

1 Article

2 **Thiourea-Derived Chelating Ligands and Their**  
3 **Organometallic Compounds: Investigations into**  
4 **Their Anticancer Inhibitory Activity**

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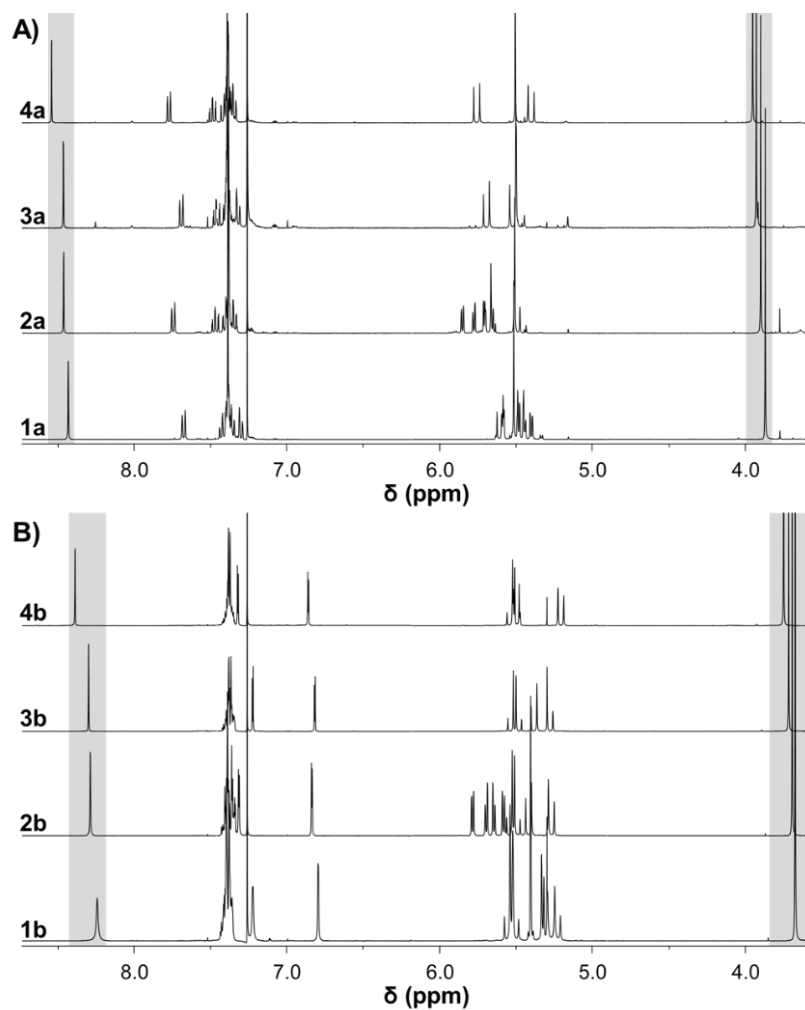
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31**Table S1.** ESI-MS data for compounds **a**, **b**, **1a-4b**, **1a<sup>Cl</sup>-4b<sup>Cl</sup>** and **1b<sup>NH3</sup>** analyzed in positive ion mode.

Compound	Observed <i>m/z</i>	Theoretical <i>m/z</i>	Assignment
<b>a</b>	358.1106	358.1102	[M + Na] <sup>+</sup>
<b>b</b>	308.0942	308.0946	[M + Na] <sup>+</sup>
<b>1a</b>	606.1034	606.1032	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>1a<sup>Cl</sup></b>	606.1024	606.1032	[M – Cl] <sup>+</sup>
<b>2a</b>	696.1576	696.1603	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>2a<sup>Cl</sup></b>	696.1576	696.1603	[M – Cl] <sup>+</sup>
<b>3a</b>	608.1125	608.1122	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>3a<sup>Cl</sup></b>	574.1487	574.1506	[M – 2Cl – H] <sup>+</sup>
<b>4a</b>	698.1672	698.1696	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>4a<sup>Cl</sup></b>	662.1949	662.1929	[M – 2Cl – H] <sup>+</sup>
<b>1b</b>	556.0836	556.0876	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>1b<sup>Cl</sup></b>	556.0871	556.0876	[M – Cl] <sup>+</sup>
<b>1b<sup>NH3</sup></b>	683.1120	683.1094	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>2b</b>	646.1422	646.1447	[M – PF <sub>6</sub> ] <sup>+</sup>
<b>2b<sup>Cl</sup></b>	646.1422	646.1447	[M – Cl] <sup>+</sup>
<b>3b</b>	524.1357	524.1324	[M – Cl – PF <sub>6</sub> – 3H + 2D] <sup>+</sup>
<b>3b<sup>Cl</sup></b>	524.1338	524.1324	[M – 2Cl – 3H + 2D] <sup>+</sup>
<b>4b</b>	612.1848	612.1769	[M – Cl – PF <sub>6</sub> – H] <sup>+</sup>
<b>4b<sup>Cl</sup></b>	612.1778	612.1773	[M – 2Cl – H] <sup>+</sup>

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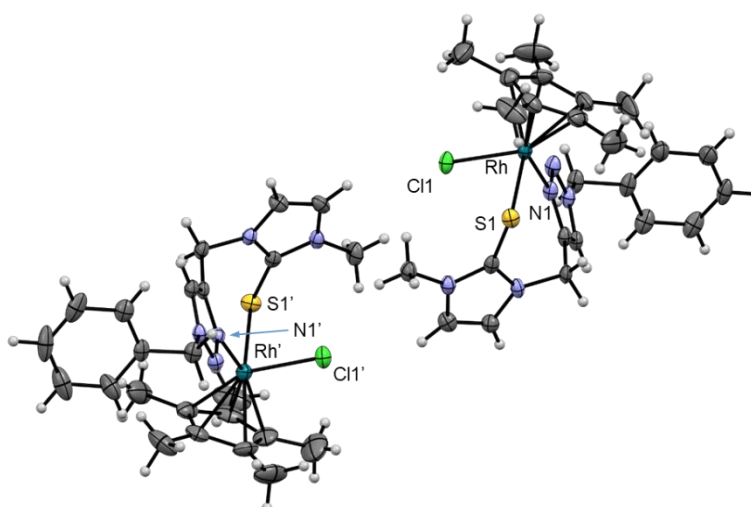
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**Figure S1.** Comparison of the  $^1\text{H}$  NMR spectra of complexes **1a-4a** (A) and **1b-4b** (B). The triazole and methyl H peaks shifting in dependence of the metal center are highlighted with grey boxes.

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**Figure S2.** Molecular structures of the two enantiomers of **3b**. Counterions have been omitted for clarity and the structures are shown at 50% probability level.

**Table S2.** X-ray crystallographic data for complex **1b<sup>NH3</sup>**, **2a**, **2a<sup>Cl</sup>**, **3b**, **3b<sup>Cl</sup>**, **4a**, and **4b<sup>Cl</sup>**.

	<b>1b<sup>NH3</sup></b>	<b>2a<sup>Cl</sup>·H<sub>2</sub>O</b>	<b>3b·toluene</b>	<b>3b<sup>Cl</sup>·H<sub>2</sub>O·toluene</b>	<b>4a·CHCl<sub>3</sub></b>	<b>4b<sup>Cl</sup>·H<sub>2</sub>O</b>
CCDC	2013780	2013781	2013782	2013783	2013784	2013785
Formula	C <sub>24</sub> H <sub>32</sub> N <sub>6</sub> RuSP <sub>2</sub> F <sub>12</sub>	C <sub>28</sub> H <sub>31</sub> Cl <sub>2</sub> N <sub>5</sub> OsS· 2.25H <sub>2</sub> O	C <sub>24</sub> H <sub>30</sub> ClN <sub>5</sub> RhSPF <sub>6</sub> · 0.5C <sub>7</sub> H <sub>8</sub> [+H <sub>2</sub> O] <sup>#</sup>	C <sub>24</sub> H <sub>30</sub> Cl <sub>2</sub> N <sub>5</sub> RhS· 1.5H <sub>2</sub> O [+ C <sub>7</sub> H <sub>8</sub> + H <sub>2</sub> O] <sup>#</sup>	C <sub>28</sub> H <sub>32</sub> ClIrN <sub>5</sub> SPF <sub>6</sub> · 3CHCl <sub>3</sub>	C <sub>24</sub> H <sub>30</sub> Cl <sub>2</sub> IrN <sub>5</sub> S· 1.25H <sub>2</sub> O
Formula weight [g mol <sup>-1</sup> ]	827.62	771.27	749.98	621.42	1201.37	706.21
Temperature [K]	99.8(3)	100.0(1)	100.0(2)	100.0(1)	100.0(1)	100.0(1)
Crystal System	monoclinic	monoclinic	orthorhombic	triclinic	monoclinic	triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>Pna</i> 2 <sub>1</sub>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1
<i>a</i> [Å]	9.06730(9)	10.77920(10)	29.9478(3)	8.49050(10)	12.49577(7)	8.3119(2)
<i>b</i> [Å]	12.95883(13)	9.14240(10)	8.43080(10)	18.6371(2)	11.25335(6)	18.9967(3)
<i>c</i> [Å]	27.5090(2)	29.8464(3)	25.6410(3)	19.1728(2)	32.00737(18)	19.2510(3)
<i>α</i> [°]	90	90	90	96.503(1)	90	62.526(1)
<i>β</i> [°]	97.9021(9)	90.727(1)	90	90.247(1)	94.3484(5)	85.408(1)
<i>γ</i> [°]	90	90	90	94.121(1)	90	80.034(1)
<i>V</i> [Å <sup>3</sup> ]	3201.66(5)	2941.06(5)	6473.94(13)	3006.32(6)	4487.90(4)	2656.20(9)
<i>Z</i>	4	4	8	4	4	4
<i>ρ</i> <sub>calc</sub> [g/cm <sup>3</sup> ]	1.717	1.742	1.539	1.478	1.778	1.766
<i>μ</i> [mm <sup>-1</sup> ]	6.424	10.818	6.640	7.124	12.506	12.540
<i>F</i> (000)	1664.0	1530.0	3048.0	1378.0	2352.0	1394.0
Crystal size [mm <sup>3</sup> ]	0.10 × 0.10 × 0.05	0.08 × 0.08 × 0.01	0.05 × 0.05 × 0.01	0.20 × 0.12 × 0.08	0.12 × 0.10 × 0.05	0.50 × 0.01 × 0.01
2 $\Theta$ range for data collection [°]	11.898 to 135.472	11.35 to 135.454	11.436 to 136.492	11.174 to 135.476	11.086 to 136.496	11.362 to 136.482
Index ranges	-10 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 15, -28 ≤ <i>l</i> ≤ 32	-12 ≤ <i>h</i> ≤ 12, -10 ≤ <i>k</i> ≤ 10, -35 ≤ <i>l</i> ≤ 35	-36 ≤ <i>h</i> ≤ 33 -7 ≤ <i>k</i> ≤ 10, -30 ≤ <i>l</i> ≤ 30	-10 ≤ <i>h</i> ≤ 10, -22 ≤ <i>k</i> ≤ 20, -23 ≤ <i>l</i> ≤ 23	-15 ≤ <i>h</i> ≤ 14, -13 ≤ <i>k</i> ≤ 13, -38 ≤ <i>l</i> ≤ 38	-10 ≤ <i>h</i> ≤ 10, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23

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Table S2. contd.

