New Journal of Chemistry

Electronic supplementary information (ESI)

The Reaction of N*H*-Indazoles with 1-Fluoro-2,4-dinitrobenzene: The Unusual Formation of Benzotriazole-*N*-oxides

Ibon Alkorta,[a] Fernando P. Cossío,[b]José Elguero,[a] Nieves Fresno,[a] Laura Hernández-Folgado,[a] Santiago García-Granda,[c] Laura Menéndez-Taboada,[c] Ruth Pérez-Fernández,[a] Felipe Reviriego[a] and Lucia Vázquez-Viñuela[c]

[a] *Instituto de Química Médica, C.S.I.C., Juan de la Cierva, 3, E-28006 Madrid, Spain,*

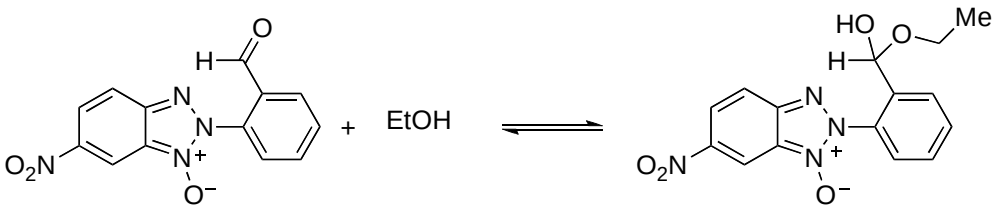
[b] *Departamento de Química Orgánica I, Kimika Fakultatea, Universidad del País Vasco – Euskal Herriko Unibertsitatea, Manuel de Lardizabal 3, 20018 San Sebastián-Donostia, Spain,*

[c] *Departamento de Química Física y Analítica, Facultad de Química, Universidad de Oviedo-CINN, E-33006 Oviedo, Spain*

1. General experimental methods

Flash column chromatography were run on silica gel 60 (0.040–0.063 nm) from Merck. Melting points were measured in open-end glass capillary tubes and are uncorrected. ^{1}H and ^{13}C NMR were recorded on a Bruker 300 MHz spectrometer. The chemical shifts are reported relative to the deuterated solvents. LC-MS chromatograms and spectra were recorded on a HPLC 2695 with a Waters 2996 photodiode array detector and Waters Micromass ZQ module. The column used was a Sunfire C18 with 3.5 μm and 50 cm x 4.6 mm. MS spectra were recorded by positive ESI.

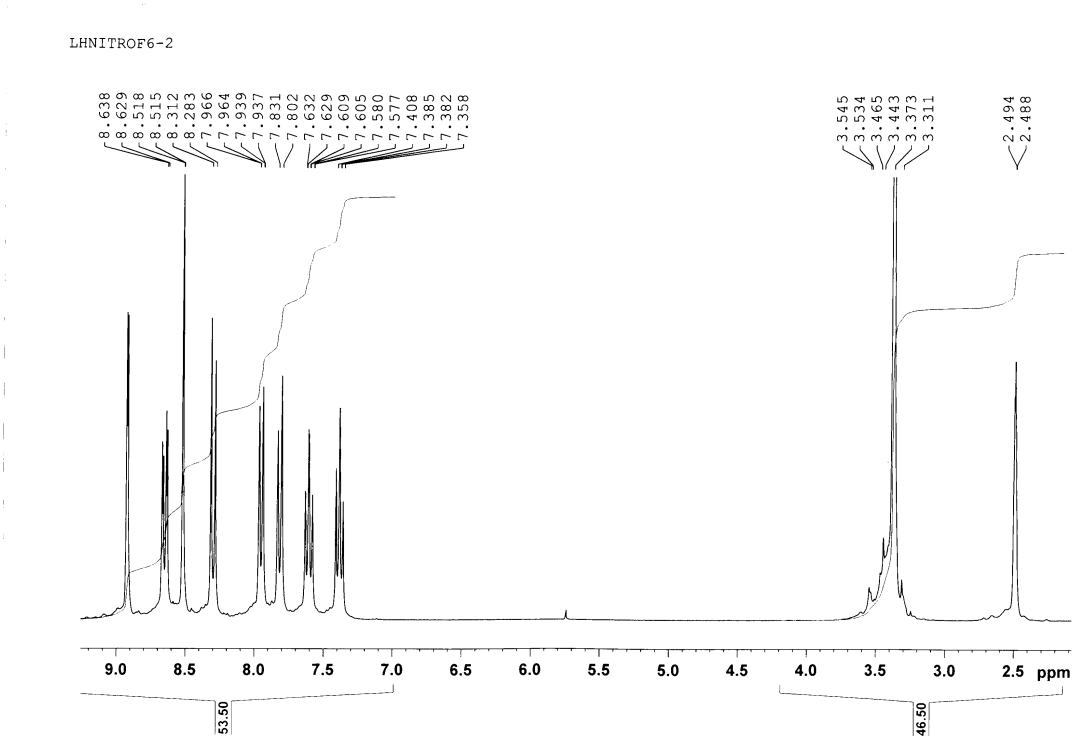
Microwave reactions were carried out using a Biotage Initiator ^{TM} 2,0. LC-MS analyses were performed using an Alliance 2695 (Waters) with a diode array UV/Vis detector Waters 2996 and interfaced to a Micromass ZQ mass spectrometer. Analyses were performed using reversed phase HPLC silica based columns: column Bridge C18 3.5 μm. (2.1 x 100 mm). Using an injection volume of 3 μL., a flow rate of 0.25 mL/min and gradient elution (5 to 95 % over 5 min) of acetonitrile in water. Acetonitrile contains 0.08 % v/v and water contains 0.1 % v/v formic acid. Analyses were monitored at 254 nm wavelength.



