

**New route to toxic nitro and nitroso products upon irradiation of micropollutants mixtures containing imidacloprid: role of NO<sub>x</sub> and effet of natural organic matter**

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**Figure SI-5**. Structures (a)-(k) of the minimum energy structures and TSs at the MN12SX/6-311++G(d,p),PCM//MN12SX/6-31+G(d,p),PCM level. Energies are given relatively to the global minimum (see Figure 4). Specific bond distances (Å) are also indicated.

**Figure SI-7** . Consumption profile of IMD (10<sup>-4</sup> M) upon irradiation in device 2.

**Figure SI-8 :** Formation of nitroso-resorcinol and nitro-resorcinol upon irradiation in device 2 of IMD ( $10^{-4}$  M) and resorcinol ( $10^{-4}$  M).

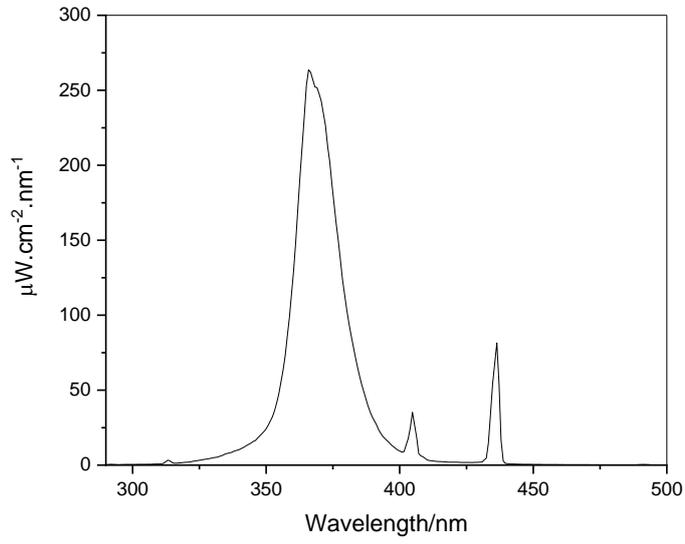
**Table SI-1.** HPLC conditions used for separation and analysis of the different compounds.

**Table SI-2 :** UPLC-HMRS of IMD and photoproducts

**Table SI-3:** Cartesian coordinates of the minimum energy structures and TSs at the MN12SX/6-311++G(d,p),PCM//MN12SX/6-31+G(d,p),PCM level.

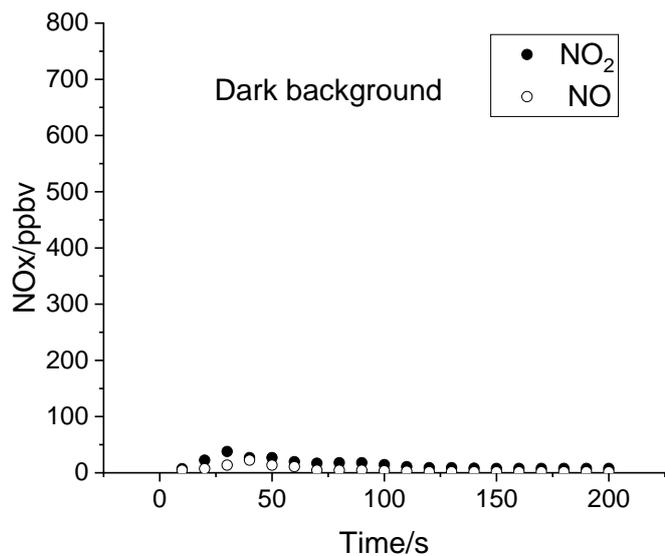
**Table SI-4 :** Photonitration and photonitrosation of the probes after 16 h of irradiation in device 2 in presence of IMD ( $10^{-5}$  or  $10^{-4}$  M) or a mixture of  $\text{NO}_3^-$  ( $2 \times 10^{-5}$  M) and  $\text{NO}_2^-$  ( $5 \times 10^{-6}$  M).

**Figure SI-1 .** Irradiance of the fluorescent tubes Sylvania F15W/BL 368S used in devices 1 and 2.

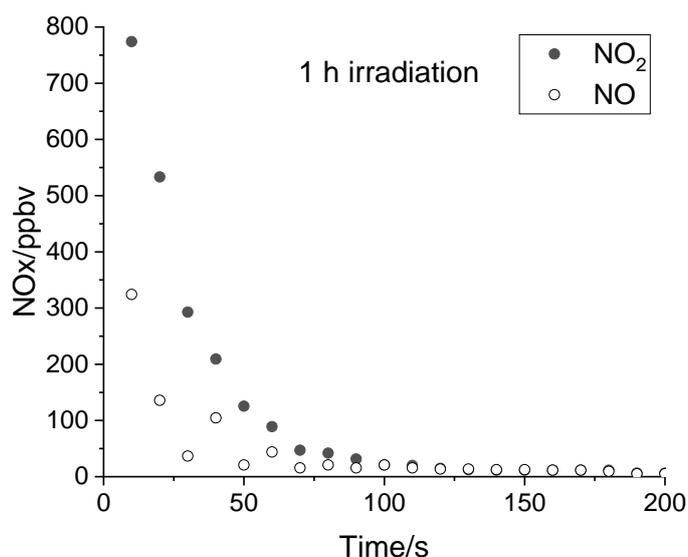


**Figure SI-2 .** Background level of NO<sub>x</sub> formation (A) and NO<sub>x</sub> formation upon irradiation of IMD ( $10^{-4}$  M) for 1 h in device 1 (B). After selected irradiation times, the light was turned off and the outlet of the reactor connected to the NO<sub>x</sub> analyzer. NO<sub>x</sub> were measured every 10 seconds for a period of 1-2 min at a flow rate of  $0.7 \text{ L min}^{-1}$ . The time profile of NO<sub>x</sub> concentrations corresponds to the decay of NO<sub>x</sub> level in the reactor due to the dilution with clean air.

