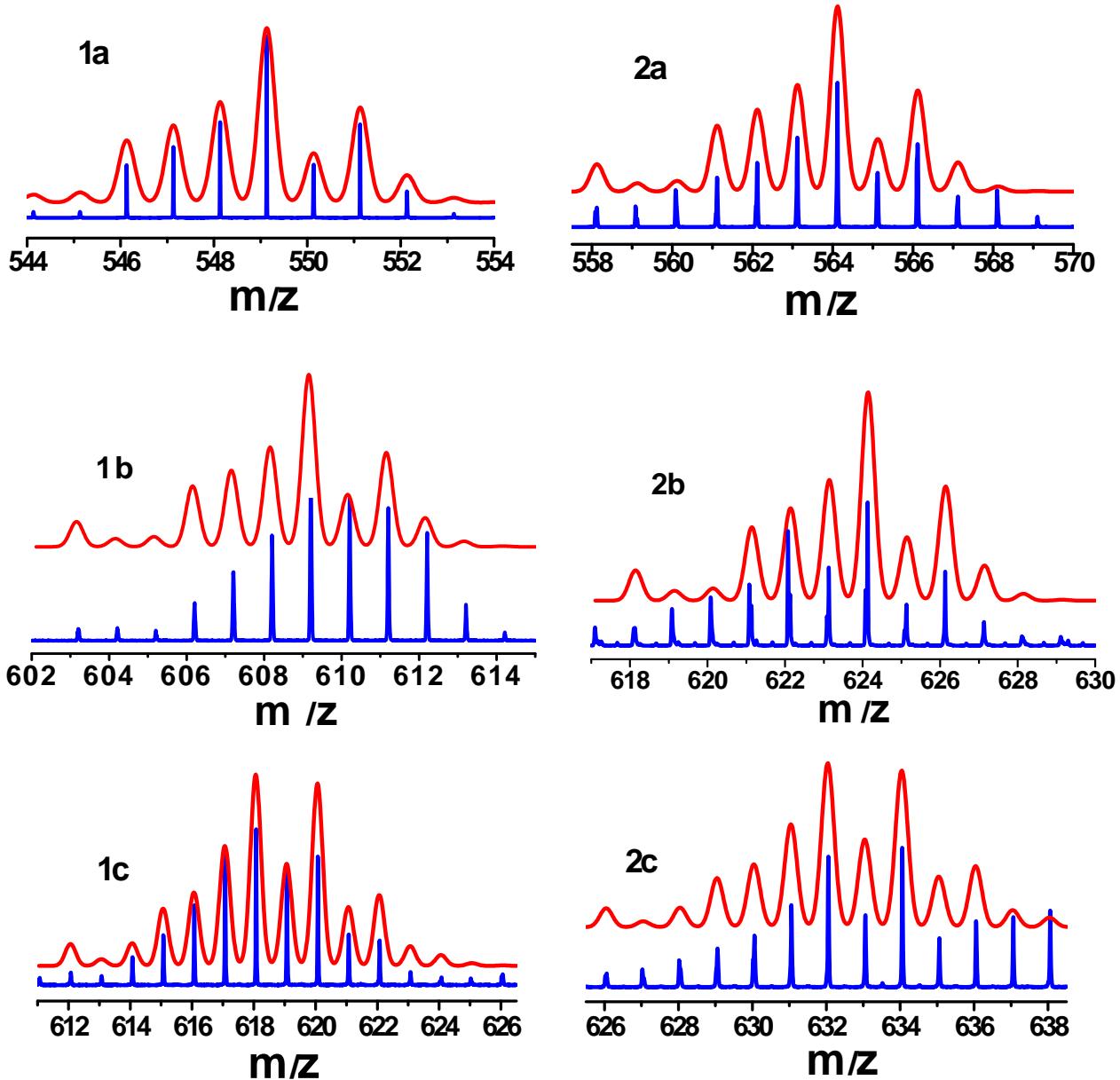


## **Supporting Information**

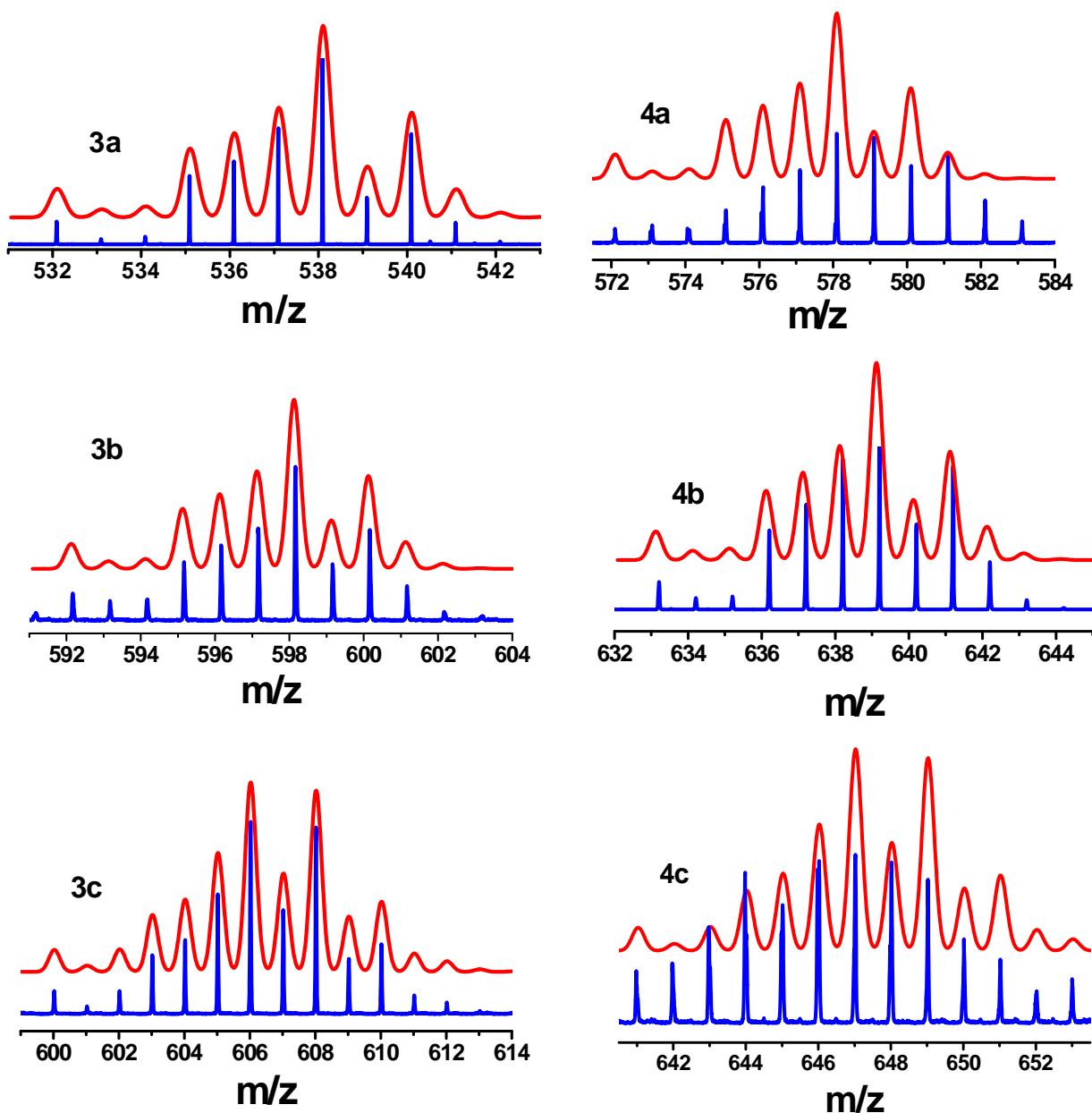
### **Ru-Complex Framework Toward Aerobic Oxidative Transformations of $\beta$ -Diketiminate and $\alpha$ -Ketodiimine**

Sanjib Panda, Abhishek Mandal, Prabir Ghosh and Goutam Kumar Lahiri\*

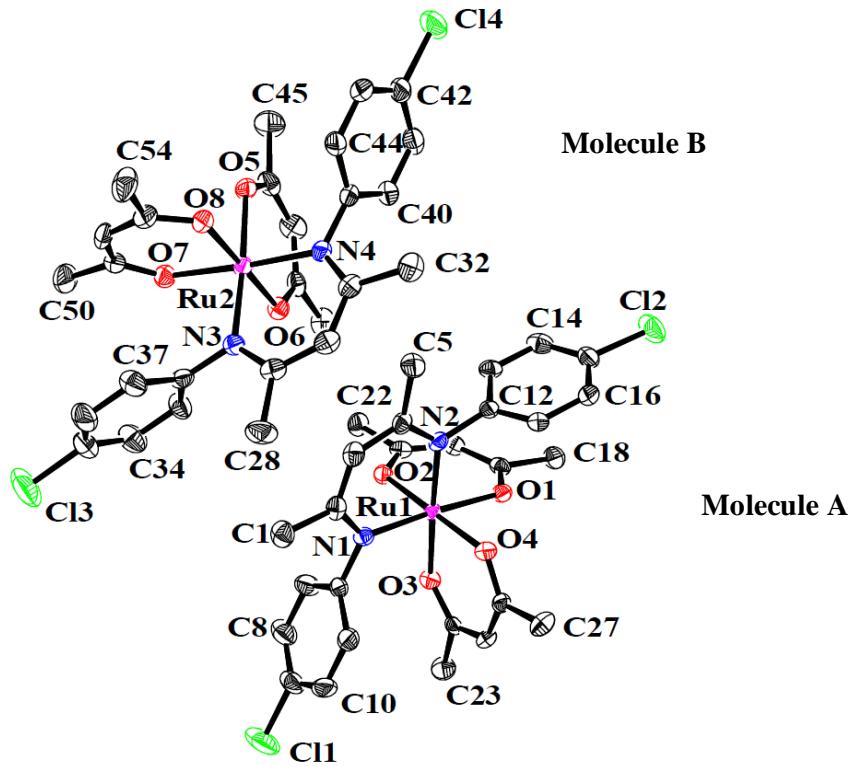
Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400076,  
India



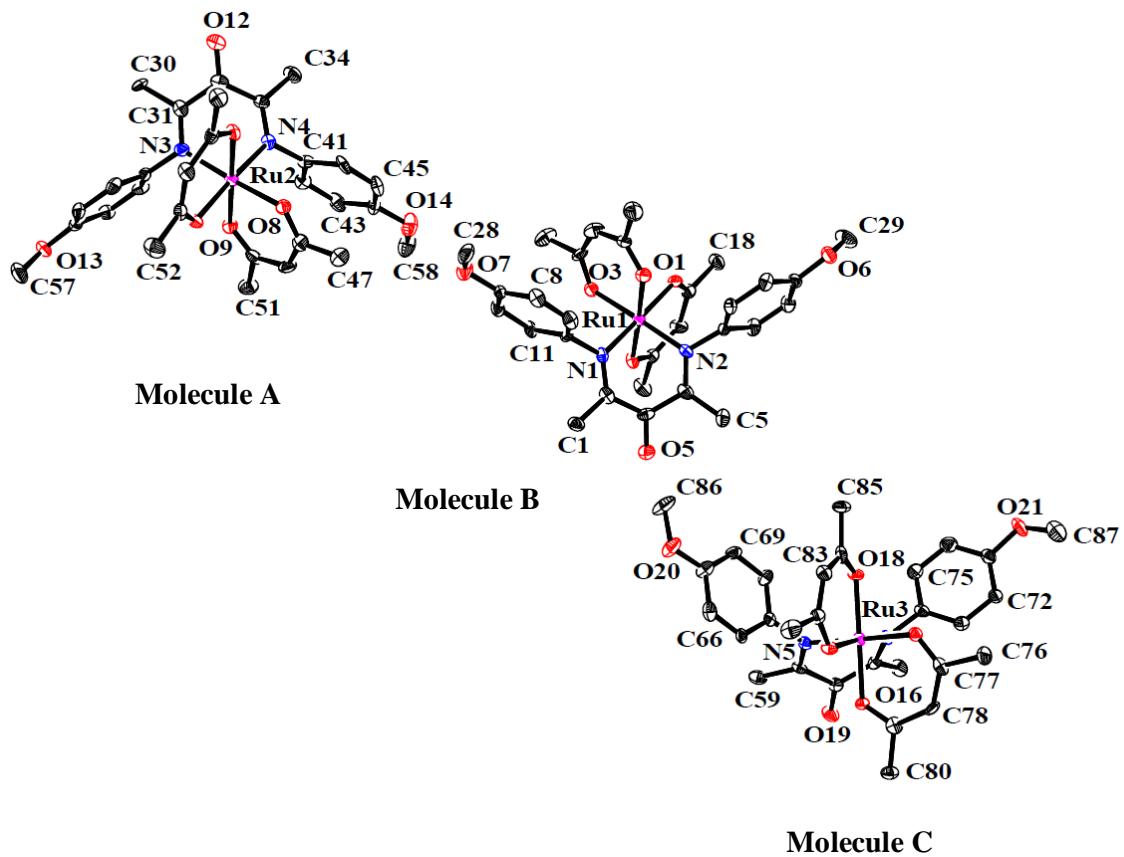
**Figure S1a.** Experimental and simulated ESI(+) mass spectra of  $\{1\text{a}\}^+$ ,  $\{1\text{b}\}^+$ ,  $\{1\text{c}\}^+$ ,  $\{2\text{a}\}^+$ ,  $\{2\text{b}\}^+$ ,  $\{2\text{c}\}^+$  in  $\text{CH}_3\text{CN}$  (blue line, experimental and red line, simulated).



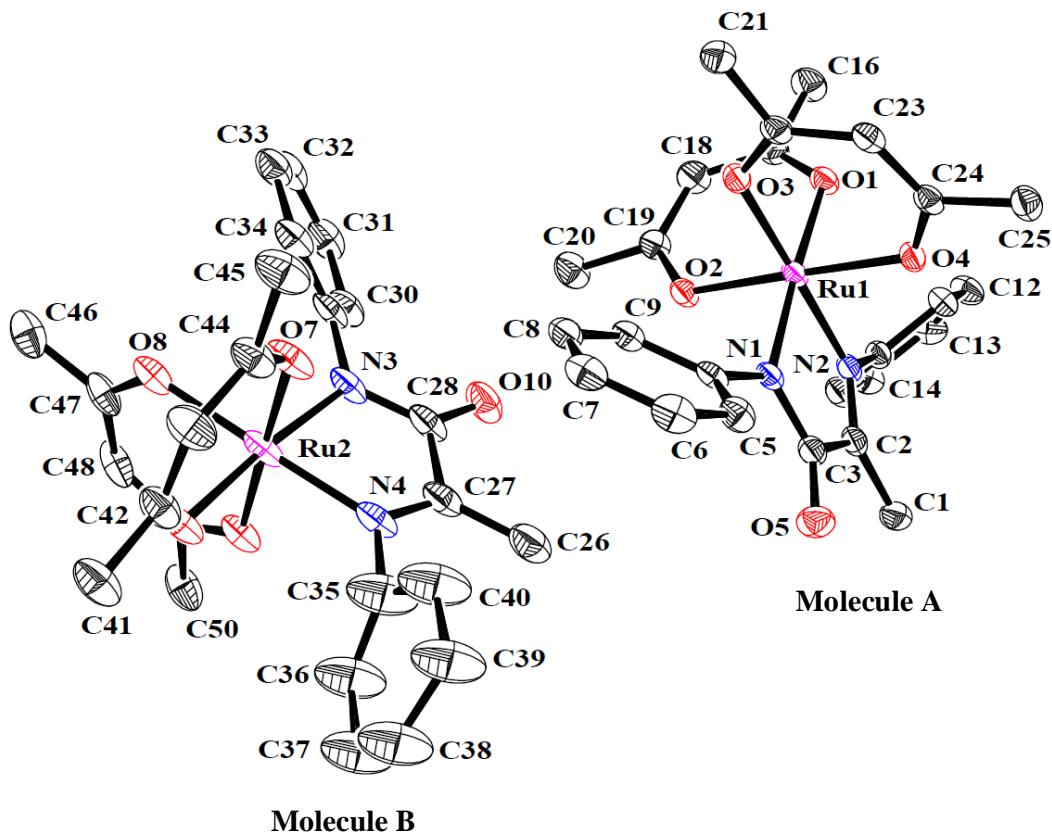
**Figure S1b.** Experimental and simulated ESI(+) mass spectra of  $\{3\text{a}+\text{H}\}^+$ ,  $\{3\text{b}+\text{H}\}^+$ ,  $\{3\text{c}+\text{H}\}^+$ ,  $\{4\text{a}\}^+$ ,  $\{4\text{b}+\text{H}\}^+$ ,  $\{4\text{c}+\text{H}\}^+$  in  $\text{CH}_3\text{CN}$  (blue line, experimental and red line, simulated).



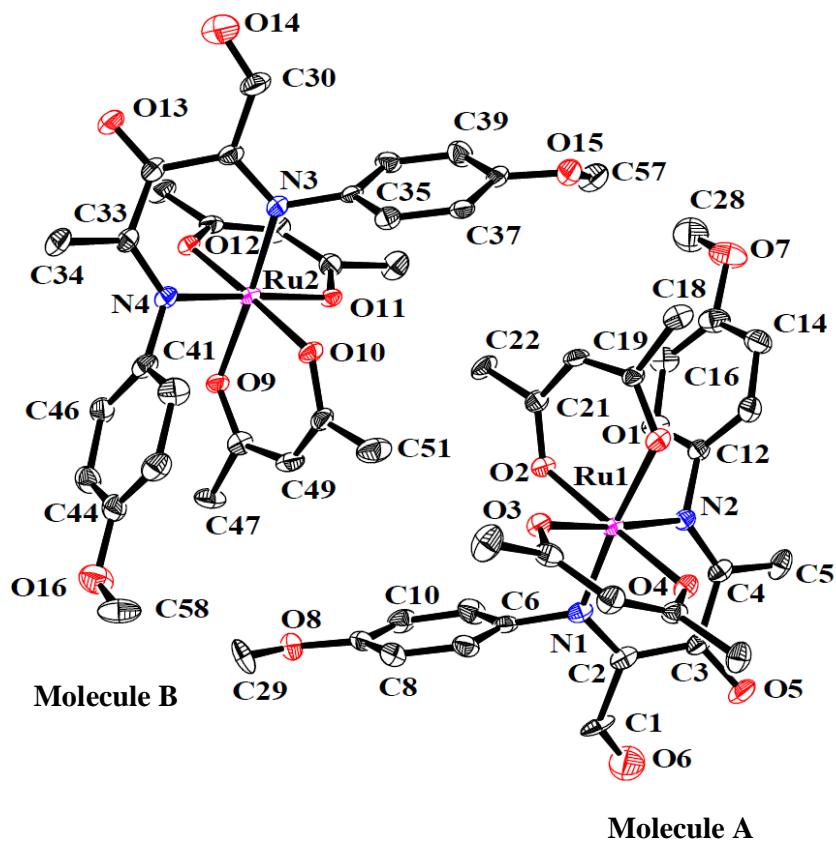
**Figure S2.** Perspective view of the asymmetric unit of **1c**, showing two independent molecules. Ellipsoids are drawn at 50% probability level. Hydrogen atoms are removed for clarity.



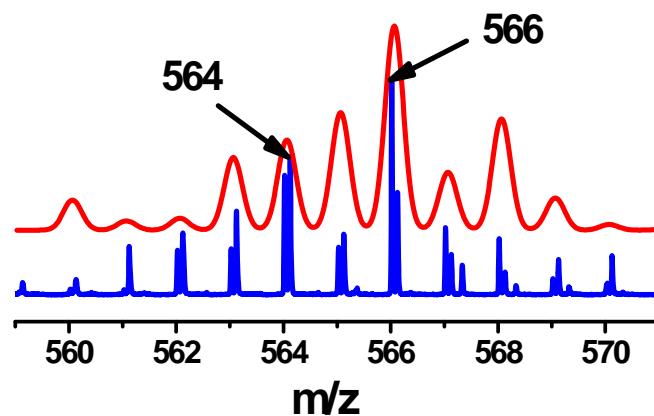
**Figure S3.** Perspective view of the asymmetric unit of **2b**, showing three independent molecules. Ellipsoids are drawn at 50% probability level. Hydrogen atoms are removed for clarity.



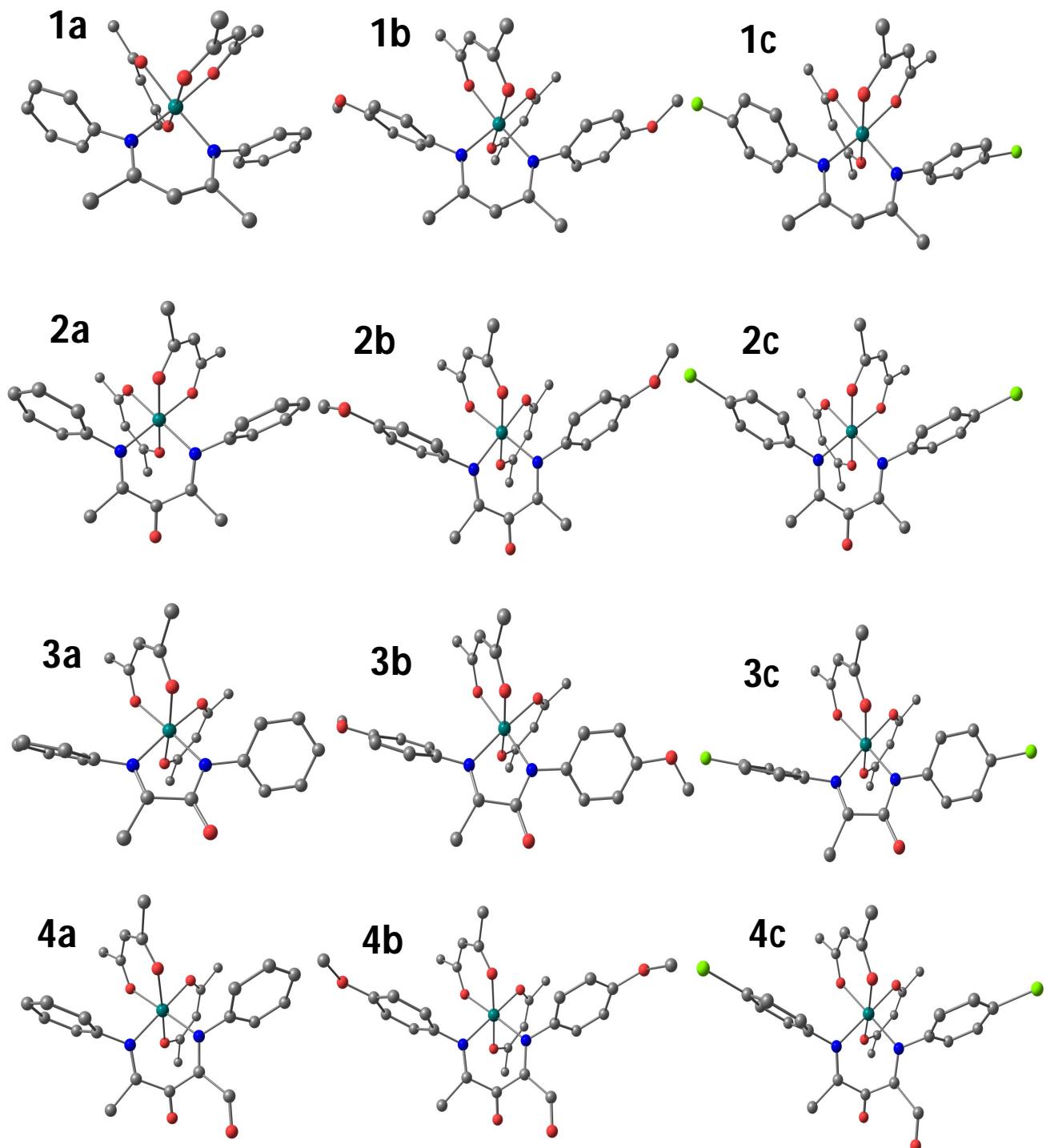
**Figure S4.** Perspective view of the asymmetric unit of **3a**, showing two independent molecules. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are removed for clarity.



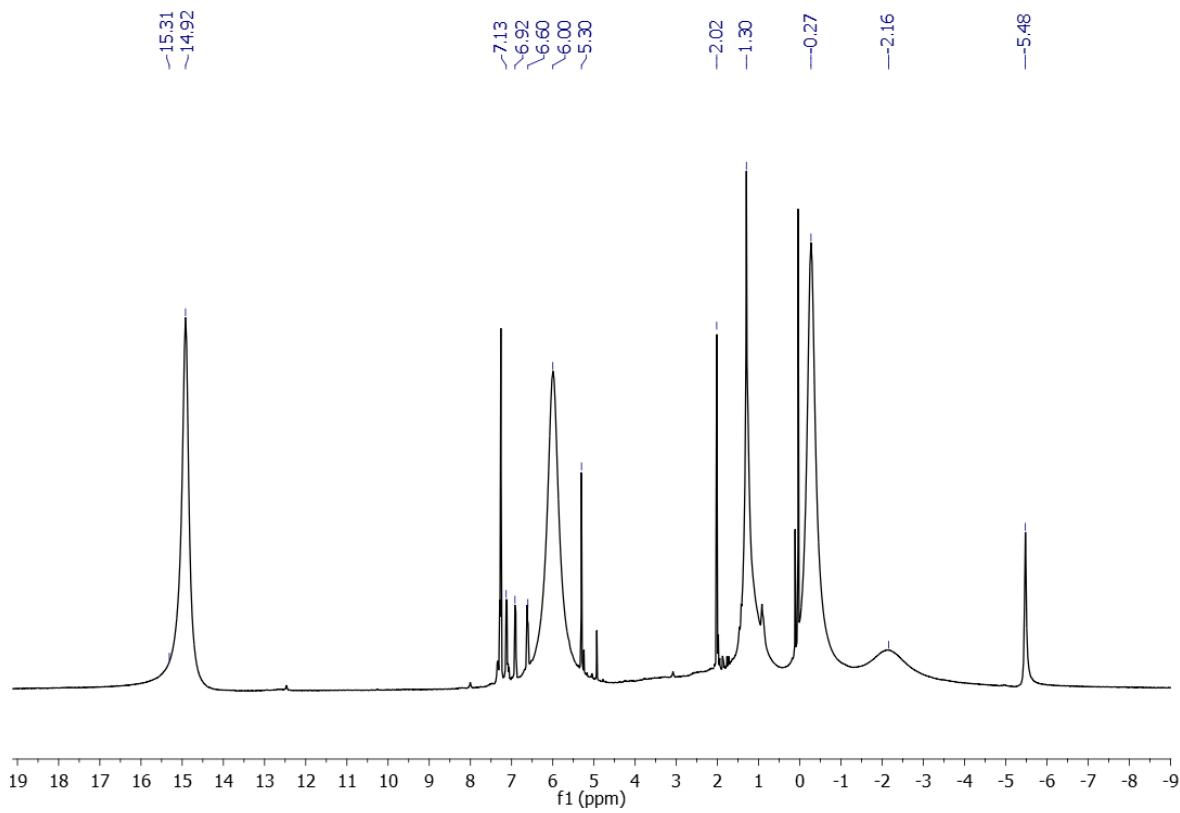
**Figure S5.** Perspective view of the asymmetric unit of **4b**, showing two independent molecules. Ellipsoids are drawn at 30% probability level. Hydrogen atoms are removed for clarity.



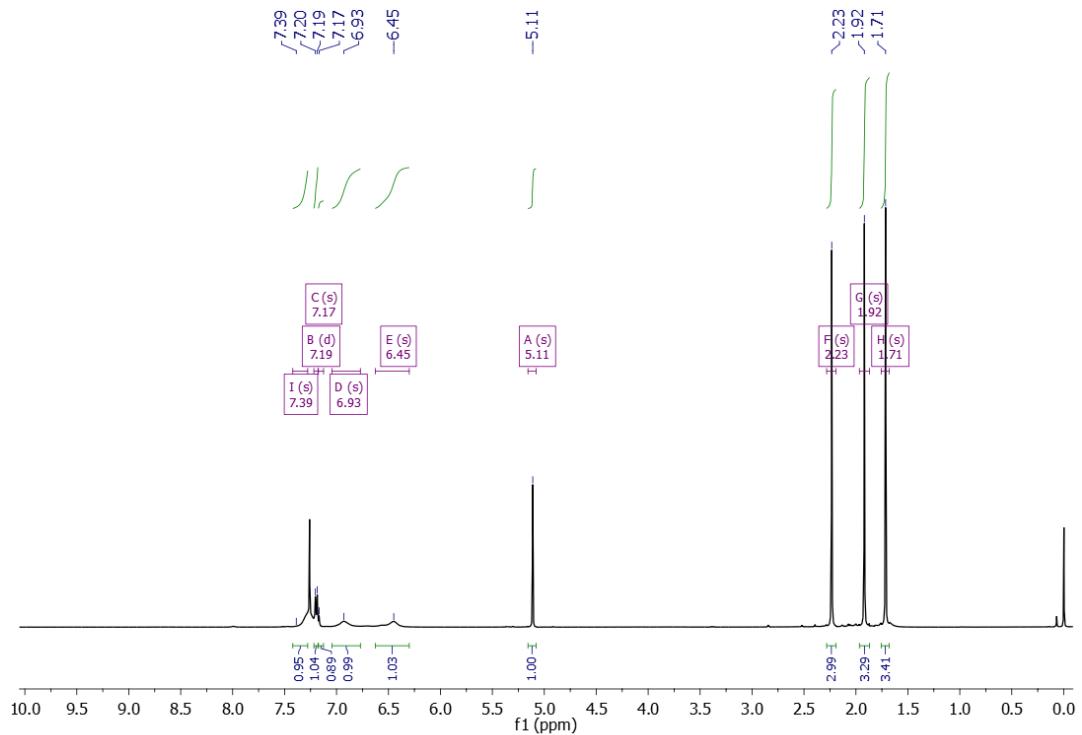
**Figure S6.** ESI-MS spectrum of the reaction mixture of **2a** and 18-O labeled **2a** during reaction of [**1a** (0.1 mM) +  $^{18}\text{O}_2$ ] in EtOH. Spectrum was recorded after 3 h of  $^{18}\text{O}_2$  purging. Peak at  $m/z = 566$  is assigned to  $\{\mathbf{2a} (^{18}\text{O})\}^+$  (blue line, experimental and red line, simulated).



