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Electronic Supplementary Information

Robust bi-directional photoswitching of thiomethyl substituted arylazopyrazoles under visible light

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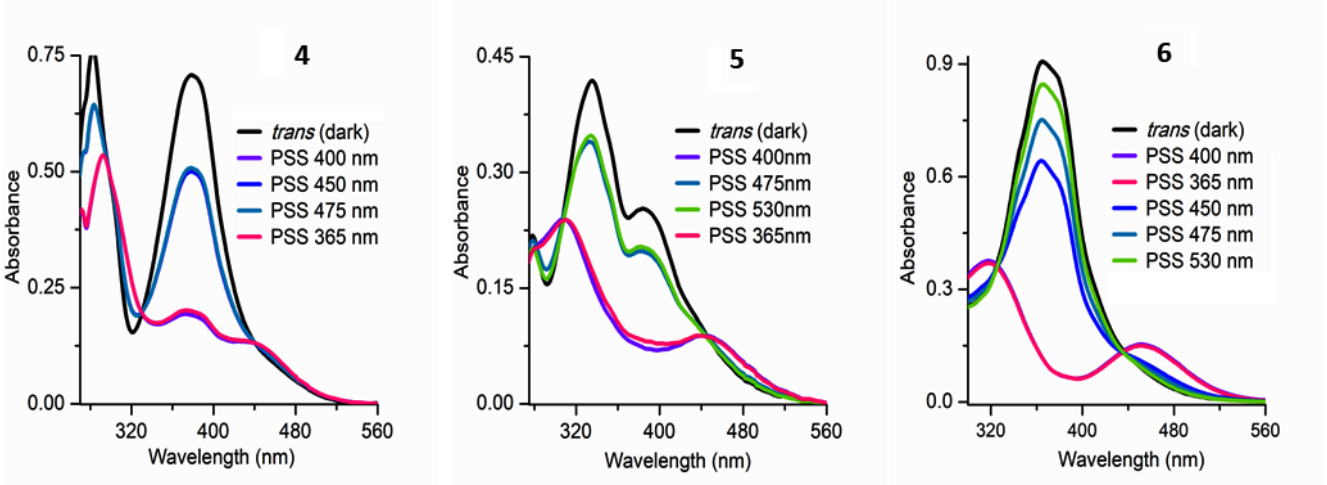
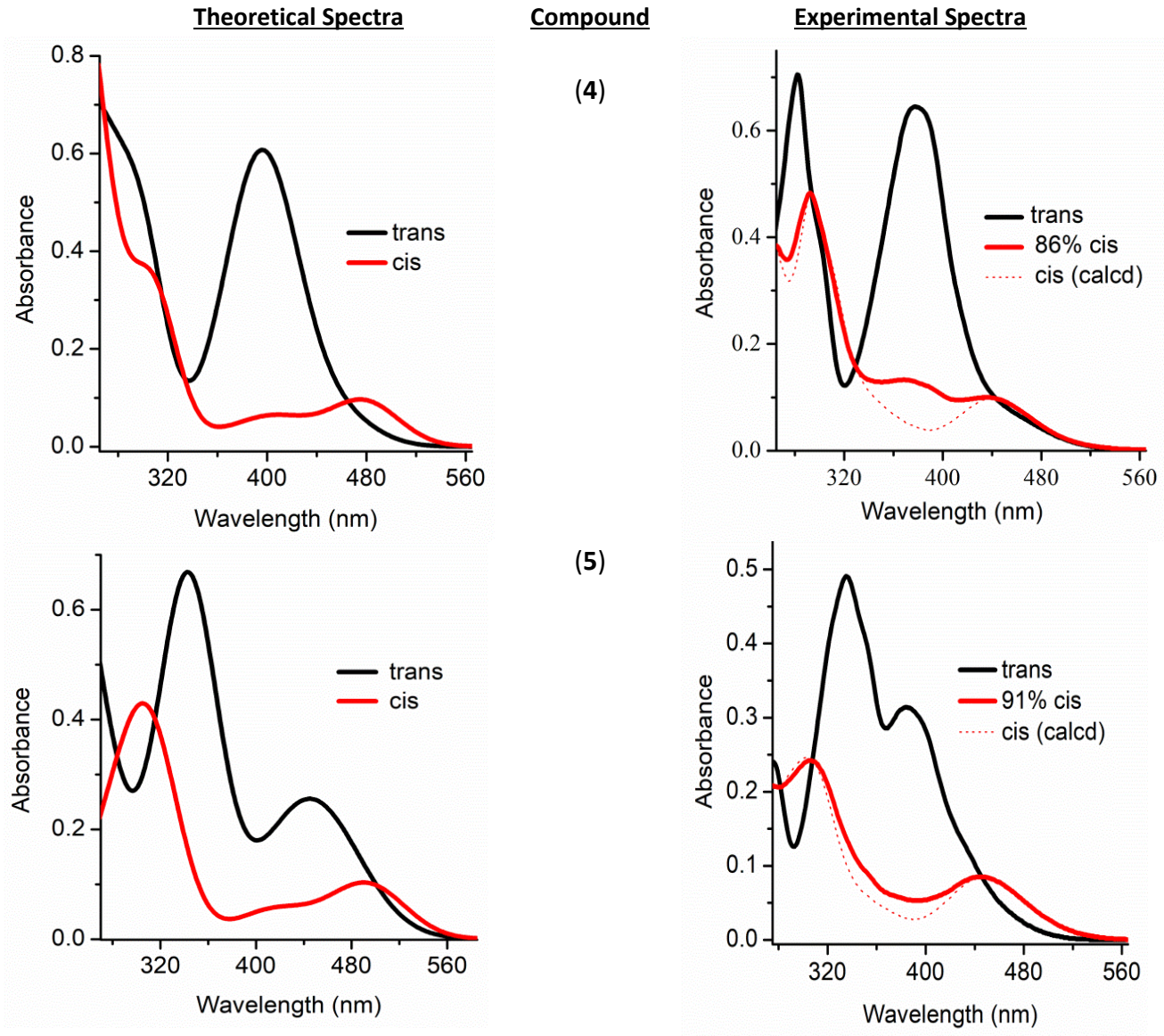


Fig. S1. Absorption spectra of PSS of **4**-**6** generated by various wavelengths of LEDs in DMSO.



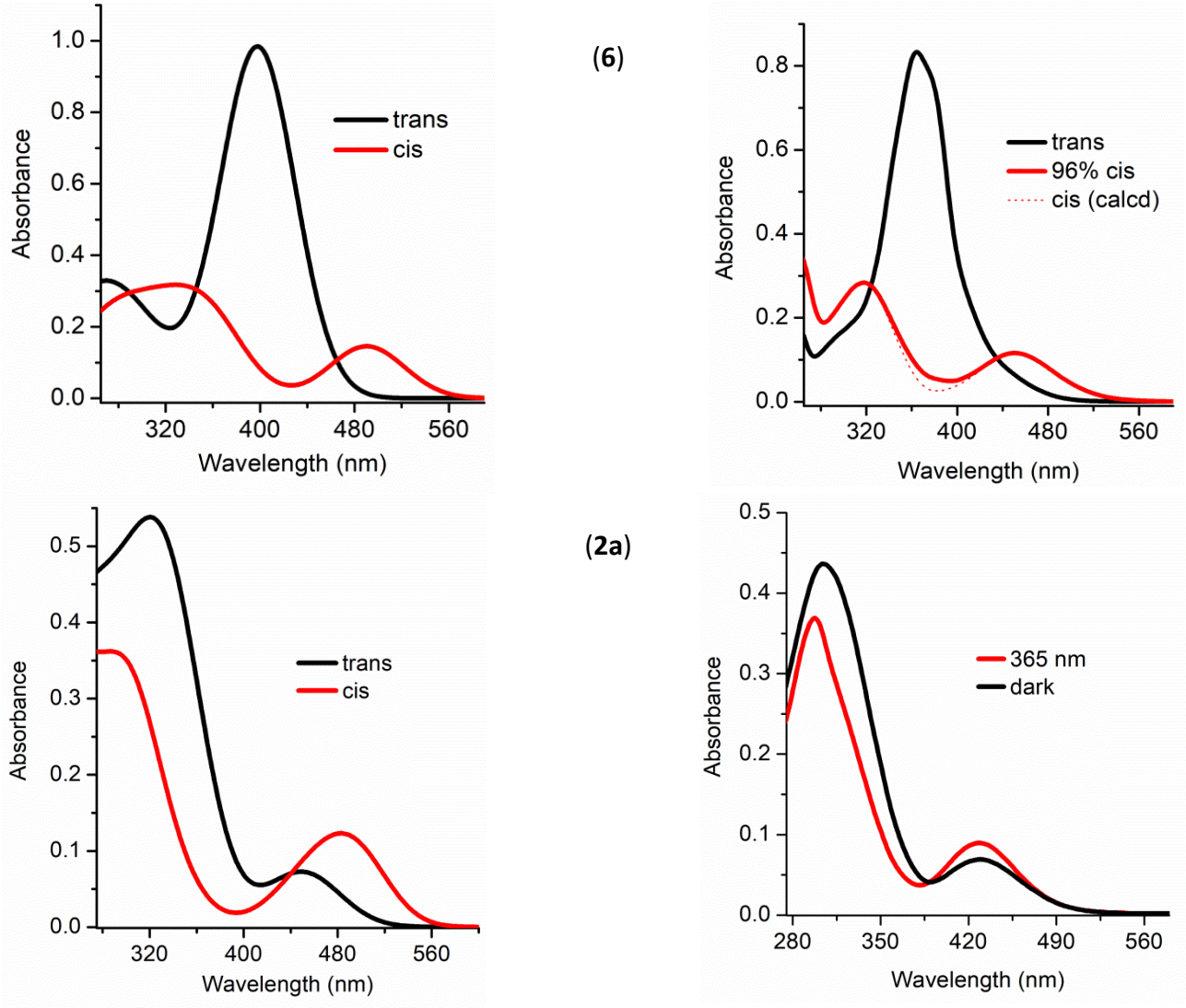


Fig. S2. Calculated vs experimental UV-Vis absorption spectra of **4-6 and 2a** in DMSO solvent. Two conformers were considered in case of both *cis* and *trans* isomers of **5.**

Table S1. **Free energies for the *trans* and *cis* isomers of switches 2a & 4-6.**

	Trans energy G° (eV)	*Cis* energy G° (eV)	Energy (G°) difference (*trans-cis*) (eV)	$t_{1/2}$ *cis*, experi-mental (day)[a]
2a	-24863.17	-24862.65	0.52 (11.99 kcal/mol)	111[b]
4	-42441.12	-42440.46	0.66 (15.22 kcal/mol)	1.1
5	-30535.87 (conf-1) -30535.75 (conf-2)	-30535.23 (conf-1) -30535.19 (conf-2)	0.60 (13.84 kcal/mol)[c]	3.3
6	-30535.96	-30535.25	0.71 (16.37(kcal/mol)	2.7

[a] Recorded in DMSO solvent at 27 °C; [b] Reported in acetonitrile; [c] Average of four energy difference values between *trans*-conformer-1/-2 and *cis*-conformer-1/-2.

The free energy difference between *cis* and *trans* isomers of **4-6** is ca. 0.60-0.71 eV, while that difference is ca. 0.52 eV for **2a**. The greater free energy difference between *cis* and *trans* isomers typically means lower activation barrier for thermal cis-to-trans reversion, leading to shorter thermal half-lives of *cis*-**4**/-**5** and -**6** in comparison to *cis*-**2a** (Table S1).

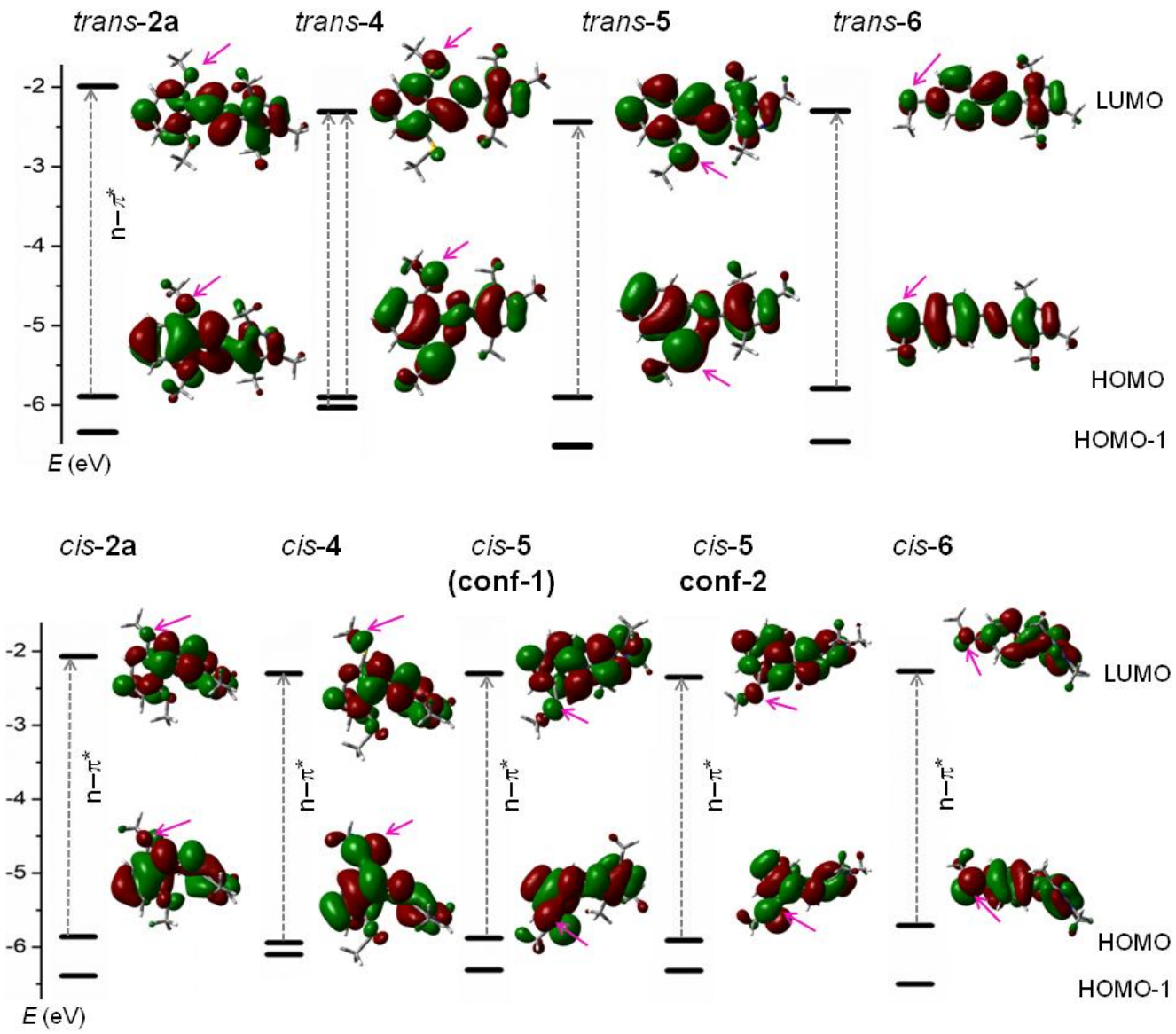


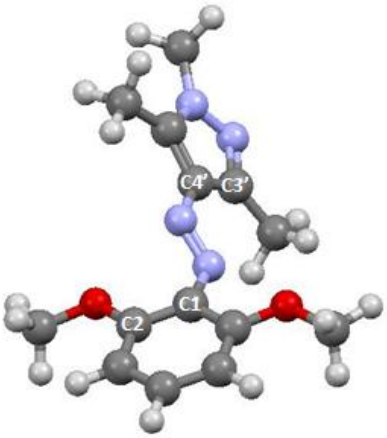
Fig. S3. Energetic diagram of frontier MOs of *trans* (top) and *cis* (bottom) isomers of **2a**, and **4-6**, and representations of LUMO (top) and HOMO (bottom). Dotted arrow illustrates long wavelength transition. Solid arrows show the lobe coefficients on the O and S atoms of –OMe and –SMe substituents, respectively.

Table S2. Atomic orbital contribution to the frontier MOs.[a]

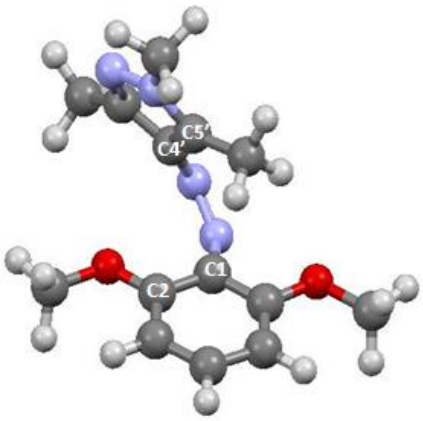
Compound	Frontier MO	Trans	Cis
2a	HOMO	C2-p=0.16 N8-p=0.16 N9-p=0.11 C4-p=0.09 C12-p=0.07 N8-s=0.06 C28-p=0.06 O37-p=0.05 N9-s=0.05 C12-s=-0.04 O38-p=0.04 C11-s=0.04 C23-p=0.04 C11-p=0.02 N13-p=0.02 N14-p=0.02 C10-p=0.01 C3-p=0.01	N30-p=0.16 C3-p=0.13 N29-p=0.12 C20-p=0.09 C5-p=0.08 C18-p=0.06 C2-p=0.05 N30-s=0.04 N29-s=0.04 C9-p=0.04 O37-p=0.03 C19-p=0.03 O38-p=0.03 N31-p=0.03 N32-p=0.02 C19-s=0.02 C2 0-s=-0.02
	LUMO[a]	**N9-p=0.29 (29%) N8-p=0.28 (28%)** C10-p=0.10 C11-p=0.07 C4-p=0.06 C23-p=0.04 C28-p=0.03 C2-p=0.02 N13-p=0.02 N14-p=0.01 C2-s=0.01 C3-s=-0.01.	**N29-p=0.32 (32%) N30-p=0.31 (31%)** C18-p=0.09 C5-p=0.05 C9-p=0.05 C2-p=0.04 C19-p=0.04 C18-s=-0.03 C20-p=0.02 N31-p=0.02 C20-d=0.01 ***(Oxygen contribution is not identified as negligible.)***
4	HOMO	**S28-p=0.26 (26%)** C2-p=0.13 C12-p=0.08 N8-p=0.06 C4-p=0.06 C23-p=0.06 N8-s=0.06 C1-p=0.05 C10-p=0.04 N9-p=0.04 N9-s=-0.04 **S30-p=0.04 (4%)** N13-p=0.03 C11-p=0.03 N14-p=0.02 C19-s=-0.02 C12-s=0.02 C29-p=0.02 C2-s=-0.02	**S14-p=0.17 (17%)** N32-p=0.12 C3-p=0.12 N31-p=0.09 C22-p=0.08 C5-p=0.07 C1-p=0.05 N32-s=0.04 C9-p=0.04 N31-s=0.03 C20-p=0.03 N33-p=0.03 C3-s=0.02 C21-p=0.02 C22-s=-0.02 S19-p=0.02 N34-p=0.02 C20-s=0.01 C21-s=0.01
	LUMO	**N9-p=0.26 (26%) N8-p=0.20 (20%)** C4-p=0.10 C10-p=0.09 C29-p=0.07 C11-p=0.06 C23-p=0.05 **S30-p=0.03 (3%)** C2-p=0.03 N13-p=0.02 **S28-p=0.01 (1%)** N14-p=0.01 C2-s=0.01	**N31-p=0.31 (31%) N32-p=0.27(27%)** C20-p=0.10 (10%) C5-p=0.05 (5%) C2-p=0.03 (3%) C21-p=0.03 (3%) C9-p=0.03 (3%) N33-p=0.03 (3%) **S14-p=0.02 (2%)** C22-p=0.02 (2%) C3-p=0.01 (1%) **S19-p=0.01 (1%)** C20-s=-0.01 (1%) C27-s=0.01 (1%) C22-d=0.01 (1%)
6	HOMO	**S33-p=0.64 (64%)** C5-p=-0.13 C1-p=0.08 C3-p=0.06 C4-p=0.05 C1-s=0.05 H30-s=0.04 C4-s=0.04 H32-s=0.03 N9-p=0.02 C29-p=0.02 C10-p=0.01 C2-s=0.01 C2-p=0.01	**S34-p=0.21 (21%)** N21-p=0.10 N20-p=0.10 C3-p=0.09 C11-p=0.08 C5-p=0.06 C9-p=0.04 C1-p=0.04 C2-p=0.03 C4-p=0.03 C8-p=0.03 N21-s=0.03 N20-s=0.03 N22-p=0.03 C10-p=0.02 N23-p=0.02 C9-s=0.01
	LUMO	**N9-p=0.26 (26%) N8-p=0.22 (22%)** C10-p=0.11 C2-p=0.08 C5-p=0.07 C23-p=0.06 **S33-s=0.04 (4%)** C3-p=0.04 C29-s=-0.03 **S33-p=0.03 (3%)** C1-s=0.02 C4-p=0.02 N13-p=0.01 C10-s=0.01	**N20-p=0.30 (18%) N21-p=0.26 (14%)** C2-p=0.07 C5-p=0.07 C8-p=0.06 C9-p=0.05 C10-p=0.04 **S34-p=0.02 (2%)** C3-p=0.02 C10-s=-0.02 C11-p=0.02 C3-s=-0.01 N22-p=0.01 N21-s=0.01 C1-p=0.01

[a] = Oxygen contribution to both LUMOs of trans and cis isomers is negligible and thus not identified in the calculation.

