Supporting information

Synthesis, characterization, and reactivity of [Pd(phosphine)(py)Cl_2] (PEPPSI) and [Pd(phosphine)Cl_2]$_2$ complexes.

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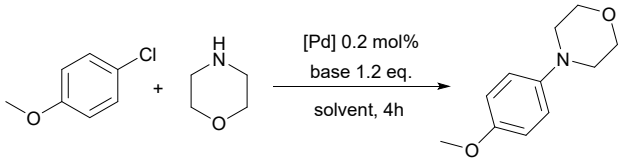
Optimization studies

Table S1. Catalyst and conditions screening in C-N coupling of morpholine and 4-chloroanisole.[a]



Entry	Catalyst	Solvent	Base	Temperature, °C	Additive[b]	GC yield (%)[c]
1	2a	THF	NaO^{t}Bu	85	-	52
2	2b	THF	NaO^{t}Bu	85	-	74
3	3a	THF	NaO^{t}Bu	85	-	33
4	3b	THF	NaO^{t}Bu	85	-	41
5	4a	THF	NaO^{t}Bu	85	-	31
6	4b	THF	NaO^{t}Bu	85	-	30
7	5a	THF	NaO^{t}Bu	85	-	42
8	5b	THF	NaO^{t}Bu	85	-	30
9	5c	THF	NaO^{t}Bu	85	-	22
10	2b	THF	NaO^{t}Bu	85	-	97[c]
11	2b	THF	KO^{t}Bu	85	-	27
12	2b	Me-THF	NaO^{t}Bu	85	-	77
13	2b	Me-THF	KO^{t}Bu	85	-	54
14	2b	^{t}BuOH	Cs_2CO_3	85	-	18
15	**2b**	**Toluene**	**NaO^{t}Bu**	**85**	**-**	**97**
16	5a	Toluene	NaO^{t}Bu	85	-	33
17	5b	Toluene	NaO^{t}Bu	85	-	31
18	5c	Toluene	NaO^{t}Bu	85	-	22
19	2b	THF	NaO^{t}Bu	60	-	24
20	5a	THF	NaO^{t}Bu	35	-	<10
21	2b	THF	NaO^{t}Bu	RT	-	<10
22	2b	Toluene	NaO^{t}Bu	85	+	71
23	5a	Toluene	NaO^{t}Bu	85	+	83
24	5b	Toluene	NaO^{t}Bu	85	+	50
25	5c	Toluene	NaO^{t}Bu	85	+	40
26	2a	THF	NaO^{t}Bu	85	+	83
27	2b	THF	NaO^{t}Bu	85	+	90
28	3b	THF	NaO^{t}Bu	85	+	88
29	5a	THF	NaO^{t}Bu	85	+	90

30	5b	THF	NaO^{t}Bu	85	+	87
31	5c	THF	NaO^{t}Bu	85	+	49
32	2b	THF	NaO^{t}Bu	RT	+	<10
33	5c	THF	NaO^{t}Bu	RT	+	<10

[a] 4-chloroanisole (1 mmol), morpholine (1.2 mmol), base (1.2 mmol), catalyst (0.2 mol% Pd) and solvent (2 mL). Reaction time 4h at indicated temperature. [b] 3-pentanone (10 mol%) [c] Yield was determined using gas chromatography with dodecane as internal standard and is average of 2 runs.

Crystallographic data of complexes

CCDC 2221473-2221475 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures

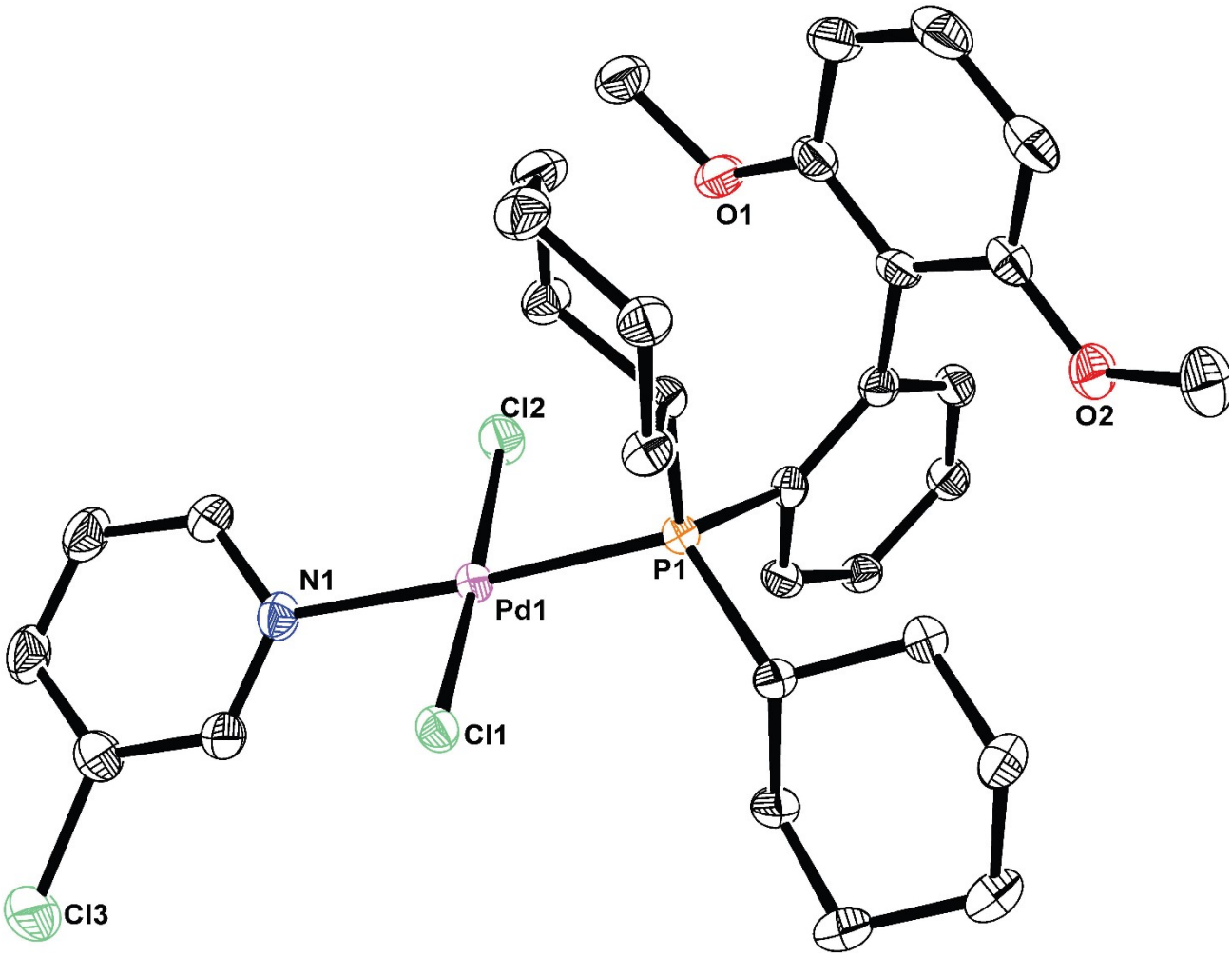


Figure S1. Molecular structure of the complex **3b**

Table S2. Crystal data and structure refinement for **3b**.

Empirical formula	$C_{31}H_{39}Cl_3NO_2PPd$
Formula weight	701.35
Temperature/K	100.0(1)
Crystal system	Orthorhombic
Space group	P212121
a/Å	8.74090(10)
b/Å	16.5403(2)
c/Å	21.5878(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3121.10(7)

Z	4
ρ_{calc}g/cm^3	1.493
μ/mm^{-1}	7.868
F(000)	1440.0
Crystal size/mm^3	0.188 × 0.105 × 0.068
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.732 to 147.7
Index ranges	-10 ≤ h ≤ 10, -20 ≤ k ≤ 20, -25 ≤ l ≤ 26
Reflections collected	27105
Independent reflections	6239 [R_{int} = 0.0393, R_{sigma} =0.0306]
Data/restraints/parameters	6239/0/354
Goodness-of-fit on F^2	1.036
Final R indexes [I>=2σ (I)]	R_1 = 0.0230, wR_2 = 0.0526
Final R indexes [all data]	R_1 = 0.0260, wR_2 = 0.0540
Largest diff. peak/hole / e Å^{-3}	0.32/-0.41

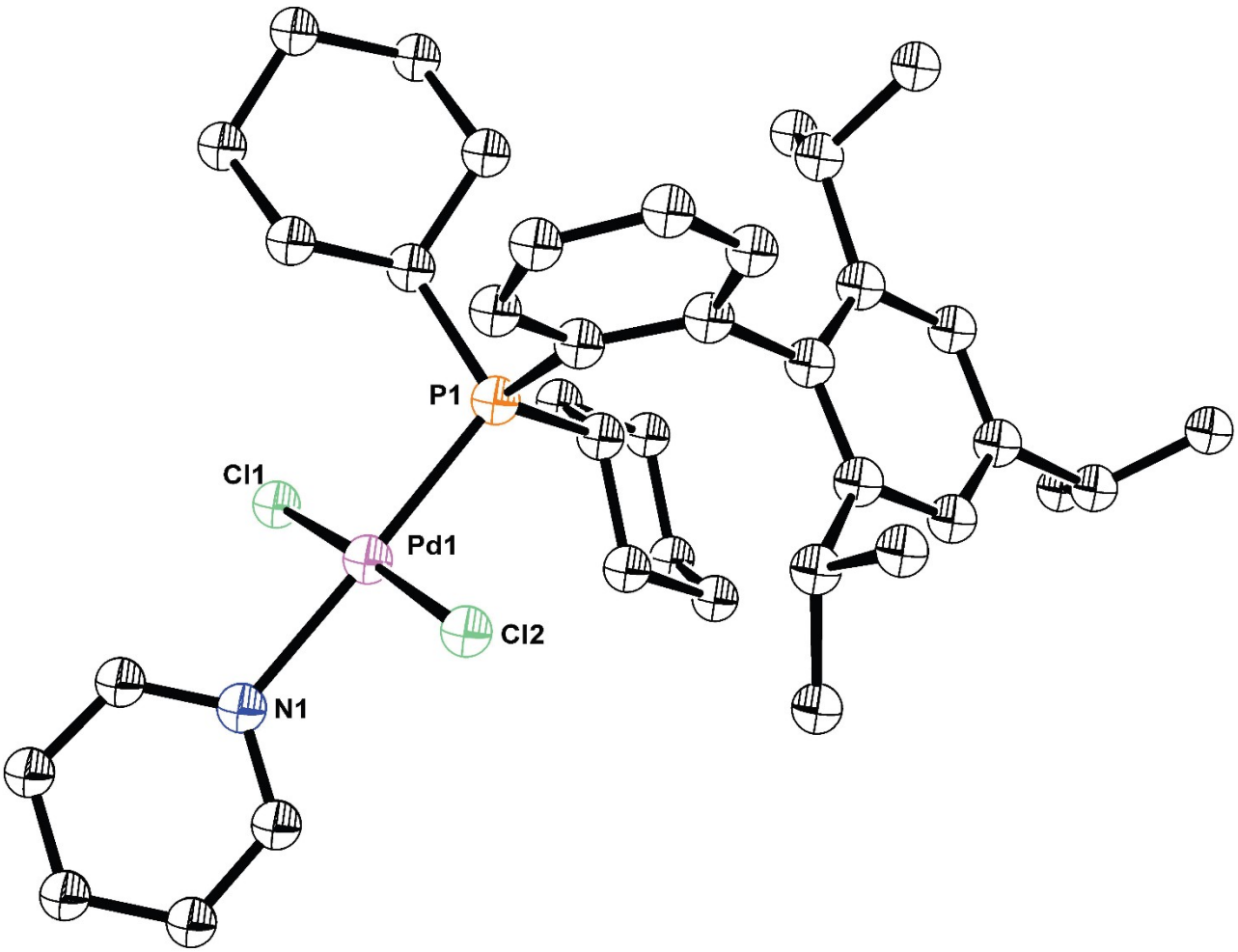


Figure S2. Molecular structure of the complex **4a**

Table S3. Crystal data and structure refinement for **4a**.

