Electronic Supplementary Material (ESI) for Dalton Transactions.

On the Mercuration, Palladation, Transmetallation and Direct Auration of a *C^N^C* Pincer Ligand[§]

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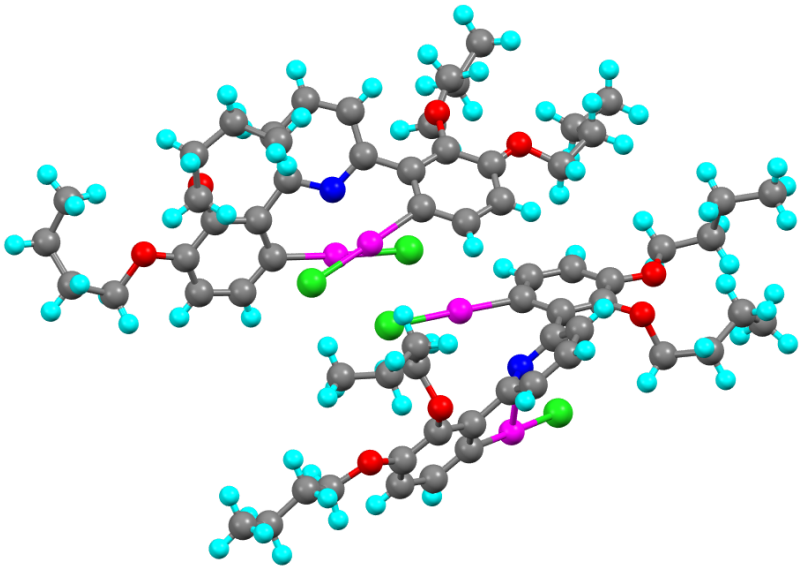
[§] Dedicated to the memory of Peter Maitlis.

Supplementary Information

Molecular Structure of the Dimercury Complex, 4-4

There are short Hg–Cl distances of 2.312(4) Å and 2.309(5) Å where the chloride is not bound to another atom and a second set of short distances, all at 2.336(4) Å by symmetry, where the chloride experiences a non-bonded contact to two other mercury centres. The two other Hg···Cl distances range are 3.032(3) Å, 3.091(3) Å, 3.065(3) Å and 3.112(3) Å, depending on the chloride in question. The spatial arrangement is as shown in Figure S1b, although the atoms are not coplanar. This extended coordination leads to four complexes being assembled through these extended Hg···Cl interactions, the core structure of which is indicated in Fig. S1c.



(a)

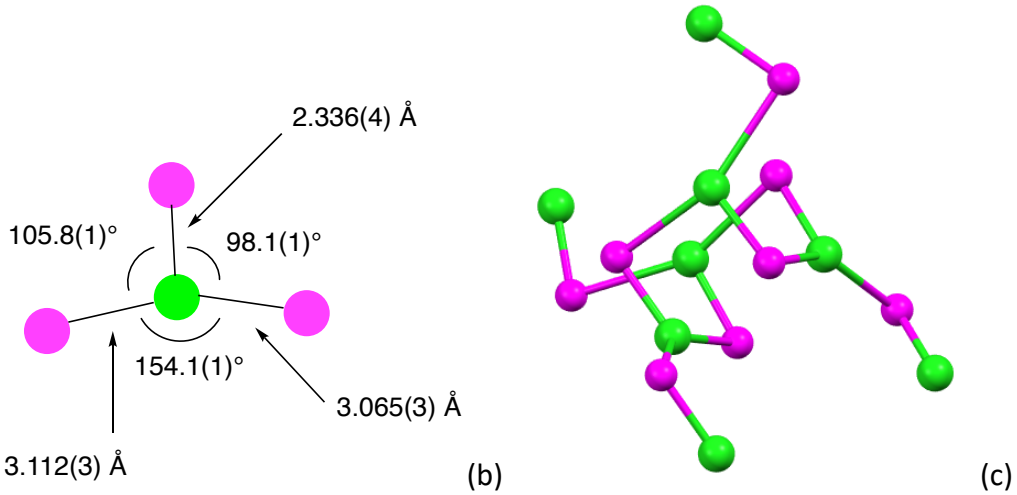


Figure S1 (a) The two complexes in the unit cell of **2**; (b) spatial disposition of mercury centres around chloride; (c) the mercury-chloride 'connectivity' in the core of the four-complex unit.

In addition, there is also a non-covalent interaction between each mercury and a pyridine nitrogen with distances of 2.75(1) Å, 2.748(9) Å, 2.767(9) Å and 2.676(9) Å, with the arrangement in each complex as exemplified in Fig. S2.

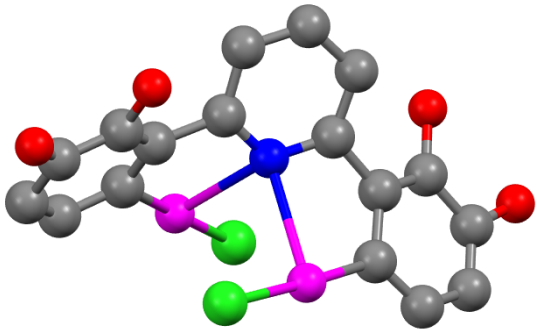


Figure S2 Cut-away of the core of a dimercury complex showing the non-covalent Hg···N interactions.

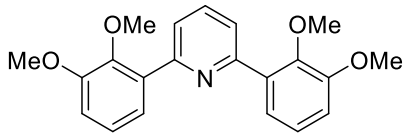
Experimental

^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Jeol ECS400 spectrometer operating at 400 MHz, with chemical shifts referenced to residual non-deuterated $CHCl_3$ signals, or appropriate residual non-deuterated solvent signal. ^{199}Hg/^{199}Hg{^{1}H} NMR spectra was recorded on a Bruker 500 AVANCE II spectrometer operating at 89.6 MHz.

APCI Mass spectroscopy data was collected on a Bruker compact® time of flight mass spectrometer; spectra were internally calibrated using sodium formate calibrant and MALDI-TOF on a Bruker Ultraflex III mass spectrometer using the University of York Chemistry department MS service.

Diffraction data were collected at 110 K on an Oxford Diffraction SuperNova dual-source X-ray diffractometer with CuKα radiation (λ = 1.54184) using a EOS CCD camera. The crystal was cooled with an Oxford Instruments Cryojet. Diffractometer control, data collection, initial unit cell determination, frame integration and unit-cell refinement was carried out with 'Crysalis'.[1] Face-indexed absorption corrections were applied using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.[2] OLEX2[3] was used for overall structure solution, refinement and preparation of computer graphics and publication data. Within OLEX2, the algorithm used for structure solution was ShelXT.[4] Refinement by full-matrix least-squares used the SHELXL-97[5] algorithm within OLEX2.[3] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using a 'riding model' and included in the refinement at calculated positions.

