Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

The Surprisingly Facile Formation of Pd(I)-Phosphido Complexes from *ortho*-Biphenylphosphines and Palladium Acetate

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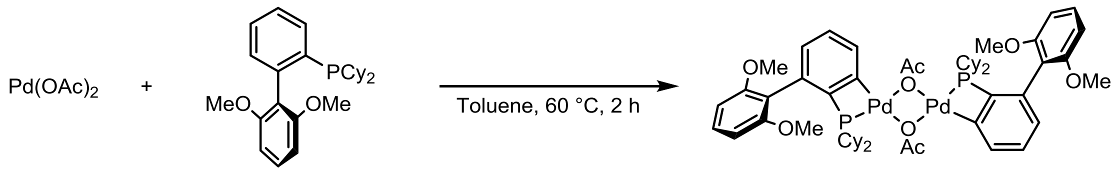
Contents

1. General Considerations

All reactions were performed under an inert atmosphere of nitrogen using standard Schlenk-line techniques unless specified otherwise. All other manipulations were performed under air. All reagents were purchased from commercial suppliers and used as received without further purification. CH_2Cl_2 and toluene and were dried using an Anhydrous Engineering alumina column drying system and all other solvents were either purchased as their anhydrous grade or dried over 3 or 4 Å molecular sieves. Morpholine was filtered through a plug of activated alumina and dried over 4 Å molecular sieves. Column chromatography was performed using technical grade silica gel, pore size 60 Å, 230-400 mesh particle size, 43-60 μm particle size. NMR spectra were recorded on Jeol ECS 300, Bruker Nano 400, Varian VNMRS500 or Bruker Advance III HD 500 cryo spectrometers. Chemical shifts (δ) are quoted in parts per million (ppm), referenced to the residual solvent peak and coupling constants (*J*) are given in Hz. Multiplicities are abbreviated as: a (apparent), br (broad), s (singlet), d (doublet), t (triplet), q (quartet), h (heptet), m (multiplet) or combinations thereof. Mass spectrometry was performed by the University of Bristol mass spectrometry service using a Synapt G2S (nanospray ionisation). GC analysis was performed on an Agilent 7820A equipped with a 5977B MSD. Infrared spectra were recorded using a Perkin Elmer Spectrum Two FT-IR spectrometer. Experimental details for single crystal X-ray diffraction are given in Section 8.

2. Synthesis of Palladium Complexes

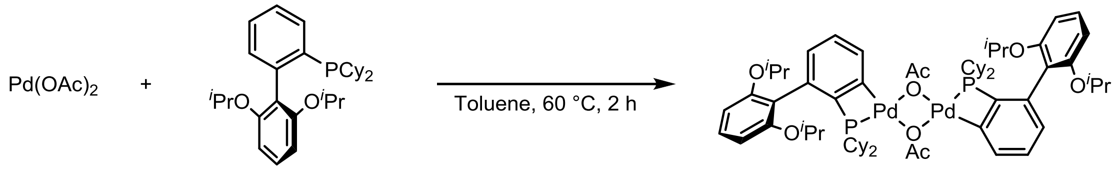
2.1 Synthesis of 1a



A dry Schlenk-tube equipped with a magnetic stirrer bar was charged with $Pd(OAc)_2$ (336.8 mg, 1.5 mmol) and SPhos (615.8 mg, 1.5 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous toluene (9 ml) added. The Schlenk-tube was sealed and the mixture stirred at 60 °C for 2 h before being cooled to room temperature. The volatiles were removed *in vacuo*, Et_2O added and the resulting suspension filtered and washed with Et_2O to afford the desired product as an air-stable dark-grey solid (282.0 mg, 33%). Crystals suitable for analysis by X-ray diffraction were grown from a solution of **1a** in toluene.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.28 (t, *J* = 8.4 Hz, 2H), 7.26 – 7.21 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 2H), 6.79 (dd, *J* = 7.6, 3.1 Hz, 2H), 6.59 (d, *J* = 8.4 Hz, 4H), 3.64 (s, 12H), 2.01 (s, 6H), 1.78 – 1.52 (bm, 24H), 1.22 – 0.98 (bm, 24H); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ 178.9, 158.5, 141.1 (d, *J* = 41.0 Hz), 138.5, 135.9, 133.7 (d, *J* = 28.7 Hz), 129.7, 129.5, 129.3, 128.7, 128.2, 128.0 (d, *J* = 8.8 Hz), 125.8, 118.7 (d, *J* = 4.3 Hz), 104.0, 55.9, 32.2 (d, *J* = 22.3 Hz), 29.8, 28.8, 27.3 (at, *J* = 15.5 Hz), 26.4, 24.7, 21.7; **^{31}P{^{1}H} NMR** (122 MHz, CD_2Cl_2) δ -47.7; **IR** (neat) ν_{max}/cm^{-1} 2925, 2852, 1588, 1470, 1411, 1248, 1110, 728; **HMRS** (nanospray) calculated for $C_{54}H_{71}O_6P_2{}^{106}Pd_2$ $[M-C_2O_2H_3]^+$: 1089.2817, found 1089.2811.

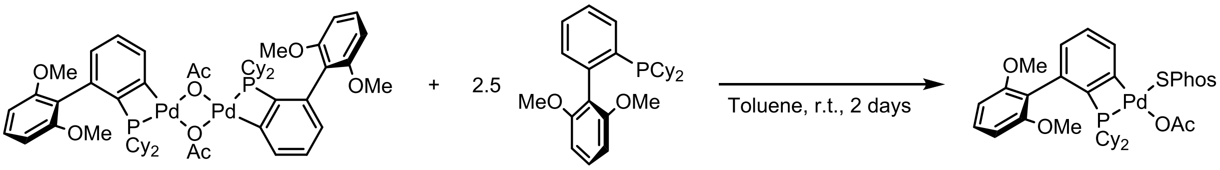
2.2 Synthesis of 1b



A dry Schlenk-tube equipped with a magnetic stirrer bar was charged with $Pd(OAc)_2$ (336.8 mg, 1.5 mmol) and RuPhos (700.0 mg, 1.5 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous toluene (9 ml) added. The Schlenk-tube was sealed and the mixture stirred at 60 °C for 2 h before being cooled to room temperature. The volatiles were removed *in vacuo*, Et_2O added and the resulting suspension filtered and washed with Et_2O to afford the desired product as an air-stable dark-grey solid (200.0 mg, 21%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.22 – 7.17 (m, 4H), 7.05 (t, *J* = 7.6 Hz, 2H), 6.80 (dd, *J* = 4.7, 2.4 Hz, 2H), 6.61 (d, *J* = 8.3 Hz, 4H), 4.32 (hept, *J* = 5.9 Hz, 4H), 2.01 (s, 6H), 1.88 – 1.27 (bm, 44H), 1.15 (d, *J* = 6.0 Hz, 12H), 1.00 (d, *J* = 5.9 Hz, 12H); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ 179.0, 157.9, 141.0 (d, *J* = 41.2 Hz), 136.7, 133.0 (d, *J* = 28.8 Hz), 129.5, 129.1, 128.7, 128.3 (d, *J* = 8.7 Hz), 128.0, 125.8, 124.1, 109.6, 73.1, 32.1 (d, *J* = 22.5 Hz), 29.6, 28.6, 27.4 (at, *J* = 14.2 Hz), 26.2, 24.7, 23.1, 22.2; **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ -47.7; **IR** (neat) ν_{max}/cm^{-1} 2978, 2923, 2852, 1587, 1538, 1456, 1413, 1236, 1108, 1052, 730; **HMRS** (nanospray) calculated for $C_{62}H_{87}O_6P_2{}^{106}Pd_2$ $[M-C_2O_2H_3]^+$: 1201.4048, found 1201.4058.

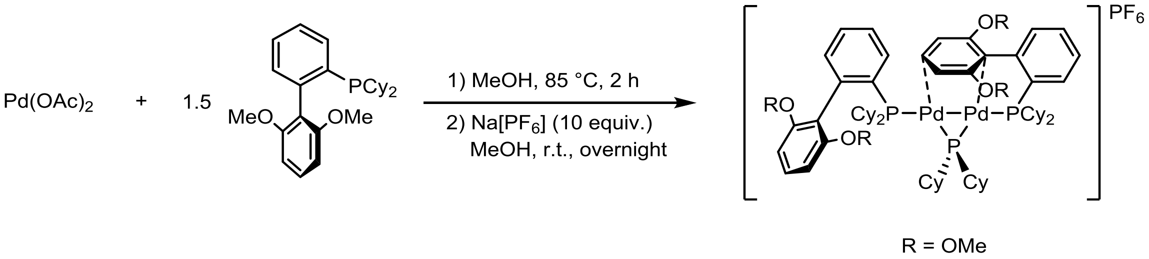
2.3 Synthesis of 3



A dry Schlenk-tube equipped with a magnetic stirrer bar was charged with **1a** (57.5 mg, 0.05 mmol) and SPhos (51.3 mg, 0.125 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous toluene (3 ml) added. The Schlenk-tube was sealed and the mixture stirred at room temperature for 2 days. The solvent was removed *in vacuo* to afford a dark-grey solid (a mixture of **3** and SPhos) which was analysed by ^{31}P NMR and HRMS.

^{31}P NMR (162 MHz, C_7H_8) δ 49.7 (d, *J* = 394.7 Hz), -49.2 (d, *J* = 394.7 Hz); **HMRS** (nanospray) calculated for $C_{52}H_{69}O_4P_2{}^{106}Pd$ $[M-C_2O_2H_3]^+$: 925.3706, found 925.3743.

2.4 Synthesis of 4a



A dry 25 ml Young's tube equipped with a magnetic stirrer bar was charged with $Pd(OAc)_2$ (224.5 mg, 1 mmol) and SPhos (615.8 mg, 1.5 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous methanol (5 ml) added. The tube was sealed and the reaction stirred vigorously at 85 °C for 2 h before being cooled to room temperature. The crude mixture was filtered through a pad of Celite, eluting with EtOAc. The volatiles were removed from the filtrate under reduced pressure and methanol (15 ml) added. To the stirred solution, $NaPF_6$ (839.8 mg, 5 mmol) was added portion-wise and the reaction left stirring overnight at room temperature. The volatiles were removed under reduced pressure and the crude product purified by column chromatography (CH_2Cl_2, collecting the first yellow band) to afford the desired product as an air-stable yellow/orange solid (266.3 mg, 39%).

Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution of **4a** layered with hexane at -18 °C.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.71 (t, *J* = 7.0 Hz, 1H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.55 – 7.41 (m, 5H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.15 (d, *J* = 7.7 Hz, 1H), 6.97 – 6.90 (bm, 1H), 6.75 (d, *J* = 8.4 Hz, 2H), 5.29 (d, *J* = 7.1 Hz, 2H), 3.77 (s, 6H), 3.26 (s, 6H), 2.33 – 2.24 (m, 2H), 2.19 – 2.10 (m, 2H), 1.98 – 1.59 (bm, 32H), 1.41 – 0.87 (bm, 30H); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ 158.4, 149.9, 144.5 (d, *J* = 31.7 Hz), 142.7 (d, *J* = 25.8 Hz), 138.6, 137.7 (d, *J* = 26.1 Hz), 134.4, 133.8, 132.7 (at, *J* = 13.7 Hz), 132.3, 130.5, 129.8, 128.8, 126.1 (d, *J* = 13.9 Hz), 119.5, 104.5, 93.4, 88.5, 55.9, 37.1 (d, *J* = 16.2 Hz), 36.9, 36.2 (d, *J* = 18.9 Hz), 32.9 (d, J = 27.1 Hz), 32.3, 30.5 (d, J = 6.6 Hz), 30.2, 29.3, 27.9 (d, J = 12.0 Hz), 27.5 (at, J = 12.1 Hz), 26.7, 26.5; **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ 280.1 (dd, *J* = 85.4, 70.8 Hz), 46.9 (dd, *J* = 91.4, 85.8 Hz), 45.1 (dd, *J* = 91.3, 70.7 Hz), -144.5 (hept, *J* = 710.4 Hz); **IR** (neat) ν_{max}/cm^{-1} 2976, 2852, 1457, 1419, 1241, 1099, 836, 731, 557; **HMRS** (nanospray) calculated for $C_{64}H_{92}O_4P_3{}^{106}Pd_2$ $[M]^+$: 1229.4278, found 1229.4304.

