Supporting Information for

Comparative Study of the Antiproliferative Activity of Heterometallic Carbene Gold(I)-Platinum(II) and Gold(I)-Palladium(II) Complexes in Cancer Cell Lines

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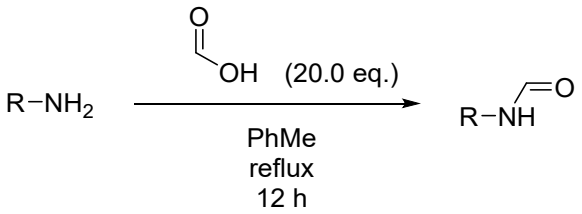
1 General Reamrks

All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Deu-terated solvents were purchased from Euriso-Top. Anhydrous solvents were dried by an MB SPS-800 with the aid of drying columns. Preparation of air- and moisture-sensitive materials was carried out in flame-dried flasks under an argon atmosphere employing standard Schlenk techniques. Thin layer chromotography (TLC) was per-formed using Polygram® precoated plastic sheets SIL G/UV254 (SiO_2, 0.20 mm thickness) from Macherey-Nagel. Column chromatography was performed using silica gel (40.0-63.0 nm particle size) from Macherey-Nagel. All cell lines were purchased from Sigma-Aldrich. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers. Chemical shifts (in ppm) were referenced to residual solvent protons. Signal multiplicity was determined as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), sex (sextet), sept (septet), m (multiplet), bs (broad signal), p (pseudo multiplicity). ^{13}C assignment was achieved via DEPT135 spectra. Mass spectra were recorded on a Vacuum Generators ZAB-2F, Finnigan MAT TSQ 700 or JEOL JMS-700 spectrometer. GC-MS spectra were recorded on a HP Agilent 5890 Series II Plus with a HP 5972 mass analysator. FT-IR spectra (in cm^{-1}) were recorded on a Bruker Vector 22 FT-IR. Crystal structure analyses were recorded on Bruker SmartCCD or Bruker APEX diffractometers.

2 Synthesis of Compounds

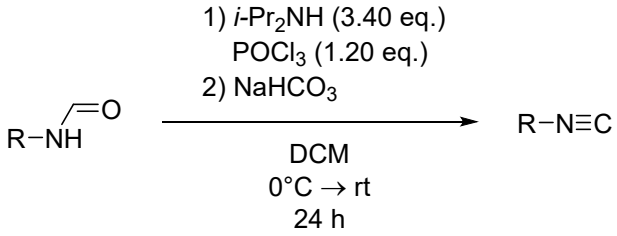
2.1 General Procedures

2.1.1 General Procedure for the Synthesis of Formamides (GP1)



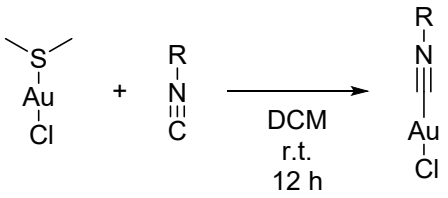
According to literature[1], in a round bottom flask, the amine (1.00 eq.) was dissolved in reagent grade toluene. Afterwards formic acid (20.0 eq.) was added to the solution, which was then refluxed with a Dean-Stark-Apparatus overnight. Removal of all volatiles *in vacuo* yielded the title compound which was used without further purification.

2.1.2 General procedure for the Synthesis of Isonitriles (GP2)



According to literature[1], in a round bottom flask, the formamide (1.00 eq.) and diisopropylamine (3.40 eq.) were dissolved in reagent grade DCM. The solution was cooled to 0 °C, then phosphoryl chloride (1.20 eq.) was added dropwise. The mixture was stirred for 3 hours for 0°C, then it was stirred over night at room temperature. Afterwards an aqueous solution of sodium hydrogen carbonate was added, and the resulting biphasic solution was stirred additional 24 hours at room temperature. The organic layer was separated, the aqueous layer was extracted with DCM. The combined organic layers were dried over sodium sulphate. Removal of all volatiles yielded title compound.

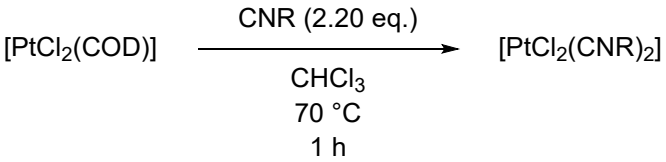
2.1.3 General Procedure for the Synthesis of Isonitrile-Gold(I)-Complexes (GP3)



R = aromatic, aliphatic

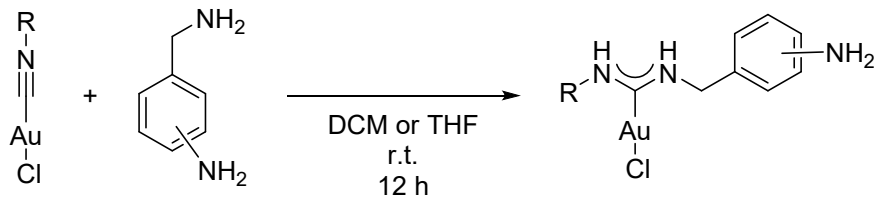
According to literature[1], in a round bottom flask, chloro(dimethyl sulfide)gold(I) (1.00 eq.) was dissolved in reagent grade DCM. Afterwards the corresponding isonitrile (1.00 eq.) was added to the solution. The reaction mixture was stirred at room temperature upon completion. Purification of the crude product was achieved by recrystallization from DCM/*n*-pentane.

2.1.4 General Procedure for the Synthesis of Isonitrile-Platinum(II)-Complexes (GP4)



Based on a modification of a literature procedure[2], in a round bottom flask, $[PtCl_2(COD)]$ (1.00 eq.) and the corresponding isonitrile (2.20 eq.) were dissolved in reagent grade chloroform. The reaction mixture was refluxed for one hour. After cooling to room temperature, the reaction volume was narrowed down to half of the original volume. Afterwards the reaction product was crystallized by the addition of *n*-pentane and dried to furnish the desired product.

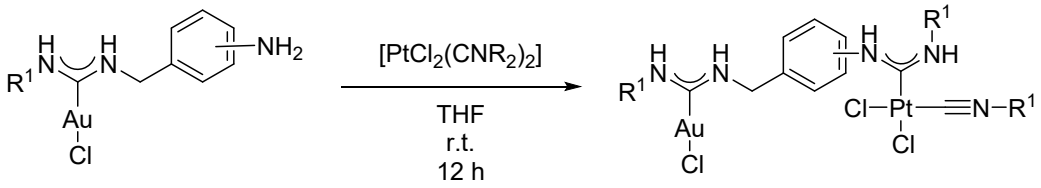
2.1.5 General Procedure for the Synthesis of acyclic diaminocarbene gold(I)-complexes (GP5)



R = aromatic, aliphatic

According to literature[1], the isonitrile gold (I) complex (1.00 eq.) and the corresponding aminobenzylamine (1.00 eq.) were dissolved in reagent grade DCM and stirred at room temperature for 12 hours. Purification of the crude product was achieved by flash column chromatography (DCM, DCM:MeOH = 99:1).

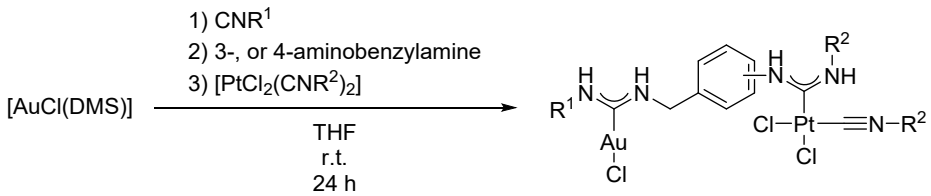
2.1.6 General Procedure for the Synthesis of heterodinuclear bis(acyclic diaminocarbene) Gold(I)- and Platinum(II)- Complexes (GP6)



R = aromatic, aliphatic
R' = aromatic

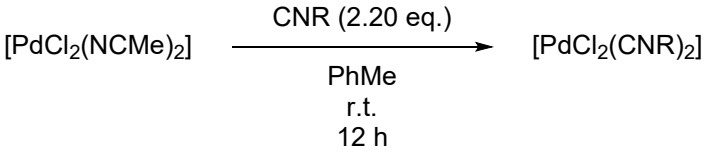
The acyclic diaminocarbene gold(I) complex (1.00 eq.) and the isonitrile platinum(II) complex (1.00 eq.) were dissolved in reagent grade THF and stirred at 40 °C for 12 hours. Afterwards the product was crystallized by the addition of *n*-pentane to the crude reaction mixture.

2.1.7 General Procedure for the One-Pot Synthesis of heterodinuclear Gold(I)- and Palladium(II)-Complexes (GP7)



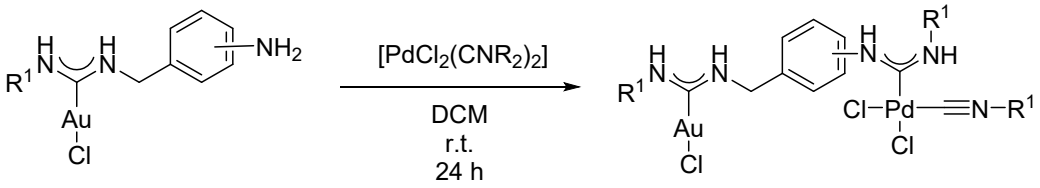
In a round bottom flask, chloro(dimethyl sulfide)gold(I) (1.00 eq.) and the corresponding isonitrile (1.00 eq.) were dissolved in reagent grade THF. The reaction mixture was stirred for 12 hours at room temperature. Afterwards the corresponding isonitrile palladium(II) complex (1.00 eq.) was added. After stirring the solution for another 12 hours at 40 °C the reaction was filtered. Addition of *n*-pentane to the filtrate furnished the desired product by crystallization.

2.1.8 General Procedure for the Synthesis of Isonitrile-Palladium(II)-Complexes (GP8)



According to literature[1], in a round bottom flask, bis(acetonitrile)palladium chloride (1.00 eq.) was dissolved in reagent grade toluene. Afterwards the corresponding isonitrile (2.00 eq.) was added to the solution. The reaction mixture was stirred at room temperature for 12 hours. The solvent was removed *in vacuo* and the residue was washed three times with *n*-pentane to obtain title compound.

2.1.9 General Procedure for the Synthesis of heterodinuclear bis(acyclic diaminocarbene) Gold(I)- and Palladium(II)- Complexes (GP9)

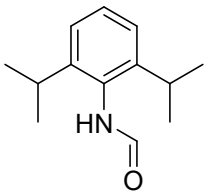


R = aromatic, aliphatic
R' = aromatic

According to literature[1], the acyclic diaminocarbene gold(I) complex (1.00 eq.) and the isonitrile palladium(II) complex (1.00 eq.) were dissolved in reagent grade DCM and stirred at room temperature upon completion. Purification of the crude product was achieved recrystallization from DCM/Et_2O.

2.2 Synthetic Procedures

2.2.1 Synthesis of *N*-(2,6-diisopropylphenyl)formamide

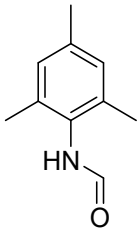


According to **GP1**, the reaction was carried out with 2,6-diisopropylaniline (5.00 g, 5.32 mL, 28.2 mmol, 1.00 eq.) and formic acid (26.0 g, 21.3 mL, 740 mmol, 20. eq.) in toluene (185 mL) to obtain title compound as a colorless solid (5.51 g, 24.4 mmol, 86 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K) δ [ppm] = 8.48 (s, 1H, Rotamers A and B, -NH(CHO)), 8.05 (s, 1H, Rotamer B, -CHO), 8.02 (d, J = 5.1 Hz, 1H, Rotamer A, -CHO), 7.39 – 7.27 (m, 1H, Rotamers A and B, $C_{Ar}H$), 7.21 (d, *J* = 3.1 Hz, 2H, Rotamer A, 2x$C_{Ar}H$), 7.19 (d, 3.1 Hz, 2H, Rotamer B, 2x$C_{Ar}H$), 3.22 (hept, *J* = 6.9 Hz, 2H, Rotamer A, 2xCH), 3.11 (hept, *J* = 6.9 Hz, 2H, Rotamer B, 2xCH), 1.22 (d, *J* = 6.9 Hz, 12H, Rotamers A and B, 4x-CH_3).

2.2.2 Synthesis of *N*-mesitylformamide

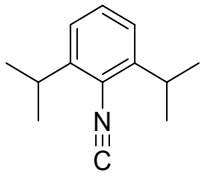


According to **GP1**, the reaction was carried out with 2,4,6-trimethylaniline (5.00 g, 5.19 mL, 37.0 mmol, 1.00 eq.) and formic acid (34.0 g, 27.9 mL, 740 mmol, 20. eq.) in toluene (185 mL) to obtain title compound as a colorless solid (5.34 g, 32.5 mmol, 88 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K) δ [ppm] = 8.41 (s, 1H, Rotamers A and B, -NH(CHO)), 8.09 – 8.02 (m, 1H, Rotamers A and B, -CHO), 8.04 (s, 1H, Rotamer A, $C_{Ar}H$), 6.94 (s, 2H, Rotamer A, 2x$C_{Ar}H$), 6.92 (s, 2H, Rotamer B, 2x$C_{Ar}H$), 2.29 (s, 3H, Rotamer A, -CH_3), 2.27 (s, 3H, Rotamer B, -CH_3), 2.26 (s, 6H, Rotamer A, 2x-CH_3), 2.22 (s, 6H, Rotamer B, 2x-CH_3).

2.2.3 Synthesis of (2,6-Diisopropylphenyl)isonitrile

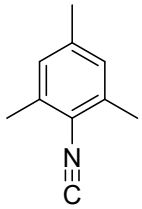


According to **GP2**, the reaction was carried out with *N*-(2,6-diisopropylphenylformamide (5.50 g, 26.8 mmol, 1.00 eq.), diisopropylamine (9.22 g, 12.9 mL, 91.9 mmol, 3.40 eq.) and phosphoryl chloride (4.93 g, 2.93 mL, 32.2 mmol, 1.20 eq.) to obtain title compound as a yellow liquid (4.90 g, 26.0 mmol, 97 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K) δ [ppm] = 7.33 (t, *J* = 7.2 Hz, 1H, $C_{Ar}\underline{H}$), 7.17 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 3.39 (hept, *J* = 6.9 Hz, 2H, 2x$C\underline{H}$), 1.29 (d, *J* = 6.9 Hz, 12H, 4x-$C\underline{H_3}$).

2.2.4 Synthesis of Mesitylisonitrile

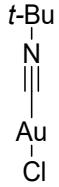


According to **GP2**, the reaction was carried out with *N*-mesitylformamide (5.00 g, 30.6 mmol, 1.00 eq.), diisopropylamine (9.30 g, 13.0 mL, 91.9 mmol, 3.40 eq.) and phosphoryl chloride (5.64 g, 3.44 mL, 36.8 mmol, 1.20 eq.) to obtain title compound as a yellow liquid (3.92 g, 27.0 mmol, 88 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K) δ [ppm] = 6.92 (s, 2H, 2x$C_{Ar}\underline{H}$), 2.40 (s, 6H, 2x-$C\underline{H_3}$), 2.31 (s, 3H, -$C\underline{H_3}$).

2.2.5 Synthesis of *tert*-Butylisonitrile gold(I) chloride

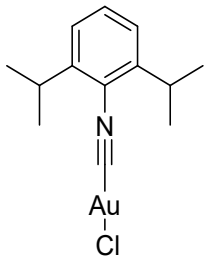


According to **GP3** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (150 mg, 509 µmol, 1.00 eq.) and tert-butyl isocyanide (42.3 mg, 509 µmol, 1.00 eq.) to obtain title compound as a colorless solid (158 mg, 501 µmol, 98 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, CD_2Cl_2, 295 K): δ [ppm] = 1.56 (t, J = 2.21 Hz, 9H, 3x-CH_3).

2.2.6 Synthesis of (2,6-Diisopropylphenyl)isonitrile gold(I) chloride

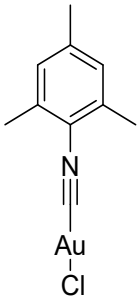


According to **GP3** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (150 mg, 509 µmol, 1.00 eq.) and 2,6-diisopropylphenyl isocyanide (95.4 mg, 509 µmol, 1.00 eq.) to obtain title compound as a colorless solid (203 mg, 484 µmol, 95 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, CD_2Cl_2, 295 K): δ [ppm] = 7.50 (t, J=7.86 Hz, 1H, $C_{Ar}\underline{H}$), 7.27 (d, J=7.82 Hz, 2H, 2x$C_{Ar}\underline{H}$), 3.25 (sept., J= 6.78 Hz, 2H, 2x$C\underline{H}$), 1.29 (d, J=6.85 Hz, 12H, 4x-CH_3).

2.2.7 Synthesis of Mesitylisonitrile gold(I) chloride

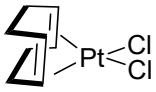


According to **GP3** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (150 mg, 509 µmol, 1.00 eq.) and mesityl isocyanide (81.1 mg, 509 µmol, 1.00 eq.) to obtain title compound as a colorless solid (190 mg, 503 µmol, 99 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, CD_2Cl_2, 295 K): δ [ppm] = 7.00 (s, 2H, 2x$C_{Ar}\underline{H}$), 2.39 (s, 6H, 2x-$C\underline{H_3}$), 2.33 (s, 3H, -$C\underline{H_3}$).

2.2.8 Synthesis of $PtCl_2$(COD)



The reaction was carried out according to a literature-known procedure[3]. In a round bottom flask, potassium tetrachloroplatinate (1.00 g, 2.41 mmol, 1.00 eq.) and 1,5-cyclopentadiene (1.04 g, 9.64 mmol, 4.00 eq.) was dissolved in a mixture of equal amounts of water and acetic acid (25 mL each). The reaction mixture was refluxed over night and was subsequently cooled down to room temperature. The formed precipitate was collected by filtration and washed with water and diethyl ether. The solid was dried in vacuo to furnish the reaction product as colorless crystals (819 mg, 2.19 mmol, 91 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ = 5.89 – 5.43 (m, 4H, 4x$C\underline{H}$), 2.93 – 2.50 (m, 4H, 2x$C\underline{H_2}$), 2.38 – 2.13 (m, 4H, 2x$C\underline{H_2}$);

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ 100.94 (d, t, $J_{Pt\text{-}C}$ = 76.3 Hz, 4x$\underline{C}H$), 31.28 (t, 4x-$\underline{C}H_2$-);

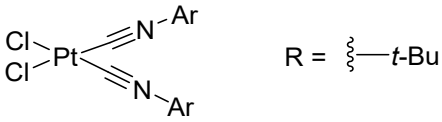
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ = -3329.76;

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3023 (w), 3009 (m), 2963 (w), 2943 (w), 2895 (w), 2838 (w), 2037 (w), 1916 (w), 1476 (w), 1451 (s), 1425 (m), 1340 (m), 1311 (s), 1227 (w), 1180 (w), 1089 (m), 1029 (s), 1010 (w), 911 (w), 872 (m), 833 (m), 811 (s), 781 (m), 695 (m);

HR-MS (EI (+)): $C_8H_{12}{}^{35}Cl_2{}^{194}Pt$ $[M]^+$ calcd. 371.99427, found 372.00362; $C_8H_{12}{}^{35}Cl^{37}Cl^{194}Pt$ $[M]^+$ calcd. 373.99132, found 374.00128; $C_8H_{12}{}^{37}Cl_2{}^{194}Pt$ $[M]^+$ calcd. 375.98837, found 376.00275; $C_8H_{12}{}^{35}Cl_2{}^{195}Pt$ $[M]^+$ calcd. 372.99638, found 372.00210; $C_8H_{12}{}^{35}Cl^{37}Cl^{195}Pt$ $[M]^+$ calcd. 374.99343, found 375.00101; $C_8H_{12}{}^{37}Cl_2{}^{195}Pt$ $[M]^+$ calcd. 376.99048, found 377.00673; $C_8H_{12}{}^{35}Cl_2{}^{196}Pt$ $[M]^+$ calcd. 373.99654, found 374.00128; $C_8H_{12}{}^{35}Cl^{37}Cl^{196}Pt$ $[M]^+$ calcd. 375.99359, found 376.00275; $C_8H_{12}{}^{37}Cl_2{}^{196}Pt$ $[M]^+$ calcd. 377.99064, found 377.99181; $C_8H_{12}{}^{35}Cl_2{}^{198}Pt$ $[M]^+$ calcd. 375.99948, found 376.00275; $C_8H_{12}{}^{35}Cl^{37}Cl^{198}Pt$ $[M]^+$ calcd. 377.99653, found 377.99181;

EA calcd for $C_8H_{12}Cl_2Pt$: C: 25.68 %, H: 3.23 %, found. C: 24.92 %, H: 3.24 %.

2.2.9 Synthesis of Bis(tert-butylisonitrile)platinum(II) chloride (1a)



According to **GP4** the reaction was carried out with $PtCl_2(cod)$ (250 mg, 668 µmol, 1.00 eq.) and *tert*-butyl isocyanide (213 mg, 1.47 mmol, 2.20 eq.). Title compound was obtained as a colorless solid (323 mg, 580 µmol, 87 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 1.56 (s, 18H, 6x-C$\underline{H}_3$).

^{13}C NMR (126 MHz, CD_2Cl_2, 295 K) δ [ppm] =59.95 (t, J = 4.5 Hz, 2C, 2x$\underline{C}_{Isonitrile}$), 45.82 (s, 2C, 2x-$\underline{C}(CH_3)_2$, 29.74 (q, 6C, 6x-$CH_3$).

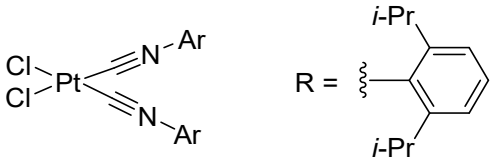
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3825.77 (p, J = 105.9 Hz).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2981 (w), 2936 (w), 2875 (w), 2256 (m), 2228 (s), 2042 (w), 1464 (w), 1400 (m), 1372 (m), 1236 (m), 1191 (s), 1046 (w), 934 (w), 859 (w), 747 (w);

HR-MS (ESI (+)): $C_{10}H_{18}{}^{35}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 453.0371, found 453.0373; $C_{10}H_{18}{}^{35}Cl^{37}Cl^{194}PtNa$ $[M+Na]^+$ calcd. 455.0342, found 455.0395; $C_{10}H_{18}{}^{37}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 457.0312, found 457.0367; $C_{10}H_{18}{}^{35}Cl_2{}^{195}PtNa$ $[M+Na]^+$ calcd. 454.0392, found 454.0394; $C_{10}H_{18}{}^{35}Cl^{37}Cl^{195}PtNa$ $[M+Na]^+$ calcd. 456.0363, found 456.0365; $C_{10}H_{18}{}^{35}Cl_2{}^{196}PtNa$ $[M+Na]^+$ calcd. 455.0394, found 455.0396; $C_{10}H_{18}{}^{35}Cl^{37}Cl^{196}PtNa$ $[M+Na]^+$ calcd. 457.0365, found 457.0367; $C_{10}H_{18}{}^{35}Cl_2{}^{198}PtNa$ $[M+Na]^+$ calcd. 457.0423, found 457.0367;

EA calcd. for $C_{10}H_{18}Cl_2N_2Pt$: C: 27.79, H: 4.20, N: 6.48; found C: 28.06, H: 4.37, N: 6.50.

2.2.10 Synthesis of Bis((2,6-diisopropylphenyl)isonitrile)platinum(II) chloride (1b)



According to **GP4** the reaction was carried out with $PtCl_2$(cod) (250 mg, 668 µmol, 1.00 eq.) and 2,6-diisopropylphenyl isocyanide (275 mg, 1.47 mmol, 2.20 eq.). Title compound was obtained as a colorless solid (364 mg, 568 µmol, 85 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.50 – 7.44 (m, 2H, 2xC_{Ar}H), 7.27 (d, *J* = 7.9 Hz, 4H, 4xC_{Ar}H), 3.34 (hept, *J* = 6.8 Hz, 4H, 4xCH), 1.30 (d, *J* = 6.9 Hz, 24H, 8x-CH_3);

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 146.70 (s, 2C, 2xC_{Ar}), 131.72 (s, 4C, 4xC_{Ar}), 124.33 (d, 6C, 6xC_{Ar}H), 30.39 (d, 4C, 4xCH), 22.84 (q, 8C, 8x-CH_3). $C_{isonitrile}$ not visible;

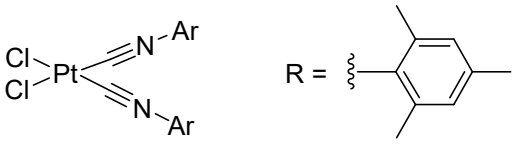
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3754.80 (p, *J* = 121.6 Hz);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2967 (m), 2929 (w), 2870 (w), 2223 (m), 2193 (s), 1588 (w), 1466 (m), 1385 (m), 1365 (w), 1334 (m), 1261 (w), 1185 (w), 1109 (w), 1062 (w), 1044 (w), 939 (w), 797 (s), 747 (s);

HR-MS (EI (+)): $C_{26}H_{34}{}^{35}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 661.1623, found 661.1626; $C_{26}H_{34}{}^{35}Cl^{37}Cl^{194}PtNa$ $[M+Na]^+$ calcd. 663.1594, found 663.1637; $C_{26}H_{34}{}^{37}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 665.1564, found 665.1641; $C_{26}H_{34}{}^{35}Cl_2{}^{195}PtNa$ $[M+Na]^+$ calcd. 662.1644, found 662.1649; $C_{26}H_{34}{}^{35}Cl^{37}Cl^{195}PtNa$ $[M+Na]^+$ calcd. 664.1615, found 664.1637; $C_{26}H_{34}{}^{37}Cl_2{}^{195}PtNa$ $[M+Na]^+$ calcd. 666.1585, found 666.1644; $C_{26}H_{34}{}^{35}Cl_2{}^{196}PtNa$ $[M+Na]^+$ calcd. 663.1646, found 663.1637; $C_{26}H_{34}{}^{35}Cl^{37}Cl^{196}PtNa$ $[M+Na]^+$ calcd. 665.1617, found 665.1641; $C_{26}H_{34}{}^{37}Cl_2{}^{196}PtNa$ $[M]^+$ calcd. 667.1587, found 667.1635; $C_{26}H_{34}{}^{35}Cl_2{}^{198}PtNa$ $[M+Na]^+$ calcd. 665.1676, found 665.11641; $C_{26}H_{34}{}^{35}Cl^{37}Cl^{198}PtNa$ $[M+Na]^+$ calcd. 667.1646, found 667.1635;

EA calcd. for $C_{26}H_{34}Cl_2N_2Pt$: C: 48.75, H: 5.35, N: 4.37; found C:48.22, H: 5.44, N: 4.42.

2.2.11 Synthesis of Bis(mesitylisonitrile)platinum(II) chloride (1c)



According to **GP4** the reaction was carried out with $PtCl_2$(cod) (250 mg, 668 µmol, 1.00 eq.) and mesityl isocyanide (213 mg, 1.47 mmol, 2.20 eq.). Title compound was obtained as a colorless solid (323 mg, 580 µmol, 87 %).

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.00 (d, *J* = 0.6 Hz, 4H, 4x$C_{Ar}\underline{H}$), 2.43 (s, 12H, 6x-$C\underline{H}_3$), 2.33 (s, 6H, 2x-CH_3).

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 141.84 (s, 2C, 2x$\underline{C}_{Ar}$), 136.27 (s, 6C, 6x$\underline{C}_{Ar}$), 129.41 (d, 4C, 4x$C_{Ar}\underline{H}$), 21.54 (q, 2C, 2x-$\underline{C}H_3$), 18.74 (q, 4C, 4x-$\underline{C}H_3$).

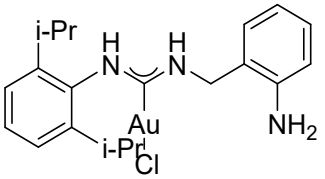
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3750.70 (p, *J* = 117.2 Hz).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 2981 (w), 2919 (w), 2858 (w), 2738 (w), 2368 (w), 2230 (m), 2195 (s), 1606 (m), 1475 (m), 1440 (m), 1377 (w), 1310 (w), 1291 (w), 1202 (w), 1033 (m), 899 (s), 852 (m), 759 (m), 714 (w);

HR-MS (ESI (+)): $C_{20}H_{22}{}^{35}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 577.0684, found 577.0681; $C_{20}H_{22}{}^{35}Cl^{37}Cl^{194}PtNa$ $[M+Na]^+$ calcd. 579.0655, found 579.0651; $C_{20}H_{22}{}^{37}Cl_2{}^{194}PtNa$ $[M+Na]^+$ calcd. 581.0625, found 581.0673; $C_{20}H_{22}{}^{35}Cl_2{}^{195}PtNa$ $[M+Na]^+$ calcd. 578.0705, found 578.0701; $C_{20}H_{22}{}^{35}Cl^{37}Cl^{195}PtNa$ $[M+Na]^+$ calcd. 580.0676, found 580.0672; $C_{20}H_{22}{}^{35}Cl_2{}^{196}PtNa$ $[M+Na]^+$ calcd. 579.0707, found 579.0704; $C_{20}H_{22}{}^{35}Cl^{37}Cl^{196}PtNa$ $[M+Na]^+$ calcd. 581.0678, found 581.0673; $C_{20}H_{22}{}^{35}Cl_2{}^{198}PtNa$ $[M+Na]^+$ calcd. 581.0736, found 581.0736;

EA calcd. for $C_{20}H_{22}Cl_2N_2Pt$: C: 43.17, H: 3.99, N: 5.03; found C: 42.34, H: 4.05, N: 4.91.

2.2.12 Synthesis of (((2-Aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (2a)

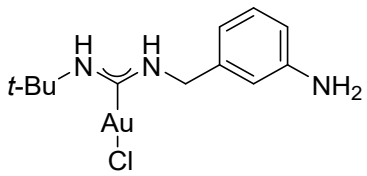


According to **GP5** the reaction was carried out with 2,6-diisopropylphenyl isocyanide gold(I) chloride (83.9 mg, 200 µmol, 1.00 eq.) and 2-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (94.0 mg, 173 µmol, 87 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.34 (s, 1H, $C_{Ar}\underline{H}$), 7.41 – 7.33 (m, 1H, $C_{Ar}\underline{H}$), 7.22 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.09 (td, *J* = 7.6, 1.5 Hz, 1H, $C_{Ar}\underline{H}$), 6.98 (dd, *J* = 7.7, 1.6 Hz, 1H, $C_{Ar}\underline{H}$), 6.71 – 6.60 (m, 2H, $C_{Ar}\underline{H}$), 6.00 (t, *J* = 5.9 Hz, 1H, $C_{Ar}\underline{H}$), 4.81 (d, *J* = 5.8 Hz, 2H, -$C\underline{H_2}$-), 3.89 (s, 2H, -$N\underline{H_2}$), 3.10 (hept, *J* = 6.9 Hz, 2H, 2x$C\underline{H}$), 1.19 (d, *J* = 6.8 Hz, 6H, 2x-$C\underline{H_3}$), 1.08 (d, *J* = 6.9 Hz, 6H, 2x-$C\underline{H_3}$);

2.2.13 Synthesis of (((3-Aminobenzyl)amino)(tert-butylamino)methylene)gold(I) chloride (2b)

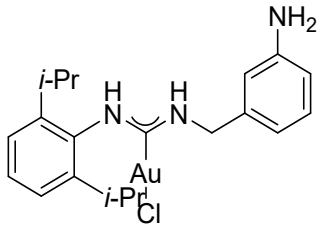


According to **GP5** the reaction was carried out with *tert*-butylisonitrile gold(I) chloride (63.1 mg, 200 µmol, 1.00 eq.) and 3-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a yellow solid (86.0 mg, 196 µmol, 98 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.16 – 7.06 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.83 – 6.17 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.67 – 6.71 (m, 2H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.61 – 6.57 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.47 – 6.13 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.45 - 5.37 (m, 1 H, Rotamers B and C, $C_{Ar}\underline{H}$), 6.19 (s, 1H, Rotamer A, $C_{Ar}\underline{H}$), 4.83 (d, J = 5.8 Hz, 2H, Rotamer C, -$C\underline{H_2}$-), 4.76 (d, J = 5.9 Hz, 2H, Rotamer B, -$C\underline{H_2}$-), 4.16 (d, J = 5.2 Hz, 2H, Rotamer A, -$C\underline{H_2}$-), 3.83 (s, 2H, Rotamers A, B and C, -$N\underline{H_2}$), 1.57 (s, 9H, Rotamer B, 3x-$C\underline{H_3}$), 1.49 (s, 9H, Rotamer A, 3x-$C\underline{H_3}$), 1.39 (s, 9H, Rotamer C, 3x-$C\underline{H_3}$).

2.2.14 Synthesis of (((3-Aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (2c)

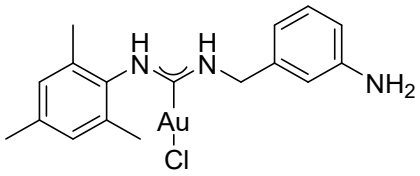


According to **GP5** the reaction was carried out with 2,6-diisopropylphenyl isocyanide gold(I) chloride (83.9 mg, 200 µmol, 1.00 eq.) and 3-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (103 mg, 190 µmol, 95 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] 8.29 (s, 1H, $C_{Ar}\underline{H}$), 7.38 (t, *J* = 7.7 Hz, 1H, $C_{Ar}\underline{H}$), 7.24 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.06 (dd, *J* = 8.8, 7.2 Hz, 1H, $C_{Ar}\underline{H}$), 6.59 – 6.55 (m, 3H, 3x$C_{Ar}\underline{H}$), 6.15 (s, 1H, $C_{Ar}\underline{H}$), 4.76 (d, J = 6.1 Hz, 2H, -C$\underline{H_2}$-), 3.74 (s, 2H, -N$\underline{H_2}$), 3.11 (hept, *J* = 7.0 Hz, 2H, 2xC$\underline{H}$), 1.19 (d, *J* = 6.9 Hz, 6H, 2x-CH_3), 1.13 (d, *J* = 6.9 Hz, 6H, 2x-C$\underline{H_3}$);

2.2.15 Synthesis of (((3-Aminobenzyl)amino)(mesitylamino)methylene)gold(I) chloride (2d)

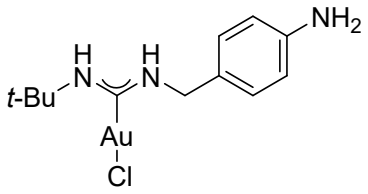


According to **GP5** the reaction was carried out with mesityl isocyanide gold(I) chloride (75.5 mg, 200 µmol, 1.00 eq.) and 3-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (98.0 mg, 196 µmol, 98 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.86 (s, 1H, $C_{Ar}\underline{H}$), 7.07 (t, *J* = 7.6 Hz, 1H, $C_{Ar}\underline{H}$), 6.96 (s, 2H, 2x$C_{Ar}\underline{H}$), 6.60 – 6.54 (m, 3H, 3x$C_{Ar}\underline{H}$), 6.21 (t, *J* = 6.2 Hz, 1H, $C_{Ar}\underline{H}$), 4.75 (d, *J* = 6.1 Hz, 2H, -C$\underline{H_2}$-), 3.79 (s, 2H, -N$\underline{H_2}$), 2.26 (s, 3H, -C$\underline{H_3}$), 2.18 (s, 6H, 2x-C$\underline{H_3}$);

2.2.16 Synthesis of (((4-Aminobenzyl)amino)(tert-butylamino)methylene)gold(I) chloride (2e)

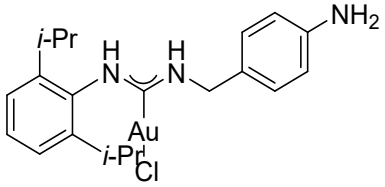


According to **GP5** the reaction was carried out with *tert*-butylisonitrile gold(I) chloride (63.0 mg, 200 µmol, 1.00 eq.) and 4-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a yellow solid (76.0 mg, 132 µmol, 87 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (700 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.10 (d, *J* = 8.1 Hz, 2H, Rotamer B, 2x$C_{Ar}\underline{H}$), 7.06 (d, *J* = 8.2 Hz, 2H, Rotamer A, 2x$C_{Ar}\underline{H}$), 6.79-6.75 (m, 2H, Rotamer C, 2x$C_{Ar}\underline{H}$), 6.68 (d, *J* = 8.4 Hz, 2H, Rotamer A, 2x$C_{Ar}\underline{H}$), 6.66-6.65 (m, 2H, Rotamer C, 2x$C_{Ar}\underline{H}$), 6.63 (d, *J* = 8.1 Hz, 2H, Rotamer B, 2x$C_{Ar}\underline{H}$), 6.46-6.15 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 6.13 (s, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 5.27 – 5.23 (m, 1H, Rotamers A, B and C, $C_{Ar}\underline{H}$), 4.79 (d, *J* = 5.8 Hz, 2H, Rotamer C, -$C\underline{H}_2$-), 4.72 (d, J = 5.8 Hz, 1H, Rotamer B, -$C\underline{H}_2$-), 4.13 (d, J = 5.0 Hz, 1H, Rotamer A, -$C\underline{H}_2$-), 3.81 (s, 2H, Rotamers A, B and C, -$N\underline{H}_2$), 1.55 (s, 9H, Rotamer B, 3x-$C\underline{H}_3$), 1.50 (s, 9H, Rotamer A, 3x-$C\underline{H}_3$), 1.36 (s, 9H, Rotamer C, 3x-$C\underline{H}_3$).

2.2.17 Synthesis of (((4-Aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (2f)

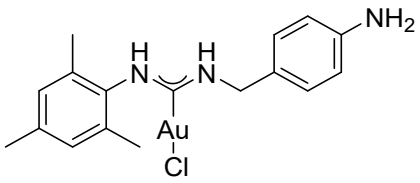


According to **GP5** the reaction was carried out with 2,6-diisopropylphenyl isocyanide gold(I) chloride (83.9 mg, 200 µmol, 1.00 eq.) and 4-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (91.0 mg, 168 µmol, 84 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (700 MHz, $CDCl_3$, 295 K): δ [ppm] = 7.25 (t, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.10 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 6.92 (d, *J* = 8.0 Hz, 2H, 2x$C_{Ar}\underline{H}$), 6.47 (d, *J* = 8.0 Hz, 2H, 2x$C_{Ar}\underline{H}$), 4.61 (d, *J* = 6.0 Hz, 2H, -C$\underline{H_2}$-), 2.94 (p, *J* = 6.8 Hz, 2H, 2xC$\underline{H}$), 1.04 (d, *J* = 6.8 Hz, 6H, 2x-C$\underline{H_3}$), 0.97 (d, *J* = 6.9 Hz, 6H, 2x-C$\underline{H_3}$);

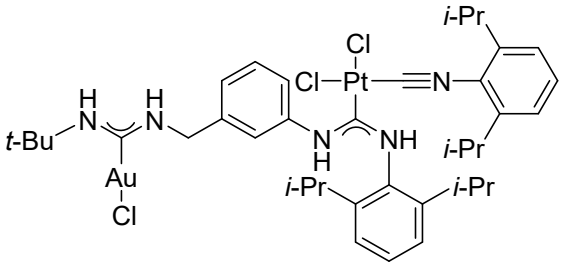
2.2.18 Synthesis of (((4-Aminobenzyl)amino)(mesitylamino)methylene)gold(I) chloride (2g)



According to **GP5** the reaction was carried out with mesityl isocyanide gold(I) chloride (75.5 mg, 200 µmol, 1.00 eq.) and 4-aminobenzylamine (24.4 mg, 200 µmol, 1.00 eq.) Title compound was obtained as a yellow solid (97.0 mg, 194 µmol, 97 % yield).