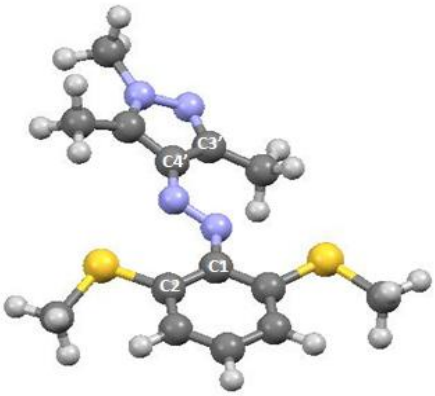
Geometry optimized structures:



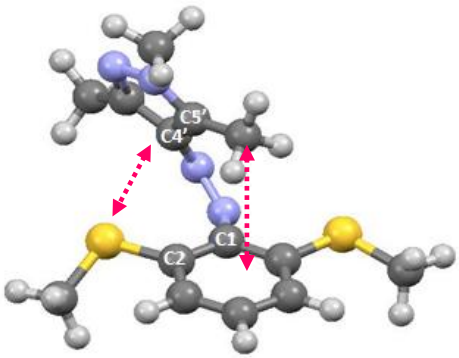
Trans-**2a**
Dihedral angle: ϕ [C2-C1-N=N] = 55.9° &
θ [C3'-C4'-N=N] = 4.1°



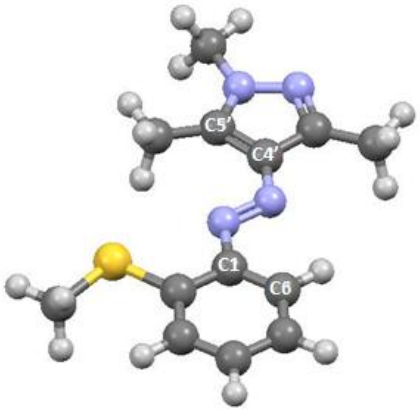
cis-**2a**
Dihedral angle: ϕ [C2-C1-N=N] = 60.6°
θ [C5'-C4'-N=N] = 43.2°



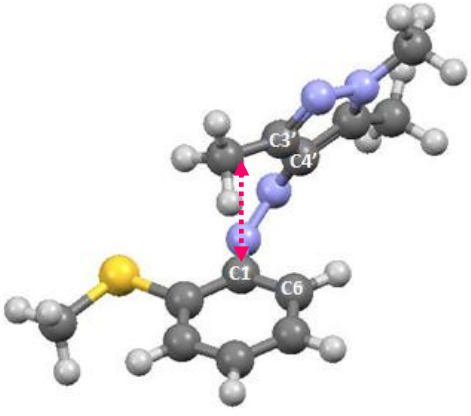
trans-**4**
Dihedral angle: ϕ [C2-C1-N=N] = 19.9°
θ [C3'-C4'-N=N] = 4.0°



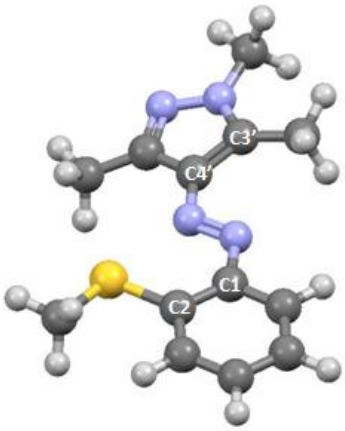
cis-**4**
Dihedral angles: ϕ [C2-C1-N=N] = 59.4°
θ [C5'-C4'-N=N] = 36.3°



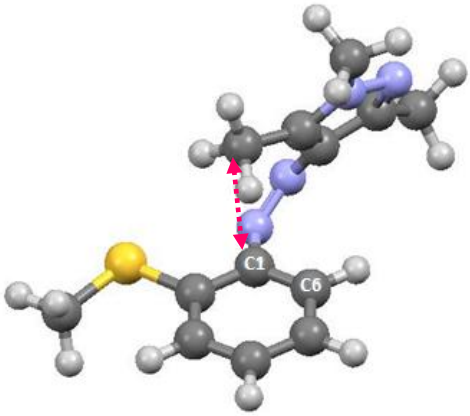
trans-**5** (conformer-1)
Dihedral angles: ϕ [C6-C1-N=N] = 0.15°
θ [C5'-C4'-N=N] = 0.9°



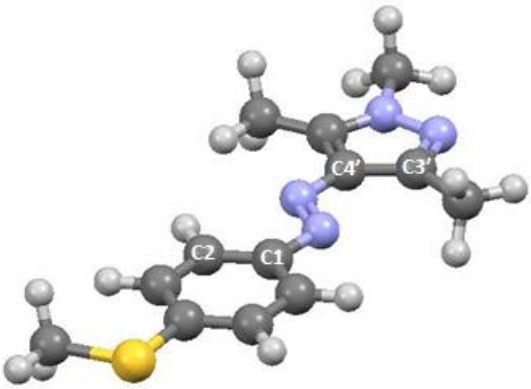
cis-**5** (conformer-1)
Dihedral angles: ϕ [C6-C1-N=N] = 50.43°
θ [C3'-C4'-N=N]= -40.0°



trans-**5** (conformer-2)
Dihedral angle: ϕ [C2-C1-N=N] = -10.1°
θ [C3'-C4'-N=N] = -5.6°

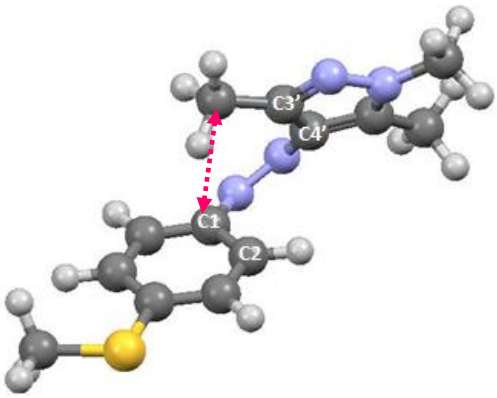


cis-**5** (conformer-2)
Dihedral angle: ϕ [C6-C1-N=N] = -50.44°
θ [C3'-C4'-N=N] = -42.5°



trans-**6**

Dihedral angles: ϕ [C2-C1-N=N] = 0.6°
θ [C3'-C4'-N=N] = 0.4°



cis-**6**
Dihedral angles: ϕ [C2-C1-N=N] = -45.1°
θ [C3'-C4'-N=N] = -43.6°

Fig. S4. Calculated structures of *trans* and *cis* isomers of **2a** and **4-6**, obtained on B3LYP/6-311++g(d,p) level of theory with DMSO solvent model. Dihedral angles are shown under each structure. The double headed arrow shows steric clash in *cis* isomer.

Table S3. **Dihedral angles and n-MO energies of *trans* and *cis* isomers of 2a & 4-6.**

	dihedral angle ϕ (*trans*)	dihedral angle θ (*trans*)	dihedral angle ϕ (*cis*)	dihedral angle θ (*cis*)
2a	55.9°	4.1°	60.6	43.2°
4	19.9°	4.0°	59.4°	36.3°
5	0.1°/-10[a]	0.9°/-5.6°	-50.43°/ -50.43°	-40.0°/-42.5°
6	0.6°	0.4°	-45.1°	-43.6°

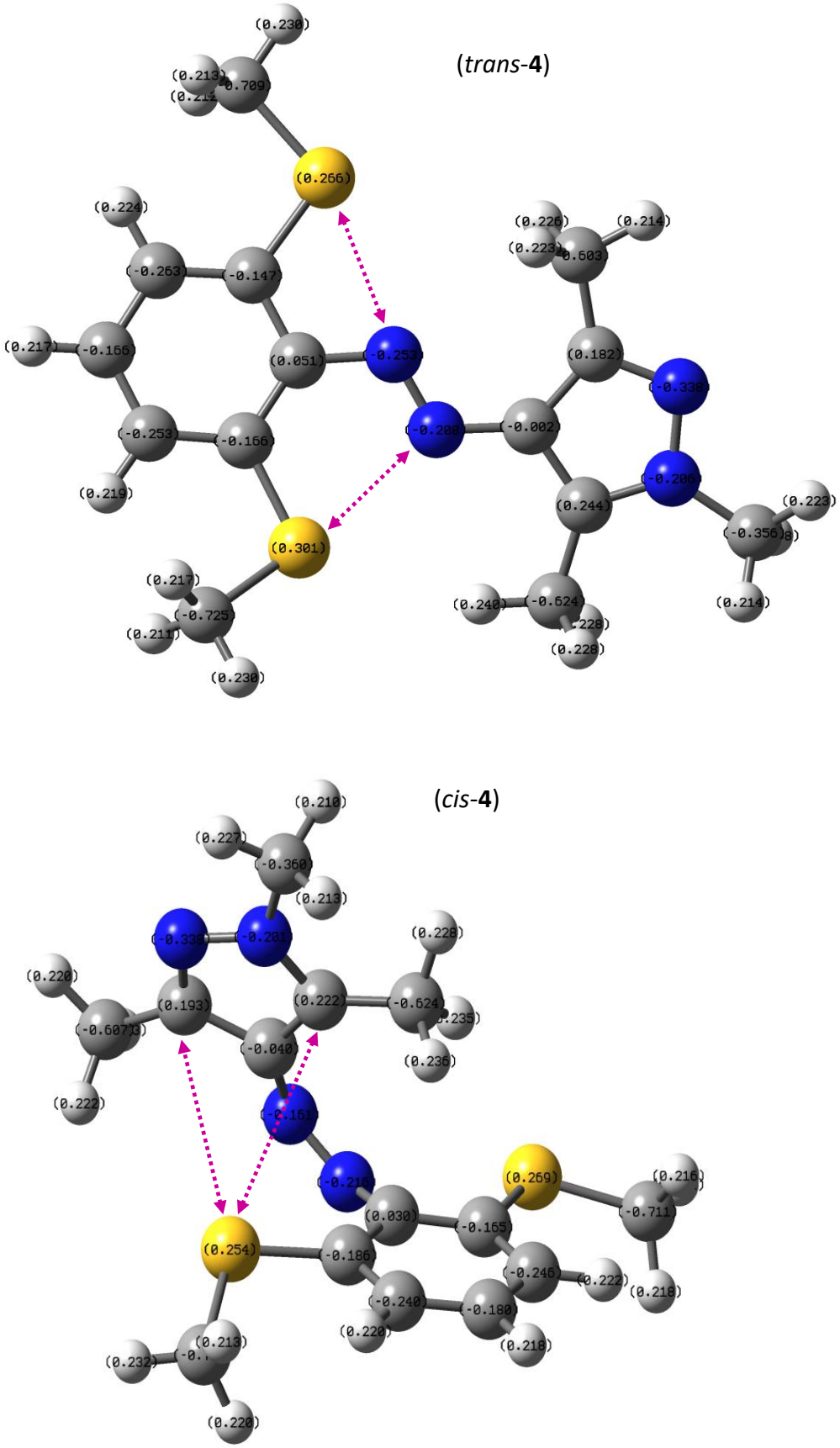
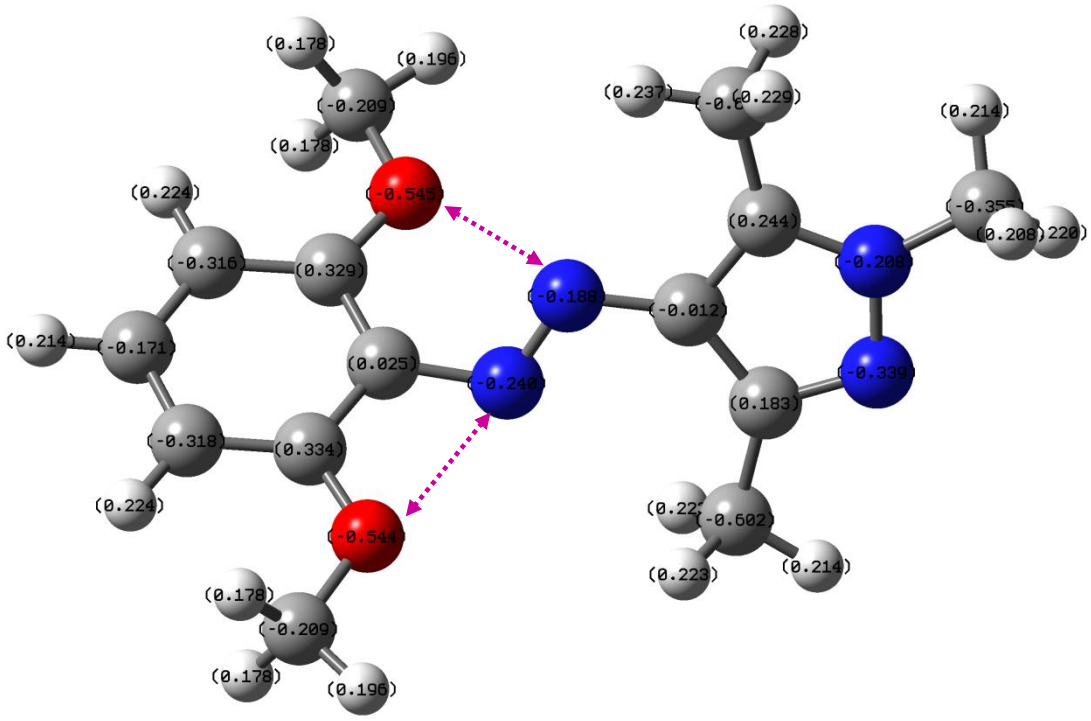


Fig. S5. Atomic charges calculated for minimum-energy geometry of *trans*-**4** and *cis*-**4**. The double headed dotted arrows indicate electrostatic attraction between positively charge S atom and negatively charged N atom in *trans*-**4** (top) leading to more planar structure than the *trans*-**2a**, and electrostatic repulsion between S atom and positively charged C atoms of pyrazole in *cis*-**4** (bottom) leading to its less thermal stable than most AAPZs.

(*trans*-**2a**)



(*cis*-**2a**)

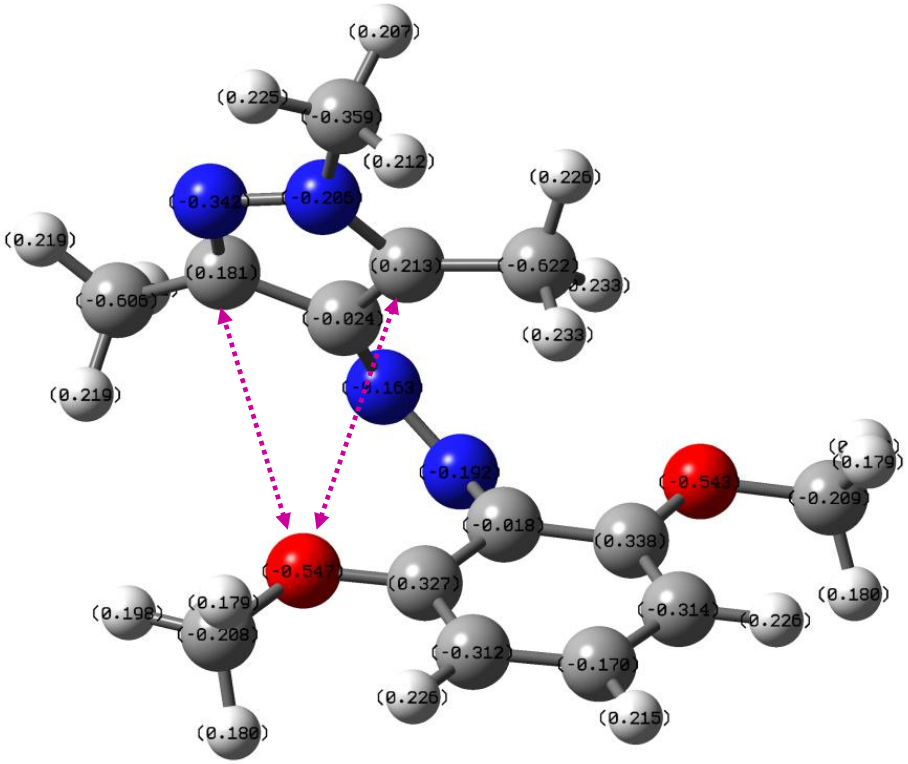


Fig. S6. Atomic charges calculated for minimum-energy geometry of *trans*-**2a** and *cis*-**2a**. The double headed dotted arrows indicate electrostatic repulsion between negatively charge O atom and negatively charged N atom in *trans*-**2a** (top) leading to more non-planar structure than the *trans*-**4**, and electrostatic attraction between O atom and positively charged C atoms of pyrazole in *cis*-**2a** (bottom) leading to its high thermal stable.

Synthesis:

General methods

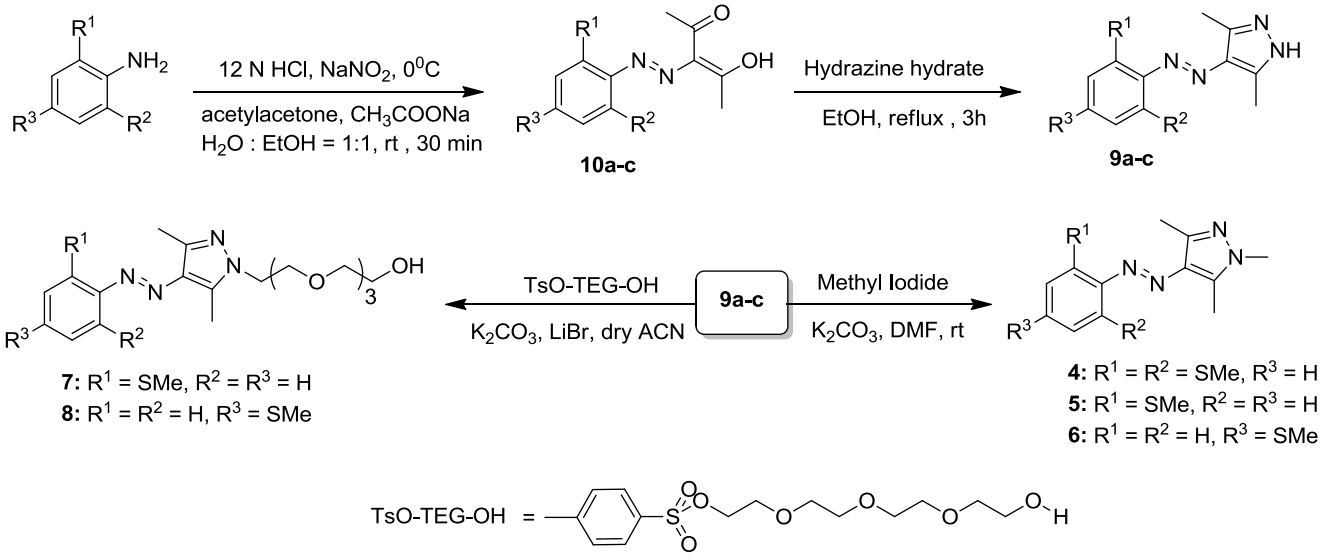
Reagents were purchased from Alfa Aesar, Sigma-Aldrich, TCI, Avra or Spectrochem and used without further purification. Reactions requiring anhydrous conditions were conducted in oven-dried glassware under an inert atmosphere (argon). Solvents were dried according to conventional methods before use. All reactions were monitored by thin-layer chromatography (TLC) using Merck silica gel 60 F254 plates (0.25 mm). Column chromatography was performed using silica gel (100 – 200 mesh particle size) treated with a solvent system specified in the individual procedures. Solvents were removed by rotary evaporator and the compounds further dried using high vacuum pumps.

^{1}H and ^{13}C NMR were recorded on a Bruker 300 MHz spectrometer. Chemical shifts (δ) are quoted in ppm (parts per million). Low resolution ESI mass spectra were recorded by the Department of Chemistry Mass Spectroscopy Service using ESI-MS (waters).

Abbreviations: DMSO: dimethyl sulfoxide, DCM: dichloromethane, ACN: acetonitrile, rt: room temperature.

Scheme S1. General synthetic route

The *thio*-substituted-arylazopyrazoles **4-8** were synthesized as outlined in the scheme below.



Experimental:

General procedure of synthesis of arylazoacetylacetone derivatives (10a-c): To a ice-cold solution of a suitably substituted aniline derivative[1-2] (1.0 mmol) in AcOH (2 mL) containing HCl (12M, 0.5 mL) was added drop-wise a 2 mL aqueous solution of $NaNO_2$ (1.2 mmol). After stirring the solution for 1 h, it was added drop-wise to a solution of pentan-2,4-dione (1.3 mmol) and NaOAc (3.0 mmol) in 50% aqueous EtOH (4 mL). The reaction was stirred for another 30 min, the yellow precipitate obtained was filtered and washed with 50% aqueous ethanol to afford a yellow solid.

(*E*)-3-((*E*)-(2,6-bis(methylthio)phenyl)diazenyl)-4-hydroxypent-3-en-2-one (10a): Yield 77% as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.14 (brs, 1H), 7.19 – 7.10 (m, 3H), 2.56 (s, 3H), 2.46 (s, 3H), 2.38 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 197.68, 137.44, 133.32, 131.00, 126.29, 125.85, 31.68, 27.62, 17.46.

(*E*)-3-((*E*)-(2-(methylthio)phenyl)diazenyl)-4-hydroxypent-3-en-2-one (10b)[3]: Yield 79% as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.00 (brs, 1H), 7.71 (dd, *J* = 8.2 Hz, 1.1 Hz, 1H), 7.43 (dd, *J* = 7.8Hz, 1.2Hz, 1H), 7.32 - 7.26 (m, 1H), 7.12 -7.06 (m, 1H), 2.57 (s, 3H), 2.45 (s, 3H), 2.40 (s, 3H).

(*E*)-3-((*E*)-(4-(methylthio)phenyl)diazenyl)-4-hydroxypent-3-en-2-one (10c): Yield 73% as a yellow solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 14.82 (brs, 1H), 7.38 – 7.28 (m, 4H), 2.61 (s, 3H), 2.52 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 197.94, 197.00, 139.09, 136.13, 133.12, 127.97, 116.80, 31.67, 26.65, 16.28.

