Electrochemical Reduction of Carbon Dioxide with a Molecular Polypyridyl Nickel Complex

Supporting Information

Lauren E. Lieske[a], Arnold L. Rheingold[b], Charles W. Machan[a,*]

* - machan@virginia.edu; 0000-0002-5182-1138

[a] – Department of Chemistry, University of Virginia, McCormick Road PO Box 400319, Charlottesville, VA 22904-4319

[b] – Department of Chemistry & Biochemistry, University of California, San Diego, La Jolla, CA 92093-0358.

Evans Method

The Evans Method for determining paramagnetic susceptibility was performed by making a concentration of 1 x 10^{-3} M $[Ni(TPEN)](PF_6)_2$ **(1)** in acetonitrile (MeCN). A capillary insert was then made with a 50% v/v mixture of MeCN and MeCN-d_3. The insert was flame sealed, and then placed in an NMR tube contain $[Ni(TPEN)](PF_6)_2$. ^{1}H NMR spectra with 64 scans were then taken using a 600 MHz Varian NMR Spectrometer.

Paramagnetic moment was then determined following the following equations[1, 2]:

χ_D(TPEN)= 46.5χ_D(en) + 49χ_D(pyr) + 49χ_D(pyr) + 49χ_D(pyr) + 49χ_D(pyr) + 6 χ_D(C) + 6 χ_D(C) + 6 χ_D(C) + 6 χ_D(C).

=267.00 x 10^{-6} emu mol^{-6}

$\chi^{dia} = \chi^{ligand} + \chi^{Ni\ 2+}$

χ^{dia} = [-267.00 + (-12.0)] x 10^{-6} emu mol^{-1}=

-279.00 x 10^{-6} emu mol^{-1}

δv^{p} = (2.22-1.99)*600 Hz

$$\chi^{para} = \frac{(138\ \text{Hz})*(770.\ \text{g/mol})}{(600\ \text{Hz})*(1.33\pi)*(1.06 \times 10^{-2}\ \text{g/mL})} - \chi^{dia}$$

=4.27 x 10^{-3} emu mol^{-1}

μ_{eff} = 3.1 Bohr Magnetons

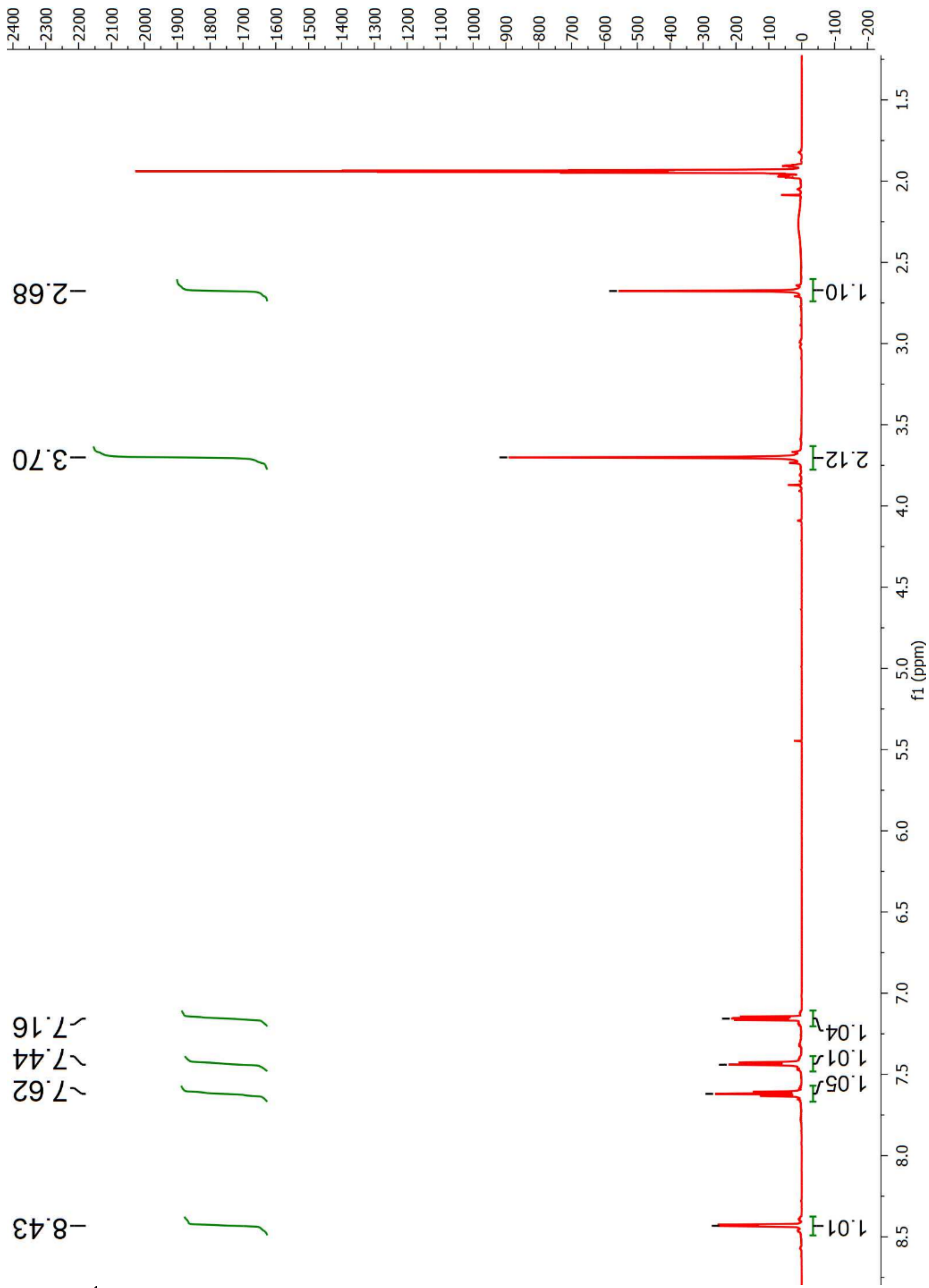

Figure S1. ^{1}H NMR of the TPEN ligand; d_3-CD_3CN; 600 MHz Varian.

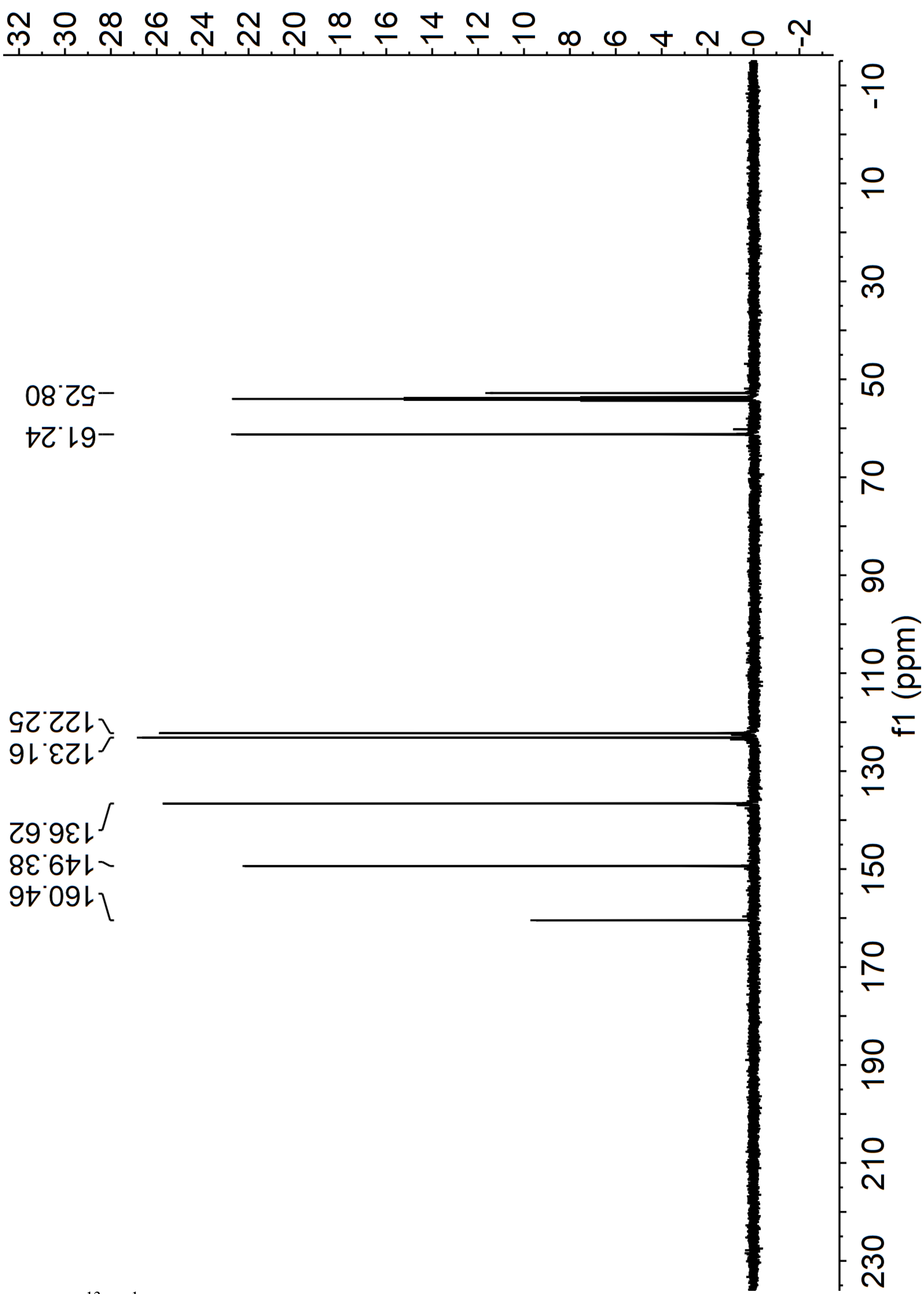

Figure S2. $^{13}C\{^{1}H\}$ NMR of the TPEN ligand; d_2-CD_2Cl_2; 600 MHz Varian.

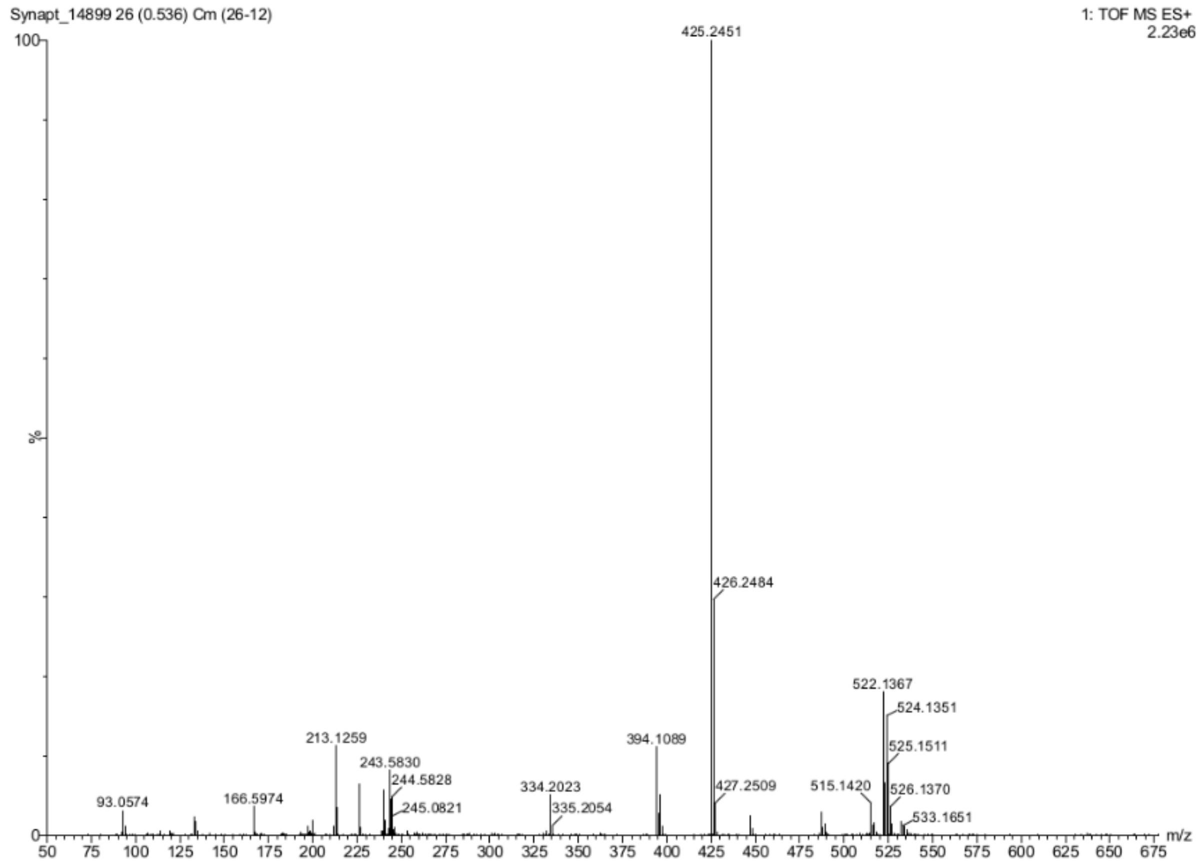

Figure S3. ESI-MS of TPEN.

