Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Light-driven rotary molecular motors without point chirality: a minimal design

Jun Wang,‡ Baswanth Oruganti‡ and Bo Durbeej*

Electronic Supplementary Information

Division of Theoretical Chemistry, IFM, Linköping University, SE-581 83 Linköping, Sweden. E-mail: bodur@ifm.liu.se
‡ These two authors contributed equally to this work and are co-first authors.

Contents

Computational details

MEP calculations. The minimum energy path (MEP) calculations on **1** and **2** were performed in the following way, consistently using the ANO-L-VDZP basis set[1] for all steps and employing active spaces of six π-electrons in six orbitals. First, ground-state (S_0) equilibrium geometries of the E_{out}, Z_{in}, E_{in} and Z_{out} isomers were optimized with the complete active space self-consistent field (CASSCF)[2] method. Then, for each species, the wavefunction at the vertically excited Franck-Condon (FC) point in the optically bright first excited singlet ππ* state (S_1) was calculated using state-averaged CASSCF (SA-CASSCF), with equal (0.5) weights for S_0 and S_1. Having obtained these points, the actual MEP calculations were carried out continuing to use SA-CASSCF. Finally, for the resulting S_1 geometries, singlepoint calculations were performed with complete active space second-order perturbation theory (CASPT2)[3] to account for dynamic electron correlation effects.

NAMD simulations. The non-adiabatic molecular dynamics (NAMD) simulations of the four isomers of **1** were carried out in the following way. First, for each isomer, 200 different initial nuclear configurations and velocities were generated by sampling from a harmonic-oscillator Wigner distribution,[4,5] where the requisite S_0 vibrational normal modes were calculated with second-order Møller-Plesset perturbation theory (MP2) in combination with the DEF2-SVP basis set.[6,7] The MP2 calculations were done within the resolution-of-identity (RI) approximation.[8,9] For each isomer, 200 trajectories were then initiated by promoting the system to the S_1 state. The trajectories were propagated classically using the velocity Verlet algorithm[10] with a fixed integration time step of 1 fs, and with nuclear forces calculated "on the fly" at the SA-CASSCF/ANO-L-VDZP level.

Following the algorithm by Robb and co-workers[11,12] as implemented in the MOLCAS 8.0 suite of programs,[13] the non-adiabatic coupling $\left\langle \Psi_1 \left| \frac{\partial}{\partial \mathbf{R}} \Psi_0 \right. \right\rangle$ between the S_1 and S_0 states was evaluated in the framework of Landau-Zener theory,[14,15] wherein the coupling is large if $\left\langle \Psi_1 \left| \frac{\partial}{\partial t} \Psi_0 \right. \right\rangle$ is large. Specifically, $\left\langle \Psi_1 \left| \frac{\partial}{\partial t} \Psi_0 \right. \right\rangle$ was computed at each step along the trajectories for which the energy gap between the two states is smaller than 0.03 a.u., using the numerical approximation

$$\left\langle \Psi_1(t) \middle| \tfrac{\partial}{\partial t} \Psi_0(t) \right\rangle \approx \frac{\left\langle \Psi_1(t) \middle| \Psi_0(t+\Delta t) \right\rangle}{\Delta t}.$$

When $\left\langle \Psi_1(t) \middle| \Psi_0(t+\Delta t) \right\rangle$ is larger than 0.25, representing the situation when the S_1 and S_0 wavefunctions start to deviate from orthogonality close to a conical intersection, the trajectory was allowed to hop to the S_0 state (but not to thereafter return to the S_1 state). After the $S_1 \rightarrow S_0$ hop, the trajectories were propagated adiabatically along the S_0 potential energy surface for up to a maximum total simulation time of 700 fs.

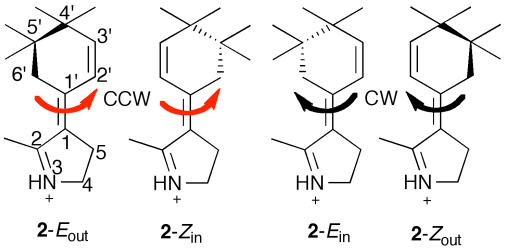
The procedure to only allow one single hop between the S_1 and S_0 states in the simulations was validated by calculating 10 complementary trajectories for the **1**-E_{out} isomer with the possibility of multiple hopping events accounted for. Specifically, in each of these 10 trajectories, five hops between the S_1 and S_0 states were allowed. The results of these simulations are compared with the corresponding results from single-hop simulations in Table S2. Encouragingly, it can be seen that the number of allowed hops plays a marginal role for the estimated percentage of successful trajectories (100% *vs.* 90%) and the preferred direction of rotation among these trajectories (100% CCW *vs.* 89% CCW).

The NAMD simulations of **2**, in turn, were carried out with the same exact protocol as those of **1**, except that only 10 different initial nuclear configurations and velocities were considered.

DFT and MP2 calculations. The $E_{out} \leftrightarrow E_{in}$ and $Z_{out} \leftrightarrow Z_{in}$ enantiomerization free-energy barriers of **1**, **2** and **3** were calculated using both MP2 and density functional theory (DFT) at the level of the M06-2X[16] global and the ωB97X-D[17] range-separated hybrid functionals to first locate the S_0 equilibrium geometries of the four isomers as well as the enantiomerization transition structures that connect these stationary points. All calculations were done with the cc-pVTZ basis set.[18] Based on the resulting geometries, frequency calculations were then performed to obtain Gibbs free energy at room temperature, and to appropriately ensure that the geometries correspond to minima (real vibrational frequencies only) or transition structures (one imaginary vibrational frequency). While the M06-2X and ωB97X-D geometries were subjected to M06-2X and ωB97X-D frequency calculations, respectively, the MP2 free-energy barriers were rather estimated by adding M06-2X thermal free-energy corrections to MP2 electronic energies. This

approach was deemed necessary because of the computational cost associated with MP2 frequency calculations.

Software used. The MEP calculations, the NAMD simulations and all other CASSCF and CASPT2 calculations were done with MOLCAS 8.0.[13] The RI-MP2 calculations were done with TURBOMOLE 6.7.[19] All other MP2 calculations and the DFT calculations were done with Gaussian 09.[20]



θ = C2 - C1 - C1' - C2'
θ' = C5 - C1 - C1' - C6'
ω = 1/2(θ + θ')
α = C1 - C2 - C5 - C1'
α' = C1' - C2' - C6' - C1

Scheme S1 The E_{out}, Z_{in}, E_{in} and Z_{out} isomers of motor **2** and relevant dihedral angles.

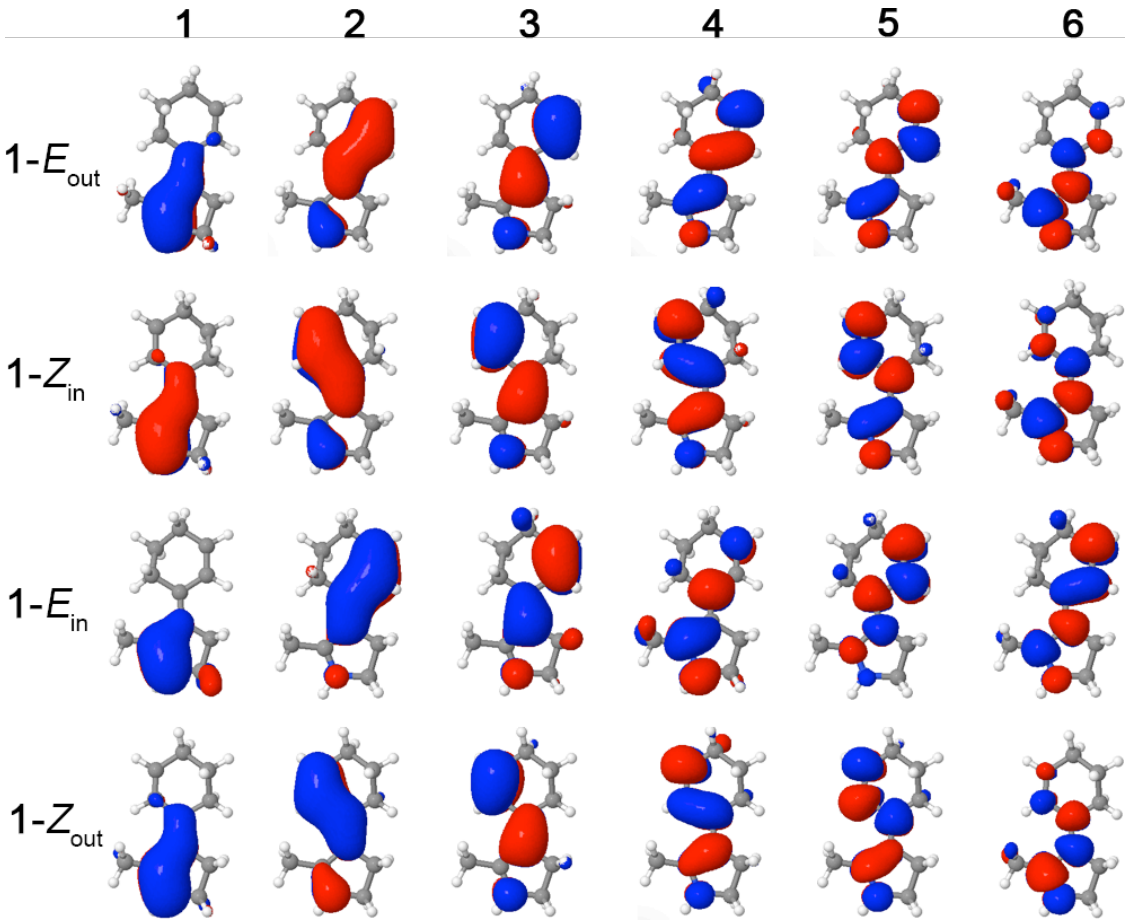


Fig. S1 Active CASSCF/ANO-L-VDZP molecular orbitals at the CASSCF S_0 equilibrium geometries of the E_{out}, Z_{in}, E_{in} and Z_{out} isomers of motor **1**.

