

Carbazole-based N₄-donor Schiff base macrocycles: obtained metal free and as Cu(II) and Ni(II) complexes

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ELECTRONIC SUPPORTING INFORMATION

Experimental

General Details

¹H and ¹³C NMR spectra were recorded at 25 °C on a Varian 400 MHz Inova spectrometer. Infrared spectra were obtained on a Perkin Elmer Spectrum BX FT-IR System as pressed KBr discs. MS spectra were collected on a Bruker MicroTOF-Q spectrometer. UV-vis spectra were obtained on a Varian 500 Scan UV-vis-NIR spectrophotometer. All cyclic voltammetry experiments were carried out on solutions containing 1 mmolL⁻¹ compound and 0.1 mmolL⁻¹ TBAPF₆ electrolyte. The complexes were run in dry, distilled (over CaH₂) MeCN in a three-compartment three-electrode cell (25 mL working volume), using a platinum working electrode (1 mm diameter) connected to a 0.01 molL⁻¹ AgNO₃ reference electrode and a platinum plate serving as a counter electrode. Measurements were recorded with an IviumStat XRe unit at room temperature. The working electrode surface was cleaned using 0.015 mm alumina, washed with water and dried before every scan. The working volume was degassed by passing a stream of Ar through it for 15 min prior to the measurements and then maintaining an inert atmosphere of Ar over the solution during the measurements. Elemental analyses were carried out by the Campbell Microanalytical Laboratory at the University of Otago.

X-Ray crystallographic data for [CuL^{tBu}(H₂O)]OAc·0.5(Ether) was collected on a Bruker Kappa Apex II area detector diffractometer at 83 K using graphite monochromated Cu-K α radiation ($\lambda = 0.71073 \text{ \AA}$). The data sets were absorption corrected using SCALE. Structures were solved using direct or Patterson methods and refined against all F² data using SHELXL-97¹ with all non-hydrogen atoms anisotropic (Table S1). One of the two ^tBu groups was rotationally disordered about the C23-C31 bond (C32-C34:C35-C37 0.75:0.25 occupancy) so EADP C32 C35, EADP C33 C36, and EADP C34 C37, were used to make the thermal parameters for these pairs of 'opposite C atoms' equal. The oxygen atom (O52) of the half occupancy diethylether (C50-C51-O52-O53A-C50A) was located on a centre of inversion, and the attached C atom was disordered 50:50 across C51 and C53A; EADP and EXYZ on the terminal C atoms, C50 and C50A, ensured that they shared the same coordinates and thermal parameters. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached, with U(H) = 1.2 U(attached atom), except for those on the amine (N3) and water (O1) atoms for which the hydrogen atoms were located from difference maps and allowed to freely refine (both coordinates and U_{iso}).

X-Ray crystallographic data for [NiL^H]OAc-EtOH was collected on an Oxford Diffraction SuperNova diffractometer with an Atlas CCD, equipped with a Cryostream N₂ open-flow cooling device, using mirror monochromated microfocus Cu K α radiation at 100 K. Scans were performed in such a way as to collect a complete set of unique reflections to a maximum resolution of 0.80 Å. Raw frame data (including data reduction, interframe scaling, unit cell refinement, and absorption corrections) were processed using CrysAlis Pro.² Structures were solved using SUPERFLIP³ and refined against all F² data using SHELXL-2014.⁴ Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached, with U(H) = 1.2 U(attached atom). The lower half of the complex was disordered over two sites 0.65:0.35 occupancy for (Ni1-N2-C14-C15-N3-C16-C17) : (Ni1B-N102-C114-C115-N103-C116-C117). The lower occupancy sites were all refined isotropically, except C117 which shared to same position as C17 (EADP and EXYZ used to ensure they had the same coordinates and thermal parameters) and was refined anisotropically; N2 was also refined isotropically. Both the acetate anion and the ethanol molecule are disordered. The acetate anion is split into two parts 0.65:0.35 occupancy (C51-C50-O50-O51) : (C151-C150-O150-O151), with all atoms anisotropic (ISOR applied to the 0.35 occupancy atoms O150 C150), that share a methyl carbon atom = C51/C151 (EADP and EXYZ to ensure they have the same coordinates and thermal parameters). The ethanol molecule is two sites for the oxygen atom O60:O160 with 0.65:0.35 occupancy; all atoms anisotropic in order to add H-atoms the full occupancy CH₂ group was split into C60/C160 (EADP and EXYZ to ensure they have the same coordinates and thermal parameters) 0.65:0.35 occupancy. Hydrogen atoms were inserted at calculated positions and rode on the atoms to which they were attached, with U(H) = 1.2 U(attached atom).

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre, CCDC 1520894-1520895.

Organic synthesis

1,8-Diformyl-3,6-di-tert-butyl-9H-carbazole (1^{tBu})

Prepared from 1,8-dibromo-3,6-di-tert-butyl-9H-carbazole,⁵⁻⁶ according to the method described by Gibson and co-workers.⁶ A solution of 1,8-dibromo-3,6-di-tert-butyl-9H-carbazole (2.50 g, 5.7 mmol) in degassed dry THF (125 mL) was cooled to 0 °C and n-BuLi (1.6 M solution in pentane: 3.87 mL, 6.2 mmol) was added. It was stirred for 1 h at this temperature. Then the reaction mixture was allowed to warm to room temperature while bubbling CO₂ (dried by passing through a CaCl₂ filled wash bottle) through the solution for 25 min. During this the colour changed from yellow to green. The solvent was then removed on a rotary evaporator, refilling the flask with argon. The dark orange residue was taken up again in dry degassed THF (125 mL), cooled to -78 °C and t-BuLi (1.5 M in hexane: 16.68 mL, 25.0 mmol) was added. This stirred solution was allowed to warm to 0 °C over 2hrs, after which it was cooled again to -78 °C. Dimethylformamide (2.01 g, 2.22 mL, 28.6 mmol) was added and then the mixture was allowed to warm up to room temperature while stirring

overnight. On addition of the DMF a white-orange precipitate formed immediately which dissolved again overnight. After 16 hrs the clear dark red solution was hydrolysed at 0 °C by addition of 1M HCl (22 mL) and was then diluted with ethyl acetate (150 mL). The organic phase was washed with 1 M aqueous NaOH (3 x 150 mL), 1M NaHCO₃ (2 x 150 mL) solutions and water (2 x 150 mL). The aqueous phases were re-extracted with 200 mL ethyl acetate, then the combined organic phases were dried over MgSO₄, filtered and the solvent removed. The resulting dark oily material was filtered through SiO₂ using a mixture of hexane and ethyl acetate (hexane : ethyl acetate = 8:1) as the eluting solvent. The filtered material was recrystallised from hot hexane, yielding **1^{tBu}** as a yellow crystalline material (0.76 g, 40.0%). R_F (hexane/EtOAc 5:1) = 0.68. ¹H-NMR (500 MHz, CDCl₃): δ (ppm) 1.52 (s, 18H, H3b), 7.94 (d, 4J(H2H4)= 1.8 Hz, 2H, H2), 8.40 (d, 4J(H4H2)= 1.8 Hz, 2H, H4), 10.24 (s, 2H, H10), 11.45 (br. s, NH). ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 31.96 (C3b), 34.90 (C3a), 120.1 (Ar-C), 123.5 (Ar-C4), 123.6 (Ar-C), 129.5 (Ar-C2), 143.2 (Ar-C3), 193.0 (Ar-C10), 142.3 (Ar-C3). IR (KBr): 3429 (s, (N-H)), 2954 (s, [C(CH₂-H)₃]), 2880 (d, (CH₂-H)), 2806 (d, (OC-H)), 2724 (s, (OC-H)), 1680 (s, (C=O)), 1592, 1482 (s, (C=C)), 1394, 1366 (s, δ(t-Bu CH₃)). ESI (-) MS (m/z): (C₂₂H₂₄NO₂)⁻ expected 334.19, found 334. Microanalysis; calc. for C₂₂H₂₅O₂N: C, 78.77; H, 7.51; N, 4.18; found: C, 78.82; H, 7.77; N, 4.22.