General procedure of synthesis of arylazopyrazole derivatives (9a-c): Synthesis of **9a** is described as a representative case. A mixture of **10a** (0.30 mmol) and hydrazine-hydrate (0.30 mmol) in ethanol (3 mL) was refluxed for 3 h. After completion of the reaction, as judged by TLC analysis, it was cooled to room temperature, concentrated on a rotary evaporator and extracted with ethyl acetate. The combined organic layer was washed with water and brine, dried with anhyd. Na_2SO_4, filtered and concentrated *in vacuo*. The crude product was subjected to a flash silica gel column chromatography to afford pure **9a**.

(*E*)-1-(2,6-bis(methylthio)phenyl)-2-(3,5-dimethyl-1*H*-pyrazol-4-yl)diazene (9a): Yield 83% as a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.19 (t, *J* = 7.9 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 2H), 2.58 (s, 3H), 2.56 (s, 3H), 2.37 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.61, 141.73, 136.69, 135.10, 128.38, 120.16, 29.72, 15.95, 12.64; LRMS (ESI): *m/z* calcd for $C_{13}H_{17}N_4S_2$: 293.0894 $[M+1]^+$; found: 293.0749.

(*E*)-1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-(2-(methylthio)phenyl)diazene (9b): Yield 80% yield as a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.22 (d, *J* = 1.2 Hz, 1H), 7.12 - 7.07 (m, 1H), 5.31 (brs, 1H), 2.57 (s, 6H), 2.43 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.27, 141.80, 139.72, 130.19, 124.36, 124.16, 115.55, 29.71, 14.46, 12.33; LRMS (ESI): m/z calcd for $C_{12}H_{15}N_4S$: 247.1017 $[M+1]^+$; found: 247.1021.

(*E*)-1-(3,5-dimethyl-1*H*-pyrazol-4-yl)-2-(4-(methylthio)phenyl)diazene (9c): Yield 81% as a yellow brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.80 (brs, 1H), 7.75 (dd, *J* = 7.1 Hz, 1.6 Hz, 2H), 7.32 (dd, *J* = 6.9 Hz, 1.5 Hz, 2H), 2.62 (s, 6H), 2.56 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.00, 141.34, 140.57, 134.66, 126.27, 122.33, 15.62, 12.18; LRMS (ESI): m/z calcd for $C_{12}H_{15}N_4S$: 247.1017 $[M+1]^+$; found: 247.0803.

General Procedure of Synthesis of arylazopyrazoles 4-6: Synthesis of **4** from **9a** is described as a representative case. A mixture of **9a** (0.10 mmol) and K_2CO_3 (0.20 mmol) in DMF (2 mL) was stirred at 40^{0}C for 20 min. Then iodomethane (0.12 mmol) was added to the reaction and it was stirred for 12 h at room temperature. The reaction mixture was diluted with ethyl acetate, and the organic layer was washed with H_2O and brine, dried over anhydrous Na_2SO_4, and filtered. The filtrate was concentrated under reduced pressure, and the crude produce was purified by column chromatography on silica gel to yield **4** as a brown-red solid.

(*E*)-1-(2,6-bis(methylthio)phenyl)-2-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazene (4): Yield 87% as a brown red solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.17 (dd, *J* = 8.4 Hz, 8.4 Hz, 1H), 7.00 (d, *J* = 7.8 Hz, 2H), 3.72 (s, 3H), 2.57 (s, 3H), 2.49 (s, 3H), 2.36 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 145.66, 142.57, 139.15, 136.39, 135.50, 128.22, 120.16, 36.06, 15.96, 14.30, 10.44; LRMS (ESI): m/z calcd for $C_{14}H_{19}N_4S_2$: 307.1051 $[M+1]^+$; found:307.0948.

(*E*)-1-(2-(methylthio)phenyl)-2-(1,3,5-trimethyl-1*H*-pyrazol-4-yl)diazene (5): Yield 85% as a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.68 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 7.38 -7.33 (m, 1H), 7.30 (d, *J* = 1.5 Hz, 1H), 7.21 -7.15 (m, 1H), 3.82 (s, 3H), 2.63 (s, 3H), 2.56 (s, 3H), 2.52 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.34, 142.94, 139.38, 138.89, 135.78, 129.86, 124.34, 124.08, 115.41, 36.07, 14.46, 14.03, 10.18; LRMS (ESI): m/z calcd for $C_{13}H_{17}N_4S$: 261.1173 $[M+1]^+$; found: 261.1170.

(*E*)-1,3,5-trimethyl-4-((4-(methylthio)phenyl)diazenyl)-1*H*-pyrazole (6): Yield 91% as a brown solid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H), 2.60 (s, 3H), 2.56 (s, 3H), 2.53 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.11, 142.38, 140.26, 138.52, 135.06, 126.36, 122.24, 35.98, 15.68, 13.82, 9.97; LRMS (ESI): m/z calcd for $C_{13}H_{17}N_4S$: 261.1173 $[M+1]^+$; found: 261.1170.

General procedure of synthesis of water soluble arylazopyrazole derivatives 7 and 8: Synthesis of **7** is described as representative. To a mixture of arylazopyrazole **9b** (0.13 mmol) and K_2CO_3 (0.65 mmol) in dry ACN (3 mL), TsO-TEG-OH[4] (0.14 mmol) and LiBr (catalytic amount) were added. After refluxing the reaction mixture for 24 h, it was concentrated under reduced pressure, and the residue obtained was diluted with EtOAc. The

organic layer was washed with water and brine, dried over Na_2SO_4, filtered and concentrated. The crude organic content was subjected to silica gel column chromatography with 2% methanol in DCM to yield **7** as red liquid.

(*E*)-2-(2-(2-(2-(3,5-dimethyl-4-((2-(methylthio)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethoxy)ethoxy)ethoxy)ethanol (7): Yield 54% as a red liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.67 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.37 - 7.32 (m, 1H), 7.28 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.20 - 7.14 (m, 1H), 4.24 (t, *J* = 5.4 Hz, 2H), 3.89 (t, *J* = 5.4 Hz, 2H), 3.72 -3.69 (m, 2H), 3.64 - 3.56 (m,10H), 2.65 (s, 3H), 2.56 (s, 3H), 2.51 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 149.38, 143.00, 140.55, 139.35, 135.65, 129.82, 124.33, 124.07, 115.40, 72.50, 70.71, 70.59, 70.50, 70.29, 69.86, 61.67, 49.04, 14.44, 14.31, 10.08; LRMS (ESI): m/z calcd for $C_{20}H_{31}N_4O4S$: 423.2066 $[M+1]^+$; found: 423.1953.

(*E*)-2-(2-(2-(2-(3,5-dimethyl-4-((4-(methylthio)phenyl)diazenyl)-1*H*-pyrazol-1-yl)ethoxy)ethoxy)ethoxy)ethanol (8): Yield 60% as a red liquid; ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.69 (d, *J* = 6.9 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.55 (t, *J* = 5.2 Hz, 1H), 4.20 (t, *J* = 5.1 Hz, 2H), 3.76 (t, *J* = 5.2 Hz, 2H), 3.51 - 3.43 (m, 12H), 2.57 (s, 3H), 2.54 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$): δ 151.10, 142.49, 140.28, 140.15, 134.90, 126.35, 122.23, 72.51, 70.69, 70.59, 70.51, 70.30, 69.88, 61.67, 49.0, 15.66, 14.06, 9.92; LRMS (ESI): m/z calcd for $C_{20}H_{31}N_4O4S$: 423.2066 $[M+1]^+$; found: 423.1975.

X-ray Crystallography: Crystals of both **4** and **5** were grown by slow evaporation of mixed solvents MeOH and Et_2O.

Compound	**4**	**5**
Identification code	CCDC 2006348	CCDC 2006349
Chemical formula	C14 H18 N4 S2	C13 H16 N4 S
Formula weight	306.44	260.36
Temperature/K	298(2)	298(2)
Radiation	MoK\α (λ = 0.71073)	MoK\α (λ = 0.71073)
Crystal system	orthorhombic	triclinic
Space group	P 21 21 21	P -1
a/Å	6.8868(8)	6.9549(12)
b/Å	14.8106(17)	8.8714(13)
c/Å	15.0914(17)	11.149(2)
α/°	90	80.680(3)
β/°	90	89.072(3)
γ/°	90	84.658(16)
Z	4	2
Volume/Å^3	1539.3(3)	675.9(2)
Crystal density g/cm^3	1.322	1.279
μ/mm^{-1}	0.342	0.228
F(000)	648	276.0
Crystal size/mm^3	0.42 × 0.31 ×0.13	0.44 × 0.30 × 0.12
Reflections collected	24711	10604
Independent reflections	4357	3091
Tmin,Tmax	0.881,0.957	0.921,0.973
Data completeness	1.67/0.95	0.986
Theta(max)	30.203	27.611
R(reflections)	0.0339(4065)	0.0726(2561)
wR2(reflections)	0.1148(4357)	0.2251(3091)
S	1.001	1.065

Absorption spectra and photoswitching:

UV-Vis absorbance spectra and thermal relaxation data were collected on a Shimadzu UV-1900 spectrophotometer or a Pre-configured fiber-optic UV–Vis spectrophotometer (AvaSpec-ULS2048L-USB2-UA-RS) coupled to a temperature controlled cuvette holder was used. Spectra were acquired in a 1 cm path length quartz cuvette. At an angle of 90° to the measuring beam, the samples were irradiated with LEDs emitting at 365 nm, 400 nm, 475 nm, 450 nm or 530 nm until no further decrease in absorbance in case of *trans*-to-*cis* and increase in absorbance for *cis*-to-*trans* was observed. Various solvents such as DMSO, acetonitrile, ethanol and toluene were used for the photoswitching experiments. However, DMSO solvent was chosen for the following studies.

(i) Determination of molar extinction coefficient: To know accurate samples concentrations, ^{1}H NMR spectra of the compounds (**4-6**) in DMSO-d_6 were recorded with a known concentration of 1,2-dichloroethane as the internal standard. These samples with known concentrations were then used to record the UV/Vis absorption spectra to calculate the molar extinction coefficients.

(ii) Determination of *cis* and *trans* % in PSSs followed by the determination of pure *cis* absorption spectra:
To determine the compositions of photostationary states (PSSs) for the *trans-cis* and the *cis-trans* isomerisations ^{1}H-NMR spectroscopy was employed. Solutions of arylazopyrazoles **4-6** (ca. 200 µM - 300 µM) in DMSO-d_6 were prepared and ^{1}H NMR spectra were acquired in the dark state (Fig. 3 and S7-S9). These samples were irradiated by 400 nm LED, 457 nm LED or 530 nm LED light for ca. 10 minutes and spectra of the achieved PSSs were recorded immediately. Signal integration of some distinct aromatic protons or the methyl group led to determine the percentages of *cis* and *trans* isomers. UV-Vis absorption spectra of these solutions were acquired after irradiating them under identical irradiation conditions. These two experiments led to determine the absorption spectra of PSSs and their compositions in terms of the percentages of *cis* and *trans* isomers. Extrapolated spectra of *cis* isomers were calculated from spectra of pure *trans*-isomer and PSS with known compositions.

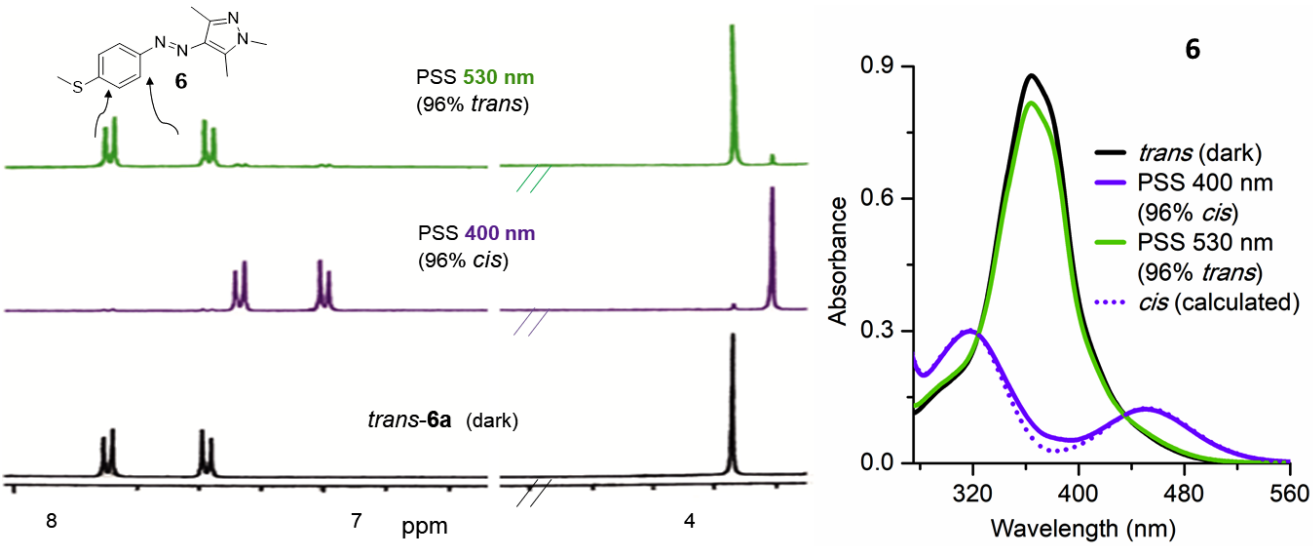


Fig. S7. ^{1}H NMR spectra of dark adapted state and PSSs of **6** in DMSO-d_6.

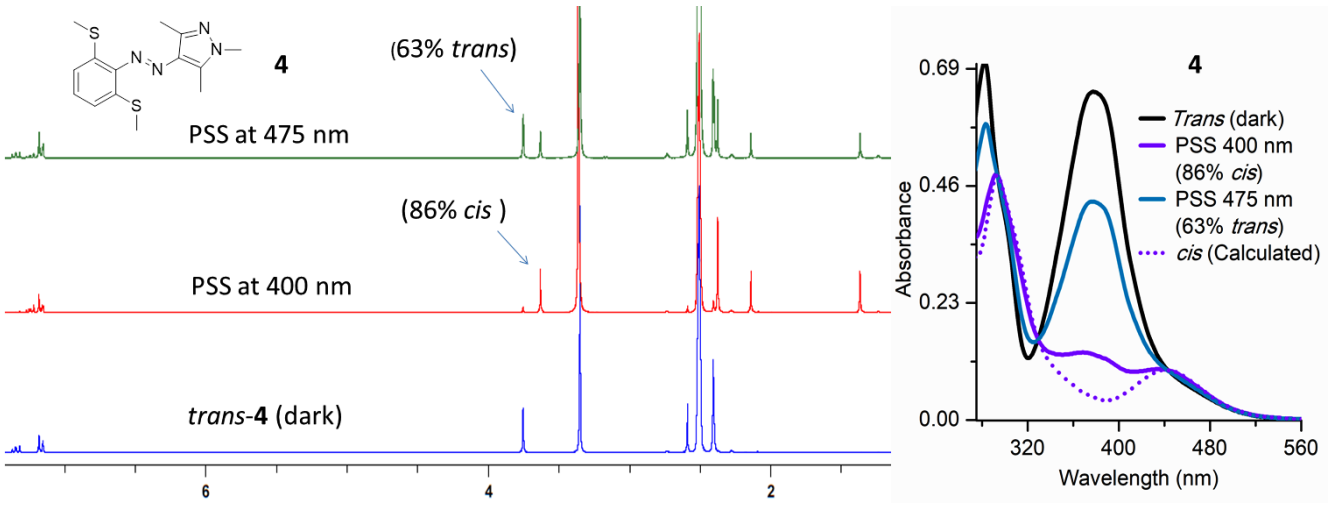


Fig. S8. ^{1}H NMR spectra of dark adapted state and PSSs of **4** in DMSO-d_6.

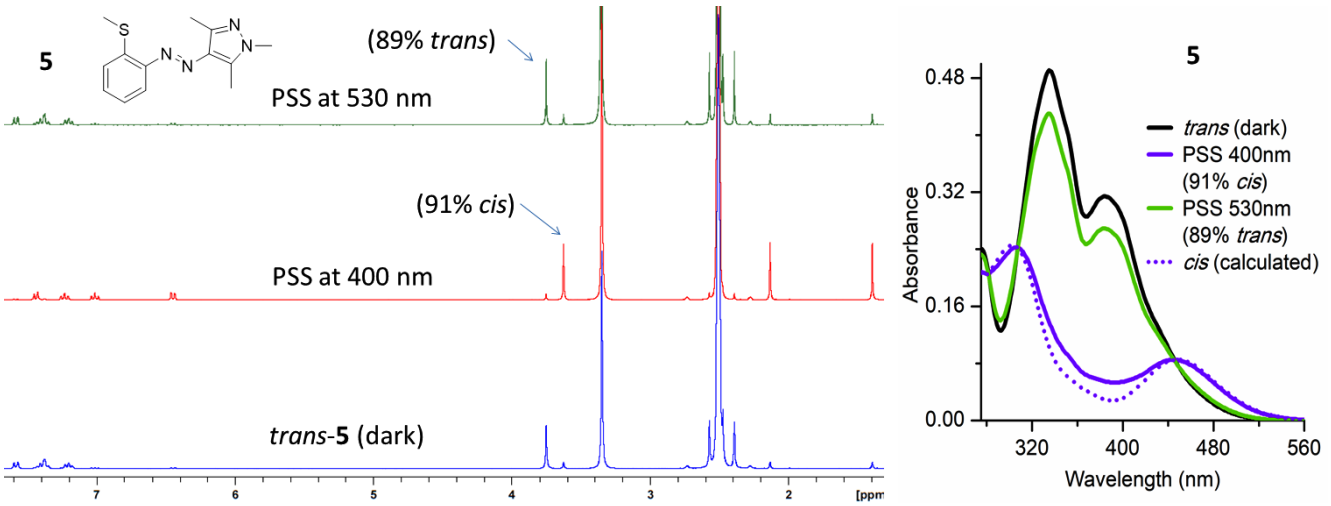


Fig. S9. ^{1}H NMR spectra of dark adapted state and PSSs of **5** in DMSO-d_6.

(iii) Photoswitching in different organic solvents:

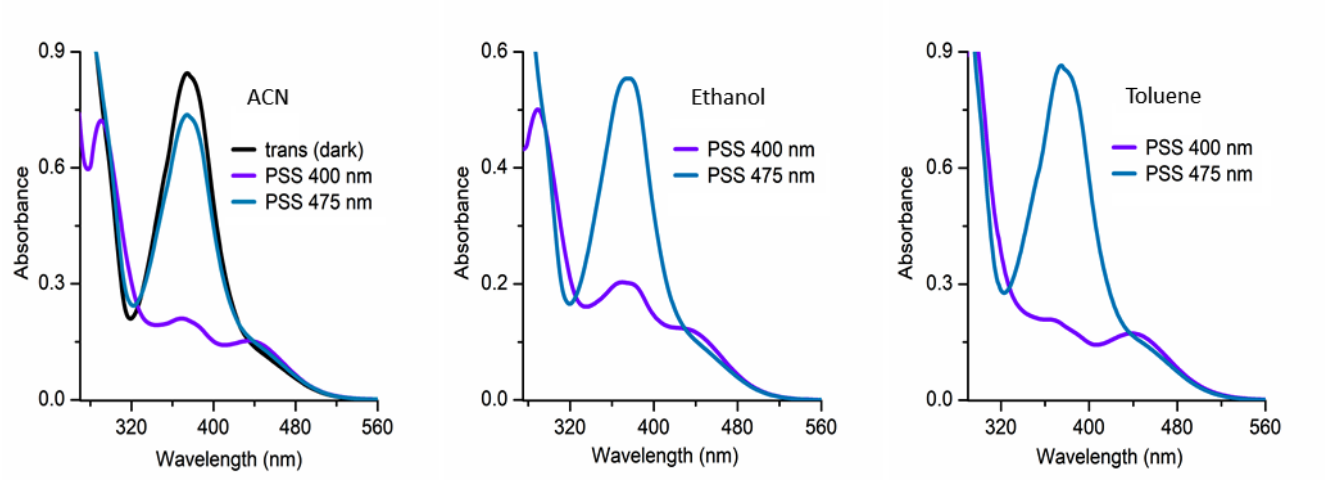


Fig. S10. Photoswitching of **4** in acetonitrile, ethanol and toluene.

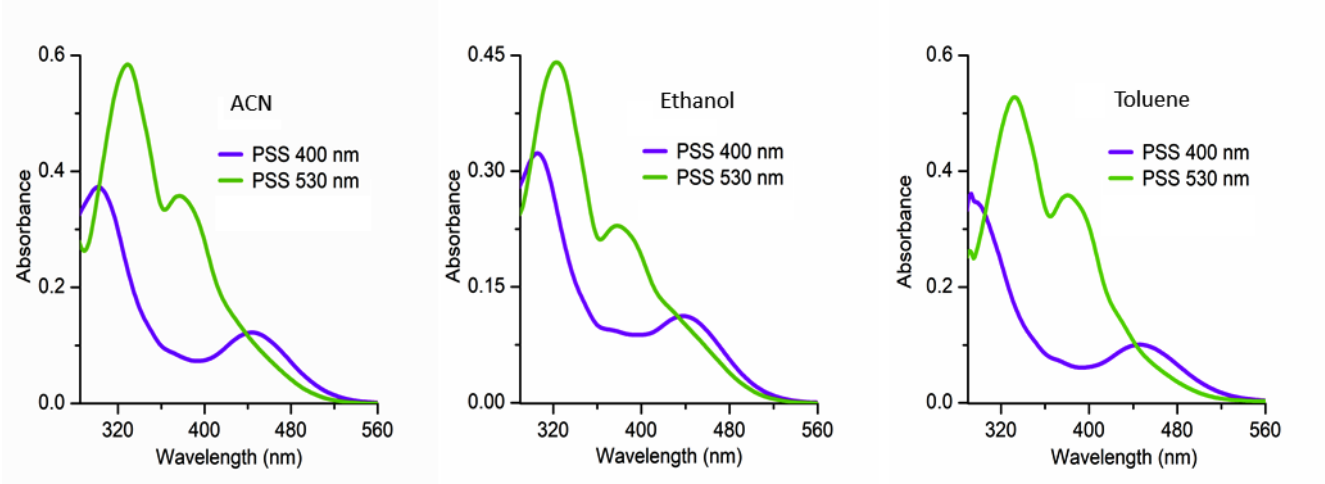


Fig. S11. Photoswitching of **5** in acetonitrile, ethanol and toluene.