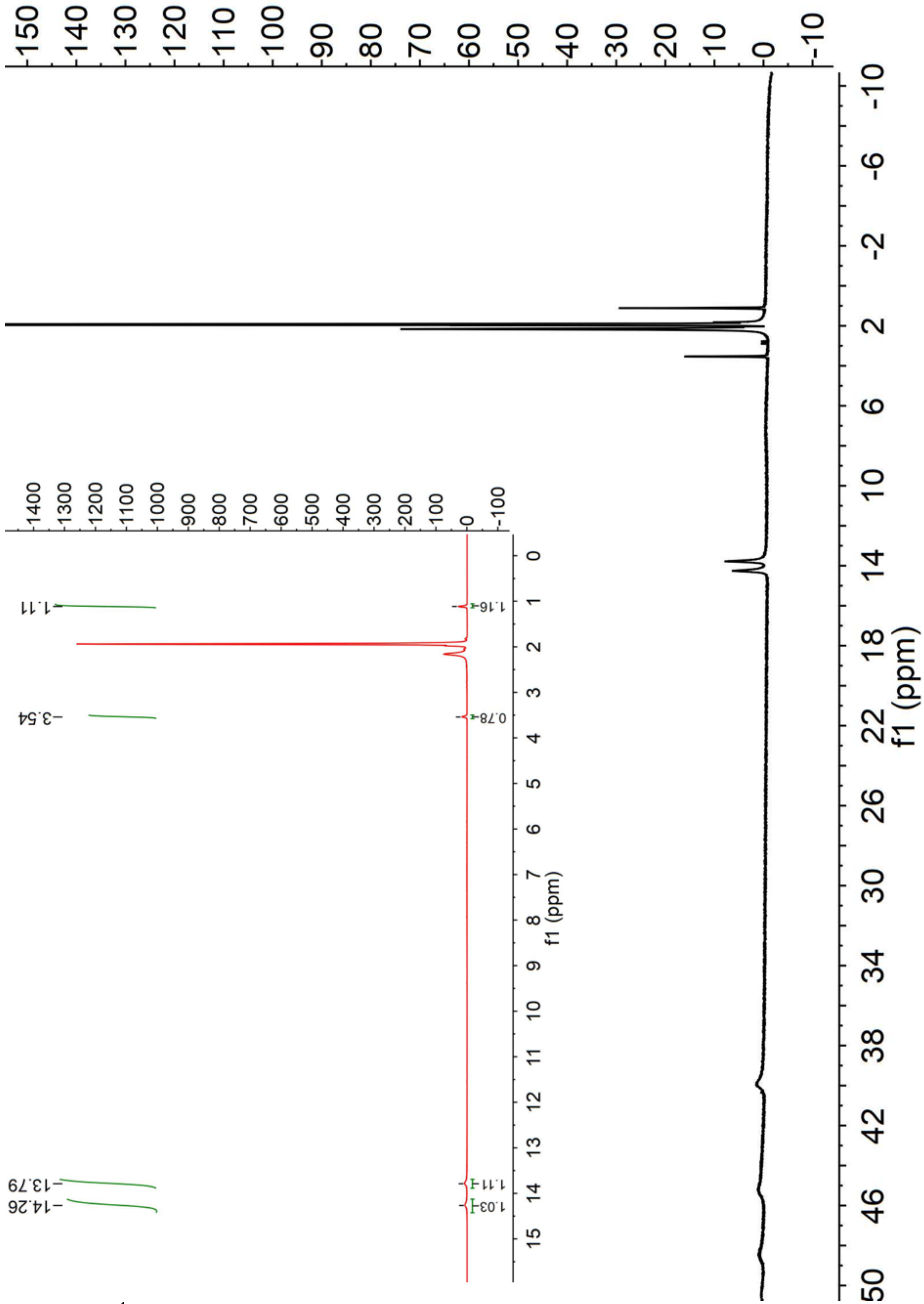

Figure S4. ^{1}H NMR of [Ni(TPEN)](PF_6)$_2$ **1**; d_3-CD_3CN; 600 MHz Varian.

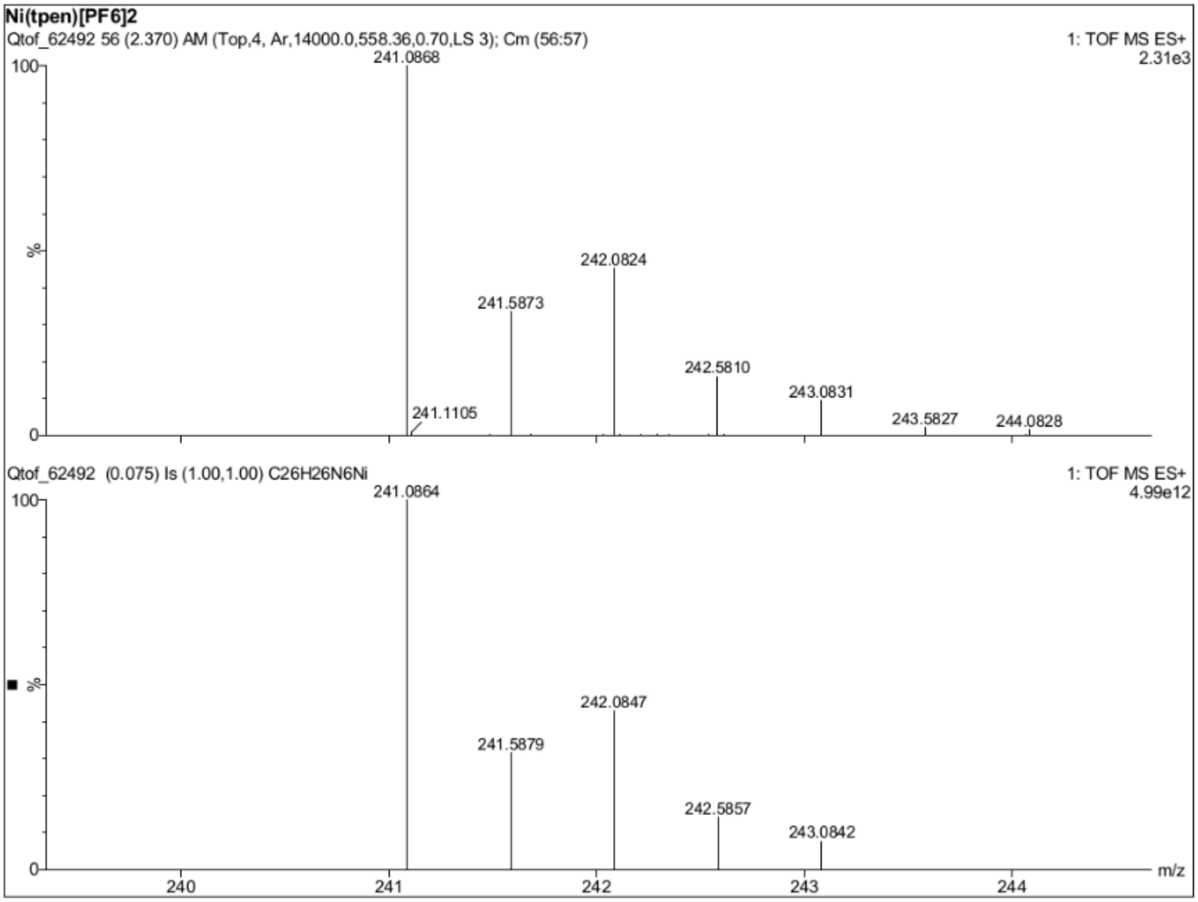

Figure S5. ESI-MS of $[Ni(TPEN)](PF_6)_2$ **1**.

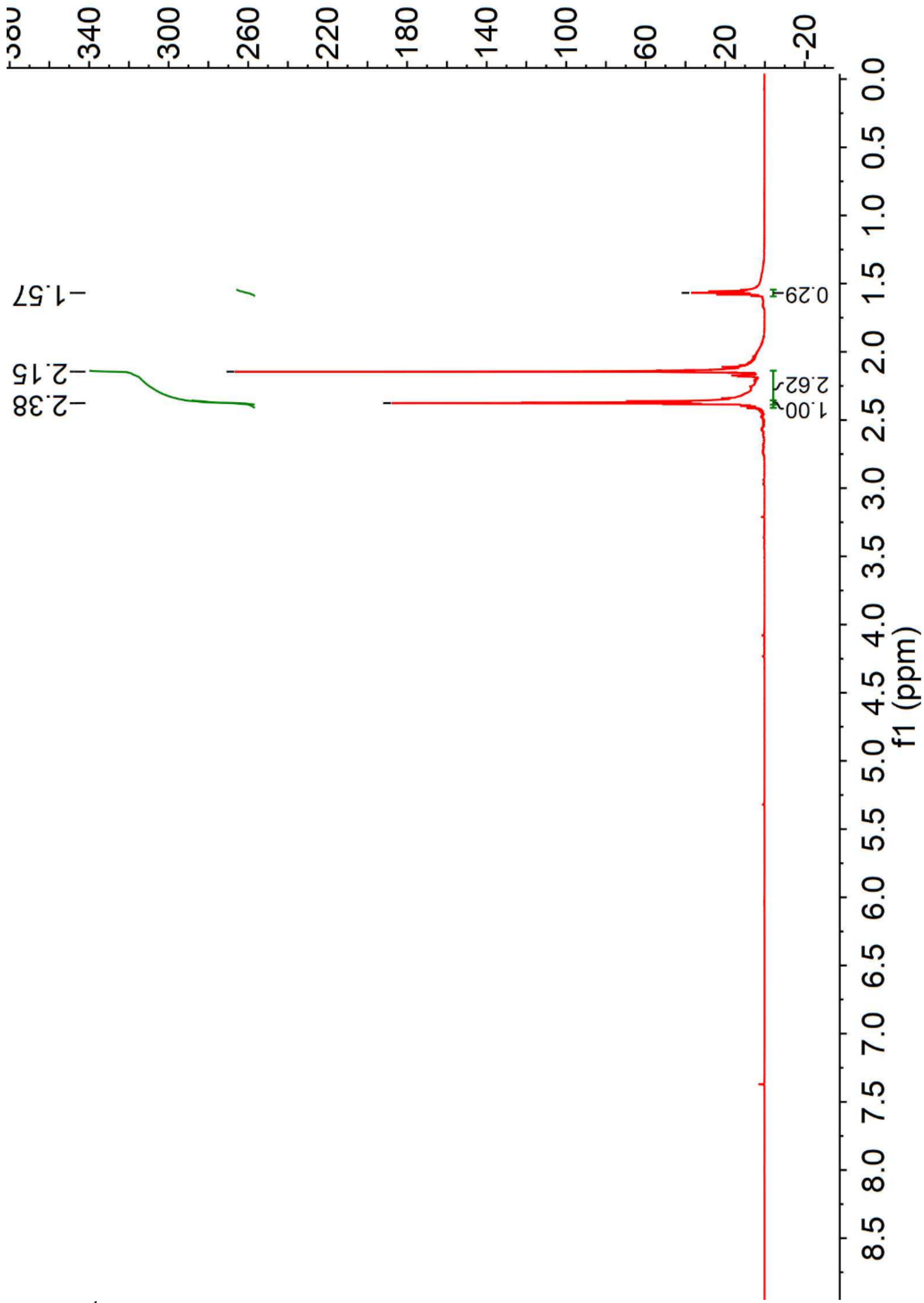

Figure S6. ^1H NMR of the TMC ligand; d_2-CD_2Cl_2; 600 MHz Varian.

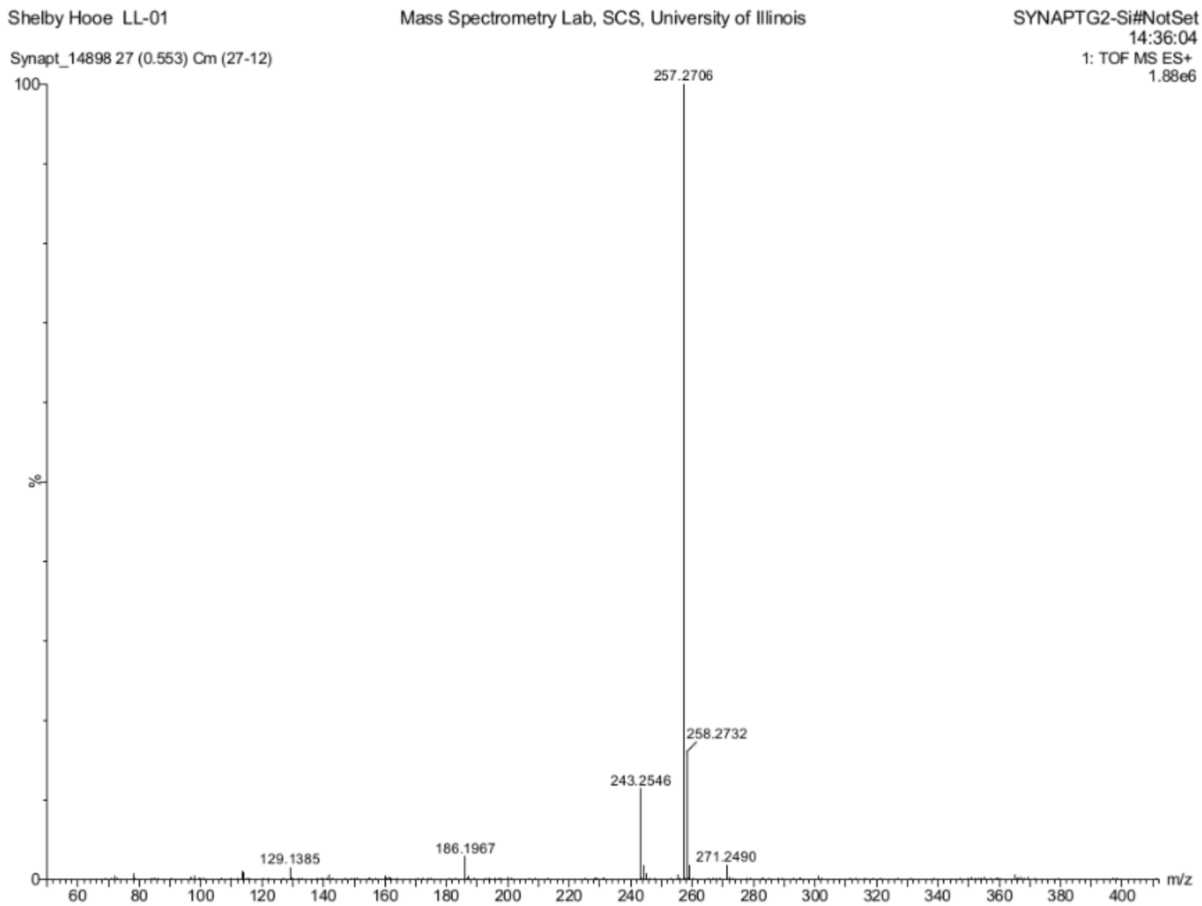

Figure S7. ESI-MS of TMC.

