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

Spiropyran as a reusable chemosensor for selective colorimetric detection of aromatic thiols

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Electronic Supplementary Information (ESI†)

CONTENTS

Details for equilibrium and kinetic analysis

1. Equilibrium analysis for compound 1

Thermodynamic equilibrium constant for the SP and MC forms (K_{eq}) is expressed as follows:[1]

$$K_{eq} = \frac{[MC]_{eq}}{[SP]_{eq}} \quad (1)$$

$$C_T = [SP]_{eq} + [MC]_{eq} = \frac{A_{MC}}{\varepsilon_{MC}}\left(1 + \frac{1}{K_{eq}}\right) \quad (2)$$

where $[SP]_{eq}$ and $[MC]_{eq}$ are the equilibrium concentrations of the SP and MC forms, C_T is the total concentration of SP and MC forms, and A_{MC} and ε_{MC} are the absorbance and the molar extinction coefficient of the MC form, respectively.[2] K_{eq} was determined by equilibrium absorption analysis: the solutions containing different concentrations of **1** (C_T) were stirred for 6 h in the dark at different temperature, and the MC absorbance (A_{MC}) was plotted against C_T (Fig. S3). It must be noted that all of the solutions attain the absorption equilibrium by 6 h stirring. Linear relationship was observed between C_T and A_{MC} for all of the solutions. The ε_{MC} value of **1** in a water/MeCN (7/3 v/v) mixture (2.36×10^4 M^{-1} cm^{-1}) was determined at 298 K according to literature procedure.[3] The K_{eq} values for respective solutions at different temperatures were therefore determined with ε_{MC} and the slope of Fig. S3. The standard enthalpy ($\Delta_r H$) and entropy ($\Delta_r S$) for isomerization were determined using the van′t Hoff equation (eq. 3).[4]

$$\ln K = -\frac{\Delta_r H}{RT} + \frac{\Delta_r S}{R} \quad (3)$$

The van't Hoff plots are shown in Fig. S4, and the obtained equilibrium parameters are summarized in Table S1.

2. Kinetic analysis for isomerization of 1

Kinetic analysis for SP→MC isomerization of **1** was carried out as follows:[5] The apparent rate constant for SP→MC isomerization (k_{obsd}) is expressed by the sum of the forward ($k_{SP\rightarrow MC}$) and backward rate constant ($k_{MC\rightarrow SP}$).[6]

$$SP \underset{k_{MC\rightarrow SP}}{\overset{k_{SP\rightarrow MC}}{\rightleftharpoons}} MC \quad (4)$$

$$k_{obsd} = k_{SP\rightarrow MC} + k_{MC\rightarrow SP} \quad (5)$$

The equilibrium constant, K_{eq} (eq. 1), is therefore rewritten as follows.

$$K_{eq} = \frac{k_{SP\rightarrow MC}}{k_{MC\rightarrow SP}} \quad (6)$$

The forward and backward rate constants are expressed as follows.

$$k_{\mathrm{SP}\rightarrow\mathrm{MC}} = \frac{K_{\mathrm{eq}}}{1+K_{\mathrm{eq}}} k_{\mathrm{obsd}} \tag{7}$$

$$k_{\mathrm{MC}\rightarrow\mathrm{SP}} = \frac{1}{1+K_{\mathrm{eq}}} k_{\mathrm{obsd}} \tag{8}$$

The relationship between the MC absorbance and k_{obsd} is expressed as follows:[7]

$$\ln\left[\frac{A_\infty - A_t}{A_\infty - A_0}\right] = -k_{\mathrm{obsd}} t \tag{9}$$

where A_0, A_t, and A_∞ are the absorbance at time 0, t, and infinity, respectively. Fig. S5 shows the plots of $\ln[(A_\infty - A_t)/(A_\infty - A_0)]$ *vs.* time during SP→MC isomerization of **1** at different temperatures. The rate constants ($k_{\mathrm{SP}\rightarrow\mathrm{MC}}$ and $k_{\mathrm{MC}\rightarrow\mathrm{SP}}$) determined using the eqs. 7 and 8 are summarized in Table S1. The activation energy (E_a) for isomerization is determined by the Arrhenius plots (Fig. S6),[8] using the following equation.

$$\ln k_{\mathrm{SP}\rightarrow\mathrm{MC}} = \ln A - \frac{E_a}{RT} \tag{10}$$

where A is frequency factor. The activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) for isomerization are expressed as follows:[9]

$$\Delta H^{\neq} = E_a - RT \tag{11}$$

$$\Delta S^{\neq} = R\left[\ln A - 1 - \ln\frac{k_B T}{h}\right] \tag{12}$$

where k_B and h are the Boltzmann′s constant and the Plank′s constant, respectively.[8] The obtained $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are summarized in Table S1.

References

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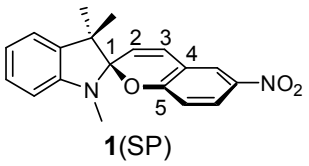
Table S1. Equilibrium and kinetic data for isomerization of **1** in a water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0) determined with different amount of **2a**.

2a / equiv	T / ℃	K_{eq}	$\Delta_r H$ / kJ mol^{-1}	$\Delta_r S$ / J K^{-1} mol^{-1}	k_{obsd} / 10^{-4} s^{-1}	$k_{SP\rightarrow MC}$ / 10^{-4} s^{-1}	$k_{MC\rightarrow SP}$ / 10^{-4} s^{-1}	$\Delta H^{\neq}$ / kJ mol^{-1}	$\Delta S^{\neq}$ / J K^{-1} mol^{-1}
0	25	2.95	−6.61 ± 0.34	−13.2 ± 1.0	0.69	0.52	0.17	107.7 ± 2.9	32.5 ± 9.1
	40	2.58			4.77	3.44	1.33		
	50	2.38			17.6	12.4	5.21		
	60	2.22			63.5	43.8	19.7		
1	15	3.39	−6.61 ± 0.79	−12.8 ± 2.6	0.22	0.17	0.05	87.0 ± 3.6	−33.6 ± 12.1
	25	3.12			0.82	0.62	0.20		
	35	2.84			2.60	1.92	0.68		
2	15	3.38	−6.74 ± 0.54	−13.2 ± 1.8	0.32	0.25	0.07	74.8 ± 1.3	−73.31 ± 4.6
	25	3.09			0.95	0.72	0.23		
	35	2.81			2.72	2.01	0.71		
10	15	3.39	−6.73 ± 0.30	−13.2 ± 1.0	2.70	2.08	0.62	45.6 ± 3.5	−157.0 ± 11.9
	25	3.07			5.20	3.92	1.28		
	35	2.82			10.4	7.68	2.72		
30	15	3.36	−6.68 ± 0.40	−13.1 ± 1.3	4.73	3.65	1.08	44.0 ± 4.7	−157.6 ± 15.7
	25	3.05			9.80	7.38	2.42		
	35	2.81			17.4	12.8	4.57		

Table S2. The dihedral angles (°) of the N–C_1–C_2–C_3, C_1–C_2–C_3–C_4, and C_2–C_3–C_4–C_5 moieties of **1** determined by DFT calculation in the absence and presence of **2a**.