2.5 Synthesis of 4b

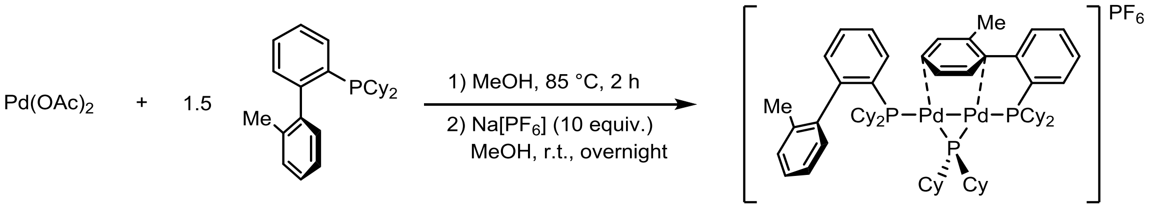
A dry 25 ml Young's tube equipped with a magnetic stirrer bar was charged with $Pd(OAc)_2$ (224.5 mg, 1 mmol) and RuPhos (700 mg, 1.5 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous methanol (5 ml) added. The tube was sealed and the reaction stirred vigorously at 85 °C for 2 h before being cooled to room temperature. The crude mixture was filtered through a pad of Celite, eluting with EtOAc. The volatiles were removed from the filtrate under reduced pressure and methanol (15 ml) added. To the stirred solution, $NaPF_6$ (839.8 mg, 5 mmol) was added portion-wise and the reaction left stirring overnight at room temperature. The volatiles were removed under reduced pressure and the crude product purified by column chromatography (CH_2Cl_2, collecting the first yellow band) to afford the desired product as an air-stable yellow/orange solid (452.6 mg, 61%). Crystals suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution of **4b** at room temperature.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.66 (t, *J* = 6.5 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.49 – 7.43 (m, 3H), 7.37 – 7.33 (m, 2H), 7.26 (d, *J* = 7.7 Hz, 1H), 7.11 (s, 1H), 7.07 (d, *J* = 7.8 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 2H), 5.25 (d, *J* = 7.2 Hz, 2H), 4.55 (hept, *J* = 6.1 Hz, 2H), 4.07 (hept, *J* = 6.1 Hz, 2H), 2.27 – 1.58 (m, 38H), 1.38 – 0.97 (bm, 28H), 1.29 (d, *J* = 6.0 Hz, 6H), 1.09 (d, *J* = 6.2 Hz, 6H), 0.91 (d, *J* = 6.0 Hz, 6H), 0.89 (d, *J* = 5.8 Hz, 6H); **^{13}C{^{1}H} NMR** (126 MHz, CD_2Cl_2) δ 157.7, 149.3, 144.4 (at, *J* = 27.5

Hz), 139.7, 137.2 (d, J = 23.4 Hz), 134.5, 133.1, 132.5 (d, J = 12.0 Hz), 131.9, 130.0, 129.4, 128.2, 125.5 (d, J = 11.8 Hz), 122.9, 107.4, 103.9, 94.6, 89.5, 72.0 (d, J = 23.8 Hz), 37.1 (b), 36.8, 36.2 (d, J = 16.5 Hz), 32.9 (d, J = 26.8 Hz), 32.6 (b), 30.8, 30.3, 29.6, 28.0 (d, J = 10.1 Hz), 27.6 (d, J = 8.2 Hz), 27.2 (d, J = 9.7 Hz), 26.7, 26.6, 22.8, 22.6, 22.3, 21.2; **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ 276.9 (dd, J = 82.5, 75.5 Hz), 46.8 (dd, J = 93.2, 83.8 Hz), 46.1 (dd, J = 94.0, 74.9 Hz), -144.5 (hept, J = 709.6 Hz); **IR** (neat) ν_{max}/cm^{-1} 2922, 2852, 1432, 1238, 1107, 1056, 836, 733, 557; **HMRS** (nanospray) calculated for $C_{72}H_{108}O_4P_3{}^{106}Pd_2$ $[M]^+$: 1341.5530, found 1341.5555.

Note: 2nd order effects observed in ^{31}P NMR.

2.6 Synthesis of 4c



A dry 25 ml Young's tube equipped with a magnetic stirrer bar was charged with $Pd(OAc)_2$ (224.5 mg, 1 mmol) and MePhos (546.8 mg, 1.5 mmol) under air. The atmosphere was evacuated and refilled with nitrogen (x 3) and anhydrous methanol (5 ml) added. The tube was sealed and the reaction stirred vigorously at 85 °C for 2 h before being cooled to room temperature. The crude mixture was filtered through a pad of Celite, eluting with EtOAc. The volatiles were removed from the filtrate under reduced pressure and methanol (15 ml) added. To the stirred solution, $NaPF_6$ (839.8 mg, 5 mmol) was added portion-wise and the reaction left stirring overnight at room temperature. The volatiles were removed under reduced pressure and the crude product purified by column chromatography (CH_2Cl_2, collecting the first yellow band) to afford the desired product as an air-stable yellow/orange solid (67.3 mg, 10%).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.74 – 7.62 (bm, 2H), 7.62 – 7.47 (bm, 4H), 7.33 – 7.23 (bm, 2H), 7.07 (bs, 2H), 6.72 (bs, 4H), 5.33 (s, 2H), 2.24 – 1.56 (bm, 42H), 1.44 – 0.77 (bm, 30H); **^{13}C NMR{^{1}H}** (126 MHz, CD_2Cl_2) δ 145.8 (b), 136.2 (b), 133.1 (b), 131.2 (b), 128.1 (b), 37.1, 36.7, 36.2 (b), 33.1, 32.6, 32.4, 30.9, 30.5 (b), 30.4 (b), 30.2, 29.8 (b), 27.6, 27.5, 27.4, 26.9, 26.6, 26.4, 26.3, 21.2; **^{31}P{^{1}H} NMR** (162 MHz, CD_2Cl_2) δ 290.4 (dd, J = 77.5, 77.1 Hz), 43.0 (bs), -144.5 (hept, J = 710.4 Hz); **IR** (neat) ν_{max}/cm^{-1} 2922, 2849, 1446, 835, 762, 732, 556; **HMRS** (nanospray) calculated for $C_{62}H_{88}P_3{}^{106}Pd_2$ $[M]^+$: 1137.4169, found 1137.4194.

Note: Due to the broad nature of the ^{13}C peaks, some resonances were not observed.

3. Solvent Screen for the Formation of 4a

A dry Young's NMR tube was charged with Pd(OAc)$_2$ (3.0 mg, 0.013 mmol) and SPhos (8.2 mg, 0.02 mmol). The atmosphere was evacuated and refilled with nitrogen (x 3) and the desired anhydrous solvent (0.7 ml) was added. The NMR tube was sealed, shaken, and then heated at 85 °C for 2 h. The reaction was subsequently analysed by ^{31}P NMR. The results are shown in Figure 1.

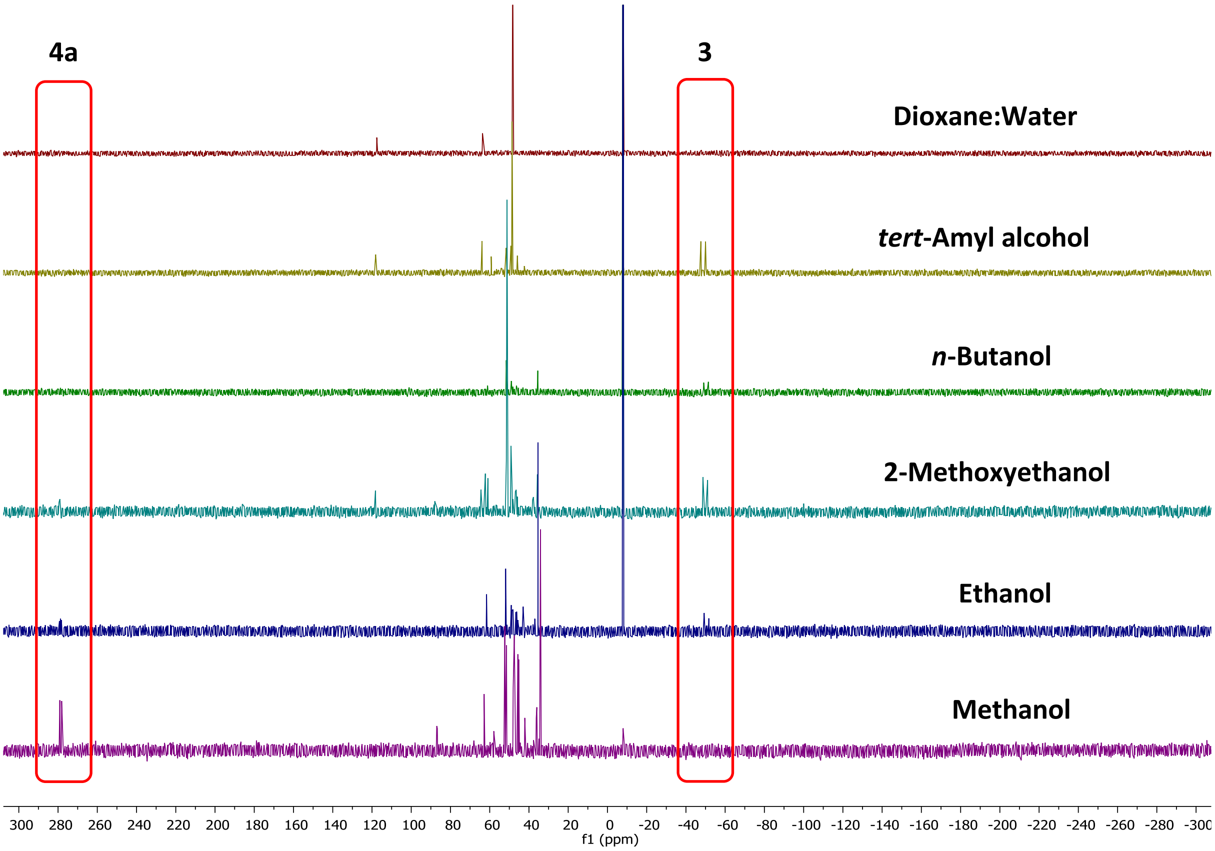


Figure 1: ^{31}P NMR spectra of the reaction between Pd(OAc)$_2$ and SPhos in various solvents.

4. Variable Temperature NMR

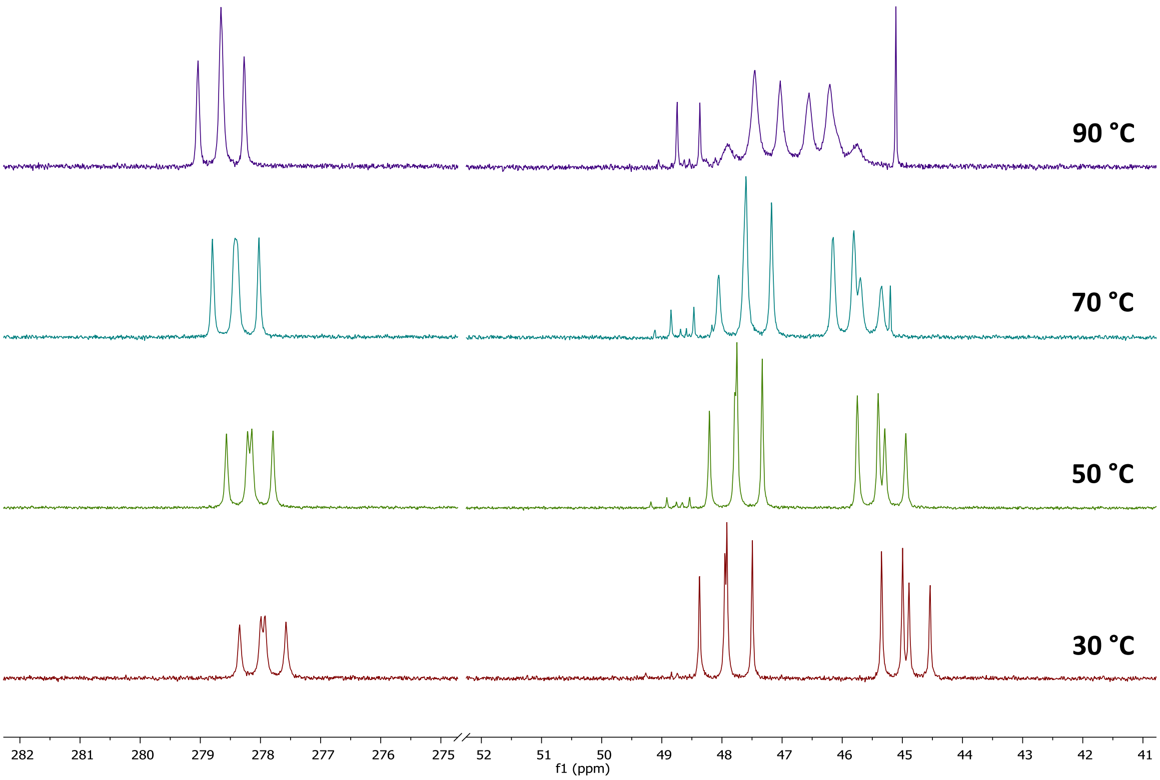


Figure 2: Variable temperature ^{31}P NMR (202 MHz, DMSO-d_6) of **4a**.