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 7.73 (s, 1H $C_{Ar}\underline{H}$), 7.04 (d, *J* = 8.4 Hz, 2H, 2x$C_{Ar}\underline{H}$), 6.94 (s, 2H, 2x$C_{Ar}\underline{H}$), 6.61 (d, *J* = 8.4 Hz, 2H, 2x$C_{Ar}\underline{H}$), 6.16 (s, 1H, $C_{Ar}\underline{H}$), 4.73 (d, *J* = 6.0 Hz, 2H, -C$\underline{H_2}$-), 3.75 (s, 2H, -N$\underline{H_2}$), 2.25 (s, 3H, -C$\underline{H_3}$), 2.16 (s, 6H, 2x-C$\underline{H_3}$);

2.2.19 Synthesis of Gold(I) Platinum(II) Complex 3a



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (50.0 mg, 114.23 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) platinum(II) chloride (73.17 mg, 114.23 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (81.0 mg, 75.12 µmol, 66 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.47 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (65.2 mg,

102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (69.0 mg, 63.99 µmol, 63 %).

m.p. = 195 – 200 °C

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.76 – 8.46 (m, 1H, N<u>H</u>), 7.83 – 7.74 (m, 1H, N<u>H</u>), 7.72 – 7.61 (m, 1H, N<u>H</u>), 7.59 – 7.47 (m, 1H, N<u>H</u>), 7.44 – 7.35 (m, 2H, 2xC_{Ar}<u>H</u>), 7.27 (d, *J* = 7.9 Hz, 2H, 2xC_{Ar}<u>H</u>), 7.18 (d, *J* = 7.9 Hz, 1H, C_{Ar}<u>H</u>), 7.14 – 7.10 (m, 1H, C_{Ar}<u>H</u>), 7.09 – 6.99 (m, 1H, 2xC_{Ar}<u>H</u>), 5.01 – 3.81 (m, 2H, -C<u>H</u>$_2$-), 3.27 (tp, *J* = 13.8, 7.0 Hz, 3H, 3x-C<u>H</u>$(CH_3)_2$), 2.89 – 2.70 (m, 1H, -C<u>H</u>$(CH_3)_2$), 1.54 – 1.36 (m, 9H, 3x-C<u>H</u>$_3$), 1.21 (d, *J* = 6.9 Hz, 9H, 3x-C<u>H</u>$_3$), 1.16 (d, *J* = 2.1 Hz, 3H, -C<u>H</u>$_3$), 1.14 (d, *J* = 2.0 Hz, 3H, -C<u>H</u>$_3$), 1.07 (d, *J* = 6.9 Hz, 9H, 3x-C<u>H</u>$_3$).

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 193.28 (s, 1C, <u>C</u>$_{Carbene}$), 169.89 (s, 1C, <u>C</u>$_{Carbene}$),147.10 (s, 1C, <u>C</u>$_{Ar}$), 146.69 (s, 1C, <u>C</u>$_{Ar}$), 145.91 (s, 1C, <u>C</u>$_{Ar}$), 140.17 (s, 1C, <u>C</u>$_{Ar}$), 139.11 (s, 1C, <u>C</u>$_{Ar}$), 137.73 (s, 1C, <u>C</u>$_{Ar}$), 131.74 (s, 2C, 2x<u>C</u>$_{Ar}$), 131.37 (d, 1C, <u>C</u>$_{Ar}$H), 130.98 (d, 1C, <u>C</u>$_{Ar}$H), 130.00 (d, 1C, <u>C</u>$_{Ar}$H), 129.68 (d, 1C, <u>C</u>$_{Ar}$H), 129.54 (s, 1C, <u>C</u>$_{Ar}$), 127.04 (d, 1C, <u>C</u>$_{Ar}$H), 125.93 (d, 1C, <u>C</u>$_{Ar}$H), 125.68 (d, 1C, <u>C</u>$_{Ar}$H), 124.33 (d, 1C, <u>C</u>$_{Ar}$H), 123.99 (d, 1C, <u>C</u>$_{Ar}$H), 122.20 (d, 1C, <u>C</u>$_{Ar}$H),54.82 (t, 1C, -<u>C</u>H_2-), 31.58 (d, 2C, 2x-<u>C</u>$H(CH_3)_2$), 30.38 (d, 2C, 2x-<u>C</u>$H(CH_3)_2$), 30.00 (q, 1C, -<u>C</u>H_3), 29.94 (s, 1C, -<u>C</u>$(CH_3)_3$), 29.09 (q, 1C, -<u>C</u>H_3), 29.00, (q, 1C, -<u>C</u>H_3), 24.66 (q, 2C, 2x-<u>C</u>H_3), 23.67 (q, 2C, 2x-<u>C</u>H_3), 22.96 (q, 2C, 2x-<u>C</u>H_3), 22.84 (q, 2C, 2x-<u>C</u>H_3);

^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3497.23 (s, 1Pt);

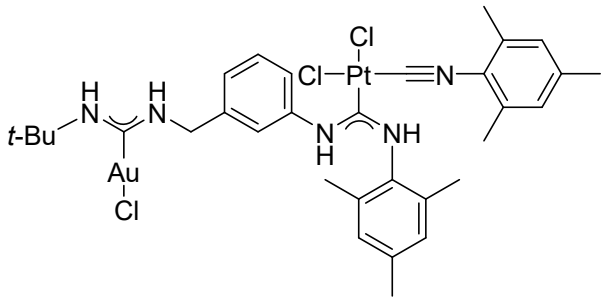
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3264 (w), 3069 (m), 2964 (w), 2928 (w), 2869 (m), 2188 (m), 1693 (w), 1626 (w), 1546 (s), 1462 (m), 1387 (m), 1364 (w), 1303 (m), 1201 (w), 1110 (w), 1061 (w), 972 (w), 936 (m), 798 (m), 748 (m), 697 (m);

HR-MS (MALDI): $C_{38}H_{53}Au^{35}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1038.2954, found 1038.2948; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1040.2924, found 1040.2959; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1042.2895, found 1042.2978; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1040.2970, found 1040.2959; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1042.2941, found 1042.2978; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1044.2911, found 1044.2979; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1041.2991, found 1041.2986; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1043.2962, found 1043.2978; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1045.2932, found 1045.2989; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1042.2993, found 1042.2978; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1044.2963, found 1044.2979; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1046.2934,

found 1046.2980; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1044.3022, found 1044.2979; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1046.2993, found 1046.2980; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1048.2963, found 1048.2992;

EA calcd. for $C_{38}H_{53}Cl_3AuN_5Pt$: C: 42.33, H: 4.95, N: 6.50; found C: 41.61, H: 5.14, N: 6.36.

2.2.20 Synthesis of Gold(I) Platinum(II) Complex 3b



According to **GP6** the reaction was carried out with (((3-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (50.0 mg, 114.23 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (63.56 mg, 114.23 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (86.0 mg, 86.51 µmol, 75 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.47 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,4,6-trimethylphenyl) platinum(II) chloride (56.67 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (74.0 mg, 74.44 µmol, 73 %).

Mixture of two rotamers: A (75 %), B (25 %).

m.p. = 212 – 217 °C;

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.07 (s, 1H, Rotamer A, N$\underline{H}$), 8.66 (s, 1H, Rotamer B, NH), 8.58 – 7.84 (m, 1H, Rotamers A and B, N$\underline{H}$), 7.72 (s, 1H, Rotamer A, 2xN$\underline{H}$), (s, 1H, Rotamer B, 2xN$\underline{H}$), 7.15 – 7.00 (m, 2H, Rotamer A and B, 2x$C_{Ar}\underline{H}$), 6.99 – 6.84 (m, 4H, Rotamer A and B, 4x$C_{Ar}\underline{H}$), 6.76 – 6.63 (m, 2H, Rotamer A and B, 2x$C_{Ar}\underline{H}$), 4.91 (m, 2H, Rotamer A, -C$\underline{H_2}$-), 4.79 – 4.04 (m, 2H, Rotamer B, -C$\underline{H_2}$-), 2.34 (s, 3H, Rotamers A and B, -C$\underline{H_3}$), 2.31 (s, 3H, Rotamers A and B, -C$\underline{H_3}$), 2.28 – 2.20 (s, 3H, Rotamers A and B, -C$\underline{H_3}$)), 2.15 (m, 3H, (s, 3H, Rotamers A and B, -C$\underline{H_3}$), 2.09 – 1.99 (m, 3H, Rotamers A and B, -C$\underline{H_3}$), 1.95 (s, 3H, Rotamers A and B, -C$\underline{H_3}$), 1.49 – 1.28 (m, 9H, Rotamers A and B, 3x-C$\underline{H_3}$);

^{13}C NMR (126 MHz, CD_2Cl_2, 295 K) δ [ppm] = 192.65 (s, 1C, Rotamer A, $\underline{C}_{Carbene}$), 192.61 (s, 1C, Rotamer B, $\underline{C}_{Carbene}$), 173.01 (s, 1C, Rotamer B, $\underline{C}_{Carbene}$), 168.01 (s, 1C, Rotamer A, $\underline{C}_{Carbene}$), 141.56 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 140.37 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 140.22 (s, 2C, Rotamer B, 2x$\underline{C}_{Ar}$), 140.19 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 140.02 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 138.55 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 136.09 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 136.06 (s, 2C, Rotamer B, 2x$\underline{C}_{Ar}$), 135.98 (s, 2C, Rotamer A, 2x$\underline{C}_{Ar}$) 135.16 (s, 2C, Rotamer A, 2x$\underline{C}_{Ar}$), 130.32 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 130.33 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 130.27 (d, 2C, Rotamer A, 2x$C_{Ar}\underline{H}$), 130.02 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 129.94 (d, 2C, Rotamer B, 2x$\underline{C}_{Ar}$H), 129.74 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 129.70 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 129.58 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 129.29 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 129.11 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 128.80 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 128.76 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 128.71 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 127.28 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 126.50 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 126.01 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 125.54 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 122.30 (d, 1C, Rotamer A, $C_{Ar}\underline{H}$), 120.93 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 120.56 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 114.07 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 113.59 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 54.64 (t, 1C, Rotamer A, -$\underline{C}H_2$-), 53.55 (t, 1C, Rotamer B, -$\underline{C}H_2$-); 31.27 (s, 1C, Rotamer A, -$\underline{C}(CH_3)_3$), 31.16 (q, 3C, Rotamers A and B, 3x-$\underline{C}H_3$), 30.21 (s, 1C, Rotamer B, -$\underline{C}(CH_3)_3$); 21.28 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 21.15 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$), 20.96 (q, 2C, Rotamer B,2x -$\underline{C}H_3$), 18.48 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 18.41 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$), 18.29 (q, 2C, Rotamer A, 2x-CH_3);

^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] -3488.05 (s, 1Pt, Rotamer A or B), -3526.87 (s, 1Pt, Rotamer A or B);

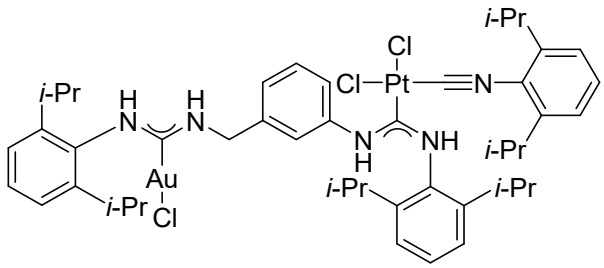
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3277 (w), 2961 (w), 2920 (w), 2862 (w), 2191 (s), 1695 (m), 1546 (s), 1477 (m), 1444 (m), 1365 (w), 1310 (w), 1229 (w), 1201 (m), 1035 (w), 971 (w), 855 (m), 800 (w), 697 (m);

HR-MS (MALDI): $C_{32}H_{41}Au^{35}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 954.2015, found 954.2014; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 956.1985, found 956.2030; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 958.1956, found 958.1269; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 956.2031, found 956.2030; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 958.2002, found 958.1269; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 960.1972, found 960.2046; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 957.2052, found 957.2055; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 959.2023, found 959.2045; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. : 961.1993, found 961.2054; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 958.2054, found 958.2045; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 960.2024, found 960.2046; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 962.1995, found 962.2044; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 960.2083, found 960.2046;

$C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 962.2054, found 962.2044; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 964.2024, found 964.2062;

EA calcd. for $C_{32}H_{41}Cl_3AuN_5Pt$: C: 38.66, H: 4.16, N: 7.04; found C: 38.17, H: 4.30, N: 6.95.

2.2.21 Synthesis of Gold(I) Platinum(II) Complex 3c



According to **GP6** the reaction was carried out with (((3-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 92.27 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) platinum(II) chloride (59.11 mg, 92.27 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (81.0 mg, 68.50 µmol, 74 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (19.08 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (65.2 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (83 mg, 70.19 µmol, 69 %).

Mixture of two rotamers: A (63 %), B (37 %)

m.p. = 192 – 197 °C

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.96 – 8.81 (m, 1H, Rotamer A, N$\underline{H}$), 8.80 (d, *J* = 17.1 Hz, 1H, Rotamer B, N$\underline{H}$), 8.42 (s, 1H, Rotamer A, N$\underline{H}$), 8.37 – 8.20 (m, 1H, Rotamer B, N$\underline{H}$), 7.84 – 7.60 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.72 (td, *J* = 6.5, 1.7 Hz, 2H, Rotamer A, 2xN$\underline{H}$), 7.63 (s, 2H, Rotamer B, 2xN$\underline{H}$), 7.53 – 7.41 (m, 4H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.29 – 7.02 (m, 6H, Rotamers A and B, 6x$C_{Ar}\underline{H}$), 7.02 – 6.75 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$); 6.58 (s, 1H, $C_{Ar}\underline{H}$), 6.57 – 6.55 (m, 1H, Rotamer B, $C_{Ar}\underline{H}$), 6.22 (t, *J* = 6.2 Hz, 1H, $C_{Ar}\underline{H}$), 6.12 (t, *J* = 6.1 Hz, 1H, Rotamer B, $C_{Ar}\underline{H}$), 5.09 – 4.83 (m, 2H, Rotamer B, -C$\underline{H_2}$-), 4.79 – 4.58 (m, 2H, Rotamer A, -C$\underline{H_2}$-), 3.35 (dt, *J* = 13.8, 6.9 Hz, 6H, 6x-C$\underline{H}(CH_3)_2$), 3.30 – 2.82 (m, 6H, Rotamer B, 6x-C$\underline{H}(CH_3)_2$), 1.30 (d, *J* = 6.8 Hz, 24H, Rotamer A, 8x-C$\underline{H_3}$), 1.17 (d, *J* = 6.8 Hz,

12H, Rotamer A 4x-C$\underline{H_3}$), 1.28 – 1.19 (m, 12H, Rotamer B, 4x-C$\underline{H_3}$), 1.15 – 1.09 (m, 18H, Rotamer B, 6x-C$\underline{H_3}$), 1.10 – 1.00 (m, 6H, Rotamer B, 2x-C$\underline{H_3}$).

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 192.10 (s, 1C, Rotamer B, $\underline{C_{Carbene}}$), 191.29 (s, 1C, Rotamer A, $\underline{C_{Carbene}}$),169.74 (s, 1C, Rotamer A, $\underline{C_{Carbene}}$), 169.33 (s, 1C, Rotamer B, $\underline{C_{Carbene}}$), 161.47 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 159.29 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 153.08 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 152.16 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 147.64 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 147.40 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 147.15 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 146.89 (s, 2C, Rotamer A, $\underline{C_{Ar}}$), 146.83 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 146.69 (s, 2C, Rotamer A, 2x$\underline{C_{Ar}}$), 145.99 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 145.98 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 145.87 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 140.38 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 139.71 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 138.90 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 138.36 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 138.19 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 138.14 (s, 2C, Rotamer B, 2x$\underline{C_{Ar}}$), 137.73 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 137.61 (s, 1C, Rotamer B, $\underline{C_{Ar}}$), 135.35 (s, 1C, Rotamer A, $\underline{C_{Ar}}$), 131.72 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 131.23 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 130.96 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 130.74 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 130.65 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 130.19 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 130.04 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 130.00 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 129.64 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 129.51 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 129.22 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 127.27 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 126.53 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 126.17 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 125.64 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 125.57 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 125.19 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 125.15 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 124.71 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H) 124.32 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 123.96 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 123.16 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 122.58 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 117.51 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H), 114.92 (d, 1C, Rotamer A, $\underline{C_{Ar}}$H), 114.13 (d, 1C, Rotamer B, $\underline{C_{Ar}}$H); 54.23 (t, 1C, Rotamer A, -$\underline{C}H_2$-), 53.06 (t, 1C, Rotamer B, -$\underline{C}H_2$-), 30.38 (d, 4C, Rotamer A, 4x-$\underline{C}H(CH_3)_2$), 29.99 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 29.94 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 29.90 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 29.10 (d, 2C, Rotamer A, 2x-$\underline{C}H(CH_3)_2$), 29.00 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 28.88 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 28.53 (d, 1C, Rotamer B, -$\underline{C}H(CH_3)_2$), 24.90 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$) , 24.83 (q, 1C, Rotamer B, -$\underline{C}H_3$), 24.67 (q, 1C, Rotamer B, -$\underline{C}H_3$), 24.64 (q, 1C, Rotamer B, -$\underline{C}H_3$), 24.10 (q, 1C, Rotamer B, -$\underline{C}H_3$), 23.85 (q, 1C, Rotamer B, -$\underline{C}H_3$), 23.65 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$), 23.59 (q, 1C, Rotamer B, -$\underline{C}H_3$), 23.15 (q, 1C, Rotamer B, -$\underline{C}H_3$), 23.12 (q, 1C, Rotamer B, -$\underline{C}H_3$), 22.96 (q, 4C, Rotamer A, 4x-$\underline{C}H_3$), 22.94 (q, 4C, Rotamer A, 4x-$\underline{C}H_3$), 22.85 (q, 4C, Rotamer A, 4x-$\underline{C}H_3$);

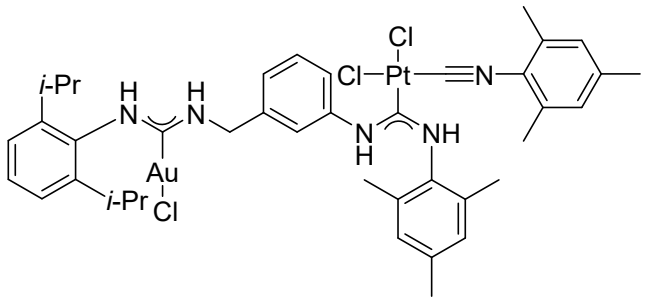
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3501.86 (s, 1Pt, Rotamer A or B), -3522.88 (s, 1Pt, Rotamer A or B);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3229 (m), 2963 (m), 2927 (w), 2868 (w), 2188 (m), 1691 (w), 1591 (s), 1546 (m), 1492 (m), 1461 (w), 1385 (w), 1364 (m), 1303 (w), 1180 (m), 1108 (w), 1060 (w), 936 (w), 799 (m), 749 (m), 695 (m);

HR-MS (ESI (+)): $C_{46}H_{61}Au^{35}Cl_2N_5{}^{192}Pt$ $[M]^+$ calcd. 1142.3580, found 1142.3586; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M]^+$ calcd. 1144.3550, found 1144.3592; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{192}Pt$ calcd. 1146.3521, found 1146.3641; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{194}Pt$ $[M]^+$ calcd. 1144.3596, found 1144.3592; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M]^+$ calcd. 1146.3567, found 1146.3641; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{194}Pt$ $[M]^+$ calcd. 1148.3537, found 1148.3605; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{195}Pt$ $[M]^+$ calcd. 1145.3617, found 1145.3617; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M]^+$ calcd. 1147.3588, found 1147.3580; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{195}Pt$ $[M]^+$ calcd. 1149.3558, found 1149.3533; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{196}Pt$ $[M]^+$ calcd. 1146.3619, found 1146.3641; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M]^+$ calcd. 1148.3589, found 1148.3605; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{196}Pt$ $[M]^+$ calcd. 1150.3560, found 1150.3610; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{198}Pt$ $[M]^+$ calcd. 1148.3648, found 1148.3605; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M]^+$ calcd. 1150.3619, found 1150.3560; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{198}Pt$ $[M]^+$ calcd. 1152.3589, found 1152.3576;

EA calcd. for $C_{46}H_{61}Cl_3AuN_5Pt$: C: 46.73, H: 5.20, N: 5.92; found C: 46.84, H: 5.41, N: 6.30.

2.2.22 Synthesis of Gold(I) Platinum(II) Complex 3d



According to **GP6** the reaction was carried out with (((3-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 92.27 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (51.34 mg, 92.27 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (82.0 mg, 74.66 µmol, 81 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (19.08 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,4,6-trimethylphenyl) platinum(II)

chloride (56.67 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (71.0 mg, 64.65 µmol, 63 %).

Mixture of two rotamers: A (48%), B (52 %).

m.p. = 189 – 204 °C;

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.93 – 8.75 (m, 1H, Rotamer A, N<u>H</u>), 8.66 (m, 1H, Rotamer B, N<u>H</u>), 8.38 – 8.14 (m, 1H, Rotamer B, N<u>H</u>), 8.04 (m, 1H, Rotamer A, N<u>H</u>), 7.88 – 7.55 (m, 2H, Rotamers A and B, 2xN<u>H</u>), 7.44 – 7.30 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 7.25 – 7.12 (m, 3H, Rotamers A and B, 3xC_{Ar}<u>H</u>), 7.05 – 6.95 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 6.90 – 6.82 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 6.58 (s, 1H, Rotamer B, C_{Ar}<u>H</u>), 6.56 (s, 1H, Rotamer A, C_{Ar}<u>H</u>), 6.23 (t, *J* = 6.2 Hz, 1H, Rotamer B, C_{Ar}<u>H</u>), 6.14 (t, *J* = 5.8 Hz, 1H, Rotamer A), 5.09 – 4.83 (m, 2H, Rotamer A, -C<u>H</u>$_2$-), 4.78 – 4.56 (m, 2H, Rotamer B, -C<u>H</u>$_2$-), 3.32 – 2.92 (m, 2H, Rotamers A and B, 2x-C<u>H</u>$(CH_3)_2$), 2.43 (s, 3H, Rotamer A, -C<u>H</u>$_3$), 2.40 – 2.29 (m, 18H, Rotamer B, 6x-C_{H3}), 2.27 – 2.23 (m, 3H, Rotamer B, -C<u>H</u>$_3$), 2.12 (s, 3H, Rotamer B, -C<u>H</u>$_3$), 2.08 (s, 3H, Rotamer B, -C<u>H</u>$_3$); 1.30 (d, *J* = 6.9 Hz, 6H, Rotamer B, 2x-C<u>H</u>$_3$), 1.18 (d, *J* = 6.9 Hz, 6H, Rotamer B, 2x-C<u>H</u>$_3$); 1.12 (d, *J* = 6.9 Hz, 6H, Rotamer A, 2x-C<u>H</u>$_3$), 1.02 (d, *J* = 6.9 Hz, 3H, Rotamer A, -C<u>H</u>$_3$), 1.00 (d, *J* = 6.9 Hz, 3H, Rotamer A, -C<u>H</u>$_3$);

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 192.49 (s, Rotamer B, 1C, <u>C</u>$_{Carbene}$), 191.65 (s, Rotamer A, 1C, <u>C</u>$_{Carbene}$), 169.27 (s, Rotamer A, 1C, <u>C</u>$_{Carbene}$), 168.79 (s, Rotamer B, 1C, <u>C</u>$_{Carbene}$), 147.67 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 147.51 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 146.91 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 146.72 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$);141.84 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 140.80 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 140.61 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 140.58 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 140.43 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 140.38 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 139.91 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 138.70 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 138.15 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 138.06 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 136.34 (s, 2C, Rotamer A, 2x<u>C</u>$_{Ar}$), 136.28 (s, 2C, Rotamer B, 2x<u>C</u>$_{Ar}$), 135.54 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 135.44 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 135.25 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 130.88 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 130.78 (d, 1C, Rotamer B, <u>C</u>$_{Ar}$H), 130.62 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 130.56 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 130.14 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 130.07 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 129.85 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 129.81 (s, 1C, Rotamer A, <u>C</u>$_{Ar}$), 129.65 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 129.62 (s, 1C, Rotamer B, <u>C</u>$_{Ar}$), 129.41 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 129.17 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 129.13 (d, 1C, Rotamer B, <u>C</u>$_{Ar}$H), 129.07 (d, 1C, Rotamer B, <u>C</u>$_{Ar}$H), 129.02 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 127.26 (d, 1C, Rotamer B, <u>C</u>$_{Ar}$H), 126.81 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 126.54 (d, 1C, Rotamer A, <u>C</u>$_{Ar}$H), 125.34 (d, 1C, Rotamer B, <u>C</u>$_{Ar}$H), 125.26 (d, 2C, Rotamer A, 2x<u>C</u>$_{Ar}$H),

125.21 (d, 2C, Rotamer B, 2x$\underline{C}_{Ar}H$), 124.36 (d, 1C, Rotamer A, $\underline{C}_{Ar}H$), 124.01 (d, 1C, Rotamer B, $\underline{C}_{Ar}H$),122.82 (d, 1C, Rotamer A, $\underline{C}_{Ar}H$), 117.54 (d, 1C, Rotamer A, $\underline{C}_{Ar}H$), 114.95(d, 1C, Rotamer B, $\underline{C}_{Ar}H$), 114.12 (d, 1C, Rotamer B, $\underline{C}_{Ar}H$), 53.71 (t, 1C, Rotamer A, -$C\underline{H}_2$-), 52.97 (t, 1C, Rotamer B, -$C\underline{H}_2$-), 29.15 (d, 1C, Rotamer A, -$C\underline{H}(CH_3)_2$), 29.10 (d, 1C, Rotamer A, -$C\underline{H}(CH_3)_2$), 28.52 (d, 2C, Rotamer B, -$C\underline{H}(CH_3)_2$), 24.77 (q, 2C, Rotamer A, 2x-$C\underline{H}_3$), 24.14 (q, 2C, Rotamer B, 2x-$C\underline{H}_3$), 23.76 (q, 2C, Rotamer B, 2x-$C\underline{H}_3$), 23.15 (q, 2C, Rotamer A, 2x-$C\underline{H}_3$), 21.23 (q, 2C, Rotamer B, 2x-CH_3), 21.21 (q, 2C, Rotamer A, 2x-CH_3), 18.75 (q, 2C, Rotamer A, 2x-CH_3), 18.69 (q, 2C, Rotamer B, 2x-CH_3), 18.43 (q, 2C, Rotamer A, 2x-CH_3), 18.38 (q, 2C, Rotamer B, 2x-CH_3).

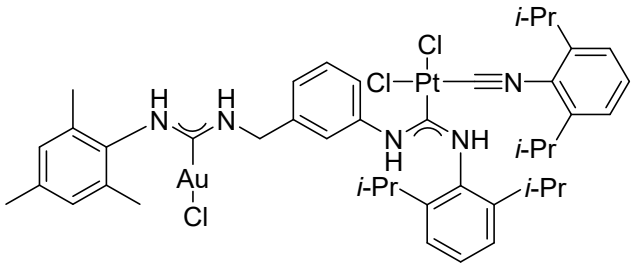
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3496.53 (s, 1Pt, Rotamer A or B), -3527.06 (s, 1Pt, Rotamer A or B);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3221 (w), 2962 (w), 2923 (w), 2865 (w), 2187 (s), 1594 (w), 1543 (s), 1382 (w), 1308 (w), 1218 (w), 1057 (w), 936 (w), 854 (w), 807 (m), 783 (m), 712 (w), 669 (w);

HR-MS (MALDI): $C_{40}H_{49}Au^{35}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1058.2641, found 1058.2647; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1060.2611, found 1060.2662; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2582, found 1062.2681; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1060.2657, found 1060.2662; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2628, found 1062.2681; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2598, found 1064.2681; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1061.2678, found 1061.2688; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1063.2649, found 1063.2681; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1065.2619, found 1065.2691; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2680, found 1062.2681; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2650, found 1064.2681; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1066.2621, found 1066.2682; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2709, found 1064.2681; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1066.2680, found 1066.2682; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1068.2650, found 1068.2703;

EA calcd. for $C_{40}H_{49}Cl_3AuN_5Pt$: C: 43.75, H: 4.50, N: 6.38; found C: 43.52, H: 4.68, N: 6.23.

2.2.23 Synthesis of Gold(I) Platinum(II) Complex 3e



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)((2,4,6-trimethylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 100.04 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) platinum(II) chloride (64.08 mg, 100.04 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (92.0 mg, 80.68 µmol, 81 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,4,6-trimethylphenyl isocyanide (14.79 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (65.2 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (87.0 mg, 73.6 µmol, 75 %).

Mixture of two rotamers: A (71 %), B (29 %).

m.p. = 244 – 249 °C;

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.27 – 9.00 (m, 1H, Rotamer A, N<u>H</u>), 9.03 – 8.92 (m, 1H, Rotamer B, N<u>H</u>), 8.66 (s, 1H, Rotamer B, N<u>H</u>), 8.62 – 8.47 (m, 1H, Rotamer A, N<u>H</u>), 8.34 – 8.05 (m, 2H, Rotamers A and B, 2xN<u>H</u>), 8.04 – 7.91 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.85 – 7.76 (m, 2H, Rotamers A and B, C_{Ar}<u>H</u>), 7.71 – 7.63 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.59 (d, *J* = 7.8 Hz, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.57 – 7.50 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.49 – 7.44 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.44 – 7.37 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.29 – 7.25 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>), 7.24 – 7.20 (m, 1H, Rotamer A, C_{Ar}<u>H</u>), 7.18 – 7.15 (m, 1H, Rotamer B, C_{Ar}<u>H</u>), 6.91 – 6.90 (m, 1H, Rotamer B, C_{Ar}H), 6.89 – 6.88 (m, 1H, Rotamer A, C_{Ar}<u>H</u>), 6.59 (dt, *J* = 12.4, 6.3 Hz, 1H, Rotamer A, C_{Ar}<u>H</u>), 6.51 (t, *J* = 6.1 Hz, 1H, Rotamer B, C_{Ar}<u>H</u>), 5.26 – 5.14 (m, 2H, Rotamer B, -C<u>H$_2$</u>-), 5.11 – 4.88 (m, 2H, Rotamer A, -C<u>H$_2$</u>-), 3.81 – 3.57 (m, 4H, Rotamer A, 4x-C<u>H</u>$(CH_3)_3$), 3.33 – 3.17 (m, 4H, Rotamer B, 4x-C<u>H</u>$(CH_3)_3$), 2.64 (s, 3H, Rotamer B, -C<u>H$_3$</u>), 2.60 – 2.56 (m, 3H, Rotamer A, -C<u>H$_3$</u>), 2.50 (s, 3H, Rotamer A, -C<u>H$_3$</u>), 2.50 – 2.48 (m, 3H, Rotamer A, -CH_3), 2.45 (s, 6H, Rotamer B, 2x-C<u>H$_3$</u>),1.62 (d, *J* = 6.9 Hz, 18H, Rotamer A, 6x-C<u>H$_3$</u>), 1.57 (dd, *J* = 6.9, 2.5 Hz, 3H, Rotamer B,

-C$\underline{H}_3$), 1.54 (dd, *J* = 6.9, 1.8 Hz, 12H, Rotamer B, 4x-C$\underline{H}_3$), 1.52 – 1.49 (m, 3H, Rotamer B, -C$\underline{H}_3$), 1.49 – 1.47 (m, 6H, Rotamer B, 2x-C$\underline{H}_3$), 1.45 (d, *J* = 6.7 Hz, 6H, Rotamer A, 2x-C$\underline{H}_3$);

^{13}C NMR (151 MHz, CD_2Cl_2, 295 K) δ [ppm] = 196.73 (s, 1C, Rotamer A, $\underline{C}_{Carbene}$), 190.97 (s, 1C, Rotamer B, $\underline{C}_{Carbene}$), 161.52 (s, 1C, Rotamer A, $\underline{C}_{Carbene}$), 159.26 (s, 1C, Rotamer B, $\underline{C}_{Carbene}$), 147.57 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 147.02 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 146.62 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 145.92 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 145.86 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 145.82 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 140.23 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 139.98 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 139.92 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 139.86 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 139.69 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 139.28 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 138.66 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 138.57 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 138.47 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 138.42 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 138.15 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 137.64 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 136.64 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 136.15 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 136.05 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 136.00 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 135.94 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 135.48 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 131.67 (s, 1C, Rotamer A, $\underline{C}_{Ar}$), 131.20 (s, 1C, Rotamer B, $\underline{C}_{Ar}$), 130.69 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 130.63 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 130.32 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 130.22 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 130.01 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 129.94 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 129.24 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 127.14 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 126.17 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 126.01 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 125.78 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 125.59 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 125.53 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 124.86 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 124.35 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 124.25 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 123.94 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 123.85 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 122.29 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 120.89 (d, 1C, Rotamer B, $\underline{C}_{Ar}\underline{H}$), 120.29 (d, 1C, Rotamer B, $\underline{C}_{Ar}$H), 117.26 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 114.76 (d, C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 113.92 (d, 1C, Rotamer A, $\underline{C}_{Ar}\underline{H}$), 53.93 (t, Rotamer B, -$\underline{C}H_2$-), 52.68 (t, Rotamer A, -$\underline{C}H_2$-), 30.43 (d, 1C, Rotamer A, -C$\underline{H}(CH_3)_2$), 30.31 (d, 2C, Rotamer A, 2x-C$\underline{H}(CH_3)_2$), 29.94 (d, 1C, Rotamer B, -C$\underline{H}(CH_3)_2$), 29.89 (d, 1C, Rotamer B, -C$\underline{H}(CH_3)_2$), 29.86 (d, 1C, Rotamer B, -C$\underline{H}(CH_3)_2$), 29.02 (d, 1C, Rotamer B, -C$\underline{H}(CH_3)_2$), 28.98 (d, 1C, Rotamer A, -C$\underline{H}(CH_3)_2$), 30.43 (q, 1C, Rotamer B, -$\underline{C}H_3$), 30.31 (q, 1C, Rotamer A, -$\underline{C}H_3$), 29.94 (q, 1C, Rotamer B, -$\underline{C}H_3$), 29.89 (q, 1C, Rotamer B, -$\underline{C}H_3$), 29.86 (q, 1C, Rotamer B, -$\underline{C}H_3$), 29.02 (q, 1C, Rotamer B, -$\underline{C}H_3$), 28.98, (q, 1C, Rotamer A, -$\underline{C}H_3$), 28.89 (q, 1C, Rotamer B, -$\underline{C}H_3$), 24.58 (q, 1C, Rotamer A, -$\underline{C}H_3$), 23.71 (q, 1C, Rotamer B, -$\underline{C}H_3$), 23.63 (q, 1C, Rotamer A, -$\underline{C}H_3$), 23.60 (q, 1C, Rotamer B, -$\underline{C}H_3$), 22.91 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 22.80 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 21.22 (q, Rotamer B, -CH_3), 21.14 (q, Rotamer B, -CH_3), 21.10 (q, Rotamer B, -CH_3), 19.03 (q, Rotamer A, -CH_3), 18.34 (q, Rotamer A, -CH_3), 18.29 (q, Rotamer A, -CH_3);

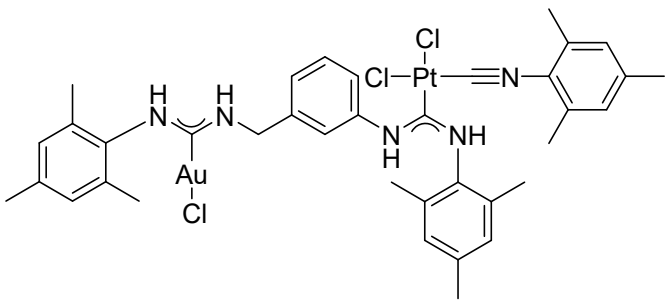
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3501.04 (s, 1Pt, Rotamer A or B), -3527.05 (s, 1Pt, Rotamer A or B);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3242 (m), 2964 (s), 2872 (m), 2188 (w), 1718 (s), 1660 (w), 1608 (w), 1551 (s), 1488 (w), 1460 (w), 1385 (w), 1365 (w), 1315 (w), 1183 (w), 1062 (m), 1035 (m), 954 (w), 855 (w), 801 (w), 750 (w), 695 (w);

HR-MS (ESI (+)): $C_{43}H_{55}Au^{35}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1100.3110, found 1100.3116; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1102.3081, found 1102.3139; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1104.3051, found 1104.3158; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1102.3127, found 1102.3139; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1104.3097, found 1104.3158; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1106.3068, found 1106.3159; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1103.3148, found 1103.3165; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1105.3118, found 1105.3160; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1107.3089, found 1107.3169; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1104.3149, found 1104.3158; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1106.3120, found 1106.3159; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1108.3090, found 1108.3162; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1106.3179, found 1106.3159; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1108.3149, found 1108.3090; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1110.3120, found 1110.3183;

EA calcd. for $C_{43}H_{55}Cl_3AuN_5Pt$: C: 45.29, H: 4.86, N: 6.14; found C: 45.57, H: 5.00, N: 6.31.

2.2.24 Synthesis of Gold(I) Platinum(II) Complex 3f



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)(2,4,6-trimethylphenylamino)methylene)gold(I) chloride (50.0 mg, 100.04 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (55.66 mg, 100.04 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (79.0 mg, 71.93 µmol, 72 % yield).

Mixture of two rotamers: A (53 %), B (47 %).

m.p. = 279 – 284 °C;

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.51 (s, 1H, Rotamer B, N<u>H</u>), 8.86 – 8.70 (m, 1H, Rotamer A, N<u>H</u>), 8.41 – 7.85 (m, 1H, Rotamers A and B, N<u>H</u>), 7.75 – 7.49 (m, 2H, Rotamers A and B, 2xN<u>H</u>), 7.38 – 7.16 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 7.03 – 6.94 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 6.94 – 6.85 (m, 3H, Rotamers A and B, 3xC_{Ar}<u>H</u>), 6.84 – 6.79 (m, 2H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 6.61 – 6.52 (m, 1H, Rotamers A and B, 2xC_{Ar}<u>H</u>), 6.31 – 6.13 (m, 1H, Rotamers A and B, C_{Ar}<u>H</u>),4.98 – 4.91 (m, 2H, Rotamer A, -C<u>H$_2$</u>-), 4.77 – 4.52 (m, 2H, Rotamer B, -C<u>H$_2$</u>-); 2.42 (s, 3H,Rotamer B, -C<u>H$_3$</u>), 2.36 – 2.34 (m, 3H, Rotamer A, -C<u>H$_3$</u>), 2.33 (s, 3H, Rotamer A, -C<u>H$_3$</u>), 2.32 (s, 3H, Rotamer B, -C<u>H$_3$</u>), 2.31 (s, 3H, Rotamer B, -C<u>H$_3$</u>), 2.30 (s, 6H, Rotamer B, 2x-C<u>H$_3$</u>), 2.26 (s, 3H, Rotamer B, -C<u>H$_3$</u>), 2.24 (s, 3H, Rotamer B, -C<u>H$_3$</u>), 2.17 (s, 3H, Rotamer A, -C<u>H$_3$</u>), 2.12 (s, 12H, Rotamer A, 4x-C<u>H$_3$</u>), 2.10 (s, 6H, Rotamer A, 2x-C<u>H$_3$</u>), 2.06 (s, 6H, Rotamer A, 2x-C<u>H$_3$</u>).

