Supporting Information

Studies of Carbon Monoxide Release from Ruthenium(II) Bipyridine Carbonyl Complexes upon UV Light Exposure

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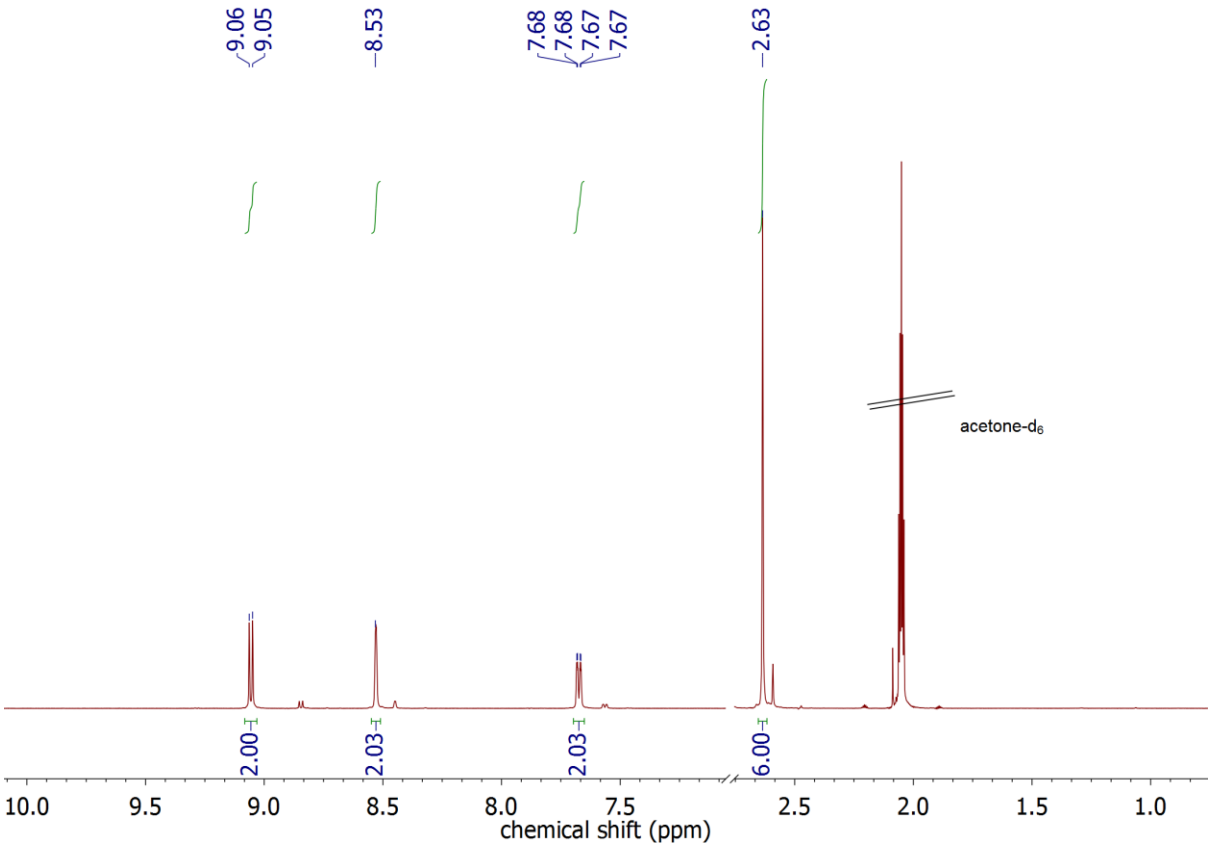

Figure S1. ^{1}H NMR spectrum of *trans*-(Cl) [Ru(4,4'-dimethyl-2,2'-bipyridine)$Cl_2(CO)_2$] (**1**) in acetone-d_6.

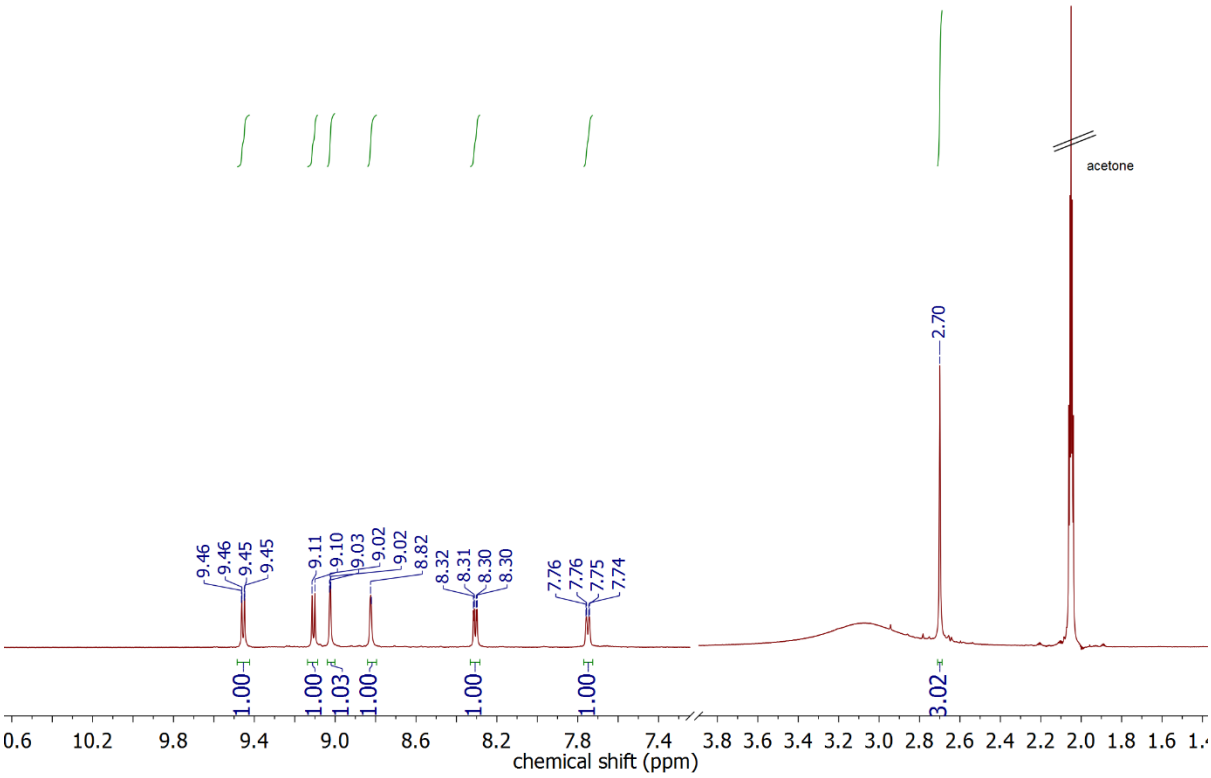

Figure S2. ^{1}H NMR spectrum of *trans*-(Cl) [Ru(4'-methyl-2,2'-bipyridine-4-carboxylic acid)$Cl_2(CO)_2$] (**2**) in acetone-d_6.

