Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for:

New Ruthenium Polypyridyl Complexes and their Applications in Acetonitrile Detection and in Catalysis for Water Oxidation

Pedro O. Abate,[a] Analía M. Peyrot,[a] Xavier Fontrodona,[b] Isabel Romero,[b] Florencia Fagalde[a]* and Néstor E. Katz[a]*

[a] Dr. P. O. Abate, Lic. Analía M. Peyrot, Dr. F. Fagalde (corresponding author) and Dr. N. E. Katz (corresponding author)
INQUINOA (CONICET-UNT)
Ayacucho 471
4000 San Miguel de Tucumán
Argentina
E-mail: nestor.katz@fbqf.unt.edu.ar florencia.fagalde@fbqf.unt.edu.ar

[b] Dr. X. Fontrodona and Dr. María I. Romero
Serveis Tècnics de Recerca and Departament de Química
Universitat de Girona
C/ M. Aurèlia Campmany
69 E-17003 Girona
Spain

Table of Contents

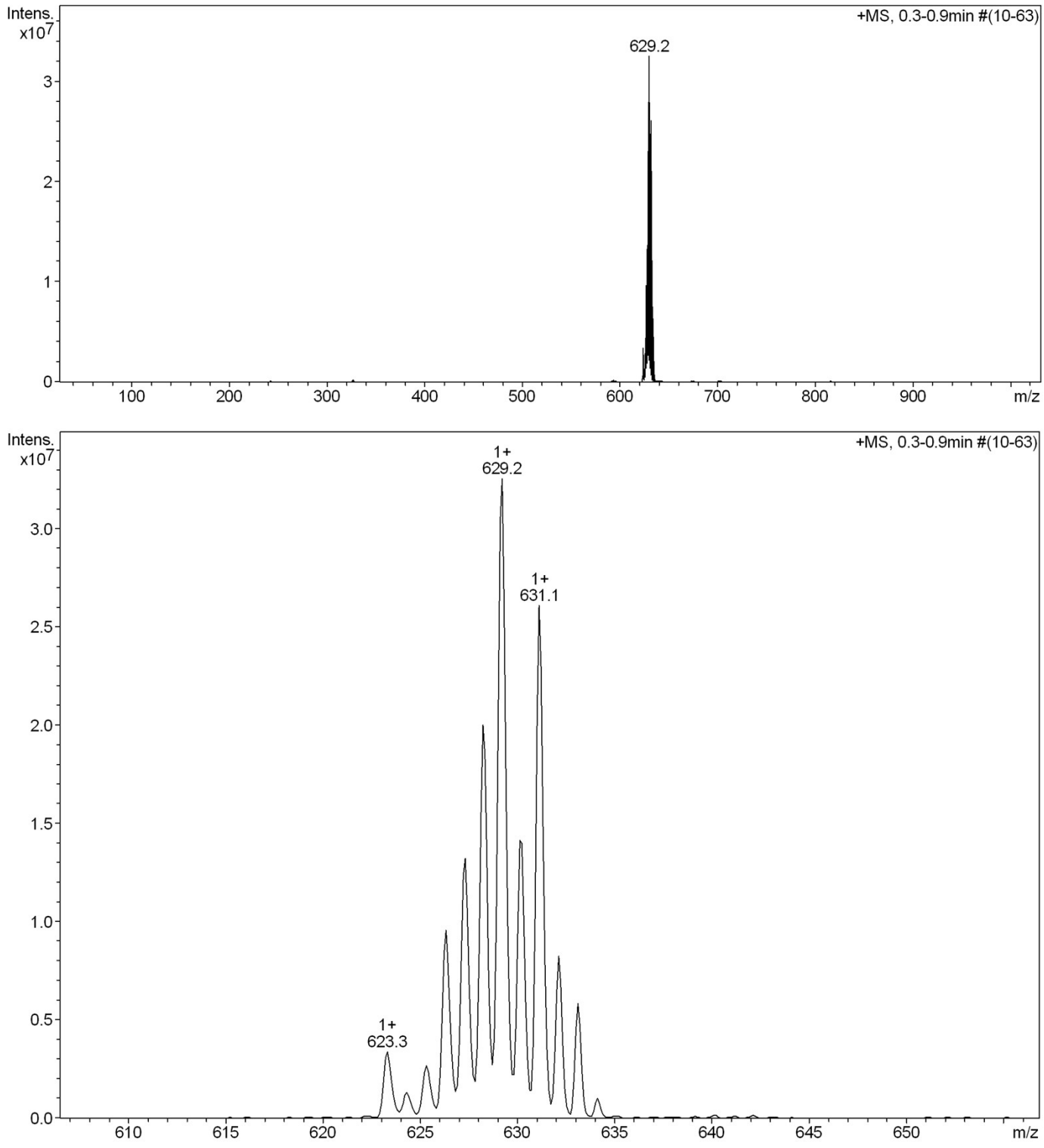


Figure S1. ESI-MS of complex **1**.