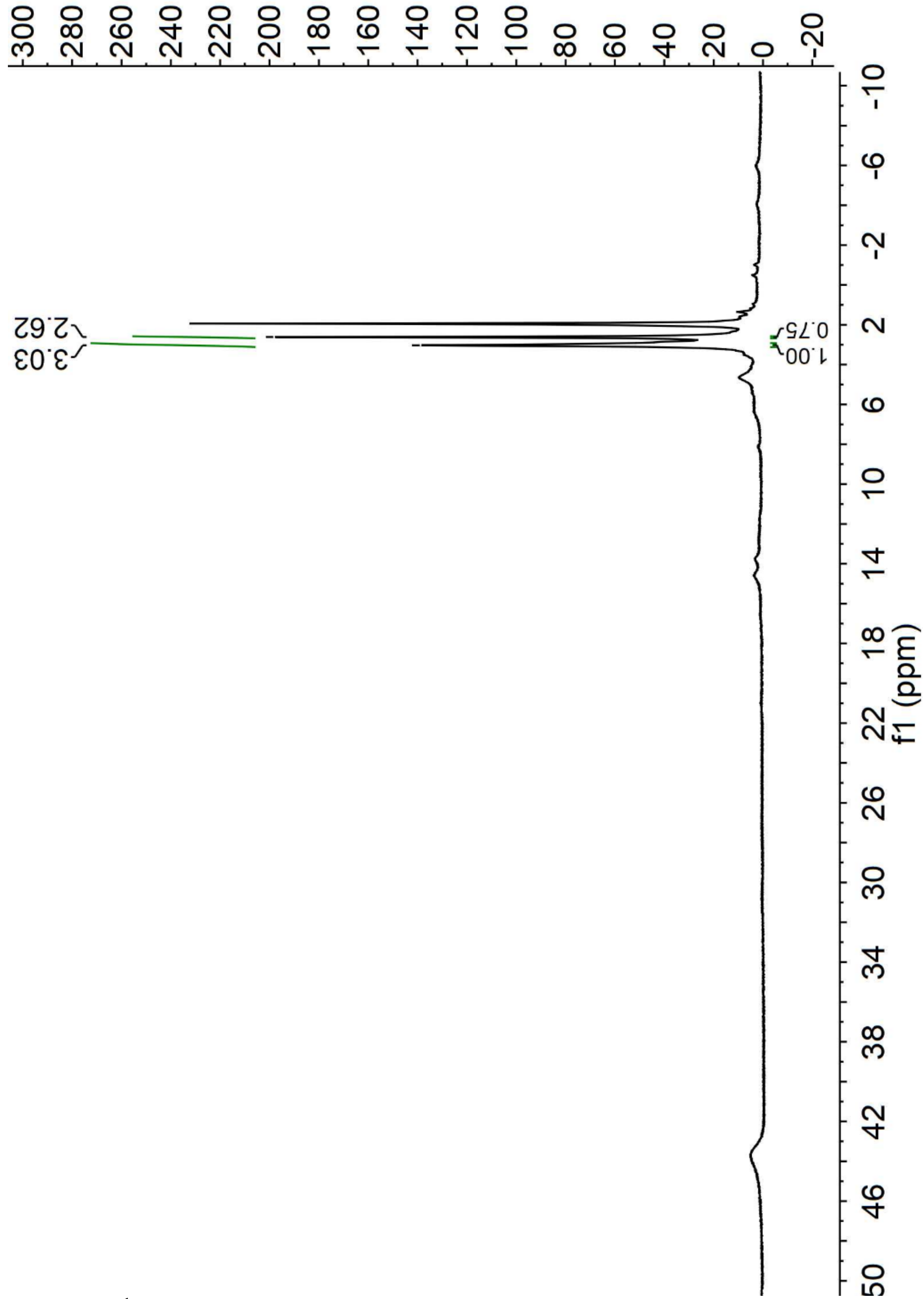

Figure S8. ^{1}H NMR of $[Ni(TMC)](PF_6)_2$; d_3-CD_3CN; 600 MHz Varian.

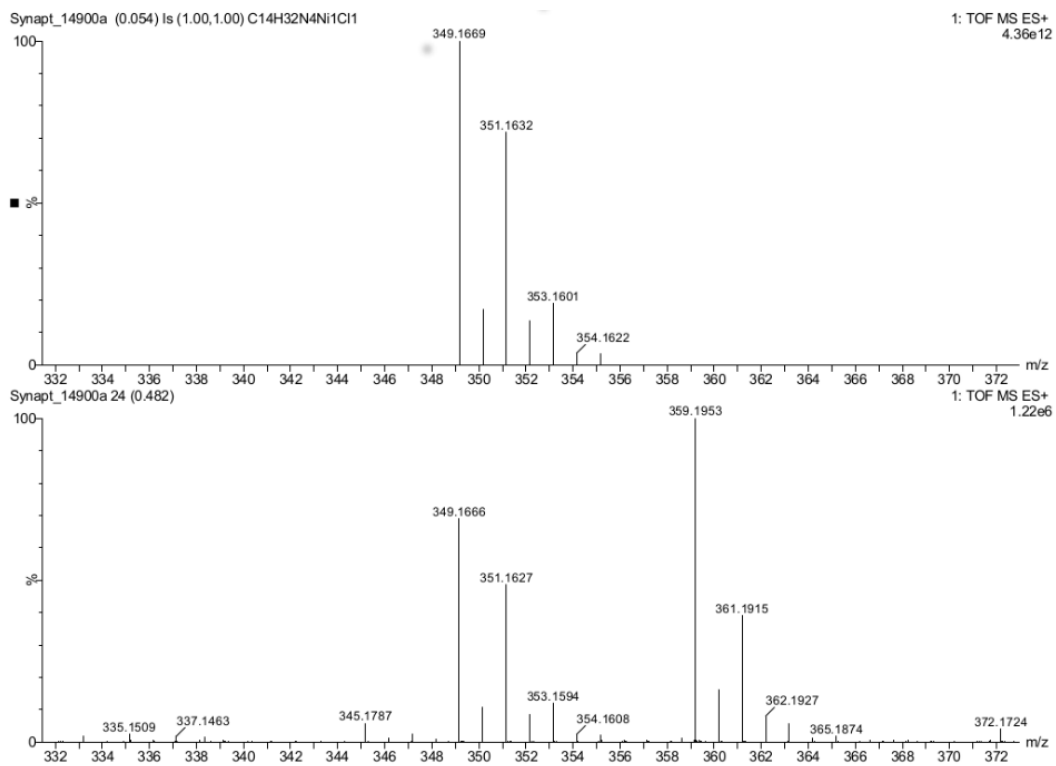

Figure S9. ESI-MS of $[Ni(TMC)](PF_6)_2$.

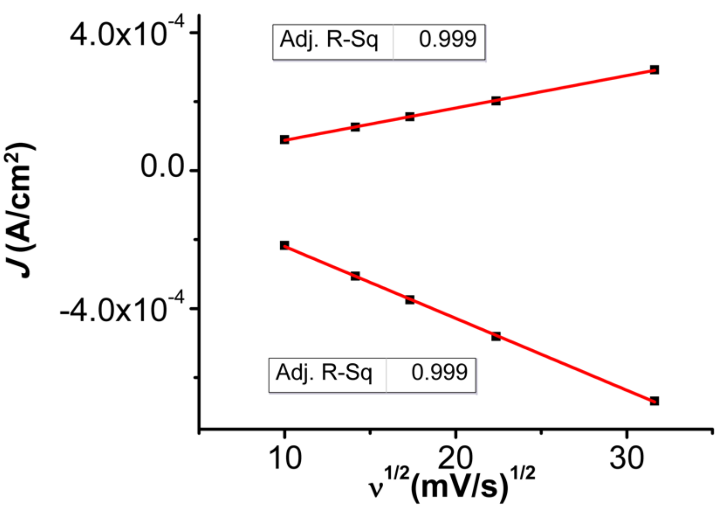

Figure S10. Linear Fit of variable scan rate data from **Figure 3** demonstrating that $[Ni(TPEN)](PF_6)_2$ **1** shows a diffusion-limited current response. Conditions: 1 mM analyte; 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, Pt wire counter electrode, Ag/AgCl pseudoreference electrode; varied scan rate; referenced to internal ferrocene standard.

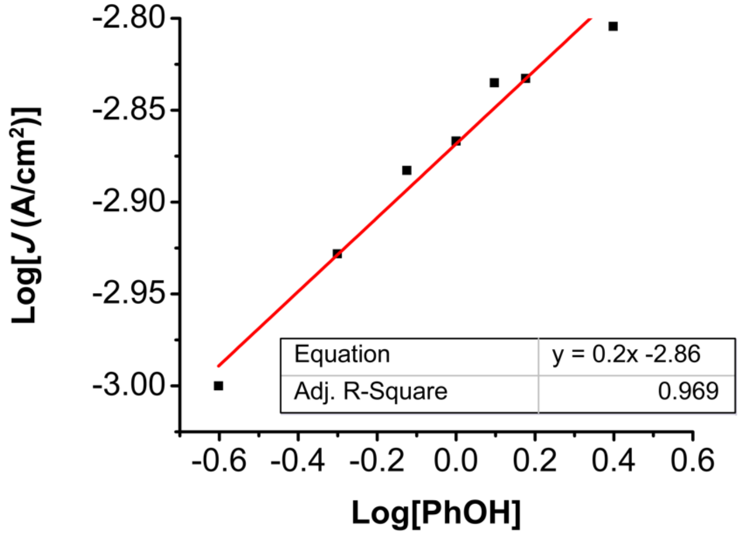

Figure S11. Log-log plot from data obtained from CVs of complex [Ni(TPEN)](PF_6)$_2$ **1**, (1 mM) with variable PhOH concentrations and CO_2 saturation at -1.93 V vs Fc/Fc$^+$. Adapted from Sathrum and Kubiak *J. Phys. Chem. Lett.* **2011**, *2*, 2372.[4] *F* is Faraday's constant, *A* is the electrode area, [*Q*] is the substrate concentration, k_{cat} is the catalytic rate, *D* is the diffusion constant of the catalyst, [*cat*] is the concentration of the catalyst, and n_{cat} is the number of electrons involved in the catalytic process. Uses data from **Figure 5** in main text.

$$(1)\quad i_{cat} = n_{cat}FA[cat](Dk_{cat}[Q]^{y})^{1/2}$$

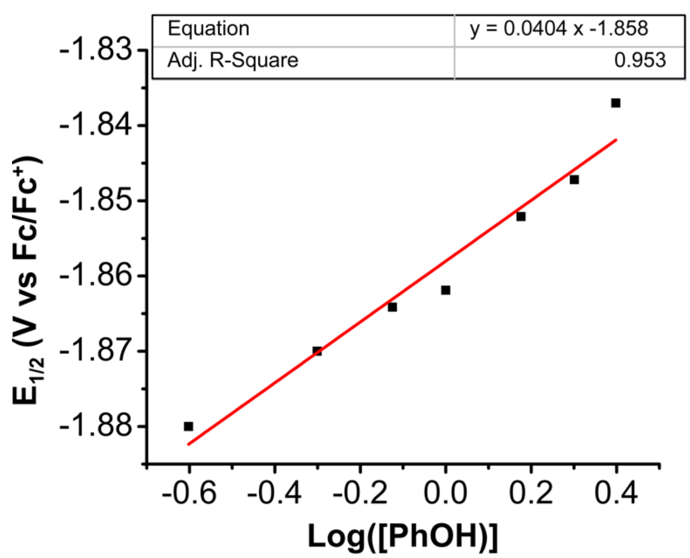

Figure S12. Plot displaying the Nernstian voltage dependence of [Ni(TPEN)](PF_6)$_2$ **1** on the concentration of PhOH in MeCN under CO_2 saturation. Conditions: 0.1 M TBAPF$_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard. Uses data from **Figure 5** in main text.

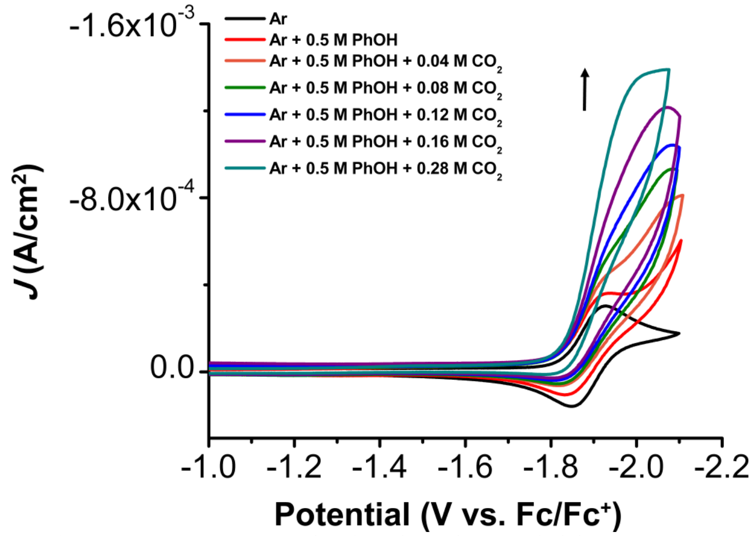

Figure S13. CVs of [Ni(TPEN)]$(PF_6)_2$ **1**, obtained under variable CO_2 concentrations with 0.5 M PhOH. Conditions: 1 mM analyte; 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

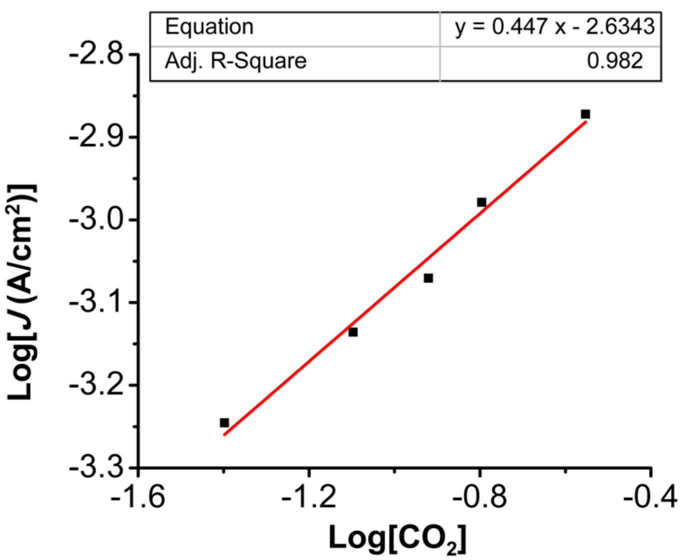

Figure S14. Log-log plot from data obtained from CVs of complex [Ni(TPEN)]$(PF_6)_2$ **1** (1 mM) under variable CO_2 concentration conditions with 0.5 M PhOH at -2.0 V vs Fc/Fc^+.

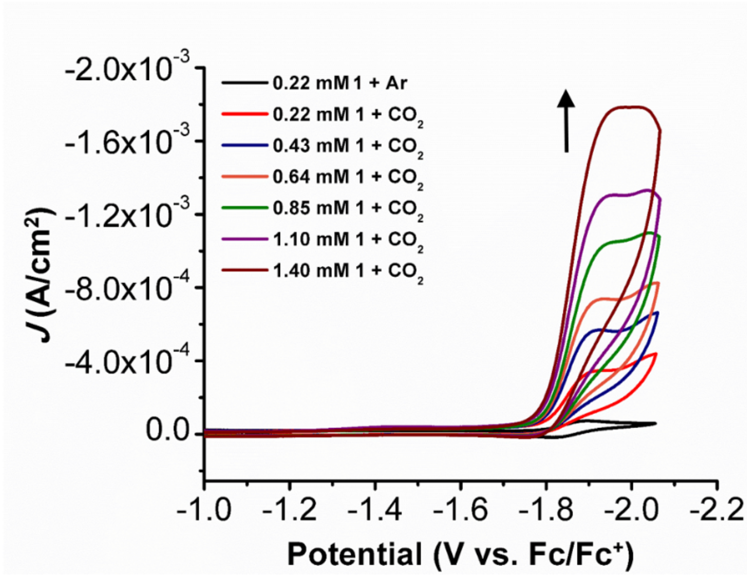

Figure S15. CVs of complex $[Ni(TPEN)](PF_6)_2$ **1** at variable concentrations, obtained under CO_2 saturation and 0.5 M PhOH. Conditions: 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

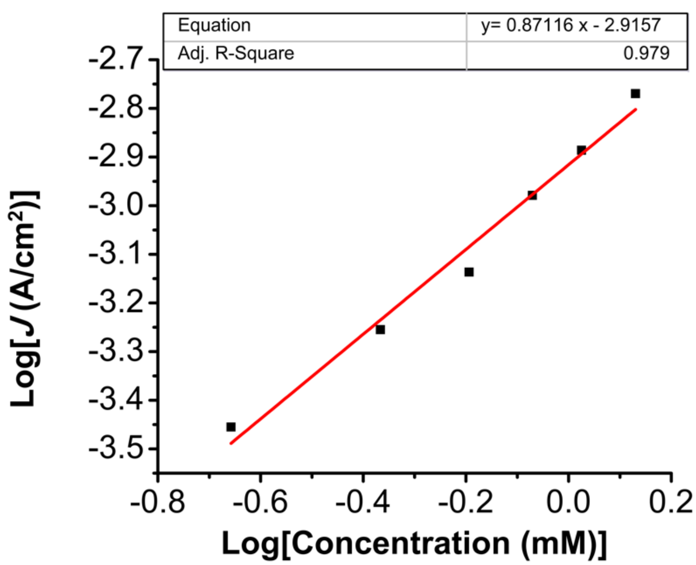

Figure S16. Log-log plot from data obtained from CVs of complex $[Ni(TPEN)](PF_6)_2$ **1** under variable concentration conditions with 0.5 M PhOH and CO_2 saturation at -1.93 V vs Fc/Fc^+.

