Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic structure and catalytic aspects of $[Ru(tpm)(bqdi)(Cl/H_2O)]^n$, tpm = tris(1-pyrazolyl)methane and bqdi = *o*-benzoquinonediimine

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Table S1 Experimental (X-ray) and DFT calculated selected bond angles (°) of $\mathbf{1}^{+}$ and $\mathbf{2}^{2+}$ (**Molecule A**)

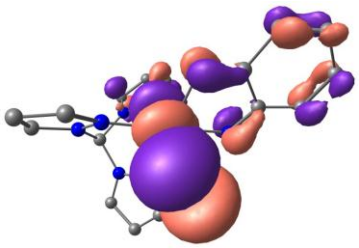
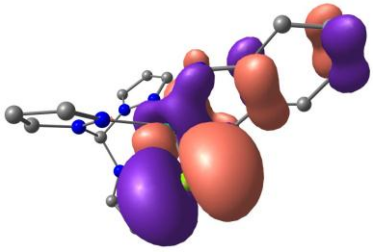
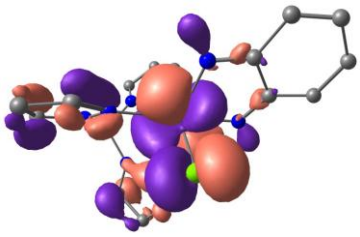
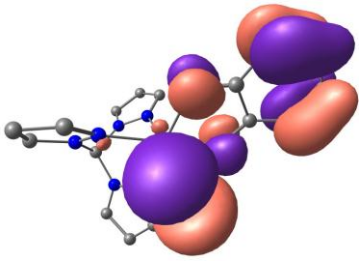
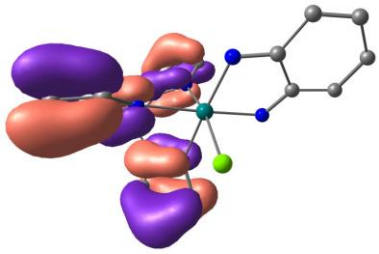
Bond angles	$\mathbf{1}^{+}$		$\mathbf{2}^{2+}$	
	X-ray	DFT	X-ray	DFT
N(1)–Ru(1)–N(2)	77.86(13)	77.115	77.90(19)	76.380
N(1)–Ru(1)–N(3)	175.06(13)	176.707	173.31(19)	175.501
N(1)–Ru(1)–N(5)	95.01(13)	97.209	93.71(18)	94.746
N(1)–Ru(1)–N(7)	98.11(13)	99.850	98.61(18)	99.817
N(2)–Ru(1)–N(3)	97.92(13)	99.793	95.76(17)	99.129
N(2)–Ru(1)–N(5)	92.12(13)	97.154	94.76(17)	94.967
N(2)–Ru(1)–N(7)	175.32(13)	176.782	176.30(17)	176.142
N(3)–Ru(1)–N(5)	82.50(13)	84.242	84.61(17)	85.303
N(3)–Ru(1)–N(7)	85.99(13)	83.219	87.68(17)	84.670
N(5)–Ru(1)–N(7)	85.82(13)	84.234	84.17(16)	84.639
N(9)–Ru(2)–N(10)	-	-	77.57(19)	-
N(9)–Ru(2)–N(11)	-	-	175.70(17)	-
N(9)–Ru(2)–N(13)	-	-	96.79(17)	-
N(9)–Ru(2)–N(15)	-	-	97.11(17)	-
N(10)–Ru(2)–N(11)	-	-	98.68(19)	-
N(10)–Ru(2)–N(13)	-	-	94.28(17)	-
N(10)–Ru(2)–N(15)	-	-	174.30(2)	-
N(11)–Ru(2)–N(13)	-	-	85.53(17)	-
N(11)–Ru(2)–N(15)	-	-	86.71(16)	-
N(13)–Ru(2)–N(15)	-	-	84.19(16)	-
N(1)–Ru(1)–Cl(1)	91.04(10)	89.984	-	-
N(2)–Ru(1)–Cl(1)	91.79(10)	89.994	-	-
N(3)–Ru(1)–Cl(1)	91.66(10)	88.877	-	-
N(5)–Ru(1)–Cl(1)	173.37(9)	170.815	-	-

N(7)–Ru(1)–Cl(1)	90.66(10)	88.926	-	-
N(1)–Ru(1)–O(1)	-	-	89.78(17)	92.384
N(2)–Ru(1)–O(1)	-	-	88.70(16)	88.738
N(3)–Ru(1)–O(1)	-	-	92.24(15)	87.754
N(5)–Ru(1)–O(1)	-	-	175.53(15)	172.569
N(7)–Ru(1)–O(1)	-	-	92.55(15)	92.092
N(9)–Ru(2)–O(2)	-	-	86.36(16)	-
N(10)–Ru(2)–O(2)	-	-	88.96(16)	-
N(11)–Ru(2)–O(2)	-	-	91.49(16)	-
N(13)–Ru(2)–O(2)	-	-	175.90(15)	-
N(15)–Ru(2)–O(2)	-	-	92.83(15)	-

Table S2 Composition and energies of selected molecular orbitals of $\mathbf{1}^{+}$ (S=0)

MO	Energy (eV)	Ru	tpm	bqdi	Cl
HOMO–10	–10.886	0.05	0.91	0.04	0.01
HOMO–9	–10.791	0.05	0.92	0.01	0.03
HOMO–8	–10.729	0.01	0.97	0.00	0.02
HOMO–7	–10.365	0.21	0.21	0.02	0.56
HOMO–6	–10.199	0.00	1.00	0.00	0.00
HOMO–5	–9.885	0.21	0.19	0.34	0.26
HOMO–4	–9.693	0.39	0.08	0.15	0.38
HOMO–3	–9.105	0.02	0.03	0.49	0.46
HOMO–2	–8.952	0.71	0.16	0.05	0.07
HOMO–1	–8.521	0.34	0.05	0.14	0.47
HOMO	–8.081	0.58	0.08	0.10	0.24
LUMO	–5.919	0.23	0.07	0.68	0.03
LUMO+1	–3.868	0.04	0.95	0.01	0.00
LUMO+2	–3.837	0.04	0.95	0.01	0.00
LUMO+3	–3.306	0.47	0.28	0.08	0.17
LUMO+4	–3.113	0.02	0.96	0.02	0.00
LUMO+5	–2.706	0.09	0.04	0.87	0.01
LUMO+6	–2.657	0.37	0.24	0.39	0.00
LUMO+7	–2.368	0.21	0.12	0.67	0.00
LUMO+8	–2.148	0.08	0.91	0.01	0.00
LUMO+9	–2.125	0.52	0.27	0.21	0.01
LUMO+10	–1.814	0.43	0.48	0.08	0.01

Contour plots of selected MOs of **1**$^{+}$

		
HOMO	HOMO–1	HOMO–2
		
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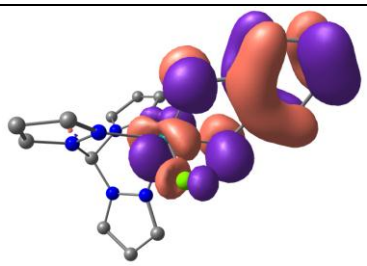
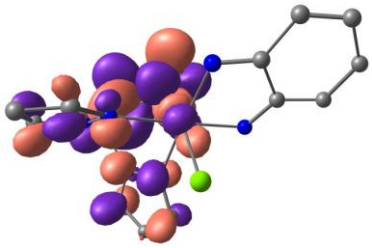
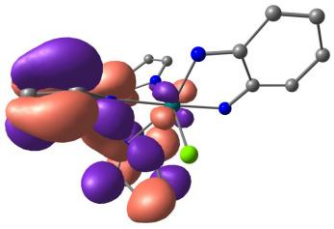
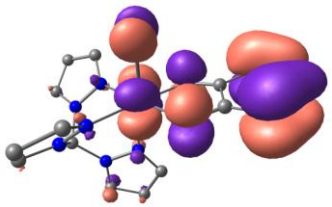
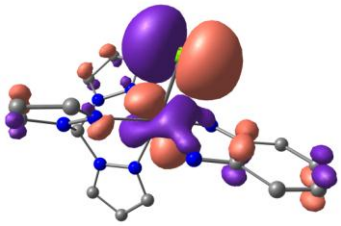
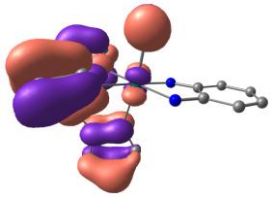
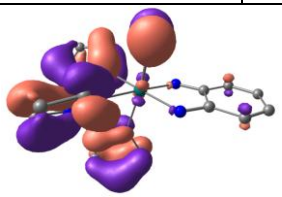
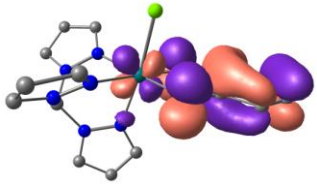
		