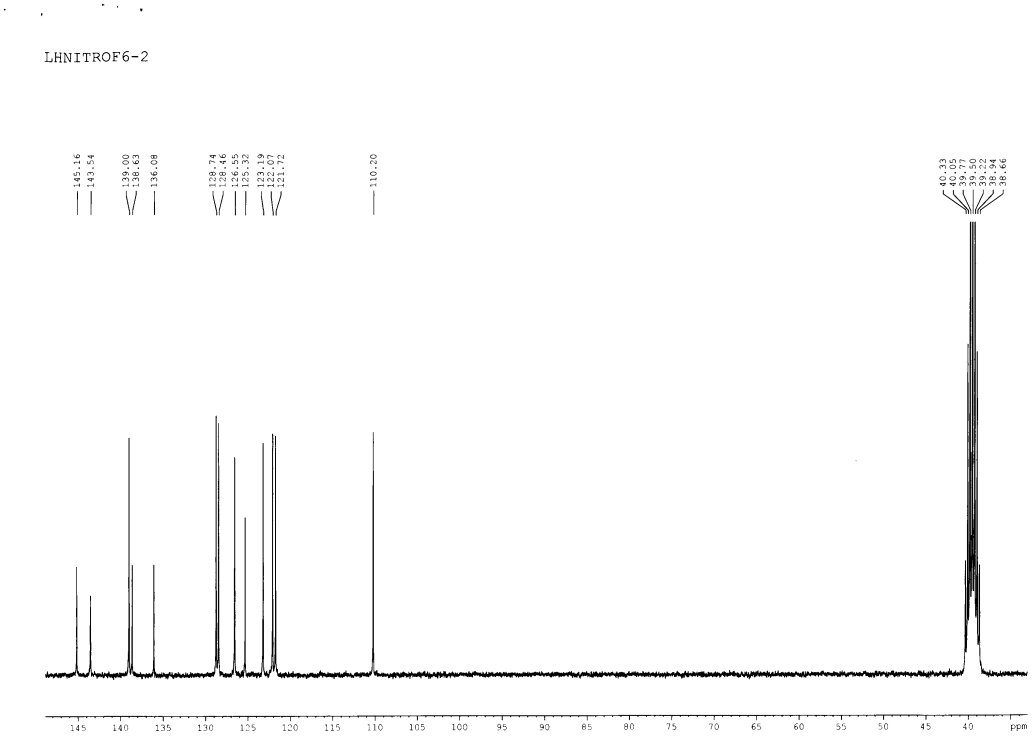
5b Hemiacetal of **5b**

Equilibrium of **11** and its hemiacetal **17**

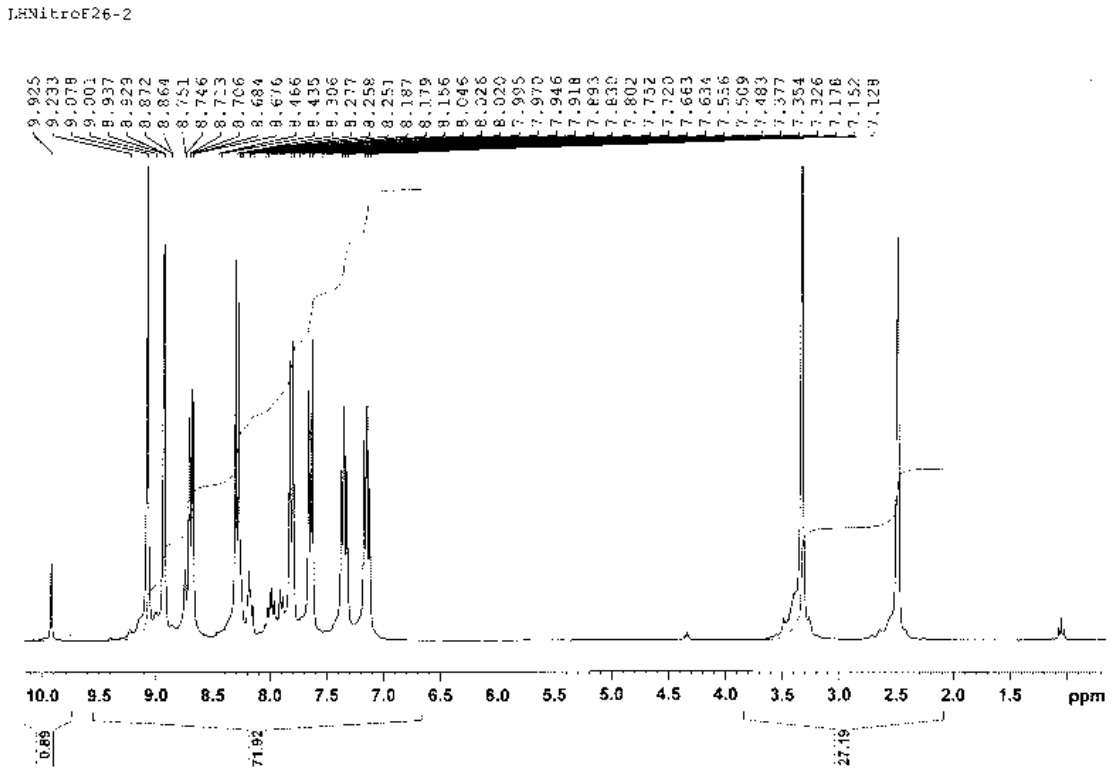
2. ^{1}H and ^{13}C-NMR spectra