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] =196.41 (s, 1C, Rotamer A, <u>C$_{Carbene}$</u>), 191.94 (s, 1C, Rotamer B, <u>C$_{Carbene}$</u>), 168.90 (s, 1C, Rotamer B, <u>C$_{Carbene}$</u>), 168.10 (s, 1C, Rotamer A, <u>C$_{Carbene}$</u>), 141.82 (s, 1C, Rotamer A, C_{Ar}), 140.72 (s, 1C, Rotamer A, C_{Ar}), 140.67 (s, 1C, Rotamer B, C_{Ar}), 140.56 (s, 1C, Rotamer B, C_{Ar}), 140.33 (s, 1C, Rotamer B, C_{Ar}), 140.24 (s, 1C, Rotamer B, C_{Ar}), 140.11 (s, 1C, Rotamer A, C_{Ar}), 139.96 (s, 1C, Rotamer A, C_{Ar}), 139.93 (s, 1C, Rotamer A, C_{Ar}), 139.84 (s, 1C, Rotamer B, C_{Ar}), 139.19 (s, 1C, Rotamer B, C_{Ar}), 138.22 (s, 1C, Rotamer A, C_{Ar}), 137.95 (s, 1C, Rotamer B, C_{Ar}), 136.70 (s, 2C, Rotamer A, 2xC_{Ar}), 136.34 (s, 2C, Rotamer B, 2xC_{Ar}), 136.30 (s, 1C, Rotamer A, C_{Ar}), 136.26 (s, 1C, Rotamer A, C_{Ar}), 136.23 (s, 2C, Rotamer B, C_{Ar}) 136.07 (s, 2C, Rotamer B, 2xC_{Ar}), 136.02 (s, 1C, Rotamer A, C_{Ar}), 135.99 (s, 2C, Rotamer B, 2xC_{Ar}), 135.58 (s, 2C, Rotamer A, 2xC_{Ar}), 135.49 (s, 2C, Rotamer A, 2xC_{Ar}), 130.51 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 130.45 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 130.35 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 130.28 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 130.25 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 130.04 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 129.96 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 129.73 (s, 129.69 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 129.39 (d, 1C, Rotamer A, C_{Ar}<u>H</u>) 129.24 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 129.03 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 127.11 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 126.92 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 126.13 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 125.81 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 124.36 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 123.09 (s, Rotamer A, <u>C$_{Ar}$</u>), 123.82 (s, Rotamer B, <u>C$_{Ar}$</u>), 122.96 (d, 1C, Rotamer A, C_{Ar}<u>H</u>), 117.32 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 114.83 (d, 1C, Rotamer B, C_{Ar}<u>H</u>) 114.03 (d, 1C, Rotamer B, C_{Ar}<u>H</u>), 53.99 (t, 1C, Rotamer B, -<u>C</u>H$_2$-), 52.69 (t, Rotamer A, -<u>C</u>H$_2$-), 21.54 , (q, 1C, Rotamer B, -<u>C</u>H$_3$), 21.42 (q, 1C, Rotamer A, -<u>C</u>H$_3$), 21.30 (q, 1C, Rotamer A, -<u>C</u>H$_3$), 21.26 (q, 1C, Rotamer A, -<u>C</u>H$_3$), 21.24 (q, 1C, Rotamer B, -<u>C</u>H$_3$), 21.15 (q, 1C, Rotamer B, -<u>C</u>H$_3$),

19.01 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$), 18.74 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$), 18.68 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 18.41 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 18.38 (q, 2C, Rotamer A, 2x-$\underline{C}H_3$), 18.34 (q, 2C, Rotamer B, 2x-$\underline{C}H_3$);

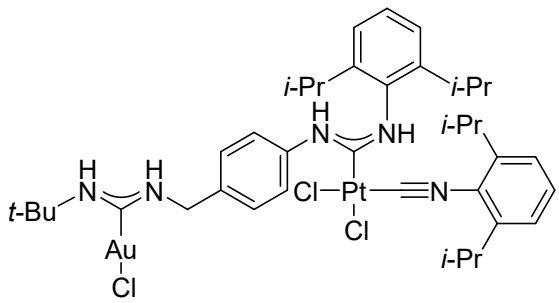
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3497.55 (s, 1Pt, Rotamer A or B), -3530.76 (s, 1Pt, Rotamer A or B);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3233 (w), 2917 (w), 2857 (w), 2189 (s), 1692 (w), 1546 (s), 1483 (m), 1379 (w), 1294 (w), 1142 (w), 1034 (w), 853 (m), 796 (w), 695 (m);

HR-MS (MALDI): $C_{37}H_{43}Au^{35}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1016.2171, found 1016.2168; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1018.2142, found 1018.2184; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 1020.2112, found 1020.2201; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1018.2188, found 1018.2184; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1020.2158, found 1020.2201; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1022.2129, found 1022.2202; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1019.2209, found 1019.2209; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1021.2179, found 1021.2202; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1023.2150, found 1023.2211; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1020.2210, found 1020.2201; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ [M-Cl]$^+$ calcd 1022.2181, found 1022.2202; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1024.2151, found 1024.2203; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1022.2240, found 1022.2202; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1024.2210, found 1024.2203; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 1026.2181, found 1026.2220;

EA calcd. for $C_{37}H_{43}Cl_3AuN_5Pt$: C: 42.08, H: 4.10, N: 6.63; found C: 42.43, H: 4.43, N: 6.59.

2.2.25 Synthesis of Gold(I) Platinum(II) Complex 3g



According to **GP6** the reaction was carried out with (((3-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (50.0 mg, 114.23 µmol, 1.00 eq.) and bis(2,6-

diisopropylphenylisonitrile) platinum(II) chloride (73.17 mg, 114.23 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (86.0 mg, 79.76 µmol, 70 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.47 mg, 102 µmol, 1.00 eq.), 4-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (65.2 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (74.0 mg, 68.63 µmol, 67 %).

m.p. = 214 – 219 °C;

^{1}H NMR (600 MHz, DMSO, 295 K) δ [ppm] = 10.85 (s, 1H, $C_{Ar}\underline{H}$), 9.58 (s, 1H, $C_{Ar}\underline{H}$), 8.28 (s, 1H, $C_{Ar}\underline{H}$), 8.24 (t, *J* = 6.1 Hz, 1H, $C_{Ar}\underline{H}$), 7.59 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 7.48 (t, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.37 (s, 1H, $C_{Ar}\underline{H}$), 7.36 (d, *J* = 2.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.33 (s, 1H, $C_{Ar}\underline{H}$), 7.32 (s, 1H, $C_{Ar}\underline{H}$), 7.24 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.03 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 6.64 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 4.77 (d, *J* = 5.9 Hz, 1H, -C$\underline{H}_2$-), 4.58 (d, *J* = 5.8 Hz, 1H, -C$\underline{H}_2$-), 3.20 – 2.99 (m, 4H, 4x-C$\underline{H}(CH_3)_2$), 1.49 (s, 9H, 3x-C$\underline{H}_3$), 1.46 (m, 12H, 4x-C$\underline{H}_3$), 1.18 (d, *J* = 6.9 Hz, 12H, 4x-C$\underline{H}_3$);

^{13}C NMR (151 MHz, DMSO, 295 K) δ [ppm] = 192.53 (s, 1C, $\underline{C}_{Carbene}$), 165.63 (s, 1C, $\underline{C}_{Carbene}$), 144.67 (s, 2C, 2x$\underline{C}_{Ar}$), 140.02 (s, 1C, $\underline{C}_{Ar}$), 136.44 (s, 1C, $\underline{C}_{Ar}$), 131.75 (s, 1C, $\underline{C}_{Ar}$), 130.62 (d, 1C, $\underline{C}_{Ar}$H), 129.05 (d, 1C, $\underline{C}_{Ar}$H), 128.68 (d, 1C, $\underline{C}_{Ar}$H), 128.35 (d, 1C, $\underline{C}_{Ar}$H), 127.42 (d, 1C, $\underline{C}_{Ar}$H), 127.15 (d, 1C, $\underline{C}_{Ar}$H), 125.89 (d, 1C, $\underline{C}_{Ar}$H), 125.77 (s, 1C, $\underline{C}_{Ar}$), 124.09 (d, 1C, $\underline{C}_{Ar}$H), 123.88 (d, 2C, 2x $\underline{C}_{Ar}$H), 123.42 (s, 1C, $\underline{C}_{Ar}$), 123.07 (s, 1C, $\underline{C}_{Ar}$), 114.98 (s, 1C, $\underline{C}_{Ar}$), 52.78 (s, 1C, -$\underline{C}(CH_3)_3$), 52.34 (t, 1C, -$\underline{C}H_2$-), 30.88 (d, 2C, 2x-$\underline{C}H(CH_3)_2$), 30.86 (d, 2C, 2x-$\underline{C}H(CH_3)_2$), 29.22 (q, 3C, 3x-$\underline{C}H_3$), 22.96 (q, 2C, 2x-$\underline{C}H_3$), 22.56 (q, 2C, 2x-$\underline{C}H_3$), 22.52 (q, 4C, 4x-$\underline{C}H_3$);

^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3539.34 (s, 1Pt);

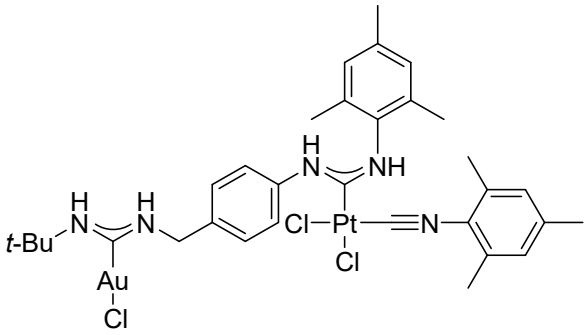
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3224 (w), 2919 (w), 2855 (w), 2185 (s), 1606 (w), 1543 (s), 1377 (w), 1294 (w), 1217 (w), 1144 (w), 1034 (w), 853 (m), 767 (w), 712 (w), 669 (w);

HR-MS (MALDI): $C_{38}H_{53}Au^{35}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1040.2970, found 1040.2924; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1042.2941, found 1042.2999; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 1044.2911, found 1044.3001; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1041.2991, found 1041.3007; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1043.2962, found 1043.3000; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 1045.2932, found 1045.3009; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1042.2993, found 1042.2999; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 1044.2963,

found 1044.3001; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1046.2934, found 1046.3002; $C_{38}H_{53}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1044.3022, found 1044.3001; $C_{38}H_{53}Au\,{}^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1046.2993, found 1046.3002; $C_{38}H_{53}Au^{37}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1048.2963, found 1048.3011;

EA calcd. for $C_{38}H_{53}Cl_3AuN_5Pt$: C: 42.33, H: 4.95, N: 6.50; found C: 42.53, H: 4.48, N: 6.48.

2.2.26 Synthesis of Gold(I) Platinum(II) Complex 3h.



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (50.0 mg, 114.23 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (63.56 mg, 114.23 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (82.0 mg, 82.49 µmol, 72 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.47 mg, 102 µmol, 1.00 eq.), 4-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,4,6-trimethylphenyl) platinum(II) chloride (56.67 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (71.0 mg, 71.42 µmol, 70 %).

m.p. = 212 – 217 °C;

^{1}H NMR (700 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.56 (d, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.78 (d, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.65 (d, *J* = 7.6 Hz, 1H, $C_{Ar}\underline{H}$), 7.52 (t, *J* = 7.7 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.33 (d, *J* = 7.5 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.05 (d, *J* = 7.5 Hz, 2H, 2x$C_{Ar}\underline{H}$), 6.99 (d, *J* = 7.6 Hz, 1H, $C_{Ar}\underline{H}$), 6.86 (d, *J* = 7.5 Hz, 2H, 2x$C_{Ar}\underline{H}$), 4.68 (s, 2H, -C$\underline{H_2}$-), 2.43 (s, 1H), 2.42 (s, 1H), 2.37 – 2.34 (m, 1H, -C$\underline{H_3}$), 2.34 (s, 3H, -C$\underline{H_3}$), 2.33 (s, 1H), 2.32 – 2.30 (m, 3H, -C$\underline{H_3}$), 2.26 - 2.25 (m, 3H, -C$\underline{H_3}$), 2.22 – 2.12 (m, 6H, 2x-C$\underline{H_3}$), 2.13 (s, 3H, -C$\underline{H_3}$), 2.12 (s, 2H, 2x-C$\underline{H_3}$), 1.50 (s, 9H, 3x-C$\underline{H_3}$);

^{13}C NMR (176 MHz, CD_2Cl_2, 295 K) δ [ppm] = 188.71 (s, 1C, $\underline{C}_{Carbene}$), 167.83 (s, 1C, $\underline{C}_{Carbene}$), 141.83 (s, 1C, $\underline{C}_{Ar}$), 140.84 (s, 2C, 2x$\underline{C}_{Ar}$), 140.58 (s, 1C, $\underline{C}_{Ar}$), 138.73 (s, 1C, $\underline{C}_{Ar}$), 138.44 (s,

1C, $\underline{C}_{Ar}$), 136.29 (s, 1C, $\underline{C}_{Ar}$), 135.54 (s, 1C, $\underline{C}_{Ar}$), 130.65 (d, 1C, $\underline{C}_{Ar}H$), 129.52 (s, 1C, $\underline{C}_{Ar}$), 129.38 (d, 1C, $\underline{C}_{Ar}H$), 129.14 (d, 1C, $\underline{C}_{Ar}H$), 128.99 (d, 1C, $\underline{C}_{Ar}H$), 128.77 (d, 1C, $\underline{C}_{Ar}H$), 126.33 (d, 1C, $\underline{C}_{Ar}H$), 126.09 (s, 1C, $\underline{C}_{Ar}$), 125.29 (d, 1C, $\underline{C}_{Ar}H$), 123.74 (s, 1C, $\underline{C}_{Ar}$), 100.96 (d, 1C, $\underline{C}_{Ar}H$), 54.20 (s, 1C, -$\underline{C}(CH_3)_3$), 53.14 (t, 1C, -$\underline{C}H_2$-), 31.50 (q, 3C, 3x-$\underline{C}H_3$), 21.44 (q, 1C, -$\underline{C}H_3$), 21.21 (q, 1C, -$\underline{C}H_3$), 18.76 (q, 2C, 2x-$\underline{C}H_3$), 18.38 (q, 2C, 2x-$\underline{C}H_3$);

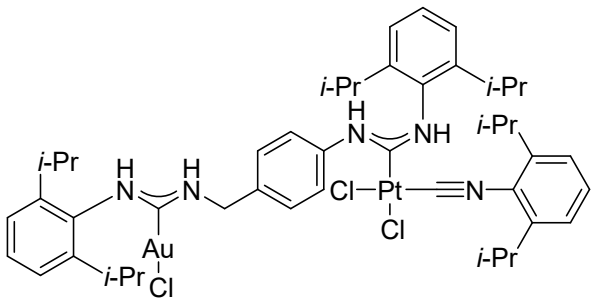
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3551.56 (s, 1Pt);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3266 (w), 2962 (w), 2919 (w), 2860 (w), 2192 (s), 1543 (s), 1475 (m), 1395 (w), 1365 (w), 1309 (w), 1199 (m), 1034 (w), 939 (w), 852 (m), 712 (w);

HR-MS (MALDI): $C_{32}H_{41}Au^{35}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 954.2015, found 954.2017; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 956.1985, found 956.2036; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{192}Pt$ [M-Cl]$^+$ calcd. 958.1956, found 958.1294; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 956.2031, found 956.2036; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 958.2002, found 958.2051; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{194}Pt$ [M-Cl]$^+$ calcd. 960.1972, found 960.2052; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 957.2052, found 957.2060; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ [M-Cl]$^+$ calcd. 959.2023, found 959.2050; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{195}Pt$ [M-Cl]$^+$ calcd. : 961.1993, found 961.2059; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 958.2054, found 958.2051; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 960.2024, found 960.2052; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{196}Pt$ [M-Cl]$^+$ calcd. 962.1995, found 962.2049; $C_{32}H_{41}Au^{35}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 960.2083, found 960.2052; $C_{32}H_{41}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 962.2054, found 962.2049; $C_{32}H_{41}Au^{37}Cl_2N_5{}^{198}Pt$ [M-Cl]$^+$ calcd. 964.2024, found 964.2063;

EA calcd. for $C_{32}H_{41}Cl_3AuN_5Pt$: C: 38.66, H: 4.16, N: 7.04; found C: 37.53, H: 4.21, N: 6.80.

2.2.27 Synthesis of Gold(I) Platinum(II) Complex 3i



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 92.27 µmol, 1.00 eq.) and

bis(2,6-diisopropylphenylisonitrile) platinum(II) chloride (59.11 mg, 92.27 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (87.0 mg, 73.58 µmol, 80 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (19.08 mg, 102 µmol, 1.00 eq.), 4-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (65.2 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (88 mg, 74.4 µmol, 73 %).

mp = 215 – 220 °C;

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.65 (s, 1H, $C_{Ar}H$), 8.01 – 7.84 (m, 1H, $C_{Ar}H$), 7.64 – 7.59 (m, 1H, $C_{Ar}H$), 7.48 (q, *J* = 7.1 Hz, 1H, $C_{Ar}H$), 7.41 – 7.36 (m, 2H, 2x$C_{Ar}H$), 7.36 – 7.32 (m, 2H, 2x$C_{Ar}H$), 7.28 (t, *J* = 8.2 Hz, 2H, 2x$C_{Ar}H$), 7.22 (dd, *J* = 7.8, 4.0 Hz, 3H, 3x$C_{Ar}H$), 7.16 (d, *J* = 7.8 Hz, 1H, $C_{Ar}H$), 7.08 (d, *J* = 8.5 Hz, 1H, $C_{Ar}H$), 6.73 (d, *J* = 8.3 Hz, 1H, $C_{Ar}H$), 6.23 – 6.09 (m, 1H, $C_{Ar}H$), 4.80 (d, *J* = 6.2 Hz, 1H, -C$\underline{H}_2$-), 4.76 (d, *J* = 6.1 Hz, 1H, -C$\underline{H}_2$-), 3.34 (pd, *J* = 6.9, 1.7 Hz, 2H, C$\underline{H}$), 3.12 – 2.94 (m, 4H, C$\underline{H}$), 1.30 (d, *J* = 6.9 Hz, 3H, -C$\underline{H}_3$), 1.22 (t, *J* = 6.8 Hz, 9H, 3x-C$\underline{H}_3$), 1.15 (dt, *J* = 6.8, 5.0 Hz, 15H, 5x-C$\underline{H}_3$), 1.07 (dd, *J* = 10.2, 6.9 Hz, 9H, 3x-C$\underline{H}_3$);

^{13}C NMR (101 MHz, CD_2Cl_2, 295 K) δ [ppm] = 192.42 (s, 1C, $C_{Carbene}$), 170.20 (s, 1$C_{Carbene}$), 147.18 (s, 2C, 2x$\underline{C}_{Ar}$), 146.91 (s, 2C, 2x$\underline{C}_{Ar}$), 146.78 (s, 1C, $\underline{C}_{Ar}$), 145.94 (s, 1C, $\underline{C}_{Ar}$), 139.24 (s, 1C, $\underline{C}_{Ar}$), 136.39 (s, 1C, $\underline{C}_{Ar}$), 131.72 (s, 1C, $\underline{C}_{Ar}$), 131.28 (d, 1C, $\underline{C}_{Ar}H$), 130.92 (d, 1C, $\underline{C}_{Ar}\underline{H}$), 130.84 (d, 1C, $\underline{C}_{Ar}H$), 130.73 (d, 1C, $\underline{C}_{Ar}H$), 129.87 (s, 1C, $\underline{C}_{Ar}$), 129.58 (s, 1C, $\underline{C}_{Ar}$), 129.48 (s, 1C, $\underline{C}_{Ar}$), 129.30 (d, 1C, $\underline{C}_{Ar}H$), 128.99 (d, 1C, $\underline{C}_{Ar}H$), 125.63 (d, 1C, $\underline{C}_{Ar}H$), 125.37 (d, 1C, $\underline{C}_{Ar}H$), 125.33 (d, 1C, $\underline{C}_{Ar}H$), 125.18 (d, 1C, $\underline{C}_{Ar}H$), 124.33 (d, 1C, $\underline{C}_{Ar}H$), 124.05 (d, 1C, $\underline{C}_{Ar}H$), 116.67 (d, 1C, $\underline{C}_{Ar}H$), 53.52 (t, 1C, -$\underline{C}H_2$-), 30.39 (d, 1C, -$\underline{C}H(CH_3)_3$), 29.98 (d, 2C, 2x-$\underline{C}H(CH_3)_3$), 29.15 (d, 2C, 2x-$\underline{C}H(CH_3)_3$), 29.05 (d, 1C, -$\underline{C}H(CH_3)_3$), 24.79 (q, 2C, 2x-$\underline{C}H_3$), 24.74 (q, 1C, -$\underline{C}H_3$), 24.62 (q, 1C, -$\underline{C}H_3$), 23.54 (q, 1C, -$\underline{C}H_3$), 23.28 (q, 1C, -$\underline{C}H_3$), 23.19 (q, 2C, 2x-$\underline{C}H_3$), 23.01 (q, 2C, 2x-$\underline{C}H_3$), 22.85 (q, 2C, 2x-$\underline{C}H_3$);

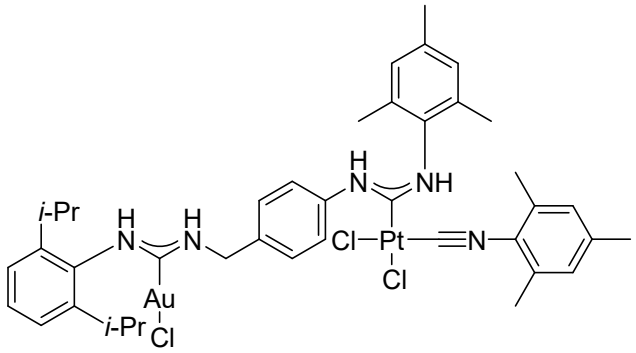
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3524.06 (s, 1Pt);

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3215 (w), 2963 (m), 2927 (w), 2868 (w), 2186 (m), 1592 (w), 1543 (s), 1462 (m), 1385 (w), 1364 (w), 1331 (w), 1300 (w), 1216 (w), 1181 (m), 1108 (m), 1058 (w), 1018 (w), 936 (w), 800 (m), 749 (m), 669 (w);

HR-MS (EI (+)): $C_{46}H_{61}Au^{35}Cl_2N_5{}^{192}Pt$ $[M]^+$ calcd. 1142.3580, found 1142.3568; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M]^+$ calcd. 1144.3550, found 1144.3592; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{192}Pt$ calcd. 1146.3521, found 1146.3616; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{194}Pt$ $[M]^+$ calcd. 1144.3596, found 1144.3592; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M]^+$ calcd. 1146.3567, found 1146.3616; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{194}Pt$ $[M]^+$ calcd. 1148.3537, found 1148.3616; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{195}Pt$ $[M]^+$ calcd. 1145.3617, found 1145.3618; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M]^+$ calcd. 1147.3588, found 1147.3617; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{195}Pt$ $[M]^+$ calcd. 1149.3558, found 1149.3626; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{196}Pt$ $[M]^+$ calcd. 1146.3619, found 1146.3616; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M]^+$ calcd. 1148.3589, found 1148.3616; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{196}Pt$ $[M]^+$ calcd. 1150.3560, found 1150.3620; $C_{46}H_{61}Au^{35}Cl_2N_5{}^{198}Pt$ $[M]^+$ calcd. 1148.3648, found 1148.3616; $C_{46}H_{61}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M]^+$ calcd. 1150.3619, found 1150.3620; $C_{46}H_{61}Au^{37}Cl_2N_5{}^{198}Pt$ $[M]^+$ calcd. 1152.3589, found 1152.3641;

EA calcd. for $C_{46}H_{61}Cl_3AuN_5Pt$: C: 46.73, H: 5.20, N: 5.92; found C: 46.68, H: 5.38, N: 6.15.

2.2.28 Synthesis of Gold(I) Platinum(II) Complex 3j



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 92.27 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (51.34 mg, 92.27 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (85.0 mg, 77.39 µmol, 84 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (19.08 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,4,6-trimethylphenyl) platinum(II) chloride (56.67 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (74.0 mg, 67.38 µmol, 66 %).

m.p. = 194 – 199 °C;

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.76 – 8.06 (m, 2H, 2x$C_{Ar}\underline{H}$), 7.59 (d, *J* = 8.5 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.44 – 7.32 (m, 2H, 2x$C_{Ar}\underline{H}$), 7.26 (d, *J* = 8.5 Hz, 1H, $C_{Ar}\underline{H}$), 7.22 (d, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.18 (d, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.07 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 7.05 (s, 1H, $C_{Ar}\underline{H}$), 7.00 (s, 3H, 3x$C_{Ar}\underline{H}$), 6.91 (s, 1H, $C_{Ar}\underline{H}$), 6.71 (d, *J* = 6.9 Hz, 1H, $C_{Ar}\underline{H}$), 6.27 – 6.08 (m, 1H, $C_{Ar}\underline{H}$), 4.82 (d, *J* = 6.2 Hz, 1H, -C$\underline{H}_2$-), 4.75 (d, *J* = 6.1 Hz, 1H, -C$\underline{H}_2$-), 3.10 – 3.00 (m, 2H, -C$\underline{H}(CH_3)_2$), 2.43 (d, *J* = 2.0 Hz, 6H, 2x-C$\underline{H}_3$), 2.34 (s, 3H, -C$\underline{H}_3$), 2.32 (s, 6H, 2x-C$\underline{H}_3$), 2.16 (s, 3H, -C$\underline{H}_3$), 1.16 (d, *J* = 6.7 Hz, 3H, -C$\underline{H}_3$), 1.13 (d, *J* = 6.7 Hz, 3H, -C$\underline{H}_3$), 1.08 (d, *J* = 6.9 Hz, 3H, -C$\underline{H}_3$), 1.05 (d, *J* = 6.9 Hz, 3H, -C$\underline{H}_3$);

^{13}C NMR (151 MHz, CD_2Cl_2, 295 K) δ [ppm] = 190.87 (s, 1C, $\underline{C}_{Carbene}$), 169.30 (s, 1C, $\underline{C}_{Carbene}$), 146.82 (s, 1C, $\underline{C}_{Ar}$), 146.69 (s, 2C, 2x$\underline{C}_{Ar}$), 141.80, (s, 1C, $\underline{C}_{Ar}$) 140.66 (s, 1C, $\underline{C}_{Ar}$), 140.40 (s, 1C, $\underline{C}_{Ar}$), 139.25 (s, 1C, $\underline{C}_{Ar}$), 136.37 (s, 1C, $\underline{C}_{Ar}$), 136.32 (s, 1C, $\underline{C}_{Ar}$), 136.23 (s, 1C, $\underline{C}_{Ar}$), 135.46 (s, 1C, $\underline{C}_{Ar}$), 130.74 (d, 1C, $\underline{C}_{Ar}$H), 130.61 (d, 1C, $\underline{C}_{Ar}$H), 130.54 (d, 1C, $\underline{C}_{Ar}$H), 129.91 (s, 1C, $\underline{C}_{Ar}$), 129.74 (s, 1C, $\underline{C}_{Ar}$), 129.60 (s, 1C, $\underline{C}_{Ar}$), 129.36 (d, 1C, $\underline{C}_{Ar}$H), 129.19 (d, 1C, $\underline{C}_{Ar}$H), 129.13 (d, 1C, $\underline{C}_{Ar}$H), 128.76 (d, 1C, $\underline{C}_{Ar}$H), 125.76 (d, 1C, $\underline{C}_{Ar}$H), 125.16 (d, 1C, $\underline{C}_{Ar}$H), 125.10 (d, 1C, $\underline{C}_{Ar}$H), 100.93 (d, 1C, $\underline{C}_{Ar}$H), 53.34 (t, 1C, -$\underline{C}H_2$-), 31.26 (q, 1C, -$\underline{C}H_3$), 29.09 (d, 2C, 2x-$\underline{C}H(CH_3)_2$), 24.80 (q, 1C, -$\underline{C}H_3$), 24.76 (q, 1C, -$\underline{C}H_3$), 23.22 (q, 1C, -$\underline{C}H_3$), 23.15 (q, 1C, -$\underline{C}H_3$), 21.52 (q, 1C, -$\underline{C}H_3$), 21.44 (q, 1C, -$\underline{C}H_3$), 21.19 (q, 1C, -$\underline{C}H_3$), 18.72 (q, 1C, -$\underline{C}H_3$), 18.36 (q, 1C,-$\underline{C}H_3$);

^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3536.97 (s, 1Pt);

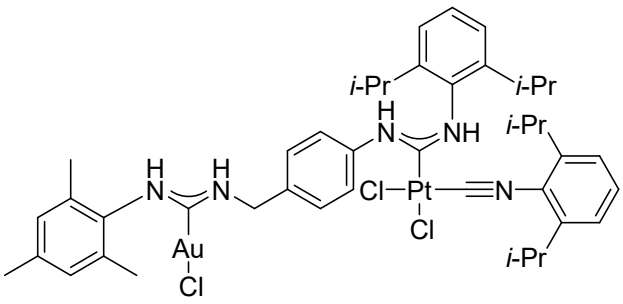
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3221 (w), 2962 (w), 2923 (w), 2865 (w), 2187 (s), 1594 (w), 1543 (s), 1382 (w), 1308 (w), 1218 (w), 1057 (w), 936 (w), 854 (w), 807 (m), 783 (m), 712 (w), 669 (w);

HR-MS (MALDI): $C_{40}H_{49}Au^{35}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1058.2641, found 1058.2630; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1060.2611, found 1060.2649; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2582, found 1062.2667; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1060.2657, found 1060.2649; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2628, found 1062.2667; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2598, found 1064.2668; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1061.2678, found 1061.2674; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1063.2649, found 1063.2669; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1065.2619, found 1065.2677; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1062.2680, found 1062.2667; $C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2650, found 1064.2668; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1066.2621, found 1066.2669; $C_{40}H_{49}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1064.2709, found 1064.2668;

$C_{40}H_{49}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1066.2680, found 1066.2669; $C_{40}H_{49}Au^{37}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1068.2650, found 1068.2686;

EA calcd. for $C_{40}H_{49}Cl_3AuN_5Pt$: C: 43.75, H: 4.50, N: 6.38; found C: 43.71, H: 5.06, N: 6.64.

2.2.29 Synthesis of Gold(I) Platinum(II) Complex 3k



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)((2,4,6-trimethylphenyl)amino)methylene)gold(I) chloride (50.0 mg, 100.04 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) platinum(II) chloride (64.08 mg, 100.04 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (79.0 mg, 75.12 µmol, 75 % yield).

According to **GP7** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (30 mg, 102 µmol, 1.00 eq.), 2,4,6-trimethylphenyl isocyanide (14.79 mg, 102 µmol, 1.00 eq.), 3-aminobenzylamine (12.4 mg, 102 µmol,1.00 eq.) and bis(2,6-diisopropylphenyl) platinum(II) chloride (56.2 mg, 102 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (69.0 mg, 65.61 µmol, 64 %).

m.p. > 300 °C;

^{1}H NMR (700 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.58 (s, 1H, $C_{Ar}\underline{H}$), 7.92 (s, 1H, $C_{Ar}\underline{H}$), 7.77 (s, 1H, $C_{Ar}\underline{H}$), 7.65 – 7.59 (m, 2H, 2x$C_{Ar}\underline{H}$), 7.48 (dt, *J* = 9.9, 7.7 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.38 (t, *J* = 7.9 Hz, 1H, $C_{Ar}\underline{H}$), 7.35 (d, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.27 (t, *J* = 7.5 Hz, 1H, $C_{Ar}\underline{H}$), 7.17 (d, *J* = 7.8 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.04 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 6.93 (s, 1H, $C_{Ar}\underline{H}$), 6.60 (d, *J* = 8.4 Hz, 1H, $C_{Ar}\underline{H}$), 6.24 (t, *J* = 6.2 Hz, 1H, $C_{Ar}\underline{H}$), 4.81 (d, *J* = 6.2 Hz, 1H, -C$\underline{H}_2$-), 4.73 (d, *J* = 6.2 Hz, 1H, -C$\underline{H}_2$-), 3.34 (hept, *J* = 6.8 Hz, 3H, 3x-C$\underline{H}(C\underline{H}_3)_3$), 3.05 (hept, *J* = 6.8 Hz, 1H, 3x-C$\underline{H}(C\underline{H}_3)_3$), 2.27 – 2.11 (m, 9H, 3x-CH_3), 1.30 (d, *J* = 7.0 Hz, 12H, 4x-C$\underline{H}_3$), 1.22 (d, *J* = 4.5 Hz, 3H, -C$\underline{H}_3$), 1.21 (d, *J* = 4.5 Hz, 3H, -C_{H3}), 1.16 (d, *J* = 6.8 Hz, 6H, 2x-C$\underline{H}_3$);

^{13}C NMR (176 MHz, CD_2Cl_2, 295 K) δ [ppm] = 191.37 (s, 1C, $\underline{C}_{Carbene}$), 169.82 (s, 1C, $\underline{C}_{Carbene}$), 146.74 (s, 1C, $\underline{C}_{Ar}$), 146.68 (s, 1C, $\underline{C}_{Ar}$), 146.26 (s, 1C, $\underline{C}_{Ar}$), 145.52 (s, 1C, $\underline{C}_{Ar}$), 139.61 (s, 1C,

$\underline{C}_{Ar}$), 139.42 (s, 1C, $\underline{C}_{Ar}$), 138.62 (s, 1C, $\underline{C}_{Ar}$), 136.45 (s, 1C, $\underline{C}_{Ar}$), 135.69 (s, 1C, $\underline{C}_{Ar}$), 135.52 (s, 1C, $\underline{C}_{Ar}$), 131.29 (s, 1C, $\underline{C}_{Ar}$), 130.86 (d, 1C, $\underline{C}_{Ar}H$), 130.39 (d, 1C, $\underline{C}_{Ar}H$), 129.95 (d, 1C, $\underline{C}_{Ar}H$), 129.81 (d, 1C, $\underline{C}_{Ar}H$), 129.64 (d, 1C, $\underline{C}_{Ar}H$), 129.41 (s, 1C, $\underline{C}_{Ar}$), 129.01 (s, 1C, $\underline{C}_{Ar}$), 128.69 (d, 1C, $\underline{C}_{Ar}H$), 128.18 (d, 1C, $\underline{C}_{Ar}H$), 125.18 (d, 1C, $\underline{C}_{Ar}H$), 125.09 (d, 1C, $\underline{C}_{Ar}H$), 123.89 (d, 1C, $\underline{C}_{Ar}H$), 123.58 (d, 1C), 114.92 (d, 1C), 52.70 (t, 1C, -$\underline{C}H_2$-), 29.95 (d, 2C, 2x-$\underline{C}H(CH_3)_2$), 29.55 (d, 1C, -$\underline{C}H(CH_3)_2$), 28.61 (d, 1C, -$\underline{C}H(CH_3)_2$), 24.20 (q, 2C, 2x-$\underline{C}H_3$), 23.12 (q, 2C, 2x-$\underline{C}H_3$), 22.62 (q, 2C, 2x-$\underline{C}H_3$), 22.42 (q, 2C, 2x-$\underline{C}H_3$), 20.71 (q, 1C, -$\underline{C}H_3$), 17.91 (q, 2C, 2x-$\underline{C}H_3$);

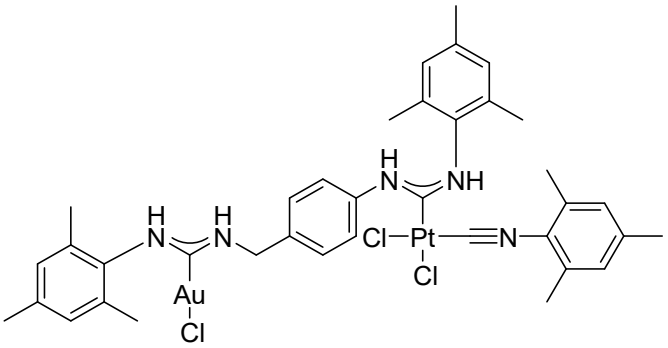
^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3532.08 (s, 1Pt).

IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3242 (m), 2964 (s), 2872 (m), 2188 (w), 1718 (s), 1660 (w), 1608 (w), 1551 (s), 1488 (w), 1460 (w), 1385 (w), 1365 (w), 1315 (w), 1183 (w), 1062 (m), 1035 (m), 954 (w), 855 (w), 801 (w), 750 (w), 695 (w);

HR-MS (ESI (+)): $C_{43}H_{55}Au^{35}Cl_2N_5{}^{192}Pt$ $[M-Cl]^+$ calcd. 1100.3110, found 1100.3116; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M-Cl]^+$ calcd. 1102.3081, found 1102.3139; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{192}Pt$ $[M-Cl]^+$ calcd. 1104.3051, found 1104.3158; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{194}Pt$ $[M-Cl]^+$ calcd. 1102.3127, found 1102.3139; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M-Cl]^+$ calcd. 1104.3097, found 1104.3158; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{194}Pt$ $[M-Cl]^+$ calcd. 1106.3068, found 1106.3159; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{195}Pt$ $[M-Cl]^+$ calcd. 1103.3148, found 1103.3165; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M-Cl]^+$ calcd. 1105.3118, found 1105.3160; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{195}Pt$ $[M-Cl]^+$ calcd. 1107.3089, found 1107.3169; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{196}Pt$ $[M-Cl]^+$ calcd. 1104.3149, found 1104.3158; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M-Cl]^+$ calcd. 1106.3120, found 1106.3159; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{196}Pt$ $[M-Cl]^+$ calcd. 1108.3090, found 1108.3162; $C_{43}H_{55}Au^{35}Cl_2N_5{}^{198}Pt$ $[M-Cl]^+$ calcd. 1106.3179, found 1106.3159; $C_{43}H_{55}Au\,{}^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M-Cl]^+$ calcd. 1108.3149, found 1108.3090; $C_{43}H_{55}Au^{37}Cl_2N_5{}^{198}Pt$ $[M-Cl]^+$ calcd. 1110.3120, found 1110.3183;

EA calcd. for $C_{43}H_{55}Cl_3AuN_5Pt$: C: 45.29, H: 4.86, N: 6.14; found C: 45.57, H: 5.00, N: 6.31.

