Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information for

Rational design of photochromic diarylbenzene with both high photoreactivity and fast thermal back reactivity

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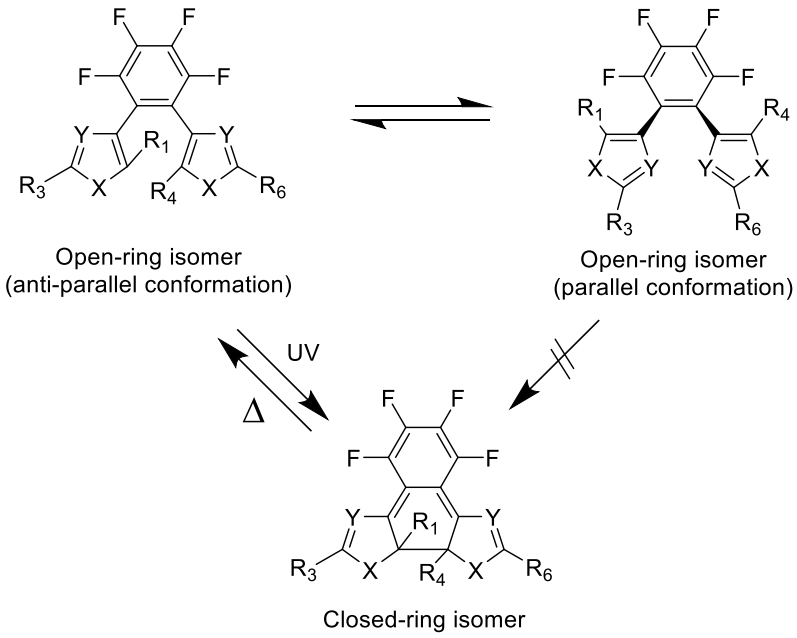

Fig. S1 Two conformations of diarylbenzene open-ring isomer with two aryl moieties in mirror symmetry and C_2 symmetry, which are called parallel and anti-parallel conformations.

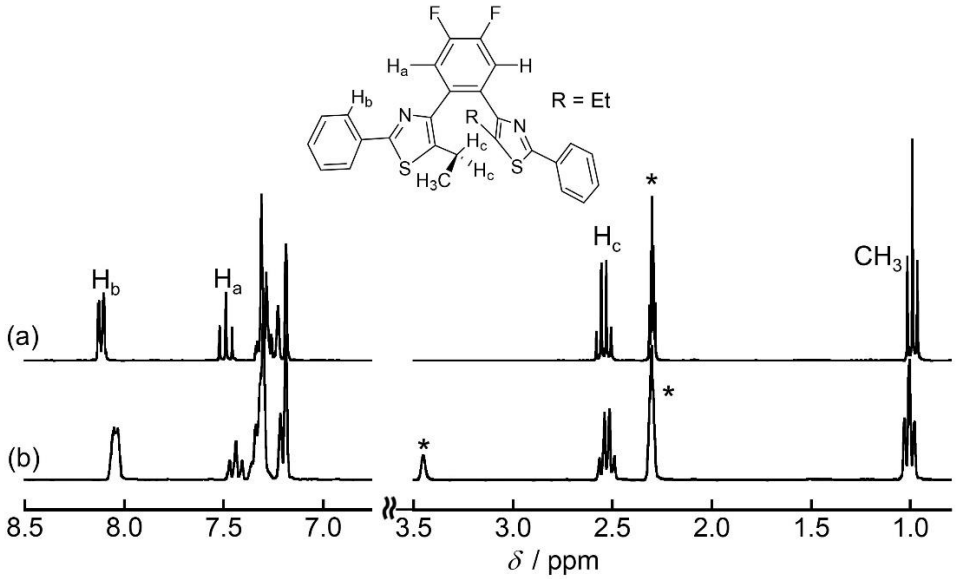

Fig. S2 ^{1}H NMR spectra of **2a** in (a) toluene-d_8 and (b) mixed solvent of toluene-d_8 and methanol-d_4 (5:1). The signals assigned to toluene and methanol was marked by asterisk.

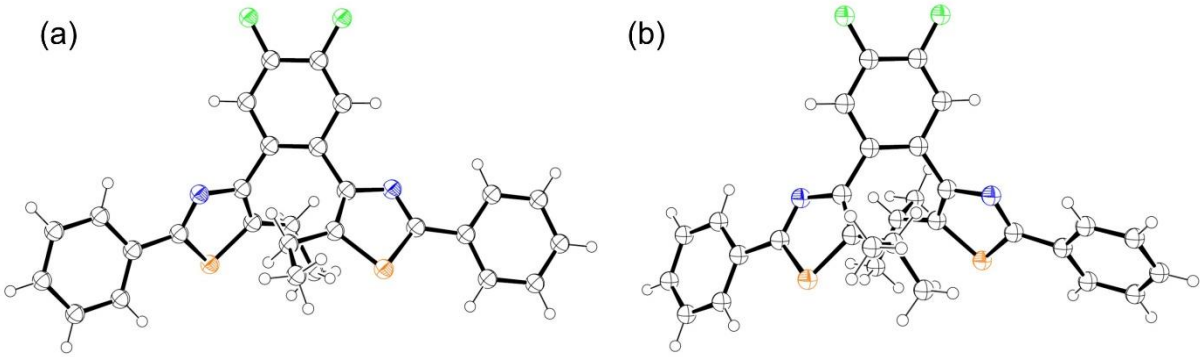

Fig. S3 ORTEP drawings (showing 50% probability displacement ellipsoids) of the open-ring isomer in (a) crystal **2a** and (b) crystal **3a**.