LUMO	LUMO+1	LUMO+2

Table S3 Composition and energies of selected molecular orbitals of $\mathbf{1}^{2+}$ (S=1/2)

MO	Energy (eV)	Ru	tpm	bqdi	Cl
		α-spin			
HOMO–10	–14.6975	0.33	0.37	0.05	0.24
HOMO–9	–14.5133	0.07	0.81	0.04	0.08
HOMO–8	–14.3391	0.44	0.10	0.23	0.23
HOMO–7	–14.1125	0.01	0.88	0.01	0.11
HOMO–6	–14.0853	0.17	0.80	0.02	0.01
HOMO–5	–13.8708	0.02	0.81	0.04	0.13
HOMO–4	–13.3821	0.05	0.79	0.02	0.15
HOMO–3	–13.3465	0.35	0.48	0.03	0.15
HOMO–2	–13.2836	0.17	0.25	0.17	0.41
HOMO–1	–12.9979	0.35	0.08	0.06	0.51
SOMO	–12.8858	0.25	0.06	0.64	0.06
LUMO	–9.9513	0.12	0.05	0.82	0.01
LUMO+1	–7.8701	0.47	0.26	0.09	0.18
LUMO+2	–7.3841	0.38	0.33	0.29	0.00
LUMO+3	–7.3063	0.15	0.78	0.06	0.00
LUMO+4	–7.1329	0.03	0.95	0.01	0.01
LUMO+5	–6.3857	0.01	0.97	0.02	0.00
LUMO+6	–6.3618	0.04	0.03	0.93	0.00
LUMO+7	–6.1713	0.02	0.03	0.95	0.00
LUMO+8	–5.2937	0.40	0.35	0.24	0.00
LUMO+9	–5.1171	0.05	0.94	0.01	0.00
LUMO+10	–4.9653	0.22	0.61	0.16	0.00

		β-spin			
HOMO–10	–14.8028	0.07	0.76	0.12	0.05
HOMO–9	–14.5829	0.19	0.46	0.06	0.29
HOMO–8	–14.2159	0.09	0.7	0.05	0.16
HOMO–7	–14.1533	0.45	0.09	0.19	0.27
HOMO–6	–14.0289	0.00	0.96	0.00	0.03
HOMO–5	–14.0248	0.18	0.79	0.02	0.00
HOMO–4	–13.6657	0.06	0.44	0.12	0.37
HOMO–3	–13.3519	0.00	0.99	0.00	0.01
HOMO–2	–13.1935	0.45	0.37	0.03	0.15
HOMO–1	–12.9514	0.00	0.02	0.74	0.24
HOMO	–12.7761	0.40	0.08	0.09	0.43
LUMO	–10.4672	0.65	0.10	0.07	0.18
LUMO+1	–9.8914	0.15	0.05	0.78	0.02
LUMO+2	–7.6124	0.47	0.27	0.09	0.17
LUMO+3	–7.2122	0.07	0.87	0.05	0.00
LUMO+4	–7.1117	0.04	0.93	0.01	0.01
LUMO+5	–7.0391	0.43	0.28	0.30	0.00
LUMO+6	–6.3719	0.01	0.96	0.03	0.00
LUMO+7	–6.3495	0.04	0.03	0.93	0.00
LUMO+8	–6.1384	0.03	0.04	0.93	0.00
LUMO+9	–5.2758	0.42	0.31	0.26	0.00
LUMO+10	–5.1150	0.05	0.94	0.01	0.00

Contour plots of selected MOs of $\mathbf{1}^{2+}$

		
HOMO(α)	HOMO–1(α)	HOMO–4(α)
		
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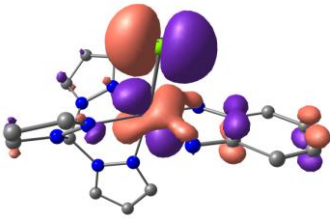	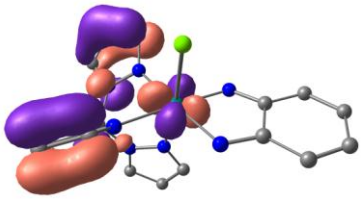	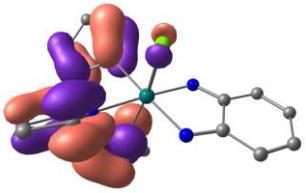
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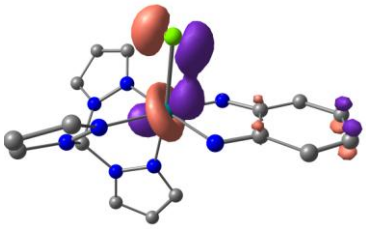	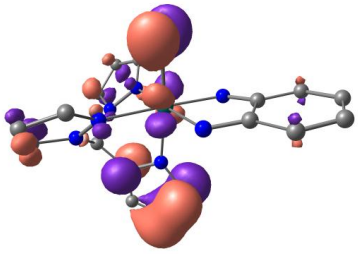	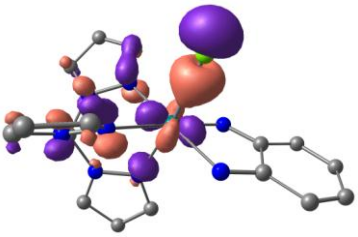
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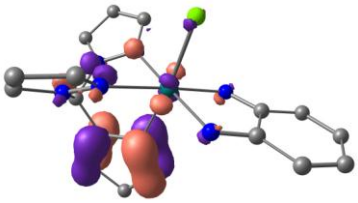
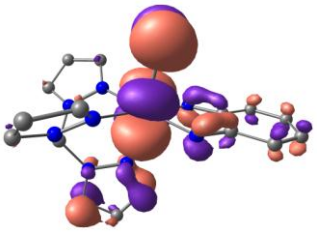
		
HOMO–10(β)	LUMO(β)	

Table S4 Composition and energies of selected molecular orbitals of **1** (*S*=1/2)

MO	Energy (eV)	Ru	tpm	bqdi	Cl
			α-spin		
HOMO–10	–7.7071	0.00	0.88	0.11	0.00
HOMO–9	–7.6410	0.00	0.55	0.44	0.00
HOMO–8	–7.2949	0.00	1.00	0.00	0.00
HOMO–7	–6.5863	0.18	0.14	0.00	0.67
HOMO–6	–6.0203	0.22	0.09	0.21	0.48
HOMO–5	–5.9702	0.35	0.08	0.15	0.43
HOMO–4	–5.2271	0.00	0.00	0.60	0.37
HOMO–3	–5.0360	0.68	0.15	0.00	0.13
HOMO–2	–4.8159	0.45	0.08	0.11	0.36
HOMO–1	–4.2194	0.59	0.11	0.15	0.16
SOMO	–3.2790	0.19	0.08	0.70	0.00
LUMO	–0.8566	0.05	0.94	0.00	0.00
LUMO+1	–0.7725	0.06	0.93	0.00	0.00
LUMO+2	–0.1453	0.00	1.00	0.00	0.00
LUMO+3	0.5513	0.07	0.93	0.00	0.00
LUMO+4	0.6699	0.43	0.36	0.08	0.13
LUMO+5	0.8003	0.62	0.31	0.06	0.00
LUMO+6	1.0795	0.33	0.54	0.12	0.00
LUMO+7	1.1285	0.15	0.46	0.38	0.00
LUMO+8	1.2558	0.24	0.55	0.21	0.00
LUMO+9	1.2896	0.32	0.55	0.12	0.00
LUMO+10	1.4493	0.12	0.86	0.00	0.00

