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High-Spin Enforcement in First-Row Metal Complexes of a Constrained Polyaromatic Ligand: Synthesis, Structure, and Properties

Lizhu Chen,[1] Hunter A. Dulaney,[1] Branford O. Wilkins,[2] Sarah Farmer,[1] Yanbing Zhang,[1] Frank R. Fronczek,[3] Jonah W. Jurss[1]*

[1]Department of Chemistry and Biochemistry, University of Mississippi, University, MS 38677, USA.
[2]Department of Chemistry, Texas A&M University, College Station, TX 77843, USA.
[3]Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803, USA.

e-mail: jwjurss@olemiss.edu

-Supplementary Information-

Contents of Supplementary Information

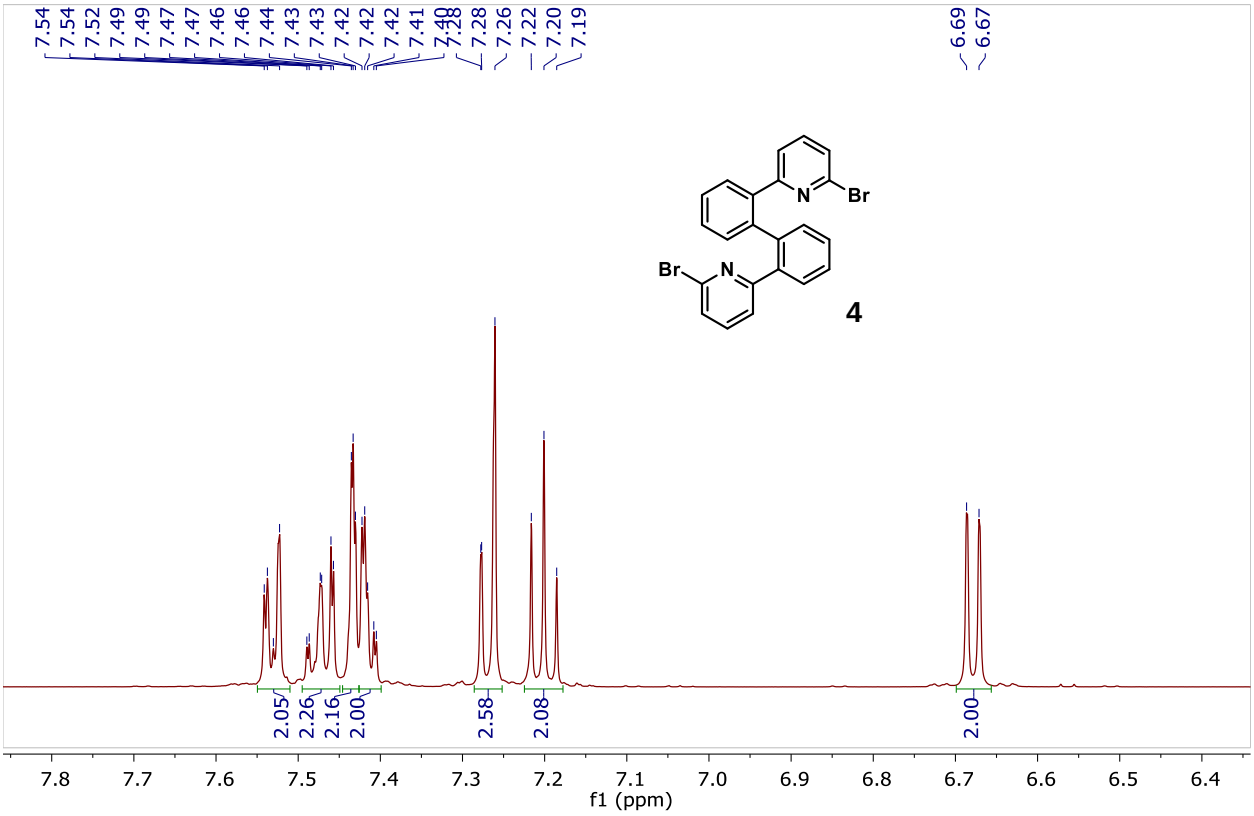

Figure S1. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **4**.

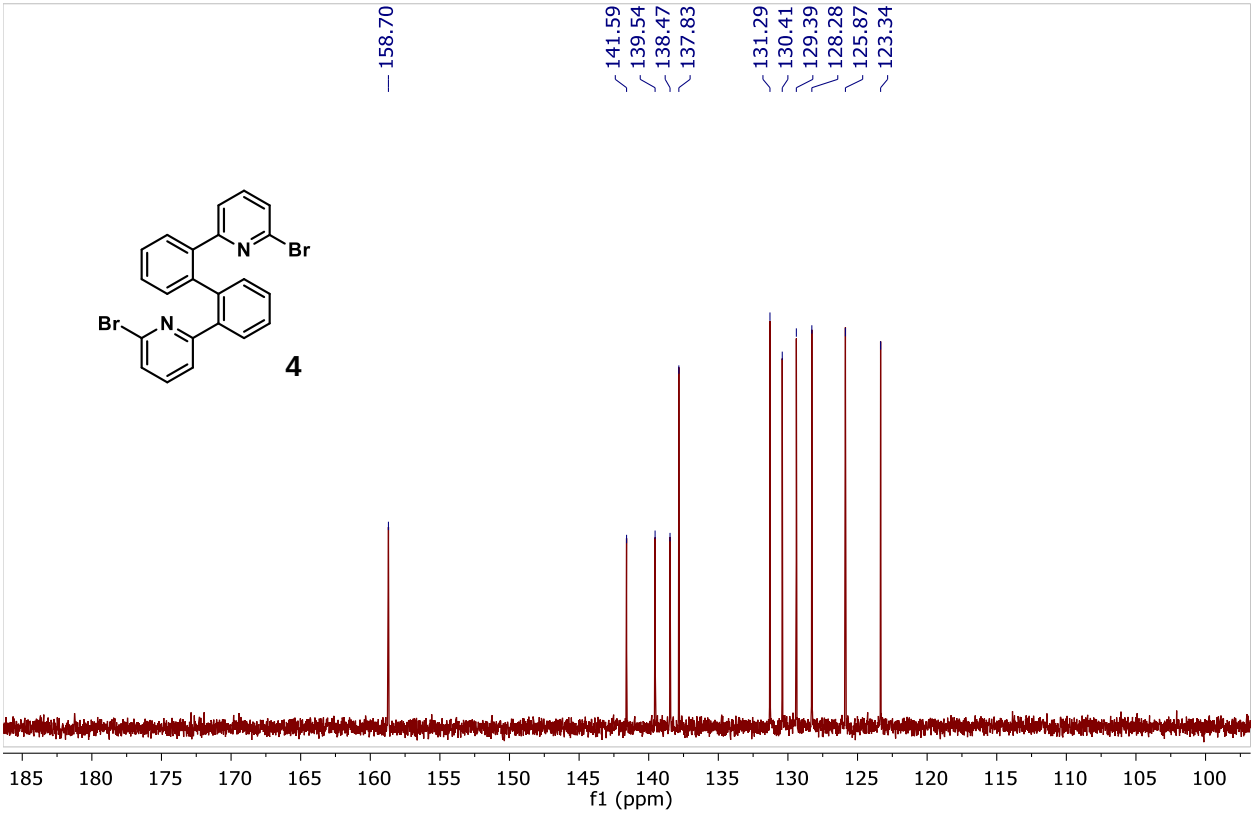

Figure S2. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **4**.

