Electronic Supplementary Material (ESI) for Dalton Transactions.

Synthesis and transition metal coordination chemistry of a novel hexadentate bispidine ligand

Peter Comba, Henning Rudolf and Hubert Wadepohl*

Universität Heidelberg, Anorganisch-Chemisches Institut, INF 270,

D-69120 Heidelberg, Germany

Electronic Supporting Information

Correspondence:

e-mail: peter.comba@aci.uni-heidelberg.de

Fax: +49-6221-546617

Table S1. Redox potentials of copper-bispidine complexes used for the correlation of with Cu^{II} complex stabilities in Figure S1 (references refer to the main text). [4, 28-30, 32]

Ligand [a]	$E(Cu^{I/II})$ [mV] (MeCN vs. Fc)	log*K*(Cu^{II})
L^1	-598	16.56(5)
Me_2-L^1	-270	9.60(7)
L^2	-776	18.31(12)
$L^{2'}$	-661	15.66(3)
L^3	-745	16.28(10)
L	-651	*16.0*
$\mathbf{L^{OH}}$	-671	*16.3*

[a] abbreviations: see Figure S1 and Chart 1 in the manuscript

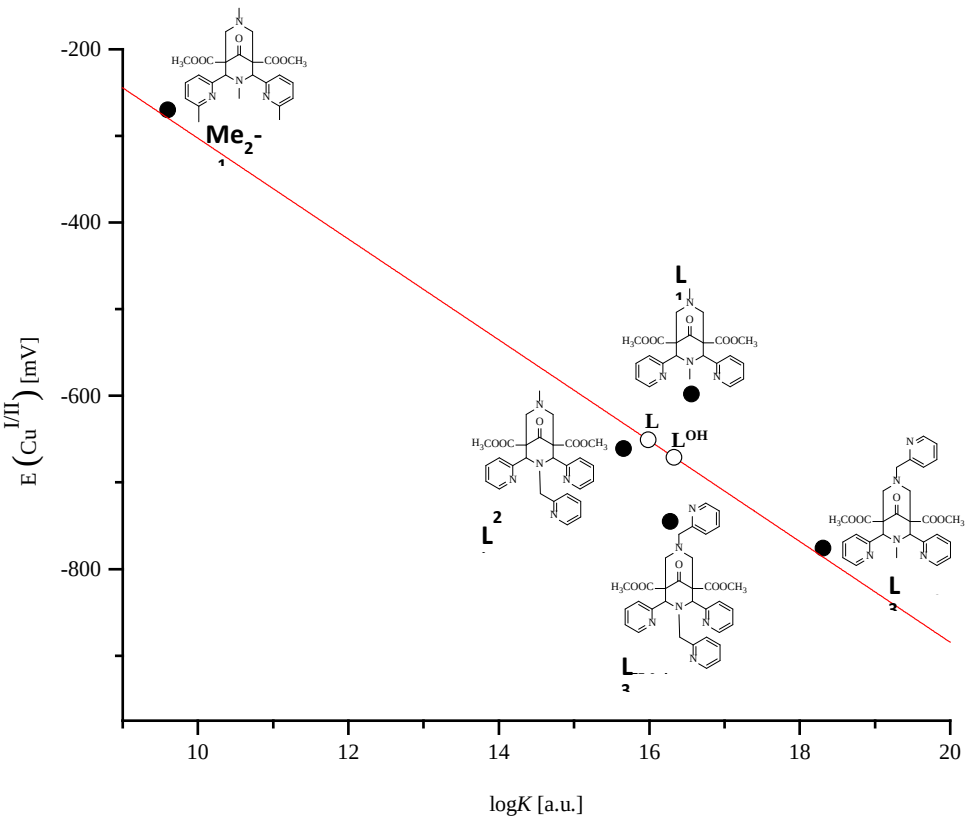

Figure S1. Plot of the redox potentials as a function of the Cu^{II} complex stability for the determination of the stability constants of ligands L and L^{OH} (data from Table S1). [4, 28-30, 32]

Table S2. Structural analysis of the manganese complex (see Table 5 and Figure 4); best plane for the pentagonal bipyramidal structure (distances in Å):

molecule	1	2
RMSD (plane)	0.376	0.378
distance from plane		
N3	0.572(1)	0.574(1)
py1	-0.492(1)	-0.354(1)
py2	-0.347(1)	-0.470(1)
py3	0.060(1)	0.054(1)
py4	0.186(1)	0.194(1)

Table S3. Details of the crystal structure determinations of $[Cu^{II}(L)]^{2+}$, $[Cu^{II}(L^{OH})]^{2+}$, $[Fe^{II}(L)OHMe]^{2+}$, $[Fe^{III}(L)OMe]^{2+}$, $[Fe^{II}(L^{OH})Cl]^{+}$, and $[Mn^{II}(L)Cl]^{+}$

