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Supporting Information

Palladium-Mediated Intramolecular Dearomatization of Ligated Dialkylterphenyl Phosphines

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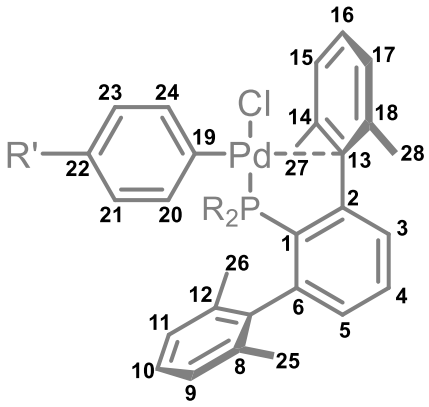
1. General considerations.

All preparations and manipulations were carried out under oxygen-free nitrogen, using conventional Schlenk techniques. Solvents were rigorously dried and degassed before use. Terphenyl phosphines[1] L1 and L2 and $Pd(CH_2SiMe_3)_2(cod)$[2] were synthesized by following previously reported procedures. Reagents were purchased from commercial suppliers and used without further purification. Solvents were dried and degassed before use. Solution NMR spectra were recorded on a Bruker Avance III 500 MHz, Bruker Avance 300 MHz and 400 Ascend/R spectrometers. The ^{1}H 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. Elemental analyses were performed by the Servicio de Microanálisis of the Instituto de Investigaciones Químicas (IIQ). X-ray diffraction studies were carried out at Centro de Investigación Tecnología e Innovación, CITIUS (Universidad de Sevilla), and Centro de Investigación en Química Sostenible, CIQSO (Universidad de Huelva).

2. General procedure for the synthesis of $Pd(Ar)Cl(PR_2Ar^{Xyl2})$ complexes 1-2.

A Schlenk tube, equipped with a magnetic stir bar, was charged with the terphenyl phosphine ligand, L, (0.2 mmol) and the corresponding aryl halide (0.6 mmol). The minimum amount of hexane was added to dissolve the solids. $Pd(CH_2SiMe_3)_2(cod)$ (0.2 mmol) was added in one portion under nitrogen flow. The reaction mixture was stirred overnight at room temperature and a suspension was obtained. The solvent was removed under vacuum and the residue was washed three times with pentane (3 x 4 mL) and dried under vacuum to provide the product. Compounds were purified by recrystallization using CH_2Cl_2 : petroleum ether (1:2) mixtures.

1. 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**, 260-272.
2. Y. Pan and G. B. Young, *J. Organomet Chem.*, 1999, **577**, 257-264.



Numbering scheme for NMR signal assignment.

2.1. Pd(Ph)Cl(P*i*Pr$_2$Ar^{Xyl2}), 1a

Following the general procedure, a mixture of Pd(CH_2SiMe_3)$_2$(cod) (77.8 mg, 0.2 mmol), L1 (80.5 mg, 0.2 mmol) and chlorobenzene (61.2 µL, 0.6 mmol) in hexane (6 mL) was stirred overnight. Complex **1a** was obtained as a pale brown solid. Yield: 92.7 mg (75%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.46 (td, 1H, J_{HH} = 7.6 Hz, J_{HP} = 2.2 Hz, CH^4), 7.45 (br, 2H, CH^{16} + CH_{ar}), 7.16 (d, 4H, J_{HH} = 7.5 Hz, CH_{ar}), 7.08-7.05 (m, 2H, CH_{ar}), 6.90-6.74 (m, 5H, CH_{ar}), 2.66-2.48 (m, 2H, C*H*i*Pr*), 2.16 (s, 12H, CH_3), 1.00 (dd, 6H, J_{HH} = 7.1 Hz, J_{HP} = 17.0 Hz, CH_3*i*Pr), 0.78 (dd, 6H, J_{HH} = 7.2 Hz, J_{HP} = 15.9 Hz, CH_3*i*Pr).

^{1}H NMR (400 MHz, $CDCl_3$, 0 ºC): δ 7.72 (br s, 1H, CH^{16}), 7.50 (td, 1H, J_{HH} = 7.6 Hz, J_{HP} = 2.2 Hz, CH^4), 7.29-7.14 (m, 5H, C$H^{15,17}$ + CH^{10} + C$H^{20,24}$), 7.10 (d, J_{HH} = 8.0 Hz, 2H, C$H^{9,11}$), 7.05 (br s, 1H, C$H^{3/5}$), 6.88 (t, 2H, J_{HH} = 7.4 Hz, C$H^{21,23}$), 6.83-6.80 (m, 1H, CH^{22}), 6.71 (m, 1H, C$H^{3/5}$), 2.64-2.51 (m, 2H, C*H*i*Pr*), 2.29 (s, 12H, CH_3), 2.07 (s, 6H, CH_3), 0.97 (dd, 6H, J_{HH} = 6.6 Hz, J_{HP} = 16.8 Hz, CH_3*i*Pr), 0.83 (br d, 6H, CH_3*i*Pr).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 0 ºC): δ 151.1 (br, $C^{2/6}$), 146.1 ($C^{2/6}$), 141.7 (C_q), 139.5 (C_q), 138.7 (C_q), 137.2 ($C^{14,18}$), 135.2 (d, J_{CP} = 24.3 Hz, C^1), 132.7 (C^{19}), 132.5 (C^{16}), 132.4 ($C^{3/5}$), 131.8 (C^4), 131.5 (CH_{ar}), 131.3 ($C^{3/5}$), 130.3 ($C^{15,17}$), 128.3-127.9 (multiple overlapping peaks), 127.3 (CH_{ar}), 123.6 (C^{22}), 26.6 (d, J_{CP} = 25.4 Hz, C*H*i*Pr*), 22.8 (CH_3), 21.6 (CH_3), 20.0 (CH_3*i*Pr), 19.2 (CH_3*i*Pr).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ 55.1.

Elemental analysis calculated (found) for $C_{34}H_{40}ClPPd$: C, 65.70 (65.57); H, 6.49 (6.79).

2.2. Pd(4-OMe-C_6H_4)Cl(P*i*Pr_2Ar^{Xyl2}), 1b

Following the general procedure, a mixture of $Pd(CH_2SiMe_3)_2(cod)$ (77.8 mg, 0.2 mmol), **L1** (80.5 mg, 0.2 mmol) and 4-chloroanisole (73.0 µL, 0.6 mmol) in hexane (6 mL) was stirred overnight. Complex **1b** was obtained as a brown solid. Yield: 85.0 mg (65%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.46 (td, 1H, J_{HH} = 7.6, J_{HP} = 2.2 Hz, C*H*^{4}), 7.45 (br, 2H, C*H*^{16} + C*H*$_{ar}$), 7.16 (d, 4H, J_{HH} = 7.3 Hz, C*H*$_{ar}$), 6.92 (dd, 2H, J_{HH} = 8.8, J_{HP} = 1.9 Hz, C*H*$_{ar}$), 6.94-6.81 (m, 2H, C*H*$_{ar}$), 6.52 (d, 2H, J_{HH} = 8.5 Hz, C*H*^{21,23}), 3.65 (s, 3H, OC*H*$_3$), 2.66-2.47 (m, 2H, C*H*i*P*r), 2.16 (br s, 12H, C*H*$_3$), 1.00 (dd, 6H, J_{HP} = 17.1 Hz, J_{HH} = 7.1 Hz, C*H*$_3$i*P*r), 0.80 (dd, 6H, J_{HP} = 15.9 Hz, J_{HH} = 7.2 Hz, C*H*$_3$i*P*r).

^{1}H NMR (400 MHz, $CDCl_3$, -20 ºC): δ 7.71 (t, 1H, J_{HH} = 7.6 Hz, C*H*^{16}), 7.48 (td, 1H, J_{HH} = 7.6 Hz, J_{HP} = 2.1 Hz, C*H*^{4}), 7.26-7.19 (m, 3H, C*H*^{15,17} and C*H*^{10}), 7.13 (d, J_{HH} = 7.5 Hz, 2H, C*H*^{9,11}), 7.05 (d, 1H, J_{HH} = 7.4 Hz, C*H*$^{3/5}$), 6.94 (br d, 2H, C*H*^{21,23}), 6.69 (d, 1H, J_{HH} = 7.7 Hz, C*H*$^{3/5}$), 6.57 (d, 2H, J_{HH} = 8.3 Hz, C*H*^{20,24}), 3.68 (s, 3H, OC*H*$_3$), 2.59-2.50 (m, 2H, C*H*i*P*r), 2.28 (s, 6H, C*H*$_3$), 2.06 (s, 6H, C*H*$_3$), 0.91 (br s, 12H, C*H*$_3$i*P*r).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, -20 ºC): δ 156.1 (*C*^{22}), 151.0 (d, J_{CP} = 22.0 Hz, *C*$^{2/6}$), 146.0 (*C*$^{2/6}$), 141.5 (*C*^{7}), 139.6 (*C*^{14,18}), 137.0 (*C*^{21,23}), 136.7 (*C*^{8,12}), 134.9 (d, J_{CP} = 23.8 Hz, *C*^{1}), 132.7 (*C*^{16}), 132.3 (d, J_{CP} = 4.3 Hz, *C*$^{3/5}$), 131.9 (*C*^{4}), 131.3 (d, J_{CP} = 11.5 Hz, *C*$^{3/5}$), 130.1 (*C*^{15,17}), 129.3 (*C*^{13}), 128.1 (*C*^{10}), 127.8 (*C*^{9,11}), 126.1 (*C*^{19}), 113.3 (*C*^{20,24}), 54.9 (O*C*H$_3$), 26.4 (d, J_{CP} = 26.0 Hz, *C*H*i*Pr), 22.8 (*C*H$_3$), 21.6 (*C*H$_3$), 19.8 (*C*H$_3$i*P*r), 19.2 (*C*H$_3$i*P*r).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ 55.9.

Elemental analysis calculated (found) for $C_{35}H_{42}ClOPPd$: C, 64.52 (64.14); H, 6.50 (6.57).

2.3. Pd(Ph)Cl(PCyp_2Ar^{Xyl2}), 2a

Following the general procedure, a mixture of $Pd(CH_2SiMe_3)_2(cod)$ (58.4 mg, 0.15 mmol), **L2** (68.2 mg, 0.15 mmol) and chlorobenzene (45.8 µL, 0.45 mmol) in hexane (3 mL) was stirred overnight. Complex **2a** was obtained as a brown solid. Yield: 65.8 mg (65%).

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.68 (br s, 1H, C*H*^{16}), 7.45 (td, 1H, J_{HH} = 7.5 Hz, J_{HP} = 1.6 Hz C*H*^{4}), 7.22-7.06 (m, 5H, C*H*^{15,17}, C*H*^{10} and C*H*^{9,11}), 7.03-6.95 (m, 3H, C*H*^{20,24} and C*H*$^{3/5}$), 6.82-6.75 (m, 3H, C*H*^{21,23} and C*H*^{22}), 6.68 (br s, 1H, C*H*$^{3/5}$), 2.70-2.53 (m, 2H, C*H*$_{Cyp}$), 2.40-2.20 (m, 2H, C*H*$_{Cyp}$), 2.24 (br s, 6H, C*H*$_3$), 2.23 (br s, 6H, C*H*$_3$), 1.95-1.75

(m, 4H, CH_{Cyp}), 1.52-1.41 (m, 4H, CH_{Cyp}), 1.34-1.22 (m, 2H, CH_{Cyp}), 1.02-0.92 (m, 2H, CH_{Cyp}), 0.87-0.74 (m, 2H, CH_{Cyp}).

^{1}H NMR (400 MHz, $CDCl_3$, -10 ºC): δ 7.69 (t, 1H, J_{HH} = 7.6 Hz, CH^{16}), 7.46 (t, 1H, J_{HH} = 7.5 Hz, CH^{4}), 7.21 (d, 1H, J_{HH} = 7.6 Hz, C$H^{15,17}$), 7.23-7.18 (m, 1H, CH^{10}), 7.09 (d, 2H, J_{HH} = 7.4 Hz, C$H^{9,11}$), 7.03 (d, 1H, J_{HH} = 7.3 Hz, C$H^{3/5}$), 6.98 (d, 2H, J_{HH} = 6.6 Hz, C$H^{20,24}$), 6.82-6.75 (m, 3H, C$H^{21,23}$ and CH^{22}), 6.67 (d, 1H, J_{HH} = 7.4 Hz, C$H^{3/5}$), 2.66-2.54 (m, 2H, CH_{Cyp}), 2.36-2.25 (m, 2H, CH_{Cyp}), 2.24 (s, 6H, CH_3), 2.01 (s, 6H, CH_3), 1.94-1.86 (m, 2H, CH_{Cyp}), 1.83-1.73 (m, 2H, CH_{Cyp}), 1.51-1.40 (m, 4H, CH_{Cyp}), 1.31-1.21 (m, 2H, CH_{Cyp}), 0.97-0.89 (m, 2H, CH_{Cyp}), 0.75-0.66 (m, 2H, CH_{Cyp}).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, -10 ºC): δ 148.7 (d, J_{CP} = 22.0 Hz, $C^{2/6}$), 145.3 ($C^{2/6}$), 139.5 (C^{7}), 139.4 ($C^{14,18}$), 138.2 (d, J_{CP} = 2.2 Hz, $C^{20,24}$), 137.0 ($C^{8,12}$), 136.4 (d, J_{CP} = 32.0 Hz, C^{1}), 133.4 (C^{19}), 132.6 (C^{16}), 132.3 (d, J_{CP} = 4.2 Hz, $C^{3/5}$), 131.5 (C^{4}), 131.1 (d, J_{CP} = 11.3 Hz, $C^{3/5}$), 130.2 ($C^{15,17}$), 129.2 (d, J_{CP} = 3.6 Hz, C^{13}), 128.2 (C^{10}), 127.2 ($C^{9,11}$), 126.5 ($C^{21,23}$), 123.9 (C^{22}), 38.1 (d, J_{CP} = 27.6 Hz, CH$_{Cyp}$), 34.4 (d, J_{CP} = 9.0 Hz, CH$_2$), 29.1 (CH$_2$), 26.1 (d, J_{CP} = 14.7 Hz, CH$_2$), 25.8 (d, J_{CP} = 9.9 Hz, CH$_2$), 22.7 (CH$_3$), 21.1 (CH$_3$).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ 46.1.

Elemental analysis calculated (found) for $C_{38}H_{44}ClPPd$ + 1/5 CH_2Cl_2: C, 66.44 (66.40); H, 6.48 (6.78).

2.4. Pd(4-OMe-C_6H_4)Cl($PCyp_2Ar^{Xyl2}$), 2b

Following the general procedure, a mixture of $Pd(CH_2SiMe_3)_2$(cod) (58.4 mg, 0.15 mmol), **L2** (68.2 mg, 0.15 mmol) and 4-chloroanisole (54.8 µL, 0.45 mmol) in hexane (3 mL) was stirred overnight. Complex **2b** was obtained as a brown solid. Yield: 66.3 mg (63%). Crystals suitable for X-ray diffraction study were obtained by vapor diffusion of petroleum ether into a dichloromethane solution of the complex.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.68 (br t, 1H, CH^{16}), 7.45 (td, 1H, J_{HH} = 7.6 Hz, J_{HP} = 1.8 Hz, CH^{4}), 7.25-7.01 (m, 6H, C$H^{9,11}$, CH^{10}, C$H^{15,17}$ and C$H^{3/5}$), 6.84 (dd, J_{HH} = 8.5, 1.8 Hz, 2H, C$H^{21,23}$), 6.67 (br s, 1H, C$H^{3/5}$), 6.48 (d, J_{HH} = 8.5 Hz, 2H, C$H^{20,24}$), 3.64 (s, 3H, OCH_3), 2.70-2.53 (m, 2H, CH_{Cyp}), 2.40-2.22 (m, 2H, CH_{Cyp}), 2.25 (br s, 6H, CH_3), 2.03 (br s, 6H, CH_3), 1.97-1.46 (m, 4H, CH_{Cyp}), 1.56-1.41 (m, 4H, CH_{Cyp}), 1.34-1.23 (m, 2H, CH_{Cyp}), 1.03-0.92 (m, 2H, CH_{Cyp}), 0.89-0.77 (m, 2H, CH_{Cyp}).

