Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Stabilisation of Gold Nanoparticles by N-Heterocyclic Thiones

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General Methods

All manipulations were carried out using standard schlenk and J. Young flasks. Manipulations of gold complexes, gold nanoparticles and catalytic experiments were performed under an atmosphere of argon or glovebox techniques of high purity nitrogen. Solution NMR spectra were acquired on Bruker DPX-300 and DRX-400 spectrometers at 298K. Elemental analysis was carried out with a LECO TruSpec CHN elementary analyser. ICP analyses were performed on SPECTROBLUE-TI. UV-Vis spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. Transmission electron microscopy (TEM) analyses were performed on a Philips CM-200 working at 200 kV with a point resolution of 2.8 Å. The approximation of the particles mean size was made through a manual analysis of enlarged micrographs by measuring *ca* 300 particles on a given grid. Just before TEM observations, a drop of the NPs dispersion was deposited on a copper grid with a reticulated amorphous carbon film and allowed to dry. The structure and the composition of the NPs at the nanoscale were analyzed by high resolution TEM (HRTEM) in a FEI Talos F200S microscope operating at an accelerating voltage of 200 kV and equipped with a Super-X energy-dispersive X-ray spectrometry (EDX) system which includes two silicon drift detectors and by coupling high-angle annular dark field imaging (HAADF) and EDX acquisitions using the scanning transmission electron microscopy (STEM) mode. The STEM-EDX elemental mapping experiments were performed over 56 x 106 pixels (0.68 nm/px) using a dwell time of 500 ms and spatial drift correction. GC analysis was performed using a Shimadzu GCMSQP2010-Plus equipped with a ZB-5MS capillary column (10 m, 0.18 mm i.d., 0.18 um film thickness). Helium carrier gas was supplied at a head pressure of 9.9 psi to provide an initial flow rate of 0.94 mL/min. A 1.0 μL injection with a split ratio of 1:100 was employed and the GC temperature was initially held at 55 °C for 5 min, then gradually increased to 270 °C at 15 °C/ min, and finally held at 270 °C for 15 min. Full-scan mass spectra were collected from 50 to 500 m/z at a data acquisition rate of 3.5 spectra/s. The MS transfer line was held at 250 °C and the ion source temperature was 200 °C. The compounds 1-methyl-3-tetradecylimidazolium bromide (**1a**),[1] 1,3-Dihexylimidazolium bromide (**1c**),[1] 1,3-Ditetradecylimidazolium bromide (**1d**),[1] 1,3-Dioctadecylimidazolium bromide (**1e**),[1] 1,3-dimesityl imidazolium tetrafluoroborate (**1f**),[2] 1,3-Dimesityl-2-thione (**2f**),[2] 1,3-bis-(2,6-diisopropylphenyl) imidazolium chloride (**1g**),[3] 1,3-bis-(2,6-diisopropylphenyl)-2-thione (**2g**),[3] 4,5-dimethyl-1,3-dimethyl-2-thione (**2h**)[4] and 4,5-dimethyl-1,3-diisopropyl-2-thione (**2i**)[4]

were prepared according to the procedure previously described in the literature. All commercially available reagents were purchased from Sigma-Aldrich or Alfa Aesar and used as received.

Synthesis of 1-methyl-3-octadecylimidazolium bromide (1b)

A schlenk flask was charged with 1-methylimidazole (0.49 mL, 6.10 mmol), 1-bromooctadecane (2.03 g, 6.10 mmol) and acetone (3.0 mL). The mixture was stirred at 85 ºC for 15 h. The reaction mixture was then cooled to room temperature and the mixture was washed with ethyl acetate. The solvent was removed under vacuum, furnishing **1b**. White solid; yield: > 99%.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.86 (3 H, t, *J* = 6.6 Hz, C***H***$_3$CH$_2$), 1.28-1.23 (28 H, m, CH$_2$C***H***$_2$), 1.90-1.88 (2 H, m, NCH$_2$C***H***$_2$), 4.12 (3 H, s, NC***H***$_3$), 4.31 (2 H, t, *J* = 7.4 Hz, NC***H***$_2$), 7.39 (1 H, s, HC=C***H***-N$^+$), 7.55 (1 H, s, ***H***C=CH-N$^+$), 10.24 (1 H, s, N$^+$=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.1 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.3, 29.0, 29.35, 29.39, 29.5, 29.61, 29.65, 29.70, 30.3 and 31.9 (CH$_2$***C***H$_2$), 36.3 (***C***H$_3$N), 50.2 (N***C***H$_2$), 121.8 (H***C***=CH-N$^+$), 123.6 (HC=***C***H-N$^+$), 137.4 (***C***=S).

Elem. Anal. Calcd. for $C_{22}H_{43}N_2Br$: C, 63.60; H, 10.43; N, 6.74.

Elem. Anal. Found: C, 63.3; H, 10.7; N, 6.9.

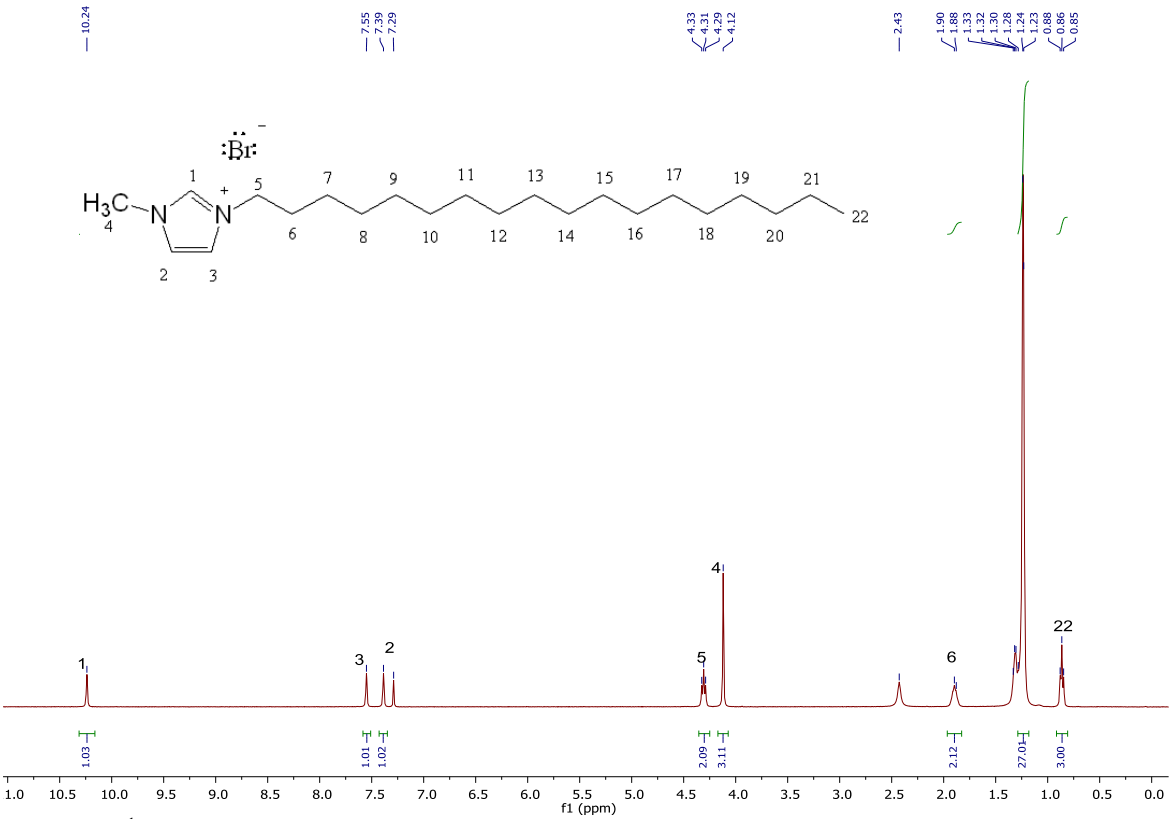

Figure S1. ^{1}H NMR spectrum of **1b**.

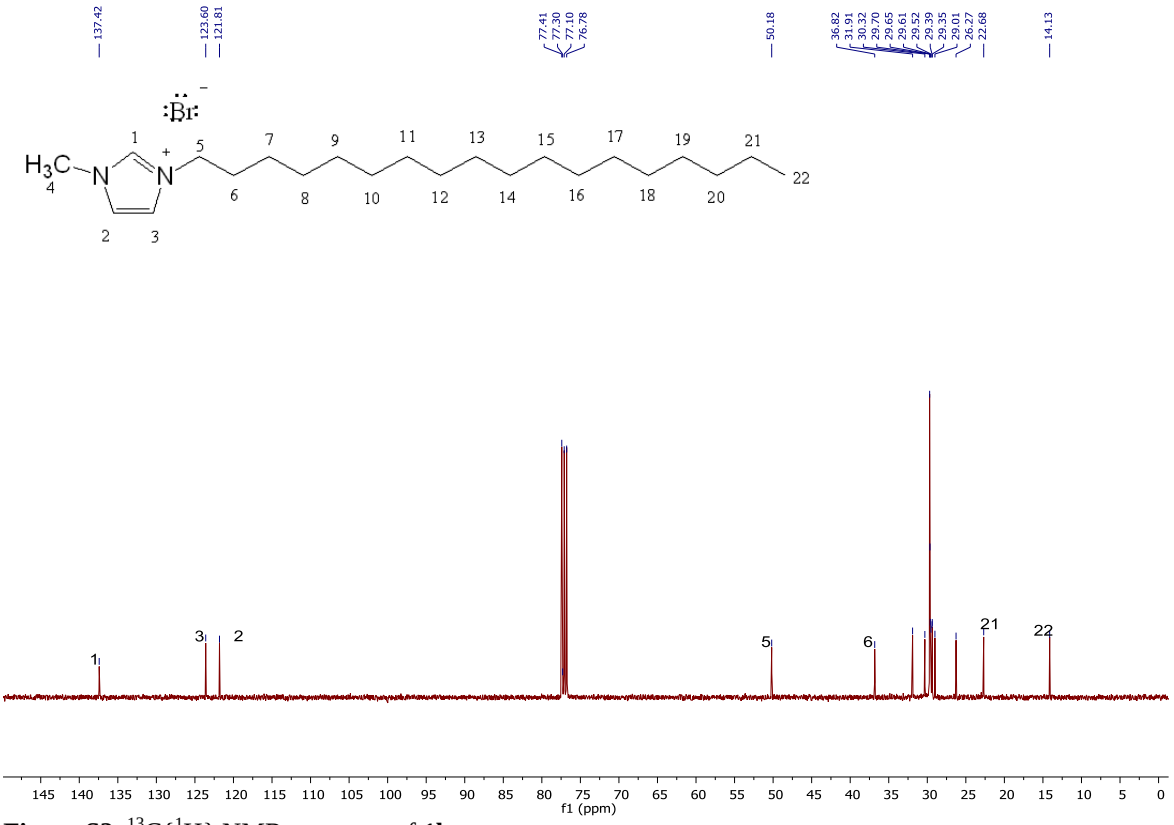

Figure S2. ^{13}C{^{1}H} NMR spectrum of **1b**.

Synthesis and characterisation of N-heterocyclic thione ligands

General Procedure (2a-e)

A schlenk flask was charged with 1,3-dialkyl imidazolium salt **1** (1.85 mmol), sulphur (1.85 mmol), potassium carbonate (1.85 mmol) and methanol (15 mL). The mixture was refluxed for 15 h. The reaction mixture was then cooled to room temperature and the mixture was washed with ethyl acetate. The solvent was removed under vacuum, furnishing the corresponding N-heterocyclic thione ligands.

1-Methyl-3-tetradecyl-2-thione, NHT^{C1,C14} (**2a**). Beige solid; yield: 97%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.5 Hz, C***H***$_3$CH$_2$), 1.30-1.26 (22 H, m, CH$_2$C***H***$_2$), 1.82-1.71 (2 H, m, NCH$_2$C***H***$_2$), 3.62 (3 H, s, NC***H***$_3$), 4.02 (2 H, t, *J* = 7.5 Hz, NC***H***$_2$), 6.69 (2 H, bs, ***H***C=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.1 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.6, 28.9, 29.2, 29.35, 29.48, 29.56, 29.62, 29.65, 29.68 and 31.9 (CH$_2$***C***H$_2$), 35.1 (***C***H$_3$N), 48.1 (N***C***H$_2$), 116.5 (CH$_3$N***C***=C), 117.6 (CH$_3$NC=***C***), 162.0 (***C***=S).

Elem. Anal. Calcd. for $C_{18}H_{34}N_2S$: C, 69.62; H, 11.04; N, 9.02; S, 10.32.

Elem. Anal. Found: C, 69.5; H, 10.8; N, 9.2; S, 10.2.

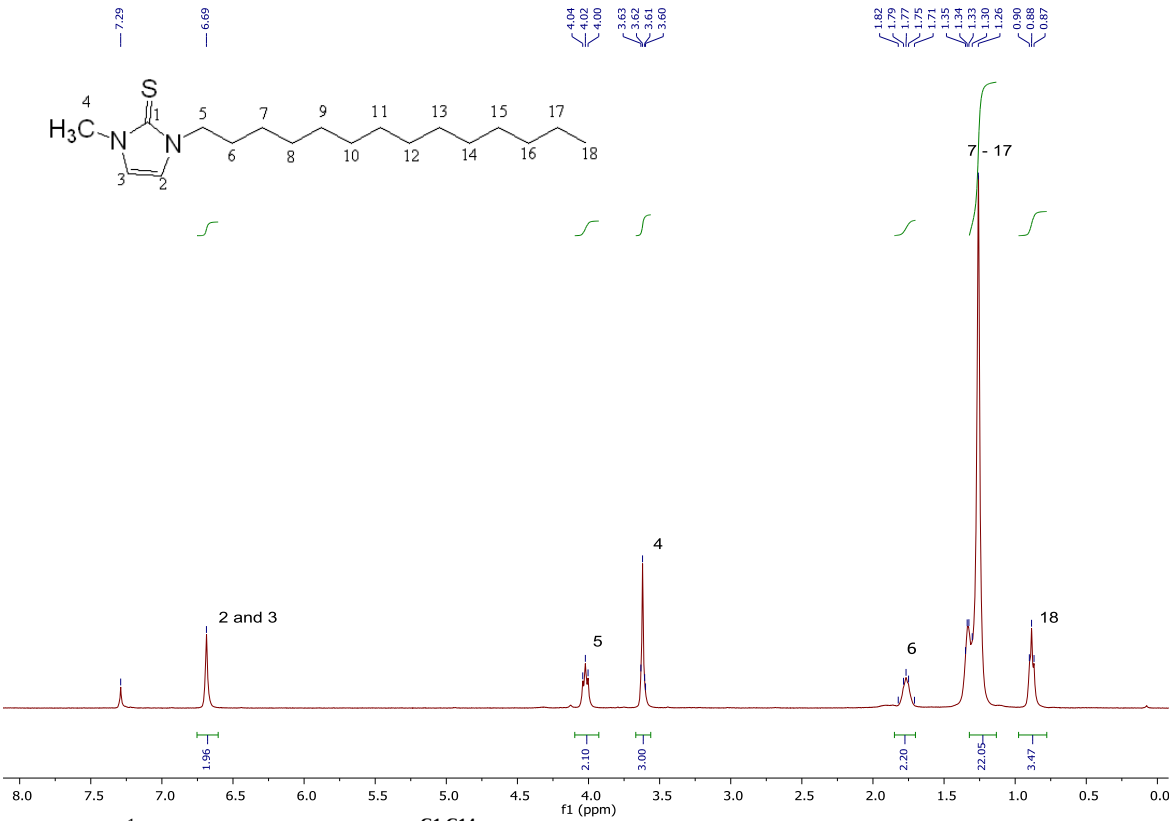

Figure S3. ^{1}H NMR spectrum of **NHT^{C1,C14}** (**2a**).

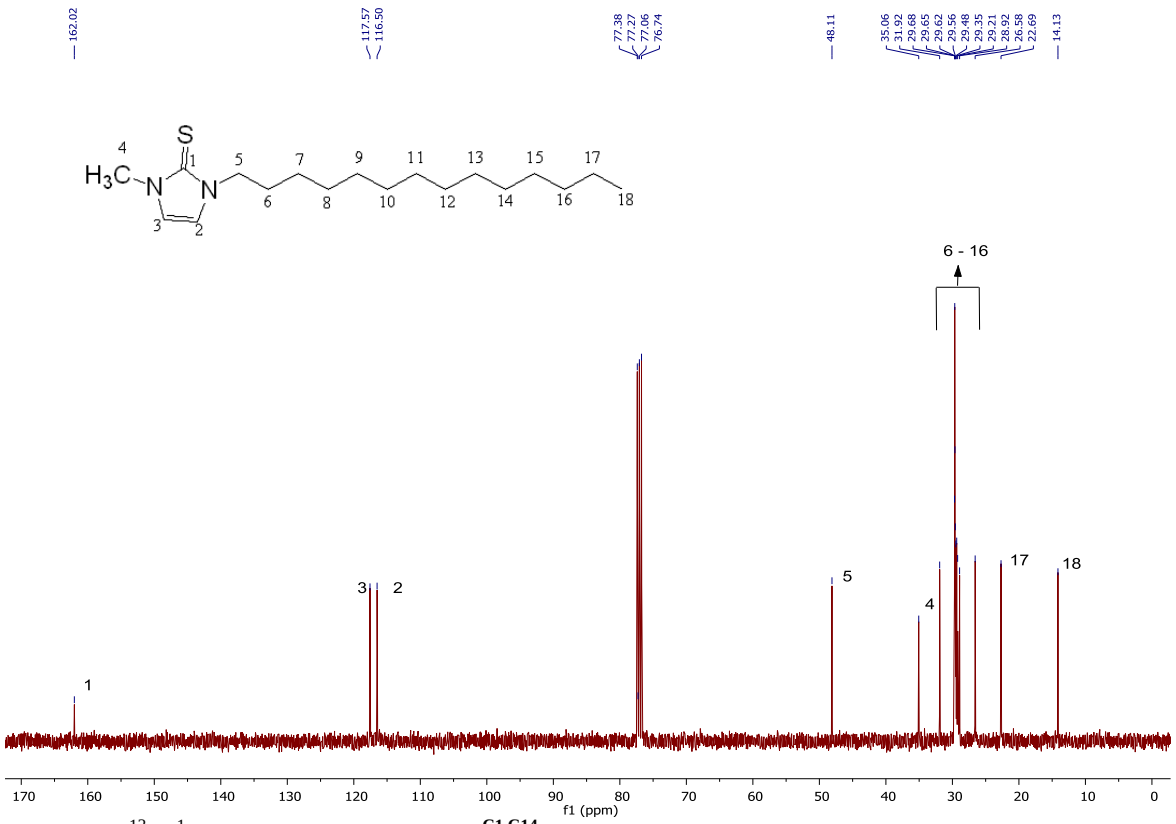

Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of **NHT^{C1,C14}** (**2a**).

1-Methyl-3-octadecyl-2-thione, NHT^{C1,C18} (**2b**). White solid; yield: 68%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.71 (3 H, t, *J* = 7.1 Hz, C***H***$_3$CH$_2$), 1.10-1.08 (30 H, m, CH$_2$C***H***$_2$), 1.56 (2 H, quint, NCH$_2$C***H***$_2$), 3.44 (3 H, s, NC***H***$_3$), 3.84 (2 H, t, *J* = 7.1 Hz, NC***H***$_2$), 6.56 (1 H, d, *J* = 4.0 Hz, HC=C***H***NCH$_2$), 6.59 (1 H, d, *J* = 4.0 Hz, ***H***C=CHNCH$_2$).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.1 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.6, 28.9, 29.2, 29.37, 29.49, 29.57, 29.63, 29.67, 29.70 and 31.9 (CH$_2$***C***H$_2$), 35.1 (***C***H$_3$N), 48.1 (N***C***H$_2$), 116.5 (CH$_3$N***C***=C), 117.6 (CH$_3$NC=***C***), 162.0 (***C***=S).

Elem. Anal. Calcd. for $C_{22}H_{42}N_2S$: C, 72.07; H, 11.55; N, 7.64; S, 8.74.

Elem. Anal. Found: C, 72.1; H, 11.4; N, 7.8; S, 8.4.

