Supplementary Information

Optically active histidin-2-ylidene stabilised gold nanoparticles

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Table of Contents

Materials and Methods 3
Synthesis of 1,3-Dimethyl-N-BOC-O-methyl-L-histidinium iodide, 1(L) 5
Synthesis of 1,3-Dimethyl-N-BOC-O-methyl-D-histidinium iodide, 1(D) 6
Synthesis of Chlorido(1,3-dimethyl-N-BOC-O-methyl-L-histidin-2-ylidene)gold(I), 2(L) 7
Synthesis of Chlorido(1,3-dimethyl-N-BOC-O-methyl-D-histidin-2-ylidene)gold(I), 2(D) 8
Synthesis of 3-NP(L) by reduction of 2(L) with $^{t}BuNH_2 \bullet BH_3$ 9
Synthesis of 3-NP(D) by reduction of 2(D) with $^{t}BuNH_2.BH_3$ 10
Figure S1. ^{1}H NMR spectrum of 1(L) 11
Figure S2. ^{13}C NMR spectrum of 1(L) 12
Figure S3. ^{1}H NMR spectrum of 1(D) 13
Figure S4. ^{13}C NMR spectrum of 1(D) 14
Figure S5. ^{1}H NMR spectrum of 2(L) 15
Figure S6. ^{13}C NMR spectrum of 2(L) 16
Figure S7. ^{1}H NMR spectrum of 2(D) 17
Figure S8. ^{13}C NMR spectrum of 2(D) 18
Figure S9. ^{1}H NMR spectrum of 3-NP(L) 19
Figure S10. ^{13}C NMR spectrum of 3-NP(L) 20
Figure S11. ^{1}H NMR spectrum of 3-NP(D) 21
Figure S12. ^{13}C NMR spectrum of 3-NP(D) 22
Figure S13. DLS histogram for 3-NP(L) in THF 23
Figure S14. DLS histogram for 3-NP(D) in THF 24

Figure S15. Photographs of 3-NP(L) synthesis: a) 2(L) in THF before addition of $^{t}BuNH_2.BH_3$, b) following reaction with $^{t}BuNH_2.BH_3$ and being stirred for 24 hrs at room temperature (25 °C), c) removal of solvent and 3-NP(L) re-dispersed in DCM. 25

Figure S16. Photographs of 3-NP(D) synthesis: a) 2(D) in THF before addition of $^{t}BuNH_2.BH_3$, b) following reaction with $^{t}BuNH_2.BH_3$ and being stirred for 24 hrs at room temperature (25 °C), c) removal of solvent and 3-NP(D) re-dispersed in DCM. 26

Table S17. Summary of NHC-coated Au NPs 3-NP(D) – 3-NP(D). Properties: Average diameter (d) and Size Distribution (Standard deviation, σ). All measurements taken from TEM images of respective samples. 27

Figure S18. UV-Vis absorption spectrum of 1(L) in DCM 28

Figure S19. UV-Vis absorption spectrum of 1(D) in DCM 28

Figure S20. UV-Vis absorption spectrum of 2(L) in DCM 29

Figure S21. UV-Vis absorption spectrum of 2(D) in DCM 29

Figure S22. UV-Vis adsorption spectrum of 3-NP(L) in DCM between 250 – 700 nm. 30

Figure S23. UV-Vis adsorption spectrum of 3-NP(L) in DCM zoomed in on the 400 – 700 nm. 30

Figure S24. UV-Vis adsorption spectrum of 3-NP(D) in DCM between 250 – 700 nm. 31

Figure S25. UV-Vis adsorption spectrum of 3-NP(D) in zoomed in on the 400 – 700 nm. 31

Figure S26. TEM images of 3-NP(L) pre-size selection 32

Figure S27. TEM images of 3-NP(L) post-size selection; white circle indicating area of EDX analysis. 33

Figure S28. EDX analysis of 3-NP(L); copper and silicon peaks have been determined to originate from the TEM grid not the sample. 34

Figure S29. TEM image of 3-NP(L) following de-protection with hydrochloric acid 35

Figure S30. TEM images of 3-NP(D) pre-size selection 36

Figure S31. TEM images of 3-NP(D) post-size selection 37

Figure S32. Thermogravimetric analysis (TGA) of 3-NP(L); organic ligand (assumed to correspond to mass loss) 26.4 wt% of 3-NP(L) 38

Figure S33. Thermogravimetric analysis (TGA) of 3-NP(D); organic ligand (assumed to correspond to mass loss) = 38.7 wt% of 3-NP(D) 39

Figure S34. Full CD spectra of synthesised compounds dissolved/ dispersed in DCM. 40

Bibliography 41

Materials and Methods

All experiments were performed in air except for the synthesis of **[2(L)** and **2(D)]** which were performed under a nitrogen atmosphere using Schlenk techniques. *N*-BOC-L-histidine was purchased from GL Biochem (Shanghai) Ltd, *N*-BOC-D-histidine was purchased from Novabiochem, sodium borohydride was purchased from Lancaster chemicals, potassium carbonate and methyl iodide were purchased from Fluorochem, chloroauric acid and borane tert-butylamine complex were purchased from Alfa Aesar, acetonitrile, dichloromethane, pentane and diethyl ether were purchased from VWR chemicals. All purchased chemicals were used as received. Chloro(dimethyl sulfide) gold was synthesised according to literature procedure.[1]

^{1}H and ^{13}C NMR spectra were recorded on a Jeol JEOL ECZ 400S spectrometer, with TMS $\delta_H = 0$ or residual protic solvent peak [$CDCl_3$, $\delta_H = 7.26$; $(CD_3)_2SO$, $\delta_H = 2.50$] as the internal standard. Chemical shifts are given in ppm (δ) and coupling constants (J) are given in Hertz (Hz). Jeol Delta v5.0.4. was used to analyse the NMR spectra. Dynamic light scattering (DLS) size measurements were obtained using a Malvern Zetasizer nano ZS-series. Ultraviolet-visible (UV-vis) spectroscopy was carried out using a PerkinElmer spectrophotometer Lambda 25 and a Jenway 7315 spectrophotometer.

The average diameter (D) and the size distribution of the nanoparticles were determined by using ImageJ software and by measuring 100 randomly selected nanoparticles in arbitrarily chosen areas of the photographs. The size distribution is reported as the standard deviation (σ) which is calculated according to the following formula: $\sigma = \{(D_i - D)^2/ (n - 1)\}^{1/2}$.

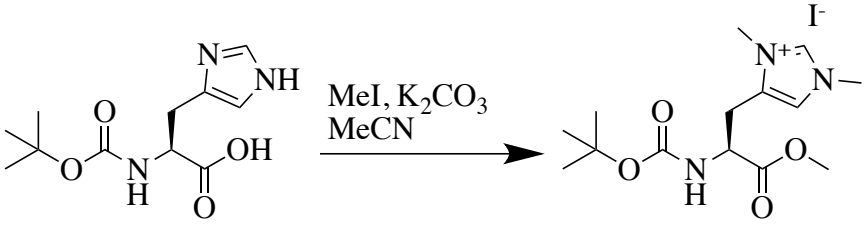
Circular dichroism measurements were recorded using a Jasco J-715 spectropolarimeter, with temperature control provided by a NesLab RTE-111 circulating chiller operating at 20 ± 0.05 °C. Spectra were recorded in a 0.2 cm pathlength quartz cell, maintaining consistent cell orientation. Samples were prepared at 1 mg mL^{-1} in dichloromethane (DCM). In the case of **1(L/D)** and **2(L/D)**, this concentration resulted in high tension (HT) voltages of > 1000 V, indicating excessive noise, and so the samples were diluted tenfold. No meaningful dichroic behaviour was observed for **1(L/D)** and **2(L/D)** at the original concentration. This was not an issue for **3-NP(L/D)**, for which HT reached a maximum of 600 V, and spectra were therefore recorded undiluted. We note that TGA results show that the final concentration of the ligands in **3-NP(L/D)** is a maximum of four times higher than that of the molecular species; the CD effects are much greater than this number. Spectra were averaged over 20 readings, and subsequently smoothed using a 9-point moving average, followed by subtraction of a similarly smoothed pure solvent baseline.

High resolution MS (HRMS) was measured at the Mass Spectrometry Centre, Faculty of Chemistry, University of Vienna utilizing a Bruker maXis UHR-TOF.

TEM solid samples were dispersed in 100% ethanol unless otherwise stated. 5 µL drops of all samples were put onto carbon-coated copper grids and allowed to air dry. Images were obtained using Gatan Digital Micrograph software with an UltraScan 4000 digital camera attached to a Jeol 2010 TEM running at 200kV. EDS data were obtained at the same time using an Oxford Instruments INCA Energy EDS system.

Thermogravimetric analysis (TGA) was performed using a Perkin Elmer TGA 4000 instrument in the temperature range of 30 – 700 °C under nitrogen atmosphere, at a heating rate of 10 °C min^{-1}.

Synthesis of 1,3-Dimethyl-N-BOC-O-methyl-L-histidinium iodide, 1(L)

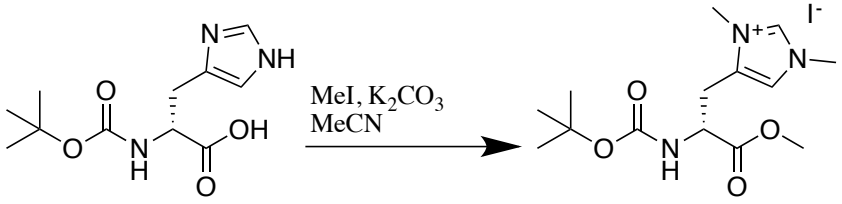


Procedure

BOC-L-His-OH (1.16 g, 4.6 mmol, 1 eq.) and K_2CO_3 (1.89 g, 13.7 mmol, 3 eq.) were suspended in MeCN (~100 mL). MeI (2.9 mL, 46.0 mmol, 10 eq.) was added to the reaction mixture. The reaction was refluxed at 90 ºC for 14 hours. The reaction was cooled and the solvent removed under reduced pressure, and the resulting residue was suspended in DCM and filtered. The resulting filtrate was concentrated under reduced pressure and Et_2O was added to precipitate the product as a white hygroscopic solid, 1.59 g (81.5%), $C_{14}H_{24}N_3O_4I \cdot ¼\ H_2O$ (425.1) requires: C 39.13, H 5.75, N 9.78%. Found: C 39.06, H 6.11, N 9.41%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (s, 1H, NC$_\varepsilon$*H*N), 7.25 (s, 1H, C$_\eta$*H*=C$_\gamma$), 5.70 (d, J = 7.2 Hz, 1H, N*H*CO), 4.53 (q, J = 6.0 Hz, 1H, C$_\alpha$*H*COO), 3.97 (s, 3H, NC*H*$_3$), 3.93 (s, 3H, NC*H*$_3$), 3.77 (s, 3H, OC*H*$_3$), 3.21 (m, 2H, C$_\beta$*H*$_a$H, C$_\beta$*H*$_b$H), 1.37 (s, 9H, (C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8 (*C*OO), 155.5 (*C*ONH), 137.4 (N*C*$_\varepsilon$N), 131.8 (*C*$_\gamma$=CH$_\eta$), 121.8 (*C*$_\eta$H=C$_\gamma$), 80.8 (*C*(CH$_3$)$_3$), 53.4 (*C*$_\alpha$HCOO), 52.2 (O*C*H$_3$), 36.9 (N*C*H$_3$), 34.5 (N*C*H$_3$), 28.3 ((*C*H$_3$)$_3$), 26.6 (*C*$_\beta$H$_2$).

ESI-MS (m/z): Calcd for $C_{14}H_{24}N_3O_4I$ [$C_{14}H_{24}N_3O_4^+$]: 298.1767, Found: 298.1753.

Synthesis of 1,3-Dimethyl-N-BOC-O-methyl-D-histidinium iodide, 1(D)

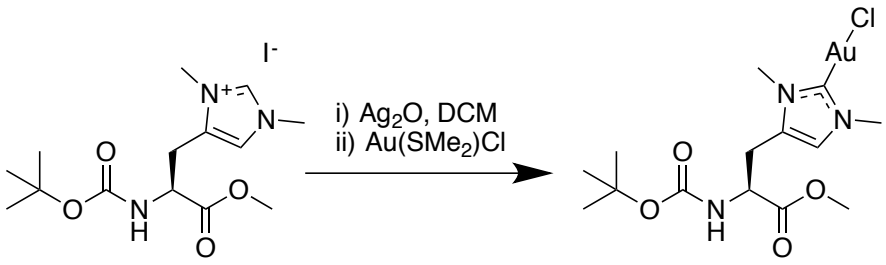


Procedure

BOC-D-His-OH (1.16 g, 4.6 mmol, 1 eq.) and K_2CO_3 (1.89 g, 13.7 mmol, 3 eq.) were suspended in MeCN (~100 mL). MeI (2.9 mL, 46.0 mmol, 10 eq.) was added to the reaction mixture. The reaction was refluxed at 90 ºC for 14 hours. The reaction was cooled and the solvent removed under reduced pressure, and the resulting residue was suspended in DCM and filtered. The resulting filtrate was concentrated under reduced pressure and Et_2O was added to precipitate the product as a white hygroscopic solid, 754 mg (42.1%), $C_{14}H_{24}N_3O_4I \cdot ¾\ H_2O$ (425.1) requires: C 38.32, H 5.86, N 9.58%. Found: C 38.16, H 6.02, N 9.34%. ^{1}H NMR (400 MHz, $CDCl_3$/ DMSO-d_6) δ 9.43 (s, 1H, NC$_\varepsilon$*H*N), 7.14 (s, 1H, C$_\eta$*H*=C$_\gamma$), 6.21(d, J = 7.6 Hz, 1H, N*H*CO), 4.25 (q, J = 7.6 Hz, 1H, C$_\alpha$*H*COO), 3.72 (s, 3H, NC*H*$_3$), 3.68 (s, 3H, NC*H*$_3$), 3.52 (s, 3H, OC*H*$_3$), 2.96 (m, 2H, C$_\beta$*H*$_a$H, C$_\beta$*H*$_b$H), 1.14 (s, 9H, (C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, $CDCl_3$/ DMSO-d_6) δ 170.8 (*C*OO), 155.6 (*C*ONH), 136.9 (N*C*$_\varepsilon$N), 131.8 (*C*$_\gamma$=CH$_\eta$), 121.7 (*C*$_\eta$H=C$_\gamma$), 80.1 (*C*(CH$_3$)$_3$), 52.9 (*C*$_\alpha$HCOO), 51.9 (O*C*H$_3$), 36.5 (N*C*H$_3$), 34.1 (N*C*H$_3$), 28.2 ((*C*H$_3$)$_3$), 25.9 (*C*$_\beta$H$_2$).

