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$LPdCl_2$(amine) Complexes Supported by Terphenyl Phosphanes: Applications in Aryl Amination Reactions

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1. General considerations.

All preparations and manipulations were carried out under oxygen-free nitrogen, using conventional Schlenk techniques. Solvents were dried with a MBraun SPS 800 solvent purification system, degassed, and stored over molecular sieves, or dried and deoxygenated using literature procedures. Dialkylterphenyl phosphanes PMe_2Ar^{Xyl2},[1] PMe_2Ar^{Dtbp2},[2] $PCyp_2Ar^{Xyl2}$,[2] and $PdCl_2(py)_2$[3] were synthesized following described procedures. All other reagents were purchased from commercial suppliers and used without further purification. Solution NMR spectra were recorded on a Bruker Avance DPX-300 and Avance 400 Ascend/R. The ^1H and ^{13}C resonances of the solvent were used as the internal standard and the chemical shifts are reported relative to TMS, while ^{31}P was referenced to external H_3PO_4. All GC analyses were performed on Agilent 7820A Gas Chromatograph with FID detector. Elemental analyses were performed by the Servicio de Microanálisis of the Instituto de Investigaciones Químicas (IIQ). X-ray diffraction studies and high resolution mass spectra were accomplished at the Centro de Investigación, Tecnología e Innovación de la Universidad de Sevilla (CITIUS).

2. Synthesis and characterization of new compounds.

2.1. $[PdCl_2(pyridine)(PMe_2Ar^{Xyl2})]$, 1a.

To a suspension of *trans*-$PdCl_2(pyridine)_2$ (97 mg, 0.29 mmol) in CH_2Cl_2 (10 mL) a solution of PMe_2Ar^{Xyl2} (100 mg, 0.29 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred at room temperature for 8 h. Volatiles were removed under vacuum and the resulting solid was purified by recrystallization from petroleum ether/CH_2Cl_2 (2:1) mixtures at -20 ºC, rendering the title compound as a yellow solid. Yield: 149 mg (85 %).

^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.74 (m, 2H, *o*-py), 7.71 (t, 1H, $^3J_{HH}$= 7.2 Hz, *p*-py), 7.55 (t, 1H, $^3J_{HH}$= 7.2 Hz, *p*-C_6H_3), 7.30-7.23 (m, 4H, *p*-Xyl, *m*-py), 7.14-7.07 (m, 6H, *m*-C_6H_3, *m*-Xyl), 2.21 (s, 12H, CH_3), 1.36 (d, 6H, $^2J_{HP}$= 13.3 Hz, P-CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 151.2 (d, $^4J_{CP}$ = 2 Hz, *o*-py), 146.0 (d, $^2J_{CP}$ = 12 Hz, *o*-C_6H_3), 141.2 (d, $^3J_{CP}$ = 3 Hz, *ipso*-Xyl), 137.8 (*p*-py), 136.8 (*o*-Xyl), 131.2 (d, $^4J_{CP}$ = 2 Hz, *o*-C_6H_3), 130.9 (d, $^1J_{CP}$ = 11 Hz, *ipso*-C_6H_3) 128.4 (*p*-C_6H_3), 127.9 (*m*-py), 124.2 (*p*-Xyl), 124.2 (*m*-Xyl), 22.1 (CH_3), 17.5 (d, $^1J_{CP}$ = 37 Hz, P-CH_3).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 2.4.

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[2] M. Marín, J. J. Moreno, C. Navarro-Gilabert, E. Álvarez, C. Maya, R. Peloso, M. C. Nicasio and E. Carmona, *Chem. Eur. J*. 2019, ***25***, 260.
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Anal. Calcd for $C_{29}H_{32}Cl_2NPPd$: C, 57.78; H, 5.35; N, 2.32. Found: C, 57.50; H, 5.59; N, 2.64.

2.2. [$PdCl_2(py)(PMe_2Ar^{Dtbp2})$], 2a.

To a suspension of *trans*-$PdCl_2(pyridine)_2$ (46 mg, 0.14 mmol) in CH_2Cl_2 (10 mL) a solution of PMe_2Ar^{Xyl2} (70 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred at room temperature for 3 h. Volatiles were removed under vacuum and the resulting solid was purified by recrystallization from petroleum ether/CH_2Cl_2 (2:1) mixtures at -20 ºC, rendering the title compound as a yellow solid. Yield: 76 mg (71 %).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 8.79 (m, 2H, *o*-py), 7.73 (d, 4H, $^5J_{HP}$ = 1.7 Hz, *o*-Dtbp), 7.69 (m, 1H, *p*-py), 7.48-7.41 (m, 3H, *p*-Dtbp, *p*-C_6H_3), 7.27 (m, 2H, *m*-py), 7.20 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 3.2 Hz, *m*-C_6H_3), 1.33 (s, 36H, *t*Bu), 0.89 (d, 6H, $^2J_{HP}$ = 10.6 Hz, P-CH_3).

^{13}C{^{1}H} NMR (75 MHz, CD_2Cl_2, 298 K): δ 153.4 (*m*-Dtbp), 151.5 (d, $^4J_{CP}$ = 1 Hz, *o*-py),151.1 (*m*-py), 147.4 (d, $^3J_{CP}$ = 3 Hz, *o*-C_6H_3), 142.6 (d, $^3J_{CP}$ = 3 Hz, *ipso*-Xyl), 138.3 (*m*-py), 131.0 (d, $^1J_{CP}$ = 9 Hz, *ipso*-C_6H_3), 129.8 (d, $^3J_{CP}$ = 3 Hz, *m*-C_6H_3), 125.2 (*p*-C_6H_3), 124.4 (d, $^4J_{CP}$ = 4 Hz, *o*-Dtbp), 121.6 (*p*-Dtbp), 35.3 (*C*(Me_3)), 31.6 (C(*Me*$_3$)), 18.2 (d, $^2J_{CP}$ = 38 Hz, P-*C*H_3).

^{31}P{^{1}H} NMR (121 MHz, CD_2Cl_2, 298 K): δ 11.6.

Anal. Calcd for $C_{41}H_{56}Cl_2NPPd$: C, 63.86; H, 7.32; N, 1.82. Found: C, 63.92; H, 6.98; N, 1.99.

2.3. [$PdCl_2$(pyridine)($PCyp_2Ar^{Xyl2}$)], 3a.

To a solution of [$PdCl_2(PCyp_2Ar^{Xyl2})]_2$ (140 mg, 0.11 mmol) in CH_2Cl_2 (10 mL), pyridine (0.5 mL) was added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. The resulting orange solution was taken to dryness and the solid residue was purified by recrystallization from petroleum ether:diethyl ether (2:1) mixtures at -20 ºC. The title compound was obtained as an orange crystalline solid. Yield: 143 mg, (91 %).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 8.70 (m, 2H, *o*-py), 7.60 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *p*-py), 7.39 (t, 1H, $^3J_{HH}$ = 7.6 Hz, *p*-C_6H_3), 7.21-7.16 (m, 4H, *p*-Xyl, *m*-py), 7.04 (d, 4H, ^3JHH = 7.4 Hz, *m*-Xyl),6.95 (dd, 2H, $^3J_{HH}$ = 7.6 Hz, $^4J_{HP}$ = 4.7 Hz, *m*-C_6H_3), 2.73-2.67 (m, 4H, Cyp), 2.20 (s, 12H, CH_3), 2.05- 1.95 (m, 2H, Cyp), 1.30-0.77 (m, 12H, Cyp).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 298 K): δ 150.2 (*o*-py), 141.9 (o-C_6H_3), 136.5 (*p*-py), 132.2 (*ipso*-Xyl), 131.7 (*o*-Xyl), 131.4 (d, $^3J_{CP}$ = 9 Hz, *m*-C_6H_3), 128.9 (d, $^4J_{CP}$= 2 Hz, *p*-C_6H_3),

127.0 (*m*-Xyl), 123.0 (*m*-py), 122.9 (*p*-Xyl), 38.8 (d, $^{2}J_{CP}$ = 27 Hz, *C*H-Cyp), 29.5 (*C*H_2-Cyp), 26.0 (d, J_{CP} = 6 Hz, *C*H_2-Cyp), 23.8 (d, J_{CP} = 13 Hz, *C*H_2-Cyp), 21.6 (*C*H_3).

$^{31}P\{^{1}H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 32.6.

Anal. Calcd for $C_{37}H_{44}Cl_2NPPd$: C, 62.50; H, 6.24; N, 1.97. Found: C, 62.86; H, 6.40, N, 2.03.

2.4. [$PdCl_2$(morpholine)(PMe_2Ar^{Xyl2})], 1b.

To a suspension of *trans*-$PdCl_2$(morpholine)$_2$ (80 mg, 0.23 mmol) in 1,2-dichloroethane (10 mL) a solution of PMe_2Ar^{Xyl2} (79 mg, 0.23 mmol) in 1,2-dichloroethane (5 mL) was added. The reaction mixture was stirred at 60 ºC for 72 h. Volatiles were removed under vacuum and the resulting solid was purified by recrystallization from petroleum ether/CH_2Cl_2 (2:1) mixtures at -20 ºC, rendering the title compound as a yellow solid. Yield: 129 mg (92 %).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ 7.62 (td, 1H, $^{3}J_{HH}$ = 7.6 Hz, $^{5}J_{HP}$ = 2.0 Hz, *p*-C_6H_3), 7.30-7.25 (m, 2H, *p*-Xyl), 7.16 (d, 4 H, $^{4}J_{HH}$ = 7.6 Hz, *m*-Xyl), 7.01 (dd, 2H, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HP}$ = 3.0 Hz, *m*-C_6H_3), 3.79 (m, 2H, OCH_2), 3.45 (m, 2H, OCH_2), 3.30-3.09 (m, 3H, NCH_2 and N*H*), 2.81 (m, 2H, NCH_2), 2.22 (s, 12H, CH_3), 1.28 (d, 6H, $^{2}J_{HP}$ = 12.4 Hz, P-CH_3).

$^{13}C\{^{1}H\}$ NMR (75 MHz, CD_2Cl_2, 298 K): δ 145.0 (d, $^{2}J_{CP}$ = 9 Hz, *o*-C_6H_3), 139.9 (d, $^{3}J_{CP}$ = 4 Hz, *ipso*-Xyl), 135.7 (*o*-Xyl), 130.8 (d, $^{3}J_{CP}$ = 2 Hz, *m*-C_6H_3), 129.9 (d, $^{1}J_{CP}$ = 9 Hz, *ipso*-C_6H_3), 127.3 (*p*-Xyl), 126.8 (*m*-Xyl), 66.9 (d, $^{4}J_{CP}$ = 3 Hz, O*C*H_2), 46.6 (d, $^{3}J_{CP}$ = 3 Hz, N*C*H_2), 20.9 (s, *C*H_3), 16.2 (d, $^{2}J_{CP}$ = 36 Hz, P-*C*H_3).

$^{31}P\{^{1}H\}$ NMR (121 MHz, CD_2Cl_2, 298 K): δ 0.6.

Anal. Calcd for $C_{28}H_{36}Cl_2NOPPd$: C, 55.05%; H, 5.97%; N, 2.29%. Found: C, 55.21%; H, 6.13%; N, 2.54%.

2.5. [$PdCl_2$(morpholine)(PMe_2Ar^{Dtbp2})], 2b.

To a suspension of *trans*-$PdCl_2$(morpholine)$_2$ (40 mg, 0.11 mmol) in CH_2Cl_2 (10 mL) a solution of PMe_2Ar^{Dtbp2} (58 mg, 0.11 mmol) in CH_2Cl_2 (5 mL) was added. The reaction mixture was stirred at room temperature for 3 h. Volatiles were removed under vacuum and the resulting solid was purified by recrystallization from petroleum ether/CH_2Cl_2 (2:1) mixtures at -20 ºC, rendering the title compound as a yellow solid. Yield: 70 mg (81 %).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.71 (d, 4H, $^{3}J_{HH}$ = 6.4 Hz, *o*-Dtbp), 7.54-7.50 (m, 1H, *p*-C_6H_3), 7.48 (t, 2H, *p*-Dtbp), 7.27 (dd, 2H, $^{3}J_{HH}$ = 7.1 Hz, $^{4}J_{HP}$ = 2.9 Hz, *m*-C_6H_3), 3.85 (d, 2H, $^{3}J_{HH}$ = 10.3 Hz, OCH_2), 3.51 (t, 2H, $^{3}J_{HH}$ = 11.4 Hz, OCH_2), 3.32 (m, 2H,

NCH_2), 2.93 (m, 3H, NCH_2 and NH), 1.43 (s, 36H, *t*Bu), 0.89 (d, 6H, $^2J_{HP}$ = 10.8 Hz, P-CH_3).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 150.8 (*m*-Dtbp), 147.4 (d, $^2J_{CP}$ = 9 Hz, *o*-C_6H_3), 142.4 (d, $^3J_{CP}$ = 3 Hz, *m*-C_6H_3), 131.1 (d, $^3J_{CP}$ = 8 Hz, *ipso*-Dtbp), 129.8 (d, $^4J_{CP}$ = 3 Hz, *o*-Dtbp), 128.4 (d, $^1J_{CP}$ = 46 Hz, *ipso*-C_6H_3), 124.8 (*p*-C_6H_3), 121.4 (*p*-Dtbp), 68.1 (d, $^4J_{CP}$ = 3 Hz, OCH_2), 47.9 (d, $^3J_{CP}$ = 3 Hz, *N*CH_2), 35.2 (*C*Me_3), 31.7 (C*Me*$_3$), 18.1 (d, $^2J_{CP}$ = 37 Hz, P-*C*H_3).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 12.1.

Anal. Calcd for $C_{40}H_{60}Cl_2NOPPd$: C, 61.66; H, 7.76; N, 1.80. Found: C, 61.36; H, 7.70; N, 2.18.

2.6. [$PdCl_2$(morpholine)($PCyp_2Ar^{Xyl2}$)], 3b.

To a solution of $[PdCl_2(PCyp_2Ar^{Xyl2})]_2$ (140 mg, 0.11 mmol) in CH_2Cl_2 (10 mL), morpholine (0.5 mL) was added under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 1 h. The resulting orange solution was taken to dryness and the solid residue was purified by recrystallization from petroleum ether:diethyl ether (2:1) mixtures at -20 ºC. The title compound was obtained as an orange crystalline solid. Yield: 143 (90 %).

^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.39 (t, 1H, $^3J_{HH}$ = 6.4 Hz, *p*-C_6H_3), 7.20-7.10 (m, 2H, *p*-Xyl), 7.03 (d, 4H, $^3J_{HH}$ = 7.8 Hz, *m*-Xyl), 6.93 (dd, 2H, $^3J_{HH}$ = 7.2 Hz, $^4J_{HP}$ = 2.9 Hz, *m*-C_6H_3), 3.72 (d, 2H, $^3J_{HH}$ = 12.4 Hz, OCH_2), 3.62 (m, 1H, NH), 3.36 (m, 2H, OCH_2), 3.16 (m, 2H, NCH_2), 2.76 (d, 2H, $^3J_{HH}$ = 12.4 Hz, NCH_2), 2.68- 2.39 (m, 5H, Cyp), 2.18 (s, 12H, CH_3), 2.02-1.81 (m, 2H, Cyp), 1.50-1.35 (m, 6H, Cyp), 1.32-0.99 (m, 5H, Cyp).

$^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, 298 K): δ 146.3 (*o*-C_6H_3), 142.8 (*ipso*-Xyl), 137.4 (*o*-Xyl), 132.4 (d, $^3J_{CP}$ = 6 Hz, *m*-C_6H_3), 132.1 (*ipso*-C_6H_3), 130.0 (*p*-C_6H_3), 128.0 (*m*-Xyl), 127.9 (*p*-Xyl), 68.0 (br, OCH_2), 47.2 (br, NCH_2), 39.4 (d, $^2J_{CP}$ = 26 Hz, *C*H-Cyp), 30.6 (*C*H_2-Cyp), 27.0 (*C*H_2-Cyp), 25.9 (d, J_{CP} = 8 Hz, *C*H_2-Cyp), 22.5 (*C*H_3).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 298 K): δ 31.2.

Anal. Calcd for $C_{37}H_{50}Cl_2NOPPd$: C, 60.62; H, 6.87; N, 1.91. Found: C, 60.54; H, 6.74, N, 2.08.

2.7. *trans*-$PdCl_2$(morpholine)$_2$, 4.

To a Schlenk tube equipped with a magnetic stir bar and charged with $PdCl_2$ (100 mg, 0.56 mmol), methanol (10 mL) was added under a nitrogen atmosphere. To the resulting reddish suspension, morpholine (0.15 mL, 1.69 mmol) was added. The mixture

was stirred at room temperature for 24 h and a grey suspension was obtained. The solid was separated by filtration, washed with methanol, and dried under vacuum. Yield: 179 mg (91%).

Anal. Calcd for $C_8H_{18}Cl_2N_2O_2Pd$: C, 27.33; H, 5.12; N, 7.97: Found: C, 27.53; H, 4.95; N, 7.68.

2.8. [$PdCl_2(PCyp_2Ar^{Xyl2})$], 5.

To a vial equipped with a J Young tap containing a magnetic bar and charged with $PdCl_2$ (40 mg, 0.22 mmol) and $PCyp_2Ar^{Xyl2}$ (100 mg, 0.22 mmol), toluene was added (5 mL). The resulting mixture was heated at 100 ºC for 24 h. The reddish solution was taken to dryness and the solid residue was recrystallized from a mixture of petroleum ether:CH_2Cl_2 (2:1). Cooling at -20 ºC afforded red crystals of the title compound. Yield: 103 mg (74%).

