Electronic Supplementary information for,

Mechanistic Variances in NO Release: *Ortho* vs. *Meta* Isomers of Nitrophenol and Nitroaniline

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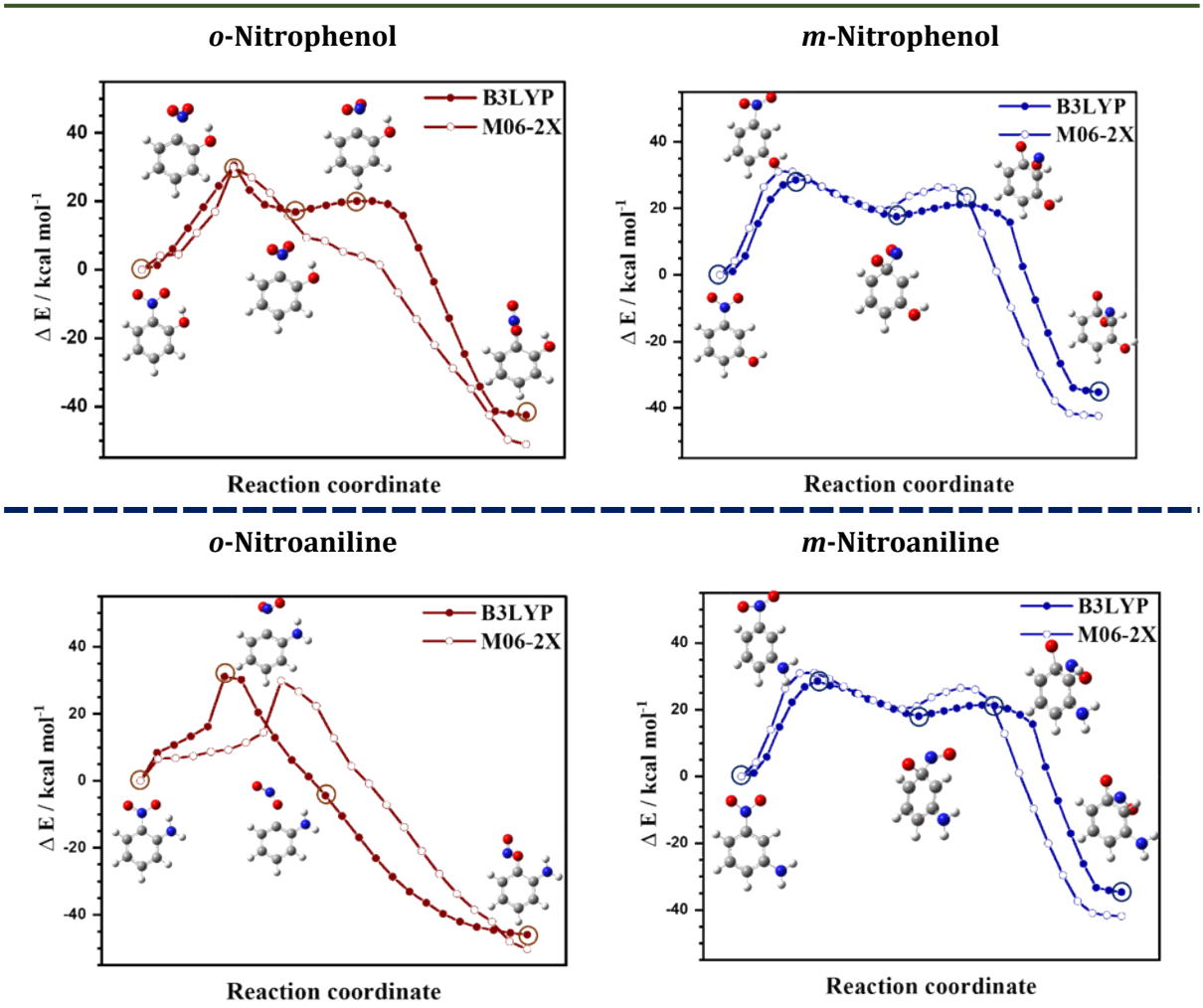