ESI-MS (m/z): Calcd for $C_{14}H_{24}N_3O_4I$ [$C_{14}H_{24}N_3O_4^+$]: 298.1767, Found: 298.1755

Synthesis of Chlorido(1,3-dimethyl-N-BOC-O-methyl-L-histidin-2-ylidene)gold(I), 2(L)

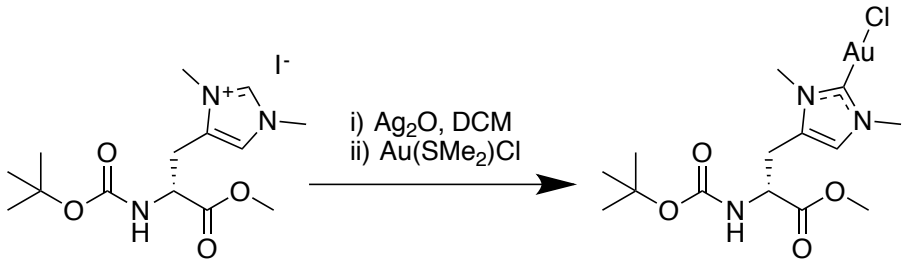


Procedure

Compound 1(L) (100 mg, 0.24 mmol, 1 eq.) and Ag_2O (28 mg, 0.12 mmol, 0.5 eq.) were suspended in dry DCM (~10 mL) and stirred at room temperature for 1 hour. To this reaction mixture [$Au(SMe_2)Cl$] (71 mg, 0.24 mmol, 1 eq.) was added. The reaction was stirred at room temperature for a further 14 hours. The resulting suspension was filtered through a Celite plug and further washed through with CH_2Cl_2 (5x10 mL). The filtrate was concentrated under reduced pressure, Et_2O was added affording 2(L) as a yellow solid, 102 mg (79%); $C_{14}H_{23}AuClN_3O_4$ (529.8) requires: C 31.74, H 4.38, N 7.93%. Found: C 31.44, H 4.35, N 7.70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.71 (s, 1H, $C_\eta H{=}C_\gamma$), 5.19 (d, J = 7.2 Hz, 1H, N*H*CO), 4.55 (q, J = 6.0 Hz, $C_\alpha H$COO), 3.76 (s, 3H, OCH_3), 3.73 (s, 6H, NCH_3), 3.15 (dd, J = 11.2, 4.4 Hz, 1H, $C_\beta H_a$H), 2.96 (dd, J = 9.6, 6.4 Hz, 1H, $C_\beta H_b$H), 1.38 (s, 9H, $(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9 (NC_εN), 171.1 (*C*OO), 155.1 (*C*ONH), 129.4 ($C_\gamma{=}CH_\eta$), 119.9 ($C_\eta H{=}C_\gamma$), 80.9 ($C(CH_3)_3$), 53.1 (C_αHCOO), 52.4 (OCH_3), 38.3 (NCH_3), 35.6 (NCH_3), 28.3 (($CH_3)_3$), 27.8 ($C_\beta H_2$).

ESI-MS (m/z): Calcd for $C_{14}H_{23}AuClN_3O_4$ [bis complex – $C_{28}H_{46}AuN_6O_8^+$]: 791.3043, Found: 791.3017.

Synthesis of Chlorido(1,3-dimethyl-N-BOC-O-methyl-D-histidin-2-ylidene)gold(I), 2(D)

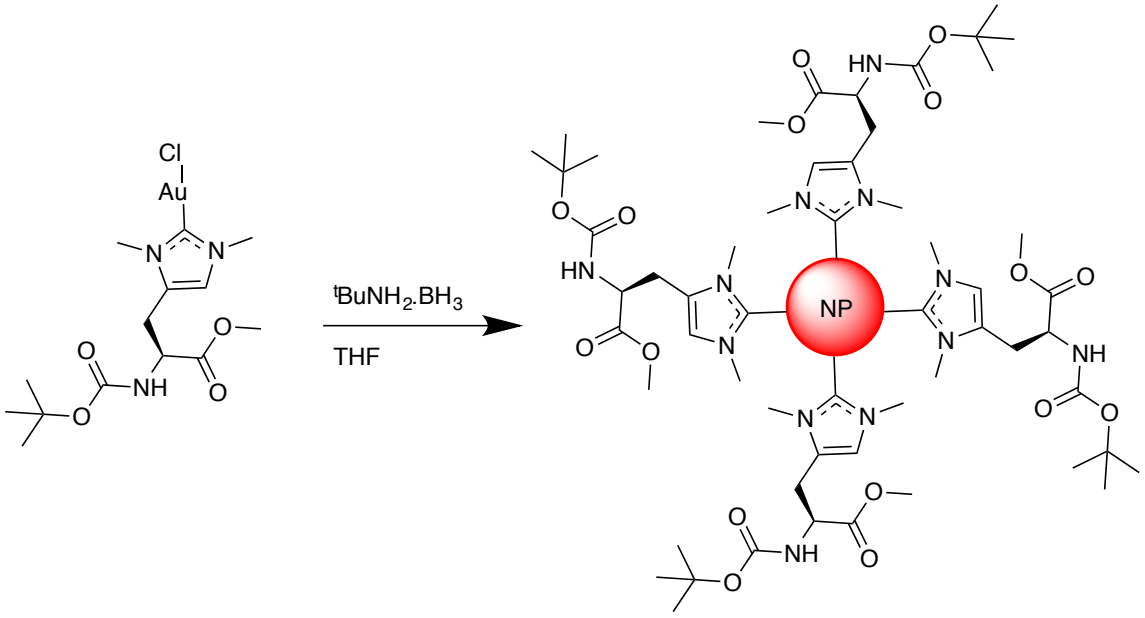


Procedure

Compound 1(D) (350 mg, 0.82 mmol, 1 eq.) and Ag_2O (95 mg, 0.41 mmol, 0.5 eq.) were suspended in dry DCM (~10 mL) and stirred at room temperature for 1 hour. To this reaction mixture [$Au(SMe_2)Cl$] (242 mg, 0.82 mmol, 1 eq.) was added. The reaction was stirred at room temperature for a further 14 hours. The resulting suspension was filtered through a Celite plug and further washed through with CH_2Cl_2 (5x10 mL). The filtrate was concentrated under reduced pressure, Et_2O and hexane was added affording 2(D) as a yellow solid, 340 mg (78 %), $C_{14}H_{23}AuClN_3O_4$ (529.8) requires: C 31.74, H 4.38, N 7.93%. Found: C 31.93, H 4.52, N 7.70%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H, $C_\eta H{=}C_\gamma$), 5.21 (d, J = 7.2 Hz, 1H, N*H*CO), 4.52 (q, J = 6.0 Hz, $C_\alpha H$COO), 3.74 (s, 3H, OCH_3), 3.72 (s, 6H, NCH_3), 3.15 (dd, J = 15.6, 5.2 Hz, 1H, $C_\beta H_a$H), 2.96 (dd, J = 15.6, 5.2 Hz, 1H, $C_\beta H_b$H), 1.37 (s, 9H, $(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.9 (NC_εN), 171.1 (*C*OO), 155.1 (*C*ONH), 129.4 ($C_\gamma{=}CH_\eta$), 120.0 (C_ηH=C_γ), 80.8 ($C(CH_3)_3$), 53.1 (C_αHCOO), 52.5 (OCH_3), 38.3 (NCH_3), 35.6 (NCH_3), 28.3 ($(CH_3)_3$), 27.8 ($C_\beta H_2$).

ESI-MS (m/z): Calcd for $C_{14}H_{23}AuClN_3O_4$ [bis complex – $C_{28}H_{46}AuN_6O_8^+$]: 791.3043, Found: 791.3019.

Synthesis of 3-NP(L) by reduction of 2(L) with $^{t}BuNH_2 \bullet BH_3$

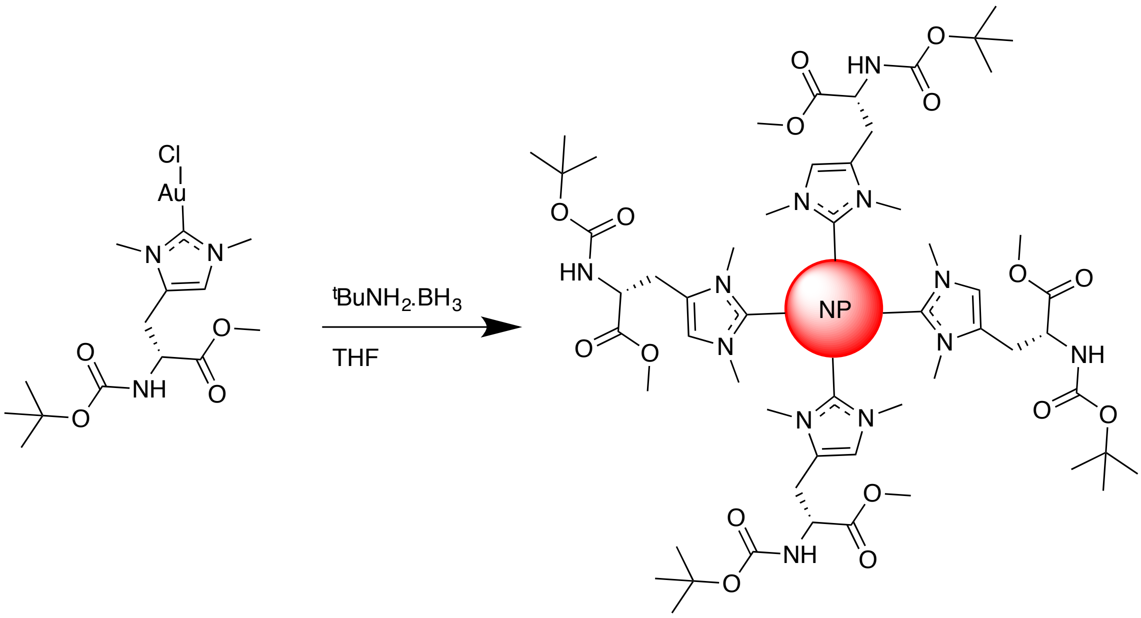


Procedure

2(L) (20 mg, 0.038 mmol, 1 eq) was dissolved in THF (1 mL) and stirred vigorously at room temperature. To this stirring solution a $^{t}BuNH_2.BH_3$ (12 mg, 0.13 mmol, 3.6 eq.) in THF (0.5 mL) solution was added quickly. The solution was stirred for 24 hours. A drop of water was added to the colourless/light pink solution to quench the borane complex, and the reaction was stirred for an additional hour at room temperature. A dark solid forms as a precipitate in the solution. The solid was isolated via centrifugation and the supernatant discarded. The solid was dried under vacuum. The resultant dark solid could be re-dispersed in organic solvents (e.g. DCM, THF, toluene) but not protic solvents (e.g. ethanol, methanol etc.), due to irreversible aggregation. Size selection was performed by dispersing the black powder in THF and centrifuging for 1 hour at 13,500 rpm. The remaining black solid was re-dispersed in THF and an aliquot taken drop-casted on a TEM grid to reveal the presence of nanoparticles (5.0 ± 0.6 nm, ± 12.0 %). These NPs are re-dispersible in THF, DCM, toluene but not in EtOH or water. UV/Vis (DCM): λ_{max}=517 nm; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H, $C_\eta H{=}C_\gamma$), 5.89 (d, J = 8.0 Hz, 1H, N*H*CO), 4.55 (br, $C_\alpha H$COO), 3.84 (s, 6H, NCH_3), 3.78 (s, 3H, OCH_3), 3.18 (br, 1H, $C_\beta H_a$H), 3.16 (dd, J = 9.6, 6.4 Hz, 1H, $C_\beta H_b$H), 1.40 (s, 9H, $(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.6 (NC_εN), 171.5 (*C*OO), 155.6 (*C*ONH), 130.7 (C_γ=CH$_\eta$), 121.4 (C_ηH=C$_\gamma$), 80.4 ($C(CH_3)_3$), 53.2 (OCH_3), 52.4 (C_αHCOO), 38.2 (NCH_3), 35.6 (NCH_3), 28.1 ($(CH_3)_3$), 27.3 ($C_\beta H_2$).

Given the average particle size (5.0 nm), the number of gold atoms in the metal core is estimated to be ~3847 by the method of Leff *et al.*[2]

Synthesis of 3-NP(D) by reduction of 2(D) with $^{t}BuNH_2.BH_3$



Procedure

2(D) (20 mg, 0.038 mmol, 1 eq) was dissolved in THF (1 mL) and stirred vigorously at room temperature. To this stirring solution a $^{t}BuNH_2.BH_3$ (12 mg, 0.13 mmol, 3.6 eq.) in THF (0.5 mL) solution was added quickly. The solution was stirred for 24 hours. A drop of water was added to the colourless/light pink solution to quench the borane complex, and the reaction was stirred for an additional hour at room temperature. A dark solid forms as a precipitate in the solution. The solid was isolated via centrifugation and the supernatant discarded. The solid was dried under vacuum. The resultant dark solid could be re-dispersed in organic solvents (e.g. DCM, THF, toluene) but not protic solvents (e.g. ethanol, methanol etc.), due to irreversible aggregation. Size selection was performed by dispersing the black powder in THF and centrifuging for 1 hour at 13,500 rpm. The obtained black solid was re-dispersed in THF and an aliquot taken drop-casted on a TEM grid to reveal the presence of nanoparticles (5.3 ± 0.8 (15.8%) nm). These NPs are re-dispersible in THF, DCM, toluene but not in EtOH or water. UV/Vis (DCM): λ_{max}=517 nm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 1H, $C_\eta H$=C_γ), 5.89 (d, J = 8.0 Hz, 1H, N*H*CO), 4.55 (br, $C_\alpha H$COO), 3.84 (s, 6H, NCH_3), 3.78 (s, 3H, OCH_3), 3.18 (br, 1H, $C_\beta H_a$H), 3.16 (dd, J = 9.6, 6.4 Hz, 1H, $C_\beta H_b$H), 1.40 (s, 9H, $(CH_3)_3$). ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.7 (NC_εN), 171.5 (*C*OO), 155.5 (*C*ONH), 130.4 (C_γ=CH_η), 121.3 (C_ηH=C_γ), 80.6 (*C*$(CH_3)_3$), 53.3 (OCH_3), 52.4 (C_αHCOO), 38.4 (NCH_3), 35.8 (NCH_3), 28.4 (($CH_3)_3$), 27.4 ($C_\beta H_2$).