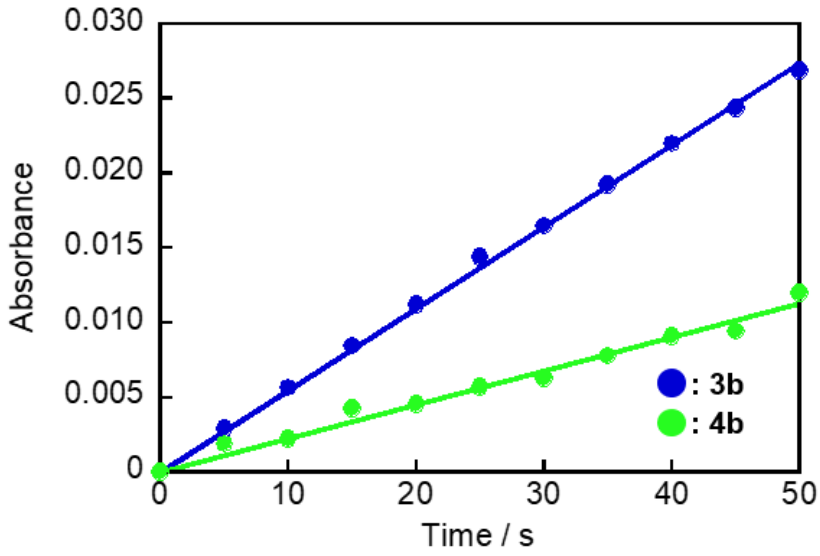

Fig. S4 Absorbance changes of **3b** (blue circle) and **4b** (green circle) at $\lambda_{max,203K}$ (718 nm for **3b**, 735 nm for **4b**) upon irradiation with 313 nm light (0.89 mW cm^{-2}) at 203 K. The initial solutions of **3a** and **4a** have the same absorbance at 313 nm (Abs_{313nm} = 0.3).

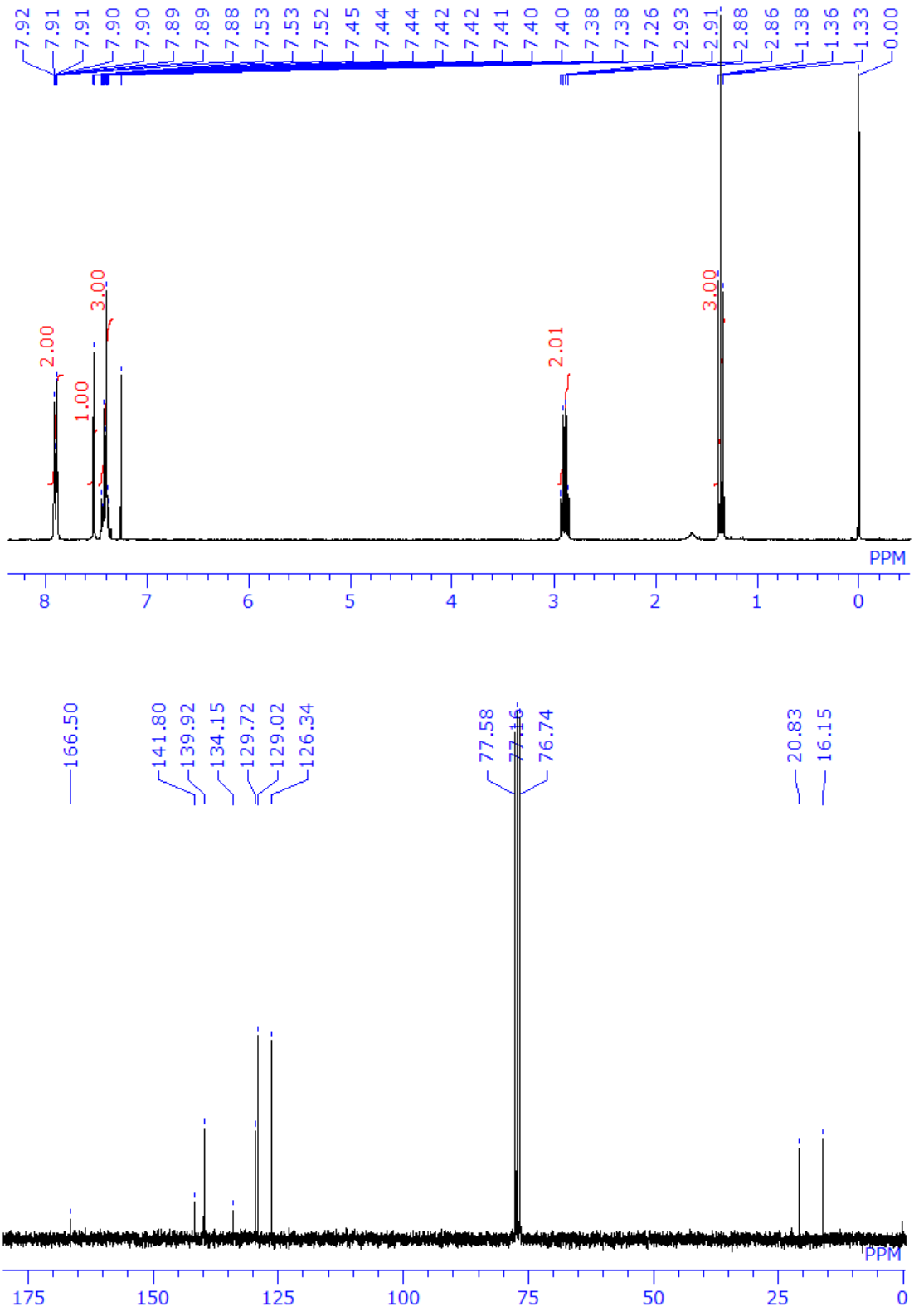

Fig. S5 ^{1}H NMR and ^{13}C NMR spectra of **9** in $CDCl_3$.

