SUPPORTING INFORMATION

Rapid, Efficient and Green Solid-state Mechanosynthesis of Palladium Complexes

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Part 1: General procedure for Mechanochemical Synthesis

Mechanochemical synthesis of all of the products has been carried out with the same approach by means of a vibrational mill (Figure S1). For all, relevant ratios of the metallic precursors are used and milled at required frequencies, depending upon their interaction. The exact milling frequency and time of milling with the resultant output has been highlighted in the table for each product. For most of the synthesis, 2 mL Eppendorfs with 3 or 4 balls inside were used (3 mm diameter, ~0.4 g) (Figure S2). To avoid oxidation to occur during milling, Eppendorf were closed in presence of argon and sealed with parafilm. However, in some particular cases, 10 mL with one ball (10 mm diameter, ~3.3 g) and 25 mL zirconia jars with one ball (15 mm diameter, ~11.4 g) were used (Figure S2).

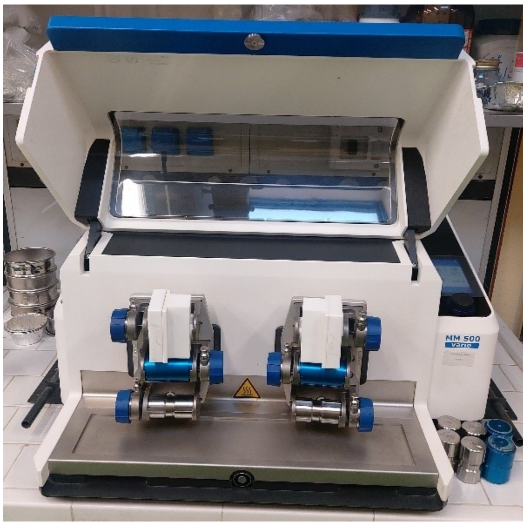


Figure S1. Retsch Ball Mill (MM 500 Vario).

Figure S2. Eppendorf with balls and zirconia jar with ball (10 mL).

Part 2: Details of Trials

[Pd(COD)Cl_2] (1a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T1 (Zr jar)	5	30	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ=97%, S=97%, light grey color, sign of degradation
T2 (Zr jar)	10	15	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ=91%, S=91%
T3 (Epp.)	20	15	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ=98%, S=98%
T4 (Zr jar)	20	15	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ=99%, S=99%
T5 (Zr jar)	30	15	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ=99%, S=99%
T6 (Zr jar)	10	30	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ>99%, grey color, degradation
T7 (Zr jar)	30	30	($Na_2[PdCl_4]$) 1:1	Yes, 2 times water.	χ>99%, grey color, degradation
T8 (Zr jar)	10	15	($PdCl_2$) 1:1	No	None
T9 (Zr jar)	20	15	($PdCl_2$) 1:1	No	χ=95%, S=95%
T10 (Zr jar)	60	15	($PdCl_2$) 1:1	No	χ>99%, grey color, degradation
T11 (Epp.)	30	20	($PdCl_2$) 1:1	No	χ=98%, S=98%
T12 (Zr jar)	30	20	($PdCl_2$) 1:1	No	χ=99%, S=99%
T13 (Zr jar)	30	20	($PdCl_2$) 1:1	No	χ=98%, S=98%
T14 (25 mL Zr jar)	20	15	($Na_2[PdCl_4]$) 1:1 gram	Yes, 2 times water.	χ=99%, S=99%

[Pd(COD)Br_2] (1b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T15 (Zr jar)	20	15	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=86%, S=86%
T16 (Zr jar)	30	15	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=98%, S=98%
T17 (Epp.)	20	15	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=36%, S=36%
T18 (Epp.)	30	15	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=77%, S=77%

[Pd(phen)$(OAc)_2$] (2a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T19 (Epp.)	120	30	($Pd(OAc)_2$) 1:1.1	Yes, 3 times pentane.	χ=71%, S=71%
T20 (Epp.)	120	30	($Pd(OAc)_2$) 1:1	No	χ=96%, S=94%
T21 (Epp.)	90	30	($Pd(OAc)_2$) 1:1	No	χ=96%, S=94%
T22 (Epp.)	60	30	($Pd(OAc)_2$) 1:1	No	χ=71%, S=71%
T23 (Epp.)	120	30	($Pd(OAc)_2$) 1:2	No	χ=50%, S=50%
T24 (Epp.)	120	30	($Pd(OAc)_2$) 1:2	Yes, 3 times Et_2O.	χ=78%, S=78%

[Pd(phen)Cl_2] (2b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T25 (Epp.)	120	30	($PdCl_2$) 1:1.4	No	χ=69%, S=69%
T26 (Epp.)	120	30	($PdCl_2$) 1:1.4	Yes, 3 times pentane.	χ=87%, S=87%
T27 (Epp.)	120	30	($PdCl_2$) 1:1.1	No	χ=90%, S=90%

T28 (Epp.)	120	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T29 (Epp.)	90	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T30 (Epp.)	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T31 (Epp.)	120	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T32 (Epp.)	90	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T33 (Epp.)	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T34 (Epp.)	120	30	($Na_2[PdCl_4]$) 1:1.1	Yes, 3 times water.	χ=90%, S=90%
T35 (Epp.)	120	30	($Na_2[PdCl_4]$) 1:2	Yes, 3 times water.	χ=50%, S=50%
T36 (Epp.)	120	30	($Na_2[PdCl_4]$) 1:2	Yes, 3 times Et_2O.	χ=77%, S=77%

[Pd(phen)Br_2] (2c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T37 (Epp.)	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=91%, S=91%
T38 (Epp.)	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=92%, S=92%
T39 (Epp.)	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=91%, S=91%
T40 (Epp.)	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 2 times water.	χ=85%, S=85%

[Pd(phen)I_2] (2d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T41 (Epp.)	120	30	(PdI_2) 1:1.3	No	χ=65%, S=65%
T42 (Epp.)	120	30	(PdI_2) 1:1.3	Yes, 3 times pentane.	χ=81%, S=81%
T43 (Epp.)	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T44 (Epp.)	90	30	(PdI_2) 1:1	No	χ>99%, S>99%
T45 (Epp.)	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

[Pd(terpy)(OAc)](OAc) (3a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T46 (Epp.)	120	30	($Pd(OAc)_2$) 1:1.1	No	χ=80%, S=80%
T47 (Epp.)	120	30	($Pd(OAc)_2$) 1:1.1	Yes, 3 times pentane.	χ=95%, S=95%
T48 (Epp.)	120	30	($Pd(OAc)_2$) 1:1.1	Yes, 3 times Et_2O.	χ=98%, S=98%
T49 (Epp.)	60	30	($Pd(OAc)_2$) 1:1	No	χ=84%, S=84%
T50 (Epp.)	90	30	($Pd(OAc)_2$) 1:1	No	χ=91%, S=91%

[Pd(terpy)Cl]Cl (3b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T51 (Epp.)	120	30	($PdCl_2$) 1:1.1	No	χ=84%, S=84%
T52 (Epp.)	120	30	($PdCl_2$) 1:1.1	Yes, 3 times pentane.	χ=95%, S=95%
T53 (Epp.)	120	30	($PdCl_2$) 1:1.1	Yes, 5 times pentane.	χ=96%, S=96%
T54 (Epp.)	120	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T55 (Epp.)	120	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T56 (Epp.)	90	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T57 (Epp.)	75	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T58 (Epp.)	60	30	($PdCl_2$) 1:1	No	χ=96%, S=96%
T59 (Epp.)	30	30	($PdCl_2$) 1:1	No	χ=94%, S=94%
T60 (Epp.)	15	30	($PdCl_2$) 1:1	No	χ=95%, S=95%
T61 (Epp.)	10	30	($PdCl_2$) 1:1	No	χ=94%, S=94%
T62 (Epp.)	5	30	($PdCl_2$) 1:1	No	χ=92%, S=92%
T63 (Epp.)	90	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

T64 (Epp.)	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T65 (Epp.)	50	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=94%, S=94%
T66 (Epp.)	40	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=93%, S=93%
T67 (Epp.)	30	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=89%, S=89%
T68 (Epp.)	15	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=84%, S=84%
T69 (Epp.)	10	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=80%, S=80%
T70 (Epp.)	5	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=78%, S=78%

[Pd(terpy)Br]Br (3c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T71 (Epp.)	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ=94%, S=94%
T72 (Epp.)	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ=94%, S=94%
T73 (Epp.)	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ=87%, S=87%

[Pd(terpy)I]I (3d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T74 (Epp.)	120	30	(PdI_2) 1:1.1	No	χ=71%, S=71%
T75 (Epp.)	120	30	(PdI_2) 1:1.1	Yes, 5 times pentane.	χ=96%, S=96%
T76 (Epp.)	120	30	(PdI_2) 1:1	No	χ=96%, S=96%
T77 (Epp.)	120	30	(PdI_2) 1:1	No	χ=96%, S=96%
T78 (Epp.)	60	30	(PdI_2) 1:1	No	χ=63%, S=63%

[Pd(PPh_3)$_2$(OAc)$_2$] (4a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T79 (Epp.)	120	30	($Pd(OAc)_2$) 1:2.2	No	100% of PPh_3O
T80 (Epp.)	120	30	($Pd(OAc)_2$) 1:2.2	No	χ>99%, S=3.5% (66% of PPh_3O)
T81 (Epp.)	30	30	($Pd(OAc)_2$) 1:2.2	No	χ=93%, S=50% (28% of PPh_3O)
T82 (Epp.)*	30	30	($Pd(OAc)_2$) 1:2	No	χ=94%, S=81%
T83 (Epp.)*	60	15	($Pd(OAc)_2$) 1:2	No	χ=86%, S=62% (17% of PPh_3O)
T84 (Epp.)*	30	30	($Pd(OAc)_2$) 1:2	Yes	100% of PPh_3O
T85 (Epp.)*	30	30	($Pd(OAc)_2$) 1:2	No	χ=94%, S=81%

*Argon atmosphere

[Pd(PPh_3)$_2$$Cl_2$] (4b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T86 (Epp.)*	30	30	($PdCl_2$) 1:2	No	χ=96%, S=88%
T87 (Epp.)*	60	30	($PdCl_2$) 1:2	No	χ>99%, S=93%
T88 (Epp.)*	30	30	($Na_2[PdCl_4]$) 1:2	Yes, 3 times water.	χ>99%, S=96%
T89 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:2	Yes, 3 times water.	χ>99%, S=98%

*Argon atmosphere

[Pd(PPh_3)$_2$$Br_2$] (4c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T90 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:2	Yes, 3 times water.	χ>99%, S>99%
T91 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:2	Yes, 3 times water.	χ>99%, S>99%
T92 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:2	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(PPh_3)$_2$$I_2$] (4d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T93 (Epp.)*	120	30	(PdI_2) 1:2	No	χ=92%, S=92%

T94 (Epp.)*	120	30	(PdI_2) 1:2	No	χ=93%, S=92%
T95 (Epp.)*	60	30	(PdI_2) 1:2	No	χ=85%, S=83%

*Argon atmosphere

[Pd(Xantphos)(OAc)$_2$] (5a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T96 (Epp.)*	90	30	($Pd(OAc)_2$) 1:1	No	Multiple products, low selectivity.
T97 (Epp.)*	30	30	($Pd(OAc)_2$) 1:1	No	χ=92%, S=69%
T98 (Epp.)*	60	15	($Pd(OAc)_2$) 1:1	No	χ=70%, S=60%
T99 (Epp.)*	30	30	($Pd(OAc)_2$) 1:1	Yes, 3 times Et_2O.	Complete degradation
T100 (Epp.)*	30	30	($Pd(OAc)_2$) 1:1	No	χ=92%, S=72%

*Argon atmosphere

[Pd(Xantphos)Cl$_2$] (5b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T101 (Epp.)*	30	30	($PdCl_2$) 1:1	No	χ=56%, S=56%
T102 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ=78%, S=78%
T103 (Epp.)*	30	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ=98%, S=98%
T104 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T105 (Epp.)*	180	30	($PdCl_2$) 1:1	No	χ>99%, S=90%
T106 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T107 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(Xantphos)Br$_2$] (5c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T108 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S=91%
T109 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S=92%
T110 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S=92%

*Argon atmosphere

[Pd(dppm)Cl$_2$] (6b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T111 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T112 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T113 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T114 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppm)Br$_2$] (6c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T115 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T116 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T117 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppm)I$_2$] (6d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T118 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T119 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T120 (Epp.)*	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

*Argon atmosphere

[Pd(dppe)(OAc)$_2$] (7a)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T121 (Epp.)*	90	30	($Pd(OAc)_2$) 1:1	No	χ>99%, S=86%
T122 (Epp.)*	30	30	($Pd(OAc)_2$) 1:1	No	χ>99%, S>99%
T123 (Epp.)*	60	15	($Pd(OAc)_2$) 1:1	No	χ>99%, S=52%. Multiple products
T124 (Epp.)*	30	30	($Pd(OAc)_2$) 1:1	No	χ>99%, S>99%

*Argon atmosphere

[Pd(dppe)Cl$_2$] (7b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T125 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T126 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T127 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T128 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppe)Br$_2$] (7c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T129 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T130 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T131 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T132 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppe)I$_2$] (7d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T133 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T134 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T135 (Epp.)*	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

*Argon atmosphere

[Pd(dppp)Cl$_2$] (8b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T136 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T137 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T138 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T139 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppp)Br$_2$] (8c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T140 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T141 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T142 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd(dppp)I$_2$] (8d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T143 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T144 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T145 (Epp.)*	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppb)Cl_2]$ (9b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T146 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T147 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T148 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T149 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T150 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppb)Br_2]$ (9c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T151 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T152 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T153 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppf)Cl_2]$ (10b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T154 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T155 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T156 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ>99%, S>99%
T157 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppf)Br_2]$ (10c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T158 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T159 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T160 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppf)I_2]$ (10d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T161 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T162 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T163 (Epp.)*	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

*Argon atmosphere

$[Pd(dppf)Cl_2]$ (11b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T164 (Epp.)*	60	30	($PdCl_2$) 1:1	No	χ=72%, S=72%
T165 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T166 (Epp.)*	60	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

$[Pd(dippf)Br_2]$ (11c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T167 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T168 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T169 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

$[Pd(dippf)I_2]$ (11d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T170 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T171 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T172 (Epp.)*	60	30	(PdI_2) 1:1	No	χ>99%, S>99%

*Argon atmosphere

[Pd((*R*)-BINAP)Cl_2] (12b)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T173 (Epp.)*	120	30	($PdCl_2$) 1:1	No	χ=17%, S=17%
T174 (Epp.)*	120	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T175 (Epp.)*	90	30	($Na_2[PdCl_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%

*Argon atmosphere

[Pd((*R*)-BINAP)Br_2] (12c)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T176 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T177 (Epp.)*	120	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T178 (Epp.)*	90	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ>99%, S>99%
T179 (Epp.)*	60	30	($Na_2[PdBr_4]$) 1:1	Yes, 3 times water.	χ=89%, S=89%

*Argon atmosphere

[Pd((*R*)-BINAP)I_2] (12d)					
Number of trial	**Time (min)**	**Frequency (Hz)**	**Ratio (M:L)**	**Washing**	**Comments**
T180 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T181 (Epp.)*	120	30	(PdI_2) 1:1	No	χ>99%, S>99%
T182 (Epp.)*	90	30	(PdI_2) 1:1	No	χ=15%, S=15%

*Argon atmosphere

Part 3: Calculations for E-factor and Effective Mass Yield (EMY)

E-factor and EMY are calculated according to the following expressions:

$$E-factor = \frac{Mass\ of\ waste}{Mass\ of\ desidered\ product}$$

$$EMY = \frac{Mass\ of\ desidered\ product}{Total\ mass\ of\ material\ used}\ x\ 100$$

Table S1: Green metrics calculation for [Pd(COD)Cl_2] **(1a)**.

[Pd(COD)Cl_2] (1a)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	50.0
1,5-Cyclooctadiene (COD)	30.5
Amount of product	78.9
Waste	1.6
Yield percentage	98
E-factor	0.02
EMY	98
Solution synthesis	
Reactant	**Amount (g)**
$K_2[PdCl_4]$	0.500
1,5-Cyclooctadiene (COD)	0.166
Amount of product	0.420
Waste: $KCl+H_2O+CH_3COOH+CH_2Cl_2+Et_2O$	0.23+30+10.5+26.6+14.2=81.5
Yield percentage	96
E-factor	194
EMY	0.51

Table S2: Green metrics calculation for [Pd(COD)Br_2] **(1b)**.

[Pd(COD)Br_2] (1b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	60.0
1,5-Cyclooctadiene (COD)	13.8
Amount of product	46.6
Waste: $NaBr+H_2O$	26+5000=5026
Yield percentage	98
E-factor	108
EMY	0.92
Solution synthesis	
Reactant	**Amount (g)**
$K_2[PdBr_4]$	0.500
1,5-Cyclooctadiene (COD)	0.107
Amount of product	0.345
Waste: $KBr+H_2O+CH_3COOH+CH_2Cl_2+Et_2O$	0.23+30+10.5+26.6+14.2=81.53
Yield percentage	93
E-factor	236
EMY	0.42

Table S3: Green metrics calculation for [Pd(phen)(OAc)$_2$] **(2a)**.

[Pd(phen)(OAc)$_2$] (2a)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
Pd(OAc)$_2$	15.0
1,10-phenanthroline (phen)	12.0
Amount of product	25.4
Waste	1.6
Yield percentage	94
E-factor	0.06
EMY	94
Solution synthesis	
Reactant	**Amount (g)**
Pd(OAc)$_2$	0.049
1,10-phenanthroline (phen)	0.036
Amount of product	0.063
Waste: CH_2Cl_2+Et_2O	9.31+3.57=12.88
Yield percentage	74
E-factor	204
EMY	0.49

Table S4: Green metrics calculation for [Pd(phen)Cl$_2$] **(2b)**.

[Pd(phen)Cl$_2$] (2b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
1,10-phenanthroline (phen)	15.2
Amount of product	30.2
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$K_2[PdCl_4]$	0.650
1,10-phenanthroline (phen)	0.360
Amount of product	0.669
Waste: KCl+MeOH+H_2O+MeCN	0.298+43.56+5+3.90=52.785
Yield percentage	94
E-factor	79
EMY	1.25

Table S5: Green metrics calculation for [Pd(phen)Br$_2$] **(2c)**.

[Pd(phen)Br$_2$] (2c)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	30.0
1,10-phenanthroline (phen)	11.5
Amount of product	25.8
Waste: NaBr+H_2O	13+2000=2013
Yield percentage	91
E-factor	78
EMY	1.26
Solution synthesis	

Reactant	Amount (g)
$K_2[PdBr_4]$	0.2033
1,10-phenanthroline (phen)	0.0727
Amount of product	0.1422
Waste: KBr+H_2O+Et_2O	0.048+30+7.13=37.178
Yield percentage	79
E-factor	261
EMY	0.38

Table S6: Green metrics calculation for [Pd(phen)I_2] **(2d)**.

[Pd(phen)I_2] (2d)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
1,10-phenanthroline (phen)	10.0
Amount of product	29.9
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$Pd(OAc)_2$ + 2.4 eq KI	0.111 + 0.200
1,10-phenanthroline (phen)	0.100
Amount of product	0.054
Waste: KI+$Pd(OAc)_2$+Phen+EtOH+H_2O	0.16+0.09+0.08+23.67+10=34
Yield percentage	20
E-factor	630
EMY	0.16

Table S7: Green metrics calculation for [Pd(terpy)(OAc)](OAc) **(3a)**.

[Pd(terpy)(OAc)](OAc) (3a)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Pd(OAc)_2$	20.0
2,2';6',2''-terpyridine (terpy)	22.8
Amount of product	40.0
Waste: Et_2O+exc.	2140+2=2142
Yield percentage	98
E-factor	54
EMY	1.83

Table S8: Green metrics calculation for [Pd(terpy)Cl]Cl **(3b)**.

[Pd(terpy)Cl]Cl (3b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
2,2';6',2''-terpyridine (terpy)	19.7
Amount of product	34.6
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**

$[Pd(COD)Cl_2]$	0.114
2,2';6',2"-terpyridine (terpy)	0.093
Amount of product	0.161
Waste: $COD+H_2O+Et_2O$	0.043+10+7.8=17.84
Yield percentage	98
E-factor	111
EMY	0.89

Table S9: Green metrics calculation for [Pd(terpy)Br]Br **(3c)**.

[Pd(terpy)Br]Br (3c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	30.0
2,2';6',2"-terpyridine (terpy)	14.8
Amount of product	29.9
Waste: $NaBr+H_2O$	13.09+2000=2013.9
Yield percentage	95
E-factor	67
EMY	1.46

Table S10: Green metrics calculation for [Pd(terpy)I]I **(3d)**.

[Pd(terpy)I]I (3d)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
2,2';6',2"-terpyridine (terpy)	13.0
Amount of product	31.7
Waste	1.3
Yield percentage	96
E-factor	0.04
EMY	96

Table S11: Green metrics calculation for $[Pd(PPh_3)_2Cl_2]$ **(4b)**.

$[Pd(PPh_3)_2Cl_2]$ (4b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
Triphenylphosphine (PPh_3)	44.4
Amount of product	55.2
Waste	4.16
Yield percentage	93
E-factor	0.08
EMY	93
Solution synthesis	
Reactant	**Amount (g)**
$PdCl_2+LiCl$	8.85+4.25
Triphenylphosphine (PPh_3)	27.5
Amount of product	32.7
Waste: LiCl+MeOH	4.25+83.16+2.54=90.2
Yield percentage	93
E-factor	2.76
EMY	26

Table S12: Green metrics calculation for $[Pd(PPh_3)_2Br_2]$ **(4c)**.

[Pd(PPh$_3$)$_2$Br$_2$] (4c)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
Na$_2$[PdBr$_4$]	20.0
Triphenylphosphine (PPh$_3$)	22.2
Amount of product	32.2
Waste: NaBr+H$_2$O	8.73+2000=2008.73
Yield percentage	>99
E-factor	62
EMY	1.58
Solution synthesis	
Reactant	**Amount (g)**
K$_2$[PdCl$_4$]+KBr	1.00+3.64
Triphenylphosphine (PPh$_3$)	1.77
Amount of product	2.37
Waste:KCl+KCl+KBr$_{exc}$+PPh$_{3exc}$+EtOH+H$_2$O+pentane+CHCl$_3$	0.72+0.46+2.2+0.16+15.8+10+6.6+14.7=50.64
Yield percentage	97
E-factor	21
EMY	4.45

Table S13: Green metrics calculation for [Pd(PPh$_3$)$_2$I$_2$] **(4d)**.

[Pd(PPh$_3$)$_2$I$_2$] (4d)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI$_2$	20.0
Triphenylphosphine (PPh$_3$)	29.1
Amount of product	45.2
Waste: CH$_2$Cl$_2$+Et$_2$O	2660+1426=4086
Yield percentage	92
E-factor	90
EMY	1.09
Solution synthesis	
Reactant	**Amount (g)**
K$_2$[PdCl$_4$]+KI	1.00+5.09
Triphenylphosphine (PPh$_3$)	1.79
Amount of product	2.63
Waste: KCl+KI+KI$_{exc}$+PPh$_{3exc}$+EtOH+H$_2$O+pentane+CHCl$_3$	0.92+1.03+3.05+0.16+15.8+10+6.6+14.7=52.26
Yield percentage	97
E-factor	20
EMY	4.78

Table S14: Green metrics calculation for [Pd(Xantphos)Cl$_2$] **(5b)**.

[Pd(Xantphos)Cl$_2$] (5b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
Na$_2$[PdCl$_4$] (Method B)	20.0
Xantphos	39.3
Amount of product	51.3
Waste: NaCl+Et$_2$O	7.95+1426=1433.95
Yield percentage	>99
E-factor	28
EMY	3.45
Solution synthesis	
Reactant	**Amount (g)**
[Pd(MeCN)$_2$Cl$_2$]	1.00

Xantphos	2.46
Amount of product	2.88
Waste: Benzene+Et_2O+exc.Xantphos	148.84+64.17+0.22=213.23
Yield percentage	98
E-factor	74
EMY	1.33

Table S15: Green metrics calculation for [Pd(Xantphos)Br_2] **(5c)**.

[Pd(Xantphos)Br_2] (5c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
Xantphos	24.5
Amount of product	33.0
Waste: NaBr+CH2Cl2+Et2O	8.7+2660+1420=4094.7
Yield percentage	92
E-factor	124
EMY	0.80
Solution synthesis	
Reactant	**Amount (g)**
$PdBr_2$	0.00532
Xantphos	0.01157
Amount of product	0.01436
Waste: MeCN+Benzene+Et_2O+pentane	7.8+8.8+14.26+6.26=37.12
Yield percentage	85
E-factor	2585
EMY	0.04

Table S16: Green metrics calculation for [Pd(dppm)Cl_2] **(6b)**.

[Pd(dppm)Cl_2] (6b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
bis(diphenylphosphino)methane (dppm)	32.5
Amount of product	47.4
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$[Pd(PhCN)_2Cl_2]$	0.965
bis(diphenylphosphino)methane (dppm)	1.01
Amount of product	1.17
Waste: PhCN+Benzene+pentane+exc.	0.52+21.975+15.75+0.33=38.575
Yield percentage	83
E-factor	33
EMY	2.95

Table S17: Green metrics calculation for [Pd(dppm)Br_2] **(6c)**.

[Pd(dppm)Br_2] (6c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
bis(diphenylphosphino)methane (dppm)	16.3

Amount of product	30.4
Waste: $NaBr+H_2O$	8.72+2000=2008.72
Yield percentage	>99
E-factor	66
EMY	1.49
Solution synthesis	
Reactant	**Amount (g)**
[Pd(dppm)Cl_2] (*E-factor*=33)	1.17
LiBr	0.265
Amount of product	1.36
Waste: $LiCl+H_2O$+Acetone	0.2+20+23.52=43.72
Yield percentage	90 ca.
E-factor	65 (32+33)
EMY	1.61

Table S18: Green metrics calculation for [Pd(dppm)I_2] **(6d)**.

[Pd(dppm)I_2] (6d).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
bis(diphenylphosphino)methane (dppm)	21.3
Amount of product	41.1
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
[Pd(dppm)Cl_2] (*E-factor*=33)	0.10
NaI	0.40
Amount of product	0.13
Waste: NaCl+NaClexc.+CH_2Cl_2+MeOH+Et_2O	0.02+0.35+26.6+23.7+21.39=72.06
Yield percentage	97
E-factor	587 (33+554)
EMY	0.15

Table S19: Green metrics calculation for [Pd(dppe)$(OAc)_2$] **(7a)**.

[Pd(dppe)$(OAc)_2$] (7a).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Pd(OAc)_2$	15.0
bis(diphenylphosphino)ethane (dppe)	26.6
Amount of product	40.8
Waste	0.8
Yield percentage	98
E-factor	0.02
EMY	98
Solution synthesis	
Reactant	**Amount (g)**
$Pd(OAc)_2$	0.50
bis(diphenylphosphino)ethane (dppe)	0.89
Amount of product	1.18
Waste: $CH_2Cl_2+Et_2O$	0.21+40+14.26=54.47
Yield percentage	85
E-factor	46
EMY	2.12

Table S20: Green metrics calculation for [Pd(dppe)Cl_2] **(7b)**.

[Pd(dppe)Cl_2] (7b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
bis(diphenylphosphino)ethane (dppe)	33.7
Amount of product	48.6
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
[Pd(PhCN)$_2$$Cl_2$]	0.965
bis(diphenylphosphino)ethane (dppe)	1.036
Amount of product	1.19
Waste: PhCN+Benzene+pentane+exc.	0.52+21.975+15.75+0.33=38.575
Yield percentage	90 ca.
E-factor	32
EMY	3.00

Table S21: Green metrics calculation for [Pd(dppe)Br_2] **(7c)**.

[Pd(dppe)Br_2] (7c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
Na_2[$PdBr_4$]	20.0
bis(diphenylphosphino)ethane (dppe)	16.9
Amount of product	28.1
Waste: NaBr+H_2O	2000+8.72=2008.72
Yield percentage	>99
E-factor	71
EMY	1.38
Solution synthesis	
Reactant	**Amount (g)**
$PdBr_2$	0.597
bis(diphenylphosphino)ethane (dppe)	0.399
Amount of product	0.8466
Waste: Toluene+Et_2O	26.01+42.78=68.79
Yield percentage	85
E-factor	81
EMY	1.21

Table S22: Green metrics calculation for [Pd(dppe)I_2] **(7d)**.

[Pd(dppe)I_2] (7d).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
bis(diphenylphosphino)ethane (dppe)	22.1
Amount of product	41.9
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	

Reactant	Amount (g)
[Pd(N,N'-dimethyl-perhydrodiazepine-2,3-dithione)I_2]	0.0300
bis(diphenylphosphino)ethane (dppe)	0.0190
Amount of product	0.0325
Waste: Acetone+EtOH+Et_2O	7.84+3.945+3.55=15.335
Yield percentage	87
E-factor	471
EMY	0.21

Table S23: Green metrics calculation for [Pd(dppp)Cl_2] **(8b)**.

[Pd(dppp)Cl_2] (8b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
bis(diphenylphosphino)propane (dppp)	34.9
Amount of product	49.8
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
[Pd(PhCN)$_2$$Cl_2$]	0.965
bis(diphenylphosphino)propane (dppp)	1.090
Amount of product	1.34
Waste: PhCN+Benzene+pentane+exc.	0.52+21.975+15.75+0.33=38.575
Yield percentage	90 ca.
E-factor	29
EMY	3.37

Table S24: Green metrics calculation for [Pd(dppp)Br_2] **(8c)**.