^{1}H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.86 (t, 1H, $^3J_{HH}$ = 7.7 Hz, p-Xyl), 7.51 (td, 1H, $^3J_{HH}$ = 7.6 Hz, $^5J_{HP}$ = 2.3 Hz, *p*-C_6H_3), 7.26-7.29 (m, 3H, *p*- and *m*-Xyl), 7.16 (d, 2H, $^3J_{HH}$ = 7.6 Hz, *m*-Xyl), 7.09 (ddd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 2.5 Hz, $^4J_{HH}$ = 1.3 Hz, *m*-C_6H_3), 6.54 (ddd, 1H, $^3J_{HH}$ = 7.5 Hz, $^4J_{HP}$ = 1.8 Hz, $^4J_{HH}$ = 1.3 Hz, *m*-C_6H_3), 2.57-2.35 (m, 6H, Cyp), 2.29 (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 1.89-1.64 (m, 6H, Cyp), 1.50-1.24 (m, 6H, Cyp).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 289 K): δ 148.1 (d, $^2J_{CP}$ = 18 Hz, *o*-C_6H_3), 145.0 (*o*-C_6H_3), 143.9 (*o*-Xyl), 138.8 (*ipso*-Xyl), 137.4 (d, $^1J_{CP}$ = 35 Hz, *ipso*-C_6H_3), 137.3 (*p*-Xyl), 136.8 (*ipso*-Xyl), 132.6 (d, $^3J_{CP}$ = 9 Hz, *p*-C_6H_3), 132.1 (d, $^3J_{CP}$ = 6 Hz, *m*-C_6H_3), 131.7 (m-Xyl), 130.8 (d, $^3J_{CP}$ = 15 Hz, *m*-C_6H_3), 128.9 (*p*-Xyl), 127.9 (*m*-Xyl), 114.2 (d, $^3J_{CP}$ = 3 Hz, *ipso*-Xyl), 41.3 (d, $^1J_{CP}$ = 30 Hz, *C*H-Cyp), 33.6 (d, J_{CP} = 5 Hz, *C*H_2-Cyp), 31.5 (*C*H_2-Cyp), 26.1 (d, J_{CP} = 11 Hz, *C*H_2-Cyp), 25.3 (d, J_{CP} = 14 Hz, *C*H_2-Cyp), 23.6 (*C*H_3), 21.2 (*C*H_3).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 298 K): δ 68.9.

^{31}P{^{1}H} NMR (121 MHz, C_6D_6, 298 K): δ 35.5.

Anal. Calcd for $C_{64}H_{78}Cl_4P_2Pd_2$: C, 60.82; H, 6.22. Found: C, 60.56; H, 6.36.

The behavior of complex **5** in solution is different upon changing the polarity of the solvent. In less polar solvent like C_6D_6 o toluene-d_8, the ^{31}P chemical shift of the phosphane ligand (35.5 ppm) agrees with a monodentate coordination mode whereas in more polar $CDCl_3$, its ^{31}P resonance shifts to higher frequency (68.9 ppm), in agreement with a P,C-bidentate coordination mode of the phosphane ligand. However, the solid state structure of **5** reveals that it consists of a dinuclear Pd(II) species formed by two $PdCl_2(PCyp_2Ar^{Xyl2})$ units linked by two bridging chlorides (see Fig S4), in which the phosphane ligands are coordinated in a classical way, through the P atom.

A combination of both forms of **5** can be obtained by dissolving it in a toluene/CH_2Cl_2 mixture. The ratio between the two compounds depends on the relative amount of solvents used, as shown in Fig S1, with the proportion of mononuclear species increasing as CH_2Cl_2 is added. Furthermore, in very concentrated CH_2Cl_2 samples of **5**, a small amount of the dinuclear species can be observed.

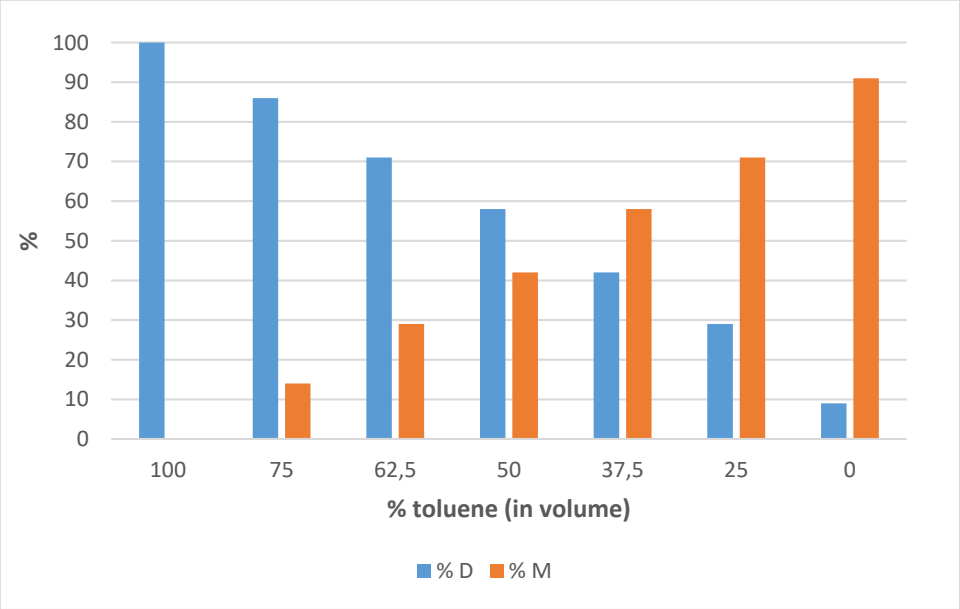


Figure S1. Variation of the ratio of dinuclear (D)/mononuclear(M) forms of **5** in toluene/dichloromethane solution, determined by ^{31}P NMR spectrospcoy.

To examine this behavior in more depth, a DOSY study has been undertaken. The DOSY spectra of **5** has been recorded in toluene-d_8 and in $CDCl_3$. For comparative purposes, DOSY spectra of compounds prepared in our group[4] $[PdCl(PMe_2Ar^{Xyl2})(\mu\text{-}Cl)]_2$ and $PtCl_2(PCyp_2Ar^{Xyl2})$, dinuclear and mononuclear species, respectively, both in solution and in the solid state, have been also recorded in $CDCl_3$. The diffusion coefficients obtained by relaxation analysis of the NMR data along with the hydrodynamic radii calculated from the said coefficients with the Stokes-Einstein equation, are gathered in Table S1. The hydrodynamic radius of **5** visibly increases from $CDCl_3$ (3.3 Å) to toluene-d_8 solution (5.5 Å). The value for compound $[PdCl(PMeAr^{Xyl2})(\mu\text{-}Cl)]_2$, which exits in solution as a dimer, is slightly lower at 5.2 Å, probably due to the reduced stric bulk of the PMe_2 moiety compared to $PCyp_2$. On the other hand, a radius of 4.3 Å is obtained

[4] Unpublished results.

for the mononuclear Pt compound, somewhat higher than expected, but still closer to the value obtained for **5** in $CDCl_3$ than to that in toluene-d_8.

Table S1. Diffusion coefficients (D) and hydrodynamic radii (r_H) gathered from the DOSY studies.

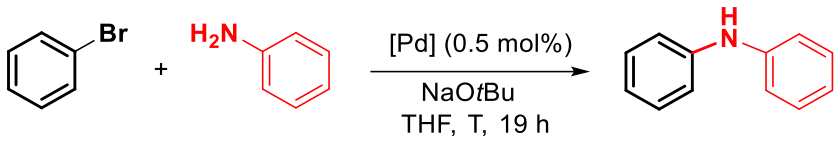
Complex	**Solvent**	**D (10^{-10} m^2 s^{-1})**	**r_H (Å)**
$PdCl_2(PCyp_2Ar^{Xyl2})$	$CDCl_3$	11.7	3.3
$[PdCl(\mu\text{-}Cl)(PCyp_2Ar^{Xyl2})]_2$	Tol-d_8	6.7	5.5
$[PdCl(\mu\text{-}Cl)(PMe_2Ar^{Xyl2})]_2$	$CDCl_3$	7.4	5.2
$PtCl_2(PCyp_2Ar^{Xyl2})$	$CDCl_3$	8.9	4.3

This study seems to support the assumption that complex **5** exist in solution as a mixture of mononuclear $PdCl_2(PCyp_2Ar^{Xyl2})$ and dinuclear $[PdCl(PCyp_2Ar^{Xyl2})(\mu\text{-}Cl)]_2$ species in dynamic equilibrium.

3. Catalytic experiments.

3.1. Screening of precatalysts

The base, NaO*t*Bu (1.2 mmol) was placed into a vial equipped with a J Young tap containing a magnetic bar. Bromobenzene (1.0 mmol) and the GC internal standard (dodecane, 50 µL) were added in turn. Then, the precatalyst (1.0 mL, 0.005 M in THF), aniline (1.2 mmol) and the additive (0.08mmol, when required) were added in turn under a nitrogen atmosphere. The reaction mixture was either stirred at room temperature or heated at a given temperature in an oil bath for 19 h. The resulting mixture was diluted with ethyl acetate (9.0 mL) and filtered through a Celite plug. Conversions were obtained on the basis of gas chromatography experiments by calibration using the pure product and dodecane as internal standard.



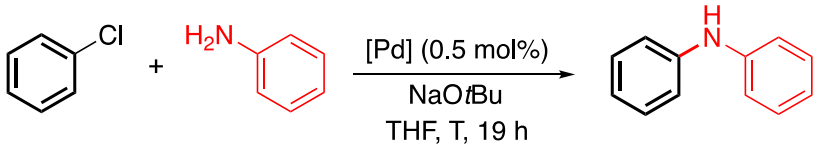
Entry	Precatalyst	T (ºC)	Conversion (%)[a]
1	**1a**	25	0
2	**2a**	25	0
3	**1b**	25	0
4	**2b**	25	0
5	**1a**	50	0
6	**2a**	50	0
7	**1b**	50	0
8	**2b**	50	0
9	**1a**	80	0
10	**2a**	80	0
11	**1b**	80	0
12	**2b**	80	0
13	**3a**	25	84
14	**3a**	50	>99
15[b]	**3a**	25	>99
16[c]	**3a**	25	>99
17	**3b**	25	>99
18[d]	**5**	25	0

[a] Average of two runs. [b] Reaction performed in the presence of acetone (8 mol%).[c] Reaction performed in the presence of 2-butanone (8 mol%). [d] 0.5 mol% of the dimer **5**.

3.2. Procedure for the reactivity profile of 3a and 3b in the arylation of aniline with bromobenzene.

Reaction mixtures were prepared as detailed in the previous section. To facilitate sampling, reactions were stirred at room temperature under a nitrogen atmosphere inside the glove box. At each time point, 35 μL of reaction mixture was removed from the catalytic reaction, poured in a vial and diluted with AcOEt (0.5-0.7 mL). The vials are kept cool (inside the glove box fridge) during the sampling for quenching the catalytic reaction. Samples were removed from the glove box and filtered through a pipette filter to eliminate solid waste. Yields were determined by gas chromatography with calibration using the pure product and, dodecane as internal standard. All experiments were performed in duplicates and yields are reported as the average of two runs.

3.3. Catalytic performance of 3a and 3b in the arylation of aniline with chlorobencene.



Entry	Precatalyst	T (ºC)	Additive (mol%)	Conversion (%)[a]
1	**3a**	25	-	10
2	**3b**	25	-	>99
3	**3a**	25	Acetone (8)	34
4	**3a**	25	2-Butanone (8)	74
5	**3a**	25	Acetone (15)	48
6	**3a**	25	2-Butanone (15)	84
7	**3a**	50	-	55
8	**3a**	50	Acetone (8)	96
9	**3a**	50	2-Butanone (8)	>99

Reaction conditions: PhCl (1 mmol), aniline (1.2 mmol), NaOtBu (1.2 mmol), precatalyst (0.005 mmol), THF (1 mL), reaction time 19 h (unoptimized). [a] Conversion determined by GC using dodecane as internal standard. Average of two runs.

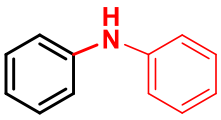
3.4. General catalytic procedure for the C-N coupling of aryl halides with aniline.

NaO*t*Bu (1.2 mmol) was placed into a vial equipped with a J Young tap containing a magnetic bar. The aryl halide (1.0 mmol), the precatalyst **3b** (1.0 mL, 0.005 M in THF) and aniline (1.2 mmol) were added in turn under a nitrogen atmosphere. The reaction mixture was stirred at room temperature for 19 h. The solution was evaporated to dryness and the residue was purified by flash chromatography on silica gel.

All C-N coupling products have been described in the literature. However, ^{1}H NMR spectra of these compounds used to identify them have been included herein along with the references where their spectroscopic characterization appeared. For the novel product, all relevant spectroscopic and analytical data are provided.

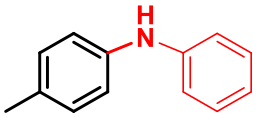
4. Characterization data for the C-N coupling products.

N,N-Diphenylamine[5] (Table 2, 6a)



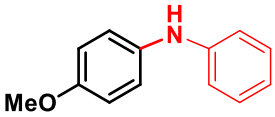
Following the general catalytic procedure, the product was isolated as a white solid after purification by flash chromatography (AcOEt/petroleum ether 1:30). Yield: 151 mg, 89% (X = Br); 158 mg, 94% (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.22 (m, 4H), 7.02 (d, 4H, J_{HH} = 8.1 Hz), 6.91 (t, 2H, J_{HH} = 7.3 Hz), 5.66 (br s, 1H).

N-(4-Methylphenyl)-*N*-phenylamine[6] (Table 2, 6b)



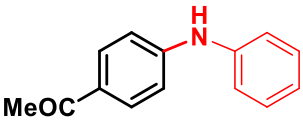
Following the general catalytic procedure, the product was isolated as a white solid after purification by flash chromatography (AcOEt/petroleum ether 1:20). Yield: 181 mg, 98% (X = Br); 180 mg, 98% (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.20 (m, 2H), 7.09 (d, 2H, J_{HH} = 8.2 Hz), 7.01-7.98 (m, 4H), 6.87 (t, 2H, J_{HH} = 7.3 Hz), 5.60 (br s, 1H), 2.30 (s, 3H)

N-(4-Methoxylphenyl)-*N*-phenylamine[7] (Table 2, 6c)



Following the general catalytic procedure, the product was isolated as a white solid after purification by flash chromatography (AcOEt/petroleum ether 1:20). Yield: 188 mg, 94% (X = Br); 91 mg, 45% (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.18 (m, 2H), 7.08-7.06 (m, 2H), 6.91-6.83. (m, 5H), 5.47 (br s, 1H), 3.80 (s, 3H).

1-(4-phenylamino)phenyl)ethan-1-one (Table 2, 6d)



Following the general catalytic procedure, the product was isolated as a yellow solid after purification by flash chromatography (AcOEt/petroleum ether 1:5). Yield: 187 mg, 88% (X = Br). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (d, 2H, J_{HH} = 6.9 Hz), 7.37-7.34 (m, 2H), 7.20-7.17 (m, 2H), 7.11-7.06 (m, 1H), 6.98 (d, 2H, J_{HH} = 6.9 Hz), 6.08 (br s, 1H), 2.53 (s, 3H). 13C{1H} NMR (75 MHz, $CDCl_3$) δ 196.5, 148.5, 140.7, 130.6, 129.5, 129.0, 123.3, 120.7, 114.4, 26.1.

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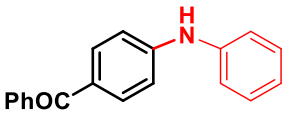
[5] Aubrey, D. W.; Lappert, M. F.; Majumdar, M. K. *J. Chem. Soc*. **1962**, 4088.
[6] Desmarets, C.; Schneider, R.; Fort, Y. *J. Org. Chem*. **2002**, *67*, 3029.
[7] Louie, J.; Driver, M. S.; Hamann, B. C.; Hartwig, J. F. *J. Org. Chem*. **1997**, *62*, 1268.

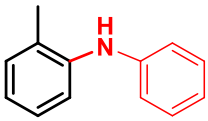
HRMS-ESI (Orbitrap): m/z calculated for $[C_{14}H_{14}ON]^+$ $[M + H]^+$ 212.10; found 212.1068

Phenyl(4-phenylamino)phenyl)methanone[8] (Table 2, 6e)



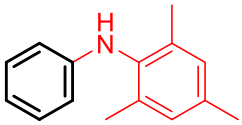
Following the general catalytic procedure, the product was isolated as a light yellow solid after purification by flash chromatography (AcOEt/petroleum ether 1:5). Yield: 241 mg, 88% (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79-7.74 (m, 4H), 7.55-7.44 (m, 3H), 7.38-7.32 (m, 2H), 7.22-7.19 (m, 2H), 7.11-7.08 (m, 1H), 7.02 (d, 2H, J_{HH} = 6.9 Hz), 6.10 (br s, 1H).

***N*-(2-Methylphenyl)-*N*-phenylamine[9] (Table 2, 6f)**



Following the general catalytic procedure, the product was isolated as a pale yellow oil after purification by flash chromatography (AcOEt/petroleum ether 1:20). Yield: 170 mg, 92% (X = Br); 169 mg, 92 % (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21-7.08 (m, 5H), 6.91-6.81 (m, 4H), 5.27 (br s, 1H), 2.17 (s, 3H).

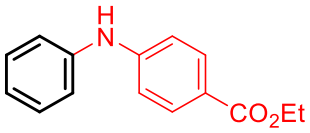
2,4,6-Trimethyl-N-phenylaniline[10] (Table 2, 6h)



Following the general catalytic procedure, the product was isolated as a colorless solid after purification by flash chromatography (petroleum ether). Yield: 187 mg, 89% (X = Br); 200 mg, 94 % (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.10 (m, 2H), 6.94 (s, 2H), 6.74-6.68 (m, 1H), 6.48-6.45 (m, 2H), 5.01 (s, 1H), 2.20 (s, 3H), 2.17 (s, 6H).

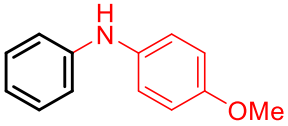
[8] Ottosen, E. R.; Sørensen, M. D.; Björkling, F.; Skak-Nielsen, T.; Fjording, M. S.; Aaes, H.; Binderup, L. *J. Med. Chem*. **2003**, *46*, 5651.
[9] Spagnolo, P.; Zanirato, P. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2615.
[10] Cortright, S. B.; Huffman, J. C.; Yoder, R. A.; Coalter, J. N., Johnston, J. N. *Organometallics* **2004**, *23*, 2238.

Ethyl 4-(phenylamino)benzoate[11] (Table 2, 6i)



Following the general catalytic procedure, the product was isolated as a colorless solid after purification by flash chromatography (AcOEt/petroleum ether 1:5). Yield: 169 mg, 69% (X = Br); 67 mg, 28 % (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94-7.91 (m, 2H), 7.36-7.31 (m, 2H), 7.18-7.15 (m, 2H), 7.09-7.00 (m, 1H), 6.97 (d, 2H, J = 8.5 Hz), 6.03 (s, 1H), 4.35 (q, 2H, *J* = 7.3 Hz), 1.38 (t, 3H, *J* = 7.3 Hz).