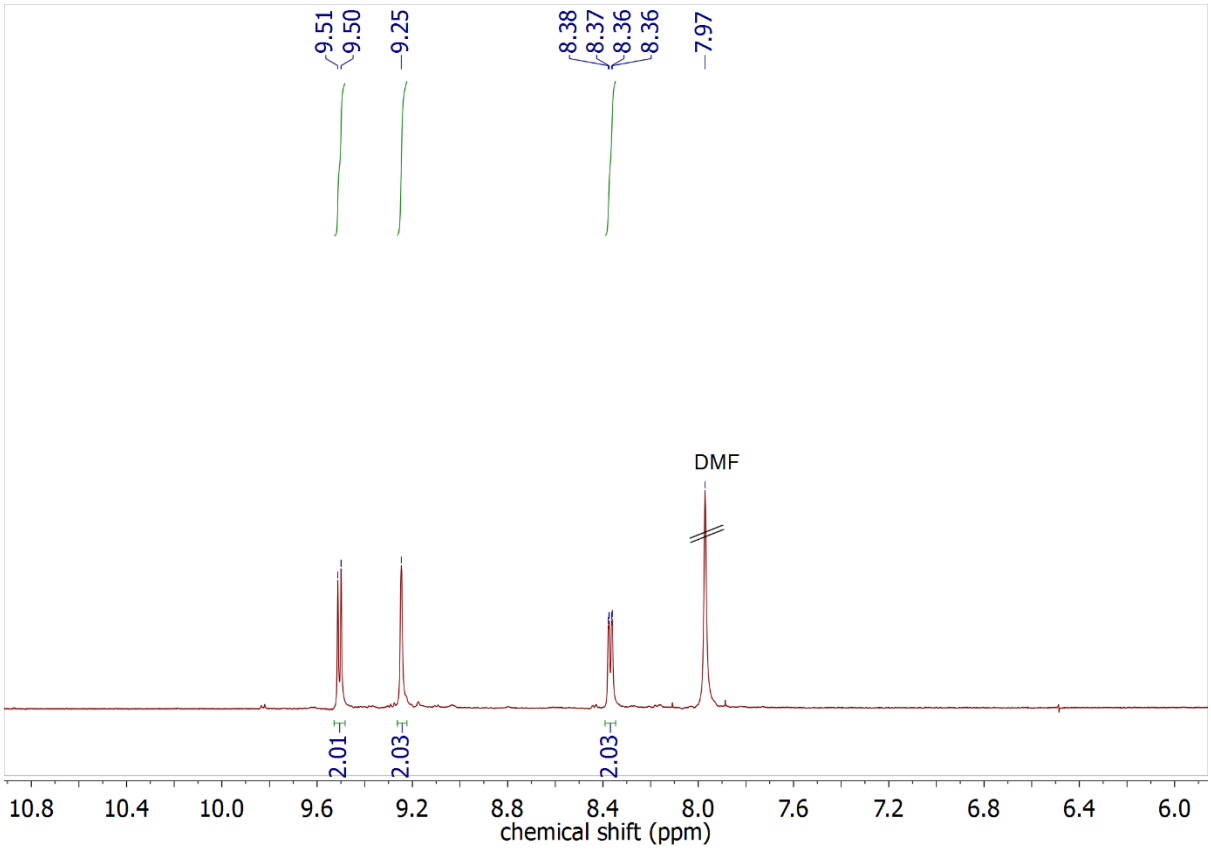

Figure S3. ^{1}H NMR spectrum of [Ru(4,4'-dicarboxylic acid-2,2'-bipyridine)$Cl_2(CO)_2$] (**3**) in acetone-d_6.

Table S1. Cartesian coordinates for DFT-calculated ground-state geometry of **1**.

Ru	-1.3325660000	-0.0000440000	0.0000400000
Cl	-1.2060070000	-0.0003920000	2.4052640000
Cl	-1.2061820000	0.0001620000	-2.4051930000
O	-3.4910090000	-2.1049200000	-0.0001170000
O	-3.4909310000	2.1048370000	0.0003730000
N	0.3303920000	-1.3199940000	-0.0001700000
N	0.3303100000	1.3199570000	0.0001320000
C	0.2591950000	-2.6584750000	-0.0003180000
C	2.6538750000	-2.8939990000	-0.0003810000
C	2.7154320000	-1.5001550000	-0.0002360000
C	1.3797550000	-3.4714780000	-0.0004230000
C	-2.6738590000	1.2999960000	0.0002460000
C	1.5488440000	0.7374370000	0.0000350000
C	1.5489560000	-0.7373160000	-0.0001280000
C	2.6535560000	2.8941900000	0.0002380000
C	3.8885110000	-3.7364740000	-0.0004880000
C	2.7153180000	1.5004110000	0.0000920000
C	1.3793610000	3.4715860000	0.0003460000
C	-2.6739390000	-1.3001000000	-0.0000520000
C	0.2589220000	2.6585080000	0.0002870000
C	3.8881860000	3.7368220000	0.0002090000
H	-0.7390610000	-3.0944980000	-0.0003570000
H	3.6881080000	-1.0103650000	-0.0002070000
H	1.2510870000	-4.5544510000	-0.0005390000
H	3.6880290000	1.0107060000	0.0000280000
H	1.2507140000	4.5545600000	0.0004820000
H	-0.7394270000	3.0942970000	0.0003730000
H	4.7984890000	3.1246030000	0.0009880000
H	3.9047370000	4.3920610000	0.8843970000
H	3.9054740000	4.3907940000	-0.8849160000
H	4.7988500000	-3.1243500000	-0.0004440000
H	3.9055080000	-4.3910700000	-0.8851370000
H	3.9055400000	-4.3912430000	0.8840330000

Table S2. Cartesian coordinates for DFT-calculated ground-state geometry of **2**.

Ru	1.4731890000	-0.7082100000	0.0000350000
Cl	1.3660840000	-0.6349700000	2.4033870000
Cl	1.3653910000	-0.6355110000	-2.4033200000
O	-5.4897970000	-1.9057410000	0.0002460000
O	-5.5161950000	0.3419050000	-0.0000330000
O	4.4481620000	-0.2212940000	-0.0011330000
O	2.0378230000	-3.6705140000	-0.0002790000
N	0.8737930000	1.3278030000	-0.0000950000
N	-0.6479140000	-0.8361270000	0.0003130000
C	-0.6557500000	5.3491460000	-0.0001950000
C	1.6994840000	2.3833160000	-0.0002510000
C	1.8285950000	-2.5434440000	0.0002480000
C	1.2464150000	3.6919330000	-0.0003260000
C	-0.9781360000	2.8439780000	-0.0000930000
C	-4.9135630000	-0.7062140000	0.0003040000
C	-0.1281710000	3.9508100000	-0.0002300000
C	-1.3048330000	0.3463540000	0.0001530000
C	-0.4575980000	1.5517850000	-0.0000170000
C	3.3180580000	-0.4123580000	-0.0002350000
C	-2.7362470000	-2.0061810000	0.0005280000
C	-2.6965250000	0.3924950000	0.0001430000
C	-3.4211870000	-0.7938480000	0.0003260000
C	-1.3487210000	-1.9766410000	0.0005140000
H	-6.4531810000	-1.7681280000	0.0000580000
H	-0.2942640000	5.8941270000	0.8850440000
H	-0.2928090000	5.8948030000	-0.8844080000
H	-1.7525700000	5.3704470000	-0.0010420000
H	2.7674270000	2.1686330000	-0.0003240000
H	1.9732220000	4.5050220000	-0.0004600000
H	-2.0561930000	2.9980350000	-0.0000450000
H	-3.2620680000	-2.9591040000	0.0006920000
H	-3.2393720000	1.3358560000	-0.0000120000
H	-0.7775960000	-2.9036570000	0.0006700000

Table S3. Cartesian coordinates for DFT-calculated ground-state geometry of **3**.