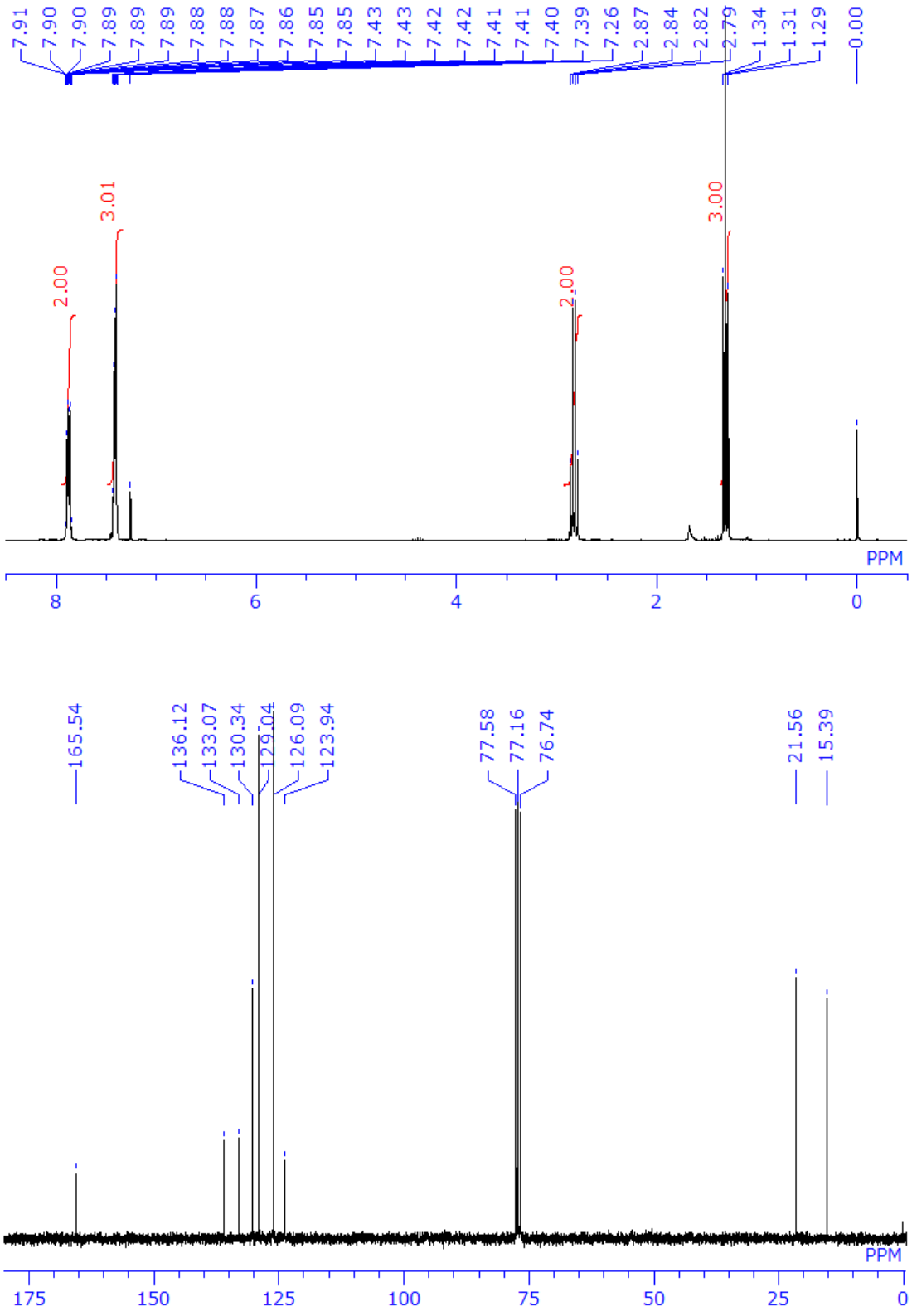

Fig. S6. ^{1}H NMR and ^{13}C NMR spectra of **11** in $CDCl_3$.

