

Supporting Information

New Ru(II) Photocages Operative with Near-IR Light: New Platform for Drug Delivery in the PDT Window

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Table S1. Crystallographic parameters for **2 – 4**.

Complex	2	3	4
CCDC Deposit Number	1841086	1841087	1841088
Empirical formula	C ₃₉ H ₃₃ N ₇ F ₁₂ P ₂ Ru	C ₄₅ H ₃₂ N ₈ OF ₁₂ P ₂ Ru	C ₃₀ H ₂₅ N ₄ O ₂ F ₃ P _{0.5} Ru
Formula weight	990.73	1091.79	647.09
Temperature (K)	150	150	150
Space group	Triclinic, P-1	Triclinic, P-1	Monoclinic, C2/m
a (Å)	11.0216(4)	11.9502(4)	18.5470(4)
b (Å)	14.4762(5)	13.3979(4)	23.5958(6)
c (Å)	14.5765(6)	13.5014(4)	17.8330(4)
α (deg)	83.804(1)	82.904(1)	90
β (deg)	85.851(1)	83.437(1)	119.975(1)
γ (deg)	69.748(1)	79.213(1)	90
Volume (Å ³)	2167.6(1)	2098.0(1)	6760.4(3)
Z	2	2	8
Density (calcd.)	1.518	1.562	1.272
Crystal size (mm)	0.31 x 0.27 x 0.12	0.19 x 0.15 x 0.08	0.31 x 0.27 x 0.08
Theta range for data collection (deg)	2.813 – 27.878	2.799-27.530	2.883-27.901
Absorption coefficient (mm ⁻¹)	0.524	0.542	0.533
F(000)	996	988	2620
Reflections collected	98530	88529	77031
Unique reflections [R(int)=0.025]	10322	9651 [R(int)=0.032]	8270 [R(int)=0.031]
R1, wR2 (I>20)	0.0298, 0.0805	0.0473, 0.1275	0.0402, 0.0456
R1, wR2 (all data)	0.0305, 0.0812	0.0500, 0.1296	0.0981, 0.1017
Goodness-of-fit on F ²	1.028	1.065	1.099
Largest diff. peak/hole (eÅ ⁻³)	1.025/-0.711	1.880/-1.302	1.266/-0.709

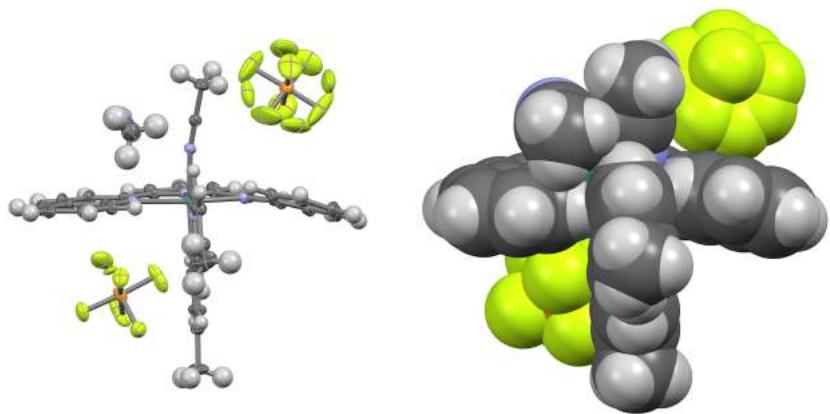


Figure S1. Thermal ellipsoid (left) and spacefill (right) drawings of complex **2** showing the steric clash of the NCCH_3 ligand with cocrystallized MeCN and PF_6^- . Disordered PF_6^- shown with all modeled partial space-occupying F atoms.

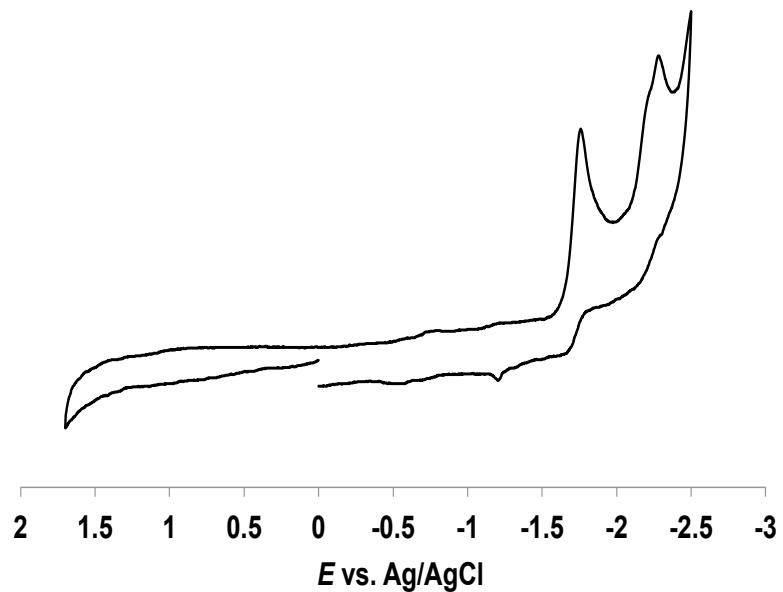


Figure S2. Cyclic voltammogram of dypy in 0.1 M TBAPF₆ in CH₃CN at 200 mV/s.

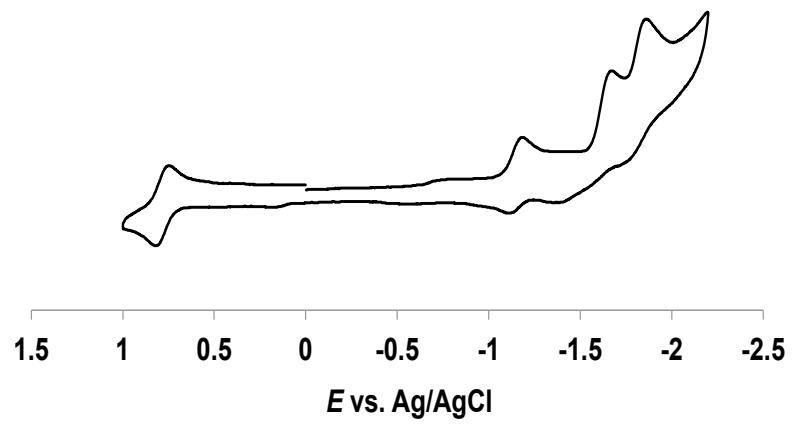


Figure S3. Cyclic voltammogram of **4** in 0.1 M TBAPF₆ in CH₃CN at 200 mV/s.

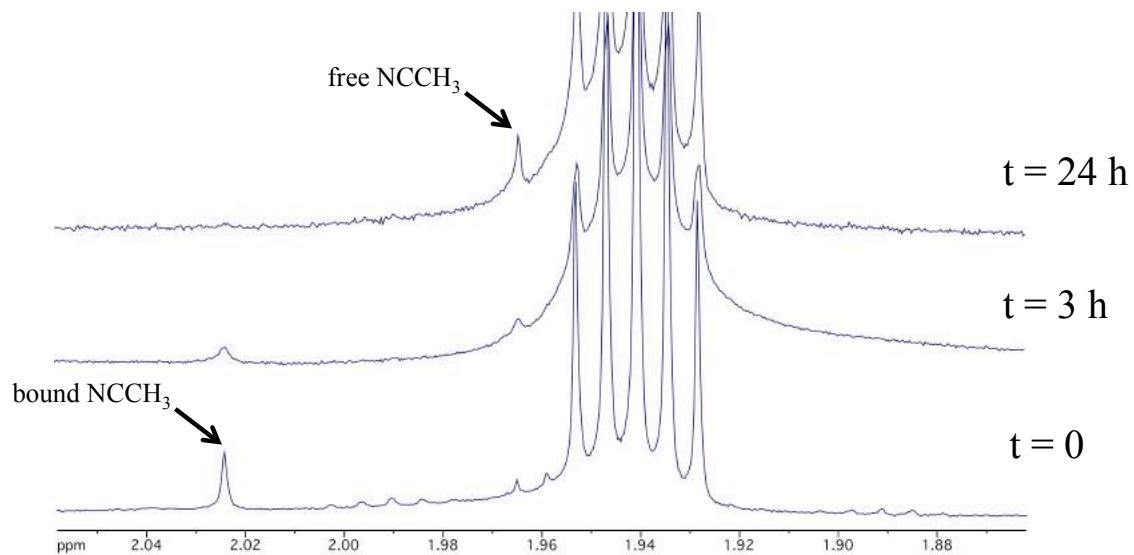
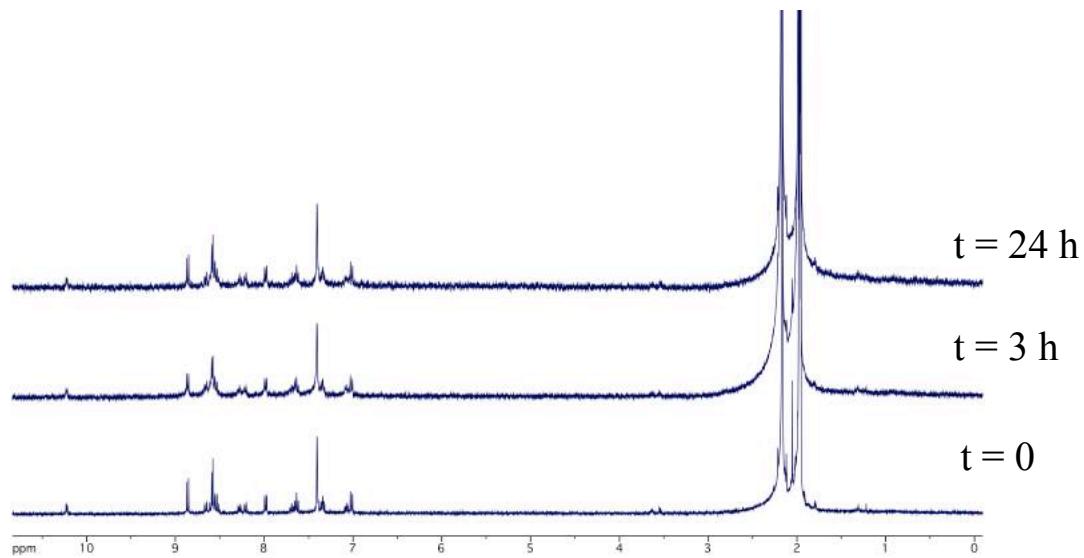


Figure S4. Photolysis of **1** in CD₃CN ($\lambda_{\text{irr}} \geq 395 \text{ nm}$): Full spectrum (top) and enhanced aliphatic region showing the appearance of free CH₃CN (bottom).