^{1}H NMR (400 MHz, $CDCl_3$, 10 ºC): δ 7.68 (t, 1H, J_{HH} = 7.5 Hz, CH^{16}), 7.45 (t, 1H, J_{HH} = 7.6 Hz, CH^{4}), 7.22-7.19 (m, 1H, CH^{10}), 7.21 (d, 2H, J_{HH} = 7.0 Hz, C$H^{15,17}$), 7.09 (d, 2H, J_{HH} = 7.3 Hz, C$H^{9,11}$), 7.03 (d, 1H, J_{HH} = 7.3 Hz, C$H^{3/5}$), 6.83 (d, 2H, J_{HH} = 8.4 Hz, C$H^{21,23}$), 6.66 (d, 1H, J_{HH} = 7.1 Hz, C$H^{3/5}$), 6.49 (d, 2H, J_{HH} = 7.9 Hz, C$H^{20,24}$), 3.65 (s, 3H, OCH_3),

2.68-2.56 (m, 2H, CH_{Cyp}), 2.36-2.27 (m, 2H, CH_{Cyp}), 2.25 (s, 6H, CH_3), 2.03 (s, 6H, CH_3), 1.95-1.89 (m, 2H, CH_{Cyp}), 1.84-1.76 (m, 2H, CH_{Cyp}), 1.52-1.44 (m, 4H, CH_{Cyp}), 1.33-1.24 (m, 2H, CH_{Cyp}), 1.01-0.92 (m, 2H, CH_{Cyp}), 0.87-0.77 (m, 2H, CH_{Cyp}).

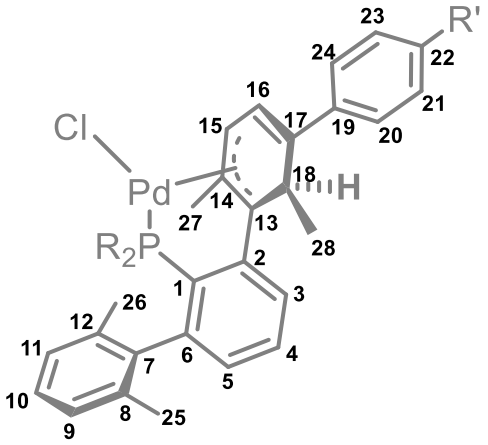
$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 10 ºC): δ 156.9 (C^{22}), 149.0 (d, J_{CP} = 21.5 Hz, $C^{2/6}$), 145.4 ($C^{2/6}$), 139.8 (C^7), 139.4 ($C^{14,18}$), 137.9 ($C^{21,23}$), 137.1 ($C^{8,12}$), 136.8 (d, J_{CP} = 26.7 Hz, C^1), 132.7 (C^{16}), 132.4 (d, J_{CP} = 2.8 Hz, $C^{3/5}$), 131.5 (d, C^4), 131.2 (d, J_{CP} = 11.2 Hz, $C^{3/5}$), 130.3 ($C^{15/17}$), 129.3 (d, J_{CP} = 3.8 Hz, C^{13}), 128.3 (C^{10}), 127.3 ($C^{9,11}$), 120.6 (C^{19}), 112.7 ($C^{20,24}$), 55.0 (OCH_3), 38.4 (d, J_{CP} = 27.7 Hz, CH$_{Cyp}$), 34.5 (d, J_{CP} = 9.1 Hz, CH$_2$), 29.3 (CH$_2$), 26.0 (d, J_{CP} = 14.9 Hz, CH$_2$), 25.9 (d, J_{CP} = 10.2 Hz CH$_2$), 22.7 (CH$_3$), 21.1 (CH$_3$).

$^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$, 25 ºC): δ 46.5

Elemental analysis calculated (found) for $C_{39}H_{46}ClOPPd$: C, 66.57 (66.63); H, 6.59 (6.61).

3. General procedure for the synthesis of complexes 3-4.

Complexes **1**-**2** (0.1 mmol) were dissolved in $CHCl_3$ (10 mL) and stirred for a given time (1 to 8 h) at 70 ºC. The solvent was removed under reduced pressure. The resulting solid was dissolved in Et_2O (10 mL) and filtered through a plug of Celite. Pure products **3**-**4** were obtained after recrystallization.



Numbering scheme for NMR signal assignment.

3.1. Synthesis of 3a

Following general procedure, complex **1a** (62.1 mg, 0.1 mmol) was stirred in $CHCl_3$ (10 mL) for 5 h at 70 ºC to give and orange solution. Complex **3a** was obtained as yellow crystals after crystallization in CH_2Cl_2:petroleum ether (1:3) at -20 ºC. Yield: 53.0 mg, 85 %.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.58 (td, 1H, J_{HH} = 7.4 Hz, J_{HP} = 2.8 Hz, C*H*^{4}), 7.50 (dt, 1H, J_{HH} = 7.5 Hz, J_{HP} = 1.4 Hz, C*H*$^{3/5}$), 7.24-7.15 (m, 7H, C*H*$_{ar}$), 7.07-7.03 (m, 2H, C*H*$^{3/5}$ + C*H*$_{ar}$), 6.13-6.10 (m, 1H, C*H*^{16}), 5.53 (dd, 1H, J_{HH} = 6.2 Hz, J_{HP} = 9.7 Hz, C*H*^{15}), 2.66 (dq, 1H, J_{HH} = 7.0 Hz, $J_{H\,P}$= 25.0 Hz, H^{18}), 2.33-2.18 (m, 2H, C*H*i*Pr*), 2.12 (s, 3H, C*H*$_3$), 1.89 (s, 3H, Me^{27}), 1.82 (s, 3H, C*H*$_3$), 1.51 (dd, 3H, J_{HH} = 7.6 Hz, J_{HP} = 23.2 Hz, C*H*$_3$*i*Pr), 1.27 (dd, 3H, J_{HH} = 6.7 Hz, J_{HP} = 18.0 Hz, C*H*$_3$*i*Pr), 1.00 (d, 3H, J_{HH} = 7.0 Hz, Me^{28}), 0.88 (dd, 3H, J_{HH} = 6.7 Hz, J_{HP} = 19.6 Hz, C*H*$_3$*i*Pr), 0.37 (dd, 3H, J_{HH} = 7.0 Hz, J_{HP} = 11.2 Hz, C*H*$_3$*i*Pr).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC): δ 151.4 (d, J_{CP} = 26.1 Hz, *C*$^{2/6}$), 147.9 (d, J_{CP} = 1.7 Hz, *C*$^{2/6}$), 143.3 (d, J_{CP} = 27.3 Hz, *C*^{1}), 140.6 (*C*^{17}), 140.1 (d, J_{CP} = 2.9 Hz, *C*^{7}), 137.8 (*C*$^{8/12}$), 137.4 (d, J_{CP} = 7.2 Hz, *C*^{19}), 135.7 (*C*$^{8/12}$), 131.9 (d, J_{CP} = 4.8 Hz, *C*$^{3/5}$), 131.7 (*C*^{4}), 128.5 (*C*H$_{ar}$), 128.4 (*C*H$_{ar}$), 128.1 (d, J_{CP} = 5.1 Hz, *C*H$_{ar}$), 126.8 (d, J_{CP} = 19.0 Hz, *C*$^{3/5}$), 126.7 (*C*H$_{ar}$), 125.8 (*C*H$_{ar}$), 122.5 (d, J_{CP} = 9.9 Hz, *C*^{16}), 111.0 (d, J_{CP} = 6.1 Hz, *C*^{14}), 99.9 (d, J_{CP} = 5.7 Hz, *C*^{13}), 88.4 (d, J_{CP} = 28.0 Hz, *C*^{15}), 43.9 (d, J_{CP} = 3.9 Hz, *C*^{18}), 27.7 (d, J_{CP} = 10.7 Hz, *C*H$_3$*i*Pr), 27.4 (d, J_{CP} = 15.7 Hz, *C*H*i*Pr), 24.6 (d, J_{CP} = 19.2 Hz, *C*H*i*Pr), 22.6 (d, J_{CP} = 7.5 Hz, *C*H$_3$*i*Pr), 21.3 (d, J_{CP} = 13.7 Hz, *C*^{28}), 21.3 (*C*H$_3$), 21.0 (*C*H$_3$), 20.8 (*C*H$_3$), 19.3 (d, J_{CP} = 6.6 Hz, *C*H$_3$*i*Pr), 17.0 (d, J_{CP} = 7.0 Hz, *C*H$_3$*i*Pr).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ 80.3.

Elemental analysis calculated (found) for $C_{34}H_{40}ClPPd$: C, 65.70 (65.73); H, 6.49 (6.65)%.

3.2. Synthesis of 3b

Following general procedure, complex **1b** (65.2 mg, 0.1 mmol) was stirred in $CHCl_3$ (10 mL) for 1 h at 70 ºC to give a bright yellow solution. Complex **3b** was obtained as yellow crystals after crystallization in CH_2Cl_2:petroleum ether (1:3) at -20 ºC. Yield: 41.5 mg, 64 %.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.57 (td, 1H, J_{HH} = 7.4 Hz, J_{HP} = 2.5 Hz, C*H*^{4}), 7.49 (br d, 1H, C*H*$^{3/5}$), 7.24-7.15 (m, 4H, C*H*$_{ar}$), 7.05 (br d, 2H, C*H*$^{3/5}$ and C*H*$_{ar}$), 6.79 (d, 2H, J_{HH} = 8.6 Hz, C*H*$_{ar}$), 6.07-6.03 (m, 1H, C*H*^{16}), 5.53 (dd, 1H, J_{HH} = 6.4 Hz, J_{HP} = 9.4 Hz, C*H*^{15}), 3.76 (s, 3H, OC*H*$_3$), 2.68-2.53 (dq, 1H, J_{HH}= 7.0 Hz, J_{HP}= 25.0 Hz, H^{18}), 2.28-2.17 (m, 2H, C*H*i*Pr*), 2.12 (s, 3H, C*H*$_3$), 1.87 (s, 3H, Me^{27}), 1.82 (s, 3H, C*H*$_3$), 1.50 (dd, 3H, J_{HH} = 7.5 Hz, J_{HP} = 23.2 Hz, C*H*$_3$*i*Pr), 1.27 (dd, 3H, J_{HH} = 6.5 Hz, J_{HP} = 18.0 Hz, C*H*$_3$*i*Pr), 1.00 (d, 3H, J_{HH} = 6.9 Hz, Me^{28}), 0.88 (dd, 3H, J_{HH} = 6.7 Hz, J_{HP} = 18.6 Hz, C*H*$_3$*i*Pr), 0.36 (dd, 3H, J_{HH} = 7.0 Hz, J_{HP} = 11.0 Hz, C*H*$_3$*i*Pr).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 25 ºC): δ 158.6 (*C*^{22}), 151.5 (d, J_{CP} = 26.2 Hz, *C*$^{2/6}$), 147.9 (*C*$^{2/6}$), 143.4 (d, J_{CP} = 27.0 Hz, *C*^{1}), 140.7 (*C*^{7}), 137.8 (*C*$^{8/12}$), 137.2 (d, J_{CP} = 7.2 Hz, *C*^{19}), 135.7 (*C*$^{8/12}$), 132.5 (d, J_{CP} = 2.8 Hz, *C*H$_{ar}$), 131.9 (d, J_{CP} = 5.1 Hz, *C*$^{3/5}$), 131.6 (*C*^{4}), 128.4 (*C*H$_{ar}$), 128.1 (d, J_{CP} = 5.1 Hz, *C*H$_{ar}$), 127.0 (*C*H$_{ar}$), 126.7 (*C*H$_{ar}$), 121.5 (d, J_{CP} = 9.8 Hz, *C*^{16}), 113.9 (*C*H$_{ar}$), 111.4 (d, J_{CP} = 6.0 Hz, *C*^{14}), 99.9 (d, J_{CP} = 5.5 Hz, *C*^{13}), 88.8 (d, J_{CP} = 27.9 Hz, *C*^{15}), 55.4 (O*C*H$_3$), 43.9 (d, J_{CP} = 3.8 Hz, *C*^{18}), 27.7 (d, J_{CP} = 10.6 Hz, *C*H$_3$*i*Pr), 27.5 (d, J_{CP} = 16.0 Hz, *C*H*i*Pr), 24.6 (d, J_{CP} = 19.3 Hz, *C*H*i*Pr), 22.6 (d, J_{CP} = 7.3 Hz, *C*H$_3$*i*Pr), 21.5 (d, J_{CP} = 13.6 Hz, *C*^{28}), 21.3 (*C*H$_3$), 21.1 (*C*H$_3$), 20.8 (*C*H$_3$), 19.3 (d, J_{CP} = 6.7 Hz, *C*H$_3$*i*Pr), 17.0 (d, J_{CP} = 7.0 Hz, *C*H$_3$*i*Pr).

^{31}P{^{1}H} NMR (121 MHz, $CDCl_3$, 25 ºC): δ 79.9.

Elemental analysis calculated (found) for $C_{35}H_{42}ClOPPd$: C, 64.52 (64.49); H, 6.50 (6.56).

3.3. Synthesis of 4a

Following general procedure, complex **2a** (82.5 mg, 0.12 mmol) was stirred in $CHCl_3$ (12 mL) for 8 h at 70 ºC to give an orange solution. Complex **4a** was obtained as yellow crystals after crystallization in Et_2O:hexane (1:1) at -20 ºC. Yield: 50 mg, 61 %.

^{1}H NMR (300 MHz, $CDCl_3$, 25 ºC): δ 7.57 (td, 1H, J_{HH} = 7.4 Hz, J_{HP} = 2.8 Hz, C*H*^{4}), 7.51 (dt, 1H, J_{HH} = 7.6 Hz, J_{HP} = 1.6 Hz, C*H*^{3}),7.26-7.14 (m, 7H, C*H*$_{ar}$), 7.07-7.03 (m, 2H,

C*H*^{9,11}), 6.13-6.10 (m, 1H, C*H*^{16}), 5.50 (dd, 1H, J_{HH} = 6.2 Hz, J_{HP} = 9.8 Hz, C*H*^{15}), 2.69 (dq, 1H, J_{HH} = 7.0 Hz, J_{HP} = 25.0 Hz, H^{18}), 2.32-2.15 (m, 2H, C*H*$_{Cyp}$), 2.11 (s, 3H, C*H*$_3$), 2.10-2.01 (m, 2H, C*H*$_{Cyp}$), 1.90 (s, 3H, C*H*$_3$), 1.84 (s, 3H, Me^{27}), 1.80-1.21 (m, 12H, C*H*$_{Cyp}$), 1.05 (d, 3H, J_{HH} = 7.0 Hz, Me^{28}), 1.01-0.72 (m, 2H, C*H*$_{Cyp}$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ 150.9 (d, J_{CP} = 26.6 Hz, *C*$^{2/6}$), 148.0 (*C*$^{2/6}$), 143.9 (d, J_{CP} = 26.6 Hz, *C*^{1}), 140.1 (*C*^{7}), 137.6 (*C*$^{8/12}$), 137.4 (d, J_{CP} = 7.3 Hz, *C*^{19}), 136.0 (*C*$^{8/12}$), 131.8 (d, J_{CP} = 4.5 Hz, *C*$^{3/5}$), 131.6 (*C*^{4}), 128.5 (*C*H$_{ar}$), 128.3 (*C*H$_{ar}$), 127.8 (*C*H$_{ar}$), 126.9 (*C*$^{3/5}$), 126.7 (*C*H$_{ar}$), 125.8 (*C*H$_{ar}$), 122.6 (d, J_{CP} = 9.9 Hz, *C*^{16}), 112.0 (d, J_{CP} = 6.3 Hz, *C*^{14}), 100.2 (d, J_{CP} = 5.8 Hz, *C*^{13}), 87.6 (d, J_{CP} = 28.8 Hz, *C*^{15}), 44.1 (d, J_{CP} = 3.5 Hz, *C*^{18}), 37.9 (d, J_{CP} = 12.5 Hz, *C*H$_{Cyp}$), 36.6 (d, J_{CP} = 14.4 Hz, *C*H$_{Cyp}$), 35.5 (d, J_{CP} = 21.3 Hz, *C*H$_{Cyp}$), 34.0 (d, J_{CP} = 9.6 Hz, *C*H$_{Cyp}$), 28.2 (d, J_{CP} = 7.0 Hz, *C*H$_{Cyp}$), 27.7 (d, J_{CP} = 4.2 Hz, *C*H$_{Cyp}$), 27.0 (d, J_{CP} = 6.1 Hz, *C*H$_{Cyp}$), 26.0-25.7 (multiple overlapping peaks), 21.7 (d, J_{CP} = 14.7 Hz, *C*^{28}), 21.4 (*C*H$_3$), 20.9 (*C*H$_3$), 20.8 (*C*H$_3$).