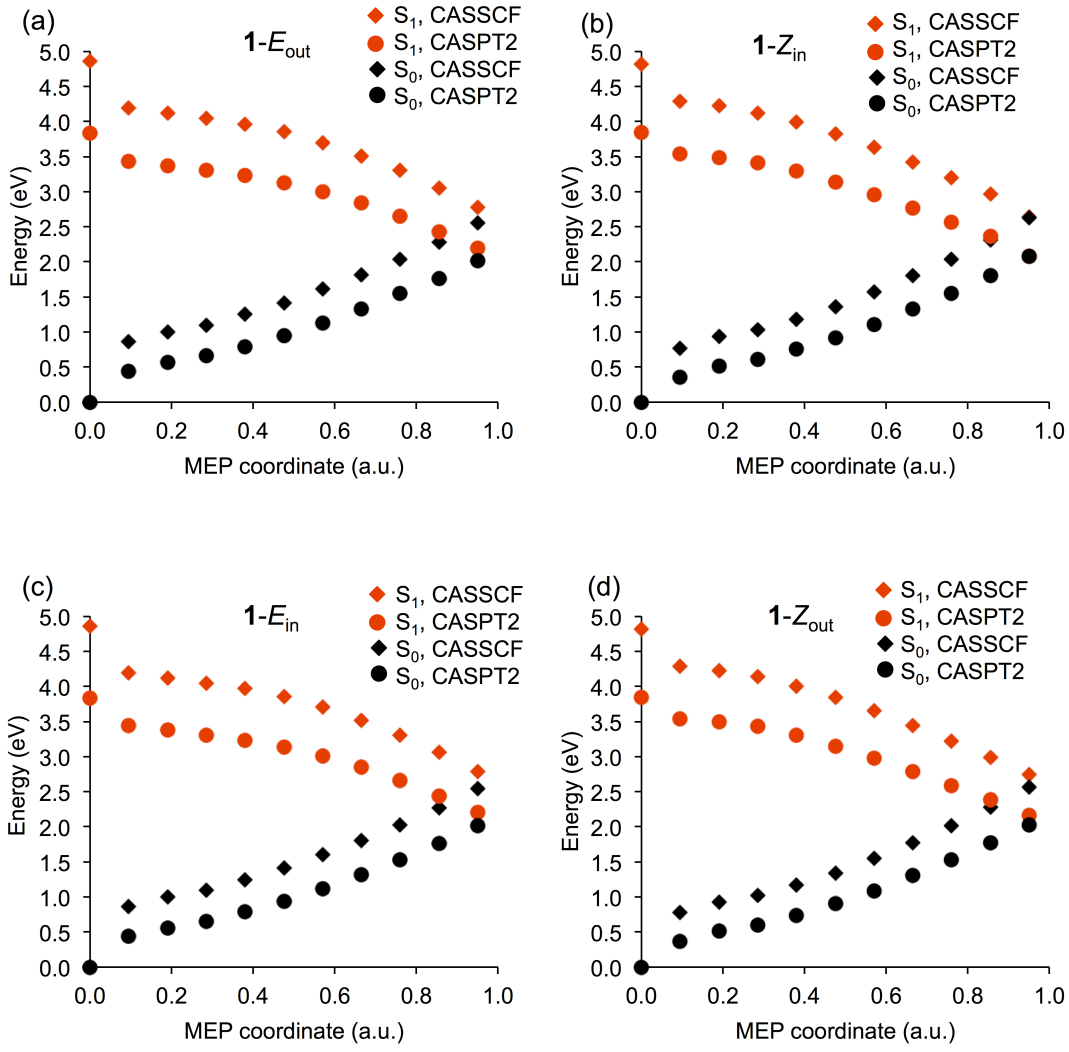


Fig. S2 Comparison of minimum energy paths (MEPs) from the S_1 Franck-Condon (FC) points of the E_{out} (a), Z_{in} (b), E_{in} (c) and Z_{out} (d) isomers of motor **1** obtained with and without CASPT2 singlepoint calculations.

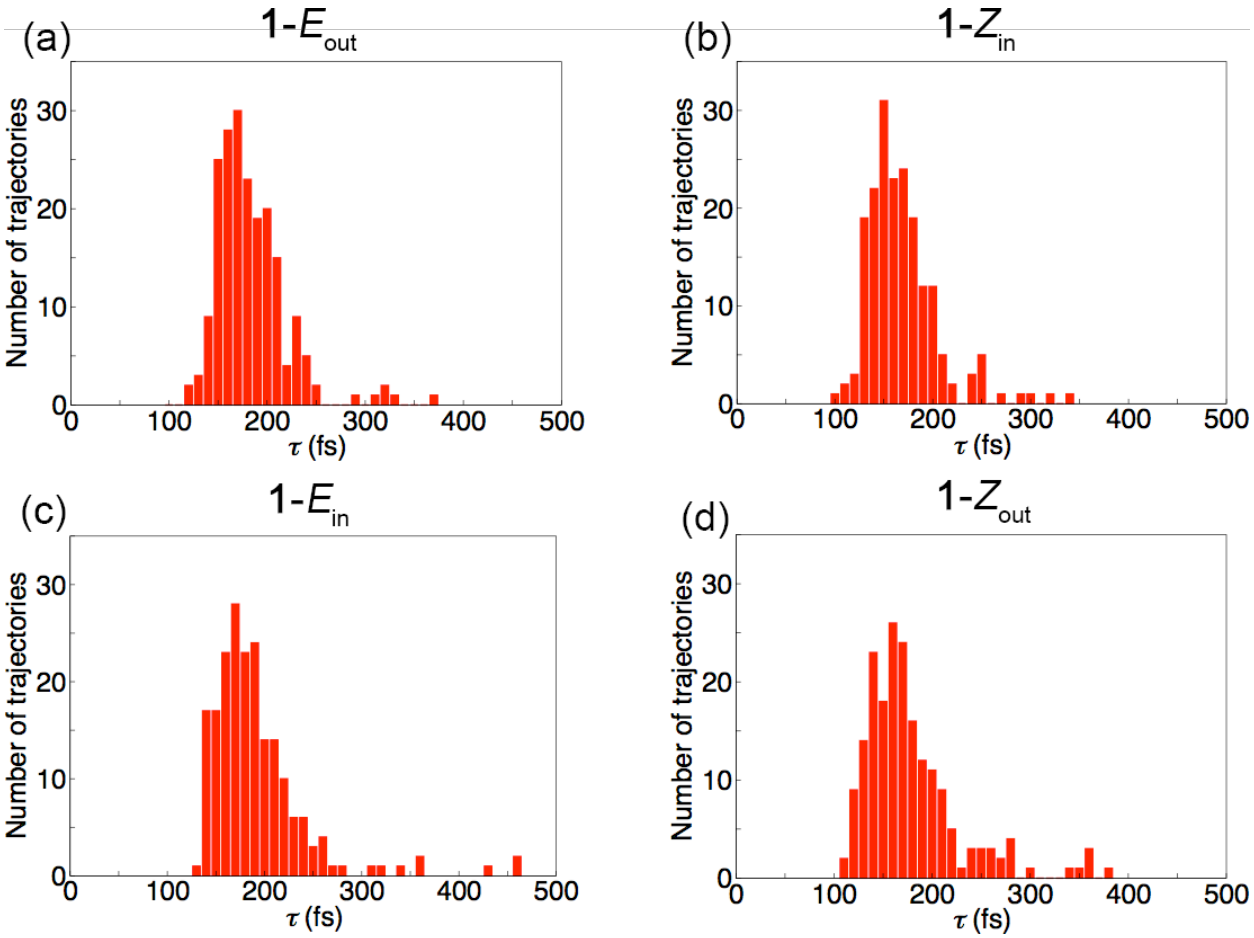


Fig. S3 Distributions of S_1 lifetimes (τ) among the **1**-E_{out} → **1**-Z_{in} (a), **1**-Z_{in} → **1**-E_{out} (b), **1**-E_{in} → **1**-Z_{out} (c) and **1**-Z_{out} → **1**-E_{in} (d) trajectories that hop to the S_0 state within 700 fs (the distributions include also those trajectories that hop to the S_0 state but do not complete the photoisomerization within 700 fs).