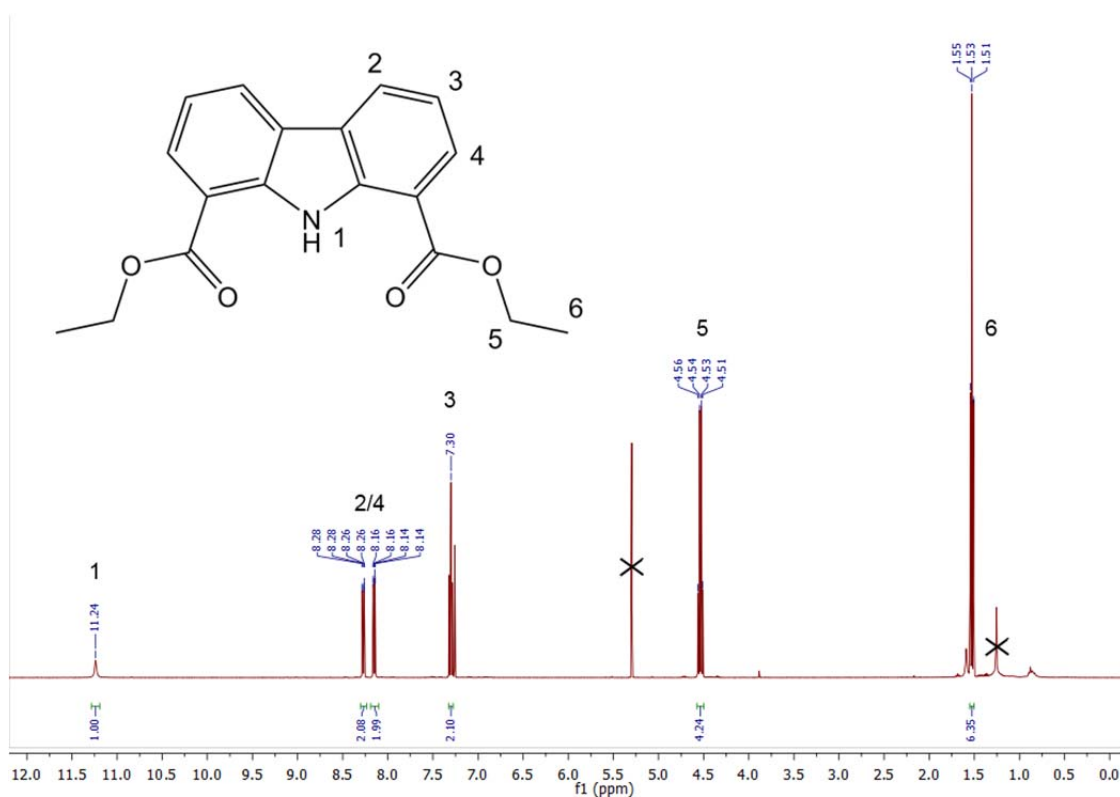


Figure S1: ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of 1,8-diethyl-dicarboxylate-carbazole

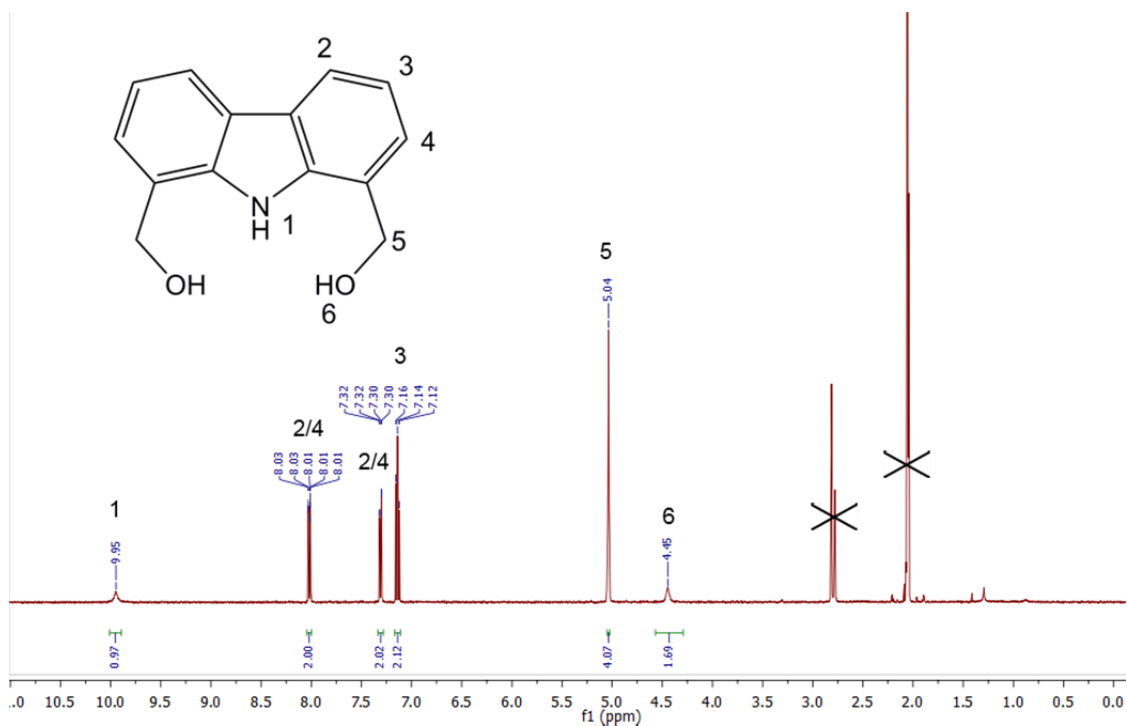


Figure S2: ¹H NMR spectrum ((CD₃)CO), 293 K, 400 MHz) of 1,8-bis(hydroxymethyl)carbazole

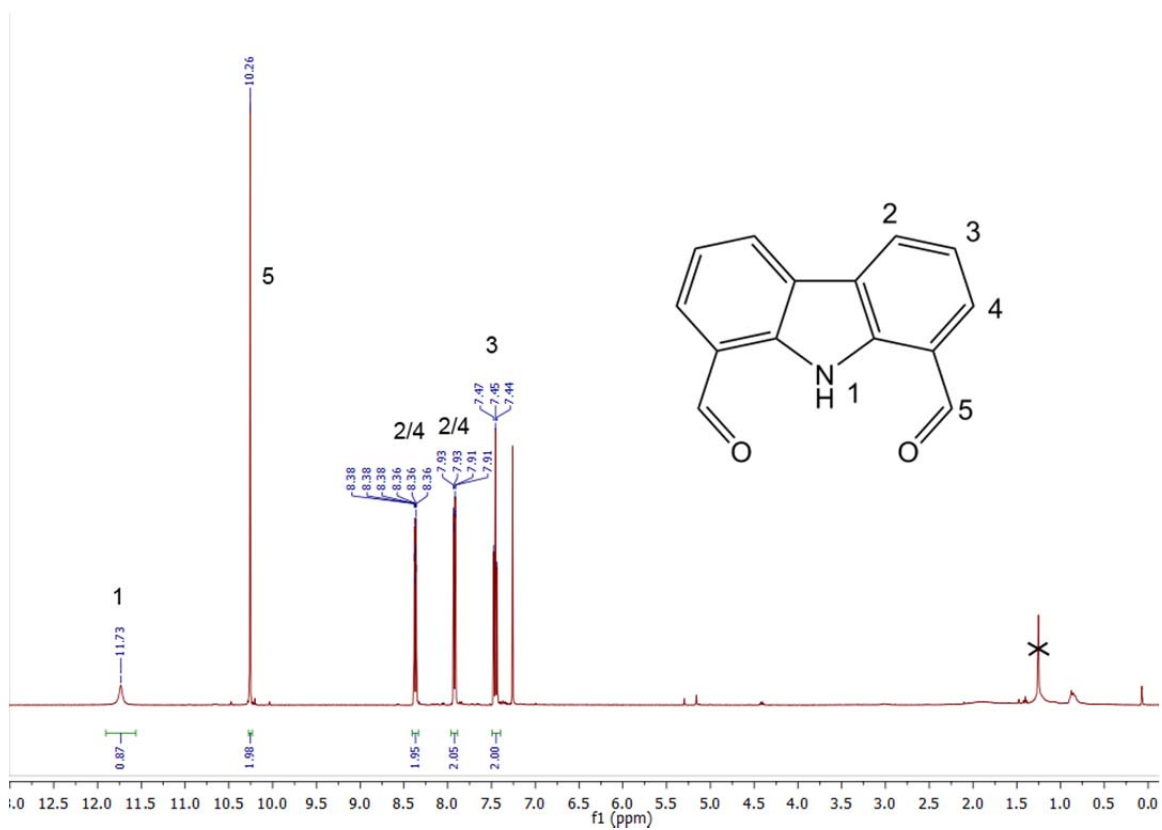


Figure S3: ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of 1,8-diformyl-carbazole

