1-(2-picolyl)-substituted 1,2,3-triazole as novel chelating ligand for the preparation of ruthenium complexes with potential anticancer activity

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SUPPORTING INFORMATION

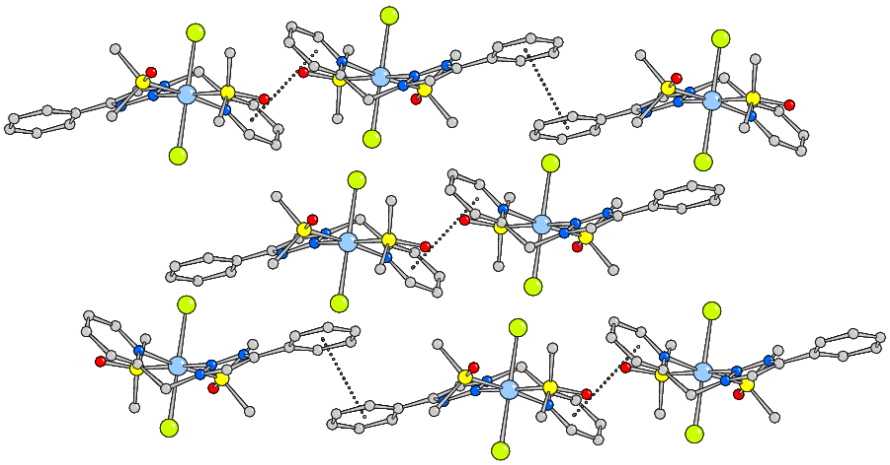

Figure S1. Crystal packing of complex **1** showing 1D arrays of complexes formed by stacking interactions between phenyl rings and between pyridyl rings of symmetry related complexes.

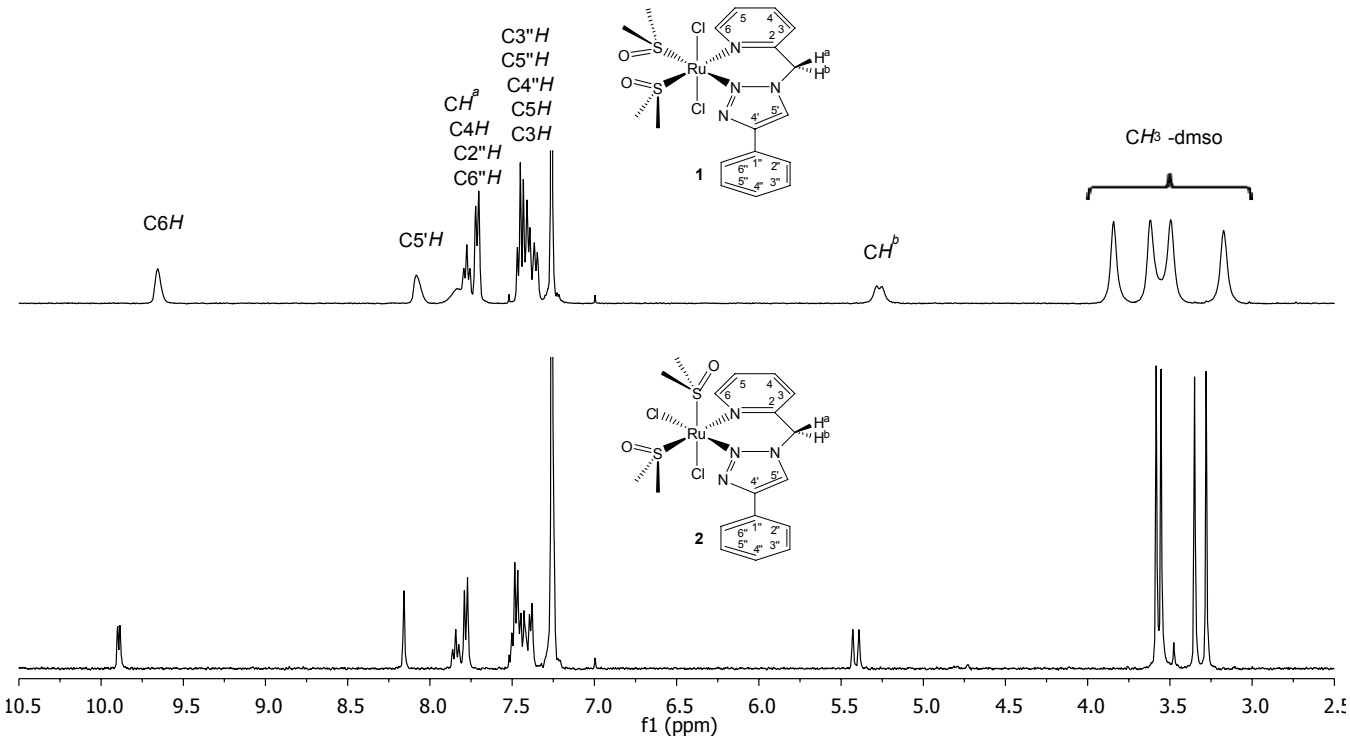

Figure S2. ^{1}H NMR spectra of **1** (top) and **2** (bottom) in $CDCl_3$ at 25.0 °C.