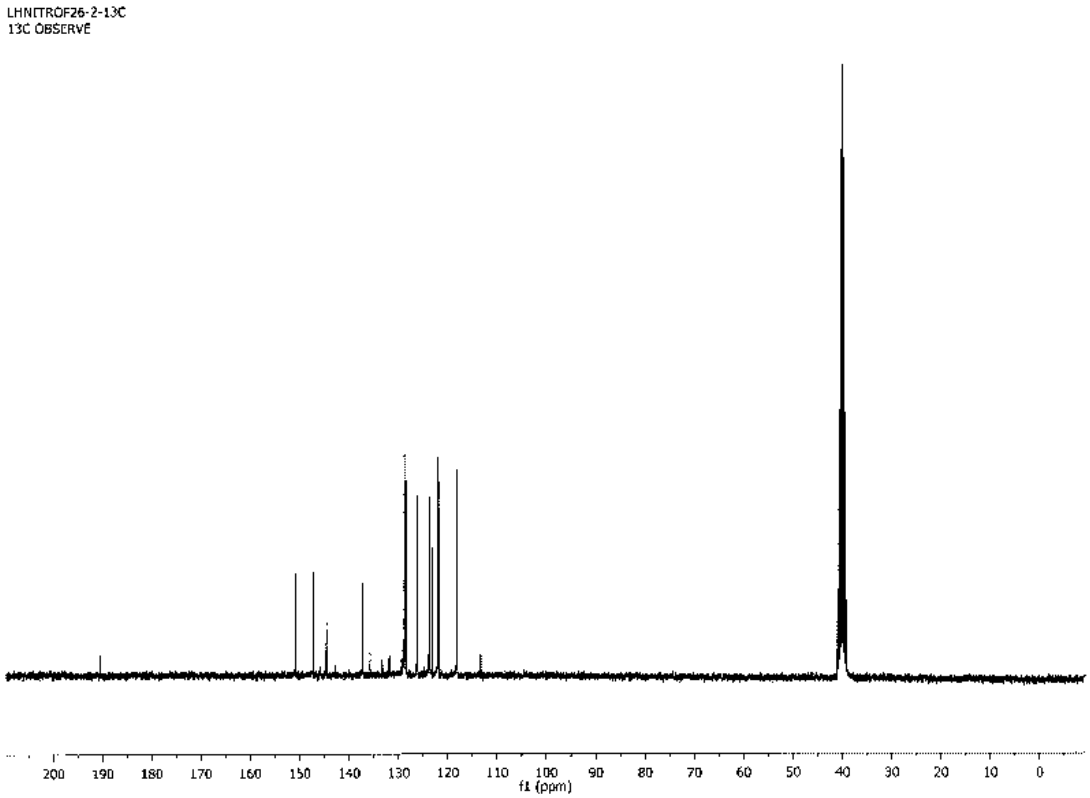
^{1}H-NMR Spectrum of **3b**



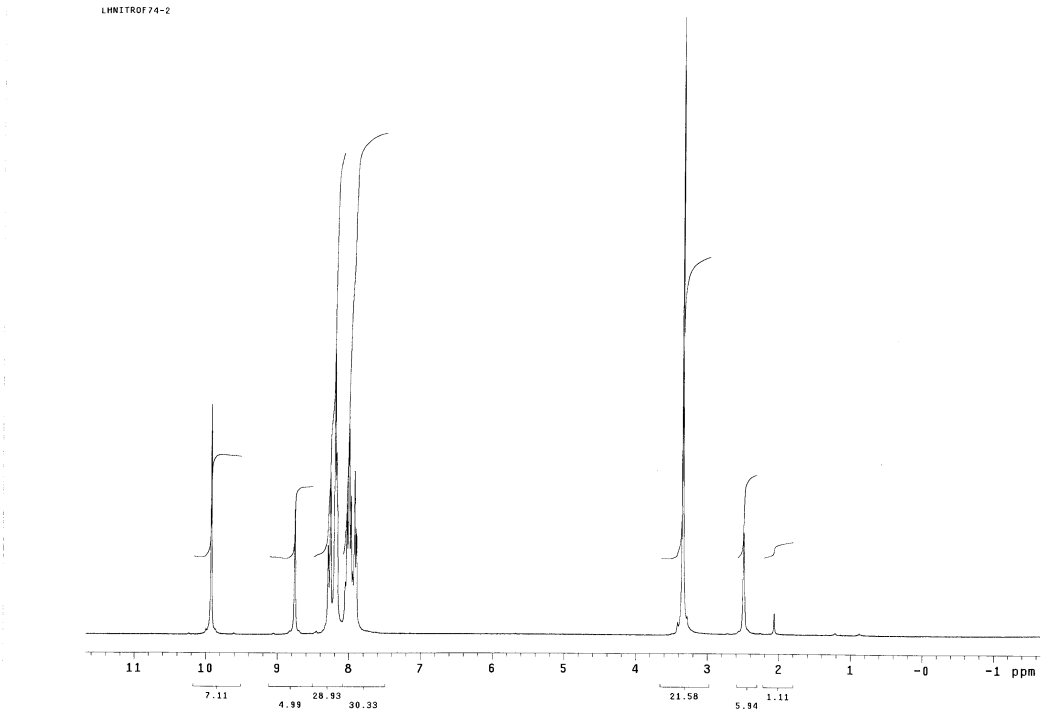
^{13}C-NMR Spectrum of **3b**



