Electronic Supporting Information

Phenolylazoindole scaffold as facilely synthesized and *bis*-functional photoswitches combining controllable fluorescence and antifungal properties with theoretical methods

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Photophysical properties

General information

The light sources used for photoisomerization are: 365 nm LED lamp (3 W), 460 nm LED lamp (5 W), 254 nm lamp (3 W), 302 nm LED lamp (3 W), 515 nm laser (80 mW), 650 nm laser (200 mW).

Photochemical isomerizations (PSSs)

PSS compositions at different wavelengths were determined as follows: 365 and 460 nm PSSs were determined by ^{1}H NMR in DMSO-d_6. The sample (1-2 mg/mL in DMSO-d_6) was sealed in a quartz cuvette and then irradiated with 365 nm or 460 nm LED light typically for 30-40 min to ensure the establishment of PSS. Then we used the UV-Vis spectra of a trans isomer and a 365 nm PSS state to deduce the spectrum of the cis isomer. A pair of trans and cis spectra were used for fitting the respective spectra at 254, 302, 515, and 650 nm PSS states. According to the fitting results, isomer fractions in the respective PSS states were obtained.
Spectral fitting follows the equation: $\alpha \times Abs_{trans}(\lambda) + (1-\alpha) \times Abs_{cis}(\lambda) = Abs_{pss}(\lambda)$.
With α the content of trans isomer in a PSS state, Abstrans (λ), Abscis (λ) and Abspss (λ) the srectra of pure trans, pure cis and pss state (at the same concentratin).

Optical cycle

To check the photostability, solutions of the synthesized switches in DMSO were exposed to 365 nm and 460 nm (515/460 nm light with equal effect on **B2**) light alternately. After 8-10 times cycles of photolysis, noticeable photobleaching was not found for any of these switches.

Thermal isomerization kinetics

Thermal cis-trans isomerization kinetics was studied at elevated temperatures. The trans sample was thermally equilibrated for at least 10 min to reach the equilibrium temperature, and the absorbance at π–π^* λmax was recorded. It was then irradiated for 10 s by 365 nm UV light to reach a cis-rich state and thermally equilibrated again for 2 min. The absorbance was read at a certain interval (typically, 60 s) with a sampling time of 1 s.
The absorbance data were fitted following first-order rate equation:

$$\ln [(A_\infty - A_0)/ (A_\infty - A_t)] = kt$$

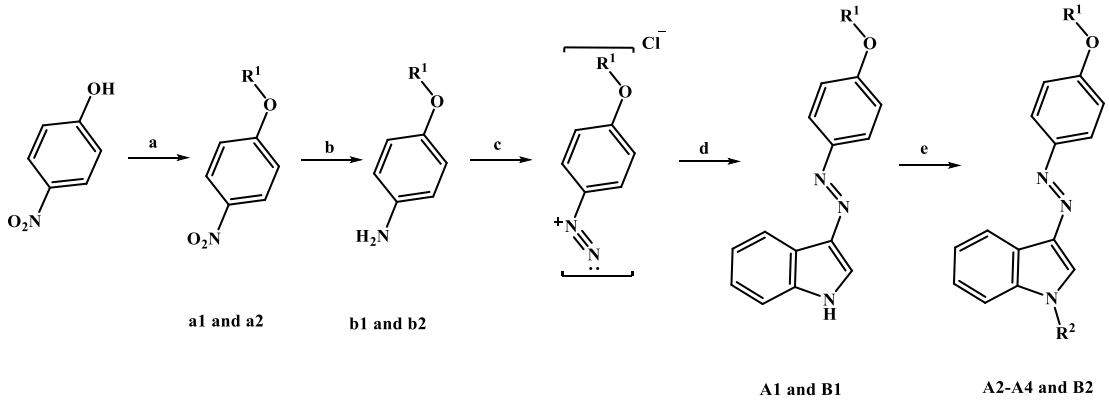
A_∞, A_0 and A_t represent the absorbances of pure trans state, at initial state (PSS_{cis}) and at reaction time *t*.
The thermal half-life $t_{1/2}$ of a first-order kinetics reaction was calculated as:

$$t_{1/2} = \ln 2/k$$

Bioassays

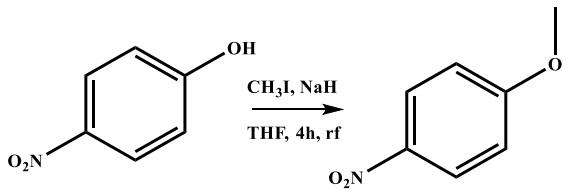
The bioactivity of all target compounds was determined *in vitro* using the standard mycelium growth inhibition technique against three representative agricultural plant pathogens, each tested compound was solubilized in DMSO and mixed with molten potato dextrose agar (PDA) to obtain the medicated medium at 50 μg/mL with three replicates. Fungus mycelium cakes (5 mm) were placed in the center of PDA medium plates with a germ-free inoculation needle and then incubated for 2−3 days at 25 ℃. In photocontrolled bioassay, the PDA was irradiated at 365 nm light for 1 hour and then inoculated with fungus.

Synthesis



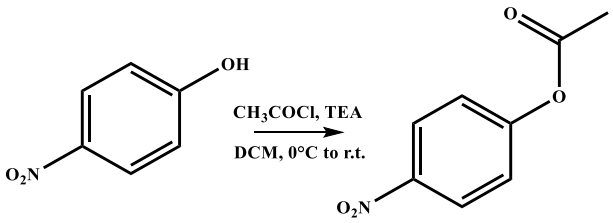
Scheme S1. Complete synthesis route of title compounds

Preparation of compound a1.



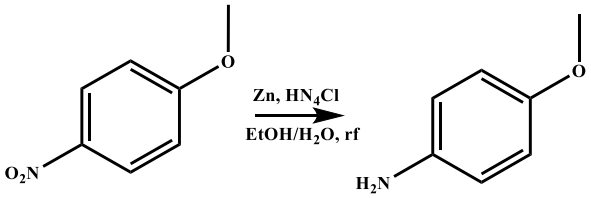
The mixtures of *p*-nitrophenol (1.39 g, 10 mmol), potassium iodide (2.11 g, 15 mmol), and 60% NaH in mineral oil (0.60 g, 15 mmol) in 50 ml of anhydrous THF stirred in the room temperature for 30mins and then the system was reflex for 4h, the reaction was monitored by TLC then mixture was concentrated and poured into water followed by the extraction with ethyl acetate. The organic layer was washed with distilled water, saturated solution of NaCl, and dried over $MgSO_4$. After the removal the solvent, the crude mixture was purified by column chromatography on silica gel (ethyl acetate: petroleum ether =1:10) to obtain1-methoxy-4-nitrobenzene after drying in vacuum as faint yellow solid. **a1**: yellow solid, yield 83 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.80 (d, J = 8.6 Hz, 2H), 7.08 (d, J = 8.8 Hz, 2H), 3.84 (s, 3H).

Preparation of compound a2.



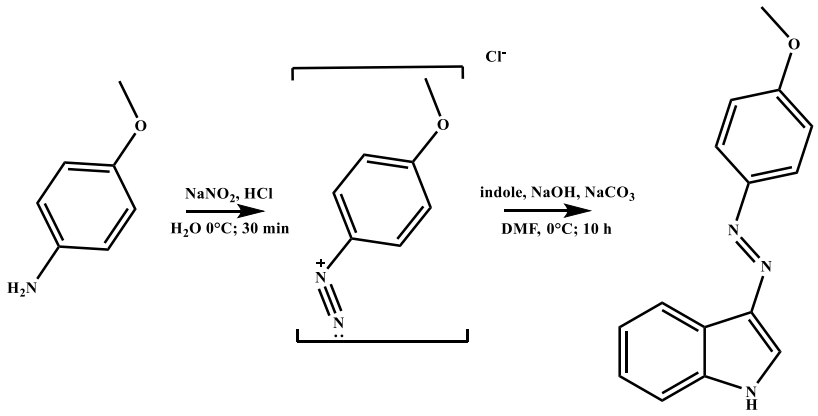
The mixtures of *p*-nitrophenol (1.39 g, 10 mmol), acetyl chloride (1.06 mL, 15 mmol), and triethylamine (4 mL, 30 mmol) in 50 ml of anhydrous DCM stirred at an ice salt bath for 30mins and then the system was stirred at room temperature for 10 h, the reaction was monitored by TLC then mixture was concentrated and poured into water followed by the extraction with ethyl acetate. The organic layer was washed with distilled water, saturated solution of NaCl, and dried over $MgSO_4$. After the removal the solvent, the crude mixture was purified by column chromatography on silica gel (ethyl acetate: petroleum ether =1: 8) to obtain1-methoxy-4-nitrobenzene after drying in vacuum as an faint yellow solid. **a2**: yellow solid, yield 87 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.84 (d, J = 8.7 Hz, 2H), 7.28 (d, J = 8.7 Hz, 2H), 2.31 (s, 3H).

Preparation of compound b1.



Taking compound **b1** as example, 1-methoxy-4-nitrobenzene (1.53 g, 10 mmol), ethanol (40 mL), water (2 mL), and ammonium chloride (1.07 g, 20 mmol) were mixed and stirred with zinc (1.3 g, 20 mmol) in the condition of reflux. After 6h, the reaction completed. After filtration, the filtrate was concentrated to get 4-methoxyaniline. **b1**: darkness brown solid, yield 67 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.84 (d, J = 8.7 Hz, 2H), 6.68 (d, J = 8.7 Hz, 2H), 5.98 – 5.68 (s, 2H), 3.84 (s, 3H). **b2**: darkness brown solid, yield 59 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.94 (d, J = 8.9 Hz, 2H), 6.69 (d, J = 8.9 Hz, 2H), 5.95 – 5.71 (s, 2H), 2.31 (s, 3H).

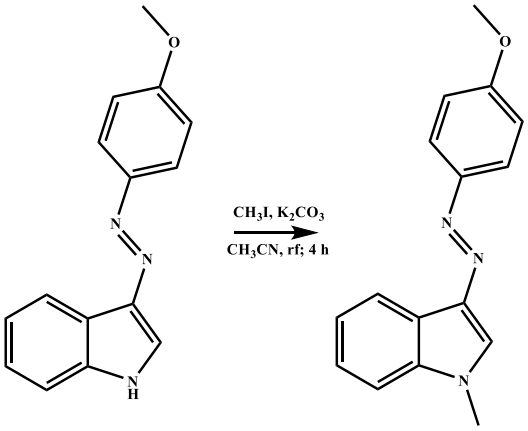
Preparation of compound A1.



Also taking compound c1 as example, **b1** was dissolved in 30 mL of water, followed by the

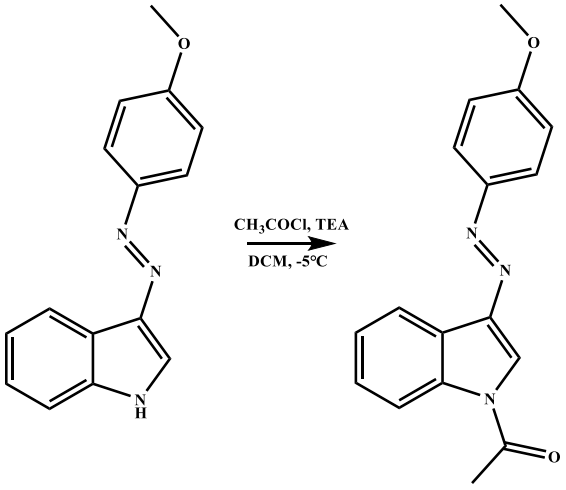
addtion of 5 mL of HCl (12.2 mol/L, 57 mmol). After the solution was cooled under 0 ℃, a pre-cooling solution of $NaNO_2$ (0.9 g, 13 mmol,) in 30 mL water was slowly added. After the mixture was stirred for 30 min in a 0 ℃ ice-salt bath, a pre-cooling solution of indole (1.4 g, 12 mmol,) and NaOH (1 g, 27 mmol) in 20 mL of water was slowly added. Then, a pre-cooling solution of Na_2CO_3 (3.8 g, 33 mmol) in 30 mL of water was slowly drip added. The brownish yellow solid precipitated continuously. After stirred for 3 h, filtered and wash with water and dry to obtained yellow solid. The crude product was subjected to flash silica gel column chromatography (ethyl acetate-Petroleum ether: 2:1) to afford the pure compound **A1**.

Preparation of compound A2



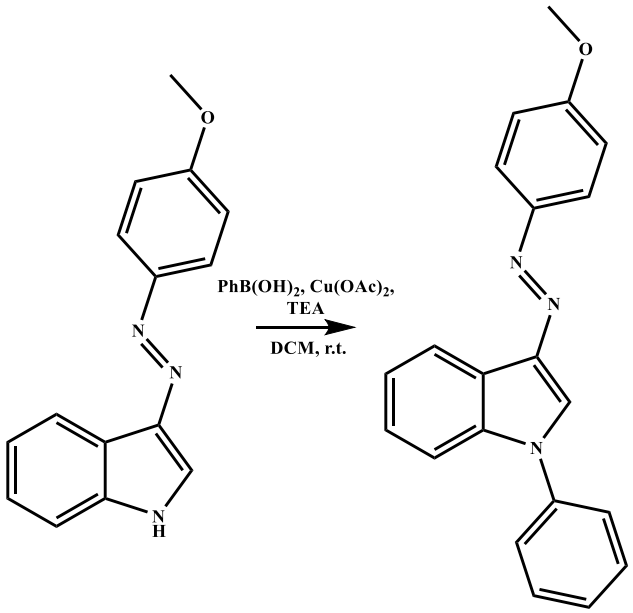
Compound **A1** (0.75 g, 3 mmol) was used for reaction, the reaction is very similar to the synthesis of compound **a1**, synthesize route can refer to that.

Preparation of compound A3



Compound **A1** (0.75 g, 3 mmol) was used for reaction, the reaction is very similar to the synthesis of compound **b1**, synthesize route can refer to that.

Preparation of compound A4



Intermediate **A1** (0.75 g, 3 mmol) was dissolved in DCM (30ml) and added to a flask, and then the phenylboronic acid and TEA (1.3 ml, 9 mmol) and $Cu(OAc)_2$ (1.2 g, 6 mmol) in dichloromethane was slowly added dropwise to the mixed solution. Reacted at r.t. for 24 hours, after the reaction, filter and wash the solution, purification by column chromatography (ethyl acetate-Petroleum ether: 1:1) gave the product **A4**. The synthesis method of compound **B2** was similar to this.

A1: Brown solid, yield 0.62 g, 2.48 mmol, 83 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 11.98 (s, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.28 (s, 1H), 7.80 (d, *J* = 8.6 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 1H), 7.26 (dd, *J* = 14.0, 6.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.47, 147.83, 137.01, 135.73, 132.73, 124.07, 123.27, 122.70, 122.64, 118.69, 114.80, 112.61, 55.90. HRMS (ESI) *m*/*z* calcd for $C_{15}H_{13}N_3O$ $[M + H]^+$252.1132, found 252.1130.

A2: Brown solid, yield 0.58 g, 2.19 mmol, 73 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.41 (d, *J* = 7.7 Hz, 1H), 8.29 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.27 (t, *J* = 7.4 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.49, 147.83, 137.54, 136.02, 134.56, 124.10, 123.27, 122.94, 122.77, 114.82, 110.93, 55.92, 33.55. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{15}N_3O$ $[M + H]^+$266.1288, found 266.1281.

A3: Brown solid, yield 0.59 g, 2.01 mmol, 67 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.80 (s, 1H), 8.49 – 8.40 (m, 2H), 7.90 (d, *J* = 8.7 Hz, 2H), 7.44 (dt, *J* = 24.3, 7.3 Hz, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.79 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 170.56, 161.86, 135.97, 126.88, 125.60, 124.16, 123.10, 116.47, 115.08, 56.08, 24.38. HRMS (ESI) *m*/*z* calcd for $C_{17}H_{15}N_3O_2$ $[M + H]^+$ 294.1237, found 294.1234.

A4: Brown solid, yield 0.61 g, 1.86 mmol, 62 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.59 (s, 1H), 8.56 – 8.50 (m, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.7 Hz, 2H),

7.61 – 7.56 (m, 1H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.36 (dd, *J* = 8.9, 5.1 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H), 3.85 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.97, 147.73, 138.36, 136.52, 136.23, 134.37, 130.44, 128.12, 125.10, 125.02, 123.77, 123.62, 123.27, 120.12, 114.91, 111.40, 55.97. HRMS (ESI) *m*/*z* calcd for $C_{21}H_{17}N_3O$ $[M + H]^+$ 328.1445, found 328.1447.

B1: Brown solid, 0.68 g, 2.43 mmol, yield 81 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 12.12 (s, 1H), 8.42 – 8.34 (m, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 1H), 7.31 – 7.25 (m, 4H), 2.31 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.07, 155.86, 145.46, 136.32, 128.08, 125.70, 125.62, 123.66, 121.31, 120.45, 119.20, 111.83, 101.42, 21.34. HRMS (ESI) *m*/*z* calcd for $C_{16}H_{13}N_3O_2$ $[M + H]^+$ 280.1081, found 280.1079.

B2: Brown solid, yield 0.56 g, 1.62 mmol, 54 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.71 (s, 1H), 8.56 – 8.52 (m, 1H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.59 (d, *J* = 4.9 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 3H), 7.32 (t, *J* = 9.5 Hz, 2H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 169.07, 155.87, 145.46, 136.33, 134.55, 133.91, 130.46, 128.09, 127.89, 127.81, 125.71, 125.62, 123.67, 121.32, 120.45, 119.21, 111.83, 101.43, 21.34. HRMS (ESI) *m*/*z* calcd for $C_{22}H_{17}N_3O_2$ $[M + H]^+$ 356.1394, found 356.1395.

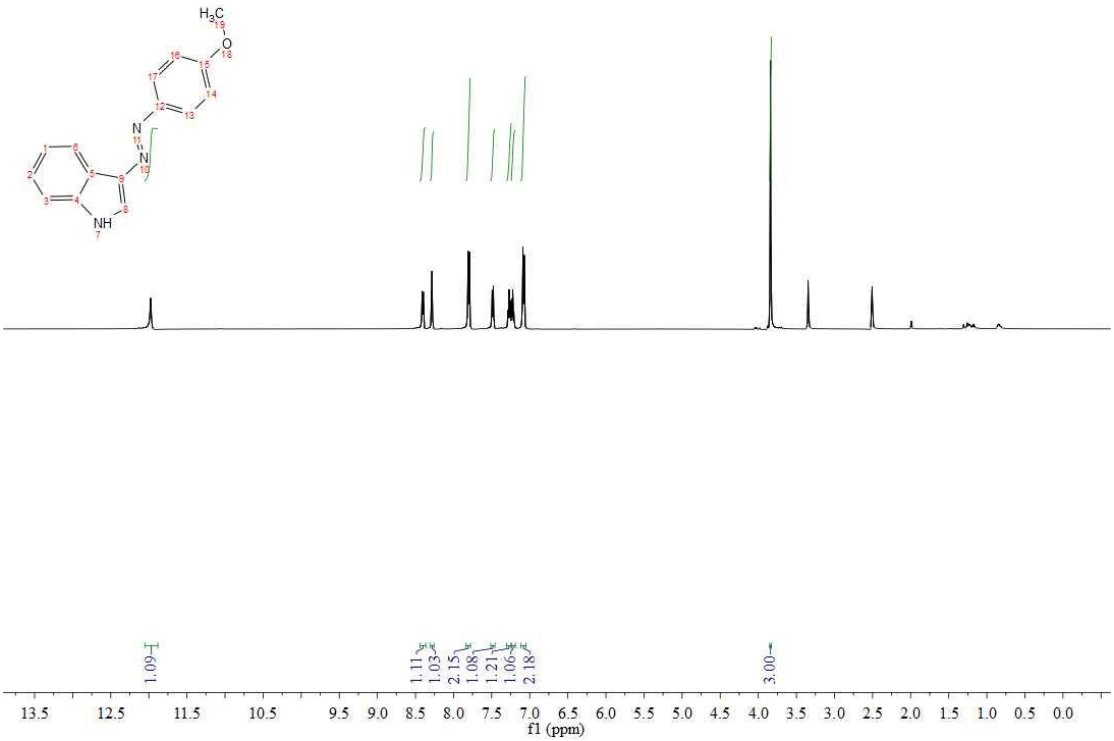


Figure S1. ^{1}H NMR spectra of compound **A1** in DMSO-d_6.

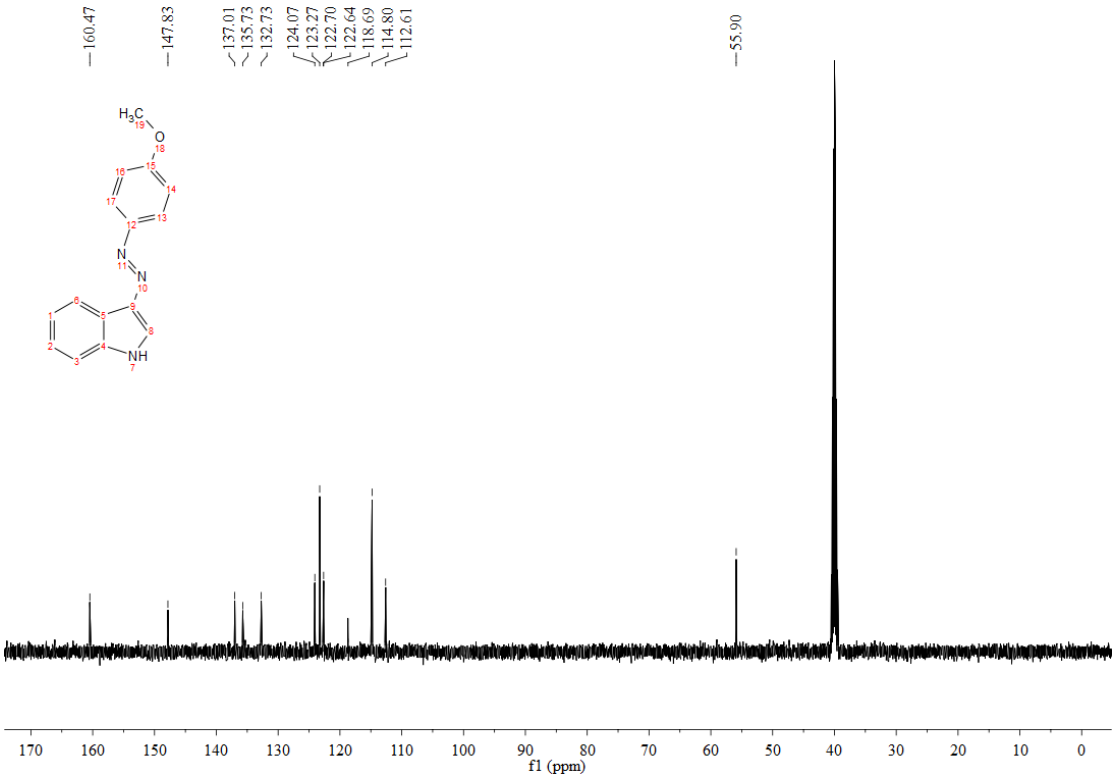


Figure S2.[13]C NMR spectra of compound **A1** in DMSO-d_6.

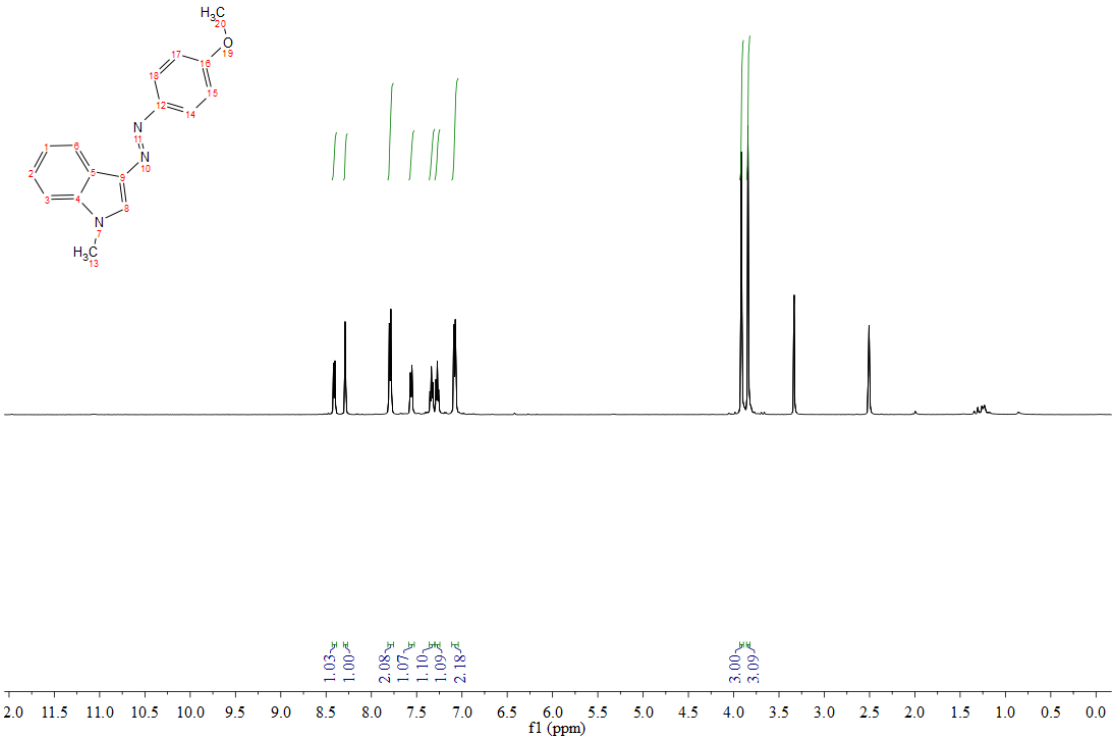


Figure S3. [1]H NMR spectra of compound **A2** in DMSO-d_6.