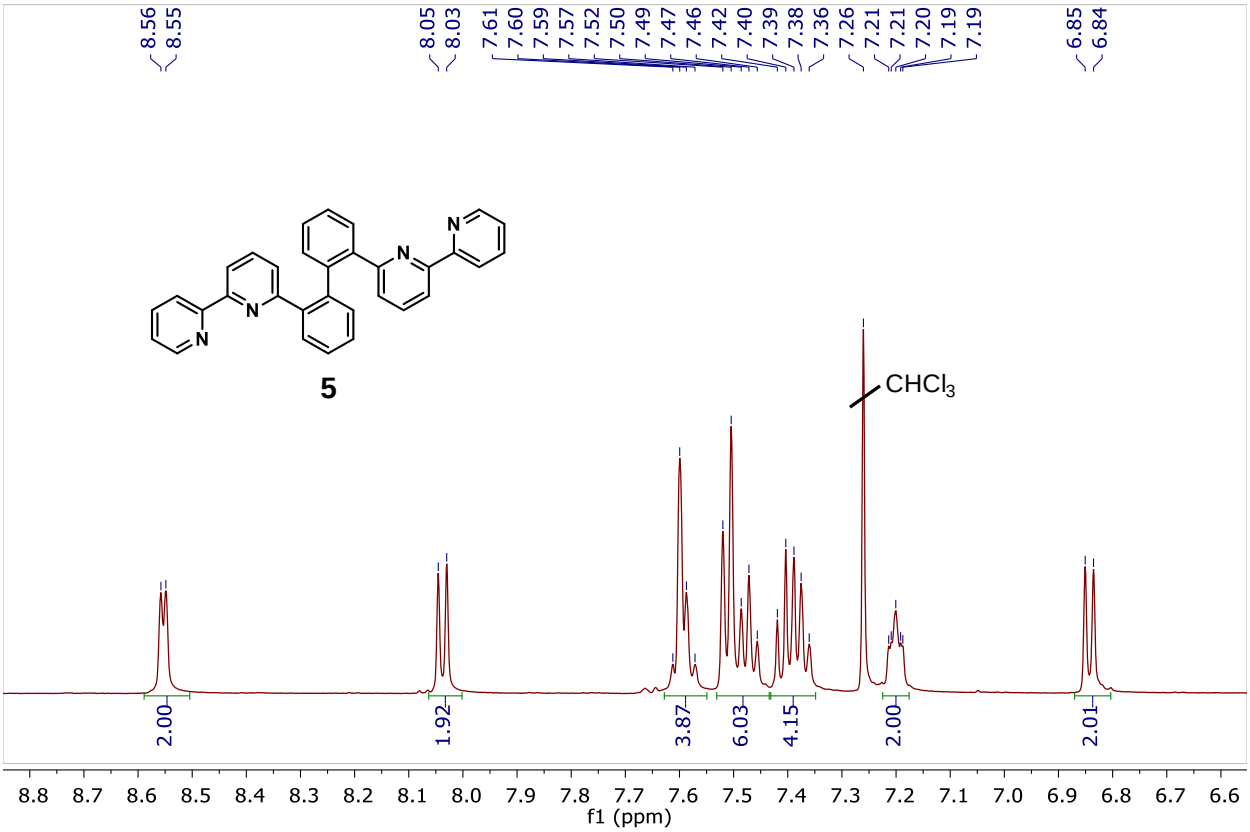

Figure S3. ^{1}H NMR spectrum (500 MHz, $CDCl_3$) of compound **5**.

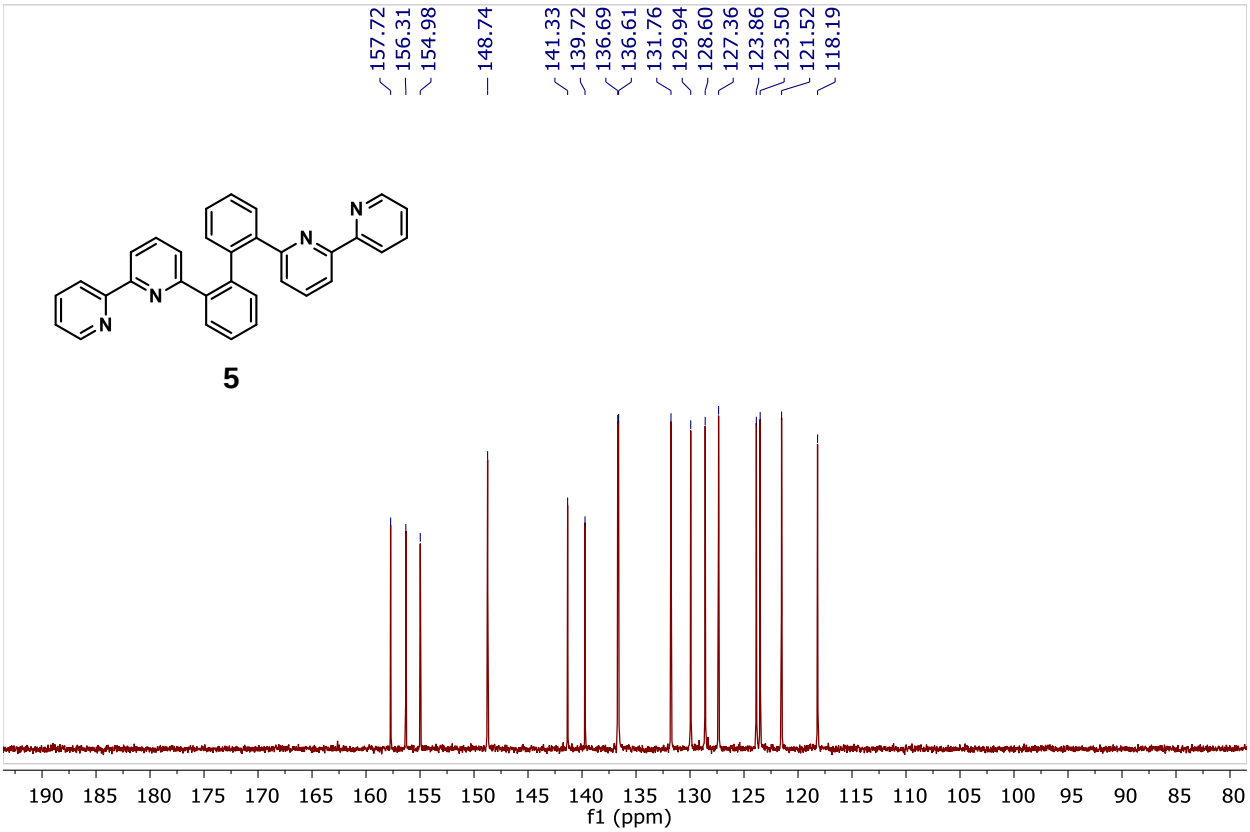

Figure S4. ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of compound **5**.

