SUPPORTING INFORMATION

New palladium catalysed reactions of bromoporphyrins: synthesis and crystal structures of nickel(II) complexes of primary 5-aminoporphyrin, 5,5'-bis(porphyrinyl) secondary amine, and 5-hydroxyporphyrin

*Louisa J. Esdaile, Mathias O. Senge and Dennis P. Arnold**

General experimental procedures. All solvents were Analytical Reagent grade unless otherwise stated. THF was distilled from sodium/benzophenone, *rac*-BINAP was obtained from Strem and other reagents were obtained from Sigma-Aldrich. TLC was performed on Merck Silica Gel 60 F254 TLC plates. Preparative column chromatography was performed on silica gel (40-63 μm), which was purchased from Qingdao Haiyang Chemical Co. Ltd., China. ^{1}H, DQF COSY and NOESY NMR experiments were conducted on a Bruker Avance 400 spectrometer operating at 400.155 MHz. All samples were prepared in $CDCl_3$ and chemical shifts were referenced to $CHCl_3$ at 7.26 ppm. Coupling constants are given in Hz. UV-visible spectra were recorded on a Varian Cary 3 or Varian Cary 50 UV-visible spectrometer in dichloromethane (DCM). Accurate mass Electrospray Ionisation (ESI) and Liquid Secondary Ion (LSI) mass spectra were recorded at the School of Chemistry, Monash University, Melbourne. ESI measurements were performed using an Agilent 1100 Series LC attached to an Agilent G1969A LC-TOF system with reference mass correction using NaI clusters. An eluent of 50:50 DCM/MeOH with 0.1% formic acid was employed using a flow rate of 0.3 mL/min. Solvent aspiration was achieved by nitrogen gas flowing at 8 L/min. The source temperature was set to 350°C and the capillary voltage to 4.0 kV. LSIMS measurements were collected using m-nitrobenzyl alcohol as proton donor and CsITEG mixture for external reference on a Kratos Concept ISQ double focussing Magnetic/Electrostatic Mass Spectrometer. NiTriPPBr (**1**) was prepared as previously described.[1]

*Synthesis of $NiTriPPNH_2$ **2**, $(NiTriPP)_2NH$ **3**, and NiTriPPOH **4**.* NiTriPPBr **1** (20.0 mg, 0.0297 mmol), hydrazine sulfate (0.5 eq., 1.9 mg, 0.015 mmol), Cs_2CO_3 (7.1 eq., 68.7 mg, 0.211 mmol), $Pd(OAc)_2$ (7 mol%, 0.5 mg, 0.002 mmol) and *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) were placed into a dry, argon-filled Schlenk flask and were dried under vacuum for 30 min. Freshly distilled, dry THF (5 cm^3) was added to the vessel and the mixture was stirred under argon for 15 h at 68 °C. The reaction was quenched with water and the mixture was extracted with DCM. After separation, the DCM was removed under reduced pressure. The products were dry-loaded onto silica and then purified using column chromatography [DCM/*n*-hexane (1:2), then DCM]. The first eluting product, after a trace amount of the debrominated starting material, was the murky green $(NiTriPP)_2NH$ (**3**). This product was recrystallised by the slow evaporation of DCM from a mixture of DCM/MeOH, to yield fine, green needles suitable for crystallographic analysis (crude yield 6.2 mg, 34%). The second product, eluting in DCM, was the purple-green $NiTriPPNH_2$ (**2**), which was recrystallised similarly to give small, purple needles suitable for crystallographic analysis (7.1 mg, 39%). The final red product, NiTriPPOH (**4**) (7.8 mg, 43%) was also recrystallised similarly to give red needles suitable for crystallographic analysis.