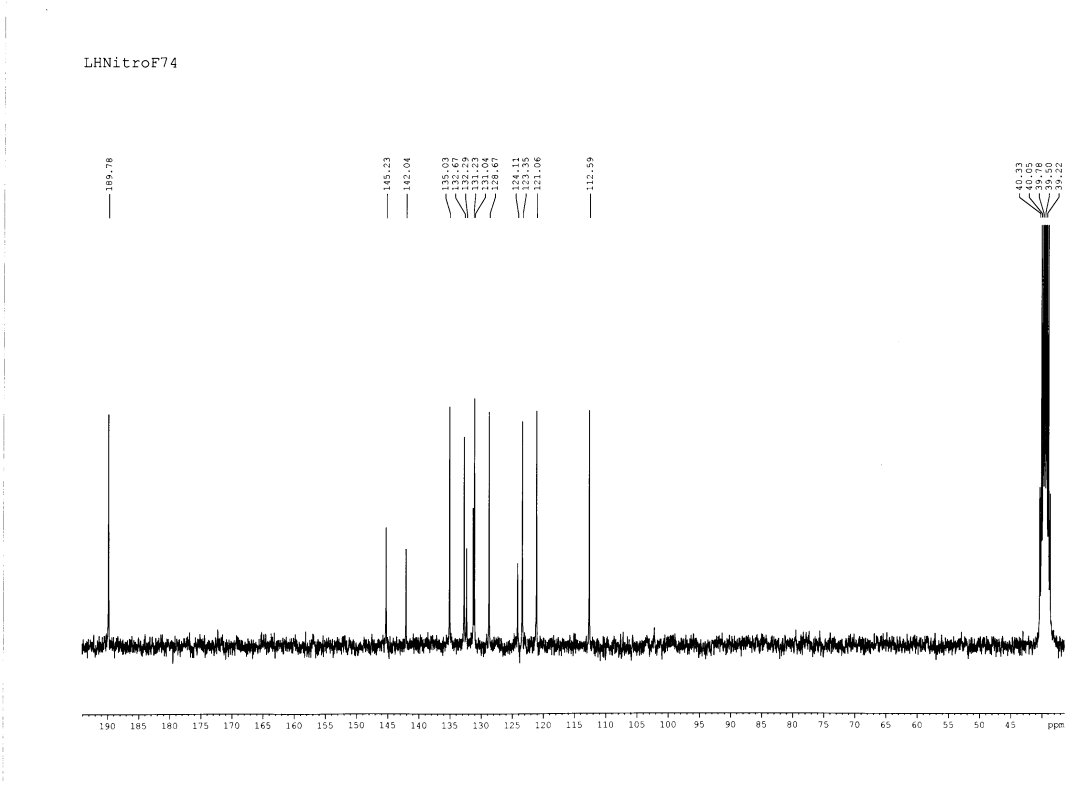
^{1}H-NMR Spectrum of **4b**



^{13}C-NMR Spectrum of **4b**



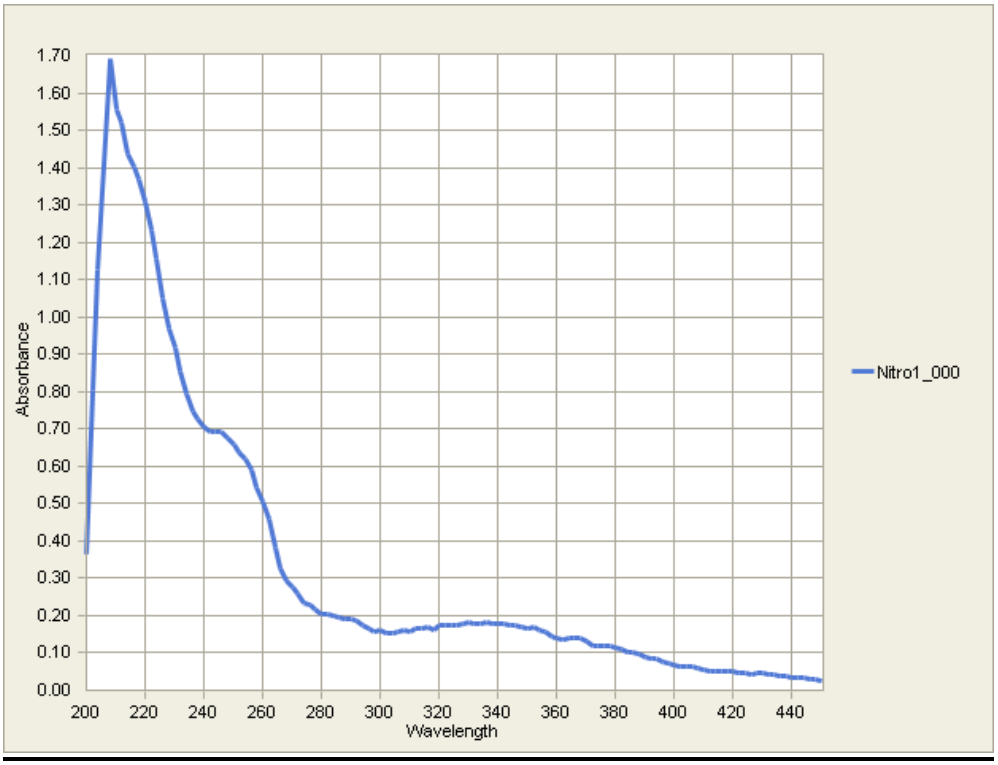
^{1}H-NMR Spectrum of **5b**

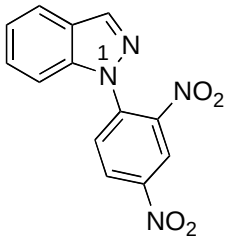