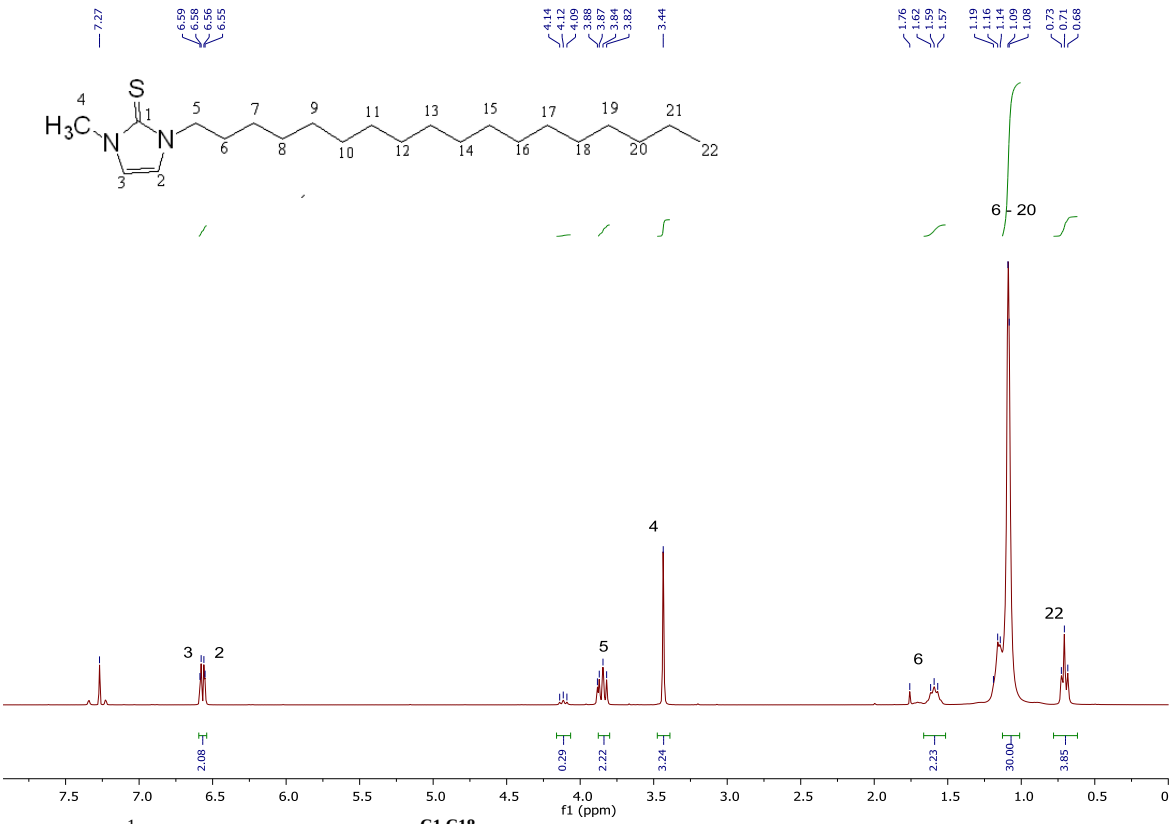

Figure S5. ^{1}H NMR spectrum of **NHT^{C1,C18}** (**2b**).

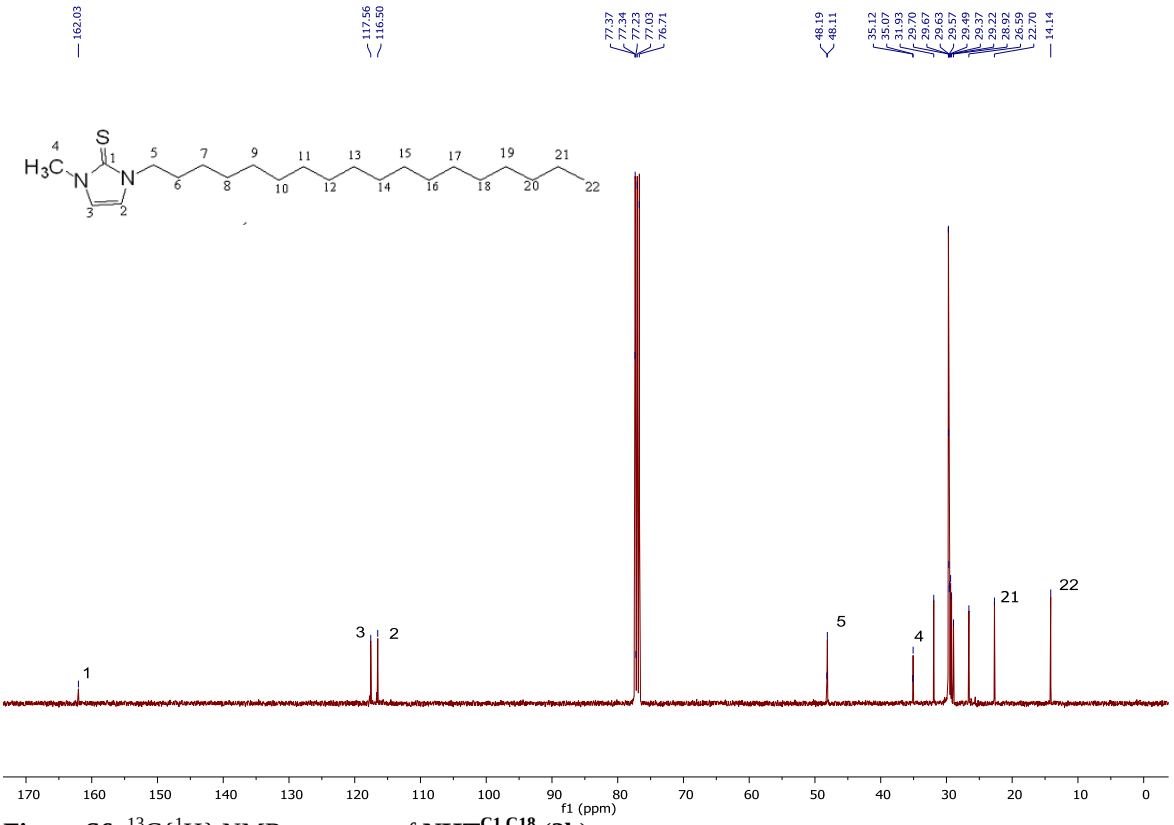

Figure S6. ^{13}C{^{1}H} NMR spectrum of **NHT^{C1,C18}** (**2b**).

1,3-Dihexyl-2-thione, NHT^{C6,C6} (**2c**). Yellow oil; yield: 89%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.77 (6 H, t, *J* = 7.0 Hz, C***H***$_3$CH$_2$), 1.24-1.20 (12 H, m, CH$_2$C***H***$_2$), 1.66 (4 H, quint, *J* = 7.5 Hz, NCH$_2$C***H***$_2$), 3.92 (4 H, t, *J* = 7.5 Hz, NC***H***$_2$), 6.62 (2 H, s, C=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 13.9 (***C***H$_3$CH$_2$), 22.4 (CH$_3$***C***H$_2$), 26.1, 28.8 and 31.3 (CH$_2$*C*H$_2$), 47.7 (N***C***H$_2$), 116.5 (***C***=C), 161.3 (***C***=S).

Elem. Anal. Calcd. for $C_{15}H_{28}N_2S$: C, 67.11; H, 10.51; N, 10.43; S, 11.94.

Elem. Anal. Found: C, 67.5; H, 10.9; N, 10.2; S, 11.6.

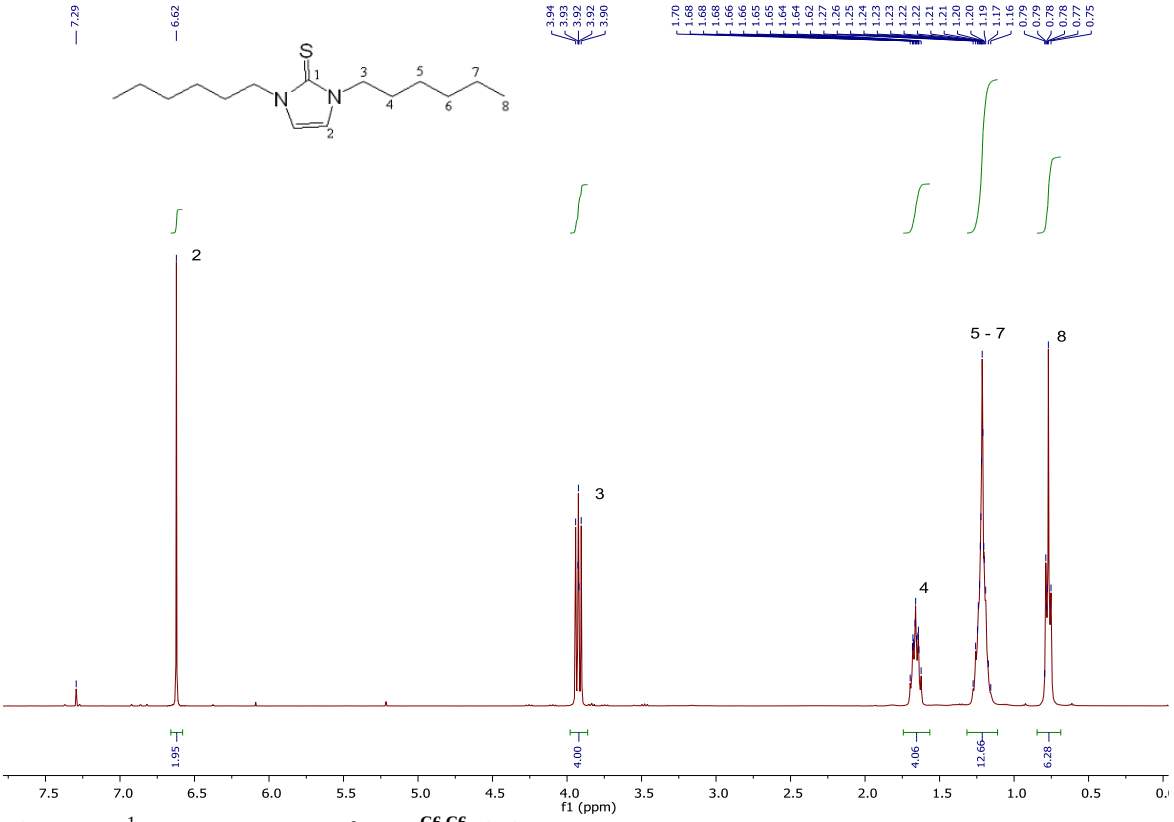

Figure S7. ^{1}H NMR spectrum of **NHT^{C6,C6}** (**2c**).

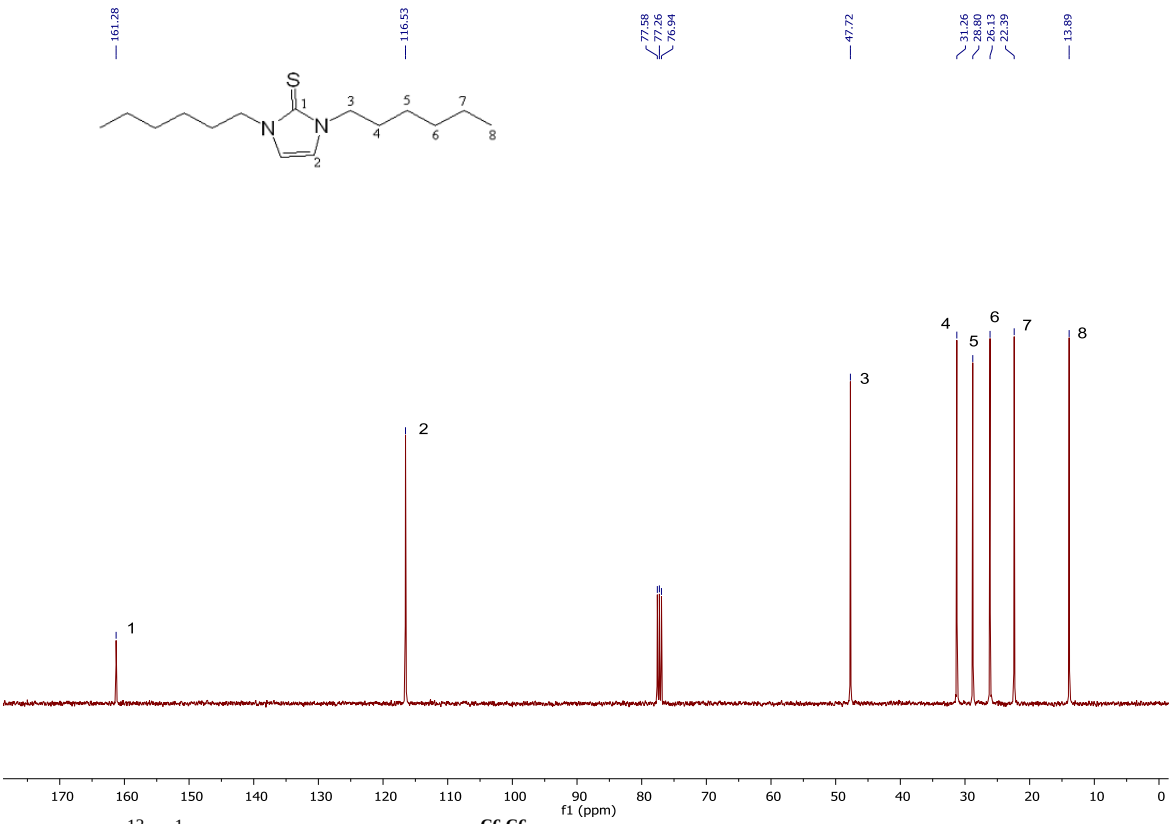

Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of **NHT^{C6,C6}** (**2c**).

1,3-Ditetradecyl-2-thione, NHT^{C14,C14} (**2d**). White solid; yield: 77%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (6 H, t, *J* = 6.9 Hz, C***H***$_3$CH$_2$), 1.31-1.27 (m, 44 H, CH$_2$C***H***$_2$), 1.78 (4 H, quint, *J* = 7.2 Hz, NCH$_2$C***H***$_2$), 4.04 (4 H, t, *J* = 7.2 Hz, NC***H***$_2$), 6.69 (2 H, s, C=C***H***).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.1 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.6, 29.0, 29.2, 29.4, 29.51, 29.58, 29.64, 29.67, 29.70 and 31.9 (CH$_2$***C***H$_2$), 47.9 (N***C***H$_2$), 116.5 (***C***=C), 161.5 (***C***=S).

Elem. Anal. Calcd. for $C_{31}H_{60}N_2S$: C, 75.54; H, 12.27; N, 5.68; S, 6.50.

Elem. Anal. Found: C, 75.9; H, 12.5; N, 5.6; S, 6.2.

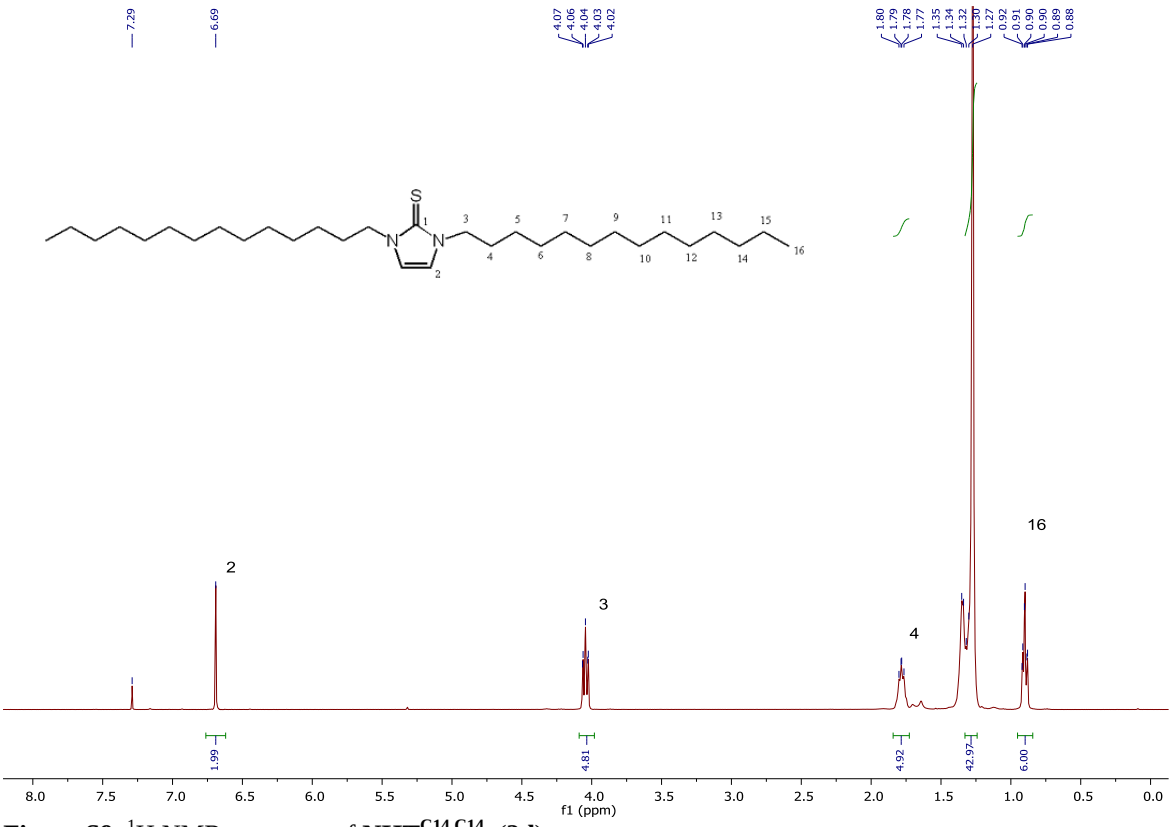

Figure S9. ^{1}H NMR spectrum of **NHT^{C14,C14}** (**2d**).

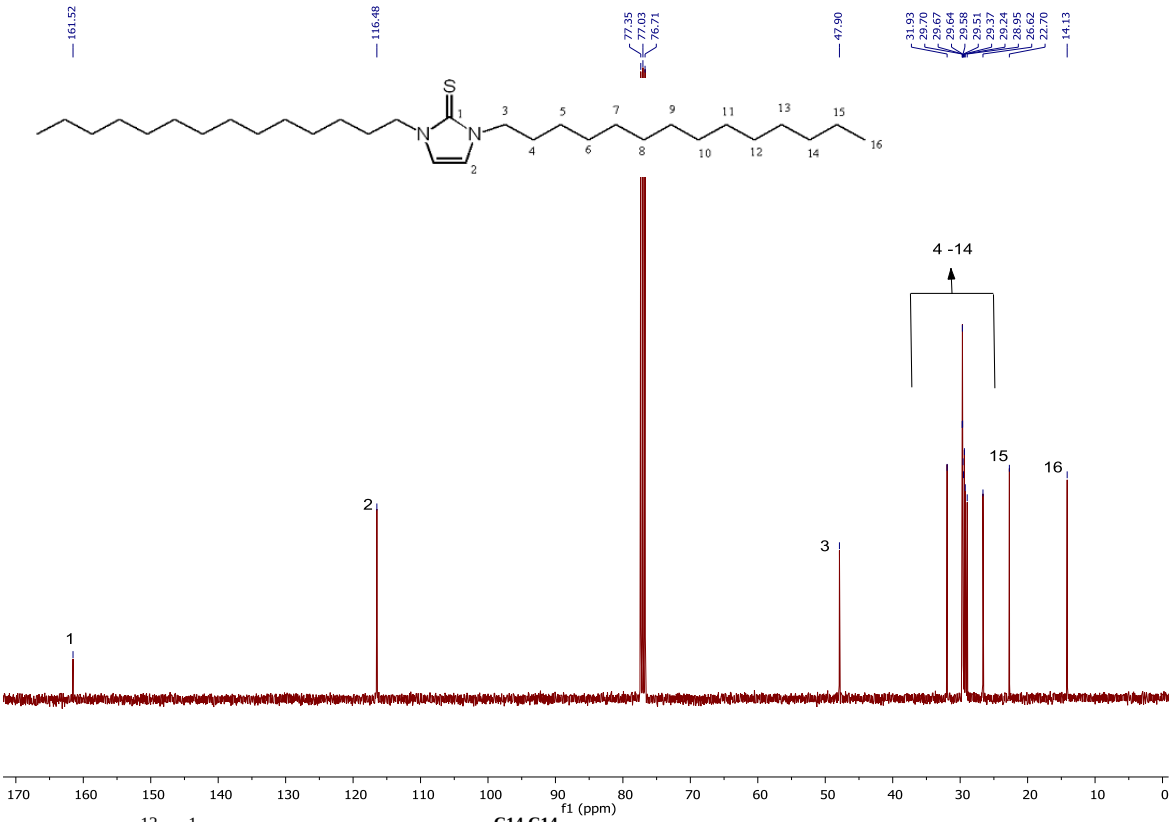

Figure S10. ^{13}C{^{1}H} NMR spectrum of **NHT^{C14,C14}** (**2d**).

1,3-Dioctadecyl-2-thione NHT^{C18,C18} (**2e**). Yellow solid; yield: 88%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (6 H, t, *J* = 7.0 Hz, C***H***$_3$CH$_2$), 1.31-1.26 (60 H, m, CH$_2$C***H***$_2$), 1.78 (4 H, quint, *J* = 7.0 Hz, NCH$_2$C***H***$_2$), 4.04 (4 H, t, *J* = 7.0 Hz, NC***H***$_2$), 6.99 (2 H, s, C=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.2 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.6, 29.0, 29.2, 29.4, 29.51, 29.58, 29.65, 29.68, 29.72 and 31.9 (CH$_2$***C***H$_2$), 47.9 (N***C***H$_2$), 116.4 (***C***=C), 161.4 (***C***=S).