2 ($NiTriPPNH_2$): δ_H 8.94 (2 H, d, *J* 4.9 Hz, *βH*), 8.49 (2 H, d, *J* 4.9 Hz, *βH*), 8.46 (2 H, d, *J* 4.9 Hz, *βH*), 8.40 (2 H, d, *J* 5.1 Hz, *βH*), 7.93-7.89 (6 H, m, phenyl *H*), 7.65-7.61 (9 H, m, phenyl *H*), 5.77 (2 H, bs, N *H*); *m/z* (HRESI) 609.1445 ($[M]^+$, $C_{38}H_{25}N_5Ni$ calc. 609.1463, overlapped with $[M - H]^+$), 632.1343 ($[M + Na]^+$, calc. $C_{38}H_{25}N_5NaNi$ 632.1361); UV Vis: λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) 426.0 (233.6), 542.5 (8.0), 598.9 (12.4).

3 [$(NiTriPP)_2NH$]: δ_H 9.86 (1 H, bs, *NH*), 8.83 (4 H, d, *J* 5.1 Hz, *βH*), 8.55 (4 H, d, *J* 5.1 Hz, *βH*), 8.52 (4 H, d, *J* 4.9 Hz, *βH*), 8.31 (4 H, d, *J* 4.9 Hz, *βH*), 7.98-7.96 (4 H, m, phenyl *H*), 7.84-7.82 (6 H, m, phenyl *H*)), 7.67-7.65 (8 H, m, phenyl *H*), 7.57-7.51 (12 H, m, phenyl *H*); *m/z* (HRESI) 1200.2552 ($[M - H]^+$, $C_{76}H_{46}N_9Ni_2$ calc. 1200.2583, overlapped with $[M]^+$), 1224.2565 ($[M + Na]^+$, calc. $C_{76}H_{47}N_9NaNi_2$ 1224.2559); UV/Vis: λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) 409.5 (135.0), 446.0 (100.1), 528.5 (19.1), 624.9 (22.8).

4 (NiTriPPOH): δ_H ($CDCl_3$ + hydrazine hydrate) 9.44 (2 H, d, *J* 4.6 Hz, *βH*), 8.72 (2 H, d, *J* 4.4 Hz, *βH*), 8.68 (2 H, d, *J* 4.9 Hz, *βH*), 8.63 (2 H, d, *J* 4.9 Hz, *βH*), 7.97-7.92 (6 H, m, phenyl *H*), 7.67-7.62 (9 H, m, phenyl *H*); *m/z* (HRESI) 609.1262 ($[M - H]^+$, $C_{38}H_{23}N_4NiO$ calc. 609.1225, overlapped with $[M]^+$). UV/Vis: λ_{max}/nm (approx. $\varepsilon/10^3$ M^{-1} cm^{-1}) 416.5 (220), 529.5 (13.0), 569.0 (7.0), (some samples show oxyl radical present by a weak band at 803 nm).

Selective synthesis of $NiTriPPNH_2$ ***2***. NiTriPPBr (20.0 mg, 0.0297 mmol), hydrazine sulfate (1.04 eq., 4.0 mg, 0.031 mmol), Cs_2CO_3 (7.1 eq., 68.7 mg, 0.211 mmol), $Pd(OAc)_2$ (7 mol%, 0.5 mg, 0.002 mmol) and *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) were placed into a dry, argon-filled Schlenk flask and were dried under vacuum for 1 h. Freshly distilled, dry THF (5 cm^3) was added to the vessel and the mixture was stirred under argon for 18 h at 68 °C. The reaction was quenched with water and the mixture was extracted with DCM. The solvent was removed under reduced pressure and the product was purified using column chromatography [DCM/*n*-hexanes (1:1) then DCM] and recrystallised by slow evaporation of DCM from a mixture of DCM/MeOH to give purple crystals (9.2 mg, 51%).