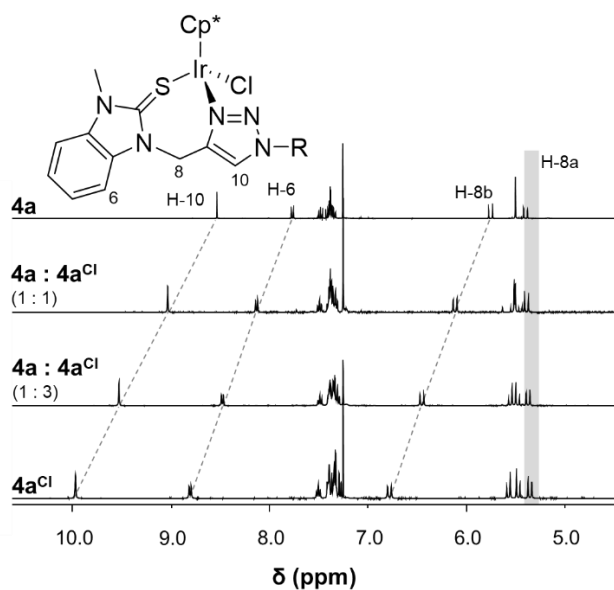
	<b>1b<sup>NH3</sup></b>	<b>2a<sup>Cl·H2O</sup></b>	<b>3b·toluene</b>	<b>3b<sup>Cl·H2O·toluene</sup></b>	<b>4a·CHCl<sub>3</sub></b>	<b>4b<sup>Cl·H2O</sup></b>
<b>Reflections collected</b>	44752	36743	50594	95171	71288	79200
<b>Independent reflections</b>	5785 [R <sub>int</sub> = 0.0399, R <sub>sigma</sub> = 0.0213]	5300 [R <sub>int</sub> = 0.0379, R <sub>sigma</sub> = 0.0216]	11382 [R <sub>int</sub> = 0.0354, R <sub>sigma</sub> = 0.0317]	10870 [R <sub>int</sub> = 0.0725, R <sub>sigma</sub> = 0.0357]	8213 [R <sub>int</sub> = 0.0506, R <sub>sigma</sub> = 0.0242]	9686 [R <sub>int</sub> = 0.0593, R <sub>sigma</sub> = 0.0278]
<b>Data / restraints / parameters</b>	5785 / 42 / 486	5300 / 0 / 396	11382 / 53 / 779	10870 / 0 / 671	8213 / 4 / 530	9686 / 0 / 658
<b>Goodness-of-fit on F<sup>2</sup></b>	1.032	1.056	1.032	1.054	1.060	1.105
<b>Final R indexes [I&gt;=2σ (I)]</b>	R <sub>1</sub> = 0.0210 wR <sub>2</sub> = 0.0502	R <sub>1</sub> = 0.0186 wR <sub>2</sub> = 0.0450	R <sub>1</sub> = 0.0327 wR <sub>2</sub> = 0.0838	R <sub>1</sub> = 0.0372 wR <sub>2</sub> = 0.0991	R <sub>1</sub> = 0.0300 wR <sub>2</sub> = 0.0718	R <sub>1</sub> = 0.0372 wR <sub>2</sub> = 0.0923
<b>Final R indexes [all data]</b>	R <sub>1</sub> = 0.0220 wR <sub>2</sub> = 0.0507	R <sub>1</sub> = 0.0205 wR <sub>2</sub> = 0.0458	R <sub>1</sub> = 0.0349 wR <sub>2</sub> = 0.0852	R <sub>1</sub> = 0.0420 wR <sub>2</sub> = 0.1026	R <sub>1</sub> = 0.0308 wR <sub>2</sub> = 0.0725	R <sub>1</sub> = 0.0414 wR <sub>2</sub> = 0.0947
<b>Largest diff. peak / hole [e Å<sup>-3</sup>]</b>	0.34 / -0.39	0.80 / -0.66	0.78 / -0.53	0.86 / -1.18	1.67 / -1.11	2.31 / -2.27
<b>Flack parameter</b>	-	-	-0.011(4)	-	-	-

44 # Highly disordered solvent; excluded with solvent mask from final refinements

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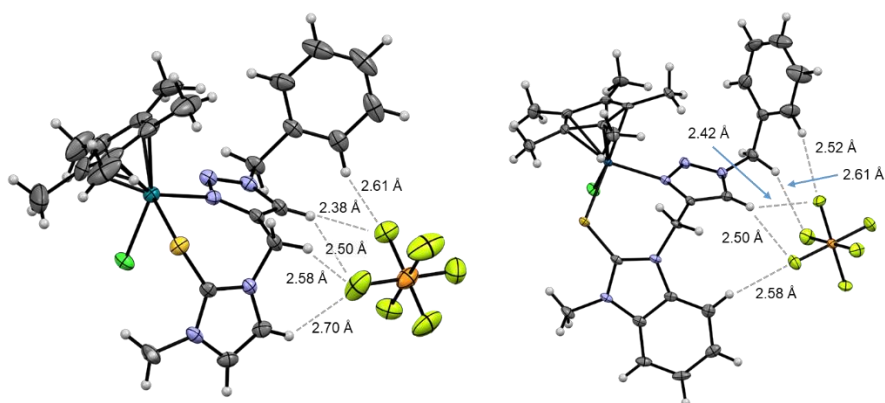
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51 **Figure S3.** The aromatic regions of the  $^1\text{H}$  NMR spectra of **4a** with its  $\text{PF}_6^-$  counterion and the chloride  
52 derivative **4a<sup>Cl</sup>** and both compounds mixed at 1 : 1 and 1 : 3 ratios, recorded in  $\text{CDCl}_3$ .

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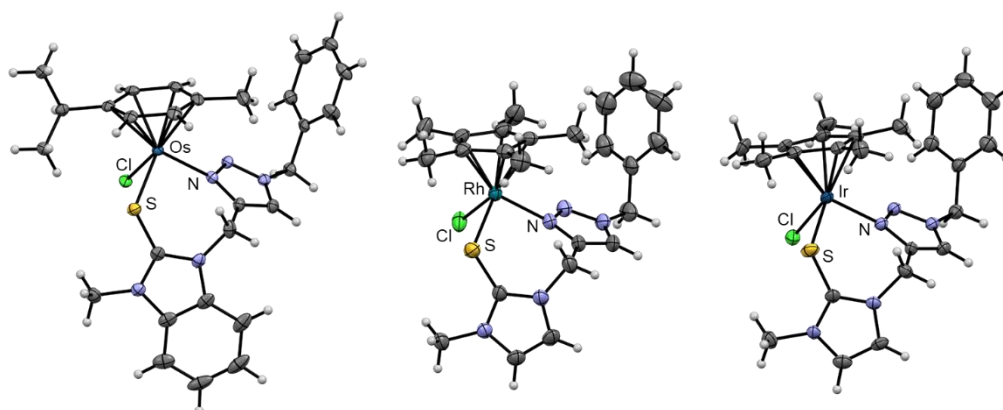


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58 **Figure S4.** Interactions between the  $\text{PF}_6^-$  counterions and the complex cations in **3b** (left) and **4a** (right)  
59 with the C–H...F distances shown. Co-crystallized solvent molecules have been omitted for clarity  
60 and the structures are drawn at 50% probability level.

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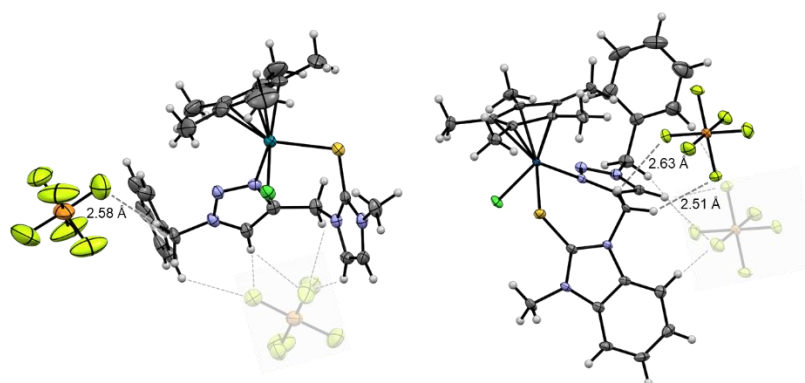
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69 **Figure S5.** Molecular structures of one of the enantiomers found for **2a<sup>Cl</sup>**, **3b<sup>Cl</sup>**, and **4b<sup>Cl</sup>**. Counterions  
70 and co-crystallized solvent molecules have been omitted for clarity and the structures are drawn at  
71 50% probability level.

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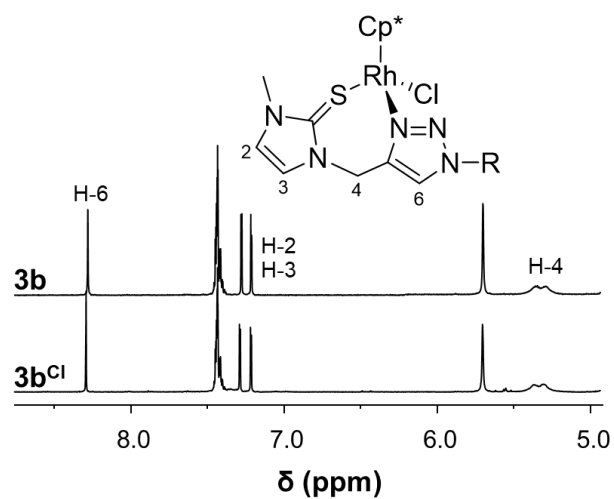


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78 **Figure S6.** Secondary interactions between the  $\text{PF}_6^-$  counterions and the complex cations in **3b** (left)  
79 and **4a** (right). Co-crystallized solvent molecules have been omitted for clarity and the structures are  
80 drawn at 50% probability level.

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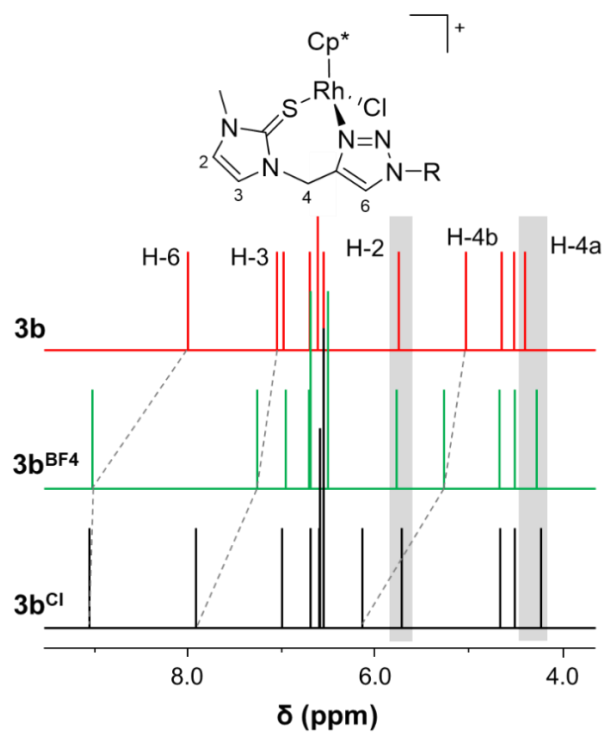
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Figure S7. The aromatic regions of the  $^1\text{H}$  NMR spectra of **3b** and **3b<sup>Cl</sup>** recorded in MeOD.

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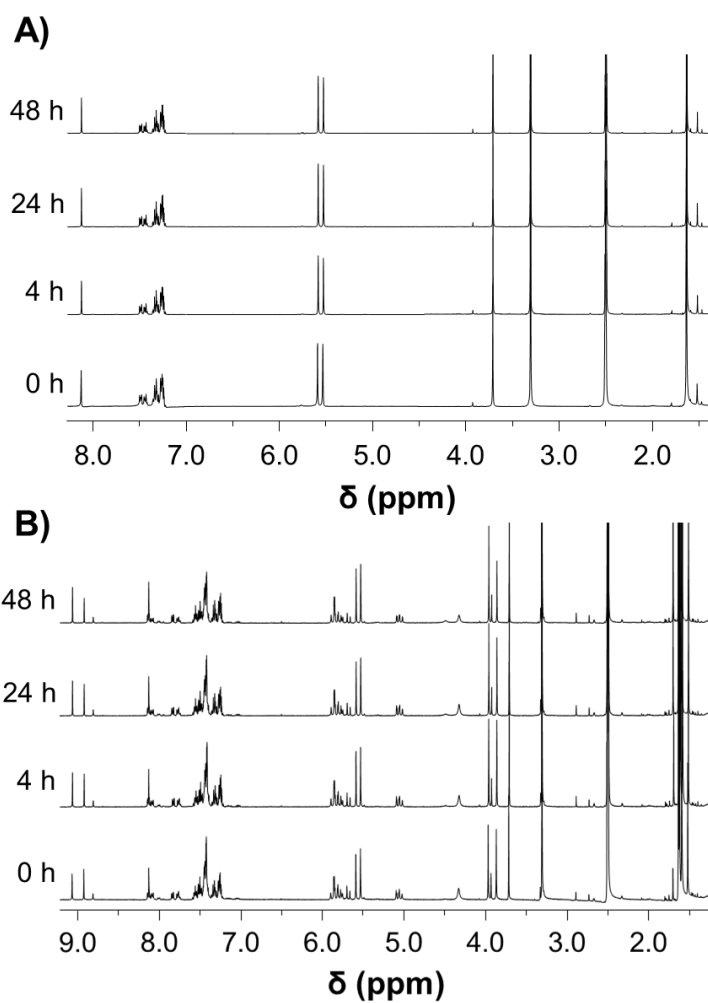
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Figure S8. DFT calculations of  $^1\text{H}$  NMR spectra of **3b**, **3b<sup>BF<sub>4</sub></sup>**, and **3b<sup>Cl</sup>**.