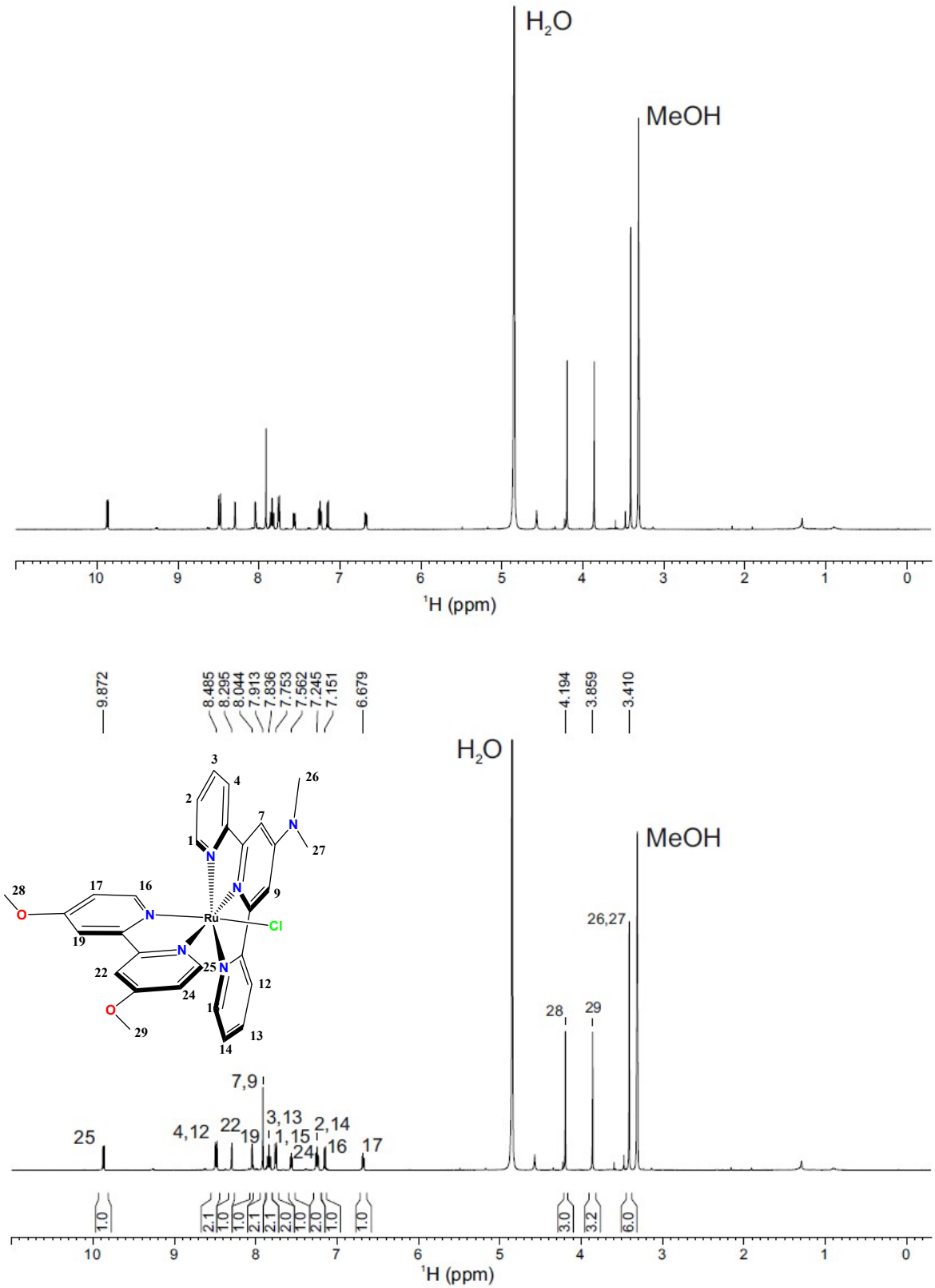


Figure S2. 400 MHz ^{1}H NMR spectrum of **1** dissolved in CD_3OD.

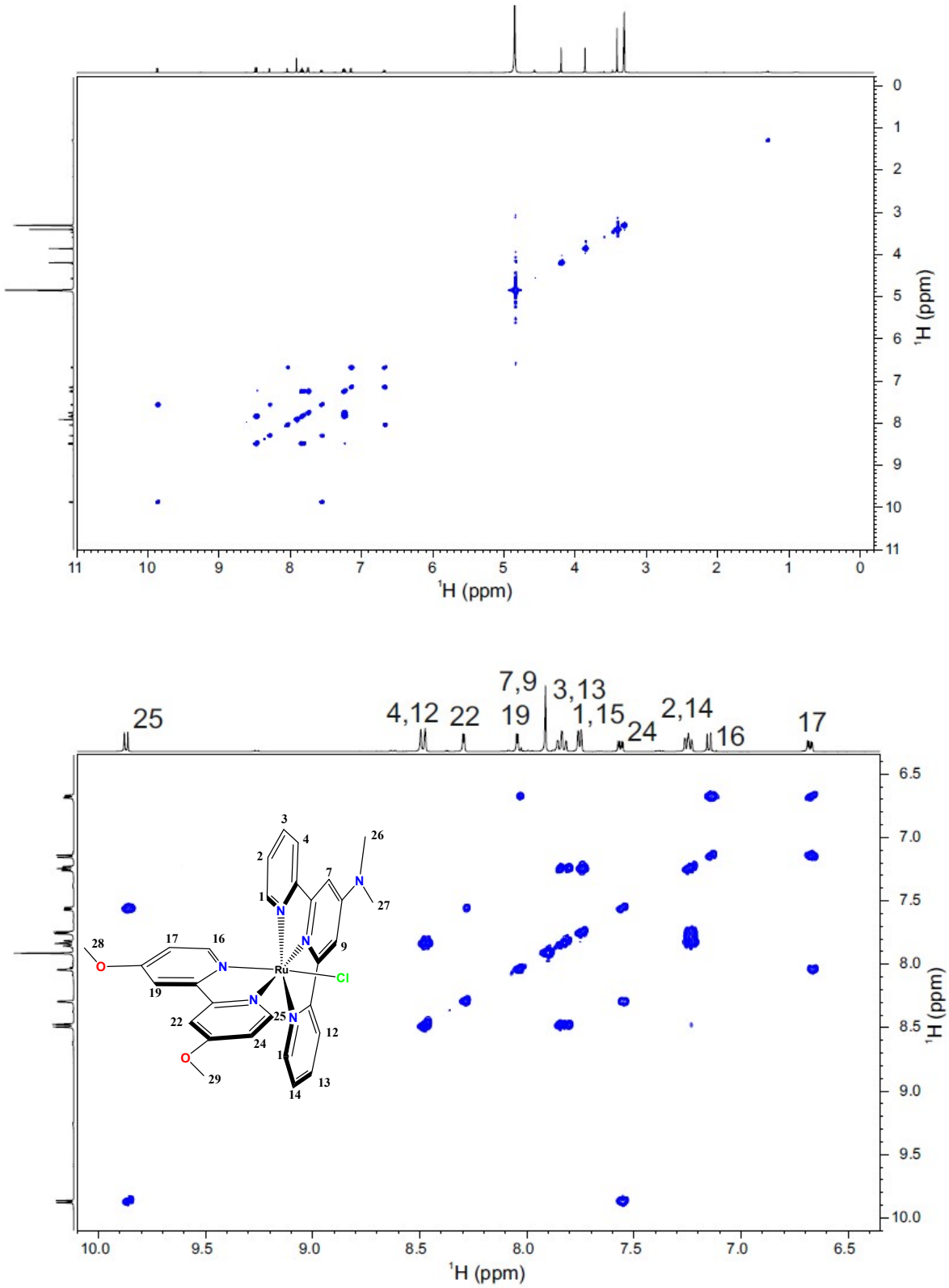


Figure S3. 2D ^{1}H-^{1}H COSY spectrum of **1** dissolved in CD_3OD.

