SUPPORTING INFORMATION

for

Understanding existing and designing novel synthetic routes to Pd-PEPPSI-NHC precatalysts

Sébastien G. Guillet,[a] Vladislav A. Voloshkin,[a] Marina Saab,[a] Marek Beliš,[a] Kristof Van Hecke,[a] Fady Nahra[a,b] and Steven P. Nolan[a,c]

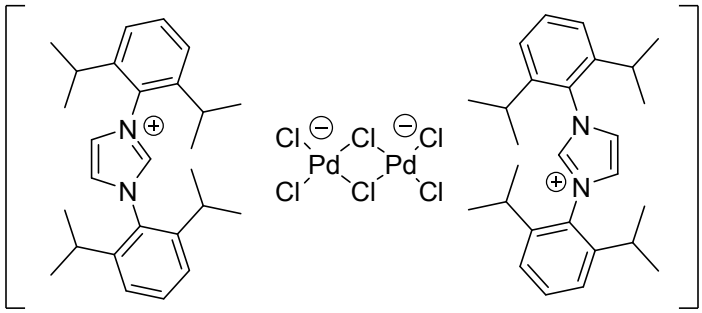
[a]Department of Chemistry and Centre for Sustainable Chemistry, Ghent University, Krijgslaan 281 - S3, 9000 Ghent, Belgium. E-mail: Catherine.cazin@ugent.be: steven.nolan@ugent.be
[b]VITO (Flemish Institute for Technological Research), Separation and Conversion Technology, Boeretang 200, B-2400 Mol, Belgium.
[c]Chemistry Department, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.

General Information

All reactions were performed in scintillation vials under air. Solvents and reagents were used as received without any further purification. Elemental analyses were performed at London Metropolitan University 166-220 Holloway Road, London, N7 8DB. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Bruker-300, 400 or 500 MHz spectrometers at room temperature using $CDCl_3$ or CD_2Cl_2 as solvent. Chemical shifts (ppm) are referenced to the residual solvent peak. Coupling constants (J) are given in hertz. Abbreviations used in the designation of the signals: s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, m = multiplet, td = triplet of doublets, tt = triplet of triplets, q = quadruplet, qt = quadruplet of triplets, hept = heptet.

Preparation of the palladate dimer

$[IPr{\cdot}H]2[PdCl_2(\mu\text{-}Cl)]_2$ **2**

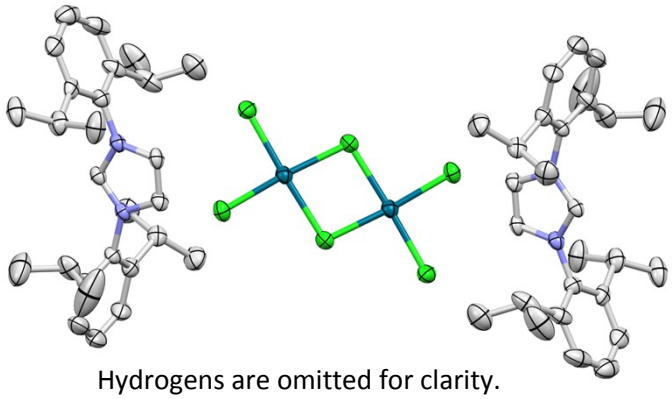


50 mg of palladium chloride (0.28 mmol, 1 equiv.) and 120 mg of IPr·HCl (0.28 mmol, 1 equiv.) were stirred in 1 mL of acetone at 60 °C for 4 h. The mixture was allowed to cool to rt, combined with 3 mL dichloromethane and filtered through microfilter to remove insolubles. The volatiles were removed under vacuum to yield 170 mg (>99%) of the palladate dimer $[IPr.H]_2[PdCl_2(\mu\text{-}Cl)]_2$ **2** as a brown microcrystalline solid.

^{1}H NMR (300 MHz, CD_2Cl_2) δ (ppm) 8.84 (t, *J* = 1.6 Hz, 2 H; C**H**-$(N)_2$), 7.99 (d, *J* = 1.6 Hz, 4 H; C**H**=C**H**), 7.67 (t, *J* = 7.9 Hz, 4 H; C_{para}**H**), 7.43 (d, *J* = 7.9 Hz, 8 H; C_{meta}**H**), 2.47 (hept, *J* = 6.8 Hz, 8 H; C**H**-$(CH_3)_2$), 1.32 (d, *J* = 6.8 Hz, 24 H; C$\mathbf{H}_3$), 1.25 (d, *J* = 6.8 Hz, 24 H; C$\mathbf{H}_3$).

^{13}C NMR (300 MHz, CD_2Cl_2) δ (ppm) 145.5 ($\mathbf{C}_{ortho}$), 137.4 (N-**C**-N) 132.8 ($\mathbf{C}_{para}$H), 130.1 ($\mathbf{C}^{Ar}$-N), 127.2 (**C**H=**C**H), 125.3 ($\mathbf{C}_{meta}$H), 29.6 (**C**H-$(CH_3)_2$), 24.7 (**C**H_3), 24.3 (**C**H_3).

Elemental analysis: calcd (%): C 53.84, H 6.19, N 4.65. Found: C 53.66, H 5.97, N 4.57.

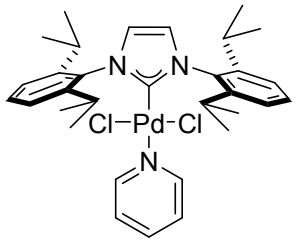


Hydrogens are omitted for clarity.

Figure S1: Molecular structure of **2**

Preparation of a PEPPSI precatalyst from the palladate dimers

$[PdCl_2(Py)(IPr)]$ 1a



100 mg of the palladate dimer **2** (0.083 mmol, 0.5 equiv.), 40 µL (0.50 mmol, 3 equiv.) of pyridine and 115 mg of potassium carbonate (0.83 mmol, 5 equiv.) were stirred in 1 mL of acetone at 60 °C for 3 h. The mixture was allowed to cool to room temperature, filtered through microfilter and the solute concentrated under reduced pressure to half its volume. Pentane (10 mL) was added to precipitate the product. The precipitate was collected by filtration leading to 86 mg (80%) of the desired $[PdCl_2(Py)(IPr)]$ complex **1a** as a pale-yellow solid.

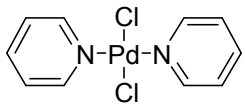
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.57-8.53 (m, 2 H; C^{Py}_{ortho}**H**), 7.53 (tt, J = 7.6 Hz, J = 1.6 Hz, 1 H; C^{Py}_{para}**H**), 7.49 (t, J = 7.7 Hz, 2 H; $C^{Ar\ NHC}_{para}$**H**), 7.35 (d, J = 8 Hz, 4 H; $C^{Ar\ NHC}_{meta}$**H**), 7.13 (s, 2 H; C**H**=C**H**), 7.12-7.07 (m, 2 H; C^{Py}_{meta}**H**), 3.19 (hept, J = 6.7 Hz, 4 H; C**H**-$(CH_3)_2$), 1.49 (d, J = 6.4 Hz, 12 H; C**H$_3$**), 1.12 (d, J = 6.4 Hz, 12 H; C**H$_3$**).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 155.0 (N-**C**-N), 151.5 ($\mathbf{C}^{Py}_{ortho}$H), 146.8 ($\mathbf{C}^{Ar\ NHC}_{ortho}$), 137.5 ($\mathbf{C}^{Py}_{para}$H), 135.3 ($\mathbf{C}^{Ar\ NHC}$-N), 130.4 ($\mathbf{C}^{Ar\ NHC}_{para}$H), 125.1 (**C**H=**C**H), 124.2 ($\mathbf{C}^{Ar\ NHC}_{meta}$H), 124.1 ($\mathbf{C}^{Py}_{meta}$H), 28.9 (**C**H), 26.4 (**C**H_3), 23.4 (**C**H_3).

The data are in agreement with the reported values.[1]

Preparation of bispyridine adducts

$[PdCl_2(Py)_2]$ 3a



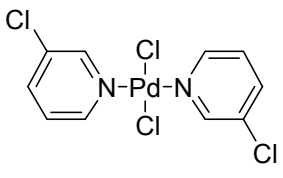
3.0 g of palladium dichloride (16.9 mmol, 1 equiv.) and 4 mL of pyridine (49.7 mmol, 3 equiv.) were stirred in 200 mL of methanol at room temperature for 3 h. After precipitation, product was filtered and washed with 100 mL of methanol, yielding 5.30 g (93%) of the desired $[PdCl_2(Py)_2]$ complex **3a** as a bright yellow solid.[2]

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.87-8.81 (m, 4 H; C_{ortho}**H**), 7.79 (tt, J = 7.6 Hz, J = 1.6 Hz, 2 H; C_{para}**H**), 7.38-7.31 (m, 4 H; C_{meta}**H**).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 153.5 (**C**$_{ortho}$), 138.7 (**C**$_{para}$), 125.1 (**C**$_{meta}$).

The data are in agreement with the reported values.[2]

$[PdCl_2(3\text{-chloropyridine})_2]$ 3b



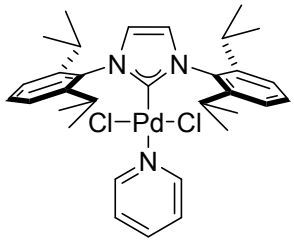
50 mg of palladium dichloride (0.28 mmol, 1 equiv.) and 80 µL of pyridine (0.85 mmol, 3 equiv.) were stirred in 5 mL of methanol at room temperature for 3 h. After precipitation product was filtered and washed with 3 mL of methanol, yielding 104 mg (92%) of the desired $[PdCl_2(3\text{-chloropyridine})_2]$ complex **3b** as a pale-yellow solid.

No NMR analysis could be performed due to insolubility of the product in any available NMR solvents.

Elemental analysis calcd (%) for $C_{10}H_8Cl_4N_2Pd$: C 29.70, H 1.99, N 6.93; found: C 29.77, H 2.00, N 6.96.