*Directed synthesis of (NiTriPP)₂NH **3**.* NiTriPPBr (20.0 mg, 0.0297 mmol), NiTriPPNH$_2$ (18.1 mg, 0.0297 mmol), Cs$_2$CO$_3$ (7.1 eq., 68.6 mg, 0.211 mmol), Pd(OAc)$_2$ (7 mol%, 0.5 mg, 0.002 mmol) and *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) were placed into a dry, argon-filled Schlenk flask and were dried under vacuum for 1.25 h. Dioxane (Sigma-Aldrich, anhydrous, 5 cm^3) was added to the vessel and the mixture was stirred under argon for 3 d at 100 °C. The reaction was quenched with water and the mixture was extracted with DCM. After separation, the DCM was removed under reduced pressure. The products were then purified using column chromatography [DCM/*n*-hexanes (1:2) then 1:1] to yield the desired olive-green product, which was recrystallised from DCM/pentane (8.9 mg, 25%). The hydroxyporphyrin **4** was the other major product.

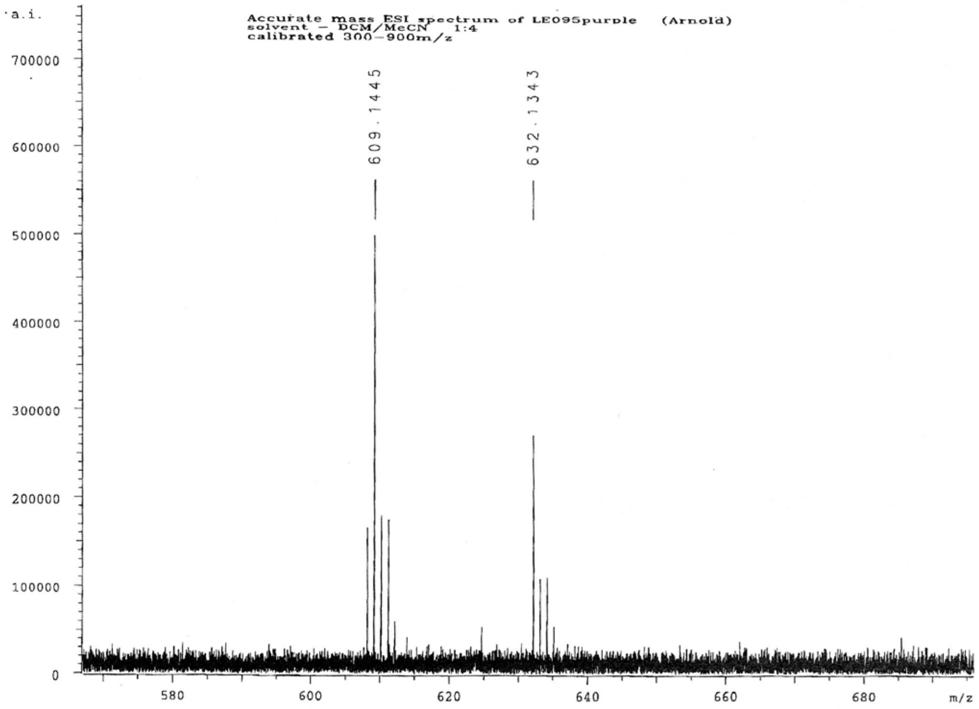
*Selective synthesis of NiTriPPOH **4**.* NiTriPPBr (20.0 mg, 0.0297 mmol), Cs$_2$CO$_3$ (7.1 eq., 68.7 mg, 0.211 mmol), Pd(OAc)$_2$ (7 mol%, 0.5 mg, 0.002 mmol) and *rac*-BINAP (20 mol%, 3.7 mg, 0.0059 mmol) were placed into a dry, argon-filled Schlenk flask and were dried under vacuum for 30 min. Freshly distilled, dry THF (5 cm^3) was added to the vessel and the mixture was stirred under argon for 4.5 d at 68 °C. The reaction was quenched with water and the mixture was extracted with DCM. After separation, the DCM was removed under reduced pressure. The product was then purified using column chromatography [DCM] to yield the desired red product, which was recrystallised from DCM/MeOH (14.4 mg, 79%).