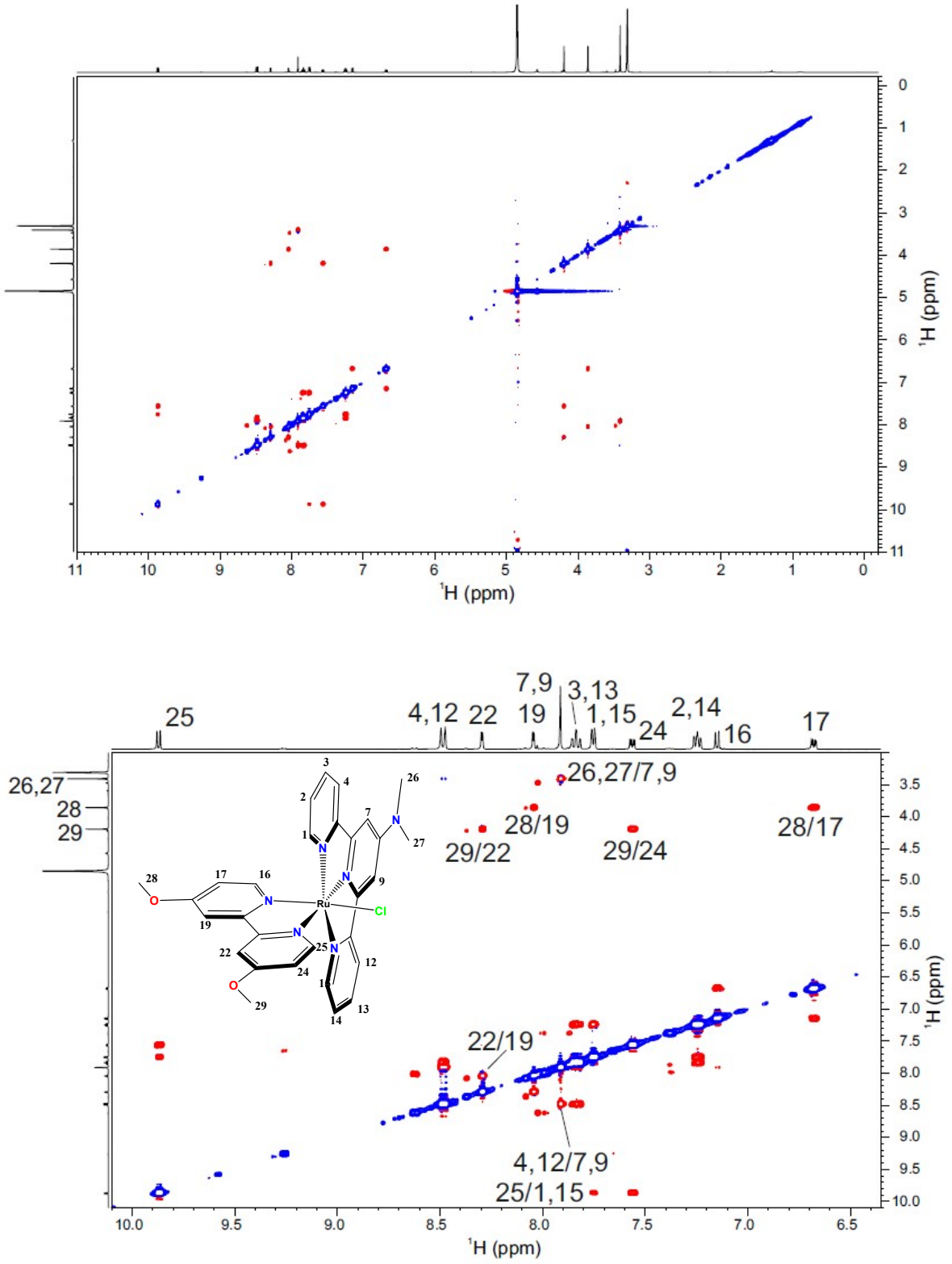


Figure S4. 2D ^{1}H-^{1}H NOESY spectrum of **1** dissolved in CD_3OD.

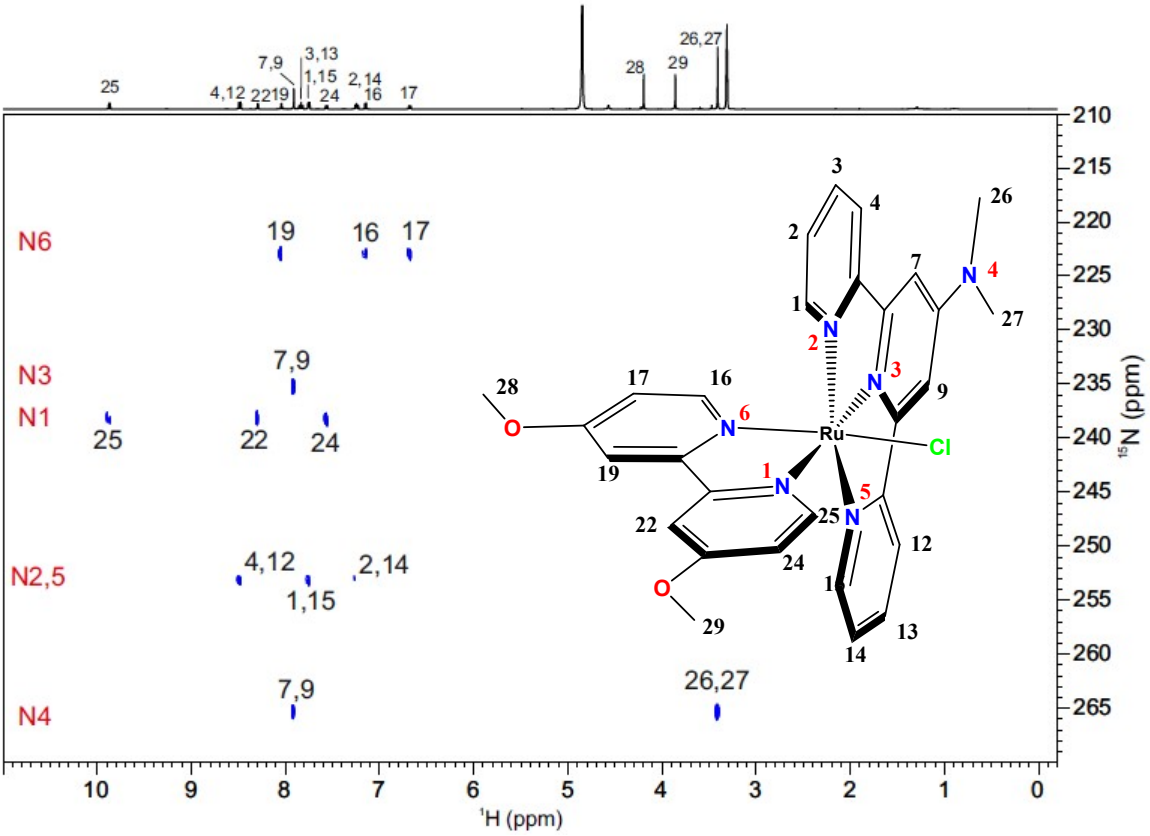


Figure S5. ^{1}H-^{15}N HMBC spectrum of **1** dissolved in CD_3OD.

