Electronic Supplementary Information

Further studies on the photoreactivities of ruthenium-nitrosyl complexes with terpyridyl ligands.

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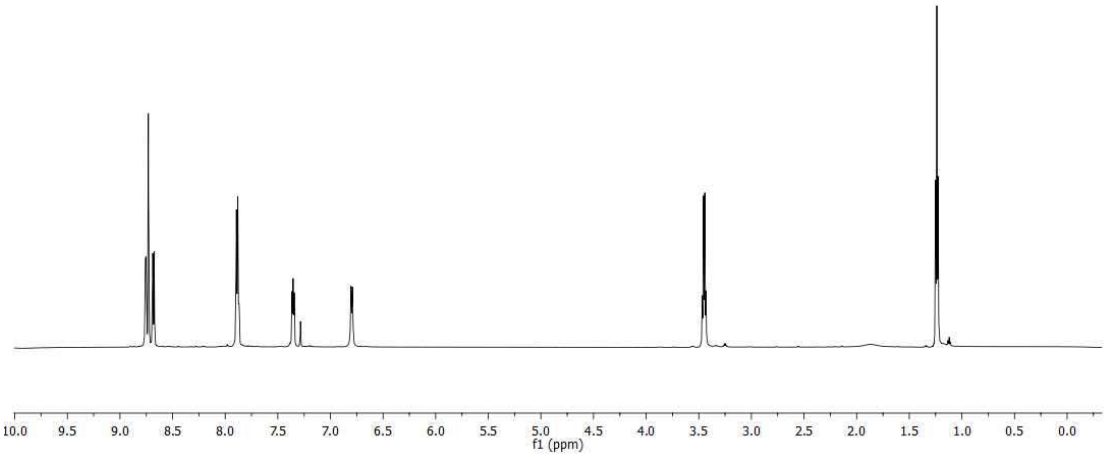


Fig. S1: ^{1}H NMR of the ligand in $CDCl_3$

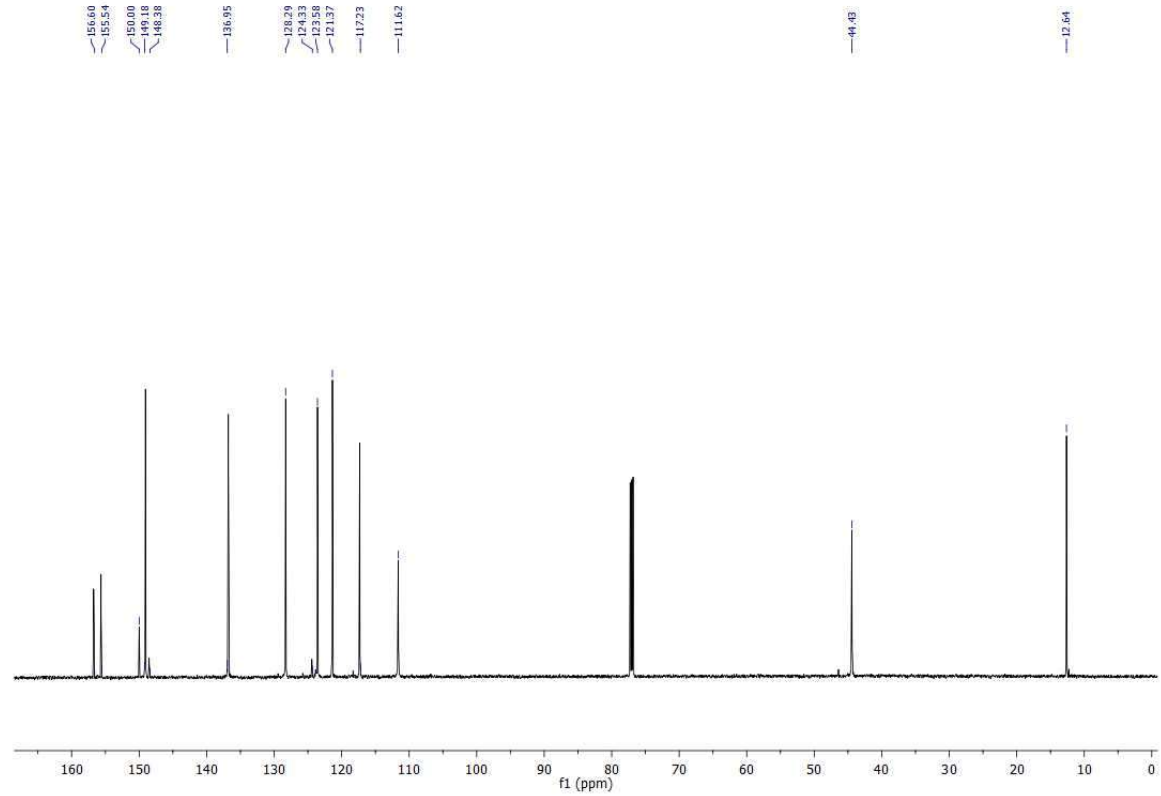


Fig. S2 : ^{13}C NMR of the ligand in $CDCl_3$.

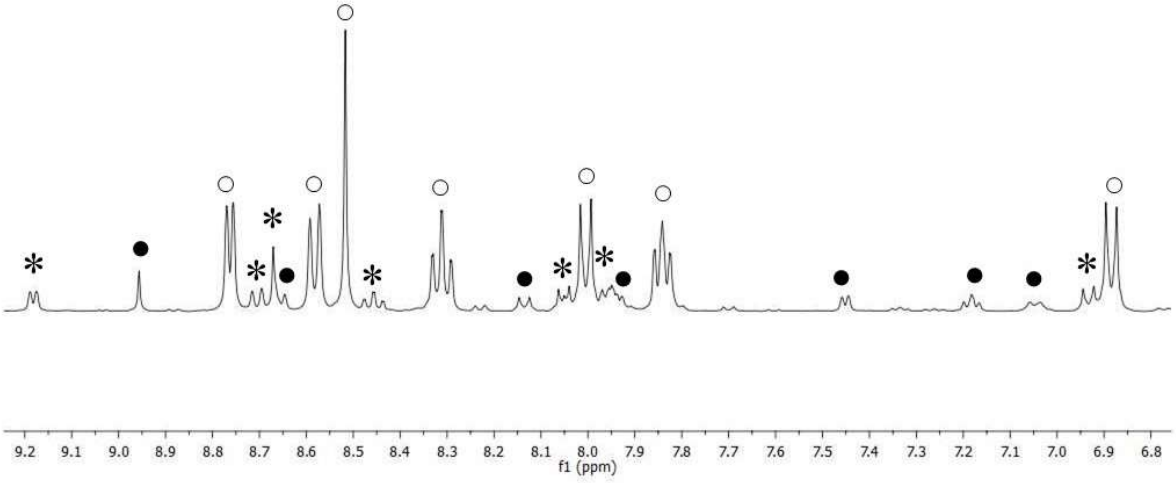


Fig. S3 : ^{1}H NMR (DMSO d6) of the crude reaction mixture in the synthesis of [**1**]$^{+}$(PF_6) : labels identify the different complexes: homoleptic (black spot), *cis* isomer (star) and *trans* isomer (white spot)