Empirical formula	$C_{39}H_{55}Cl_5NPPd$
Formula weight	852.46
Temperature/K	100.0(1)
Crystal system	triclinic
Space group	P-1
a/Å	9.5074(2)
b/Å	10.9513(2)
c/Å	21.0209(5)
α/°	89.4832(17)
β/°	79.552(2)
γ/°	74.1193(19)
Volume/Å^3	2068.32(8)
Z	2
ρ_{calc} g/cm^3	1.369
μ/mm^{-1}	7.155
F(000)	884.0
Crystal size/mm^3	0.171 × 0.082 × 0.065
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.402 to 147.782
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 13, -26 ≤ l ≤ 26
Reflections collected	38851
Independent reflections	8258 [R_{int} = 0.0591, R_{sigma} = 0.0408]
Data/restraints/parameters	8258/11/443
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0459, wR_2 = 0.1186
Final R indexes [all data]	R_1 = 0.0520, wR_2 = 0.1241
Largest diff. peak/hole / e Å^{-3}	1.62/-1.24

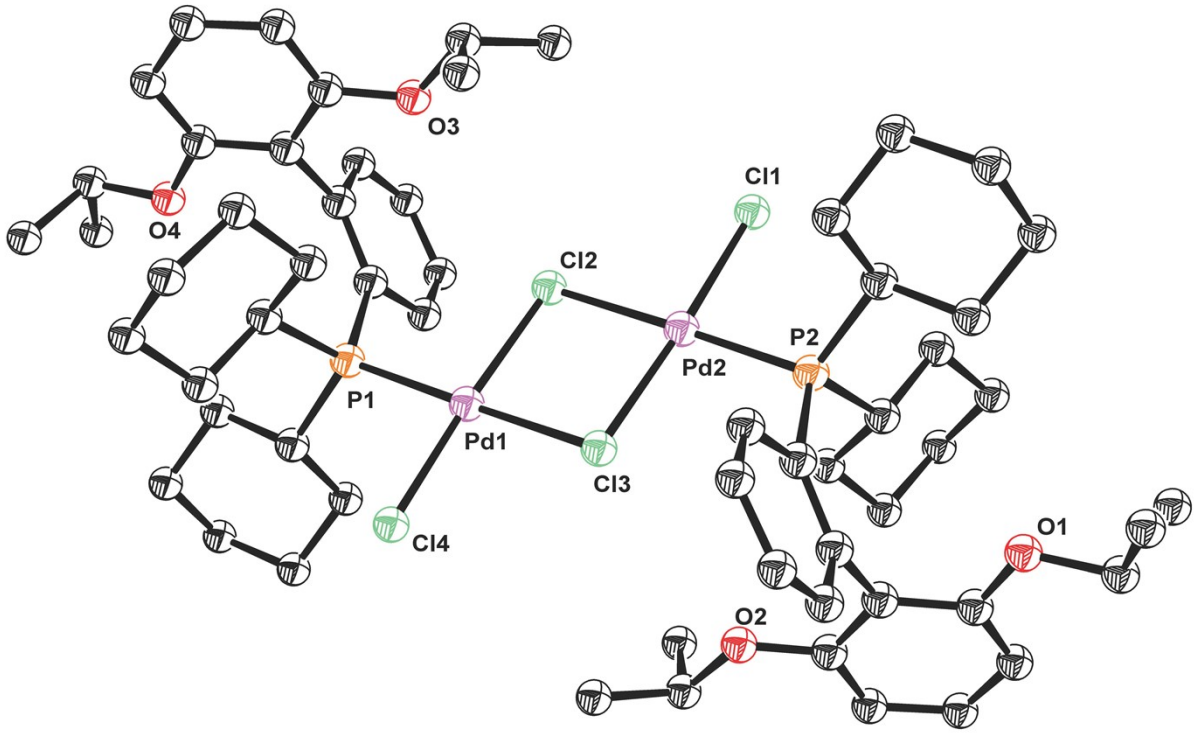


Figure S3. Molecular structure of the complex **5a**

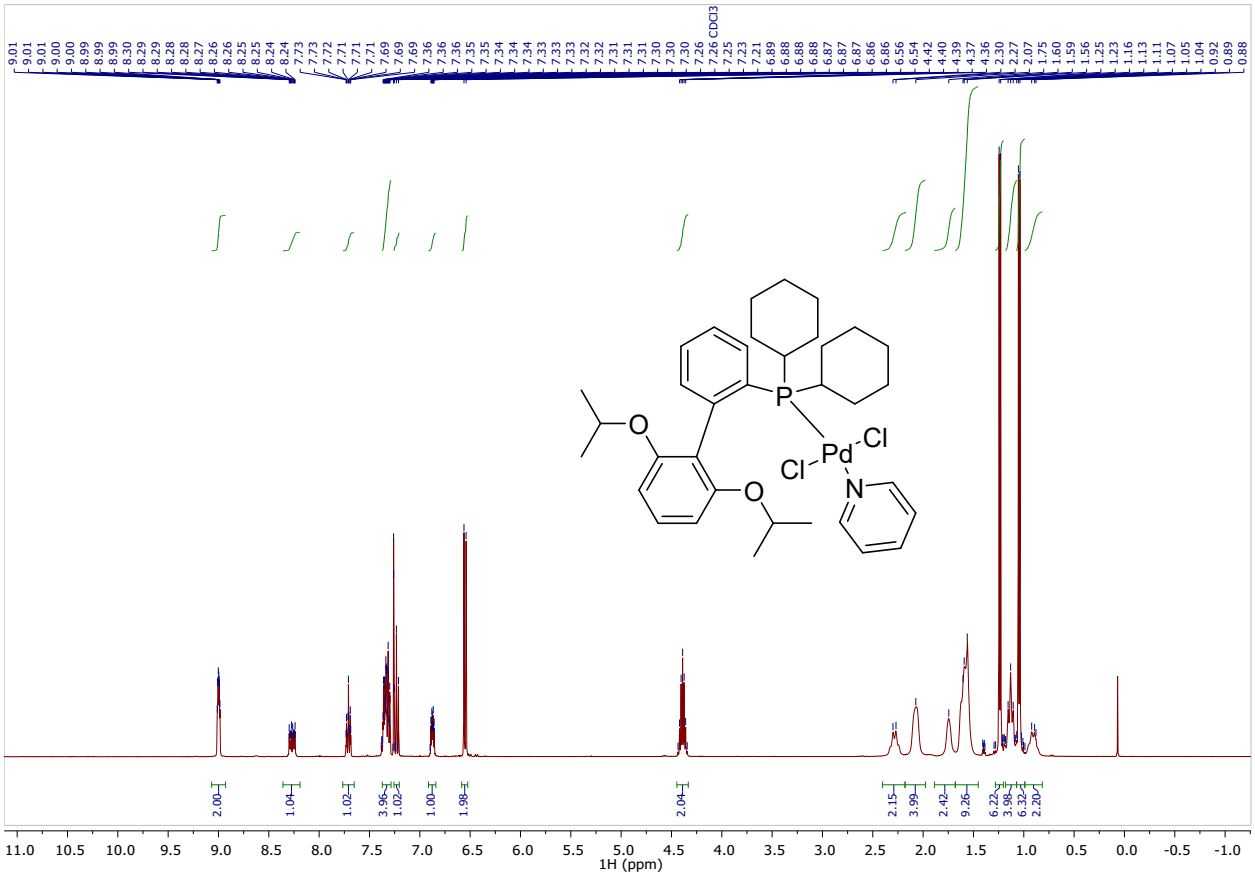
Table S4. Crystal data and structure refinement for **5a.**

Empirical formula	$C_{60}H_{86}Cl_4O_4P_2Pd_2$
Formula weight	1287.83
Temperature/K	100.0(1)
Crystal system	monoclinic
Space group	P21/n
a/Å	9.8194(3)
b/Å	16.4376(4)
c/Å	18.6502(5)
α/°	90
β/°	95.314(2)
γ/°	90
Volume/Å^3	2997.34(14)
Z	2
ρ_{calc}g/cm^3	1.427
μ/mm^{-1}	7.326
F(000)	1336.0
Crystal size/mm^3	0.16 × 0.065 × 0.029
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.182 to 147.962
Index ranges	-11 ≤ h ≤ 12, -20 ≤ k ≤ 20, -23 ≤ l ≤ 20

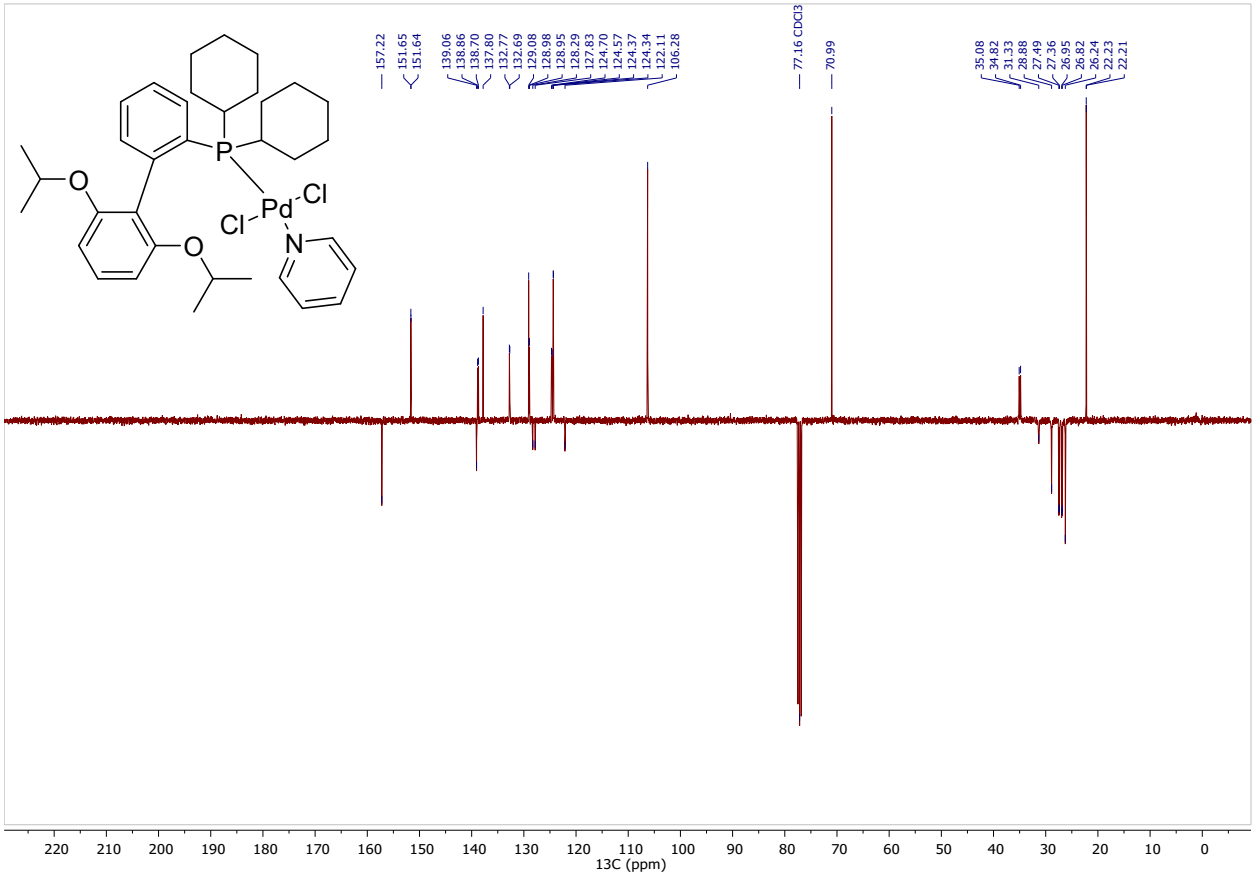
Reflections collected	28583
Independent reflections	6074 [R_{int} = 0.0893, R_{sigma} = 0.0653]
Data/restraints/parameters	6074/0/338
Goodness-of-fit on F^2	1.005
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.0957
Final R indexes [all data]	R_1 = 0.0649, wR_2 = 0.1086
Largest diff. peak/hole / e $Å^{-3}$	0.69/-0.89