Elem. Anal. Calcd. for $C_{39}H_{76}N_2S$: C, 77.41; H, 12.66; N, 4.63; S, 5.30.

Elem. Anal. Found: C, 77.5; H, 12.4; N, 4.7; S, 5.3.

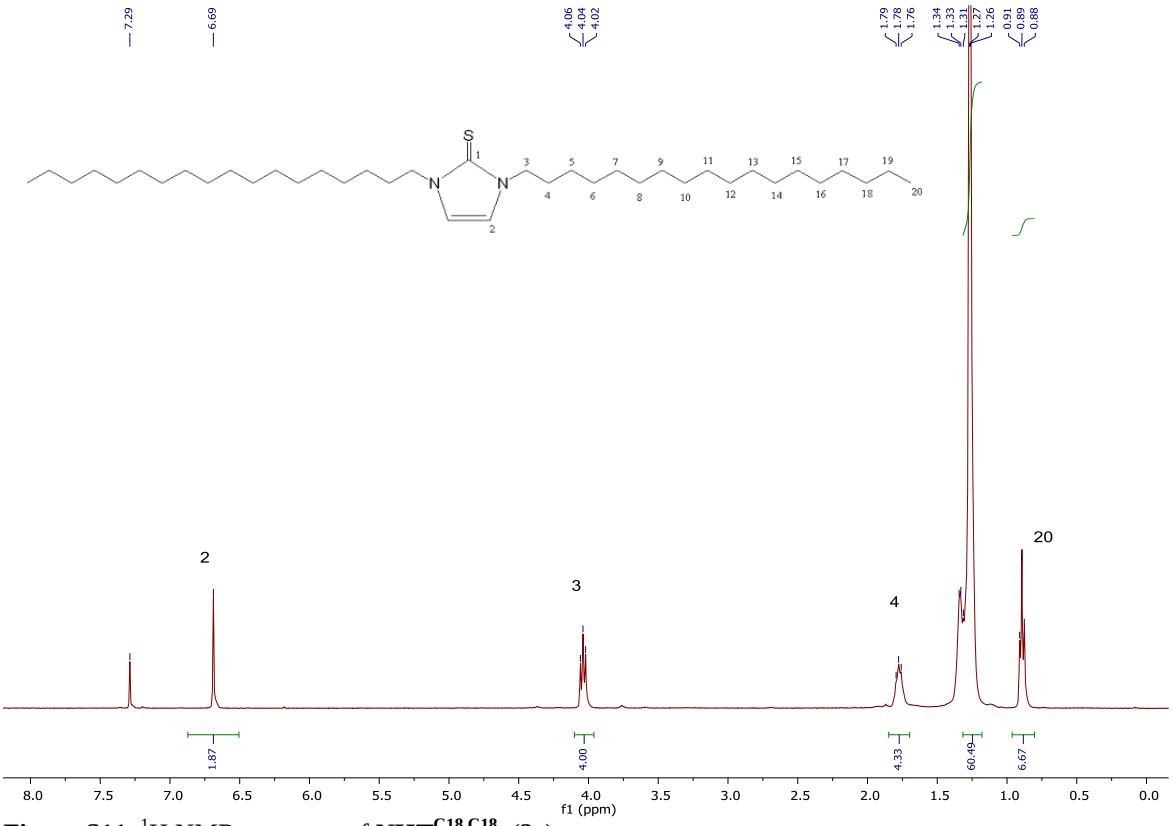

Figure S11. ^{1}H NMR spectrum of **NHT^{C18,C18}** (**2e**).

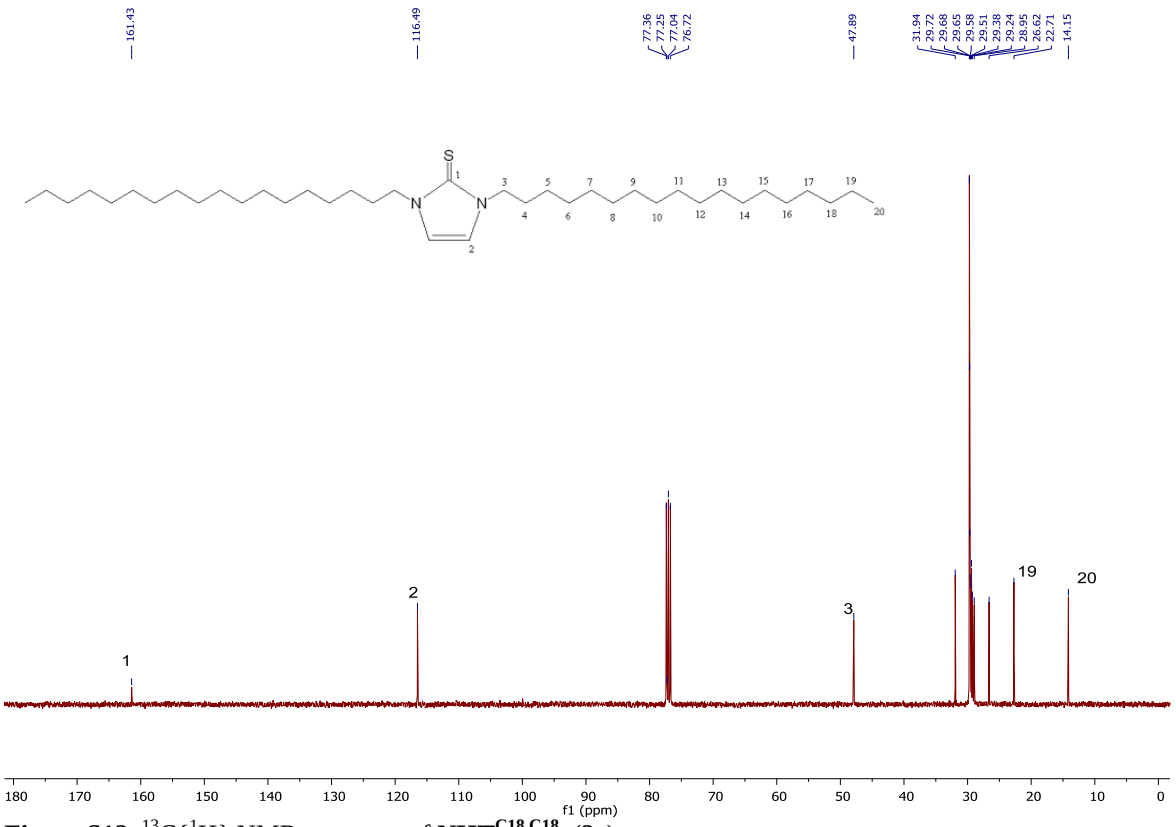

Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of **NHT^{C18,C18}** (**2e**).

Synthesis and characterisation of gold complexes

General Procedure (3a-i)

A J. Young flask was charged with N-heterocyclic thione ligand **2** (0.20 mmol), chloro(tetrahydrothiophene)gold(I)[6] (0.20 mmol) and dry dichloromethane (5.0 mL). The mixture was stirred at room temperature for 10 h. The resulting solution was then filtered under argon via cannula and the solvent was evaporated under vacuum, furnishing the corresponding N-heterocyclic thione complexes.

1-Methyl-3-tetradecyl-2-thione complex (3a). Orange solid; yield: 90%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.7 Hz, C***H***$_3$CH$_2$), 1.30-1.26 (22 H, m, CH$_2$C***H***$_2$), 1.87-1.84 (2 H, m, NCH$_2$C***H***$_2$), 3.91 (3 H, s, NC***H***$_3$), 4.26 (2 H, t, *J* = 7.5 Hz, NC***H***$_2$), 7.04 (1 H, s, ***H***C=CHNCH$_2$), 7.07 (1 H, s, HC=C***H***NCH$_2$).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.2 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.4, 29.1, 29.35, 29.43, 29.5, 29.62, 29.65, 29.68 and 31.9 (CH$_2$***C***H$_2$), 36.5 (***C***H$_3$N), 49.6 (N***C***H$_2$), 119.9 (CH$_3$N***C***=C), 121.3 (CH$_3$NC=***C***), 149.7 (***C***=S).

Elem. Anal. Calcd. for $C_{18}H_{34}N_2SAuCl$: C, 39.82; H, 6.31; N, 5.16; S, 5.90.

Elem. Anal. Found: C, 39.8; H, 6.6; N, 5.1; S, 5.8.

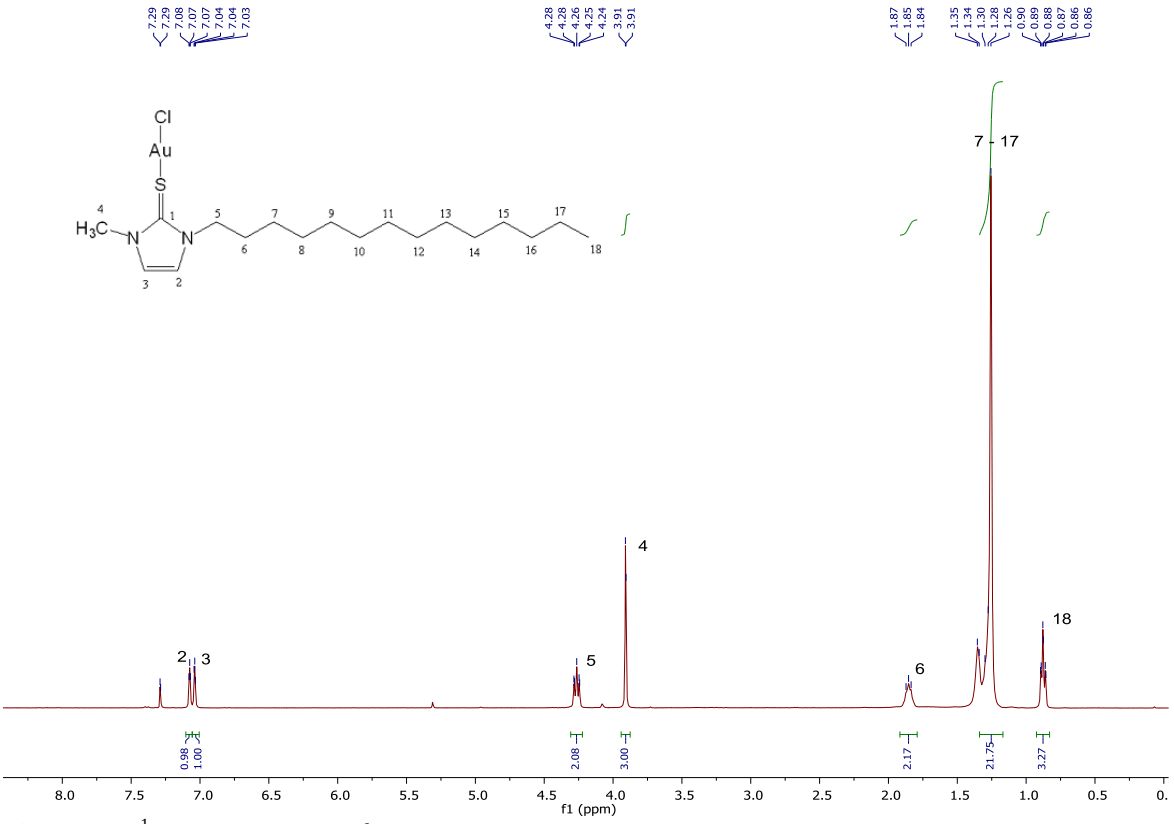

Figure S13. ^{1}H NMR spectrum of **3a**.

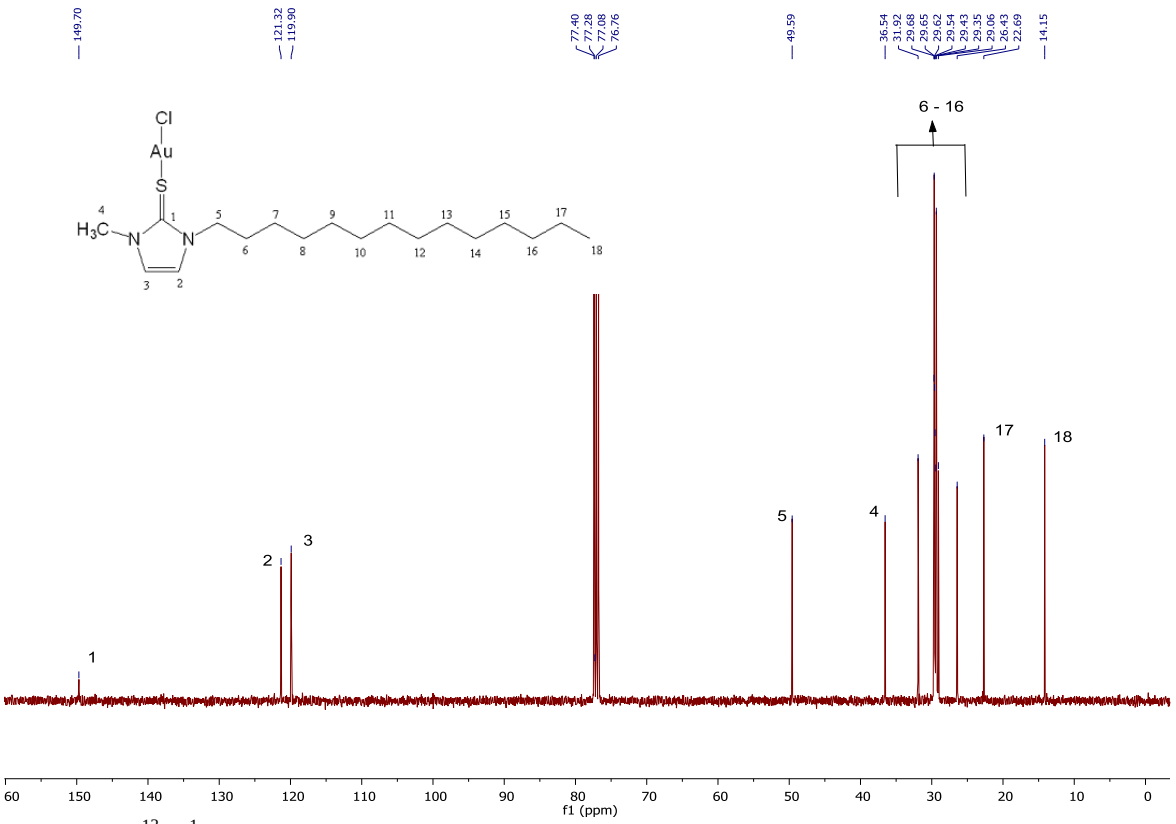

Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of **3a**.

1-Methyl-3-octadecyl-2-thione complex (3b). Orange solid; yield: 94%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.88 (3 H, t, *J* = 6.7 Hz, C***H***$_3$CH$_2$), 1.30-1.26 (30 H, m, CH$_2$C***H***$_2$), 1.90-1.79 (2 H, m, NCH$_2$C***H***$_2$), 3.88 (3 H, s, NC***H***$_3$), 4.23 (2 H, t, *J* = 7.3 Hz, NC***H***$_2$), 7.01 (1 H, s, ***H***C=CHNCH$_2$), 7.12 (1 H, s, HC=C***H***NCH$_2$),

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.1 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.5, 29.1, 29.32, 29.37, 29.45, 29.55, 29.63, 29.67, 29.71 and 31.9 (CH$_2$***C***H$_2$), 36.3 (***C***H$_3$N), 49.4 (N***C***H$_2$), 119.4 (CH$_3$N***C***=C), 121.0 (CH$_3$NC=***C***), 151.3 (***C***=S).

Elem. Anal. Calcd. for $C_{22}H_{42}N_2SAuCl$: C, 44.11; H, 7.07; N, 4.68; S, 5.35.

Elem. Anal. Found: C, 44.1; H, 6.8; N, 4.5; S, 5.1.

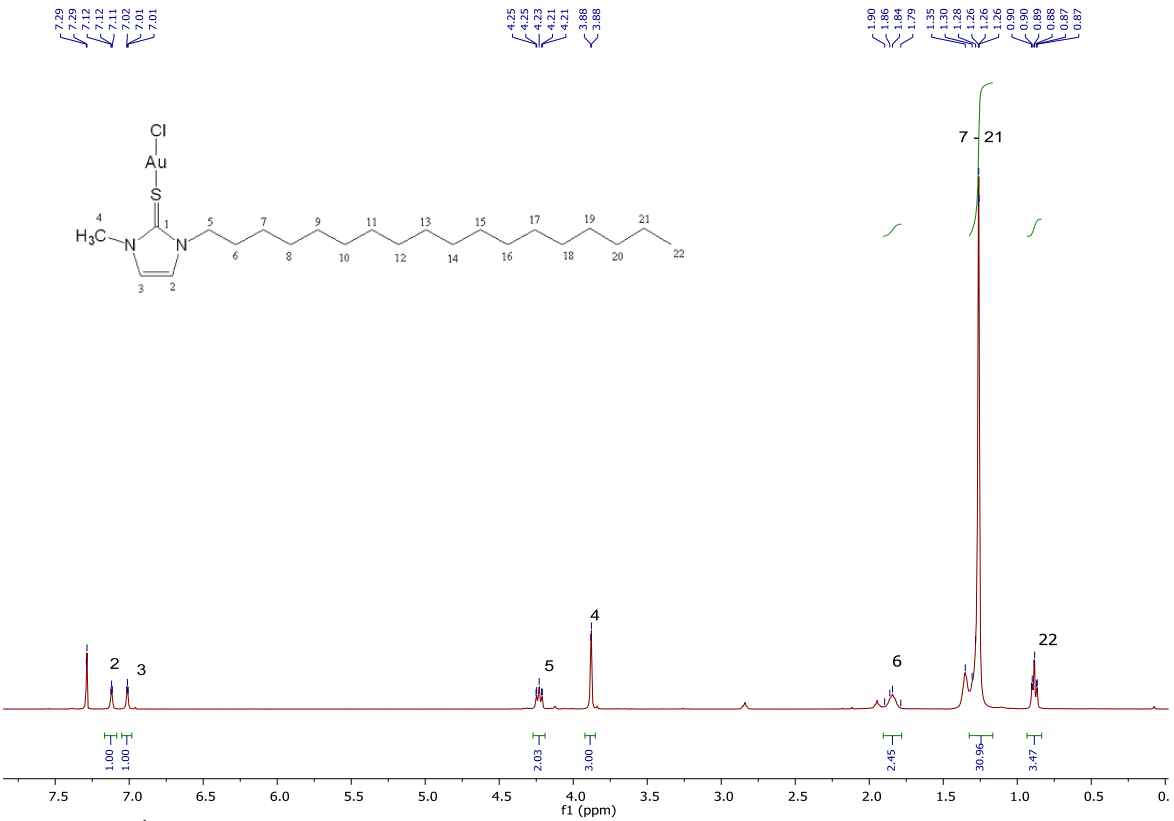

Figure S15. ^{1}H NMR spectrum of **3b**.

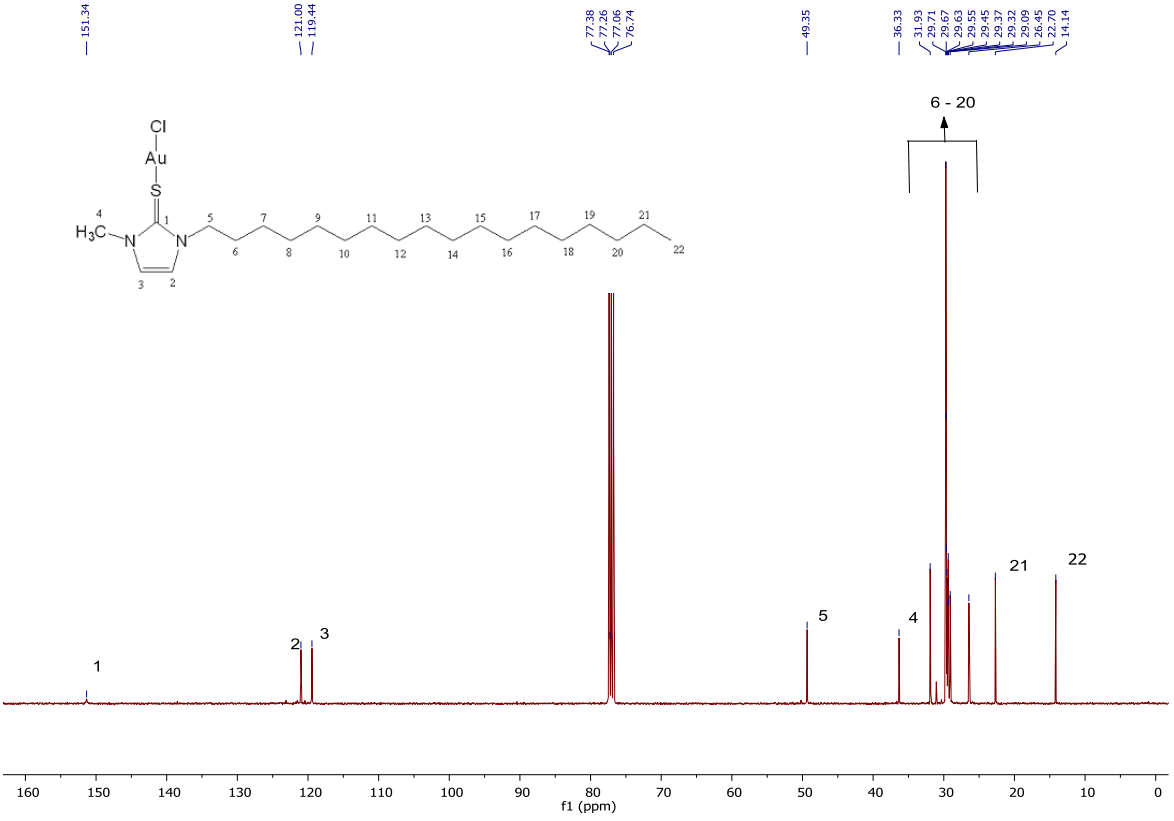

Figure S16. ^{13}C{^{1}H} NMR spectrum of **3b**.