[Pd(dppp)Br_2] (8c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	15.0
bis(diphenylphosphino)propane (dppp)	17.5
Amount of product	28.7
Waste	8.7
Yield percentage	>99
E-factor	143
EMY	0.70
Solution synthesis	
Reactant	**Amount (g)**
$PdCl_2$	0.200
bis(diphenylphosphino)propane (dppp)	0.460
Amount of product	0.570
Waste: CH_2Cl_2+H_2O+KBr exc.+Na_2SO_4+esano	0.2+19.95+10+5.73+10+3.3=49.18
Yield percentage	75
E-factor	86
EMY	1.14

Table S25: Green metrics calculation for [Pd(dppp)I_2] **(8d)**.

[Pd(dppp)I_2] (8d).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**

PdI_2	20.0
bis(diphenylphosphino)propane (dppp)	22.9
Amount of product	42.8
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$[Pd(PhCN)_2Cl_2]$+NaI	0.250+0.816
bis(diphenylphosphino)butane (dppb)	0.270
Amount of product	0.288
Waste: exc.+PhCN+CH_2Cl_2+Et_2O+NaI+H_2O+EtOH	0.1+0.13+53.2+32.09+.78+10+7.89=104.19
Yield percentage	57
E-factor	362
EMY	0.28

Table S26: Green metrics calculation for $[Pd(dppb)Cl_2]$ **(9b)**.

$[Pd(dppb)Cl_2]$ (9b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
bis(diphenylphosphino)butane (dppb)	36.1
Amount of product	51.0
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$PdCl_2$	0.287
bis(diphenylphosphino)butane (dppb)	0.67
Amount of product	0.600
Waste: exc.+MeCN+Et_2O	0.37+39+14.26=53.63
Yield percentage	61
E-factor	89
EMY	1.11

Table S27: Green metrics calculation for $[Pd(dppb)Br_2]$ **(9c)**.

$[Pd(dppb)Br_2]$ (9c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
bis(diphenylphosphino)butane (dppb)	18.1
Amount of product	29.3
Waste: NaBr+H_2O	8.7+2000=2008.7
Yield percentage	>99
E-factor	69
EMY	1.44
Solution synthesis	
Reactant	**Amount (g)**
$K_2[PdBr_4]$	0.2526
bis(diphenylphosphino)butane (dppb)	0.2124
Amount of product	0.1412
Waste: KBr+exc.+MeOH+H_2O+Acetone	0.281+15.84+20+15.68=51.801
Yield percentage	41

E-factor	367
EMY	0.28

Table S28: Green metrics calculation for [Pd(dppf)Cl_2] **(10b)**.

[Pd(dppf)Cl_2] (10b).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$PdCl_2$ (Method A)	15.0
bis(diphenylphosphino)ferrocene (dppf)	46.9
Amount of product	61.4
Waste	0
Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
[Pd(NBD)Cl_2]	2.69
Bicyclo[2.2.1]hepta-2,5-diene (NBD)	5.54
Amount of product	6.95
Waste: NBD+Acetone+Et_2O	0.37+0.92+78.4+78.61=158.3
Yield percentage	95
E-factor	23
EMY	4.21

Table S29: Green metrics calculation for [Pd(dppf)Br_2] **(10c)**.

[Pd(dppf)Br_2] (10c).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
bis(diphenylphosphino)ferrocene (dppf)	23.5
Amount of product	34.7
Waste: NaBr+H_2O	8.7+2000=2008.7
Yield percentage	>99
E-factor	58
EMY	1.70
Solution synthesis	
Reactant	**Amount (g)**
[Pd(NBD)Br_2]	3.58
Bicyclo[2.2.1]hepta-2,5-diene (NBD)	5.54
Amount of product	7.8
Waste: NBD+Acetone+Et_2O	0.37+0.92+78.4+78.61=158.3
Yield percentage	95
E-factor	20
EMY	4.70

Table S30: Green metrics calculation for [Pd(dppf)I_2] **(10d)**.

[Pd(dppf)I_2] (10d).	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
bis(diphenylphosphino)ferrocene (dppf)	30.8
Amount of product	50.7
Waste	0

Yield percentage	>99
E-factor	0
EMY	100
Solution synthesis	
Reactant	**Amount (g)**
$[Pd(COD)Cl_2]$+NaI	2.855+3.2
bis(diphenylphosphino)ferrocene (dppf)	5.54
Amount of product	8.96
Waste: exc.NaI+NaCl+COD+Et2O+Acetone+EtOH	1.7+0.58+1.08+106.95+39.2+138.1=287.61
Yield percentage	98
E-factor	32
EMY	2.94

Table S31: Green metrics calculation for $[Pd(dippf)Cl_2]$ **(11b)**.

$[Pd(dippf)Cl_2]$ (11b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdCl_4]$ (Method B)	15.0
bis(diisopropylphosphino)ferrocene (dippf)	21.3
Amount of product	30.2
Waste: NaCl+H_2O	6+2000=2006
Yield percentage	>99
E-factor	66
EMY	1.48
Solution synthesis	
Reactant	**Amount (g)**
$[Pd(COD)Cl_2]$	0.0179
bis(diisopropylphosphino)ferrocene (dippf)	0.0262
Amount of product	0.0224
Waste: exc.+$HCl_{37\%}$+EtOH+Et_2O+H_2O	0.027+2.38+1.578+1.438+100=105.42
Yield percentage	38
E-factor	4706
EMY	0.02

Table S32: Green metrics calculation for $[Pd(dippf)Br_2]$ **(11c)**.

$[Pd(dippf)Br_2]$ (11c)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
bis(diisopropylphosphino)ferrocene (dippf)	17.72
Amount of product	28.8
Waste: NaBr+H_2O	8.7+2000=2008.7
Yield percentage	>99
E-factor	69
EMY	1.48

Table S33: Green metrics calculation for $[Pd(dippf)I_2]$ **(11d)**.

$[Pd(dippf)I_2]$ (11d)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	20.0
bis(diisopropylphosphino)ferrocene (dippf)	23.2
Amount of product	43.2
Waste	0
Yield percentage	>99

E-factor	0
EMY	100

Table S34: Green metrics calculation for [Pd((*R*)-BINAP)Cl_2] **(12b)**.

[Pd((*R*)-BINAP)Cl_2] (12b)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdCl_4]$	15.0
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)	31.7
Amount of product	40.4
Waste: NaCl+H_2O	6+2000=2006
Yield percentage	>99
E-factor	50
EMY	1.97
Solution synthesis	
Reactant	**Amount (g)**
[Pd(COD)Cl_2]	0.23
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)	0.50
Amount of product	0.62
Waste: COD+CH_2Cl_2+hexane+Et_2O	0.09+19.95+13.22+7.13=47.52
Yield percentage	97
E-factor	77
EMY	1.29

Table S35: Green metrics calculation for [Pd((*R*)-BINAP)Br_2] **(12c)**.

[Pd((*R*)-BINAP)Br_2] (12c)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
$Na_2[PdBr_4]$	20.0
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)	26.4
Amount of product	37.4
Waste: NaBr+H_2O	8.7+2000=2008.7
Yield percentage	>99
E-factor	54
EMY	1.83
Solution synthesis	
Reactant	**Amount (g)**
[Pd(MeCN)$_2Br_2$]	0.174
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)	0.311
Amount of product	0.395
Waste: MeCN+Benzene+Et_2O	0.073+0.041+8.787+21.39=30.29
Yield percentage	85
E-factor	77
EMY	1.29

Table S36: Green metrics calculation for [Pd((*R*)-BINAP)I_2] **(12d)**.

[Pd((*R*)-BINAP)I_2] (12d)	
Mechanochemical synthesis	
Reactant	**Amount (mg)**
PdI_2	15.0
(*R*)-2,2′-bis(diphenylphosphino)-1,1′-binaphthyl ((*R*)-BINAP)	25.9
Amount of product	40.5
Waste	0

Yield percentage	>99
E-factor	0
EMY	100

Part 4. NMR's characterizations spectra's

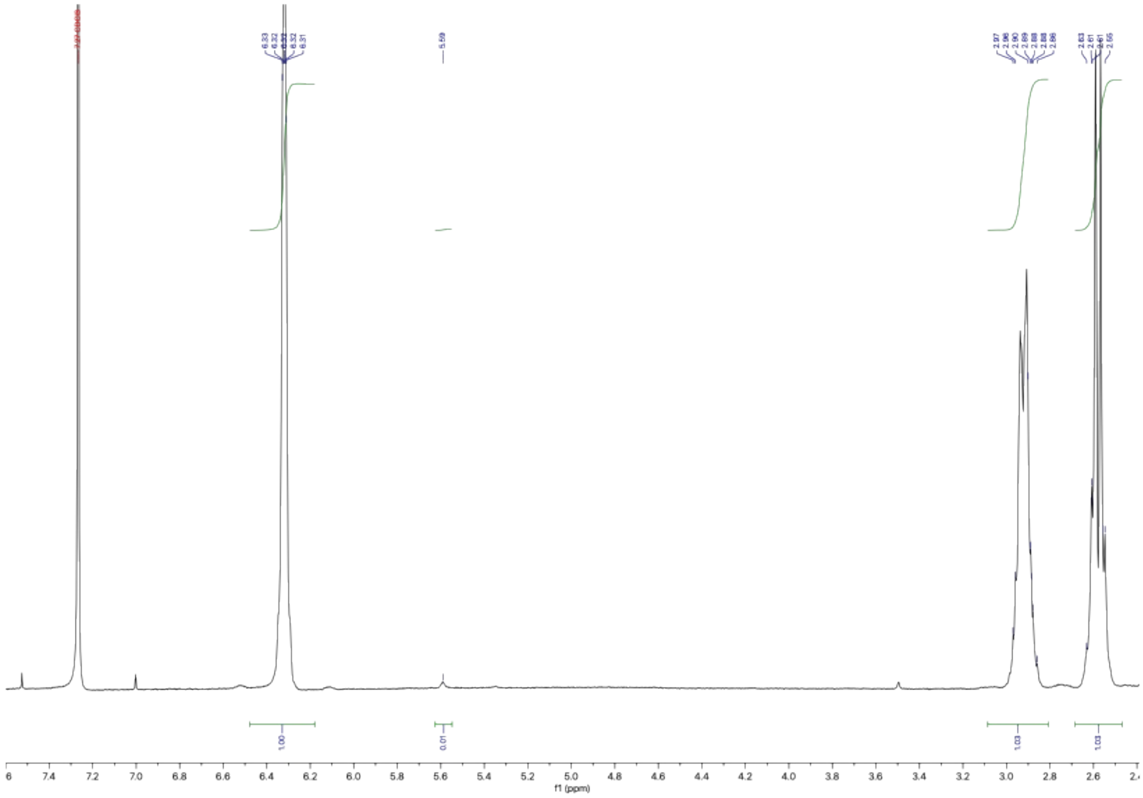
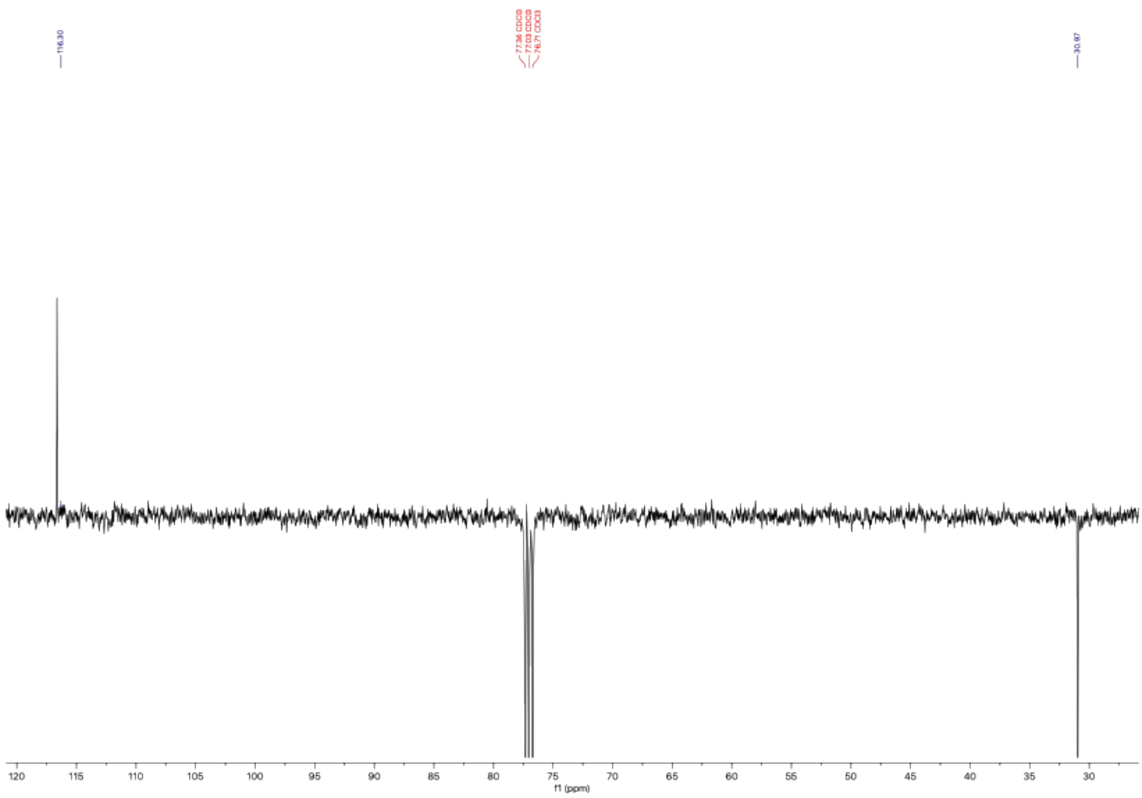


Figure S3. ^1H NMR spectra of $[Pd(COD)Cl_2]$ **(1a)** (400.1 MHz, $CDCl_3$, 298K).



FigureS4. $^{13}C\{^1H\}$ NMR spectra of [Pd(COD)Cl_2] **(1a)** (100.6 MHz, $CDCl_3$, 298K).

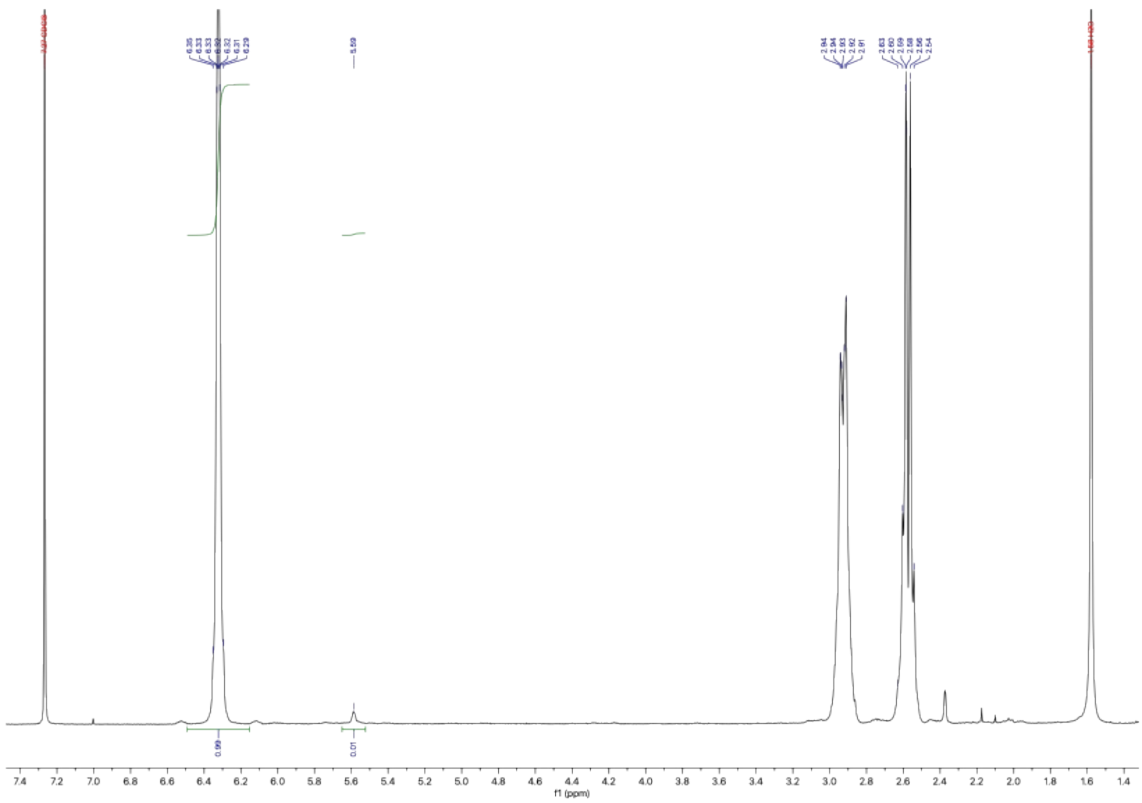


Figure S5. ^1H NMR spectra of [Pd(COD)Cl_2] **(1a)**, gram scale synthesis (400.1 MHz, $CDCl_3$, 298K).

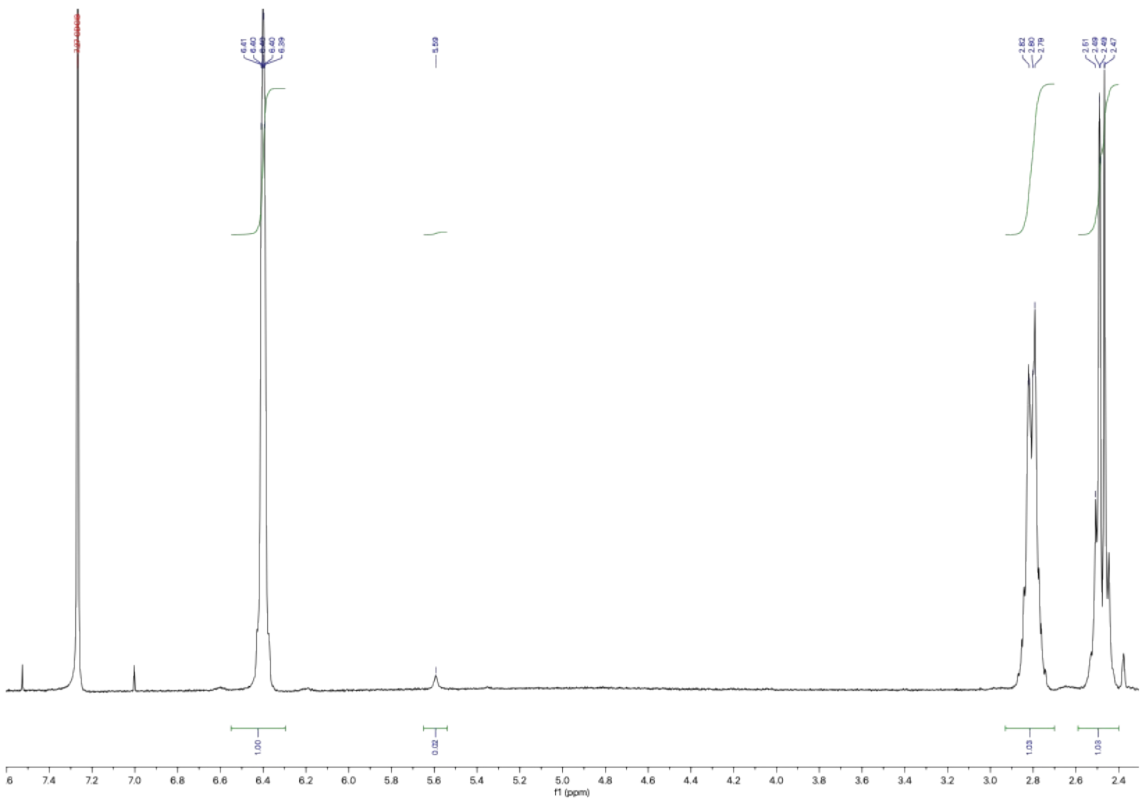


Figure S6. ^{1}H NMR spectra of $[Pd(COD)Br_2]$ **(1b)** (400.1 MHz, $CDCl_3$, 298K).

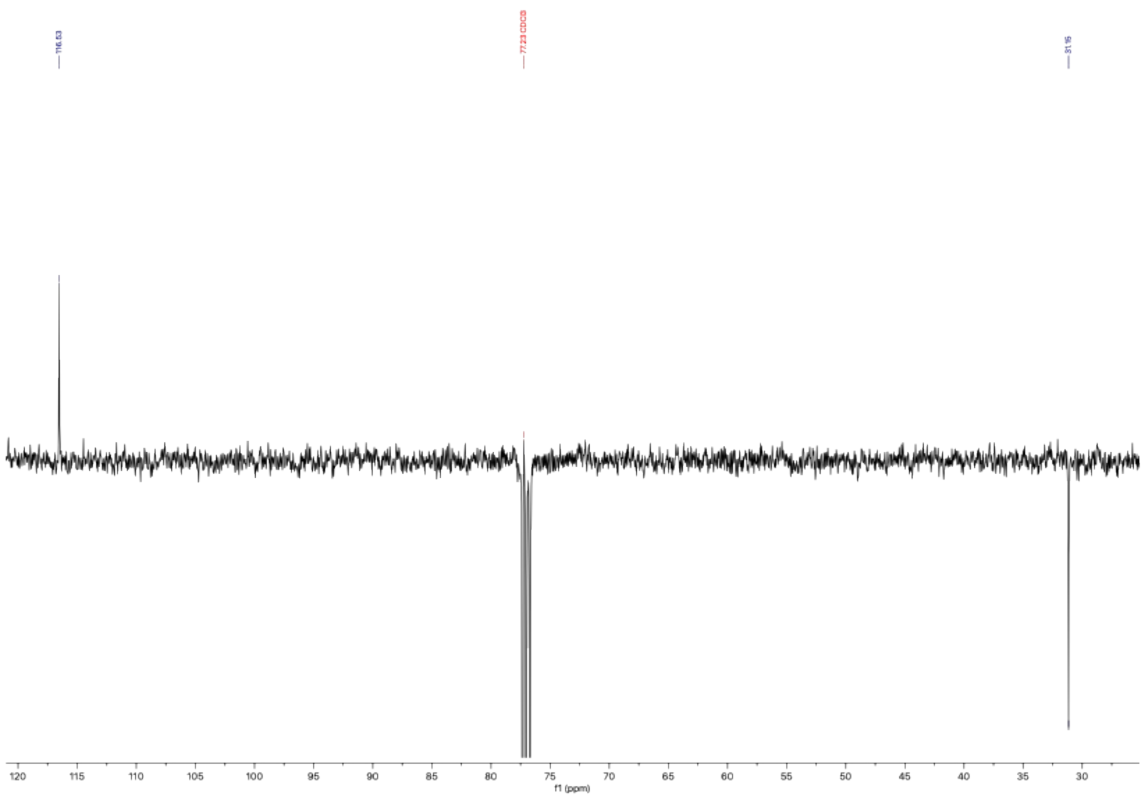


Figure S7. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(COD)Br_2]$ **(1b)** (100.6 MHz, $CDCl_3$, 298K).

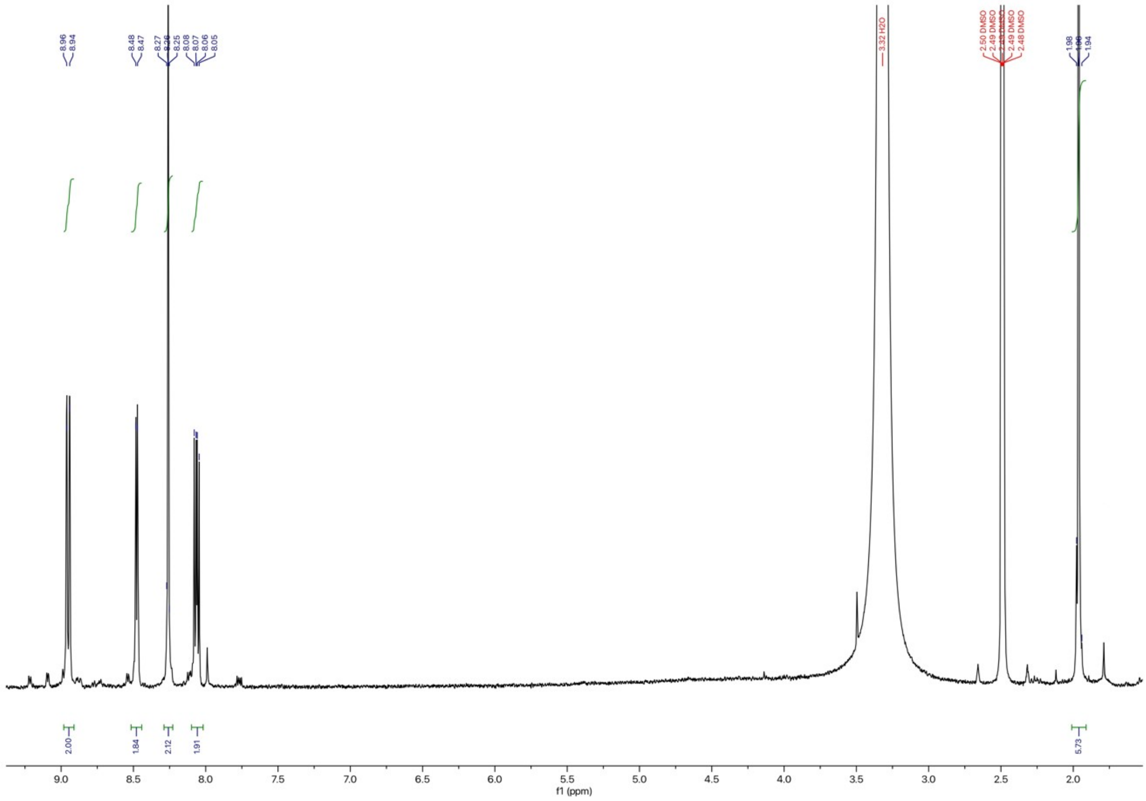


Figure S8. ^{1}H NMR spectra of [Pd(phen)(OAc)$_2$] **(2a)** (400.1 MHz, DMSO-d$_6$, 298K).

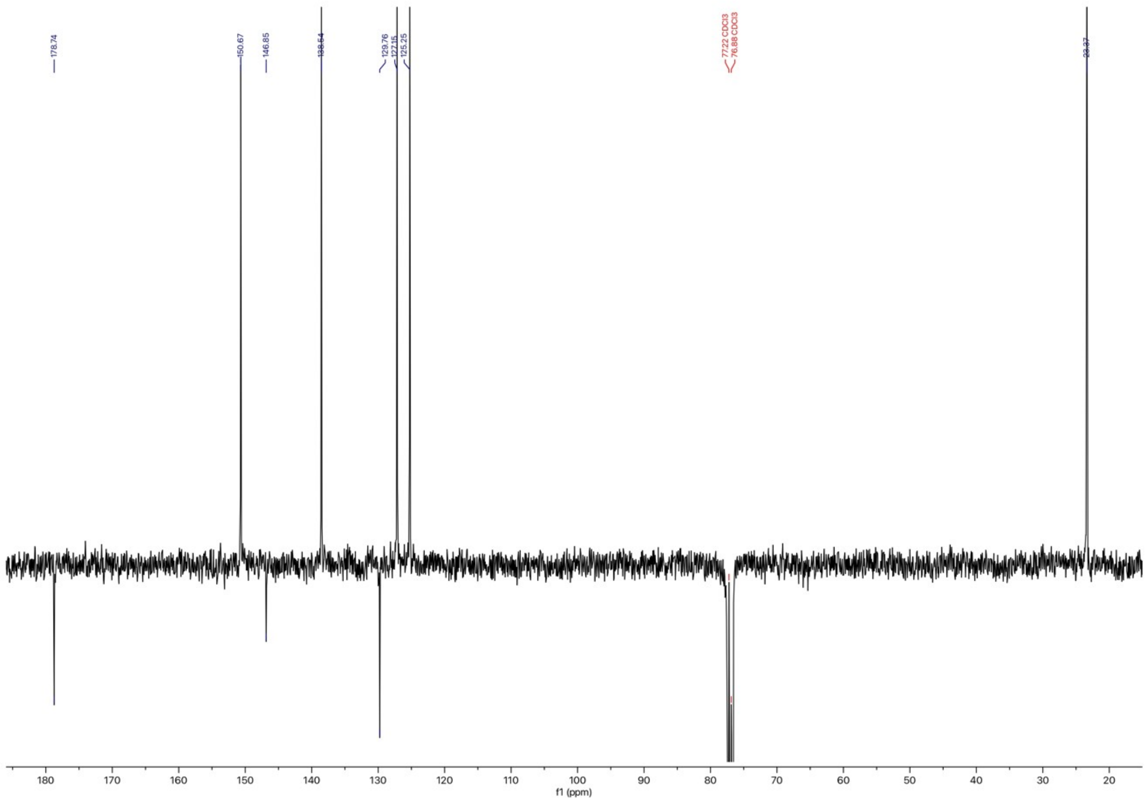


Figure S9. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(phen)(OAc)$_2$] **(2a)** (100.6 MHz, $CDCl_3$, 298K).

