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

The curious case of the photochemistry of 2-hydroxyphenylazo-3,5-dimethylisoxazole: Unravelling the process among tautomerization, photoisomerization, and conformational changes

Chitranjan Sah[†], Anjali Mahadevan[†], Pravesh Kumar and Sugumar Venkataramani*

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector-81, Knowledge City, SAS Nagar, Mohali, Punjab – 140306, India.

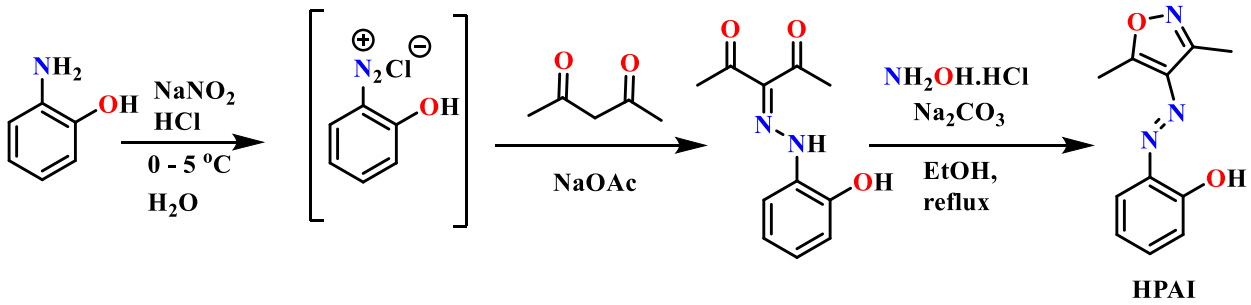
E-mail: sugumarv@iisermohali.ac.in

S1: General methods

All the geometrical optimization for all the conformers of *E*- and *Z*- isomers of HPAI and the transition states have been performed at density functional theory[1] with M06-2X[2] and ωB97X-D[3] functional using cc-pVTZ[4,5] and def2tzvp[6] basis set respectively. The optimized geometries have been verified to minima/transition state by frequency calculations. (That is zero and one imaginary frequency corresponding to minima and transition state respectively). Intrinsic reaction coordinate[7] (IRC) analysis has been performed at the B3LYP/cc-pVTZ level of theory to verify the true transition states[8], which are part of the potential energy surfaces connecting reactant and the product. The relative energies have been estimated using vibrational zero-point energy (ZPE) corrected electronic energy or thermal corrected energy (at 298 K).

For UV-vis spectroscopic studies, spectroscopic grade solvent (DMSO) purchased from Spectrochem has been used. Analysis of UV-vis photoswitching and kinetics studies have been performed on a Cary 60 UV-vis spectrophotometer from Agilent technology attached with a temperature controller Peltier assembly, and data processing was done using OriginPro 2017 (64-bit). The experiments were performed using a quartz Cuvette of 1 cm path length from Sigma Aldrich until the attainment of photostationary state (PSS). For the forward *E*-*Z* and reverse *Z*-*E* photoisomerization steps, the spectral data have been collected under simultaneous irradiation of light at a right angle to the optical beam from the light source of the spectrophotometer. For forward (*E*-*Z*) photoisomerization, a commercial LED torch (Convoy S2+, 365 nm, 40 mW) and for the reverse (*Z*-*E*) photoisomerization a light of wavelength 470 nm from Applied Photophysics (SX20 LED) have been used.

S2: Synthesis and characterization data



Scheme S1. Synthesis of 2-hydroxyphenylazo-3,5-dimethylisoxazole (**HPAI**).

Synthesis of HPAI[9]

In a RB flask 2-hydroxyaniline (5.0 mmol) in distilled water was cooled to 0 °C. Then conc. HCl (37%, 1.6 ml) was added dropwise and stirred. A cold aqueous solution of $NaNO_2$ (5.5 mmol) in 5 ml of distilled water was added dropwise to the reaction mixture. The reaction mixture was stirred at 0 °C for half an hour. In another flask, a mixture of sodium acetate (17.5 mmol) and acetylacetone (5.0 mmol) in water (25 ml) and methanol (3 ml) was cooled to 0 °C, and was charged into the diazonium salt. The reaction was then stirred at room temperature for 2 hours and monitored for completion by TLC. The resulting yellow to orange precipitate was filtered and washed with water and dried under vacuum. Without further purification, the acetylacetone derivative (1.0 mmol) was refluxed along with hydroxylamine hydrochloride (1.5 mmol), and sodium carbonate (1.5 mmol) in 10 ml ethanol. The reaction was monitored by TLC and upon completion, the solvent was evaporated and purified by column chromatography using ethylacetate/hexane mixture.

***(E)*-2-((3,5-dimethylisoxazole-4-yl)diazenyl)phenol**: yellow solid, mp = 114 °C, 201.9 mg, 93% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.53 (s, 3H), 2.70 (s, 3H), 7.01 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.05 (td, *J* = 8.0, 1.2 Hz, 1H), 7.31-7.366 (m, 1H), 7.82 (dd, *J* = 7.9 Hz, 1.6 Hz, 1H), 11.94 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 12.1, 12.1, 118.2, 120.2, 130.8, 132.2, 133.2, 137.7, 152.1, 154.1, 167.4; HRMS (ESI-TOF): calcd. for $C_{11}H_{11}N_3O_2$ $[M+H]^+$ 218.0930, found 218.0923; IR (ATR, cm^{-1}) 3510, 3178, 1591, 1220, 779.

S3: Deposition spectrum of HPAI and computed IR data of various conformers

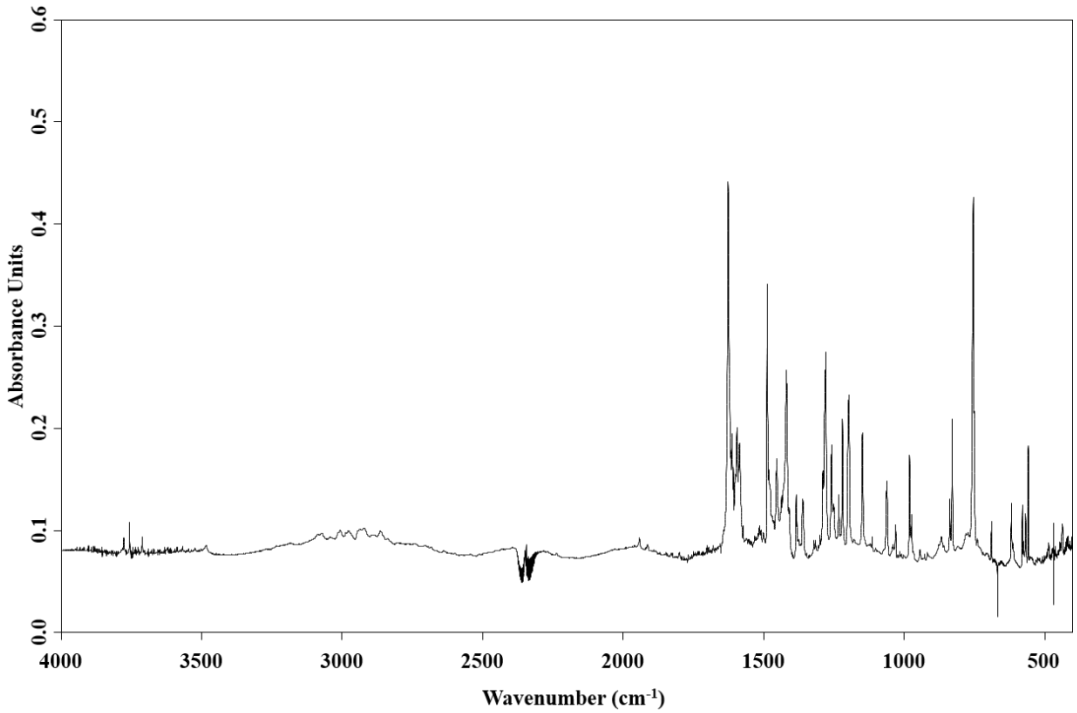


Figure S1. Experimental IR spectrum of **HPAI** isolated in Ar matrix at 4K**.**

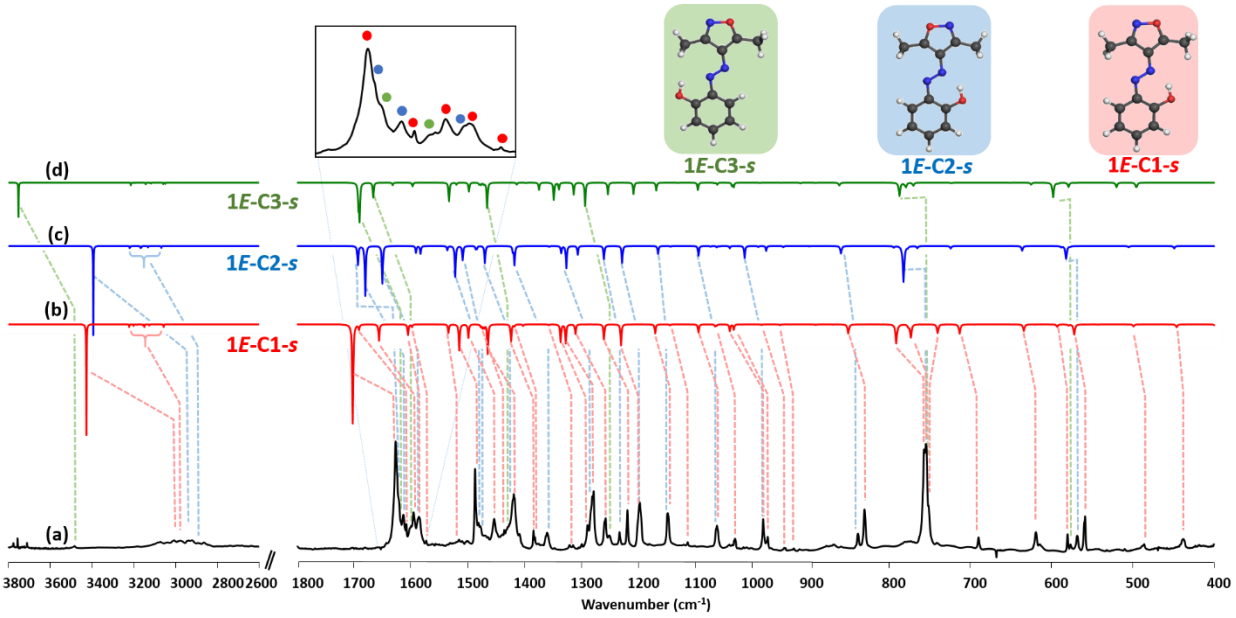


Figure S2. Matrix isolation infrared spectroscopic studies on **HPAI**. (**a**) Deposition spectrum of *E*-**HPAI** (Ar, 4 K); (**b-d**) Computed spectra of the conformers **1*E*-C1-*s*** (red)*,* **1*E*-C2-*s*** (blue), and **1*E*-C3-*s*** (green) (M06-2X/cc-pVTZ level of theory, unscaled). The zoomed portion with assignments of the features around 1600 cm^{-1} corresponding to the three conformers (in their respective colour codes) and the optimized structures of them are included at the top.

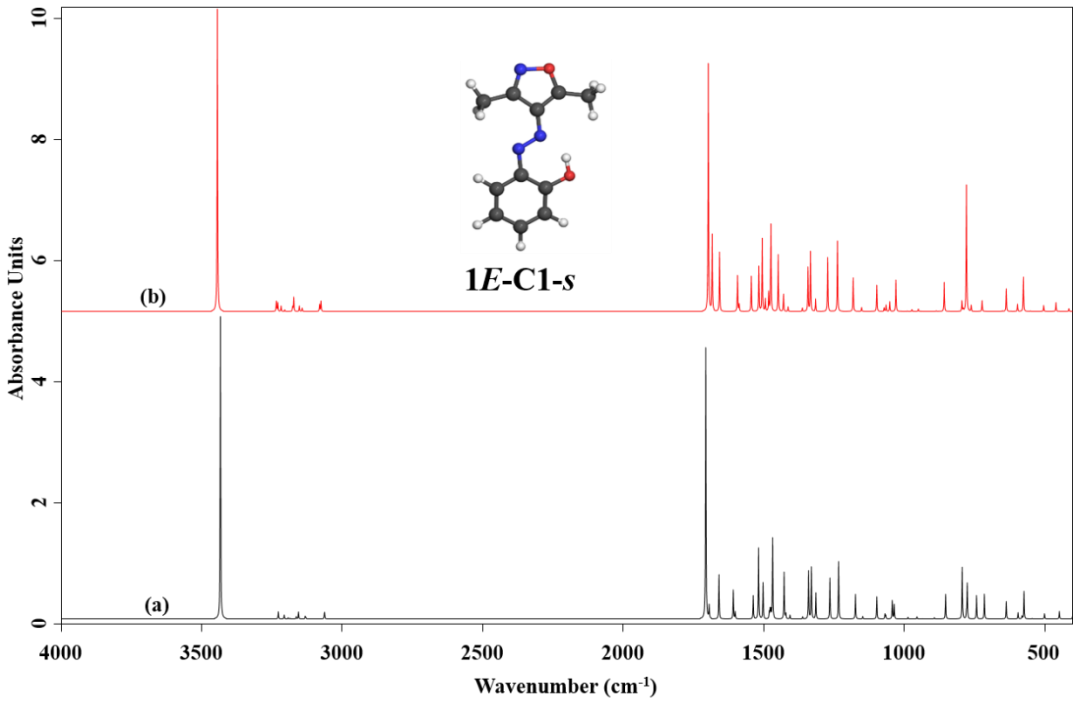


Figure S3. Simulated IR spectra of **1*E*-C1-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 3432.5/3445.2 cm^{-1}; I_{abs}: 290.6/258.6

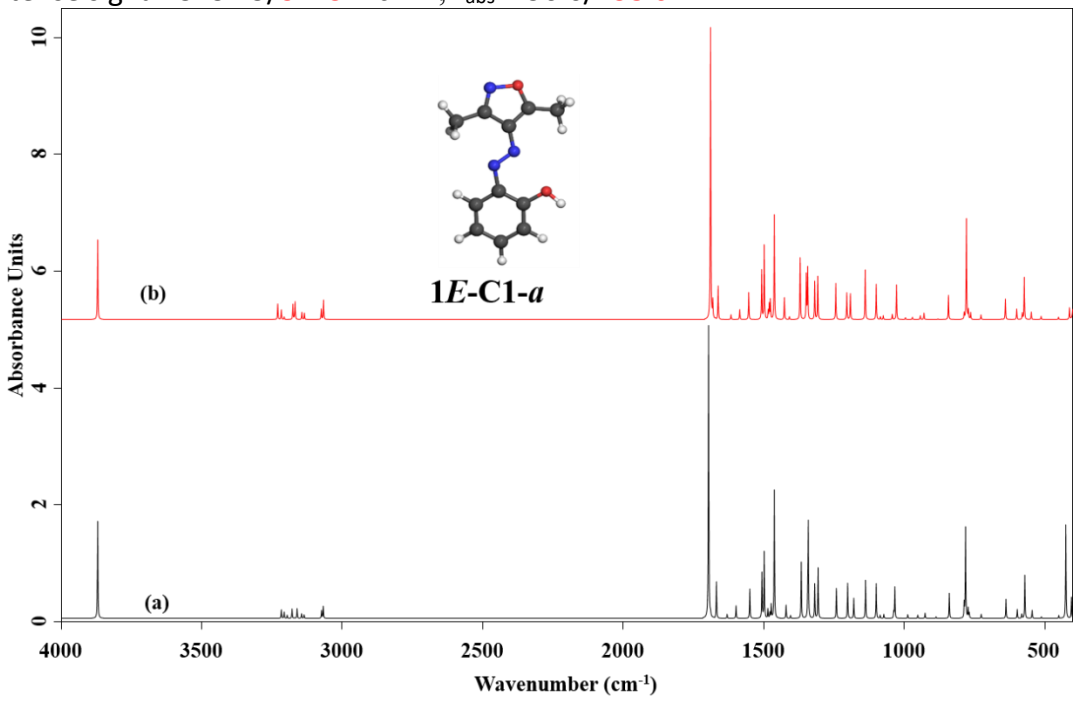


Figure S4. Simulated IR spectra of **1*E*-C1-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1696.5/1689.1 cm^{-1}; I_{abs}: 214.3/213.8

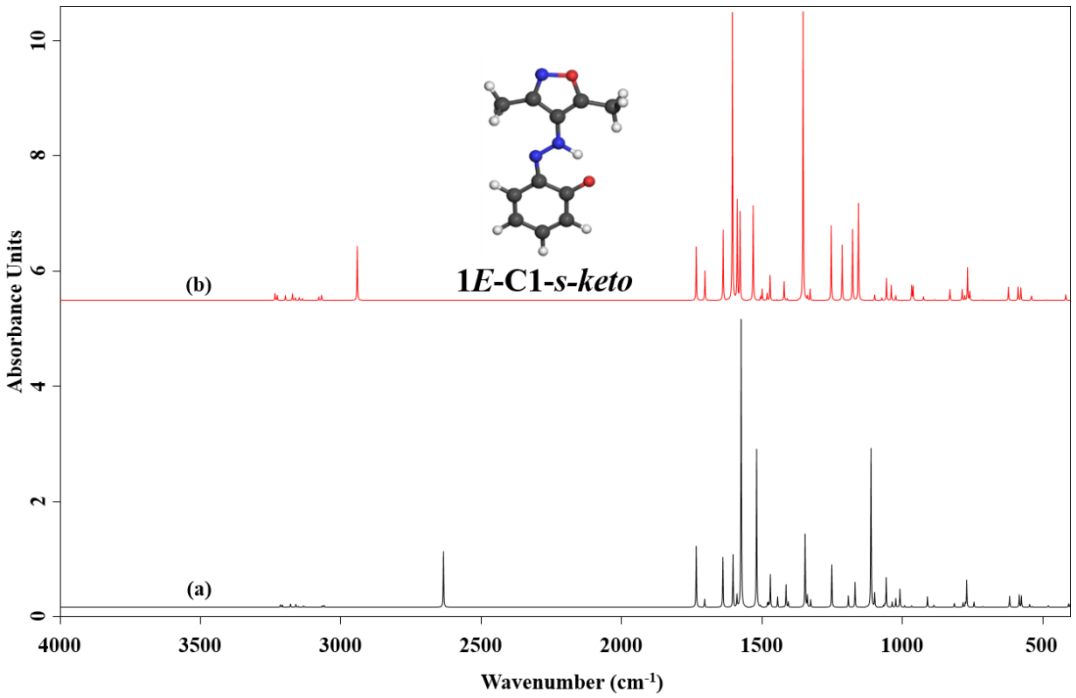


Figure S5. Simulated IR spectra of **1*E*-C1-*s-keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1574.1/1353.3 cm^{-1}; I_{abs}: 619.1/477.4

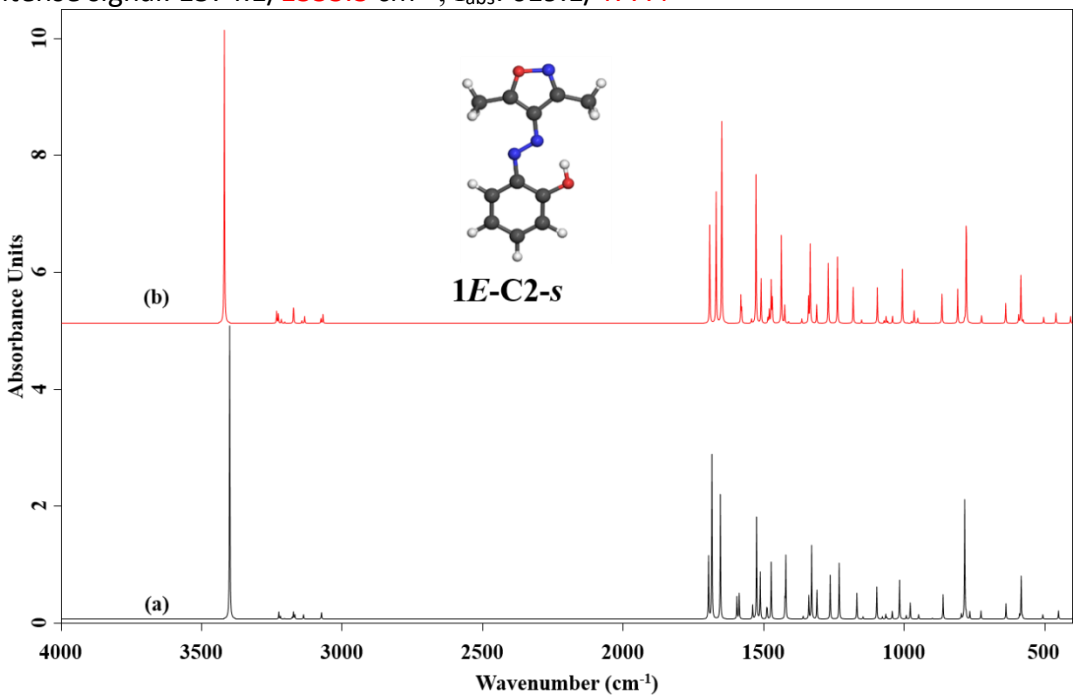


Figure S6. Simulated IR spectra of **1*E*-C2-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 3401.7/3420.6 cm^{-1}; I_{abs}: 274.5/241.2