1,3-Dihexyl-2-thione complex (3c). Orange oil; yield: 96%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.89 (6 H, t, *J* = 6.9 Hz, C***H***$_3$CH$_2$), 1.39-1.30 (12 H, m, CH$_2$C***H***$_2$), 1.87 (4 H, quint, *J* = 7.5 Hz, NCH$_2$C***H***$_2$), 4.29 (4 H, t, *J* = 7.5 Hz, NC***H***$_2$), 7.06 (2 H, s, C=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.0 (***C***H$_3$CH$_2$), 22.5 (CH$_3$***C***H$_2$), 26.1, 29.3 and 31.2 (CH$_2$***C***H$_2$), 49.4 (N***C***H$_2$), 120.1 (***C***=C), 149.0 (***C***=S).

Elem. Anal. Calcd. for $C_{15}H_{28}N_2SAuCl$: C, 35.97; H, 5.63; N, 5.59; S, 6.40.

Elem. Anal. Found: C, 36.2; H, 5.6; N, 5.7; S, 6.3.

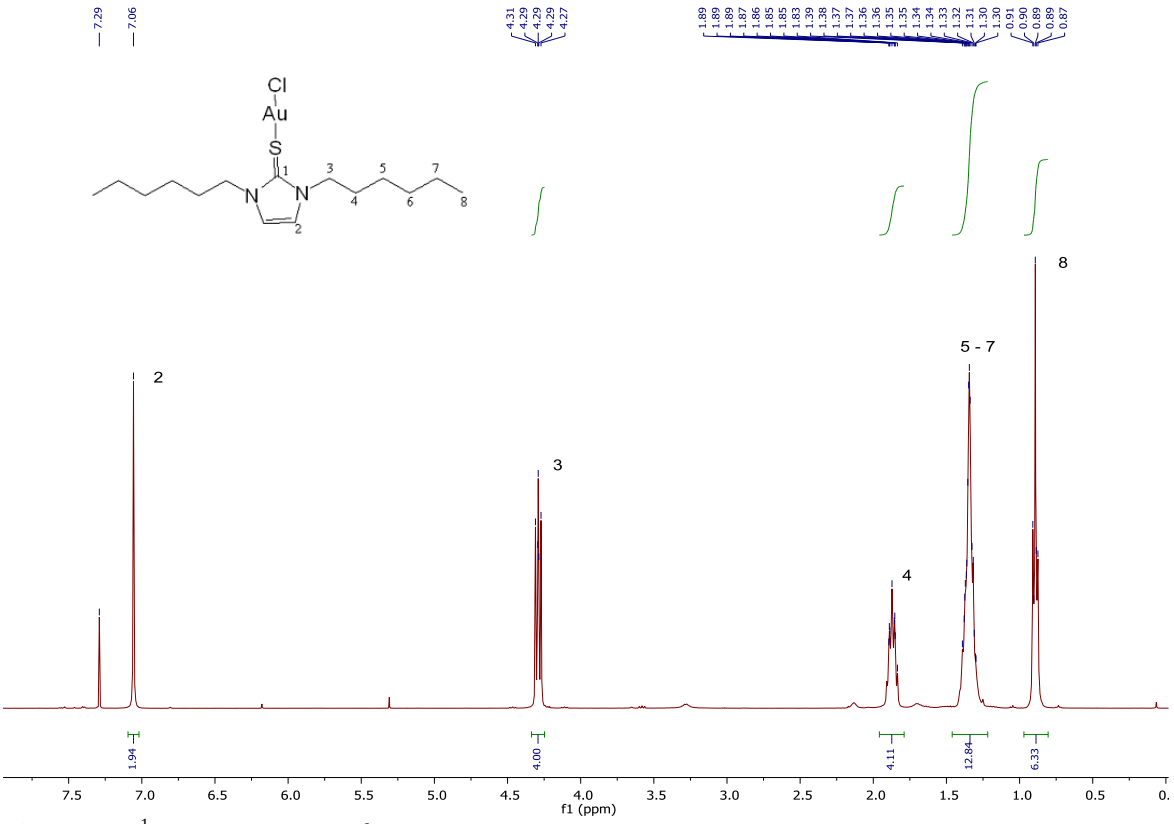

Figure S17. ^{1}H NMR spectrum of **3c**.

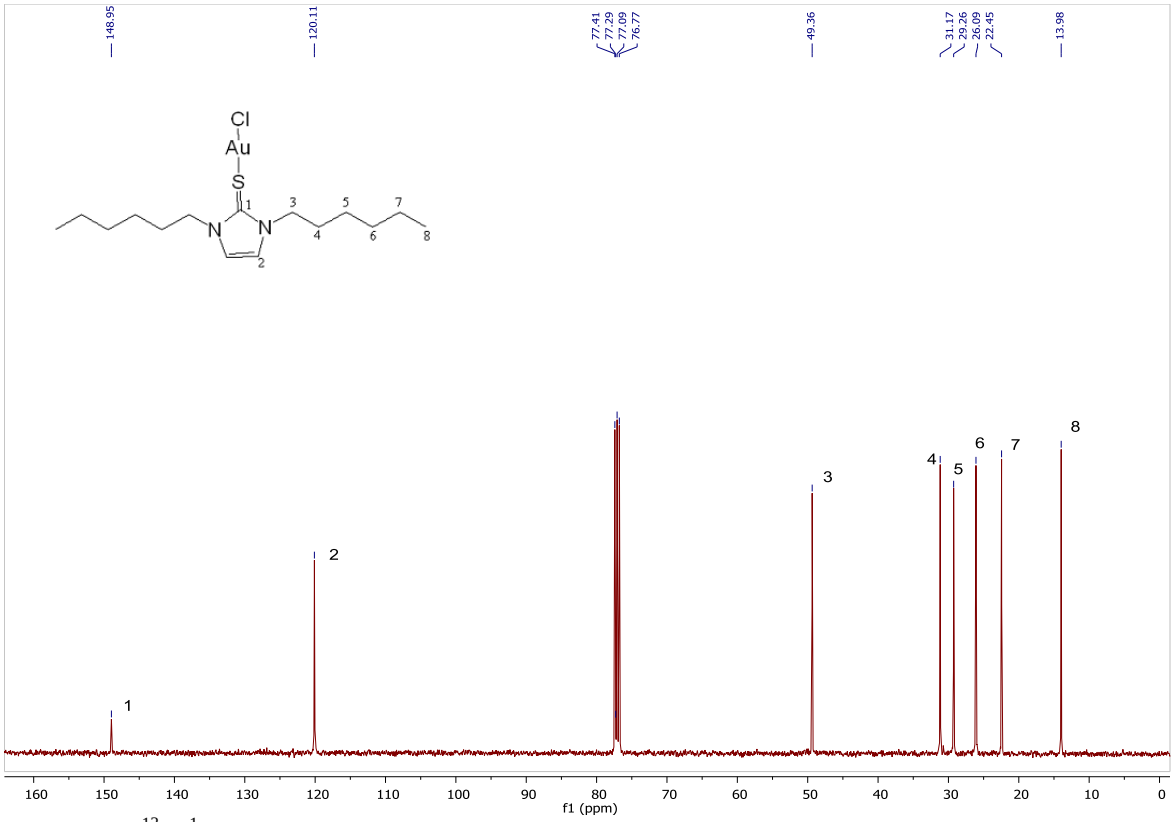

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of **3c**.

1,3-Ditetradecyl-2-thione complex (3d). Orange solid; yield: 92%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.90 (6 H, t, *J* = 6.8 Hz, CH_3CH_2), 1.30-1.28 (44 H, m, CH_2CH_2), 1.88 (4 H, quint, *J* = 7.3 Hz, NCH_2CH_2), 4.30 (4 H, t, *J* = 7.3 Hz, NCH_2), 7.02 (2 H, s, C=CH).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 14.1 (CH_3CH_2), 22.7 (CH_3CH_2), 26.5, 29.1, 29.27, 29.38, 29.43, 29.5, 29.63, 29.67, 29.70 and 31.9 (CH_2CH_2), 49.4 (NCH_2), 119.8 (C=C).

Elem. Anal. Calcd. for $C_{31}H_{60}N_2SAuCl$: C, 51.34; H, 8.34; N, 3.86; S, 4.42.

Elem. Anal. Found: C, 51.0; H, 8.7; N, 3.6; S, 4.1.

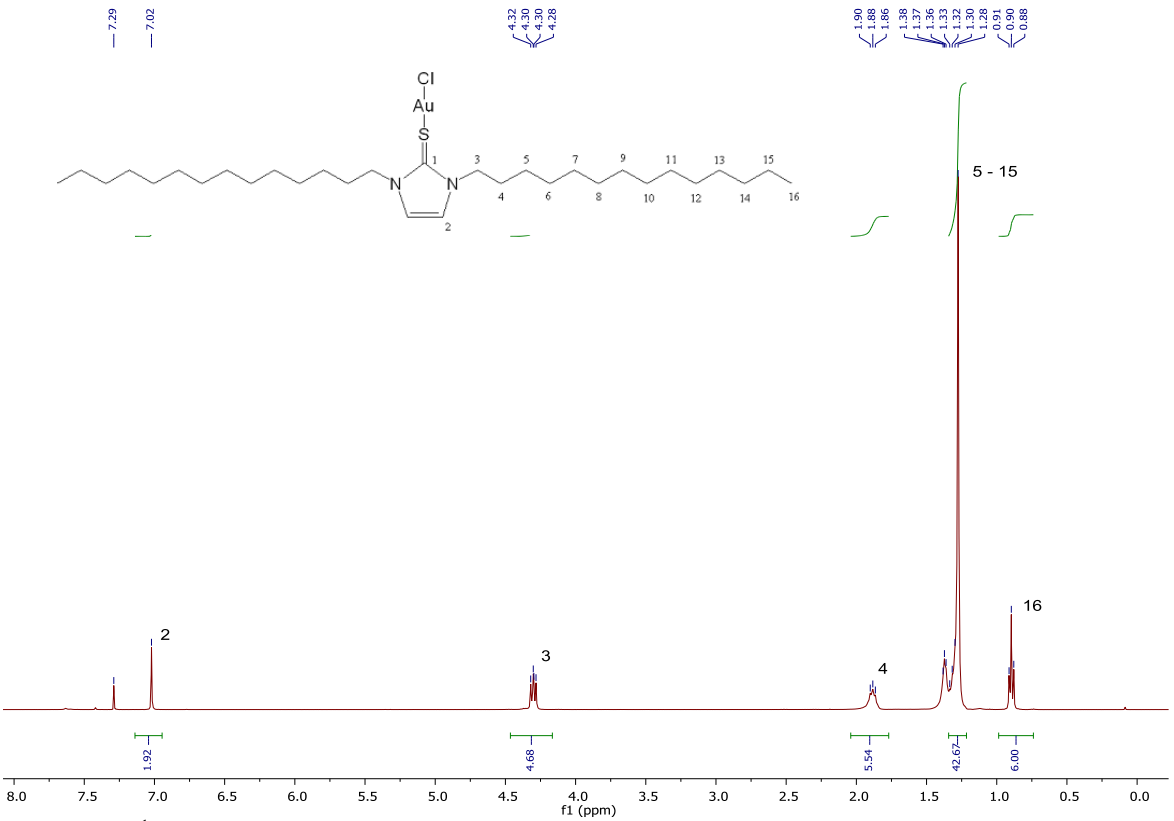

Figure S19. ^{1}H NMR spectrum of **3d**.

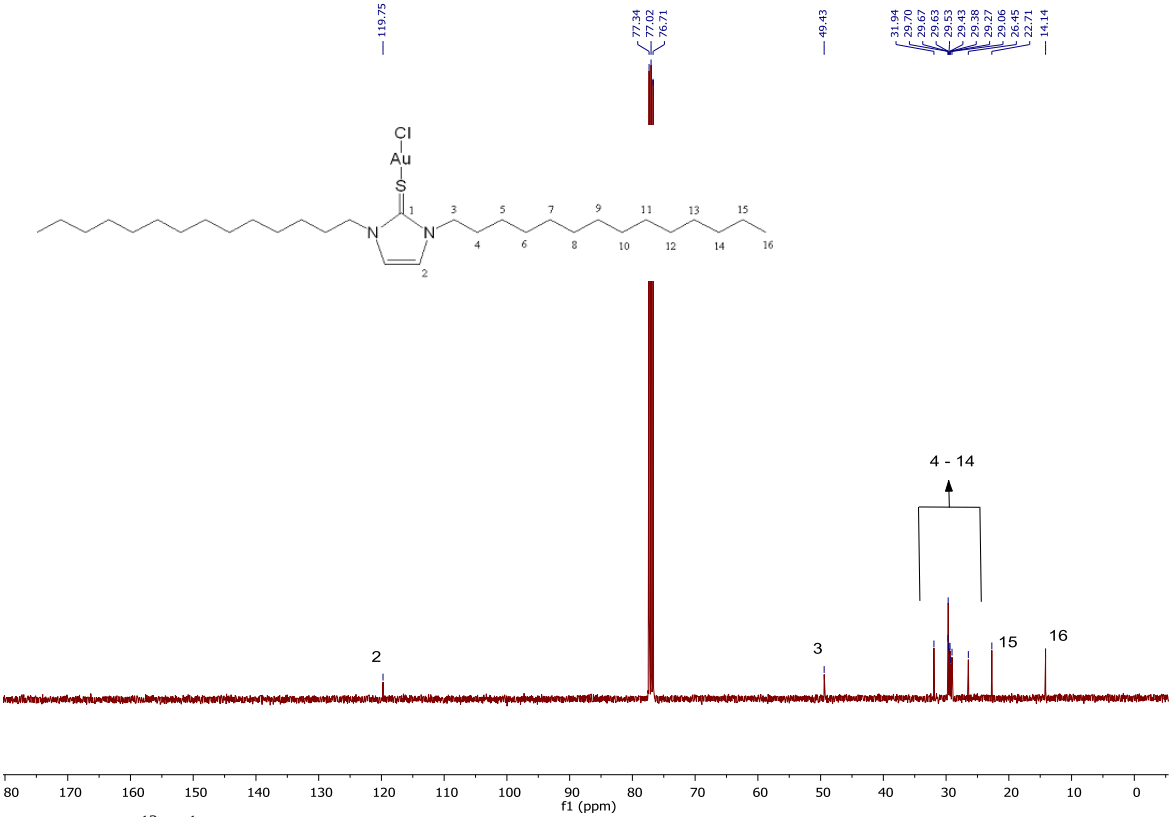

Figure S20. ^{13}C{^{1}H} NMR spectrum of **3d**.

1,3-Dioctadecyl-2-thione complex (3e). Orange solid; yield: 98%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.94-0.84 (6 H, m, C***H***$_3$CH$_2$), 1.32-1.23 (60 H, m, CH$_2$C***H***$_2$), 1.88 (4 H, m, NCH$_2$C***H***$_2$), 4.31 (4 H, t, *J* = 7.3 Hz, NC***H***$_2$), 6.99 (2 H, s, C=C***H***).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 14.2 (***C***H$_3$CH$_2$), 22.7 (CH$_3$***C***H$_2$), 26.5, 29.1, 29.29, 29.39, 29.45, 29.54, 29.64, 29.69, 29.73 and 32.0 (CH$_2$***C***H$_2$), 49.4 (N***C***H$_2$), 119.8 (***C***=C), 149.5 (***C***=S).

Elem. Anal. Calcd. for $C_{39}H_{76}N_2SAuCl$: C, 55.93; H, 9.15; N, 3.34; S, 3.83.

Elem. Anal. Found: C, 55.6; H, 8.9; N, 3.0; S, 4.1.

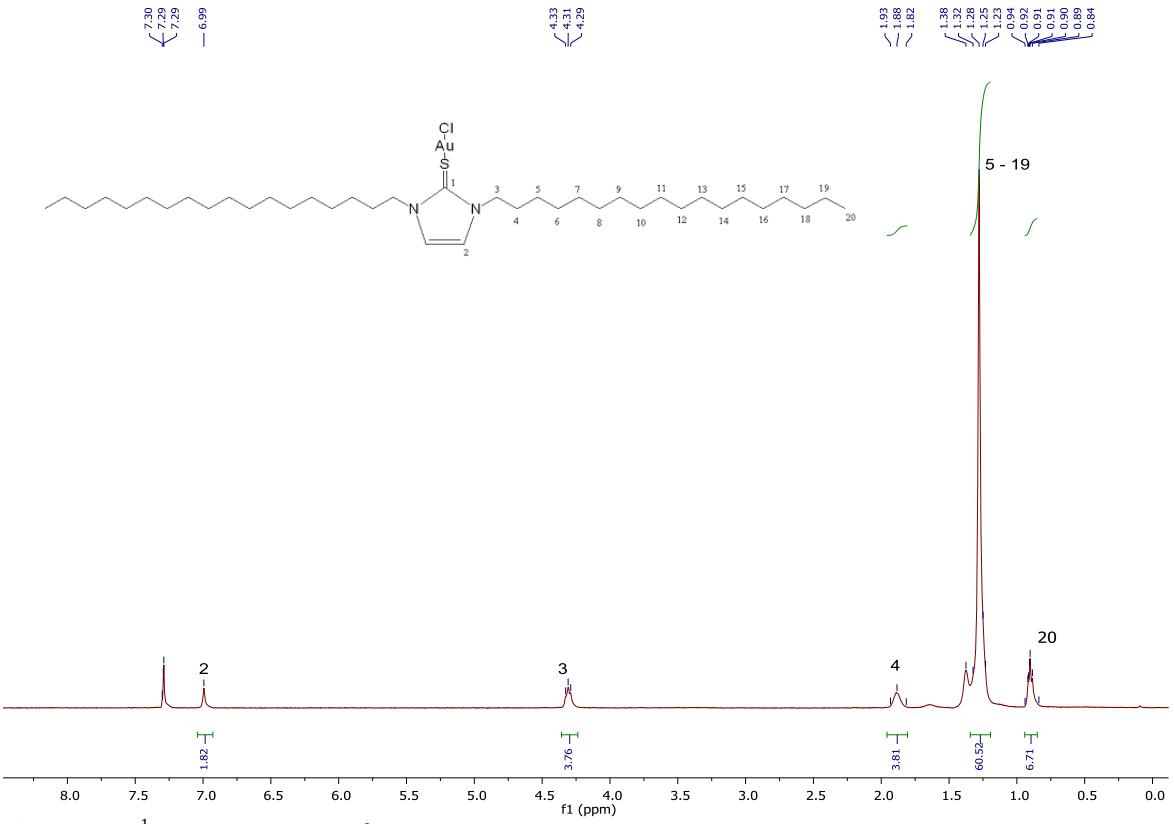

Figure S21. ^{1}H NMR spectrum of **3e**.

