Supporting Information for

Improving Photosensitivity without Changing Thermal Reactivity in Photochromic Diarylbenzenes Based on Accurate Prediction by DFT Calculations

Daichi Kitagawa*, Naoko Takahashi, Tatsumoto Nakahama, and Seiya Kobatake*

Department of Applied Chemistry, Graduate School of Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

*E-mail: kitagawa@osaka-cu.ac.jp; kobatake@a-chem.eng.osaka-cu.ac.jp

Table S1. Oscillator strength of **1a**, **5a**, and **6a** calculated by time−dependent density functional theory (TD−DFT) at the MPW1PW91/6−31G(d)//M06-2X/6−31G(d) level.

1a		**5a**		**6a**	
Wavelength /nm	Oscillator Strength	Wavelength /nm	Oscillator Strength	Wavelength /nm	Oscillator Strength
306.2	0.050	328.6	0.281	356.0	1.273
290.1	0.019	312.2	0.022	339.7	0.046
286.8	0.649	302.2	0.697	326.9	0.028
274.3	0.001	301.6	0.021	325.7	0.639
267.3	0.046	290.8	0.160	314.3	0.029
264.5	0.368	277.5	0.079	295.4	0.026

Table S2. The Results for the TDDFT calculation of **1a**, **5a**, and **6a**.

Excitation energies and oscillator strengths pf **1a**:

Excited State 1: Singlet-A 4.0496 eV 306.17 nm f=0.0504 <S**2>=0.000

127 ->128 0.65550

127 ->130 -0.24858

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2273.06566911

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 4.2746 eV 290.05 nm f=0.0191 <S**2>=0.000

126 ->128 -0.23228

126 ->130 0.11495

127 ->129 0.64198

Excited State 3: Singlet-A 4.3237 eV 286.76 nm f=0.6486 <S**2>=0.000

127 ->128 0.25340

127 ->130 0.64431

Excited State 4: Singlet-A 4.5195 eV 274.33 nm f=0.0010 <S**2>=0.000

126 ->128 0.61321

126 ->130 -0.19525

127 ->129 0.26393

Excited State 5: Singlet-A 4.6378 eV 267.33 nm f=0.0463 <S**2>=0.000

124 ->128 -0.19924

126 ->130 -0.14930

127 ->131 0.63069

Excited State 6: Singlet-A 4.6877 eV 264.49 nm f=0.3684 <S**2>=0.000

125 ->128 0.10755

126 ->129 0.68583

Excitation energies and oscillator strengths of **5a**:

Excited State 1: Singlet-A 3.7734 eV 328.57 nm f=0.2813 <S**2>=0.000

137 ->138 0.68980

137 ->140 -0.13498

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -2993.25858826

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.9716 eV 312.18 nm f=0.0221 <S**2>=0.000

136 ->138 -0.16737

137 ->139 0.67274

Excited State 3: Singlet-A 4.1034 eV 302.15 nm f=0.6966 <S**2>=0.000

136 ->139 0.25461

137 ->138 0.12544

137 ->140 0.63777

Excited State 4: Singlet-A 4.1114 eV 301.56 nm f=0.0214 <S**2>=0.000

136 ->138 0.66571

136 ->140 -0.11418

137 ->139 0.17922

Excited State 5: Singlet-A 4.2633 eV 290.82 nm f=0.1599 <S**2>=0.000

136 ->139 0.64658

137 ->140 -0.24186

Excited State 6: Singlet-A 4.4682 eV 277.48 nm f=0.0792 <S**2>=0.000

136 ->138 0.12035

136 ->140 0.57064

137 ->141 0.35803

Excitation energies and oscillator strengths of **6a**:

Excited State 1: Singlet-A 3.4830 eV 355.97 nm f=1.2730 <S**2>=0.000

168 ->171 0.14252

169 ->170 0.68892

This state for optimization and/or second-order correction.

Total Energy, E(TD-HF/TD-KS) = -3376.66378857

Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State 2: Singlet-A 3.6500 eV 339.69 nm f=0.0458 <S**2>=0.000