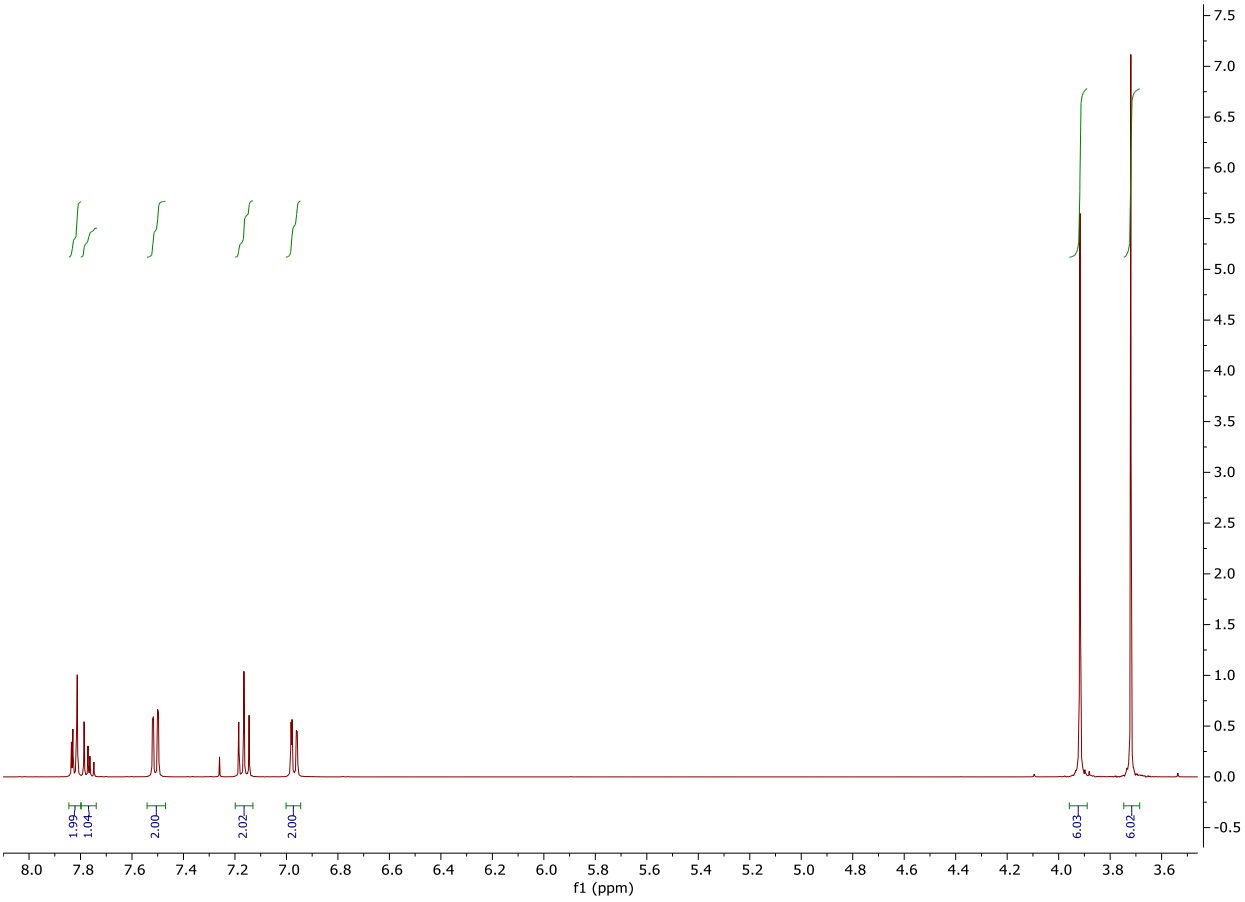
2,6-*Bis*(2,3-dimethoxyphenyl)pyridine



2,6-Dibromopyridine (6.74 g, 28.46 mmol) and 2,3-dimethoxyphenyl boronic acid (15.54 g, 85.37 mmol) were added to a flask containing [$Pd_3(OAc)_6$] (22.0 mg, 0.5 mol%) and K_3PO_4 (18.12 g, 85.37 mmol). Ethylene glycol (200 mL) was added, and the reaction mixture heated to 80 °C for 2 hr with vigorous stirring. The reaction mixture was cooled to room temperature, and the solid precipitate isolated by filtration and washed with water (150 mL), after which it was air dried. The resulting grey solid was dissolved in warm CH_2Cl_2 (~50 mL) and filtered through Celite® and reduced to dryness. The cubic crystalline, off-white residue was recrystallized from the minimum amount of hot ethanol to give the pure product as white broad rectangular crystals. Yield: 8.91 g (89.1%)

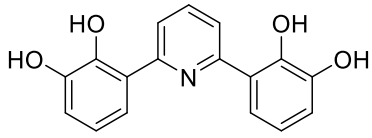
^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: 7.81 (3H, m), 7.51 (2H, dd, $^{3}J_{HH}$ = 7.9 H, $^{4}J_{HH}$ = 1.6 Hz), 7.17 (2H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 8.0 Hz), 6.97 (2H, d, $^{3}J_{HH}$ = 8.2 Hz, $^{4}J_{HH}$ = 1.5 Hz),), 3.92 (6H, s), 3.72 (6H, s).

$^{13}C\{^{1}H\}$ NMR (100.5 MHz, $CDCl_3$) δ^{H} ppm: 155.23, 152.97, 147.20, 136.02, 134.59, 124.18, 123.02, 122.88, 112.46, 60.97, 55.92.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **2,6-*bis*(2,3-dimethoxyphenyl)pyridine**

