

Electronic Supplementary Information (ESI)
for manuscript

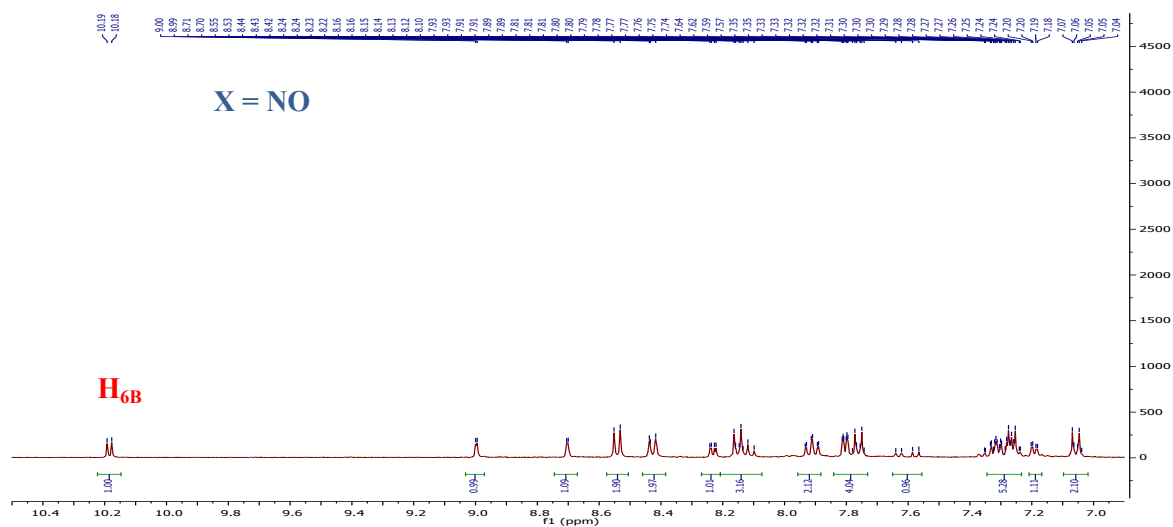
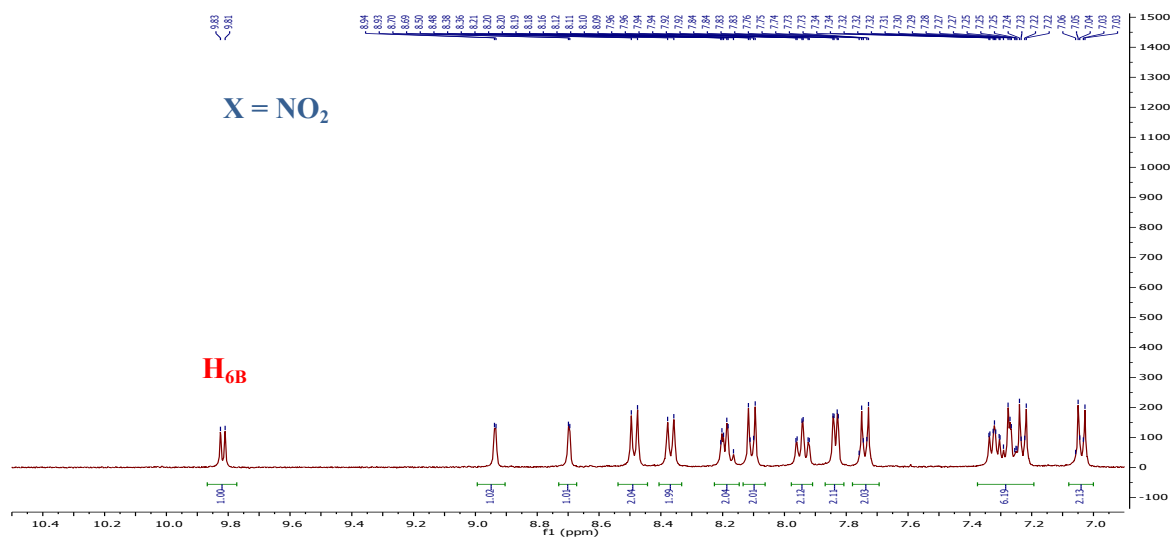
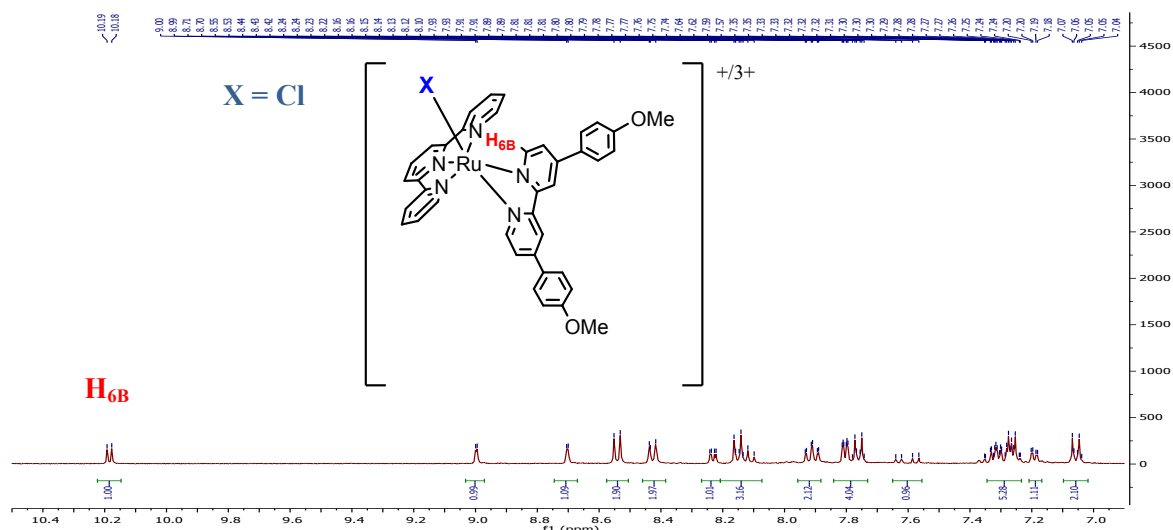
**Nitric oxide (NO) photo-release in a series of ruthenium-nitrosyl complexes:
new experimental insights in the search of a comprehensive mechanism**