^{31}P{^{1}H} NMR (160 MHz, $CDCl_3$, 25 ºC): δ 65.3.

Elemental analysis calculated (found) for $C_{38}H_{44}ClPPd$: C, 67.76 (67.42); H, 6.58 (6.97).

3.4. Synthesis of 4b

Following general procedure, complex **2b** (53.3 mg, 0.08 mmol) was stirred in $CHCl_3$ (8 mL) for 2 h at 70 ºC to give a bright yellow solution. Complex **4b** was obtained as yellow crystals after crystallization in Et_2O:hexane (1:1) at -20 ºC. Yield: 42.9 mg, 80 %.

^{1}H NMR (500 MHz, $CDCl_3$, 25 ºC): δ 7.56 (td, 1H,J_{HH} = 7.5 Hz, J_{HP} = 2.7 Hz, C*H*^{4}), 7.50 (d, 1H, J_{HH} = 7.5 Hz, C*H*^{3}), 7.21 (t, 1H, J_{HH} = 7.6 Hz, C*H*^{10}), 7.18 (d, 2H, J_{HH} = 8.8 Hz, C*H*^{20,24}), 7.15 (d, 1H, J_{HH} = 7.7 Hz, C*H*^{5}), 7.06-7.04 (m, 2H, C*H*^{9,11}), 6.80 (d, 2H, J_{HH} = 8.8 Hz, C*H*^{21,23}), 6.06-6.04 (m, 1H, C*H*^{16}), 5.49 (dd, 1H, J_{HH} = 6.2 Hz, J_{HP} = 9.8 Hz, C*H*^{15}), 3.77 (s, 3H, OC*H*$_3$), 2.64 (dq, 1H, J_{HH} = 7.0 Hz, J_{HP} = 25.0 Hz, H^{18}), 2.28-2.16 (m, 3H, C*H*$_{Cyp}$), 2.11 (s, 3H, C*H*$_3$), 2.09-2.03 (m, 2H, C*H*$_{Cyp}$), 1.89 (s, 3H, Me^{27}), 1.84 (s, 3H, C*H*$_3$), 1.80-1.24 (m, 11H, C*H*$_{Cyp}$), 1.05 (d, J_{HH} = 7.0 Hz, 3H, Me^{28}), 1.03-0.89 (m, 1H, C*H*$_{Cyp}$), 0.87-0.77 (m, 1H, C*H*$_{Cyp}$).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, 25 ºC): δ 158.6 (*C*^{22}), 151.1 (d, J_{CP} = 26.6 Hz, *C*$^{2/6}$), 148.0 (d, J_{CP} = 2.3 Hz, *C*$^{2/6}$), 144.0 (d, J_{CP} = 29.1 Hz, *C*^{1}), 140.1 (d, J_{CP} = 1.9 Hz, *C*^{7}), 137.6 (*C*$^{8/12}$), 137.2 (d, J_{CP} = 7.5 Hz, *C*^{19}), 136.1 (*C*$^{8/12}$), 132.5 (d, J_{CP} = 3.3 Hz, *CH*$_{ar}$), 131.8 (d, J_{CP} = 4.8 Hz, *C*$^{3/5}$), 131.6 (d, J_{CP} = 1.9 Hz, *C*^{4}), 128.3 (*CH*$_{ar}$), 127.9 (d, J_{CP} = 1.1 Hz, *CH*$_{ar}$), 127.0 (d, J_{CP} = 1.8 Hz, *CH*$_{ar}$), 126.9 (*CH*$_{ar}$), 126.7 (*CH*$_{ar}$), 121.5 (d, J_{CP} = 10.1 Hz, *C*^{16}), 113.9 (*CH*$_{ar}$), 111.6 (d, J_{CP} = 6.4 Hz, *C*^{14}), 100.2 (d, J_{CP} = 5.9 Hz, *C*^{13}), 88.0 (d, J_{CP} = 28.7

Hz, C^{15}), 55.4 (OCH_3), 44.1 (d, J_{CP} = 4.1 Hz, C^{18}), 37.8 (d, J_{CP} = 12.2 Hz, CH_{Cyp}), 36.6 (d, J_{CP} = 14.6 Hz, CH_{Cyp}), 35.5 (d, J_{CP} = 21.4 Hz, CH_{Cyp}), 34.0 (d, J_{CP} = 9.8 Hz, CH_{Cyp}), 28.2 (d, J_{CP} = 7.3 Hz, CH_{Cyp}), 27.7 (d, J_{CP} = 4.5 Hz, CH_{Cyp}), 27.0 (d, J_{CP} = 6.2 Hz, CH_{Cyp}), 26.1-25.7 (multiple overlapping peaks), 21.9 (d, J_{CP} = 14.7 Hz, C^{28}), 21.4 (CH_3), 20.9 (CH_3), 20.8 (CH_3).

$^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 25 ºC): δ 64.9.

Elemental analysis calculated (found) for $C_{39}H_{46}ClOPPd$: C, 66.57 (66.64); H, 6.59 (6.31.

4. Variable Temperature NMR Studies

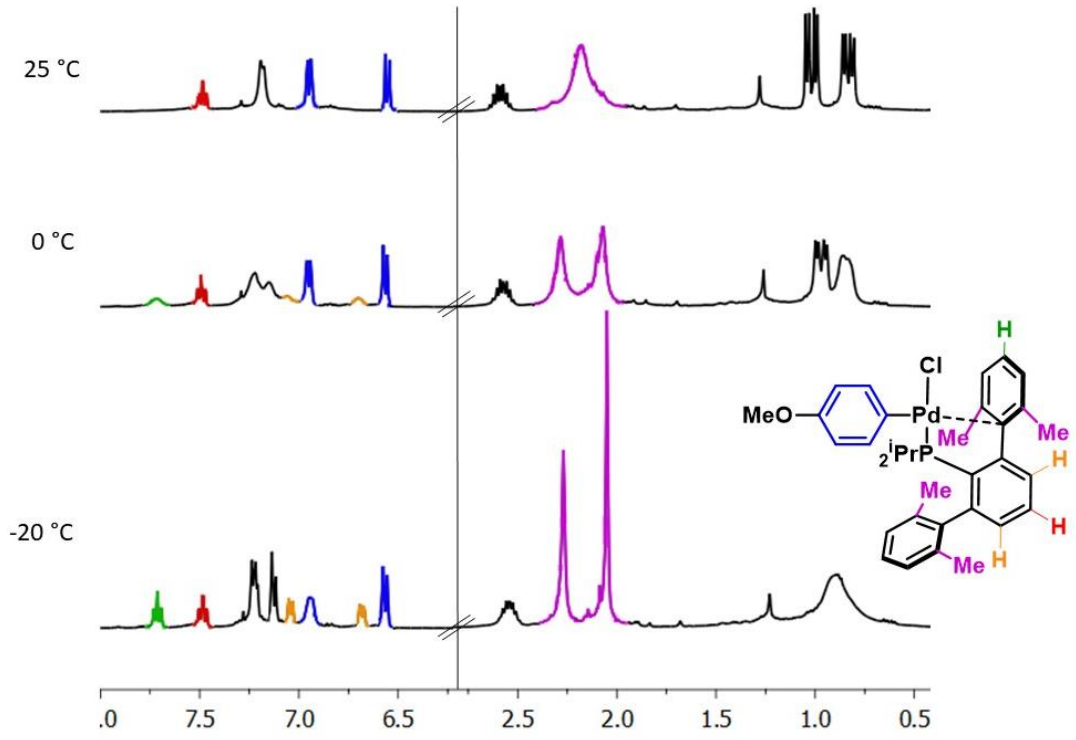
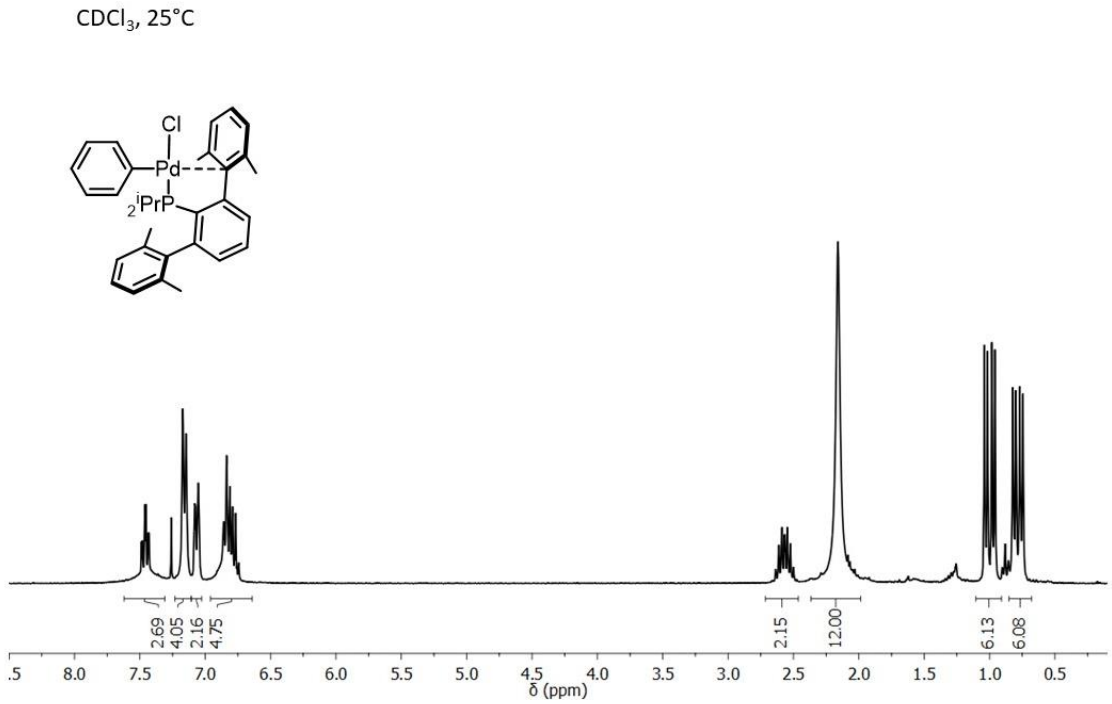


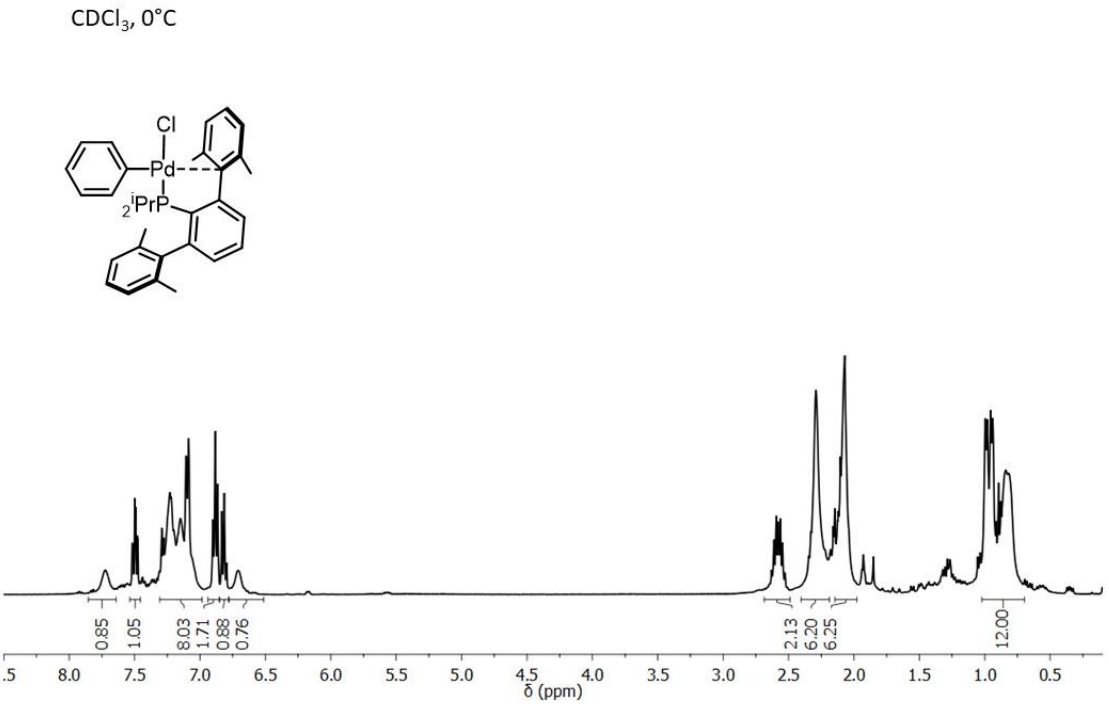
Figure S1. ^1H-NMR spectra of **1b** at 25, 0 and -20 ºC ($CDCl_3$).