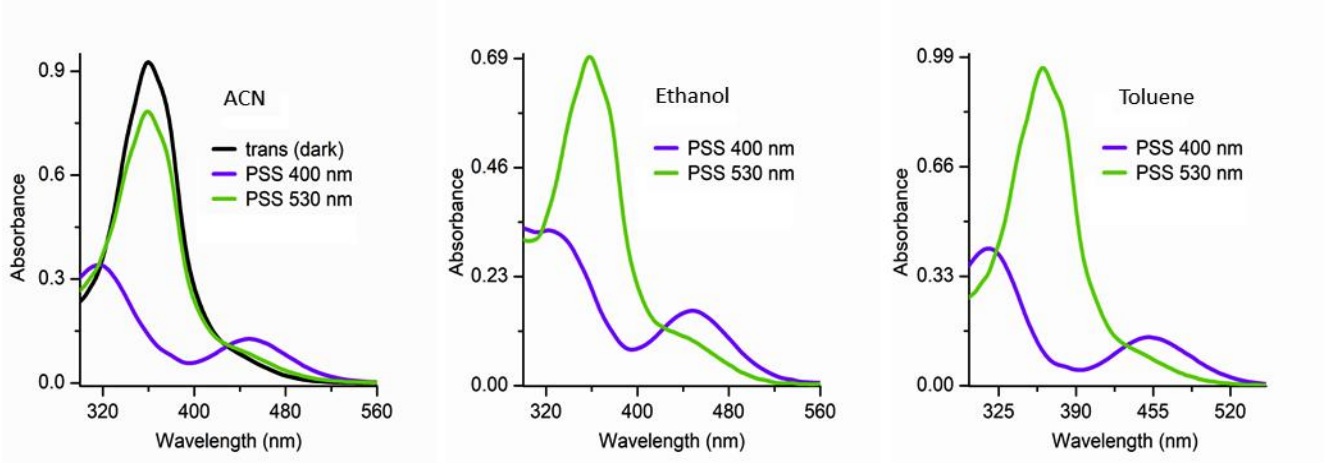


Fig. S12. Photoswitching of **6** in acetonitrile, ethanol and toluene.

(iv) Determination of thermal half-lives of *cis*-isomers: This was done in two ways: i) by acquiring UV-Vis absorption spectra of irradiated solutions at a particular time interval (4 h or 6 h), and ii) by recording absorbance at 395 nm as a function of time after irradiating samples at 400 nm in DMSO solvent at 27^{0}C. The resulting curves obtained from both experiments were nicely fitted with mono-exponential functions, resulting in *cis* half-lives of **4**-**8**.

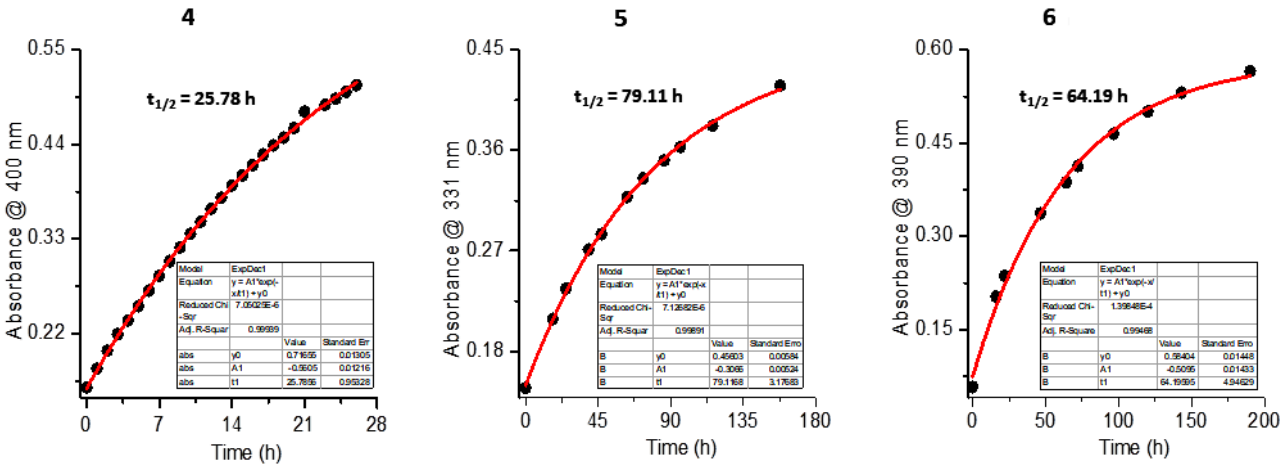
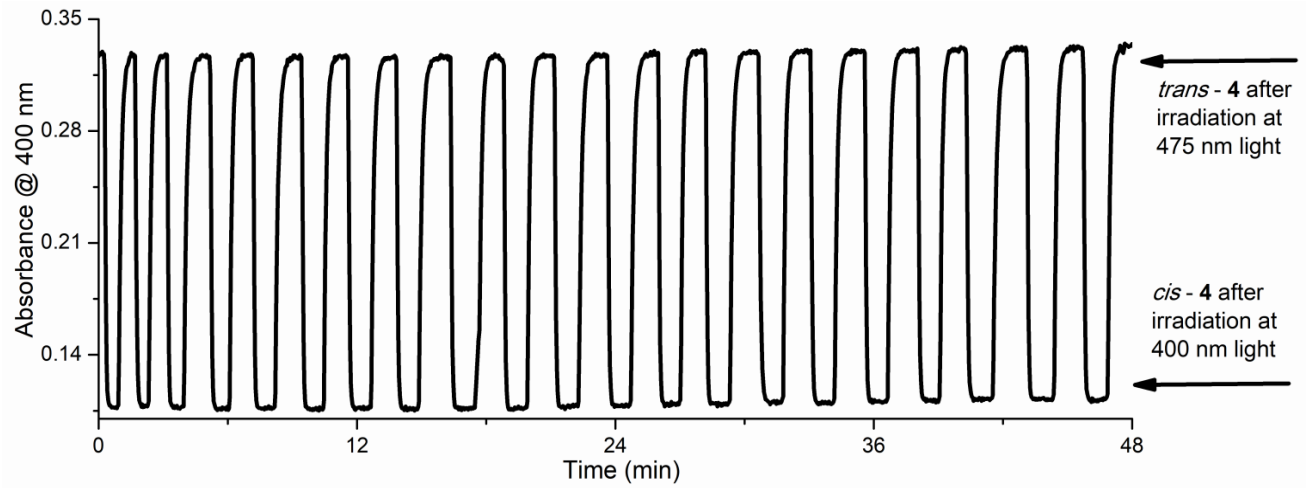


Fig. S13. Thermal *cis*-to-*trans* relaxation rates for **4**, **5** and **6** at 27^{o}C in DMSO solvent.

(v) Photobleaching: To check the photostability, solutions of switches **4**-**6** in DMSO were exposed to 400 nm and 475 nm /530 nm light alternately. After many cycles of photolysis, considerable photobleaching was not found for any of these switches (Fig. S14).

Repeated cycles of photoswitching:



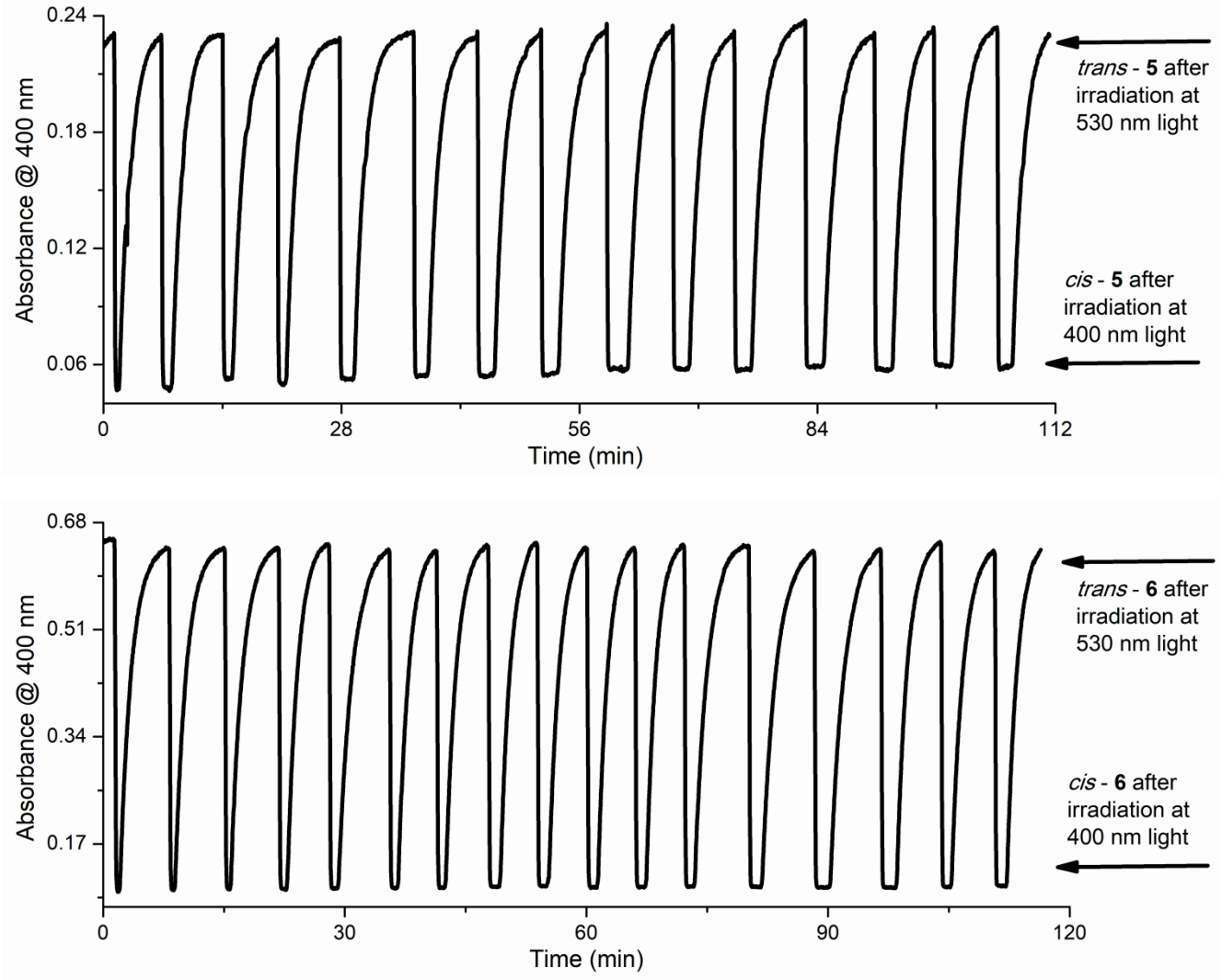


Fig. S14. Multiple rounds of photoswitching of **4-6** in DMSO.

Photoswitching and kinetic studies on AAPZs 7 and 8:

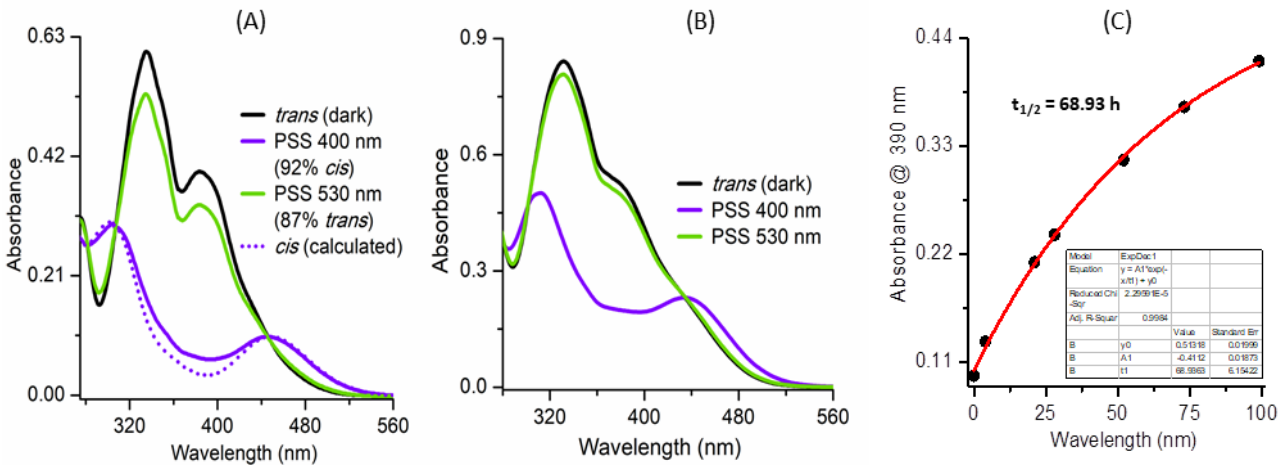


Fig. S15. Photoswitching of **7** in DMSO (A) and phosphate buffer (B). Thermal *cis*-to-*trans* relaxation rates in DMSO at 31°C (C).

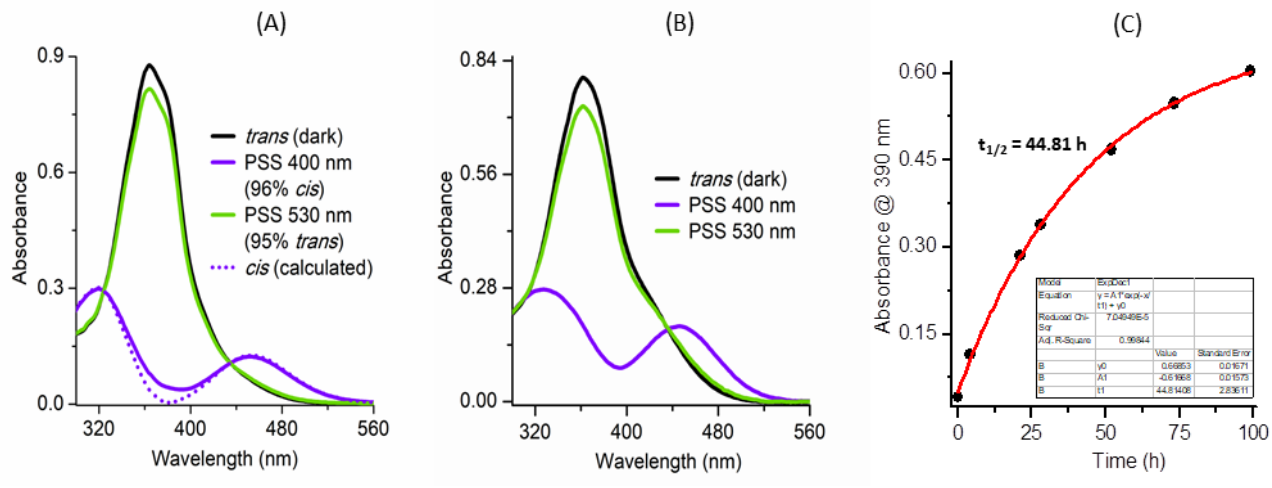


Fig. S16. Photoswitching of **8** in DMSO (A) and in phosphate buffer (B). Thermal *cis*-to-*trans* relaxation rates in DMSO at 31°C (C).

Glutathione stability: A 50 uM solution of trans-**7/-8** in 100 mM sodium phosphate buffer, (pH 7.4) was mixed with 0.25M glutathione to give a final concentration of 10 mM reduced glutathione (GSH). To suppress the GSH self-oxidation, the resulting solution was supplemented with 5 mM TCEP. During the incubation period of 12 h at 31°C, UV-Vis absorption spectra were recorded every 4 h interval in a Shimadzu uv-1900 spectrophotometer (Fig. S17). Similarly, *cis*-**8** was incubated with 10 mM GSH for 2 h, and absorption spectrum of the mixed solution was collected every 1 h interval (Fig. 3B). No reduction of the absorption intensity was noticed, suggesting that compound **7** and **8** are stable to reduction by glutathione. Finally, multiple rounds of photoswitching were tested by alternating irradiation of these solutions with violet and green. Photoswitching behaviour of **7**/**8** remained unchanged after GSH treatment as shown in Fig. S17.

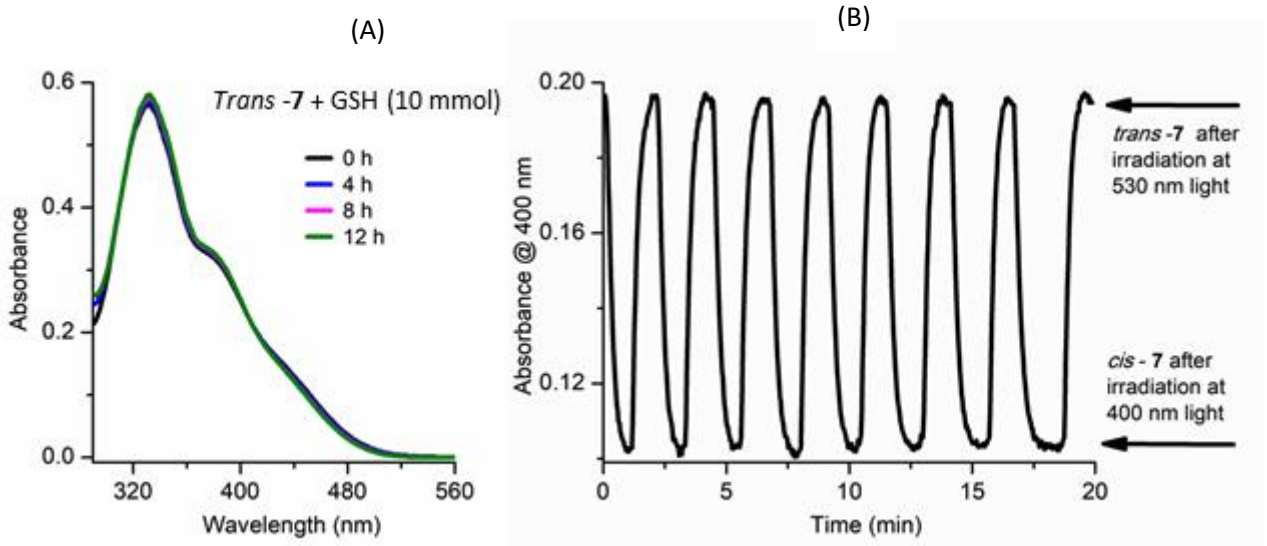


Fig. S17. UV-vis absorption scans of *trans*-**7** (A) incubated with 10 mM GSH and TCEP (5 mmol) in phosphate buffer (pH 7.4) at 31°C; spectra were acquired at 4h intervals over a period of 12 h. After this, multiple rounds of photoswitching were carried out upon alternating exposure to 400 nm and 530 nm light for *trans*-**7** (B).

^{1}H and ^{13}C NMR spectra of all compounds:

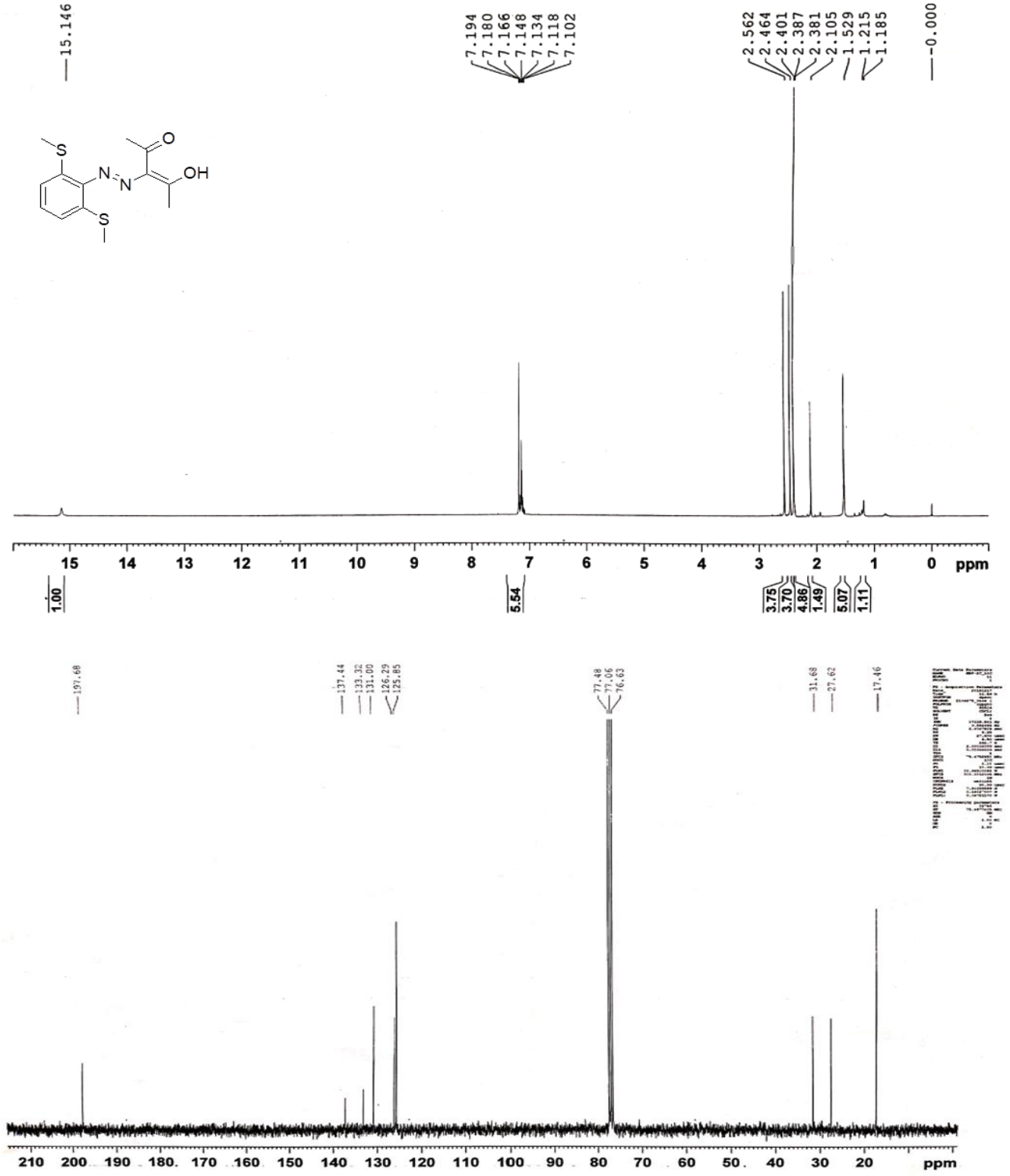


Fig. S18. ^{1}H and ^{13}C NMR spectra of (*E*)-3-((*E*)-(2,6-bis(methylthio)phenyl)diazenyl)-4-hydroxypent-3-en-2-one (**10a)** in $CDCl_3$.