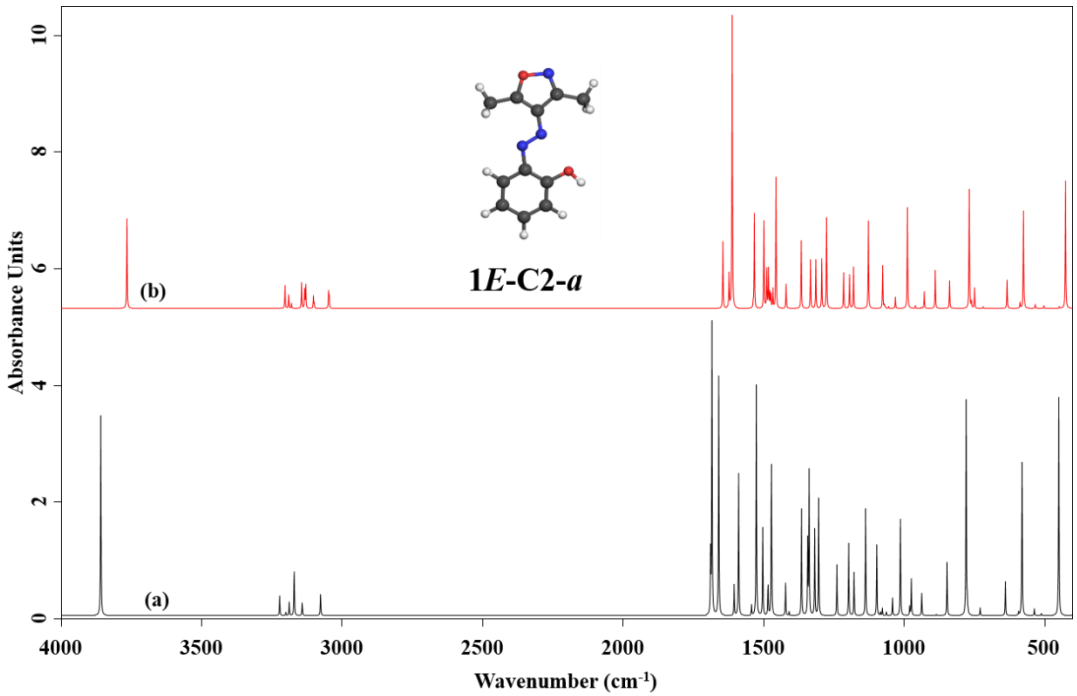


Figure S7. Simulated IR spectra of **1*E*-C2-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1684.3/1612.3 cm^{-1}; I_{abs}: 107.3/165.4

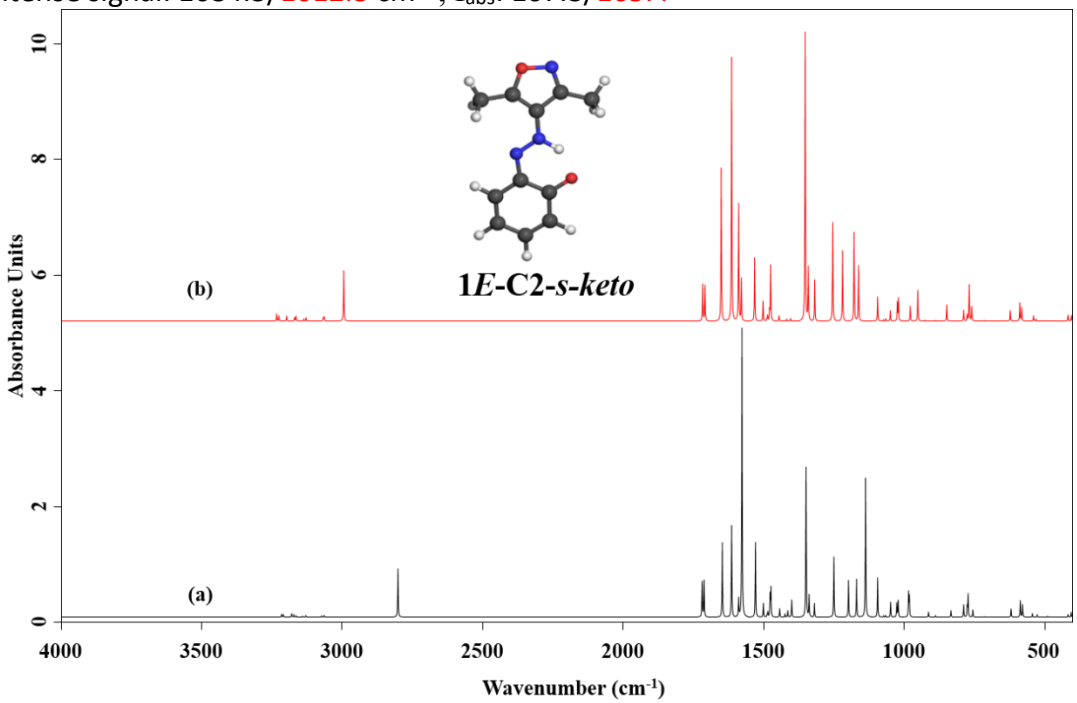


Figure S8. Simulated IR spectra of **1*E*-C2-*s-keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1577.4/1352.8 cm^{-1}; I_{abs}: 563.9/446.9

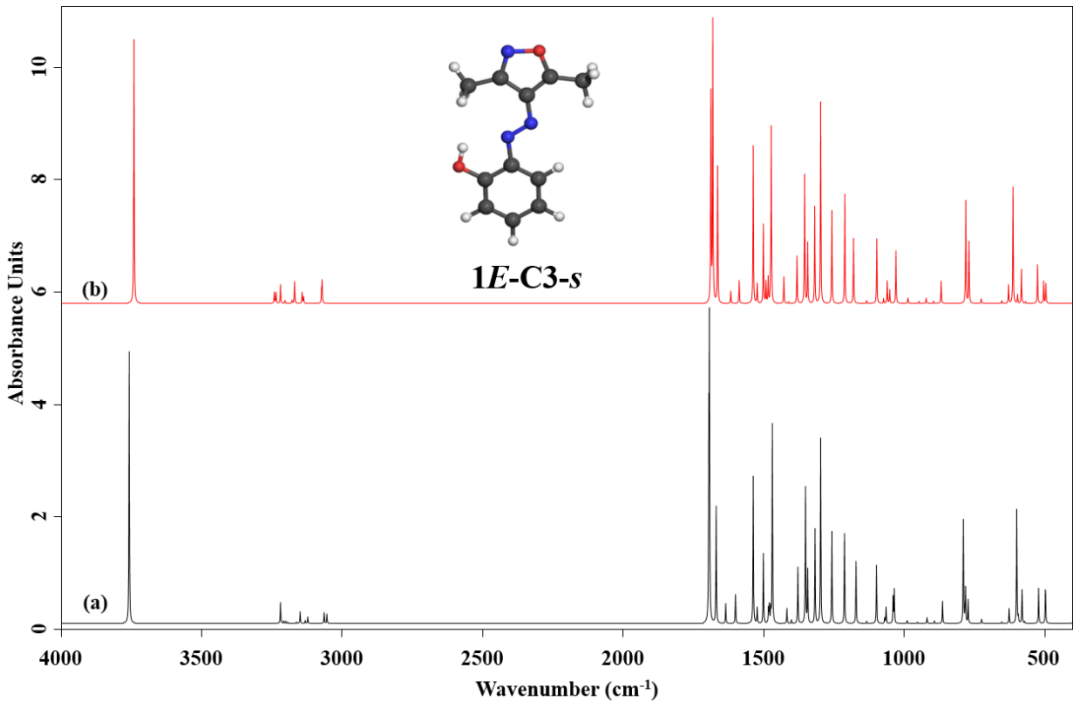


Figure S9. Simulated IR spectra of **1*E*-C3-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1693.8/1681.6 cm^{-1}; I_{abs}: 147.8/146.1

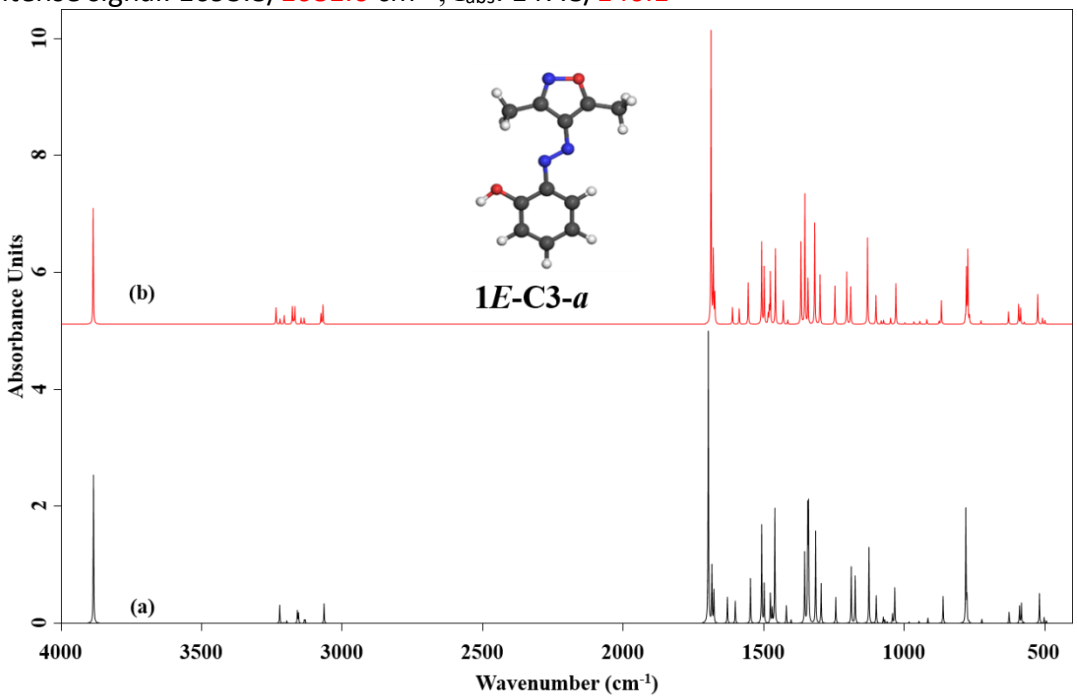


Figure S10. Simulated IR spectra of **1*E*-C3-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1697.0/1687.2 cm^{-1}; I_{abs}: 190.9/197.1

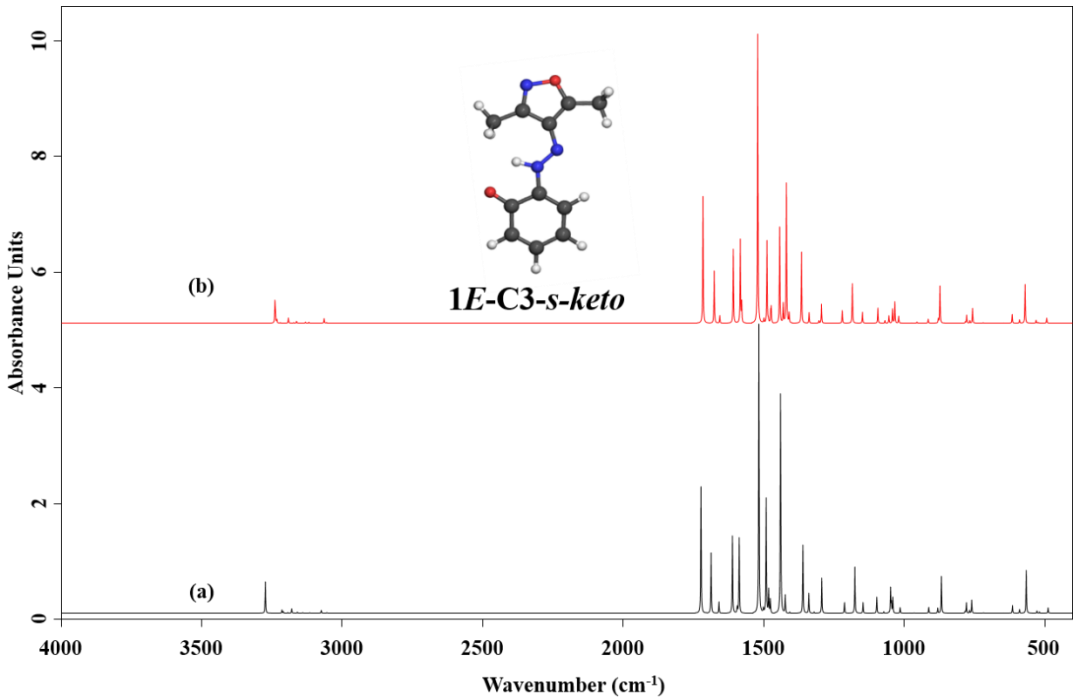


Figure S11. Simulated IR spectra of **1*E*-C3-*s*-*keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1517.7/1521.9 cm^{-1}; I_{abs}: 703.3/753.8

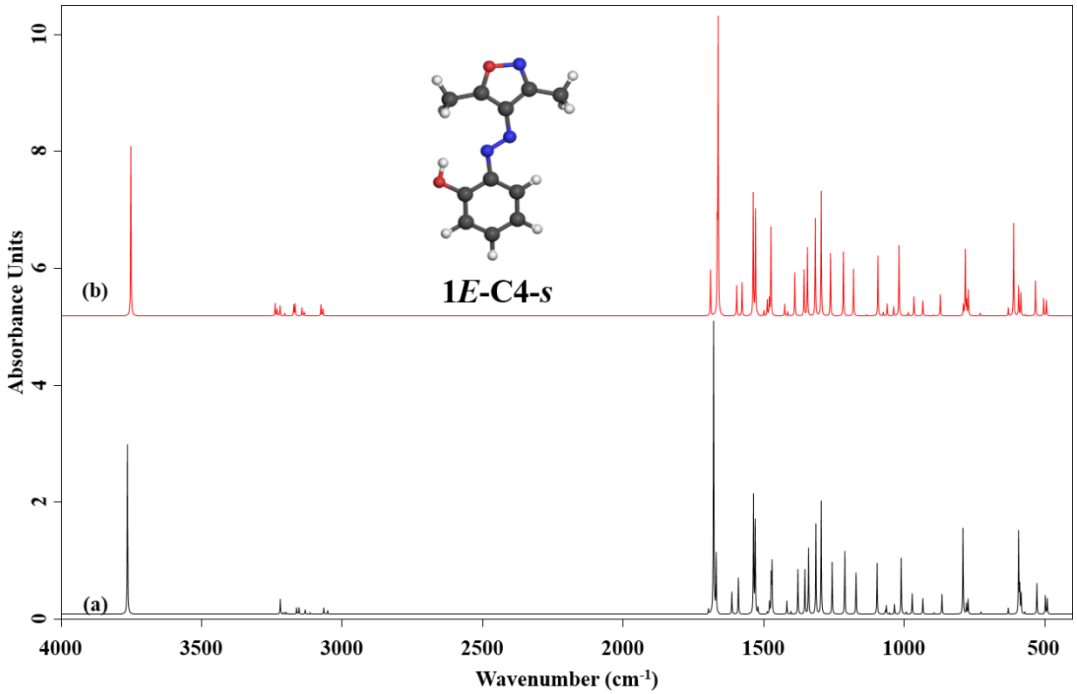


Figure S12. Simulated IR spectra of **1*E*-C4-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1672.3/1662.6 cm^{-1}; I_{abs}: 204.6/200.6

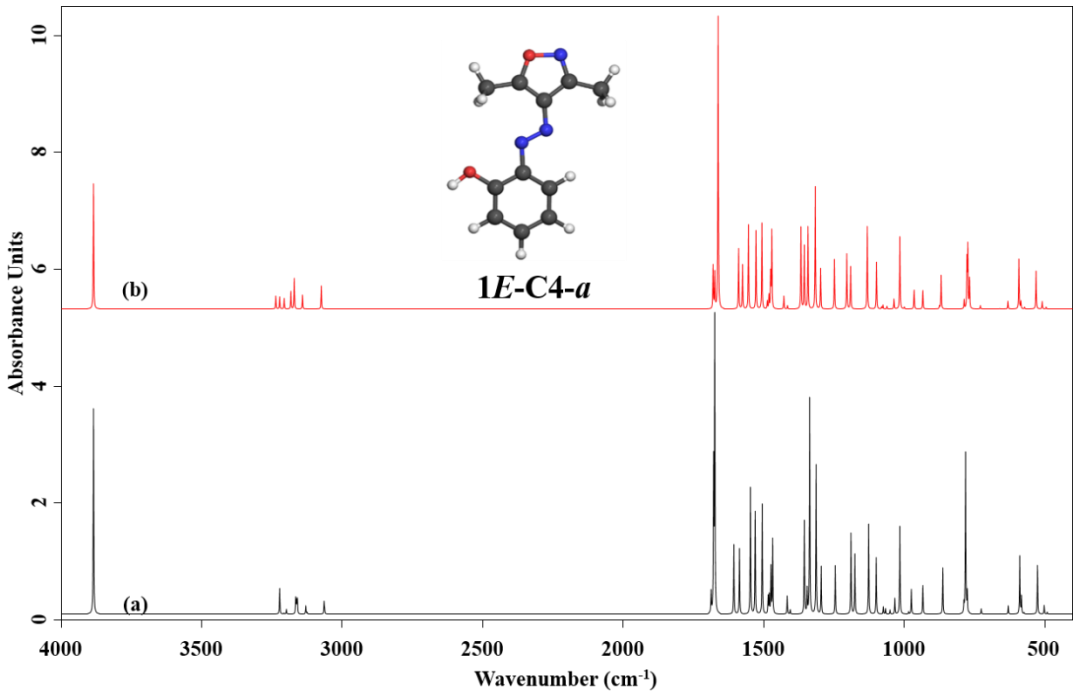


Figure S13. Simulated IR spectra of **1*E*-C4-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1674.2/1662.3 cm^{-1}; I_{abs}: 133.3/175.7

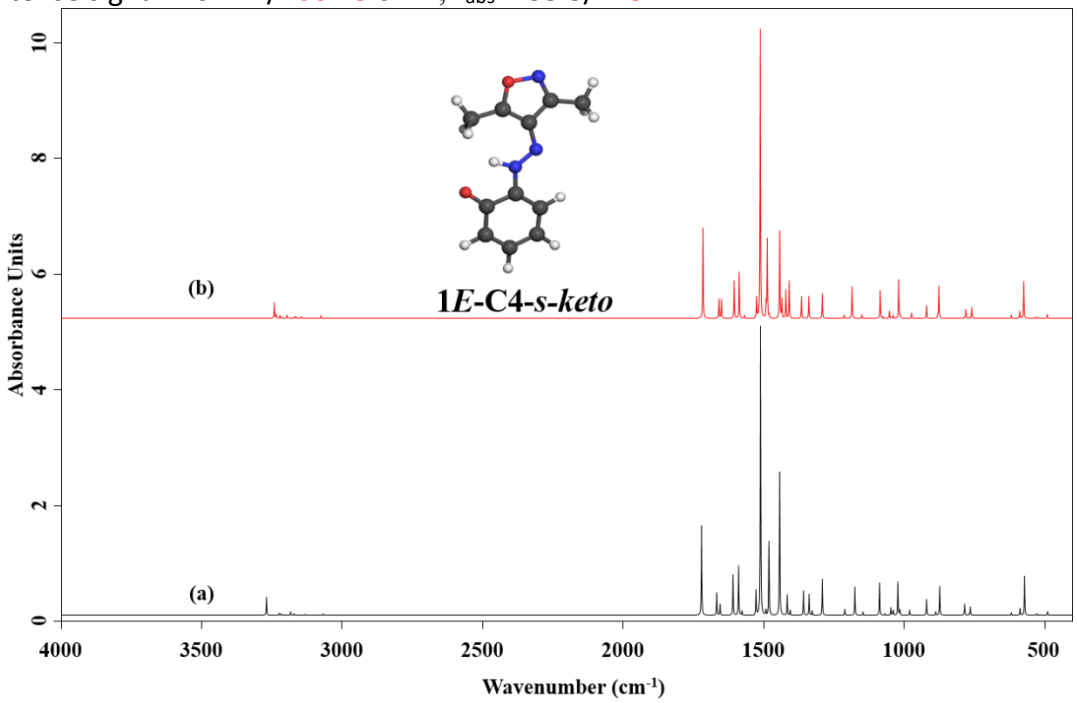


Figure S14. Simulated IR spectra of **1*E*-C4-*s-keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1511.8/1512.1 cm^{-1}; I_{abs}: 873.6/903.8

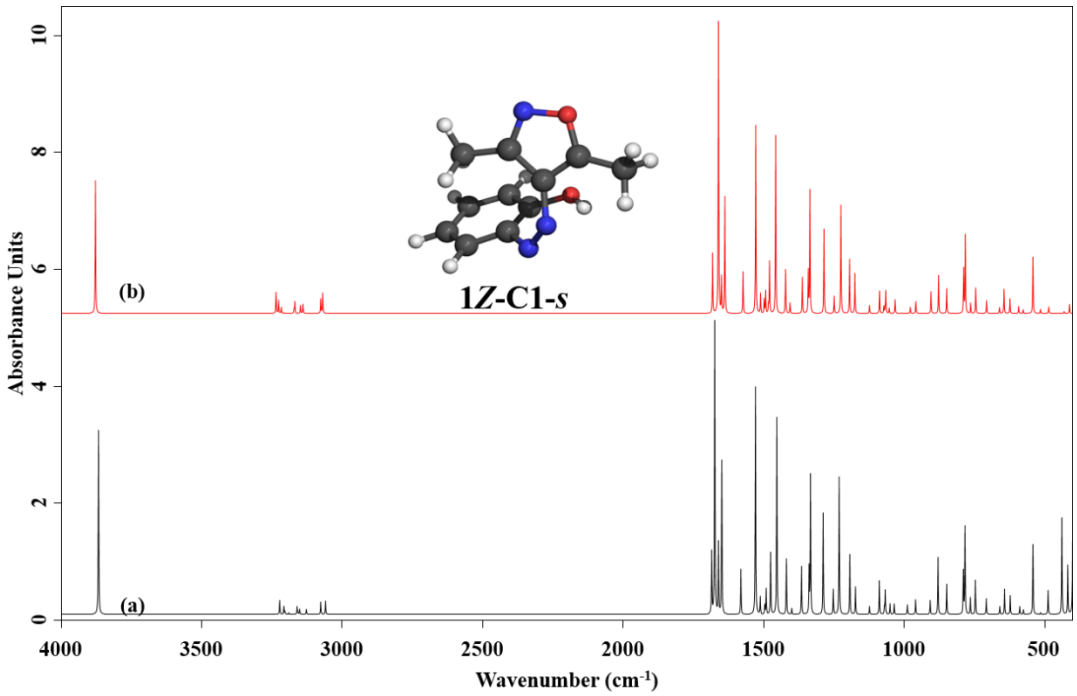


Figure S15. Simulated IR spectra of **1*Z*-C1-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1674.3/1661.7 cm^{-1}; I_{abs}: 103.0/117.0