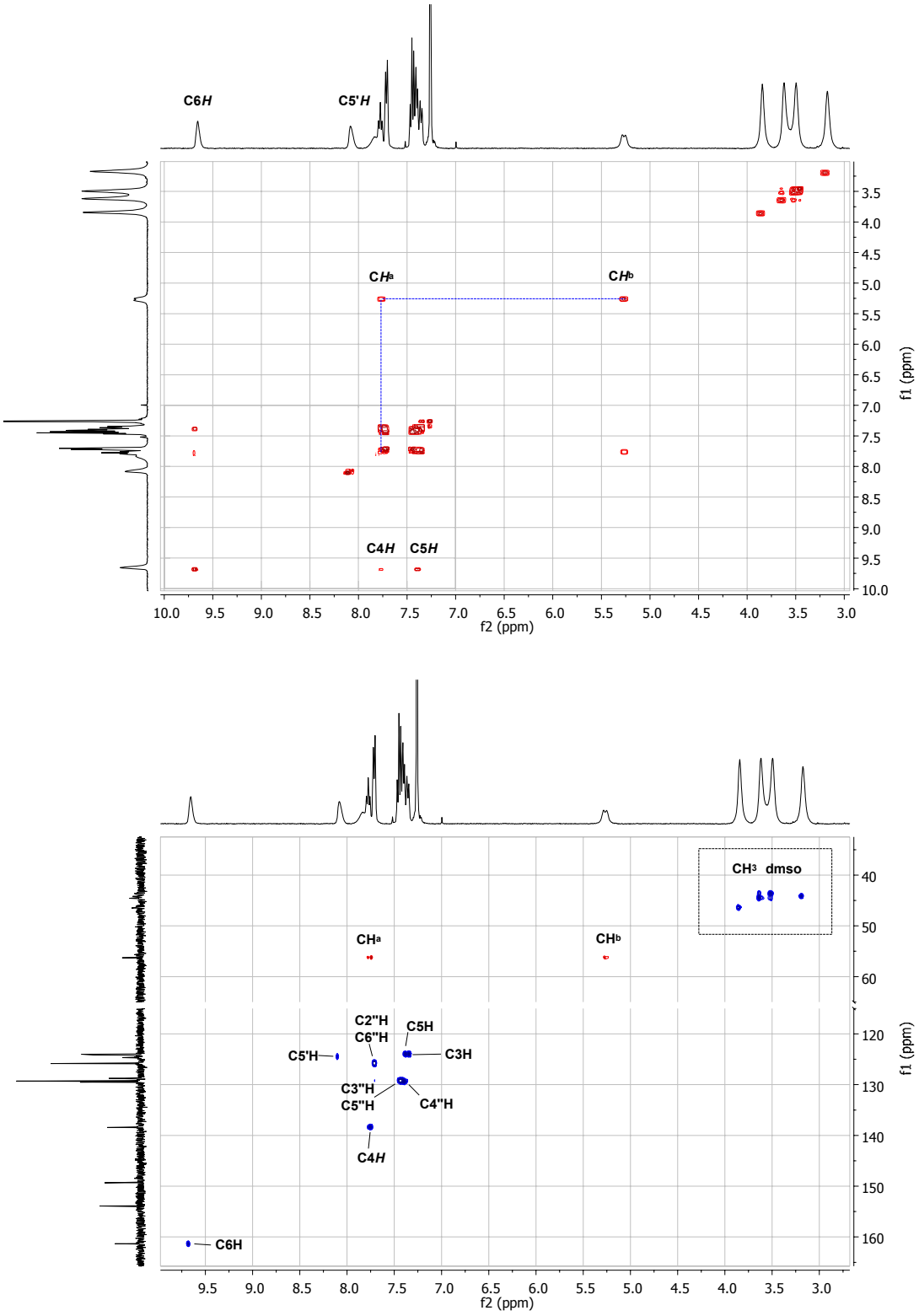

Figure S3. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear phase-sensitive ^{1}H-^{13}C HSQC (bottom, red cross-peaks = CH_2; blue cross-peaks = CH or CH_3) NMR spectra of **1** in $CDCl_3$ at 25.0 °C.