A)



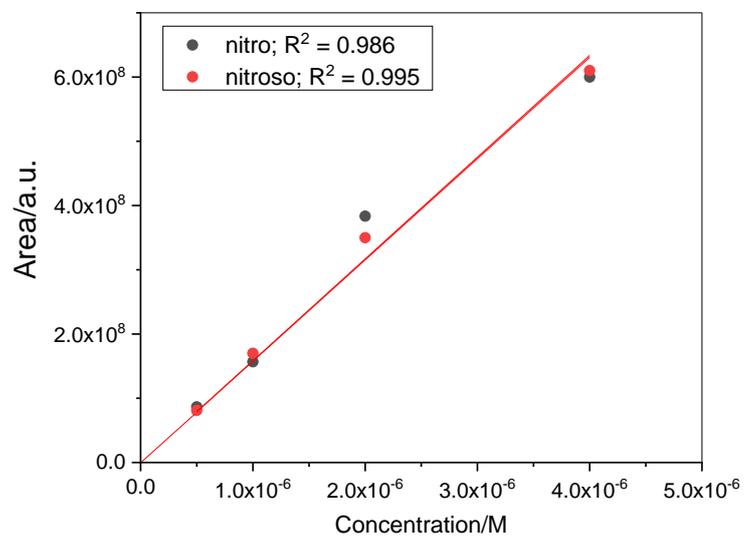
B)



**Table SI-2.** HPLC conditions used for separation and analysis of the different compounds.

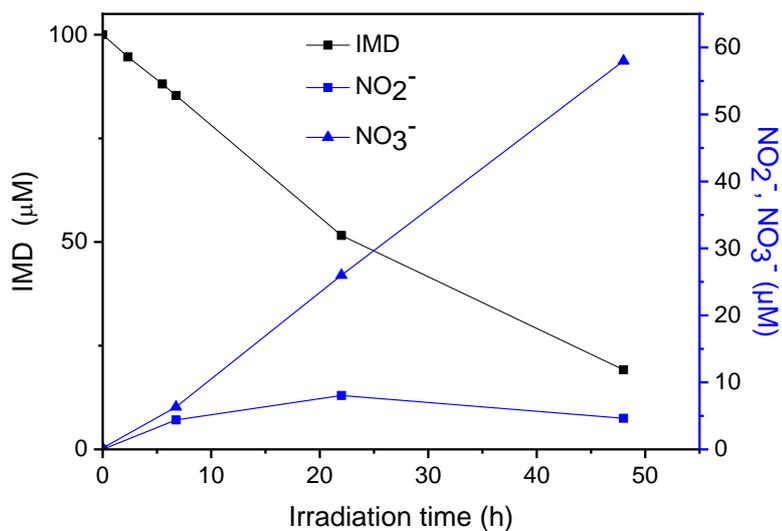
<b>Compound</b>	<b>H<sub>2</sub>O (%)</b>	<b>ACN</b>	<b>Detection wavelength/nm</b>
IMD	60	40	270
Phenol	60	40	270
L-tryptophan	85	15	280
Resorcinol	70	30	274
NO <sub>2</sub> <sup>-</sup> (derivatized)	60	40	307

**Figure SI-3 .** Calibration curve for nitroso-phenol (open circles) and for nitro-phenol (black circles). Area were obtained by UPLC-HR-MS analyses in electrospray negative mode. For nitrosophenol  $m/z= 122.0237$  (5 ppm) and for nitrophenol  $m/z=138.0186$  (5 ppm).

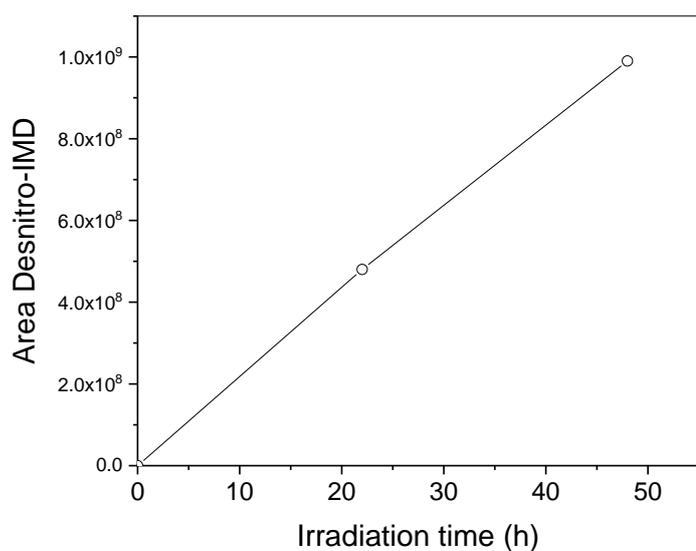


**Figure SI-4.** Consumption profile of aqueous IMD ( $10^{-4}$  M) irradiated in device 1, formation of  $\text{NO}_3^-$  and  $\text{NO}_2^-$  (A) and area UPLC-HRMS of desnitro-IMD (B). IMD was analyzed by HPLC-UV,  $\text{NO}_3^-$  by ionic chromatography,  $\text{NO}_2^-$  by HPLC-UV after derivatization by DNPH. Desnitro-IMD was identified by UPLC-HRMS ( $m/z = 22.0740/213.0709$ ,  $\Delta = 2.2$  ppm)

A)