Given the average particle size (5.3 nm), the number of gold atoms in the metal core is estimated to be ~4585 by the method of Leff *et al.*[2]

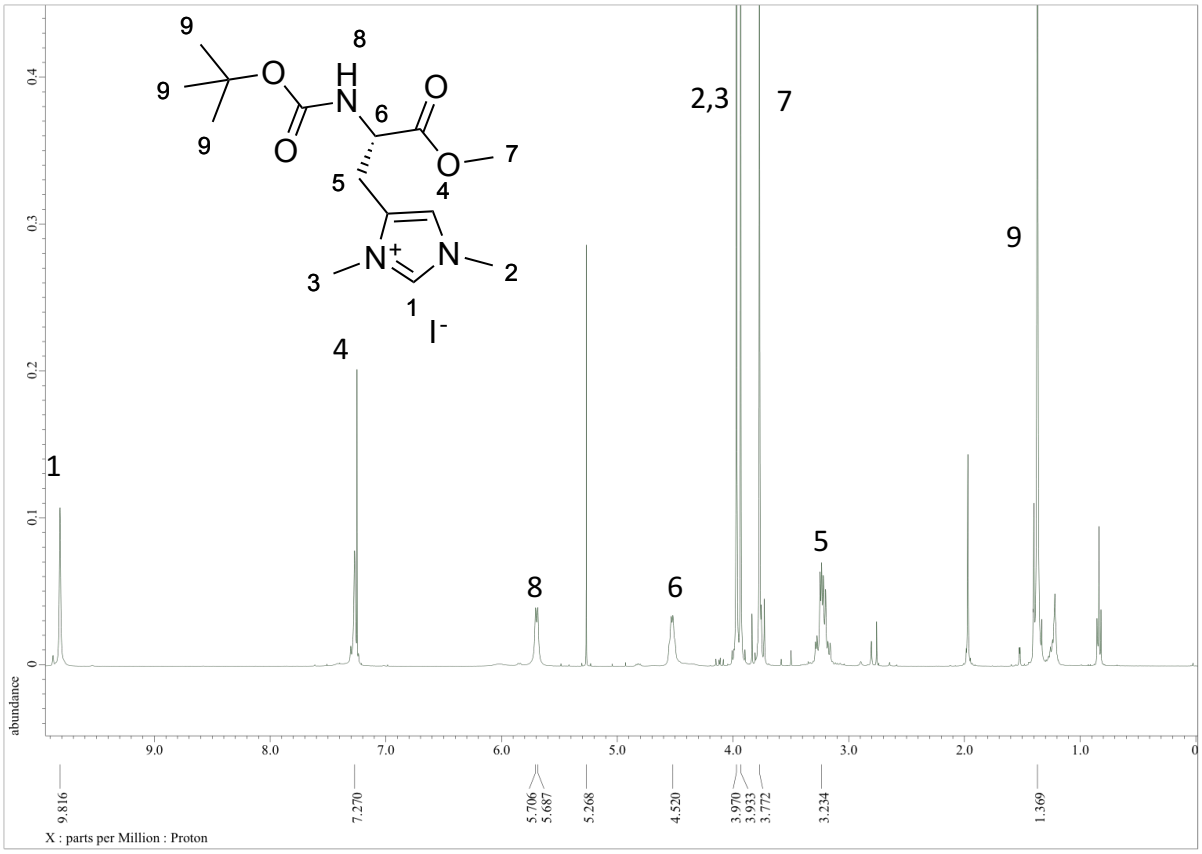


Figure S1. ^{1}H NMR spectrum of **1(L)**

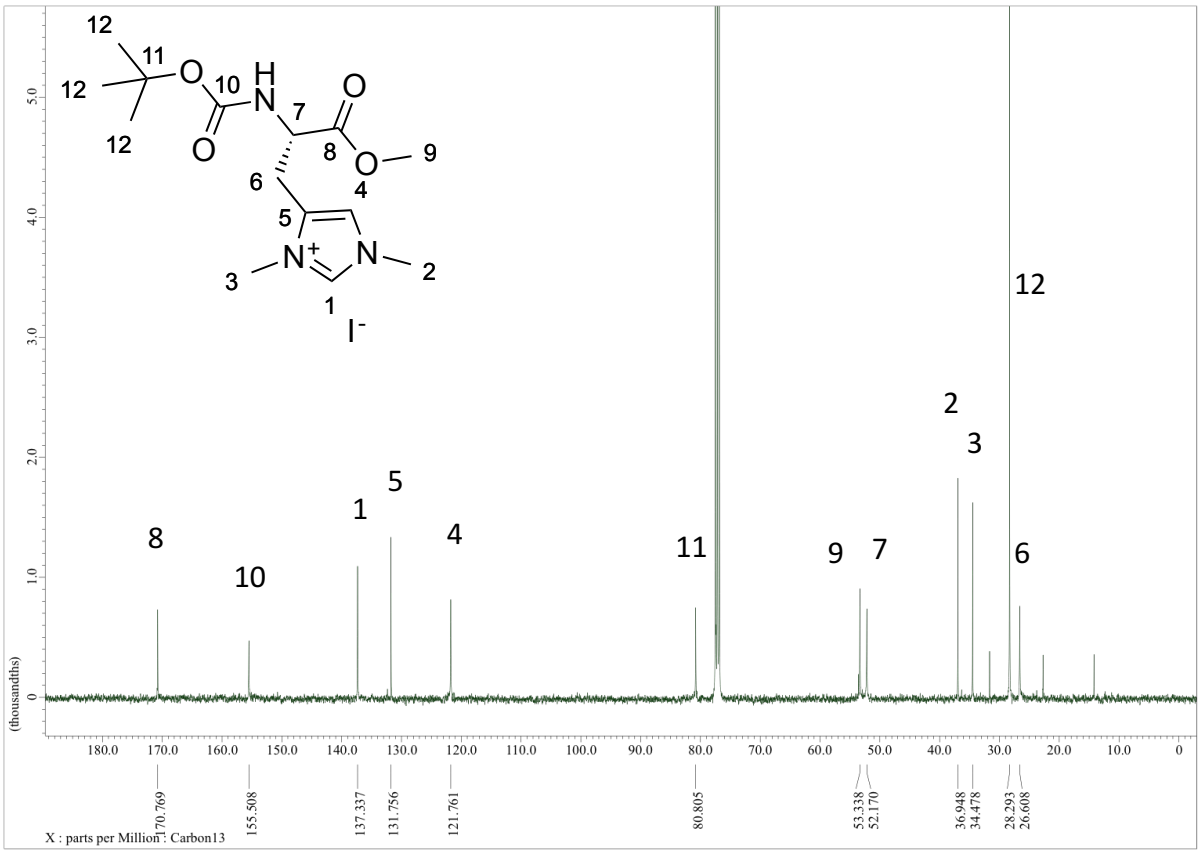


Figure S2. ^{13}C NMR spectrum of **1(L)**

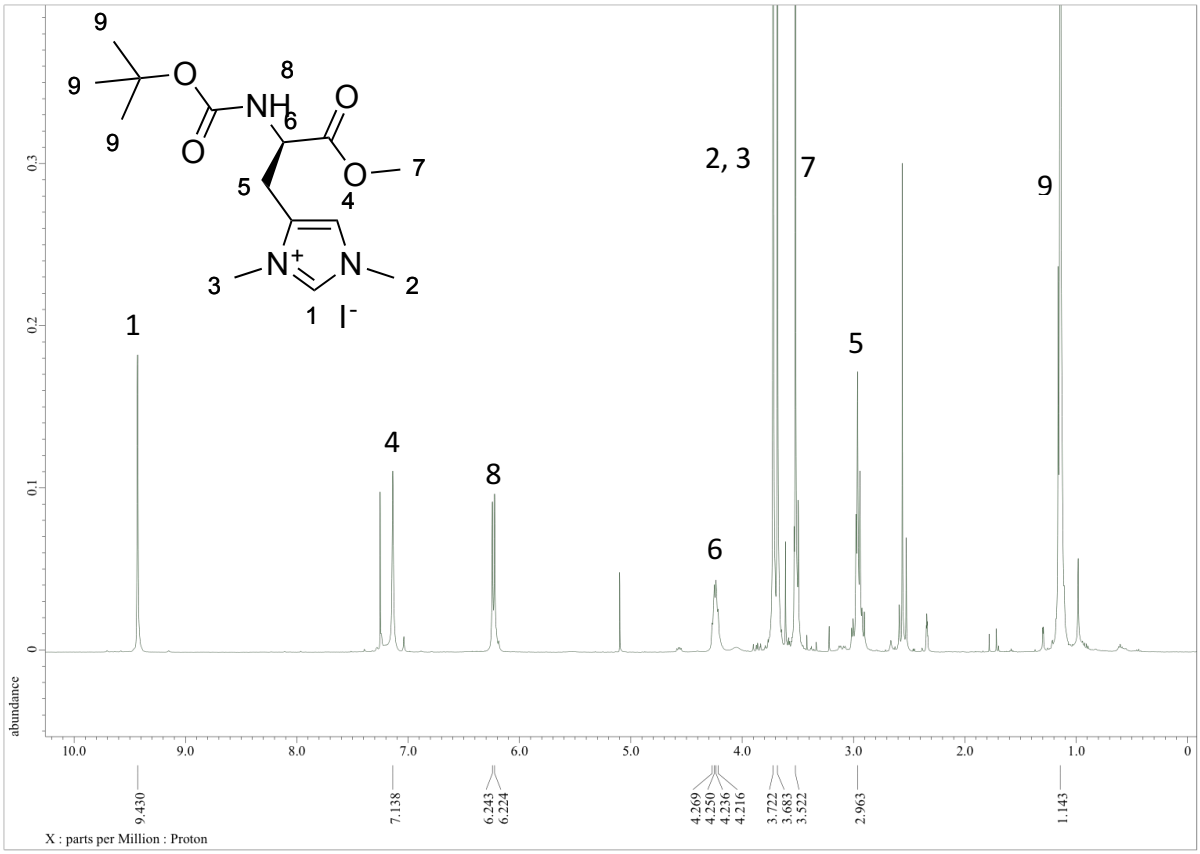


Figure S3. ^{1}H NMR spectrum of **1(D)**

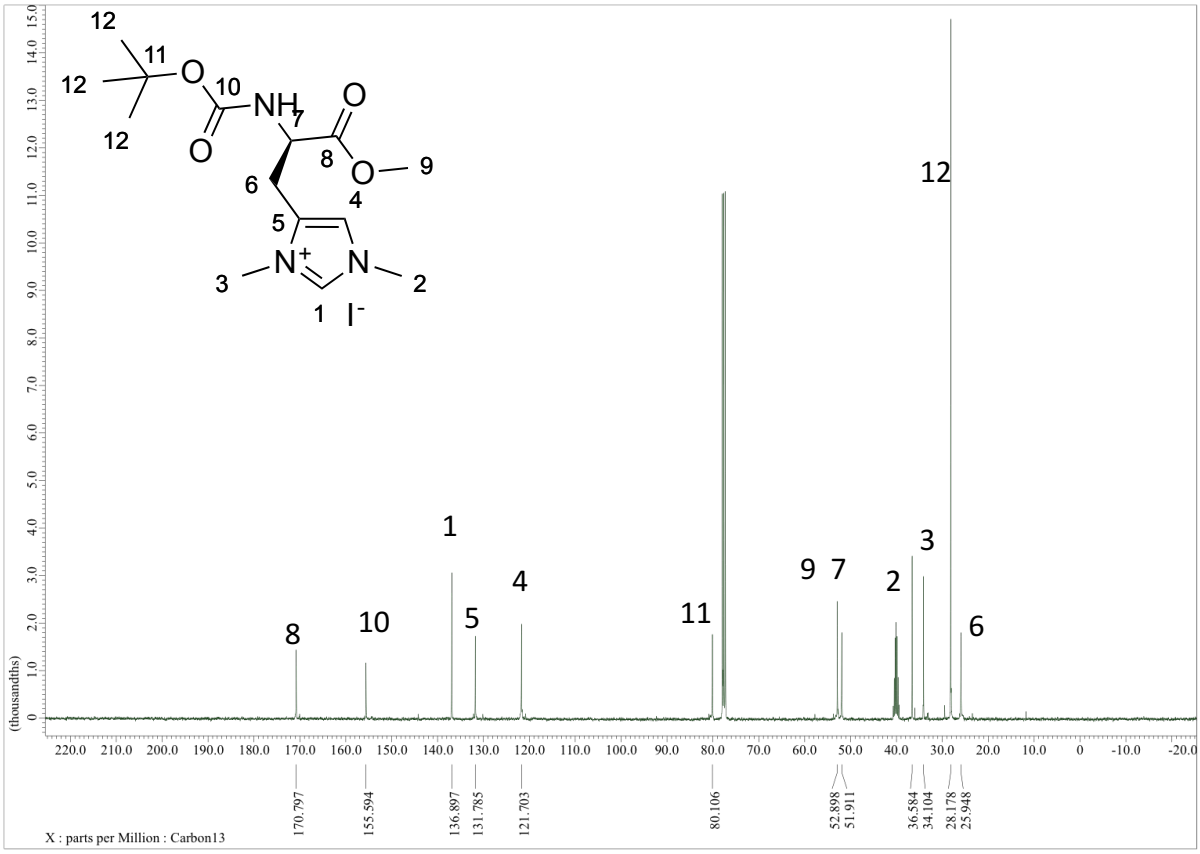


Figure S4. ^{13}C NMR spectrum of **1(D)**

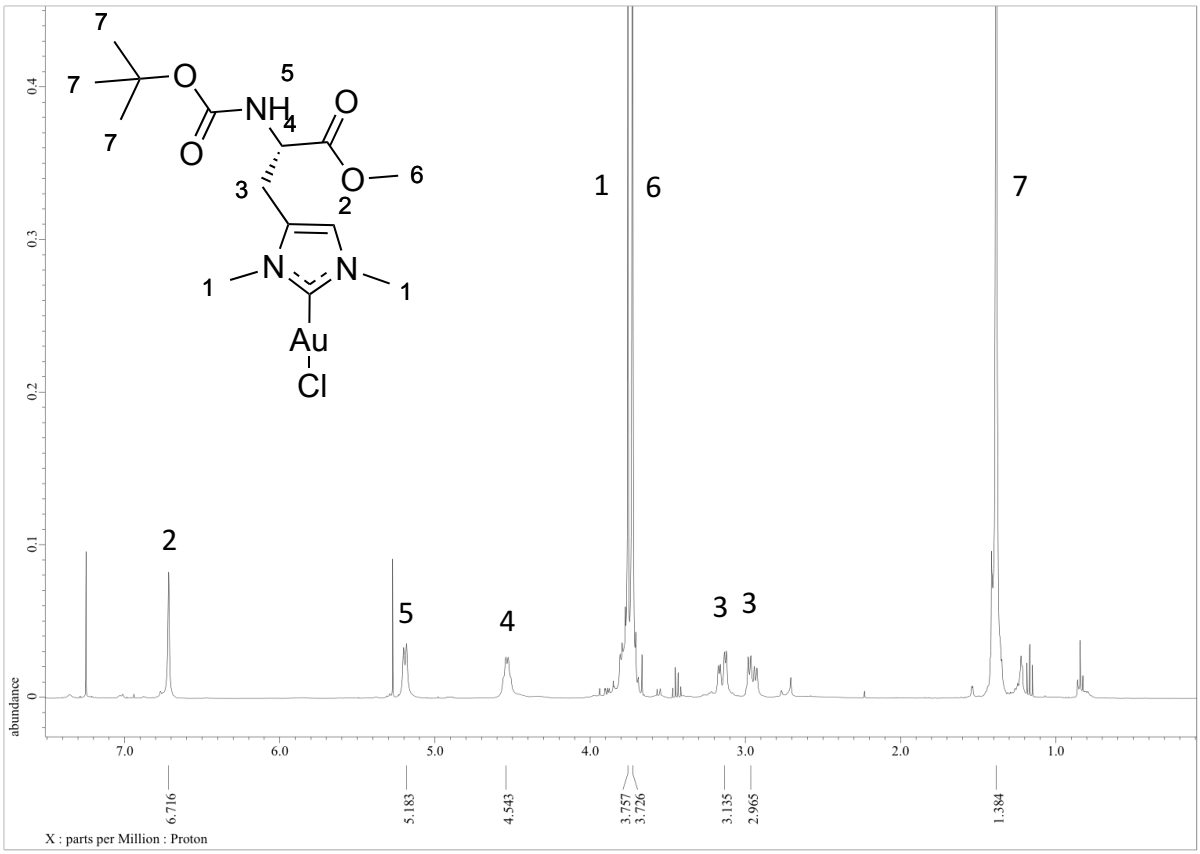


Figure S5. ^{1}H NMR spectrum of **2(L)**

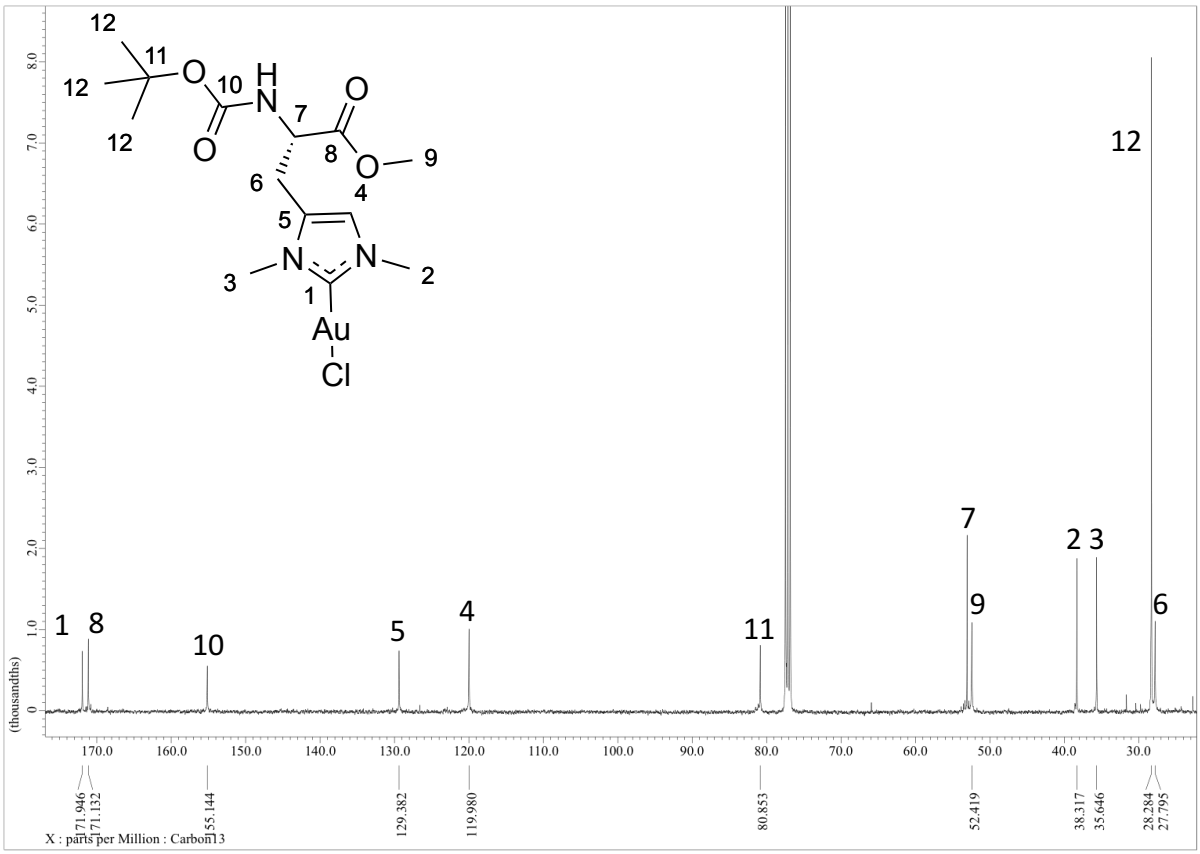


Figure S6. ^{13}C NMR spectrum of **2(L)**

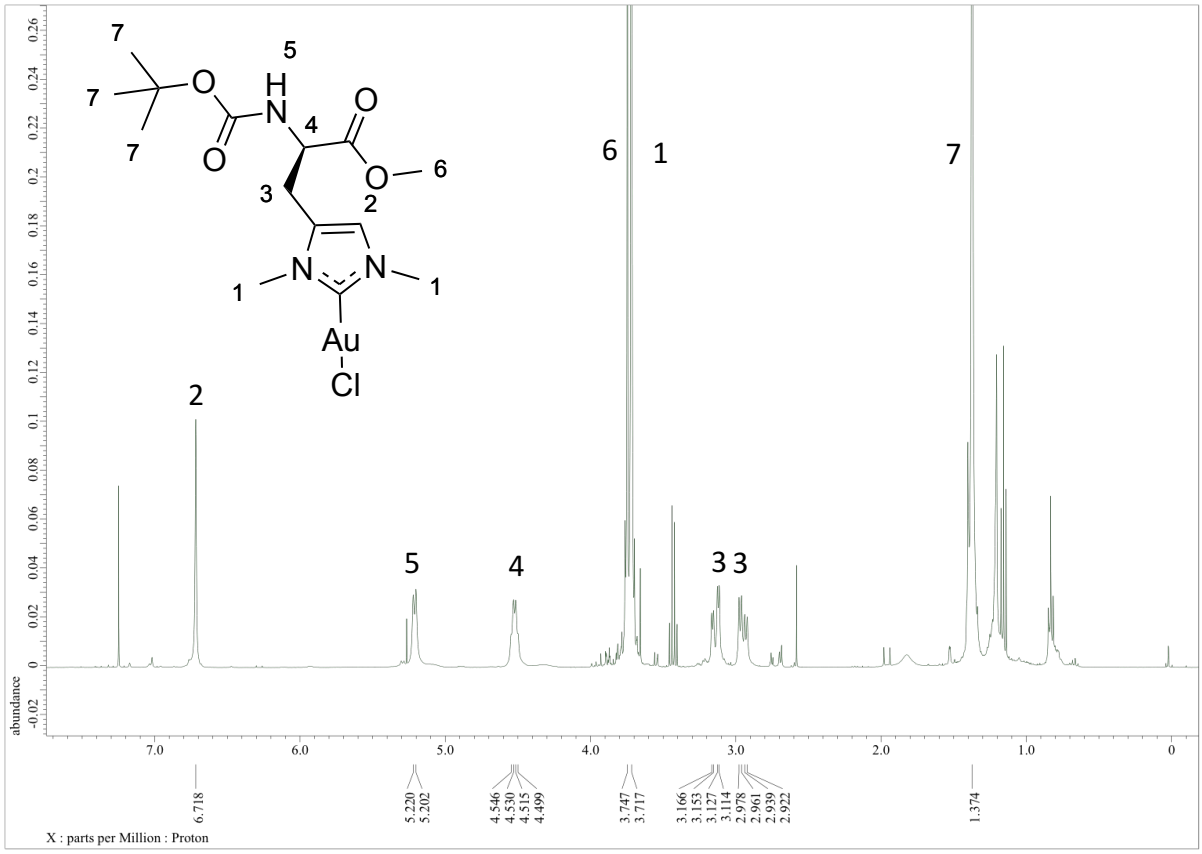


Figure S7. ^{1}H NMR spectrum of **2(D)**