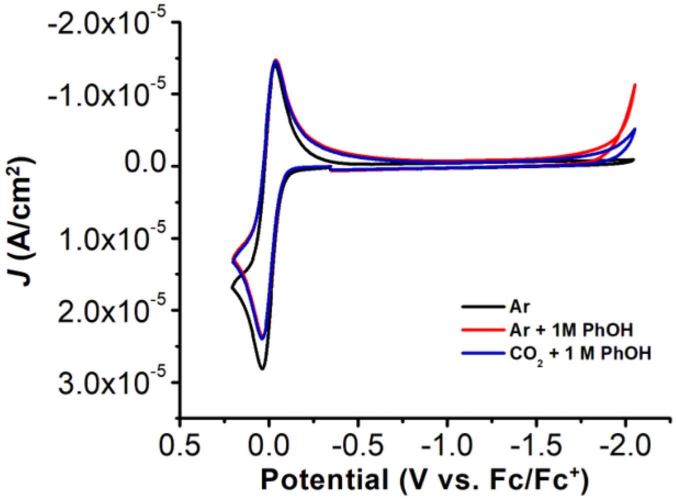

Figure S17. CVs showing CO_2 and PhOH control responses. Conditions: 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

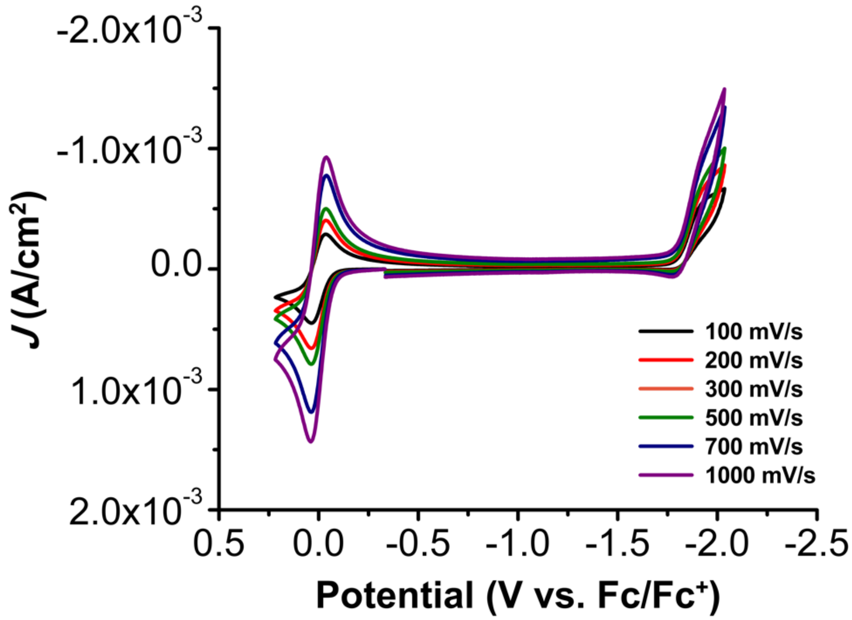

Figure S18. Cyclic voltammogram of $[Ni(TPEN)](PF_6)_2$ **(1)** (1 mM) under CO_2 saturation and 0.5 M PhOH. Conditions: 0.1 M $TBAPF_6$/MeCN; glassy carbon working electrode, glassy carbon counter electrode; Ag/AgCl pseudoreference electrode; varied scan rate; referenced to internal ferrocene standard.

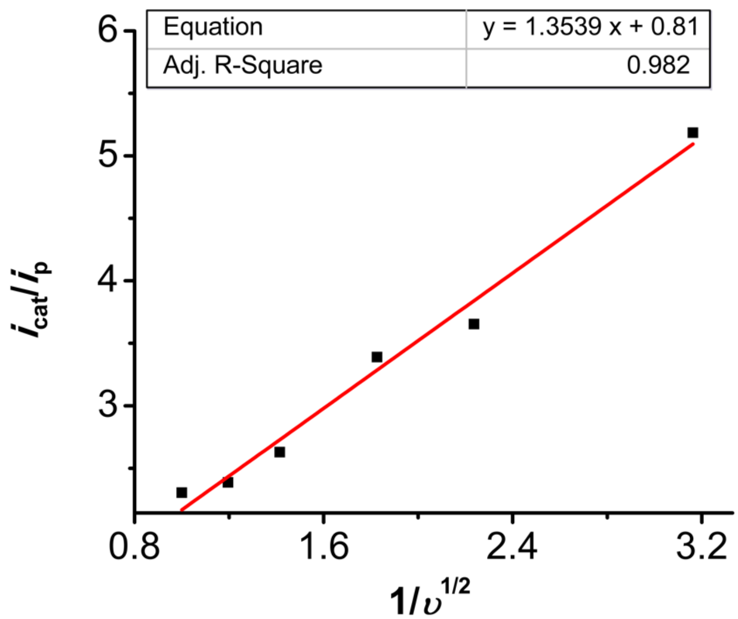

Figure S19. Linear fit between peak catalytic current over non-catalytic vs the inverse square root of the scan rate from the variable scan rate data in **Figure S18**.[3] This establishes the validity of using the equations for the FOWA.[3]

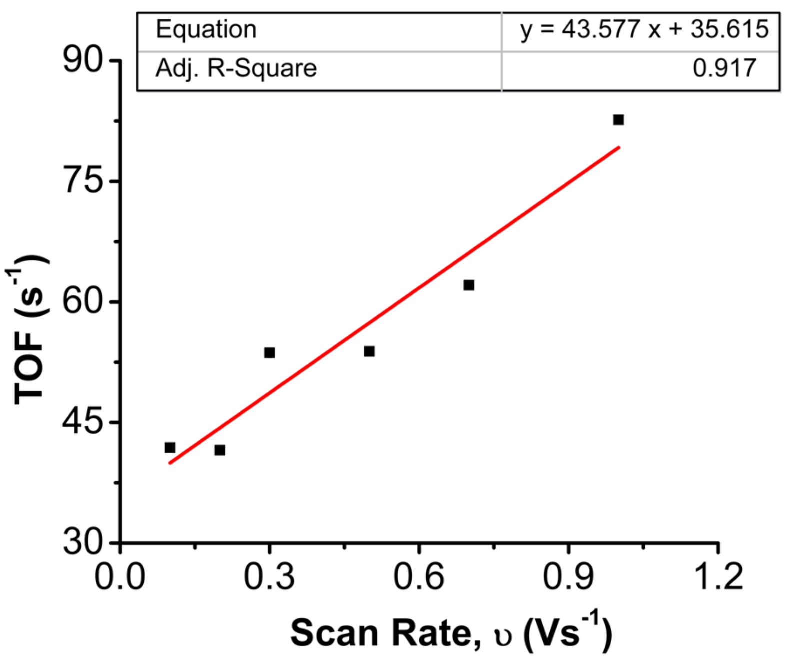

Figure S20. Linear fit plot of TOF (s^{-1}) vs scan rate of the variable scan rate data from **Figure S18** demonstrating that $[Ni(TPEN)](PF_6)_2$ **1** can be analyzed by FOWA using these data.[3]

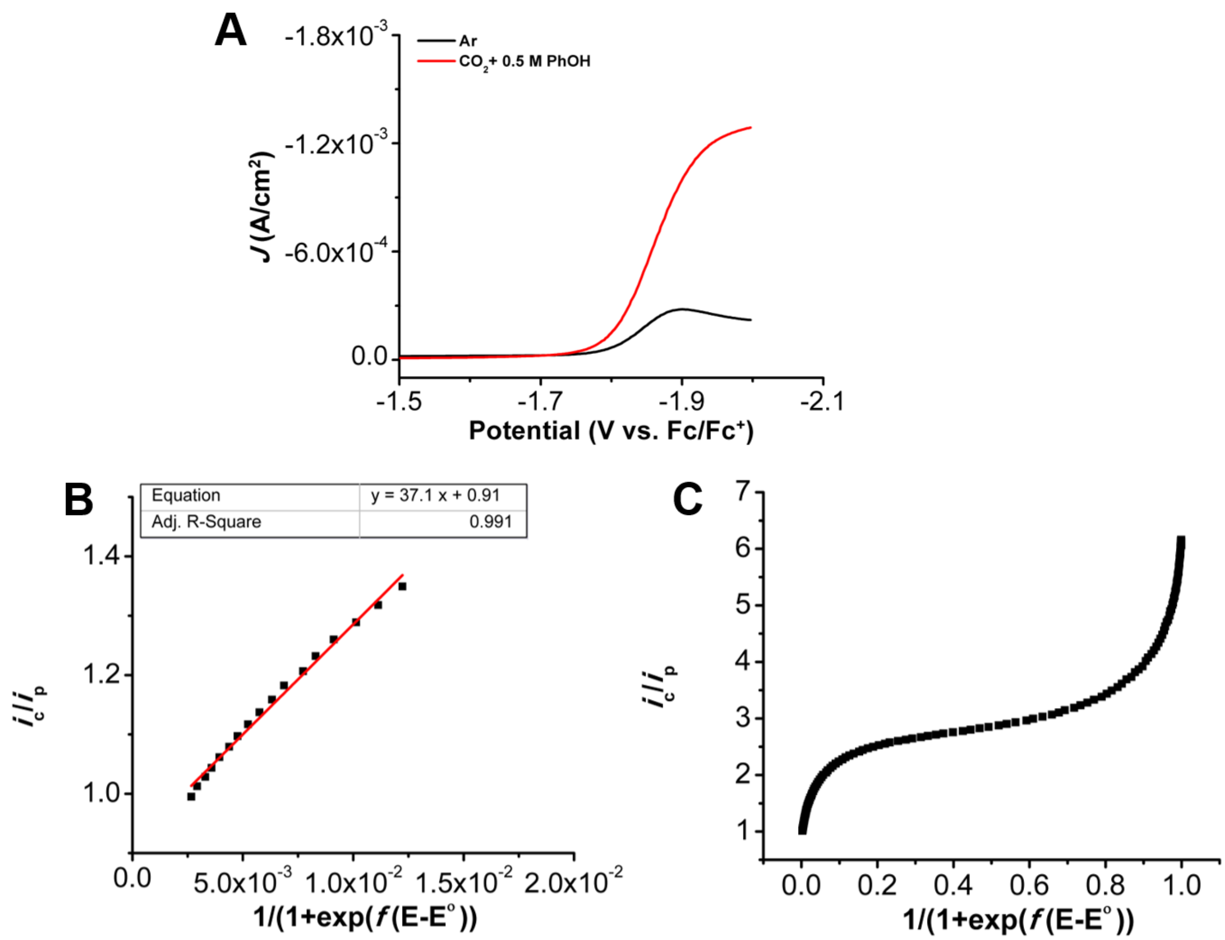

Figure S21. A) CV overlay between catalytic current under CO_2 and 0.5 M phenol and $[Ni(TPEN)](PF_6)_2$ **1** under argon. **B)** Linear region from the FOWA. **C)** Entire region of i_c/i_p vs 1/(1+exp(f (E-E^o)). Conditions: 1 mM analyte; 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

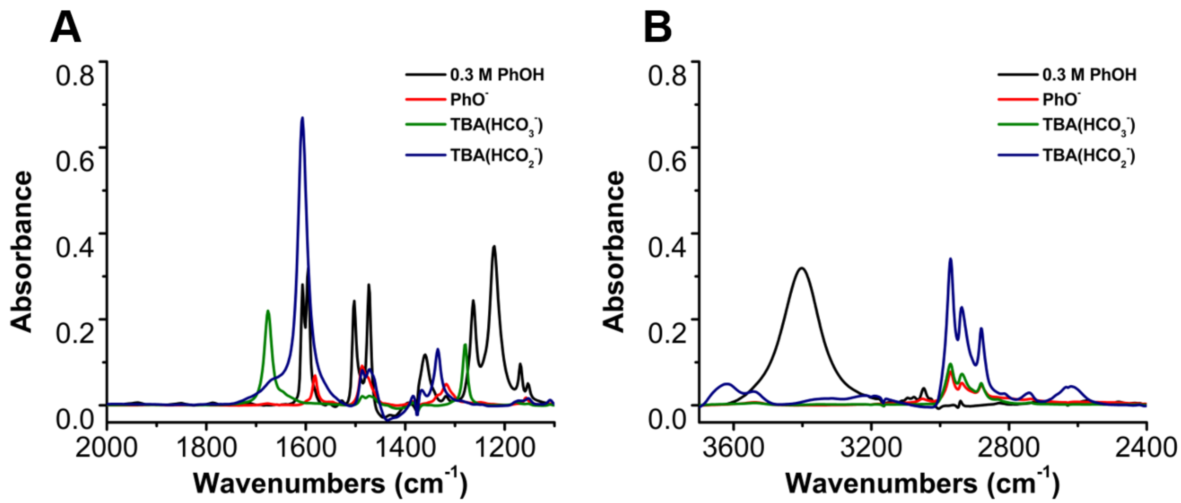

Figure S22. IR controls for the following with their corresponding v_{max}/cm^{-1} taken in MeCN: TBA(HCO_2^-) 1333 cm^{-1} and 1608 cm^{-1},[6] TBA(HCO_3^-) (1676 cm^{-1}), PhO^- (1589 cm^{-1}) and PhOH (3408 cm^{-1}) in MeCN.