169 ->171 0.69660

Excited State 3: Singlet-A 3.7930 eV 326.87 nm f=0.0276 <S**2>=0.000

168 ->170 0.69453

Excited State 4: Singlet-A 3.8063 eV 325.74 nm f=0.6389 <S**2>=0.000

168 ->171 0.53399

169 ->172 0.44050

Excited State 5: Singlet-A 3.9446 eV 314.32 nm f=0.0293 <S**2>=0.000

168 ->171 -0.42783

169 ->170 0.10694

169 ->172 0.53521

Excited State 6: Singlet-A 4.1969 eV 295.42 nm f=0.0259 <S**2>=0.000

168 ->172 0.66245

169 ->173 0.16215

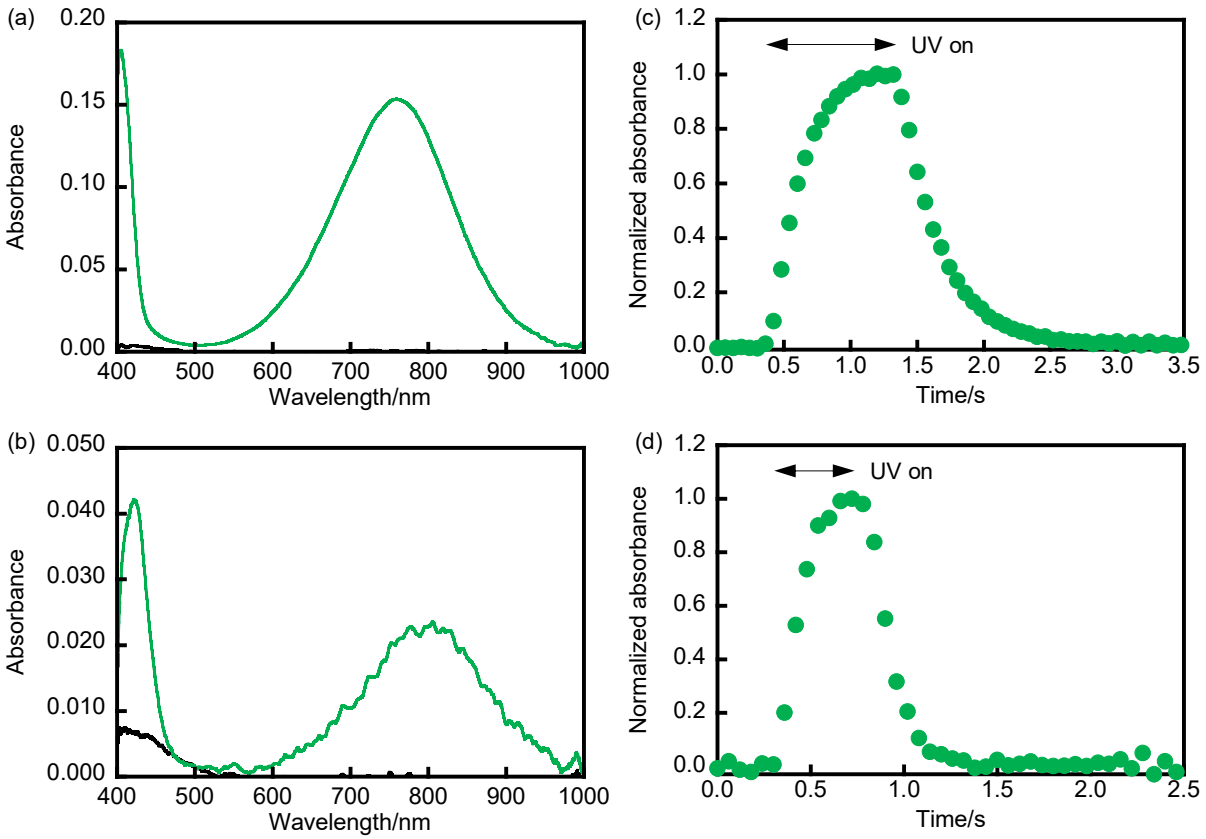

Figure S1. Absorption spectra of (a) **5b** ([**5a**] = 9.8 × 10^{-5} M) and (b) **6b** ([**6a**] = 4.2 × 10^{-5} M) in THF upon irradiation with 313 nm light at 298 K (69 mW cm^{-2}) and absorbance change of (c) **5b** and (d) **6b** in THF relative to time upon irradiation with 313 nm light (69 mW cm^{-2}) for 0.7 s (**5b**) and 0.3 s (**6b**) and thermal bleaching at 298 K. The data points of each absorbance were averaged over the data from 740 to 770 nm (**5b**) and from 775 to 805 nm (**6b**) and were recorded at 60 ms intervals for **5b** and **6b**.

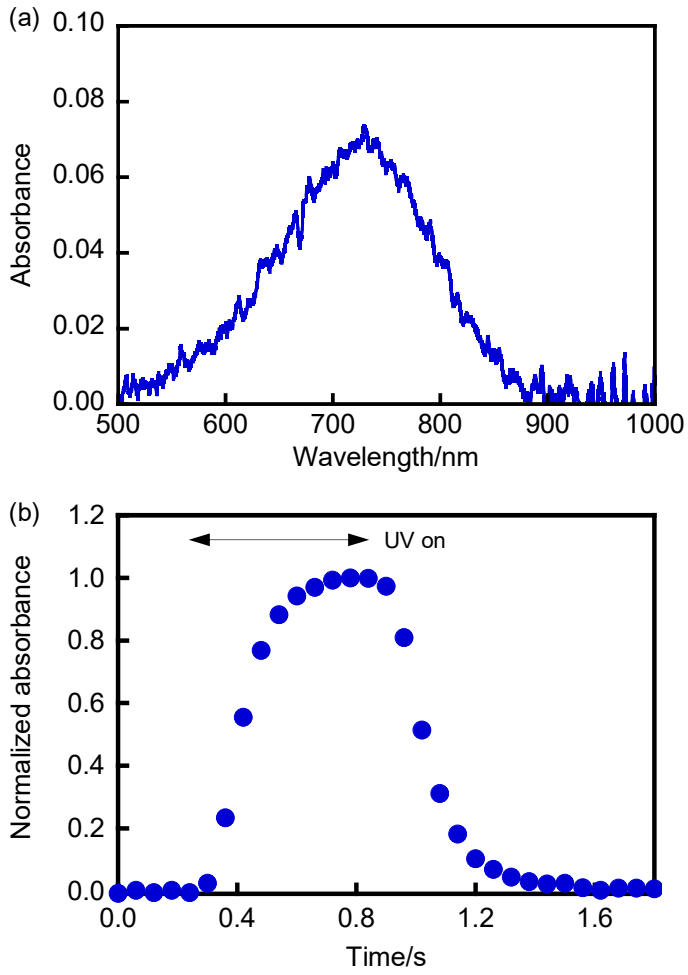

Figure S2. (a) Absorption spectra of **1b** in THF ([**1a**] = 3.8×10^{-5} M) upon irradiation with 313 nm light at 298 K (69 mW cm^{-2}) and (b) absorbance change of **1b** in THF relative to time upon irradiation with 313 nm light (69 mW cm^{-2}) for 0.4 s and thermal bleaching at 298 K. The data points of each absorbance were averaged over the data from 710 to 740 nm and were recorded at 60 ms intervals.