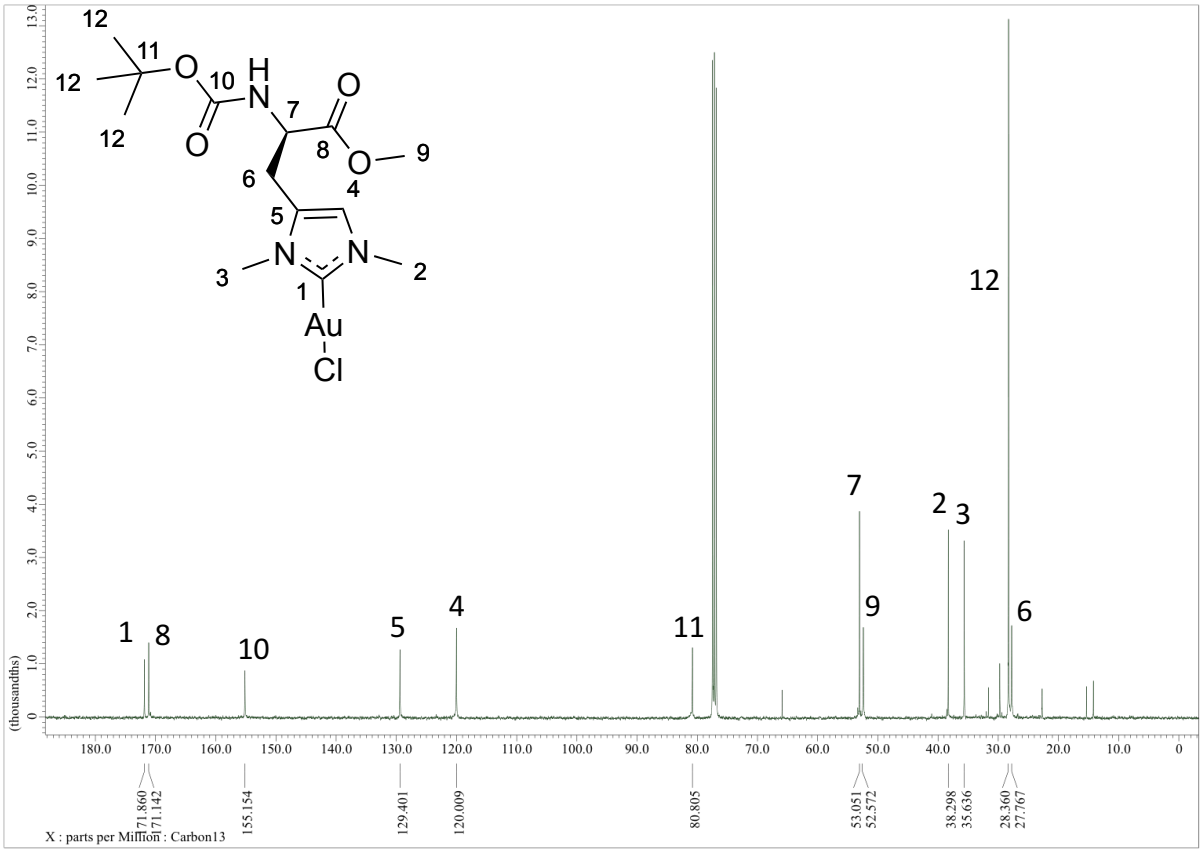


Figure S8. ^{13}C NMR spectrum of **2(D)**

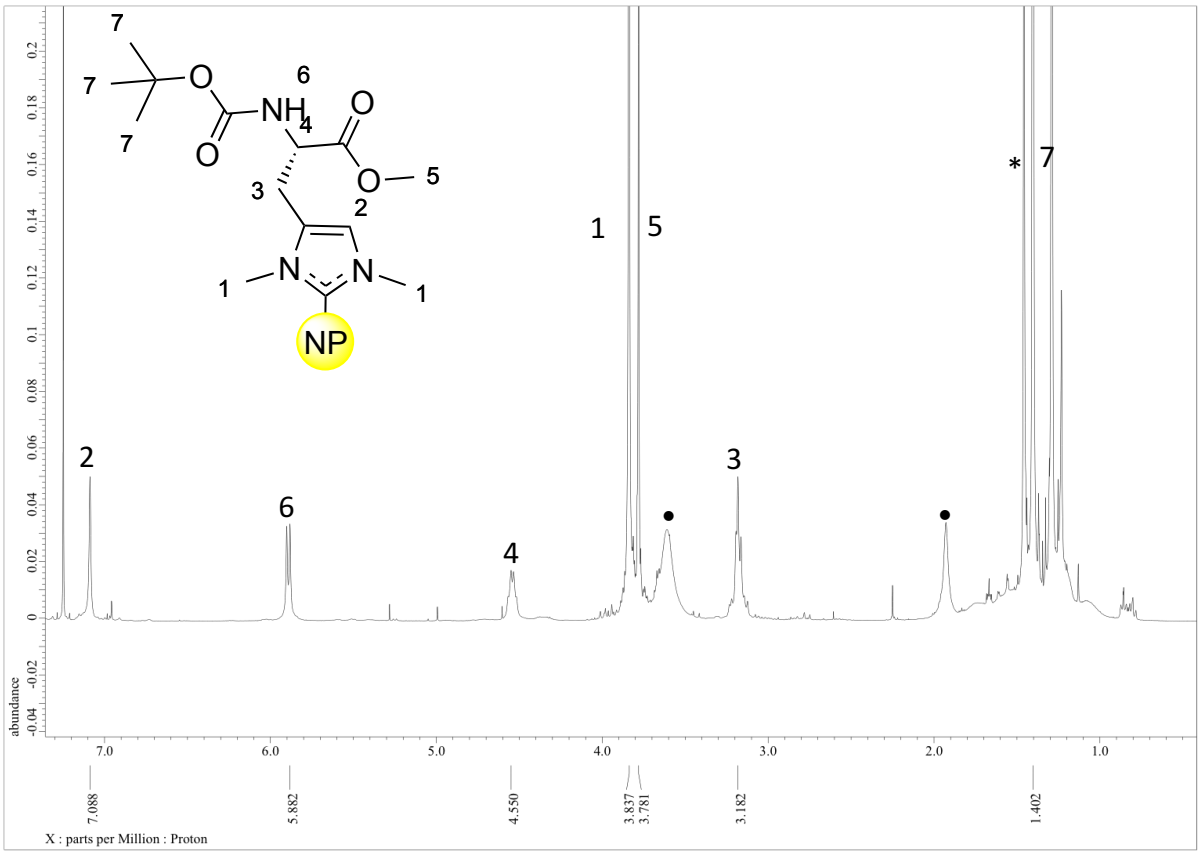


Figure S9. ^{1}H NMR spectrum of **3-NP(L)**

*=^{t}Bu from the borane complex

•=THF

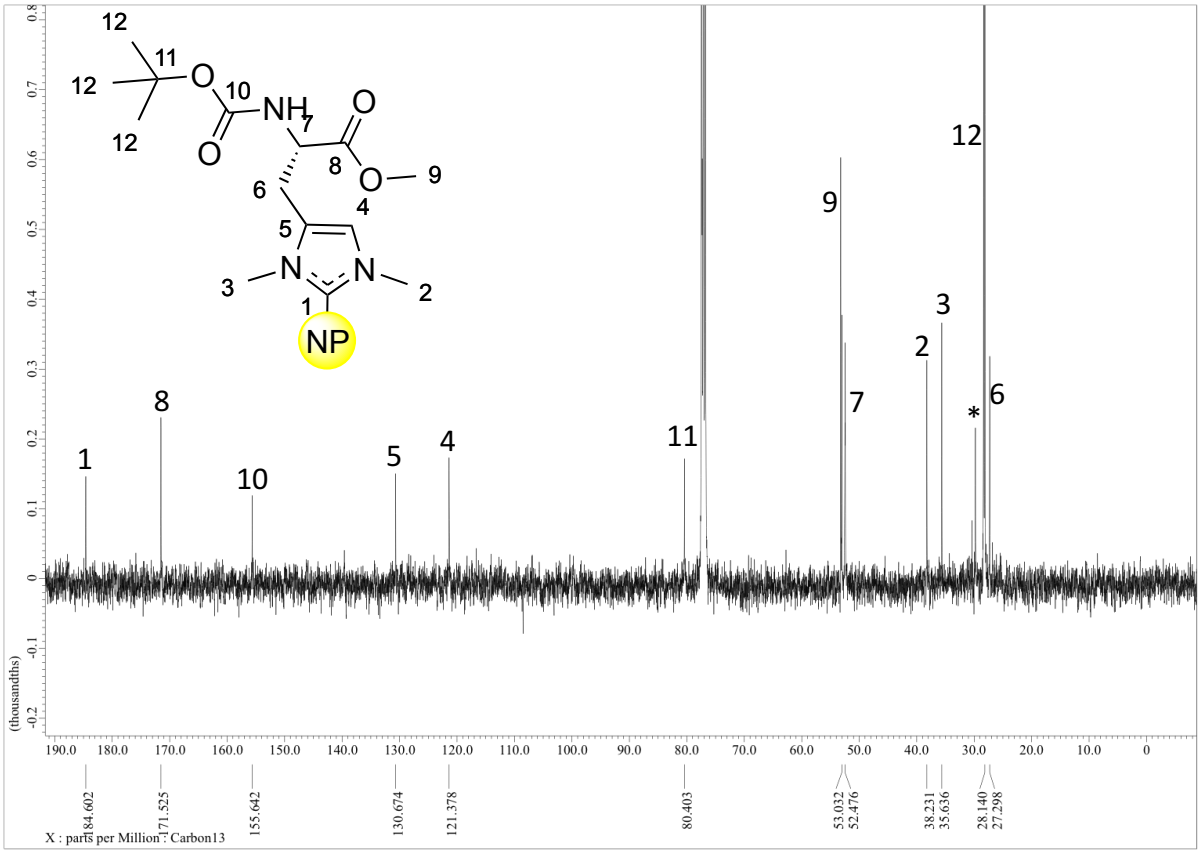


Figure S10. ^{13}C NMR spectrum of **3-NP(L)**
*=^{t}Bu from the borane complex

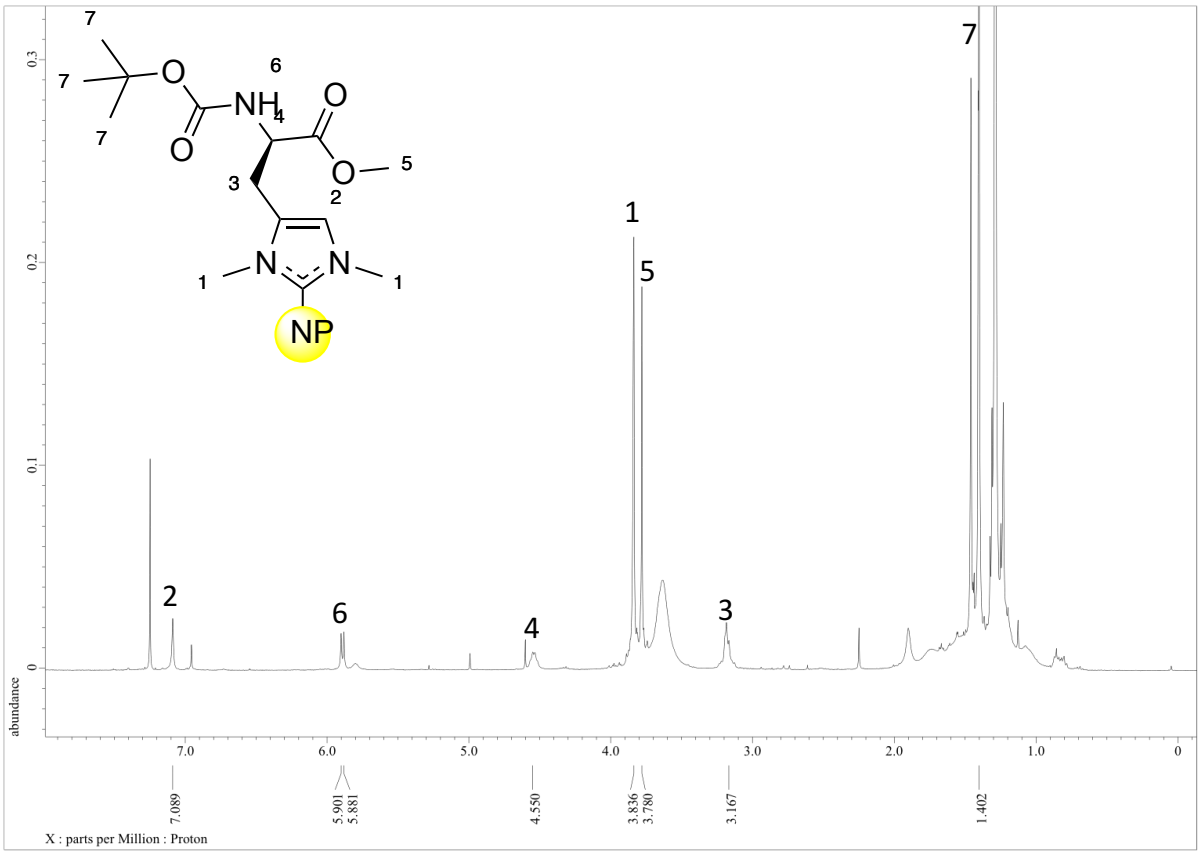


Figure S11. ^{1}H NMR spectrum of **3-NP(D)**

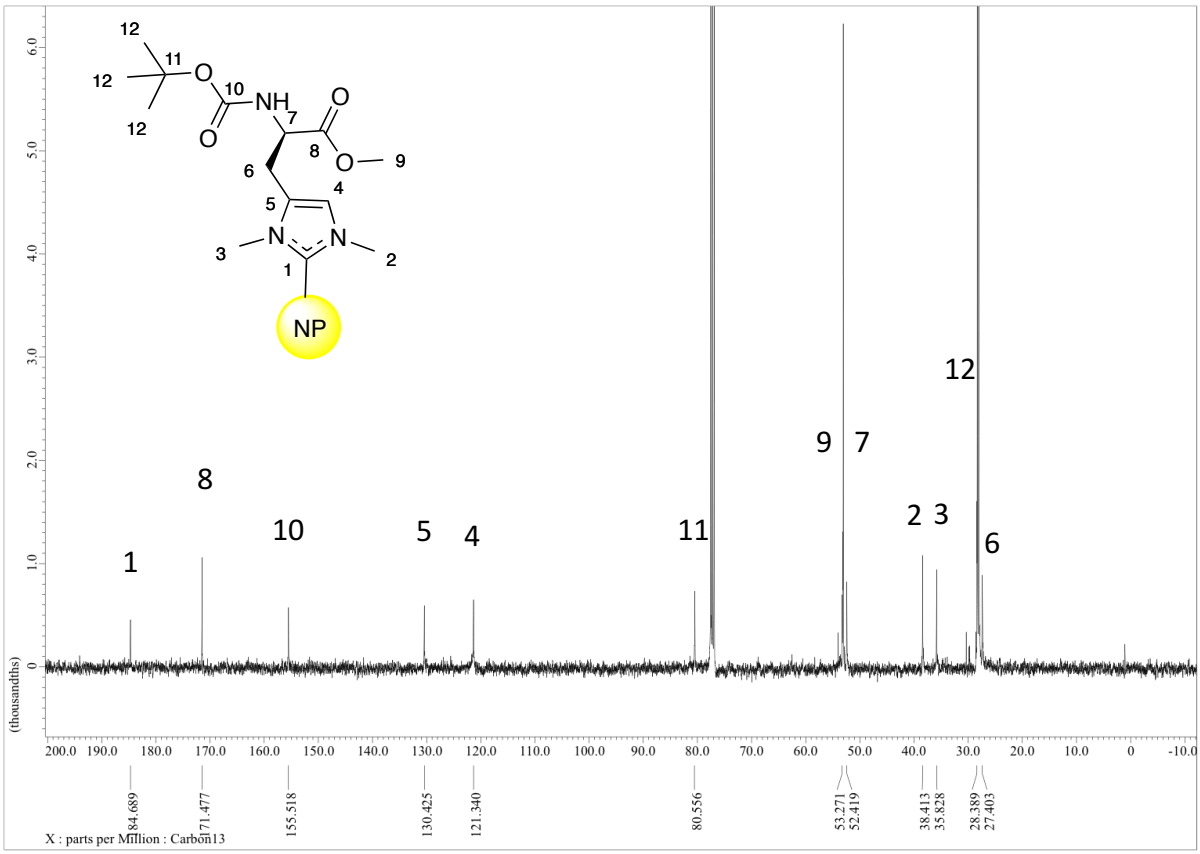


Figure S12. ^{13}C NMR spectrum of **3-NP(D)**

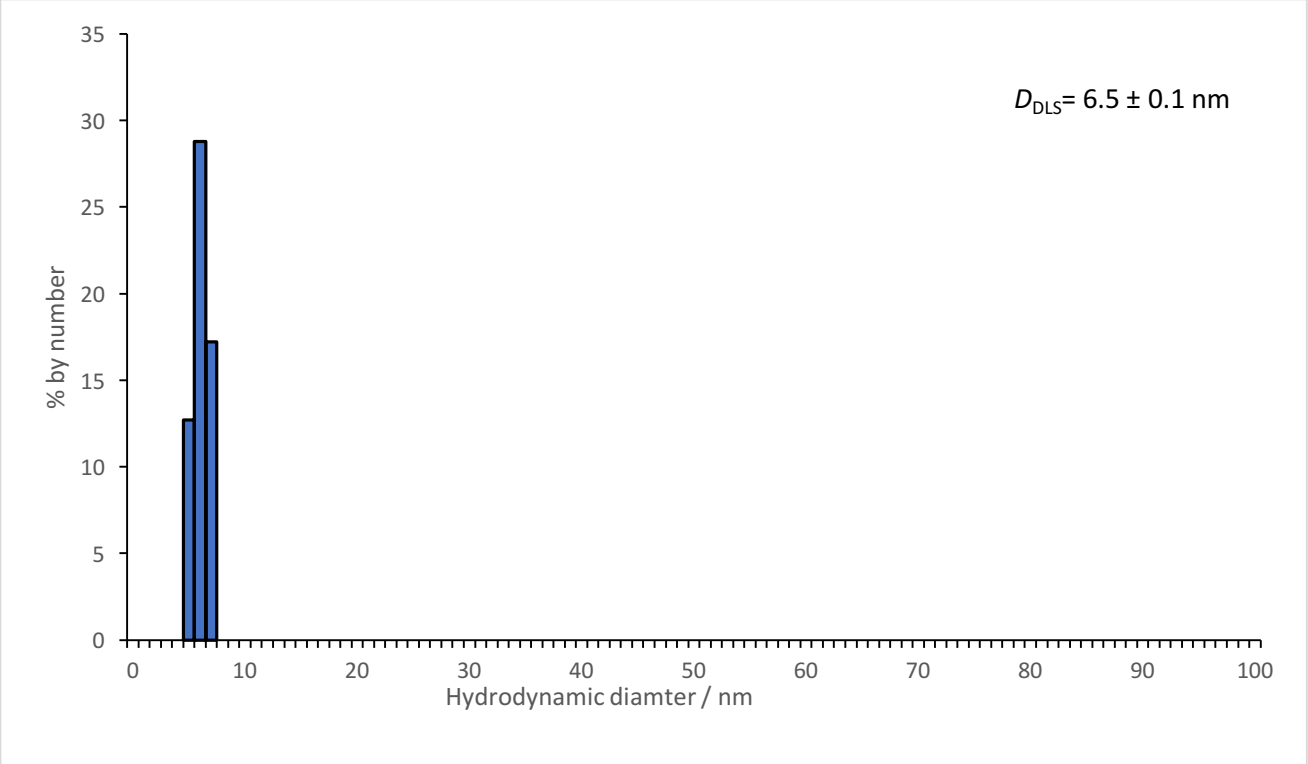


Figure S13. DLS histogram for **3-NP(L)** in THF

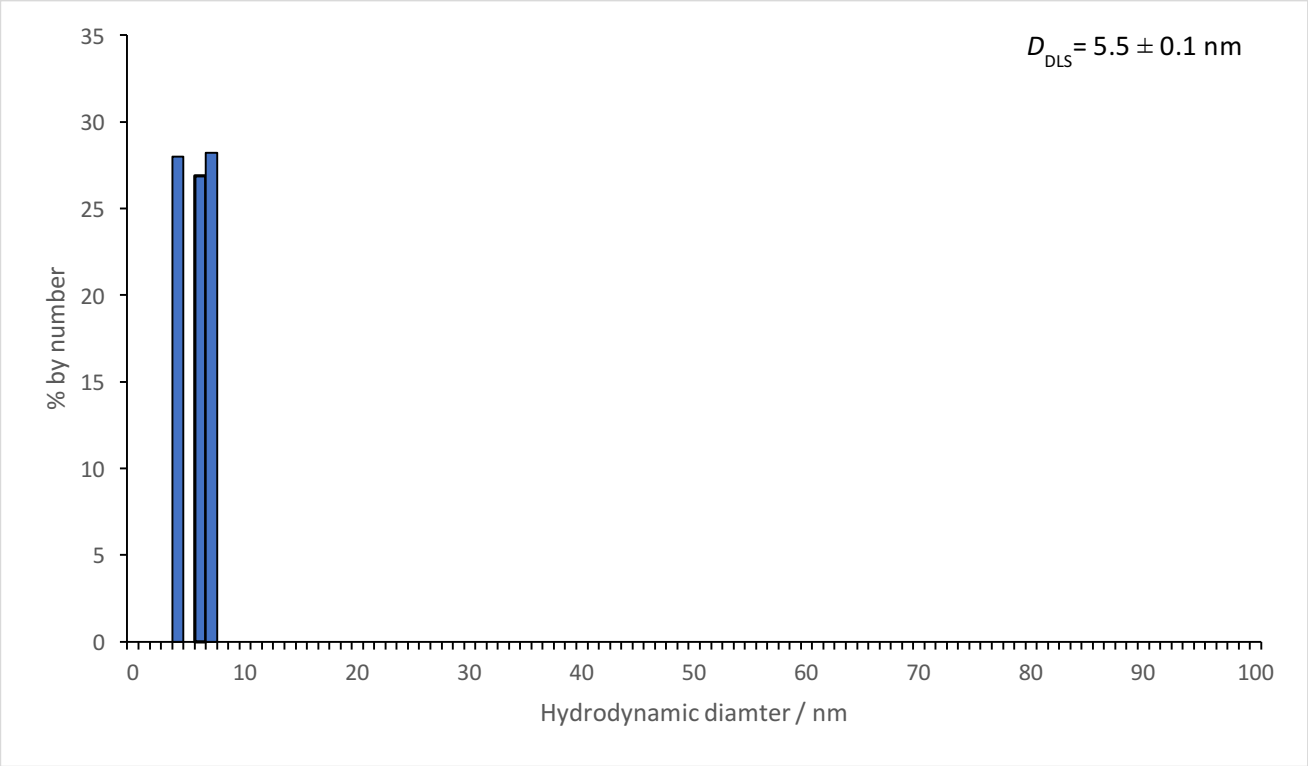


Figure S14. DLS histogram for **3-NP(D)** in THF

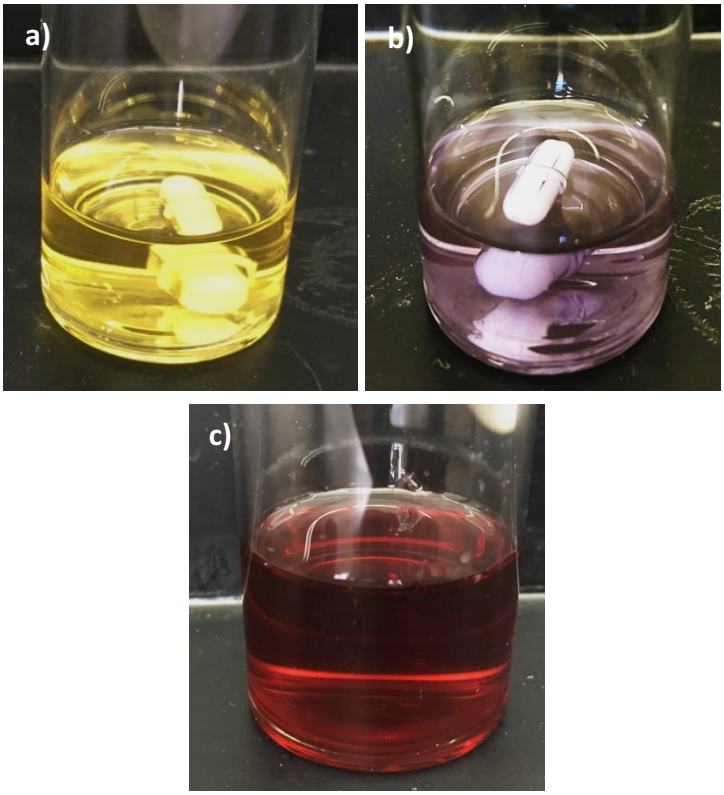