^{13}C-NMR Spectrum of **5b**

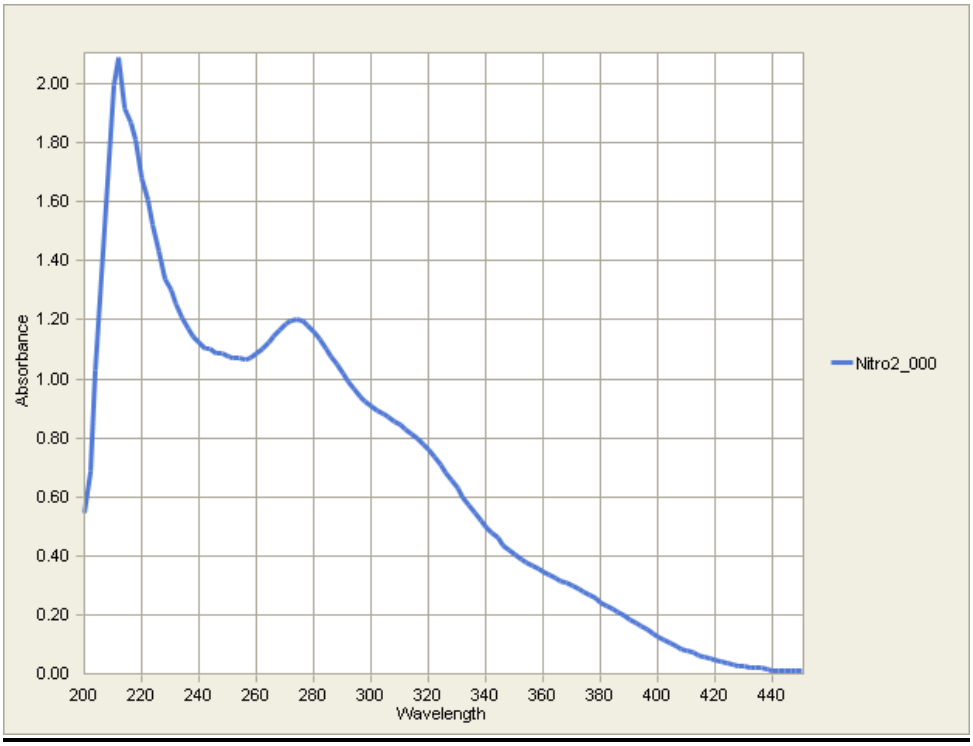
3. Electronic spectra

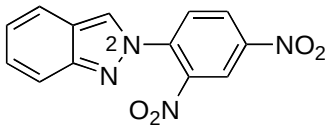