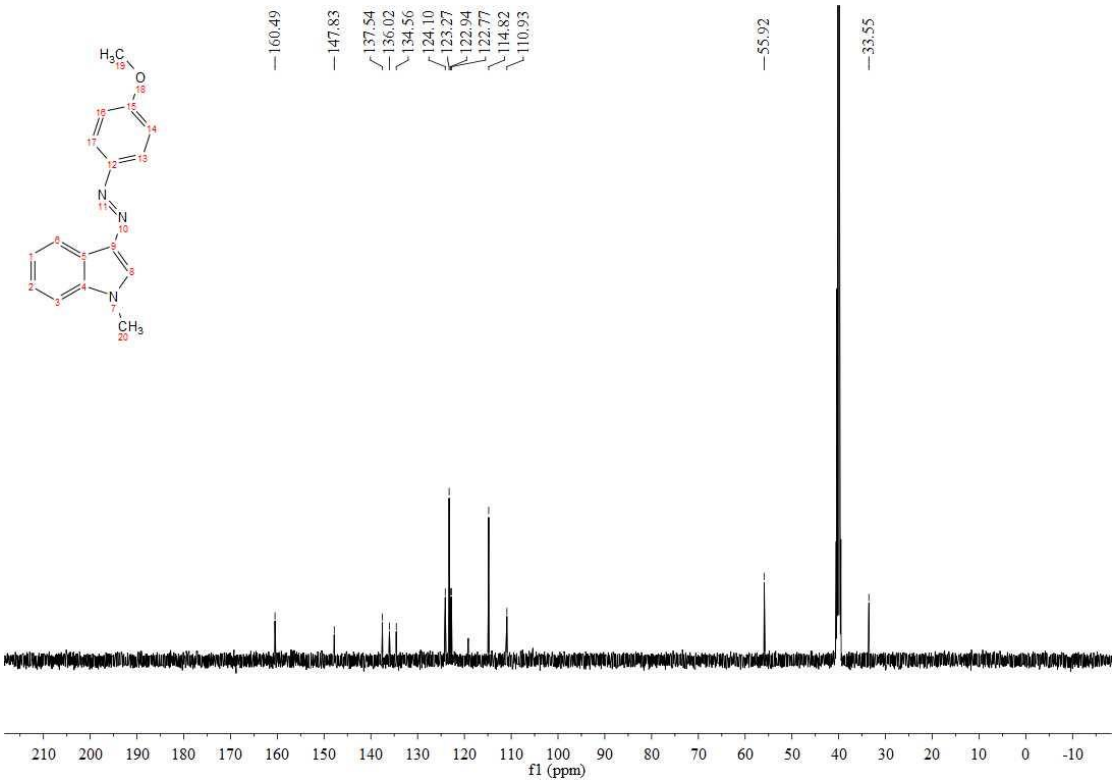


Figure S4. ^{13}C NMR spectra of compound **A2** in DMSO-d_6.

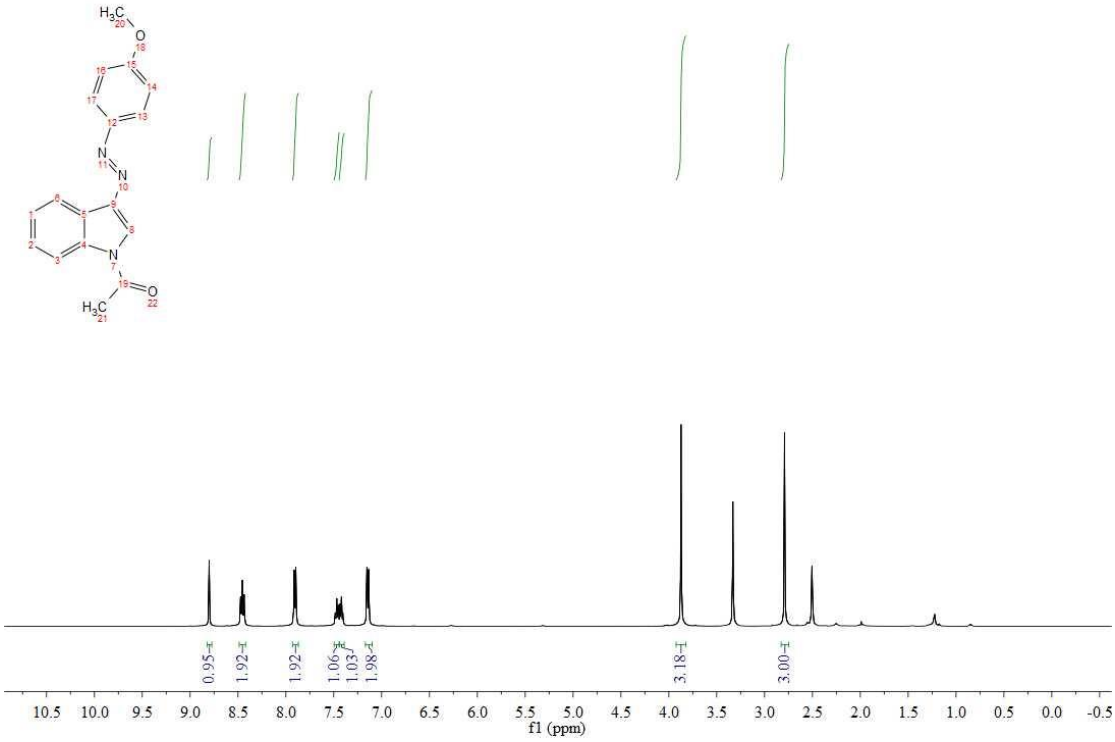


Figure S5. ^{1}H NMR spectra of compound **A3** in DMSO-d_6.

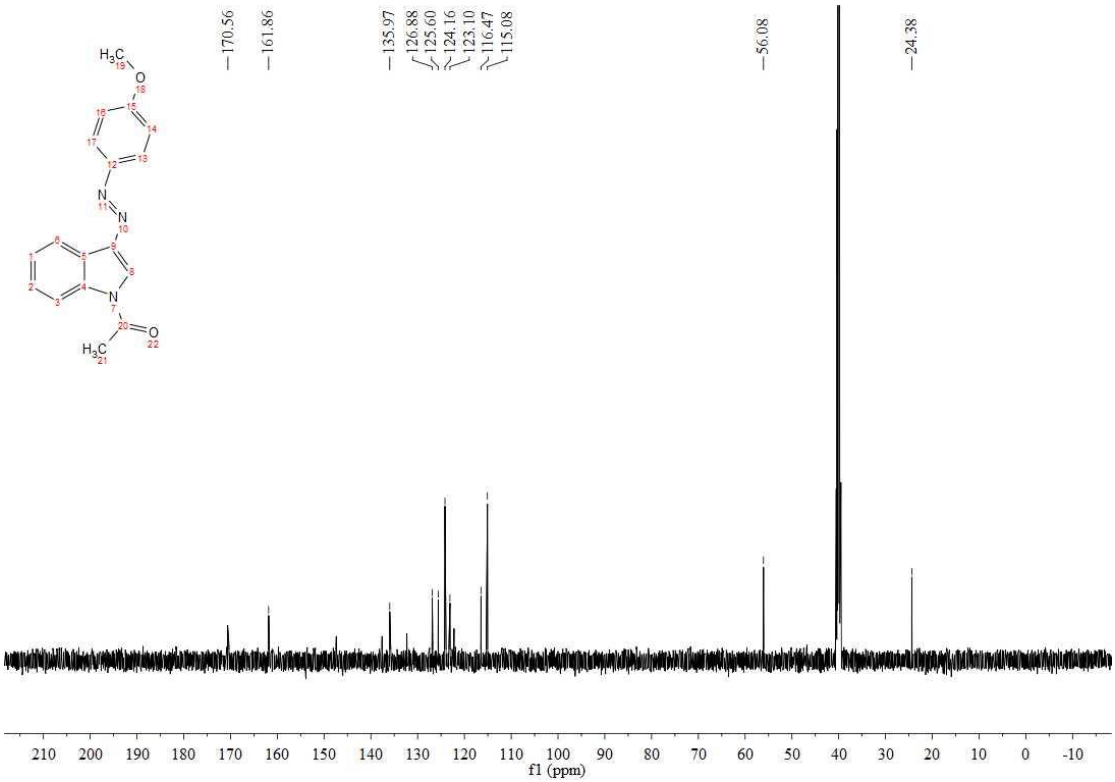


Figure S6. ^{13}C NMR spectra of compound **A3** in DMSO-d_6.

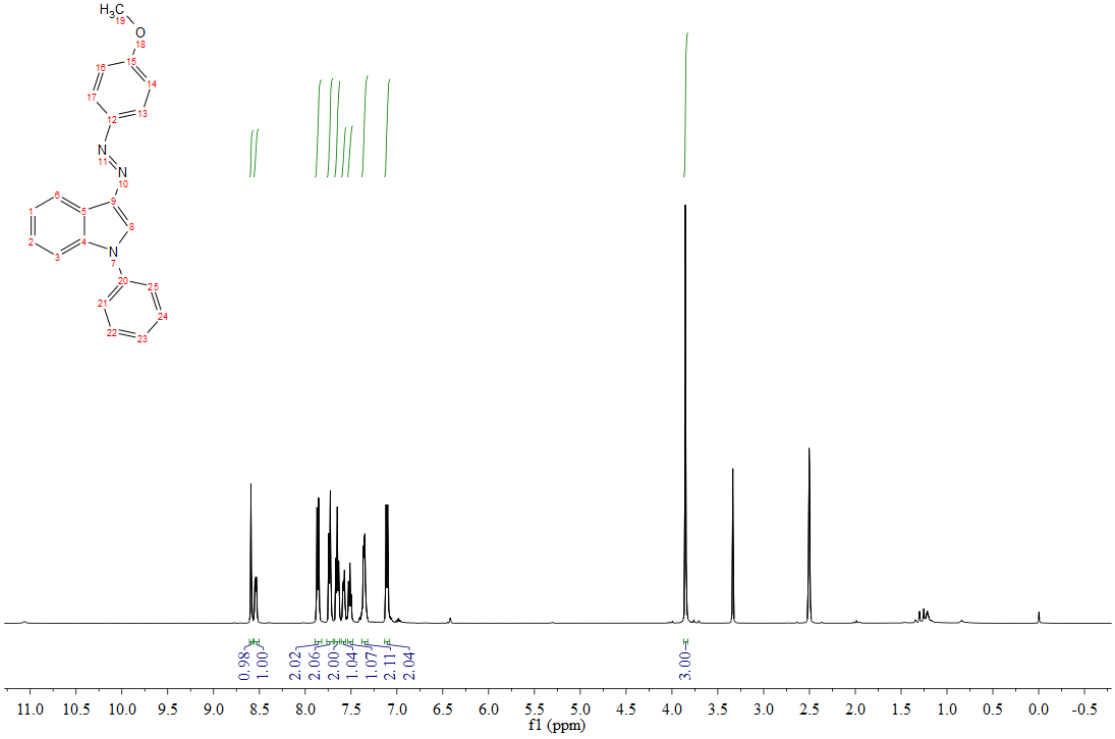


Figure S7. ^{1}H NMR spectra of compound **A4** in DMSO-d_6.

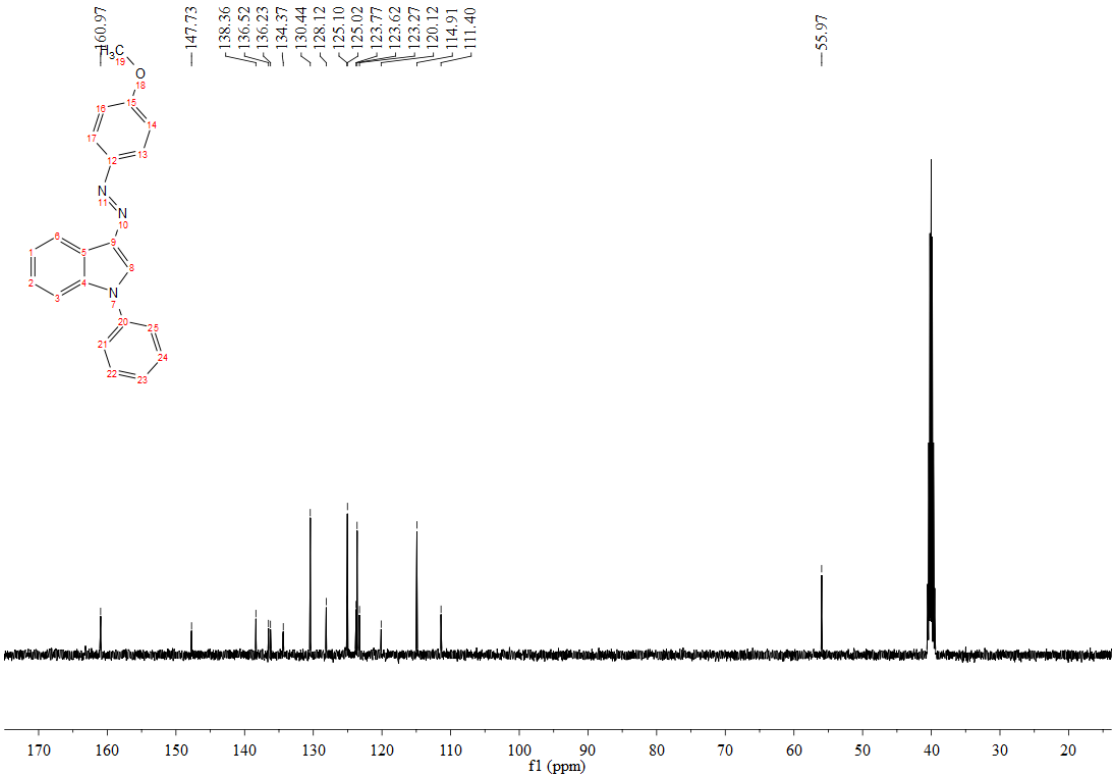


Figure S8. ^{13}C NMR spectra of compound **A4** in DMSO-d_6.

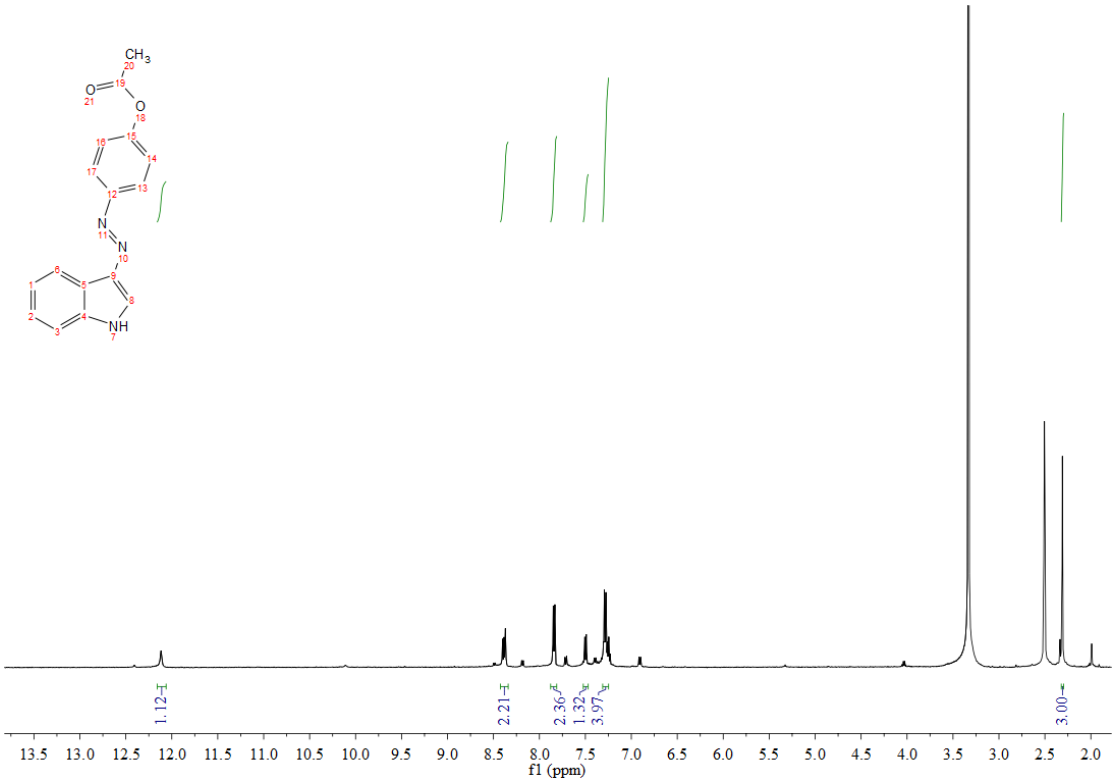


Figure S9. ^{1}H NMR spectra of compound **B1** in DMSO-d_6.

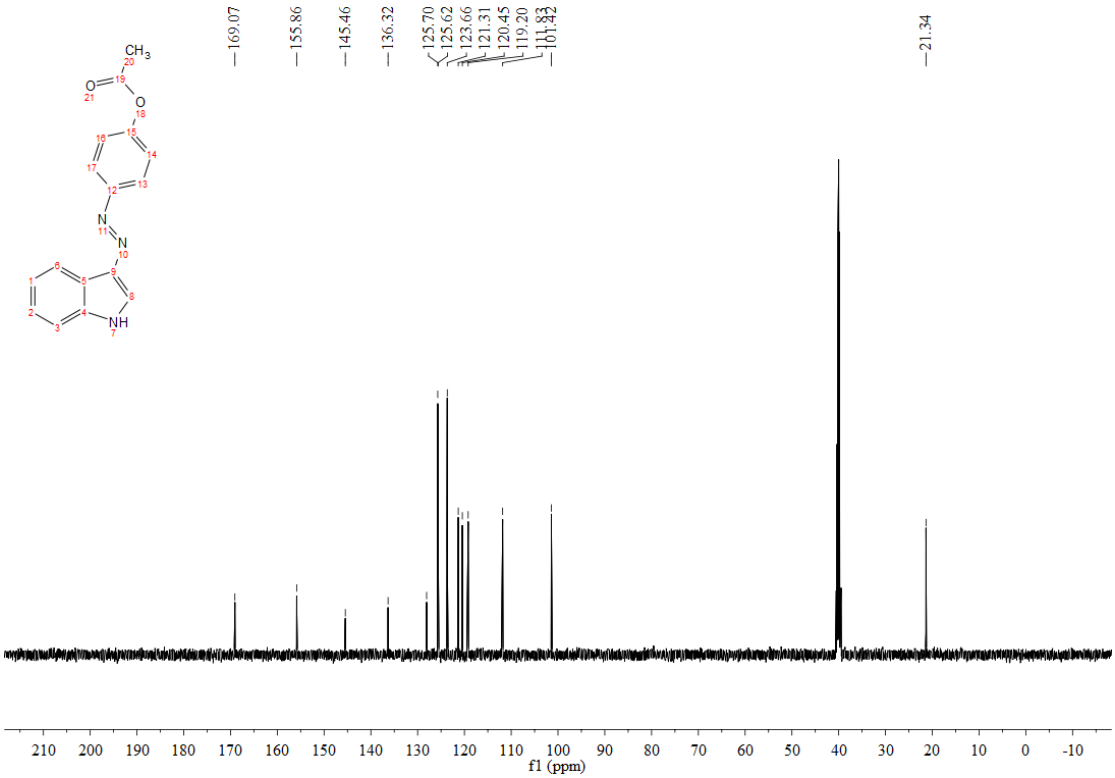


Figure S10. ^{13}C NMR spectra of compound **B1** in DMSO-d_6.

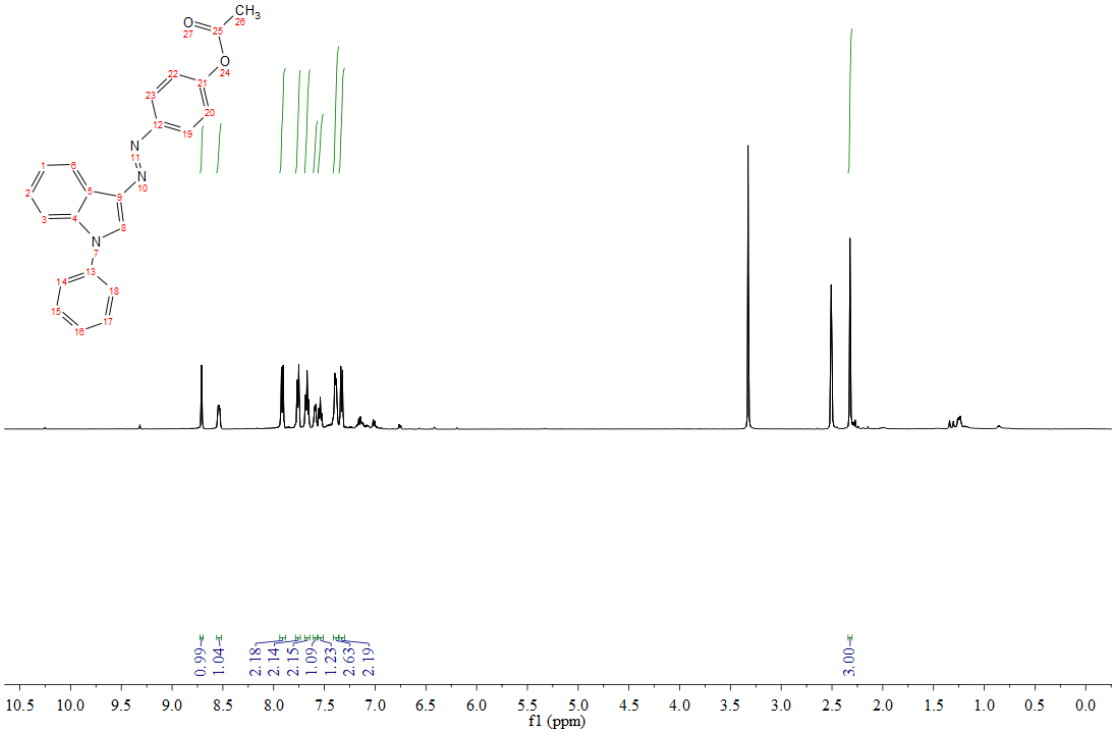


Figure S11. ^{1}H NMR spectra of compound **B2** in DMSO-d_6.

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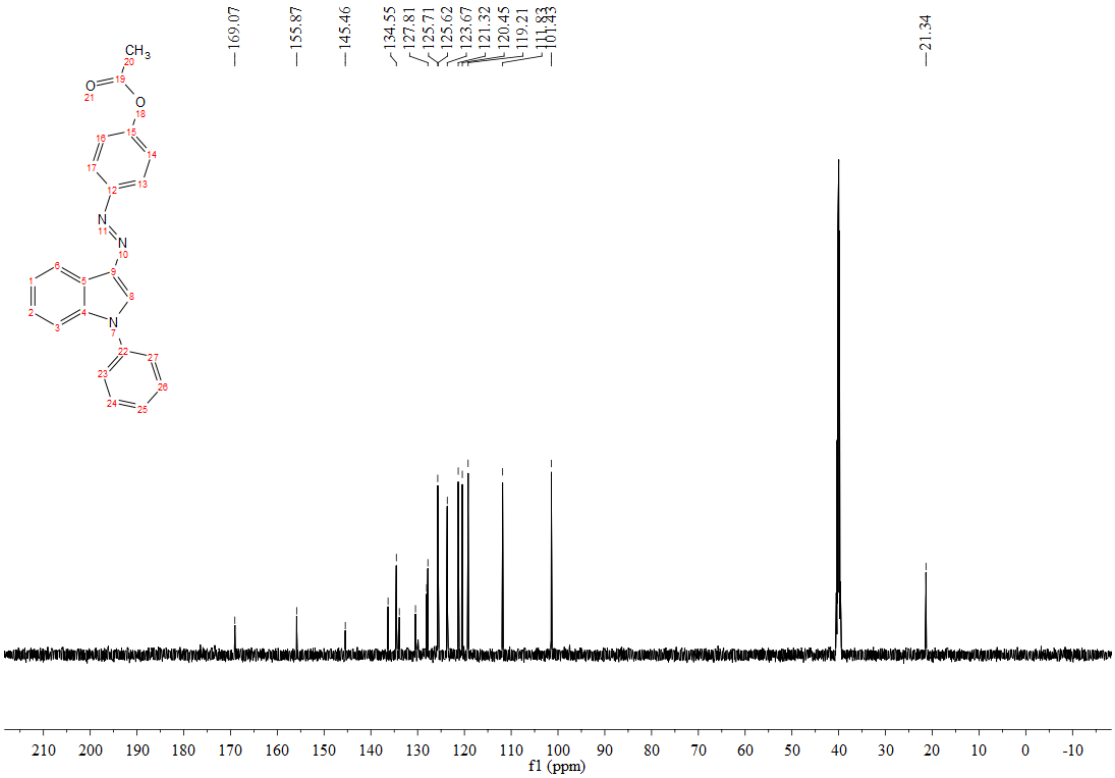


Figure S12. ^{13}C NMR spectra of compound **B2** in DMSO-d_6.

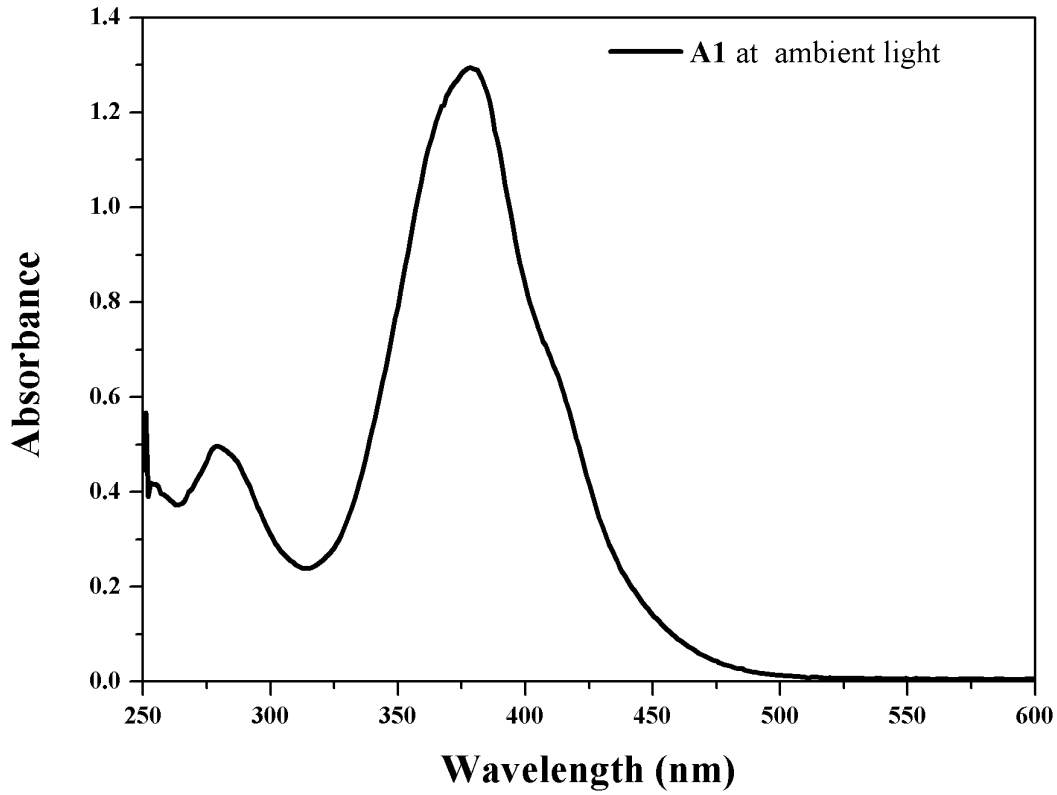


Figure S13. UV/Vis absorption spectra of **A1** in DMSO.