Figure S15. Photographs of **3-NP(L)** synthesis: a) **2(L)** in THF before addition of $^{t}BuNH_2.BH_3$, b) following reaction with $^{t}BuNH_2.BH_3$ and being stirred for 24 hrs at room temperature (25 ºC), c) removal of solvent and **3-NP(L)** re-dispersed in DCM.

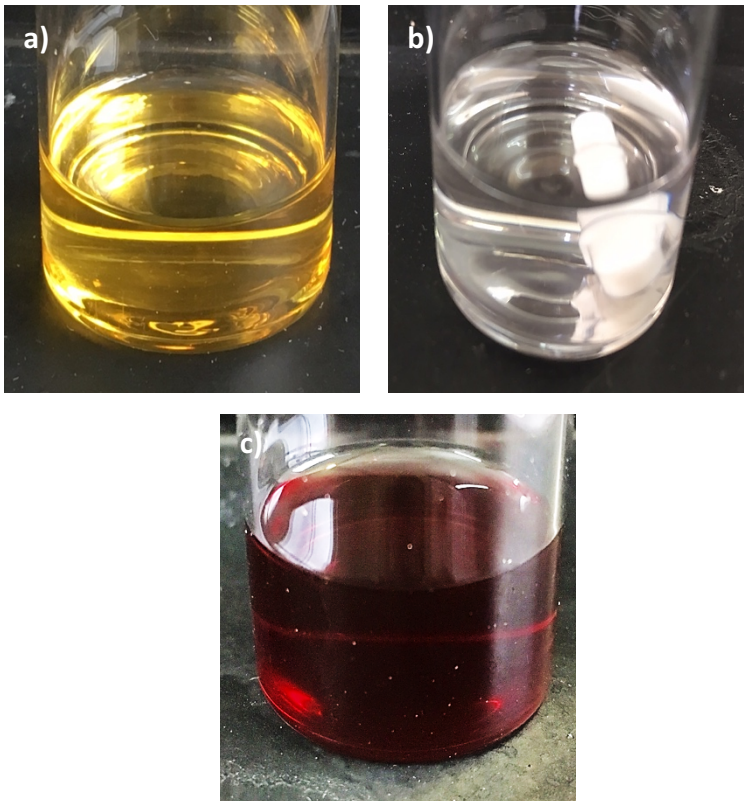


Figure S16. Photographs of **3-NP(D)** synthesis: a) **2(D)** in THF before addition of $^{t}BuNH_2.BH_3$, b) following reaction with $^{t}BuNH_2.BH_3$ and being stirred for 24 hrs at room temperature (25 ºC), c) removal of solvent and **3-NP(D)** re-dispersed in DCM.

Table S17. Summary of NHC-coated Au NPs **3-NP(D) – 3-NP(D)**. Properties: Average diameter (d) and Size Distribution (Standard deviation, σ). All measurements taken from TEM images of respective samples.