Fig. S1. One-dimensional cuts of the T_1-2D-PES along the minimum energy pathway for *ortho* and *meta* isomers of nitrophenol (top panel) and nitroaniline (bottom panel) resulting in NO release. The energy scale is relative to the intact molecule on the T_1 surface. Also shown are selected structures along the minimum energy path calculated at the B3LYP level. Note that in the case of *meta* isomers, the NO release follows an oxaziridine ring intermediate, while the NO_2 roaming intermediate is observed for *ortho* isomers.

o-nitrophenol	m-nitrophenol

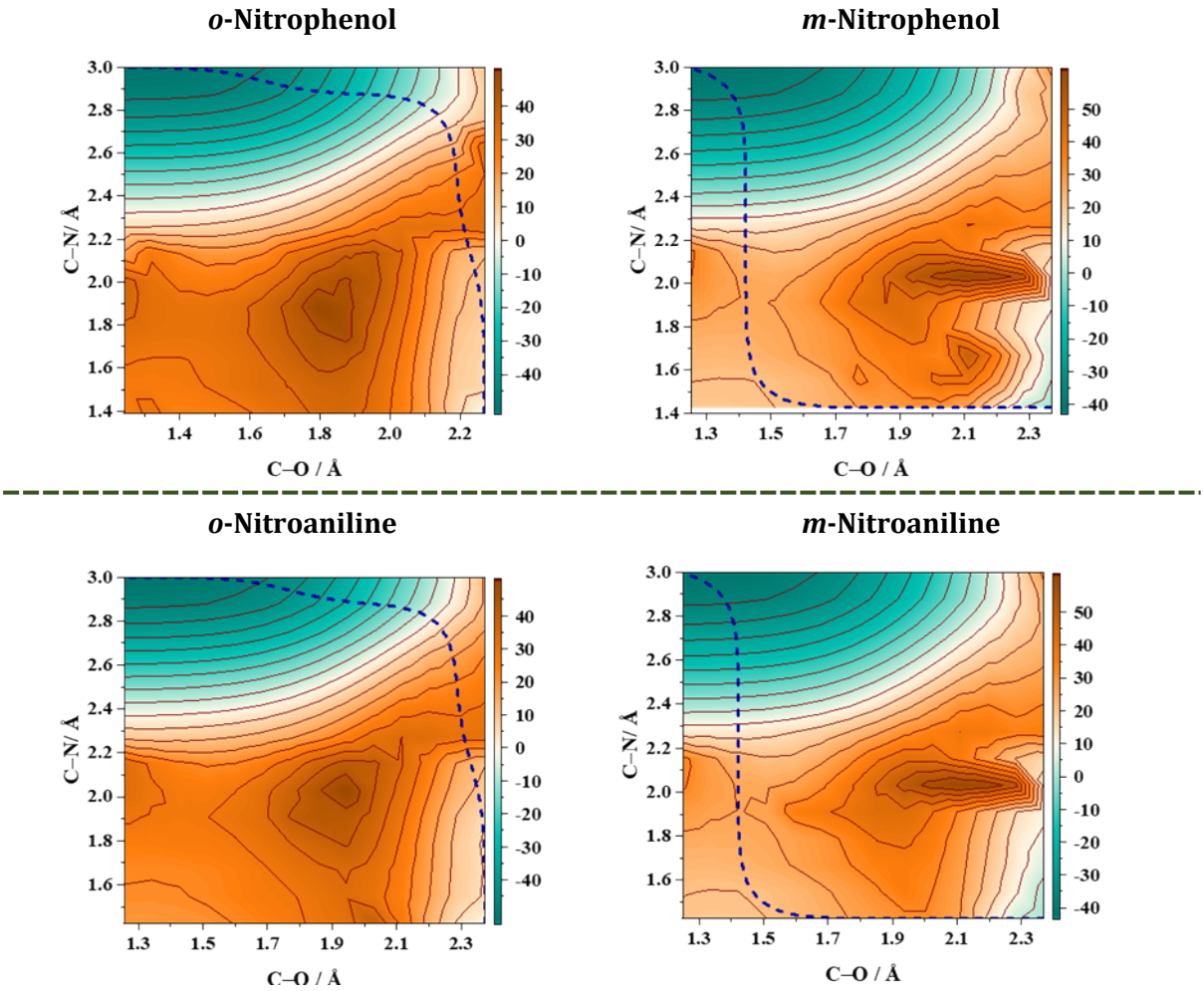

Fig. S2. Two-dimensional potential energy surface (2D-PES) plots of *o*-nitrophenol, *m*-nitrophenol, *o*-nitroaniline, and *m*-nitroaniline calculated using M06-2X/6-311++G(d,p) level of theory. The blue dashed lines represent the minimum energy paths (MEP) connecting the starting structure (bottom right corner) with the formation of NO and the co-fragment phenoxy radical (top left corner) in the T_1 state. The energy scale is in kcal mol^{-1} relative to the starting geometry on the T_1 surface.