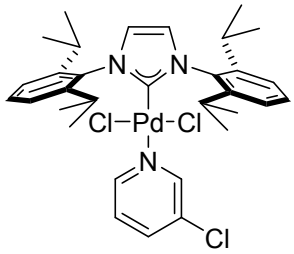
Preparation of the PEPPSI precatalysts from the bis(pyridine) adducts

[$PdCl_2$(Py)(IPr)] 1a



1.5 g of [$PdCl_2(Py)_2$] **3a** (4.47 mmol, 1 equiv.), 1.9 g of IPr·HCl (4.47 mmol, 1 equiv.) and 3.1 g of K_2CO_3 (22.35 mmol, 5 equiv.) were stirred in 25 mL of acetone at 60 °C for 3 hours. The mixture was cooled down, filtered through a frit and dried under vacuum. Pentane (100 mL) was added to triturate the product. The precipitate was filtered, leading to 2.63 g (91%) of the desired [$PdCl_2$(Py)(IPr)] complex **1a** as a pale-yellow solid. The data are in agreement with the reported values.[3]

[$PdCl_2$(3-chloropyridine)(IPr)] 1b



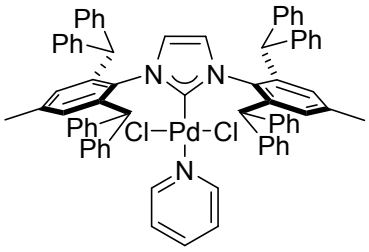
50 mg of [$PdCl_2$(3-chloropyridine)$_2$] **3b** (0.12 mmol, 1 equiv.), 53 mg of IPr·HCl (0.12 mmol, 1 equiv.) and 85 mg of K_2CO_3 (0.62 mmol, 5 equiv.) were stirred in 1 mL of acetone at 60 °C during 3 hours. The mixture was cooled down, filtered through a microfilter and dried under vacuum. Pentane (10 mL) was added to triturate the product. The precipitate was filtered, leading to 62.4 mg (74%) of the desired [$PdCl_2$(3-chloropyridine)(IPr)] complex **1b** as a pale-yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.60 (d, J = 2.4 Hz, 1 H; $C^{Py}{}_2$**H**), 8.52 (dd, J = 5.6 Hz, J = 1.3 Hz, 1 H; $C^{Py}{}_6$**H**), 7.55 (ddd, J = 8.2 Hz, J = 2.4 Hz, J = 1.3 Hz, 1 H; $C^{Py}{}_4$**H**) 7.53-7.46 (m, 2 H; $C^{Ar\ NHC}{}_{para}$**H**), 7.35 (d, J = 7.8 Hz, $C^{Ar\ NHC}{}_{meta}$**H**), 7.14 (s, 2 H; C**H**=C**H**), 7.06 (dd, J = 8.2 Hz, J = 5.6 Hz, 1 H; $C^{Py}{}_5$**H**), 3.16 (hept, J = 6.8 Hz, 4 H; C**H**-$(CH_3)_2$), 1.48 (d, J = 6.6 Hz, 12 H; C$\mathbf{H}_3$), 1.20 (d, J = 6.9 Hz, 12 H; C$\mathbf{H}_3$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 153.6 (N-**C**-N), 150.6 (**C**$^{Py}{}_2$H), 149.5 (**C**$^{Py}{}_6$H), 146.8 (**C**$^{Ar\ NHC}{}_{ortho}$), 137.6 (**C**$^{Py}{}_4$H), 135.1 (**C**$^{Ar\ NHC}$-N), 132.1 (**C**$^{Py}{}_3$), 130.5 (**C**$^{Ar\ NHC}{}_{para}$H), 125.3 (**C**H=**C**H), 124.5 (**C**$^{Py}{}_5$H), 124.2 (**C**$^{Ar\ NHC}{}_{meta}$H), 28.9 (**C**H-$(CH_3)_2$), 26.5 (**C**H_3), 23.4 (**C**H_3).

The data match the reported values.[3]

[$PdCl_2$(Py)(IPr*)] 1c



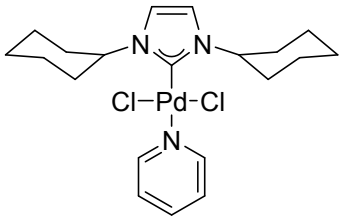
287 mg of [$PdCl_2(Py)_2$] **3a** (0.85 mmol, 1 equiv.), 811 mg of IPr*·HCl (0.85 mmol, 1 equiv.) and 590 mg of K_2CO_3 (4.27 mmol, 5 equiv.) were stirred in 10 mL of acetone at 60 °C for 16 hours. The mixture was allowed to cool to rt, filtered through a frit and volatiles removed under vacuum. Pentane (100 mL) was added to triturate the product. The precipitate was collected by filtration and lead to isolation of 924 mg (92%) of the desired [$PdCl_2$(Py)(IPr*)] complex **1c** as a pale-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.12-9.06 (m, 2 H; $C^{Py}{}_{ortho}$**H**), 7.78 (tt, J = 7.8 Hz, J = 1.4 Hz, 1 H; $C^{Py}{}_{para}$**H**), 7.47-7.39 (m, 8 H; C^{Ar}**H**), 7.38-7.31 (m, 2 H; $C^{Py}{}_{meta}$**H**), 7.24-7.14 (m, 12 H; C^{Ar}**H**), 7.10-6.96 (m, 12 H; C^{Ar}**H**), 6.79-6.69 (m, 12 H; C^{Ar}**H**), 6.38 (s, 4 H; C**H**-$(Ph)_2$), 4.89 (s, 2 H; C**H**=C**H**), 2.19 (s, 6 H; C$\mathbf{H_3}$).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 152.1 (**C**$^{Py}{}_{ortho}$H), 151.0 (N-**C**-N), 144.8 (**C**^{Ar}), 144.1 (**C**^{Ar}), 141.7 (**C**^{Ar}), 138.3 (**C**^{Ar}), 138.1 (**C**$^{Py}{}_{para}$H), 135.6 (**C**^{Ar}), 131.0 (**C**^{Ar}H), 130.7 (**C**^{Ar}H), 129.6 (**C**^{Ar}H), 128.3 (**C**^{Ar}H), 127.9 (**C**^{Ar}H), 126.7 (**C**^{Ar}H), 126.1 (**C**^{Ar}H), 124.4 (**C**$^{Py}{}_{meta}$H), 124.2 (**C**H=**C**H), 51.0 (**C**H-$(Ph)_2$), 21.9 (**C**H_3).

The data match the reported values.[4]

[$PdCl_2(Py)(ICy)$] **1d**



300 g of [$PdCl_2(Py)_2$] **3a** (0.89 mmol, 1 equiv.), 240 mg of ICy·HCl (0.89 mmol, 1 equiv.) and 618 mg of K_2CO_3 (4.47 mmol, 5 equiv.) were stirred in 6 mL of acetone at 60 °C for 3 hours. The mixture was allowed to cool to rt, filtered through a frit and the volatiles evaporated under vacuum. Pentane (50 mL) was added to triturate the product. The precipitate was filtered leading to 332 mg (76%) of the desired [$PdCl_2(Py)(ICy)$] complex **1d** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.05-9.01 (m, 2 H; C^{Py}_{ortho}**H**), 7.76 (tt, J = 7.6 Hz, J = 1.6 Hz, 1 H; C^{Py}_{para}**H**), 7.36-7.32 (m, 2 H; C^{Py}_{meta}**H**), 6.96 (s, 2 H; C**H**=C**H**), 5.42-5.32 (m, 2 H; C_1**H**$_{ax}$-N), 2.37 (br d, J = 10.5 Hz, 4 H; C_2**H**$_{eq}$), 1.91 (br d, J = 12.8 Hz, 4 H; C_3**H**$_{eq}$), 1.77 (br d, J = 13.3 Hz, 2 H; C_4**H**$_{eq}$), 1.67-1.45 (m, 8 H; C_2**H**$_{ax}$ and C_3**H**$_{ax}$) 1.22 (qt, J = 12.7 Hz, J = 3.7 Hz, 2 H; C_4**H**$_{ax}$).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 151.4 (**C**$^{Py}_{ortho}$H), 146.3 (N-**C**-N), 138.0 (**C**$^{Py}_{para}$H), 124.5 (**C**$^{Py}_{meta}$H), 118.3 (**C**H=**C**H), 60.3 (**C**$_1$H-N), 33.8 (**C**$_2$-(H)$_2$), 25.7 (**C**$_3$-(H)$_2$), 25.5 (**C**$_4$-(H)$_2$).

Elemental analysis calcd (%): C 49.04, H 6.17, N 8.58. Found: C 49.06, H 5.83, N 8.45.

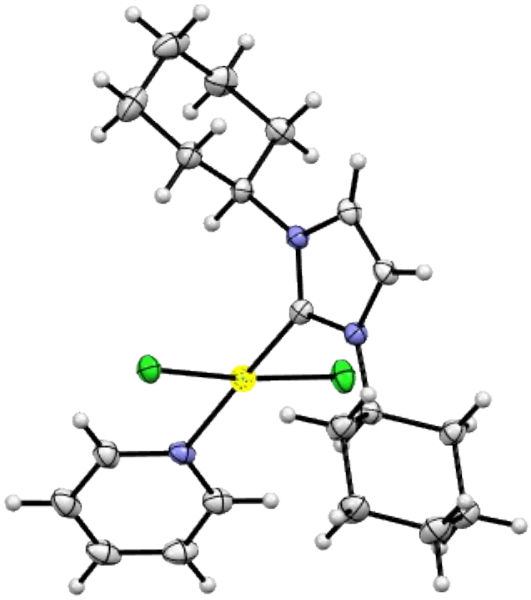
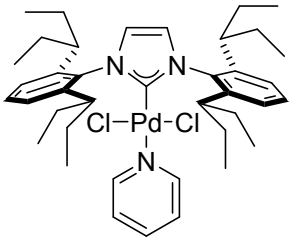


Figure S2: Molecular structure of **1d**

[$PdCl_2$(Py)(IPent)] **1e**



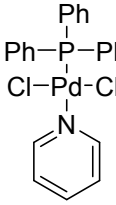
250 mg of [$PdCl_2(Py)_2$] **3a** (0.75 mmol, 1 equiv.), 400 mg of IPent·HCl (0.75 mmol, 1 equiv.) and 515 mg of K_2CO_3 (3.73 mmol, 5 equiv.) were stirred in 5 mL of ethyl acetate at 60 °C for 4 hours. The mixture was allowed to cool to room temperature, filtered and volatiles removed under vacuum. Pentane (50 mL) was added to triturate the product. The precipitate was collected by filtration leading to 335 mg (60%) of the desired [$PdCl_2$(Py)(IPent)] complex **1e** as a pale-yellow solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.60-8.55 (m, 2 H; C^{Py}_{ortho}**H**), 7.53 (tt, J = 7.6 Hz, J = 1.6 Hz, 1 H; C^{Py}_{para}**H**), 7.43 (t, J = 7.8 Hz, 2H, $C^{Ar\ NHC}_{para}$**H**), 7.23 (d, J = 7.8 Hz, 4 H; $C^{Ar\ NHC}_{meta}$**H**), 7.11-7.04 (m, 4 H; **H**$^{Py}_{meta}$ and C**H**=C**H**), 2.87-2.74 (m, 4H, C**H**-(C_2H_5)$_2$), 2.22-2.04 (m, 4H, C**H**$_2$-CH_3), 1.94-1.76 (m, 4H, C**H**$_2$-CH_3), 1.60-1.47 (m, 4H, C**H**$_2$-CH_3), 1.12 (t, J = 7.3 Hz, 12H, C**H**$_3$), 0.79 (t, J = 7.3 Hz, 12H, C**H**$_3$).