	Before Centrifugation		After Centrifugation at 13.5k RPM (Isolated particle sizes)	
	Overall Distribution		Isolated Particles	
	d (nm)	σ (%)	d (nm)	σ (%)
3-NP(L)	4.1	58.0	5.0	12.0
3-NP(D)	4.0	36.1	5.3	15.8

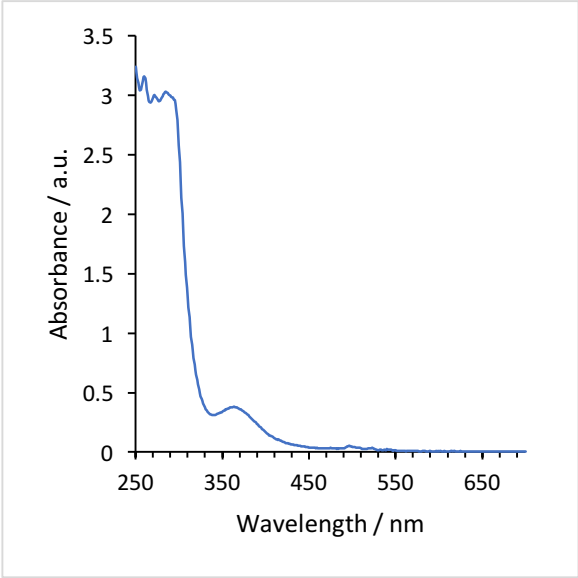


Figure S18. UV-Vis absorption spectrum of **1(L)** in DCM

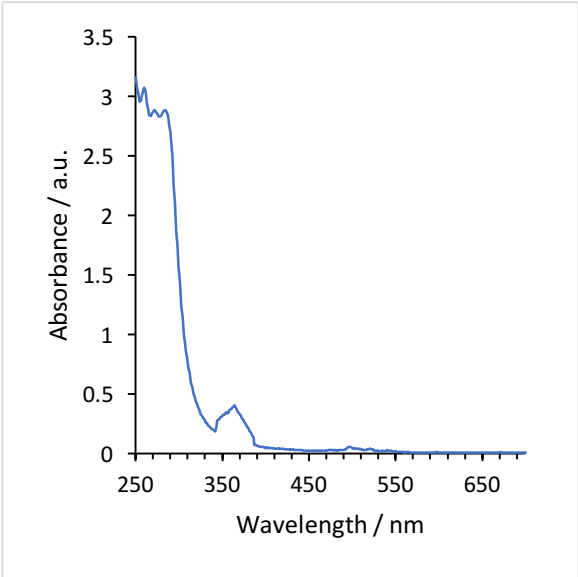


Figure S19. UV-Vis absorption spectrum of **1(D)** in DCM

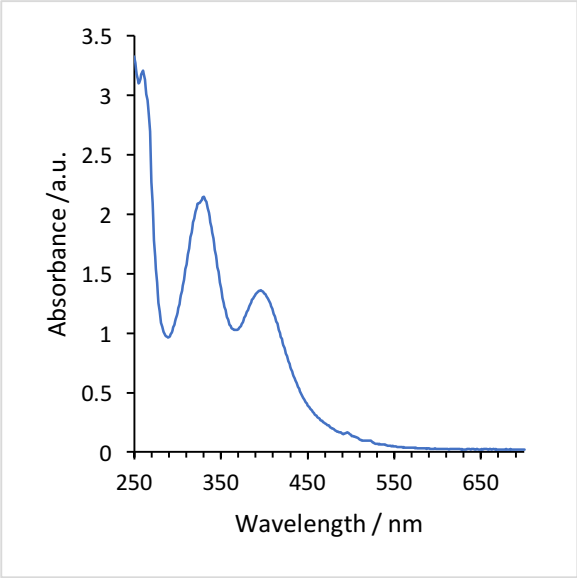


Figure S20. UV-Vis absorption spectrum of **2(L)** in DCM

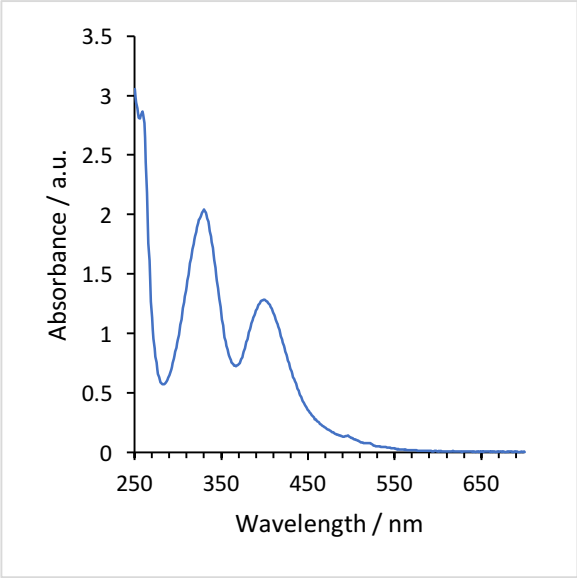


Figure S21. UV-Vis absorption spectrum of **2(D)** in DCM

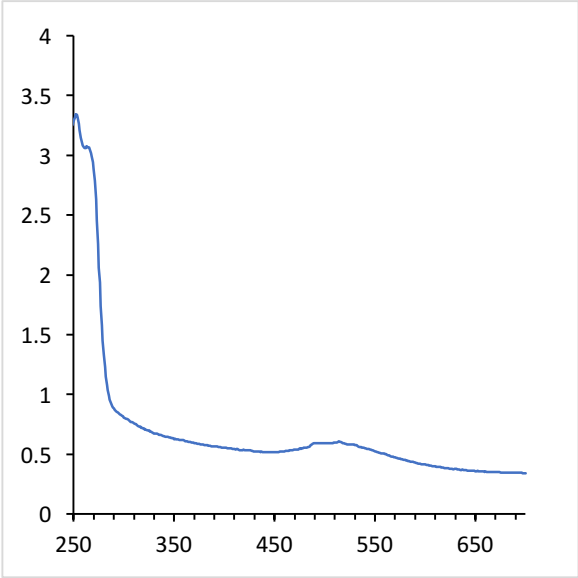


Figure S22. UV-Vis adsorption spectrum of **3-NP(L)** in DCM between 250 – 700 nm.