1(SP)

	N–C_1–C_2–C_3	C_1–C_2–C_3–C_4	C_2–C_3–C_4–C_5
1(SP)	116.6	2.4	−0.7
TS1	81.8	6.3	10.9
CCC	43.5	15.3	16.6
TS2	−2.6	96.4	−2.8
CTC	17.9	178.3	2.6
TS3	94.2	178.6	−0.5
TTC (MC)	179.9	180.0	0
TS4	−4.9	63.3	8.2
CCC-2a	6.9	47.1	68.8
TS5	−14.1	157.5	117.8
CTT-2a	3.3	−122.5	112.0
TS6	−3.4	−159.8	155.1

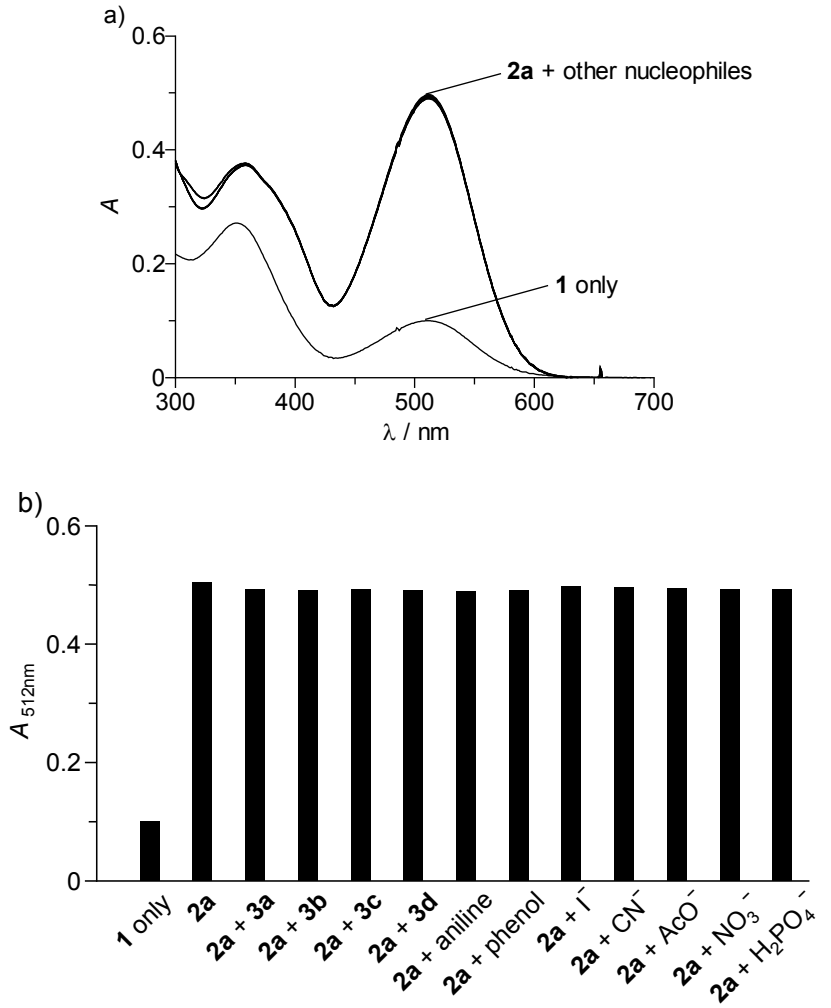


Fig. S1 (a) Absorption spectra of **1** (30 μM) measured in a water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0) with **2a** (30 equiv) together with each respective nucleophile (30 equiv) for 60 min at 25℃ in the dark. (b) Absorbance of solutions at 512 nm.

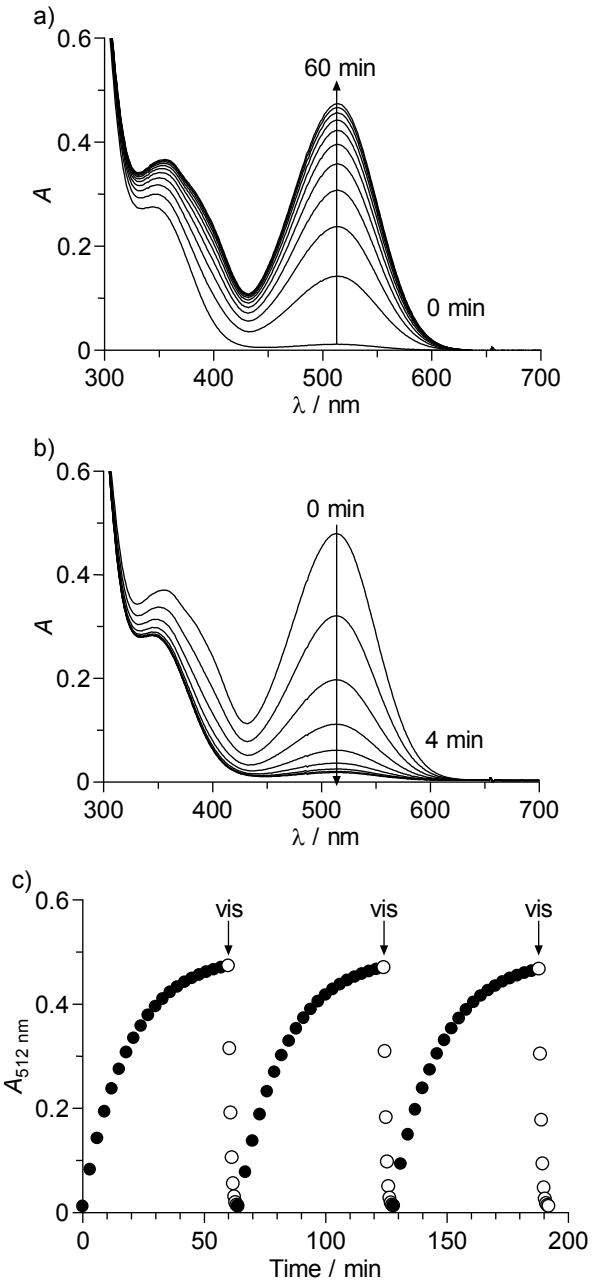


Fig. S2 (a) Time-dependent change in the absorption spectra of **1** (30 μM) measured in the presence of 30 equiv of **2a** in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1 M, pH 7.0) at 25℃ in the dark. (b) Change in absorption spectra of the solution (a) when irradiated with 550 nm monochromatic light. (c) Change in 512 nm absorbance during the repeated stirring under the dark and 550 nm irradiation conditions.