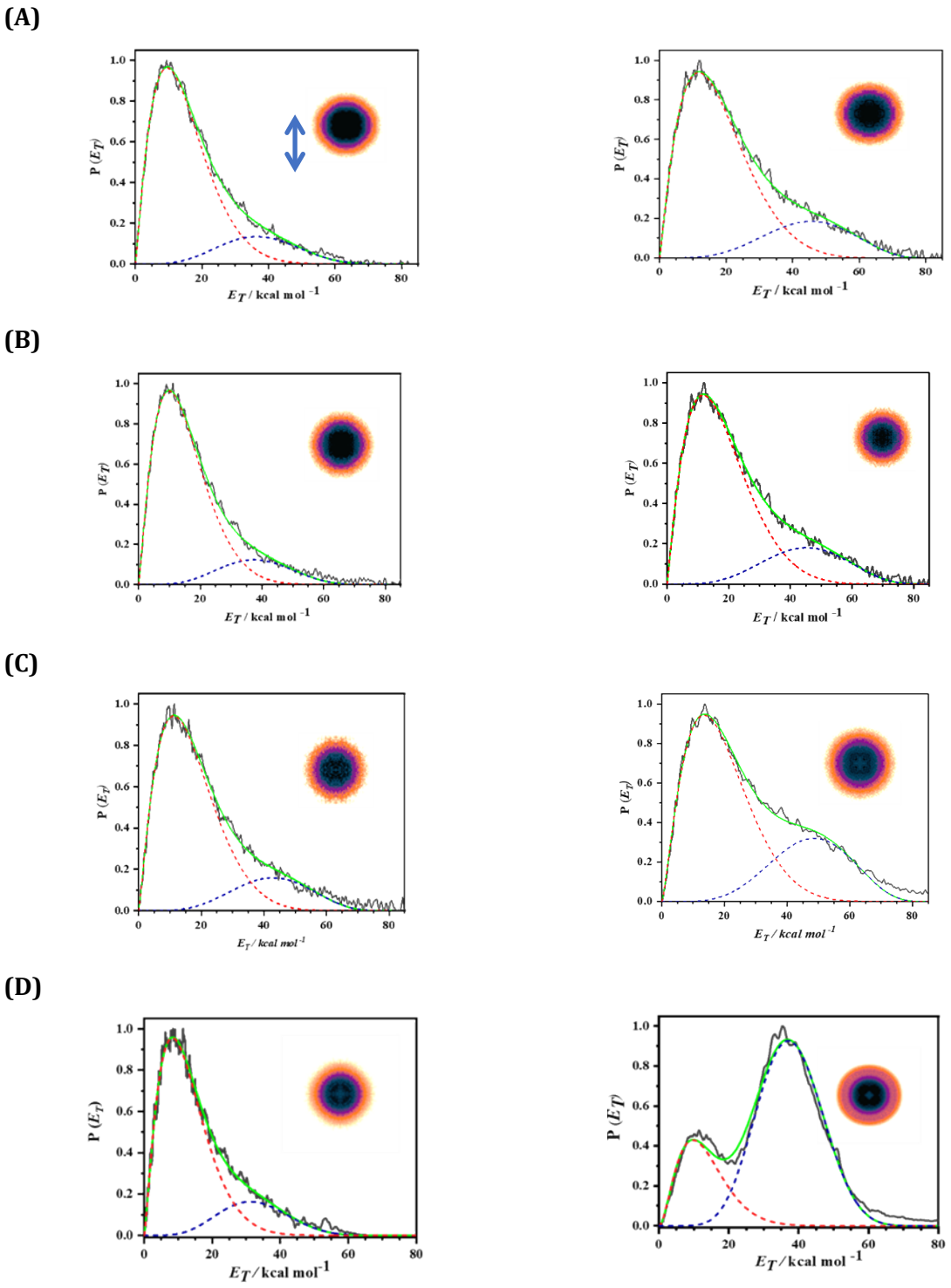

Fig. S3. Symmetrized raw velocity mapped images of NO photofragment obtained from the 266 nm photolysis of *o*-nitrophenol and *m*-nitrophenol at various product states: (A) v=0; J=21.5, (B) v=0; J=29.5, (C) v=0; J=33.5 and (D) v=1; J=50.5. The total translational energy distributions $[P(E_T)]$ are extracted from the corresponding velocity map images. The experimental data (black solid curves) were fitted with an empirical bimodal empirical function, with slow (red dotted curve) and fast (blue dotted curve) translational energy components, and the cumulative fit is shown by green solid curves. The *s/f* is the ratio of the area under the slow and the fast components.