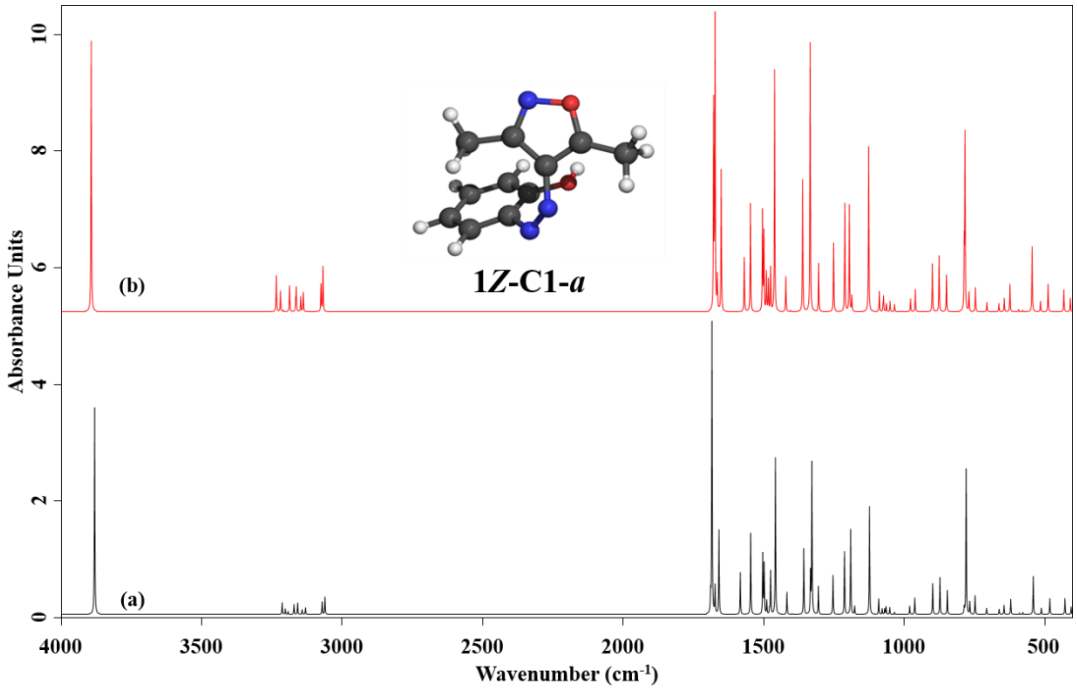


Figure S16. Simulated IR spectra of **1*Z*-C1-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1684.7/1673.3cm^{-1}; I_{abs}: 122.4/78.0

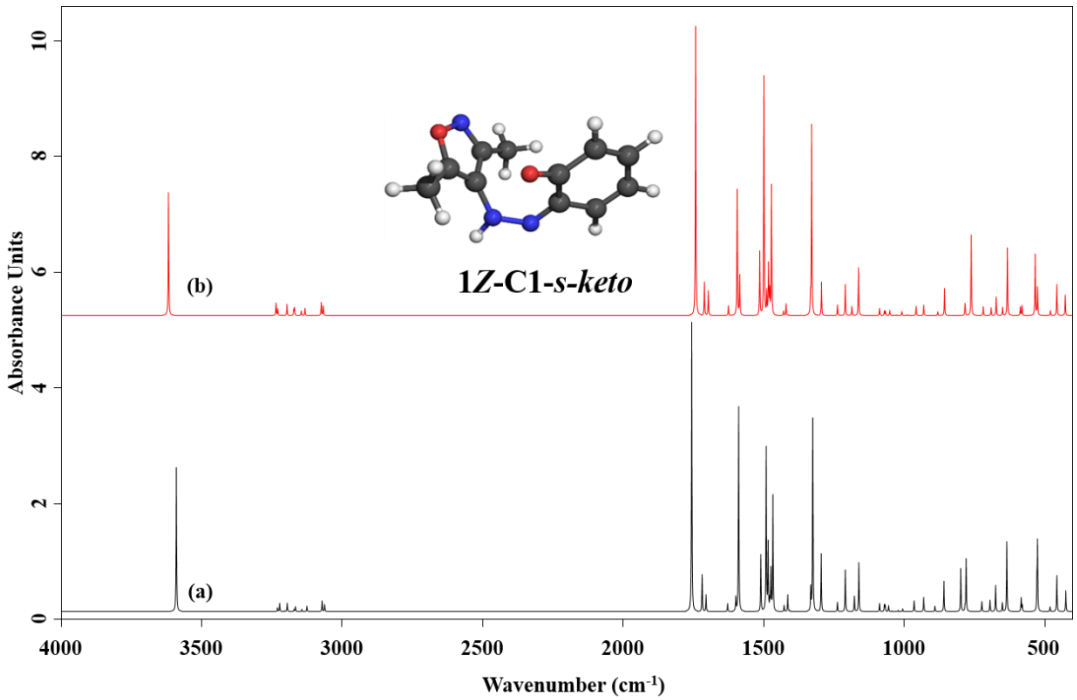


Figure S17. Simulated IR spectra of **1*Z*-C1-*s*-*keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1756.9/1742.1 cm^{-1}; I_{abs}: 228.1/238.9

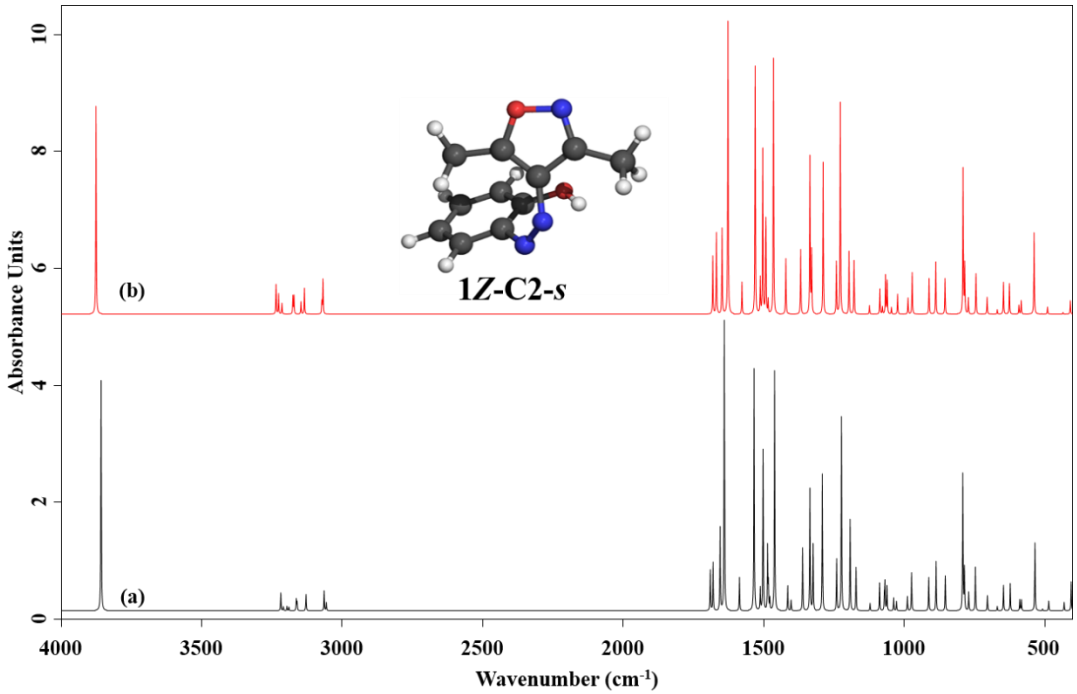


Figure S18. Simulated IR spectra of **1*Z*-C2-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1640.8/1661.7 cm^{-1}; I_{abs}: 82.5/117.0

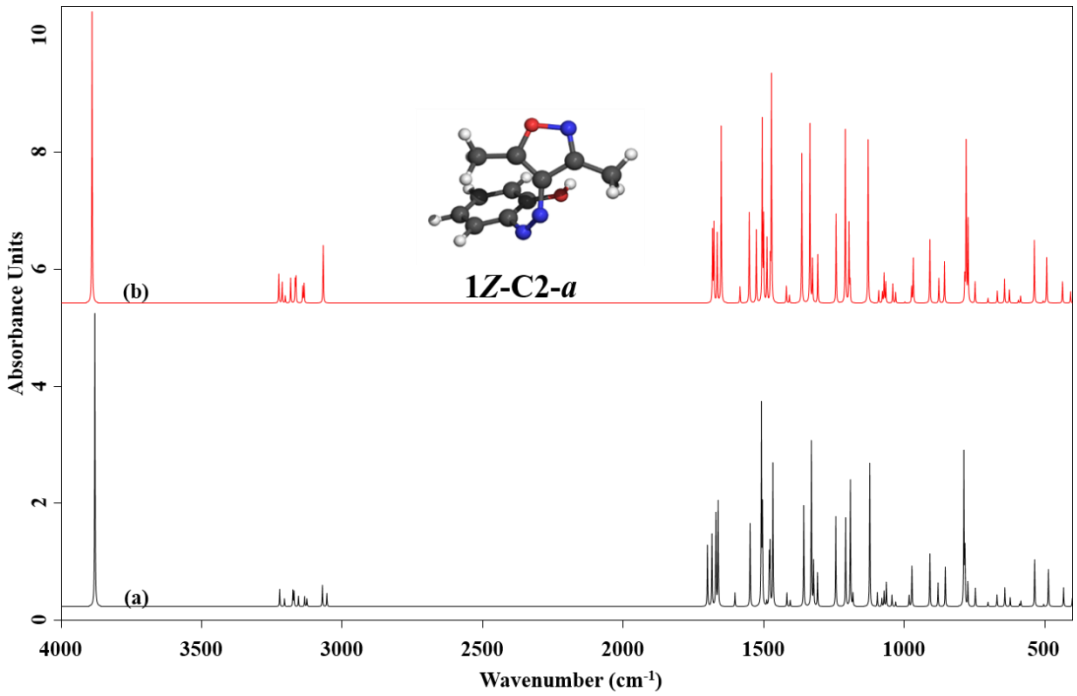


Figure S19. Simulated IR spectra of **1*Z*-C2-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 3881.7/3891.0cm^{-1}; I_{abs}: 90.3 /75.6

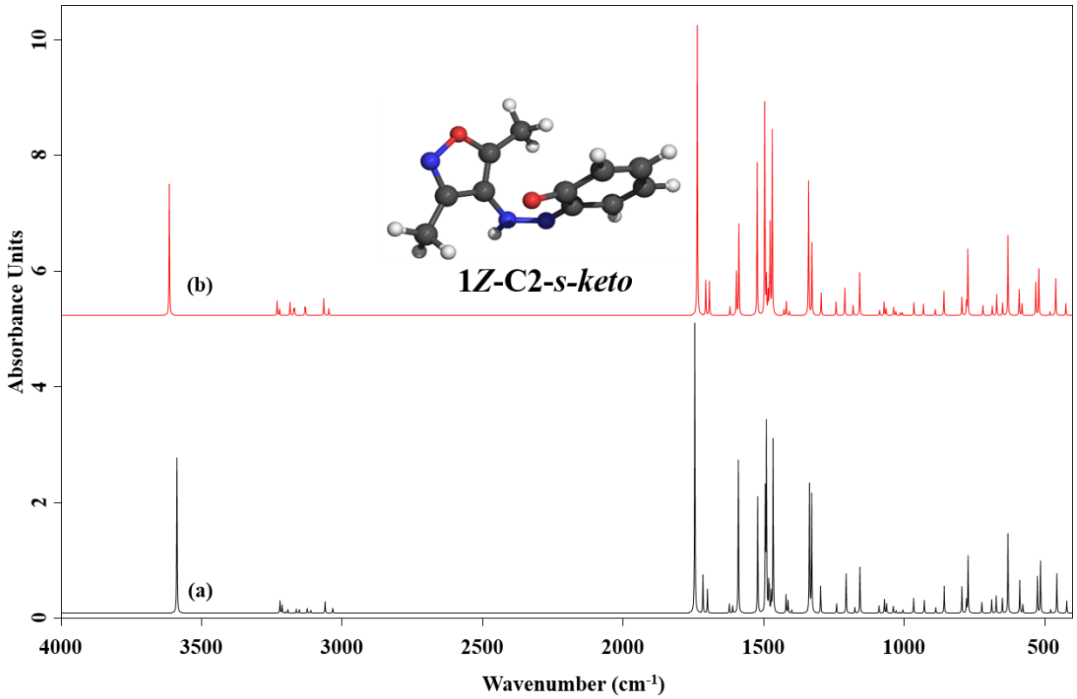


Figure S20. Simulated IR spectra of **1*Z*-C2-*s-keto*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1745.4/1736.4cm^{-1}; I_{abs}: 219.5/223.0

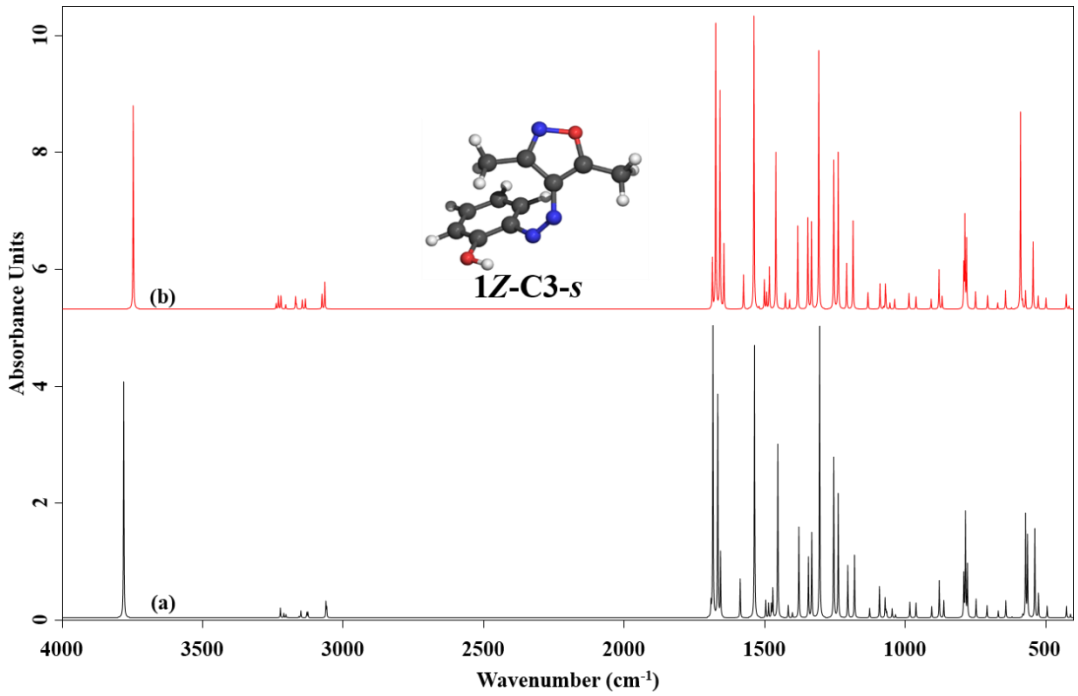


Figure S21. Simulated IR spectra of **1*Z*-C3-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1304.1/1538.0 cm^{-1}; I_{abs}: 119.5/118.2

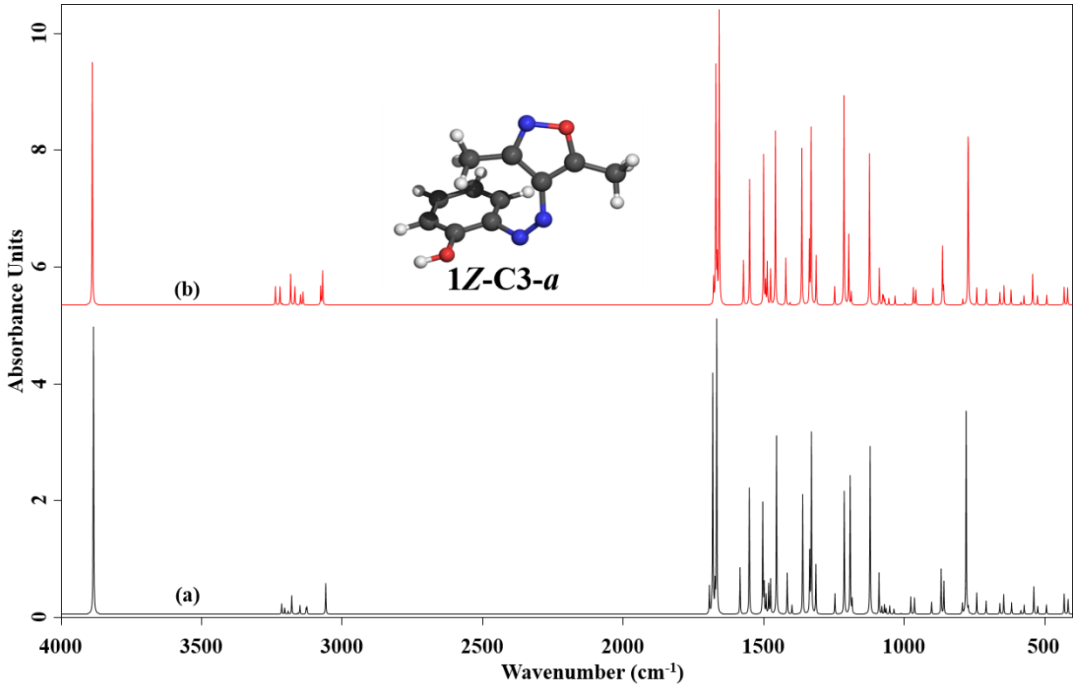


Figure S22. Simulated IR spectra of **1*Z*-C3-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1667.5/1658.1 cm^{-1}; I_{abs}: 105.5/102.2

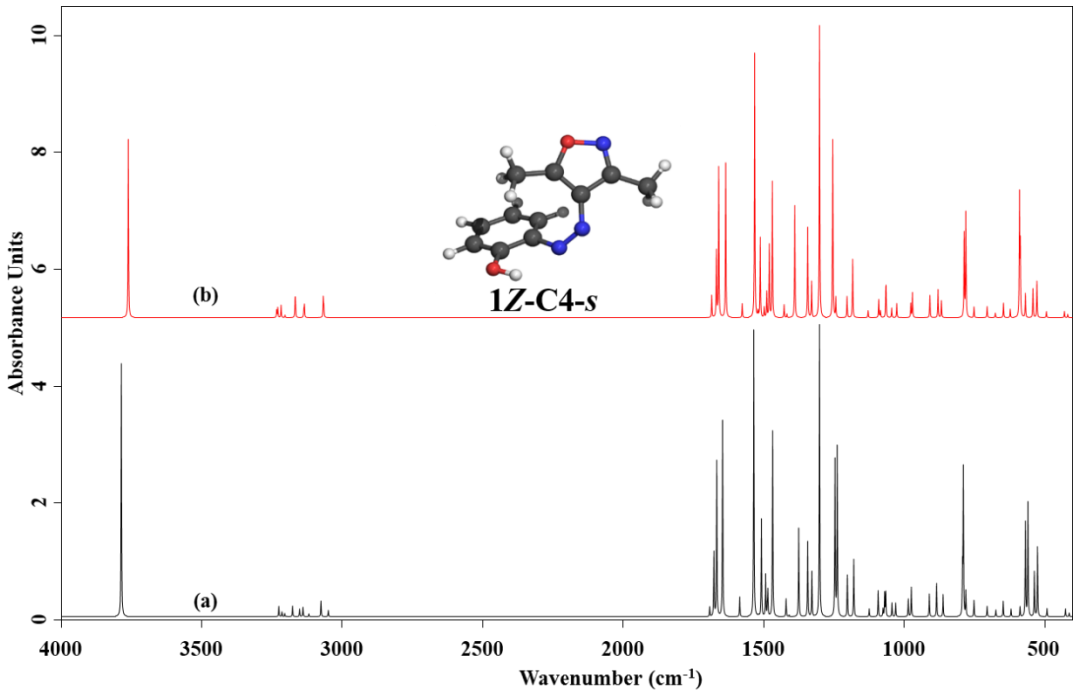


Figure S23. Simulated IR spectra of **1*Z*-C4-*s*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 1301.7/1301.8cm^{-1}; I_{abs}: 127.9/109.8

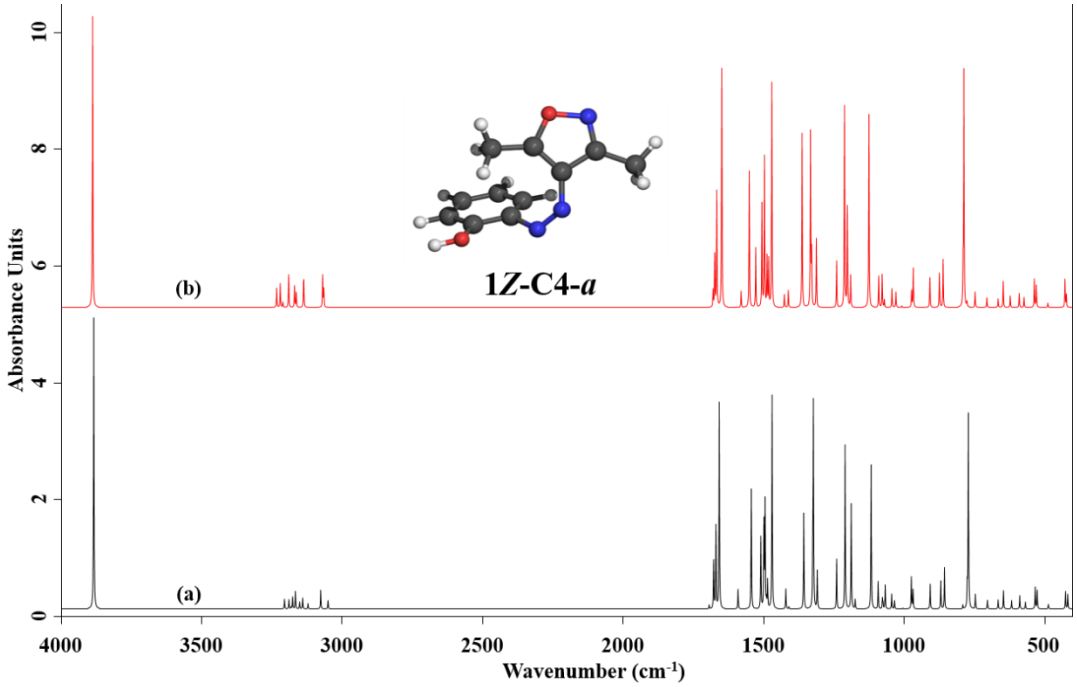


Figure S24. Simulated IR spectra of **1*Z*-C4-*a*** based on M06-2x/cc-pVTZ (black) and ωB97X-D/def2tzvp (red) harmonic vibrational frequencies, (unscaled).
Most intense signal: 3885.8/3889.5 cm^{-1}; I_{abs}: 102.8/84.6

S4: AIM analysis

Table S1. Electron density [$\rho(r_c)$], Laplacian of electron density [$\nabla^2\rho(r_c)$], local electronic kinetic energy density [$G(r_c)$], local electronic potential energy density [$V(r_c)$] and hydrogen bonding energy (E_{HB}) values for the hydrogen bonded interactions in the different conformers of HPAI at M06-2x/cc-pVTZ. The values for $\rho(r_c)$, $\nabla^2\rho(r_c)$, $G(r_c)$ and $V(r_c)$ are given in atomic units and for E_{HB}, in kcal mol^{-1}

Species	Interaction	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$G(r_c)$	$V(r_c)$	E_{HB}
1*E*-C1-*s*	N---O-H	0.04777	0.09419	0.03378	-0.04402	-13.8
1*E*-C2-*s*	N---O-H	0.04898	0.09449	0.03461	-0.04559	-14.3
1*E*-C3-*s*	N---O-H	0.02250	0.09790	0.02150	-0.01852	-5.8
1*E*-C4-*s*	N---O-H	0.02234	0.09720	0.02132	-0.01834	-5.8
1*Z*-C1-*s*	H-O---C	0.01225	0.04654	0.00964	-0.00765	-2.4
1*Z*-C2-*s*	H-O---C	0.01189	0.04583	0.00943	-0.00740	-2.3
1*Z*-C3-*s*	H-O---C	0.01127	0.04023	0.00834	-0.00663	-2.1
1*Z*-C4-*s*	H-O---C	0.01053	0.03846	0.00788	-0.00613	-1.9

S5: Assignment of conformers (experiment vs computational)

Table S2. Computed harmonic frequencies (bold: absolute and normal: scaled) and intensities of **1*E*-C1-*s***, **1*E*-C2-*s*** (blue) and **1*E*-C3-*s*** (green) at M06-2X/cc-pVTZ level of theory along with the experimental frequency and intensity of the deposited **HPAI** (Ar matrix, 4 K).