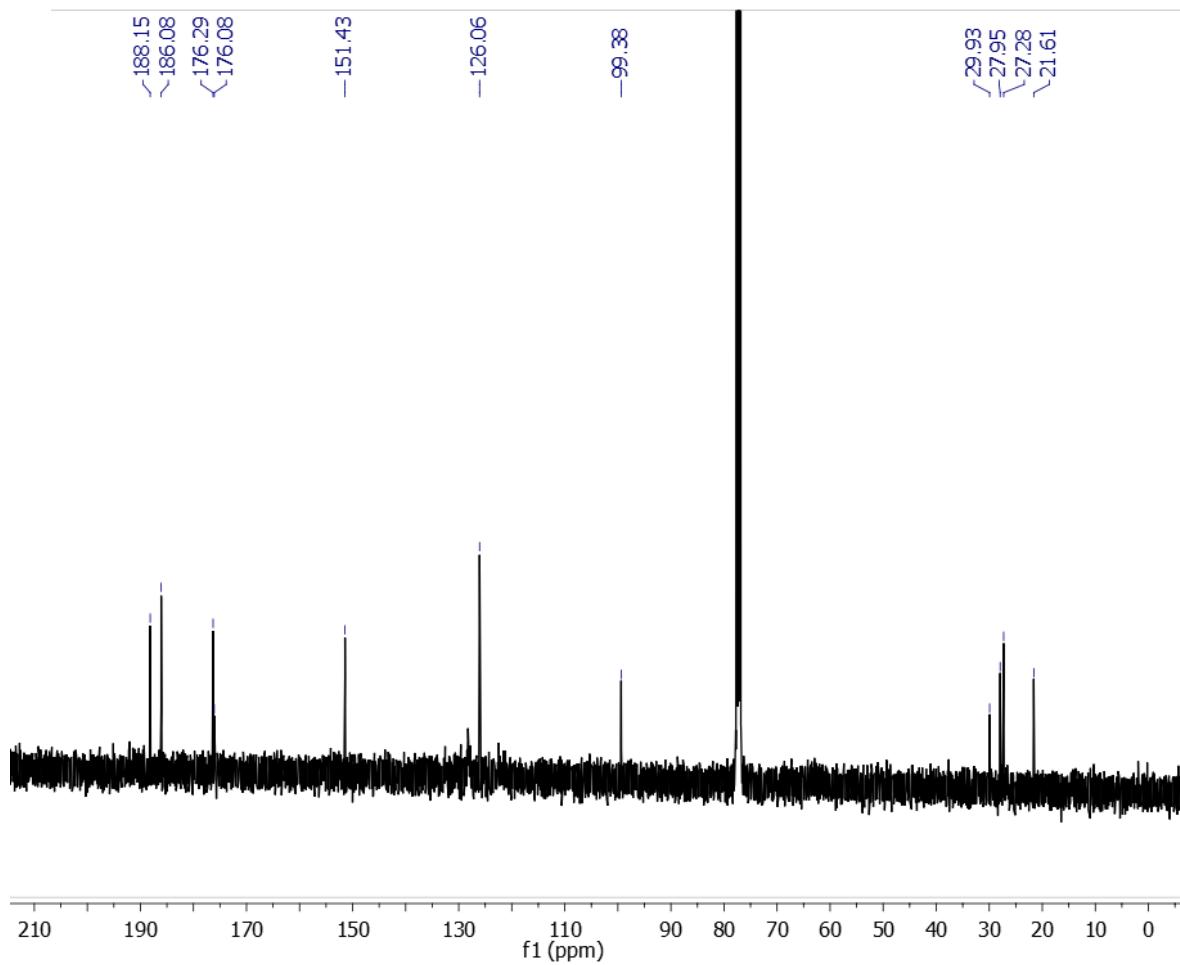
**Figure S7.** DFT optimized structures of **1-4** derivatives.



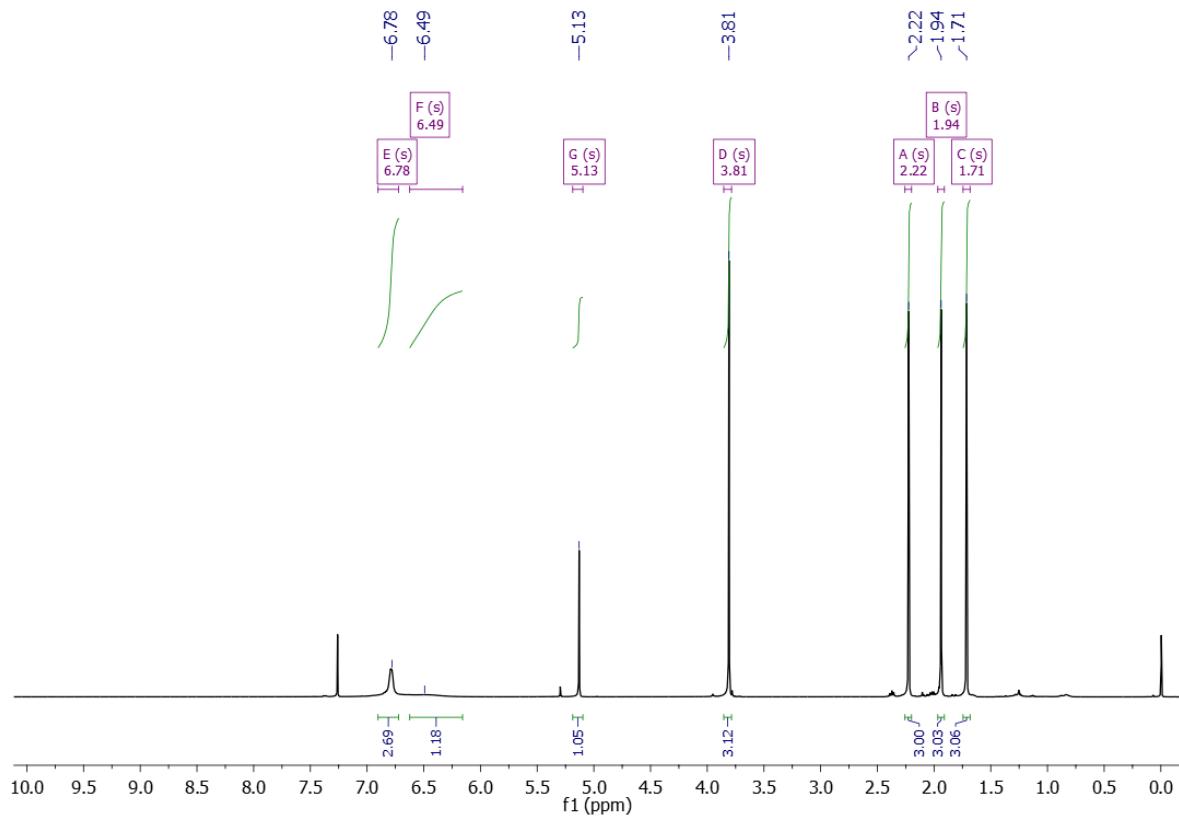
**Figure S8a.** <sup>1</sup>H NMR of [Ru(acac)<sub>2</sub>(nacnac<sup>Cl,Cl</sup>)], **1c** in <sup>13</sup>CDCl<sub>3</sub> with TMS (  $\delta$ = 0 ppm) as internal standard.



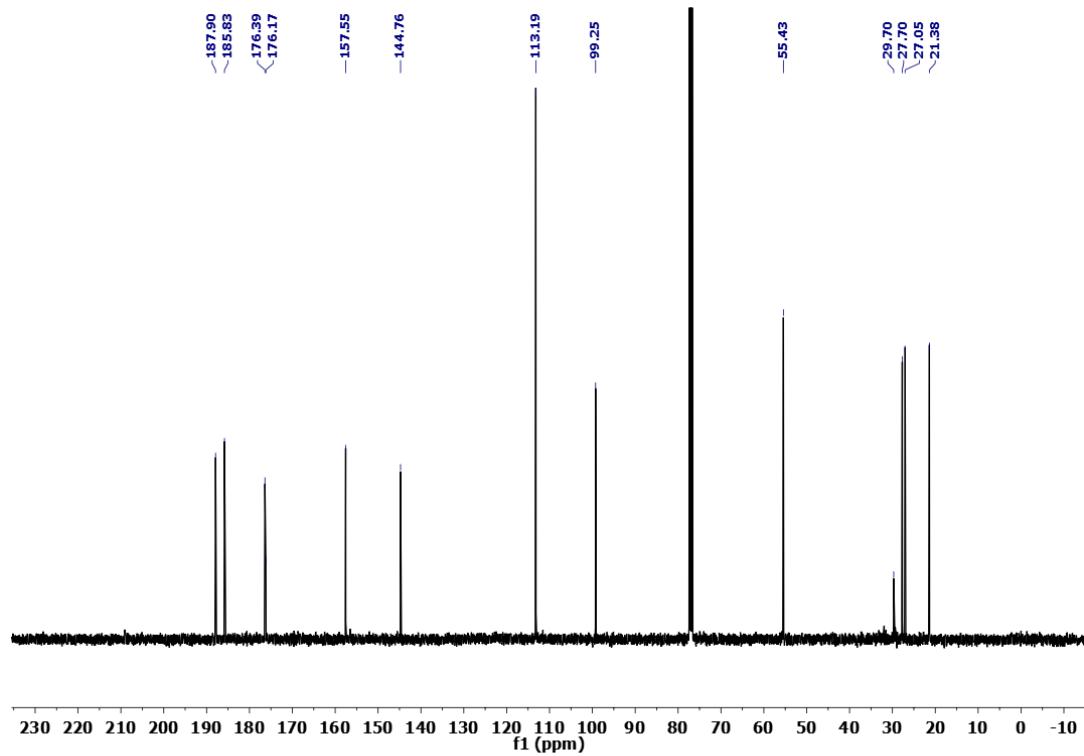
**Figure S8b.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^{1\text{H},\text{H}})]$ , **2a** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



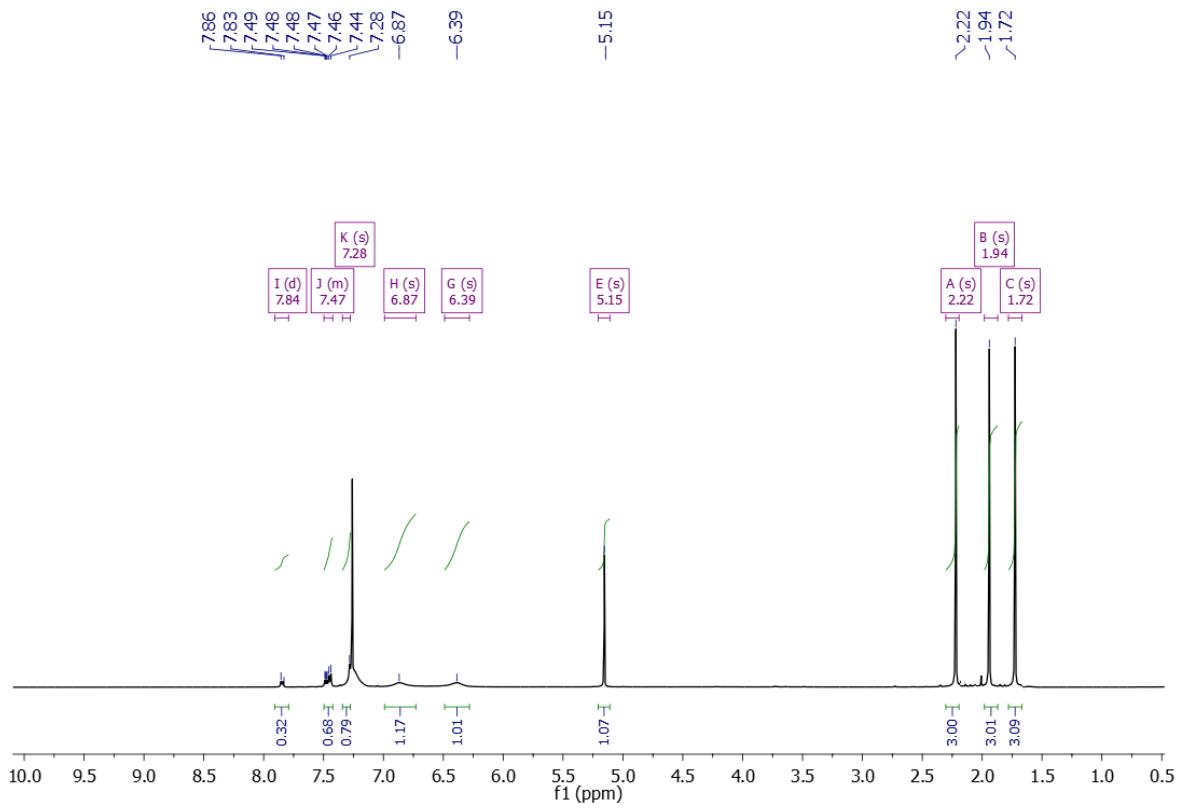
**Figure S8c.**  $^{13}\text{C}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^{\text{1 H,H}})]$ , **2a** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



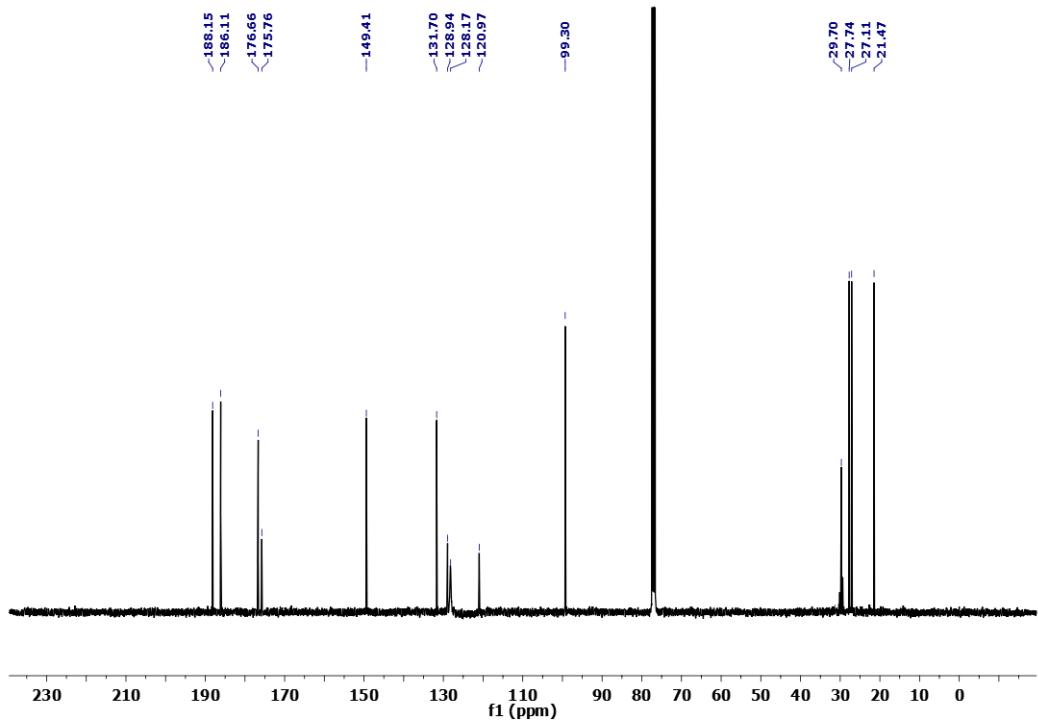
**Figure S8d.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^1\text{OMe},\text{OMe})]$ , **2b** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



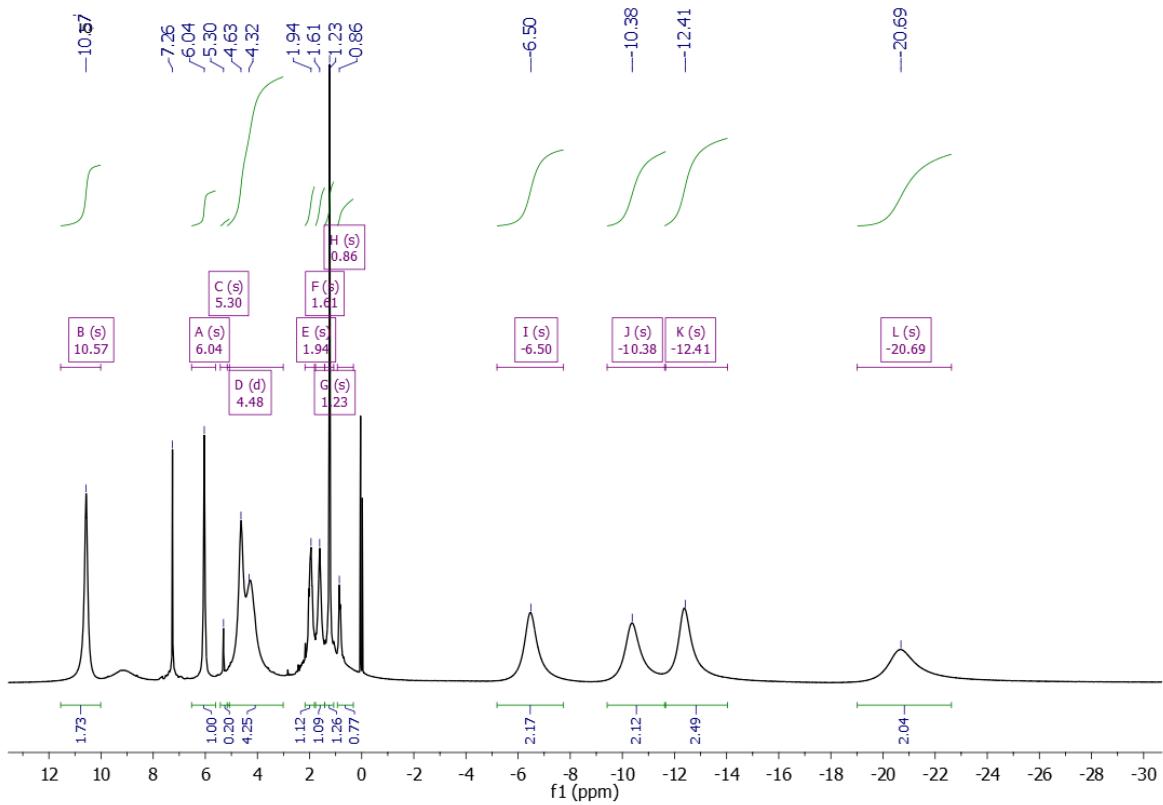
**Figure S8e.**  $^{13}\text{C}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^1\text{OMe,OMe})]$ , **2b** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



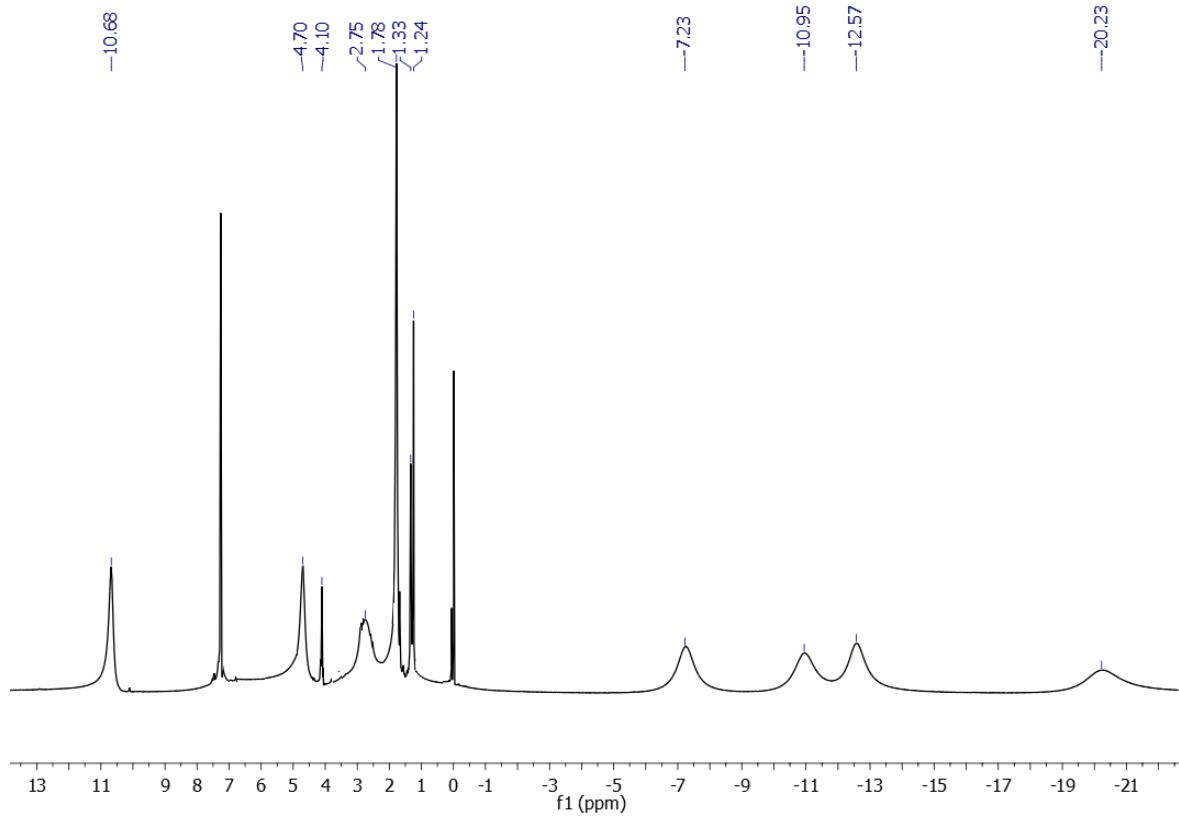
**Figure S8f.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^1\text{Cl},\text{Cl})]$ , **2c** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



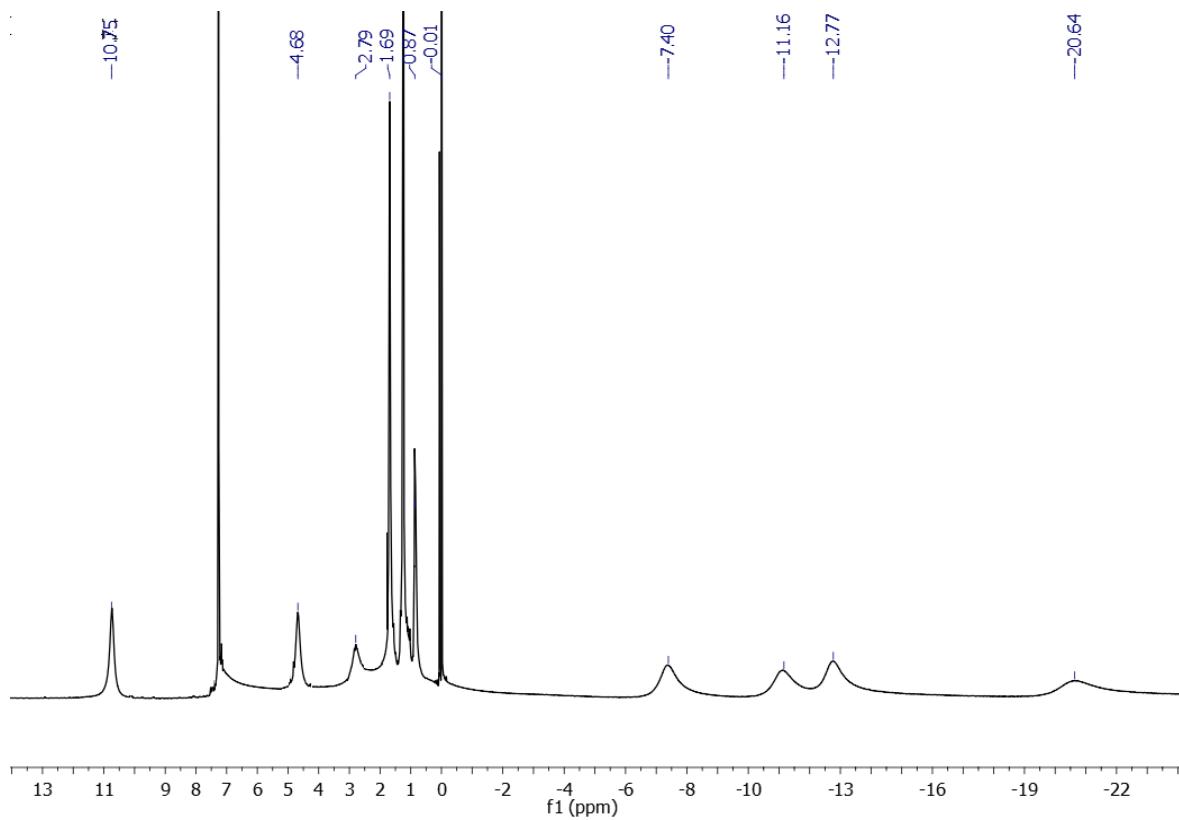
**Figure S8g.** <sup>13</sup>C NMR of [Ru(acac)<sub>2</sub>(L<sup>1</sup>Cl,Cl)], **2c** in CDCl<sub>3</sub> with TMS ( $\delta = 0$  ppm) as internal standard.