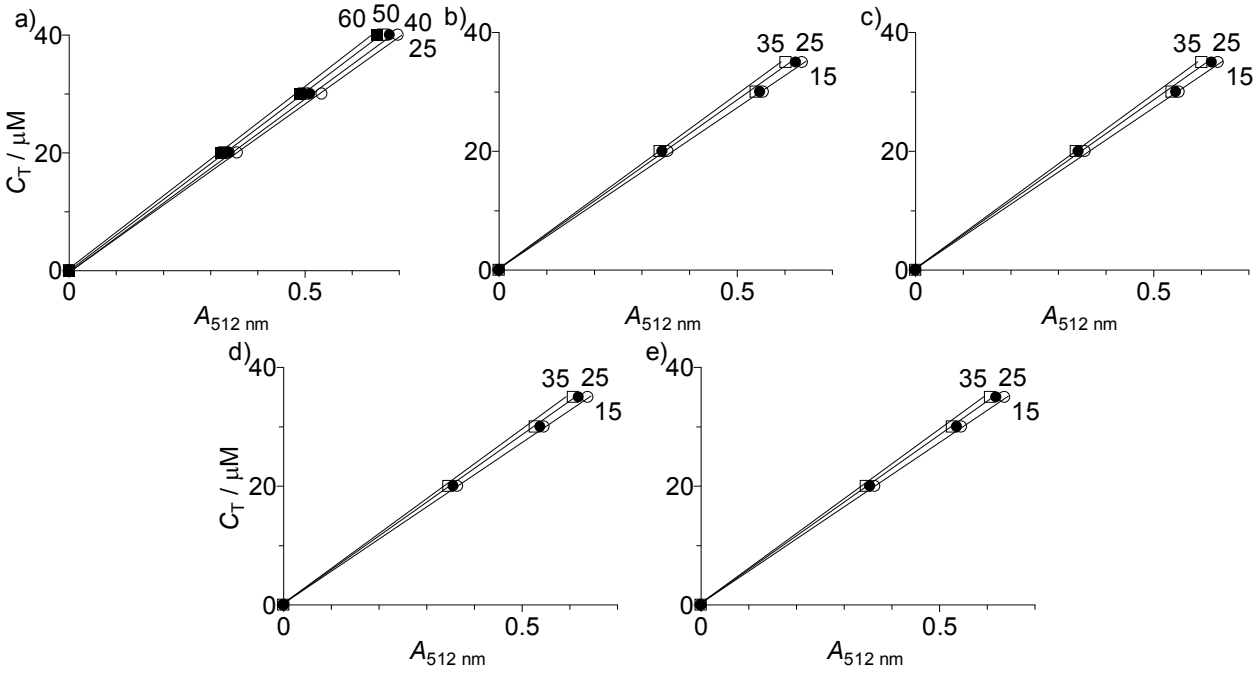


Fig. S3 Plots of C_T *vs.* A_{MC} obtained by the equilibrium absorption experiments for **1** (6 h) at different temperatures (15−60 ℃) in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1M, pH 7.0), (a) in the absence of **2a** and in the presence of (b) 1 equiv, (c) 2 equiv, (d) 10 equiv, and (e) 30 equiv of **2a**.

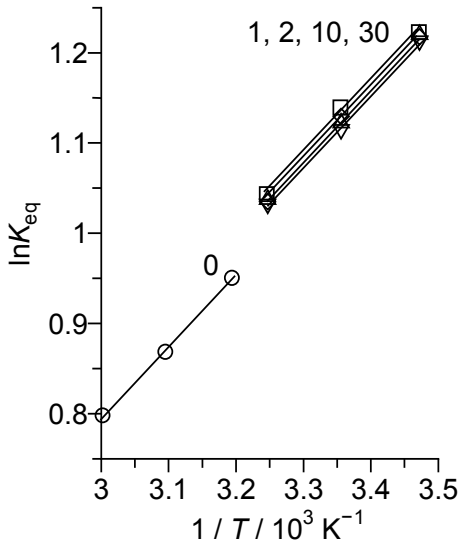


Fig. S4 van′t Hoff plots of the K_{eq} data for **1** obtained by equilibrium absorption experiments with different amount of **2a** in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1M, pH 7.0) at different temperatures. The numbers in the figure denote the amount of **2a** added relative to that of **1** (equiv).

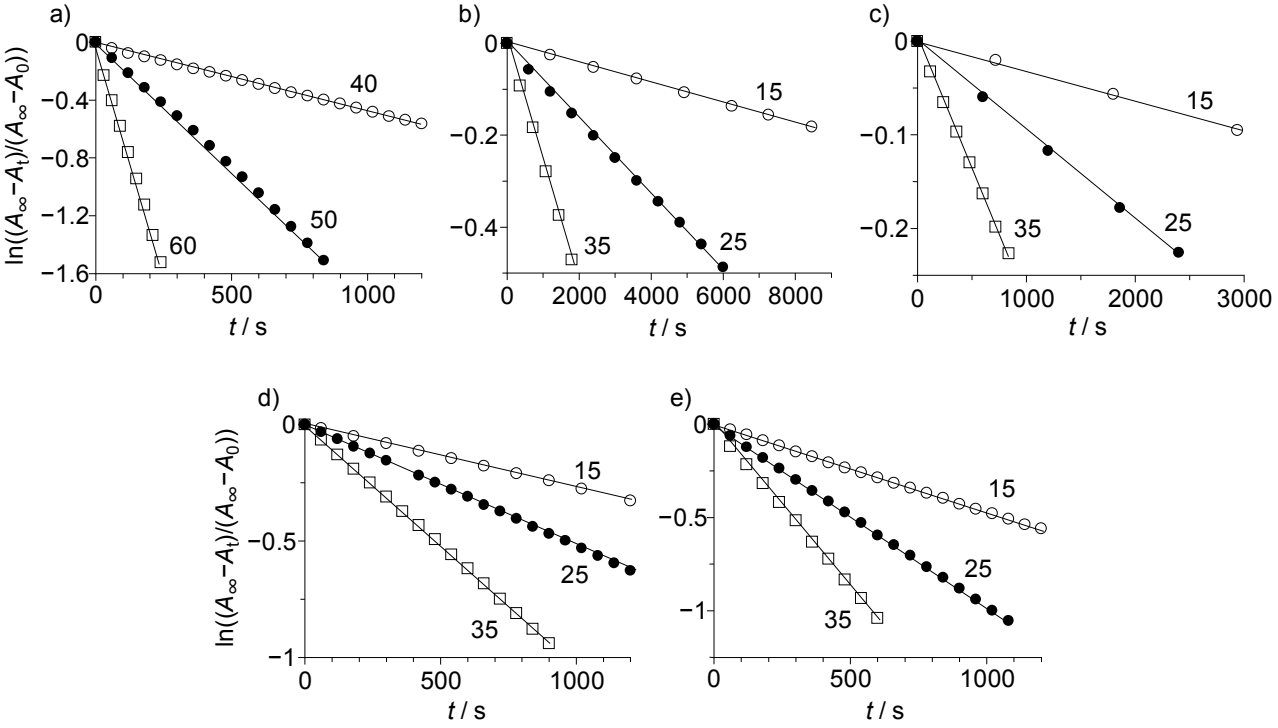


Fig. S5 Kinetic absorption data for the SP→MC isomerization of **1** in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1M, pH 7.0) in the (a) absence of **2a** and presence of (b) 1 equiv, (c) 2 equiv, (d) 10 equiv, and (e) 30 equiv of **2a** at different temperatures. The numbers in the figure denote the temperature.