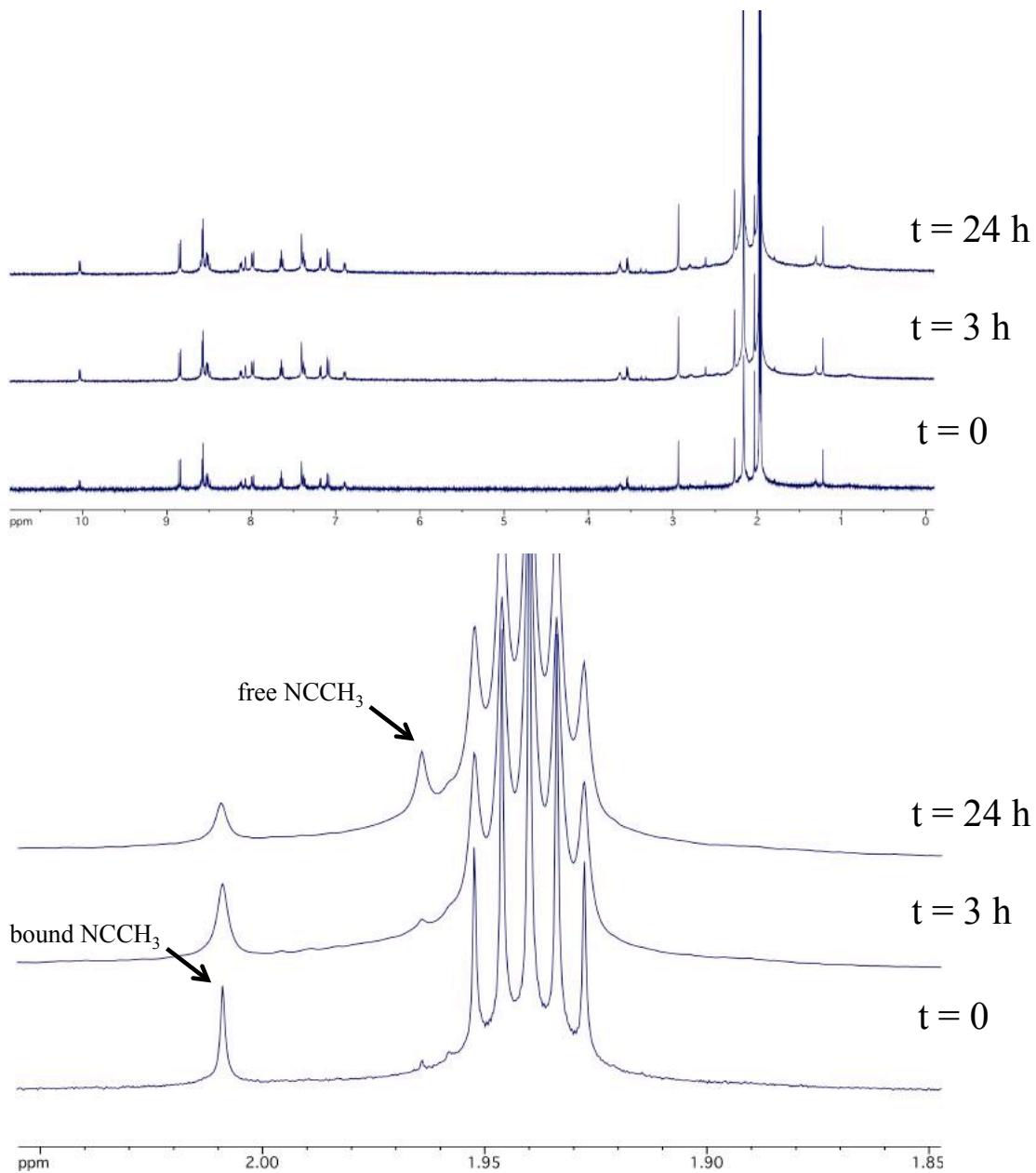


Figure S5. Photolysis of **2** in CD_3CN ($\lambda_{\text{irr}} \geq 395 \text{ nm}$): Full spectrum (top) and enhanced aliphatic region showing the appearance of free CH_3CN (bottom).

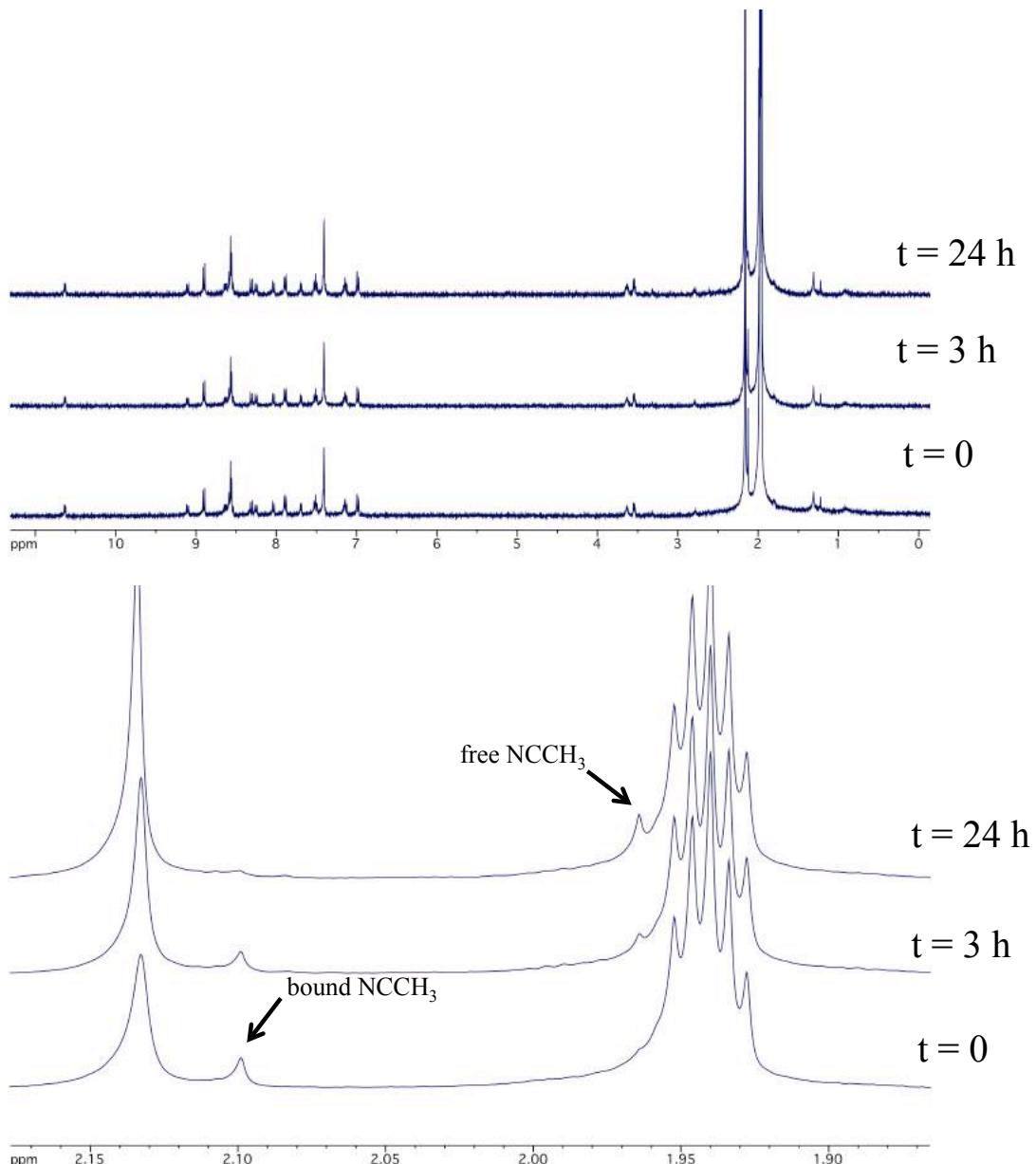


Figure S6. Photolysis of **3** in CD_3CN ($\lambda_{\text{irr}} \geq 395 \text{ nm}$): Full spectrum (top) and enhanced aliphatic region showing the appearance of free CH_3CN (bottom).

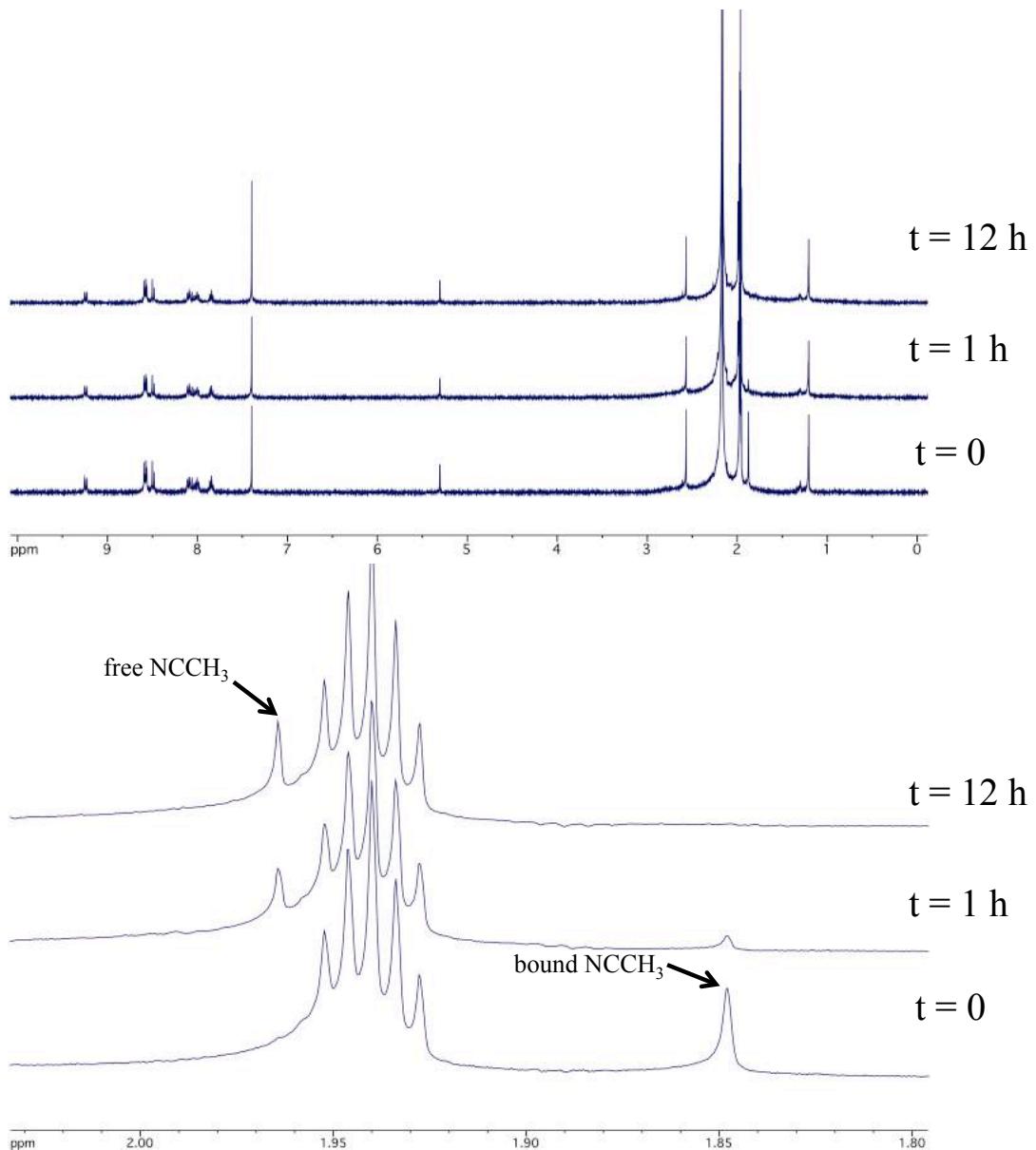


Figure S7. Photolysis of **4** in CD_3CN ($\lambda_{\text{irr}} \geq 395 \text{ nm}$): Full spectrum (top) and enhanced aliphatic region showing the appearance of free CH_3CN (bottom).