		β-spin			
HOMO–10	–7.6927	0.98	0.00	0.00	0.00
HOMO–9	–7.3820	0.12	0.00	0.77	0.07
HOMO–8	–7.2946	0.00	0.99	0.00	0.00
HOMO–7	–7.1896	0.00	0.19	0.74	0.00
HOMO–6	–6.5468	0.17	0.14	0.00	0.68
HOMO–5	–5.9520	0.20	0.09	0.17	0.54
HOMO–4	–5.7634	0.21	0.06	0.14	0.59
HOMO–3	–4.9623	0.76	0.15	0.00	0.00
HOMO–2	–4.8839	0.14	0.00	0.45	0.36
HOMO–1	–4.5275	0.51	0.09	0.11	0.29
HOMO	–3.9936	0.49	0.10	0.33	0.08
LUMO	–1.5230	0.14	0.19	0.65	0.00
LUMO+1	–0.7997	0.07	0.88	0.00	0.00
LUMO+2	–0.7674	0.06	0.93	0.00	0.00
LUMO+3	–0.1396	0.00	1.00	0.00	0.00
LUMO+4	0.5554	0.07	0.93	0.00	0.00
LUMO+5	0.7320	0.43	0.37	0.08	0.12
LUMO+6	0.8117	0.62	0.32	0.06	0.00
LUMO+7	1.0993	0.23	0.74	0.00	0.00
LUMO+8	1.2727	0.27	0.67	0.06	0.00
LUMO+9	1.3293	0.49	0.28	0.21	0.00
LUMO+10	1.3696	0.29	0.47	0.24	0.00

Contour plots of selected MOs of **1**

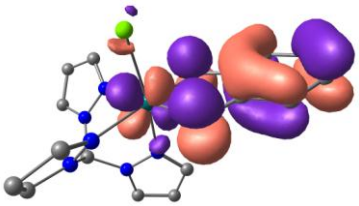
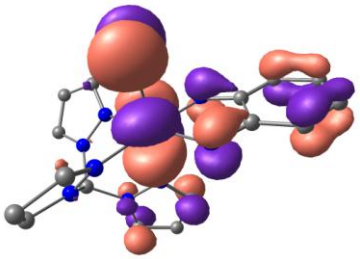
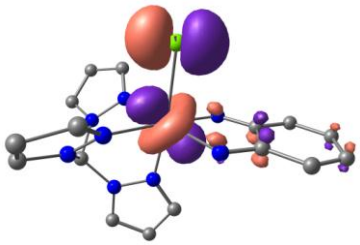
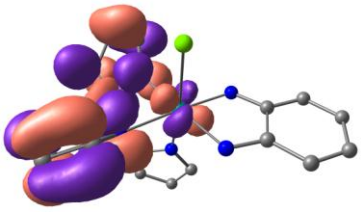
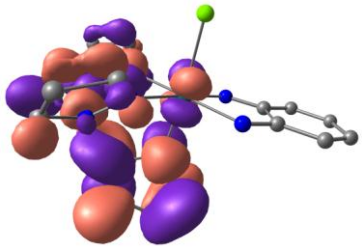
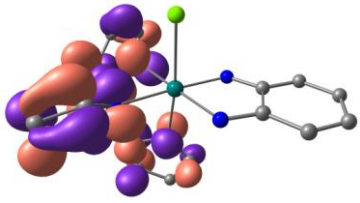
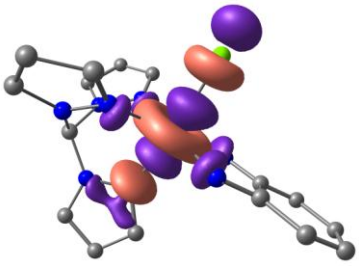
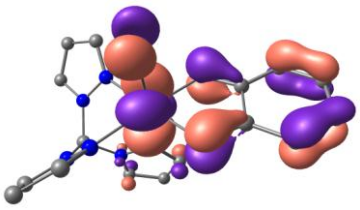
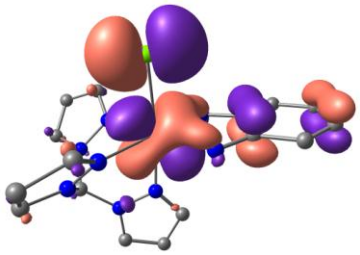
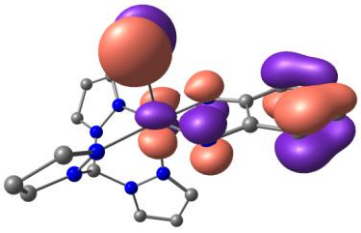
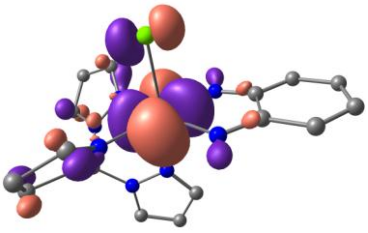
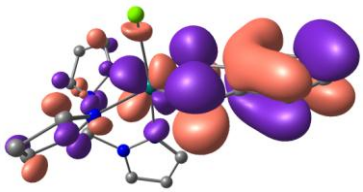
		
HOMO(α)	HOMO−1(α)	HOMO−2(α)
		
LUMO(α)	LUMO+1(α)	LUMO+2(α)
		
LUMO+4(α)	HOMO(β)	HOMO−1(β)
		
HOMO−2(β)	HOMO−3(β)	LUMO(β)

Table S5 DFT calculated selected bond distances (Å) of $\mathbf{1}^{n}$ (n = 2+, 1+, 0)

Bond distances	DFT		
	$\mathbf{1}^{+}$	$\mathbf{1}^{2+}$	**1**
Ru(1)–N(1)	2.020	2.034	2.0527
Ru(1)–N(2)	2.020	2.033	2.0525
Ru(1)–N(3)	2.139	2.134	2.132
Ru(1)–N(5)	2.127	2.116	2.086
Ru(1)–N(7)	2.139	2.134	2.129
Ru(1)–Cl(1)	2.405	2.328	2.452
C(1)–N(1)	1.318	1.312	1.342
C(6)–N(2)	1.318	1.312	1.343
C(1)–C(2)	1.434	1.435	1.419
C(2)–C(3)	1.364	1.363	1.383
C(3)–C(4)	1.442	1.451	1.416
C(4)–C(5)	1.364	1.363	1.383
C(5)–C(6)	1.434	1.435	1.419
C(6)–C(1)	1.468	1.484	1.453

Table S6 TD-DFT calculated electronic transitions of $\mathbf{2}^{2+}$ (**Molecule A**)

Energy (eV)	λ (nm)	f^a	$\lambda_{expt.}$ (nm) (ε ($dm^3mol^{-1}cm^{-1}$))	Transition	Character
1.86	667.71	0.0212	720(1210)	HOMO-2→LUMO (0.60)	Ru(dπ)→Q(π*)
2.87	432.48	0.3620	497(19800)	HOMO-3→LUMO (0.55)	Ru(dπ)→Q(π*)
4.13	300.43	0.0313	316(5500)	HOMO→LUMO+2 (0.50)	Ru(dπ)→tpm(π*)

[a]Oscillator strength

Table S7 Composition and energies of selected molecular orbitals of $\mathbf{2}^{2+}$ (*S*=0) (**Molecule A**)

MO	Energy (eV)	Ru	tpm	bqdi	H_2O
HOMO–10	–14.947	0.13	0.05	0.81	0.00
HOMO–9	–14.404	0.07	0.85	0.06	0.02
HOMO–8	–14.347	0.08	0.81	0.10	0.01
HOMO–7	–13.769	0.08	0.90	0.02	0.00
HOMO–6	–13.713	0.01	0.99	0.01	0.00
HOMO–5	–13.708	0.08	0.90	0.02	0.00
HOMO–4	–13.103	0.00	1.00	0.00	0.00
HOMO–3	–12.765	0.79	0.08	0.12	0.01
HOMO–2	–12.749	0.17	0.14	0.67	0.01
HOMO–1	–12.211	0.70	0.19	0.11	0.00
HOMO	–11.741	0.63	0.12	0.23	0.02
LUMO	–9.359	0.18	0.05	0.76	0.02
LUMO+1	–7.036	0.42	0.34	0.06	0.17
LUMO+2	–6.846	0.07	0.91	0.01	0.01
LUMO+3	–6.758	0.14	0.82	0.01	0.03
LUMO+4	–6.124	0.41	0.27	0.32	0.00
LUMO+5	–6.105	0.05	0.92	0.03	0.00
LUMO+6	–5.930	0.23	0.08	0.63	0.06
LUMO+7	–5.675	0.38	0.13	0.22	0.28
LUMO+8	–5.649	0.02	0.02	0.95	0.00
LUMO+9	–5.058	0.52	0.24	0.21	0.03
LUMO+10	–5.011	0.59	0.32	0.07	0.02