	$[Cu^{II}(L)](BF_4)_2$	$[Cu^{II}(L^{OH})](BF_4)_2 \cdot 2H_2O$	$[Fe^{II}(L)OHMe](BF_4)_2 \cdot OEt_2$	$[Fe^{III}(L)OMe](ClO_4)_2 \cdot H_2O \cdot NCMe$	$[Fe^{II}(L^{OH})Cl]Cl \cdot solv$	$2[Mn^{II}(L)Cl][MnCl_4] \cdot MeO \cdot solv$
formula	$C_{33.57}H_{34.13}B_2CuF_8N_6O_6$	$C_{33}H_{38}B_2CuF_8N_6O_7$	$C_{38.7}H_{48.7}B_2F_8FeN_6O_{7.7}$	$C_{36}H_{42}Cl_2FeN_7O_{16}$	$C_{33}H_{34}Cl_2FeN_6O_5$	$C_{34.5}H_{38}Cl_3Mn_{1.5}N_6O_{6.5}$
M_r	854.75	867.85	950.18	955.51	720.38	829.47
crystal system	monoclinic	monoclinic	monoclinic	triclinic	triclinic	monoclinic
space group	$P\ 2_1/c$	$P\ 2_1/c$	$P\ 2_1/n$	P -1	P -1	$P2_1/a$
a /Å	20.74985(19)	20.7553(3)	10.538(5)	13.353(6)	8.40726(19)	20.546(2)
b /Å	10.42825(8)	10.30900(12)	15.040(7)	13.488(6)	14.6959(3)	15.8473(17)
c /Å	17.69608(16)	17.8036(2)	27.068(14)	13.681(6)	15.2169(4)	23.647(2)
α /°				61.283(7)	79.632(2)	
β /°	102.4417(9)	103.2779(13)	99.311(8)	69.065(14)	84.430(2)	104.361(12)
γ /°				68.674(11)	76.8063(18)	
V /Å^3	3739.23(6)	3707.55(8)	4233(3)	1962.1(15)	1797.48(8)	7458.9(14)
Z	4	4	4	2	2	8
F_{000}	1746	1780	1969	990	747	3492
d_c /Mg·m^{-3}	1.518	1.555	1.491	1.617	1.331	1.477
X-radiation, λ /Å	Cu-*K*α, 1.5418	Mo-*K*α, 0.71073	Mo-*K*α, 0.71073	Mo-*K*α, 0.71073	Mo-*K*α, 0.71073	Mo-*K*α, 0.71073
μ /mm^{-1}	1.652	0.685	1.491	0.606	0.613	0.784
max., min. transmission factors	0.957, 0.785	0.965, 0.912	0.7462, 0.6976	0.7464, 0.7022	1.0000, 0.7692	0.898, 0.587
data collect. temperat. /K	110(1)	110(1)	100(2)	100(2)	110(1)	200(2)
θ range /°	4.8 to 70.8	3.2 to 25.7	1.5 to 31.0	1.7 to 32.5	3.3 to 29.9	2.6 to 30.5
index ranges (indep. set) *h,k,l*	-25 ... 25, -12 ... 12, -	-25 ... 25, -12 ... 12, -	-15 ... 15, -21 ... 21, -	-19 ... 20, -20 ... 20, -	-11 ... 11, -20 ... 20, -	-29 … 29, -22 … 22, -

	$[Cu^{II}(L)](BF_4)_2$	$[Cu^{II}(L^{OH})]$ $(BF_4)_2 \cdot 2H_2O$	$[Fe^{II}(L)OHMe]$ $(BF_4)_2 \cdot OEt_2$	$[Fe^{III}(L)OMe]$ $(ClO_4)_2 \cdot H_2O \cdot NCMe$	$[Fe^{II}(L^{OH})Cl]Cl \cdot solv$	$2[Mn^{II}(L)Cl]$ $[MnCl_4] \cdot MeO \cdot solv$
	21 ... 21	21 ... 21	39 ... 39	20 ... 20	21 ... 21	33 … 32
reflections measured	92804	70356	103429	50130	97442	88584
unique [R_{int}]	7169 [0.0403]	7025 [0.0649]	13502 [0.0516]	13127 [0.0449]	9872 [0.0727]	22313 [0.0947]
observed [$I \geq 2\sigma(I)$]	6735	5859	10336	10051	8736	11153
parameters refined	528	524	613	571	449	940
GooF on F^2	1.050	1.042	1.043	1.033	1.210	0.795
R indices [$F>4\sigma(F)$] $R(F)$, $wR(F^2)$	0.0803, 0.2317	0.0434, 0.0991	0.0589, 0.1608	0.0429, 0.1030	0.0659, 0.1307	0.0473, 0.1073
R indices (all data) $R(F)$, $wR(F^2)$	0.0830, 0.2343	0.0556, 0.1055	0.0809, 0.1757	0.0646, 0.1152	0.0775, 0.1346	0.1034, 0.1190
Difference density: max, min /e·Å^{-3}	2.137, -1.166	0.908, -0.773	1.504, -0.788	0.893, -0.688	0.486, -0.503	1.51, -0.99