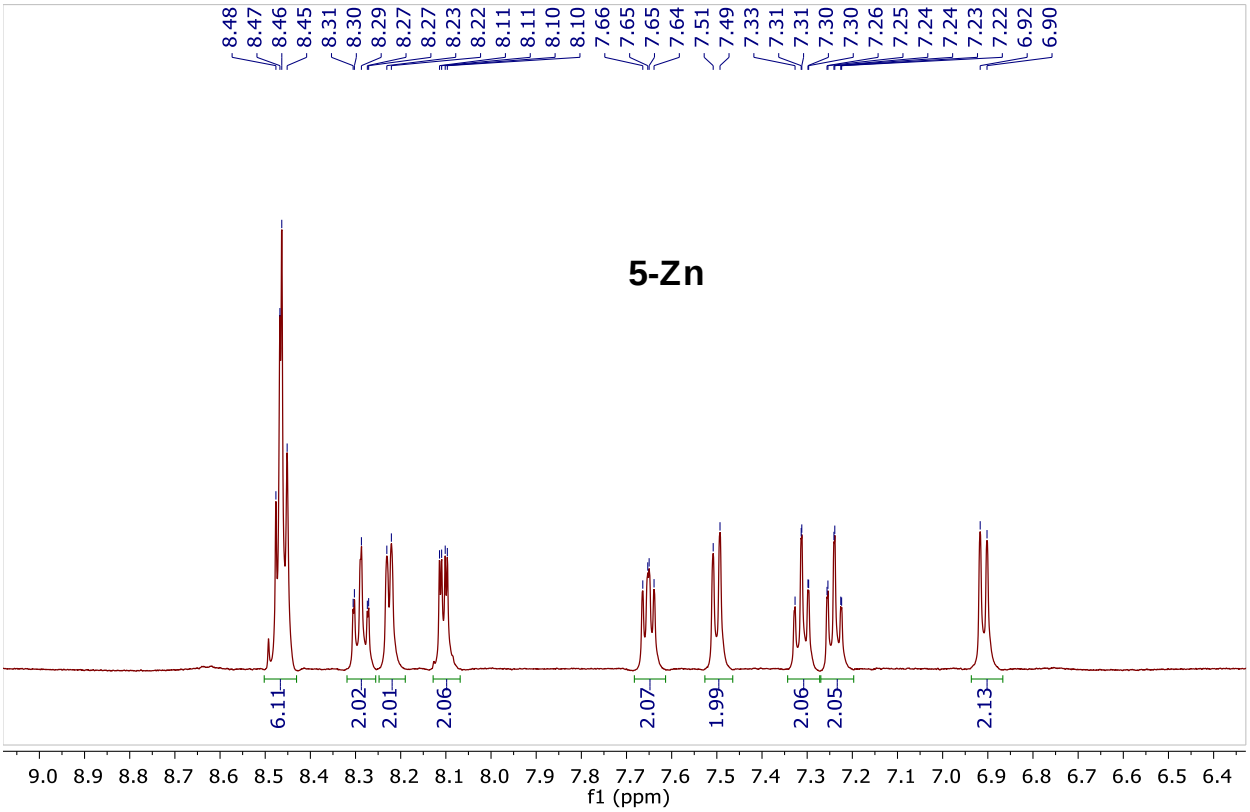

Figure S5. ^{1}H NMR spectrum (500 MHz, CD_3CN) of zinc complex **5-Zn**.

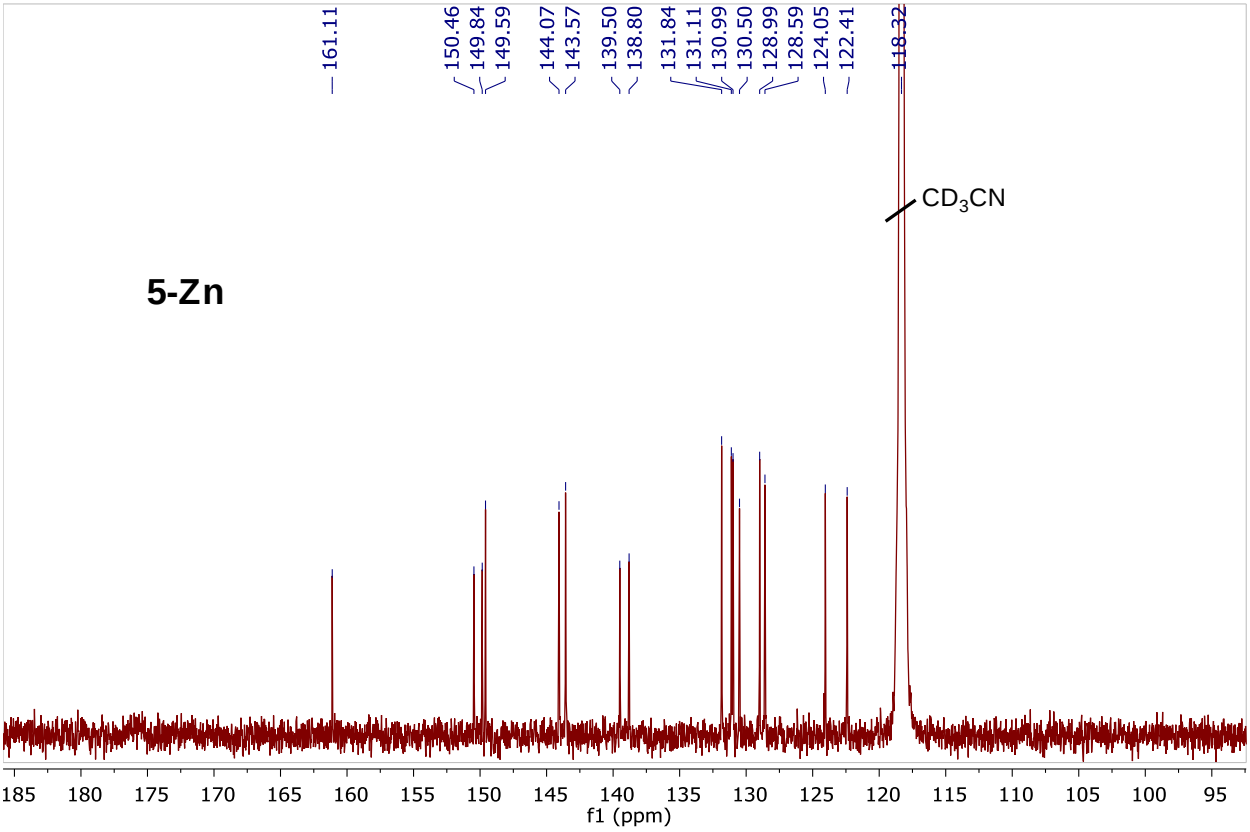

Figure S6. ^{13}C NMR spectrum (126 MHz, CD_3CN) of zinc complex **5-Zn**.

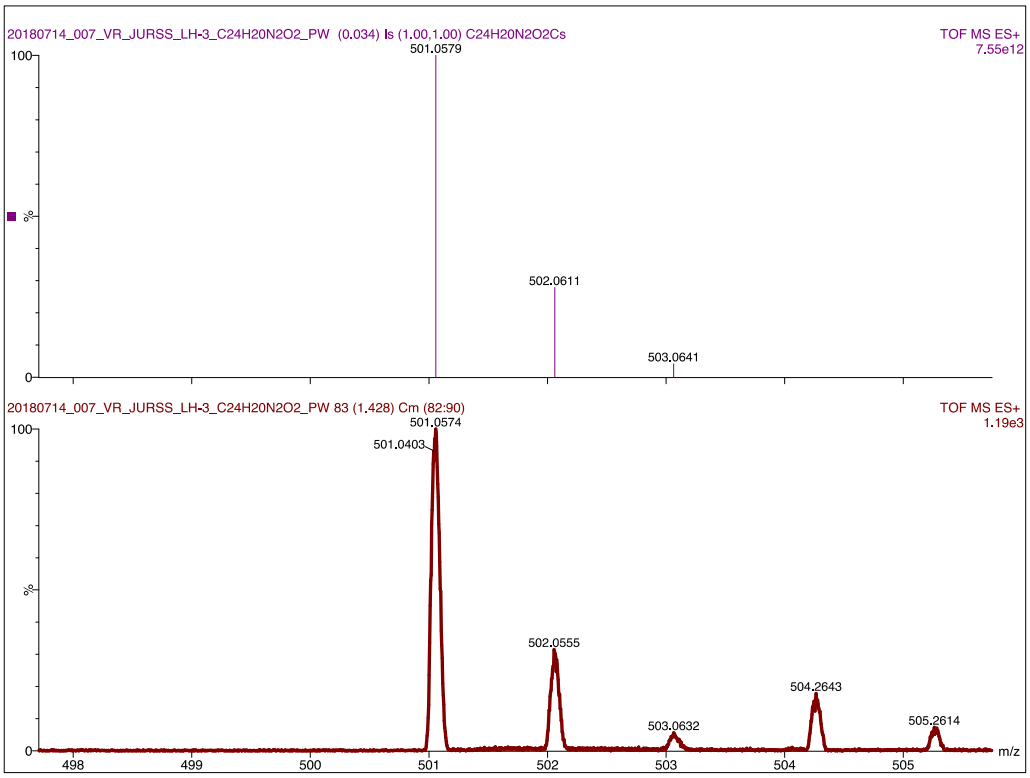

Figure S7. Theoretical and experimental high resolution mass spectra for compound **2**.