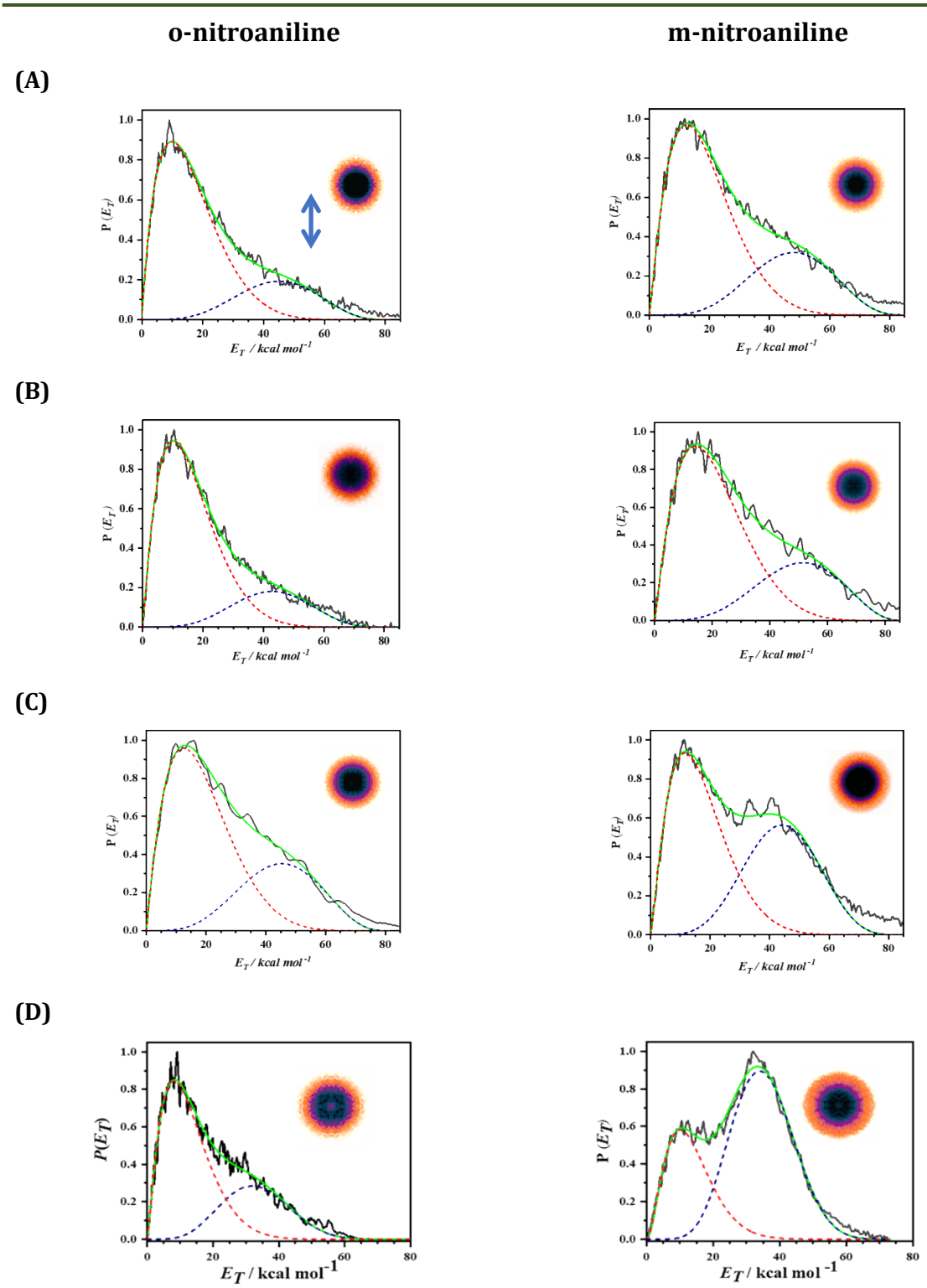

Fig. S4: Symmetrized raw velocity mapped images of NO photofragment obtained from the 266 nm photolysis of *o*-nitroaniline and *m*-nitroaniline at various product states: (A) v=0; J=21.5, (B) v=0; J=29.5, (C) v=0; J=33.5 and (D) v=1; J=50.5. The total translational energy distributions $[P(E_T)]$ are extracted from the corresponding velocity map images. The experimental data (black solid curves) were fitted with an empirical bimodal empirical function, with slow (red dotted curve) and fast (blue dotted curve) translational energy components, and the cumulative fit is shown by green solid curves. The *s/f* is the ratio of the area under the slow and the fast components.