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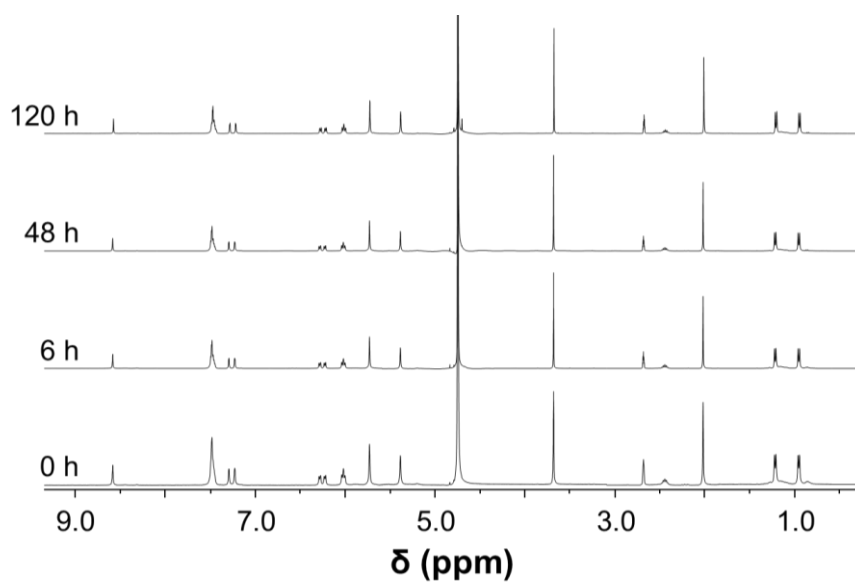
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Figure S9. Stability of 4a (A) and 4a<sup>Cl</sup> (B) in DMSO-*d*<sub>6</sub> investigated by <sup>1</sup>H NMR spectroscopy.

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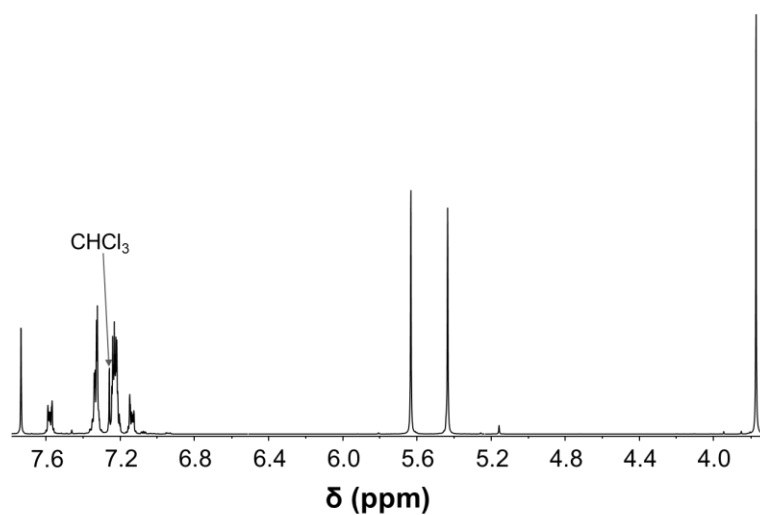
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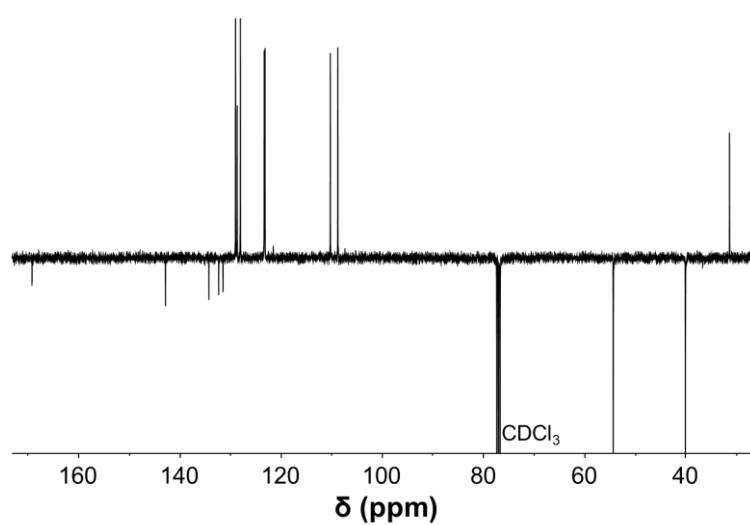
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Figure S10. Stability of 1b in 15% DMSO-*d*<sub>6</sub>/D<sub>2</sub>O investigated by <sup>1</sup>H NMR spectroscopy.



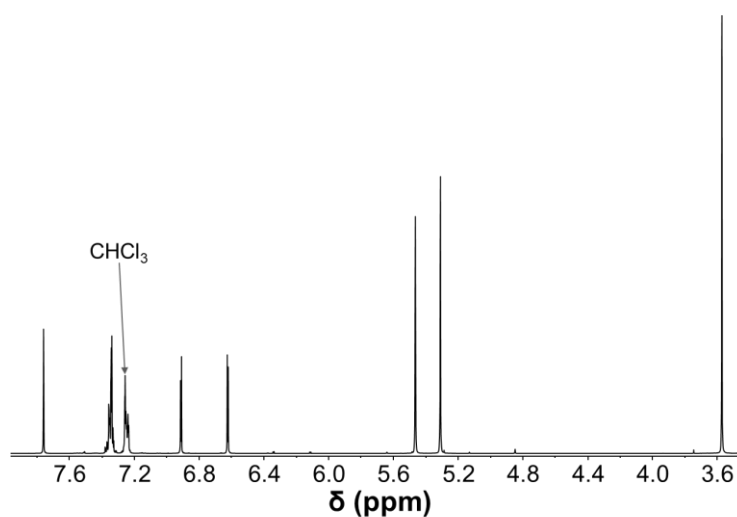
103 **Figure S11.**  $^1\text{H}$  NMR spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-methylbenzimidazole-2-  
104 thione **a** recorded in  $\text{CDCl}_3$ .

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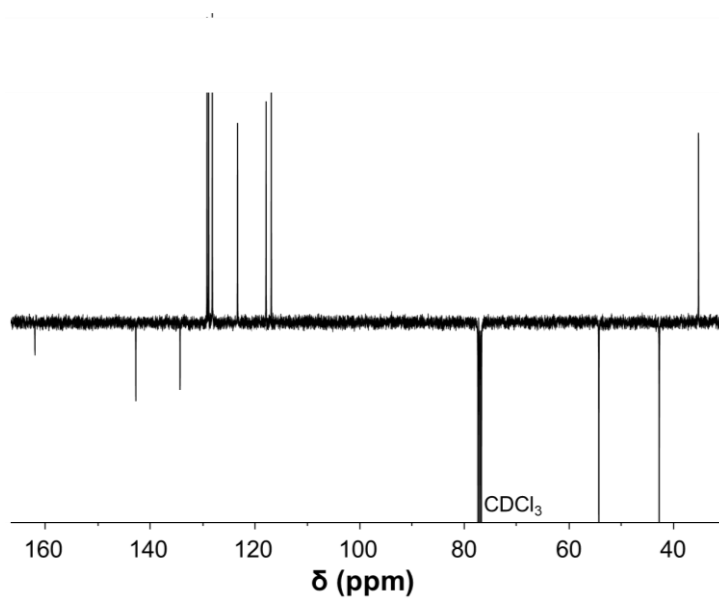
111 **Figure S12.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-  
112 methylbenzimidazole-2-thione **a** recorded in  $\text{CDCl}_3$ .

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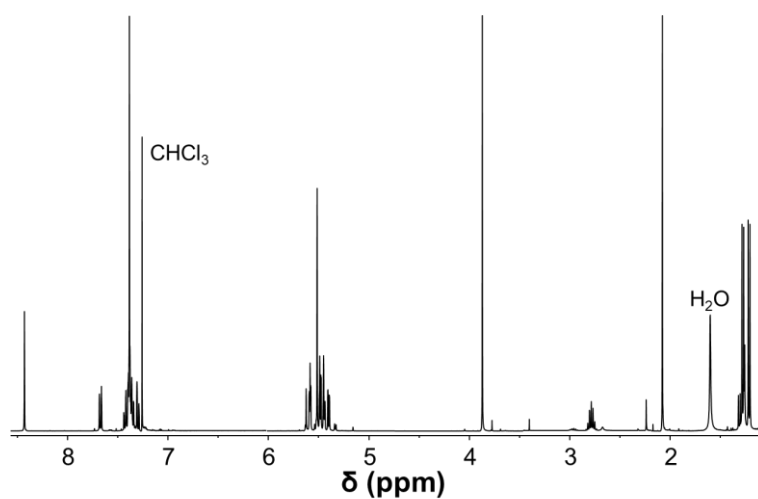
**Figure S13.**  $^1\text{H}$  NMR spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-methylimidazole-2-thione **b** recorded in  $\text{CDCl}_3$ .

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**Figure S14.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-methylimidazole-2-thione **b** recorded in  $\text{CDCl}_3$ .

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**Figure S15.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylbenzimidazole-2-thione- $\kappa\text{S}$ ]( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1a** recorded in  $\text{CDCl}_3$ .

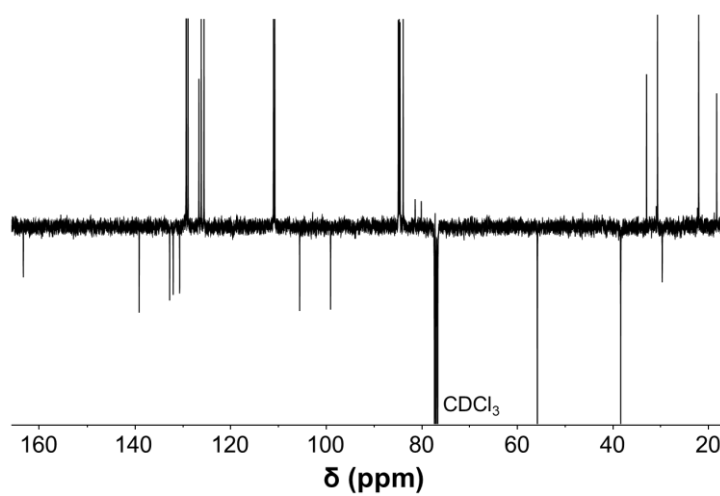
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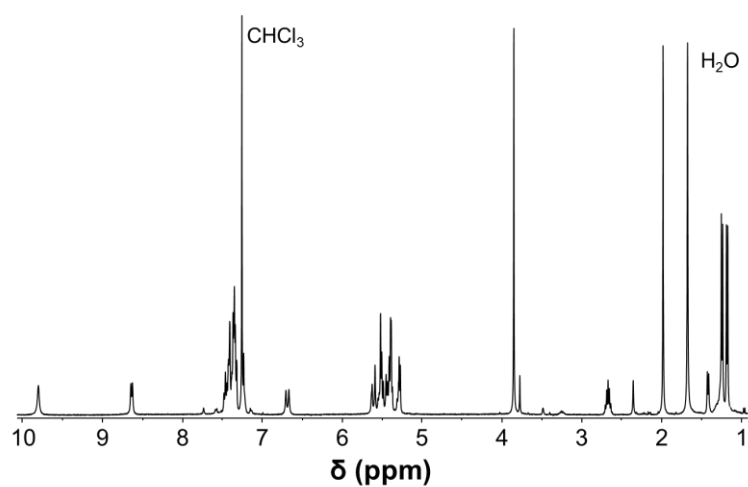
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**Figure S16.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylbenzimidazole-2-thione- $\kappa\text{S}$ ]( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1a** recorded in  $\text{CDCl}_3$ .

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**Figure S17.** <sup>1</sup>H NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-κN)methyl]-3-methylbenzimidazole-2-thione-κS}(η<sup>6</sup>-*p*-cymene)ruthenium(II)] chloride **1a<sup>Cl</sup>** recorded in CDCl<sub>3</sub>.