Ru	-1.8582580000	-0.0000810000	0.0000200000
Cl	-1.7305520000	-0.0005810000	-2.4017590000
Cl	-1.7305530000	0.0004830000	2.4017930000
O	-4.0217630000	2.1002610000	-0.0006950000
O	-4.0214810000	-2.1006860000	0.0003220000
O	4.4658690000	3.1544400000	0.0004720000
O	3.1543310000	4.9803730000	-0.0001110000
O	4.4661970000	-3.1540910000	-0.0006220000
O	3.1547560000	-4.9801980000	0.0001600000
N	-0.1967340000	1.3250240000	-0.0002080000
N	-0.1966020000	-1.3250010000	0.0003020000
C	-0.2778400000	2.6607390000	-0.0003580000
C	2.0989590000	2.8827320000	-0.0000640000
C	2.1872520000	1.4950930000	0.0001140000
C	0.8421820000	3.4813070000	-0.0003350000
C	-3.2028420000	-1.2991980000	0.0003440000
C	1.0205900000	-0.7361120000	0.0000380000
C	1.0205250000	0.7362400000	-0.0000350000
C	2.0991910000	-2.8825180000	0.0000730000
C	3.3714620000	3.6677810000	0.0000490000
C	2.1873790000	-1.4948960000	-0.0001750000
C	0.8424540000	-3.4812040000	0.0004680000
C	-3.2030280000	1.2988770000	-0.0002510000
C	-0.2776270000	-2.6607340000	0.0005250000
C	3.3718340000	-3.6674910000	-0.0001670000
H	-1.2774570000	3.0921480000	-0.0004930000
H	3.1733940000	1.0342680000	0.0004110000
H	0.7261160000	4.5634600000	-0.0004890000
H	3.1734890000	-4.5633650000	0.0007100000
H	-1.2772240000	-3.0921910000	0.0007350000
H	4.0219850000	5.4212420000	0.0000630000
H	4.0224810000	-5.4210200000	-0.0000610000

Table S4. Selected bond distances (Å) and angles (°) for the DFT-calculated structures of complexes **1**–**3** and two reported crystal structures.[1-2]

	Homanen[1]	**1**	**2**	**3**	Bischof[2]
Ru-Cl1	2.404	2.409	2.407	2.405	2.398
Ru-Cl2	2.391	2.409	2.407	2.405	2.390
Ru-CO1	1.879	1.868	1.869	1.870	1.865
Ru-CO2	1.866	1.868	1.868	1.870	1.883
C-O1	1.118	1.147	1.146	1.146	1.125
C-O2	1.129	1.147	1.146	1.146	1.130
Ru-N(bpy)1	2.129	2.123	2.125	2.125	2.104
Ru-N(bpy)1	2.118	2.123	2.122	2.125	2.106
Cl-Ru-Cl	175.3	174	173.8	173.9	175.8
CO-Ru-CO	88.3	88.2	88.2	88.0	88.4

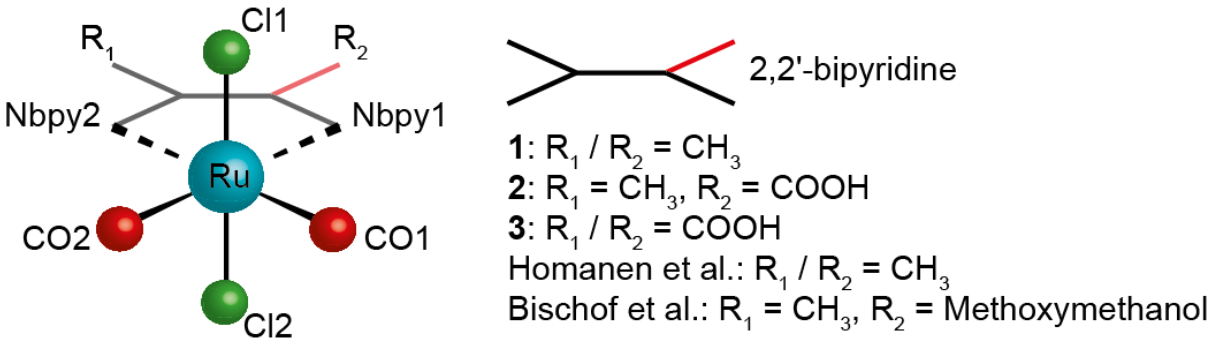

Table S5. Selected low-lying electronic transitions of complexes **1**–**3** predicted by TD-DFT with oscillator strength larger than 0.001.

Complex	Transition energy		Oscillator strength	Main contribution (%)
	nm	eV		
1	364	3.40	0.0288	HOMO-1->LUMO (99%)
	354	3.50	0.0034	HOMO-1->LUMO+2 (92%)
	296	4.19	0.0033	HOMO->LUMO+4 (89%)
	288	4.31	0.1004	HOMO-2->LUMO (43%), HOMO->LUMO+1 (52%)
	279	4.44	0.282	HOMO-2->LUMO (48%), HOMO->LUMO+1 (45%)
	276	4.49	0.0038	HOMO-1->LUMO+1 (97%)
	271	4.57	0.0135	HOMO->LUMO+3 (95%)
2	419	2.96	0.0013	HOMO->LUMO (99%)
	399	3.10	0.0296	HOMO-1->LUMO (99%)
	353	3.51	0.0031	HOMO-1->LUMO+3 (92%)
	320	3.87	0.0097	HOMO->LUMO+1 (97%)
	299	4.14	0.2795	HOMO-2->LUMO (88%)
	297	4.17	0.0032	HOMO->LUMO+4 (88%)
	280	4.44	0.0261	HOMO->LUMO+2 (90%)
	272	4.55	0.0108	HOMO-1->LUMO+2 (93%)
	269	4.62	0.0891	HOMO-5->LUMO (88%)
3	447	2.77	0.0017	HOMO->LUMO (99%)
	423	2.93	0.028	HOMO-1->LUMO (99%)
	352	3.52	0.003	HOMO-1->LUMO+3 (92%)
	337	3.68	0.0217	HOMO->LUMO+1 (99%)
	328	3.78	0.0037	HOMO-1->LUMO+1 (98%)
	319	3.89	0.0027	HOMO->LUMO+2 (92%)
	303	4.10	0.3261	HOMO-2->LUMO (87%)
	299	4.15	0.0037	HOMO->LUMO+4 (88%)
	272	4.56	0.0447	HOMO-6->LUMO (71%), HOMO-2->LUMO+1 (24%)