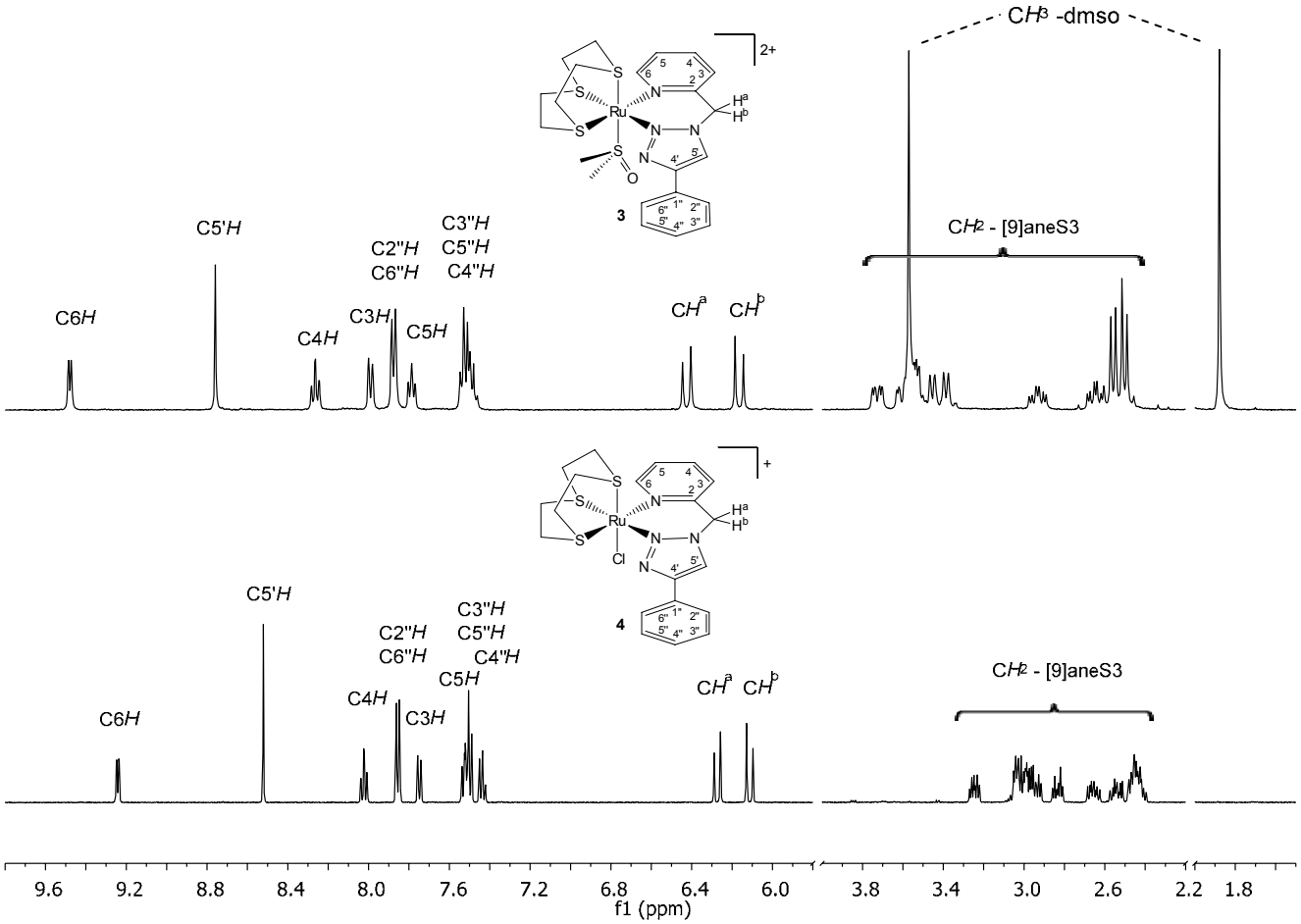

Figure S4. ^{1}H NMR spectra of **3** (top) and **4** (bottom) in CD_3NO_2 at 25.0 °C.

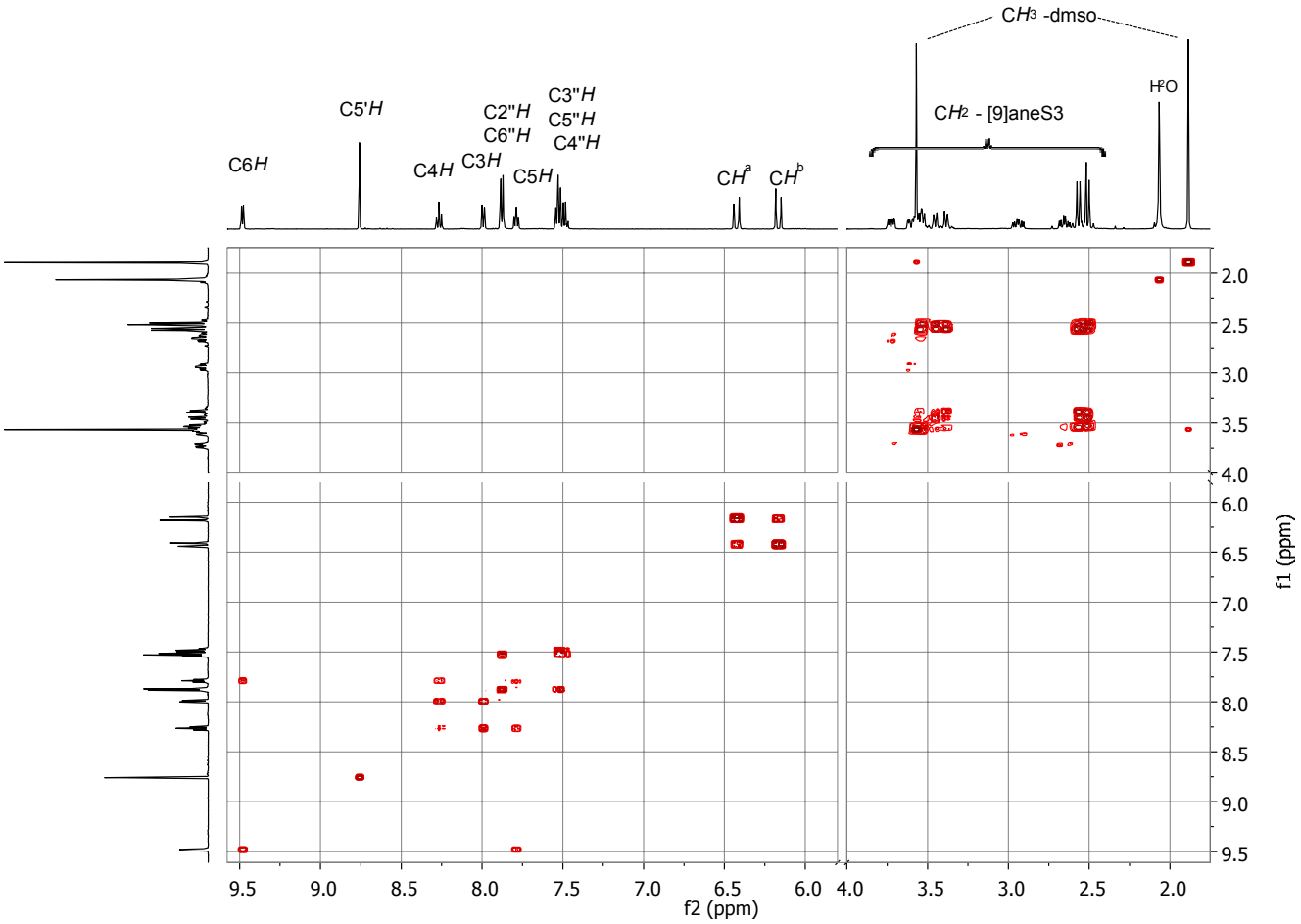

Figure S5. The ^{1}H-^{1}H COSY NMR spectrum of **3** in CD_3NO_2 at 25.0 °C.