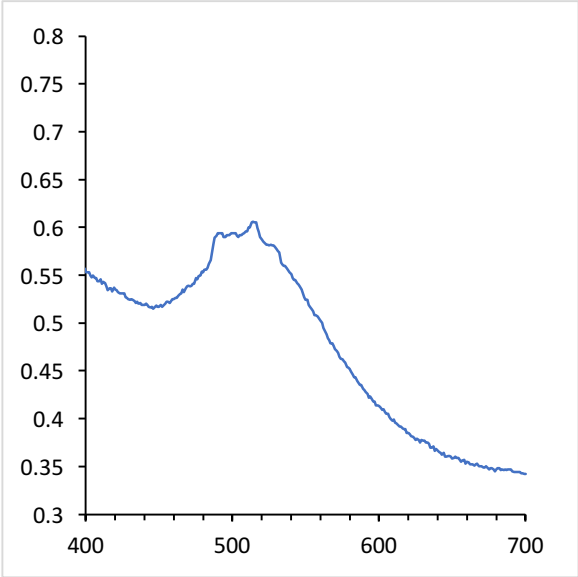


Figure S23. UV-Vis adsorption spectrum of **3-NP(L)** in DCM zoomed in on the 400 – 700 nm.

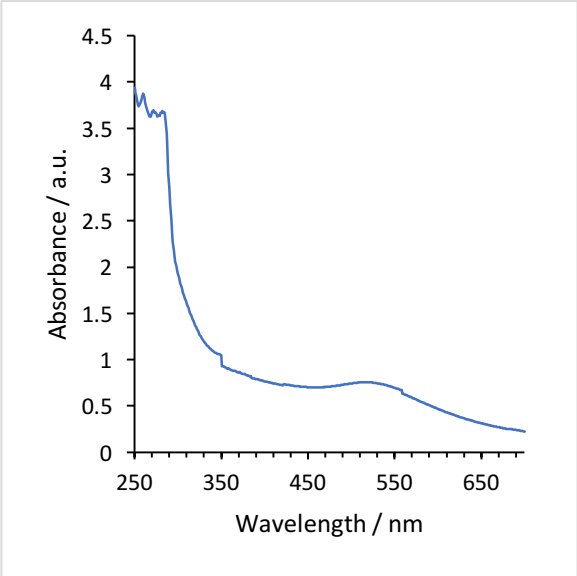


Figure S24. UV-Vis adsorption spectrum of **3-NP(D)** in DCM between 250 – 700 nm.

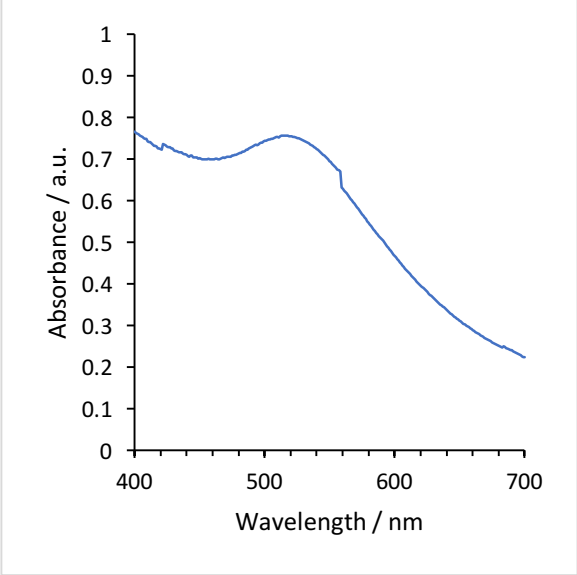


Figure S25. UV-Vis adsorption spectrum of **3-NP(D)** in zoomed in on the 400 – 700 nm.

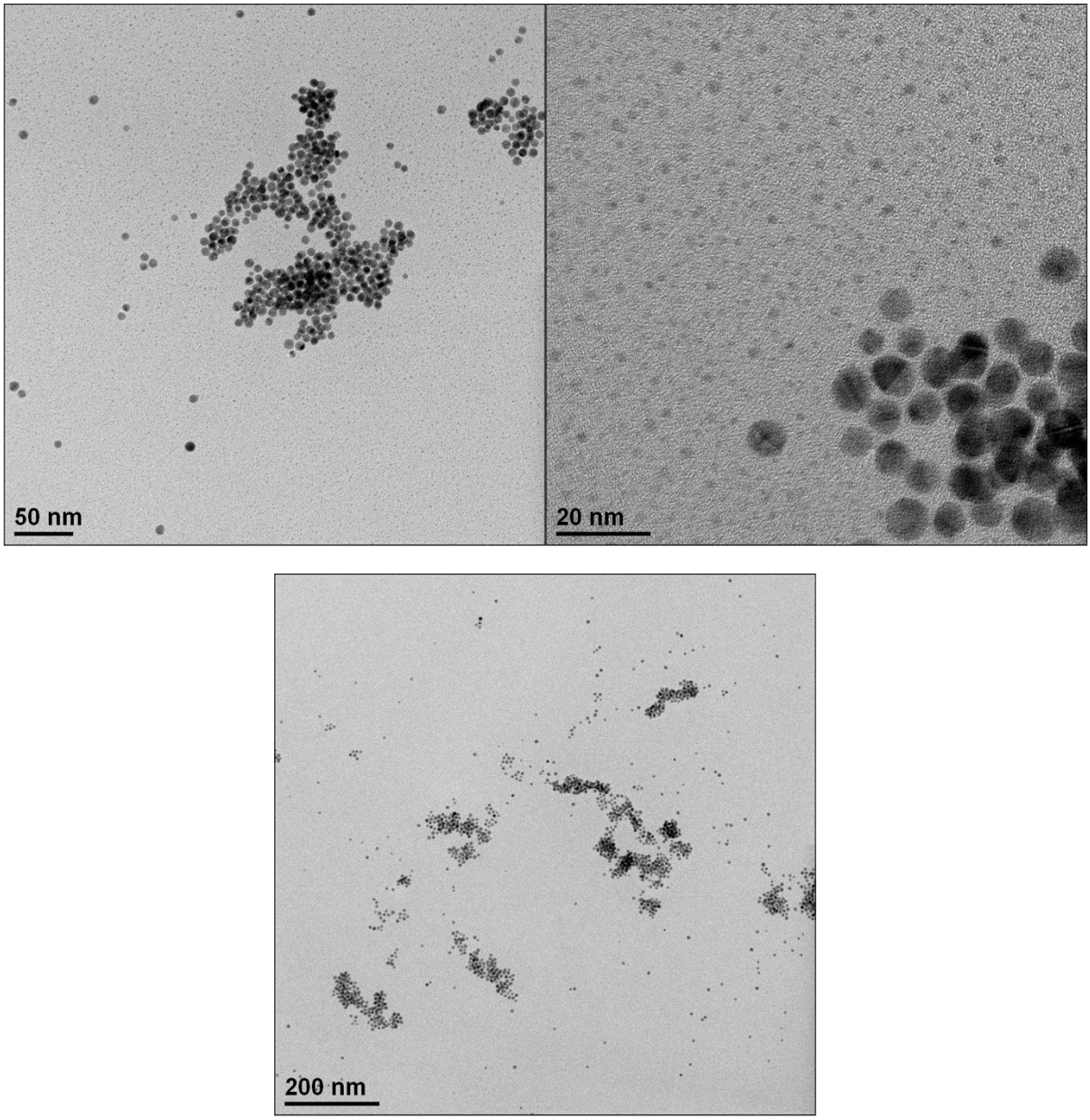


Figure S26. TEM images of **3-NP(L)** pre-size selection

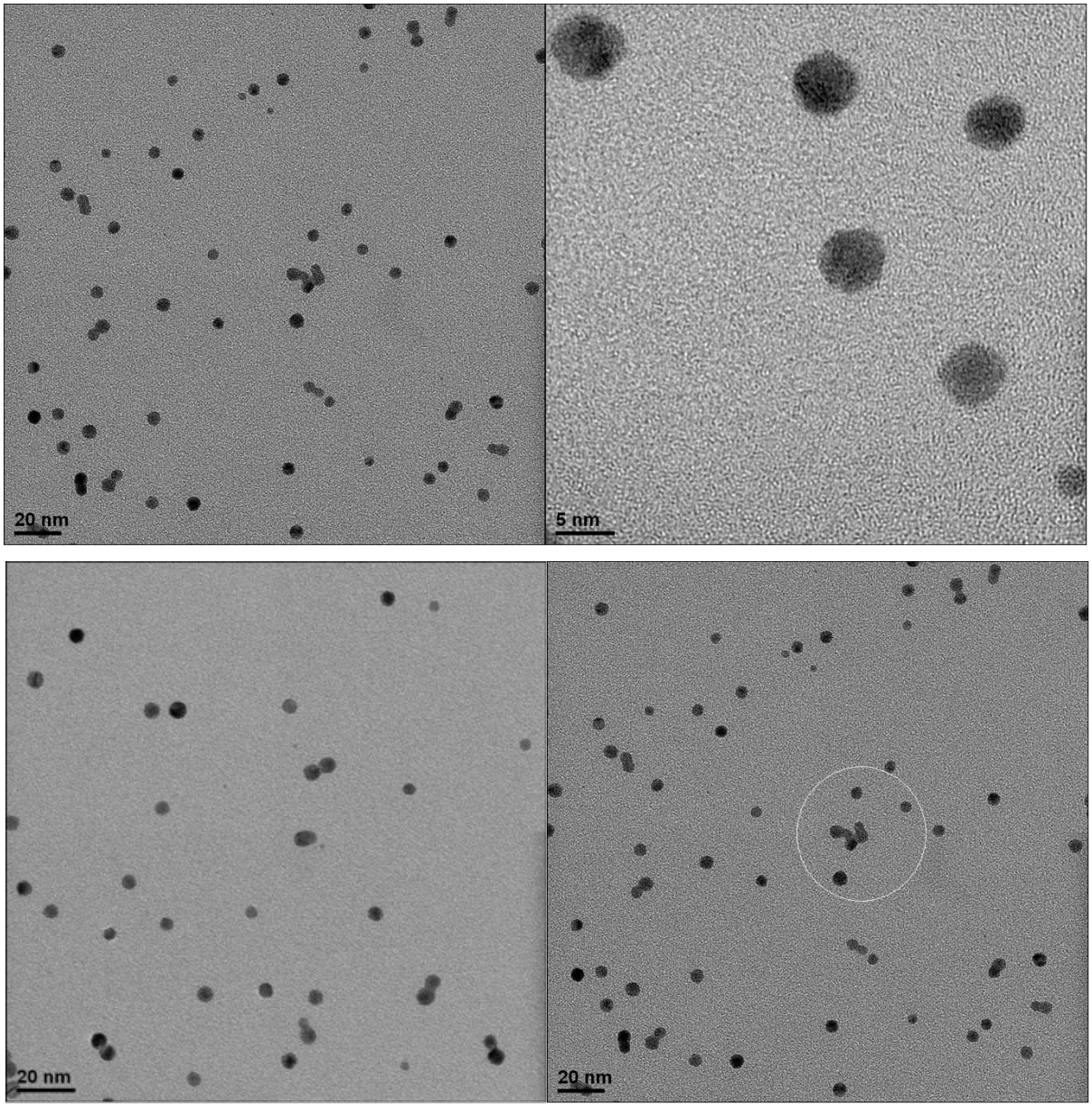


Figure S27. TEM images of **3-NP(L)** post-size selection; white circle indicating area of EDX analysis.

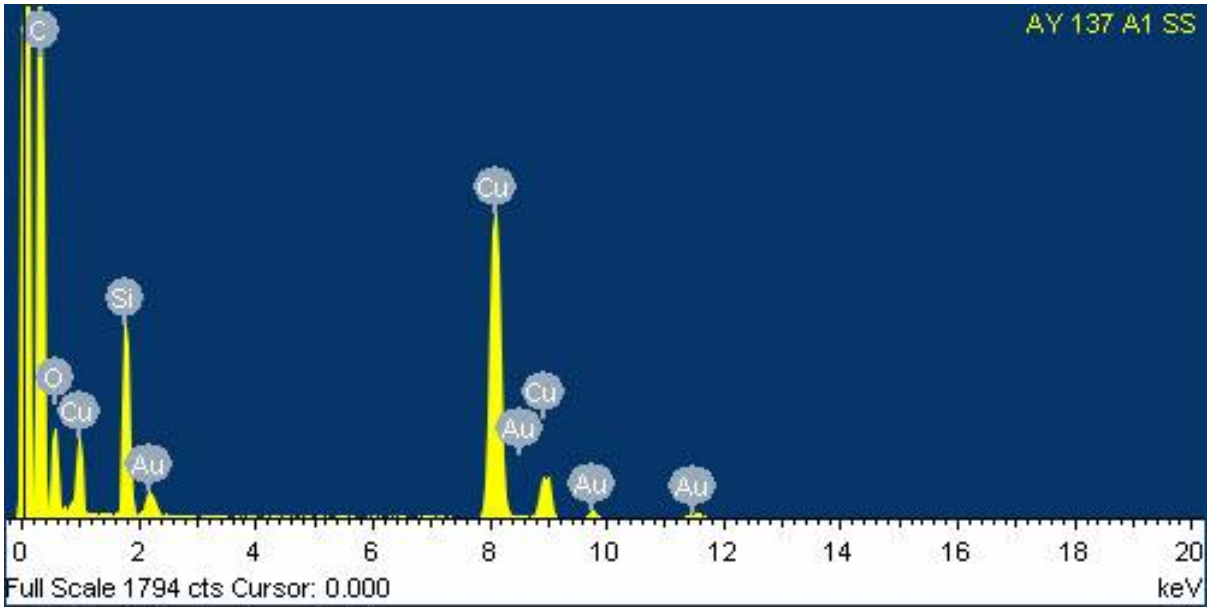


Figure S28. EDX analysis of **3-NP(L); c**opper and silicon peaks have been determined to originate from the TEM grid not the sample.