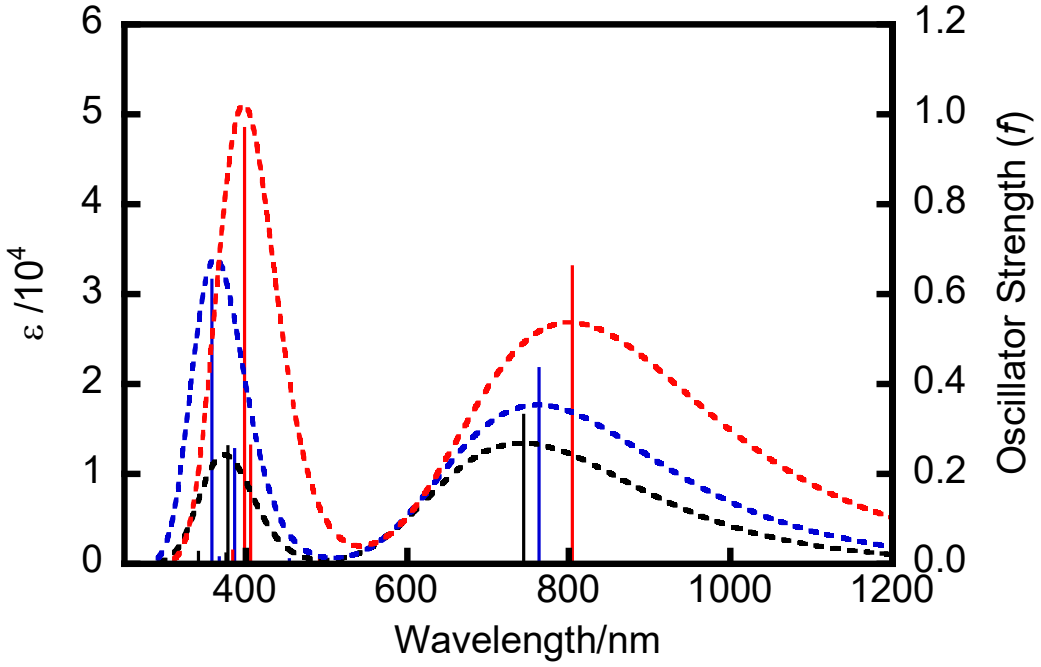

Figure S3. Calculated absorption spectra of **1b** (black), **5b** (blue), and **6b** (red) by TD-DFT (MPW1PW91/6-31G(d)//M06-2X/6-31G(d) level of the theory), modeled with a HWHM of 2000 cm^{-1}.

Table S3. Oscillator strength of **1b**, **5b**, and **6b** calculated by time−dependent density functional theory (TD−DFT) at the MPW1PW91/6−31G(d)//M06-2X/6−31G(d) level.

1b		**5b**		**6b**	
Wavelength /nm	Oscillator Strength	Wavelength /nm	Oscillator Strength	Wavelength /nm	Oscillator Strength
741.6	0.330	761.1	0.434	801.0	0.660
428.6	0.001	452.0	0.006	488.1	0.016
375.7	0.260	389.7	0.003	421.6	0.001
373.7	0.020	383.9	0.253	402.8	0.261
357.1	0.006	364.6	0.015	396.3	0.968
339.5	0.026	355.9	0.632	381.0	0.030

Table S4. HOMO and LUMO level data of the 1,2-diarylbenzenes calculated by DFT at the M06-2X/6-31G(d) level

Compound	E_{HOMO}/eV	E_{LUMO}/eV	$E_{HOMO-LUMO}$/eV
1b	−0.20479	−0.07654	−0.12825
5b	−0.19969	−0.07679	−0.12290
6b	−0.20060	−0.08152	−0.11908

Kinetic analysis of thermal back-reaction

The reaction kinetics of the thermal back-reaction was analyzed as follows: If the thermal back-reaction from the closed-ring isomer to the open-ring isomer obey a first-order kinetics, the kinetic equation is expressed as following equation by using Lambert-Beer law.

$$\ln\frac{A_t}{A_0} = -kt$$

where k is reaction rate constant, t is reaction time, and A_0 and A_t are absorbance of the closed-ring isomer at initial state (t = 0 s) and at arbitrary reaction time t, respectively. The k value can be calculated from the slope of the linear plot. The calculated k values are summarized in Table S5 and S6.

Arrhenius equation can be described as follows.

$$\ln k = \ln A - \frac{E_a}{RT}$$

where A is frequency factor, E_a is activation energy, R is gas constant, and T is absolute temperature. The linear relationship can be obtained by plotting ln$k$ relative to 1/T as shown in Figure 6. The E_a and A values can be determined from the slope and intercept of the linear plot. The results are summarized in Table 4.

Eyring equation can be described as follows.

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\ddagger}}{R}\frac{1}{T} + ln\frac{k_B}{h} + \frac{\Delta S^{\ddagger}}{R}$$

where $\Delta H^{\ddagger}$ is enthalpy of activation, $\Delta S^{\ddagger}$ is entropy of activation, and k_B is Boltzmann constant. The linear relationship can be obtained by plotting ln(k/T) relative to $1/T$ as shown in Figures S5–S7. The $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ values can be determined from the slope and intercept of the linear plot. The Gibbs energy of activation ($\Delta G^{\ddagger}$) was also determined using the relationship of $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$. The results are summarized in Table S8.

Table S5. First-order rate constants for the thermal back-reaction of **5b**.

T/K	k/s^{-1}
238	0.002630
233	0.001267
228	0.000591
223	0.000267

Table S6. First-order rate constants for the thermal back-reaction of **6b**.