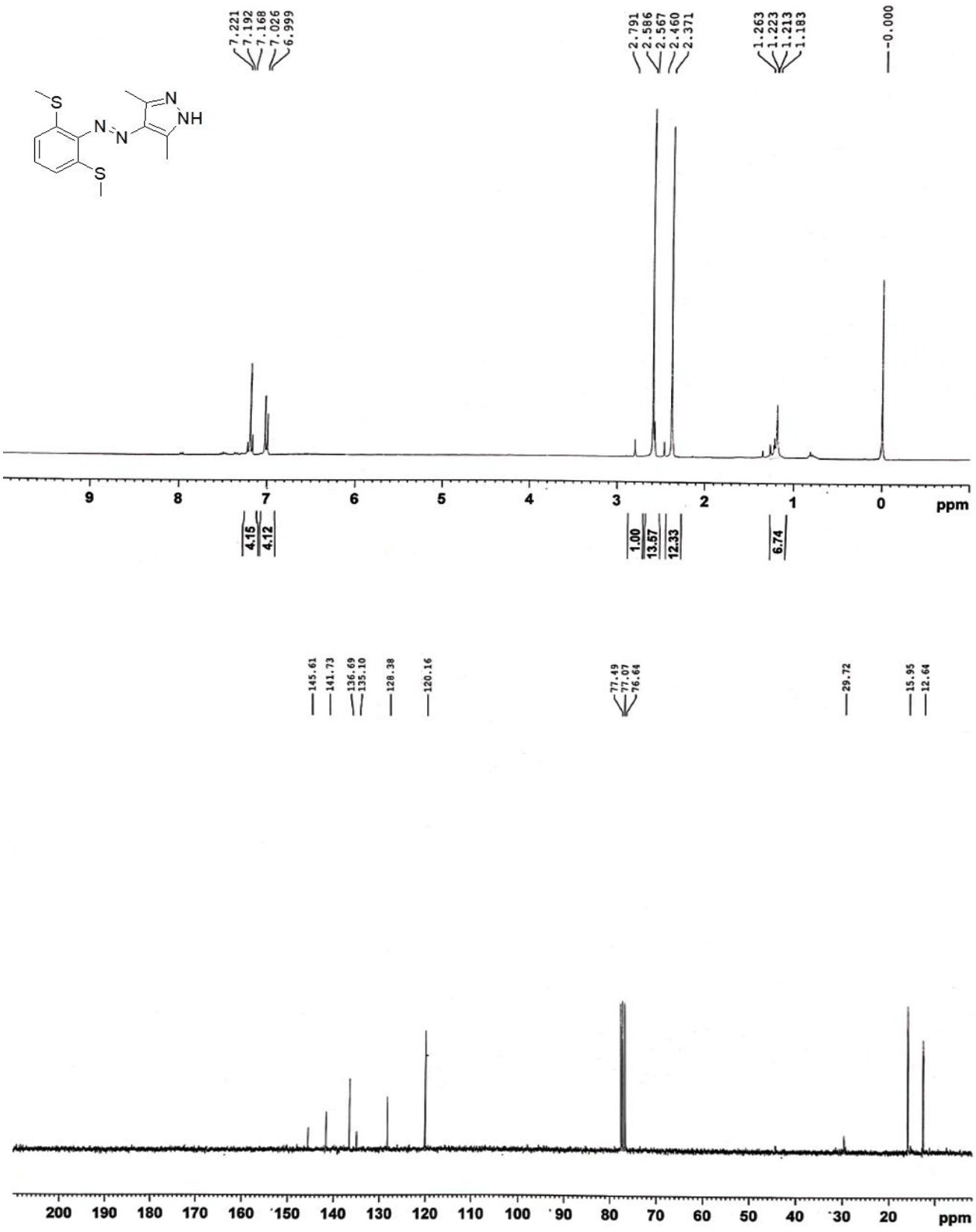


Fig. S19. ^{1}H and ^{13}C NMR spectra of (*E*)-4-((2,6-bis(methylthio)phenyl)diazenyl)-3,5-dimethyl-1H-pyrazole (**9a**) in $CDCl_3$ . .

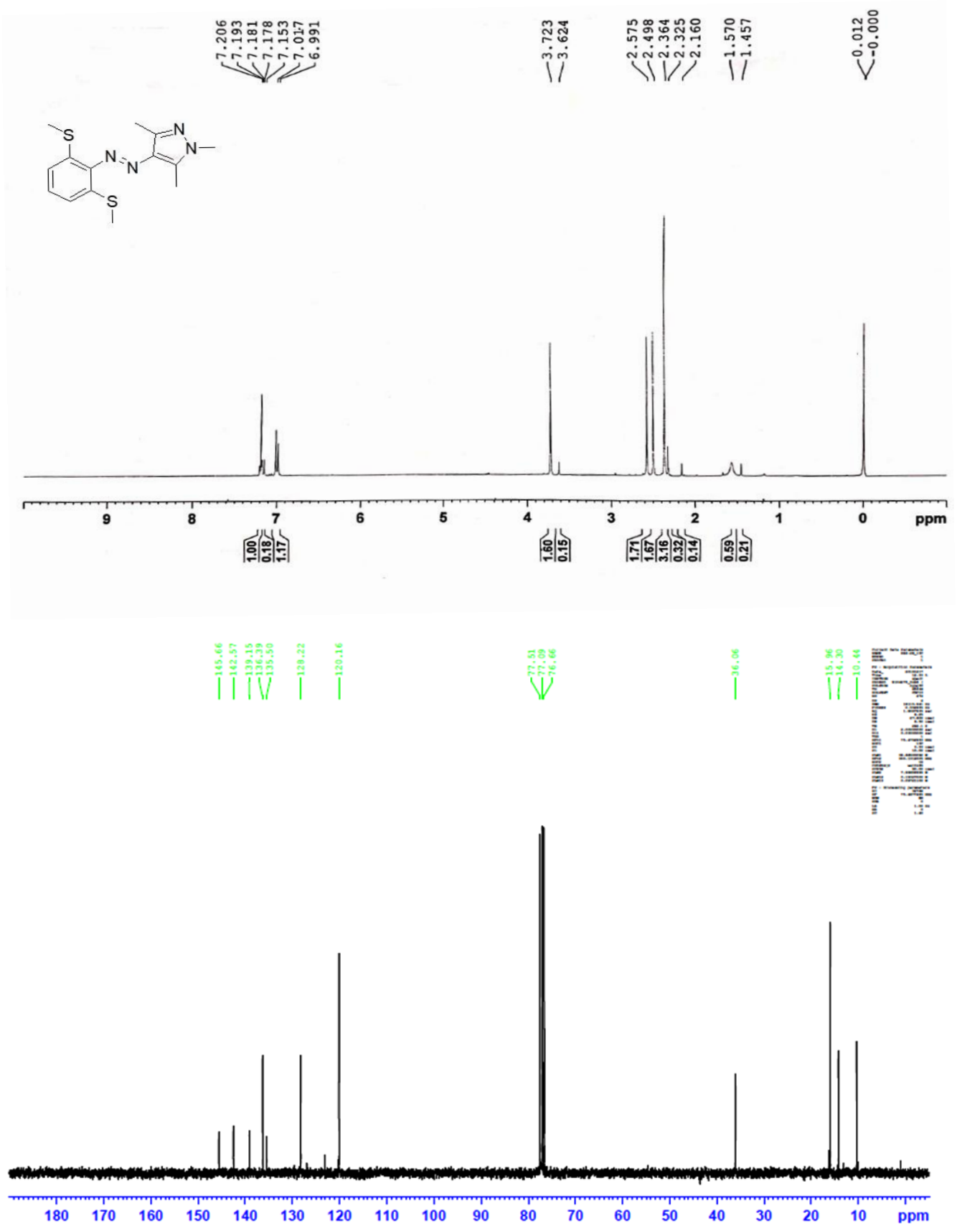


Fig. S20. ^{1}H and ^{13}C NMR spectra of (*E*)-4-((2,6-bis(methylthio)phenyl)diazenyl)-1,3,5-trimethyl-1H-pyrazole (**4**) in $CDCl_3$.

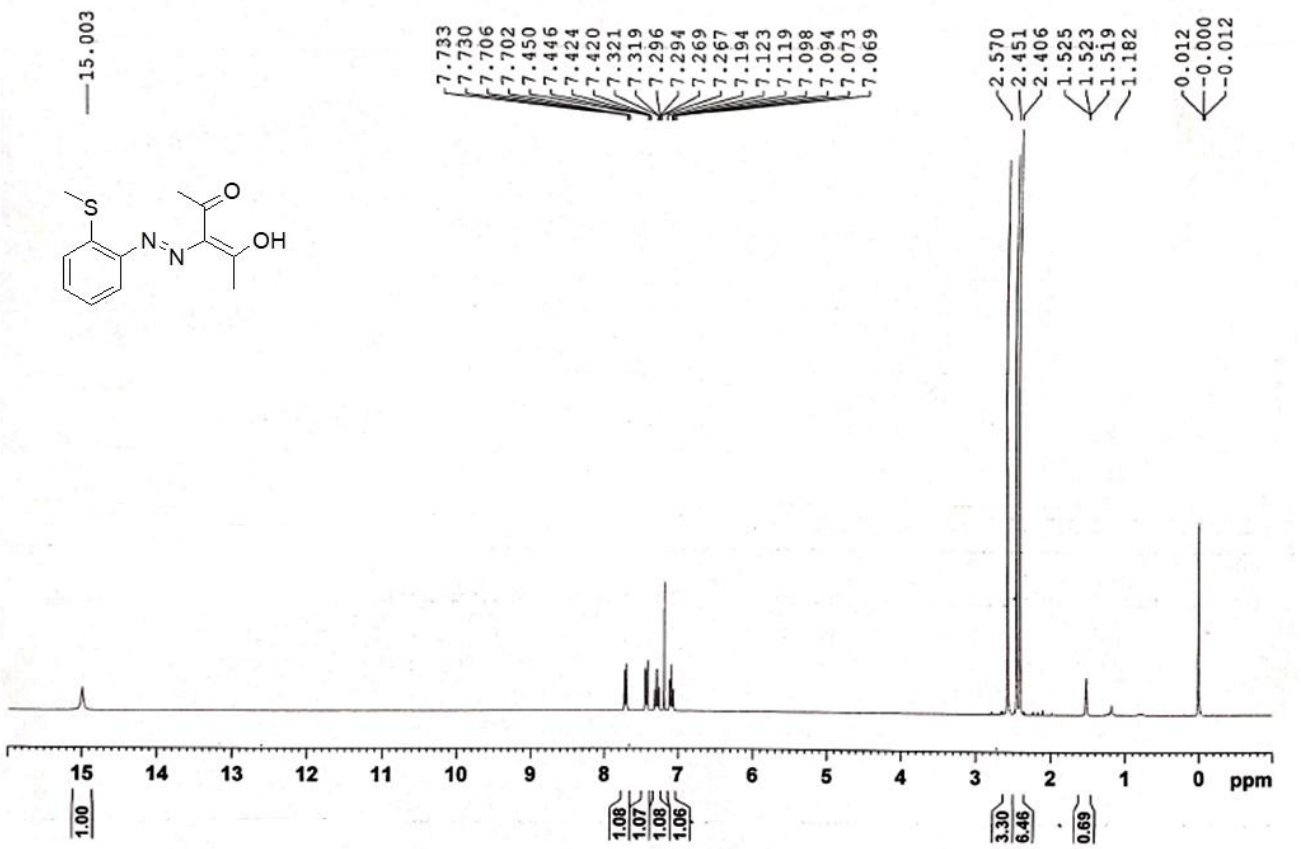


Fig. S21. ^{1}H NMR spectrum of (*E*)-4-hydroxy-3-((*E*)-(2-(methylthio)phenyl)diazenyl)pent-3-en-2-one (**10b**) in $CDCl_3$.

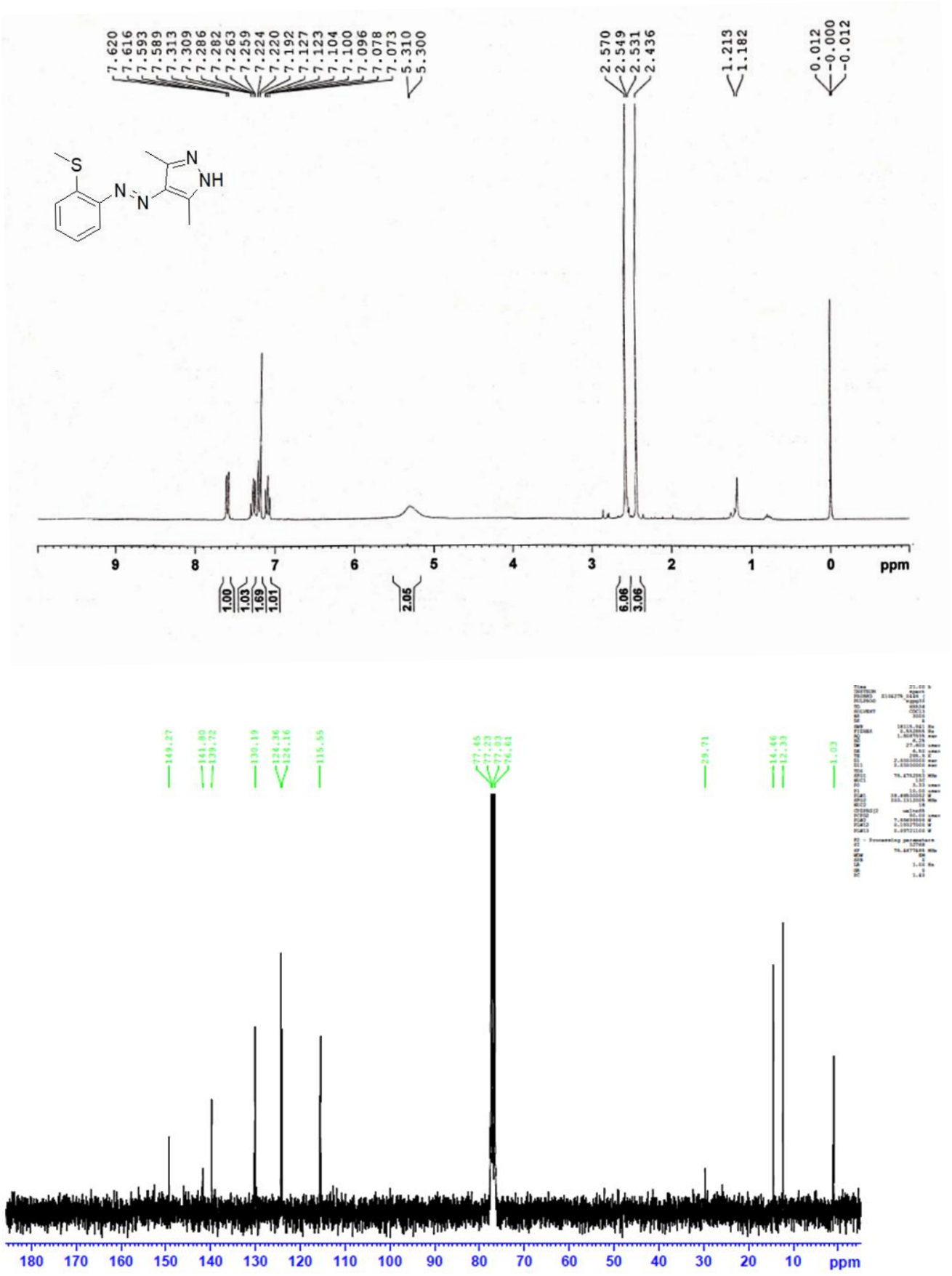


Fig. S22. ^{1}H and ^{13}C NMR spectra of (*E*)-3,5-dimethyl-4-((2-(methylthio)phenyl)diazenyl)-1H-pyrazole (**9b**) in $CDCl_3$.

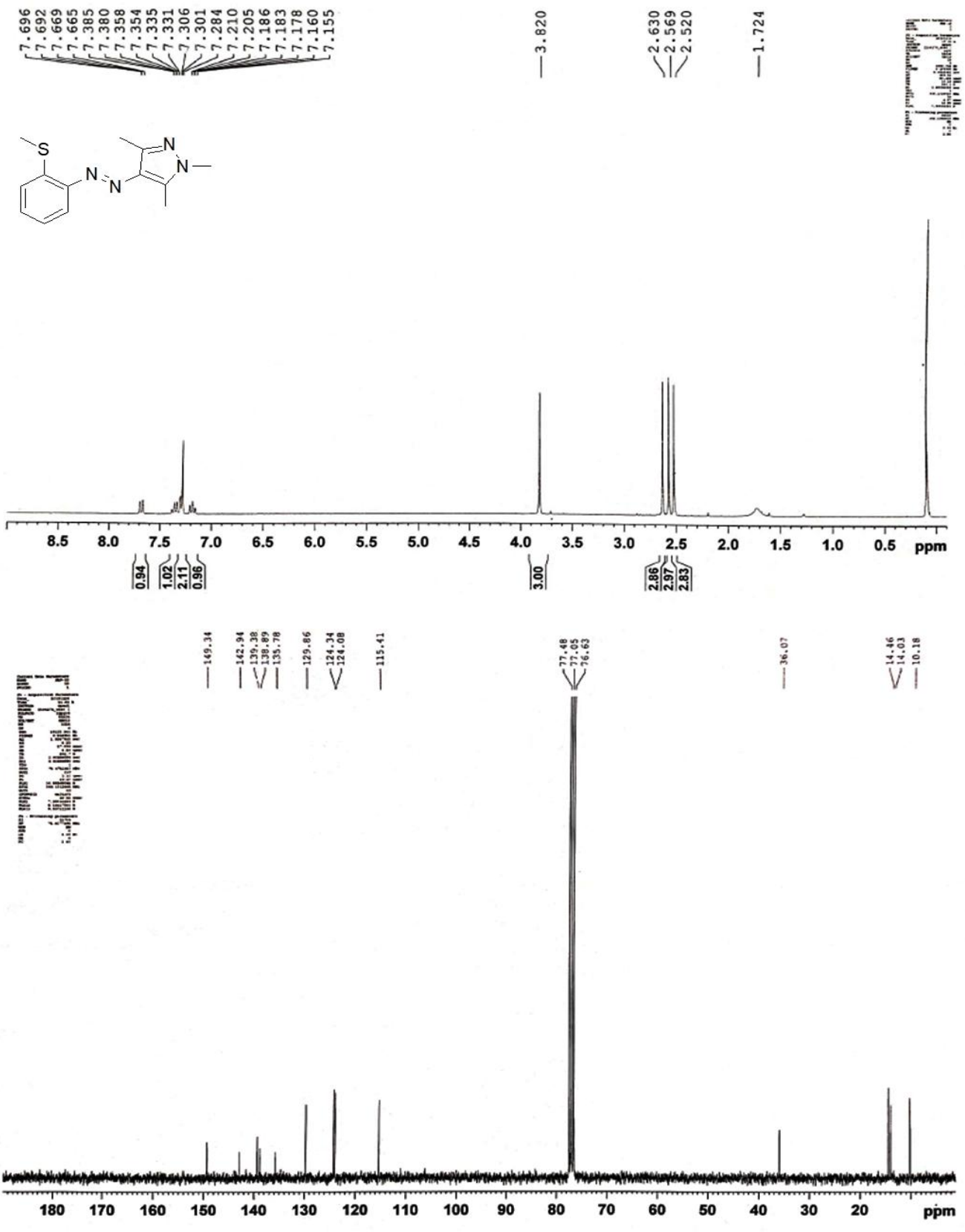


Fig. S23. ^{1}H and ^{13}C NMR spectra of (*E*)-1,3,5-trimethyl-4-((2-(methylthio)phenyl)diazenyl)-1H-pyrazole (**5**) in $CDCl_3$.