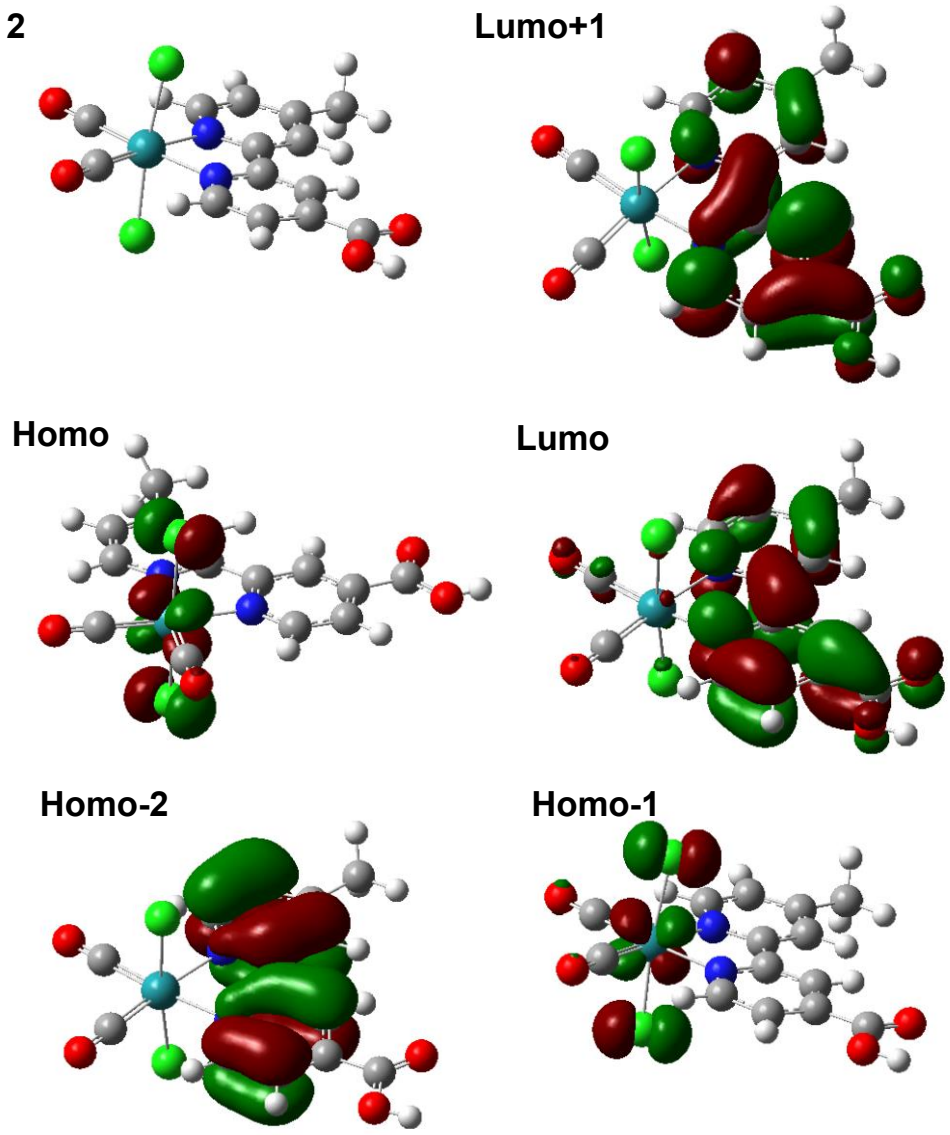

Figure S4. Main molecular orbitals of complex **2** involved in the electronic transitions discussed in this work.

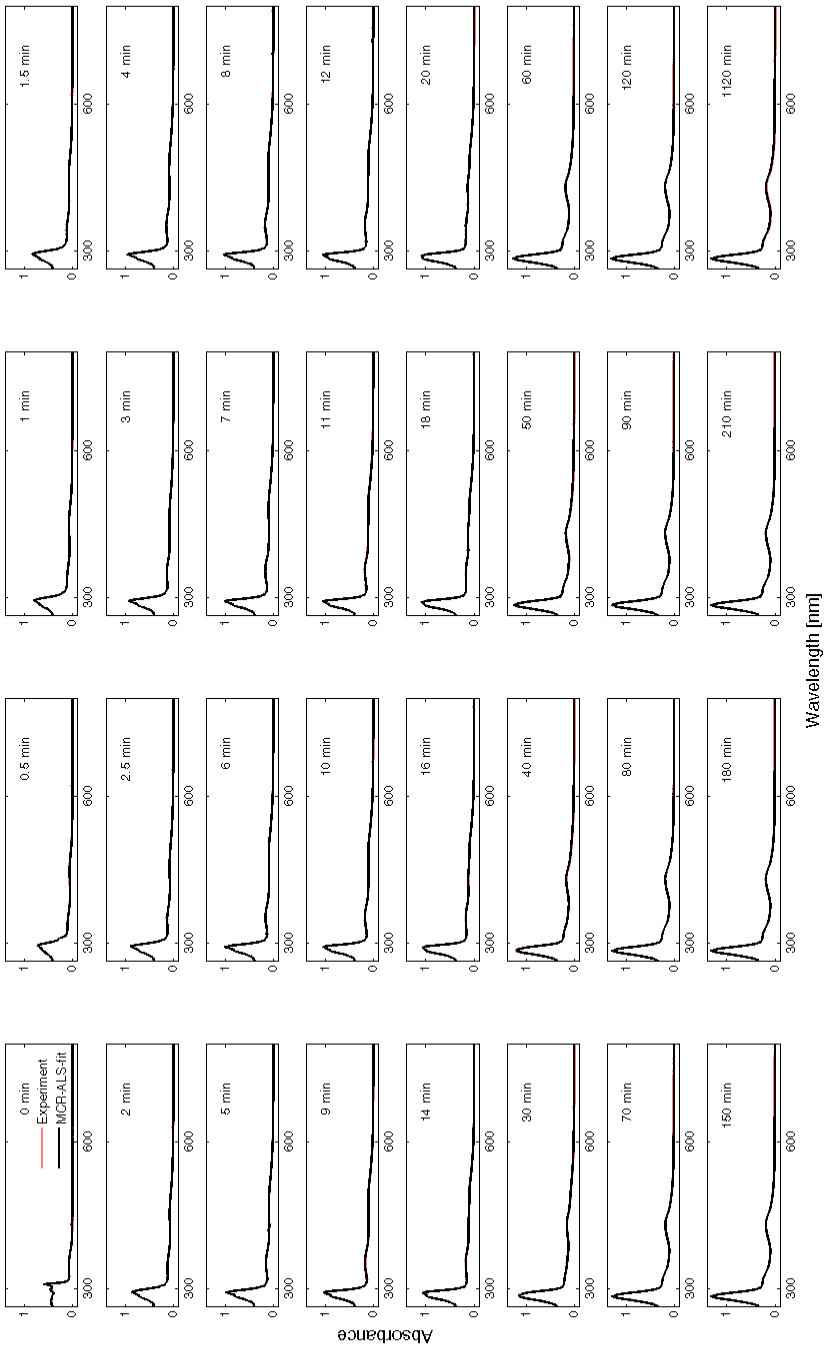

Figure S5. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **1** in acetonitrile.