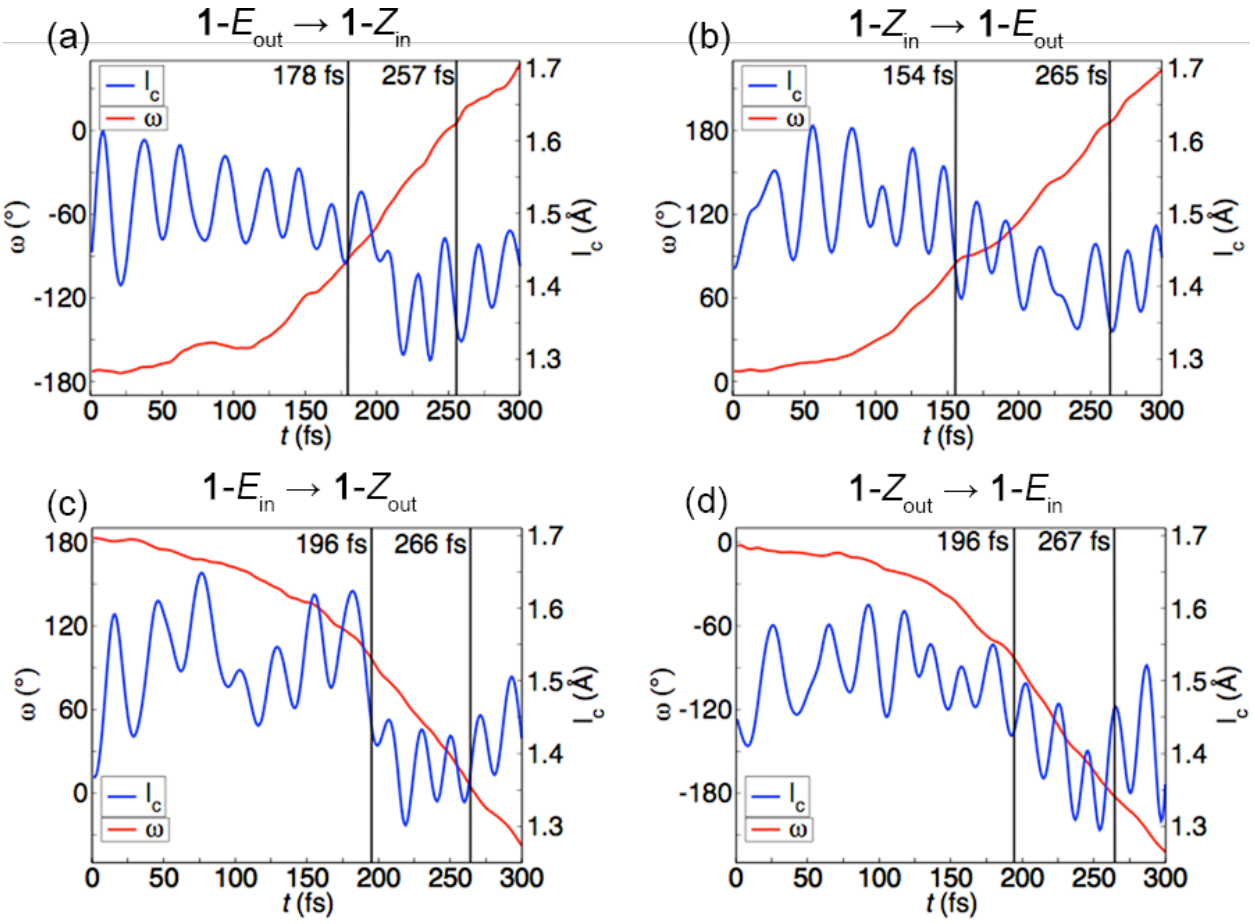


Fig. S4 Changes in the central olefinic bond length (l_c) and the ω dihedral angle along typical **1**-E_{out} → **1**-Z_{in} (a), **1**-Z_{in} → **1**-E_{out} (b), **1**-E_{in} → **1**-Z_{out} (c) and **1**-Z_{out} → **1**-E_{in} (d) photoisomerization trajectories. S_1 lifetimes and photoisomerization times (PITs) are indicated with vertical lines. A typical trajectory is one whose PIT is close to the average PIT for all successful trajectories; see Table S6.

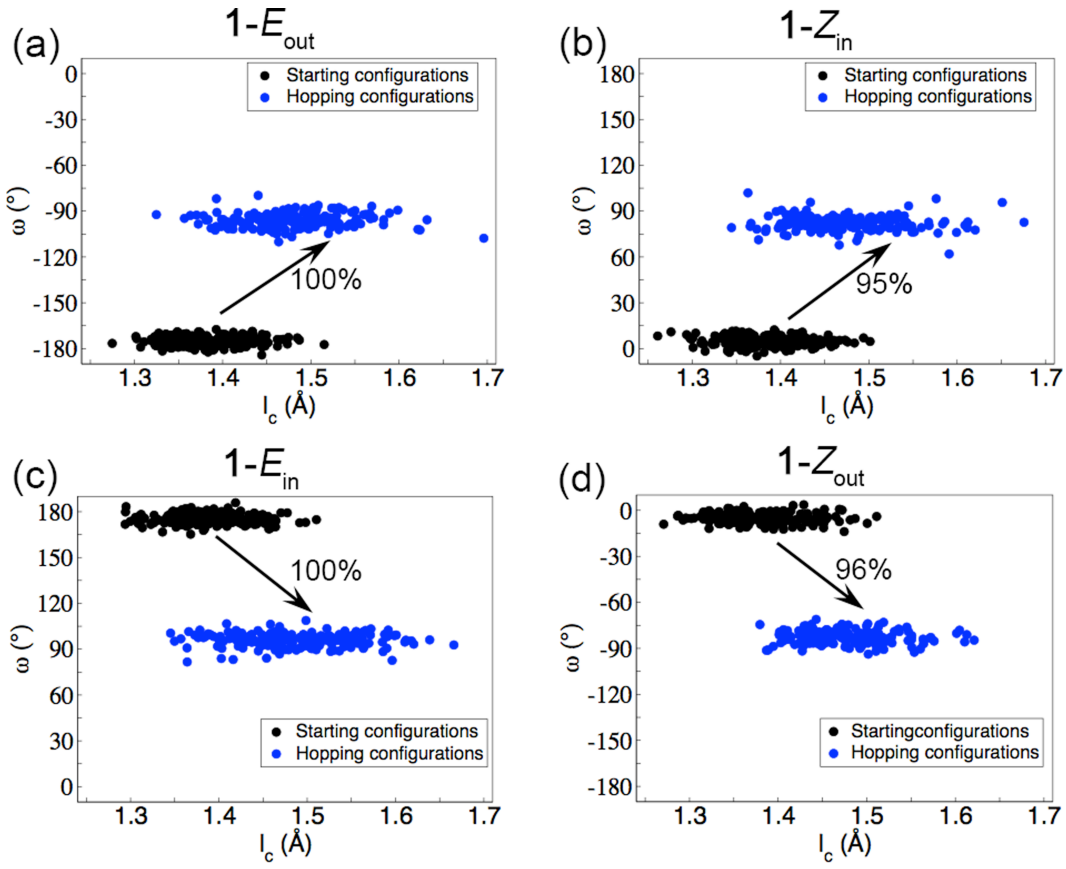


Fig. S5 Distributions of central olefinic bond lengths (l_c) and ω dihedral angles in the starting and $S_1 \rightarrow S_0$ hopping configurations of the **1**-E_{out} → **1**-Z_{in} (a), **1**-Z_{in} → **1**-E_{out} (b), **1**-E_{in} → **1**-Z_{out} (c) and **1**-Z_{out} → **1**-E_{in} (d) trajectories. Shown are also the percentages of trajectories that hop to the S_0 state.