2.2.30 Synthesis of Gold(I) Platinum(II) Complex 3l



According to **GP6** the reaction was carried out with (((4-aminobenzyl)amino)(2,4,6-trimethylphenylamino)methylene)gold(I) chloride (50.0 mg, 100.04 µmol, 1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) platinum(II) chloride (55.66 mg, 100.04 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (83.0 mg, 83.49 µmol, 83 % yield).

m.p. = 264 – 269 °C;

^{1}H NMR (700 MHz, CD_2Cl_2, 295 K) δ [ppm] = 8.56 (s, 1H, $C_{Ar}\underline{H}$), 7.95 (s, 1H, $C_{Ar}\underline{H}$), 7.55 (s, 1H, $C_{Ar}\underline{H}$), 7.54 – 7.44 (m, 2H, 2x $C_{Ar}\underline{H}$), 7.31 – 7.11 (m, 2H, 2x$C_{Ar}\underline{H}$), 6.97 – 6.90 (m, 3H, 3x$C_{Ar}\underline{H}$), 6.80 (d, *J* = 12.2 Hz, 3H, 3x$C_{Ar}\underline{H}$), 6.20 (t, *J* = 6.4 Hz, 1H, $C_{Ar}\underline{H}$), 4.73 (d, *J* = 6.4 Hz, 2H, -$C\underline{H}_2$-), 2.35 (s, 2H, 2x-$C\underline{H}_3$), 2.26 (s, 6H), 2.24 (m, 3H, -$C\underline{H}_3$), 2.19 (s, 4H, -CH_3 and $C\underline{H}_3$), 2.12 (m, 4H, -CH_3 and $C\underline{H}_3$), 2.07 (s, 6H, 2x-$C\underline{H}_3$), 2.03 (s, 3H, -$C\underline{H}_3$);

^{13}C NMR (176 MHz, CD_2Cl_2, 295 K) δ [ppm] = 191.43 (s, 1C), 169.29 (s, 1C), 141.81 (s, 1C), 140.62 (s, 1C), 140.40 (s, 1C), 139.91 (s, 1C), 139.18 (s, 1C), 136.88 (s, 1C), 136.71 (s, 1C), 136.35 (s, 1C), 136.25 (s, 1C), 135.94 (s, 1C), 135.51 (s, 1C), 130.59 (d, 1C), 130.54 (d, 1C), 130.26 (d, 1C), 129.94 (s, 1C), 129.65 (s, 1C), 129.37 (d, 1C), 129.26 (d, 1C), 129.12 (d, 1C), 128.56 (d, 1C), 125.82 (d, 1C), 125.61 (s, 1C), 123.99 (s, 1C), 115.36 (d, 1C), 100.96 (d, 1C), 31.27 (t, 1C), 21.44 (q, 1C), 21.20 (q, 1C), 21.08 (q, 1C), 18.73 (q, 2C), 18.37 (q, 2C), 18.30 (q, 2C);

^{195}Pt NMR (86 MHz, CD_2Cl_2, 295 K) δ [ppm] = -3539.34 (s, 1Pt);

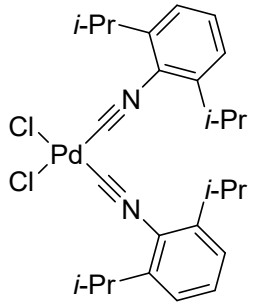
IR (ATR) $\tilde{\nu}$ [cm^{-1}] = 3224 (w), 2919 (w), 2855 (w), 2185 (m), 1606 (w), 1543 (s), 1377 (w), 1294 (w), 1217 (w), 1144 (w), 1034 (w), 853 (m), 767 (w), 712 (w), 669 (w);

HR-MS (MALDI): $C_{37}H_{43}Au^{35}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1016.2171, found 1016.2166; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1018.2142, found 1018.2182; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{192}Pt$ $[M\text{-}Cl]^+$ calcd. 1020.2112, found 1020.2200; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1018.2188,

found 1018.2182; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1020.2158, found 1020.2200; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{194}Pt$ $[M\text{-}Cl]^+$ calcd. 1022.2129, found 1022.2200; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1019.2209, found 1019.2207; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1021.2179, found 1021.2199; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{195}Pt$ $[M\text{-}Cl]^+$ calcd. 1023.2150, found 1023.2209; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1020.2210, found 1020.2200; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd 1022.2181, found 1022.2200; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{196}Pt$ $[M\text{-}Cl]^+$ calcd. 1024.2151, found 1024.2202; $C_{37}H_{43}Au^{35}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1022.2240, found 1022.2200; $C_{37}H_{43}Au^{35}Cl^{37}ClN_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1024.2210, found 1024.2202; $C_{37}H_{43}Au^{37}Cl_2N_5{}^{198}Pt$ $[M\text{-}Cl]^+$ calcd. 1026.2181, found 1026.2222;

EA calcd. for $C_{37}H_{43}Cl_3AuN_5Pt$: C: 42.08, H: 4.10, N: 6.63; found C: 42.25, H: 4.27, N: 6.61.

2.2.31 Synthesis of Bis((2,6-diisopropylphenyl)isonitrile)palladium(II) chloride (4a)

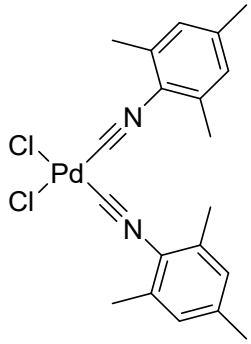


According to **GP8** the reaction was carried out with bis(acetonitrile)palladium chloride (150 mg, 509 µmol, 1.00 eq.) and 2,6-diisopropylphenyl isocyanide (104 mg, 509 µmol, 1.00 eq.) to obtain title compound as a colorless solid (176 mg, 404 µmol, 80 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ [ppm] = 7.38 (t, J=7.77 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.16 (d, J=7.78 Hz, 4H, 4x$C_{Ar}\underline{H}$), 3.29 (sept., J=6.91 Hz, 4H, 4x$C\underline{H}$), 1.22 (d, J=6.89 Hz, 24H, 8x-$C\underline{H}_3$).

2.2.32 Synthesis of Bis(mesitylisonitrile)palladium(II) chloride (4b)

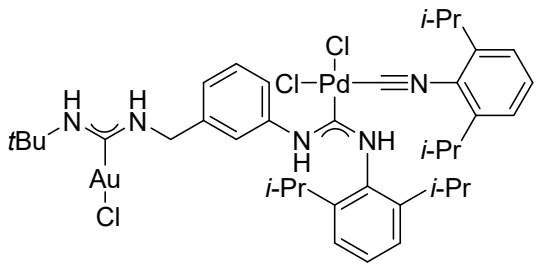


According to **GP8** the reaction was carried out with bis(acetonitrile)palladium chloride (150 mg, 509 µmol, 1.00 eq.) and mesityl isocyanide (104 mg, 509 µmol, 1.00 eq.) to obtain title compound as a colorless solid (176 mg, 404 µmol, 80 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (300 MHz, $CDCl_3$, 295 K): δ [ppm] = 6.94 (s, 4H, 4x$C_{Ar}\underline{H}$), 2.44 (s, 12H, 4x-C$\underline{H_3}$), 2.32 (s, 6H, 2x-C$\underline{H_3}$).

2.2.33 Synthesis of Gold(I) Palladium(II) Complex 5a



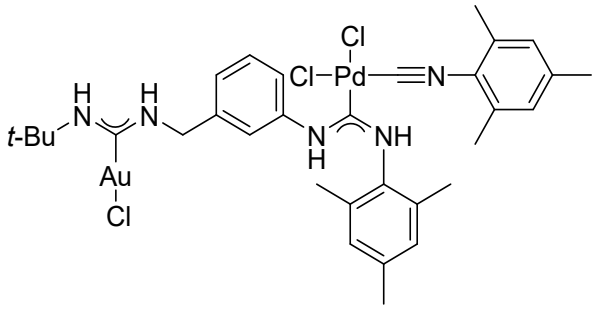
According to **GP9** the reaction was carried out with (((3-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (65.7 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol µmol, 1.00 eq.) Title compound was obtained as a colorless solid (123 mg, 124 µmol, 83 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (500 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.11 – 8.20 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 8.15 – 7.78 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.77 – 7.57 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.41 – 7.24 (m, 6H, Rotamers A and B, 6x$C_{Ar}\underline{H}$), 7.24 – 7.05 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 7.05 – 6.58 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 5.17 – 4.11 (m, 2H, Rotamers

A and B, -C$\underline{H}_2$-), 3.43 – 2.74 (m, 4H, Rotamers A and B, 4xC$\underline{H}$), 1.53 – 1.38 (m, 9H, Rotamers A, and B, 3x-C$\underline{H}_3$), 1.30 – 1.07 (m, 24H, Rotamers A and B, 8x-C$\underline{H}_3$);

2.2.34 Synthesis of Gold(I) Palladium(II) Complex 5c

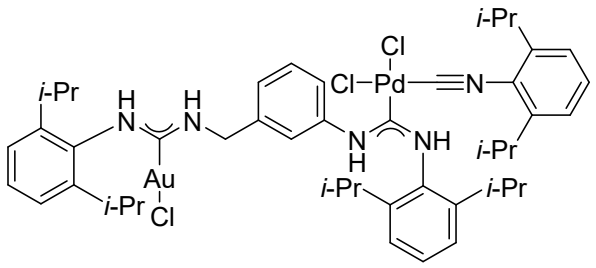


According to **GP9** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (29.5 mg, 100 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.41 mg, 100 µmol, 1.00 eq.), 3-aminobenzylamine (12.2 mg, 100 µmol,1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) palladium(II) chloride (46.8 mg, 100 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (70.0 mg, 77.8 µmol, 78 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.92 – 9.73 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 9.05 – 8.78 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.95 – 7.85 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.71 – 7.58 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.47 (t, J = 5.7 Hz, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.32 – 7.11 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 7.05 – 6.95 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 6.87 – 6.73 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 5.16 – 4.65 (m, 2H, Rotamers A and B, -C$\underline{H}_2$-), 2.45 – 2.21 (m, 18H, Rotamers A and B, 6x-C$\underline{H}_3$), 1.47 – 1.34 (m, 9H, Rotamers A and B, 3x-C$\underline{H}_3$);

2.2.35 Synthesis of Gold(I) Palladium(II) Complex 5c

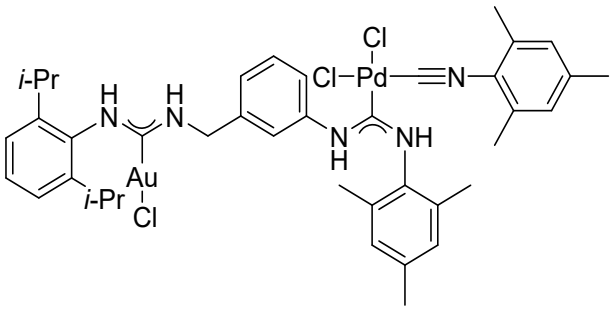


According to **GP9** the reaction was carried out with (((3-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (81.2 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (128 mg, 117 µmol, 78 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.37 – 8.78 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 8.19 – 7.83 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.83 – 7.52 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.53 – 7.02 (m, 12H, Rotamers A and B, 12x$C_{Ar}\underline{H}$), 6.91 – 6.50 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 5.18 – 4.51 (m, 2H, Rotamers A and B, -$C\underline{H_2}$-), 3.49 – 2.81 (m, 6H, Rotamers A and B, 2x-$C\underline{H_3}$), 1.34 – 0.91 (m, 36H, Rotamers A and B, 12x-$C\underline{H_3}$);

2.2.36 Synthesis of Gold(I) Palladium(II) Complex 5d

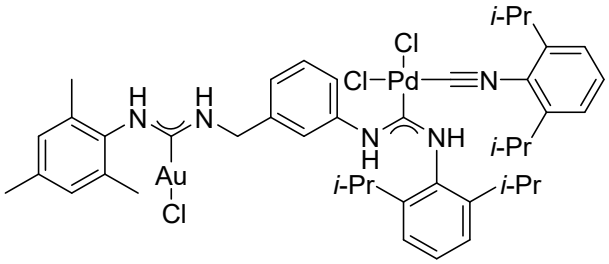


According to **GP9** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (29.5 mg, 100 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (18.8 mg, 100 µmol, 1.00 eq.), 3-aminobenzylamine (12.2 mg, 100 µmol,1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) palladium(II) chloride (46.8 mg, 100 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (72.0 mg, 71.3 µmol, 71 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.28 – 8.28 (m, 2H, Rotamers A and B, $C_{Ar}\underline{H}$), 8.01 – 7.66 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.59 – 7.24 (m, 5H, Rotamers A and B, 5x$C_{Ar}\underline{H}$), 7.23 – 6.88 (m, 6H, Rotamers A and B, 6x$C_{Ar}\underline{H}$), 6.87 – 6.15 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 5.34 – 4.72 (m, 2H, Rotamers A and B, -$C\underline{H_2}$-), 3.46 – 3.00 (m, 2H, Rotamers A and B, 2x$C\underline{H}$), 2.65 – 2.10 (m, 18H, Rotamers A and B, 6x-CH_3), 1.50 – 0.99 (m, 12H, Rotamers A and B, 4x-CH_3).

2.2.37 Synthesis of Gold(I) Palladium(II) Complex 5e

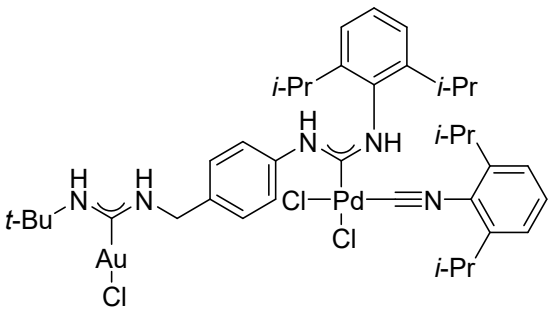


According to **GP9** the reaction was carried out with (((3-aminobenzyl)amino)(mesitylamino)methyl)gold(I) chloride (75.0 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (126 mg, 120 µmol, 80 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.17 (s, 1H, Rotamer A, $C_{Ar}\underline{H}$), 8.87 (s, 1H, Rotamer B, $C_{Ar}\underline{H}$), 8.18 – 7.55 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 7.51 – 7.08 (m, 9H, Rotamers A and B, 9x$C_{Ar}\underline{H}$), 6.96 – 6.81 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 6.69 – 6.52 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 5.18 – 4.65 (m, 2H, Rotamers A and B, -$C\underline{H}_2$-), 3.40 – 2.79 (m, 4H, Rotamers A and B, 4x$C\underline{H}$), 2.40 – 2.01 (m, 9H, Rotamers A and B, 3x-$C\underline{H}_3$), 1.34 – 1.00 (m, 24H, Rotamers A and B, 8x-$C\underline{H}_3$).

2.2.38 Synthesis of Gold(I) Palladium(II) Complex 5f

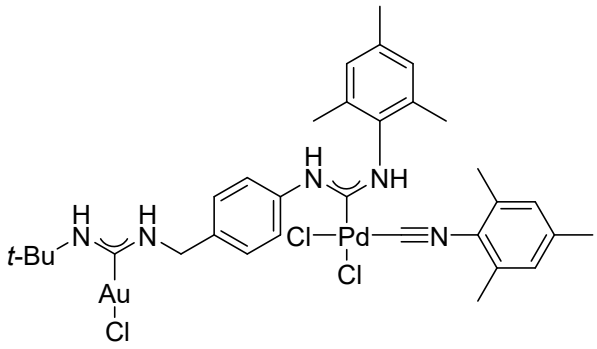


According to **GP9** the reaction was carried out with (((4-aminobenzyl)amino)(*tert*-butylamino)methylene)gold(I) chloride (65.7 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (136 mg, 137 µmol, 92 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, THF-d_8, 295 K) δ [ppm] = 10.84 (s, 1H, $C_{Ar}\underline{H}$), 9.17 (s, 1H, $C_{Ar}\underline{H}$), 8.84 (t, *J* = 6.5 Hz, 1H, $C_{Ar}\underline{H}$), 8.44 (s, 1H, $C_{Ar}\underline{H}$), 8.14 (d, *J* = 6.9 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.96 (d, *J* = 7.4 Hz, 2H,2x$C_{Ar}\underline{H}$), 7.75 (t, *J* = 7.8 Hz, 1H, $C_{Ar}\underline{H}$), 7.70 (t, *J* = 8.5 Hz, 1H, $C_{Ar}\underline{H}$), 7.62 (d, *J* = 7.7 Hz, 3H, 3x$C_{Ar}\underline{H}$), 7.60 – 7.58 (m, 3H, 3x$C_{Ar}\underline{H}$), 5.17 (d, *J* = 6.1 Hz, 2H, -CH_2-), 3.80 – 3.33 (m, 4H, 4x$C\underline{H}$), 1.81 (d, *J* = 1.7 Hz, 9H, 3x-CH_3), 1.60 – 1.46 (m, 24H, 8x-$C\underline{H_3}$).

2.2.39 Synthesis of Gold(I) Palladium(II) Complex 5g

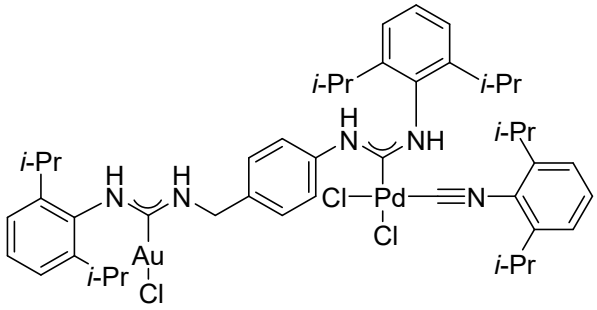


According to **GP9** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (29.5 mg, 100 µmol, 1.00 eq.), *tert*-butyl isocyanide (8.41 mg, 100 µmol, 1.00 eq.), 4-aminobenzylamine (12.2 mg, 100 µmol,1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile) palladium(II) chloride (46.8 mg, 100 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (66.0 mg, 72.8 µmol, 73 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.34 (s, 1H, $C_{Ar}\underline{H}$), 8.00 (d, *J* = 13.6 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.92 – 7.72 (m, 1H, $C_{Ar}\underline{H}$), 7.64 (d, *J* = 8.4 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.54 (s, 1H, $C_{Ar}\underline{H}$), 7.39 (d, *J* = 8.4 Hz, 2H, 2x$C_{Ar}\underline{H}$), 7.01 (s, 3H, 3x$C_{Ar}\underline{H}$), 6.85 (s, 3H, 3x$C_{Ar}\underline{H}$), 4.66 (d, *J* = 6.1 Hz, 2H, -$C\underline{H_2}$-), 2.33 (s, 6H, 2x-$C\underline{H_3}$), 2.30 (s, 3H, -$C\underline{H_3}$), 2.25 (s, 3H, -$C\underline{H_3}$), 2.14 (s, 6H, 2x-$C\underline{H_3}$), 1.47 (s, 9H, 3x-$C\underline{H_3}$).

2.2.40 Synthesis of Gold(I) Palladium(II) Complex 5h

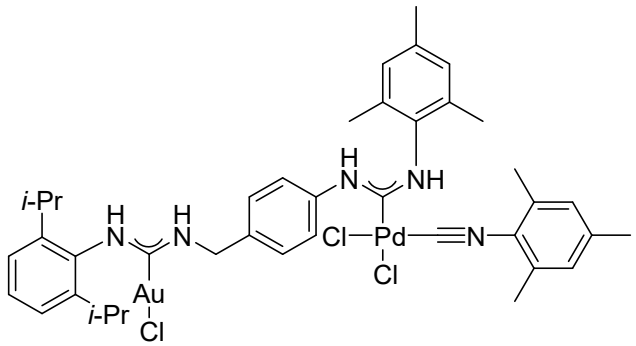


According to **GP9** the reaction was carried out with (((4-aminobenzyl)amino)((2,6-diisopropylphenyl)amino)methylene)gold(I) chloride (81.2 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (122 mg, 112 µmol, 74 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (400 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.38 – 8.05 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 7.64 (d, *J* = 8.4 Hz, 2H, Rotamer A, 2x$C_{Ar}\underline{H}$), 7.48 (d, *J* = 8.2 Hz, 2H, Rotamer B, 2x$C_{Ar}\underline{H}$), 7.45 – 7.35 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 7.35 – 7.21 (m, 5H, Rotamers A and B, 5x$C_{Ar}\underline{H}$), 7.21 – 7.02 (m, 5H, Rotamers A and B, 5x$C_{Ar}\underline{H}$), 6.99 – 6.43 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 6.09 (t, *J* = 6.2 Hz, 1H, Rotamer A, $C_{Ar}\underline{H}$), 5.97 (t, *J* = 6.0 Hz, 1H, Rotamer B, $C_{Ar}\underline{H}$), 4.77 (d, *J* = 6.2 Hz, 2H, Rotamer A, -$C\underline{H}_2$-), 4.65 (d, *J* = 6.0 Hz, 2H, Rotamer B, -$C\underline{H}_2$-), 3.40 – 2.79 (m, 6H, Rotamers A and B, 2x-$C\underline{H}_3$), 1.24 – 0.85 (m, 36H, Rotamers A and B, 12x-$C\underline{H}_3$).

2.2.41 Synthesis of Gold(I) Palladium(II) Complex 5i



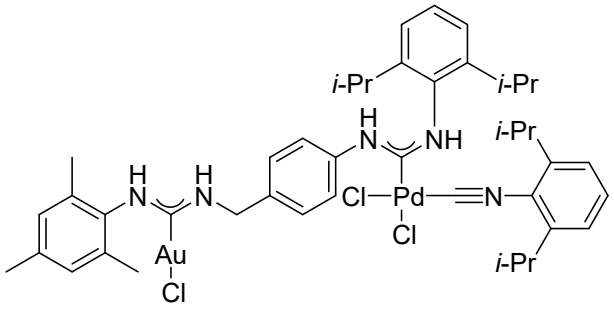
According to **GP9** the reaction was carried out with chloro(dimethyl sulfide)gold(I) (29.5 mg, 100 µmol, 1.00 eq.), 2,6-diisopropylphenyl isocyanide (14.6 mg, 100 µmol, 1.00 eq.), 4-aminobenzylamine (12.2 mg, 100 µmol,1.00 eq.) and bis(2,4,6-trimethylphenylisonitrile)

palladium(II) chloride (46.8 mg, 100 µmol, 1.00 eq.). Title compound was obtained as a colorless solid (81.0 mg, 80.2 µmol, 80 %).

Analytical data is in accordance with literature.[1]

^{1}H NMR (600 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.47 (s, 1H, Rotamer A, $C_{Ar}\underline{H}$), 9.21 (s, 1H, Rotamer B, $C_{Ar}\underline{H}$), 8.37 – 8.00 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.72 (d, *J* = 8.2 Hz, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.48 (s, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 7.42 – 7.28 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 7.25 – 7.08 (m, 3H, Rotamers A and B, 3x$C_{Ar}\underline{H}$), 7.02 (s, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 6.88 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 6.25 (t, *J* = 6.3 Hz, 1H, Rotamer A, $C_{Ar}\underline{H}$), 6.20 (t, *J* = 6.4 Hz, 1H, Rotamer B, $C_{Ar}\underline{H}$) 5.11 – 4.71 (m, 2H, Rotamers A and B, -$C\underline{H}_2$-), 3.23 – 3.18 (m, 2H, Rotamer B, 2x$C\underline{H}$), 3.16 – 2.99 (m, 2H, Rotamer A, 2x$C\underline{H}$), 2.50 – 2.20 (m, 18H, Rotamers A and B, 6x-CH_3), 1.23 – 0.94 (m, 12H, Rotamers A and B, 4x-CH_3).

2.2.42 Synthesis of Gold(I) Palladium(II) Complex 5j



According to **GP9** the reaction was carried out with (((4-aminobenzyl)amino)(mesitylamino)methyl)gold(I) chloride (75.0 mg, 150 µmol, 1.00 eq.) and bis(2,6-diisopropylphenylisonitrile) palladium(II) chloride (82.8 mg, 150 µmol, 1.00 eq.) Title compound was obtained as a colorless solid (131 mg, 120 µmol, 83 % yield).

Analytical data is in accordance with literature.[1]

^{1}H NMR (700 MHz, CD_2Cl_2, 295 K) δ [ppm] = 9.51 – 8.43 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 7.65 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 7.51 – 7.15 (m, 7H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 7.09 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 6.88 – 6.70 (m, 2H, Rotamers A and B, 2x$C_{Ar}\underline{H}$), 6.25 – 5.90 (m, 1H, Rotamers A and B, $C_{Ar}\underline{H}$), 4.87 – 4.76 (d, *J* = 5.9 Hz, 2H, Rotamer A, -$C\underline{H}_2$-), 4.73 (d, *J* = 5.9 Hz, 2H, Rotamer B, -$C\underline{H}_2$-), 3.37 – 3.20 (m, 2H, Rotamers A and B, 2x$C\underline{H}$), 3.01 (m, 2H, Rotamers A and B, 2x$C\underline{H}$), 2.23 – 1.99 (m, 9H, Rotamers A and B, 3x-$C\underline{H}_3$), 1.31 – 0.98 (m, 24H, Rotamers A and B, 8x-$C\underline{H}_3$).

3 NMR Spectra

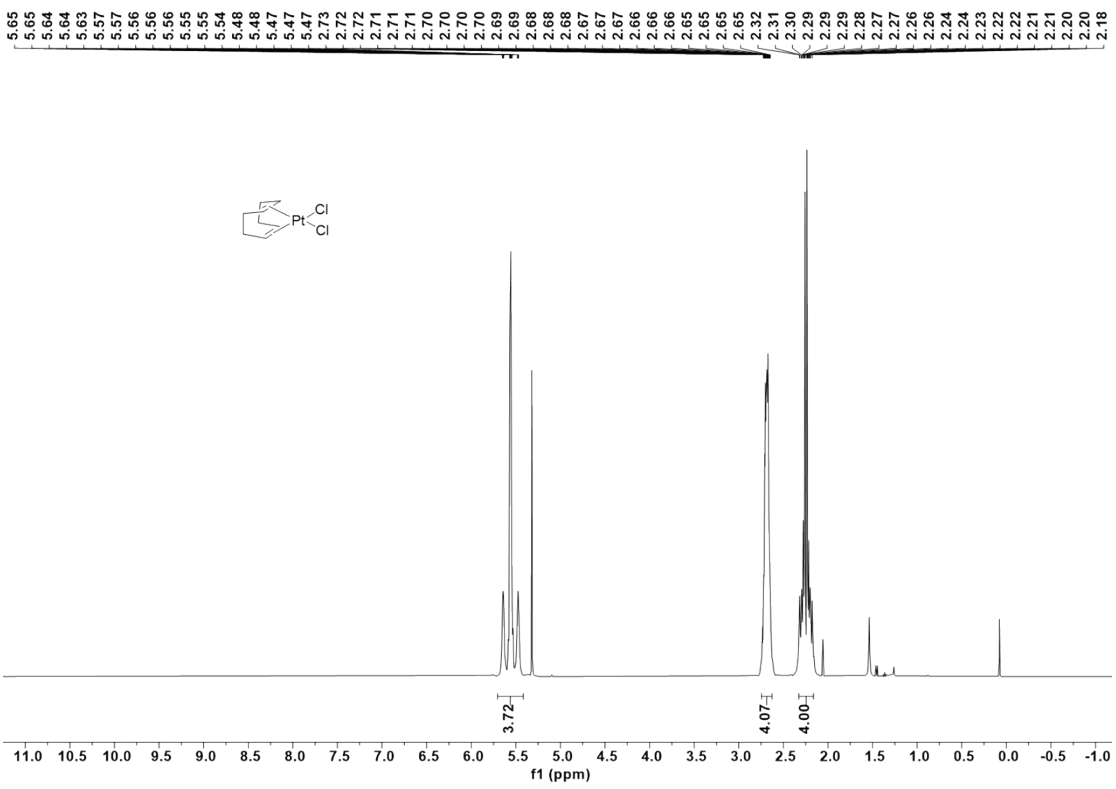


Figure S1. ^{1}H NMR of [$\mathbf{PtCl_2(COD)}$] in CD_2Cl_2 (400 MHz, 295K).

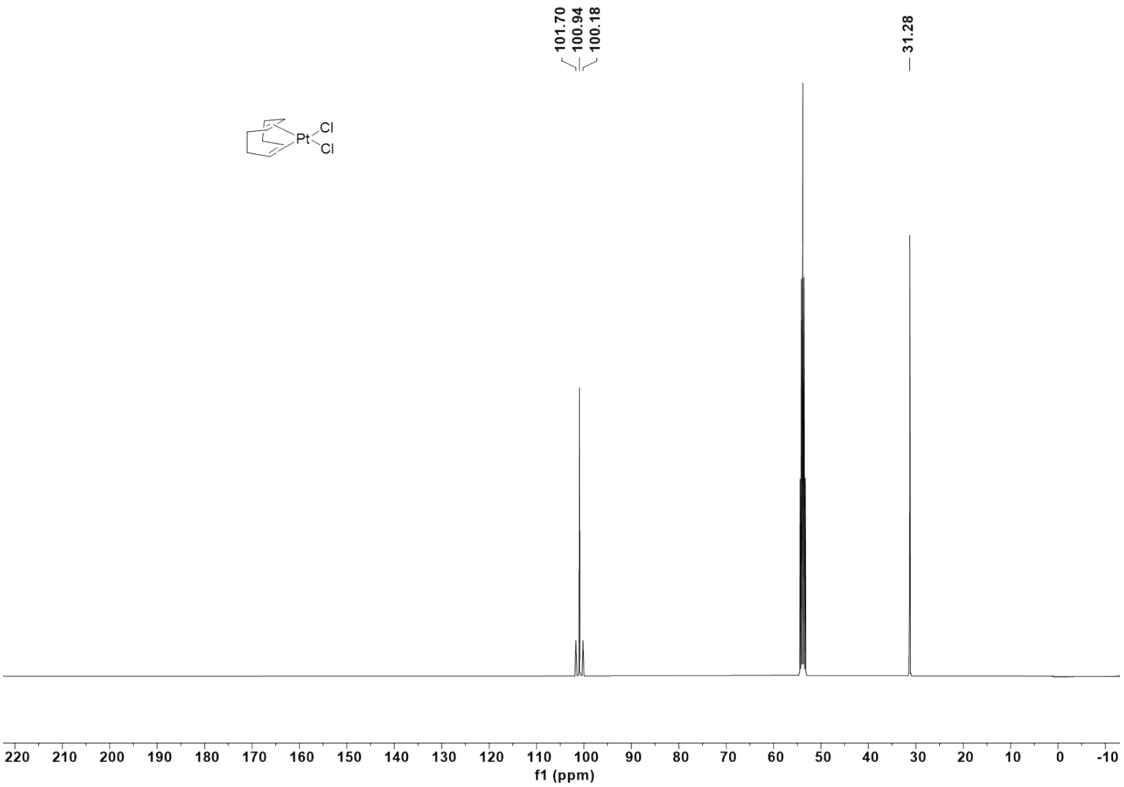


Figure S2. ^{13}C NMR of [**$PtCl_2$(COD)**] in CD_2Cl_2 (101 MHz, 295 K).

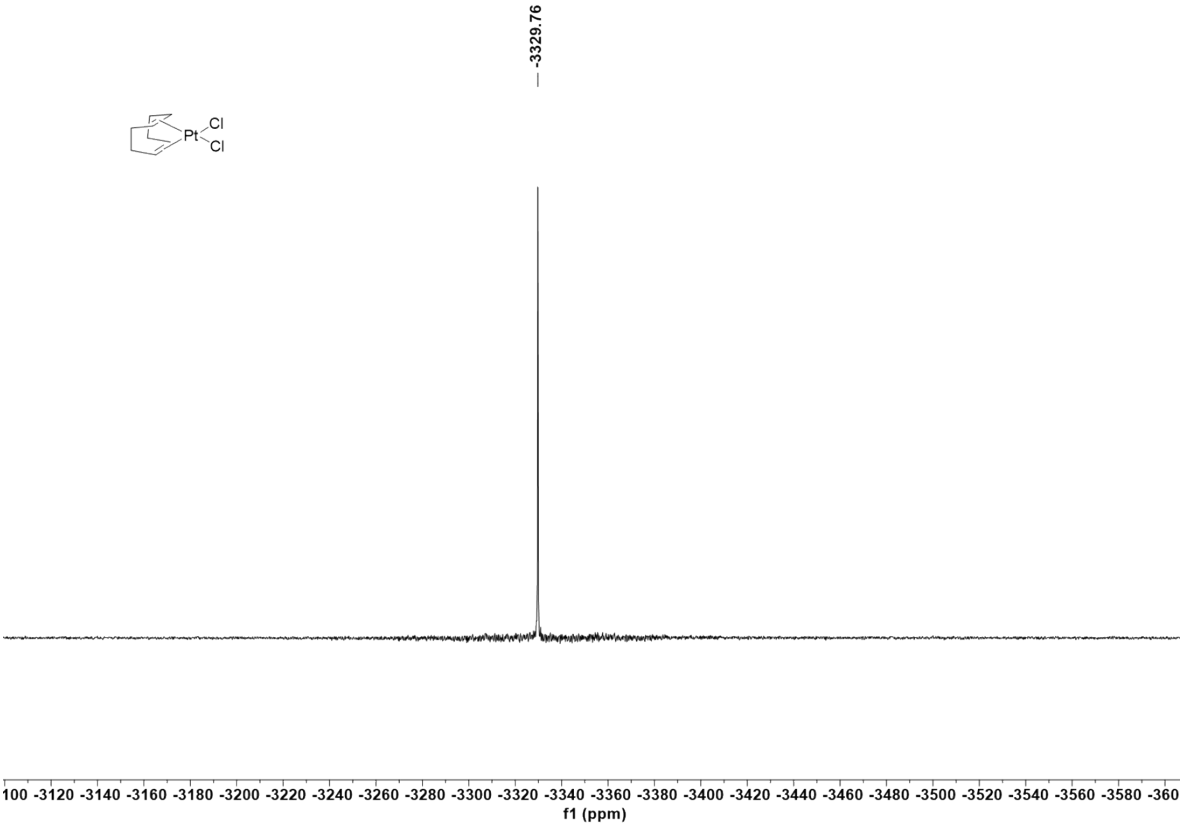


Figure S3. ^{195}Pt NMR of [**PtCl2(COD)**] in CD_2Cl_2 (86 MHz, 295 K).

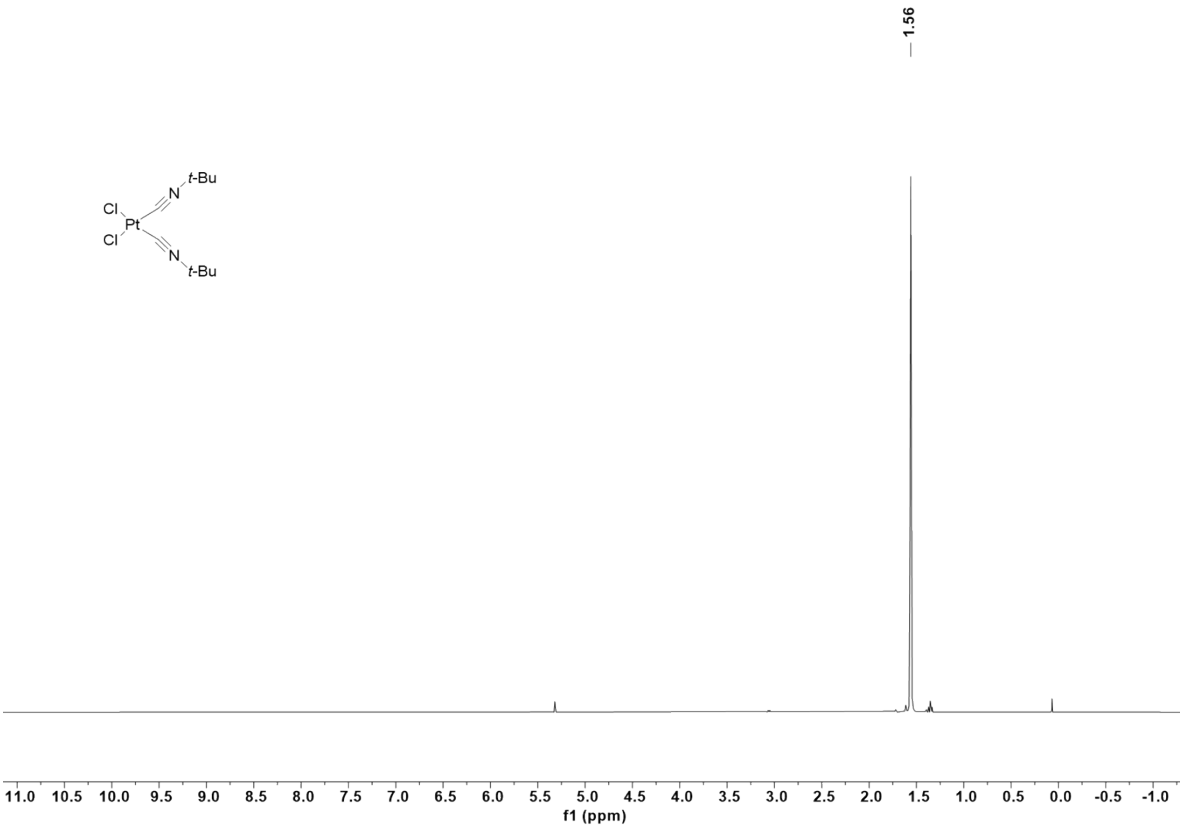


Figure S4. ^{1}H NMR of **1a** in CD_2Cl_2 (400 MHz, 295 K).

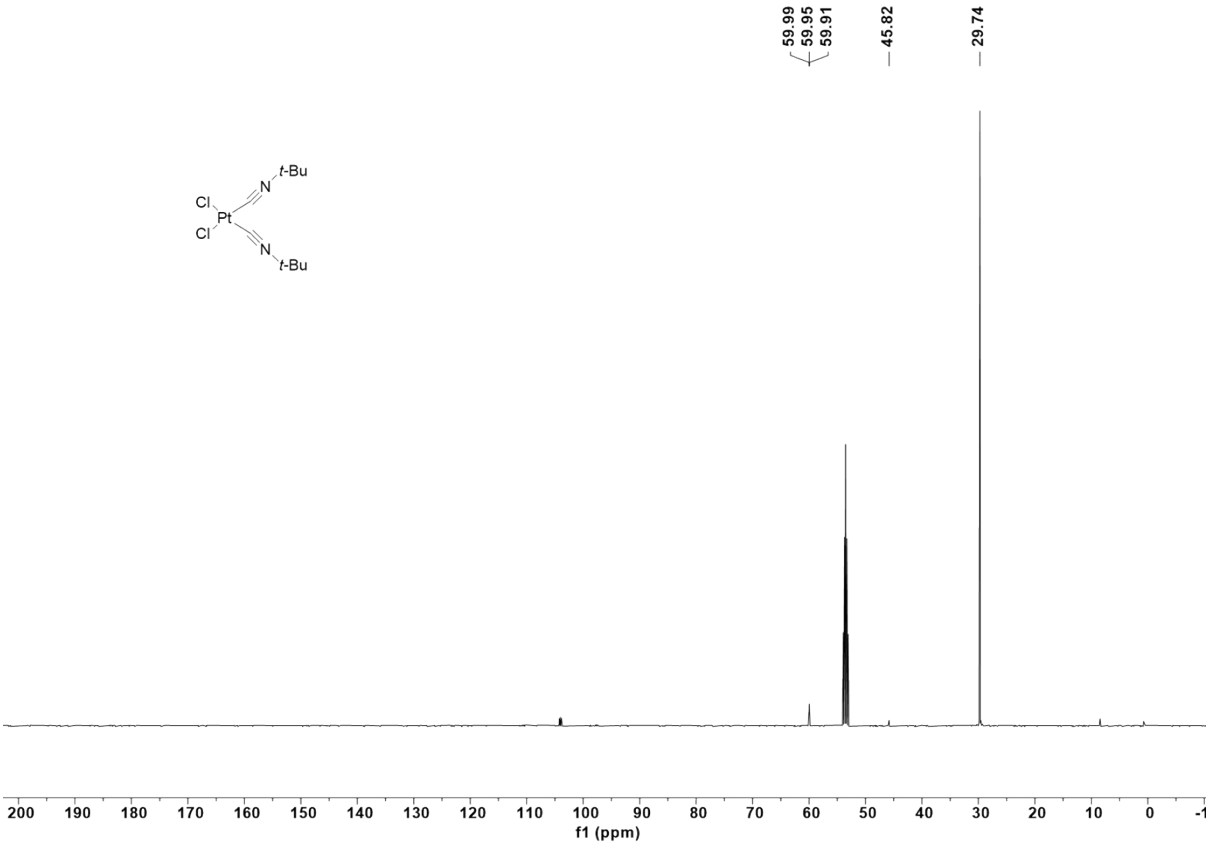


Figure S5. ^{13}C NMR of **1a** in CD_2Cl_2 (126 MHz, 295 K).