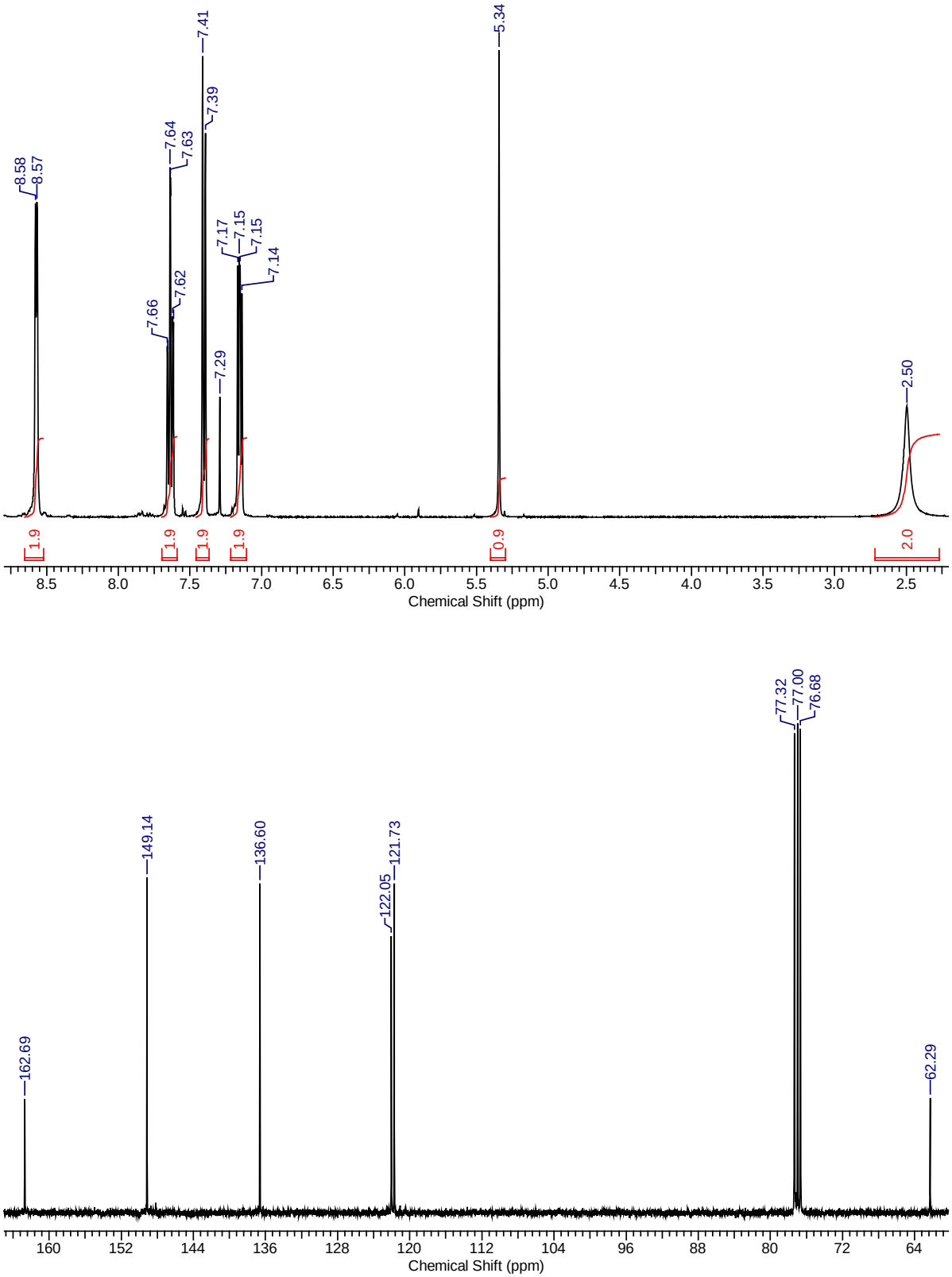

Figure S2: NMR Spectra of Di(2-pyridyl)methylamine

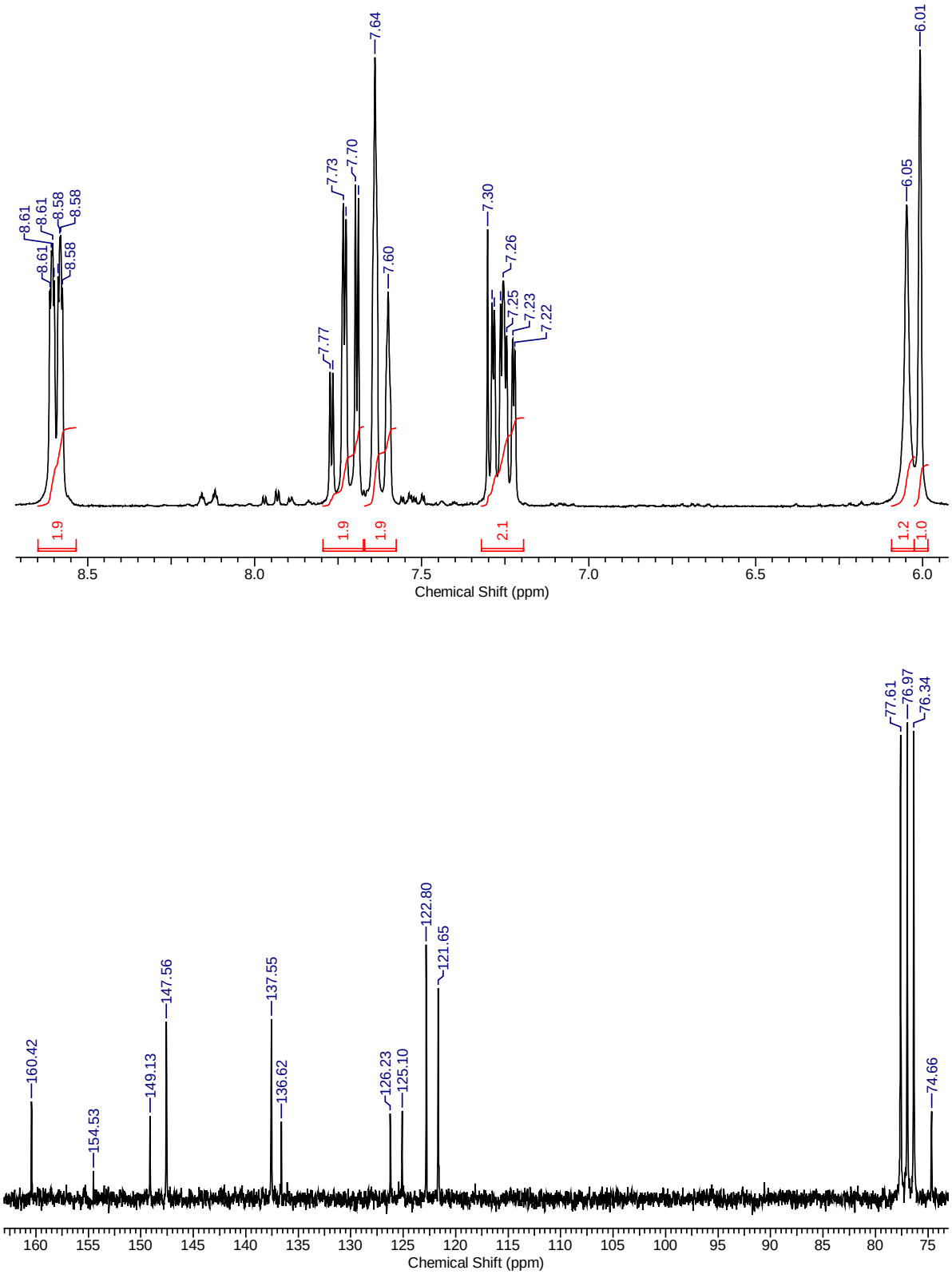

Figure S3: NMR Spectra of Di(2-pyridyl)methanol

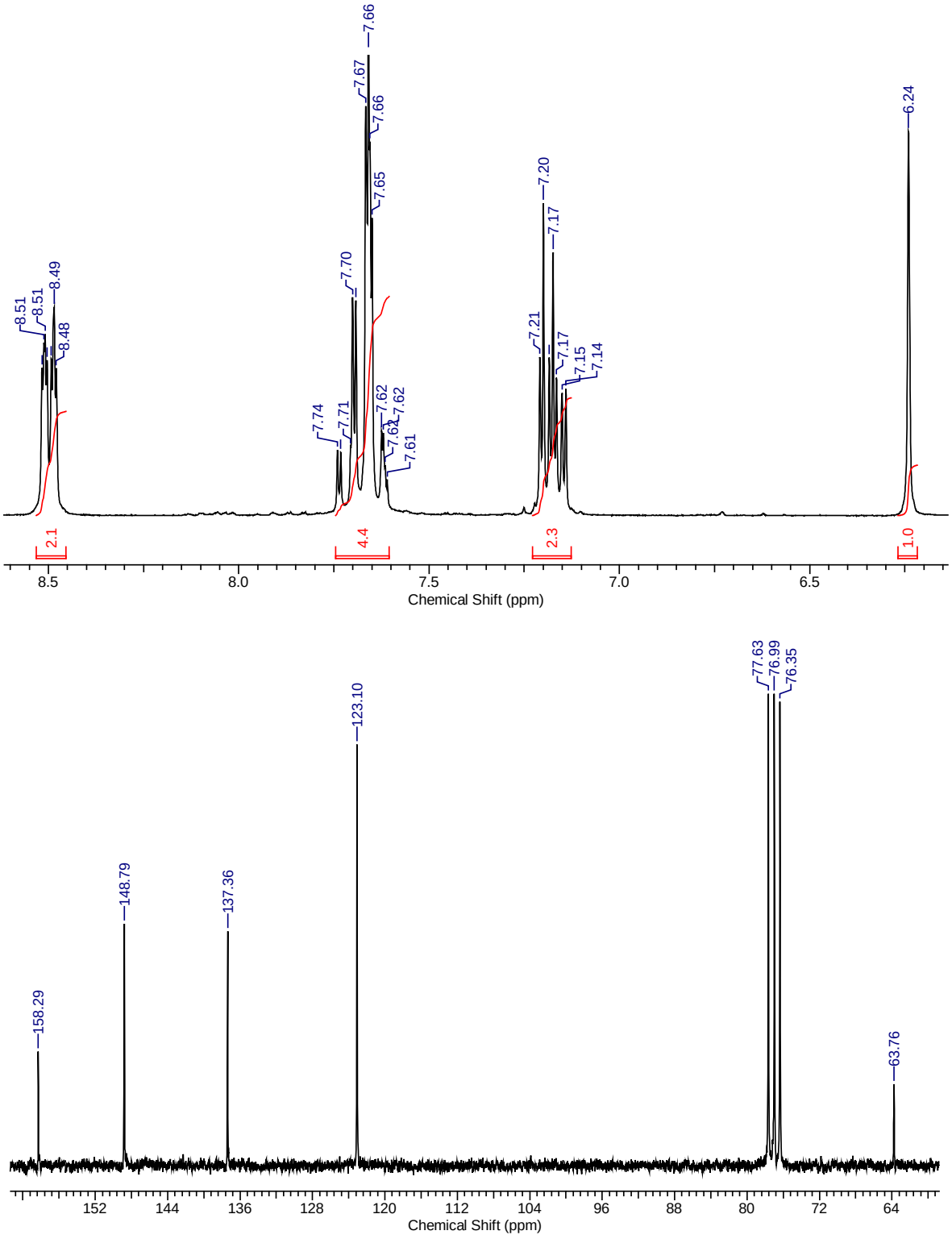