NMR spectra of compounds

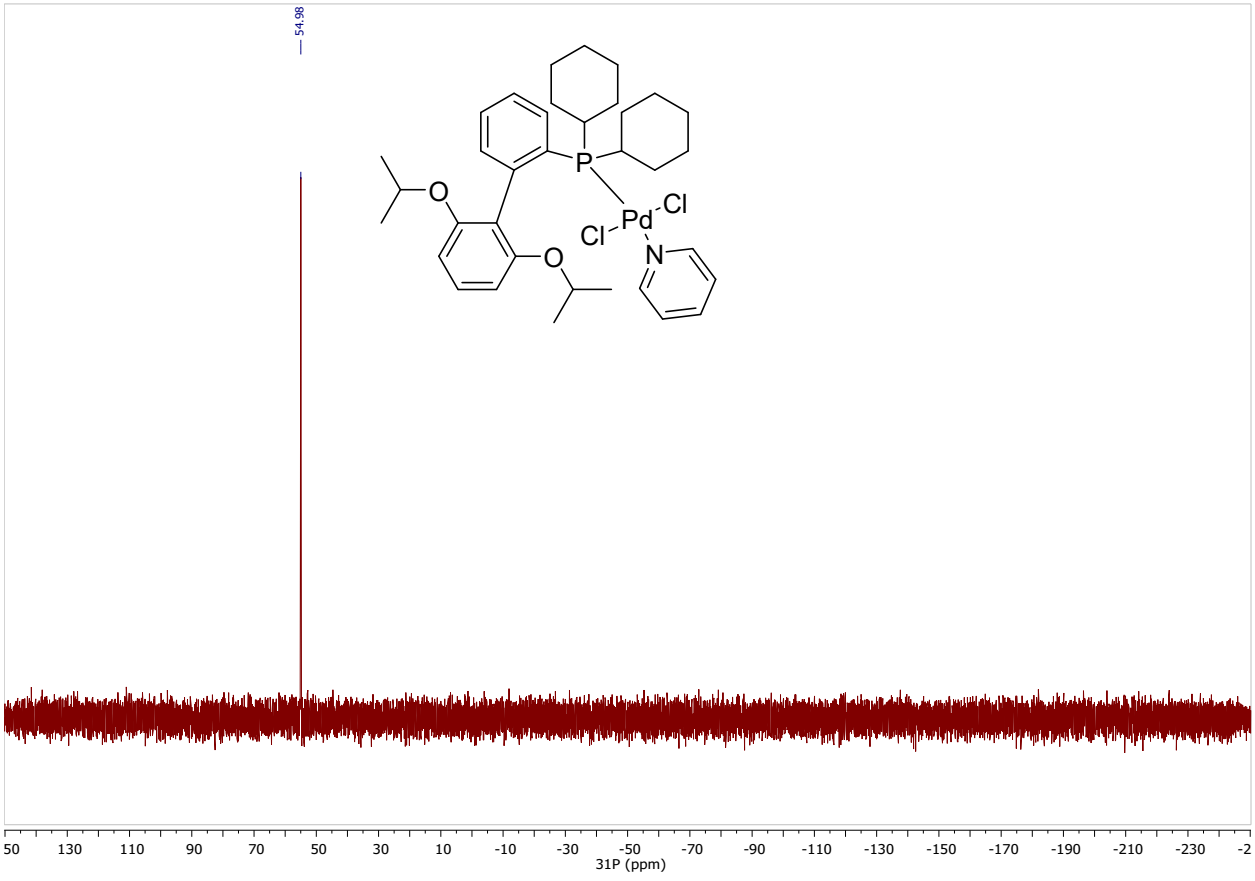
^{1}H NMR of **2a** in $CDCl_3$



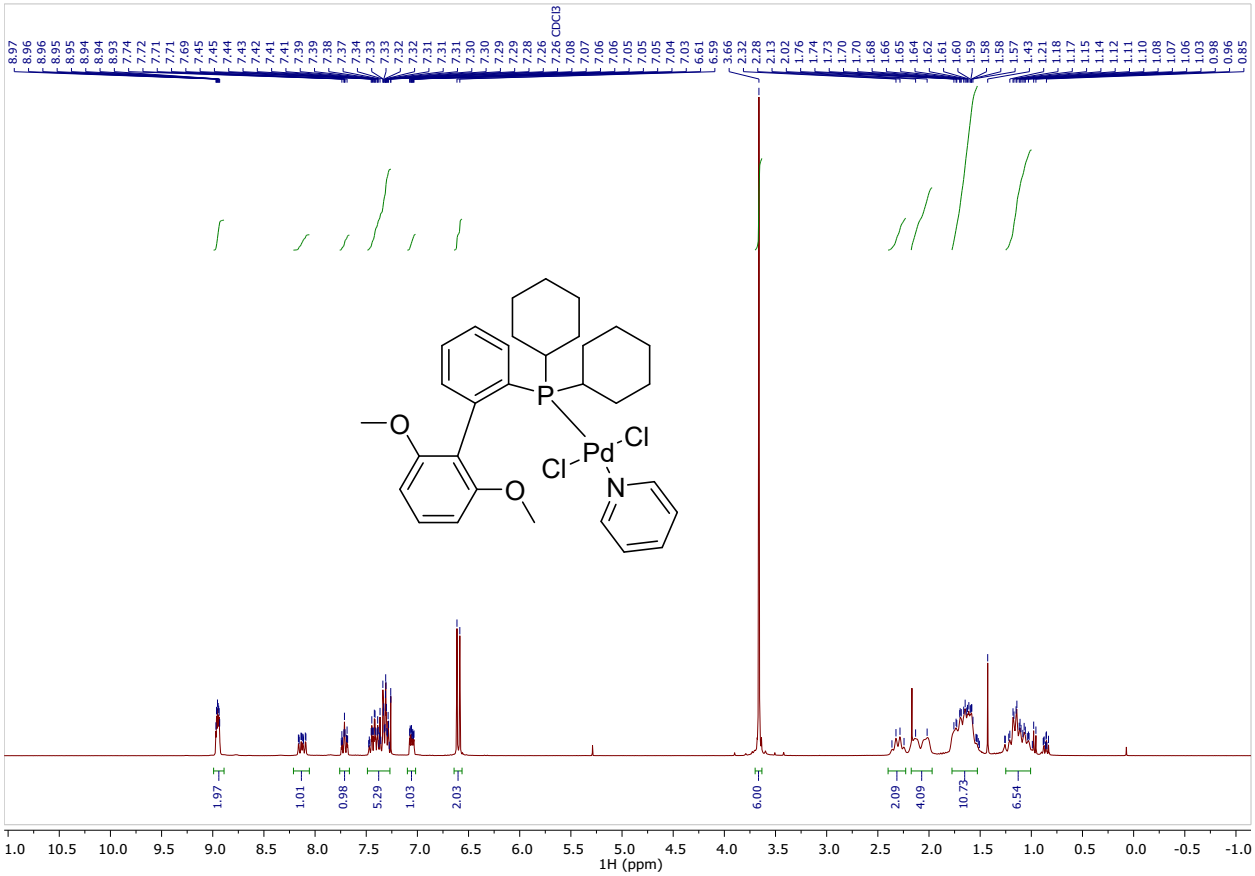
^{13}C DEPT NMR of **2a** in $CDCl_3$



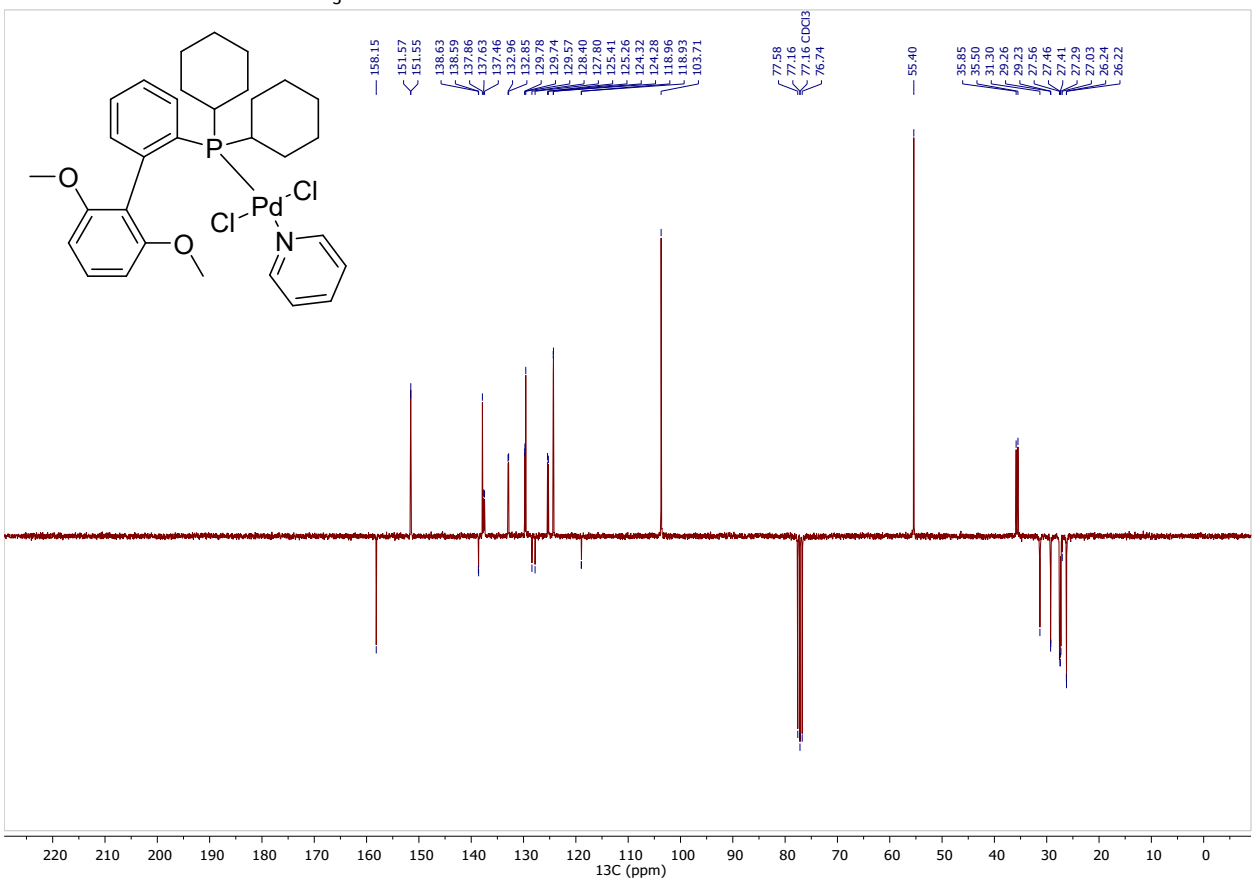
^{31}P NMR of **2a** in $CDCl_3$



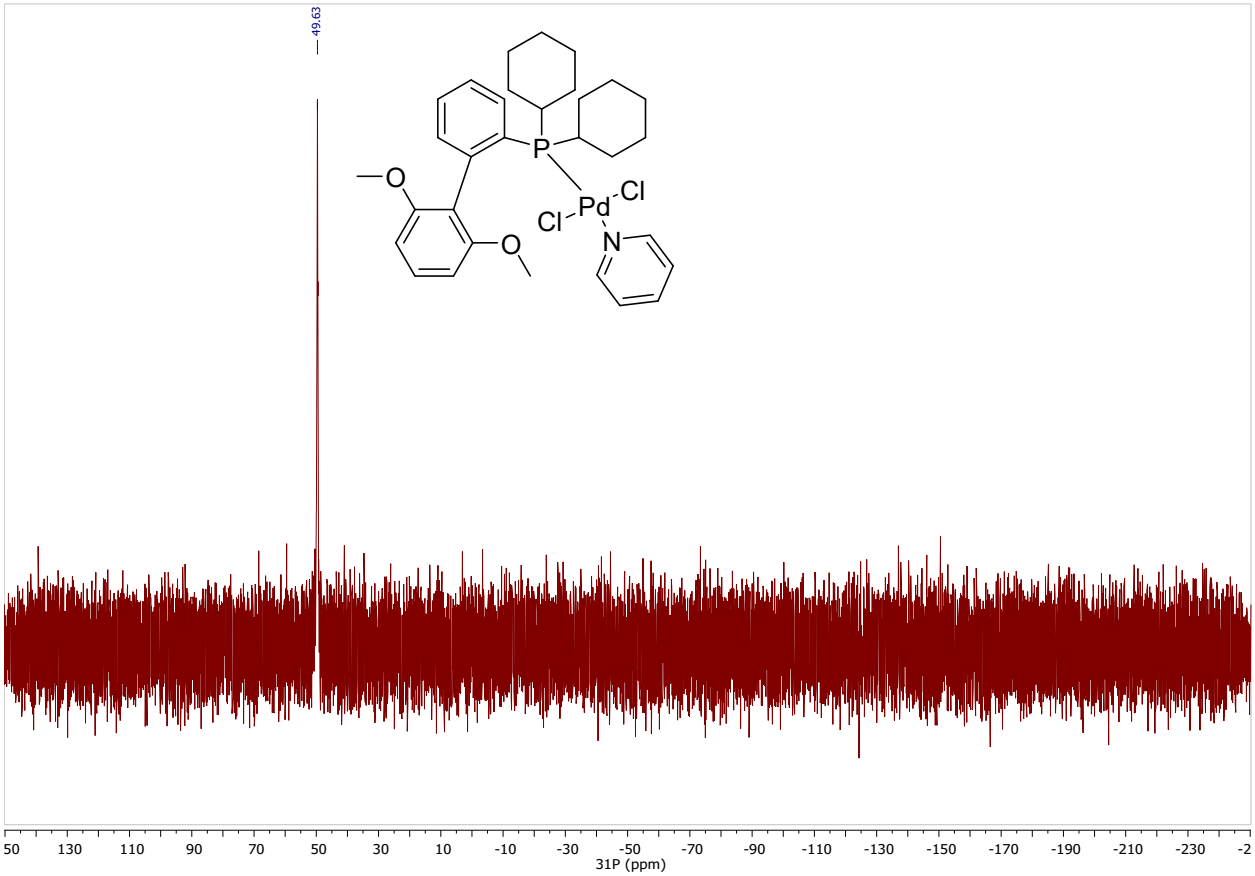
^{1}H NMR of **3a** in $CDCl_3$



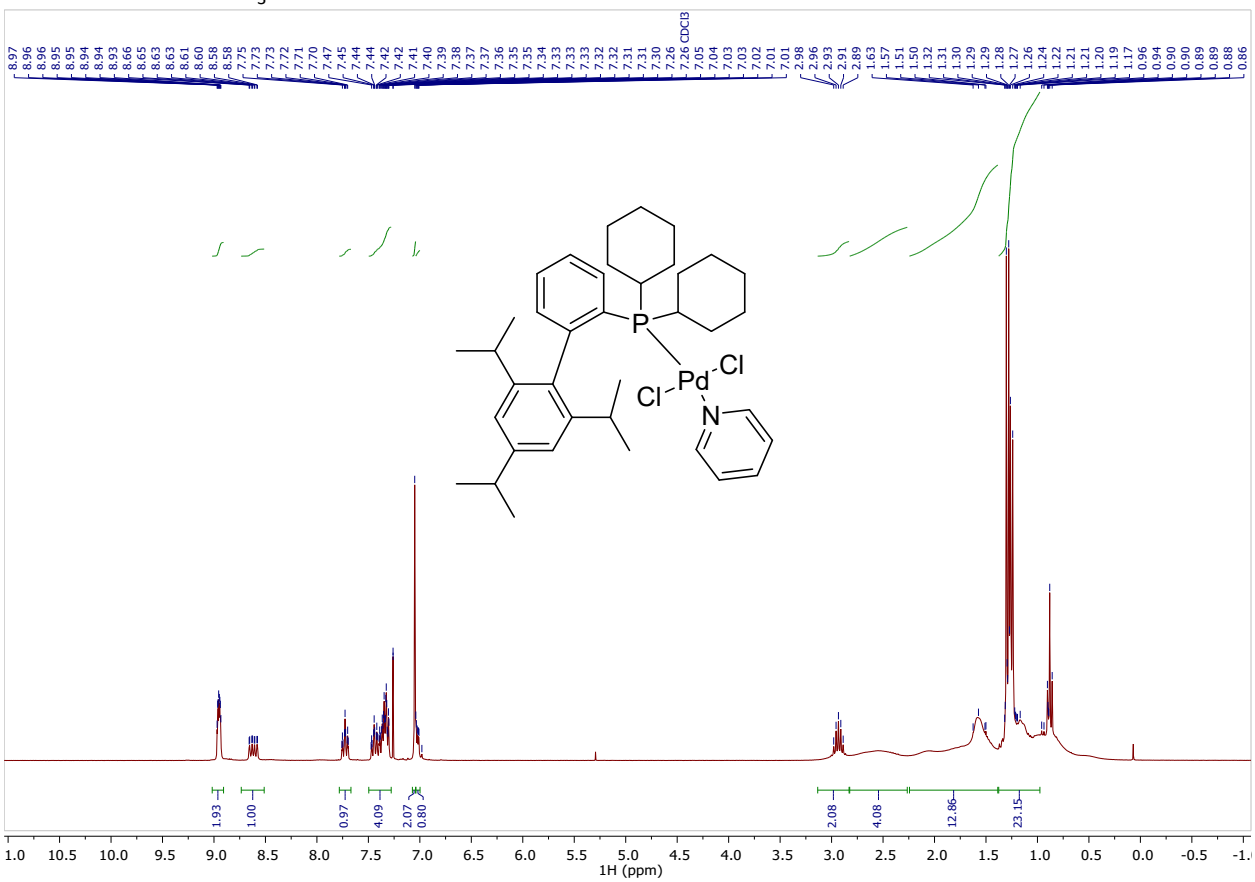