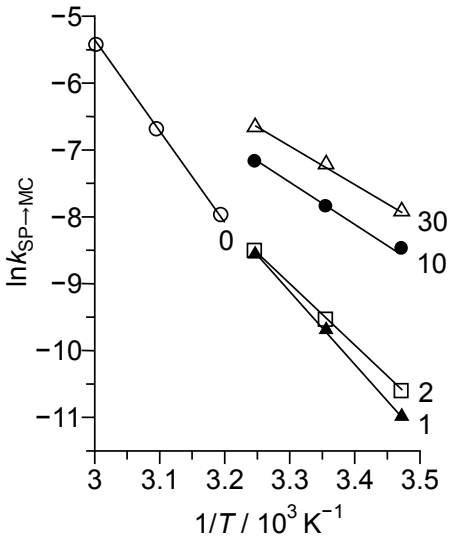
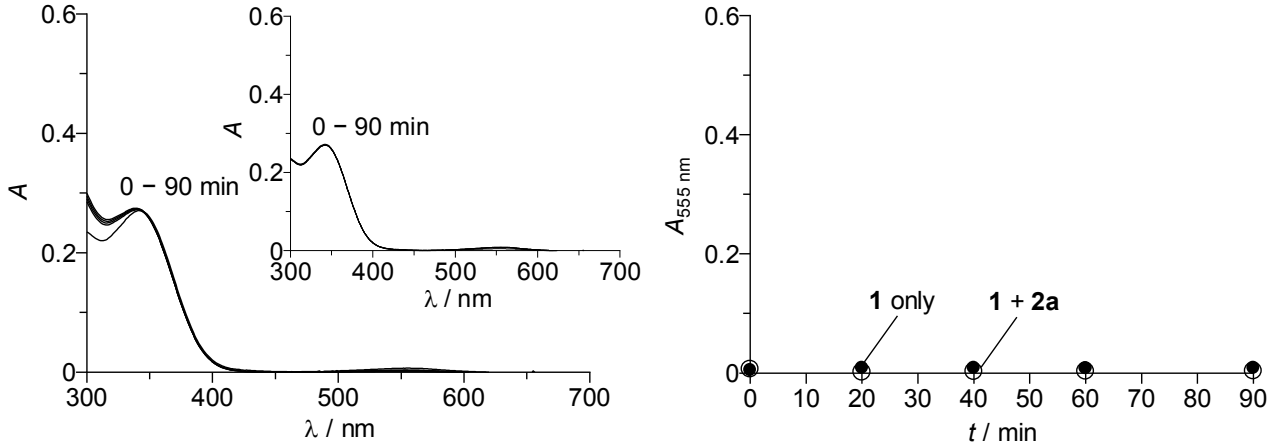
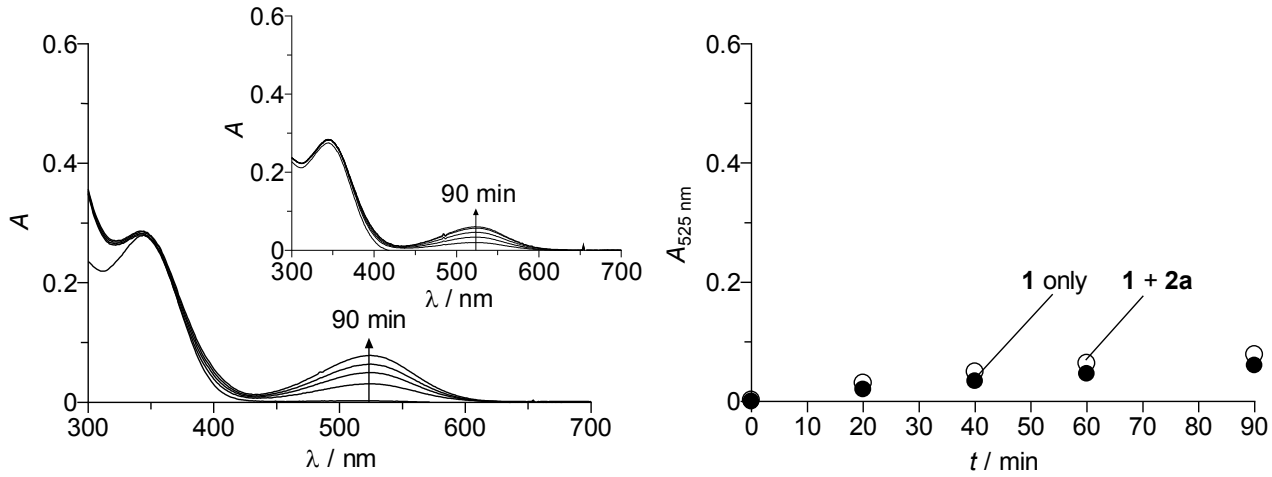


Fig. S6 Arrhenius plots of the kinetic absorption data for **1** in a buffered water/MeCN mixture (7/3 v/v; HEPES 0.1M, pH 7.0) at different temperatures obtained with different amount of **2a**. The numbers in the figure denote the amount of **2a** relative to that of **1** (equiv).

a (MeCN)



b (water/MeCN = 3/7 v/v)



c (water/MeCN = 5/5 v/v)

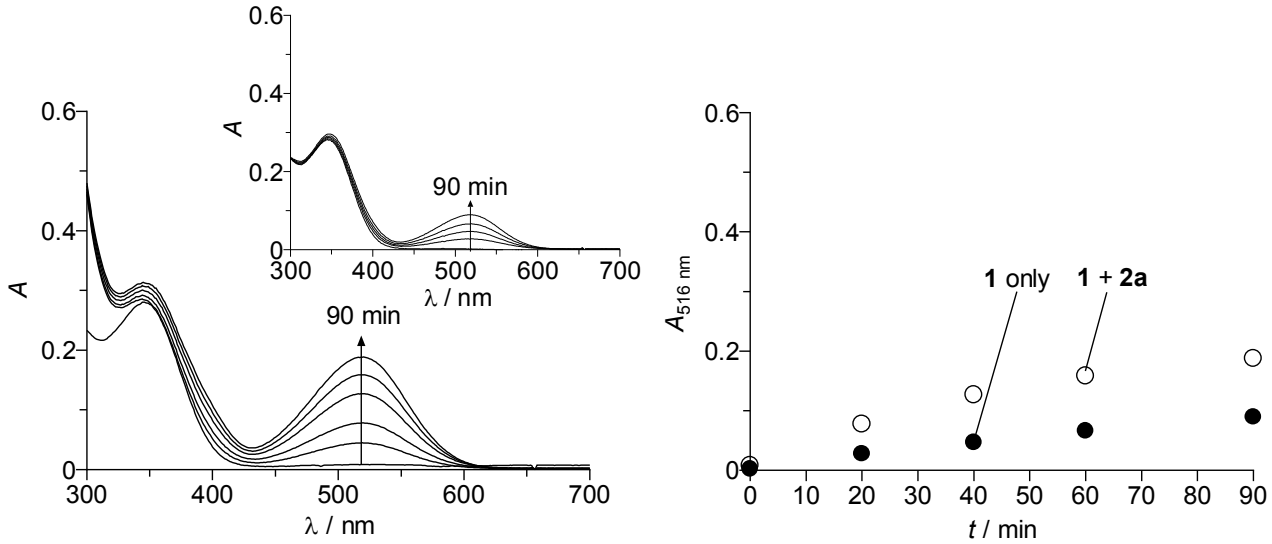
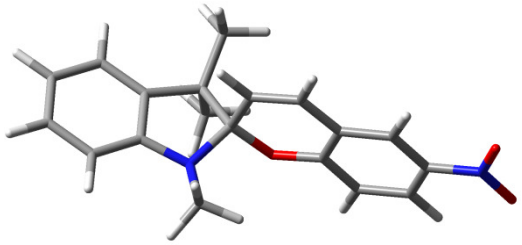


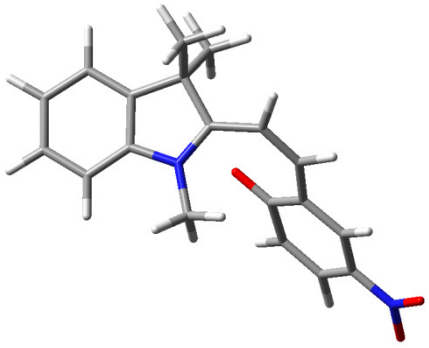
Fig. S7 (Left) Effect of water concent on the time-dependent change in the absorption spectra of **1** (30 μM) in the absence (inset) and presence of 30 equiv of benzenethiol (**2a**) in the dark at 25 °C. (Right) Change in MC absorbance.