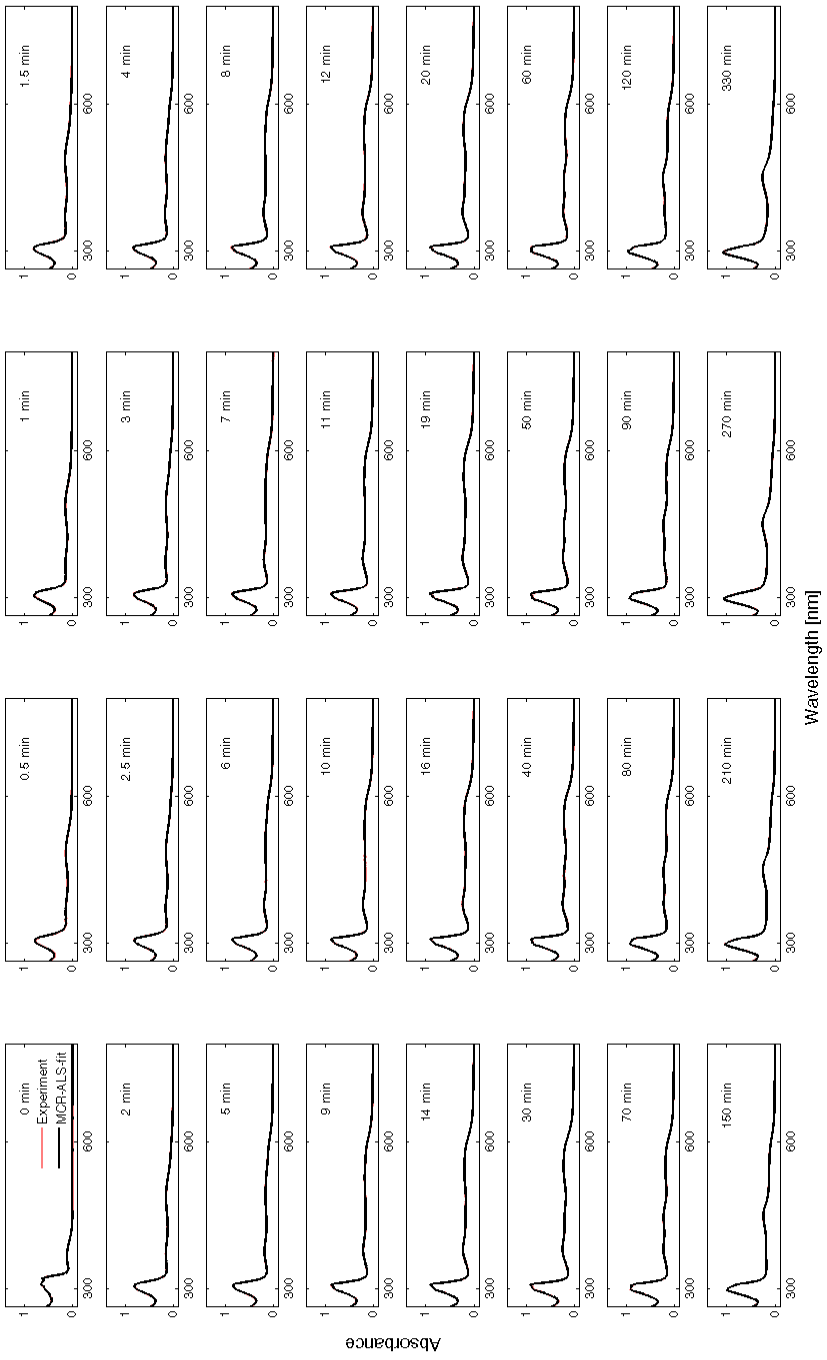

Figure S6. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **2** in acetonitrile.

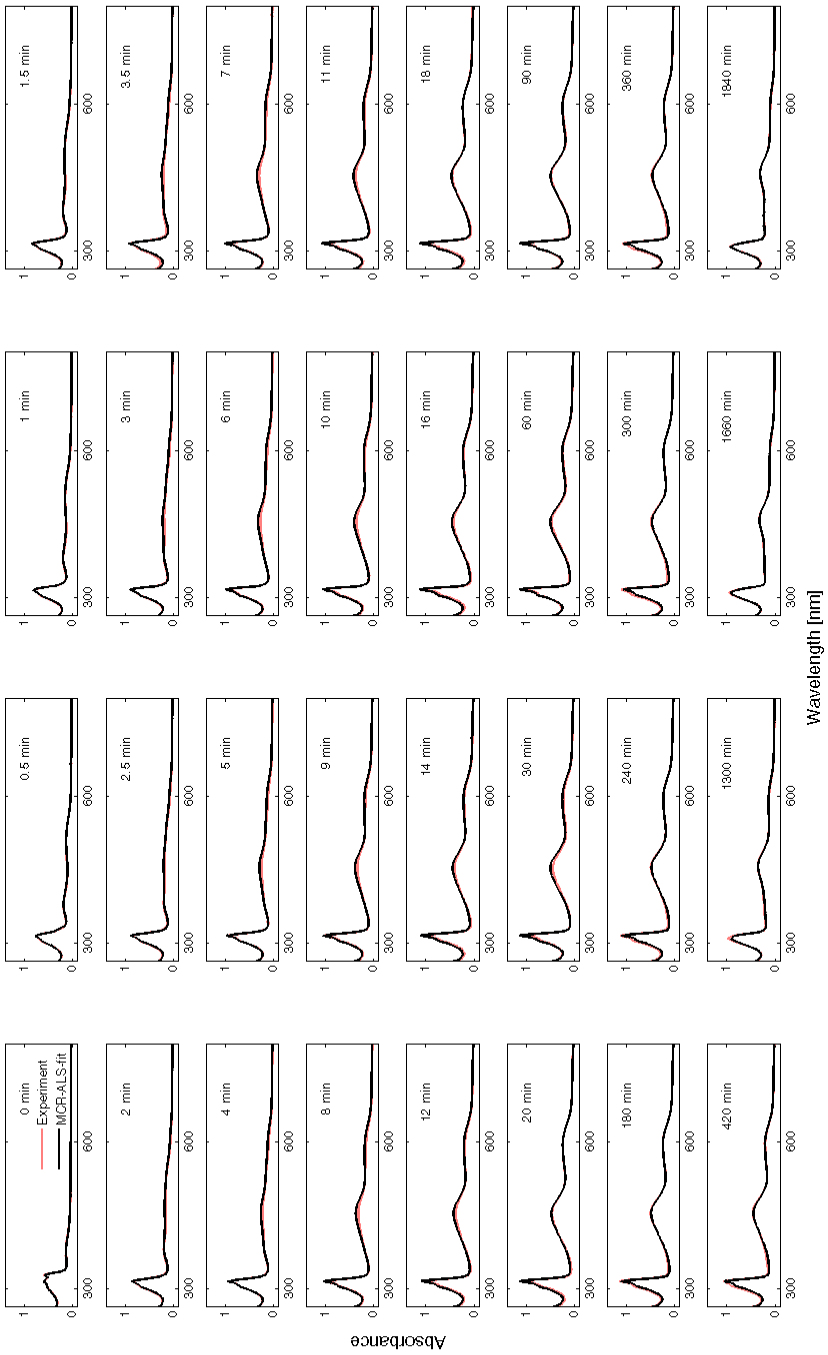

Figure S7. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **3** in acetonitrile.