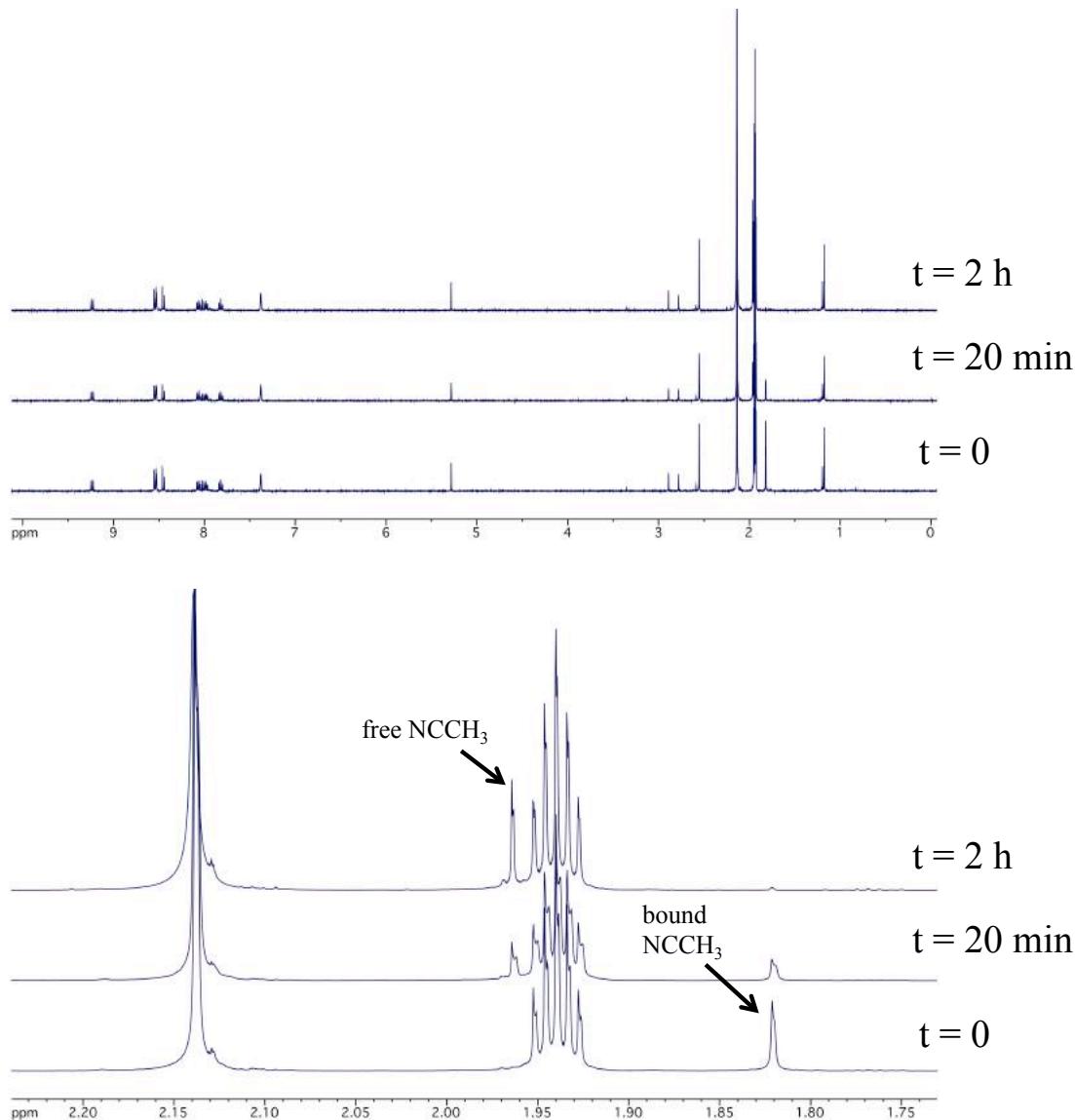


Figure S8. Photolysis of **4** in CD₃CN ($\lambda_{\text{irr}} = 735 \pm 15$ nm): Full spectrum (top) and enhanced aliphatic region showing the appearance of free CH₃CN (bottom).

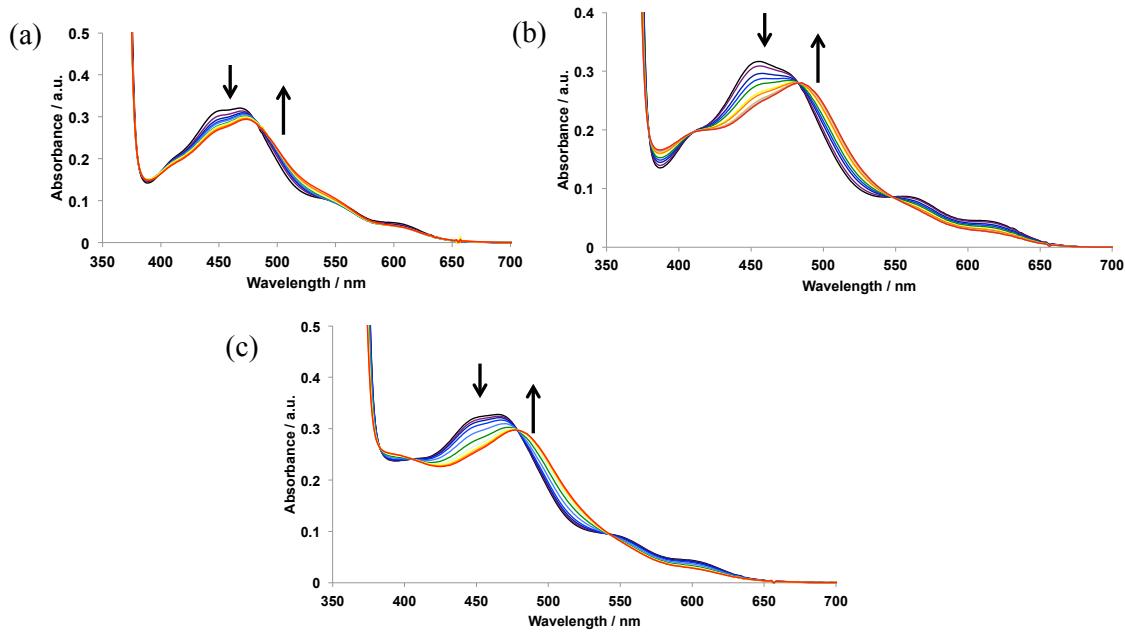


Figure S9. Changes in the electronic absorption spectra upon irradiation of **1** (a), **2** (b), and **3** (c) ($\lambda_{\text{irr}} \geq 395$ nm, $t_{\text{irr}} = 0 - 30$ min) in H_2O (5% acetone).

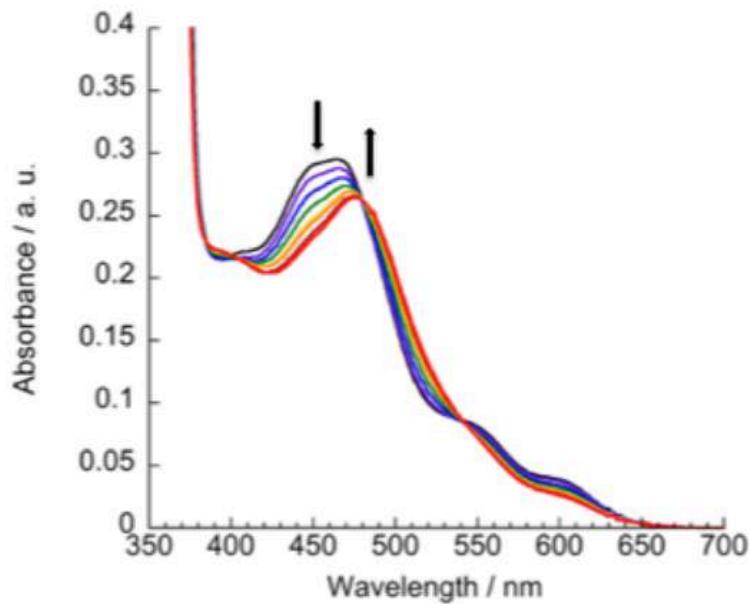


Figure S10. Changes in the electronic absorption spectra upon irradiation of **2** ($\lambda_{\text{irr}} \geq 610$ nm, $t_{\text{irr}} = 0 - 2$ h) in H_2O (5% acetone).

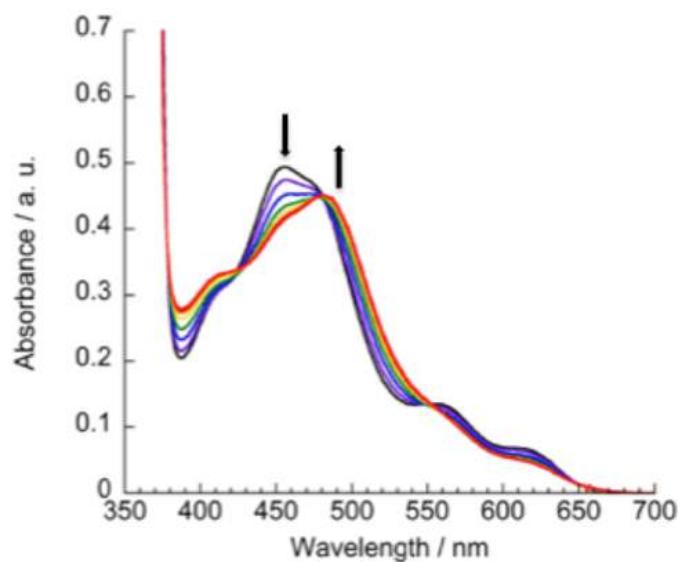


Figure S11. Changes in the electronic absorption spectra upon irradiation of **3** ($\lambda_{\text{irr}} \geq 610$ nm, $t_{\text{irr}} = 0 - 2$ h) in H_2O (5% acetone).

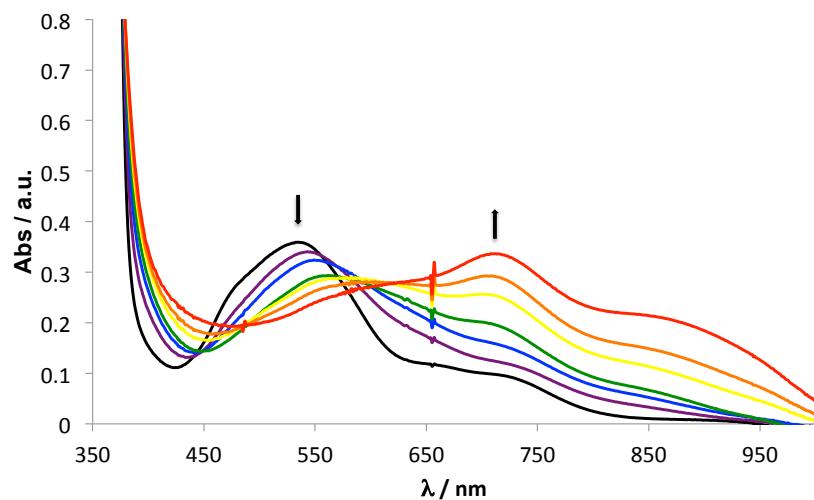


Figure S12. Photolysis of **4** in H_2O (5% acetone) ($\lambda_{\text{irr}} \geq 715$ nm) for 0 – 2 h in air.

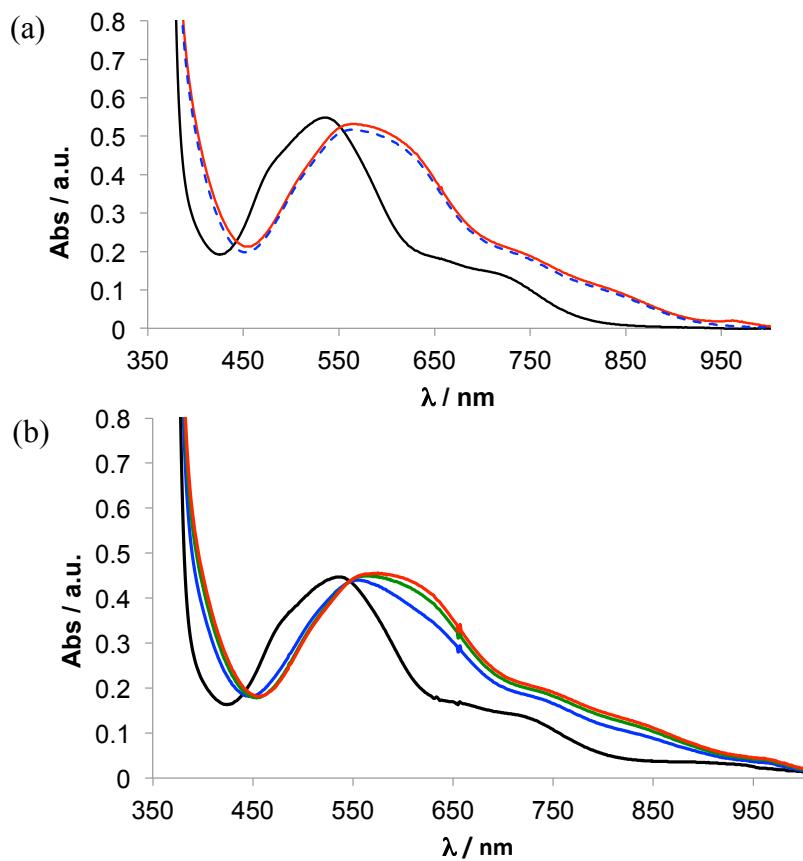


Figure S13. Photolysis of **4** ($\lambda_{\text{irr}} \geq 610$ nm): (a) in N_2 purged H_2O (5% acetone) at $t = 0$ (—) and $t = 45$ min (—) and aerated in the dark after photolysis $t = 45$ min (---) and (b) in aerated H_2O (5% acetone) with 10 equiv added ascorbic acid $t = 0$ (—), $t = 15$ min (—), $t = 30$ min (—), and $t = 45$ min (—).