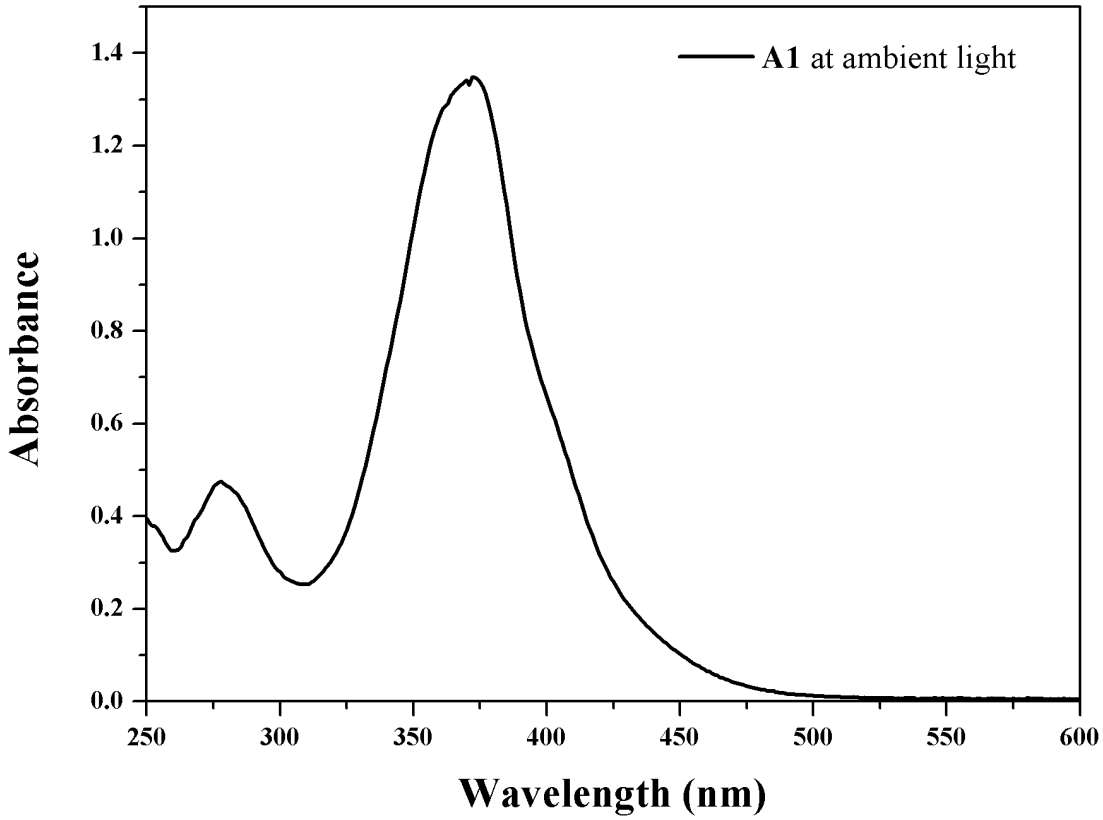


Figure S14. UV/Vis absorption spectra of **A1** in CH_3CN.

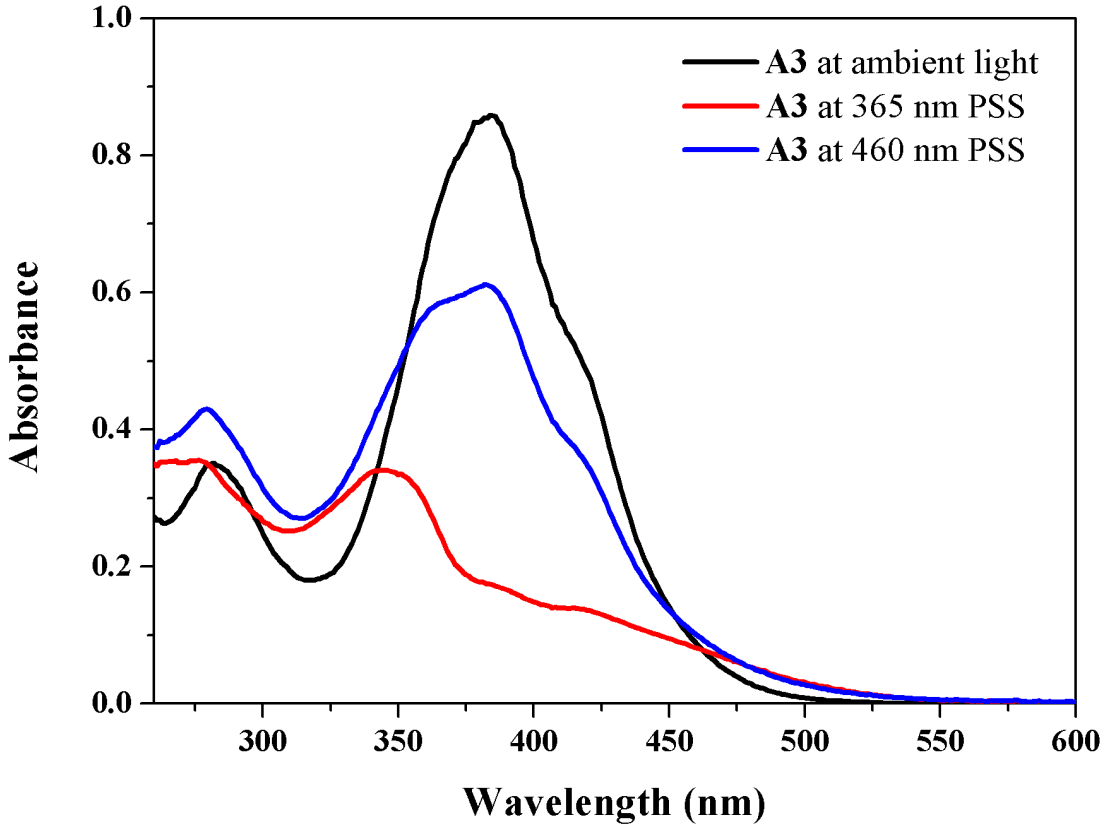


Figure S15. UV/Vis absorption spectra of **A2** at initial state, 365, and 460 nm PSSs in DMSO.

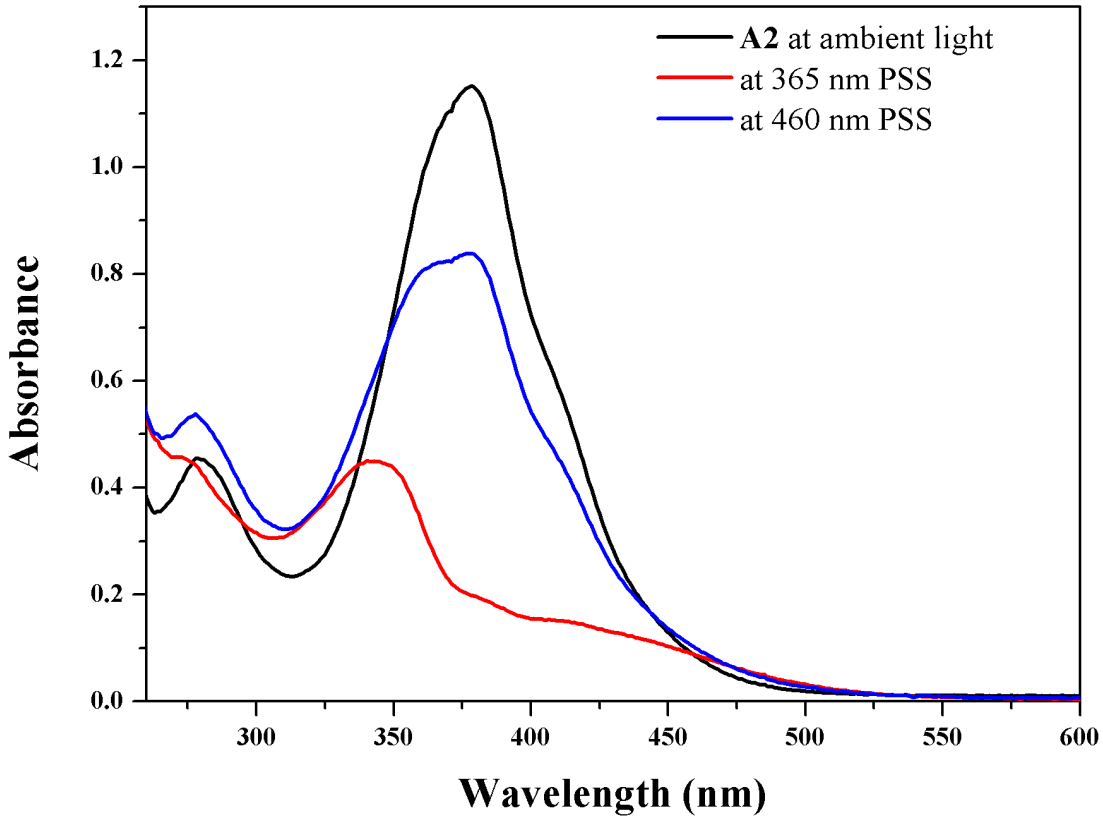


Figure S16. UV/Vis absorption spectra of **A2** at initial state, 365, and 460 nm PSSs in CH_3CN.

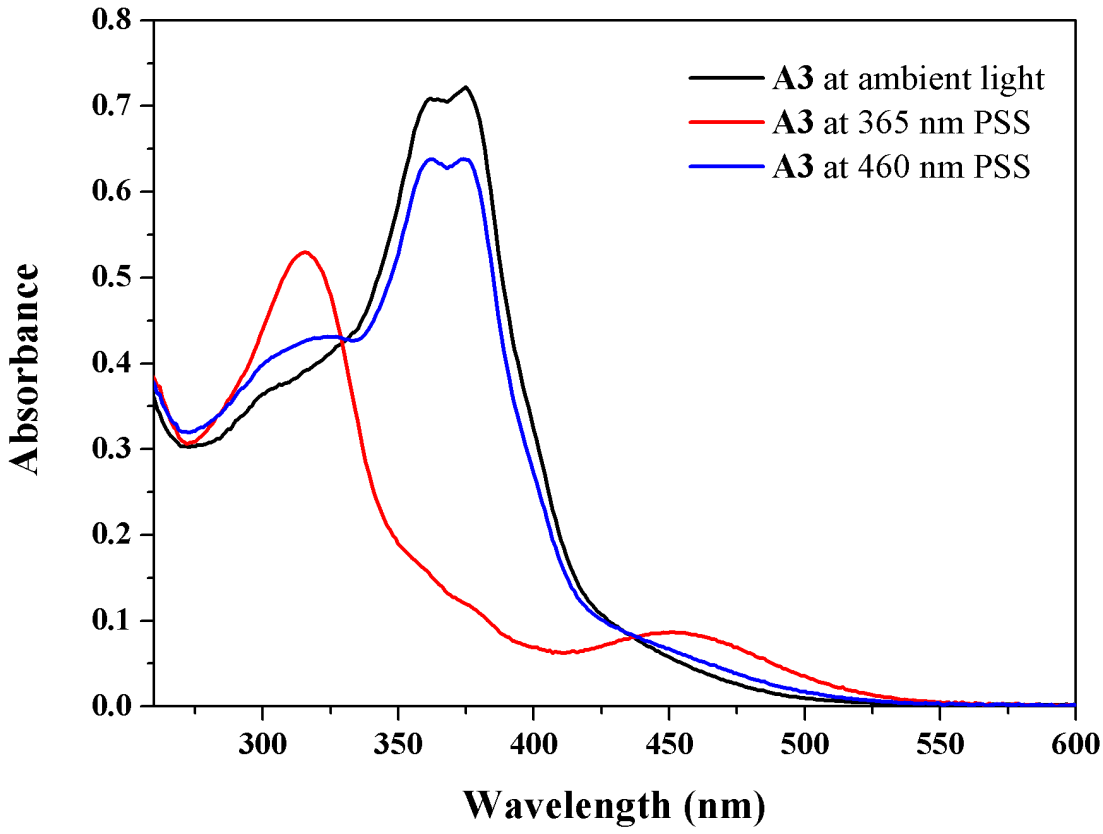


Figure S17. UV/Vis absorption spectra of **A3** at initial state, 365, and 460 nm PSSs in DMSO.

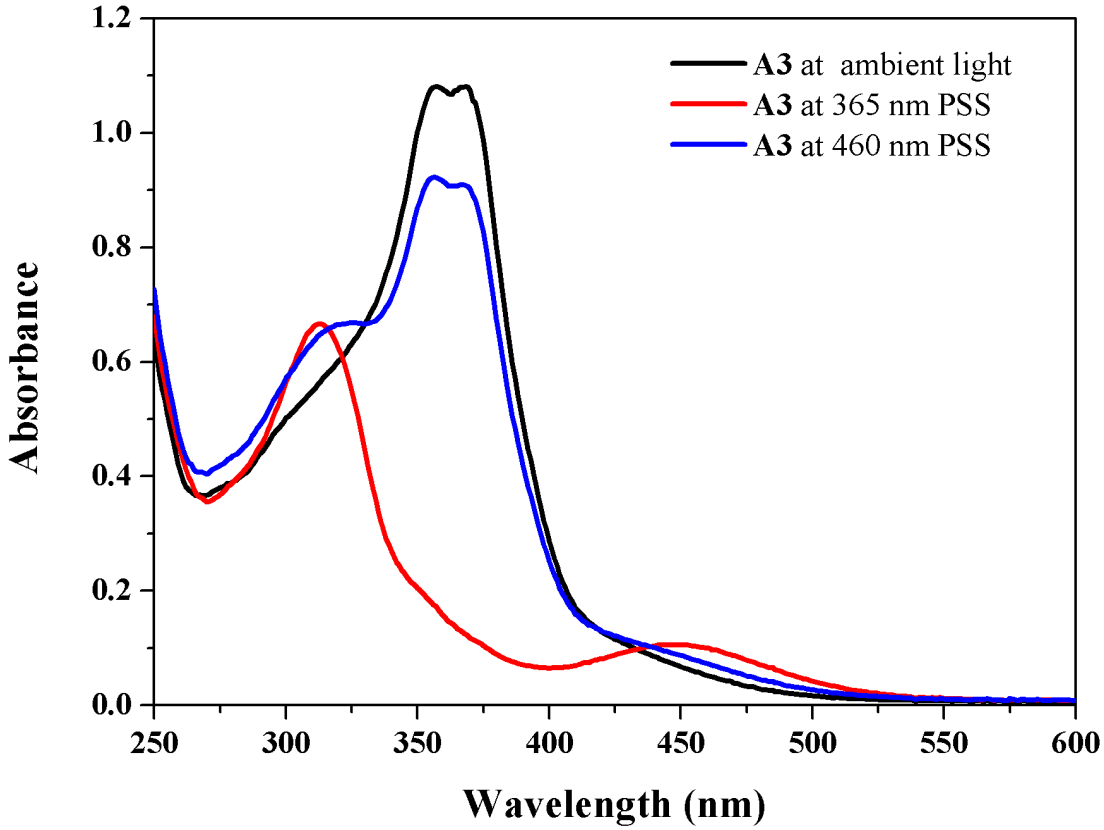


Figure S18. UV/Vis absorption spectra of **A3** at initial state, 365, and 460 nm PSSs in CH_3CN.

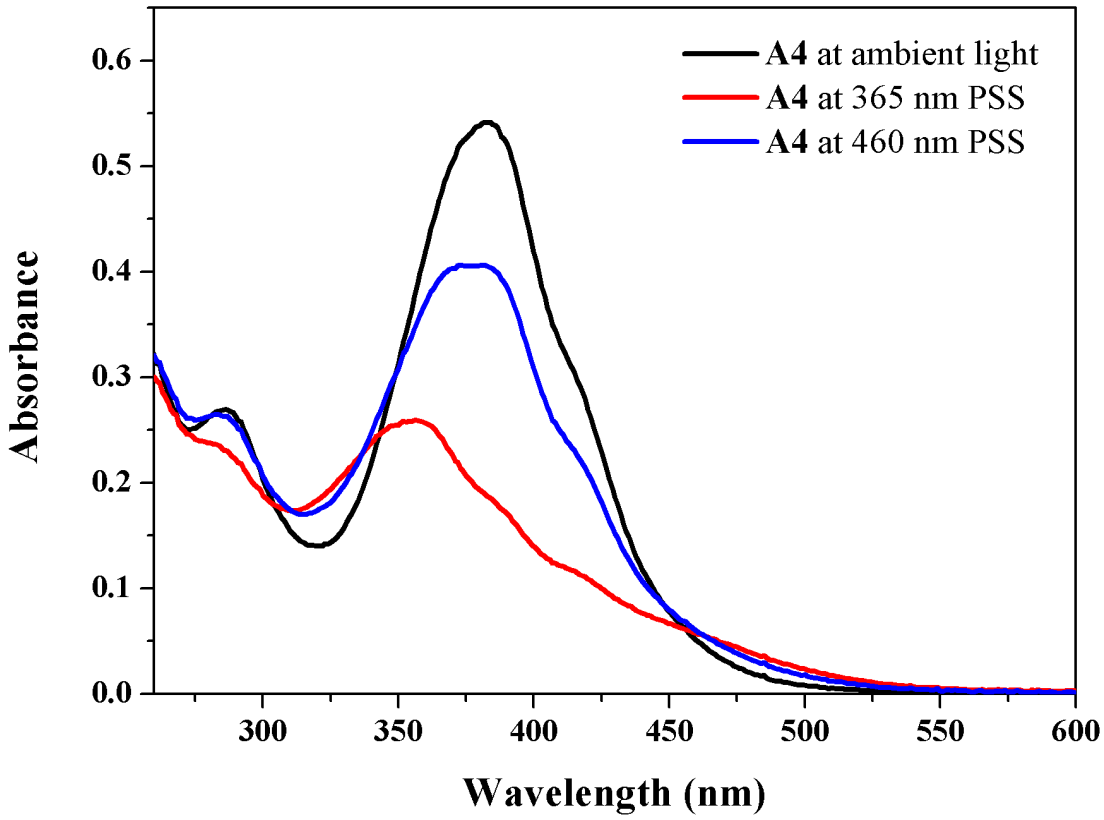


Figure S19. UV/Vis absorption spectra of **A4** at initial state, 365, and 460 nm PSSs in DMSO.

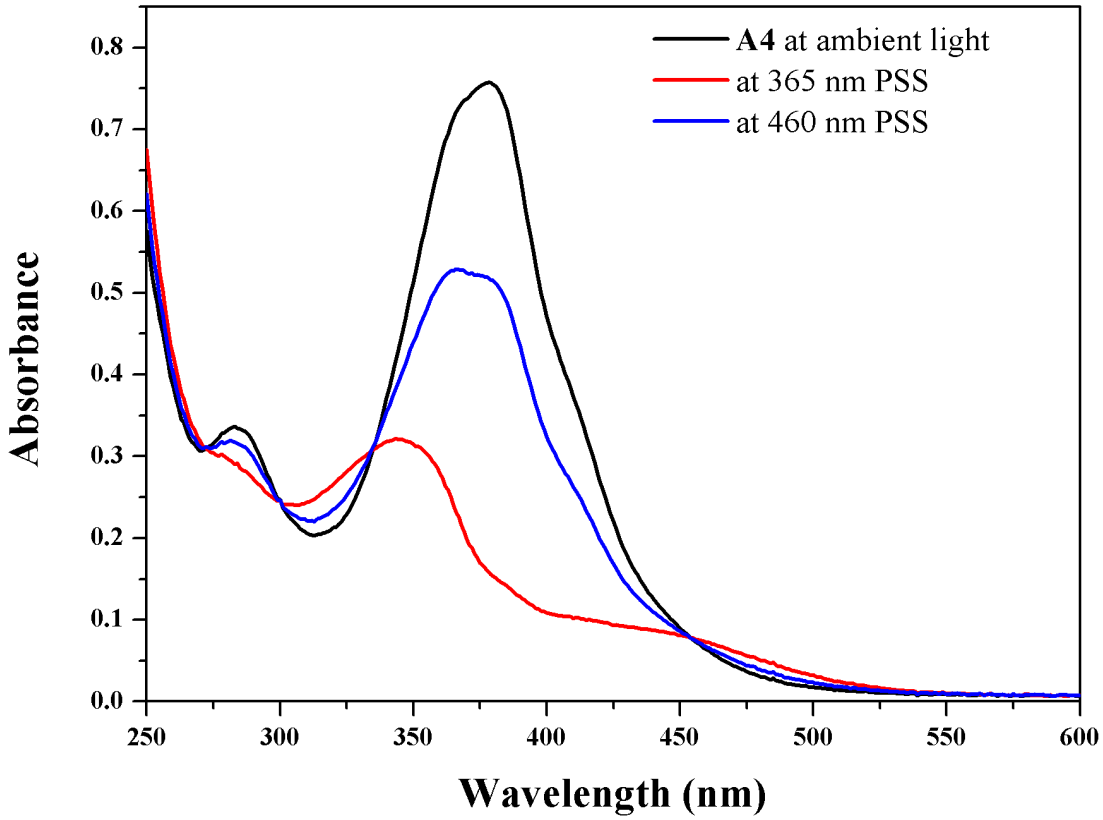


Figure S20. UV/Vis absorption spectra of **A4** at initial state, 365, and 460 nm PSSs in CH_3CN.

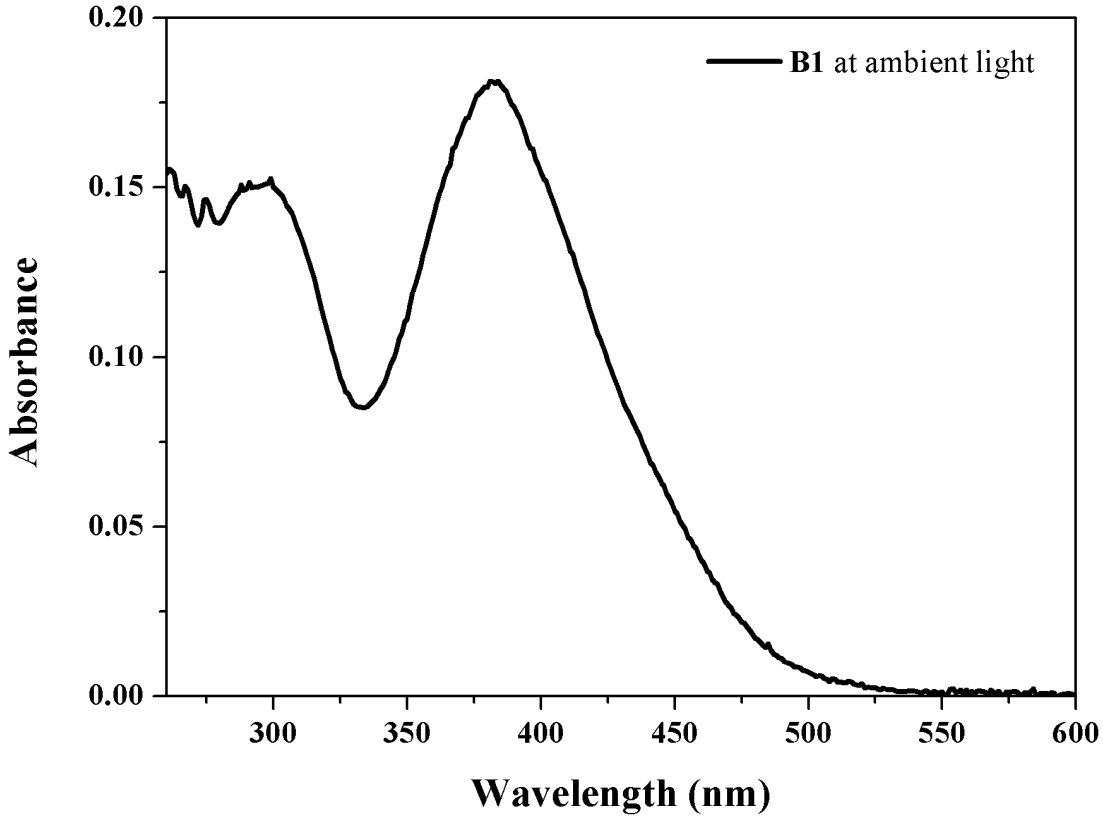


Figure S21. UV/Vis absorption spectra of **B1** in DMSO.

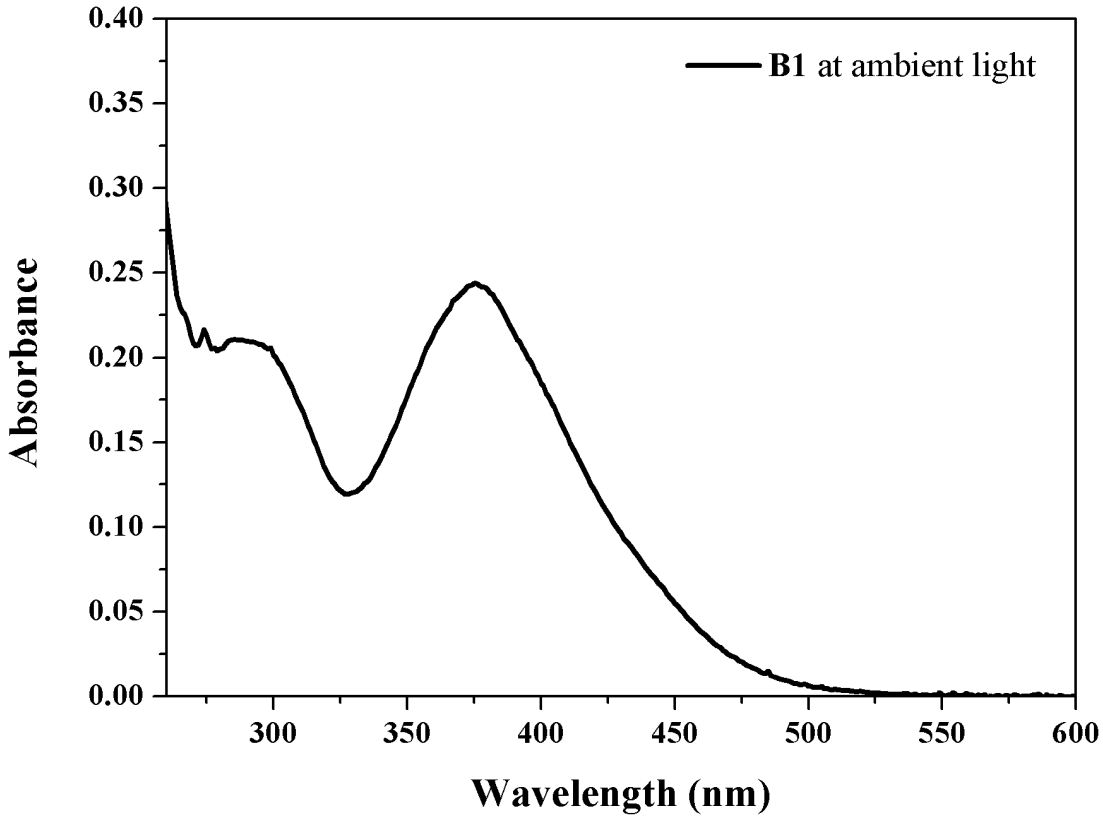


Figure S22. UV/Vis absorption spectra of **B1** in CH_3CN.