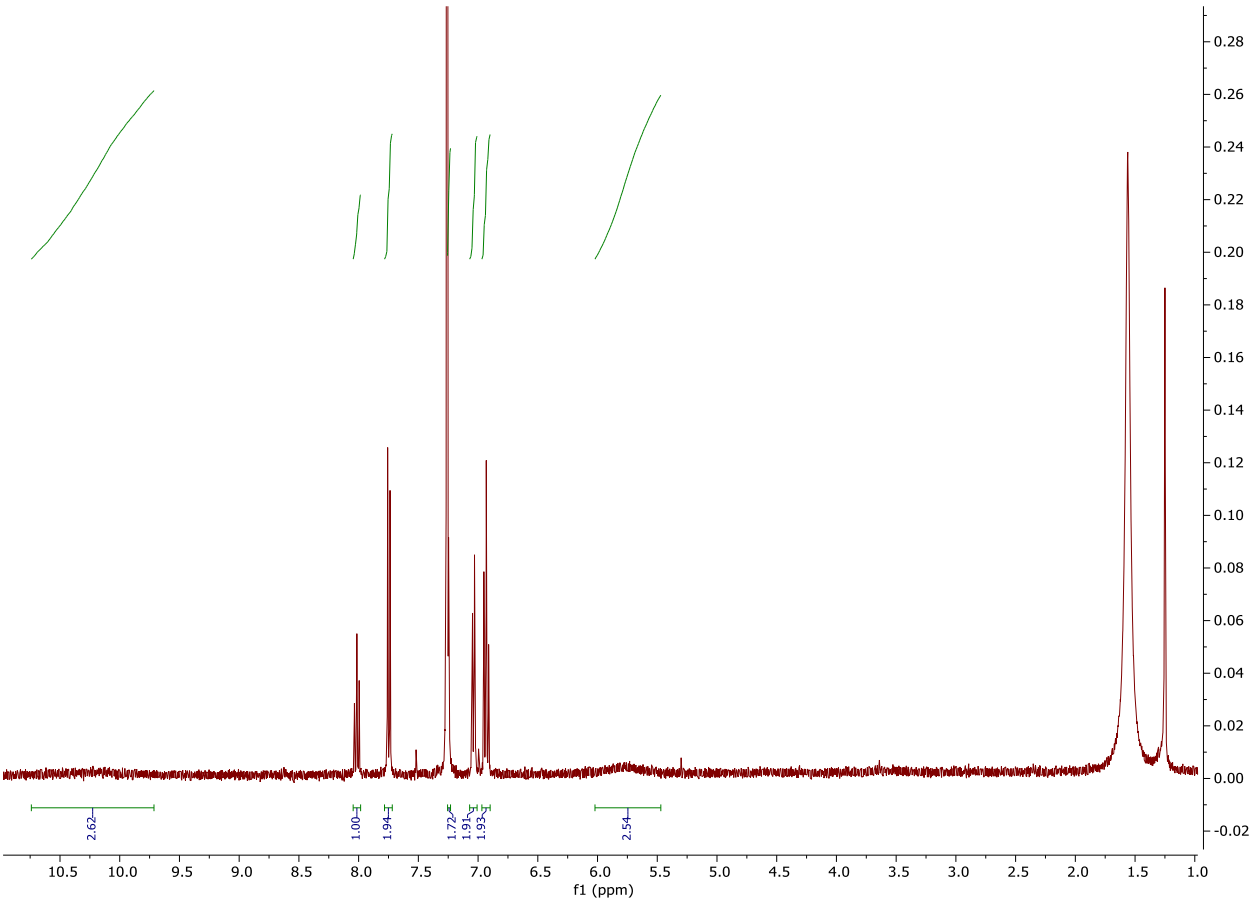
2,6-*Bis*(2,3-dihydroxyphenyl)pyridine



2,6-*Bis*(2,3-dimethoxyphenyl)pyridine (8.50 g, 24.19 mmol) was added to molten pyridinium chloride (38.93 g, 336.88 mmol) at 200 °C and stirred for 16 hr. The still molten mixture was

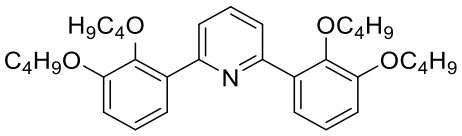
added carefully to distilled water (350 mL) and the resulting mustard yellow precipitate was isolated by filtration, air-dried and was used without further purification. Yield: 6.42 g (89.9%).

^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: ~10.18 (2H, s br), 8.01 (1H, t, $^{3}J_{HH}$ = 8.2 Hz), 7.75 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 7.25 (2H, dd, $^{3}J_{HH}$ ~ 8 Hz, $^{4}J_{HH}$ = 1.4 Hz), 7.04 (2H, dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 1.4 Hz), 6.93 (2H, dd, $^{3}J_{HH}$ = 8.0 Hz, $^{3}J_{HH}$ = 7.9 Hz), 5.78 (2H, s br).



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **2,6-*bis*(2,3-dihydroxyphenyl)pyridine** (compound not very soluble).

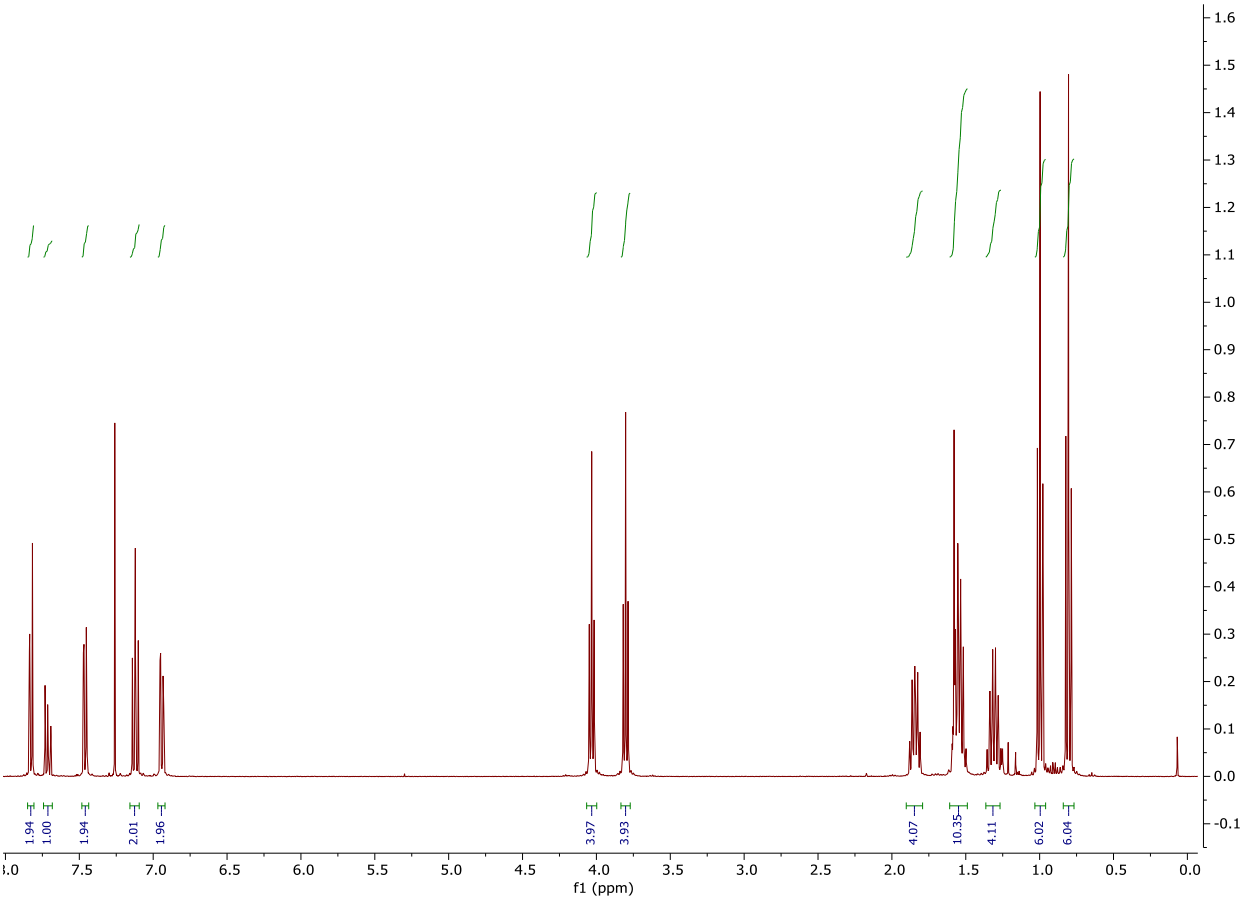
2,6-Bis(2,3-dibutyloxyphenyl)pyridine



2,6-*Bis*(2,3-dihydroxyphenyl)pyridine (1.4083 g, 4.7692 mmol), 1-bromobutane (9.5 mL, 12.12 g, 88.47 mmol), K_2CO_3 (10.23 g, 74.02 mmol) were heated to reflux in 2-butanone (100 mL) for 89 hr. Then the resulting solution was filtered, washed with acetone (50 mL) and reduced to dryness *in vacuo* to give an orange oil. The product was purified *via* column chromatography (silica, 95:5

petroleum ether (40-60 °C):ethyl acetate, R_f = 0.23) to give an orange oil, then on a second column to give a viscous yellow oil. Yield: 1.165 g (52.5%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^H ppm: 7.83 (2H, m), 7.71 (1H, m), 7.46 (2H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.5 Hz), 7.12 (2H, dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.9 Hz), 6.94 (2H, dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 1.6 Hz), 4.03 (4H, t, $^3J_{HH}$ = 6.6 Hz), 3.80 (4H, t, $^3J_{HH}$ = 6.6 Hz), 1.85 (4H, m), 1.55 (8H, m), 1.30 (4H, m), 1.00 (6H, t, $^3J_{HH}$ = 7.3 Hz), 0.88 (6H, t, $^3J_{HH}$ = 7.3 Hz).