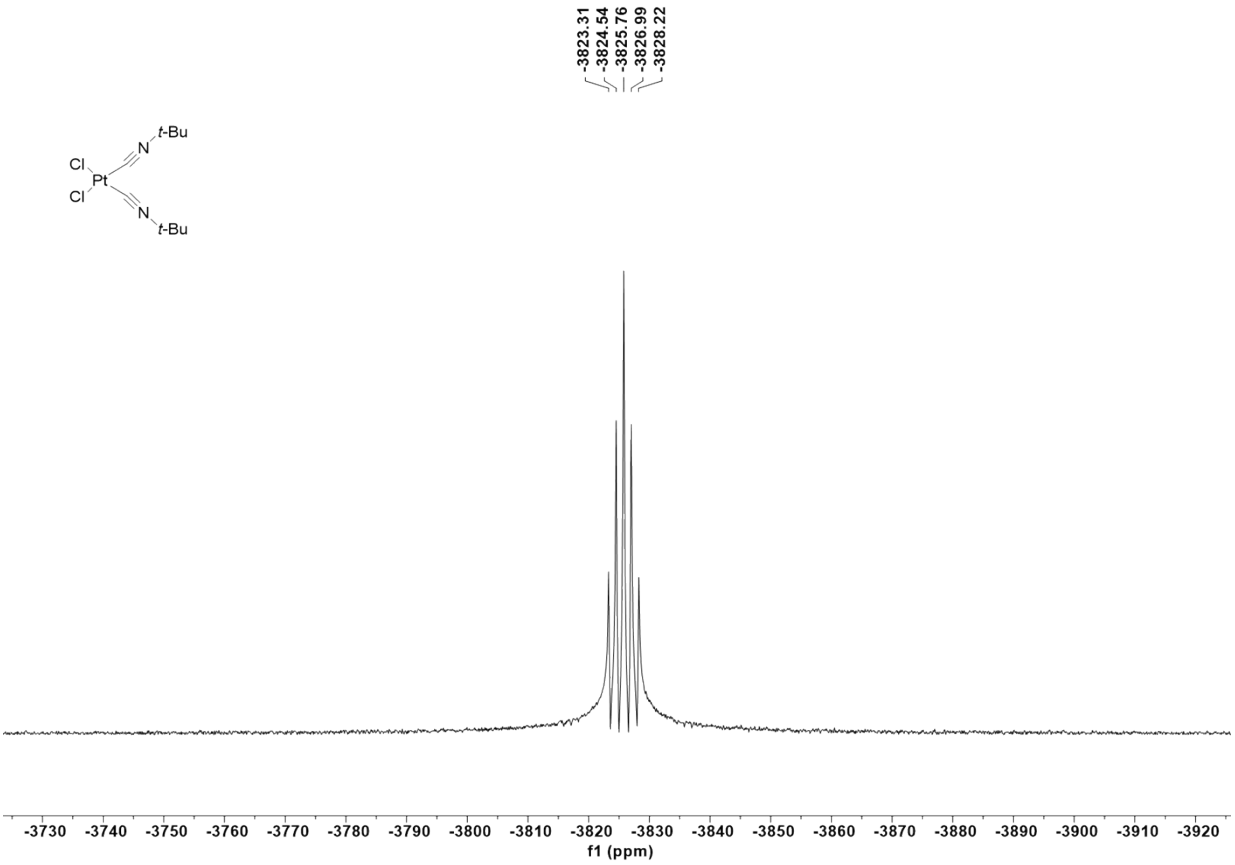


Figure S6. ^{195}Pt NMR of **1a** in CD_2Cl_2 (86 MHz, 295K).

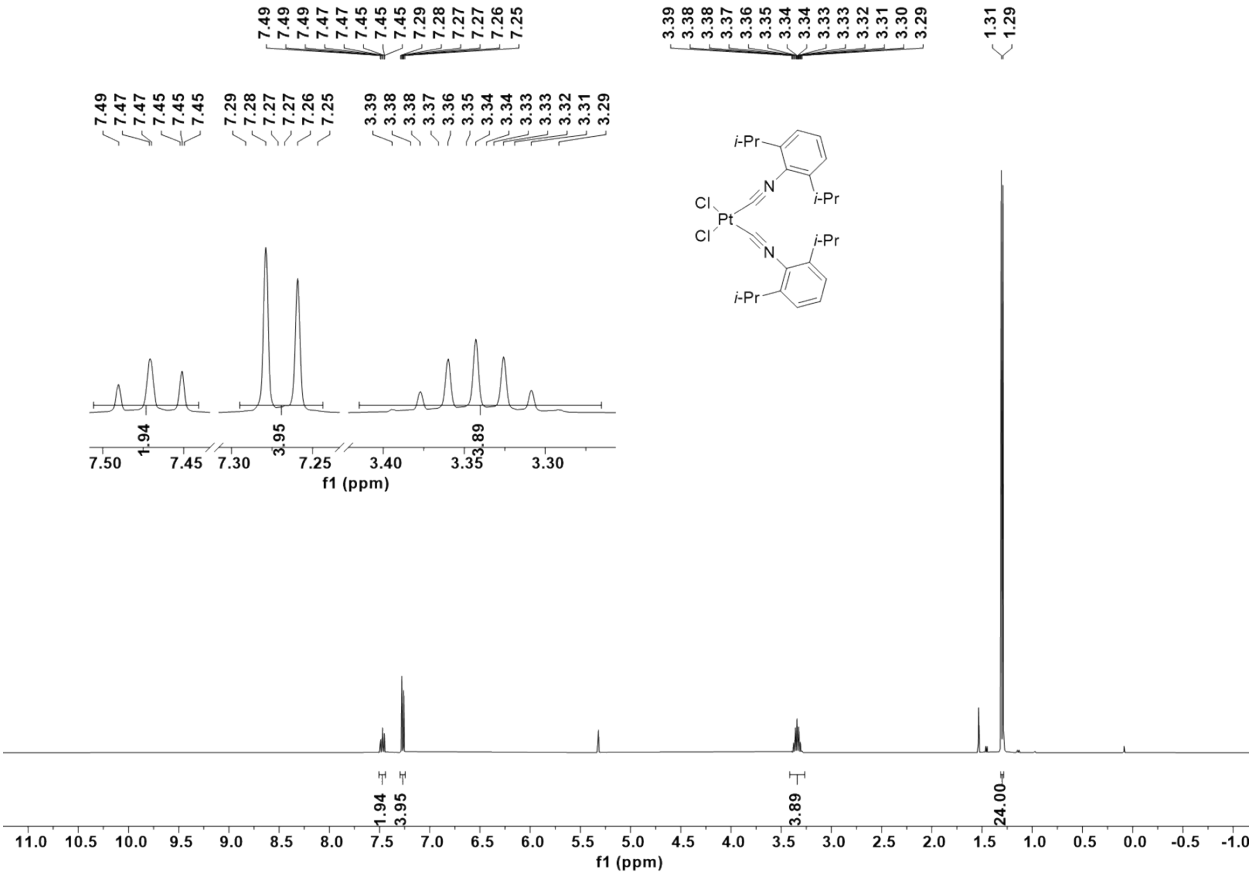


Figure S7. ^{1}H NMR of **1b** in CD_2Cl_2 (400MHz, 295K).

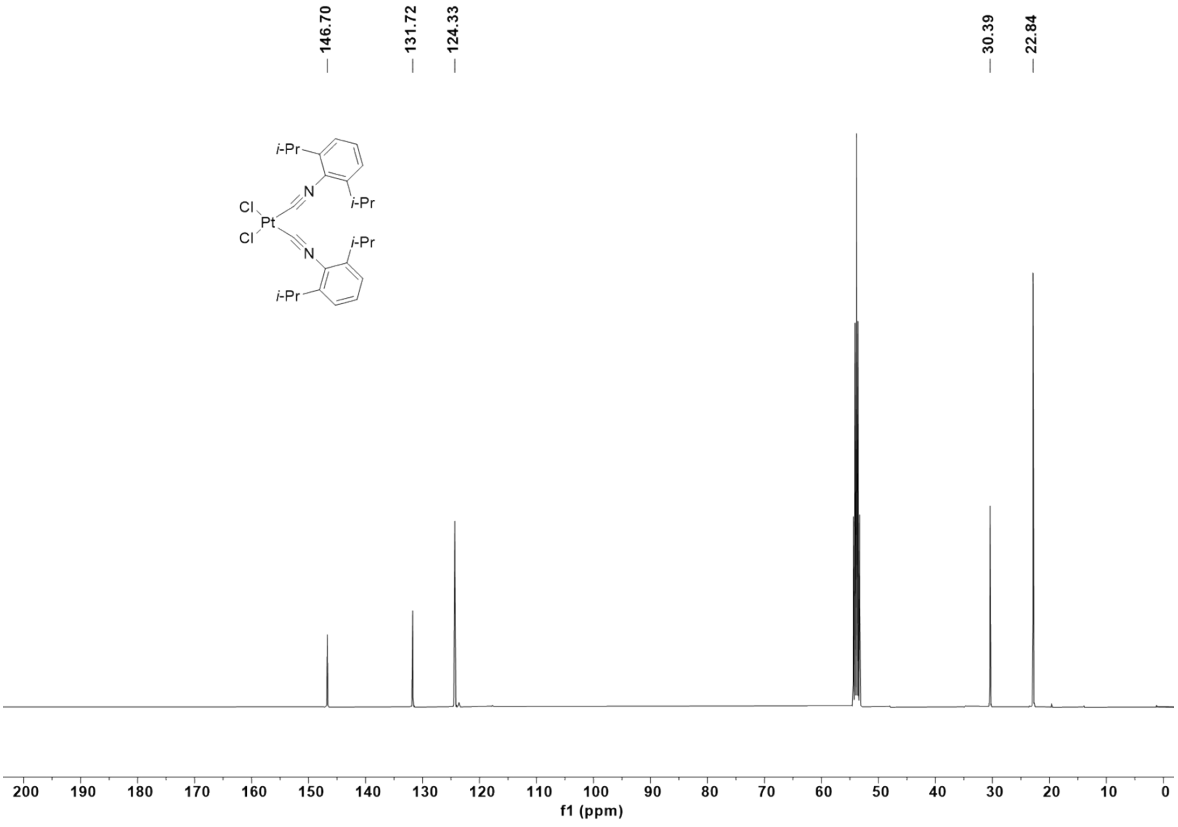


Figure S8. ^{13}C NMR of **1b** in CD_2Cl_2 (101 MHz, 295K).

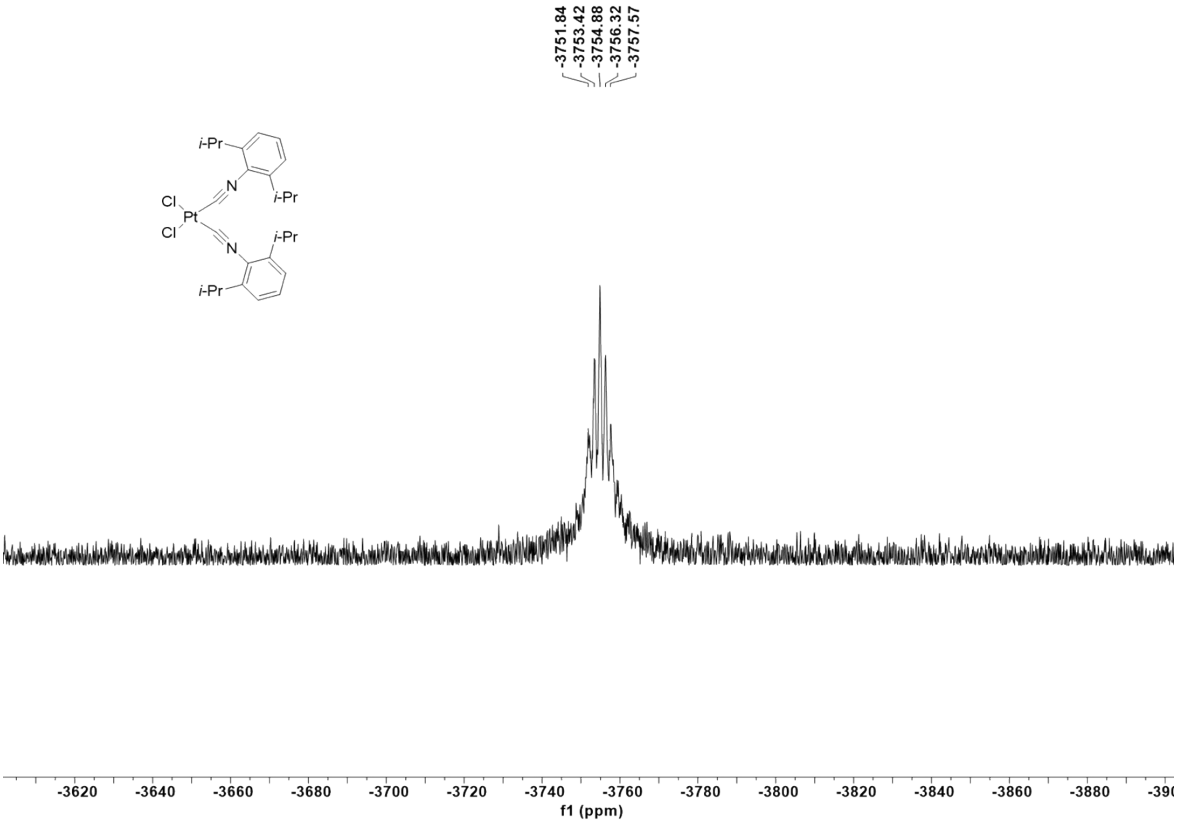


Figure S9. ^{195}Pt NMR of **1b** in CD_2Cl_2 (86 MHz, 295K).

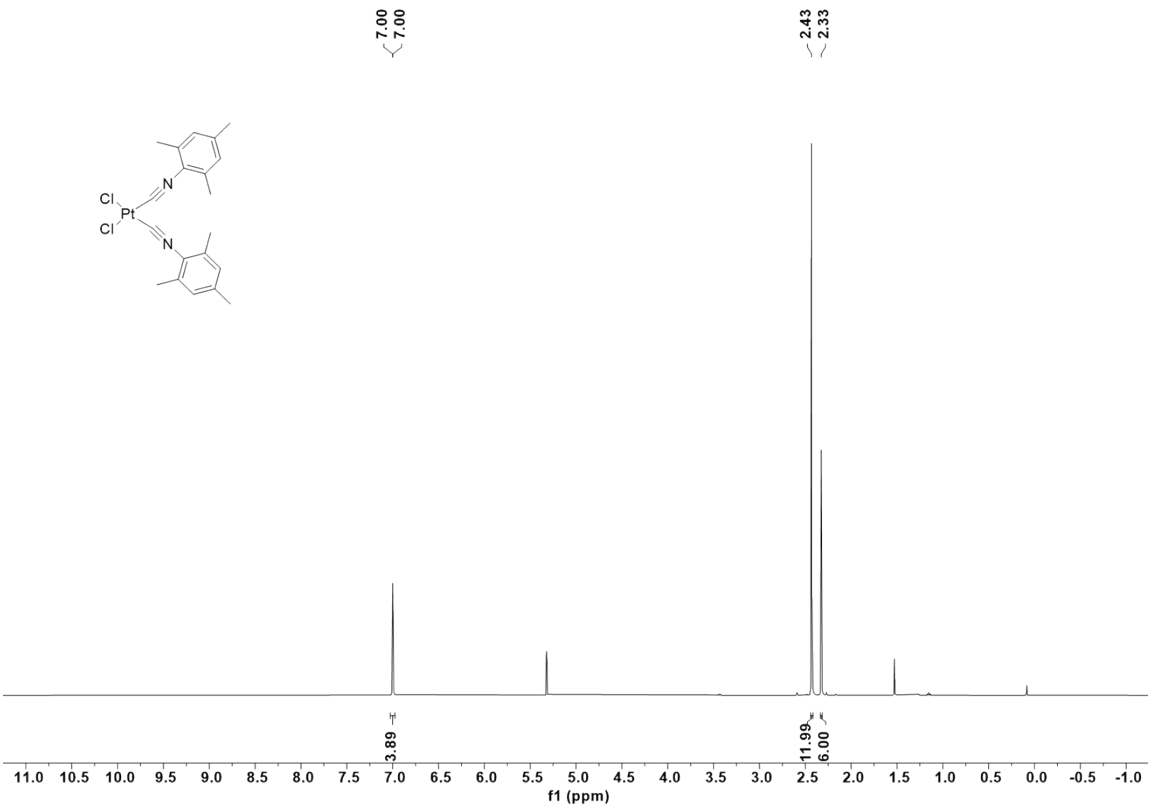


Figure S10. ^{1}H NMR of **1c** in CD_2Cl_2 (400 MHz, 295K).

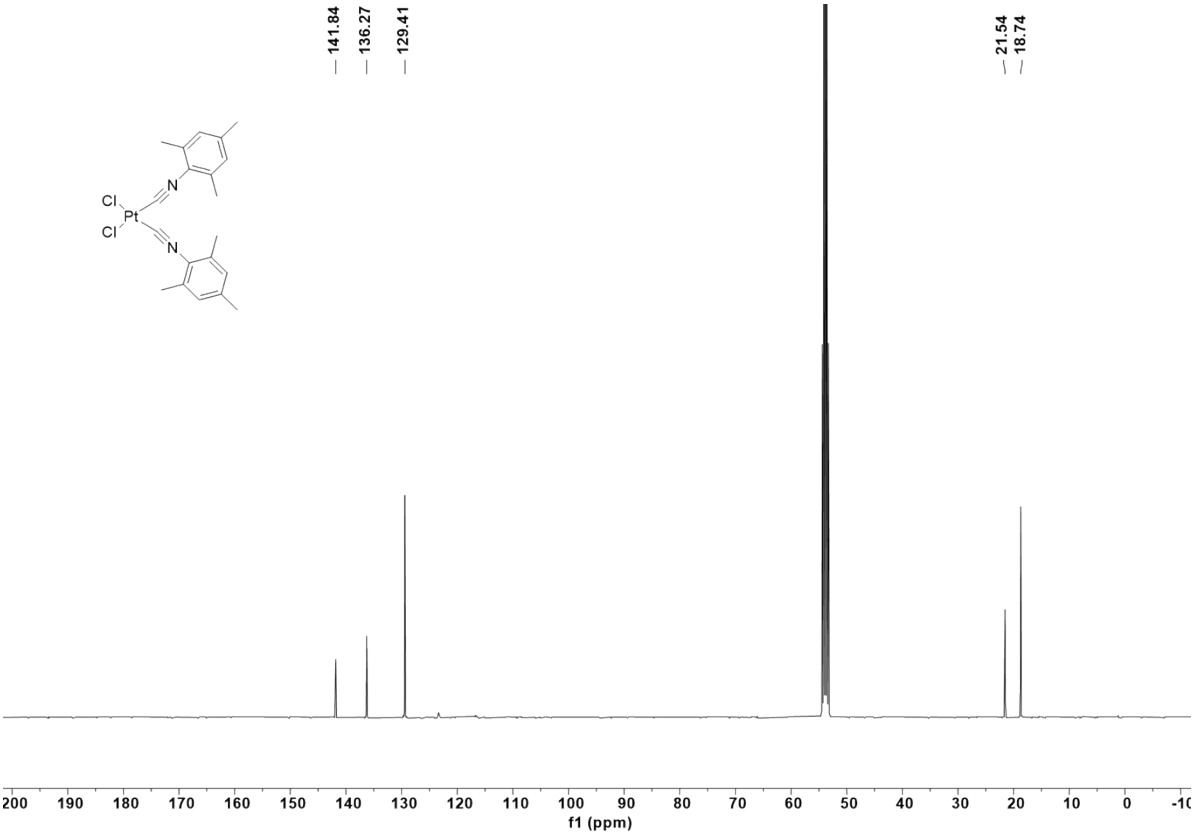


Figure S11. ^{13}C NMR of **1c** in CD_2Cl_2 (101 MHz, 295K).

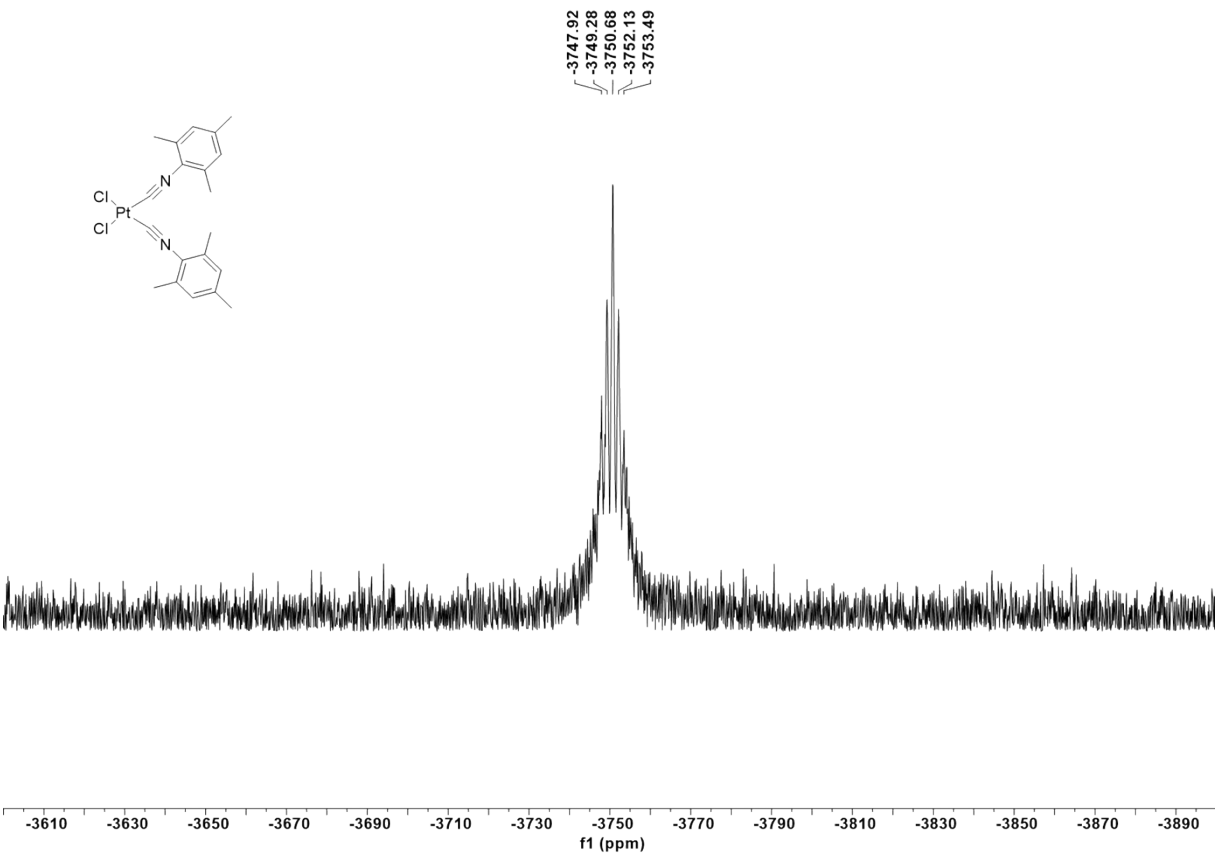


Figure S12. ^{195}Pt NMR of **1c** in CD_2Cl_2 (86 MHz, 295K).

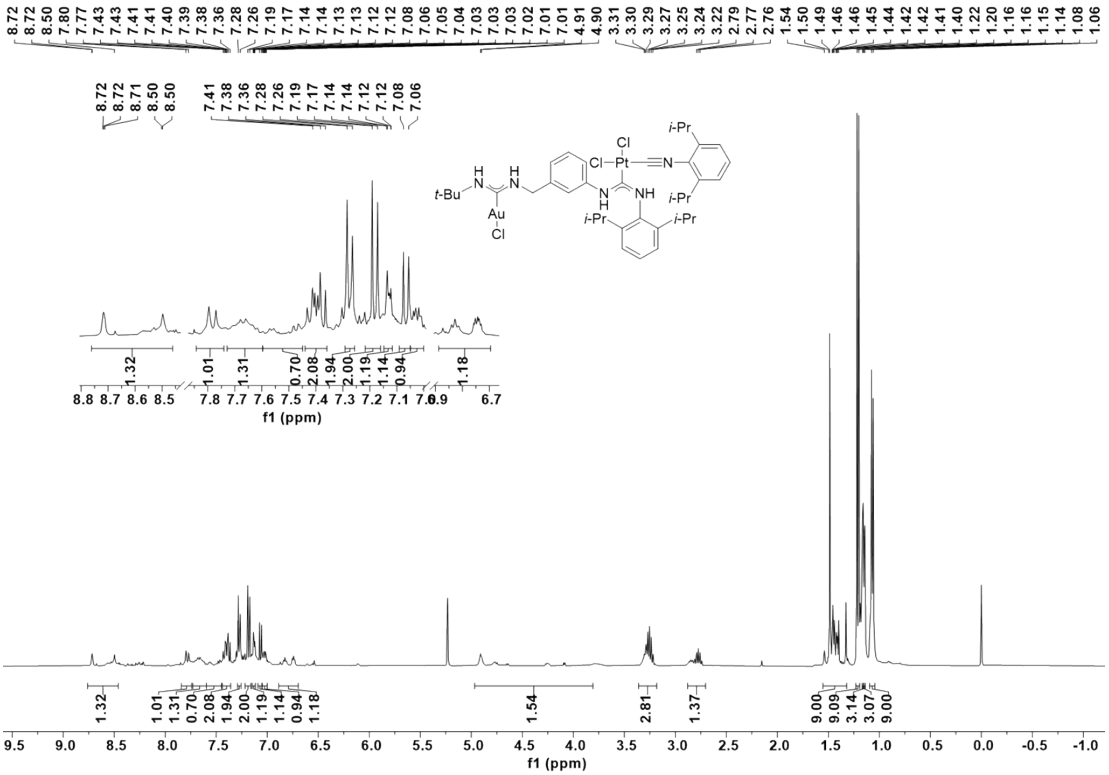


Figure S13. ^{1}H NMR of **3a** in CD_2Cl_2 (400 MHz, 295K).

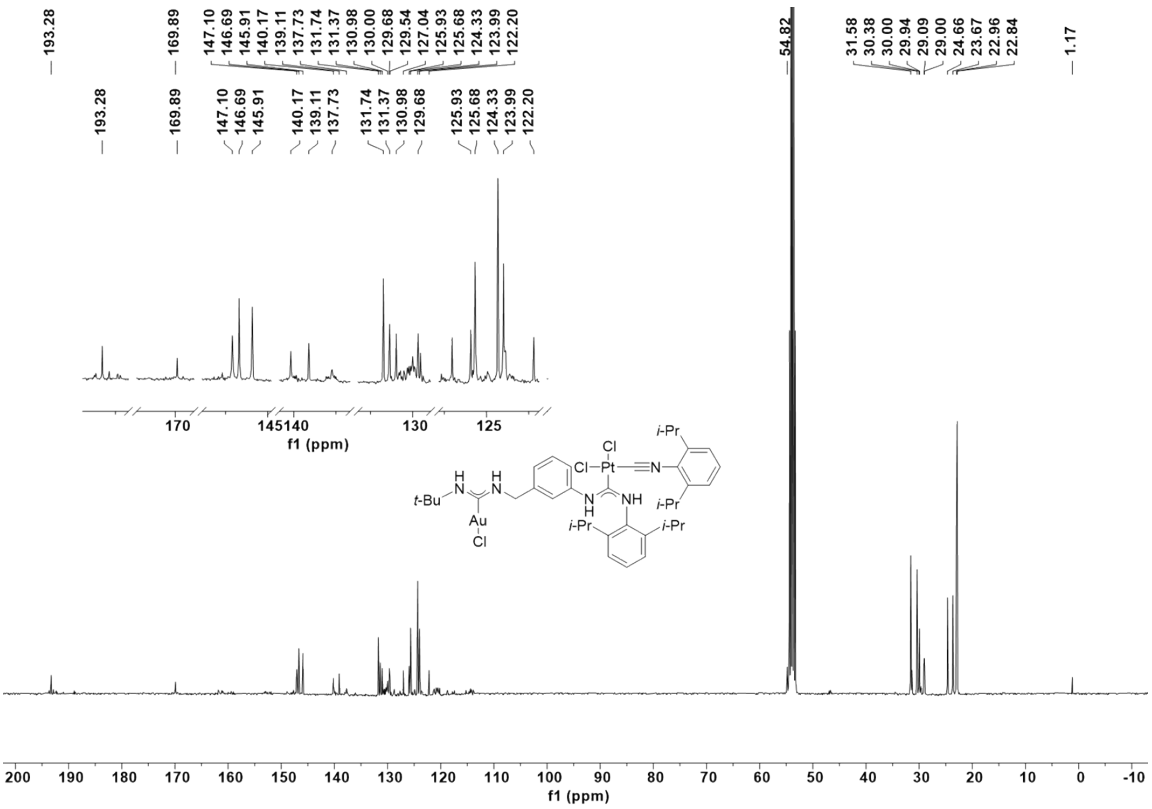


Figure S14. ^{13}C NMR of **3a** in CD_2Cl_2 (101 MHz, 295K).

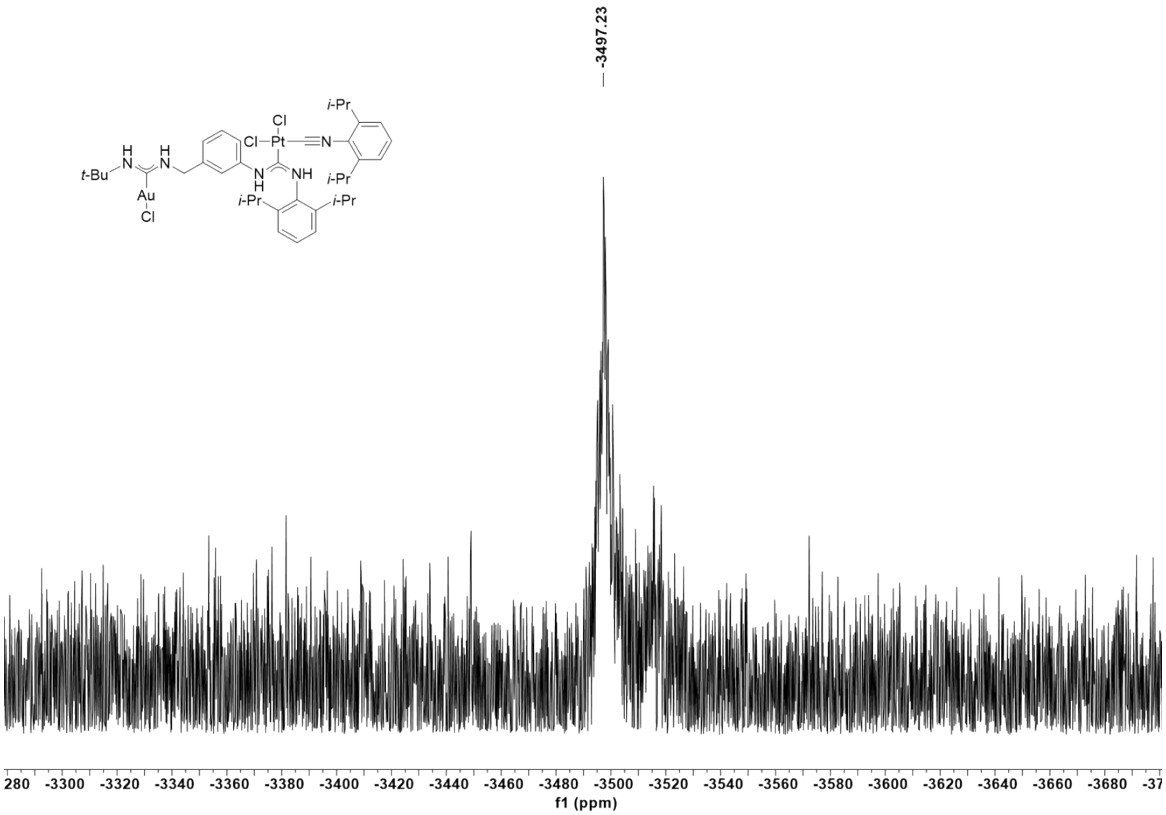


Figure S15. ^{195}Pt NMR of **3a** in CD_2Cl_2 (86 MHz, 295K).

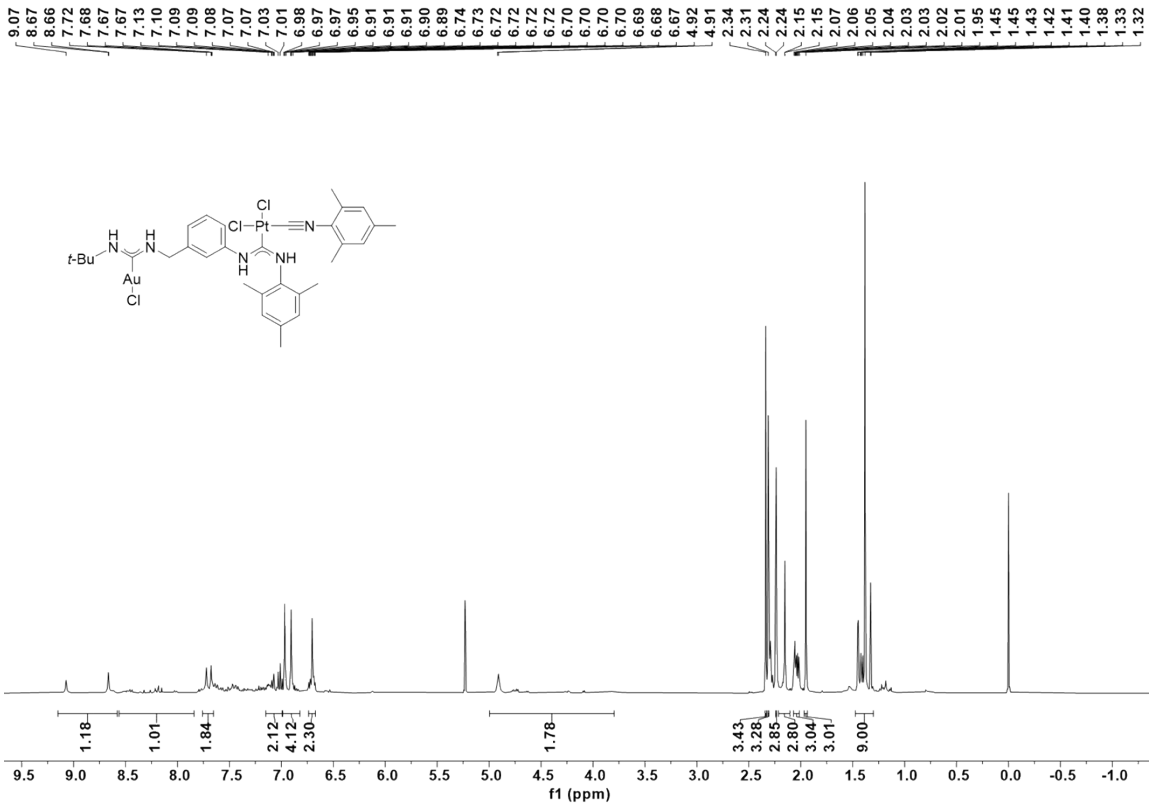


Figure S16. ^{1}H NMR of **3b** in CD_2Cl_2 (400 MHz, 295K).

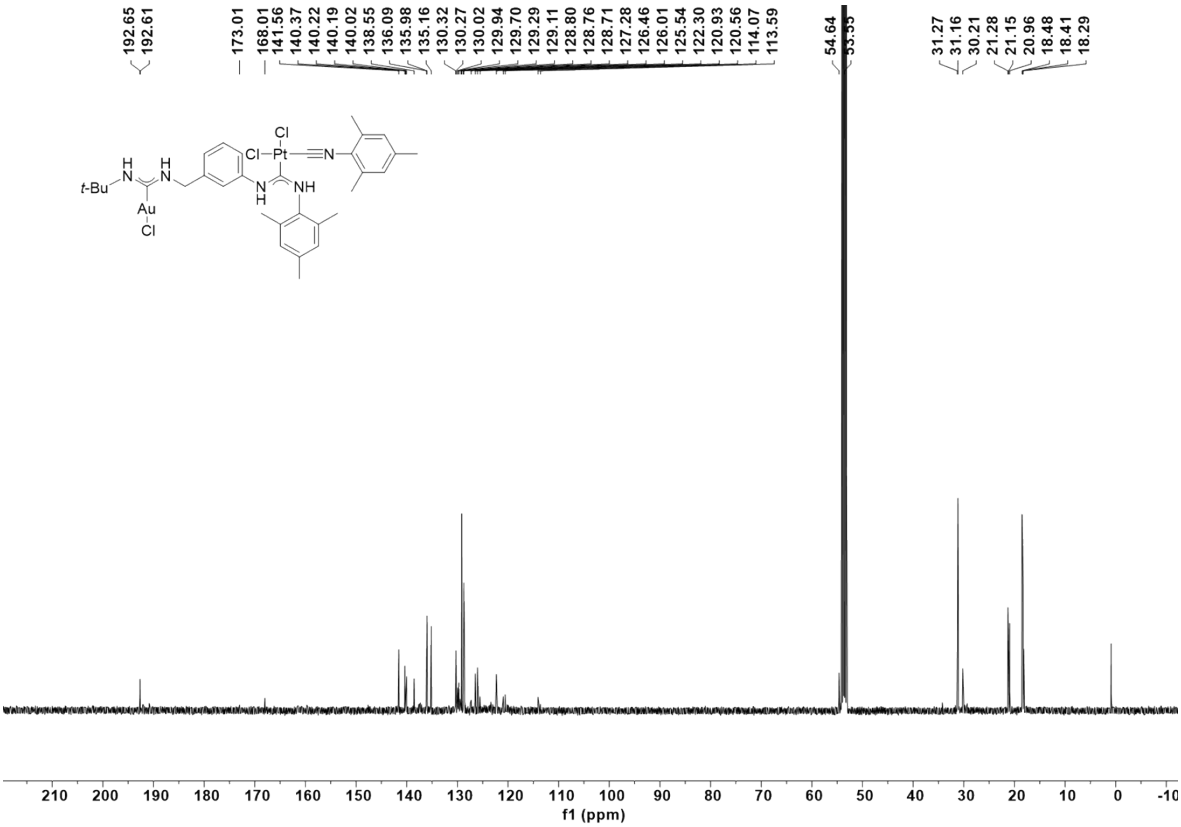


Figure S17. ^{13}C NMR of **3b** in CD_2Cl_2 (126 MHz, 295K).