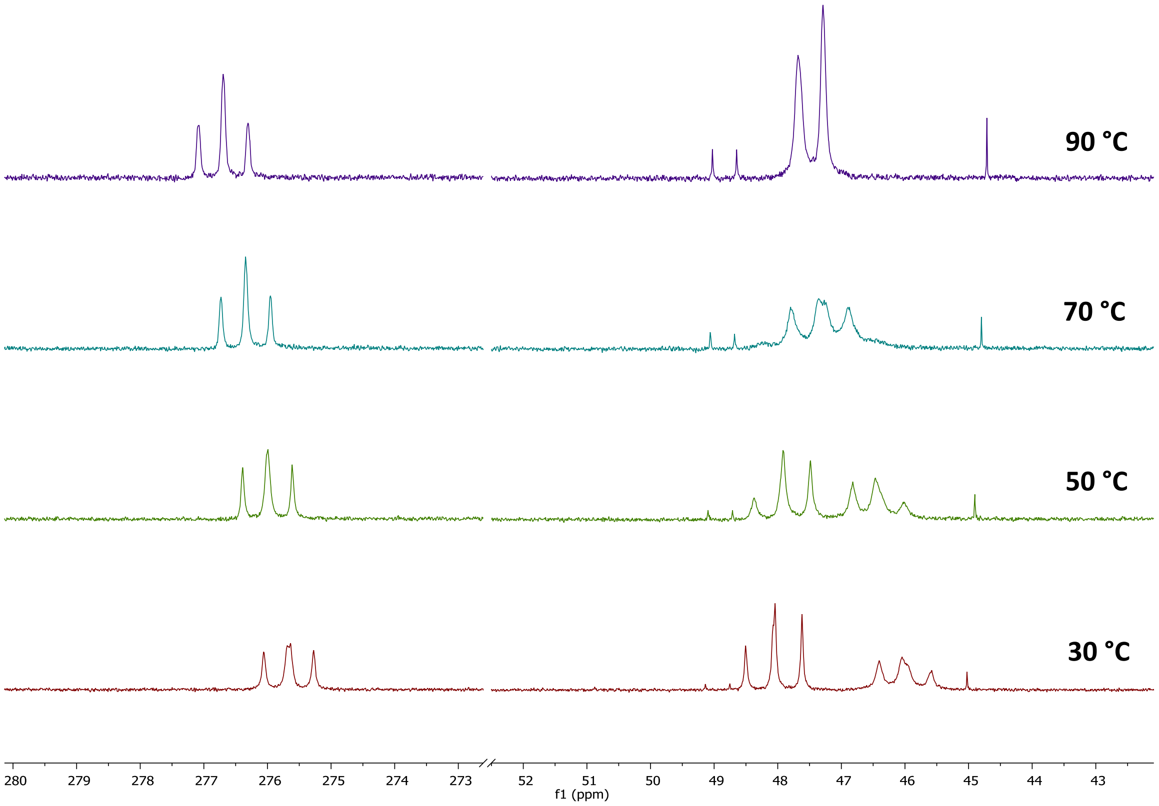
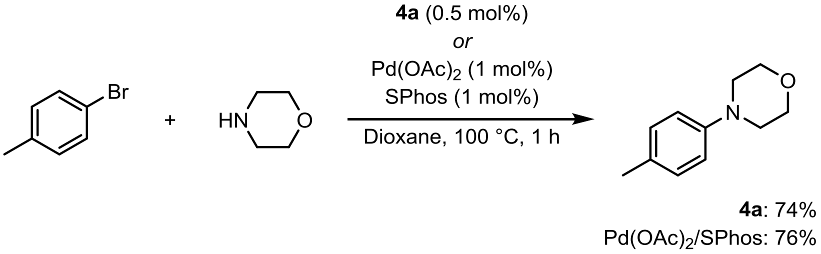


Figure 3: Variable temperature ^{31}P NMR (202 MHz, DMSO-d_6) of **4b**.

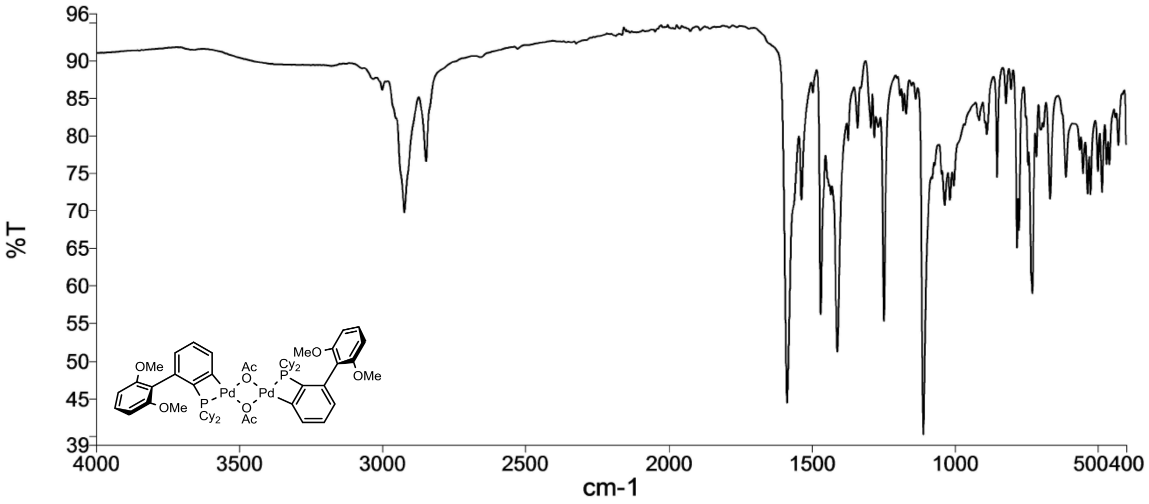
5. Amination



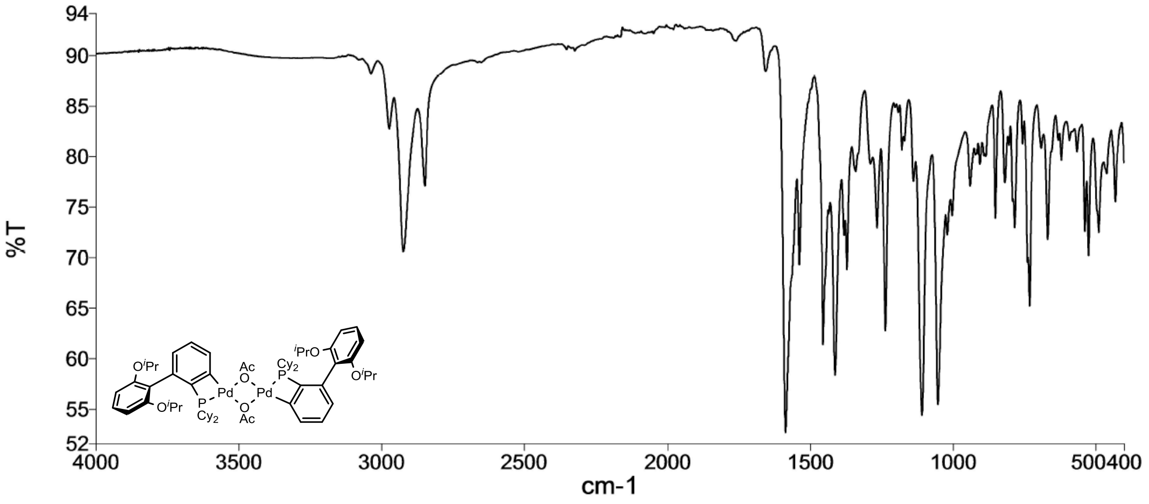
A dry Schlenk-tube equipped with a magnetic stirrer bar was charged with either **4a** (6.9 mg, 0.01 mmol) or a mixture of $Pd(OAc)_2$ (4.5 mg, 0.02 mmol) and SPhos (8.2 mg, 0.02 mmol) under air. NaO^tBu (269.1 mg, 2.8 mmol) and 4-bromotoluene (342.1 mg, 2.0 mmol) were added and the atmosphere evacuated and refilled with nitrogen (x 3). Morpholine (245 µl, 2.8 mmol) and anhydrous 1,4-dioxane (2 ml) were added, the Schlenk-tube sealed and the mixture stirred at 100 °C for 1 h. After cooling to room temperature, dodecane (454 µl, 2.0 mmol) was added to the mixture and an aliquot removed and passed through a plug of Celite, eluting with EtOAc, for analysis by GC.

6. IR Spectra

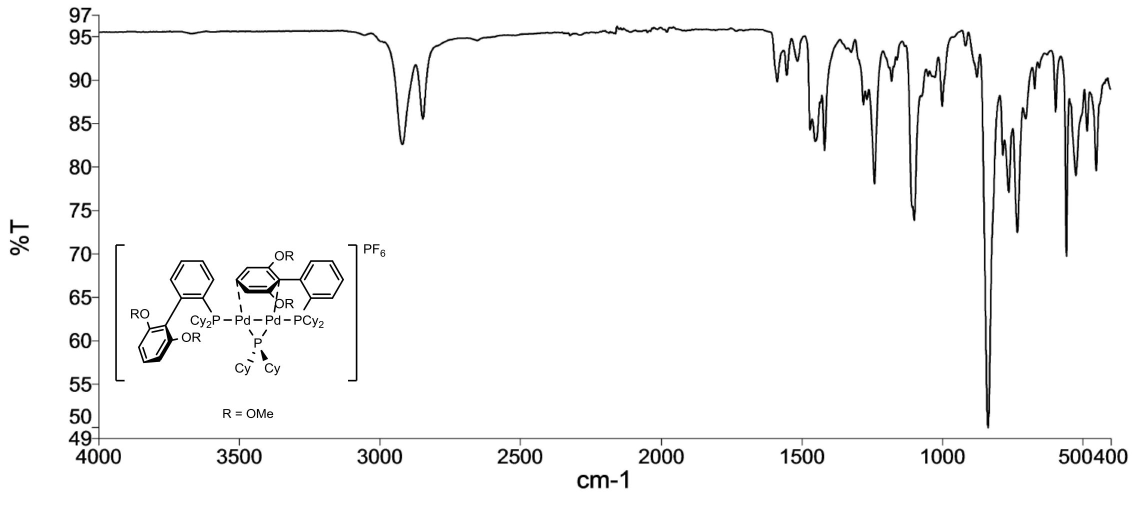
1a:



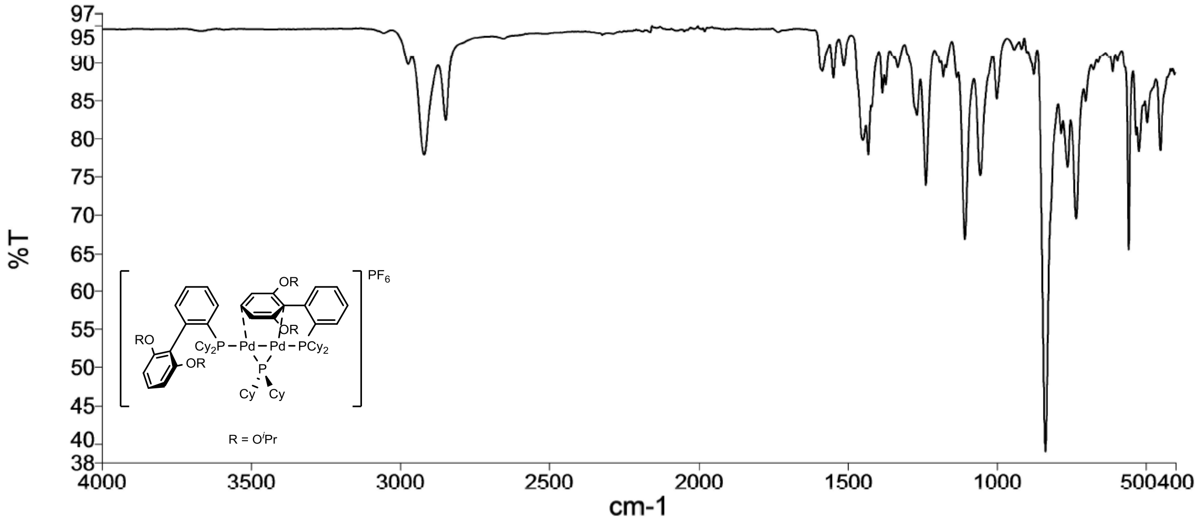
1b:



4a:



4b: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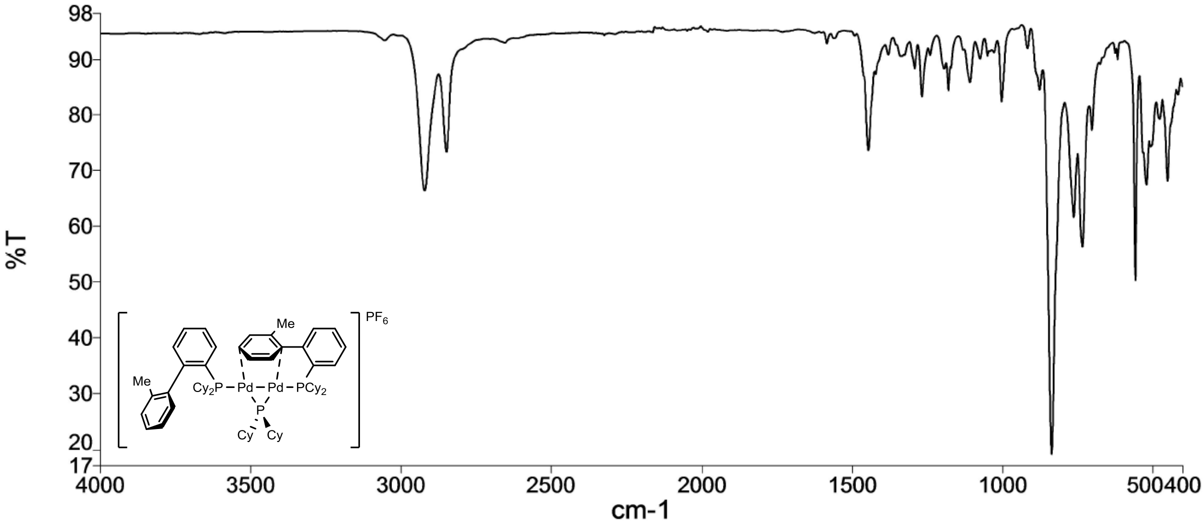
4c: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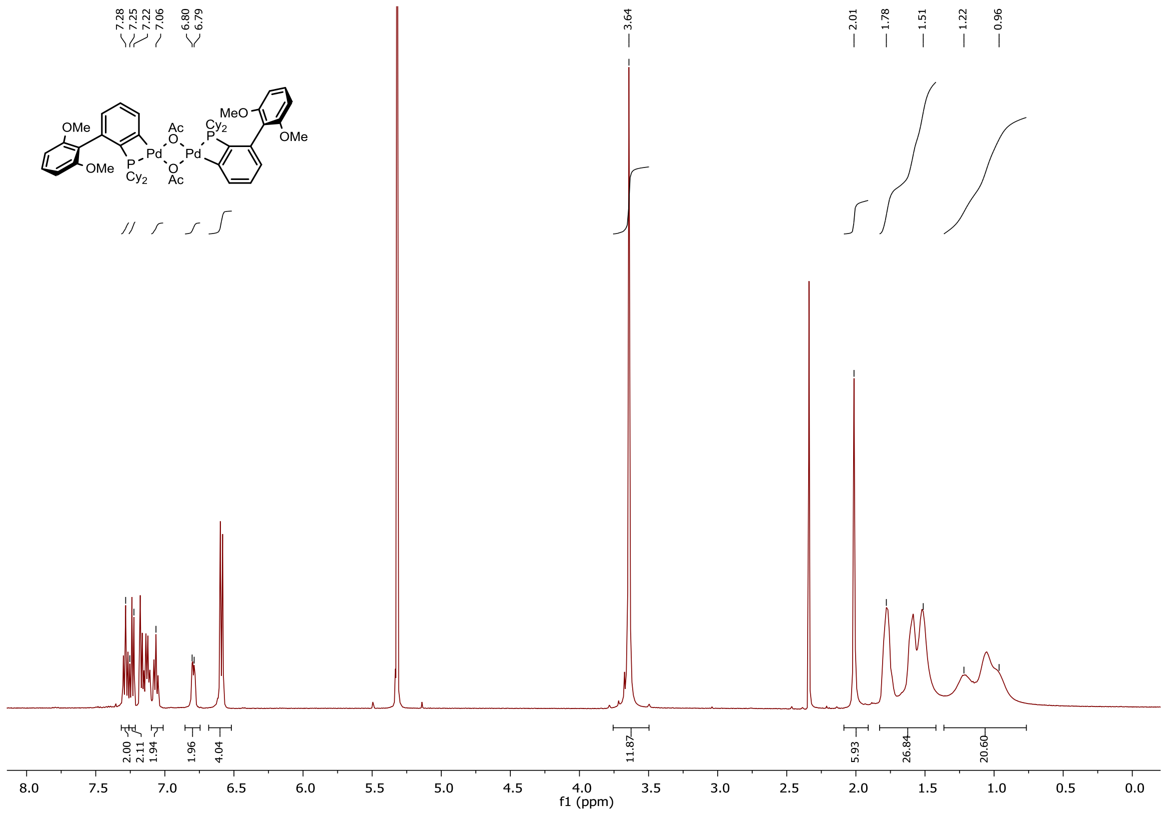
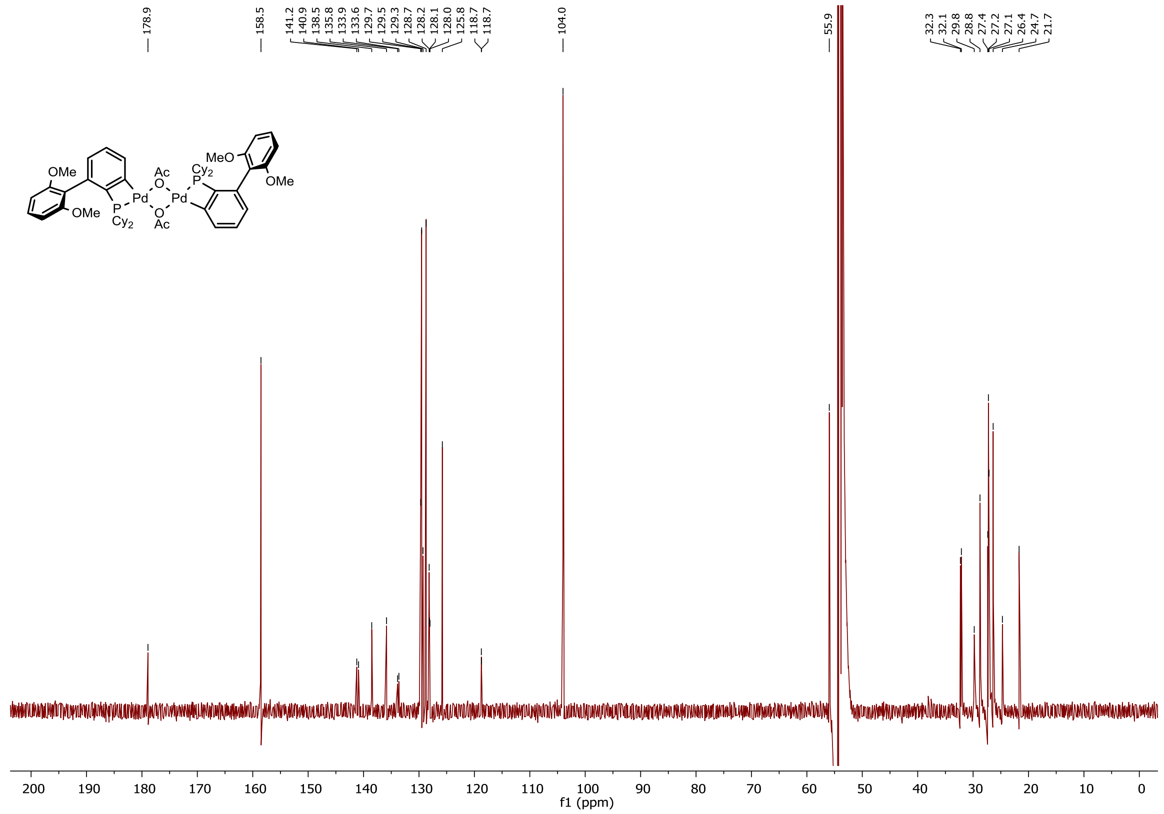
Cy
Cy

7. NMR Spectra

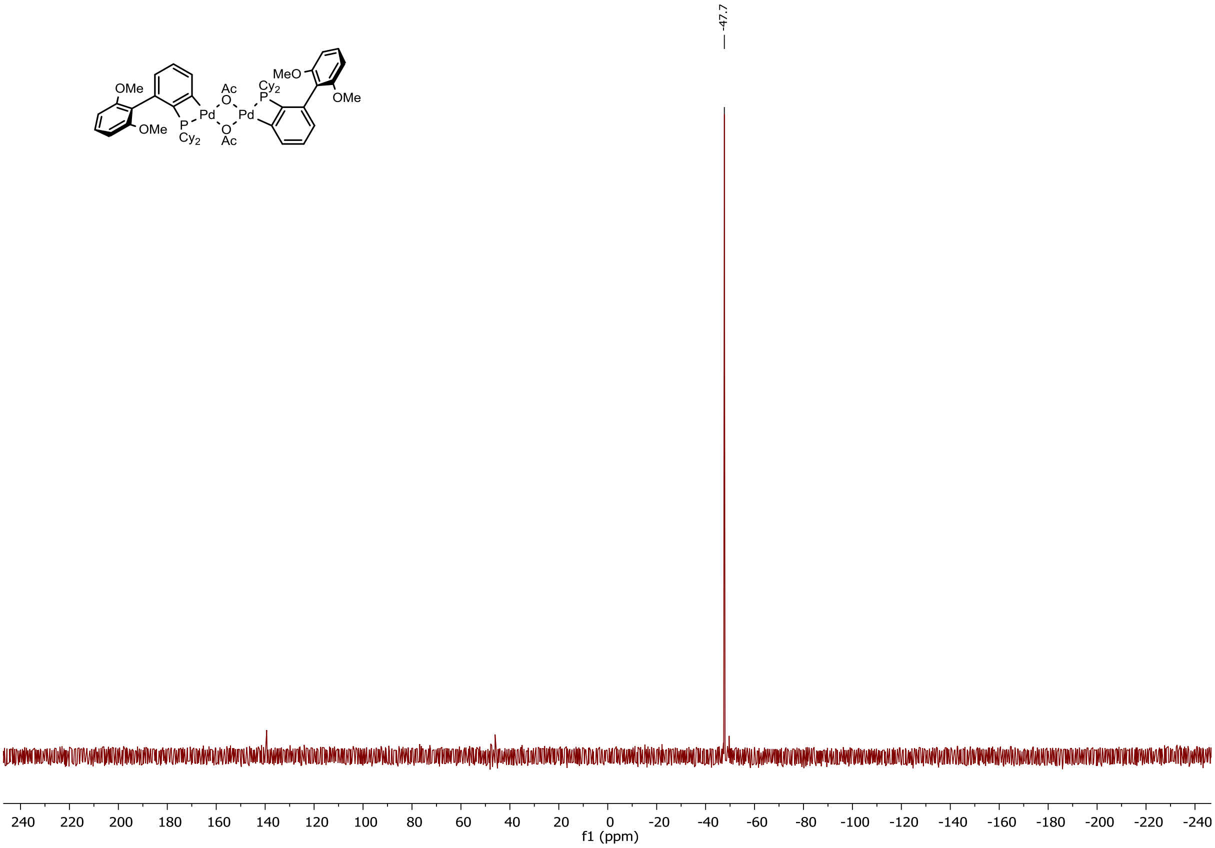
1a (^{1}H NMR, 500 MHz, CD_2Cl_2):



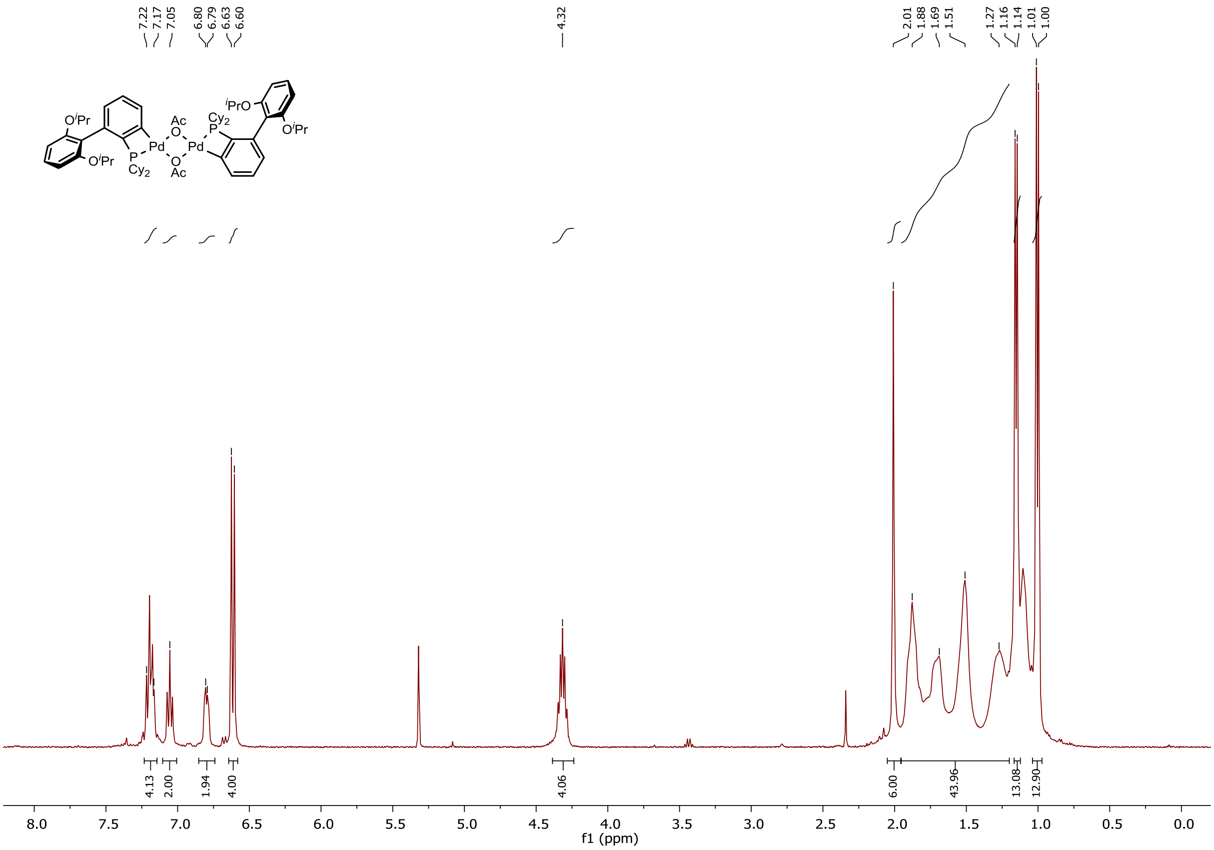
1a (^{13}C NMR, 126 MHz, CD_2Cl_2):