T/K	k/s^{-1}
228	0.003179
223	0.001542
218	0.000746
213	0.000304

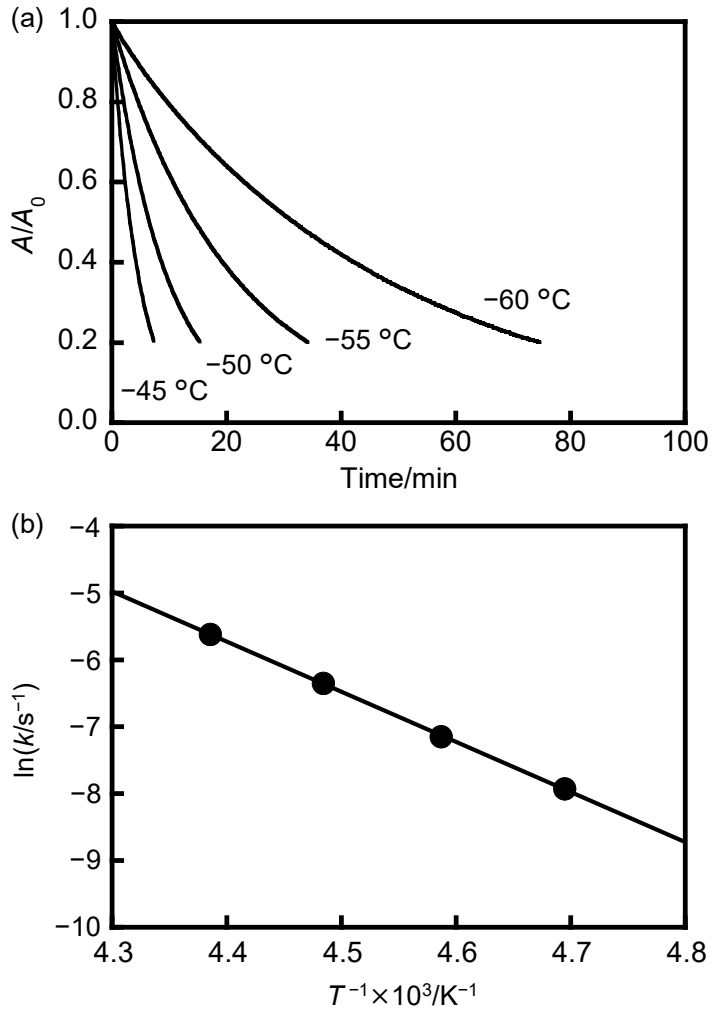

Figure S4. (a) Absorption decay curves at λ_{max} for **1b** in THF at various temperatures and (b) temperature dependence of the rate constant (k) for thermal back-reaction of **1b**.

Table S7. First-order rate constants for the thermal back-reaction of **1b**.

T/K	k/s^{-1}
228	0.003624
223	0.001750
218	0.000787
213	0.000361

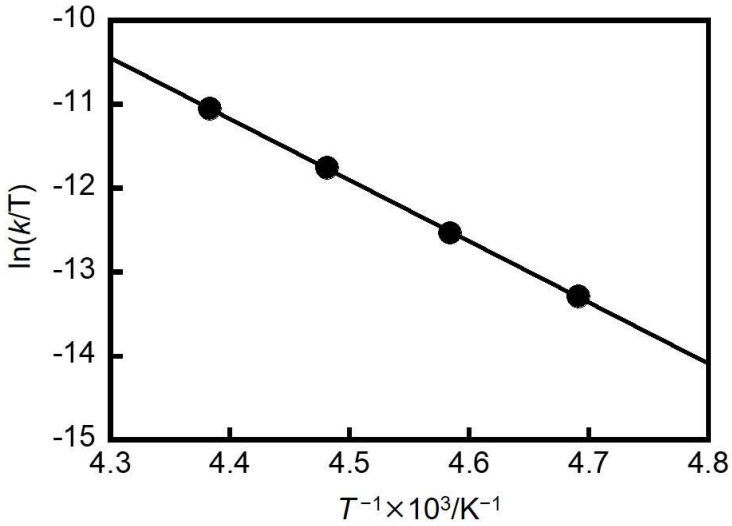

Figure S5. Eyring plot for the thermal back-reaction of **1b**.

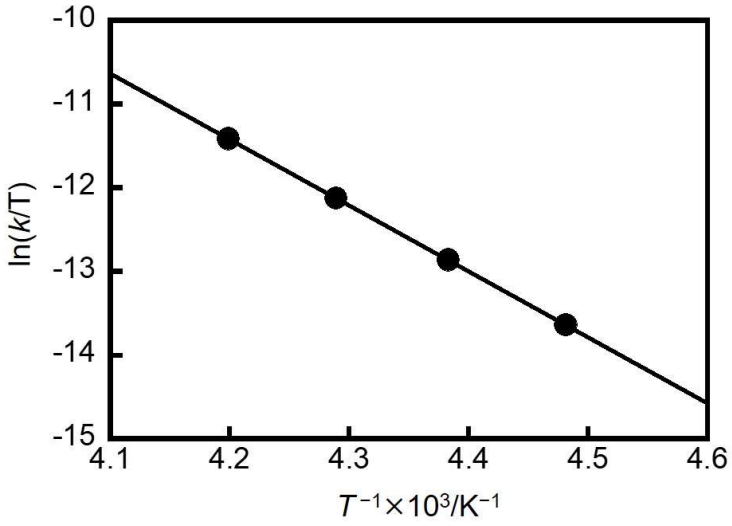

Figure S6. Eyring plot for the thermal back-reaction of **5b**.

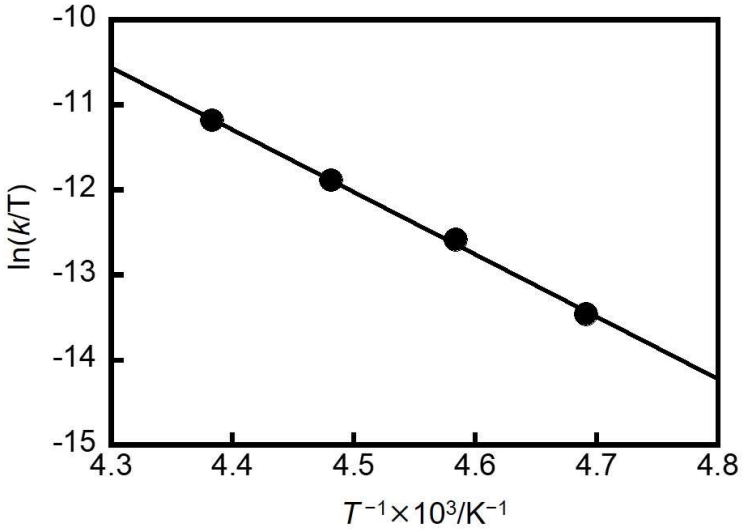

Figure S7. Eyring plot for the thermal back-reaction of **6b**.

Table S8. $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$. and $\Delta G^{\ddagger}$ values for **1**, **5**, and **6** estimated from the Eyring plot.