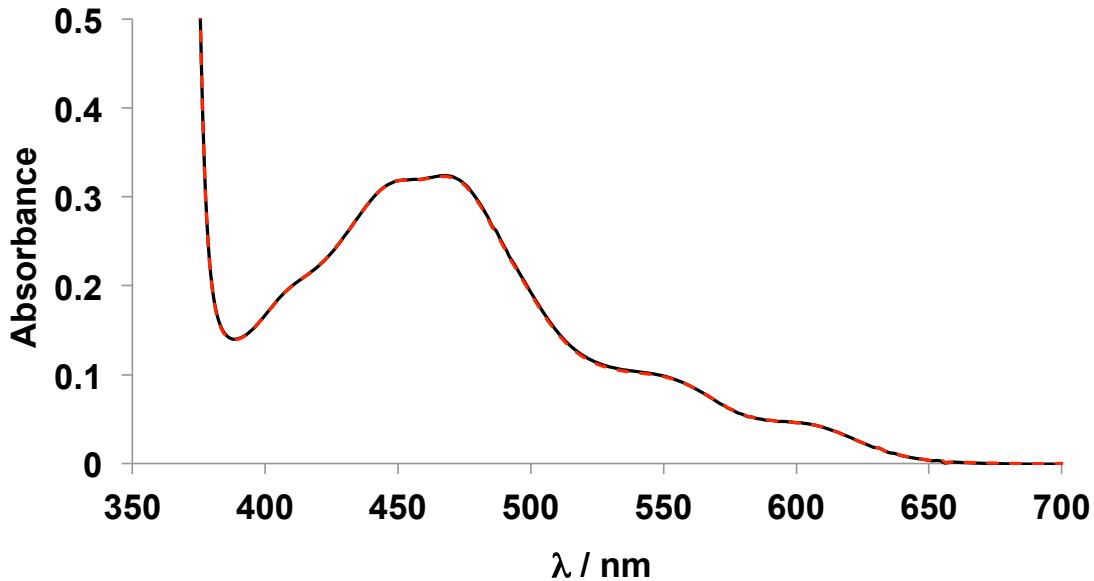


Figure S14. Absorption spectrum of **1** in H₂O (5% acetone) at $t = 0$ (—) and $t = 48 \text{ h}$ (- -) in the dark at room temperature.

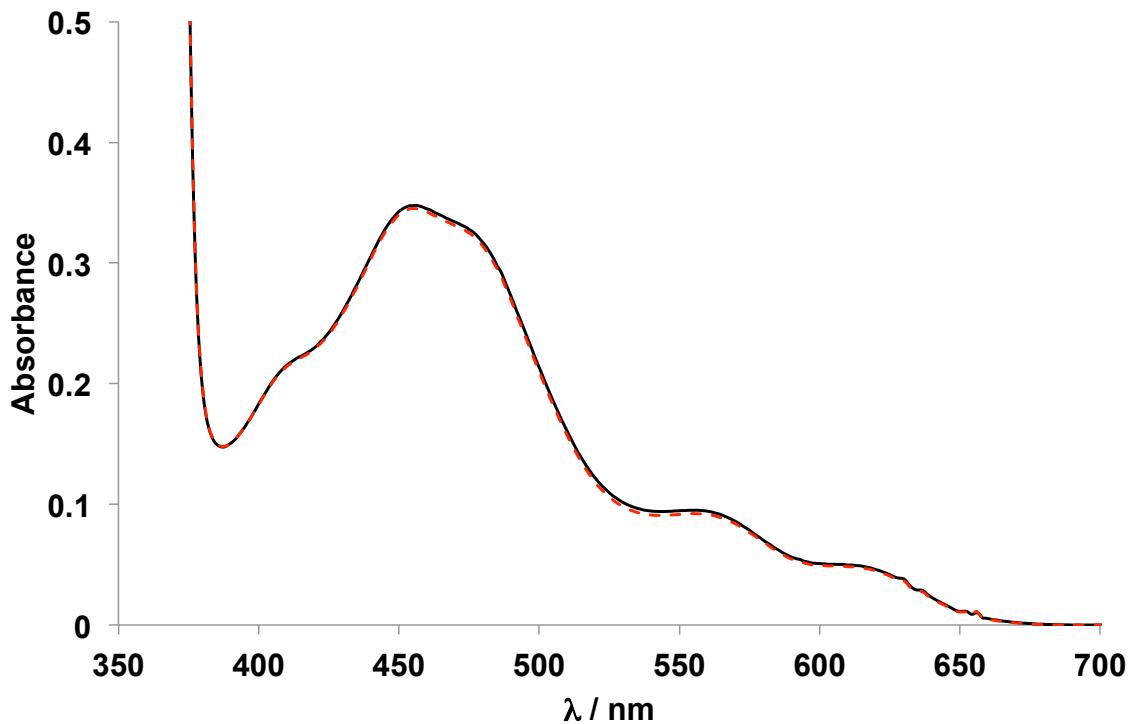


Figure S15. Absorption spectrum of **2** in H₂O (5% acetone) at $t = 0$ (—) and $t = 48 \text{ h}$ (- -) in the dark at room temperature.

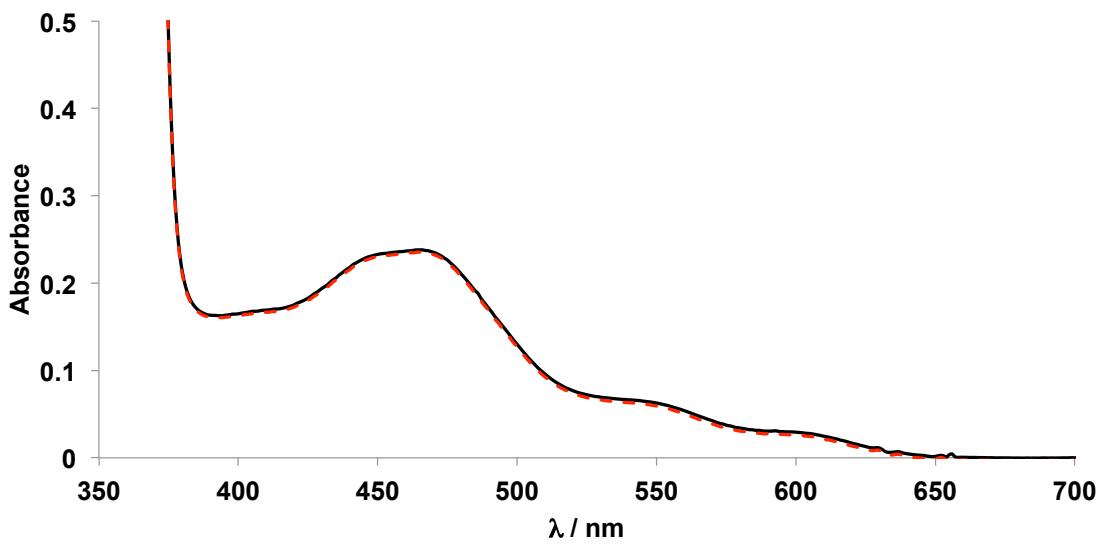


Figure S16. Absorption spectrum of **3** in H₂O (5% acetone) at t = 0 (—) and t = 48 h (- -) in the dark at room temperature.

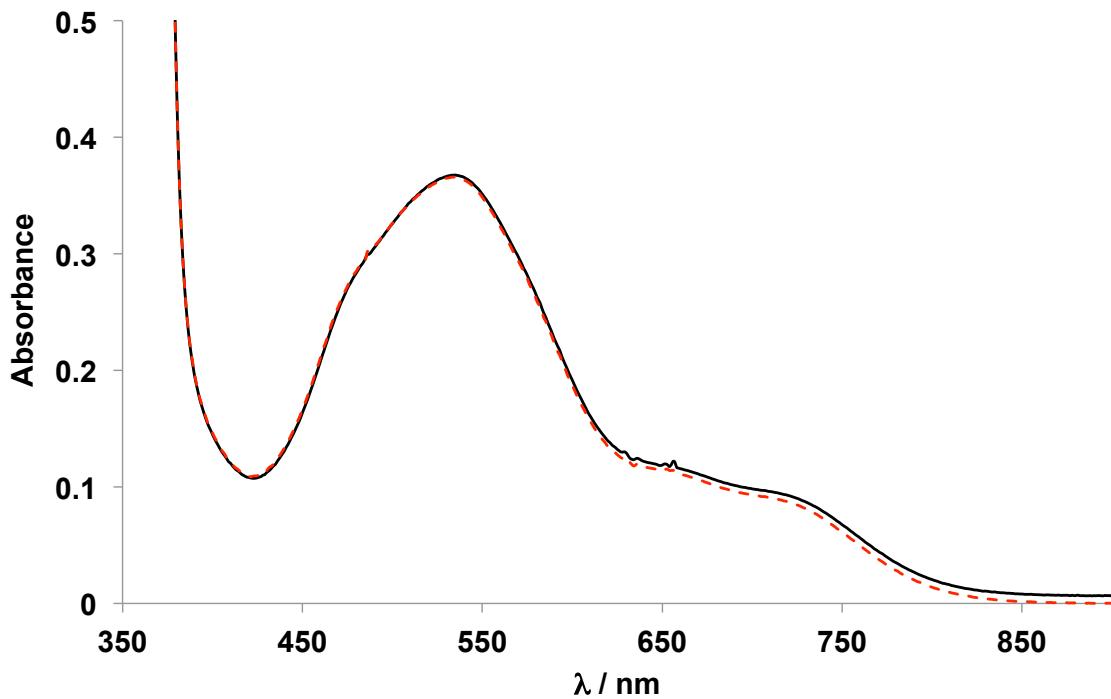


Figure S17. Absorption spectrum of **4** in H₂O (5% acetone) at t = 0 (—) and t = 48 h (- -) in the dark at room temperature.

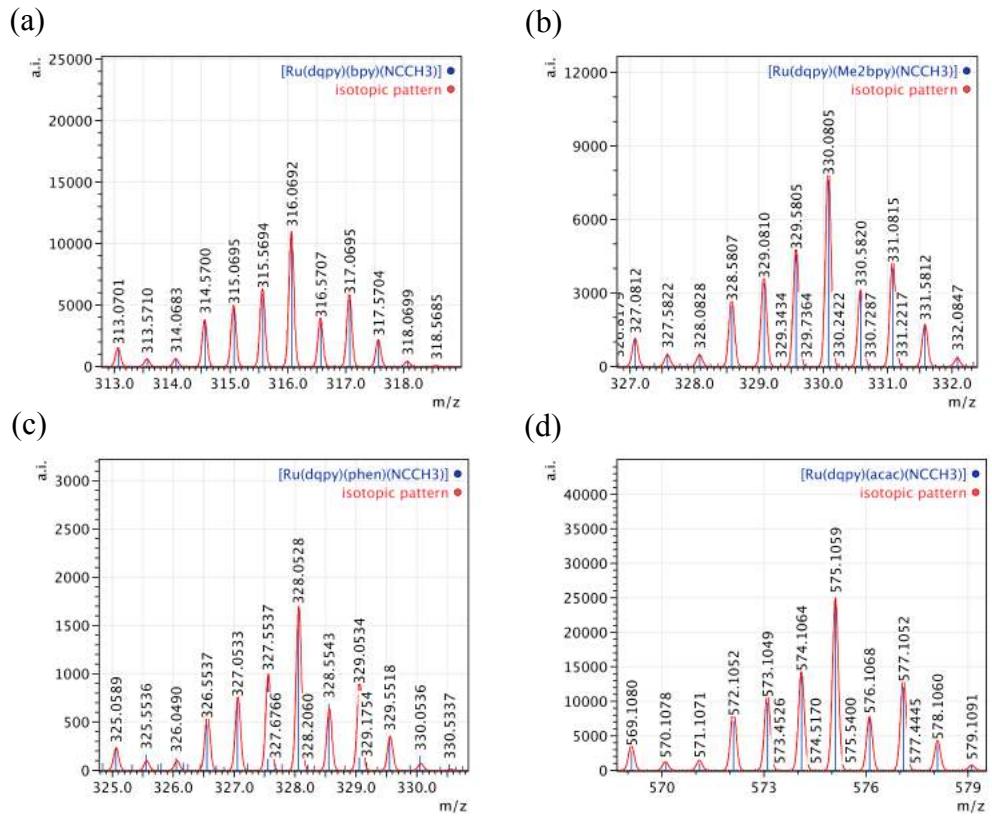


Figure S18. Calculated (—) and experimental (—) ESI mass spectra of (a) **1**, (b) **2**, (c) **3**, and (d) **4**.