*Synthesis of NiTriPPOAc **5**.*[2] NiTriPPOH **4** (5.0 mg, 0.0082 mmol) was dried and the flask was filled with argon. Pyridine (1.26 cm^3, 0.0156 mmol) was added, which gave a green solution, followed the addition of acetic anhydride (0.38 cm^3, 0.0041 mmol). The resulting red solution was stirred at 75 °C under argon for 10 mins. The solvent was removed and the product was purified by column chromatography, and recrystallised from DCM/MeOH to obtain red, cubic crystals (4.1 mg, 77%). δ_H 9.11 (2 H, d, *J* 4.9 Hz, βH), 8.80 (2 H, d, *J* 4.9 Hz, βH), 8.71 (2 H, d, *J* 4.9 Hz, βH), 8.70 (2 H, d, *J* 4.6 Hz, βH), 8.01-7.98 (6 H, m, phenyl *H*), 7.72-7.66 (9 H, m, phenyl *H*), 2.87 (3 H, s, Me *H*); *m/z* (LSIMS) 651.7 ([M – 1]$^+$, $C_{40}H_{25}N_4NiO_2$ calc. 651.1); UV Vis: λ_{max}/nm ($\varepsilon/10^3$ M^{-1} cm^{-1}) 412.0 (267.9), 525.0 (19.2).

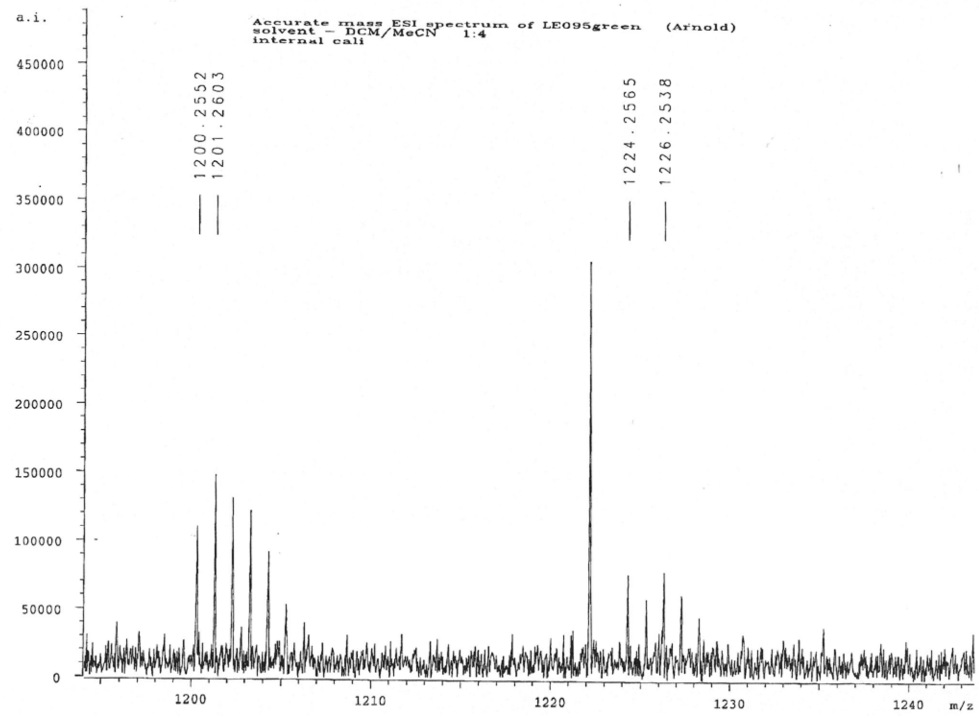
1. R. D. Hartnell, A. J. Edwards and D. P. Arnold, *J. Porphyrins Phthalocyanines*, 2002, **6**, 695–707.
2. R. G. Khoury, L. Jaquinod, R. Paolesse and K. M. Smith, *Tetrahedron*, 1999, **55**, 6713–6732.

Mass spectra of 2-5.