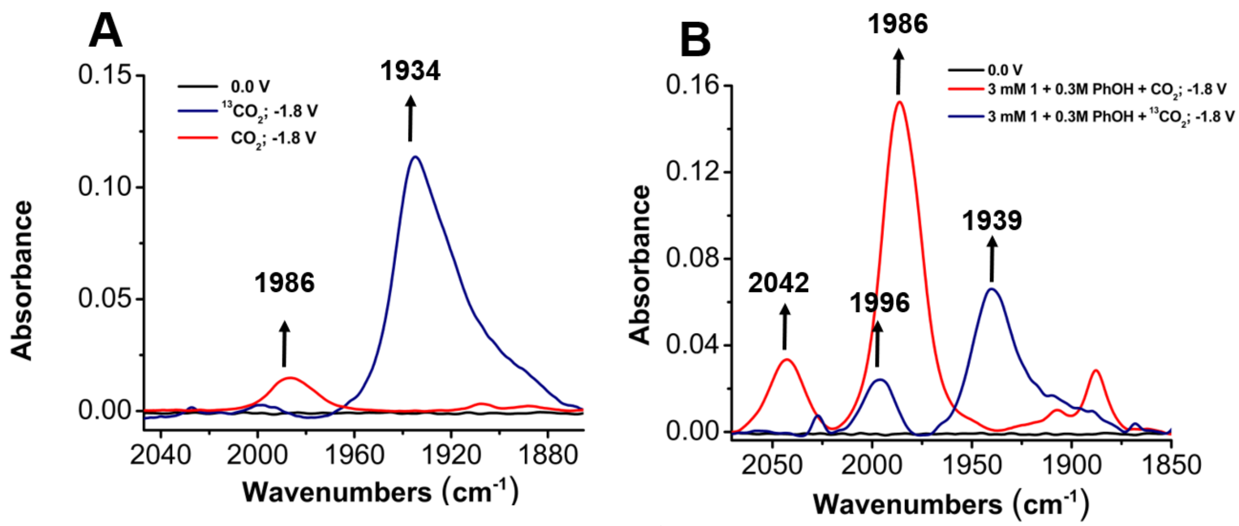

Figure S23. A comparison of the [Ni(TPEN)(CO)]$^+$ stretch with labeled CO_2 without **(A)** and with 0.3 M solution of PhOH **(B)**. Conditions: 3 mM solution of **(1)**; $^{13}CO_2$ and CO_2 sparged for ~ 30s; 0.1 M $TBAPF_6$/MeCN; referenced to internal ferrocene standard.

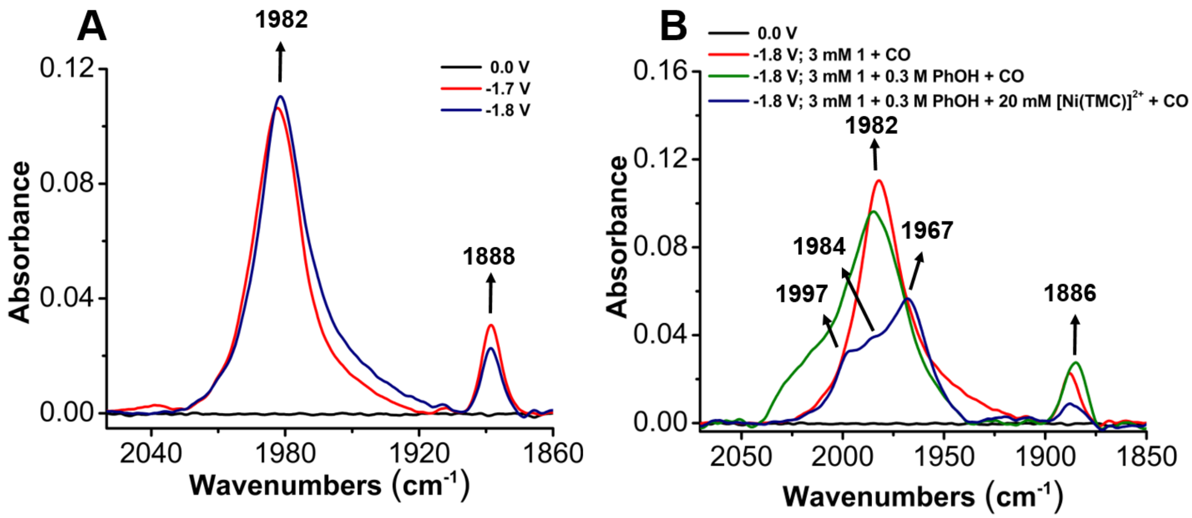

Figure S24. A) IR-SEC analysis of a 3 mM solution of $[Ni(TPEN)](PF_6)_2$ **1** with CO sparged into solution for ~30 s. **B)** Different conditions with catalyst under CO. Ni-CO stretch from $[Ni(TMC)(CO)]^+$ grows in at 1967 cm^{-1} with a shoulder associated with Ni-CO stretch from $Ni(\kappa^4\text{-}TPEN)(CO)]^+$ at 1984 cm^{-1}. Conditions: 0.1 M $TBAPF_6$/MeCN; referenced to internal ferrocene standard.

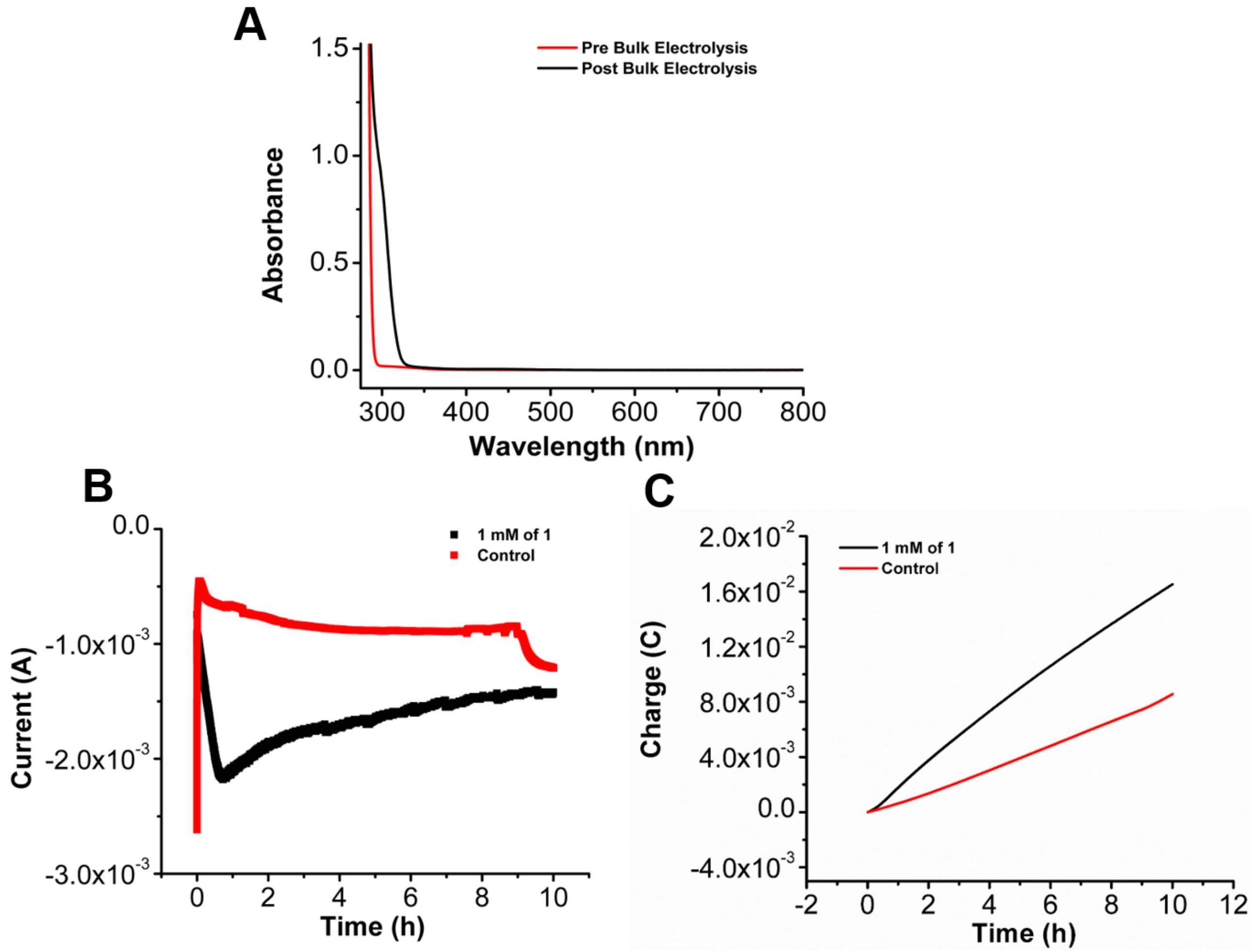

Figure S25. **A)** UV-Vis of the bulk solution before and after electrolysis. **B)** Current vs time plot of electrolysis experiment held at -2.05 V vs Fc/Fc$^+$. **C)** Charge passed during electrolysis experiment. Conditions: 1 mM of $[Ni(TPEN)](PF_6)_2$ **1**; 0.5 M PhOH; 0.1 M $TBAPF_6$/MeCN, graphite working electrode, graphite carbon counter electrode, Ag/AgCl pseudoreference electrode, and 0.5 M Fc was used as a sacrificial oxidant.

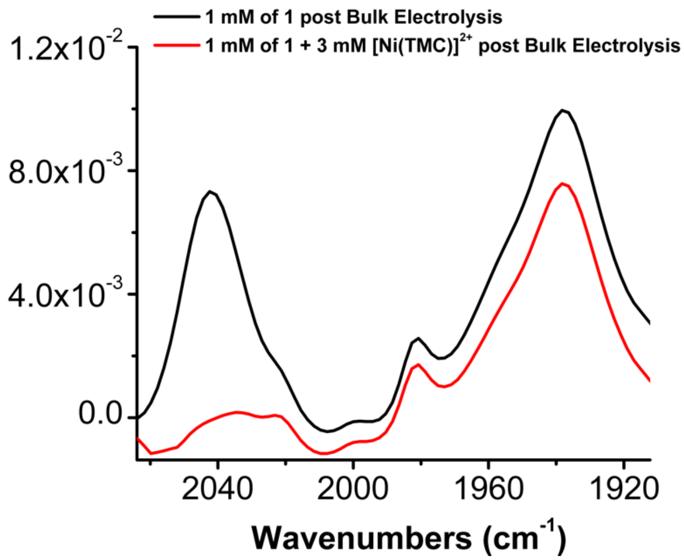

Figure S26. IR comparison between the post bulk electrolysis experiments of [Ni(TPEN)](PF_6)$_2$ **1** with and without [Ni(TMC)]$^{2+}$. Ni(CO)$_4$ appears at 2042 cm^{-1} while the Ni-CO stretch is observed at 1981 cm^{-1} in both solutions.

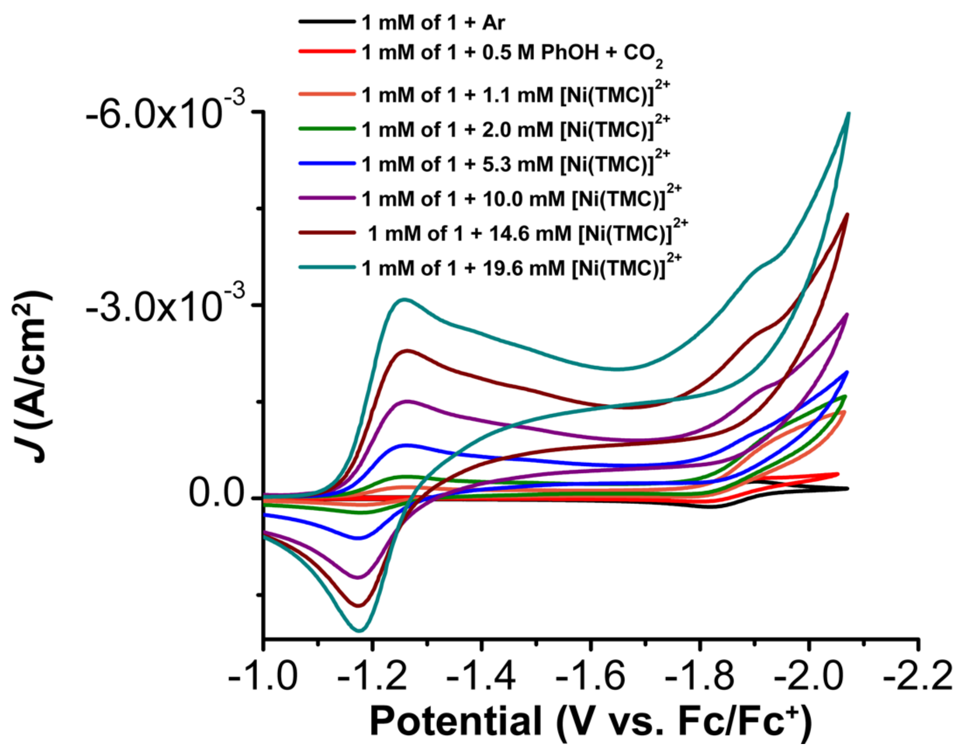

Figure S27. CVs of [Ni(TPEN)](PF_6)$_2$ **1** at 1 mM, obtained under CO_2 saturation with 0.5 M PhOH and with [Ni(TMC)]$^{2+}$ titrations. Conditions: 1 mM analyte; 0.1 M TBAPF$_6$/MeCN glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