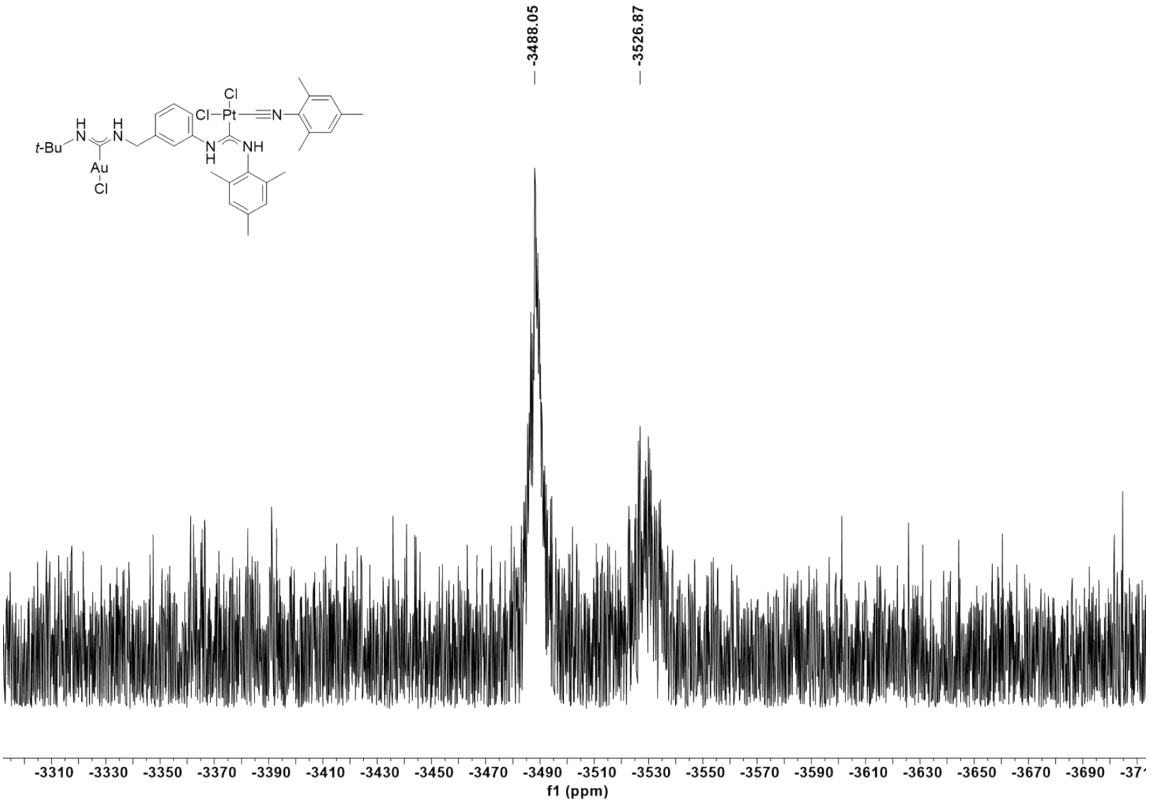


Figure S18. ^{195}Pt NMR of **3b** in CD_2Cl_2 (86 MHz, 295K).

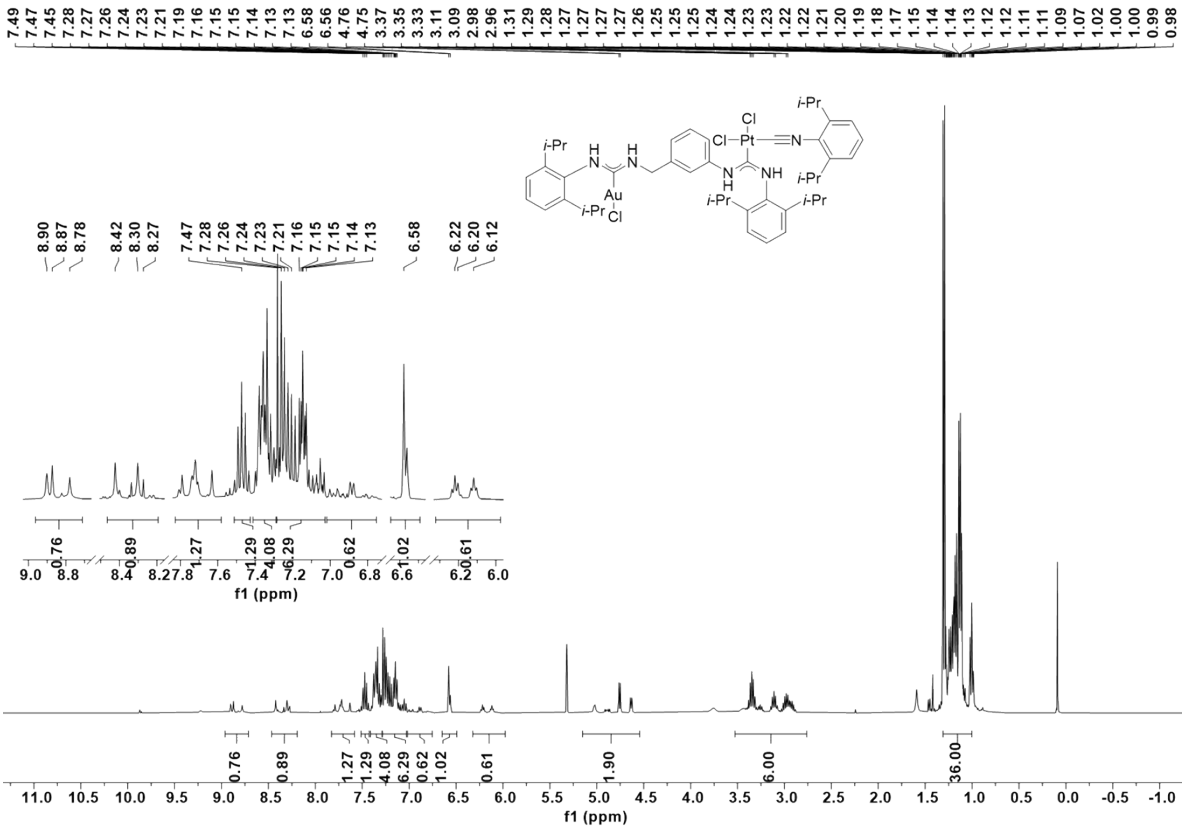


Figure S19. ^{1}H NMR of **3c** in CD_2Cl_2 (400 MHz, 295K).

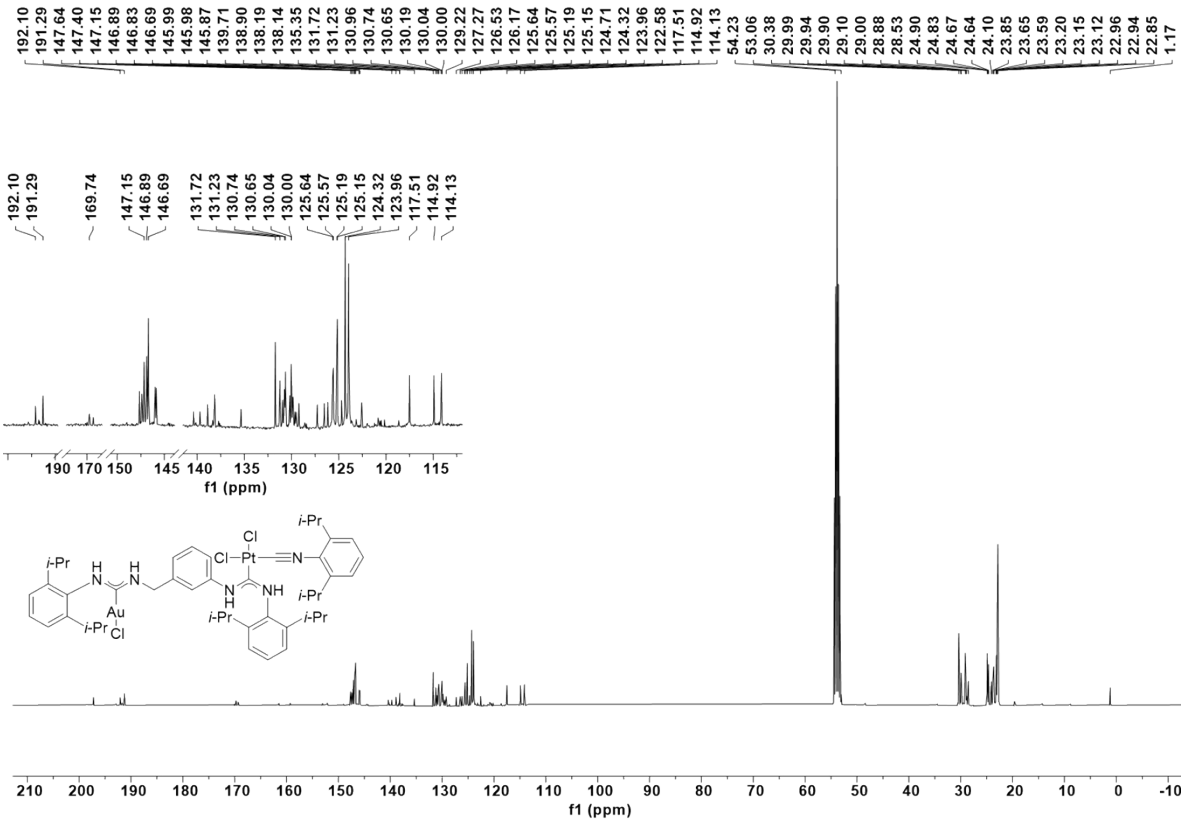


Figure S20. ^{13}C NMR of **3c** in CD_2Cl_2 (101 MHz, 295K).

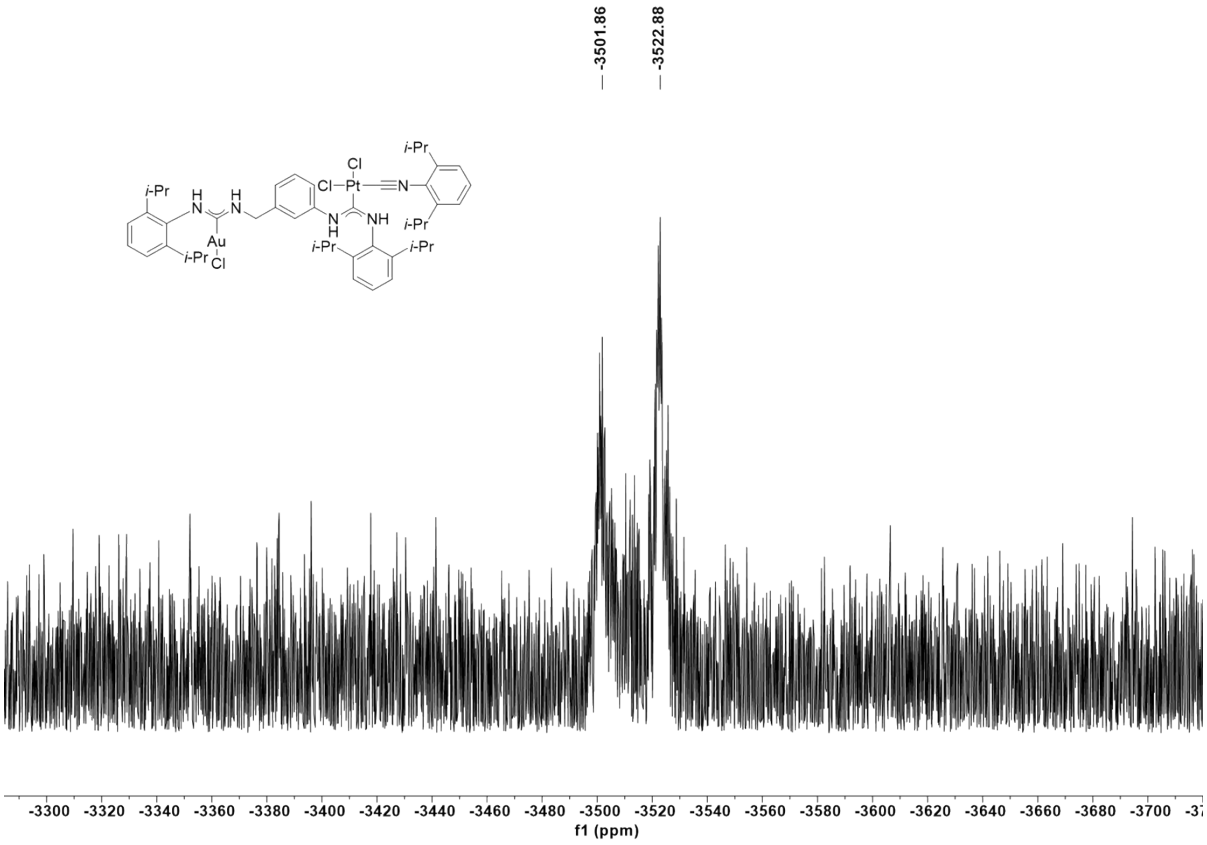


Figure S21. ^{195}Pt NMR of **3c** in CD_2Cl_2 (86 MHz, 295K).

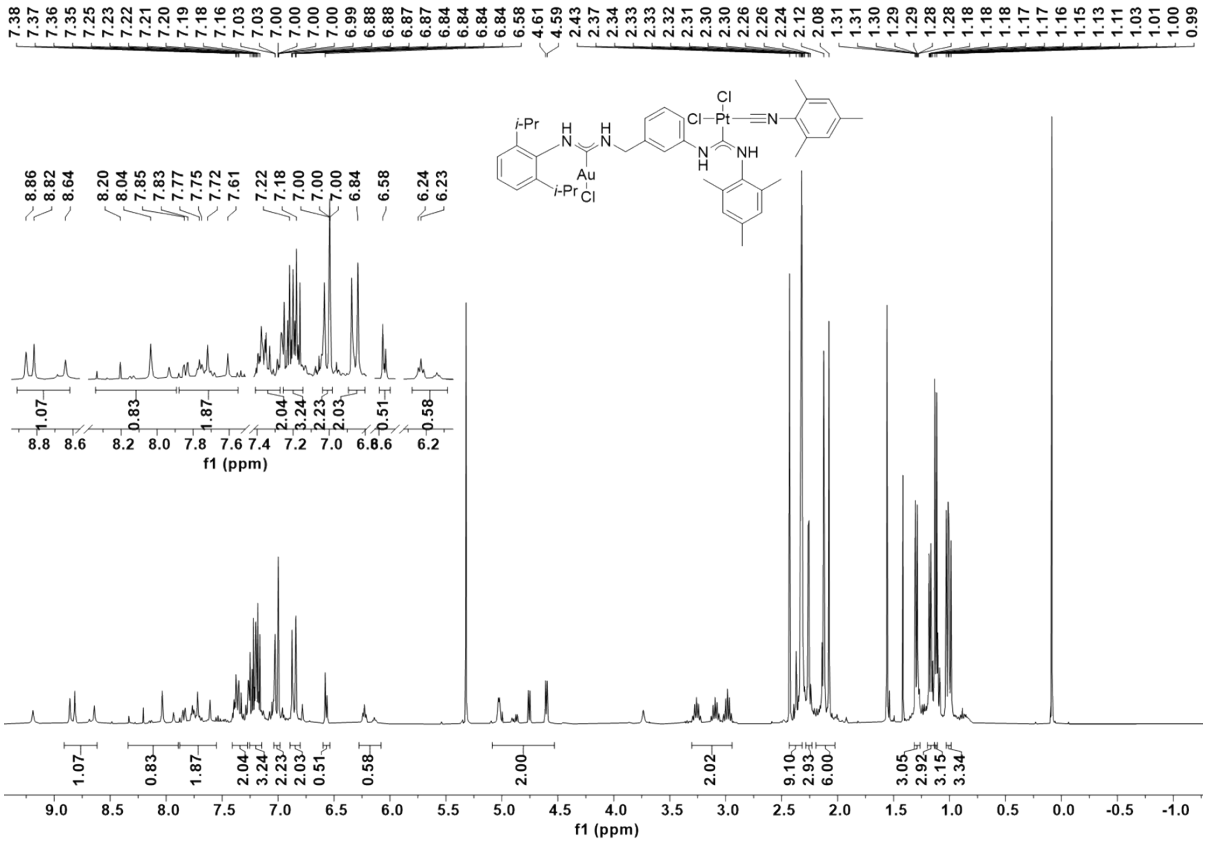


Figure S22. ^{1}H NMR of **3d** in CD_2Cl_2 (400 MHz, 295K).

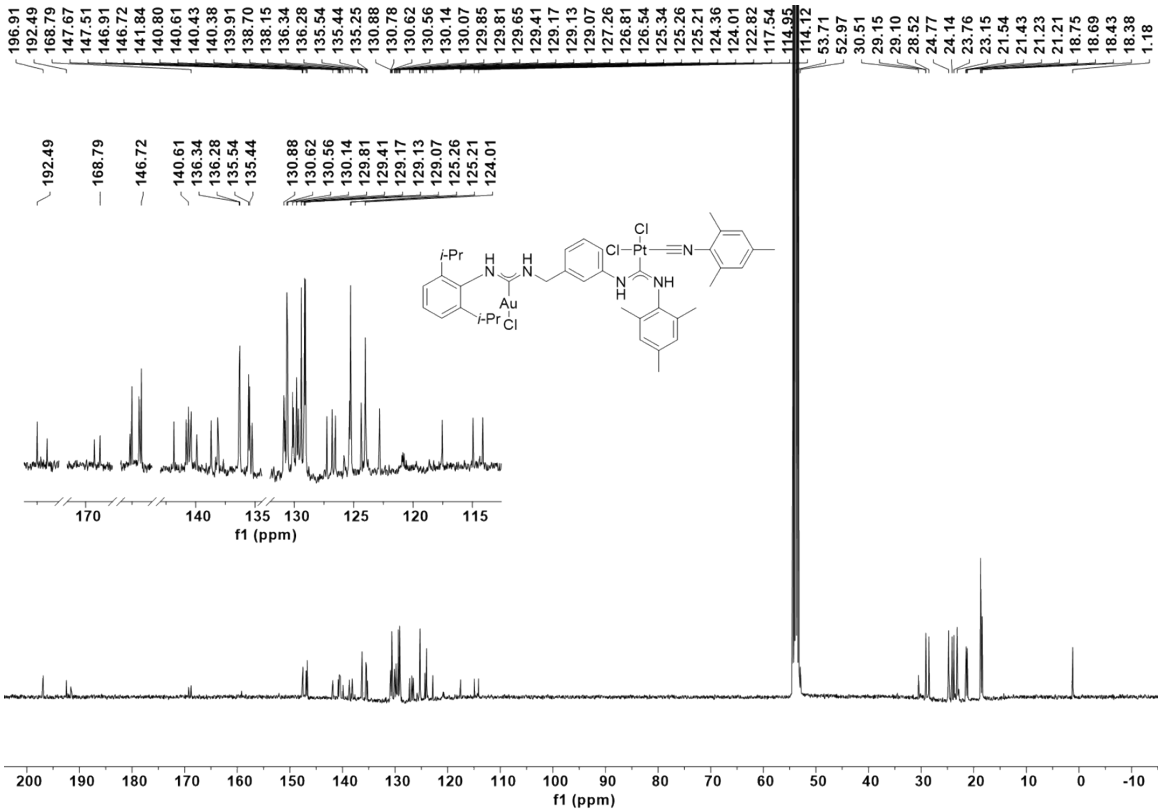


Figure S23. ^{13}C NMR of **3d** in CD_2Cl_2 (101 MHz, 295K).

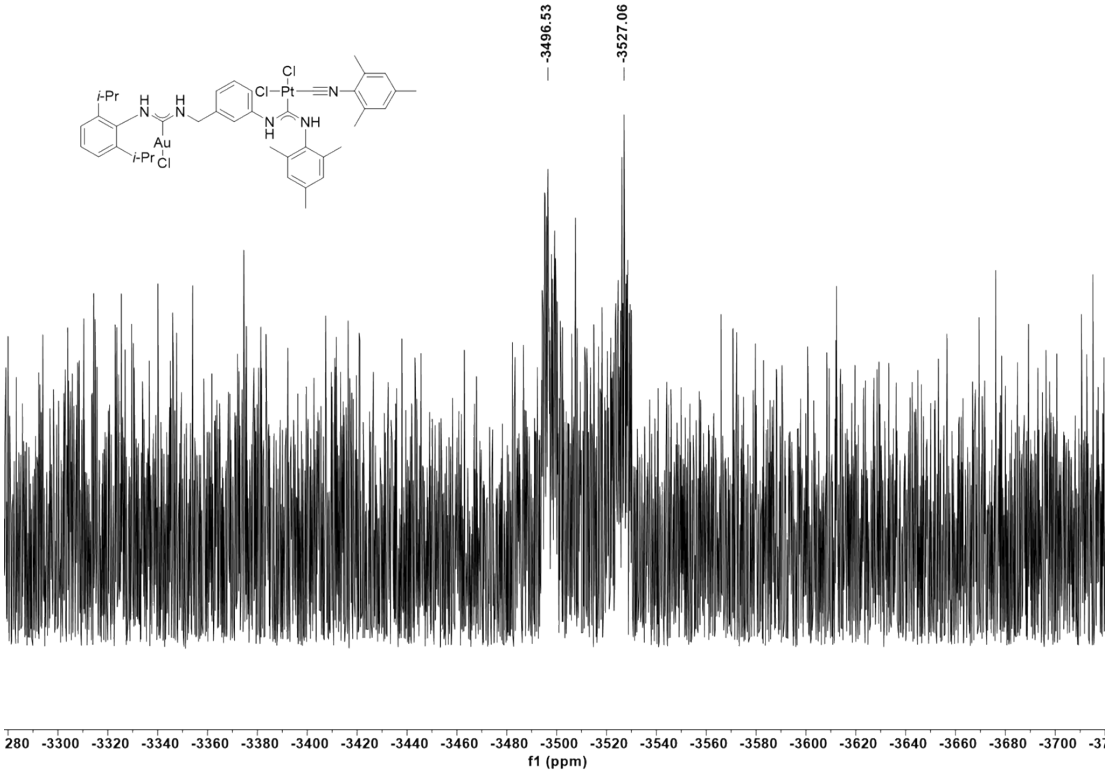


Figure S24. ^{195}Pt NMR of **3d** in CD_2Cl_2 (86 MHz, 295K).

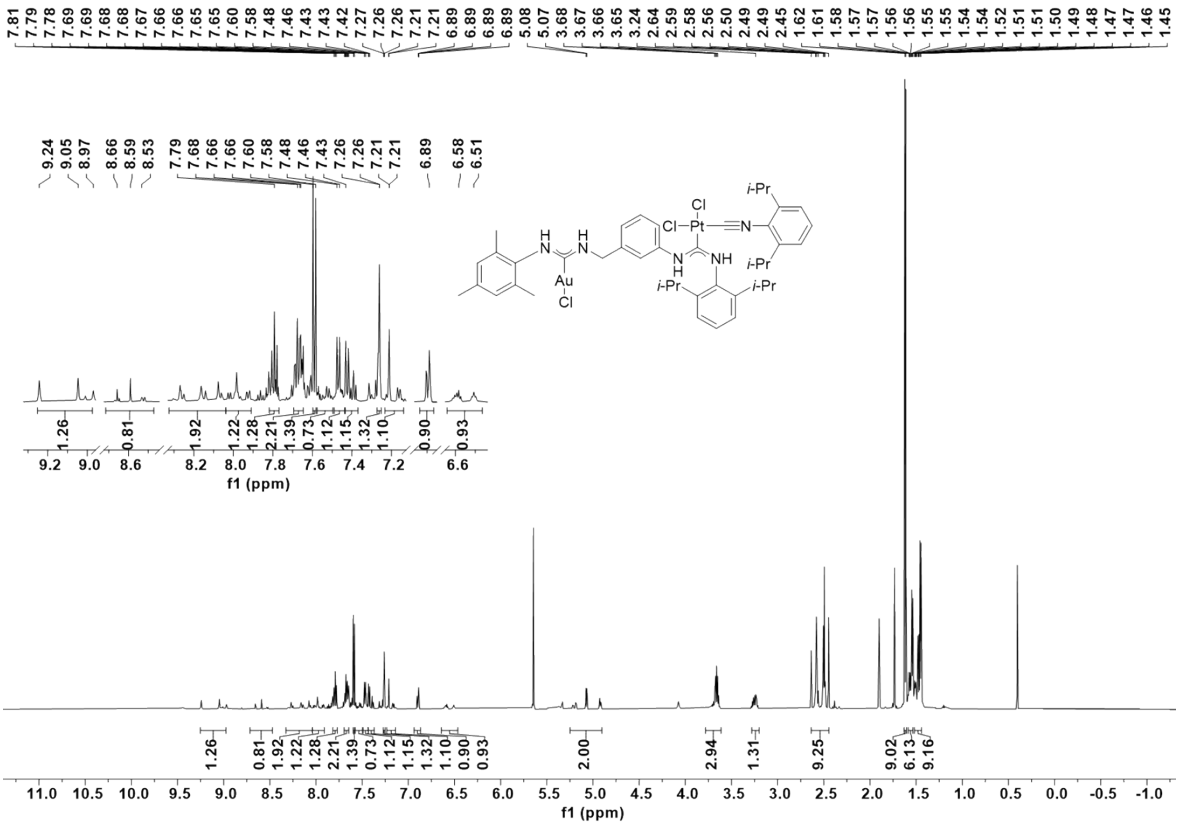


Figure S25. ^{1}H NMR of **3e** in CD_2Cl_2 (600 MHz, 295K).

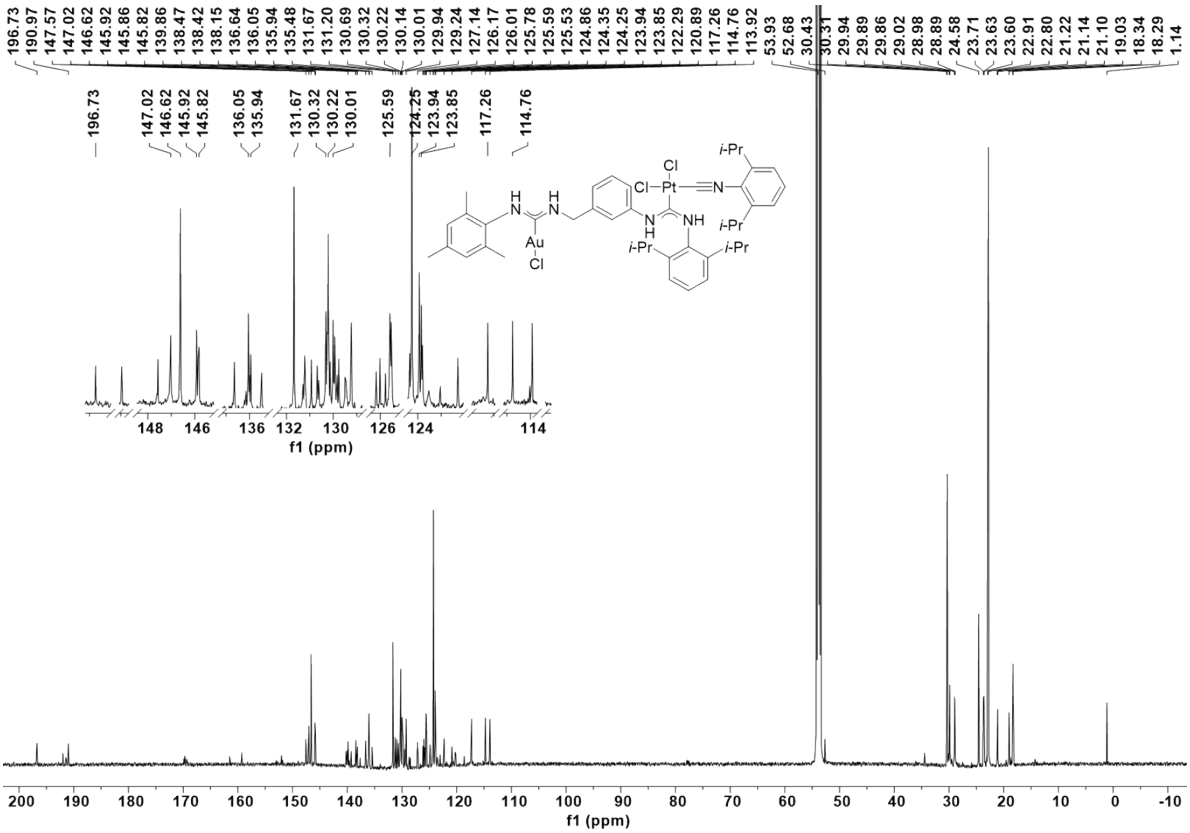


Figure S26. ^{13}C NMR of **3e** in CD_2Cl_2 (151 MHz, 295K).

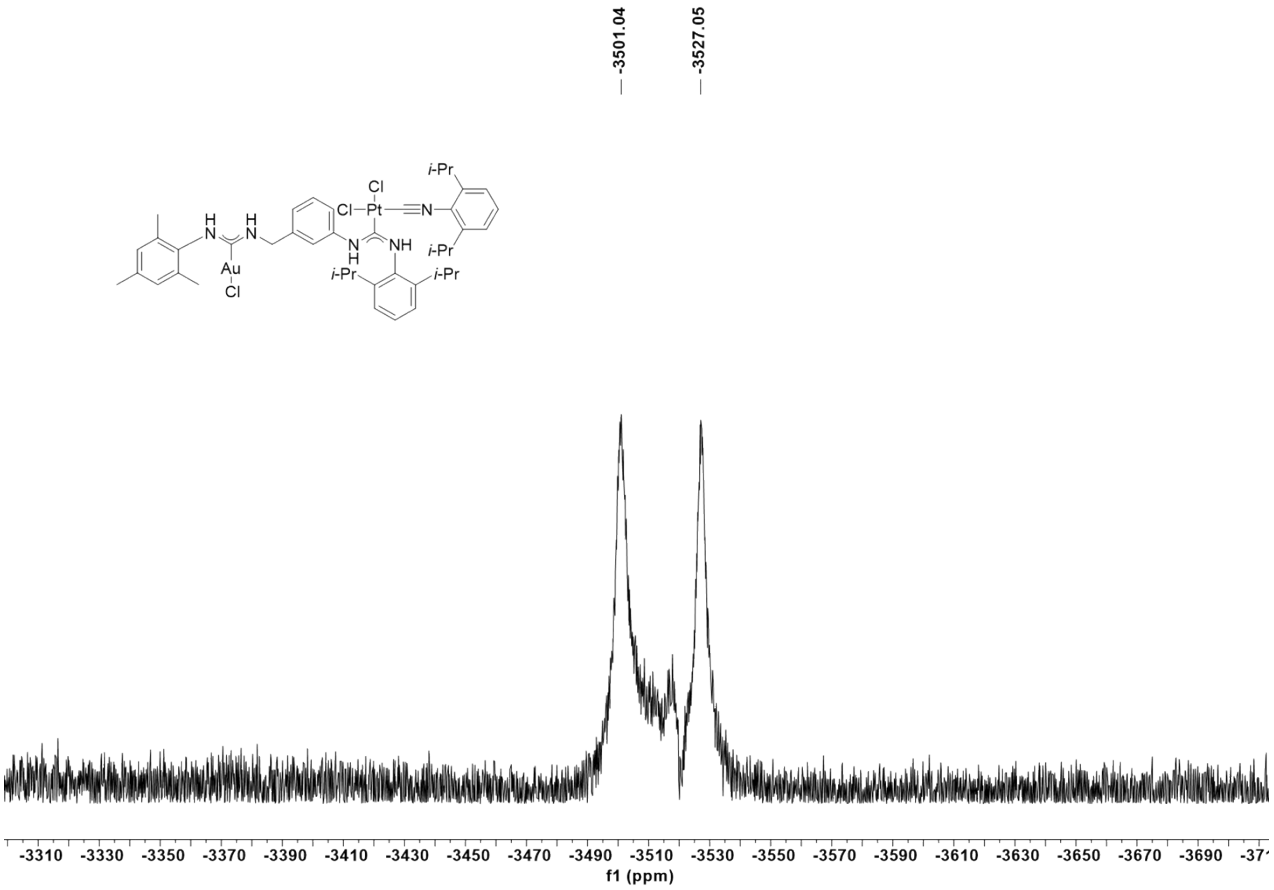


Figure S27. ^{195}Pt NMR of **3e** in CD_2Cl_2 (86 MHz, 295K).

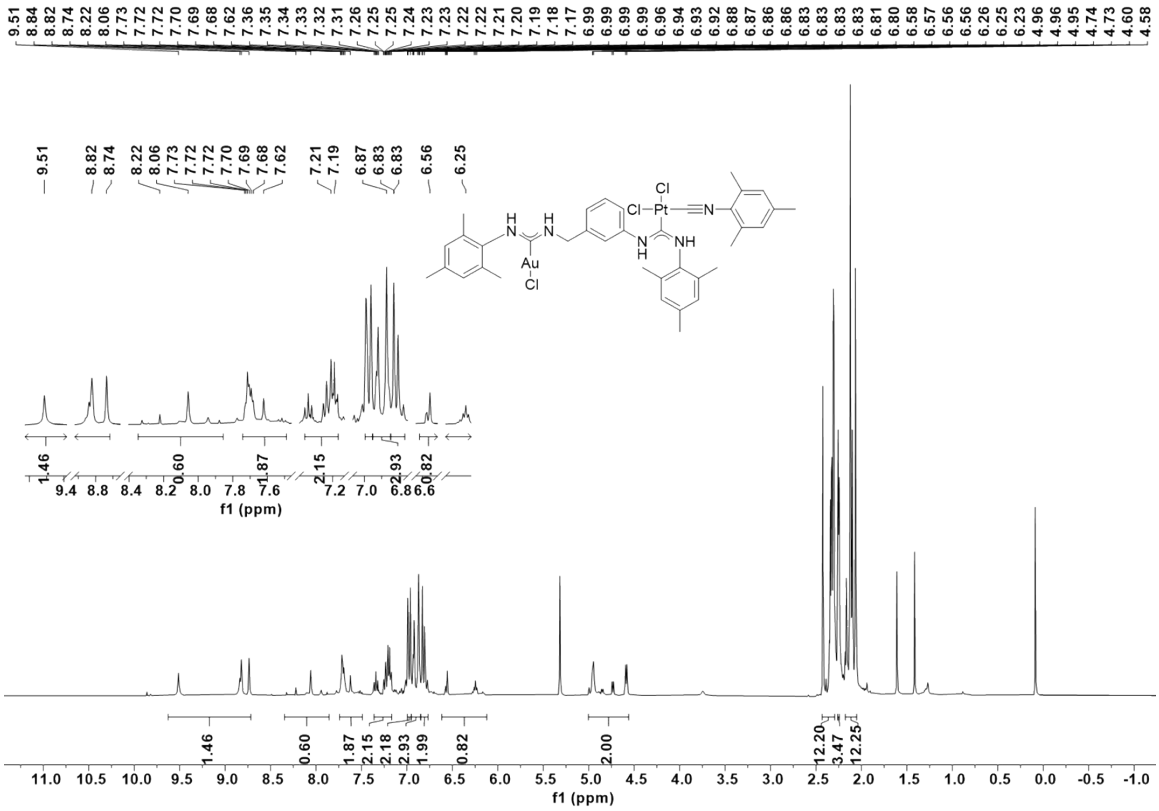


Figure S28. ^{1}H NMR of **3f** in CD_2Cl_2 (400 MHz, 295K).

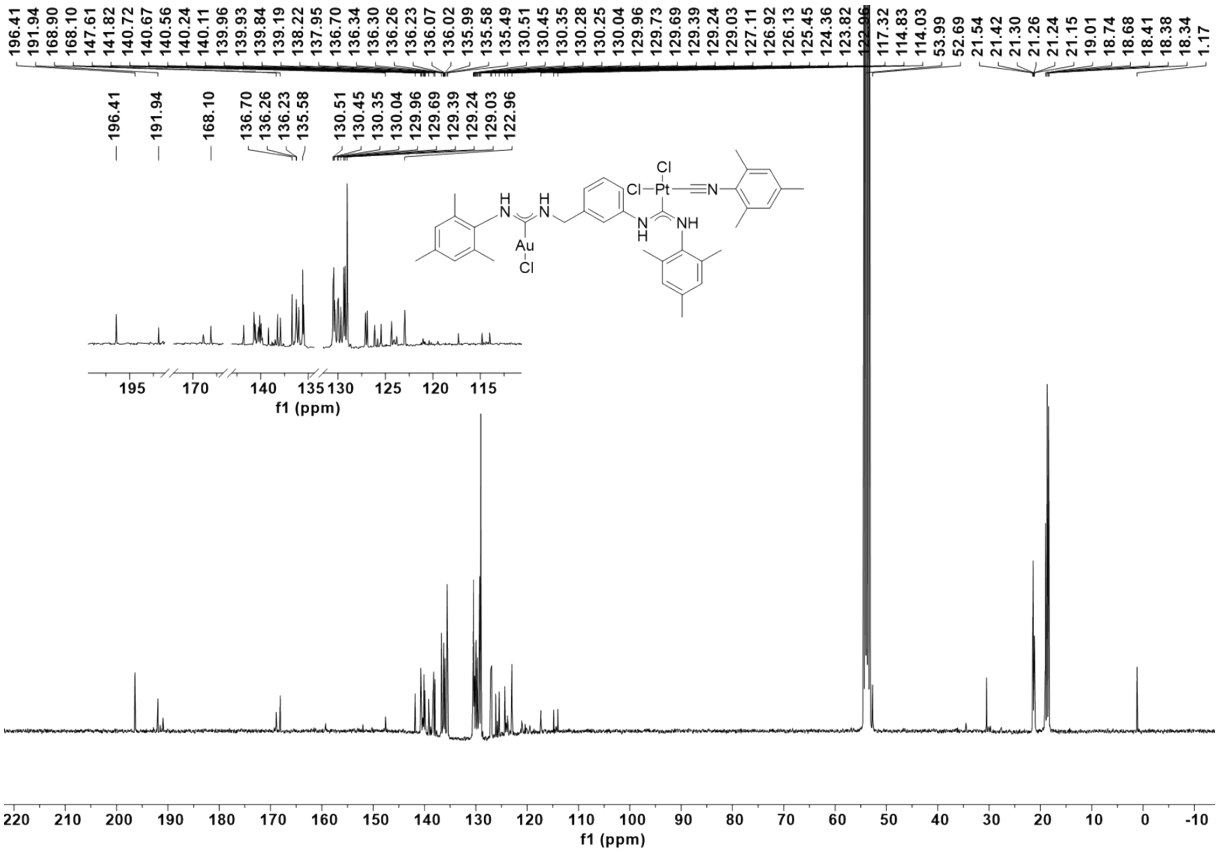


Figure S29. ^{13}C NMR of **3f** in CD_2Cl_2 (101 MHz, 295K).

