Supporting information:

Cp_2Ni[1] and $[CpNi(COD)]BF_4$[2] were both synthesized according to literature procedures. DIB ligands were synthesised by sonication of the corresponding aniline with 2,3-butadione.

Synthesis of 1. A solution of $[Ni(cp)(cod)]BF_4$ (100 mg (0.314 mmol)) and Ph-DAB_{Me} (74 mg (0.314 mmol)) in dry THF (25 mL) were refluxed under Argon atmosphere for one hour. After the solution turned dark pink the solvent was removed and the solid recrystallized with DCM/ *n*-Hexane. Red crystals were obtained. Yield: 112 mg; 80%. Anal. Calc. for $C_{21}H_{21}N_2NiBF_4$ (found): C, 56.44 (55.65), H, 4.74 (4.72), N, 6.27 (6.15). ^{1}H NMR (250 MHz, CD_2Cl_2) δ [ppm]: 7.35 (dt, *J* = 28.0, 7.3 Hz, 6H), 7.06 (d, *J* = 7.4 Hz, 4H), 4.97 (s, 5H), 2.07 (s, 6H). ESI-MS: ($C_{21}H_{21}N_2Ni$) m/z 359.11

Synthesis of 2. A solution of $[Ni(cp)(cod)]BF_4$ (100 mg (0.314 mmol)) and 2-CF_3Ph-DAB_{Me} (116 mg (0.314 mmol)) in dry THF (25 mL) were refluxed under Argon atmosphere for one hour. After the solution turned dark purple the solvent was removed and the solid recrystallized with DCM/ *n*-Hexane. Purple crystals were obtained. Yield: 165 mg; 90%. Anal. Calc. for $C_{23}H_{19}BF_{10}N_2Ni$ (found): C, 47.39 (47.64), H, 3.29 (3.54), N, 4.81 (5.04). ^{1}H NMR (250 MHz, $CDCl_3$) δ [ppm]: 7.73 (m, 6H), 7.47 (t, *J* = 7.5 Hz, 2H), 4.95 (s, 5H), 2.10 (s, 6H). **MS:** m/z: ($C_{23}H_{19}F_6N_2Ni^+$): 495.08

Synthesis of 3. A solution of $[Ni(cp)(cod)]BF_4$ (100 mg (0.314 mmol)) and 2-OMePh-DAB_{Me} (93 mg (0.314 mmol)) in dry THF (25 mL) were refluxed under Argon atmosphere for one hour. After the solution turned dark red, the solvent was removed and the solid recrystallized with DCM/ *n*-Hexane. Red crystals were obtained. Yield: 151 mg; 95%. Anal. Calc. for $C_{23}H_{25}BF_4N_2NiO_2$ (found) C, 54.44 (54.42), H, 4.97 (5.01), N, 5.53 (5.61)**:** ^{1}H NMR (250 MHz, CD_2Cl_2) δ [ppm]: 7.38 (t, *J* = 6.7 Hz, 2H), 7.10 (dd, *J* = 18.2, 7.6 Hz, 6H), 5.00 (s, 5H), 3.95 (s, 6H), 2.05 (s, 6H). ESI-MS: m/z: ($C_{23}H_{25}N_2NiO_2^+$) 419.13

[1] W. L. Jolly, D. J. Chazan, N. A. D. Carey, H. C. Clark, in *Inorganic Syntheses*, John Wiley & Sons, Inc., **2007**, pp. 122-123.

[2] A. Salzer, T. L. Court, H. Werner, *J. Organomet. Chem.* **1973**, *54*, 325-330.