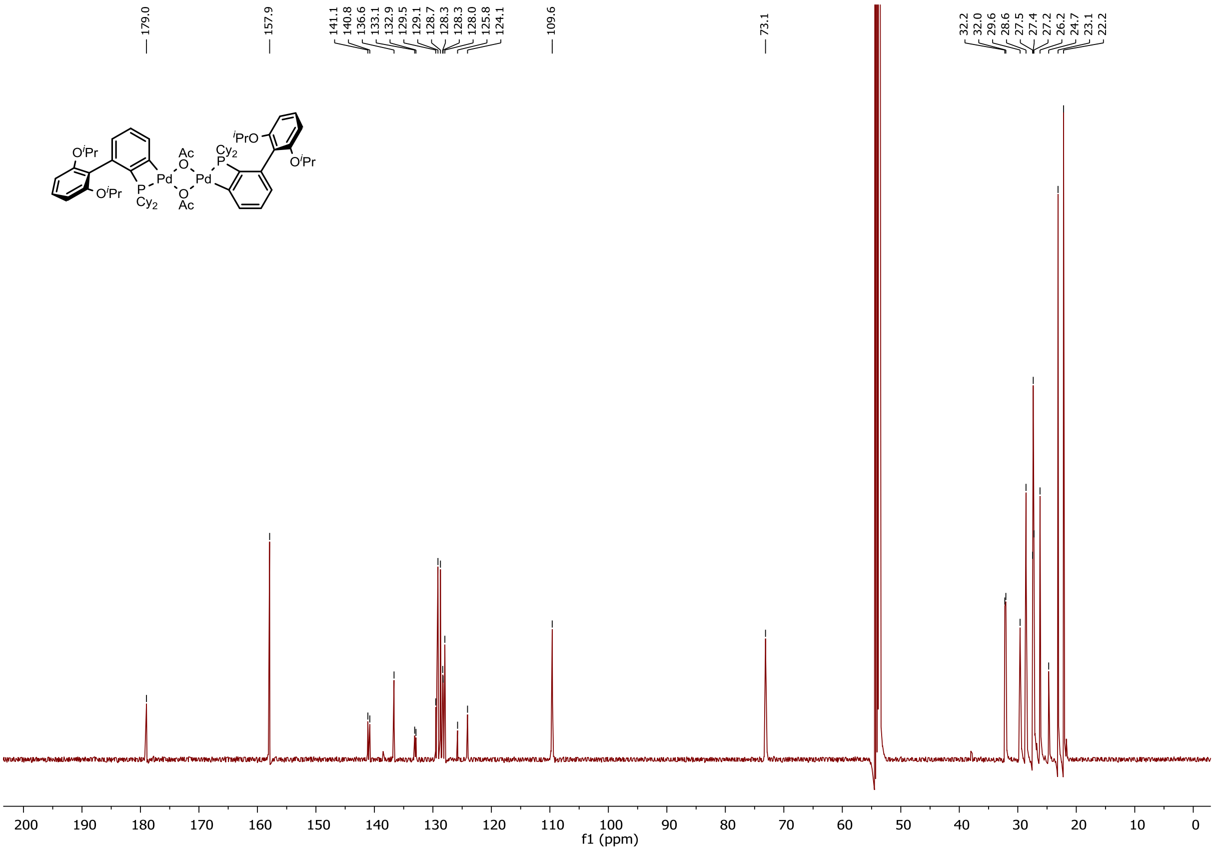
1a (^{31}P NMR, 122 MHz, CD_2Cl_2):



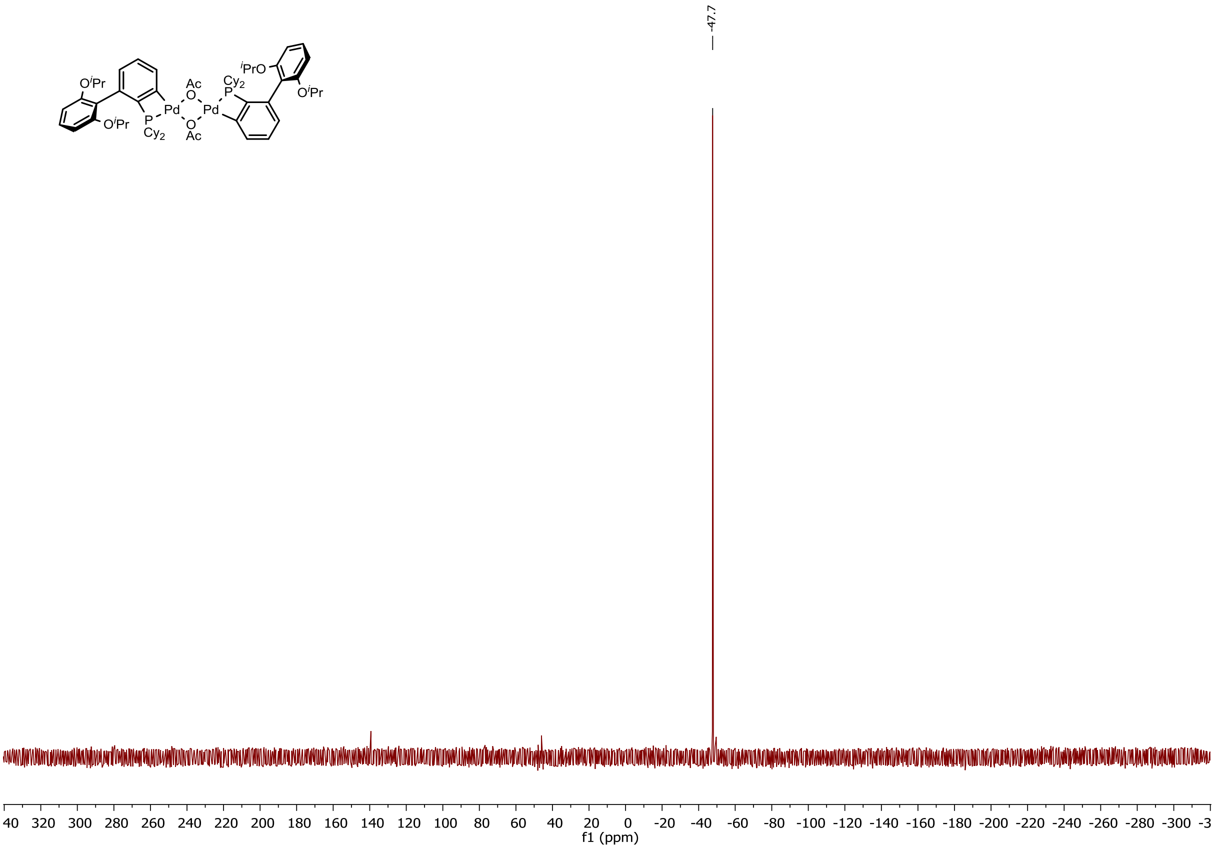
1b (^{1}H NMR, 400 MHz, CD$_2$Cl$_2$):



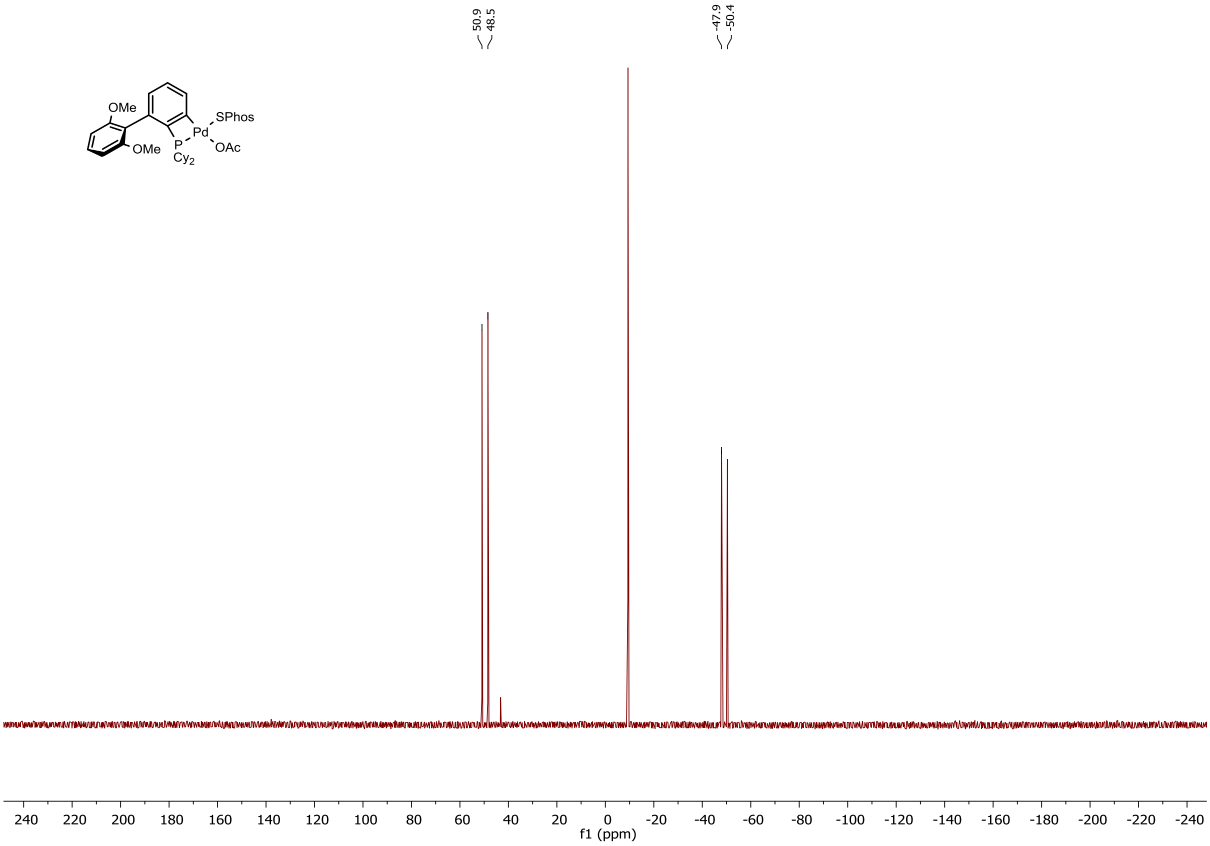
1b (^{13}C NMR, 126 MHz, CD$_2$Cl$_2$):



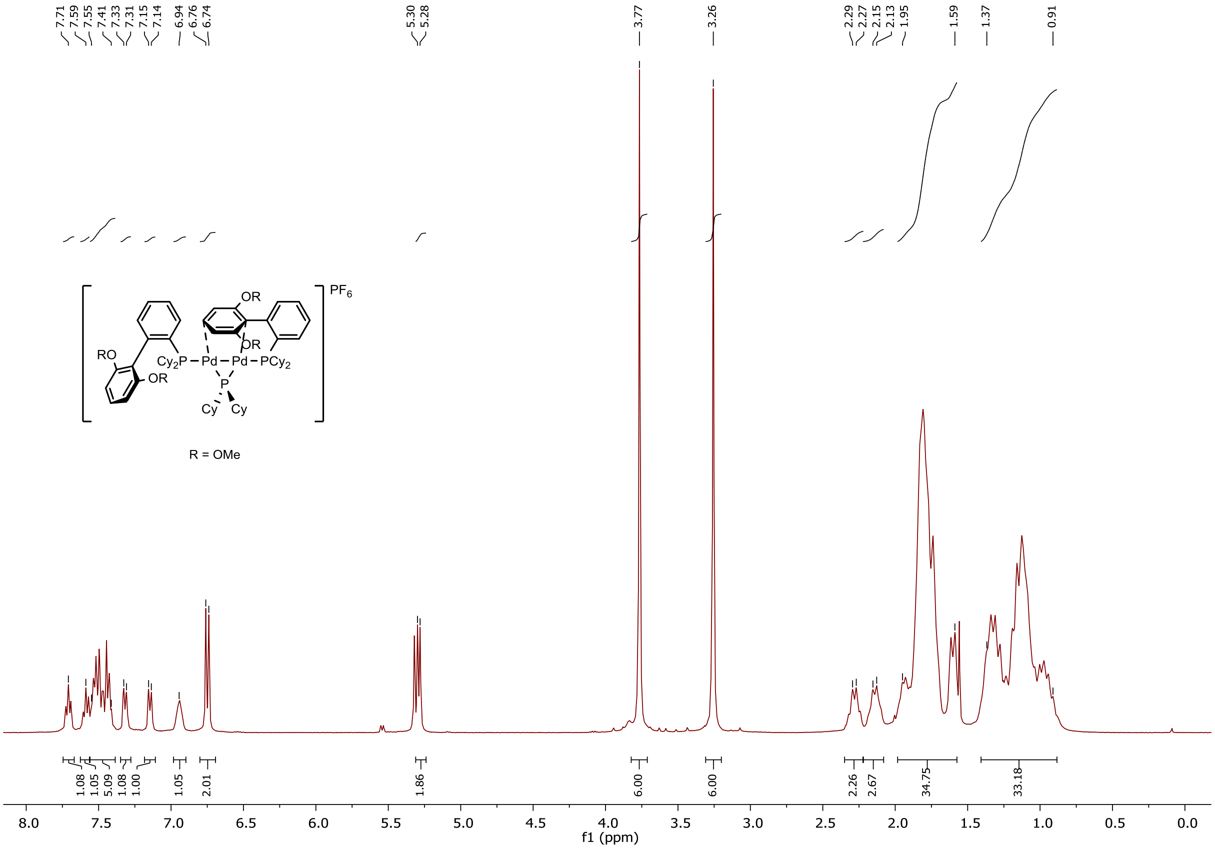
1b (^{31}P NMR, 162 MHz, CD_2Cl_2):