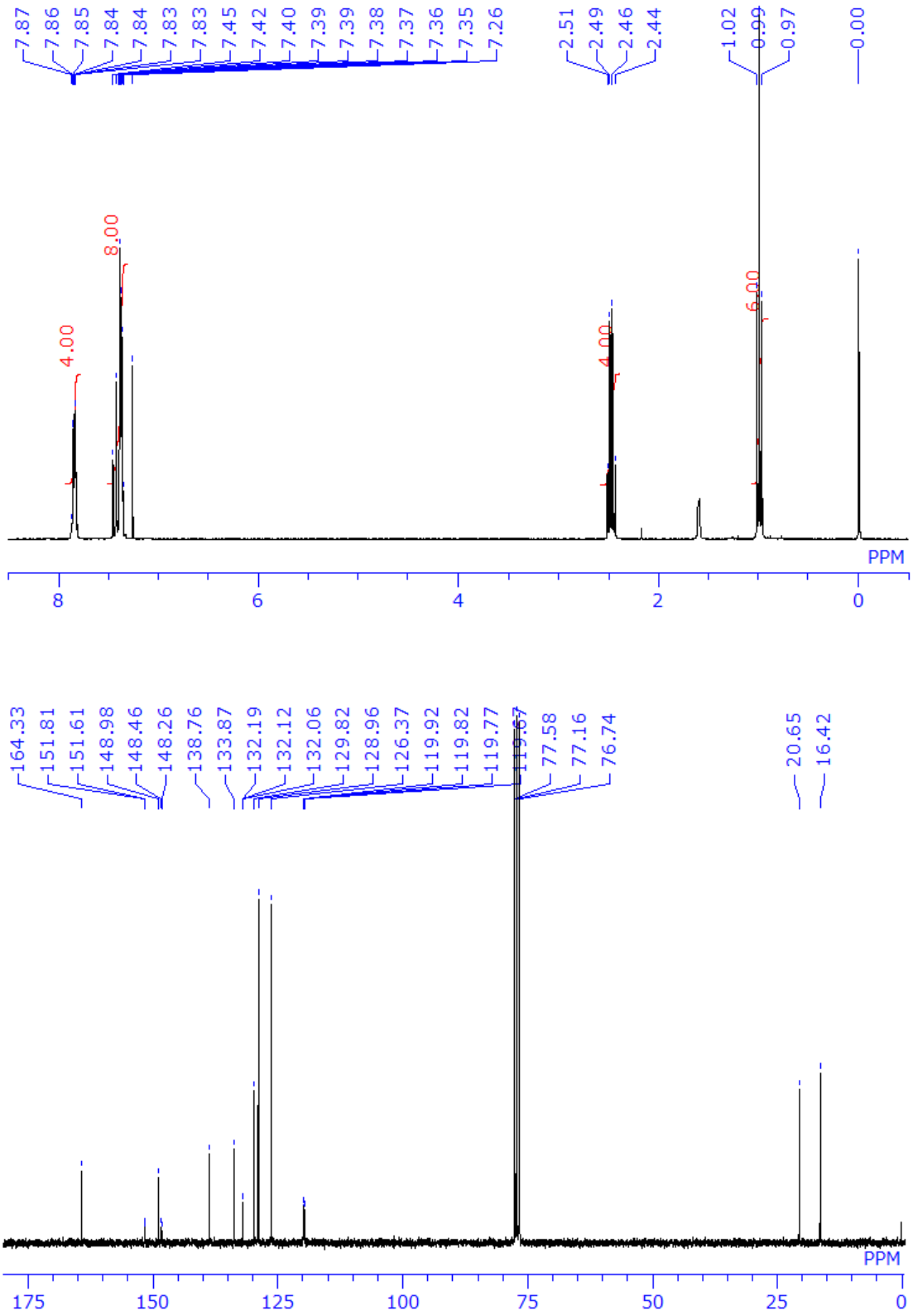

Fig. S7 ^{1}H NMR and ^{13}C NMR spectra of **2a** in $CDCl_3$.

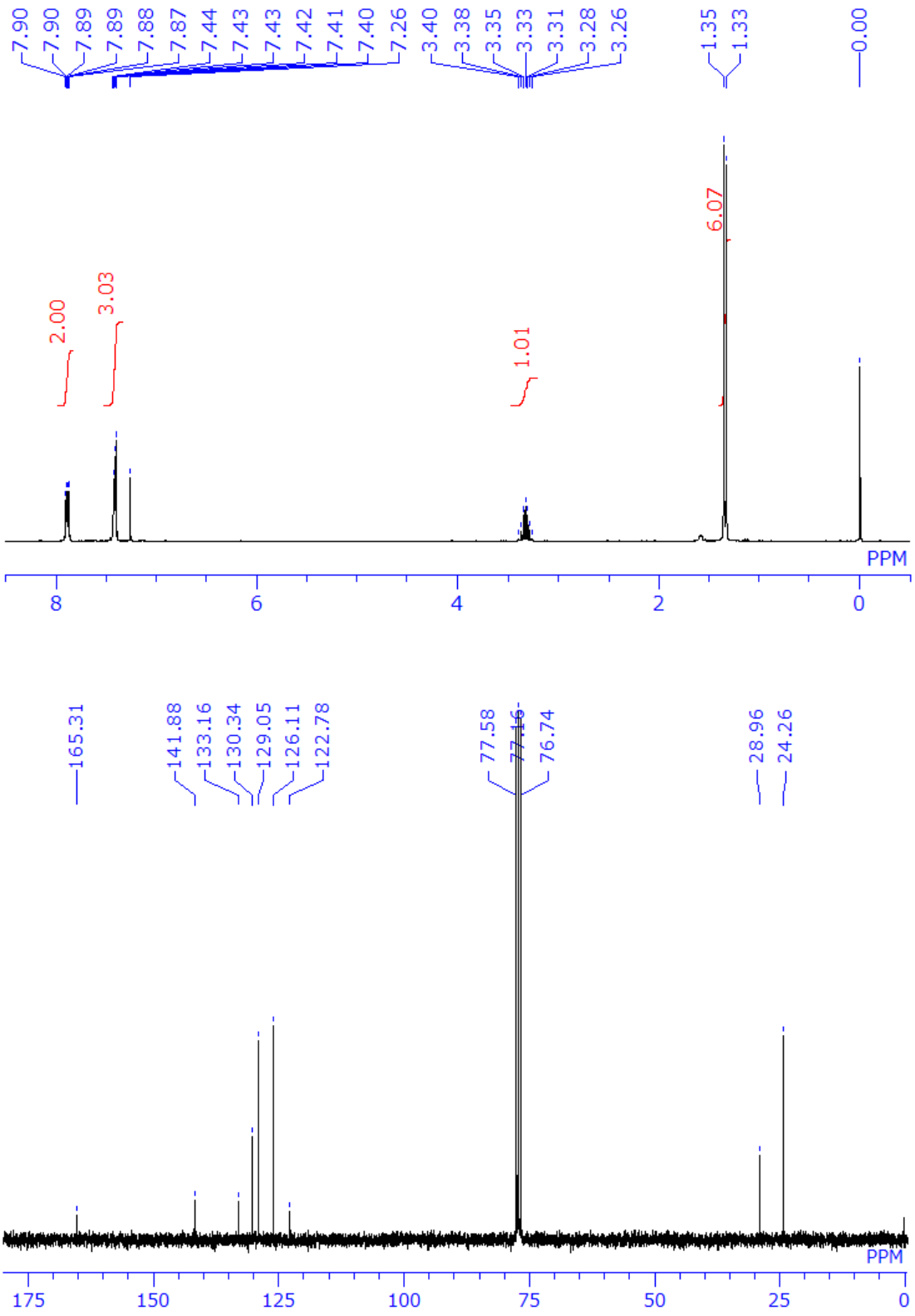

Fig. S8 ^{1}H NMR and ^{13}C NMR spectra of **12** in $CDCl_3$.