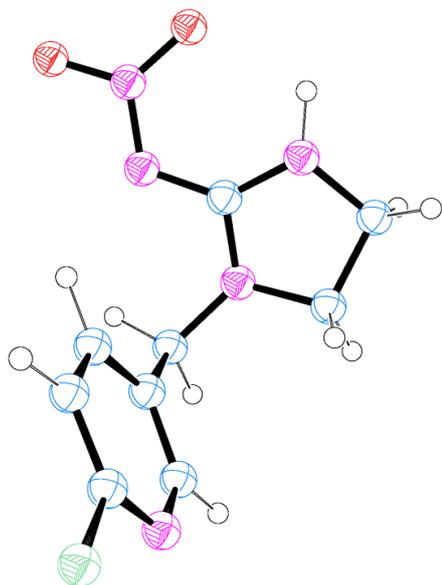
B)



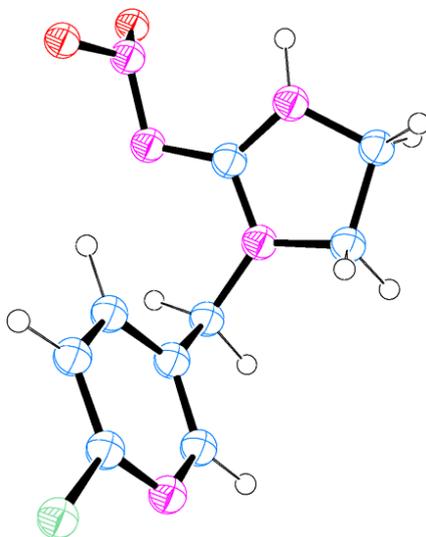
**Table SI-2 : UPLC-HMRS of IMD and photoproducts**

Name	m/z exp. in ES <sup>+</sup>	m/z theor. in ES <sup>+</sup>	Δppm	Formula of the neutral molecule
IMD	256.0603/ 258.0571	256.0596/ 258.0566	2.82	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>2</sub>
IMD+O	272.0549/ 274.0517	272.0545/ 274.0515	1.38	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O <sub>3</sub>
IMD-O	240.0650/ 242.0620	240.0647/ 242.0617	1.52	C <sub>9</sub> H <sub>10</sub> ClN <sub>5</sub> O
Desnitro-IMD	211.0746/ 213.0717	211.0745/ 213.0716	0.33	C <sub>9</sub> H <sub>11</sub> ClN <sub>4</sub>
Desnitro-IMD+2O	243.0650/ 245.0619	243.0643/ 245.0614	2.84	C <sub>9</sub> H <sub>11</sub> ClN <sub>4</sub> O <sub>2</sub>

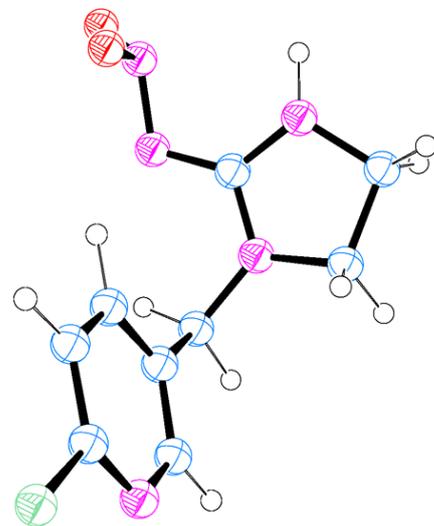
**Figure SI-5.** Structures (a)-(k) of the minimum energy structures and TSs at the MN12SX/6-311++G(d,p),PCM/MN12SX/6-31+G(d,p),PCM level. Energies are given relatively to the global minimum (see Figure 4). Specific bond distances (Å) are also indicated.



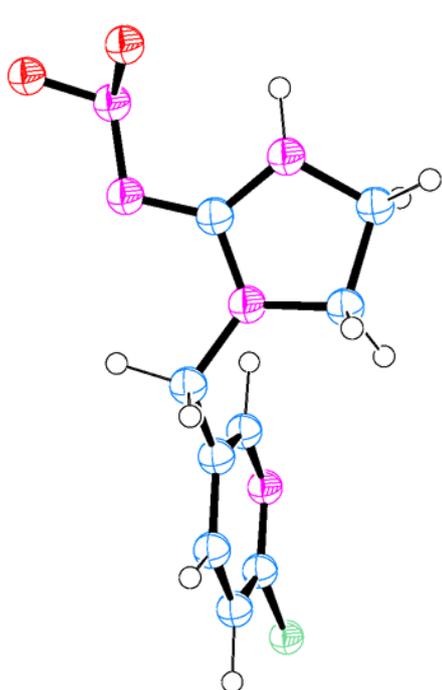
Global min in  $S_0$ ,  ${}^1\text{RNNNO}_2$  (a)  
 $0.0 \text{ kcal mol}^{-1}$



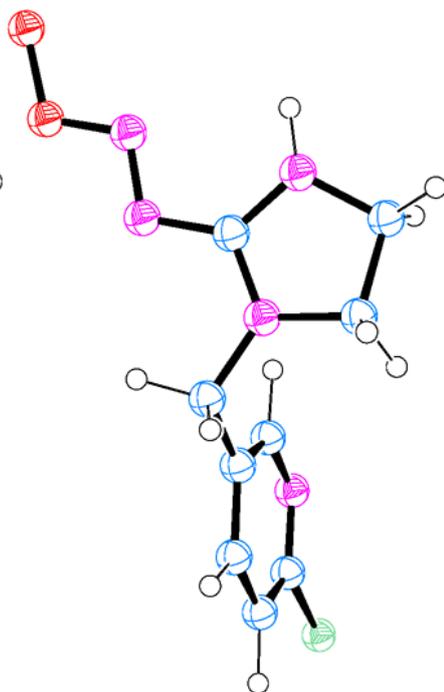
Min in  $S_1$  (b)  
 $79.3 \text{ kcal mol}^{-1}$