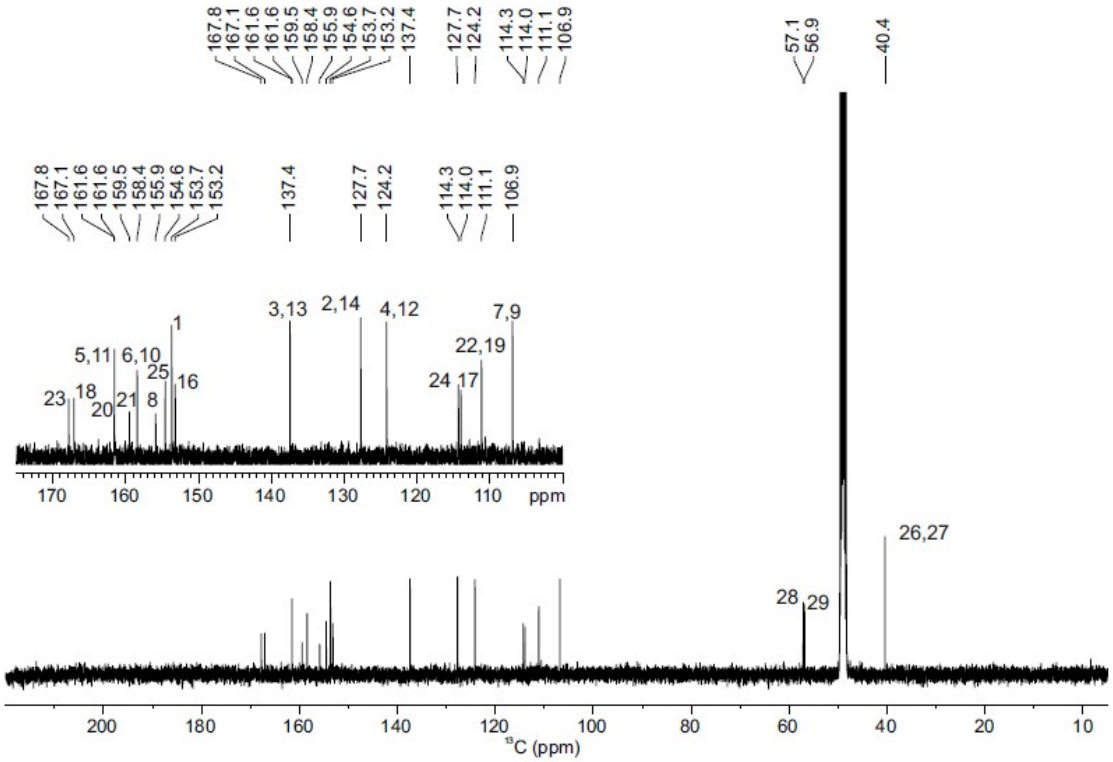


Figure S6. 100 MHz ^{13}C NMR spectrum of **1** dissolved in CD_3OD.

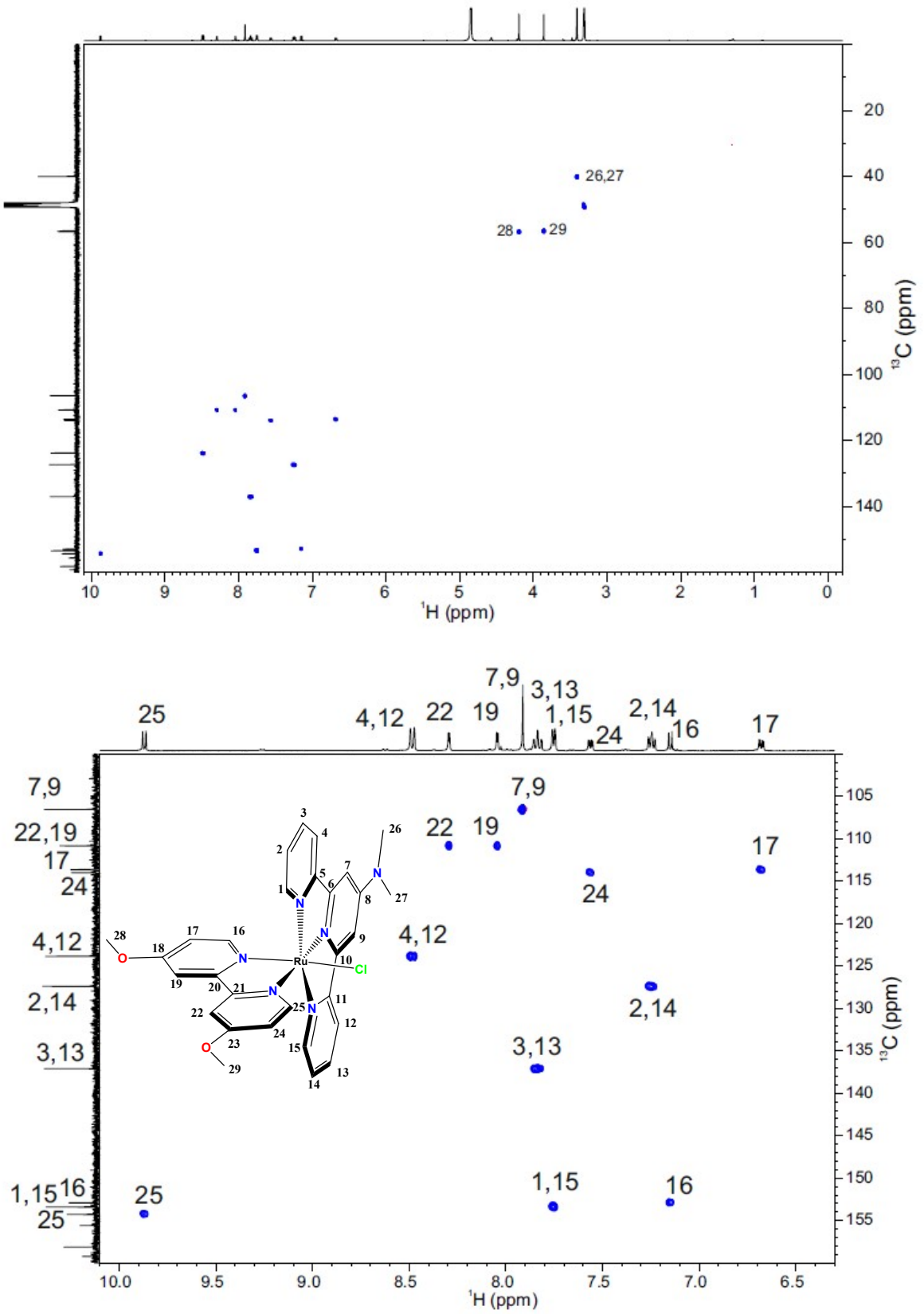


Figure S7. 2D ^{1}H-^{13}C HSQC spectrum of **1** dissolved in CD_3OD.