Table 1 Crystal data and structure refinement for of [CpNiL]BF4

Identification code	ac353_[CpNi(dab)]BF4	ac352_[CpNi(dabf)]BF4	ac354_[CpNi(dabome)]BF4
Empirical formula	$C_{21}H_{21}BN_2F_4Ni$	$C_{23}H_{19}BN_2F_{10}Ni$	C23H25BN2O2F4Ni
Formula weight	446.93	582.11	506.47
Temperature/K	100.02	99.99	100
Crystal system	orthorhombic	orthorhombic	monoclinic
Space group	Pnma	$Pca2_1$	Cc
a/Å	11.9844(8)	19.7420(17)	9.1415(8)
b/Å	15.3276(11)	7.5757(5)	21.906(2)
c/Å	10.8448(8)	15.8268(13)	11.8206(10)
α/°	90	90	90
β/°	90	90	104.863(4)
γ/°	90	90	90
Volume/Å^3	1992.1(2)	2367.0(3)	2287.9(4)
Z	4	4	4
ρ_{calc}g/cm^3	1.49	1.6333	1.4702
μ/mm^{-1}	1.019	0.913	0.903
F(000)	921.9	1176.8	1048.8
Crystal size/mm^3	0.594 × 0.194 × 0.167	0.209 × 0.188 × 0.116	0.322 × 0.198 × 0.105
Radiation	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.6 to 52.94	4.12 to 52.78	3.72 to 52.88
Index ranges	-15 ≤ h ≤ 15, -13 ≤ k ≤ 19, -12 ≤ l ≤ 13	-23 ≤ h ≤ 24, -9 ≤ k ≤ 6, -19 ≤ l ≤ 17	-11 ≤ h ≤ 11, -26 ≤ k ≤ 27, -14 ≤ l ≤ 14
Reflections collected	24840	16211	15856
Independent reflections	2133 [R_{int} = 0.0312, R_{sigma} = 0.0160]	4737 [R_{int} = 0.0703, R_{sigma} = 0.0946]	4550 [Rint = 0.0312, Rsigma = 0.0498]
Data/restraints/parameters	2133/90/139	4737/21/336	4550/108/334
Goodness-of-fit on F^2	1.067	1.008	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0311, wR_2 = 0.1099	R_1 = 0.0473, wR_2 = 0.0778	R1 = 0.0552, wR2 = 0.1373
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.1290	R_1 = 0.0834, wR_2 = 0.0892	R1 = 0.0673, wR2 = 0.1453
Largest diff. peak/hole / e Å^{-3}	0.69/-0.60	0.76/-0.70	0.55/-0.42
Flack parameter		-0.00(2)	8.539(15)

Bond	**1$^+$**	**2$^+$**	**3$^+$**	**Free Ligand (Ph){Kovach, 2011 #236}**	**Free Ligand (*o*-CF3){Bomfim, 2007 #235}**	**Free Ligand (*o*-Me)**
Ni1–N1	1.8544(16)	1.870(3)	1.866(4)			
Ni1–N2	1.8544(16)	1.867(3)	1.881(6)			
Ni1–Cp	1.699	1.714	1.718			
N1–C6	1.307(3)	1.301(5)	1.319(6)	1.281	1.280	1.280(2)
N2–C7	1.307(3)	1.317(5)	1.304(7)	1.281	1.280	1.280(2)
C6–C7	1.465(4)	1.472(6)	1.461(7)	1.503	1.513	1.502(2)

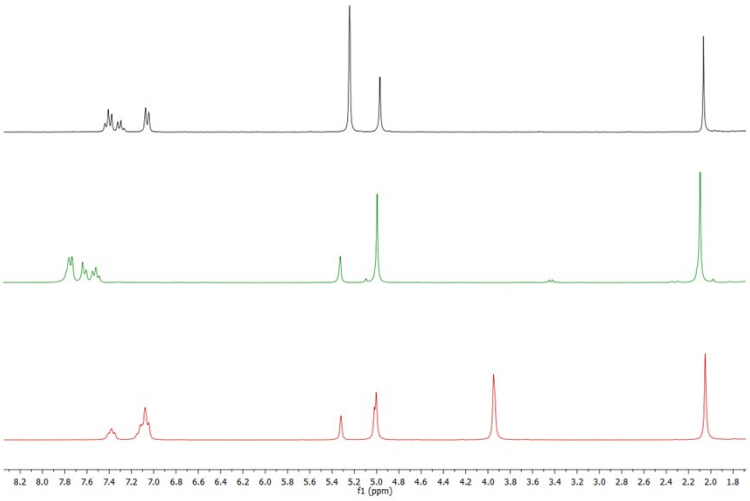

Figure S1. 1H-NMR of complexes $\mathbf{1}^{+}$,$\mathbf{2}^{+}$, and $\mathbf{3}^{+}$ in CD_2Cl_2