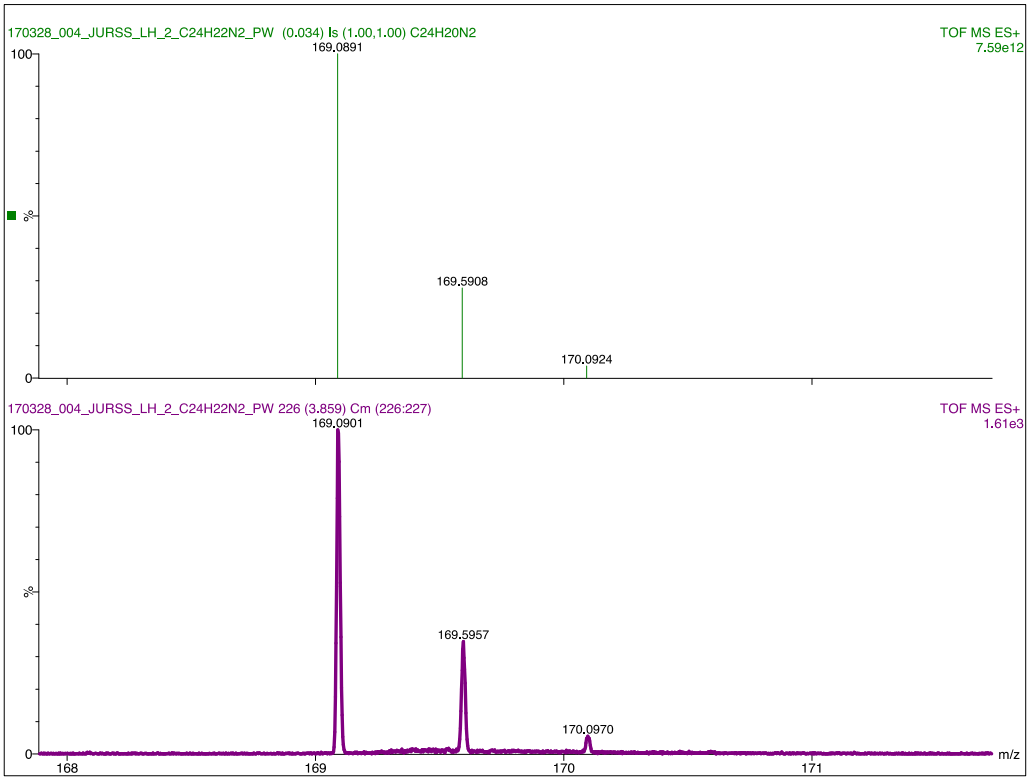

Figure S8. Theoretical and experimental high resolution mass spectra for compound **3**.

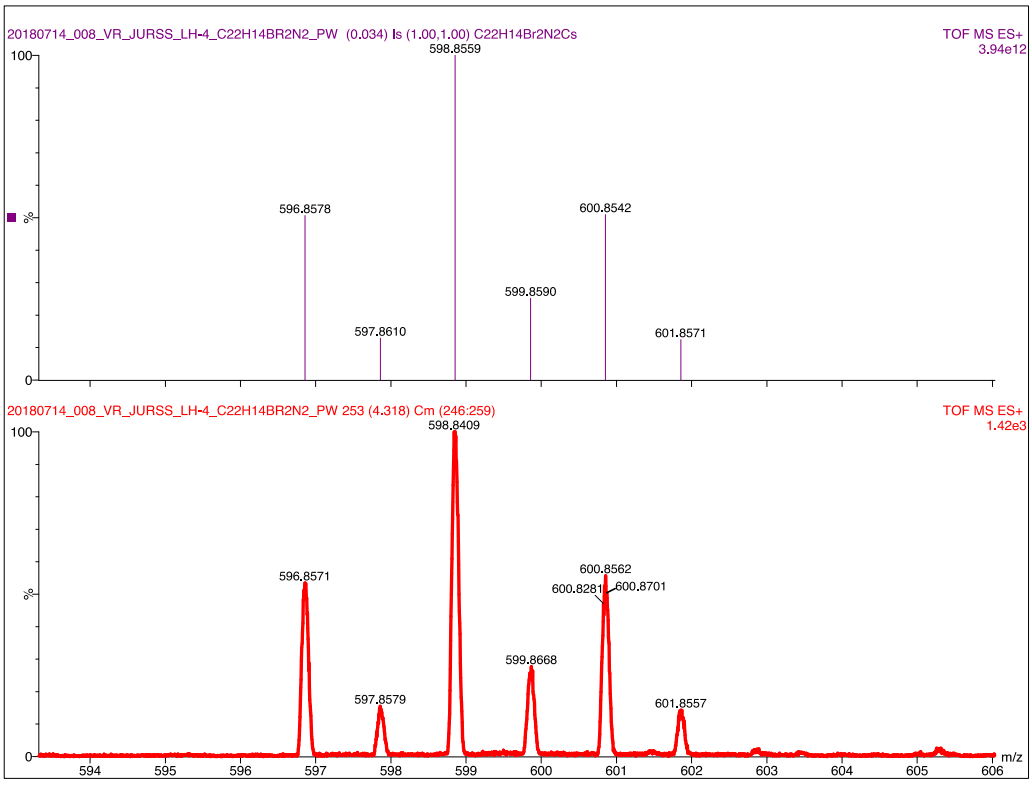

Figure S9. Theoretical and experimental high resolution mass spectra for compound **4**.

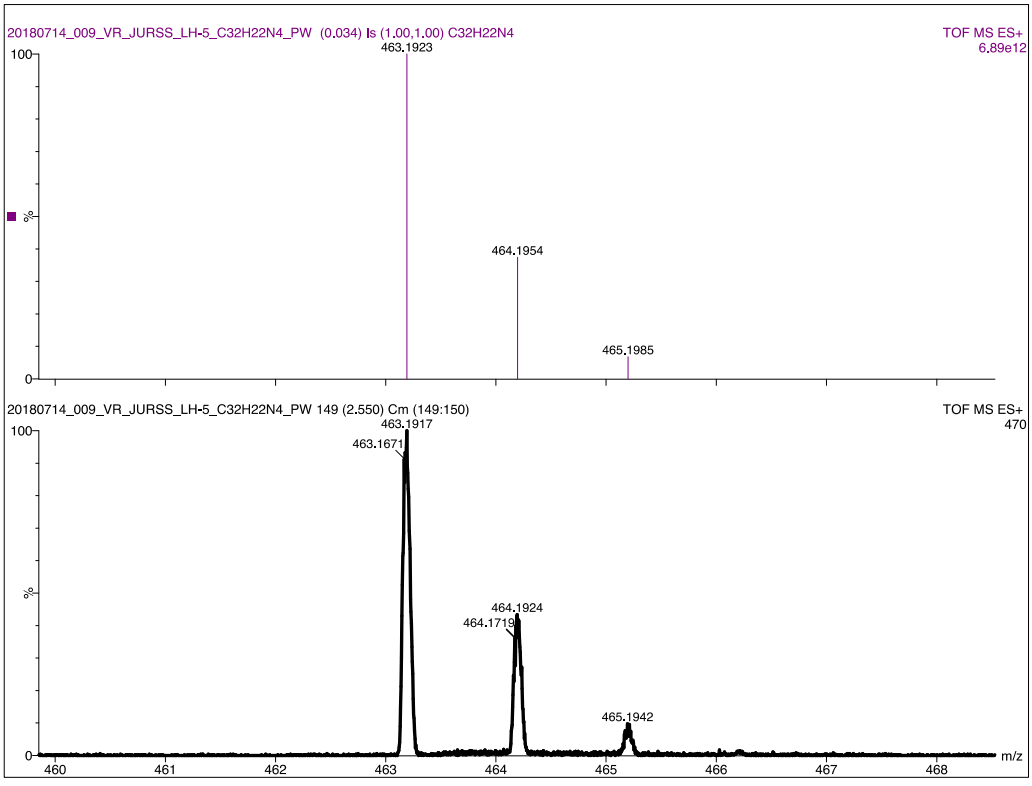

Figure S10. Theoretical and experimental high resolution mass spectra for compound **5**.