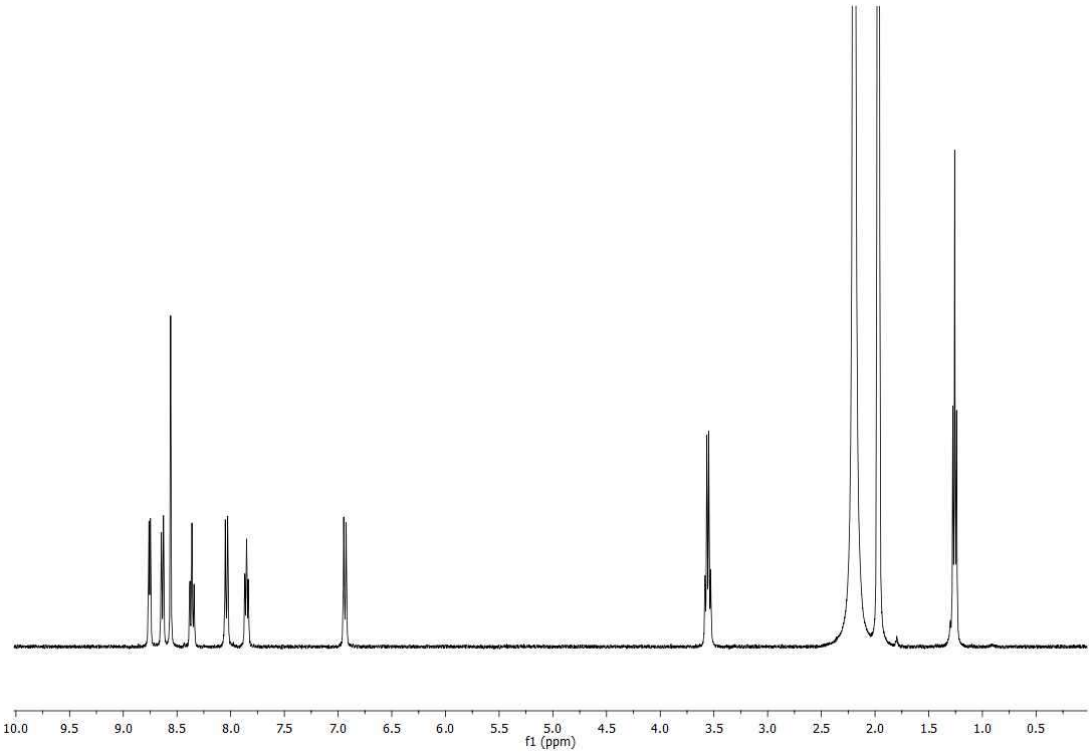


Fig. S4 : ^{1}H NMR of [**1t**]$^{+}$(PF_6) in CD_3CN.

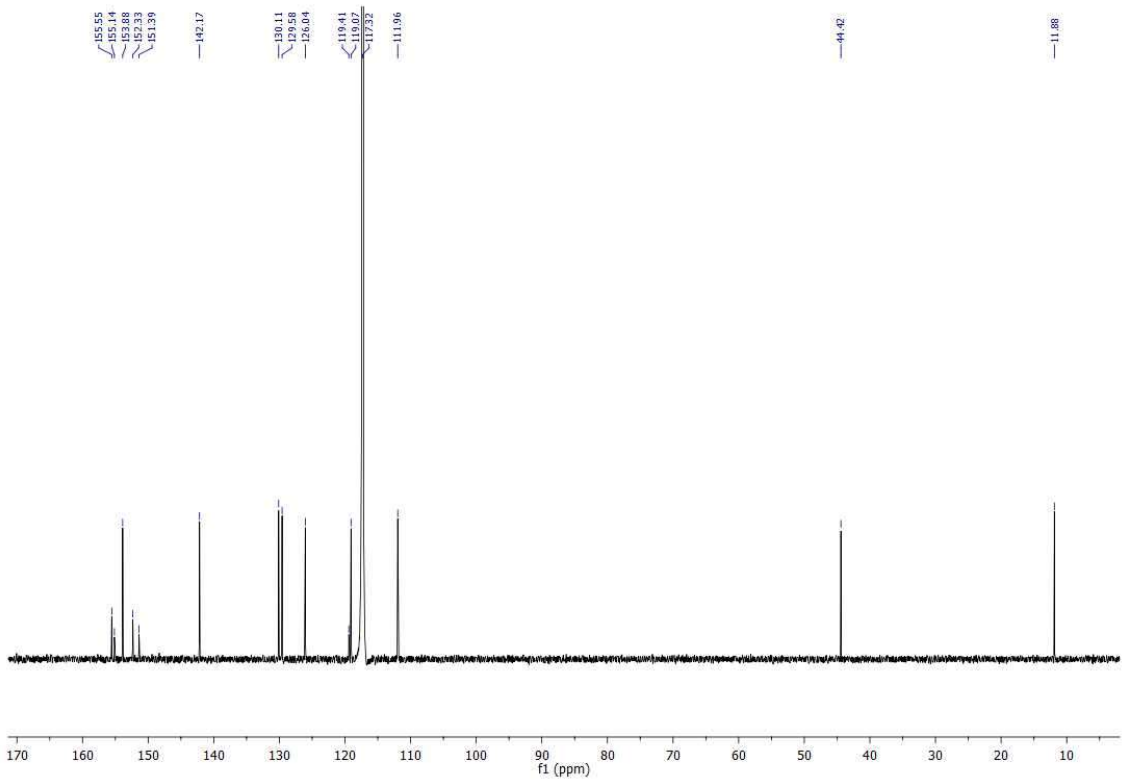


Fig. S5 : ^{13}C NMR of [**1t**]$^{+}$(PF_6) in CD_3CN.

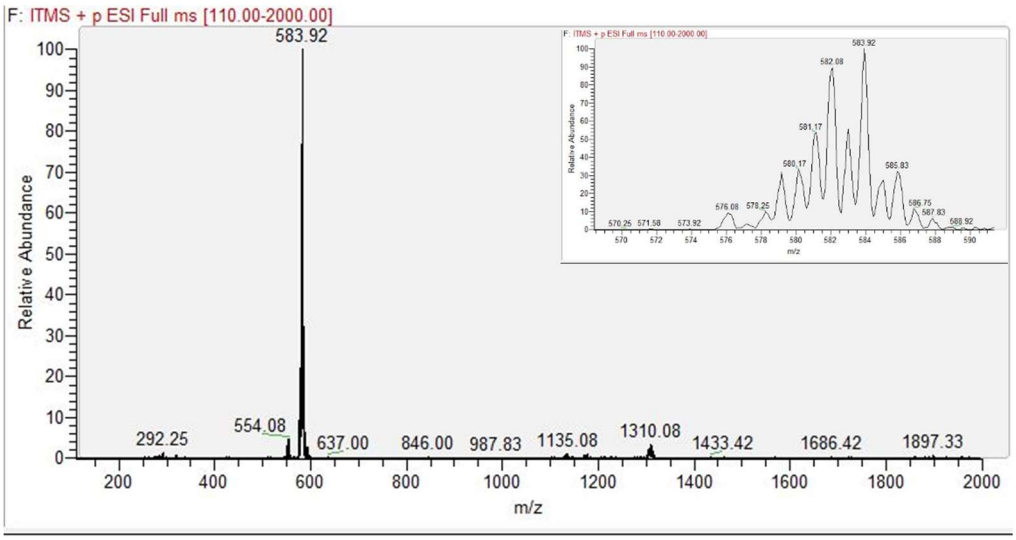


Fig. S6 : ESI mass spectrum of [**1t**]$^{+}$(PF_6)

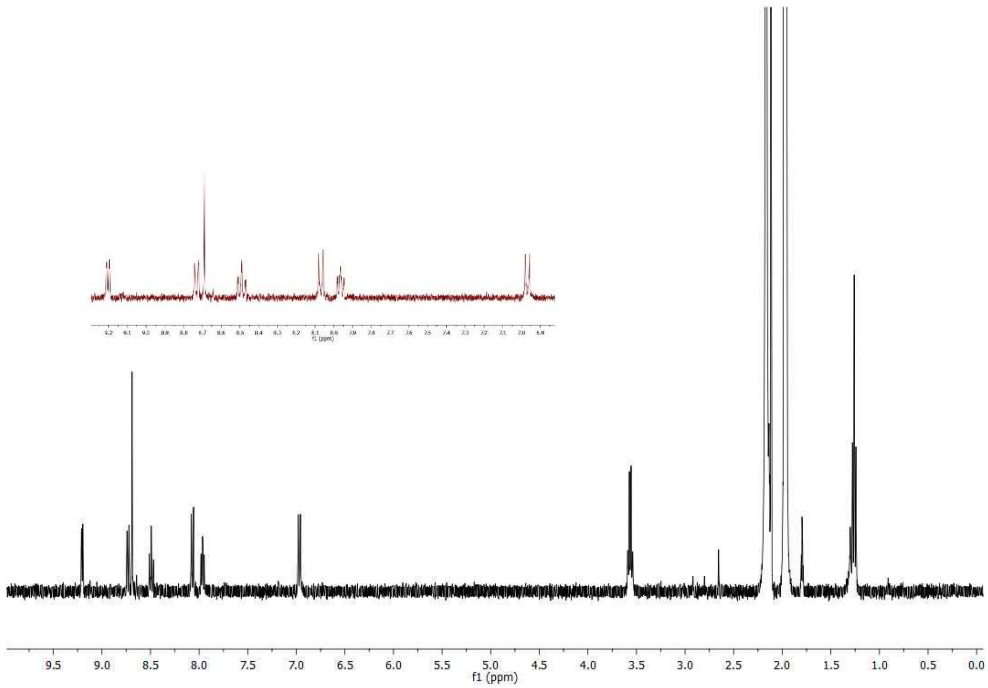


Fig. S7 : ^{1}H NMR of [**1c**]$^{+}(PF_6)$ in CD_3CN.