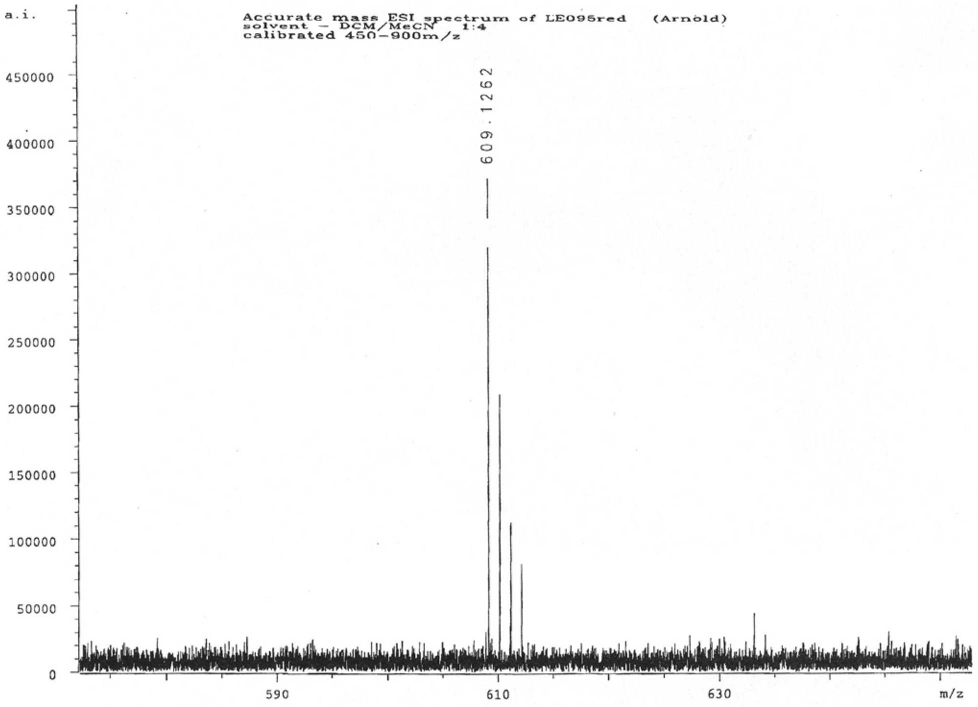
NiTriPPNH$_2$ **2**



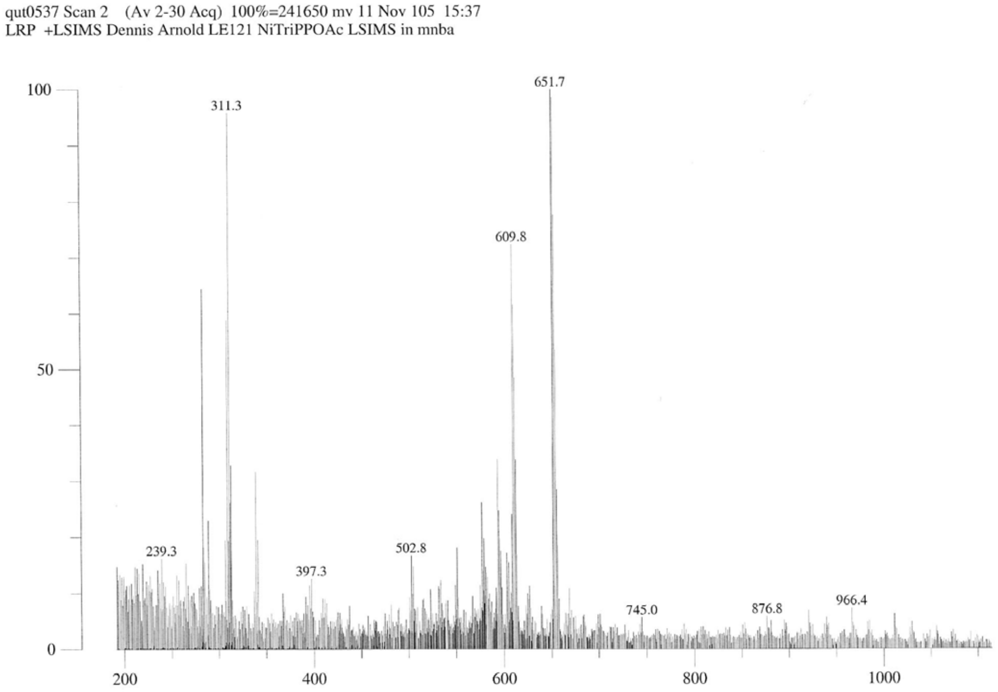