Figure S4: NMR Spectra of Di(2-pyridyl)methylchloride

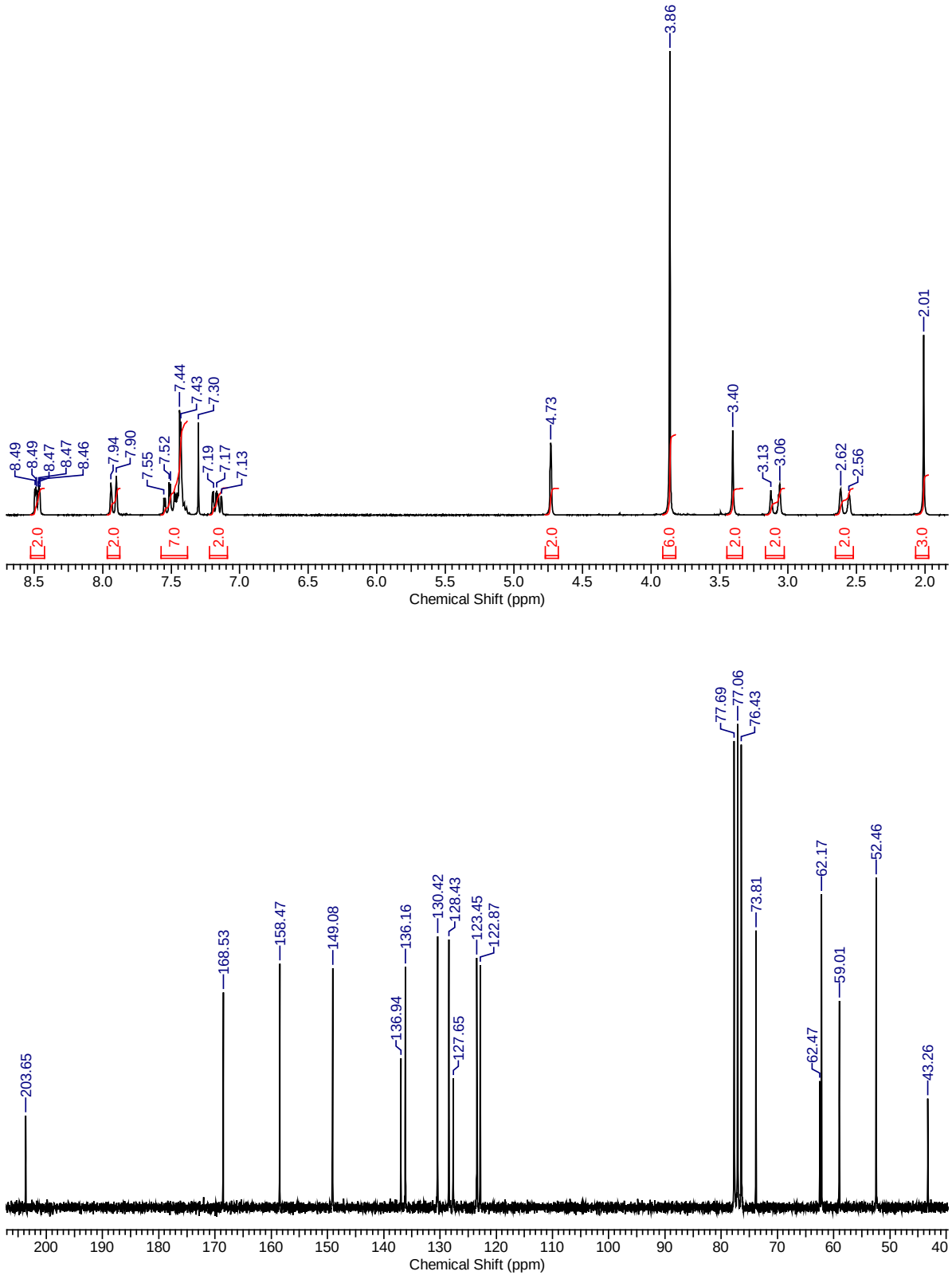

Figure S5: NMR Spectra of Dimethyl-(7-benzyl-3-methyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate