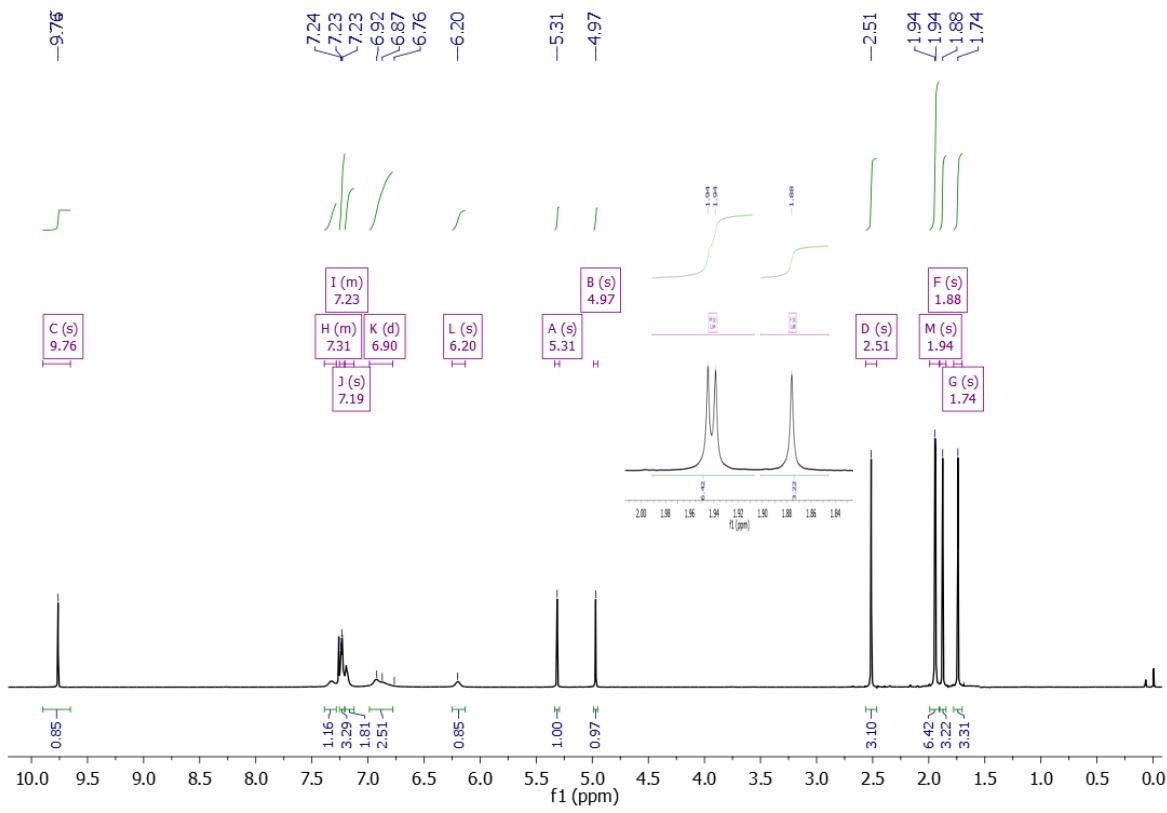
**Figure S8h.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^{5\text{H},\text{H}})]$ , **3a** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



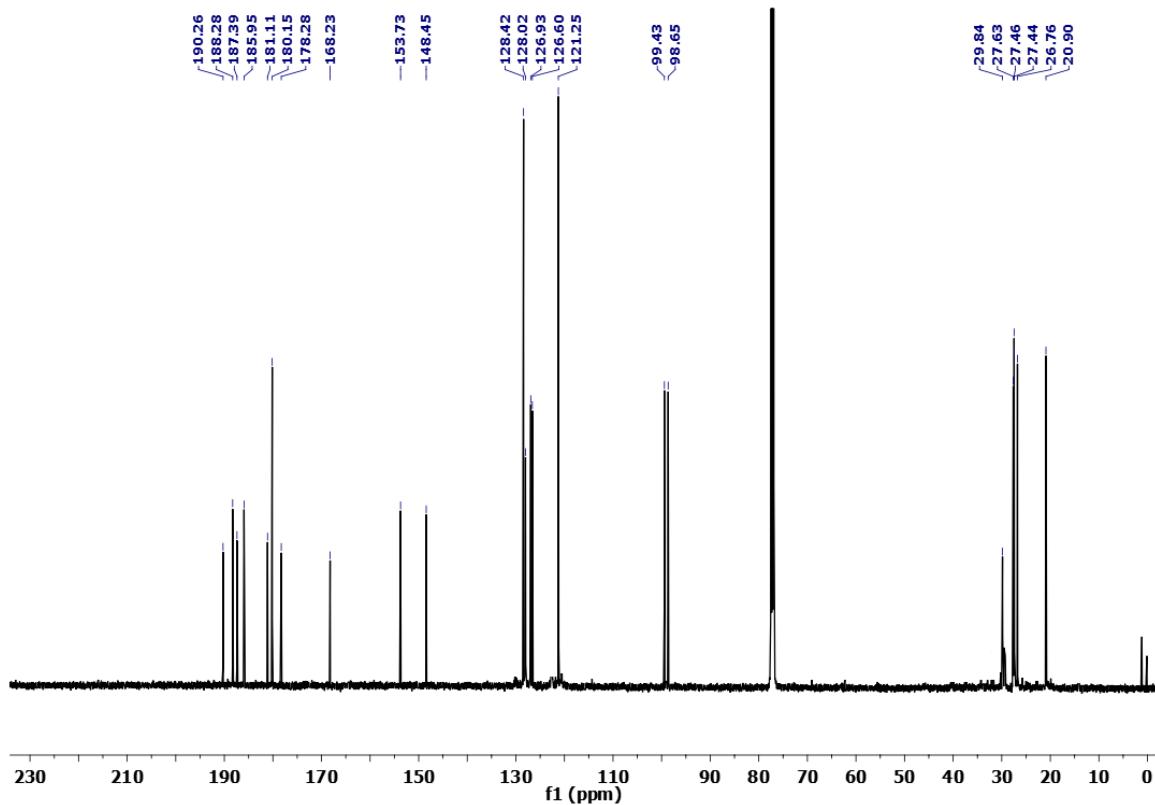
**Figure S8i.** <sup>1</sup>H NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^5\text{OMe},\text{OMe})]$ , **3b** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



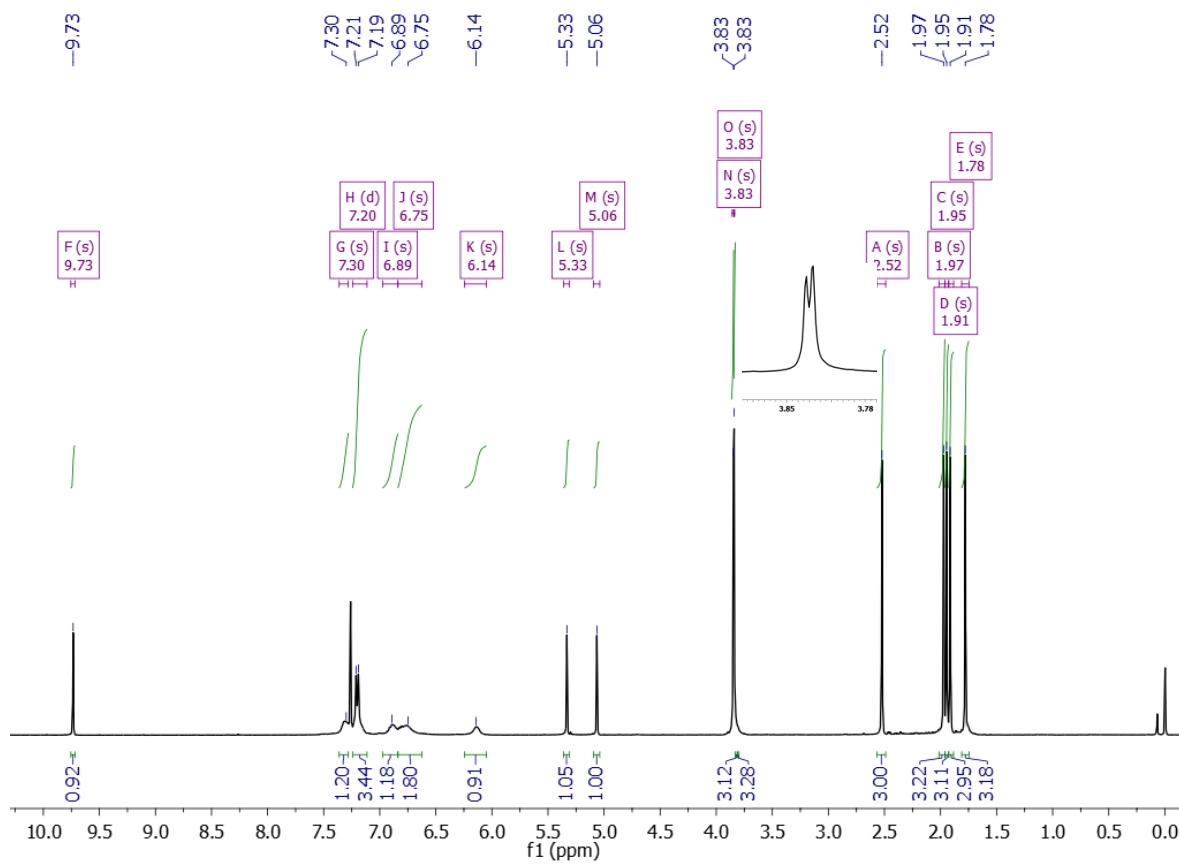
**Figure S8j.** <sup>1</sup>H NMR of [Ru(acac)<sub>2</sub>(L<sup>5</sup>Cl<sub>5</sub>)], **3c** in CDCl<sub>3</sub> with TMS (  $\delta$  = 0 ppm) as internal standard.



**Figure S8k.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^{6\text{H},\text{H}})]$ , **4a** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.

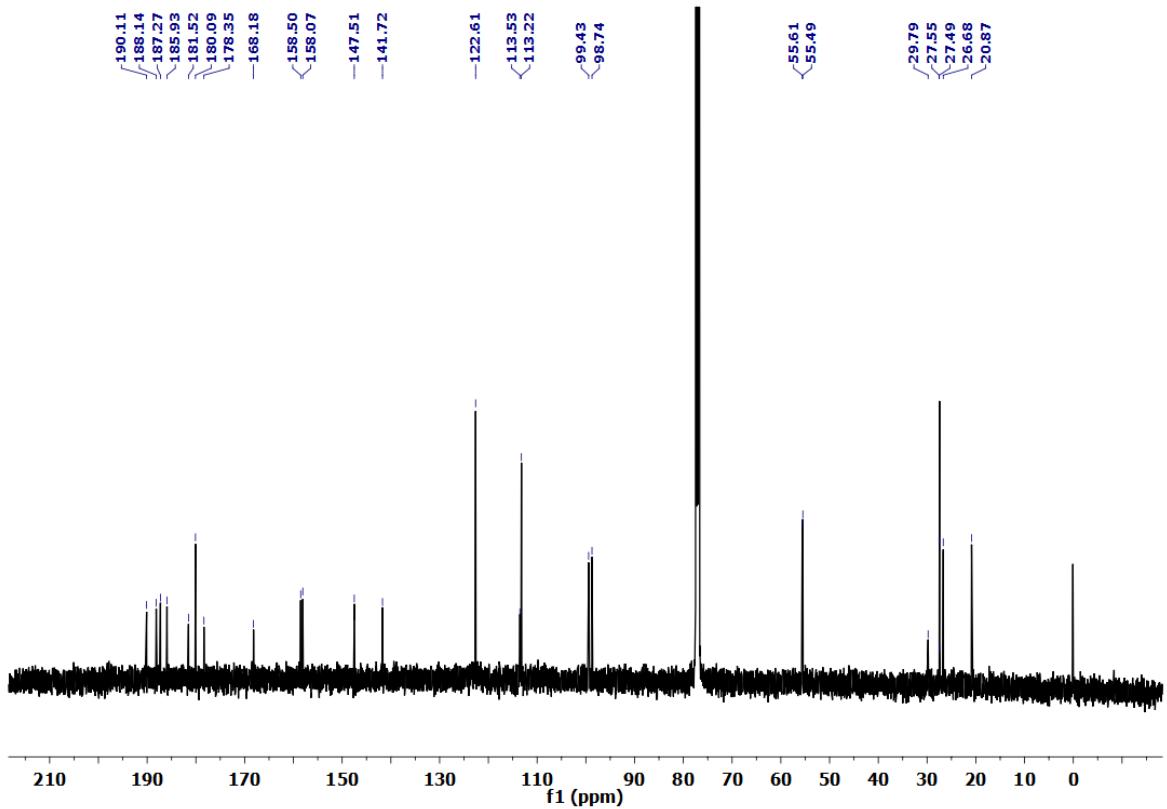


**Figure S8l.**  $^{13}\text{C}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^{\text{6H,6}})]$ , **4a** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.

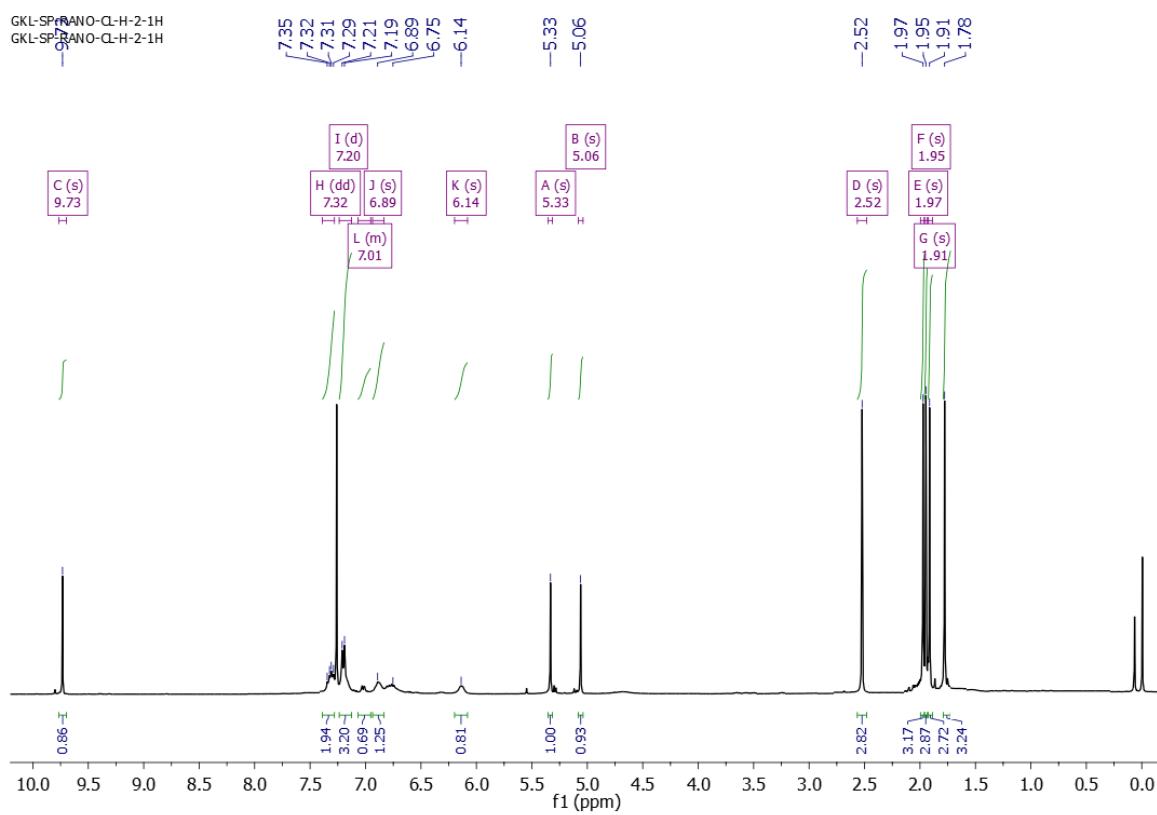


**Figure S8m.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^6\text{OMe},\text{OMe})]$ , **4b** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as

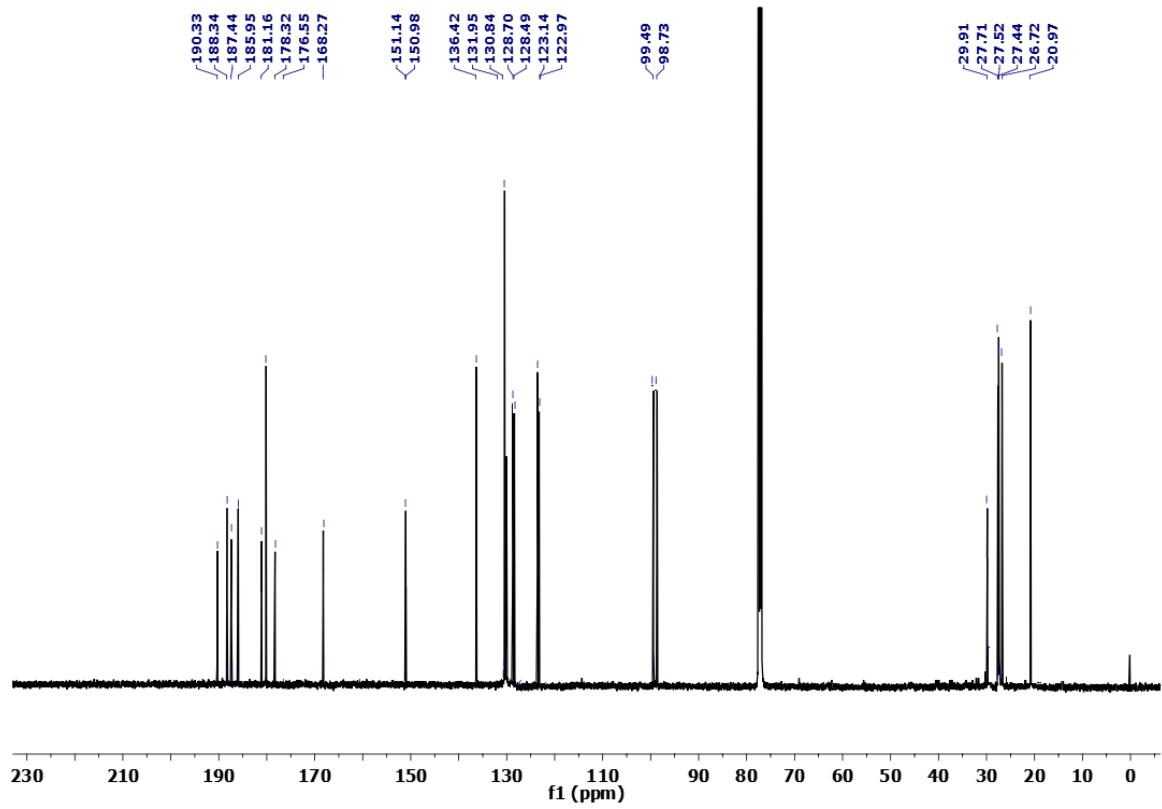
internal standard.



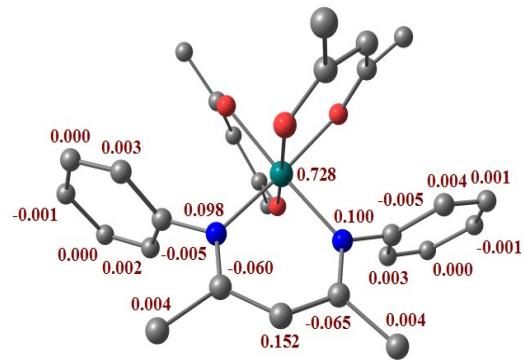
**Figure S8n.**  $^{13}\text{C}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^6\text{OMe},\text{OMe})]$ , **4b** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



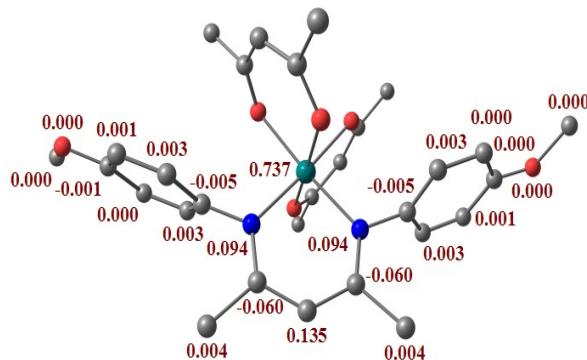
**Figure S8o.**  $^1\text{H}$  NMR of  $[\text{Ru}(\text{acac})_2(\text{L}^6\text{Cl}_2)]$ , **4c** in  $\text{CDCl}_3$  with TMS ( $\delta = 0$  ppm) as internal standard.



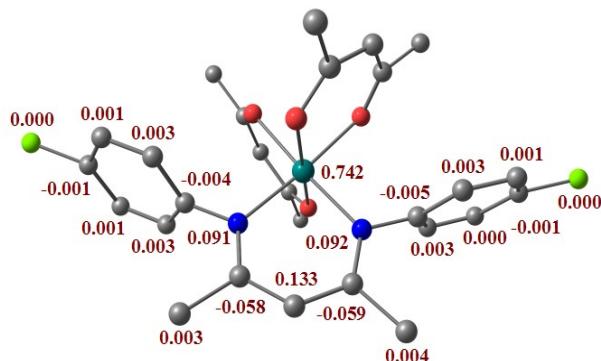
**Figure S8p.** <sup>13</sup>C NMR of [Ru(acac)<sub>2</sub>(L<sup>6-</sup>Cl<sub>2</sub>)], **4c** in CDCl<sub>3</sub> with TMS ( $\delta = 0$  ppm) as internal standard.



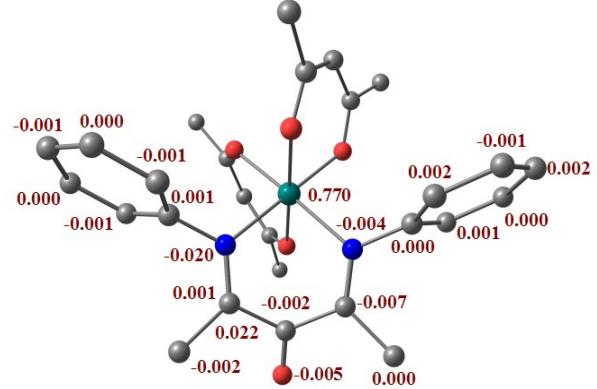
**1a**



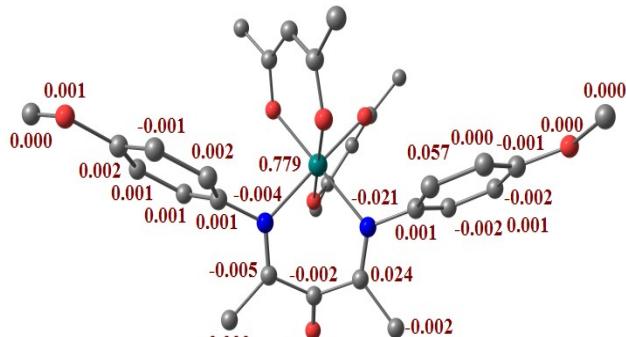
**1b**



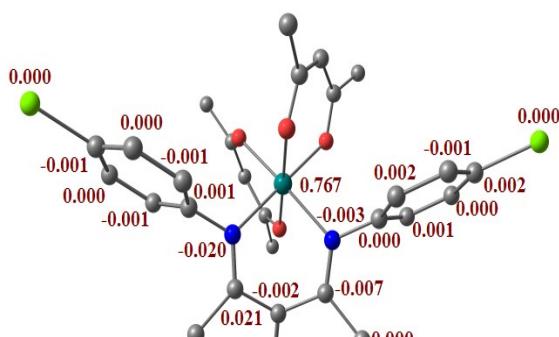
**1c**



**2a<sup>+</sup>**

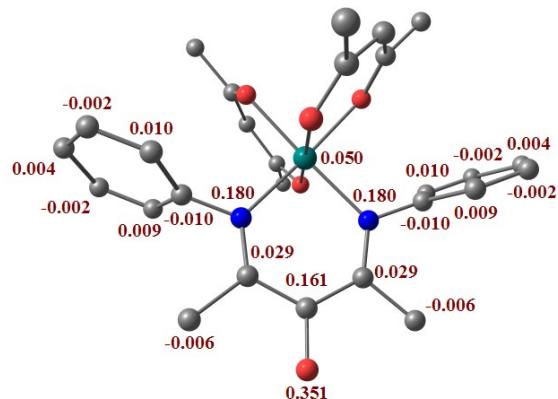


**2b<sup>+</sup>**

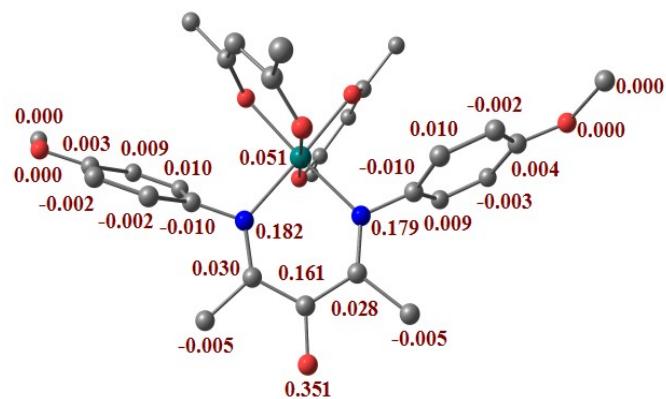


**2c<sup>+</sup>**

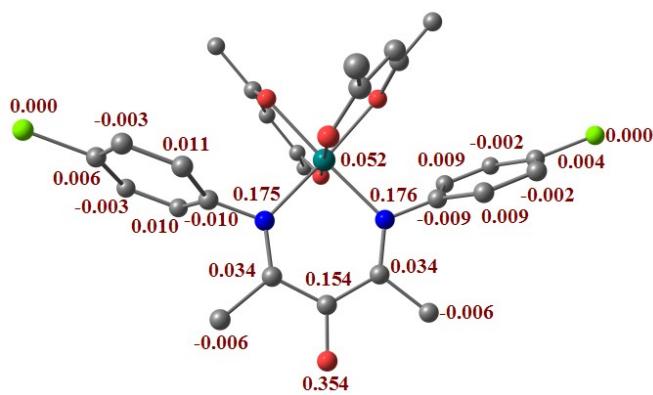
**Figure S9a.** Mulliken spin density plots showing atomic spin density values (spin density values of acac moieties are omitted for clarity).



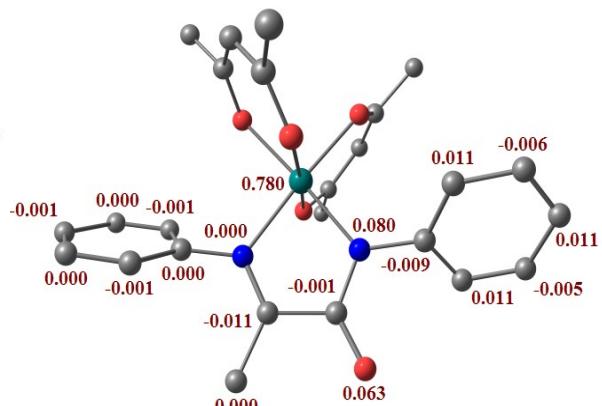
$2\text{a}^-$



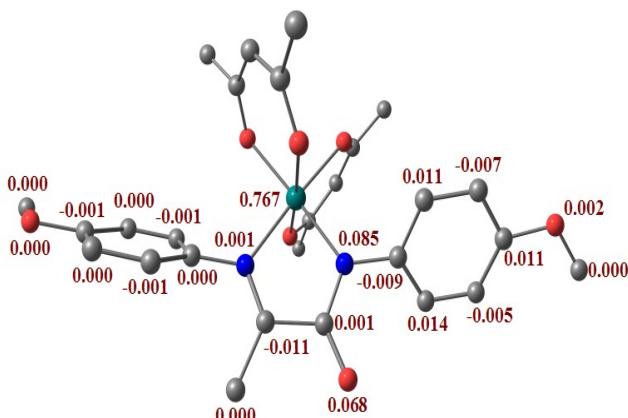
$2\text{b}^-$



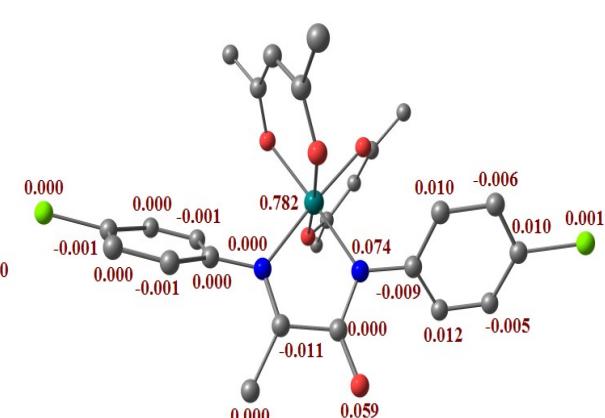
$2\text{c}^-$



$3\text{a}$

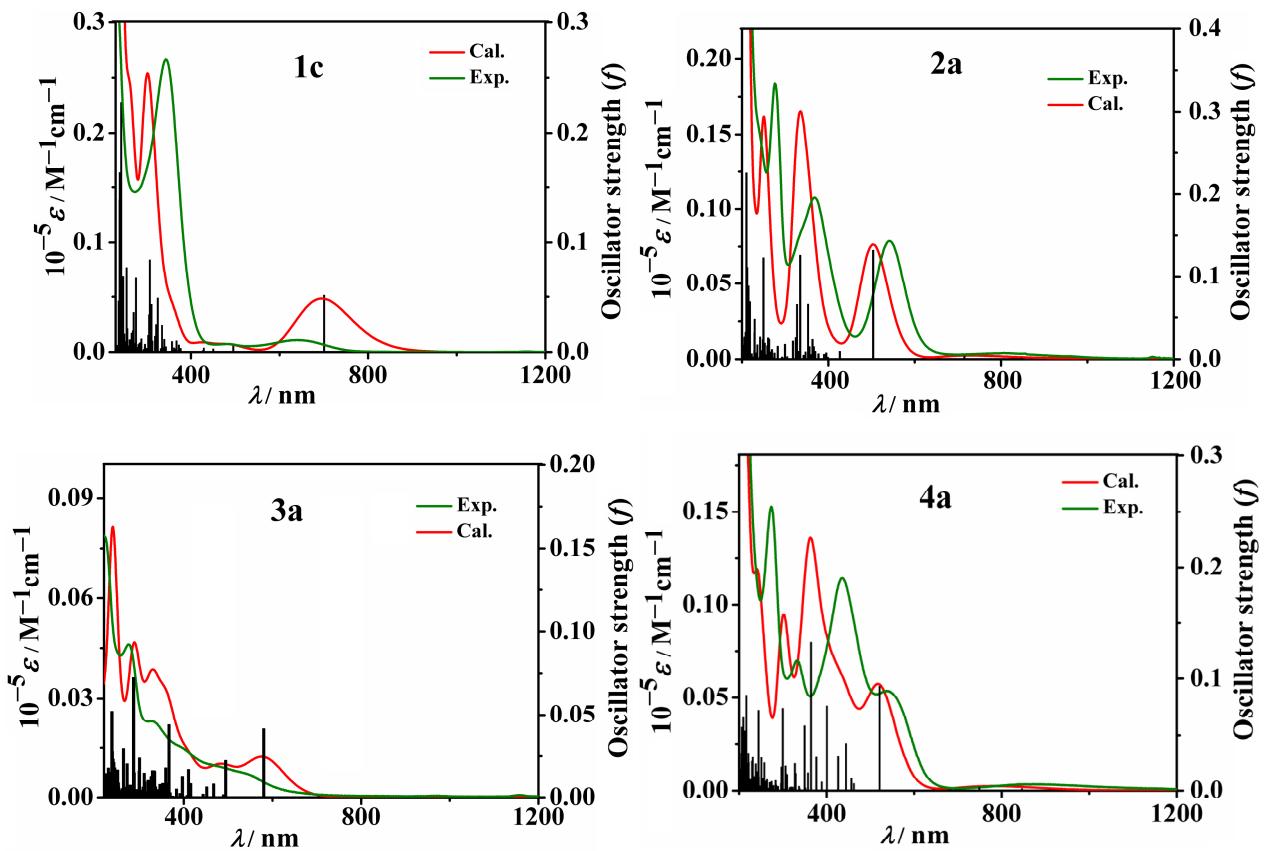


$3\text{b}$

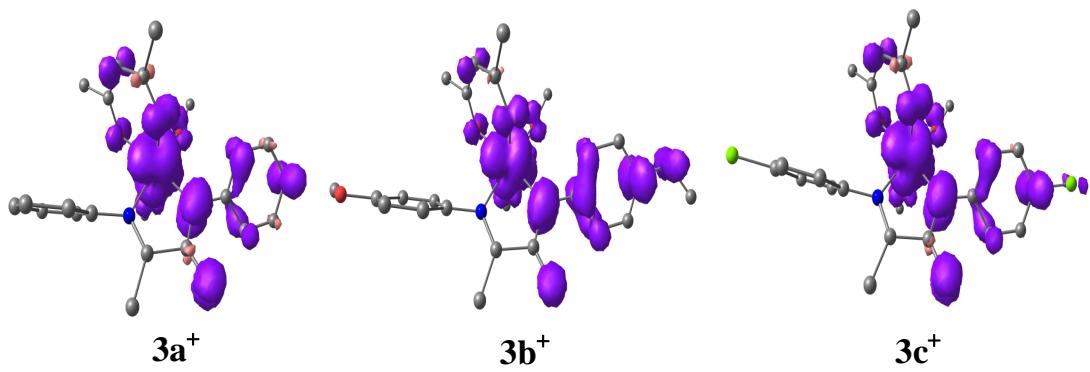


$3\text{c}$

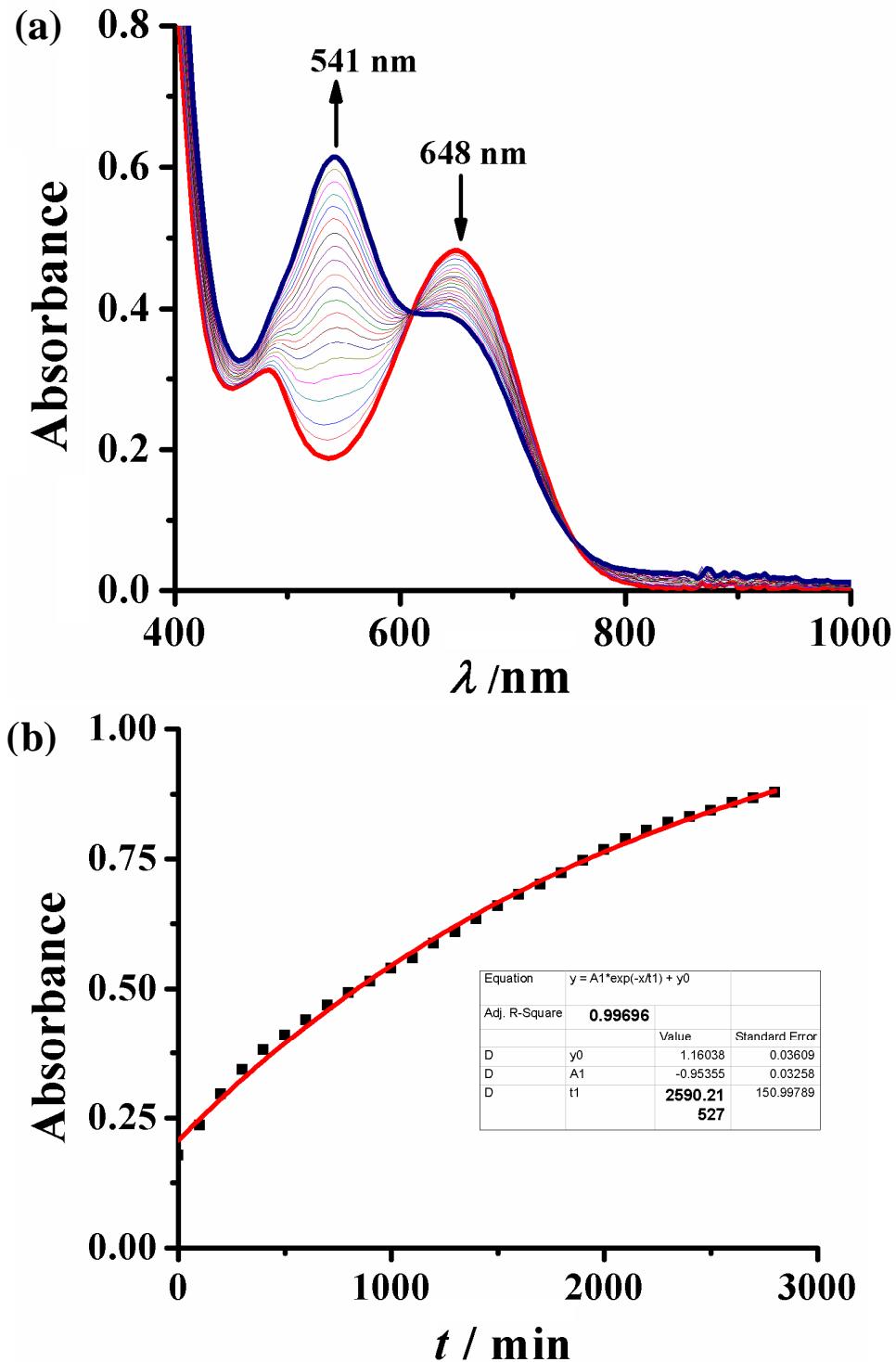
**Figure S9b.** Mulliken spin density plots showing atomic spin density values (spin density values of acac moieties are omitted for clarity).