^{13}C DEPT NMR of **3a** in $CDCl_3$



^{31}P NMR of **3a** in $CDCl_3$



^{1}H NMR of **4a** in $CDCl_3$



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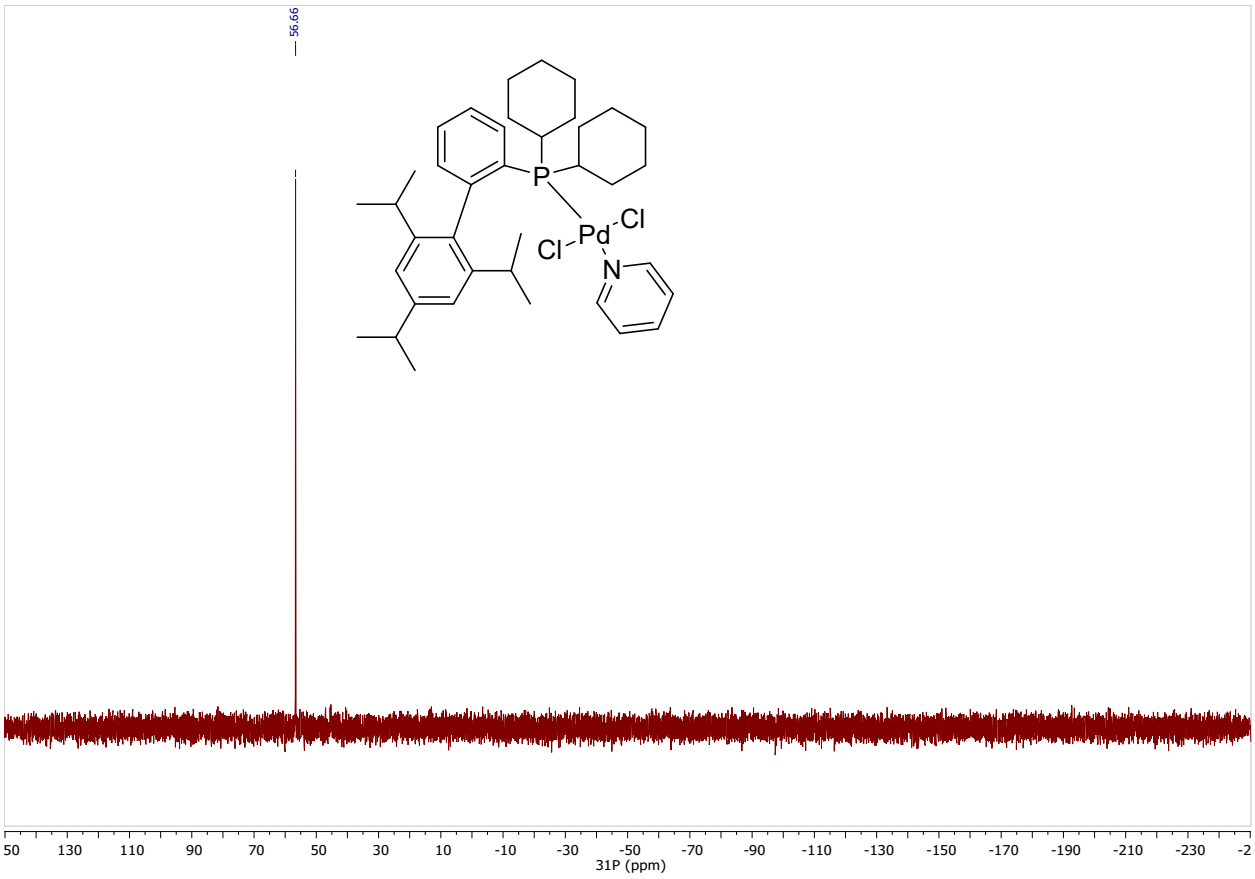

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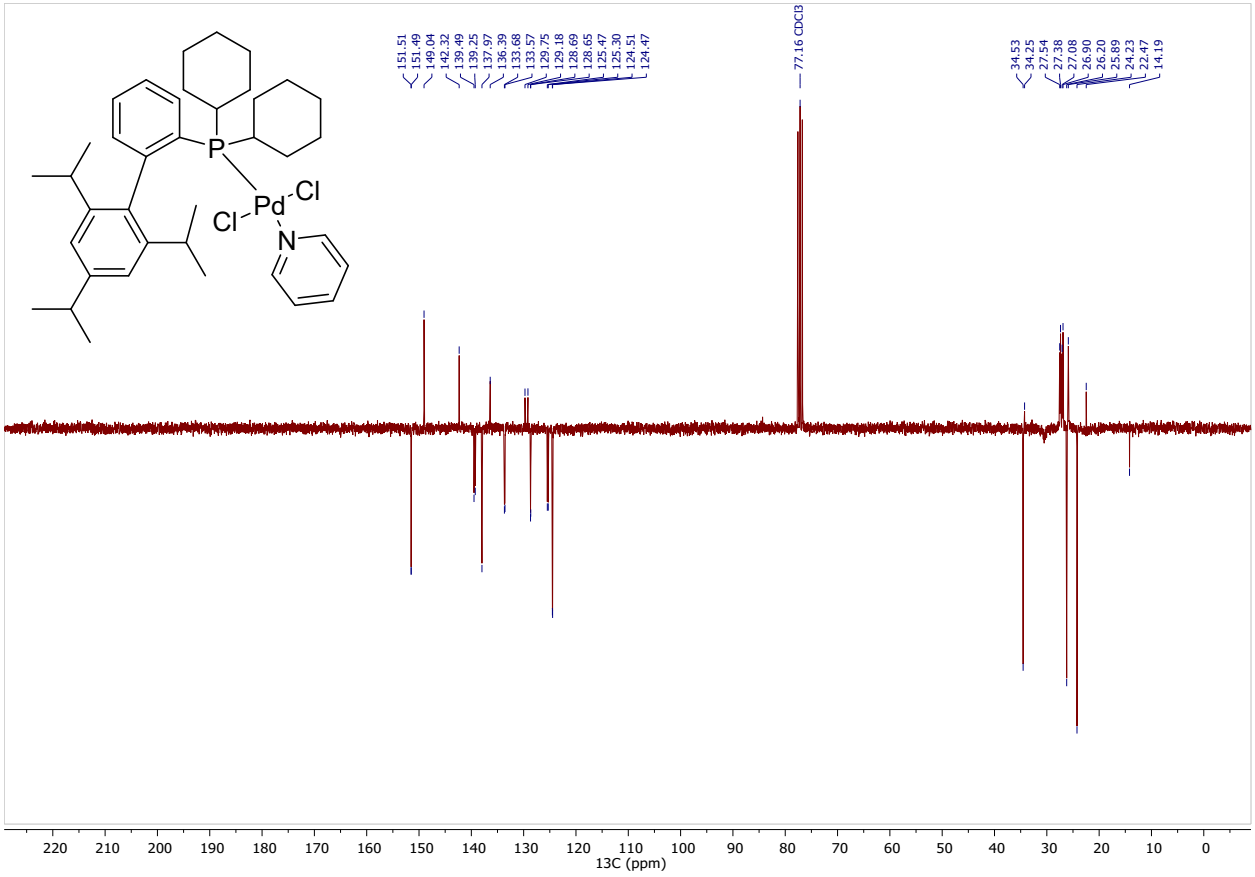
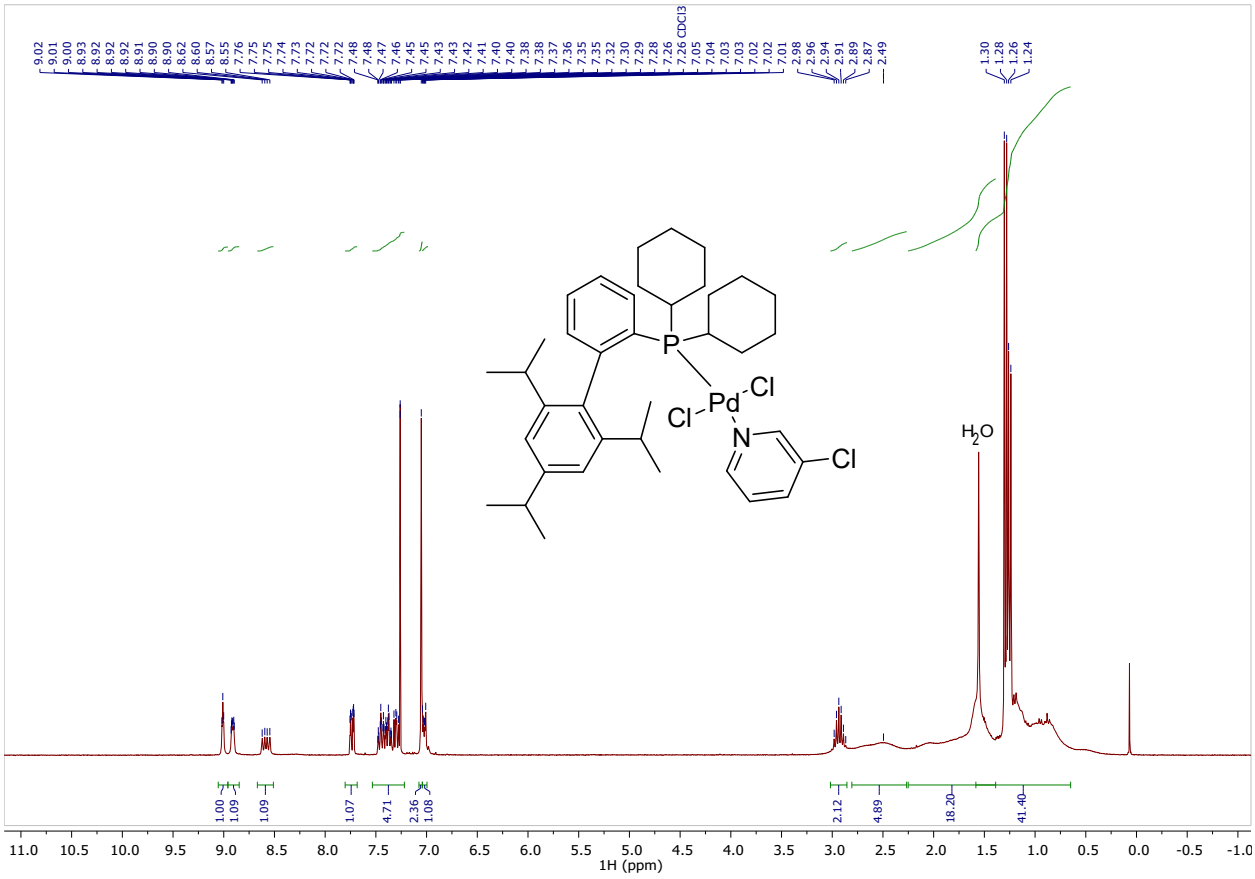
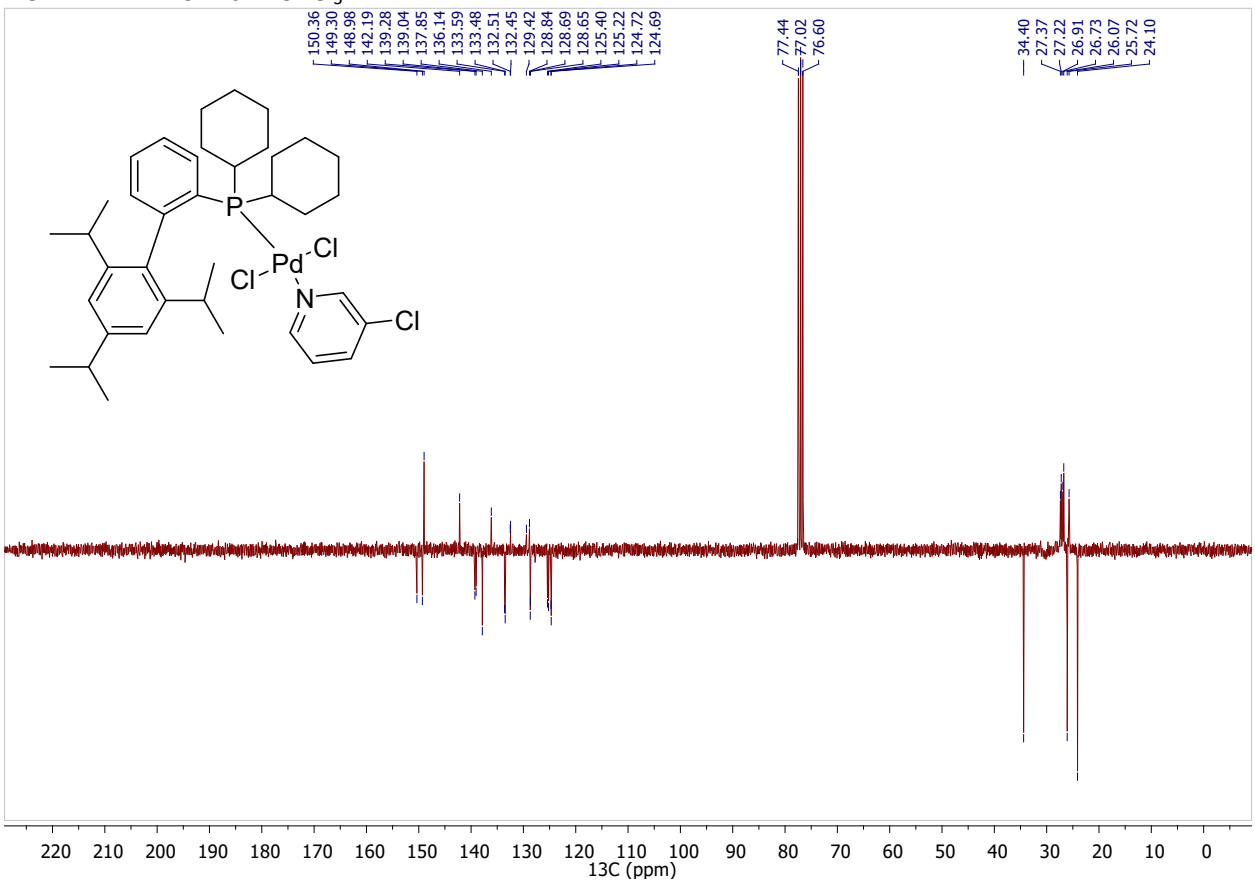