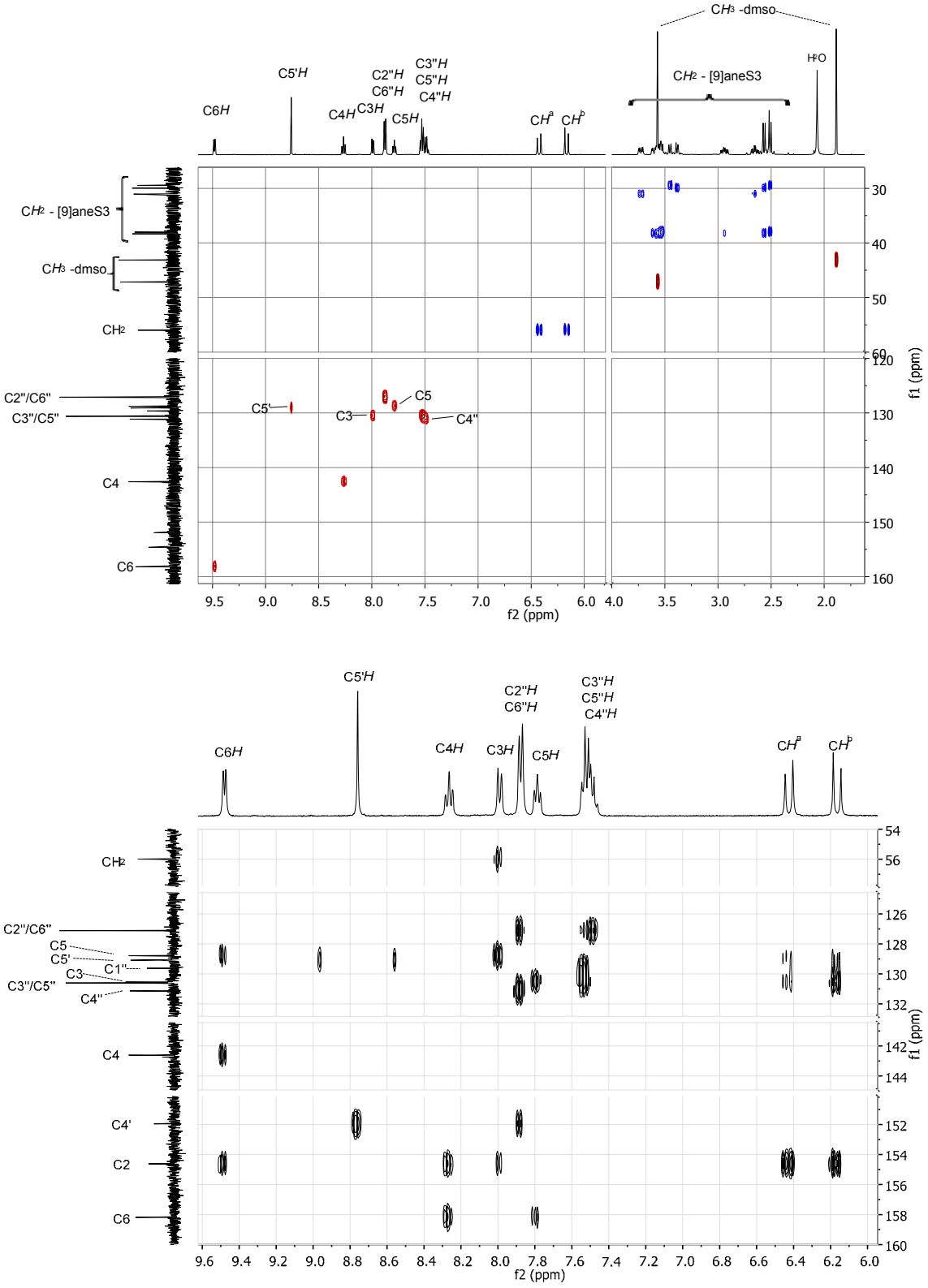

Figure S6. The 2D heteronuclear phase-sensitive ^{1}H-^{13}C HSQC (top, blue cross-peaks = CH_2; red cross-peaks = CH or CH_3) and HMBC (downfield region, bottom) NMR spectra of **3** in CD_3NO_2 at 25.0 °C.