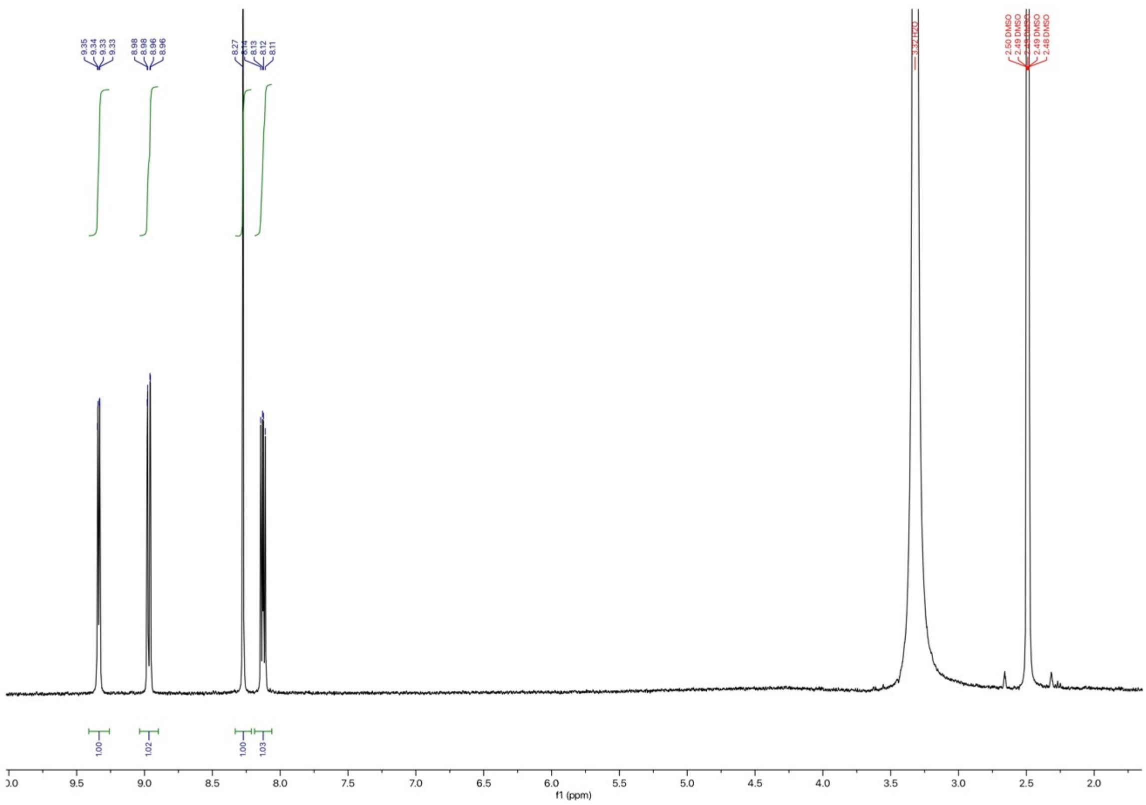


Figure S10. ^{1}H NMR spectra of $[Pd(phen)Cl_2]$ **(2b)** (400.1 MHz, DMSO-d_6, 298K).

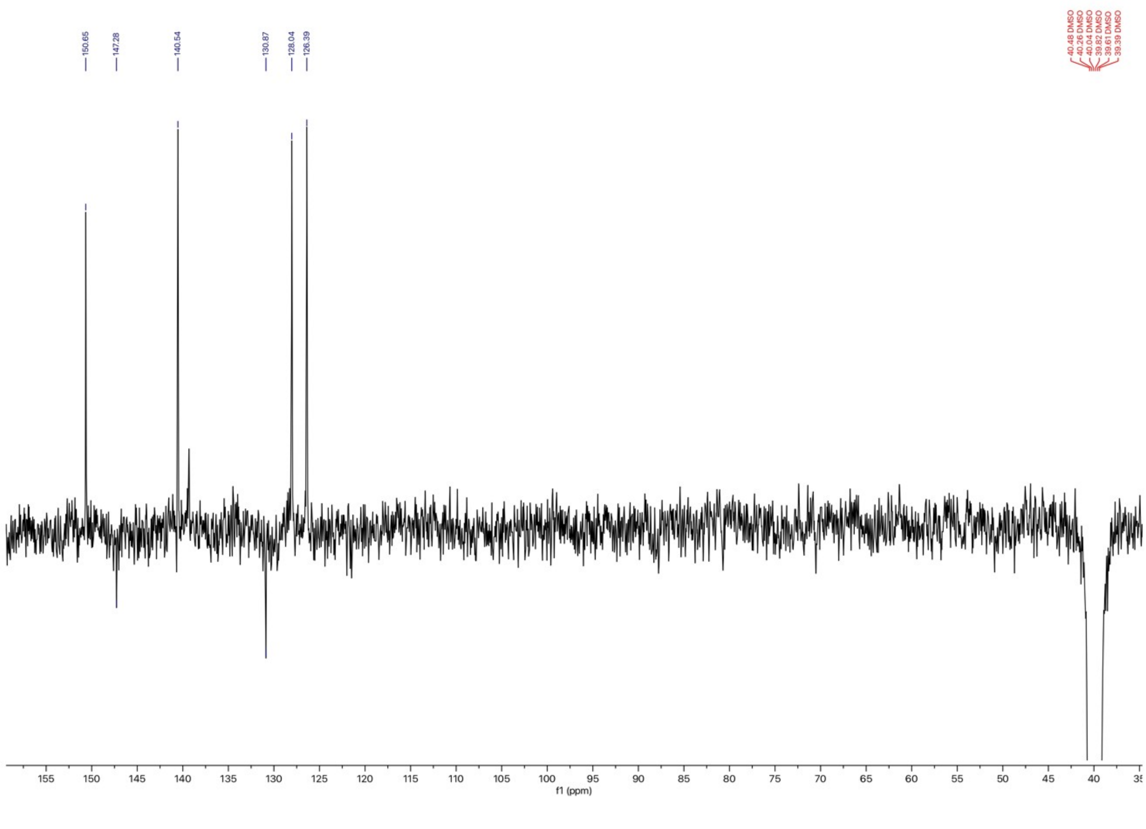


Figure S11. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(phen)Cl_2]$ **(2b)** (100.6 MHz, DMSO-d_6, 298K).

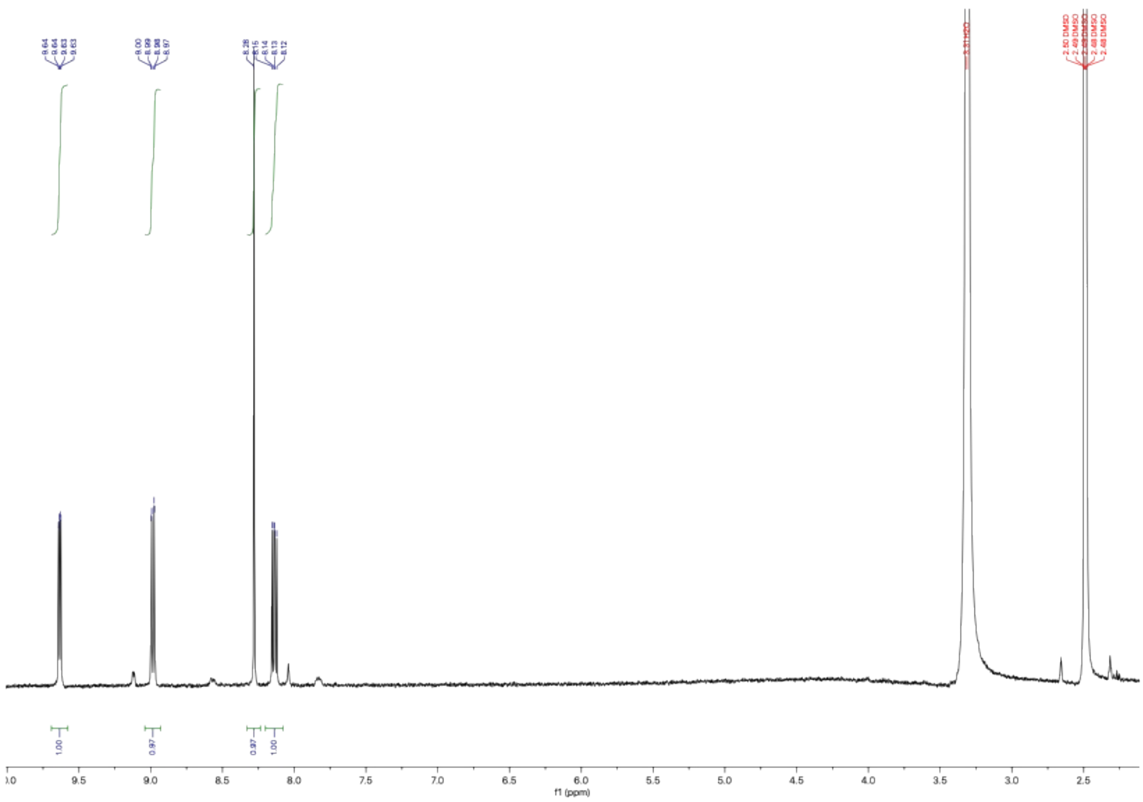


Figure S12. ^{1}H NMR spectra of $[Pd(phen)Br_2]$ **(2c)** (400.1 MHz, DMSO-d_6, 298K).

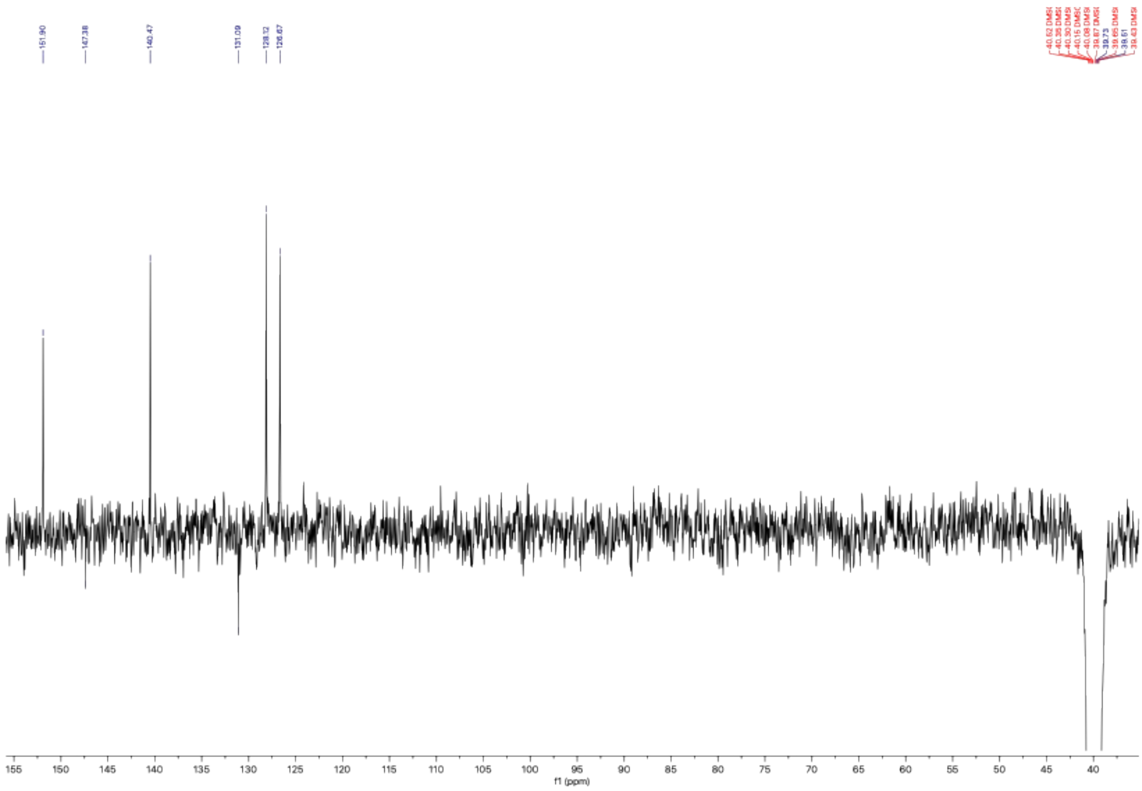


Figure S13. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(phen)Br_2]$ **(2c)** (100.6 MHz, DMSO-d_6, 298K).

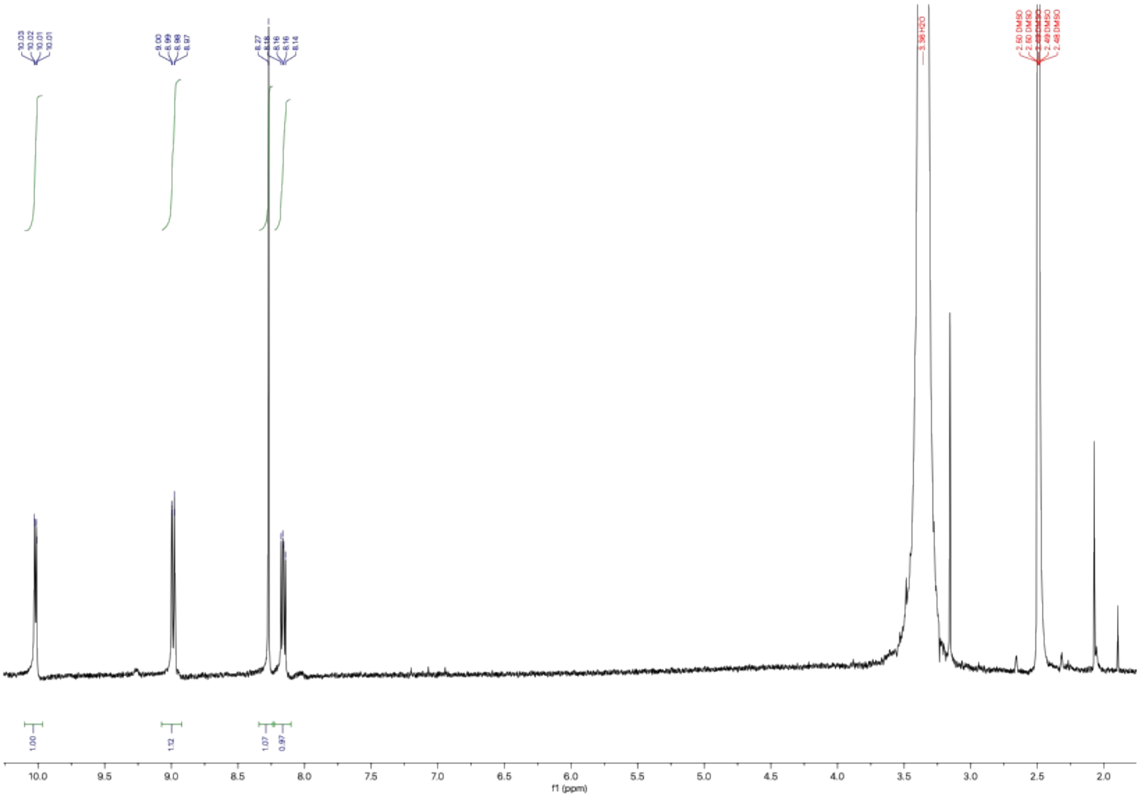


Figure S14. ^{1}H NMR spectra of $[Pd(phen)I_2]$ **(2d)** (400.1 MHz, DMSO-d_6, 298K).

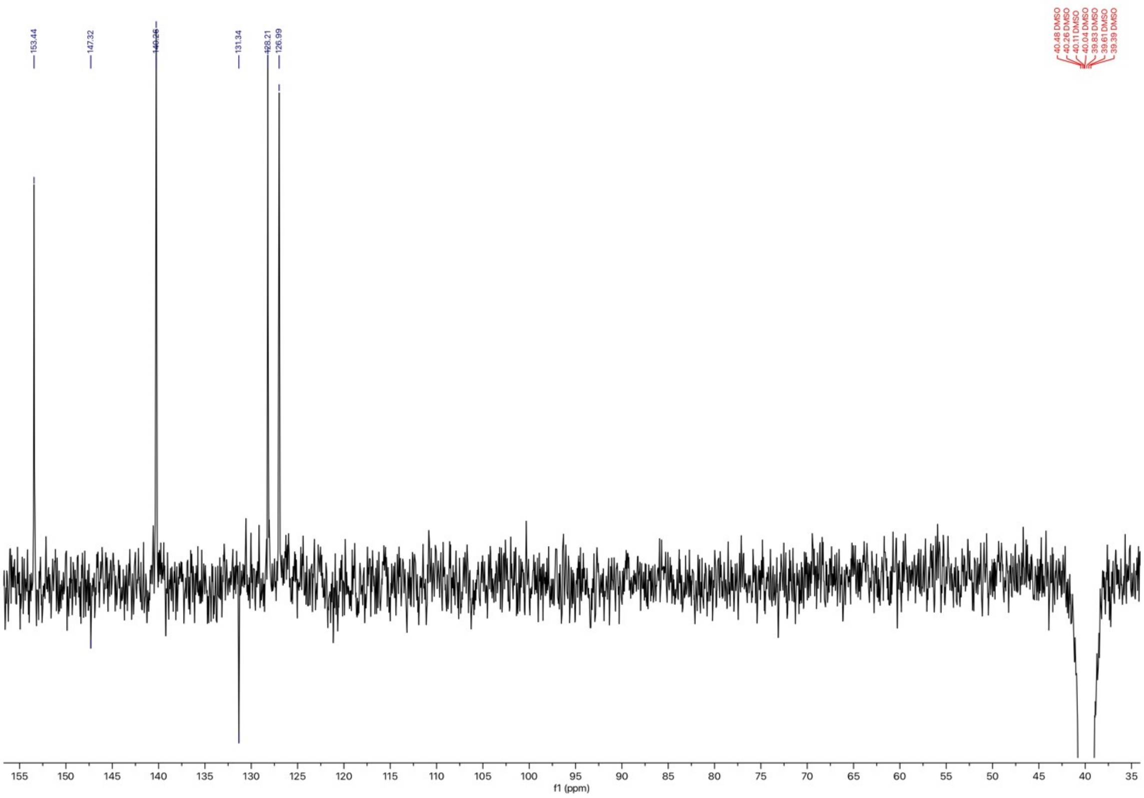


Figure S15. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(phen)I_2]$ **(2d)** (100.6 MHz, DMSO-d_6, 298K).

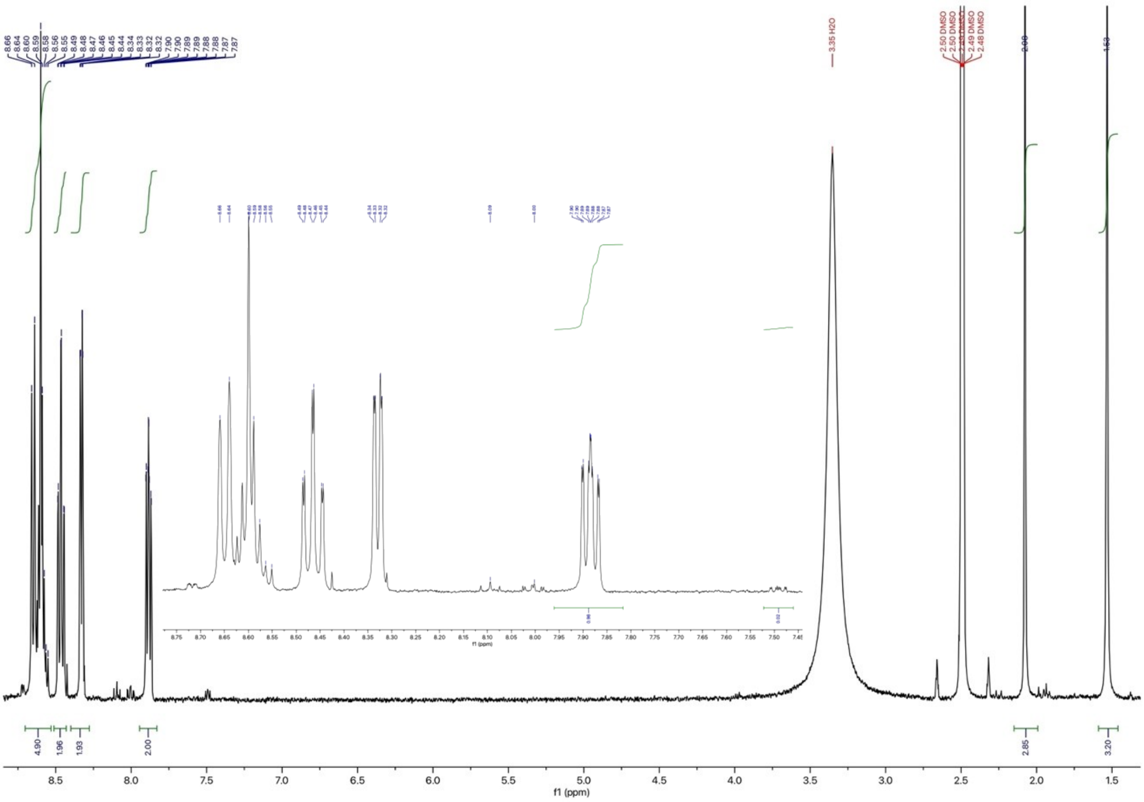


Figure S16. ^{1}H NMR spectra of [Pd(terpy)(OAc)](OAc) **(3a)** (400.1 MHz, DMSO-d_6, 298K).

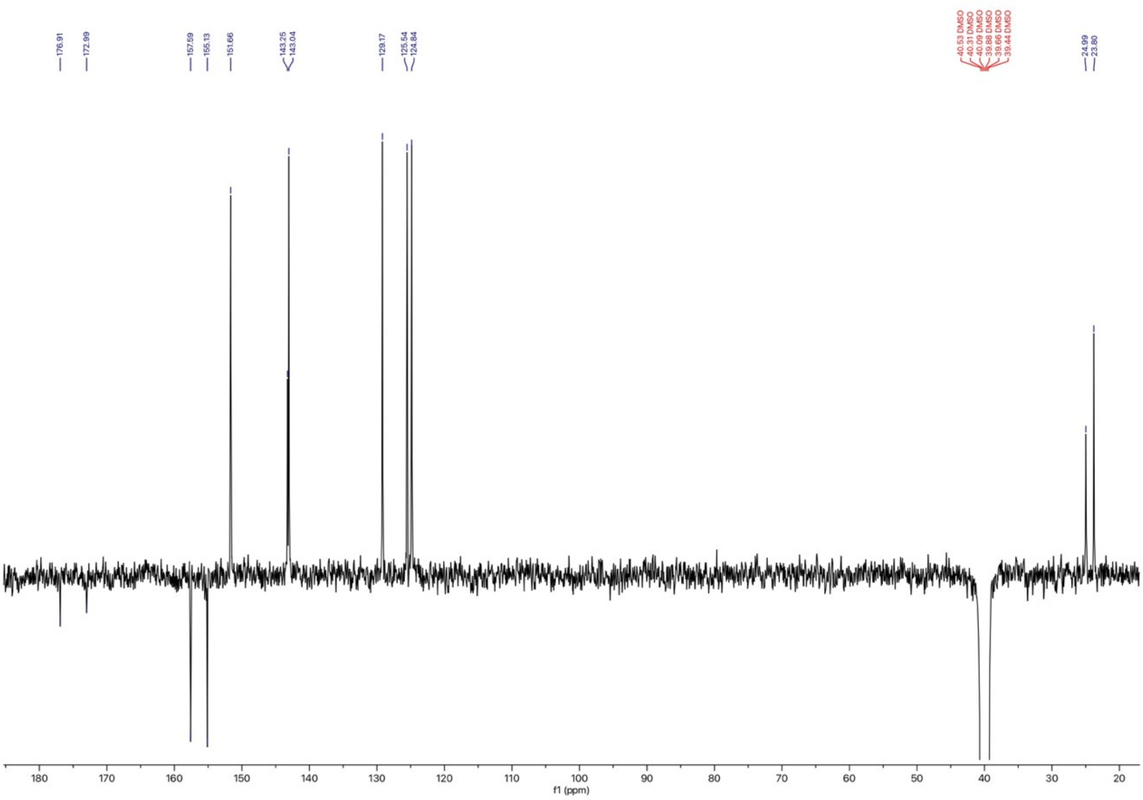


Figure S17. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(terpy)(OAc)](OAc) **(3a)** (100.6 MHz, DMSO-d_6, 298K).

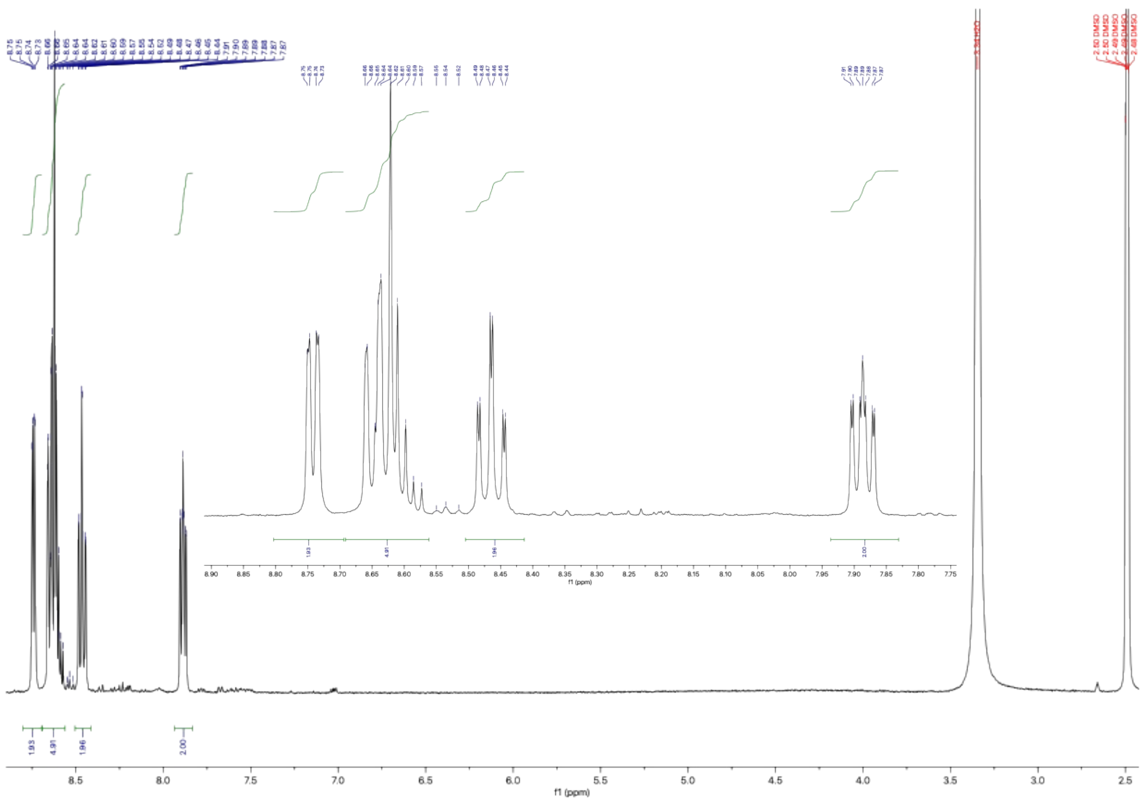


Figure S18. ^{1}H NMR spectra of [Pd(terpy)Cl]Cl **(3b)** (400.1 MHz, DMSO-d_6, 298K).

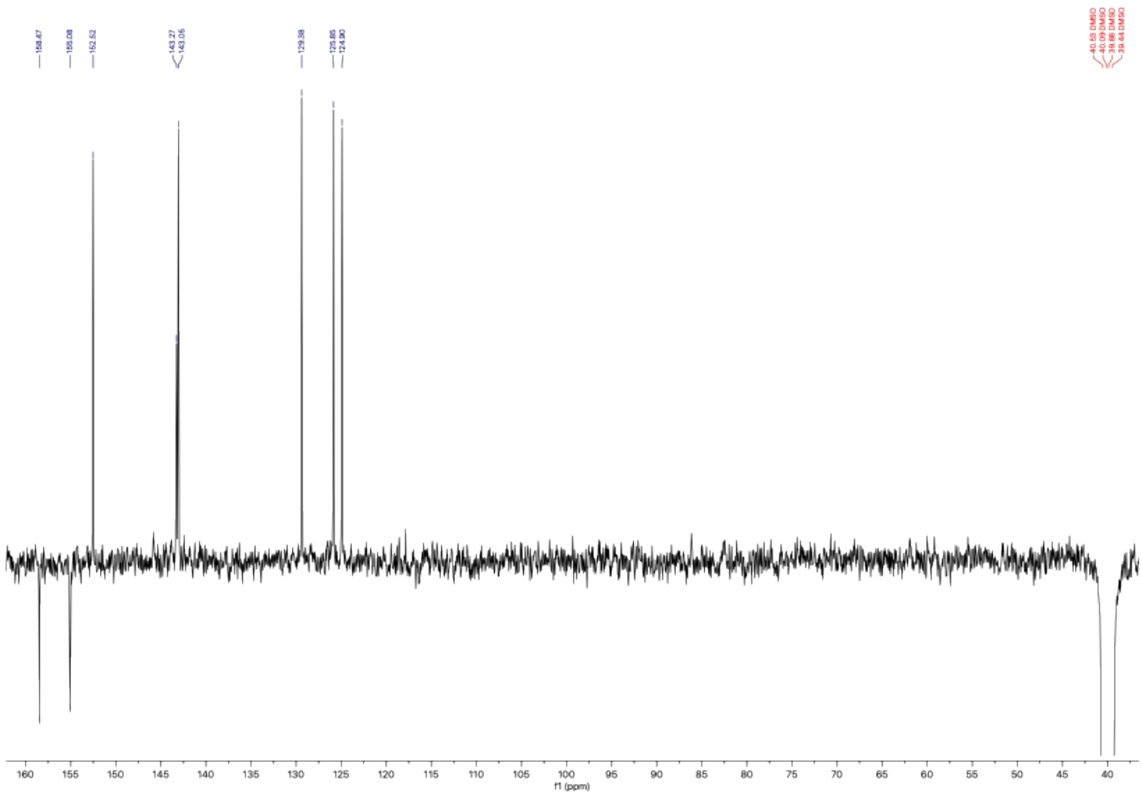


Figure S19. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(terpy)Cl]Cl **(3b)** (100.6 MHz, DMSO-d_6, 298K).