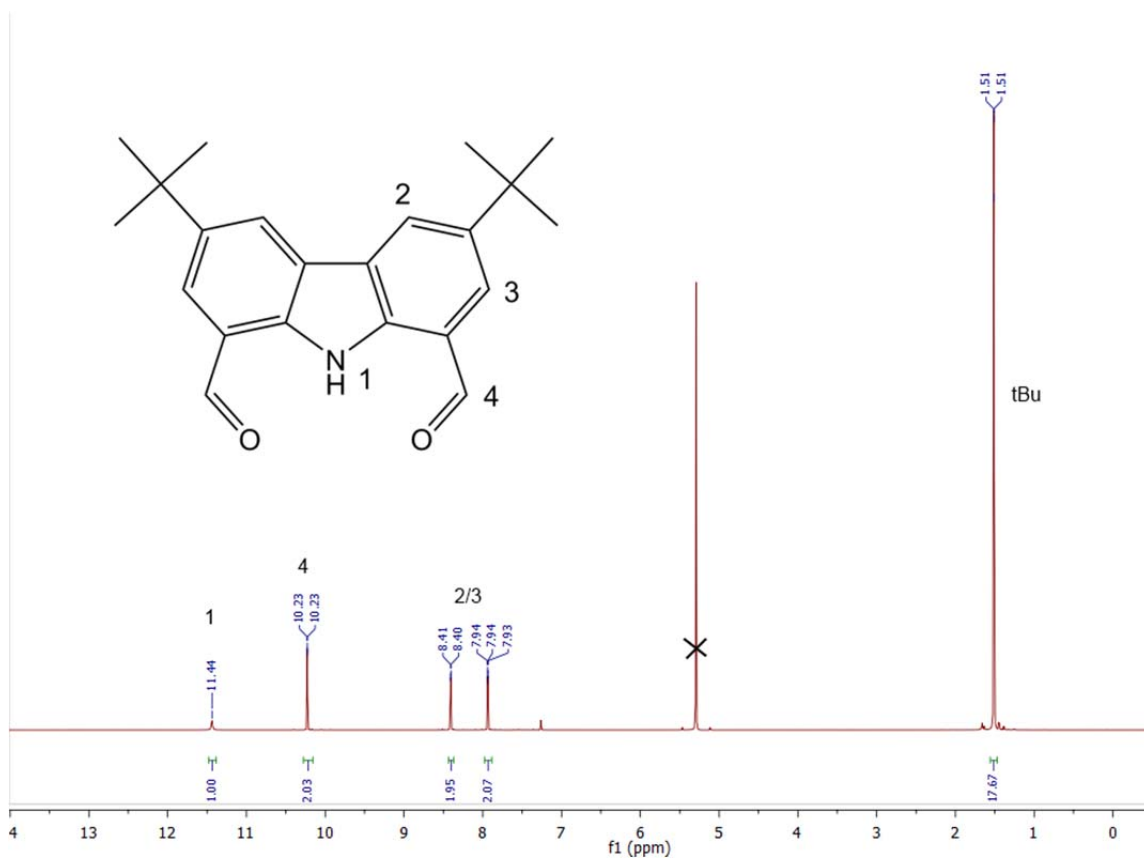


Figure S4: ^1H NMR spectrum (CDCl_3 , 293 K, 400 MHz) of 1,8-diformyl-3,6-di-tert-butyl-9H-carbazole

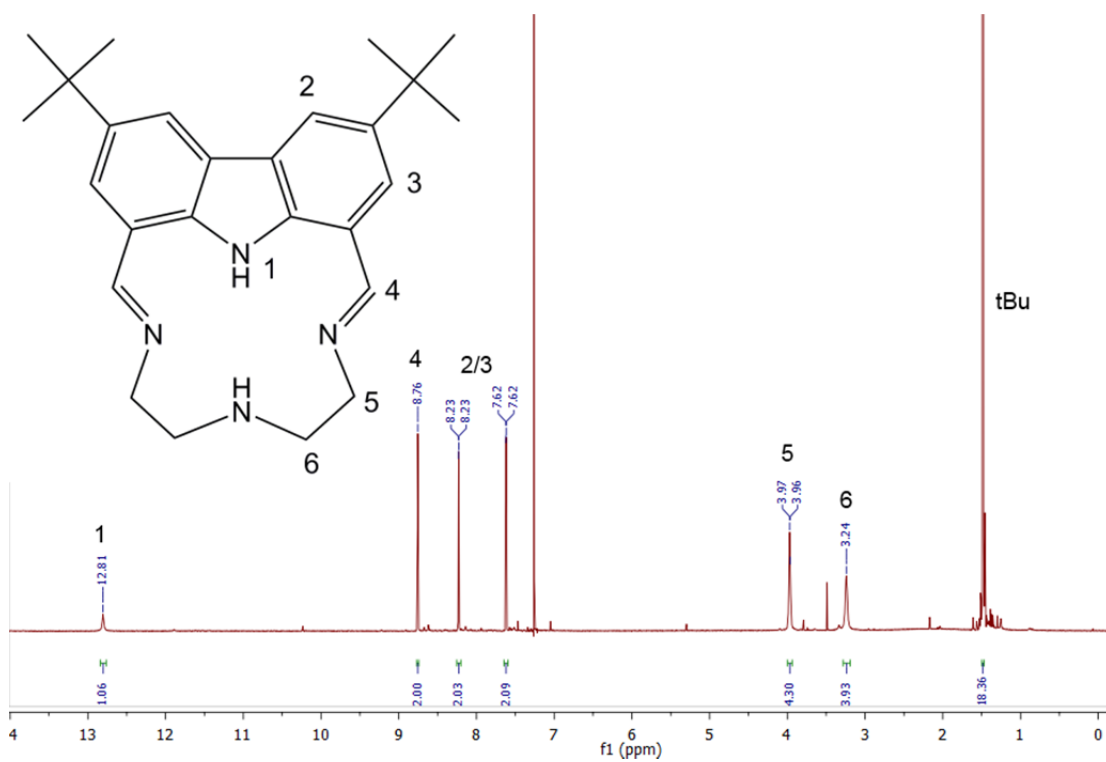


Figure S5: ^1H NMR spectrum (CDCl_3 , 293 K, 500 MHz) of HL^{tBu}.