Contour plots of selected MOs of $\mathbf{2}^{2+}$

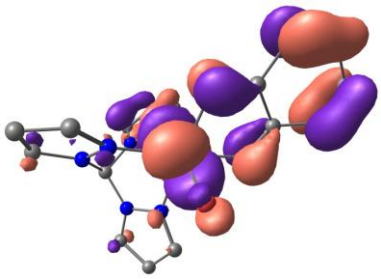
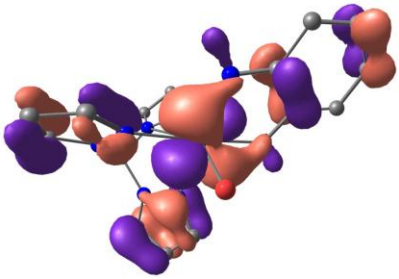
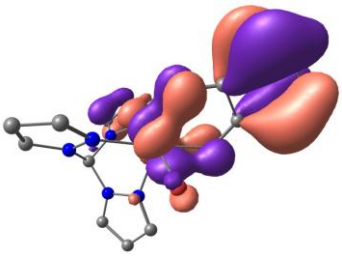
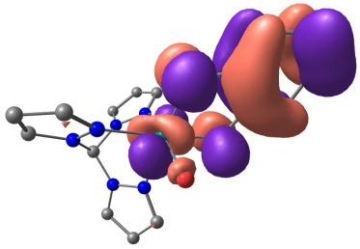
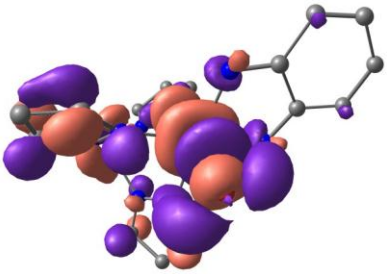
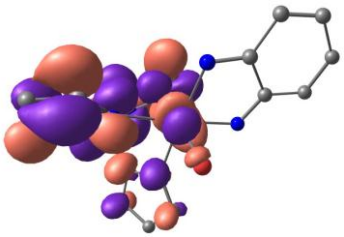
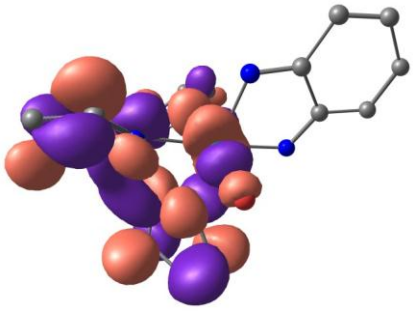
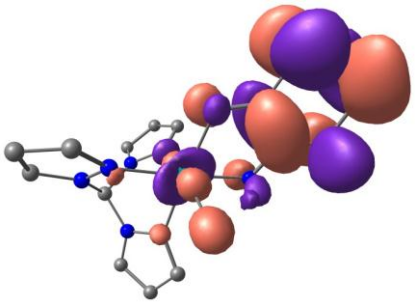
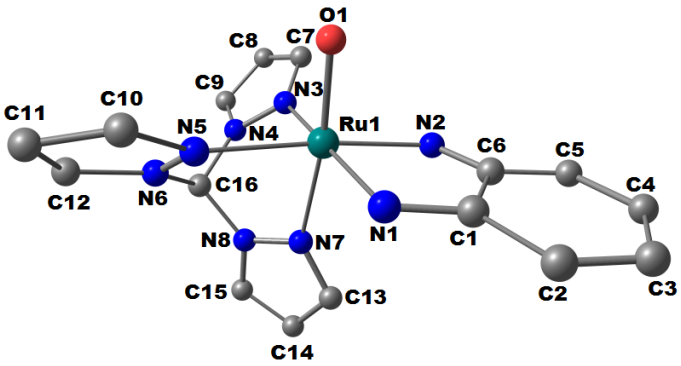
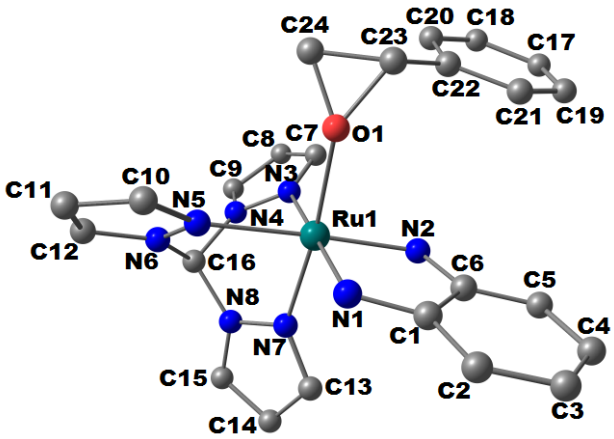
		
HOMO	HOMO–1	HOMO–2
		
LUMO	LUMO+1	LUMO+2
		
LUMO+3	LUMO+6	

Table S8 DFT calculated selected bond distances (Å) based on the optimised structures of $\mathbf{3}^{2+}$ and ($\mathbf{3}^{2+}$ + styrene) adduct (**A**)



$\mathbf{3}^{2+}$



A

Bond distances	$\mathbf{3}^{2+}$ (Å)	**A** (Å)
Ru(1)–O(1)	1.782	2.172
C(23)–C(24)	-	1.472
O(1)–C(23)	-	1.509
O(1)–C(24)	-	1.447
Ru(1)–N(1)	2.081	2.001
Ru(1)–N(2)	2.081	2.007
Ru(1)–N(3)	2.129	2.169
Ru(1)–N(5)	2.129	2.158
Ru(1)–N(7)	2.252	2.072

Fig. S1 ESI(+) mass spectra of (a) $[\mathbf{1}]^{+}$ in CH_3CN, (b) $\{[\mathbf{2}](ClO_4)_2\text{-}ClO_4\text{-}H_2O\}^{+}$ in H_2O, (c) *in situ* generated $\{[\mathbf{3}](ClO_4)_2\text{-}ClO_4\}^{+}$ and (d) *in -situ* generated adduct of $\mathbf{3}^{2+}$ + styrene (**A**) (*m*/2).