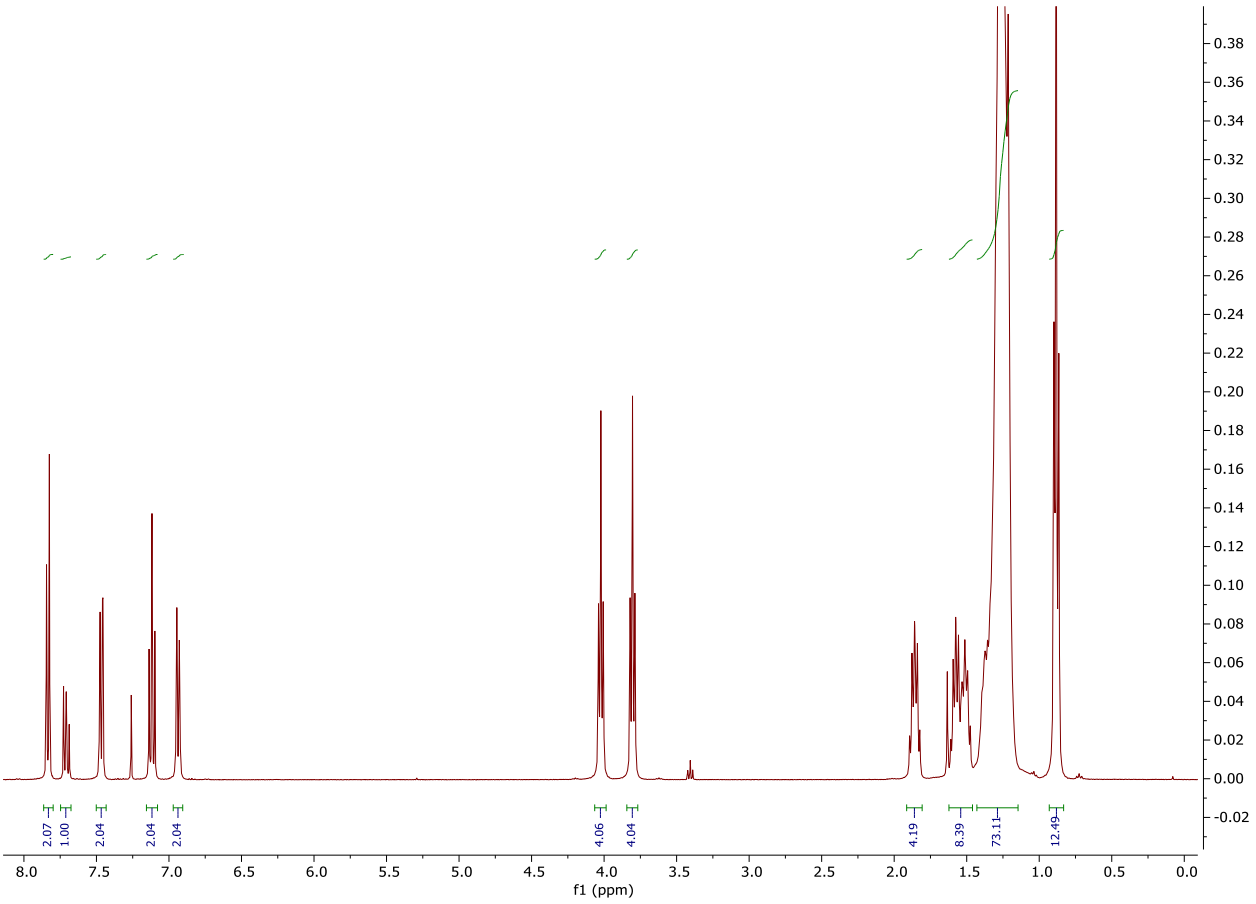
^{1}H NMR spectrum (400 MHz, $CDCl_3$) **2,6-*Bis*(2,3-dibutyloxyphenyl)pyridine** (compound is an oil and contains small amounts of occluded solvent which are readily removed at the next step).

2,6-Bis(2,3-didodecyloxyphenyl)pyridine was similarly prepared in 64% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ^H ppm: 7.83 (2H, d, $^3J_{HH}$ = 7.7 Hz), 7.70 (1H, m), 7.47 (2H, dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.3 Hz), 7.12 (2H, dd, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 8.2 Hz), 6.94 (2H, dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.3

Hz), 4.02 (4H, t, $^{3}J_{HH}$ = 6.5 Hz), 3.80 (4H, t, $^{3}J_{HH}$ = 6.6 Hz), 1.86 (4H, m), 1.59 (4H, m), 1.51 (4H, m), 1.27 (68H, broad m), 0.88 (6H, t, $^{3}J_{HH}$ = 7.2 Hz), 0.88 (6H, t, $^{3}J_{HH}$ = 7.0 Hz).

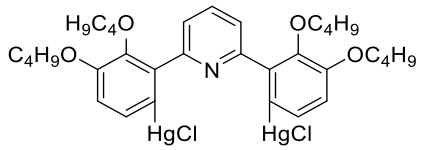
$^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) δ^{C} ppm: 155.45, 152.59, 146.57, 135.28, 135.11, 123.93, 123.34, 122.69, 113.37, 73.77, 68.68, 31.91, 30.19, 29.71, 29.70, 26.69, 29.68, 29.66, 29.63, 29.52, 29.45, 29.36, 29.17, 26.03, 22.67, 14.10.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **2,6-*Bis*(2,3-didodecyloxyphenyl)pyridine** (there is a very small amount of residual and difficult-to-remove 1-bromododecane in the sample, but it is readily removed at the next step).