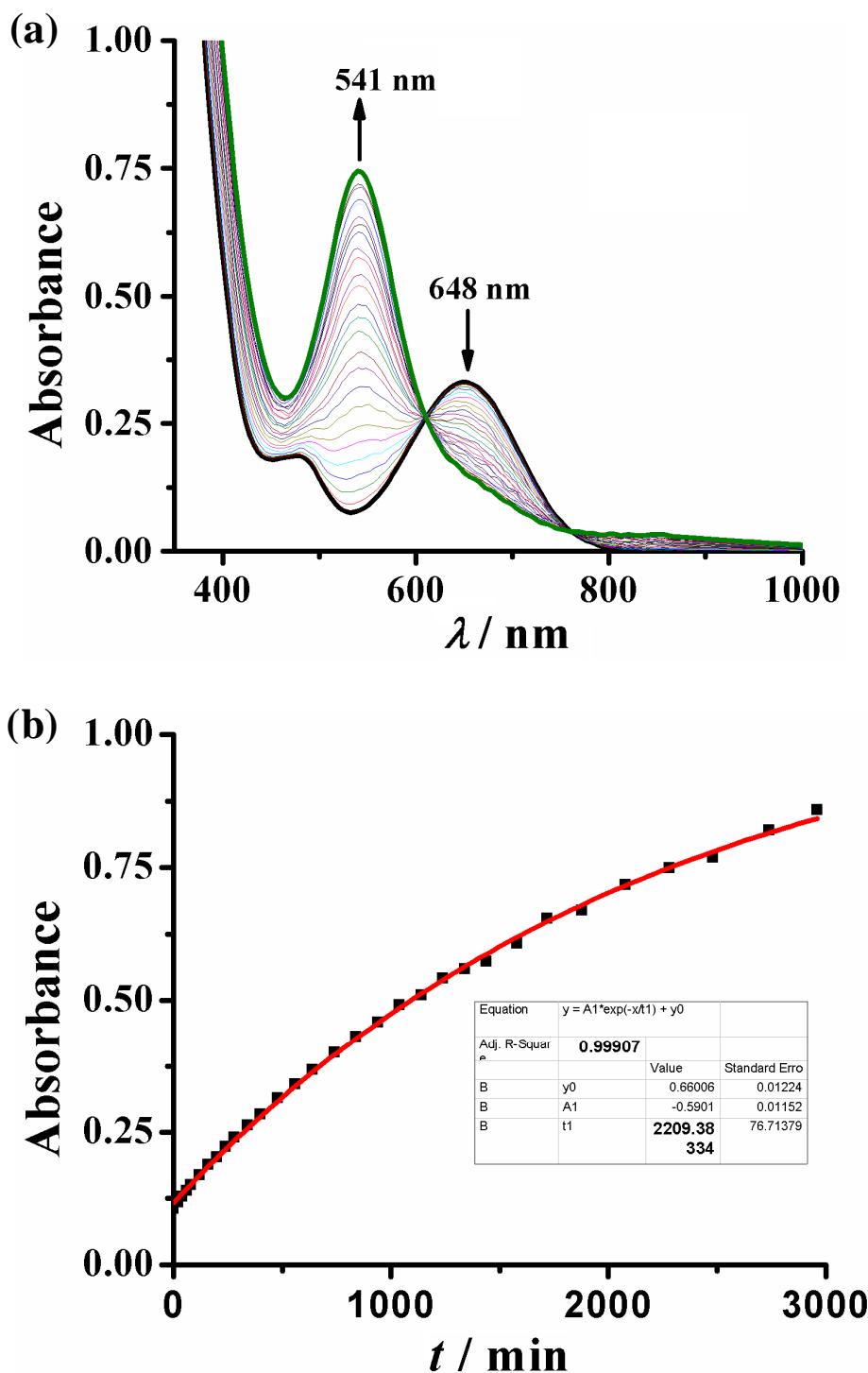
**Figure S10.** Experimental ( $\text{CH}_3\text{CN}$ ) and TD-DFT ((U)B3LYP/CPCM/ $\text{CH}_3\text{CN}$ ) calculated electronic spectra of representative complexes. Oscillator strengths are shown by the black vertical lines; the spectra (red) are convoluted with a Gaussian function having full width at half-maximum of  $3000 \text{ cm}^{-1}$ .



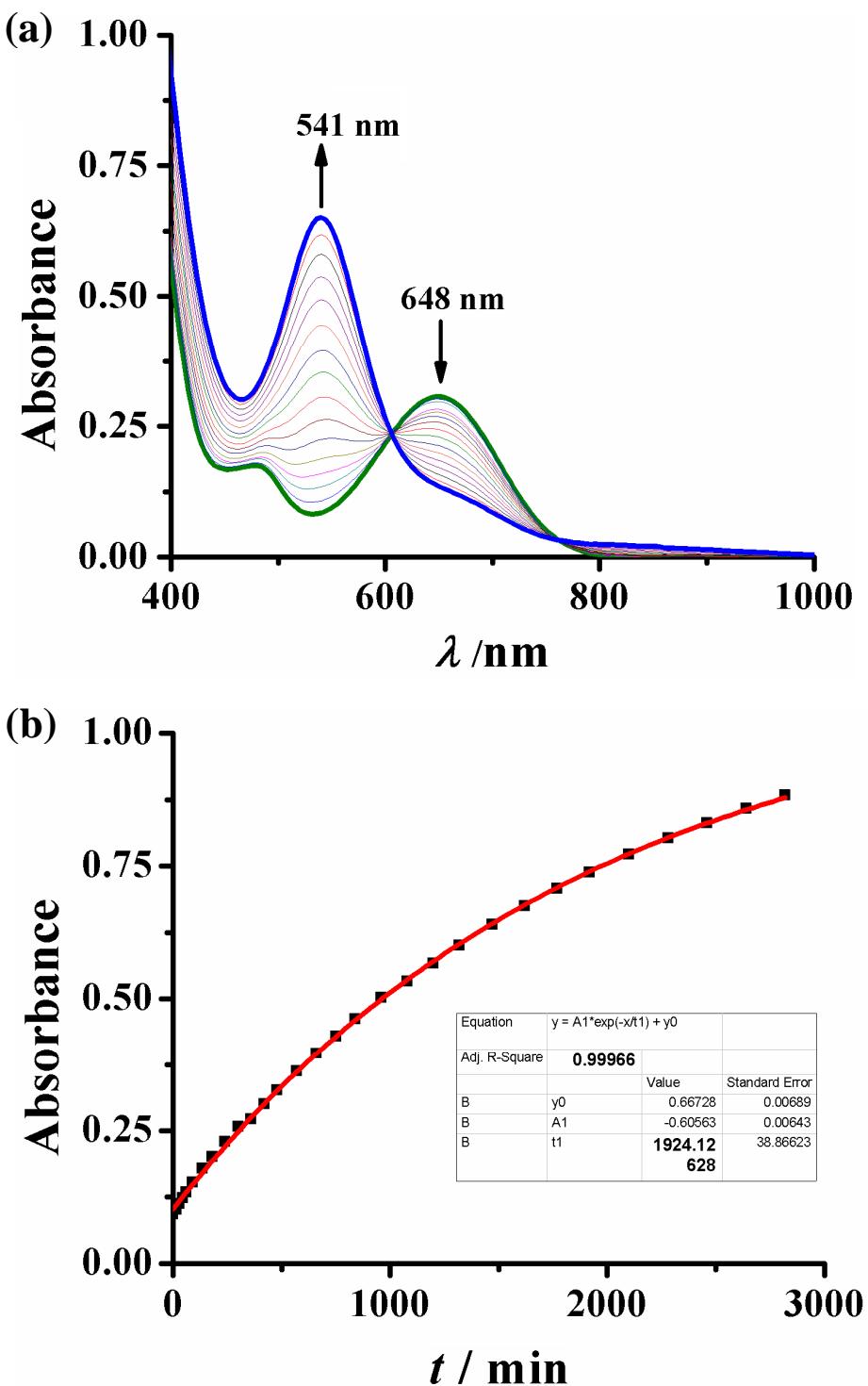
**Figure S11.** Spin density representations of  $\mathbf{3}^n$  ( $n = +1$ ).



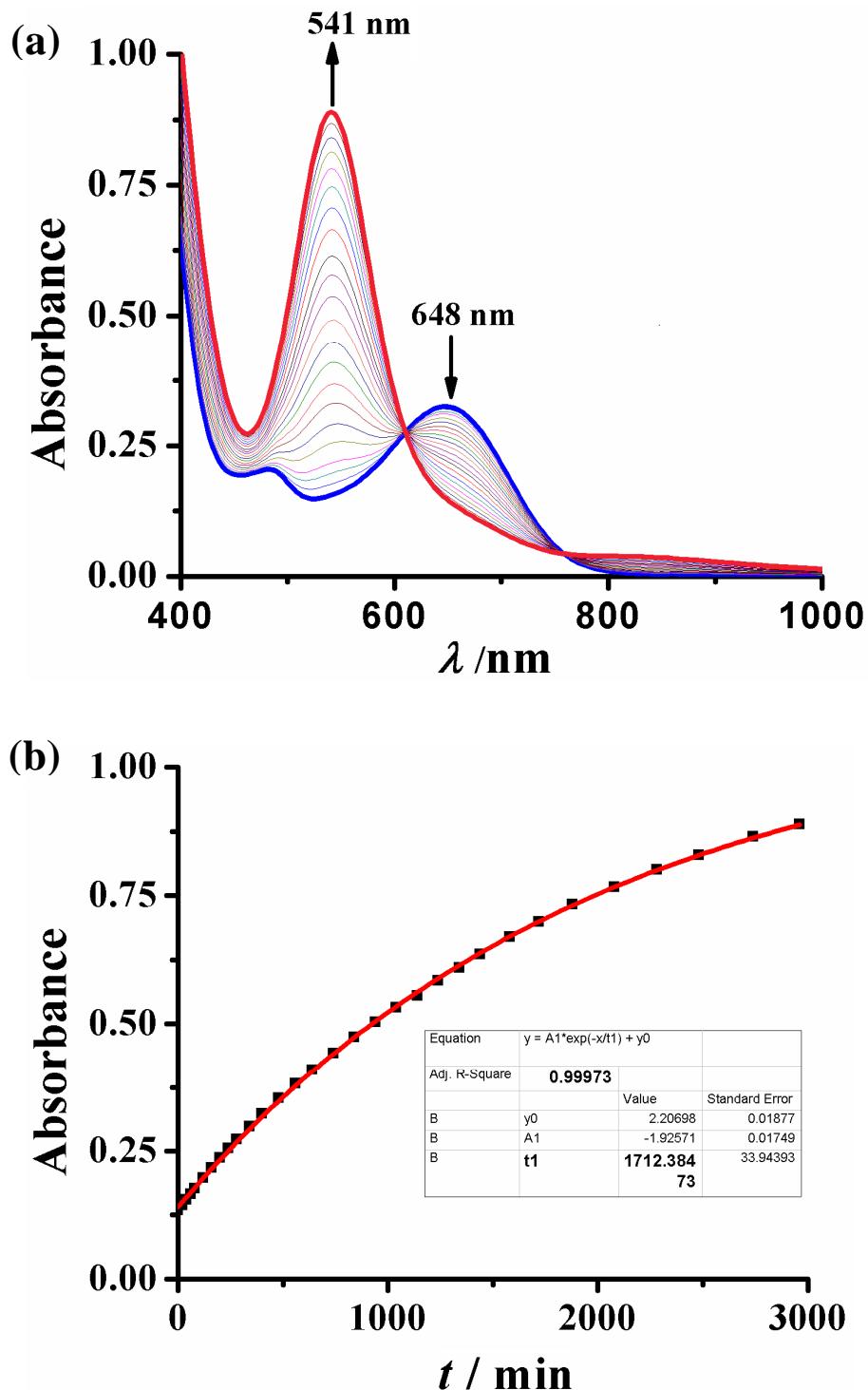
**Figure S12a.** (a) UV-vis change at 541 nm and 648 nm in presence of oxygen for **1a** at 303 K. (b) Rate constant is calculated based on the growing feature of absorbance of 541 nm band as a function of time ( $t$ ).



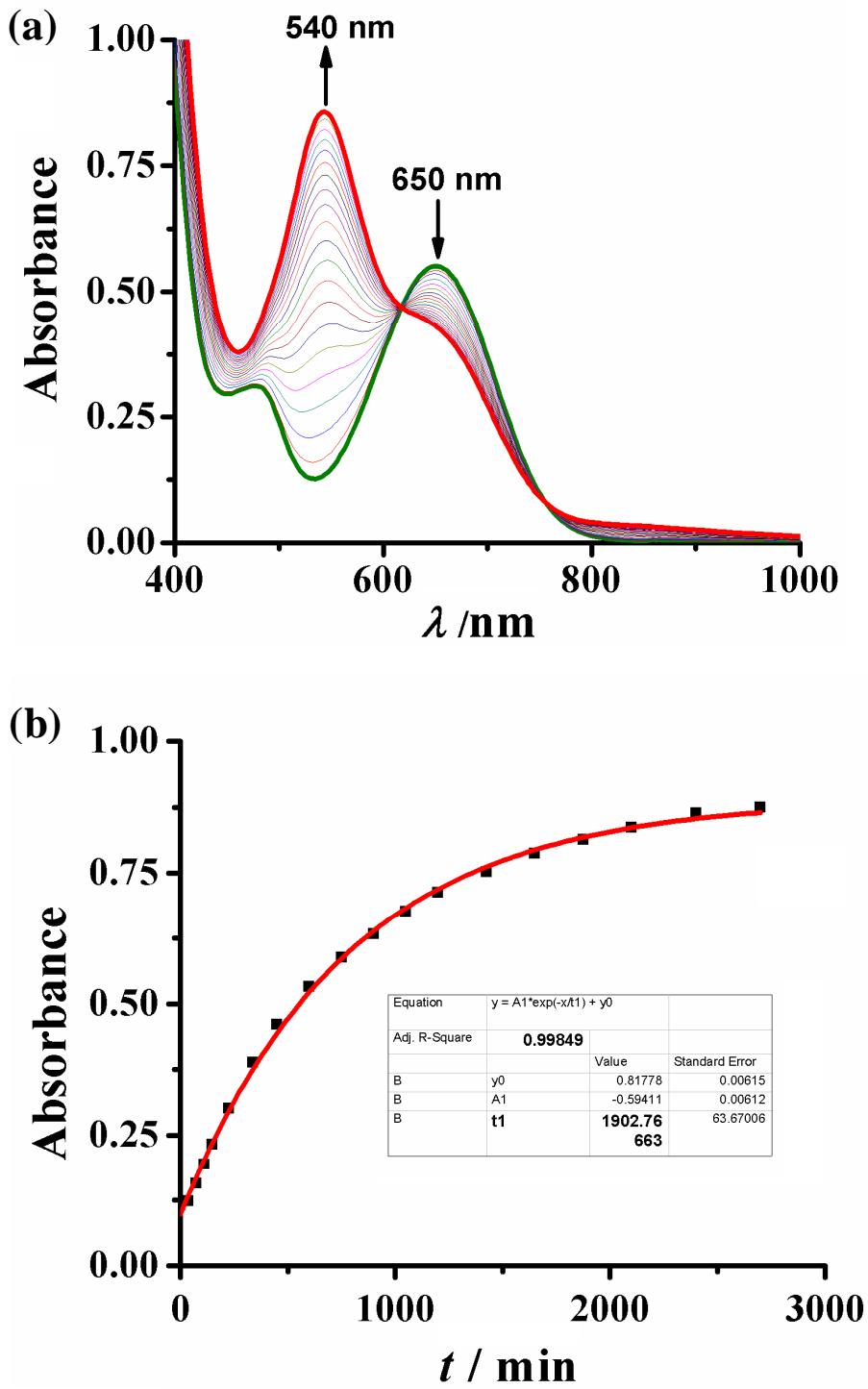
**Figure S12b.** (a) UV-vis change at 541 nm and 648 nm in presence of oxygen for **1a** at 313 K. (b) Rate constant is calculated based on the growing feature of absorbance of 541 nm band as a function of time ( $t$ ).



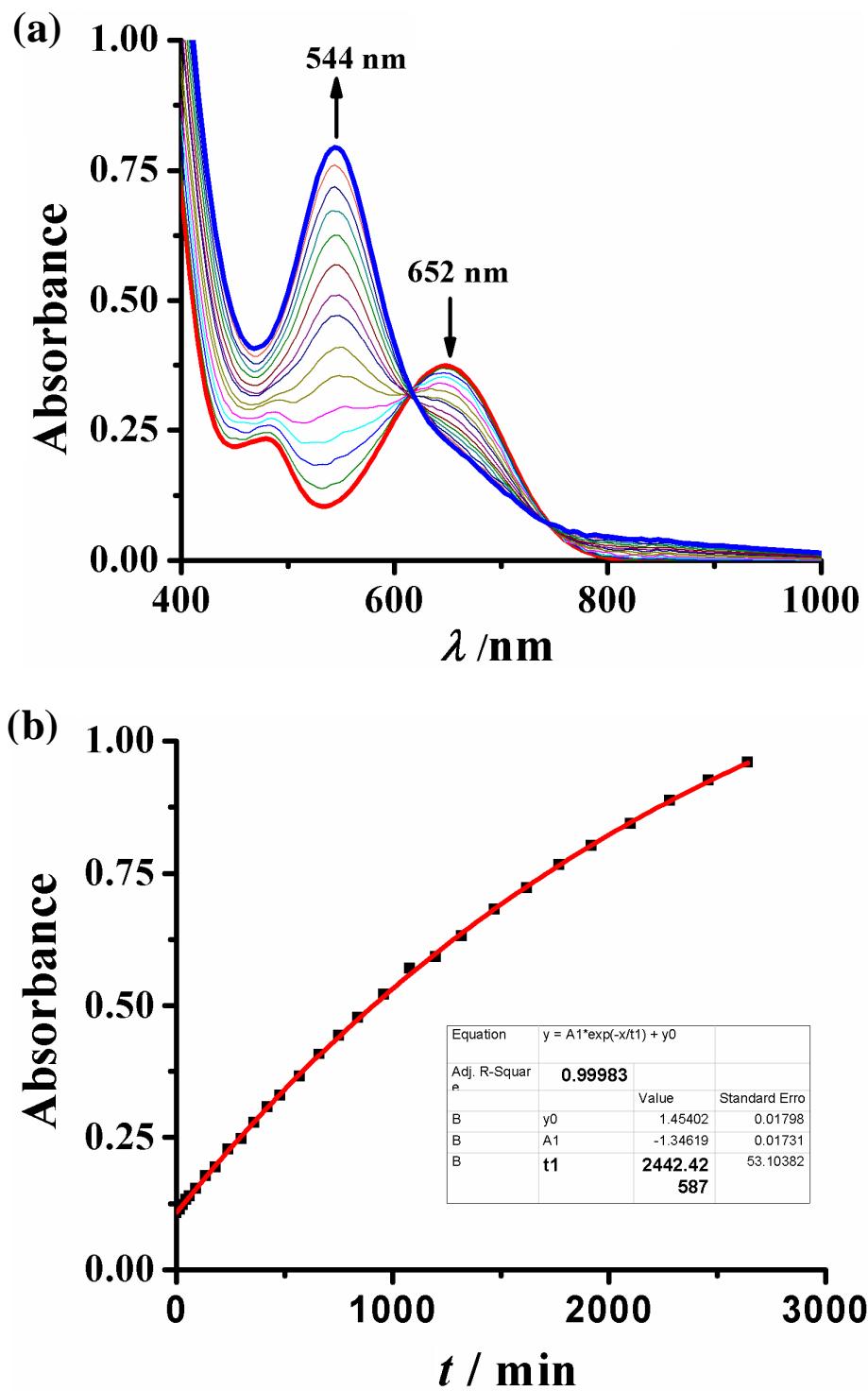
**Figure S12c.** (a) UV-vis change at 541 nm and 648 nm in presence of oxygen for **1a** at 323 K. (b) Rate constant is calculated based on the growing feature of absorbance of 541 nm band as a function of time ( $t$ ).



**Figure S12d.** (a) UV-vis change at 541 nm and 648 nm in presence of oxygen for **1a** at 333 K. (b) Rate constant is calculated based on the growing feature of absorbance of 541 nm band as a function of time ( $t$ ).



**Figure S12e.** (a) UV-vis change at 540 nm and 650 nm in presence of oxygen for **1b** at 333 K. (b) Rate constant is calculated based on the growing feature of absorbance of 540 nm band as a function of time ( $t$ ).

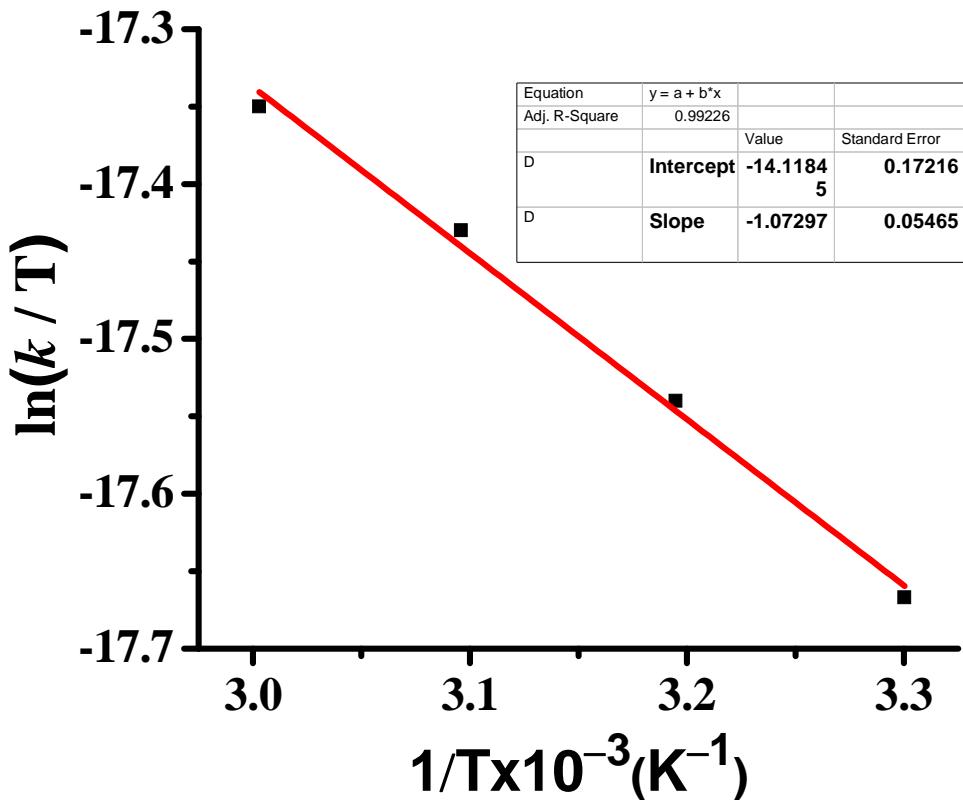


**Figure S12f.** (a) UV-vis change at 544 nm and 652 nm in presence of oxygen for **1c** at 333 K. (b) Rate constant is calculated based on the growing feature of absorbance of 544 nm band as a function of time ( $t$ ).

Activation enthalpy ( $\Delta H^\ddagger$ ) and activation entropy ( $\Delta S^\ddagger$ ) values for the conversion of **1a**→**2a** were obtained from the slope and intercept of plots of  $\ln(k/T)$  versus  $1/T$  using the following equation:

$$\ln(k/T) = \ln(R/Nh) + \Delta S^\ddagger / R - \Delta H^\ddagger / RT$$

where N = Avogadro's number, R = universal gas constant, and h = Planck's constant.