Compound	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}	$\Delta G^{\ddagger}$/kJ mol^{-1} at 25 °C
1	60.6	−23.9	67.7
5	65.5	−17.5	70.7
6	61.0	−22.9	67.8

Table S9. Cartesian coordinates of **1a** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.653589	1.686643	0.269377
C	0.653587	1.686641	-0.269374
C	1.272635	2.913970	-0.506794
C	0.644333	4.124730	-0.254271
C	-0.644332	4.124732	0.254266
C	-1.272635	2.913974	0.506793
C	-1.419057	0.456306	0.580414
C	-2.736745	0.230660	0.064073
C	-3.262928	-0.980078	0.409719
H	-3.248249	0.938963	-0.578981
C	1.419053	0.456302	-0.580408
C	2.736741	0.230657	-0.064067
C	3.262928	-0.980078	-0.409718
H	3.248244	0.938960	0.578988
S	-2.140847	-1.855340	1.409031
S	2.140847	-1.855341	-1.409029
C	-0.965467	-0.587451	1.346590
C	0.965466	-0.587453	-1.346589
C	0.328279	-0.733005	2.085862

H	1.033447	-1.371447	1.540968
H	0.797322	0.245737	2.215882
H	0.166211	-1.169064	3.075905
C	-0.328280	-0.733007	-2.085862
H	-1.033453	-1.371439	-1.540962
H	-0.797317	0.245737	-2.215891
H	-0.166213	-1.169078	-3.075899
F	-2.507548	2.959801	1.015461
F	-1.263539	5.273577	0.507396
F	1.263543	5.273573	-0.507405
F	2.507548	2.959793	-1.015462
C	4.569034	-1.544155	-0.041243
C	4.755933	-2.926235	0.080233
C	5.654116	-0.693454	0.205872
C	5.994271	-3.443753	0.442777
H	3.919546	-3.598449	-0.093899
C	6.887625	-1.212637	0.579642
H	5.529706	0.378320	0.081340
C	7.063637	-2.589537	0.698534
C	-4.569033	-1.544156	0.041243
C	-4.755930	-2.926236	-0.080240
C	-5.654117	-0.693456	-0.205866

C	-5.994268	-3.443755	-0.442784
H	-3.919542	-3.598449	0.093889
C	-6.887626	-1.212640	-0.579637
H	-5.529709	0.378318	-0.081329
C	-7.063636	-2.589539	-0.698536
H	-8.029196	-2.993711	-0.985920
H	8.029198	-2.993708	0.985918
H	-7.718312	-0.539073	-0.767090
H	-6.121025	-4.518158	-0.534347
H	6.121030	-4.518156	0.534335
H	7.718310	-0.539070	0.767099

Table S10. Cartesian coordinates of **1b** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.740019	1.767262	-0.000393
C	0.740020	1.767264	0.000395
C	1.396598	3.049966	0.103103
C	0.716290	4.212823	0.059481
C	-0.716299	4.212820	-0.059481
C	-1.396602	3.049961	-0.103102
C	-1.427705	0.582406	0.119438
C	-2.834236	0.312933	0.074410
C	-3.160515	-1.007519	0.053503
H	-3.582487	1.089333	0.004798
C	1.427707	0.582408	-0.119435
C	2.834238	0.312934	-0.074409
C	3.160517	-1.007518	-0.053501
H	3.582490	1.089333	-0.004799
S	-1.763637	-2.089238	0.056274
C	-0.630435	-0.681282	0.430823
C	0.630438	-0.681281	-0.430818
C	-0.351181	-0.696146	1.949679
H	0.166792	-1.609661	2.246423
H	0.258432	0.166720	2.232853

H	-1.305917	-0.642225	2.478292
C	0.351181	-0.696142	-1.949673
H	-0.166769	-1.609668	-2.246422
H	-0.258455	0.166711	-2.232840
H	1.305915	-0.642193	-2.478288
F	-2.731952	3.096112	-0.195721
F	-1.330140	5.392142	-0.122753
F	1.330127	5.392147	0.122753
F	2.731948	3.096125	0.195724
C	4.514208	-1.570514	-0.007858
C	4.732094	-2.883125	0.430901
C	5.618942	-0.801568	-0.404272
C	6.017906	-3.407864	0.485239
H	3.890082	-3.493823	0.745364
C	6.902262	-1.327435	-0.347246
H	5.465399	0.204777	-0.781080
H	6.168315	-4.425062	0.832918
H	7.745731	-0.720432	-0.660948
C	-4.514206	-1.570516	0.007857
C	-4.732087	-2.883131	-0.430892
C	-5.618943	-0.801568	0.404257
C	-6.017898	-3.407873	-0.485234

H	-3.890072	-3.493831	-0.745344
C	-6.902262	-1.327437	0.347227
H	-5.465405	0.204780	0.781057
H	-6.168304	-4.425074	-0.832905
H	-7.745734	-0.720433	0.660918
S	1.763639	-2.089237	-0.056271
C	7.107388	-2.632141	0.098813
H	8.111318	-3.042901	0.139557
C	-7.107384	-2.632147	-0.098822
H	-8.111313	-3.042908	-0.139569

Table S11. Cartesian coordinates of transition state of **1** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.635212	1.865161	0.324418
C	-0.635222	1.865170	-0.324453
C	-1.224100	3.083997	-0.624799
C	-0.615738	4.299243	-0.312671
C	0.615739	4.299235	0.312671
C	1.224095	3.083982	0.624782
C	1.316281	0.590981	0.608983
C	2.669078	0.341280	0.385600
C	3.029334	-0.998425	0.469726
H	3.378366	1.117262	0.115005
C	-1.316298	0.590998	-0.609040
C	-2.669091	0.341295	-0.385640
C	-3.029352	-0.998408	-0.469794
H	-3.378373	1.117273	-0.115017
S	1.646679	-1.986274	0.886428
S	-1.646707	-1.986248	-0.886547
C	0.524807	-0.600720	0.832969
C	-0.524829	-0.600699	-0.833061
C	-0.511118	-0.637139	1.940661
H	-0.003942	-0.669522	2.908466