4-Methoxy-N-phenylaniline[12] (Table 2, 6j)

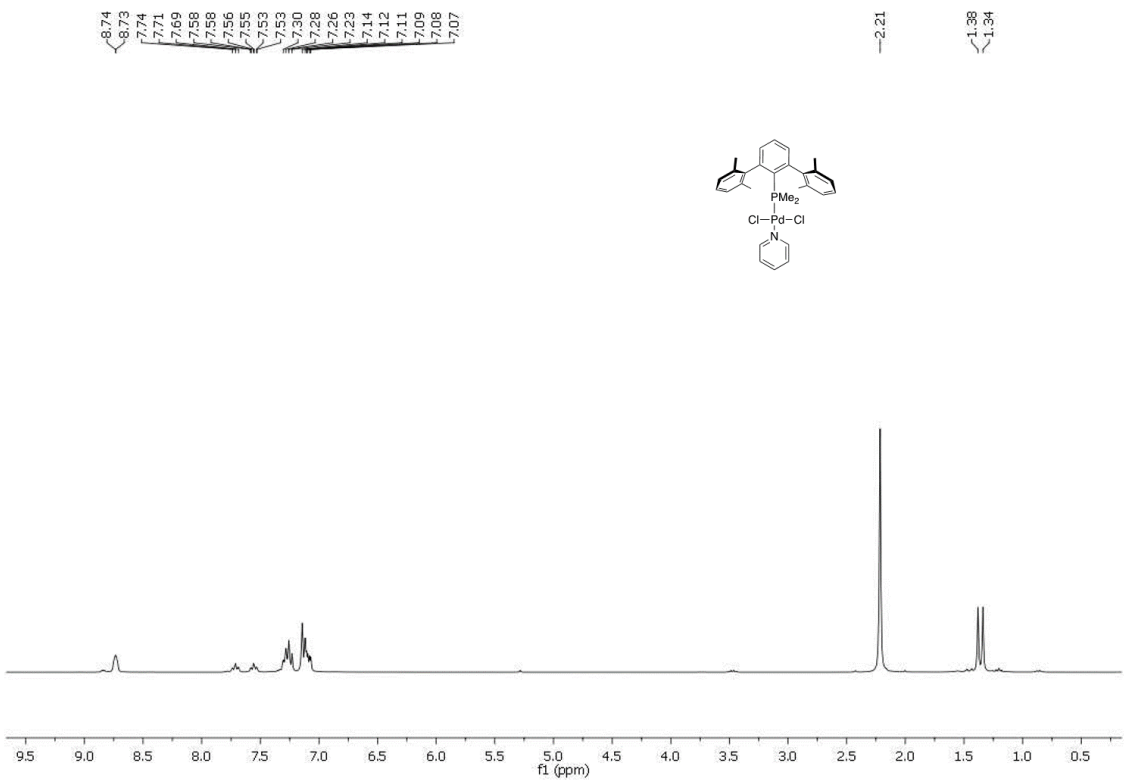


Following the general catalytic procedure, the product was isolated as a colorless solid after purification by flash chromatography (AcOEt/petroleum ether 1:10). Yield: 144 mg, 72% (X = Br); 33 mg, 17 % (X = Cl). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26-7.19 (m, 2H), 7.07 (br, 2H), 6.93-6.85 (m, 5 H), 5.45 (br , 1H), 3.81 (s, 3H).

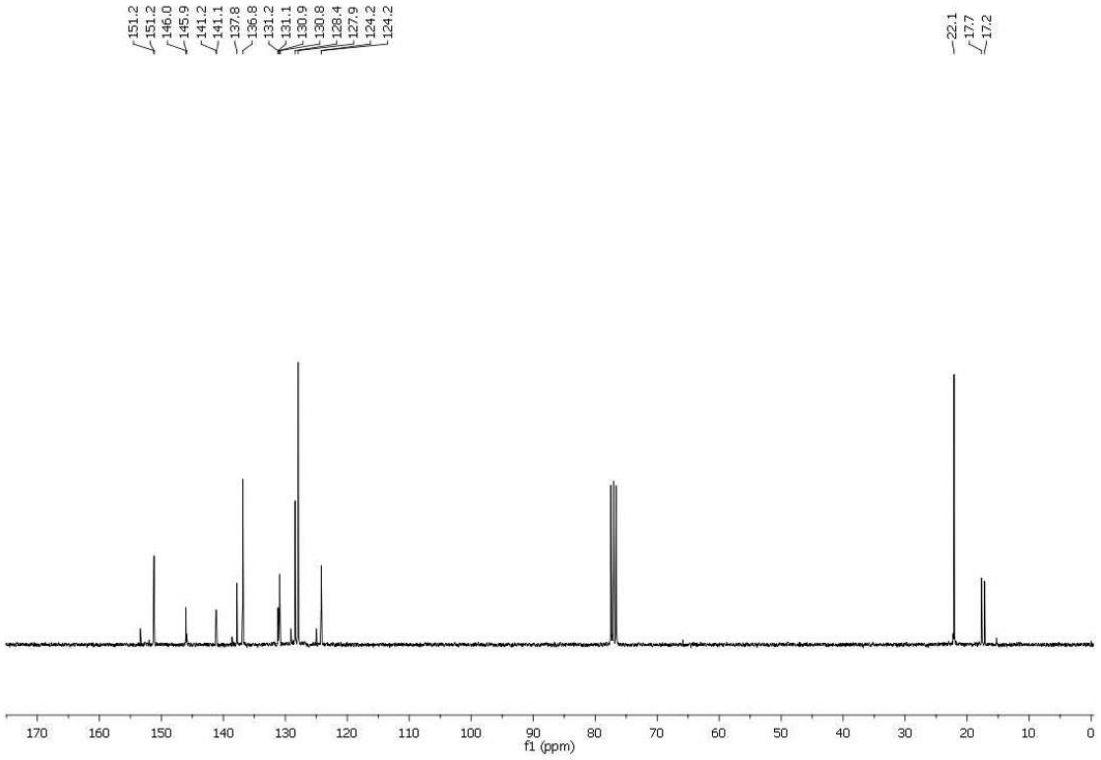
[11] Fors, B. P.; Buchwald, S. L. *J. Am. Chem. Soc*. **2010**, *132*, 15914.
[12] Carroll, M. A.; Wood R. A. *Tetrahedron* **2007**, *63*, 11349.

5. NMR Spectra of compounds.

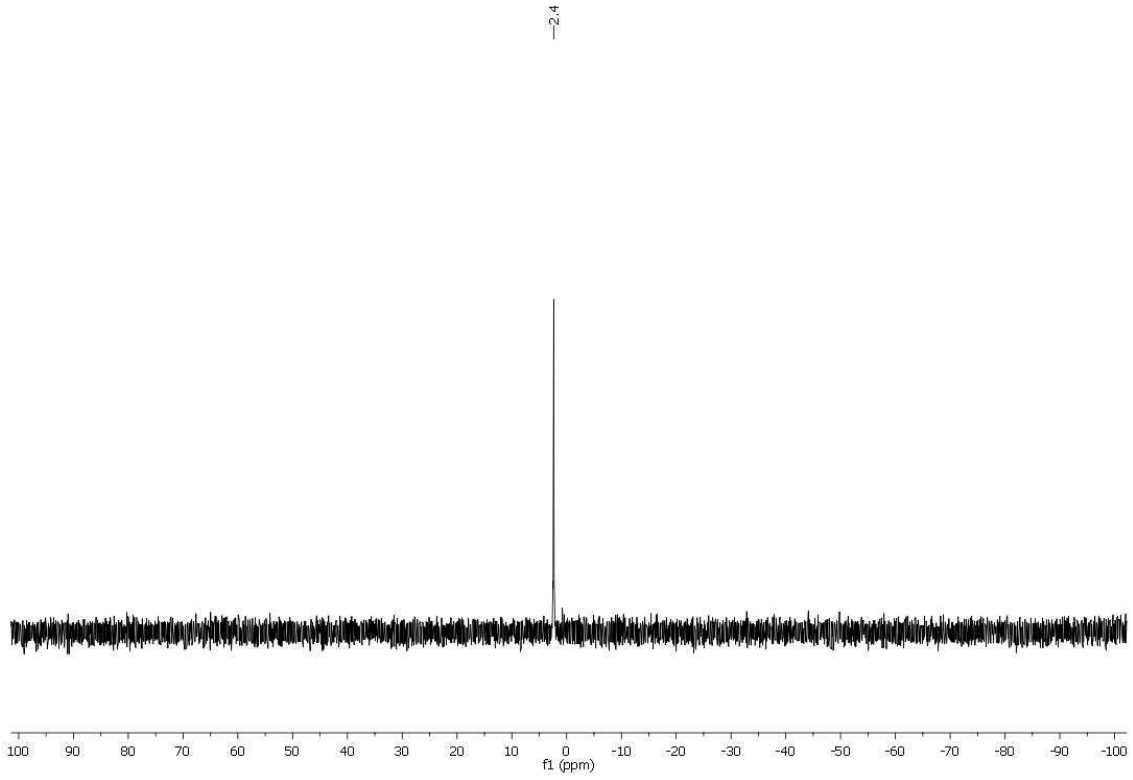
^{1}H NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Xyl2})], **1a**, (300 MHz, $CDCl_3$, 298 K).



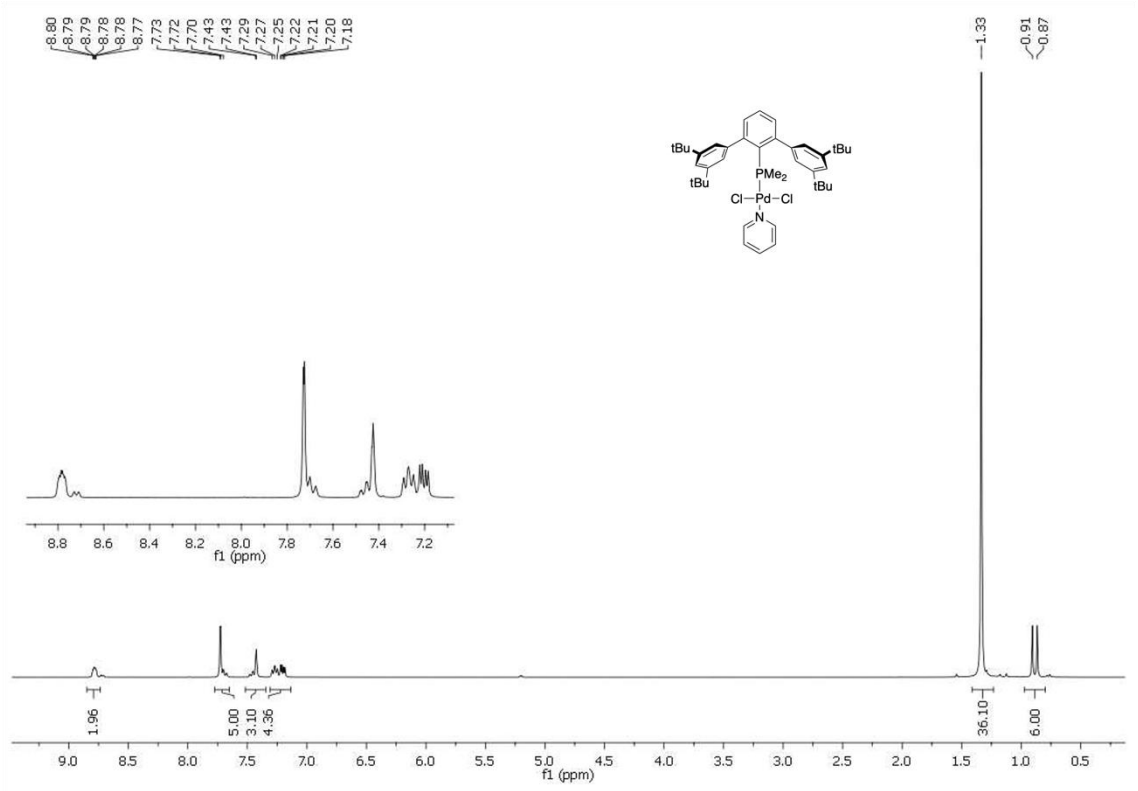
$^{13}C\{^{1}H\}$ NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Xyl2})], **1a**, (75 MHz, $CDCl_3$, 298 K)



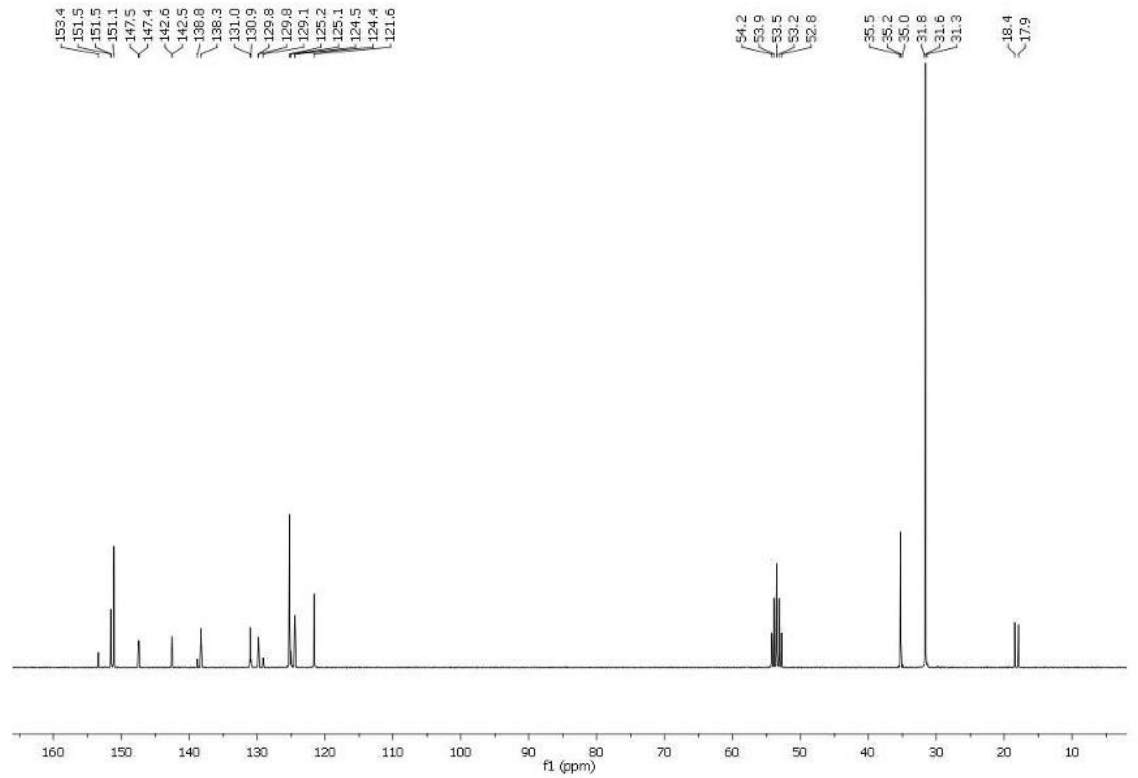
$^{31}P\{^{1}H\}$ NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Xyl2})], **1a**, (121 MHz, $CDCl_3$, 298 K)



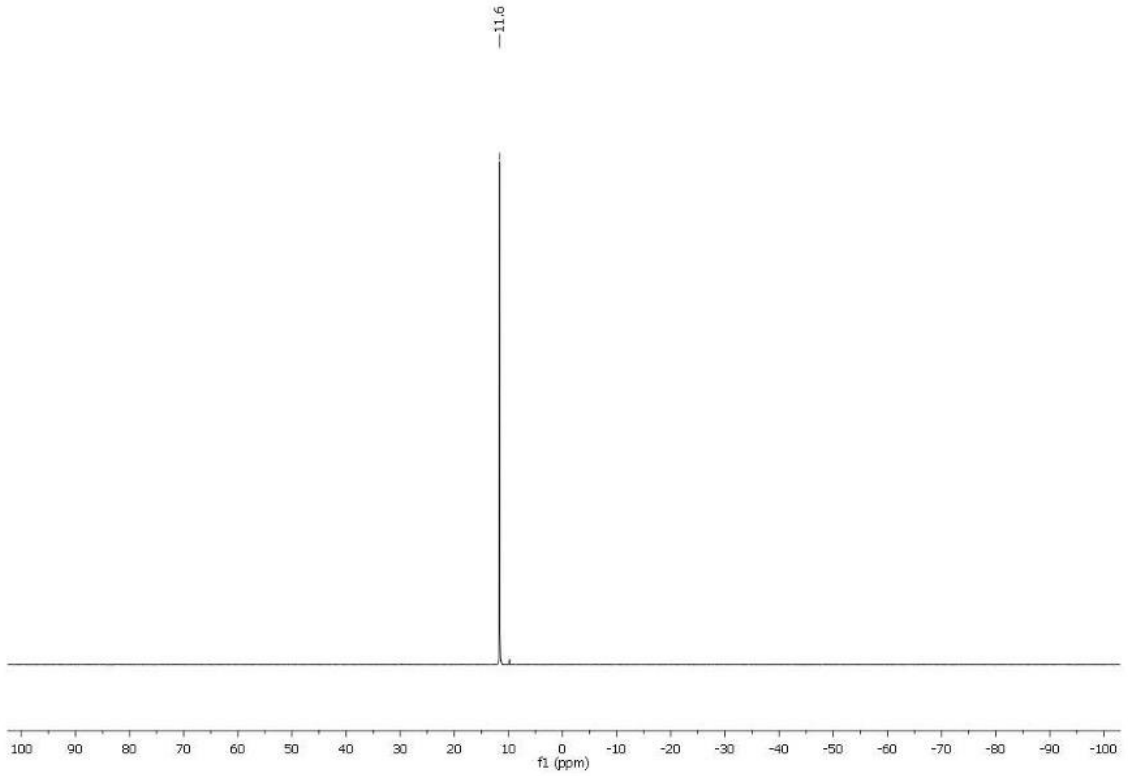
^{1}H NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Dtbp2})], **2a**, (300 MHz, CD_2Cl_2, 298 K)