Cartesian Coordinates (in Å) of 1(SP)



C	0.00124	-0.01494	-0.013306	N	10.879425	1.823404	1.960002
C	-0.006895	-0.014158	1.382163	O	11.005083	3.051214	2.039333
C	1.187243	-0.005697	2.118207	O	11.825343	1.036139	2.082577
C	2.391917	-0.008195	1.413454	H	-0.93495	-0.011835	-0.564025
C	2.410752	-0.000293	0.006701	H	-0.953969	-0.01045	1.915673
C	1.223353	-0.012061	-0.708069	H	1.165808	0.007251	3.20333
N	3.69444	-0.019901	1.920168	H	1.232545	-0.010055	-1.795389
C	4.605318	0.416514	0.849094	H	6.124008	3.548424	1.233819
C	3.855807	-0.058685	-0.467637	H	3.934447	2.510765	0.802241
O	5.8382	-0.328731	0.993413	H	10.249495	-0.760274	1.739378
C	7.038961	0.242644	1.230685	H	8.635339	3.22248	1.639357
C	7.204275	1.642837	1.321029	H	5.034176	0.203268	3.503037
C	6.019323	2.469567	1.156375	H	3.422707	-0.349419	3.962788
C	4.828815	1.905361	0.915626	H	3.682102	1.364888	3.555723
C	8.12917	-0.625186	1.383114	H	5.237374	0.812894	-1.909531
C	9.393591	-0.108162	1.621707	H	3.850335	1.858608	-1.544121
C	9.556545	1.27935	1.71047	H	3.641772	0.430978	-2.567456
C	8.478083	2.153166	1.564087	H	5.258565	-1.616778	-1.115461
C	3.968093	0.332929	3.304098	H	3.573268	-1.877355	-1.609333
C	4.164193	0.820787	-1.687053	H	4.06379	-2.180624	0.068748
C	4.216272	-1.527105	-0.795056	H	7.966486	-1.694832	1.308943

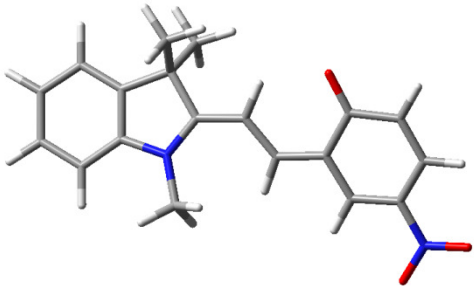
Cartesian Coordinates (in Å) of CCC



C	-0.006163	-0.006033	-0.008096	H	1.227942	3.915186	5.489147
C	-0.005353	0.004003	1.395197	H	1.861822	4.040447	7.890532
C	1.279559	0.005681	2.117821	H	1.137341	2.289204	9.480661
C	2.475353	0.048292	1.289189	H	-0.244495	0.371119	8.710979
C	2.432358	0.087053	-0.074639	H	-2.63145	-0.436245	3.610282
C	1.174994	0.055538	-0.737794	H	-2.067221	-0.500111	1.394749
C	-1.278683	-0.129984	2.050095	H	3.425418	0.057786	1.815607
C	-1.672663	0.012841	3.357709	H	3.338429	0.131137	-0.667586

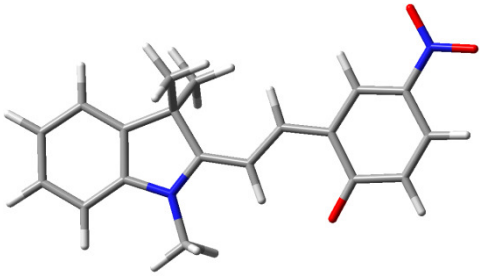
C	-1.023383	0.614555	4.476037	H	-0.947145	-0.047826	-0.546084
N	-0.369432	1.770842	4.489564	C	-0.499577	-1.370336	5.941604
C	0.132233	2.064077	5.786542	H	-0.486746	-1.730285	6.975372
C	-0.284393	1.062299	6.665256	H	-1.102562	-2.060277	5.342698
C	-1.107855	0.05018	5.89516	H	0.519615	-1.369865	5.54831
C	0.069135	1.135868	8.006094	C	-2.576324	0.026052	6.391514
C	0.847162	2.219639	8.436637	H	-3.175933	-0.677657	5.805932
C	1.256886	3.210543	7.538217	H	-2.596993	-0.30089	7.435577
C	0.90269	3.15015	6.185485	H	-3.036761	1.016906	6.332144
O	1.362911	-0.044753	3.369208	C	-0.197837	2.687856	3.36927
N	1.124688	0.071379	-2.165618	H	-0.942544	2.4608	2.60834
O	0.017497	0.035855	-2.734836	H	-0.342192	3.707925	3.73034
O	2.195535	0.120428	-2.799779	H	0.803566	2.583715	2.94612

Cartesian Coordinates (in Å) of CTC



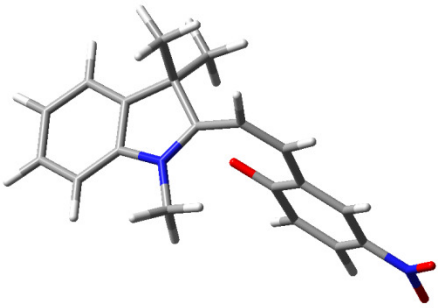
C	0.004344	-0.017369	0.001257	H	-6.820437	-0.510179	3.573178
C	0.000899	0.009414	1.409653	H	-8.203187	0.026176	5.559483
C	1.28873	0.033371	2.139509	H	-7.159182	0.860986	7.642947
C	2.487696	0.033803	1.310021	H	-4.696756	1.177545	7.782647
C	2.445645	0.005551	-0.051911	H	-0.642225	0.204177	4.050352
C	1.186328	-0.021374	-0.720083	H	-2.111491	0.00162	1.369813
C	-1.268809	0.012496	2.054588	H	3.436813	0.054447	1.837571
C	-1.51218	0.088038	3.415597	H	3.352487	0.003147	-0.645233
C	-2.756356	0.125299	4.074759	H	-0.936696	-0.036957	-0.538098
N	-3.972709	-0.219769	3.617661	C	-2.101213	-0.363688	6.471056
C	-4.976795	0.024698	4.594729	H	-2.258377	-0.055573	7.509541
C	-4.370059	0.50493	5.757395	H	-1.02707	-0.330837	6.264994
C	-2.875598	0.593085	5.530235	H	-2.4474	-1.395957	6.36182
C	-5.148391	0.806436	6.866985	C	-2.353426	2.040627	5.684367
C	-6.536067	0.626529	6.785226	H	-1.283689	2.093435	5.460307
C	-7.126039	0.153408	5.609002	H	-2.505245	2.376075	6.715115
C	-6.351856	-0.156498	4.484801	H	-2.883632	2.726852	5.017025
O	1.373031	0.051349	3.388037	C	-4.280236	-0.852855	2.33807
N	1.143246	-0.052812	-2.150462	H	-3.459603	-1.514322	2.05688
O	0.038747	-0.078972	-2.722794	H	-4.439507	-0.104726	1.555951
O	2.218294	-0.053041	-2.777183	H	-5.185253	-1.449294	2.452187

Cartesian Coordinates (in Å) of TTC



C	0.005968	0.001688	-0.015669	C	4.144167	1.276227	-1.306686
C	-0.002224	0.003561	1.382743	C	4.142568	-1.283018	-1.302484
C	1.190541	0.003541	2.114118	C	4.07468	0.001857	3.283383
C	2.379286	0.001511	1.390001	H	-0.933536	0.001774	-0.559901
C	2.406569	-0.000207	-0.006571	H	-0.947888	0.005139	1.916325
C	1.216514	-0.000189	-0.721664	H	1.168884	0.005221	3.198101
N	3.713693	0.000867	1.866166	H	1.217288	-0.001501	-1.808018
C	4.604932	-0.000268	0.855439	H	6.324453	0.002954	2.1381
C	3.848995	-0.001852	-0.48227	H	6.671346	-0.00432	-0.90623
C	5.988218	0.000389	1.109602	H	10.946311	0.005282	2.66511
C	6.973665	-0.001711	0.137096	H	12.305144	0.000499	0.585451
C	8.381586	-0.000876	0.337104	H	8.736491	-0.006093	-1.796663
C	9.015129	0.002661	1.675792	H	5.181293	1.306947	-1.649554
C	10.473198	0.002837	1.687504	H	3.948172	2.177361	-0.717768
C	11.222056	0.000205	0.54902	H	3.495334	1.295536	-2.187938
C	10.576411	-0.003015	-0.722695	H	5.17964	-1.316128	-1.645303
C	9.195304	-0.003534	-0.813625	H	3.493635	-1.304437	-2.183605
O	8.365342	0.004888	2.744982	H	3.945492	-2.181957	-0.710584
N	11.364971	-0.005818	-1.917831	H	4.664775	-0.887152	3.520331
O	12.604569	-0.005442	-1.811107	H	3.16831	-0.004512	3.884308
O	10.791181	-0.008503	-3.021631	H	4.654046	0.897466	3.522281