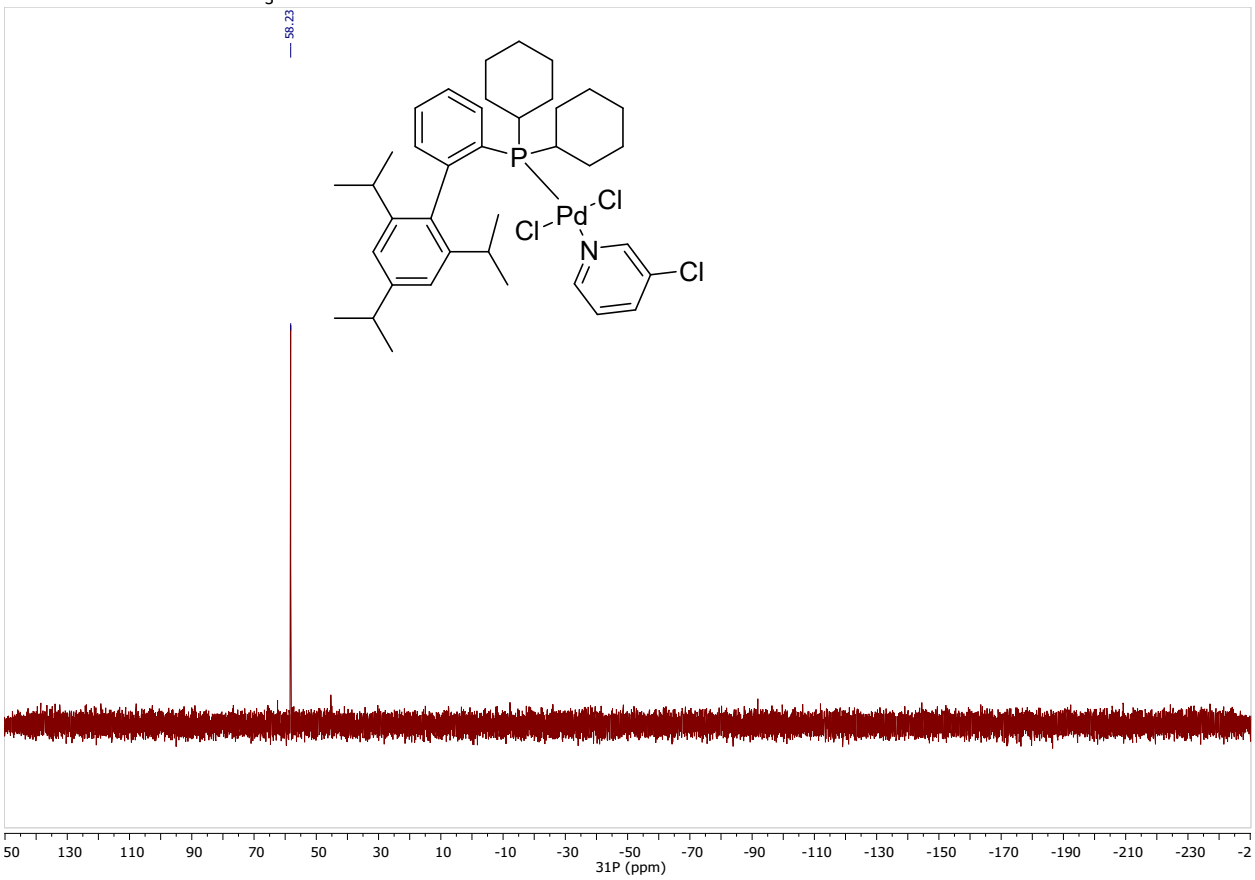
^{1}H NMR of **4b** in $CDCl_3$



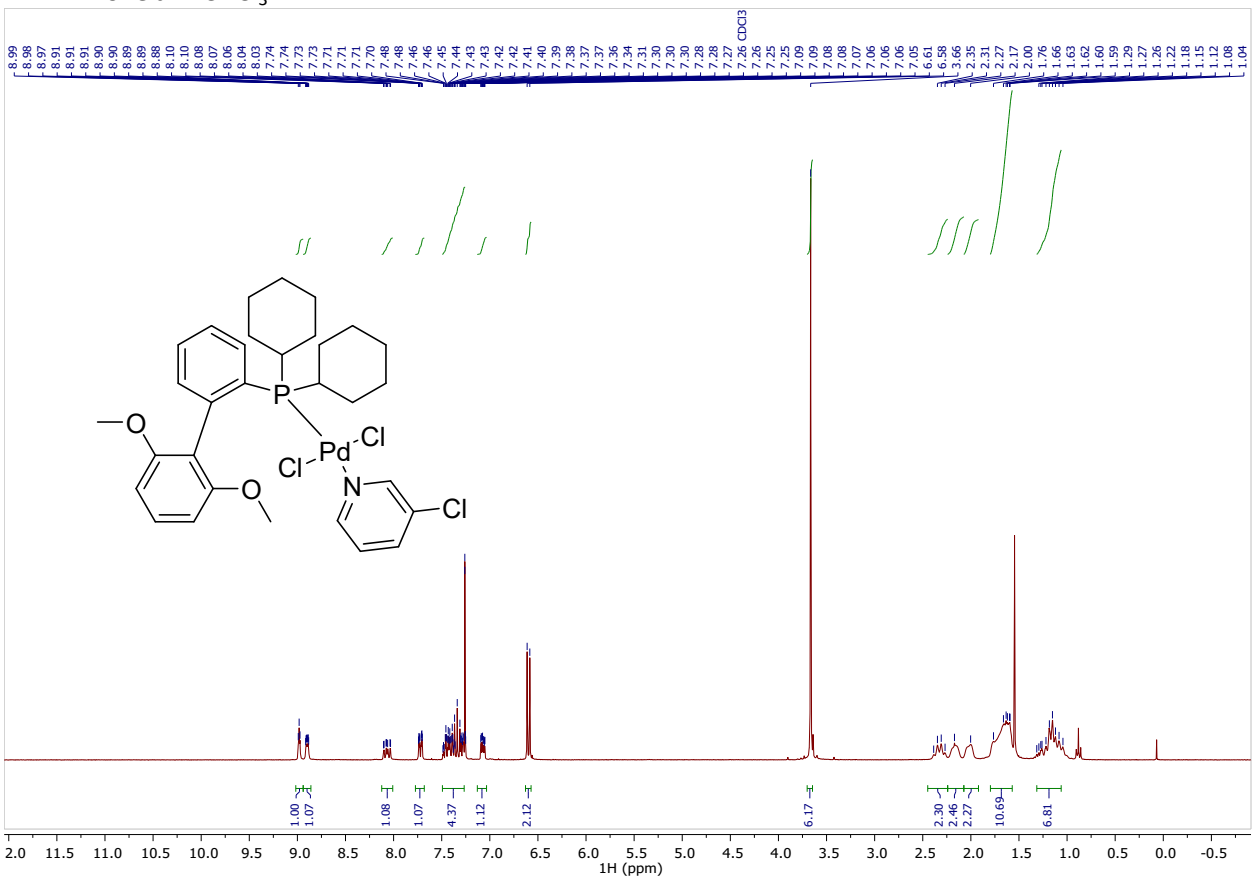
^{13}C DEPT NMR of **4b** in $CDCl_3$



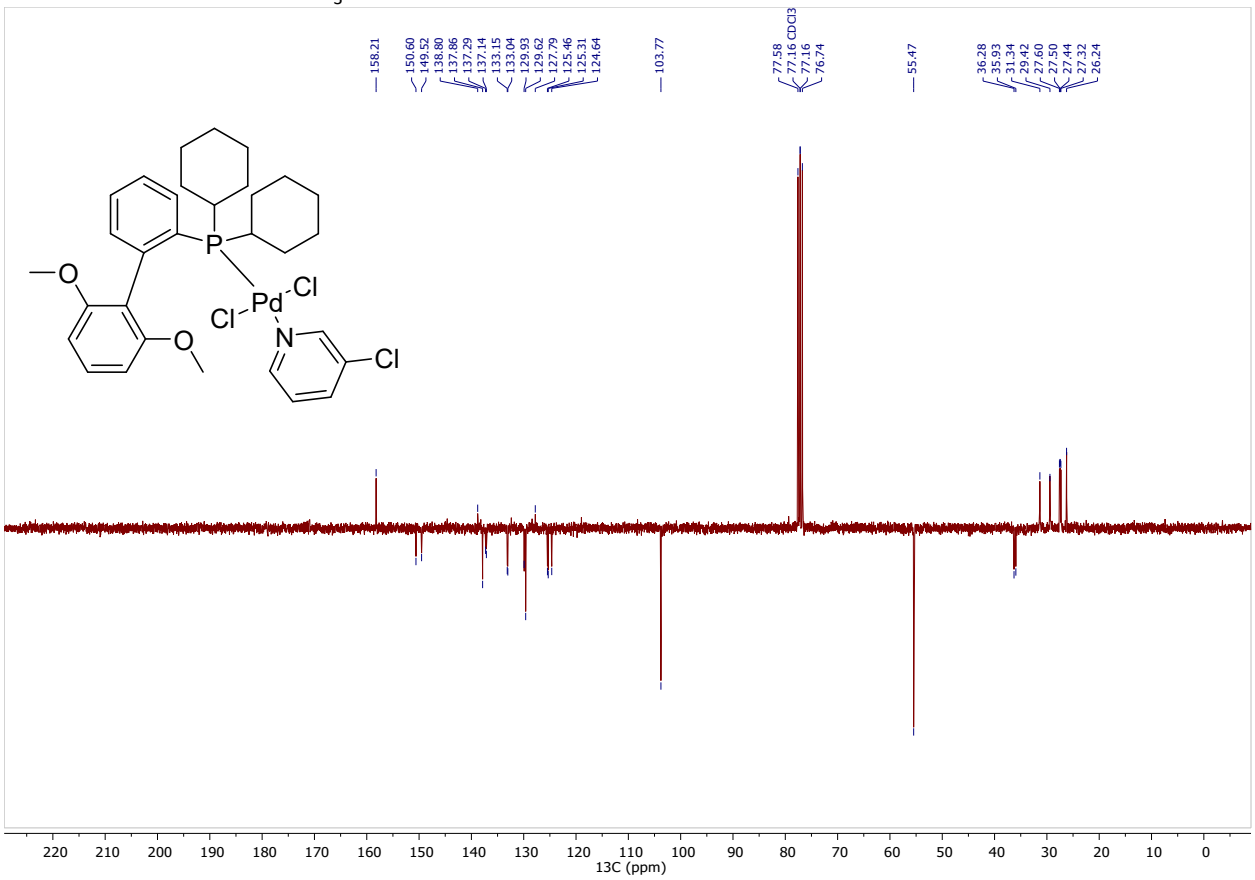
^{31}P NMR of **4b** in $CDCl_3$



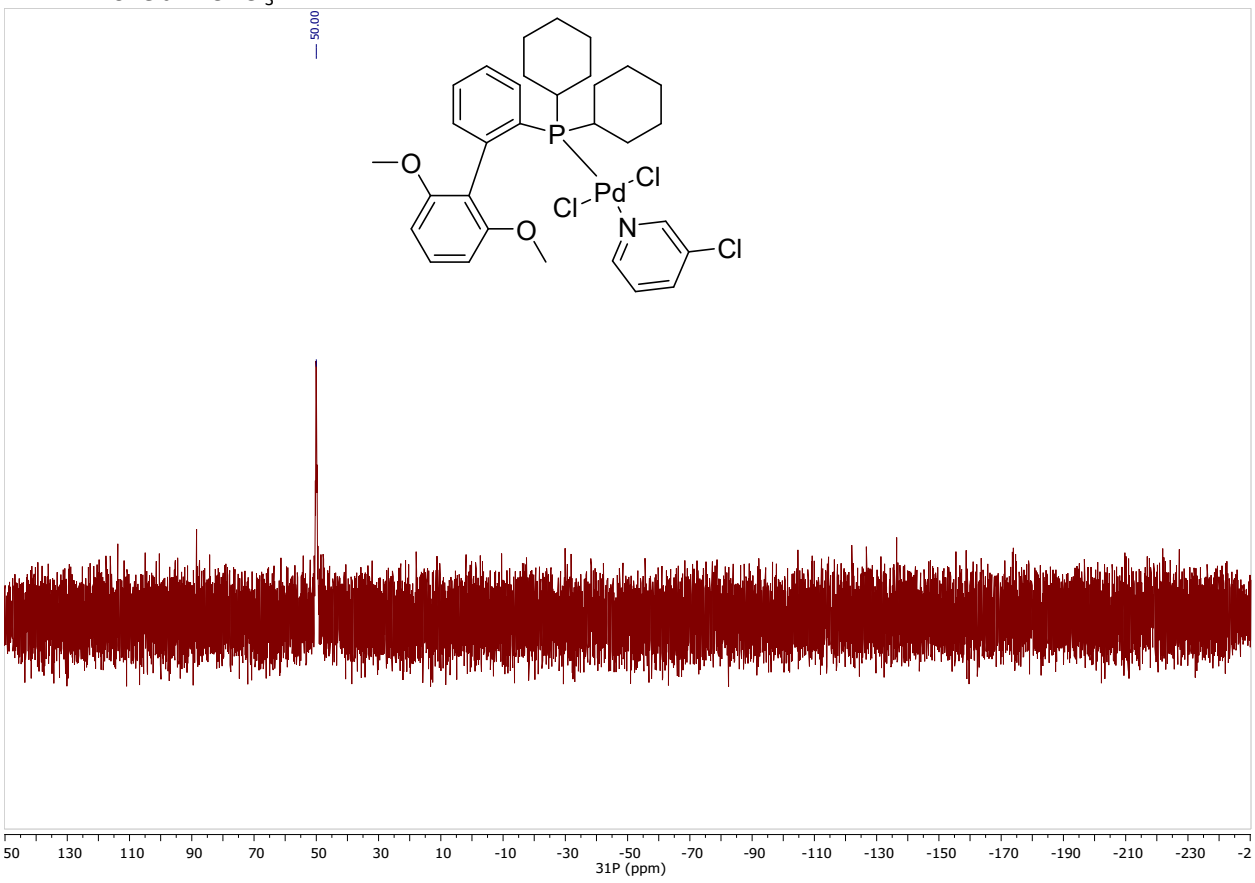
^{1}H NMR of **3b** in $CDCl_3$