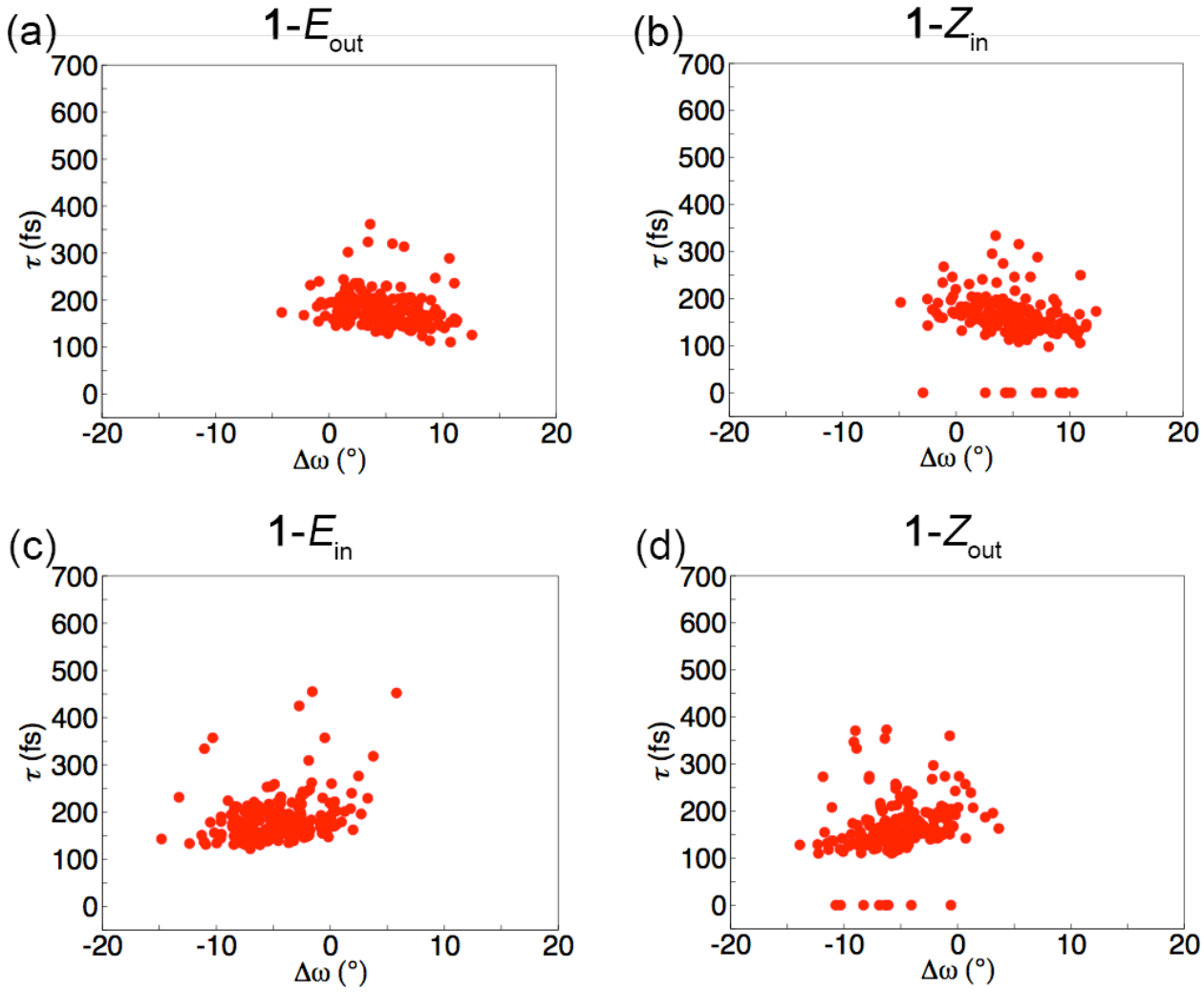


Fig. S6 S_1 lifetimes (τ) plotted against initial Δω values for all 200 trajectories run for the E_{out} (a), Z_{in} (b), E_{in} (c) and Z_{out} (d) isomers of motor **1**. Data points at τ = 0 correspond to trajectories that do not hop to the S_0 state within 700 fs.

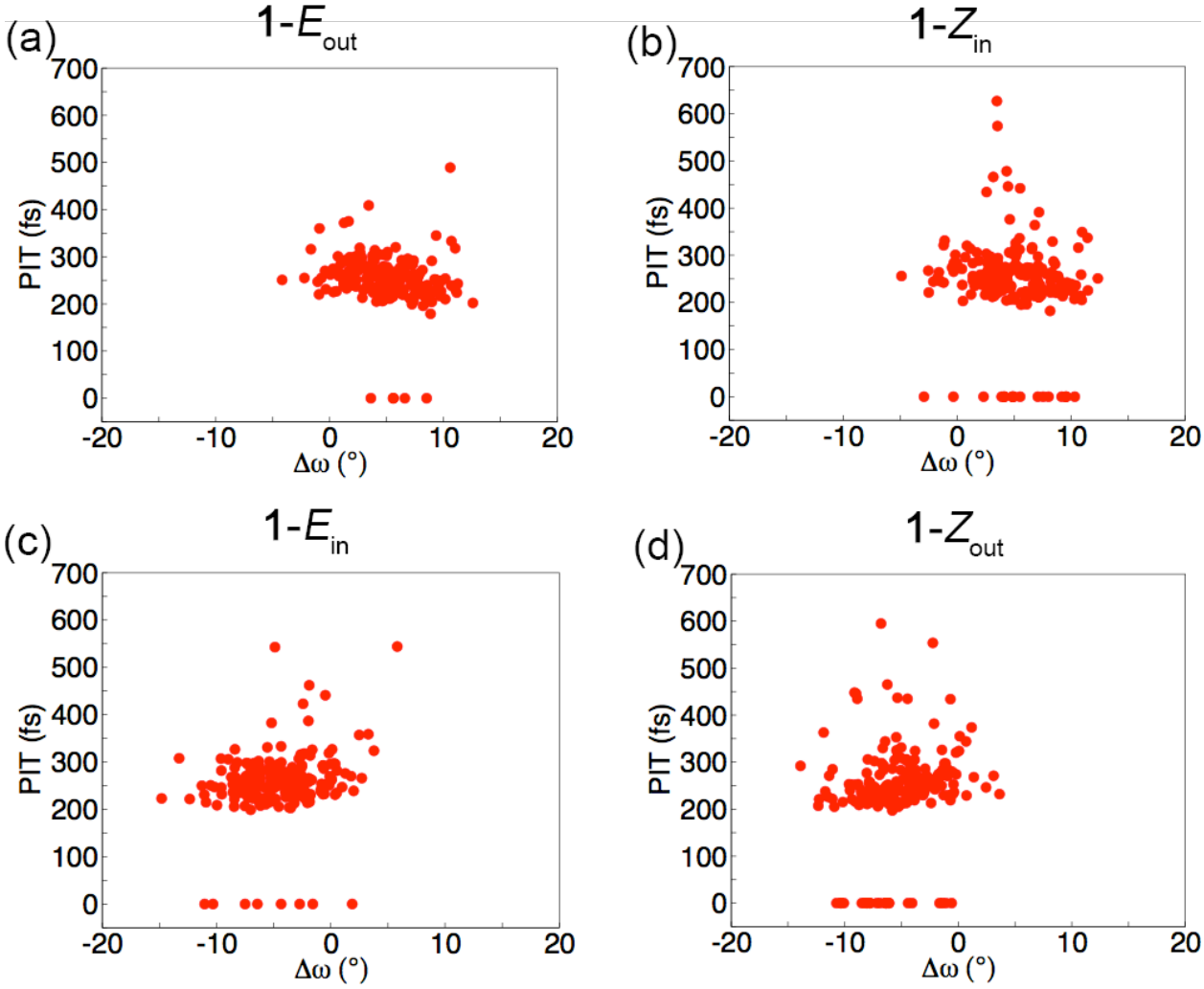


Fig. S7 Photoisomerization times (PITs) plotted against initial Δω values for all 200 trajectories run for the E_{out} (a), Z_{in} (b), E_{in} (c) and Z_{out} (d) isomers of motor **1**. Data points at PIT = 0 correspond to trajectories that do not complete the photoisomerization within 700 fs.

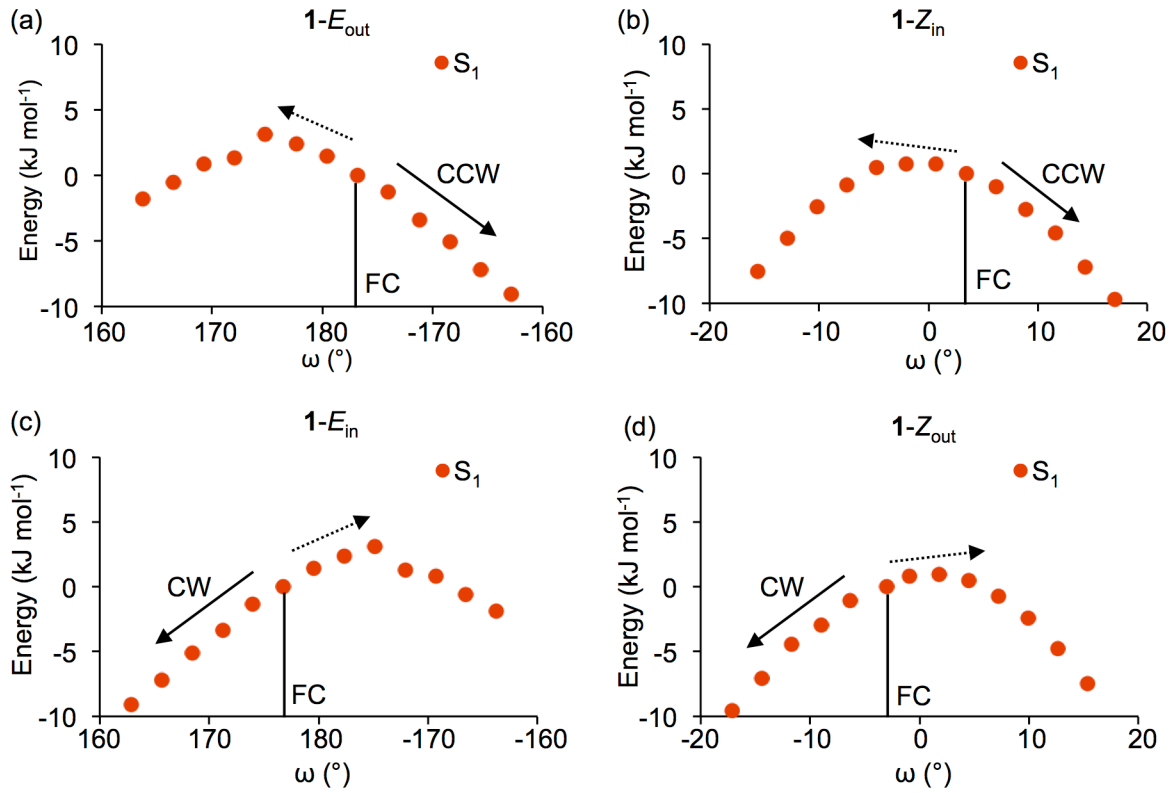


Fig. S8 Asymmetry in the S_1 potential energy surface (PES) with respect to clockwise (CW) and counterclockwise (CCW) rotations from the Franck-Condon (FC) points of the E_{out} (a), Z_{in} (b), E_{in} (c) and Z_{out} (d) isomers of motor **1**. The energy profiles were calculated for 13 different values of the ω dihedral angle by first performing constrained S_1 geometry optimizations at the SA-CASSCF/ANO-L-VDZP level of theory with equal (0.5) weights for S_0 and S_1, followed by CASPT2/ANO-L-VDZP singlepoint calculations at the resulting geometries. For each point along the energy profiles, two dihedral constraints were enforced in the geometry optimizations: one for the θ dihedral angle and one for the θ' dihedral angle (see Scheme 1). Following the definitions of dihedral angles in Scheme 1, the ω value for each point was obtained as the average of the θ and θ' values at that point. The selection of θ and θ' values was done by first relating θ' to θ through linear regression analyses of the geometries obtained from the minimum energy path calculations in Fig. 1. Then, for each energy profile, 13 different θ values were selected manually in increments of 3° from the value at the FC point, whereafter the 13 corresponding θ' values were calculated by the regression formula in question.