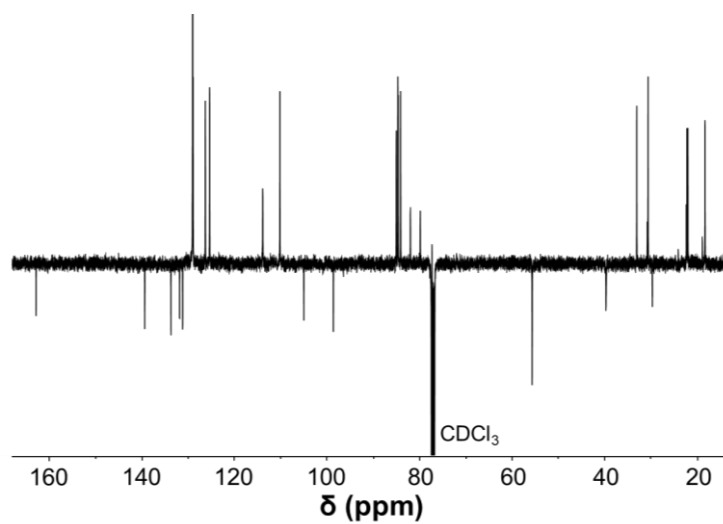
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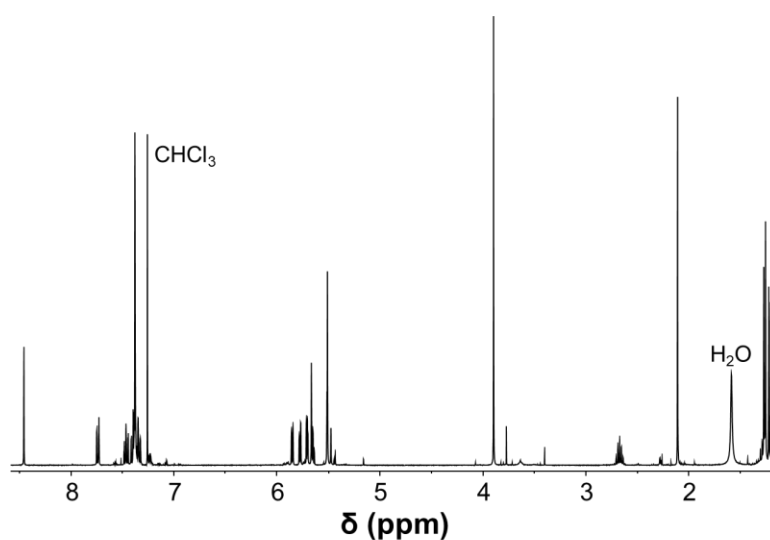
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**Figure S18.** <sup>13</sup>C{<sup>1</sup>H} DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-κN)methyl]-3-methylbenzimidazole-2-thione-κS}(η<sup>6</sup>-*p*-cymene)ruthenium(II)] chloride **1a<sup>Cl</sup>** recorded in CDCl<sub>3</sub>.

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157 **Figure S19.** <sup>1</sup>H NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-κN)methyl]-3-  
158 methylbenzimidazole-2-thione-κS}(η<sup>6</sup>-*p*-cymene)osmium(II)] hexafluorophosphate **2a** recorded in  
159 CDCl<sub>3</sub>.

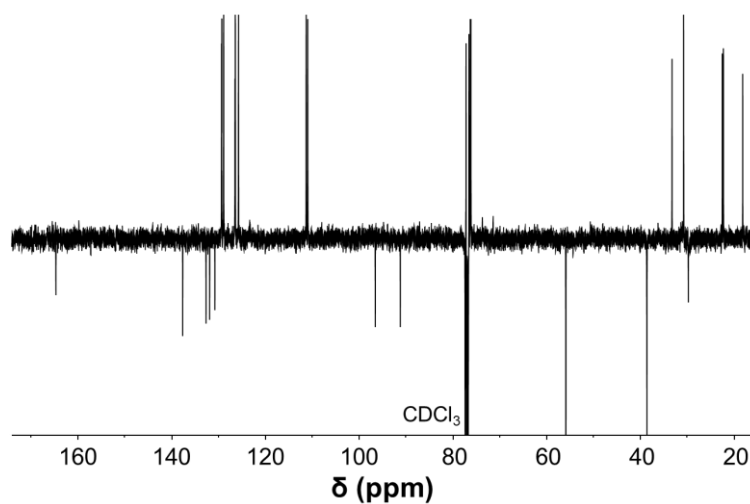
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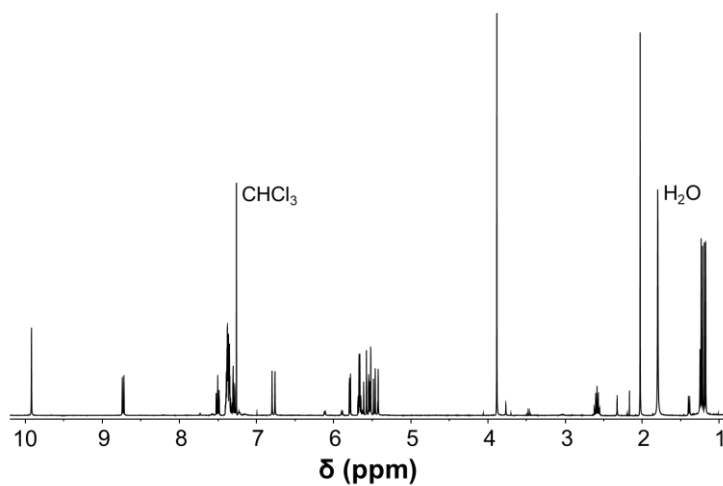
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166 **Figure S20.** <sup>13</sup>C{<sup>1</sup>H} DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-κN)methyl]-  
167 3-methylbenzimidazole-2-thione-κS}(η<sup>6</sup>-*p*-cymene)osmium(II)] hexafluorophosphate **2a** recorded in  
168 CDCl<sub>3</sub>.

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171 **Figure S21.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-  
172 methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2a<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

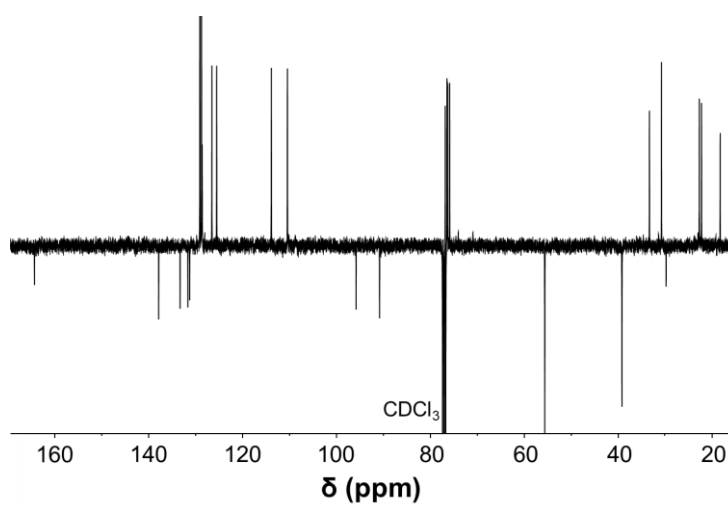
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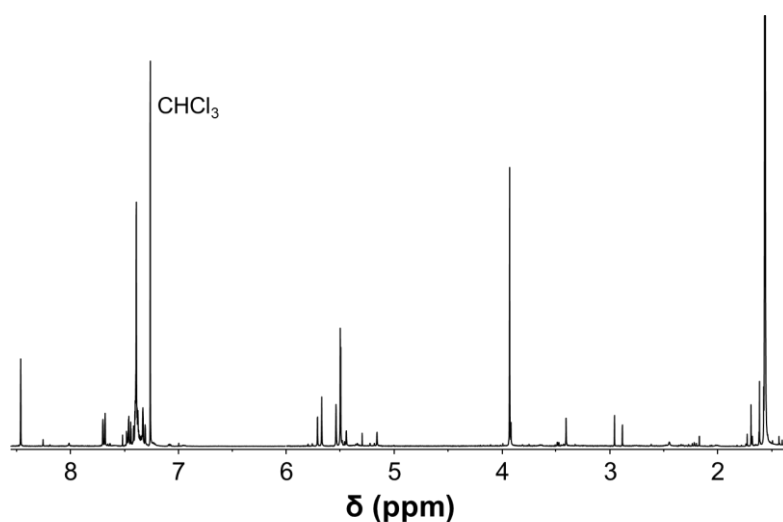
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179 **Figure S22.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-  
180 3-methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2a<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

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183 **Figure S23.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-  
184 methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)]  
185 hexafluorophosphate **3a** recorded in  $\text{CDCl}_3$ .

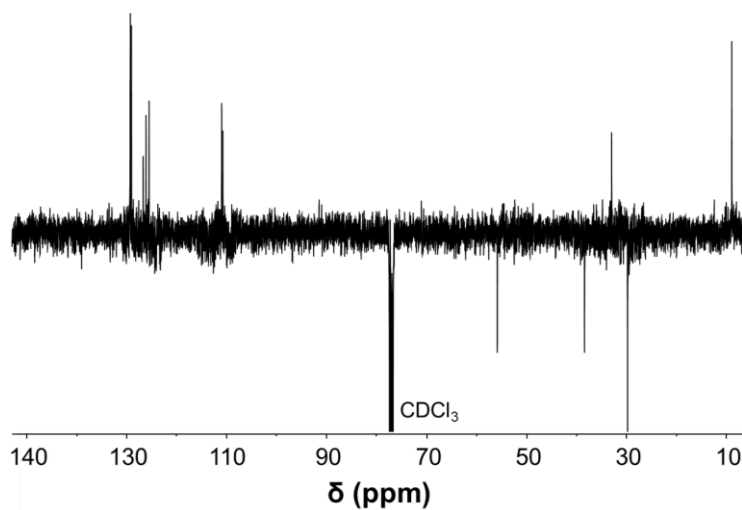
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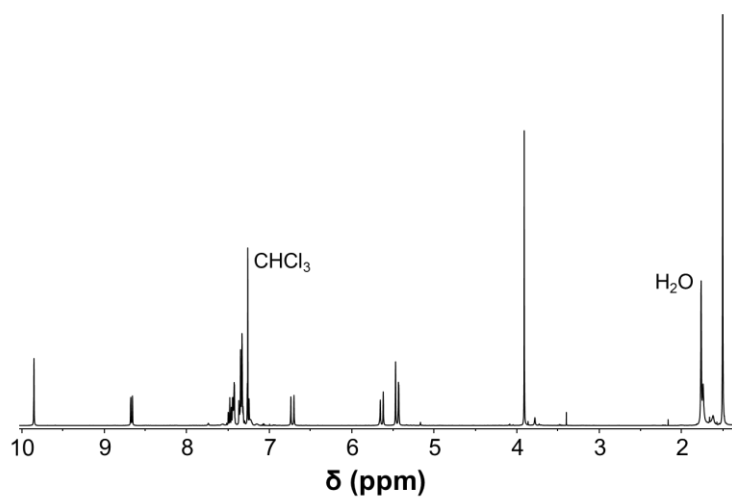


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192 **Figure S24.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-  
193 3-methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)]  
194 hexafluorophosphate **3a** recorded in  $\text{CDCl}_3$ .

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**Figure S25.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylbenzimidazole-2-thione- $\kappa\text{S}$ ]( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] chloride **3a<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

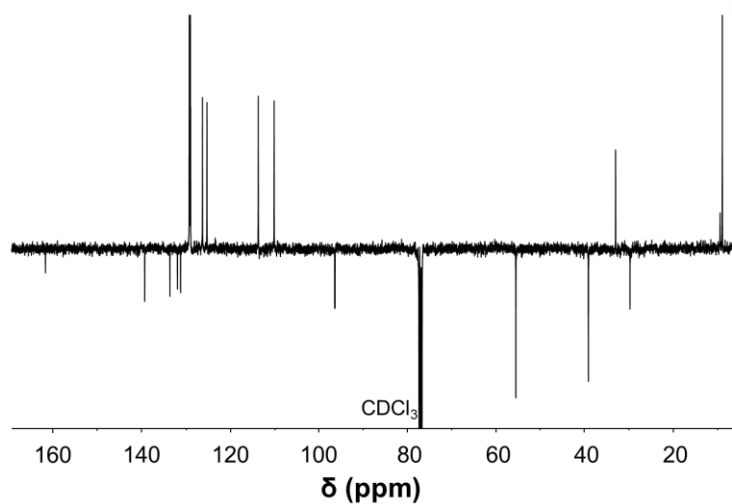
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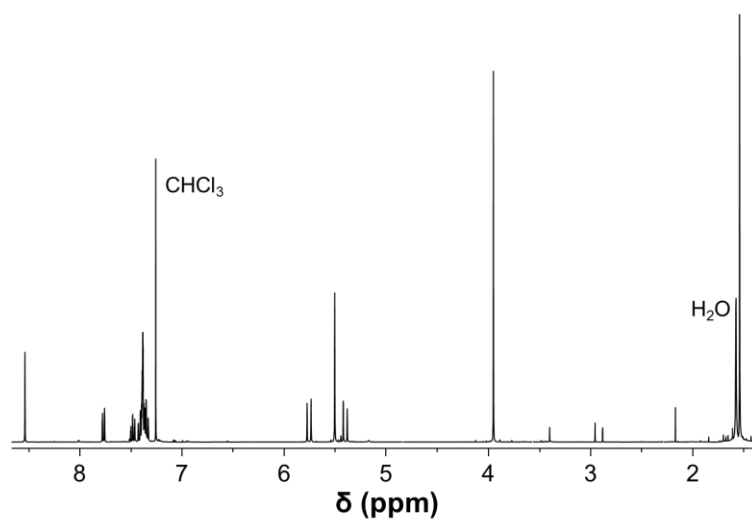
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**Figure S26.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylbenzimidazole-2-thione- $\kappa\text{S}$ ]( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] chloride **3a<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

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211 **Figure S27.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-  
212 methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)]  
213 hexafluorophosphate **4a** recorded in  $\text{CDCl}_3$ .