H	-1.136655	0.257180	1.912994
H	-1.154601	-1.518376	1.856209
C	0.511095	-0.637098	-1.940754
H	0.003921	-0.669430	-2.908562
H	1.136655	0.257205	-1.913050
H	1.154557	-1.518353	-1.856337
F	2.410617	3.134647	1.239127
F	1.214845	5.445783	0.618920
F	-1.214837	5.445799	-0.618904
F	-2.410621	3.134676	-1.239143
C	4.308436	-1.591871	0.207882
C	4.652821	-2.924524	0.216792
C	6.020065	-3.150262	-0.096077
H	3.942969	-3.714150	0.438710
C	6.722276	-2.004207	-0.341125
H	6.476195	-4.133321	-0.139286
C	-4.308446	-1.591858	-0.207924
C	-4.652855	-2.924505	-0.216954
C	-6.020075	-3.150255	0.096012
H	-3.943040	-3.714118	-0.439031
C	-6.722242	-2.004215	0.341259
H	-6.476220	-4.133309	0.139144

S	5.697673	-0.610975	-0.193130
S	-5.697628	-0.610985	0.193334
C	8.170106	-1.859796	-0.691835
H	8.710778	-1.274544	0.058990
H	8.631476	-2.848826	-0.748282
H	8.304468	-1.366598	-1.659847
C	-8.170039	-1.859820	0.692115
H	-8.710777	-1.274503	-0.058612
H	-8.631411	-2.848851	0.748524
H	-8.304307	-1.366699	1.660179

Table S12. Cartesian coordinates of **5a** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.632026	1.772497	-0.316772
C	-0.632020	1.772583	0.316784
C	-1.232798	2.999430	0.598259
C	-0.624289	4.209799	0.299816
C	0.624479	4.209715	-0.300082
C	1.232895	2.999266	-0.598386
C	1.365865	0.539356	-0.688601
C	2.721959	0.306865	-0.286920
C	3.212269	-0.900150	-0.694699
H	3.307155	1.024411	0.278814
C	-1.365953	0.539539	0.688753
C	-2.722043	0.307064	0.287052
C	-3.212393	-0.899912	0.694900
H	-3.307195	1.024553	-0.278798
S	2.004843	-1.770909	-1.594632
S	-2.005065	-1.770590	1.595036
C	0.849196	-0.491176	-1.431995
C	-0.849347	-0.490935	1.432271
C	-0.497265	-0.621373	-2.073344
H	-1.156222	-1.279132	-1.494867

H	-0.977338	0.358329	-2.139289
H	-0.409540	-1.028909	-3.084621
C	0.497103	-0.621117	2.073644
H	1.156003	-1.279058	1.495307
H	0.977264	0.358554	2.139381
H	0.409346	-1.028434	3.085008
F	2.427816	3.044895	-1.193612
F	1.223557	5.358797	-0.596004
F	-1.223279	5.358961	0.595599
F	-2.427716	3.045221	1.193478
C	4.524188	-1.478451	-0.456176
C	5.188784	-2.430061	-1.180557
C	6.467420	-2.750363	-0.637873
H	4.783275	-2.870003	-2.085315
C	6.772370	-2.045559	0.489821
H	7.146316	-3.474778	-1.074387
C	-4.524298	-1.478221	0.456309
C	-5.189178	-2.429426	1.180958
C	-6.467692	-2.749878	0.638070
H	-4.783952	-2.868964	2.086039
C	-6.772276	-2.045577	-0.490040
H	-7.146761	-3.474043	1.074732

C	-8.019624	-2.108611	-1.316290
H	-8.698498	-2.854385	-0.895429
H	-8.540985	-1.146180	-1.333429
H	-7.804812	-2.390471	-2.351942
C	8.019936	-2.108309	1.315766
H	8.698636	-2.854331	0.895063
H	8.541382	-1.145915	1.332319
H	7.805376	-2.389675	2.351604
S	-5.471600	-0.979237	-0.916025
S	5.471900	-0.978914	0.915661

Table S13. Cartesian coordinates of **5b** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.003217	-0.739112	1.797720
C	0.003217	0.739112	1.797720
C	0.104648	1.395598	3.079397
C	0.060594	0.715732	4.243184
C	-0.060594	-0.715732	4.243184
C	-0.104648	-1.395598	3.079397
C	0.109011	-1.429910	0.612020
C	0.076152	-2.834713	0.346276
C	0.058240	-3.159265	-0.977138
H	0.050332	-3.588278	1.122394
C	-0.109011	1.429910	0.612020
C	-0.076152	2.834713	0.346276
C	-0.058240	3.159265	-0.977138
H	-0.050332	3.588278	1.122394
S	0.033045	-1.762250	-2.059560
C	0.426110	-0.634074	-0.652012
C	-0.426110	0.634074	-0.652012
C	1.946374	-0.366696	-0.666534
H	2.247565	0.147750	-1.580510
H	2.233570	0.242701	0.195241

H	2.467408	-1.325495	-0.610174
C	-1.946374	0.366696	-0.666534
H	-2.247565	-0.147750	-1.580510
H	-2.233570	-0.242701	0.195241
H	-2.467408	1.325495	-0.610174
F	-0.201742	-2.730457	3.124098
F	-0.125849	-1.330486	5.422066
F	0.125849	1.330486	5.422066
F	0.201742	2.730457	3.124098
S	-0.033045	1.762250	-2.059560
C	0.038276	-4.482971	-1.553443
C	0.084851	-4.820649	-2.883303
C	0.049333	-6.223685	-3.104267
H	0.153979	-4.081949	-3.674556
C	-0.023737	-6.952513	-1.950244
H	0.079378	-6.684009	-4.085538
C	-0.038276	4.482971	-1.553443
C	-0.084851	4.820649	-2.883303
C	-0.049333	6.223685	-3.104267
H	-0.153979	4.081949	-3.674556
C	0.023737	6.952513	-1.950244
H	-0.079378	6.684009	-4.085538