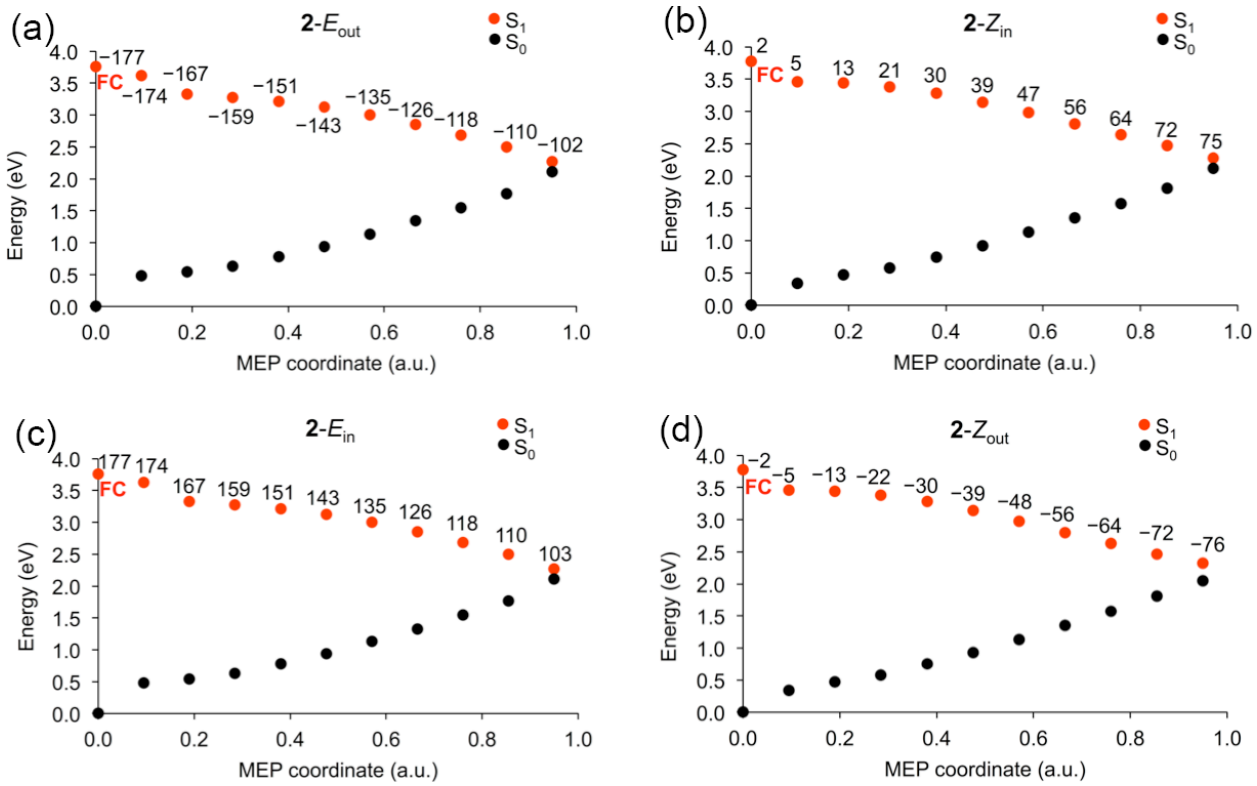


Fig. S9 Minimum energy paths (MEPs) from the S_1 Franck-Condon (FC) points of the E_{out} (a), Z_{in} (b), E_{in} (c) and Z_{out} (d) isomers of motor **2**. Shown are also the corresponding changes in the ω dihedral angle (degrees).

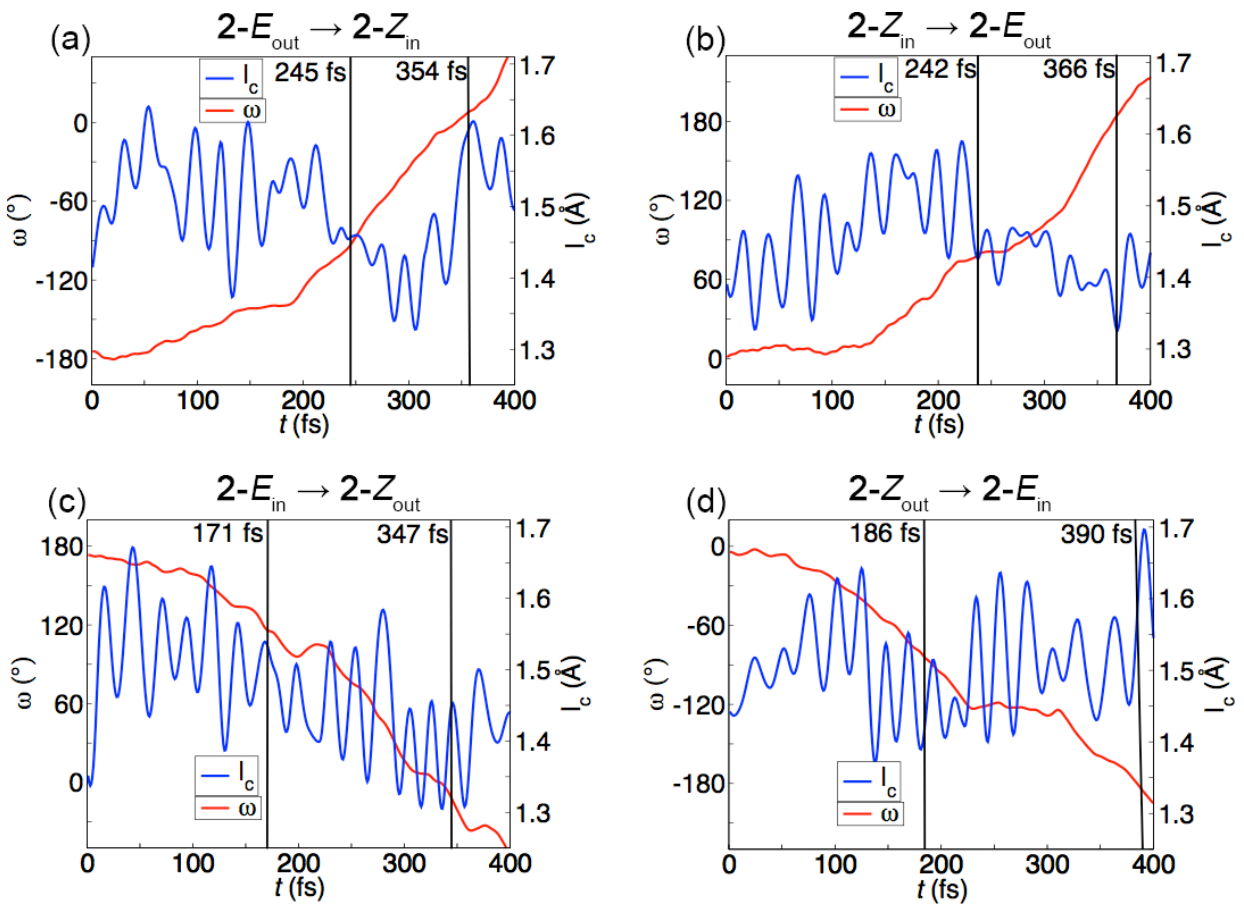


Fig. S10 Changes in the central olefinic bond length (l_c) and the ω dihedral angle along typical **2**-E_{out} → **2**-Z_{in} (a), **2**-Z_{in} → **2**-E_{out} (b), **2**-E_{in} → **2**-Z_{out} (c) and **2**-Z_{out} → **2**-E_{in} (d) photoisomerization trajectories taken from Table S8. S_1 lifetimes and photoisomerization times (PITs) are indicated with vertical lines.

Table S1 CASSCF/ANO-L-VDZP occupation numbers for active molecular orbitals in the S_0 and S_1 states of different isomers of motor **1**[a]

		Active molecular orbital					
Isomer	State	1	2	3	4	5	6
E_{out}	S_0	1.97	1.94	1.91	0.10	0.03	0.05
	S_1	1.97	1.92	1.06	0.94	0.08	0.03
Z_{in}	S_0	1.97	1.94	1.91	0.10	0.03	0.05
	S_1	1.97	1.91	1.11	0.89	0.09	0.03
E_{in}	S_0	1.97	1.94	1.91	0.10	0.03	0.05
	S_1	1.97	1.92	1.06	0.94	0.08	0.03
Z_{out}	S_0	1.97	1.94	1.91	0.10	0.03	0.05
	S_1	1.97	1.91	1.11	0.89	0.09	0.03

[a] Calculations carried out at CASSCF S_0 equilibrium geometries.