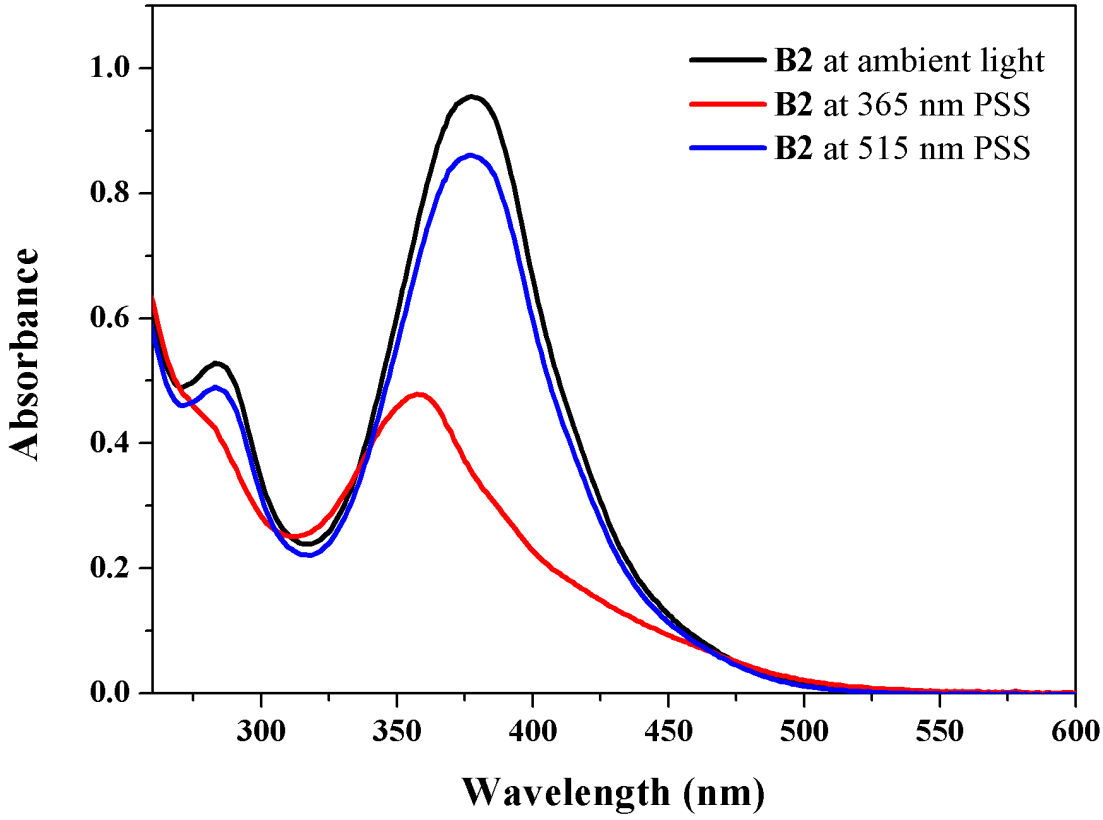
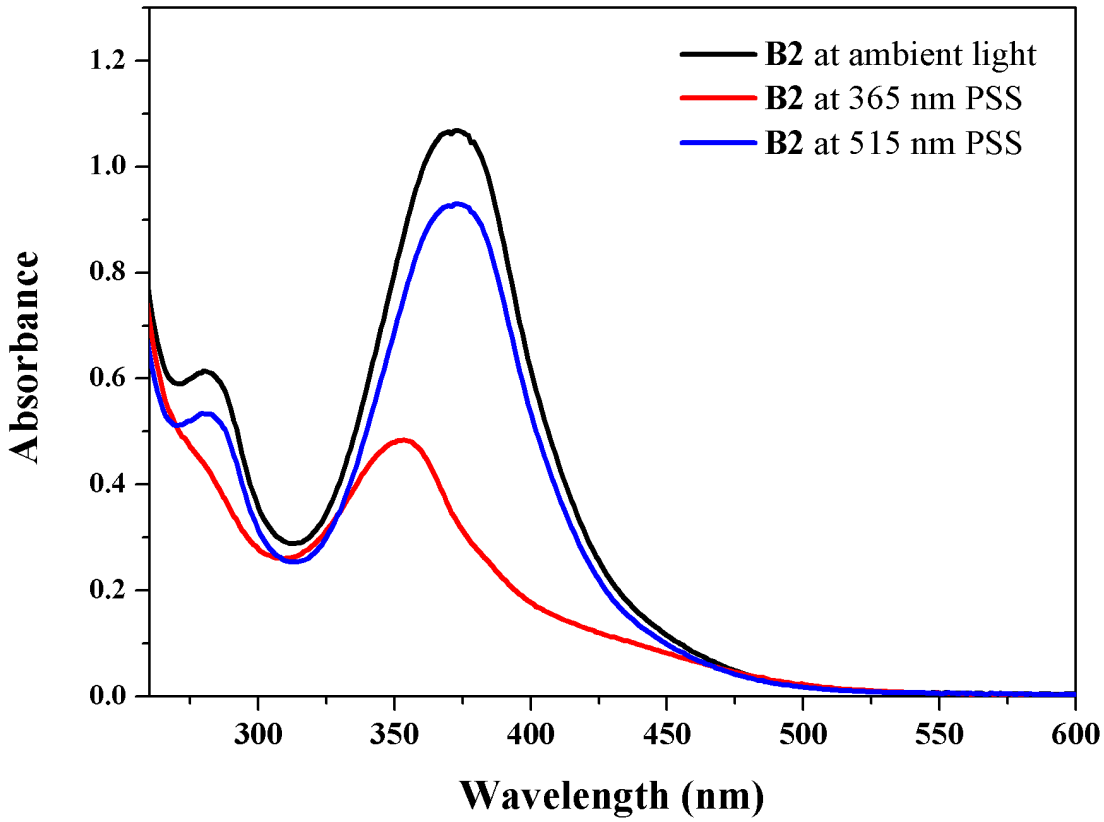


Figure S23. UV/Vis absorption spectra of **B2** at initial state, 365, and 515 nm PSSs in DMSO



. Figure S24. UV/Vis absorption spectra of **B2** at initial state, 365, and 515 nm PSSs in CH_3CN

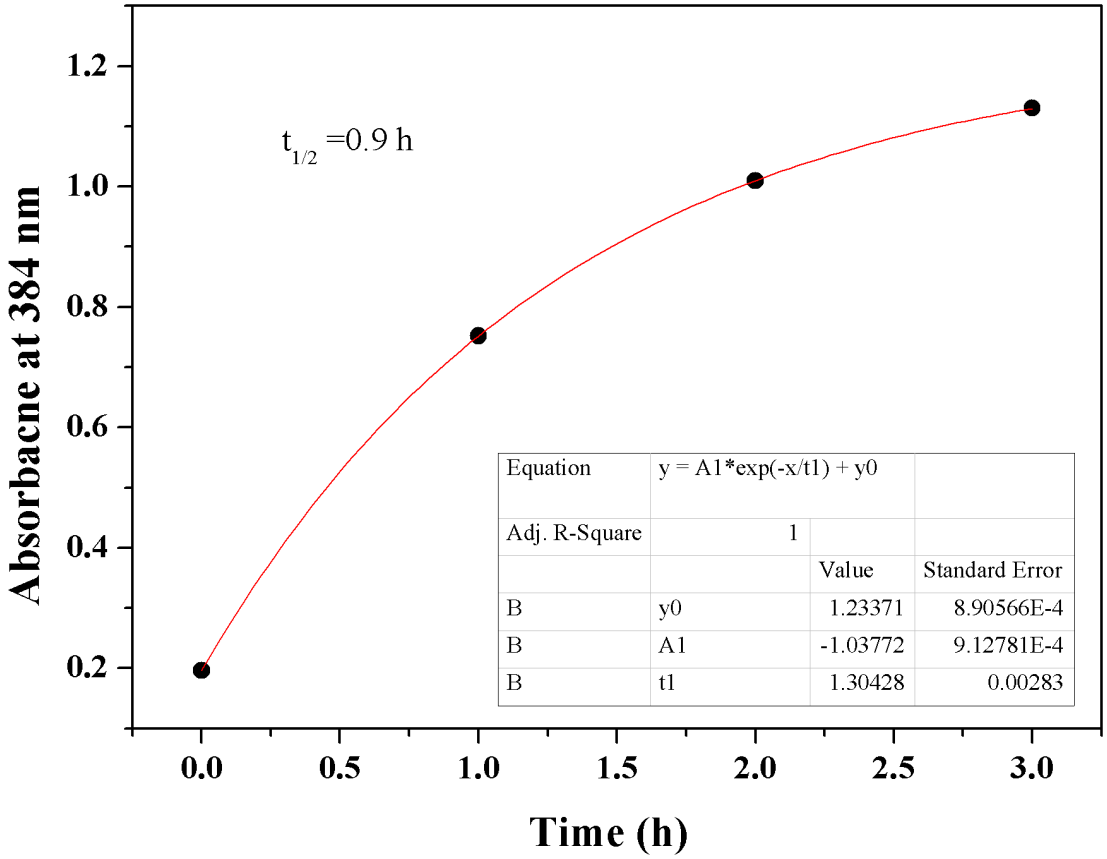


Figure S25. Thermal relaxation curve for isomerization of compound **A2** at PSS_{cis} in DMSO.

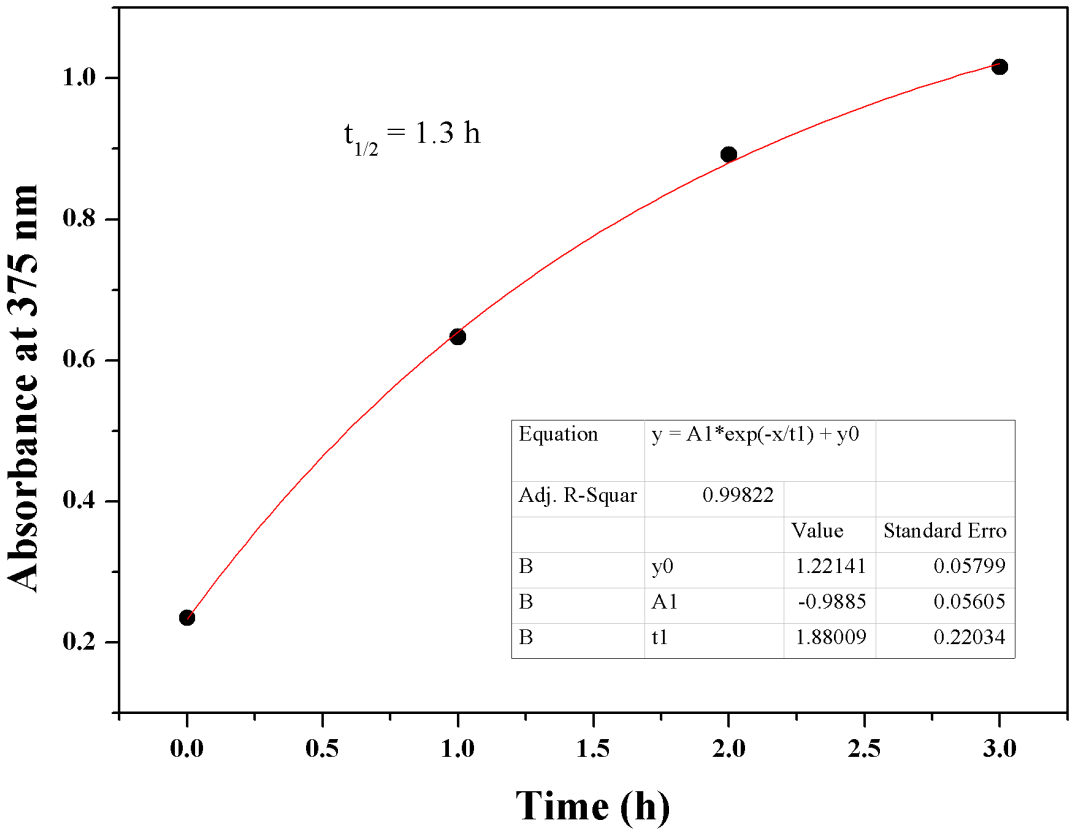


Figure S26. Thermal relaxation curve for isomerization of compound **A3** at PSS_{cis} in DMSO.

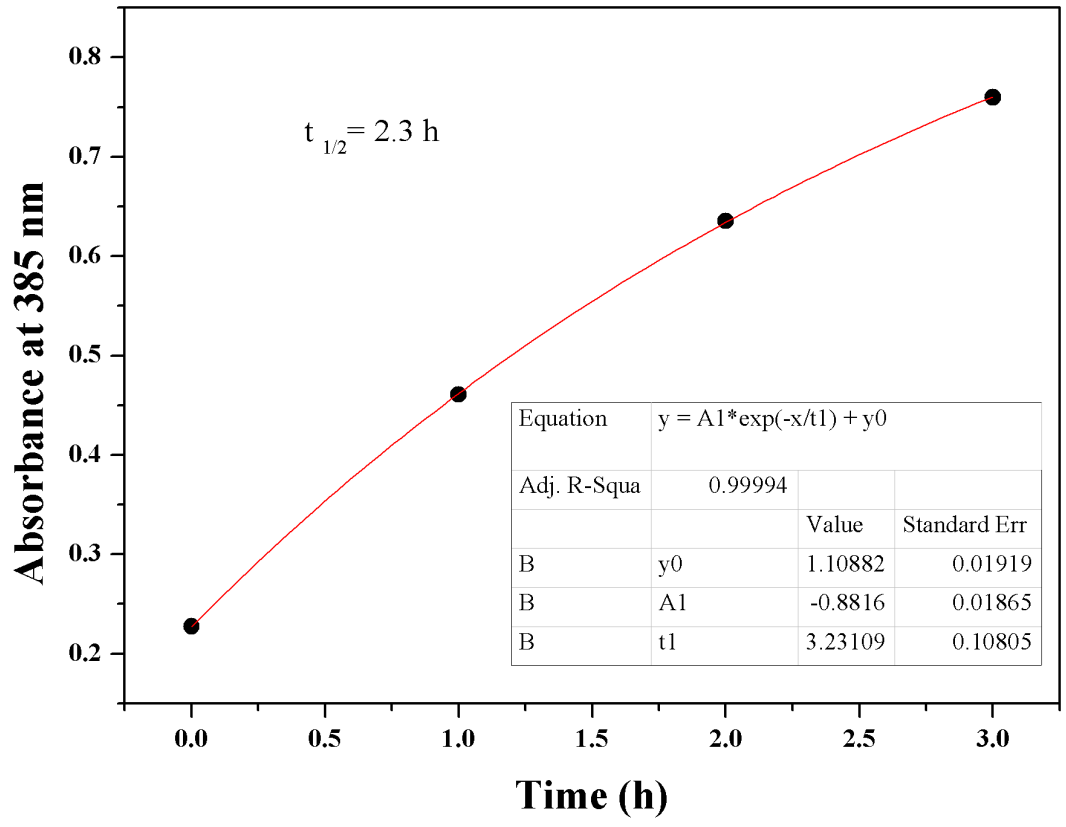


Figure S27. Thermal relaxation curve for isomerization of compound **A4** at PSS_{cis} in DMSO.

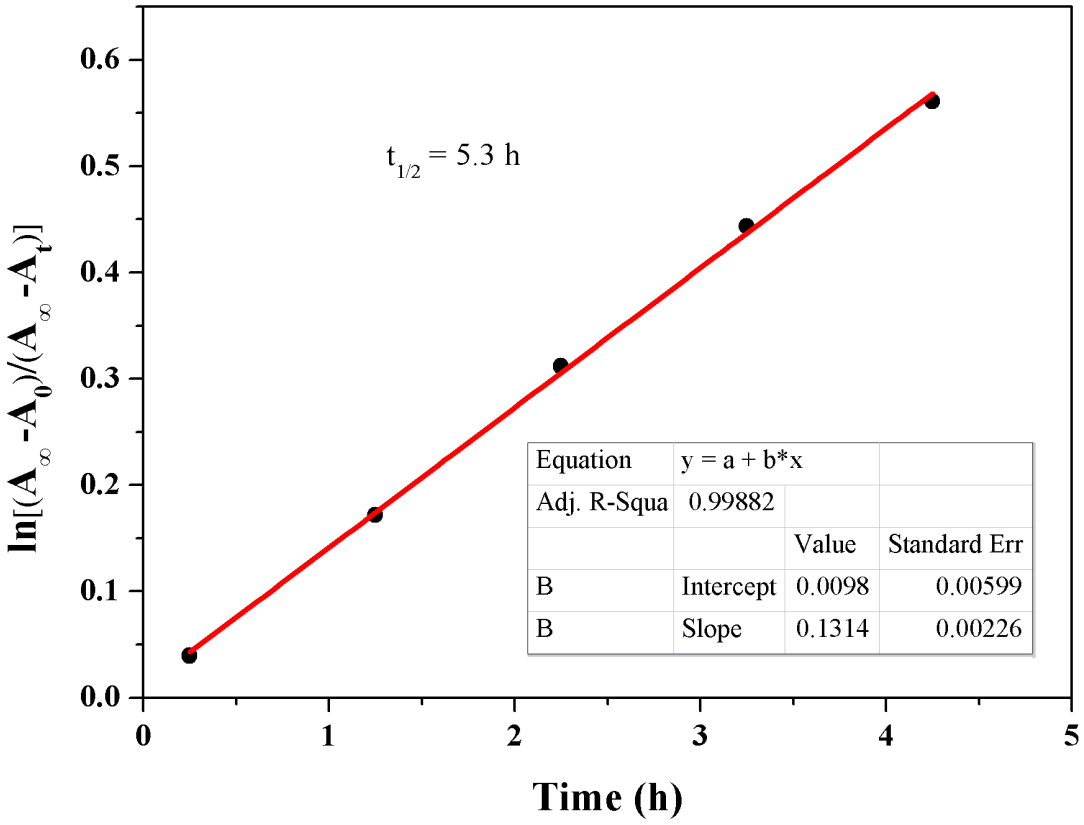


Figure S28. Thermal relaxation fitting curve for isomerization of compound **B2** at PSS_{cis} in DMSO.

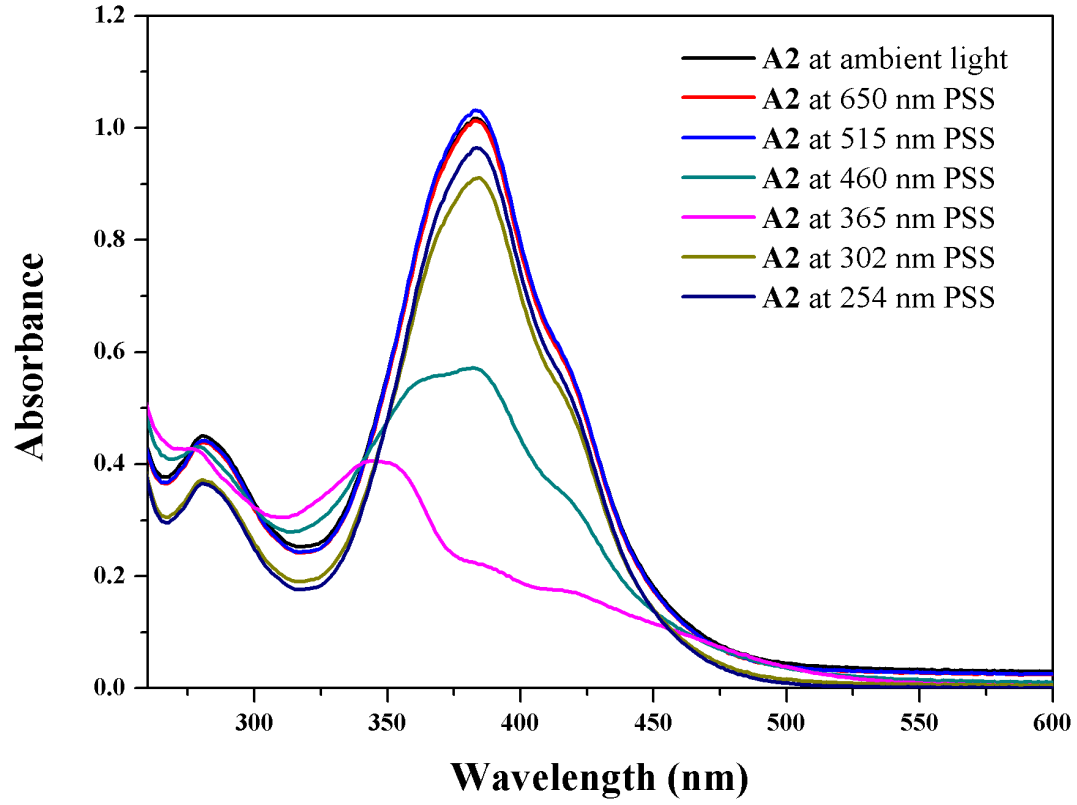


Figure S29. The UV/Vis spectra of compound **A2** at various PSSs in DMSO.

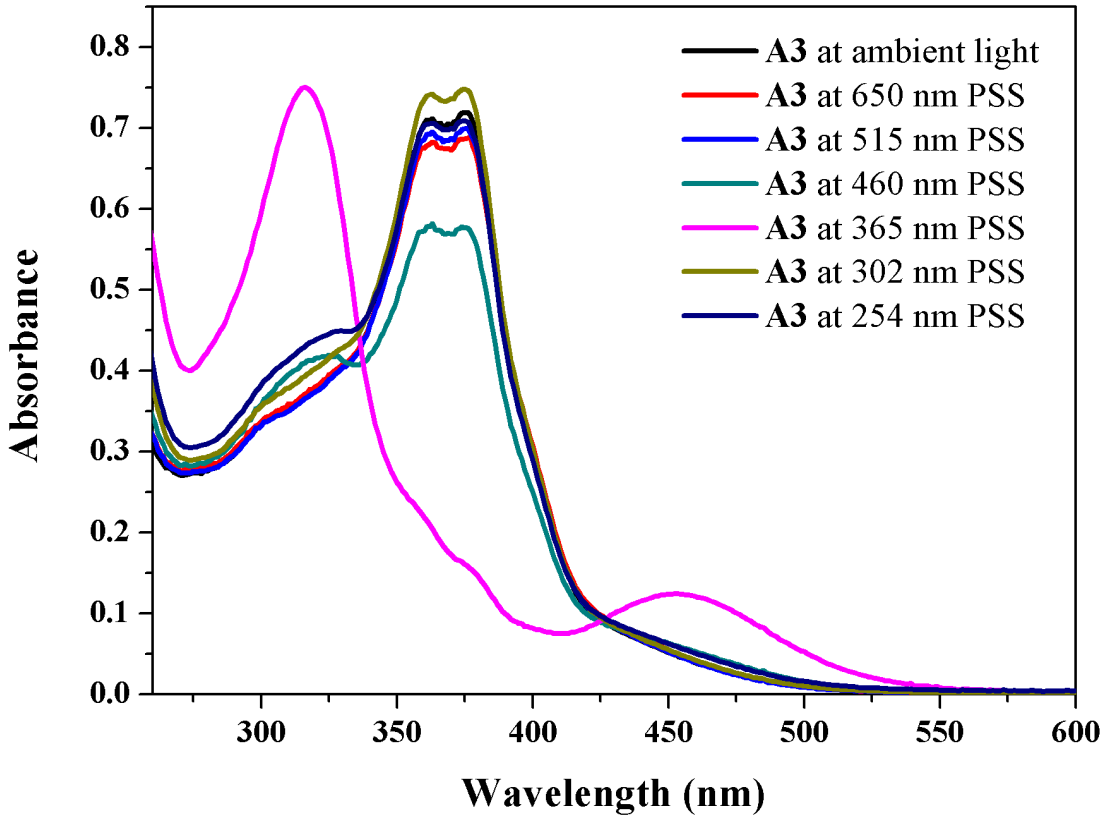


Figure S30. The UV/Vis spectra of compound **A3** at various PSSs in DMSO.

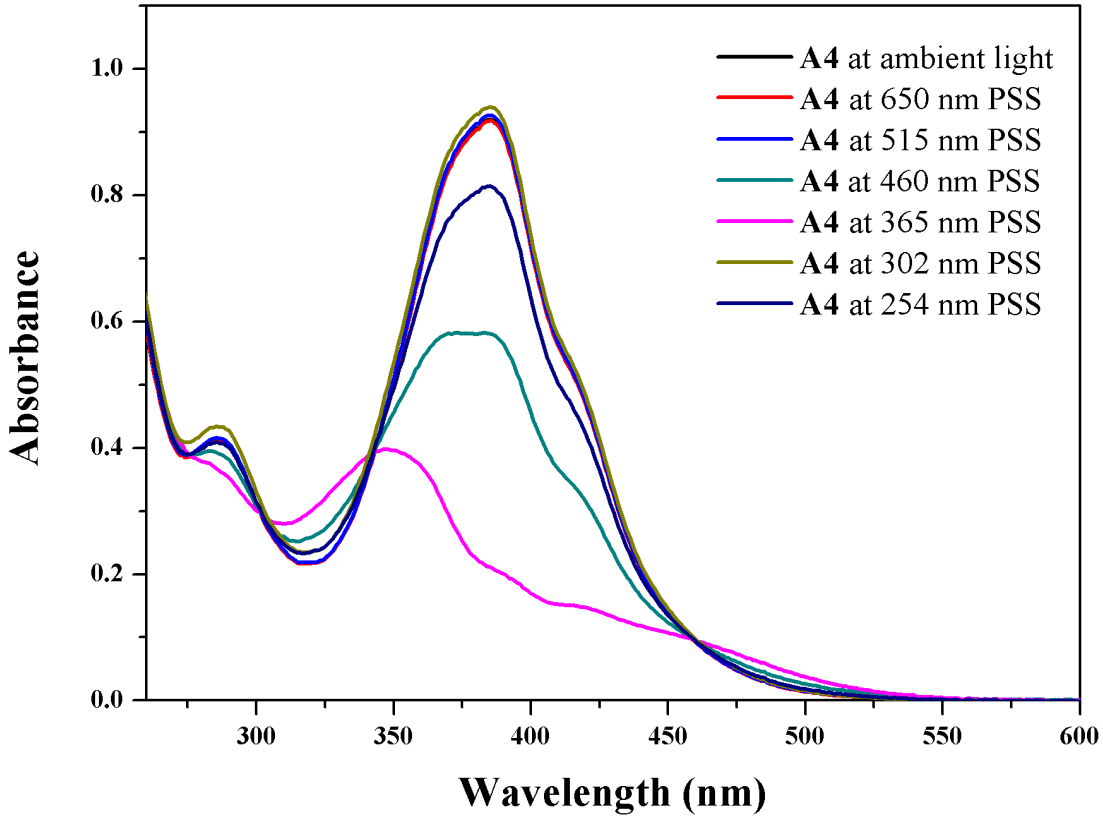


Figure S31. The UV/Vis spectra of compound **A4** at various PSSs in DMSO.