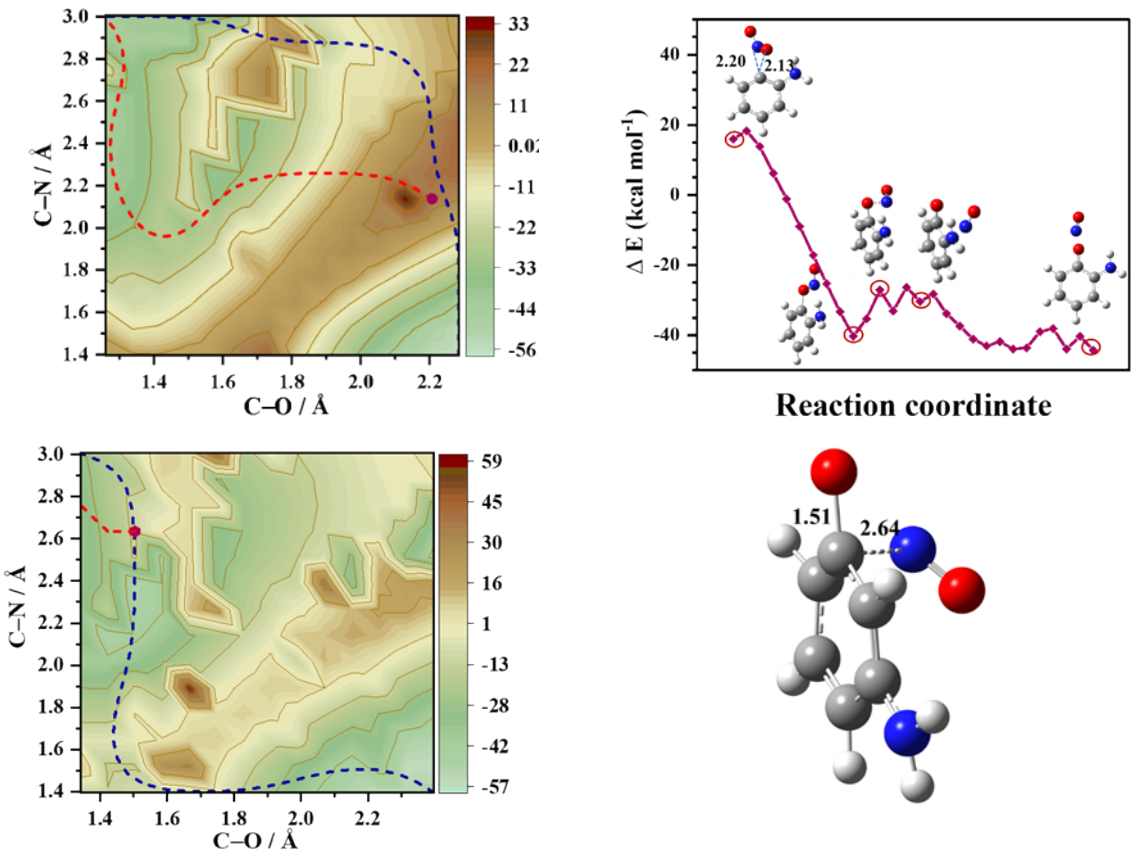

Fig. S5. Ground state (S_0) 2D-PES plots of *o*-nitroaniline (top left), and *m*-nitroaniline (bottom left) with the projected minimum energy path (MEP) that connect the reactant (bottom right corner) to the product (top left corner) in the T_1 state (blue dashed line). The purple dot represents the T_1/S_0 crossing point along the T_1 MEP and the red dashed lines represent the MEPs in the S_0 state. Note that the T_1/S_0 crossing for *o*-nitroaniline and *m*-nitroaniline are early and late relative to the reactant, respectively. The S_0-MEP and selected structures after the T_1/S_0 crossing point for *o*-nitroaniline are shown (top right) along with the T_1/S_0 crossing point of *m*-nitroaniline (bottom right). The distances are shown in Å and the energy scale is in kcal mol^{-1} relative to the starting geometry in the T_1 state.