Mercury Complex 4-4

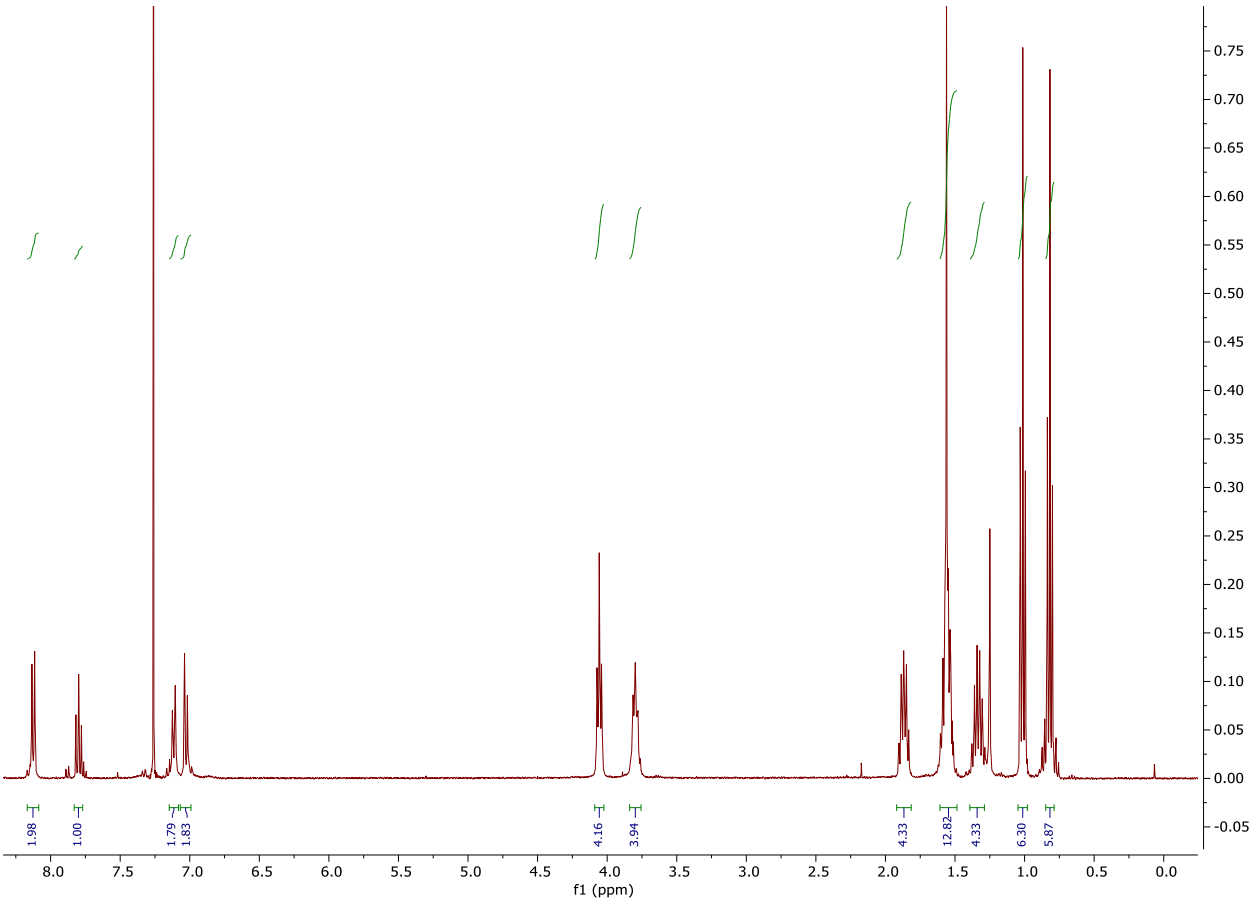
Mercury complexes are toxic and should be handled and disposed of with proper care for personal health and the environment.



2,6-*Bis*(2,3-butyloxyphenyl)pyridine (1.00 g, 1.92 mmol) and $Hg(OAc)_2$ (1.31 g, 4.11 mmol) were added to ethanol (200 mL) and heated to vigorous reflux for 24 hr. The resulting mixture was cooled to 50 °C and a solution of LiCl (0.19 g, 4.48 mmol) in methanol (50 mL) was added and the resulting mixture allowed to stir for 15 min, then distilled water (200 mL) was added and the resulting solution cooled to room temperature and filtered. The white precipitate was washed with copious amounts of water, a small amount of ethanol (<5 mL) and air-dried. Yield = 1.0443 g (55.0%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^H ppm: 8.12 (2H, d, $^3J_{HH}$ = 7.9 Hz), 7.80 (1H, t, $^3J_{HH}$ = 7.9 Hz), 7.11 (2H, d, $^3J_{HH}$ = 8.1 Hz), 7.03 (2H, d, $^3J_{HH}$ = 8.1 Hz), 4.06 (4H, t, $^3J_{HH}$ = 6.5 Hz), .380 (4H, m), 1.87 (4H, m), 1.55 (8H, m), 1.34 (4H, m), 1.01 (6H, t, $^3J_{HH}$ = 7.3 Hz), 0.82 (6H, t, $^3J_{HH}$ = 7.3 Hz).

Elemental Analysis: Found (%): C 40.0 H 4.5, N 1.7; Calc (%) for $C_{33}H_{43}Cl_2Hg_2NO_4$: C 40.1, H 4.4, N 1.4.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **Mercury Complex 4**-4 (complex prepared to grow single crystals and so given the toxicity of the material, purification was not exhaustive).

Mercury Complex 4-12 was similarly prepared in 75% yield.

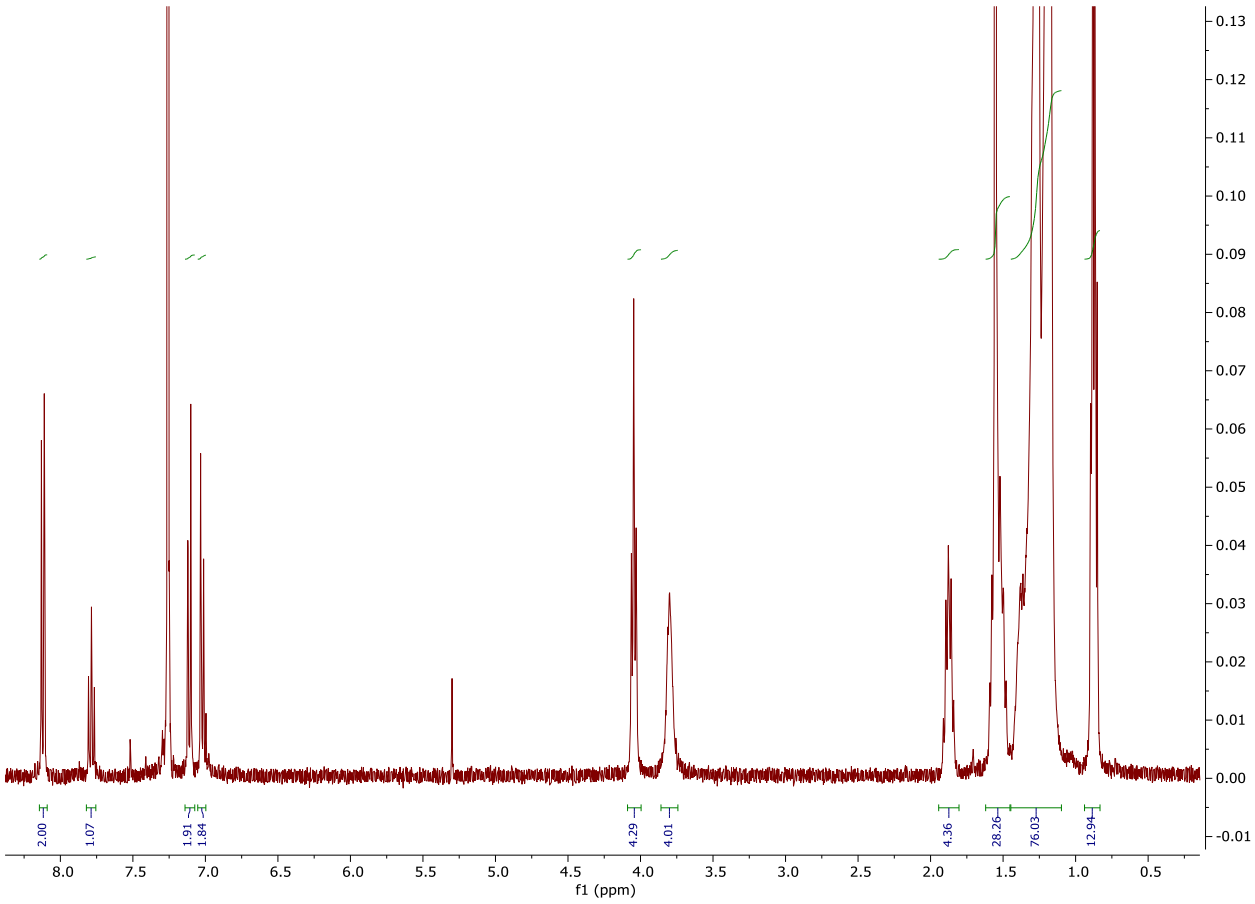
^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: 8.12 (2H, d, $^{3}J_{HH}$ = 7.9 Hz), 7.79 (1H, t, $^{3}J_{HH}$ = 8.1 Hz), 7.11 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 7.01 (2H, m), 4.05 (4H, t, $^{3}J_{HH}$ = 6.3 Hz), 3.90 (4H, broad m), 1.88 (4H, m), 1.55 (4H, m), 1.42-1.18 (72H, broad m), 0.88 (6H, t, $^{3}J_{HH}$ = 6.4 Hz), 0.87 (6H, t, $^{3}J_{HH}$ = 7.3 Hz).