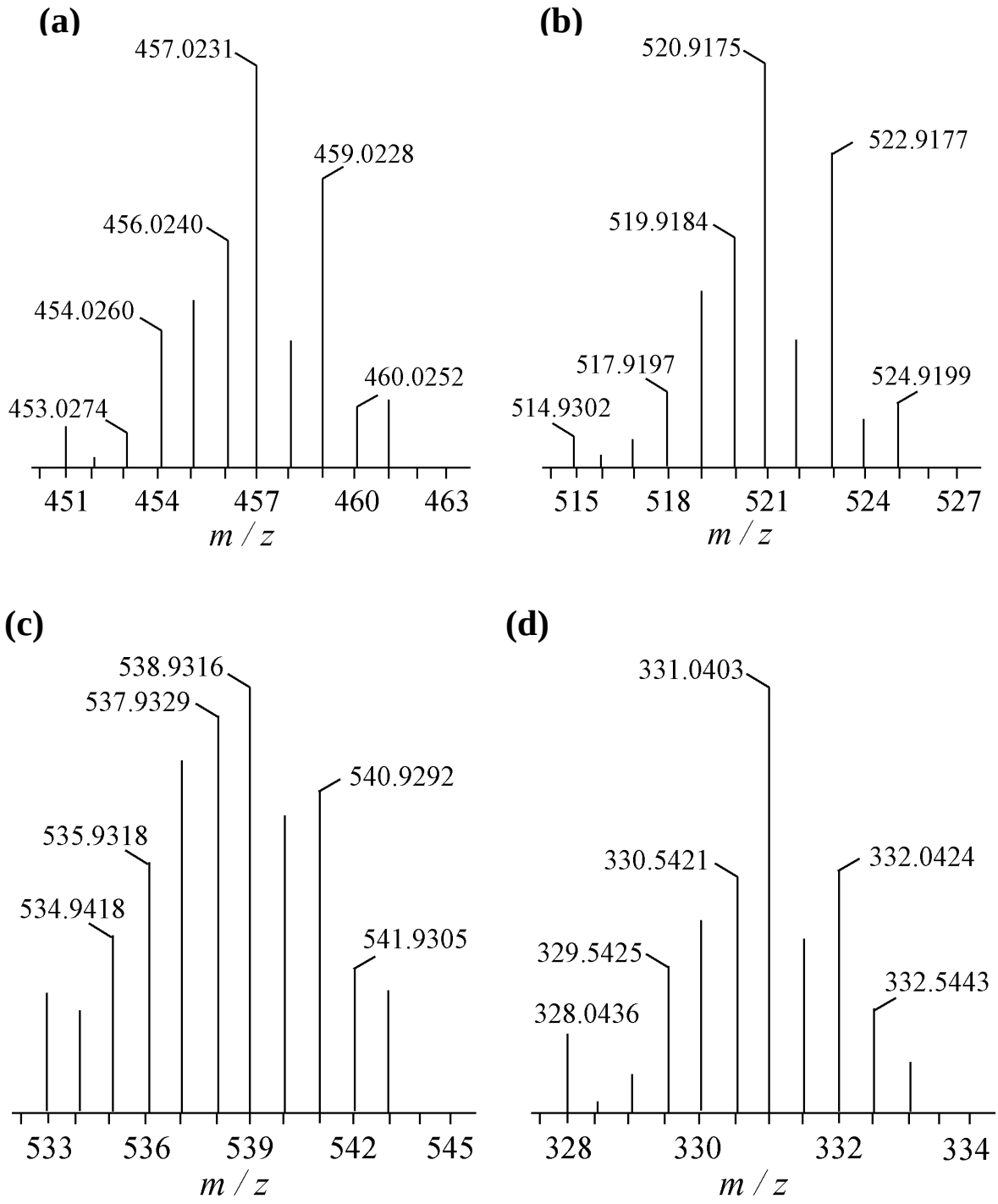


Fig. S2 DFT optimised structures of (a) $\mathbf{1}^{+}$ and (b) $\mathbf{2}^{2+}$ (**Molecule A**, see Fig. 2 in the text).

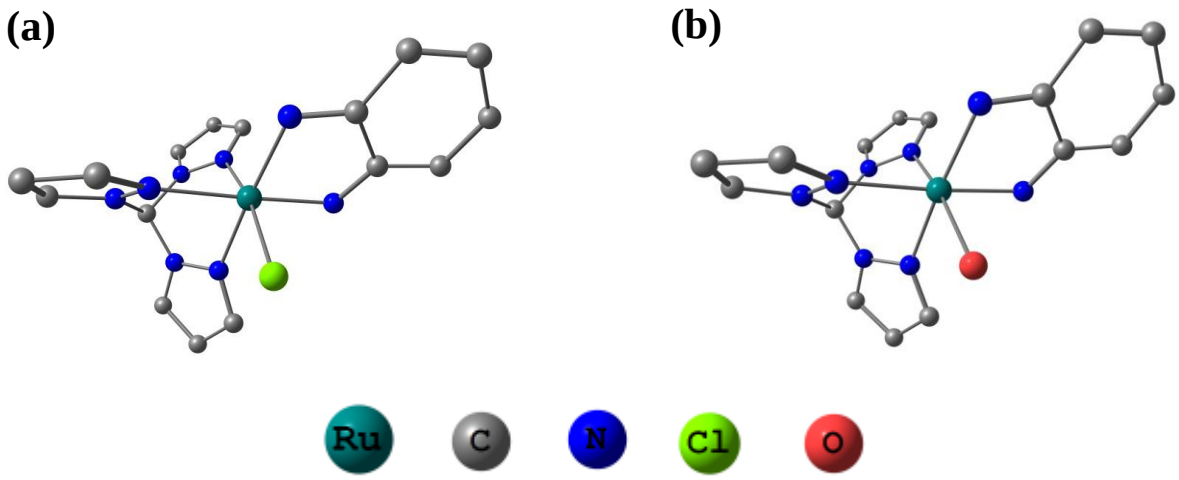
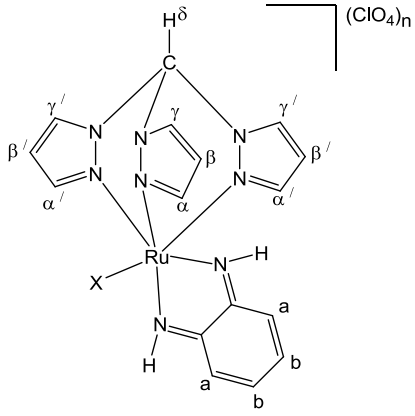


Fig. S3(a) ^{1}H NMR spectra of [**1**]ClO_4 in (a) $CDCl_3$, (b) $(CD_3)_2SO$, (c) CD_3CN, (d) $(CD_3)_2CO$, and [**2**]$(ClO_4)_2$ in (e) $(CD_3)_2CO$, (f) D_2O.