S	-0.049333	-5.914414	-0.562679
S	0.049333	5.914414	-0.562679
C	0.080526	8.440632	-1.797263
H	1.010415	8.760032	-1.316107
H	0.027258	8.911479	-2.781849
H	-0.753253	8.814761	-1.194914
C	-0.080526	-8.440632	-1.797263
H	-0.027258	-8.911479	-2.781849
H	0.753253	-8.814761	-1.194914
H	-1.010415	-8.760032	-1.316107

Table S14. Cartesian coordinates of transition state of **5** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.635212	1.865161	0.324418
C	-0.635222	1.865170	-0.324453
C	-1.224100	3.083997	-0.624799
C	-0.615738	4.299243	-0.312671
C	0.615739	4.299235	0.312671
C	1.224095	3.083982	0.624782
C	1.316281	0.590981	0.608983
C	2.669078	0.341280	0.385600
C	3.029334	-0.998425	0.469726
H	3.378366	1.117262	0.115005
C	-1.316298	0.590998	-0.609040
C	-2.669091	0.341295	-0.385640
C	-3.029352	-0.998408	-0.469794
H	-3.378373	1.117273	-0.115017
S	1.646679	-1.986274	0.886428
S	-1.646707	-1.986248	-0.886547
C	0.524807	-0.600720	0.832969
C	-0.524829	-0.600699	-0.833061
C	-0.511118	-0.637139	1.940661
H	-0.003942	-0.669522	2.908466

H	-1.136655	0.257180	1.912994
H	-1.154601	-1.518376	1.856209
C	0.511095	-0.637098	-1.940754
H	0.003921	-0.669430	-2.908562
H	1.136655	0.257205	-1.913050
H	1.154557	-1.518353	-1.856337
F	2.410617	3.134647	1.239127
F	1.214845	5.445783	0.618920
F	-1.214837	5.445799	-0.618904
F	-2.410621	3.134676	-1.239143
C	4.308436	-1.591871	0.207882
C	4.652821	-2.924524	0.216792
C	6.020065	-3.150262	-0.096077
H	3.942969	-3.714150	0.438710
C	6.722276	-2.004207	-0.341125
H	6.476195	-4.133321	-0.139286
C	-4.308446	-1.591858	-0.207924
C	-4.652855	-2.924505	-0.216954
C	-6.020075	-3.150255	0.096012
H	-3.943040	-3.714118	-0.439031
C	-6.722242	-2.004215	0.341259
H	-6.476220	-4.133309	0.139144

S	5.697673	-0.610975	-0.193130
S	-5.697628	-0.610985	0.193334
C	8.170106	-1.859796	-0.691835
H	8.710778	-1.274544	0.058990
H	8.631476	-2.848826	-0.748282
H	8.304468	-1.366598	-1.659847
C	-8.170039	-1.859820	0.692115
H	-8.710777	-1.274503	-0.058612
H	-8.631411	-2.848851	0.748524
H	-8.304307	-1.366699	1.660179

Table S15. Cartesian coordinates of **6a** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.592761	2.109981	0.385603
C	0.592756	2.109931	-0.385574
C	1.160275	3.336854	-0.728779
C	0.588904	4.547211	-0.365012
C	-0.588830	4.547260	0.364847
C	-1.160241	3.336950	0.728710
C	-1.278004	0.877651	0.841976
C	-2.674006	0.651814	0.611106
C	-3.116362	-0.554260	1.074629
H	-3.320354	1.375654	0.125454
C	1.277964	0.877548	-0.841854
C	2.673969	0.651711	-0.611009
C	3.116304	-0.554392	-1.074479
H	3.320341	1.375579	-0.125429
S	-1.811435	-1.431155	1.819544
S	1.811335	-1.431340	-1.819258
C	-0.678870	-0.155558	1.517448
C	0.678806	-0.155688	-1.517264
C	0.736494	-0.293157	1.985480
H	1.323675	-0.929837	1.313257

H	1.216152	0.688607	2.017285
H	0.776214	-0.726044	2.989152
C	-0.736564	-0.293286	-1.985282
H	-1.323769	-0.929864	-1.312984
H	-1.216183	0.688493	-2.017209
H	-0.776302	-0.726296	-2.988900
F	-2.283718	3.383958	1.450316
F	-1.154115	5.695952	0.720721
F	1.154229	5.695857	-0.720973
F	2.283757	3.383767	-1.450383
C	4.452995	-1.118442	-1.010740
C	4.991402	-2.136806	-1.754363
C	6.346347	-2.409835	-1.426840
H	4.440772	-2.652078	-2.534108
C	6.841194	-1.600654	-0.437755
H	6.950617	-3.153200	-1.934203
C	-4.453050	-1.118316	1.010859
C	-4.991500	-2.136621	1.754532
C	-6.346424	-2.409679	1.426948
H	-4.440918	-2.651825	2.534355
C	-6.841207	-1.600592	0.437754
H	-6.950725	-3.153005	1.934332

C	8.191839	-1.586720	0.139097
C	8.746193	-0.410968	0.660152
C	8.954804	-2.761712	0.170795
C	10.028316	-0.409624	1.196745
H	8.174409	0.512613	0.625340
C	10.240571	-2.755056	0.697415
H	8.524743	-3.686916	-0.201468
C	10.782382	-1.580187	1.214537
H	10.442436	0.512055	1.593673
H	10.817934	-3.674318	0.714932
H	11.784953	-1.578119	1.630503
C	-8.191809	-1.586725	-0.139200
C	-8.746147	-0.411018	-0.660375
C	-8.954749	-2.761734	-0.170876
C	-10.028228	-0.409736	-1.197066
H	-8.174382	0.512576	-0.625581
C	-10.240476	-2.755138	-0.697594
H	-8.524697	-3.686903	0.201485
C	-10.782270	-1.580315	-1.214838
H	-10.442336	0.511908	-1.594089
H	-10.817819	-3.674413	-0.715093
H	-11.784809	-1.578294	-1.630880