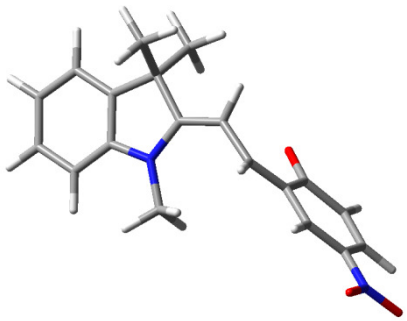
Cartesian Coordinates (in Å) of TS1



C	0.008223	-0.170587	-0.011222	H	0.975724	4.13406	5.7518
C	-0.009612	-0.060458	1.377169	H	2.131437	4.004136	7.951355
C	1.238276	0.036692	2.110607	H	2.198504	1.880107	9.218579
C	2.455331	0.012701	1.343197	H	1.096986	-0.162905	8.325179
C	2.446504	-0.074521	-0.026766	H	-2.527265	-0.114431	3.762581
C	1.215389	-0.166501	-0.715474	H	-2.126242	-0.431833	1.480633
C	-1.273307	-0.124732	2.083641	H	3.39099	0.077879	1.890225
C	-1.523182	0.089378	3.394227	H	3.369836	-0.078786	-0.593916

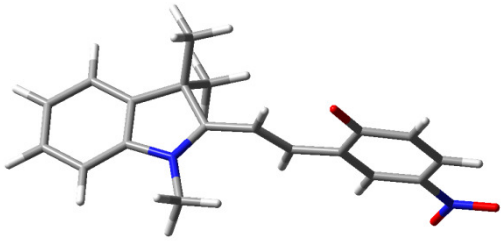
C	-0.604031	0.566059	4.432617	H	-0.921639	-0.256757	-0.562686
N	-0.314722	1.854197	4.619335	C	0.323467	-1.552878	5.578372
C	0.398614	2.043679	5.83377	H	0.41536	-2.039566	6.554912
C	0.421448	0.834629	6.533723	H	-0.271864	-2.203406	4.929393
C	-0.370506	-0.193008	5.748931	H	1.312753	-1.43456	5.137182
C	1.066226	0.765038	7.761201	C	-1.757809	-0.402338	6.428286
C	1.684301	1.9199	8.262951	H	-2.365766	-1.111873	5.858696
C	1.646492	3.12049	7.547482	H	-1.600879	-0.814341	7.429197
C	0.996455	3.203943	6.30941	H	-2.308877	0.538076	6.527482
O	1.270801	0.128091	3.38313	C	-0.490105	2.922333	3.642809
N	1.204657	-0.268671	-2.140747	H	-1.212586	2.603162	2.893353
O	0.112378	-0.358467	-2.732019	H	-0.858957	3.816215	4.150384
O	2.290487	-0.264898	-2.750384	H	0.466871	3.143874	3.160415

Cartesian Coordinates (in Å) of TS2



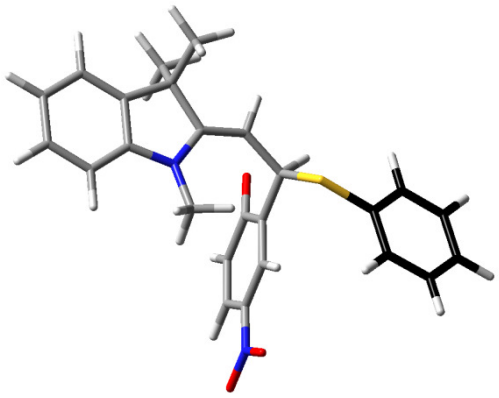
C	-0.00163	0.002511	-0.000708	H	-1.831708	5.032795	4.890235
C	0.009213	-0.00764	1.443828	H	-2.28945	5.802276	7.197503
C	1.335152	-0.016438	2.156454	H	-2.670852	4.176318	9.031154
C	2.526637	0.005678	1.297119	H	-2.596358	1.728689	8.563522
C	2.449514	0.023931	-0.053506	H	-1.547204	-1.115876	3.893955
C	1.160651	0.01955	-0.703025	H	-2.070283	-0.05548	1.419591
C	-1.201778	-0.01665	2.084657	H	3.485061	0.00567	1.806047
C	-1.485121	-0.090899	3.52518	H	3.338454	0.039875	-0.672337
C	-1.74489	0.881166	4.422476	H	-0.950493	0.000487	-0.525425
N	-1.767482	2.262904	4.226003	C	-0.964172	-0.210822	6.5943
C	-1.980885	2.93406	5.43529	H	-1.193652	-0.342183	7.657692
C	-2.183896	2.005791	6.468258	H	-0.865805	-1.205045	6.145006
C	-2.082254	0.596949	5.90353	H	0.00089	0.298805	6.511515
C	-2.435831	2.443037	7.759404	C	-3.429224	-0.150563	6.022297
C	-2.477293	3.822474	8.022719	H	-3.365125	-1.14002	5.555788
C	-2.263929	4.735955	6.988759	H	-3.696938	-0.286778	7.076252
C	-2.008599	4.30805	5.678215	H	-4.234656	0.407544	5.533768
O	1.438763	-0.049888	3.384088	C	-1.502833	2.945538	2.974676
N	1.111131	0.033086	-2.158436	H	-1.910812	2.371212	2.140813
O	0.00876	0.02773	-2.714628	H	-2.003416	3.916456	2.979534
O	2.185125	0.04939	-2.769312	H	-0.429516	3.101734	2.804517

Cartesian Coordinates (in Å) of TS3



C	0.081836	0.371658	0.044344	H	-6.250103	-1.735377	4.950962
C	0.01588	0.080077	1.403059	H	-7.94089	-0.405445	6.207425
C	1.206537	-0.422156	2.104614	H	-7.499068	1.952459	6.802763
C	2.399259	-0.579434	1.291058	H	-5.363916	3.049477	6.166844
C	2.432457	-0.283258	-0.044508	H	-0.7158	-0.315827	4.02662
C	1.263927	0.199722	-0.686667	H	-2.054822	0.663679	1.446681
C	-1.251691	0.288112	2.081278	H	3.285534	-0.950425	1.798772
C	-1.516749	0.055564	3.387728	H	3.337639	-0.409806	-0.627361
C	-2.80972	0.31518	4.014893	H	-0.796791	0.742397	-0.473461
N	-3.756631	-0.582627	4.15951	C	-2.222289	1.978239	5.800091
C	-4.876272	-0.055404	4.876721	H	-2.551709	2.895425	6.296872
C	-4.598797	1.272749	5.202157	H	-1.225721	2.146756	5.381856
C	-3.22522	1.625637	4.67176	H	-2.163454	1.181522	6.547408
C	-5.545364	2.012675	5.900291	C	-3.268202	2.760798	3.619158
C	-6.748653	1.389452	6.256264	H	-2.275466	2.921531	3.190039
C	-7.000726	0.054214	5.919704	H	-3.589349	3.685487	4.107682
C	-6.058062	-0.701259	5.214546	H	-3.971812	2.534814	2.812368
O	1.213956	-0.704448	3.332432	C	-3.722639	-1.966085	3.677271
N	1.29036	0.509569	-2.071678	H	-2.784694	-2.130339	3.151278
O	0.2528	0.934956	-2.623157	H	-4.565948	-2.125051	3.001759
O	2.35381	0.348972	-2.707788	H	-3.80372	-2.640831	4.532241