^{13}C DEPT NMR of **3b** in $CDCl_3$



^{31}P NMR of **3b** in $CDCl_3$



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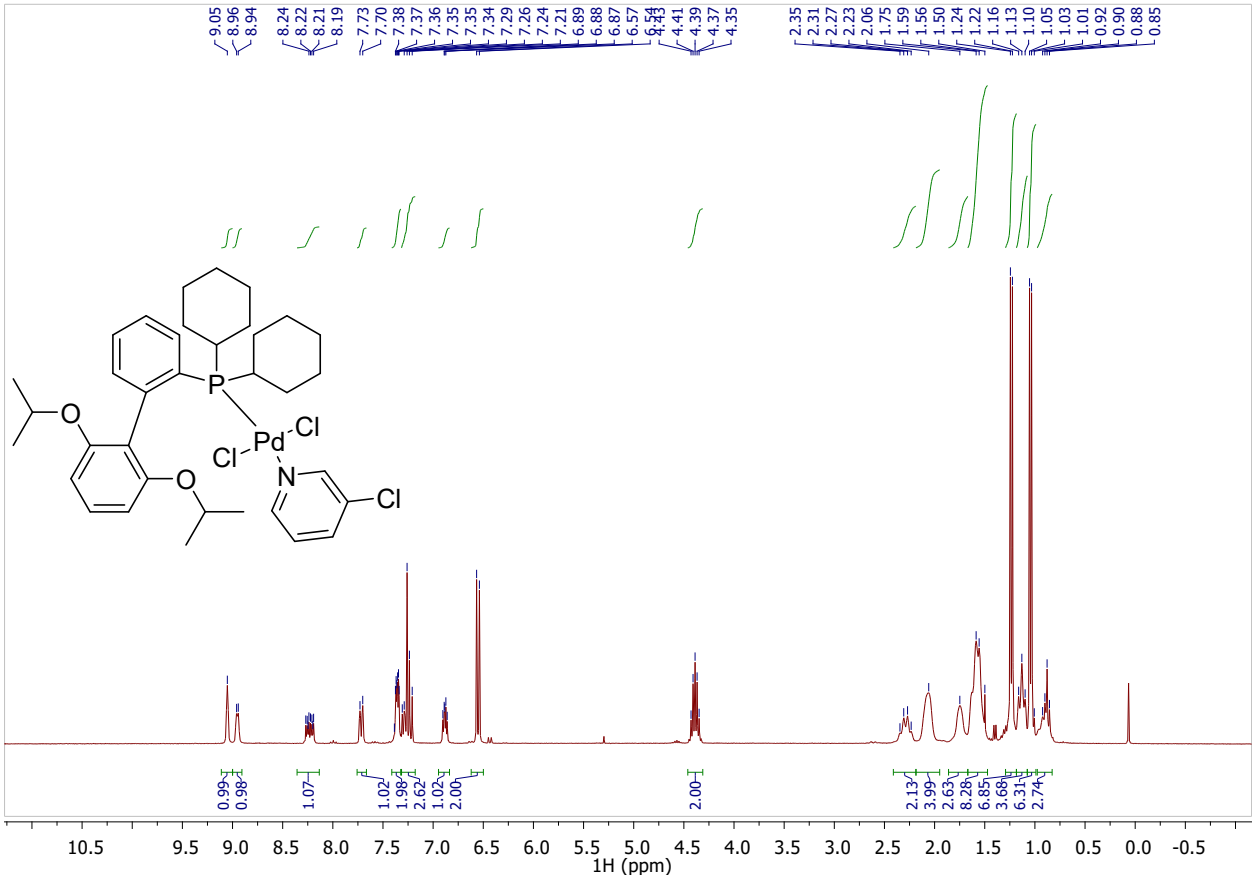

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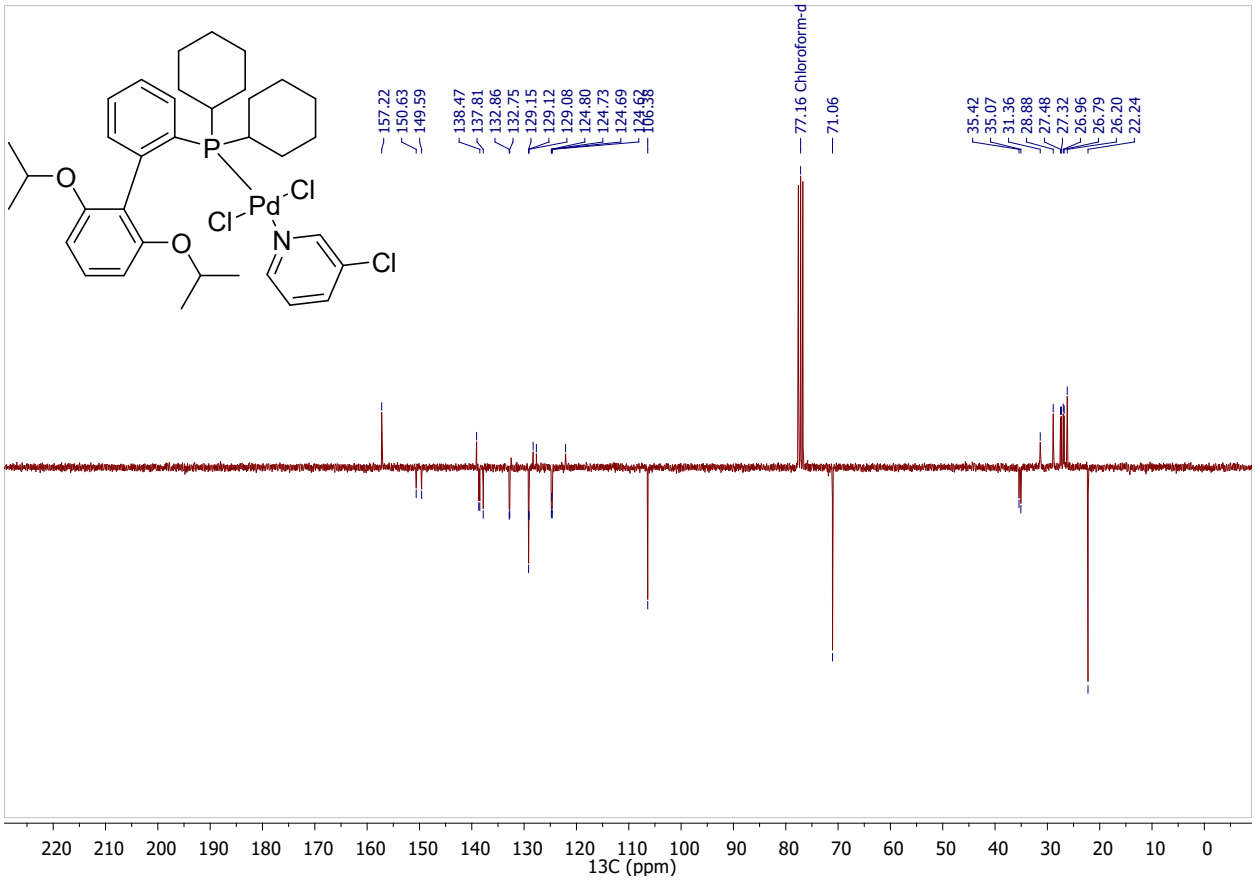
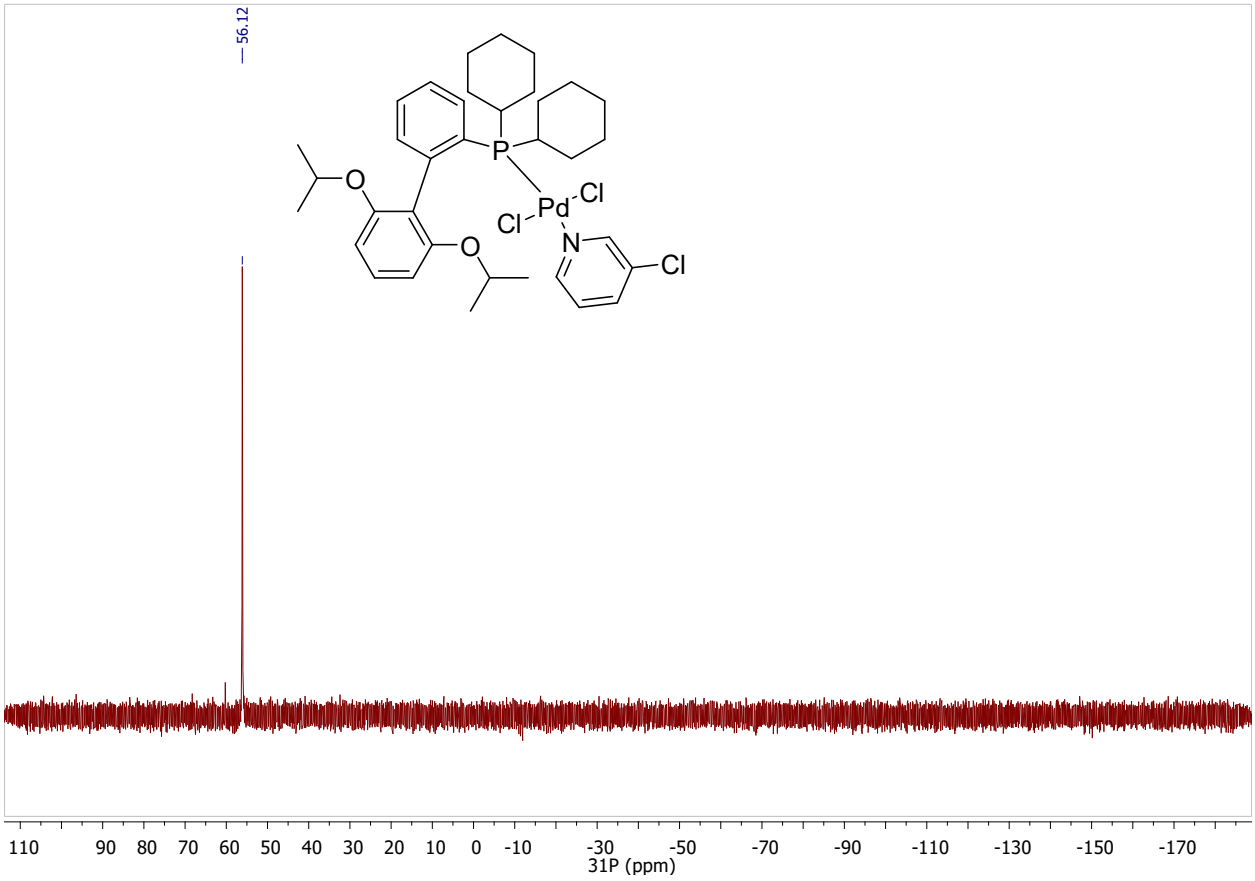
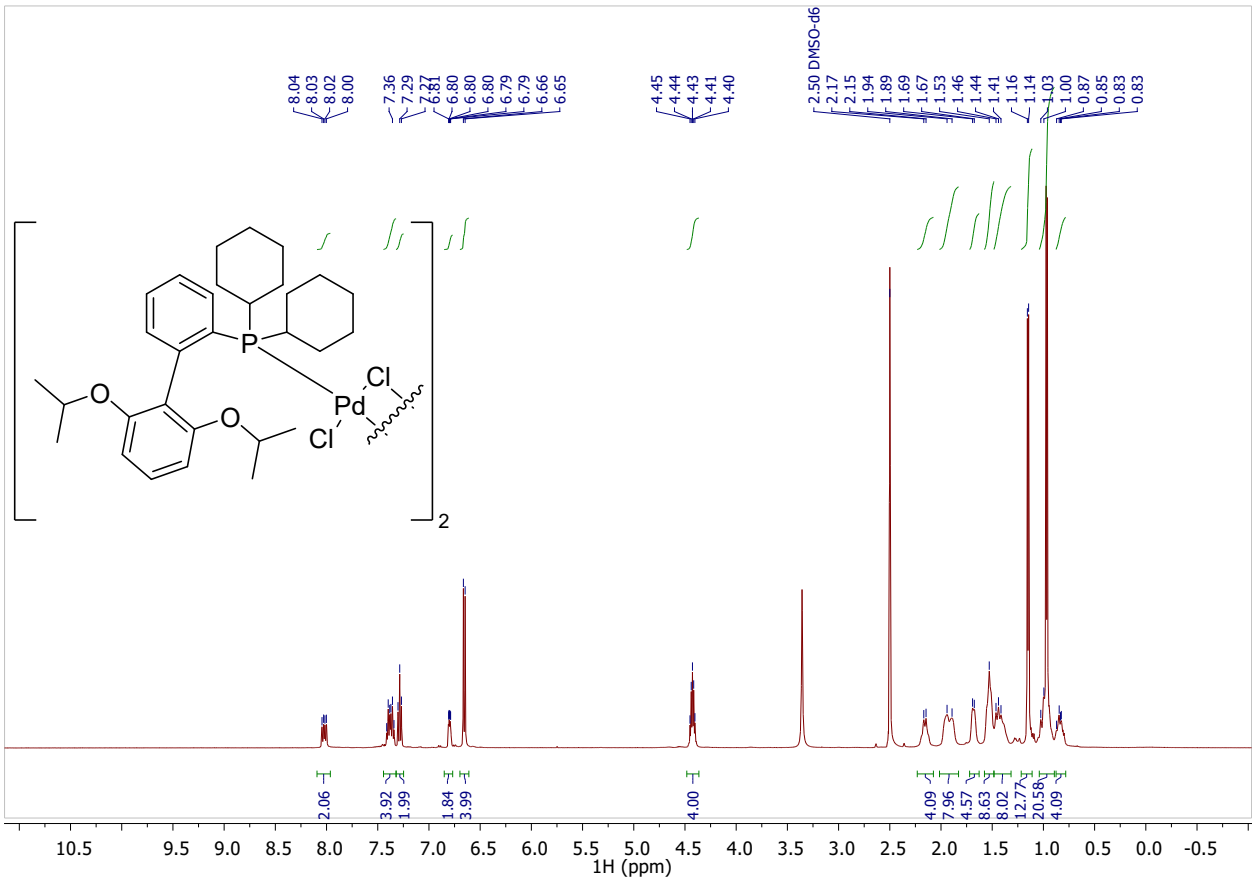