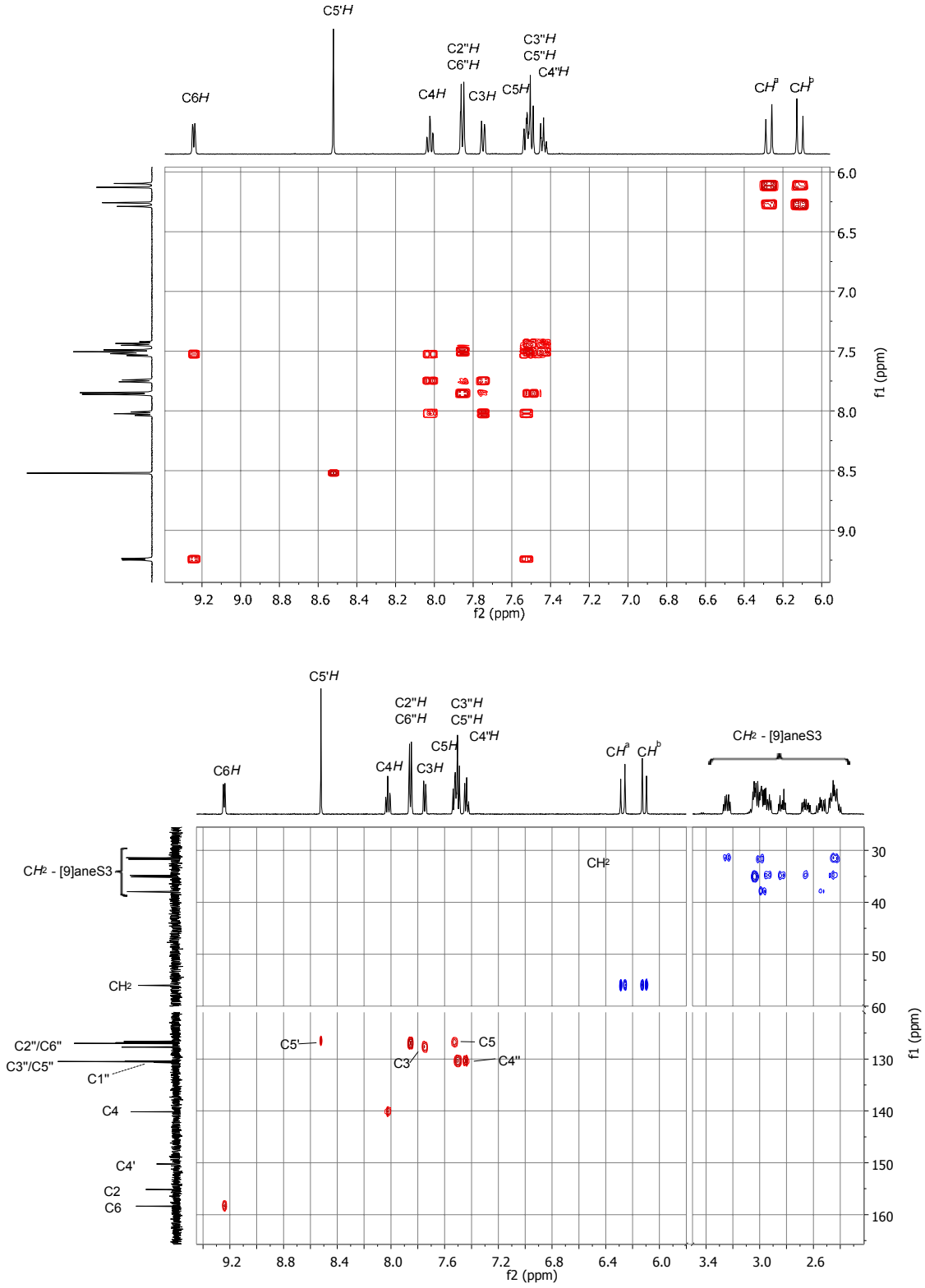

Figure S7. The 2D homonuclear ^{1}H-^{1}H COSY (downfield region, top) and heteronuclear phase-sensitive ^{1}H-^{13}C HSQC (bottom, blue cross-peaks = CH_2; red cross-peaks = CH or CH_3) NMR spectrum of **4** in CD_3NO_2 at 25.0 °C.

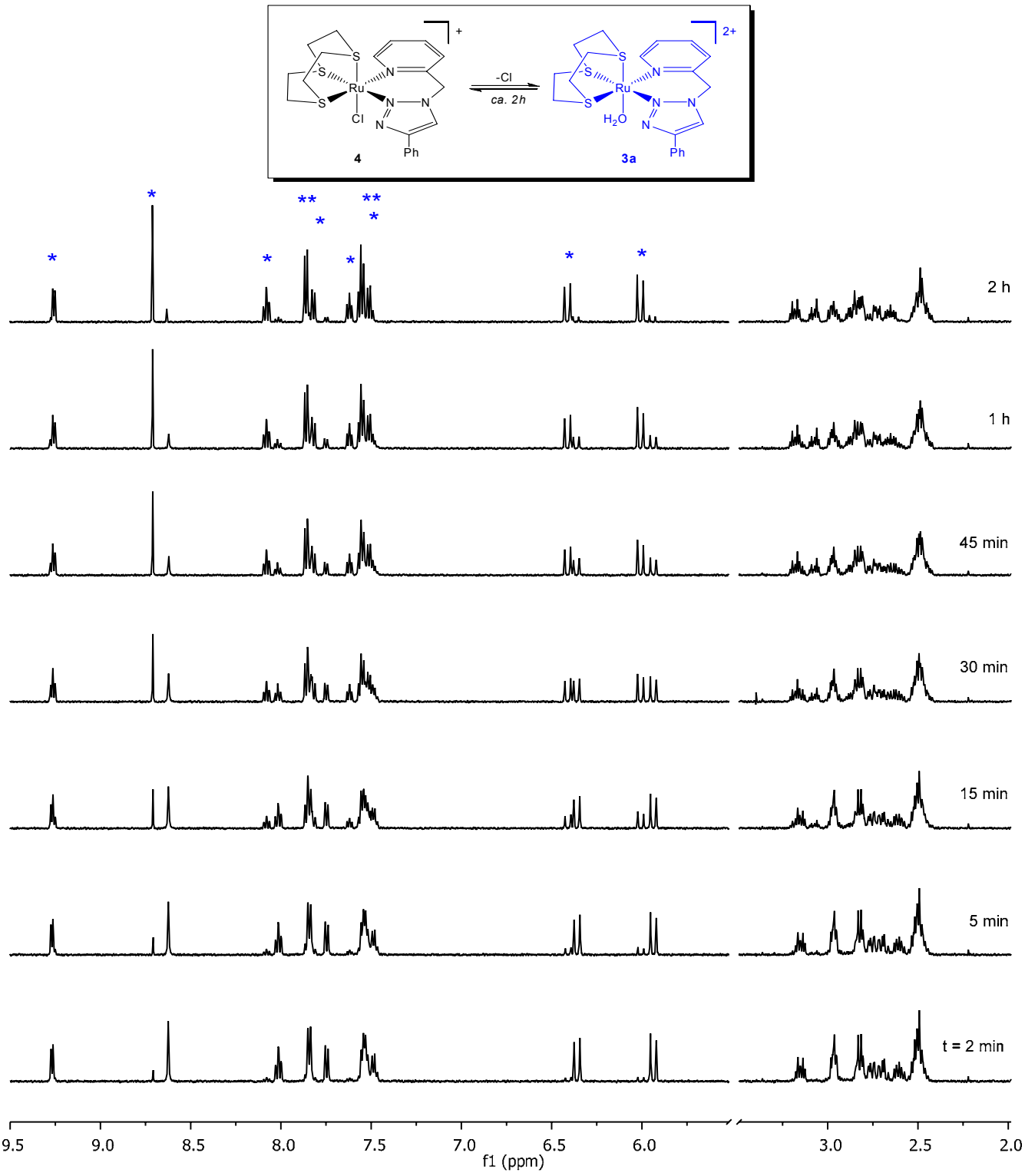

Figure S8. ^{1}H NMR spectral changes during the hydrolysis of **4** (2.0 mM) in D_2O at 25.0 °C. With (*) are indicated the resonances of the **ppt** ligand of the aqua species **3a**.