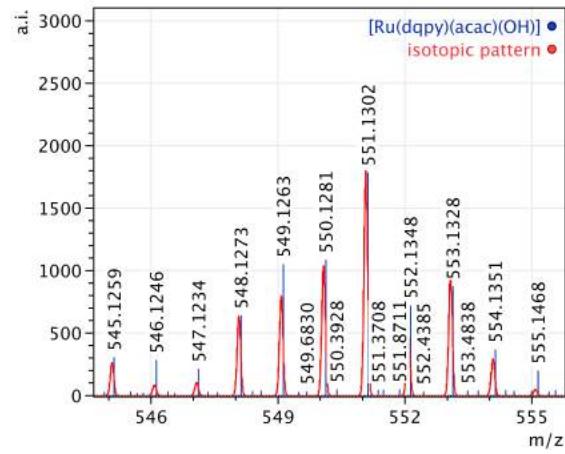


Figure S19. Calculated (—) and experimental (—) ESI mass spectrum of species generated from photolysis of **4** in aerated H₂O (5% acetone) consistent with [Ru(dqpy)(acac)(OH)]⁺.

Table S2. Calculated Bond Lengths for **1**.

Source	Ru–N / Å					
	dppy			bpy		CH ₃ CN
	N2	N3	N4	N5	N6	N1
Calcd	2.169	1.988	2.166	2.090	2.063	2.017

Table S3. Experimental and Calculated Bond Lengths for **2**.

Source	Ru–N / Å					
	dppy			(CH ₃) ₂ bpy		CH ₃ CN
	N2	N3	N4	N5	N6	N1
Experiment	2.129(2)	1.979(2)	2.174(1)	2.099(2)	2.054(1)	2.044(1)
Calcd	2.163	1.986	2.170	2.095	2.067	2.014

Table S4. Experimental and Calculated Bond Lengths for **3**.

Source	Ru–N / Å					
	dppy			phen		CH ₃ CN
	N2	N3	N4	N5	N6	N1
Experiment	2.160(2)	1.971(3)	2.146(2)	2.103(3)	2.059(2)	2.038(2)
Calcd	2.170	1.986	2.165	2.103	2.072	2.013

Table S5. Experimental and Calculated Bond Lengths for **4**.

Source	Ru–N / Å			Ru–O / Å		
	dppy			CH ₃ CN	acac	
	N2	N3	N4	N1	O1	O2
Experiment	2.096(3)	1.937(2)	2.124(2)	2.011(*)	2.090(2)	2.053(2)
Calcd	2.113	1.951	2.113	1.987	2.100	2.057

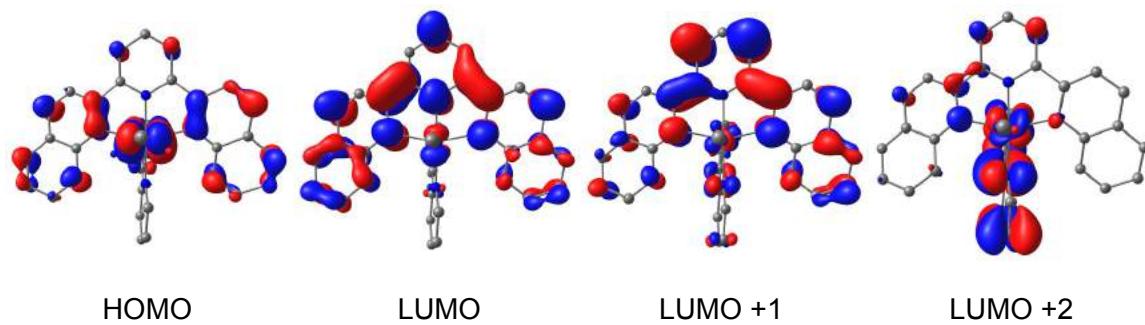


Figure S20. Calculated frontier molecular orbitals for **1**.

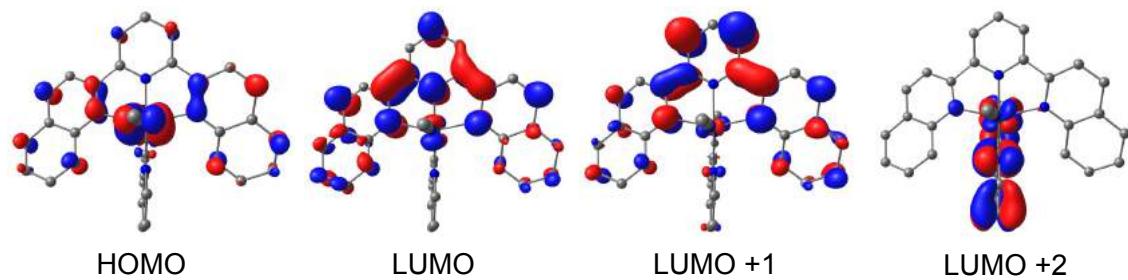


Figure S21. Calculated frontier molecular orbitals for **3**.

Table S5. Calculated Electronic Absorption Transitions and Assignments for **1 – 4**.

Complex	Exptl. λ (nm)	Calcd. λ (nm)	Assignment
1	471	448	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow bpy $\pi^*/$ dqry π^*
	550	529	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow dqry π^*
	609	560	Ru $d_{yz}/dqry \pi$ \longrightarrow dqry π^* (HOMO \longrightarrow LUMO)
2	456	446	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow Me ₂ bpy $\pi^*/$ dqry π^*
	558	544	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow dqry π^*
	608	570	Ru $d_{yz}/dqry \pi$ \longrightarrow dqry π^* (HOMO \longrightarrow LUMO)
3	469	458	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow phen $\pi^*/$ dqry π^*
	534	532	Ru $d_{yz}/d_{xz}/d_{xy}$ \longrightarrow dqry π^*
	600	557	Ru $d_{yz}/dqry \pi$ \longrightarrow dqry π^* (HOMO \longrightarrow LUMO)
4	540	517	Ru d_{xy} \longrightarrow dqry π^*
	703	598	Ru d_{yz}/d_{xy} \longrightarrow dqry π^*
	770	730	Ru $d_{yz}/acac \pi$ \longrightarrow dqry π^* (HOMO \longrightarrow LUMO)

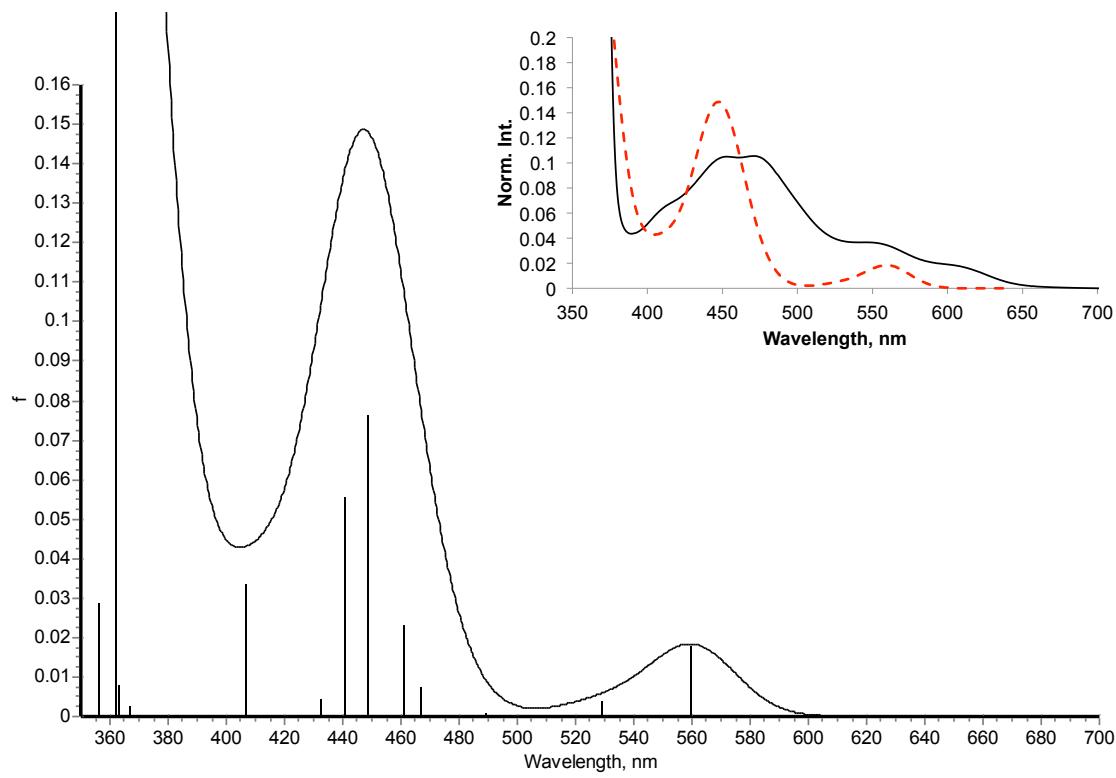


Figure S22. Calculated absorption spectrum of **1**. Inset: overlay of experimental (—) and calculated (---) absorption spectra of **1**.

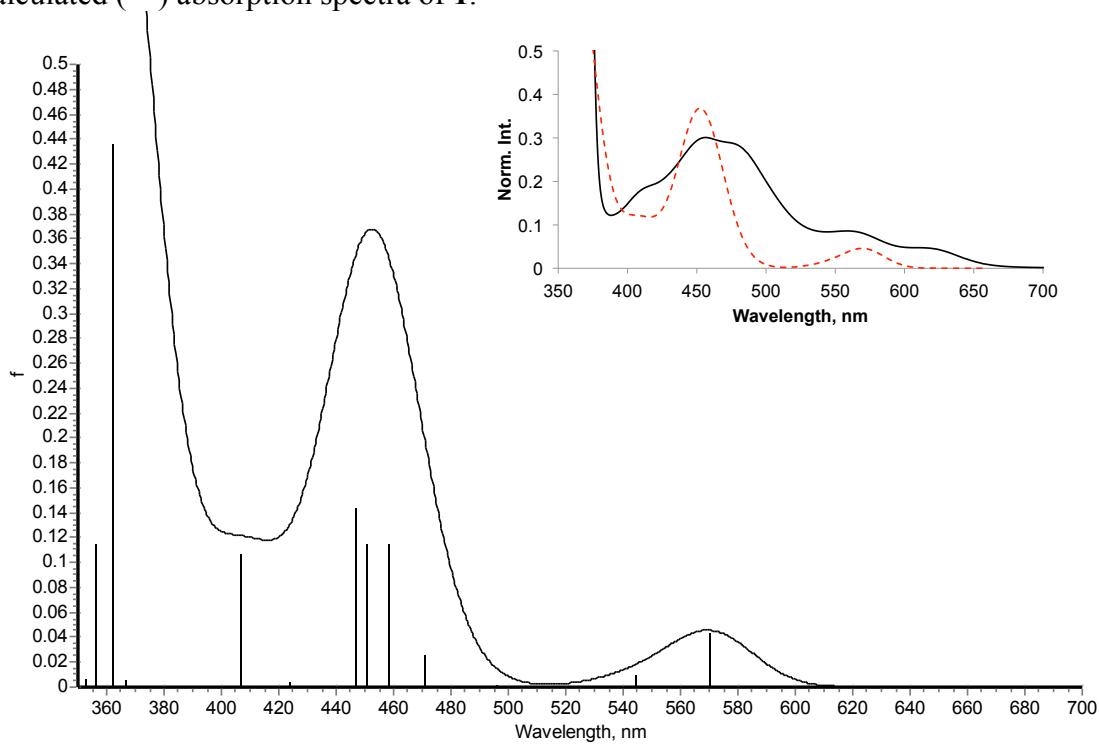


Figure S23. Calculated absorption spectrum of **2**. Inset: overlay of experimental (—) and calculated (---) absorption spectra of **2**.