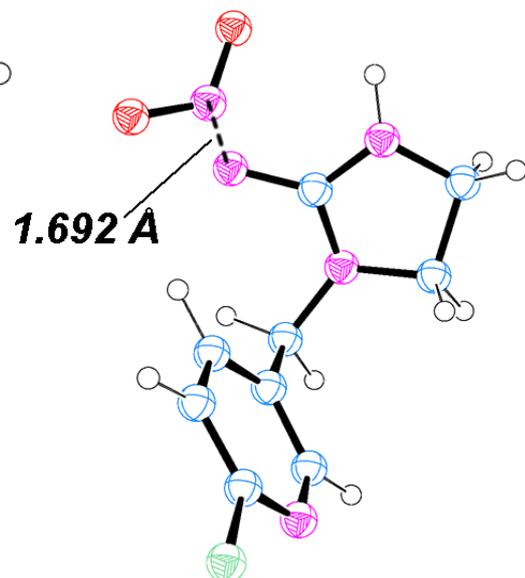
Min in  $T_1$ ,  ${}^3\text{RNNNO}_2$  (c)  
 $67.3 \text{ kcal mol}^{-1}$



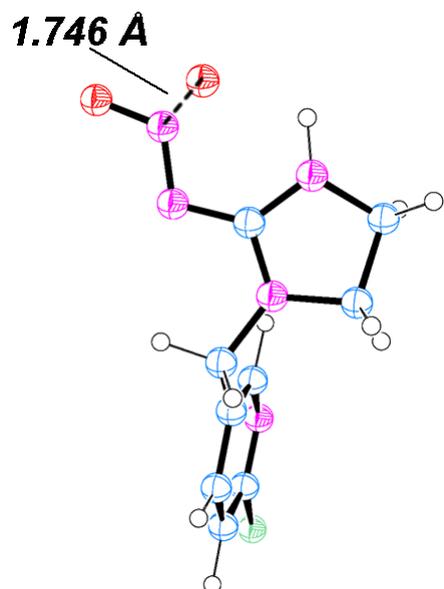
TS in  $S_0$  (d)  
 $106.1 \text{ kcal mol}^{-1}$



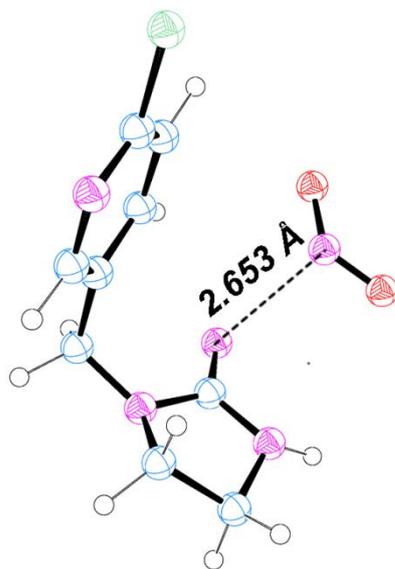
${}^1\text{RNNNO-O}$  (e)  
 $56.4 \text{ kcal mol}^{-1}$



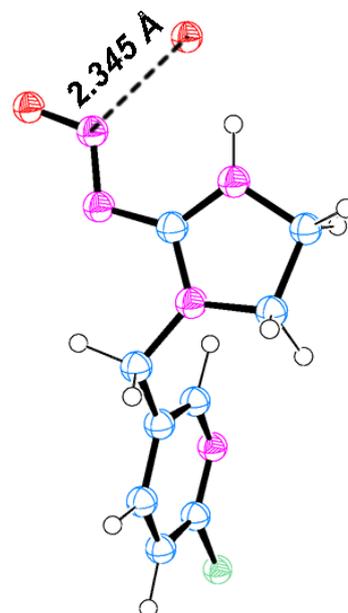
TS $_1$  in  $T_1$  (f)  
 $73.4 \text{ kcal mol}^{-1}$



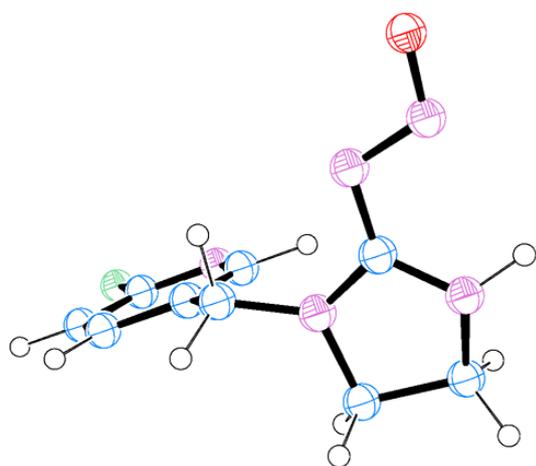
**TS<sub>2</sub> in T<sub>1</sub> (g)**  
78.7 kcal mol<sup>-1</sup>