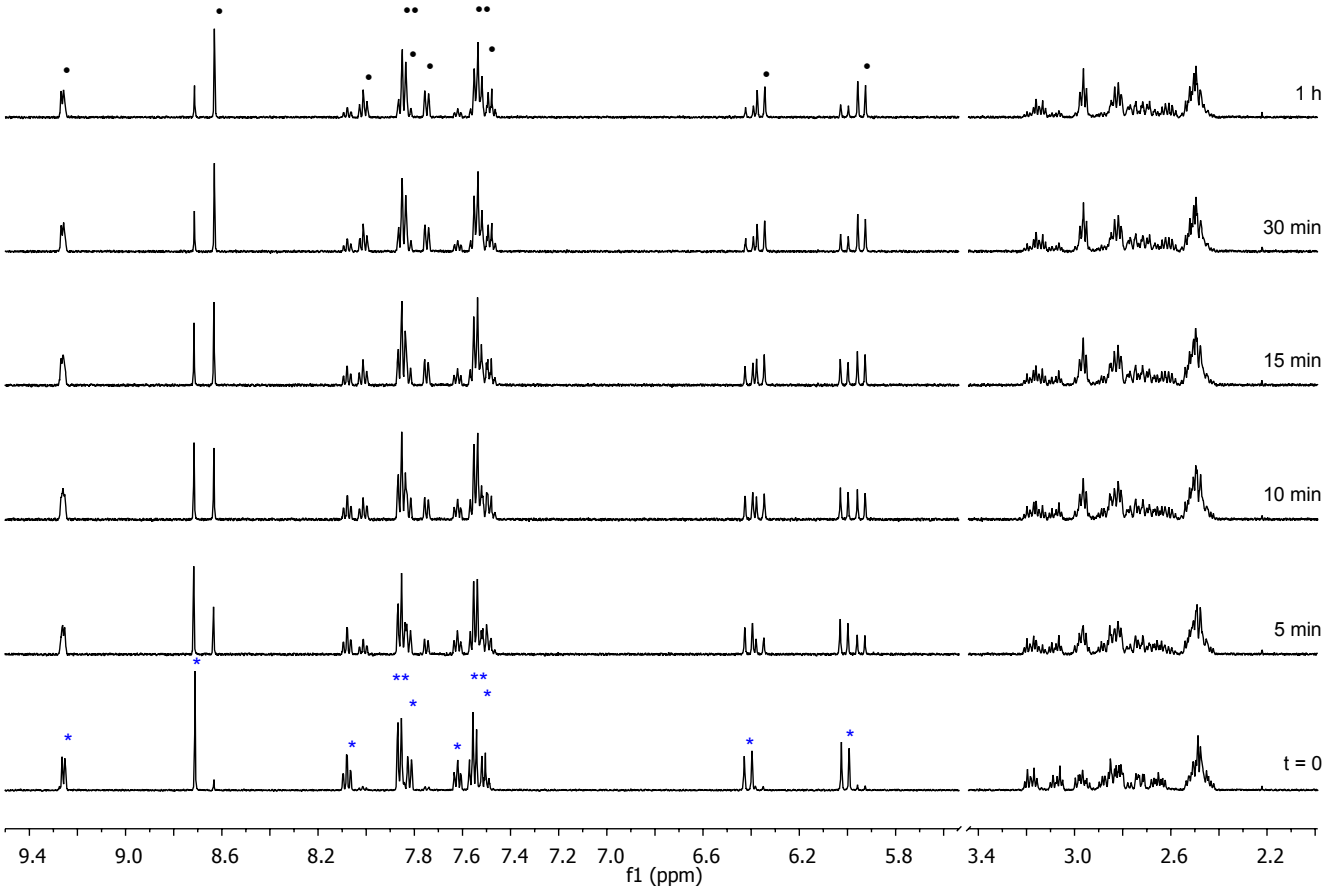

Figure S9. ^{1}H NMR spectral changes upon addition of 100mM NaCl to equilibrated solution (after 1d) of **4** and **3a** in D_2O at 25.0 °C. With (*) and (•) are indicated the resonances of the **ppt** ligand of the aqua species **3a** and of the **4**, respectively.