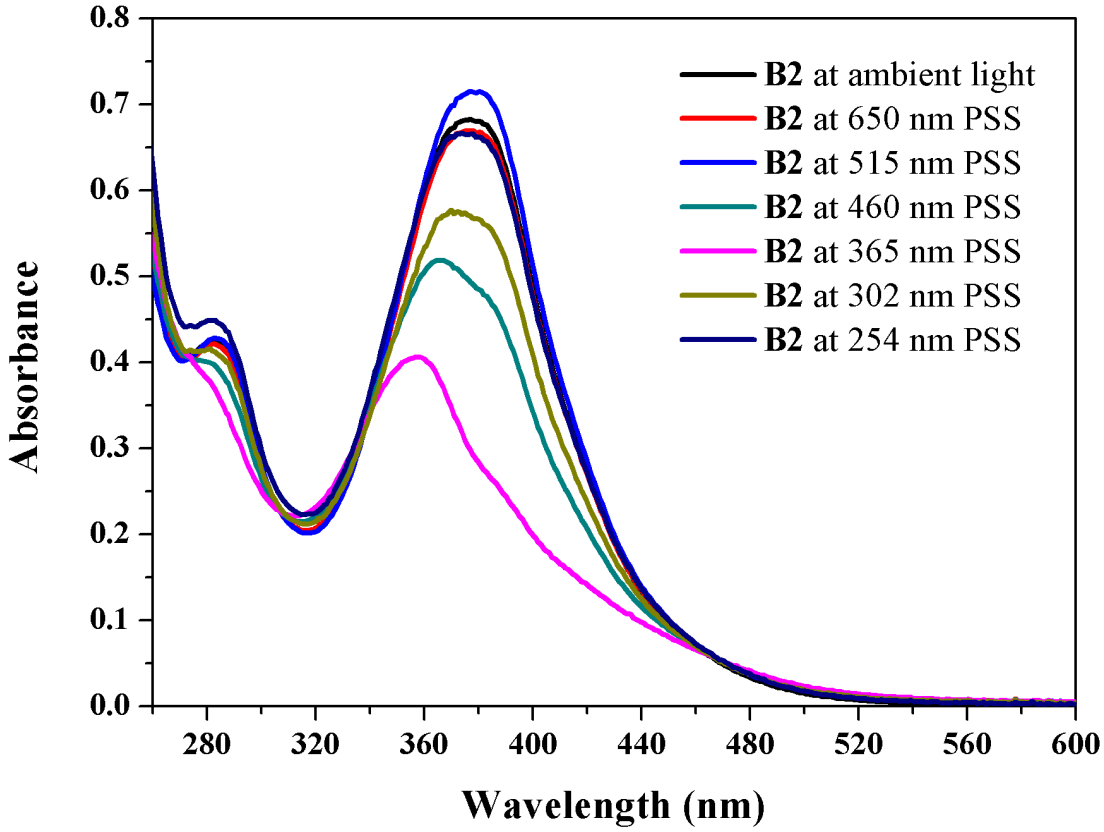


Figure S32. The UV/Vis spectra of compound **B2** at various PSSs in DMSO.

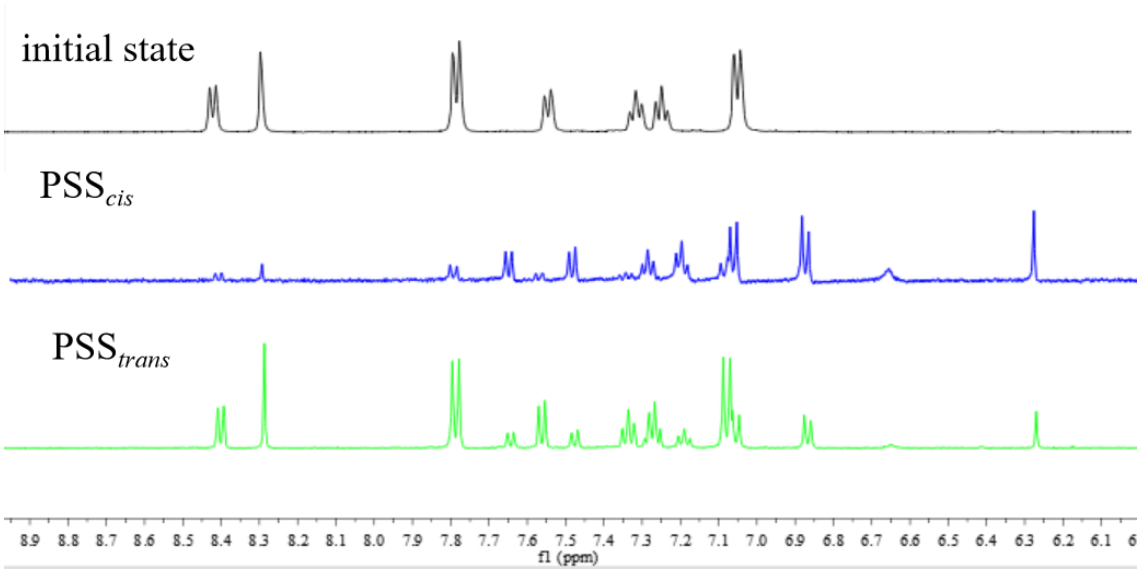


Figure S33. Expanded ^{1}H NMR spectra showing proton signals of **A2** in DMSO-d_6.

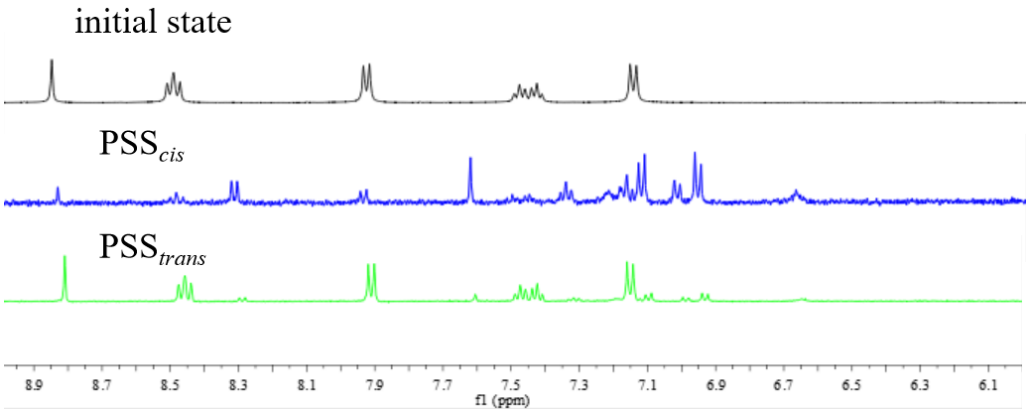


Figure S34. Expanded ^{1}H NMR spectra showing proton signals of **A3** in DMSO-d_6.

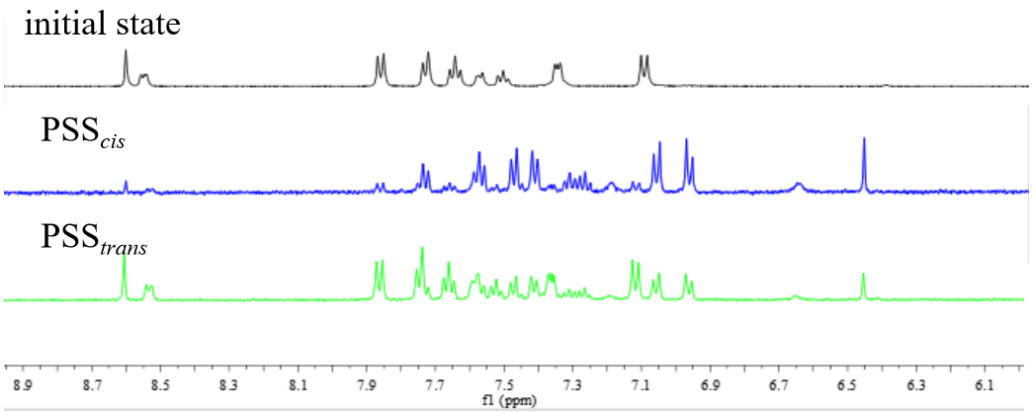


Figure S35. Expanded ^{1}H NMR spectra showing proton signals of **A4** in DMSO-d_6.

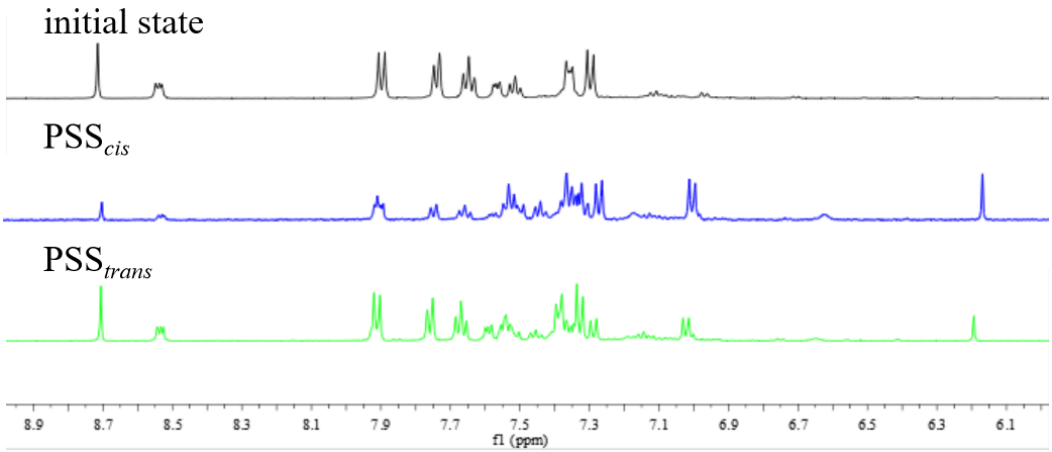


Figure S36. Expanded ^{1}H NMR spectra showing proton signals of **B2** in DMSO-d_6.

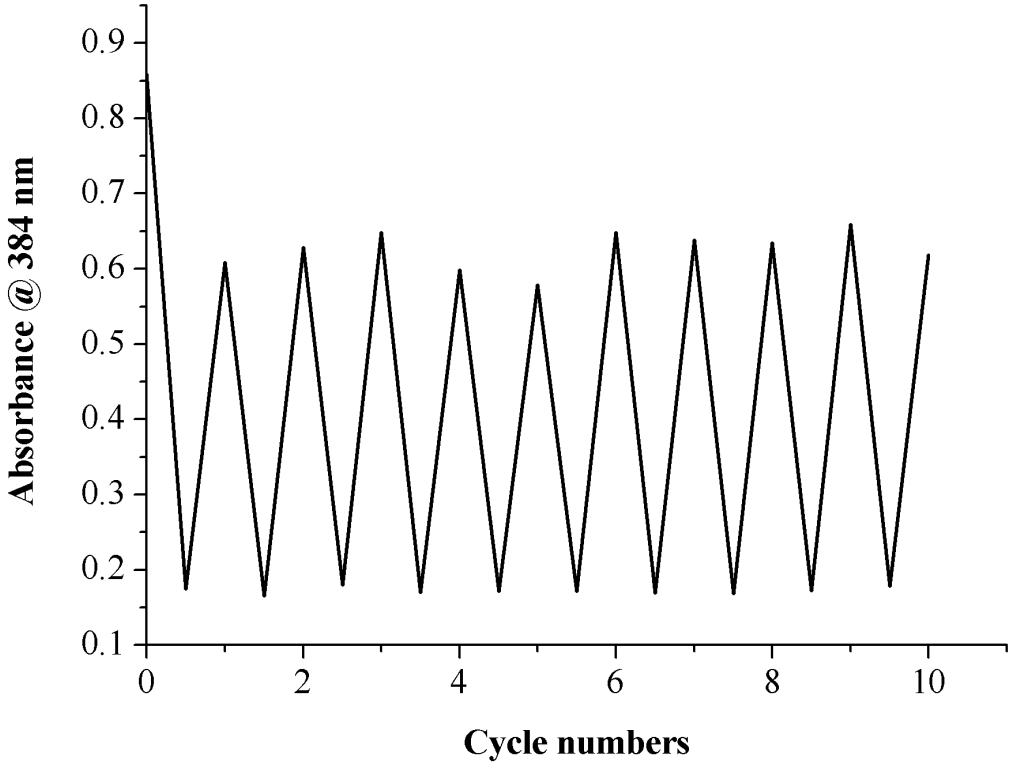


Figure S37. Multiple rounds of photoswitching of **A2** by alternating 365 nm and 460 nm light irradiations in DMSO.

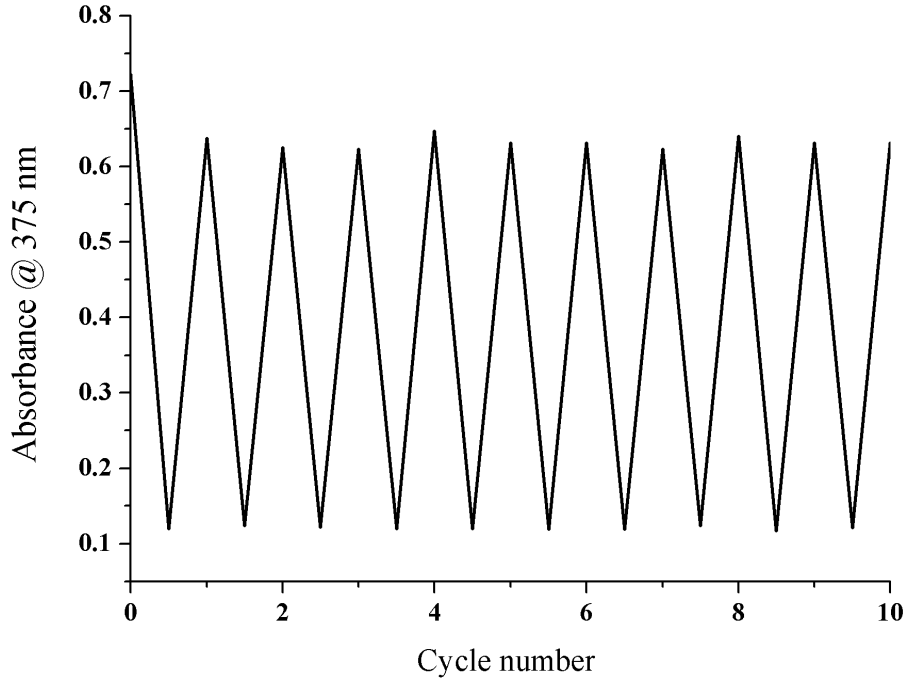


Figure S38. Multiple rounds of photoswitching of **A3** by alternating 365 nm and 460 nm light irradiations in DMSO.

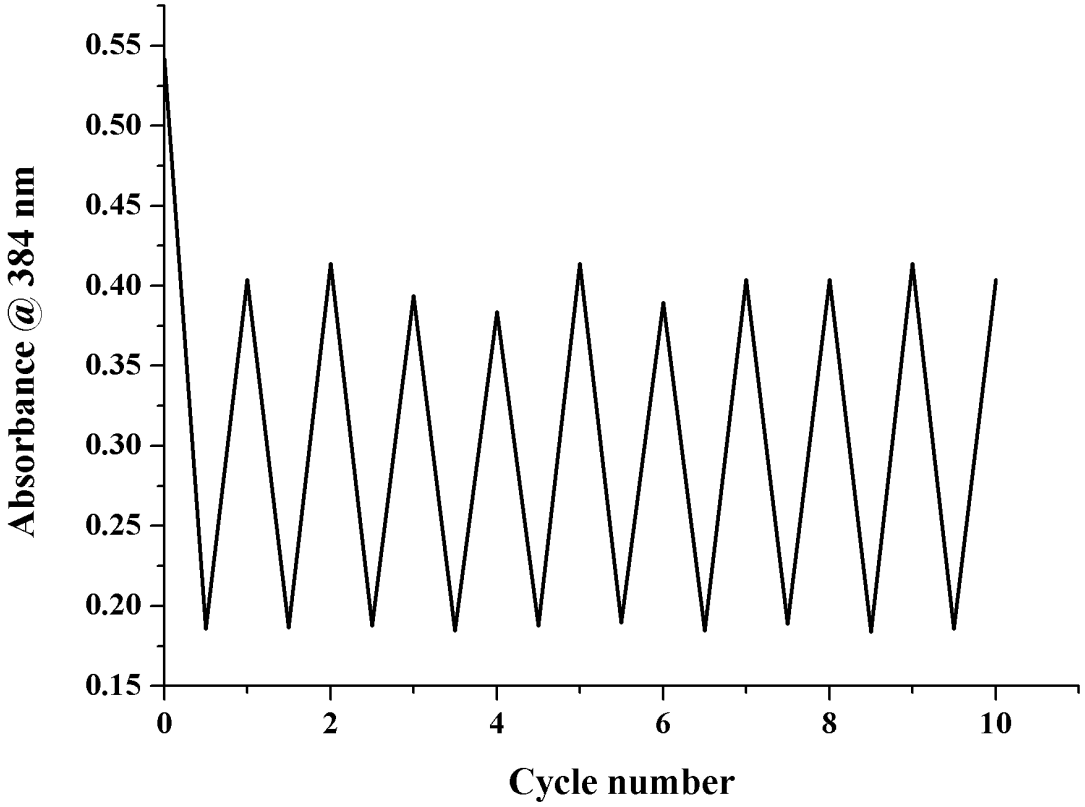


Figure S39. Multiple rounds of photoswitching of **A4** by alternating 365 nm and 460 nm light irradiations in DMSO.

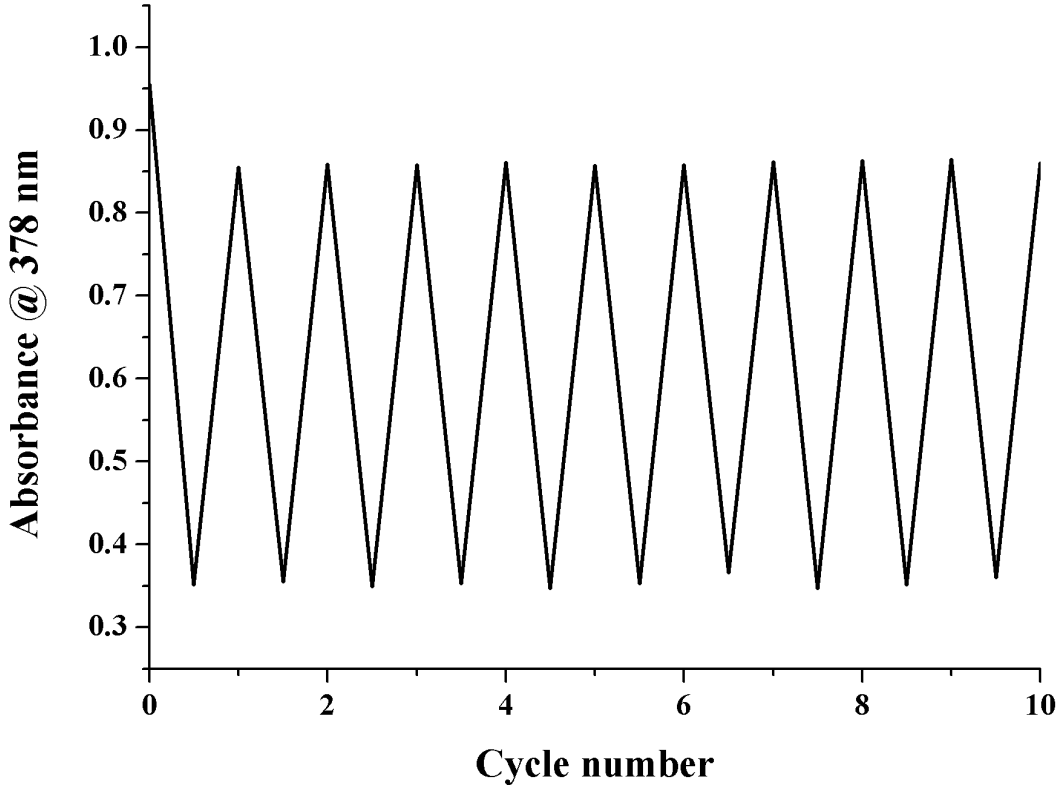
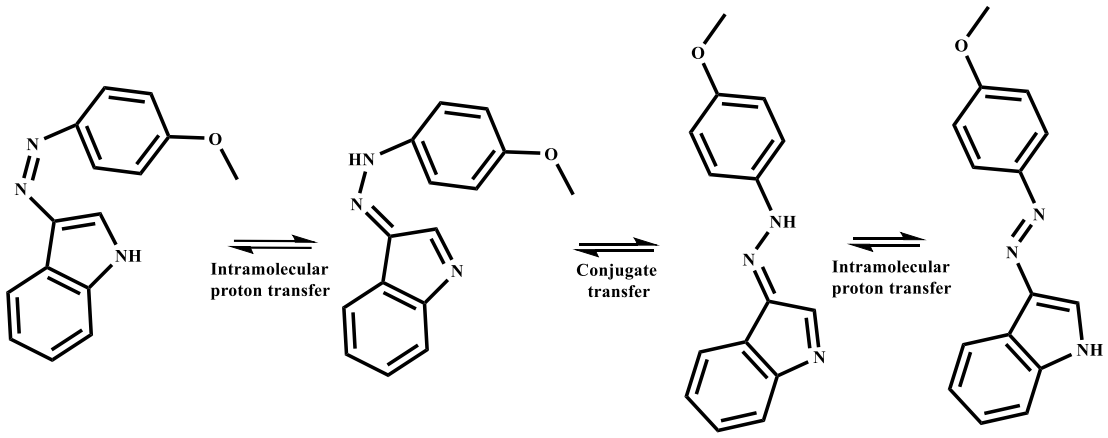


Figure S40. Multiple rounds of photoswitching of **B2** by alternating 365 nm and 460 nm light irradiations in DMSO.



Scheme S2. The possible intermolecular hydrazine mechanism for compounds **A1** and **B1**.