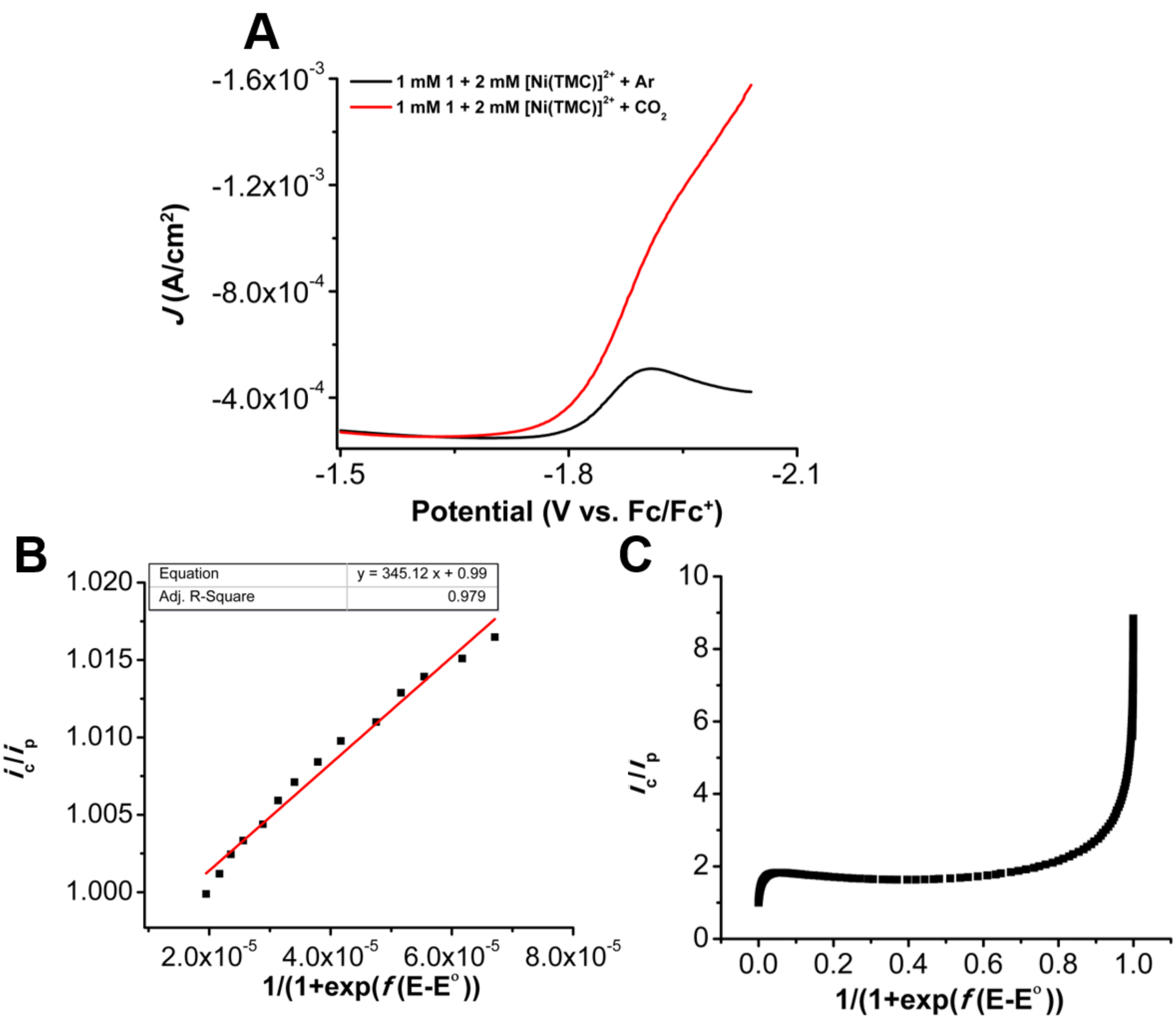

Figure S28. A) CV overlay between catalytic current under CO_2 with phenol (red trace) and 1 mM of $[Ni(TPEN)](PF_6)_2$ **1**, and 2 mM $[Ni(TMC)]^{2+}$ under Ar (black trace) **B.)** Linear region from the FOWA. **C.)** Entire region of i_c/i_p vs 1/(1+exp(*f* (E-E°)). Conditions: 1 mM **1**; 2 mM $Ni(TMC)[PF_6]_2$; 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

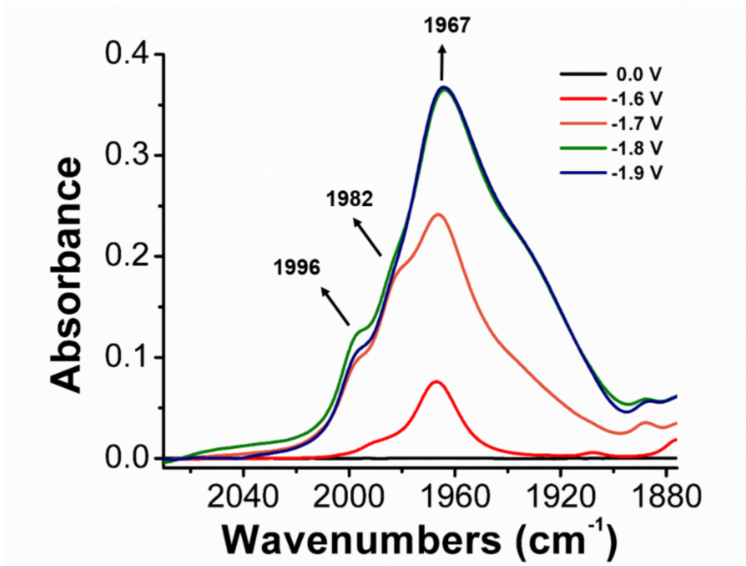

Figure S29. IR-SEC analysis of a 3 mM solution of $[Ni(TPEN)](PF_6)_2$ **1** with CO_2 in a solution containing 20 mM of $[Ni(TMC)](PF_6)_2$. Ni-CO stretch from $[Ni(TMC)(CO)]^+$ grows in at 1967 cm^{-1} with a shoulder associated with Ni-CO stretch from $Ni(\kappa^4\text{-TPEN})(CO)]^+$ at 1982 cm^{-1}. Conditions: 0.1 M $TBAPF_6$/MeCN; referenced to internal ferrocene standard.

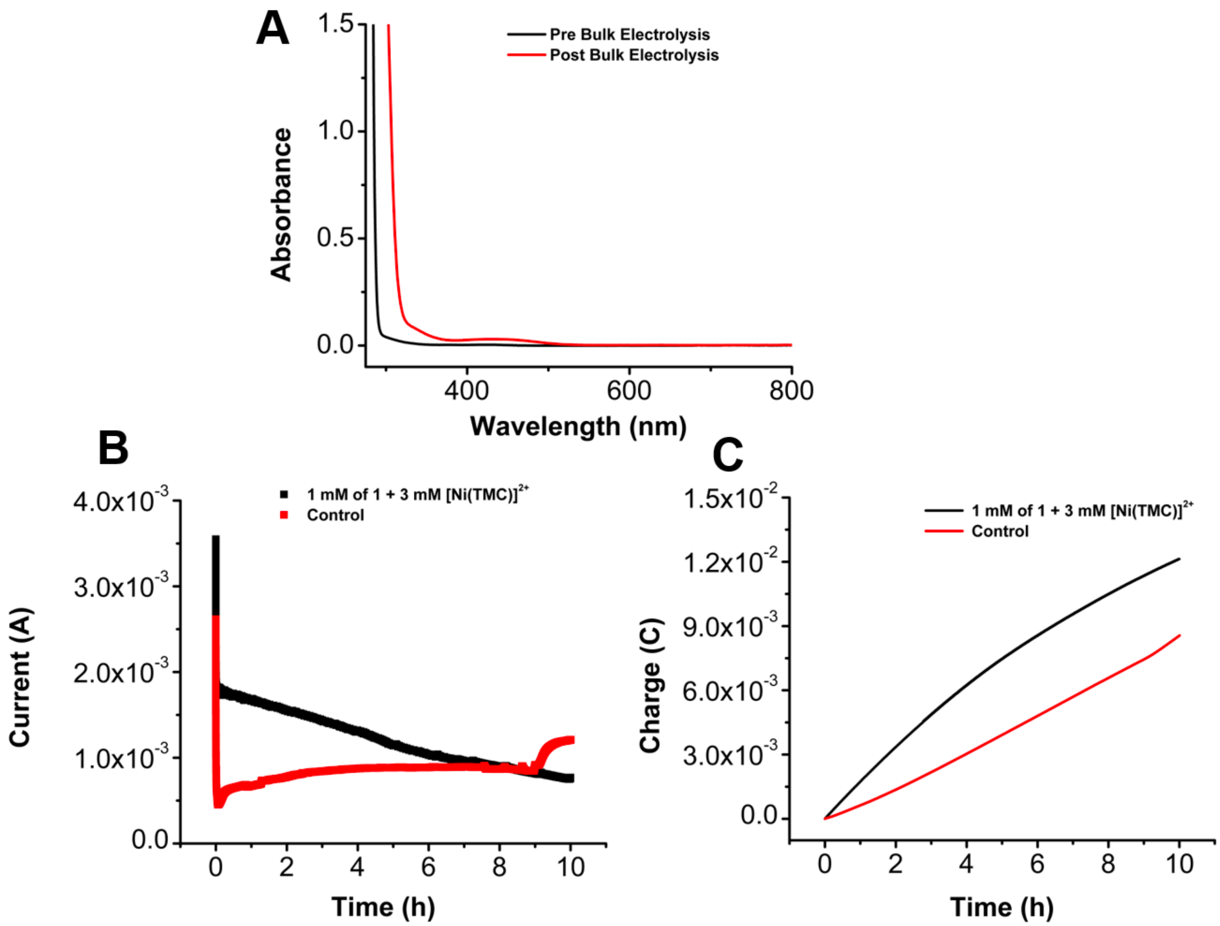

Figure S30. **A)** UV-Vis of the bulk solution before and after electrolysis. **B)** Current vs time plot of control electrolysis experiment held at -2.05 V vs Fc/Fc^{+}. **C)** Charge passed during control electrolysis experiment. Conditions: 1 mM of $[Ni(TPEN)](PF_6)_2$ **1**; 3 mM $[Ni(TMC)]^{2+}$; 0.5 M PhOH; 0.1 M $TBAPF_6$/MeCN, graphite working electrode, graphite carbon counter electrode, Ag/AgCl pseudoreference electrode, and 0.5 M Fc was used as a sacrificial oxidant.

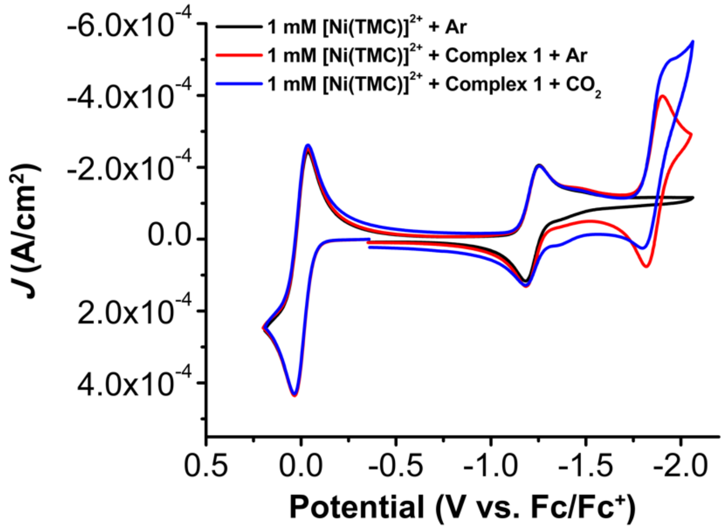

Figure S31. CVs of [Ni(TPEN)](PF_6)$_2$**1** (1 mM) obtained under Ar and then Ar and CO_2 upon the addition of 1 mM of [Ni(TMC)]$^{2+}$. Conditions: 0.1 M $TBAPF_6$/MeCN, glassy carbon working electrode, glassy carbon counter electrode, Ag/AgCl pseudoreference electrode; scan rate 100 mV/s; referenced to internal ferrocene standard.

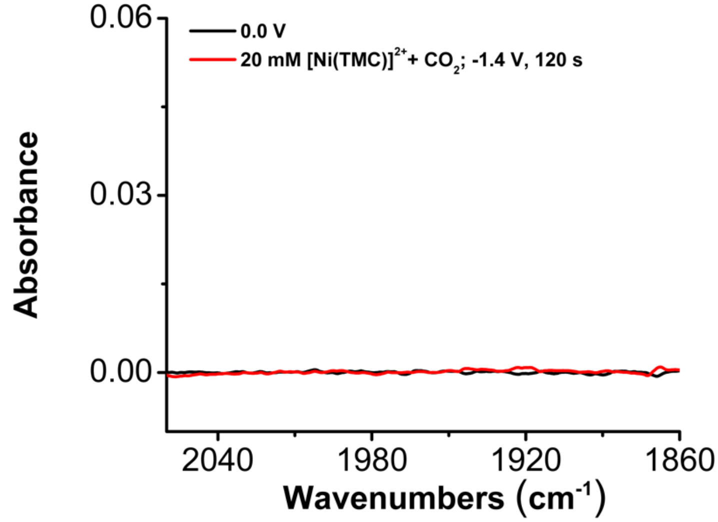

Figure S32. IR-SEC analysis of a 20 mM solution of [Ni(TMC)]$^{2+}$with CO_2, without the addition of [Ni(TPEN)](PF_6)$_2$ **1**. No carbonyl-containing species are observed. Conditions: 0.1 M $TBAPF_6$/MeCN; referenced to internal ferrocene standard.

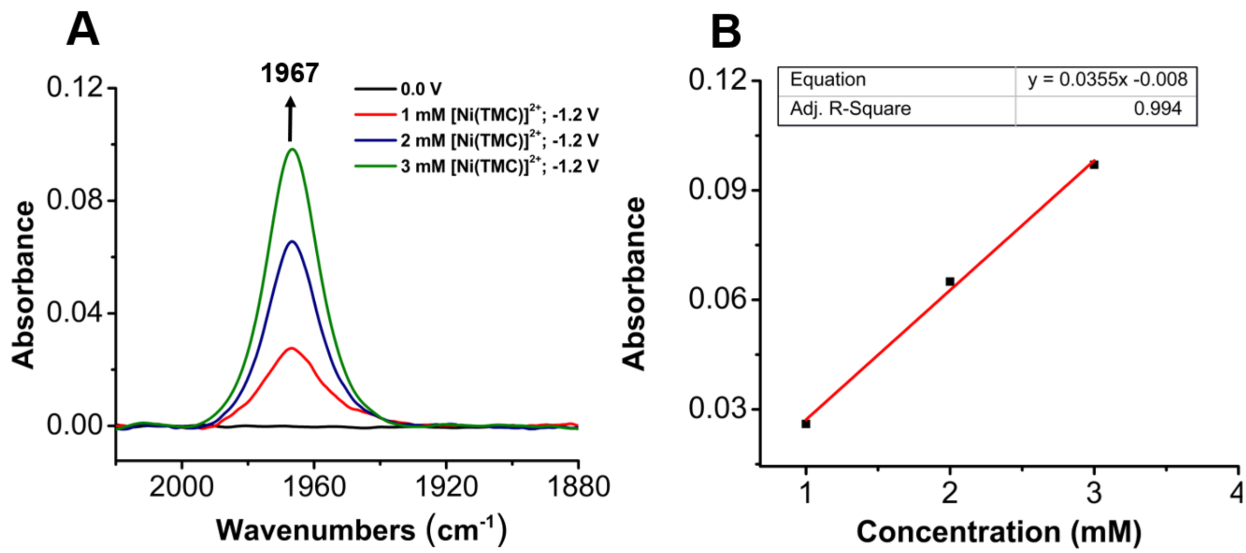

Figure S33. A) IR-SEC analysis of $[Ni(TMC)]^{2+}$ **1** with CO sparged into solution for ~30 s to show the $[Ni(TMC)(CO)]^{+}$ stretch at 1967 cm^{-1}. Conditions: 0.1 M $TBAPF_6$/MeCN; referenced to internal ferrocene standard. **B)** Linear fit of $[Ni(TMC)(CO)]^{+}$ absorbance.