**Figure S12g.** Plot of { $\ln(k/T)$ } versus  $1/T$  for the reaction of **1a** with molecular oxygen.

To determine the errors in activation parameters we have also used the simplified form of the above equation-

$$R[\ln(K_B/h) - \ln(k/T)] = \Delta H^\ddagger / T - \Delta S^\ddagger \quad (\text{where, } R/N = K_B)$$

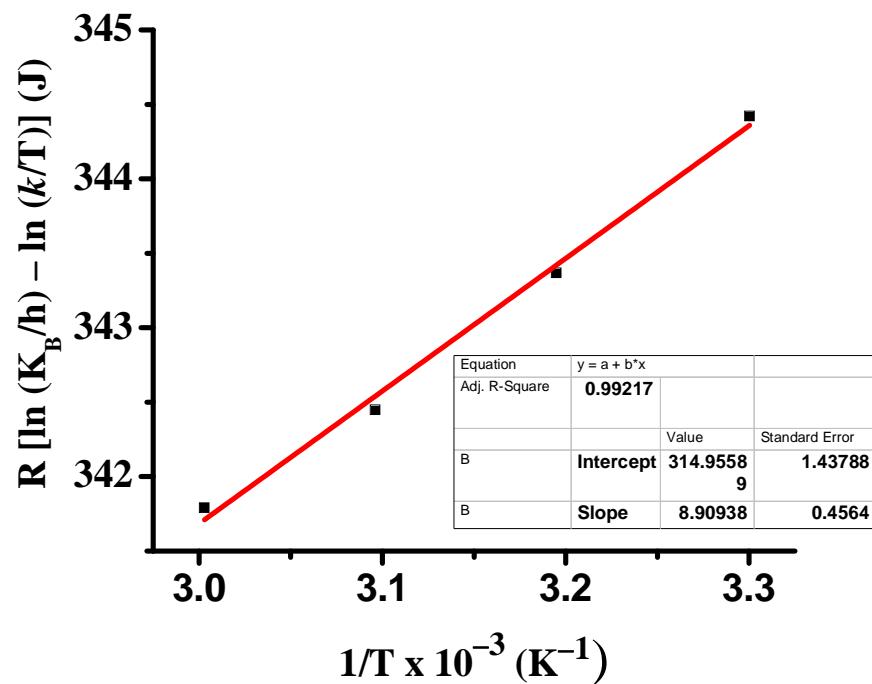
Plot of  $R[\ln(K_B/h) - \ln(k/T)]$  vs  $1/T$  directly gives the values as well as errors in the activation parameters,  $\Delta H^\ddagger$  (=Slope) and  $\Delta S^\ddagger$  (= -Intercept). Now from the inset of figure S7h –

$$\Delta H^\ddagger = \text{Slope} = 8.91 \text{ kJ mol}^{-1} = 2.13 \text{ kcal mol}^{-1}$$

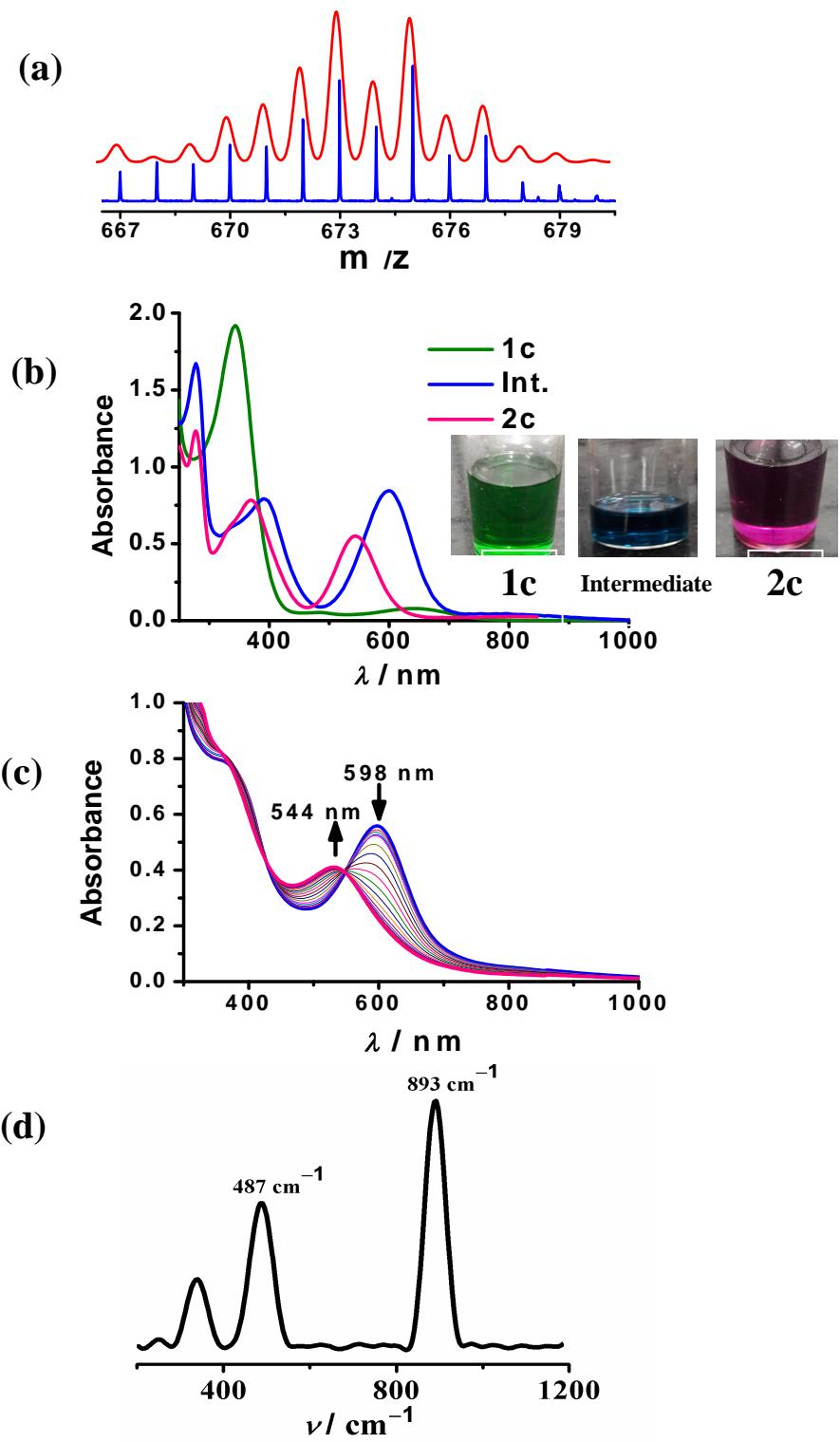
$$\text{Error in } \Delta H^\ddagger = \pm 0.46 \text{ kJ mol}^{-1} = \pm 0.11 \text{ kcal mol}^{-1}$$

$$\Delta S^\ddagger = -(\text{Intercept}) = -315 \text{ J mol}^{-1}\text{K}^{-1} = -75.28 \text{ cal mol}^{-1}\text{K}^{-1}$$

$$\text{Error in } \Delta S^\ddagger = \pm 1.44 \text{ mol}^{-1}\text{K}^{-1} = \pm 0.34 \text{ cal mol}^{-1}\text{K}^{-1}$$



**Figure S12h.** Plot of  $\{R[\ln(K_B/h) - \ln(k/T)]\}$  vs  $1/T$  for the reaction of **1a** with molecular oxygen.



**Figure S13.** (a) ESI(+) mass spectra of  $\{\text{Intermediate}+\text{Na}\}^+$  in  $\text{CH}_3\text{CN}$  (blue, experimental and red, simulated). (b) Electronic spectra in  $\text{CH}_3\text{CN}$  of **1c**, intermediate and **2c**. Inset shows the difference in color. (c) UV-vis change for  $\text{Intermediate} \rightarrow \mathbf{2c}$  conversion at 298 K. (d) Raman spectrum of intermediate for  $\mathbf{1c} \rightarrow \mathbf{2c}$  conversion.

**Table S1. Selected Crystallographic Parameters**

	<b>1b</b>	<b>1c</b>	<b>2a</b>	<b>1.5x2b</b>	<b>3a</b>	<b>4b</b>
empirical formula	C <sub>29</sub> H <sub>35</sub> N <sub>2</sub> O <sub>6</sub> Ru	C <sub>27</sub> H <sub>29</sub> N <sub>2</sub> O <sub>4</sub> Cl <sub>2</sub> Ru	C <sub>27</sub> H <sub>30</sub> N <sub>2</sub> O <sub>5</sub> Ru	C <sub>43.50</sub> H <sub>51</sub> N <sub>3</sub> O <sub>10.50</sub> Ru <sub>1.50</sub>	C <sub>50</sub> H <sub>54</sub> N <sub>4</sub> O <sub>10</sub> Ru <sub>2</sub>	C <sub>29</sub> H <sub>26</sub> N <sub>2</sub> O <sub>8</sub> Ru
formula weight	608.66	617.49	563.60	935.47	1073.11	637.63
crystal system	Triclinic	Monoclinic	Triclinic	Triclinic	triclinic	monoclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub>
<i>a</i> (Å)	8.7263(19)	29.7932(10)	8.640(2)	12.8937(7)	8.3547(3)	12.8560(6)
<i>b</i> (Å)	10.199(2)	8.549(3)	12.194(4)	15.2287(10)	12.3211(3)	15.4998(7)
<i>c</i> (Å)	15.806(4)	23.075(7)	12.282(4)	24.1360(12)	23.6301(6)	15.3235(8)
$\alpha$ (deg)	84.398(6)	90.00	104.803(5)	73.227(5)	76.431(2)	90
$\beta$ (deg)	85.611(7)	110.315(5)	91.430(5)	75.505(5)	88.605(2)	114.065(6)
$\gamma$ (deg)	78.741(6)	90.00	93.581(5)	65.542(6)	86.731(3)	90
<i>V</i> (Å <sup>3</sup> )	1370.7(5)	5512(3)	1247.5(6)	4083.6(4)	2360.56(12)	2788.1(3)
<i>Z</i>	2	8	2	4	2	4
$\mu$ (mm <sup>-1</sup> )	0.617	0.797	0.669	0.626	0.703	0.616
$\rho_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.475	1.488	1.500	1.522	1.510	1.519
<i>T</i> (K)	100(2)	100(2)	100(2)	100(2)	150(2)	150(2)
<i>F</i> (000)	630	2520	580	1932	1100	1312
$\theta$ range (deg)	3.1 to 25.0	3.0 to 25.00	3.0 to 25.00	1.8 to 25.0	3.0 to 25.00	2.1 to 25.0
data/restraints /parameters	4760/0/351	9610/0/661	4395/0/322	13674/0/078	8219 / 0 / 575	9750/13/723
$R_1, wR_2[I > 2\sigma(I)]$	0.0362, 0.0805	0.0409, 0.0827	0.0288, 0.0765	0.0719, 0.1503	0.0515, 0.1284	0.0614, 0.1481
$R_1, wR_2(\text{all data})$	0.0424, 0.0846	0.0507, 0.0886	0.0322, 0.0784	0.1026, 0.1688	0.0625, 0.1365	0.0687, 0.1556
<i>GOF</i> on <i>F</i> <sup>2</sup>	1.056	1.061	1.086	1.081	1.031	1.035
largest difference in peak and hole (e Å <sup>-3</sup> )	0.435, -0.504	0.534, -0.556	0.525, -0.338	1.496, -1.070	1.532, -1.691	3.522, -0.595

**Table S2. Selected Experimental and DFT Calculated Bond Lengths (Å) for **1a**, **1b** and **1c****

bond lengths	DFT	X-ray	DFT	X-ray	DFT
	<b>1a</b> (S=1/2)	<b>1b</b>	<b>1b</b> (S=1/2)	<b>1c</b> <b>(Molecule A)</b>	<b>1c</b> (S=1/2)
Ru(1)-N(1)	2.040	2.009(2)	2.046	2.012(3)	2.050
Ru(1)-N(2)	2.054	2.003(2)	2.046	2.007(3)	2.045
Ru(1)-O(1)	2.101	2.071(2)	2.109	2.064(2)	2.101
Ru(1)-O(2)	2.080	2.020(2)	2.061	2.029(2)	2.054
Ru(1)-O(3)	2.088	2.061 (2)	2.108	2.067(2)	2.106
Ru(1)-O(4)	2.054	2.024(2)	2.061	2.021(2)	2.066
C(2)-N(1)	1.339	1.338(4)	1.335	1.336(4)	1.334
C(4)-N(2)	1.330	1.326(4)	1.336	1.333(4)	1.337
C(2)-C(3)	1.402	1.400(4)	1.405	1.398(5)	1.405
C(3)-C(4)	1.410	1.397(4)	1.404	1.397(5)	1.403
C(6)-N(1)	1.435	1.443(4)	1.436	1.444(5)	1.432
C(12)-N(2)	1.433	1.441(4)	1.436	1.448(4)	1.433

**Table S3. Selected Experimental and DFT Calculated Bond Angles [deg] for **1a**, **1b** and **1c****

bond angle [deg]	DFT	X-ray	DFT	X-ray	DFT
	<b>1a</b> (S=1/2)	<b>1b</b>	<b>1b</b> (S=1/2)	<b>1c</b> <b>(Molecule A)</b>	<b>1c</b> (S=1/2)
N(1)-Ru(1)-N(2)	90.38	91.67(10)	91.84	91.07(11)	91.47
N(1)-Ru(1)-O(1)	176.72	176.88(8)	175.58	175.75(10)	175.67
N(1)-Ru(1)-O(2)	91.96	87.40(9)	88.48	88.97(10)	88.04
N(1)-Ru(1)-O(3)	92.67	92.26(9)	92.31	92.52(10)	92.33
N(1)-Ru(1)-O(4)	91.05	93.31(9)	94.33	92.83(10)	94.42
N(2)-Ru(1)-O(1)	92.24	91.40(9)	92.26	93.05(10)	92.49
N(2)-Ru(1)-O(2)	94.55	93.07(9)	94.30	92.04(10)	93.56
N(2)-Ru(1)-O(3)	176.41	176.07(9)	175.50	176.26(10)	176.17
N(2)-Ru(1)-O(4)	86.98	89.15(9)	88.41	89.11(10)	89.76
O(1)-Ru(1)-O(2)	89.80	91.88(8)	89.54	91.92(9)	89.96
O(1)-Ru(1)-O(3)	84.65	84.68(8)	83.65	83.38(9)	83.73
O(1)-Ru(1)-O(4)	87.12	87.30(8)	87.32	86.20(9)	87.36
O(2)-Ru(1)-O(3)	87.26	87.01(8)	87.44	86.98(10)	87.06
O(2)-Ru(1)-O(4)	176.62	177.65(8)	176.04	177.85(9)	175.83
O(3)-Ru(1)-O(4)	91.06	90.72(8)	89.56	91.76(9)	89.47

**Table S4. Selected Experimental and DFT Calculated Bond Lengths (Å) for **2a**, **2b** and **2c****

bond lengths	X-ray	DFT	X-ray	DFT	DFT
	<b>2a</b>	<b>2a (S=0)</b>	<b>2b (Molecule B)</b>	<b>2b (S=0)</b>	<b>2c (S=0)</b>
Ru(1)-N(1)	1.978(2)	2.041	1.973(5)	2.038	2.041
Ru(1)-N(2)	1.974(2)	2.036	1.960(6)	2.038	2.036
Ru(1)-O(1)	2.0346(19)	2.079	2.024(4)	2.099	2.062
Ru(1)-O(2)	2.0182(17)	2.063	2.001(6)	2.099	2.077
Ru(1)-O(3)	2.0529(17)	2.095	2.035(4)	2.081	2.097
Ru(1)-O(4)	2.0504(18)	2.095	2.037(7)	2.063	2.093
C(2)-N(1)	1.311(3)	1.303	1.31(1)	1.307	1.304
C(4)-N(2)	1.316(3)	1.306	1.31(1)	1.303	1.307
C(2)-C(3)	1.486(4)	1.498	1.48(1)	1.495	1.498
C(3)-C(4)	1.481(4)	1.495	1.47(1)	1.498	1.496
C(3)-O(5)	1.240(3)	1.233	1.25(1)	1.233	1.232
C(6)-N(1)	1.453(3)	1.439	1.44(1)	1.439	1.437
C(12)-N(2)	1.449(3)	1.440	1.436(9)	1.440	1.438

**Table S5. Selected Experimental and DFT Calculated Bond Angles [deg] for **2a**, **2b** and **2c****

bond angle [deg]	X-ray	DFT	X-ray	DFT	DFT
	<b>2a</b>	<b>2a</b> ( <i>S</i> =0)	<b>2b</b> (Molecule B)	<b>2b</b> ( <i>S</i> =0)	<b>2c</b> ( <i>S</i> =0)
N(1)-Ru(1)-N(2)	87.19(9)	88.48	87.9(2)	88.74	88.41
N(1)-Ru(1)-O(1)	178.68(7)	176.38	178.4(2)	174.16	84.74
N(1)-Ru(1)-O(2)	87.49(8)	84.75	86.7(2)	94.75	176.45
N(1)-Ru(1)-O(3)	94.07(8)	93.30	94.3(2)	92.57	95.54
N(1)-Ru(1)-O(4)	93.15(8)	95.52	93.3(2)	86.48	93.12
N(2)-Ru(1)-O(1)	92.65(8)	93.12	92.4(2)	93.59	86.48
N(2)-Ru(1)-O(2)	86.49(8)	86.61	88.6(2)	94.69	93.13
N(2)-Ru(1)-O(3)	172.79(7)	174.84	173.5(2)	176.98	94.32
N(2)-Ru(1)-O(4)	94.85(8)	94.11	93.3(2)	85.22	174.78
O(1)-Ru(1)-O(2)	93.81(7)	92.10	94.9(2)	90.39	92.16
O(1)-Ru(1)-O(3)	86.26(7)	84.84	85.7(2)	84.85	179.16
O(1)-Ru(1)-O(4)	85.55(7)	87.61	85.1(2)	88.39	88.69
O(2)-Ru(1)-O(3)	86.47(7)	88.73	85.3(2)	87.91	87.54
O(2)-Ru(1)-O(4)	178.54(6)	179.24	178.1(2)	178.77	85.08
O(3)-Ru(1)-O(4)	92.18(7)	90.55	92.8(2)	92.14	90.51

**Table S6. Selected Experimental and DFT Calculated Bond Lengths ( $\text{\AA}$ ) for **3a**, **3b** and **3c****

bond lengths	X-ray	DFT	DFT	DFT
	<b>3a</b>	<b>3a</b> ( $S=1/2$ )	<b>3b</b> ( $S=0$ )	<b>3c</b> ( $S=1/2$ )
	(Molecule A)			
Ru(1)-N(1)	2.000(3)	2.024	2.021	2.029
Ru(1)-N(2)	2.016(4)	2.087	2.086	2.088
Ru(1)-O(1)	2.030(3)	2.089	2.093	2.086
Ru(1)-O(2)	2.004(3)	2.061	2.062	2.060
Ru(1)-O(3)	2.031(3)	2.042	2.043	2.040
Ru(1)-O(4)	1.998(3)	2.080	2.083	2.078
C(1)-N(1)	1.352(6)	1.371	1.372	1.371
C(2)-N(2)	1.284(5)	1.292	1.293	1.293
C(3)-C(2)	1.499(6)	1.516	1.514	1.516
C(2)-C(1)	1.474(6)	1.497	1.498	1.497
C(1)-O(5)	1.224(5)	1.232	1.233	1.231
C(4)-N(1)	1.352(6)	1.422	1.421	1.419
C(10)-N(2)	1.425(5)	1.430	1.429	1.428

**Table S7. Selected Experimental and DFT Calculated Bond Angles [deg] for **3a**, **3b** and **3c****

bond angle [deg]	X-ray	DFT	DFT	DFT
	<b>3a</b>	<b>3a</b> ( <i>S</i> =1/2)	<b>3b</b> ( <i>S</i> =0)	<b>3c</b> ( <i>S</i> =1/2)
	(Molecule A)			
N(1)-Ru(1)-N(2)	79.70(14)	79.64	79.81	79.50
N(1)-Ru(1)-O(1)	176.00(13)	176.68	177.06	176.49
N(1)-Ru(1)-O(2)	90.35(12)	91.63	91.64	91.53
N(1)-Ru(1)-O(3)	97.88(13)	91.85	91.90	91.86
N(1)-Ru(1)-O(4)	89.97(12)	96.91	96.87	97.02
N(2)-Ru(1)-O(1)	96.35(12)	97.05	97.25	96.99
N(2)-Ru(1)-O(2)	91.25(13)	93.01	92.94	93.25
N(2)-Ru(1)-O(3)	177.56(12)	176.15	176.30	176.02
N(2)-Ru(1)-O(4)	86.79(12)	86.30	86.40	86.06
O(1)-Ru(1)-O(2)	90.41(11)	88.41	88.47	88.44
O(1)-Ru(1)-O(3)	86.06(11)	88.04	87.92	88.10
O(1)-Ru(1)-O(4)	89.13(11)	86.41	86.07	86.49
O(2)-Ru(1)-O(3)	89.15(12)	88.79	88.79	88.76
O(2)-Ru(1)-O(4)	177.92(11)	176.27	176.22	176.36
O(3)-Ru(1)-O(4)	92.85(11)	92.13	92.09	92.15

**Table S8. Selected Experimental and DFT Calculated Bond Lengths ( $\text{\AA}$ ) for **4a**, **4b** and **4c****

bond lengths	DFT	X-ray	DFT	DFT
	<b>4a</b> ( $S=0$ )	<b>4b</b> (Molecule A)	<b>4b</b> ( $S=0$ )	<b>4c</b> ( $S=0$ )
Ru(1)-N(1)	2.001	1.934(8)	2.001	2.002
Ru(1)-N(2)	2.072	2.002(8)	2.071	2.073
Ru(1)-O(1)	2.091	2.052(7)	2.092	2.088
Ru(1)-O(2)	2.099	2.031(6)	2.104	2.098
Ru(1)-O(3)	2.074	2.029(7)	2.076	2.072
Ru(1)-O(4)	2.051	2.020(7)	2.050	2.051
C(2)-N(1)	1.323	1.333(14)	1.323	1.324
C(4)-N(2)	1.296	1.285(13)	1.296	1.296
C(2)-C(3)	1.496	1.468(16)	1.496	1.496
C(3)-C(4)	1.513	1.499(15)	1.512	1.512
C(3)-O(5)	1.222	1.241(13)	1.222	1.221
C(1)-O(6)	1.216	1.164(15)	1.216	1.215

**Table S9. Selected Experimental and DFT Calculated Bond Angles [deg] for **4a**, **4b** and **4c****

bond angle [deg]	DFT	X-ray	DFT	DFT
	<b>4a</b>	<b>4b</b> (Molecule A)	<b>4b</b> ( <i>S</i> =0)	<b>4c</b> ( <i>S</i> =0)
N(1)-Ru(1)-N(2)	88.55	88.3(3)	88.51	88.54
N(1)-Ru(1)-O(1)	175.19	174.2(3)	174.63	175.51
N(1)-Ru(1)-O(2)	95.16	92.9(3)	95.55	94.96
N(1)-Ru(1)-O(3)	92.85	96.6(3)	93.11	92.94
N(1)-Ru(1)-O(4)	87.48	88.8(3)	87.24	87.55
N(2)-Ru(1)-O(1)	92.51	90.7(3)	92.29	92.25
N(2)-Ru(1)-O(2)	94.48	93.1(3)	94.76	94.53
N(2)-Ru(1)-O(3)	177.05	174.8(3)	176.79	176.96
N(2)-Ru(1)-O(4)	87.94	88.0(3)	87.54	88.12
O(1)-Ru(1)-O(2)	89.44	92.9(3)	89.68	89.39
O(1)-Ru(1)-O(3)	85.89	84.5(3)	85.85	86.07
O(1)-Ru(1)-O(4)	84.98	85.4(3)	84.86	84.88
O(2)-Ru(1)-O(3)	87.98	85.0(3)	87.84	88.0
O(2)-Ru(1)-O(4)	177.29	178.0(3)	177.18	177.41
O(3)-Ru(1)-O(4)	92.49	93.8(3)	92.45	92.52

**Table S10. EPR Data in CH<sub>3</sub>CN/Toluene (1:1) at 100 K**

complex	<i>g</i> <sub>1</sub>	<i>g</i> <sub>2</sub>	<i>g</i> <sub>3</sub>	<i>&lt;g&gt;<sup>a</sup></i>	<i>Δg<sup>b</sup></i>
<b>1a</b>	2.185	2.111	1.871	2.060	0.314
<b>1b</b>	2.192	2.099	1.872	2.059	0.320
<b>1c</b>	2.185	2.114	1.880	2.064	0.305
<b>2a<sup>+</sup></b>	2.496	2.220	1.882	2.214	0.614
<b>2a<sup>-</sup></b>	2.079	2.005	–	2.030	0.074
<b>2b<sup>+</sup></b>	2.412	2.141	1.805	2.134	0.607
<b>2b<sup>-</sup></b>	2.088	2.006	–	2.034	0.082
<b>2c<sup>+</sup></b>	2.365	2.116	1.872	2.127	0.493
<b>2c<sup>-</sup></b>	2.086	2.006	–	2.033	0.080
<b>3a</b>	2.392	2.215	1.810	2.153	0.582
<b>3b</b>	2.379	2.226	1.813	2.153	0.566
<b>3c</b>	2.398	2.212	1.811	2.154	0.587

$$^a \langle g \rangle = \{(1/3)(g_1^2 + g_2^2 + g_3^2)\}^{1/2}. \quad ^b \Delta g = g_1 - g_3.$$

**Table S11. DFT Calculated (UB3LYP/LanL2DZ/6-31G\*) Mulliken Spin Densities**

complex	Ru	nacnac	<b>L<sup>1</sup></b>	<b>L<sup>5</sup></b>	acac
<b>1a</b> ( $S=1/2$ )	0.728	0.221	–	–	0.051
<b>1b</b> ( $S=1/2$ )	0.742	0.195	–	–	0.063
<b>1c</b> ( $S=1/2$ )	0.737	0.200	–	–	0.063
<b>2a<sup>+</sup></b> ( $S=1/2$ )	0.770	–	-0.014	–	0.244
<b>2a<sup>-</sup></b> ( $S=1/2$ )	0.050	–	0.940	–	0.006
<b>2b<sup>+</sup></b> ( $S=1/2$ )	0.779	–	-0.009	–	0.230
<b>2b<sup>-</sup></b> ( $S=1/2$ )	0.051	–	0.950	–	-0.001
<b>2c<sup>+</sup></b> ( $S=1/2$ )	0.767	–	-0.013	–	0.246
<b>2c<sup>-</sup></b> ( $S=1/2$ )	0.052	–	0.947	–	0.001
<b>3a</b> ( $S=1/2$ )	0.780	–	–	0.138	0.082
<b>3a<sup>+</sup></b> ( $S=1$ )	1.077	–	–	0.609	0.315
<b>3b</b> ( $S=1/2$ )	0.767	–	–	0.182	0.051
<b>3b<sup>+</sup></b> ( $S=1$ )	0.914	–	–	0.763	0.280
<b>3c</b> ( $S=1/2$ )	0.782	–	–	0.132	0.086
<b>3c<sup>+</sup></b> ( $S=1$ )	1.044	–	–	0.656	0.303

**Table S12. Electronic Spectral Data of Complexes**

complex	$\lambda$ [nm] ( $\varepsilon$ [ $M^{-1} cm^{-1}$ ])
<b>1c</b>	640(1100), 342(26670), 228(35140)
<b>2a</b>	826(420), 541(8160), 369(11030), 278(18370), 206(39440)
<b>2b</b>	844(490), 541(9000), 367(13150), 277(21000), 226(29970)
<b>2c</b>	831(450), 544(7270), 370(10490), 278(16950), 227(36410)
<b>3a</b>	539(770), 478(950), 395(1530), 332(2290), 275(4690), 222(7840)
<b>3b</b>	534(790), 479(1010), 394(1650), 328(2450), 273(4980), 222(8410)
<b>3c</b>	542(710), 478(910), 376(1610), 330(2210), 277(4430), 224(7510)
<b>4a</b>	864(370), 540(5370), 436(11420), 332(6950), 274(15170)
<b>4b</b>	862(370), 546(5630), 439(12030), 335(7360), 279(16060)
<b>4c</b>	869(340), 548(4920), 436(10740), 339(6530), 275(15860), 234(24090)