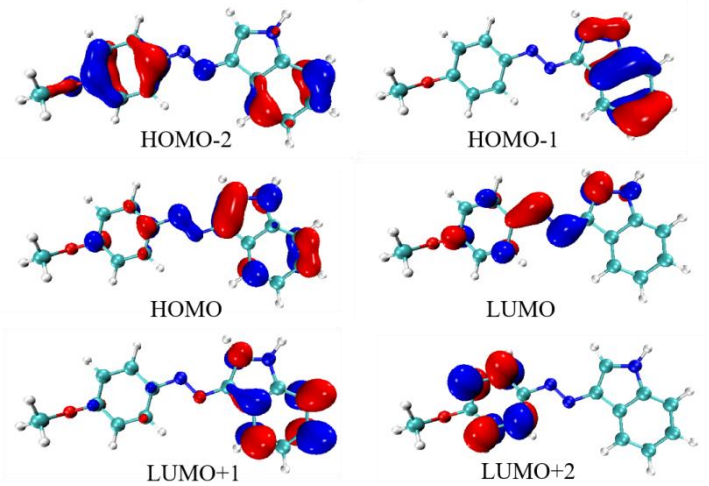


Figure S41. Frontier MOs of **A1** *trans.*

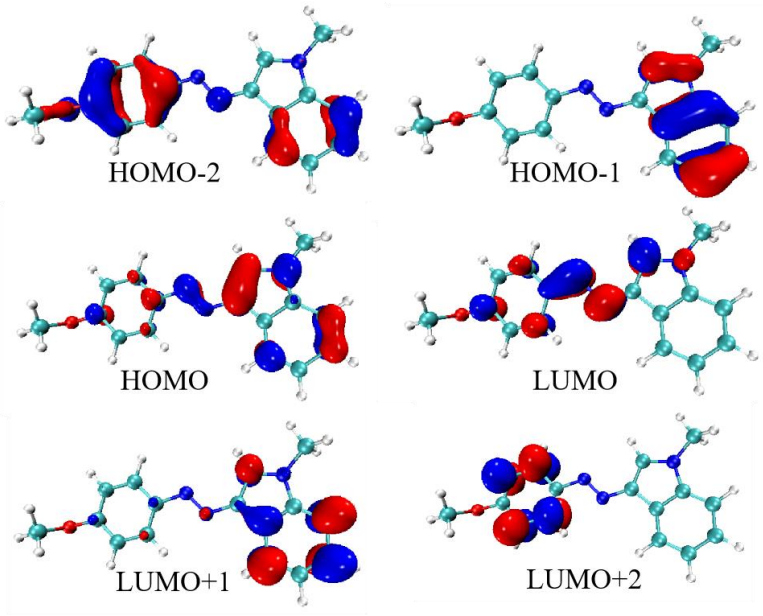


Figure S42. Frontier MOs of **A2** *trans.*

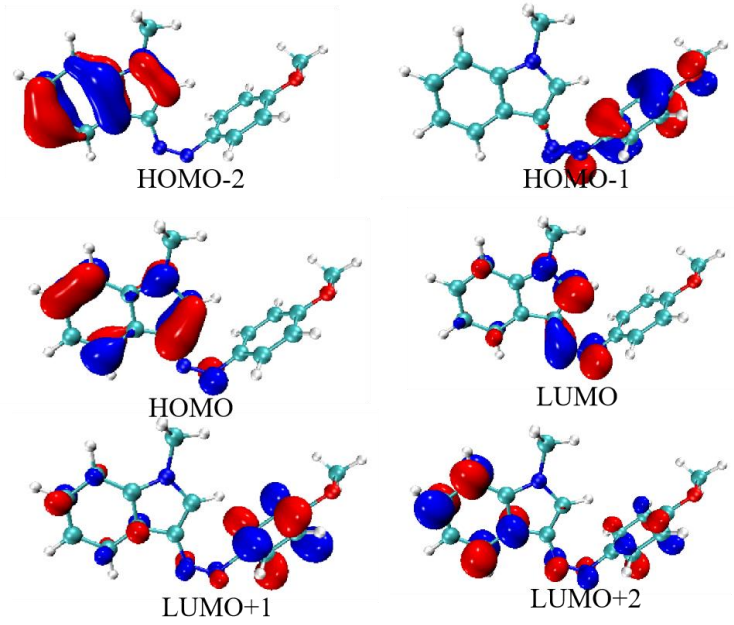


Figure S43. Frontier MOs of **A2** *cis.*

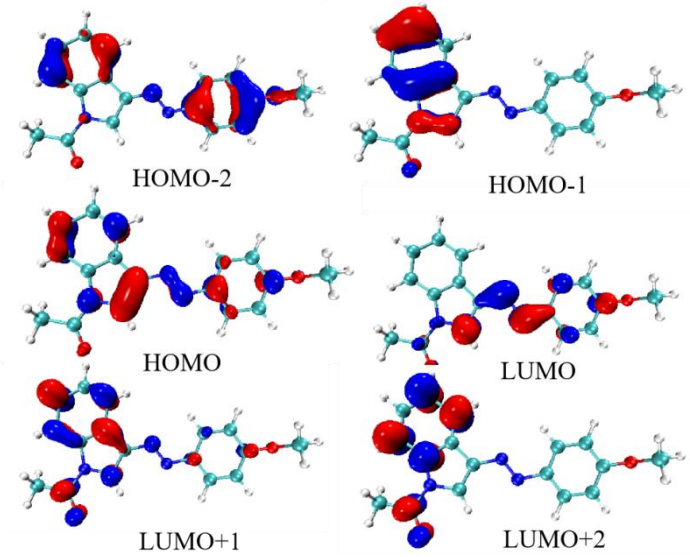


Figure S44. Frontier MOs of **A3** *trans.*

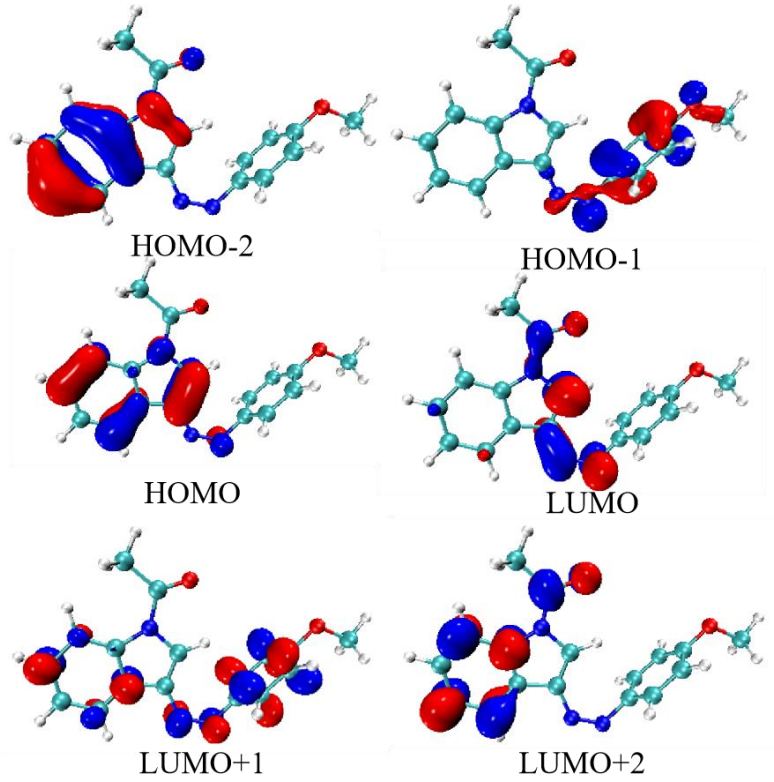


Figure S45. Frontier MOs of **A3** *cis.*

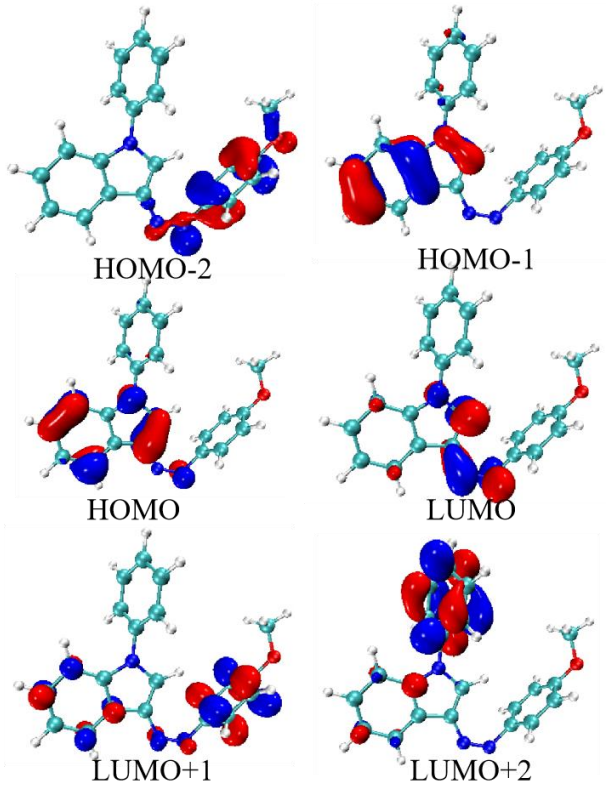


Figure S46. Frontier MOs of **A4** *trans.*

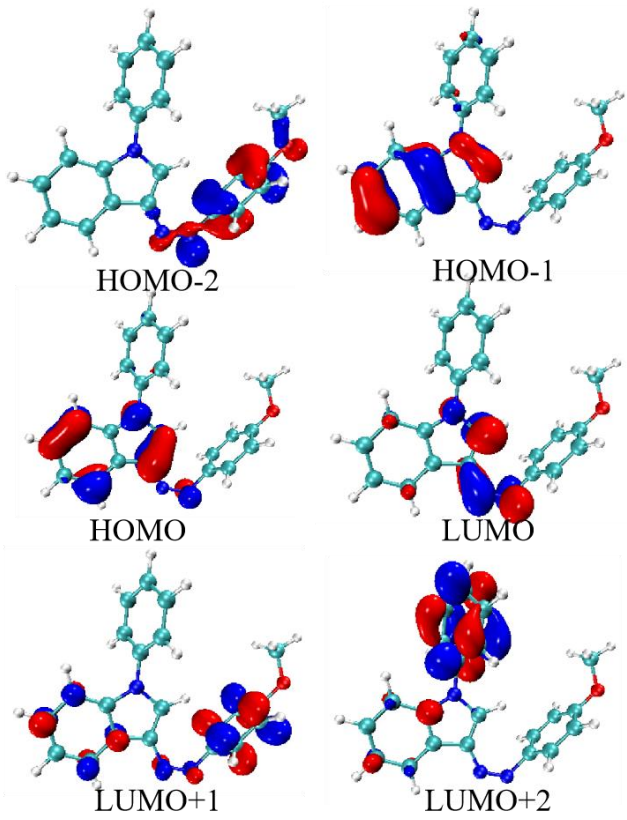


Figure S47. Frontier MOs of **A4** *cis.*

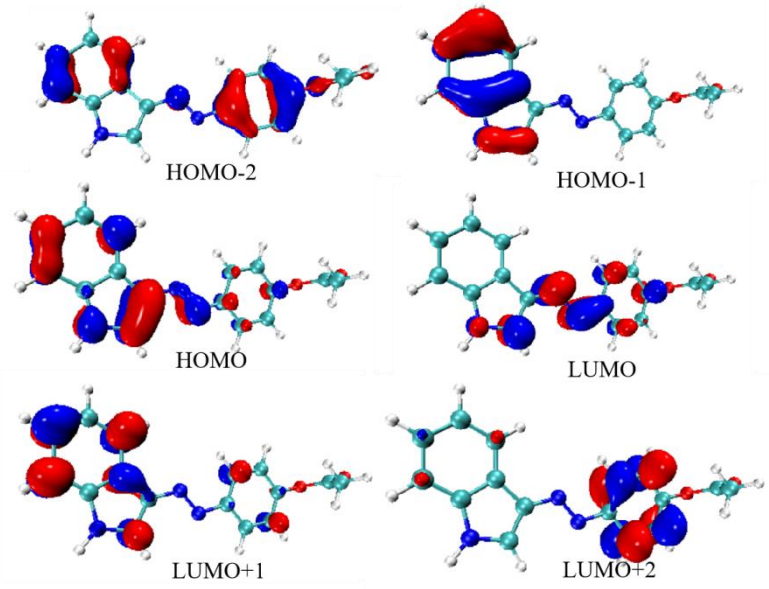


Figure S48. Frontier MOs of **B1** *trans.*

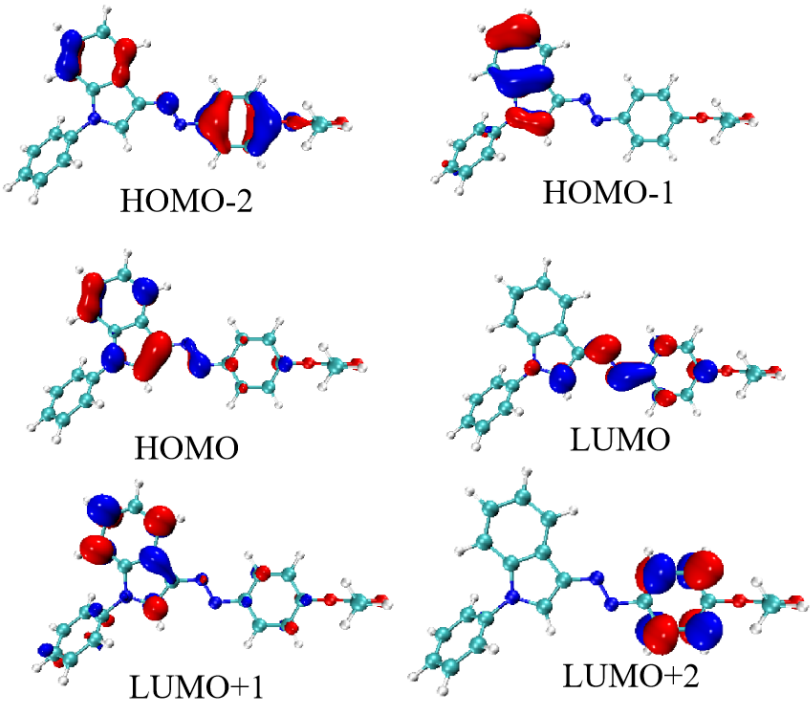


Figure S49. Frontier MOs of **B2** *trans.*

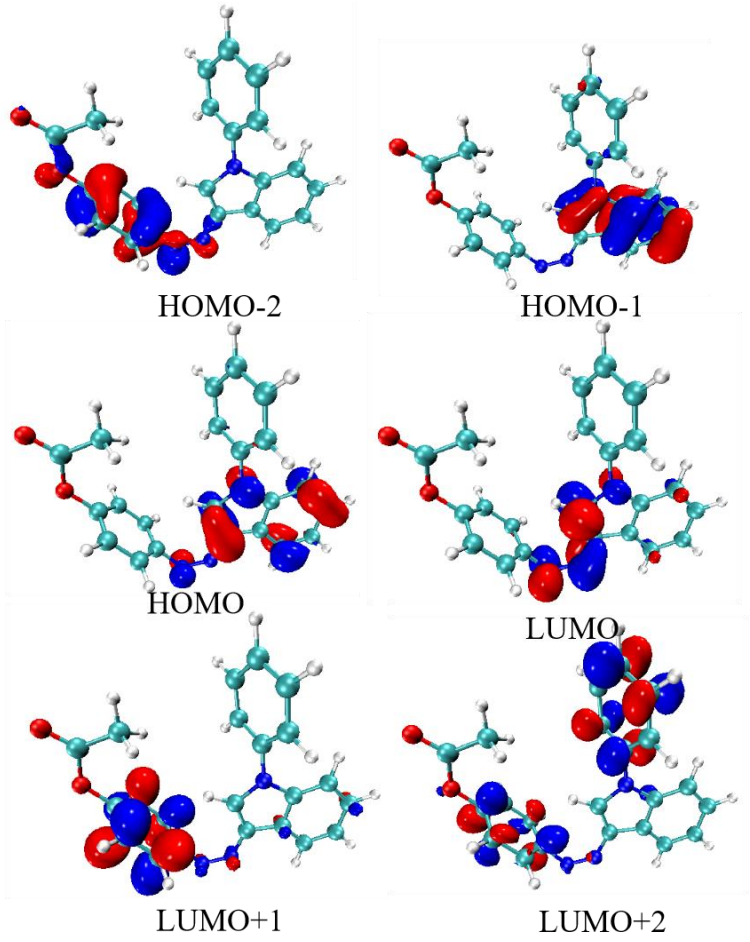


Figure S50. Frontier MOs of **B2** *cis.*

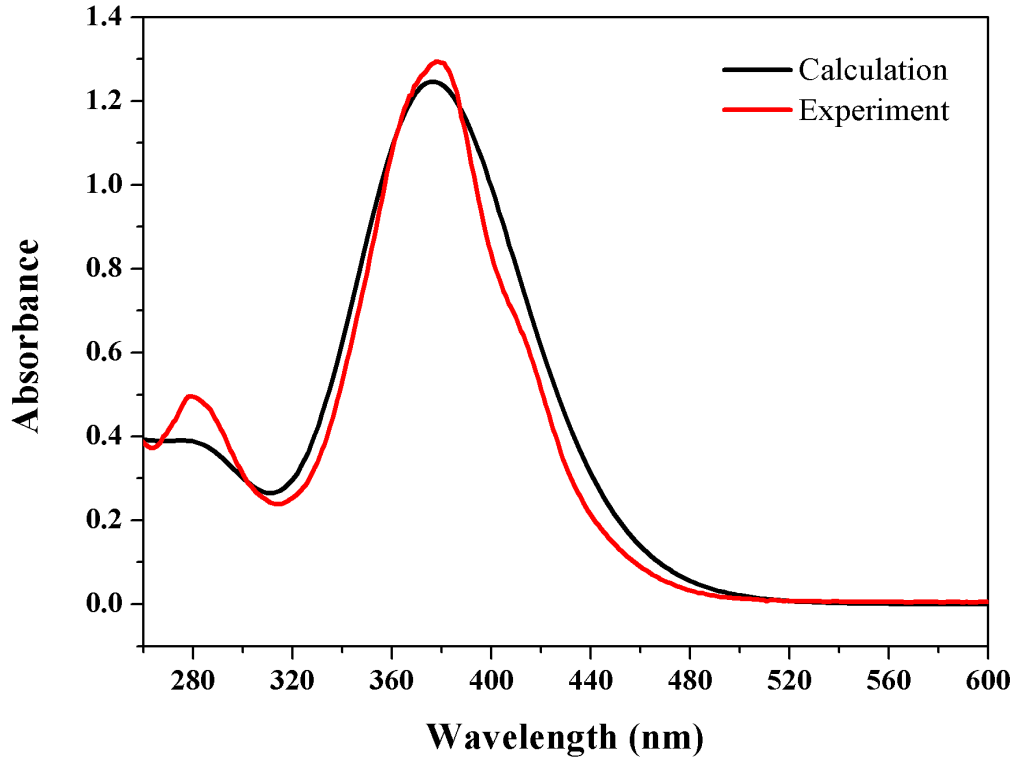


Figure S51. Experimental and calculated UV/Vis absorption spectra of **A1** at ambient light in DMSO.

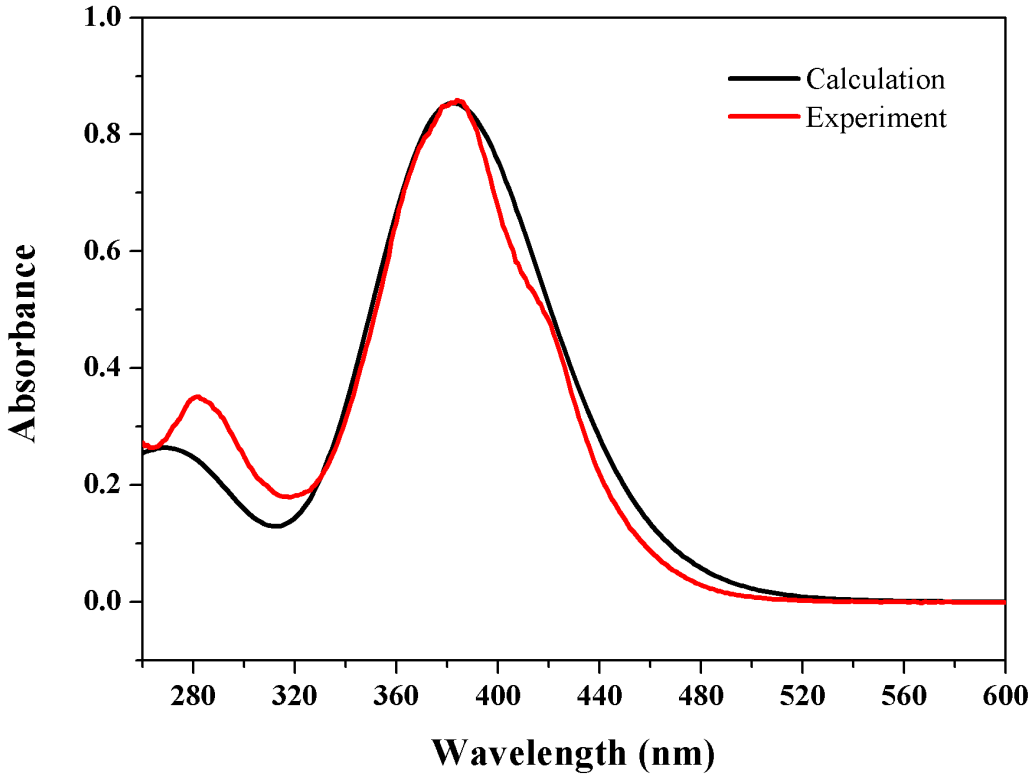


Figure S52. Experimental and calculated UV/Vis absorption spectra of **A2** at ambient light in DMSO.

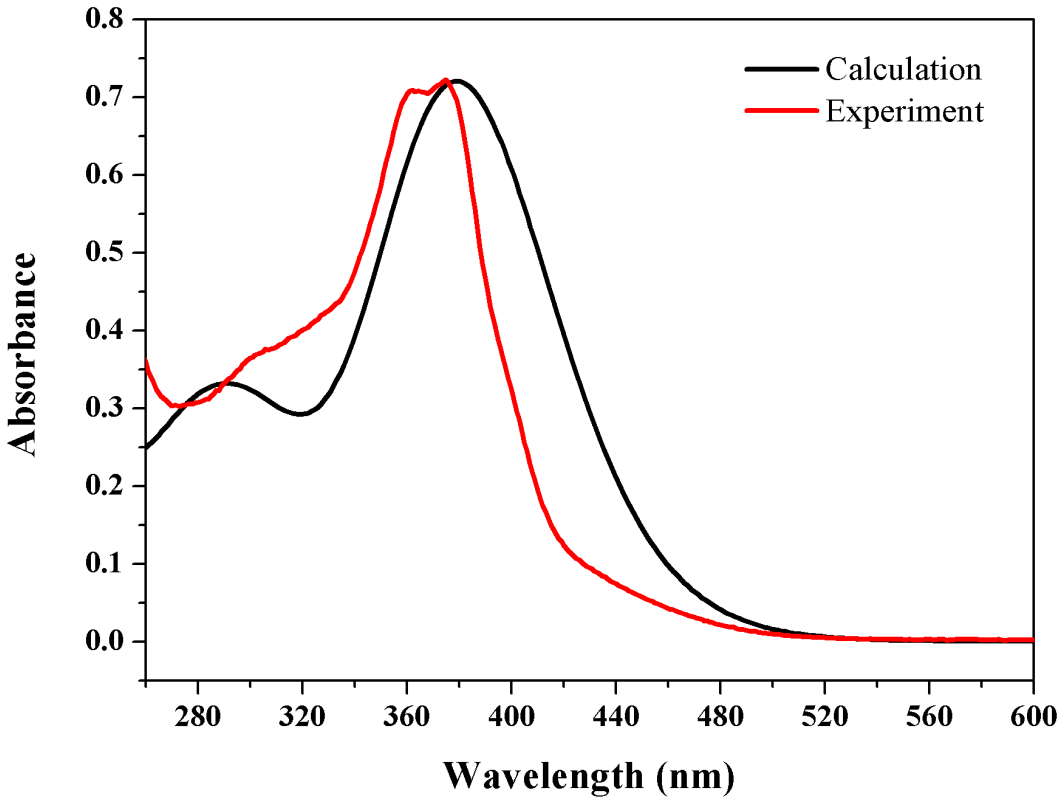


Figure S53. Experimental and calculated UV/Vis absorption spectra of **A3** at ambient light in DMSO.

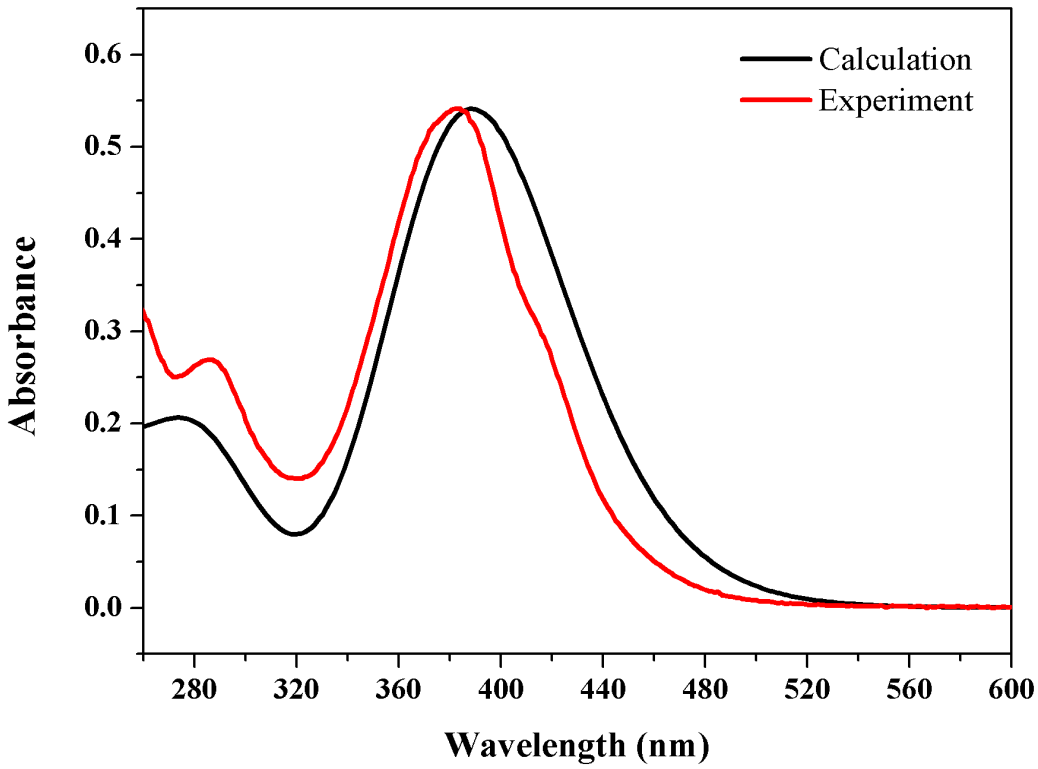


Figure S54. Experimental and calculated UV/Vis absorption spectra of **A4** at ambient light in DMSO.

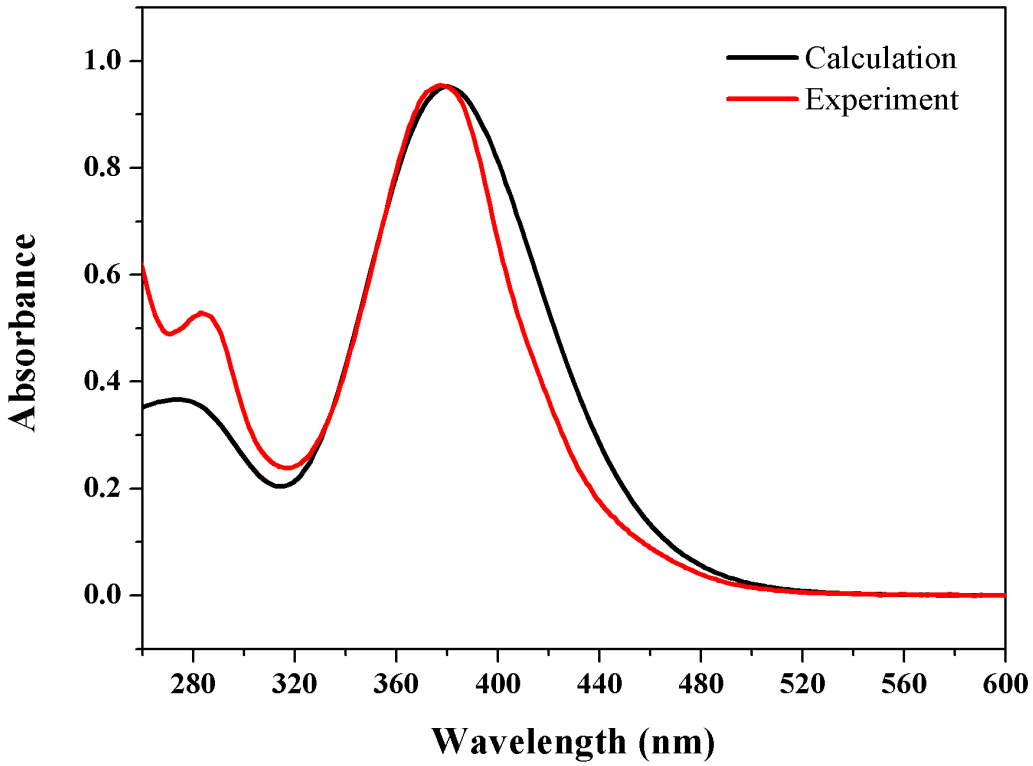


Figure S55. Experimental and calculated UV/Vis absorption spectra of **B1** at ambient light in DMSO.

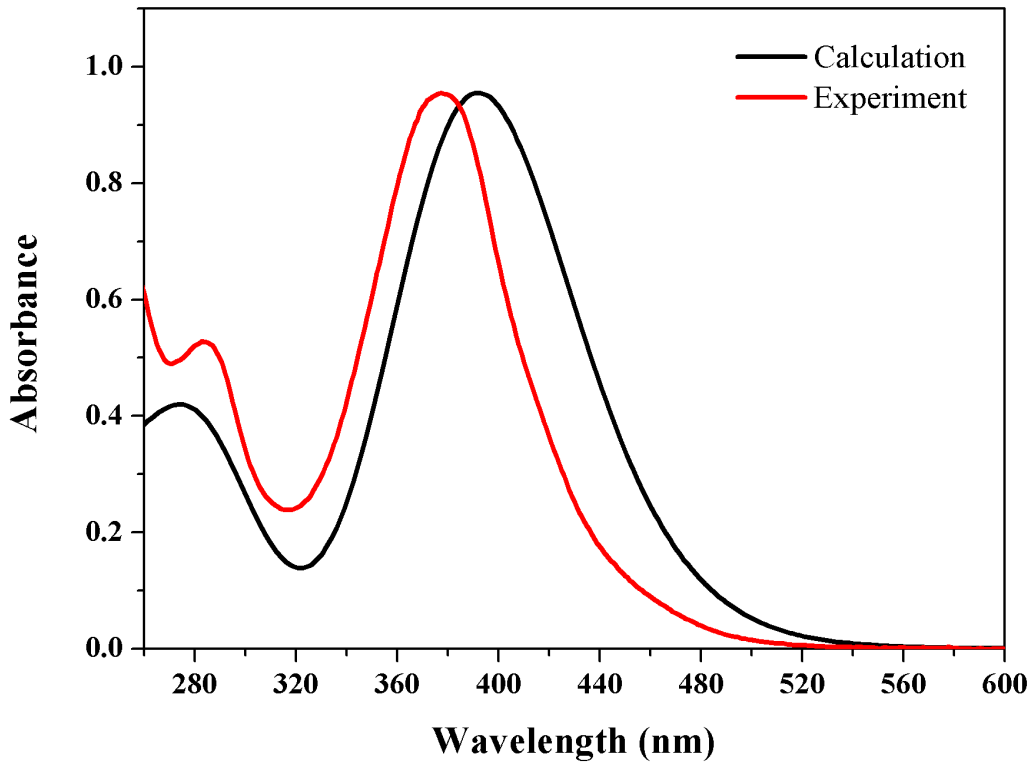


Figure S56. Experimental and calculated UV/Vis absorption spectra of **B2** at ambient light in DMSO.