Normal Mode	Symmetry	Computed				Experimental (Ar, 4 K)		Tentative Assignments
		$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*E*-C1-*s***	$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*E*-C2-*s***	$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*E*-C3-*s***	I_{rel}	$\bar{\upsilon}$ (cm^{-1})	I_{rel}	
75	A			**3759.6**, 3646.8	49	3484.0	2	ν(OH)
75	A+ A′	**3434.5**, 3331.5	**3401.7**, 3299.7		100	3072.0 3041.5 3007.5 2987.5 2974.5 2944.5 2936.5 2921.0 2864.0	br	ν(OH)
64	A	**1706.1**, 1654.9			90	1627.0	100	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)+δ_{ph}(NNC)+ ν_{iso}(CC)+ν_{iso}(CN)
64	A′		**1696.6**, 1645.7		21	1623.5	o	ν_{ph}(CC)+δ(OH)+ δ_{ph}(CH)
63	A			**1693.8**, 1643.0	51	1621.0	o	ν_{ph}(CC)+ν_{iso}(CC)+ ν_{iso}(CN)+ν(NN)+$\delta_{iso}(CH_3)$+$\delta_{iso}(CNN_{azo})$
63	A′		**1684.0**, 1633.5		53	1613.0	29	ν_{ph}(CC) + ν_{iso}(CC) +ν_{iso}(CN)+ν(NN)+$\delta_{iso}(CH_3)$+δ(OH)
63	A	**1694.4**, 1643.6			4	1608.0	19	ν_{ph}(CC)+ ν_{iso}(CC)+δ(OH)+ δ_{ph}(CH)
62	A			**1669.4**, 1619.4	42	1599	7	ν_{ph}(CC)+δ(OH)+ δ_{ph}(CH)
62	A	**1659.6**, 1609.8			15	1595.0	31	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)+ν(NN)
61+62	A	**1608.2**, 1560.0	**1654.2**, 1604.6		10+ 43	1585.5	27 o	ν(NN)+ δ(OH)+δ_{ph}(CH)+ ν_{iso}(CN) δ(OH)+ ν_{ph}(CC)+ δ_{ph}(CH)+ ν_{iso}(CC)
60	A	**1601.2**, 1553.2			2	1573.0	5	ν_{iso}(CN)+ $\nu_{iso}(CCH_3)$+ $\delta_{iso}(CH_3)$+ ν_{azo}(NN)
59	A	**1537.1**, 1491.0			8	1515.3	<5	δ_{ph}(CH)+δ(OH)
59	A			**1537.0**, 1490.9		1500.5	<5	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)+ ν_{ph}(CO)

58	A	**1518.6**, 1473.0			23	1487.0	73	$\nu_{ph}(CC)+\delta_{ph}(CH)+\nu(NN)+\nu_{ph}(CO)$
58	A’		**1525.4**, 1479.7		35	1481.5	21	$\delta_{ph}(CH)+\nu_{iso}(CC)+\delta(OH)+\delta_{iso}(CH_3)$
57	A’		**1512.8**, 1467.4		16	1477.0	18	$\nu_{ph}(CC)+\delta_{ph}(CH)+\nu(NN)+\nu_{ph}(CO)+\delta_{iso}(CH_3)$
57	A	**1502.7**, 1457.6			12	1453.5	25	$\nu_{iso}(CC)+\delta_{iso}(CH_3)$
56	A	**1480.7**, 1436.3			2	1436.0	5	$\delta_{iso}(CH_3)+\nu_{iso}(CN_{azo})+\nu_{iso}(CC)$
53	A’		**1473.2**, 1429.0		15	1421.0	47	$\delta_{iso}(CH_3)$
53	A	**1468.6**, 1424.5			27	1419.0	49	$\nu_{ph}(CC)+\nu_{iso}(CC)+\delta_{iso}(CH_3)+\delta(OH)+\delta_{ph}(CH)$
52	A	**1427.4**, 1384.6			16	1385.0	19	$\nu_{ph}(CC)+\delta_{ph}(CH)+\delta(OH)$
51	A	**1421.5**, 1378.9			2	1382.0	8	$\delta_{iso}(CH_3)$
51	A’		**1421.4**, 1378.8		21	1361.0	16	$\delta_{ph}(CH)+\delta(OH)+\delta_{iso}(CH_3)$
49	A	**1421.5**, 1378.9			1	1321.5	5	$\delta_{ph}(CH)$
48	A	**1340.3**, 1300.1			16	1290.0	22	$\delta_{iso}(CH_3)+\nu_{iso}(ring)$
47	A’		**1329.8**, 1289.9		25	1281.5	50	$\nu_{ph}(CO)+\nu_{ph}(CC)+\delta_{ph}(CH)+\delta(OH)$
47	A	**1330.7**, 1290.8			17	1279.0	55	$\nu_{ph}(CO)+\nu_{ph}(CC)+\delta_{ph}(CH)+\delta(OH)$
46	A	**1314.0**, 1274.6			9	1258.0	28	$\nu_{ph}(CNazo)+\nu_{iso}(CN_{azo})\delta(OH)+\delta_{ph}(CH)+\delta_{iso}(CH_3)$
46	A			**1297.1**, 1258.2	34	1251.5	12	$\nu_{ph}(CC)+\nu_{iso}(CC)+\nu_{ph}(CO)+\delta(OH)+\delta_{ph}(CH)$
45	A’		**1263.8**, 1225.9		15	1233.5	15	$\nu_{ph}(CN_{ahzo})+\nu_{iso}(CN_{azo})+\delta(OH)+\delta_{ph}(CH)$
45	A	**1264.5**, 1226.6			14	1220.0	36	$\nu_{iso}(CN_{azo})+\delta(OH)+\delta_{ph}(CH)$
44+44	A+ A’	**1233.5**, 1196.5	**1231.7**, 1194.7		19+19	1198.0	44	$\nu_{ph}(CNazo)+\delta(OH)+\delta_{ph}(CH)+\nu_{ph}(CC)$
43+43	A+A’	**1173.5**, 1138.3	**1168.5**, 1133.4		8+9	1149.0	31	$\delta_{ph}(CH)$
42	A	**1147.7**, 1113.3				1114.0	<5	$\delta_{ph}(CH)$
41+41	A+A’	**1097.9**, 1064.9	**1097.3**,1064.4		7+11	1062.5	21	$\nu_{iso}(C\text{-}CH_3)+\delta_{ph}(CH)+\delta_{iso}(CH_3)+\delta_{Ph}(ring)+\delta_{iso}(CCO)$
40	A	**1068.4**, 1036.3			2	1031.0	10	$\delta_{ph}(CH)$
37+36	A+A’	**1042.8**, 1011.6	**1016.1**, 985.6		6+ 13	981.5	30	$\gamma_{iso}(CH_3)+\nu_{iso}(ON)$
36	A	**1035.2**, 1004.2			5	973.5	13	$\delta_{iso}(CH_3)+\delta_{iso}(ring)$
34	A	**986.9**, 957.3			1	943.5	5	$\gamma_{ph}(CH)$
33	A	**954.3**, 925.9			1	927.5	5	$\delta_{iso}(CH_3)+\nu_{iso}(ON)$
30	A’		**861.4**, 835.5		8	838.0	15	$\tau_{iso}(CN_{azo})+\tau_{iso}(CH_3)+\tau_{Ph}(ring)$
30	A	**852.6**, 827.0			8	830.0	38	$\delta_{Ph}(ring)+\delta_{ph}(CH)+\nu_{ph}(CO)+\delta(NN)+\nu_{iso}(CC)$
29	A	**793.5**, 769.7			17	756.5	93	$\gamma(OH)+\gamma_{iso}(CH_3)+\gamma_{iso}(ring)+\gamma_{ph}(CH)$
26+27+29	A + A″+A	**775.4**, 752.1	**784.4**, 760.9	**789.3**, 765.6	12 + 38 + 19	754.5	98	$\gamma_{ph}(CH)+\gamma_{ph}(CN_{azo})+\gamma(OH)$
25	A	**742.4**, 720.1			8	751.0	46	$\gamma_{ph}(CH)+\gamma(OH)+\gamma_{iso}(CH_3)+\gamma_{iso}(ring)$
24	A	**714.5**, 693.1			8	690.0	11	$\delta_{Ph}(ring)+\delta_{iso}(ring)$

22	A	**636.2**, 617.1			6	619.5	17	δ_{Ph}(ring)+δ_{iso}(ring)
21	A	**594.3**, 576.4			2	580.0	16	τ(OH)+ τ_{iso}(CH_3)+ τ_{Ph}(ring)
22	A			**599.4**, 581.4	21	576.5	7	γ(OH)
20	A′		**583.5**, 566.0		14	568.5	15	γ_{iso}(CH_3)+δ_{iso}(ring)+$\underline{\tau}$(CNNC)+$\underline{\tau}_{Ph}$(ring)
19	A	**573.6**, 556.4			9	559.0	34	$\underline{\tau}_{Ph}$(ring)+δ_{iso}(ring)+δ_{ph}(N_{azo}CC)+ $\underline{\tau}$(OH)+$\underline{\tau}$(CNNC)
17	A	**500.8**, 485.8			2	486.0	5	γ_{ph}(CH)+γ_{ph}(CN_{azo})
16	A	**447.9**, 434.5			3	438.0	9	$\underline{\tau}_{Ph}$(ring)+$\underline{\tau}_{iso}$(ring)+$\underline{\tau}$(CNNC)

br - broad; o - overlap; ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ – torsion; Scaling factor used: 0.97 below 2000 cm^{-1} and 0.95 above 2000 cm^{-1}.

Table S3. Computed harmonic frequencies and intensities of **1*E*-C1-*s***, **1*E*-C2-*s*** (blue) and **1*E*-C3-*s*** (green) at ωB97X-D /def2tzvp level of theory (unscaled) along with the experimental frequency and intensity of the deposited **HPAI** (Ar matrix, 4 K)

Normal Mode	Symmetry	Computed				Experimental (Ar, 4 K)		Tentative Assignments
		$\bar{\nu}_{cal}$ (cm^{-1}) **1*E*-C1-*s***	$\bar{\nu}_{cal}$ (cm^{-1}) **1*E*-C2-*s***	$\bar{\nu}_{cal}$ (cm^{-1}) **1*E*-C3-*s***	I_{rel}	$\bar{\nu}$ (cm^{-1})	I_{rel}	
75	A			3742.9	53	3484.0	2	ν(OH)
75	A	3445.2	3420.6		100	3072.0 3041.5 3007.5 2987.5 2974.5 2944.5 2936.5 2921.0 2864.0	br	ν(OH)
64	A	1697.2			82	1627.0	100	ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)+ δ_{ph}(NNC)+ ν_{iso}(CC)+ ν_{iso}(CN)
63	A′		1669.5		42	1613.0	29	ν_{ph}(CC)+ ν_{iso}(CC)+ ν_{iso}(CN)+ ν(NN)+ δ_{iso}(CH_3)+ δ(OH)
63	A			1681.7	56	1608.0	19	ν_{ph}(CC)+ ν_{iso}(CC)+ν_{iso}(CN)+ ν(NN)+ δ_{iso}(CH_3)+ δ_{iso}(CNN_{azo})
62	A	1657.7			20	1595.0	31	ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)+ ν(NN)
61+62	A	1593.7	1649.5		12+69	1585.5	27	
58	A	1517.6			15	1487.0	73	ν_{ph}(CC)+ δ_{ph}(CH)+ ν(NN)+ ν_{ph}(CO)

57	A	1505.5			24	1481.5	21	ν_{iso}(CC)+ δ_{iso}(CH_3)
53	A	1474.3			27	1453.5	25	ν_{iso}(CC)+ δ_{iso}(CH_3)
58	A′		1527.7		47	1419.5	49	ν_{ph}(CC)+ ν_{iso}(CC)+δ_{iso}(CH_3)+ δ(OH)+ δ_{ph}(CH)
52	A	1448.6			19	1385.0	19	ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)
51	A		1425.3		6	1361.0	16	δ_{ph}(CH)+δ(OH)+ δ_{iso}(CH_3)
49	A	1362.4			1	1321.5	5	δ_{ph}(CH)
48	A	1342.2			15	1290.0	22	δ_{iso}(CH_3)+ ν_{iso}(ring)
47	A		1334.6		27	1281.5	50	ν_{ph}(CO)+ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)
47	A	1333.5			20	1279.0	55	ν_{ph}(CO)+ ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)
46	A	1315.9			4	1258.0	28	ν_{ph}(CNazo)+ ν_{iso}(CN_{azo}) δ(OH)+ δ_{ph}(CH)+ δ_{iso}(CH_3)
46	A			1297.4	41	1251.5	12	ν_{ph}(CC)+ ν_{iso}(CC)+ ν_{ph}(CO)+ δ(OH)+ δ_{ph}(CH)
45	A		1270.4		21	1233.5	15	ν_{ph}(CN_{ahzo})+ν_{iso}(CN_{azo})+δ(OH)+δ_{ph}(CH)
45	A	1272.0			18	1220.0	36	ν_{iso}(CN_{azo})+ δ(OH)+ δ_{ph}(CH)
44	A	1237.2			23	1198.0	44	ν_{ph}(CNazo)+ δ(OH)+ δ_{ph}(CH)+ ν_{ph}(CC)
43	A	1181.2			11	1149.0	31	δ_{ph}(CH)
41	A	1097.6			9	1062.5	21	ν_{iso}(C-CH_3)+ δ_{ph}(CH)+ δ_{iso}(CH_3)+ δ_{Ph}(ring)+ δ_{iso}(CCO)
40	A	1072.0			1	1031.0	10	δ_{ph}(CH)
37	A	1051.4			3	981.5	30	γ_{iso}(CH_3)+ ν_{iso}(ON)
36	A	1029.6			10	973.5	13	δ_{iso}(CH_3)+ δ_{iso}(ring)
30	A		865.5		10	838.0	15	τ_{iso}(CN_{azo})+ τ_{iso}(CH_3)+ τ_{Ph}(ring)
30	A	857.3			10	830.0	38	δ_{Ph}(ring)+δ_{ph}(CH)+ ν_{ph}(CO)+ δ(NN)+ ν_{iso}(CC)
29	A	794.8			3	756.5	93	γ(OH)+ γ_{iso}(CH_3)+ γ_{iso}(ring)+ γ_{ph}(CH)
27+ 27+ 28	A + A″+ A	778.1	779.7	780.6	41 + 23 + 13	754.5	98	γ_{ph}(CH)+ γ_{ph}(CN_{azo})+ γ(OH)
24	A	722.6			4	690.0	11	δ_{Ph}(ring)+δ_{iso}(ring)
22	A	636.8			8	619.5	17	δ_{Ph}(ring)+ δ_{iso}(ring)
22	A			612.4	23	580.0	16	γ(OH)
20	A′		584.9		15	568.5	15	γ_{iso}(CH_3)+ δ_{iso}(ring)+ $\underline{\tau}$(CNNC)+ $\underline{\tau_{Ph}}$(ring)
19	A	575.6			11	559.0	34	$\underline{\tau_{Ph}}$(ring)+ δ_{iso}(ring)+ δ_{ph}(N_{azo}CC)+ $\underline{\tau}$(OH)+ $\underline{\tau}$(CNNC)
17	A	503.0			2	486.0	5	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
16	A	459.5			3	438.0	9	$\underline{\tau_{Ph}}$(ring)+ $\underline{\tau_{iso}}$(ring)+ $\underline{\tau}$(CNNC)

br - broad; o - overlap; ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ - torsion.

Table S4. Computed harmonic frequencies and intensities of the three most abundant conformers of ***E*-HPAI** (M06-2X/cc-pVTZ level of theory, unscaled)

	1*E*-C1-*s*				**1*E*-C2-*s***				**1*E*-C3-*s***			
Mode	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}
16	A	447.9	7.3	3	A'	450.8	7.8	3	A	496.2	10.8	7
17	A	500.8	5.1	2	A"	506.2	4.1	2	A	497.8	12.4	8
18	A	544.6	0.5	0	A'	537.2	0	0	A	521.1	18.6	13
19	A	573.6	26.7	9	A"	578.8	2.3	1	A	571.6	1	1
20	A	580.2	2.6	1	A'	583.5	40.1	15	A	580.8	17.7	12
21	A	594.3	6.2	2	A'	589.9	4.2	2	A	593.5	3.4	2
22	A	636.2	16.9	6	A'	637.9	14.4	5	A	599.4	60	41
23	A	648.5	0.3	0	A"	658.6	0	0	A	626.5	7.9	5
24	A	714.5	24	8	A"	726.1	7.7	3	A	652.6	0.8	1
25	A	742.4	22.6	8	A"	766.8	6.9	3	A	724.6	2.3	2
26	A	775.4	34.1	12	A'	779.5	4.6	2	A	772.3	12.4	8
27	A	778	6.2	2	A"	784.4	111.1	41	A	781.2	17.7	12
28	A	790.1	2.2	1	A'	786.2	3.6	1	A	783.5	5	3
29	A	793.5	49.6	17	A"	796.4	4.6	2	A	789.3	54.4	37
30	A	852.6	23.8	8	A'	861.4	22.9	8	A	863.6	11.7	8
31	A	892.6	1.3	0	A"	899.9	0.9	0	A	892.6	1.4	1
32	A	935	0.2	0	A'	948.9	4.2	2	A	918.6	3.1	2
33	A	954.5	2.2	1	A'	978.1	15.1	6	A	952.2	0.7	0
34	A	986.9	1.6	1	A"	992.3	3.5	1	A	989.2	1.5	1
35	A	1018.9	0.2	0	A"	1012.6	0.1	0	A	1017.4	0.1	0
36	A	1035.2	13.8	5	A'	1016.1	36.5	13	A	1035.2	17.6	12
37	A	1042.8	17.8	6	A'	1042.3	7.4	3	A	1039	13.7	9
38	A	1061.4	0.2	0	A"	1061	1.5	1	A	1064.4	8.4	6
39	A	1065.5	3.5	1	A'	1065.6	4.6	2	A	1064.5	0.2	0
40	A	1068.4	4.8	2	A"	1077	2.3	1	A	1069.3	2.9	2
41	A	1097.9	21.4	7	A'	1097.3	30.2	11	A	1098.5	30.7	21
42	A	1147.7	2.5	1	A'	1146.8	2.3	1	A	1133.8	1.2	1