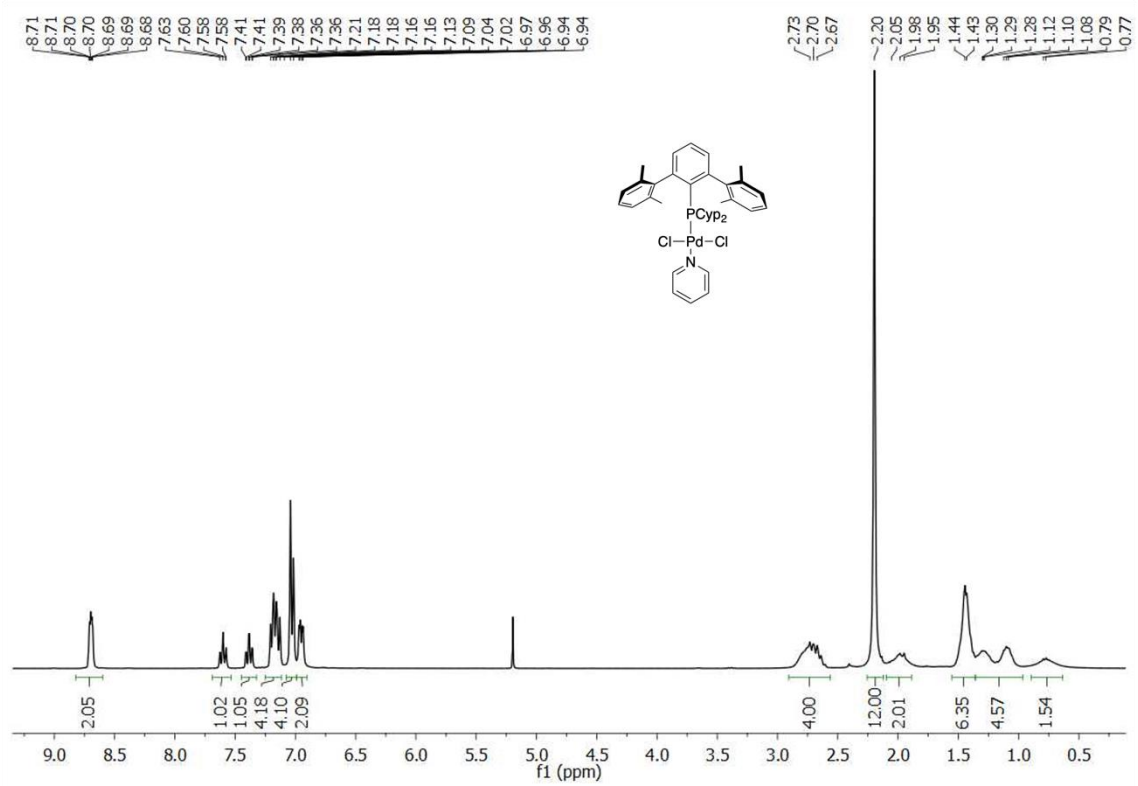
^{13}C{^{1}H} NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Dtbp2})], **2a** (75 MHz, CD_2Cl_2, 298 K)



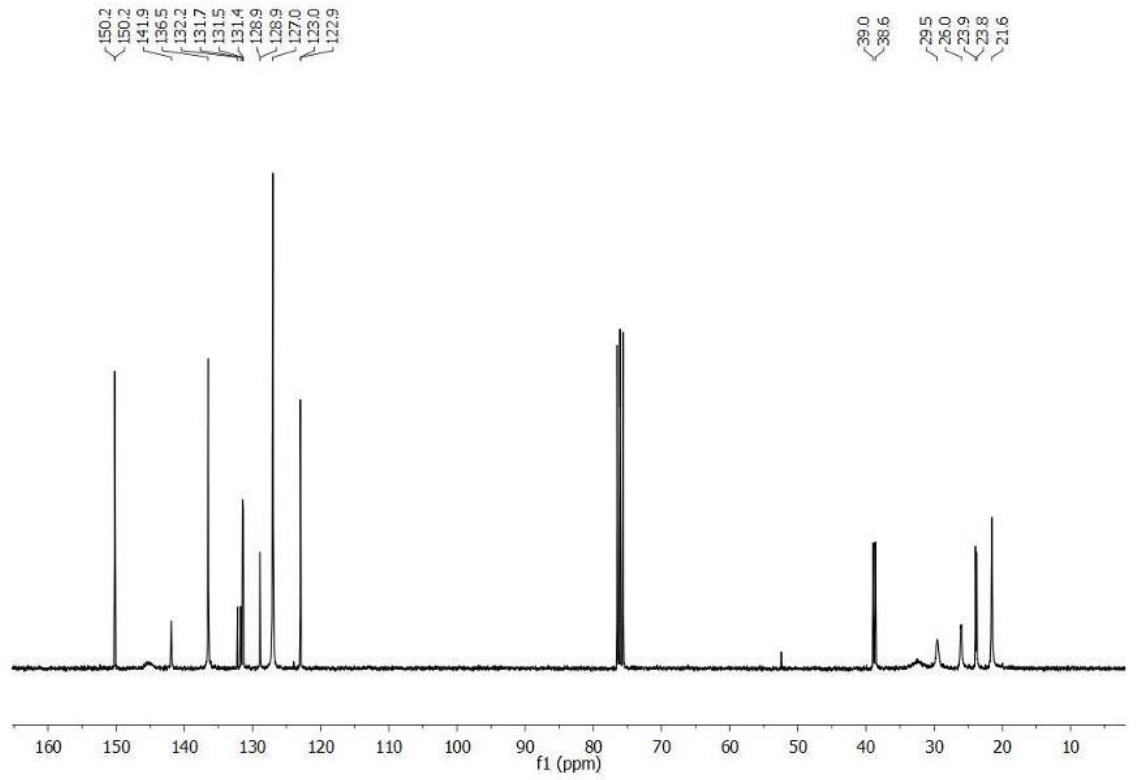
$^{31}P\{^{1}H\}$ NMR spectrum of [$PdCl_2$(pyridine)(PMe_2Ar^{Dtbp2})], **2a**, (121 MHz, CD_2Cl_2, 298 K)



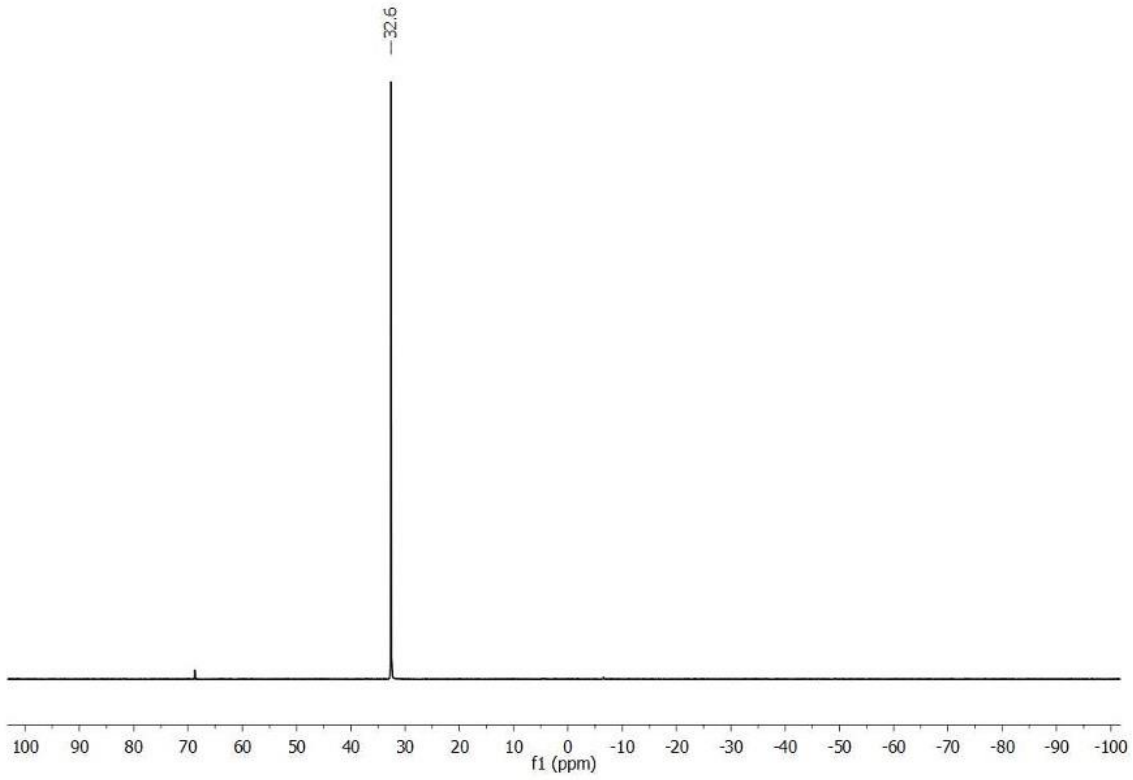
^{1}H NMR spectrum of [$PdCl_2$(pyridine)($PCyp_2Ar^{Xyl2}$)], **3a**, (300 MHz, $CDCl_3$, 298 K.



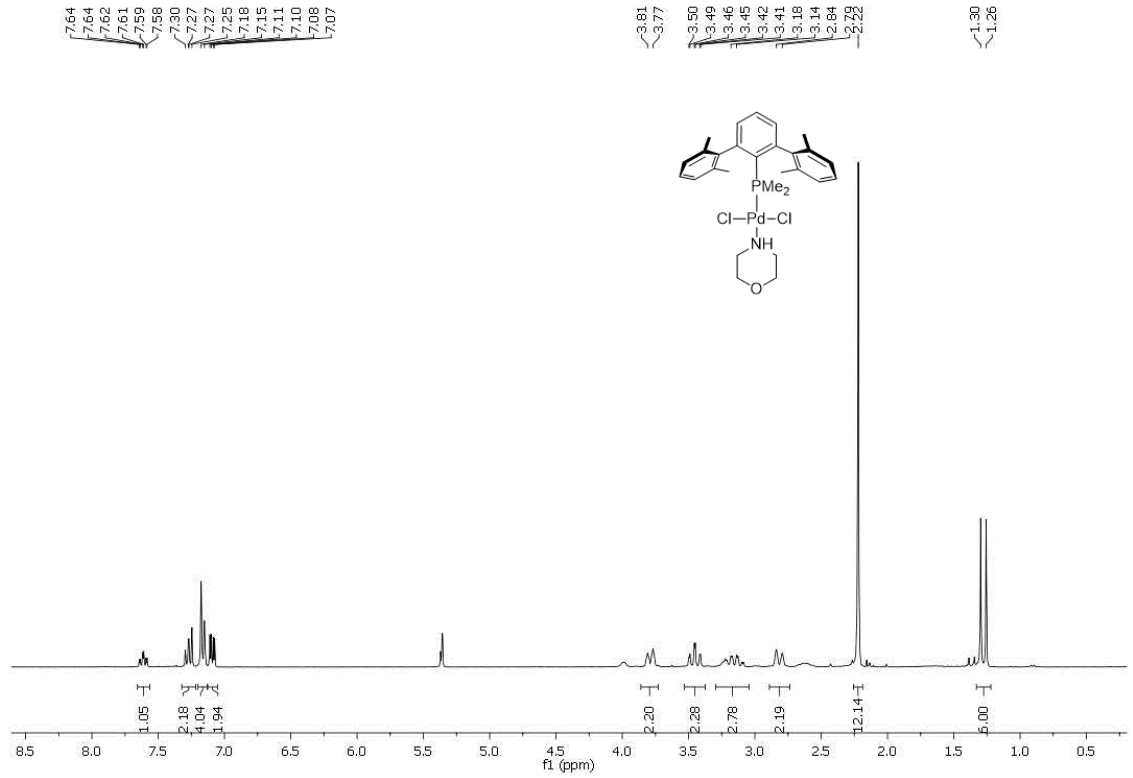
^{13}C{^{1}H} NMR spectrum of [$PdCl_2$(pyridine)($PCyp_2Ar^{Xyl2}$)], **3a**, (75 MHz, $CDCl_3$, 298 K)



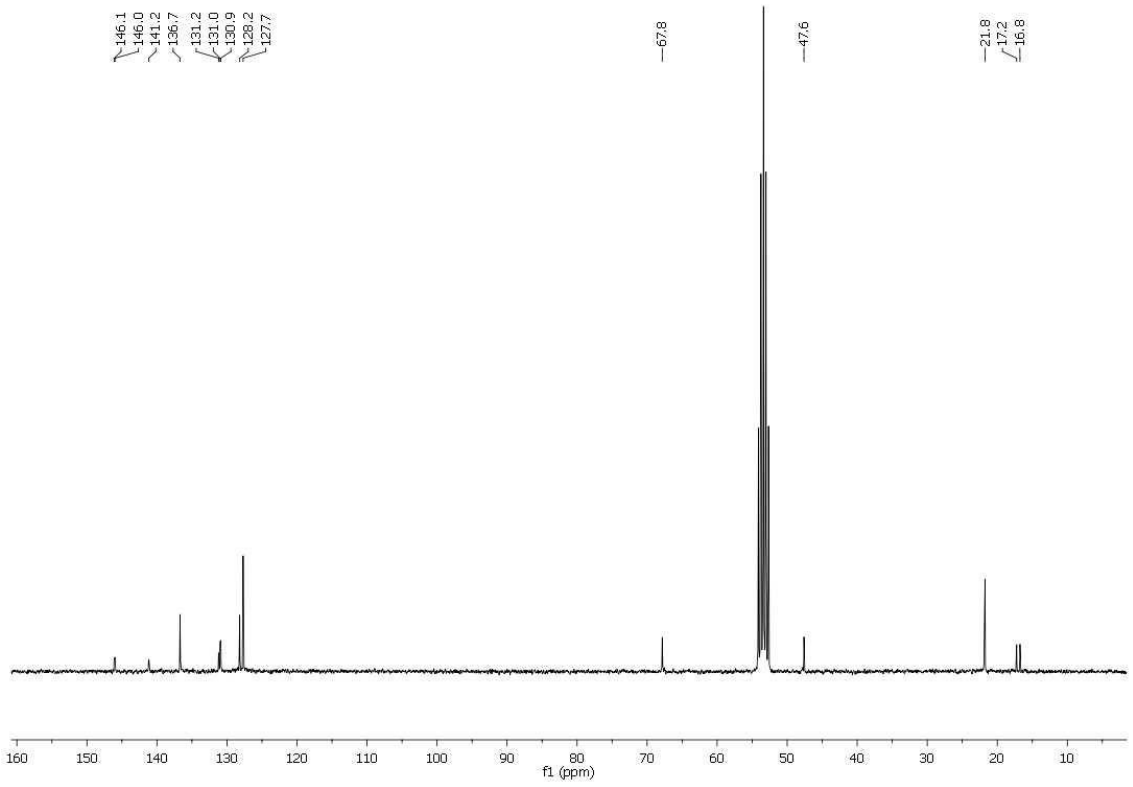
$^{31}P\{^{1}H\}$ NMR spectrum of [$PdCl_2$(pyridine)($PCyp_2Ar^{Xyl2}$)], **3a**, (121 MHz, $CDCl_3$, 298 K)



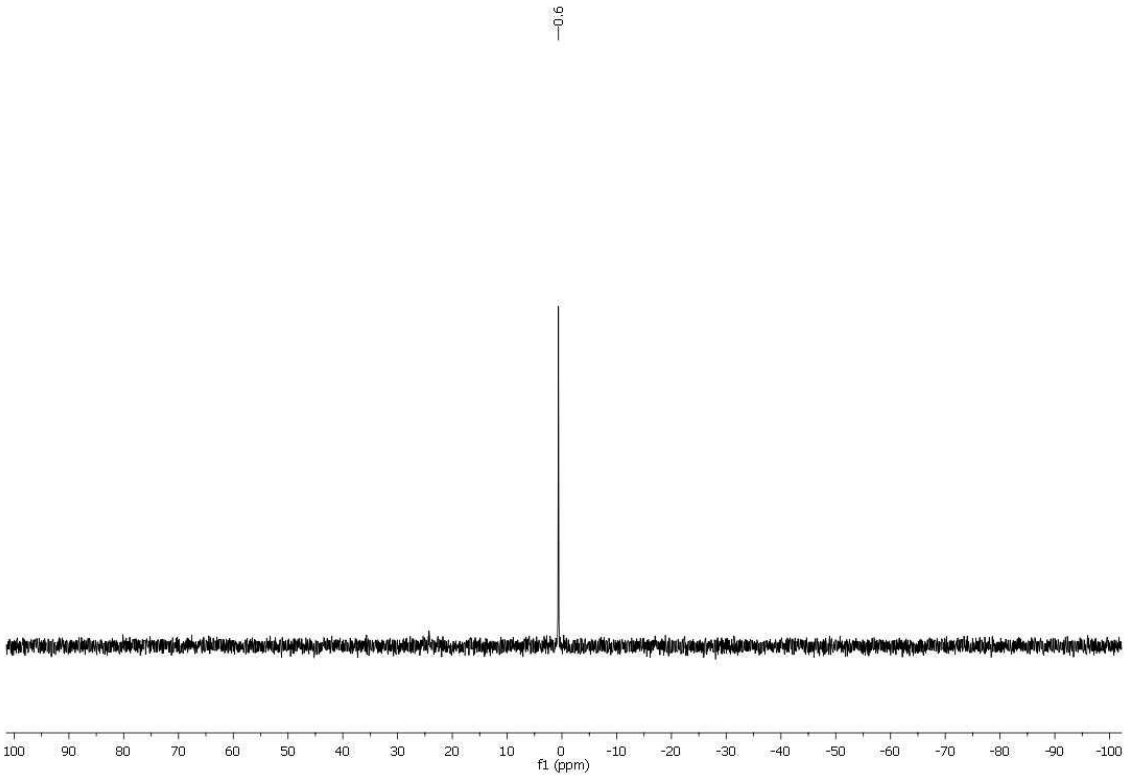
^{1}H NMR spectrum of [$PdCl_2$(morpholine)(PMe_2Ar^{Xyl2})], **1b**, (300 MHz, CD_2Cl_2, 298 K)