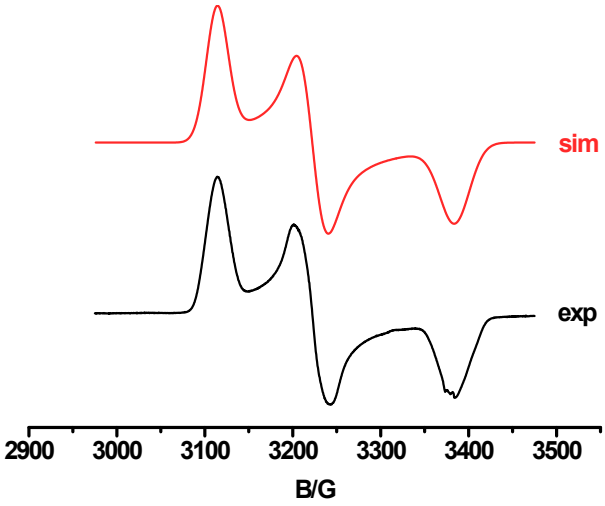

Figure S2. ESR Spectrum of the chemically reduced species $\mathbf{1}^{+}$ with Cp_2Co in toluene, 120 K

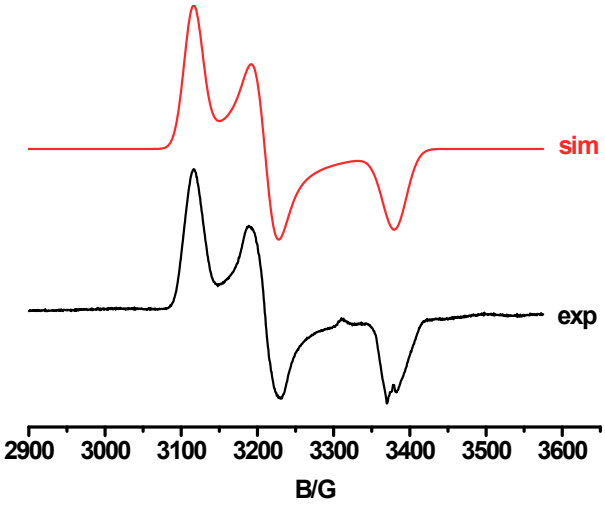

Figure S3. ESR Spectrum of the chemically reduced species $\mathbf{2}^{+}$ with Cp_2Co in toluene, 120 K

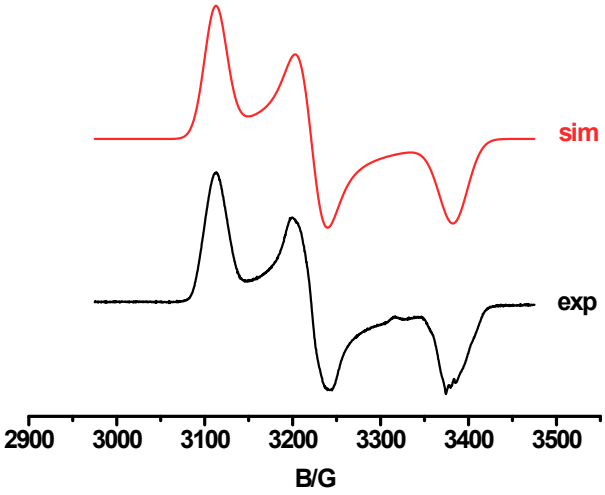

Figure S3. ESR Spectrum of the chemically reduced species $\mathbf{3}^{+}$ with Cp_2Co in toluene, 120 K

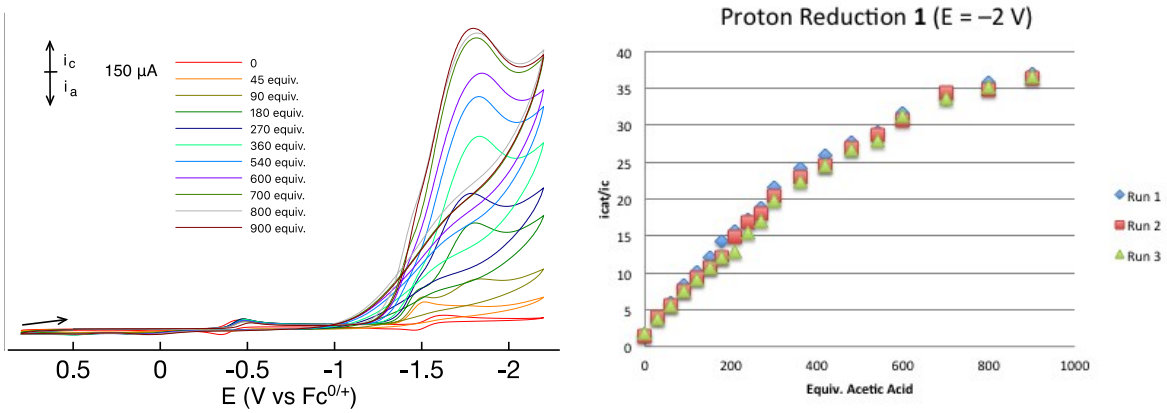

Figure S4. Electrocatalytic reduction of acetic acid by **1** in CH_3CN/0.1 M Bu_4NPF_6 at 298 K, the scan rate was 100 mV/s with a 1 mm glassy carbon working electrode, Pt counter electrode, Ag reference electrode. Catalytic current (ic) to the peak current of the Ni(II/I) couple in the absence of acid (i_c) as a function of the concentration of acetic acid. Select voltammograms displayed as example of a typical run, select plots are

displayed for clarity, full runs were performed at 30 equiv. of acetic acid intervals.