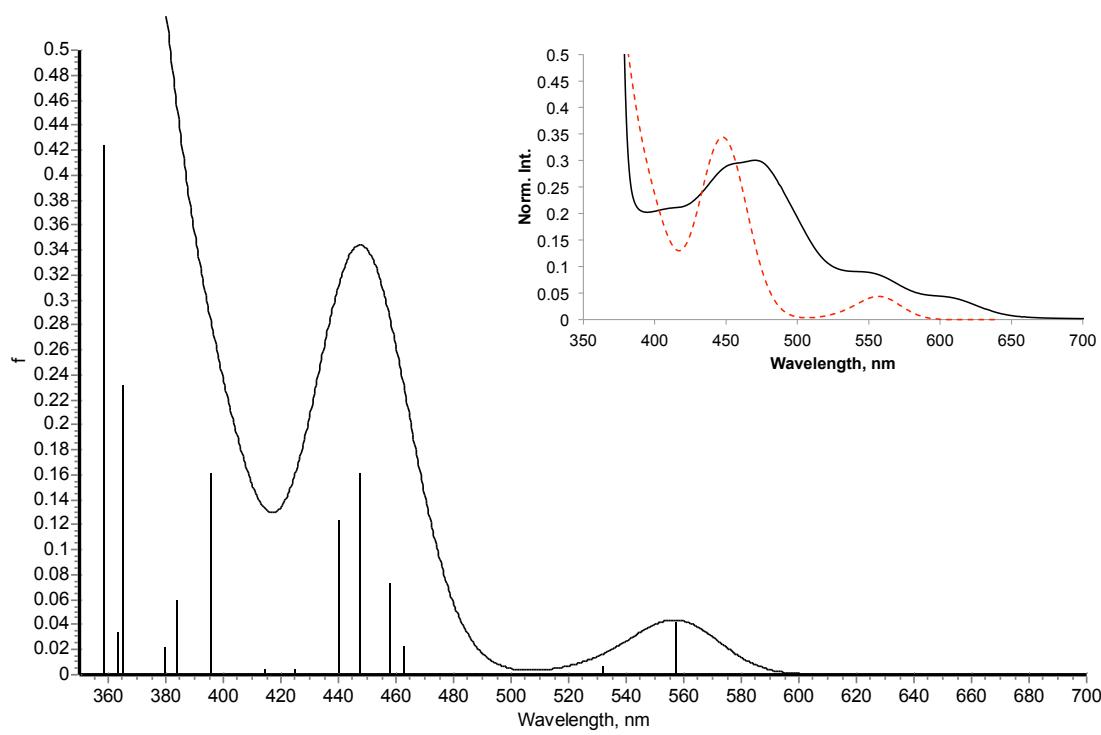


Figure S24. Calculated absorption spectrum of **3**. Inset: overlay of experimental (—) and calculated (---) absorption spectra of **3**.

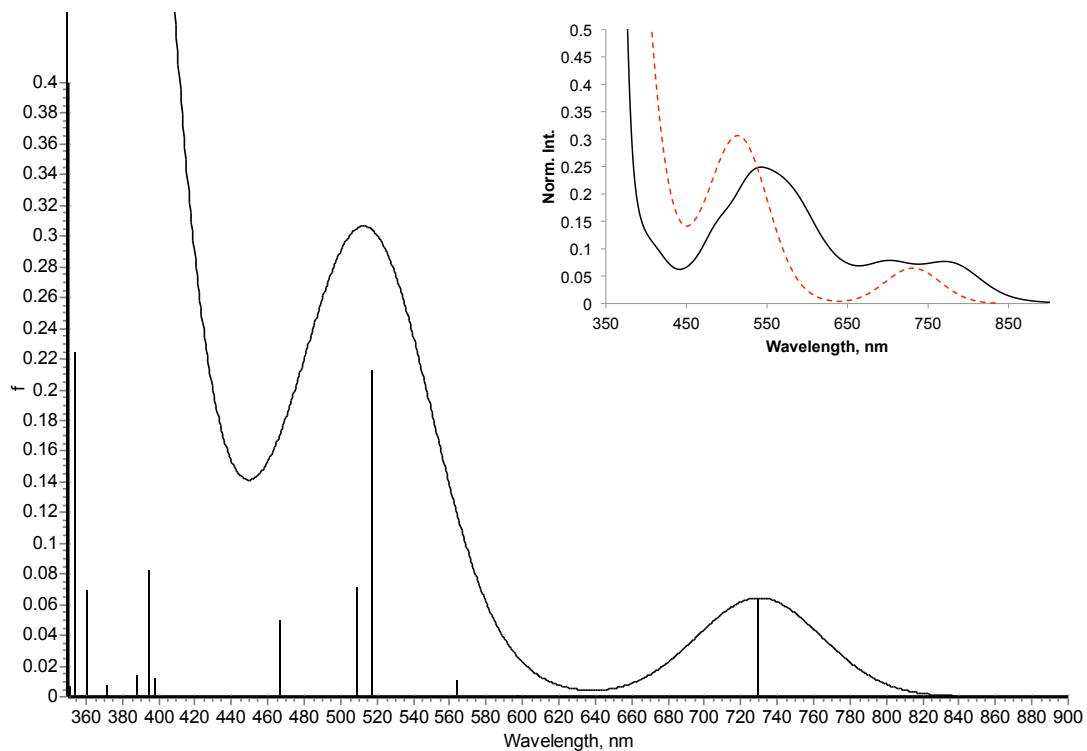


Figure S25. Calculated absorption spectrum of **4**. Inset: overlay of experimental (—) and calculated (---) absorption spectra of **4**.

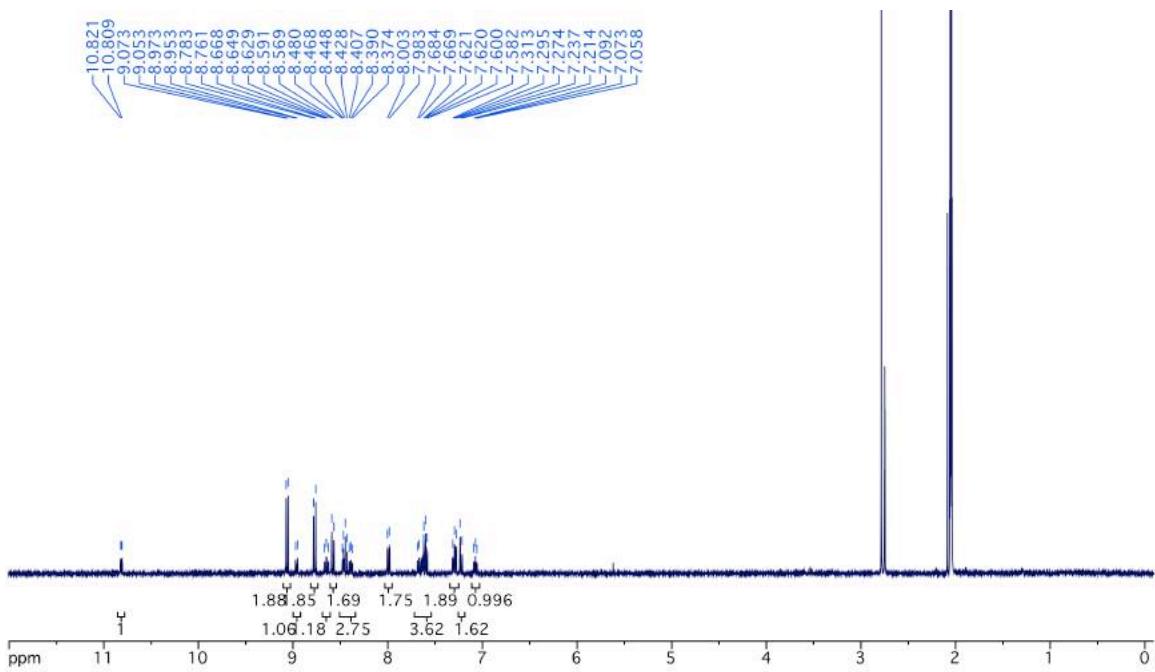
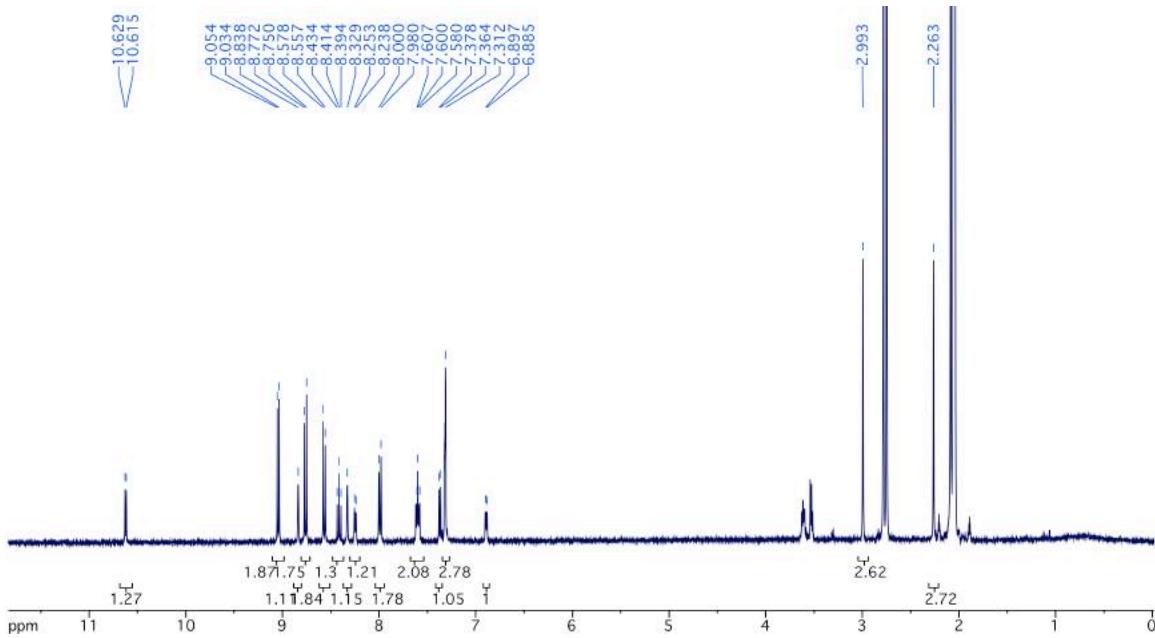


Figure S25. 400 MHz ^1H NMR spectrum of **1-Cl** in acetone- d_6 .