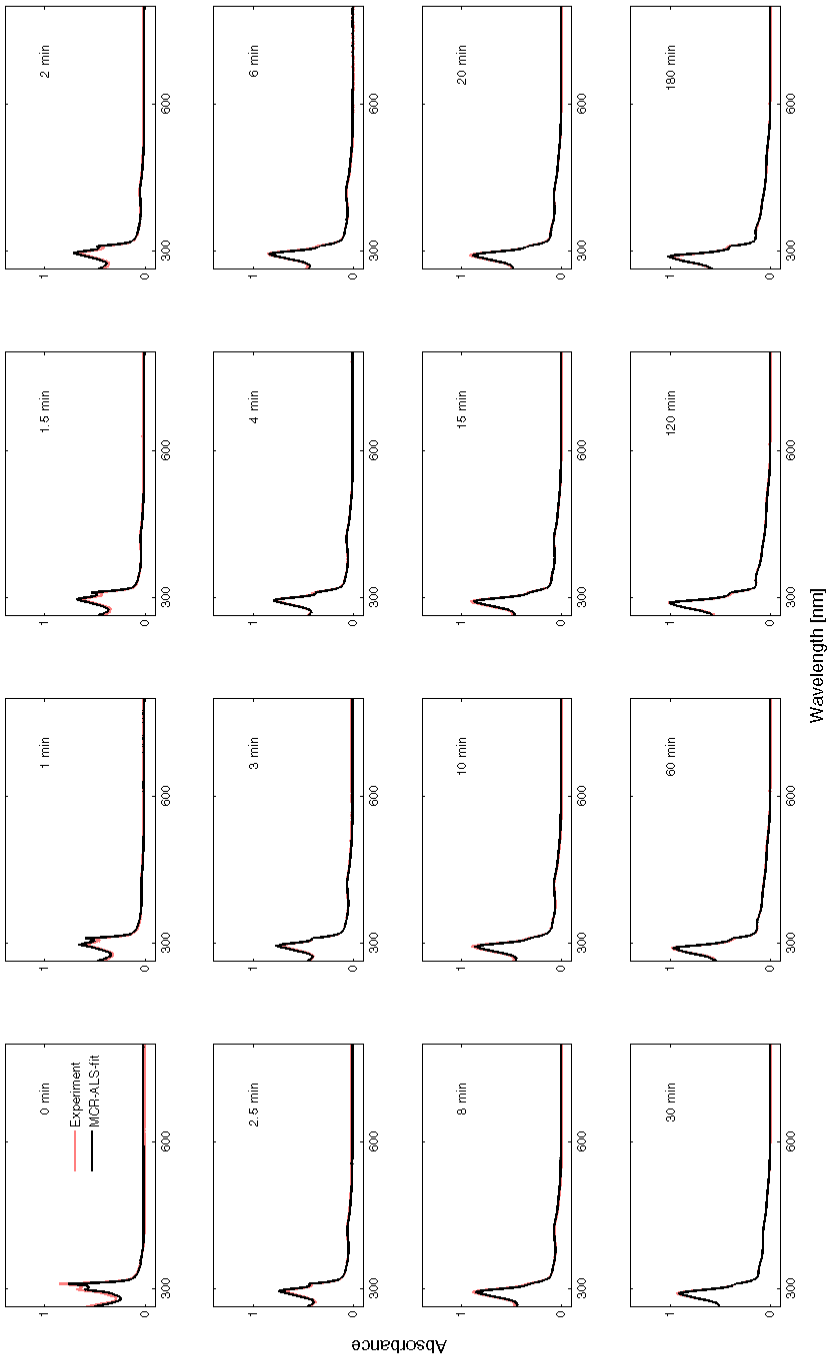

Figure S8. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **1** in 1% DMSO in water.

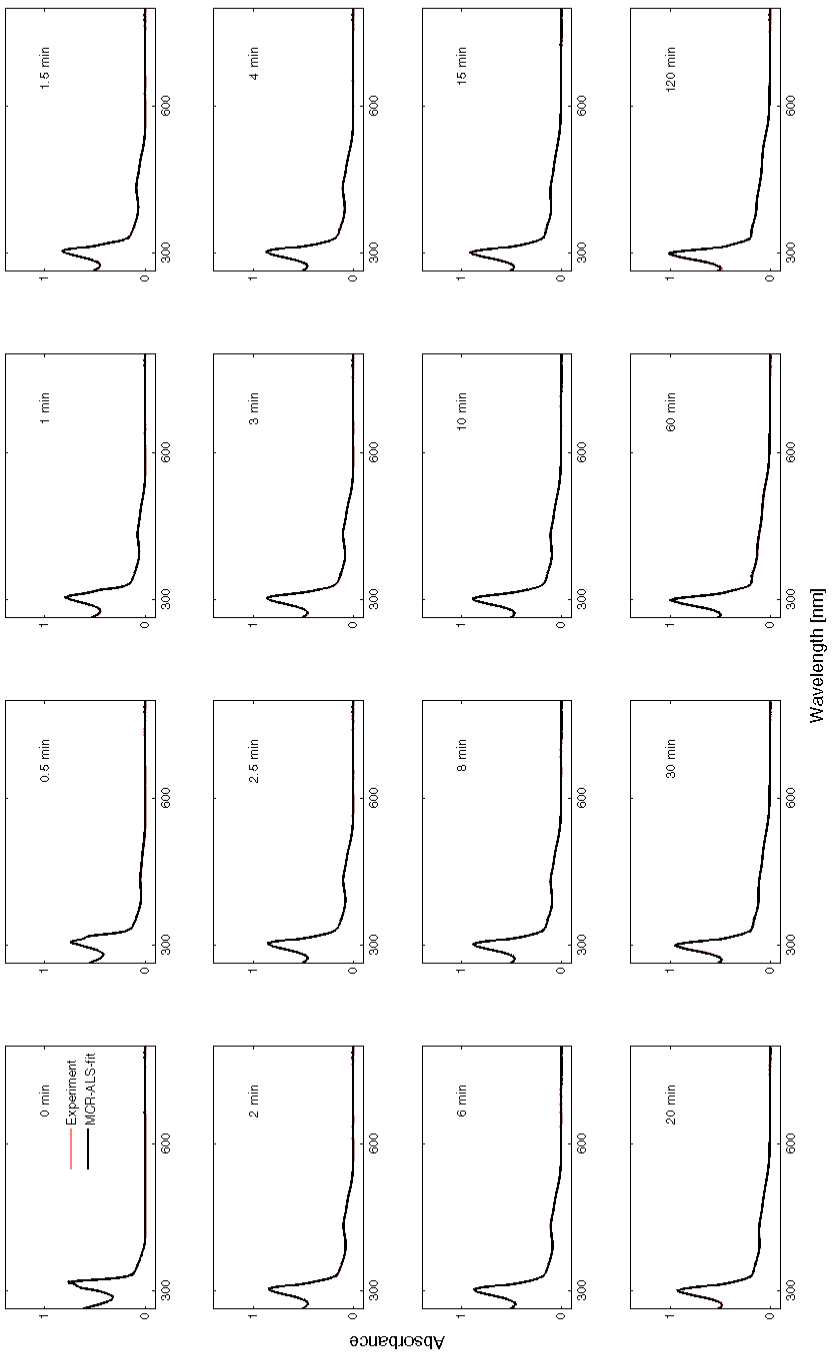

Figure S9. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **2** in 1% DMSO in water.