^{13}C NMR (400 MHz, $CDCl_3$) δ (ppm) 153.8 (N-**C**-N), 151.6 (**C**$^{Py}_{ortho}$H), 144.7 (**C**$^{Ar\ NHC}_{ortho}$), 137.3 (**C**$^{Py}_{para}$H), 136.9 (**C**$^{Ar\ NHC}$-N), 129.2 (**C**$^{Ar\ NHC}_{para}$H), 125.4 (**C**H=**C**H and **C**$^{Ar\ NHC}_{meta}$H), 124.0 (**C**$^{Py}_{meta}$H), 41.3 (**C**H), 28.9 (**C**H$_2$), 27.3 (**C**H$_2$), 13.0 (**C**H$_3$), 11.3 (**C**H$_3$).

The data match the reported values.[5]

[$PdCl_2$(Py)(PPh_3)] **4a**



In a scintillation vial flushed with argon, 100 mg of [$PdCl_2(Py)_2$] **3a** (0.30 mmol, 1 equiv.) and 262 mg of PPh_3 (0.30 mmol, 1 equiv.) were stirred in 3 mL of ethyl acetate at room temperature for 18 hours. The volatiles were removed using vacuum. The crude product was washed with pentane (25 mL) and dried under vacuum, leading to 153 mg (98%) of the desired [$PdCl_2$(Py)(PPh_3)] complex **4a** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 9.03-8.98 (m, 2 H; C^{Py}_{ortho}**H**), 7.86-7.75 (m, 7 H; C^{Py}_{para}**H** and C^{Ph}_{meta}**H**), 7.53-7.46 (m, 3H, C^{Ph}_{para}**H**), 7.46-7.40 (m, 6 H; C^{Ph}_{ortho}**H**), 7.40-7.34 (m, 2 H; C^{Py}_{meta}**H**).

^{13}C NMR (300 MHz, $CDCl_3$) δ (ppm) 151.8 (d, $J_{C\text{-}P}$ = 1.7 Hz, **C**$^{Py}_{ortho}$H), 138.4 (**C**$^{Py}_{para}$H), 135.0 (d, $J_{C\text{-}P}$ = 10.4 Hz, **C**$^{Ph}_{meta}$H), 131.2 (d, $J_{C\text{-}P}$ = 3.0 Hz, **C**$^{Ph}_{para}$**H**), 129.4 (d, $J_{C\text{-}P}$ = 57.6 Hz, P-**C**), 128.3 (d, $J_{C\text{-}P}$ = 11.3 Hz, **C**$^{Ph}_{ortho}$H), 124.7 (d, $J_{C\text{-}P}$ = 3.4 Hz, **C**$^{Py}_{meta}$H).

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 28.9 (**P**Ph_3).

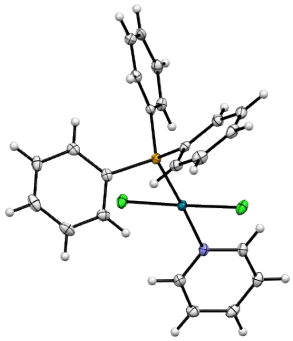
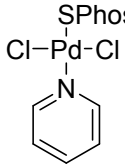


Figure 2: Molecular structure of **1f**

[$PdCl_2$(Py)(SPhos)] **4b**



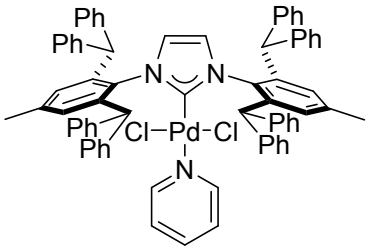
In a vial flushed with argon, 67 mg of [$PdCl_2(Py)_2$] **3a** (0.20 mmol, 1 equiv.) and 90 mg of SPhos (0.22 mmol, 1.1 equiv.) were stirred in 2 mL of dichloromethane at room temperature for 24 hours. The volatiles were removed using vacuum. 10 mL of pentane were added to the crude product to triturate it, and it was then washed with pentane (5 mL) and dried under vacuum, leading to 129 mg (97%) of the desired [$PdCl_2$(Py)(SPhos)] complex **4b** as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.98-8.92 (m, 2 H; C^{Py}_{ortho}**H**),8.13 (ddd, J = 12.7 Hz, J = 7.6 Hz, J = 1.5 Hz, 1 H, $C^{Ar\ SPhos}$**H**), 7.72 (tt, J = 7.6 Hz, J = 1.6 Hz, 1 H, C^{Py}_{para}**H**), 7.49-7.35 (m, 2 H, $C^{Ar\ SPhos}$**H**), 7.35-7.27 (m, 3 H, $C^{Ar\ SPhos}$**H** and C^{Py}_{meta}**H**), 7.09-7.02 (m, 1 H, $C^{Ar\ SPhos}$**H**), 6.60 (d, J = 8.4 Hz, 2 H, $C^{Ar\ SPhos}$**H**), 3.66 (s, 6 H, O-C**H**$_3$), 2.22-2.40 (m, 2 H $C^{Cy\ SPhos}$**H**), 2.21-1.96 (m, 4 H, $C^{Cy\ SPhos}$**H**), 1.82-1.46 (m, 10 H, $C^{Cy\ SPhos}$**H**), 1.24-0.98 (m, 6 H, $C^{Cy\ SPhos}$**H**).

^{31}P NMR (162 MHz, $CDCl_3$) δ (ppm) 49.6 (**P**Ph_3).

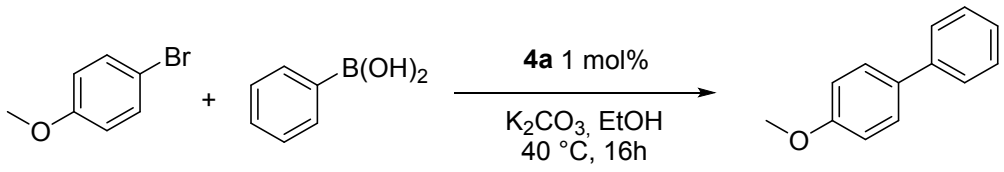
One pot synthesis of the PEPPSI precatalyst from $PdCl_2$

[$PdCl_2$(Py)(IPr*)] **1c**



30 mg of $PdCl_2$ (0.18 mmol, 1 equiv.), 161 mg of IPr*·HCl (0.18 mmol, 1 equiv.), 13.6 µL of pyridine (0.18 mmol, 1 equiv.) and 117 mg of K_2CO_3 (0.85 mmol, 5 equiv.) were stirred in 3 mL of acetone at 60 °C for 16 hours. The mixture was allowed to cool to room temperature, filtered through a microfilter and volatiles evaporated under vacuum. Pentane (25 mL) was added to triturate the product. The precipitate was collected by filtration leading to 172 mg (86%) of the desired [$PdCl_2$(Py)(IPr*)] complex **1c** as a pale-yellow solid.

Catalytic test of [$PdCl_2(Py)(PPh_3)$] 4a



Suzuki-Miyaura coupling of 4-bromoanisole and phenylboronic acid was chosen as a test reaction. A vial was charged with 97 mg of K_2CO_3 (0.7 mmol, 1.4 equiv) and 2.6 mg of [$PdCl_2(Py)(PPh_3)$] **1f** (5 µmol, 1 mol%), 1 mL of ethanol was added followed by 63 µL of 4-bromoanisole (0.5 mmol, 1 equiv) and 73 mg of phenylboronic acid (0.6 mmol, 1.2 equiv). The mixture was stirred at 40 °C for 16 h. Volatiles were removed under reduced pressure and the residue was analysed by ^{1}H NMR. The spectrum showed complete conversion to the expected cross-coupling product. The reaction was performed twice.