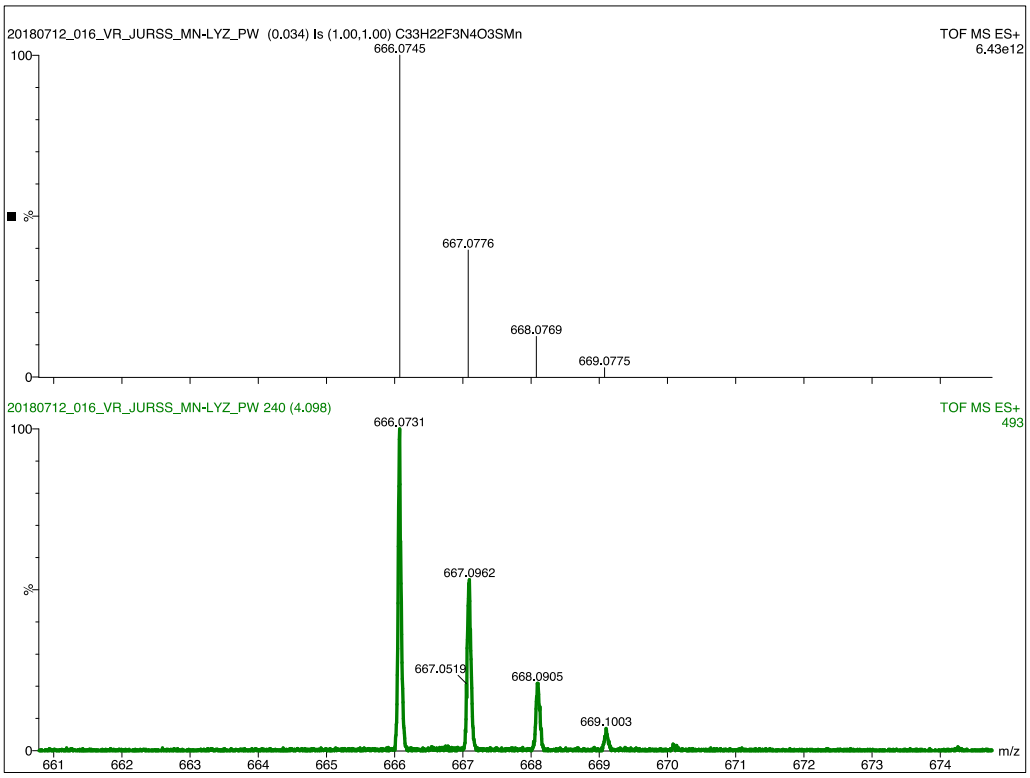

Figure S11. Theoretical and experimental high resolution mass spectra for $[Mn(bpbb)(OTf)]^+$.

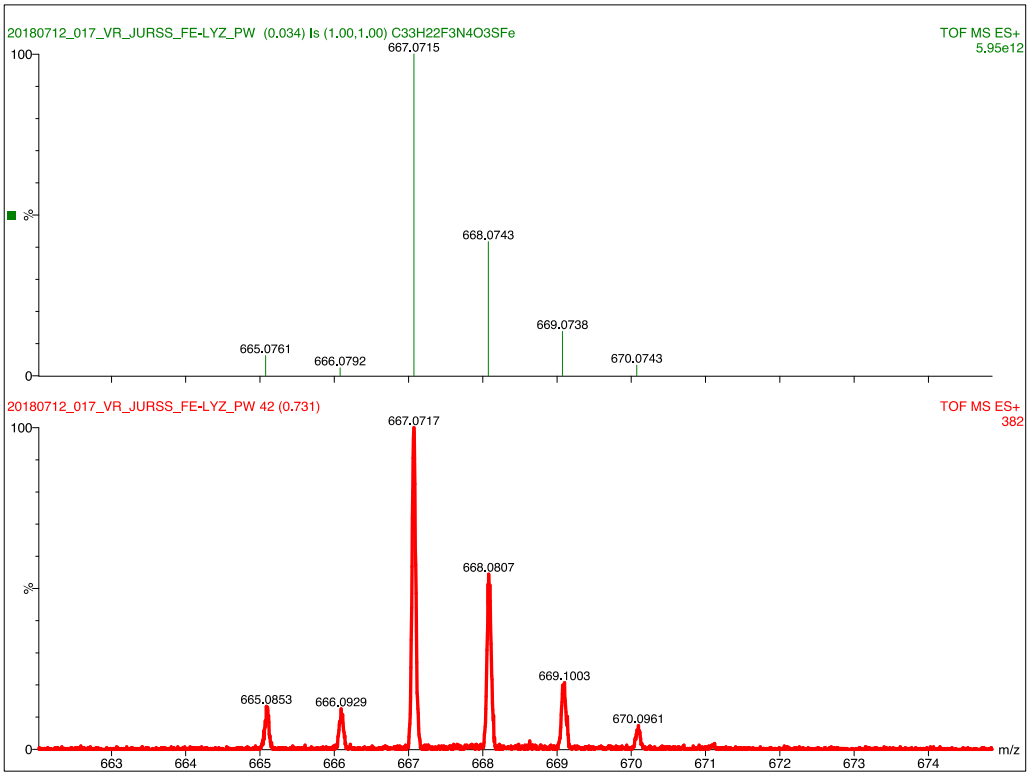

Figure S12. Theoretical and experimental high resolution mass spectra for $[Fe(bpbb)(OTf)]^+$.

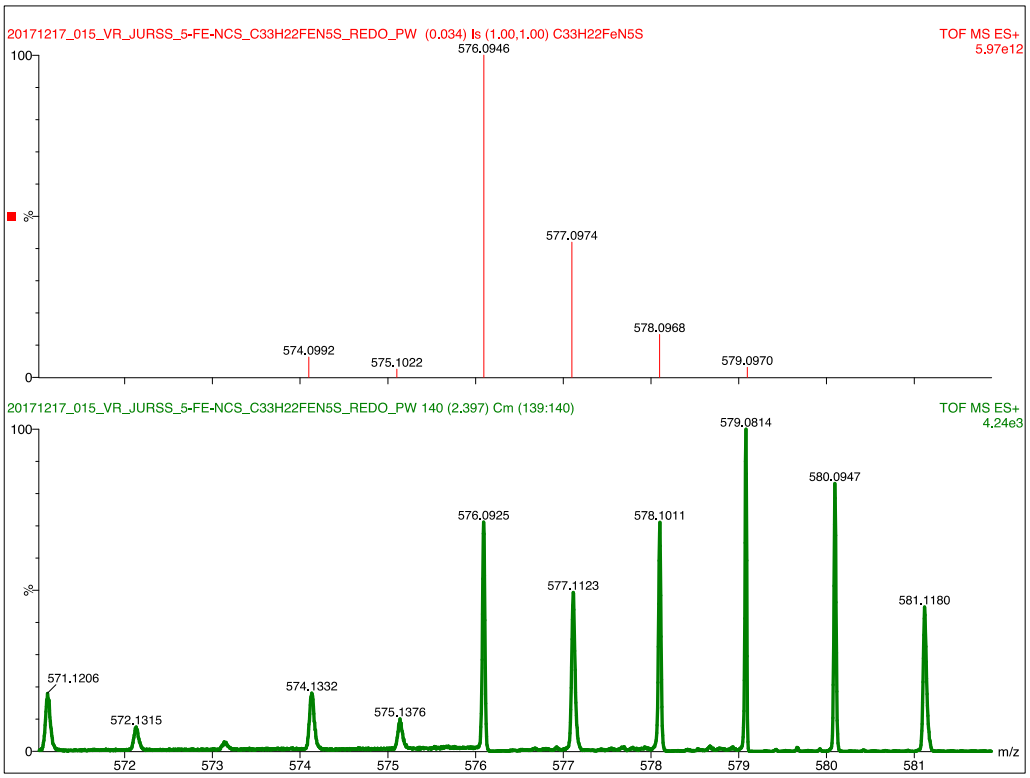

Figure S13. Theoretical and experimental high resolution mass spectra for $[Fe(bpbb)(NCS)]^{+}$.