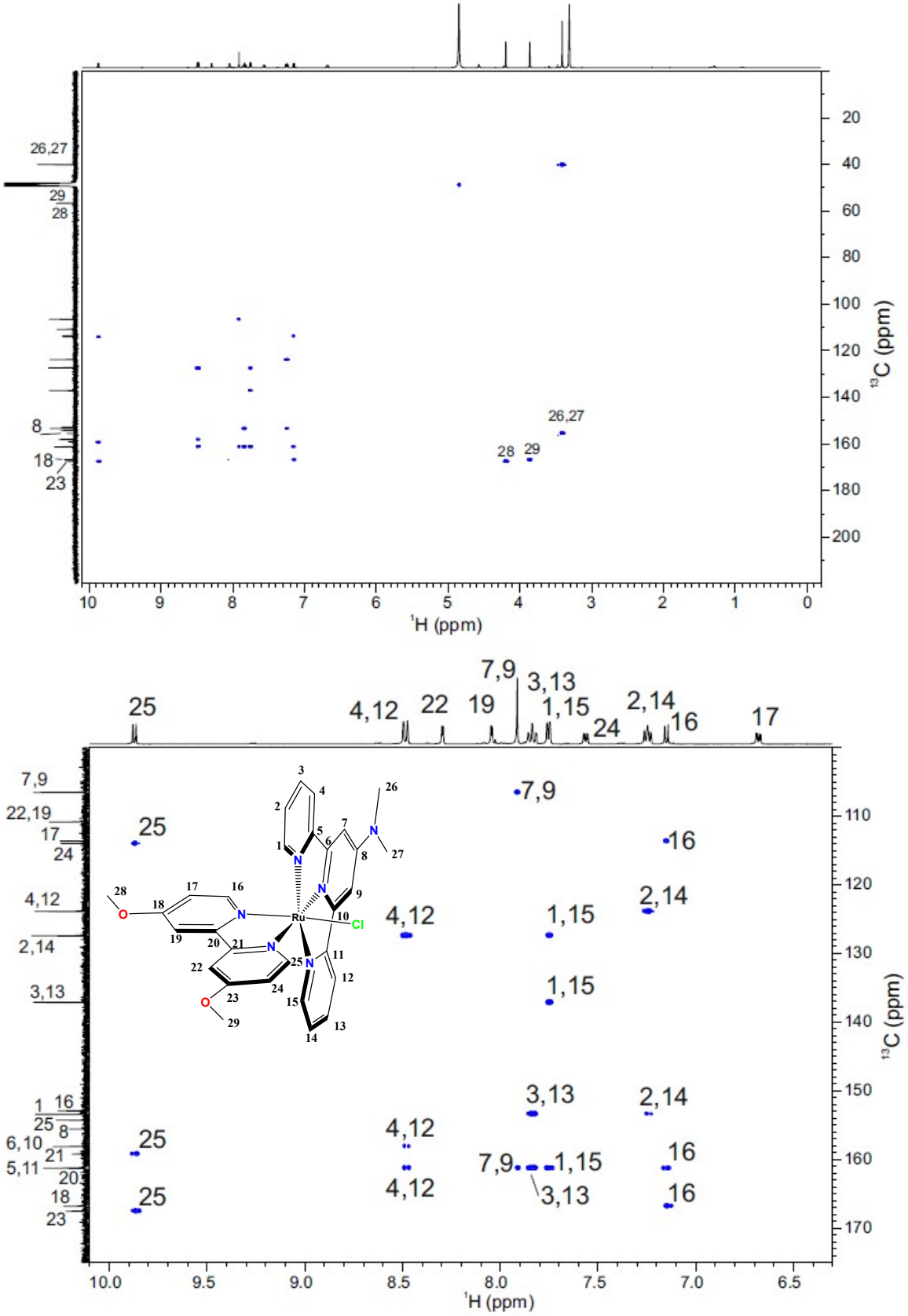


Figure S8. 2D ^{1}H-^{13}C HMBC spectrum of **1** dissolved in CD_3OD.

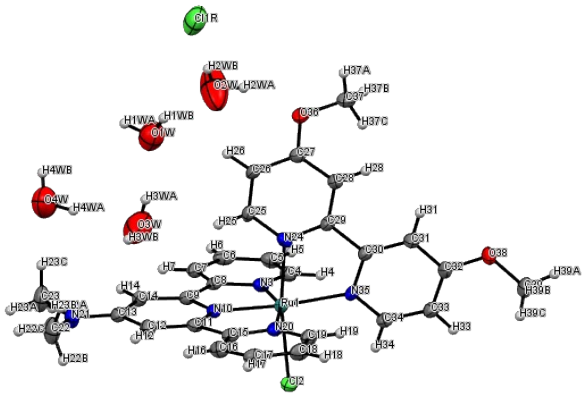


Figure S9. Crystal structure of **1·3H$_2$O** with counter-anion and solvent molecules.

Table S1. Sample and crystal data for 1·3H$_2$O.

Chemical formula	$C_{29}H_{36}Cl_2N_6O_6Ru$	
Formula weight	736.61 g/mol	
Temperature	1001 K	
Wavelength	0.71076 Å	
Crystal size	0.060 x 0.120 x 0.500 mm	
Crystal habit	black needle	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.869(13) Å	α = 107.961°
	b = 11.422(13) Å	β = 110.491°
	c = 14.735(17) Å	γ = 94.301°
Volume	1595.1 Å^3	
Z	2	
Density (calculated)	1.533 g/cm^3	
Absorption coefficient	0.710 mm^{-1}	
F(000)	756	

Table S2. Data collection and structure refinement for 1·3H_2O.

Diffractometer	D8 QUEST ECO three-circle diffractometer
Radiation source	Ceramic x-ray tube (Mo Kα, λ = 0.71076 Å)
Theta range for data collection	2.89 to 29.11°
Index ranges	-14<=h<=14, -15<=k<=15, -20<=l<=20
Reflections collected	110330
Independent reflections	8564 [R(int) = 0.0639]
Coverage of independent reflections	99.70%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7458 and 0.6599
Structure solution technique	direct methods
Structure solution program	SHELXT 2014/5 (Sheldrick, 2014)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2017/1 (Sheldrick, 2017)
Function minimized	$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8564 / 0 / 401
Goodness-of-fit on F^2	1.057
Final R indices	7188 data; I>2σ(I) R1 = 0.0445, wR2 = 0.1072
	all data R1 = 0.0597, wR2 = 0.1200
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0495P)^2+5.8501P]$ where $P=(F_o^2+2F_c^2)/3$
Largest diff. peak and hole	3.604 and -2.276 eÅ^{-3}
R.M.S. deviation from mean	0.126 eÅ^{-3}

Table S3. Bond lengths (Å) for 1·3H_2O.

Ru1-N10	1.9771	Ru1-N24	2.0501	C23-H23A	0.98	C23-H23B	0.98
Ru1-N3	2.0731	Ru1-N20	2.0841	C23-H23C	0.98	N24-C25	1.357(4)
Ru1-N35	2.0931	Ru1-Cl2	2.4311	N24-C29	1.371(4)	C25-C26	1.385(5)
N3-C4	1.346(4)	N3-C8	1.374(4)	C25-H25	0.95	C26-C27	1.406(4)
C4-C5	1.394(4)	C4-H4	0.95	C26-H26	0.95	C27-O36	1.354(4)
C5-C6	1.396(5)	C5-H5	0.95	C27-C28	1.396(4)	C28-C29	1.403(4)
C6-C7	1.393(5)	C6-H6	0.95	C28-H28	0.95	C29-C30	1.475(4)
C7-C8	1.399(4)	C7-H7	0.95	C30-N35	1.369(4)	C30-C31	1.387(4)
C8-C9	1.488(4)	C9-N10	1.353(4)	C31-C32	1.402(4)	C31-H31	0.95
C9-C14	1.392(4)	N10-C11	1.353(4)	C32-O38	1.351(4)	C32-C33	1.395(5)
C11-C12	1.386(4)	C11-C15	1.491(4)	C33-C34	1.390(4)	C33-H33	0.95
C12-C13	1.421(4)	C12-H12	0.95	C34-N35	1.347(4)	C34-H34	0.95
C13-N21	1.364(4)	C13-C14	1.421(5)	O36-C37	1.460(4)	C37-H37A	0.98
C14-H14	0.95	C15-N20	1.376(4)	C37-H37B	0.98	C37-H37C	0.98
C15-C16	1.393(4)	C16-C17	1.394(5)	O38-C39	1.433(4)	C39-H39A	0.98
C16-H16	0.95	C17-C18	1.381(5)	C39-H39B	0.98	C39-H39C	0.98
C17-H17	0.95	C18-C19	1.398(5)	O1W-H1WA	0.877	O1W-H1WB	0.9101
C18-H18	0.95	C19-N20	1.357(4)	O2W-H2WA	0.87	O2W-H2WB	0.87
C19-H19	0.95	N21-C22	1.460(5)	O3W-H3WA	0.87	O3W-H3WB	0.87
N21-C23	1.460(4)	C22-H22A	0.98	O4W-H4WA	0.87	O4W-H4WB	0.87
C22-H22B	0.98	C22-H22C	0.98				

