

Supplementary Table S3. Enthalpies (H), relative enthalpies (ΔH), entropies (S), relative entropies (ΔS), free Gibbs energies (G), and relative Gibbs free energies (ΔG) for the TSs and CAs involved in the I32CA of (*E*)-*N*-((2-((methylbut-2-en-1-yl)thio)-1*H*-indol-3-yl)methylene)methanamine oxide **1**.

System	H(a.u)	$\Delta H(\text{kcal/mol})$	S (cal mol ⁻¹ K ⁻¹)	ΔS (cal mol ⁻¹ K ⁻¹)	G(a.u)	$\Delta G(\text{kcal/mol})$
(E)- 1	-1164.9945		169.145		-1165.0892	
TS2n	-1164.9615	20.8	146.904	-22.2	-1165.0437	28.6
TS2x	-1164.9377	35.7	148.844	-20.3	-1165.0210	42.8
TS3n	-1164.9456	30.7	145.874	-23.3	-1165.0272	38.9
CA2n	-1165.0177	-14.5	142.506	-26.6	-1165.0974	-5.2
CA2x	-1165.0126	-11.3	144.386	-24.8	-1165.0933	-2.6
CA3n	-1165.0059	-7.1	141.710	-27.4	-1165.0852	2.5