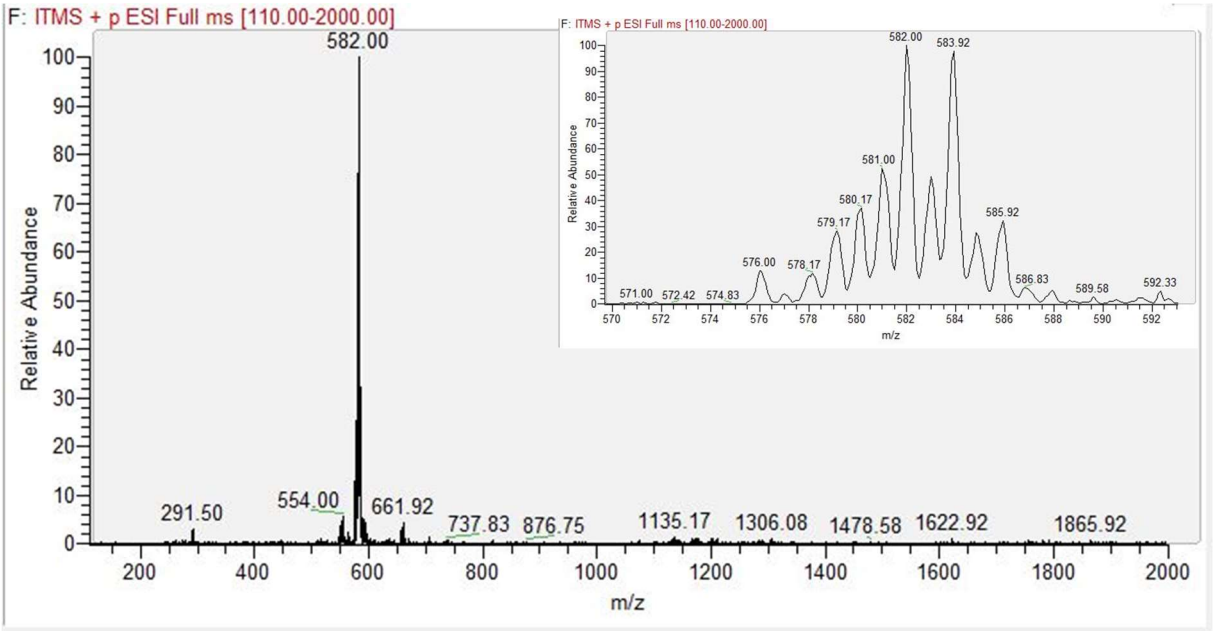


Fig. S8 : ESI mass spectrum of [**1c**]$^{+}(PF_6)$

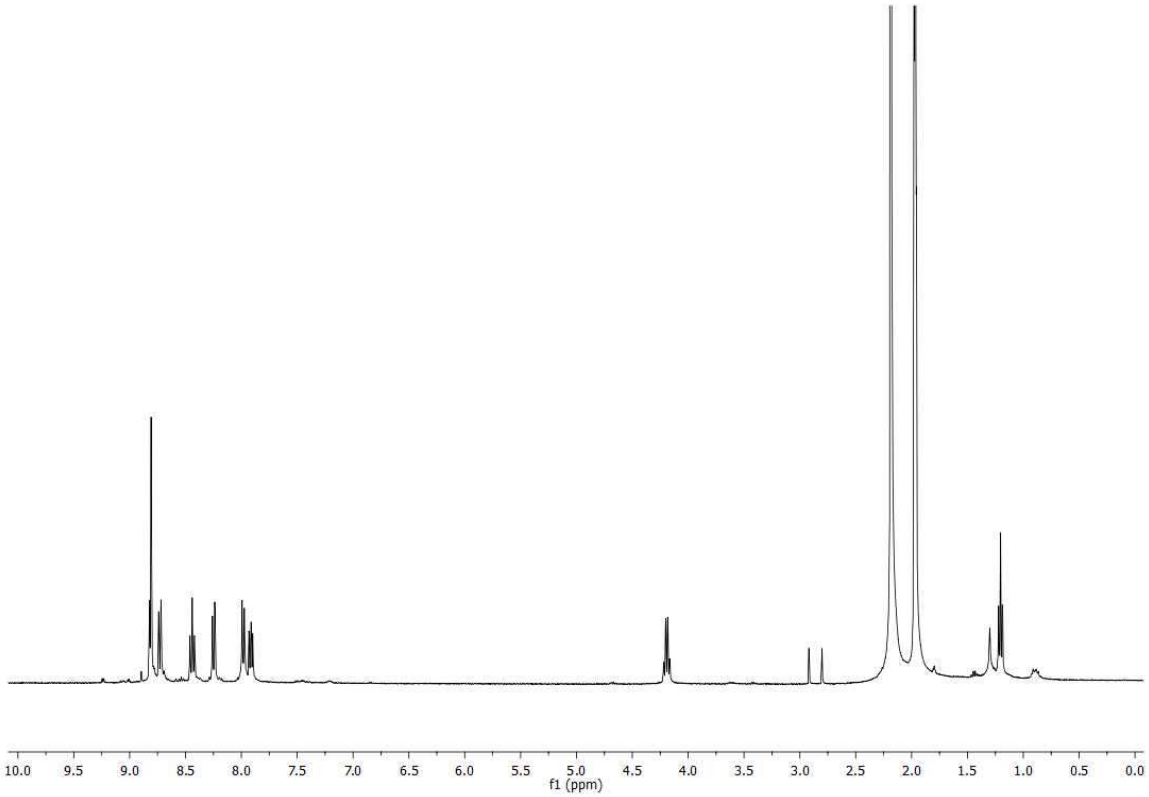


Fig. S9: ^{1}H NMR of [**2t**]$^{+}$(PF_6) in CD_3CN.

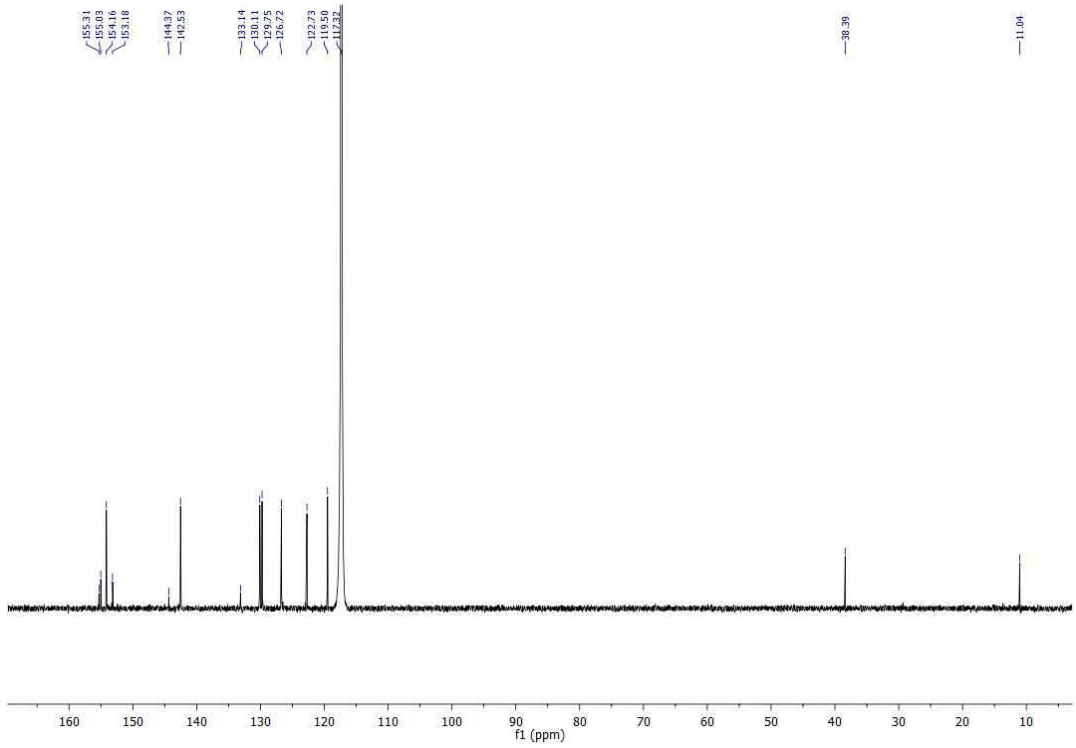


Fig. S10: ^{13}C NMR of [**2t**]$^{+}$(PF_6) in CD_3CN.