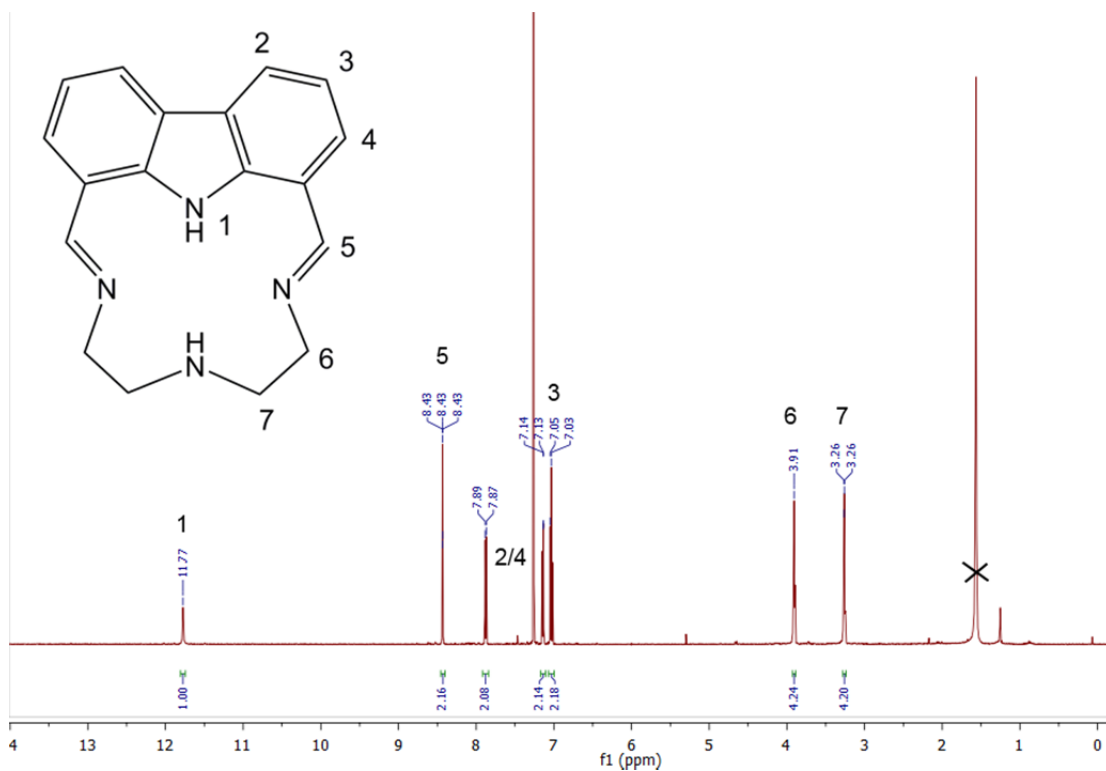


Figure S6: ^1H NMR spectrum (CDCl_3 , 293 K, 500 MHz) of HL^{H} .

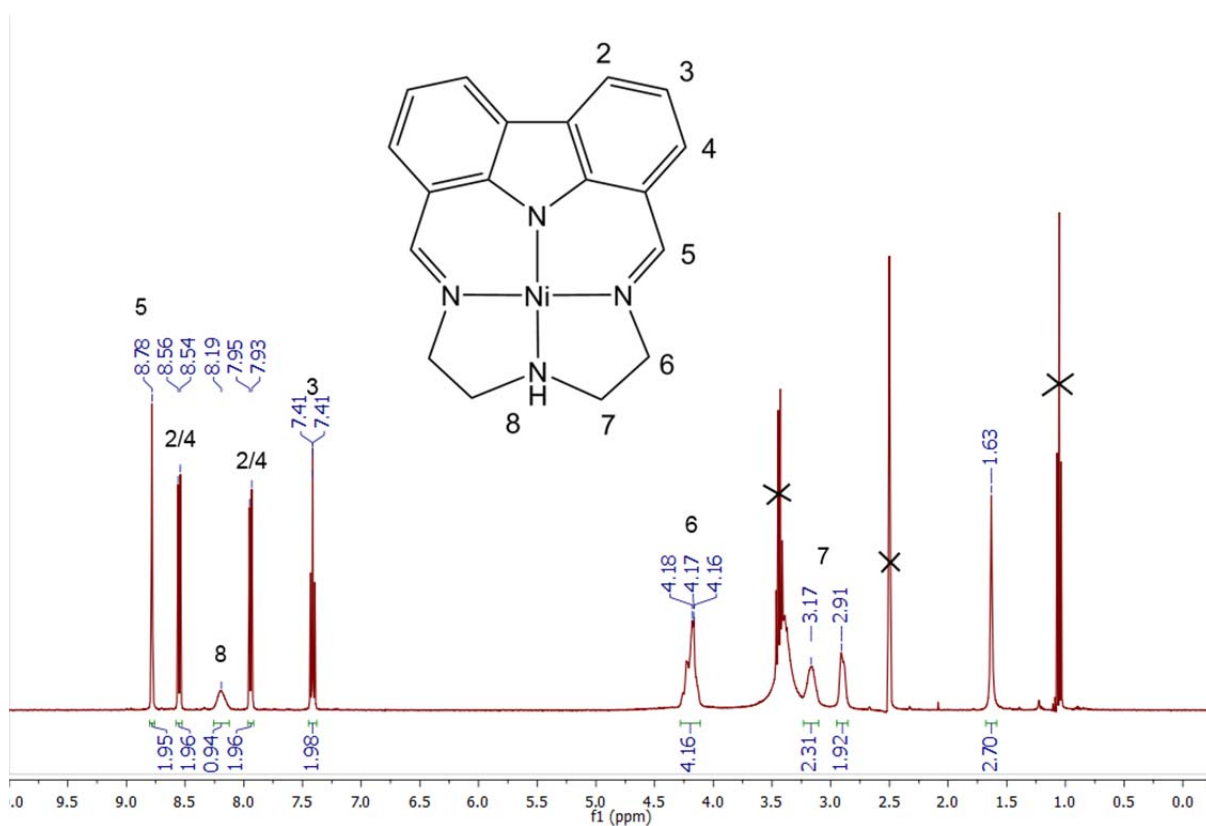


Figure S7: ^1H NMR spectrum ($(\text{CD}_3)_2\text{SO}$, 293 K, 400 MHz) of $[\text{NiL}^{\text{H}}]\text{OAc}$.