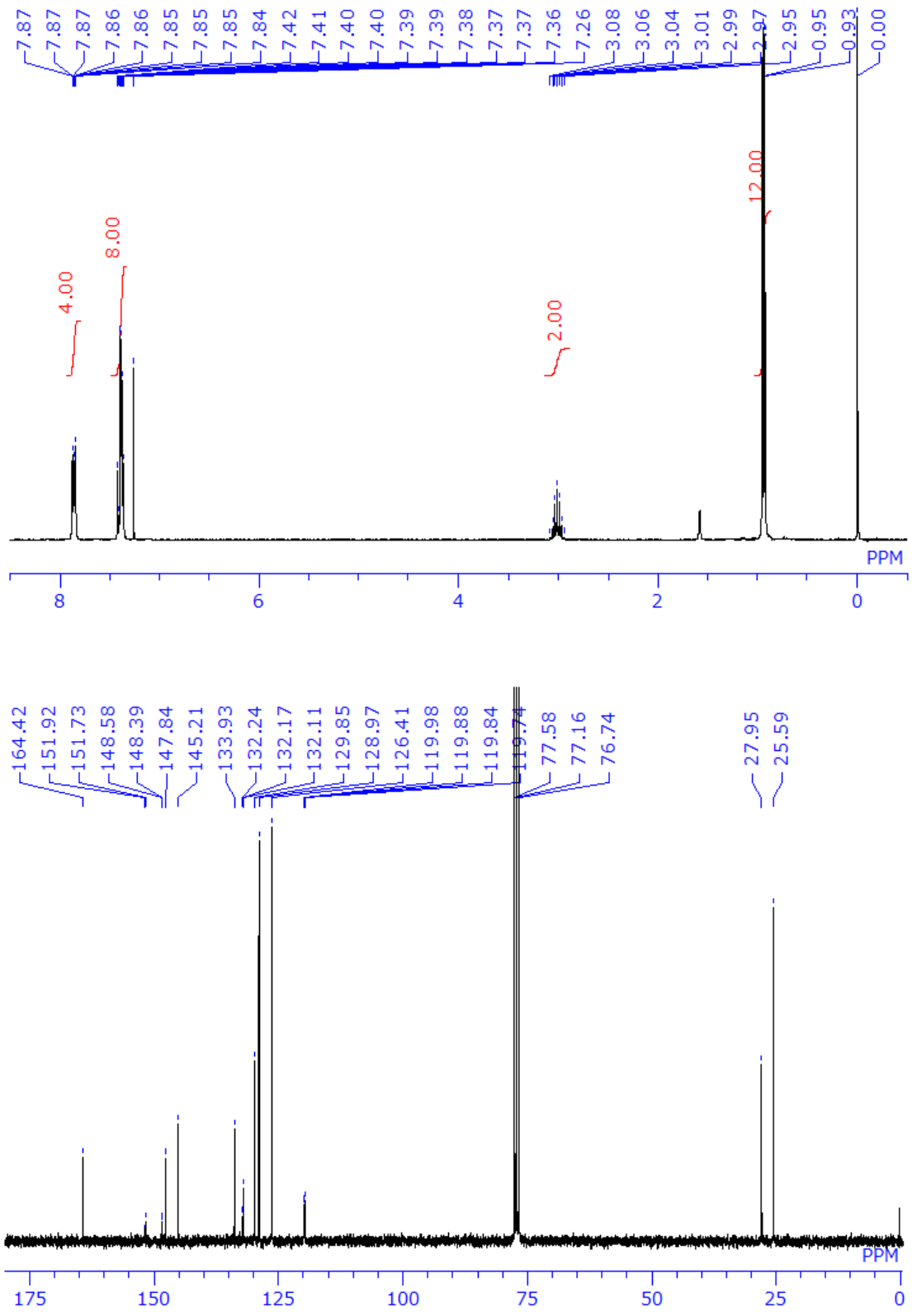

Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of **3a** in $CDCl_3$.

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 obeys a first-order kinetics, the kinetic equation is expressed as the following equation using Lambert-Beer law.

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

where k is the rate constant of the reaction, 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 S1 and S2.

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 2. The E_a and A values can be determined from the slope and intercept of the linear plot. The results are summarized in Table 2.

Table S1. First-order rate constants for the thermal back reaction in *n*-hexane of **2b**.

T/K	k/s^{-1}
293	0.012699
288	0.007206
283	0.003460
278	0.001874
273	0.000979

Table S2. First-order rate constants for the thermal back reaction in crystal of **3b**.

T/K	k/s^{-1}
263	0.033965
258	0.018694
253	0.009818
248	0.005261
243	0.002662

Table S3. Relative initial slope of the absorbance change against the UV irradiation time and the estimated photocyclization quantum yield for DABs **1**–**4**. The relative initial slope was calculated using the slope of **1** as a standard.

Compound	Initial slope	$\Phi_{o\rightarrow c}$
1	1	0.91
2	0.928	0.84
3	0.917	0.83
4	0.344	0.34

Table S4. X-ray crystallographic data for **2a** and **3a**.