References

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2. Rajputa, J.; Mossa, J.R.; Huttona, A.T.; Hendricks, D.T.; Arendse, C.E.; Imriec, C. *J. Organomet. Chem*. **2004**, *689*, 1553-1568
3. O'Brien, C.J.; Kantchev, E.A.B.; Valente, C.; Hadei, N.; Chass, G.A.; Loug H; A.; Hopkinson, A.C.; Organ, M.G. *Chem. Eur. J*. **2006**, *12*, 4743 – 4748
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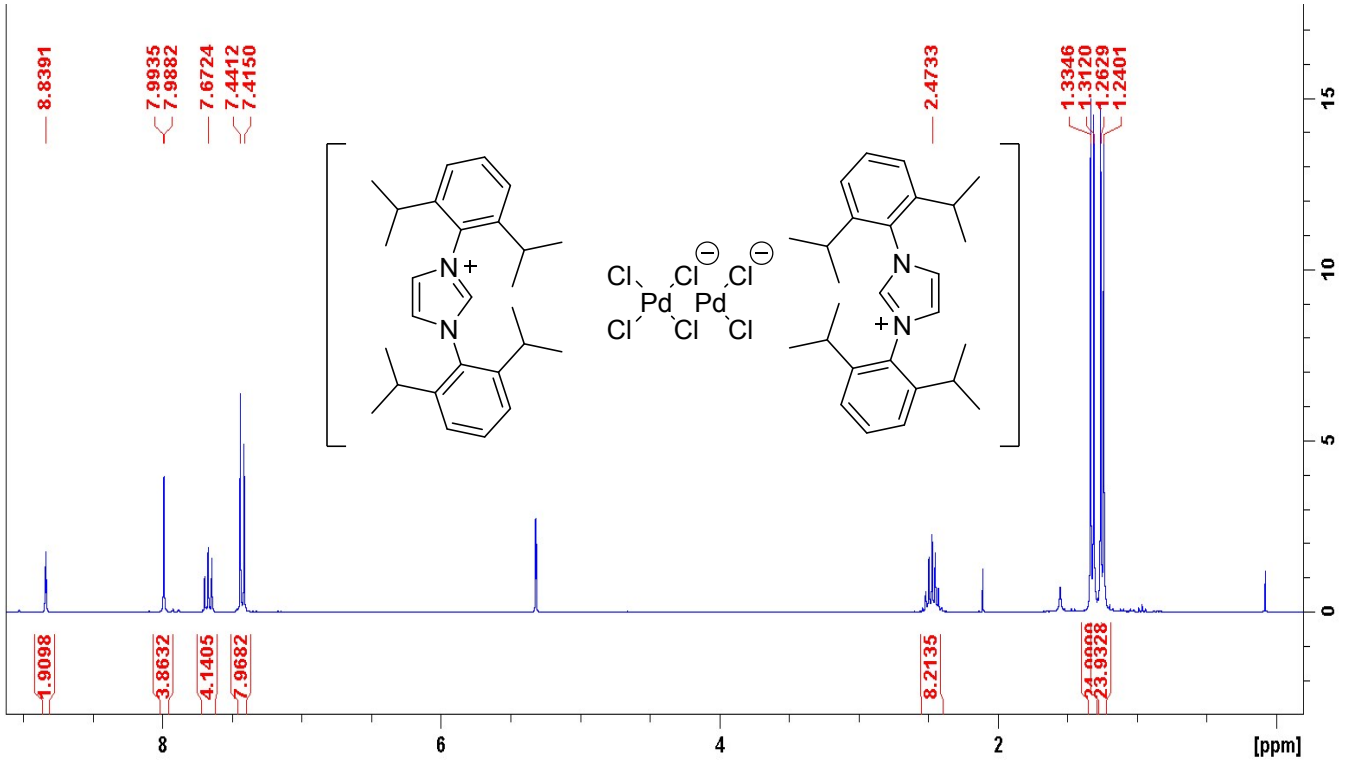
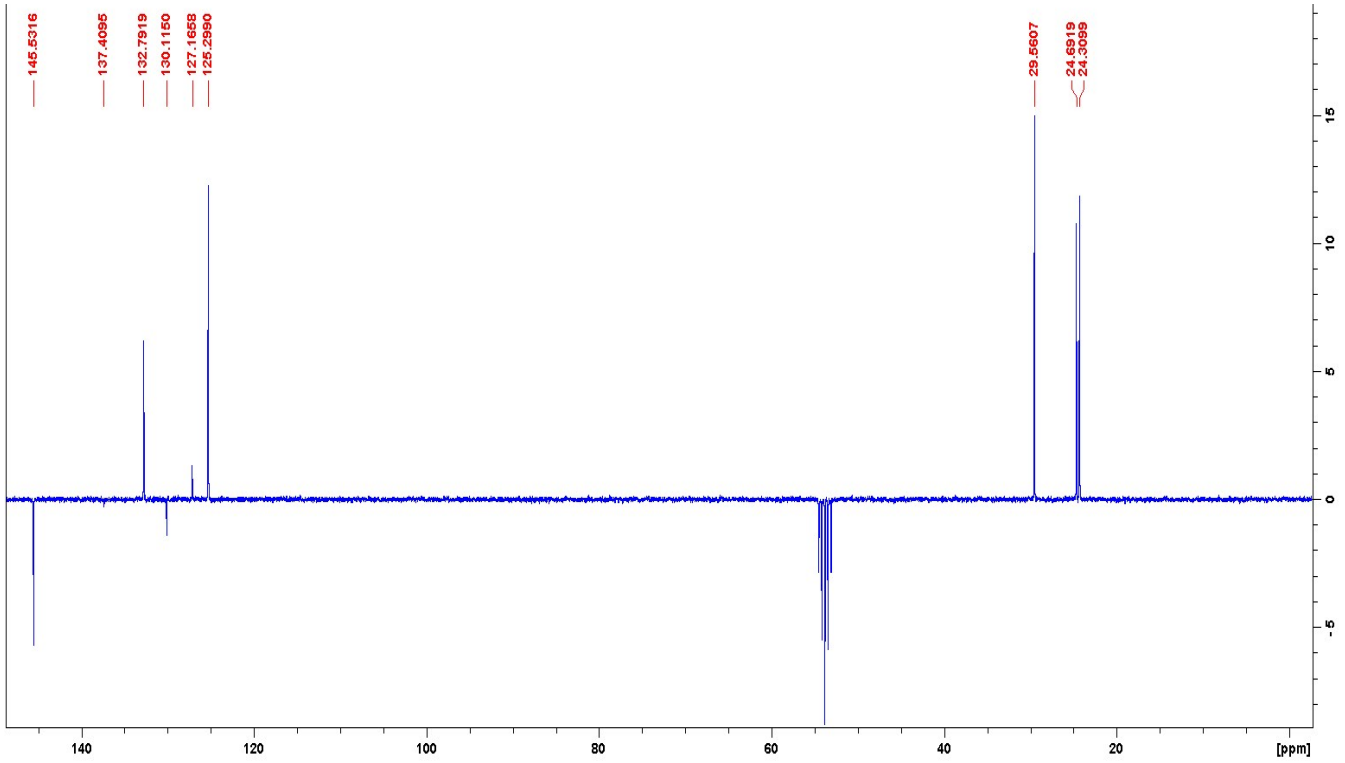
6. CCDC 1978988, 1978989 and 1990911 (**2**, **1d** and **4a**) contain the crystallographic data for this paper and can be obtained via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44-1223-336033; or deposit@ccdc.cam.ac.uk).

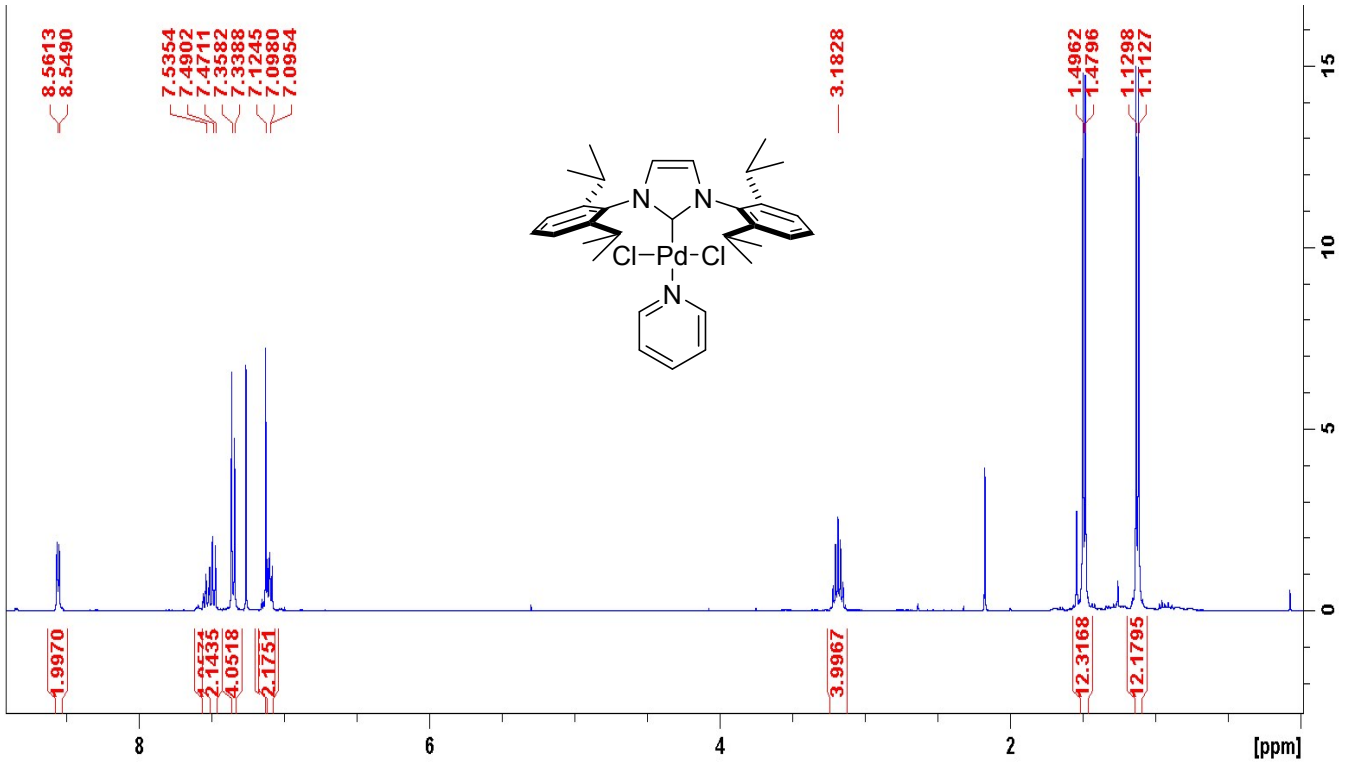
NMR spectra

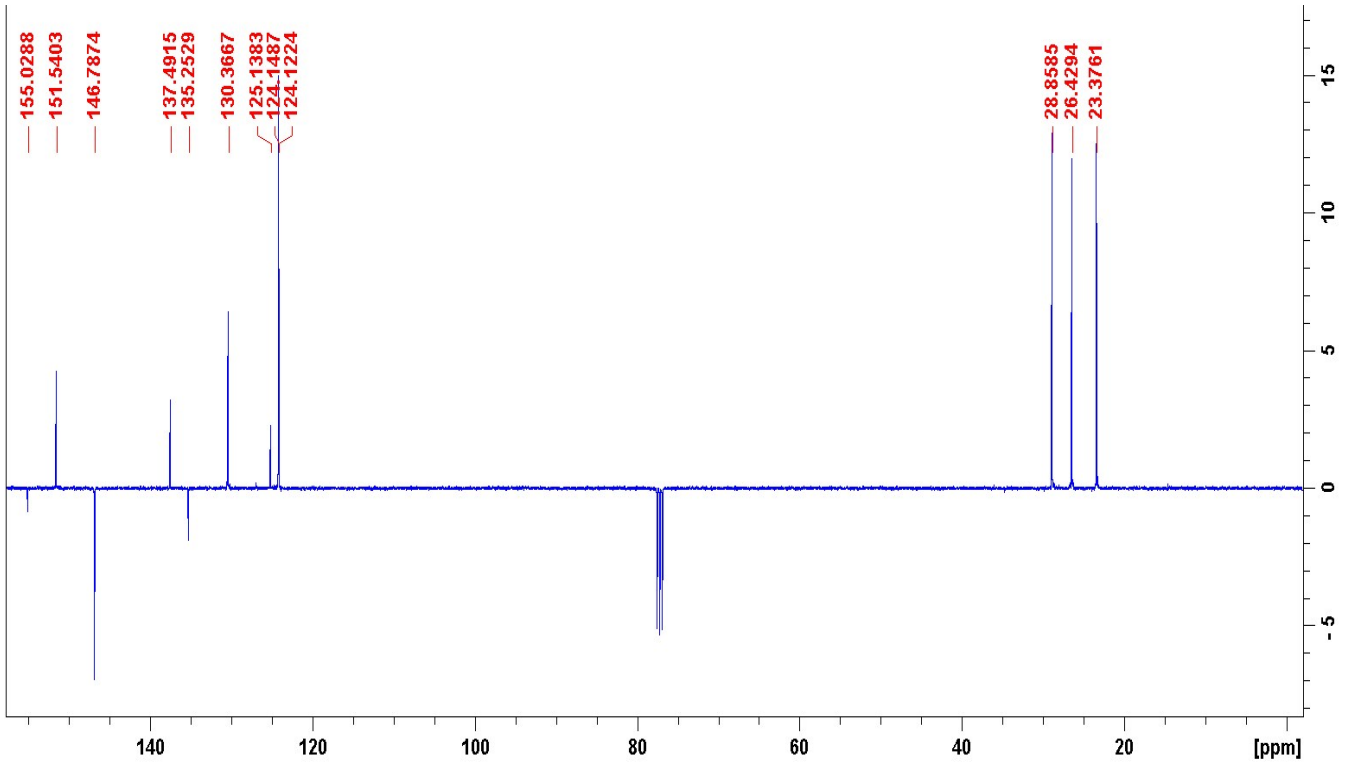
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(\mu\text{-}Cl)]_2[IPr.H]_2$ (**2**)