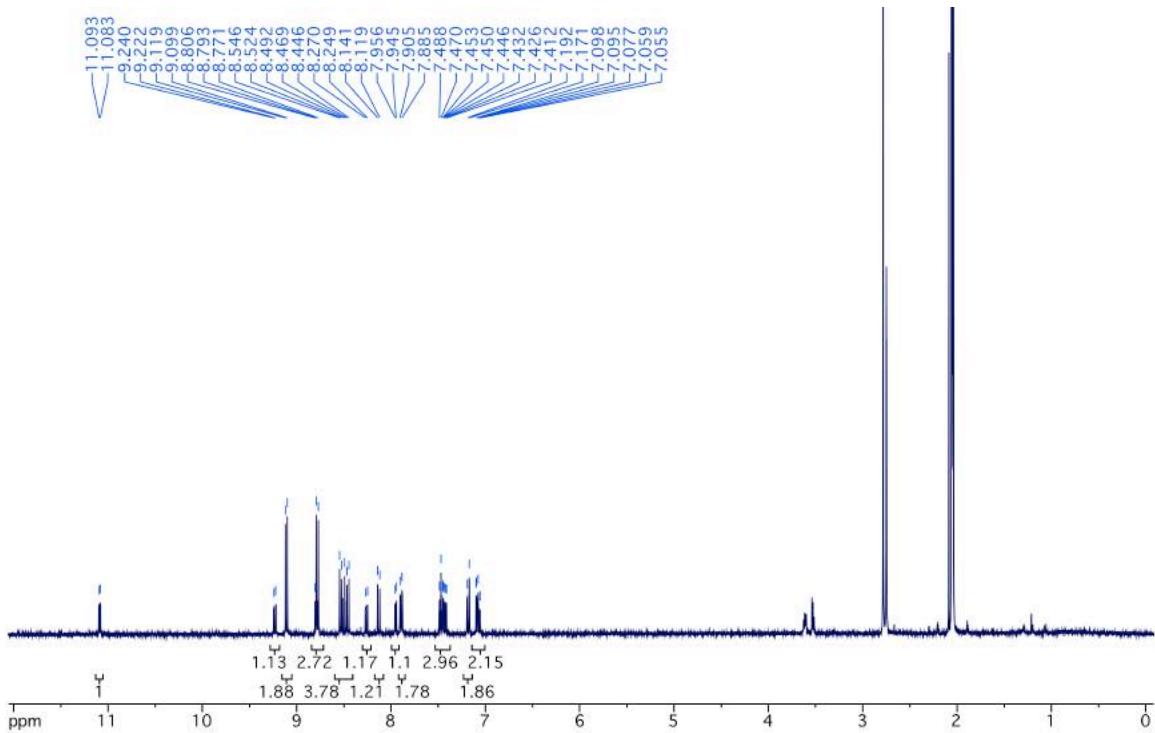


Figure S27. 400 MHz ^1H NMR spectrum of **3-Cl** in acetone- d_6 .

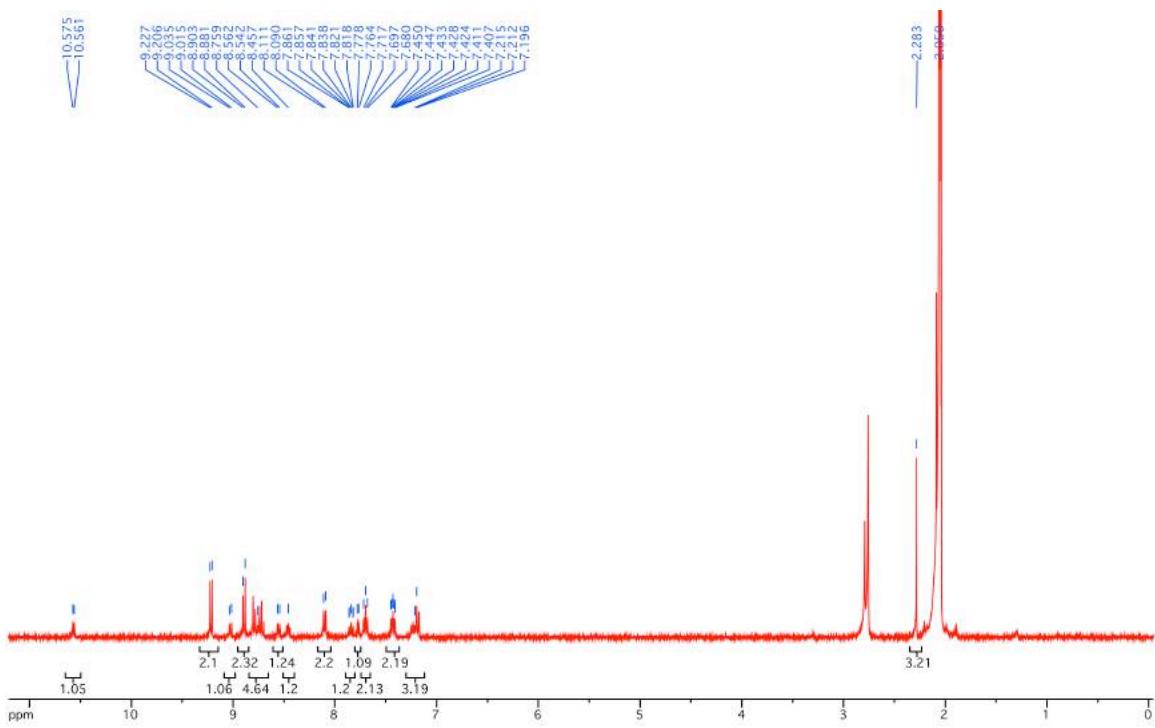


Figure S28. 400 MHz ¹H NMR spectrum of **1** in acetone-*d*₆.

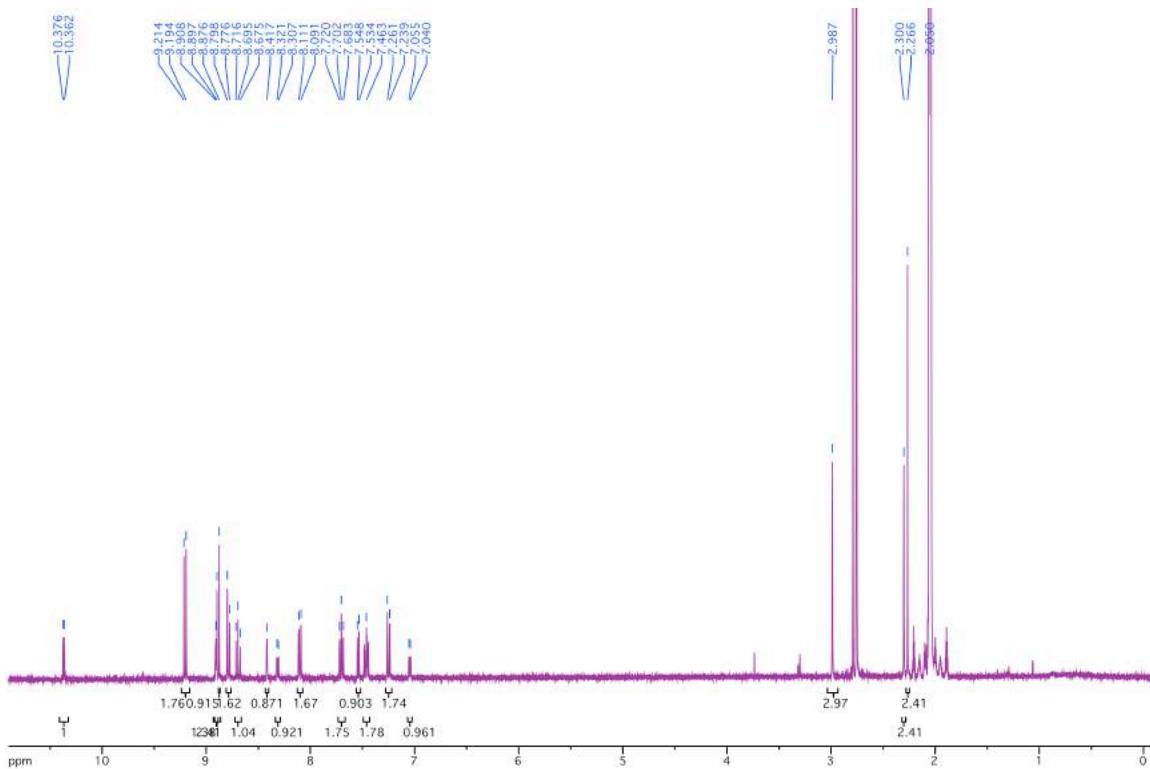


Figure S29. 400 MHz ^1H NMR spectrum of **2** in acetone- d_6 .

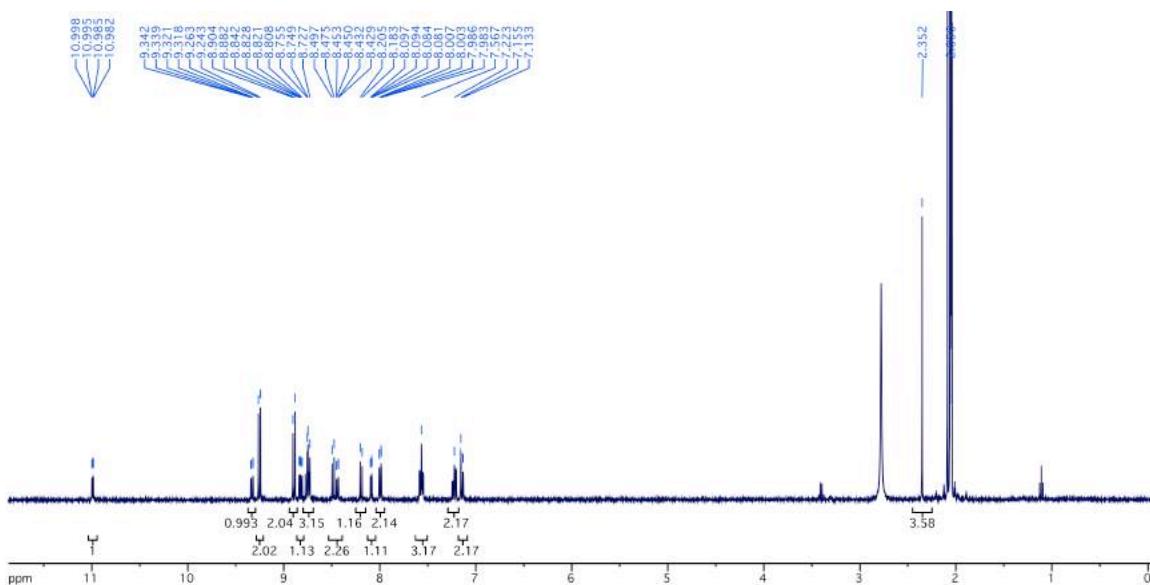


Figure S30. 400 MHz ^1H NMR spectrum of **3** in acetone- d_6 .

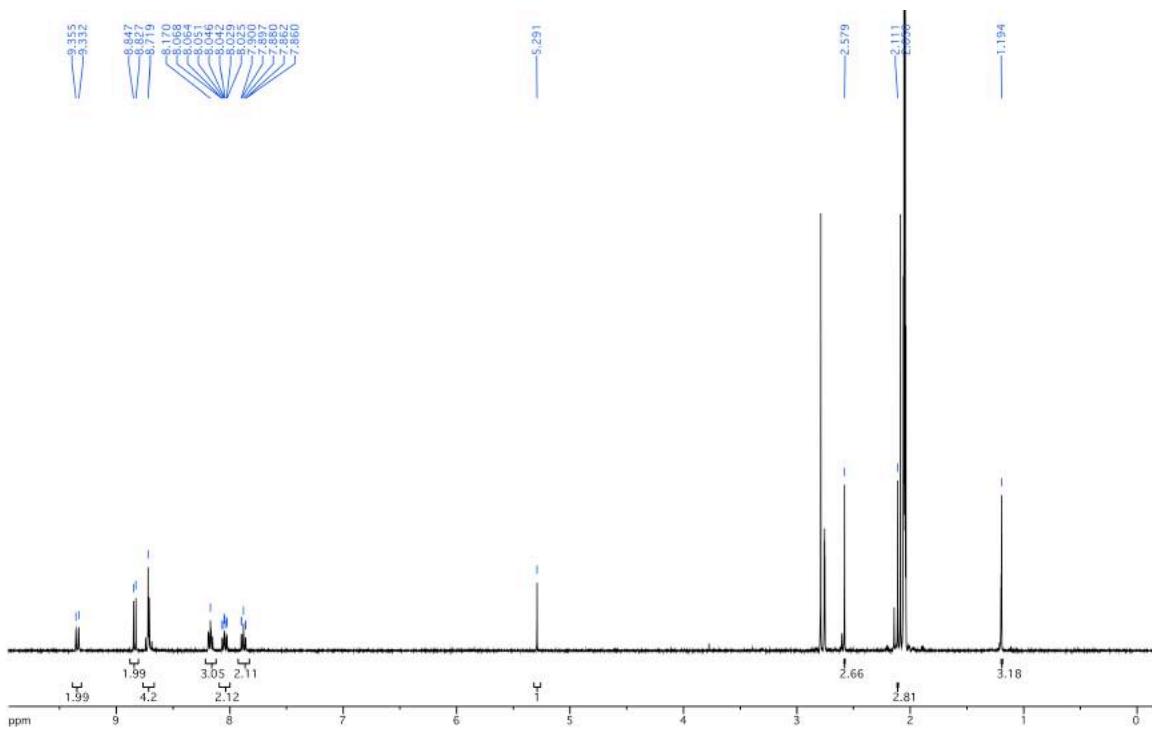


Figure S31. 400 MHz ^1H NMR spectrum of **4** in acetone- d_6 .