S	-5.616834	-0.500493	-0.120841
S	5.616842	-0.500533	0.120846

Table S16. Cartesian coordinates of **6b** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.739229	2.106424	-0.052268
C	-0.738242	2.107037	-0.047753
C	-1.395419	3.386007	-0.169780
C	-0.715067	4.550586	-0.154723
C	0.716903	4.552478	-0.045542
C	1.396923	3.389242	0.016396
C	1.428981	0.917293	-0.142668
C	2.832728	0.652572	-0.108471
C	3.157974	-0.670775	-0.061709
H	3.586130	1.429223	-0.097755
C	-1.428735	0.923612	0.095191
C	-2.833007	0.658853	0.079103
C	-3.158979	-0.664998	0.095123
H	-3.585942	1.435081	0.041398
S	1.761176	-1.752692	-0.010349
C	0.630863	-0.353297	-0.426375
C	-0.630958	-0.333389	0.434871
C	0.352850	-0.401376	-1.944103
H	-0.164794	-1.320997	-2.221780
H	-0.257232	0.454872	-2.246057

H	1.308032	-0.357902	-2.472905
C	-0.352431	-0.313884	1.953191
H	0.163966	-1.221154	2.270841
H	0.259203	0.553740	2.217037
H	-1.307285	-0.245730	2.479973
F	2.732545	3.435686	0.100439
F	1.332556	5.731829	-0.009803
F	-1.330639	5.727620	-0.238089
F	-2.730984	3.429204	-0.256347
S	-1.763062	-1.748803	0.082338
C	-4.482885	-1.238533	0.099951
C	-4.821273	-2.569239	0.184232
C	-6.952068	-1.634423	0.068218
C	-6.219245	-2.791627	0.165867
H	-4.082057	-3.357315	0.278304
H	-6.675986	-3.770252	0.257072
C	4.481802	-1.243325	-0.029970
C	4.820026	-2.576022	0.011956
C	6.218078	-2.796484	0.042020
H	4.080517	-3.369529	0.026053
C	6.951598	-1.635718	0.022449
H	6.672832	-3.778013	0.108587

S	-5.909338	-0.249104	-0.011509
S	5.909786	-0.249000	-0.041793
C	8.412091	-1.486960	0.044745
C	9.019713	-0.350544	0.592940
C	9.225635	-2.496595	-0.486298
C	10.404160	-0.228438	0.611341
H	8.402671	0.432547	1.025733
C	10.609436	-2.376431	-0.457203
H	8.765866	-3.367137	-0.944505
C	11.204394	-1.241732	0.090154
H	10.858429	0.658093	1.042658
H	11.225782	-3.166609	-0.874810
H	12.285478	-1.146644	0.107285
C	-8.412308	-1.488038	0.026219
C	-9.041925	-0.334110	0.509090
C	-9.203520	-2.517953	-0.499345
C	-10.426169	-0.214664	0.469331
H	-8.443124	0.465274	0.937673
C	-10.587577	-2.400047	-0.528379
H	-8.725640	-3.403450	-0.907745
C	-11.204550	-1.247869	-0.045719
H	-10.897482	0.685709	0.850913

H	-11.186230	-3.206283	-0.941042
H	-12.285583	-1.154823	-0.074200

Table S17. Cartesian coordinates of transition state of **6** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.614781	2.204502	0.361705
C	-0.614785	2.204504	-0.361721
C	-1.186366	3.423242	-0.693997
C	-0.597379	4.638318	-0.346646
C	0.597374	4.638316	0.346648
C	1.186361	3.423237	0.693990
C	1.274981	0.929734	0.690806
C	2.638514	0.678260	0.562461
C	2.991199	-0.662179	0.680351
H	3.366885	1.452765	0.343832
C	-1.274985	0.929739	-0.690829
C	-2.638518	0.678264	-0.562483
C	-2.991203	-0.662175	-0.680380
H	-3.366889	1.452768	-0.343848
S	1.581073	-1.647241	0.998712
S	-1.581078	-1.647235	-0.998750
C	0.468588	-0.260284	0.867393
C	-0.468593	-0.260279	-0.867424
C	-0.640302	-0.292976	1.902090
H	-0.200647	-0.337349	2.901843

H	-1.253330	0.608045	1.838851
H	-1.285199	-1.167069	1.767329
C	0.640297	-0.292963	-1.902123
H	0.200641	-0.337335	-2.901875
H	1.253321	0.608060	-1.838882
H	1.285197	-1.167055	-1.767364
F	2.336183	3.474558	1.374592
F	1.178868	5.784524	0.684515
F	-1.178873	5.784529	-0.684505
F	-2.336187	3.474567	-1.374599
C	-4.284810	-1.256194	-0.524436
C	-4.634493	-2.585651	-0.642852
C	-6.012522	-2.822109	-0.429269
H	-3.918805	-3.361820	-0.891876
C	-6.728362	-1.684320	-0.148163
H	-6.474577	-3.798894	-0.515725
C	-8.165566	-1.558255	0.116435
C	-8.855436	-0.368473	-0.150059
C	-8.878185	-2.643881	0.644100
C	-10.218724	-0.268623	0.101955
H	-8.323084	0.477154	-0.577806
C	-10.242781	-2.544864	0.884206

H	-8.350058	-3.561005	0.887209
C	-10.919120	-1.356510	0.616278
H	-10.736900	0.660740	-0.113214
H	-10.777952	-3.395544	1.295125
H	-11.984204	-1.278407	0.810140
S	-5.684596	-0.293326	-0.130990
C	4.284807	-1.256197	0.524410
C	4.634486	-2.585658	0.642803
C	6.012517	-2.822113	0.429235
H	3.918792	-3.361831	0.891800
C	6.728363	-1.684320	0.148164
H	6.474570	-3.798902	0.515677
C	8.165572	-1.558252	-0.116408
C	8.855440	-0.368478	0.150126
C	8.878197	-2.643868	-0.644088
C	10.218733	-0.268627	-0.101863
H	8.323084	0.477140	0.577884
C	10.242797	-2.544850	-0.884168
H	8.350070	-3.560984	-0.887228
C	10.919135	-1.356503	-0.616199
H	10.736909	0.660729	0.113338
H	10.777972	-3.395521	-1.295098

H	11.984222	-1.278400	-0.810040
S	5.684600	-0.293323	0.131005