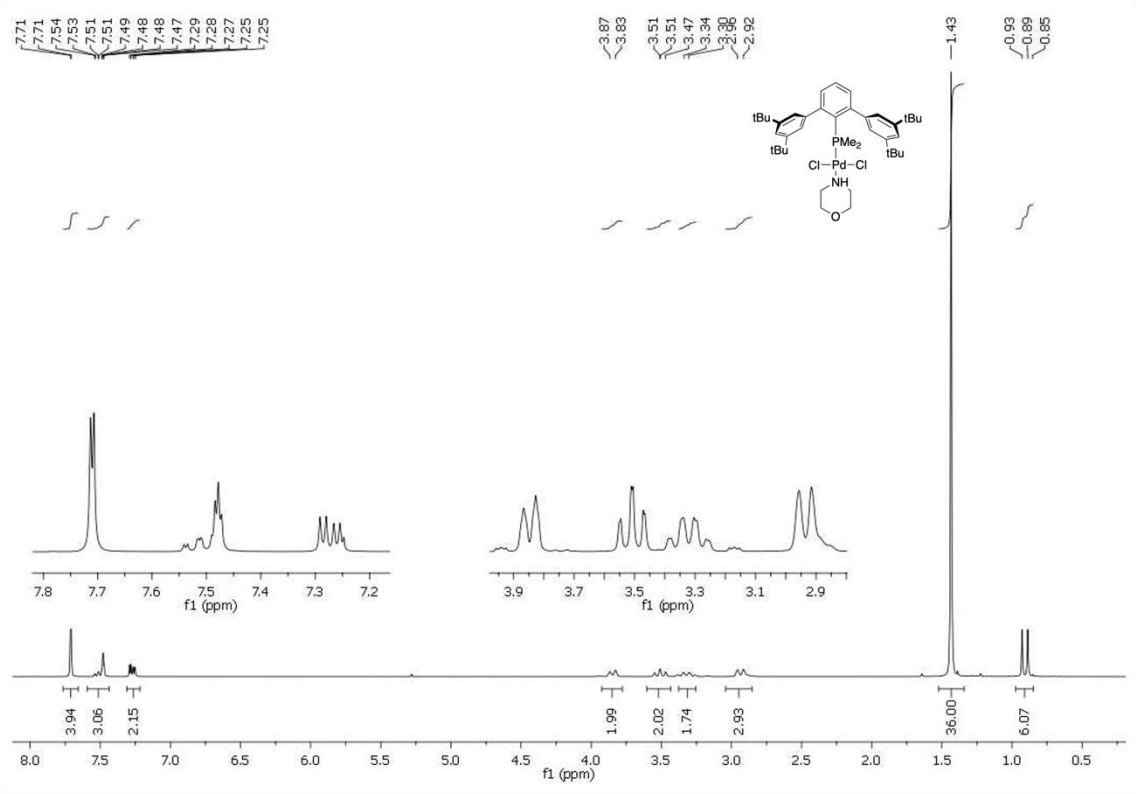
$^{13}C\{^{1}H\}$ NMR spectrum of [$PdCl_2$(morpholine)(PMe_2Ar^{Xyl2})], **1b**, (75 MHz, CD_2Cl_2, 298 K)



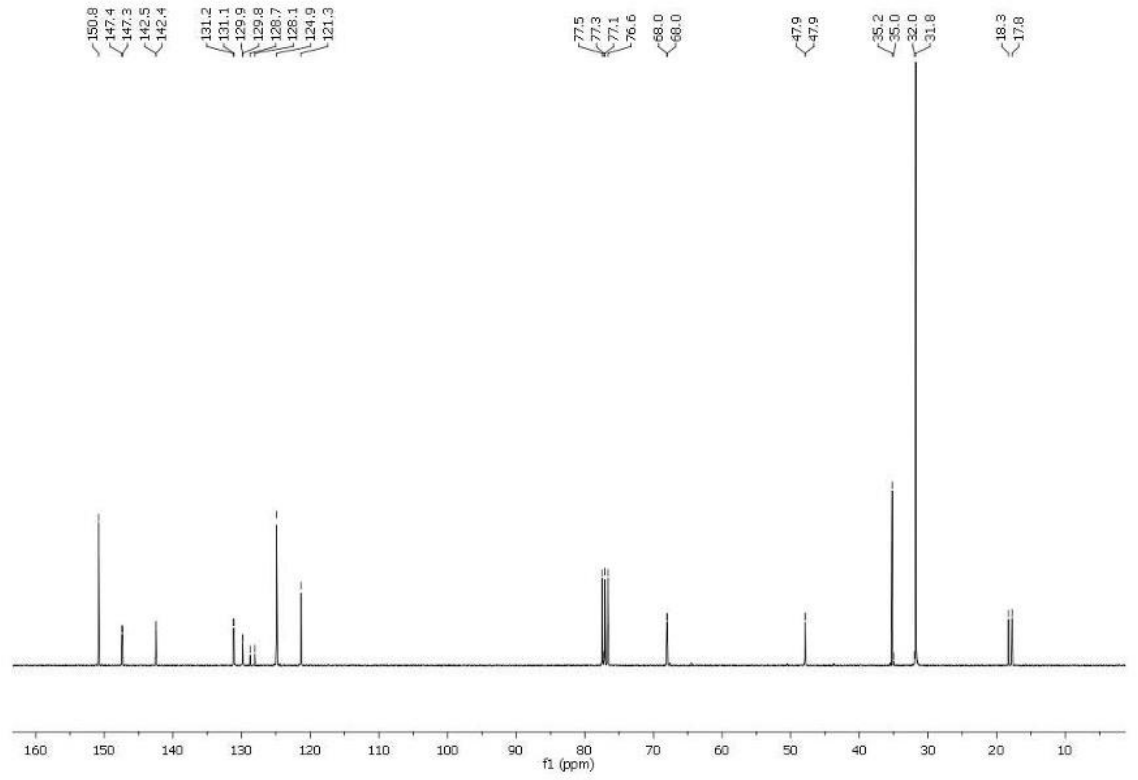
$^{31}P\{^{1}H\}$ NMR spectrum of $[PdCl_2(morpholine)(PMe_2Ar^{Xyl2})]$, **1b**, (121 MHz, CD_2Cl_2, 298 K)



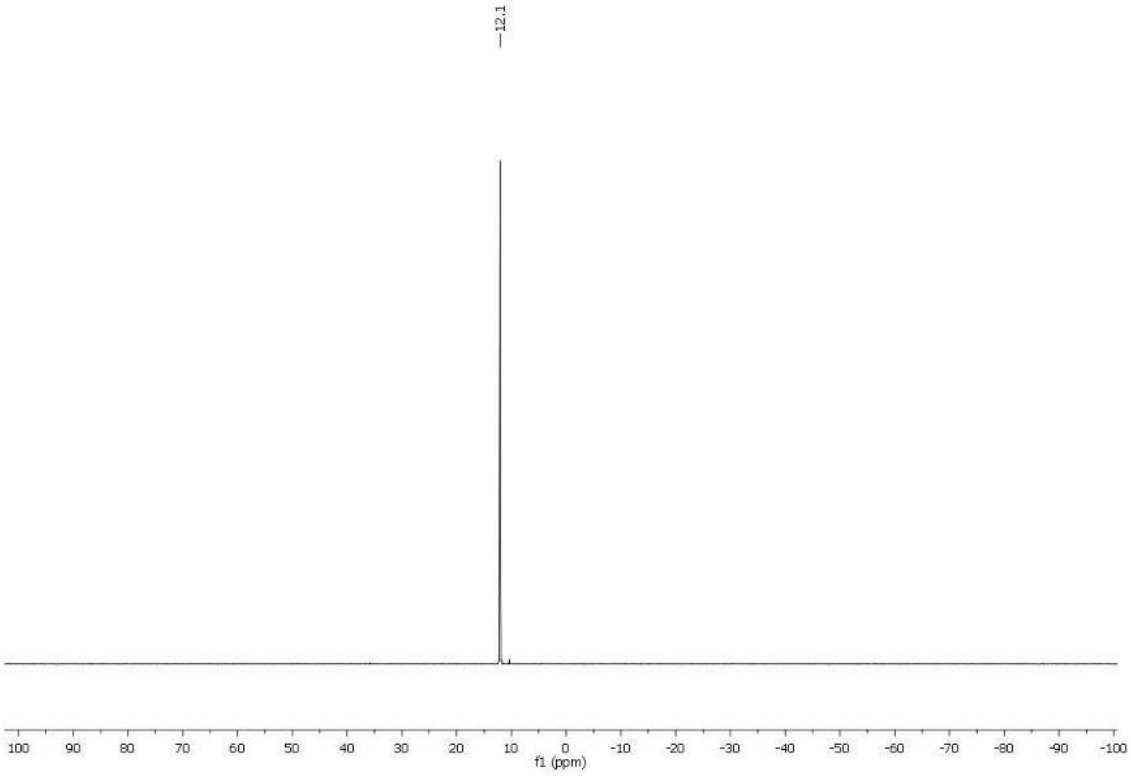
^{1}H NMR spectrum of [$PdCl_2$(morpholine)(PMe_2Ar^{Dtbp2})], **2b**, (300 MHz, $CDCl_3$, 298 K)



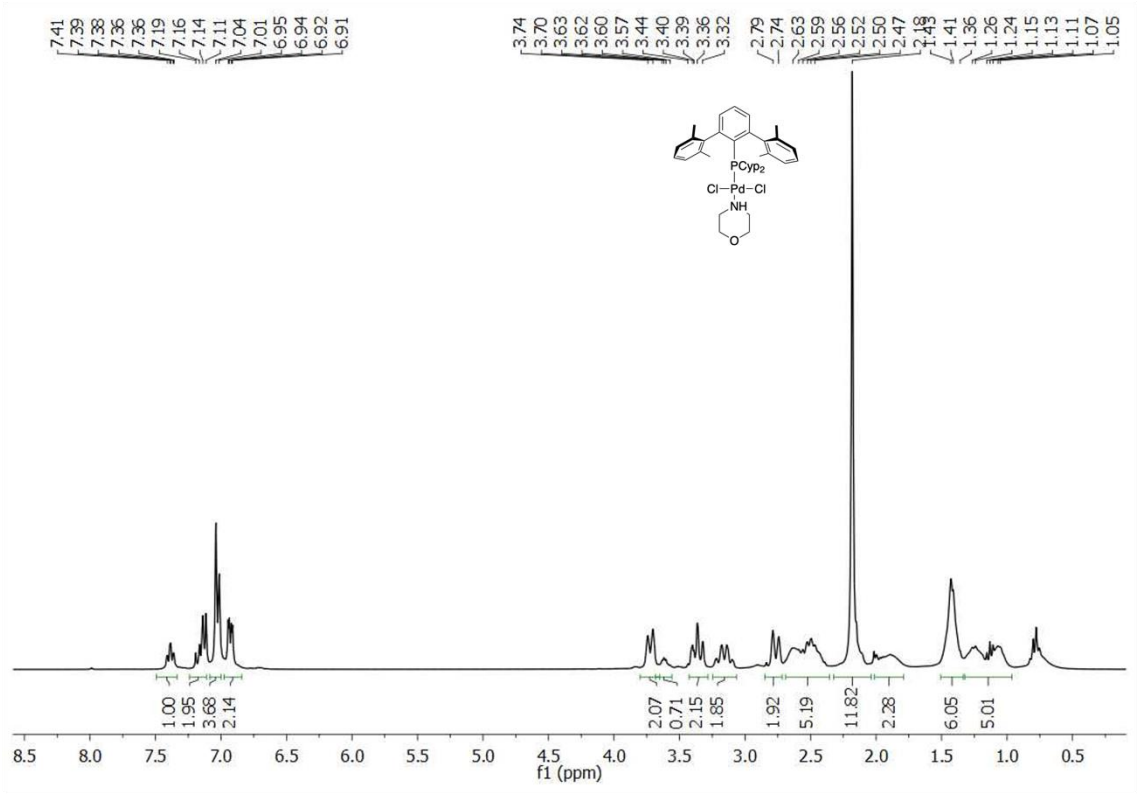
^{13}C{^{1}H} NMR spectrum of [$PdCl_2$(morpholine)(PMe_2Ar^{Dtbp2})], **2b**, (75 MHz, $CDCl_3$, 298 K)



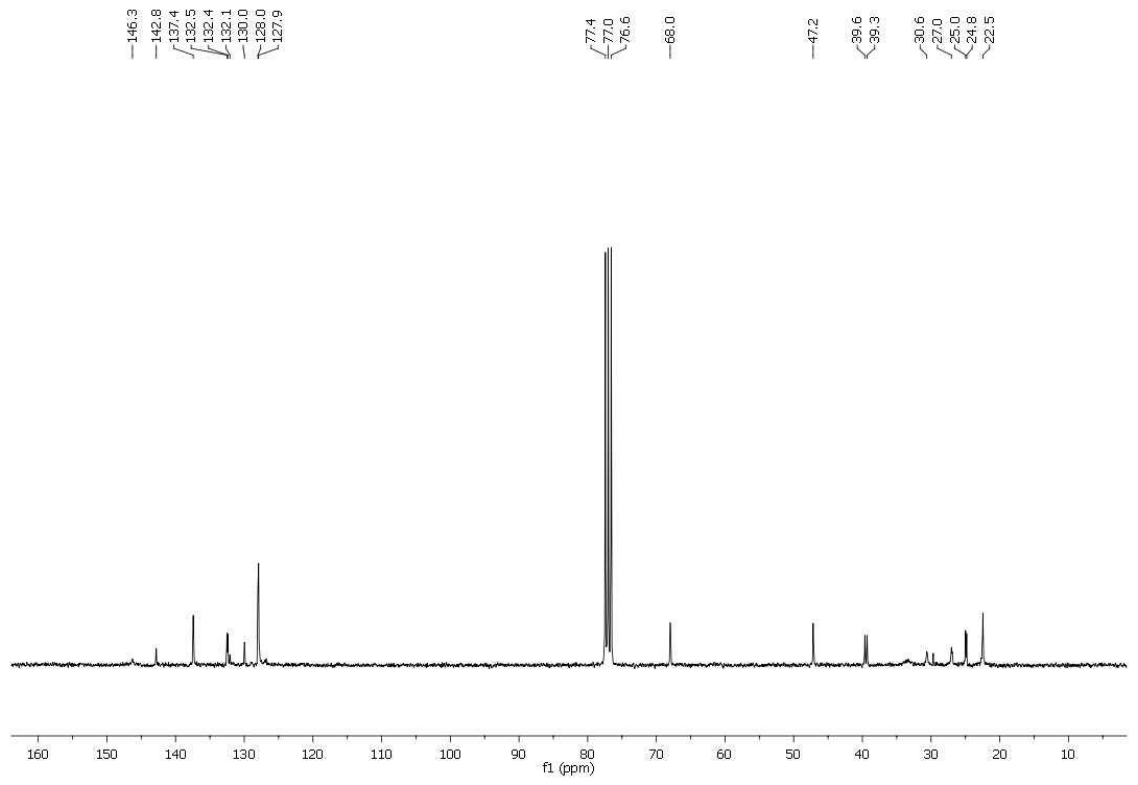
$^{31}P\{^{1}H\}$ NMR spectrum of $[PdCl_2(morpholine)(PMe_2Ar^{Dtbp2})]$, **2b**, (121 MHz, $CDCl_3$, 298 K)



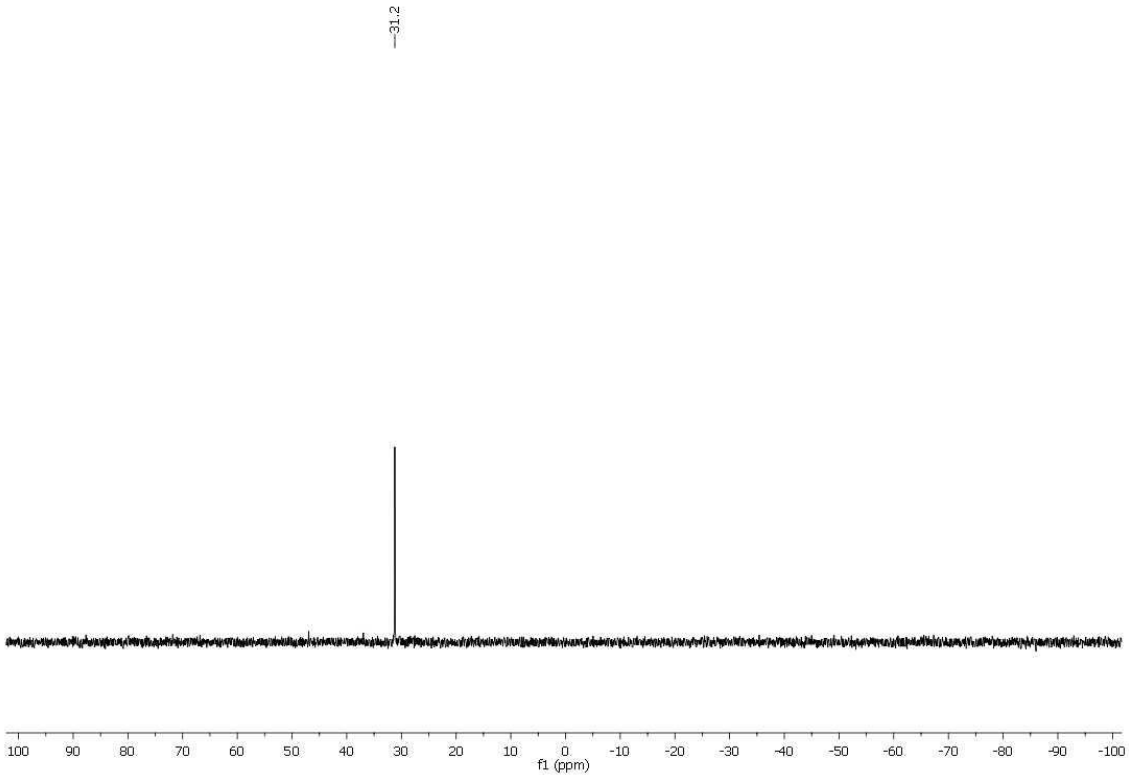
^{1}H NMR spectrum of [$PdCl_2$(morpholine)($PCyp_2Ar^{Xyl2}$)], **3b**, (300 MHz, $CDCl_3$, 298 K)