<u>Compound 3 (246 nm, Abs= 0.69) [50 % EtOH, 50% PBS]</u>



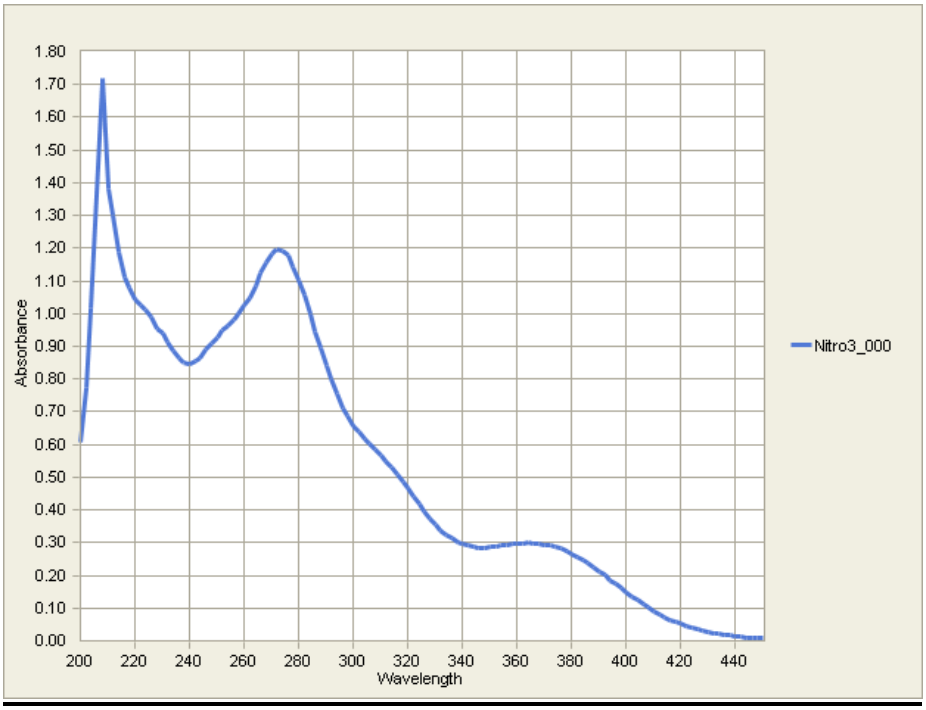


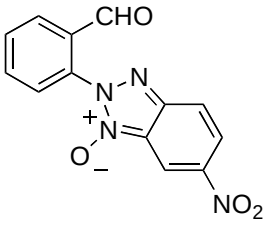
Compound 4 (274 nm, Abs= 1.20) [20 % EtOH, 80% PBS]