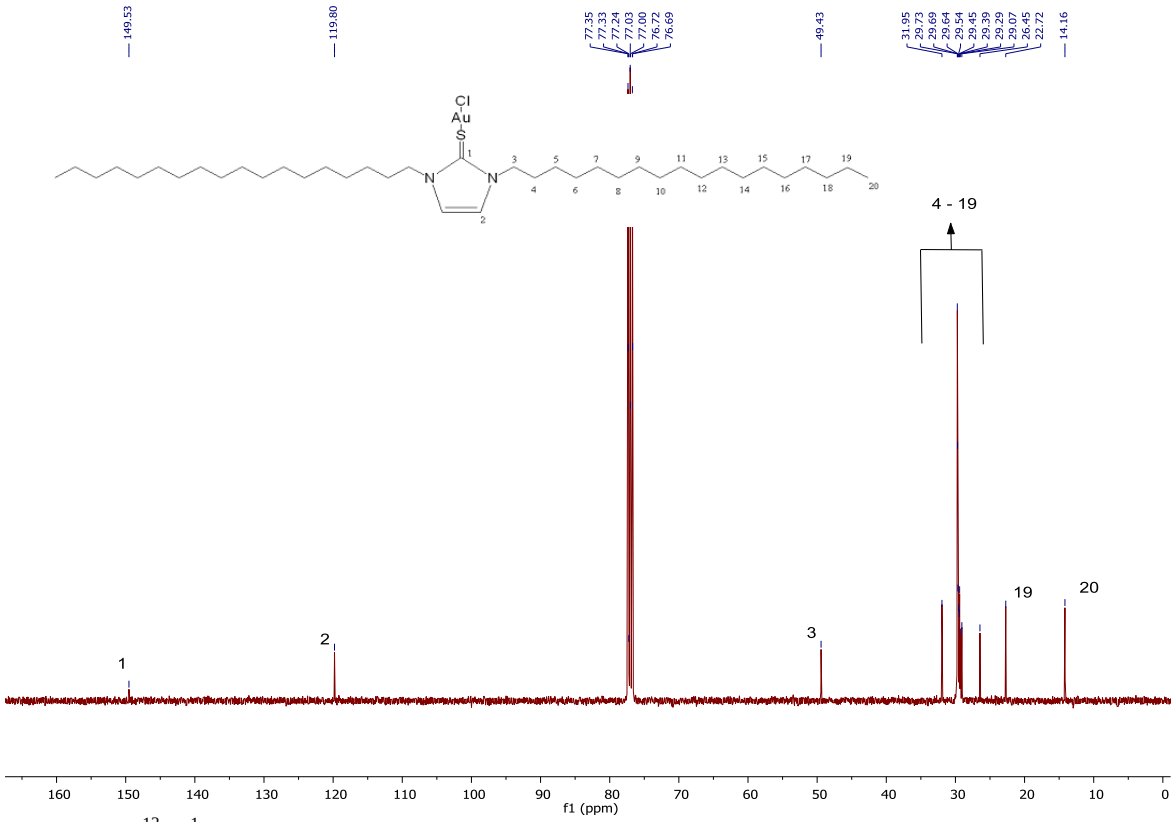

Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of **3e**.

1,3-Dimesityl-2-thione complex (3f). Beige solid; yield: 92%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.12 (12 H, s,C***H***$_3$), 2.42 (6 H, s, C***H***$_3$), 7.08 (2 H, s, C=C***H***), 7.10 (4 H, s, Ph-**H***m*).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 17.8 (*o*-**C**H_3), 21.3 (*p*-**C**H_3), 121.2 (***C***=C), 130.0 (**C**q, Ph-H*m*), 131.9 (**C**q, Ph-C*o*), 135.0 (**C**q, Ph-C*p*), 141.2 (**C**q-N), 154.4 (***C***=S).

Elem. Anal. Calcd. for $C_{21}H_{24}N_2SAuCl$: C, 44.34; H, 4.25; N, 4.92; S, 5.64.

Elem. Anal. Found: C, 44.2; H, 4.5; N, 4.7; S, 5.7.

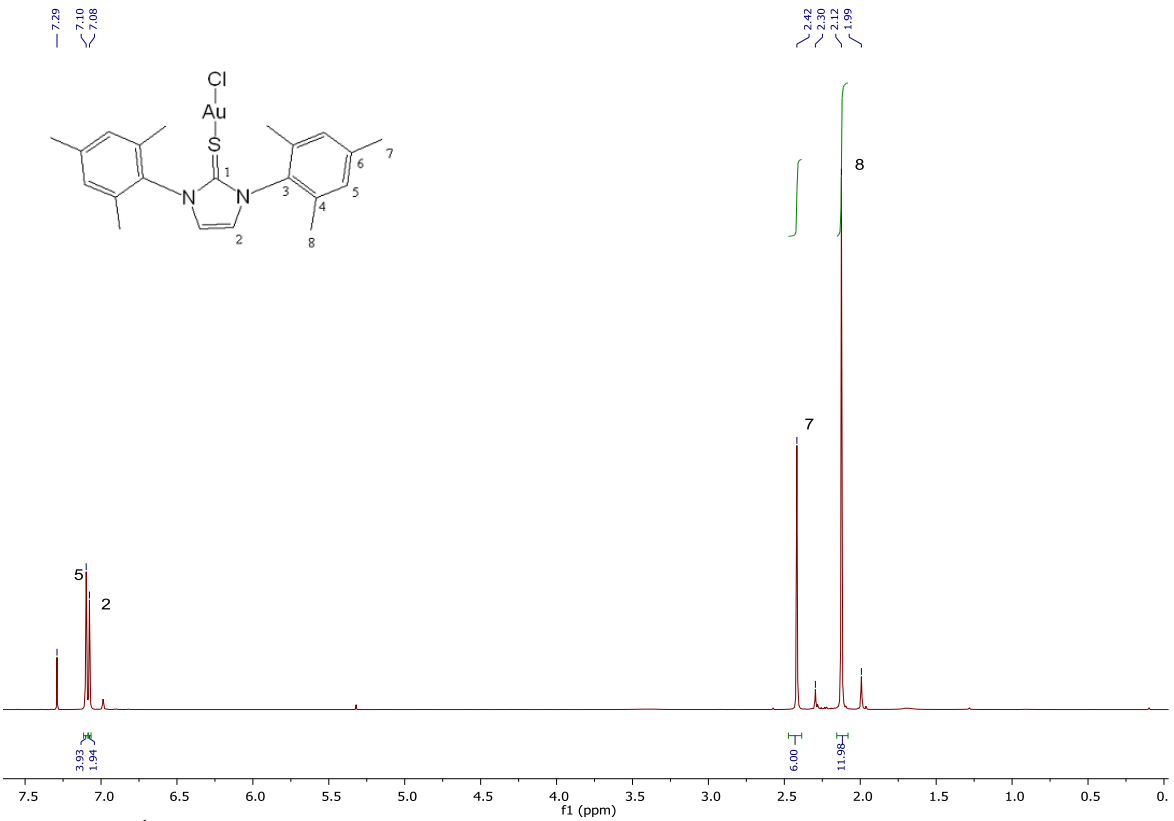

Figure S23. ^{1}H NMR spectrum of **3f**.

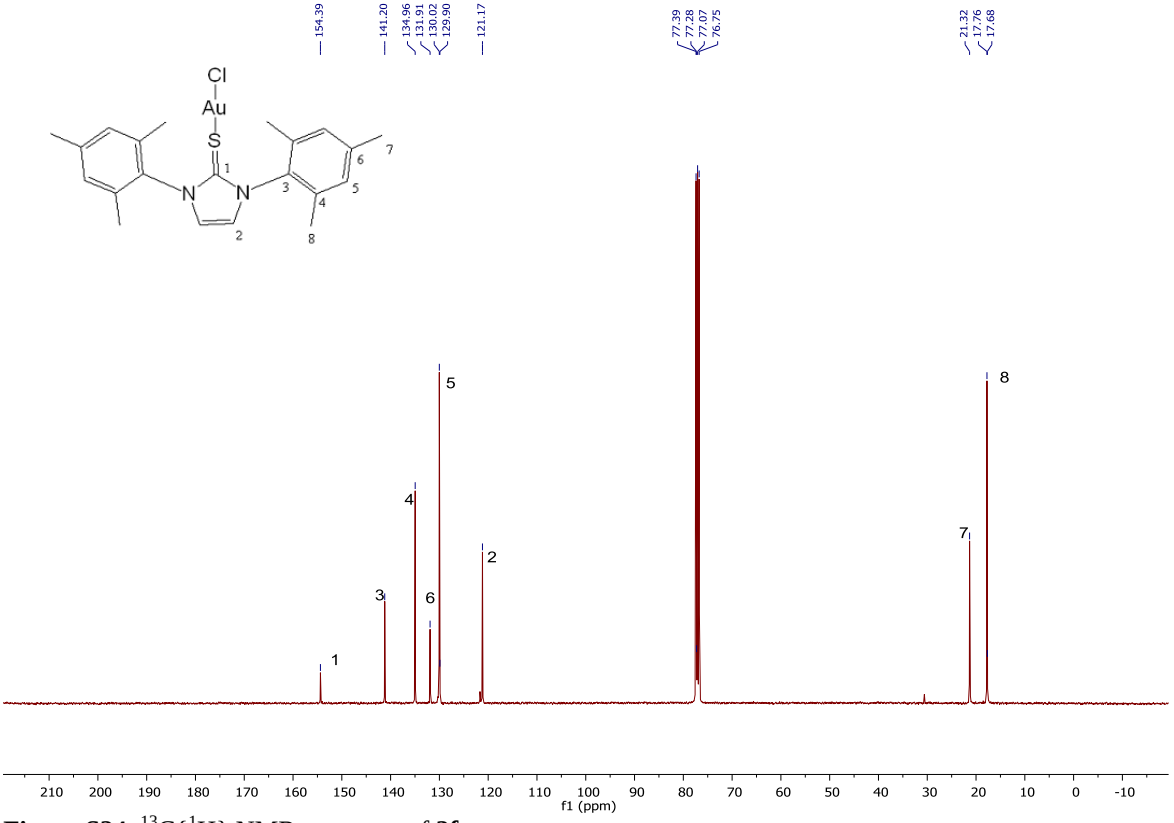

Figure S24. ^{13}C{^{1}H} NMR spectrum of **3f**.

1,3-bis-(2,6-diisopropylphenyl)-2-thione complex (3g). Gray solid; yield: > 99%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (12 H, d, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 1.40 (12 H, d, *J* = 6.8 Hz, CH(C***H***$_3$)$_2$), 2.53 (4 H, sep, *J* = 6.8 Hz, C***H***(CH$_3$)$_2$), 7.11 (2 H, s, C=C***H***), 7.40 (4 H, d, *J* = 7.8 Hz, Ph-**H***m*), 7.64 (2 H, t, *J* = 7.8 Hz, Ph-**H***p*).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 23.4 (CH(***C***H$_3$)$_2$), 24.5 (CH(***C***H$_3$)$_2$), 29.2 (***C***H(CH$_3$)$_2$), 122.0 (***C***=C), 125.1 (**C**q, Ph-H*m*), 131.7 (**C**q, Ph-H*p*), 131.9 (**C**q, Ph-C*o*), 145.7 (**C**q-N), 157.9 (***C***=S).

Elem. Anal. Calcd. for $C_{27}H_{36}N_2SAuCl$: C, 49.66; H, 5.56; N, 4.29; S, 4.91.

Elem. Anal. Found: C, 49.5; H, 6.0; N, 4.2; S, 4.5.

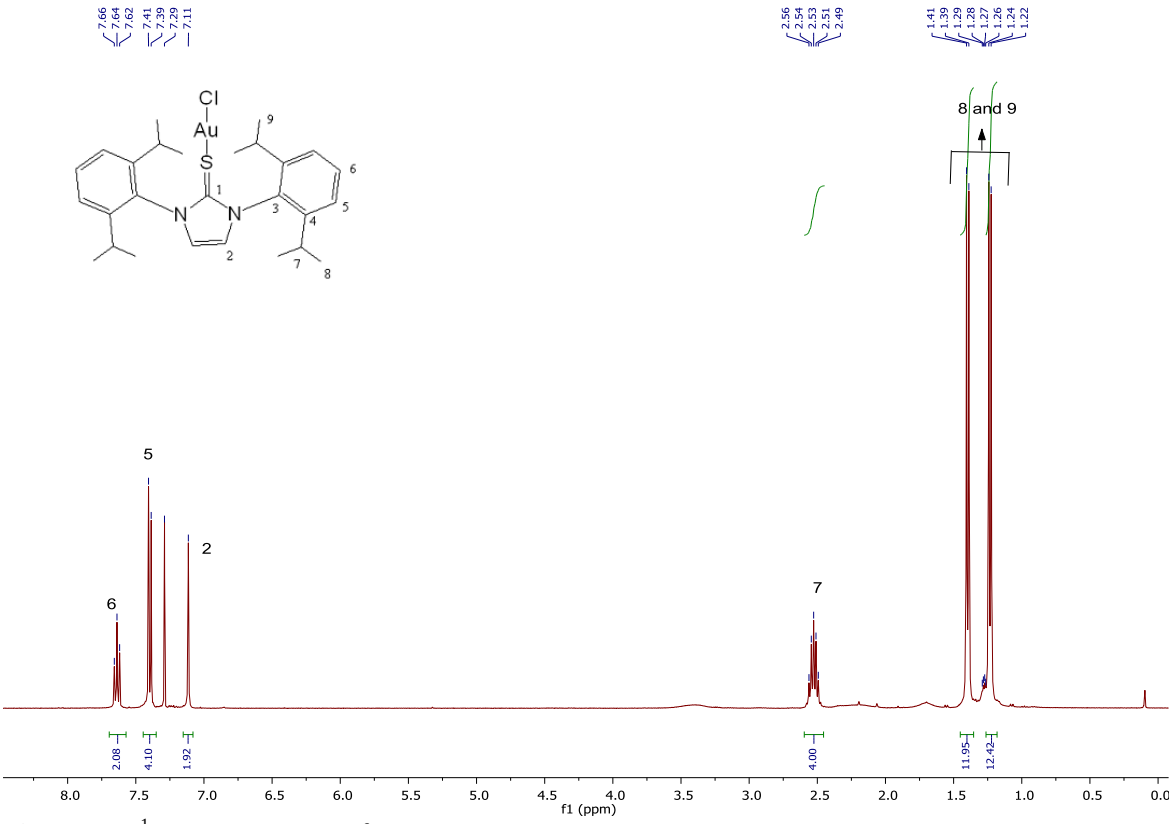

Figure S25. ^{1}H NMR spectrum of **3g**.

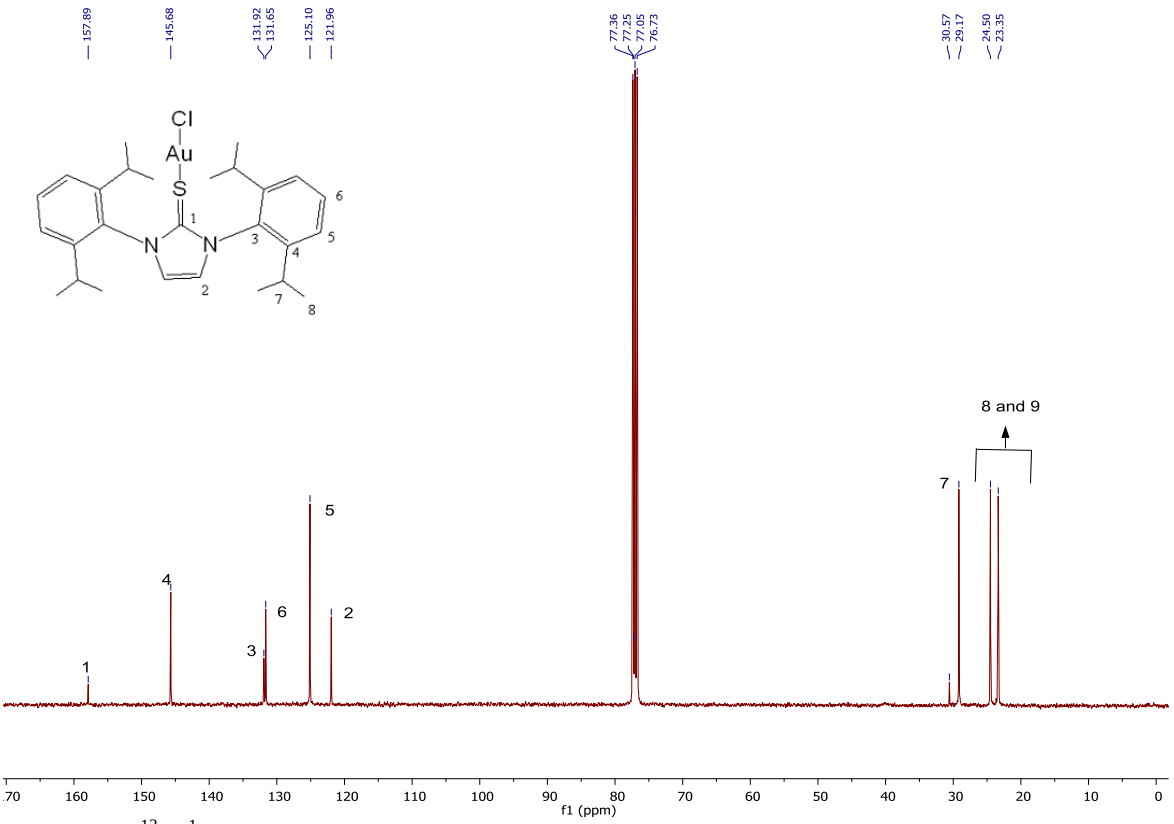

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **3g**.

4,5-Dimethyl-1,3-dimethyl-2-thione complex (3h). Red solid; yield: > 99%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.18 (6 H, s, C=CC***H***$_3$), 3.73 (6 H, s, NC***H***$_3$).

$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): δ = 9.5 (C=C***C***H_3), 33.3 (N***C***H_3), 125.2 (C=***C***), 147.0 (***C***=S).

Elem. Anal. Calcd. for $C_7H_{12}N_2SAuCl$: C, 21.63; H, 3.11; N, 7.21; S, 8.25.

Elem. Anal. Found: C, 21.8; H, 3.1; N, 7.3; S, 8.5.

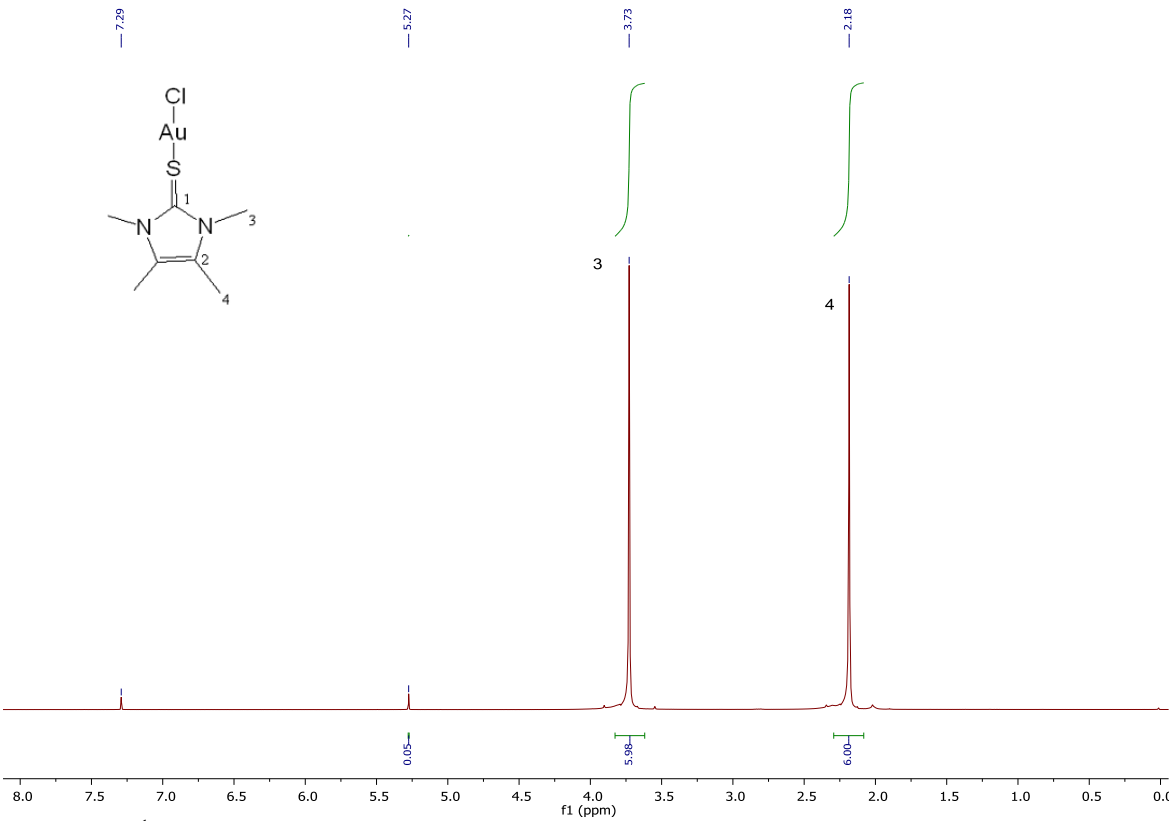

Figure S27. ^{1}H NMR spectrum of **3h**.