43	A	1173.5	23.8	8	A'	1168.5	24.2	9	A	1171.9	32.7	22
44	A	1233.5	55.3	19	A'	1231.7	52.4	19	A	1212	47.4	32
45	A	1264.5	39.4	14	A'	1263.8	41.2	15	A	1257	48.5	33
46	A	1314	25.1	9	A'	1310.5	27	10	A	1297.1	97.5	66
47	A	1330.7	49.8	17	A'	1329.8	68.9	25	A	1317.6	49.8	34
48	A	1340.3	46.1	16	A'	1339.5	21.8	8	A	1343.5	28	19
49	A	1361.1	2.3	1	A'	1360	2.8	1	A	1351.8	71.7	48
50	A	1406.2	3.9	1	A'	1410.5	0.2	0	A	1378.6	29.7	20
51	A	1421.5	4.9	2	A'	1421.4	58.6	21	A	1401.7	1.9	1
52	A	1427.4	45.1	15	A'	1424	15.7	6	A	1417.8	8	5
53	A	1468.6	78	27	A'	1473.2	42.3	15	A	1469.2	105.1	71
54	A	1474.3	8	3	A"	1473.2	11.2	4	A	1475.7	7.1	5
55	A	1477.2	8.9	3	A'	1487.2	8.3	3	A	1480.2	9.2	6
56	A	1480.7	6.5	2	A"	1489.3	9.3	3	A	1483.9	7.5	5
57	A	1502.7	34.9	12	A'	1512.8	43.8	16	A	1501.4	37	25
58	A	1518.6	68.2	23	A'	1525.4	95.5	35	A	1523.8	8.2	6
59	A	1537.1	22.4	8	A'	1539.9	13	5	A	1537	77.6	52
60	A	1601.2	6.8	2	A'	1587.1	24	9	A	1600.8	15.3	10
61	A	1608.2	27.9	10	A'	1595.2	20.9	8	A	1635.3	10.5	7
62	A	1659.6	42.6	15	A'	1654.2	116.8	43	A	1669.4	61.8	42
63	A	1694.4	12.5	4	A'	1684	153.9	56	A	1693.8	147.8	100
64	A	1706.1	260.7	90	A'	1696.6	58.5	21	A	1695.5	91.7	62
65	A	3063.5	4.9	2	A'	3074.5	5.2	2	A	3055.6	5	3
66	A	3064.2	3.3	1	A'	3075.8	1.7	1	A	3065.3	5.8	4
67	A	3129.5	1.1	0	A"	3138.4	3.7	1	A	3123.8	3.5	2
s68	A	3132.6	2.8	1	A"	3139.1	0.9	0	A	3132.9	1.6	1
69	A	3156.1	6.9	2	A'	3170	4.2	2	A	3150.2	6.2	4
70	A	3164.8	2.3	1	A'	3174	6.8	2	A	3163.4	0.7	0
71	A	3186.4	0.7	0	A'	3179.5	1.7	1	A	3194.7	0.7	0
72	A	3193	1.2	0	A'	3206.6	0.6	0	A	3201.9	1.2	1
73	A	3207.6	3.9	1	A'	3220.7	2.6	1	A	3209.8	1.4	1

74	A	3228.9	6.9	2	A'	3226.9	6.8	2	A	3220.9	11.1	8
75	A	3434.5	290.6	100	A'	3401.7	274.5	100	A	3759.6	143	97

Table S5. Computed harmonic frequencies and intensities of the three most abundant conformers of ***Z*-HPAI** (M06-2X/cc-pVTZ level of theory, unscaled)

	1*Z*-C3-*s*				**1*Z*-C4-*s***				**1*Z*-C1-*s***			
Mode	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}	Symmetry	Wavenumber (cm^{-1})	I_{abs}	I_{rel}
16	A	495	4.8	4	A	491.9	3.1	3	A	438.9	34	33
17	A	525.1	10	8	A	525.5	26.2	24	A	487.2	8.4	8
18	A	538.5	36.6	30	A	536.6	16.9	15	A	514.6	0.6	1
19	A	564.2	33.5	28	A	559.9	42.9	39	A	541	24.6	24
20	A	571.5	42.3	35	A	568.5	35.5	32	A	575.3	1.7	2
21	A	581.4	1.1	1	A	587.5	3.8	3	A	588.2	2.8	3
22	A	619.3	0.4	0	A	619.8	2.9	3	A	622.8	6.6	6
23	A	641.8	7.1	6	A	647.1	5.8	5	A	642.6	8.9	9
24	A	668.2	2.8	2	A	673.4	2.6	2	A	659.7	2.8	3
25	A	708.2	5	4	A	704.5	4	4	A	707.5	5.5	5
26	A	747.1	7.8	6	A	751.6	6.2	6	A	746.5	12.1	12
27	A	778.1	21.5	18	A	780.8	9.4	9	A	764.4	5.9	6
28	A	785.9	43	36	A	789.9	55.3	50	A	783.5	30.8	30
29	A	791	17.6	15	A	792.2	17.1	16	A	789.2	15	15
30	A	862.3	7.1	6	A	861.5	8.4	8	A	848.1	10.6	10
31	A	878	15.3	13	A	884.8	12.6	11	A	879.8	20.1	19
32	A	905.8	4.7	4	A	910.7	8.6	8	A	907.7	5	5
33	A	962	6.2	5	A	974	11.1	10	A	960	5.2	5
34	A	983.9	6.5	5	A	985.7	6.7	6	A	988.1	3.4	3
35	A	1022.8	0	0	A	1023.8	0.1	0	A	1018.2	0.1	0
36	A	1034.1	1.3	1	A	1030.3	5.1	5	A	1035.1	3.7	4
37	A	1046.5	3.8	3	A	1043	5.3	5	A	1050	3.8	4
38	A	1065.5	2.2	2	A	1065.1	9.1	8	A	1063	0.4	0

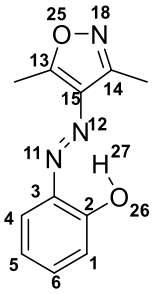
39	A	1068.6	2.6	2	A	1069.7	8.9	8	A	1067.8	8.4	8
40	A	1071.3	8	7	A	1075.8	3	3	A	1070.5	2.4	2
41	A	1091.5	12.9	11	A	1092.3	9.9	9	A	1088.4	11.9	12
42	A	1126.8	3.9	3	A	1124.5	3	3	A	1123.5	2.9	3
43	A	1180.6	25.7	21	A	1179.6	21.6	20	A	1173.2	9.7	9
44	A	1204.8	21.5	18	A	1202.6	15.7	14	A	1193.3	21.1	20
45	A	1238.6	50.8	42	A	1238.3	63.6	58	A	1231.5	48.4	47
46	A	1254.3	65.7	55	A	1246.9	58.8	53	A	1252.2	9	9
47	A	1304.1	119.5	100	A	1301.8	109.8	100	A	1289	35.7	35
48	A	1332.6	34.9	29	A	1328.1	17	15	A	1333.7	48.9	48
49	A	1344.4	24.8	21	A	1343.2	28.3	26	A	1338.8	16	15
50	A	1378.4	37.2	31	A	1375	33.3	30	A	1365.2	16.9	16
51	A	1402	2.2	2	A	1409.3	0.6	1	A	1400.1	2.2	2
52	A	1416.7	5.1	4	A	1420.2	6.8	6	A	1419.4	19.6	19
53	A	1453	71.2	59	A	1468.7	69.9	64	A	1453.9	69.3	67
54	A	1471.5	12	10	A	1485.1	9.6	9	A	1475.9	21.9	21
55	A	1476.6	5.6	5	A	1487.8	3.5	3	A	1479.2	0.4	0
56	A	1486.9	6	5	A	1493.7	15.8	14	A	1491	9.1	9
57	A	1496.5	7.3	6	A	1508.3	36.8	33	A	1496.8	3.2	3
58	A	1520.9	0.1	0	A	1519.5	0.4	0	A	1512.1	6.2	6
59	A	1536.2	111.7	93	A	1535.8	107.8	98	A	1529.6	80	78
60	A	1587.3	16	13	A	1585.8	7.5	7	A	1581.1	15.9	15
61	A	1657.5	26.5	22	A	1646.1	73.9	67	A	1649.9	54.1	53
62	A	1667.2	91.1	76	A	1667.7	58.6	53	A	1661.8	25	24
63	A	1684.8	119.4	99	A	1678	24.1	22	A	1674.3	103	100
64	A	1692	5.7	5	A	1692.6	3.7	3	A	1685.9	21.9	21
65	A	3059	4.1	3	A	3050.9	2.4	2	A	3060.3	4.7	5
66	A	3062.6	6.5	5	A	3076.4	5.9	5	A	3077.7	4.3	4
67	A	3126.9	2.4	2	A	3119.6	1.1	1	A	3128.7	1.8	2
68	A	3130.1	2.2	2	A	3140.2	3.6	3	A	3152.6	1.8	2
69	A	3151.2	2.9	2	A	3152.8	2.9	3	A	3157.8	0.4	0

70	A	3158.8	0.5	0	A	3177.4	4	4	A	3161.6	2.8	3
71	A	3197.5	0.2	0	A	3198.7	0.1	0	A	3191.4	0.6	1
72	A	3204.1	1.3	1	A	3205.1	1.3	1	A	3204.6	1	1
73	A	3212.9	1.9	2	A	3215.6	1.8	2	A	3208.3	2.9	3
74	A	3224.1	4.1	3	A	3226.7	3.9	4	A	3223.9	4.9	5
75	A	3782.8	96.7	81	A	3787.9	95.1	86	A	3868.6	64.7	63

Table S6. Computational O-H stretching data

S. No	HPAI	OH frequency (cm^{-1})	
		M06-2X/cc-pVTZ	ωB97X-D/ def2tzvp
1	**1*E*-C1-*s***	3434.5	3445.2
2	**1*E*-C2-*s***	3401.7	3420.6
3	**1*E*-C3-*s***	3759.6	3742.9
4	**1*E*-C4-*s***	3774.5	3753.2
5	**1*E*-C3-*a***	3886.4	3787.1
6	**1*E*-C4-*a***	3886.4	3886.8
7	**1*E*-C1-*a***	3871.8	3871.3
8	**1*E*-C1-*s*-*keto***	.....	.....
9	**1*E*-C2-*s*-*keto***	.....	.....
10	**1*E*-C2-*a***	3860.8	3767.7
11	**1*E*-C3-*s*-*keto***	.....	.....
12	**1*E*-C4-*s*-*keto***	.....	.....
13	**1*Z*-C3-*s***	3782.8	3749.0
14	**1*Z*-C4-*s***	3787.9	3762.4
15	**1*Z*-C1-*s***	3868.6	3880.0
16	**1*Z*-C2-*s***	3859.4	3877.9
17	**1*Z*-C2-*a***	3881.7	3891.0
18	**1*Z*-C1-*a***	3882.2	3894.8
19	**1*Z*-C3-*a***	3886.1	3890.2
19	**1*Z*-C4-*a***	3885.8	3889.5
21	**1*Z*-C2-*s*-*keto***	.....	.....
22	**1*Z*-C1-*s*-*keto***	.....	.....

Table S7. NBO Analysis of 1*E*-C1-*s*



Donor	Acceptor	$\langle E^2 \rangle$ (kcal/mol)
$n_{(N12)}$	$\sigma^*_{(O26\text{-}H27)}$	23.24
$\pi_{(N11\text{-}N12)}$	$\pi^*_{(C2\text{-}C3)}$	10.03
$\pi_{(N11\text{-}N12)}$	$\pi^*_{(C13\text{-}C15)}$	12.05
$\pi_{(C2\text{-}C3)}$	$\pi^*_{(N11\text{-}N12)}$	32.14

Table S8. Computed harmonic frequency and intensity of **1*Z*-C3-*s*** at M06-2X/cc-pVTZ level of theory (bold: absolute and normal: scaled) along with the experimental frequency and intensity of the photoproduct after irradiation at 365 nm in Ar matrix at 4 K.

Normal Mode	Symmetry	Computed		Experimental (Ar, 4 K)		$\bar{\upsilon}_{diff.}$ (cm^{-1})	Tentative Assignments
		$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*Z*-C3-*s***	I_{rel}	$\bar{\upsilon}$ (cm^{-1})	I_{rel}		
75	A	**3782.8**, 3593.6	81	3484.0	39	298.8	ν(OH)
63	A	**1684.8**, 1634.3	99	1629.5	--	55.3	ν_{ph}(CC)+ ν_{iso}(CC)+ν_{iso}(CN)+ ν(NN)+δ_{iso}(CH_3)
62	A	**1667.2**, 1617.1	76	1600.5	36	66.7	ν_{ph}(CC)+ ν_{iso}(CC)+ν(NN)+δ_{ph}(CH)+δ(OH)
61	A	**1657.5**, 1607.8	22	1587.0	25	70.5	ν(NN)+ν_{ph}(CC)+ν_{iso}(CC)+δ_{ph}(CH)+δ(OH)
59	A	**1536.2**, 1490.1	93	1482.0	58	54.2	ν_{ph}(CO)+ ν_{ph}(CC)+δ_{ph}(CH)
57	A	**1496.5**, 1451.6	6	1467.0	16	29.5	ν_{iso}(CO)+ ν_{iso}(CC)+δ_{iso}(CH_3)
56	A	**1486.9**, 1442.3	5	1439.0	16	47.9	δ_{iso}(CH_3)
54	A	**1471.5**, 1427.3	10	1431.0	15	40.5	γ_{iso}(CH_3)
53	A	**1453.0**, 1409.4	59	1414.0	67	39.0	ν_{iso}(CO)+ ν_{iso}(CC)+δ_{iso}(CH_3)
52	A	**1416.7**, 1375.2	<5	1380.5	16	36.2	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)+ ν_{iso}(CC)+ ν(NN)

50	A	**1378.4**, 1337.1	31	1348.0	34	30.4	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)
49	A	**1344.4**, 1304.1	21	1317.0	50	26.9	δ_{ph}(CH)+ δ_{ph}(OH)+ ν_{iso}(ring)
48	A	**1332.6**, 1292.6	29	1316.0	58	16.6	ν_{iso}(CO)+ ν_{iso}(CC)+δ_{iso}(CH_3)
47	A	**1304.1**, 1265.0	100	1250.0	100	54.1	ν_{ph}(CO)+ ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)
46	A	**1254.3**, 1216.6	55	1217.0	45	37.3	ν_{iso}(CN_{azo})+ δ_{ph}(CH)+δ(OH)
45	A	**1238.6**, 1201.5	42	1182.0	53	56.6	ν_{iso}(CN_{azo})+ν_{ph}(CN_{azo})+δ_{ph}(CH)+δ(OH)
44	A	**1204.8**, 1168.6	18	1176.5	20	28.3	δ_{ph}(CH)+ δ_{ph}(OH)
43	A	**1180.6**, 1145.2	21	1145.0	22	35.6	δ_{ph}(CH)
41	A	**1091.5**, 1058.7	11	1028.0	10	63.5	δ_{iso}(CH_3)+ τ_{iso}(ring)
40	A	**1071.3**, 1039.1	7	1024.0	26	47.3	δ_{ph}(CH)+ δ_{ph}(OH)
34	A	**983.9**, 954.4	5	970.0	40	13.9	γ_{ph}(CH)
33	A	**962.0**, 933.1	5	966.0	41	-4.0	ν_{iso}(NO)+γ_{iso}(CH_3)
32	A	**905.8**, 878.6	4	905.0	16	0.8	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
31	A	**878.0**, 851.7	13	846.0	32	32.0	γ_{ph}(CH)+γ_{ph}(CN_{azo})
30	A	**862.3**, 836.4	6	841.0	33	21.3	δ_{ph}(ring)+ν_{ph}(CO)
28	A	**785.9**, 762.4	36	o	-	-	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
27	A	**778.1**, 754.8	18	743.0	20	35.1	γ_{ph}(CH)+ γ_{ph}(ring)+ γ_{iso}(ring)
20	A	**571.5**, 554.4	35	577.0	34	-5.5	γ(OH)+δ_{ph}(ring)
19	A	**564.2**, 547.3	28	565.0	31	-0.8	γ(OH)
18	A	**538.5**, 522.4	31	553.0	28	-14.5	γ(OH)+ γ_{ph}(CH)
17	A	**525.1**, 509.4	8	510.0	31	15.1	γ(OH)+δ_{ph}(ring)
16	A	**495.0**, 480.1	4	485.0	41	10.0	τ_{iso}(ring)+γ_{ph}(CH)+ γ(OH)+ γ_{iso}(CH_3)+ γ_{ph}(CN_{azo})

o - overlapping; ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ - torsion.

Table S9. Computed frequency and intensity of **1*Z*-C3-*s*** at ωB97X-D/def2tzvp level of theory (unscaled) along with the experimental frequency and intensity of the photoproduct after irradiation at 365 nm in Ar matrix at 4 K.

Normal Mode	Symmetry	Computed		Experimental (Ar, 4 K)		$\bar{\upsilon}_{diff.}$ (cm^{-1})	Tentative Assignments
		$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*Z*-C3-*s***	I_{rel}	$\bar{\upsilon}$ (cm^{-1})	I_{rel}		
75	A	3749.0	70	3484.0	39	265	ν(OH)
63	A	1674.4	97	1611.0	13	63.4	ν_{ph}(CC)+ ν_{iso}(CC) ν_{iso}(CN)+ ν(NN)+ δ_{iso}(CH_3)
62	A	1659.9	74	1600.5	36	59.4	ν_{ph}(CC)+ ν_{iso}(CC)+ ν(NN)+ δ_{ph}(CH) + δ(OH)
61	A	1645.1	22	1587.0	25	58.1	ν_{ph}(CC)+ ν_{iso}(CC)+ ν(NN)+ δ_{ph}(CH) + δ(OH)
59	A	1538.0	100	1482.0	58	56.0	ν_{ph}(CO)+ ν_{ph}(CC)+ δ_{ph}(CH)

57	A	1501.7	10	1467.0	16	34.7	ν_{iso}(CO)+ ν_{iso}(CC)+ δ_{iso}(CH_3)
56	A	1494.0	6	1439.0	16	55.0	δ_{iso}(CH_3)
54	A	1483.5	14	1431.0	15	52.5	δ_{iso}(CH_3)
53	A	1460.3	54	1414.0	67	46.3	ν_{iso}(CO)+ ν_{iso}(CC)+ δ_{iso}(CH_3)
52	A	1428.2	9	1380.5	16	47.7	ν_{ph}(CC)+δ_{ph}(CH)+δ(OH)+ ν_{iso}(CC)+ ν(NN)
50	A	1382.5	28	1348.0	34	34.5	ν_{ph}(CC)+ δ_{ph}(CH) +δ(OH)
49	A	1354.1	46	1317.0	50	37.1	δ_{ph}(CH)+ δ_{ph}(OH)+ ν_{iso}(ring)
48	A	1333.4	30	1316.0	58	17.4	ν_{iso}(CO)+ ν_{iso}(CC)+ δ_{iso}(CH_3)
47	A	1307.1	88	1250.0	100	57.1	ν_{ph}(CO)+ ν_{ph}(CC)+ δ_{ph}(CH**)** + δ(OH)
45	A	1238.5	54	1182.0	53	56.5	ν_{iso}(CN_{azo})+ ν_{ph}(CN_{azo}) +ν_{ph}(CC)+ δ_{ph}(CH**)** + δ(OH)
44	A	1211.5	39	1176.5	20	35.0	δ_{ph}(CH)+ δ_{ph}(OH)
43	A	1180.3	23	1145.0	22	35.3	δ_{ph}(CH)
41	A	1097.0	23	1028.0	10	69	δ_{iso}(CH_3)+ τ_{iso}(ring)
40	A	1070.4	8	1024.0	26	46.4	ν_{ph}(CC)+ δ_{ph}(CH)
34	A	986.6	5	970.0	40	16.6	γ_{ph}(CH)
33	A	961.9	4	966.0	41	−4.1	ν_{iso}(NO)+ γ_{iso}(CH_3)
32	A	907.8	3	905.0	16	2.8	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
31	A	879.4	14	846.0	32	33.4	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
30	A	868.7	4	841.0	33	27.7	δ_{ph}(ring)+ ν_{ph}(CO)
28	A	787.3	31	743.0	20	44.3	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
21	A	589.4	67	577.0	34	12.4	γ(OH)
19	A	571.4	6	565.0	31	6.4	γ(OH)+ δ_{ph}(ring)
18	A	544.6	23	553.0	28	-8.4	γ(OH)+ γ_{ph}(CH)
17	A	526.5	5	510.0	31	16.5	γ(OH)+ δ_{ph}(ring)
16	A	498.4	4	485.0	41	13.4	$\underline{\tau}_{iso}$(ring)+ γ_{ph}(CH)+ γ(OH)+ γ_{iso}(CH_3)+ γ_{ph}(CN_{azo})

ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ - torsion.

Table S10. Computed frequency and intensity of **1*Z*-C4-*s*** at M06-2X/cc-pVTZ level of theory (bold: absolute and normal: scaled) along with the experimental frequency and intensity of the photoproduct after irradiation at 365 nm in Ar matrix at 4 K.

Normal Mode	Symmetry	Computed		Experimental (Ar, 4 K)		$\bar{\upsilon}_{diff.}$ (cm^{-1})	Tentative Assignments
		$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*Z*-C4-*s***	I_{rel}	$\bar{\upsilon}$ (cm^{-1})	I_{rel}		
75	A	**3787.9**, 3598.5	86	3484.0	39	303.9	ν(OH)

63	A	**1678.0**, 1627.6	22	1611.0	13	67.0	ν_{iso}(CN)+ ν_{ph}(CC)+ ν_{iso}(CC)+ν(NN)+δ_{iso}(CH_3)+ δ(OH)
62	A	**1667.7**, 1617.7	53	1600.5	36	67.2	ν_{ph}(CC)+δ_{ph}(CH)+ δ(OH)
61	A	**1646.1**, 1596.8	67	1587.0	25	59.1	ν_{iso}(CN)+ ν_{ph}(CC)+ ν_{iso}(CC)+ν(NN)+δ(OH**)**
59	A	**1535.8**, 1489.7	98	1482.0	58	53.8	ν_{ph}(CC)+δ_{ph}(CH)
57	A	**1508.3**, 1463.0	33	1467.0	16	41.3	ν_{iso}(CC)+ ν_{iso}(CO)+δ_{iso}(CH_3)
56	A	**1493.7**, 1448.9	14	1439.0	16	54.7	δ_{iso}(CH_3)
54	A	**1485.1**, 1440.5	9	1431.0	15	54.1	δ_{iso}(CH_3)
53	A	**1468.7**, 1424.7	64	1414.0	67	54.7	ν_{iso}(CC)+δ_{iso}(CH_3)
50	A	**1375.0**, 1333.8	30	1348.0	34	27.0	ν_{ph}(CC)+δ_{ph}(CH)+ δ(OH)
48	A	**1328.1**, 1288.2	15	1316.0	58	12.1	ν_{iso}(CC)+ ν_{iso}(CO)+δ_{iso}(CH_3)
47	A	**1301.8**, 1262.7	100	1250.0	100	51.8	ν_{ph}(CC)+ ν_{ph}(CO)+δ_{ph}(CH)+δ(OH)
45	A	**1238.3**, 1201.1	58	1182.0	53	56.3	ν_{ph}(CN_{azo})+δ_{ph}(CH)+ δ(OH)
39	A	**1069.7**, 1037.6	8	1024.0	26	45.7	ν_{ph}(CC)+δ_{ph}(CH)
34	A	**985.7**, 956.2	6	970.0	40	15.7	γ_{ph}(CH)
33	A	**974.0**, 944.8	10	966.0	41	8.0	γ_{iso}(CH_3)+ν_{iso}(NO)
32	A	**910.7**, 883.4	8	905.0	16	5.7	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
31	A	**884.8**,858.3	11	846.0	32	38.8	γ_{ph}(CH)+γ_{ph}(CN_{azo})
30	A	**861.5**,835.7	8	841.0	33	20.5	δ_{ph}(ring)+ν_{ph}(CO)
28	A	**789.9**, 766.2	50	743.0	20	46.9	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
20	A	**568.5**, 551.4	32	577.0	34	-8.5	γ(OH)+δ_{ph}(ring)+$\underline{\tau}$(CNNC)
19	A	**559.9**, 543.1	39	565.0	31	-5.1	γ(OH)
17	A	**525.5**, 520.5	24	510.0	31	15.5	γ(OH)+δ_{ph}(ring)
16	A	**491.9**, 477.1	3	485.0	41	6.9	γ_{ph}(CH)+ γ_{ph}(CN_{azo})+ γ_{iso}(CH_3)+$\underline{\tau}$(CNNC)+ $\underline{\tau}_{ph}$(ring)+ $\underline{\tau}_{iso}$(ring)

ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ – torsion; Scaling factor used: 0.97 below 2000 cm^{-1} and 0.95 above 2000 cm^{-1}.