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$) δ^{C} ppm: 157.13, 153.19, 148.04, 137.35, 136.67, 132.38, 125.47, 113.93, 74.41, 68.60, 31.92, 31.90, 30.32, 29.71, 29.67, 29.65, 29.51, 29.43, 29.40, 29.37, 29.34, 26.18, 26.15, 22.68, 14.11.

^{199}Hg NMR (89.6 MHz, $CDCl_3$) δ^{Hg} ppm: -1012 (d, $^{3}J_{HHg}$ = 154.1 Hz)

ACPI MS: m/z = 968.8454 [ligand], 1204.7689 $[M+H]^+$, 1438.7045 $[M+H^+]$, 2334.5929 [Dimer]

Elemental Analysis: Found (%): C 53.5, H 7.4, N 1.2; Calc (%) for $C_{65}H_{107}Cl_2Hg_2NO_4$: C 54.3, H 7.5, N 1.0. Formally impure (further purification was not undertaken), but confirms assignment as dimercurated complex.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **mercury complex 4**-12.

Gold Complex 6-12

$Na[AuCl_4]$ (1.4678 g, 3.6898 mmol) and **4**-12 (4.50 g, 3.1279 mmol) were heated to reflux in 1:1 chloroform:acetonitrile (400 mL) under nitrogen for 24 hr. The reaction mixture was cooled to room temperature and reduced to dryness under reduced pressure, then extracted into acetonitrile (50 mL) and the insoluble solid isolated by filtration. The brown solid was washed sequentially with distilled water (50 mL) and ethanol (25 mL), dried *in vacuo* and crystallised out

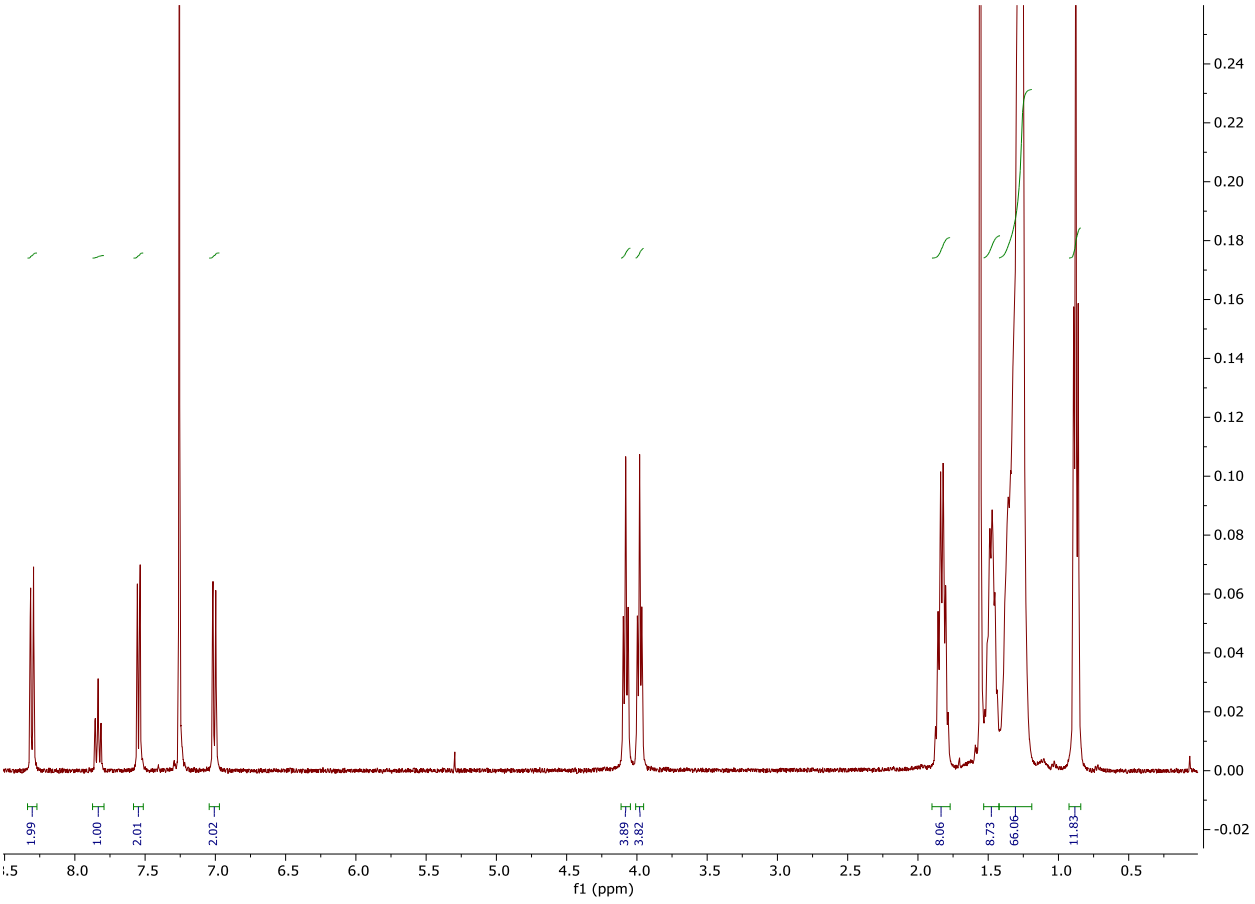
of CH_2Cl_2. The resulting dirty yellow solid was isolated by filtration, washed with ethyl acetate and then redissolved in CH_2Cl_2 and a hot filtrate was done to give a yellow solid on solvent removal, which was recrystallised out of chloroform/hexane to give the titular product as a microcrystalline yellow solid. Yield: 1.041 g (24%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^H ppm: 8.31 (2H, d, $^3J_{HH}$ = 8.3 Hz), 7.84 (1H, t, $^3J_{HH}$ = 8.4 Hz), 7.55 (2H, d, $^3J_{HH}$ = 8.4 Hz), 7.01 (2H, d, $^3J_{HH}$ = 7.9 Hz), 4.08 (4H, t, $^3J_{HH}$ = 6.8 Hz), 3.98 (4H, t, $^3J_{HH}$ = 6.4 Hz), 1.83 (8H, m), 1.54-1.19 (72H, broad m), 0.88 (6H, t, $^3J_{HH}$ = 5.9 Hz), 0.88 (6H, t, $^3J_{HH}$ = 6.5 Hz).

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ^C ppm: 164.45, 160.42, 151.62, 148.31, 142.72, 140.14, 128.31, 122.08, 116.53, 73.40, 68.86, 31.92, 30.37, 29.70, 29.66, 29.65, 29.55, 29.45, 29.37, 26.23, 26.10, 22.69, 14.11.