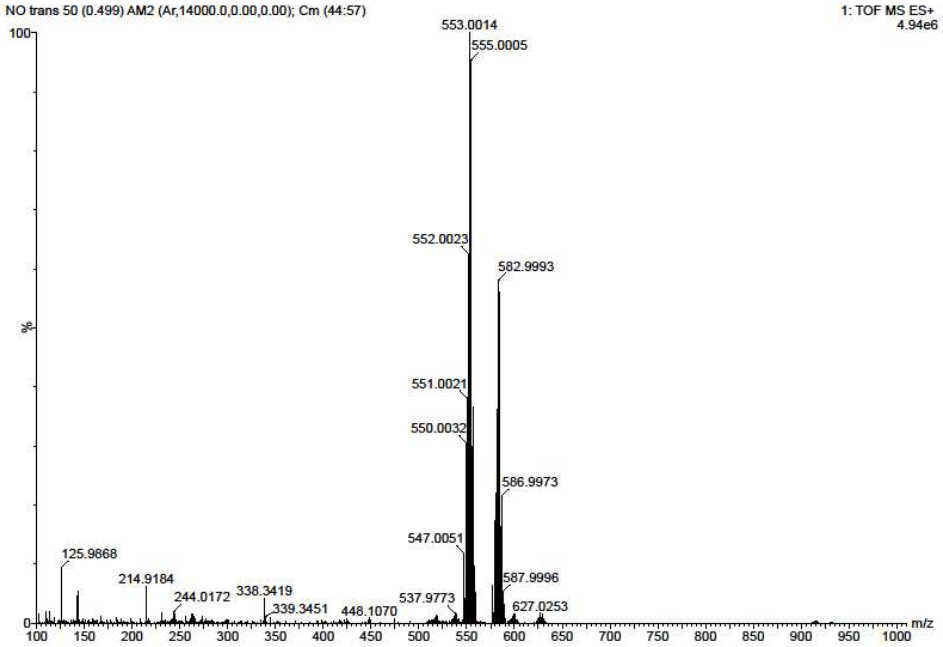


Fig. S11 : HR ES mass spectrum of [**2t**]$^{+}$(PF_6)

S1: synthesis of [**3**]$^{+}$(PF_6)

To a dark-blue solution of about 10 mg of [**1t**]$^{+}$(PF_6) in 1mL of MeCN in a a tube, were added 2 drops of nitric acid (65%). Instantaneously, the solution became colorless. The tube was left in a closed flask for diffusion with diethyloxide. After few days, brown crystals appeared and some of them were collected for ^{1}H NMR measurement.

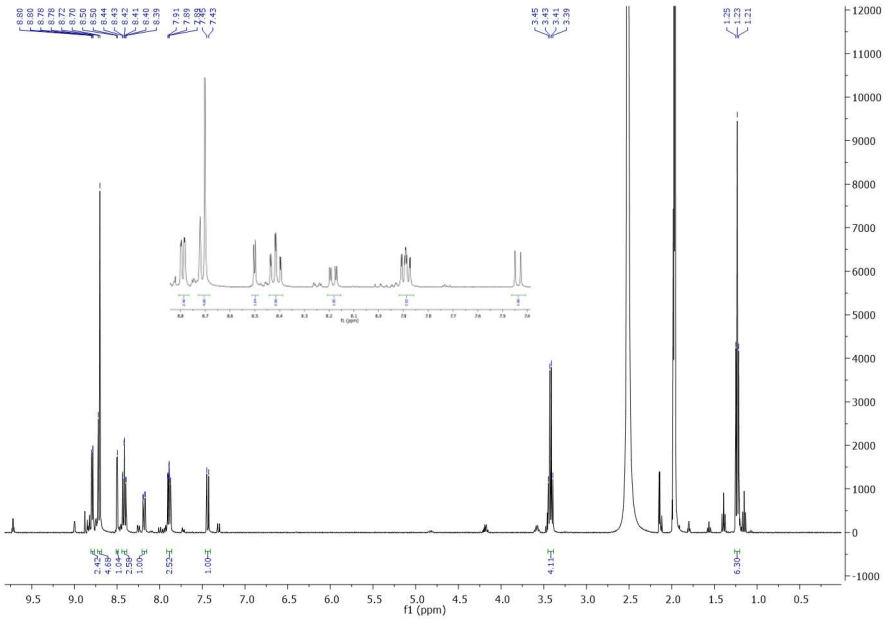
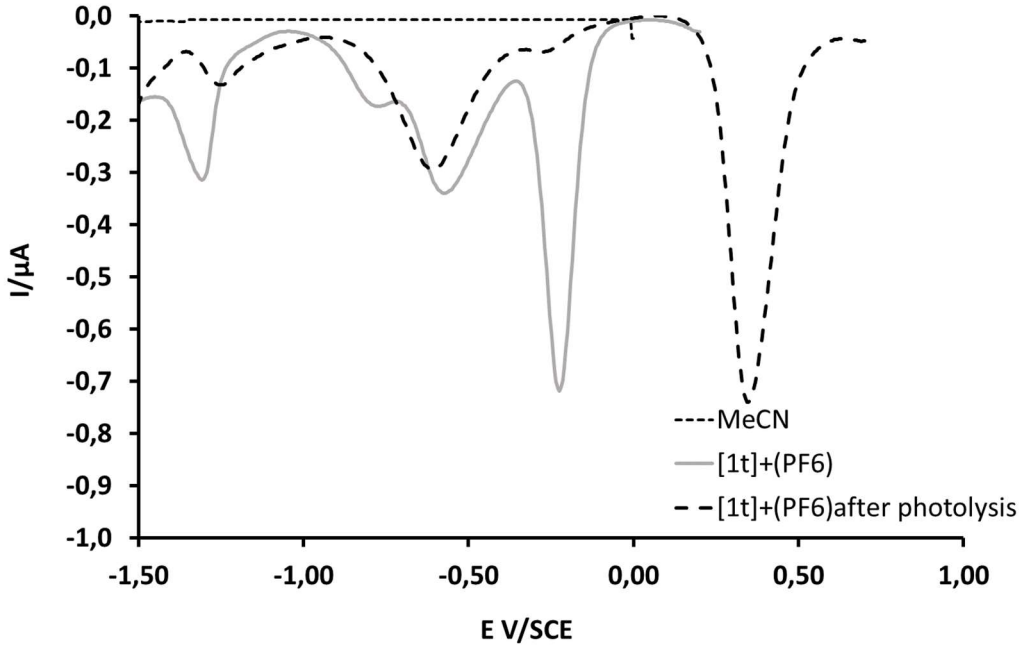
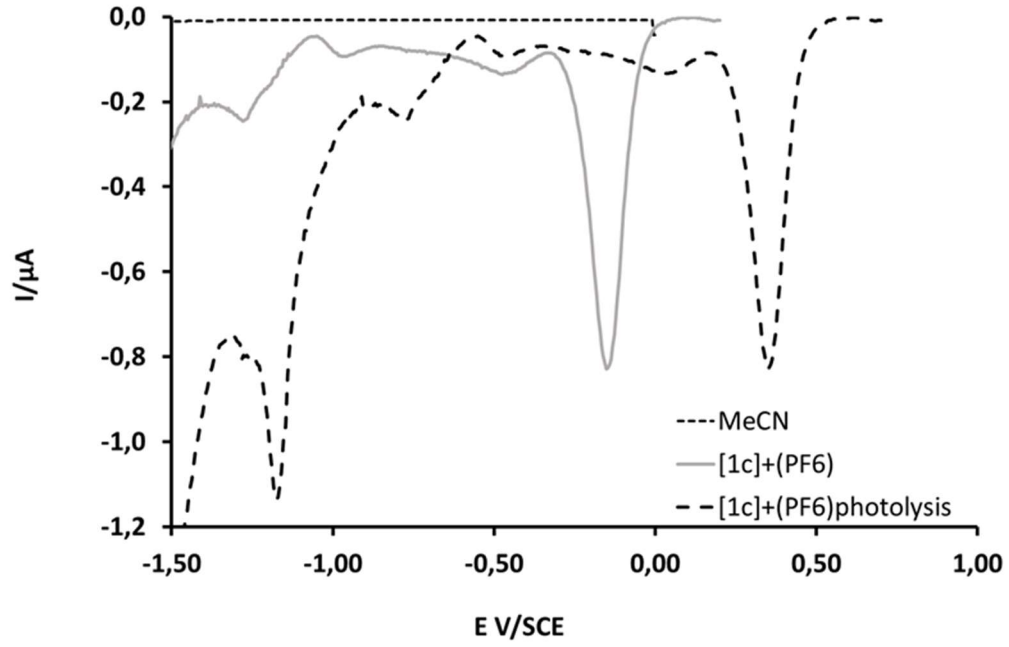