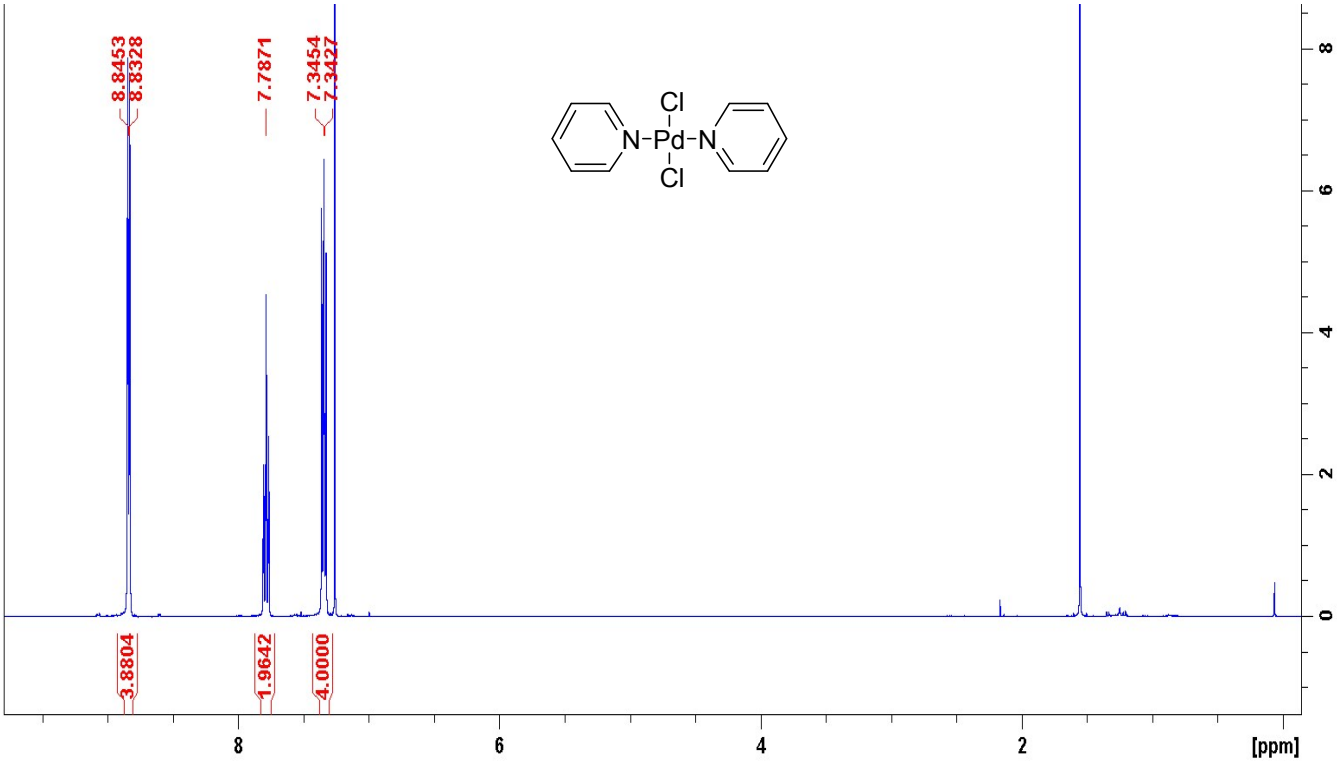


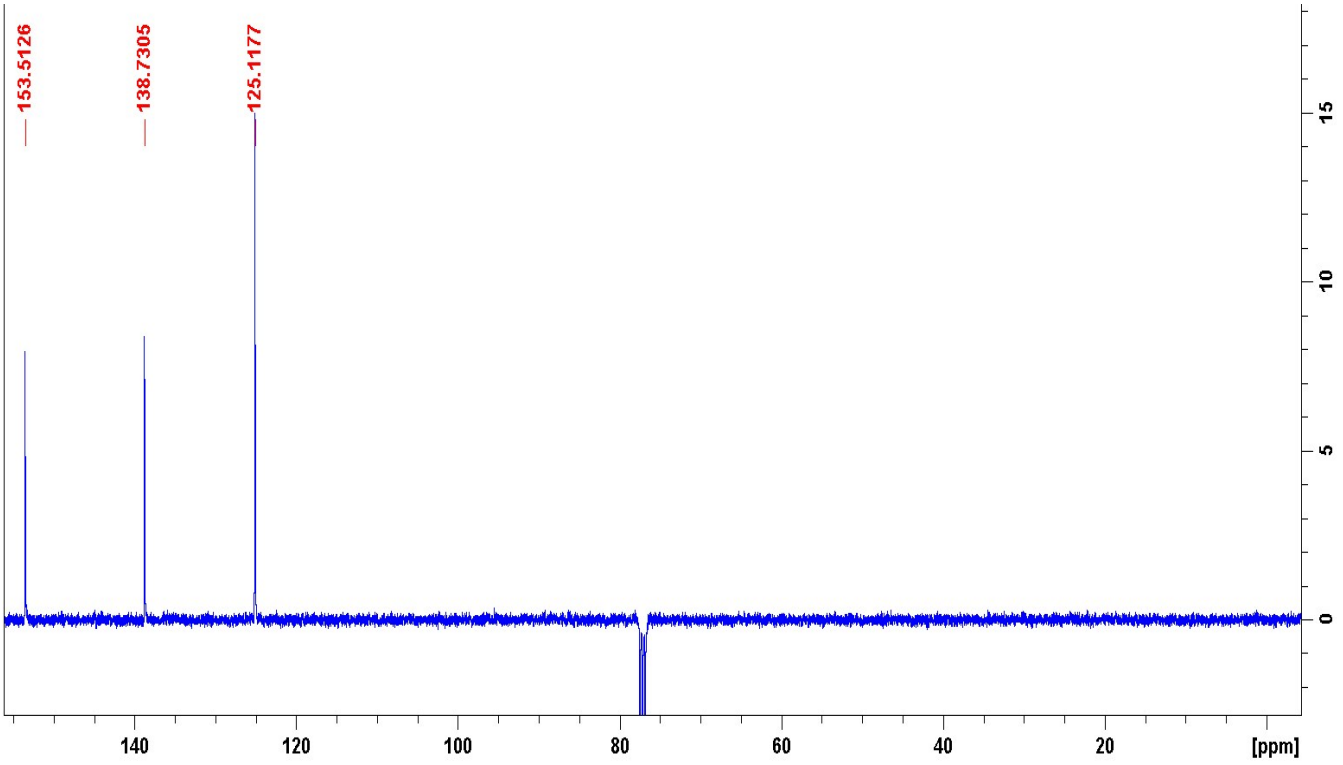
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(Py)IPr]$ (**1a**)