by

Max Roose, Marine Tassé, Pascal G. Lacroix, and Isabelle Malfant

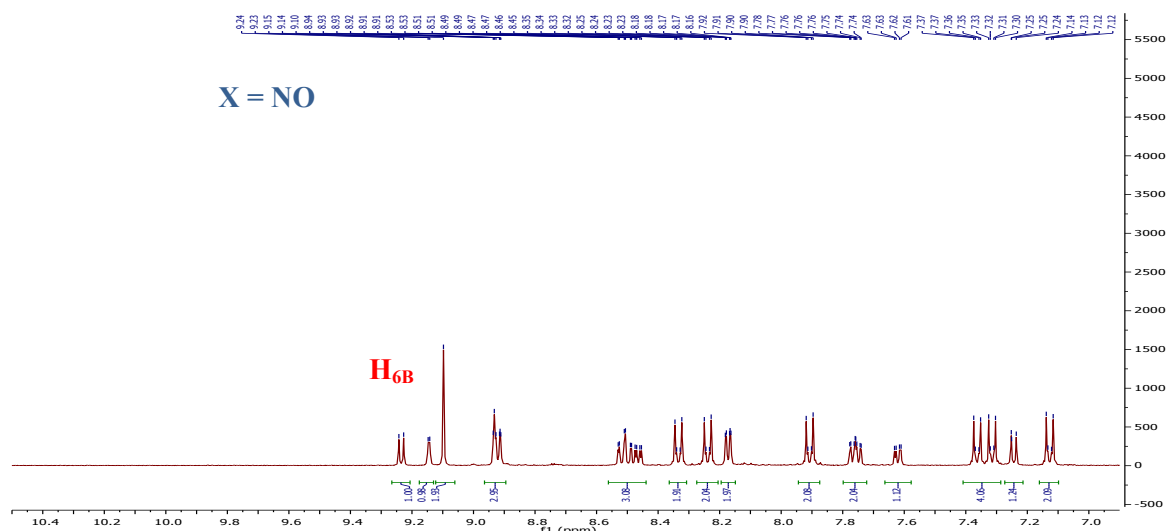
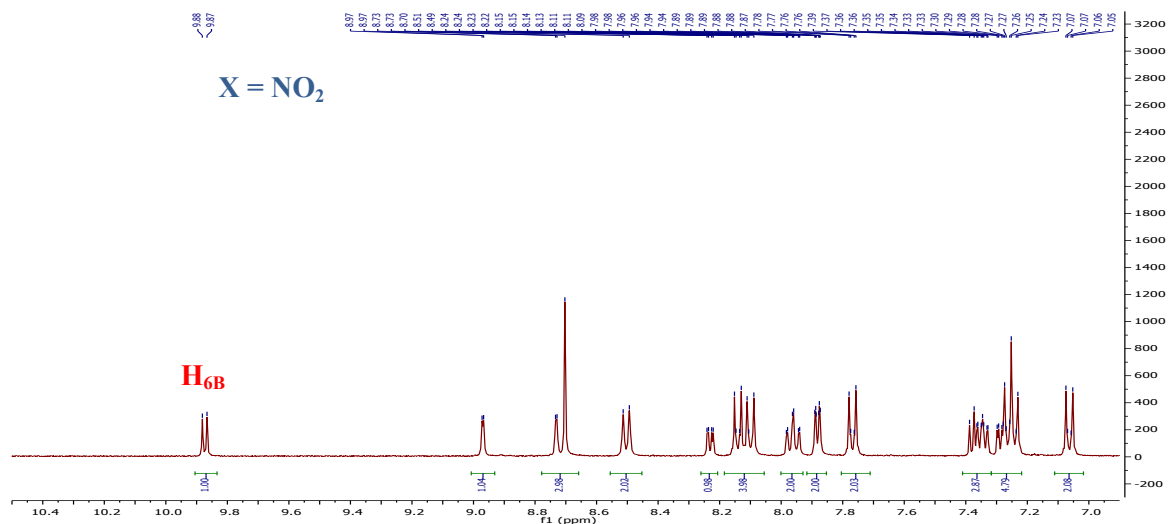
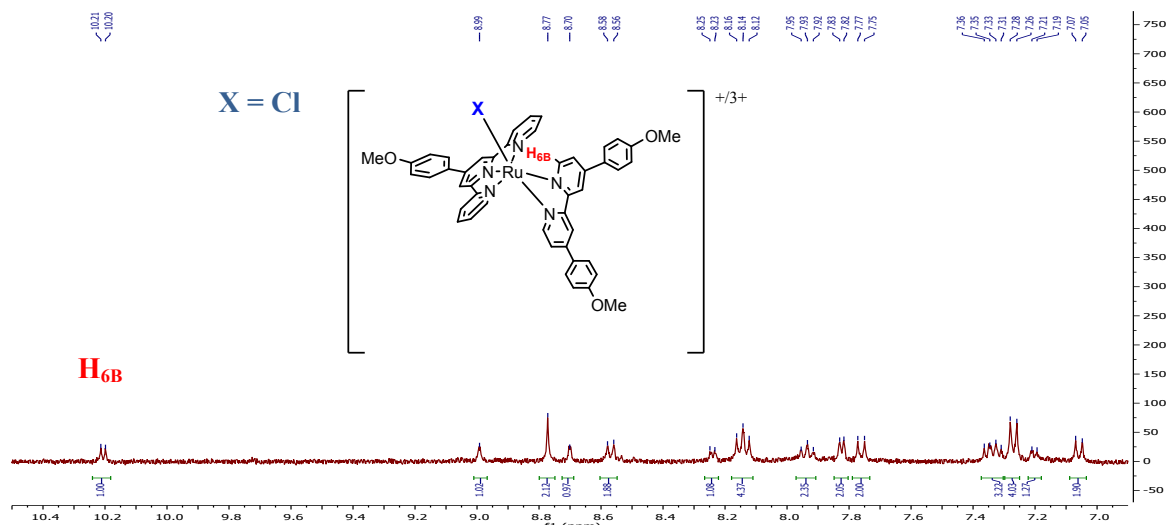
- Fig S1- ¹H-NMR for [Ru^{II}(terpy)(MP₂bipy)Cl](Cl), [Ru^{II}(terpy)(MP₂bipy)(NO₂)](PF₆), and [Ru^{II}(terpy)(MP₂bipy)(NO)](PF₆)₃ (**[RuT0B2](PF₆)₃**)
- Fig S2- ¹H-NMR for [Ru^{II}(MPterpy)(MP₂bipy)Cl](Cl), [Ru^{II}(MPterpy)(MP₂bipy)(NO₂)](PF₆), and [Ru^{II}(MPterpy)(MP₂bipy)(NO)](PF₆)₃ (**[RuT1B2](PF₆)₃**)
- Fig S3- Atom assignment for ¹H- and ¹³C-NMR
- Table S4- Optimized geometries
- Table S5- UV-visible spectra computed by TD-DFT
- Fig and Table S6- Electrochemical data
- Fig S7- Photorelease on [RuT1B0](PF₆)₃ and [RuT0B2](PF₆)₃
- Fig S8- ¹H-NMR of the photoproduct of [RuT1B2](PF₆)₃
- Fig S9- IR spectra for [RuT1B2](PF₆)₃ and its photoproduct

-S1- ^1H -NMR for $[\text{Ru}^{\text{II}}(\text{terpy})(\text{MP}_2\text{bipy})\text{Cl}](\text{Cl})$, $[\text{Ru}^{\text{II}}(\text{terpy})(\text{MP}_2\text{bipy})(\text{NO}_2)](\text{PF}_6)$, and $[\text{Ru}^{\text{II}}(\text{terpy})(\text{MP}_2\text{bipy})(\text{NO})](\text{PF}_6)_3$

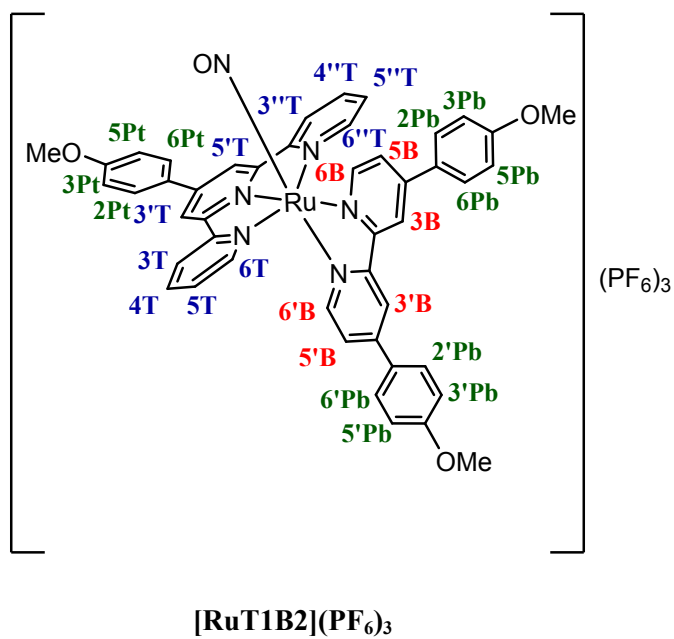
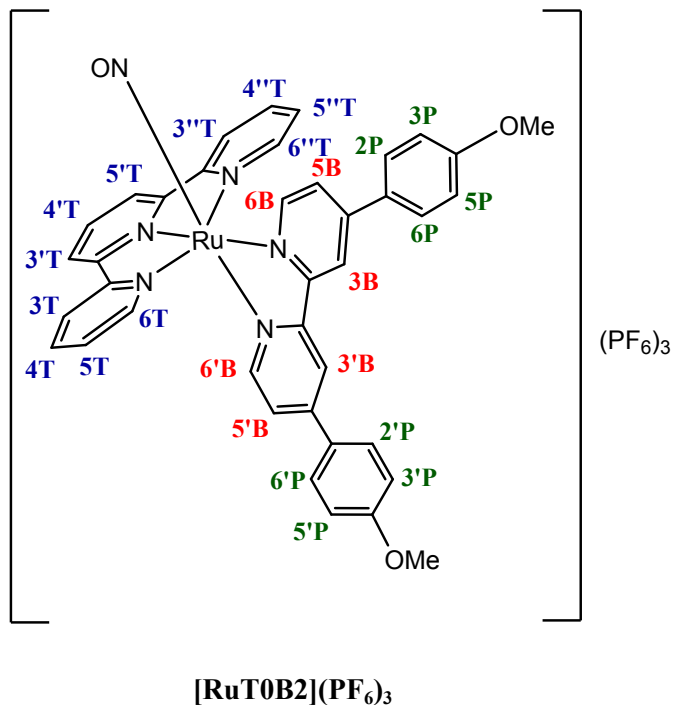


-S2-

¹H-NMR for [Ru^{II}(MPterpy)(MP₂bipy)Cl](Cl), [Ru^{II}(MPterpy)(MP₂bipy)(NO₂)](PF₆), and [Ru^{II}(MPterpy)(MP₂bipy)(NO)](PF₆)₃



-S3- Atom assignment for ^1H - and ^{13}C -NMR



-S4- Optimized geometries

[RuTOBO]³⁺

Ru	0.044278	-0.000002	-0.577078
N	-0.253436	0.000186	-2.321655
N	0.605552	-0.000010	1.441035
N	-1.899223	-0.000090	-0.116215
C	-2.512845	1.192980	0.014683
C	-1.613453	2.353390	-0.134481
N	-0.302212	-2.065761	-0.396096
N	-0.302394	2.065736	-0.395961
C	0.221839	4.391598	-0.424621
H	0.974331	5.161825	-0.548028
C	-2.512720	-1.193222	0.014718
C	-3.878464	-1.215021	0.289450
H	-4.412687	-2.150022	0.404069
C	0.222185	-4.391586	-0.425046
H	0.974703	-5.161746	-0.548710
C	-1.613220	-2.353541	-0.134451
C	-4.551151	-0.000216	0.418252
C	-2.033118	3.672106	-0.011401
H	-3.072003	3.898363	0.196276
C	-3.878591	1.214653	0.289410
H	-4.412909	2.149603	0.403974
C	0.587620	3.054226	-0.539978
H	1.607953	2.762252	-0.755893
C	0.587843	-3.054173	-0.540367
H	1.608121	-2.762106	-0.756426
C	-2.032738	-3.672290	-0.011305
H	-3.071555	-3.898642	0.196604
C	-1.105125	-4.702552	-0.157515
H	-1.424069	-5.735163	-0.063535
C	-1.105563	4.702446	-0.157391
H	-1.424606	5.735030	-0.063463
N	2.155625	0.000088	-0.703737
H	-5.615094	-0.000273	0.629261
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C	2.863879	0.000231	-1.847332
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C	4.929563	0.000182	-0.643936
C	4.199025	0.000068	0.538847
C	2.806616	0.000035	0.488146
C	-0.248985	-0.000003	2.479281
C	0.183509	-0.000005	3.796387
C	1.550443	-0.000043	4.051071
C	2.436839	-0.000062	2.980068
C	1.946520	-0.000024	1.676807
H	2.306537	0.000323	-2.774600
H	4.775682	0.000387	-2.806371
H	6.013903	0.000209	-0.612803
H	4.714340	0.000022	1.490912
H	-1.305818	-0.000014	2.252580
H	-0.548379	0.000017	4.595657
H	1.926977	-0.000064	5.068422
H	3.503697	-0.000102	3.162884