APCI MS: m/z = 1198.7565 $[M + H]^+$

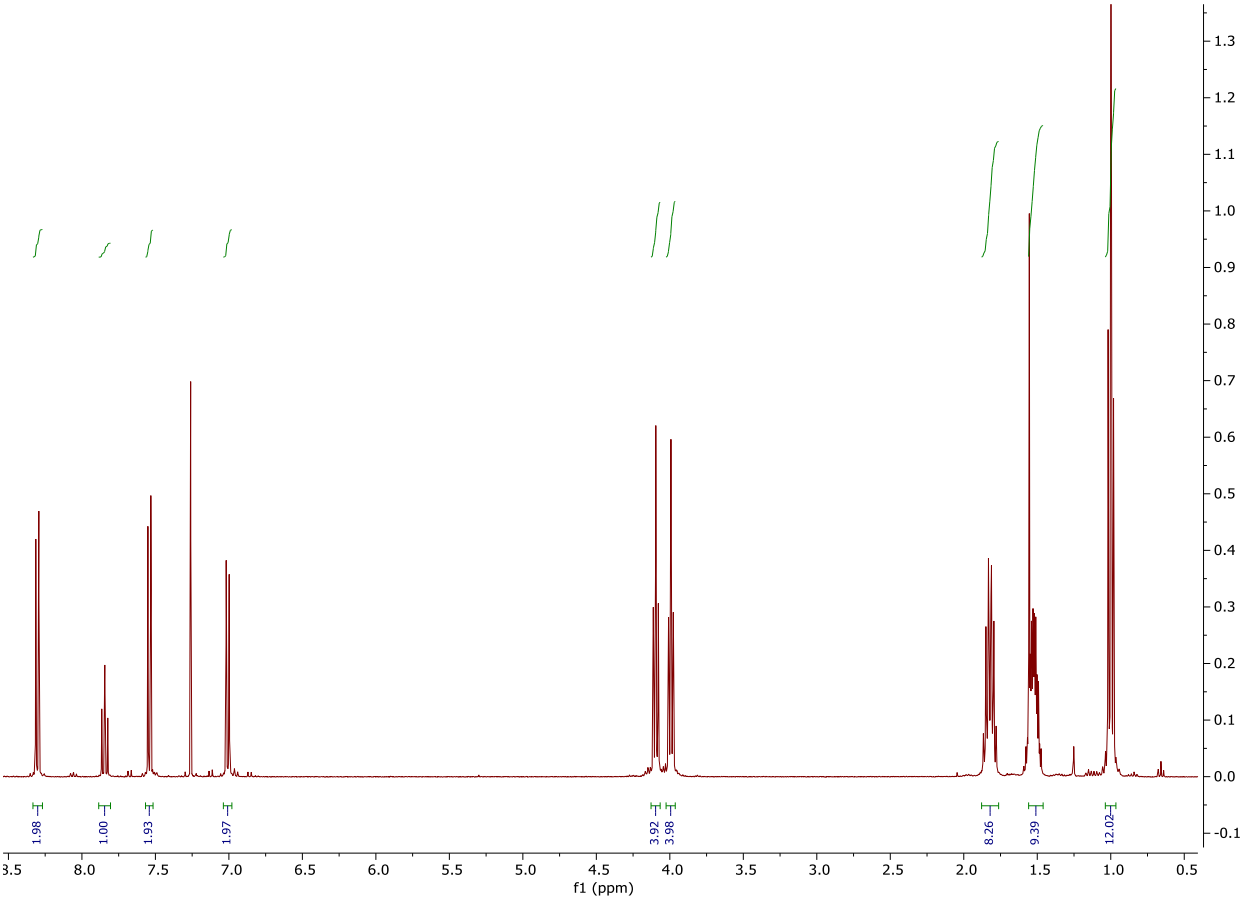
Elemental Analysis: Found (%): C 70.0, H 9.1, N 0.9; Calc (%) for $C_{78}H_{122}AuNO_4$: C 70.2, H 9.2, N 1.1.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **Gold Complex 6**-12

Gold Complex 6-4 was similarly prepared in 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: 8.30 (2H, d, $^{3}J_{HH}$ = 8.2 Hz), 7.84 (1H, t, $^{3}J_{HH}$ = 8.2 Hz), 7.54 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 7.01 (2H, d, $^{3}J_{HH}$ = 8.2 Hz), 4.10 (4H, t, $^{3}J_{HH}$ = 6.9 Hz), 3.99 (4H, t, $^{3}J_{HH}$ = 6.4 Hz), 1.82 (8H, m), 1.00 (6H, t, $^{3}J_{HH}$ = 7.5 Hz), 1.00 (6H, t, $^{3}J_{HH}$ = 7.3 Hz).



^{1}H NMR (400 MHz, $CDCl_3$) **Gold Complex 6**-4 (complex prepared for growing single crystals therefore purification not exhaustive).