^{31}P NMR of **2b** in $CDCl_3$



^{1}H NMR of **5a** in DMSO-d_6



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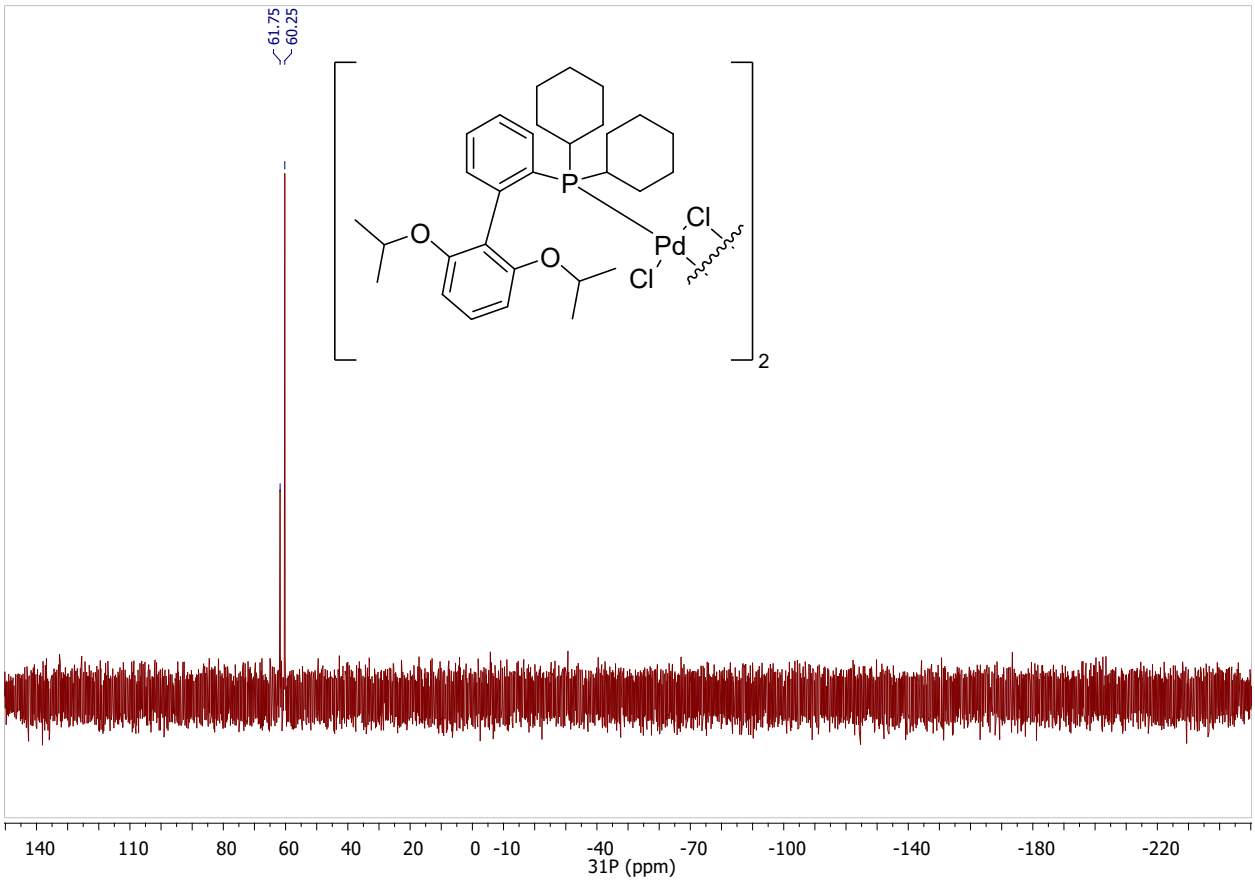
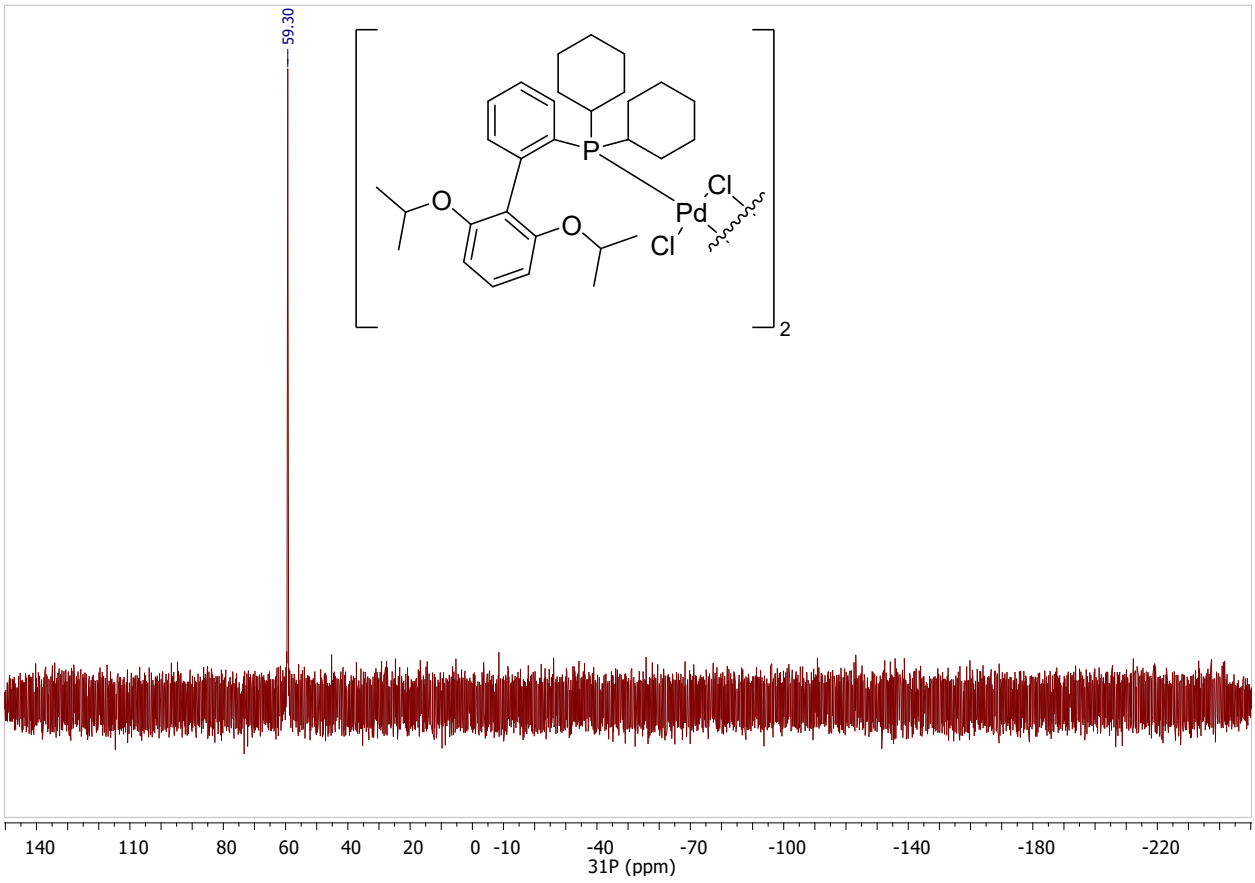


^{31}P NMR of **5a** in DMSO-d_6



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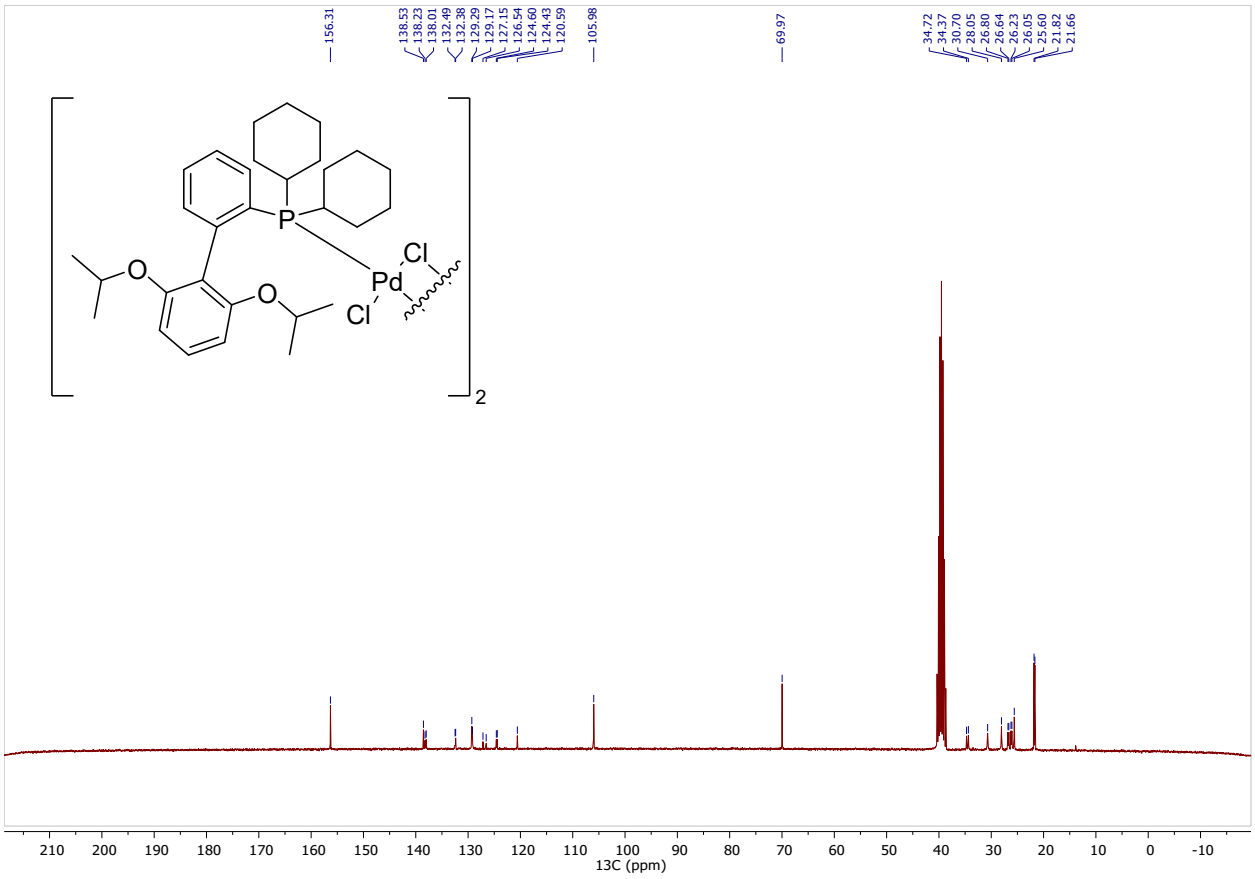