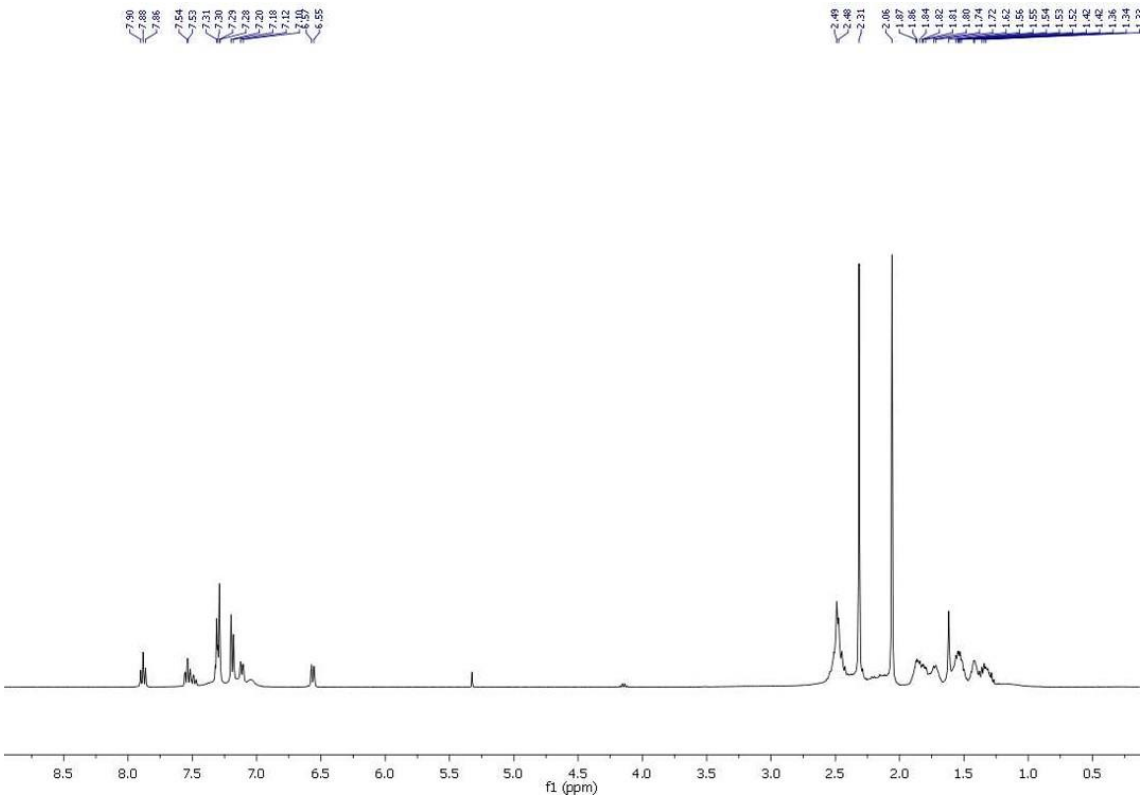
^{13}C{^{1}H} NMR spectrum of [$PdCl_2$(morpholine)($PCyp_2Ar^{Xyl2}$)], **3b**, (300 MHz, $CDCl_3$, 298 K)



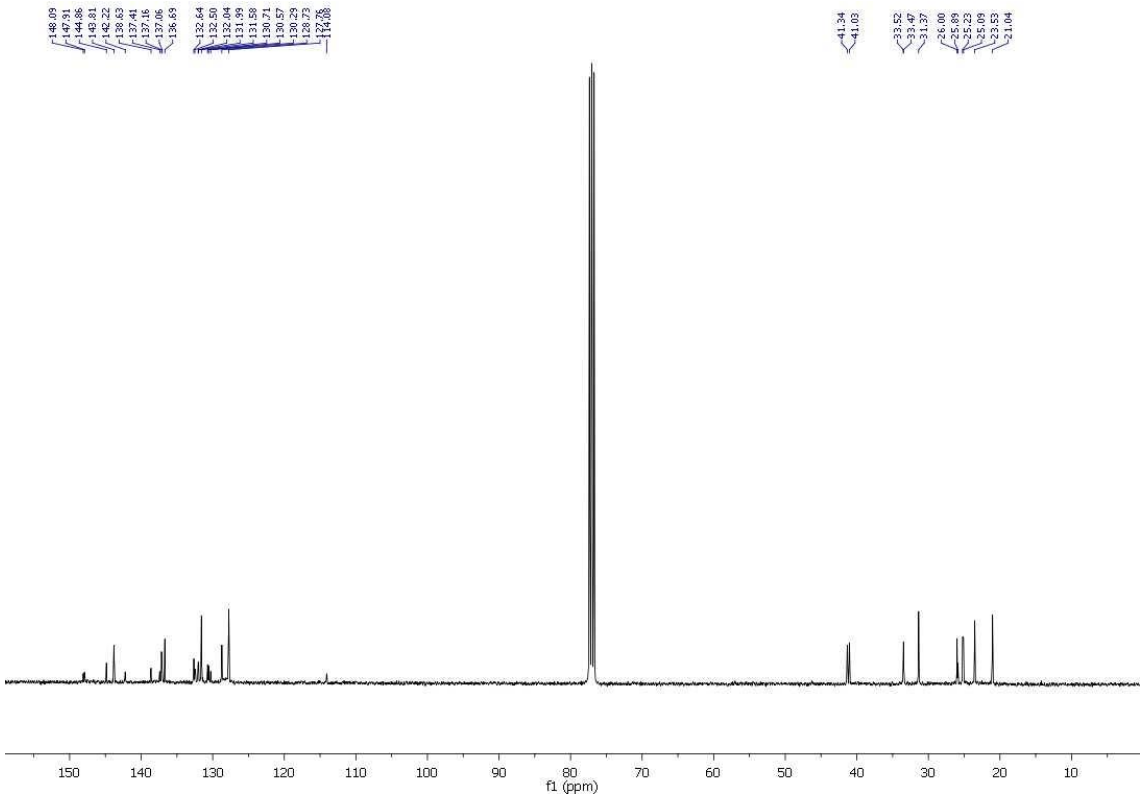
$^{31}P\{^{1}H\}$ NMR spectrum of [$PdCl_2$(morpholine)($PCyp_2Ar^{Xyl2}$)], **3b**, (75 MHz, $CDCl_3$, 298 K).



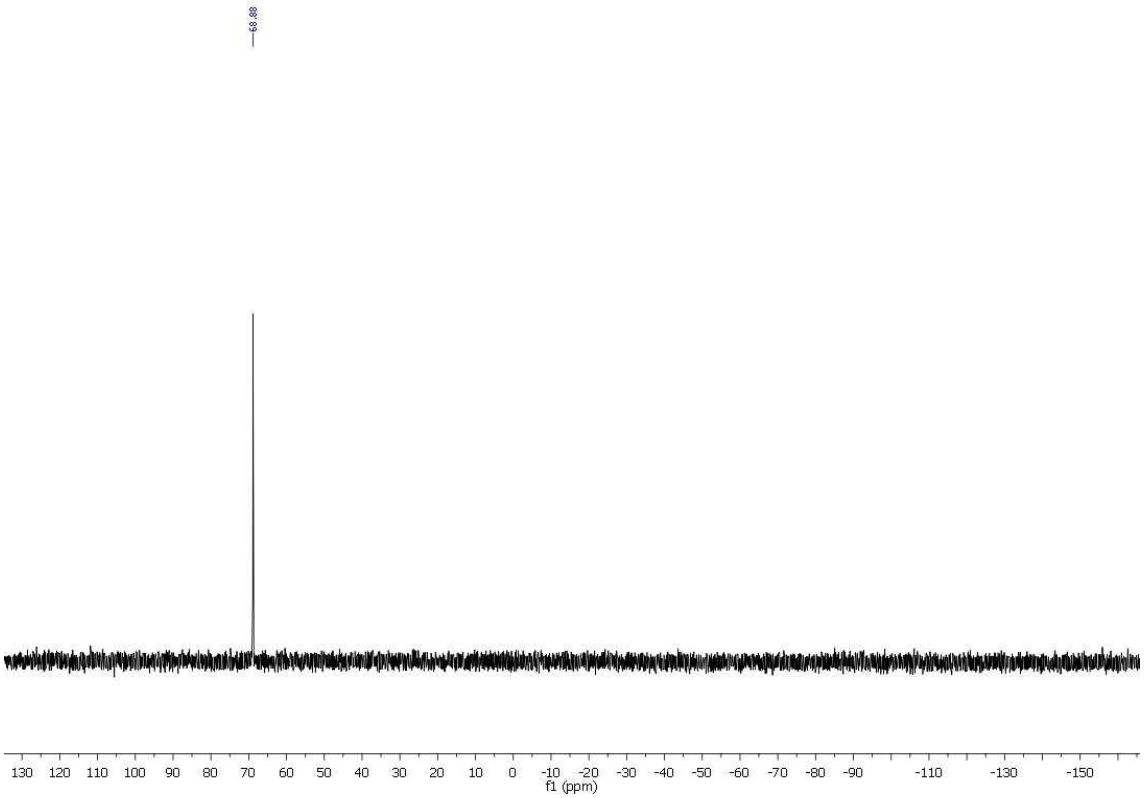
^{1}H NMR spectrum of [$PdCl_2(PCyp_2Ar^{Xyl2})]_2$, **5**, (300 MHz, $CDCl_3$, 298 K).



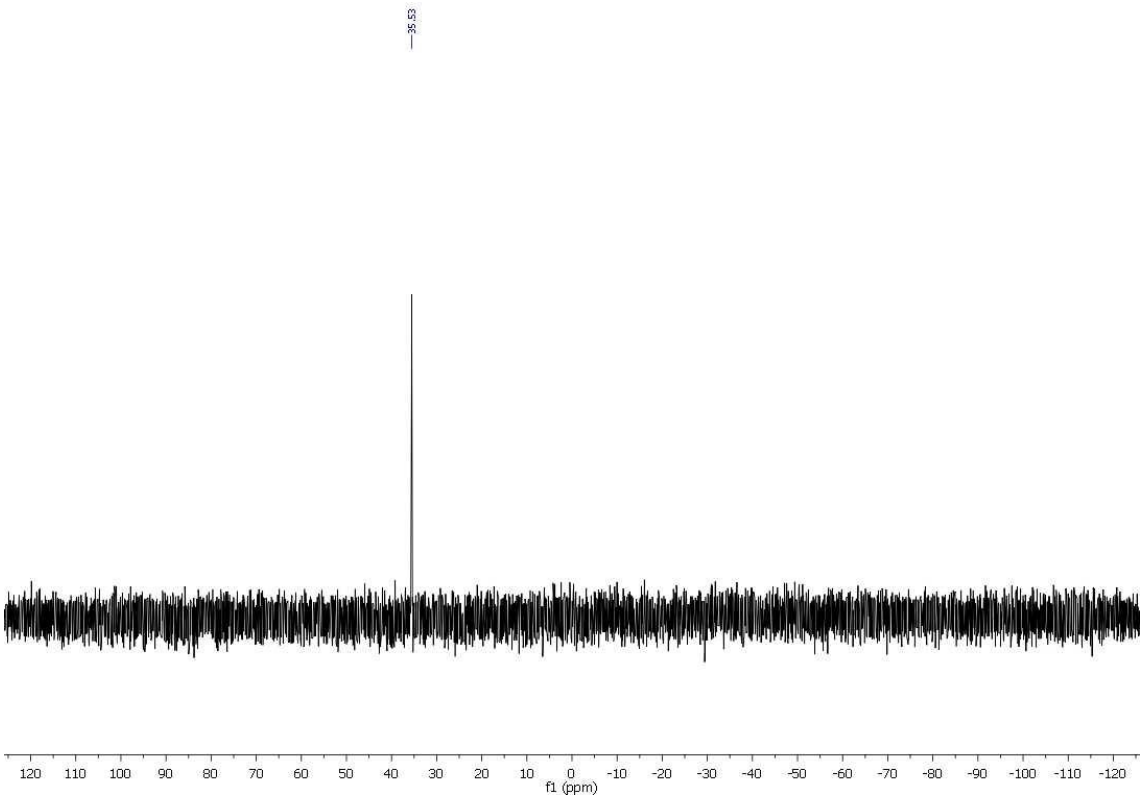
^{13}C{^{1}H} NMR spectrum of [$PdCl_2(PCyp_2Ar^{Xyl2})]_2$, **5** (100 MHz, $CDCl_3$, 298).



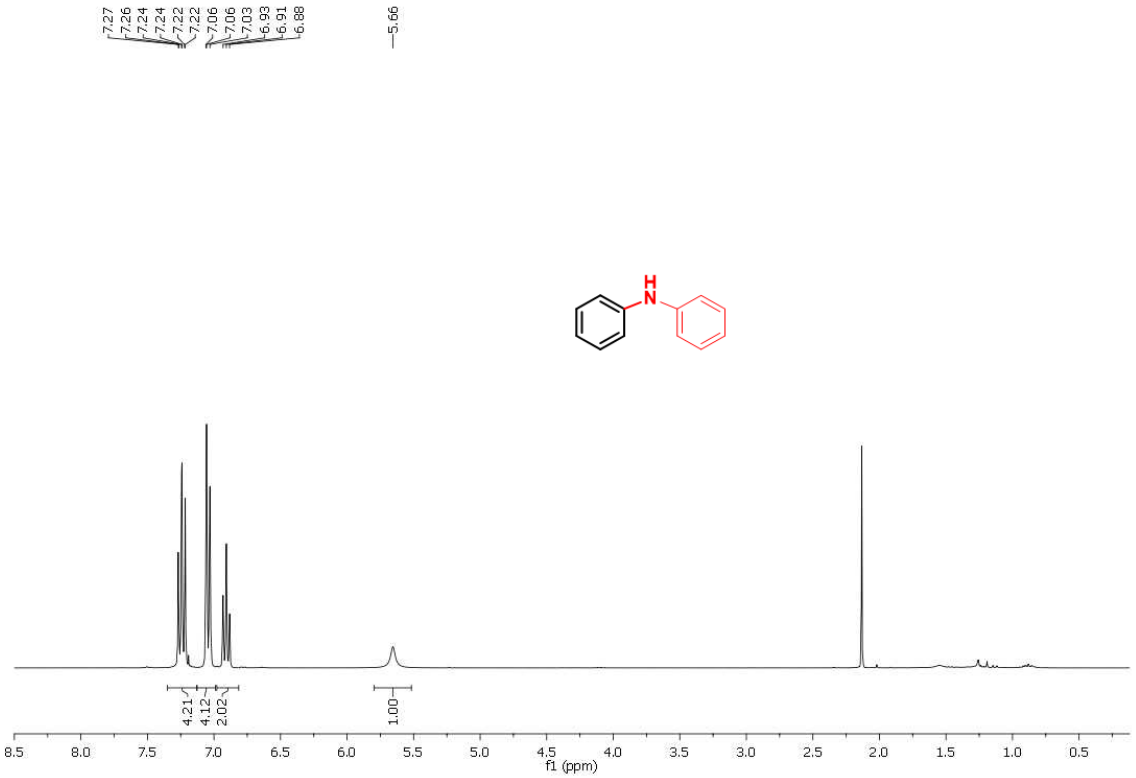
$^{31}P\{^{1}H\}$ NMR spectrum of $[PdCl_2(PCyp_2Ar^{Xyl2})]_2$, **5**, (121 MHz, $CDCl_3$, 298 K).



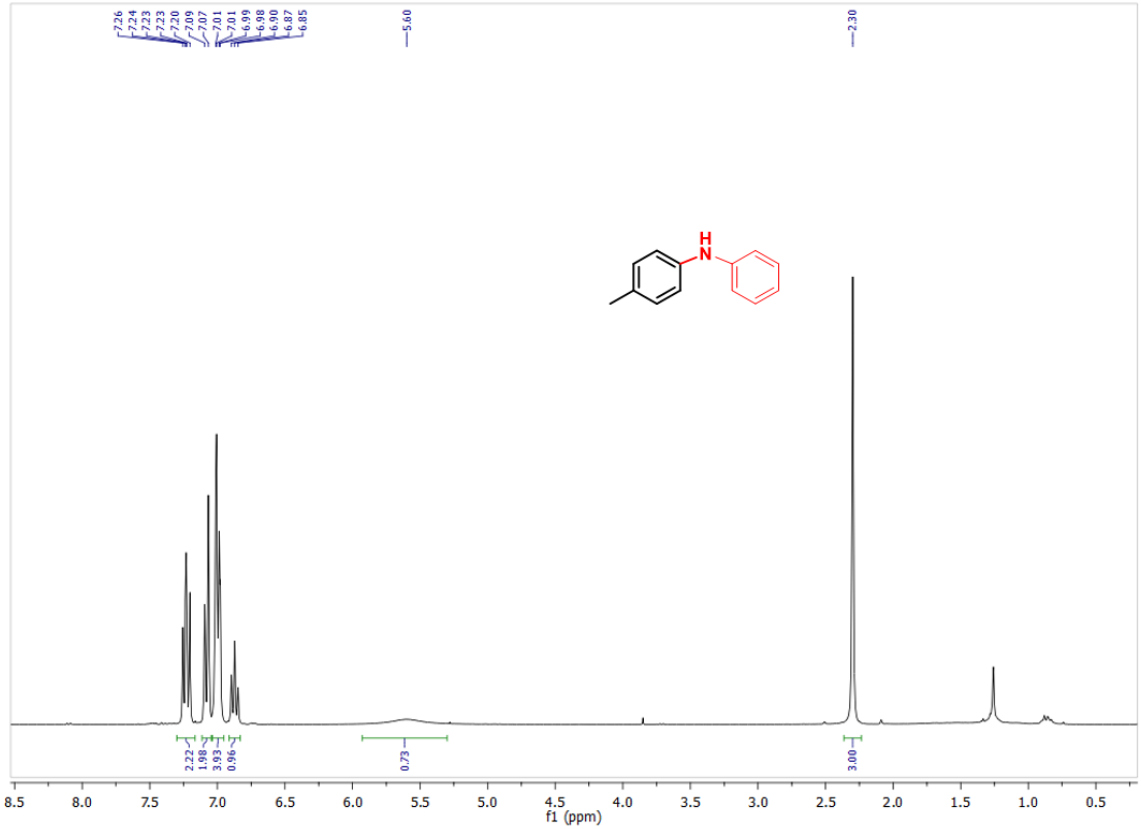
$^{31}P\{^{1}H\}$ NMR spectrum of $[PdCl_2(PCyp_2Ar^{Xyl2})]_2$, **5**, (121 MHz, C_6D_6, 298 K).