5. NMR Spectra of compounds.

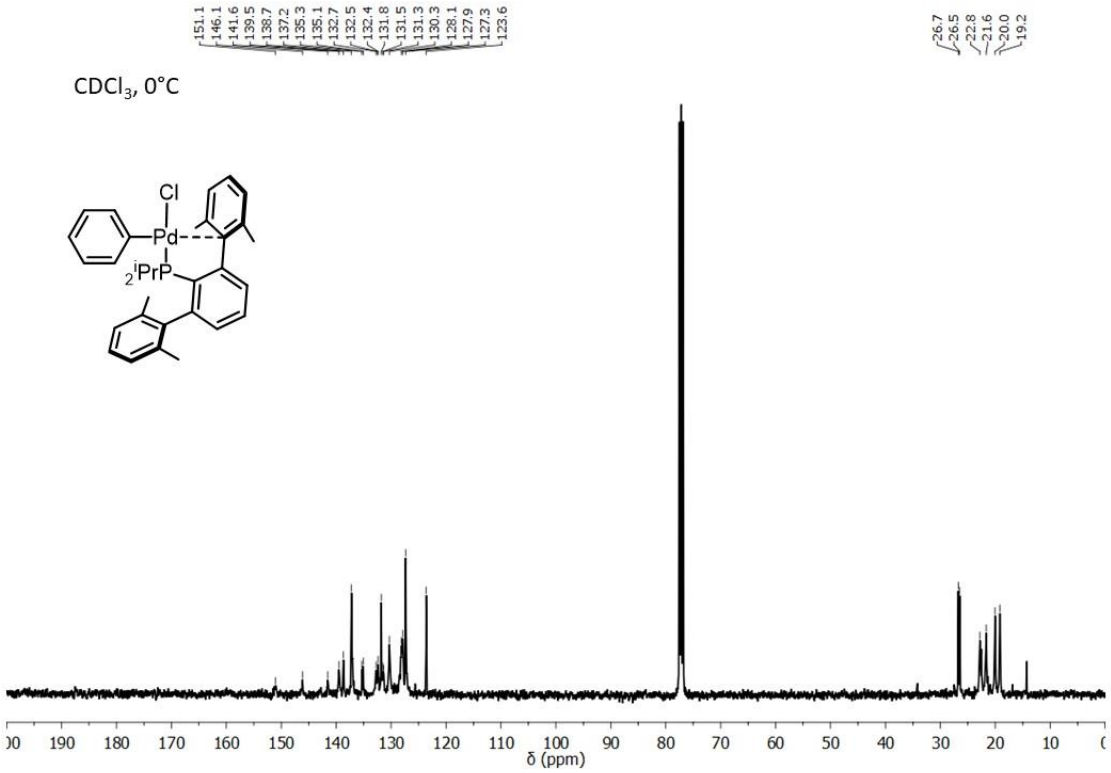
^{1}H NMR spectrum of **1a** at 25 ºC



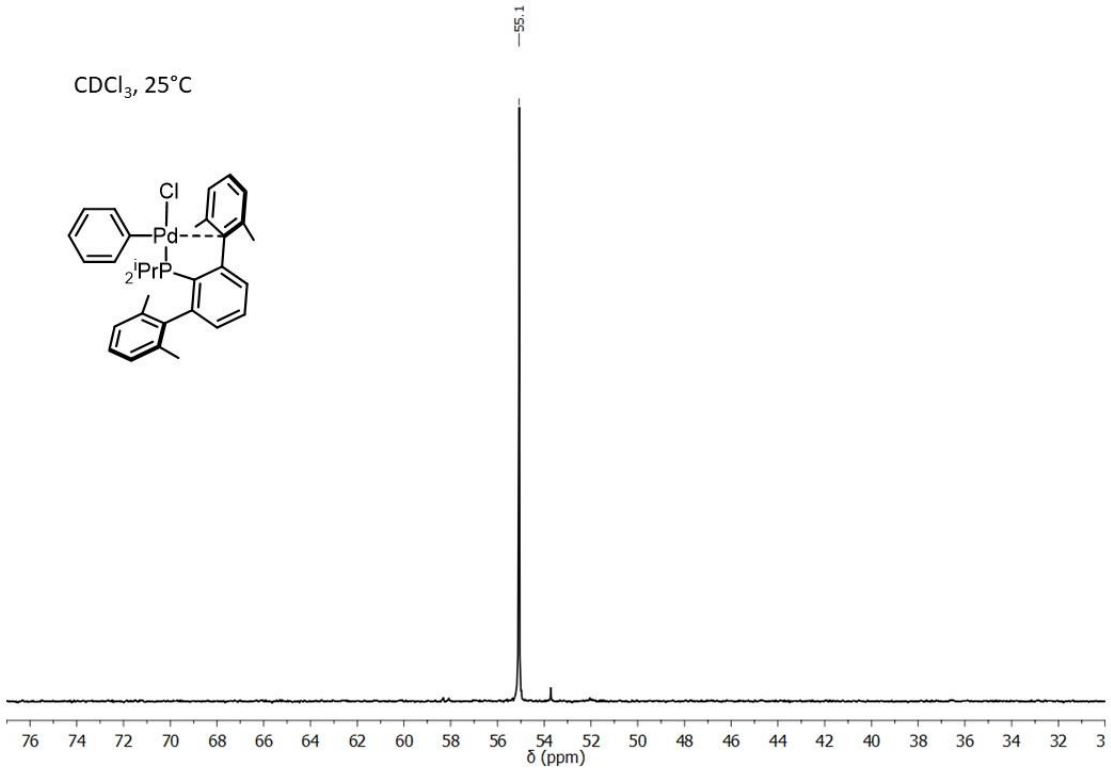
^{1}H NMR spectrum of **1a** at 0 ºC



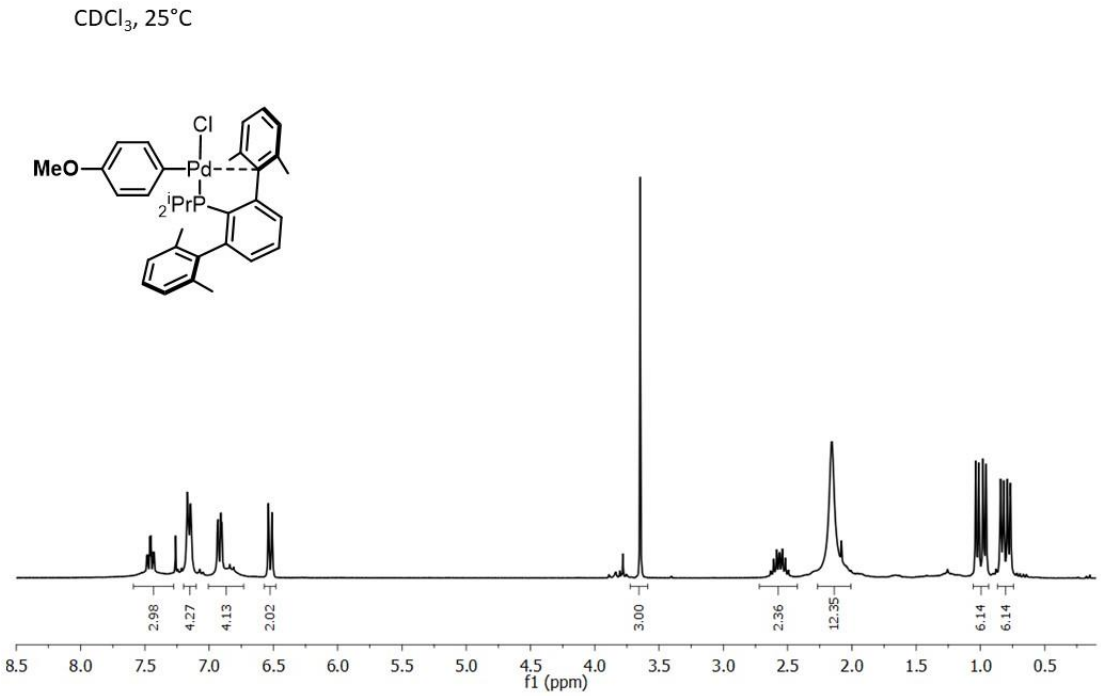
$^{13}C\{^{1}H\}$ NMR spectrum of **1a**



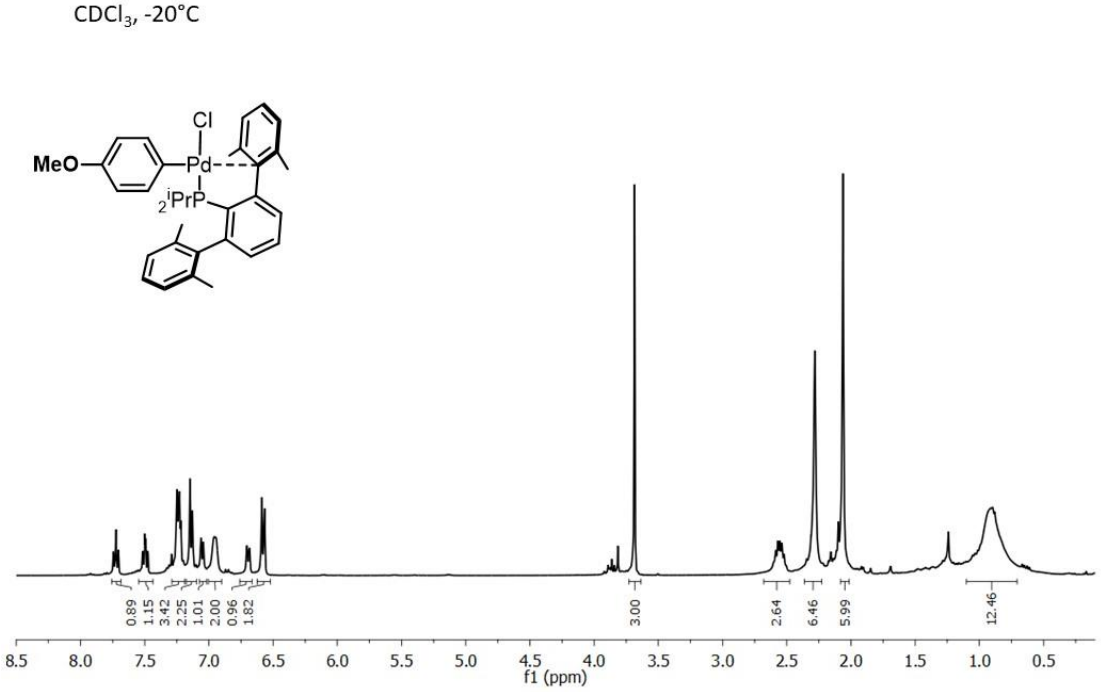
$^{31}P\{^{1}H\}$ NMR spectrum of **1a**



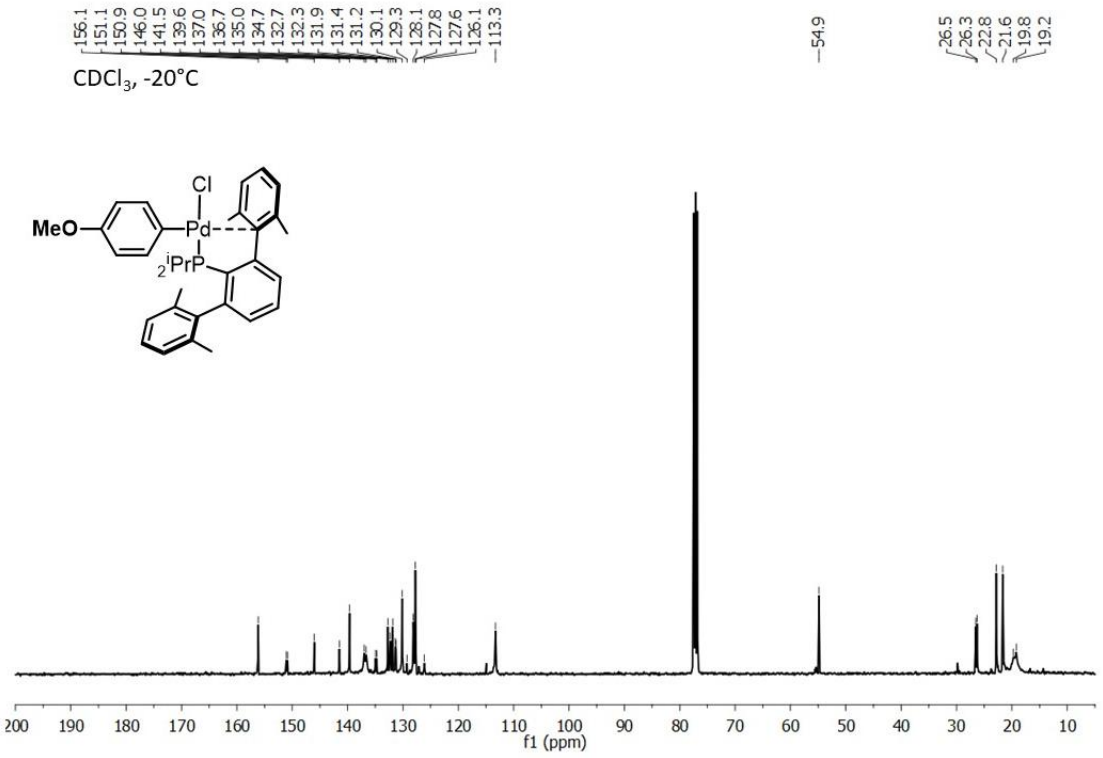
^{1}H NMR spectrum of **1b** at 25 ºC



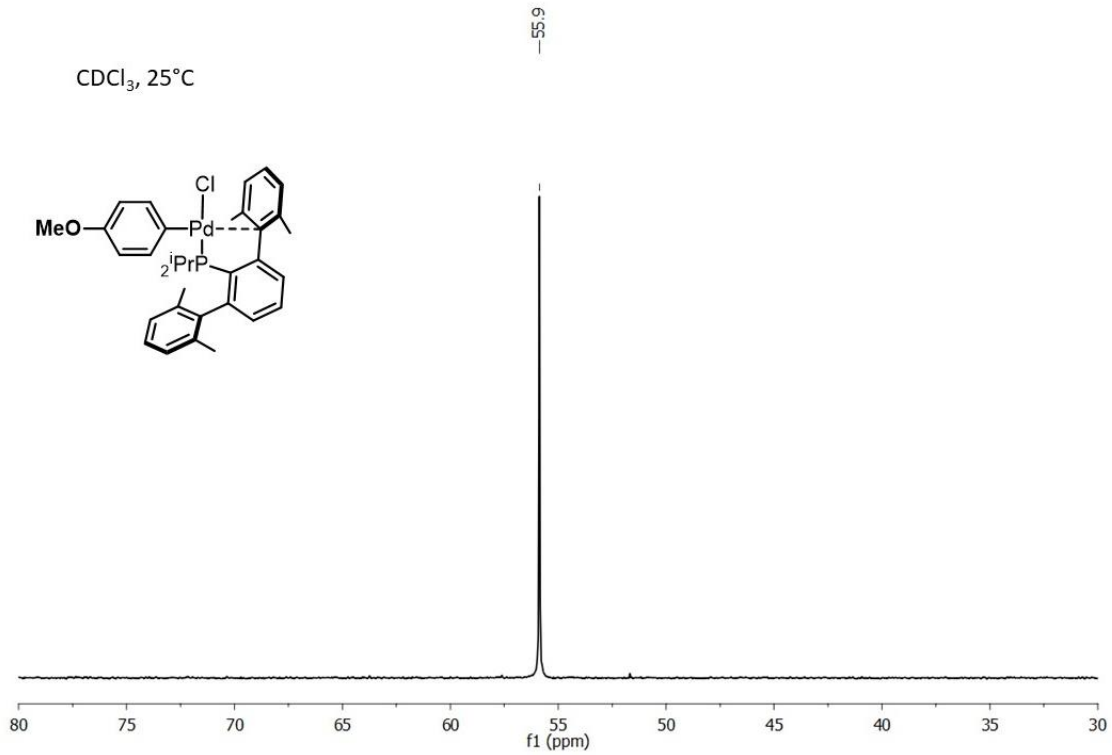
^{1}H NMR spectrum of **1b** at -20 ºC



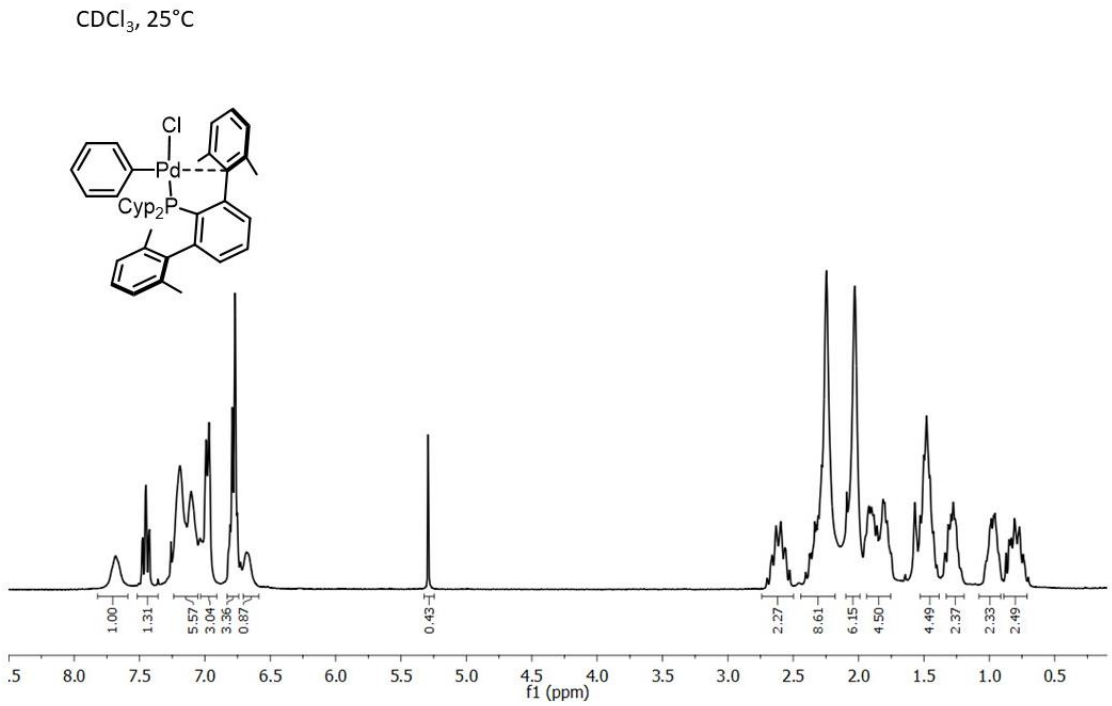
$^{13}C\{^{1}H\}$ NMR spectrum of **1b**