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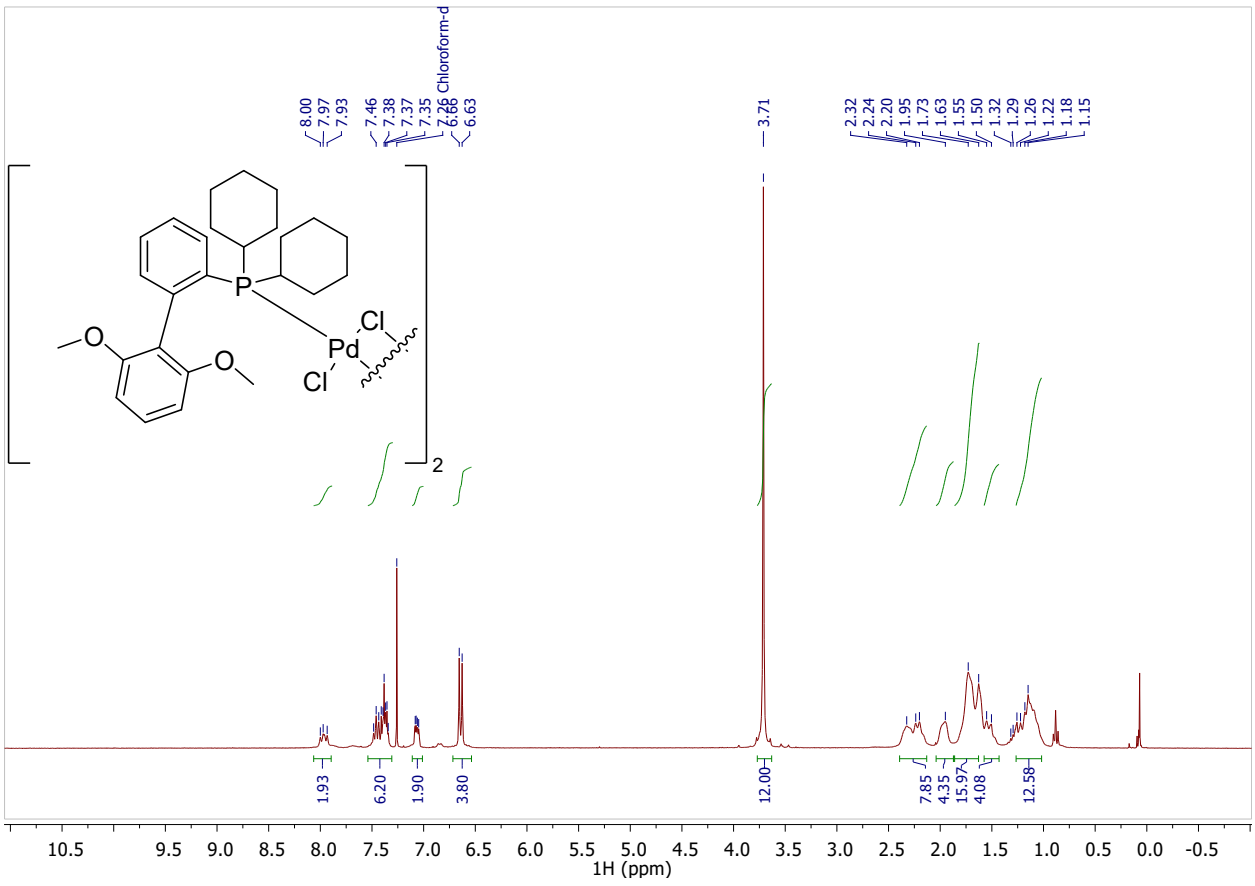

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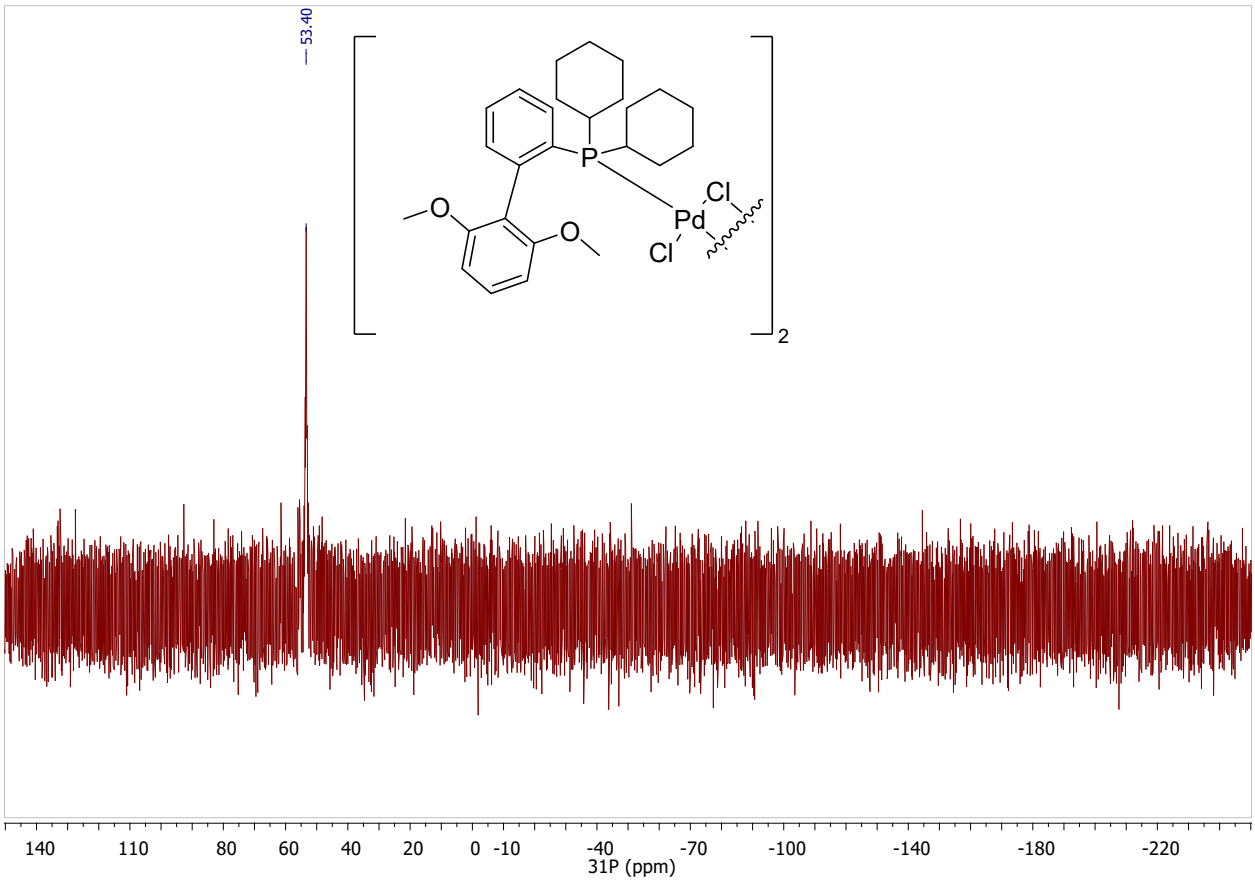

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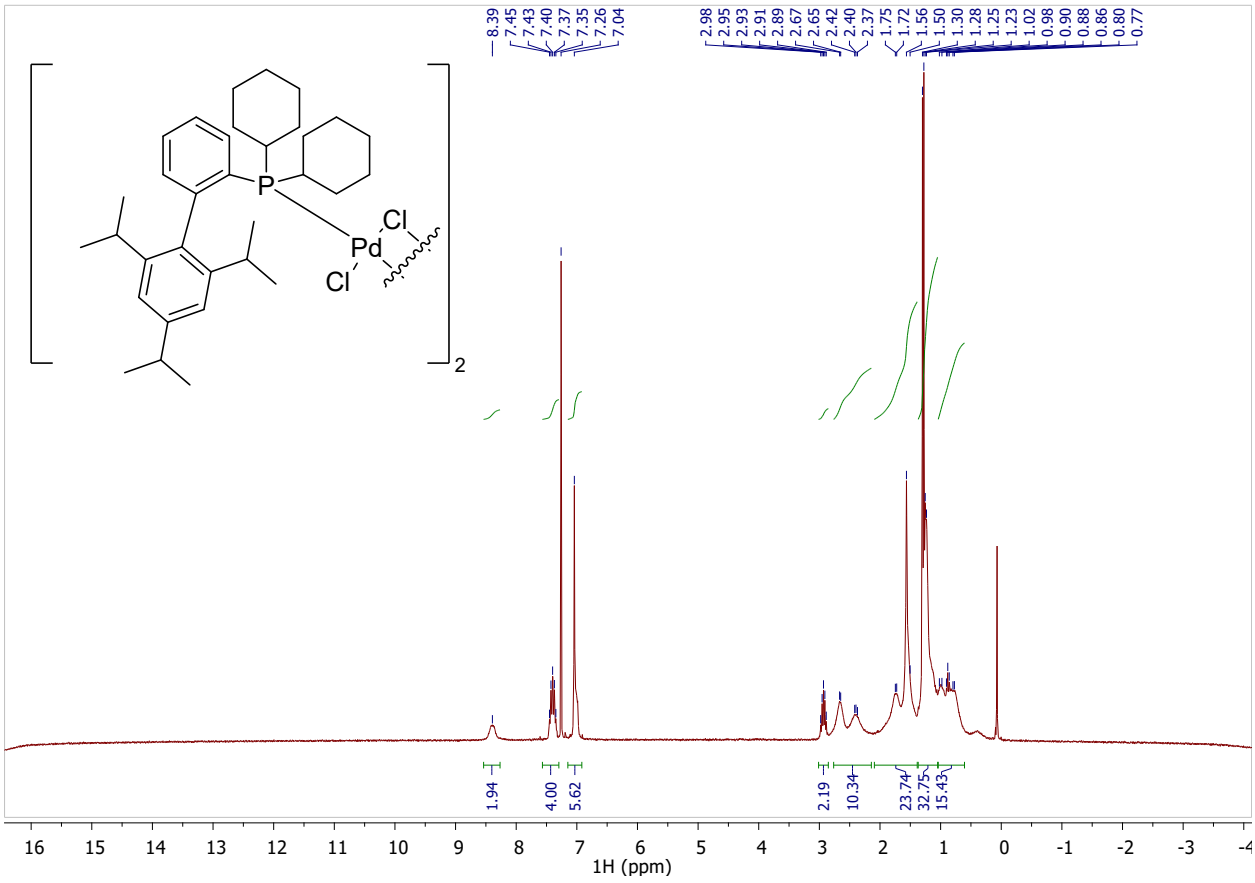

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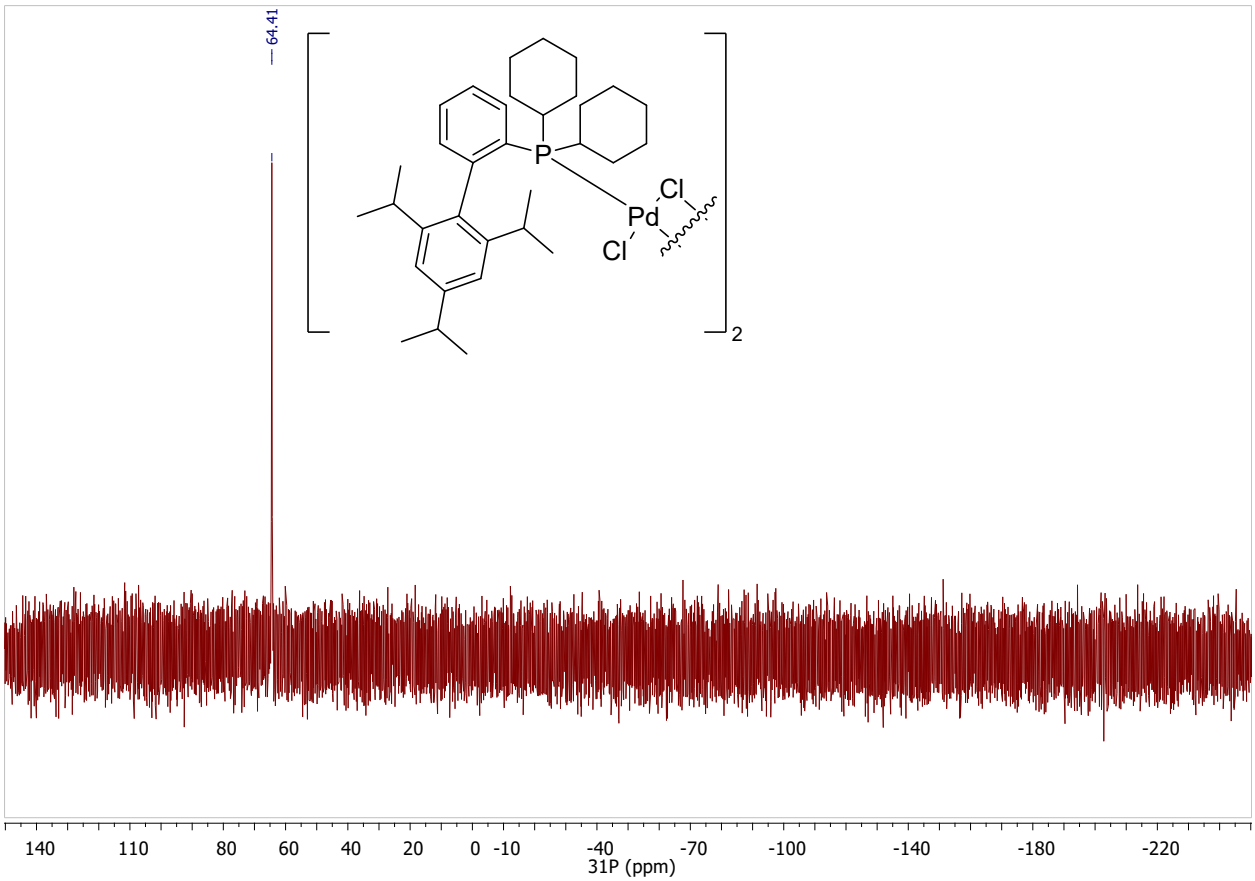

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