(NiTriPP)$_2$NH **3**



NiTriPPOH **4**

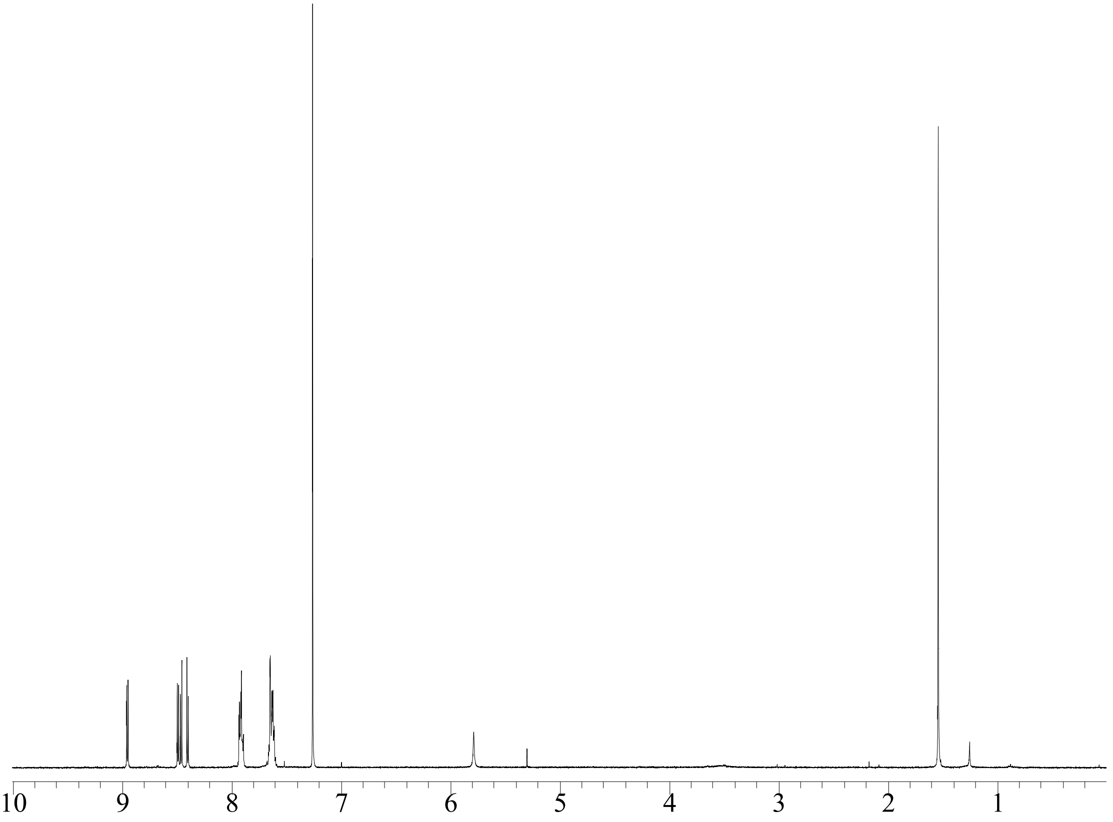


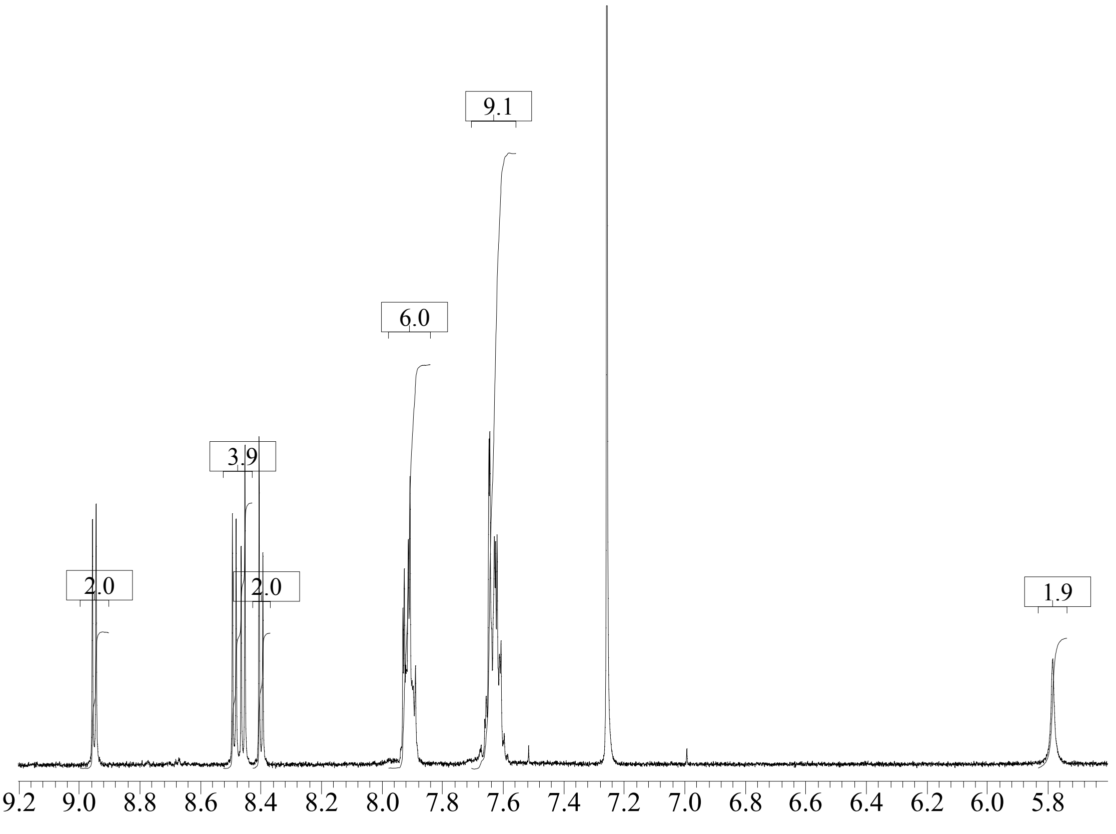