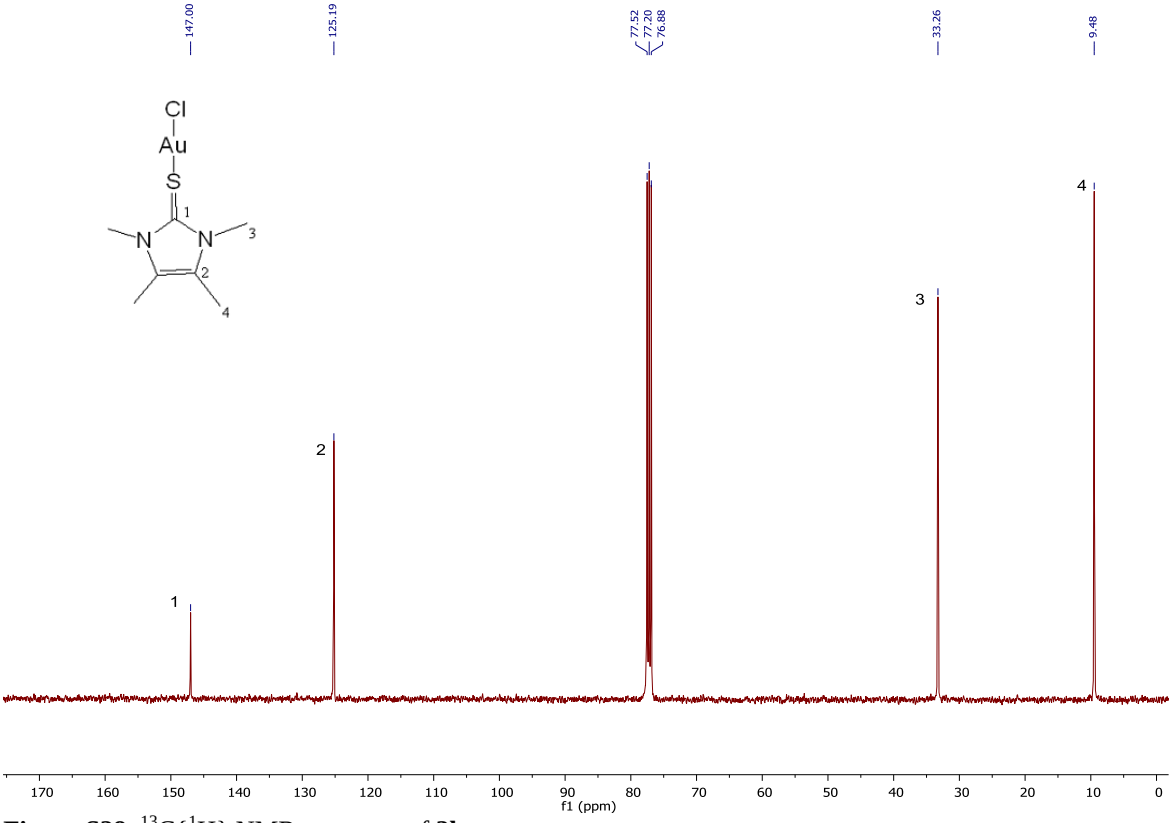

Figure S28. ^{13}C{^{1}H} NMR spectrum of **3h**.

4,5-Dimethyl-1,3-diisopropyl-2-thione complex (3i). Pink solid; yield: 94%

^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.57 (6 H, s, CH(C***H***$_3$)$_2$), 1.59 (6 H, s, CH(C***H***$_3$)$_2$), 2.29 (6 H, s, C=CC***H***$_3$), 5.69 (2 H, m, C***H***(CH$_3$)$_2$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ = 10.4 (C=C***C***H$_3$), 20.7 (CH(***C***H$_3$)$_2$), 51.4 (***C***H(CH$_3$)$_2$), 125.5 (C=***C***), 146.3 (***C***=S).

Elem. Anal. Calcd. for $C_{11}H_{20}N_2SAuCl$: C, 29.71; H, 4.53; N, 6.30; S, 7.21.

Elem. Anal. Found: C, 29.7; H, 4.8; N, 6.3; S, 7.1.

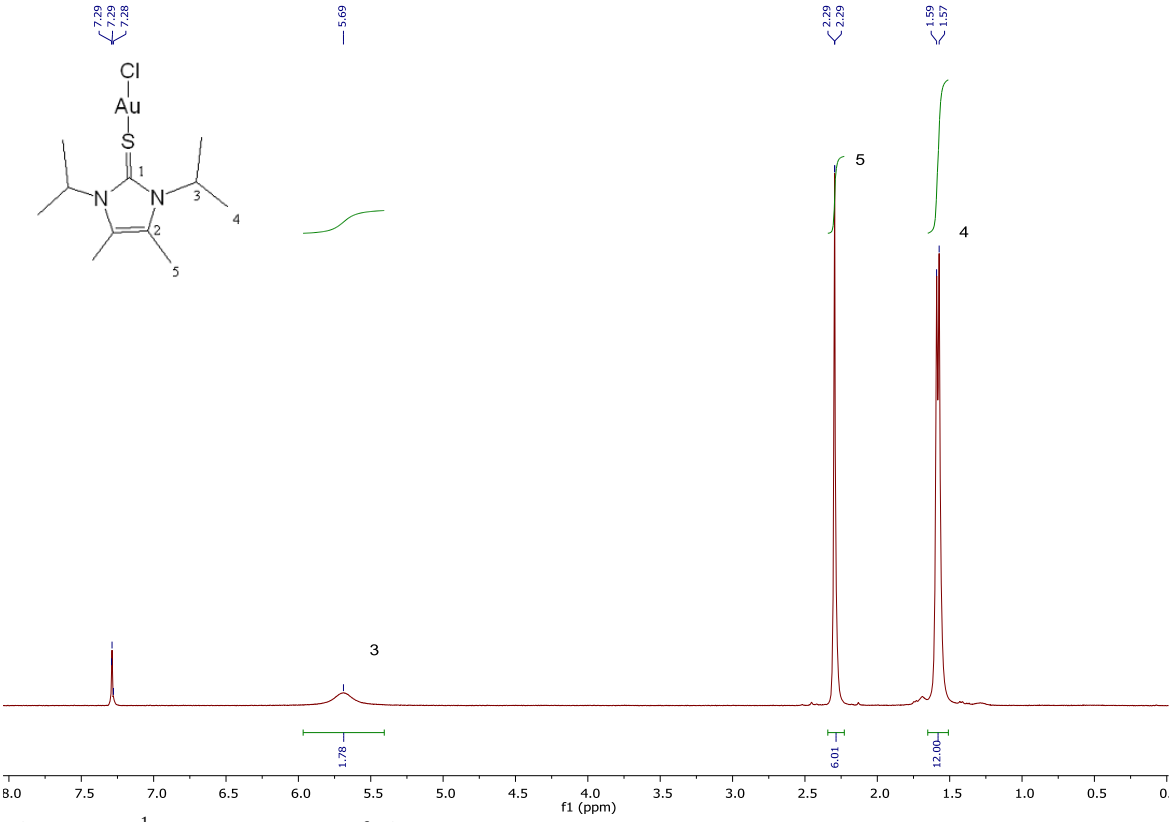

Figure S29. ^{1}H NMR spectrum of **3i**.

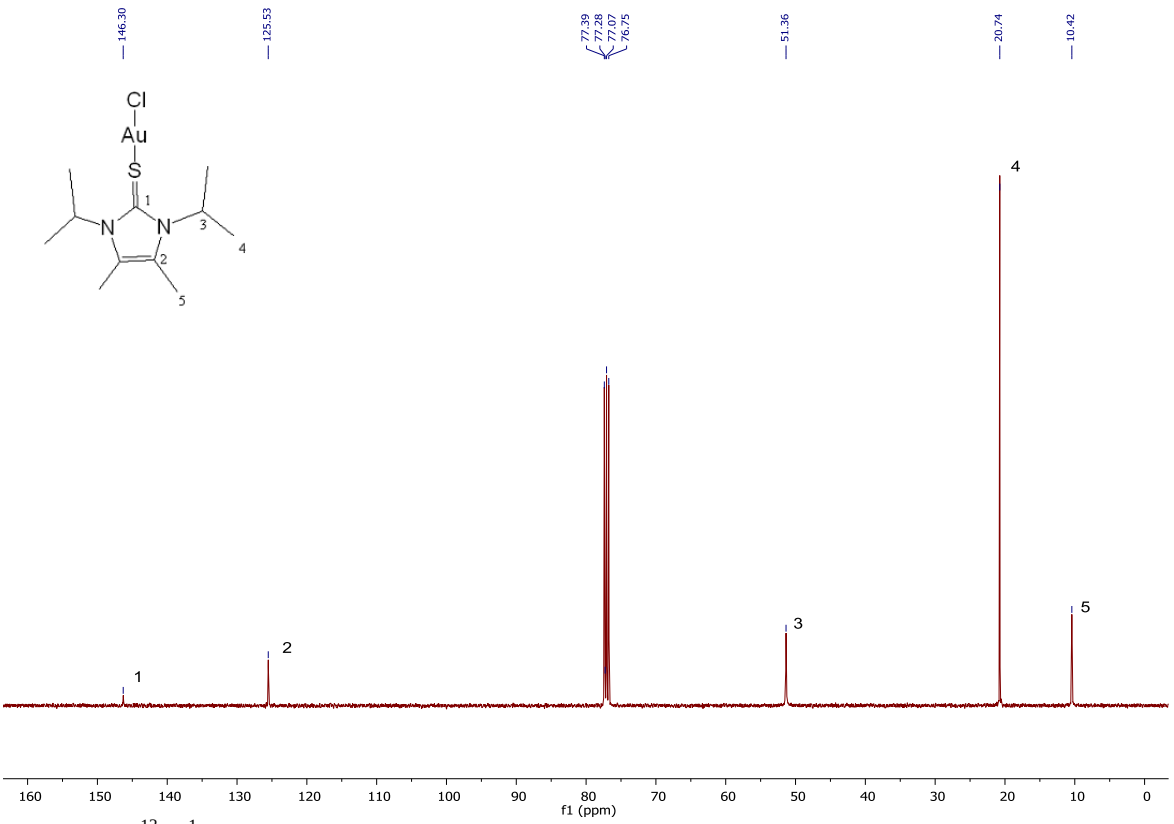

Figure S30. $^{13}C\{^{1}H\}$ NMR spectrum of **3i**.

Synthesis and characterisation of gold nanoparticles (AuNPs)

General Procedure AuNP-NHT^{Cx,Cy}

A J. Young flask was charged with gold complex **3** (0.14 mmol) and dry tetrahydrofuran (20 mL). Potassium triethylborohydride solution (0.14 mmol, 1 M in THF) was added in one portion and the mixture was stirred at room temperature for 1 h. The resulting red solution was quenched with 0.1 mL of dry ethanol and the solvent was evaporated under vacuum. The dark solid powder was washed with dry ethanol (3 x 5 mL), filtered under argon via cannula and again drying under vacuum, furnishing the corresponding AuNPs.

AuNP-NHT^{C1,C14}.

TEM: NPs of 3.8 (0.8) nm. **DLS (THF):** NPs of 7.8 (0.5) nm. **Au content (ICP):** 90%.

UV-Vis (THF): λmax = 512 nm.

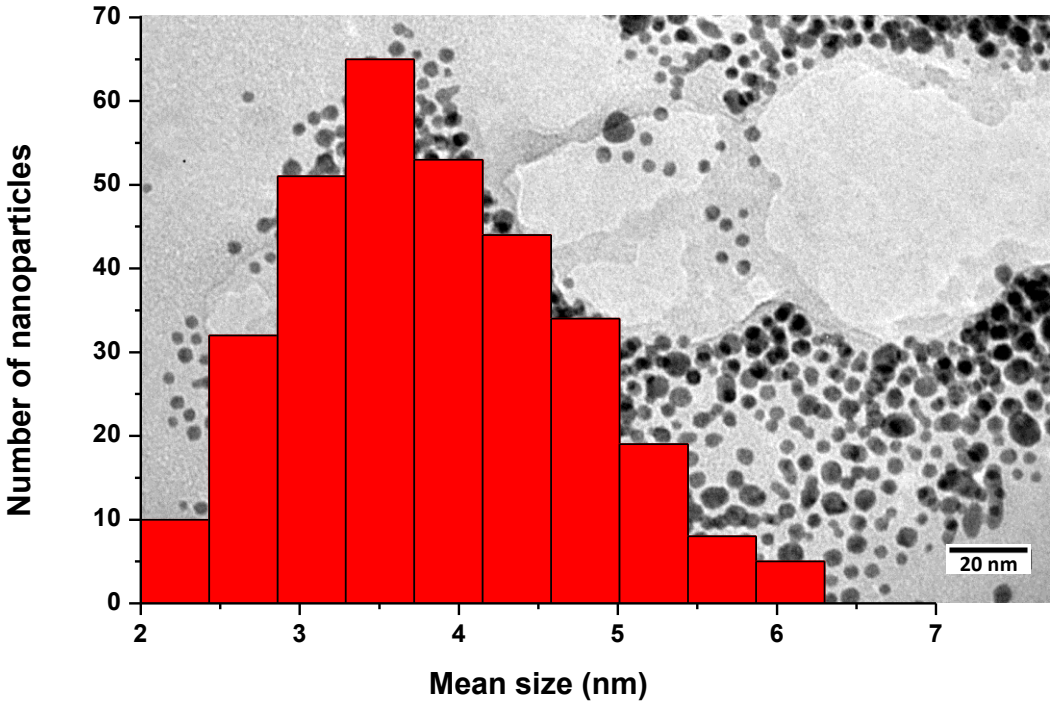

Figure S31. TEM image of AuNPs **AuNP-NHT^{C1,C14}**.

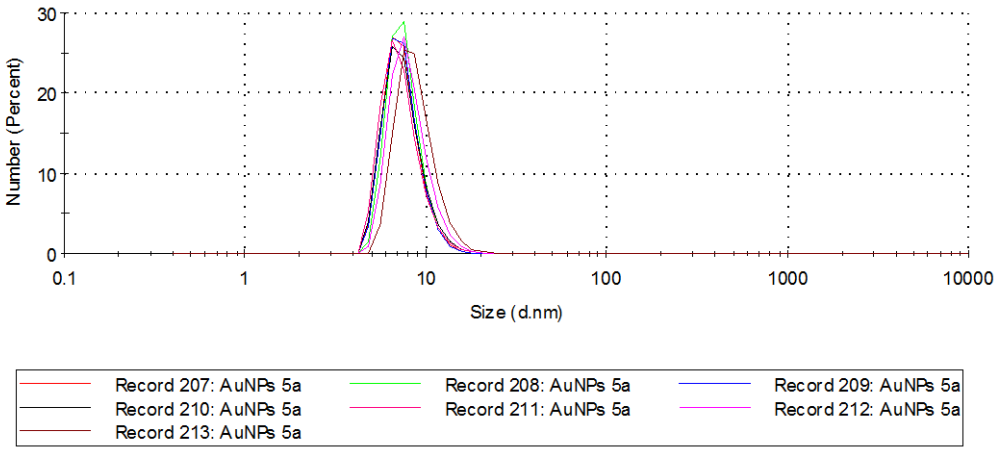

Figure S32. Size distribution by DLS of AuNPs **AuNP-NHT^{C1,C14}**.

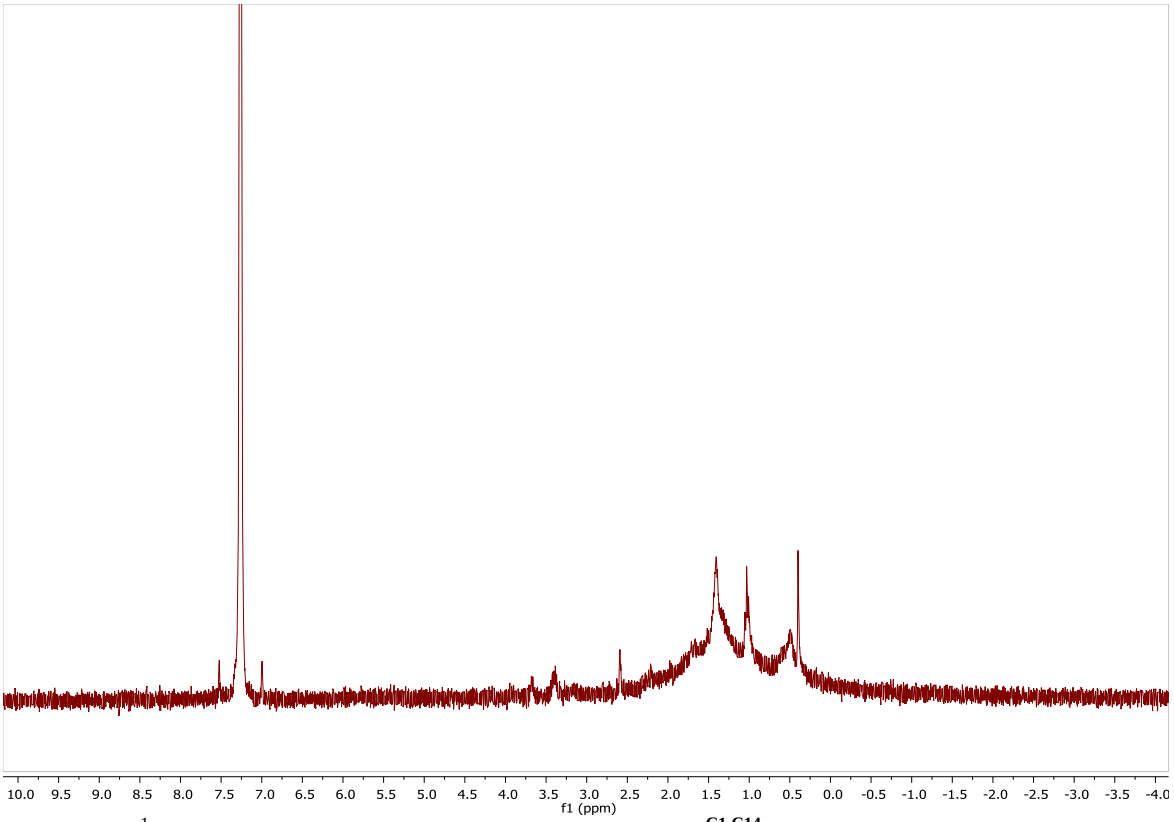

Figure S33. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **AuNP-NHT^{C1,C14}**.

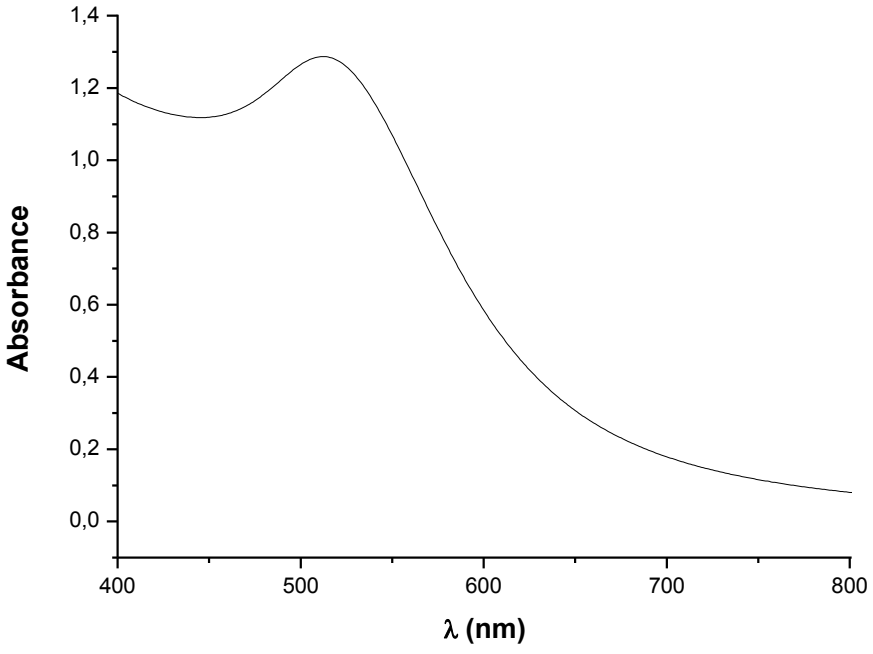

Figure S34. UV-Vis spectrum of AuNPs **AuNP-NHT^{C1,C14}**.

AuNP-NHT^{C1,C18}.

TEM: NPs of 3.7 (0.7) nm. **DLS (THF):** NPs of 8.2 (0.4) nm **Au content (ICP):** 74%.

UV-Vis (THF): λmax = 515 nm.