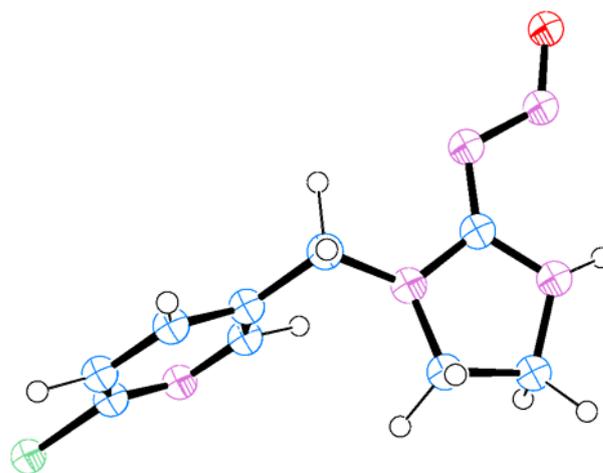
**<sup>3</sup>RN---NO<sub>2</sub> (h)**  
59.8 kcal mol<sup>-1</sup>



**<sup>3</sup>RNNO-O in T<sub>1</sub> (i)**  
76.1 kcal mol<sup>-1</sup>



**<sup>1</sup>RNNO (j)**  
80.4 kcal/mol



**<sup>3</sup>RNNO (k)**  
121.4 kcal/mol

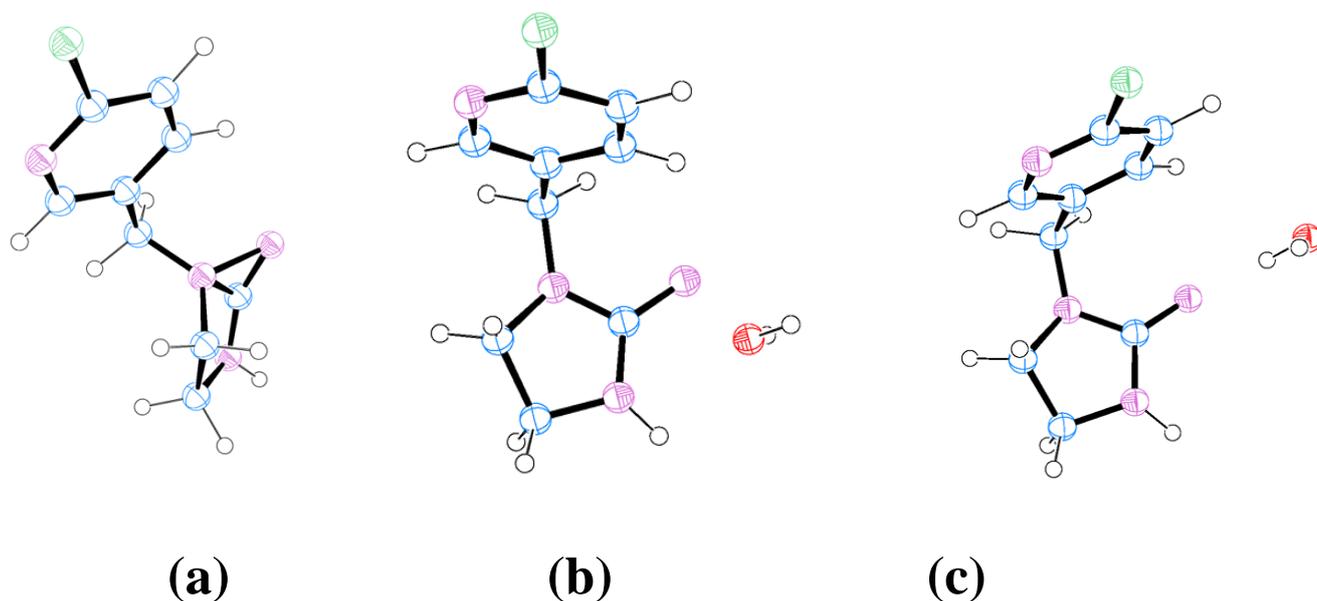
**Table SI-3:** Cartesian coordinates of the minimum energy structures and TSs at the MN12SX/6-311++G(d,p),PCM/MN12SX/6-31+G(d,p),PCM level.