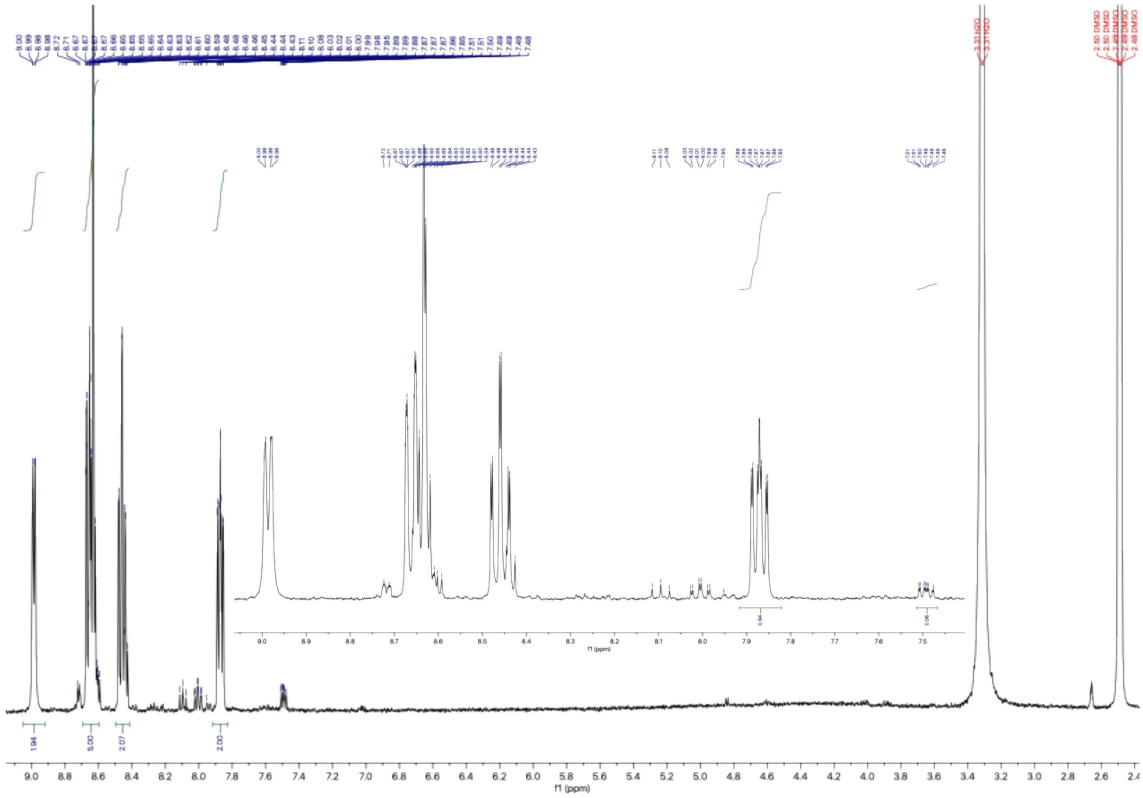


Figure S20. ^{1}H NMR spectra of [Pd(terpy)Br]Br **(3c)** (400.1 MHz, DMSO-d_6, 298K).

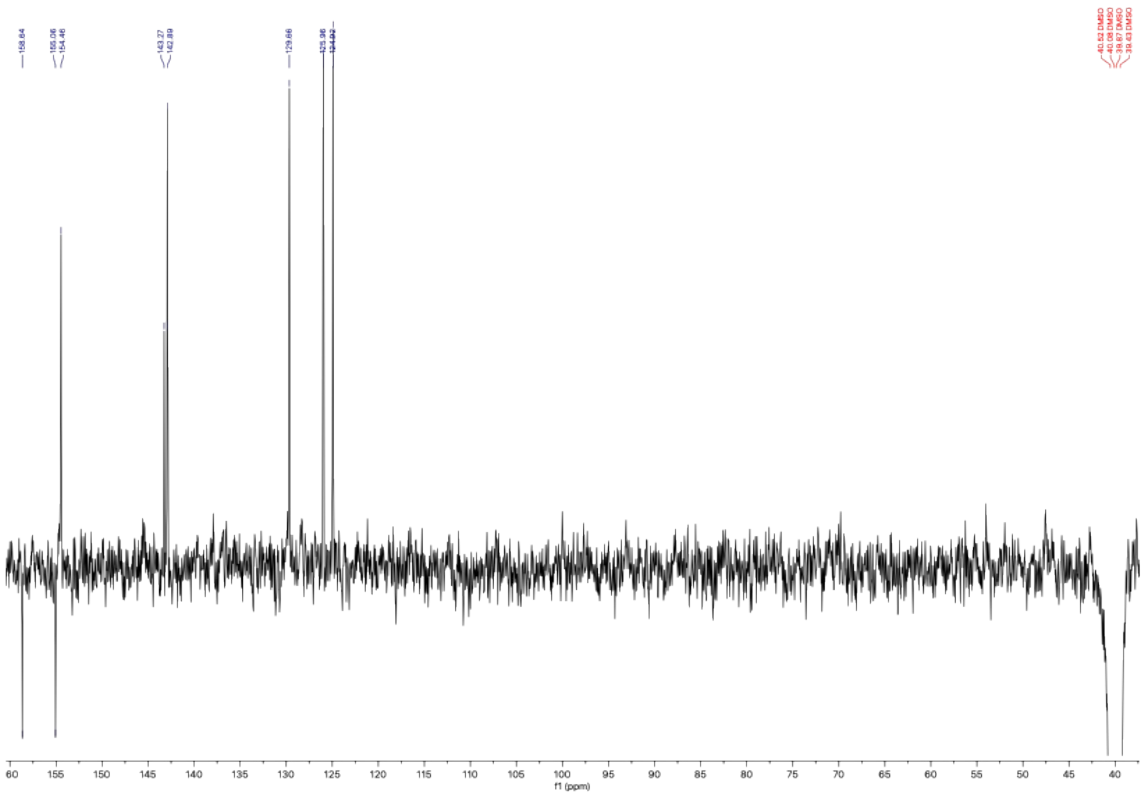


Figure S21. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(terpy)Br]Br **(3c)** (100.6 MHz, DMSO-d_6, 298K).

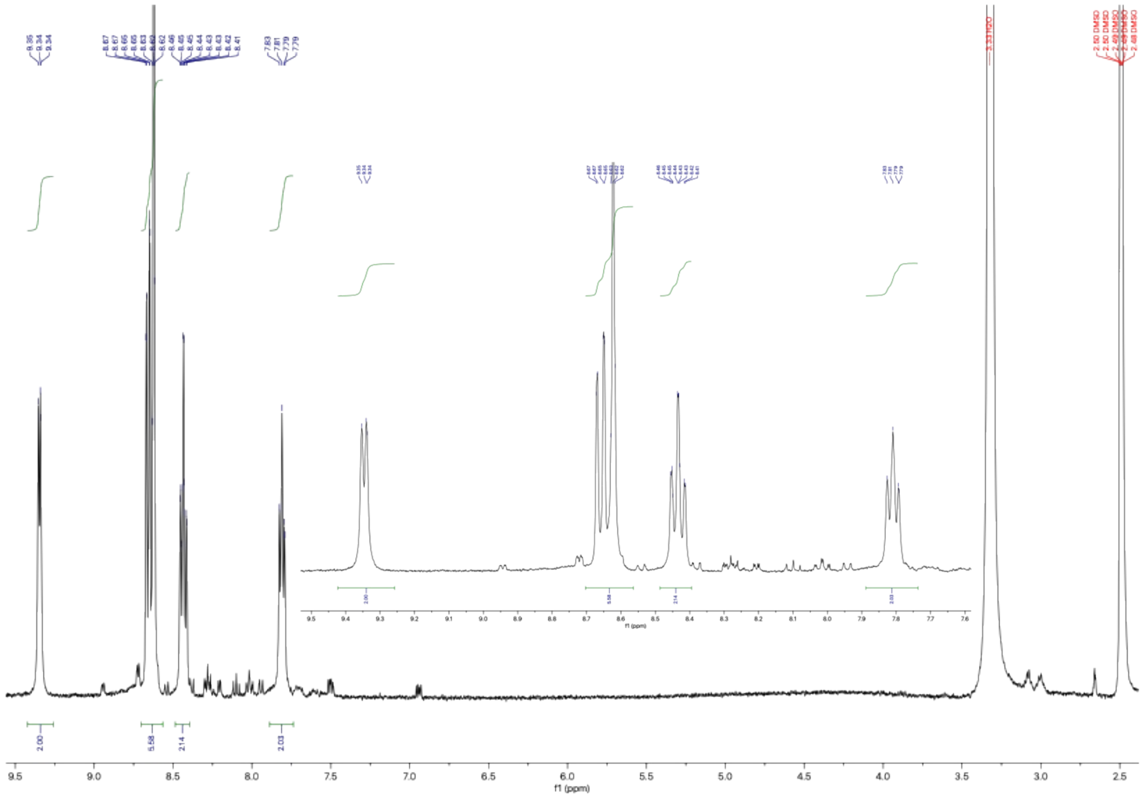


Figure S22. ^{1}H NMR spectra of [Pd(terpy)I]I **(3d)** (400.1 MHz, DMSO-d_6, 298K).

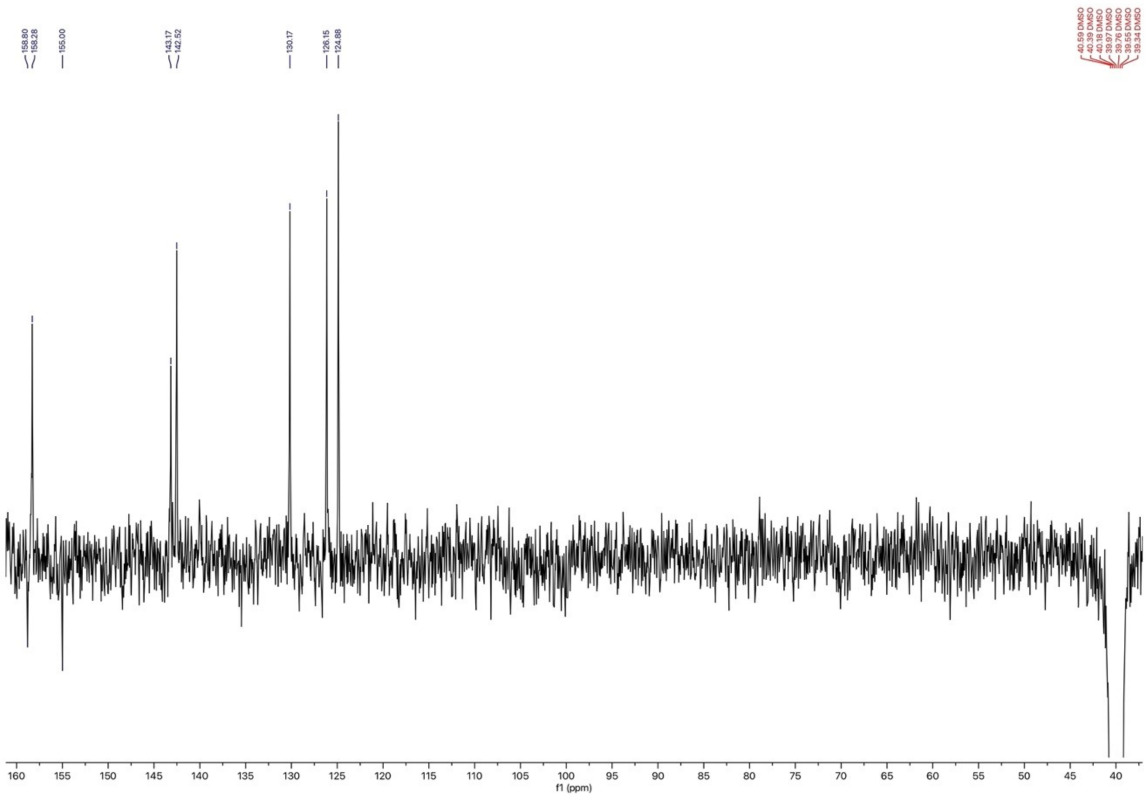


Figure S23. ^{13}C{^{1}H} NMR spectra of [Pd(terpy)I]I **(3d)** (100.6 MHz, DMSO-d_6, 298K).

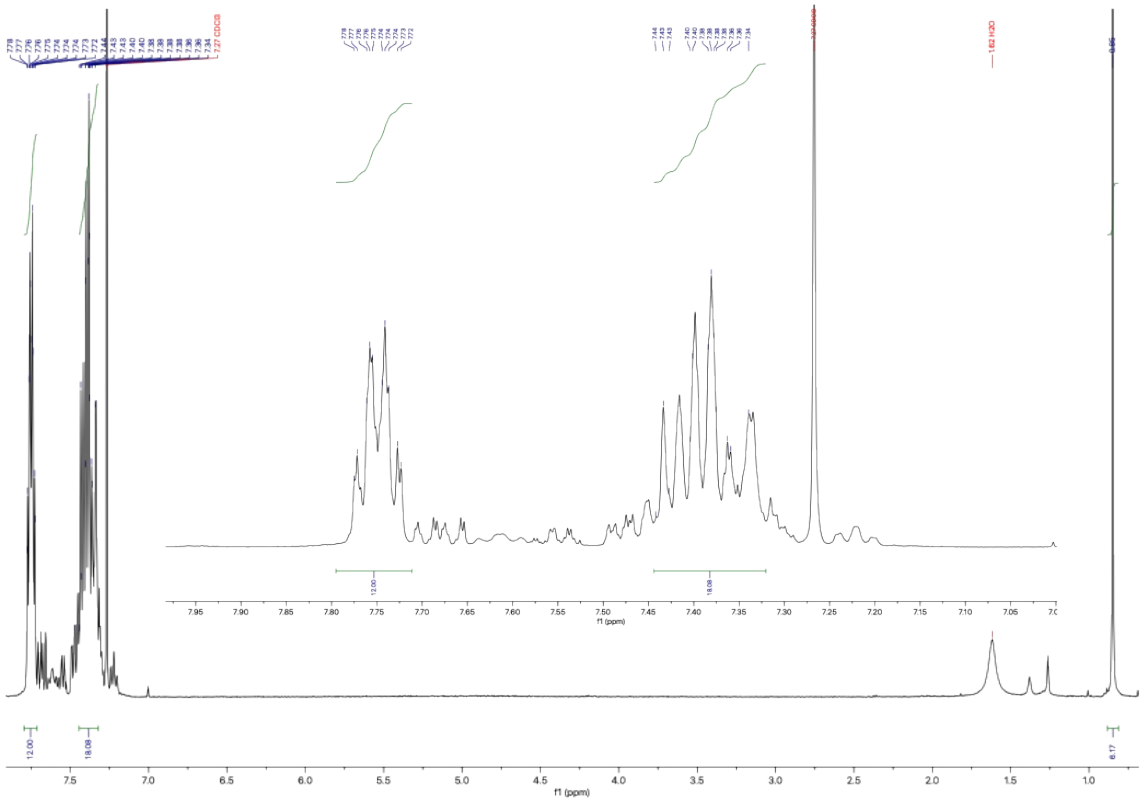


Figure S24. ^{1}H NMR spectra of $[Pd(PPh_3)_2(OAc)_2]$ **(4a)** (400.1 MHz, $CDCl_3$, 298K).

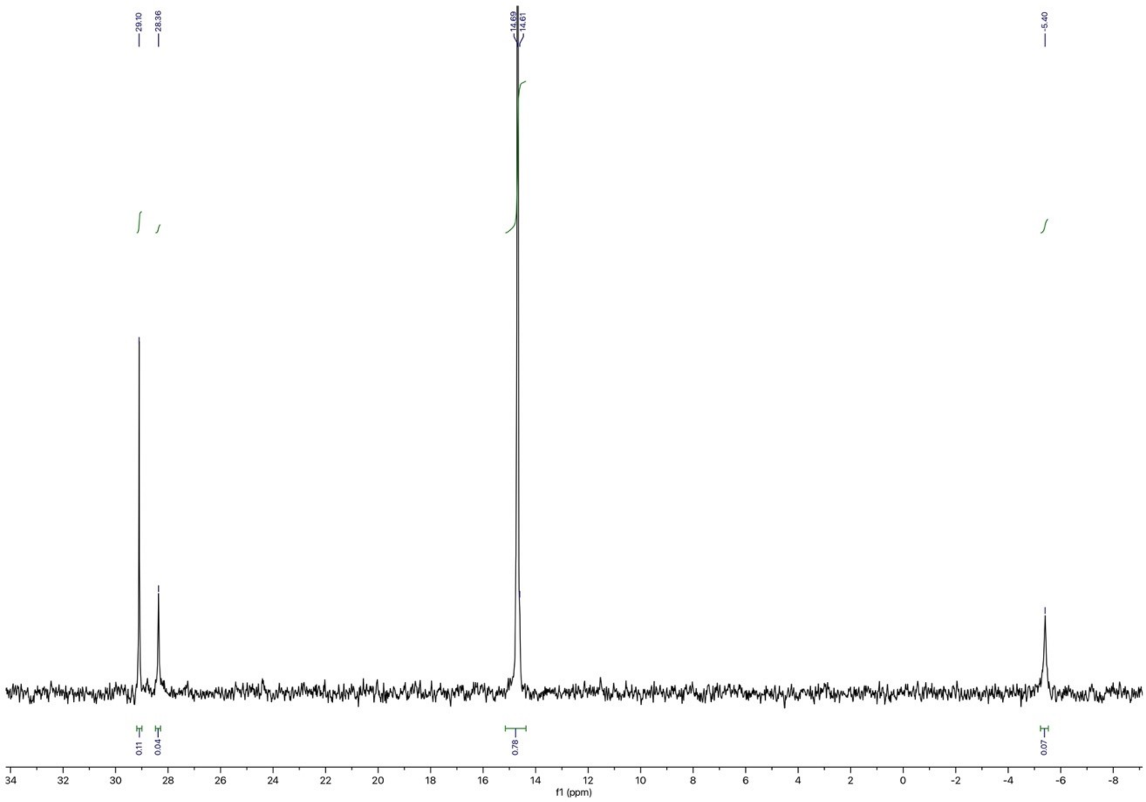


Figure S25. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(PPh_3)_2(OAc)_2]$ **(4a)** (162.0 MHz, $CDCl_3$, 298K).

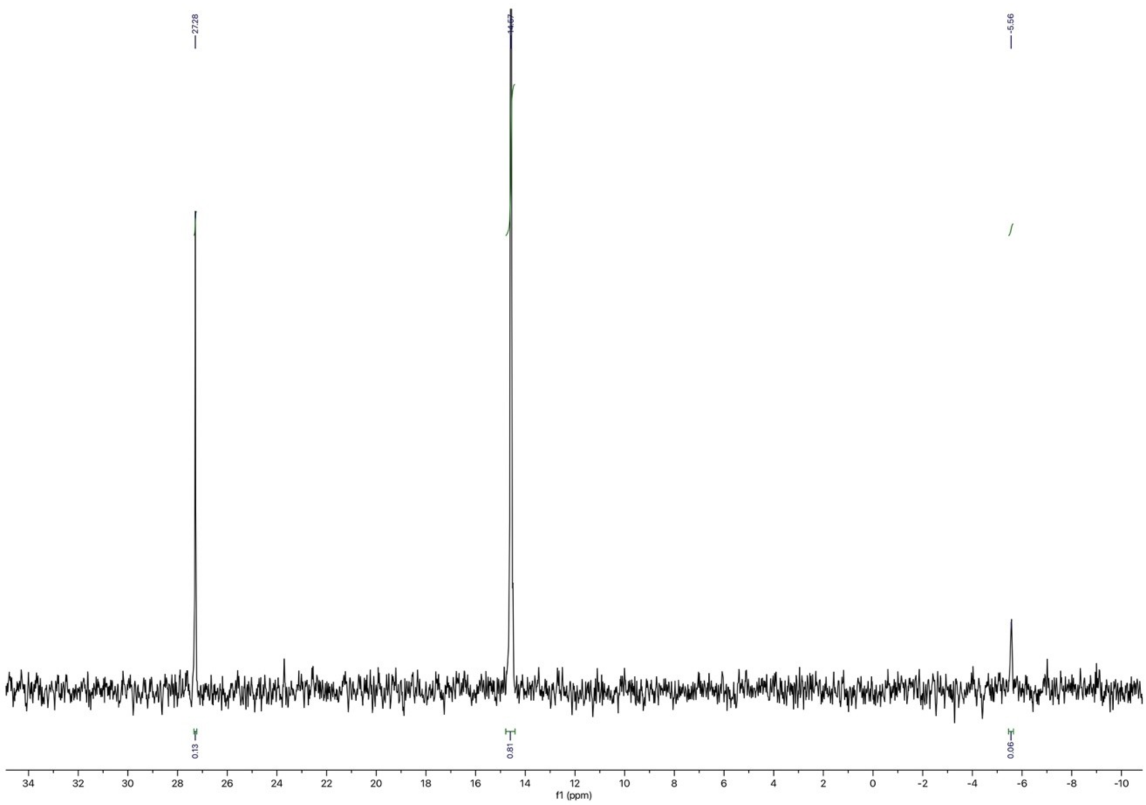


Figure S26. $^{31}P\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2(OAc)_2]$ **(4a)** (162.0 MHz, CD_2Cl_2, 298K).

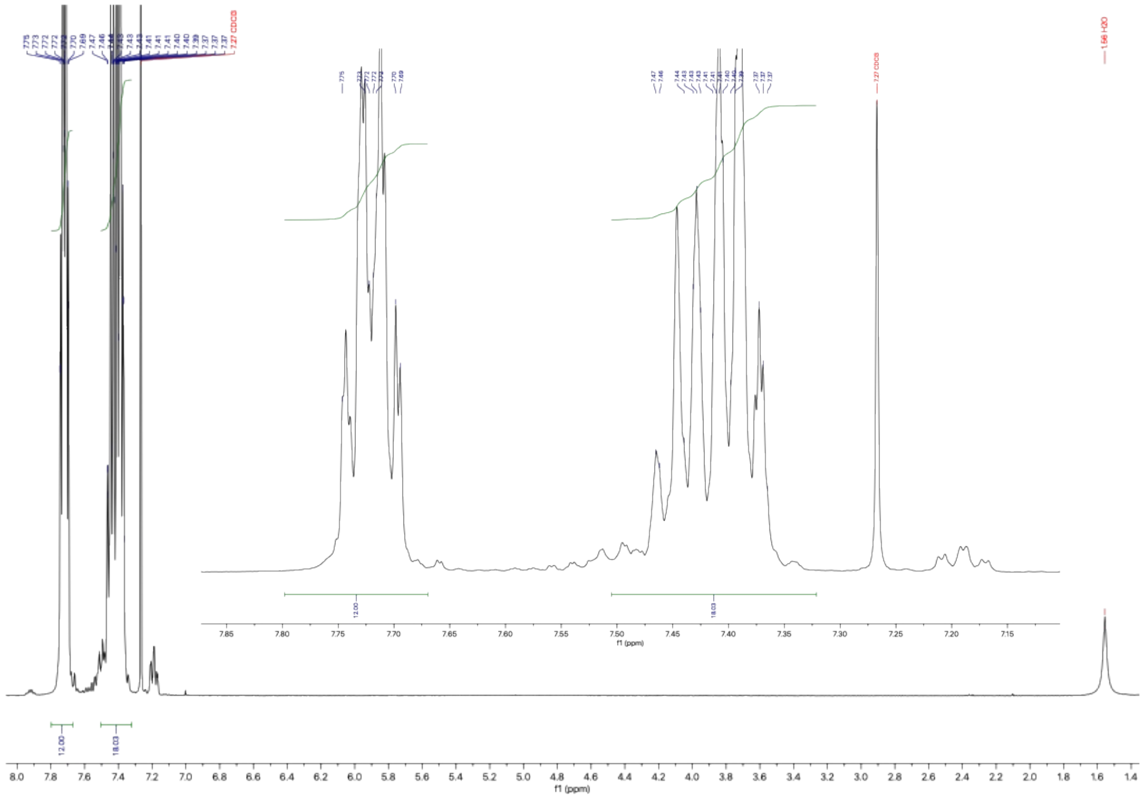


Figure S27. ^1H NMR spectra of $[Pd(PPh_3)_2Cl_2]$ **(4b)** (400.1 MHz, $CDCl_3$, 298K).

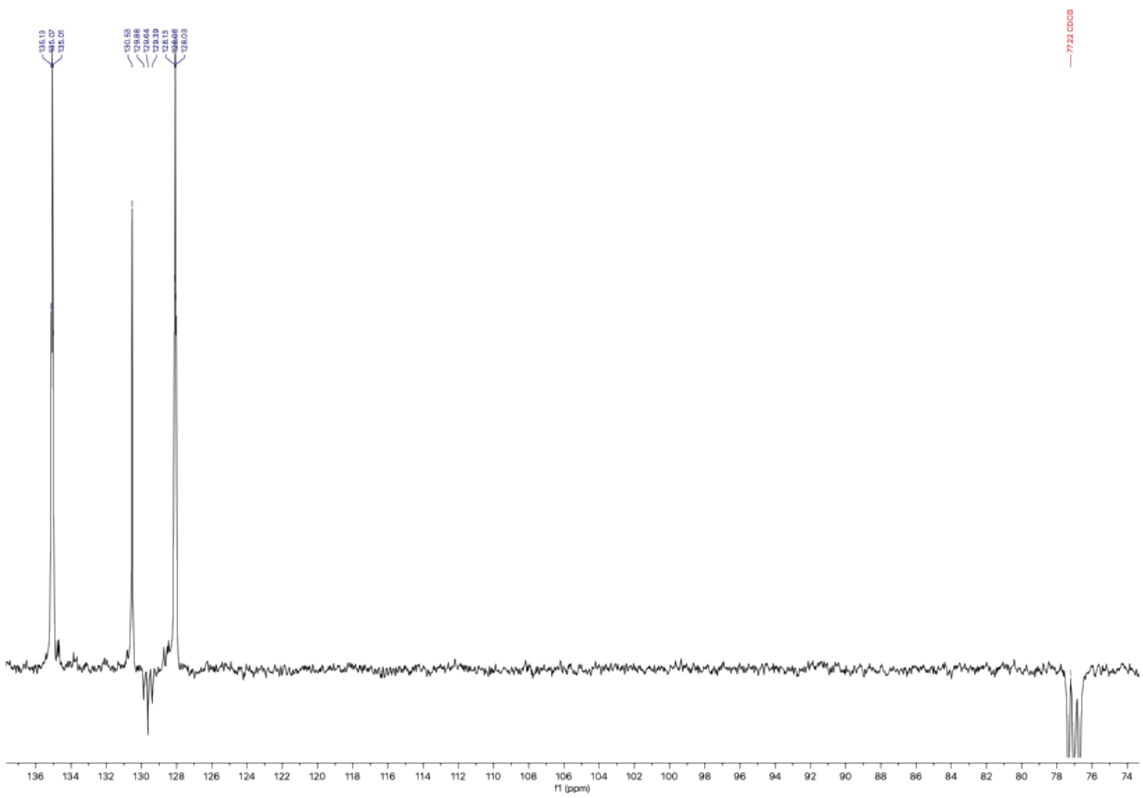


Figure S28. $^{13}C\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2Cl_2]$ **(4b)** (100.6 MHz, $CDCl_3$, 298K).

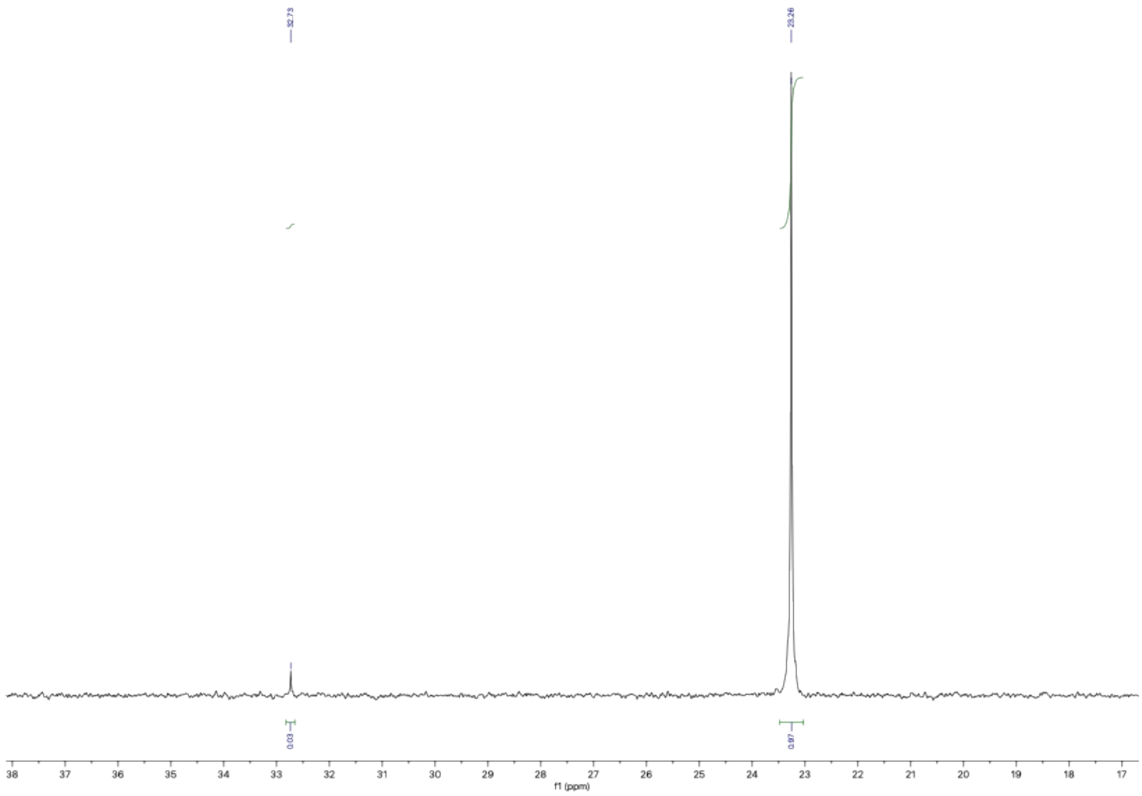


Figure S29. $^{31}P\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2Cl_2]$ **(4b)** (162.0 MHz, $CDCl_3$, 298K).