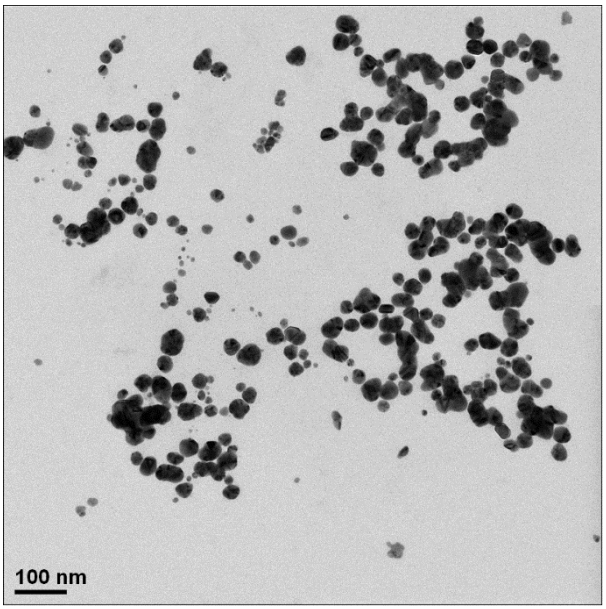


Figure S29. TEM image of **3-NP(L)** following de-protection with hydrochloric acid

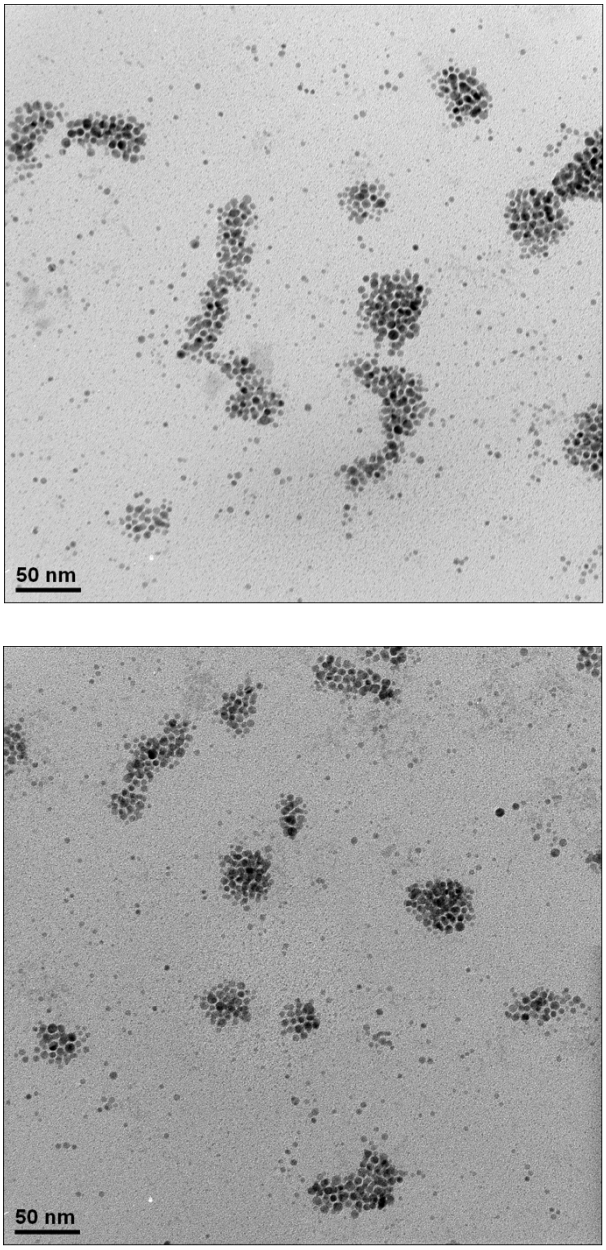


Figure S30. TEM images of **3-NP(D)** pre-size selection

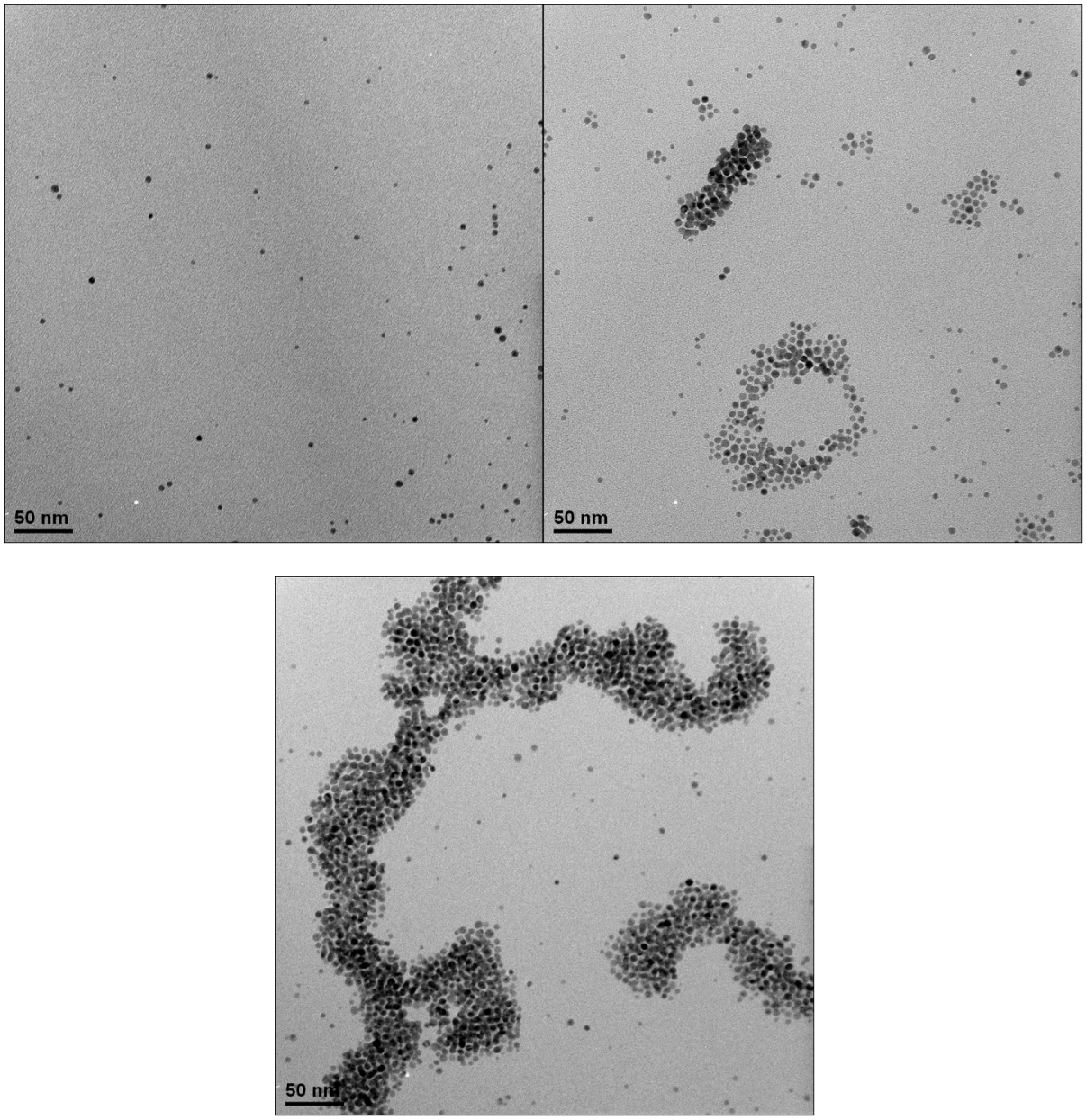


Figure S31. TEM images of **3-NP(D)** post-size selection

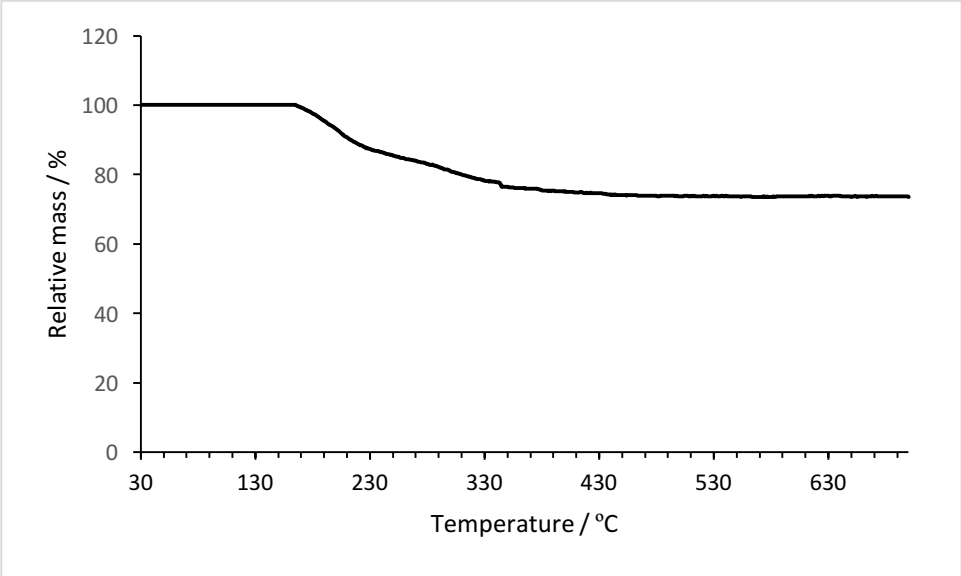


Figure S32. Thermogravimetric analysis (TGA) of **3-NP(L);** organic ligand (assumed to correspond to mass loss) 26.4 wt% of **3-NP(L)**

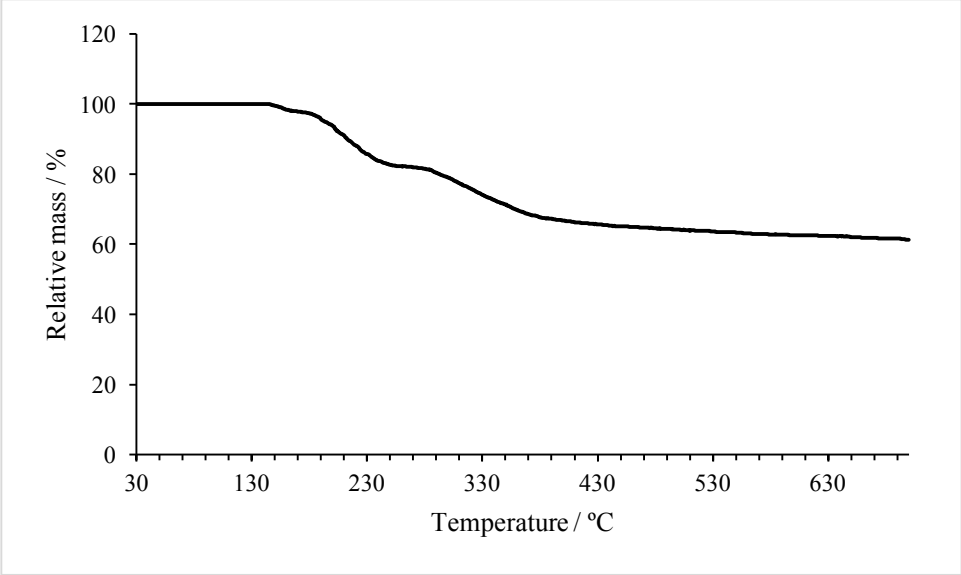


Figure S33. Thermogravimetric analysis (TGA) of **3-NP(D); o**rganic ligand (assumed to correspond to mass loss) = 38.7 wt% of 3-NP(D)

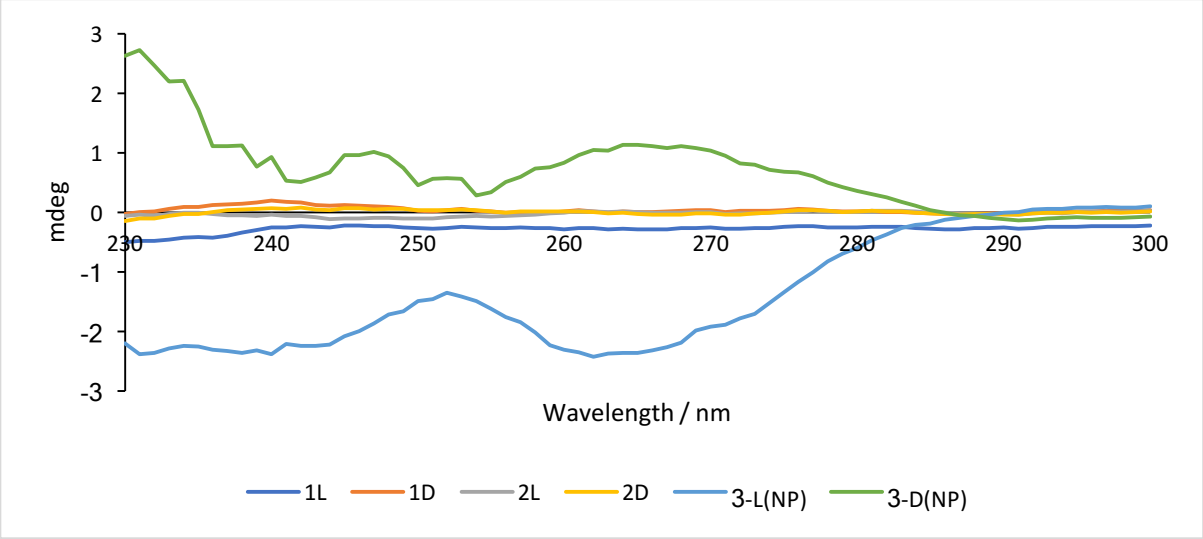


Figure S34. Full CD spectra of synthesised compounds dissolved/ dispersed in DCM.

Bibliography

1 T. N. Hooper, C. P. Butts, M. Green, M. F. Haddow, J. E. McGrady and C. A. Russell, *Chem. - A Eur. J.*, 2009, **15**, 12196–12200.

2 D. V. Leff, P. C. Ohara, J. R. Heath and W. M. Gelbart, *J. Phys. Chem.*, 1995, **99**, 7036–7041.