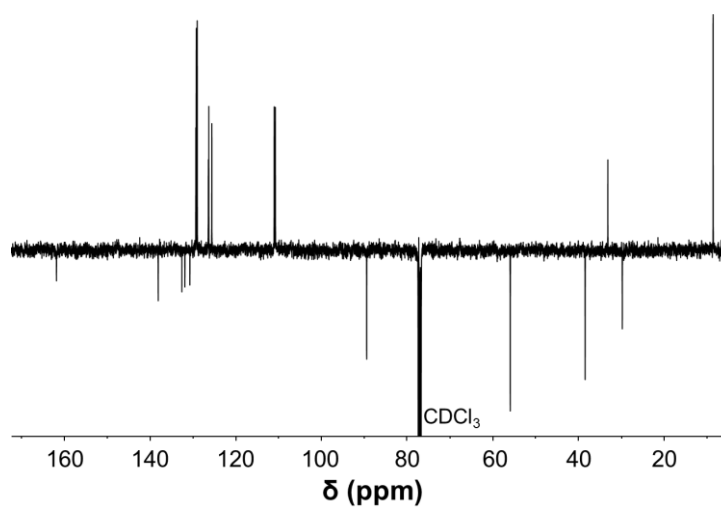
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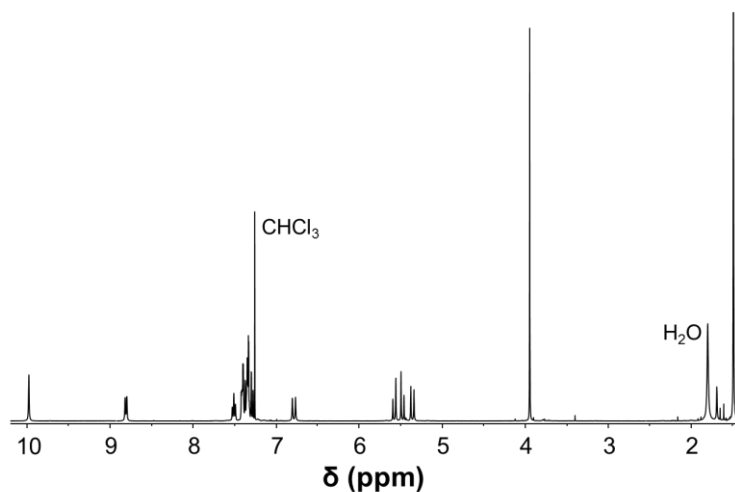
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220 **Figure S28.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-  
221 3-methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)]  
222 hexafluorophosphate **4a** recorded in  $\text{CDCl}_3$ .

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225 **Figure S29.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-  
226 methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] chloride **4a<sup>Cl</sup>**  
227 recorded in  $\text{CDCl}_3$ .

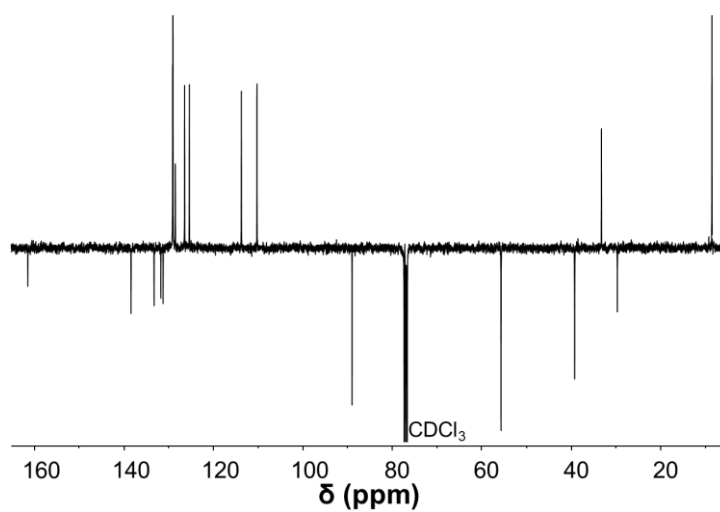
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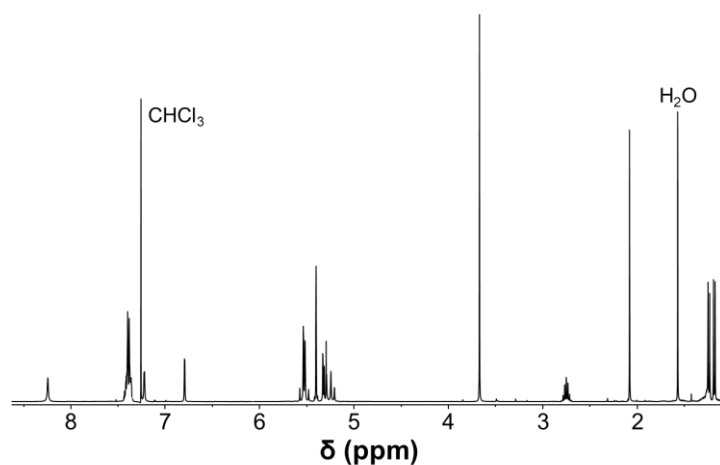
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234 **Figure S30.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-  
235 3-methylbenzimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] chloride **4a<sup>Cl</sup>**  
236 recorded in  $\text{CDCl}_3$ .

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**Figure S31.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1b** recorded in  $\text{CDCl}_3$ .

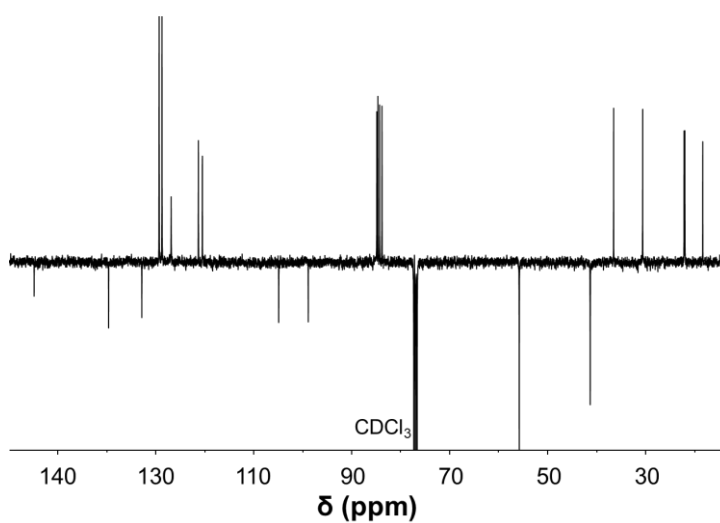
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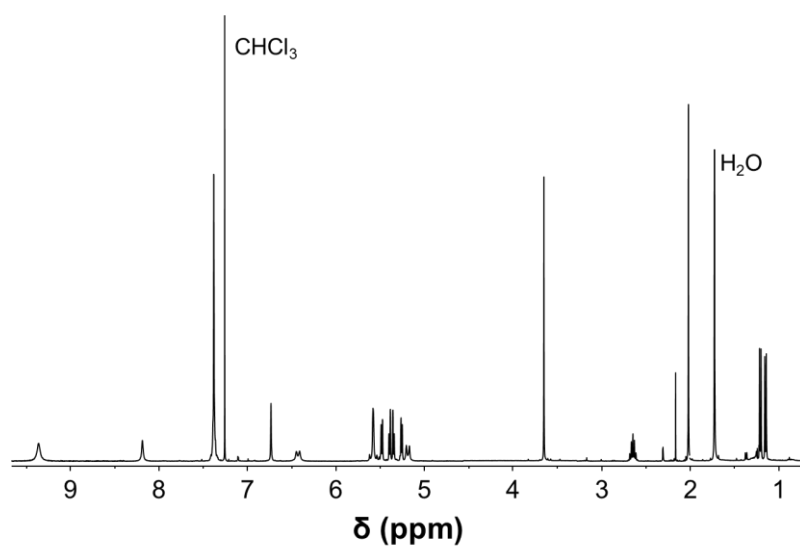
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**Figure S32.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1b** recorded in  $\text{CDCl}_3$ .



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**Figure S33.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)ruthenium(II)] chloride **1b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

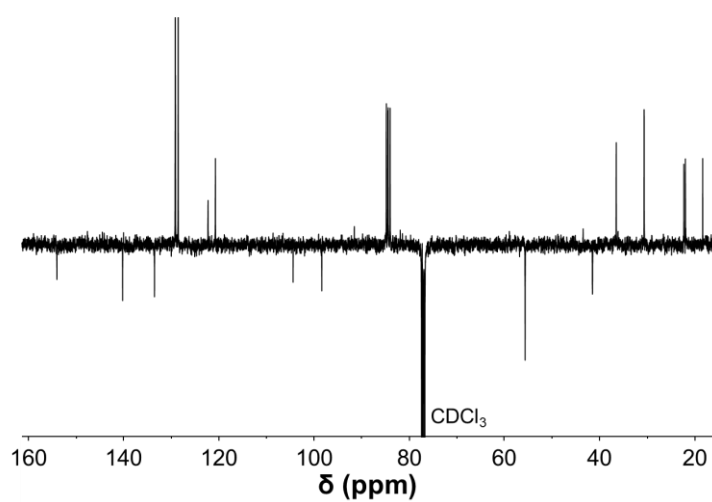
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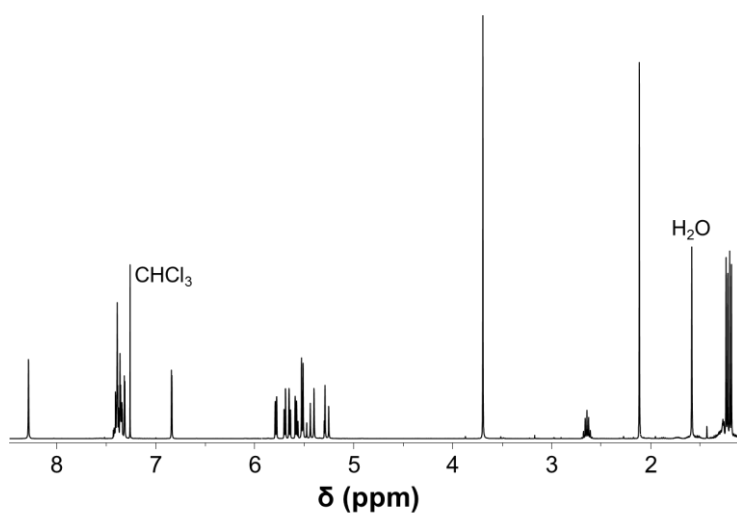
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**Figure S34.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)ruthenium(II)] chloride **1b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

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**Figure S35.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] hexafluorophosphate **2b** recorded in  $\text{CDCl}_3$ .

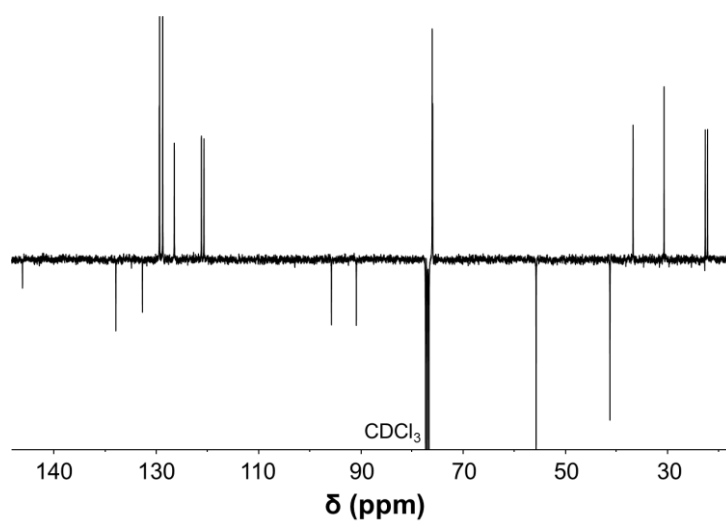
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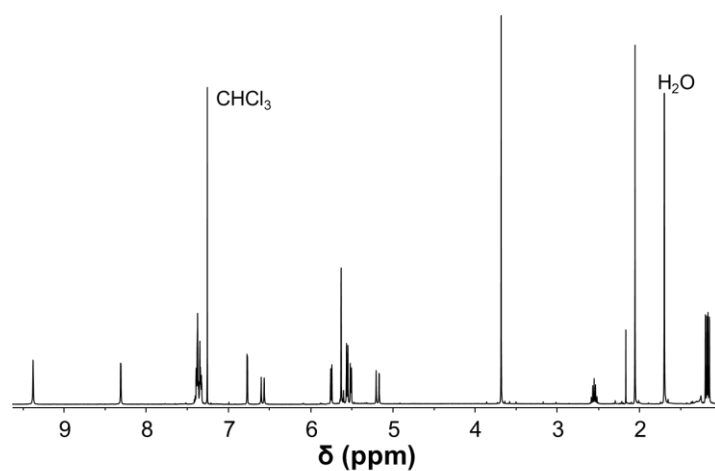
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**Figure S36.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] hexafluorophosphate **2b** recorded in  $\text{CDCl}_3$ .