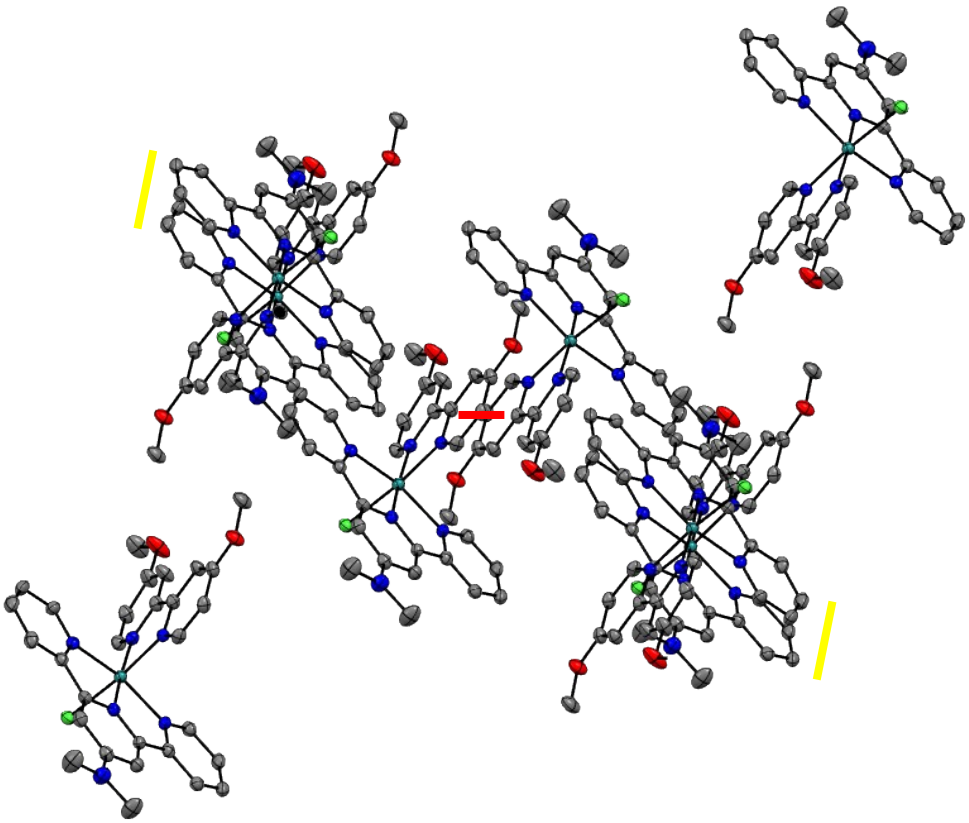


Figure S10. View of the two-dimensional layer formed by the cationic part of **1·3H$_2$O**, showing intermolecular π_{tpy}-π_{tpy} (yellow line) and π_{bpy}-π_{bpy} (red line) stacking interactions.

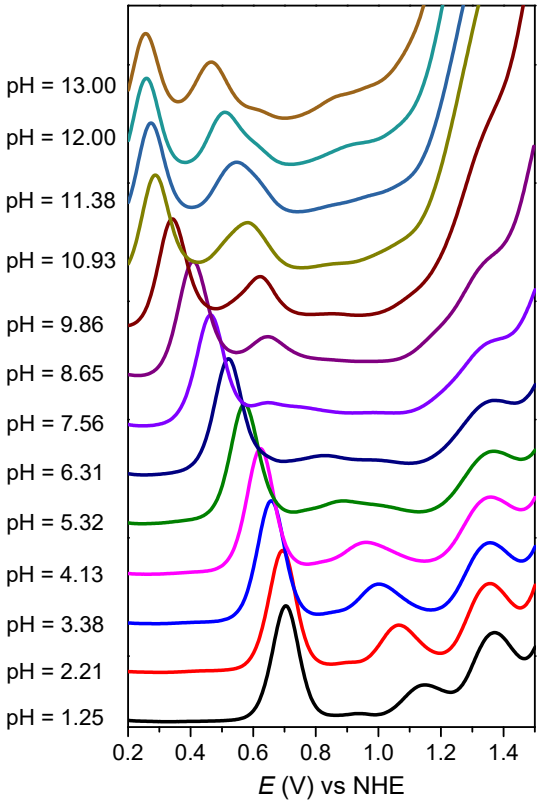


Figure S11. DPV of **2** vs pH.

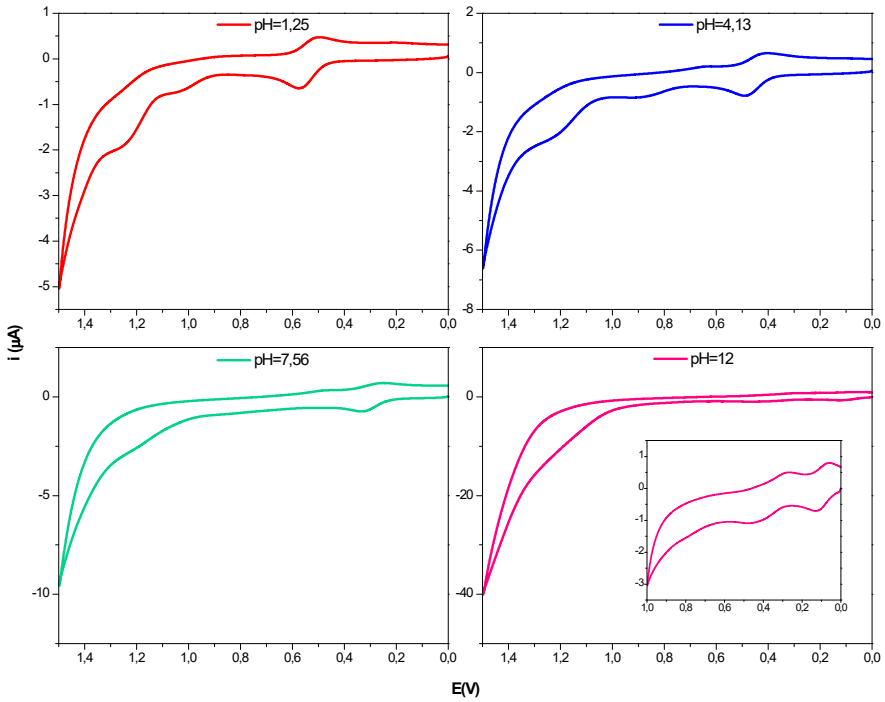


Figure S12. CV of **2** at different pH.

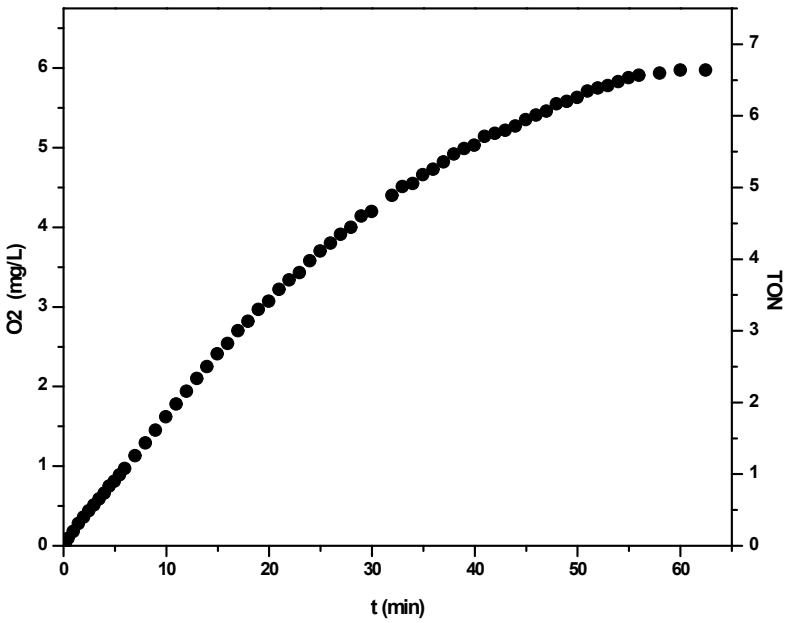


Figure S13. $[O_2]$ vs t for **2** in $HClO_4$ 0.1 M, C= 3.10^{-5} M after adding 30 equivalents of Ce(IV). V_f= 7.5 mL.