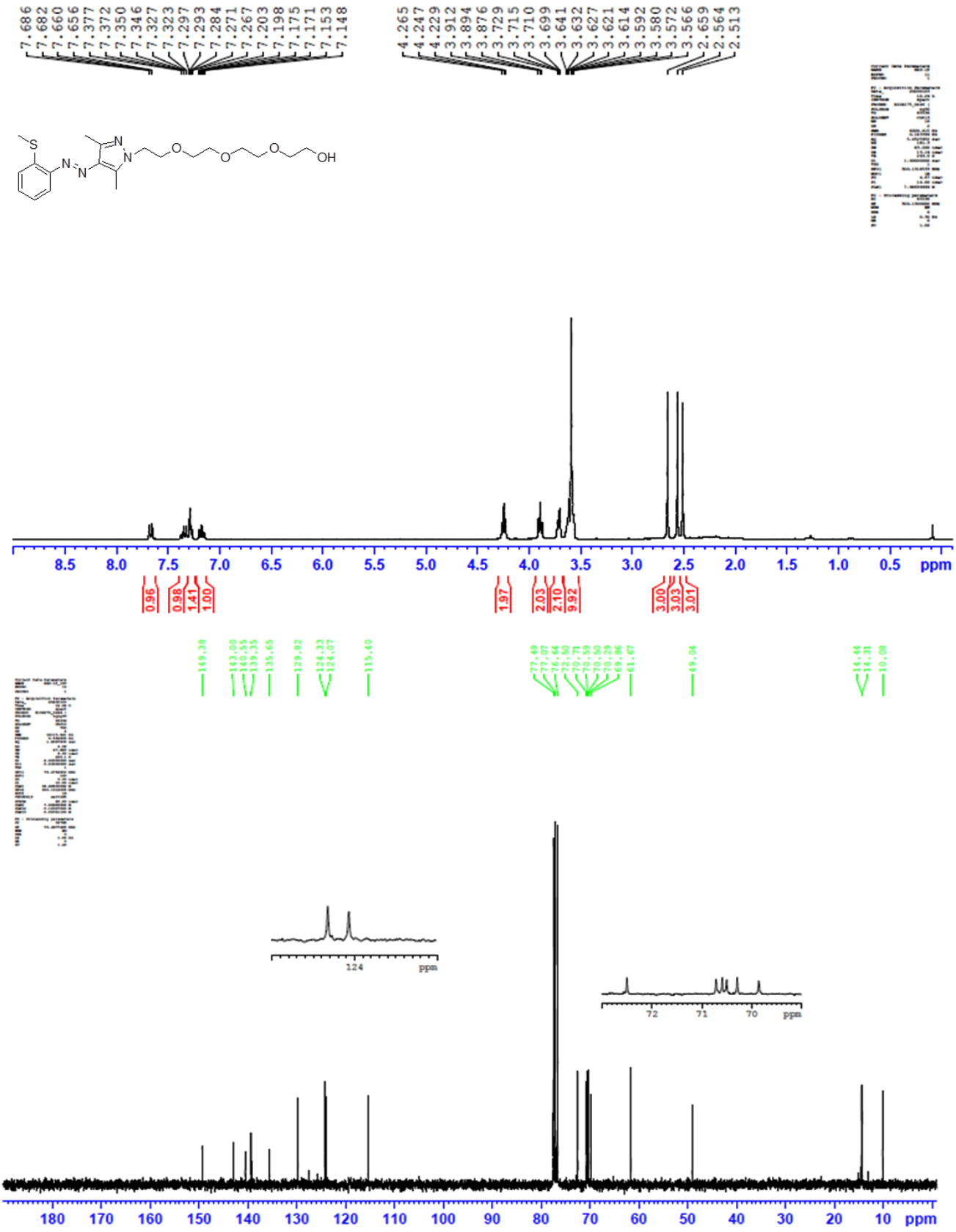


Fig. S24. ^{1}H and ^{13}C NMR spectra of (*E*)-2-(2-(2-(2-(3,5-dimethyl-4-((2-(methylthio)phenyl)diazenyl)-1H-pyrazol-1-yl)ethoxy)ethoxy)ethoxy)ethanol (**7**) in $CDCl_3$.

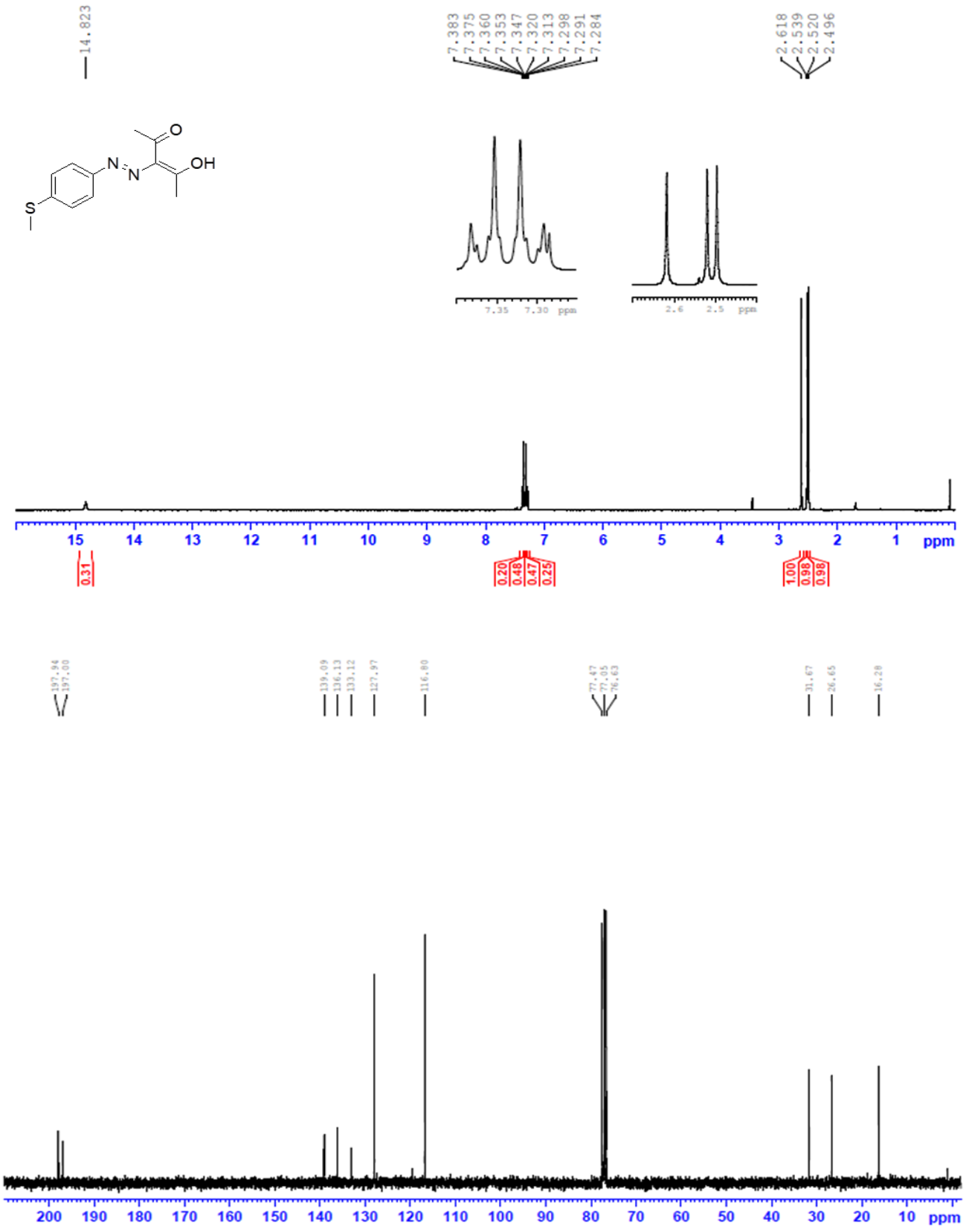


Fig. S25. ^{1}H and ^{13}C NMR spectra of (*E*)-4-hydroxy-3-((*E*)-(4-(methylthio)phenyl)diazenyl)pent-3-en-2-one (**10c**) in $CDCl_3$.

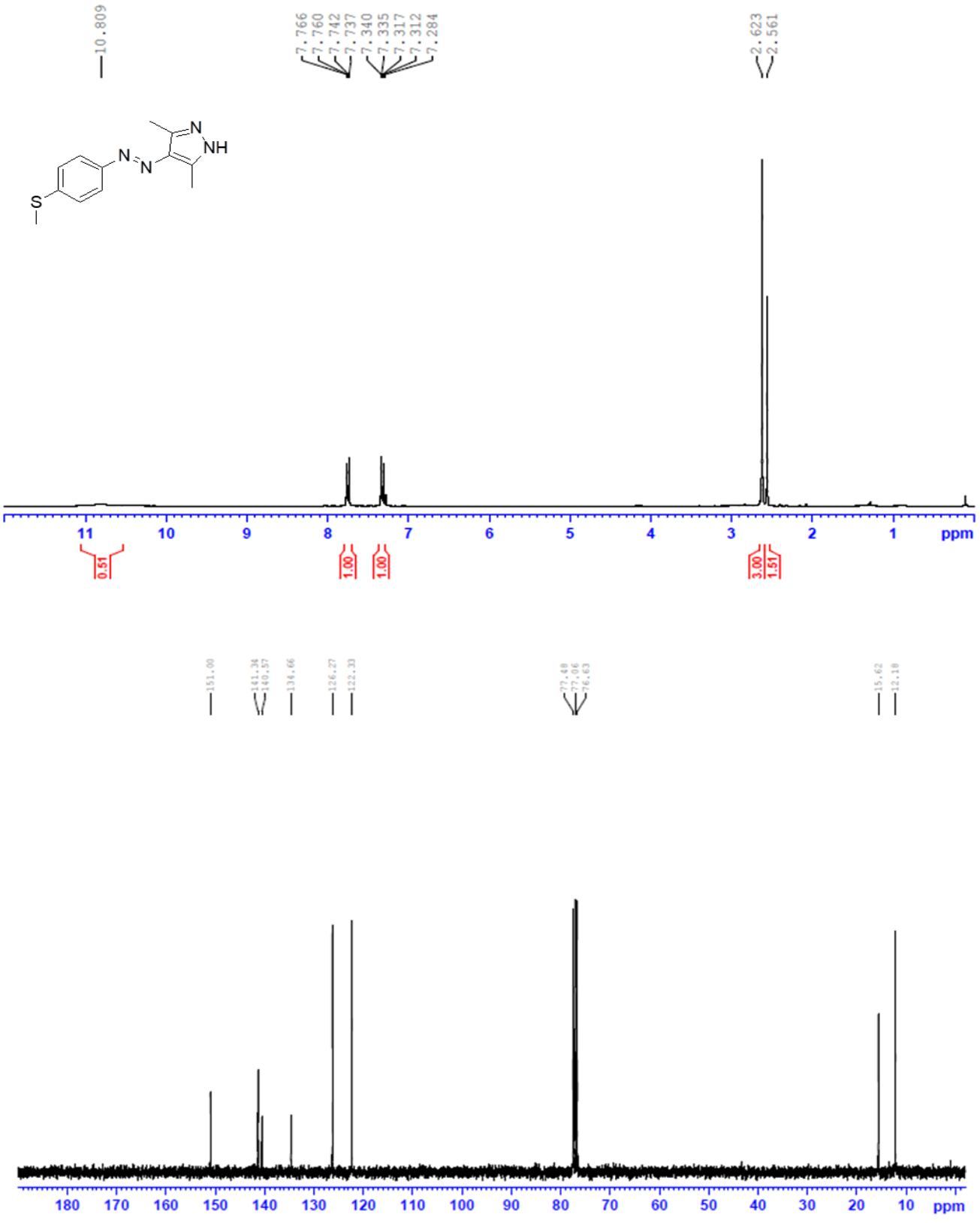


Fig. S26. ^{1}H and ^{13}C NMR spectra of (*E*)-3,5-dimethyl-4-((4-(methylthio)phenyl)diazenyl)-1H-pyrazole(**9c**) in $CDCl_3$.

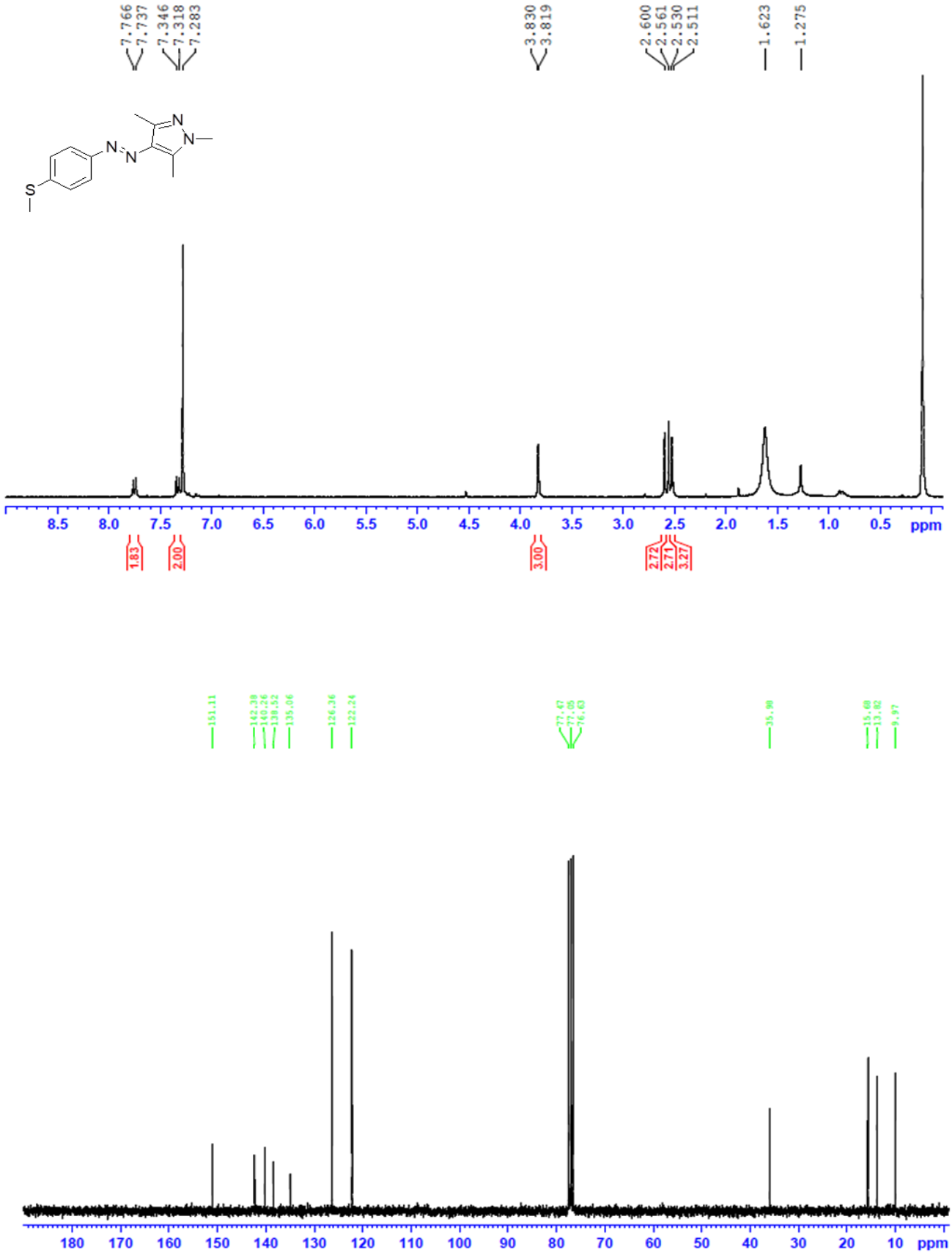


Fig. S27. ^{1}H and ^{13}C NMR spectra of (*E*)-1,3,5-trimethyl-4-((4-(methylthio)phenyl)diazenyl)-1H-pyrazole (**6**) in $CDCl_3$.

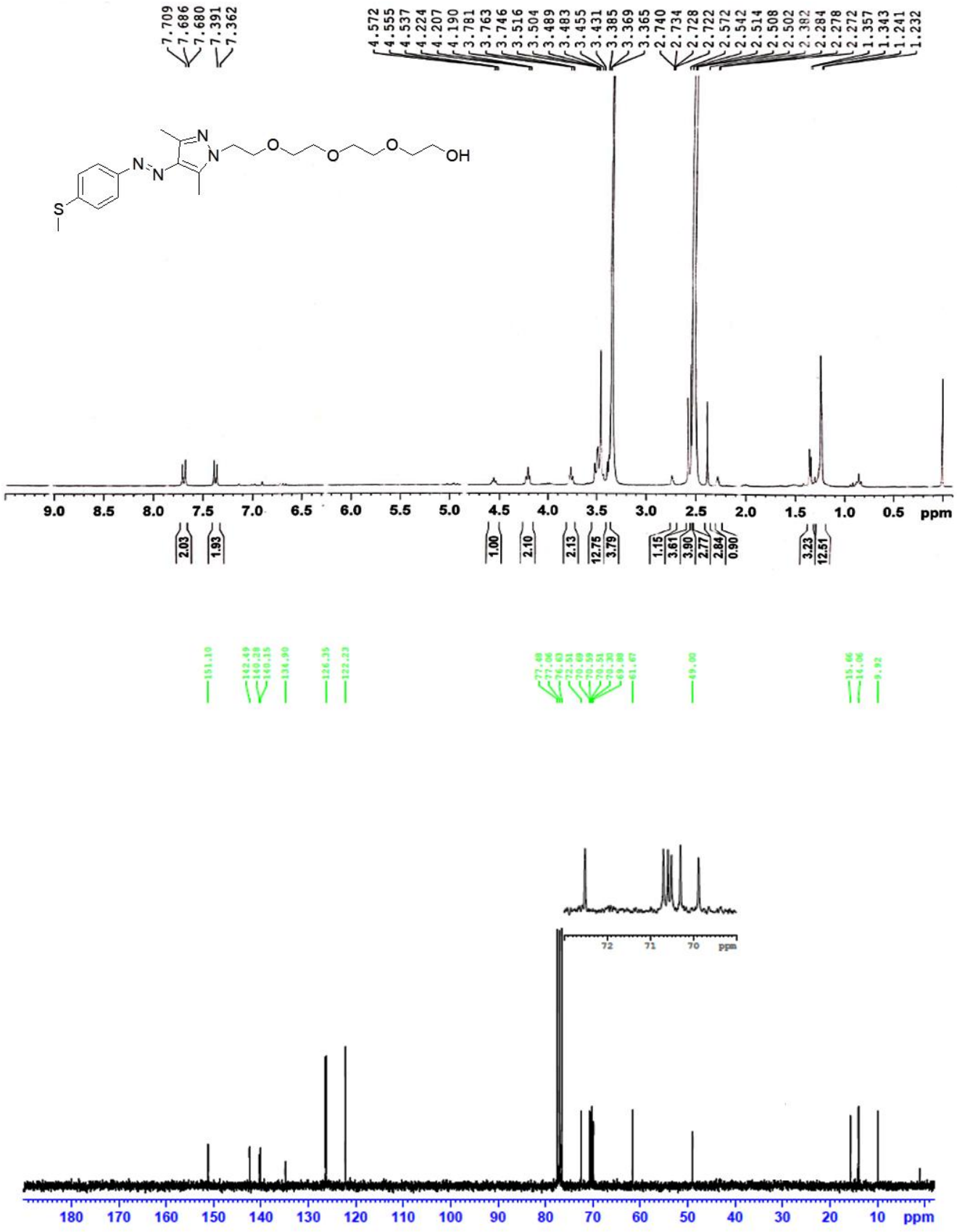


Fig. S28. ^{1}H and ^{13}C NMR spectra of (*E*)-2-(2-(2-(2-(3,5-dimethyl-4-((4-(methylthio)phenyl)diazenyl)-1H-pyrazol-1-yl)ethoxy)ethoxy)ethoxy)ethanol (**8**) inDMSO-d_6 and $CDCl_3$, respectively .

Computational Chemistry:

Geometries of *cis* and *trans* forms of **2a, 4-6** were calculated with the nonlocal hybrid Becke three-parameter Lee-Yang-Parr (B3LYP) functional[5] and the 6-311++g(d,p) basis set with a DMSO solvent model (CPCM) using the Gaussian 09 suit of programs.[6] On the basis of the optimized geometries, singlet excited-states were calculated by time dependent DFT (TD-DFT)[7] method using same method and basis set, and the DMSO solvent model. Singlet excited-states having oscillator strength (f) higher than 0.01 were considered. The simulated UV-vis spectra were generated by fitting excited state energies to a Gaussian curve with full-width-at-half-maximum of the experimentally observed UV-vis spectra of compounds **4-6** (Figure S2).

Ground state free energies (sum of electronic and thermal free energies) of *trans* and *cis* isomers of **2a** and **4-6** shown in Table S1 were calculated from frequency calculations.

Table S4. XYZ coordinates optimized molecular geometry of *trans*-4.