**Table S13. TD-DFT ((U)B3LYP/CPCM/CH<sub>3</sub>CN) Calculated Electronic Transitions for 1c, 2a, 3a, 4a**

$\lambda/\text{nm}$ expt (DFT)	$\varepsilon/\text{M}^{-1}\text{cm}^{-1}$ ( <i>f</i> )	transitions	character
<b>1c(S=1/2)</b>			
648 (695)	1100 (0.052)	HOMO-1( $\beta$ )→LUMO( $\beta$ ) (0.92)	Ru(d $\pi$ )/nacnac( $\pi$ )→Ru(d $\pi$ )/nacnac ( $\pi^*$ )
342 (298)	26670 (0.084)	HOMO-11( $\beta$ )→LUMO( $\beta$ ) (0.63)	acac( $\pi$ )→Ru(d $\pi$ )/nacnac( $\pi^*$ )
		HOMO-12( $\beta$ )→LUMO( $\beta$ ) (0.32)	nacnac( $\pi$ )/acac( $\pi$ )→Ru(d $\pi$ )/nacnac ( $\pi^*$ )
228 (227)	35140 (0.046)	HOMO-9( $\alpha$ )→LUMO+1( $\alpha$ ) (0.32)	nacnac( $\pi$ )→acac( $\pi^*$ )
		HOMO-7( $\beta$ )→LUMO+1( $\beta$ ) (0.30)	acac( $\pi$ )→acac( $\pi^*$ )
<b>2a(S=0)</b>			
826 (847)	420 (0.002)	HOMO→LUMO (0.66)	Ru(d $\pi$ )/acac( $\pi$ )→L <sup>1</sup> ( $\pi^*$ )/Ru(d $\pi$ )
541 (504)	8160 (0.132)	HOMO-2→LUMO (0.44)	Ru(d $\pi$ )/L <sup>1</sup> ( $\pi$ )→L <sup>1</sup> ( $\pi^*$ )/Ru(d $\pi$ )
		HOMO→LUMO (0.22)	Ru(d $\pi$ )/acac( $\pi$ )→L <sup>1</sup> ( $\pi^*$ )/Ru(d $\pi$ )
369(335)	11030 (0.126)	HOMO-2→LUMO+1 (0.52)	Ru(d $\pi$ )/L <sup>1</sup> ( $\pi$ )→L <sup>1</sup> ( $\pi^*$ )/acac( $\pi^*$ )
278 (250)	18370 (0.123)	HOMO-4→LUMO+2(0.42)	acac( $\pi$ )→acac( $\pi^*$ )/L <sup>1</sup> ( $\pi^*$ )
		HOMO-3→LUMO+1(0.14)	acac( $\pi$ )/Ru(d $\pi$ )→L <sup>1</sup> ( $\pi^*$ )/acac( $\pi^*$ )
206 (210)	39440 (0.226)	HOMO-5→LUMO+5(0.51)	L <sup>1</sup> ( $\pi$ )/acac( $\pi$ )→ L <sup>1</sup> ( $\pi^*$ )
		HOMO-4→LUMO+8(0.17)	acac( $\pi$ )→Ru(d $\pi$ )/acac( $\pi^*$ )
<b>3a(S=1/2)</b>			
539 (580)	770 (0.042)	HOMO-2( $\beta$ )→LUMO( $\beta$ ) (0.82)	Ru(d $\pi$ )/acac( $\pi$ )/L <sup>5</sup> ( $\pi$ )→Ru(d $\pi$ )
478 (494)	950 (0.023)	HOMO-3( $\beta$ )→LUMO( $\beta$ ) (0.87)	acac( $\pi$ )/L <sup>5</sup> ( $\pi$ )→Ru(d $\pi$ )
395 (366)	1530 (0.044)	HOMO-2( $\alpha$ )→LUMO+1( $\alpha$ ) (0.64)	acac( $\pi$ )/Ru(d $\pi$ )→acac( $\pi^*$ )
		HOMO-2( $\beta$ )→LUMO+2( $\beta$ ) (0.29)	Ru(d $\pi$ )/L <sup>5</sup> ( $\pi$ )→L <sup>5</sup> ( $\pi^*$ )
332 (329)	2290 (0.016)	HOMO-1( $\beta$ )→LUMO+3( $\beta$ ) (0.35)	Ru(d $\pi$ )/L <sup>5</sup> ( $\pi$ )→acac( $\pi^*$ )
		HOMO-11( $\beta$ )→LUMO( $\beta$ ) (0.33)	acac( $\pi$ )→Ru(d $\pi$ )
222 (238)	7840 (0.028)	HOMO-15( $\beta$ )→LUMO+1( $\beta$ ) (0.59)	L <sup>5</sup> ( $\pi$ )→ Ru(d $\pi$ )
		HOMO-14( $\beta$ )→LUMO+1( $\beta$ ) (0.43)	L <sup>5</sup> ( $\pi$ )/ acac( $\pi$ )→Ru(d $\pi$ )
<b>4a(S=0)</b>			
864 (846)	370 (0.002)	HOMO→LUMO (0.60)	Ru(d $\pi$ )/ acac( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/Ru(d $\pi$ )
540 (521)	5370 (0.093)	HOMO-2→LUMO (0.39)	Ru(d $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/Ru(d $\pi$ )
		HOMO-1→LUMO (0.37)	Ru(d $\pi$ )/acac( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/ Ru(d $\pi$ )
436 (444)	11420 (0.042)	HOMO→LUMO+1 (0.40)	Ru(d $\pi$ )/acac( $\pi$ )→acac( $\pi^*$ )/L <sup>6</sup> ( $\pi^*$ )
		HOMO-5→LUMO (0.20)	Ru(d $\pi$ )/acac( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/Ru(d $\pi$ )
332 (364)	6950 (0.133)	HOMO-2 →LUMO+1 (0.38)	Ru(d $\pi$ )→L <sup>6</sup> ( $\pi^*$ )
		HOMO-6 →LUMO+1 (0.34)	L <sup>6</sup> ( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/Ru(d $\pi$ )
274 (258)	15167 (0.025)	HOMO-3→LUMO+2(0.43)	acac( $\pi$ )/L <sup>6</sup> ( $\pi$ )→acac( $\pi^*$ )
		HOMO-10→LUMO+2(0.25)	acac( $\pi$ )/L <sup>6</sup> ( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )
233 (231)	22710 (0.030)	HOMO-15→LUMO(0.38)	L <sup>6</sup> ( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )/Ru(d $\pi$ )
		HOMO-4→LUMO+5(0.31)	L <sup>6</sup> ( $\pi$ )→L <sup>6</sup> ( $\pi^*$ )

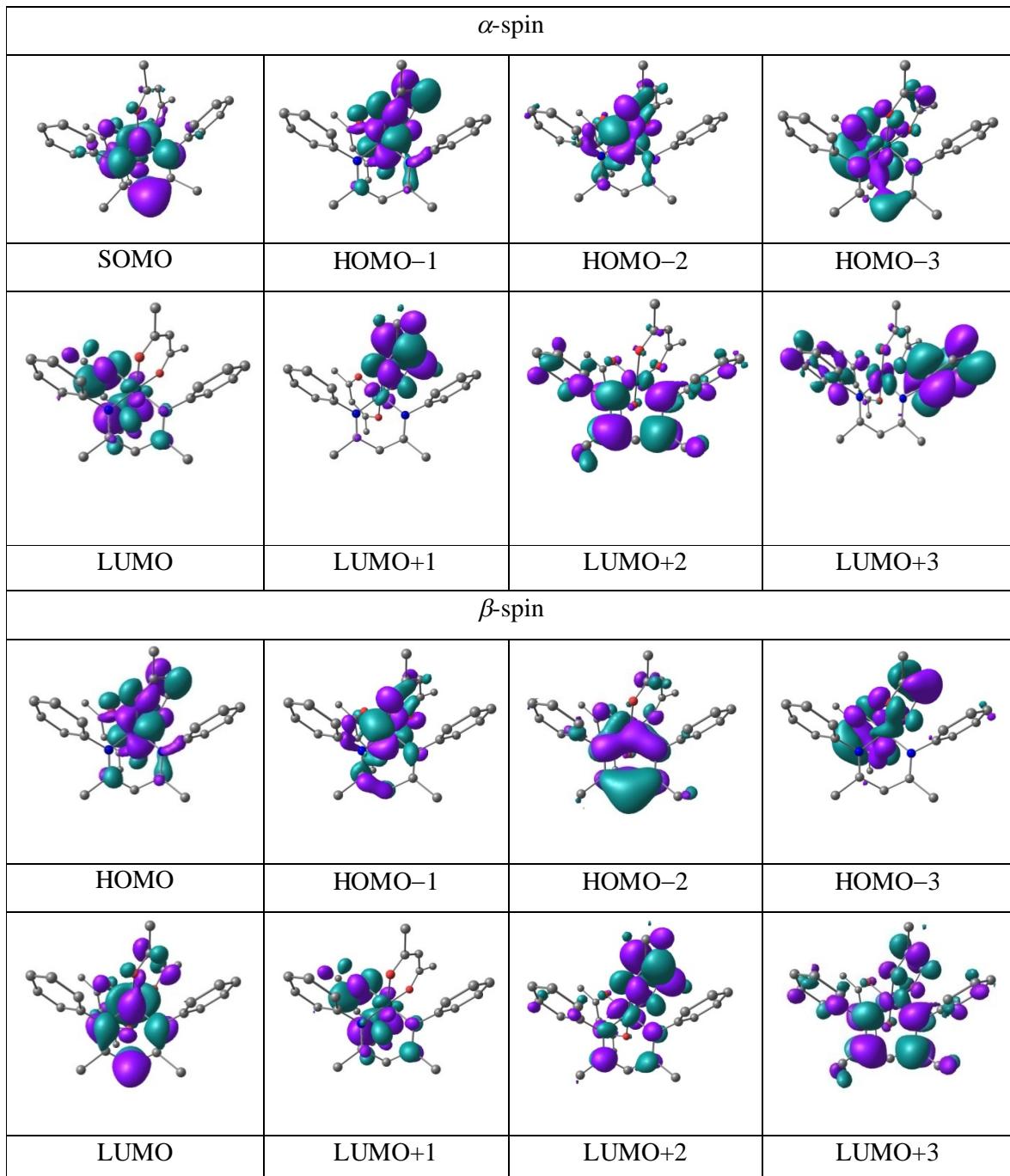
**Table S14. Electrochemical Data<sup>a</sup>**

complex	$E^{\circ}_{298}/\text{V} (\Delta E/\text{mV})^b$	
	Ox1	Red1
<b>1c</b>	0.44 <sup>c</sup>	-1.06(80)
<b>2a</b>	0.28(70)	-1.31(100)
<b>2b</b>	0.27(70)	-1.36(80)
<b>2c</b>	0.34(70)	-1.25(80)
<b>3a</b>	0.95(70)	-0.71(70)
<b>3b</b>	0.79(70)	-0.67(70)
<b>3c</b>	1.05(70)	-0.58(70)

<sup>a</sup>From cyclic voltammetry in CH<sub>3</sub>CN/0.1 M Et<sub>4</sub>NClO<sub>4</sub> at 100 mVs<sup>-1</sup>. <sup>b</sup>Potentials in V versus SCE; peak potential differences ΔE[mV] (in parentheses). <sup>c</sup>Irreversible Process.

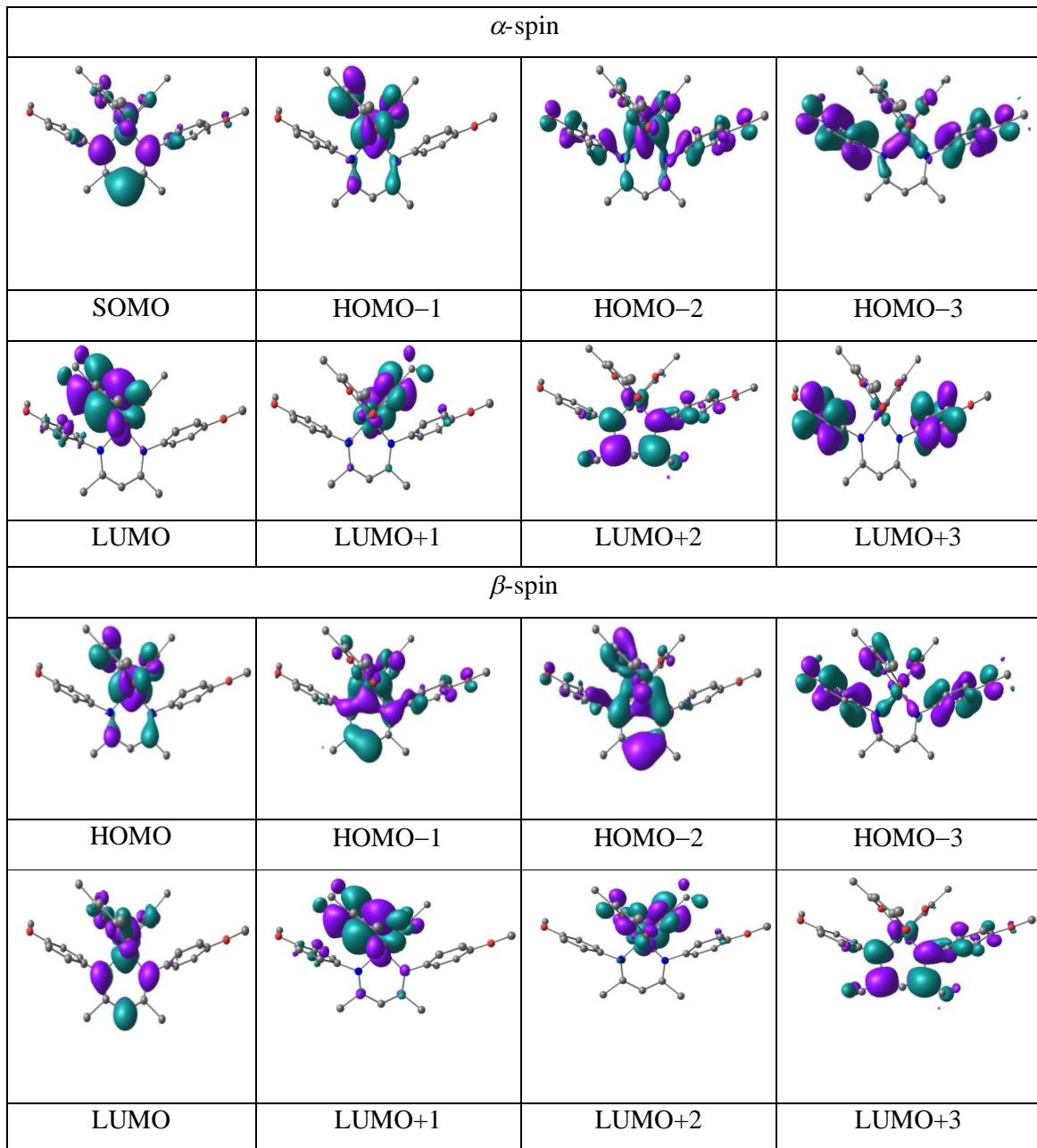
**Table S15. Composition and Energies of Selected Molecular Orbitals of 1a ( $S=1/2$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-6.249	0.05	0.69	0.25
HOMO-4	-5.844	0.29	0.17	0.54
HOMO-3	-5.809	0.06	0.18	0.76
HOMO-2	-5.072	0.71	0.09	0.20
HOMO-1	-4.809	0.57	0.07	0.36
SOMO	-4.360	0.33	0.53	0.14
LUMO	-0.461	0.03	0.07	0.89
LUMO+1	-0.291	0.03	0.07	0.89
LUMO+2	-0.136	0.04	0.92	0.04
LUMO+3	0.096	0.10	0.80	0.10
LUMO+4	0.131	0.02	0.93	0.04
LUMO+5	0.239	0.09	0.82	0.09
$\beta$ -spin				
HOMO-5	-6.244	0.03	0.71	0.26
HOMO-4	-5.881	0.19	0.10	0.71
HOMO-3	-5.729	0.12	0.06	0.82
HOMO-2	-5.273	0.24	0.64	0.12
HOMO-1	-4.789	0.70	0.12	0.18
SOMO	-4.594	0.63	0.08	0.29
LUMO	-1.918	0.48	0.38	0.14
LUMO+1	-0.449	0.04	0.09	0.87
LUMO+2	-0.190	0.06	0.23	0.71
LUMO+3	-0.118	0.04	0.78	0.18
LUMO+4	0.121	0.06	0.88	0.06
LUMO+5	0.145	0.05	0.88	0.0



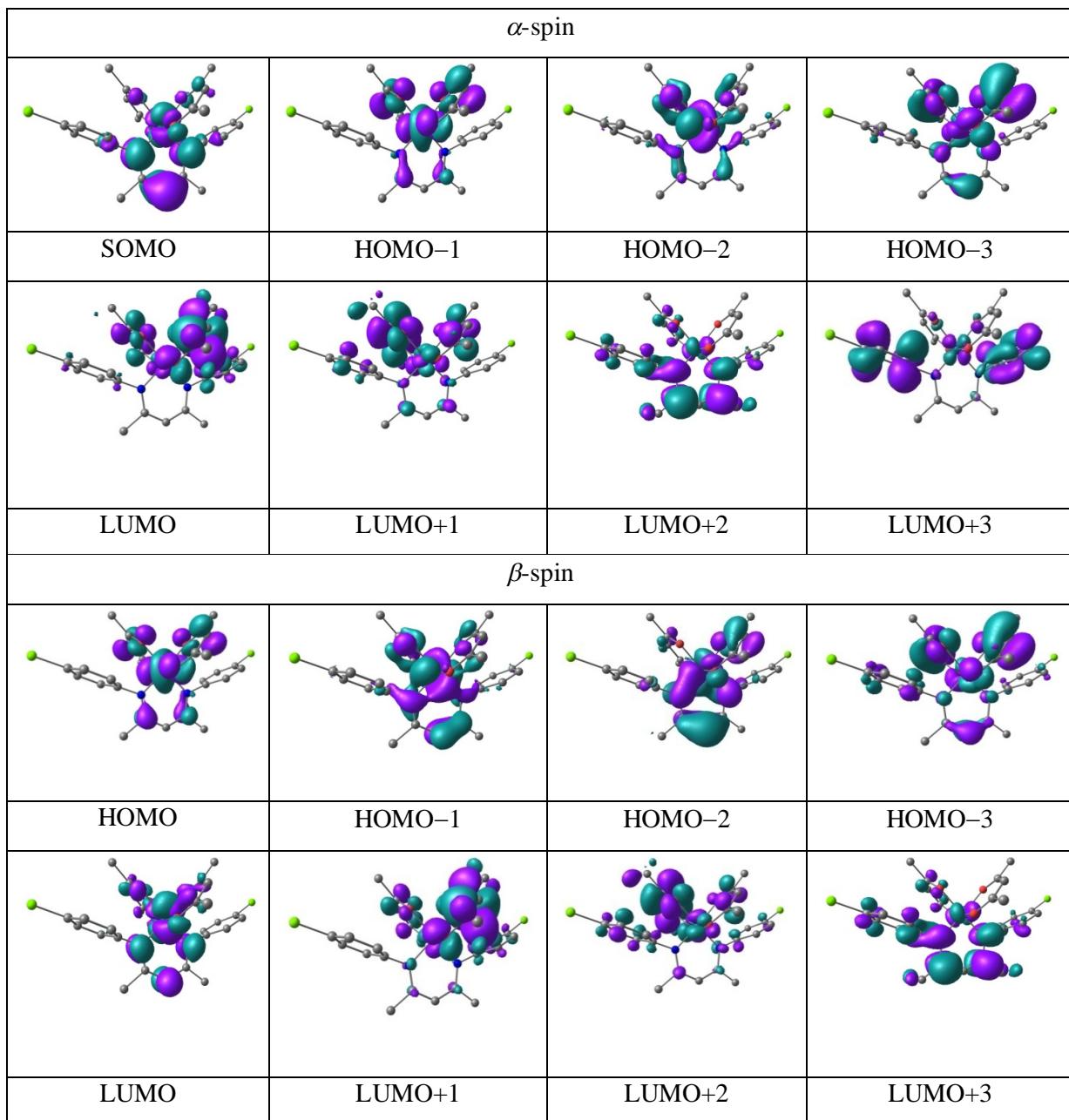
**Table S16. Composition and Energies of Selected Molecular Orbitals of 1b ( $S=1/2$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-5.568	0.24	0.53	0.23
HOMO-4	-5.545	0.04	0.38	0.58
HOMO-3	-5.523	0.06	0.83	0.10
HOMO-2	-5.303	0.56	0.31	0.13
HOMO-1	-4.917	0.56	0.10	0.35
SOMO	-4.633	0.28	0.62	0.10
LUMO	-0.520	0.03	0.12	0.85
LUMO+1	-0.443	0.03	0.08	0.89
LUMO+2	-0.146	0.06	0.92	0.02
LUMO+3	0.235	0.03	0.93	0.04
LUMO+4	0.293	0.00	0.93	0.06
LUMO+5	0.421	0.26	0.54	0.19
$\beta$ -spin				
HOMO-5	-5.861	0.09	0.26	0.65
HOMO-4	-5.522	0.06	0.84	0.10
HOMO-3	-5.503	0.02	0.81	0.17
HOMO-2	-5.111	0.36	0.48	0.16
HOMO-1	-5.012	0.50	0.35	0.16
SOMO	-4.674	0.62	0.11	0.28
LUMO	-2.156	0.58	0.27	0.16
LUMO+1	-0.478	0.05	0.14	0.81
LUMO+2	-0.373	0.05	0.07	0.88
LUMO+3	-0.073	0.07	0.91	0.03
LUMO+4	0.243	0.02	0.94	0.04
LUMO+5	0.299	0.00	0.93	0.07



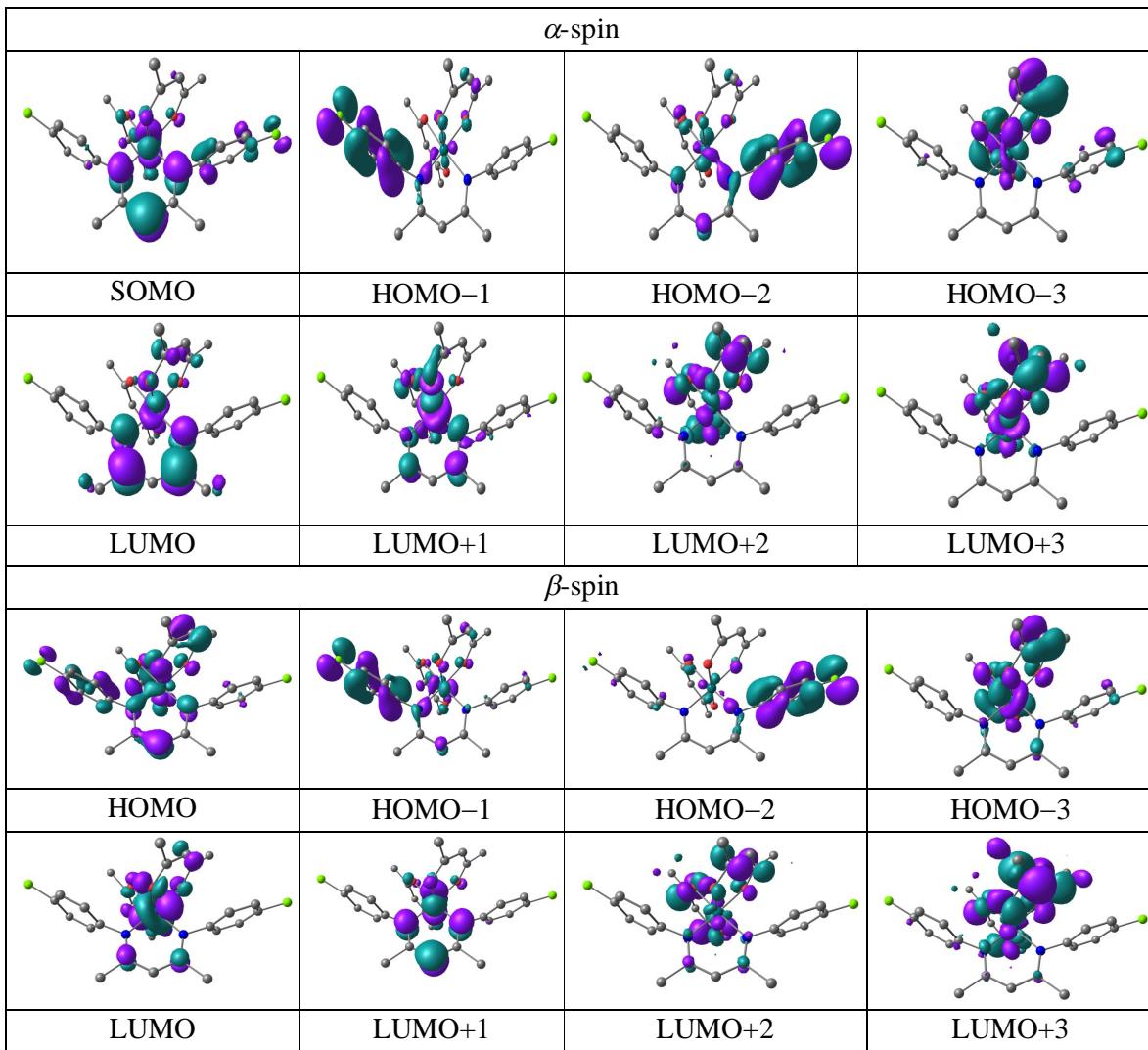
**Table S17. Composition and Energies of Selected Molecular Orbitals of 1c ( $S=1/2$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-6.330	0.05	0.79	0.16
HOMO-4	-6.288	0.03	0.85	0.13
HOMO-3	-5.851	0.09	0.18	0.73
HOMO-2	-5.706	0.69	0.13	0.19
HOMO-1	-5.231	0.54	0.09	0.37
SOMO	-5.020	0.29	0.62	0.10
LUMO	-0.787	0.03	0.16	0.81
LUMO+1	-0.750	0.03	0.18	0.78
LUMO+2	-0.505	0.05	0.90	0.05
LUMO+3	-0.248	0.05	0.90	0.05
LUMO+4	-0.220	0.11	0.73	0.17
LUMO+5	-0.179	0.04	0.86	0.09
$\beta$ -spin				
HOMO-5	-6.320	0.07	0.66	0.27
HOMO-4	-6.284	0.07	0.68	0.25
HOMO-3	-6.075	0.09	0.19	0.72
HOMO-2	-5.474	0.27	0.53	0.20
HOMO-1	-5.394	0.60	0.22	0.17
SOMO	-4.996	0.60	0.10	0.30
LUMO	-2.506	0.59	0.26	0.15
LUMO+1	-0.738	0.04	0.19	0.77
LUMO+2	-0.693	0.05	0.18	0.77
LUMO+3	-0.433	0.06	0.89	0.05
LUMO+4	-0.238	0.01	0.96	0.03
LUMO+5	-0.180	0.03	0.87	0.10



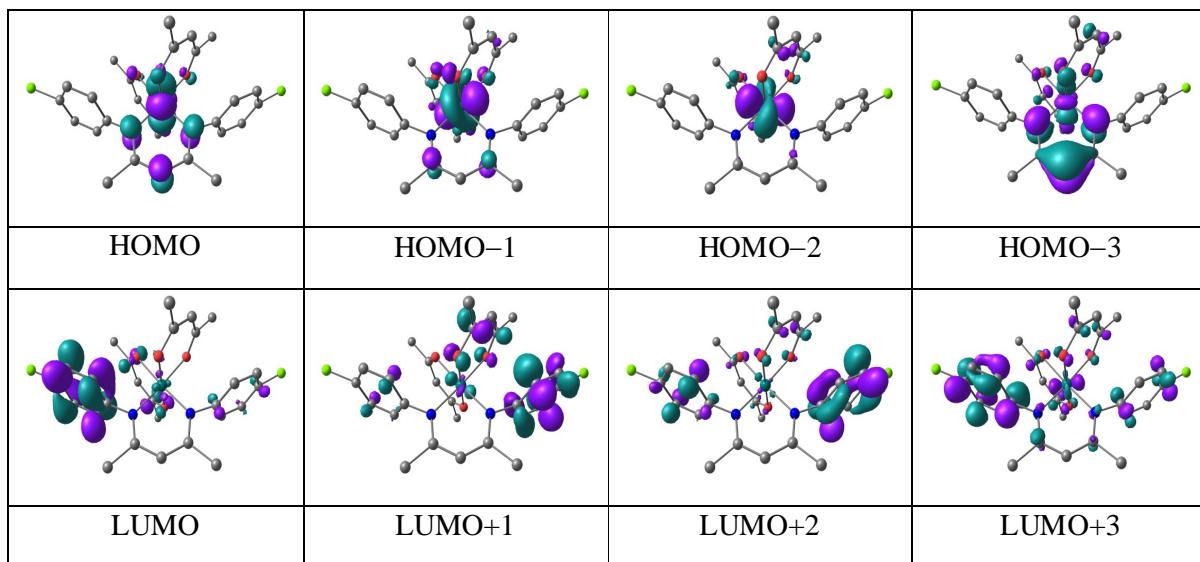
**Table S18. Composition and Energies of Selected Molecular Orbitals of  $1\mathbf{c}^+$  ( $S=1$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-9.987	0.04	0.86	0.10
HOMO-4	-9.534	0.01	0.35	0.64
HOMO-3	-9.446	0.11	0.17	0.72
HOMO-2	-9.323	0.07	0.84	0.09
HOMO-1	-9.209	0.04	0.89	0.07
HOMO	-9.096	0.21	0.66	0.13
LUMO	-4.406	0.10	0.74	0.15
LUMO+1	-4.337	0.33	0.28	0.39
LUMO+2	-4.298	0.10	0.15	0.75
LUMO+3	-4.257	0.16	0.11	0.73
LUMO+4	-4.061	0.38	0.34	0.28
LUMO+5	-3.195	0.01	0.96	0.03
$\beta$ -spin				
HOMO-5	-9.893	0.35	0.58	0.07
HOMO-4	-9.760	0.29	0.40	0.31
HOMO-3	-9.531	0.31	0.15	0.54
HOMO-2	-9.271	0.04	0.91	0.06
HOMO-1	-9.221	0.07	0.80	0.14
HOMO	-9.116	0.11	0.44	0.46
LUMO	-7.247	0.64	0.12	0.24
LUMO+1	-6.890	0.44	0.45	0.11
LUMO+2	-4.254	0.04	0.16	0.80
LUMO+3	-4.222	0.03	0.10	0.87
LUMO+4	-4.041	0.10	0.80	0.10
LUMO+5	-3.886	0.48	0.20	0.31



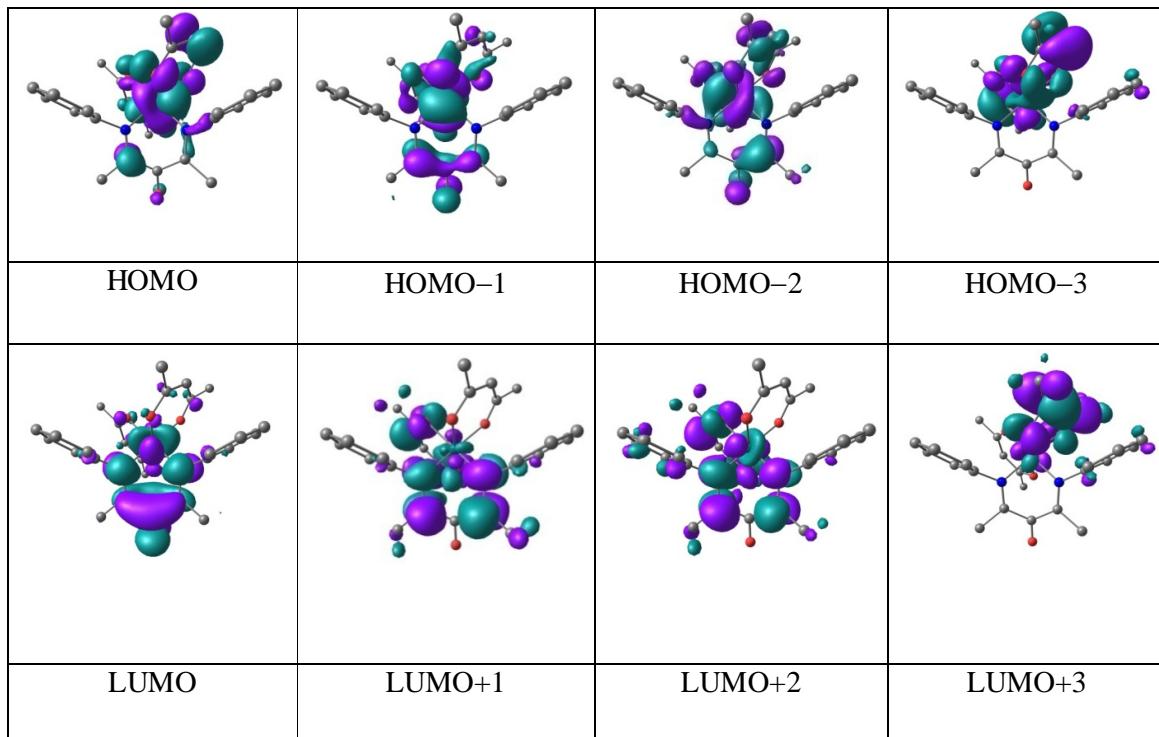
**Table S19. Composition and Energies of Selected Molecular Orbitals of  $1c^-$  ( $S=0$ )**