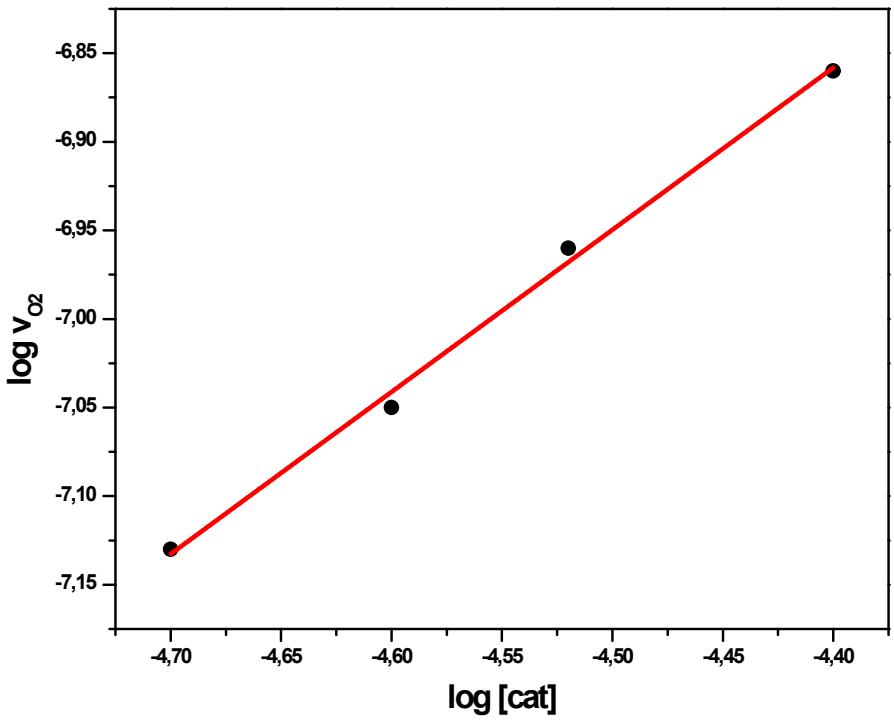


Figure S14. $^{\log v_{O_2}}$ vs. ($^{\log [cat]_0}$) for **2** in $HClO_4$ 0.1 M at *T*=20°C. $[cat]_0$=2x10^{-5} M, 2.5x10^{-5} M, 3x10^{-5} M y 4.10^{-5} M. $[Ce(IV)]_0$=8.4x10^{-3} M, 1.05x10^{-2} M, 1.26x10^{-2} M y 1.68x10^{-2} M. V_f=7,5 ml.

Table S4. Energies and percent contributions of selected MOs of complexes 1, 2 and 3 in their ground state.

Complex 1	E (eV)	Ru	dmapy	py	dmobpy	Cl
L+4	-1.45	1	8	91	0	0
L+3	-1.61	2	0	37	61	0
L+2	-2.29	5	28	27	41	0
L+1	-2.36	5	27	67	0	1
LUMO	-2.39	1	21	23	55	0
HOMO	-5.41	59	30	2	2	7
H-1	-5.45	71	2	11	7	9
H-2	-5.63	74	1	7	17	1
H-3	-6.52	11	68	2	1	19
H-4	-7.09	2	24	29	1	44

Complex 2	E (eV)	Ru	dmapy	py	dmobpy	H_2O
L+4	-1.53	1	9	91	0	0
L+3	-1.67	1	1	48	50	0
L+2	-2.35	4	17	17	62	0
L+1	-2.44	1	31	33	35	0
LUMO	-2.50	5	27	67	0	1
HOMO	-5.61	58	37	1	2	1
H-1	-5.77	77	1	8	13	0
H-2	-5.84	71	2	12	14	0
H-3	-6.73	25	69	4	1	2
H-4	-7.24	1	44	52	3	0

Complex 3	E (eV)	Ru	dmapy	py	dmobpy	CH_3CN
L+4	-1.52	1	8	91	0	0
L+3	-1.67	1	0	41	58	0
L+2	-2.38	4	22	21	53	1
L+1	-2.45	1	27	29	44	0
LUMO	-2.47	3	28	67	0	1
HOMO	-5.75	50	44	1	2	3
H-1	-5.87	77	2	9	11	2
H-2	-5.93	69	2	10	16	3
H-3	-6.8	30	62	4	1	3
H-4	-7.25	1	44	52	3	0

Table S5. Selected singlet excited state transitions with their group contributions for complex 1 obtained from TD-DFT calculations in ethanol.

No.	Wavelength (nm)	Osc. Strength	Major contributions
6	516.7	0.0632	H-2->L+1 (37%) HOMO->L+2 (45%)
7	504.0	0.0856	H-2->L+2 (40%) H-1->LUMO (12%) H-1->L+2 (15%) HOMO->L+1 (26%)
8	491.4	0.1263	H-2->LUMO (85%)
18	367.5	0.0584	H-2->L+5 (15%) H-1->L+5 (61%)
27	324.9	0.1095	H-2->L+5 (38%) H-2->L+6 (10%) H-1->L+5 (14%) H-1->L+6 (15%)
32	292.4	0.3654	H-5->L+1 (86%)
47	266.6	0.6334	HOMO->L+7 (24%) HOMO->L+8 (37%)
99	216.5	0.3319	H-8->L+5 (65%)

No.	Ru	dmapy	py	dmobpy	Cl
6	65-->5 (-60)	17-->27 (10)	5-->45 (40)	8-->23 (15)	5-->0 (-5)
7	69-->4 (-65)	9-->26 (17)	7-->37 (30)	11-->33 (22)	5-->0 (-5)
8	73-->2 (-71)	2-->21 (19)	7-->25 (18)	16-->52 (36)	2-->0 (-2)
18	69-->8 (-61)	6-->4 (-2)	9-->51 (42)	9-->36 (27)	7-->0 (-7)
27	66-->6 (-60)	5-->5 (0)	9-->39 (30)	13-->50 (37)	7-->0 (-7)
32	6-->6 (0)	21-->26 (5)	29-->66 (37)	9-->1 (-8)	35-->1 (-34)
47	44-->23 (-21)	26-->28 1	10-->24 (14)	5-->23 (18)	15-->2 (-13)
99	6-->10 (4)	11-->7 (-4)	6-->45 (39)	71-->38 (-33)	6-->1 (-5)

Table S6. Selected singlet excited state transitions with their group contributions for complex 2 obtained from TD-DFT calculations in ethanol.