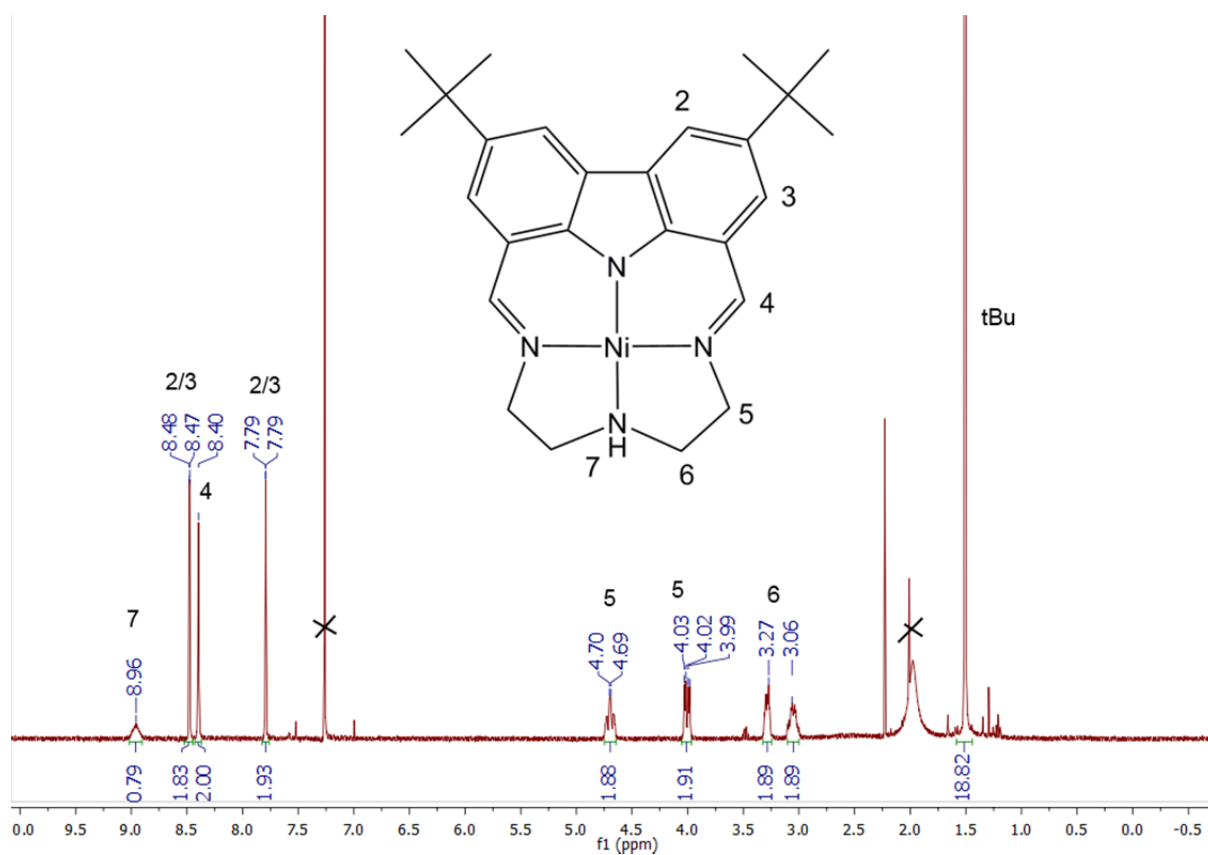


Figure S8: ¹H NMR spectrum (CDCl₃, 293 K, 400 MHz) of [NiL^{tBu}]OAc

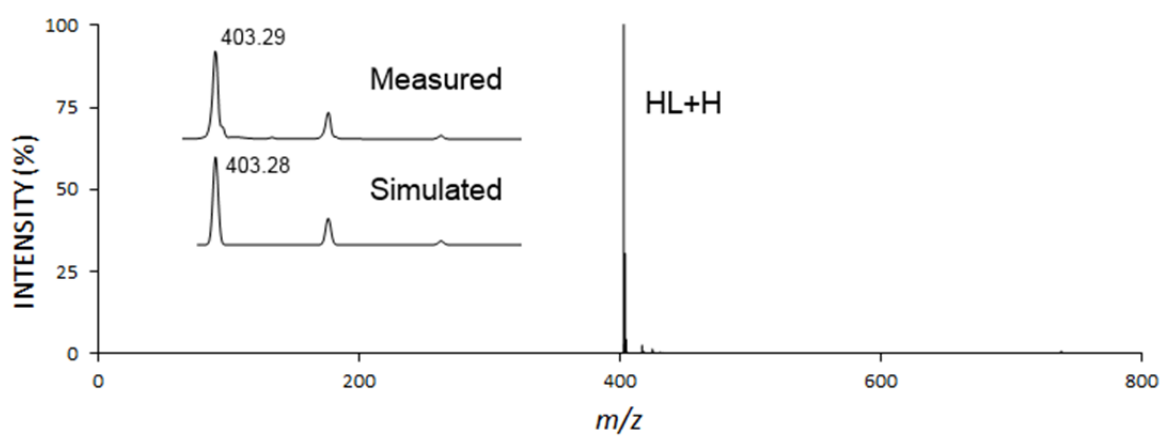


Figure S9: ESI(+) mass spectrum of HL^{tBu}

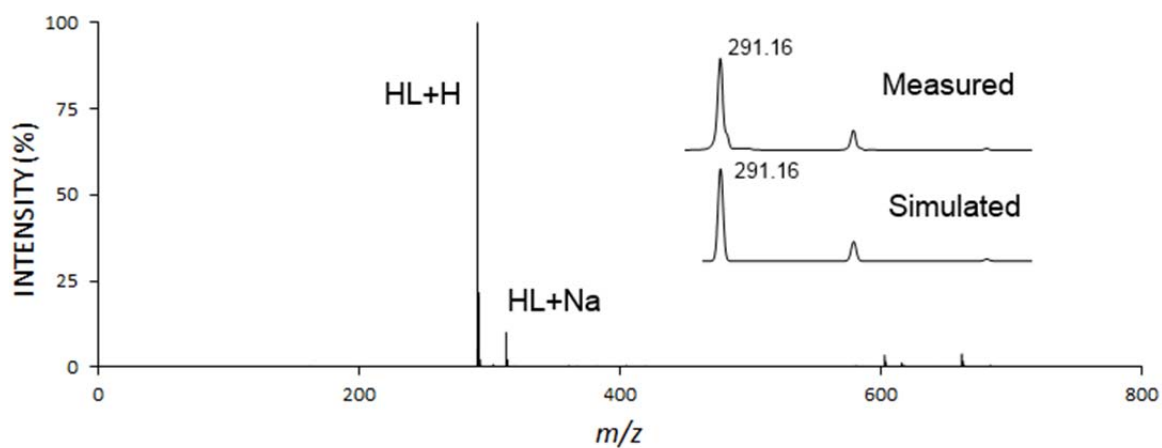


Figure S10: ESI(+)-mass spectrum of HL^H

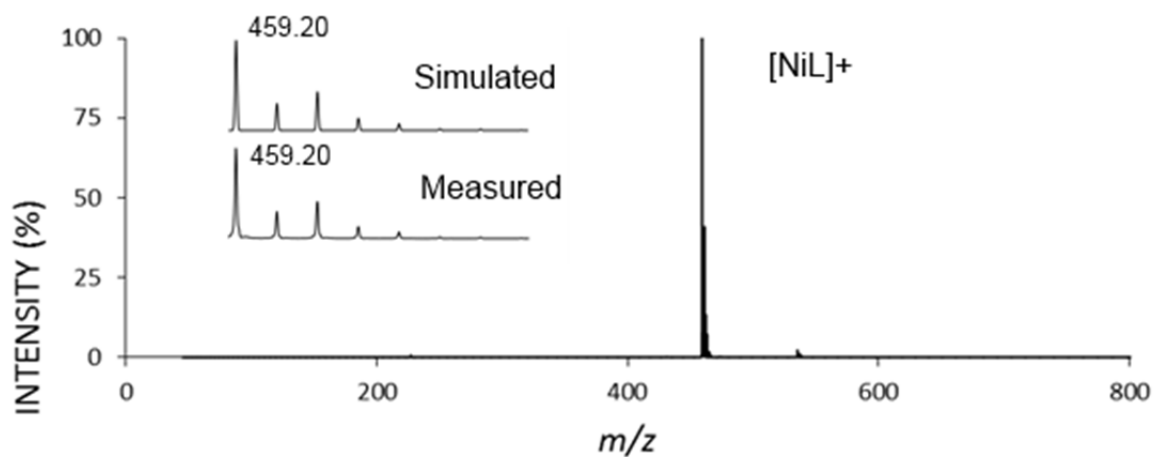


Figure S11: ESI(+)-mass spectrum of $[NiL^{tBu}]OAc$.

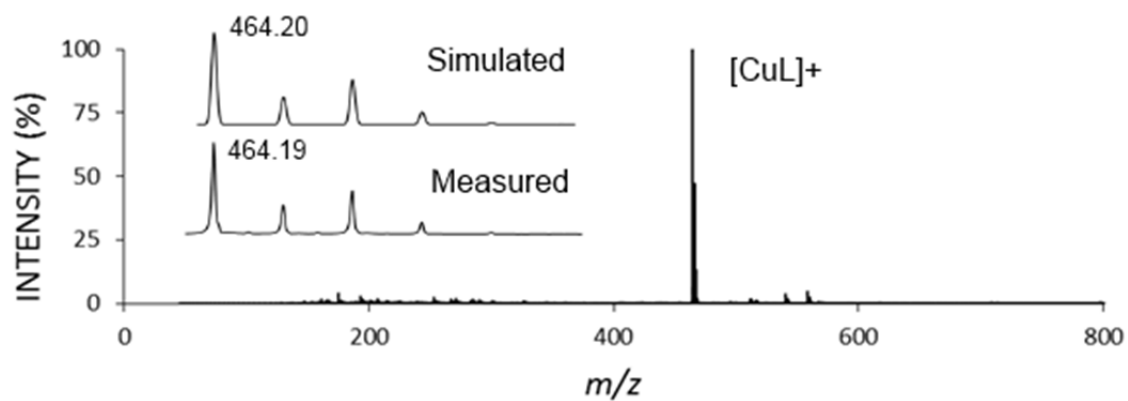


Figure S12: ESI(+)-mass spectrum of $[CuL^{tBu}]OAc$.