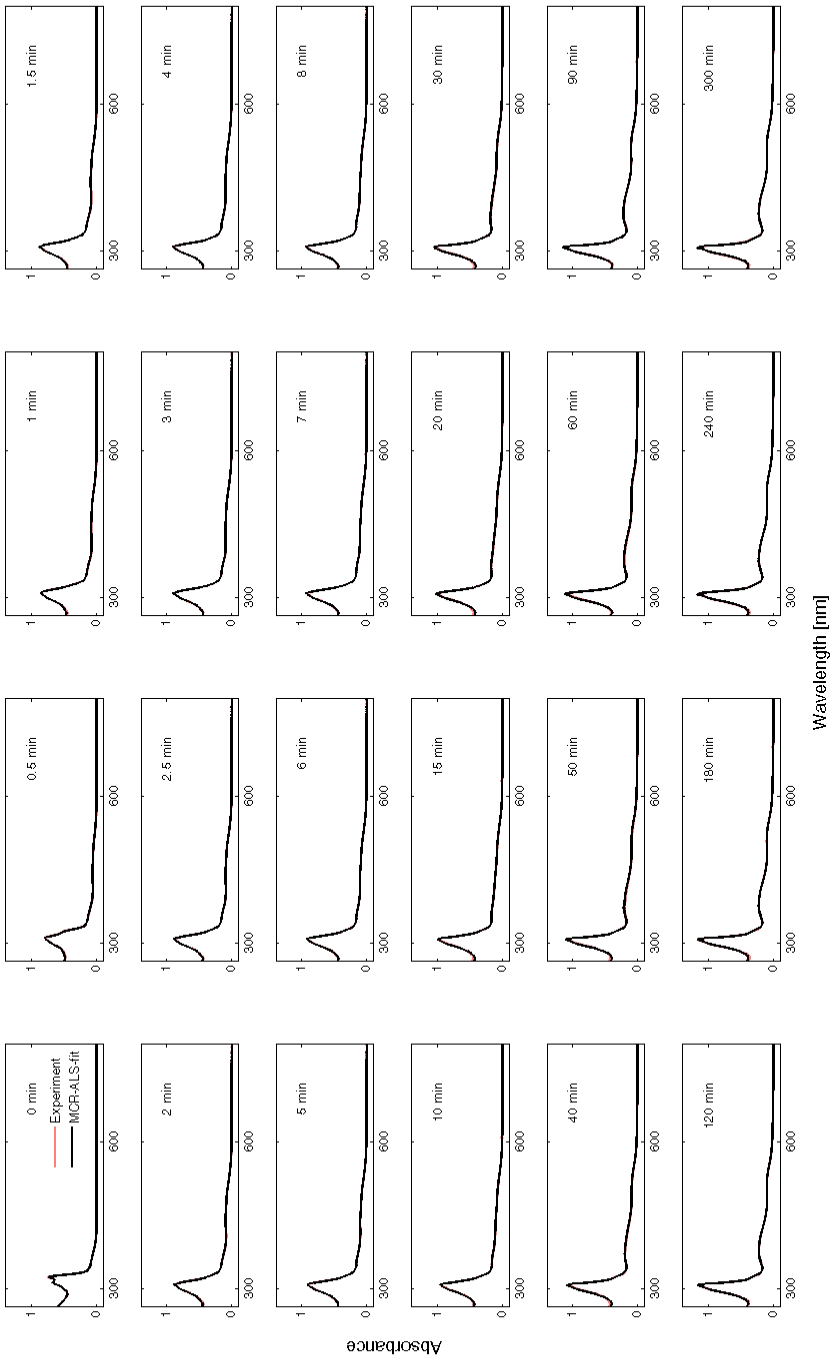

Figure S10. Comparison of MCR-ALS fit and experimental UV-Vis absorbance spectra recorded upon UV irradiation of complex **3** in 1% DMSO in water.

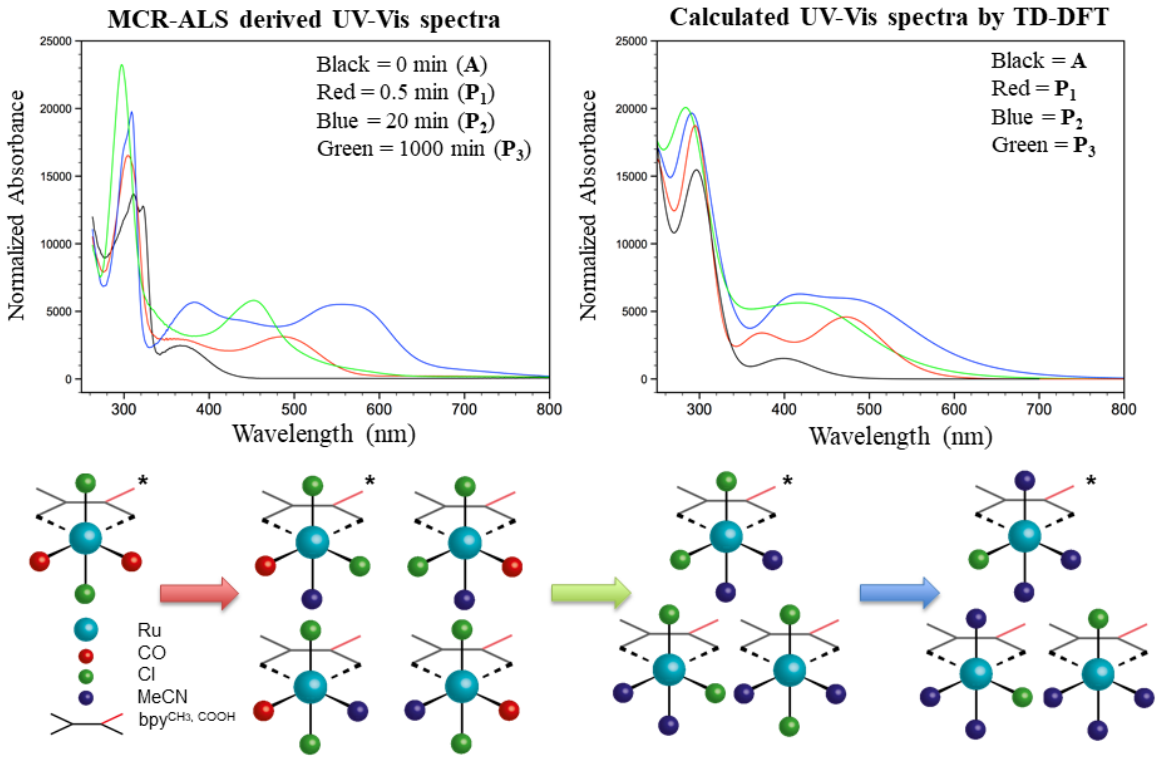

Figure S11. Comparison of MCR-ALS derived (top left) and TD-DFT-predicted UV-Vis absorbance spectra (top right) for proposed photoproducts of **2** in acetonitrile (*indicates the structures associated with the predicted spectra).