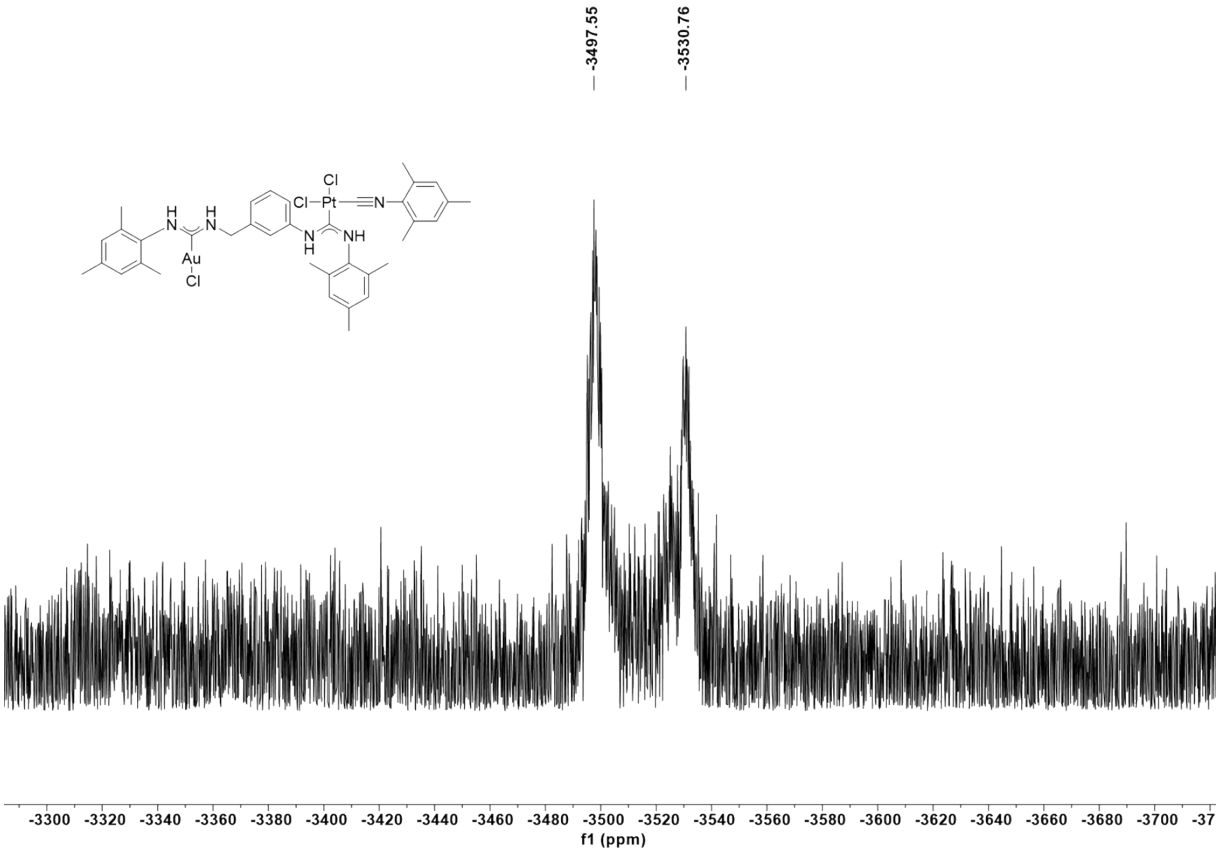


Figure S30. ^{195}Pt NMR of **3f** in CD_2Cl_2 (86 MHz, 295K).

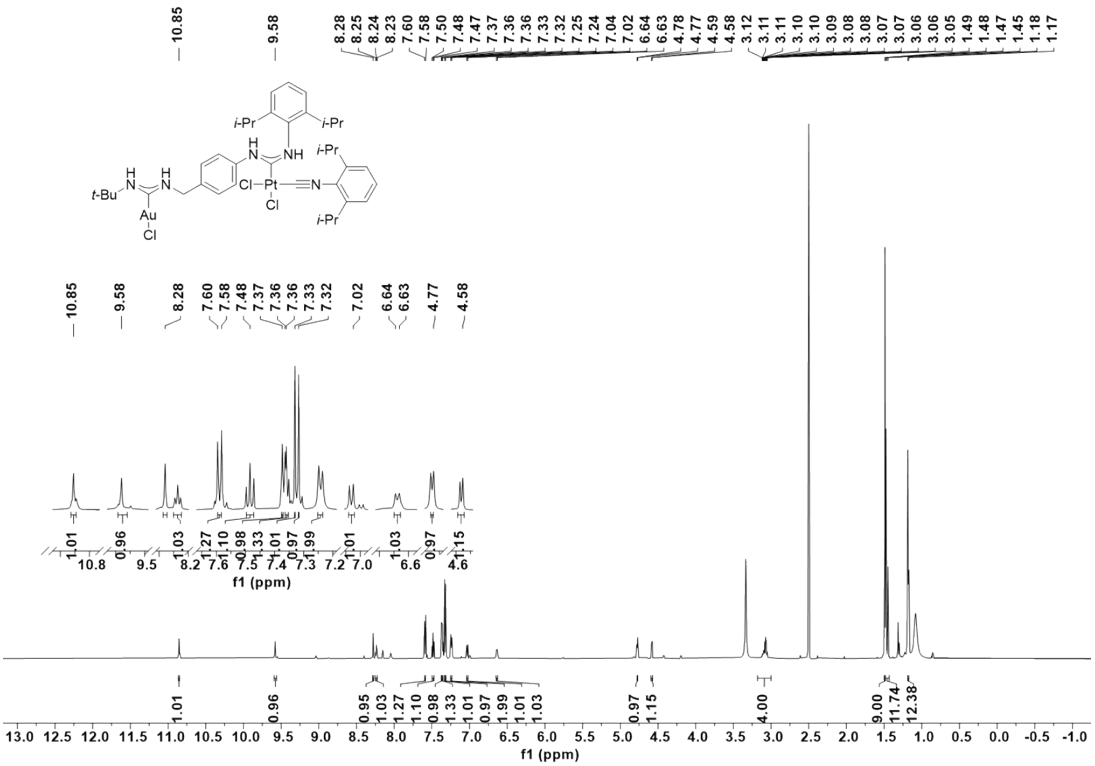


Figure S31. ^{1}H NMR of **3g** in DMSO-d_6 (600 MHz, 295K).

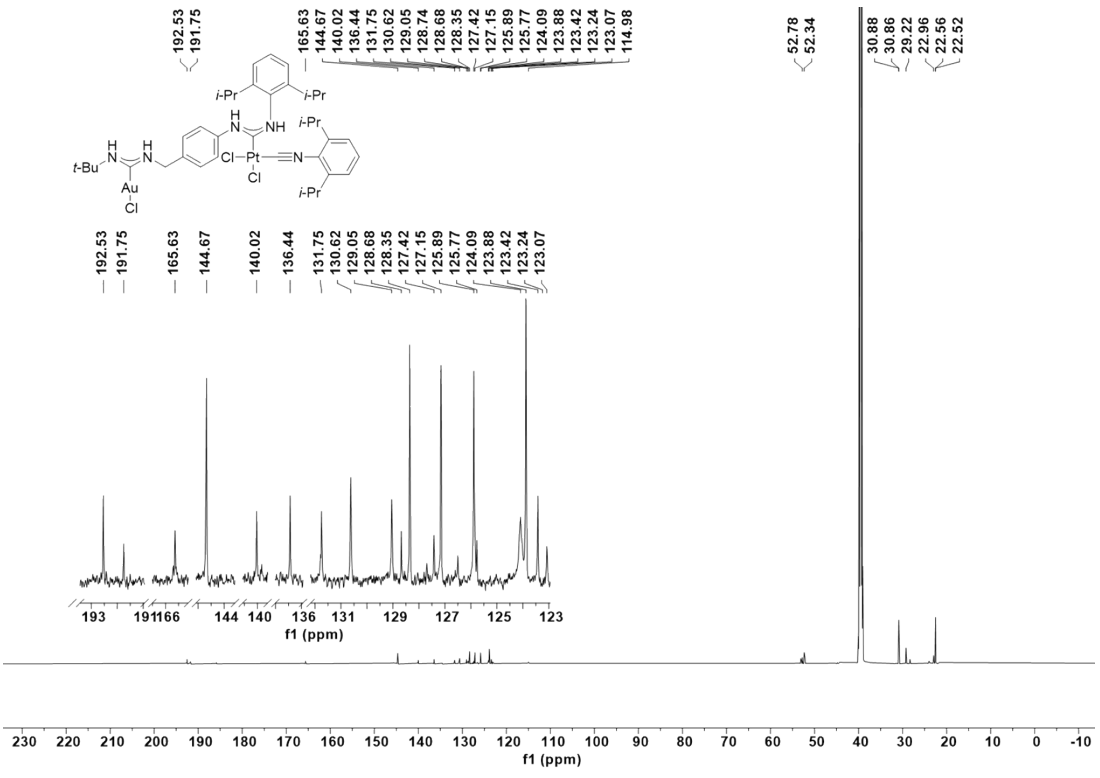


Figure S32. ^{13}C NMR of **3g** in DMSO-d_6 (151 MHz, 295K).

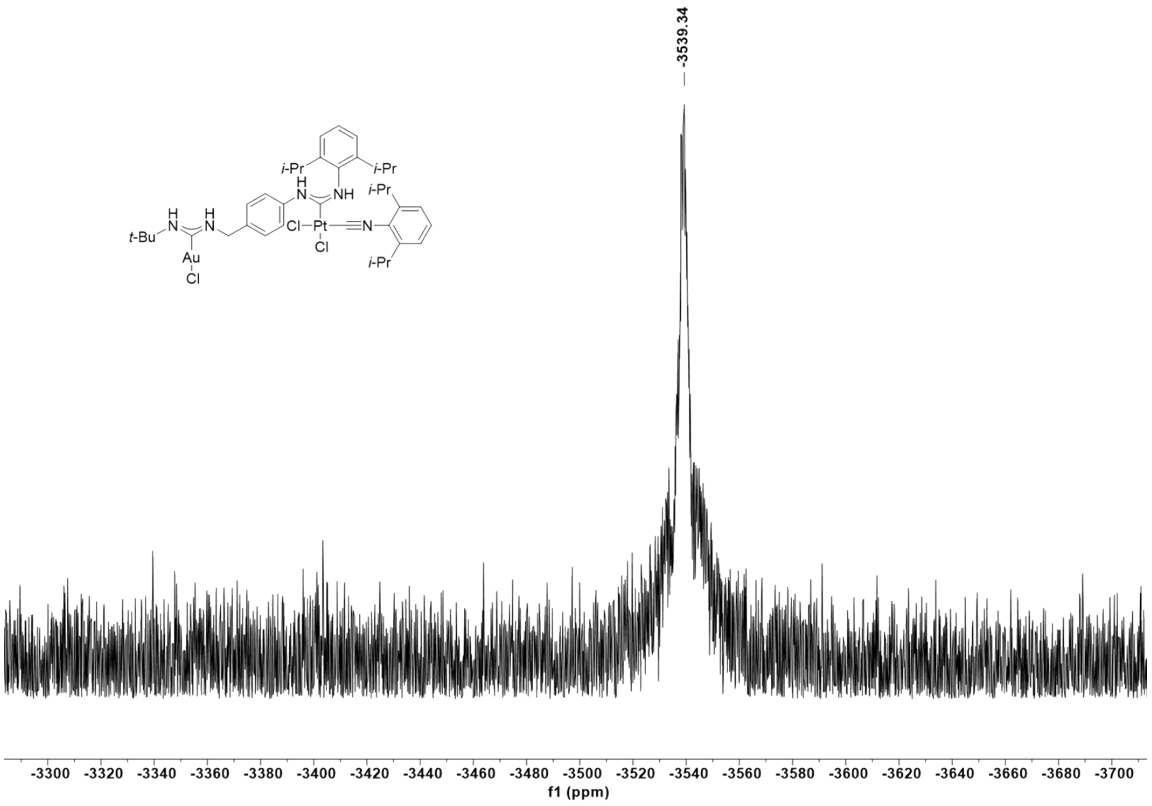


Figure S33. ^{195}Pt NMR of **3g** in DMSO-d_6 (86 MHz, 295K).

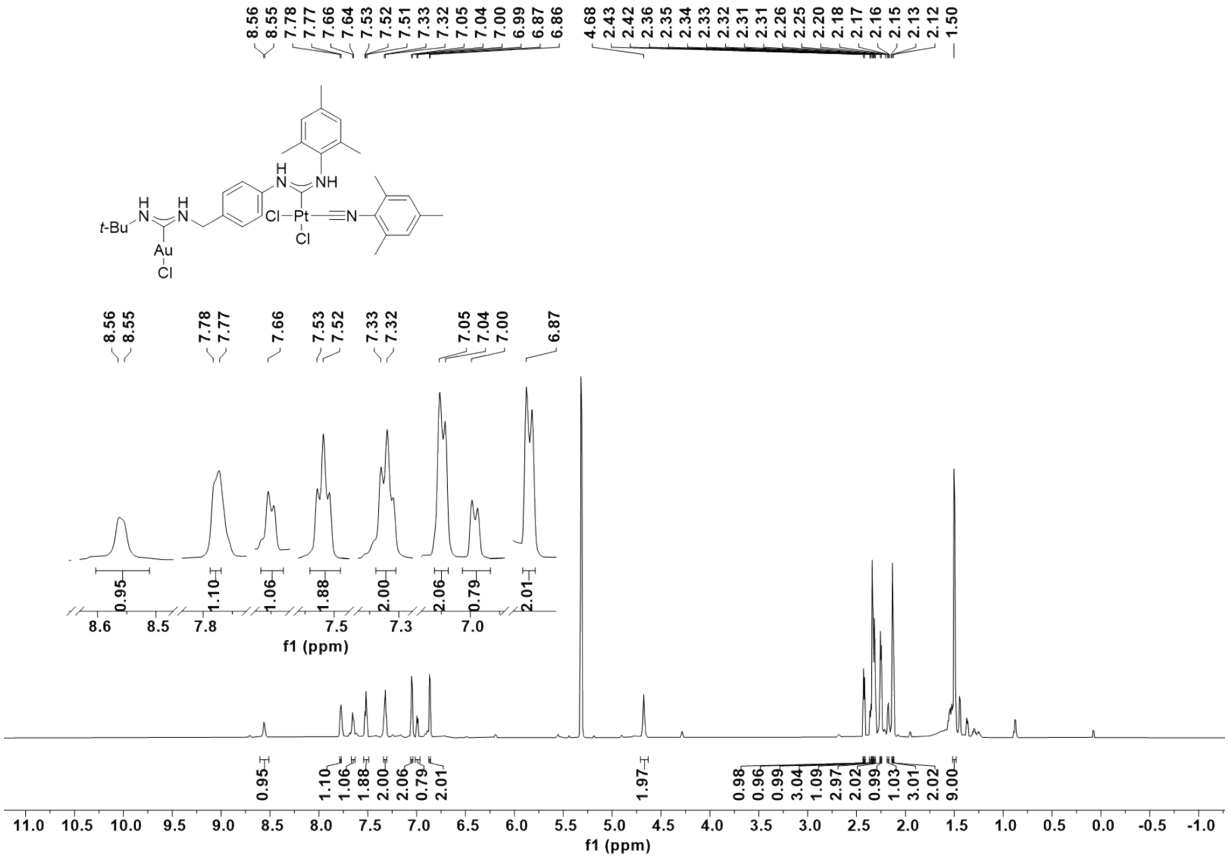


Figure S34. ^{1}H NMR of **3h** in CD_2Cl_2 (700 MHz, 295K).

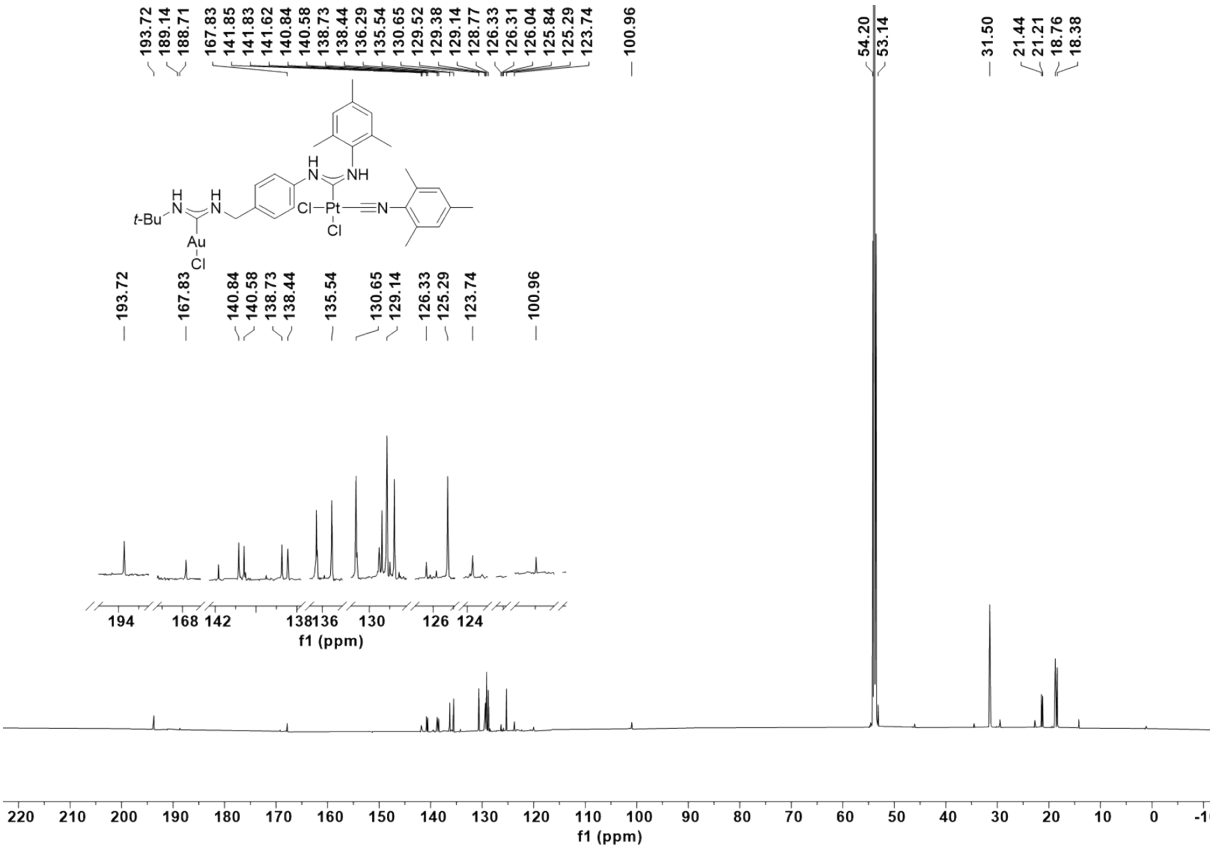


Figure S35. ^{13}C NMR of **3h** in CD_2Cl_2 (176 MHz, 295K).

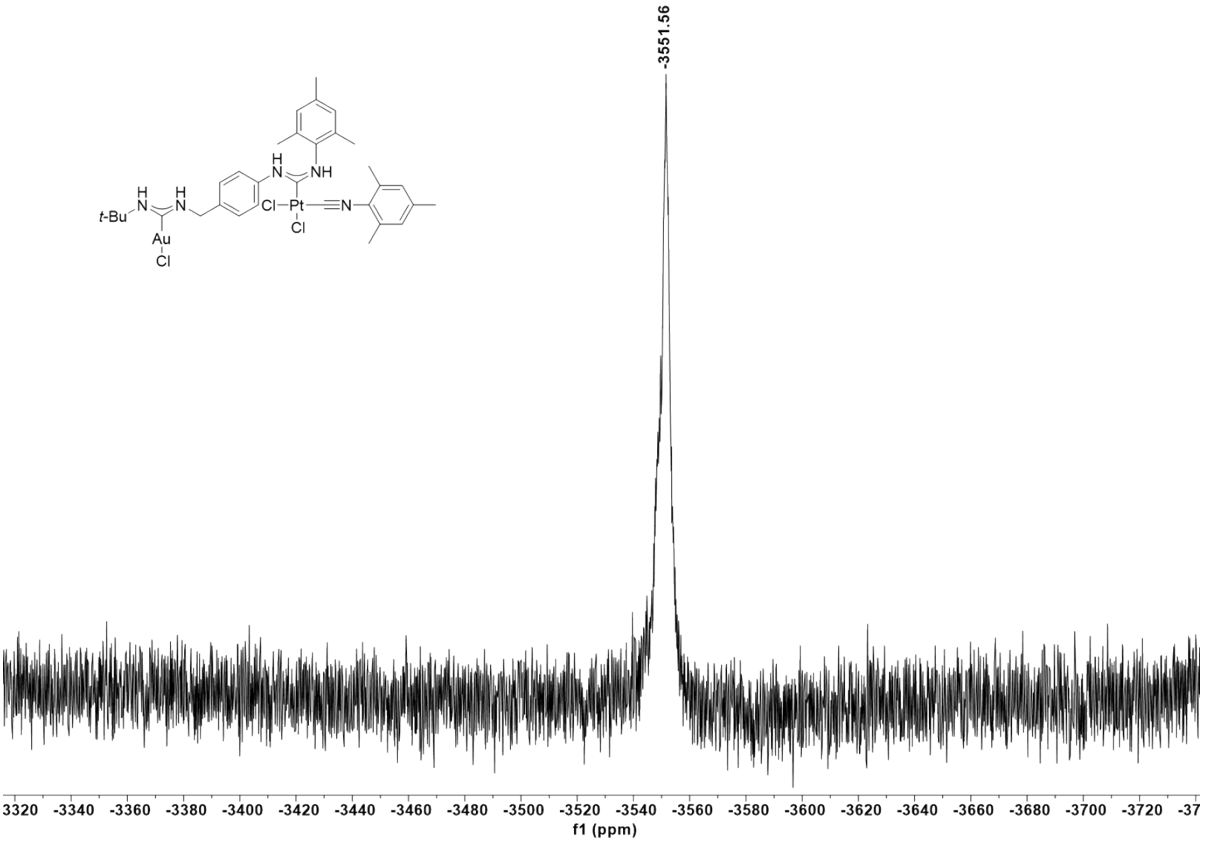


Figure S36. ^{195}Pt NMR of **3h** in CD_2Cl_2 (86 MHz, 295K).

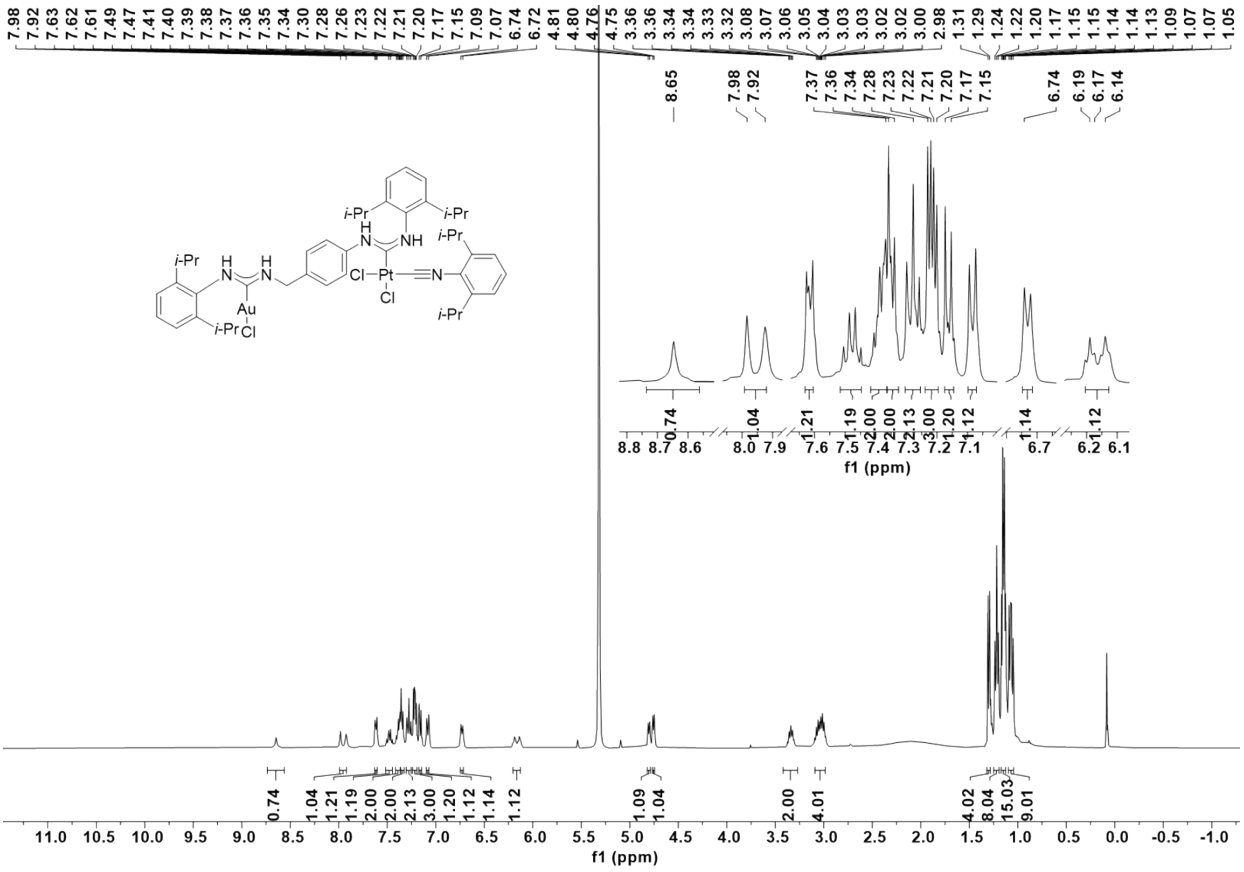


Figure S37. ^{1}H NMR of **3i** in CD_2Cl_2 (400 MHz, 295K).

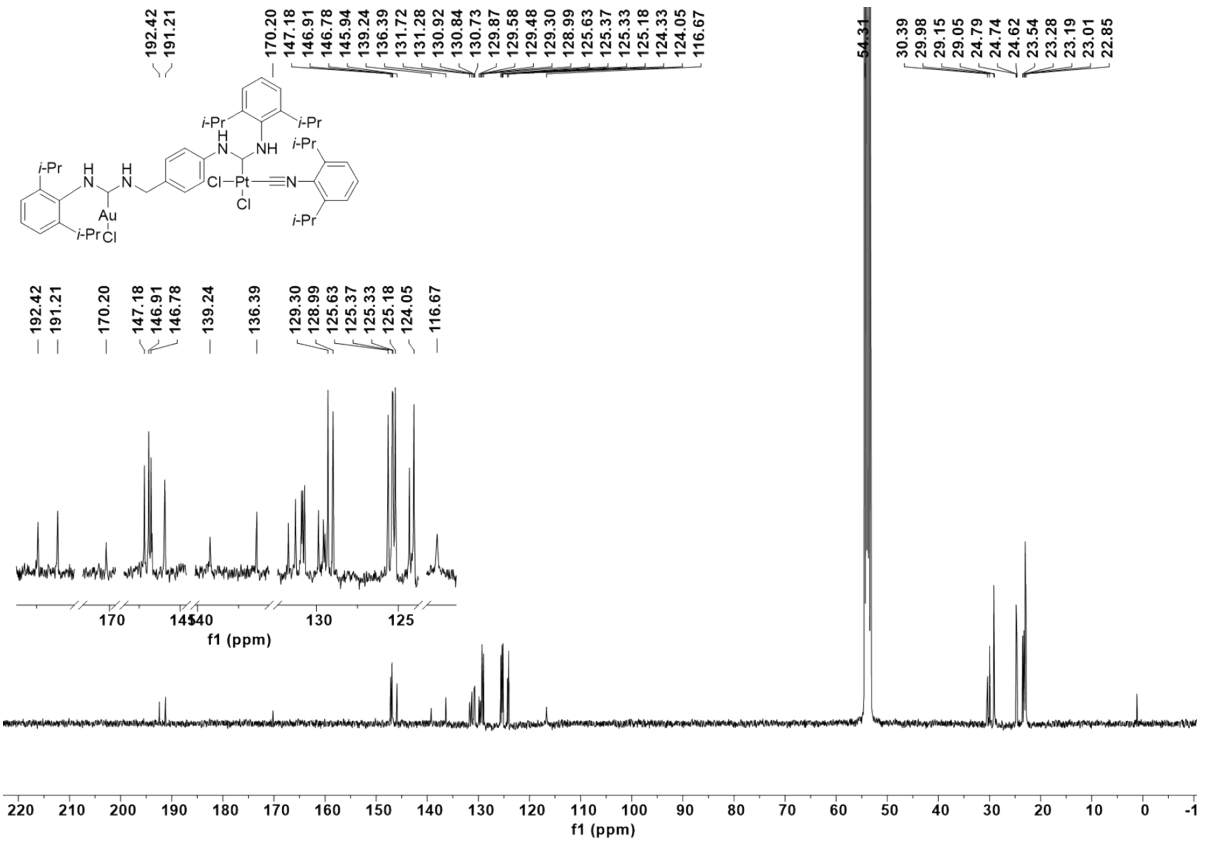


Figure S38. ^{13}C NMR of **3i** in CD_2Cl_2 (100 MHz, 295K).

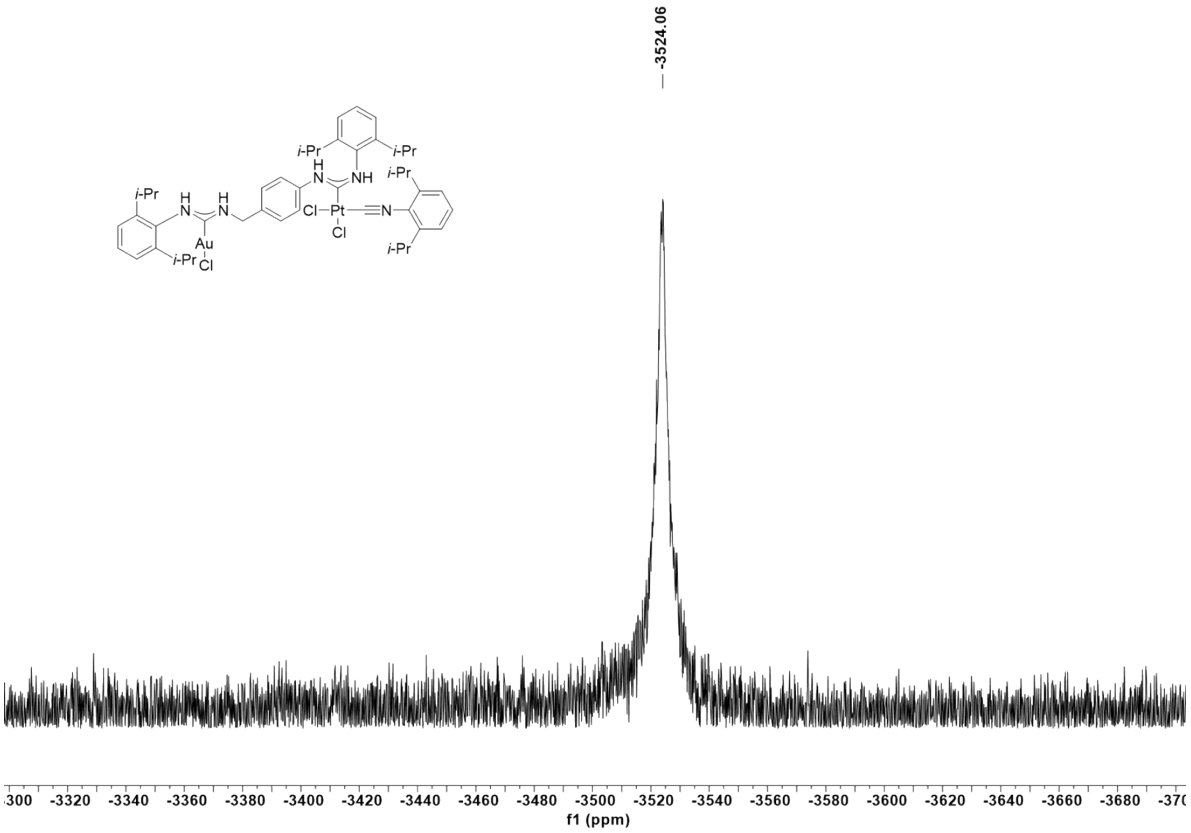


Figure S39. ^{195}Pt NMR of **3i** in CD_2Cl_2 (86 MHz, 295K).

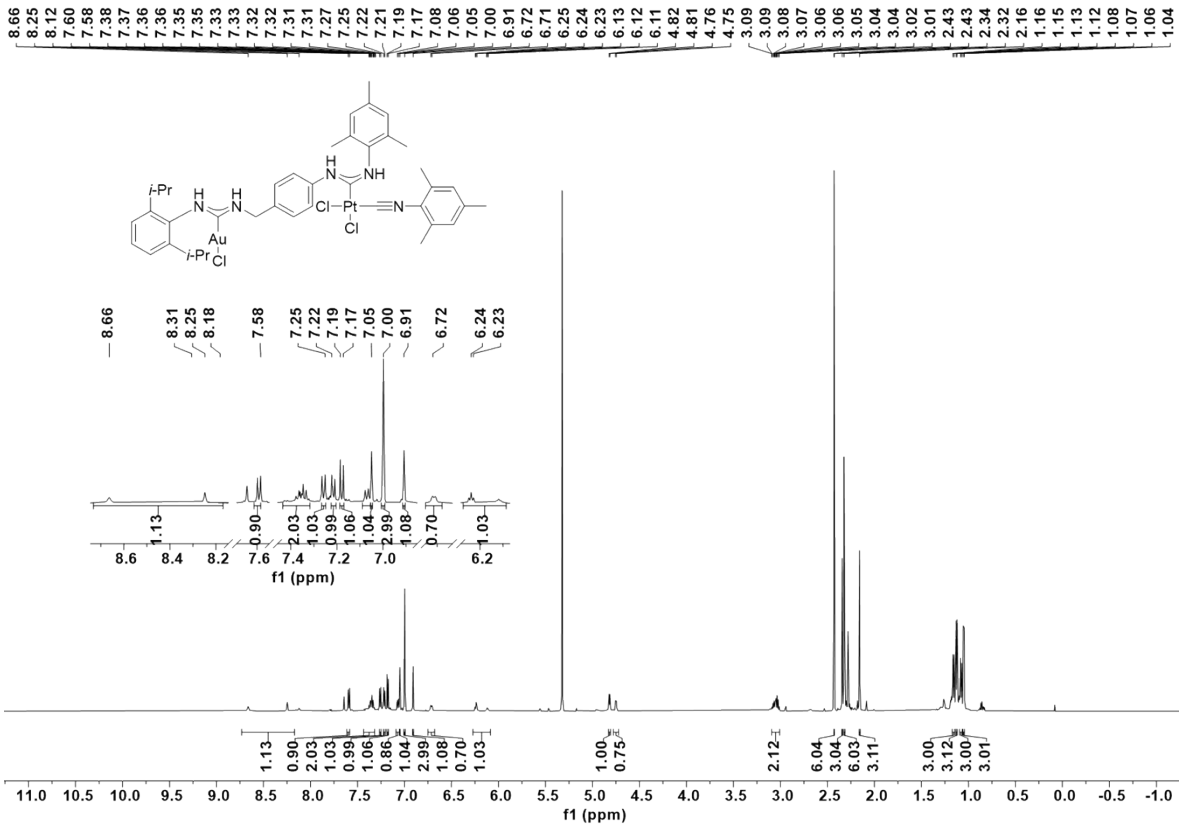


Figure S40. ^{1}H NMR of **3j** in CD_2Cl_2 (600 MHz, 295K).

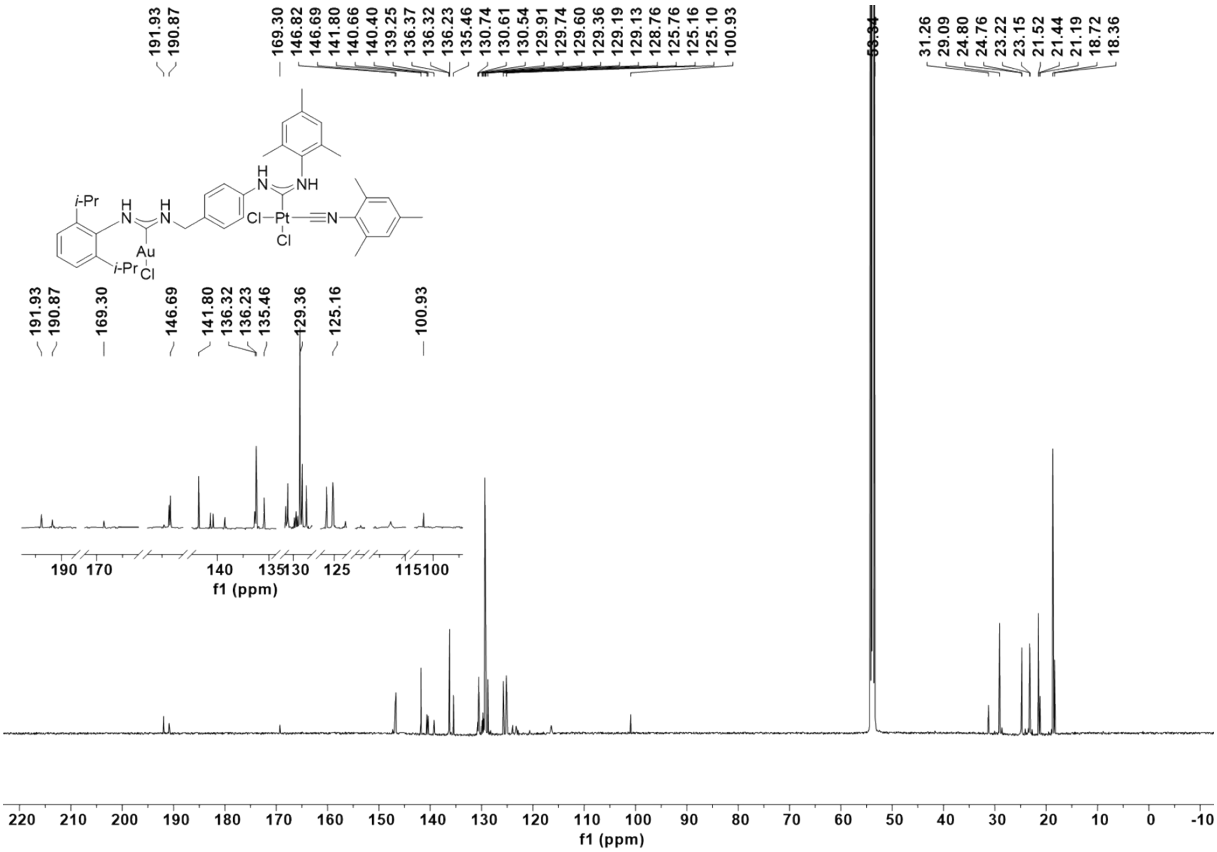


Figure S41. ^{13}C NMR of **3j** in CD_2Cl_2 (100 MHz, 295K).