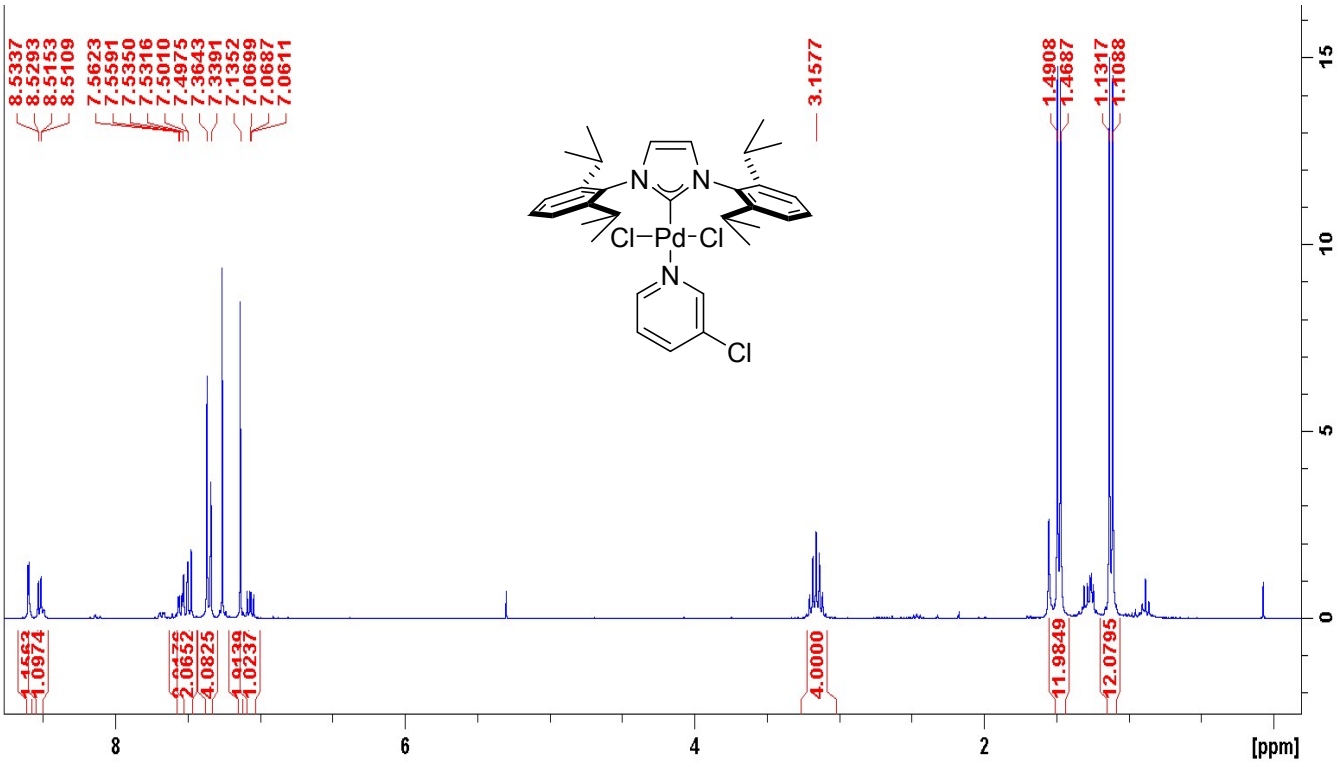


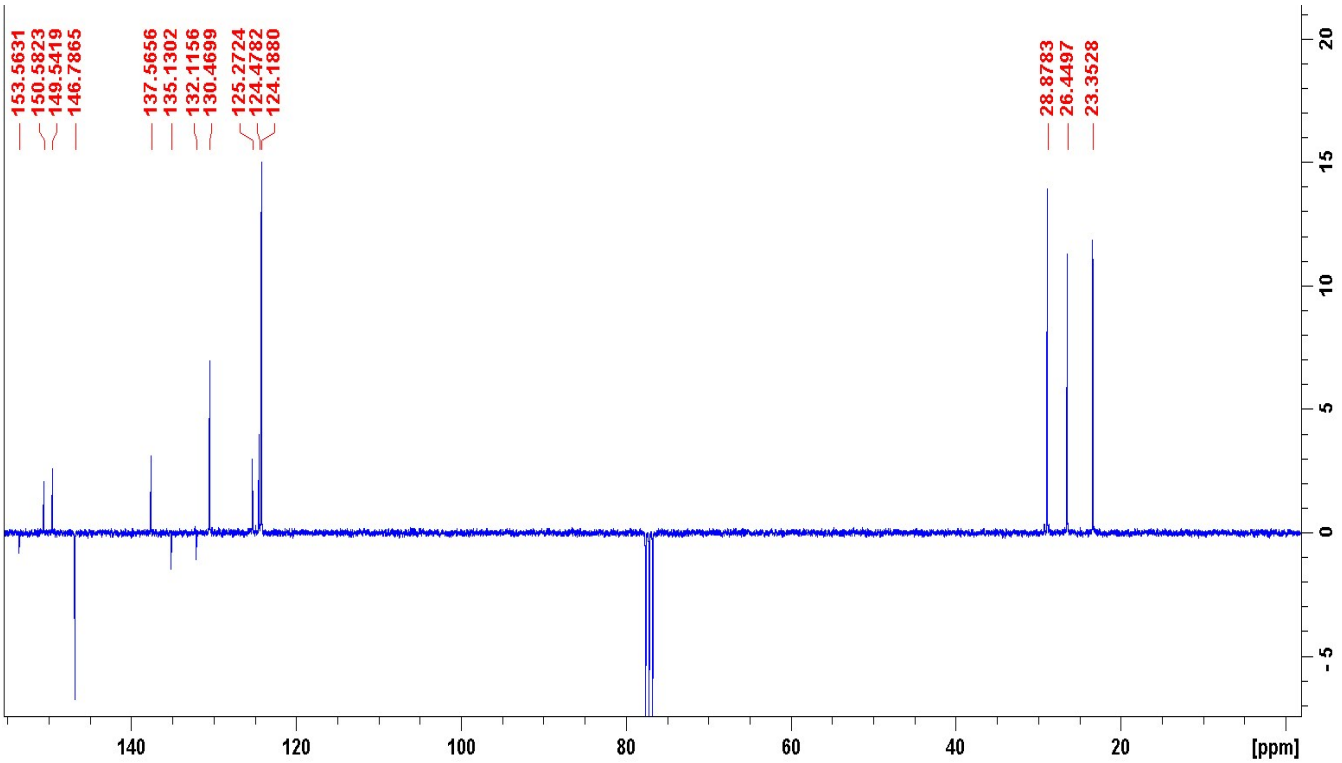
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(Py)_2]$ (**3a**)



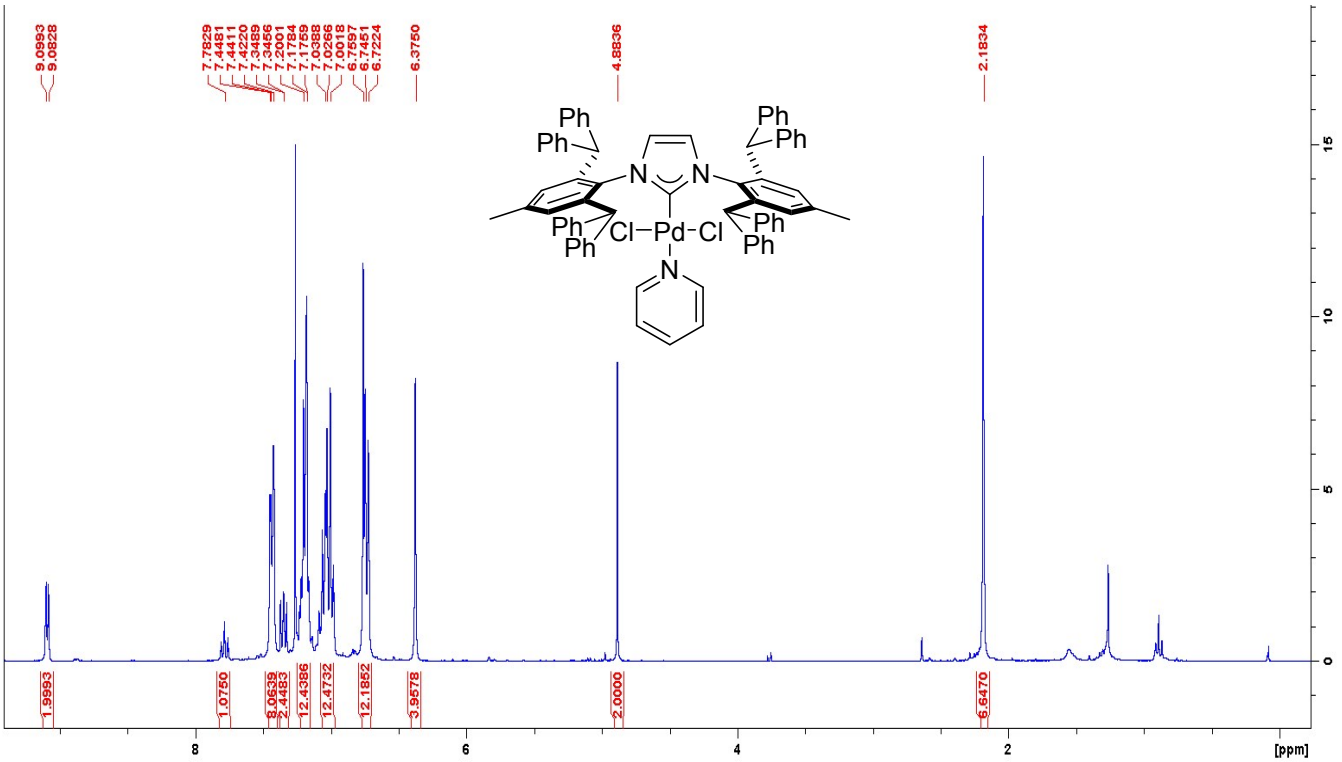


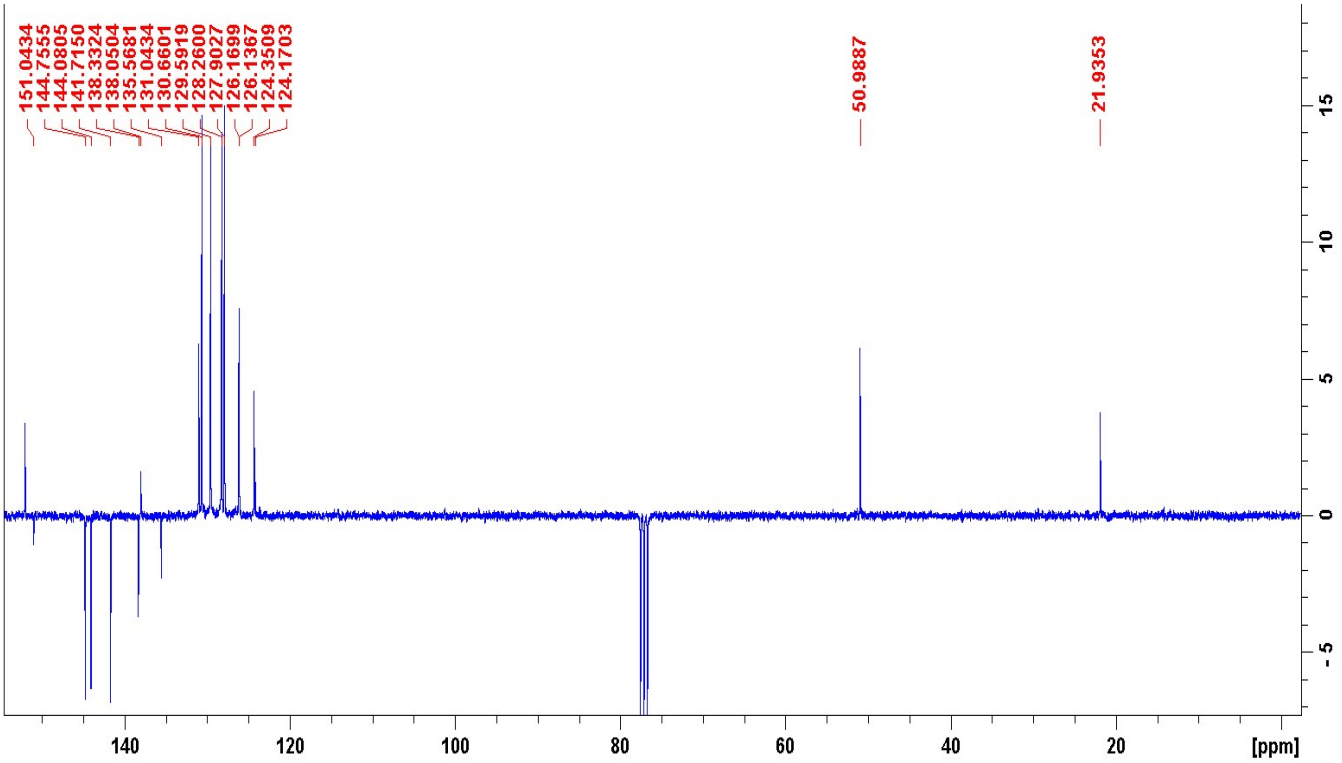
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(3\text{-chloropyridine})IPr]$ (**1b**)