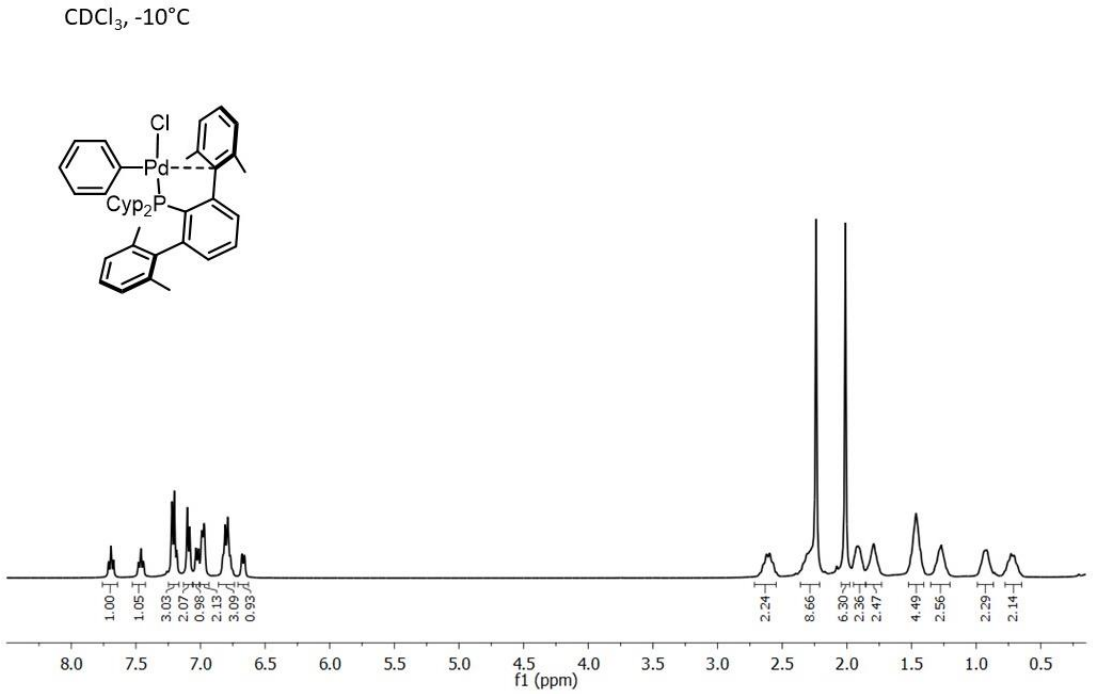
$^{31}P\{^{1}H\}$ NMR spectrum of **1b**



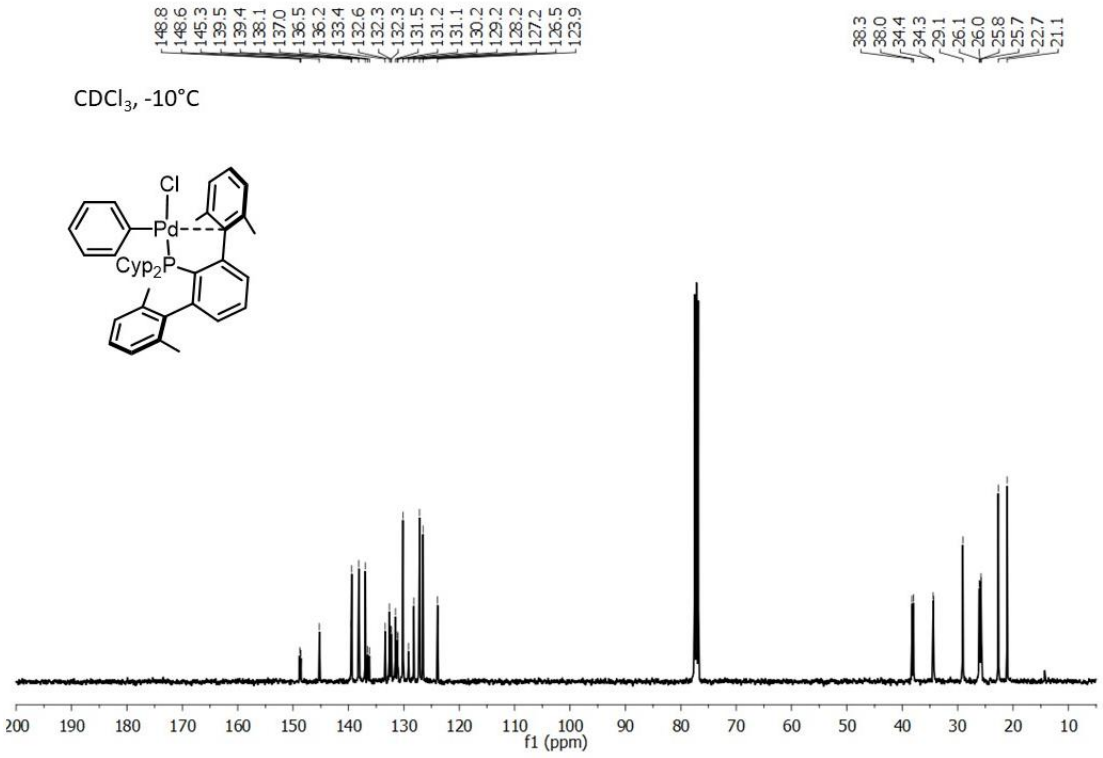
^{1}H NMR spectrum of **2a** at 25 ºC



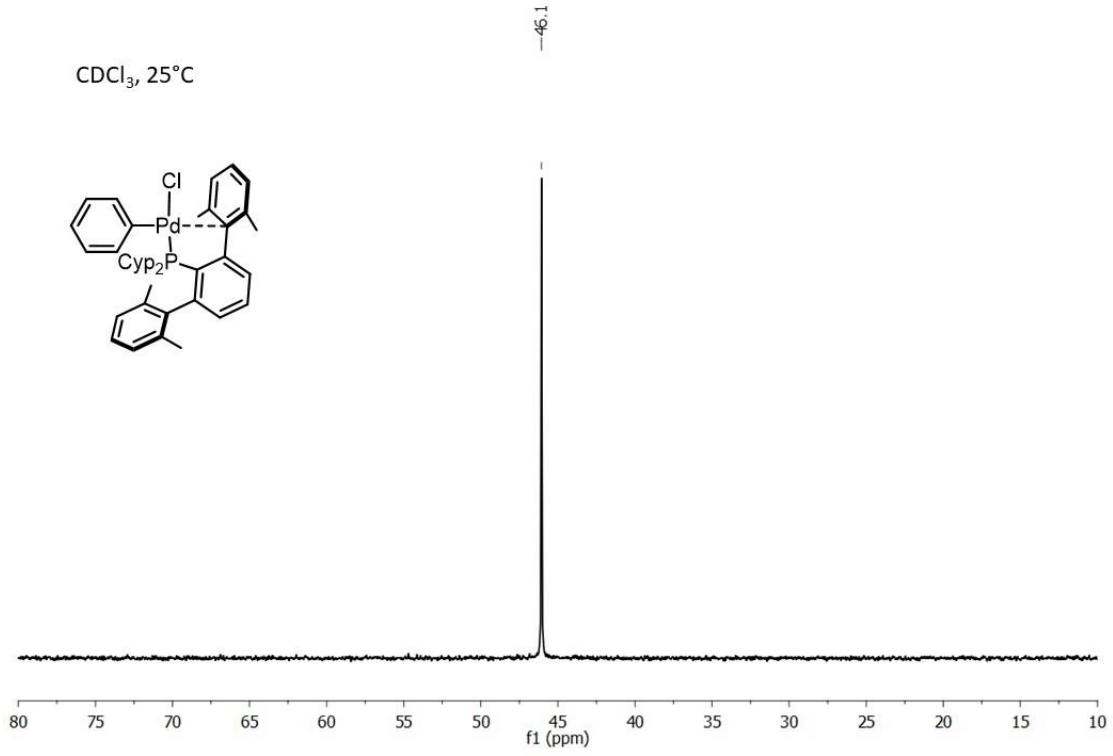
^{1}H NMR spectrum of **2a** at -10 ºC



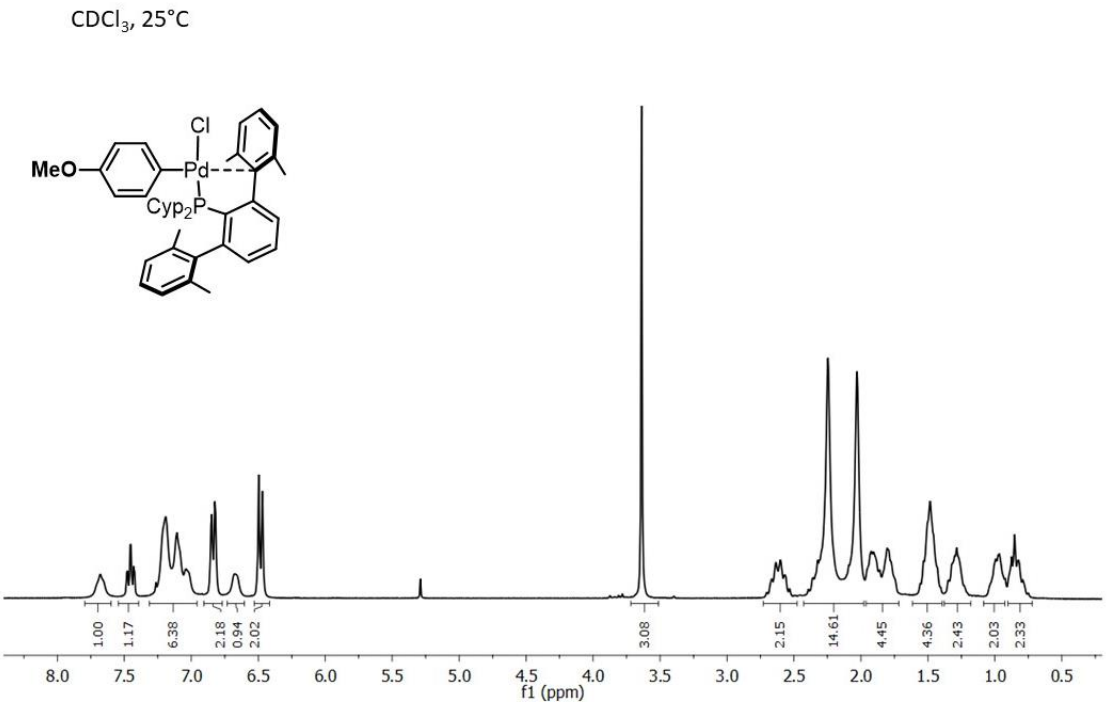
$^{13}C\{^{1}H\}$ NMR spectrum of **2a**



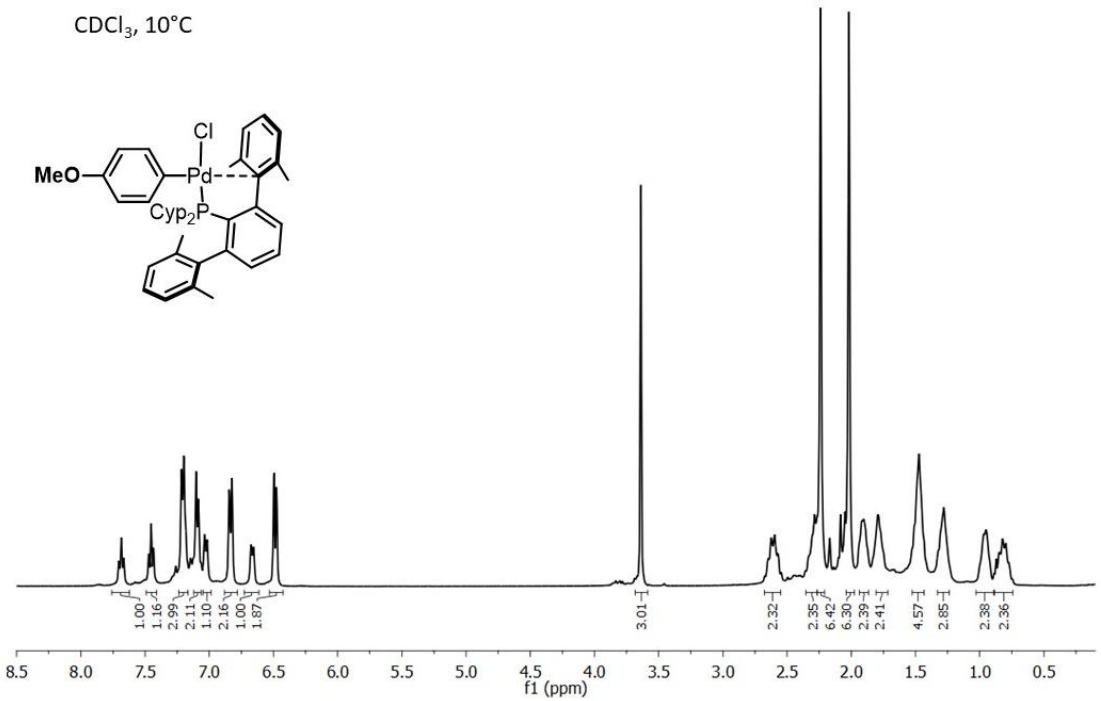
$^{31}P\{^{1}H\}$ NMR spectrum of **2a**