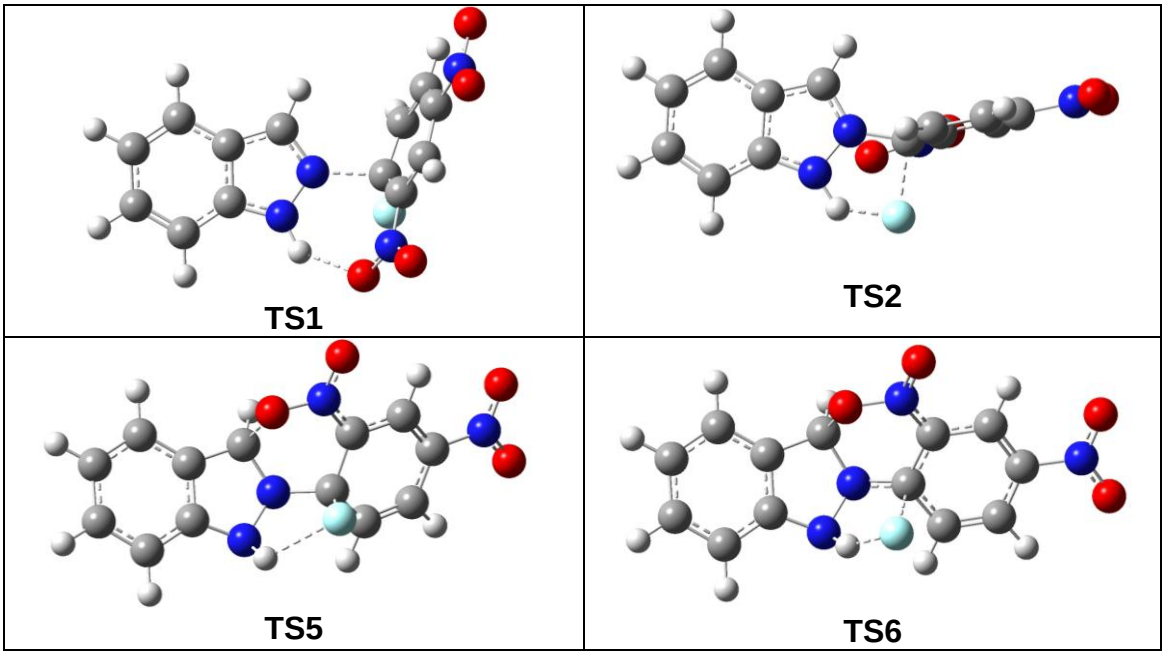


Compound 5 (272 nm, Abs = 1.20; 274 nm, Abs =1.19) [20 % EtOH, 80% PBS]





4. Computational data



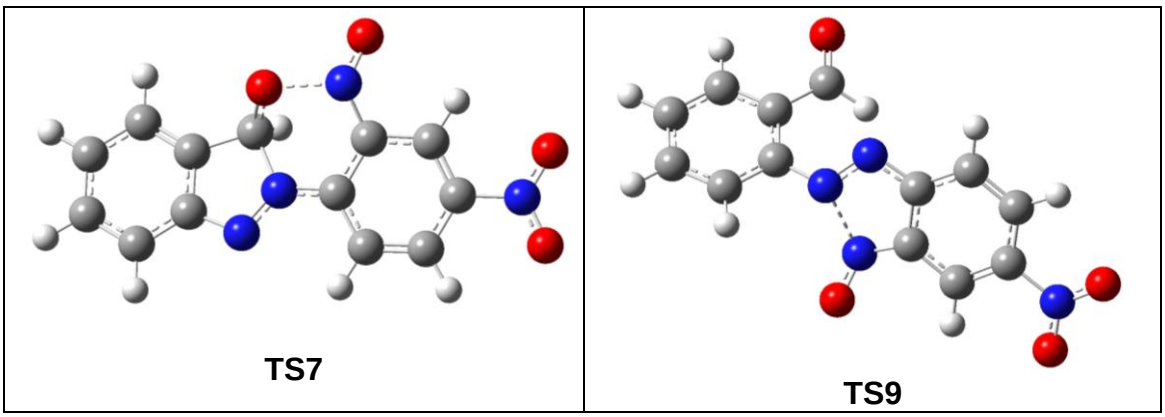


Figure S1. Fully optimized transition structures [B3LYP(PCM)/6-31G(d) level of theory] associated with the reaction profile represented in Figure 15.

Photochemical mechanism.

Supporting Information

9

B3LYP/6-31G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.154819	0.978152	-0.000392
2	6	0	2.508099	1.172480	-0.000433
3	6	0	3.073337	-0.135267	-0.000047
4	7	0	2.153896	-1.077423	0.000224
5	7	0	0.951081	-0.390339	0.000036
6	6	0	-0.165484	-1.196109	0.000236
7	6	0	-1.503856	-1.011810	0.000093
8	7	0	-2.274833	0.197655	0.000065
9	8	0	-3.499299	0.050269	-0.000982
10	8	0	-1.710659	1.299958	0.001234
11	1	0	0.318969	1.654220	-0.000601
12	1	0	3.026698	2.120115	-0.000733
13	1	0	4.119320	-0.414282	0.000041
14	1	0	0.147323	-2.234891	0.000332
15	1	0	-2.145134	-1.880894	-0.000072

E(B3LYP)= -508.091357 a.u.
NIMAG=0
ZPVE= 0.107873 a.u.
E(TDB3LYP,S1)= -507.957788 a.u.