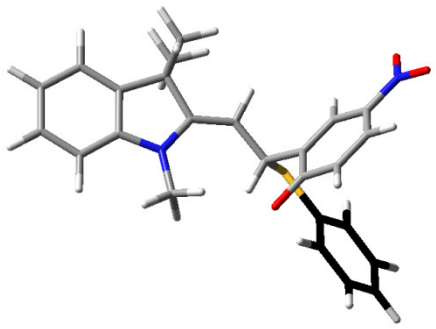
Cartesian Coordinates (in Å) of CCC-2a



C	-0.034081	0.008793	-0.004836	H	-0.962185	-0.060244	-0.558107
C	-0.040198	0.016156	1.367544	C	-0.85187	3.206063	5.181598
C	1.224933	0.044762	2.114036	H	-0.972613	3.949338	5.978131
C	2.43204	0.138642	1.312663	H	-0.896847	2.211215	5.63698

C	2.411187	0.161593	-0.057607	H	0.142147	3.333579	4.740777
C	1.173645	0.090108	-0.738944	C	-3.347537	3.165876	4.755626
C	-1.641114	1.080227	3.107366	H	-3.427146	2.163401	5.190394
C	-1.742726	2.415967	2.915518	H	-3.516751	3.898055	5.553793
N	-1.66087	3.197799	1.756984	H	-4.142995	3.281105	4.011829
C	-1.699704	4.559838	2.069709	C	-1.788708	2.748163	0.382353
C	-1.869218	4.73936	3.449702	H	-2.211819	1.745038	0.361851
C	-1.955911	3.377745	4.117969	H	-2.470547	3.419907	-0.151863
C	-1.95198	6.017223	3.981058	H	-0.827571	2.736019	-0.142646
C	-1.856962	7.12649	3.123215	C	-1.280573	-0.104962	2.238601
C	-1.684476	6.934884	1.751022	H	-1.058185	-0.904621	2.950503
C	-1.601693	5.647987	1.200278	S	-2.843071	-0.693734	1.361675
O	1.262694	-0.023134	3.370931	C	-2.450891	-2.382375	0.883421
N	1.139684	0.091264	-2.147493	C	-2.540454	-2.75667	-0.464586
O	0.035183	0.022679	-2.740287	C	-2.114966	-3.347958	1.844284
O	2.215972	0.161961	-2.789402	C	-2.300645	-4.079562	-0.844871
H	-1.455914	5.51294	0.133388	H	-2.79407	-2.012107	-1.213486
H	-1.607752	7.79576	1.091848	C	-1.853328	-4.66281	1.456827
H	-1.91573	8.132151	3.529523	H	-2.064418	-3.073613	2.894236
H	-2.090358	6.16477	5.049683	C	-1.949768	-5.033639	0.112374
H	-1.821483	0.78582	4.137508	H	-2.376977	-4.359335	-1.892171
H	3.374661	0.177662	1.853309	H	-1.587762	-5.401298	2.208547
H	3.326659	0.225402	-0.635097	H	-1.754702	-6.060051	-0.185537

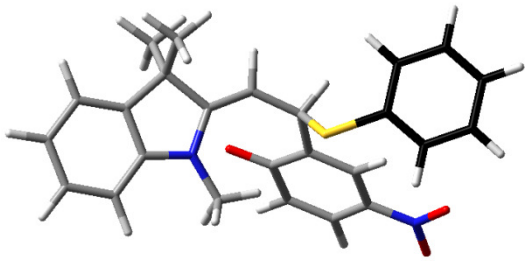
Cartesian Coordinates (in Å) of CTT-2a



C	-0.005604	0.00766	0.025853	H	-0.936903	0.006781	-0.530566
C	-0.014962	-0.010504	1.402345	C	-4.528521	3.170078	1.8109
C	1.238925	-0.028538	2.155981	H	-5.118756	4.066719	1.589712
C	2.452409	-0.018055	1.364577	H	-4.331506	2.653118	0.865541
C	2.44069	0.00324	-0.007124	H	-5.132345	2.510159	2.442291
C	1.20665	0.014125	-0.697348	C	-2.369603	4.474427	1.597445
C	-2.017832	1.368087	2.037039	H	-2.129909	3.967523	0.656228
C	-2.403291	2.303686	2.934604	H	-2.924856	5.389409	1.360491
N	-2.192473	2.371466	4.315278	H	-1.429886	4.760348	2.081468
C	-2.856096	3.472843	4.868139	C	-1.344185	1.491208	5.100847
C	-3.475141	4.220933	3.854961	H	-1.854276	0.555359	5.365199
C	-3.210712	3.55757	2.513786	H	-0.426394	1.251519	4.556615

C	-4.179712	5.373417	4.167047	H	-1.066201	2.001431	6.025298
C	-4.275753	5.780397	5.508179	C	-1.295428	0.059282	2.209752
C	-3.664594	5.023485	6.509389	H	-1.035449	-0.125325	3.246688
C	-2.948244	3.856747	6.207805	S	-2.565588	-1.258628	1.751562
O	1.268339	-0.06234	3.421387	C	-1.749199	-2.8337	1.997328
N	1.185619	0.030903	-2.110792	C	-2.342954	-3.955328	1.393221
O	0.085062	0.037572	-2.709331	C	-0.598848	-3.007446	2.782205
O	2.269175	0.040079	-2.739793	C	-1.80398	-5.227665	1.581223
H	-2.493952	3.275361	7.003361	H	-3.227189	-3.829871	0.773338
H	-3.746194	5.335727	7.547332	C	-0.059299	-4.285954	2.951489
H	-4.82838	6.679629	5.764546	H	-0.113194	-2.160686	3.25658
H	-4.656075	5.95878	3.38399	C	-0.656112	-5.400547	2.359691
H	-2.269318	1.59638	1.003592	H	-2.278436	-6.083722	1.108388
H	3.393116	-0.032137	1.909219	H	0.835471	-4.406005	3.557283
H	3.362548	0.007778	-0.577639	H	-0.231542	-6.390673	2.499634