NiTriPPOAc **5**



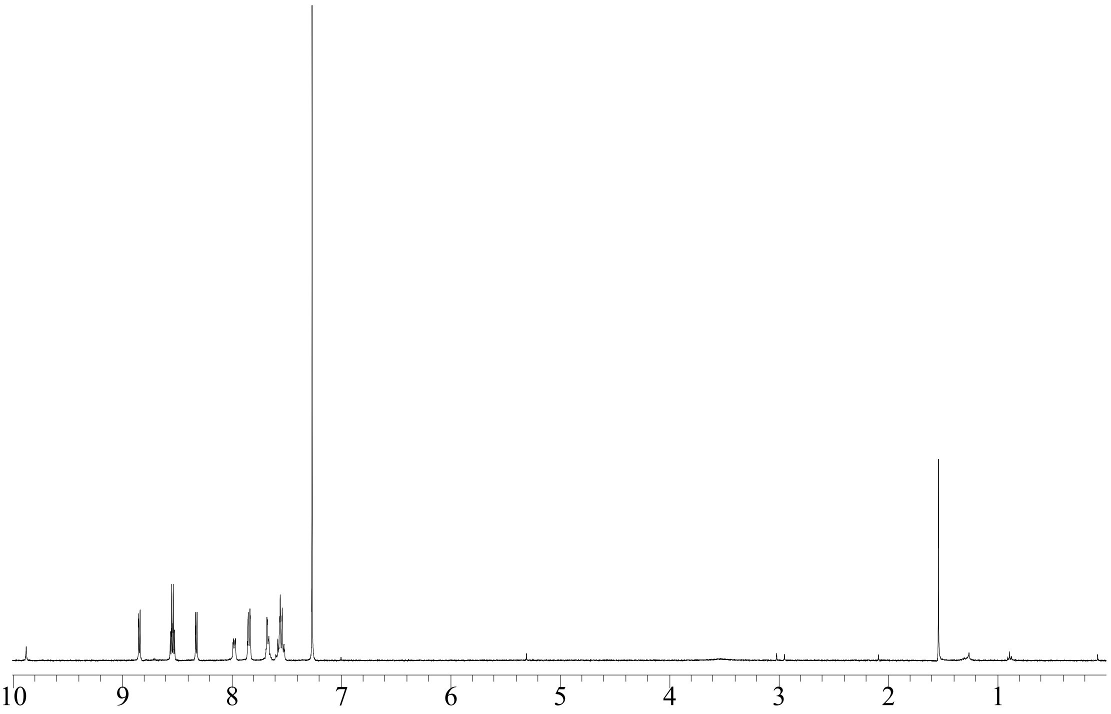
400 MHz ^{1}H NMR spectra of 2, 3, 5