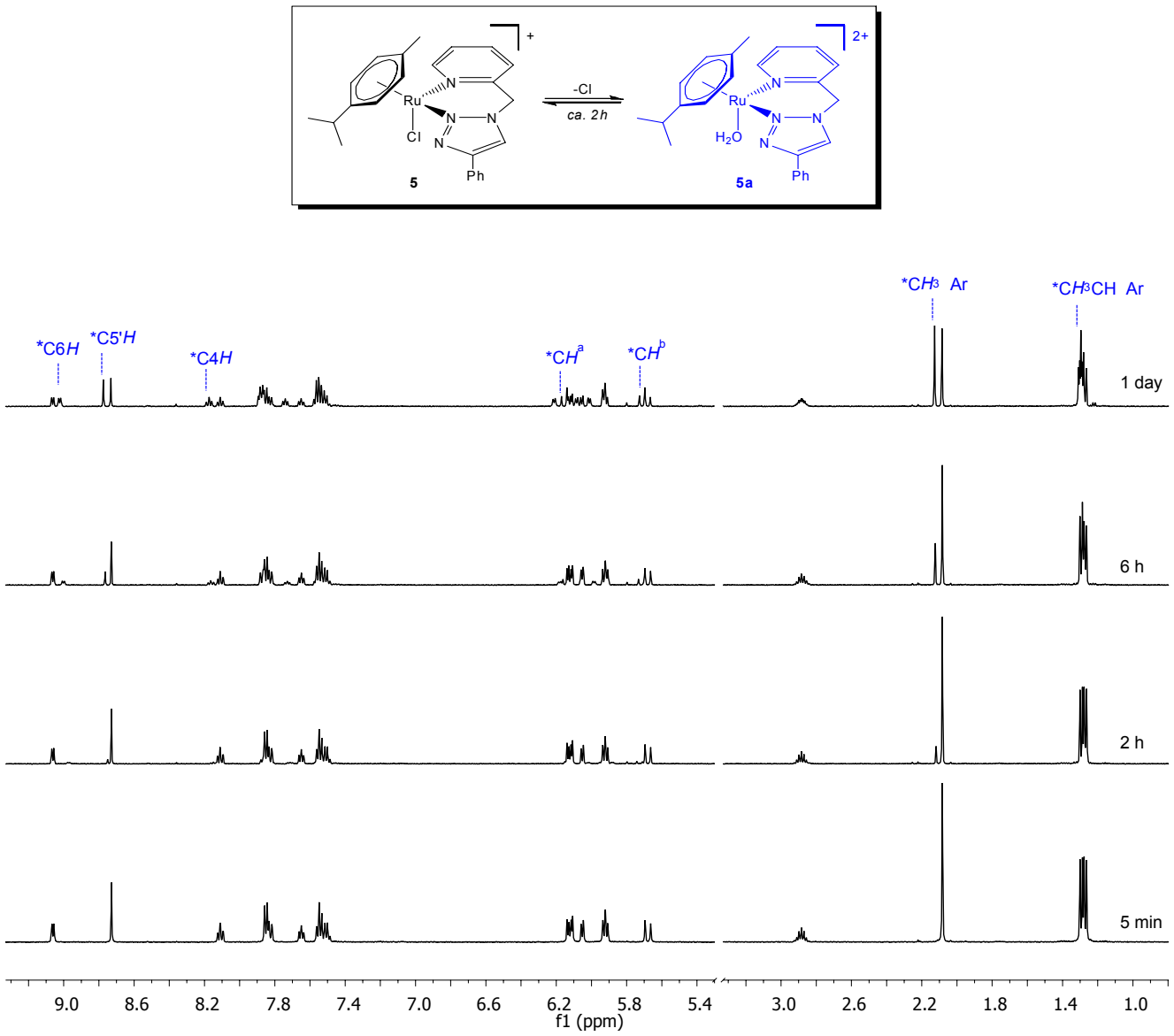

Figure S10. ^{1}H NMR spectral changes during the hydrolysis of **5** (2.0 mM) in D_2O at 25.0 °C. With (*) are indicated selected resonances of the aqua species **5a**.

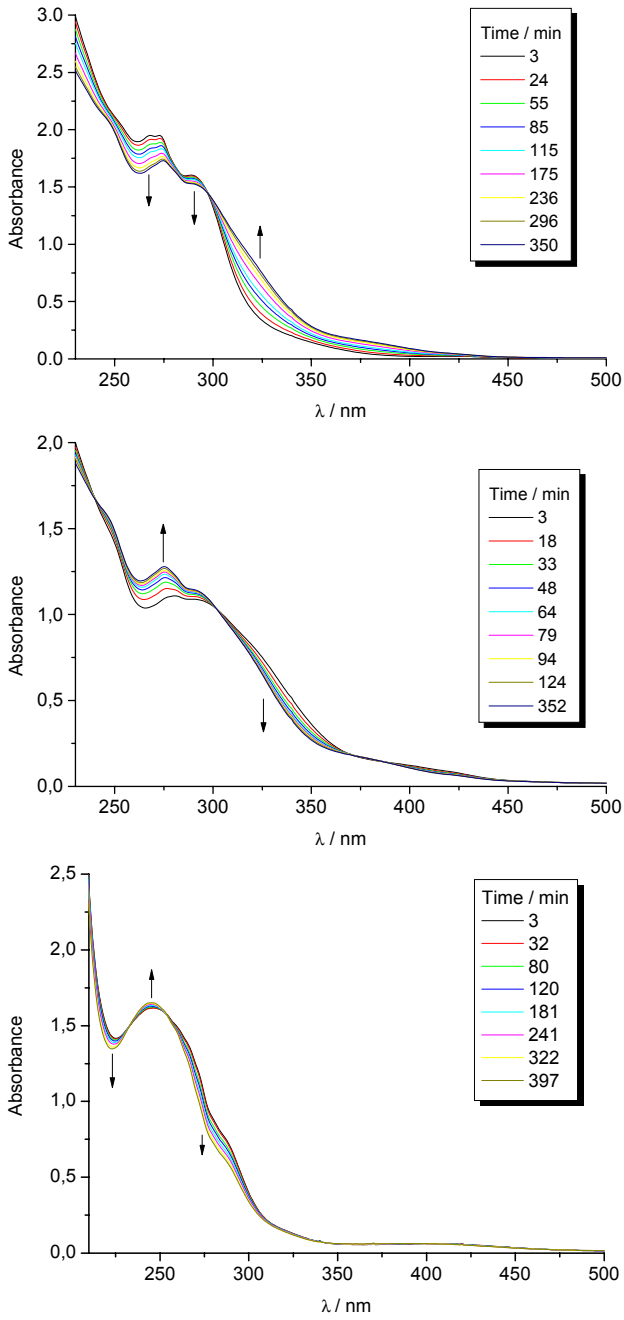

Figure S11. Time evolution of UV-Vis spectra of complexes **3** (top), **4** (middle) and **5** (bottom) in H_2O at 25.0 °C.