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**Figure S37.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

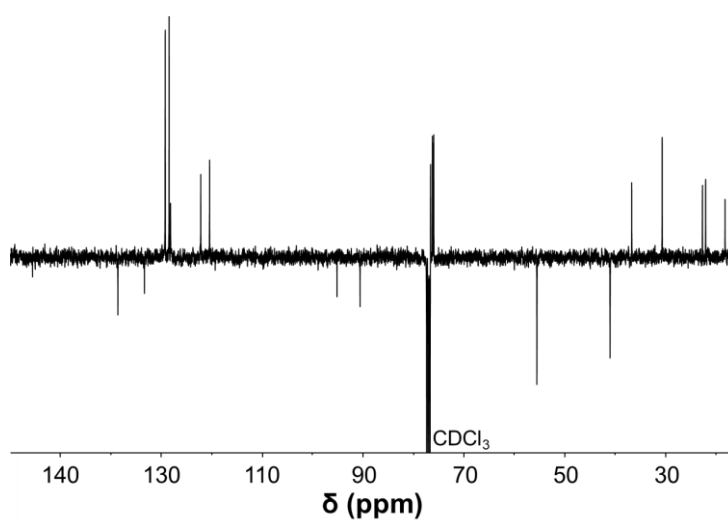
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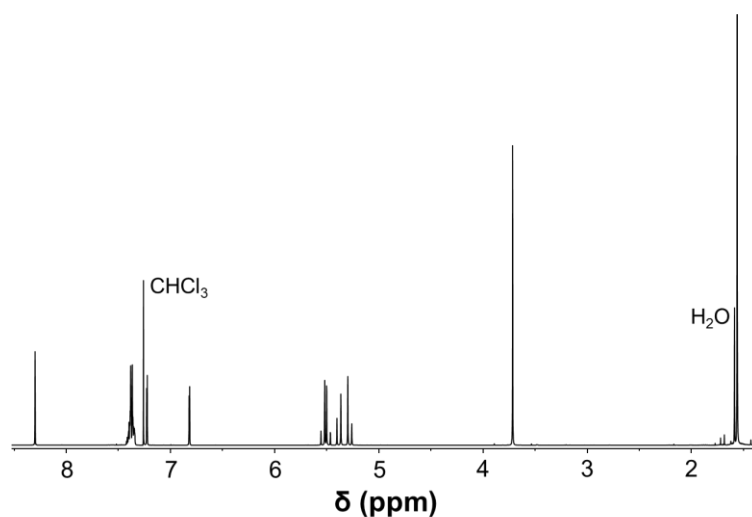
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**Figure S38.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

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**Figure S39.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] hexafluorophosphate **3b** recorded in  $\text{CDCl}_3$ .

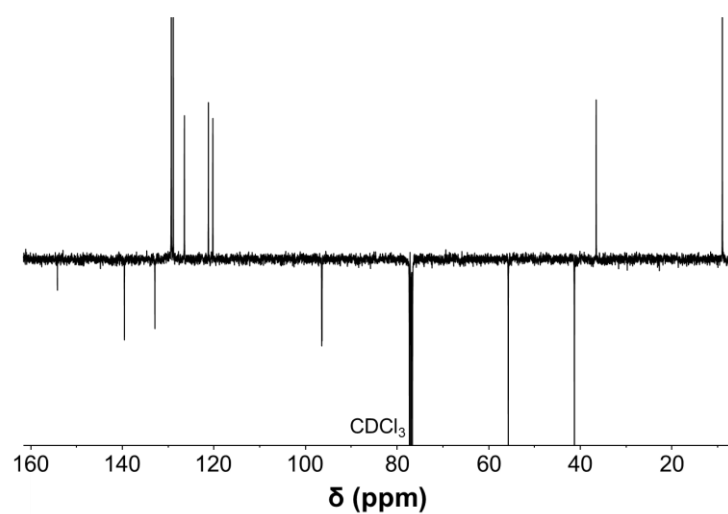
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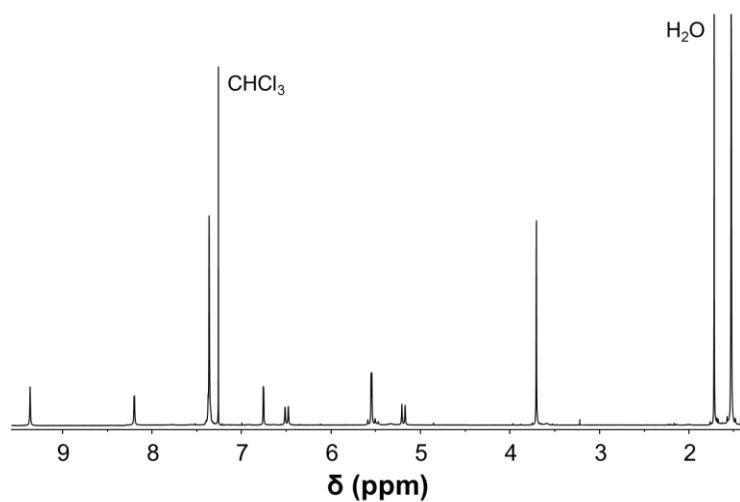
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**Figure S40.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] hexafluorophosphate **3b** recorded in  $\text{CDCl}_3$ .





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**Figure S41.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] chloride **3b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .

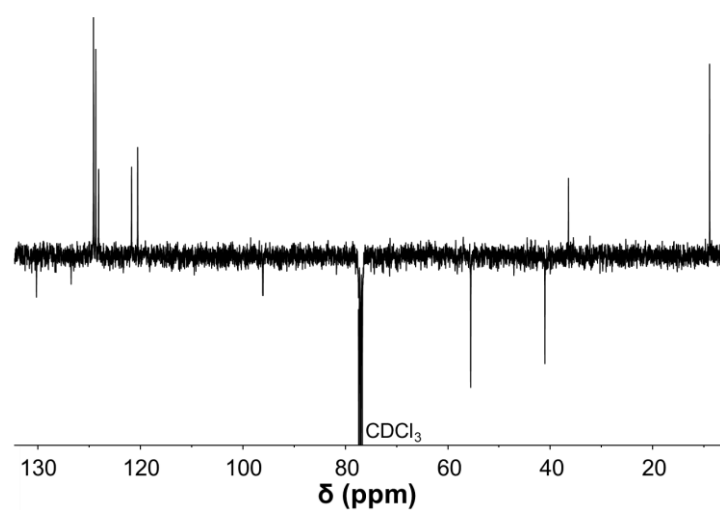
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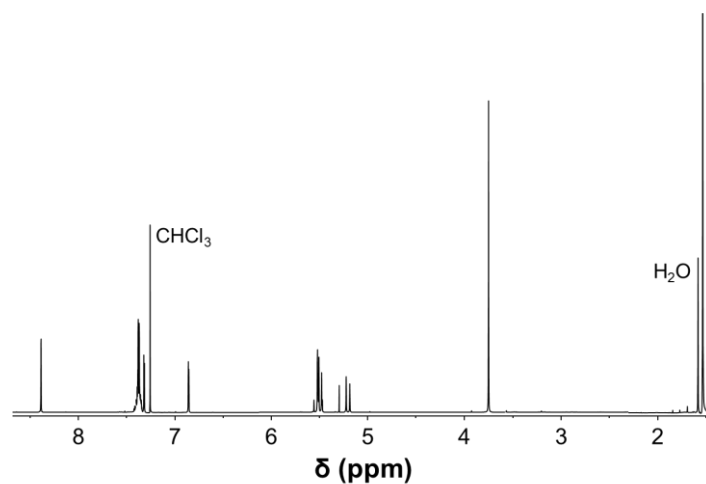
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**Figure S42.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] chloride **3b<sup>Cl</sup>** recorded in  $\text{CDCl}_3$ .



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**Figure S43.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] hexafluorophosphate **4b** recorded in  $\text{CDCl}_3$ .

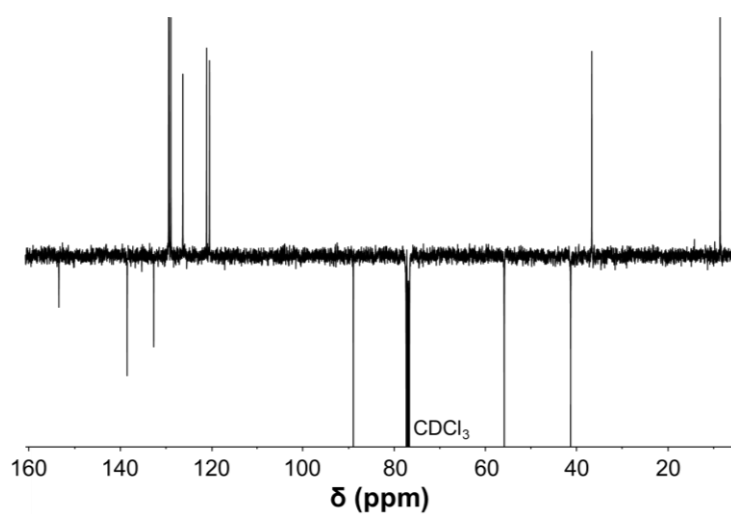
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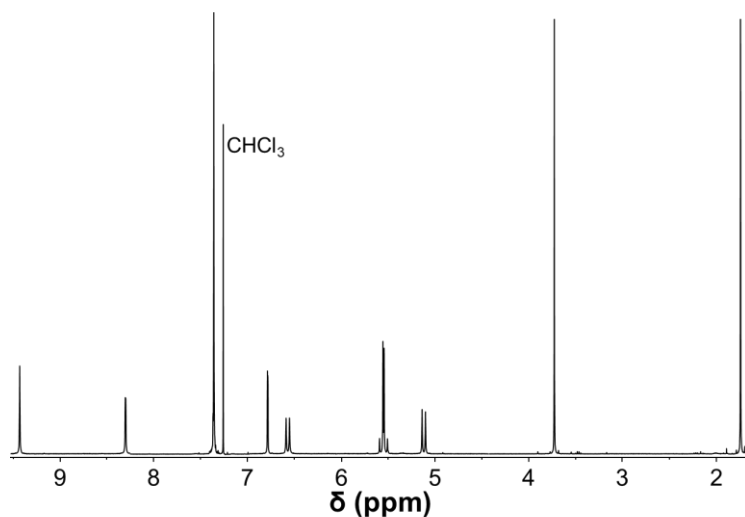
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**Figure S44.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] hexafluorophosphate **4b** recorded in  $\text{CDCl}_3$ .



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328 **Figure S45.**  $^1\text{H}$  NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-3-  
329 methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] chloride **4b<sup>Cl</sup>** recorded in  
330  $\text{CDCl}_3$ .