	2a	**3a**
Formula	$C_{28}H_{22}F_2N_2S_2$	$C_{30}H_{26}F_2N_2S_2$
Formula weight	488.60	516.65
Temperature/K	150(2)	150(2)
Crystal system	Triclinic	Monoclinic
Space group	*P*–1	$P2_1/c$
a/Å	7.83940(10)	9.0824(5)
b/Å	12.4027(5)	19.6538(9)
c/Å	12.7386(6)	15.2420(8)
α/deg	74.717(4)	90
β/deg	83.855(2)	99.908(2)
γ/deg	89.388(2)	90
Volume/Å^3	1187.71(8)	2680.2(2)
Z	2	4
Density/g cm^{-3}	1.366	1.280
Goodness-of-fit on F^2	1.047	1.056
R ($I > 2\sigma(I)$)	$R_1 = 0.0375$	$R_1 = 0.0485$
R (all data)	$wR_2 = 0.0963$	$wR_2 = 0.1152$
CCDC No.	2105051	2105052

Table S5. Cartesian coordinates of **2a** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.65592	1.783588	0.252601
C	0.655903	1.783715	-0.25253
C	1.312689	3.004379	-0.45988
C	0.659847	4.194933	-0.22197
C	-0.66015	4.194816	0.2224
C	-1.31285	3.004151	0.460127
C	-1.39923	0.547091	0.594178
C	-3.22951	-0.70087	0.501137
C	1.399305	0.547323	-0.59426
C	3.229557	-0.70067	-0.5012
S	-2.17505	-1.69828	1.473705
S	2.17506	-1.69808	-1.47374
C	-0.93633	-0.49052	1.361456
C	0.936385	-0.49027	-1.36154
C	0.383248	-0.65846	2.055547
H	1.021132	-1.33688	1.472263
H	0.890475	0.311714	2.052284
C	-0.38311	-0.65815	-2.0558
H	-1.0208	-1.33724	-1.47308
H	-0.89067	0.311842	-2.05188

F	-1.27102	5.364612	0.427479
F	1.27058	5.364832	-0.42686
C	4.594962	-1.1136	-0.13961
C	5.147456	-2.31407	-0.59534
C	5.356838	-0.27652	0.684261
C	6.440617	-2.67369	-0.23292
H	4.569137	-2.97257	-1.23868
C	6.648559	-0.63935	1.042937
H	4.916512	0.652107	1.031194
C	7.194831	-1.83802	0.586796
H	6.859561	-3.60788	-0.59313
H	7.232478	0.015697	1.681957
C	-4.59494	-1.11375	0.139576
C	-5.14735	-2.31436	0.595051
C	-5.35693	-0.27649	-0.68401
C	-6.44054	-2.67392	0.232672
H	-4.56893	-2.97302	1.238142
C	-6.64867	-0.63927	-1.04265
H	-4.91666	0.65224	-1.03075
C	-7.19486	-1.83807	-0.58675
H	-6.85941	-3.60822	0.592682
H	-7.23267	0.01592	-1.68145

H	2.334684	3.021002	-0.8224
H	-2.33485	3.020604	0.822653
N	2.691	0.422143	-0.13146
N	-2.69093	0.421932	0.131379
H	-8.20454	-2.11942	-0.86887
H	8.204487	-2.11942	0.868952
C	-0.25411	-1.17509	-3.49066
H	0.186308	-2.17711	-3.51629
H	-1.23814	-1.23138	-3.96273
H	0.37926	-0.51298	-4.08771
C	0.254585	-1.17655	3.490013
H	-0.18544	-2.17877	3.514908
H	1.238691	-1.23286	3.961921
H	-0.37896	-0.51516	4.087676

Table S6. Cartesian coordinates of **2b** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.735049	1.796835	-0.00787
C	-0.73505	1.796835	0.00788
C	-1.43176	3.061903	-0.07951
C	-0.72303	4.202827	-0.04839
C	0.723025	4.202828	0.048391
C	1.431754	3.061903	0.079521

C	1.399908	0.609483	-0.12831
C	3.145839	-0.75068	0.012739
C	-1.39991	0.609481	0.128322
C	-3.14584	-0.75068	-0.01277
S	1.857203	-1.98622	0.019594
S	-1.85721	-1.98622	-0.01962
C	0.637062	-0.684	-0.43175
C	-0.63706	-0.684	0.431744
C	0.338867	-0.76004	-1.95475
H	-0.44371	-0.02451	-2.17506
H	-0.08401	-1.7456	-2.1709
C	-0.33887	-0.76007	1.954739
H	0.084001	-1.74564	2.170865
H	0.443722	-0.02454	2.175038
F	1.303409	5.403641	0.094985
F	-1.30341	5.403641	-0.095
C	-4.55584	-1.14776	-0.09223
C	-4.93743	-2.4937	-0.08223
C	-5.53968	-0.15279	-0.18276
C	-6.28154	-2.84035	-0.16349
H	-4.18491	-3.27319	-0.00202
C	-6.87927	-0.5042	-0.26326

H	-5.2293	0.886296	-0.18958
C	-7.25402	-1.84819	-0.25418
H	-6.56886	-3.88675	-0.15361
H	-7.63601	0.27063	-0.334
C	4.555842	-1.14775	0.092221
C	4.937426	-2.4937	0.082205
C	5.539675	-0.15279	0.182794
C	6.281535	-2.84036	0.163479
H	4.184905	-3.27318	0.00197
C	6.879263	-0.50421	0.263305
H	5.2293	0.886295	0.189621
C	7.254018	-1.84819	0.254201
H	6.568861	-3.88675	0.153579
H	7.636008	0.270623	0.334071
N	-2.76598	0.480245	0.054319
N	2.765976	0.480245	-0.05431
H	-2.51394	3.077947	-0.12529
H	2.513939	3.077943	0.125299
H	8.30302	-2.12027	0.317218
H	-8.30302	-2.12027	-0.31718
C	-1.54046	-0.50292	2.859999
H	-2.33165	-1.24203	2.702031

H	-1.22784	-0.57036	3.905439
H	-1.96039	0.494267	2.699251
C	1.54047	-0.50288	-2.85999
H	1.960408	0.494297	-2.69922
H	2.331667	-1.242	-2.70203
H	1.227875	-0.57032	-3.90544