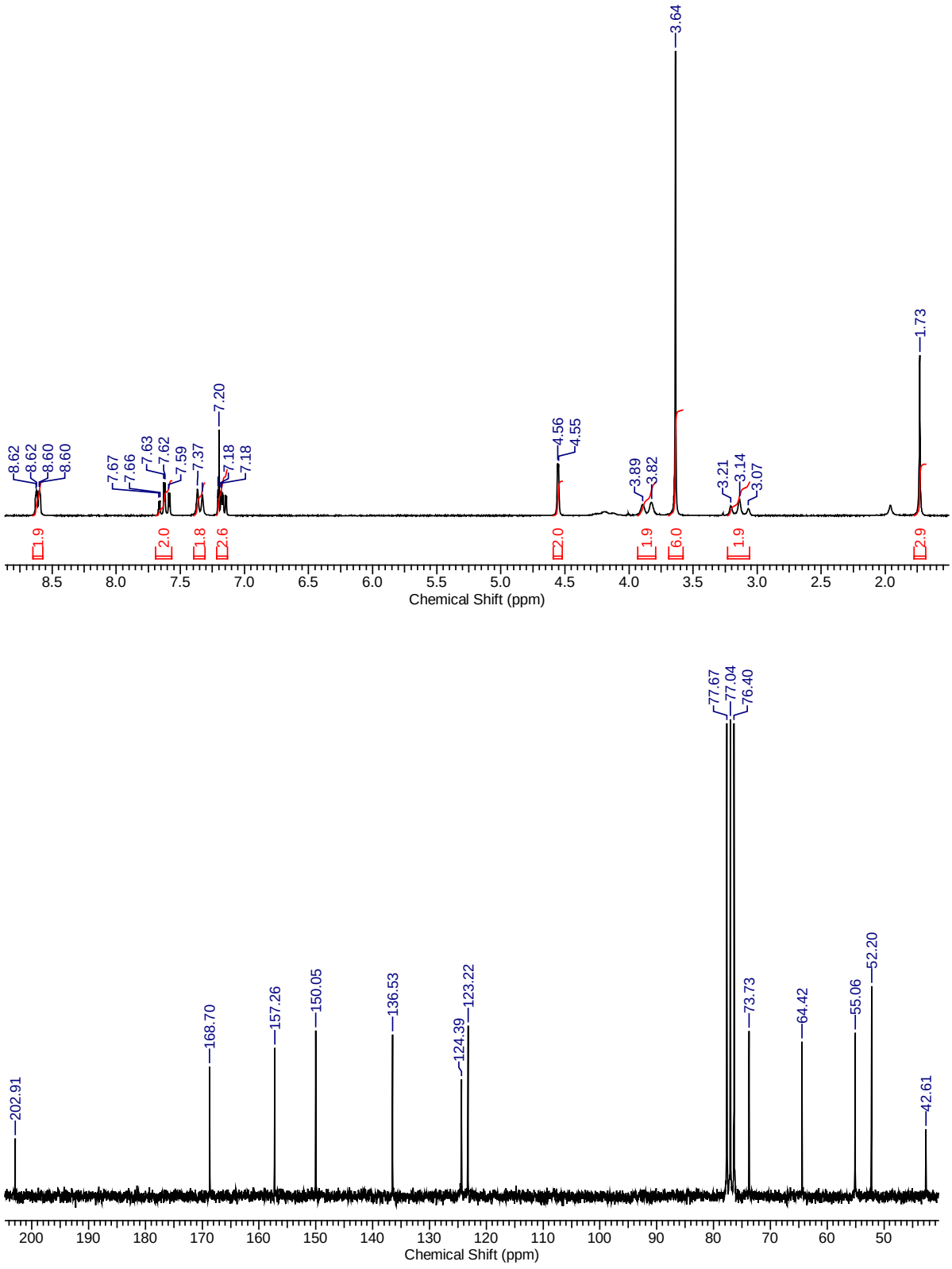

Figure S6: NMR Spectra of Dimethyl-(3-methyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate

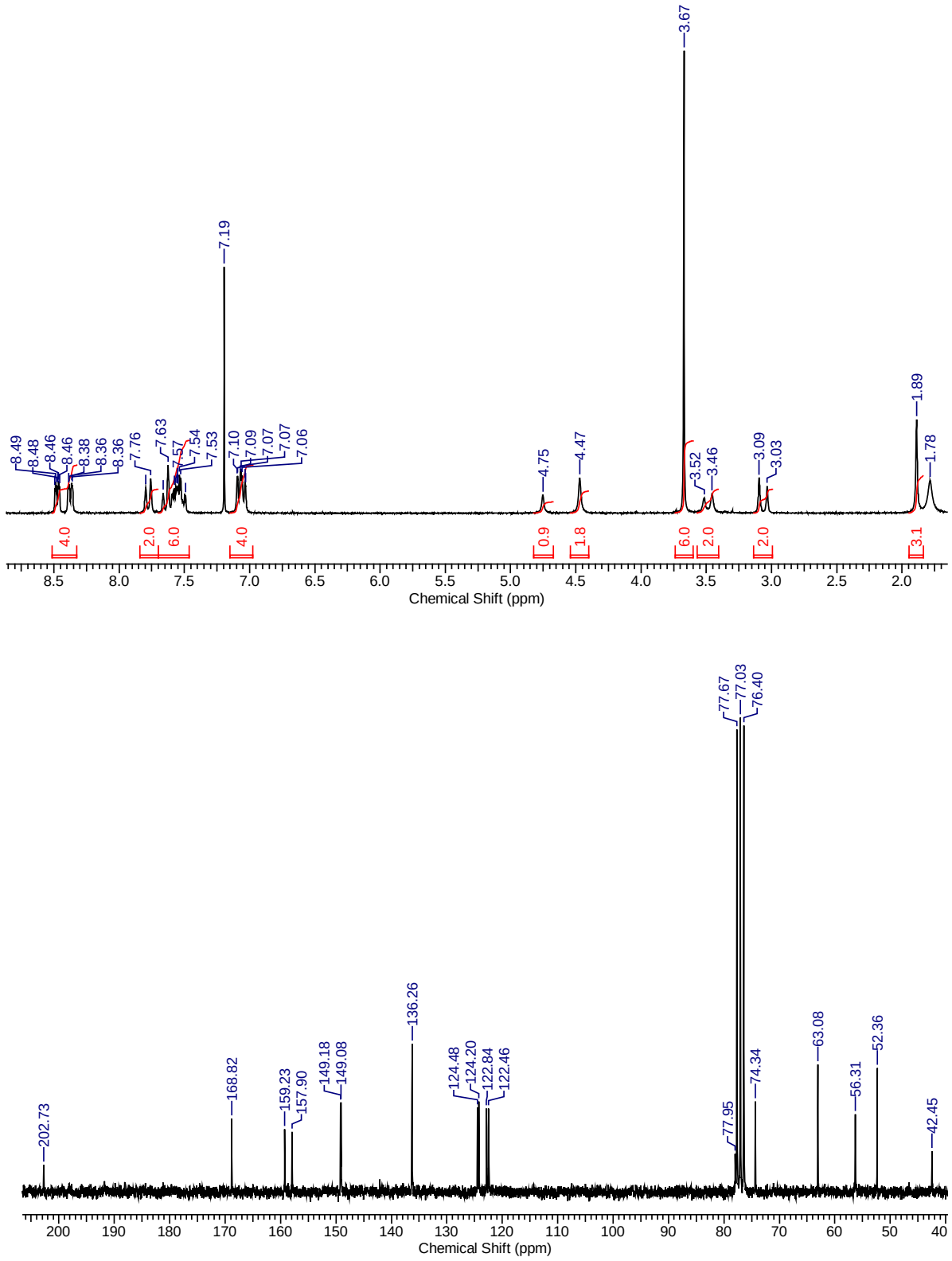

Figure S7: NMR Spectra of Dimethyl-(3-methyl-7-bis(2-pyridyl)methyl-9-oxo-2,4-bis(2-pyridyl)-3,7-diazabicyclo[3.3.1]nonane)-1,5-dicarboxylate

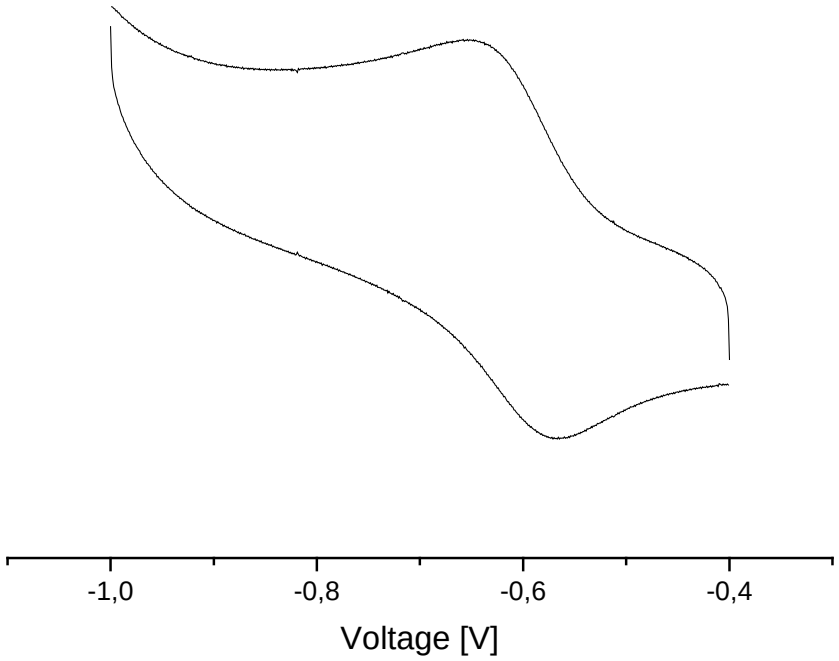

Figure S8: Cyclovoltammogramm of $[Cu(L)](BF_4)_2$ in acetonitrile with 0.1M $(Bu_4N)PF_6$ as supporting electrolyte vs. $Ag/AgNO_3$

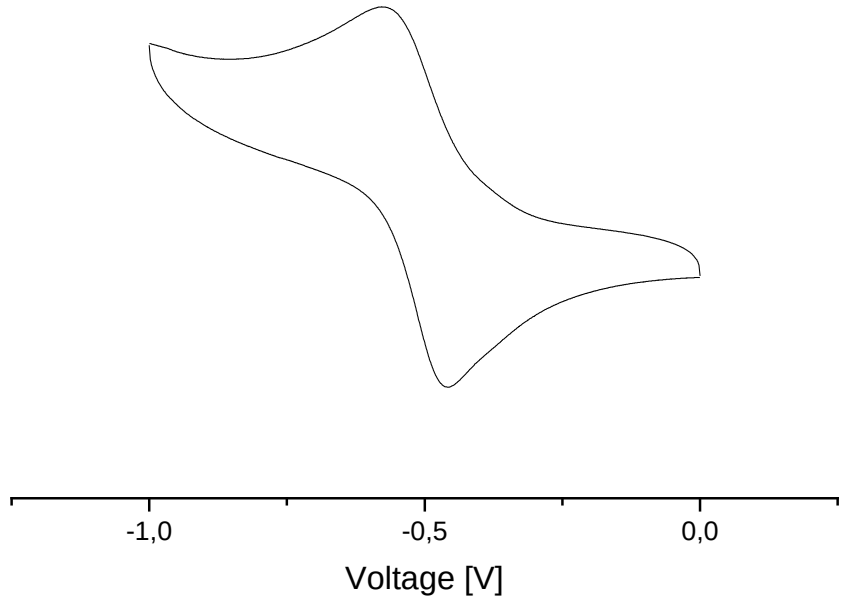

Figure S9: Cyclovoltammogramm of $[Cu(L)](BF_4)_2$ in water with 3M NaCl as supporting electrolyte vs. Ag/AgCl

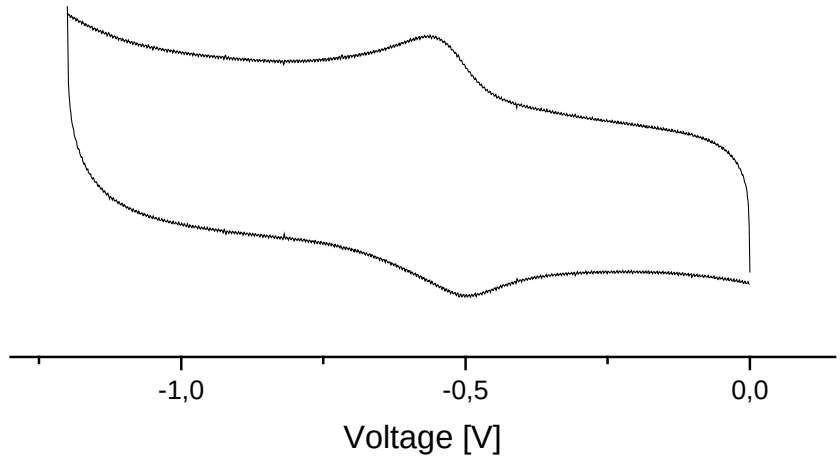

Figure S10: Cyclovoltammogramm of $[Cu(L^{OH})](BF_4)_2$ in acetonitrile with 0.1M $(Bu_4N)PF_6$ as supporting electrolyte vs. $Ag/AgNO_3$