Table S11. Computed frequency and intensity of **1*Z*-C4-*s*** at ωB97X-D/def2tzvp level of theory (unscaled) along with the experimental frequency and intensity of the photoproduct after irradiation at 365 nm in Ar matrix at 4 K.

Normal Mode	Symmetry	Computed		Experimental (Ar, 4 K)		$\bar{\upsilon}_{diff.}$ (cm^{-1})	Tentative Assignments
		$\bar{\upsilon}_{cal}$ (cm^{-1}) **1*Z*-C4-*s***	I_{rel}	$\bar{\upsilon}$ (cm^{-1})	I_{rel}		
75	A	3762.4	61	3484.0	39	278.4	ν(OH)

63	A	1668.4	23	1611.0	13	57.4	ν_{iso}(CN)+ ν_{ph}(CC)+ ν_{iso}(CC)+ν(NN)+ δ_{iso}(CH_3)+ δ(OH)
62	A	1660.3	51	1600.5	36	59.8	ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)
61	A	1635.4	53	1587.0	25	48.4	ν_{iso}(CN)+ ν_{ph}(CC)+ ν_{iso}(CC)+ν(NN)+ δ(OH)
59	A	1533.0	90	1482.0	58	51.0	ν_{ph}(CC)+ δ_{ph}(CH)
57	A	1512.3	27	1467.0	16	45.3	ν_{iso}(CC)+ ν_{iso}(CO)+ δ_{iso}(CH_3)
56	A	1498.1	4	1439.0	16	59.1	δ_{iso}(CH_3)
54	A	1480.6	25	1431.0	15	49.6	δ_{iso}(CH_3)
53	A	1469.6	47	1414.0	67	55.6	ν_{iso}(CC)+ δ_{iso}(CH_3)
50	A	1389.7	38	1348.0	34	41.7	ν_{ph}(CC)+ δ_{ph}(CH)+ δ(OH)
48	A	1329.3	12	1316.0	58	13.3	ν_{iso}(CC)+ ν_{iso}(CO)+ δ_{iso}(CH_3)
47	A	1301.7	100	1250.0	100	51.7	ν_{ph}(CC)+ ν_{ph}(CO)+ δ_{ph}(CH)+ δ(OH)
45	A	1243.9	7	1182.0	53	61.9	ν_{iso}(CN_{azo})+ δ_{ph}(CH)+ δ(OH)
39	A	1064.1	7	1024.0	26	40.1	ν_{ph}(CC)+ δ_{ph}(CH)
34	A	976.5	5	970.0	40	6.5	γ_{ph}(CH)
33	A	970.2	9	966.0	41	4.2	γ_{iso}(CH_3)+ ν_{iso}(NO)
32	A	908.9	8	905.0	16	3.9	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
31	A	879.7	10	846.0	32	33.7	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
30	A	867.3	6	841.0	33	26.3	δ_{ph}(ring)+ ν_{ph}(CO)
28	A	786.7	29	743.0	20	43.7	γ_{ph}(CH)+ γ_{ph}(CN_{azo})
21	A	589.8	41	577.0	34	12.8	γ(OH)+ δ_{ph}(ring)
19	A	568.3	8	565.0	31	3.3	γ(OH)+ δ_{ph}(ring)+ δ_{iso}(ring)+ $\underline{\tau}$(CNNC)
17	A	527.6	12	510.0	31	17.6	γ(OH)+ δ_{ph}(ring)+ γ_{ph}(CH)
16	A	493.1	2	485.0	41	8.1	γ_{ph}(CH)+ γ_{ph}(CN_{azo})+ γ_{iso}(CH_3)+ $\underline{\tau}$(CNNC)+ $\underline{\tau}_{ph}$(ring)+ $\underline{\tau}_{iso}$(ring)

ν - stretching; δ - in-plane-bending; γ - out-of-plane bending; τ - torsion.

S6: Solution phase photoswitching and kinetics data: UV-Vis spectroscopic studies

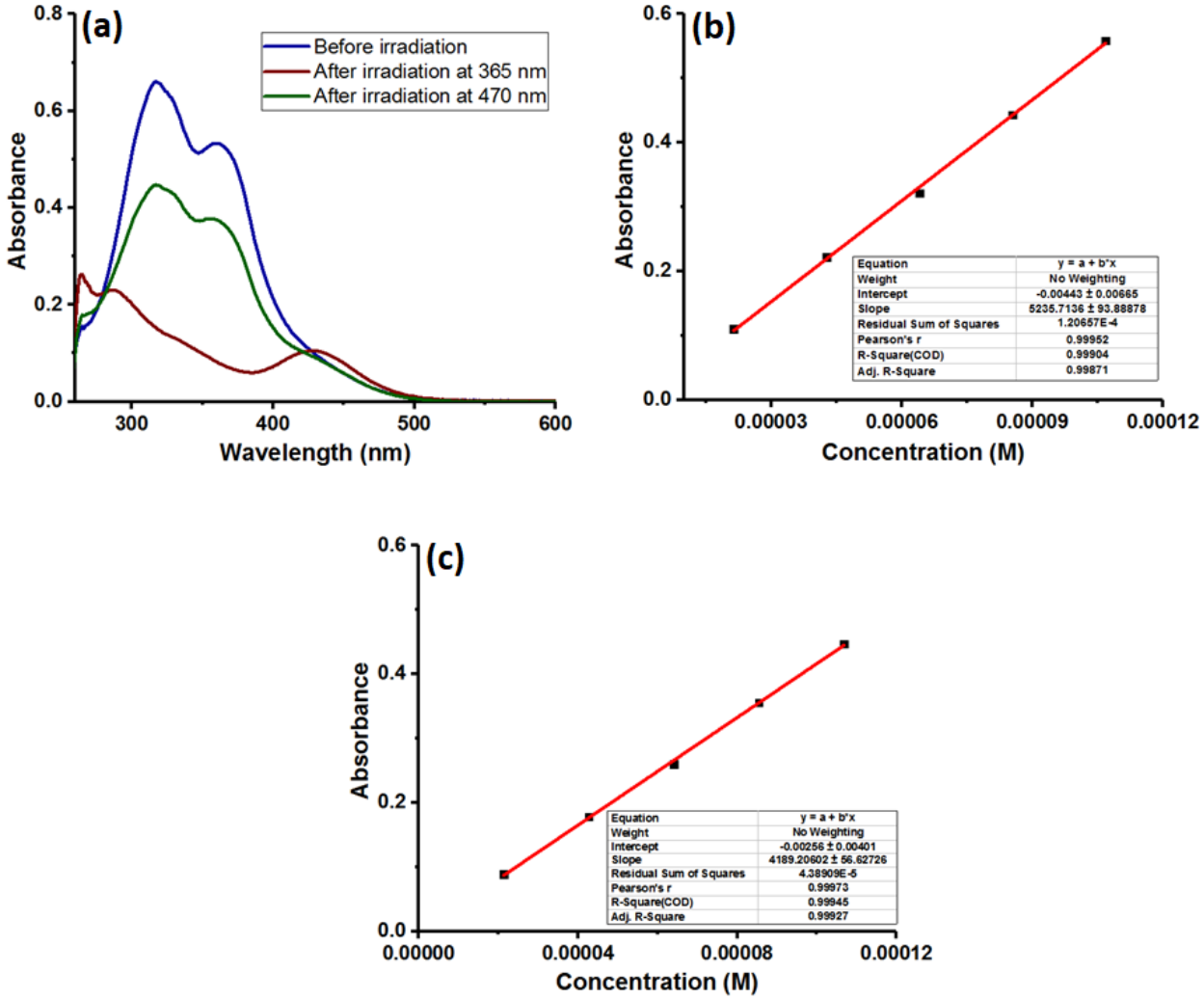


Figure S25. (a) UV-Vis spectral data depicting the photoswitching in **HPAI** (126 μM, DMSO) at different irradiation conditions; Estimation of molar absorption coefficient corresponding to the $\lambda_{max}(\pi-\pi^*)$: (b) 317 nm (ε, 5236 ± 94 M^{-1} cm^{-1}), and (c) 360 nm (ε, 4189 ± 57 M^{-1} cm^{-1}) in DMSO.

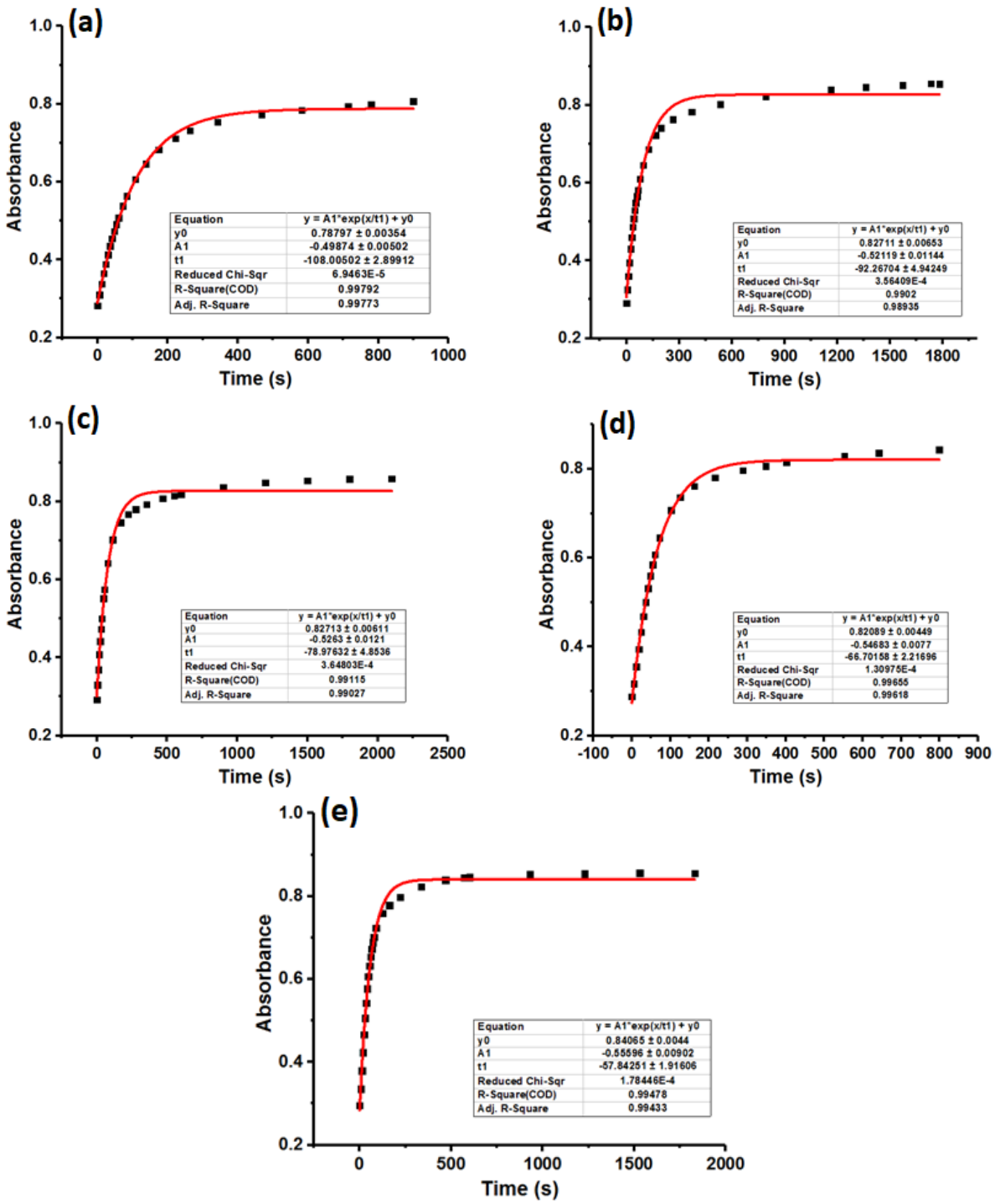


Figure S26. Kinetics data for the thermal reverse isomerization of **HPAI** at (a) 25 °C, (b) 30 °C, (c) 35 °C, (d) 40 °C and (e) 45 °C in DMSO (152 μM). Kinetics data have been followed by the absorption changes at $\lambda_{max}(\pi-\pi^*)$ = 317 nm of *E*-isomer.

Table S12. Half-lives and rate constants for the thermal reverse isomerization of **HPAI** at variable temperature.

Compound	Temperature (°C)	Rate constant (s^{-1})	Half-life (s)	Conc. [μM]
HPAI	25	$9.3 \times 10^{-3} \pm 2.5 \times 10^{-4}$	75	152
	30	$1.1 \times 10^{-2} \pm 5.8 \times 10^{-4}$	64	152
	35	$1.3 \times 10^{-2} \pm 7.8 \times 10^{-4}$	55	152
	40	$1.5 \times 10^{-2} \pm 5.0 \times 10^{-4}$	46	152
	45	$1.7 \times 10^{-2} \pm 5.7 \times 10^{-4}$	40	152

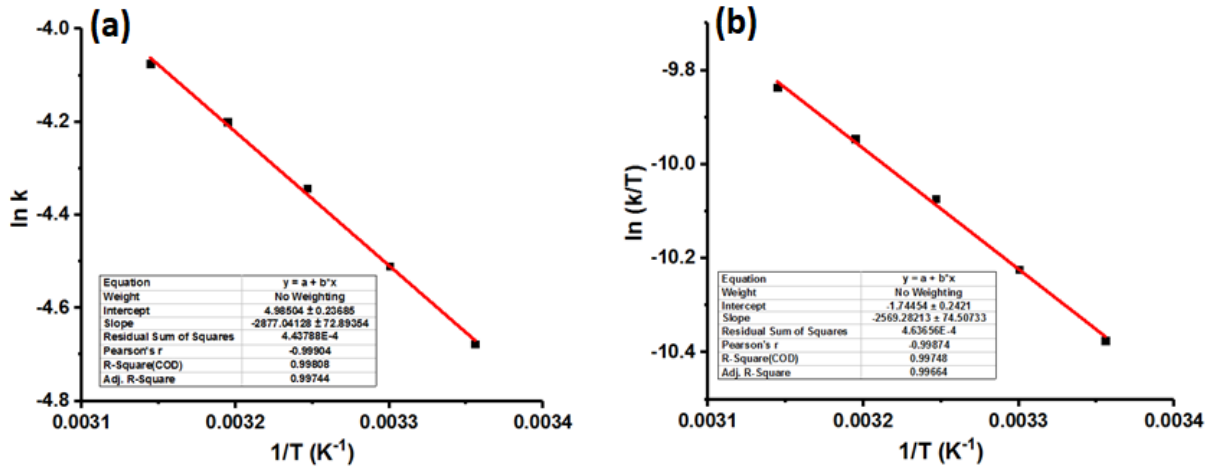


Figure S27. Arrhenius plot (a) and Eyring plot (b) for the thermal reverse isomerization of **HPAI**.

Table S13. Activation parameters derived from Arrhenius and Eyring plots for **HPAI**.

Compound	E_a kcal mol^{-1}	$\Delta G^{\ddagger}$ (298K) kcal mol^{-1}	$\Delta H^{\ddagger}$ kcal mol^{-1}	$\Delta S^{\ddagger}$ cal K^{-1}
HPAI	5.7 ± 0.1	20.2 ± 0.2	5.1 ± 0.1	-50.7 ± 0.5

S7: Computational mechanistic aspects

Table S14. Computational data corresponding to the *E*- and *Z*- isomers of **HPAI** related to the thermal isomerization channels at M06-2X/cc-pVTZ (normal) and ωB97X-D/def2tzvp (*italics*).

species	Absolute energy (Hartree)	ZPVE (Hartree)	Thermal energy (Hartree)	Thermal correction (Hartree)	Free energy (G) (Hartree)	Enthalpy (H) (Hartree)	Lowest frequency	Point group
1*E*-C1-*s*	-740.179777 *-740.236827*	0.210560 *0.211320*	-740.165807 *-740.222993*	0.224530 *0.225154*	-740.222419 *-740.279306*	-740.164863 *-740.222049*	13.87 *13.94*	C_1 *C_1*
TS$_{1E\text{-}C1\text{-}s\text{-}ph}$	-740.106018 *-740.163219*	0.208022 *0.208291*	-740.091887 *-740.149139*	0.222152 *0.222371*	-740.147928 *-740.205156*	-740.090943 *-740.148195*	500.25i *513.57i*	C_1 *C_1*
TS$_{1E\text{-}C1\text{-}s\text{-}ox}$	-740.103918 *-740.160673*	0.208273 *0.208344*	-740.090008 *-740.146760*	0.222183 *0.222257*	-740.145003 *-740.201708*	-740.089064 *-740.145816*	510.88i *522.85i*	C_1 *C_1*
1*E*-C1-*a*	-740.164931 *-740.221349*	0.210428 *0.210279*	-740.150749 *-740.207072*	0.224611 *0.224556*	-740.206964 *-740.263524*	-740.149805 *-740.206128*	21.13 *23.35*	C_1 *C_1*
1*E*-C1-*s*-*keto*	-740.164918 *-740.225365*	0.208953 *0.210650*	-740.150886 *-740.211564*	0.222986 *0.224452*	-740.208373 *-740.267292*	-740.149941 *-740.210620*	7.25 *21.43*	C_1 *C_1*
1*E*-C2-*s*	-740.177942 *-740.236295*	0.211163 *0.210791*	-740.164280 *-740.222317*	0.224825 *0.224769*	-740.218713 *-740.278514*	-740.163336 *-740.221373*	39.96 *20.06*	C_1 *C_1*
1*E*-C2-*a*	-740.162306 *-740.482002*	0.210478 *0.206889*	-740.148131 *-740.467383*	0.224653 *0.221508*	-740.204513 *-740.525138*	-740.147187 *-740.466439*	17.69 *15.57*	Cs *Cs*
1*E*-C2-*s*-*keto*	-740.163694 *-740.225400*	0.209819 *0.210491*	-740.149819 *-740.211499*	0.223694 *0.224392*	-740.205348 *-740.267361*	-740.148875 *-740.210555*	28.79 *23.86*	C_1 *C_1*
1*E*-C3-*s*	-740.177515 *-740.233980*	0.210719 *0.210939*	-740.163517 *-740.219893*	0.224717 *0.225026*	-740.219379 *-740.276416*	-740.162572 *-740.218949*	26.90 *26.20*	C_1 *C_1*
1*E*-C3-*a*	-740.169981 *-740.225427*	0.209616 *0.210182*	-740.155478 *-740.211014*	0.224119 *0.224594*	-740.213775 *-740.268045*	-740.154534 *-740.210070*	6.31 *20.39*	C_1 *C_1*
1*E*-C3-*s*-*keto*	-740.144853 *-740.206118*	0.211196 *0.210813*	-740.131064 *-740.192108*	0.224985 *0.224823*	-740.186347 *-740.248184*	-740.130120 *-740.191164*	25.02 *25.69*	Cs Cs
1*E*-C4-*s*	-740.174993 *-740.231639*	0.210784 *0.211134*	-740.160881 *-740.217679*	0.224896 *0.225094*	-740.217187 *-740.273393*	-740.159936 *-740.216735*	19.81 *26.45*	C_1 *C_1*
1*E*-C4-*a*	-740.167989 *-740.223863*	0.209807 *0.210217*	-740.153592 *-740.209470*	0.224204 *0.224610*	-740.210694 *-740.266530*	-740.152648 *-740.208525*	15.11 *16.94*	C_1 *C_1*
1*E*-C4-*s*-*keto*	-740.143454	0.210942	-740.129533	0.224864	-740.185258	-740.128589	24.39	C_1

	-740.204765	*0.210866*	*-740.190769*	*0.224863*	*-740.246921*	*-740.189825*	*19.38*	*C_1*
1*Z*-C1-*s*	-740.150894	0.210632	-740.137108	0.224418	-740.191326	-740.136164	39.11	C_1
	-740.207400	*0.210440*	*-740.193418*	*0.224422*	*-740.248294*	*-740.192473*	*38.06*	*C_1*
1*Z*-C1-*a*	-740.150003	0.210270	-740.136069	0.224204	-740.190604	-740.135124	40.38	C_1
	-740.206480	*0.210441*	*-740.192450*	*0.224472*	*-740.247484*	*-740.191506*	*40.61*	*C_1*
1*Z*-C1-*s*-*keto*	-740.137961	0.211340	-740.124031	0.225270	-740.178985	-740.123087	40.06	C_1
	-740.199743	*0.211096*	*-740.185666*	*0.225173*	*-740.241295*	*-740.184722*	*33.67*	*C_1*
1*Z*-C2-*s*	-740.150698	0.210233	-740.136745	0.224186	-740.191491	-740.135801	37.88	C_1
	-740.206778	*0.210723*	*-740.192901*	*0.224599*	*-740.247411*	*-740.191957*	*37.09*	*C_1*
1*Z*-C2-*a*	-740.150441	0.210462	-740.136499	0.224404	-740.191058	-740.135555	42.01	C_1
	-740.206738	*0.210749*	*-740.192847*	*0.224640*	*-740.247431*	*-740.191903*	*43.61*	*C_1*
1*Z*-C2-*s*-*keto*	-740.138480	0.210805	-740.124507	0.224778	-740.179720	-740.123563	27.02	C_1
	-740.199999	*0.210947*	*-740.185901*	*0.225046*	*-740.241674*	*-740.184957*	*27.60*	*C_1*
1*Z*-C3-*s*	-740.156052	0.210659	-740.142152	0.224559	-740.197050	-740.141208	50.63	C_1
	-740.212651	*0.211371*	*-740.198946*	*0.225076*	*-740.253402*	*-740.198002*	*43.93*	*C_1*
1*Z*-C3-*a*	-740.149016	0.210339	-740.135040	0.224315	-740.190111	-740.134096	40.03	C_1
	-740.205779	*0.210583*	*-740.191787*	*0.224575*	*-740.247088*	*-740.190843*	*32.77*	*C_1*
1*Z*-C4-*s*	-740.154858	0.211322	-740.141251	0.224929	-740.195346	-740.140307	50.31	C_1
	-740.212344	0.211328	-740.198656	0.225016	-740.253190	-740.197712	39.68	C_1
1*Z*-C4-*a*	-740.148585	0.210496	-740.134757	0.224324	-740.189417	-740.133812	32.70	C_1
	-740.205546	*0.211075*	*-740.191720*	*0.224901*	*-740.246356*	*-740.190776*	*43.57*	*C_1*