Table S7. Cartesian coordinates of transition state of **2** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.6464	1.872816	-0.28951
C	0.646402	1.872815	0.28951
C	1.282335	3.083159	0.557028
C	0.638364	4.277334	0.273541
C	-0.63836	4.277334	-0.27354
C	-1.28234	3.08316	-0.55703
C	-1.3265	0.592038	-0.54508
C	-3.04098	-0.79665	-0.3623
C	1.326503	0.592037	0.545078
C	3.040976	-0.79666	0.362294
S	-1.76546	-1.93642	-0.77247
S	1.76546	-1.93643	0.772465
C	-0.56424	-0.62082	-0.79497
C	0.564244	-0.62082	0.794976

C	0.408949	-0.69261	-1.96799
H	1.21201	0.032911	-1.80502
H	0.8743	-1.68437	-1.98441
C	-0.40895	-0.69262	1.967992
H	-1.21201	0.032916	1.805029
H	-0.87431	-1.68437	1.984402
F	-1.23349	5.445253	-0.5263
F	1.23349	5.445252	0.526308
C	4.408605	-1.21144	0.086979
C	4.797636	-2.55693	0.154842
C	5.365663	-0.24095	-0.25256
C	6.11063	-2.92331	-0.112
H	4.070764	-3.32091	0.418618
C	6.675801	-0.61404	-0.51409
H	5.057082	0.797359	-0.30615
C	7.054904	-1.95502	-0.44633
H	6.397958	-3.96853	-0.05659
H	7.407328	0.144367	-0.77518
C	-4.40861	-1.21144	-0.08698
C	-4.79764	-2.55693	-0.15484
C	-5.36566	-0.24095	0.252555
C	-6.11063	-2.92331	0.111996

H	-4.07076	-3.32091	-0.41862
C	-6.6758	-0.61404	0.514091
H	-5.05708	0.797359	0.306142
C	-7.05491	-1.95502	0.446329
H	-6.39796	-3.96853	0.056587
H	-7.40733	0.144367	0.775176
N	-2.63317	0.457085	-0.29774
N	2.633174	0.457085	0.297742
H	-2.27649	3.1003	-0.99007
H	2.276486	3.100299	0.990068
C	0.266393	-0.39954	3.308148
H	-0.46416	-0.4617	4.119484
H	1.069461	-1.11202	3.515457
H	0.695707	0.607271	3.310624
C	-0.2664	-0.39952	-3.30815
H	0.464158	-0.46166	-4.11948
H	-1.06946	-1.112	-3.51547
H	-0.69572	0.607284	-3.31061
H	8.08074	-2.24304	-0.65291
H	-8.08074	-2.24304	0.652906

Table S8. Cartesian coordinates of **3a** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å

C	-0.64877	1.872107	-0.2694
C	0.648555	1.872226	0.269014
C	1.298819	3.091993	0.499716
C	0.651734	4.282233	0.24187
C	-0.65227	4.282114	-0.2426
C	-1.2992	3.091754	-0.50028
C	-1.38093	0.634813	-0.64146
C	-3.19595	-0.63796	-0.59566
C	1.380889	0.635086	0.641281
C	3.196043	-0.63748	0.595747
S	-2.19364	-1.50192	-1.73459
S	2.193961	-1.50117	1.735062
C	-0.95077	-0.30721	-1.5386
C	0.950939	-0.30668	1.538806
C	0.333934	-0.37554	-2.31662
H	0.941678	0.474321	-1.98648
C	-0.33365	-0.37482	2.31702
H	-0.94149	0.474902	1.986699
F	-1.25507	5.455092	-0.4674
F	1.254387	5.455321	0.466507
C	4.522316	-1.12672	0.185934
C	5.171144	-2.15775	0.873606

C	5.145475	-0.54243	-0.92429
C	6.422799	-2.59908	0.456373
H	4.705572	-2.61406	1.743545
C	6.397256	-0.98432	-1.33576
H	4.633824	0.253587	-1.45491
C	7.039396	-2.01394	-0.64803
H	6.91802	-3.39851	0.997878
H	6.871856	-0.52694	-2.1981
H	8.016112	-2.35903	-0.97178
C	-4.52229	-1.12711	-0.18591
C	-5.16976	-2.16028	-0.87164
C	-5.1469	-0.54058	0.922321
C	-6.42148	-2.6015	-0.45449
H	-4.70305	-2.61847	-1.73999
C	-6.39873	-0.98239	1.333728
H	-4.63634	0.257092	1.451483
C	-7.03951	-2.01413	0.647929
H	-6.9156	-3.40262	-0.99449
H	-6.87444	-0.52324	2.194511
H	-8.01626	-2.35915	0.971633
N	2.643991	0.44193	0.123665
N	-2.64407	0.441687	-0.12394

H	2.306418	3.112939	0.901062
H	-2.3068	3.112502	-0.90162
C	0.084534	-0.22996	-3.82294
H	1.036708	-0.22716	-4.36189
H	-0.51491	-1.06602	-4.20029
H	-0.44505	0.700263	-4.04696
C	1.103539	-1.66447	-2.00611
H	2.105112	-1.62507	-2.44605
H	1.202587	-1.8123	-0.92656
H	0.582684	-2.53475	-2.42267
C	-1.10326	-1.66389	2.007025
H	-2.10472	-1.62442	2.447201
H	-1.20257	-1.81199	0.927527
H	-0.58225	-2.53402	2.423675
C	-0.08401	-0.22882	3.823255
H	-1.03608	-0.22578	4.362379
H	0.515414	-1.06485	4.200733
H	0.445713	0.701399	4.046941

Table S9. Cartesian coordinates of **3b** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	-0.73169	1.871773	0.001011
C	0.731738	1.871777	-0.00106