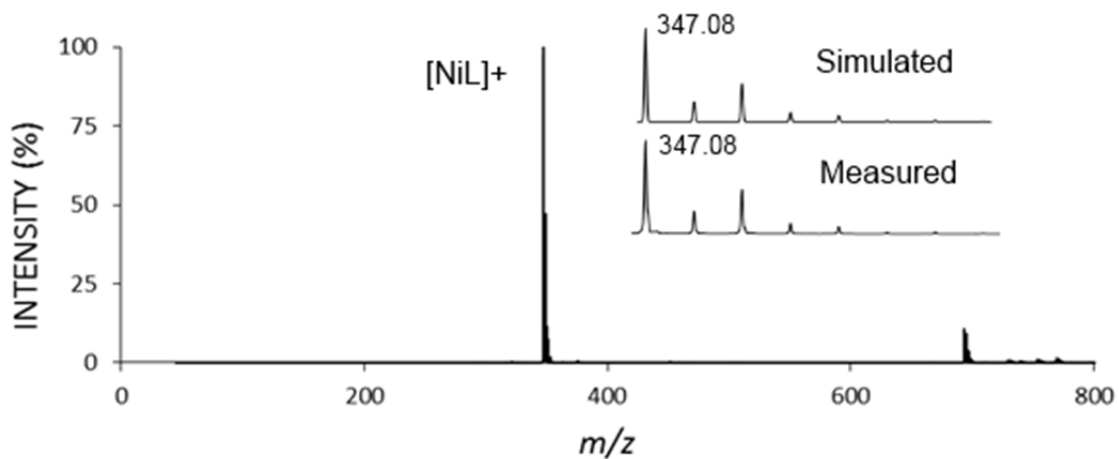


Figure S13: ESI(+) mass spectrum of $[\text{NiL}^{\text{H}}]\text{OAc}$.

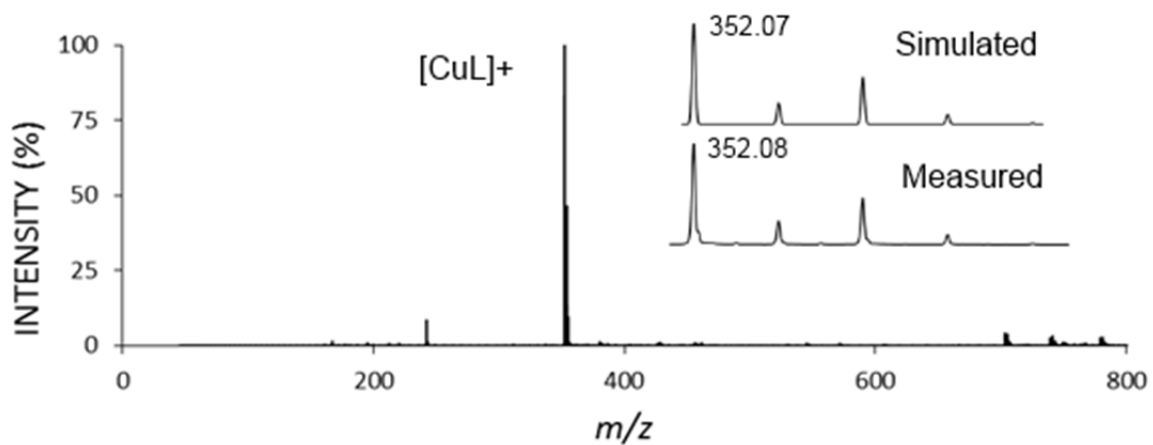


Figure S14: ESI(+) mass spectrum of $[\text{CuL}^{\text{H}}]\text{OAc}$.

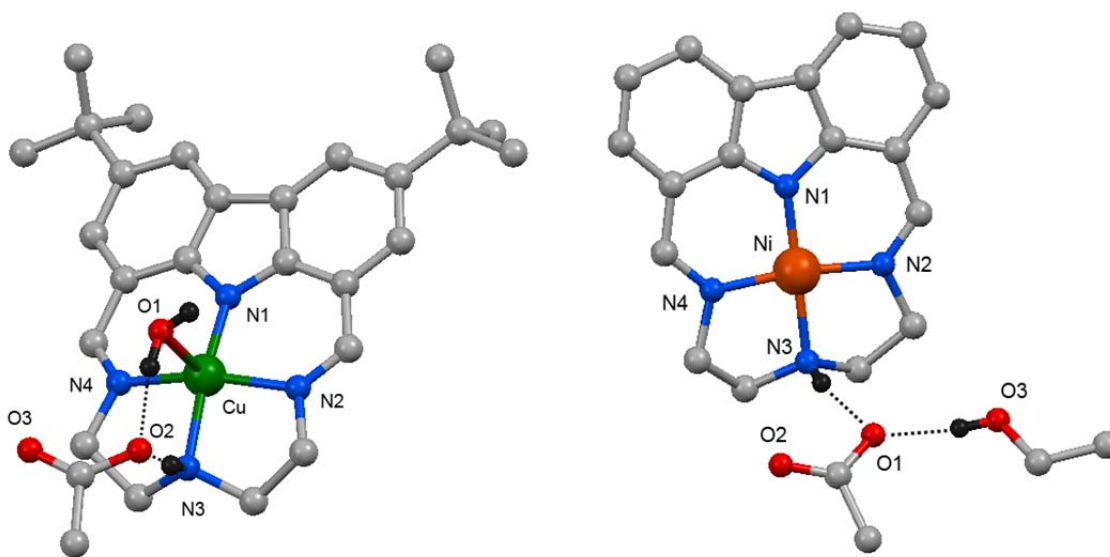


Figure S15 and S16: Hydrogen bonding interactions in the structures of $[\text{CuL}^{\text{tBu}}(\text{H}_2\text{O})]\text{OAc}\cdot 0.5\text{Ether}$ (left) and $[\text{NiL}^{\text{H}}]\text{OAc}\cdot \text{EtOH}$ (right).

Table S1. Crystal data and structure refinement for [CuL^{tbu}(H₂O)]OAc·0.5(Ether) and [NiL^H]OAc·EtOH.

Identification code	[CuL ^{tbu} (H ₂ O)]OAc·0.5(Ether)	[NiL ^H]OAc·EtOH
Empirical formula	C ₃₀ H ₄₃ Cu N ₄ O _{3.50}	C ₂₂ H ₂₆ N ₄ Ni O ₃
Formula weight	579.22	453.18
Temperature	83 K	100 K
Wavelength	0.71073 Å	1.54184 Å
Crystal system	Monoclinic	Orthorhombic
Space group	P2 ₁ /c	P 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions	15.2496(4) Å, 16.9526(5) Å 11.4962(3) Å β = 98.699(2)°	6.6646(3) Å 12.9442(4) Å 23.1878(7) Å
Volume	2937.81(14) Å ³	2000.37(11) Å ³
Z	4	4
Density (calculated)	1.310 Mg/m ³	1.505 Mg/m ³
Absorption coefficient	0.782 mm ⁻¹	1.671 mm ⁻¹
F(000)	1232	952.0
Crystal size	0.40 x 0.16 x 0.08 mm ³	0.20 x 0.08 x 0.05 mm ³
Theta range for data collection	1.81 to 26.35°	5.09 to 76.13°
Index ranges	-19<=h<=19, -21<=k<=21, -14<=l<=14	-8<=h<=5, -15<=k<=16, -25<=l<=29
Reflections collected	58913	13219
Independent reflections	5978 [R(int) = 0.0458]	4086 [R(int) = 0.0498]
Completeness to theta = 26.00/76.29°	100 %	100 %
Absorption correction	Semi-empirical from equivalents	multi-scan
Max. and min. transmission	1.000 and 0.847	1.000 and 0.69218
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	5978 / 18 / 386	4086 / 22 / 331
Goodness-of-fit on F ²	1.102	1.226
Final R indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.1042	R1 = 0.0887, wR2 = 0.2532
R indices (all data)	R1 = 0.0649, wR2 = 0.1213	R1 = 0.1005, wR2 = 0.2554
Largest diff. peak and hole	1.216 and -0.566 e.Å ⁻³	1.60 and -0.99 e.Å ⁻³