X = Cl, n = 1: [**1**]ClO_4

X = H_2O, n = 2: [**2**]$(ClO_4)_2$

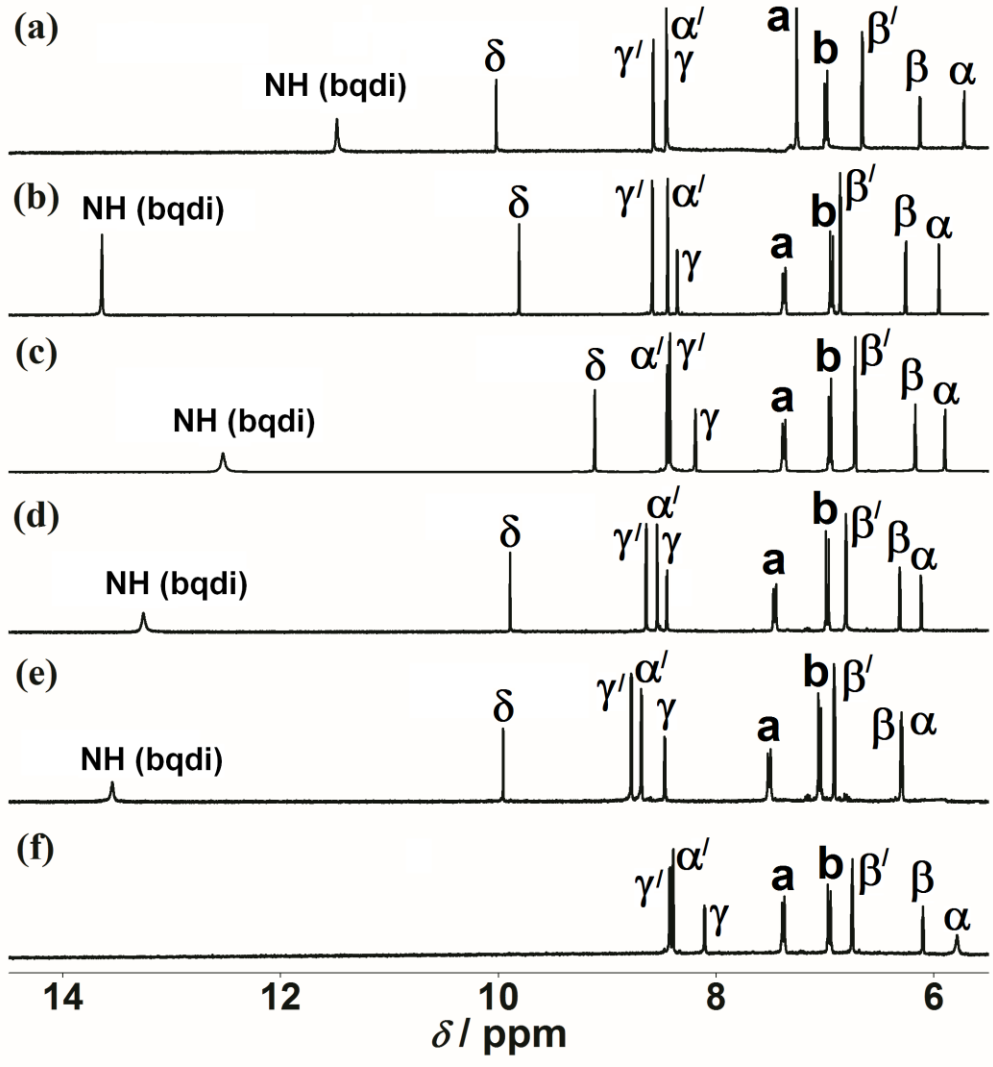
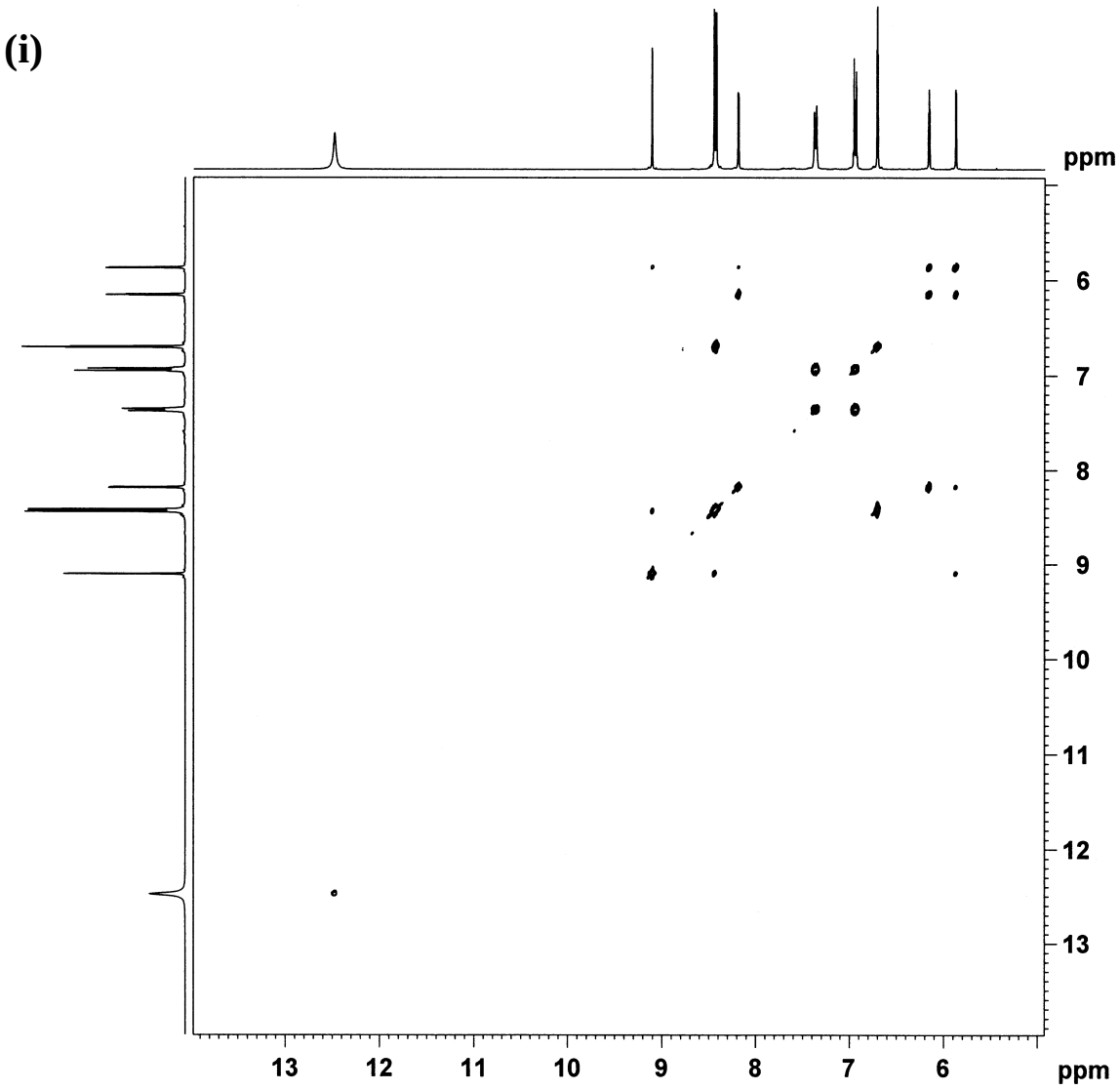


Fig. S3(b) ^{1}H-^{1}H COSY NMR of [**1**]ClO_4 in CD_3CN: (i) full range, (ii) expanded.



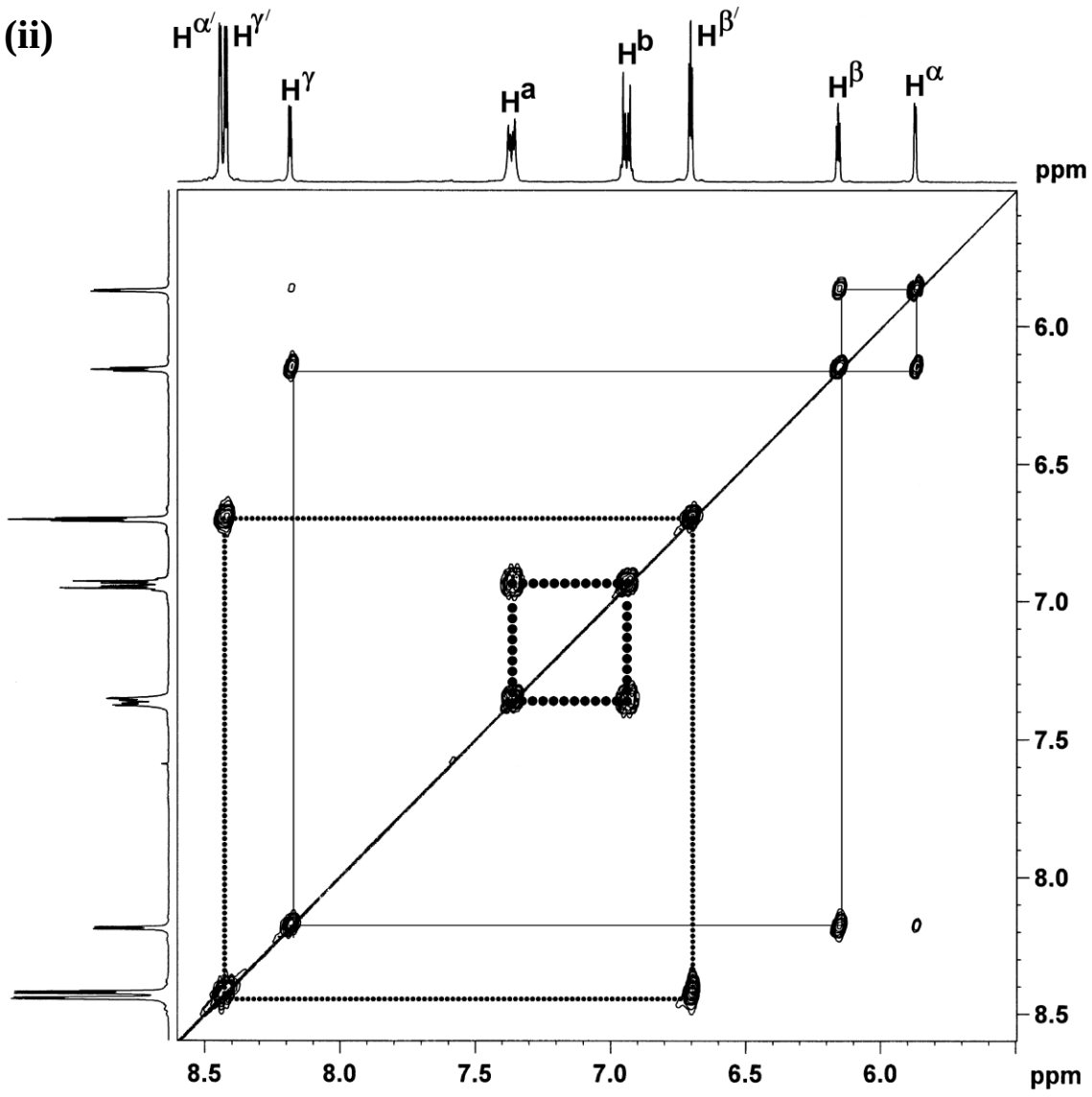
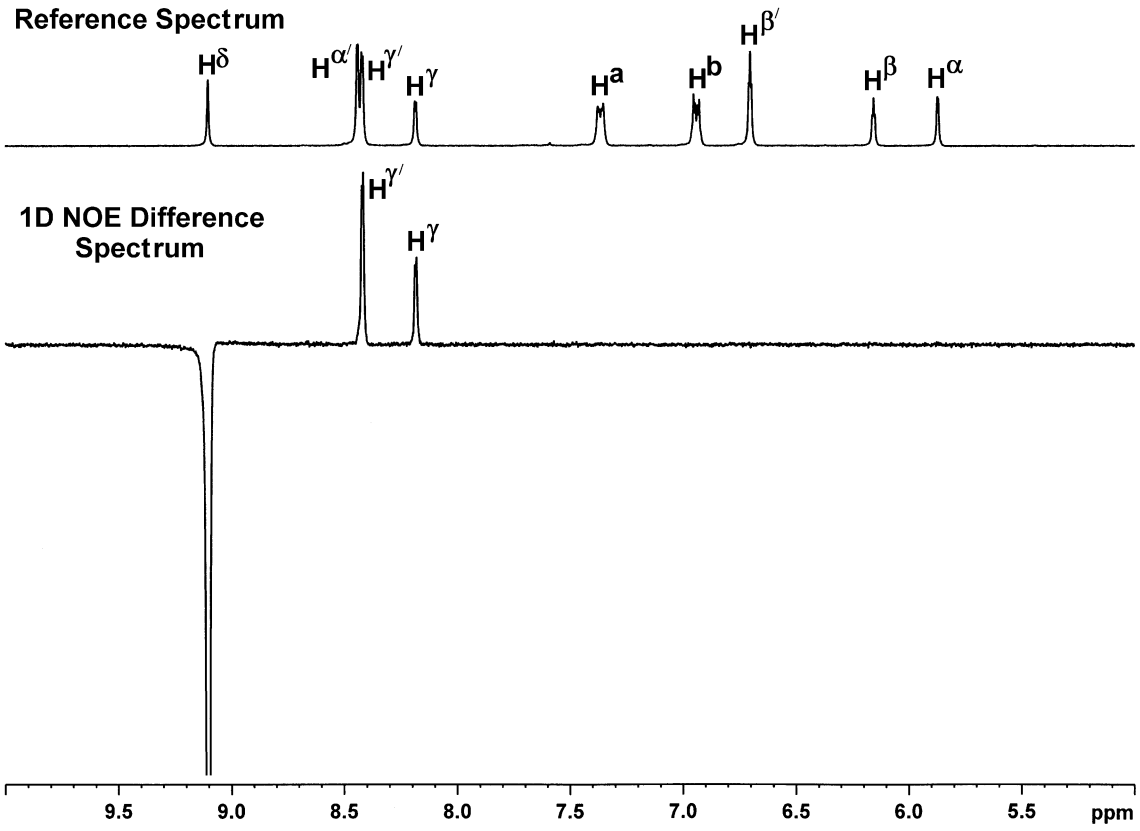