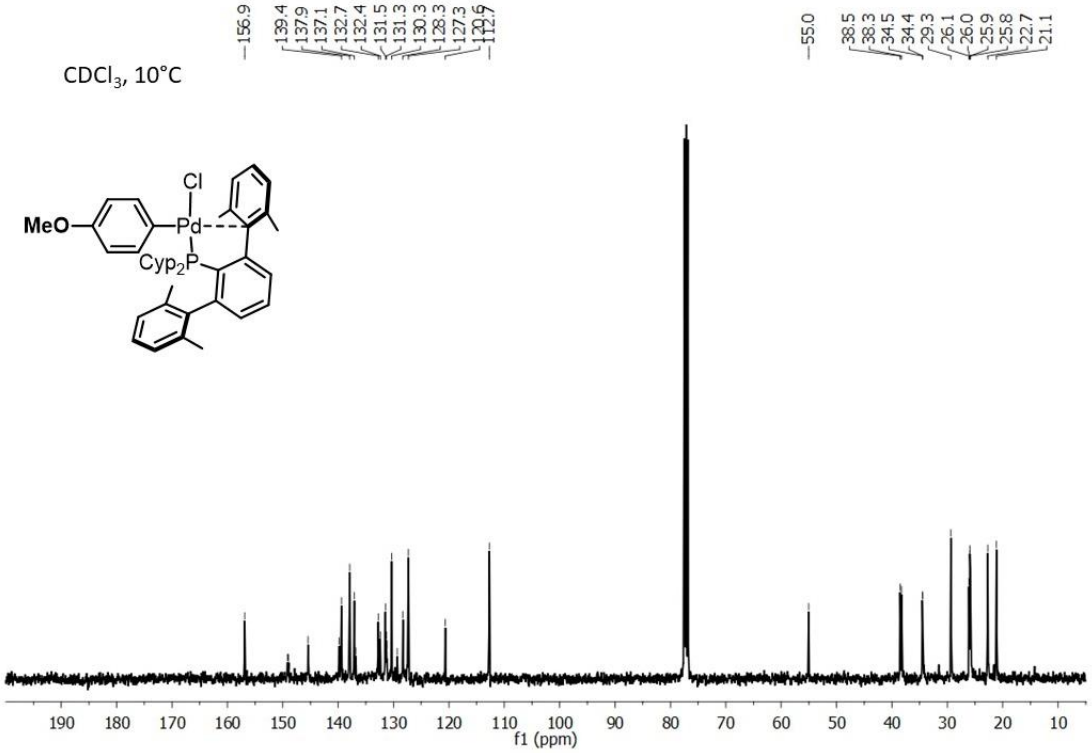
^{1}H NMR spectrum of **2b** at 25 ºC



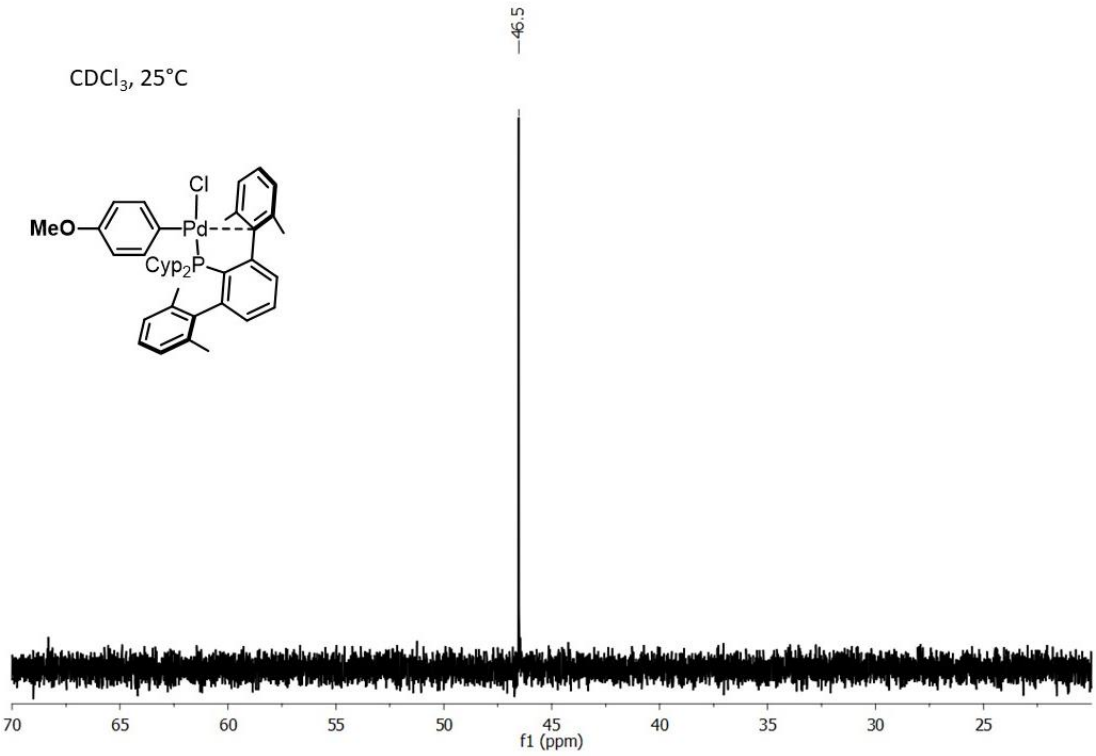
^{1}H NMR spectrum of **2b** at 10 ºC



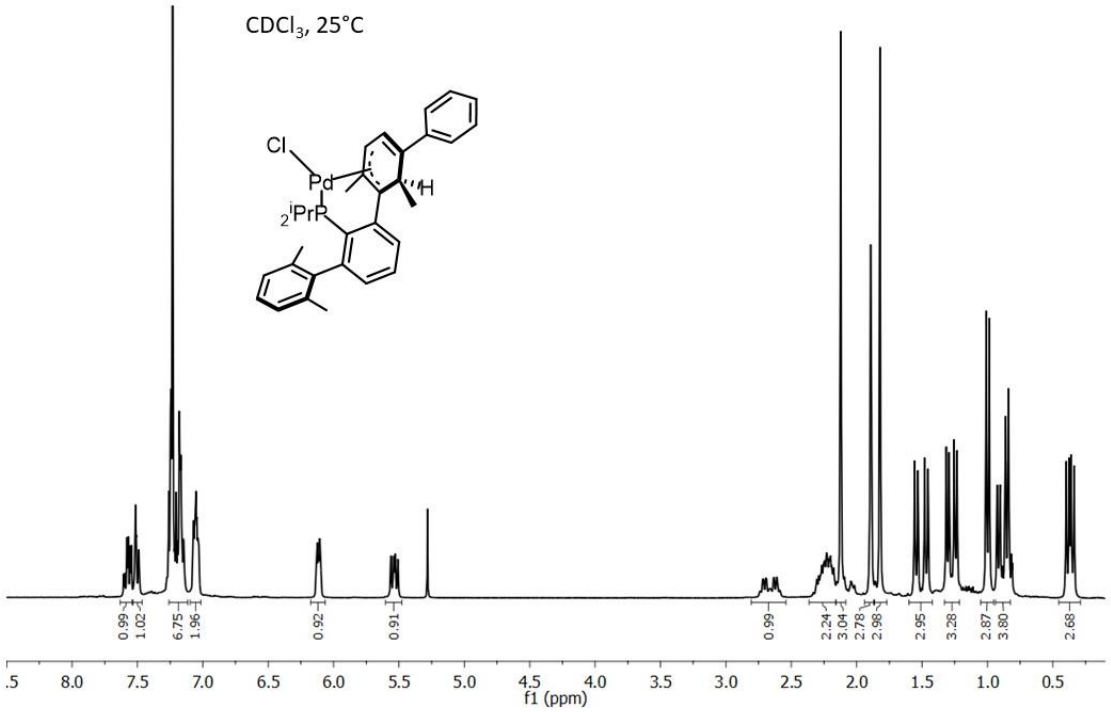
$^{13}C\{^{1}H\}$ NMR spectrum of **2b**



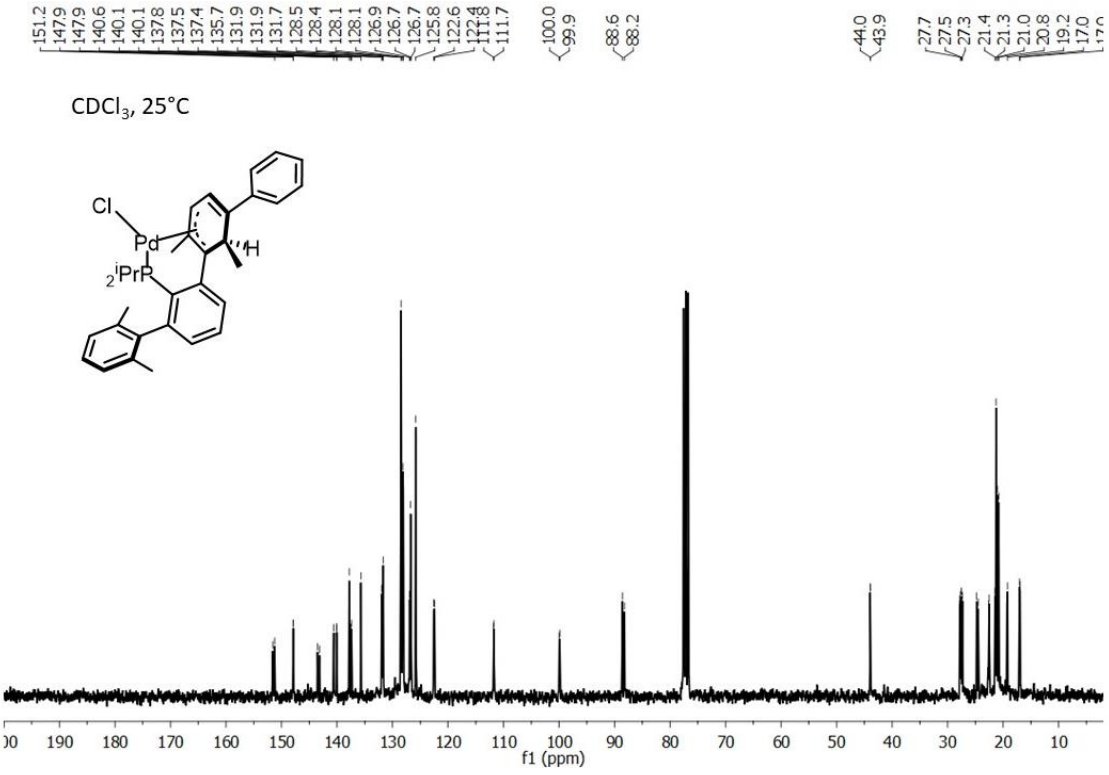
$^{31}P\{^{1}H\}$ NMR spectrum of **2b**



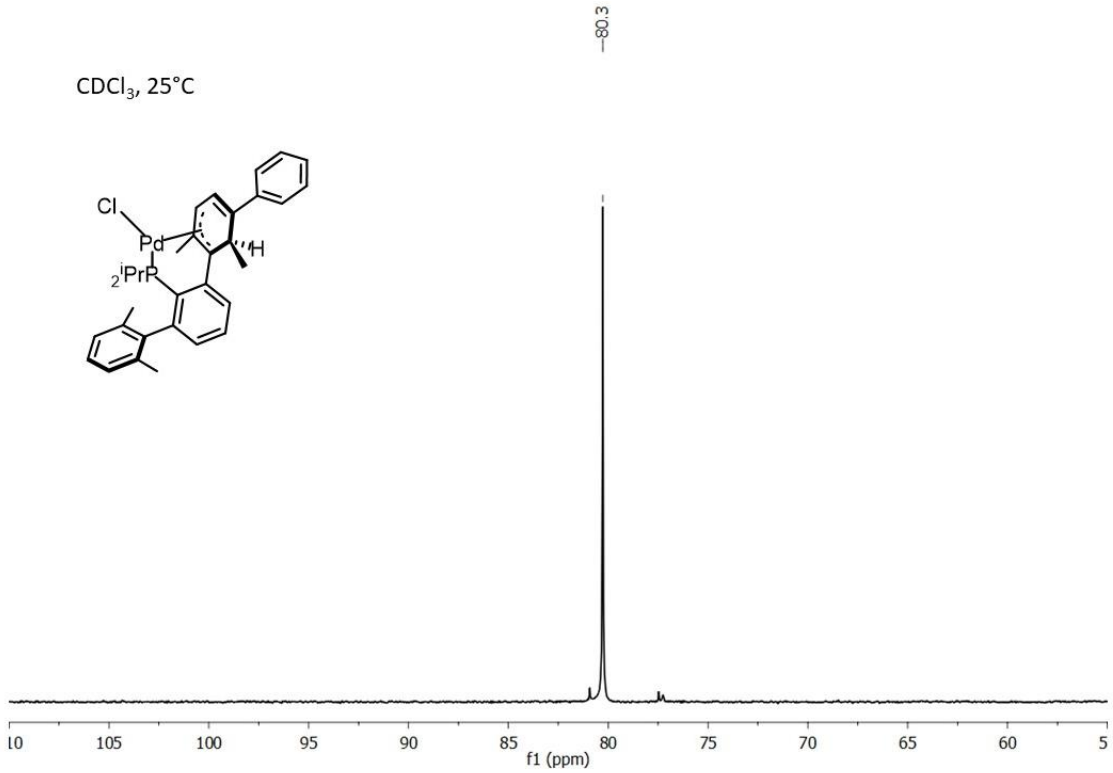
^{1}H NMR spectrum of **3a**



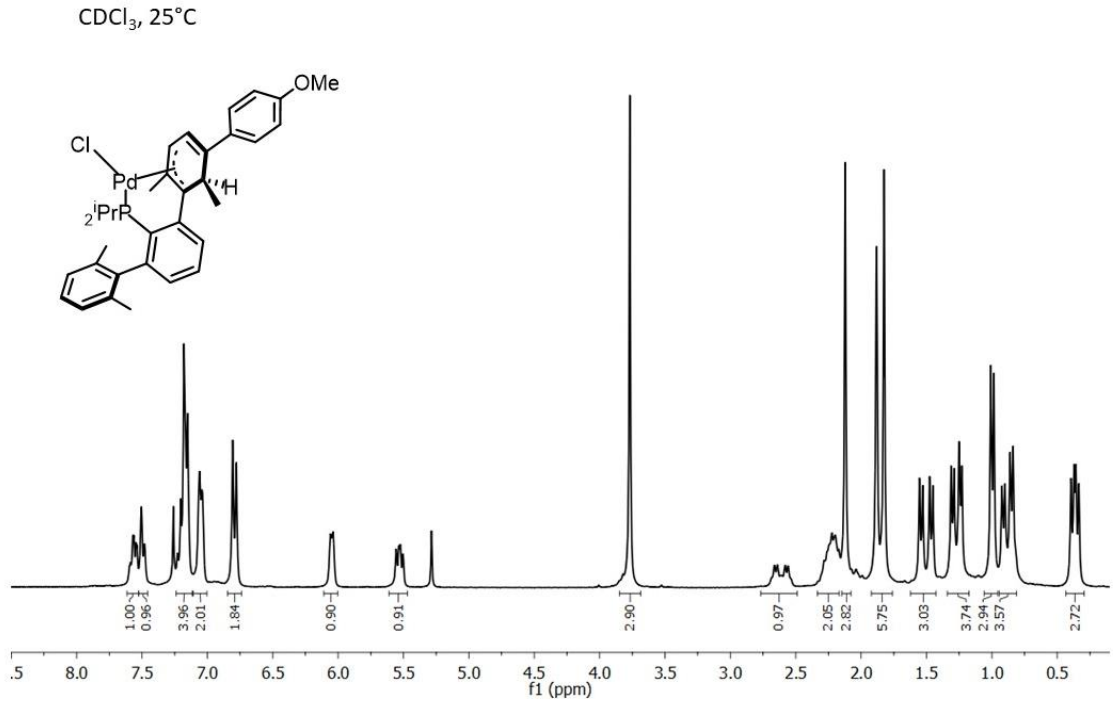
^{13}C{^{1}H} NMR spectrum of **3a**



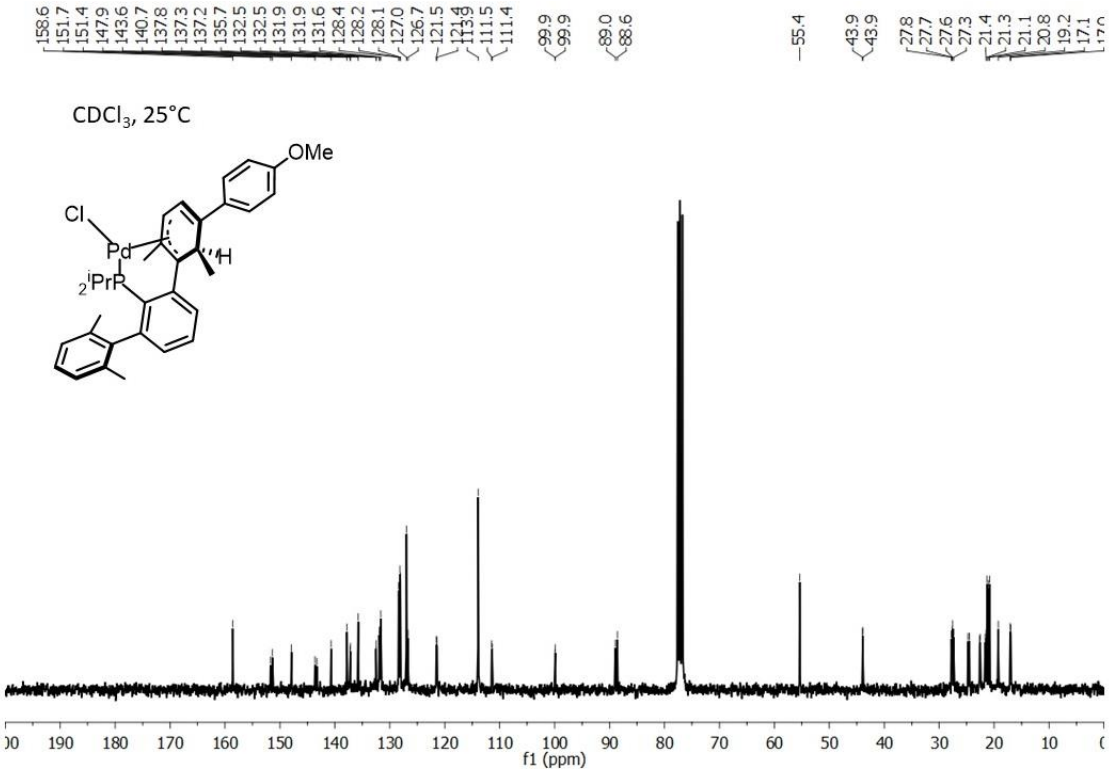
$^{31}P\{^{1}H\}$ NMR spectrum of **3a**