No.	Wavelength (nm)	Osc. Strength	Major contributions
2	511.6	0.0638	HOMO->LUMO (78%)
	490.6	0.0747	H-2->LUMO (31%)
			HOMO->L+1 (18%)
5			HOMO->L+2 (47%)
8	459.2	0.1771	H-2->L+1 (81%)
			H-1->L+2 (11%)
18	349.5	0.0454	H-1->L+5 (73%)
27	310.3	0.0006	H-1->L+7 (22%)
			H-1->L+10 (12%)
			H-1->L+12 (55%)
32	279.1	0.0004	H-5->LUMO (95%)
47	257.8	0.2246	H-7->L+1 (19%)
			H-7->L+2 (14%)
			H-6->L+2 (49%)
99	206.2	0.0059	H-11->L+1 (53%)
			H-10->L+2 (35%)

No.	Ru	dmapy	py	dmobpy	H_2O
2	60-->5 (-55)	31-->26 (-5)	3-->60 (57)	4-->8 (4)	1-->1 (0)
5	61-->5 (-56)	26-->22 (-4)	5-->36 (31)	6-->36 (30)	1-->0 (-1)
8	71-->2 (-69)	3-->29 (26)	11-->32 (21)	14-->38 (24)	0-->0 (0)
18	74-->9 (-65)	6-->2 (-4)	8-->42 (34)	12-->46 (34)	0-->1 1
27	74-->67 (-7)	4-->8 (4)	8-->7 (-1)	14-->12 (-2)	0-->6 (6)
32	0-->5 (5)	0-->27 (27)	0-->67 (67)	99-->0 (-99)	0-->1 1
47	6-->4 (-2)	1-->20 (19)	5-->21 (16)	89-->55 (-34)	0-->0 (0)
99	4-->2 (-2)	3-->25 (22)	47-->30 (-17)	47-->43 (-4)	0-->0 (0)

Table S7. Selected singlet excited state transitions with their group contributions for complex 3 obtained from TD-DFT calculations in ethanol.

No.	Wavelength (nm)	Osc. Strength	Major contributions
2	477.2	0.0103	H-2->LUMO (79%) HOMO->L+2 (15%)
6	463.8	0.0589	H-2->LUMO (17%) HOMO->L+1 (12%) HOMO->L+2 (66%)
8	445.6	0.1695	H-2->L+1 (86%)
20	331.8	0.0678	H-3->LUMO (49%) H-2->L+5 (24%) H-1->L+6 (19%)
27	308.1	0.1194	H-2->L+5 (51%) H-1->L+6 (21%)
28	295.3	0.4253	H-4->LUMO (91%)
49	254.1	0.6217	HOMO->L+7 (79%)
68	228.7	0.3324	H-6->L+3 (27%) H-4->L+6 (18%) H-2->L+10 (16%)
97	209.3	0.2122	H-7->L+6 (81%)

No.	Ru	dmapy	py	dmobpy	CH_3CN
2	65-->3 (-62)	10-->27 (17)	9-->59 (50)	13-->10 (-3)	3-->1 (-2)
6	53-->3 (-50)	37-->23 (-14)	3-->31 (28)	4-->41 (37)	3-->1 (-2)
8	69-->1 (-68)	3-->26 (23)	10-->29 (19)	15-->43 (28)	3-->0 (-3)
20	50-->4 (-46)	34-->16 (-18)	7-->50 (43)	7-->29 (22)	3-->2 (-1)
27	65-->4 (-61)	9-->5 (-4)	10-->38 (28)	13-->50 (37)	3-->3 (0)
28	5-->4 (-1)	41-->27 (-14)	50-->67 (17)	4-->1 (-3)	0-->1 1
49	45-->4 (-41)	41-->53 (12)	4-->33 (29)	7-->7 (0)	3-->2 (-1)
68	30-->10 (-20)	18-->3 (-15)	15-->18 1	35-->42 (7)	2-->27 (25)
97	9-->2 (-7)	4-->6 1	8-->6 (-2)	78-->86 (8)	1-->1 (0)

Complex 1	Complex 2	Complex 3

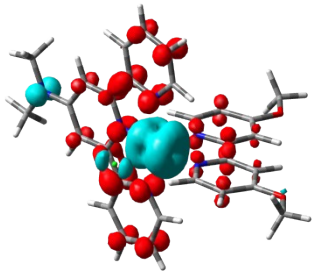
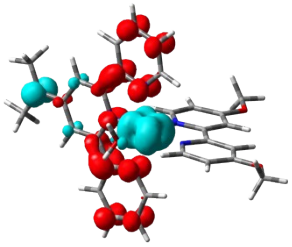
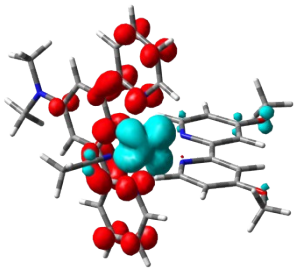
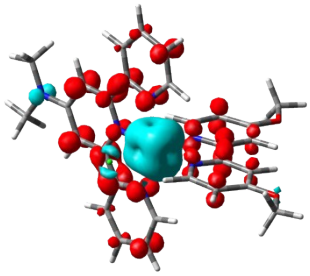
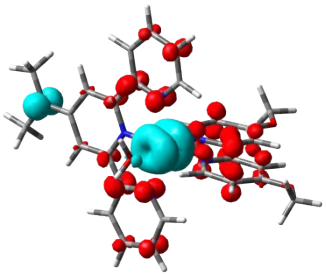
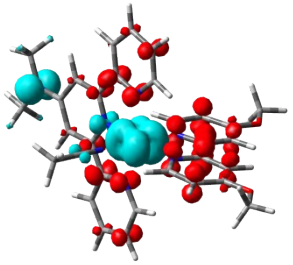
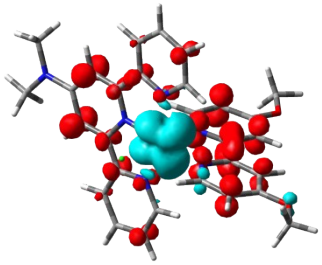
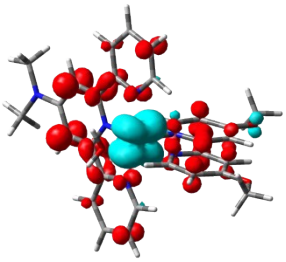
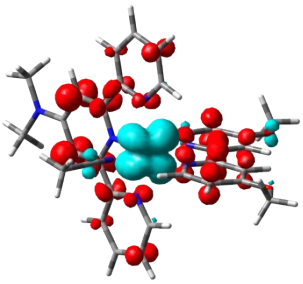
 Transition 6 (λ = 516.7 nm, f = 0.063)	 Transition 2 (λ = 511.6 nm, f = 0.064)	 Transition 2 (λ = 477.2 nm, f = 0.010)
 Transition 7 (λ = 504.0 nm, f = 0.086)	 Transition 5 (λ = 490.6 nm, f = 0.075)	 Transition 6 (λ = 463.8 nm, f = 0.059)
 Transition 8 (λ = 491.4 nm, f = 0.126)	 Transition 8 (λ = 459.2 nm, f = 0.075)	 Transition 8 (λ = 4457 nm, f = 0.117)

Figure S15. EDDM obtained for the three transitions with major contributions to the lowest MLCTs in complexes 1-3.