Table S2 Comparison of 10 trajectories run for the E_{out} isomer of motor **1** with 1 or 5 hops allowed between the S_1 and S_0 states

Trajectory	Allowed hops	Observed hops	PIT (fs)[a]
1	1	1	319
	5	5	312
2	1	1	217
	5	1	217
3	1	1	218
	5	1	218
4	1	1	232
	5	3	316
5	1	1	251
	5	5	–[e]
6	1	1	227
	5	1	227
7	1	1	239
	5	5	283
8	1	1	251
	5	1	251
9	1	1	294
	5	5	310
10	1	1	252
	5	5	266
1–10	1		<PIT>[b] = 250 fs S[c] = 100% D[d] = 100% CCW
1–10	5		<PIT>[b] = 267 fs S[c] = 90% D[d] = 89% CCW

[a] Photoisomerization time. [b] Average photoisomerization time. [c] Percentage of successful trajectories. [d] Direction of rotation among successful trajectories. [e] Trajectory does not complete photoisomerization within 700 fs.

Table S3 Relative energies (E, kJ mol^{-1}) and optimized S_0 geometric parameters (Å and degrees) for different isomers of motors **1** and **2** at different levels of theory

		CASSCF[a]		RI-MP2[b]		M06-2X[c]		ωB97X-D[c]	
Isomer	Energy/ Parameter[d]	**1**	**2**	**1**	**2**	**1**	**2**	**1**	**2**
E_{out}	*E*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
	l_c	1.36	1.36	1.38	1.38	1.36	1.36	1.36	1.36
	θ	-175	-175	-173	-172	-173	-174	-174	-175
	θ'	-180	-180	-179	-179	-179	-179	-180	-179
	ω	-177	-177	-176	-175	-176	-176	-177	-177
	Δω	3	3	4	5	4	4	3	3
Z_{in}	*E*	*0.3*	*0.1*	*0.4*	*0.7*	*1.0*	*0.6*	*0.4*	*0.4*
	l_c	1.36	1.36	1.38	1.38	1.36	1.36	1.36	1.36
	θ	5	4	9	9	6	6	6	6
	θ'	1	0	2	1	1	1	1	2
	ω	3	2	6	5	3	4	3	4
	Δω	3	2	6	5	3	4	3	4
E_{in}	*E*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
	l_c	1.36	1.36	1.38	1.38	1.36	1.36	1.36	1.36
	θ	175	175	172	172	173	174	174	175
	θ'	180	180	179	179	179	179	180	179
	ω	177	177	176	175	176	176	177	177
	Δω	-3	-3	-4	-5	-4	-3	-3	-3
Z_{out}	*E*	*0.3*	*0.1*	*0.4*	*0.7*	*1.0*	*0.6*	*0.4*	*0.4*
	l_c	1.36	1.36	1.38	1.38	1.36	1.36	1.36	1.36
	θ	-5	-4	-9	-9	-6	-6	-6	-6
	θ'	0	0	-2	-1	-1	-1	-1	-2
	ω	-3	-2	-6	-5	-3	-4	-3	-4
	Δω	-3	-2	-6	-5	-3	-4	-3	-4

[a] Calculations carried out using the ANO-L-VDZP basis set. [b] Calculations carried out using the DEF2-SVP basis set. [c] Calculations carried out using the cc-pVTZ basis set. [d] l_c is the central olefinic bond length.

Table S4 Vertical $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_2$ excitation energies (eV) for different isomers of motors **1** and **2**[a]

Isomer	Excitation	State-averaging[b]	**1**	**2**
E_{out}	$S_0 \rightarrow S_1$	S_0, S_1	3.83 (0.93)	3.76 (0.94)
	$S_0 \rightarrow S_1$	S_0, S_1, S_2	3.78 (0.91)	3.69 (0.92)
	$S_0 \rightarrow S_2$	S_0, S_1, S_2	5.21 (0.08)	5.13 (0.08)
Z_{in}	$S_0 \rightarrow S_1$	S_0, S_1	3.84 (0.73)	3.76 (0.75)
	$S_0 \rightarrow S_1$	S_0, S_1, S_2	3.79 (0.72)	3.73 (0.74)
	$S_0 \rightarrow S_2$	S_0, S_1, S_2	5.31 (0.15)	5.22 (0.15)
E_{in}	$S_0 \rightarrow S_1$	S_0, S_1	3.83 (0.93)	3.78 (0.94)
	$S_0 \rightarrow S_1$	S_0, S_1, S_2	3.78 (0.91)	3.71 (0.92)
	$S_0 \rightarrow S_2$	S_0, S_1, S_2	5.21 (0.08)	5.10 (0.08)
Z_{out}	$S_0 \rightarrow S_1$	S_0, S_1	3.84 (0.73)	3.78 (0.75)
	$S_0 \rightarrow S_1$	S_0, S_1, S_2	3.80 (0.72)	3.73 (0.75)
	$S_0 \rightarrow S_2$	S_0, S_1, S_2	5.31 (0.15)	5.22 (0.15)

[a] CASPT2 calculations carried out using the ANO-L-VDZP basis set, with oscillator strengths in parentheses obtained with the complete active space state-interaction (CASSI) method (Ref. 21). [b] SA-CASSCF wavefunctions at the FC points obtained using equal weights for the indicated states.

Table S5 α and α' pyramidalization dihedral angles (degrees) along the photoisomerization minimum energy paths (MEPs) for different isomers of motors **1** and **2**

		α		α'	
Isomer	MEP point	**1**	**2**	**1**	**2**
E_{out}	1	-1	-1	-1	-1
	2	0	0	0	0
	3	0	0	0	0
	4	0	1	0	0
	5	0	1	0	0
	6	1	2	0	0
	7	1	3	0	0
	8	3	4	0	0
	9	4	4	-1	0
	10	5	6	-1	1
	11	5	6	-1	1
Z_{in}	1	0	0	-2	-2
	2	-3	-3	-1	-1
	3	-3	-4	-1	-1
	4	-3	-2	-1	-1
	5	-1	-1	-1	-2
	6	0	1	-1	-2
	7	1	2	-2	-2
	8	2	3	-2	-2
	9	3	4	-2	-3
	10	4	4	-3	-3
	11	4	4	-3	-3
E_{in}	1	1	1	1	1
	2	0	0	0	0
	3	0	0	0	0
	4	0	-1	0	0
	5	0	-1	0	0

Table S5 Continued

		α		α'	
Isomer	MEP point	**1**	**2**	**1**	**2**
	6	0	-2	0	0
	7	0	-3	0	0
	8	-2	-4	0	0
	9	-4	-4	-1	0
	10	-5	-6	-1	-1
	11	-5	-6	-1	-1
Z_{out}	1	0	0	2	2
	2	3	3	1	1
	3	3	4	1	1
	4	3	2	1	1
	5	1	1	1	2
	6	0	-1	1	2
	7	-1	-2	2	2
	8	-2	-3	2	2
	9	-3	-4	2	3
	10	-4	-4	3	3
	11	-4	-4	3	3

Table S6 S_1 lifetimes (τ, fs) and photoisomerization times (PITs, fs) for different isomers of motor **1**

	τ			PIT		
Isomer	Slowest[a]	Fastest[b]	Average[c]	Slowest[a]	Fastest[b]	Average[d]
E_{out}	362	111	179	489	179	257
Z_{in}	334	98	165	627	182	265
E_{in}	455	122	187	544	199	266
Z_{out}	373	110	174	595	197	267

[a] Slowest trajectory. [b] Fastest trajectory. [c] Averaged value over all trajectories that hop to the S_0 state within 700 fs. [d] Averaged value over all trajectories that complete the photoisomerization within 700 fs.

Table S7 Enantiomerization free-energy barriers (kJ mol^{-1}) for motors **1**, **2** and **3** at different levels of theory[a]

	M06-2X			ωB97X-D			MP2		
Enantiomerization	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
$E_{in} \leftrightarrow E_{out}$	27.8	48.7	78.3	26.8	45.7	72.9	25.2	49.6	82.5
$Z_{in} \leftrightarrow Z_{out}$	23.6	43.2	76.8	24.2	46.5	73.9	26.9	43.6	80.9

[a] Calculations carried out using the cc-pVTZ basis set.

Table S8 S_1 lifetimes (τ, fs) and photoisomerization times (PITs, fs) for each of the 10 trajectories run for the different isomers of motor **2**

	E_{out}		Z_{in}		E_{in}		Z_{out}	
Trajectory	τ	PIT	τ	PIT	τ	PIT	τ	PIT
1	172	346	192	334	174	330	135	276
2	267	411	156	304	170	349	186	390
3	245	354	156	252	193	318	172	474
4	180	424	167	361	235	331	165	528
5	194	–[a]	158	294	211	324	143	256
6	170	–[a]	242	366	186	342	–[b]	–[a]
7	204	469	171	346	171	347	250	445
8	196	433	170	–[a]	172	368	381	514
9	174	–[a]	269	378	192	–[a]	186	456
10	163	311	160	391	225	329	158	266

[a] Trajectory does not complete photoisomerization within 700 fs. [b] Trajectory does not hop to the S_0 state within 700 fs.