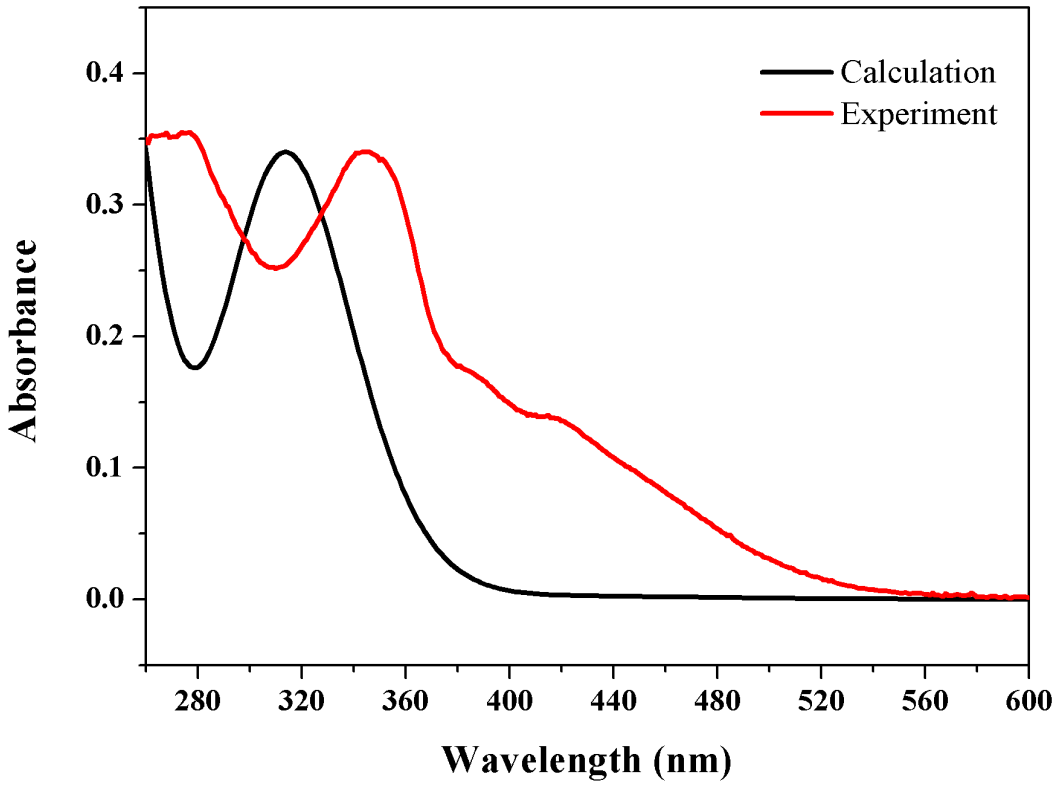


Figure S57. Experimental and calculated UV/Vis absorption spectra of **A2**$_{cis}$ in DMSO.

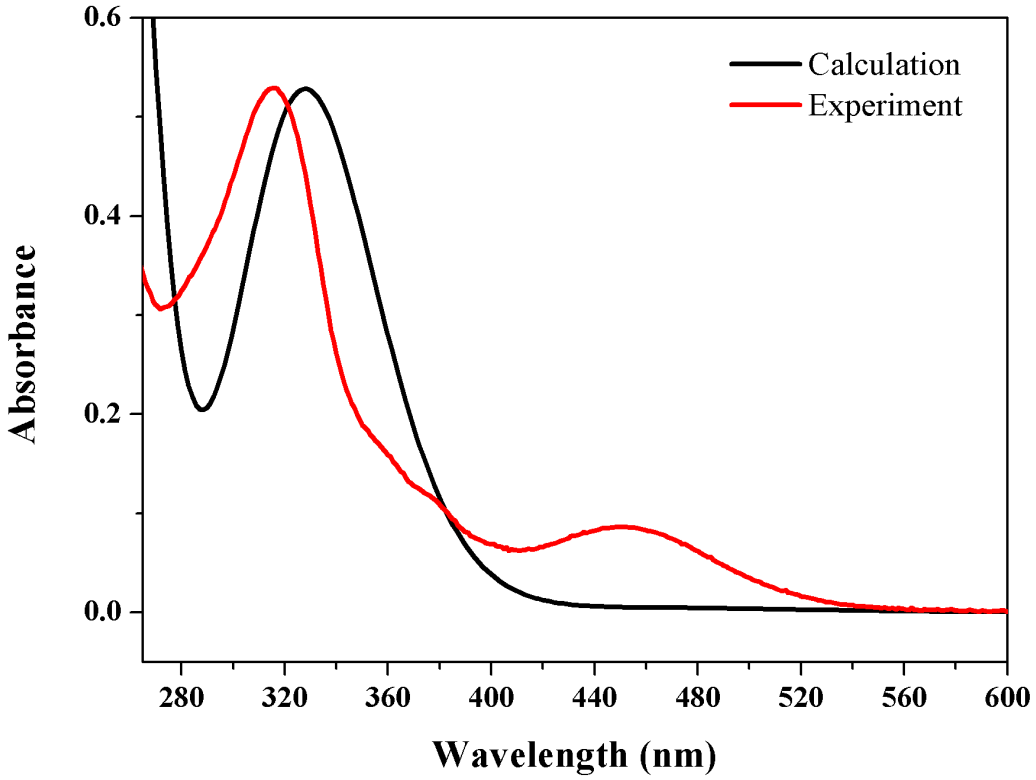


Figure S58. Experimental and calculated UV/Vis absorption spectra of **A3**$_{cis}$ in DMSO.

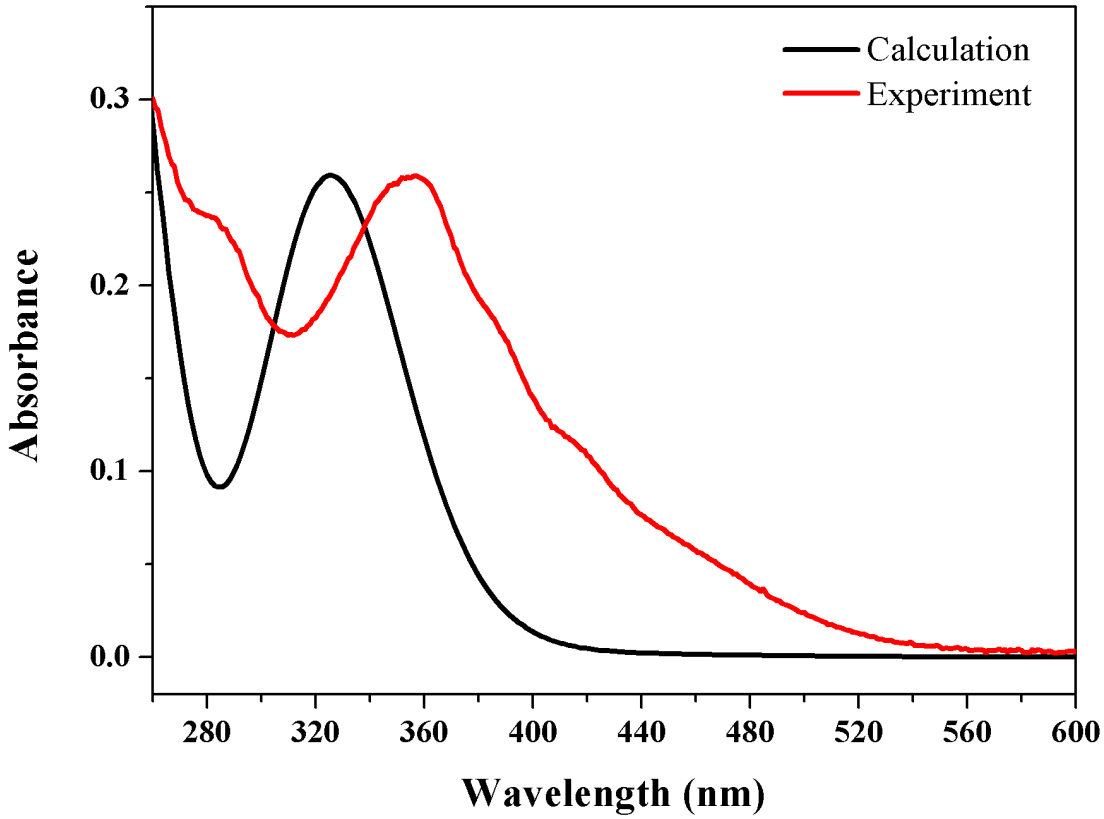


Figure S59. Experimental and calculated UV/Vis absorption spectra of **A4**$_{cis}$ in DMSO.

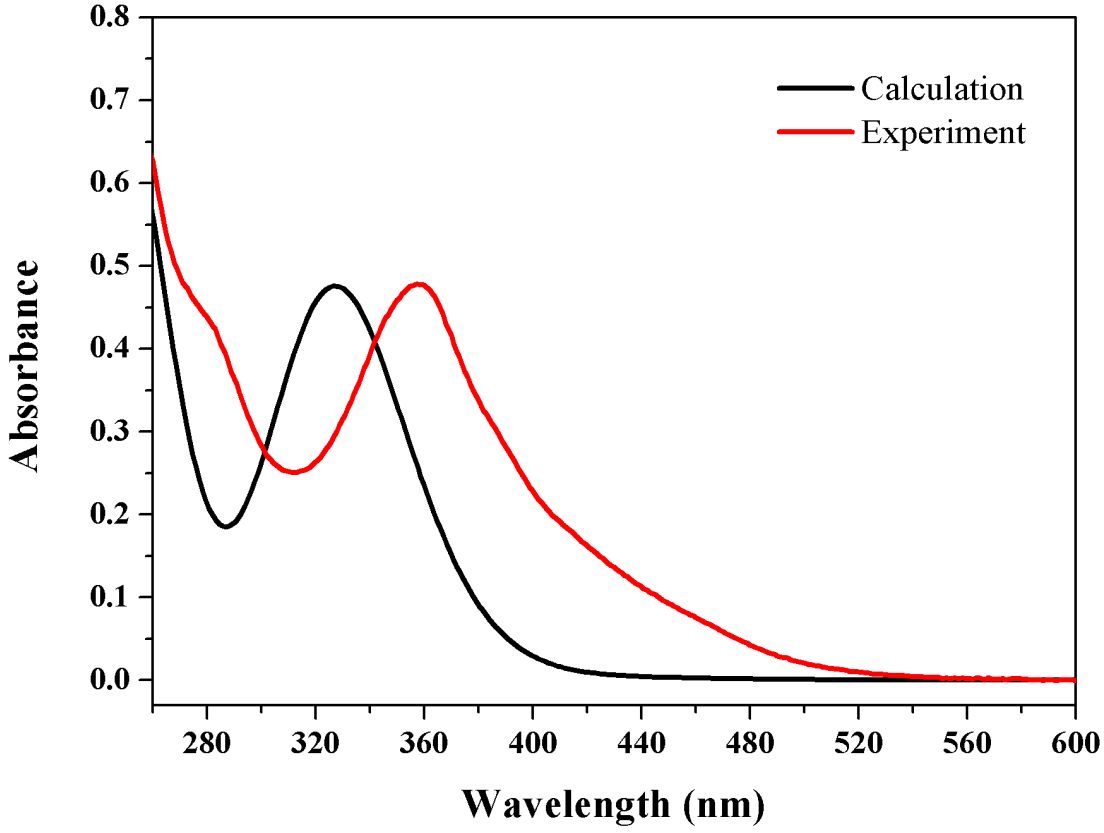


Figure S60. Experimental and calculated UV/Vis absorption spectra of **B2**$_{cis}$ in DMSO.

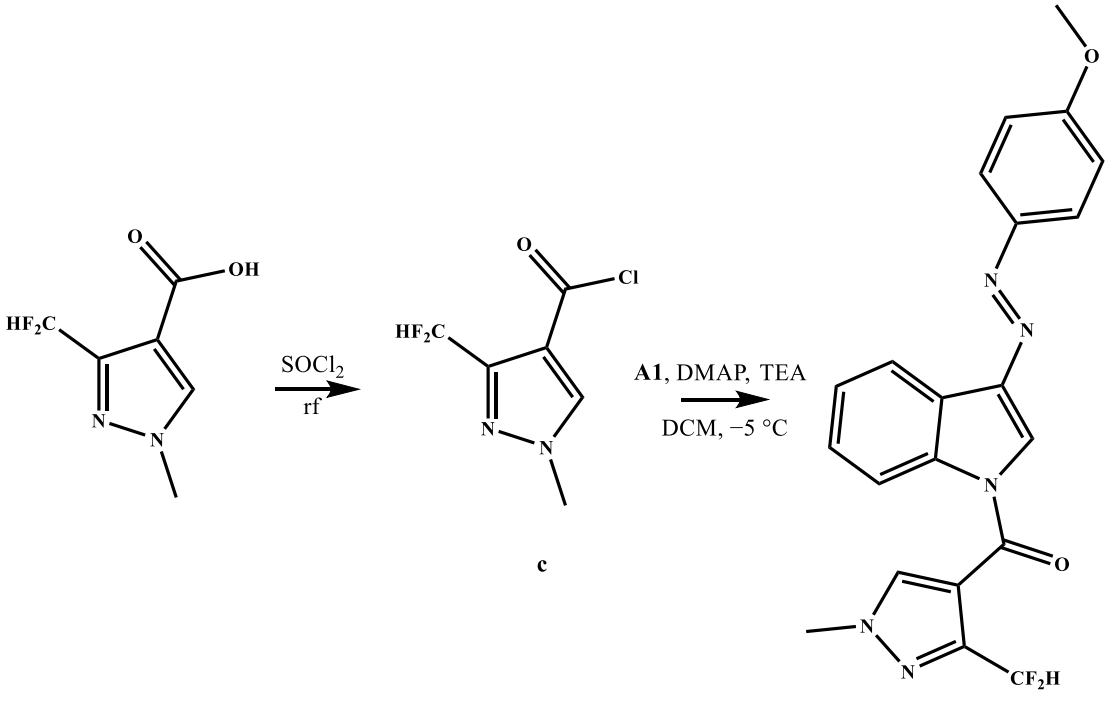
Table S1. The energy (eV) of Frontier MOs at *trans*-isomer.

Comp.	**A1**	**A2**	**A3**	**A4**	**B1**	**B2**
HOMO-2	-8.983	-9.267	-9.394	-8.951	-9.481	-9.495
HOMO-1	-8.514	-8.699	-9.065	-8.420	-8.787	-8.751
HOMO	-7.510	-7.623	-8.104	-7.436	-7.810	-7.812
LUMO	2.052	1.761	1.439	2.008	1.612	1.528
LUMO+1	3.679	3.421	3.065	3.469	3.374	2.292
LUMO+2	3.980	3.688	3.567	3.546	3.451	3.434

Table S2. The energy (eV) of Frontier MOs at *cis*-isomer.

Comp.	**A2**	**A3**	**A4**	**B2**
HOMO-2	-8.741	-9.112	-8.981	-9.239
HOMO-1	-8.582	-9.034	-8.775	-8.805
HOMO	-8.064	-8.557	-8.168	-8.205
LUMO	2.400	1.890	2.224	2.163
LUMO+1	3.403	3.291	3.353	3.164
LUMO+2	3.767	3.549	3.422	3.341

Preparation of compound C1



C1

(0.58g 3mmol) 3-(difluoromethyl)-1-methyl-1H-pyrazole-4-carboxylic acid was dissolved into 12 mL of dichlorosulfoxide, reflux reaction for 5 hours then remove solvent to obtain intermediate pyrazole formyl chloride **c**. Then, a pre-cooling solution of **A1** (0.5 g, 2 mmol), 4-dimethylaminopyridine (0.73 g, 6 mmol), and 1 mL triethylamine in 30 mL of dichloromethane

was slowly drip added, stirred for 12h, the solution was washed by saturated sodium bicarbonate solution and dried with anhydrous magnesium sulfate, concentrated with solvent, and purified by column chromatography (ethyl acetate/petroleum ether = 1/1, V/V) to afford the compound **C1**.

C1: Yellow solid, yield 0.60 g, 1.48 mmol 74 %; ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (s, 1H), 8.68 (s, 1H), 8.52 (d, J = 7.6 Hz, 1H), 8.40 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.9 Hz, 2H), 7.52 (t, J = 7.2 Hz, 1H), 7.47 (t, J = 7.2 Hz, 1H), 7.38 – 7.17 (m, 1H), 7.17 – 7.13 (m, 2H), 4.03 (s, 3H), 3.88 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 161.93, 161.51, 147.38, 137.74, 136.67, 136.35, 132.57, 126.86, 125.96, 124.24, 123.31, 122.44, 116.23, 115.07, 113.51, 110.40 (t, J = 234.7 Hz), 56.08, 39.95. ^{19}F NMR (470 MHz, DMSO-d_6) δ -114.05. MS (ESI) *m/z* calcd for $C_{21}H_{17}F_2N_5O_2$ $[M + H]^+$410.13, found 410.06.

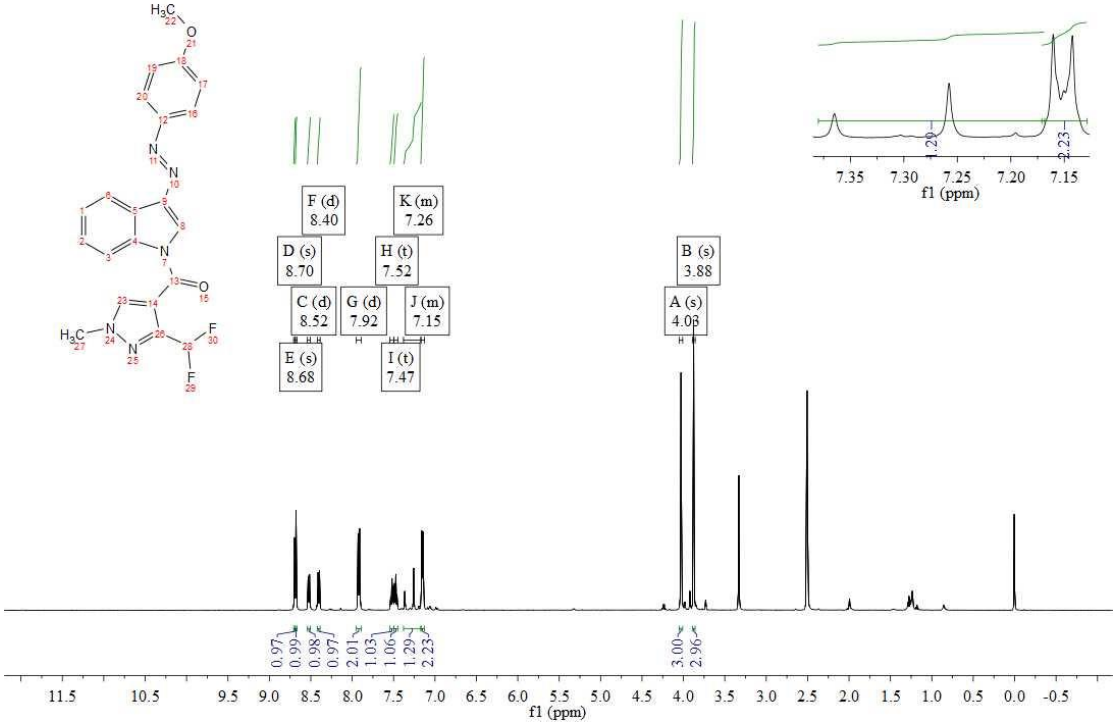


Figure S61. ^{1}H NMR of compound **C1**.in DMSO-d_6.

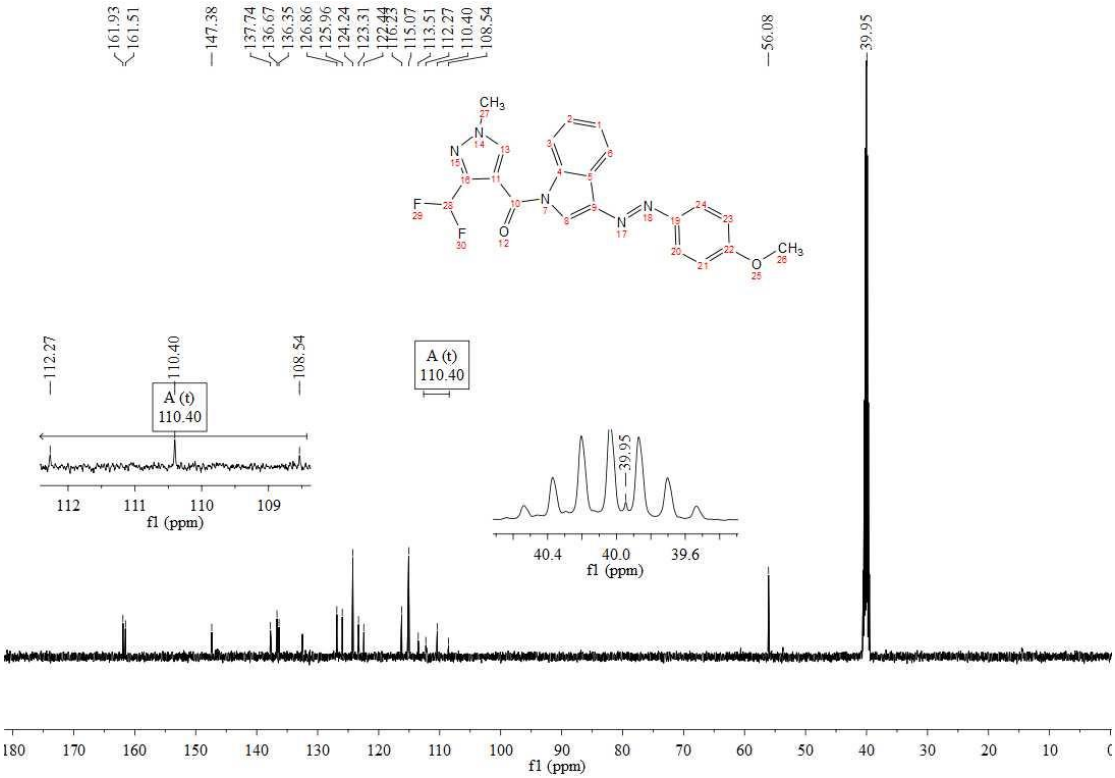


Figure S62. ^{13}C NMR of compound **C1** in DMSO-d_6.

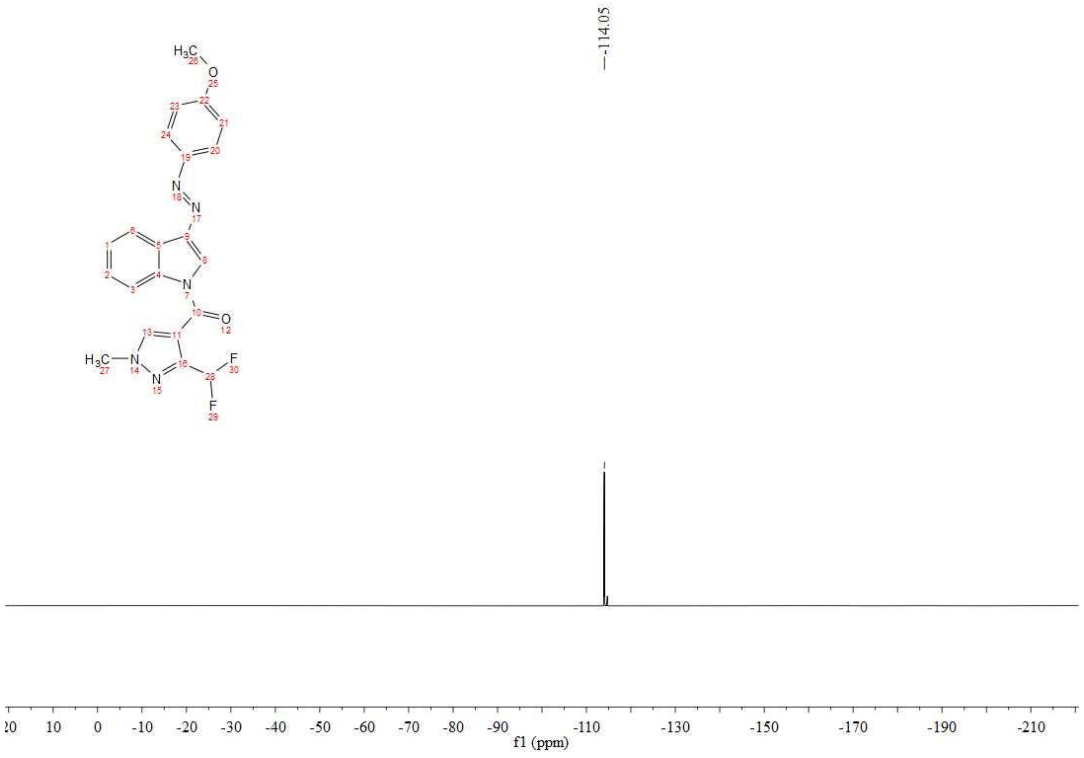


Figure S63. ^{19}F NMR of compound **C1** in DMSO-d_6.

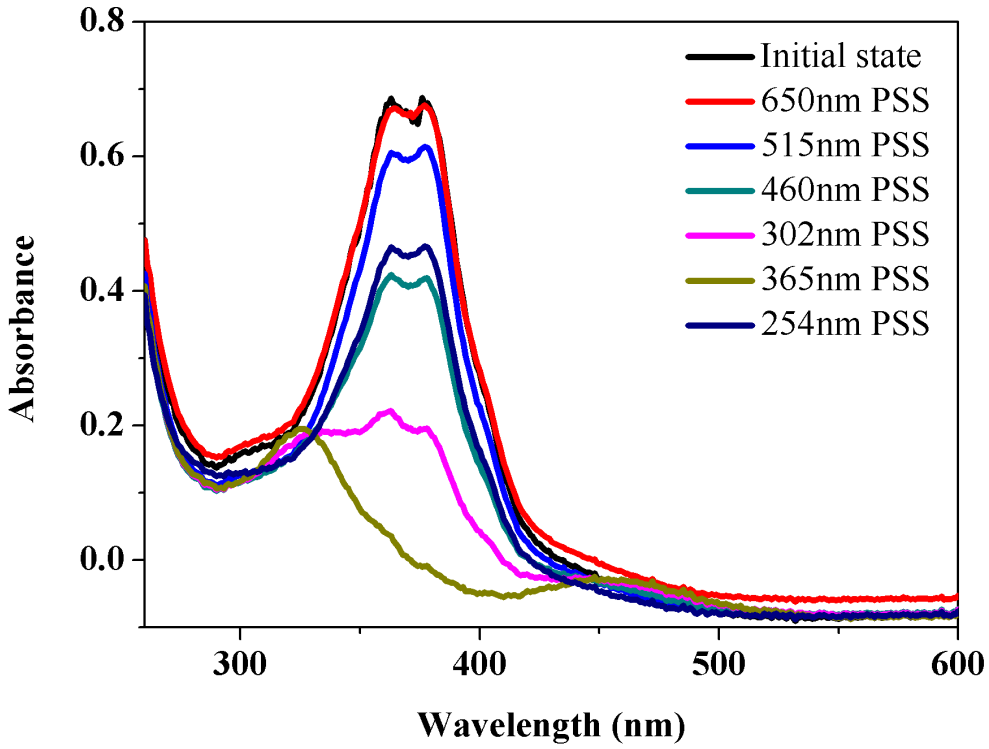


Figure S64. The UV/Vis spectra of compound **C1** at various PSSs.