MO	energy (eV)	Composition		
		Ru	L	$\text{acac}^-$
HOMO-5	-2.644	0.13	0.07	0.80
HOMO-4	-2.535	0.11	0.12	0.77
HOMO-3	-1.908	0.13	0.64	0.22
HOMO-2	-1.020	0.74	0.10	0.15
HOMO-1	-0.662	0.69	0.13	0.18
HOMO	-0.158	0.57	0.29	0.14
LUMO	2.630	0.03	0.78	0.19
LUMO+1	2.650	0.03	0.77	0.20
LUMO+2	2.712	0.02	0.83	0.15
LUMO+3	2.884	0.07	0.76	0.18
LUMO+4	3.015	0.06	0.45	0.50
LUMO+5	3.044	0.04	0.40	0.56



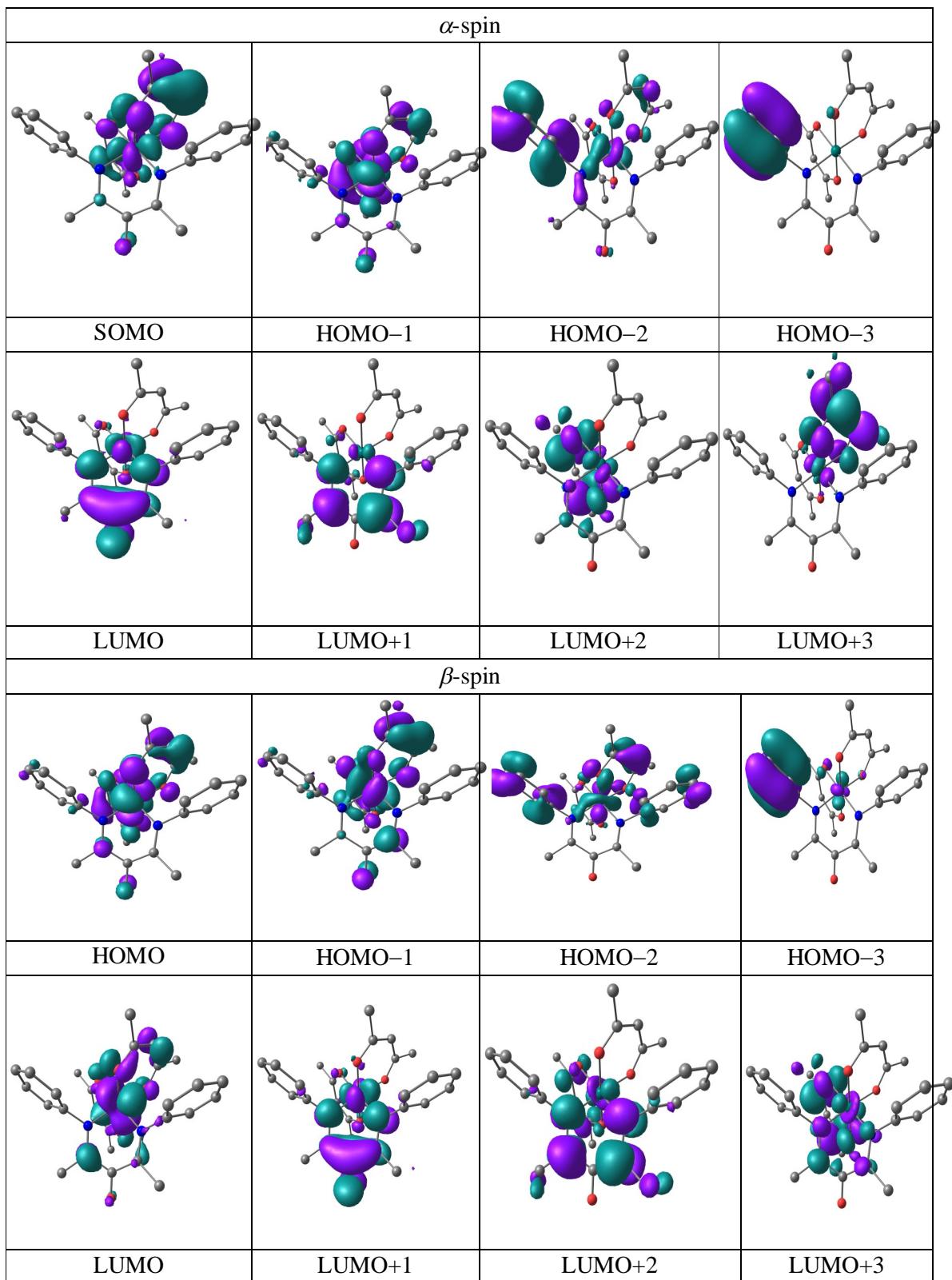
**Table S20. Composition and Energies of Selected Molecular Orbitals of 2a ( $S=0$ )**

MO	energy (eV)	Composition		
		Ru	L	acac <sup>-</sup>
HOMO-5	-6.474	0.03	0.55	0.42
HOMO-4	-6.104	0.19	0.11	0.70
HOMO-3	-5.881	0.20	0.07	0.73
HOMO-2	-5.083	0.63	0.21	0.17
HOMO-1	-4.899	0.61	0.17	0.21
HOMO	-4.765	0.59	0.10	0.31
LUMO	-2.079	0.22	0.71	0.07
LUMO+1	-0.664	0.02	0.58	0.40
LUMO+2	-0.522	0.06	0.47	0.47
LUMO+3	-0.324	0.04	0.09	0.87
LUMO+4	-0.097	0.03	0.90	0.06
LUMO+5	-0.065	0.06	0.85	0.09



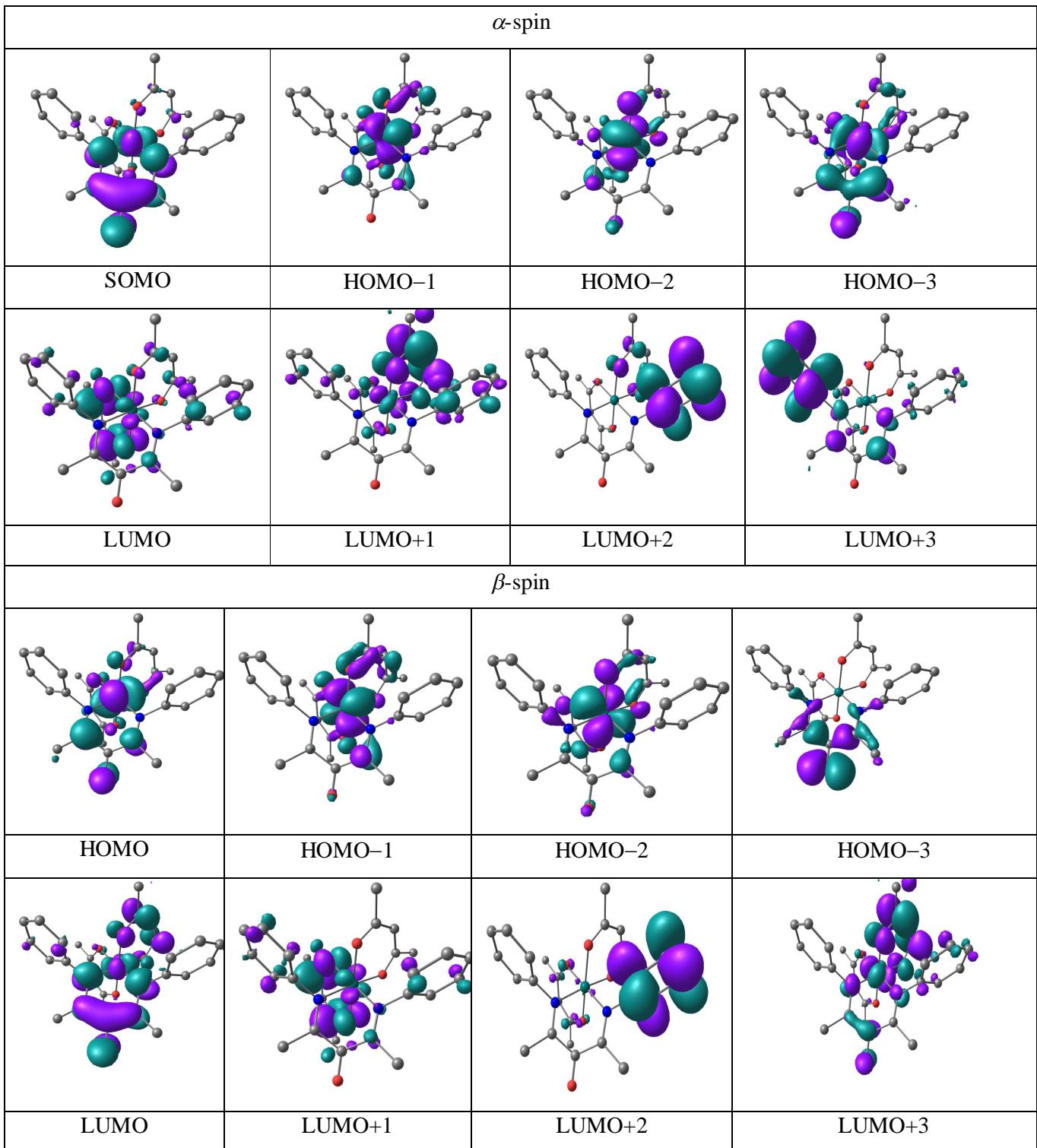
**Table S21. Composition and Energies of Selected Molecular Orbitals of 2a<sup>+</sup> (S=1/2)**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-9.874	0.14	0.76	0.11
HOMO-4	-9.731	0.09	0.79	0.12
HOMO-3	-9.641	0.01	0.96	0.03
HOMO-2	-9.550	0.12	0.75	0.13
HOMO-1	-9.223	0.27	0.13	0.60
SOMO	-9.172	0.19	0.09	0.71
LUMO	-6.080	0.12	0.84	0.04
LUMO+1	-4.409	0.03	0.93	0.04
LUMO+2	-4.181	0.04	0.09	0.87
LUMO+3	-3.997	0.05	0.06	0.90
LUMO+4	-3.829	0.45	0.21	0.34
LUMO+5	-3.609	0.36	0.44	0.20
$\beta$ -spin				
HOMO-5	-9.762	0.24	0.30	0.46
HOMO-4	-9.650	0.19	0.65	0.16
HOMO-3	-9.643	0.06	0.87	0.07
HOMO-2	-9.550	0.22	0.50	0.28
HOMO-1	-9.105	0.38	0.18	0.44
SOMO	-9.025	0.38	0.13	0.49
LUMO	-7.009	0.65	0.12	0.22
LUMO+1	-6.031	0.17	0.78	0.05
LUMO+2	-4.345	0.04	0.84	0.12
LUMO+3	-4.145	0.05	0.17	0.78
LUMO+4	-3.939	0.04	0.05	0.91
LUMO+5	-3.601	0.41	0.31	0.28



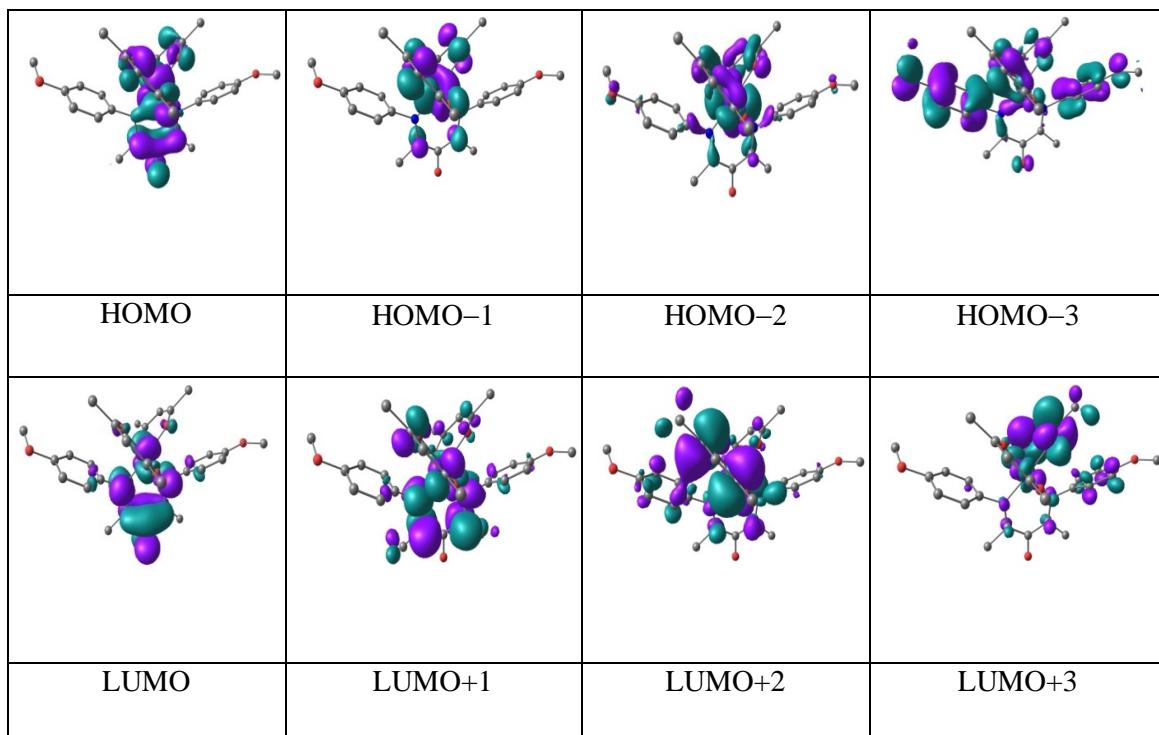
**Table S22. Composition and Energies of Selected Molecular Orbitals of  $2\text{a}^-$  ( $S=1/2$ )**

MO	energy (eV)	Composition		
		Ru	L	$\text{acac}^-$
$\alpha$ -spin				
HOMO-5	-2.542	0.08	0.05	0.88
HOMO-4	-2.067	0.00	0.98	0.01
HOMO-3	-1.336	0.55	0.29	0.16
HOMO-2	-1.005	0.72	0.10	0.18
HOMO-1	-0.865	0.72	0.09	0.19
SOMO	0.694	0.73	0.73	0.07
LUMO	2.768	0.04	0.16	0.79
LUMO+1	2.868	0.06	0.21	0.73
LUMO+2	2.897	0.01	0.85	0.14
LUMO+3	3.009	0.02	0.93	0.05
LUMO+4	3.060	0.06	0.80	0.15
LUMO+5	3.152	0.04	0.86	0.10
$\beta$ -spin				
HOMO-5	-2.642	0.09	0.09	0.82
HOMO-4	-2.523	0.06	0.05	0.88
HOMO-3	-1.896	0.00	0.99	0.01
HOMO-2	-0.994	0.71	0.12	0.17
HOMO-1	-0.800	0.73	0.09	0.19
SOMO	-0.623	0.60	0.25	0.14
LUMO	2.505	0.09	0.64	0.26
LUMO+1	2.779	0.05	0.17	0.78
LUMO+2	2.901	0.01	0.92	0.07
LUMO+3	3.016	0.13	0.25	0.62
LUMO+4	3.054	0.01	0.91	0.08
LUMO+5	3.067	0.05	0.80	0.15



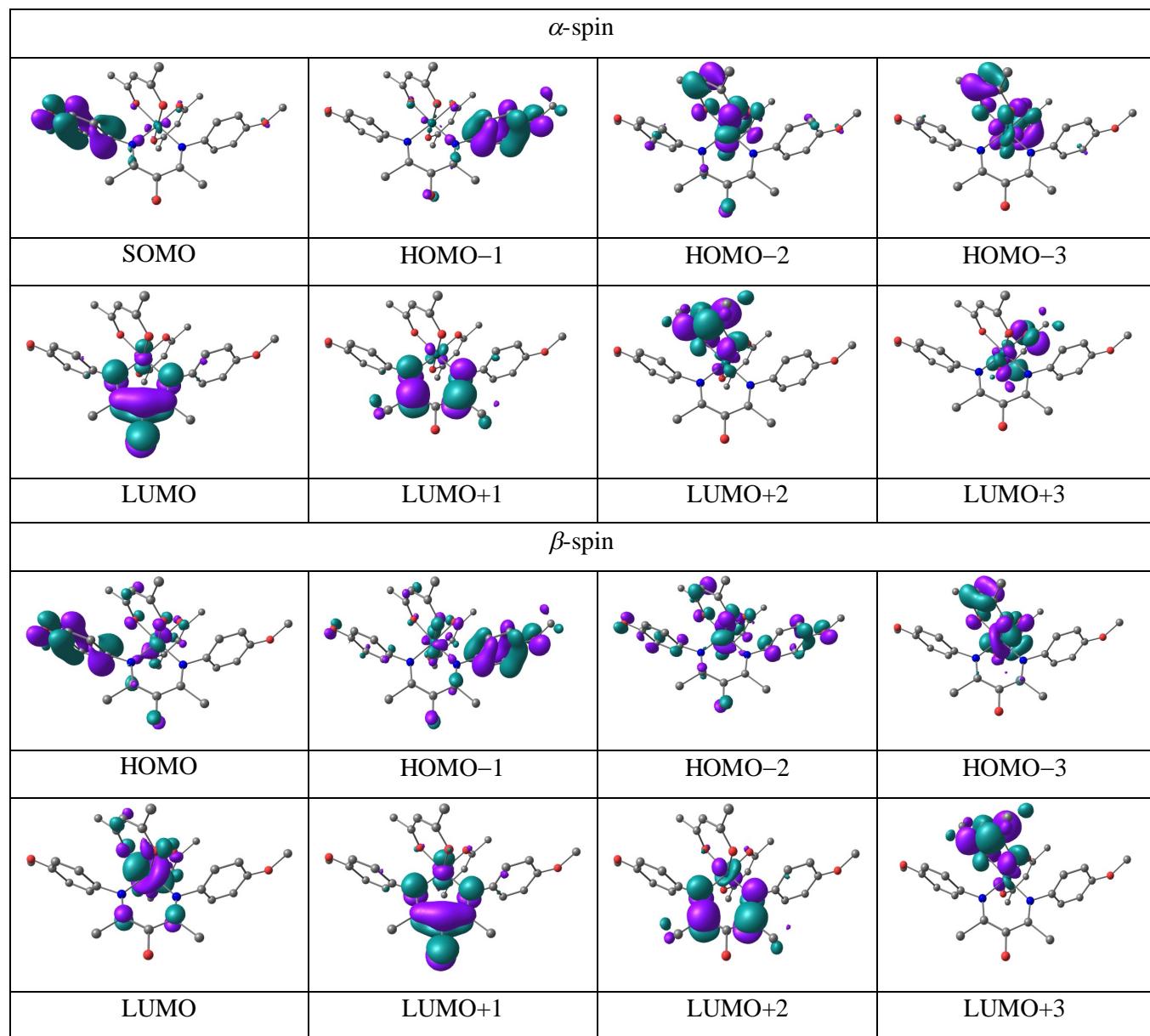
**Table S23. Composition and Energies of Selected Molecular Orbitals of 2b ( $S=0$ )**

MO	energy (eV)	Composition		
		Ru	L	acac <sup>-</sup>
HOMO-5	-5.884	0.10	0.27	0.63
HOMO-4	-5.790	0.03	0.86	0.12
HOMO-3	-5.715	0.04	0.78	0.19
HOMO-2	-5.119	0.71	0.13	0.16
HOMO-1	-4.722	0.60	0.10	0.29
HOMO	-4.709	0.51	0.24	0.25
LUMO	-2.511	0.19	0.76	0.05
LUMO+1	-0.655	0.04	0.81	0.15
LUMO+2	-0.487	0.05	0.21	0.73
LUMO+3	-0.399	0.05	0.18	0.77
LUMO+4	-0.012	0.02	0.92	0.06
LUMO+5	0.049	0.00	0.88	0.11



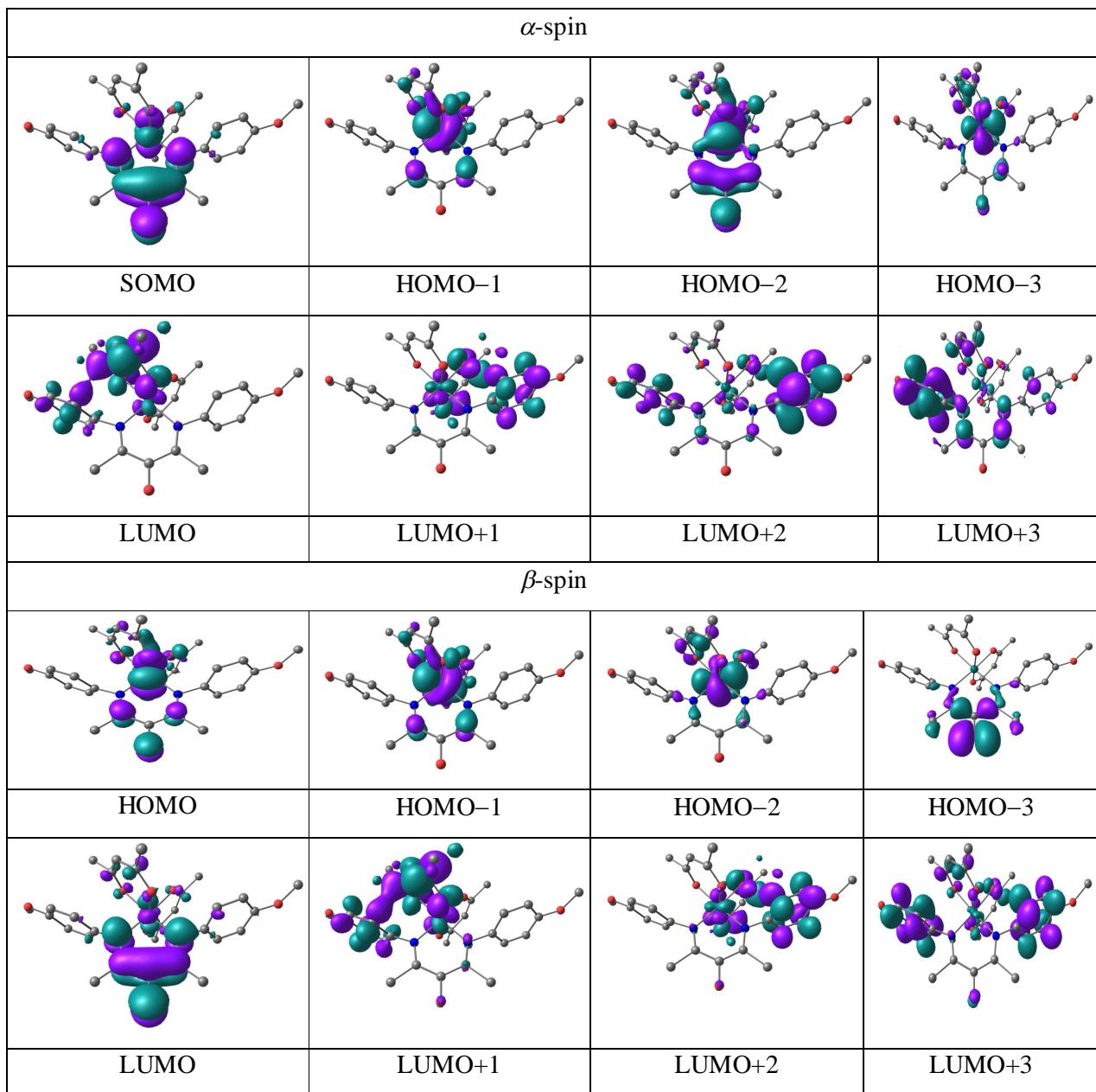
**Table S24. Composition and Energies of Selected Molecular Orbitals of 2b<sup>+</sup> (S=1/2)**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-9.720	0.59	0.23	0.18
HOMO-4	-9.636	0.32	0.46	0.21
HOMO-3	-9.066	0.15	0.09	0.76
HOMO-2	-8.929	0.29	0.14	0.57
HOMO-1	-8.647	0.02	0.94	0.04
SOMO	-8.596	0.03	0.94	0.04
LUMO	-6.366	0.08	0.90	0.02
LUMO+1	-4.419	0.03	0.96	0.01
LUMO+2	-3.983	0.06	0.11	0.83
LUMO+3	-3.922	0.05	0.06	0.89
LUMO+4	-3.665	0.49	0.16	0.35
LUMO+5	-3.527	0.42	0.33	0.25
$\beta$ -spin				
HOMO-5	-9.602	0.46	0.40	0.14
HOMO-4	-9.404	0.33	0.23	0.43
HOMO-3	-9.175	0.37	0.10	0.53
HOMO-2	-8.683	0.26	0.44	0.29
HOMO-1	-8.624	0.09	0.79	0.13
SOMO	-8.574	0.09	0.76	0.15
LUMO	-6.848	0.63	0.14	0.23
LUMO+1	-6.418	0.14	0.83	0.04
LUMO+2	-4.276	0.08	0.87	0.05
LUMO+3	-3.936	0.05	0.11	0.84
LUMO+4	-3.870	0.04	0.08	0.88
LUMO+5	-3.383	0.48	0.20	0.31



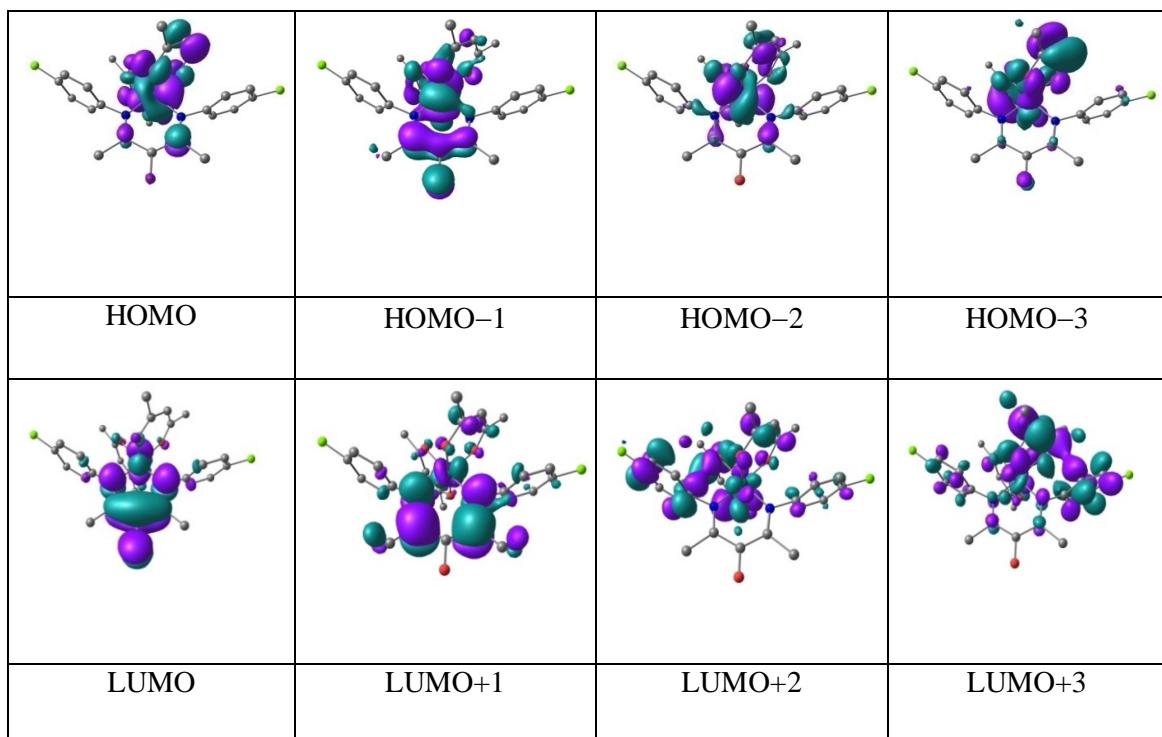
**Table S25. Composition and Energies of Selected Molecular Orbitals of 2b<sup>-</sup> (S=1/2)**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-2.577	0.07	0.11	0.82
HOMO-4	-2.246	0.00	0.99	0.00
HOMO-3	-1.192	0.72	0.12	0.15
HOMO-2	-1.072	0.55	0.26	0.19
HOMO-1	-0.812	0.70	0.12	0.19
SOMO	0.167	0.22	0.72	0.06
LUMO	2.679	0.05	0.29	0.66
LUMO+1	2.759	0.04	0.30	0.65
LUMO+2	2.929	0.03	0.80	0.17
LUMO+3	2.969	0.02	0.83	0.14
LUMO+4	3.153	0.07	0.75	0.18
LUMO+5	3.447	0.07	0.81	0.12
$\beta$ -spin				
HOMO-5	-2.713	0.13	0.09	0.79
HOMO-4	-2.536	0.04	0.11	0.85
HOMO-3	-2.016	0.00	0.99	0.00
HOMO-2	-1.146	0.75	0.10	0.15
HOMO-1	-0.796	0.70	0.11	0.18
SOMO	-0.587	0.66	0.16	0.18
LUMO	2.182	0.06	0.83	0.11
LUMO+1	2.710	0.06	0.34	0.61
LUMO+2	2.788	0.06	0.37	0.58
LUMO+3	2.961	0.02	0.74	0.24
LUMO+4	3.014	0.02	0.67	0.31
LUMO+5	3.537	0.10	0.85	0.04