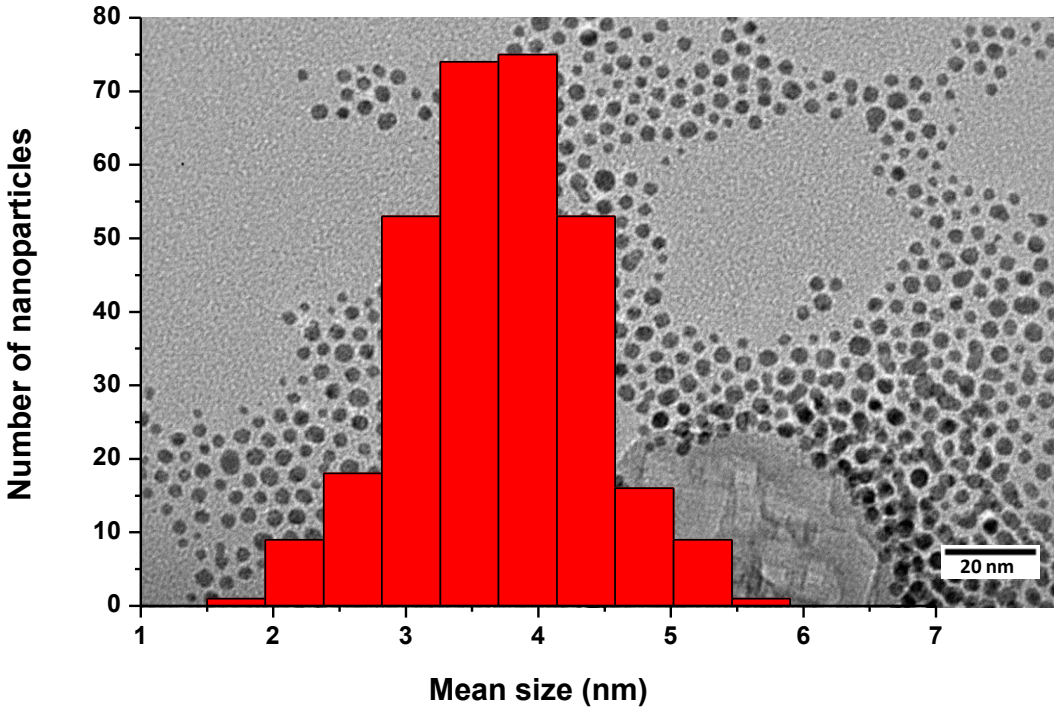

Figure S35. TEM image of AuNPs **AuNP-NHT^{C1,C18}**.

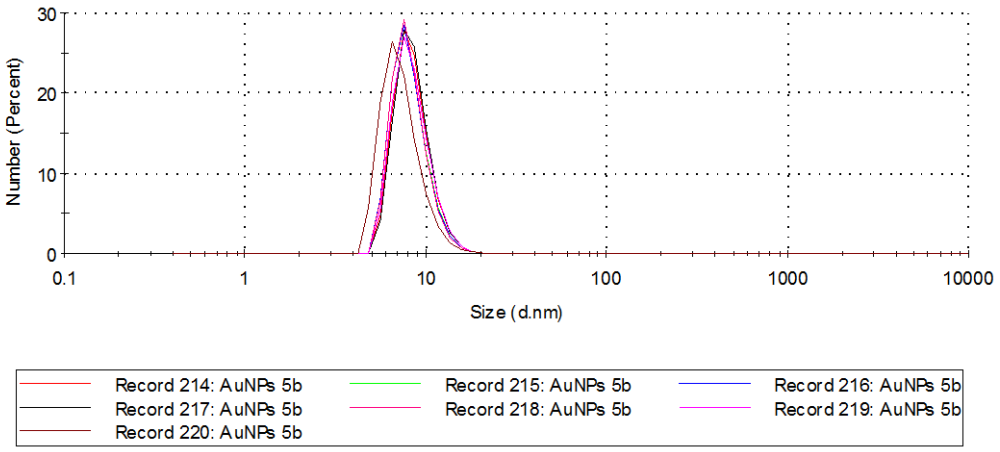

Figure S36. Size distribution by DLS of AuNPs **AuNP-NHT^{C1,C18}**.

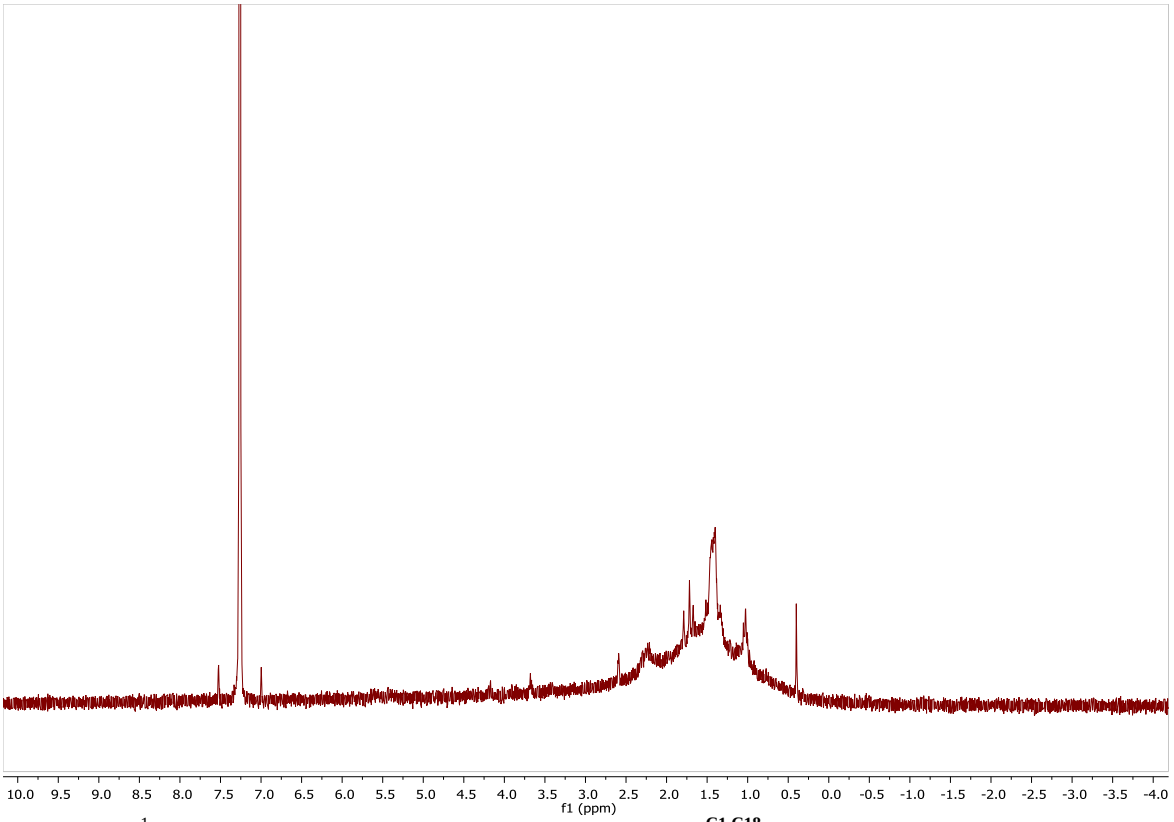

Figure S37. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **AuNP-NHT^{C1,C18}**.

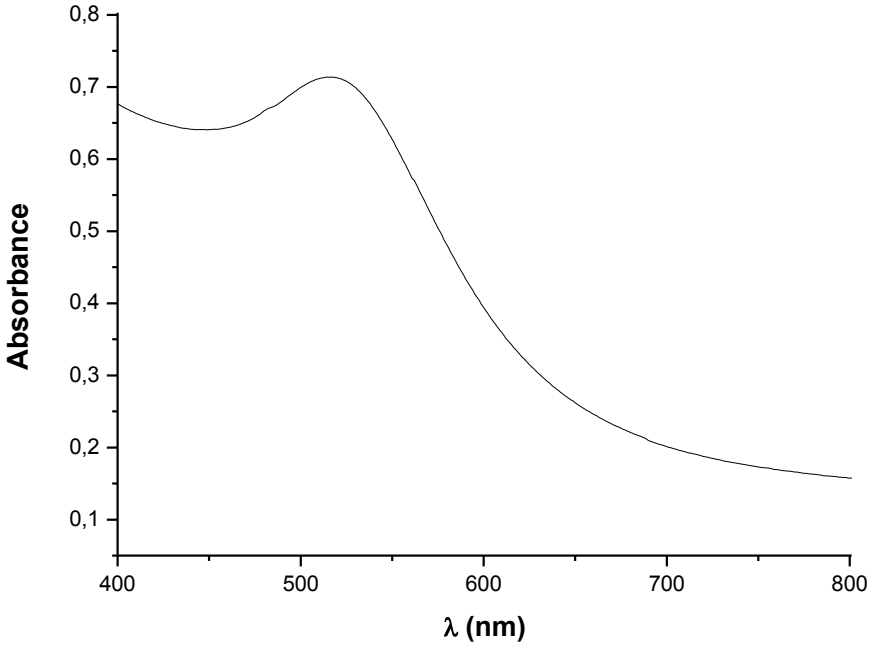

Figure S38. UV-Vis spectrum of AuNPs **AuNP-NHT^{C1,C18}**.

AuNP-NHT^{C6,C6}.

TEM: NPs of 2.9 (0.7) nm. **DLS (THF):** NPs of 4.4 (0.5) nm **Au content (ICP):** 55%.

UV-Vis (THF): λmax = 506 nm.

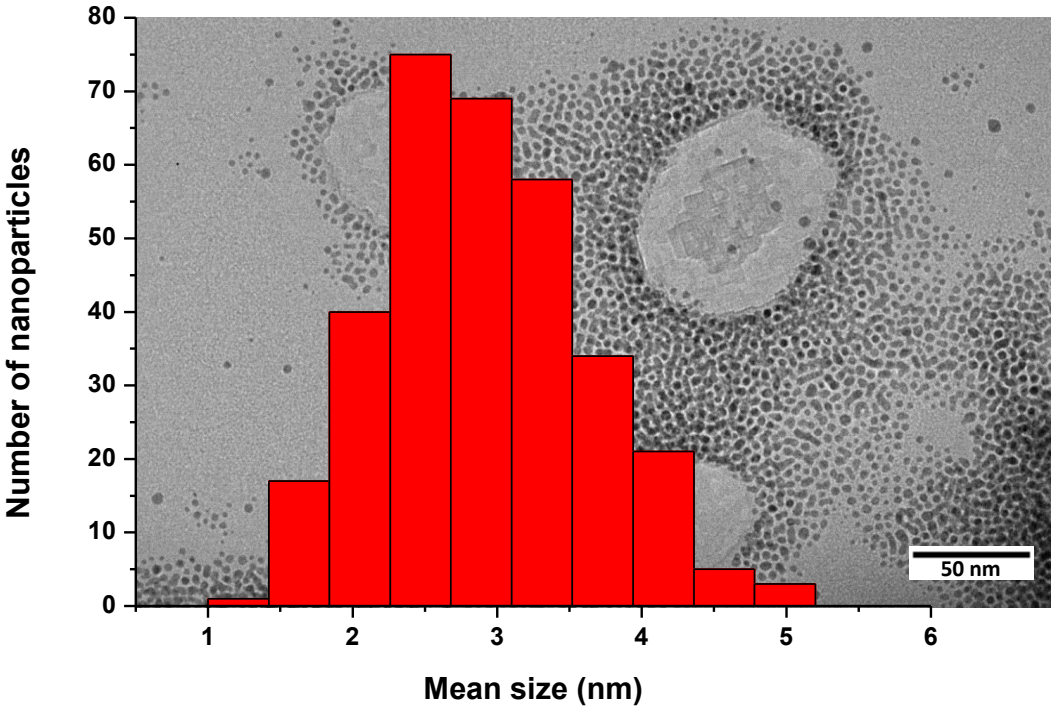

Figure S39. TEM image of AuNPs **AuNP-NHT^{C6,C6}**.

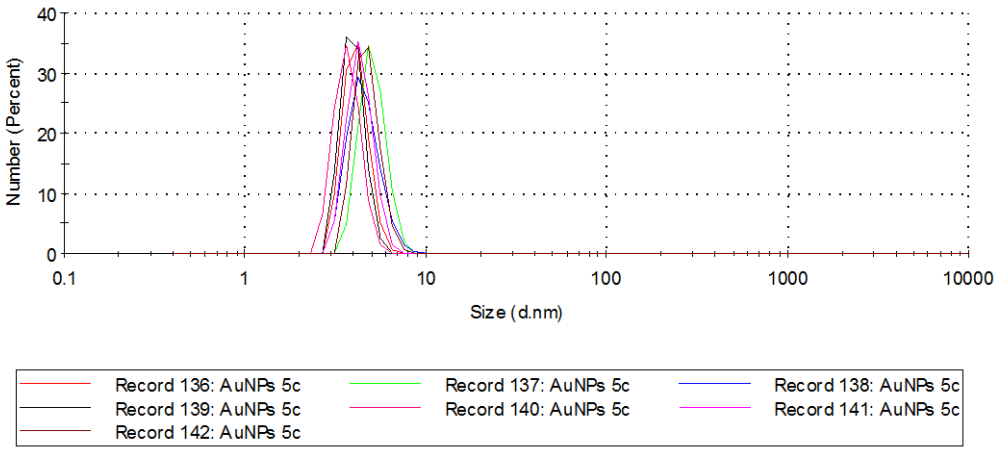

Figure S40. Size distribution by DLS of AuNPs **AuNP-NHT^{C6,C6}**.

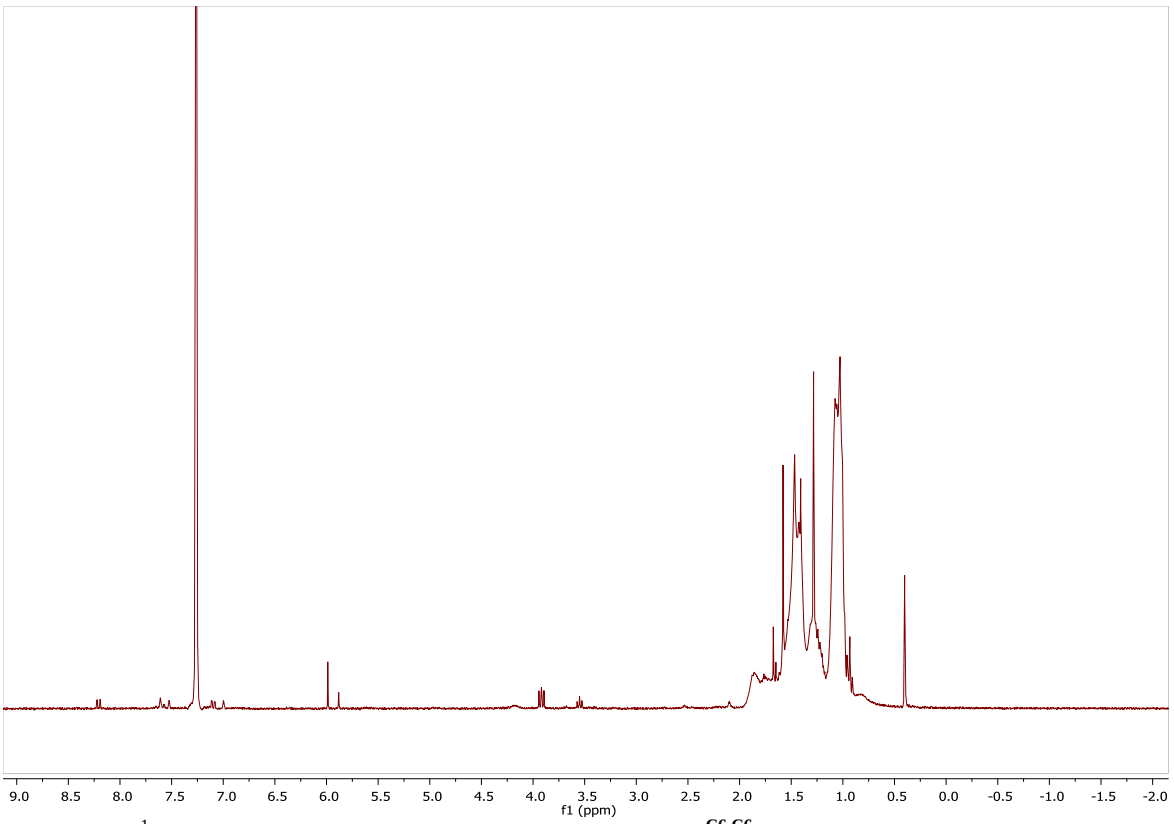

Figure S41. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **AuNP-NHT^{C6,C6}**.

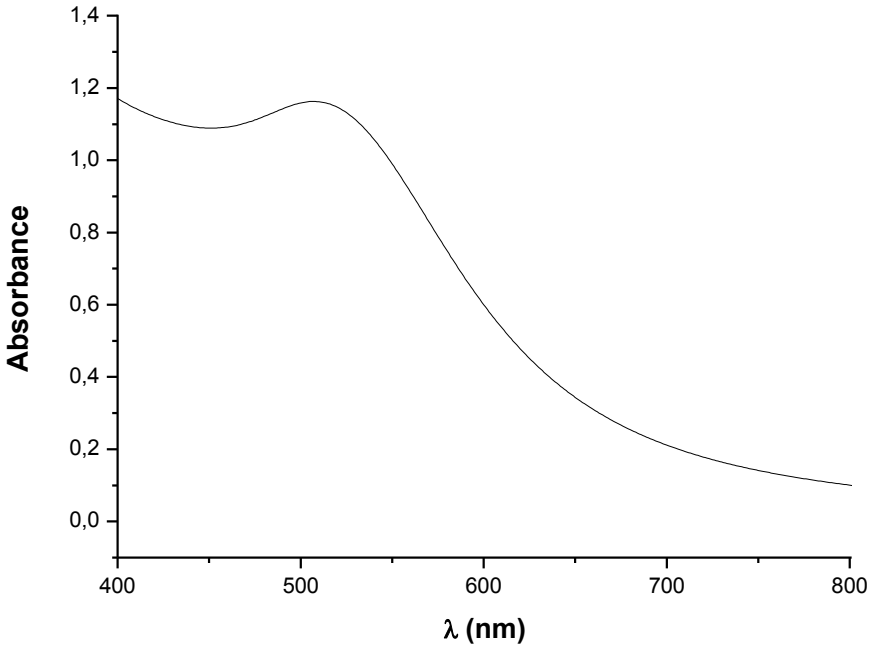

Figure S42. UV-Vis spectrum of AuNPs **AuNP-NHT^{C6,C6}**.

AuNP-NHT^{C14,C14}.

TEM: NPs of 3.5 (1.0) nm. **DLS (THF):** NPs of 8.5 (0.3) nm **Au content (ICP):** 88%.

UV-Vis (THF): λmax = 526 nm.

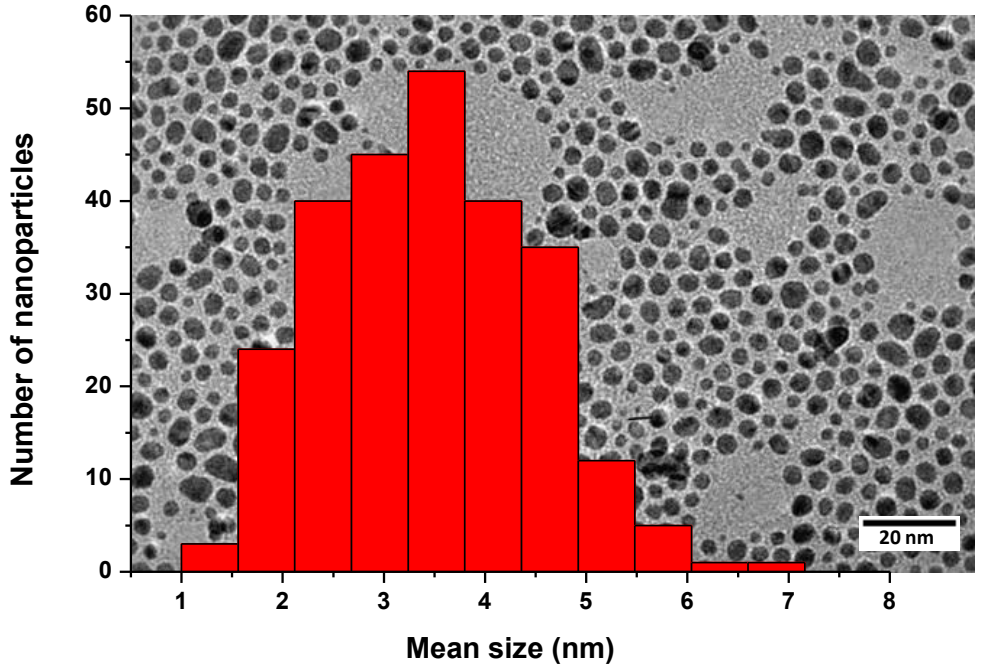

Figure S43. TEM image of AuNPs **AuNP-NHT^{C14,C14}**.