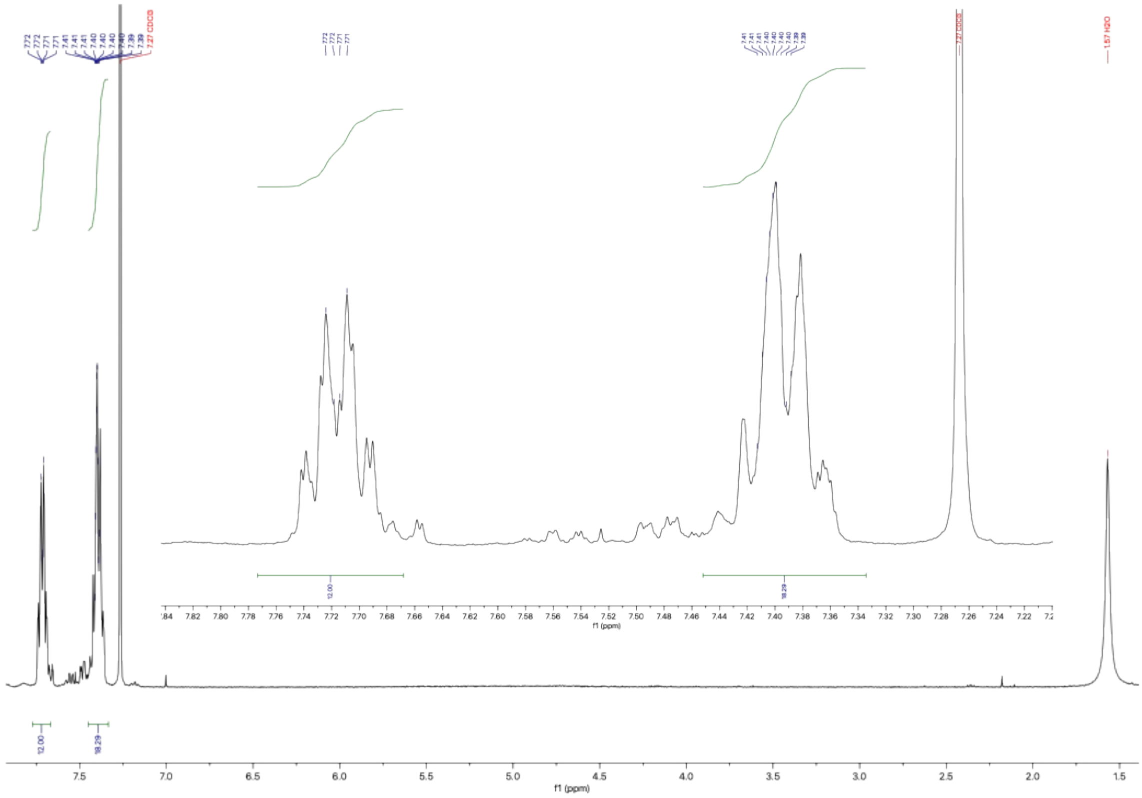


Figure S30. ^{1}H NMR spectra of $[Pd(PPh_3)_2Br_2]$ **(4c)** (400.1 MHz, $CDCl_3$, 298K).

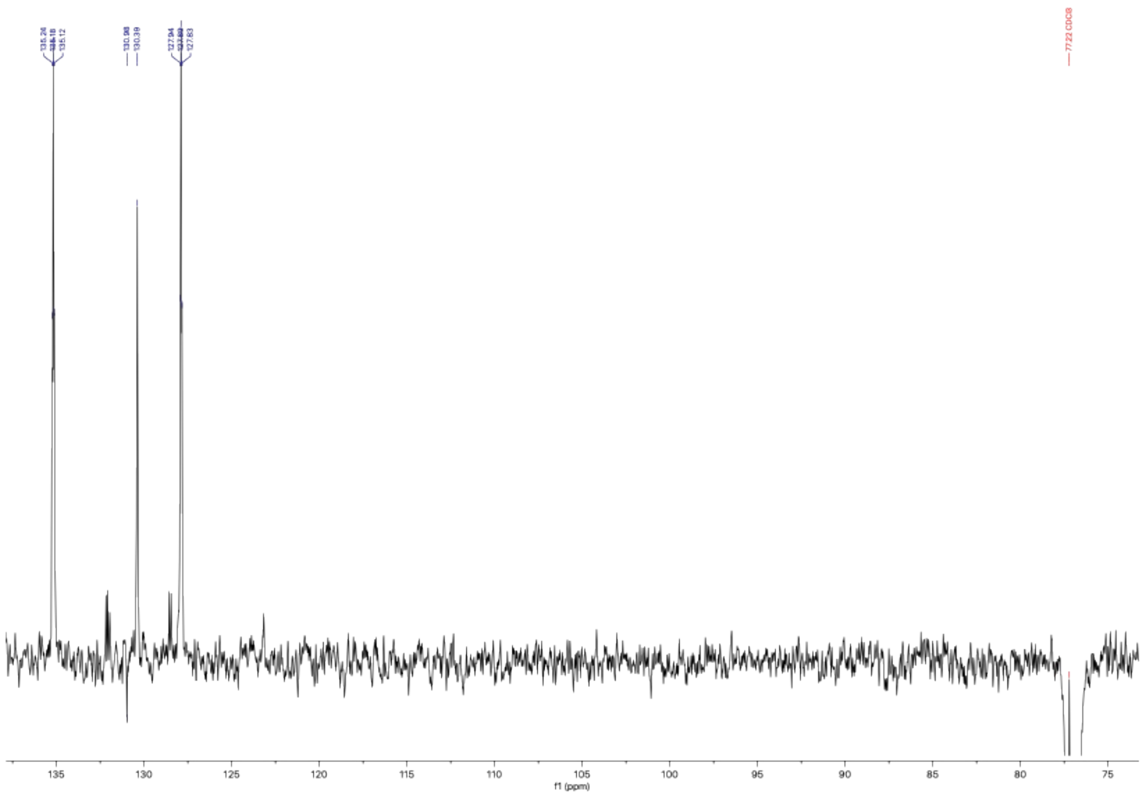


Figure S31. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(PPh_3)_2Br_2]$ **(4c)** (100.6 MHz, $CDCl_3$, 298K).

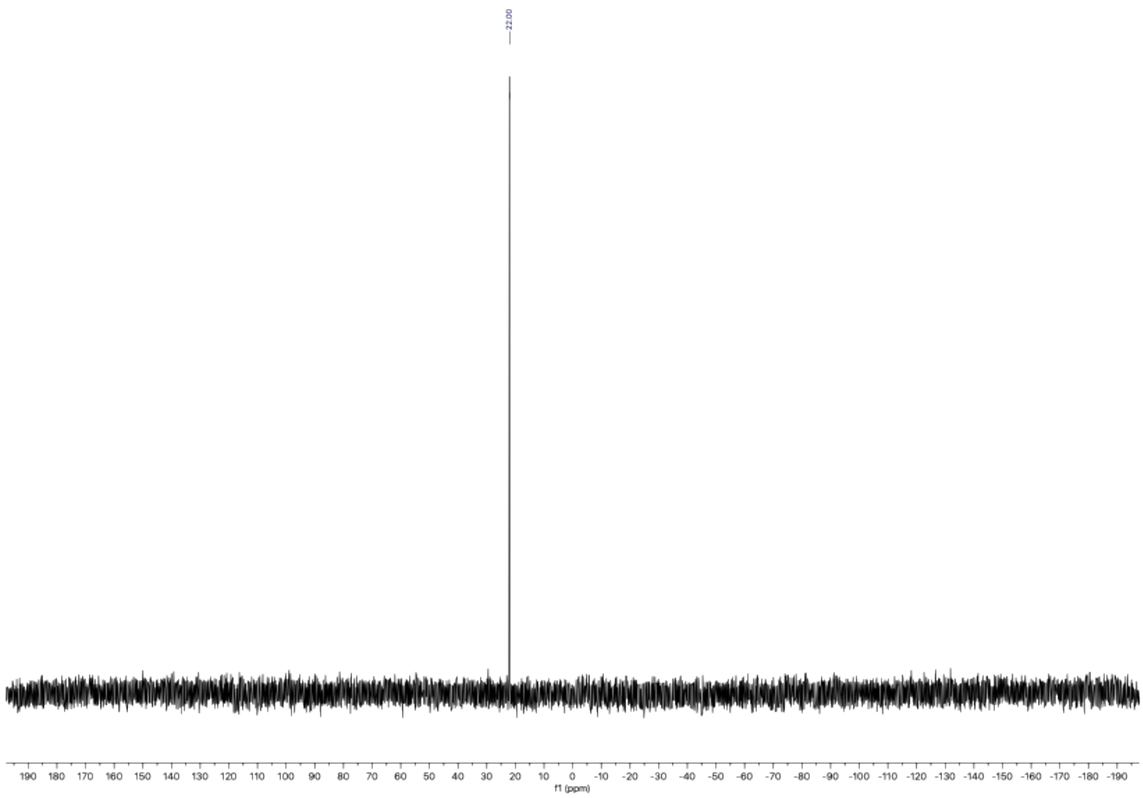


Figure S32. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(PPh_3)_2Br_2]$ **(4c)** (162.0 MHz, $CDCl_3$, 298K).

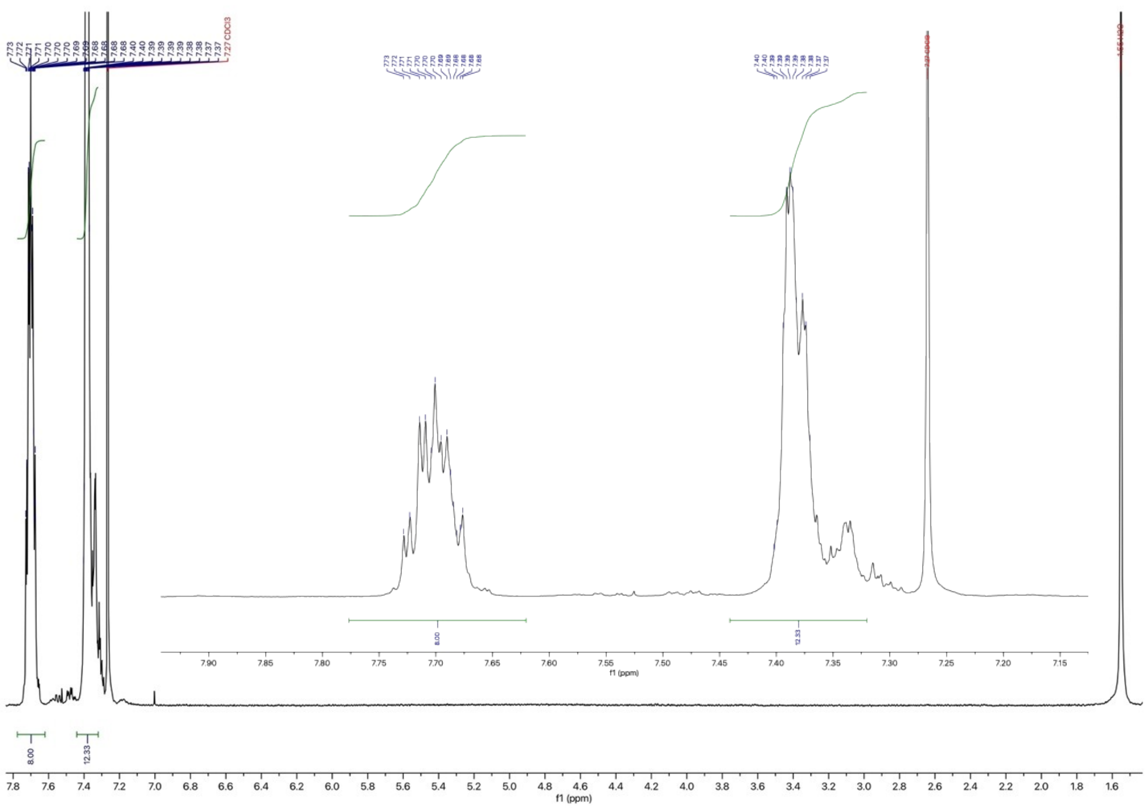


Figure S33. ^{1}H NMR spectra of $[Pd(PPh_3)_2I_2]$ **(4d)** (400.1 MHz, $CDCl_3$, 298K).

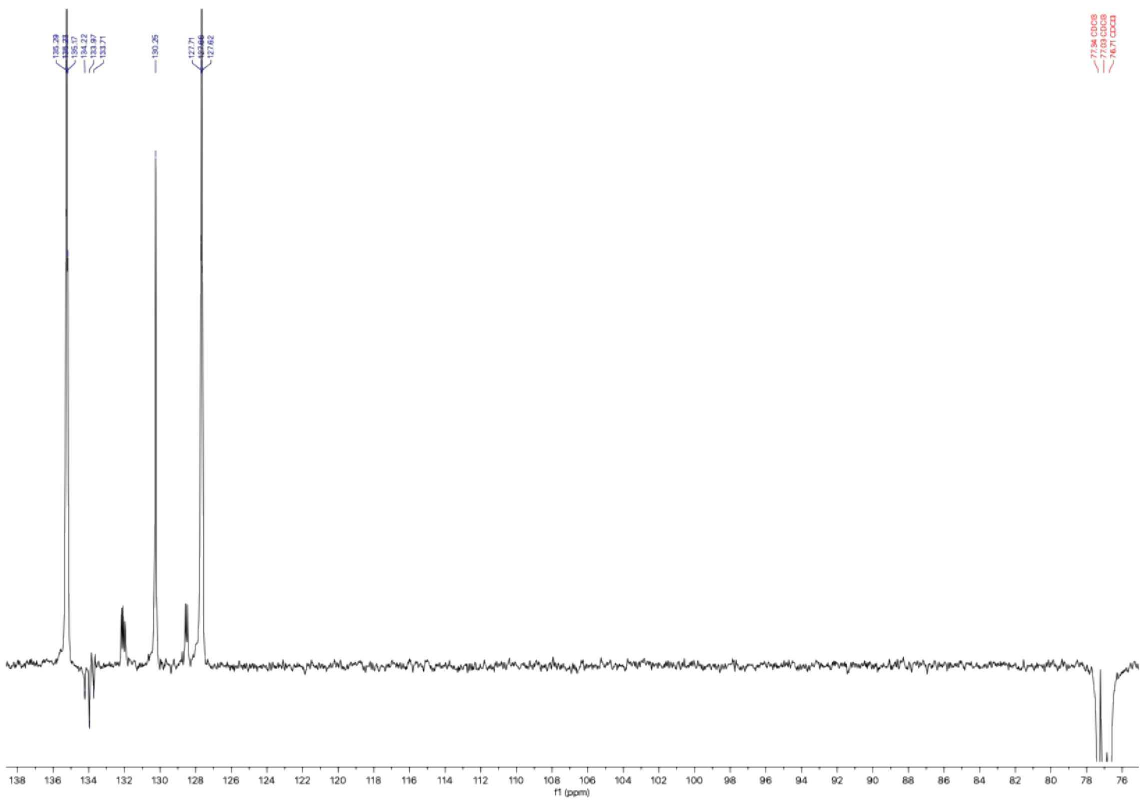


Figure S34. $^{13}C\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2I_2]$ **(4d)** (100.6 MHz, $CDCl_3$, 298K).

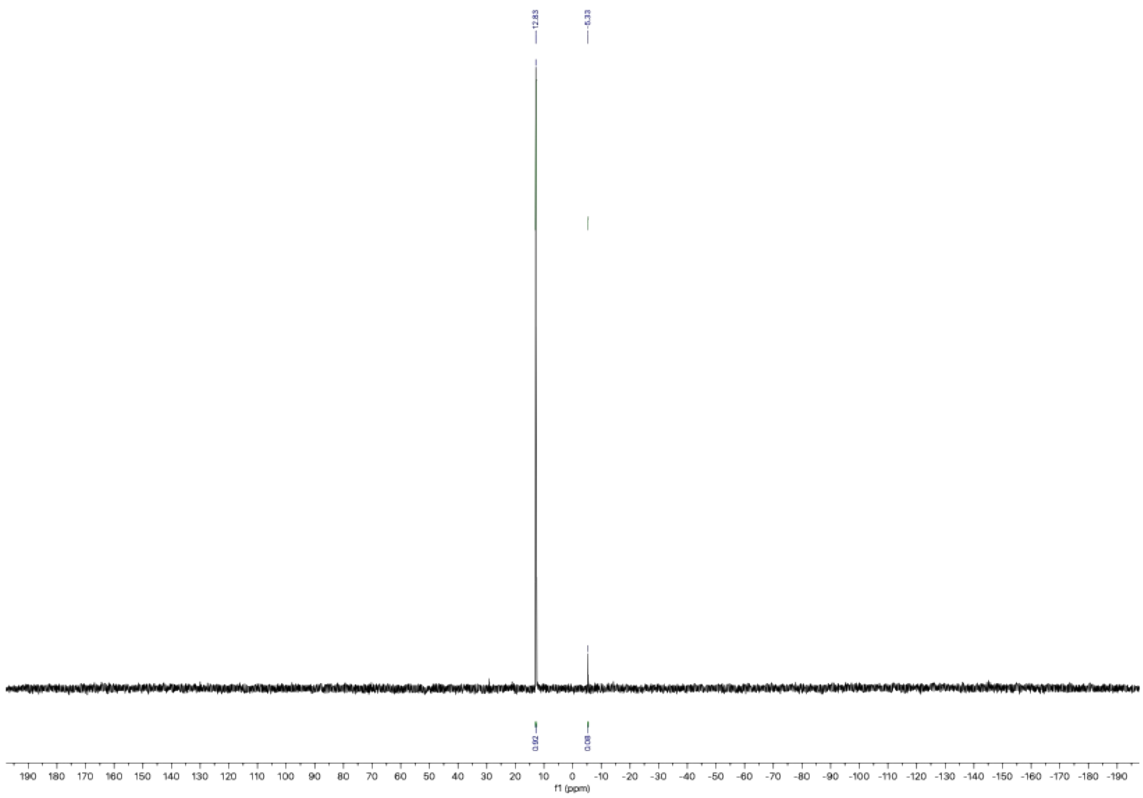


Figure S35. $^{31}P\{^1H\}$ NMR spectra of $[Pd(PPh_3)_2I_2]$ **(4d)** (162.0 MHz, $CDCl_3$, 298K).

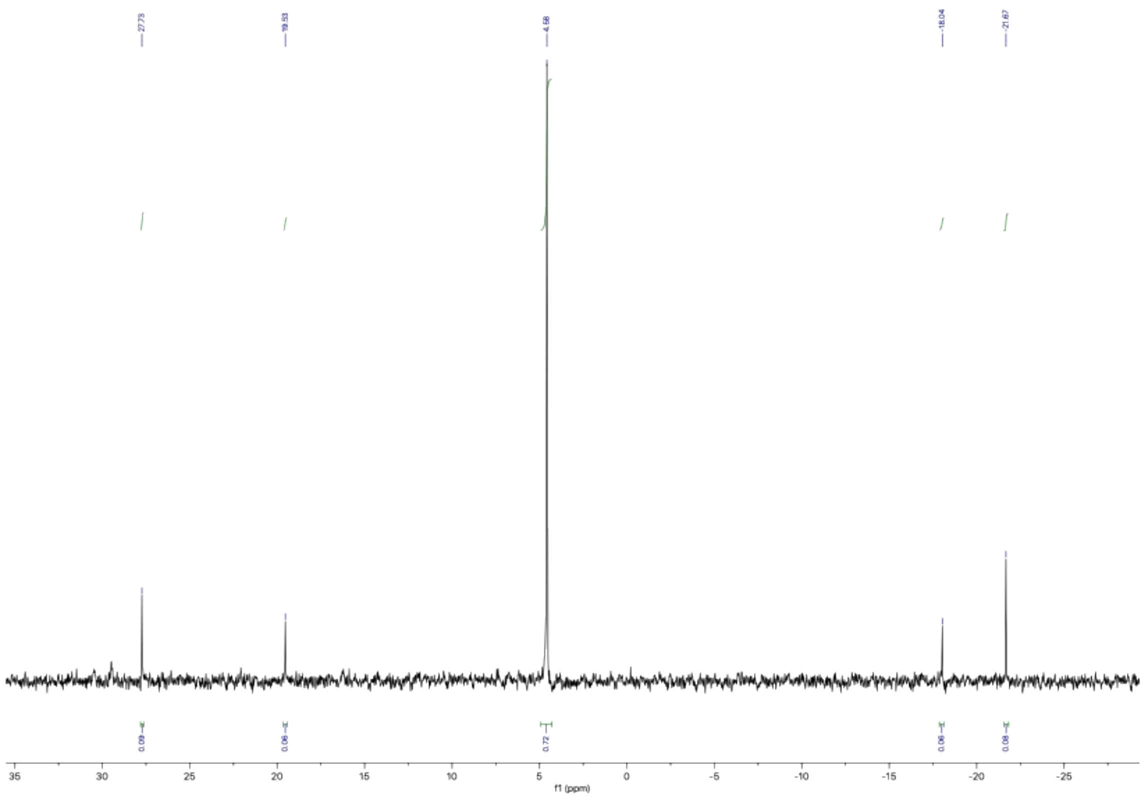


Figure S36. $^{31}P\{^1H\}$ NMR spectra of [Pd(Xantphos)(OAc)$_2$] **(5a)** (162.0 MHz, $CDCl_3$, 298K).

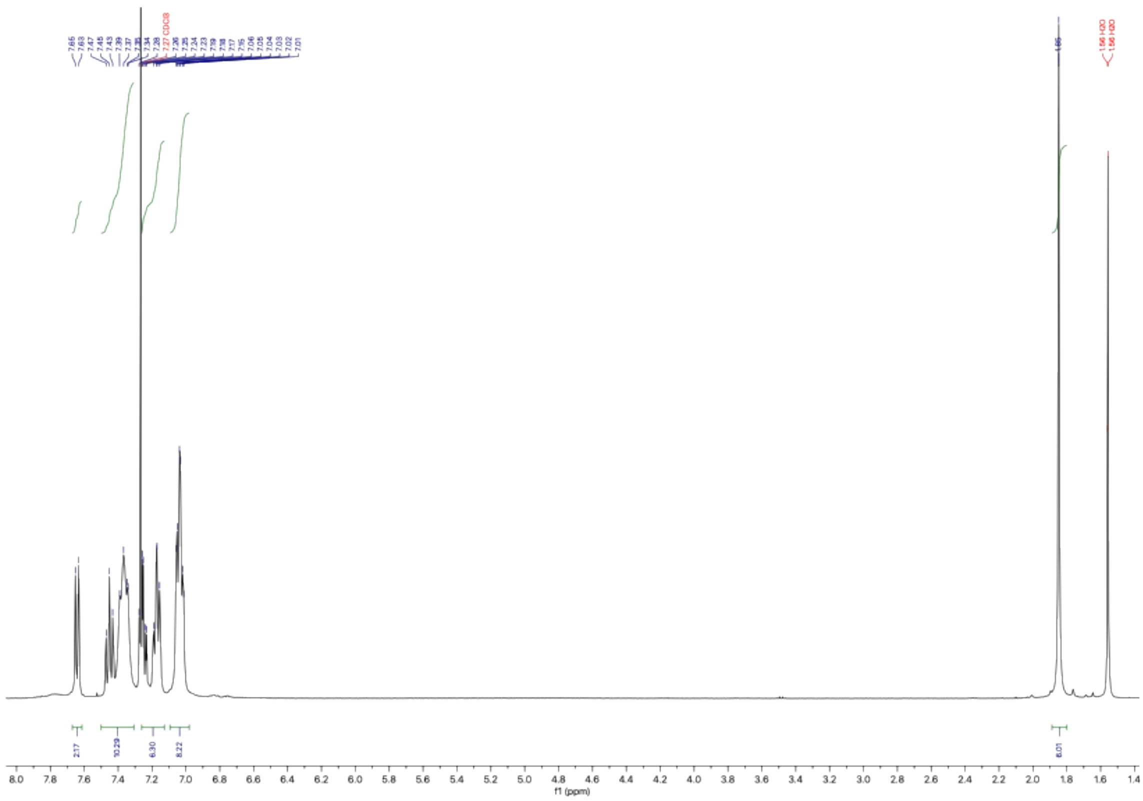


Figure S37. ^1H NMR spectra of [Pd(Xantphos)Cl$_2$] **(5b)** (400.1 MHz, $CDCl_3$, 298K).

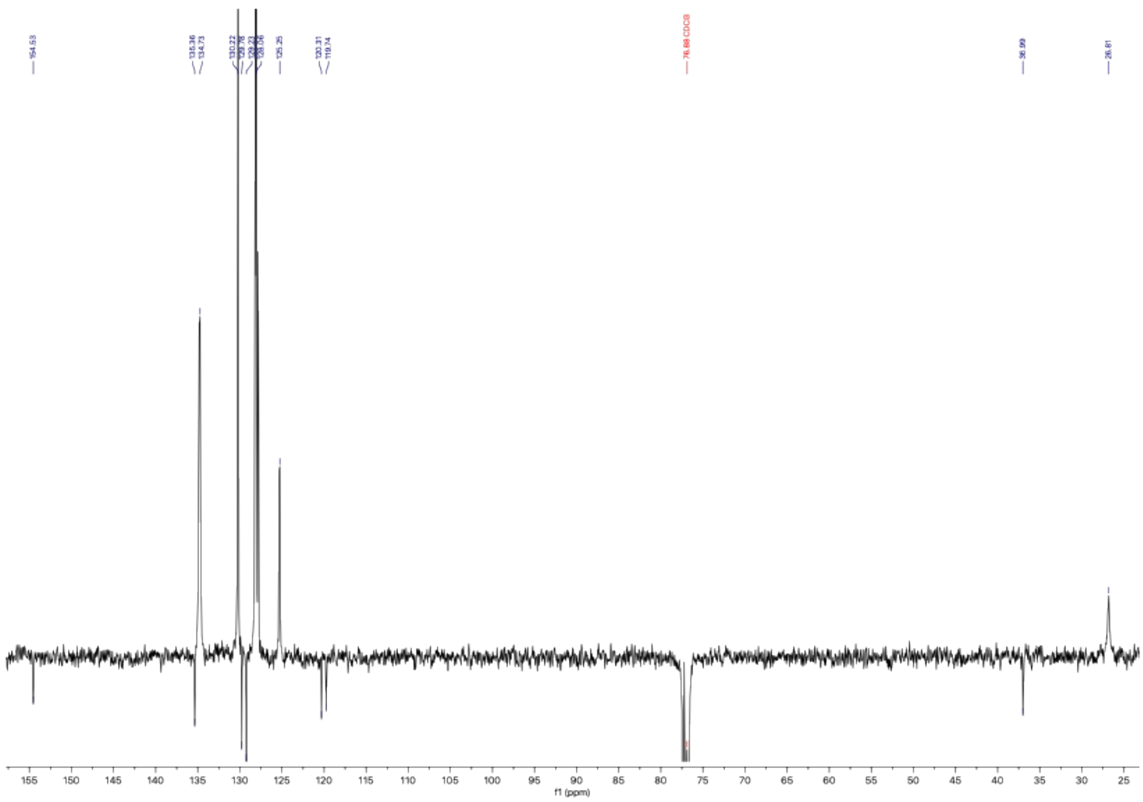


Figure S38. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(Xantphos)Cl_2]$ **(5b)** (100.6 MHz, $CDCl_3$, 298K).

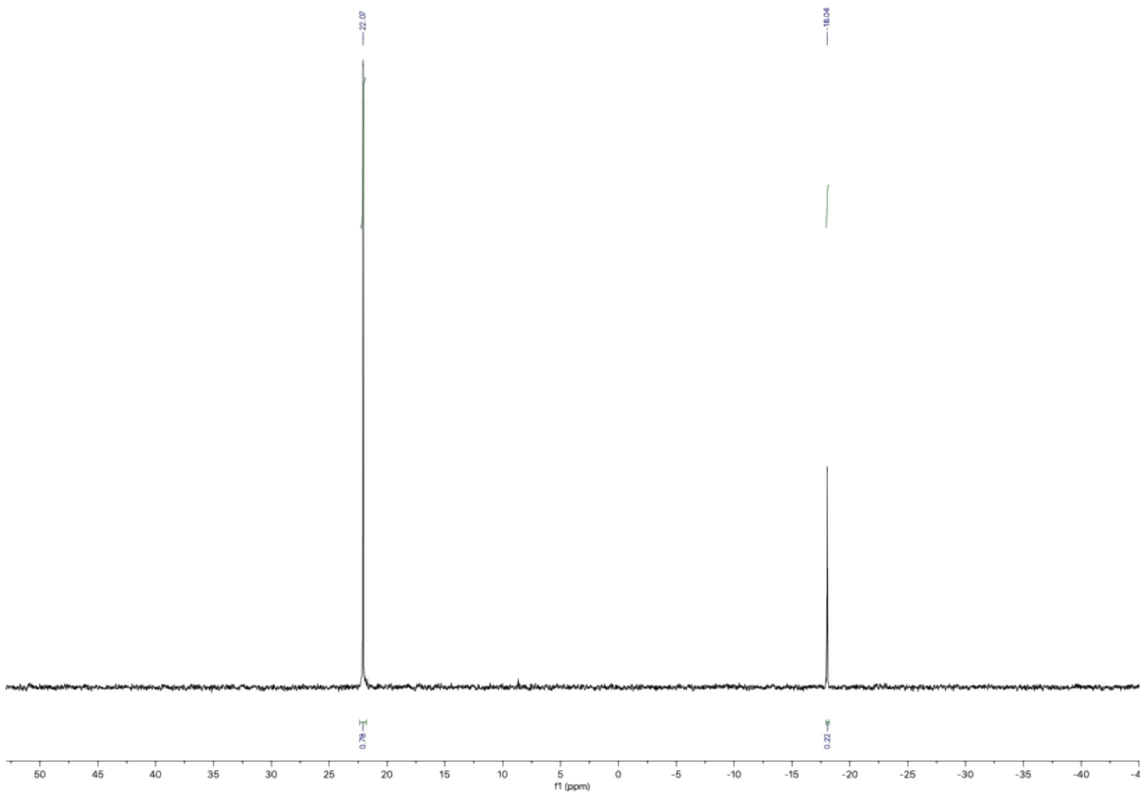


Figure S39. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(Xantphos)Cl_2]$ Method A **(5b)** (162.0 MHz, $CDCl_3$, 298K).