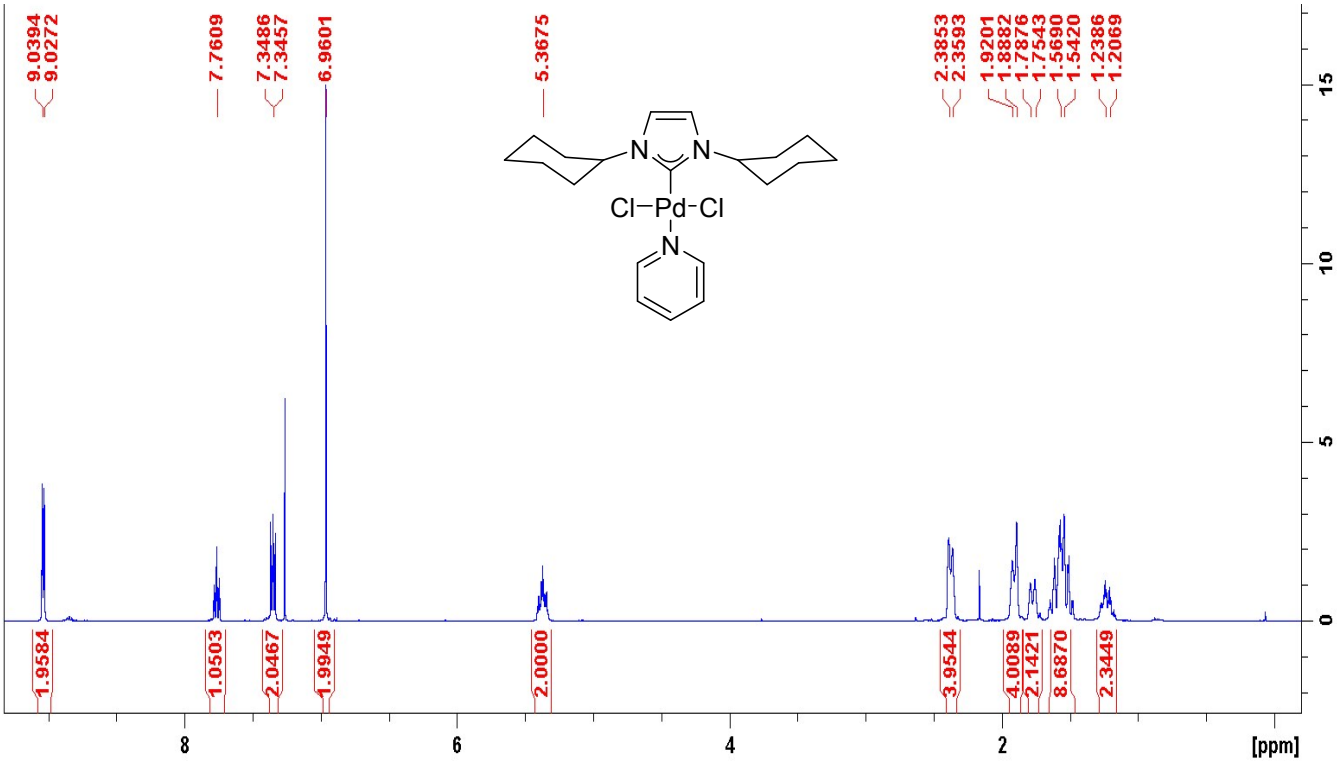


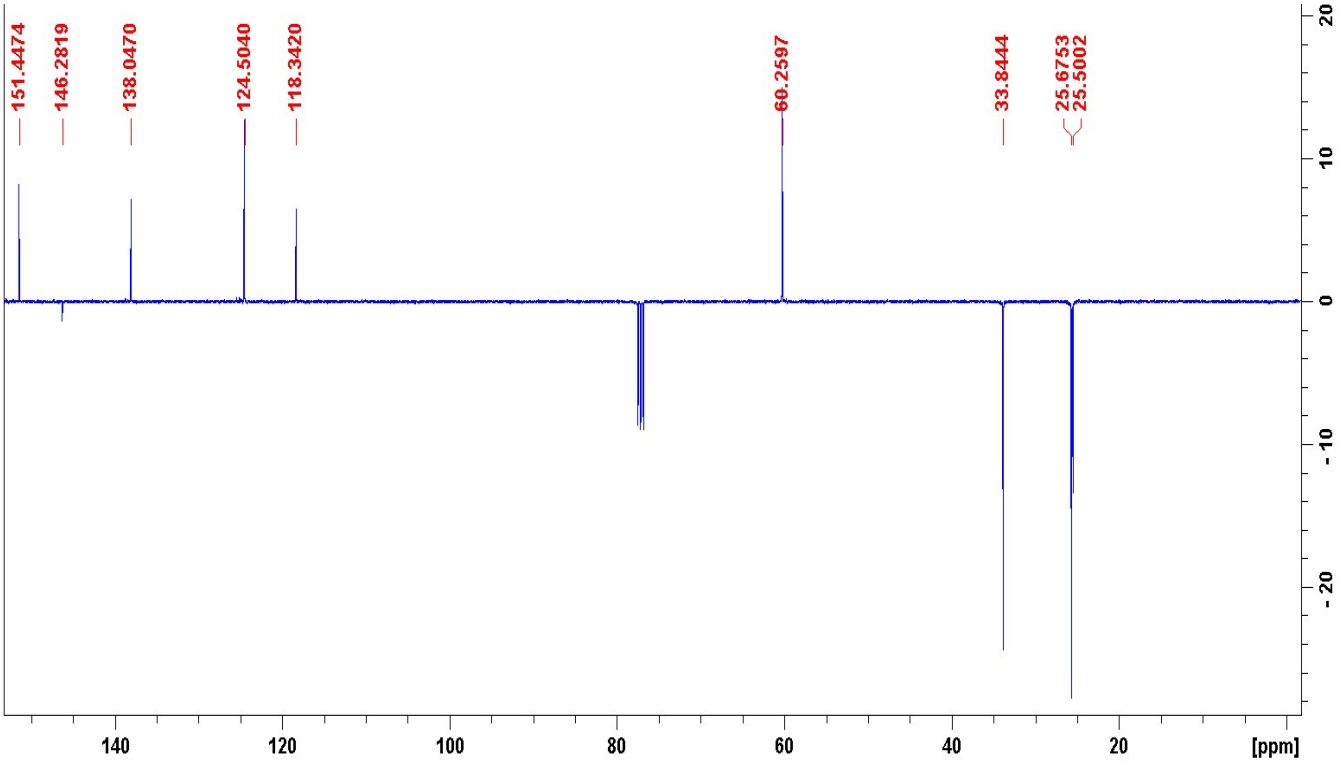
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(Py)IPr^*]$ (**1c**)



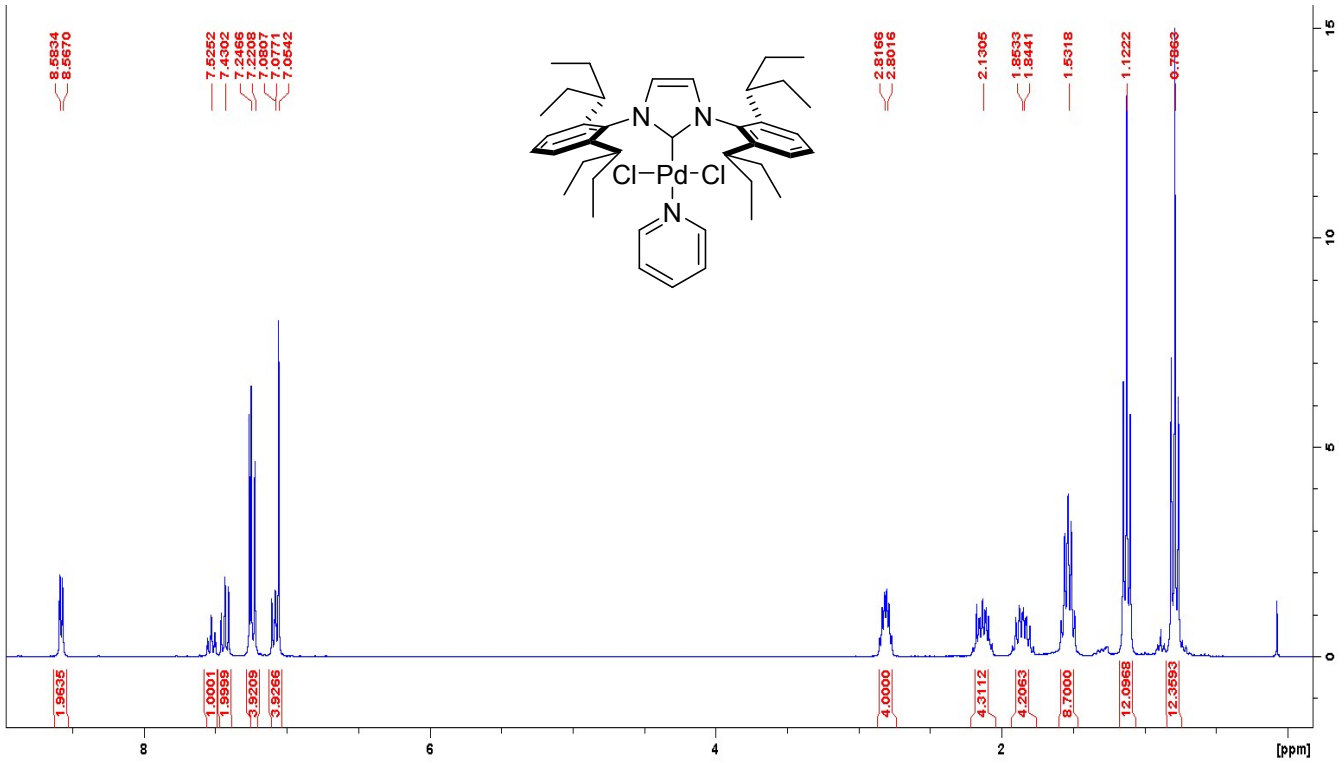


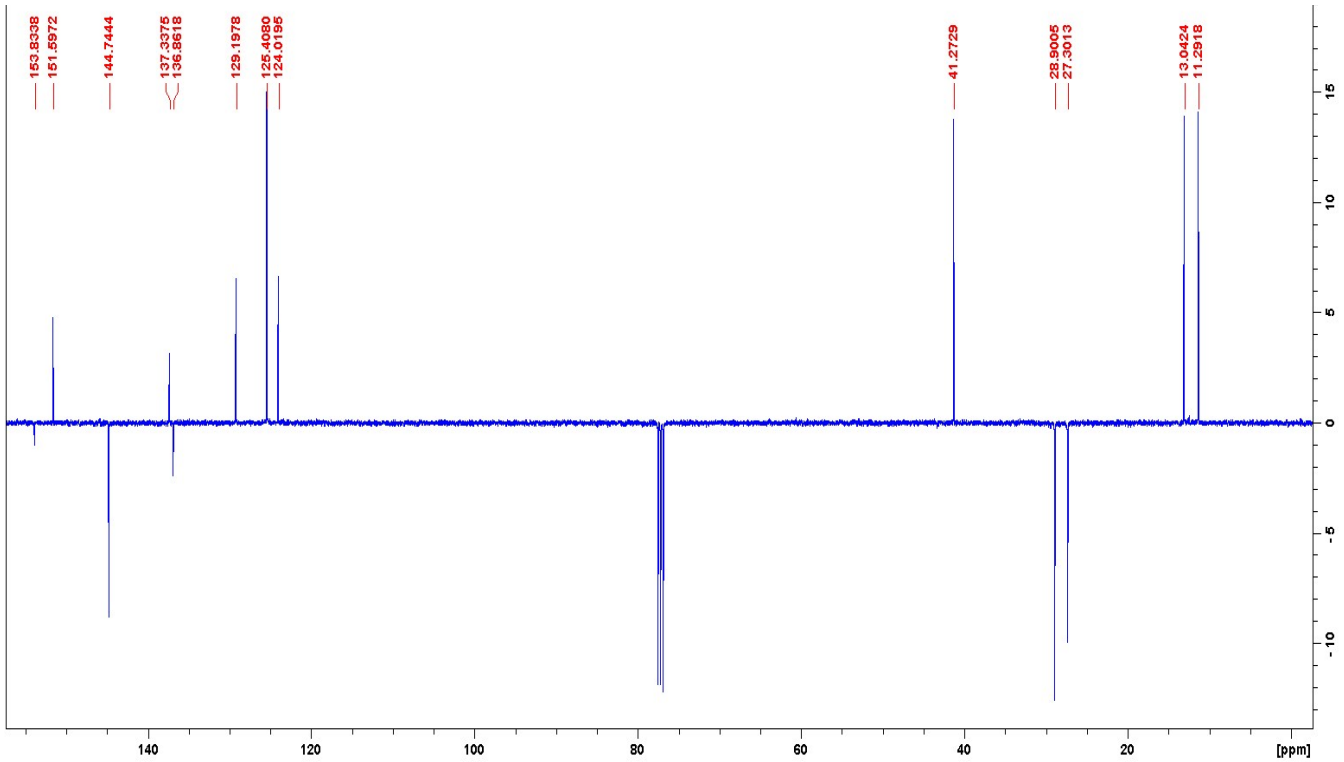
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(Py)ICy]$ (**1d**)