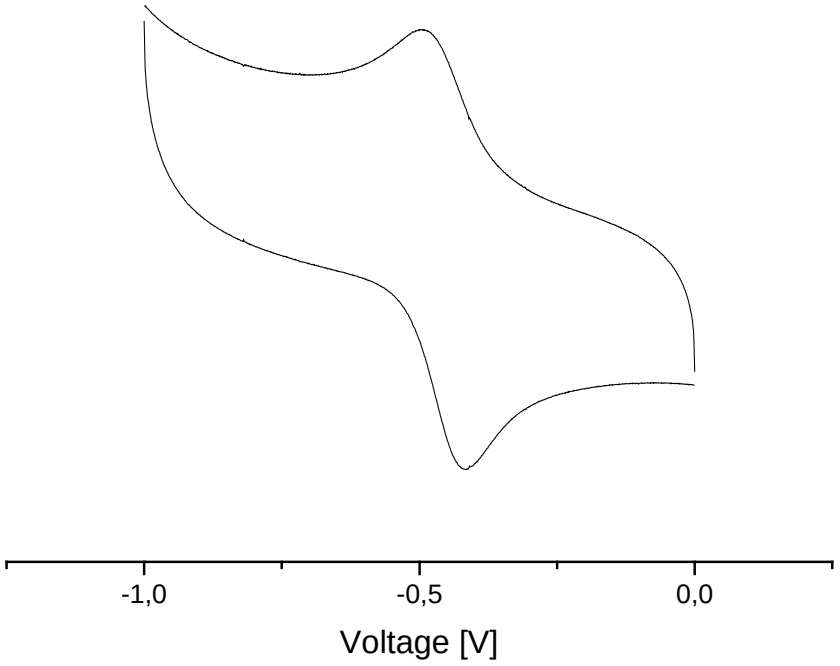

Figure S11: Cyclovoltammogramm of $[Cu(L^{OH})](BF_4)_2$ in water with 3M NaCl as supporting electrolyte vs. Ag/AgCl

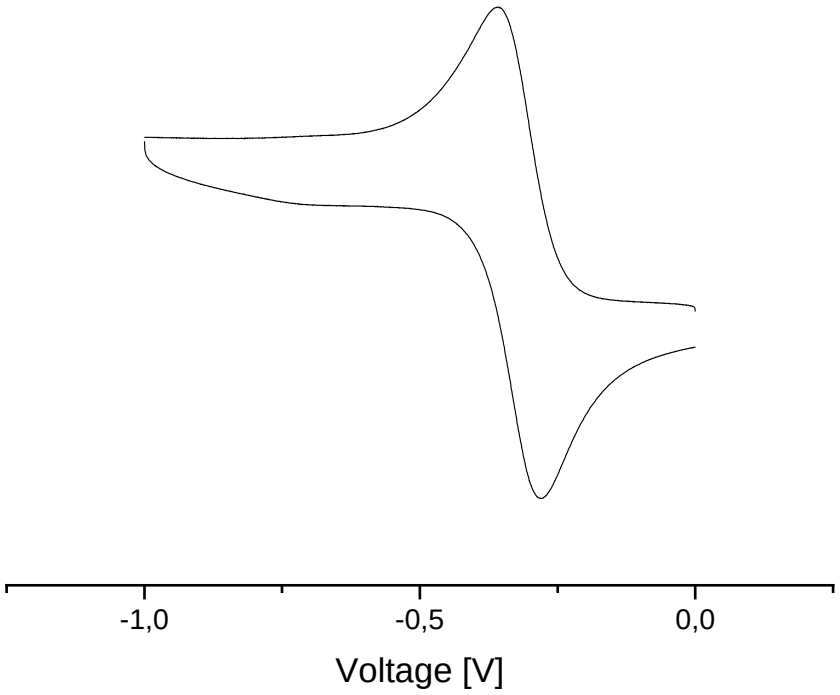

Figure S12: Cyclovoltammogramm of $[Cu(L)](ClO_4)_2$ in acetonitrile with 0.1M $(Bu_4N)PF_6$ as supporting electrolyte vs. $Ag/AgNO_3$

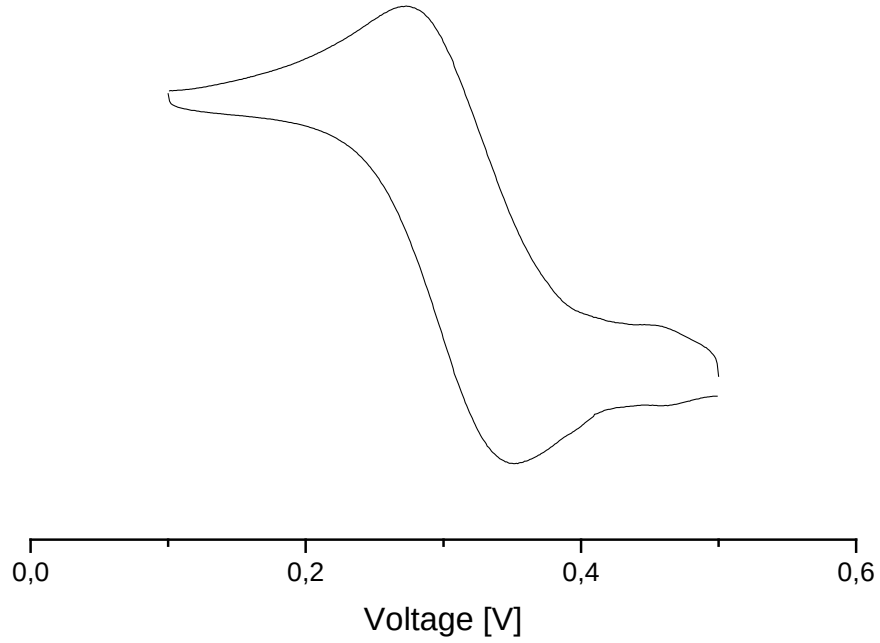

Figure S13: Cyclovoltammogramm of $[Fe(L^{OH})(Cl)]Cl$ in acetonitrile with 0.1M $(Bu_4N)PF_6$ as supporting electrolyte vs. $Ag/AgNO_3$