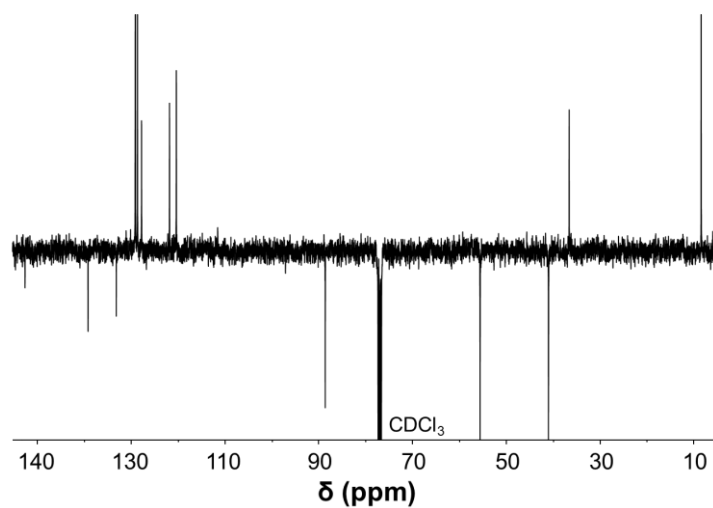
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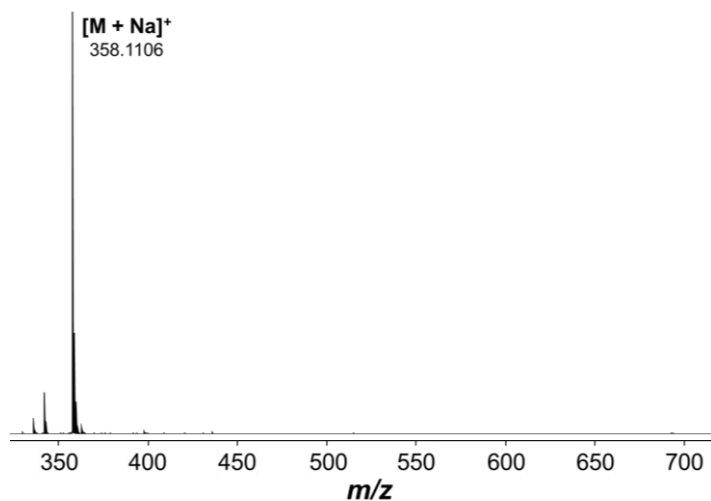
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337 **Figure S46.**  $^{13}\text{C}\{^1\text{H}\}$  DEPT-Q NMR spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa\text{N}$ )methyl]-  
338 3-methylimidazole-2-thione- $\kappa\text{S}$ }( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] chloride **4b<sup>Cl</sup>** recorded  
339 in  $\text{CDCl}_3$ .



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341 **Figure S47.** Electrospray ionization mass spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-  
342 methylbenzimidazole-2-thione **a**.

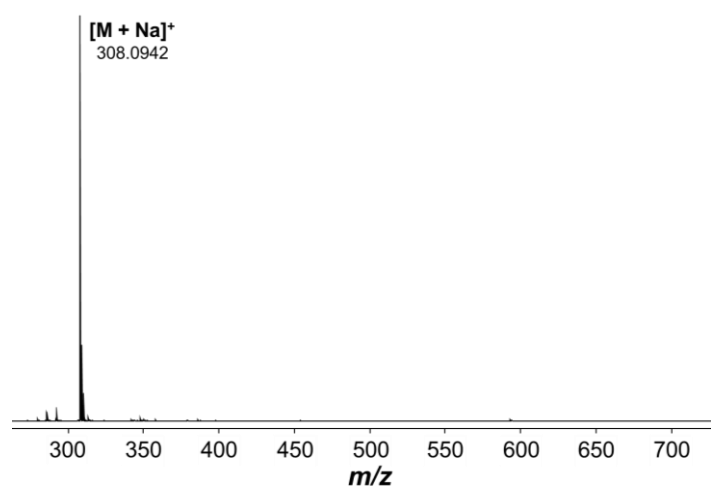
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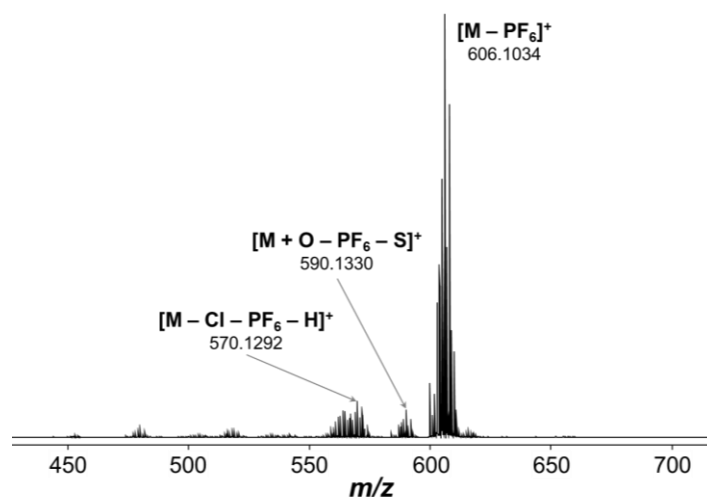
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349 **Figure S48.** Electrospray ionization mass spectrum of 1-[(1-benzyl-1,2,3-triazol-4-yl)methyl]-3-  
350 methylimidazole-2-thione **b**.

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**Figure S49.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1a**.

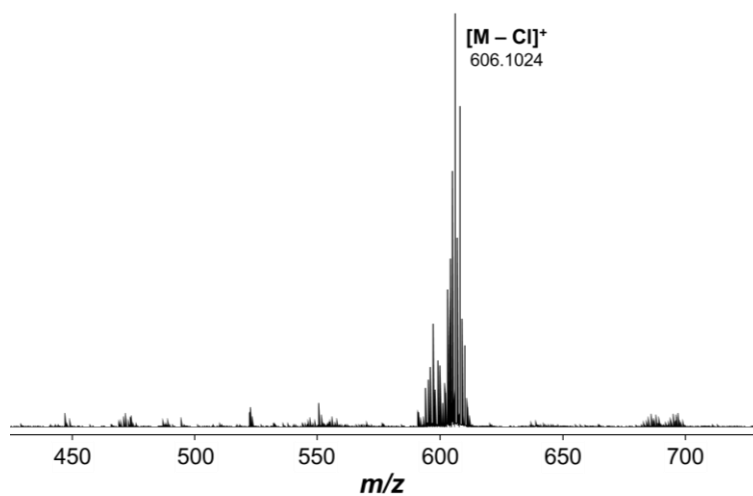
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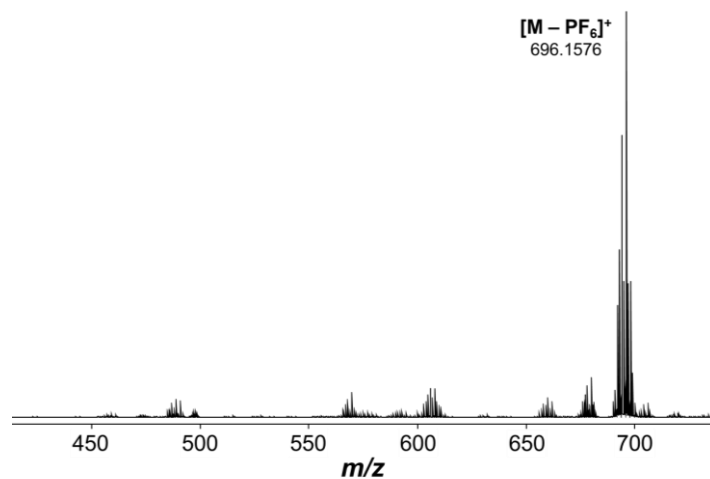
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**Figure S50.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)ruthenium(II)] chloride **1a<sup>Cl</sup>**.

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**Figure S51.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)osmium(II)] hexafluorophosphate **2a**.

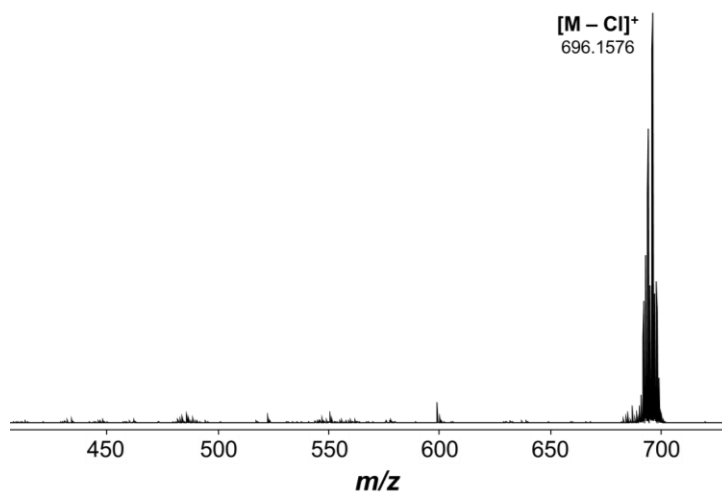
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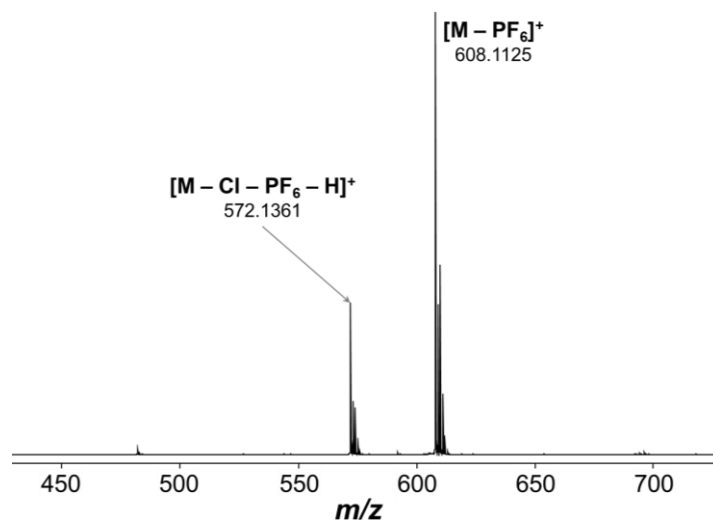
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**Figure S52.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2a<sup>Cl</sup>**.

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378 **Figure S53.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
379  $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)]  
380 hexafluorophosphate **3a**.

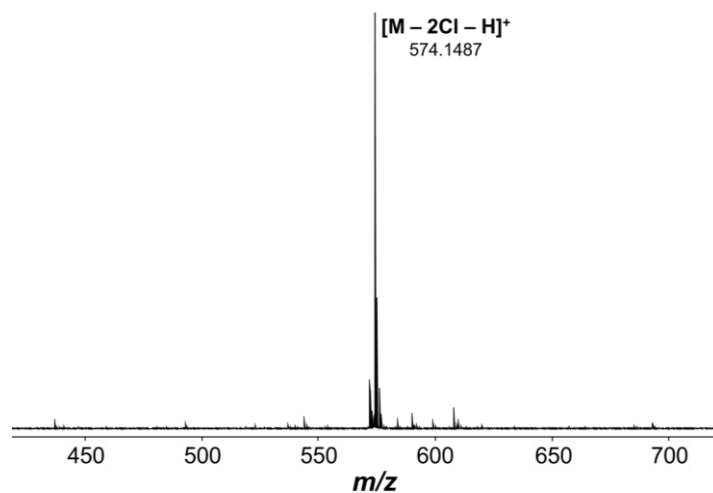
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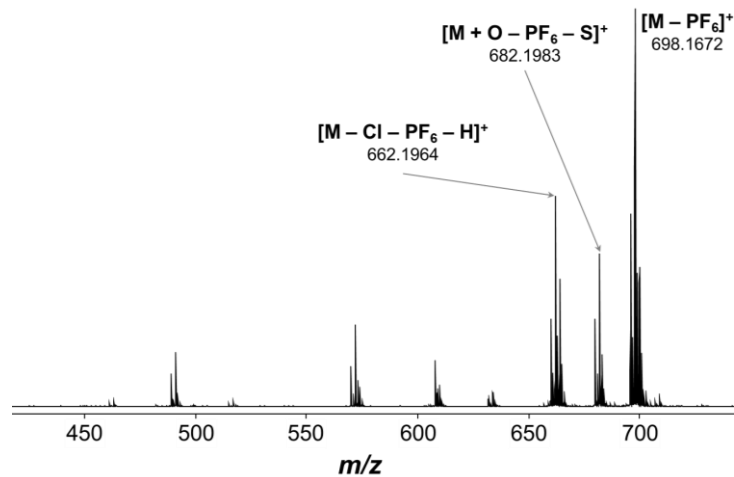
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387 **Figure S54.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
388  $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)]  
389 chloride **3a<sup>Cl</sup>**.



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391 **Figure S55.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
392  $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)]  
393 hexafluorophosphate **4a**.