Fig. S12: ^{1}H NMR of complex **3** (with zoom of the aromatic part as insert)



(a)



(b)

Fig. S13 : Square wave voltammograms in reduction for (a) [**1t**]$^{+}$(PF_6) and (b) [**1c**]$^{+}$(PF_6) before (in grey) and after irradiation (with a Xenon lamp (complex 1mM in MeCN), 0.1M (nBu_4)[PF_6]

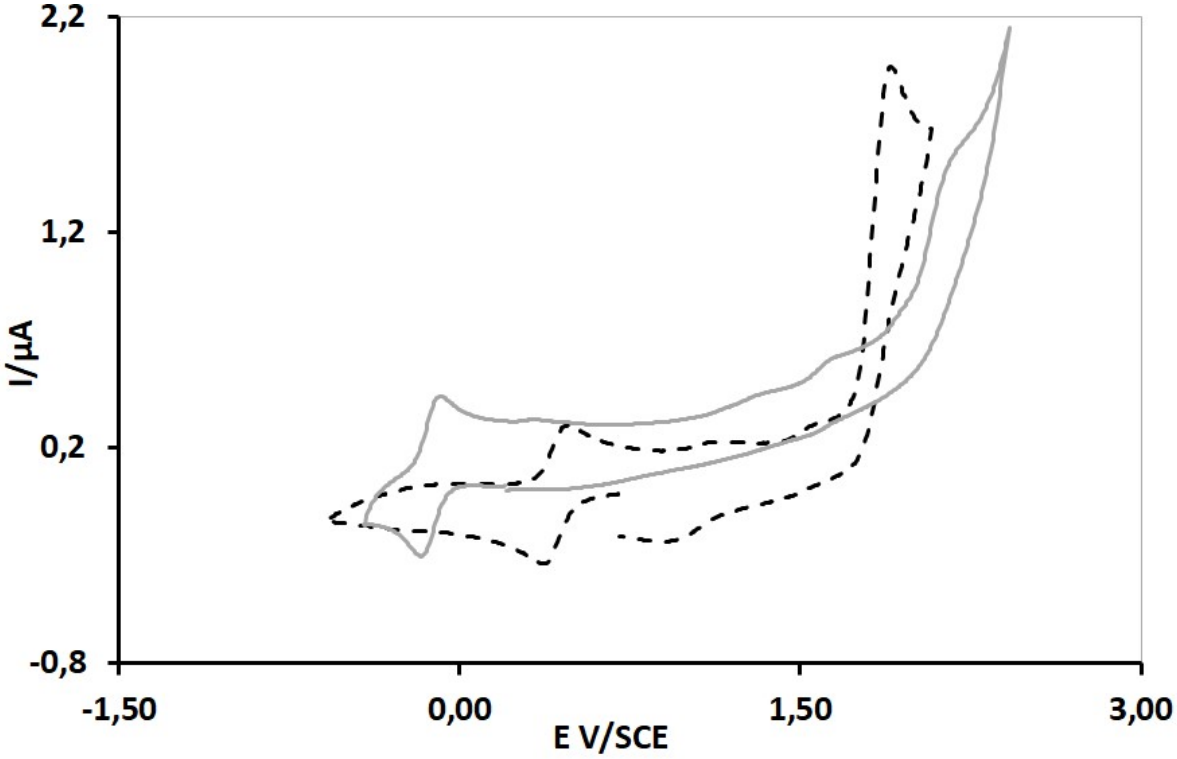


Fig. S14: CV of [**2t**]$^{+}$(PF_6) before (in grey) and after irradiation (with a Xenon lamp (complex 1mM in MeCN), 0.1M (nBu_4)[PF_6], working electrode Pt disk, scan 0.2 V/s

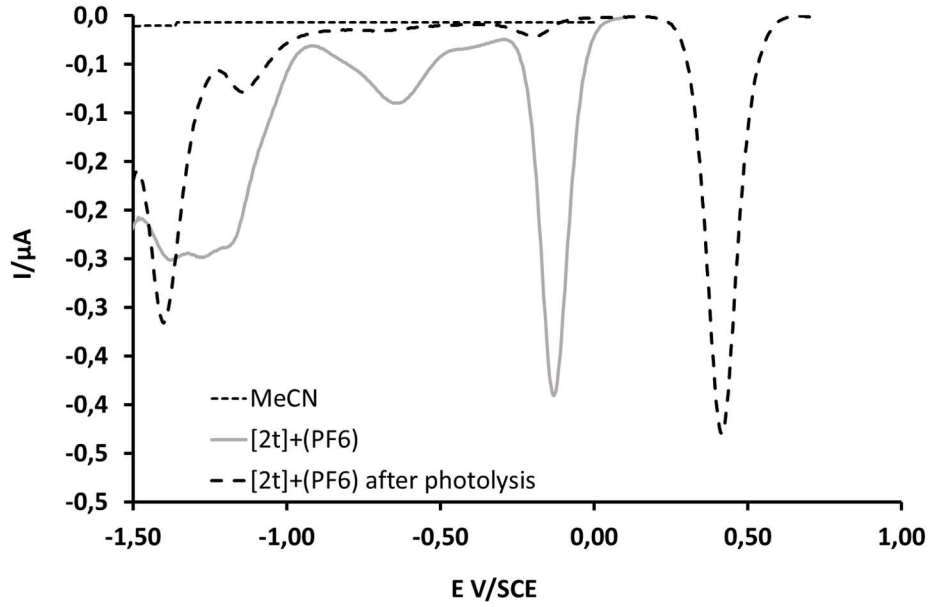


Fig. S15 : Square wave voltammograms in reduction for (a) [**2t**]$^{+}$(PF_6) before (in grey) and after irradiation (with a Xenon lamp (complex 1mM in MeCN), 0.1M (nBu_4)[PF_6]

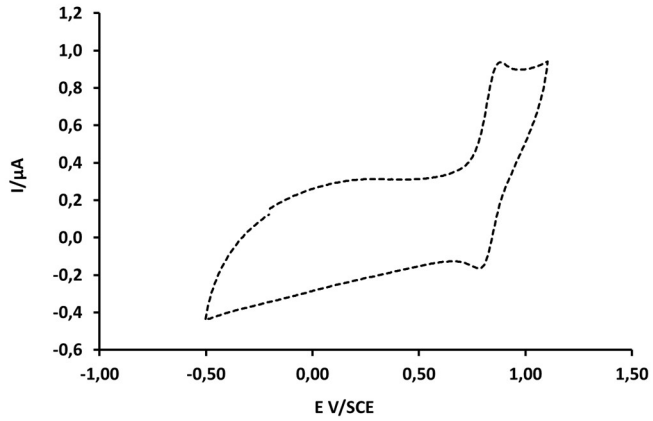


Fig. S16 : CV of ligand NEt_2Phtpy in MeCN, 0.1M $(nBu_4)[PF_6]$, working electrode Pt disk, scan 0.2 V/s

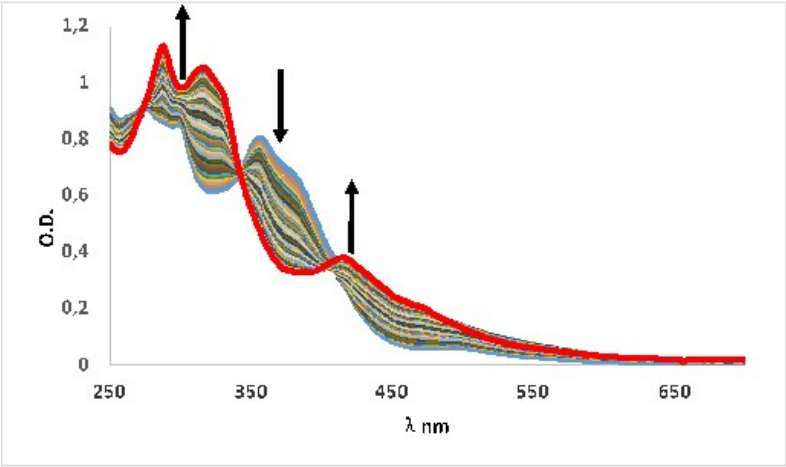


Fig. S17 : Evolution of the electronic spectrum of $[\mathbf{2t}]^+(PF_6)$ during irradiation at 365 nm.