CASSCF(4,4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.168984	0.974812	0.000039
2	6	0	2.499215	1.166066	0.000125
3	6	0	3.057085	-0.151977	0.000097
4	7	0	2.130047	-1.062219	0.000013
5	7	0	0.946796	-0.380659	-0.000020
6	6	0	-0.173862	-1.183599	-0.000156
7	6	0	-1.505981	-1.009221	-0.000205
8	7	0	-2.272618	0.205496	-0.000006
9	8	0	-3.455900	0.065330	0.000458
10	8	0	-1.713120	1.264002	-0.000405
11	1	0	0.361832	1.665895	0.000013
12	1	0	3.019801	2.099896	0.000193
13	1	0	4.088500	-0.439148	0.000128
14	1	0	0.125233	-2.212262	-0.000108
15	1	0	-2.145428	-1.863842	0.000035

E(CASSCF,S0)= -505.187342 a. u.
E(CASSCF-MP2,S0)= -506.621541 a. u.
E(CASSCF,S1)= -504.936567 a. u.
ECASSCF-MP2,S1)= -506.430792 a. u.

10

B3LYP/6-31G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-0.434195	-0.649688	0.422418
2	6	0	-1.723904	-1.325675	0.117130
3	6	0	-2.607620	-0.326541	-0.143930
4	7	0	-2.078516	0.953654	-0.192651
5	7	0	-0.787312	0.769560	0.075872
6	6	0	0.220300	1.624546	0.015658
7	6	0	1.537475	1.111078	0.113083
8	7	0	1.822280	-0.182672	-0.029921
9	8	0	0.669130	-1.053108	-0.352937
10	8	0	2.912791	-0.740574	-0.098105
11	1	0	-0.142290	-0.649550	1.488459
12	1	0	-1.907723	-2.382454	0.232140
13	1	0	-3.669131	-0.425454	-0.336140
14	1	0	0.013993	2.674657	-0.141696
15	1	0	2.402293	1.746133	0.246311

E(B3LYP)= -508.032642 a. u.
NIMAG=0
ZPVE= 0.106989
E(TDB3LYP,S1)=-507.971319 a. u.

CASSCF(4,4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.419265	-0.619917	0.416405
2	6	0	-1.701610	-1.314101	0.106801
3	6	0	-2.579420	-0.350618	-0.145090
4	7	0	-2.046874	0.941769	-0.168290
5	7	0	-0.778965	0.762397	0.085021
6	6	0	0.225200	1.631976	0.021008
7	6	0	1.537837	1.103421	0.080168
8	7	0	1.769514	-0.198981	-0.055804
9	8	0	0.681173	-0.996381	-0.347952
10	8	0	2.845934	-0.770414	-0.063014
11	1	0	-0.142406	-0.659636	1.466352
12	1	0	-1.859437	-2.368178	0.185440
13	1	0	-3.626431	-0.452928	-0.346488
14	1	0	0.017356	2.669889	-0.126274
15	1	0	2.411880	1.704349	0.206463

E(CASSCF,S0)= -505.114617 a. u.
E(CASSCF-MP2,S0)= -506.562533 a. u.
E(CASSCF,S1)= -504.989975 a. u.
ECASSCF-MP2,S1)= -506.429923 a. u.

12

B3LYP/6-31G*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.590763	-0.630593	0.596753
2	6	0	-1.802318	-1.274019	0.214969
3	6	0	-2.591787	-0.269172	-0.340575
4	7	0	-2.040550	0.958776	-0.401840
5	7	0	-0.799400	0.738658	0.154136
6	6	0	0.228988	1.566384	0.133095
7	6	0	1.528464	1.063985	0.265947
8	7	0	1.806863	-0.232153	-0.066989
9	8	0	0.809530	-1.127031	-0.225039
10	8	0	2.940143	-0.613935	-0.349157
11	1	0	-0.147699	-0.704313	1.593345
12	1	0	-2.084364	-2.288063	0.449227

13	1	0	-3.605947	-0.379558	-0.708416
14	1	0	0.033211	2.610798	-0.084162
15	1	0	2.403510	1.692397	0.325292

E(B3LYP)= -508.018027 a. u.
NIMAG=1 (-737.9960 cm^{-1})
ZPVE= 0.105616 a. u.
E(TDB3LYP,S1)= -507.971319 a. u.

CASSCF(4,4)

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.502606	-0.633285	0.585671
2	6	0	-1.731960	-1.275982	0.219341
3	6	0	-2.523460	-0.270030	-0.340013
4	7	0	-1.990587	0.915542	-0.300384
5	7	0	-0.781251	0.728933	0.352715
6	6	0	0.247118	1.580017	0.119250
7	6	0	1.516108	1.116799	-0.009228
8	7	0	1.737641	-0.225197	-0.166497
9	8	0	0.700221	-0.988363	-0.434476
10	8	0	2.833492	-0.741686	-0.045152
11	1	0	-0.007759	-0.854157	1.517198
12	1	0	-1.962110	-2.311959	0.340634
13	1	0	-3.500984	-0.386349	-0.764876
14	1	0	0.016673	2.625526	0.079985
15	1	0	2.392658	1.727278	0.013120

E(CASSCF,S0-S1)=- 505.0761925 a. u.
E(CASSCF-MP2, S0-S1)= -506.529006 a. u.