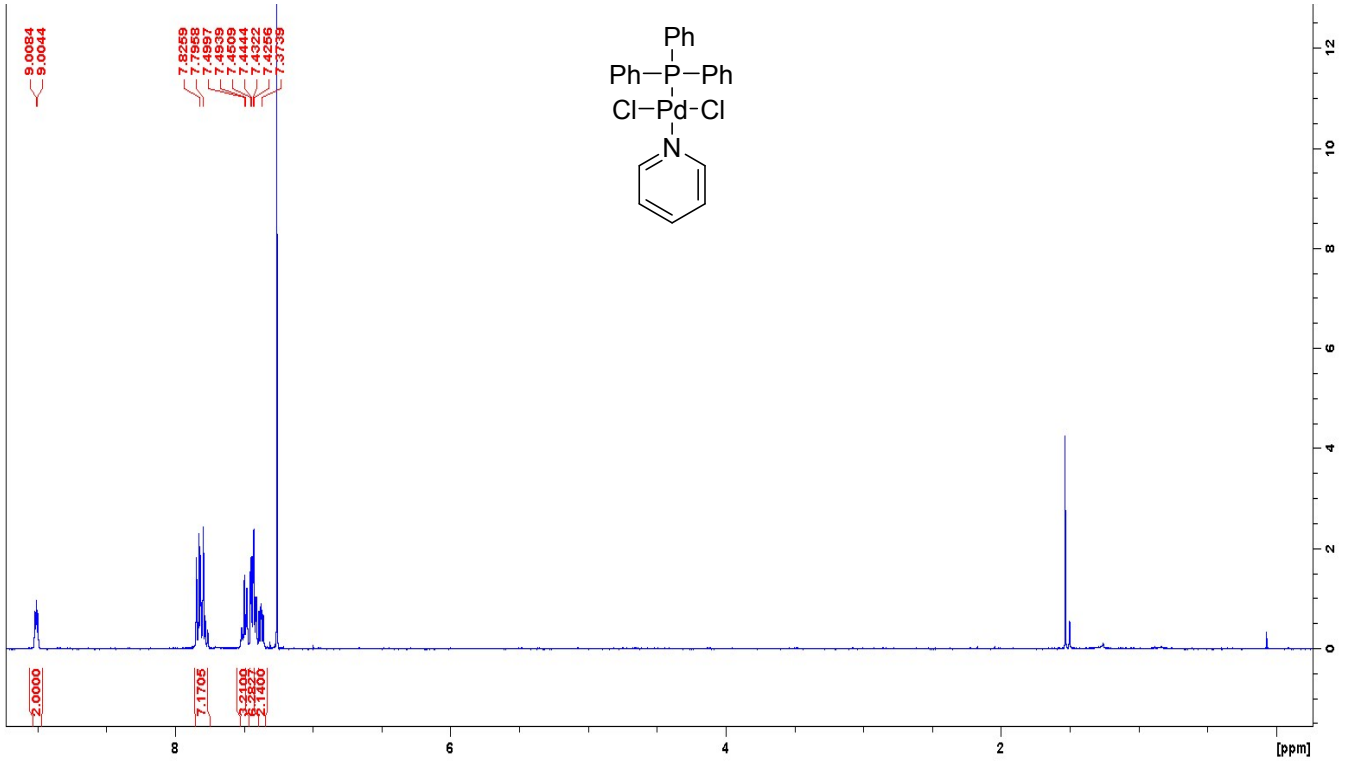


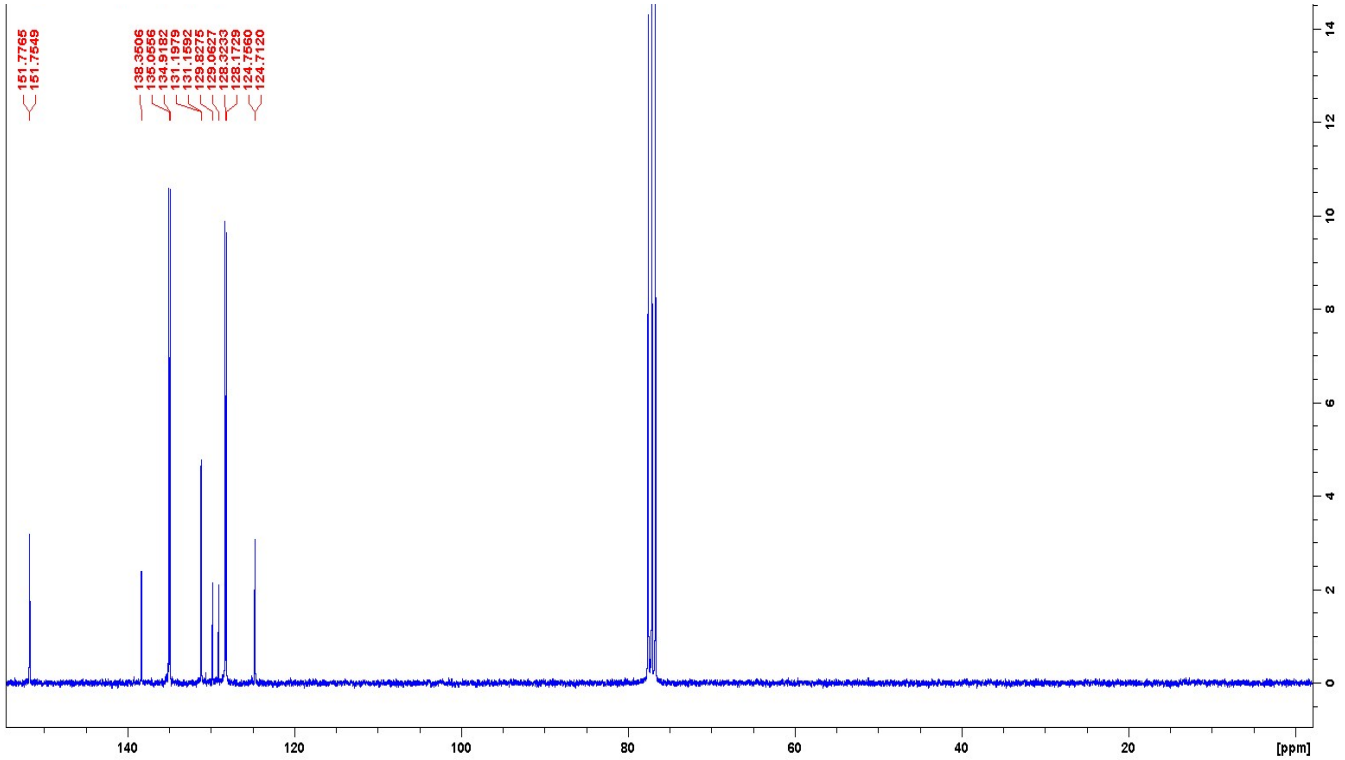
^{1}H and $^{13}C\{^{1}H\}$ apt NMR of $[PdCl_2(Py)IPent]$ (**1e**)

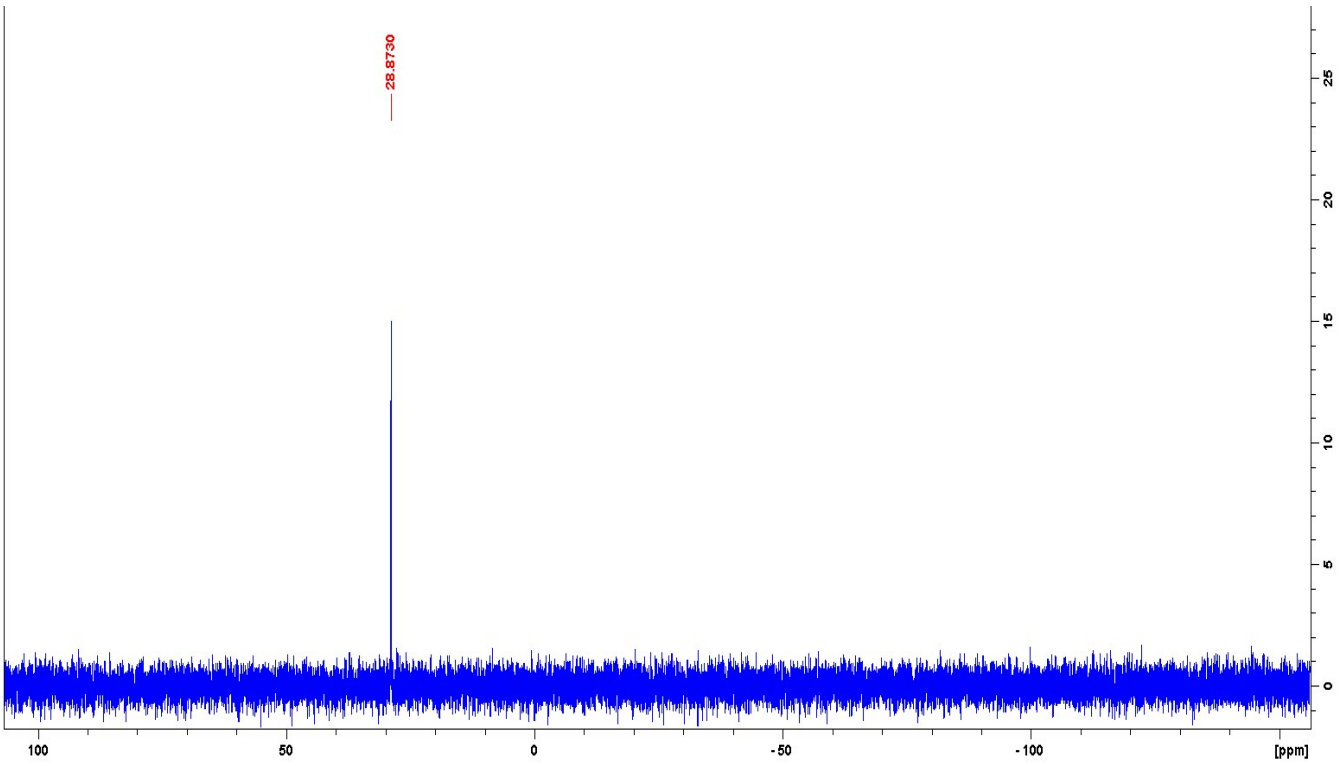




^{1}H, $^{13}C\{^{1}H\}$ and ^{31}P NMR of $[PdCl_2(Py)(PPh_3)]$ (**4a**)






28.8730
25
20
15
10
5
0
100
50
0
-50
-100
[ppm]

^{1}H and ^{31}P NMR of $[PdCl_2(Py)(SPhos)]$ (**4b**)