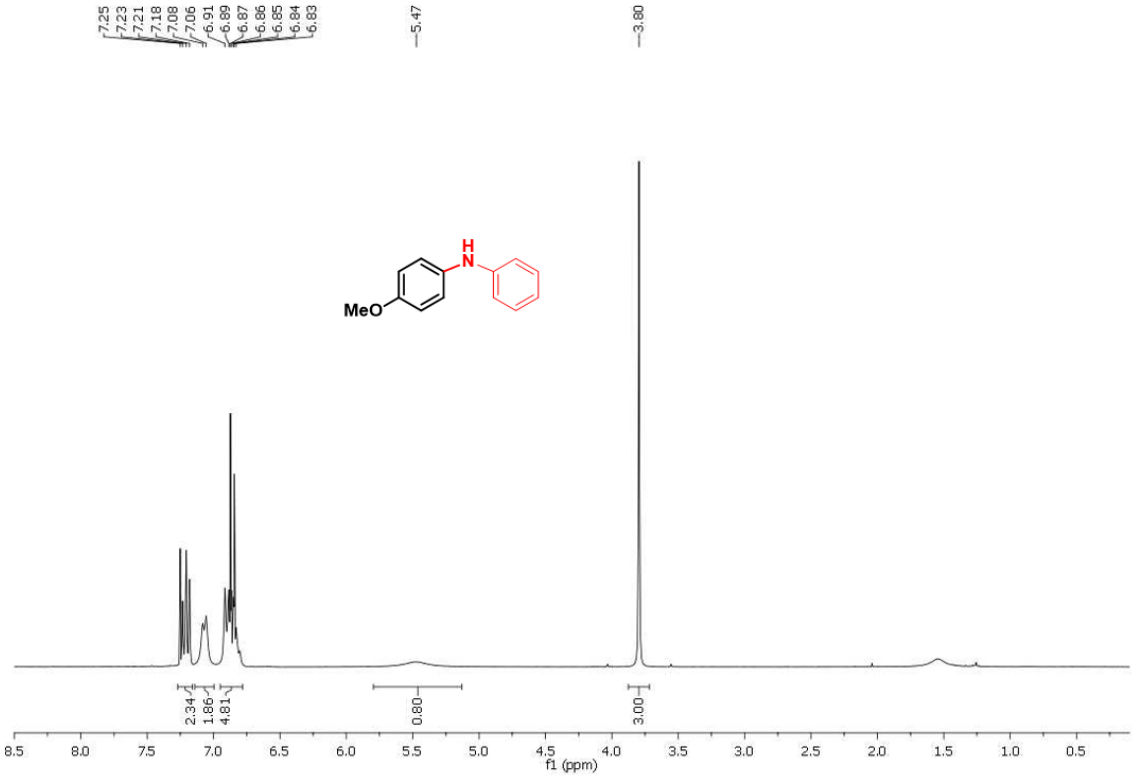
^{1}H NMR spectrum of *N,N*-Diphenylamine, **6a** (300 MHz, $CDCl_3$, 298 K).



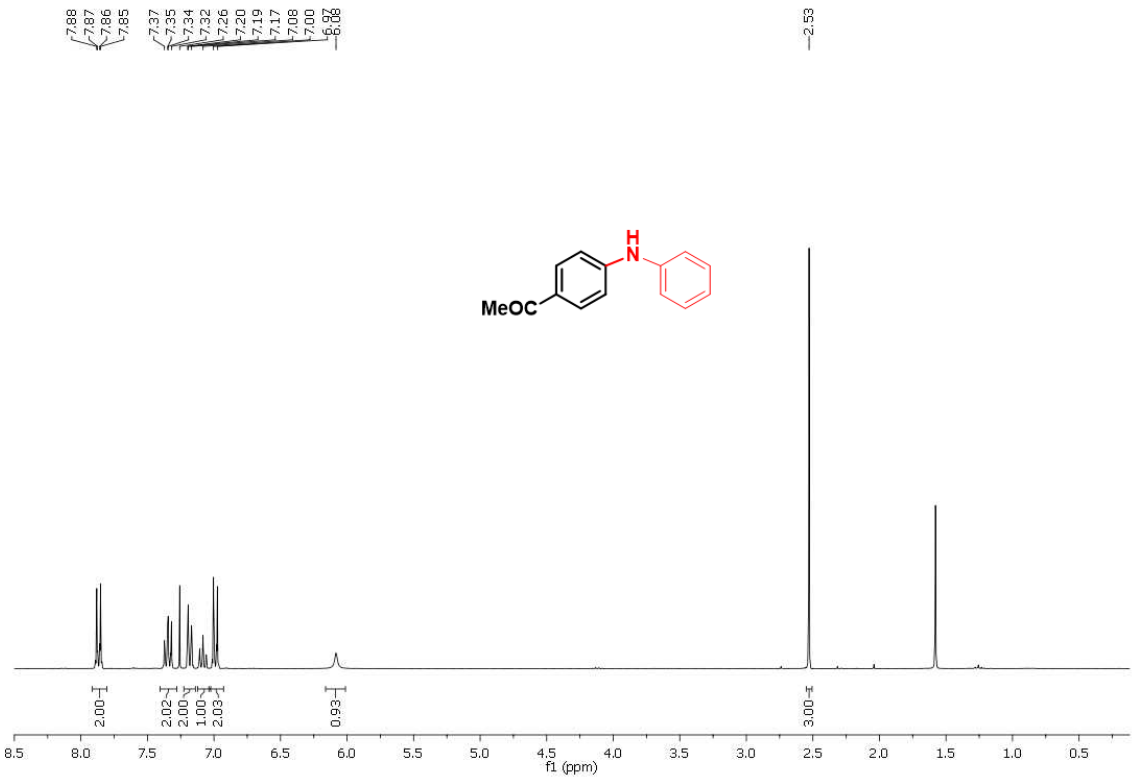
^{1}H NMR spectrum of *N*-(4-Methylphenyl)-*N*-phenylamine, **6b**, (300 MHz, $CDCl_3$, 298 K).



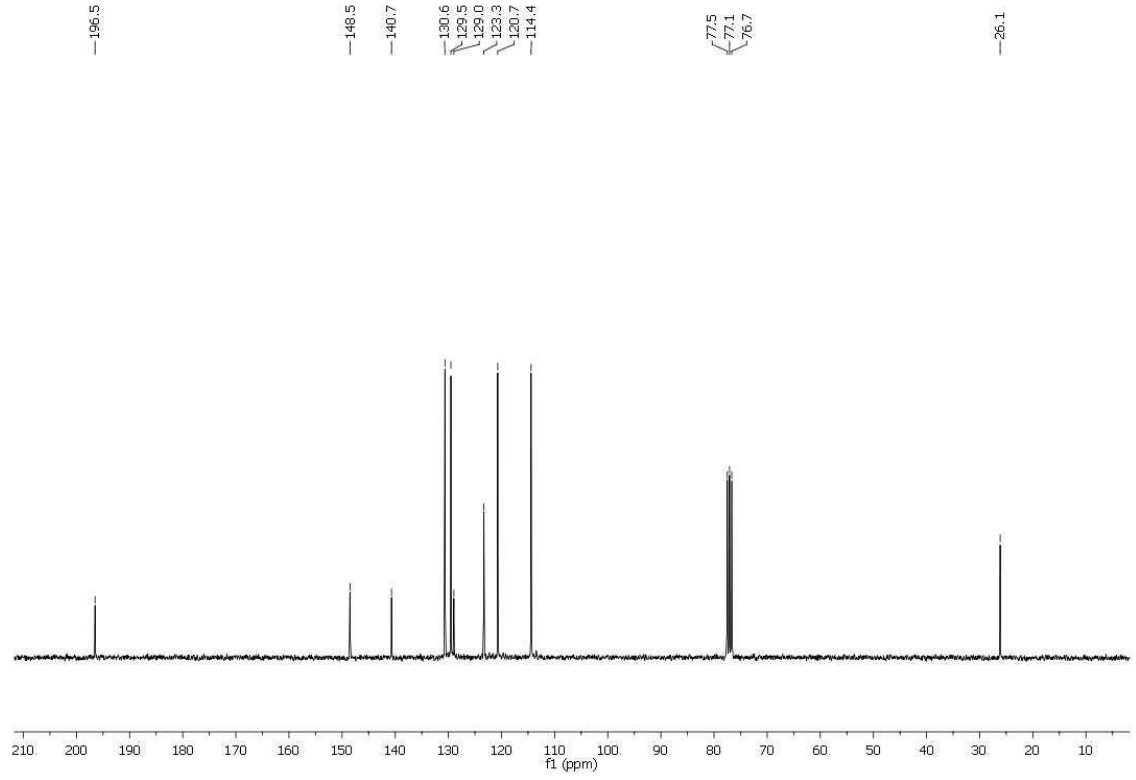
^{1}H NMR spectrum of *N*-(4-Methoxylphenyl)-*N*-phenylamine, **6c**, (300 MHz, $CDCl_3$, 298 K).



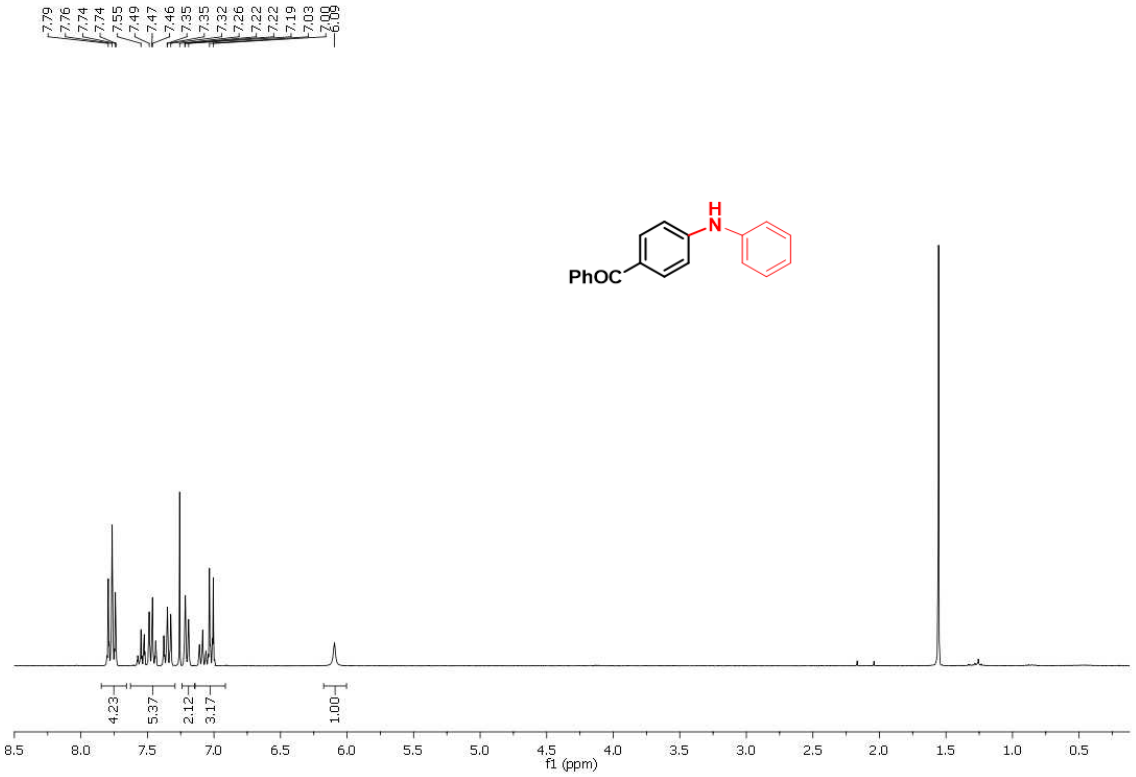
^{1}H NMR spectrum of 1-(4-phenylamino)phenyl)ethan-1-one, **6d**, (300 MHz, $CDCl_3$, 298 K).



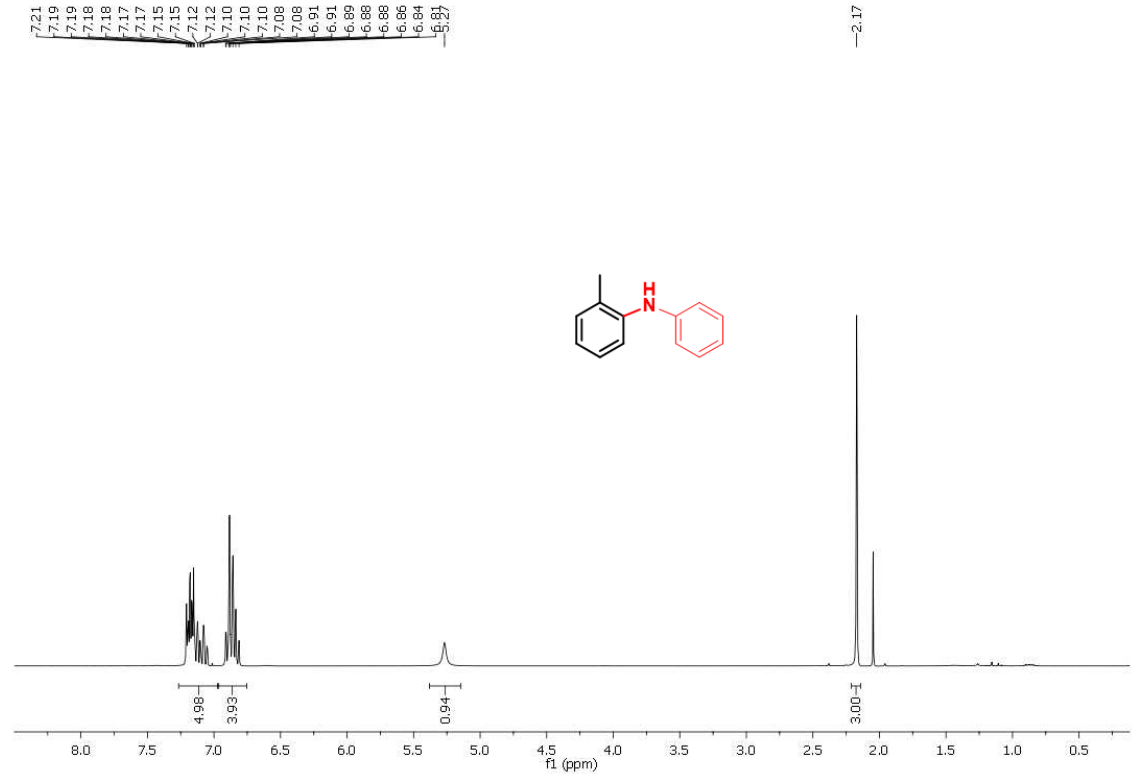
$^{13}C\{^{1}H\}$ NMR spectrum of Phenyl(4-phenylamino)phenyl)methanone, **6d**, (75 MHz MHz, $CDCl_3$, 298 K).



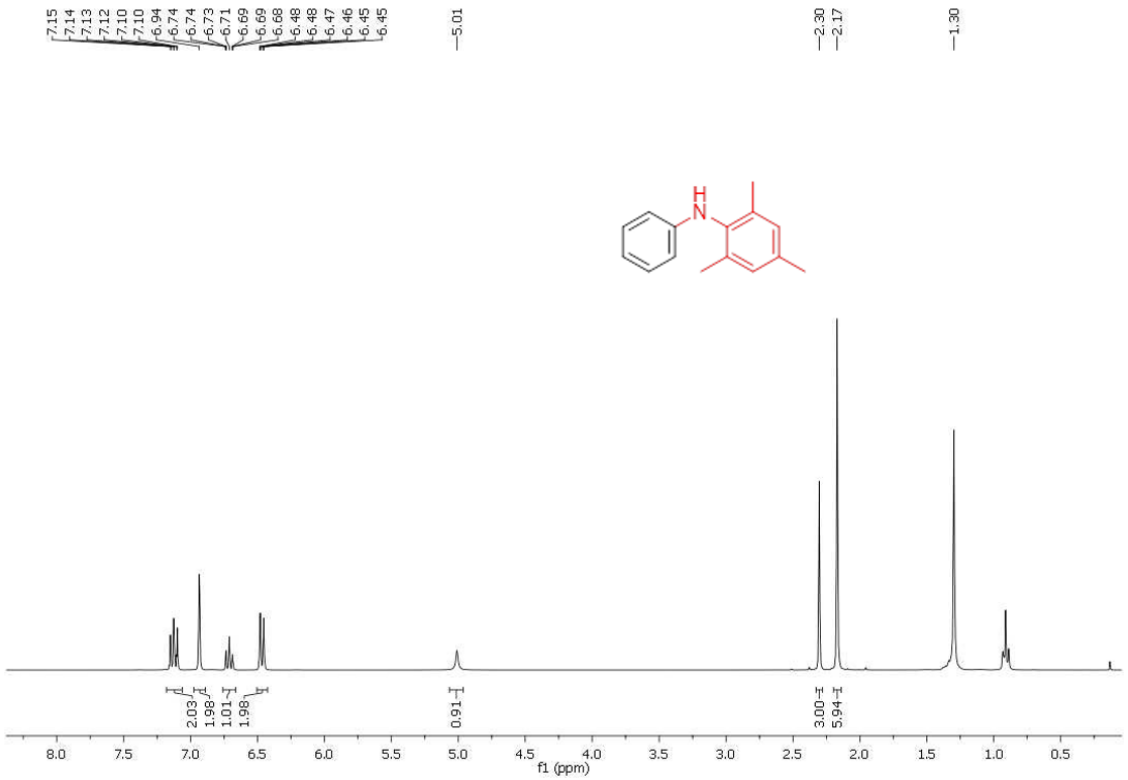
^{1}H NMR spectrum of Phenyl(4-phenylamino)phenyl)methanone, **6e**, (300 MHz, $CDCl_3$, 298 K).