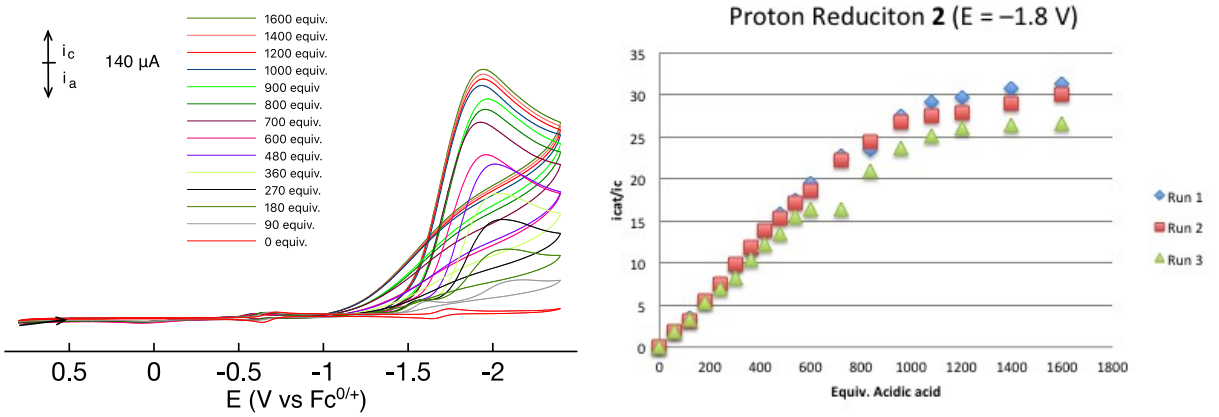

Figure S5. Electrocatalytic reduction of acetic acid by **2** in CH_3CN/0.1 M Bu_4NPF_6 at 298 K, the scan rate 100 mV/s with a 1 mm glassy carbon working electrode, Pt counter electrode, Ag reference electrode. Catalytic current (ic) to the peak current of the Ni(II/I) couple in the absence of acid (i_c) as a function of the concentration of acetic acid. Select voltammograms displayed as example of a typical run, select plots are displayed for clarity, full runs were performed at 30 equiv. of acetic acid intervals.