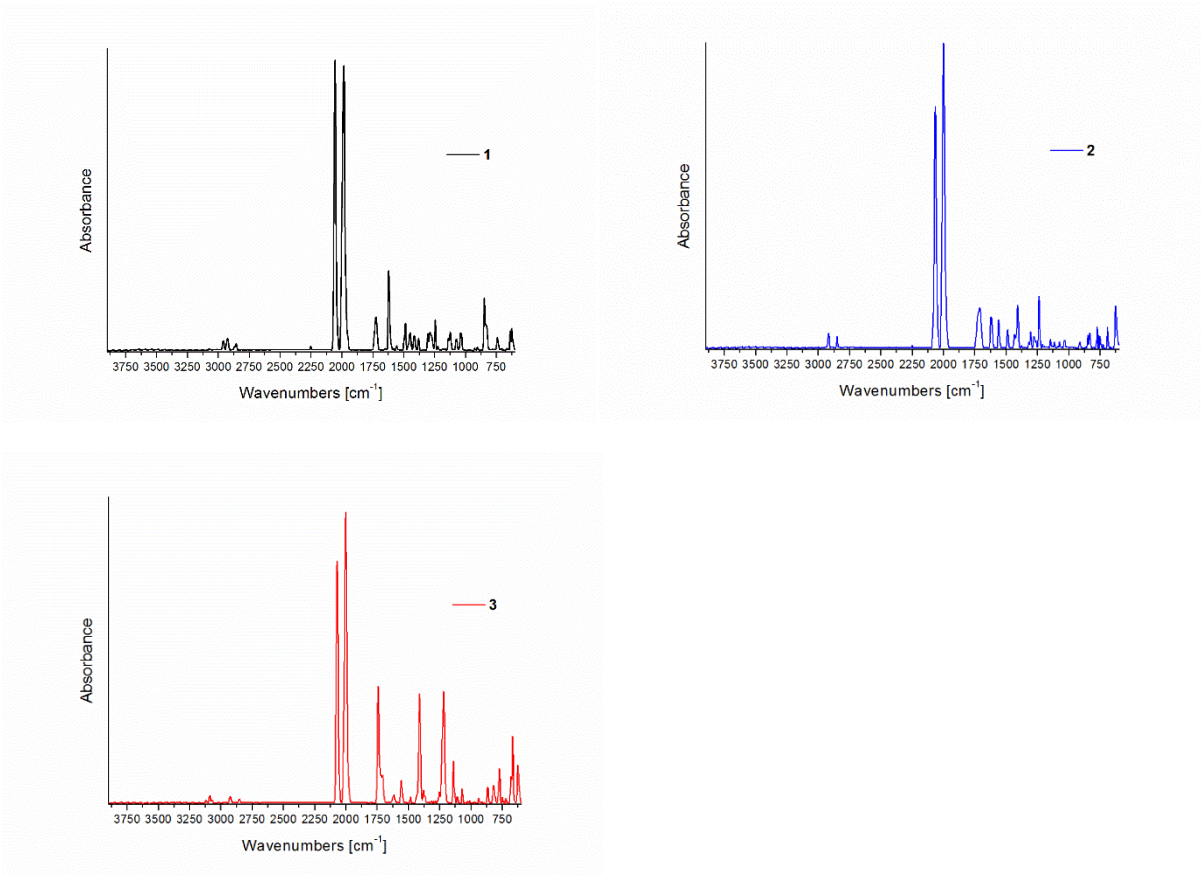

Figure S12. Infrared spectra of complexes **1** (black), **2** (blue) and **3** (red).

Table S6. Selected infrared bands (cm^{-1}) observed upon UV irradiation of complexes **1**–**3** in acetonitrile.

Time [min]	**1**		**2**		**3**	
	ν(MeCN)	ν(CO)	ν(MeCN)	ν(CO)	ν(MeCN)	ν(CO)
0	2253	2054; 1985	2251	2065; 1998	2251	2069; 2002
0.5		2056; 1992; 1963		2056; 1992; 1963(sh)		2067; 2004(sh); 1981
3	2268; 2249	2056 (w); 1959	2286; 2243	2056, 1963	2279	2067; 1981
10	2270; 2251	1959	2243	1961	2278	2067; 1981
20	2271	1959	2266 (w); 2241	1961	2276	2067; 1979
60	2272	1961	2266	1961	2276	2067; 1979
150	2276	-	2266; 2241 (sh)	1962	2276	-
330	2278	-	2266; 2241	1961	2276	-
1080	-	-	2283 (sh); 2272; 2245	-	-	-
1440	-	-	2285; 2245	-	-	-

ν(non-bound MeCN) = 2252 cm^{-1}

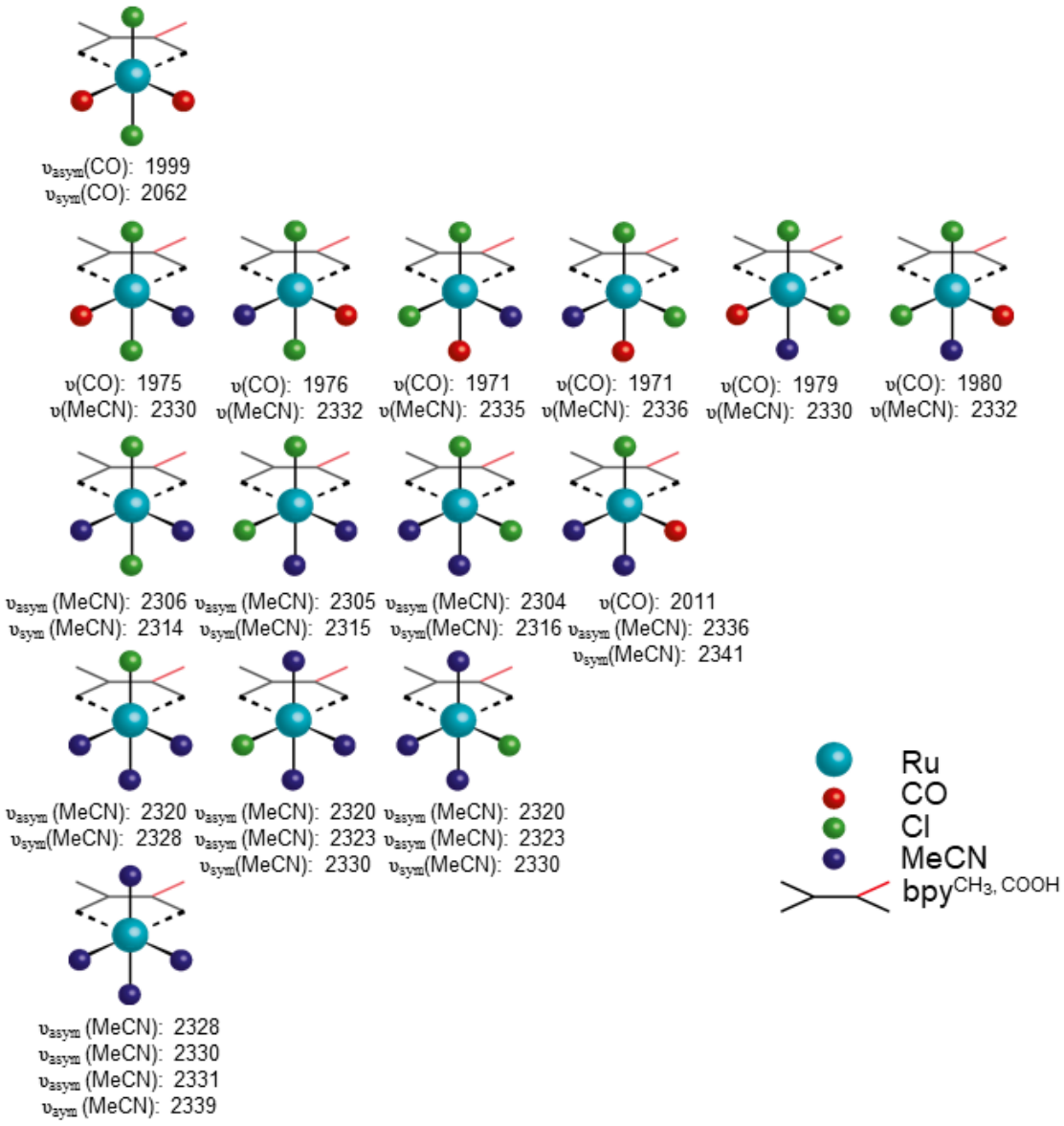

Figure S13. Simplified representation of complex **2** and its acetonitrile-substituted derivatives, together with the corresponding carbonyl and acetonitrile stretching vibrations (cm^{-1}) calculated by DFT. A uniform scaling factor of 0.965 was applied to the calculated frequencies.

References

1. Homanen, P.; Haukka, M.; Luukkanen, S.; Ahlgrén, M.; Pakkanen, T. A., Selective Formation of cis(X)- and trans(X)-Ru(dmbpy)$(CO)_2X_2$ Complexes (X = Cl, Br, I, SCN) from Monomeric and Dimeric Ru–mono(dmbpy) Carbonyl Complexes (Dmbpy = 4,4′-Dimethyl-2,2′-bipyridine). *Eur. J. Inorg. Chem.* **1999,** *1999*, 101-106.

2. Bischof, C.; Joshi, T.; Dimri, A.; Spiccia, L.; Schatzschneider, U., Synthesis, Spectroscopic Properties, and Photoinduced CO-Release Studies of Functionalized Ruthenium(II) Polypyridyl Complexes: Versatile Building Blocks for Development of CORM−Peptide Nucleic Acid Bioconjugates. *Inorg. Chem.* **2013,** *52*, 9297-9308.