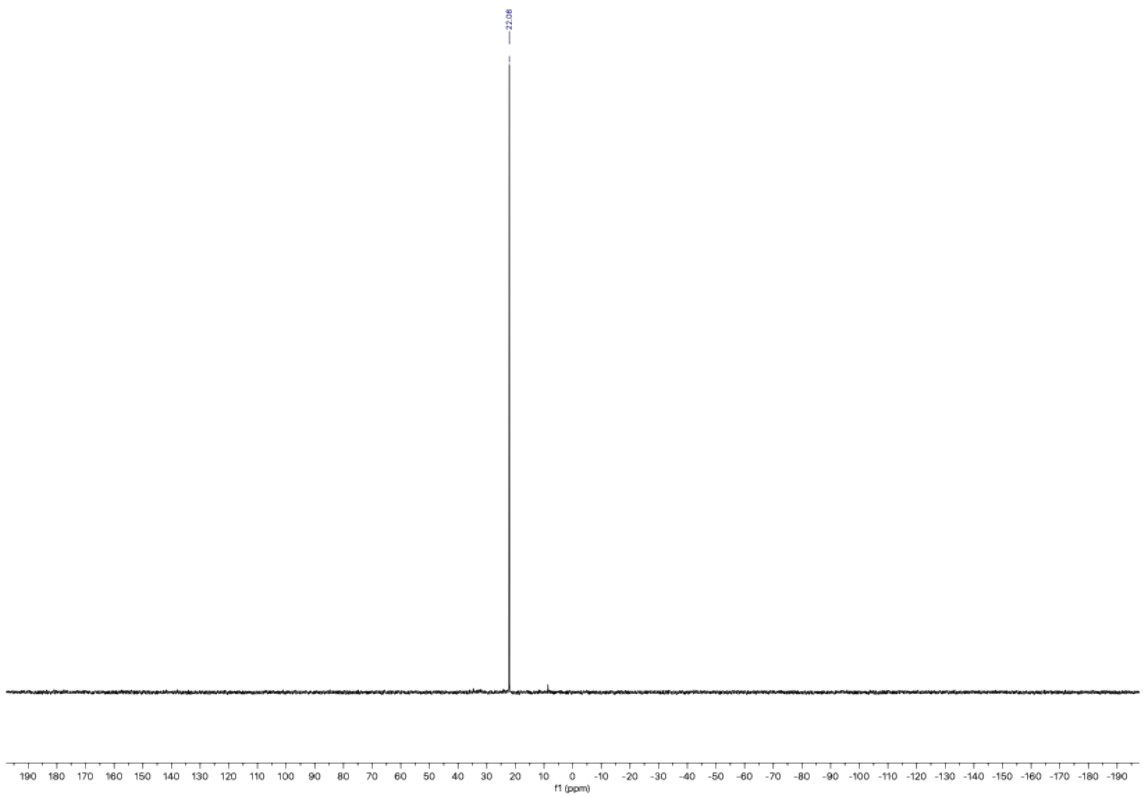


Figure S40. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(Xantphos)Cl_2] Method B **(5b)** (162.0 MHz, $CDCl_3$, 298K).

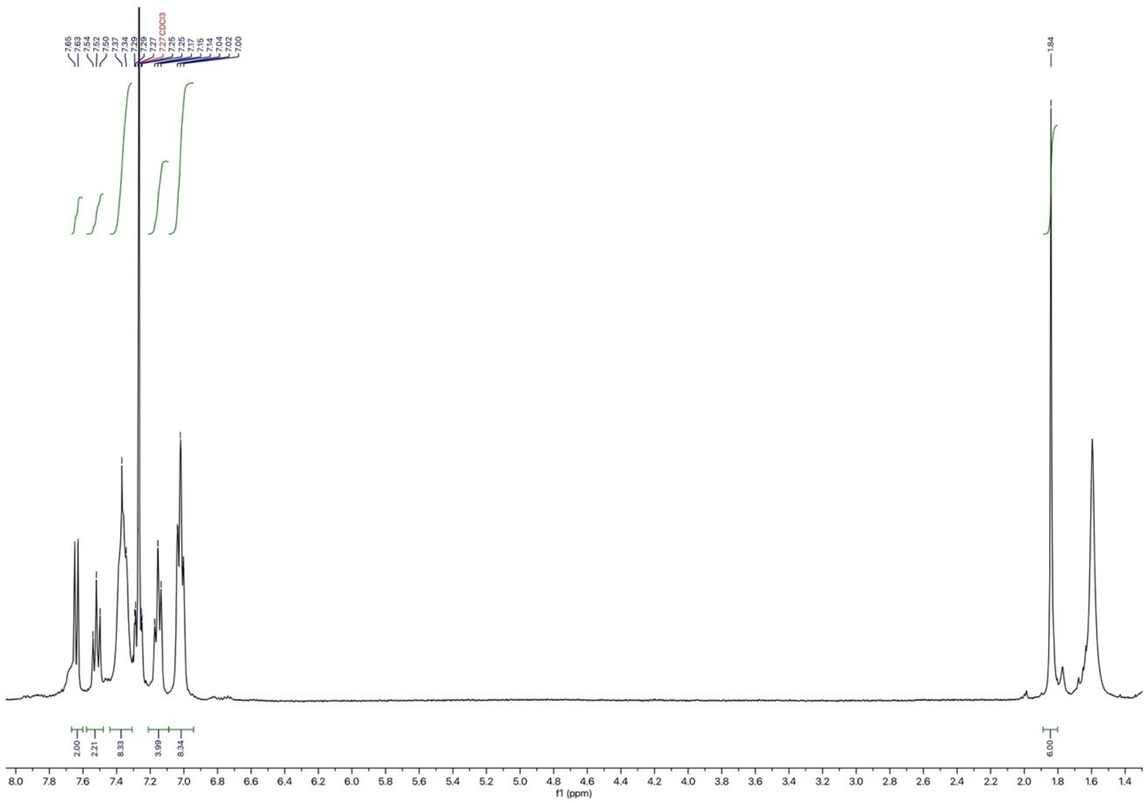


Figure S41. ^{1}H NMR spectra of [Pd(Xantphos)Br_2] **(5c)** (400.1 MHz, $CDCl_3$, 298K).

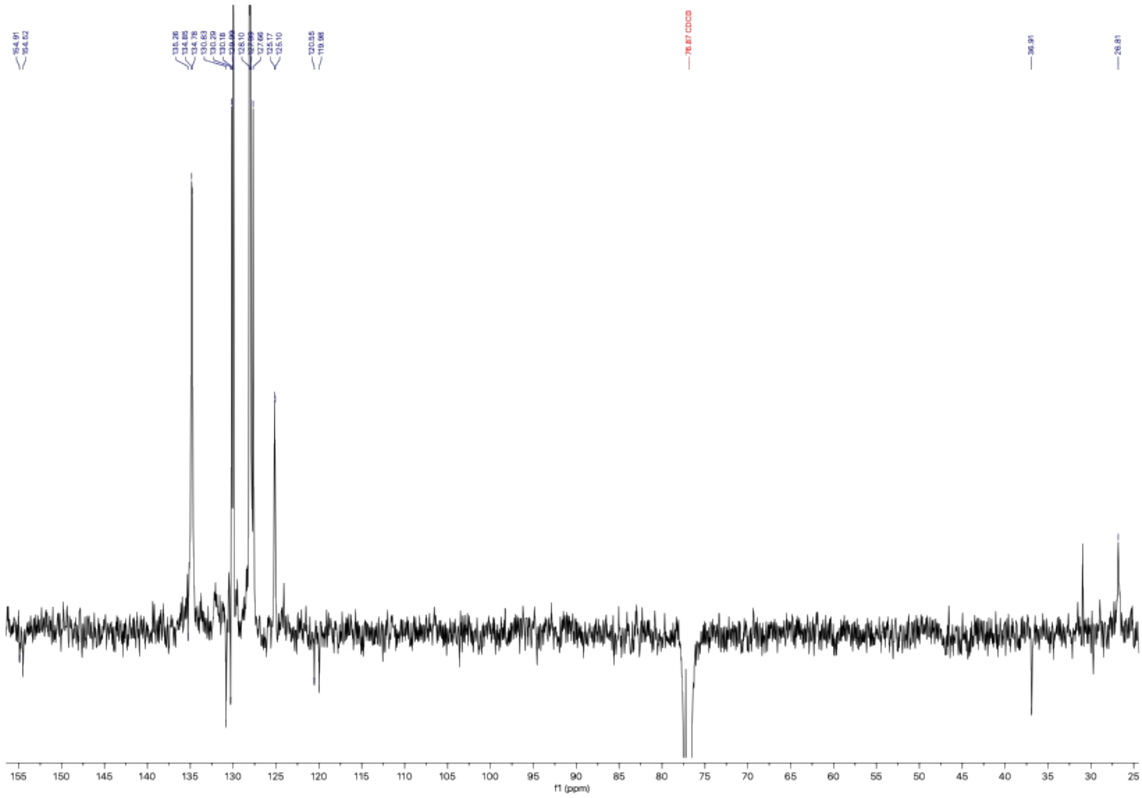


Figure S42. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(Xantphos)Br_2] **(5c)** (100.6 MHz, $CDCl_3$, 298K).

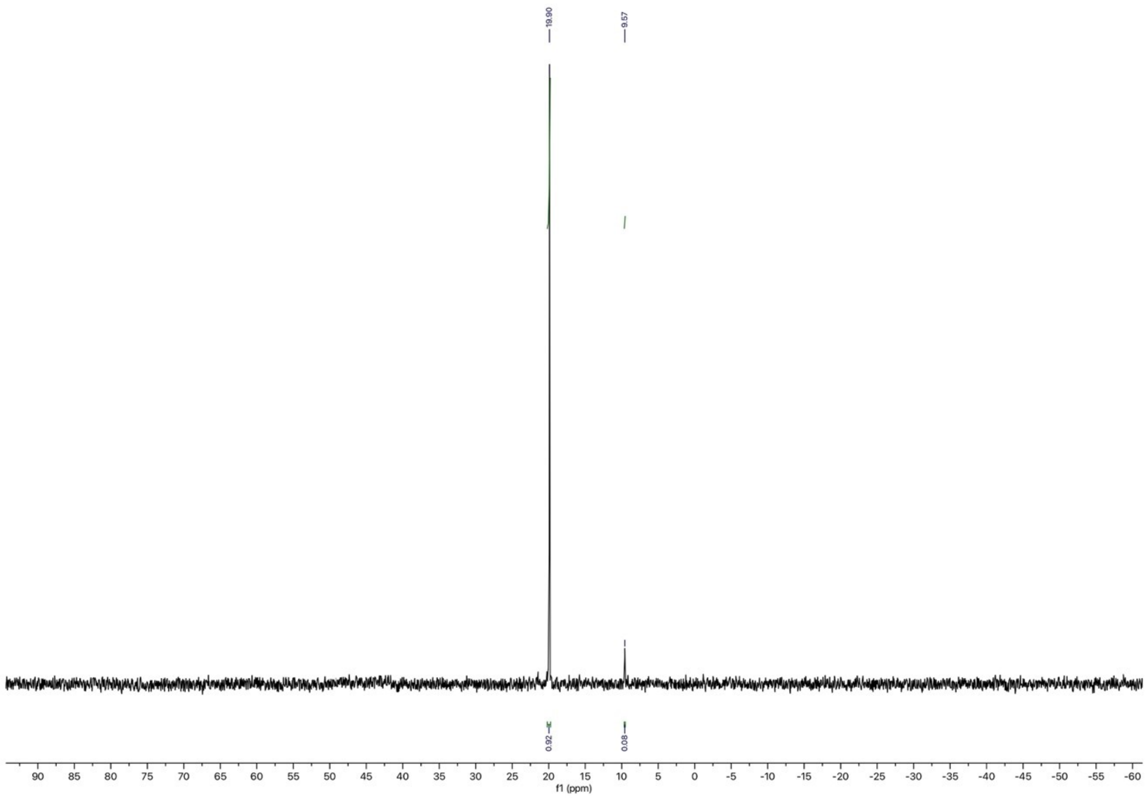


Figure S43. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(Xantphos)Br_2] **(5c)** (162.0 MHz, $CDCl_3$, 298K).

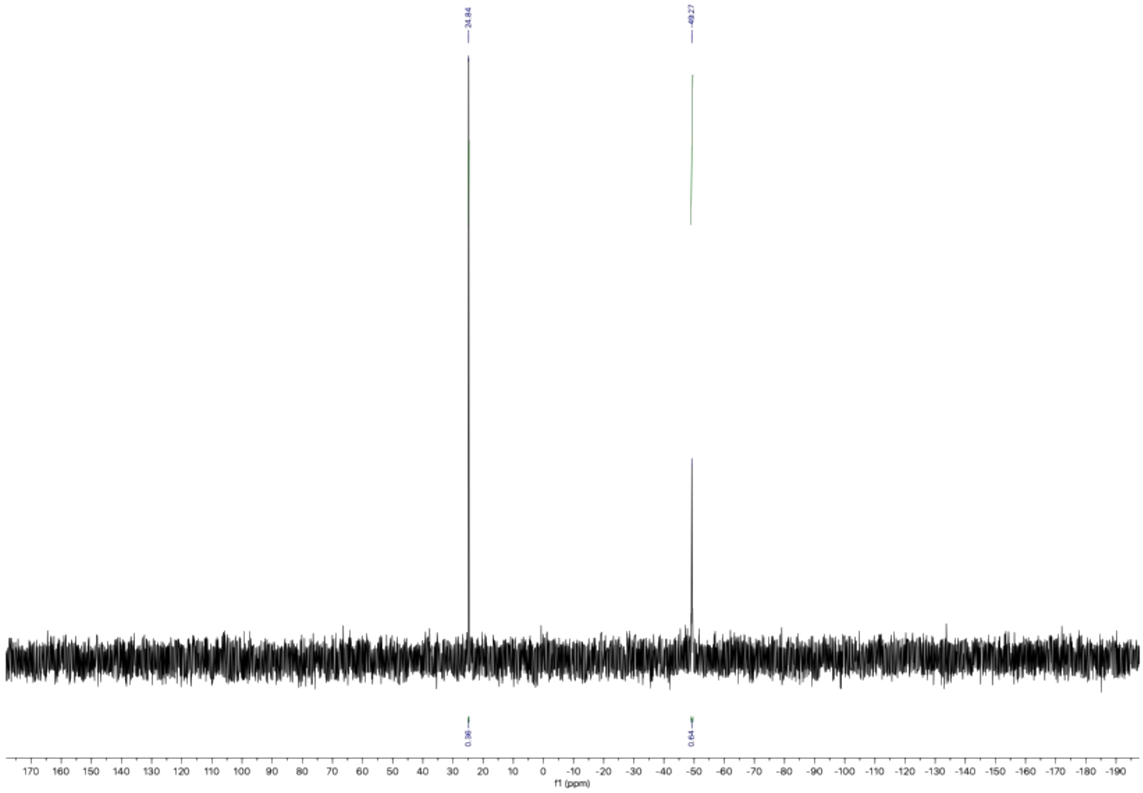


Figure S44. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppm)(OAc)_2]$ **(6a)** (162.0 MHz, $CDCl_3$, 298K).

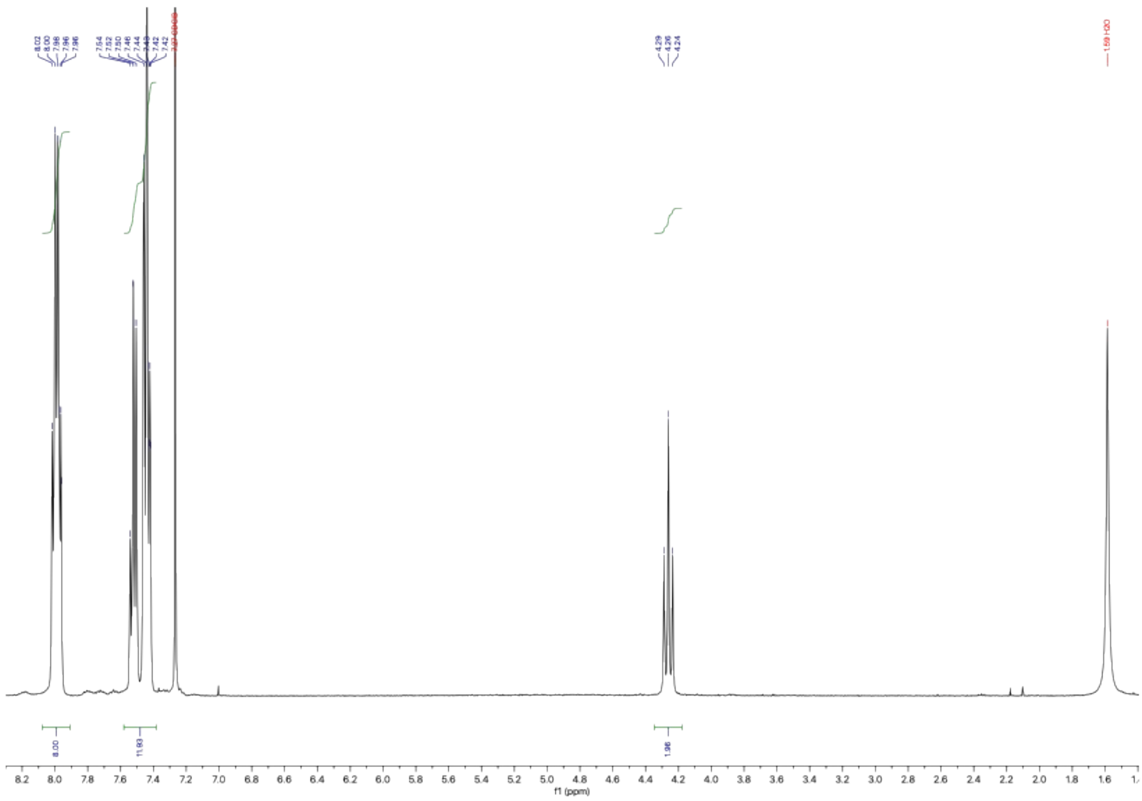


Figure S45. ^{1}H NMR spectra of $[Pd(dppm)Cl_2]$ **(6b)** (400.1 MHz, $CDCl_3$, 298K).

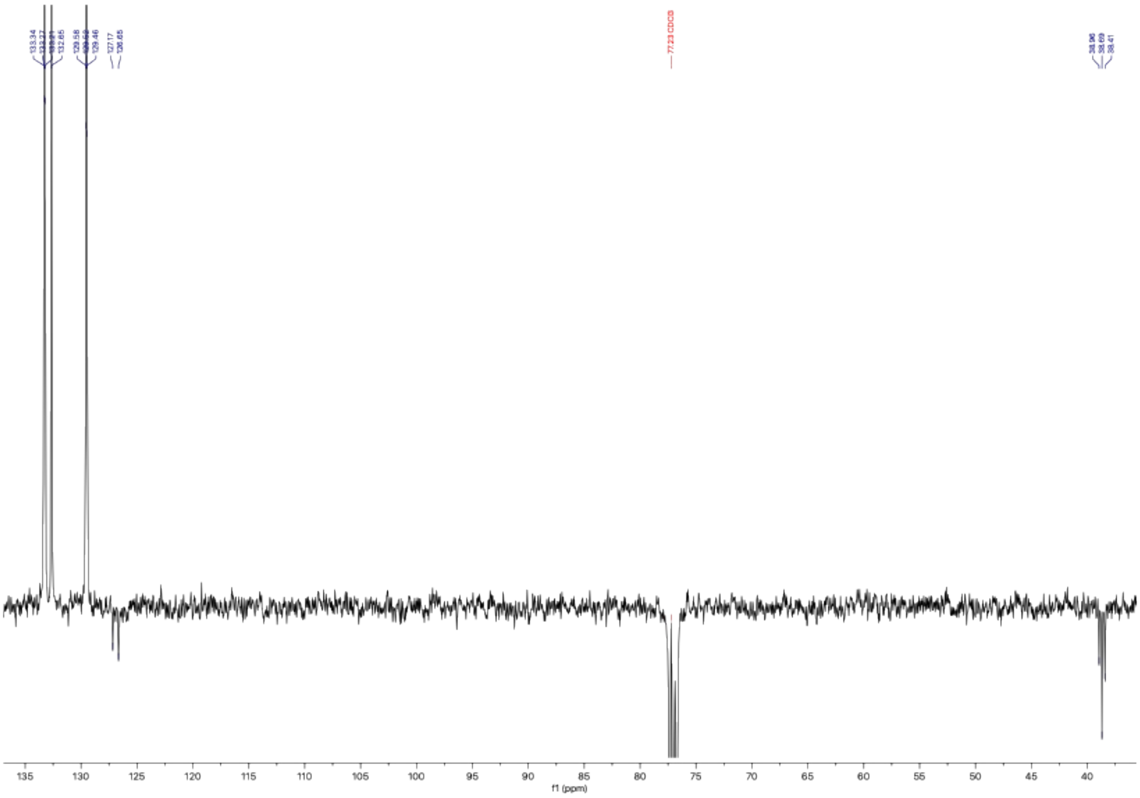


Figure S46. $^{13}C\{^1H\}$ NMR spectra of $[Pd(dppm)Cl_2]$ **(6b)** (100.6 MHz, $CDCl_3$, 298K).

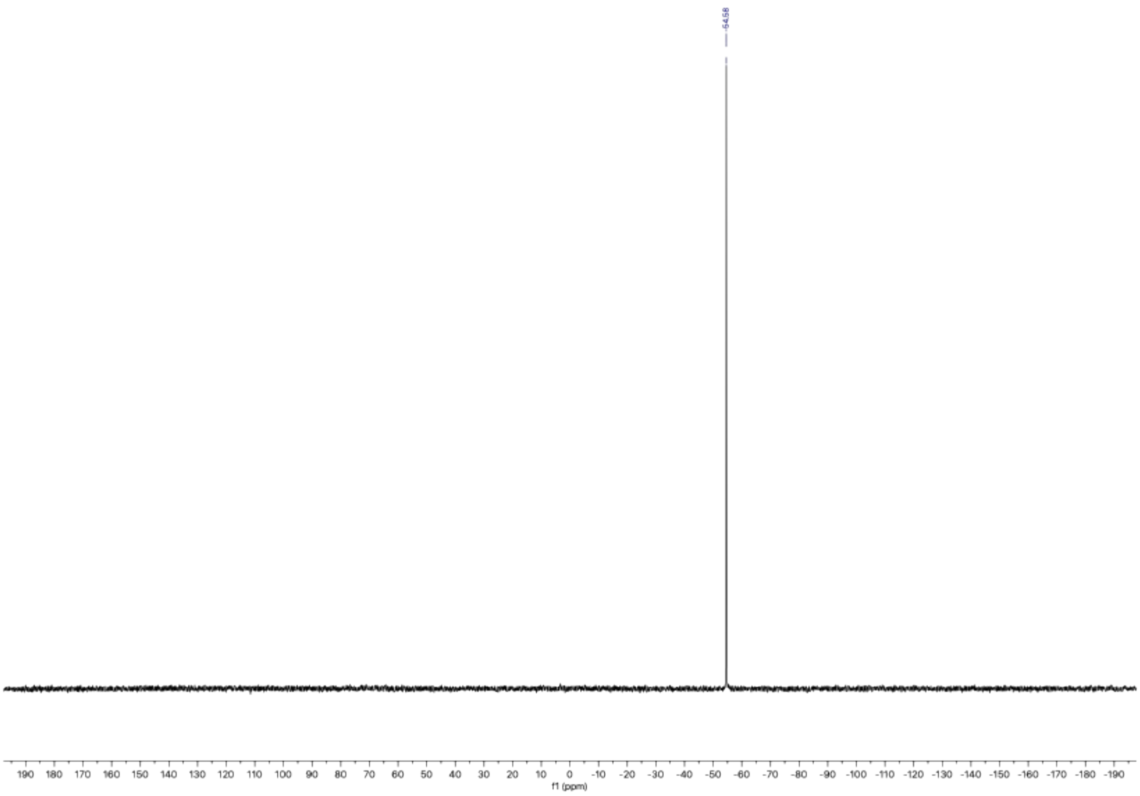


Figure S47. $^{31}P\{^1H\}$ NMR spectra of $[Pd(dppm)Cl_2]$ **(6b)** (162.0 MHz, $CDCl_3$, 298K).

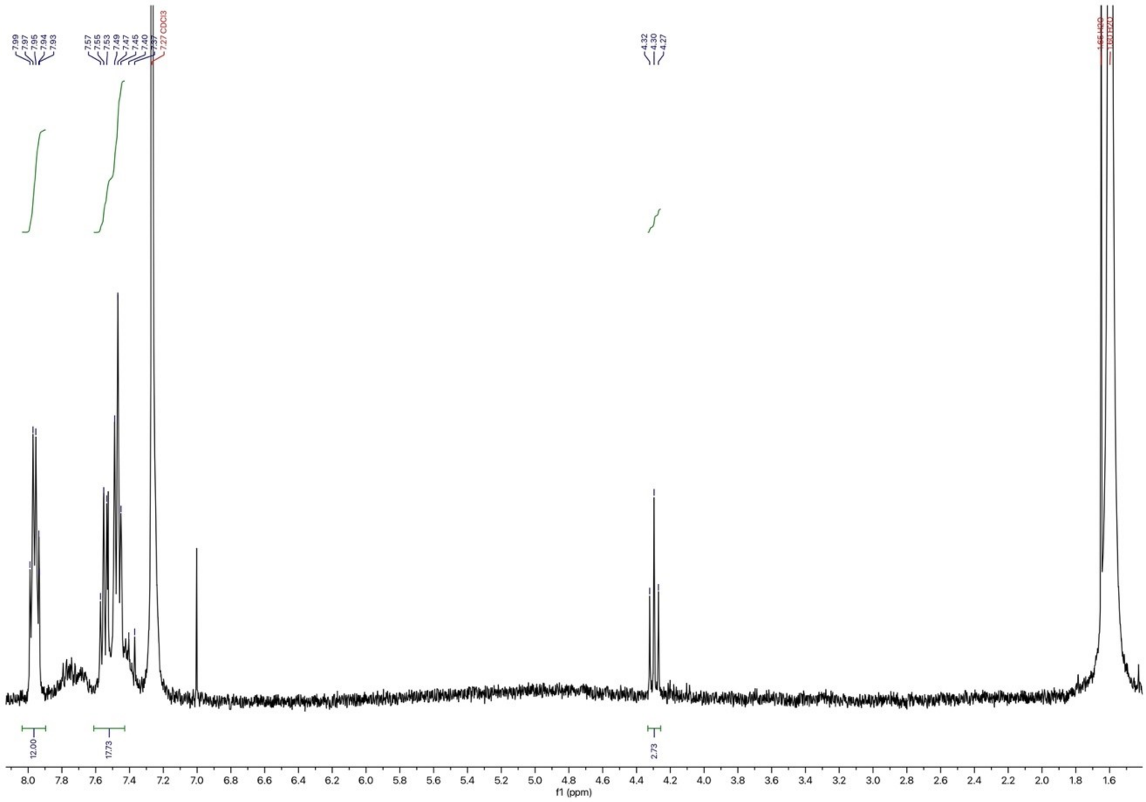


Figure S48. ^{1}H NMR spectra of [Pd(dppm)Br_2] **(6c)** (400.1 MHz, $CDCl_3$, 298K).