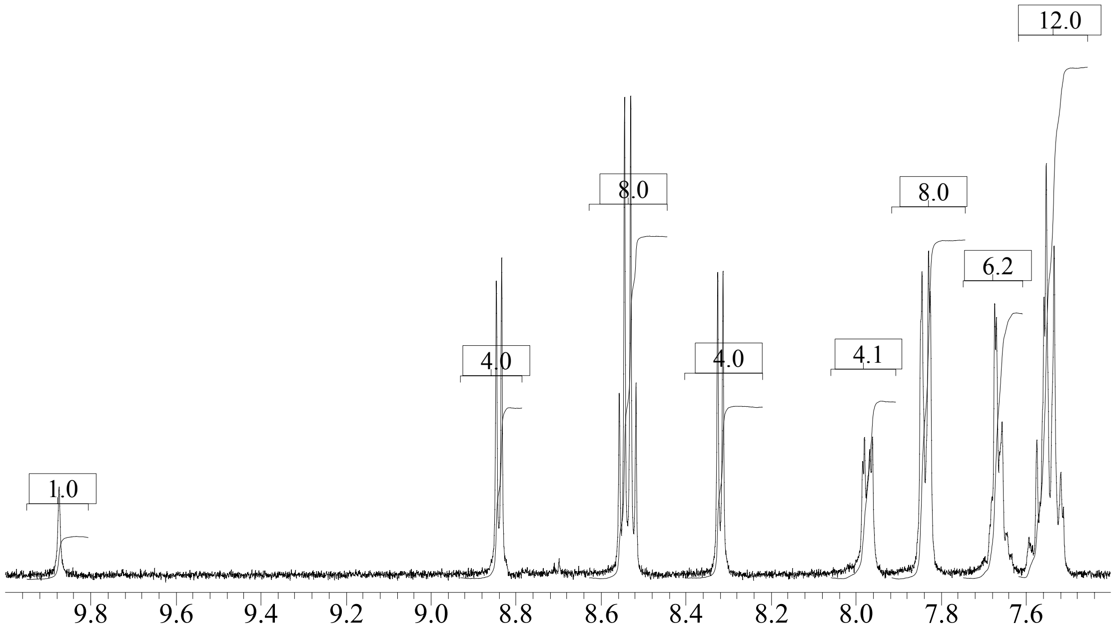
NiTriPPNH$_2$ **2**





(NiTriPP)$_2$NH **3**





NiTriPPOAc **5**