C	-6.04858	0.34439	-0.36968
C	-3.94918	1.5229	-0.06088
C	-5.28711	1.92665	-2.04549
C	-6.24074	1.00639	-1.58982
H	-6.7767	-0.35825	-0.02176
H	-5.43382	2.43211	-2.9771
H	-7.11557	0.80921	-2.17351
N	-2.74731	1.7938	0.74101
N	-2.57838	1.21182	1.81366
C	-1.04826	0.93267	3.78323
C	-0.24467	2.43248	2.27542
C	-1.37651	1.48271	2.61555
N	0.13144	1.63977	4.32997
N	0.65091	2.37272	3.21944
C	-1.77217	-0.25147	4.45059
H	-2.80603	-0.23851	4.17517
H	-1.32818	-1.16945	4.12641
H	-1.68526	-0.1692	5.51388
C	-0.16131	3.31297	1.01471
H	-0.67633	2.83235	0.20931
H	-0.61436	4.26205	1.21191
H	0.86469	3.45626	0.74695
C	-4.14133	2.1849	-1.28103
C	-3.73255	4.6024	-2.84234
H	-4.21328	4.14246	-3.68035
H	-4.46233	5.11027	-2.24704
H	-3.00443	5.30503	-3.19026
S	-2.93007	3.35378	-1.85981
C	-4.9028	0.60264	0.39479
S	-4.65874	-0.23821	1.94457
C	-6.23956	-0.60689	2.67496
H	-6.77554	0.30367	2.84376
H	-6.80056	-1.23363	2.01361
H	-6.09285	-1.11235	3.60657
C	1.11472	0.70792	4.90069
H	1.95934	1.25718	5.261
H	0.66778	0.16941	5.71011
H	1.43275	0.01888	4.14638

Table S5. Details of electronic transitions of *trans*-4.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (81 = HOMO, 82 = LUMO)	
1	2.6989 eV, 459.39 nm	0.0428	79 -> 82	0.58287
			81 -> 82	0.38829
2	3.0107 eV, 411.82 nm	0.0988	79 -> 82	0.22148
			80 -> 82	0.54326

			81 -> 82	-0.38554
3	3.1616 eV, 392.15 nm	0.3975	79 -> 82	-0.32471
			80 -> 82	0.44230
			81 -> 82	0.43657
4	4.0763 eV, 304.16 nm	0.0477	77 -> 82	0.51322
			78 -> 82	-0.47945
5	4.1740 eV, 297.04 nm	0.2843	77 -> 82	0.47443
			78 -> 82	0.49790
6	4.5991 eV , 269.58 nm	0.2056	80 -> 83	0.12290
			80 -> 88	0.16832
			81 -> 83	0.64594
7	4.8514 eV, 255.56 nm	0.1901	76 -> 82	-0.25428
			79 -> 83	-0.10944
			80 -> 83	0.61714
			81 -> 83	-0.10724
8	4.9313 eV, 251.42 nm	0.0176	76 -> 82	-0.11020
			80 -> 85	0.15168
			81 -> 84	0.60817
			81 -> 85	-0.19234
			81 -> 86	0.11979
10	5.0192 eV, 247.02 nm	0.0126	76 -> 82	-0.21538
			80 -> 84	0.55374
			80 -> 86	-0.11658
			81 -> 84	0.15400
			81 -> 85	0.22124
			81 -> 86	-0.11211
11	5.0864 eV, 243.75 nm	0.0881	75 -> 82	0.11998
			76 -> 82	0.48974
			80 -> 83	0.20513
			80 -> 84	0.13197
			81 -> 83	-0.10837
			81 -> 84	0.15581
			81 -> 85	0.10821
			81 -> 88	-0.32734
13	5.2475 eV, 236.27 nm	0.0167	75 -> 82	0.15062
			80 -> 84	0.11866
			80 -> 86	-0.11011
			81 -> 85	0.12479
			81 -> 86	0.60440
15	5.3053 eV, 233.70 nm	0.0498	75 -> 82	0.18393
			79 -> 87	0.17343
			80 -> 85	-0.22007
			80 -> 86	0.11945
			81 -> 87	0.56909
16	5.3103 eV, 233.48 nm	0.0215	74 -> 82	0.11953
			75 -> 82	-0.13398
			80 -> 84	0.12462
			80 -> 85	-0.33538
			80 -> 86	0.35924
			80 -> 88	0.17192
			81 -> 85	-0.20275
			81 -> 86	0.14874
			81 -> 87	-0.20337
			81 -> 88	-0.14914
17	5.3379 eV, 232.27 nm	0.0921	74 -> 82	0.13580
			75 -> 82	0.27461
			76 -> 82	-0.10277
			80 -> 85	0.36577
			80 -> 86	0.24677
			80 -> 88	0.36553
18	5.3503 eV, 231.73 nm	0.0154	74 -> 82	0.13850
			75 -> 82	0.29977
			76 -> 82	-0.16397

			79 -> 84	-0.19305
			79 -> 88	-0.29673
			80 -> 84	-0.12894
			80 -> 85	-0.25214
			80 -> 86	-0.19049
			81 -> 87	-0.16681
			81 -> 88	-0.13665
19	5.3837 eV, 230.29 nm	0.1000	74 -> 82	0.10015
			79 -> 84	0.24618
			79 -> 88	0.25267
			80 -> 84	-0.15786
			80 -> 85	-0.10775
			80 -> 86	-0.28098
			80 -> 88	0.39127
			81 -> 89	0.14336
20	5.4395 eV, 227.93 nm	0.0473	74 -> 82	0.32494
			76 -> 82	-0.10091
			78 -> 83	-0.12231
			79 -> 84	0.40199
			79 -> 87	-0.14292
			80 -> 88	-0.25638
			81 -> 88	-0.21021

Table S6. XYZ coordinates optimized molecular geometry of *cis*-4.

C	-6.11442	0.47	-0.249
C	-4.94811	0.70615	0.49119
C	-3.97233	1.58405	0.00021
C	-5.32916	1.98965	-1.97115
C	-6.30495	1.11176	-1.48017
H	-6.85946	-0.20029	0.12587
H	-5.47463	2.47964	-2.91118
H	-7.19545	0.93145	-2.04532
C	-4.16285	2.2258	-1.23096
C	-3.70052	4.59426	-2.85136
H	-4.21012	4.13279	-3.67127
H	-4.40306	5.13888	-2.25578
H	-2.95548	5.26456	-3.22624
S	-2.92345	3.34087	-1.85458
C	-5.53026	-1.68658	2.03554
H	-6.57685	-1.5402	1.86782
H	-5.12455	-2.29129	1.25157
H	-5.38479	-2.17657	2.97557
S	-4.70612	-0.10898	2.05497
C	-2.08777	0.19041	-2.01384
C	-2.77002	-1.27717	-0.43168
C	-2.13731	-0.05597	-0.64492
C	-1.44444	1.4709	-2.57783
H	-2.12366	1.94176	-3.25743
H	-1.22136	2.14159	-1.77452
H	-0.54131	1.21902	-3.09341
C	-2.98157	-1.83612	0.98762
H	-2.84096	-1.05363	1.70374
H	-3.97501	-2.22414	1.07373
H	-2.27571	-2.61897	1.17152
N	-1.60791	0.82823	0.40333
N	-2.69068	1.84356	0.81361
N	-2.69462	-0.88368	-2.67939
N	-3.12723	-1.8141	-1.67638
C	-2.8578	-1.03035	-4.13292
H	-1.92791	-0.82106	-4.61914
H	-3.16089	-2.0314	-4.35859

H -3.60337 -0.34535 -4.47905

Table S7. Details of electronic transitions of *cis*-4.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (81 = HOMO, 82 = LUMO)	
1	2.5987 eV 477.10 nm	0.0744	77 -> 82	0.16040
			79 -> 82	-0.12045
			80 -> 82	0.17932
			81 -> 82	0.64859
2	3.0508 eV 406.40 nm	0.0442	80 -> 82	0.67412
			81 -> 82	-0.19640
3	3.4360 eV 360.83 nm	0.0147	77 -> 82	-0.19317
			79 -> 82	0.64838
			81 -> 82	0.14968
4	4.0250 eV 308.04 nm	0.2384	77 -> 82	0.62693
			78 -> 82	-0.11890
			79 -> 82	0.20528
			81 -> 82	-0.11825
			81 -> 84	-0.12603
6	4.3728 eV 283.53 nm	0.0660	80 -> 84	0.29473
			81 -> 83	0.62092
8	4.6960 eV 264.02 nm	0.0143	76 -> 82	-0.27731
			80 -> 83	-0.36233
			81 -> 84	0.49901
9	4.8257 eV 256.92 nm	0.2391	76 -> 82	-0.10800
			79 -> 83	0.13565
			80 -> 83	-0.30356
			80 -> 84	0.44733
			81 -> 83	-0.17451
			81 -> 84	-0.32778
10	4.8917 eV 253.46 nm	0.1660	75 -> 82	0.11231
			76 -> 82	0.16449
			79 -> 83	0.24880
			80 -> 83	0.32568
			80 -> 84	0.34902
			81 -> 83	-0.21307
			81 -> 84	0.28315
11	5.0455 eV 245.73 nm	0.0174	80 -> 85	-0.11063
			80 -> 86	0.12481
			81 -> 85	0.61801
			81 -> 86	-0.18394
12	5.0666 eV 244.71 nm	0.1453	79 -> 83	0.51954
			80 -> 83	-0.12168
			80 -> 84	-0.17464
			80 -> 85	-0.26255
			80 -> 86	-0.14296
			81 -> 85	-0.17214
			81 -> 86	-0.16828
13	5.1583 eV 240.36 nm	0.1408	75 -> 82	-0.12637
			79 -> 83	0.31785
			80 -> 84	-0.13403
			80 -> 85	0.39136
			81 -> 85	0.15271
			81 -> 86	0.35086
			81 -> 87	-0.14989
14	5.1866 eV 239.05 nm	0.0193	80 -> 85	-0.26275
			80 -> 86	0.14009
			81 -> 86	0.42474
			81 -> 87	0.41790
			81 -> 88	0.13697
15	5.2343 eV 236.87 nm	0.0606	75 -> 82	0.11688
			79 -> 83	0.14809
			79 -> 84	0.10989
			80 -> 85	0.29830
			80 -> 86	0.36175
			81 -> 85	-0.15745

			81 -> 86	-0.26566
			81 -> 87	0.27660
			81 -> 89	-0.10914
16	5.2642 eV 235.52 nm	0.0294	75 -> 82	0.63233
			79 -> 84	-0.14715
			80 -> 86	-0.14163
			81 -> 85	0.10228
18	5.3118 eV 233.41 nm	0.0123	79 -> 84	0.60645
			80 -> 86	-0.24507
			81 -> 88	0.13993
19	5.3621 eV 231.22 nm	0.0146	74 -> 82	0.57540
			79 -> 84	-0.15675
			80 -> 88	0.11158
			81 -> 88	0.15531
			81 -> 89	-0.26639

Table S8. XYZ coordinates optimized molecular geometry of *trans*-5 (conf-1).

C	-6.34194	1.10883	0.02373
C	-5.06585	1.17135	0.59956
C	-4.06325	1.94472	-0.00094
C	-5.61285	2.59307	-1.75313
C	-6.61545	1.8197	-1.15262
H	-7.10745	0.51834	0.48223
H	-5.82168	3.13584	-2.65129
H	-7.58978	1.77197	-1.59228
N	-2.72469	2.0103	0.60308
N	-2.48424	1.38537	1.63723
C	-0.67844	0.75991	3.50735
C	-1.14568	1.45094	2.24126
N	1.095	1.76122	2.58901
C	-1.53417	-0.16632	4.39133
H	-2.56113	0.12688	4.32576
H	-1.42958	-1.17676	4.05521
H	-1.20638	-0.09263	5.40721
C	-0.12274	3.1768	0.65813
H	-0.88204	2.91089	-0.04731
H	-0.3329	4.14594	1.06001
H	0.82884	3.19216	0.16909
C	-4.33675	2.65559	-1.17729
C	-0.09701	2.14258	1.79889
N	0.56239	1.08759	3.73046
C	1.90991	2.92941	2.95253
H	2.26227	3.40912	2.06335
H	1.31563	3.61706	3.51722
H	2.74499	2.61237	3.54161
S	-3.0633	3.6379	-1.94003
C	-3.32842	3.69066	-3.69939
H	-4.28454	4.12566	-3.90312
H	-2.56292	4.28115	-4.15789
H	-3.29718	2.69687	-4.09475
H	-4.85702	0.62858	1.49773

Table S9. Details of electronic transitions of *trans*-5 (conf-1).

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
2	2.8888 eV 429.20 nm	0.2981	67 -> 70	0.12959
			69 -> 70	0.68981
3	3.5610 eV 348.18 nm	0.5080	67 -> 70	0.65686
			68 -> 70	-0.19980
			69 -> 70	-0.14476

4	3.9823 eV	311.33 nm	0.0210	66 -> 70	0.70362
5	4.5971 eV	269.70 nm	0.0785	64 -> 70	0.15086
				65 -> 70	0.48920
				69 -> 71	0.45103
				69 -> 74	-0.10649
6	4.8434 eV	255.99 nm	0.1710	65 -> 70	-0.46837
				69 -> 71	0.49447
10	5.0996 eV	243.13 nm	0.0101	63 -> 70	-0.22915
				64 -> 70	0.56467
				67 -> 71	-0.27048
				69 -> 71	-0.11525
				69 -> 74	0.13794
12	5.2207 eV	237.48 nm	0.1608	67 -> 71	0.34447
				68 -> 71	-0.10250
				69 -> 74	0.54689
				69 -> 77	-0.15155
15	5.4826 eV	226.14 nm	0.1372	64 -> 70	0.25974
				67 -> 71	0.42091
				68 -> 71	-0.12603
				69 -> 74	-0.37133
				69 -> 77	-0.25746
17	5.5993 eV	221.43 nm	0.0107	67 -> 72	-0.27285
				69 -> 75	-0.10500
				69 -> 76	0.46097
				69 -> 78	-0.33931
				69 -> 80	0.15980
				69 -> 86	-0.10679
19	5.6529 eV	219.33 nm	0.0221	64 -> 70	0.12910
				65 -> 71	0.15934
				67 -> 71	0.23245
				67 -> 74	-0.17062
				68 -> 72	-0.11417
				69 -> 77	0.56583

Table S10. XYZ coordinates optimized molecular geometry of *trans*-5 (conf-2).

C	-6.29841	1.04378	-0.01968
C	-5.03314	1.12243	0.57767
C	-4.00132	1.82722	-0.05679
C	-5.50004	2.37472	-1.88596
C	-6.53186	1.66992	-1.2515
H	-7.08622	0.50566	0.46474
H	-5.67829	2.85279	-2.82648
H	-7.49792	1.60987	-1.70759
N	-2.67411	1.90972	0.5698
N	-2.46888	1.35927	1.65271
C	-0.71594	0.83805	3.60335
C	-1.14168	1.44177	2.27931
N	1.09796	1.72996	2.65188
C	-1.61017	-0.00095	4.53505
H	-2.62868	0.30809	4.42532
H	-1.52172	-1.03575	4.27763
H	-1.30142	0.14188	5.54953
C	-0.04805	3.02194	0.59458
H	-0.79874	2.71988	-0.10551
H	-0.24428	4.02273	0.91832
H	0.91334	2.98047	0.1267
C	-4.23477	2.45336	-1.28861
H	-3.44696	2.99149	-1.77304
C	-0.06886	2.07597	1.80961
N	0.52723	1.15532	3.82849
C	1.93161	2.9047	2.94496
H	2.31268	3.30876	2.0304
H	1.34177	3.64519	3.44363

H	2.7472	2.61525	3.5742
C	-5.78085	-1.1072	2.2861
H	-6.80671	-0.80896	2.22635
H	-5.56095	-1.78957	1.4918
H	-5.6026	-1.58527	3.22662
S	-4.73661	0.32713	2.14227

Table S11. Details of electronic transitions of *trans*-5(conf-2).

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
1	2.7449 eV 451.68 nm	0.0162	67 -> 70	0.27332
			68 -> 70	0.61634
			69 -> 70	0.19942
2	3.1465 eV 394.04 nm	0.3770	68 -> 70	-0.23351
			69 -> 70	0.66229
			69 -> 70	-0.14476
3	3.7103 eV 334.17 nm	0.4620	67 -> 70	0.63579
			68 -> 70	-0.23833
			69 -> 70	-0.13528
			69 -> 71	-0.12465
4	4.0813 eV 303.79 nm	0.0236	66 -> 70	0.70260
5	4.6586 eV 266.14 nm	0.1824	65 -> 70	0.24001
			67 -> 70	0.10970
			69 -> 71	0.61830
6	4.8736 eV 254.40 nm	0.0140	65 -> 70	-0.19217
			67 -> 71	0.20150
			68 -> 71	0.64609
7	4.9815 eV 248.89 nm	0.0364	65 -> 70	0.34546
			68 -> 71	0.11309
			69 -> 71	-0.17647
			69 -> 72	0.5200
			69 -> 74	-0.13983
8	5.0223 eV 246.87 nm	0.0562	65 -> 70	0.43991
			68 -> 71	0.13231
			68 -> 74	-0.11141
			69 -> 71	-0.19679
			69 -> 72	-0.41085
			69 -> 73	0.13815
			69 -> 74	-0.11244
12	5.2698 eV 235.27 nm	0.0389	64 -> 70	-0.25242
			65 -> 70	0.12502
			67 -> 71	0.25941
			67 -> 72	-0.11283
			69 -> 73	0.14048
			69 -> 74	0.51206
13	5.3440 eV 232.01 nm	0.0382	64 -> 70	0.11030
			67 -> 71	-0.11957
			67 -> 74	0.18203
			68 -> 72	-0.23881
			68 -> 73	-0.21464
			68 -> 74	0.49388
			68 -> 76	0.16393
			69 -> 73	0.11119
15	5.4619 eV 227.00 nm	0.0196	67 -> 74	0.12739
			68 -> 72	0.60836
			68 -> 73	-0.13267
			68 -> 74	0.18786
			69 -> 73	-0.15383
			67 -> 74	-0.17062
			68 -> 72	-0.11417
			69 -> 77	0.56583

16	5.4800 eV 226.25 nm	0.0173	64 -> 70	-0.25336
			65 -> 71	0.10686
			67 -> 71	0.39300
			68 -> 71	-0.13932
			68 -> 74	0.15952
			69 -> 74	-0.37821
			69 -> 76	0.18345
17	5.5881 eV 221.87 nm	0.1043	67 -> 71	-0.16545
			67 -> 76	0.10438
			68 -> 76	0.14095
			69 -> 76	0.60137

Table S12. XYZ coordinates optimized molecular geometry of *cis*-5 (conformer-1)

C	-6.11442	0.47	-0.249
C	-4.94811	0.70615	0.49119
C	-3.97233	1.58405	0.00021
C	-5.32916	1.98965	-1.97115
C	-6.30495	1.11176	-1.48017
H	-6.85946	-0.20029	0.12587
H	-5.47463	2.47964	-2.91118
H	-7.19545	0.93145	-2.04532
C	-4.16285	2.2258	-1.23096
C	-5.53026	-1.68658	2.03554
H	-6.57685	-1.5402	1.86782
H	-5.12455	-2.29129	1.25157
H	-5.38479	-2.17657	2.97557
S	-4.70612	-0.10898	2.05497
C	-2.08777	0.19041	-2.01384
C	-2.77002	-1.27717	-0.43168
C	-2.13731	-0.05597	-0.64492
C	-1.44444	1.4709	-2.57783
H	-2.12366	1.94176	-3.25743
H	-1.22136	2.14159	-1.77452
H	-0.54131	1.21902	-3.09341
C	-2.98157	-1.83612	0.98762
H	-2.84096	-1.05363	1.70374
H	-3.97501	-2.22414	1.07373
H	-2.27571	-2.61897	1.17152
N	-1.60791	0.82823	0.40333
N	-2.69068	1.84356	0.81361
N	-2.69462	-0.88368	-2.67939
N	-3.12723	-1.8141	-1.67638
C	-2.8578	-1.03035	-4.13292
H	-1.92791	-0.82106	-4.61914
H	-3.16089	-2.0314	-4.35859
H	-3.60337	-0.34535	-4.47905
H	-3.41782	2.8961	-1.60583

Table S13. Details of electronic transitions of *cis*-5 (conformer-1)

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
1	2.5689 eV 482.64 nm	0.0969	66 -> 70	0.16505
			68 -> 70	-0.22645
			69 -> 70	0.64305
2	3.1843 eV 389.36 nm	0.0541	68 -> 70	0.64688
			69 -> 70	0.25445
3	3.9768 eV 311.77 nm	0.1370	66 -> 70	-0.38822
			67 -> 70	0.55622

				68 -> 70	-0.11339
4	4.0401 eV	306.89 nm	0.1598	66 -> 70	0.53050
				67 -> 70	0.42510
				68 -> 70	0.10087
5	4.2730 eV	290.16 nm	0.0140	65 -> 70	0.57778
				69 -> 71	0.35616
				69 -> 72	-0.13271
6	4.4962 eV	275.75 nm	0.1066	65 -> 70	-0.33726
				68 -> 71	-0.12184
				68 -> 72	-0.14259
				69 -> 71	0.56717
7	4.8229 eV	257.07 nm	0.0626	68 -> 71	0.27538
				69 -> 72	0.61069
8	4.9549 eV	250.23 nm	0.0846	65 -> 71	0.10116
				68 -> 71	0.57197
				68 -> 72	-0.21906
				69 -> 72	-0.25020
				69 -> 73	-0.11304
9	5.0042 eV	247.76 nm	0.0226	68 -> 71	0.10127
				68 -> 74	-0.11373
				69 -> 73	0.66325
				69 -> 74	-0.11146
10	5.1014 eV	243.04 nm	0.0333	64 -> 70	-0.17309
				68 -> 72	-0.28587
				68 -> 73	-0.14956
				69 -> 73	0.13346
				69 -> 74	0.51644
				69 -> 76	-0.12402
11	5.1598 eV	240.29 nm	0.0511	64 -> 70	0.64306
				68 -> 71	-0.11345
				68 -> 72	-0.14369
				69 -> 74	0.12604
				69 -> 75	0.11569
12	5.2083 eV	238.05 nm	0.0610	68 -> 71	0.13349
				68 -> 72	0.28998
				68 -> 73	-0.10288
				69 -> 74	0.23219
				69 -> 75	0.53676
13	5.2615 eV	235.65 nm	0.1102	64 -> 70	0.12080
				65 -> 71	-0.13678
				68 -> 72	0.43490
				68 -> 73	-0.10197
				69 -> 71	0.11193
				69 -> 74	0.25290
				69 -> 75	-0.38541
14	5.4156 eV	228.94 nm	0.0209	63 -> 70	0.44072
				68 -> 72	-0.12852
				68 -> 73	-0.13465
				69 -> 76	0.45521
				69 -> 78	0.12071
16	5.4574 eV	227.19 nm	0.0212	63 -> 70	0.15061
				68 -> 73	0.58526
				68 -> 74	-0.24682
				69 -> 74	0.21216
17	5.5199 eV	224.61 nm	0.0120	68 -> 74	0.20869
				69 -> 77	0.56979
				69 -> 78	0.28630
18	5.5621 eV	222.91 nm	0.0130	68 -> 73	0.22646
				68 -> 74	0.48414
				68 -> 75	-0.20618
				68 -> 76	-0.15807
				69 -> 73	0.11007
				69 -> 76	0.25452
				69 -> 77	-0.15232
				69 -> 78	-0.14395
19	5.6292 eV	220.25 nm	0.0142	68 -> 74	0.10019
				69 -> 77	-0.34955
				69 -> 78	0.53498

			69 -> 80	0.10536
20	5.6334 eV 220.09 nm	0.0790	66 -> 71	0.61768
			67 -> 71	-0.26383

Table S14. XYZ coordinates optimized molecular geometry of *cis*-5 (conformer-2)

C	-6.11442	0.47	-0.249
C	-4.94811	0.70615	0.49119
C	-3.97233	1.58405	0.00021
C	-5.32916	1.98965	-1.97115
C	-6.30495	1.11176	-1.48017
H	-6.85946	-0.20029	0.12587
H	-5.47463	2.47964	-2.91118
H	-7.19545	0.93145	-2.04532
C	-4.16285	2.2258	-1.23096
C	-5.53026	-1.68658	2.03554
H	-6.57685	-1.5402	1.86782
H	-5.12455	-2.29129	1.25157
H	-5.38479	-2.17657	2.97557
S	-4.70612	-0.10898	2.05497
C	-2.08777	0.19041	-2.01384
C	-2.13731	-0.05597	-0.64492
C	-1.44444	1.4709	-2.57783
H	-2.12366	1.94176	-3.25743
H	-1.22136	2.14159	-1.77452
H	-0.54131	1.21902	-3.09341
C	-2.98157	-1.83612	0.98762
H	-2.84096	-1.05363	1.70374
H	-3.97501	-2.22414	1.07373
H	-2.27571	-2.61897	1.17152
N	-1.60791	0.82823	0.40333
N	-2.69068	1.84356	0.81361
N	-3.12723	-1.8141	-1.67638
H	-3.41782	2.8961	-1.60583
C	-2.77002	-1.27717	-0.43168
N	-2.69462	-0.88368	-2.67939
C	-4.27883	-2.657	-2.02888
H	-4.08835	-3.15024	-2.95911
H	-4.43368	-3.38781	-1.26283
H	-5.15269	-2.04648	-2.12128

Table S15. Details of electronic transitions of *cis*-5 (conformer-2).