[RuT1B0]³⁺

Ru	1.605281	0.011138	-0.608790
N	1.564630	0.112859	-2.373832
N	1.896912	-0.096368	1.464396
N	-0.368649	0.053941	-0.390986
C	-0.976384	1.254354	-0.281654
C	-0.036795	2.393042	-0.244670
N	1.179236	-2.046728	-0.567338
N	1.289078	2.075935	-0.353145
C	1.877485	4.378260	-0.156035
H	2.660560	5.127057	-0.126319
C	-1.037576	-1.118851	-0.389457
C	-2.418839	-1.109777	-0.292202
H	-2.967397	-2.042449	-0.323979
C	1.643969	-4.384476	-0.625396
H	2.386015	-5.172300	-0.684415
C	-0.161085	-2.303193	-0.481403
C	-3.114263	0.114958	-0.191470
C	-0.431515	3.716477	-0.092682
H	-1.482007	3.966391	-0.006304
C	-2.356910	1.307080	-0.178469
H	-2.853814	2.260959	-0.054334
C	2.217580	3.038816	-0.311081
H	3.248977	2.722992	-0.409678
C	2.055071	-3.056202	-0.637231
H	3.102126	-2.787719	-0.706497
C	-0.625990	-3.612616	-0.466187
H	-1.688181	-3.814147	-0.396455
C	0.285260	-4.664293	-0.539990
H	-0.069410	-5.689493	-0.529786
C	0.534715	4.719606	-0.047202
H	0.234484	5.755290	0.072066
N	3.716173	-0.055068	-0.455456
C	-4.573208	0.146858	-0.096284
O	1.592242	0.187101	-3.504811
C	4.570740	-0.041683	-1.494234
C	5.947251	-0.054820	-1.321323
C	6.458996	-0.079155	-0.028494
C	5.577734	-0.100092	1.046437
C	4.204057	-0.093412	0.811345
C	0.909314	-0.130383	2.375445
C	1.159831	-0.203354	3.737199
C	2.480013	-0.242959	4.171574
C	3.503413	-0.206530	3.231238
C	3.193689	-0.131137	1.875393
H	4.142883	-0.022523	-2.487926
H	6.592480	-0.043237	-2.192095
H	7.529588	-0.083790	0.146193
H	5.961781	-0.119924	2.058169
H	-0.105020	-0.099542	2.002942
H	0.327557	-0.228992	4.430806
H	2.715902	-0.301841	5.228838
H	4.534941	-0.240253	3.557929
C	-5.286433	-0.920835	0.476348
C	-6.670543	-0.900318	0.576058
C	-7.385769	0.201332	0.081446
C	-6.687678	1.276116	-0.499050
C	-5.309580	1.250441	-0.577957

O	-8.723332	0.322199	0.115446
C	-9.493531	-0.737889	0.675200
H	-4.756117	-1.771921	0.893610
H	-7.180389	-1.734638	1.043672
H	-7.254008	2.115540	-0.889942
H	-4.801417	2.080738	-1.059452
H	-10.533770	-0.424305	0.586408
H	-9.246104	-0.890269	1.731516
H	-9.343083	-1.670274	0.119946

[RuTOB2]³⁺

Ru	1.853813	-1.454910	-0.042362
N	2.332740	-3.158106	-0.127672
N	1.086445	0.478207	0.043826
N	3.733093	-0.779903	0.042926
C	4.292721	-0.635300	1.260168
C	3.387261	-0.951793	2.382256
N	2.230744	-1.123025	-2.083431
N	2.124722	-1.348412	2.040333
C	1.545430	-1.554095	4.344129
H	0.791916	-1.800529	5.083177
C	4.355476	-0.507299	-1.121206
C	5.675562	-0.063143	-1.083866
H	6.215399	0.170480	-1.993131
C	1.768008	-1.075774	-4.421666
H	1.052989	-1.238159	-5.219868
C	3.509125	-0.696806	-2.316348
C	6.294286	0.083039	0.157386
C	3.755510	-0.849943	3.718169
H	4.756608	-0.535579	3.987384
C	5.611910	-0.194139	1.341426
H	6.102162	-0.063520	2.298317
C	1.231607	-1.642062	2.991526
H	0.251169	-1.957910	2.655483
C	1.386561	-1.308850	-3.104002
H	0.390646	-1.654429	-2.854896
C	3.943302	-0.452195	-3.613541
H	4.956431	-0.115349	-3.797831
C	3.063090	-0.643040	-4.677537
H	3.393527	-0.454738	-5.693561
C	2.824596	-1.154076	4.710106
H	3.103367	-1.077614	5.755729
N	-0.222265	-1.799711	-0.111180
H	7.322287	0.426222	0.202702
O	2.605798	-4.256611	-0.186822
C	-0.819953	-3.005084	-0.185678
C	-2.191992	-3.157014	-0.210886
C	-3.030640	-2.030623	-0.150257
C	-2.388279	-0.783543	-0.071503
C	-1.003941	-0.688773	-0.058388
C	1.816517	1.609390	0.105773
C	1.249322	2.865173	0.150222
C	-0.149005	3.012909	0.126274
C	-0.893599	1.821842	0.059292
C	-0.272982	0.583480	0.022265
H	-0.177263	-3.874509	-0.237486
H	-2.596372	-4.158169	-0.303345

H	-2.982237	0.117220	0.012119
H	2.891954	1.503516	0.131005
H	1.908164	3.721377	0.230471
H	-1.972755	1.871343	0.002154
C	-5.301922	-1.110747	-0.675922
H	-4.849903	-0.221142	-1.104997
C	-6.679421	-1.223072	-0.689352
H	-7.299838	-0.432969	-1.100905
C	-7.302488	-2.374193	-0.176674
C	-6.514006	-3.411242	0.342195
H	-6.966227	-4.305497	0.755481
C	-5.129741	-3.290553	0.338091
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C	-4.491956	-2.144650	-0.163420
C	-2.098743	4.485225	0.679642
H	-2.633733	3.635604	1.093609
C	-2.703937	5.726274	0.716422
H	-3.699550	5.850043	1.130881
C	-2.031293	6.858928	0.223786
C	-0.736666	6.719305	-0.298594
H	-0.198495	7.572000	-0.696417
C	-0.134730	5.468202	-0.317015
H	0.856655	5.383702	-0.752267
C	-0.795335	4.324844	0.163758
O	-2.706344	8.019915	0.296649
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H	-2.798692	10.007695	-0.013895
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H	-1.846704	9.133081	-1.244925
O	-8.648116	-2.386497	-0.227655
C	-9.337191	-3.529677	0.267150
H	-10.397485	-3.321313	0.121853
H	-9.061468	-4.430643	-0.292466
H	-9.137407	-3.681223	1.333984

[RuT1B2]³⁺

Ru	-0.387627	-1.663811	0.067209
N	-0.668826	-3.408179	0.150222
N	0.186928	0.337769	-0.026820
N	-2.317459	-1.187174	-0.001213
C	-2.915977	-1.114079	-1.208410
C	-1.990723	-1.315838	-2.342146
N	-0.785524	-1.367045	2.113919
N	-0.690619	-1.579146	-2.010316
C	-0.101914	-1.696763	-4.317529
H	0.669651	-1.854227	-5.062273
C	-2.968850	-0.987493	1.163536
C	-4.325590	-0.708605	1.140981
H	-4.866055	-0.577934	2.069805
C	-0.315959	-1.261423	4.449697
H	0.417935	-1.339799	5.243483
C	-2.101545	-1.085095	2.354797
C	-5.012053	-0.634202	-0.090236
C	-2.371774	-1.236805	-3.676269
H	-3.401283	-1.025892	-3.939536
C	-4.271717	-0.835958	-1.275493
H	-4.758537	-0.740950	-2.237662