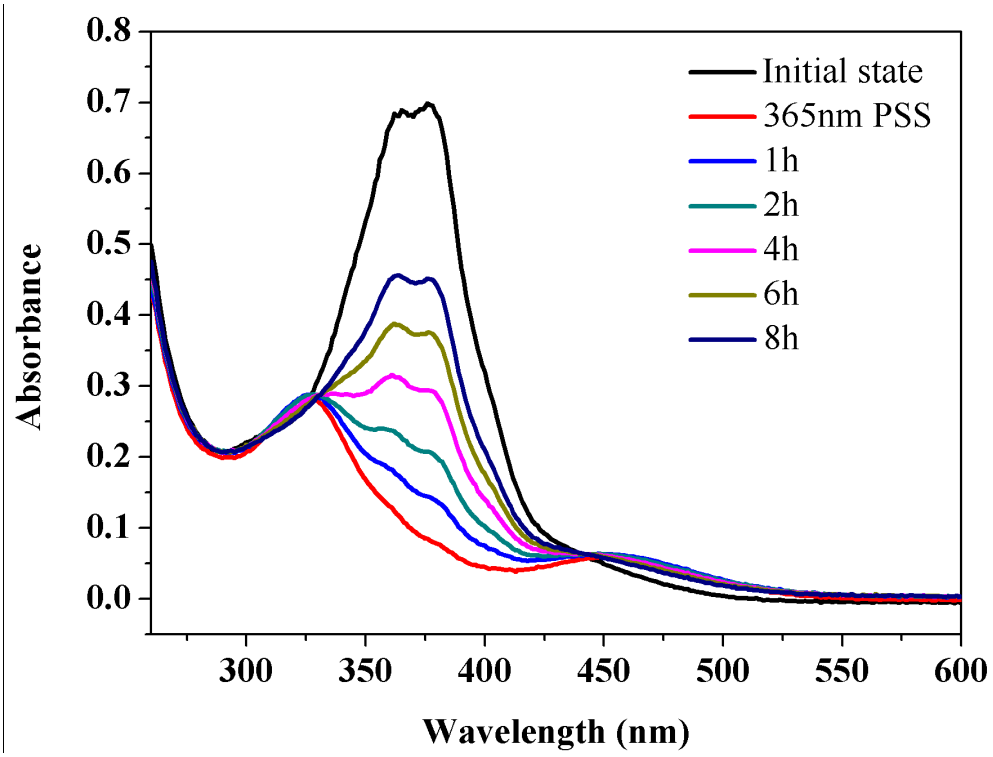


Figure S65. UV/Vis spectra of **C1**$_{cis}$ of thermal relaxtion at different times.

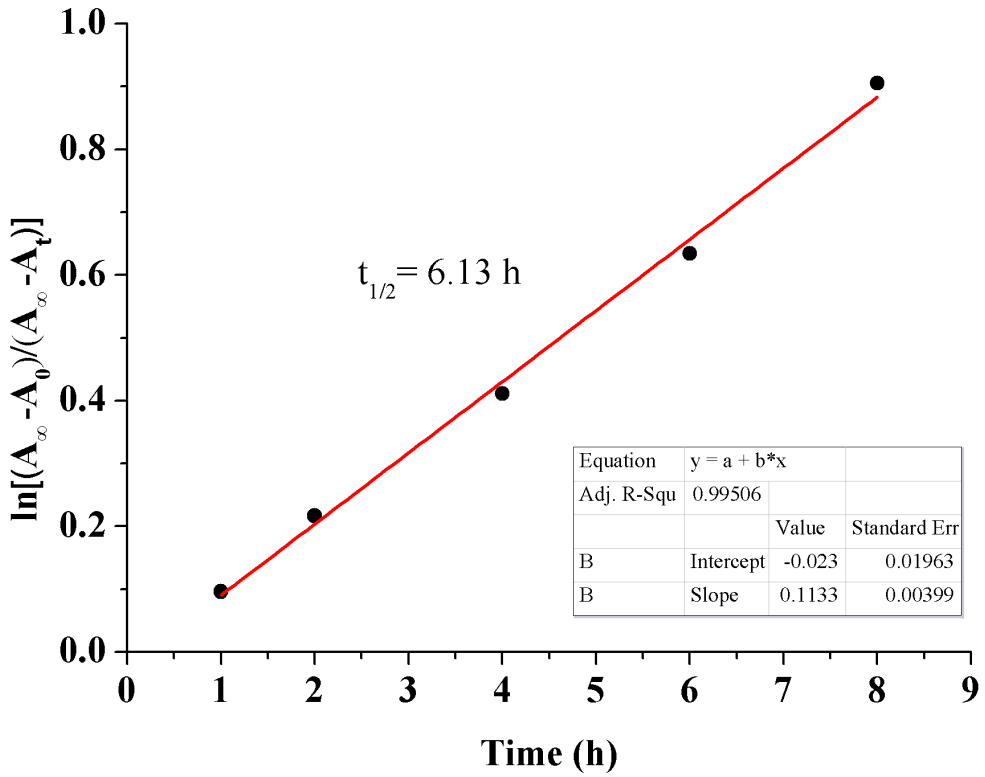


Figure S66. Thermal relaxation fitting curve for isomerization of compound **C1** at PSS_{cis} in DMSO.

XYZ coordinates optimized molecular geometry of **A1**.

C	2.94431502	-0.26198687	0.00979941
C	3.09035805	-1.64367862	-0.05419256
C	4.35855885	-2.17329270	-0.03011131
C	5.48407317	-1.34221012	0.05700889
C	5.35774237	0.02559336	0.12095573
C	1.79635443	0.61207444	0.00788117
H	2.22477273	-2.27080407	-0.12101050
H	4.49538206	-3.23508430	-0.07857076
H	6.46123680	-1.78239560	0.07380742
H	6.22055027	0.65769557	0.18725422
N	0.48216007	0.15389003	-0.06806772
N	-0.41091793	1.02130068	-0.05587072
C	-1.74956770	0.54235346	-0.13485440
C	-2.74583117	1.50172830	-0.11637197
C	-2.09381537	-0.79883656	-0.23125006
C	-4.07505168	1.13312018	-0.18499273
H	-2.46110223	2.53114648	-0.04868287
C	-3.41896530	-1.16798573	-0.30098928
H	-1.31527035	-1.53035585	-0.25240020

C	-4.41227296	-0.20260358	-0.27884106
H	-4.85218023	1.86885722	-0.18289583
H	-3.69694017	-2.19798457	-0.38987882
C	2.26003493	1.88640892	0.09036429
H	1.70443462	2.79311387	0.11300839
C	4.07463352	0.55704791	0.09633336
N	3.63148568	1.86761644	0.14445751
H	4.21139433	2.67341380	0.20695049
O	-5.74495819	-0.57571599	-0.36162822
C	-6.40572494	-0.88576279	0.89326092
H	-6.40666106	-0.02478737	1.54948843
H	-7.41707405	-1.15549237	0.63654513
H	-5.91701928	-1.71306252	1.39177476

XYZ coordinates optimized molecular geometry of **A2**.

C	2.64539902	-0.60427123	-0.00340642
C	2.70969176	-1.99464378	-0.04128857
C	3.94652027	-2.59711114	-0.01318938
C	5.12038285	-1.83147347	0.05228131
C	5.07463945	-0.45621020	0.09037652
C	1.55652522	0.34035188	-0.01667203
H	1.81083685	-2.57586591	-0.09135839
H	4.02039915	-3.66607095	-0.04151472
H	6.07025398	-2.32769044	0.07292452
H	5.97345428	0.12390996	0.14034816
N	0.21921721	-0.03171165	-0.07741246
N	-0.62666938	0.88453220	-0.08379601
C	-1.99049942	0.47634970	-0.14676198
C	-2.93319241	1.49033070	-0.15888240
C	-2.41014925	-0.84675309	-0.19707604
C	-4.28156631	1.19370300	-0.21730713
H	-2.59671666	2.50586954	-0.12191643
C	-3.75472885	-1.14418511	-0.25593967
H	-1.67832402	-1.62545797	-0.19016715
C	-4.69324200	-0.12429553	-0.27007813
H	-5.01369878	1.97432773	-0.23215250
H	-4.08666748	-2.16106464	-0.30168613
C	2.11188551	1.58676616	0.03947959
H	1.62416739	2.53282656	0.04846049
C	3.82386060	0.15030586	0.06172222
C	4.41164709	2.60861153	0.15278951
H	3.85384531	3.53229972	0.15078023
H	5.07218461	2.59253134	-0.70336071

H	4.99852299	2.55128024	1.05937171
N	3.47106493	1.48822925	0.08675266
O	-6.04356995	-0.42618730	-0.35393001
C	-6.73658730	-0.63976729	0.91270092
H	-6.69158274	0.25155639	1.52316243
H	-7.75928250	-0.86321722	0.65765733
H	-6.29763943	-1.46933263	1.44959208

XYZ coordinates optimized molecular geometry of **A3**.

C	-2.13399229	1.06488811	-0.01408691
C	-2.01866619	2.44575346	-0.03011081
C	-3.16910031	3.20326057	0.00412571
C	-4.41782389	2.58402197	0.05337607
C	-4.54460033	1.20878894	0.06973315
C	-1.13160142	0.02038553	-0.04104300
H	-1.05061506	2.90218335	-0.06845597
H	-3.10876045	4.27284802	-0.00726788
H	-5.30460128	3.18503833	0.07920303
H	-5.51699244	0.77591260	0.10721181
N	0.23784236	0.29695928	-0.09157841
N	1.00213399	-0.68431993	-0.11071992
C	2.39652580	-0.39948262	-0.16092772
C	3.24239129	-1.49483641	-0.18486986
C	2.93053306	0.88237708	-0.18768398
C	4.61196593	-1.31917751	-0.23141905
H	2.81545882	-2.47619066	-0.16597867
C	4.29608100	1.05870197	-0.23475036
H	2.27111851	1.72318393	-0.17178296
C	5.13914716	-0.04203295	-0.26038084
H	5.27200798	-2.16116009	-0.25514086
H	4.71861854	2.04186265	-0.26239397
C	-1.77251675	-1.15968614	-0.00836628
H	-1.38661753	-2.14827111	-0.01381086
C	-3.38661013	0.44221236	0.03581428
C	-4.02090459	-2.04572521	0.08147753
N	-3.15247030	-0.95009043	0.03946031
C	-5.49800445	-1.78004887	0.13677338
H	-5.82475696	-1.23727150	-0.74031220
H	-5.99774373	-2.73516577	0.16848663
H	-5.75438247	-1.21499356	1.02303568
O	-3.55193123	-3.16544668	0.07257158
O	6.51010092	0.13837505	-0.33221089
C	7.21197104	0.28085592	0.94043906

H	8.25163859	0.41422445	0.69172355
H	6.84500815	1.14247581	1.48060994
H	7.08395015	-0.60748295	1.54325112

XYZ coordinates optimized molecular geometry of **A4**

C	-1.26761829	1.69966023	-0.06743129
C	-0.99586675	3.06272711	-0.10574682
C	-2.05092568	3.94389961	-0.10390110
C	-3.37307558	3.48091542	-0.07039867
C	-3.65886738	2.13594806	-0.03202879
C	-0.42706259	0.52796850	-0.07314384
H	0.01826773	3.40528153	-0.13900957
H	-1.86640300	4.99919124	-0.13304993
H	-4.17761771	4.18915447	-0.07824165
H	-4.66924692	1.78364270	-0.01518454
N	0.96518493	0.58336479	-0.10824688
N	1.56522906	-0.50761319	-0.11111618
C	2.98686433	-0.44010396	-0.14746070
C	3.65789517	-1.64967854	-0.14485421
C	3.71087600	0.74344226	-0.18887831
C	5.03817456	-1.68524557	-0.17522849
H	3.08259672	-2.55175253	-0.11938173
C	5.08742857	0.70956141	-0.22040875
H	3.18123920	1.67140410	-0.19801024
C	5.75382477	-0.50497900	-0.21452636
H	5.56567950	-2.61631053	-0.18499536
H	5.65706878	1.61477726	-0.26671021
C	-1.24469951	-0.55335326	-0.03342982
H	-0.98771678	-1.58529958	-0.00999381
C	-2.58960739	1.24925537	-0.02320716
N	-2.56030092	-0.14278386	0.00007214
C	-3.68390516	-1.01346337	0.04967848
C	-3.87098996	-1.95504959	-0.94860532
C	-4.58274252	-0.93034471	1.10130053
C	-4.95131426	-2.81694450	-0.89035384
H	-3.18120323	-1.99858363	-1.76669329
C	-5.67075527	-1.78270901	1.14568798
H	-4.42010155	-0.21067407	1.87713546
C	-5.85567588	-2.73006536	0.15335620
H	-5.09079653	-3.54499635	-1.66406140
H	-6.36417855	-1.71451010	1.95977438
H	-6.69593765	-3.39365278	0.19348624
O	7.13911778	-0.53654384	-0.25873713

C	7.82546109	-0.47525572	1.01906278
H	8.87838412	-0.50598008	0.79127835
H	7.58610835	0.44231052	1.54113330
H	7.55561425	-1.31953786	1.64056241

XYZ coordinates optimized molecular geometry of **B1**.

C	-3.58705576	0.30345215	0.00860383
C	-3.67557390	1.68710480	-0.12458603
C	-4.91949189	2.27321969	-0.08441675
C	-6.07716625	1.49853185	0.08686205
C	-6.00746509	0.13070437	0.22008096
C	-2.48146498	-0.62498686	0.01462086
H	-2.78929544	2.27499050	-0.25506925
H	-5.01204385	3.33631963	-0.18471898
H	-7.03306775	1.98256938	0.11431817
H	-6.89098778	-0.46056852	0.35078210
N	-1.15573987	-0.23595751	-0.13139158
N	-0.29194052	-1.13430847	-0.10372600
C	1.05830297	-0.70405966	-0.25752716
C	2.02336590	-1.69552601	-0.21484058
C	1.44051803	0.61750173	-0.44619203
C	3.36132860	-1.37792317	-0.35255951
H	1.71470174	-2.71034528	-0.07442296
C	2.77400313	0.93863299	-0.58467405
H	0.69088736	1.37760213	-0.48412671
C	3.72730645	-0.06111105	-0.53159354
H	4.11264537	-2.13930189	-0.32835394
H	3.08065925	1.95222529	-0.73934146
C	-3.00614859	-1.87381096	0.18350517
H	-2.50157585	-2.80876385	0.23770721
C	-4.74920751	-0.45814404	0.17906838
N	-4.36331945	-1.78341430	0.28275864
O	5.07126075	0.26125717	-0.71814879
C	5.94666135	0.59500470	0.28980789
C	5.39296753	0.60246069	1.68613843
H	4.57851033	1.31038546	1.76819884
H	5.01396166	-0.37628572	1.95003868
H	6.18372625	0.87968672	2.36419330
O	7.07638329	0.85248960	-0.01901088
H	-4.97755444	-2.55903330	0.41079732

XYZ coordinates optimized molecular geometry of **B2**.

C	-1.91670163	1.70190930	0.03364468
C	-1.66308870	3.06891496	0.10353854
C	-2.72838244	3.92890444	0.23816756
C	-4.04176903	3.44187397	0.30815330
C	-4.30890753	2.09328222	0.23982444
C	-1.06389748	0.54473201	-0.09008620
H	-0.65703727	3.43409822	0.05525204
H	-2.55823398	4.98555584	0.29380254
H	-4.85315067	4.13331013	0.41861360
H	-5.31164511	1.72412320	0.29667793
N	0.32144453	0.62381455	-0.18364715
N	0.94468828	-0.45044172	-0.28414481
C	2.36268840	-0.34278626	-0.37773051
C	3.05866552	-1.53444606	-0.48463317
C	3.05671838	0.85982175	-0.37017147
C	4.43746060	-1.53436023	-0.57743071
H	2.51054873	-2.45328205	-0.49474165
C	4.43217296	0.86431642	-0.46252989
H	2.51319202	1.77625435	-0.29326883
C	5.11477687	-0.33394720	-0.56006179
H	4.98261865	-2.45042128	-0.66841217
H	4.97862171	1.78441798	-0.46583355
C	-1.87096772	-0.55059241	-0.09752093
H	-1.60746521	-1.57786440	-0.18429803
C	-3.23083066	1.22816437	0.09529571
N	-3.18285677	-0.16157747	0.01090605
O	6.50223100	-0.32362513	-0.69764784
C	7.39538424	-0.37484152	0.34847043
C	6.80904865	-0.44042793	1.72987732
H	6.19027656	0.42653441	1.92152247
H	6.19226786	-1.32288894	1.83968071
H	7.61789968	-0.47290105	2.44164303
O	8.56417936	-0.36285618	0.08112585
C	-4.29846355	-1.05080294	0.03782357
C	-5.29264764	-0.94488810	-0.92184681
C	-4.37590631	-2.02580825	1.01859352
C	-6.37094953	-1.81171053	-0.89106199
H	-5.21676944	-0.19845440	-1.68567141
C	-5.44827063	-2.90092370	1.03436999
H	-3.60932133	-2.09151391	1.76358493
C	-6.44943234	-2.79280736	0.08373207
H	-7.13956456	-1.72655284	-1.63249465
H	-5.50436056	-3.65608913	1.79222227
H	-7.28229494	-3.46650466	0.10159206

XYZ coordinates optimized molecular geometry of **A2**$_{cis}$.

C	-2.63115146	-0.48214590	-0.05953862
C	-3.74830331	-1.30873861	-0.13771660
C	-4.99574656	-0.72771912	-0.14025690
C	-5.14315179	0.66551577	-0.06598597
C	-4.04785242	1.49568937	0.01201942
C	-1.20939366	-0.74457675	-0.03408624
H	-3.62833924	-2.37153977	-0.19404893
H	-5.87119337	-1.34332960	-0.19974126
H	-6.12715747	1.09038027	-0.07003983
H	-4.16423024	2.55872140	0.06843459
N	-0.76363257	-2.06721277	-0.10061208
N	0.41153120	-2.47674924	-0.08356587
C	1.52607042	-1.55686723	0.02283380
C	2.15547781	-1.09281333	-1.11273139
C	2.02063117	-1.20493052	1.27129850
C	3.25849295	-0.25758805	-1.01457262
H	1.78713262	-1.37623319	-2.07784875
C	3.11557516	-0.37674883	1.37192456
H	1.54462095	-1.57752201	2.15556814
C	3.74125650	0.10835557	0.22854543
H	3.72439352	0.09195058	-1.91101460
H	3.50635956	-0.09276518	2.32649000
C	-0.59286201	0.48053320	0.05274868
H	0.43797970	0.72930555	0.09553088
C	-2.78995643	0.90374495	0.01445141
C	-1.24890944	2.90339636	0.17216184
H	-0.18096443	3.04842654	0.22547746
H	-1.70718898	3.31589926	1.06038082
H	-1.63324075	3.41293536	-0.70066836
N	-1.52754293	1.46763470	0.08240517
C	5.54269225	1.48342923	-0.69003362
H	5.97200873	0.70119045	-1.30123662
H	6.32822159	2.08105033	-0.25876491
H	4.90039148	2.10686734	-1.29729033
O	4.81893769	0.92846715	0.43060139

XYZ coordinates optimized molecular geometry of **A3**$_{cis}$.

C	-2.49228920	-0.96663910	-0.00002175
C	-3.47341530	-1.94522607	0.00011256
C	-4.79372218	-1.55213317	0.00032028

C	-5.12513264	-0.19710234	0.00040679
C	-4.15499213	0.78546838	0.00027117
C	-1.04421162	-1.07051218	-0.00024179
H	-3.19591016	-2.97900814	0.00005037
H	-5.57304385	-2.28729574	0.00042768
H	-6.15624803	0.09452183	0.00057742
H	-4.44965568	1.80890407	0.00034044
N	-0.47049794	-2.35559079	-0.00036747
N	0.73738107	-2.63634399	-0.00036065
C	1.76389495	-1.61430790	-0.00017061
C	2.28446899	-1.16218835	1.19964341
C	2.28480095	-1.16206045	-1.19979458
C	3.31377447	-0.23914777	1.19714652
H	1.88665788	-1.52778029	2.12426201
C	3.31410452	-0.23901932	-1.19690802
H	1.88724671	-1.52756063	-2.12455991
C	3.82414586	0.22933545	0.00021726
H	3.71739024	0.12572729	2.11894213
H	3.71797795	0.12596330	-2.11854832
C	-0.55584550	0.18802890	-0.00030293
H	0.43533716	0.55981142	-0.00046424
C	-2.82294635	0.39025860	0.00004551
C	-1.32359361	2.47741141	-0.00021059
N	-1.60518010	1.10355987	-0.00013601
C	6.20283939	0.65409708	0.00027928
H	6.84894470	1.51628630	0.00033202
H	6.37996634	0.05655068	-0.88328761
H	6.38007985	0.05636597	0.88370134
O	4.83883605	1.17387314	0.00040943
C	-2.47794223	3.43666165	-0.00012599
H	-3.08908064	3.30258453	0.88240461
H	-2.06976648	4.43483017	-0.00023205
H	-3.08929437	3.30247971	-0.88249508
O	-0.16460519	2.83596374	-0.00033455

XYZ coordinates optimized molecular geometry of **A4**$_{cis}$.

C	-2.25264306	-1.65637925	0.02281206
C	-3.25875260	-2.61701841	0.06523086
C	-4.56643898	-2.19458357	0.12866621
C	-4.88109905	-0.82790850	0.15485426
C	-3.89643832	0.13291925	0.11311107
C	-0.80965912	-1.74931883	-0.03001867
H	-3.00825156	-3.65802812	0.05068208

H	-5.35945632	-2.91475609	0.16179424
H	-5.90802236	-0.52620756	0.20984361
H	-4.13760556	1.17515848	0.13627356
N	-0.21695581	-3.01774865	-0.06739279
N	0.99649353	-3.28598050	-0.08856088
C	2.00371265	-2.24617338	-0.06904755
C	2.50454141	-1.79261917	1.13920729
C	2.52832611	-1.77200151	-1.25879418
C	3.50991387	-0.84380899	1.15534015
H	2.10852704	-2.17772497	2.05670408
C	3.53339570	-0.82246505	-1.23846060
H	2.15074534	-2.14143581	-2.19038888
C	4.02449541	-0.35683205	-0.03245240
H	3.90508153	-0.48665726	2.08387105
H	3.94616009	-0.44912777	-2.15287586
C	-0.33555656	-0.46621695	-0.04162445
H	0.65738350	-0.09523961	-0.08848737
C	-2.57783893	-0.30025009	0.04097406
N	-1.38376251	0.41500116	-0.00202873
C	4.63383843	1.98042948	-0.01866430
H	4.03387133	2.20165316	0.85338652
H	4.06933334	2.20515234	-0.91314029
H	5.54295515	2.55839071	0.00067383
O	5.04630815	0.58056555	-0.01304433
C	-1.24828011	1.83659027	0.00292242
C	-0.53126631	2.45350671	1.01447657
C	-1.82302506	2.59054089	-1.00767332
C	-0.38367984	3.82987404	1.01033955
H	-0.10221920	1.86245999	1.79777207
C	-1.68633506	3.96758563	-0.99737205
H	-2.36273691	2.10335227	-1.79360733
C	-0.96420109	4.58913072	0.00830567
H	0.17359665	4.30501465	1.79222759
H	-2.13325790	4.54965571	-1.77782741
H	-0.85505273	5.65490397	0.01053399

XYZ coordinates optimized molecular geometry of **B2**$_{cis}$.

C	2.90390087	-1.32913974	-0.02219750
C	4.07339868	-2.08302833	-0.05490372
C	5.27830880	-1.42137951	-0.10932126
C	5.33009990	-0.01987758	-0.13554338
C	4.18175378	0.73815979	-0.10291340
C	1.50355378	-1.69121345	0.02103803

H	4.02421929	-3.15262472	-0.03989468
H	6.19308411	-1.97913676	-0.13505358
H	6.28222651	0.46975981	-0.18313212
H	4.22177427	1.80722198	-0.12539903
N	1.15654946	-3.04646514	0.05460995
N	0.01442744	-3.53665477	0.07558557
C	-1.16915498	-2.70621328	0.06126651
C	-1.75154733	-2.35623539	-1.14510392
C	-1.76924459	-2.34243251	1.25440432
C	-2.91709100	-1.61317793	-1.15743379
H	-1.29600542	-2.66089870	-2.06465616
C	-2.93483601	-1.59878444	1.24086858
H	-1.32731313	-2.63662237	2.18392459
C	-3.49443630	-1.22883649	0.03535779
H	-3.37911031	-1.33782886	-2.08250370
H	-3.40999401	-1.31222766	2.15583293
C	0.79700105	-0.51930174	0.02764774
H	-0.24794654	-0.34035191	0.06710598
C	2.96825616	0.06387427	-0.04029214
N	1.66062902	0.54196535	-0.00675067
C	-4.77405971	0.86510135	0.01815704
O	-4.68915529	-0.50902853	0.02158768
C	1.26005601	1.91321991	-0.01158887
C	0.46395315	2.39137601	-1.03903049
C	1.65782777	2.75358383	1.01551350
C	0.05751905	3.71481816	-1.03310835
H	0.17513270	1.73668628	-1.83593444
C	1.26237317	4.07977380	1.00728840
H	2.26192029	2.37073414	1.81227100
C	0.45916279	4.56146541	-0.01344654
H	-0.56045482	4.08268319	-1.82706976
H	1.57216701	4.72937397	1.80080299
H	0.14942260	5.58705101	-0.01394637
C	-3.47578198	1.62088270	0.03501789
H	-3.69657050	2.67597436	0.02891004
H	-2.90357961	1.37520913	0.92032907
H	-2.87646164	1.37057010	-0.83046408
O	-5.86957356	1.35236601	0.00275041