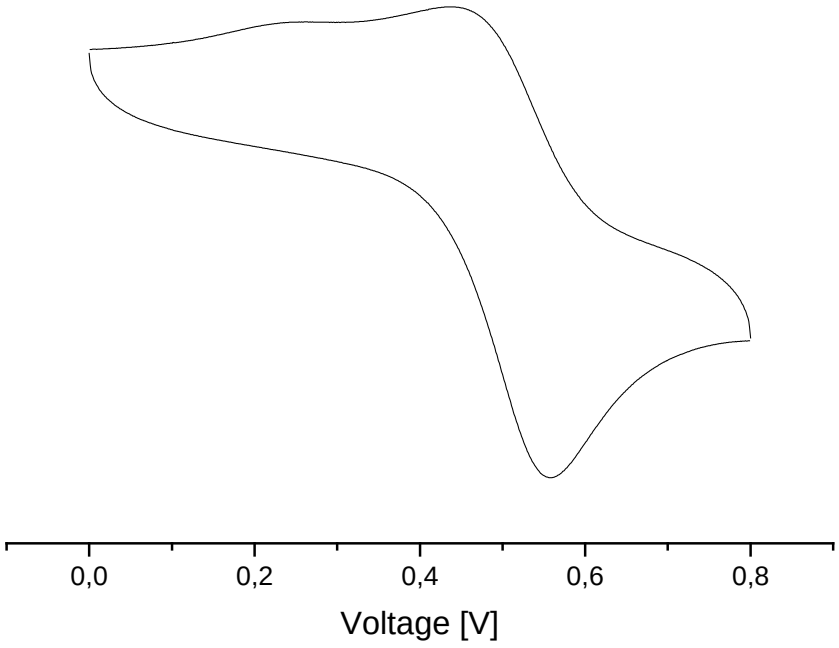

Figure S14: Cyclovoltammogramm of [Fe(L^{OH})(Cl)]Cl in water with 3M NaCl as supporting electrolyte vs. Ag/AgCl

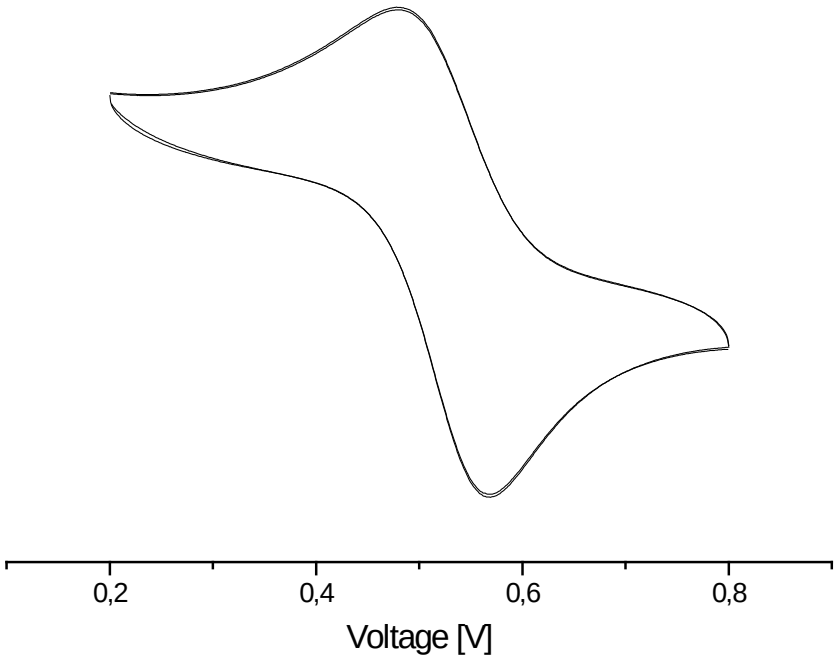

Figure S15: Cyclovoltammogramm of [Fe(L)(OHMel)]$(BF_4)_2$ in water with 3M NaCl as supporting electrolyte vs. Ag/AgCl

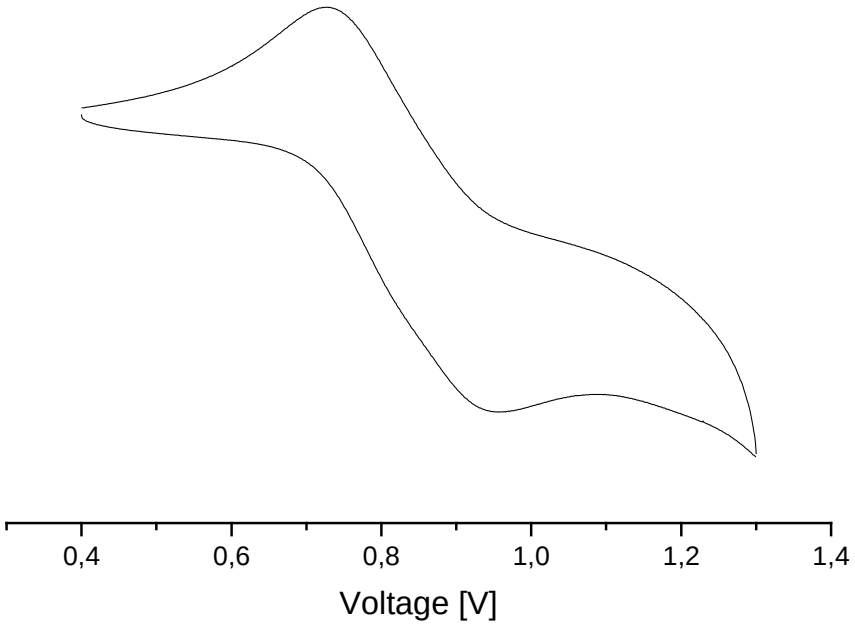

Figure S16: Cyclovoltammogramm of $[Mn(L)(Cl)]_2[MnCl_4]$ in acetonitrile with 0.1M $(Bu_4N)PF_6$ as supporting electrolyte vs. $Ag/AgNO_3$