Fig. S3(c) 1D NOE (Nuclear Overhauser Enhancement) difference spectrum of [**1**]ClO_4 in CD_3CN on selective irradiation at δ 9.11 ppm (corresponding to H^{δ}): (i) excluding N-H resonance, (ii) expanded.

(i)



(ii)

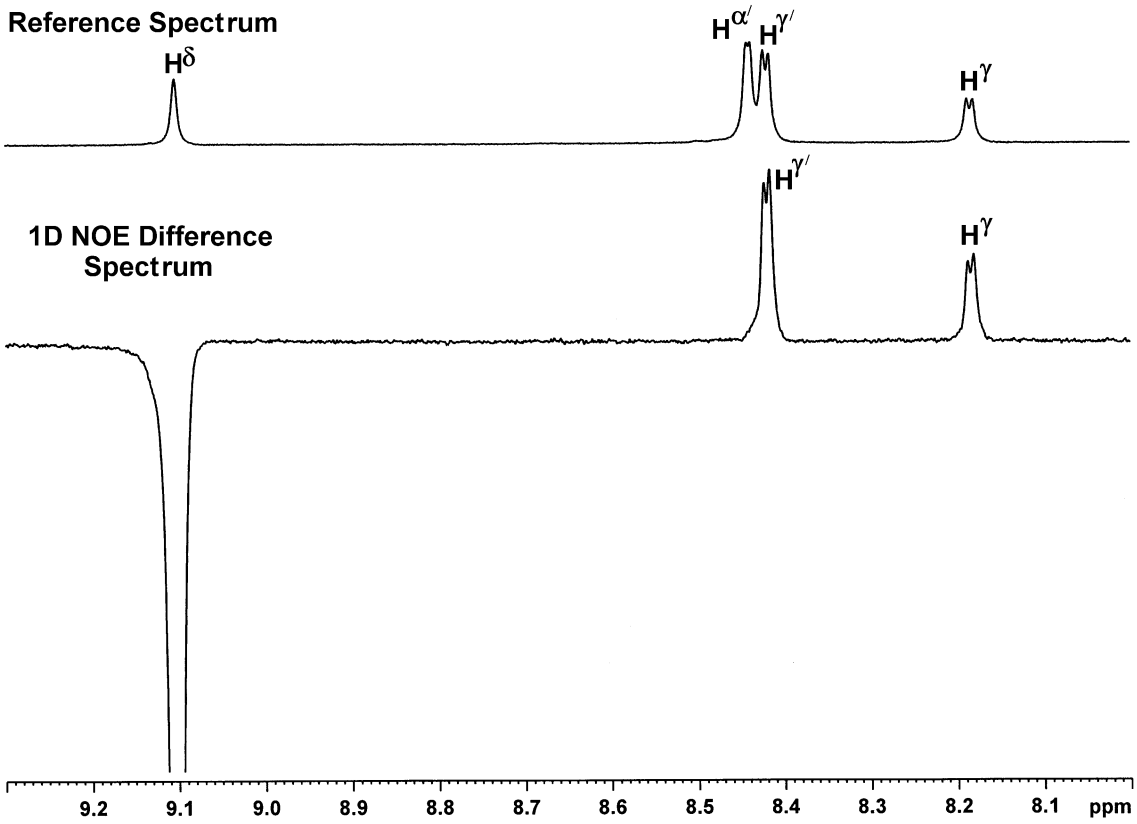
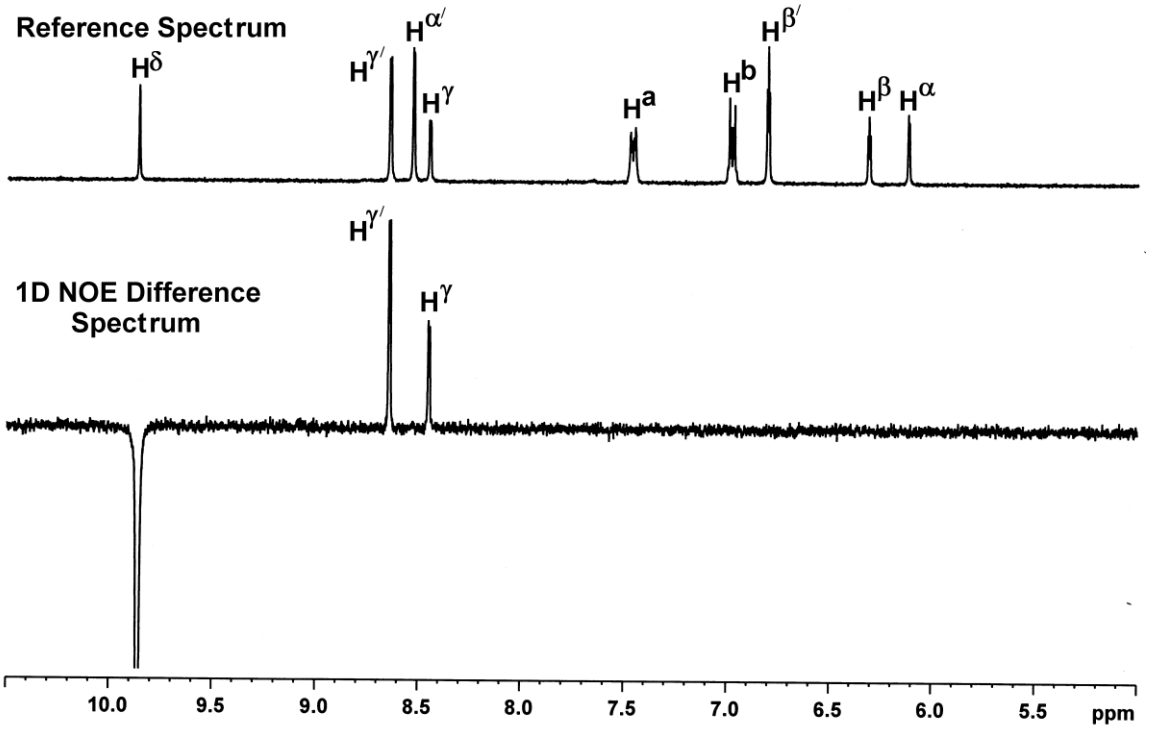