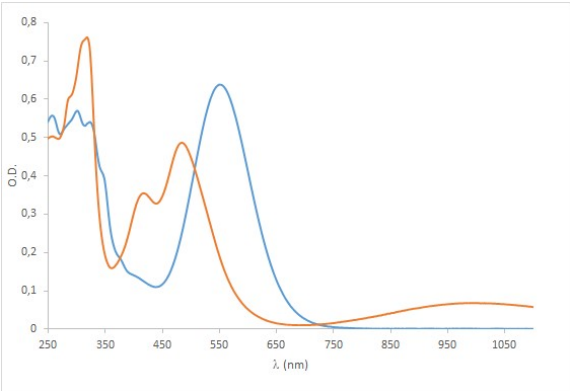


Fig. S18 : Absorption spectra of $[\mathbf{1t}]^+(PF_6)$ (blue) and of the photoproduct $[\mathbf{4}]^+(PF_6)$ (orange)

Table S1: DFT coordinates

[1c]$^+$ cis(Cl,Cl)[(NEt$_2$Phtpy)RuCl$_2$(NO)]$^+$

Ru	-3.081505	-0.008093	0.109561
Cl	-2.940018	0.163693	-2.245702
N	-1.110923	-0.007365	0.093639
C	-0.473600	-1.185342	-0.026583
C	-1.386751	-2.339056	-0.158755
N	-2.716091	2.042106	0.163314
N	-2.716436	-2.043851	-0.140404
C	-3.260390	-4.337598	-0.450410
H	-4.027361	-5.094892	-0.564715
C	-0.473924	1.176002	0.135776
C	0.908256	1.202984	0.115018
H	1.428850	2.149493	0.189844
C	-3.258729	4.356650	0.209394
H	-4.025571	5.122636	0.216326
C	-1.386201	2.336486	0.183765
C	1.640924	-0.002186	0.030147
C	-0.962380	-3.651469	-0.318135
H	0.095331	-3.886497	-0.332463
C	0.908544	-1.207837	-0.057578
H	1.429018	-2.148449	-0.187450
C	-3.627427	-3.007688	-0.284378
H	-4.662870	-2.685135	-0.265249
C	-3.626568	3.017150	0.172719
H	-4.662547	2.696567	0.148682
C	-0.961058	3.657643	0.222439
H	0.096856	3.891482	0.238110
C	-1.907734	4.677896	0.236702
H	-1.586370	5.713747	0.266935
C	-1.909662	-4.660740	-0.464591
H	-1.588749	-5.689463	-0.590694
Cl	-5.514668	0.013052	-0.098452
N	-3.344994	-0.137268	1.833572
O	-3.644831	-0.221404	2.926870
C	3.835789	-1.130809	0.423508
H	3.323216	-2.016487	0.788298
C	5.214021	-1.137059	0.433514
H	5.720466	-2.023275	0.796796
C	5.959866	-0.002200	0.018060
C	5.212950	1.131829	-0.397988
H	5.718607	2.017619	-0.763381
C	3.834872	1.125956	-0.384617
H	3.322493	2.011922	-0.748703
C	3.095335	-0.002128	0.021156
N	7.319446	-0.001034	0.018929
C	8.378597	-1.379749	1.803212
C	8.091971	-1.199160	0.316971
H	8.987268	-2.275806	1.964381
H	7.452791	-1.485765	2.378099

H	8.927851	-0.519542	2.200994
H	7.576799	-2.073891	-0.091624
H	9.033642	-1.120727	-0.236845
C	8.381889	1.378437	-1.762647
C	8.090466	1.198569	-0.277251
H	8.987706	2.276607	-1.922941
H	7.457718	1.480126	-2.340962
H	8.935830	0.519701	-2.157210
H	7.571907	2.072535	0.128712
H	9.030295	1.122537	0.279990

[1t]$^{+}$ trans(Cl,Cl)[(NEt$_2$Phtpy)RuCl$_2$(NO)]$^{+}$

C	3.029030	0.036504	3.646367
H	2.740577	0.034558	4.690127
C	4.366331	0.049826	3.274057
H	5.131963	0.059045	4.041174
C	4.685664	0.049947	1.922671
H	5.720313	0.059378	1.596719
C	3.659129	0.036974	0.985394
H	3.884381	0.035107	-0.074365
C	2.339172	0.025282	1.417842
C	1.177070	0.009167	0.516221
C	1.204948	0.013409	-0.864921
H	2.155480	0.057927	-1.380947
C	0.000000	0.000000	-1.601941
C	-1.204948	-0.013409	-0.864921
H	-2.155480	-0.057927	-1.380947
C	-1.177070	-0.009167	0.516221
C	-2.339172	-0.025282	1.417842
C	-3.659129	-0.036974	0.985394
H	-3.884381	-0.035107	-0.074365
C	-4.685664	-0.049947	1.922671
H	-5.720313	-0.059378	1.596719
C	-4.366331	-0.049826	3.274057
H	-5.131963	-0.059045	4.041174
C	-3.029030	-0.036504	3.646367
H	-2.740577	-0.034558	4.690127
N	2.041898	0.024867	2.744519
N	0.000000	0.000000	1.167696
N	-2.041898	-0.024867	2.744519
Cl	0.030934	-2.400829	3.020798
Ru	0.000000	0.000000	3.161429
C	-1.115097	0.439270	-3.796293
H	-1.995454	0.818116	-3.285327
C	-1.122133	0.448017	-5.173933
H	-2.013064	0.800223	-5.679638
C	0.000000	0.000000	-5.921029
C	1.122133	-0.448017	-5.173933
H	2.013064	-0.800223	-5.679638
C	1.115097	-0.439270	-3.796293
H	1.995454	-0.818116	-3.285327

C	0.000000	0.000000	-3.055126
N	0.000000	0.000000	-7.280079
C	-2.215965	-0.464672	-8.315586
C	-1.107645	0.547908	-8.051922
H	-3.008236	-0.009828	-8.919537
H	-2.658993	-0.821472	-7.380137
H	-1.828019	-1.332361	-8.859939
H	-1.500701	1.435640	-7.546759
H	-0.692903	0.903167	-9.001011
C	2.215965	0.464672	-8.315586
C	1.107645	-0.547908	-8.051922
H	3.008236	0.009828	-8.919537
H	2.658993	0.821472	-7.380137
H	1.828019	1.332361	-8.859939
H	1.500701	-1.435640	-7.546759
H	0.692903	-0.903167	-9.001011
Cl	-0.030934	2.400829	3.020798
N	0.000000	0.000000	4.920963
O	0.000000	0.000000	6.056970

[2t]$^{+}$ trans(Cl,Cl)[((Et)(ON)NPhtpy)RuCl$_2$(NO)]$^{+}$

C	3.519900	3.083632	0.167294
H	4.572209	2.829008	0.156955
C	3.105101	4.407386	0.235990
H	3.848159	5.195175	0.280502
C	1.745066	4.684749	0.245740
H	1.387044	5.707285	0.299147
C	0.839895	3.630667	0.185454
H	-0.226440	3.822547	0.191861
C	1.314935	2.327638	0.117663
C	0.448301	1.141433	0.049286
C	-0.937518	1.127398	0.043906
H	-1.491241	2.055415	0.114375
C	-1.621417	-0.097579	-0.016904
C	-0.865549	-1.280059	-0.068758
H	-1.363173	-2.239101	-0.144876
C	0.518857	-1.211775	-0.057991
C	1.456197	-2.343618	-0.114702
C	1.062330	-3.673486	-0.177750
H	0.009903	-3.930569	-0.186610
C	2.030290	-4.670656	-0.229824
H	1.735364	-5.713345	-0.279787
C	3.370785	-4.311100	-0.216276
H	4.160490	-5.052430	-0.254842
C	3.703653	-2.964196	-0.150040
H	4.738204	-2.645088	-0.134819
N	2.650008	2.070675	0.110657
N	1.126211	-0.016039	-0.001474
N	2.773187	-2.006095	-0.100734
Cl	2.976584	0.168293	-2.387708
Ru	3.127688	0.044776	0.006227