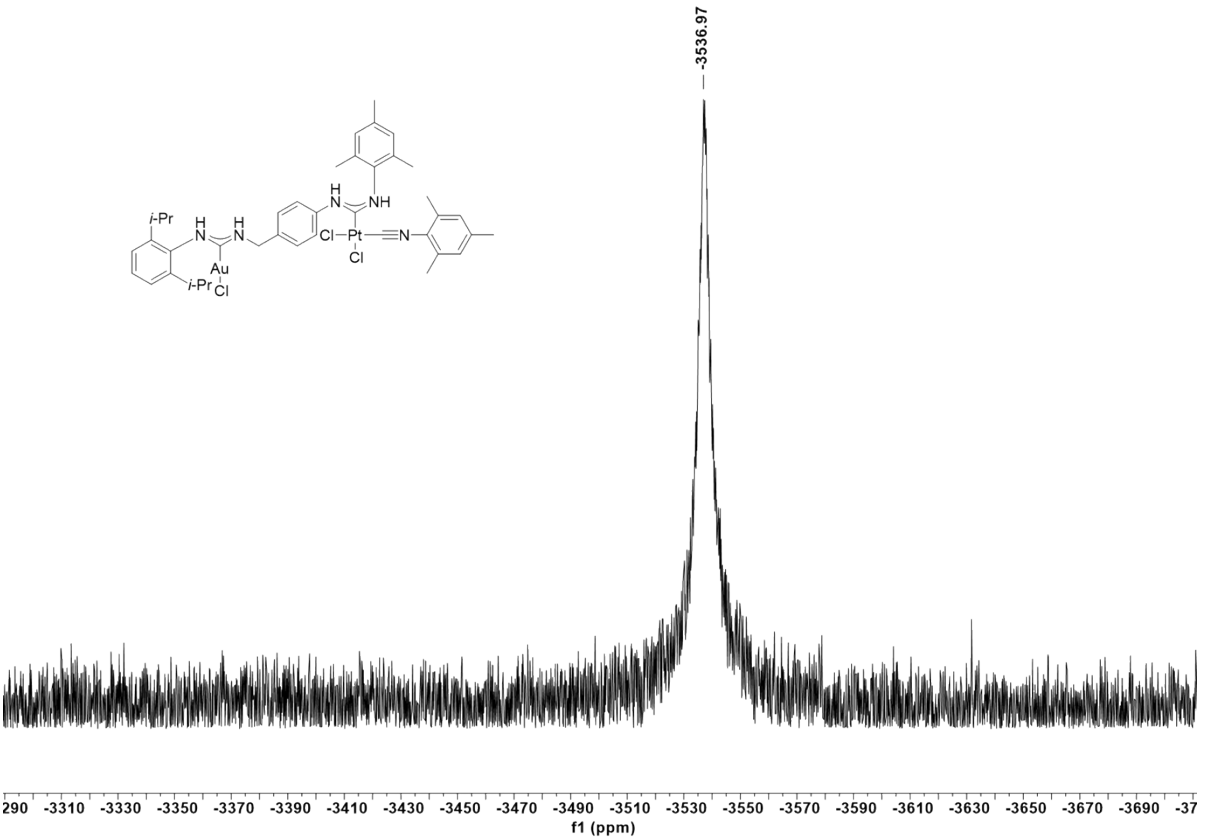


Figure S42. ^{195}Pt NMR of **3j** in CD_2Cl_2 (86 MHz, 295K).

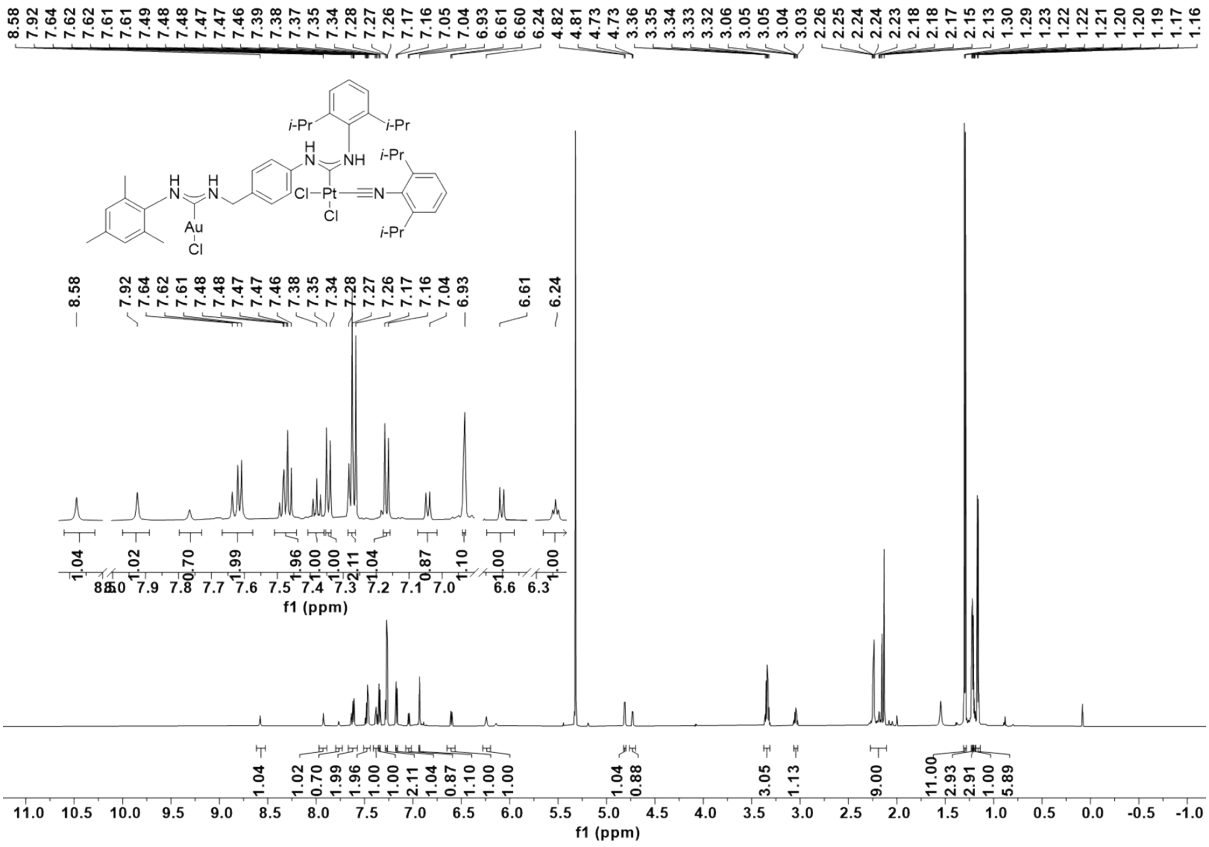


Figure S43. ^{1}H NMR of **3k** in CD_2Cl_2 (700 MHz, 295K).

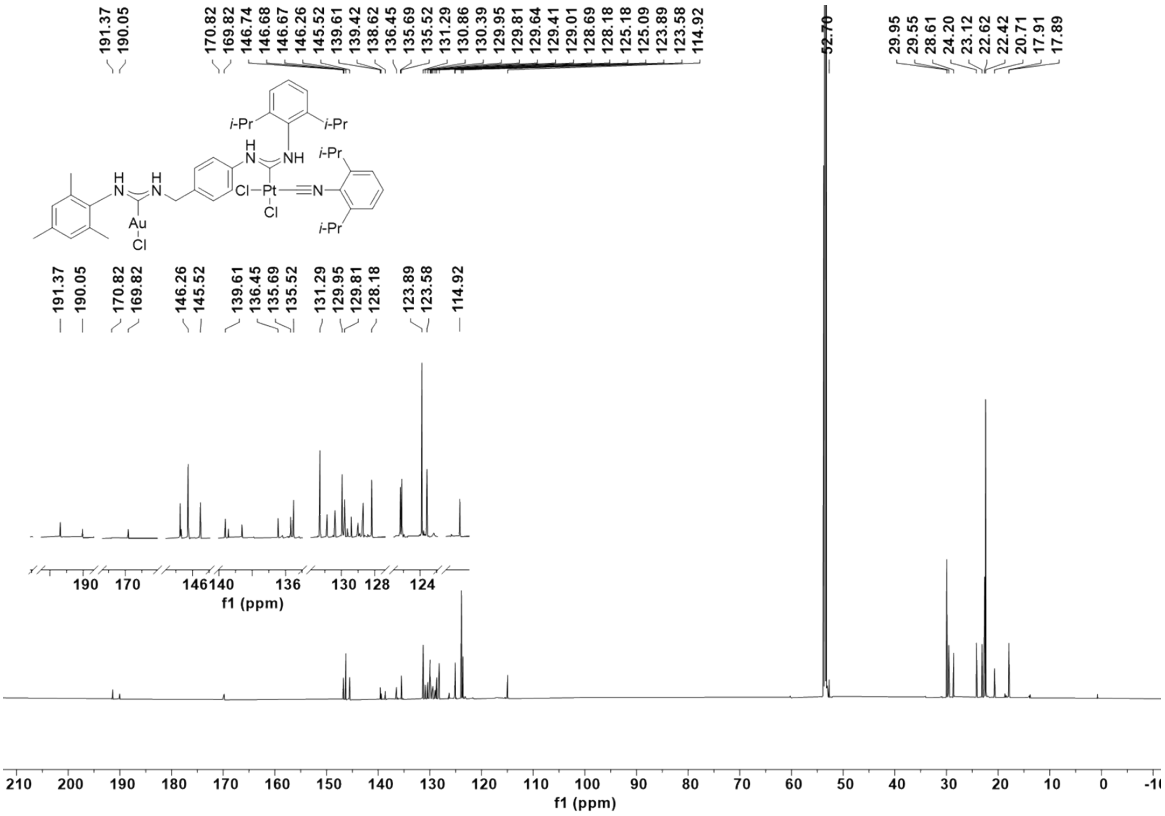


Figure S44. ^{13}C NMR of **3k** in CD_2Cl_2 (176 MHz, 295K).

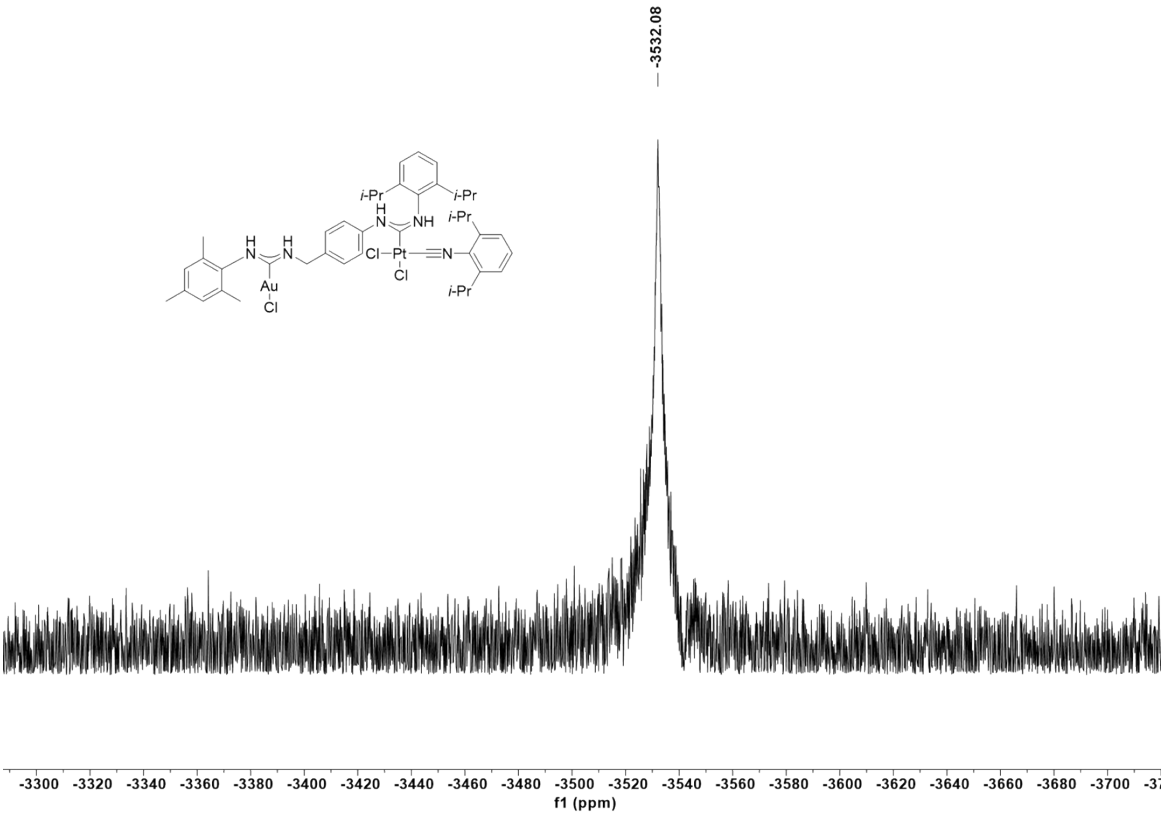


Figure S45. ^{195}Pt NMR of **3k** in CD_2Cl_2 (86 MHz, 295K).

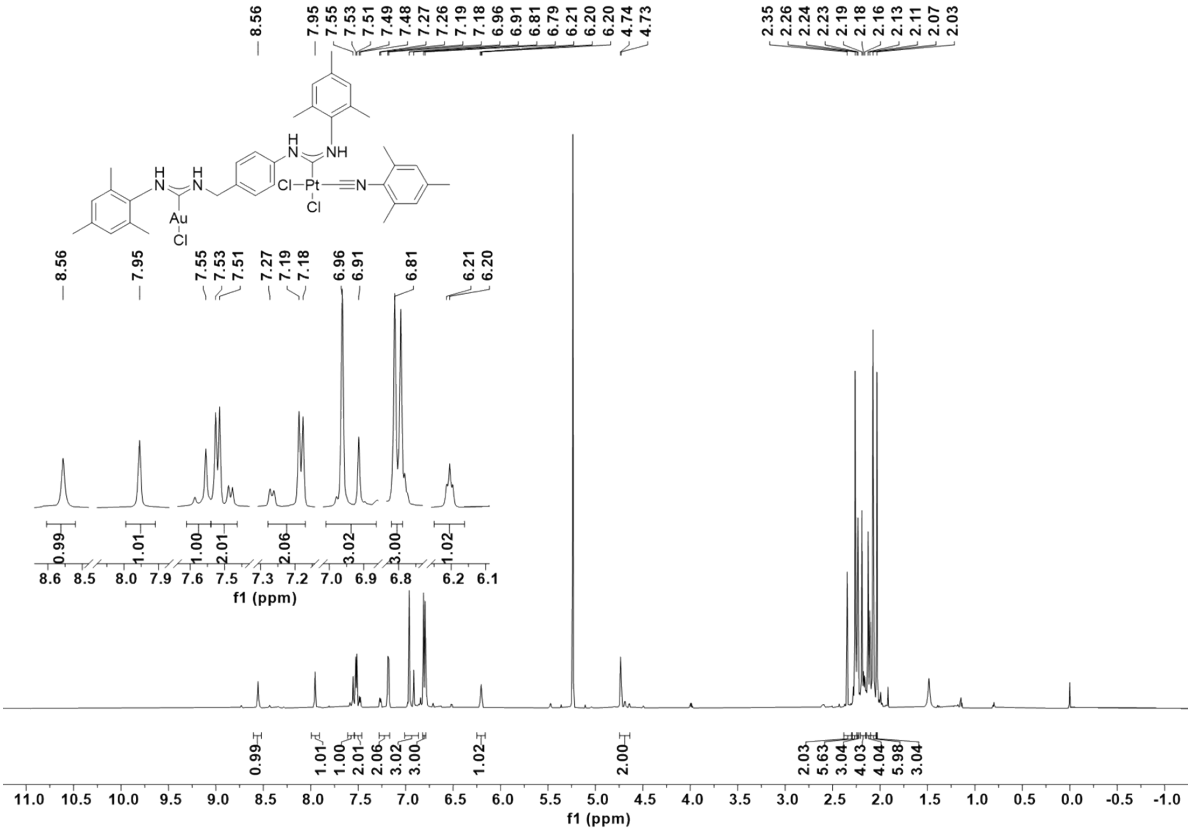


Figure S46. ^{1}H NMR of **3l** in CD_2Cl_2 (700 MHz, 295K).

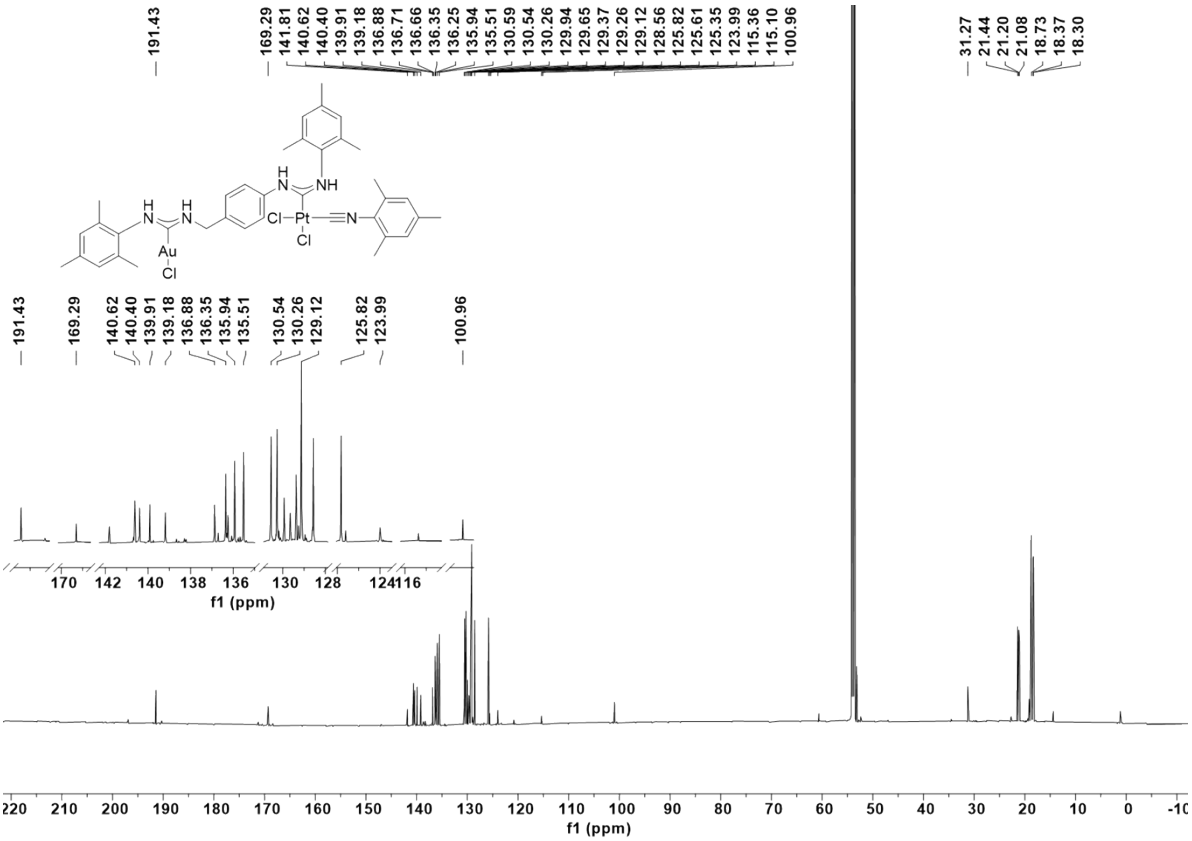


Figure S47. ^{13}C NMR of **3l** in CD_2Cl_2 (176 MHz, 295K).

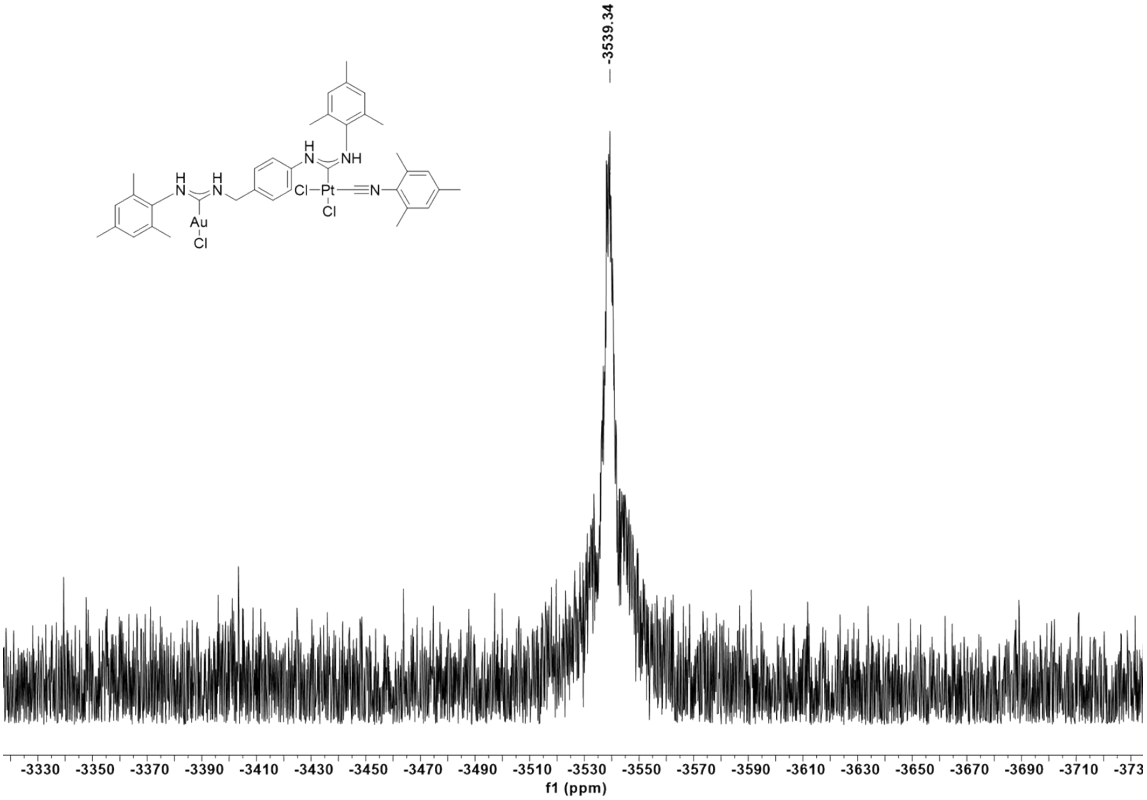


Figure S48. ^{195}Pt NMR of **3l** in CD_2Cl_2 (86 MHz, 295K).

4 DNA Docking

The docking studies with the DNA were carried using the AutoDock Vina 1.1.1 software,[5] using the B-DNA dodecamer crystallographic structure from the Protein Data Bank (PDB ID 1BNA), according to previous studies.[2,6-9] The 3D model of complex **3h** was obtained by quantum chemical calculations, and the DNA receptor was prepared using the Chimera 1.8 software.[10,11] Complex **3h** and cisplatin were fully optimized using a Density Functional Theory (DFT) approach as implemented in the Amsterdam Density Functional program (ADF2019.307)[12,13] with the BLYP functional[14], combined with a TZ2P basis set and a small frozen core approximation. Scalar relativistic effect was included at the Zeroth Order Regular Approximation (ZORA) level.[15] The effect of dispersive interactions was taken into account in the geometry optimizations using Grimme D3 dispersion correction[16,17] and the Becke-Johnson[18,19] damping function (BLYP-D3(BJ)). The Hirshfeld atomic charges of the optimized geometry were used for the docking simulation. For the blind docking, the grid box was positioned in the center of the DNA molecule (coordinates xyz: 14.75, 20.98, and 9.23; size: 50×50×50 Å), and an exhaustiveness of 50 was used. Since AutoDock Vina does not recognize the Au and Pt atoms, they were replaced by Cu and Zn for docking simulations, however, keeping all the metal features obtained from the DFT calculations. To represent the binding mode of interaction, the conformer of the ligand with the lowest predicted binding free energy (ΔG) from the most populated cluster was chosen.

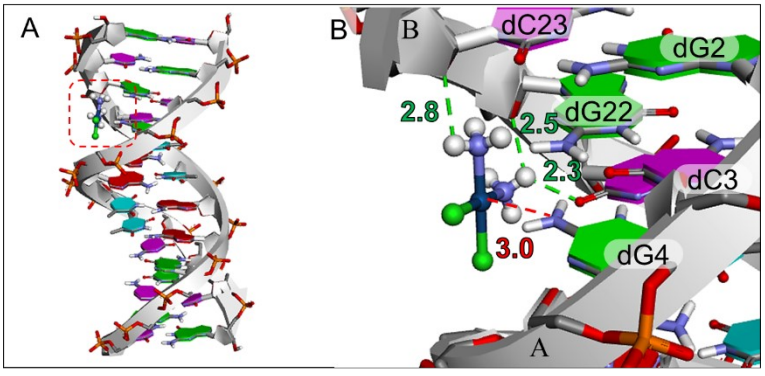


Figure S49. Cisplatin interaction with DNA obtained from molecular docking simulations. (A) Overview and (B) close view of the cisplatin interaction with DNA. ΔG = -3.2 kcal/mol. Hydrophobic, H-bonds, and Pt···N interactions are represented by purple, green, and red dashed lines with their respective distances in Å.

Table S1. Cartesian coordinates (Å) and energy (Hartree) of complex **3h** and cisplatin. Level of theory: ZORA-BLYP-D3(BJ)/TZ2P.

Complex 3h

E= -17.01051802 a.u.

Au	2.013308000	-5.339156000	-2.997968000
Cl	3.545542000	-7.081034000	-3.063236000
C	0.703016000	-3.791929000	-2.960909000
N	-0.402610000	-3.701315000	-3.711781000
N	0.934292000	-2.724937000	-2.156878000
H	-0.993814000	-2.877779000	-3.594941000
H	0.340988000	-1.898388000	-2.239573000
C	-0.921834000	-4.672263000	-4.735648000
C	-1.233925000	-6.026502000	-4.069352000
H	-1.658341000	-6.711741000	-4.810934000
H	-0.324037000	-6.477736000	-3.662228000
H	-1.955691000	-5.899320000	-3.254988000
C	-2.219298000	-4.039874000	-5.274889000
H	-2.955510000	-3.904164000	-4.472891000
H	-2.662533000	-4.693919000	-6.031080000
H	-2.019744000	-3.068387000	-5.744178000
C	0.098992000	-4.834811000	-5.878712000
H	1.034794000	-5.261762000	-5.505686000
H	-0.308016000	-5.506172000	-6.642449000

H	0.316880000	-3.866455000	-6.342969000
C	1.999615000	-2.634822000	-1.203970000
C	2.890247000	-1.558697000	-1.256950000
C	3.962799000	-1.502164000	-0.367931000
C	4.162006000	-2.529781000	0.565100000
C	3.251714000	-3.592198000	0.630494000
C	2.167047000	-3.631353000	-0.236236000
H	2.763117000	-0.782416000	-2.007238000
H	4.657163000	-0.665744000	-0.411028000
H	1.460166000	-4.451896000	-0.179049000
H	3.386319000	-4.376845000	1.364056000
N	5.345196000	-2.489795000	1.348478000
C	5.629890000	-3.131617000	2.507371000
N	6.943141000	-3.145815000	2.814726000
H	6.085965000	-1.926182000	0.931835000
H	7.602340000	-2.821123000	2.105200000
C	7.532947000	-3.879801000	3.909192000
C	8.178813000	-5.092162000	3.600402000
C	8.740389000	-5.826065000	4.649297000
C	8.663157000	-5.384812000	5.976983000
C	8.038489000	-4.159550000	6.237124000
C	7.475175000	-3.376739000	5.220264000
H	8.631524000	-6.625936000	2.153309000

H	9.235186000	-6.768875000	4.423964000
H	9.554816000	-5.607620000	7.939774000
H	7.989327000	-3.793334000	7.260844000
H	7.165982000	-1.690202000	6.517972000
C	8.250611000	-5.601741000	2.178350000
H	7.266877000	-5.596215000	1.698764000
H	8.915307000	-4.983406000	1.558124000
C	6.829326000	-2.051806000	5.541907000
H	7.064973000	-1.296079000	4.784909000
H	5.736734000	-2.137361000	5.563047000
C	9.215078000	-6.229129000	7.104411000
H	8.441855000	-6.906415000	7.493049000
H	10.054674000	-6.846867000	6.767578000
Pt	4.240725000	-3.914713000	3.737884000
Cl	2.600297000	-4.746930000	5.248754000
C	4.869041000	-5.688664000	3.525353000
N	5.252214000	-6.786179000	3.344142000
H	4.598647000	-7.396732000	-0.468488000
C	5.652110000	-7.977951000	2.769116000
C	6.282184000	-8.951075000	3.569777000
C	6.706753000	-10.125176000	2.940944000
C	6.510706000	-10.345124000	1.569428000
C	5.869335000	-9.353300000	0.811965000

C	5.426178000	-8.158398000	1.384246000
H	7.048288000	-9.528486000	5.500548000
H	7.200627000	-10.889082000	3.538964000
H	6.121095000	-12.366541000	0.914399000
H	5.705129000	-9.510815000	-0.252104000
Cl	3.414196000	-1.709043000	3.969948000
C	6.468508000	-8.718035000	5.049260000
H	6.981719000	-7.768868000	5.237500000
H	5.498750000	-8.659539000	5.559750000
C	6.947224000	-11.641934000	0.924150000
H	7.255730000	-11.485678000	-0.115286000
H	7.780105000	-12.099325000	1.468984000
C	4.726619000	-7.097297000	0.573887000
H	3.734739000	-6.880925000	0.990071000
H	5.283110000	-6.150819000	0.589313000

Cisplatin

E= -1.78954433 a.u.

Pt	-0.173672000	-0.809134000	0.043548000
Cl	1.195828000	1.064754000	0.098932000
Cl	1.552541000	-2.357694000	0.153123000
N	-1.712945000	0.644899000	-0.055930000

H	-1.176778000	1.525549000	-0.035877000
H	-2.259460000	0.614828000	-0.919034000
H	-2.350551000	0.632431000	0.742695000
N	-1.380290000	-2.551456000	-0.003257000
H	-2.007522000	-2.645147000	0.798202000
H	-1.920591000	-2.661809000	-0.863725000
H	-0.674451000	-3.301911000	0.041324000

5 Cell viability assay and cellular uptake

Five cancer cells lines (A2780, OVCAR-3, HCT116, A549, MDA-MB-231) and one non-tumoral cell type (MRC-5) were employed and grown in accordance with the supplier's instructions and maintained at 37°C in humidified atmosphere of 5% of CO_2. A defined number of cells (A2780 1000 cells per well, OVCAR-3 2000 cpw, HCT116 1000 cpw, A549 1000 cpw, MDA-MB-231 1000 cpw and MRC-5 8000 cpw) was seeded in 96 well and treated after 24h with six different concentrations of the tested complexes (0.001, 0.01, 0.1, 1, 10, 100 μM). In particular, a 10 mM stock solution in DMSO was prepared for each complex. This solution was directly diluted in the culture medium, resulting in the desired six different concentrations.

After 96 h from the treatment, cell viability was measured with a CellTiter glow assay (Promega, Madison, WI, USA) with BioTek Synergy H1. IC_{50} values were calculated from logistical dose response curves. Averages were obtained from triplicates and error bars are standard deviations.

As far as concerned the cellular uptake experiments, A549 cancer cells were seeded at $2 \cdot 10^6$ cells/plate in 10 cm dishes. After overnight culture at 37 °C and 5% CO_2, cells were treated at 1 μM concentrations of compounds **3h** and **3e** for 3, 6 and 24 hours in duplicate samples. Cells were washed twice with PBS, the washing solution was removed and cells isolated by scraping. Pellets of $2 \cdot 10^6$ cells were collected and desegregated overnight in a 2:1 HNO_3:H_2O_2 mixture. After a 1:10 dilution, samples were analysed by ICP-MS iCAP RQ Thermo Scientific in STDS mode.

6 Stability of complex 3h in solution

In order to assess the stability of the used complexes in solution for the antiproliferative studies, exemplarily complex **3h** was dissolved in a 100 mM saline solution in D_2O and DMSO-d_6 in the rationand was left to stand at room temperature. ^1H NMR spectra of the solution were measured after t = 0 h, 3 h, 6 h, 12 h, 24 h and 48 h. No decomposition was observed.

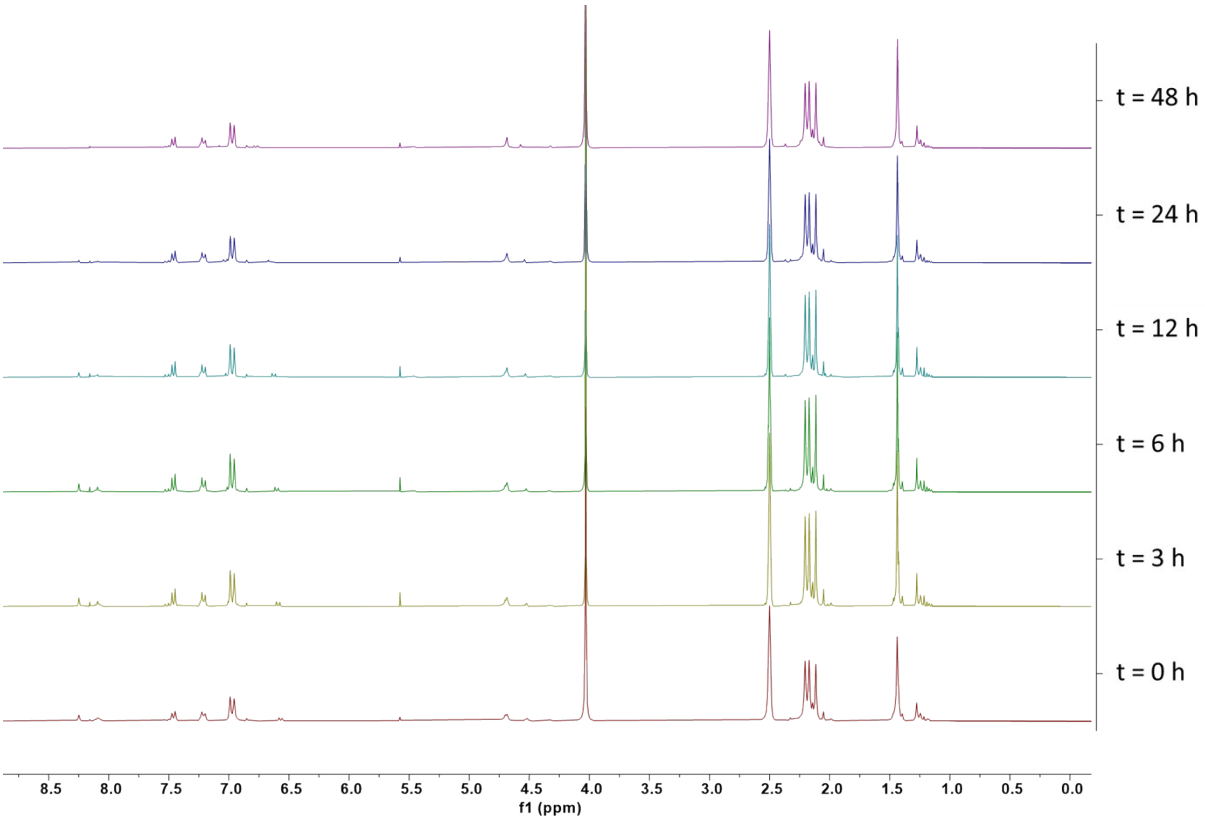
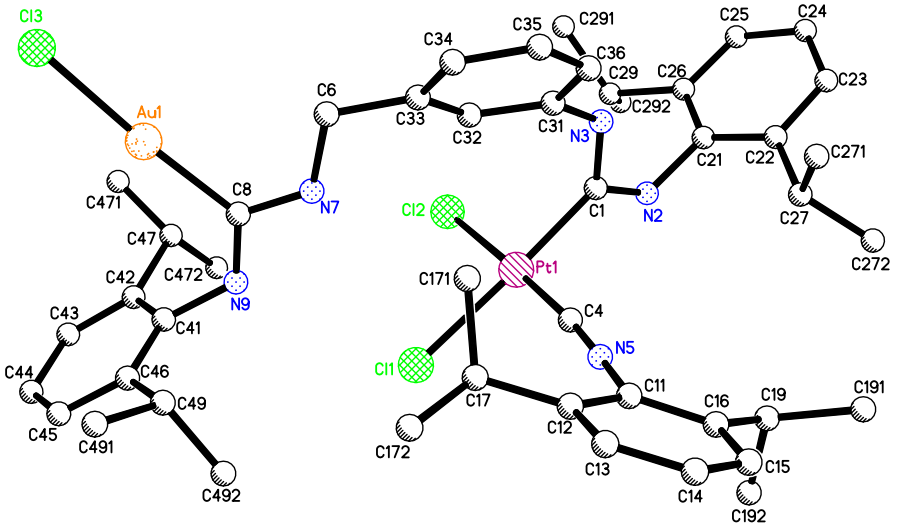


Figure S50. Stability studies of complex **3h** via ^1H NMR experiments in a 100 mM saline solution in D_2O and DMSO-d_6 at 300 MHz and 295 K.

7 Single Crystal Structure of 3c

Empirical formula	$C_{46.70}H_{61.91}Au_{0.73}Cl_{3.43}N_5O_{0.54}Pt$	
Formula weight	1162.23	
Temperature	200(2) K	
Wavelength	1.54178 Å	
Crystal system	monoclinic	
Space group	$P2_1/n$	
Z	8	
Unit cell dimensions	a = 19.7827(5) Å	α = 90 deg.
	b = 24.1706(7) Å	β =103.752(2) deg.
	c = 21.6782(6) Å	γ = 90 deg.
Volume	10068.5(5) $Å^3$	
Density (calculated)	1.53 g/cm^3	
Absorption coefficient	11.03 mm^{-1}	
Crystal shape	needle	
Crystal size	0.390 x 0.018 x 0.018 mm^3	
Crystal colour	colourless	
Theta range for data collection	2.7 to 62.0 deg.	
Index ranges	-20≤h≤22, -27≤k≤24, -20≤l≤24	
Reflections collected	52287	
Independent reflections	15181 (R(int) = 0.0550)	
Observed reflections	10268 (I > 2σ(I))	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.71 and 0.24	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	15181 / 967 / 1124	
Goodness-of-fit on F^2	1.01	
Final R indices (I>2sigma(I))	R1 = 0.050, wR2 = 0.095	
Largest diff. peak and hole	0.83 and -1.18 $eÅ^{-3}$	



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