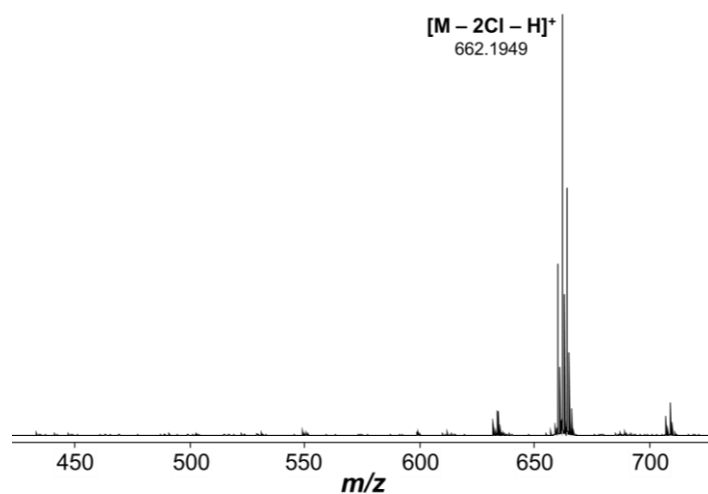
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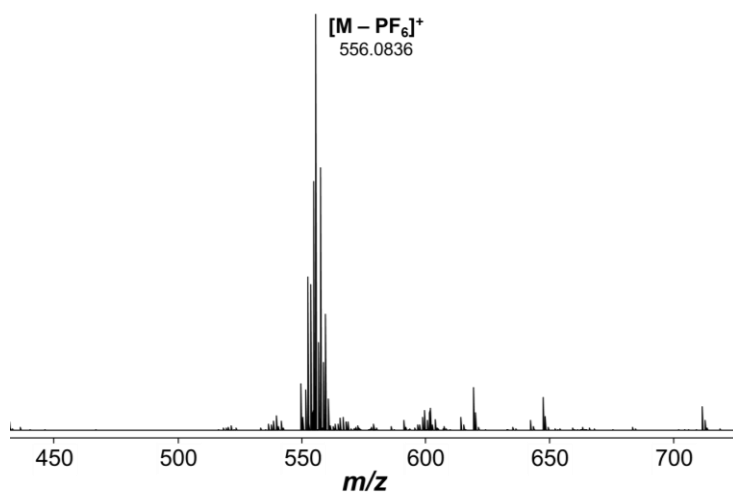
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400 **Figure S56.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
401  $\kappa$ N)methyl]-3-methylbenzimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)]  
402 chloride **4a<sup>Cl</sup>**.





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**Figure S57.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate **1b**.

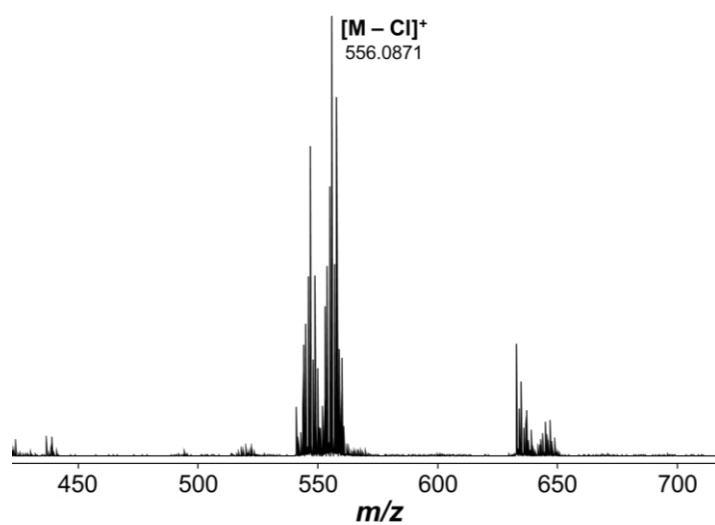
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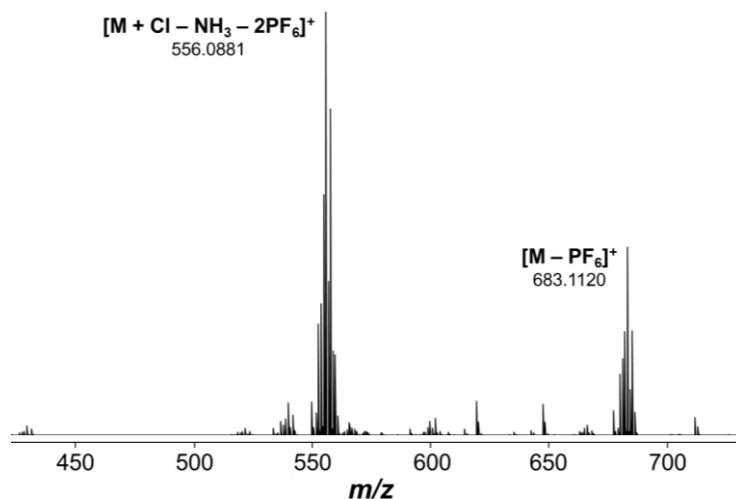
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**Figure S58.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)ruthenium(II)] chloride **1b<sup>Cl</sup>**.

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416 **Figure S59.** Electrospray ionization mass spectrum of [ammine{1-[(1-benzyl-1,2,3-triazol-4-yl-  
417  $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)ruthenium(II)] hexafluorophosphate  
418 **1b**<sup>NH<sub>3</sub></sup>.

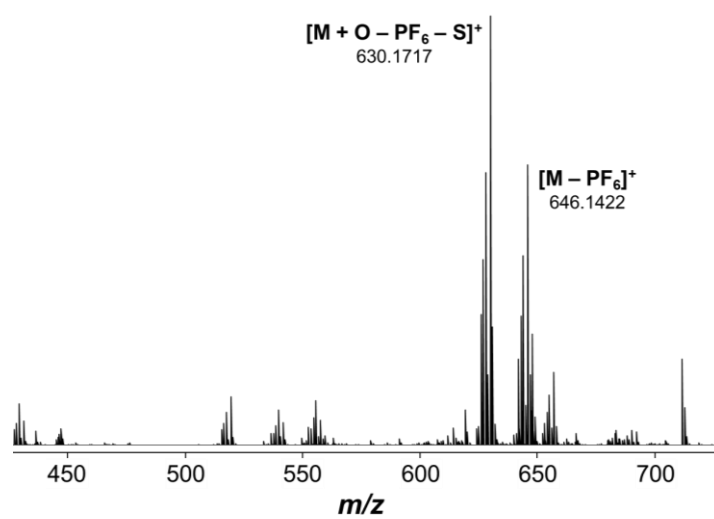
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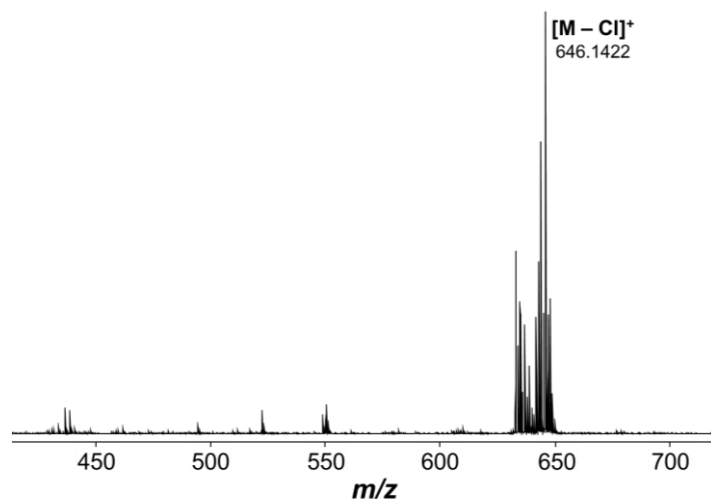
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425 **Figure S60.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
426  $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^6$ -*p*-cymene)osmium(II)] hexafluorophosphate **2b**.



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**Figure S61.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S)}( $\eta^6$ -*p*-cymene)osmium(II)] chloride **2b<sup>Cl</sup>**.

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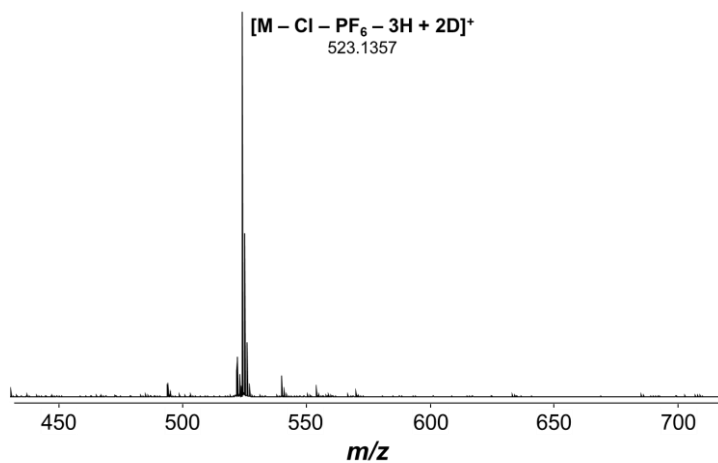
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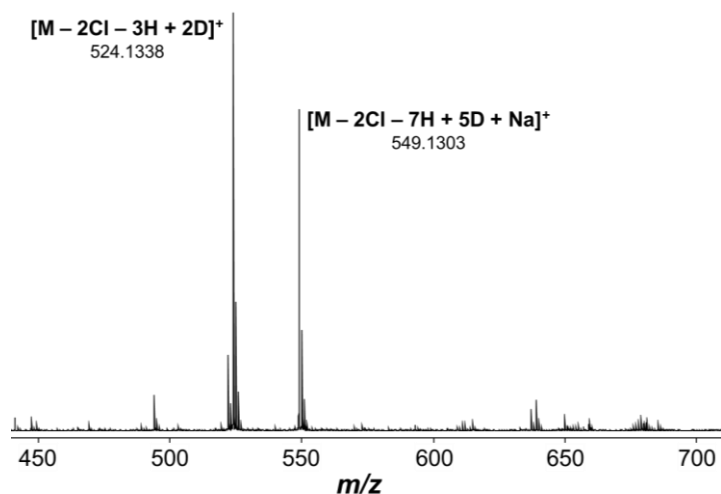
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**Figure S62.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S)}( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] hexafluorophosphate **3b**.



440

441 **Figure S63.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
442  $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)rhodium(III)] chloride  
443 **3b<sup>Cl</sup>**.

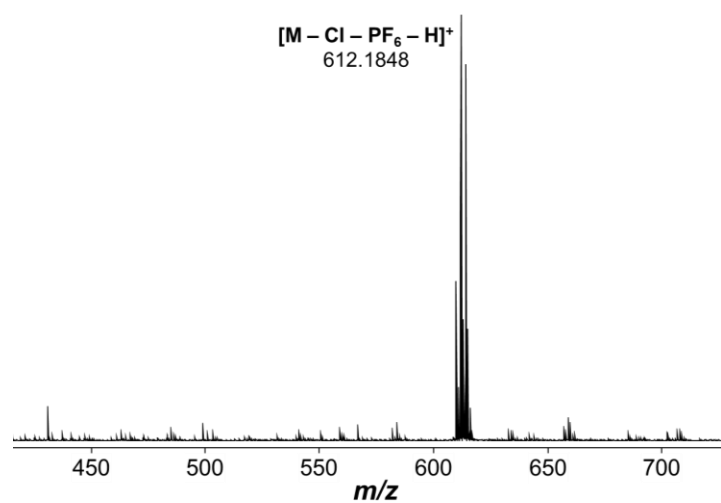
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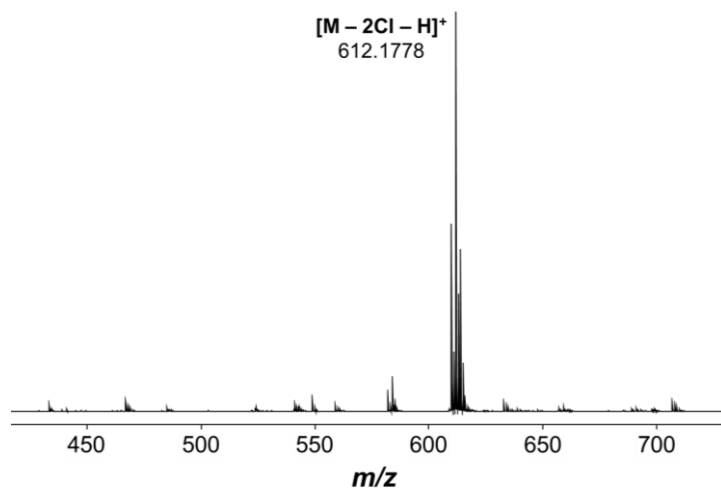
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449

450 **Figure S64.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl-  
451  $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)]  
452 hexafluorophosphate **4b**.



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**Figure S65.** Electrospray ionization mass spectrum of [chlorido{1-[(1-benzyl-1,2,3-triazol-4-yl- $\kappa$ N)methyl]-3-methylimidazole-2-thione- $\kappa$ S}( $\eta^5$ -pentamethylcyclopentadiene)iridium(III)] chloride **4b<sup>Cl</sup>**.

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