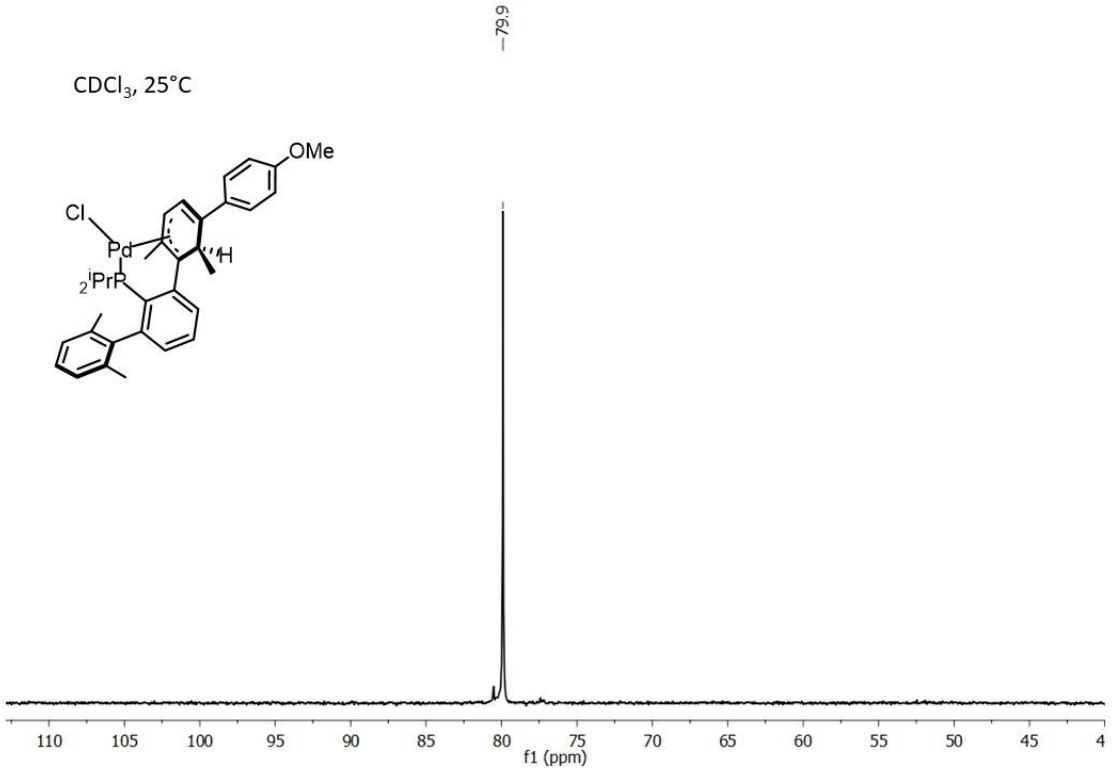
^{1}H NMR spectrum of **3b**



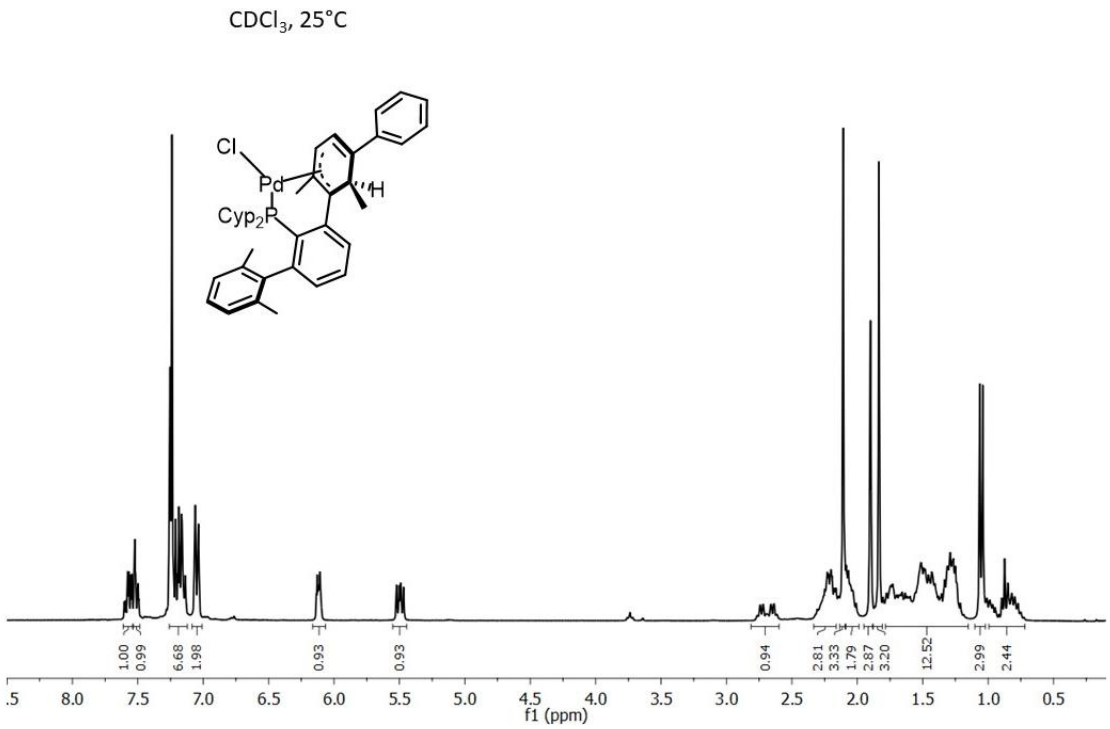
$^{13}C\{^{1}H\}$ NMR spectrum of **3b**



$^{31}P\{^{1}H\}$ NMR spectrum of **3b**



^{1}H NMR spectrum of **4a**



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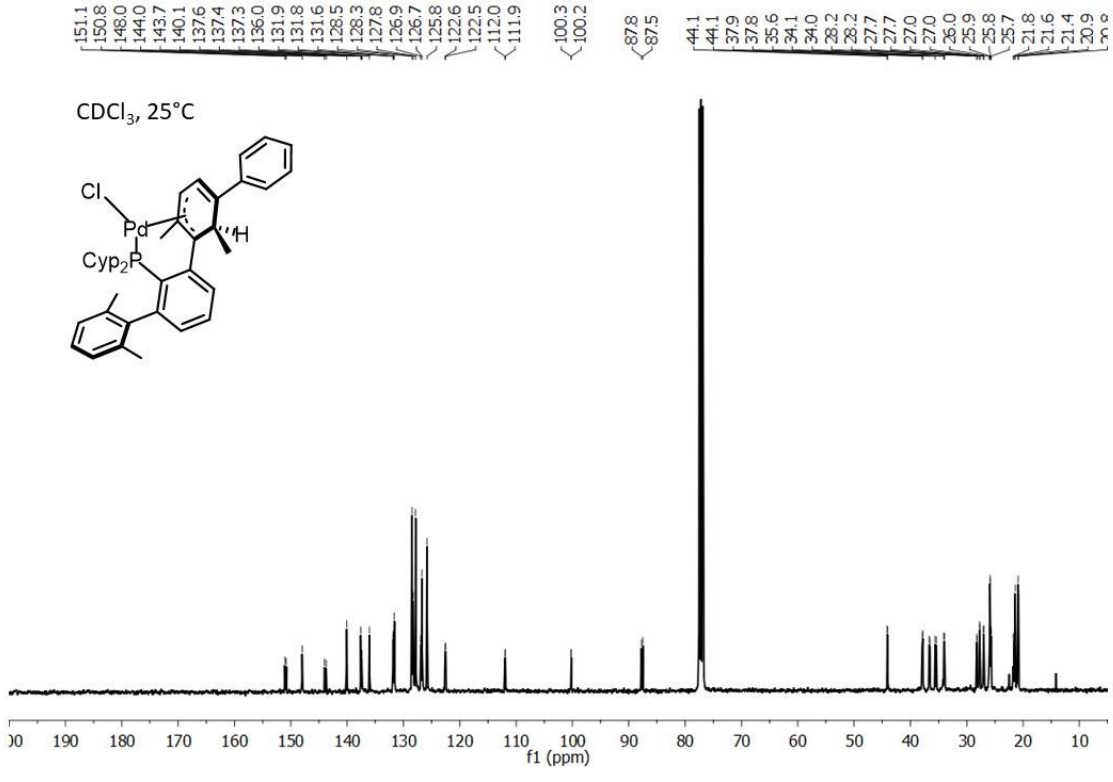
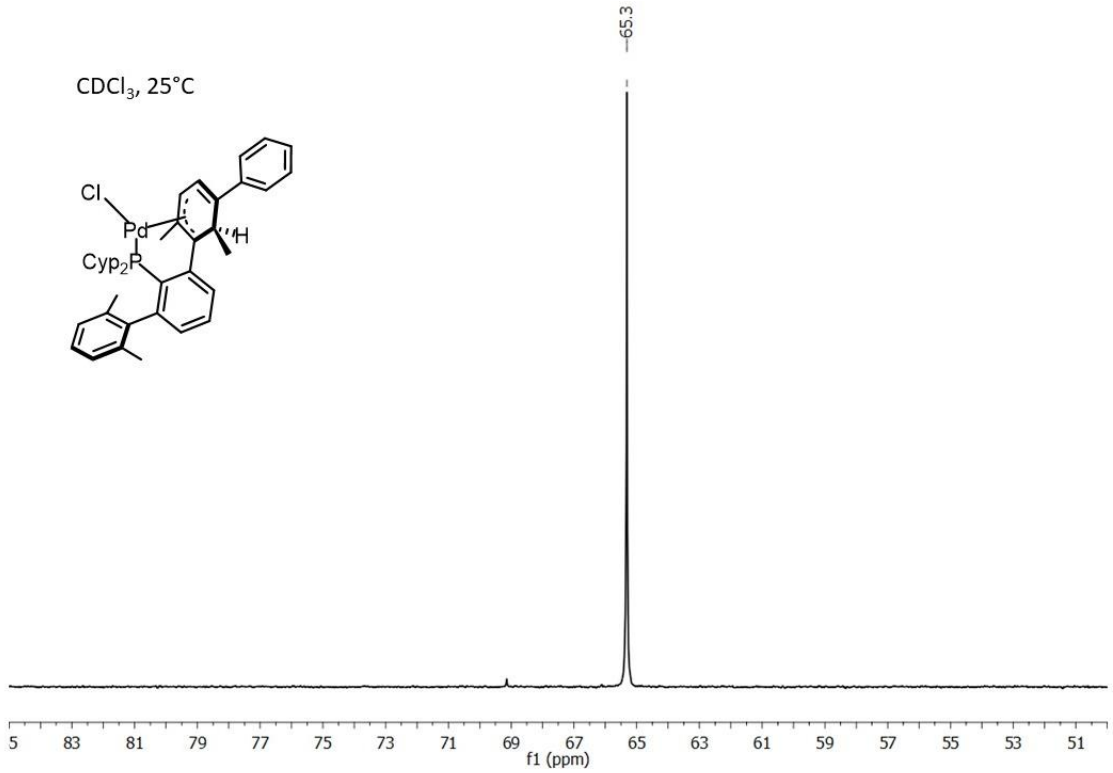
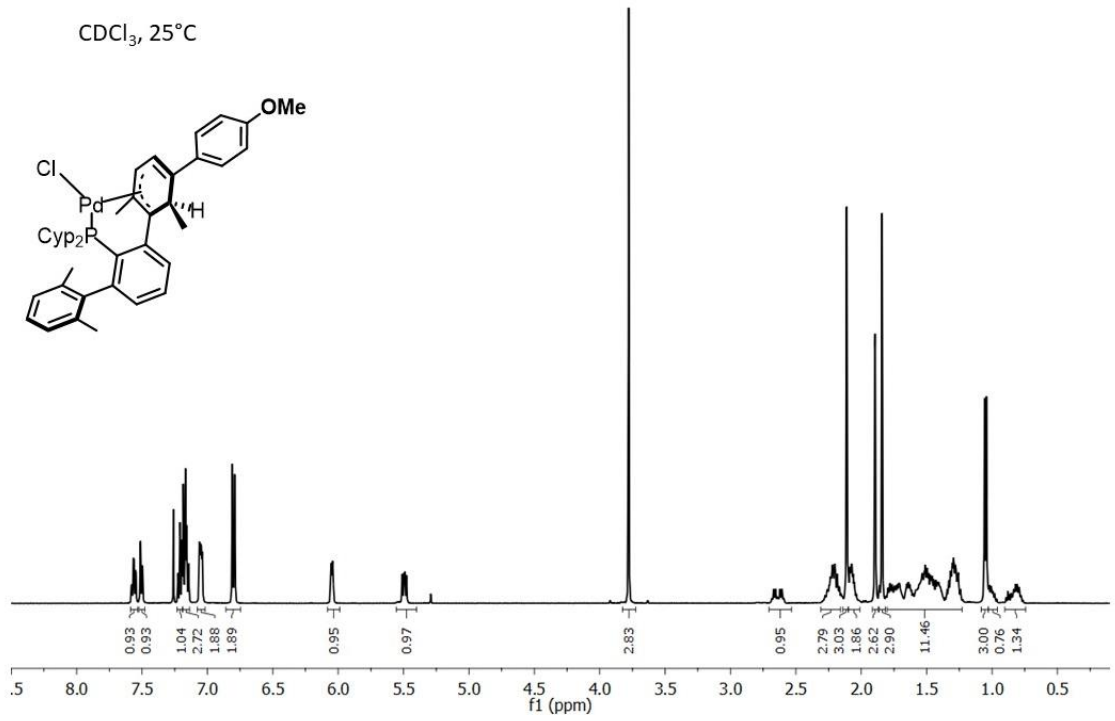