C	-3.784478	-1.206734	0.568299
H	-3.239663	-2.004489	1.064351
C	-5.166841	-1.256703	0.562307
H	-5.682457	-2.088037	1.026056
C	-5.903576	-0.228467	-0.044286
C	-5.224470	0.839018	-0.641429
H	-5.765449	1.650068	-1.114634
C	-3.837833	0.878708	-0.627133
H	-3.339312	1.707496	-1.120693
C	-3.090470	-0.140478	-0.025002
N	-7.310355	-0.270255	-0.058813
N	-7.886572	-1.097776	0.817083
O	-9.106052	-1.104503	0.794164
C	-8.597186	1.842831	-0.303841
C	-8.132270	0.545573	-0.950635
H	-9.225380	2.396673	-1.008260
H	-7.753758	2.480588	-0.021709
H	-9.187756	1.633084	0.592099
H	-7.554883	0.723469	-1.859760
H	-8.991815	-0.076003	-1.213310
Cl	2.967664	-0.088159	2.398673
N	4.885492	0.091096	0.009323
O	6.019987	0.113190	0.007467

[4]$^{+}$ trans(Cl,Cl)[(NEt$_2$Phtpy)RuCl$_2$(MeCN)]$^{+}$

C	3.440821	3.031503	0.052997
H	4.479467	2.721435	0.053736
C	3.076624	4.371144	0.071004
H	3.844915	5.135713	0.086464
C	1.725156	4.696527	0.067735
H	1.405445	5.733295	0.080551
C	0.780358	3.676905	0.047204
H	-0.277967	3.909947	0.043002
C	1.206129	2.353799	0.031072
C	0.296818	1.195731	0.007903
C	-1.087932	1.219621	0.013229
H	-1.610201	2.167006	0.063288
C	-1.815277	0.012339	-0.006296
C	-1.077809	-1.192970	-0.027054
H	-1.597410	-2.141776	-0.075933
C	0.304533	-1.165174	-0.022627
C	1.211355	-2.333929	-0.044061
C	0.770601	-3.650838	-0.066456
H	-0.289608	-3.874665	-0.069590
C	1.705008	-4.682335	-0.084345
H	1.371840	-5.714829	-0.102304
C	3.059646	-4.374924	-0.078485
H	3.818502	-5.148841	-0.091450
C	3.438064	-3.038456	-0.054623
H	4.479668	-2.738985	-0.048013
N	2.534308	2.050262	0.033564

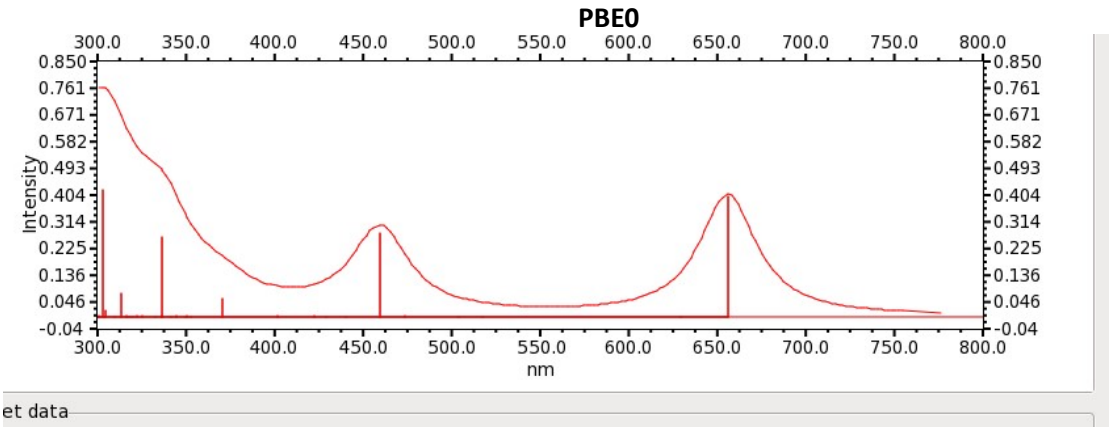
N	0.945728	0.018236	-0.007159
N	2.543099	-2.048870	-0.038098
Cl	2.938723	0.082275	-2.360138
Ru	2.898415	0.015767	0.000366
C	-4.006203	-1.099025	0.470819
H	-3.488843	-1.963994	0.876233
C	-5.385143	-1.112509	0.482456
H	-5.885681	-1.994582	0.863519
C	-6.138064	-0.009628	0.000959
C	-5.397751	1.100144	-0.484665
H	-5.908311	1.977187	-0.864103
C	-4.018745	1.099721	-0.479273
H	-3.510833	1.969335	-0.886724
C	-3.272619	0.003985	-0.005585
N	-7.499209	-0.016063	0.004393
C	-8.527377	-2.253207	-0.369437
C	-8.263339	-1.104641	0.597455
H	-9.125795	-3.029844	0.118647
H	-7.591782	-2.705880	-0.713564
H	-9.077481	-1.901621	-1.248969
H	-7.752364	-1.461046	1.497414
H	-9.212937	-0.681183	0.941312
C	-8.546141	2.211122	0.385220
C	-8.276786	1.065578	-0.583797
H	-9.153950	2.982704	-0.099256
H	-7.612834	2.671849	0.724842
H	-9.088557	1.854105	1.267339
H	-7.774216	1.427242	-1.486366
H	-9.224262	0.633423	-0.922667
Cl	2.914904	-0.002512	2.362096
N	4.973469	-0.043108	0.011004
C	6.128316	-0.081611	0.018834
C	7.574923	-0.132537	0.029630
H	7.980379	0.828167	-0.299879
H	7.927092	-0.344303	1.043069
H	7.921054	-0.920773	-0.644794

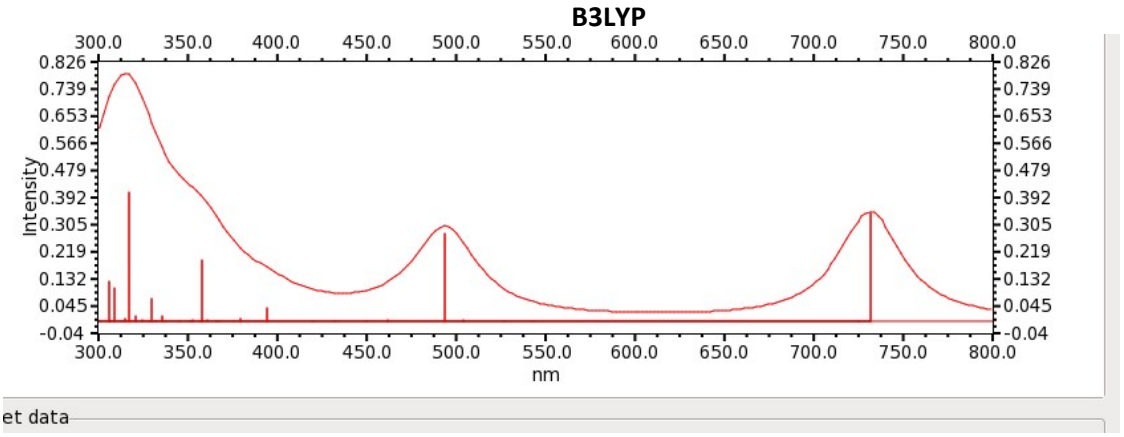
S2: Selection of the TD-DFT method for the computation of the UV-Vis spectra

It was achieved based on the capability to reproduce satisfactory the energy of the low lying transition of **1t**. PBE0 outperform the standard B3LYP, B3PW91 and CAM-B3LYP methods.