Description of multimedia files

Motor 1:

1e_out_and_z_in.mpg: Movie from the NAMD simulations showing two representative trajectories merged together to illustrate the full **1**-E_{out} → **1**-Z_{in} → **1**-E_{out} rotary process

1e_in_and_z_out.mpg: Movie from the NAMD simulations showing two representative trajectories merged together to illustrate the full **1**-E_{in} → **1**-Z_{out} → **1**-E_{in} rotary process

Motor 2:

2e_out_and_z_in.mpg: Movie from the NAMD simulations showing two representative trajectories merged together to illustrate the full **2**-E_{out} → **2**-Z_{in} → **2**-E_{out} rotary process

2e_in_and_z_out.mpg: Movie from the NAMD simulations showing two representative trajectories merged together to illustrate the full **2**-E_{in} → **2**-Z_{out} → **2**-E_{in} rotary process

References for the Electronic Supplementary Information

(1) P. O. Widmark, P.-Å. Malmqvist and B. O. Roos, *Theor. Chim. Acta* 1990, **77**, 291–306.

(2) B. O. Roos, P. R. Taylor and P. E. M. Siegbahn, *Chem. Phys.* 1980, **48**, 157–173.

(3) K. Andersson, P.-Å. Malmqvist and B. O. Roos, *J. Chem. Phys.* 1992, **96**, 1218–1226.

(4) J. P. Dahl and M. Springborg, *J. Chem. Phys.* 1988, **88**, 4535–4547.

(5) R. Schinke, *Photodissociation Dynamics: Spectroscopy and Fragmentation of Small Polyatomic Molecules*, Cambridge University Press, Cambridge, U.K., 1993.

(6) F. Weigend, *Phys. Chem. Chem. Phys.* 2006, **8**, 1057−1065.

(7) F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* 2005, **7**, 3297−3305.

(8) M. Feyereisen, G. Fitzgerald and A. Komornicki, *Chem. Phys. Lett.* 1993, **208**, 359−363.

(9) O. Vahtras, J. Almlöf and M. W. Feyereisen, *Chem. Phys. Lett.* 1993, **213**, 514−518.

(10) L. Verlet, *Phys. Rev.* 1967, **159**, 98−103.

(11) G. Groenhof, M. Bouxin-Cademartory, B. Hess, S. P. de Visser, H. J. C. Berendsen, M. Olivucci, A. E. Mark and M. A. Robb, *J. Am. Chem. Soc.* 2004, **126**, 4228−4233.

(12) L. V. Schäfer, G. Groenhof, M. Boggio-Pasqua, M. A. Robb and H. Grubmüller, *PLoS Comput. Biol.* 2008, **4**, e1000034.

(13) F. Aquilante, J. Autschbach, R. K. Carlson, L. F. Chibotaru, M. G. Delcey, L. De Vico, I. Fdez. Galván, N. Ferré, L. M. Frutos, L. Gagliardi, M. Garavelli, A. Giussani, C. E. Hoyer, G. L. Manni, H. Lischka, D. Ma, P.-Å. Malmqvist, T. Müller, A. Nenov, M. Olivucci, T. B. Pedersen, D. Peng, F. Plasser, B. Pritchard, M. Reiher, I. Rivalta, I. Schapiro, J. Segarra-Martí, M. Stenrup, D. G. Truhlar, L. Ungur, A. Valentini, S. Vancoillie, V. Veryazov, V. P. Vysotskiy, O. Weingart, F. Zapata and R. Lindh, *J. Comput. Chem.* 2016, **37**, 506–541.

(14) M. Desouter-Lecomte and J. C. Lorquet, *J. Chem. Phys.* 1979, **71**, 4391–4403.

(15) C. Wittig, *J. Phys. Chem. B* 2005, **109**, 8428–8430.

(16) Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.* 2008, **120**, 215–241.

(17) J.-D. Chai and M. Head-Gordon, *Phys. Chem. Chem. Phys.* 2008, **10**, 6615−6620.

(18) T. H. Dunning, Jr., *J. Chem. Phys.* 1989, **90**, 1007−1023.

(19) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.* 1989, **162**, 165−169.

(20) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, *Revision D.01*, Gaussian, Inc., Wallingford CT, USA, 2009.

(21) P.-Å. Malmqvist and B. O. Roos, *Chem. Phys. Lett.* 1989, **155**, 189−194.

Cartesian coordinates (Å) for CASSCF S_0 equilibrium geometries of 1 and 2

1-E_{out}

C	-3.02226651	-1.22814938	0.24260189
C	-1.82896997	0.76704447	-0.05335875
C	-0.80655670	-0.27886349	-0.03627781
C	-1.55144875	-1.61173270	0.02385595
C	0.54750487	-0.14632461	-0.10440878
C	1.37676012	-1.35712645	-0.18554492
C	1.30852829	1.16351017	-0.16084413
C	2.72510286	-1.31994594	-0.19194173
C	2.66604849	1.06283731	0.54199525
H	1.46398412	1.41615768	-1.21336890
H	0.74542170	1.97039194	0.28593898
C	3.52194521	-0.05425776	-0.04629781
H	3.18038251	2.01944507	0.46185634
H	2.50326820	0.87243800	1.60465751
H	4.39073014	-0.23974082	0.58514635
H	3.91054319	0.23474093	-1.02715096
H	-3.70460264	-1.65904251	-0.48438836
H	3.26715812	-2.24828327	-0.31460850
H	0.88457747	-2.31044607	-0.28387419
H	-1.19280238	-2.24003066	0.83271467
H	-1.43731729	-2.16359597	-0.90654736
H	-3.38457987	-1.44958894	1.24380677
H	-3.83928780	0.78543352	0.07597188
C	-1.70895001	2.25080561	-0.21149293
H	-1.26267473	2.67824160	0.68345322
H	-1.07549486	2.48711000	-1.06037939
H	-2.68877495	2.69676231	-0.36012055
N	-2.99907784	0.23296092	0.06984827

1-Z_{in}

C	3.01233832	-1.26253730	-0.10182050
C	1.51899378	-1.61203504	-0.02492485
C	0.80263147	-0.26329415	-0.04384249
C	1.84247188	0.75956375	0.08067605
H	3.61335859	-1.71253385	0.68299256
H	3.46174633	-1.48790728	-1.06622668
H	1.22570933	-2.24008004	-0.85991685
H	1.30374008	-2.15366536	0.89357513
C	-0.54629910	-0.10224589	-0.13850061
C	-1.24355175	1.18681910	-0.23901884
C	-1.44320184	-1.32215779	-0.22008803
C	-2.58969191	1.28037002	-0.22836966
C	-2.77220467	-1.10132576	0.50574282
H	-1.63259449	-1.52314258	-1.27879574
H	-0.94616159	-2.19684859	0.18573219
C	-3.51418763	0.10841481	-0.05446688
H	-3.38430999	-1.99765482	0.41854525
H	-2.57685814	-0.94777653	1.56900090
H	-4.33876714	0.38865299	0.60106292
H	-3.96057854	-0.13070387	-1.02407363
H	3.85505674	0.73098474	0.15646882
H	-3.03673395	2.25616009	-0.36611131
C	1.74007246	2.24493490	0.22960895
H	1.37907714	2.68037425	-0.69937807
H	1.04186756	2.49222619	1.02360589
H	2.71223168	2.67172987	0.46110228
H	-0.67743797	2.08781540	-0.37562181
N	3.00595835	0.19808475	0.07681019

1-E_{in}

C	3.02362275	-1.22864399	0.23557540
C	1.82911814	0.76738728	-0.05170014
C	0.80660536	-0.27841932	-0.03496207
C	1.55082139	-1.61146750	0.02804913
C	-0.54745971	-0.14613899	-0.10428112
C	-1.37631490	-1.35745086	-0.18285421
C	-1.30897100	1.16308259	-0.16538121
C	-2.72469343	-1.32084285	-0.18961452
C	-2.66695338	1.06415628	0.53677095
H	-0.74671735	1.97186311	0.27890117
H	-1.46373343	1.41213082	-1.21889567
C	-3.52209212	-0.05497482	-0.04870431
H	-3.91003856	0.23082676	-1.03076911
H	-4.39130173	-0.23871802	0.58265937
H	3.39503521	-1.45440381	1.23242237
H	-3.26636181	-2.24975101	-0.30944350
H	-0.88384657	-2.31102401	-0.27673074
H	1.43035084	-2.16927541	-0.89786998
H	1.19633329	-2.23415889	0.84315449
H	3.69933768	-1.65654559	-0.49938023
H	3.83949030	0.78571620	0.07414546
C	1.70891722	2.25168070	-0.20367576
H	1.07675722	2.49180019	-1.05241768
H	1.26106955	2.67477377	0.69254405
H	2.68878496	2.69870474	-0.34869252
H	-3.18145913	2.02040083	0.45351841
H	-2.50487046	0.87695713	1.60012572
N	2.99941562	0.23308264	0.06874127