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
1	2.5542 eV 485.41 nm	0.0912	66 -> 70	-0.16020
			68 -> 70	0.21504
			69 -> 70	0.64714
2	3.1590 eV 392.48 nm	0.0447	68 -> 70	0.64999
			69 -> 70	-0.24438
3	3.9108 eV 317.03 nm	0.1283	65 -> 70	0.10573
			66 -> 70	0.55452
			67 -> 70	-0.36925
			68 -> 70	0.13636
			69 -> 70	0.11575
4	3.9579 eV 313.25 nm	0.0816	66 -> 70	0.35144
			67 -> 70	0.59812
5	4.2473 eV 291.92 nm	0.0269	65 -> 70	0.62200
			69 -> 71	0.26773
			69 -> 72	0.13401
6	4.5028 eV 275.35 nm	0.0833	65 -> 70	-0.24876
			68 -> 71	0.11685
			68 -> 72	-0.16127

				69 -> 71	0.60767
7	4.8129 eV	257.61 nm	0.0907	68 -> 71	0.21303
				69 -> 72	0.62443
8	4.9754 eV	249.20 nm	0.0524	64 -> 70	-0.13152
				65 -> 71	-0.10163
				68 -> 71	0.55275
				68 -> 72	0.26059
				69 -> 72	-0.17088
				69 -> 73	0.22206
9	4.9978 eV	248.08 nm	0.0298	68 -> 71	-0.17778
				68 -> 74	-0.10598
				69 -> 72	0.13496
				69 -> 73	0.63559
10	5.1129 eV	242.49 nm	0.0441	64 -> 70	0.58173
				68 -> 73	-0.12772
				69 -> 74	0.28795
11	5.1312 eV	241.63 nm	0.0854	63 -> 70	-0.11029
				64 -> 70	-0.30679
				68 -> 71	-0.20858
				68 -> 72	0.35015
				68 -> 73	-0.15545
				69 -> 74	0.39293
12	5.2238 eV	237.34 nm	0.0959	63 -> 70	-0.24707
				64 -> 70	0.13709
				65 -> 71	-0.11517
				68 -> 71	-0.12612
				68 -> 72	0.41672
				68 -> 73	0.13474
				69 -> 71	0.13153
				69 -> 74	-0.38712
				69 -> 75	0.11067
13	5.2931 eV	234.24 nm	0.0361	69 -> 75	0.66443
14	5.3248 eV	232.84 nm	0.0943	63 -> 70	0.61450
				68 -> 71	-0.11425
				68 -> 72	0.22707
15	5.4455 eV	227.68 nm	0.0205	68 -> 73	0.52996
				68 -> 74	0.17873
				69 -> 74	0.26725
				69 -> 76	-0.10226
				69 -> 77	0.24583
				69 -> 78	0.10231
17	5.4897 eV	225.85 nm	0.0127	68 -> 74	0.19862
				69 -> 76	0.60800
				69 -> 77	0.21736
				69 -> 78	-0.10945
18	5.6146 eV	220.83 nm	0.0131	68 -> 74	0.51264
				68 -> 78	0.10114
				69 -> 76	-0.15853
				69 -> 77	-0.23613
				69 -> 78	-0.28791
19	5.6923 eV	217.81 nm	0.0399	66 -> 71	0.63928
				67 -> 71	-0.23506
20	5.6334 eV	220.09 nm	0.0120	68 -> 74	0.27035
				68 -> 75	0.34082
				69 -> 77	-0.10668
				69 -> 78	0.46393
				69 -> 80	-0.11690

Table S16. XYZ coordinates optimized molecular geometry of *trans*-6.

C	-6.21894	0.69909	-0.24854
C	-5.02005	0.84572	0.46215
C	-4.04586	1.7481	0.01428
C	-5.46946	2.35721	-1.85498
C	-6.44364	1.45483	-1.4071
H	-6.96275	0.0101	0.09343
H	-5.64103	2.93423	-2.73958

N	-2.78829	1.90192	0.75976
N	-2.59075	1.23754	1.77828
C	-0.96976	0.74421	3.62961
C	-0.17327	2.30618	2.18236
C	-1.33317	1.39136	2.52377
N	0.27461	1.35184	4.15205
N	0.76931	2.13552	3.0651
C	-1.71708	-0.44741	4.25664
H	-2.76259	-0.36413	4.0448
H	-1.34135	-1.3607	3.84478
H	-1.56653	-0.44534	5.31599
C	-0.11394	3.26893	0.98187
H	-0.69806	2.87269	0.17769
H	-0.50416	4.22269	1.26993
H	0.90162	3.38034	0.66387
C	-4.27057	2.50385	-1.14429
H	-3.52676	3.19283	-1.48626
C	1.23738	0.33459	4.59835
H	2.12885	0.8147	4.94432
H	0.80847	-0.23752	5.39436
H	1.47561	-0.31384	3.78124
C	-7.87541	-0.15086	-2.70943
H	-8.15335	-0.79941	-1.90505
H	-8.61974	-0.19523	-3.47684
H	-6.93257	-0.46162	-3.10866
S	-7.76111	1.29369	-2.18808
H	-4.84848	0.2687	1.34675

Table S17. Details of electronic transitions of *trans*-6.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
2	3.1163 eV 397.86 nm	0.9835	69 -> 70	0.70472
3	4.1017 eV 302.27 nm	0.0143	66 -> 70	0.64377
			67 -> 70	-0.28106
4	4.1808 eV 296.55 nm	0.0723	65 -> 70	0.26061
			66 -> 70	0.24949
			67 -> 70	0.54743
			69 -> 71	0.24278
5	4.2373 eV 292.60 nm	0.0837	65 -> 70	0.41859
			66 -> 70	-0.12664
			67 -> 70	-0.32760
			69 -> 71	0.43750
6	4.7106 eV 263.20 nm	0.1658	65 -> 70	0.49787
			69 -> 71	-0.48257
11	5.2592 eV 235.75 nm	0.0236	64 -> 70	-0.25627
			67 -> 71	0.11798
			69 -> 76	0.63046
13	5.3032 eV 233.79 nm	0.0717	69 -> 74	0.63682
			69 -> 75	-0.24321

Table S18. XYZ coordinates optimized molecular geometry of *cis*-6.

C	-6.11442	0.47	-0.249
C	-4.94811	0.70615	0.49119
C	-3.97233	1.58405	0.00021
C	-5.32916	1.98965	-1.97115
C	-6.30495	1.11176	-1.48017
H	-6.85946	-0.20029	0.12587
H	-5.47463	2.47964	-2.91118
C	-4.16285	2.2258	-1.23096
C	-2.08777	0.19041	-2.01384
C	-2.77002	-1.27717	-0.43168
C	-2.13731	-0.05597	-0.64492
C	-1.44444	1.4709	-2.57783
H	-2.12366	1.94176	-3.25743

H	-1.22136	2.14159	-1.77452
H	-0.54131	1.21902	-3.09341
C	-2.98157	-1.83612	0.98762
H	-2.84096	-1.05363	1.70374
H	-3.97501	-2.22414	1.07373
H	-2.27571	-2.61897	1.17152
N	-1.60791	0.82823	0.40333
N	-2.69068	1.84356	0.81361
N	-2.69462	-0.88368	-2.67939
N	-3.12723	-1.8141	-1.67638
C	-2.8578	-1.03035	-4.13292
H	-1.92791	-0.82106	-4.61914
H	-3.16089	-2.0314	-4.35859
H	-3.60337	-0.34535	-4.47905
H	-3.41782	2.8961	-1.60583
C	-7.79048	-0.66508	-2.46013
H	-8.03465	-1.09827	-1.5127
H	-8.58822	-0.84411	-3.15039
H	-6.89023	-1.1071	-2.83303
H	-4.80265	0.21616	1.43121
S	-7.5866	0.85225	-2.29357

Table S19. Details of electronic transitions of *cis*-6.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (69 = HOMO, 70 = LUMO)	
1	2.5281 eV 490.43 nm	0.1457	66 -> 70	0.14436
			68 -> 70	0.23801
			69 -> 70	0.64527
2	3.5046 eV 353.78 nm	0.2285	66 -> 70	0.18694
			68 -> 70	0.61373
			69 -> 70	-0.27241
3	3.9936 eV 310.46 nm	0.1283	66 -> 70	0.17404
			67 -> 70	0.64930
			69 -> 71	0.16830
4	4.0330 eV 307.42 nm	0.1297	66 -> 70	0.60956
			67 -> 70	-0.22684
			68 -> 70	-0.19435
			69 -> 72	-0.11250
6	4.5693 eV 271.34 nm	0.0948	65 -> 70	0.58923
			68 -> 71	-0.13918
			69 -> 71	-0.26027
			69 -> 72	0.19168
7	4.7716 eV 259.84 nm	0.0867	65 -> 70	-0.15365
			68 -> 71	0.12648
			69 -> 72	0.61129
			69 -> 73	0.19829
8	4.8364 eV 256.36 nm	0.0296	69 -> 72	-0.16291
			69 -> 73	0.64280
			69 -> 74	-0.13689
10	4.9272 eV 251.63 nm	0.0246	65 -> 70	0.15477
			68 -> 71	0.66168
11	5.0382 eV 246.09 nm	0.0222	64 -> 70	0.64823
			69 -> 75	-0.17749
12	5.0904 eV 243.57 nm	0.0533	64 -> 70	0.17574
			69 -> 75	0.66132
14	5.3654 eV 231.08 nm	0.0147	68 -> 72	-0.11479
			68 -> 73	-0.11364
			69 -> 77	0.65891
16	5.4974 eV 225.53 nm	0.0236	68 -> 72	0.61961
			69 -> 78	-0.22101
			69 -> 79	-0.13170
17	5.5172 eV 224.72 nm	0.0219	63 -> 70	0.43653
			66 -> 71	0.15074
			68 -> 72	0.15947
			69 -> 78	0.47425
18	5.5728 eV 222.48 nm	0.0739	63 -> 70	-0.11015

				65 -> 71	-0.12800
				66 -> 71	0.38518
				67 -> 71	0.55820
19	5.6186 eV 220.67 nm	0.0175		66 -> 71	0.52069
				67 -> 71	-0.40781
				69 -> 79	-0.14725

Table S20. XYZ coordinates optimized molecular geometry of *trans*-2a.

C	-6.07296	0.39044	-0.33798
C	-3.96675	1.55845	-0.03564
C	-5.31207	1.97403	-2.01281
C	-6.26777	1.05683	-1.55532
H	-6.80266	-0.30987	0.01132
H	-5.46081	2.48284	-2.94227
H	-7.14621	0.86533	-2.13547
N	-2.75993	1.82154	0.76138
N	-2.58867	1.2357	1.83157
C	-1.05067	0.94389	3.79315
C	-0.24726	2.44436	2.28589
C	-1.38184	1.49879	2.62859
N	0.1348	1.64401	4.33638
N	0.65244	2.37778	3.22553
C	-1.77687	-0.23885	4.46049
H	-2.81194	-0.22037	4.18995
H	-1.33861	-1.15791	4.13161
H	-1.68463	-0.16004	5.52359
C	-0.16574	3.32808	1.02732
H	-0.68672	2.85215	0.22298
H	-0.61351	4.27865	1.22936
H	0.85964	3.46746	0.75518
C	-4.16156	2.22484	-1.25298
C	-3.83013	4.16908	-2.50325
H	-4.31686	3.71376	-3.34031
H	-4.55479	4.67856	-1.90308
H	-3.10043	4.86938	-2.85255
C	-4.92245	0.64125	0.42185
C	-5.99225	-0.33081	2.25589
H	-6.52326	0.58171	2.4298
H	-6.5592	-0.95307	1.59539
H	-5.84351	-0.83961	3.18535
C	1.11645	0.70604	4.89982
H	1.96525	1.25039	5.25774
H	0.67084	0.16724	5.70978
H	1.4278	0.01773	4.14206
O	-4.72367	-0.03874	1.66403
O	-3.18636	3.16076	-1.71981

Table S21. Details of electronic transitions of *trans*-2a.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (73 = HOMO, 74 = LUMO)	
1	2.7561 eV 449.86 nm	0.0722	71 -> 74	-0.29866
			73 -> 74	0.63069
2	3.6343 eV 341.15 nm	0.0226	72 -> 74	0.69981
3	3.7415 eV 331.38 nm	0.4438	69 -> 74	-0.22861
			71 -> 74	0.58703
			73 -> 74	0.30988
4	4.3810 eV 283.00 nm	0.0184	70 -> 74	0.69670
5	4.5661 eV 271.53 nm	0.2796	69 -> 74	0.61063
			71 -> 74	0.20936
			73 -> 75	-0.10766
			73 -> 76	-0.23272
6	4.9051 eV 252.76 nm	0.0120	69 -> 74	0.11424
			73 -> 75	0.65969

9	5.1685 eV	239.88 nm	0.0222	71 -> 78	-0.10910
				73 -> 77	0.50412
				73 -> 78	0.45520
12	5.4294 eV	228.36 nm	0.0166	72 -> 75	0.46949
				72 -> 76	-0.16163
				72 -> 77	-0.27068
				72 -> 78	0.13471
				73 -> 80	-0.34105
				73 -> 81	-0.12548
14	5.5752 eV	222.38 nm	0.0811	68 -> 74	0.24631
				69 -> 79	0.13426
				71 -> 75	0.16977
				71 -> 79	-0.30593
				72 -> 76	0.35509
				72 -> 77	0.19160
				73 -> 79	0.23709
				73 -> 80	-0.10926
15	5.5798 eV	222.20 nm	0.0333	68 -> 74	0.61452
				71 -> 75	0.11039
				71 -> 79	0.14587
				72 -> 76	-0.17069
				73 -> 79	-0.11982
16	5.6157 eV	220.78 nm	0.0280	68 -> 74	-0.21430
				71 -> 75	0.46030
				71 -> 76	0.23799
				71 -> 77	0.10706
				72 -> 79	0.16059
				73 -> 76	0.18135
				73 -> 82	-0.20576
19	5.7359 eV	216.16 nm	0.0356	71 -> 75	-0.28835
				71 -> 76	0.53993
				72 -> 78	-0.12763
				72 -> 79	0.15332
				72 -> 80	-0.12946
				73 -> 82	0.12285
20	5.7558 eV	215.41 nm	0.0191	72 -> 78	0.30975
				72 -> 79	0.24128
				72 -> 80	0.51905
				73 -> 83	0.10735

Table S22. XYZ coordinates optimized molecular geometry of *cis*-2a.

C	-6.10509	0.45961	-0.26345
C	-4.93878	0.69576	0.47674
C	-3.963	1.57366	-0.01424
C	-5.31983	1.97926	-1.9856
C	-6.29561	1.10136	-1.49462
H	-6.85013	-0.21068	0.11142
H	-5.46529	2.46925	-2.92563
H	-7.18612	0.92106	-2.05977
C	-4.15352	2.21541	-1.24541
C	-3.74689	4.53375	-2.83779
H	-4.25649	4.07228	-3.65769
H	-4.44943	5.07837	-2.2422
H	-3.00186	5.20405	-3.21266
C	-5.48389	-1.62607	2.02197
H	-6.53048	-1.47969	1.85424
H	-5.07818	-2.23078	1.23799
H	-5.33842	-2.11606	2.96199
C	-2.07844	0.18002	-2.02829
C	-2.76069	-1.28756	-0.44613
C	-2.12798	-0.06636	-0.65937
C	-1.43511	1.4605	-2.59228
H	-2.11433	1.93137	-3.27188
H	-1.21203	2.1312	-1.78897
H	-0.53198	1.20863	-3.10786

C	-2.97224	-1.84652	0.97317
H	-2.83163	-1.06402	1.68929
H	-3.96568	-2.23453	1.05928
H	-2.26638	-2.62937	1.15707
N	-1.59858	0.81784	0.38888
N	-2.68134	1.83316	0.79916
N	-2.68528	-0.89408	-2.69384
N	-3.1179	-1.8245	-1.69083
C	-2.84847	-1.04075	-4.14737
H	-1.91858	-0.83145	-4.63359
H	-3.15156	-2.0418	-4.37304
H	-3.59404	-0.35575	-4.4935
O	-2.96982	3.28036	-1.841
O	-4.69679	-0.11937	2.04052

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Table S23. Details of electronic transitions of *cis*-2a.

Excited State	Energy (eV), λ (nm)	Oscillator Strength (f)	MOs, coefficients (73 = HOMO, 74 = LUMO)	
	2.6873 eV 461.37 nm	0.0743	69 -> 74	0.17839
			73 -> 74	0.68072
1	3.5716 eV 347.14 nm	0.0260	72 -> 74	0.70170
3	3.8516 eV 321.91 nm	0.0239	69 -> 74	-0.33606
			71 -> 74	0.60076
4	4.1019 eV 302.26 nm	0.2198	69 -> 74	0.56088
			70 -> 74	0.20222
			71 -> 74	0.30908
			73 -> 74	-0.16075
5	4.1644 eV 297.72 nm	0.0204	69 -> 74	-0.17401
			70 -> 74	0.67002
			71 -> 74	-0.11866
6	4.8036 eV 258.11 nm	0.0996	73 -> 75	0.64572
			73 -> 76	-0.12903
8	4.9886 eV 248.53 nm	0.0245	73 -> 76	0.67180
			73 -> 77	-0.10843
9	5.2127 eV 237.85 nm	0.0337	72 -> 75	0.11211
			73 -> 77	-0.23243
			73 -> 78	-0.33521
			73 -> 79	0.47482
			73 -> 80	-0.22777
			73 -> 81	-0.12775
11	5.3697 eV 230.90 nm	0.0715	68 -> 74	0.12836
			71 -> 77	0.11372
			72 -> 75	0.35597
			73 -> 77	-0.24830
			73 -> 79	-0.33826
			73 -> 80	-0.18221
			73 -> 81	-0.29531
12	5.4256 eV 228.52 nm	0.0413	68 -> 74	0.61128
			73 -> 79	0.11741
			73 -> 80	0.22211
			73 -> 81	-0.14539
13	5.4502 eV 227.48 nm	0. .0160	72 -> 75	0.22291
			72 -> 76	-0.42530
			72 -> 79	0.12056
			73 -> 78	-0.10180
			73 -> 79	0.10785
			73 -> 80	0.43229
14	5.4601 eV 227.07 nm	0. .0602	68 -> 74	-0.13014
			71 -> 77	0.12816
			72 -> 75	0.16915
			72 -> 76	0.48770
			72 -> 79	-0.10028
			73 -> 77	-0.18929
			73 -> 80	0.35167
15	5.4920 eV 225.76 nm	0.0212	68 -> 74	0.24519
			72 -> 75	0.18262
			73 -> 80	-0.14523

			73 -> 81	0.57353
18	5.7697 eV 214.89 nm	0.0248	72 -> 78	0.66179
19	5.7936 eV 214.00 nm	0.0282	67 -> 74	-0.21562
			69 -> 75	-0.13536
			72 -> 76	0.11059
			72 -> 77	-0.42568
			72 -> 79	0.43585
			72 -> 82	0.10126
20	5.8074 eV 213.49 nm	0.0438	67 -> 74	0.26498
			69 -> 75	0.19135
			72 -> 76	0.10485
			72 -> 77	0.29088
			72 -> 79	0.44338
			72 -> 81	0.17289
			72 -> 82	0.11646

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