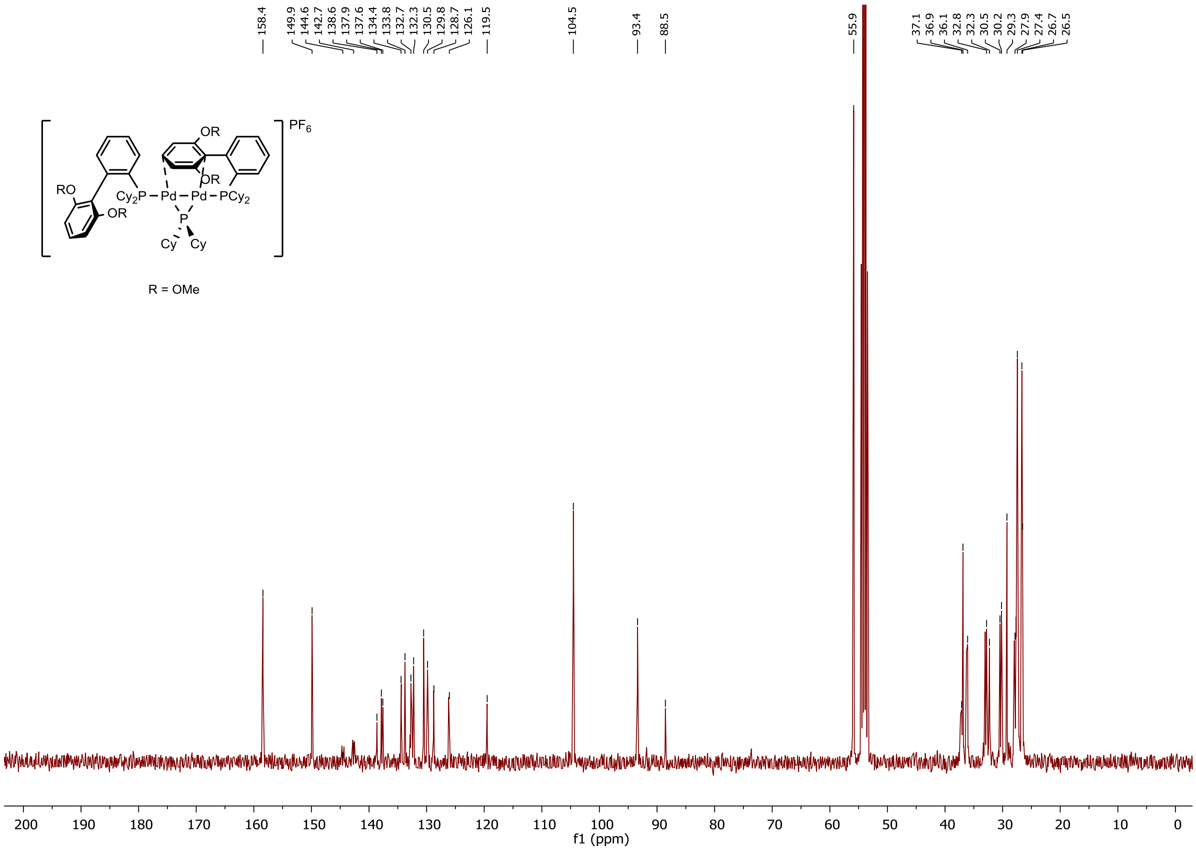
3 (^{31}P NMR, 162 MHz, C_7H_8):



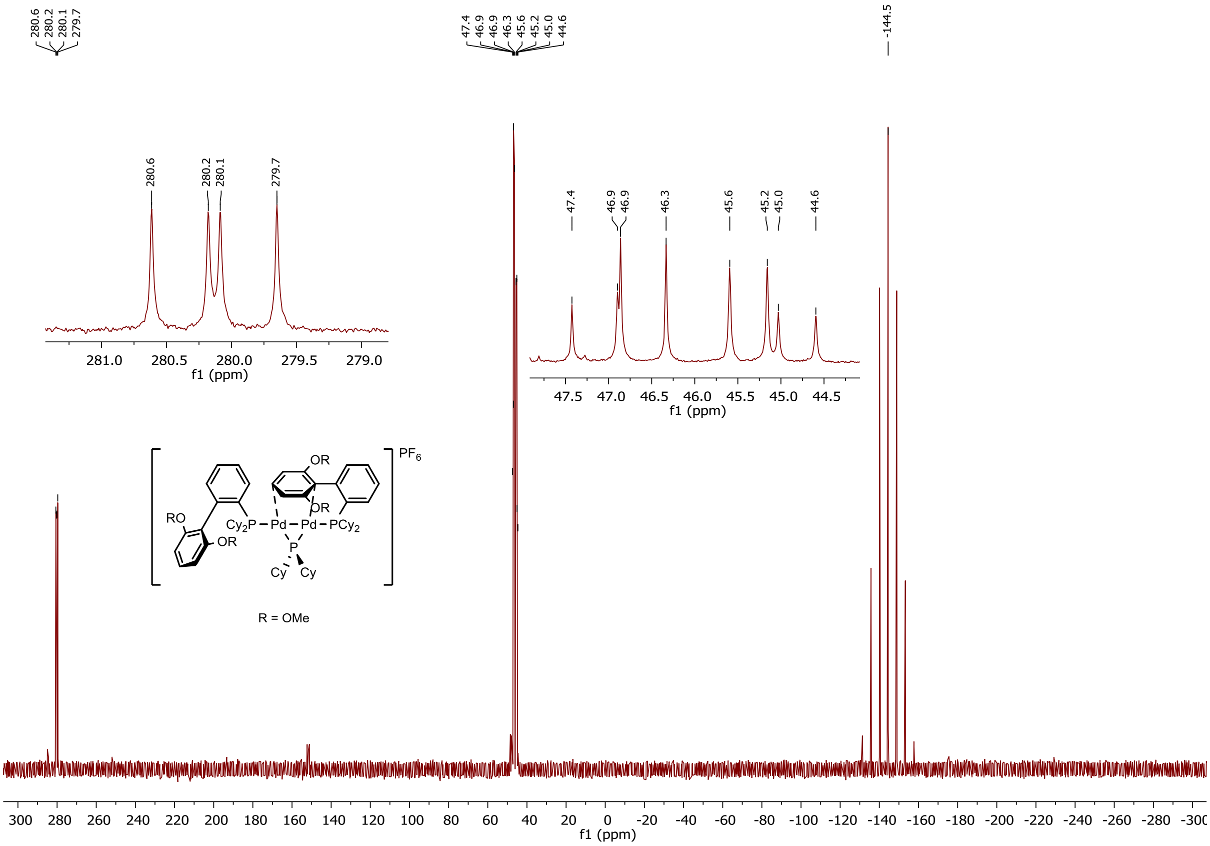
4a (^{1}H NMR, 400 MHz, CD_2Cl_2):



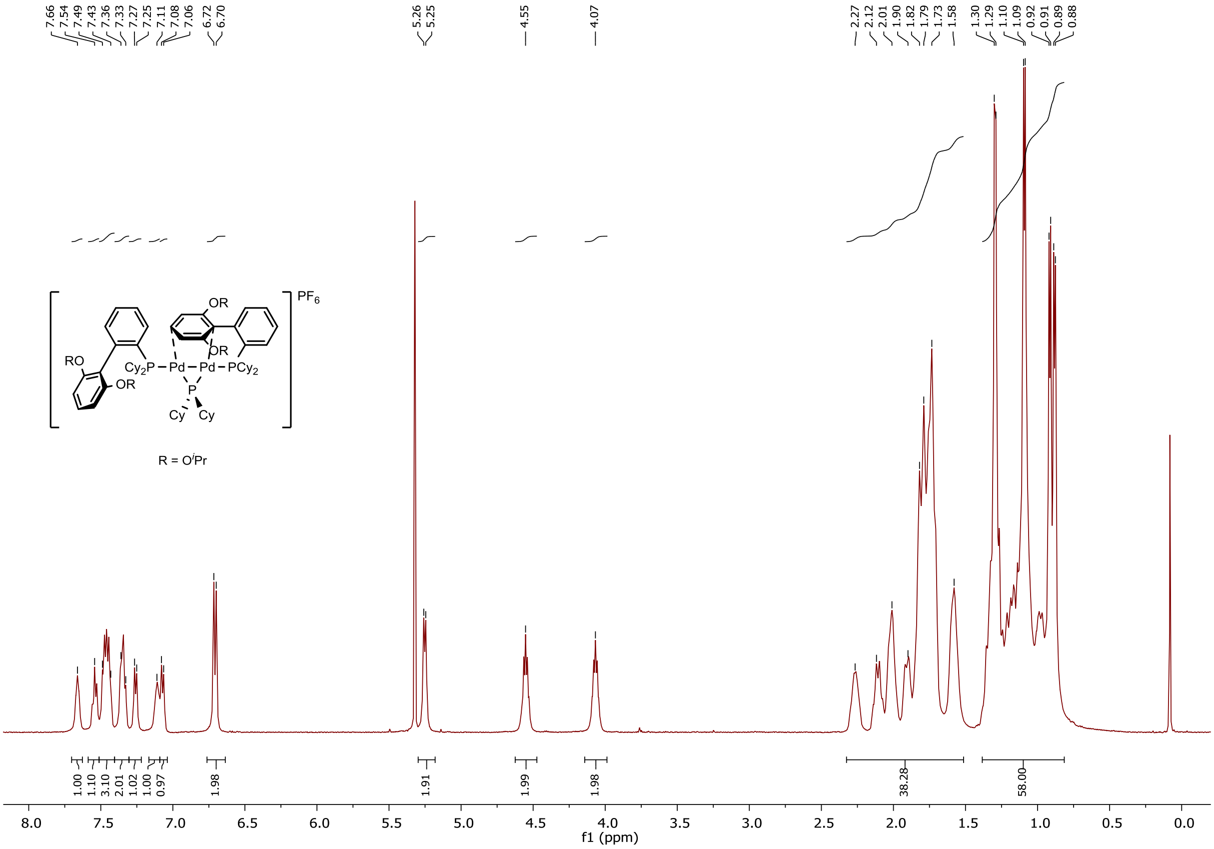
4a (^{13}C NMR, 126 MHz, CD_2Cl_2):