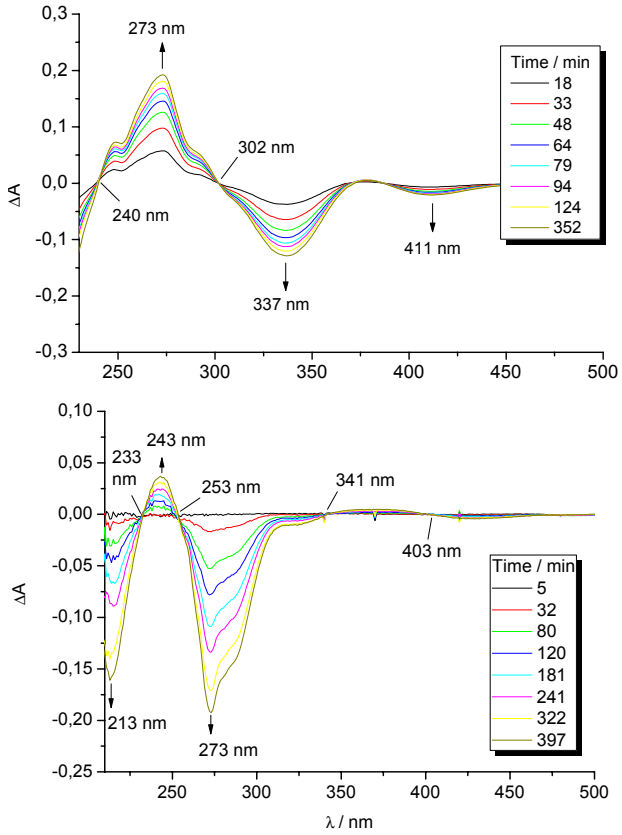

Figure S12. Time evolution of UV-Vis difference spectra during the aquation of complexes **4** (top) and **5** (bottom) in H_2O at 25.0 °C. $\Delta A = A_t - A_0$, where A_t = absorbance at time t and A_0 = absorbance at $t = 2$ min (i.e. the time at which the first spectrum was recorded).

Table S1. Assignments of ^{1}H resonances (δ) for complexes **1** – **5** in various solvents and for hydrolysis products **3a** and **5a**.

	Free ppt			1		2		3		3a	4		5		5a
	D_2O	**$CDCl_3$**	**DMF***	**$CDCl_3$**	**CD_3NO_2**	**$CDCl_3$**	**CD_3NO_2**	**D_2O**	**CD_3NO_2**	**D_2O**	**D_2O**	**CD_3NO_2**	**D_2O**	**DMF***	**D_2O**
3	7.41-7.49	7.20-7.35	7.31-7.43	7.48-7.31	7.65	7.52-7.36	7.67	7.95	7.99	7.82	7.74	7.74	7.94-7.72	8.00	n.a.
4	7.92	7.69	7.87	7.92-7.64	7.97	7.83	8.02	8.23	8.26	8.08	8.01	8.02	8.11	8.25	8.17
5	7.41-7.49	7.20-7.35	7.31-7.43	7.48-7.31	7.53-7.40	7.52-7.36	7.56-7.48	7.74	7.79	7.62	7.49	7.60-7.38	7.65	7.76	7.74
6	8.52	8.61	8.59	9.67	9.56	9.90	9.74	9.34	9.48	9.26	9.27	9.24	9.06	9.24	9.02
CH[a]	5.82	5.70	5.84	7.92-7.64	7.59	7.52-7.36	7.01	6.32	6.42	6.41	6.36	6.28	6.17-6.08	6.48	n.a.
CH[b]				5.26	5.69	5.41	5.87	6.11	6.16	6.01	5.94	6.10	5.68	5.96	5.71
5'	8.37	7.94	8.70	8.11	8.56	8.16	8.58	8.83	8.76	8.71	8.62	8.52	8.72	9.15	8.77
2''/6''	7.83	7.82	7.92-7.98	7.92-7.64	7.87	7.78	7.92	7.89	7.88	7.86	7.84	7.85	7.94-7.72	7.96-7.90	n.a.
3''/5''	7.53	7.41	7.43-7.50	7.48-7.31	7.53-7.40	7.52-7.36	7.56-7.48	7.54	7.59-7.42	7.59-7.53	7.53	7.60-7.38	7.58-7.45	7.58-7.50	n.a.
4''	7.41-7.49	7.20-7.35	7.31-7.43	7.48-7.31	7.53-7.40	7.52-7.36	7.45	7.54	7.59-7.42	7.53-7.48	7.53	7.60-7.38	7.58-7.45	7.49-7.42	n.a.
CH_3 - dmso				3.86/ 3.64/ 3.52/ 3.19	3.78/ 3.52/ 3.37/ 3.17	3.59/ 3.56/ 3.35/ 3.28	3.41/ 3.41/ 3.40/ 3.19	3.54/ 1.99	3.57/ 1.88						

*from the ref.: D. Urankar, B. Pinter, A. Pevec, F. De Proft, I. Turel and J. Košmrlj, *Inorg. Chem.*, 2010, **49**, 4820-4829.

n.a.: not assigned. These resonances are not well resolved since they are overlapped with resonances of **5**.

Table S2. Assignments of ^{13}C resonances (δ) for complexes **1** – **5** in various solvents.

	Free ppt	1		2	3	4	5
	DMF*	**$CDCl_3$**	**CD_3NO_2**	**$CDCl_3$**	**CD_3NO_2**	**CD_3NO_2**	**DMF***
2	156.1	153.9	156.3	151.8	154.6	155.1	154.2
3	122.9	124.0	125.9	124.1	130.5	127.7	127.1
4	138.0	138.4	140.1	138.6	142.6	140.2	141.2
5	123.9	124.2	124.5	124.3	128.8	126.8	126.7
6	150.3	161.4	161.8	159.9	158.2	158.4	159.1
CH_2	55.7	56.3	56.7	56.1	56.0	56.0	55.2
4'	147.7	149.3	149.9	148.8	152.0	150.2	150.1
5'	122.7	124.7	126.9	125.1	129.1	126.6	127.5
1''	132.0	128.8	126.7	128.4	129.6	130.7	129.8
2''/6''	126.0	125.8	126.8	125.6	127.1	127.0	126.1
3''/5''	129.5	129.3	130.4	129.5	130.6	130.5	129.8
4''	128.5	129.5	130.3	129.8	131.1	130.4	129.8
CH_3 - dmso		46.5/44.6/ 44.2/43.7	46.4/44.6/ 44.5/43.8	45.9/45.8 45.3/44.5	47.2/43.1		
CH_2 [9]aneS_3					38.4/38.3/ 38.1/31.1/ 30.0/29.5	37.9/35.1/ 34.9/34.8/ 31.7/31.4	

*from the ref.: D. Urankar, B. Pinter, A. Pevec, F. De Proft, I. Turel and J. Košmrlj, *Inorg. Chem.*, 2010, **49**, 4820-4829.