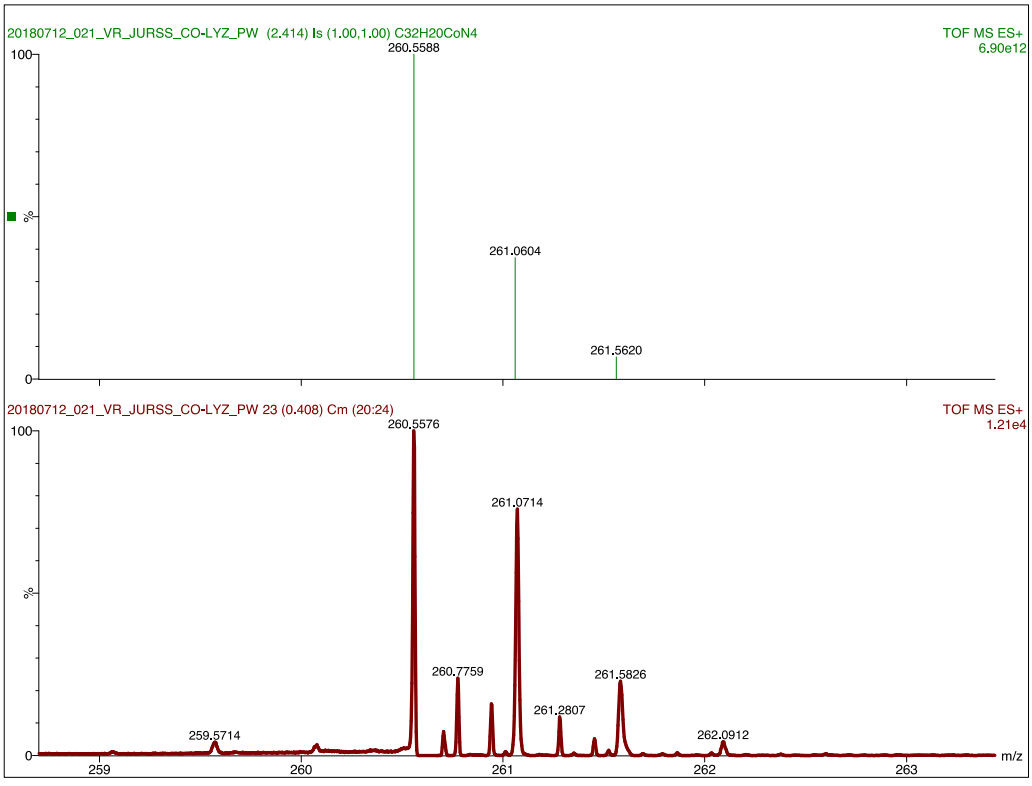

Figure S14. Theoretical and experimental high resolution mass spectra for $[Co(bpbb)]^{2+}$.

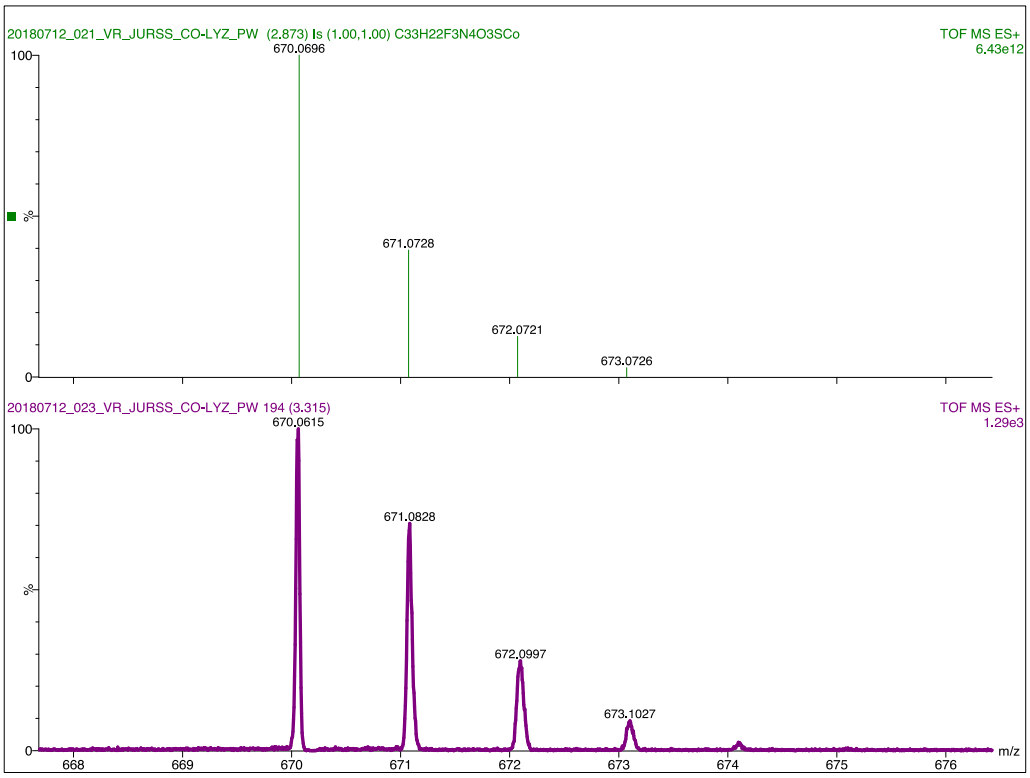

Figure S15. Theoretical and experimental high resolution mass spectra for $[Co(bpbb)(OTf)]^+$.