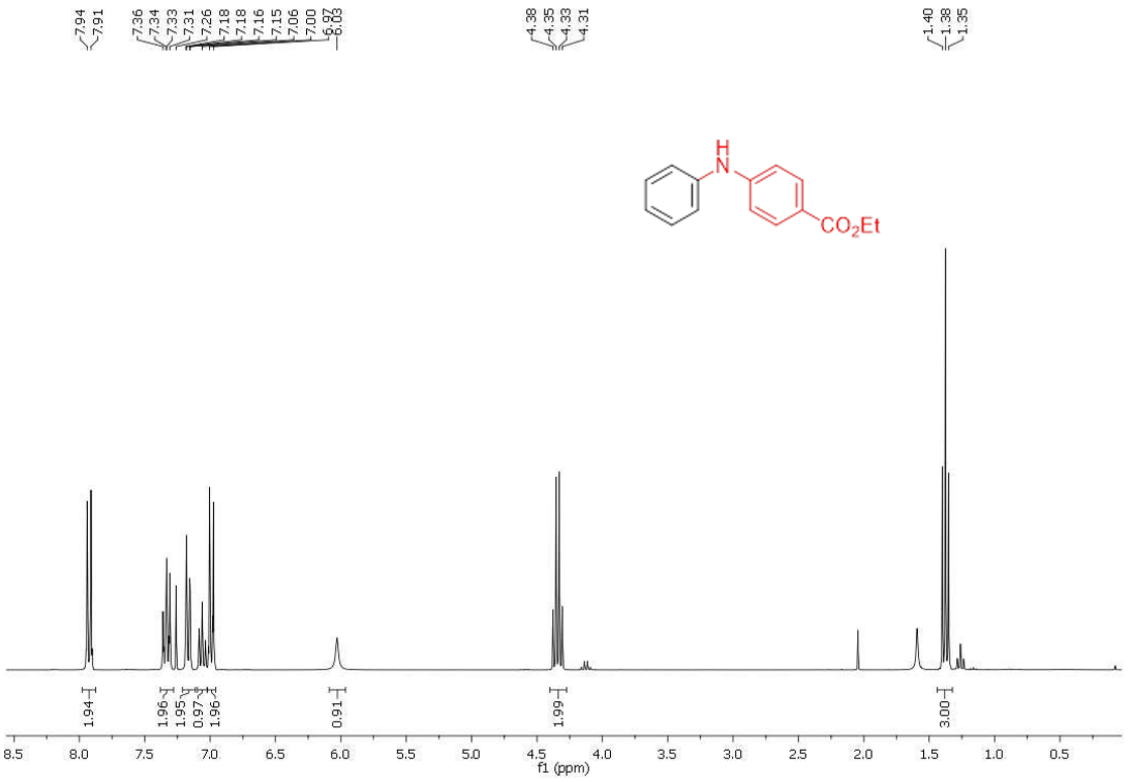
^{1}H NMR spectrum of *N*-(2-Methylphenyl)-*N*-phenylamine, **6f**, (300 MHz, $CDCl_3$, 298 K).



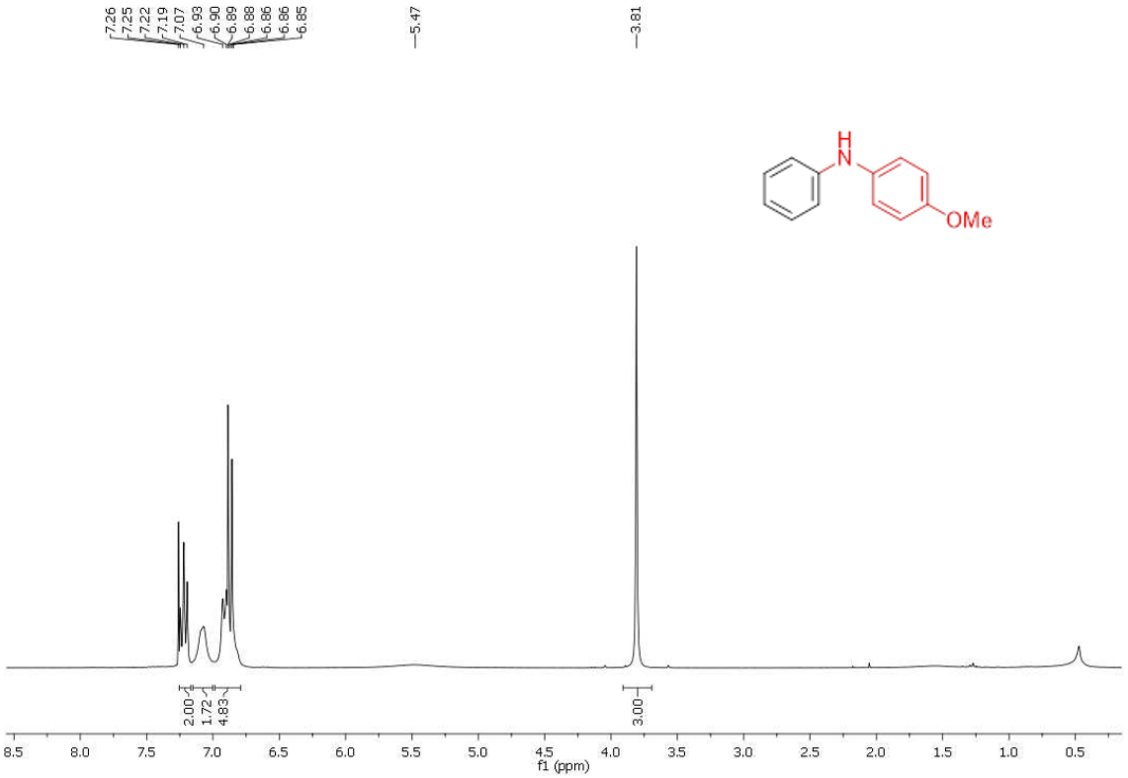
^{1}H NMR spectrum of 2,4,6-trimethyl-N-phenylaniline, **6h**, (300 MHz, $CDCl_3$, 298 K).



^{1}H NMR spectrum of ethyl 4-(phenylamino)benzoate, **6i**, (300 MHz, $CDCl_3$, 298 K).



^{1}H NMR spectrum of 4-methoxy-*N*-phenylaniline, **6j**, (300 MHz, $CDCl_3$, 298 K).



6. X-ray structural characterization of new complexes 1b, 2a and 3a.

Single crystals for X-ray diffraction analyses were grown by slow evaporation of solution of the complexes in petroleum ether:CH_2Cl_2 (2:1) mixtures cooled to -20 °C. Crystals of suitable size were mounted in a loop fibre covered with perfluoropolyether oil (FOMBLIN®, Aldrich). Data collections were performed on a Bruker-AXSX8Kappa diffractometer equipped with an Apex-II CCD area detector, using a graphite monochromator Ag Kα1 (λ=0.56086 Å) and a Bruker Cryo-Flex low-temperature device.[13] Data collections were processed with APEX-W2D-NT (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multiscan method applied by SADABS[14]. The structures were solved by SHELXT and the starting models were refined by full-matrix least-squares procedures with SHELXL, using the software package Olex2 suite[15]. Non-hydrogen atoms were refined with anisotropic displacement parameters and hydrogen atoms were introduced into the geometrically calculated positions and refined riding on the corresponding parent atoms. Weighted R factors (*wR*) and all goodness-of-fit (S) are based on F^2, conventional *R* factors (*R*) are based on *F*. A summary of the fundamental crystal and refinement data are provided in Table S3. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in cif files. A summary of cell parameters, data collection, structures solution, and the refinement of crystal structures are provided below. The corresponding crystallographic data were deposited with the Cambridge Crystallographic Data Centre as supplementary publications. CCDC 2158769 (**1b**), 2158767 (**2a**), 2158768 (**3a**) and 2158770 (**5**). The data can be obtained free of charge via: https://www.ccdc.cam.ac.uk/structures/

[13] (a) Bruker APEX2; Bruker AXS, Inc.; Madison, WI, 2007. (b) Bruker Advanced X-ray solutions. SAINT and SADABS programs. Bruker AXS Inc. Madison, WI, 2004.
[14] G. M. Sheldrick, SADABS; Bruker Analytical X-ray Division, Madison, WI, 2008.
[15] O.V. Dolomanov, L.J. Bourhis, R.J. Gildea, J.A.K. Howard, H. Puschmann, OLEX2 J. Appl. Cryst., 2009, 42 339-341.

Table S3. Crystal data and structure refinement for **1b, 2a**, **3a** and **5.**

	1b	**2a**	**3a**	**5**
formula	$C_{29}H_{38}PdCl_4NOP$	$C_{41}H_{56}PdCl_2NP$	$C_{38}H_{46}PdCl_4NP$	$C_{65}H_{80}Pd_2Cl_6P_2$
fw	695.77	771.13	795.93	1348.73
cryst.size, mm	0.22 × 0.18 × 0.16	0.40 × 0.26 × 0.23	0.14 × 0.13 × 0.08	0.23 x 0.17 x 0.14
crystal system	Monoclinic	Triclinic	Orthorhombic	Triclinic
space group	P2_1 /c	*P-1*	Pbca	*P*-1
a, Å	23.6446(16)	9.1723(5)	15.2644(6)	12.9169(8)
b, Å	22.8590(14)	11.6910(8)	18.3812(6)	15.0027(9)
c, Å	11.6653(7)	18.9911(13)	25.6270(9)	15.8900(10)
α, deg	90	97.274(2)	90	95.311(3)
β, deg	103.717(3)	97.470(2)	90	98.986(3)
γ, deg	90	102.579(2)	90	98.963(3)
V, Å^3	6125.2(7)	1945.3(2)	7190.4(4)	2982.7(3)
T, K	173	173	173	173
Z	8	2	8	2
ρ_{calc}, g cm^{-3}	1.509	1.317	1.470	1.502
μ, mm^{-1} (AgKα)	0.534	0.360	0.461	0.509
F(000)	2848.0	808.0	3280.0	1388.0
absorption corrections	multi-scan, 0.63-0.75	multi-scan, 0.65 -0.75	multi-scan, 0.62-0.74	multi-scan, 0.64-0.75
θ range, deg	3.13 to 49.12	3.09 to 45.68	3.01 to 44.00	3.18 to 47.36
no. of rflns measd	138141	35017	64427	65774
R_{int}	0.106	0.050	0.057	0.073
no. of rflns unique	20727	10675	8977	18172
no. of params / restraints	697 / 0	429 / 0	423 / 4	697 / 0
R_1 ($I > 2\sigma(I)$) [a]	0.048	0.036	0.036	0.053
R_1 (all data)	0.091	0.051	0.054	0.101
wR_2 ($I > 2\sigma(I)$)	0.092	0.073	0.069	0.119
wR_2 (all data)	0.108	0.081	0.075	0.144
Diff.Fourier.peaks min/max, eÅ^{-3}	-1.32 / 0.85	-0.66 / 0.61	-0.71 / 0.58	-1.26 / 1.09
CCDC number	2158769	2158767	2158768	2158770

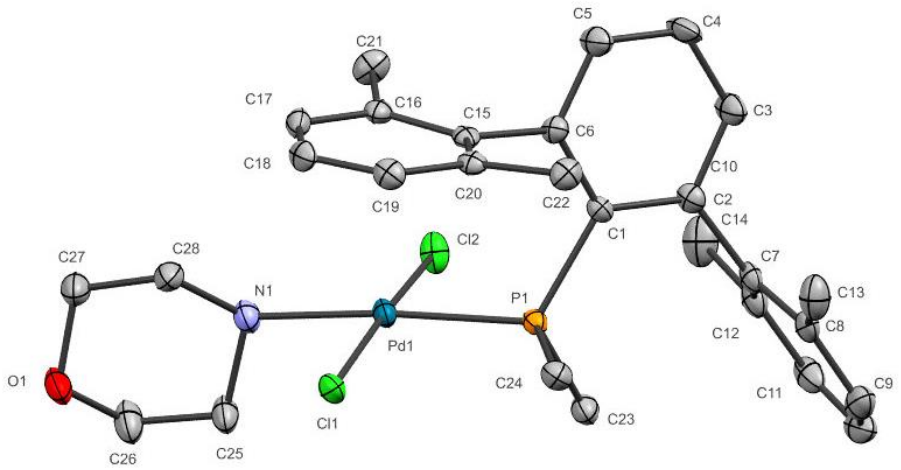


Figure S2

. Molecular structure of **[PdCl$_2$(morpholine)(PMe$_2$Ar^{Xyl2})], 1b.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

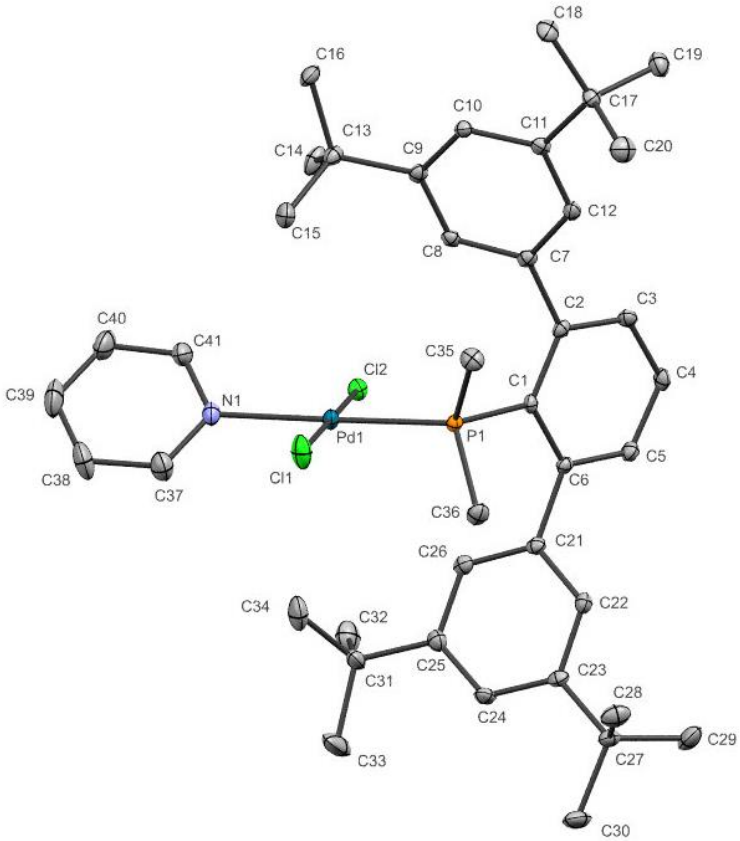


Figure S3. Molecular structure of **[PdCl$_2$(pyridine)(PMe$_2$Ar^{Dtbp2})], 2a.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

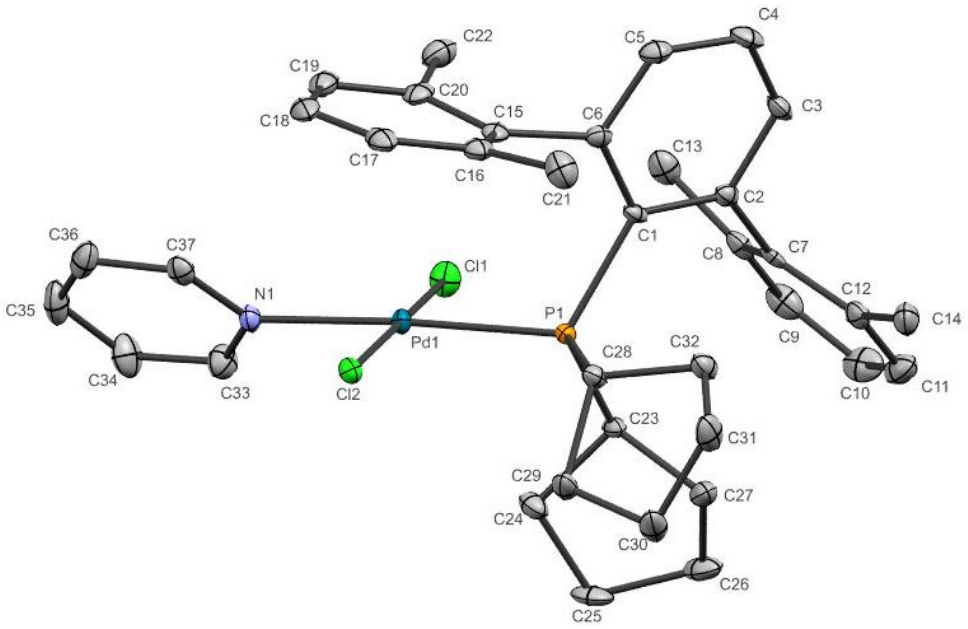


Figure S4. Molecular structure of **[PdCl$_2$(pyridine)(PCyp$_2$Ar^{Xyl2})], 3a.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability.

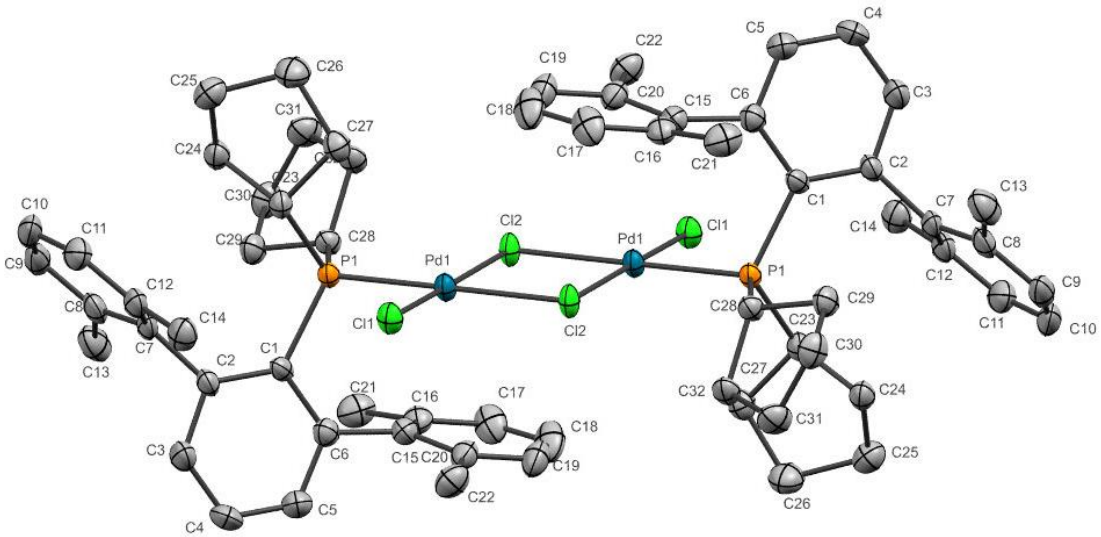


Figure S5. Molecular structure of **[PdCl$_2$(PCyp$_2$Ar^{Xyl2})]$_2$, 5.** Hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [°]: Pd1-P1 2.2408(10), Pd1-Cl1 2.2878(10), Pd1-Cl2(cis-P1),

2.3423(19), Pd1-Cl2(trans-P1) 2.4285(9), P1-Pd1-Cl1 86.11(4), Cl1-Pd1-Cl2(trans-P1) 91.28(3), Cl2-Pd1-Cl2 84.90(3), P1-Pd1-Cl2 97.68(3).