Min S <sub>0</sub> , <sup>1</sup> RNNO <sub>2</sub> (a)			Min S <sub>1</sub> (b)			Min T <sub>1</sub> , <sup>3</sup> RNNO <sub>2</sub> (c)			TS S <sub>0</sub> (d)			<sup>1</sup> RNNO-O (e)							
C	-3.904635	0.765039	0.032387	C	-3.398081	0.341802	0.079196	C	-3.362675	-0.347631	-0.074888	C	-0.203027	-0.349078	1.121773	C	-0.154117	0.191187	1.381299
C	-2.651975	1.265986	-0.317873	C	-2.294923	1.176317	0.255215	C	-2.232460	-1.117072	-0.347477	H	-0.281192	-0.106962	2.195510	H	-0.106941	0.737387	2.336454
C	-1.771163	0.388254	-0.933223	C	-1.082502	0.731770	-0.248795	C	-1.023506	-0.662472	0.156625	C	-0.927867	1.995016	0.518132	C	-0.739947	2.341866	0.147460
C	-2.166764	-0.931261	-1.177332	C	-1.017011	-0.505420	-0.896764	C	-0.987178	0.524124	0.897419	C	-2.038247	2.499264	-0.402607	C	-1.809222	2.629975	-0.911387
C	-3.448748	-1.301054	-0.779059	C	-2.191008	-1.246366	-0.998624	C	-2.187175	1.202458	1.087676	H	0.065289	2.357516	0.229170	H	0.281189	2.492397	-0.221553
N	-4.312703	-0.469965	-0.181967	N	-3.370853	-0.830912	-0.525888	N	-3.364975	0.775416	0.614761	H	-1.113855	2.266057	1.571397	H	-0.881746	2.940803	1.060570
H	-0.776932	0.727778	-1.229275	H	-0.190402	1.353466	-0.141601	H	-0.110339	-1.235334	-0.023647	H	-1.666108	2.679980	-1.422076	H	-1.412985	2.518630	-1.930749
H	-2.387350	2.301614	-0.116328	H	-2.391683	2.132733	0.763368	H	-2.306763	-2.033495	-0.928024	H	-2.521117	3.407213	-0.029650	H	-2.254452	3.623066	-0.803036
H	-3.809069	-2.319038	-0.948182	H	-2.192201	-2.220737	-1.492300	H	-2.212382	2.137059	1.652683	N	-1.031695	0.548155	0.348818	N	-0.982752	0.931296	0.453497
Cl	-5.046843	1.828429	0.817110	Cl	-4.947854	0.860345	0.690667	Cl	-4.909736	-0.885948	-0.680589	N	-2.954805	1.363624	-0.384090	N	-2.783146	1.578648	-0.630835
C	-1.232405	-1.933964	-1.814625	C	0.284558	-1.025771	-1.465310	C	0.307430	1.054822	1.468931	H	-3.762834	1.318289	-0.997301	H	-3.601560	1.412056	-1.206440
H	-1.798679	-2.809084	-2.160279	H	0.121930	-1.973713	-1.994034	H	0.132063	1.999553	1.999723	C	-2.283558	0.237601	-0.063034	C	-2.199555	0.582978	0.040735
H	-0.725483	-1.498193	-2.682400	H	0.717191	-0.252771	-2.173030	H	0.737372	0.344379	2.185474	N	-2.734621	-1.004600	-0.084846	N	-2.702912	-0.649266	0.324821
C	-0.574092	-3.204168	0.277229	C	1.131843	-2.341972	0.556493	C	1.135361	2.343184	-0.572120	N	-3.959398	-1.067285	-0.660242	N	-3.874881	-0.779031	-0.195123
C	0.789058	-3.429027	0.931785	C	2.423456	-2.204628	1.370553	C	2.415193	2.194510	-1.400977	O	-4.611643	-2.141095	-0.408242	O	-4.346713	-1.939414	0.072304
H	-1.068425	-4.135321	-0.020573	H	1.028070	-3.311187	0.056855	H	1.036222	3.327626	-0.102311	O	-5.110203	-0.465414	0.134532	O	-5.621750	-2.141845	-0.462369
H	-1.253750	-2.632790	0.931988	H	0.232750	-2.158848	1.167751	H	0.230410	2.138675	-1.167309	H	-0.594941	-1.366250	0.989337	H	-0.644501	-0.770714	1.576793
H	1.249157	-4.371466	0.600354	H	3.217372	-2.862363	0.989606	H	3.203420	2.879828	-1.057836	C	1.242504	-0.290799	0.691388	C	1.240908	-0.022062	0.843308
H	0.746251	-3.415572	2.024795	H	2.272044	-2.399108	2.435751	H	2.245955	2.346043	-2.470799	C	1.593661	-0.164240	-0.652341	C	1.469772	-0.258065	-0.511323
N	-0.214848	-2.410322	-0.893377	N	1.268626	-1.268798	-0.425800	N	1.301086	1.300108	0.439606	C	2.279394	-0.394872	1.619394	C	2.348739	-0.015140	1.691979
N	1.544992	-2.291783	0.421331	N	2.767602	-0.804712	1.131045	N	2.786811	0.811780	-1.113668	H	0.821427	-0.066346	-1.418580	H	0.640957	-0.266019	-1.222977
H	2.526684	-2.126330	0.609672	H	3.643477	-0.393806	1.439213	H	3.658194	0.398663	-1.430265	C	3.598640	-0.382619	1.185131	C	3.615398	-0.245686	1.172933
C	0.977749	-1.810901	-0.690410	C	2.172605	-0.379626	0.008438	C	2.210014	0.409620	0.025425	H	2.509851	-0.483432	2.684555	H	2.226772	0.173523	2.759720
N	1.360434	-0.869752	-1.568602	N	2.361218	0.770849	-0.659494	N	2.440532	-0.712142	0.738625	C	3.810872	-0.256142	-0.184742	C	3.706360	-0.466007	-0.198603
N	2.579242	-0.334902	-1.426154	N	3.279295	1.593014	0.010847	N	3.347063	-1.548856	0.067730	H	4.433881	-0.460282	1.877288	H	4.503037	-0.245919	1.801116
O	2.875910	0.546229	-2.242636	O	4.420065	1.561650	-0.596315	O	4.205043	-2.174075	0.755423	Cl	5.450699	-0.230562	-0.787984	Cl	5.279412	-0.743932	-0.906833
O	3.377159	-0.691010	-0.533892	O	2.747453	2.691061	0.409641	O	2.498420	-2.230334	-0.725516	N	2.857413	-0.145456	-1.090040	N	2.682984	-0.474873	-1.031162