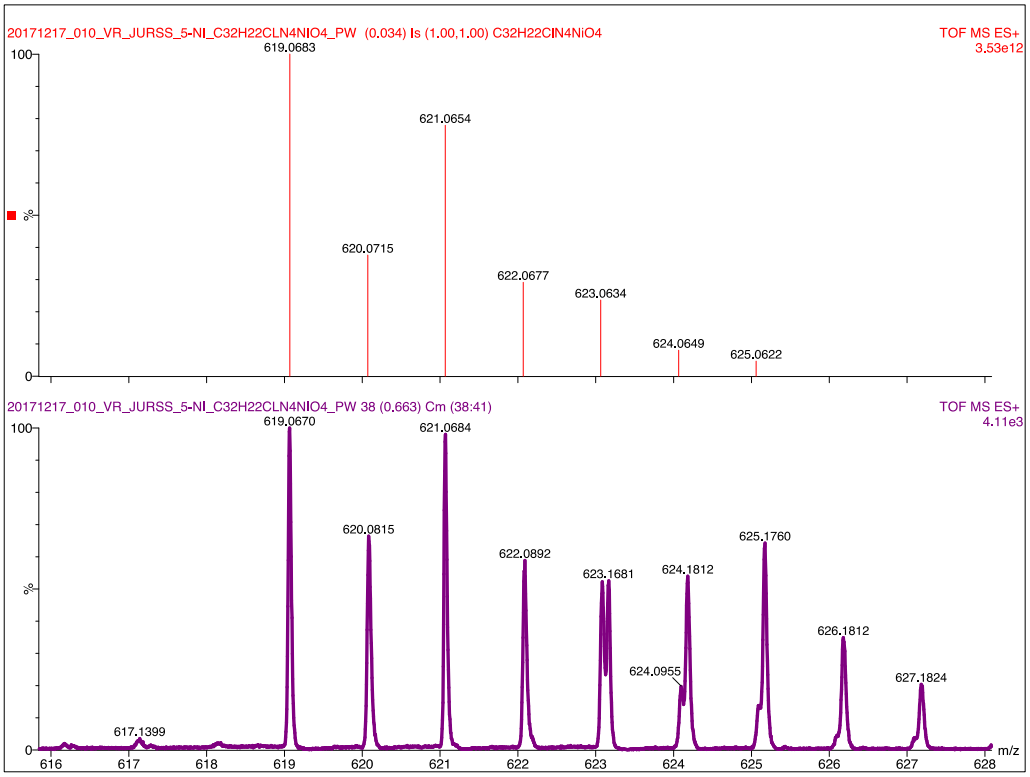

Figure S16. Theoretical and experimental high resolution mass spectra for $[Ni(bpbb)(ClO_4)]^+$.

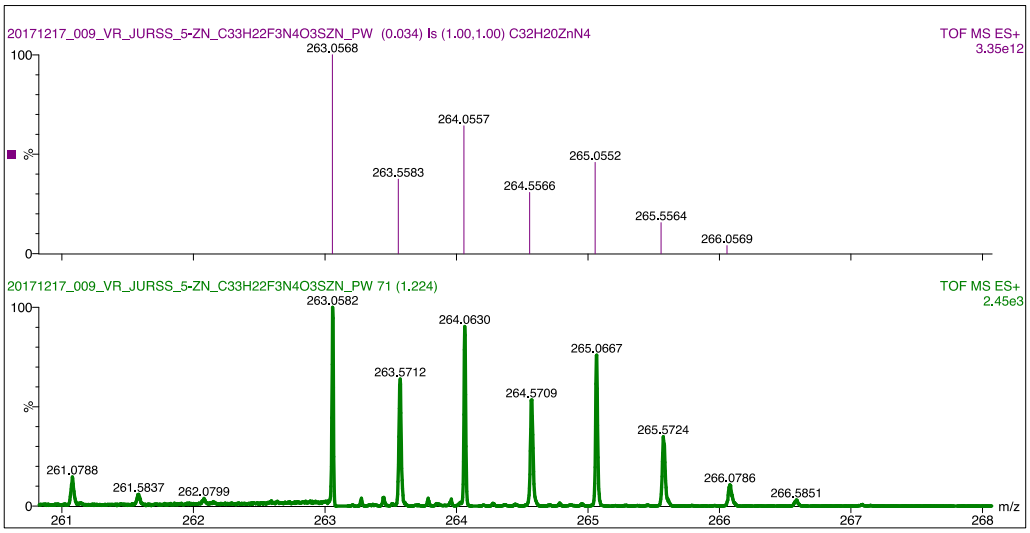

Figure S17. Theoretical and experimental high resolution mass spectra for $[Zn(bpbb)]^{2+}$.

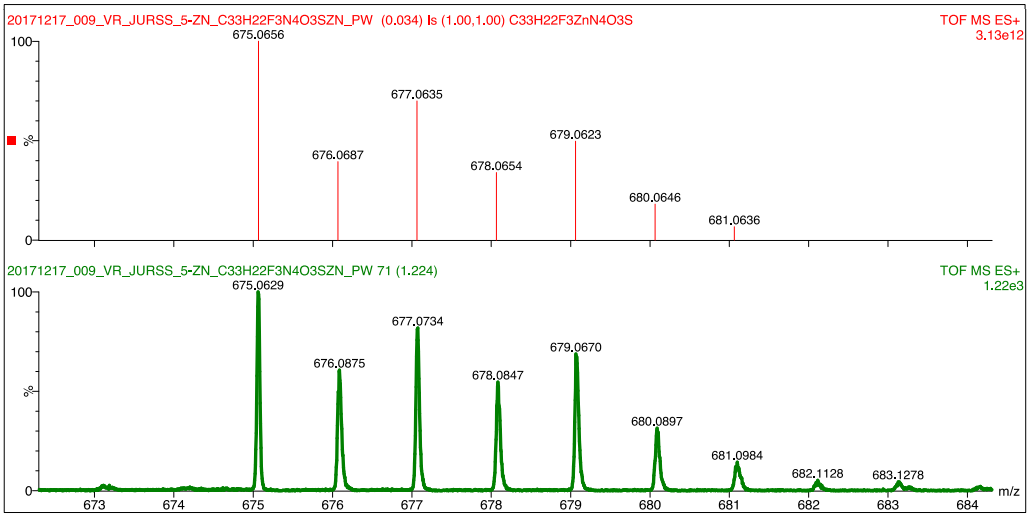

Figure S18. Theoretical and experimental high resolution mass spectra for $[Zn(bpbb)(OTf)]^{+}$.

Table S1. Selected Bond Distances of **5-Mn** and Related Manganese(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Mn(bpy)_2$ Complexes	**Mn-N**[a,b]	**Mn-N**[a,c]	**Mn-O**	**Mn-L**	**Avg Mn-N (bpy)**	**Ref.**	**CCDC Deposition #**
[Mn(bpbb)(OTf)(MeCN)](OTf)	2.238 **2.275**	**2.235** 2.238	2.200	2.227	2.247	*This work*	1837621
$[Mn(bpy)_2(OH_2)(tipba)](ClO_4)$[d]	2.252 2.290	2.265 2.242	2.186	2.126	2.262	1	765619
$[Mn(bpy)_2(OH_2)(sac)](sac)$[e]	2.253 2.249	2.273 2.259	2.127	2.229	2.259	2	131045
$[Mn(bpy)_2(OH_2)(N_3)](ClO_4)$	2.269 2.269	2.254 2.254	2.178	2.129	2.262	3	623967
$[Mn(bpy)_2(OH_2)(ONO_2)](NO_3)$	2.334 2.266	2.283 2.257	2.156	2.251	2.285	4	254464
$[Mn(bpy)_2(OH_2)Cl](ClO_4)$	2.235 2.292	2.260 2.268	2.167	2.447	2.264	5	1294032

a. Mn-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b*. Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c*. Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. *d*. tipba = 2,4,6-triisopropylbenzoate. *e*. sac = 1,2-benzisothiazol-3(2*H*)-onate 1,1-dioxide. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S2. Selected Bond Distances of **5-Fe** and Related Iron(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Fe(bpy)_2$ Complexes	**Fe-N**[a,b]	**Fe-N**[a,c]	**Fe-L**	**Fe-L**	**Avg Fe-N (bpy)**	**Ref.**	**CCDC Deposition #**
[Fe(bpbb)(OTf)(MeCN)](OTf)[d]	2.150 **2.208**	**2.197** 2.175	2.149	2.161	2.183	*This work*	1837622
$Fe(bpy)_2Cl_2$ (220 K)	2.180 2.180	2.159 2.159	2.409	2.409	2.170	6	248214
$Fe(bpy)_2(CN)_2$ (123 K)	1.992 2.000	1.957 1.959	1.912	1.901	1.977	7	1015599
$Fe(bpy)_2(NCS)_2$ (110 K)	1.964 1.964	1.969 1.969	1.945	1.945	1.967	8	1153555
$Fe(bpy)_2(NCS)_2$ (298 K)	2.181 2.181	2.166 2.166	2.053	2.053	2.174	8	1153557