Palladium Complex 5-12

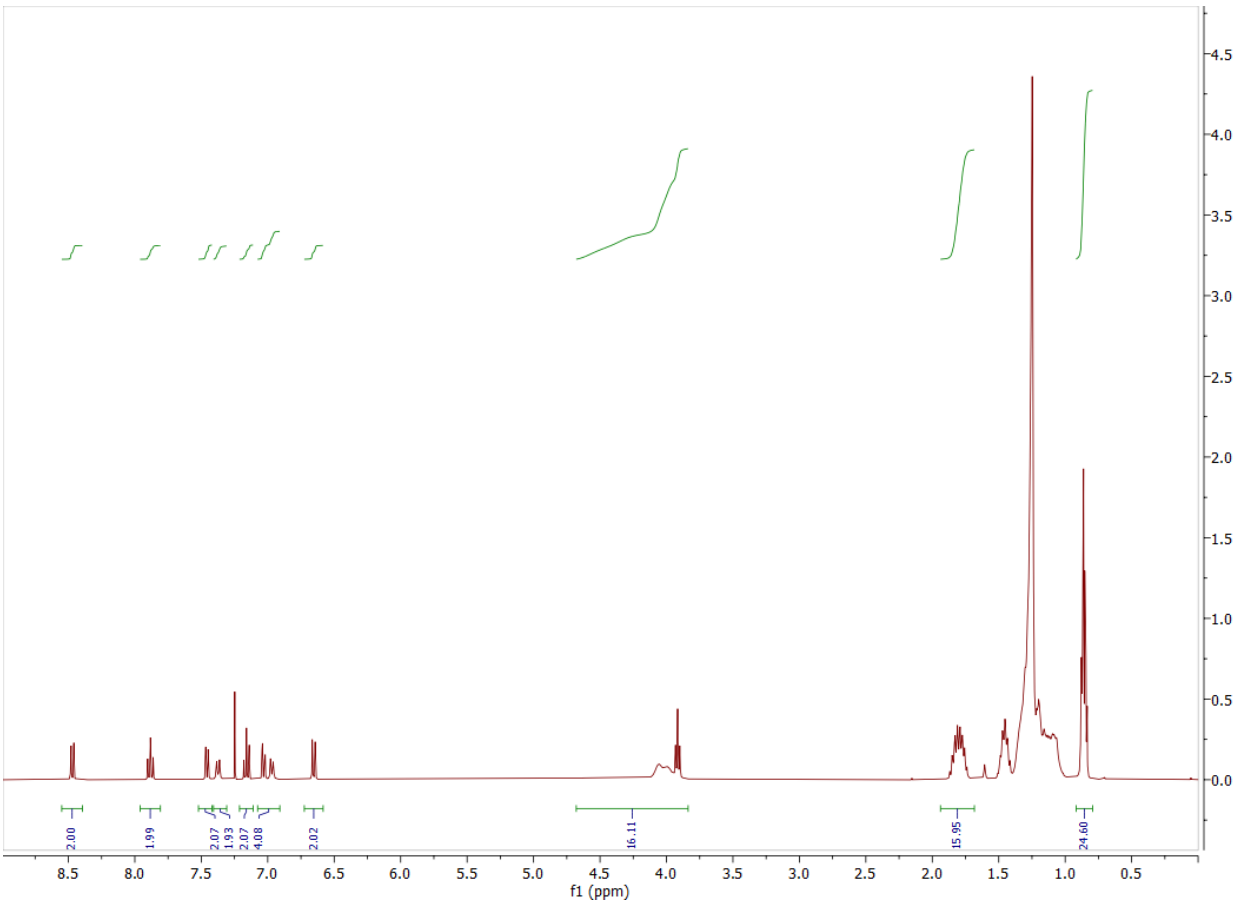
2,6-*Bis*(2,3-didodecylphenyl)pyridine (0.5004 g, 0.5166 mmol) and $K_2[PdCl_4]$ (0.1125 g, 0.3446 mmol) were heated to reflux in ethanol (50 mL) for 24 hr. The solution was cooled to room temperature and the resulting yellow precipitate was isolated *via* filtration. The solid was washed by distilled water (15 mL), then ethanol (2.5 mL) and air dried. A second crop was isolated *via* the same method. The combined product was purified by column chromatography (silica, 95:5 petroleum ether (40 – 60 °C):ethyl acetate, R_f = 0.03, then 7:3 CH_2Cl_2: petroleum ether (40 – 60 °C), R_f = 0.47) to give a yellow oil, which solidified on standing to give a golden glassy solid. Yield: 0.1188 g (31%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^H ppm: 8.48 (2H, d, $^3J_{HH}$ = 8.3 Hz), 7.89 (2H, t, $^3J_{HH}$ = 8.6 Hz), 7.46 (2H, t, $^3J_{HH}$ = 7.6 Hz), 7.38 (2H, d, $^3J_{HH}$ = 8.6 Hz), 7.16 (2H, dd, $^3J_{HH}$ = 7.4 Hz, $^3J_{HH}$ = 7.4 Hz), 7.04 (2H, d, $^3J_{HH}$ = 7.4 Hz), 6.97 (2H,d, $^3J_{HH}$ = 7.4 Hz), 6.66 (2H, d, $^3J_{HH}$ = 8.7 Hz), 4.07 (2H, br s), 4.00 (2H, br s), 3.92 (2H, t, $^3J_{HH}$ = 6.3 Hz), 1.80 (16H, m), 1.46 (16H, m), 1.4 – 1.0 (136H, br m), 0.86 (24H, m).

Note that integration of the area between 4.6 > δ > 3.8 gives an integration of 16 hydrogens, consistent with the fluxional nature of the unmetallated ring.

^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ^C ppm: 164.11, 155.28, 152.47, 150.07, 146.30, 143.44, 139.37, 137.70, 136.57, 131.62, 131.54, 126.06, 124.12, 122.27, 121.90, 117.24, 114.61, 78.97, 77.33, 73.24, 70.40, 69.10, 32.02, 31.99, 30.50, 29.81, 29.79, 29.75, 29.69, 29.61, 29.54, 29.50, 29.47, 29.43, 29.29, 26.30, 26.22, 26.18, 25.57, 22.79, 14.21.

MALDI-TOF MS: m/z = 2180.435632 $[M + H]^+$



^{1}H NMR spectrum (400 MHz, $CDCl_3$) **palladium complex 5**-12

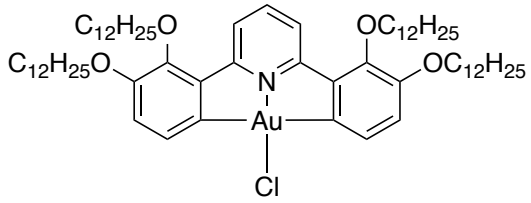
Gold Complex 6-12 **from Palladium Complex 5**-12

5-12 (0.0995, 0.0448 mmol) and $Na[AuCl_4]$ (0.0365 g, 0.0918 mmol) were heated to reflux in 1:1 chloroform:acetonitrile (50 mL) for 24 hr under a dinitrogen atmosphere. The solution was cooled to room temperature and reduced to dryness under reduced pressure. The off-white to purple solid was extracted into acetonitrile (15 mL) and the insoluble solid isolated *via* filtration, washed with acetonitrile (10 mL) and air dried. The purple solid was dissolved in CH_2Cl_2 and filtered through Celite® to remove elemental gold and the resulting yellow solution reduced to dryness. The remaining mustard yellow solid was recrystallised out of CH_2Cl_2/hexane to give a pale yellow solid. Yield: 0.0467 g (48%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: 8.31 (2H, d, $^{3}J_{HH}$ = 8.1 Hz), 7.84 (1H, t, $^{3}J_{HH}$ = 8.5 Hz), 7.55 (2H, d, $^{3}J_{HH}$ = 7.9 Hz), 7.01 (2H, d, $^{3}J_{HH}$ = 9.1 Hz), 4.08 (4H, t, $^{3}J_{HH}$ = 7.0 Hz), 3.98 (4H, t, $^{3}J_{HH}$ = 6.8 Hz), 1.83 (8H, m), 1.47 (8H, m), 1.4-1.1 (68H, br m), 0.88 (6H, t, $^{3}J_{HH}$ = 6.9 Hz), 0.88 (6H, t, $^{3}J_{HH}$ = 6.9 Hz).

APCI MS: m/z = 1198.7599 $[M + H]^{+}$

Gold Complex 6-12 **(Direct Auration from Ligand 1-**12**)**



$Na[AuCl_4]$ (0.1024 g, 0.2574 mmol), NaOBz (0.0447 g, 0.3102 mml) and $[Cp^*RhCl_2]_2$ (4.14 mg, 6.70 µmol) were added to a solution of 2,6-*bis*(2,3-didodecylphenyl)pyridine (0.2951 g, 0.3047 mmol) in ethyl acetate (20 mL) and heated at 60 °C for 19 hr. The resulting cloudy straw-coloured solution was cooled to room temperature and the light brown precipitate isolated *via* filtration and washed with distilled water (20 mL), ethanol (10 mL) and air dried. The solid was dissolved in chloroform and filtered through a Celite® plug to remove elemental gold and the resulting yellow solution reduced to dryness to give a pale yellow microcrystalline solid. Yield: 0.0316 g (11%)

^{1}H NMR (400 MHz, $CDCl_3$) δ^{H} ppm: 8.31 (2H, d, $^{3}J_{HH}$ = 8.2 Hz), 7.84 (1H, t, $^{3}J_{HH}$ = 8.4 Hz), 7.55 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 7.01 (2H, d, $^{3}J_{HH}$ = 8.0 Hz), 4.08 (4H, t, $^{3}J_{HH}$ = 6.9 Hz), 3.98 (4H, t, $^{3}J_{HH}$ = 6.4 Hz), 1.83 (8H, m), 1.47 (8H, m), 1.4-1.1 (68H, br m), 0.88 (6H, t, $^{3}J_{HH}$ = 6.8 Hz), 0.88 (6H, t, $^{3}J_{HH}$ = 6.8 Hz).

APCI MS: m/z = 1198.7627 $[M + H]^{+}$