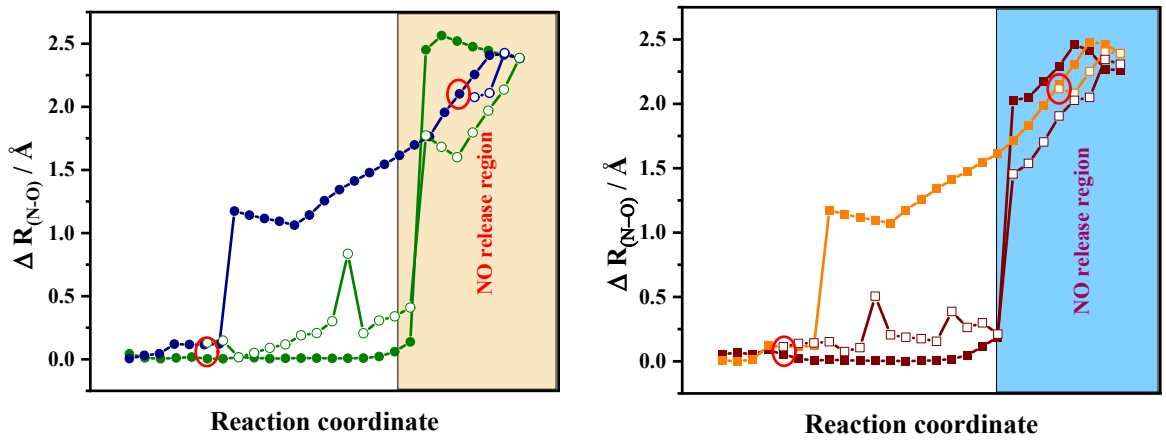

Fig. S6. The roaming and oxaziridine pathways for the NO release in nitrophenols (left panel) and nitroanilines (right panel) is analysed by the evaluating the difference between two N-O bond lengths of the NO_2 group ($^{\Delta R_{N-O}}$) along the minimum energy path in T_1 (solid symbols) and S_0 (open symbols) surfaces. The red circles represent the T_1/S_0 crossing points. The green and blue curves represent *ortho* and *meta* nitrophenols, respectively, while *ortho* and *meta* nitroanilines are represented by brown and orange curves. The roaming path is characterized by sudden and late change in the $^{\Delta R_{N-O}}$ values, whereas the oxaziridine pathway is measured.