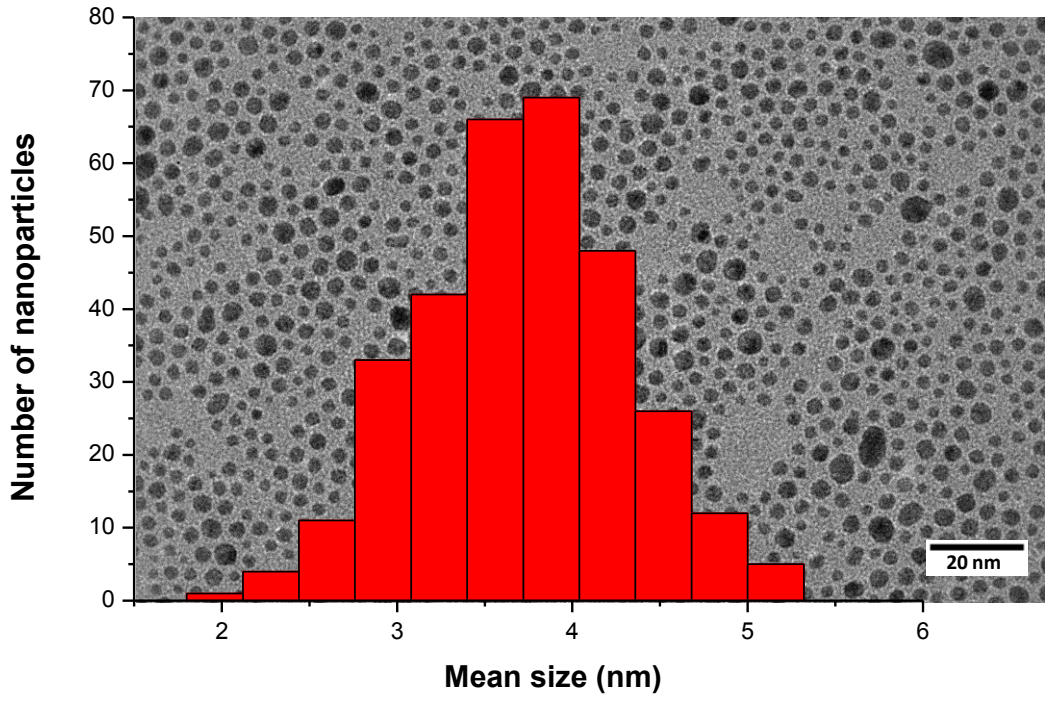

Figure S44. TEM image of AuNPs **AuNP-NHT^{C14,C14}** after exposure to air for *ca.* two months. Mean size: 3.7 (0.6) nm

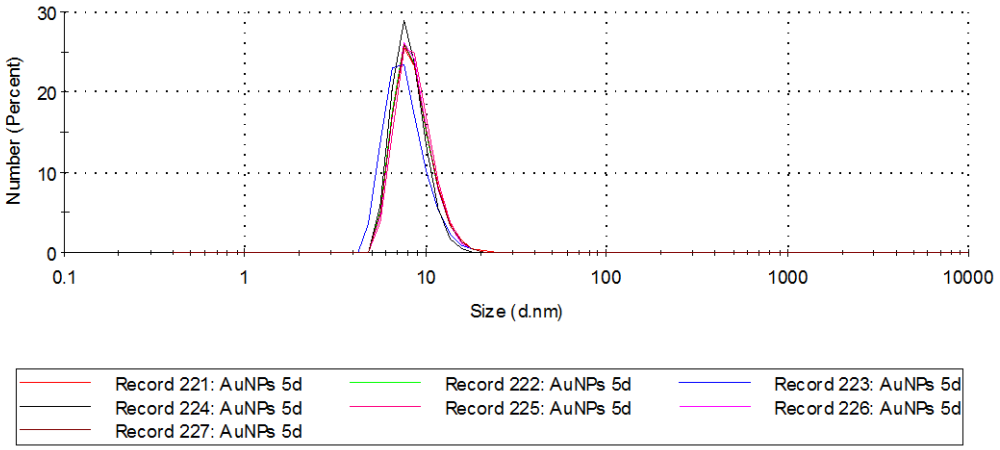

Figure S45. Size distribution by DLS of AuNPs **AuNP-NHT^{C14,C14}**.

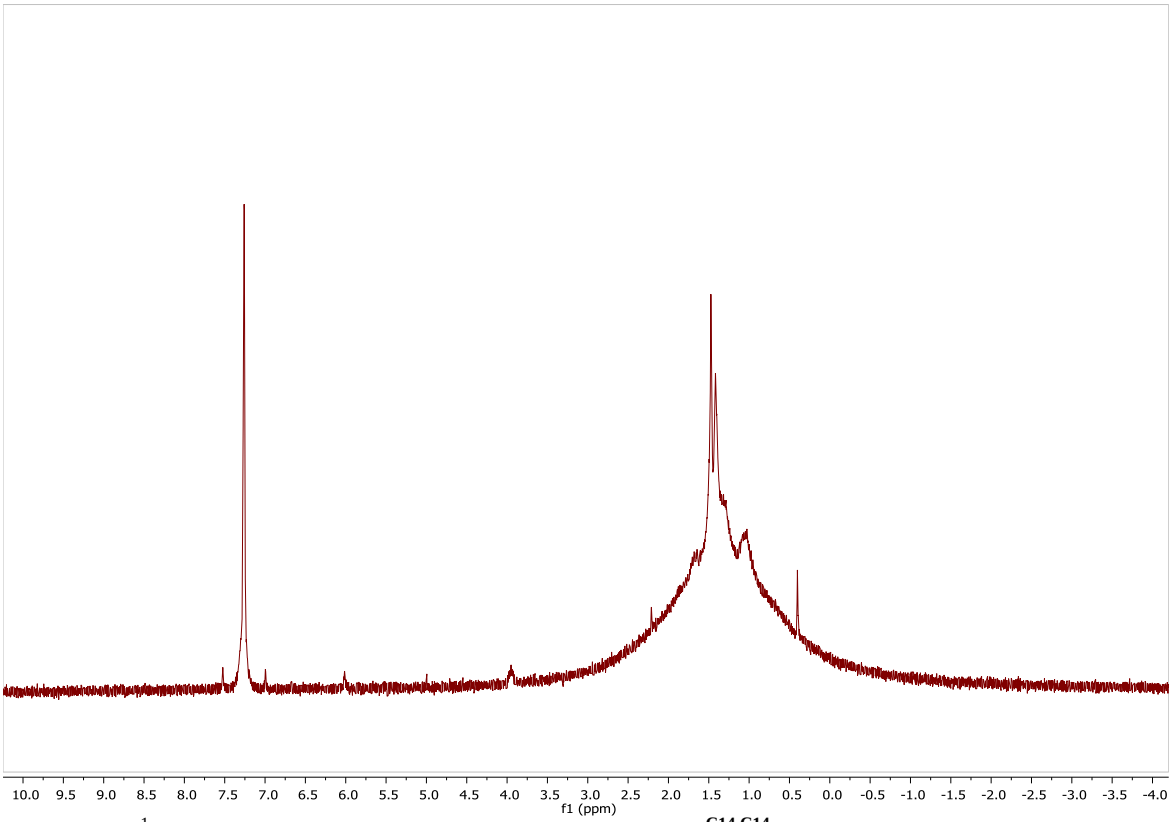

Figure S46. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **AuNP-NHT^{C14,C14}**.

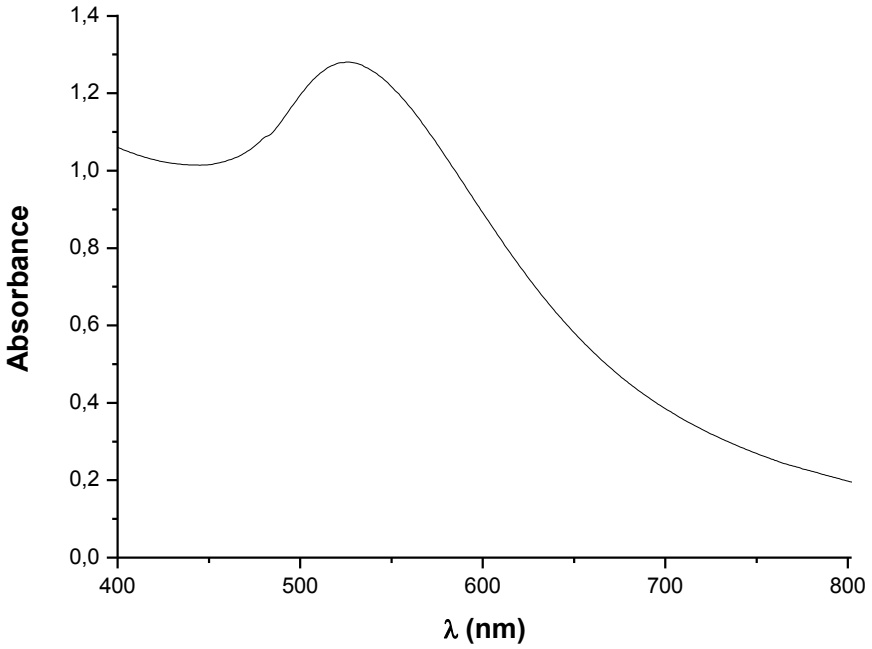

Figure S47. UV-Vis spectrum of AuNPs **AuNP-NHT^{C14,C14}**.

AuNP-NHT^{C18,C18}.

TEM: NPs of 2.9 (0.8) nm. **DLS (THF):** NPs of 8.6 (0.4) nm **Au content (ICP):** 56%. **UV-Vis (THF):** λmax = 515 nm.

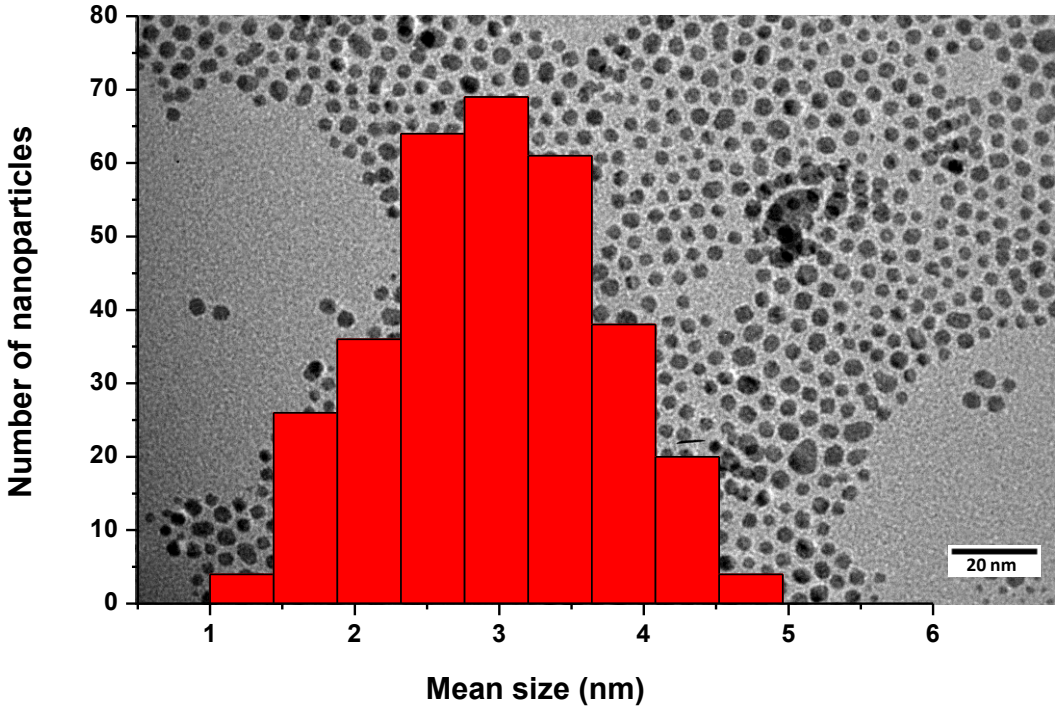

Figure S48. TEM image of AuNPs **AuNP-NHT^{C18,C18}**.

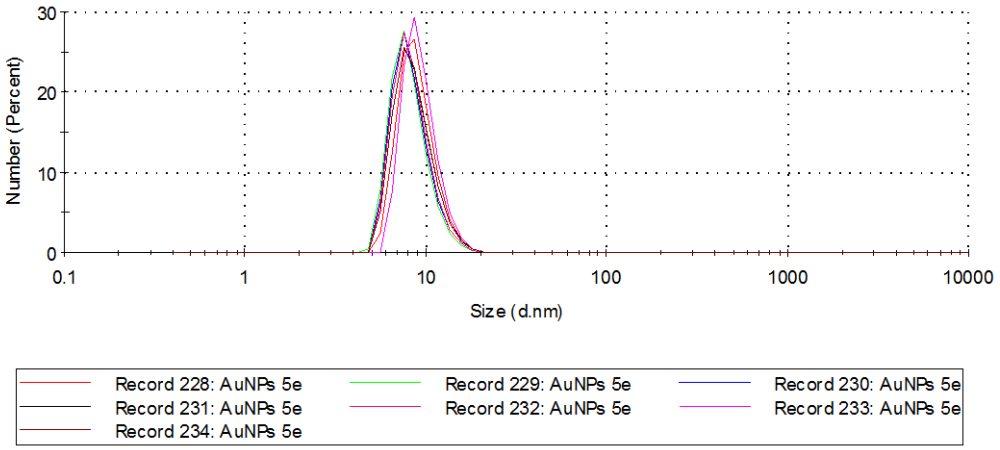

Figure S49. Size distribution by DLS of AuNPs **AuNP-NHT**^{C18,C18}.

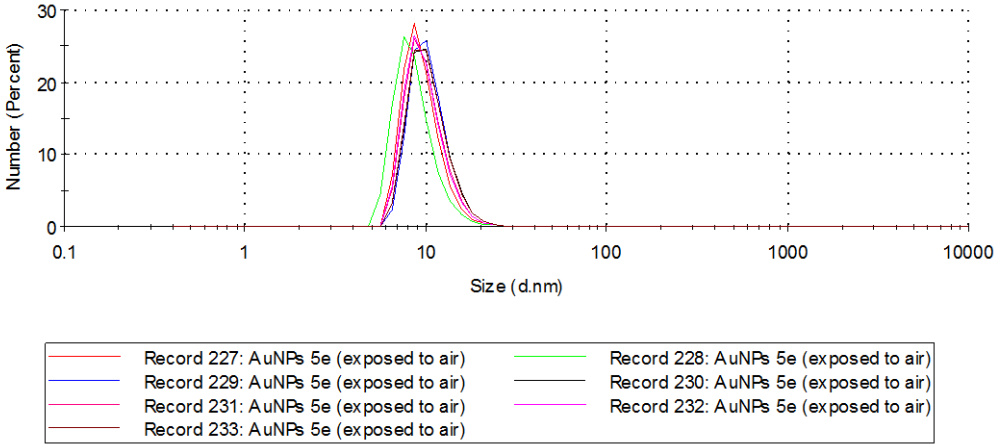

Figure S50. Size distribution by DLS of AuNPs **AuNP-NHT**^{C18,C18} after exposure to air for two weeks. Mean size: 9.9 (0.6) nm

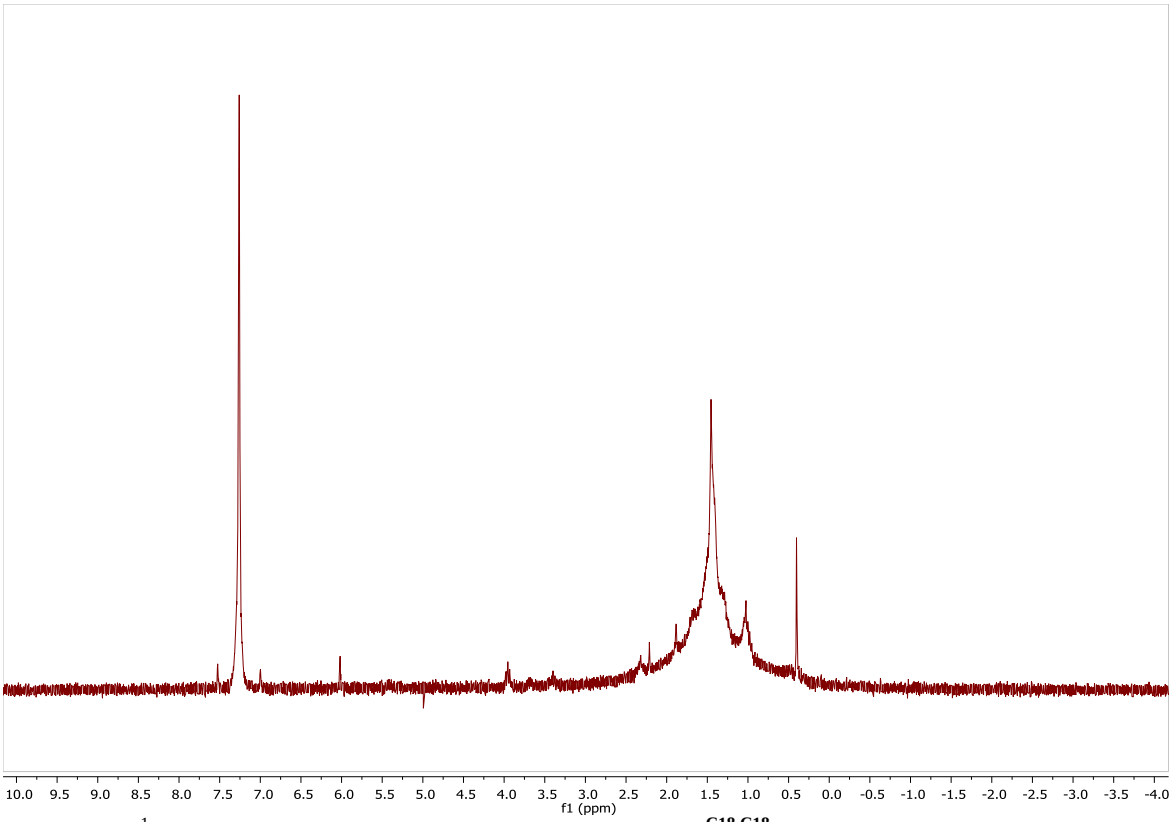

Figure S51. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **AuNP-NHT^{C18,C18}**.

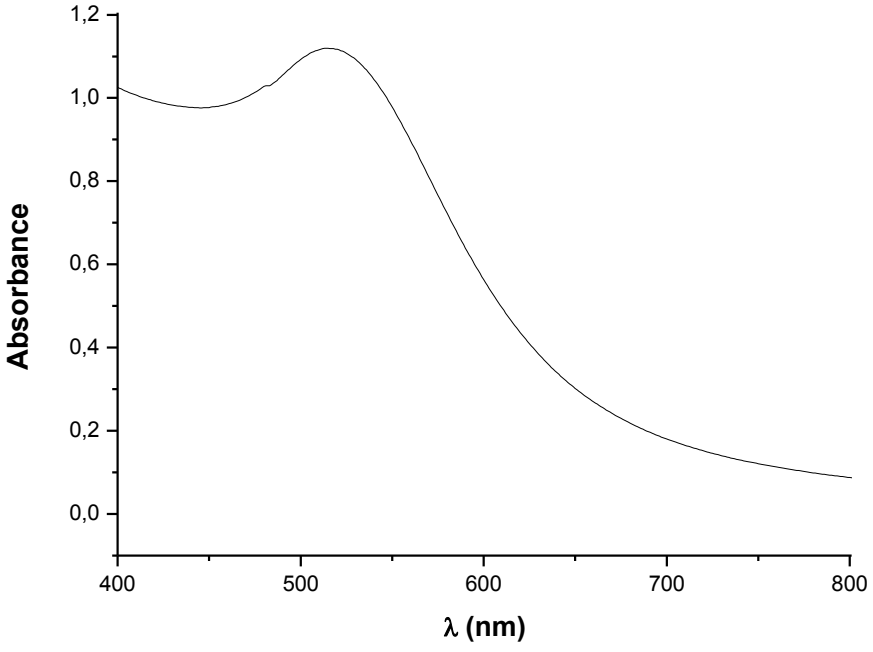

Figure S52. UV-Vis spectrum of AuNPs **AuNP-NHT^{C18,C18}**.

Catalytic experiments

General Procedure

A J. Young flask was charged with nitroarene (0.45 mmol) (See Table 1 and 2), sodium borohydride (85.12 mg, 2.24 mmol), AuNPs-NHT^{Cx,Cy} (1.0 mol% Au), tetrahydrofuran (2.0 mL) and water (5.0 mL). The mixture was stirred at room temperature. After complete conversion of the nitroarene (See Table 1 and 2), an aliquot of the reaction mixture was filtered under argon via cannula and analyzed by GC-MS or by ^{1}H NMR.

References

[1] Rohini, R.; Lee C. K.; Lu, J. T.; Lin, I. J. B. *J. Chin. Chem. Soc.* **2013**, 60, 745-754.

[2] Ramnial, T.; Taylor, S. A.; Bender, M. L.; Gorodetsky, B.; Lee, P. T. K.; Dickie, D. A.; McCollum, B. M.; Pye, C. C.; Walsby, C. J.; Clyburne, J. A. C. *J. Org. Chem*. **2008**, 73, 801-812.

[3] Zeng, W.; Wang, E.; Qiu, R.; Sohail, M.; Wu, S.; Chen, F. X. *J. Organomet. Chem*. **2013**, 743, 44-48.

[4] Kuhn, N.; Kratz, T. *Synthesis*. **1993**, 561-562.

[5] Uson, R.; Laguna, A.; Laguna, M.; Briggs, D. A.; Murray, H. H.; Fackler Jr, J. P. *Inorganic Syntheses*. Volume 26. 2007.