Cyclic Voltammetry - Full Scan rate studies

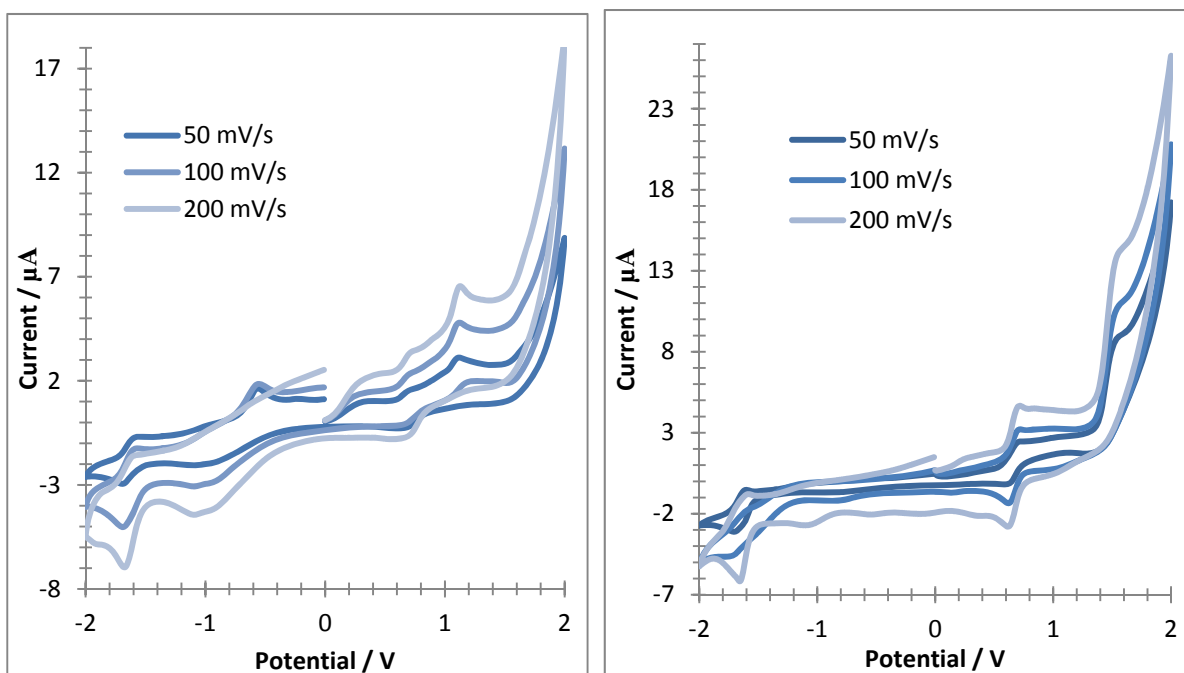


Figure S17 and S18: Full scan rate studies of [CuL^H]OAc (left) and [CuL^{tBu}]OAc (right) at speeds of 50, 100 and 200 mV/s, going 0 to 2 to -2V, in 0.1 molL⁻¹ NBu₄PF₆ MeCN vs 0.01 molL⁻¹ AgNO₃/Ag.

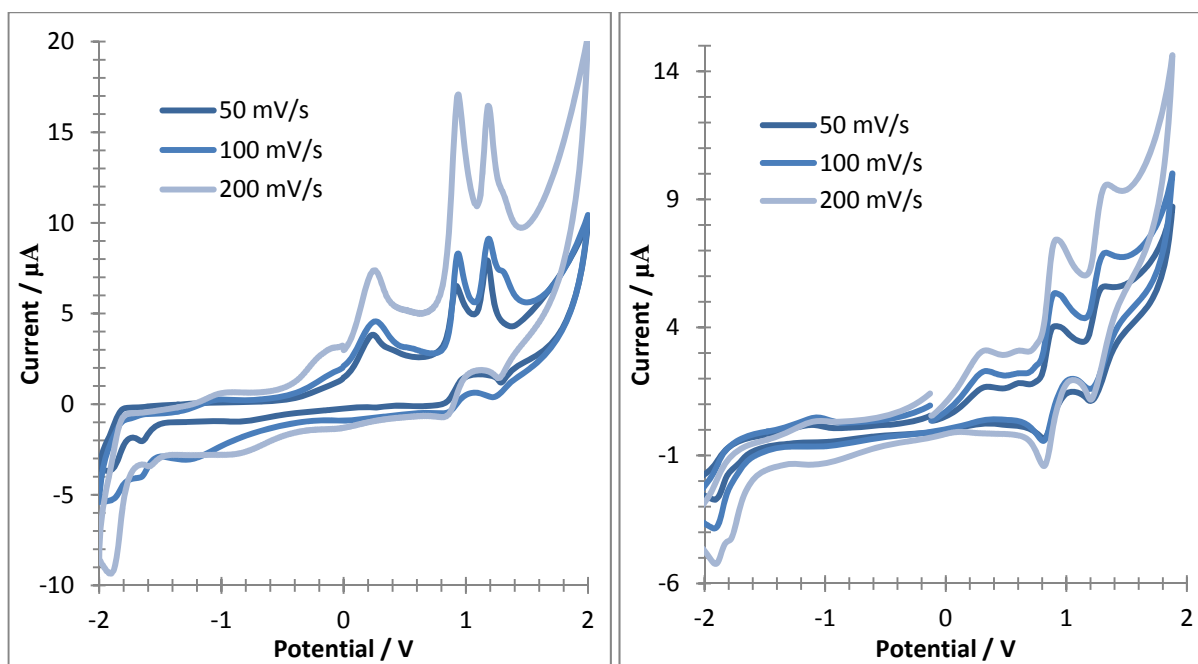


Figure S19 and S20: Full scan rate studies of [NiL^H]OAc (left) and [NiL^{tBu}]OAc (right) at speeds of 50, 100 and 200 mV/s, going 0 to 2 to -2V, in 0.1 molL⁻¹ NBu₄PF₆ MeCN vs 0.01 molL⁻¹ AgNO₃/Ag.

Stack Plot

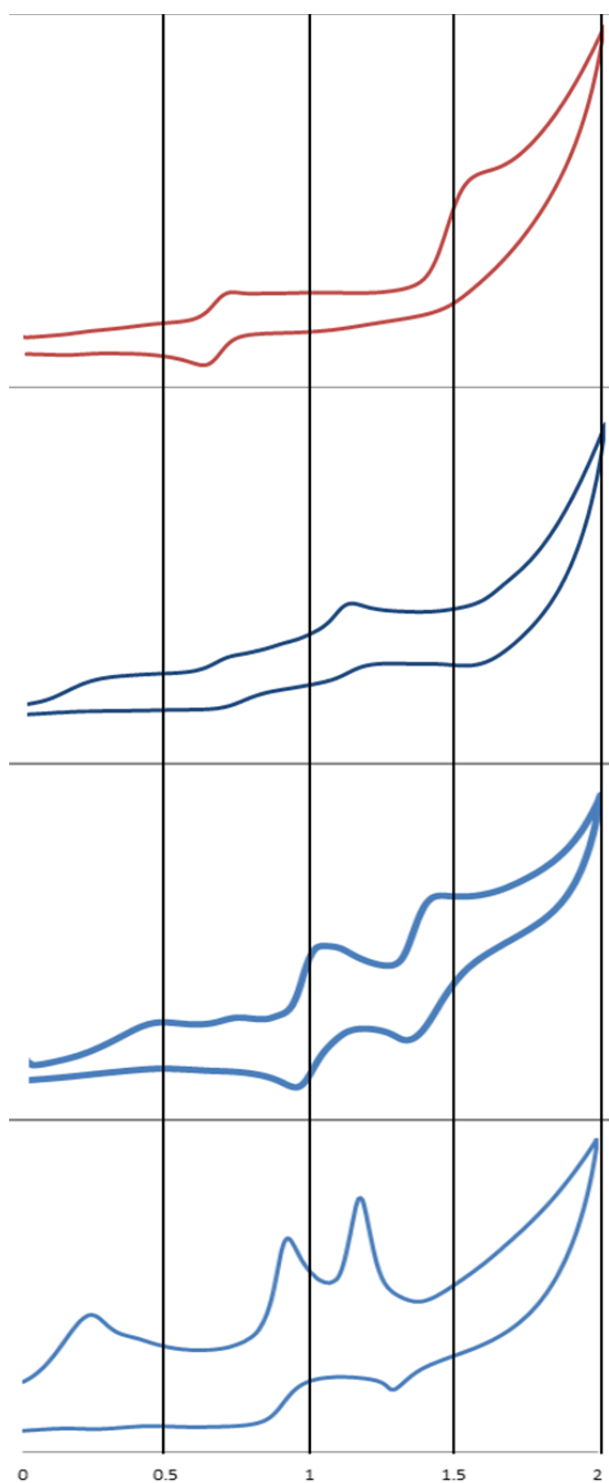


Figure S21: Stack plot of cyclic voltammograms of all four complexes, from 0 to 2V at 100 mV/s in 0.1 molL⁻¹ NBu₄PF₆ MeCN vs 0.01 molL⁻¹ AgNO₃/Ag. Top: [CuL^{tBu}]OAc, top middle: [CuL^H]OAc, bottom middle: [NiL^{tBu}]OAc, bottom: [NiL^H]OAc