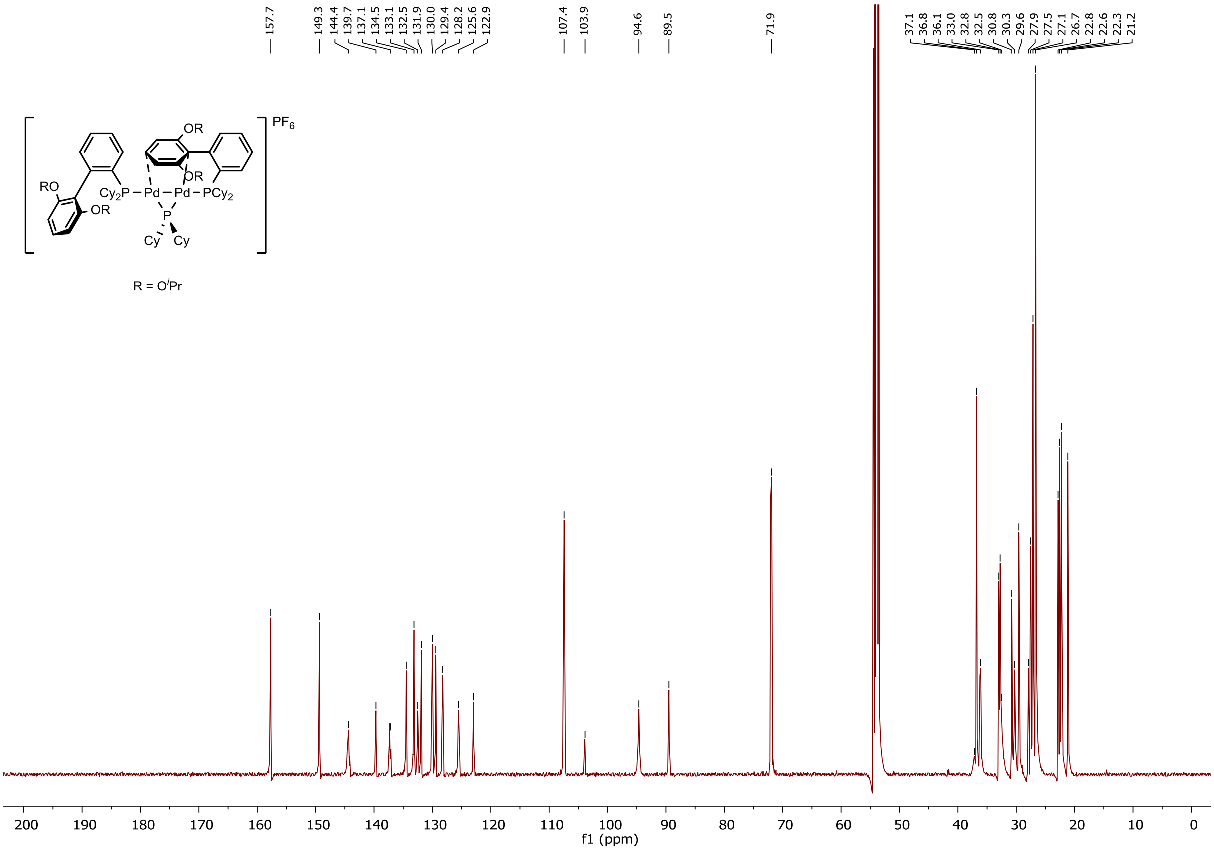
4a (^{31}P NMR, 162 MHz, CD$_2$Cl$_2$):



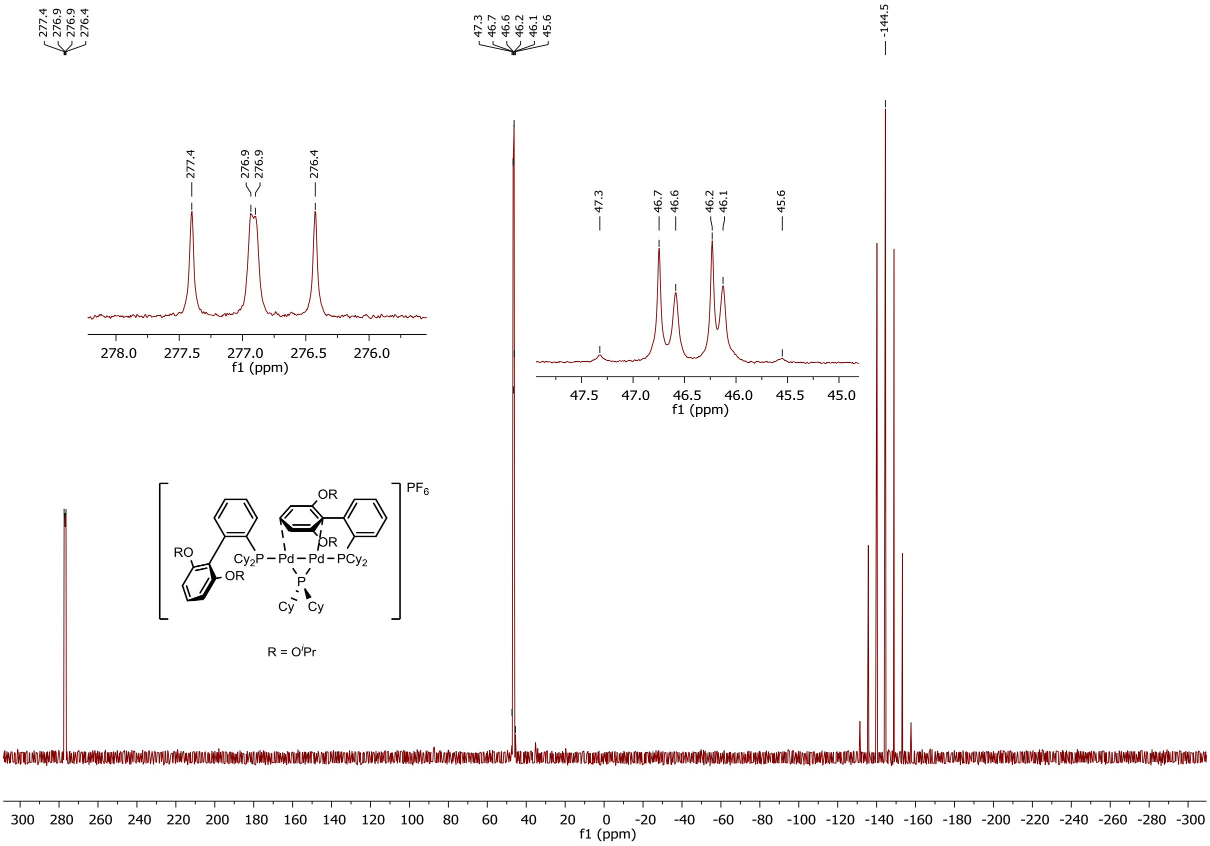
4b (^{1}H NMR, 500 MHz, CD_2Cl_2):



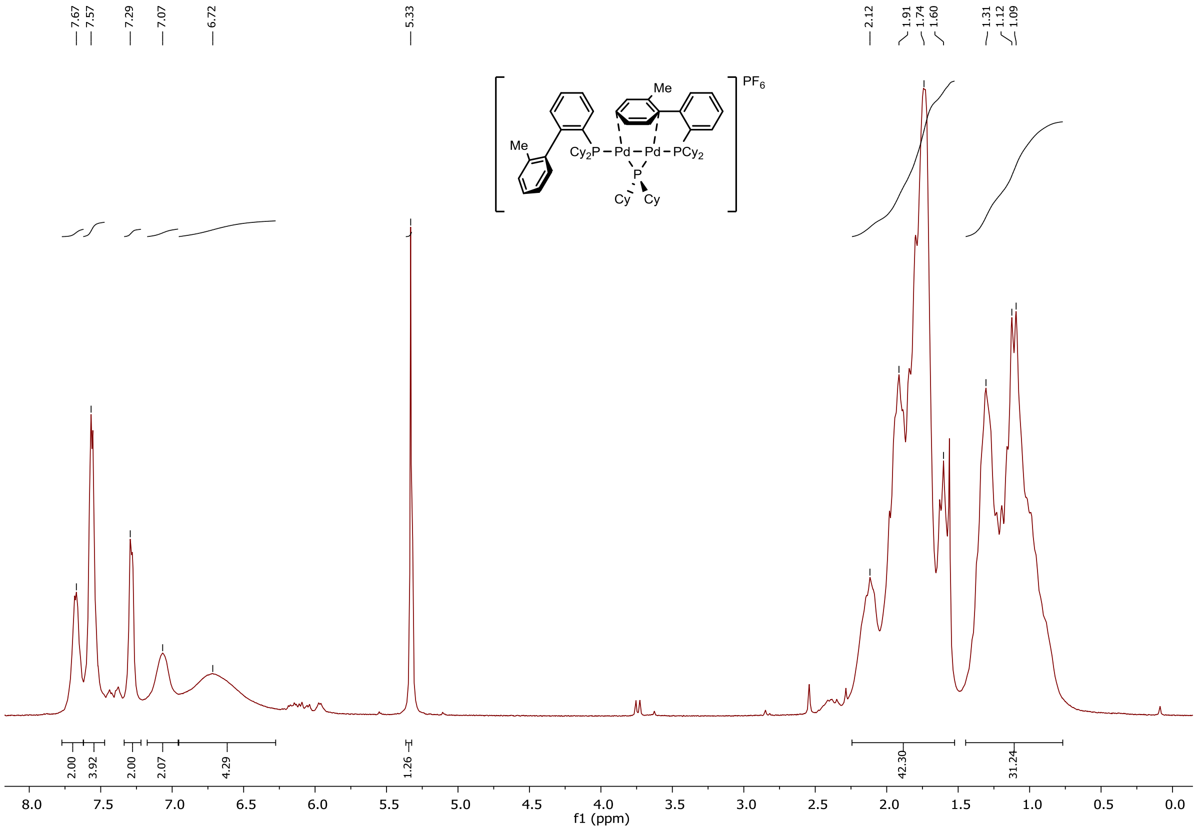
4b (^{13}C NMR, 126 MHz, CD_2Cl_2):



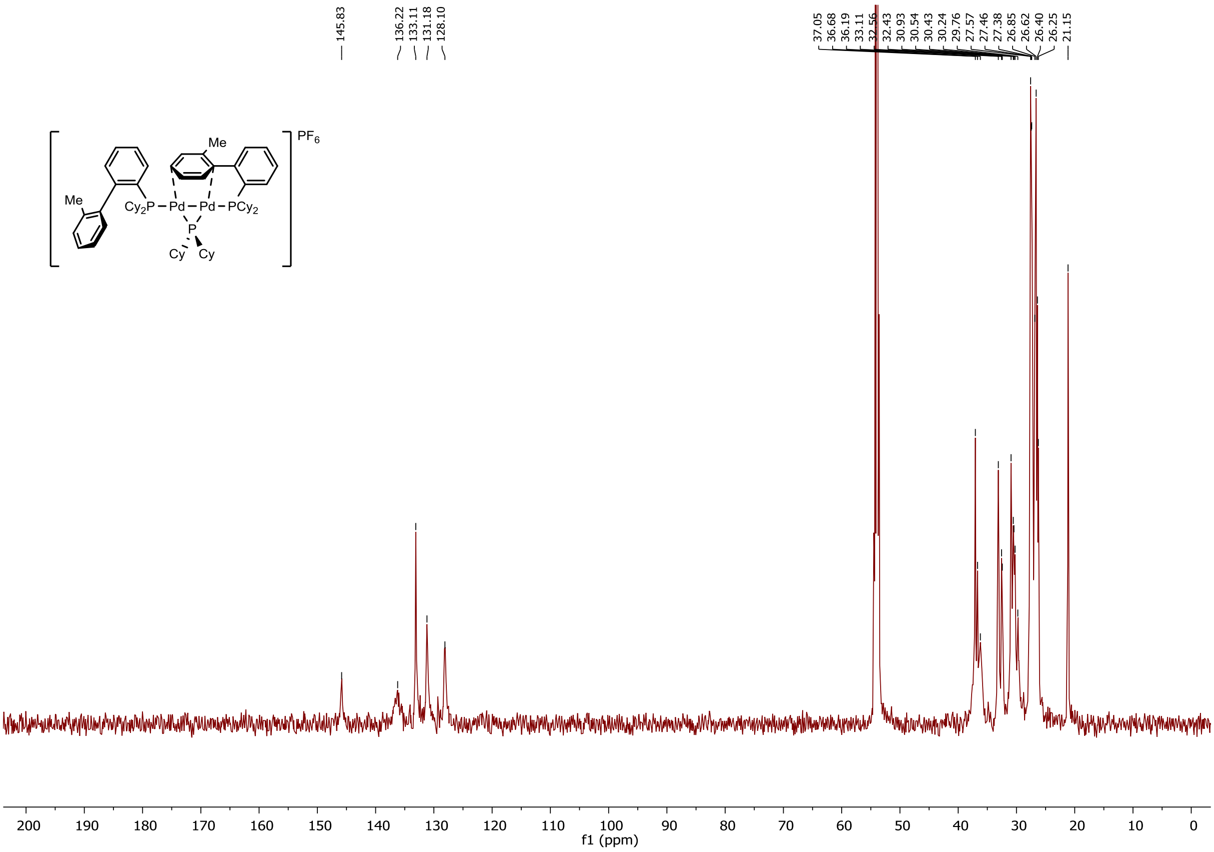
4b (^{31}P NMR, 162 MHz, CD$_2$Cl$_2$):