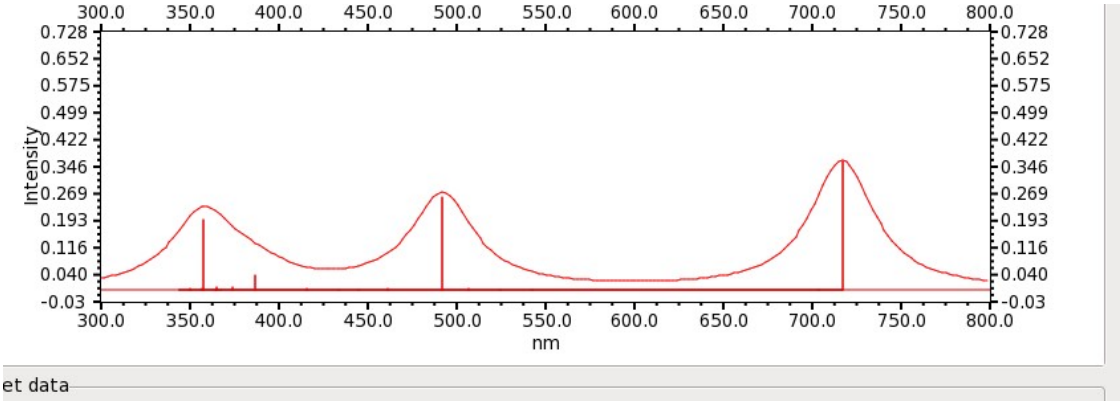
Exp. (UV-Vis) 550 nm

PBE0 656 nm (Δ vs exp. = 2940 cm^{-1})
B3LYP 732 nm (Δ vs exp. = 4520 cm^{-1})
B3PW91 717 nm (Δ vs exp. = 4230 cm^{-1})
CAM-B3LYP 451 nm (Δ vs exp. = 3390 cm^{-1})



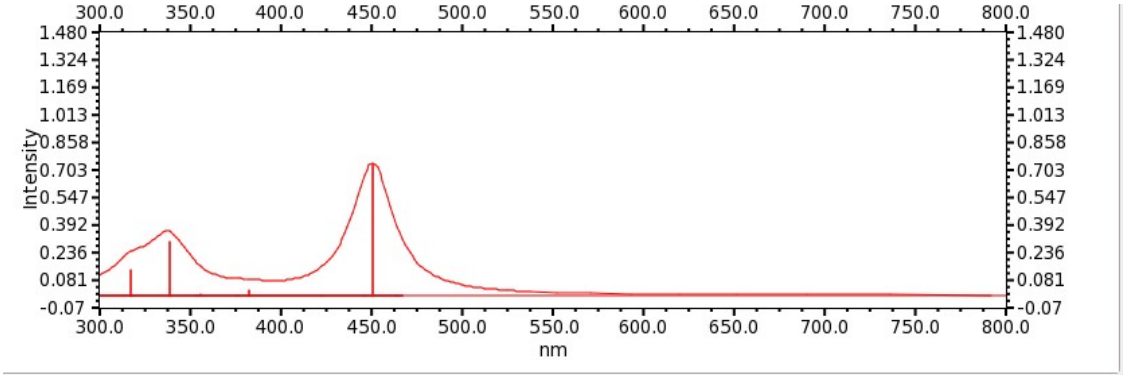


B3PW91



et data

CAM-B3LYP



et data

Table S2: Crystal data of complex **[1c]$^+$(CF_3CO_2)**

Crystals obtained after diffusion of diethyloxide in a solution of the complex in acetonitrile.

Empirical formula	C25 H24 Cl2 N5 O Ru, C2 F3 O2
Formula weight	695.48
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P b c n
Unit cell dimensions	a = 25.0164(18) A alpha = 90 deg. b = 15.6581(11) A beta = 90 deg. c = 14.4095(11) A gamma = 90 deg.
Volume	5644.3(7) A^3
Z, Calculated density	8, 1.637 Mg/m^3
Absorption coefficient	0.804 mm^-1
Max. and min. transmission	0.7454 and 0.6802
F(000)	2800
Crystal size	0.200 x 0.060 x 0.020 mm
Theta range for data collection	1.534 to 26.395 deg.
Limiting indices	-31<=h<=30, -19<=k<=19,-18<=l<=18
Reflections collected / unique	96772 / 5775 [R(int) = 0.0624]
Completeness to theta = 25.242	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5775 / 579 / 520
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0812, wR2 = 0.2006
R indices (all data)	R1 = 0.1138, wR2 = 0.2260
Largest diff. peak and hole	1.913 and -0.811 e.A^-3

Table S3: Crystal data of complex **[2t]$^{+}$(PF_6)**

Crystals obtained after diffusion of diethyloxide in a solution of the complex in acetone.

Empirical formula	C23 H19 Cl2 N6 O2 Ru, F6 P, 2(C3 H6 O)
Formula weight	844.54
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 11.7489(10) A alpha = 92.726(3) deg. b = 12.6748(11) A beta = 106.873(3) deg. c = 13.5235(12) A gamma = 117.004(3) deg.
Volume	1678.6(3) A^3
Z, Calculated density	2, 1.671 Mg/m^3
Absorption coefficient	0.752 mm^-1
F(000)	852
Crystal size	0.10 x 0.04 x 0.02 mm
Theta range for data collection	1.61 to 26.73 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -17<=l<=17
Reflections collected / unique	53504 / 7112 [R(int) = 0.0492]
Completeness to theta = 26.73	100.0 %
Max. and min. transmission	0.7459 and 0.7060
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7112 / 0 / 447
Goodness-of-fit on F^2	1.042
Final R indices [I>2sigma(I)]	R1 = 0.0315, wR2 = 0.0714
R indices (all data)	R1 = 0.0402, wR2 = 0.0761
Largest diff. peak and hole	1.073 and -0.539 e.A^-3

Table S4: Crystal data of complex **[3]$^{+}$(PF_6)**

Crystals obtained after diffusion of diethyloxide in a solution of the complex in acetonitrile.

Empirical formula	C25 H23 Cl2 N6 O3 Ru, F6 P
Formula weight	772.43
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 11.546(4) A alpha = 97.082(12) deg. b = 12.407(4) A beta = 100.947(13) deg. c = 13.352(4) A gamma = 116.663(13) deg.
Volume	1630.1(10) A^3
Z, Calculated density	2, 1.574 Mg/m^3
Absorption coefficient	0.765 mm^-1
Max. and min. transmission	0.7465 and 0.7040
F(000)	772
Crystal size	0.14 x 0.12 x 0.04 mm
Theta range for data collection	1.60 to 31.51 deg.
Limiting indices	-16<=h<=16, -18<=k<=18, 0<=l<=19
Reflections collected / unique	10868 / 10868 [R(int) = 0.0000]
Completeness to theta = 31.51	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10868 / 162 / 443
Goodness-of-fit on F^2	1.076
Final R indices [I>2sigma(I)]	R1 = 0.0454, wR2 = 0.1353
R indices (all data)	R1 = 0.0552, wR2 = 0.1437
Largest diff. peak and hole	1.140 and -1.536 e.A^-3

Table S5 : Crystal data of complex **[4]$^{+}$(PF_6)**

Crystals obtained after diffusion of diethyloxide in a solution of the complex in acetonitrile.

Empirical formula	C27 H27 Cl2 N5 Ru, F6 P
Formula weight	738.48
Temperature	298(2) K
Wavelength	0.71073 A
Crystal system, space group	monoclinic, C 2/c
Unit cell dimensions	a = 8.5133(9) A alpha = 90 deg. b = 39.637(4) A beta = 106.784(3) deg. c = 10.0803(11) A gamma = 90 deg.
Volume	3256.6(6) A^3
Z, Calculated density	4, 1.506 Mg/m^3
Absorption coefficient	0.754 mm^-1
F(000)	1472
Crystal size	0.22 x 0.20 x 0.18 mm
Theta range for data collection	5.11 to 26.37 deg.
Limiting indices	-10<=h<=10, -44<=k<=49, -12<=l<=12
Reflections collected / unique	13715 / 3323 [R(int) = 0.0544]
Completeness to theta = 26.37	99.2 %
Max. and min. transmission	0.7459 and 0.6348
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3323 / 380 / 310
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0469, wR2 = 0.1066
R indices (all data)	R1 = 0.0714, wR2 = 0.1177
Largest diff. peak and hole	1.002 and -0.556 e.A^-3

Table S6: Selected bond lengths and angles of [**1c**]$^+$ (PF_6) and of the photoproduct: [**4**](PF_6)

Selected bonds (Å)	[**4**]$^+$	[**1c**]$^+$
Ru-N(1)	2.074(4)	1.836(8)
Ru-N(2)	2.072(3)	2.075(7)
Ru-N(3)	1.942(6)	1.964(6)
Ru-N(2)i	2.072(3)	2.090(7)
Ru-Cl(1)	2.3444(9)	2.319(2)
Ru-Cl(2)	2.3444(9)	2.403(2)
N(1)-O(1)		1.055(10)
N(5)-C(19)	1.359(9)	1.384(12)
Selected angles (°)		
C(1)-N(1)-Ru(1)	180.00(1)	
O(1)-N(1)-Ru(1)		163.7(9)
N(3)-Ru(1)-N(2)	80.07(8)	79.2(3)
N(2)-Ru(1)-N(1)	99.93(8)	94.8(3)
C7-C8-C9 and C17-C16-C21	10.51(45)	19.42(63)