1-Z_{out}

C	-3.01207969	-1.26409473	-0.09304931
C	-1.84380096	0.76044769	0.07718448
C	-0.80258785	-0.26157686	-0.04245930
C	-1.51754218	-1.61123704	-0.02749844
C	0.54678597	-0.10029726	-0.13226623
C	1.24501102	1.18879237	-0.22344225
C	1.44241361	-1.32100745	-0.21933260
C	2.59127366	1.28128381	-0.21599710
C	2.77525253	-1.10514145	0.50066683
H	0.94570665	-2.19583284	0.18657239
H	1.62644662	-1.52006456	-1.27937882
C	3.51542342	0.10706316	-0.05645006
H	3.95499384	-0.12614873	-1.03059587
H	4.34469914	0.38163396	0.59550892
H	-3.47078845	-1.49777942	-1.05100232
H	3.03846859	2.25809722	-0.34576622
H	0.67962480	2.09178285	-0.34851143
H	-1.29568367	-2.15897121	0.88562703
H	-1.22824234	-2.23303733	-0.86866573
H	-3.60473523	-1.70874935	0.70120258
H	-3.85630865	0.73008857	0.15165625
C	-1.74431330	2.24700122	0.21617100
H	-1.05738427	2.50077156	1.01803286
H	-1.37071824	2.67555577	-0.71095300
H	-2.71973715	2.67495979	0.43109960
H	3.38602471	-2.00153497	0.40504171
H	2.58579304	-0.95745942	1.56579870
N	-3.00665966	0.19768964	0.07464136

2-E_{out}

C	-4.11920928	-1.06643524	0.35020118
C	-2.76143570	0.77430724	-0.15933834
C	-1.83895382	-0.35626558	-0.07885839
C	-2.69804985	-1.60340607	0.12488742
C	-0.48223903	-0.35999927	-0.20103016
C	0.23287003	-1.63811325	-0.19107180
C	0.39887999	0.85031862	-0.40847209
C	1.57771467	-1.70600508	-0.19636337
C	1.77418862	0.75304995	0.29593443
H	0.54403046	0.96775873	-1.48227737
H	-0.07951526	1.75190316	-0.05633653
C	2.53057311	-0.52916588	-0.19334199
H	-4.86410351	-1.49389892	-0.31478883
H	2.03382147	-2.68719295	-0.22771078
H	-0.33524041	-2.55377555	-0.19499168
H	-2.36751453	-2.18779108	0.97741553
H	-2.66908347	-2.24441198	-0.75338902
H	-4.46278146	-1.16486873	1.37733465
H	-4.75529702	0.99331352	0.03010738
C	-2.51356446	2.22128416	-0.45149555
H	-1.99099722	2.67756785	0.38545637
H	-1.89884520	2.32386340	-1.33986411
H	-3.45415769	2.74406551	-0.60370420
N	-3.97037219	0.36524798	0.04525303
C	2.53932831	2.04557645	-0.03441480
H	2.02550649	2.90223104	0.40215741
H	3.54533762	2.02814906	0.37745306
H	2.61549714	2.21543543	-1.10559119
C	1.53689846	0.72574513	1.81928983
H	2.46838196	0.85149565	2.36418324
H	0.88290328	1.54943586	2.10680023
H	1.07708503	-0.20144762	2.15410339
C	3.07718539	-0.38658484	-1.63208050
H	3.90259538	0.32004103	-1.66844461
H	3.45377347	-1.34864040	-1.97720841
H	2.31531178	-0.06361239	-2.33795956
C	3.72033687	-0.89519099	0.71634775
H	4.26515761	-1.73359414	0.28426952
H	4.41705452	-0.06551780	0.80919353
H	3.40095042	-1.18792101	1.71308933

2-Z_{in}

C	3.92751166	-1.36506699	-0.21457002
C	2.40752737	-1.58645144	-0.22433448
C	1.80869786	-0.18451151	-0.12991103
C	2.92596157	0.72902500	0.10568470
H	4.45112205	-1.92619805	0.55412135
H	4.40025344	-1.55456547	-1.17544880
H	2.09802869	-2.09947110	-1.12929927
H	2.10798871	-2.19552280	0.62497487
C	0.48151535	0.10217514	-0.23640660
C	-0.10841839	1.44184553	-0.21630369
C	-0.51421281	-1.01233314	-0.46822950
C	-1.44311351	1.62544038	-0.20066909
C	-1.86335400	-0.81405532	0.25947122
H	-0.67793967	-1.07729901	-1.54452827
H	-0.09993853	-1.96647248	-0.16203295
C	-2.50341649	0.54392323	-0.18972498
H	4.92611226	0.52121423	0.22614534
H	-1.80849035	2.64418812	-0.22624067
C	2.94476531	2.20118281	0.37226784
H	2.63075282	2.73703892	-0.52041639
H	2.26026209	2.44144503	1.18016311
H	3.94588897	2.52649852	0.64207589
H	0.52131648	2.31016406	-0.24073181
N	4.03831213	0.07169679	0.08228860
C	-2.74879718	-2.02275305	-0.08612374
H	-2.30949297	-2.93176893	0.32450329
H	-3.74373382	-1.92167724	0.34088835
H	-2.85315352	-2.16144502	-1.15933573
C	-1.60241536	-0.84364735	1.77902598
H	-2.53303705	-0.89839726	2.33718826
H	-1.01951316	-1.72807622	2.03618531
H	-1.05710615	0.03158283	2.12621659
C	-3.63197068	1.00624463	0.75340513
H	-4.10352357	1.90087891	0.34858135
H	-4.40249380	0.24488051	0.84827795
H	-3.26466744	1.24728892	1.74751868
C	-3.09321416	0.48147021	-1.61727430
H	-3.98310909	-0.14228163	-1.64446769
H	-3.38371316	1.48124844	-1.93781610
H	-2.38231290	0.09906879	-2.34607072

2-E_{in}

C	4.11823903	-1.06609279	0.35356735
C	2.76130014	0.77438776	-0.15895958
C	1.83882389	-0.35630743	-0.08002911
C	2.69787024	-1.60339652	0.12418097
C	0.48220690	-0.36008389	-0.20313226
C	-0.23290944	-1.63820656	-0.19348394
C	-0.39900251	0.85020226	-0.41022421
C	-1.57775548	-1.70603596	-0.19783330
C	-1.77374281	0.75300845	0.29534009
H	0.07966536	1.75185955	-0.05866219
H	-0.54502820	0.96744073	-1.48393904
C	-2.53062278	-0.52921031	-0.19320191
H	4.45878893	-1.16430416	1.38174316
H	-2.03392820	-2.68718539	-0.22941029
H	0.33518177	-2.55387679	-0.19891260
H	2.67125922	-2.24316217	-0.75510709
H	2.36558383	-2.18913426	0.97507999
H	4.86519893	-1.49345860	-0.30916129
H	4.75477811	0.99365575	0.03423034
C	2.51384548	2.22116165	-0.45250006
H	1.90032470	2.32297422	-1.34179668
H	1.99018067	2.67820586	0.38334035
H	3.45465993	2.74378168	-0.60390474
N	3.96989192	0.36550896	0.04800598
C	-3.71918697	-0.89551874	0.71794759
H	-4.41588535	-0.06593995	0.81180534
H	-4.26445484	-1.73391765	0.28642644
H	-3.39850060	-1.18836911	1.71423750
C	-3.07910437	-0.38636785	-1.63121392
H	-3.45604544	-1.34838149	-1.97607364
H	-3.90462158	0.32019342	-1.66637951
H	-2.31814302	-0.06317229	-2.33797738
C	-1.53518961	0.72583399	1.81849849
H	-0.88069687	1.54935510	2.10536630
H	-2.46619133	0.85196208	2.36412812
H	-1.07540627	-0.20146583	2.15306805
C	-2.53915605	2.04551534	-0.03447234
H	-2.02514327	2.90218662	0.40184235
H	-2.61598800	2.21542013	-1.10559214
H	-3.54491908	2.02798215	0.37799886

2-Z_{out}

C	-3.92769091	-1.36419276	-0.21816990
C	-2.92522173	0.72841787	0.10783013
C	-1.80854323	-0.18514550	-0.13037032
C	-2.40790947	-1.58681077	-0.22483202
C	-0.48152353	0.10154471	-0.23839720
C	0.10809435	1.44140959	-0.22068228
C	0.51442265	-1.01281471	-0.46958404
C	1.44274843	1.62522036	-0.20512228
C	1.86288360	-0.81364625	0.25927338
H	0.10021573	-1.96699784	-0.16340041
H	0.67906345	-1.07790149	-1.54572714
C	2.50321779	0.54389715	-0.19085427
H	-4.39788583	-1.54939827	-1.18115613
H	1.80809355	2.64391267	-0.23321538
H	-0.52190884	2.30947524	-0.24833959
H	-2.11049758	-2.19521258	0.62575703
H	-2.09704219	-2.10094921	-1.12865095
H	-4.45392538	-1.92789012	0.54680961
H	-4.92543610	0.52106992	0.22919051
C	-2.94284049	2.19971203	0.37920035
H	-2.25510466	2.43727683	1.18513151
H	-2.63231622	2.73849566	-0.51294342
H	-3.94289483	2.52421824	0.65390701
N	-4.03786128	0.07157903	0.08384867
C	1.60038711	-0.84154849	1.77859684
H	1.01700319	-1.72555497	2.03611770
H	2.53043116	-0.89588550	2.33776834
H	1.05494376	0.03418779	2.12428756
C	2.74878244	-2.02263366	-0.08405926
H	2.85402948	-2.16264821	-1.15700975
H	3.74335648	-1.92088491	0.34364293
H	2.30923998	-2.93118358	0.32733231
C	3.09530494	0.47948847	-1.61737801
H	3.38606619	1.47886073	-1.93893283
H	3.98540731	-0.14406316	-1.64221298
H	2.38568604	0.09580153	-2.34674704
C	3.63018441	1.00792240	0.75336636
H	4.40060793	0.24677875	0.85080606
H	4.10233235	1.90190581	0.34780495
H	3.26120496	1.25061120	1.74646197