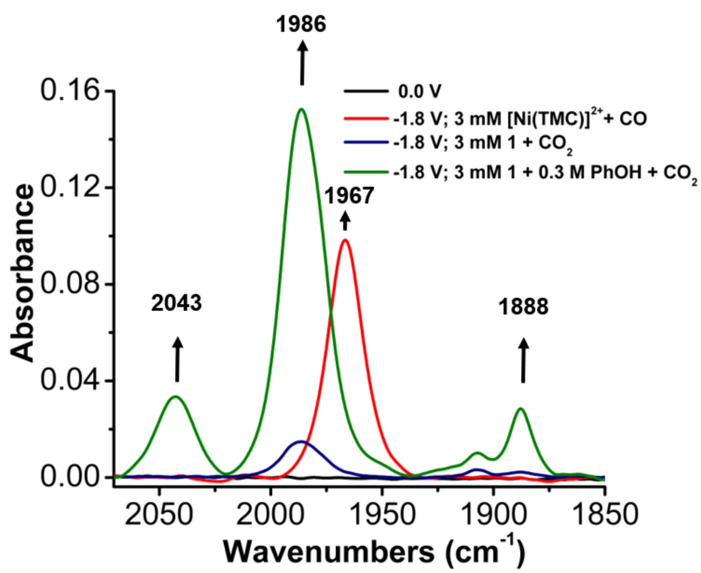

Figure S34. A comparison of the 3 mM solution of **(1)** with a 3 mM solution of $[Ni(TMC)]^{2+}$ to show the catalytic activity of $[Ni(TPEN)]^{2+}$.

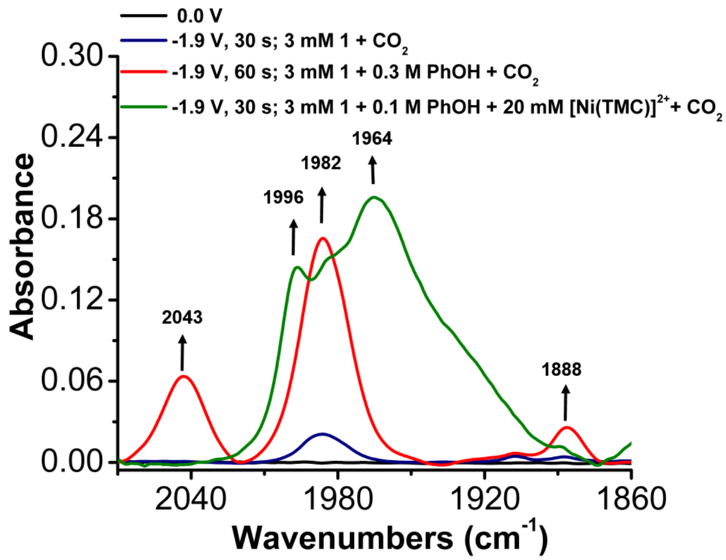

Figure S35. IR-SEC spectra overlaying of 3 mM Ni(TPEN)[PF_6]$_2$ **1** with the addition of 20 mM [Ni(TMC)]$^{2+}$ to show the loss of Ni(CO)$_4$ formation upon the addition of the CO scavenger. Timepoints: blue 60 s; red 30 s; green 60 s.

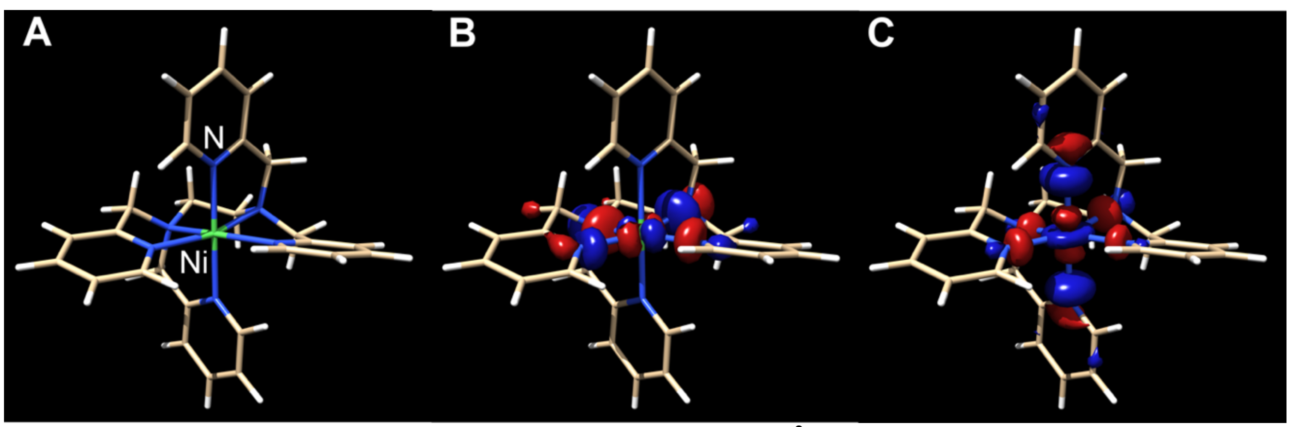

Figure 36. Kohn-Sham orbital representations of [Ni(TPEN)]$^{2+}$ **1** (A); SOMO-I (B); and SOMO-II (C). ORCA 4.0; B3LYP/G; ZORA; def2-TZVP; CPCM(Acetonitrile), 2S+1 = 3.

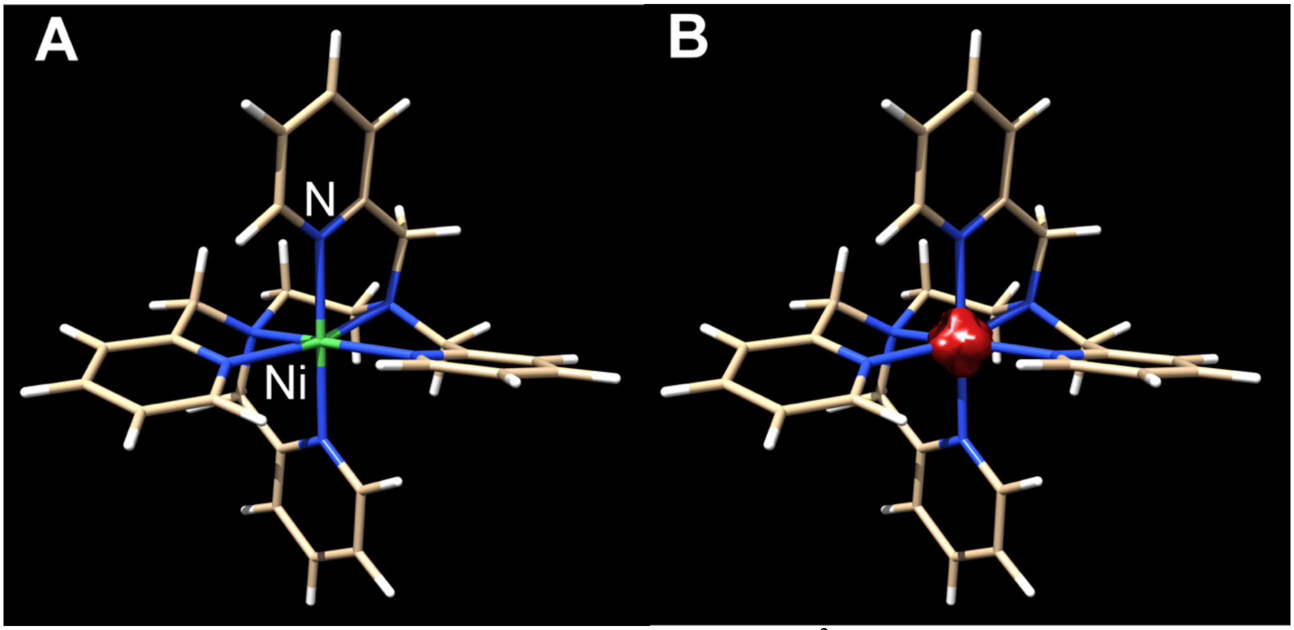

Figure S37. Calculated spin density localization of $[Ni(TPEN)]^{2+}$ **1**. ORCA 4.0; B3LYP/G; def2-TZVP; CPCM(Acetonitrile), 2S+1 = 3.

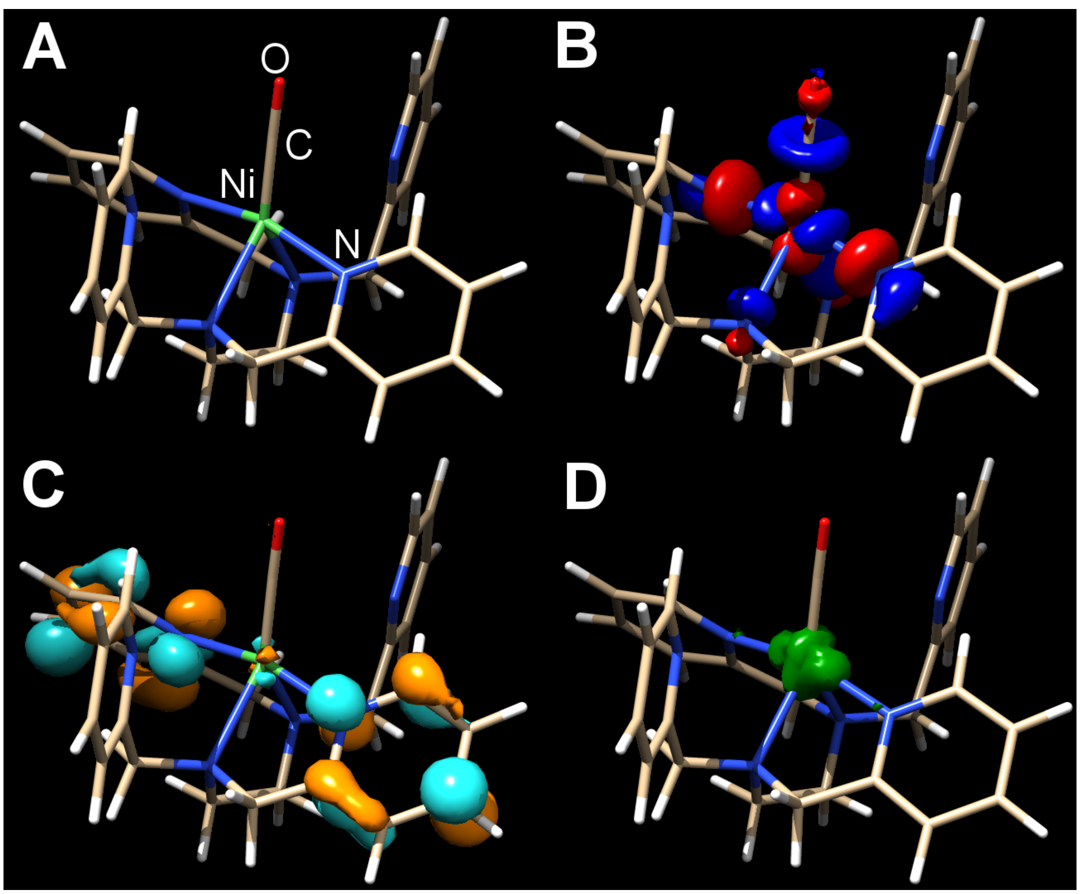

Figure S38. Kohn-Sham orbital representations of the SOMO (B) and LUMO (C) of $[Ni(TPEN)(CO)]^{+}$ **5** (A); spin density (D). ORCA 4.0; B3LYP/G; def2-TZVP; CPCM(Acetonitrile), 2S+1 = 2.

Table S1. The peak to peak separation as well as the peak current ratio for both **1** and the internal Fc/Fc^+ reference at 100 mV/s.

Scan Rate (100mV/s)	i_{pa} **(*J*(A/cm²))**	i_{pc} **(*J*(A/cm²))**	E_{pa} **(V)**	E_{pc} **(V)**	**|ΔE| (V)**	$\|i_{pa}/i_{pc}\|$ **(*J*(A/cm²))**
Fc/Fc^+	4.88×10^{-4}	-5.00×10^{-4}	0.035	-0.032	0.067	9.76×10^{-1}
1	2.06×10^{-4}	-2.23×10^{-4}	-1.82	-1.89	0.07	9.26×10^{-1}

Foot-of-the-Wave Calculations[5]

$$\frac{i_c}{i_p} = \frac{2.24 n_{cat}^{\sigma} \sqrt{\frac{RT}{F\nu} k_{cat} C_{substrate}}}{1 + \exp\left[\frac{F}{RT}(E - E^0)\right]}$$

where $n_{cat}^{\sigma} = 2$, $\frac{RT}{F\nu} = 0.256796$ s, $k_{cat} = k_{obs}$[catalyst]; $E^{\circ} = E_{1/2}$(1 mM Ni(II)/Ni(I)) = -1.86 V vs Fc/Fc^+.[5]

Table S2. FOWA analysis of **1** with PhOH titrations; $\boldsymbol{k_{cat}}$ assumes first-order concentration dependences for [PhOH] and [CO_2] for simplicity.

Phenol Concentration (M)	$\mathbf{TOF_{max}}$ (s^{-1})	[Ni(TPEN)](PF_6)$_2$ $\boldsymbol{k_{cat}}$ ($M^{-2}s^{-1}$)
0.24	2.18×10^2	3.24×10^3
0.5	2.67×10^2	3.97×10^3
0.75	4.02×10^3	6.00×10^4
1.0	3.60×10^4	5.36×10^5
1.48	1.02×10^5	1.51×10^6
1.98	3.70×10^5	5.51×10^6
2.49	7.72×10^8	1.15×10^{10}

Table S3. FOWA analysis of **1** with $[Ni(TMC)]^{2+}$ titrations at 0.5 M PhOH.