Table S6. Optimized Atomic Coordinates (atomic number, x , y , z) for singlet $[\mathbf{1}]^{2+}$.

44	8.030418000	3.760839000	3.623646000
7	8.303041000	5.767178000	4.392890000
7	9.885997000	3.675100000	4.332498000
7	7.320648000	3.126265000	5.401235000
7	8.538929000	4.471771000	1.754498000
7	6.158983000	3.958638000	2.714168000
7	8.576277000	1.707971000	3.182680000
6	6.162418000	4.576580000	1.489759000
6	6.952876000	2.771925000	6.448515000
6	7.417013000	6.828293000	4.486405000
6	10.473569000	4.814349000	4.786127000
6	4.966645000	4.838288000	0.807641000
6	7.495803000	4.858534000	0.951325000
6	10.533180000	2.480277000	4.351925000
6	6.022361000	6.624109000	4.370478000
6	9.602442000	5.993041000	4.729537000
6	7.882068000	8.165511000	4.760306000
6	9.760818000	1.378226000	3.769904000
6	6.953104000	9.236546000	4.809969000
6	5.140482000	7.684578000	4.455654000
6	5.603141000	9.005533000	4.653520000
6	9.802326000	4.629503000	1.296671000
6	11.778680000	4.775780000	5.290836000
6	7.881467000	0.704541000	2.523771000
6	7.730804000	5.427768000	-0.305808000
6	10.101512000	7.280234000	5.029464000
6	6.487312000	2.338422000	7.748400000
1	5.974447000	1.368425000	7.669370000
1	5.787569000	3.075510000	8.169641000
1	7.336813000	2.229719000	8.438880000
6	9.258397000	8.364822000	5.006543000
6	11.841028000	2.402492000	4.848084000
6	3.750388000	4.452725000	1.362813000
6	3.756539000	3.790625000	2.594876000
6	10.088804000	5.181931000	0.053845000
6	4.969227000	3.563944000	3.232682000
6	8.333512000	-0.665097000	2.559611000
6	9.034661000	5.598295000	-0.761670000
6	10.251472000	0.054055000	3.816299000
6	12.461500000	3.559238000	5.319396000
6	7.585019000	-1.672961000	1.899353000
6	6.030354000	-0.007316000	1.112134000
6	6.447509000	-1.355059000	1.188980000

6	6.790414000	10.867345000	13.381082000
1	7.730188000	11.035126000	12.868282000
6	5.352235000	8.194130000	9.634858000
6	4.576598000	9.829162000	13.464462000
6	4.663585000	7.138427000	9.025973000
1	3.789915000	6.696062000	9.502082000
6	9.510451000	8.164400000	11.104690000
6	4.332966000	13.830714000	8.678945000
6	5.118575000	6.644308000	7.802947000
1	4.593605000	5.821357000	7.316921000
6	9.813021000	12.123152000	8.071123000
1	9.251650000	12.476726000	8.926316000
6	9.397885000	12.015480000	11.481241000
1	9.978962000	11.094930000	11.525838000
6	6.246241000	7.204770000	7.203316000
1	6.595554000	6.828250000	6.243296000
6	4.175584000	12.549750000	8.122822000
1	3.358999000	12.337972000	7.430625000
6	6.610273000	11.328274000	14.671261000
1	7.417108000	11.874636000	15.163093000
6	10.179132000	10.471314000	6.306697000
6	9.847745000	13.177964000	12.086638000
1	10.802869000	13.165319000	12.614741000
6	5.040086000	8.794890000	10.935601000
6	10.447773000	7.203545000	11.646001000
1	11.463220000	7.404555000	11.273714000
1	10.161435000	6.184229000	11.347290000
1	10.457212000	7.254922000	12.744918000
6	3.859596000	8.449103000	11.630969000
1	3.144444000	7.767645000	11.173253000
6	8.727734000	8.562560000	6.153570000
1	8.399255000	7.652196000	5.655220000
6	4.410090000	10.344753000	14.775473000
1	3.486954000	10.116377000	15.311983000
6	7.888695000	14.279721000	11.288121000
1	7.272574000	15.173038000	11.183313000
6	9.792294000	9.276255000	5.661567000
1	10.329258000	8.941568000	4.771843000
6	5.406125000	11.088485000	15.371453000
1	5.278121000	11.470924000	16.384888000
6	11.235628000	11.274544000	5.806259000
1	11.769481000	10.936269000	4.915907000
6	11.565274000	12.465885000	6.416018000
1	12.373088000	13.083674000	6.021800000
6	3.608652000	8.990866000	12.868058000
1	2.686595000	8.759436000	13.404942000

6	9.081594000	14.356773000	12.013894000
6	10.834122000	12.892923000	7.547018000
1	11.072999000	13.852374000	8.009109000
6	3.401150000	14.954415000	8.339230000
1	2.352618000	14.626021000	8.373523000
1	3.590385000	15.312522000	7.314420000
1	3.522439000	15.806613000	9.019455000
6	9.525772000	15.623972000	12.680510000
1	9.423197000	15.540436000	13.774400000
1	8.933285000	16.487722000	12.354144000
1	10.586224000	15.830740000	12.476361000

Table S8. Optimized Atomic Coordinates (atomic number, x , y , z) for singlet $[3]^{2+}$.

44	8.053645000	3.739345000	3.638243000
7	8.322302000	5.750772000	4.391549000
7	9.907540000	3.661430000	4.345156000
7	7.317645000	3.118216000	5.405836000
7	8.593297000	4.439293000	1.764132000
7	6.170126000	3.920473000	2.720198000
7	8.598703000	1.681000000	3.217673000
6	6.228310000	4.502722000	1.476549000
6	5.255833000	5.365469000	-0.604025000
6	6.930240000	2.768780000	6.447627000
6	7.433874000	6.810158000	4.480499000
6	10.495241000	4.805573000	4.786876000
6	5.077999000	4.769306000	0.688841000
6	7.527834000	4.775104000	0.963638000
6	10.556439000	2.467604000	4.374379000
6	6.040486000	6.601664000	4.359888000
6	9.621418000	5.981754000	4.725705000
6	7.894610000	8.149061000	4.752491000
6	9.783105000	1.358215000	3.808224000
6	6.962170000	9.217228000	4.798945000
6	6.505177000	5.634360000	-1.093222000
6	5.155147000	7.659518000	4.440398000
6	5.613334000	8.981926000	4.639232000
6	9.830301000	4.640998000	1.281088000
6	11.802503000	4.773302000	5.286522000
6	7.903032000	0.669398000	2.572529000
6	7.683259000	5.331650000	-0.331787000
6	10.116965000	7.271388000	5.021448000
6	6.442040000	2.341265000	7.741219000
1	5.906024000	1.384666000	7.653143000

1	5.756997000	3.093603000	8.159624000
1	7.282183000	2.208401000	8.438881000
6	9.270398000	8.353175000	4.998009000
6	11.866236000	2.396335000	4.865974000
6	3.821618000	4.412065000	1.227895000
6	3.773137000	3.800343000	2.471748000
6	10.066201000	5.188408000	0.010787000
6	4.957657000	3.566866000	3.185666000
6	8.351478000	-0.700601000	2.630212000
6	8.999755000	5.543354000	-0.798924000
6	10.271771000	0.034067000	3.874260000
6	12.487370000	3.558243000	5.323452000
6	7.600601000	-1.716618000	1.985327000
6	6.053017000	-0.058630000	1.168160000
6	6.465134000	-1.406451000	1.268292000
6	9.550077000	-0.992580000	3.317108000
6	6.750073000	0.951359000	1.803600000
1	10.659514000	4.355165000	1.927196000
1	6.625982000	6.075817000	-2.084259000
1	7.334209000	10.225840000	4.989808000
1	5.672739000	5.589875000	4.236983000
1	4.939620000	3.084307000	4.162671000
1	11.173413000	7.404189000	5.248612000
1	12.279825000	5.680026000	5.654823000
1	4.083156000	7.469344000	4.362684000
1	11.095482000	5.325593000	-0.321230000
1	9.165575000	5.971948000	-1.789037000
1	2.909035000	4.603760000	0.660427000
1	2.823479000	3.492122000	2.910104000
1	11.211888000	-0.168800000	4.384185000
1	13.505984000	3.516890000	5.710521000
1	9.643107000	9.360806000	5.192569000
1	4.899733000	9.805355000	4.688136000
1	12.402787000	1.449123000	4.884455000
1	4.369909000	5.588322000	-1.201603000
1	9.900355000	-2.024572000	3.382410000
1	7.954126000	-2.747415000	2.053265000
1	5.896673000	-2.190521000	0.766606000
1	6.431911000	1.980257000	1.696173000
1	5.175200000	0.190591000	0.569437000

Table S9. Optimized Atomic Coordinates (atomic number, x , y , z) for singlet $[4]^+$.

44	3.230037000	6.931500000	4.044855000
8	4.018610000	5.200474000	4.933652000
8	1.796944000	5.779671000	3.123545000

7	4.344429000	6.982276000	2.250372000
7	2.291260000	8.352137000	3.091860000
7	1.825566000	7.507101000	5.514439000
7	4.628502000	8.015983000	4.949329000
6	3.782038000	7.819408000	1.334199000
6	1.148953000	8.850552000	3.646569000
6	1.659637000	4.502246000	3.226506000
6	2.593062000	8.550677000	1.776428000
6	7.980608000	5.082754000	1.285575000
1	8.918689000	4.577143000	1.051638000
6	0.931376000	8.412038000	5.026532000
6	5.541258000	6.363427000	1.930009000
6	2.641777000	5.958839000	8.763868000
1	3.409851000	5.314018000	9.195295000
6	7.414157000	4.959280000	2.574279000
1	7.928542000	4.364871000	3.331866000
6	2.725241000	6.314650000	7.430414000
1	3.539943000	5.954907000	6.804556000
6	4.328439000	8.003096000	0.042643000
1	3.833245000	8.672912000	-0.658921000
6	1.744265000	7.155705000	6.851628000
6	3.565629000	4.002724000	4.780546000
6	7.347760000	5.851626000	0.330694000
1	7.778583000	5.971124000	-0.665726000
6	6.131787000	6.517460000	0.627338000
6	-0.125823000	8.928477000	5.811402000
1	-0.823494000	9.639136000	5.370628000
6	6.221954000	5.581919000	2.894633000
1	5.786133000	5.481251000	3.887005000
6	5.476992000	7.343010000	-0.318159000
1	5.903399000	7.464318000	-1.315920000
6	1.775395000	9.371317000	0.991439000
1	2.005031000	9.537911000	-0.060024000
6	0.310365000	9.675526000	2.888657000
1	-0.604503000	10.079892000	3.319422000
6	5.462248000	8.619613000	5.495652000
6	0.641727000	9.952280000	1.561525000
1	-0.004853000	10.591440000	0.959769000
6	-0.265244000	8.537044000	7.119977000
1	-1.084064000	8.916540000	7.734451000
6	0.622346000	7.253606000	9.046006000
1	-0.194383000	7.631870000	9.664563000
6	0.683548000	7.652371000	7.686907000
6	1.583061000	6.419028000	9.578859000
1	1.532291000	6.120231000	10.626956000
6	2.463556000	3.639365000	3.989789000

1	2.205561000	2.581677000	3.963941000
6	0.510273000	3.939601000	2.428943000
1	-0.429837000	4.412249000	2.750171000
1	0.422082000	2.852982000	2.540956000
1	0.644878000	4.181936000	1.364238000
6	4.321142000	2.938651000	5.537254000
1	5.376313000	2.935832000	5.224070000
1	3.901075000	1.938962000	5.377923000
1	4.305671000	3.164192000	6.614450000
6	6.498158000	9.368817000	6.174454000
1	7.492596000	9.021984000	5.856711000
1	6.413070000	9.239880000	7.263624000
1	6.411142000	10.440487000	5.941741000