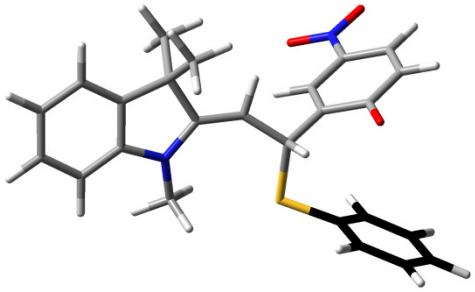
Cartesian Coordinates (in Å) of TS4



C	0.332768	0.505442	-0.004339	H	3.483388	-0.796057	1.806135
C	0.185001	0.088784	1.305023	H	3.674386	0.002635	-0.544313
C	1.362169	-0.435385	2.021855	H	-0.52268	0.8751	-0.55589
C	2.613622	-0.424046	1.270227	C	-1.404744	-1.89563	5.987791
C	2.725376	0.011335	-0.019952	H	-1.767129	-2.276574	6.949806
C	1.568271	0.483806	-0.683345	H	-1.857903	-2.4973	5.192521
C	-1.234396	0.069626	1.88632	H	-0.32037	-2.039321	5.948952
C	-1.521425	-0.320989	3.30956	C	-3.308371	-0.232563	5.879808
C	-1.192288	0.18768	4.516379	H	-3.792811	-0.809959	5.084668
N	-0.360907	1.254684	4.868869	H	-3.700091	-0.58285	6.841997
C	-0.28396	1.397366	6.254085	H	-3.590463	0.818724	5.758988
C	-1.097463	0.446557	6.887989	C	0.423673	2.107856	3.998774
C	-1.773999	-0.405699	5.827485	H	0.231152	3.161176	4.236585
C	-1.178901	0.410512	8.271032	H	1.495597	1.910185	4.118541
C	-0.436184	1.333245	9.028543	H	0.162081	1.937661	2.958497
C	0.372946	2.272474	8.386244	S	-2.196074	1.733311	1.553347
C	0.464917	2.320478	6.987728	C	-3.038583	1.482474	-0.01053
O	1.349607	-0.870905	3.198949	C	-3.921691	0.407617	-0.204129
N	1.647154	0.933765	-2.016772	C	-2.872406	2.423749	-1.038676
O	0.612574	1.344611	-2.596123	C	-4.604996	0.267033	-1.412645
O	2.755725	0.913884	-2.605013	H	-4.081233	-0.313043	0.592922
H	1.102264	3.051939	6.501535	C	-3.578439	2.29191	-2.236748

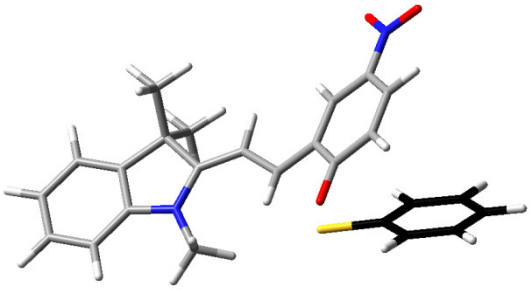
H	0.94744	2.98202	8.97634	H	-2.186225	3.253903	-0.899403
H	-0.491586	1.313022	10.113202	C	-4.440719	1.210838	-2.430779
H	-1.808097	-0.323177	8.769896	H	-5.279848	-0.573334	-1.552023
H	-2.253006	-1.123037	3.369854	H	-3.442917	3.030164	-3.022621
H	-1.817194	-0.617611	1.267922	H	-4.982442	1.104492	-3.3664

Cartesian Coordinates (in Å) of TS5



C	-0.004846	-0.009116	0.037045	H	-0.942084	0.005936	-0.50945
C	-0.00711	0.001484	1.412307	C	-3.08397	3.831856	0.282209
C	1.251025	0.00311	2.163892	H	-3.280944	4.900948	0.140075
C	2.460587	-0.03961	1.35894	H	-2.016826	3.655232	0.107395
C	2.44065	-0.062995	-0.011123	H	-3.650945	3.276831	-0.472629
C	1.2019	-0.04514	-0.696868	C	-2.674756	4.188115	2.754718
C	-2.076213	1.31882	1.871798	H	-1.59882	4.03055	2.624661
C	-3.318998	1.854713	1.889389	H	-2.870932	5.261684	2.652647
N	-4.605334	1.311384	2.045868	H	-2.943403	3.88708	3.772689
C	-5.570536	2.322985	2.112233	C	-4.98282	-0.078134	1.876355
C	-4.976561	3.57857	1.925381	H	-4.368634	-0.534974	1.096315
C	-3.485615	3.39552	1.709462	H	-4.873644	-0.661969	2.795549
C	-5.750704	4.72905	1.940006	H	-6.024736	-0.124957	1.550921
C	-7.135467	4.625462	2.152357	C	-1.300086	0.051936	2.205242
C	-7.71635	3.370785	2.345737	H	-1.001856	0.106585	3.257799
C	-6.944896	2.200473	2.332615	S	-2.218641	-1.5943	2.081206
O	1.291775	0.049158	3.422368	C	-0.981151	-2.74588	2.686444
N	1.172226	-0.063135	-2.106624	C	-0.263521	-3.540677	1.781944
O	0.067846	-0.040552	-2.701263	C	-0.779641	-2.917567	4.063932
O	2.252171	-0.101845	-2.744138	C	0.644541	-4.493968	2.249901
H	-7.413259	1.236737	2.504112	H	-0.418767	-3.411314	0.715438
H	-8.786802	3.292395	2.517637	C	0.135628	-3.863511	4.528056
H	-7.750647	5.520479	2.170234	H	-1.342789	-2.312413	4.768439
H	-5.293838	5.704342	1.788287	C	0.847582	-4.655074	3.622162
H	-1.333856	2.087939	1.668994	H	1.193824	-5.107747	1.541024
H	3.405282	-0.047287	1.897253	H	0.286444	-3.987953	5.597044
H	3.35885	-0.092235	-0.587124	H	1.55425	-5.396339	3.985211

Cartesian Coordinates (in Å) of TS6



C	0.002522	-0.000888	0.002899	H	-0.926808	-0.015121	-0.554657
C	0.003219	0.001385	1.392426	C	-5.448611	0.529012	0.765607
C	1.280747	-0.000809	2.129825	H	-6.350813	0.948141	0.306523
C	2.484689	0.011602	1.315429	H	-4.77813	0.203739	-0.03687
C	2.450033	0.017688	-0.051398	H	-5.737736	-0.349922	1.35064
C	1.199766	0.008425	-0.724608	C	-4.355271	2.816552	0.807402
C	-2.445027	0.542446	1.70823	H	-3.673181	2.524698	0.002359
C	-3.551509	0.988038	2.392496	H	-5.242284	3.270225	0.351925
N	-3.805732	1.01262	3.744499	H	-3.858959	3.574586	1.421621
C	-5.037763	1.641628	4.016487	C	-2.948854	0.488563	4.798818
C	-5.658434	1.998542	2.81324	H	-2.533066	-0.475554	4.501779
C	-4.765456	1.592679	1.656359	H	-2.133039	1.181901	5.034862
C	-6.898226	2.620628	2.825706	H	-3.546884	0.334022	5.697366
C	-7.514246	2.89062	4.057381	C	-1.205371	0.031487	2.196764
C	-6.879733	2.538333	5.250701	H	-0.975365	0.137782	3.24711
C	-5.627784	1.908979	5.251203	S	-1.710385	-2.36443	2.605344
O	1.332189	-0.000209	3.385125	C	-0.426293	-3.36426	1.903367
N	1.162081	0.009413	-2.14306	C	-0.68818	-4.182229	0.783611
O	0.056542	-0.00155	-2.727364	C	0.877352	-3.383365	2.441975
O	2.238946	0.021715	-2.778732	C	0.30204	-5.00306	0.243821
H	-5.146003	1.654325	6.188998	H	-1.682579	-4.173999	0.345463
H	-7.358595	2.756793	6.201178	C	1.868603	-4.197309	1.891777
H	-8.484195	3.37848	4.081755	H	1.108045	-2.741343	3.286043
H	-7.388376	2.898995	1.896176	C	1.587475	-5.016254	0.794362
H	-2.548266	0.60752	0.629404	H	0.070495	-5.630363	-0.613878
H	3.433131	0.016105	1.846003	H	2.866076	-4.193454	2.32536
H	3.360889	0.02701	-0.638988	H	2.359948	-5.652746	0.371093