Other Scan Rate studies

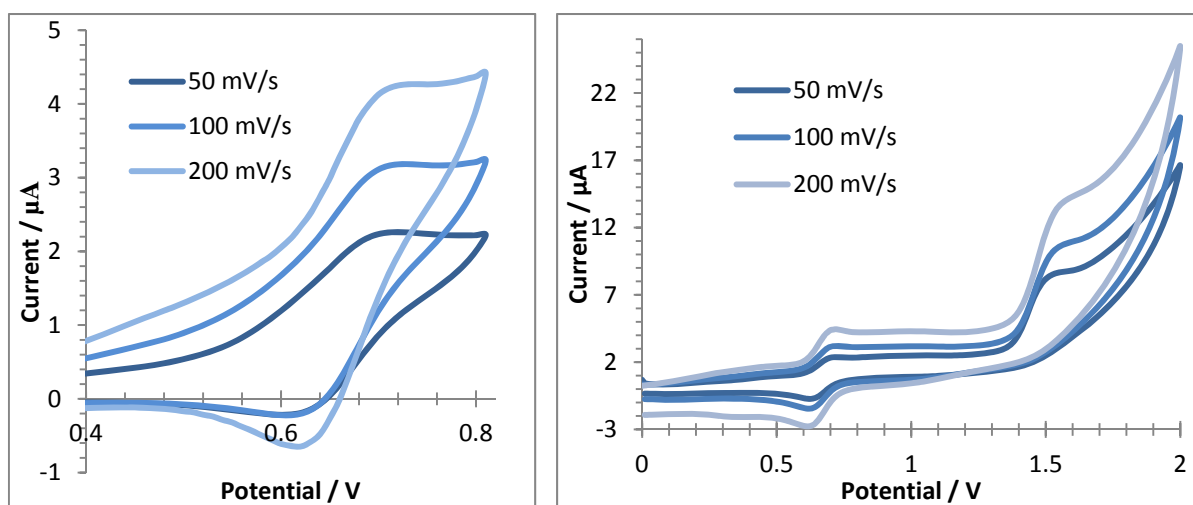


Figure S22 and S23: Scan rate study of [CuL^{tBu}]OAc, from 0 to 0.8 V (left) and from 0 to 2 V (right), in 0.1 molL⁻¹ NBu₄PF₆ MeCN vs 0.01 molL⁻¹ AgNO₃/Ag.

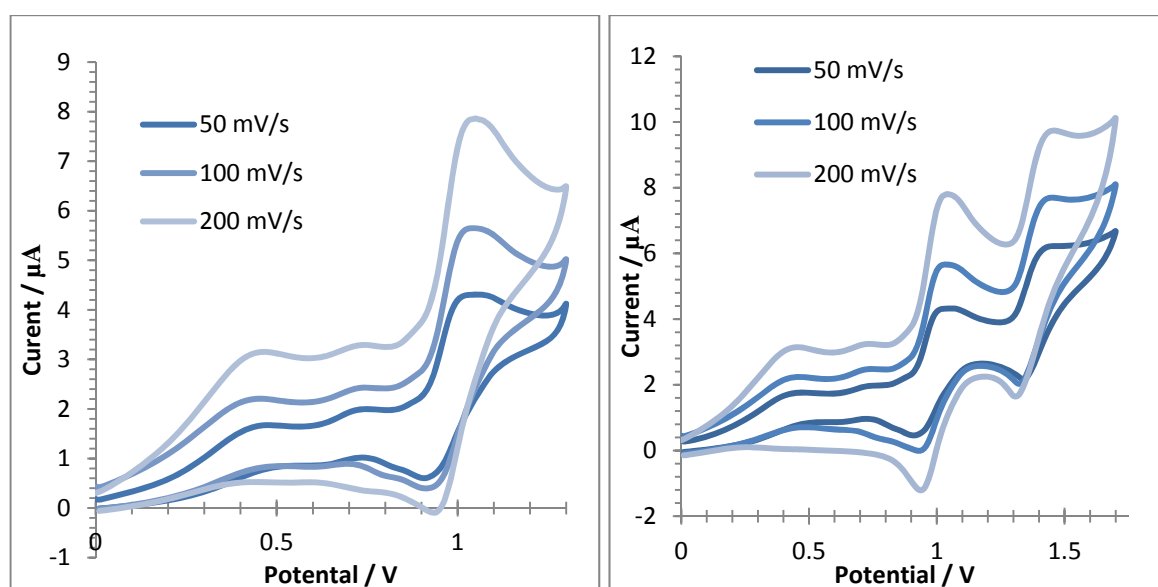


Figure S24 and S25: Scan rate study of [NiL^{tBu}]OAc, from 0 to 1.3 V (left) and from 0 to 1.7 V (right), in 0.1 molL⁻¹ NBu₄PF₆ MeCN vs 0.01 molL⁻¹ AgNO₃/Ag.

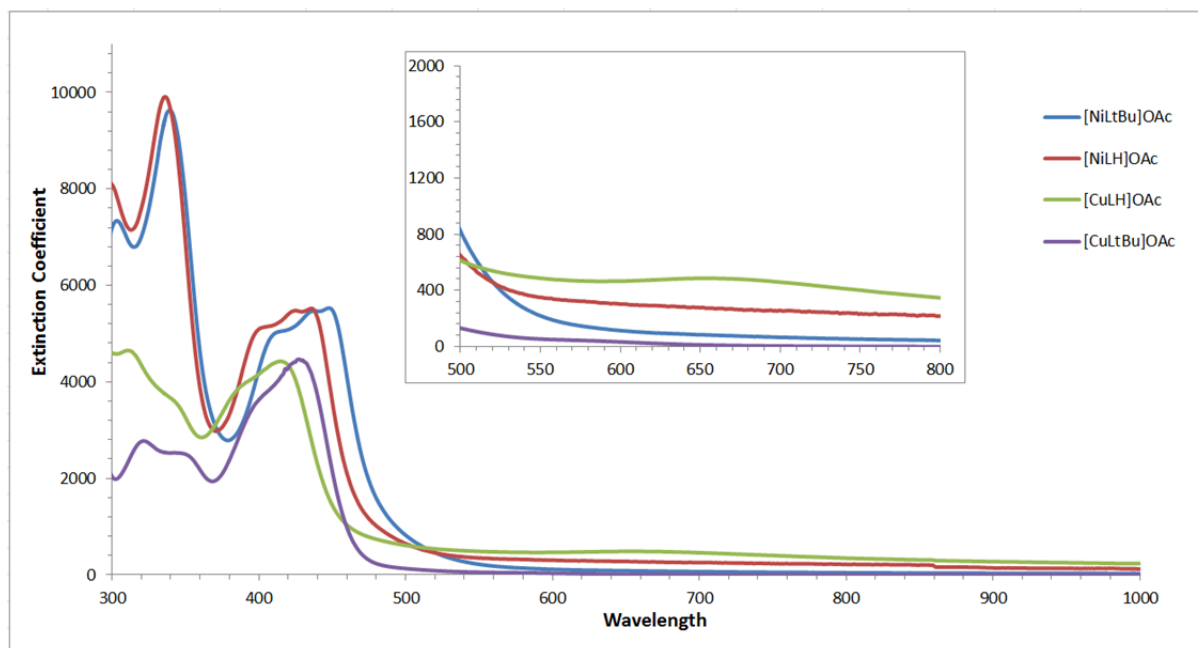


Figure S26: UV-vis spectra in MeCN at 0.25 mmolL⁻¹ for [CuL^H(H₂O)]OAc, [CuL^tBu(H₂O)]OAc, [NiL^H]OAc and [NiL^tBu]OAc (colour). Inset 500-800nm window.

References

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