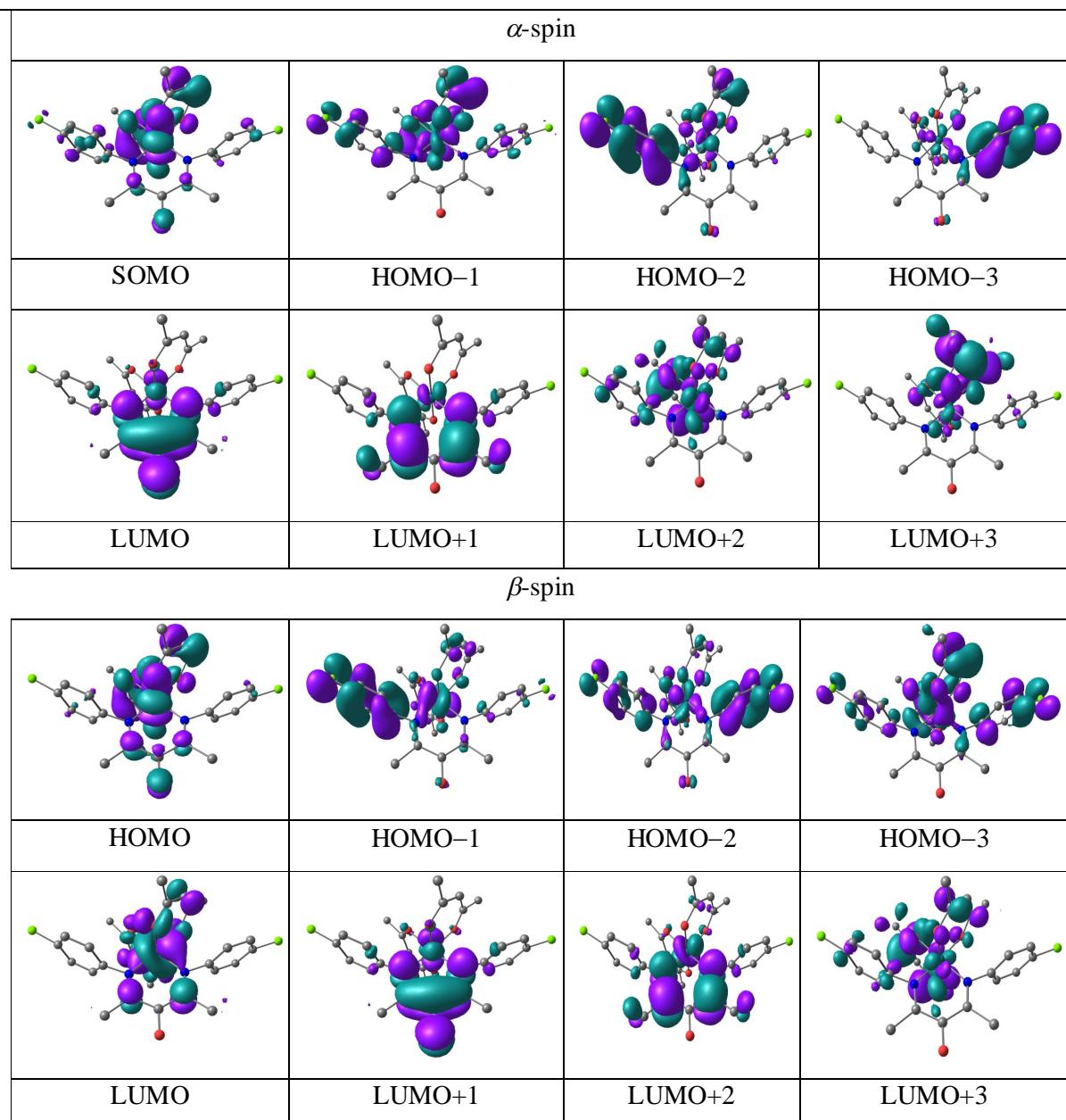
**Table S26. Composition and Energies of Selected Molecular Orbitals of 2c ( $S=0$ )**

MO	energy (eV)	Composition		
		Ru	L	acac <sup>-</sup>
HOMO-5	-6.532	0.01	0.83	0.16
HOMO-4	-6.347	0.29	0.12	0.59
HOMO-3	-6.058	0.12	0.09	0.79
HOMO-2	-5.419	0.73	0.11	0.16
HOMO-1	-5.020	0.53	0.22	0.25
HOMO	-4.992	0.59	0.10	0.31
LUMO	-2.770	0.18	0.78	0.04
LUMO+1	-0.939	0.05	0.88	0.07
LUMO+2	-0.768	0.04	0.31	0.65
LUMO+3	-0.692	0.06	0.38	0.56
LUMO+4	-0.487	0.01	0.92	0.07
LUMO+5	-0.393	0.01	0.77	0.22



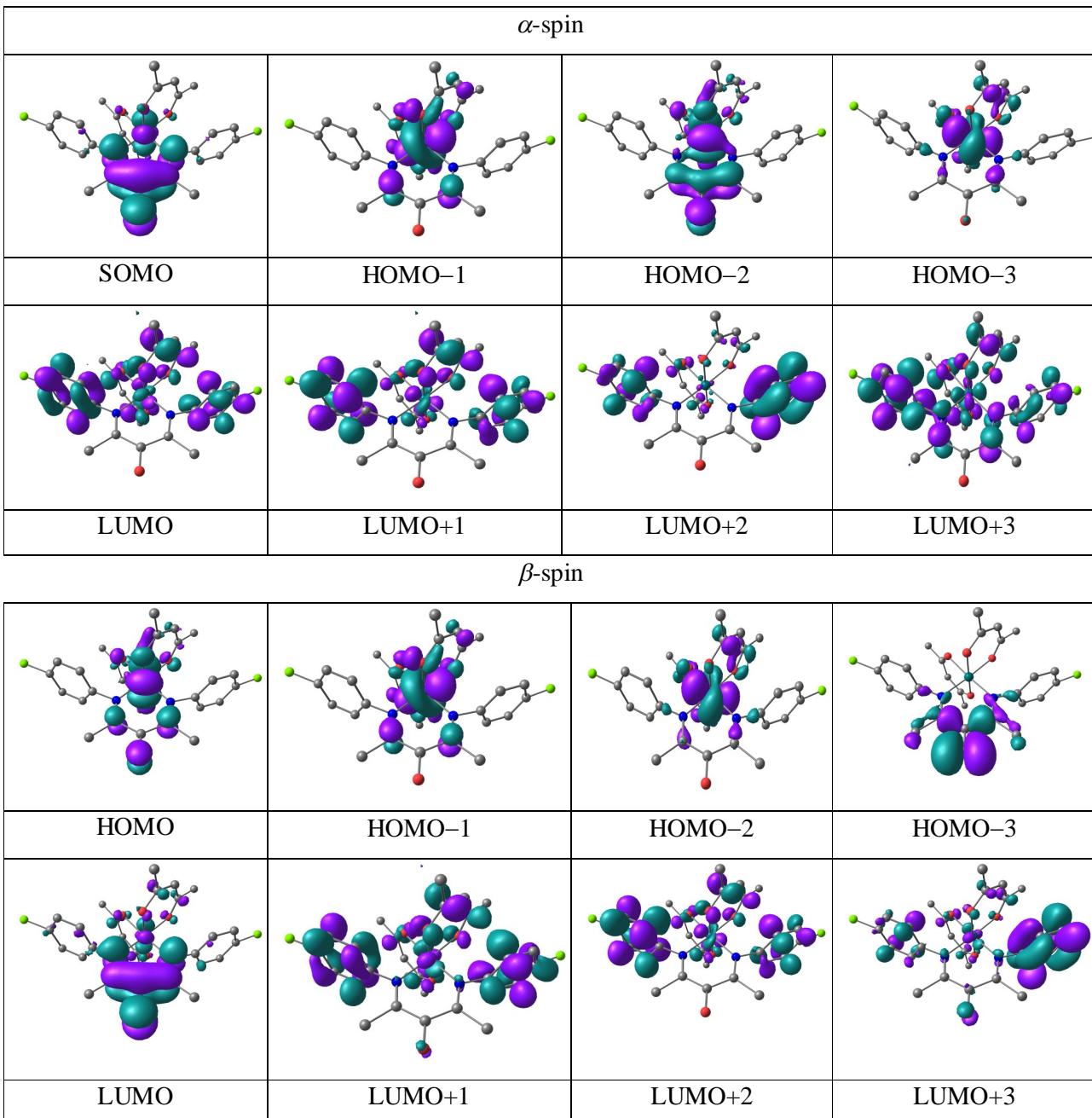
**Table S27. Composition and Energies of Selected Molecular Orbitals of  $2c^+$  ( $S=1/2$ )**

MO	energy (eV)	Composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-10.036	0.64	0.16	0.20
HOMO-4	-9.927	0.42	0.21	0.37
HOMO-3	-9.494	0.04	0.89	0.08
HOMO-2	-9.417	0.05	0.77	0.18
HOMO-1	-9.313	0.16	0.24	0.60
SOMO	-9.226	0.28	0.14	0.59
LUMO	-6.617	0.07	0.90	0.02
LUMO+1	-4.721	0.03	0.96	0.01
LUMO+2	-4.225	0.06	0.15	0.79
LUMO+3	-4.206	0.04	0.10	0.86
LUMO+4	-3.987	0.45	0.24	0.30
LUMO+5	-3.917	0.39	0.32	0.29
$\beta$ -spin				
HOMO-5	-9.952	0.50	0.31	0.19
HOMO-4	-9.658	0.36	0.18	0.46
HOMO-3	-9.521	0.15	0.41	0.44
HOMO-2	-9.453	0.13	0.74	0.12
HOMO-1	-9.354	0.21	0.69	0.10
SOMO	-8.965	0.35	0.13	0.51
LUMO	-7.155	0.62	0.13	0.24
LUMO+1	-6.640	0.12	0.85	0.03
LUMO+2	-4.562	0.08	0.88	0.04
LUMO+3	-4.187	0.04	0.13	0.84
LUMO+4	-4.152	0.05	0.12	0.83
LUMO+5	-3.759	0.38	0.38	0.23



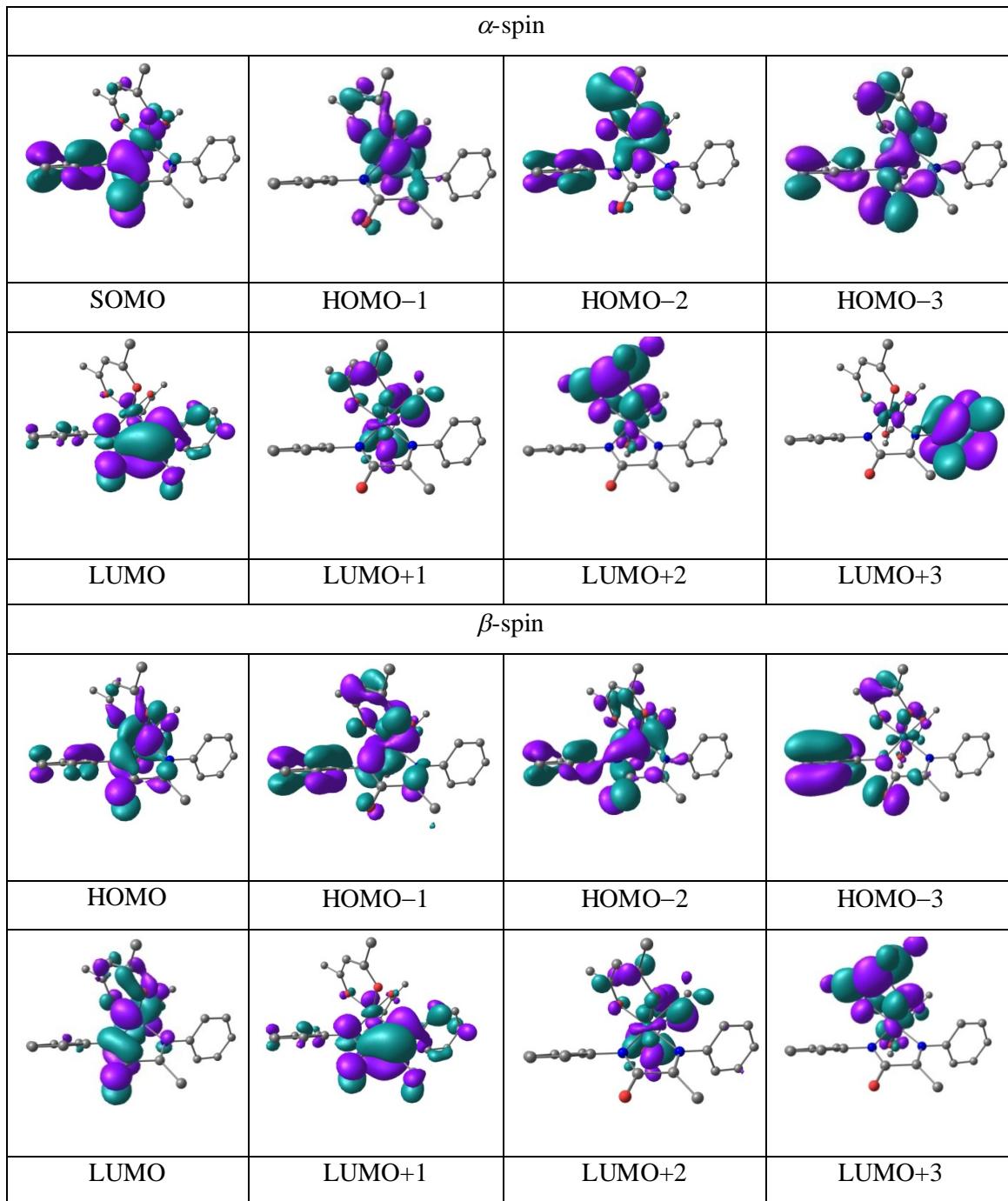
**Table S28. Composition and Energies of Selected Molecular Orbitals of  $2c^-$  ( $S=1/2$ )**

MO	energy (eV)	Composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-2.832	0.06	0.07	0.87
HOMO-4	-2.637	0.00	0.99	0.01
HOMO-3	-1.526	0.74	0.11	0.15
HOMO-2	-1.380	0.58	0.24	0.19
HOMO-1	-1.143	0.69	0.11	0.19
SOMO	-0.052	0.19	0.76	0.05
LUMO	2.337	0.03	0.56	0.41
LUMO+1	2.364	0.04	0.69	0.27
LUMO+2	2.454	0.01	0.88	0.11
LUMO+3	2.567	0.04	0.67	0.28
LUMO+4	2.702	0.06	0.64	0.30
LUMO+5	2.728	0.04	0.55	0.41
$\beta$ -spin				
HOMO-5	-3.017	0.14	0.07	0.79
HOMO-4	-2.799	0.04	0.07	0.88
HOMO-3	-2.412	0.00	0.99	0.01
HOMO-2	-1.495	0.75	0.10	0.15
HOMO-1	-1.133	0.70	0.11	0.19
SOMO	-0.963	0.68	0.14	0.18
LUMO	1.970	0.05	0.83	0.12
LUMO+1	2.359	0.04	0.64	0.31
LUMO+2	2.371	0.04	0.73	0.24
LUMO+3	2.482	0.02	0.87	0.11
LUMO+4	2.616	0.05	0.60	0.35
LUMO+5	2.708	0.38	0.62	0.32



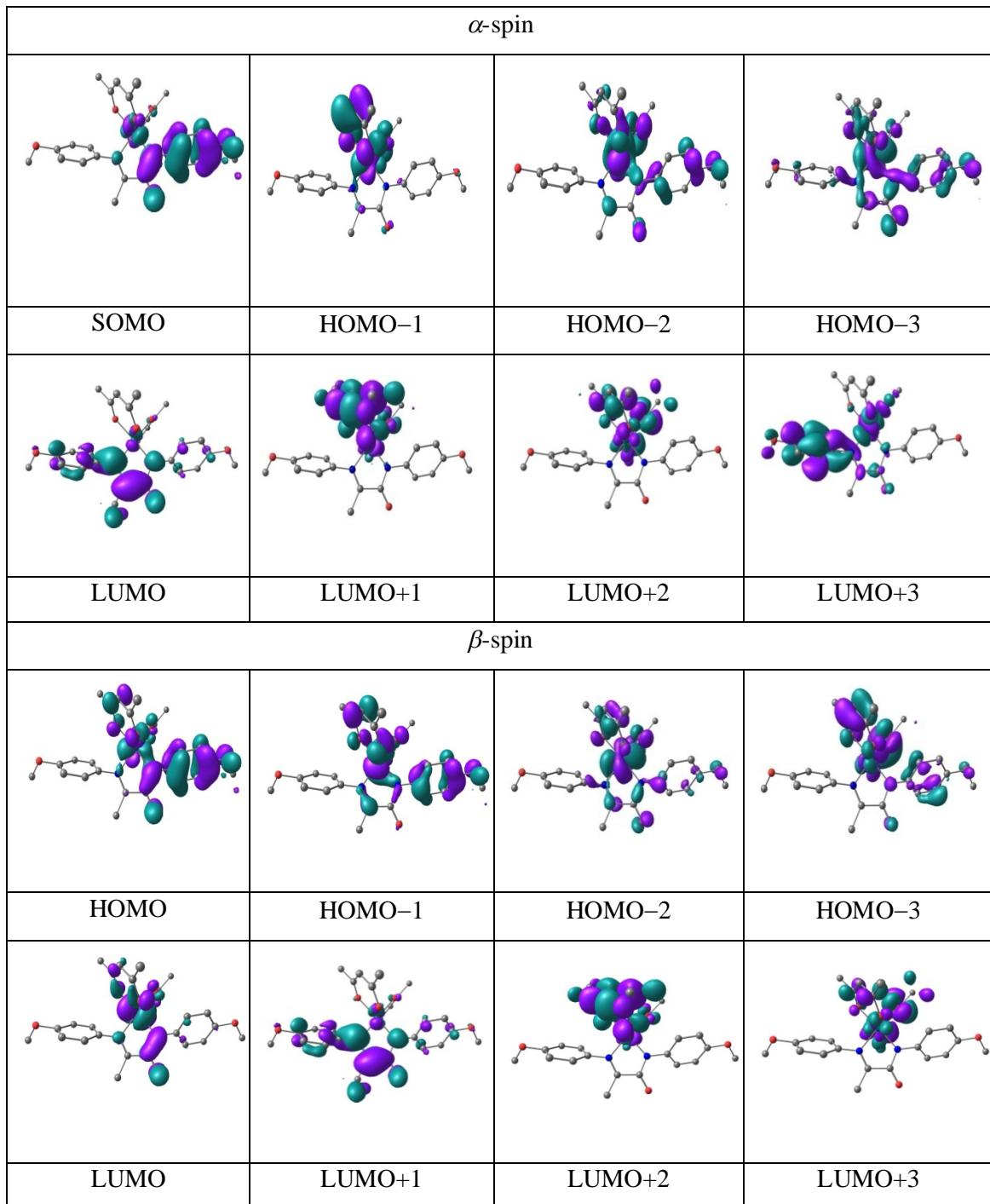
**Table S29. Composition and Energies of Selected Molecular Orbitals of 3a ( $S=1/2$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-6.375	0.20	0.26	0.53
HOMO-4	-6.098	0.20	0.67	0.14
HOMO-3	-6.046	0.32	0.45	0.23
HOMO-2	-5.683	0.44	0.18	0.38
HOMO-1	-5.437	0.50	0.07	0.43
SOMO	-5.157	0.28	0.64	0.08
LUMO	-1.478	0.04	0.93	0.03
LUMO+1	-0.847	0.03	0.04	0.952
LUMO+2	-0.756	0.04	0.05	0.91
LUMO+3	-0.230	0.06	0.90	0.04
LUMO+4	-0.164	0.18	0.73	0.10
LUMO+5	0.198	0.43	0.26	0.31
$\beta$ -spin				
HOMO-5	-6.429	0.08	0.57	0.35
HOMO-4	-6.173	0.07	0.31	0.63
HOMO-3	-6.058	0.04	0.81	0.15
HOMO-2	-5.676	0.47	0.35	0.18
HOMO-1	-5.429	0.47	0.30	0.23
SOMO	-5.105	0.50	0.24	0.26
LUMO	-2.589	0.65	0.19	0.16
LUMO+1	-1.412	0.06	0.90	0.04
LUMO+2	-0.832	0.04	0.05	0.91
LUMO+3	-0.696	0.05	0.06	0.89
LUMO+4	-0.224	0.04	0.93	0.04
LUMO+5	-0.070	0.13	0.81	0.06



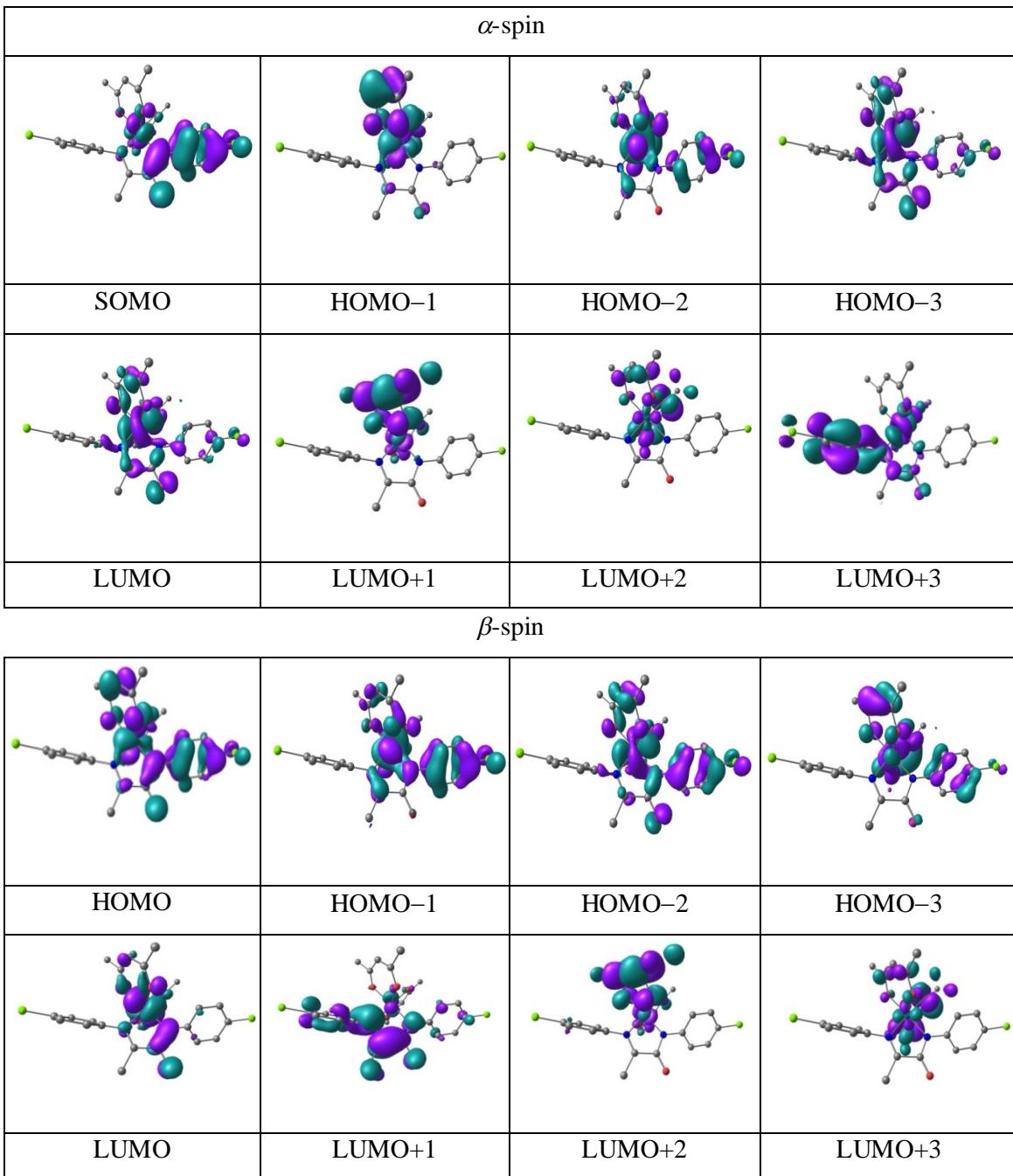
**Table S30. Composition and Energies of Selected Molecular Orbitals of 3b ( $S=1/2$ )**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-6.351	0.05	0.76	0.20
HOMO-4	-6.263	0.16	0.32	0.52
HOMO-3	-6.132	0.57	0.30	0.13
HOMO-2	-5.775	0.45	0.19	0.35
HOMO-1	-5.555	0.43	0.07	0.50
SOMO	-5.071	0.15	0.82	0.03
LUMO	-1.666	0.04	0.94	0.02
LUMO+1	-1.027	0.05	0.04	0.91
LUMO+2	-0.966	0.05	0.04	0.91
LUMO+3	-0.479	0.32	0.51	0.17
LUMO+4	-0.387	0.14	0.76	0.09
LUMO+5	-0.227	0.39	0.32	0.29
$\beta$ -spin				
HOMO-5	-6.439	0.22	0.28	0.50
HOMO-4	-6.318	0.02	0.92	0.07
HOMO-3	-6.139	0.09	0.15	0.76
HOMO-2	-5.754	0.64	0.16	0.20
HOMO-1	-5.474	0.51	0.25	0.25
SOMO	-5.105	0.24	0.60	0.16
LUMO	-2.758	0.65	0.20	0.15
LUMO+1	-1.588	0.05	0.91	0.03
LUMO+2	-1.006	0.04	0.05	0.91
LUMO+3	-0.913	0.05	0.05	0.89
LUMO+4	-0.387	0.06	0.91	0.03
LUMO+5	-0.282	0.23	0.65	0.12



**Table S31. Composition and Energies of Selected Molecular Orbitals of 3c (S=1/2)**

MO	energy (eV)	composition		
		Ru	L	acac <sup>-</sup>
$\alpha$ -spin				
HOMO-5	-6.677	0.12	0.75	0.13
HOMO-4	-6.538	0.18	0.40	0.42
HOMO-3	-6.442	0.52	0.25	0.23
HOMO-2	-5.087	0.40	0.18	0.42
HOMO-1	-5.813	0.42	0.07	0.51
SOMO	-5.508	0.23	0.70	0.07
LUMO	-1.967	0.04	0.94	0.02
LUMO+1	-1.256	0.05	0.05	0.90
LUMO+2	-1.180	0.04	0.05	0.91
LUMO+3	-0.836	0.26	0.61	0.13
LUMO+4	-0.721	0.11	0.81	0.07
LUMO+5	-0.538	0.39	0.31	0.30
$\beta$ -spin				
HOMO-5	-6.690	0.26	0.20	0.54
HOMO-4	-6.628	0.03	0.92	0.05
HOMO-3	-6.380	0.11	0.14	0.75
HOMO-2	-6.062	0.54	0.27	0.19
HOMO-1	-5.841	0.44	0.32	0.23
SOMO	-5.487	0.40	0.35	0.25
LUMO	-3.016	0.66	0.19	0.15
LUMO+1	-1.897	0.05	0.92	0.03
LUMO+2	-1.235	0.04	0.05	0.90
LUMO+3	-1.128	0.05	0.05	0.89
LUMO+4	-0.736	0.08	0.88	0.04
LUMO+5	-0.668	0.14	0.78	0.08



**Table S32. Temperature Dependent Kinetic Data of 1a**

Temp. (K)	$k(s^{-1}) [=1/(t1*60)]$	$\ln(k/T)$	$1/T \times 10^{-3}$
303	$6.44 \times 10^{-6}$	-17.67	3.3003
313	$7.54 \times 10^{-6}$	-17.54	3.1949
323	$8.66 \times 10^{-6}$	-17.43	3.0960
333	$9.74 \times 10^{-6}$	-17.35	3.0030
Value from $\ln(k/T)$ versus $1/T$ plot			
	Value	Standard Error	
Intercept	-14.12	$\pm 0.17$	
Slope	-1.07	$\pm 0.05$	

Activation enthalpy ( $\Delta H^\ddagger$ ) and activation entropy ( $\Delta S^\ddagger$ ) values were obtained from the slope and intercept of plots of  $\ln(k/T)$  versus  $1/T$  using the following equation:

$$\ln(k/T) = \ln(R/Nh) + \Delta S^\ddagger / R - \Delta H^\ddagger / RT$$

where N = Avogadro's number, R = universal gas constant, and h = Planck's constant.

**Table S33. Change in Rate Constant Values of 1 on Varying Substituents**

complex	Rate Constants ( $k$ ) (in $s^{-1}$ ) at 333 K $k = [=1/(t1*60)]$	Standard Error
<b>1a</b>	$9.74 \times 10^{-6}$	$\pm 1.9 \times 10^{-7}$
<b>1b</b>	$8.76 \times 10^{-6}$	$\pm 2.8 \times 10^{-7}$
<b>1c</b>	$6.83 \times 10^{-6}$	$\pm 1.5 \times 10^{-7}$