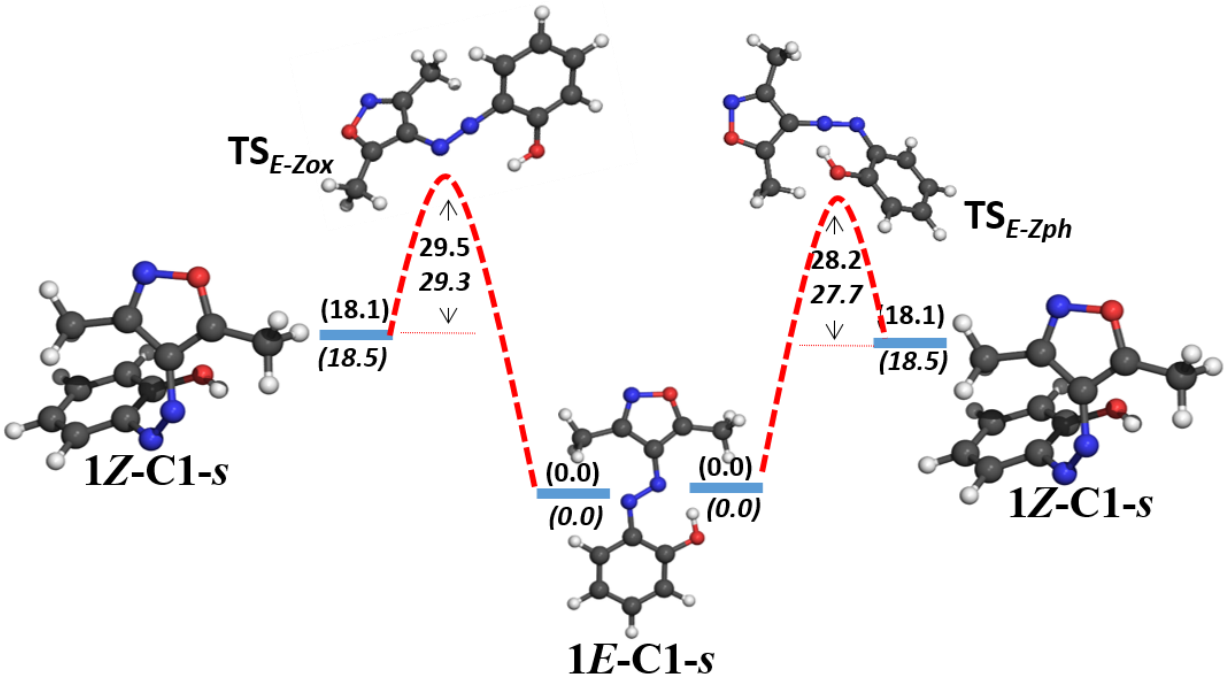


Figure S28. Computed energy profiles corresponding to the thermal reverse isomerization of **1*Z*-C1-*s*** to **1*E*-C1-*s*** (Computed barriers (in kcal/mol) for the thermal isomerization step involving inversion along the phenyl ring at M06-2x/cc-pVTZ (normal) and ωB97X-D/def2tzvp (italics) levels of theory).

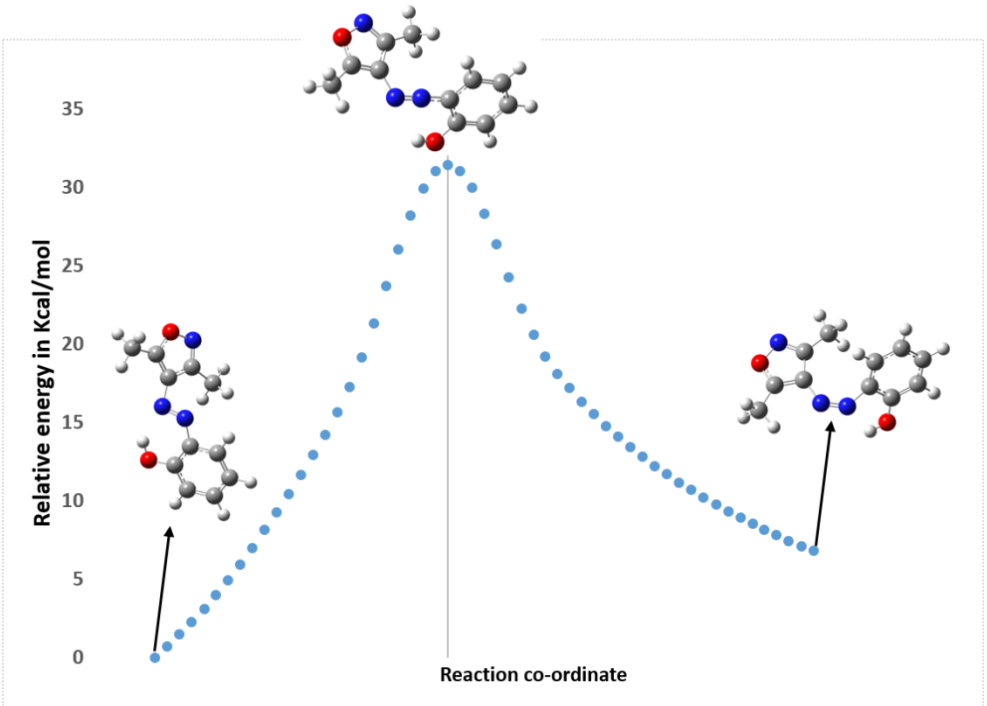


Figure S29 a. IRC analysis of transition state connecting **1*Z*-C1-*s*** to **1*E*-C1-*s*** inversion along phenyl ring at M06-2x/cc-pVTZ level of theory

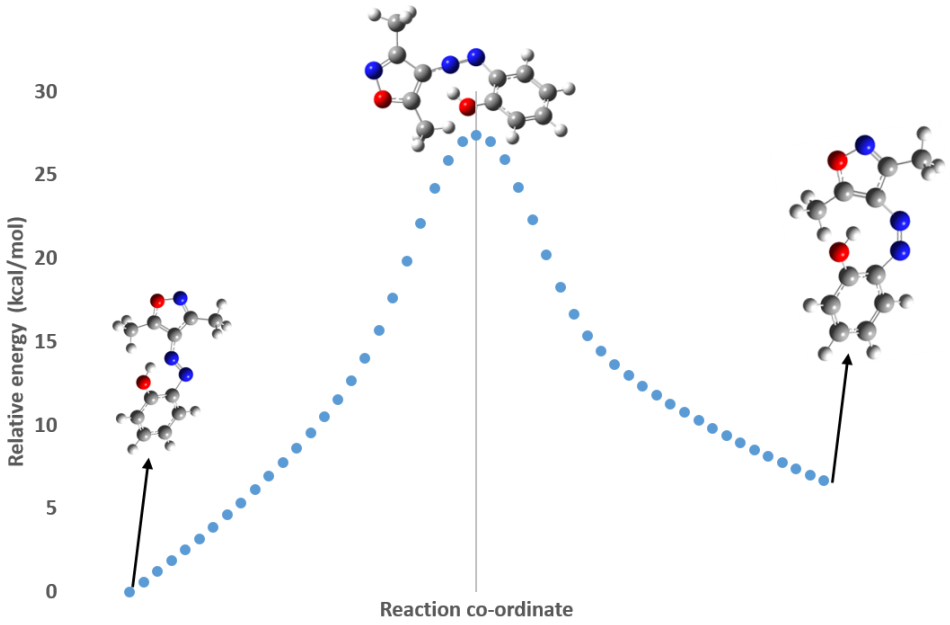


Figure S29 b. IRC analysis of transition state connecting **1*Z*-C1-*s*** to **1*E*-C1-*s*** inversion along oxazole ring at M06-2x/cc-pVTZ level of theory

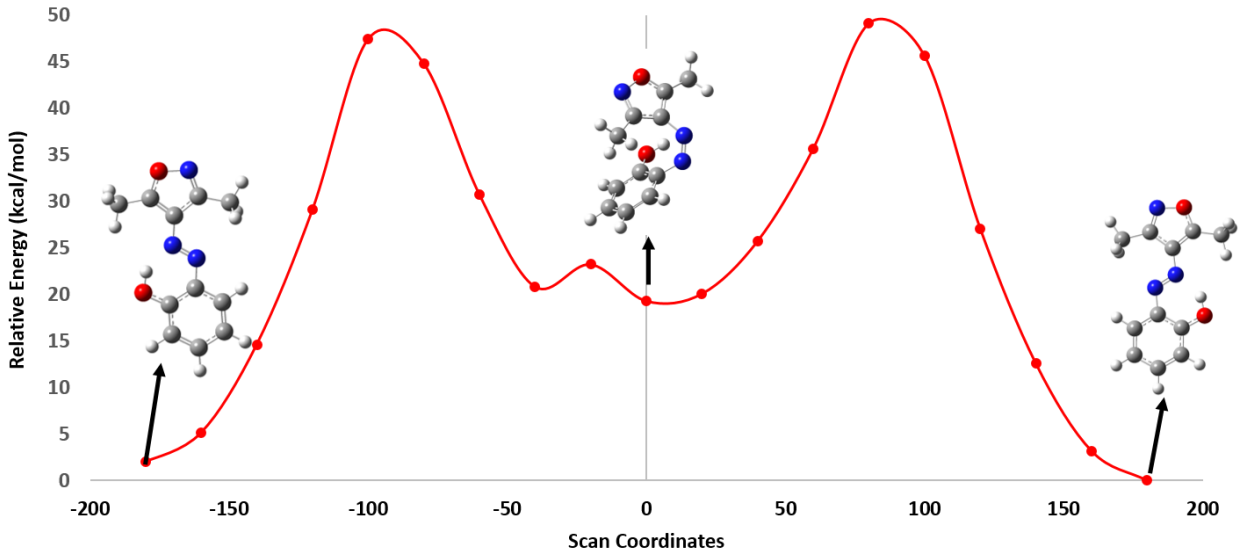


Figure 30. Computed energy profile corresponding to the rotational isomerization of **1*E*-C1-*s*** to **1*Z*-C1-*s***. Dihedral scan around C_{ph}-N=N-C_{iso}

S9: Cartesian Coordinates

1*E*-C1-*s*				**1*E*-C1-*a***			
C	3.95179500	1.30310600	-0.00858500	C	-3.90104800	-1.34446800	0.29990100
C	2.58199200	1.44711600	-0.00957800	C	-2.52425600	-1.44108300	0.23436200
C	1.73646800	0.33441300	-0.00296500	C	-1.71316700	-0.32914400	0.01558400
C	2.29456300	-0.96112300	0.00518200	C	-2.32284300	0.92442000	-0.17830900
C	3.68119900	-1.09686400	0.00660800	C	-3.71068200	1.01220200	-0.12269100
C	4.49520400	0.01889500	-0.00036200	C	-4.49411000	-0.10310800	0.11928900
H	4.59453400	2.17113800	-0.01377000	H	-4.50304300	-2.22239000	0.48345100
H	2.11440300	2.42273900	-0.01565500	H	-2.02321300	-2.39202100	0.35654200
H	4.08984300	-2.09755800	0.01337600	H	-4.17553400	1.98024600	-0.27262100
H	5.56903900	-0.11171500	0.00080700	H	-5.56962800	0.00196900	0.16000400
N	0.36409200	0.62892500	-0.00389500	N	-0.32927800	-0.62072100	-0.02589300
N	-0.41875400	-0.34606200	-0.00171300	N	0.44010700	0.34960600	0.09227500
C	-2.76529200	-0.95571900	-0.00434200	C	2.76902300	0.96570400	0.15077700
C	-2.46151800	1.23642100	0.00395200	C	2.50391000	-1.21326100	-0.11363700
C	-1.77080500	-0.02430300	-0.00127600	C	1.79038500	0.02452300	0.04323500
C	-2.75871400	-2.43525900	-0.00991500	C	2.70770900	2.43259000	0.32617900
C	-1.91892100	2.62180000	0.00958500	C	1.98001600	-2.59550900	-0.28159600
N	-3.74514700	1.03883500	0.00395900	N	3.78436300	-0.99578900	-0.09540200
H	-3.29851100	-2.81058600	-0.87887200	H	3.21803900	2.93394300	-0.49587600
H	-1.73631000	-2.80212600	-0.03950300	H	1.66459600	2.73879100	0.34933200
H	-3.24943100	-2.81837200	0.88451800	H	3.19604500	2.72500500	1.25560700
H	-1.29408200	2.78734000	-0.86638900	H	1.34742600	-2.65253200	-1.16578100
H	-2.74464200	3.32911000	0.01559800	H	2.81209200	-3.28952600	-0.37346200
H	-1.28925400	2.77814500	0.88380400	H	1.35927200	-2.86841700	0.57017400
O	-3.93969500	-0.33596700	-0.00151300	O	3.95543000	0.37551100	0.07054500
O	1.54451800	-2.07047900	0.01246100	O	-1.57285100	2.01973700	-0.44353700
H	0.60865200	-1.77933400	0.01022100	H	-2.16265700	2.75407500	-0.63885400
1*E*-C1-*s*-*keto*				**1*E*-C2-*s***			
C	4.01100500	1.23363000	-0.01374800	C	1.39344100	-3.92684800	0.00000000
C	2.67673000	1.47415000	-0.01607500	C	0.43306100	-2.93988200	0.00000000
C	1.74727200	0.39661000	-0.00487300	C	0.78420400	-1.58684500	0.00000000
C	2.20609800	-0.98488100	0.00890400	C	2.14821800	-1.22337400	0.00000000
C	3.62908700	-1.17592500	0.01102000	C	3.11212200	-2.23009200	0.00000000
C	4.47672800	-0.11402300	0.00015400	C	2.73910000	-3.55936600	0.00000000
H	4.72126500	2.04697100	-0.02254600	H	1.10920800	-4.96896600	0.00000000
H	2.27272900	2.47795700	-0.02664900	H	-0.62269100	-3.17637300	0.00000000
H	3.98669400	-2.19591300	0.02149700	H	4.15135200	-1.93233700	0.00000000
H	5.54469600	-0.29284900	0.00202800	H	3.50544200	-4.32295500	0.00000000
N	0.44504100	0.72184000	-0.00804600	N	-0.29245300	-0.68731600	0.00000000
N	-0.39259400	-0.24580600	0.00202900	N	0.00000000	0.52958000	0.00000000
C	-2.71460600	-0.97941500	-0.00687300	C	-0.94294900	2.82773000	0.00000000
C	-2.48258800	1.22084800	0.00629100	C	-2.42743300	1.19099300	0.00000000
C	-1.75915000	-0.01344500	-0.00001000	C	-1.07707000	1.40771600	0.00000000
C	-2.65365800	-2.45882900	-0.01526600	C	0.31786800	3.61717400	0.00000000
C	-1.97497100	2.61961700	0.01624800	C	-3.26949500	-0.02558900	0.00000000
N	-3.76095700	0.98002800	0.00330100	H	0.08873100	4.67942600	0.00000000
H	-3.17439800	-2.85377500	-0.88717200	H	0.91467900	3.37797800	0.88000300

H	-1.61964200	-2.79699400	-0.04218600	H	0.91467900	3.37797800	-0.88000300
H	-3.13091700	-2.86353200	0.87694800	H	-3.04363700	-0.63456200	0.87462100
H	-1.35517600	2.80658700	-0.85910200	H	-4.32033000	0.25327800	0.00000000
H	-2.81967000	3.30374900	0.02328600	H	-3.04363700	-0.63456200	-0.87462100
H	-1.35229200	2.79267900	0.89252300	O	-3.04032700	2.37061100	0.00000000
O	-3.91234400	-0.39177100	-0.00490200	N	-2.10912400	3.39969400	0.00000000
O	1.39456500	-1.94750200	0.01902100	O	2.55772300	0.05031500	0.00000000
H	0.05684600	-1.21314900	0.01281100	H	1.75168300	0.61029300	0.00000000
1*E*-C2-*a*				**1*E*-C2-*s*-keto**			
C	1.36562400	-3.90771300	0.00000000	C	4.00273400	1.25754900	0.08118500
C	0.44072500	-2.88200600	0.00000000	C	2.66861900	1.48779500	0.10218300
C	0.81755800	-1.53879400	0.00000000	C	1.74392700	0.40476000	0.03422200
C	2.19124100	-1.22543900	0.00000000	C	2.21474800	-0.97400600	-0.05342100
C	3.11726300	-2.26505600	0.00000000	C	3.64267600	-1.15134400	-0.07512200
C	2.71655800	-3.58943100	0.00000000	C	4.48023600	-0.08574000	-0.01043800
H	1.04106400	-4.93804100	0.00000000	H	4.70778300	2.07390000	0.13304400
H	-0.62167200	-3.08548200	0.00000000	H	2.25731600	2.48630700	0.17098300
H	4.17299800	-2.01768800	0.00000000	H	4.00821000	-2.16628800	-0.14335500
H	3.46385700	-4.37113600	0.00000000	H	5.54976000	-0.25421300	-0.02788900
N	-0.27392300	-0.64068200	0.00000000	N	0.44525700	0.72208500	0.05477000
N	0.00000000	0.57427500	0.00000000	N	-0.40003800	-0.24219700	-0.00473000
C	-1.00876500	2.83693700	0.00000000	C	-2.76180700	-1.01517700	0.04102100
C	-2.45522900	1.16935900	0.00000000	C	-2.45614800	1.17216300	-0.04206100
C	-1.10940400	1.41364600	0.00000000	C	-1.76494600	0.00108300	-0.00348700
C	0.23771200	3.64802500	0.00000000	O	-3.76165200	0.88045700	-0.01846400
C	-3.27134800	-0.06513500	0.00000000	N	-3.94848600	-0.48386500	0.03230200
H	-0.00733500	4.70685600	0.00000000	O	1.41529900	-1.93883600	-0.10625900
H	0.83822000	3.40978500	0.87702500	H	0.02592400	-1.20698200	-0.06138900
H	0.83822000	3.40978500	-0.87702500	C	-2.54921400	-2.48699300	0.09036600
H	-3.03178000	-0.66896200	0.87447900	H	-2.01193600	-2.82673300	-0.79574100
H	-4.32831600	0.19024700	0.00000000	H	-1.95310100	-2.75907200	0.96184900
H	-3.03178000	-0.66896200	-0.87447900	H	-3.50846600	-2.99482900	0.14123200
O	-3.09621800	2.33404900	0.00000000	C	-2.06835000	2.60037800	-0.10089300
N	-2.18624200	3.38537600	0.00000000	H	-1.65273900	2.92504400	0.85317800
O	2.60486200	0.06108400	0.00000000	H	-1.30121200	2.75164700	-0.85754300
H	3.56691500	0.07339000	0.00000000	H	-2.94269900	3.20328800	-0.33430100
1*E*-C3-*s*				**1*E*-C3-*a***			
C	3.47000000	-1.77857200	-0.00040600	C	3.41045600	-1.82338100	-0.00058100
C	2.12135700	-1.48968100	-0.00037700	C	2.07080700	-1.48682600	-0.00059200
C	1.69386700	-0.16268300	-0.00003300	C	1.66994400	-0.15237100	-0.00012100
C	2.63177000	0.87739200	0.00022900	C	2.64025500	0.85679800	0.00033600
C	3.99124700	0.58189700	0.00020100	C	3.98894900	0.51343900	0.00036300
C	4.39981400	-0.73787600	-0.00010700	C	4.36995000	-0.81646000	-0.00009400
H	3.80608300	-2.80555900	-0.00067900	H	3.71073400	-2.86150700	-0.00096700
H	1.37677800	-2.27266100	-0.00063400	H	1.30311800	-2.24691700	-0.00100000
H	4.69924800	1.39822900	0.00041800	H	4.73554200	1.29884300	0.00075300
H	5.45766100	-0.96369500	-0.00013600	H	5.42192900	-1.06756800	-0.00008100
N	0.35123000	0.26765800	0.00002600	N	0.32303900	0.28123900	-0.00014600
N	-0.51075700	-0.62918800	0.00006500	N	-0.52397200	-0.62961800	0.00006200
C	-2.89382000	-1.02672500	0.00012300	C	-2.91870000	-1.00538000	0.00025400
C	-2.41209400	1.13178500	-0.00018400	C	-2.40264800	1.14643500	-0.00030500