C	0.225092	-1.766223	-2.967624
H	1.234518	-1.980396	-2.637699
C	0.080547	-1.452477	3.130324
H	1.107614	-1.682577	2.874422
C	-2.552221	-0.889120	3.654651
H	-3.595789	-0.667635	3.843524
C	-1.650766	-0.978515	4.713397
H	-1.994331	-0.827407	5.731302
C	-1.418077	-1.428554	-4.674156
H	-1.707529	-1.368295	-5.718005
N	1.719736	-1.797144	0.116910
O	-0.795242	-4.534914	0.204561
C	2.435754	-2.936055	0.186913
C	3.816304	-2.950383	0.207056
C	4.536777	-1.745093	0.148142
C	3.772060	-0.568891	0.074114
C	2.385077	-0.613530	0.063594
C	-0.652957	1.389734	-0.090612
C	-0.214480	2.695829	-0.148754
C	1.162417	2.982115	-0.138495
C	2.022918	1.872374	-0.069066
C	1.528920	0.578432	-0.017451
H	1.883213	-3.865096	0.240566
H	4.318979	-3.906425	0.296169
H	4.273110	0.386999	-0.005996
H	-1.712600	1.174765	-0.106414
H	-0.955923	3.481786	-0.230012
H	3.092372	2.030099	-0.023917
C	6.701487	-0.601939	0.680576
H	6.159091	0.232925	1.115031
C	8.083250	-0.571878	0.693940
H	8.619482	0.274836	1.111206
C	8.821086	-1.649077	0.173144
C	8.143563	-2.758024	-0.353664
H	8.685811	-3.597879	-0.772790
C	6.754113	-2.780635	-0.349286
H	6.252788	-3.639060	-0.787080
C	6.002362	-1.709966	0.160196
C	2.950520	4.633728	-0.728186
H	3.559155	3.837090	-1.145836
C	3.432419	5.927290	-0.779376
H	4.405603	6.144189	-1.208661
C	2.660503	6.992385	-0.281934
C	1.393206	6.731494	0.260071
H	0.781127	7.530393	0.662522
C	0.915180	5.427971	0.292672
H	-0.057427	5.249769	0.741910
C	1.676474	4.351253	-0.192359
O	3.219600	8.212879	-0.369702
C	2.487126	9.335881	0.110197
H	3.126094	10.201577	-0.065546
H	1.546477	9.458011	-0.438360
H	2.281730	9.244734	1.182669
O	10.161030	-1.522906	0.224715
C	10.964377	-2.583524	-0.281154
H	11.997527	-2.268452	-0.132356
H	10.783246	-3.514266	0.268307
H	10.781600	-2.743479	-1.349840
C	-7.251189	-0.840009	-1.188339

H	-6.819038	-1.465183	-1.964186
C	-8.607317	-0.582360	-1.226815
H	-9.228186	-0.977216	-2.024830
C	-9.211752	0.191292	-0.219311
C	-8.426637	0.694497	0.829324
H	-8.862183	1.306721	1.610610
C	-7.067484	0.414796	0.864728
H	-6.478053	0.840394	1.671508
C	-6.446896	-0.351373	-0.136896
O	-10.534576	0.391248	-0.347547
C	-11.209362	1.156385	0.646826
H	-12.255797	1.178095	0.342106
H	-11.123860	0.684879	1.632100
H	-10.818859	2.179148	0.689532

-S5- UV-visible spectra computed by TD-DFT

[RuTOBO]³⁺

Excitation energies and oscillator strengths:

Excited State	1:	Singlet-A	2.9902 eV	414.63 nm	f=0.0002
<S**2>=0.000					
102 ->117		0.21840			
107 ->117		0.22185			
110 ->118		-0.13018			
112 ->117		0.38500			
113 ->117		0.39552			
115 ->117		-0.10852			
116 ->117		0.14866			
Excited State	2:	Singlet-A	3.1378 eV	395.13 nm	f=0.0021
<S**2>=0.000					
104 ->118		0.18872			
107 ->118		0.20874			
113 ->118		0.61655			
Excited State	3:	Singlet-A	3.1457 eV	394.14 nm	f=0.0024
<S**2>=0.000					
102 ->117		-0.18215			
104 ->117		0.17769			
110 ->118		0.17030			
112 ->117		-0.27305			
113 ->117		0.47388			
114 ->118		0.10137			
116 ->117		-0.21866			
Excited State	4:	Singlet-A	3.4193 eV	362.60 nm	f=0.0008
<S**2>=0.000					
101 ->117		-0.13141			
102 ->118		0.17578			
103 ->117		-0.11690			
110 ->117		-0.27816			
112 ->118		0.32935			
114 ->117		-0.19468			
115 ->118		-0.10633			
116 ->118		0.41208			
Excited State	5:	Singlet-A	3.4439 eV	360.01 nm	f=0.0097
<S**2>=0.000					
101 ->118		0.20431			
103 ->118		0.18483			
105 ->118		0.13825			
110 ->118		0.41386			
112 ->117		0.12473			
114 ->118		0.25542			
116 ->117		0.33757			
Excited State	6:	Singlet-A	3.5909 eV	345.28 nm	f=0.0583
<S**2>=0.000					
102 ->117		-0.15447			
110 ->118		-0.13148			
112 ->117		-0.26623			
113 ->117		0.10111			
113 ->122		-0.11095			
114 ->118		-0.11536			
116 ->117		0.54324			
116 ->119		0.11697			
Excited State	7:	Singlet-A	3.6828 eV	336.66 nm	f=0.0172
<S**2>=0.000					

102 ->118	-0.12748				
110 ->117	0.17981				
112 ->118	-0.23246				
114 ->117	0.13372				
115 ->118	0.14019				
116 ->118	0.56785				
Excited State	8:	Singlet-A	3.8261 eV	324.05 nm	f=0.0023
<S**2>=0.000					
112 ->117	0.10856				
115 ->117	0.68255				
Excited State	9:	Singlet-A	3.8298 eV	323.73 nm	f=0.0417
<S**2>=0.000					
112 ->118	0.11308				
115 ->118	0.66332				
115 ->120	0.11906				
Excited State	10:	Singlet-A	4.0750 eV	304.25 nm	f=0.0082
<S**2>=0.000					
104 ->122	0.16888				
104 ->123	0.13001				
107 ->122	0.15709				
107 ->123	0.11630				
113 ->122	0.41572				
113 ->123	0.29951				
113 ->125	0.11036				
116 ->117	0.10270				
116 ->119	-0.29805				
Excited State	11:	Singlet-A	4.2037 eV	294.94 nm	f=0.2802
<S**2>=0.000					
104 ->122	0.12516				
113 ->122	0.20384				
113 ->123	0.16859				
116 ->119	0.58452				
Excited State	12:	Singlet-A	4.4423 eV	279.10 nm	f=0.0143
<S**2>=0.000					
110 ->117	-0.12316				
112 ->118	0.16685				
114 ->117	0.63933				
116 ->121	0.12775				
Excited State	13:	Singlet-A	4.5040 eV	275.27 nm	f=0.0003
<S**2>=0.000					
110 ->118	-0.20169				
113 ->123	0.15243				
114 ->118	0.60369				
Excited State	14:	Singlet-A	4.5838 eV	270.48 nm	f=0.2749
<S**2>=0.000					
115 ->118	-0.12947				
115 ->120	0.64401				
115 ->121	-0.15697				
Excited State	15:	Singlet-A	4.7098 eV	263.25 nm	f=0.0323
<S**2>=0.000					
104 ->122	-0.10502				
104 ->123	0.13351				
107 ->119	-0.10481				
107 ->123	0.12469				
110 ->118	0.17366				
112 ->117	0.11326				
113 ->119	-0.31896				
113 ->122	-0.26910				
113 ->123	0.36815				
114 ->118	-0.15384				

Excited State 16: Singlet-A 4.7916 eV 258.75 nm f=0.2083
 <S**2>=0.000
 114 ->117 -0.14587
 114 ->119 0.32470
 116 ->120 0.10384
 116 ->121 0.55644

Excited State 17: Singlet-A 4.9650 eV 249.72 nm f=0.0158
 <S**2>=0.000
 102 ->122 0.26050
 112 ->119 0.16356
 112 ->122 0.44946
 115 ->119 -0.27185
 115 ->122 -0.14351
 116 ->122 0.22705

Excited State 18: Singlet-A 5.0494 eV 245.54 nm f=0.0001
 <S**2>=0.000
 102 ->122 0.10495
 111 ->117 -0.10149
 112 ->122 0.19964
 113 ->123 -0.13966
 115 ->119 0.58068
 116 ->122 0.14261

Excited State 19: Singlet-A 5.1711 eV 239.76 nm f=0.0418
 <S**2>=0.000
 102 ->118 -0.10906
 109 ->117 0.15865
 110 ->117 0.18695
 111 ->118 0.47912
 112 ->118 0.26589
 113 ->120 0.10758
 115 ->127 0.11630

Excited State 20: Singlet-A 5.1862 eV 239.07 nm f=0.0352
 <S**2>=0.000
 102 ->117 -0.11014
 107 ->119 0.11803
 109 ->118 0.15086
 111 ->117 0.35753
 112 ->117 0.13057
 112 ->119 0.23834
 113 ->119 0.30412
 113 ->123 0.10028
 115 ->119 0.17943
 116 ->125 0.11173

[RuT1B0]³⁺

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 2.9079 eV 426.37 nm f=0.0002 <S**2>=0.000
 125 ->145 -0.14794
 126 ->146 0.10737
 131 ->145 0.10167
 132 ->146 0.20926
 137 ->145 -0.24378
 138 ->146 -0.20113
 139 ->145 0.13279
 140 ->146 0.18584
 144 ->146 0.45811

Excited State 2: Singlet-A 2.9746 eV 416.81 nm f=0.2267
 <S**2>=0.000
 137 ->146 -0.14840