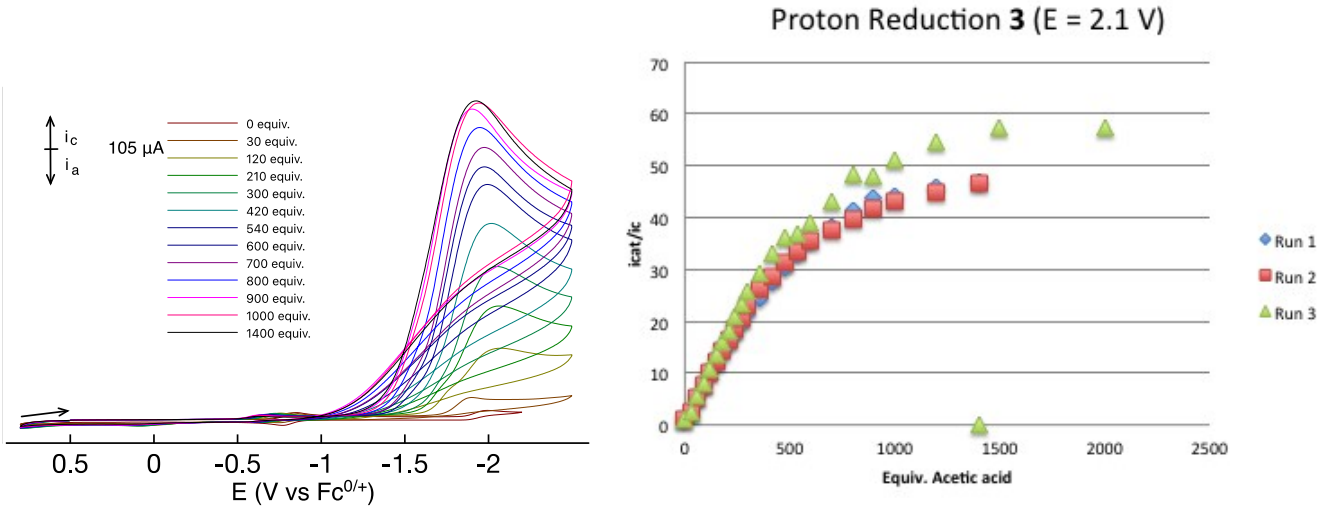

Figure S6. Electrocatalytic reduction of acetic acid by **3** in CH_3CN/0.1 M Bu_4NPF_6 at 298 K, the scan rate was 100 mV/s with a 1 mm glassy carbon working electrode, Pt counter electrode, Ag reference electrode. Catalytic current (ic) to the peak current of the Ni(II/I) couple in the absence of acid (i_c) as a function of the concentration of acetic acid. Select voltammograms displayed as example of a typical run, select plots are displayed for clarity, full runs were performed at 30 equiv. of acetic acid intervals.

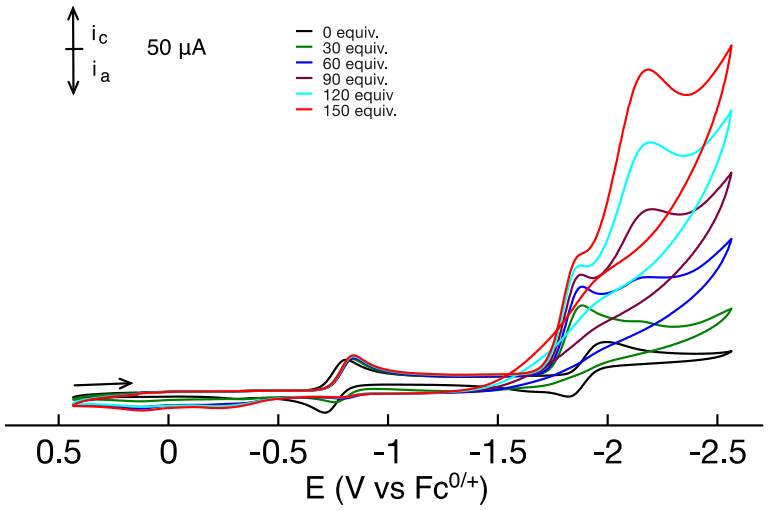

Figure S7. Electrocatalytic reduction of acetic acid at lower concentrations by **3** in CH_3CN/0.1 M Bu_4NPF_6 at 298 K, the scan rate was 100 mV/s with a 1 mm glassy carbon working electrode, Pt counter electrode, Ag reference electrode.

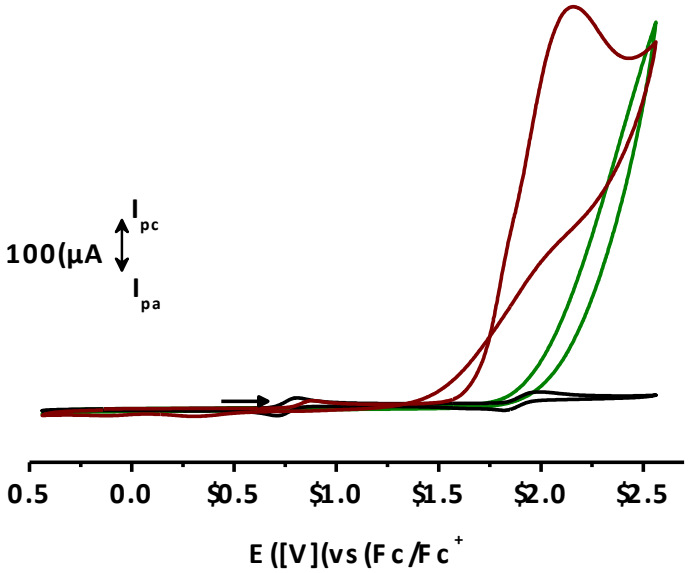

Figure S8. Cyclic voltammetry of acetic acid with **3** (red) and without **3** (green) in CH_3CN/0.1 M Bu_4NPF_6 at 298 K, the scan rate was 100 mV/s with a 1 mm glassy carbon working electrode, Pt counter electrode, Ag reference electrode.