C	-1.82431600	-0.18072700	0.00005000	C	-1.83800300	-0.17633800	-0.00000400
C	-2.99800100	-2.50165800	0.00048400	C	-3.04628600	-2.47893500	0.00063100
C	-1.76016900	2.46994300	-0.00031300	C	-1.71582300	2.46615400	-0.00067200
N	-3.70713200	1.04141400	-0.00027500	N	-3.69922100	1.07724000	-0.00022600
H	-3.54040000	-2.84163000	-0.88147700	H	-3.59355600	-2.81107400	-0.88136700
H	-2.00024400	-2.93174200	0.00073900	H	-2.05531300	-2.92473400	0.00096000
H	-3.54054100	-2.84108800	0.88257900	H	-3.59392900	-2.81058000	0.88258100
H	-1.12766600	2.58219500	-0.88049300	H	-1.06858600	2.55352000	-0.87184900
H	-2.52454800	3.24331900	-0.00063700	H	-2.45859200	3.26043400	-0.00081900
H	-1.12807700	2.58253600	0.88012400	H	-1.06844900	2.55395200	0.87036000
O	-4.01354400	-0.31385200	-0.00010000	O	-4.02827700	-0.27546800	0.00012700
O	2.23849500	2.16677400	0.00049200	O	2.22802700	2.14684500	0.00077500
H	1.27077700	2.16895400	0.00035800	H	2.99678100	2.72376500	0.00107600
1*E*-C3-*s*-*keto*				**1*E*-C4-*s***			
C	-1.88663300	3.53312700	0.00000000	C	-3.46812300	-1.77410300	0.00004600
C	-1.68153700	2.18942900	0.00000000	C	-2.11976700	-1.48532800	0.00003900
C	-0.35510500	1.71346900	0.00000000	C	-1.69289300	-0.15763300	0.00000000
C	0.82014400	2.57510900	0.00000000	C	-2.63149200	0.88223200	-0.00002100
C	0.51856400	3.98810900	0.00000000	C	-3.99074200	0.58665400	-0.00001000
C	-0.76748200	4.42293900	0.00000000	C	-4.39854700	-0.73330600	0.00001900
H	-2.88828400	3.93649500	0.00000000	H	-3.80382700	-2.80108200	0.00008200
H	-2.49863900	1.48116100	0.00000000	H	-1.37352200	-2.26665700	0.00006800
H	1.35445500	4.67324700	0.00000000	H	-4.69931500	1.40242400	-0.00002800
H	-0.96180200	5.48822400	0.00000000	H	-5.45609700	-0.95997300	0.00002700
N	0.00000000	0.41000000	0.00000000	N	-0.35097200	0.27241900	0.00003100
N	-0.75088800	-0.60592400	0.00000000	N	0.51203300	-0.62484100	-0.00008800
C	-0.81944600	-3.00883900	0.00000000	C	2.36589900	1.08383000	0.00001200
C	1.25961600	-2.24553000	0.00000000	C	2.95968500	-1.04340900	-0.00002600
C	-0.12312300	-1.83231900	0.00000000	C	1.82663600	-0.17415300	-0.00001100
C	-2.26753000	-3.30300600	0.00000000	C	1.79144900	2.44809200	0.00004000
C	2.51250500	-1.43598100	0.00000000	C	2.96196300	-2.53054500	-0.00003800
N	1.33546400	-3.54218700	0.00000000	N	4.06470400	-0.36141800	0.00001800
H	-2.53588500	-3.88446000	0.88188400	H	2.59098700	3.18476700	0.00019300
H	-2.82361300	-2.36953700	0.00000000	H	1.16334000	2.59001400	-0.87967400
H	-2.53588500	-3.88446000	-0.88188400	H	1.16311000	2.58986900	0.87961200
H	2.57352100	-0.79280400	0.87998400	H	2.44038500	-2.90811700	-0.87842100
H	3.36713200	-2.10727700	0.00000000	H	3.98492600	-2.89714100	-0.00047100
H	2.57352100	-0.79280400	-0.87998400	H	2.44116600	-2.90812700	0.87880900
O	0.03766500	-4.02240000	0.00000000	O	3.69004400	0.97616100	0.00003800
O	1.96104700	2.08399700	0.00000000	O	-2.23819300	2.17202200	-0.00006600
H	1.03392000	0.34717300	0.00000000	H	-1.27073300	2.17145500	0.00000300
1*E*-C4-*a*				**1*E*-C4-*s*-*keto***			
C	-3.40719988	-1.81971911	0.00143599	C	3.63617700	1.68573100	-0.07422400
C	-2.06798289	-1.48216105	0.01087601	C	2.28270900	1.56544300	-0.05814900
C	-1.66899895	-0.14691803	0.01012998	C	1.72723900	0.27147800	0.00840700
C	-2.64020999	0.86105192	-0.00005907	C	2.51657700	-0.95332400	0.05751900
C	-3.98845498	0.51655887	-0.01048808	C	3.94477000	-0.74095400	0.03648100
C	-4.36789392	-0.81381615	-0.00954205	C	4.45692200	0.51474200	-0.02603200
H	-3.70641784	-2.85815012	0.00300701	H	4.10072800	2.65930700	-0.12532600
H	-1.29855886	-2.24057702	0.02000504	H	1.62490700	2.42293900	-0.09383000
H	-4.73595801	1.30106884	-0.01970412	H	4.57734100	-1.61667900	0.07028800

H	-5.41953491	-1.06618619	-0.01715607	H	5.53185100	0.64425100	-0.04116500
N	-0.32289897	0.28661102	0.02128999	N	0.40795400	-0.00840500	0.02628500
N	0.52484407	-0.62472294	-0.00346596	N	-0.57218400	0.79074600	-0.01143400
C	2.35628300	1.09745913	-0.00005998	C	-2.25816800	-1.09172100	-0.04094700
C	2.98493009	-1.02035984	-0.00284790	C	-3.02865300	0.98132500	0.02466300
C	1.83973505	-0.17018089	0.00125005	C	-1.82307800	0.21052200	-0.00535700
C	1.74580394	2.44466811	0.00083098	C	-1.58401600	-2.41211300	-0.09471600
C	3.01332915	-2.50762284	-0.00520586	C	-3.14852700	2.46214400	0.06694800
N	4.07949706	-0.32058279	-0.00442790	N	-4.07018400	0.20834300	0.01298500
H	2.52058491	3.20264214	-0.08576703	H	-2.33146100	-3.19340200	-0.20587400
H	1.03141295	2.52996106	-0.81691404	H	-0.88759000	-2.47025500	-0.93457800
H	1.17483192	2.59387711	0.91750696	H	-1.00851300	-2.60624100	0.81375000
H	2.49205818	-2.89293188	-0.88059786	H	-2.65393300	2.90516400	-0.79653800
H	4.04260916	-2.85652280	-0.01372183	H	-4.19752700	2.74584500	0.06972500
H	2.50597615	-2.89622584	0.87686714	H	-2.66399400	2.85429200	0.96028800
O	3.68243400	1.01176519	-0.00363495	O	-3.58957600	-1.08975700	-0.02897700
O	-2.22916605	2.15232794	-0.00203809	O	1.95499900	-2.06062500	0.10908600
H	-2.99928607	2.72740191	-0.00983412	H	0.29399900	-1.03658500	0.07998700
1*Z*-C1-*s*				**1*Z*-C1-*a***			
C	2.34450200	-0.10200500	1.53034600	C	2.27566400	-0.17087600	1.54940200
C	1.30070500	-0.72147500	0.85139800	C	1.24279400	-0.74130600	0.81519400
C	1.32868500	-0.76818500	-0.54652100	C	1.31441300	-0.74094700	-0.58146100
C	2.43918300	-0.28515100	-1.23050700	C	2.45603500	-0.25404400	-1.20519000
C	3.46688300	0.34318900	-0.55342300	C	3.47823500	0.32439400	-0.47313900
C	3.40874600	0.44085800	0.83329900	C	3.37953800	0.37158100	0.91090700
H	2.29663800	-0.06663600	2.60971700	H	2.20819000	-0.15828200	2.63097600
H	2.45937900	-0.39640900	-2.30655900	H	2.50901200	-0.32506800	-2.28361000
H	4.31115000	0.74308900	-1.09613000	H	4.34735800	0.72511400	-0.97430200
H	4.20842600	0.92475500	1.37687300	H	4.17007600	0.81514100	1.50002500
N	0.32860200	-1.45499800	-1.30119400	N	0.33231600	-1.36863000	-1.40764000
N	-0.87533600	-1.16560100	-1.21510100	N	-0.86890600	-1.08012100	-1.34034400
C	-0.98279900	1.30483200	-0.25825800	C	-0.98018000	1.32002700	-0.25934600
C	-2.62983100	-0.13763800	0.05183100	C	-2.59386800	-0.15152200	0.05105000
C	-1.38215300	-0.06237200	-0.49507000	C	-1.38008300	-0.03076300	-0.55064100
C	-3.60870500	-1.24443800	0.12611000	C	-3.53977400	-1.28464000	0.13433500
C	0.21106100	2.07939400	-0.70285200	C	0.19479400	2.11521600	-0.71933800
H	0.45995800	1.83761400	-1.73494300	H	0.43156100	1.88081900	-1.75617900
H	-0.01645500	3.13976200	-0.62539500	H	-0.04216300	3.17296400	-0.63337200
H	1.08190400	1.85501400	-0.08848200	H	1.07856300	1.89908500	-0.11965100
H	-3.30763700	-2.03209400	-0.56065700	H	-3.31260400	-1.99330400	-0.65902100
H	-3.65672700	-1.65108500	1.13689800	H	-3.44114900	-1.79469500	1.09327900
H	-4.60077800	-0.88204700	-0.13850100	H	-4.56399000	-0.92912600	0.03752400
O	0.31380800	-1.27259400	1.59953600	O	0.16945400	-1.32326100	1.40878800
H	-0.31005700	-1.74569700	1.04066300	H	0.27103700	-1.28332000	2.36376600
O	-2.94126700	1.02373800	0.60952800	O	-2.88862500	0.97809100	0.68697100
N	-1.92237900	1.93239000	0.38427900	N	-1.89025700	1.90722500	0.46282000
1*Z*-C1-*s-keto*				**1*Z*-C2-*s***			
C	2.11887000	-1.07863800	1.33068700	C	2.30823700	-0.35663100	1.53007100
C	1.10229400	-0.97155700	0.28617700	C	1.27876100	-0.85467200	0.73978600
C	1.42143000	-0.02183900	-0.82305400	C	1.32688700	-0.66284100	-0.64478400
C	2.78338300	0.45320000	-0.95367000	C	2.44570600	-0.06913000	-1.21856500

C	3.69151400	0.24288200	0.01422000
C	3.33091200	-0.51180900	1.19187700
H	1.85421600	-1.67629100	2.19190000
H	3.00987500	1.03120500	-1.83943200
H	4.69256400	0.63974200	-0.07362300
H	4.07282800	-0.63744400	1.97053600
N	0.62059000	0.35482900	-1.78289100
N	-0.69017800	0.20863400	-1.71822100
C	-1.34890200	1.34550100	0.45208900
C	-2.41047400	-0.51202700	-0.07487700
C	-1.44649400	0.31965800	-0.53580200
C	-2.92368700	-1.80804500	-0.56355000
C	-0.41737600	2.50649000	0.48678500
H	-0.31787500	2.94829900	-0.50457300
H	-0.78559300	3.25489500	1.18383900
H	0.57675300	2.18573100	0.80291100
H	-2.35990100	-2.10233100	-1.44515200
H	-2.77858700	-2.56353700	0.20744700
H	-3.98491800	-1.75047500	-0.80367600
O	0.10798500	-1.68117200	0.27336200
O	-2.88964000	-0.02045600	1.06594900
N	-2.21707700	1.14201700	1.39897900
H	-1.12828600	0.56197600	-2.55502400

C	3.46309300	0.43426700	-0.42880300
C	3.38327700	0.29630800	0.95255600
H	2.24481800	-0.50779700	2.59866200
H	2.48400100	0.00391000	-2.29756500
H	4.31582000	0.91642200	-0.88449400
H	4.17354400	0.67802400	1.58393600
N	0.33908300	-1.21102400	-1.52573000
N	-0.86694500	-0.93800200	-1.41307800
C	-0.99618100	1.29438300	-0.17676400
C	-2.64693700	-0.14131000	0.11155500
C	-1.37199300	0.02523700	-0.51476200
C	-3.52171600	-1.34312000	0.06230700
C	0.13752000	2.18247100	-0.52487900
N	-2.97113800	0.91608100	0.78995100
H	0.47597500	1.98506000	-1.53918500
H	-0.18065000	3.21934500	-0.44197800
H	0.98022700	2.01183300	0.14839400
H	-3.68569900	-1.64239500	-0.97206100
H	-3.05319200	-2.18198500	0.57814400
H	-4.47326500	-1.12662900	0.54029700
O	-1.94694800	1.82318200	0.59350500
O	0.28129800	-1.52527500	1.36630100
H	-0.30328900	-1.93819800	0.72309000

1*Z*-C2-*a*

C	-2.20758700	-0.71375700	-1.45798900
C	-1.19800300	-0.97929700	-0.54178800
C	-1.30986700	-0.48883900	0.76319400
C	-2.46445800	0.18351400	1.14079100
C	-3.46557000	0.45693600	0.22343400
C	-3.32959500	0.00942100	-1.08269800
H	-2.11022400	-1.08678600	-2.47079700
H	-2.55029800	0.49709100	2.17299800
H	-4.34787300	1.00103800	0.52796900
H	-4.10377800	0.20463000	-1.81159600
N	-0.35887300	-0.79258800	1.79164700
N	0.84738400	-0.54970200	1.66344600
C	1.01771600	1.35633700	0.00763100
C	2.56168500	-0.20930300	-0.11542600
C	1.36213500	0.16376700	0.56119800
C	3.36047400	-1.44344800	0.10095400
C	-0.06025700	2.34032500	0.26097800
N	2.87450100	0.67094400	-1.01763400
H	-0.39488300	2.27186400	1.29385700
H	0.30669500	3.34582300	0.06467900
H	-0.92005900	2.14334900	-0.38320400
H	3.65005300	-1.52116700	1.14837500
H	2.75995800	-2.32075900	-0.13919200
H	4.24872600	-1.42756800	-0.52509400
O	1.91901700	1.66683400	-0.93169200
O	-0.10779800	-1.72290400	-0.85934700
H	-0.16919100	-2.01346600	-1.77358800

1*Z*-C2-*s-keto*

C	2.25170600	0.48949700	1.57181500
C	1.15811900	-0.22442900	0.91657400
C	1.44358200	-0.69913400	-0.46647600
C	2.80834900	-0.66864700	-0.94445500
C	3.78048500	-0.05119000	-0.25001600
C	3.47837600	0.56090100	1.02047400
H	2.02797800	0.91547900	2.54014700
H	2.99105600	-1.12579200	-1.90768300
H	4.78855100	-0.00227600	-0.63540100
H	4.27240800	1.07475000	1.54793100
N	0.59651400	-1.26766300	-1.28653900
N	-0.70807300	-1.23107900	-1.13497500
C	-1.29280200	1.13434800	-0.66051100
C	-2.61351700	-0.35379100	0.28230600
C	-1.47050400	-0.20474200	-0.55345300
C	-3.19950100	-1.62264300	0.78510500
C	-0.25347100	1.96189400	-1.30999000
N	-3.08437600	0.80926200	0.61756600
H	0.13615000	1.45601100	-2.19133700
H	-0.66129600	2.93023200	-1.59165800
H	0.58196300	2.11944100	-0.62022000
H	-3.52440600	-2.26074300	-0.03709200
H	-2.43993900	-2.16061900	1.35293500
H	-4.05010400	-1.40954200	1.42682000
O	-2.25203000	1.74790600	0.03656400
O	0.11153500	-0.48200700	1.49413800
H	-1.17179800	-1.77016400	-1.85065800

1*Z*-C3-*s*			
C	-3.39249300	-0.32070000	-0.05155400
C	-2.44849800	0.67484200	-0.26451000
C	-1.21438000	0.61292200	0.38907400
C	-0.96407700	-0.39508200	1.31489200
C	-1.91611200	-1.37222000	1.54392100
C	-3.11925300	-1.34052900	0.84406700
H	-4.33018600	-0.26926300	-0.58646100
H	-0.02686500	-0.40154300	1.85364300
H	-1.72564000	-2.15349500	2.26539700
H	-3.85945100	-2.11091900	1.01138800
N	-0.35641500	1.72417300	0.15499100
N	0.86910100	1.61975900	0.00338700
C	1.22926100	-0.80393900	-0.91694900
C	2.80267000	0.18820200	0.27531100
C	1.52449600	0.37988900	-0.15122600
C	3.71700000	1.03772100	1.06879300
C	0.03695700	-1.14578900	-1.74459800
H	-0.35466000	-0.25499900	-2.23565600
H	0.32605900	-1.87464900	-2.49777000
H	-0.76017900	-1.56499500	-1.13061600
H	3.30666000	2.04343800	1.12514200
H	3.83250700	0.64570600	2.07958900
H	4.70040300	1.06595100	0.60196200
O	-2.71984300	1.66950000	-1.13613100
H	-2.02729000	2.33982000	-1.05095800
O	3.22585600	-1.00710800	-0.12553500
N	2.24975700	-1.60908700	-0.89918600

1Z-C3-*a*			
C	-3.32841700	-0.30192300	-0.11647500
C	-2.35957600	0.65349400	-0.38539100
C	-1.20387600	0.70577200	0.39599300
C	-1.04772200	-0.17895500	1.45394000
C	-2.01974800	-1.13026600	1.72549100
C	-3.15829800	-1.19112800	0.93506400
H	-4.21474200	-0.34948200	-0.73816000
H	-0.15911000	-0.10687500	2.06685200
H	-1.88992900	-1.81505400	2.55094500
H	-3.92121300	-1.93047100	1.13535600
N	-0.29761700	1.78714900	0.18412000
N	0.91419400	1.60798600	0.02279200
C	1.17659400	-0.88597000	-0.82638200
C	2.81579400	0.15882300	0.22049800
C	1.51664500	0.34033000	-0.14888400
C	3.77561900	1.04893700	0.90914500
C	-0.05223500	-1.29027200	-1.56806100
H	-0.44992900	-0.44960100	-2.13612500
H	0.20169200	-2.09957600	-2.24839500
H	-0.82764100	-1.63230900	-0.88270200
H	3.38557500	2.06402400	0.89462300
H	3.91840200	0.74009400	1.94501200
H	4.74179500	1.01367500	0.40829500
O	-2.44386600	1.51942500	-1.42556700
H	-3.29511400	1.41979800	-1.86065300
O	3.21317800	-1.05840100	-0.13164900
N	2.19299900	-1.69734400	-0.81361900

1*Z*-C4-*s*			
C	3.38035400	-0.33625600	0.05537000
C	2.43095300	0.65434500	0.27216500
C	1.21009600	0.60851100	-0.40462700
C	0.97436900	-0.38413100	-1.35047400
C	1.92935500	-1.35805600	-1.58028100
C	3.12280200	-1.33918700	-0.86259700
H	4.30939300	-0.29297000	0.60591000
H	0.04566600	-0.38147800	-1.90433800
H	1.74989100	-2.12597600	-2.31887000
H	3.86594600	-2.10590100	-1.03342400
N	0.34985300	1.72261400	-0.16648800
N	-0.87413400	1.61852300	-0.00314300
C	-1.22264700	-0.70171700	0.93694700
C	-2.84946800	0.12364500	-0.30261200
C	-1.52059000	0.37599900	0.15573500
C	-3.68378100	0.99728000	-1.16968200
C	-0.06935200	-1.06432100	1.79148500
N	-3.27388200	-1.02622700	0.12763300
H	0.39077300	-0.16706900	2.20398000
H	-0.40186200	-1.70781800	2.60287100
H	0.69098000	-1.58708700	1.20610800
H	-3.77195200	1.98669600	-0.72196200
H	-3.22218600	1.12106200	-2.14892900

1Z-C4-*a*			
C	3.30497999	-0.38854787	0.01455089
C	2.35624098	0.56014897	0.37053729
C	1.18582397	0.68568827	-0.37796665
C	0.98821497	-0.13195228	-1.48287298
C	1.93749298	-1.07577012	-1.84099138
C	3.09718499	-1.20180242	-1.08909344
H	4.20696899	-0.48593111	0.60722185
H	0.08669397	-0.00720405	-2.06804992
H	1.77559298	-1.70176276	-2.70659264
H	3.84580199	-1.93290230	-1.36087575
N	0.31551396	1.78646414	-0.09450218
N	-0.90068604	1.63950206	0.07051077
C	-1.19103100	-0.71945631	0.94922879
C	-2.81563502	0.08547419	-0.30235486
C	-1.50863102	0.37089800	0.19757724
C	-3.65651604	0.95512154	-1.16728550
C	-0.04446699	-1.07089966	1.81656964
N	-3.20992100	-1.09117197	0.08200465
H	0.42001400	-0.16799782	2.21121501
H	-0.38548998	-1.69600400	2.63928638
H	0.71032901	-1.61666541	1.24578240
H	-3.76566404	1.93762735	-0.70945009
H	-3.18662505	1.09821595	-2.14023444

H	-4.67153400	0.56115800	-1.29219000	H	-4.63498103	0.50329159	-1.30675768
O	-2.26251500	-1.53685700	0.92143200	O	-2.19986799	-1.59176229	0.88320344
O	2.68525600	1.62770600	1.17453000	O	2.47851098	1.35324352	1.46534762
H	2.00755300	2.31153500	1.07857100	H	3.34191998	1.22050936	1.86655956

References:

1 R. E. Stratmann, J. C. Burant, G. E. Scuseria and M. J. Frisch, *J*. *Chem*. *Phys*., 1997, **106**, 10175–10183.

2 Y. Zhao and D. G. Truhlar, *Theor*. *Chem*. *Acc*., 2008, **120**, 215−241.

3 J.-D. Chai and M. Head-Gordon, *Phys*. *Chem*. *Chem*. *Phys*., 2008, **10**, 6615-6620.

4 R. A. Kendall, T. H. Dunning and R. J. Harrison, *J*. *Chem*. *Phys*., 1992, **96**, 6796−6806.

5 T. H. Dunning, *J*. *Chem*. *Phys*., 1989, **90**, 1007–1023.

6 F. Weigend and R. Ahlrichs, *Phys*. *Chem*. *Chem*. *Phys*., 2005, **7**, 3297−3305.

7 K. Fukui, *Acc*. *Chem*. *Res*., 1981, **14**, 363–368.

8 T. A. Halgren and W. N. Lipscomb, *Chem*. *Phys*. *Lett*., 1977, **49**, 225−232.

9 P. Kumar, A. Srivastava, C. Sah, S. Devi and S. Venkataramani, *Chem*. – *Eur*. *J*., 2019, **25**, 11924–11932.