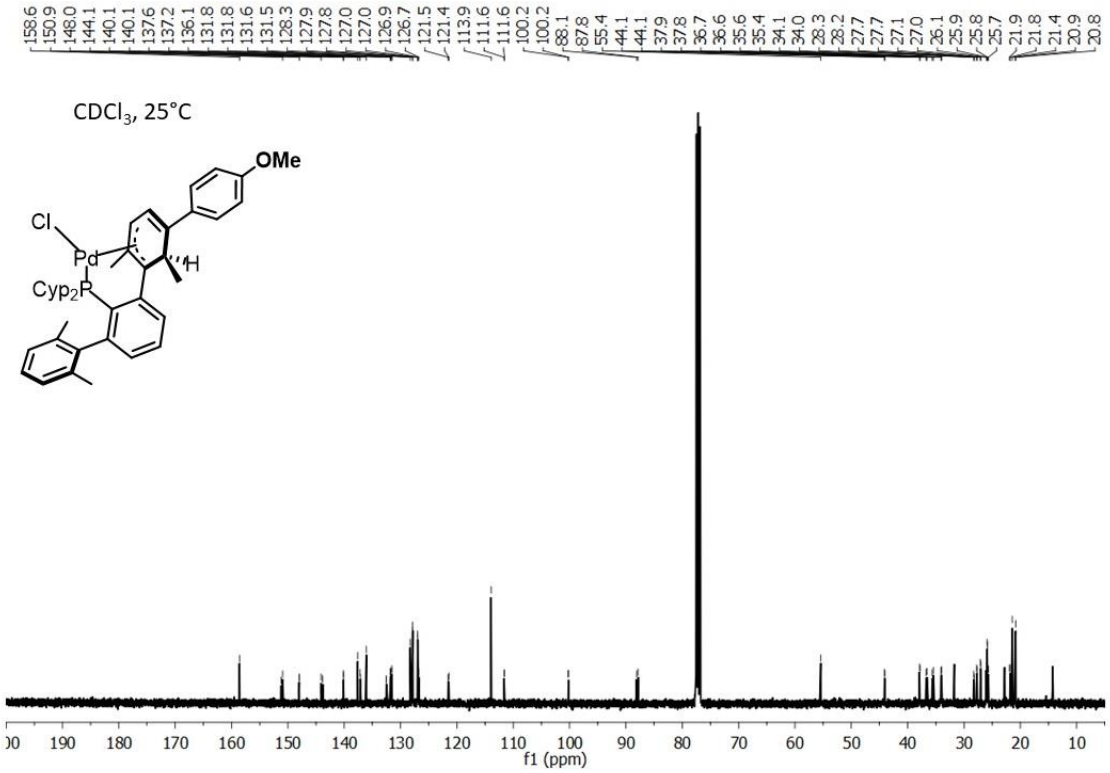
$^{31}P\{^{1}H\}$ NMR spectrum of **4a**



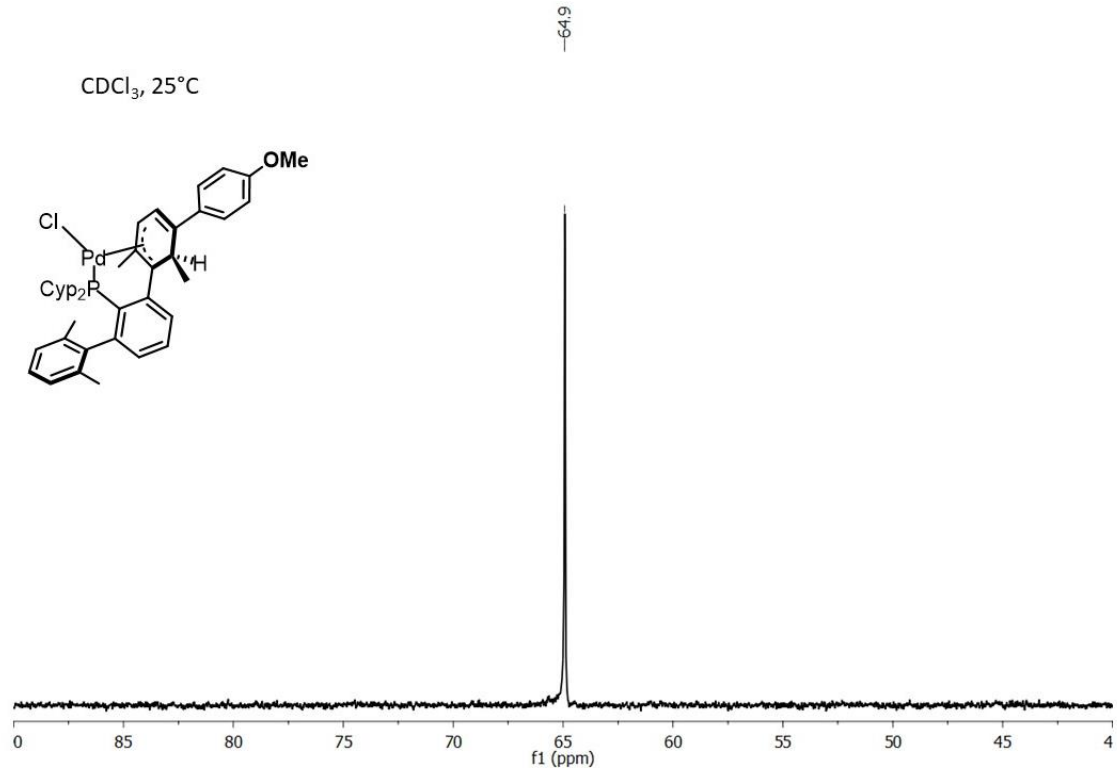
^{1}H NMR spectrum of **4b**



$^{13}C\{^{1}H\}$ NMR spectrum of **4b**



$^{31}P\{^{1}H\}$ NMR spectrum of **4b**



6. X-ray structural data of new complexes

Single crystals of suitable size for X-ray diffraction analysis of each compound were selected and coated with FOMBLIN oil, mounted on a glass fibre and fixed in a cold nitrogen stream (T = 100 K) to the goniometer head. Data collection have been performed on two difractometers:

- 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 (used with **2b** and **3a**), and
- A Bruker Chi-Fixed QUEST diffractometer equipped with a Photon II CMOS detector, using MoKα1 (λ=0.71073 Å, microfocus sealed x-ray tube) and a Oxford Cryosystems low-temperature device (Cryostream 800), (used with **4b**).

Data collections were processed with APE-W2D-ND (Bruker, 2004), cell refinement and data reduction with SAINT-Plus (Bruker, 2004) and the absorption was corrected by multiscan method applied by SADABS.[3] The space-group assignment was based upon systematic absences, E statistics, and successful refinement of the structure. The structures were solved by direct methods and refined against all *F2* data by full-matrix least-squares techniques (SHELXTL-6.12)[4] minimizing $w[Fo^2-Fc^2]^2$.

Thermal parameters for all non-hydrogen atoms were refined anisotropically while hydrogen atoms were included in calculated positions and allowed to ride on the attached atoms with the isotropic temperature factors (*U*iso values) fixed at 1.2 times (1.5 times for methyl groups) those *U*eq values of the corresponding attached atoms.

A summary of the fundamental crystal and refinement data are given in the Table S1. Atomic coordinates, anisotropic displacement parameters and bond lengths and angles can be found in the cif files which have been deposited in the Cambridge Crystallographic Data Centre with no. 1944960-1944961 and 1943362. These data can be obtained free for charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

3 G. M. Sheldrick, SADABS, Program for Empirical Absorption Correction of Area Detector Data. Göttingen: University of Göttingen, 1996.
4 G. M. Sheldrick, SHELXTL, versión 6.14. Program for solution and refinement of crystal structures, Universität Göttingen, Germany, 2000.

Table S1. *Crystal data and structure refinement for **2b**, **3a** and **4b***

Identification code	**2b**	**3a**	**4b**
Empirical formula	C39 H46 Cl O P Pd	C34 H40 Cl P Pd	C43 H56 Cl O2 P Pd
Formula weight	703.58	621.48	777.69
Temperature	100.0 K	100.0 K	100.0 K
Wavelength	0.56086 Å	0.56086 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	$P2_1/n$	$P2_1/c$
Unit cell dimensions	a = 11.8653(5) Å b = 12.3384(5) Å c = 12.5433(5) Å α = 82.432(2)° β = 75.828(2)° γ = 69.560(2)°	a = 15.8449(6) Å b = 13.4470(6) Å c = 15.8973(6) Å α = 90° β = 118.1371(14)° γ = 90°	a = 14.0644(5) Å b = 13.7583(5) Å c = 20.8100(7) Å α = 90° β = 109.162(2)° γ = 90°
Volume	1666.18(12) $Å^3$	2986.9(2) $Å^3$	3803.7(2) $Å^3$
Z	2	4	4
Density (calculated)	1.402 Mg/m^3	1.382 Mg/m^3	1.358 Mg/m^3
Absorption coefficient	0.382 mm^{-1}	0.421 mm^{-1}	0.635 mm^{-1}
F(000)	732	1320	1632
Crystal size	0.3 x 0.3 x 0.2 mm^3	0.11 x 0.08 x 0.06 mm^3	0.31 x 0.11 x 0.06 mm^3
Theta range for data collection	2.784 to 45.778°	3.312 to 44.082°	2.138 to 30.033°
Index ranges	-15<=h<=15, -16<=k<=16, -16<=l<=15	-17<=h<=21, -17<=k<=15, -21<=l<=21	-19<=h<=19, -19<=k<=19, -29<=l<=29
Reflections collected	23319	26078	124219
Independent reflections	8083 [R(int) = 0.0355]	7465 [R(int) = 0.0397]	11130 [R(int) = 0.0816]
Completeness to theta = 22.00°	95.4 %	99.9 %	99.9 %
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.7447 and 0.6141	0.7447 and 0.5960	0.7462 and 0.6806
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	8083 / 0 / 393	7465 / 0 / 342	11130 / 0 / 440
Goodness-of-fit on F^2	1.063	0.901	1.044

Final R indices [I>2sigma(I)]	R1 = 0.0364, wR2 = 0.0801	R1 = 0.0346, wR2 = 0.0858	R1 = 0.0399, wR2 = 0.0947
R indices (all data)	R1 = 0.0520, wR2 = 0.0930	R1 = 0.0497, wR2 = 0.0933	R1 = 0.0582, wR2 = 0.1057
Largest diff. peak and hole	1.15 and -1.18 e.Å^{-3}	1.03 and -0.61 e.Å^{-3}	1.371 and -0.962 e.Å^{-3}

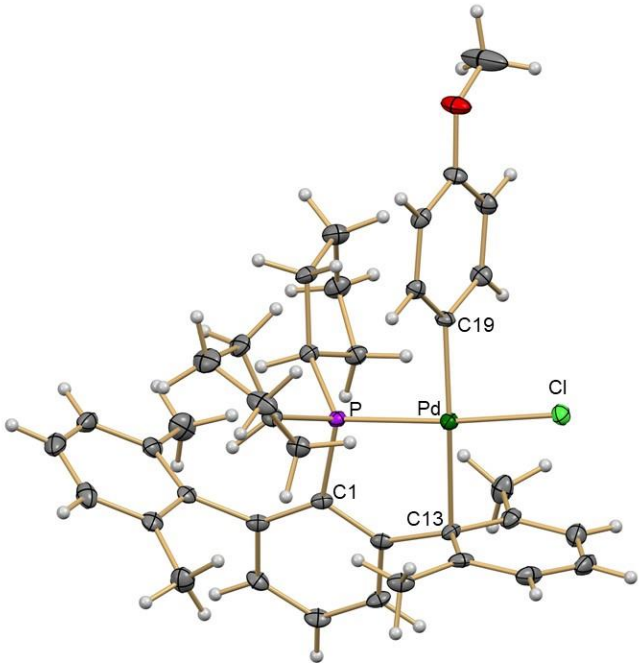


Figure S2. Molecular structure of **2b.** Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [º]: Pd-P 2.2575(7), Pd-Cl 2.3518(7), Pd-C13 2.426(2), Pd-C19 2.002(2); Cl-Pd-C19 84.57(8), P-Pd-C13 83.50(7), P-Pd-Cl 172.02(2), C13-Pd-C19 162.01(9).

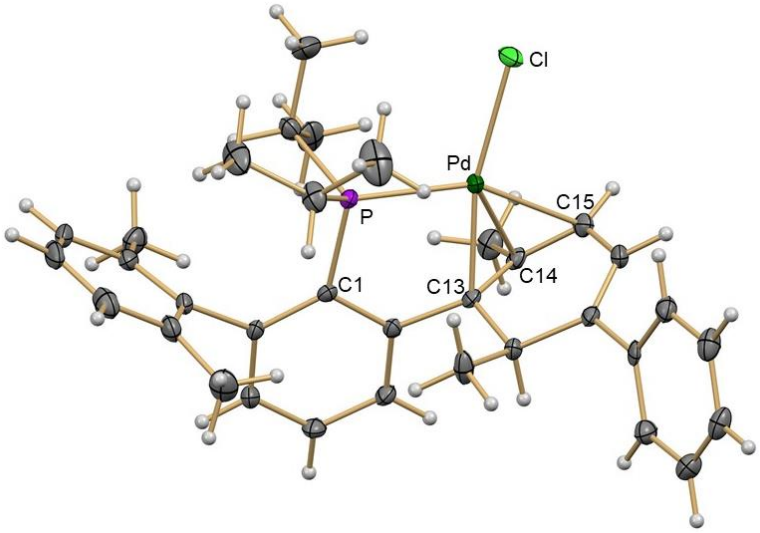


Figure S3. Molecular structure of **3a.** Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [º]: Pd-P 2.2673(6), Pd-Cl 2.3915(7), Pd-C13 2.084(2), Pd-C14 2.154(2), Pd-C15 2.270(2); P-Pd-C13 84.99(6), P-Pd-Cl 107.76(2), Cl-Pd-C13 166.75(6).

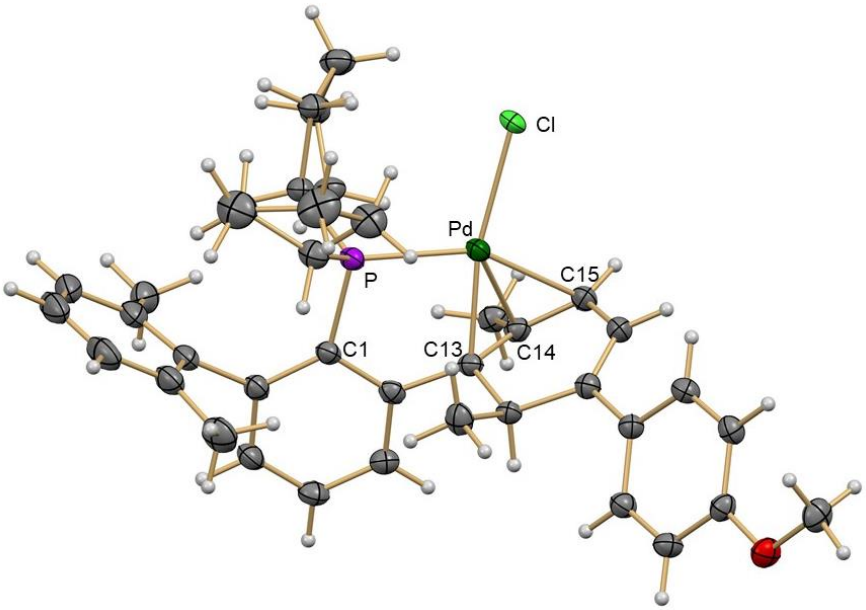


Figure S4. Molecular structure of **4b.** Thermal ellipsoids are shown at 50% probability. Selected bond lengths [Å] and angles [º]: Pd-P 2.2688(7), Pd-Cl 2.4121(6), Pd-C13 2.085(2), Pd-C14 2.156(2), Pd-C15 2.279(3); P-Pd-C13 84.84(7), P-Pd-Cl 105.95(2), Cl-Pd-C13 168.84(7).

Determination of the distortion parameter (τ_4) of complex 2b.[5]

The distortion parameter for four coordinated complexes can be obtained by the following equation.

$$\tau_4 = \frac{360° - (\alpha + \beta)}{141°} = \frac{360 - (172.02 + 162.01)}{141} = \mathbf{0.18}$$

P-Pd-Cl (α): 172.02°

C13-Pd-C19 (β): 162.01°

5 L. Yang, D. R. Powell and R. P. Houser, *Dalton Trans.*, 2007, 955-964.