138 ->145	-0.14734				
140 ->145	0.11646				
144 ->145	0.61782				
144 ->147	-0.11506				
Excited State	3:	Singlet-A	3.0567 eV	405.62 nm	f=0.0001
<S**2>=0.000					
125 ->145	-0.11244				
127 ->145	0.12202				
131 ->145	0.20340				
137 ->145	-0.20727				
139 ->145	0.50503				
139 ->147	0.10347				
144 ->146	-0.26938				
Excited State	4:	Singlet-A	3.1679 eV	391.38 nm	f=0.0312
<S**2>=0.000					
127 ->146	0.19216				
131 ->146	0.18653				
139 ->146	0.61710				
144 ->145	-0.11200				
Excited State	5:	Singlet-A	3.2276 eV	384.13 nm	f=0.0043
<S**2>=0.000					
125 ->145	0.21811				
127 ->145	0.16049				
137 ->145	0.37409				
139 ->145	0.33168				
142 ->145	-0.29010				
144 ->146	0.23264				
Excited State	6:	Singlet-A	3.4906 eV	355.19 nm	f=0.2652
<S**2>=0.000					
125 ->146	-0.14064				
132 ->145	0.17361				
137 ->146	-0.27016				
140 ->145	0.17080				
142 ->146	0.38782				
144 ->145	-0.15467				
144 ->147	0.30825				
Excited State	7:	Singlet-A	3.6090 eV	343.54 nm	f=0.0623
<S**2>=0.000					
125 ->145	0.12100				
137 ->145	0.20629				
142 ->145	0.59349				
142 ->147	-0.11807				
143 ->145	0.11644				
144 ->146	0.11299				
Excited State	8:	Singlet-A	3.6928 eV	335.75 nm	f=0.0181
<S**2>=0.000					
124 ->146	-0.13406				
126 ->146	-0.16100				
132 ->146	-0.28633				
135 ->146	0.12010				
137 ->145	-0.11810				
138 ->146	0.15955				
139 ->150	-0.12346				
140 ->146	-0.26239				
142 ->146	0.12661				
144 ->146	0.34370				
144 ->147	-0.13384				
144 ->149	-0.14532				
Excited State	9:	Singlet-A	3.6985 eV	335.23 nm	f=0.1755
<S**2>=0.000					
142 ->146	0.45678				

144 ->146	-0.10107				
144 ->147	-0.44475				
Excited State	10:	Singlet-A	3.7910 eV	327.05 nm	f=0.1907
<S**2>=0.000					
125 ->146	0.11655				
132 ->145	-0.14872				
137 ->146	0.23569				
140 ->145	-0.13244				
141 ->146	-0.29180				
142 ->146	0.29806				
144 ->145	0.21382				
144 ->147	0.32952				
Excited State	11:	Singlet-A	3.8767 eV	319.82 nm	f=0.0036
<S**2>=0.000					
141 ->145	0.65654				
141 ->146	-0.14726				
Excited State	12:	Singlet-A	3.8927 eV	318.50 nm	f=0.0186
<S**2>=0.000					
137 ->146	0.15843				
141 ->145	0.17564				
141 ->146	0.59513				
141 ->148	0.11276				
144 ->147	0.10591				
Excited State	13:	Singlet-A	3.9832 eV	311.27 nm	f=0.0103
<S**2>=0.000					
138 ->149	-0.10656				
142 ->145	-0.14308				
142 ->147	-0.24156				
144 ->146	0.10119				
144 ->149	0.58936				
Excited State	14:	Singlet-A	4.1078 eV	301.83 nm	f=0.0011
<S**2>=0.000					
127 ->150	0.18598				
127 ->152	0.11997				
131 ->150	0.15315				
131 ->152	0.10144				
137 ->145	-0.10122				
139 ->150	0.44255				
139 ->152	0.27669				
139 ->153	0.21300				
142 ->147	-0.15087				
144 ->149	-0.10396				
Excited State	15:	Singlet-A	4.2772 eV	289.87 nm	f=0.0041
<S**2>=0.000					
142 ->145	-0.11598				
143 ->145	0.59998				
143 ->147	-0.29131				
143 ->156	-0.11249				
Excited State	16:	Singlet-A	4.2991 eV	288.40 nm	f=0.2557
<S**2>=0.000					
139 ->150	0.11763				
140 ->146	-0.11727				
140 ->149	0.10606				
142 ->147	0.57005				
143 ->147	0.10047				
144 ->149	0.26124				
Excited State	17:	Singlet-A	4.4793 eV	276.79 nm	f=0.0250
<S**2>=0.000					
137 ->146	0.16257				
138 ->145	0.14887				

140 ->145	0.62109				
142 ->149	-0.14660				
Excited State 18: Singlet-A 4.5441 eV 272.84 nm f=0.0012					
<S**2>=0.000					
132 ->146	-0.13680				
138 ->146	0.19110				
139 ->147	-0.10790				
139 ->152	0.17083				
140 ->146	0.55776				
143 ->146	-0.11361				
Excited State 19: Singlet-A 4.5610 eV 271.84 nm f=0.0003					
<S**2>=0.000					
142 ->146	-0.12846				
143 ->146	0.67873				
Excited State 20: Singlet-A 4.5941 eV 269.87 nm f=0.2656					
<S**2>=0.000					
141 ->146	-0.13971				
141 ->148	0.65775				

[RuTOB2]³⁺

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-A	2.8117 eV	440.95 nm	f=0.0001	<S**2>=0.000
157 ->173	0.15530				
162 ->173	0.19078				
166 ->173	0.39801				
171 ->173	0.22666				
172 ->173	0.41562				
Excited State 2:	Singlet-A	2.8580 eV	433.82 nm	f=0.0288	
<S**2>=0.000					
157 ->174	0.13506				
162 ->174	0.18071				
166 ->174	0.39600				
171 ->174	0.30838				
172 ->174	0.40465				
Excited State 3:	Singlet-A	2.9611 eV	418.71 nm	f=0.0005	
<S**2>=0.000					
147 ->173	-0.16507				
148 ->173	-0.14783				
161 ->174	0.15025				
163 ->173	-0.29782				
164 ->173	-0.28243				
168 ->173	-0.16669				
171 ->173	0.37694				
Excited State 4:	Singlet-A	3.1513 eV	393.44 nm	f=0.2755	
<S**2>=0.000					
161 ->173	0.12616				
164 ->174	-0.15757				
171 ->174	0.48425				
171 ->176	0.10299				
172 ->174	-0.39603				
172 ->176	-0.10480				
Excited State 5:	Singlet-A	3.3405 eV	371.16 nm	f=0.0012	
<S**2>=0.000					
147 ->174	0.10373				
148 ->174	-0.11348				
161 ->174	0.25179				
163 ->173	-0.13981				
165 ->174	0.15764				

166 ->173	-0.10201			
168 ->173	-0.11898			
171 ->173	-0.32235			
172 ->173	0.44017			
Excited State	6:	Singlet-A	3.4418 eV	360.23 nm f=0.0356
<S**2>=0.000				
147 ->174	-0.10068			
148 ->173	-0.10266			
157 ->174	-0.13693			
161 ->173	0.23922			
162 ->174	-0.15796			
163 ->174	-0.23080			
164 ->174	-0.12581			
165 ->173	0.16757			
166 ->174	-0.18554			
167 ->174	0.12237			
168 ->174	-0.22291			
172 ->174	0.32017			
172 ->176	0.12852			
Excited State	7:	Singlet-A	3.4486 eV	359.52 nm f=0.0020
<S**2>=0.000				
147 ->174	0.13689			
148 ->174	-0.16412			
153 ->174	0.10855			
157 ->173	0.10769			
161 ->174	0.36481			
162 ->173	0.13857			
163 ->173	0.13445			
165 ->174	0.22831			
166 ->173	0.16339			
168 ->173	0.16906			
172 ->173	-0.28323			
Excited State	8:	Singlet-A	3.5280 eV	351.43 nm f=0.0267
<S**2>=0.000				
157 ->173	-0.10653			
162 ->173	-0.18186			
166 ->173	-0.22675			
168 ->173	0.44746			
171 ->173	0.34293			
172 ->173	0.17677			
Excited State	9:	Singlet-A	3.5360 eV	350.64 nm f=0.1224
<S**2>=0.000				
150 ->174	-0.10517			
157 ->174	-0.11151			
161 ->173	-0.11775			
162 ->174	-0.19725			
163 ->174	0.12672			
166 ->174	-0.26325			
168 ->174	0.33384			
171 ->174	0.32081			
171 ->176	0.15190			
172 ->174	0.19234			
Excited State	10:	Singlet-A	3.6784 eV	337.06 nm f=0.0479
<S**2>=0.000				
147 ->173	-0.10539			
163 ->173	-0.21968			
164 ->173	-0.15154			
166 ->173	0.15362			
166 ->178	0.11432			
167 ->173	0.10260			
168 ->173	0.44445			
168 ->175	0.13001			
171 ->173	-0.25756			

Excited State	11:	Singlet-A	3.7406 eV	331.46 nm	f=0.1341
<S**2>=0.000					
	161 ->173	0.12508			
	163 ->174	-0.12069			
	164 ->174	-0.10805			
	166 ->174	0.11697			
	167 ->174	0.23549			
	168 ->174	0.53524			
	171 ->176	-0.12475			
	172 ->176	0.14809			
Excited State	12:	Singlet-A	3.8085 eV	325.55 nm	f=0.3886
<S**2>=0.000					
	161 ->173	-0.11599			
	163 ->174	0.13365			
	167 ->174	0.37490			
	167 ->176	0.11140			
	168 ->174	-0.19812			
	172 ->174	-0.10252			
	172 ->176	0.42005			
	172 ->179	0.12490			
Excited State	13:	Singlet-A	3.8664 eV	320.67 nm	f=0.0025
<S**2>=0.000					
	167 ->173	0.66311			
Excited State	14:	Singlet-A	3.9019 eV	317.76 nm	f=0.1728
<S**2>=0.000					
	167 ->174	0.48294			
	171 ->179	-0.10553			
	172 ->174	0.11729			
	172 ->176	-0.40370			
	172 ->179	-0.13231			
Excited State	15:	Singlet-A	4.0096 eV	309.22 nm	f=0.3427
<S**2>=0.000					
	166 ->178	-0.10718			
	167 ->174	0.10361			
	171 ->174	-0.19418			
	171 ->176	0.56661			
	171 ->179	-0.12106			
	172 ->179	0.11344			
Excited State	16:	Singlet-A	4.0146 eV	308.83 nm	f=0.0369
<S**2>=0.000					
	150 ->178	0.13778			
	157 ->178	0.15950			
	162 ->178	0.21001			
	162 ->181	-0.12578			
	166 ->178	0.35907			
	166 ->181	-0.21036			
	166 ->182	-0.13307			
	168 ->173	-0.10419			
	168 ->175	0.12601			
	171 ->176	0.17094			
	171 ->178	0.12156			
	172 ->178	0.13242			
Excited State	17:	Singlet-A	4.2181 eV	293.94 nm	f=0.1098
<S**2>=0.000					
	168 ->175	-0.43611			
	171 ->175	0.46724			
Excited State	18:	Singlet-A	4.2272 eV	293.30 nm	f=0.1593
<S**2>=0.000					
	168 ->175	0.46013			
	171 ->175	0.46147			