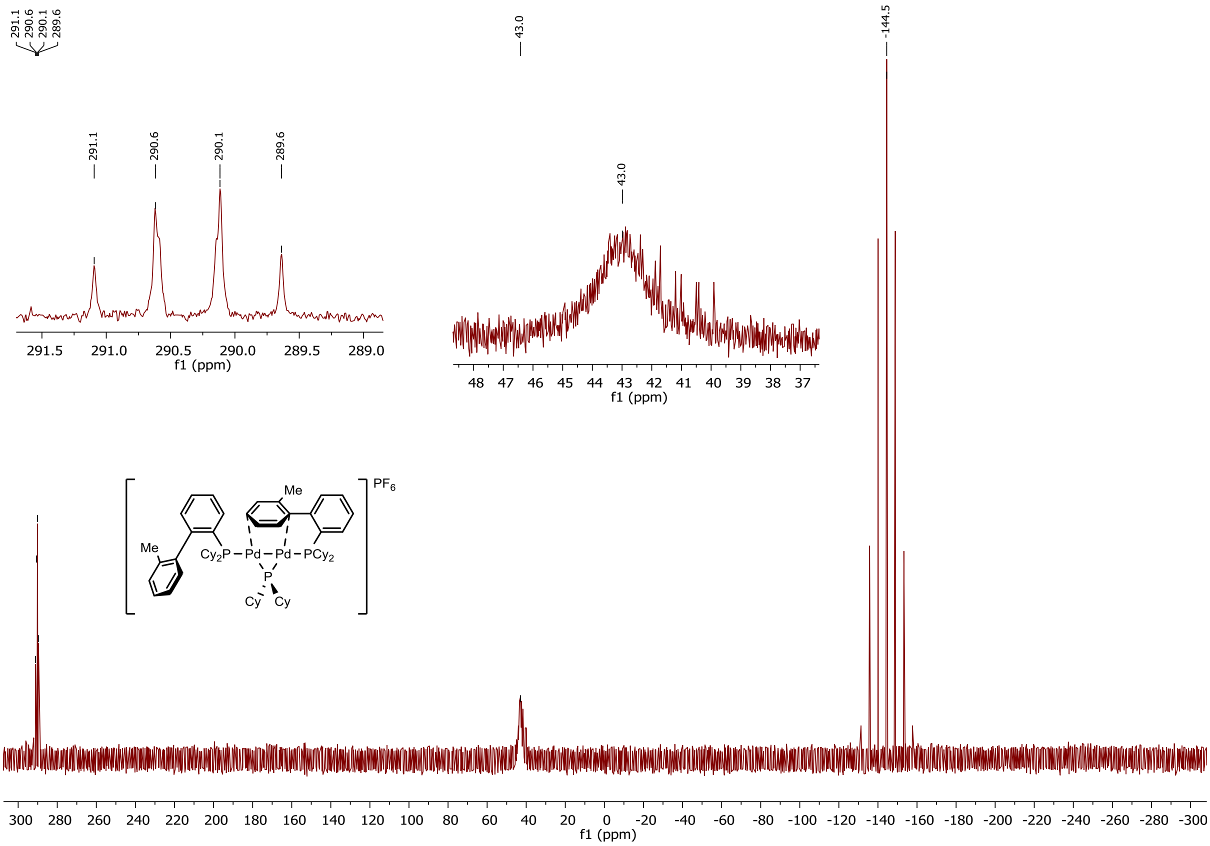
4c (^{1}H NMR, 400 MHz, CD_2Cl_2):



4c (^{13}C NMR, 126 MHz, CD_2Cl_2):



4c (^{31}P NMR, 162 MHz, CD_2Cl_2):



8. Single Crystal X-Ray Diffraction

X-ray diffraction experiments on **1a**, **2**, **4a** and **4b** were carried out at 100(2) K on a Bruker APEX II CCD diffractometer using Mo-K_α radiation (λ = 0.71073 Å). Intensities were integrated in SAINT[1] and absorption corrections based on equivalent reflections were applied using SADABS.[2] Structures **1a**, **2**, **4a** and **4b** were solved using ShelXT,[3] all of the structures were refined by full matrix least squares against F^2 in ShelXL[4, 5] using Olex2.[6] All of the non-hydrogen atoms were refined anisotropically, while all of the hydrogen atoms were located geometrically and refined using a riding model. In **4a** one of the PF_6^- was disordered and necessarily modelled at 50% occupancy. Squeeze within Platon[7, 8] was used to remove disordered solvent from the lattice of **4b** that could not be sensibly modelled. Crystal structure and refinement data are given in Table 1. Crystallographic data for compounds **1a**, **2**, **4a** and **4b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 1884584-1884587. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax(+44) 1223 336033, e-mail: deposit@ccdc.cam.ac.uk].

Table 1: Crystal data and structure refinement for **1a**, **2**, **4a** and **4b**.

Identification code	**1a**	**2**	**4a**	**4b**
Empirical formula	$C_{63}H_{82}O_8P_2Pd_2$	$C_{52}H_{68}Cl_2O_4P_2Pd_2$	$C_{64}H_{92}F_6O_4P_4Pd_2$	$C_{72}H_{108}F_6O_4P_4Pd_2$
Formula weight	1242.02	1102.70	1376.05	1488.26
Temperature/K	100(2)	100(2)	100(2)	100(2)
Crystal system	monoclinic	triclinic	monoclinic	triclinic
Space group	*P*2/*n*	*P*-1	*C*2/*c*	*P*-1
a/Å	12.7552(6)	9.3085(2)	28.2770(6)	11.5721(4)
b/Å	11.4178(6)	10.5148(3)	10.8401(2)	15.3228(5)
c/Å	19.7866(11)	13.9103(3)	41.2461(9)	22.4790(7)
α/°	90	74.2420(10)	90	85.7858(14)
β/°	100.144(3)	72.2210(10)	98.0020(10)	75.7187(15)
γ/°	90	69.1100(10)	90	69.5539(15)
Volume/Å^3	2836.6(3)	1190.83(5)	12519.9(4)	3619.0(2)
Z	2	1	8	2
ρ_{calc}g/cm^3	1.454	1.538	1.460	1.366
μ/mm^{-1}	0.746	0.980	0.741	0.646
F(000)	1292.0	568.0	5712.0	1556.0
Crystal size/mm^3	0.39 × 0.29 × 0.15	0.48 × 0.40 × 0.31	0.45 × 0.44 × 0.18	0.69 × 0.52 × 0.42
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	3.536 to 55.992	4.218 to 55.822	3.988 to 55.87	1.87 to 56.154

Index ranges	$-16 \le h \le 15$, $-14 \le k \le 15$, $-26 \le l \le 25$	$-12 \le h \le 12$, $-13 \le k \le 13$, $-18 \le l \le 18$	$-37 \le h \le 21$, $-14 \le k \le 14$, $-54 \le l \le 54$	$-15 \le h \le 15$, $-20 \le k \le 20$, $-26 \le l \le 29$
Reflections collected	25647	21946	56350	67277
R_{int} / R_{sigma}	0.0444 / 0.0421	0.0166 / 0.0149	0.0569 / 0.0531	0.0229 / 0.0207
Data/restraints/parameters	6850/0/344	5702/0/282	14958/0/758	17529/0/804
Goodness-of-fit on F^2	1.006	1.073	1.032	1.031
Final R indexes [I>=2σ (I)]	$R_1 = 0.0312$, $wR_2 = 0.0646$	$R_1 = 0.0199$, $wR_2 = 0.0508$	$R_1 = 0.0412$, $wR_2 = 0.0893$	$R_1 = 0.0263$, $wR_2 = 0.0600$
Final R indexes [all data]	$R_1 = 0.0449$, $wR_2 = 0.0702$	$R_1 = 0.0217$, $wR_2 = 0.0518$	$R_1 = 0.0603$, $wR_2 = 0.0970$	$R_1 = 0.0305$, $wR_2 = 0.0618$
Largest diff. peak/hole / e Å^{-3}	1.11/-0.54	0.56/-0.24	1.06/-0.64	1.45/-0.72

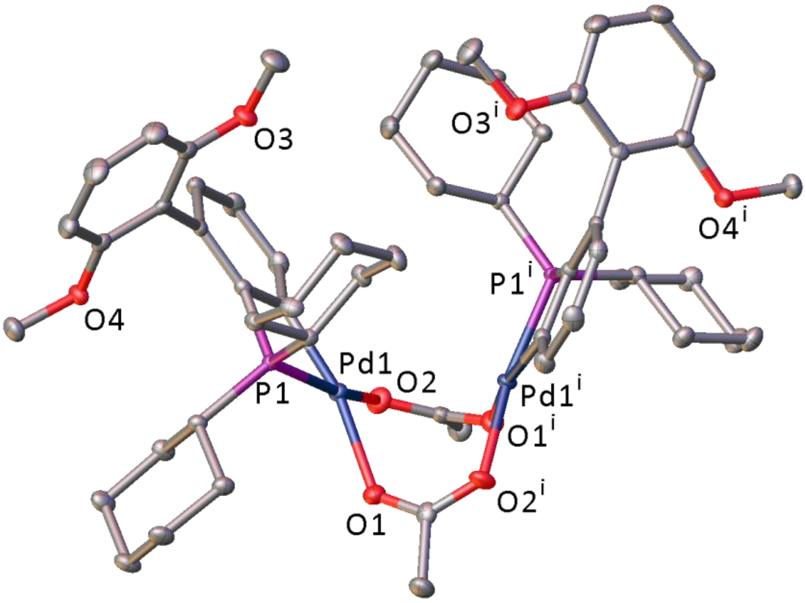


Figure 4: Crystal structure of **1a**, with hydrogen atoms and toluene solvent omitted for clarity. Symmetry code ^{i} ½-x, +y, ½-z.

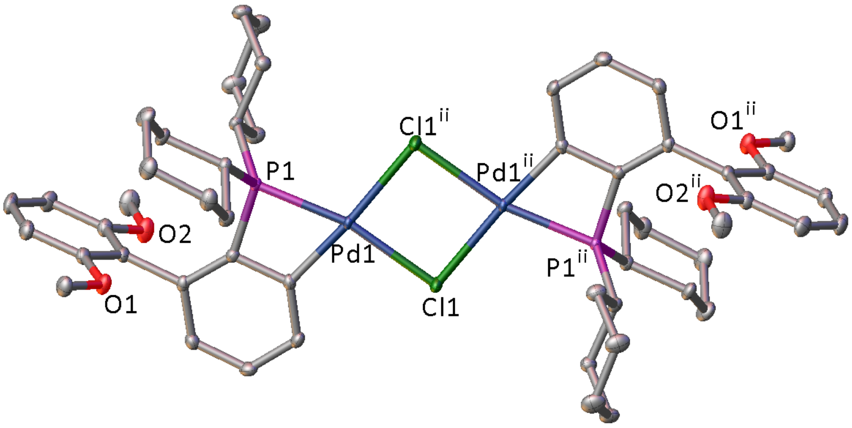


Figure 5: Crystal structure of **2**, with hydrogen atoms omitted for clarity. Symmetry code ^{ii} 1-x, -y, -z.

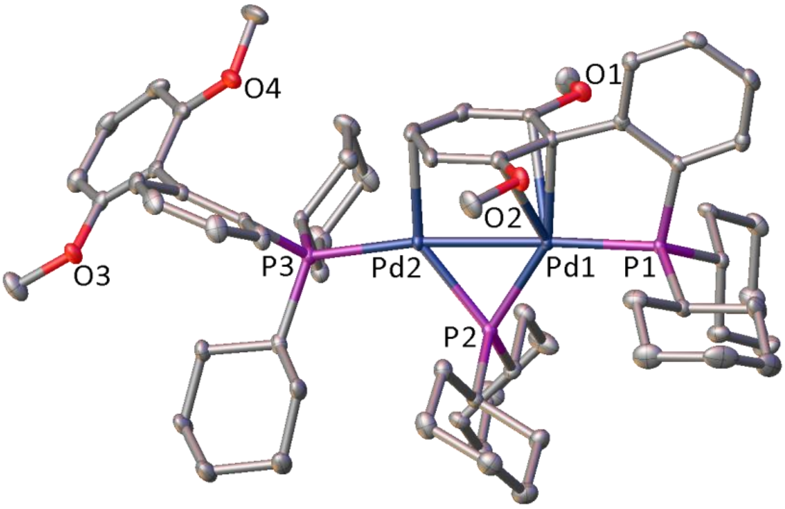


Figure 6: Crystal structure of **4a**, with hydrogen atoms and PF_6^- counterions omitted for clarity.

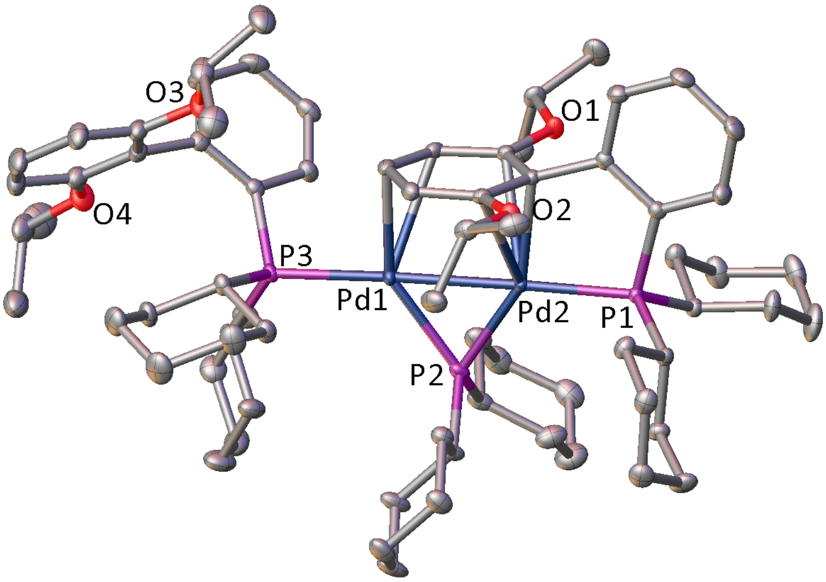


Figure 7: Crystal structure of **4b**, with hydrogen atoms and PF_6^- counterion omitted for clarity.

9. References

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