TS <sub>1</sub> , T <sub>1</sub> (f)			TS <sub>2</sub> , T <sub>1</sub> (g)			<sup>3</sup> RN---NO <sub>2</sub> (h)			<sup>3</sup> RNNO-O in T <sub>1</sub> (i)						
C	3.187194	0.227055	-0.124355	C	-0.205293	-0.060599	1.314892	C	2.814838	-0.330504	-0.104796	C	-0.119348	0.059714	1.469669
C	2.151026	1.138337	0.074237	H	-0.225749	0.396895	2.317390	C	2.114400	0.556284	0.708377	H	-0.069546	0.605839	2.425420
C	0.975015	0.646553	0.621106	C	-1.037432	2.128770	0.331767	C	0.901175	0.115662	1.220359	C	-1.011961	2.155277	0.347300
C	0.879107	-0.711259	0.943283	C	-2.129584	2.411617	-0.703288	C	0.436348	-1.163967	0.903215	C	-2.178567	2.355329	-0.625482
C	1.988973	-1.514046	0.692219	H	-0.045765	2.465962	0.008335	C	1.243134	-1.952450	0.083372	H	-0.044390	2.445562	-0.078388
N	3.132100	-1.057506	0.166573	H	-1.264221	2.578975	1.311582	N	2.416805	-1.548618	-0.417693	H	-1.158771	2.696668	1.295427
H	0.138042	1.327863	0.800686	H	-1.716339	2.479670	-1.720069	H	0.313353	0.770053	1.867321	H	-1.840656	2.350273	-1.672011
H	2.270553	2.187294	-0.186483	H	-2.695331	3.321754	-0.483212	H	2.507230	1.545953	0.930126	H	-2.733398	3.278748	-0.434443
H	1.966680	-2.580645	0.929145	N	-1.088372	0.671828	0.437138	H	0.939235	-2.968736	-0.181882	N	-1.065274	0.715845	0.595987
Cl	4.689901	0.800493	-0.804530	N	-2.966371	1.222997	-0.571628	Cl	4.350410	0.173373	-0.772346	N	-2.997235	1.179441	-0.350447
C	-0.389542	-1.299857	1.516466	H	-3.745817	1.032188	-1.193510	C	-0.908128	-1.653261	1.387958	H	-3.826097	0.923517	-0.890056
H	-0.200563	-2.300278	1.925345	C	-2.262716	2.019044	-0.023736	H	-0.902819	-2.744665	1.506130	C	-2.262662	0.235823	0.242243
H	-0.778435	-0.671310	2.328589	N	-2.607783	-1.069180	0.109505	H	-1.139081	-1.213097	2.368362	N	-2.592191	-1.049179	0.519810
C	-1.356164	-2.374792	-0.593330	N	-3.779593	-1.321407	-0.472256	C	-2.131166	-1.961989	-0.816481	N	-3.771921	-1.362575	0.037006
C	-2.639341	-2.062339	-1.370850	O	-4.195045	-2.471112	-0.504790	C	-3.316312	-1.199517	-1.397255	O	-4.181012	-2.488907	0.271856
H	-1.313314	-3.403713	-0.220838	O	-5.077016	-0.351132	0.178466	H	-2.317457	-3.035770	-0.700481	O	-5.042584	-0.382344	-1.673348
H	-0.452574	-2.169155	-1.190489	H	-0.599483	-1.080291	1.416376	H	-1.226612	-1.815491	-1.433860	H	-0.503267	-0.945154	1.687434
H	-3.477316	-2.694880	-1.044078	C	1.214956	-0.100755	0.803031	H	-4.270264	-1.631624	-1.055222	C	1.260847	-0.028331	0.862984
H	-2.515145	-2.155929	-2.453515	C	1.507667	-0.062886	-0.559029	H	-3.306916	-1.162074	-2.491041	C	1.450728	-0.180374	-0.509285
N	-1.441694	-1.426608	0.518570	C	2.288934	-0.215521	1.688497	N	-1.997941	-1.317254	0.485603	C	2.399265	0.002449	1.670371
N	-2.871707	-0.672843	-0.985360	H	0.708298	0.036117	-1.296650	N	-3.085288	0.122779	-0.824530	H	0.597108	-0.199956	-1.190479
H	-3.677759	-0.121158	-1.268011	C	3.583197	-0.300980	1.195184	H	-3.789700	0.848562	-0.910140	C	3.655784	-0.128373	1.096183
C	-2.250335	-0.412582	0.167004	H	2.116853	-0.238813	2.765821	C	-2.443143	-0.018085	0.379887	H	2.307632	0.129040	2.750445
N	-2.366870	0.699289	0.925083	C	3.736657	-0.256583	-0.188209	N	-2.271254	0.910898	1.266655	C	3.706095	-0.278963	-0.287035
N	-2.480190	2.017349	-0.129050	H	4.444850	-0.392440	1.852223	N	-0.783212	2.567466	-0.175823	H	4.565384	-0.108351	1.691679
O	-3.713558	2.017662	-0.435706	Cl	5.345353	-0.362644	-0.862800	O	-1.580424	2.968442	-0.977686	Cl	5.264756	-0.448675	-1.059718
O	-1.882135	3.011505	0.314613	N	2.749246	-0.137062	-1.053440	O	-0.042379	3.151509	0.565595	N	2.654169	-0.302675	-1.082295

**Figure SI-6.** Structures of  $\text{RN}^+$  (a),  $\text{RN}^+\cdot\text{H}_2\text{O}$  (b) and  $\text{RN}\cdot\text{H}_2\text{O}$  (c) obtained at the MN12SX/6-31+G(d,p),PCM level and calculation of  $\text{RN}^+$  energy:



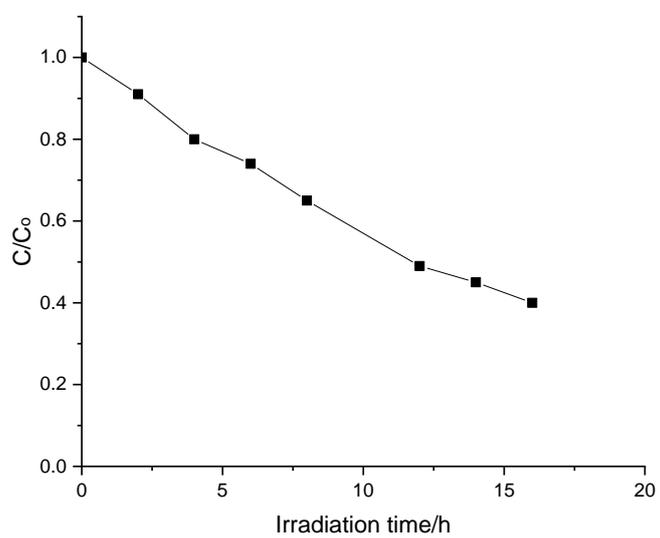
#### Calculation of $\text{RN}^+$ energy:

Optimization of  $\text{RN}^+$  at the MN12SX/6-31+G(d,p),PCM level gave rise to the high energy cyclized species in Fig SI-6a. This structure is similar to that found in the gas phase (MN12SX/6-31+G(d,p)) and it became clear that the PCM model was not sufficient to account for solvent effects here. It was thus decided to optimize  $\text{RN}^+$  at the MN12SX/6-31+G(d,p),PCM level in the presence of one water molecule (implicit + explicit solvation model). The obtained geometry is shown below in Figure SI-6b (no spurious cyclization). Thus, the more accurate energy of  $\text{RN}^+$  ( $\text{RN}^+/\text{NO}_2^-$  at 69.0 kcal/mol in Figure 4) was that of  $\text{RN}^+$  obtained at the MN12SX/6-31+G(d,p),PCM level and corrected with the energy difference below, i.e:

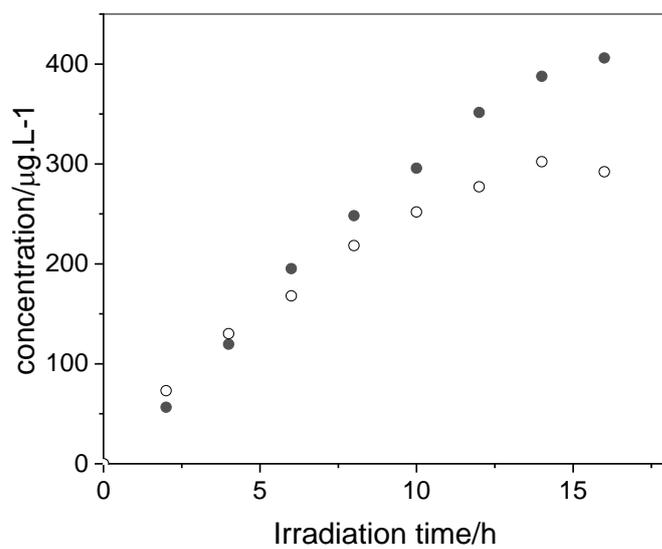
$$E_{\text{text}}(\text{RN}^+) = E(\text{RN}^+) + \underbrace{[E(\text{RN}^+, \text{H}_2\text{O}) - E(\text{RN}, \text{H}_2\text{O})] - [E(\text{RN}^+) - E(\text{RN})]}_{\substack{\text{These species computed at the} \\ \text{MN12SX/6-311++G(d,p),PCM // MN12SX/6-31+G(d,p),PCM} \\ \text{level}}}$$

i.e: 
$$E_{\text{text}}(\text{RN}^+) = E(\text{RN}) + [E(\text{RN}^+, \text{H}_2\text{O}) - E(\text{RN}, \text{H}_2\text{O})]$$

**Figure SI-7 .** Consumption profile of IMD ( $10^{-4}$  M) upon irradiation in device 2. The concentrations of IMD were determined by HPLC-UV.



**Figure SI-8 :** Formation of nitroso-resorcinol (open circles) and nitro-resorcinol (full circles) upon irradiation in device 2 of IMD ( $10^{-4}$  M) and resorcinol ( $10^{-4}$  M). The concentrations of nitroso and nitro-resorcinols were estimated using calibration curves of Figure SI-3.



**Table SI-4 :** Photonitration and photonitrosation of the probes after 16 h of irradiation in device 2 in presence of IMD ( $10^{-5}$  or  $10^{-4}$  M) or a mixture of  $\text{NO}_3^-$  ( $2 \times 10^{-5}$  M) and  $\text{NO}_2^-$  ( $5 \times 10^{-6}$  M). The concentrations of IMD and of the probes were obtained by HPLC-UV while the amounts of nitro and nitro-derivatives by UPLC-HRMS.

Conditions	% of converted IMD	% of converted probe	Nitroso derivative formed ( $\mu\text{g.L}^{-1}$ )	Nitro derivative formed ( $\mu\text{g.L}^{-1}$ )	Sum ( $\mu\text{g.L}^{-1}$ )
Phenol ( $10^{-4}$ M)	-	< 0.5	-	-	-
Phenol ( $10^{-4}$ M)+ IMD ( $10^{-4}$ M)	56±3	14±1	34±2	202±10	236±12
Phenol ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	3.4±0.1	0.28±0.02	34±2	34±2
Resorcinol ( $10^{-4}$ M)	-	< 0.5	-	-	-
Resorcinol ( $10^{-4}$ M)+IMD ( $10^{-4}$ M)	58±3	29±1	406±40	292±29	498±69
Resorcinol ( $10^{-4}$ M)+IMD ( $10^{-5}$ M)	61±3	46±5	43±4	16±2	59±6
Resorcinol ( $10^{-5}$ M)+IMD ( $10^{-4}$ M)	62±3	58±5	3.6±0.8	100±20	104±21
Resorcinol ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	6.2±0.3	99±9	70.8±7	170±16
Tryptophan ( $10^{-4}$ M)	-	91±5	-	-	-
Tryptophan ( $10^{-4}$ M)+IMD ( $10^{-4}$ M)	60±3	95±5	19±2	9.4±0.9	28±3
Tryptophan ( $10^{-4}$ M)+ $\text{NO}_2^-/\text{NO}_3^-$	-	96±5	7.4±0.7	6.2±0.6	14±2