172 ->175	-0.14244				
Excited State 19:	Singlet-A	4.3025 eV	288.17 nm	f=0.0034	
<S**2>=0.000					
166 ->175	0.16975				
171 ->175	0.12360				
172 ->175	0.64262				
Excited State 20:	Singlet-A	4.4204 eV	280.48 nm	f=0.0034	
<S**2>=0.000					
169 ->174	0.59590				
169 ->176	0.24594				
169 ->179	-0.16124				

[RuT1B2]³⁺

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-A	2.8333 eV	437.59 nm	f=0.0000	<S**2>=0.000
182 ->201 0.12246					
187 ->201 0.18816					
188 ->201 -0.11489					
192 ->201 0.39836					
199 ->201 -0.19757					
200 ->201 -0.39466					
Excited State 2:	Singlet-A	2.8904 eV	428.95 nm	f=0.0307	
<S**2>=0.000					
173 ->202 0.10280					
182 ->202 0.10740					
187 ->202 0.18311					
192 ->202 0.40993					
199 ->202 -0.30236					
200 ->202 -0.39047					
Excited State 3:	Singlet-A	2.9201 eV	424.59 nm	f=0.0002	
<S**2>=0.000					
170 ->201 -0.15028					
171 ->202 0.12348					
181 ->202 0.19456					
188 ->201 -0.20062					
189 ->202 -0.18283					
190 ->201 -0.19060					
191 ->202 0.17278					
192 ->201 -0.12254					
194 ->201 -0.10847					
198 ->202 0.36665					
199 ->201 0.26525					
Excited State 4:	Singlet-A	3.0041 eV	412.71 nm	f=0.2687	
<S**2>=0.000					
181 ->201 0.10081					
188 ->202 -0.11325					
189 ->201 -0.15204					
190 ->202 -0.12676					
191 ->201 0.12740					
198 ->201 0.56902					
198 ->203 -0.11291					
199 ->202 0.19911					
Excited State 5:	Singlet-A	3.1065 eV	399.11 nm	f=0.0007	
<S**2>=0.000					
170 ->201 0.14373					
181 ->202 0.10641					
188 ->201 0.20346					
189 ->202 -0.12931					

190 ->201	0.21344			
191 ->202	0.11322			
194 ->201	0.14203			
198 ->202	0.40395			
199 ->201	-0.31713			
200 ->201	0.13210			
Excited State	6:	Singlet-A	3.2422 eV	382.41 nm f=0.3591
<S**2>=0.000				
198 ->201	-0.25507			
199 ->202	0.43280			
199 ->204	0.10541			
200 ->202	-0.42327			
200 ->204	-0.13139			
Excited State	7:	Singlet-A	3.4033 eV	364.30 nm f=0.0033
<S**2>=0.000				
187 ->201	0.12621			
188 ->201	-0.19604			
192 ->201	0.14955			
194 ->201	-0.21067			
198 ->202	-0.10027			
199 ->201	-0.24067			
200 ->201	0.51359			
Excited State	8:	Singlet-A	3.5016 eV	354.08 nm f=0.1266
<S**2>=0.000				
170 ->202	-0.10189			
181 ->201	0.15916			
187 ->202	0.13923			
188 ->202	-0.19464			
190 ->202	-0.11667			
191 ->201	0.15273			
192 ->202	0.17128			
194 ->202	-0.23470			
198 ->201	-0.16643			
198 ->203	0.27006			
199 ->202	0.12580			
200 ->202	0.26281			
Excited State	9:	Singlet-A	3.5490 eV	349.34 nm f=0.0388
<S**2>=0.000				
187 ->201	0.19443			
192 ->201	0.24447			
194 ->201	0.37085			
199 ->201	0.36977			
200 ->201	0.21046			
Excited State	10:	Singlet-A	3.5573 eV	348.54 nm f=0.3169
<S**2>=0.000				
173 ->202	0.10983			
187 ->202	0.19656			
192 ->202	0.26279			
194 ->202	0.27196			
198 ->203	-0.17340			
199 ->202	0.30987			
199 ->204	0.16564			
200 ->202	0.21001			
Excited State	11:	Singlet-A	3.6794 eV	336.97 nm f=0.0402
<S**2>=0.000				
170 ->201	-0.10683			
181 ->202	0.13011			
188 ->201	-0.15768			
190 ->201	-0.11247			
192 ->201	-0.13204			
194 ->201	0.46033			
194 ->203	-0.10302			

198 ->202	-0.21807				
199 ->201	-0.23623				
Excited State	12:	Singlet-A	3.7167 eV	333.59 nm	f=0.0064
<S**2>=0.000					
171 ->202	-0.16992				
181 ->202	-0.26061				
186 ->202	0.10404				
188 ->201	-0.13645				
189 ->202	0.14438				
191 ->202	-0.23917				
192 ->206	0.13846				
194 ->203	-0.10242				
198 ->202	0.33685				
198 ->205	-0.16249				
199 ->201	-0.13664				
Excited State	13:	Singlet-A	3.7405 eV	331.47 nm	f=0.2539
<S**2>=0.000					
194 ->202	0.49617				
195 ->202	0.10386				
198 ->201	0.12416				
198 ->203	0.42835				
Excited State	14:	Singlet-A	3.7938 eV	326.81 nm	f=0.5795
<S**2>=0.000					
193 ->202	0.41328				
193 ->204	0.12487				
194 ->202	0.19651				
198 ->201	-0.12385				
198 ->203	-0.19516				
200 ->204	0.35721				
Excited State	15:	Singlet-A	3.8749 eV	319.97 nm	f=0.0410
<S**2>=0.000					
181 ->201	-0.13759				
188 ->202	0.17370				
190 ->202	0.11456				
191 ->201	-0.11727				
194 ->202	-0.21086				
198 ->201	0.17841				
198 ->203	0.31067				
199 ->204	0.13319				
200 ->202	-0.10475				
200 ->204	0.35286				
200 ->207	0.12016				
Excited State	16:	Singlet-A	3.8975 eV	318.11 nm	f=0.0030
<S**2>=0.000					
193 ->201	0.65803				
Excited State	17:	Singlet-A	3.9363 eV	314.98 nm	f=0.1107
<S**2>=0.000					
188 ->202	0.11804				
193 ->202	0.50841				
200 ->202	0.10093				
200 ->204	-0.33223				
200 ->207	-0.10858				
Excited State	18:	Singlet-A	4.0073 eV	309.39 nm	f=0.0106
<S**2>=0.000					
189 ->205	-0.10532				
194 ->201	0.13861				
194 ->203	0.21542				
198 ->205	0.59318				
Excited State	19:	Singlet-A	4.0329 eV	307.43 nm	f=0.0283
<S**2>=0.000					