[Ni(TMC)](PF_6)$_2$ (mM)	$\mathbf{TOF_{max}}$ (s^{-1})	[Ni(TPEN)](PF_6)$_2$ $\boldsymbol{k_{cat}}$ ($M^{-2}s^{-1}$)
1	7.96×10^5	4.02×10^9
2	2.31×10^4	1.17×10^8
5	2.74×10^4	1.39×10^8

Table S4. Crystal data and structure refinement for machan02q.
CCDC 1816890

Identification code	CWM-002	
Empirical formula	C26 H28 F12 N6 Ni P2	
Formula weight	773.19	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 13.8699(6) Å	α = 90°.
	b = 17.1455(7) Å	β = 100.970(2)°.
	c = 14.2982(8)	γ = 90°.
Volume	3338.1(3) $Å^3$	
Z	4	
Density (calculated)	1.539 Mg/m^3	
Absorption coefficient	0.772 mm^{-1}	
F(000)	1568	
Crystal size	0.26 x 0.15 x 0.1 mm^3	
Theta range for data collection	2.565 to 26.027°.	
Index ranges	-11<=h<=17, -21<=k<=20, -17<=l<=12	
Reflections collected	15877	
Independent reflections	6314 [R(int) = 0.0550]	
Completeness to theta = 25.242°	96.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.4293 and 0.3852	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6314 / 0 / 424	
Goodness-of-fit on F^2	1.011	
Final R indices [I>2sigma(I)]	R1 = 0.0471, wR2 = 0.0906	
R indices (all data)	R1 = 0.0902, wR2 = 0.1046	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.516 and -0.424 e.$Å^{-3}$	
SQUEEZE	154e/unit cell (roughly four hexane)	

Geometry-Optimized DFT Coordinates

[Ni(κ^6-TPEN)]$^{2+}$; 2S+1=3

Ni	6.271361	12.877217	12.070347
N	4.546489	11.748955	11.624644
N	7.936293	14.087427	12.527486
N	5.058258	13.480623	13.715087
N	7.024973	12.616755	10.126526
C	6.535656	11.845593	14.750365
N	6.833099	11.444606	13.501538
C	3.576296	11.831845	12.538833
N	5.618725	14.697368	11.155956
C	6.406484	13.416597	9.239812
C	5.907552	13.213023	14.886690
H	5.349323	13.281472	15.823029
H	6.692694	13.968886	14.918500
C	5.297967	14.290995	9.778850
H	5.142508	15.150513	9.123087
H	4.368197	13.722437	9.797535
C	7.900229	15.314867	12.002038
C	3.819018	12.675347	13.761941
H	2.958269	13.324167	13.932900
H	3.864995	12.003809	14.620573
C	9.017743	13.702631	13.221490
H	9.002092	12.699586	13.619779
C	8.011045	11.815257	9.715605
H	8.488527	11.207445	10.472294
C	4.460657	15.107491	11.977819
H	3.608520	14.492736	11.693341
H	4.191151	16.149349	11.789786
C	8.417213	11.759507	8.393091
H	9.219919	11.097748	8.101392
C	4.784874	14.910118	13.453637
H	5.672241	15.480456	13.725282
H	3.959857	15.273811	14.070922
C	6.702182	15.703772	11.177287
H	6.314867	16.659921	11.534054
H	7.044122	15.880644	10.156783
C	2.383279	11.130242	12.402149
H	1.615355	11.227172	13.157743
C	4.375841	10.952721	10.559385
H	5.191496	10.911660	9.852024
C	7.394720	10.248139	13.308788
H	7.597290	9.967393	12.284144
C	6.808396	11.045282	15.848836
H	6.547165	11.387638	16.840315
C	3.224207	10.217993	10.358707
H	3.130969	9.589368	9.484939
C	6.763936	13.420503	7.900419
H	6.257644	14.082718	7.211899
C	7.704542	9.399007	14.357726
H	8.159670	8.439790	14.159227
C	7.408749	9.808994	15.651119
H	7.631720	9.170171	16.494747
C	2.203276	10.314367	11.299258
H	1.283476	9.759379	11.174035
C	8.949450	16.212301	12.173973
H	8.884387	17.201677	11.742847
C	7.777435	12.575479	7.469279
H	8.072253	12.563805	6.428770
C	10.101926	14.532456	13.426588
H	10.952441	14.179189	13.991381
C	10.063463	15.817502	12.894195
H	10.891159	16.498708	13.038750

[Ni(κ5-TPEN)]+; 2S+1=2

Ni	6.498403	12.830453	12.138965
N	4.779259	11.681902	11.833517
N	8.131724	13.971546	12.345123
N	5.026442	13.663898	13.802202
N	6.780289	12.497202	9.102165
C	6.392302	11.997532	14.954334
N	6.900211	11.562878	13.788527
C	3.813609	11.734480	12.758405
N	5.773472	14.606858	11.017891
C	6.298621	13.697707	8.761356
C	5.841937	13.407138	14.975108
H	5.298063	13.564475	15.915899
H	6.680947	14.106113	14.963860
C	5.254938	14.297484	9.666689
H	4.841067	15.196920	9.196696
H	4.444847	13.580913	9.796498
C	8.010086	15.244017	11.927687
C	3.799992	12.889507	13.746113
H	2.963656	13.540639	13.476973
H	3.554091	12.492016	14.735126
C	9.169738	13.661847	13.143815
C	7.720005	11.948849	8.333776
H	8.084334	10.975020	8.642128
C	4.665175	15.122519	11.851073
H	3.780032	14.533299	11.612826
H	4.440029	16.161237	11.580918
C	8.224510	12.557747	7.189704
H	8.989629	12.068675	6.602352
C	4.922775	15.044128	13.351952
H	5.853231	15.554358	13.602070
H	4.114879	15.587747	13.861264
C	6.897287	15.554525	10.961550
H	6.556220	16.583863	11.109851
H	7.333364	15.518926	9.962572
C	2.806738	10.774710	12.815549
H	2.044702	10.844316	13.581382
C	4.759607	10.690254	10.930272
C	7.395730	10.323970	13.720540
C	6.365889	11.188817	16.082491
H	5.933875	11.564696	16.999847
C	3.792498	9.700944	10.923720
C	6.736842	14.374668	7.626548
C	7.406612	9.457452	14.803552
C	6.880621	9.900726	16.009249
C	2.795348	9.742519	11.892148
C	8.904506	16.234631	12.314413
H	8.756657	17.249010	11.968569
C	7.714619	13.795822	6.826875
C	10.106862	14.589581	13.557753
C	9.970891	15.909695	13.139354
H	8.072703	14.305205	5.942067
H	6.322001	15.343042	7.381318
H	9.227701	12.632115	13.464528
H	10.676090	16.667421	13.453091
H	10.919834	14.282204	14.200860
H	7.812591	8.461554	14.696671
H	6.860492	9.252918	16.875622
H	7.791257	10.020003	12.759881
H	5.549988	10.724976	10.193507
H	3.823092	8.917869	10.178457
H	2.024007	8.983956	11.925911

[Ni(κ[5]-TPEN)(CO_2)]$^+$; 2S+1=2

Ni	6.651240	12.675429	12.287086
N	5.006555	11.488279	11.828454
N	8.074521	14.085183	12.746304
N	5.250869	13.482674	13.772450
N	6.154596	12.223867	8.550470
C	6.556162	11.967004	15.161011
N	7.069067	11.462233	14.025737
C	3.894818	11.785604	12.517488
N	5.868106	14.376693	11.044059
C	6.124314	13.555880	8.641062
C	5.924525	13.330799	15.065960
H	5.242075	13.490372	15.905253
H	6.703498	14.090897	15.135244
C	5.238747	14.138491	9.708197
H	4.825373	15.087520	9.350582
H	4.413266	13.451088	9.873179
C	7.980223	15.234278	12.066394
C	4.009896	12.693254	13.714629
H	3.136264	13.346734	13.768191
H	3.963137	12.054386	14.598336
C	9.012716	13.956323	13.692328
C	6.913952	11.666494	7.609032
H	6.915583	10.581988	7.572558
C	4.793233	14.970624	11.888383
H	3.873422	14.434027	11.660225
H	4.631769	16.014660	11.604034
C	7.672941	12.401218	6.706965
H	8.274005	11.898867	5.961234
C	5.057158	14.884017	13.376531
H	5.947807	15.443250	13.652231
H	4.213368	15.336156	13.908992
C	7.011641	15.295150	10.920679
H	6.673642	16.324181	10.766962
H	7.580921	15.000265	10.040948
C	2.666720	11.215992	12.204790
H	1.789009	11.496089	12.770828
C	4.936667	10.575306	10.849776
C	7.646515	10.256883	14.053628
C	6.614463	11.272606	16.360422
H	6.177930	11.703904	17.250494
C	3.754748	9.946815	10.501123
C	6.830351	14.372406	7.760213
C	7.747786	9.507032	15.215268
C	7.223414	10.025727	16.390801
C	2.592410	10.285875	11.180744
C	8.813718	16.310831	12.346086
H	8.700131	17.232356	11.792242
C	7.621928	13.786238	6.782383
C	9.889524	14.976007	14.012625
C	9.780879	16.181961	13.329514
C	8.045688	11.838936	10.917955
O	8.023349	10.624314	11.013539
O	8.642920	12.700869	10.307075
H	8.183821	14.399795	6.090323
H	6.755909	15.448950	7.837450
H	9.051212	13.005119	14.201938
H	10.439961	17.008146	13.560055
H	10.632078	14.826135	14.783191
H	8.221518	8.536314	15.190101
H	7.275885	9.465202	17.314525
H	8.025869	9.898217	13.108368
H	5.858095	10.361017	10.339625
H	3.750312	9.217652	9.703273
H	1.646631	9.829020	10.922196

[Ni(κ[5]-TPEN)(CO_2H)]$^+$; 2S+1=3

Ni	6.719180	12.560728	12.224117
N	4.932973	11.424931	11.818142
N	8.112603	14.148695	12.757103
N	5.271604	13.425537	13.768801
N	6.088724	12.223591	8.546930
C	6.586222	11.907447	15.173465
N	7.119290	11.399198	14.052880
C	3.840929	11.788348	12.499591
N	5.872136	14.391102	11.026507
C	6.112858	13.555641	8.637482
C	5.944456	13.267489	15.063029
H	5.260126	13.428285	15.901076
H	6.722762	14.027859	15.135227
C	5.237478	14.173582	9.694441
H	4.855110	15.133570	9.328424
H	4.390978	13.511043	9.855463
C	7.973987	15.285681	12.068729
C	4.018030	12.653047	13.722507
H	3.155823	13.314503	13.835366
H	3.998462	11.980474	14.582261
C	9.032831	14.070438	13.722294
C	6.836076	11.634353	7.615865
H	6.792910	10.550627	7.580185
C	4.819447	14.966383	11.901140
H	3.889566	14.450477	11.665411
H	4.666214	16.023650	11.658980
C	7.637030	12.335305	6.723636
H	8.225597	11.807633	5.985445
C	5.088982	14.833739	13.387822
H	5.982691	15.381542	13.673394
H	4.248562	15.281995	13.929779
C	7.030485	15.287975	10.898544
H	6.711490	16.312373	10.678928
H	7.619857	14.938675	10.050474
C	2.579269	11.315864	12.157179
H	1.712814	11.645337	12.714177
C	4.820023	10.550015	10.812272
C	7.726827	10.210331	14.092154
C	6.649133	11.224854	16.380605
H	6.198588	11.654168	17.264741
C	3.602329	10.012457	10.433096
C	6.865421	14.341189	7.765793
C	7.835107	9.472884	15.261029
C	7.285177	9.991912	16.425875
C	2.457906	10.416186	11.109112
C	8.746415	16.405693	12.358422
H	8.600322	17.318162	11.797145
C	7.643537	13.721454	6.798082
C	9.850150	15.135344	14.059185
C	9.695119	16.330373	13.366021
C	8.081565	11.783654	10.904251
O	8.089254	10.404827	10.748888
O	8.924024	12.404655	10.273540
H	8.239232	14.310514	6.113001
H	6.835401	15.420011	7.841829
H	9.106689	13.122835	14.238018
H	10.304447	17.190942	13.607803
H	10.580485	15.028960	14.848608
H	8.331898	8.513462	15.251280
H	7.341656	9.441333	17.355362
H	8.125980	9.851407	13.153086
H	5.736009	10.295938	10.305670
H	3.555059	9.306507	9.615931
H	1.486263	10.033287	10.826925
H	8.796432	10.186530	10.111160

Ni(κ^5-TPEN)(CO)]$^+$; 2S+1=2

Ni	6.709516	12.554690	11.854048
N	4.903527	11.515842	11.580364
N	8.138192	14.022629	12.305718
N	5.501650	13.244079	13.679174
N	6.627046	12.549895	8.584806
C	6.728044	11.940737	15.423525
N	7.704959	11.377684	14.704833
C	3.948905	11.678901	12.501354
N	5.763633	14.406812	10.903894
C	6.146113	13.795163	8.508895
C	6.229540	13.287348	14.969032
H	5.587502	13.715429	15.747850
H	7.078608	13.954964	14.835667
C	5.156506	14.214314	9.564670
H	4.655563	15.135790	9.245891
H	4.397005	13.441389	9.666565
C	7.919995	15.257172	11.843463
C	4.322333	12.372516	13.781647
H	3.458604	12.921575	14.171762
H	4.538576	11.584517	14.503385
C	9.180222	13.801807	13.119627
C	7.521246	12.155267	7.680526
H	7.890258	11.140294	7.780535
C	4.692775	14.754011	11.859440
H	3.844381	14.102431	11.659055
H	4.351122	15.782384	11.690309
C	7.976279	12.971128	6.650661
H	8.705537	12.601940	5.942363
C	5.119210	14.621679	13.308755
H	5.971257	15.268722	13.507952
H	4.297939	14.973472	13.945341
C	6.799207	15.449066	10.859065
H	6.362854	16.445889	10.983471
H	7.257792	15.434328	9.870141
C	2.666714	11.167928	12.325205
H	1.915062	11.334223	13.085163
C	4.623974	10.821720	10.468176
C	8.155733	10.179691	15.072393
C	6.187886	11.321656	16.547997
H	5.400841	11.809329	17.107178
C	3.379359	10.267712	10.229222
C	6.535520	14.675847	7.502735
C	7.670500	9.485989	16.175608
C	6.668102	10.075958	16.931802
C	2.377221	10.450826	11.176114
C	8.737474	16.324763	12.201465
H	8.523152	17.314435	11.822000
C	7.464660	14.257610	6.558376
C	10.045760	14.808148	13.507736
C	9.815608	16.098261	13.041176
C	7.869607	11.276959	11.292266
O	8.636975	10.512763	10.920372
H	7.784796	14.926222	5.770140
H	6.120662	15.674076	7.467621
H	9.279990	12.789886	13.484293
H	10.463898	16.914215	13.331398
H	10.872025	14.585575	14.168057
H	8.073071	8.515933	16.431749
H	6.263336	9.576401	17.801916
H	8.945483	9.755280	14.461607
H	5.425087	10.753711	9.746280
H	3.199698	9.716600	9.317066
H	1.387409	10.043707	11.019303

IR Frequencies Calibration: 2077 cm^{-1} by calculation, 2043 cm^{-1} by experiment, 0.983

$[Ni(CO)_4]^0$; 2S+1=1

Ni	-6.263080	7.635617	-0.398814
O	-6.238815	6.641085	-3.200318
O	-9.015277	8.467393	0.356204
O	-4.466348	9.989314	-0.124617
O	-5.346613	5.462036	1.410211
C	-6.247694	7.023147	-2.131169
C	-7.965909	8.146801	0.065024
C	-5.149117	9.088720	-0.232440
C	-5.698459	6.293252	0.721472

References

1. G. A. Bain and J. F. Berry, *Journal of Chemical Education*, 2008, **85**, 532.
2. C. Piguet, *Journal of Chemical Education*, 1997, **74**, 815.
3. K. T. Ngo, M. McKinnon, B. Mahanti, R. Narayanan, D. C. Grills, M. Z. Ertem and J. Rochford, *Journal of the American Chemical Society*, 2017, **139**, 2604-2618.
4. A. J. Sathrum and C. P. Kubiak, *The Journal of Physical Chemistry Letters*, 2011, **2**, 2372-2379.
5. C. Costentin, S. Drouet, M. Robert and J.-M. Savéant, *Journal of the American Chemical Society*, 2012, **134**, 11235-11242.
6. C. A. B. Stephen C. Cheng, Michael G. Hill, and Kent R. Mann, *Inorg. Chem.*, 1996, **35**, 7704-7708.