a. Fe-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b*. Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c*. Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. *d*. Data collected at a temperature of 100 K. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S3. Selected Bond Distances of **5-Co** and Related Cobalt(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Co(bpy)_2$ Complexes	**Co-N**[a,b]	**Co-N**[a,c]	**Co-L**	**Co-L**	**Avg Co-N (bpy)**	**Ref.**	**CCDC Deposition #**
[Co(bpbb)(OTf)(MeCN)](OTf)	2.096 **2.171**	**2.157** 2.131	2.181	2.134	2.139	*This work*	1837623
$[Co(bpy)_2(O_2NO)](NO_3)$[d]	1.939 1.939	1.924 1.924	1.898	1.898	1.932	9	1568416
$Co(bpy)_2(OH_2)(O_2C\text{-}R\text{-}CO_2)$[e]	2.104 2.103	2.081 2.091	2.125	2.106	2.095	10	251573
$Co(bpy)_2Cl_2$	2.152 2.152	2.131 2.131	2.430	2.430	2.142	11	820066
$[Co(bpy)_2(OH_2)_2]^{2+}$ (complex anion)	2.058 2.065	2.064 2.059	2.047	2.093	2.062	12	654576

a. Co-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b.* Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c.* Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. *d*. Nitrato ligand is bidentate (κ^2). *e*. $O_2C\text{-}R\text{-}CO_2$ = benzene-1,4-dioxyacetate. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S4. Selected Bond Distances of **5-Ni** and Related Nickel(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Ni(bpy)_2$ Complexes	**Ni-N**[a,b]	**Ni-N**[a,c]	**Ni-O**	**Ni-L**	**Avg Ni-N (bpy)**	**Ref.**	**CCDC Deposition #**
$[Ni(bpbb)(ClO_4)(MeCN)](ClO_4)$	2.041 **2.134**	**2.137** 2.062	2.221	2.058	2.094	*This work*	1837624
$[Ni(bpy)_2(OH_2)(O_2C\text{-}R)](R\text{-}CO_2)$[d]	2.095 2.096	2.079 2.065	2.075	2.078	2.084	13	717183
$[Ni(bpy)_2(OH_2)(ONO_2)](NO_3)$	2.065 2.081	2.045 2.044	2.058	2.151	2.059	14	1524290
$[Ni(bpy)_2(OH_2)_2](CdBr_4)$	2.081 2.078	2.079 2.061	2.113	2.103	2.075	15	116631
$[Ni(bpy)_2(OH_2)_2](ClO_4)_2$	2.075 2.061	2.066 2.062	2.084	2.094	2.066	16	133580
$Ni(bpy)_2Cl_2$	2.101 2.101	2.080 2.080	2.413	2.413	2.091	17	1237075

a. Ni-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b.* Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c.* Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. *d*. $R\text{-}CO_2$ = 1*H*-indole-2-carboxylate. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S5. Selected Bond Distances of Previously Reported Copper Complex (**5-Cu′** in the main text) and Related Copper(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Cu(bpy)_2$ Complexes	**Cu-N**[a,b]	**Cu-N**[a,c]	**Cu-L**	**Cu-Cl**	**Avg Cu-N (bpy)**	**Ref.**	**CCDC Deposition #**
$[Cu(bpbb)Cl](ClO_4)$	2.061 **2.204**	**2.037** 1.981	-	2.305	2.071	18	1162810
$[Cu(bpy)_2Cl](R\text{-}SO_3)$	2.104 2.110	1.978 1.990	-	2.280	2.046	19	749881
$[Cu(bpy)_2Cl](ClO_4)$	2.127 2.067	1.985 1.981	-	2.260	2.040	20	926638
$[Cu(bpy)_2Cl](BF_4)$	2.079 2.142	2.006 1.982	-	2.285	2.052	21	1259100

a. Cu-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b.* Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c.* Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S6. Selected Bond Distances of **5-Zn** and Related Zinc(II) Compounds Containing Two Unsubstituted 2,2'-Bipyridine (bpy) Ligands.

$Zn(bpy)_2$ Complexes	**Zn-N**[a,b]	**Zn-N**[a,c]	**Zn-O**	**Zn-L**	**Avg Zn-N (bpy)**	**Ref.**	**CCDC Deposition #**
$[Zn(bpbb)(OTf)](OTf)$	2.061 **2.085**	**2.112** 2.092	2.231	-	2.088	*This work*	1837625
$[Zn(bpy)_2Cl](BF_4)$	2.124 2.072	1.984 1.985	-	2.255	2.041	22	271110
$[Zn(bpy)_2(OH_2)](ClO_4)_2$	2.069 2.077	2.090 2.079	2.029	-	2.079	23	702343

a. Zn-N bond distances that are side-by-side in adjacent columns indicate that these nitrogen donors are from the same bipyridine (or bipyridine unit in the case of bpbb). *b.* Bipyridine-based nitrogen donor *trans* to a monodentate ligand. *c.* Bipyridine-based nitrogen donor *trans* to another bipyridine-based nitrogen donor. Bold bond distances correspond to the pyridine donors that are closest to the biphenyl backbone.

Table S7. Electrochemical data for selected *bis*(2,2'-bipyridine) and *tris*(2,2'-bipyridine) complexes of Mn, Fe, Co, Ni, Cu, and Zn.[a]

$M(bpy)_n$ Complex	**Redox Potentials (V vs $Fc^{+/0}$)**				**Reference** (Conditions)
	***E*$_1$**	***E*$_2$**	***E*$_3$**	***E*$_4$**	
5-Mn	0.67	-1.71	-2.30	-	*This work*
$[Mn(bpy)_3]^{2+}$	0.93	-1.74	-1.92	-2.13	25 (*b*)
5-Fe	0.95	-1.53	-2.30	-	*This work*
$[Fe(bpy)_3]^{2+}$	0.69	-1.72	-1.91	-2.16	26 (*c*)
$[Fe(bpy)_2(MeCN)_2]^{2+}$	1.02	-1.47	-	-	27 (*b*)
5-Co	0.74	-1.03	-1.69	-1.96	*This work*
$[Co(bpy)_3]^{2+}$	-0.04	-1.33	-1.95 ($2e^-$)	-	25 (*b*)
$[Co(bpy)_2(\kappa^2\text{-}O_2NO)]^+$	-	-1.20	-1.78	-	9 (*b*)
$Co(bpy)_2Cl_2$	-0.07	-1.26	-1.46	*ca.* -1.84	28 (*d*)
5-Ni	-	-1.03	-1.57	-2.38	*This work*
$[Ni(bpy)_3]^{2+}$	1.08	-1.93 ($2e^-$)	-	-	29, 30 (*b*)
$Ni(bpy)_2Br_2$	0.43	-0.08	-1.90	-2.66	31 (*e*)
5-Cu (ref. 18)	0.09	-0.71	-2.07	-2.26	*This work*
$[Cu(bpy)_3]^{2+}$	-0.49	-	-	-	32 (*c*)
$[Cu(bpy)_2Br]^+$	-0.62	-1.26	-	-	33 (*c*)
5-Zn	-	-1.47	-1.58	-2.17	*This work*
$[Zn(bpy)_3]^{2+}$	>1.92	-1.75 ($2e^-$)	-2.23	-	25 (*b*)

a. Reported potentials were converted to the ferrocenium/ferrocene ($Fc^{+/0}$) couple when necessary using conversions provided in the source reference or in reference 24; *b*. MeCN / 0.1 M R_4NClO_4 (where R is ethyl or *n*-butyl); *c*. MeCN / 0.1 M Bu_4NPF_6; *d*. 4:1 MeCN:H_2O / 0.1 M Bu_4NClO_4; *e*. DMF / 0.1 M Bu_4NBF_4.

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