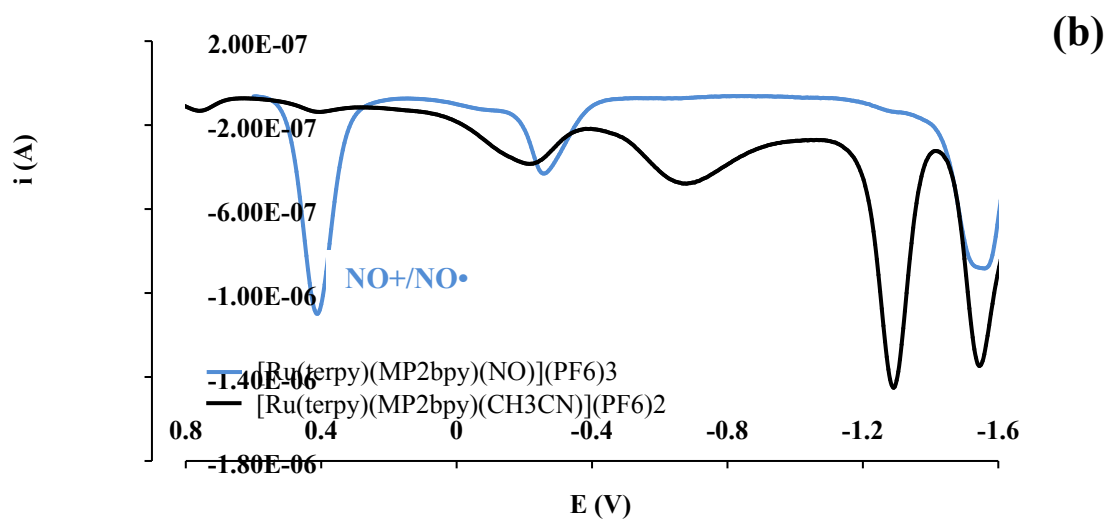
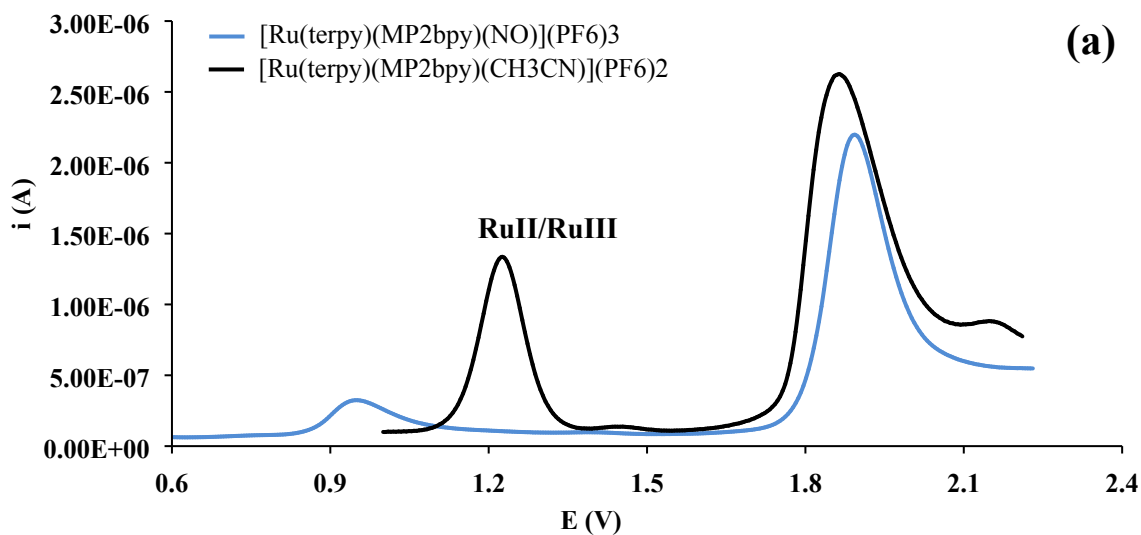
173 ->206	0.13714
173 ->210	-0.10454
182 ->206	0.11753
187 ->206	0.19893
187 ->210	-0.14553
188 ->201	0.10784
192 ->206	0.35233
192 ->210	-0.25095
194 ->201	-0.10396
194 ->203	-0.10655
199 ->204	-0.15448
199 ->206	-0.11677
200 ->206	-0.12744

Excited State	20:	Singlet-A	4.0376 eV	307.07 nm	f=0.3048
<S**2>=0.000					
193 ->202		0.10869			
199 ->202		-0.20490			
199 ->204		0.56789			
199 ->207		-0.11811			
200 ->207		0.11095			

-S6- Electrochemical data

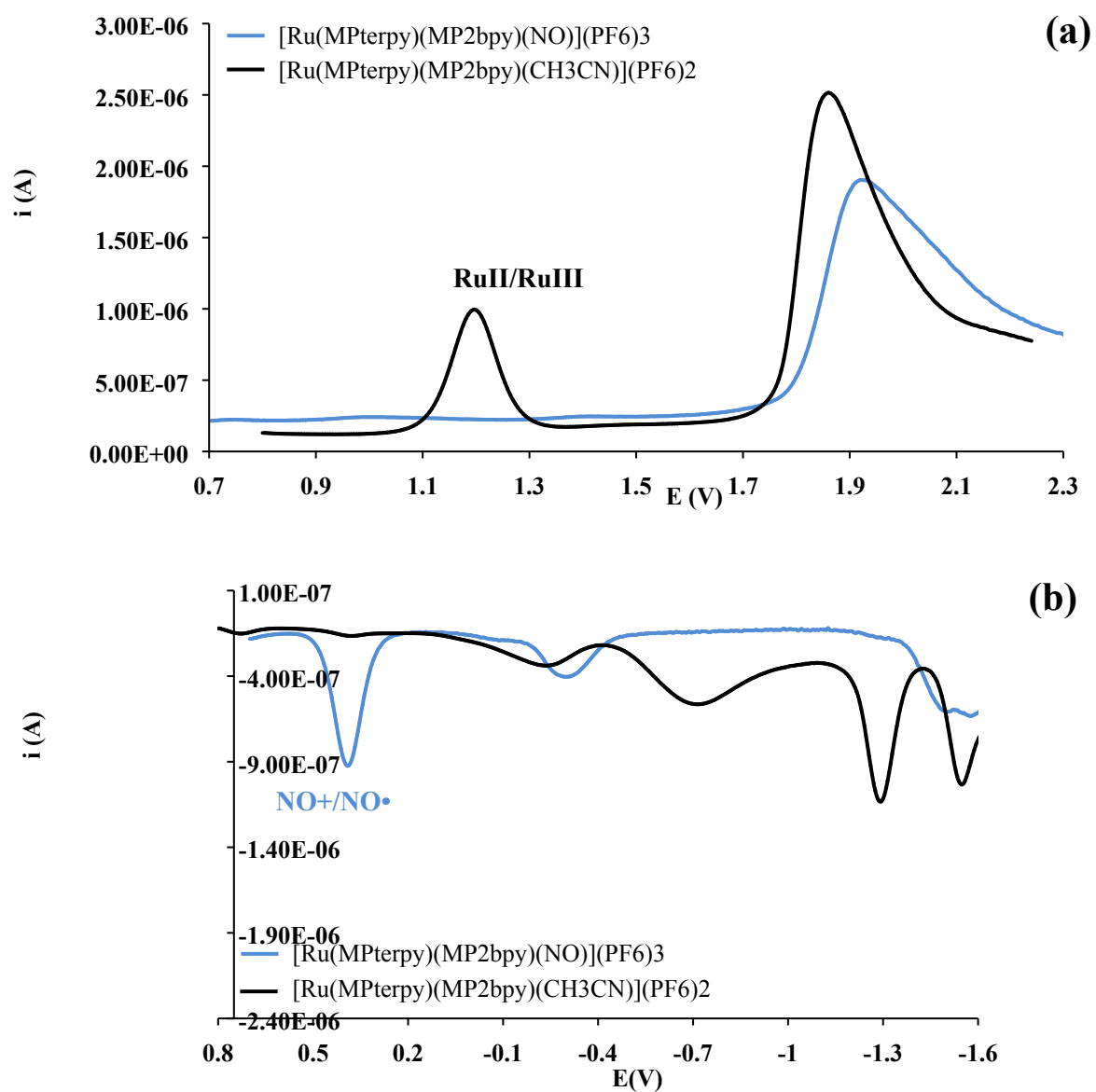
Square wave voltammograms

[RuT0B2](PF₆)₃ and photoproduct



(a) oxidation and (b) reduction. The irradiation was performed with the Hg lamp. Potentials vs SCE.

[RuT1B2](PF₆)₃ and photoproduct

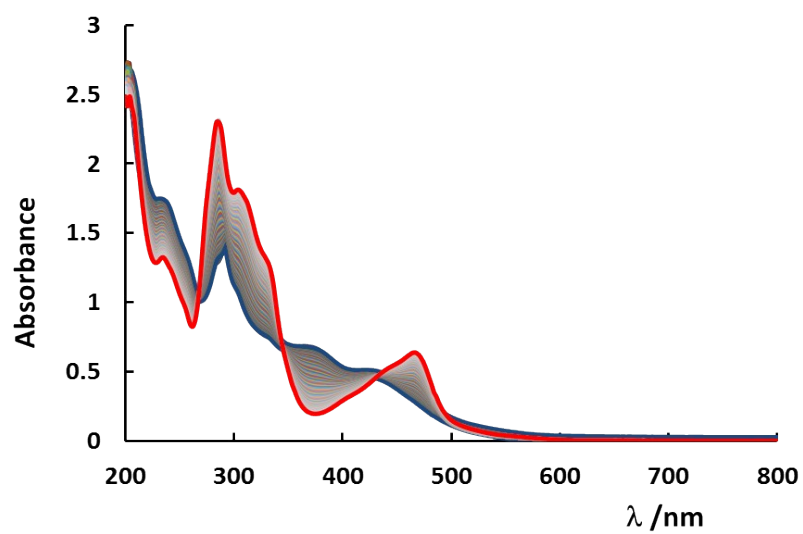


(a) oxidation and **(b)** reduction. The irradiation was performed with the Hg lamp. Potentials vs SCE.

The data are summarized in the following table, where the potential are in Volt vs SCE. E_{eq} indicates the equilibrium potentials.