TABLE S1: Weighted average of the translational energy values for the slow component (*s*) and fast component (*f*) from the $P(E_T)$ profiles from the NO^+ fragment from 266 nm photolysis (Figure 3). ΔE_{avg} refers to the energy difference between the two average values, while *s/f* represents the ratio of the area under the slow and fast bands. E_T^{max} refers to maximum translational energy values extracted from the fit from equation 1.

NO product state		s_{mp}	s_{avg}	f_{mp}	f_{avg}	ΔE_{avg}	E_T^{max}	*s/f* (Slow / Fast)
		(kcal mol $^{-1}$)						
v=0, J=21.5	o-Nitrophenol	9.55	13.05	35.90	36.38	26.83	80.88	4.92
	m-Nitrophenol	11.71	14.95	45.13	45.56	30.61	85.00	3.17
	o-Nitroaniline	9.37	14.41	43.74	45.00	30.59	81.58	3.23
	m-Nitroaniline	12.40	16.15	48.09	47.49	31.34	86.26	2.28
v=0, J=29.5	o-Nitrophenol	9.87	13.29	36.78	37.39	24.10	80.88	5.40
	m-Nitrophenol	11.71	14.95	45.13	45.56	30.61	85.00	3.78
	o-Nitroaniline	10.12	14.01	42.05	42.71	28.70	81.58	3.67
	m-Nitroaniline	14.16	14.79	51.34	48.89	34.10	86.26	2.38
v=0, J=33.5	o-Nitrophenol	11.22	14.75	42.24	42.82	27.50	80.88	4.31
	m-Nitrophenol	13.63	15.91	48.76	48.82	32.91	85.00	2.31
	o-Nitroaniline	12.42	16.35	44.34	45.12	28.77	81.58	2.05
	m-Nitroaniline	11.37	15.30	43.57	44.20	28.90	86.26	1.21
***v*=1, *J* =50.5**	o-Nitrophenol	8.33	12.56	31.15	32.34	19.78	80.88	3.85
	m-Nitrophenol	9.74	12.30	36.99	36.94	24.64	85.00	0.33
	o-Nitroaniline	8.17	12.64	31.79	32.99	20.35	81.58	1.92
	m-Nitroaniline	10.11	12.70	34.00	34.01	21.31	86.26	0.45

TABLE S2: The parameters used to fit the $P(E_T)$ function in equation 1: a_1 and b_1 for slow component (*s*) and a_2 and b_2 for fast component (*f*) following 266 nm photolysis shown in Figure 2.

NO product state		a_1	b_1	a_2	b_2
v=0, J=21.5	o-Nitrophenol	1.20	8.99	4.76	5.80
	m-Nitrophenol	1.13	6.68	4.47	3.46
	o-Nitroaniline	0.94	6.83	4.43	3.58
	m-Nitroaniline	1.15	6.85	4.61	3.67
v=0, J=29.5	o-Nitrophenol	1.25	9.04	1.25	5.72
	m-Nitrophenol	1.14	7.18	4.54	3.98
	o-Nitroaniline	1.08	7.58	4.70	4.24
	m-Nitroaniline	1.14	5.82	4.22	2.86
v=0, J=33.5	o-Nitrophenol	1.24	7.72	4.87	4.32
	m-Nitrophenol	1.39	7.40	5.19	3.89
	o-Nitroaniline	1.10	6.09	4.13	3.29
	m-Nitroaniline	1.29	8.39	5.28	5.04
v=1, J =50.5	o-Nitrophenol	1.36	11.82	5.36	8.54
	m-Nitrophenol	1.95	15.11	8.17	10.59
	o-Nitroaniline	1.24	11.22	5.20	8.13
	m-Nitroaniline	1.98	14.97	7.26	11.18