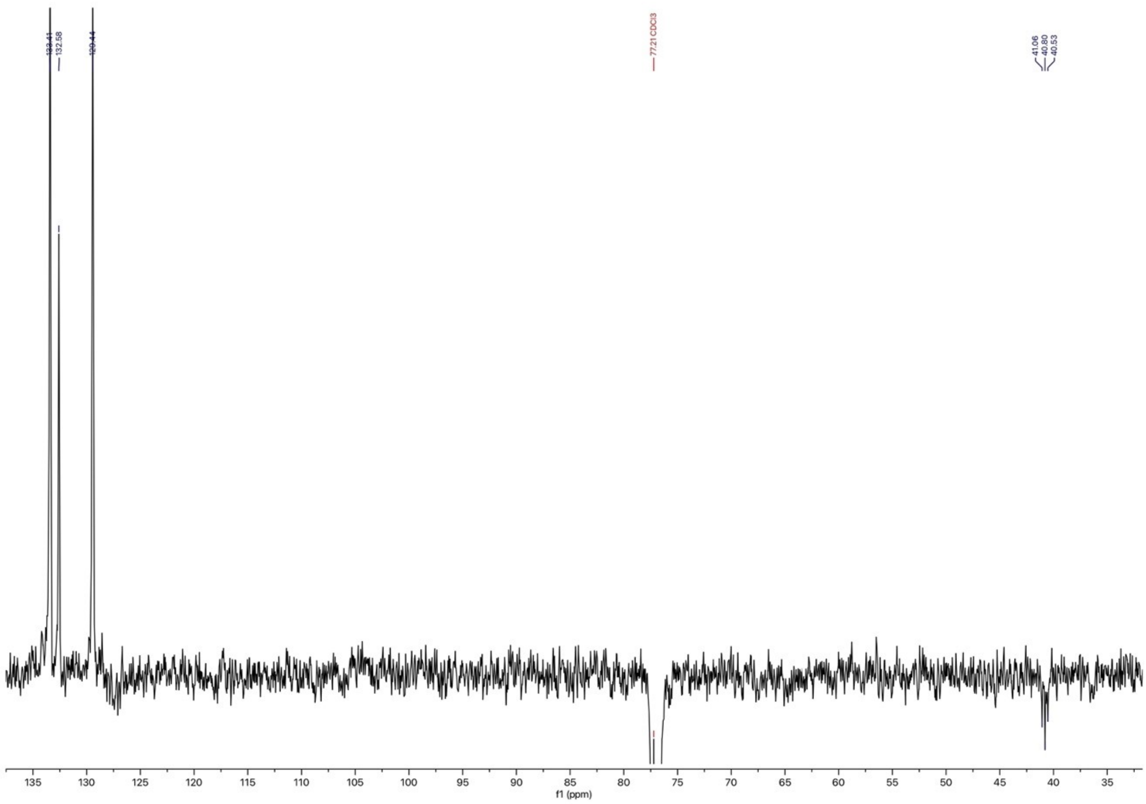


Figure S49. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(dppm)Br_2] **(6c)** (100.6 MHz, $CDCl_3$, 298K).

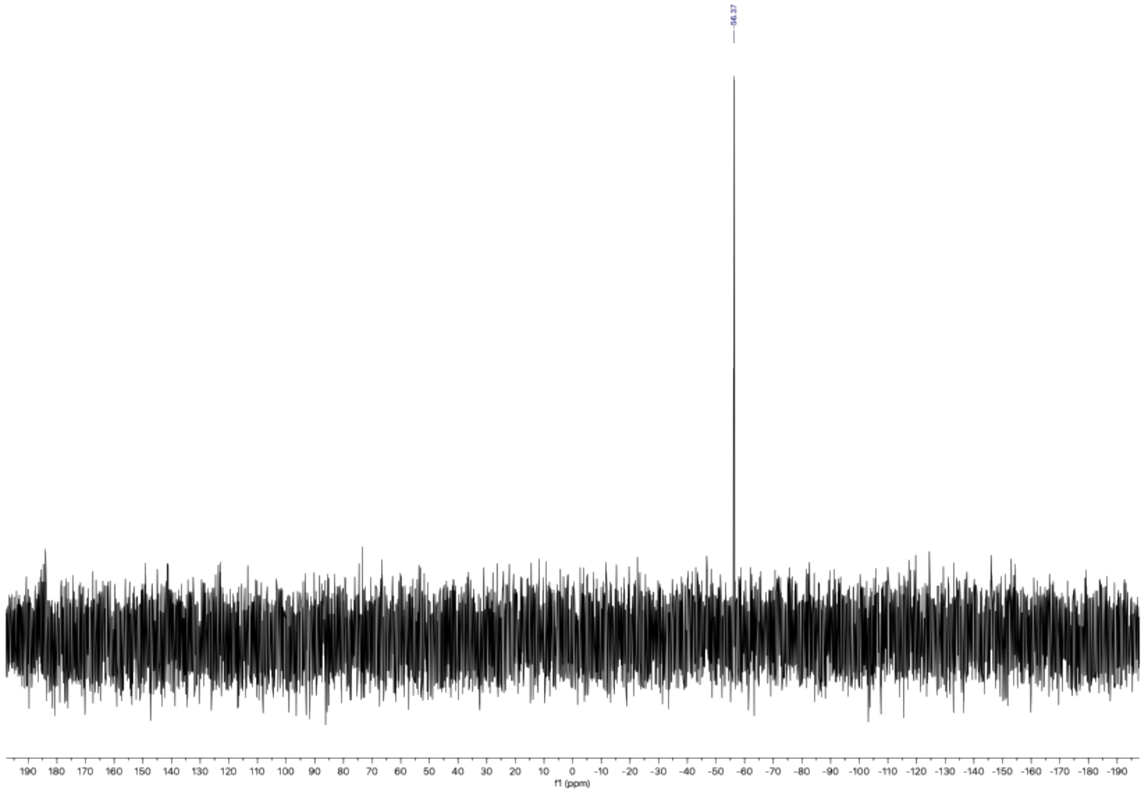


Figure S50. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppm)Br_2]$ **(6c)** (162.0 MHz, $CDCl_3$, 298K).

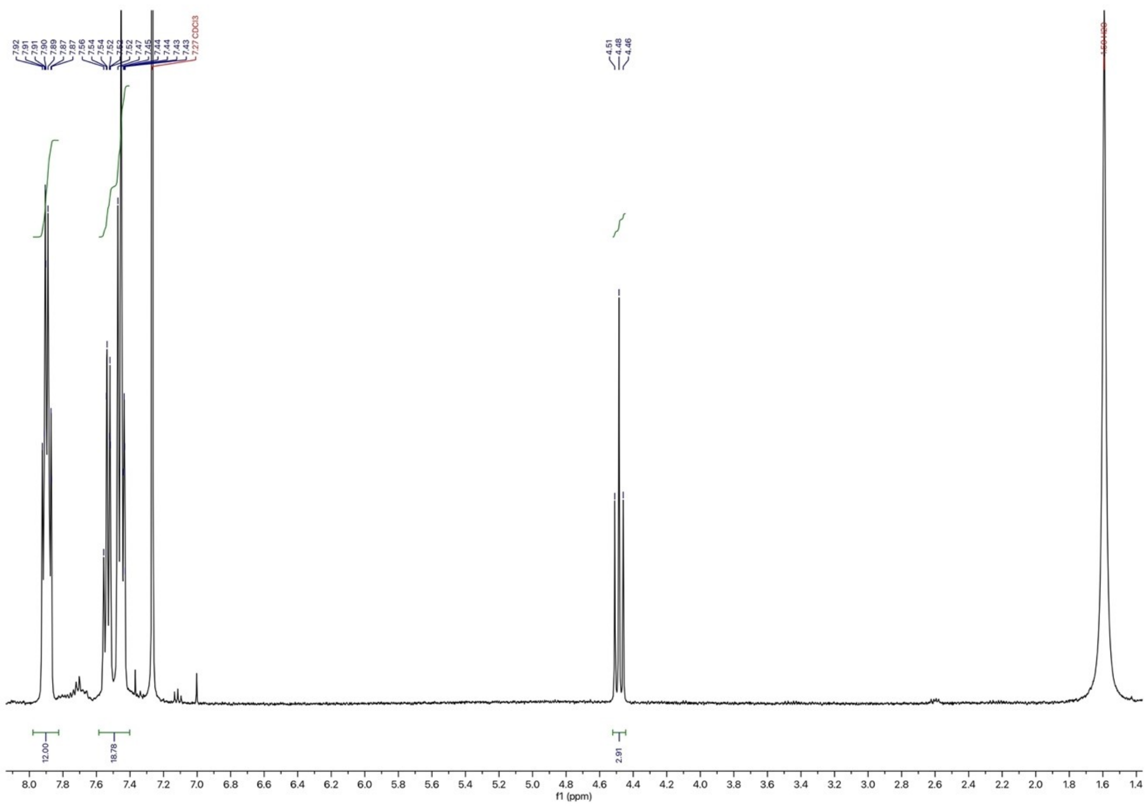


Figure S51. ^{1}H NMR spectra of $[Pd(dppm)I_2]$ **(6d)** (400.1 MHz, $CDCl_3$, 298K).

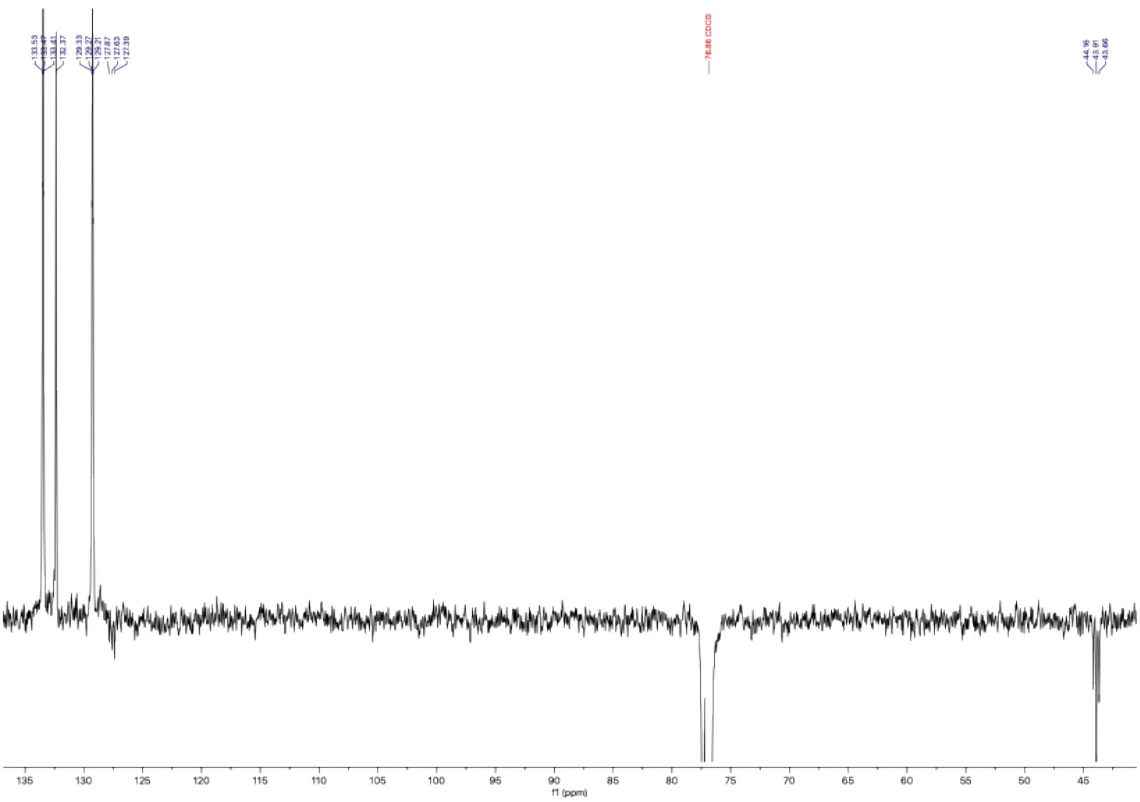


Figure S52. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppm)I_2]$ **(6d)** (100.6 MHz, $CDCl_3$, 298K).

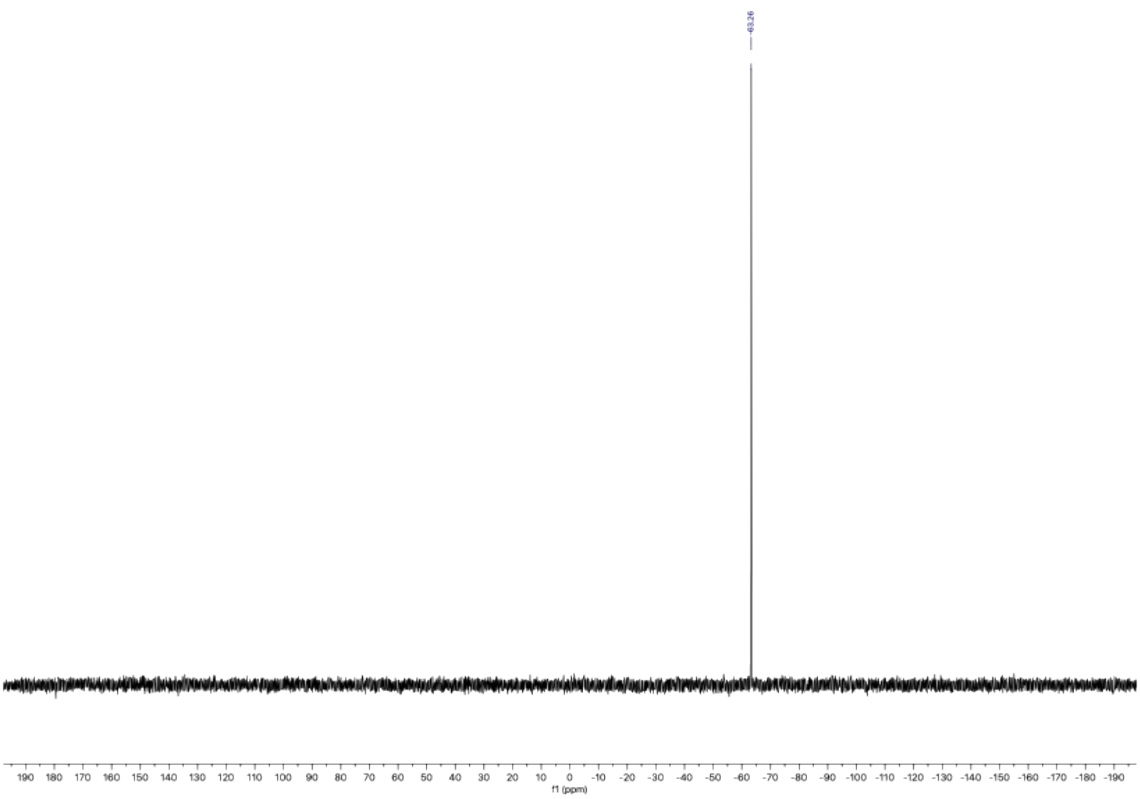


Figure S53. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppm)I_2]$ **(6d)** (162.0 MHz, $CDCl_3$, 298K).

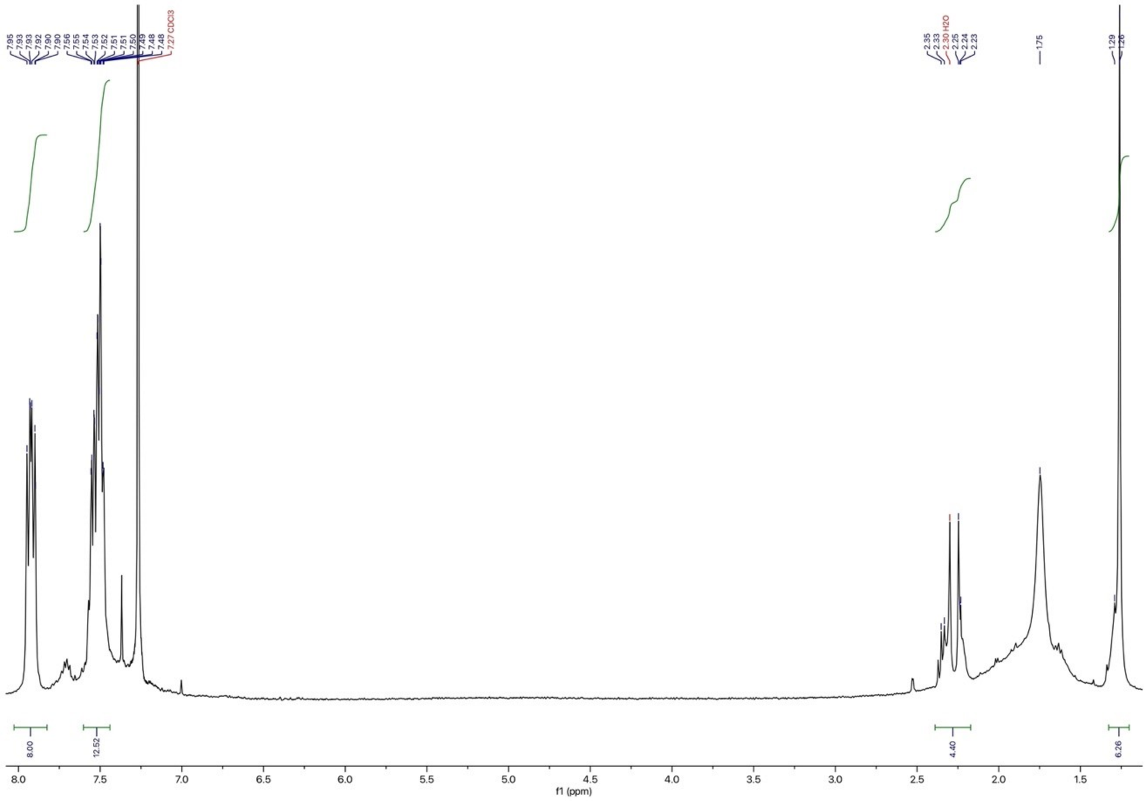


Figure S54. ^{1}H NMR spectra of $[Pd(dppe)(OAc)_2]$ **(7a)** (400.1 MHz, $CDCl_3$, 298K).

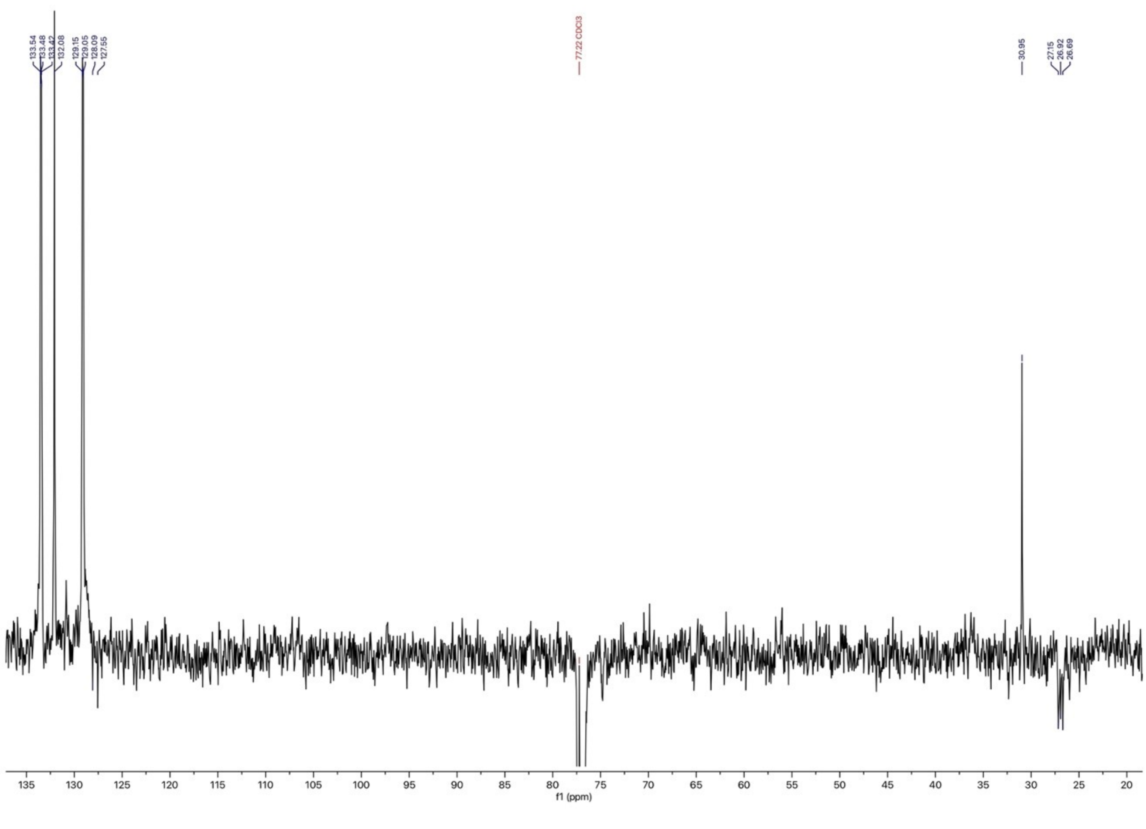


Figure S55. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppe)(OAc)_2]$ **(7a)** (100.6 MHz, $CDCl_3$, 298K).

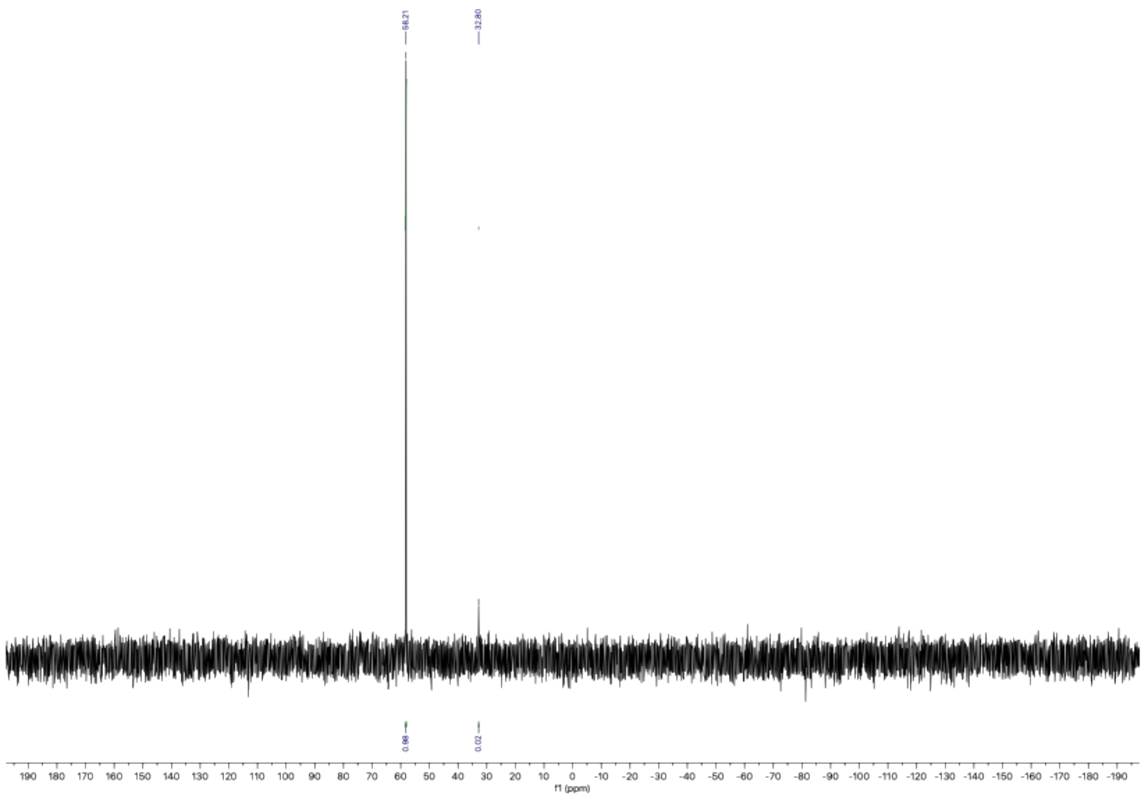


Figure S56. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppe)(OAc)_2]$ **(7a)** (162.0 MHz, $CDCl_3$, 298K).

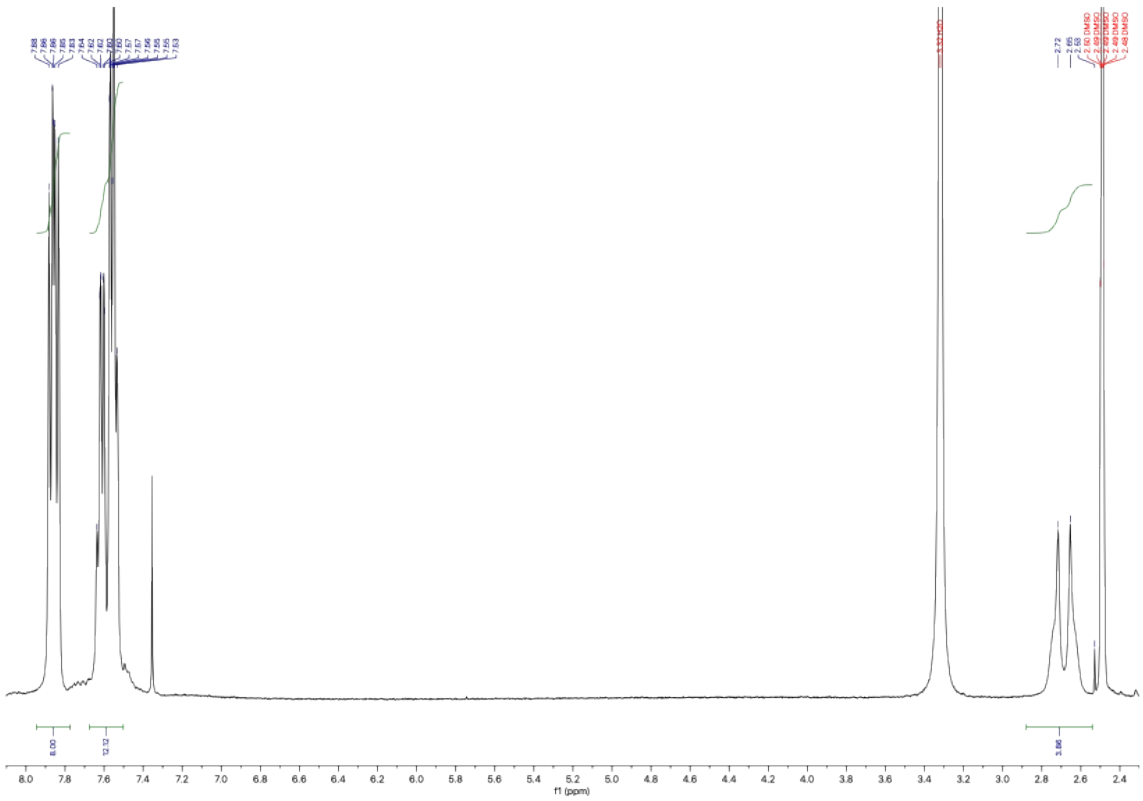


Figure S57. ^{1}H NMR spectra of $[Pd(dppe)Cl_2]$ **(7b)** (400.1 MHz, DMSO-d_6, 298K).

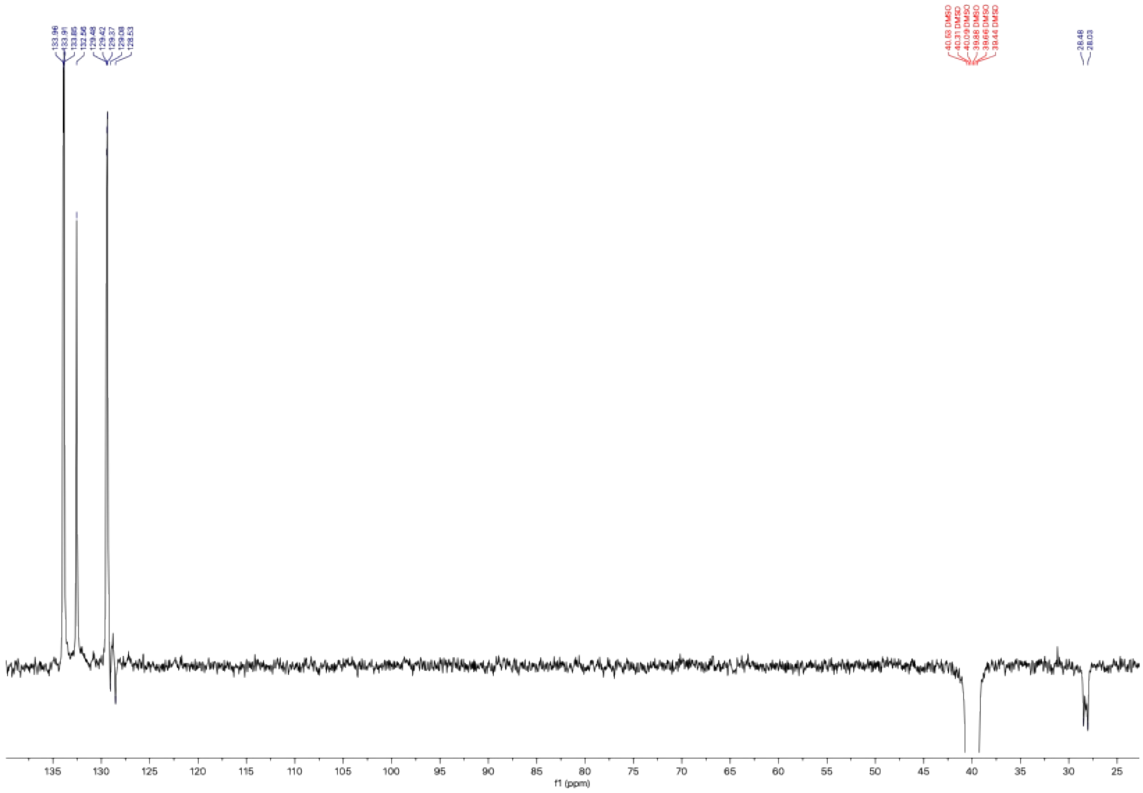


Figure S58. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(dppe)Cl_2] **(7b)** (100.6 MHz, DMSO-d_6, 298K).