Complexes	Before irradiation				After irradiation		
	E _{eq}	Reduction		Oxidation	E _{eq}	Oxidation	
		NO⁺/NO[•]	Polypyridyl ligands	MP₂bpy or MPterpy		MP₂bpy or MPterpy	Ru^{III/II}
[RuT0B0](PF ₆) ₃	0.50	0.47			0.79		1.29
[RuT1B0](PF ₆) ₃	0.48	0.44	-1.49, -1.62, -1.71	1.99	0.69	1.93	1.27
[RuT0B2](PF ₆) ₃	0.55	0.42	-1.58	1.89	0.79	1.87	1.23
[RuT1B2](PF ₆) ₃	0.45	0.39	-1.48; -1,58	1.92	0.80	1.86	1.20

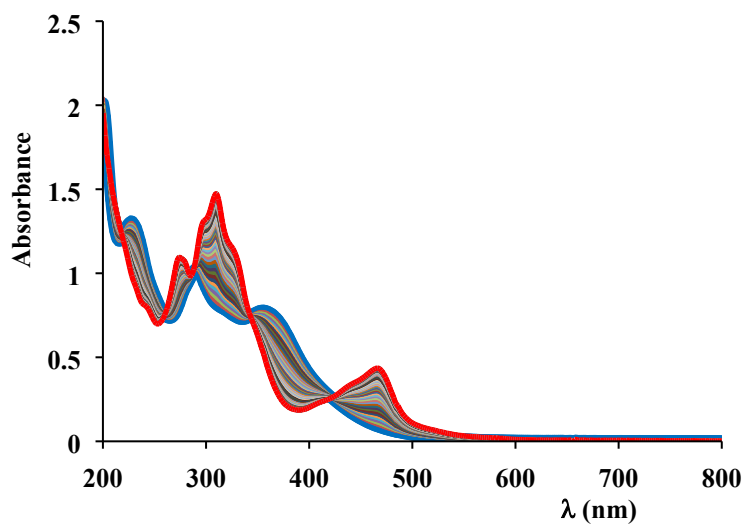
-S7- Photorelease on [RuT1B0](PF₆)₃ and [RuT0B2](PF₆)₃



[RuT1B0](PF₆)₃

Blue: before irradiation

Red: after 40 mn irradiation at 436 nm

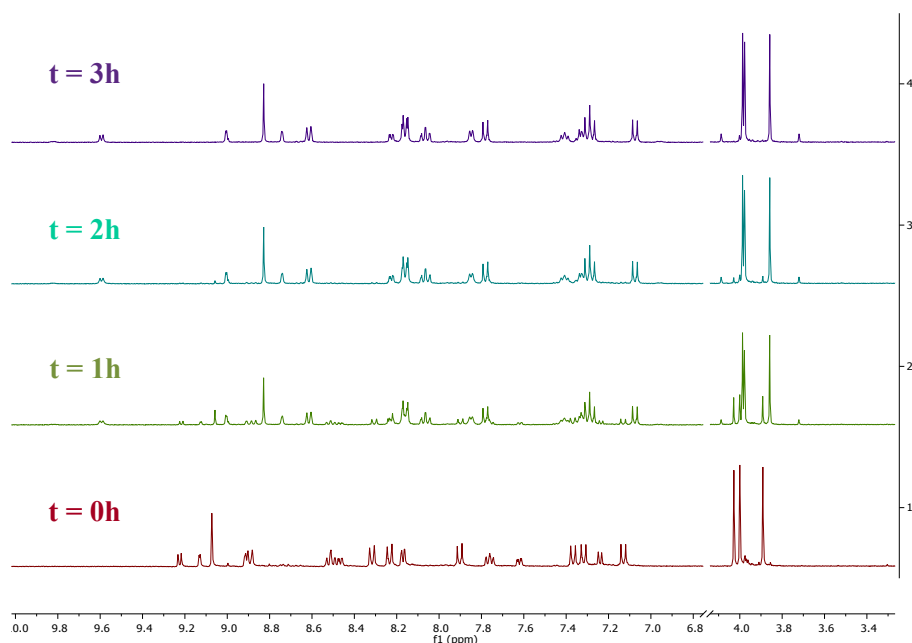


[RuT0B2](PF₆)₃

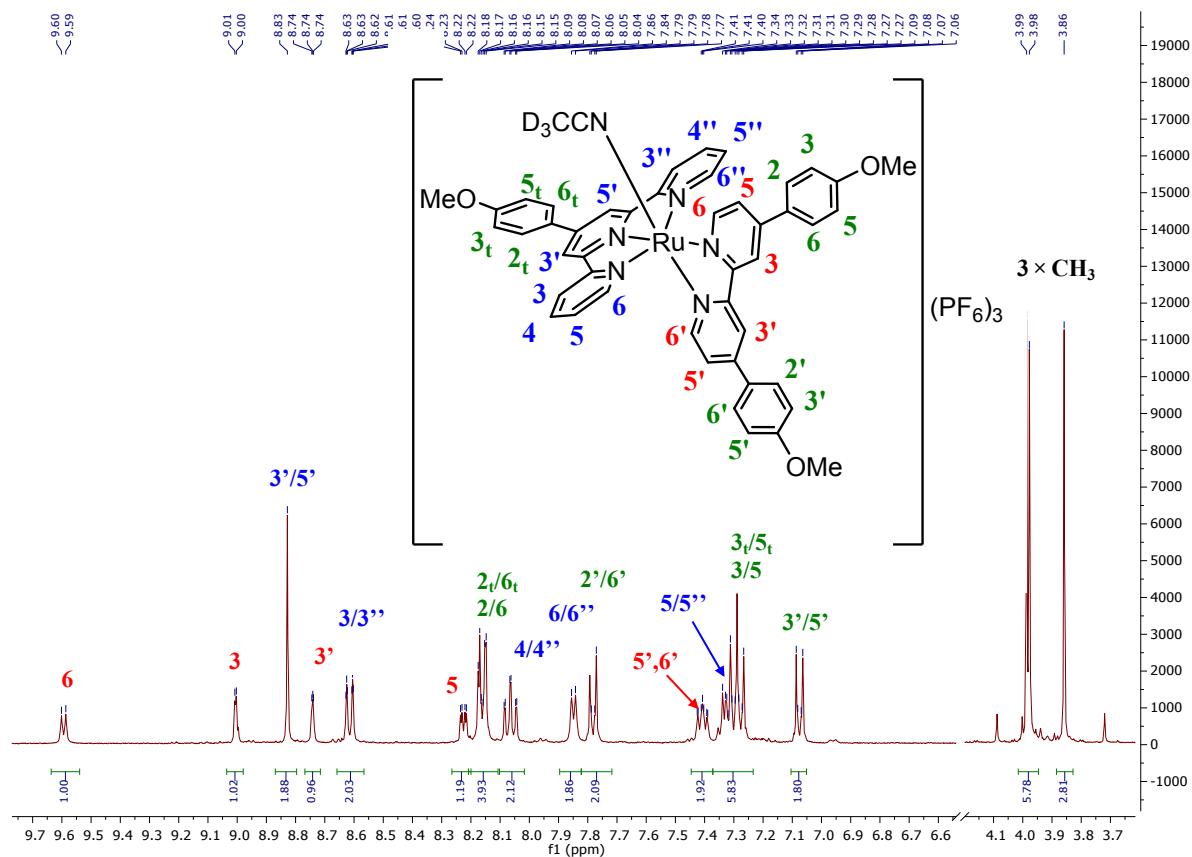
Blue: before irradiation

Red: after 45 mn irradiation at 365 nm

-S8- ^1H -NMR of the photoproduct obtained from $[\text{RuT1B2}](\text{PF}_6)_3$.

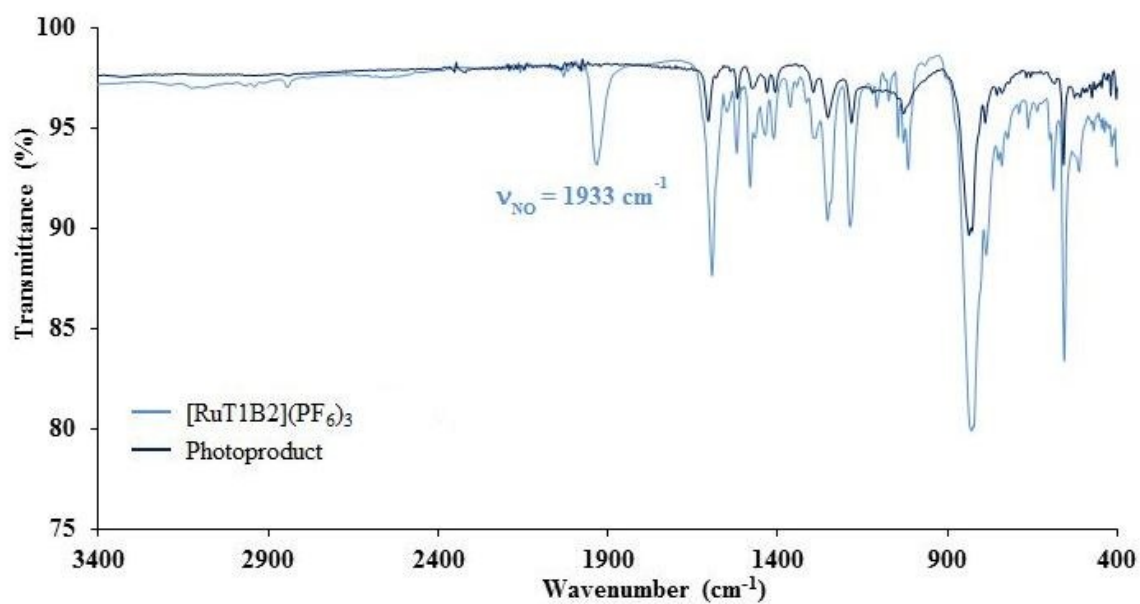


Complete NO release obtained from intense irradiation, using a Xenon lamp.
Until these conditions, a single photoproduct is evidenced.



^1H NMR of the photoproduct in CD_3CN

-S9- IR spectra for $[\text{RuT1B2}](\text{PF}_6)_3$ and its photoproduct



IR spectra showing the disappearance of the ν_{NO} band, after irradiation of the RuNO complex $[\text{RuT1B2}]^{3+}$.