Reference Spectrum
Hδ
Hα/
Hγ/
Hγ
1D NOE Difference Spectrum
Hγ/
Hγ
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
ppm

Fig. S3(d) 1D NOE (Nuclear Overhauser Enhancement) difference spectrum of [**1**]ClO_4 in $(CD_3)_2CO$ on selective irradiation at δ 9.89 ppm (corresponding to H^{δ}): (i) excluding N-H resonance, (ii) expanded.

(i)



(ii)

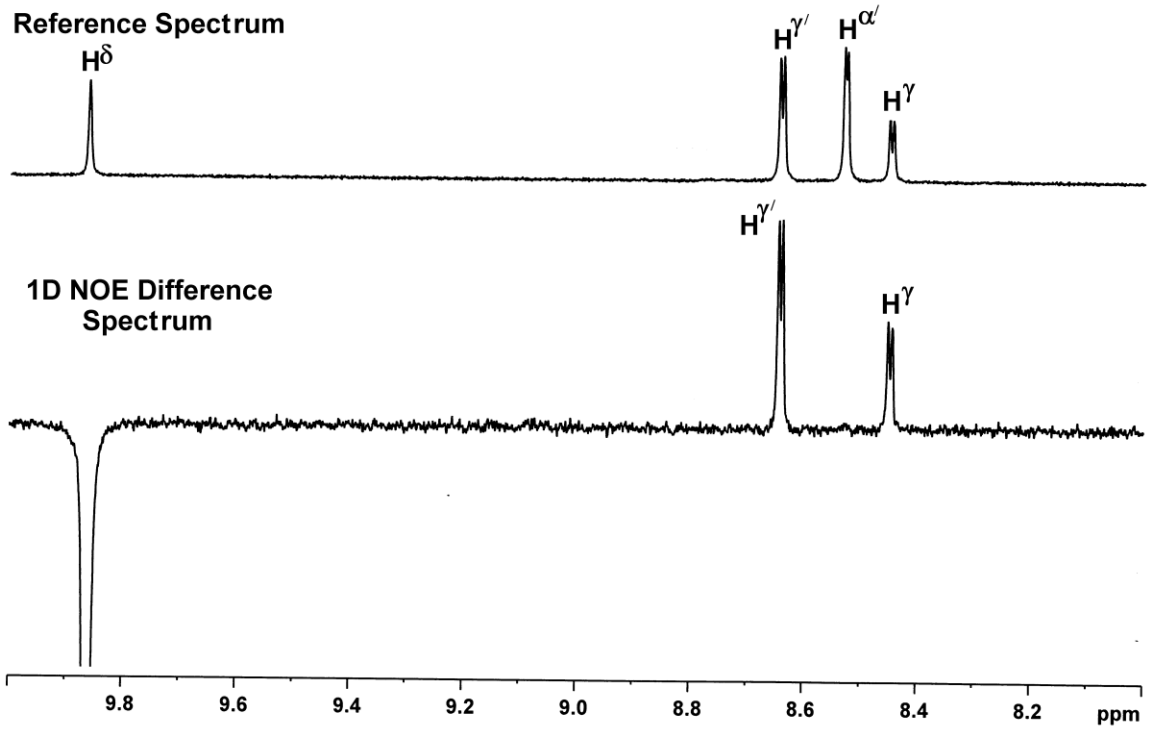

Reference Spectrum
Hδ
Hγ′
Hα′
Hγ
1D NOE Difference Spectrum
Hγ′
Hγ
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
ppm

Fig. S4 Cyclic (solid) and differential pulse (dotted) voltammograms of [**2**]$(ClO_4)_2$ at pH 7.0 *versus* SCE. Scan rate 100 mV s^{-1}.

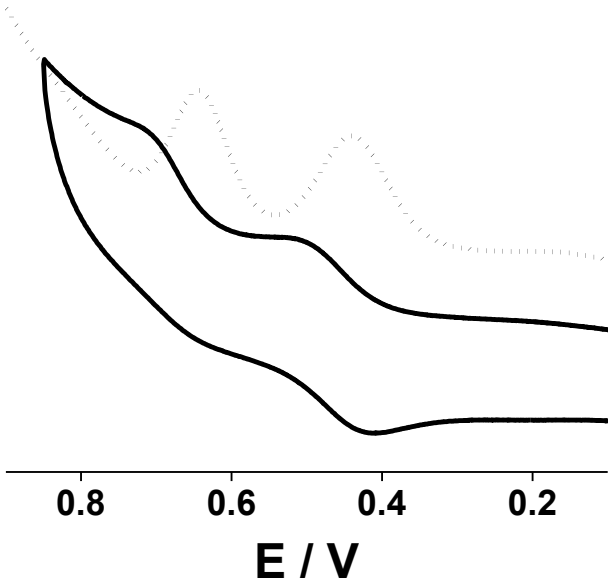


Fig. S5 Visible spectra of a solution of $[Ru(tpm)(bqdi)(H_2O)]^{2+}$ ($\mathbf{2}^{2+}$) + $PhI(OAc)_2$ in CH_2Cl_2 (black, in situ generated $[Ru(tpm)(bqdi)(O)]^{2+}$ ($\mathbf{3}^{2+}$)) and $\mathbf{2}^{2+}$ + $PhI(OAc)_2$ + methyl *p*-tolyl sulfide in CH_2Cl_2 (red, in situ generated $\mathbf{2}^{2+}$ + *p*-tolyl sulfoxide).

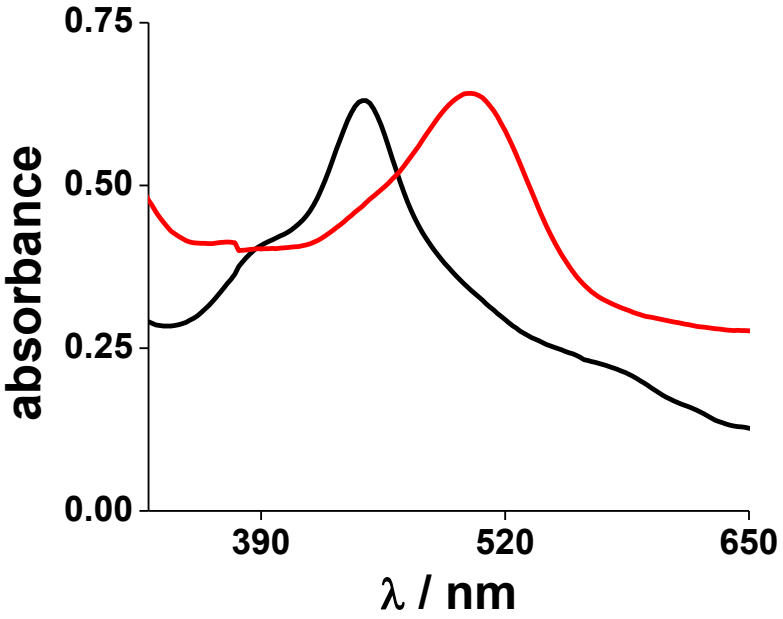


Fig. S6 ^{31}P NMR spectra of (a) PPh_3 in $CDCl_3$ (δ = -5.47 ppm) and (b) $\mathbf{2}^{2+}$ + $PhI(OAc)_2$ + PPh_3 in $CDCl_3$ (δ = 29.83 ppm).