C	1.43086	3.135242	-0.09299
C	0.722662	4.276429	-0.0548
C	-0.72261	4.276428	0.054745
C	-1.43081	3.13524	0.092934
C	-1.3917	0.684792	-0.13436
C	-3.16975	-0.63359	-0.01036
C	1.391743	0.684802	0.134283
C	3.169775	-0.63361	0.010216
S	-1.91465	-1.89213	-0.03491
S	1.914691	-1.89215	0.03516
C	-0.63512	-0.62282	-0.45113
C	0.635146	-0.62277	0.451127
C	-0.30079	-0.70837	-1.99197
H	0.674989	-0.22416	-2.11491
C	0.300723	-0.70807	1.991942
H	-0.67501	-0.22373	2.11472
F	-1.3028	5.477314	0.103858
F	1.302848	5.477315	-0.10392
C	4.588163	-0.99896	-0.07724
C	5.000408	-2.33592	-0.0731
C	5.548541	0.018121	-0.17212
C	6.351415	-2.65176	-0.16415

H	4.266342	-3.13261	0.008692
C	6.895336	-0.30259	-0.26182
H	5.214659	1.049934	-0.17454
C	7.300659	-1.63763	-0.25852
H	6.662402	-3.69142	-0.15925
H	7.633786	0.489463	-0.33521
C	-4.58814	-0.99893	0.077165
C	-5.00039	-2.33589	0.073197
C	-5.54851	0.01817	0.171935
C	-6.3514	-2.65171	0.164304
H	-4.26634	-3.13259	-0.00851
C	-6.8953	-0.30252	0.261691
H	-5.21461	1.049981	0.174233
C	-7.30064	-1.63756	0.258553
H	-6.6624	-3.69137	0.159528
H	-7.63374	0.489551	0.335003
N	-2.75963	0.586905	-0.05907
N	2.759666	0.586893	0.058891
H	-2.51243	3.150121	0.146406
H	2.512478	3.150122	-0.14647
C	1.311823	0.043168	2.865152
H	1.047216	-0.09706	3.91777

H	2.322293	-0.35751	2.724096
H	1.332266	1.115636	2.660897
C	-1.31189	0.042813	-2.86523
H	-1.04754	-0.09785	-3.91786
H	-2.32243	-0.35756	-2.72381
H	-1.33202	1.115358	-2.66136
H	8.355123	-1.88571	-0.32892
H	-8.3551	-1.88562	0.329002
C	-0.19585	-2.14435	-2.52736
H	-1.19232	-2.55233	-2.71902
H	0.352428	-2.13313	-3.47457
H	0.324178	-2.82479	-1.85147
C	0.195564	-2.14395	2.527544
H	1.191973	-2.55196	2.719467
H	-0.35292	-2.13256	3.47463
H	-0.32435	-2.82448	1.851644

Table S10. Cartesian coordinates of transition state of **3** optimized at the M06-2X/6-31G(d) level.

Atom	X/Å	Y/Å	Z/Å
C	0.653433	1.952688	0.267877
C	-0.65375	1.952243	-0.26701
C	-1.30098	3.162377	-0.51557
C	-0.64848	4.355257	-0.25277

C	0.647145	4.355675	0.25234
C	1.300134	3.163201	0.515842
C	1.327607	0.672216	0.52277
C	3.064214	-0.69303	0.397852
C	-1.32732	0.6714	-0.52148
C	-3.06398	-0.69394	-0.39803
S	1.809016	-1.83475	0.841483
S	-1.80787	-1.83607	-0.83811
C	0.565467	-0.54805	0.797497
C	-0.56473	-0.54897	-0.79474
C	-0.38822	-0.59189	2.013647
C	0.389148	-0.5931	-2.01074
F	1.247909	5.524864	0.485065
F	-1.24971	5.524068	-0.48619
C	-4.43835	-1.09333	-0.13757
C	-4.84498	-2.43296	-0.22345
C	-5.38525	-0.11424	0.206806
C	-6.16469	-2.78455	0.029373
H	-4.12584	-3.20366	-0.48865
C	-6.70206	-0.47283	0.454554
H	-5.0635	0.919203	0.275058
C	-7.09863	-1.8077	0.368129

H	-6.46537	-3.82521	-0.03973
H	-7.42529	0.292224	0.719392
C	4.438229	-1.09251	0.135684
C	4.845698	-2.43169	0.224709
C	5.38397	-0.11398	-0.21344
C	6.165075	-2.78338	-0.02969
H	4.127476	-3.20196	0.493622
C	6.700465	-0.47265	-0.46273
H	5.061582	0.919107	-0.28406
C	7.097869	-1.80707	-0.37315
H	6.466418	-3.82368	0.041916
H	7.422817	0.291976	-0.73118
N	2.637091	0.55419	0.301166
N	-2.63719	0.553426	-0.30205
H	2.306818	3.178766	0.918848
H	-2.30766	3.177299	-0.9186
C	0.739876	-2.01538	-2.46502
H	1.579847	-1.97516	-3.16487
H	1.02736	-2.6642	-1.63473
H	-0.10706	-2.47309	-2.98729
C	-0.73664	-2.01428	2.469487
H	-1.57718	-1.97481	3.168695

H	-1.02245	-2.66448	1.639663
H	0.110769	-2.46994	2.992761
H	-8.12966	-2.08437	0.564076
H	8.128653	-2.0838	-0.57031
C	-0.22097	0.174889	-3.18992
H	-1.19418	-0.25033	-3.46079
H	-0.36047	1.233739	-2.95472
H	0.435918	0.100436	-4.06249
C	0.219942	0.178626	3.192017
H	1.193186	-0.24533	3.464697
H	0.358702	1.237185	2.955185
H	-0.43784	0.105038	4.063995
H	-1.31607	-0.08748	1.724888
H	1.315929	-0.08631	-1.72288