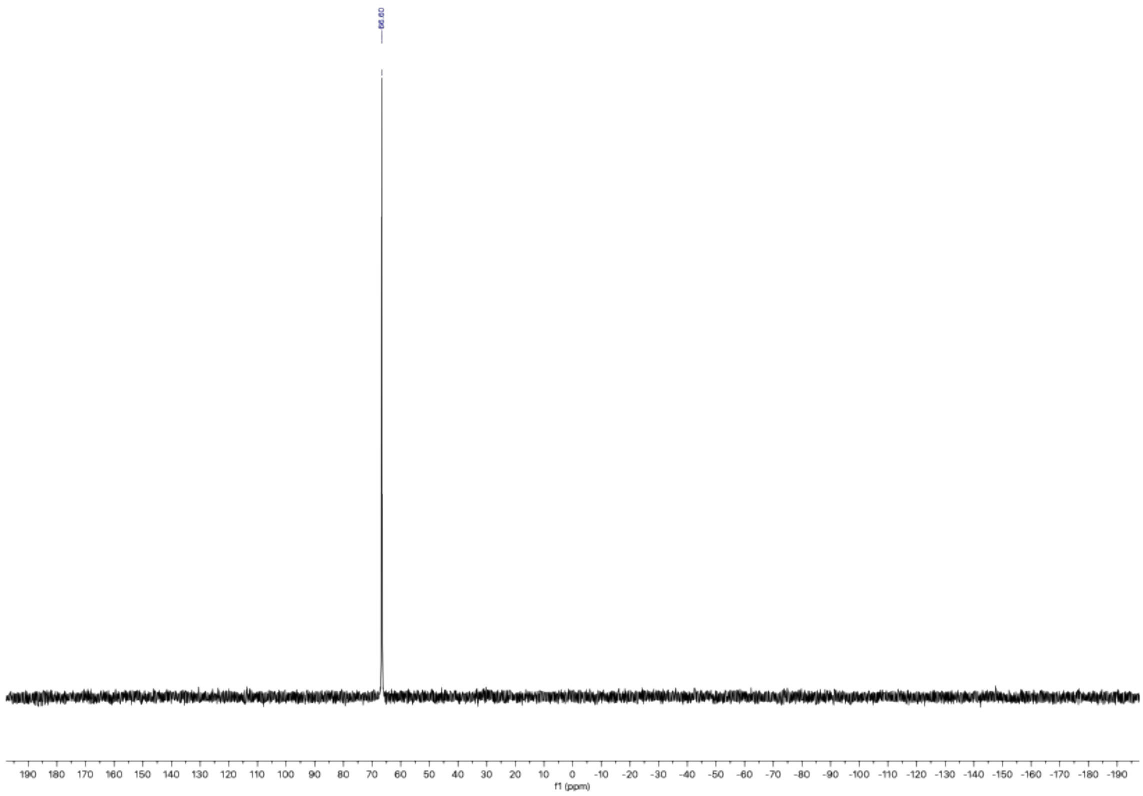


Figure S59. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(dppe)Cl_2] **(7b)** (162.0 MHz, DMSO-d_6, 298K).

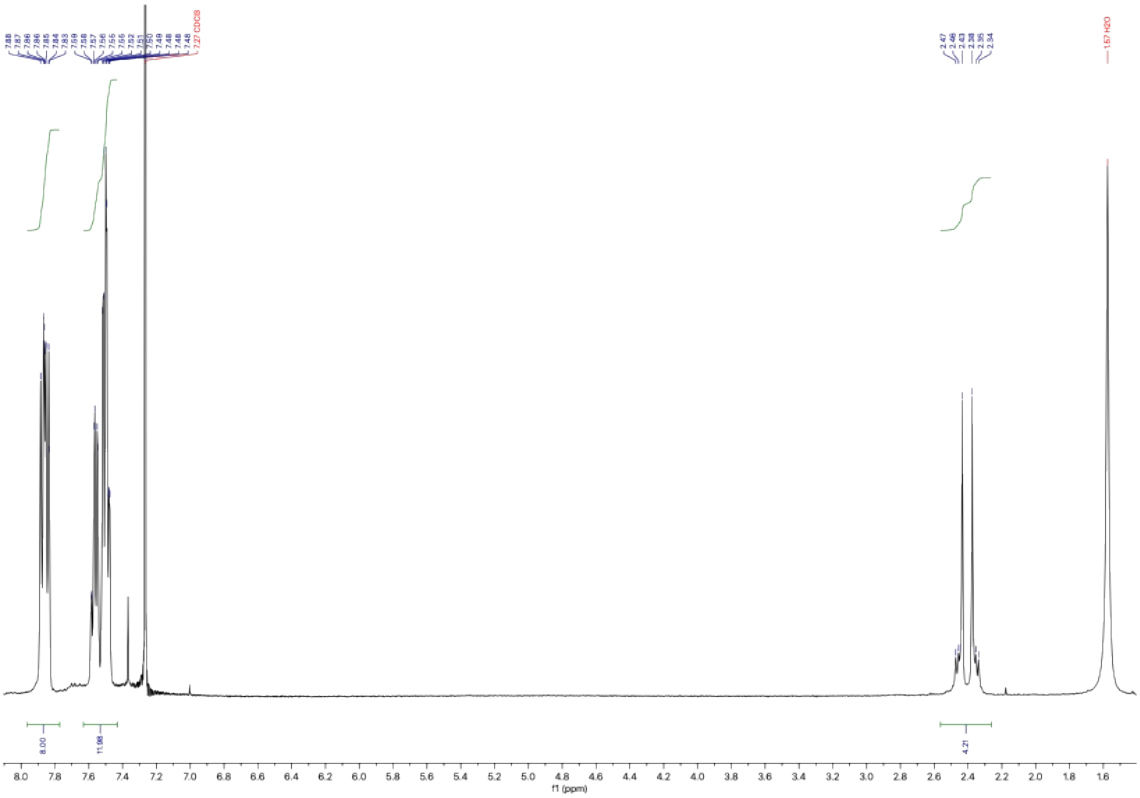


Figure S60. ^{1}H NMR spectra of [Pd(dppe)Br_2] **(7c)** (400.1 MHz, $CDCl_3$, 298K).

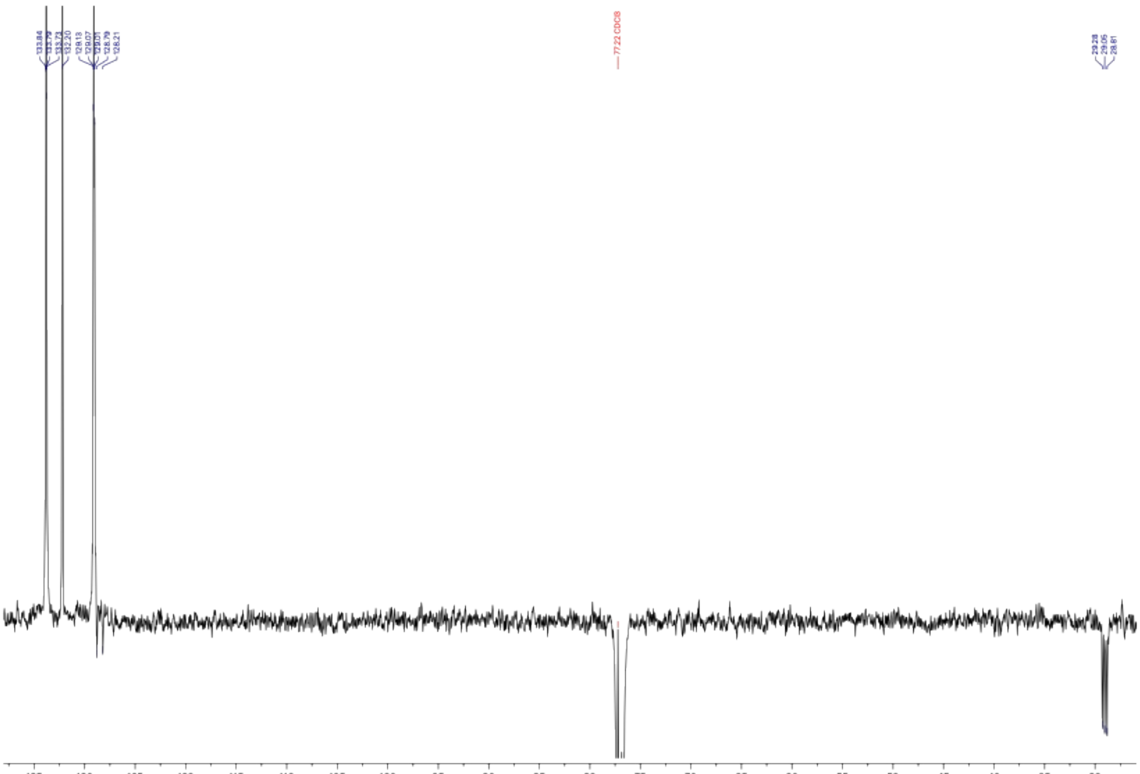


Figure S61. $^{13}C\{^1H\}$ NMR spectra of [Pd(dppe)Br_2] **(7c)** (100.6 MHz, $CDCl_3$, 298K).

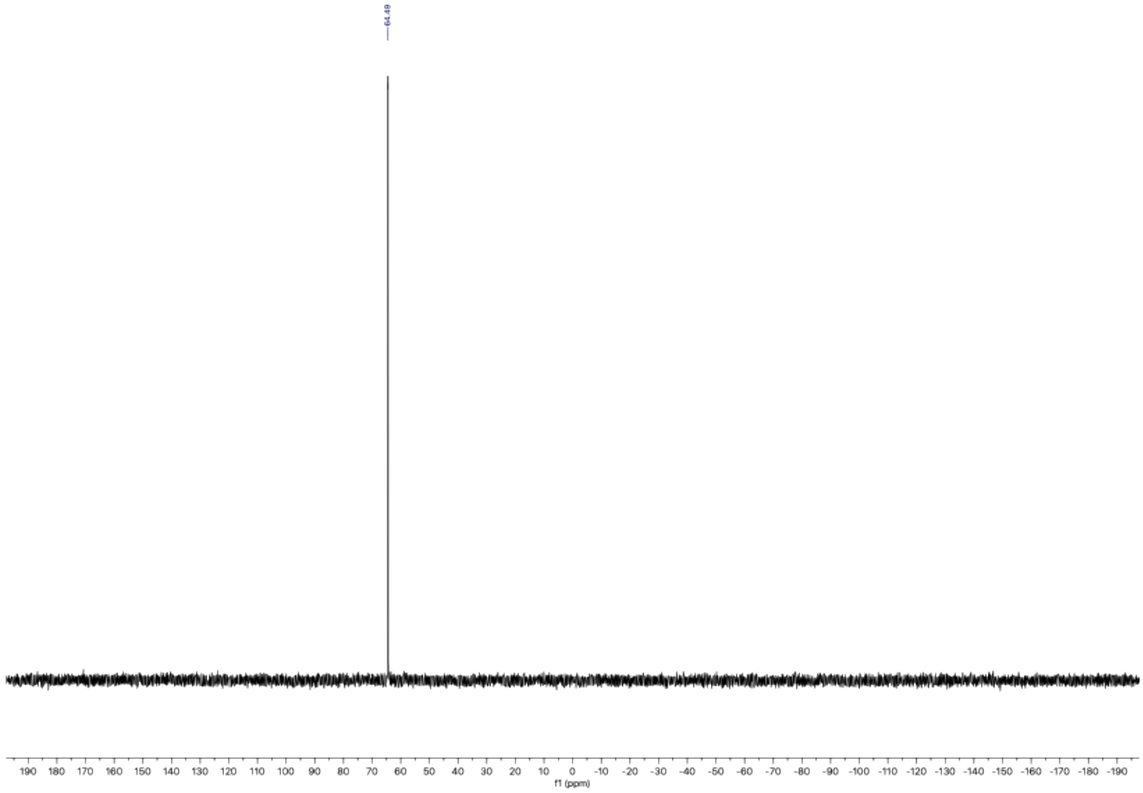


Figure S62. $^{31}P\{^1H\}$ NMR spectra of [Pd(dppe)Br$_2$] **(7c)** (162.0 MHz, $CDCl_3$, 298K).

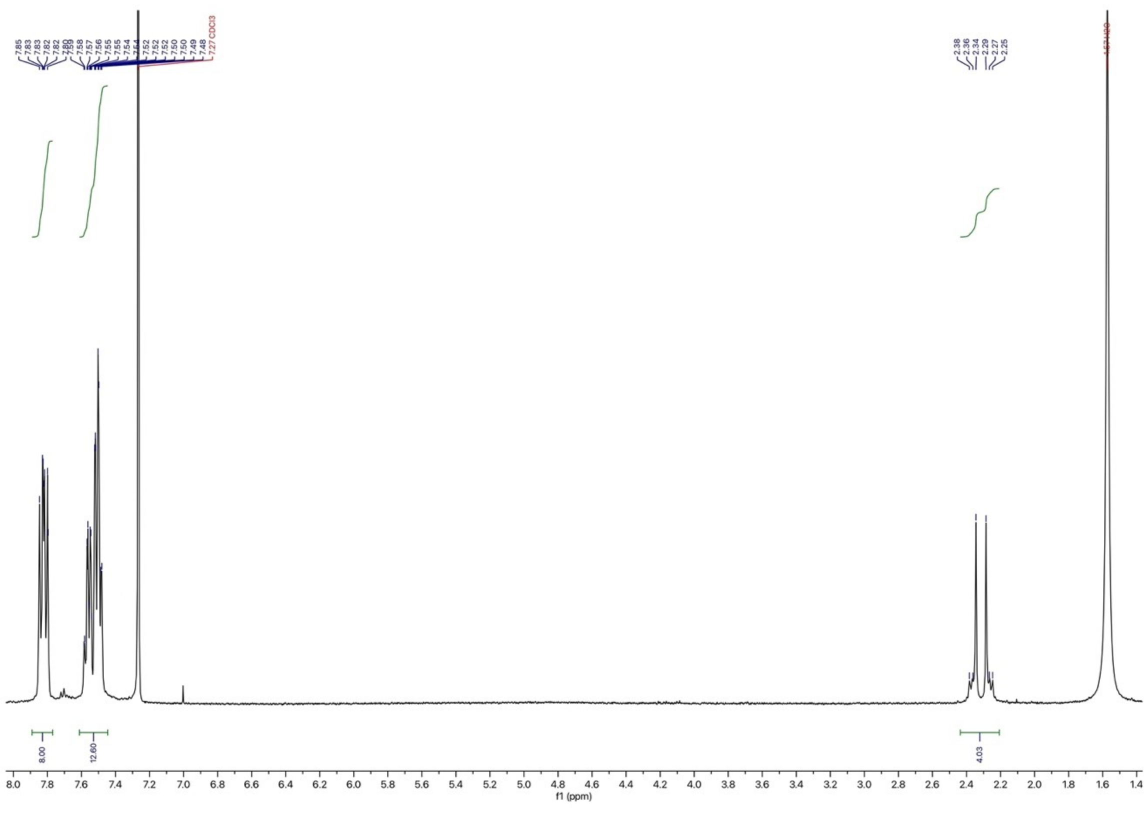


Figure S63. ^1H NMR spectra of [Pd(dppe)I$_2$] **(7d)** (400.1 MHz, $CDCl_3$, 298K).

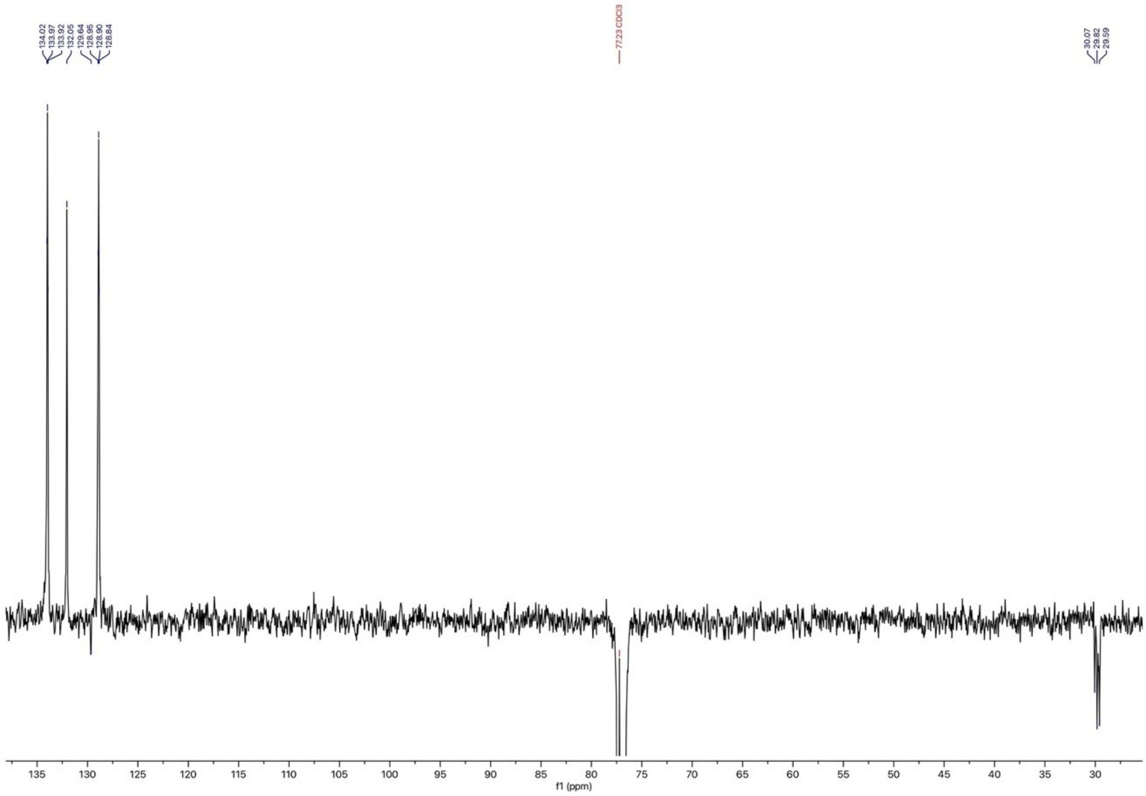


Figure S64. $^{13}C\{^1H\}$ NMR spectra of $[Pd(dppe)I_2]$ **(7d)** (100.6 MHz, $CDCl_3$, 298K).

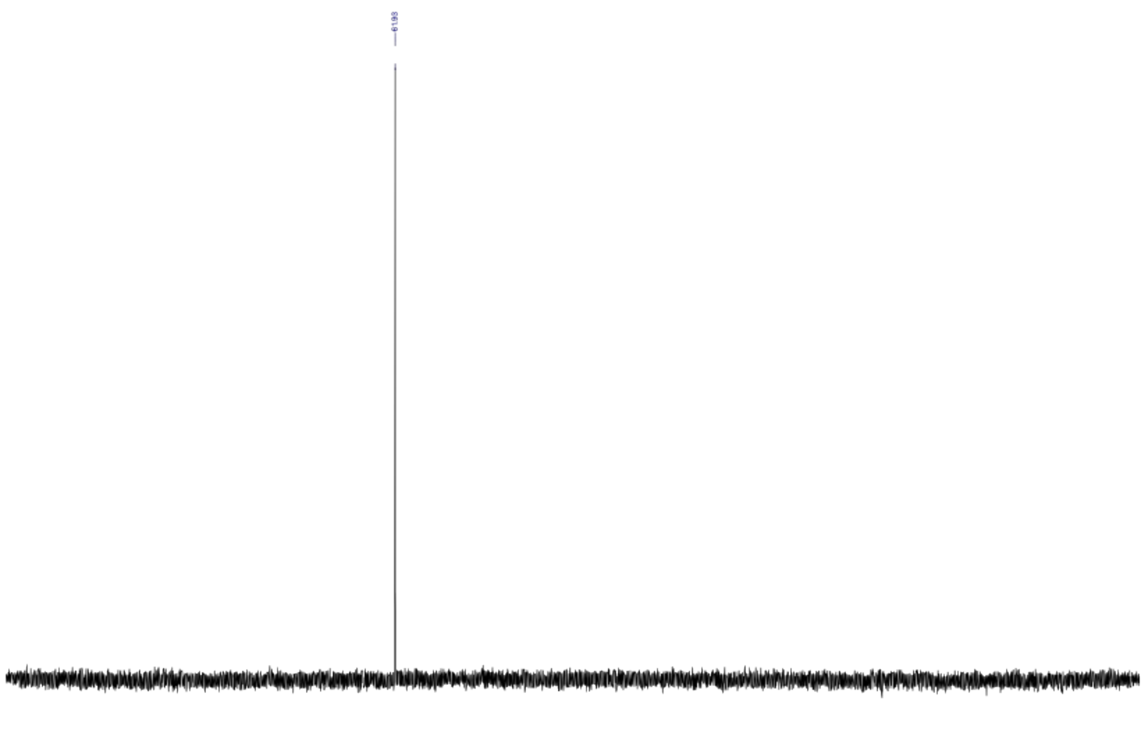


Figure S65. $^{31}P\{^1H\}$ NMR spectra of $[Pd(dppe)I_2]$ **(7d)** (162.0 MHz, $CDCl_3$, 298K).

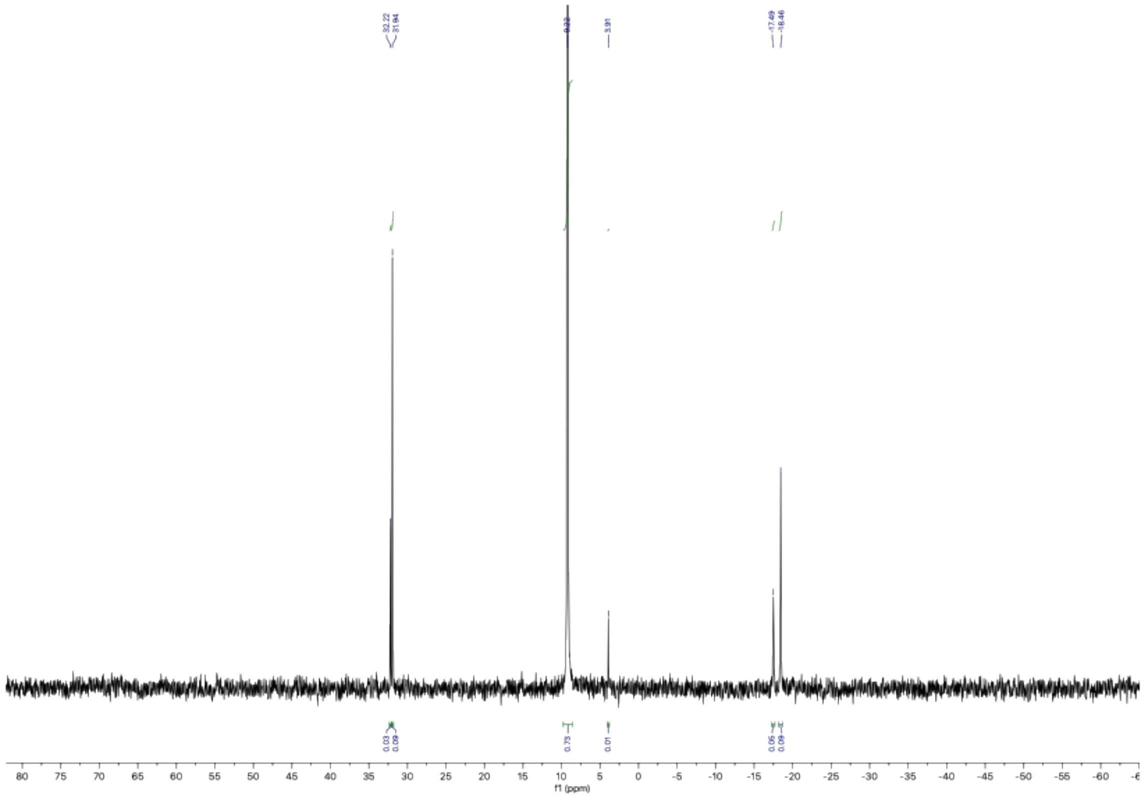


Figure S66. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppp)(OAc)_2]$ **(8a)** (162.0 MHz, $CDCl_3$, 298K).

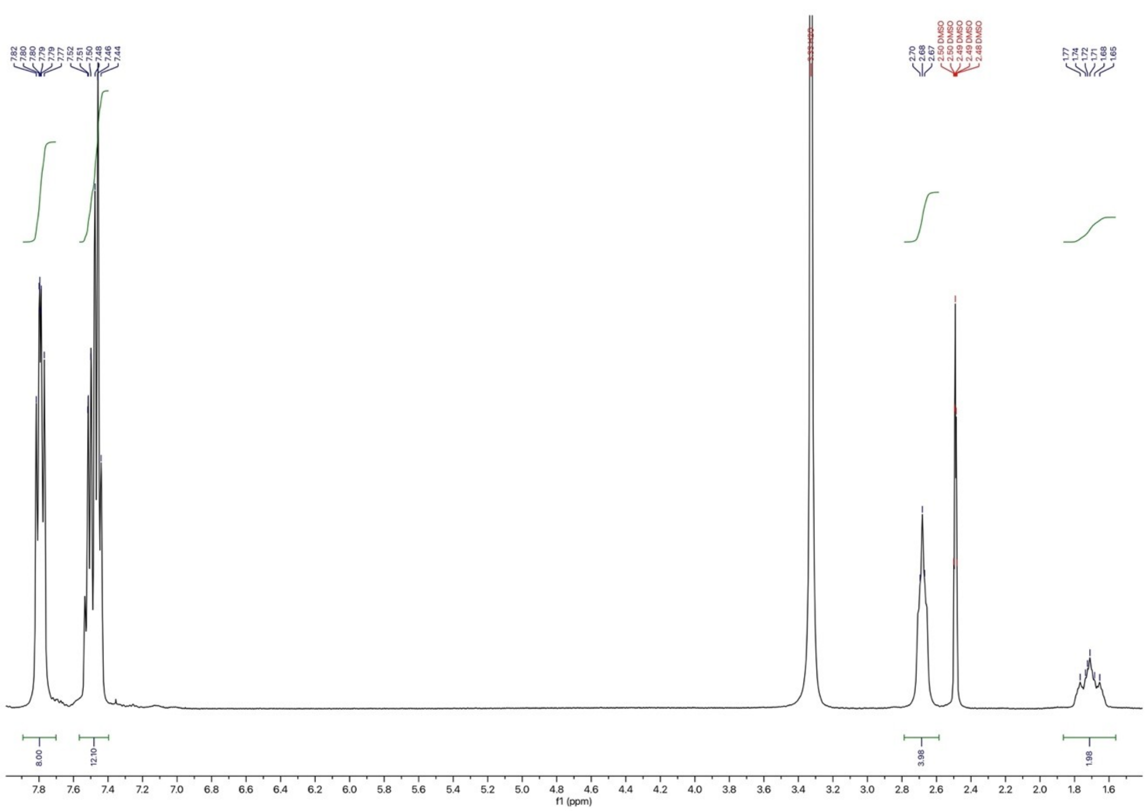


Figure S67. ^{1}H NMR spectra of $[Pd(dppp)Cl_2]$ **(8b)** (400.1 MHz, DMSO-d_6, 298K).

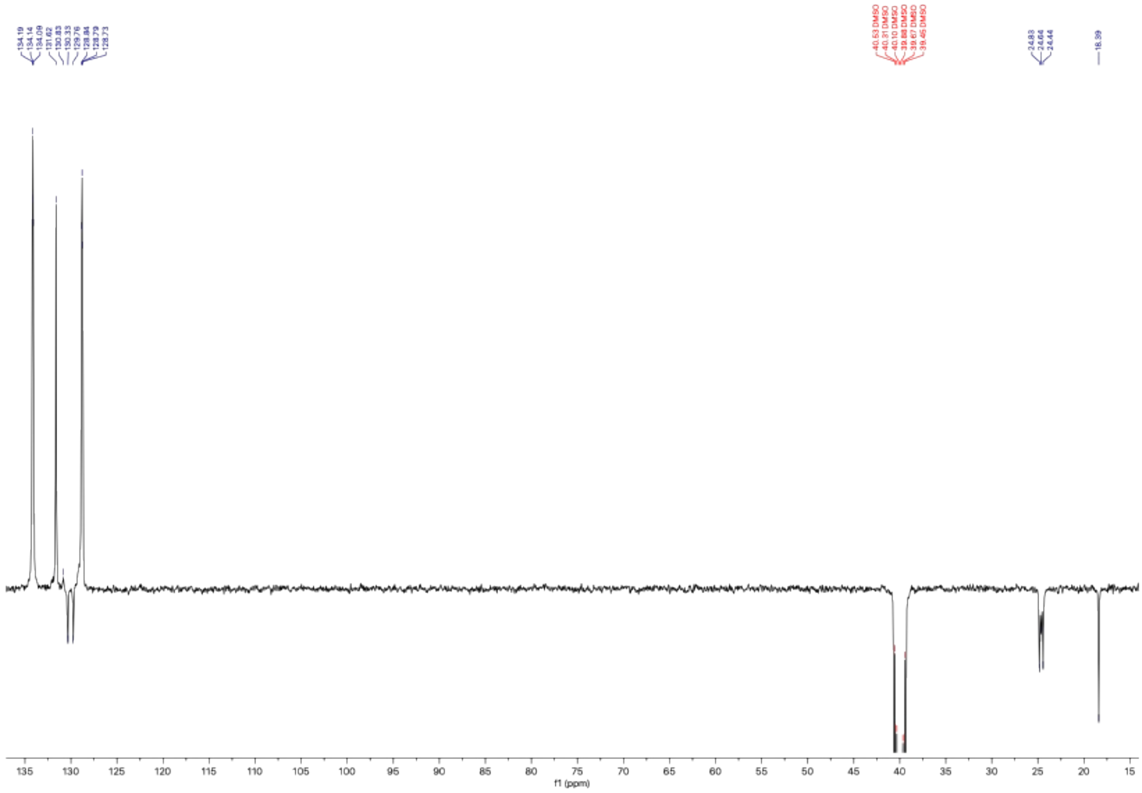


Figure S68. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppp)Cl_2]$ **(8b)** (100.6 MHz, DMSO-d_6, 298K).

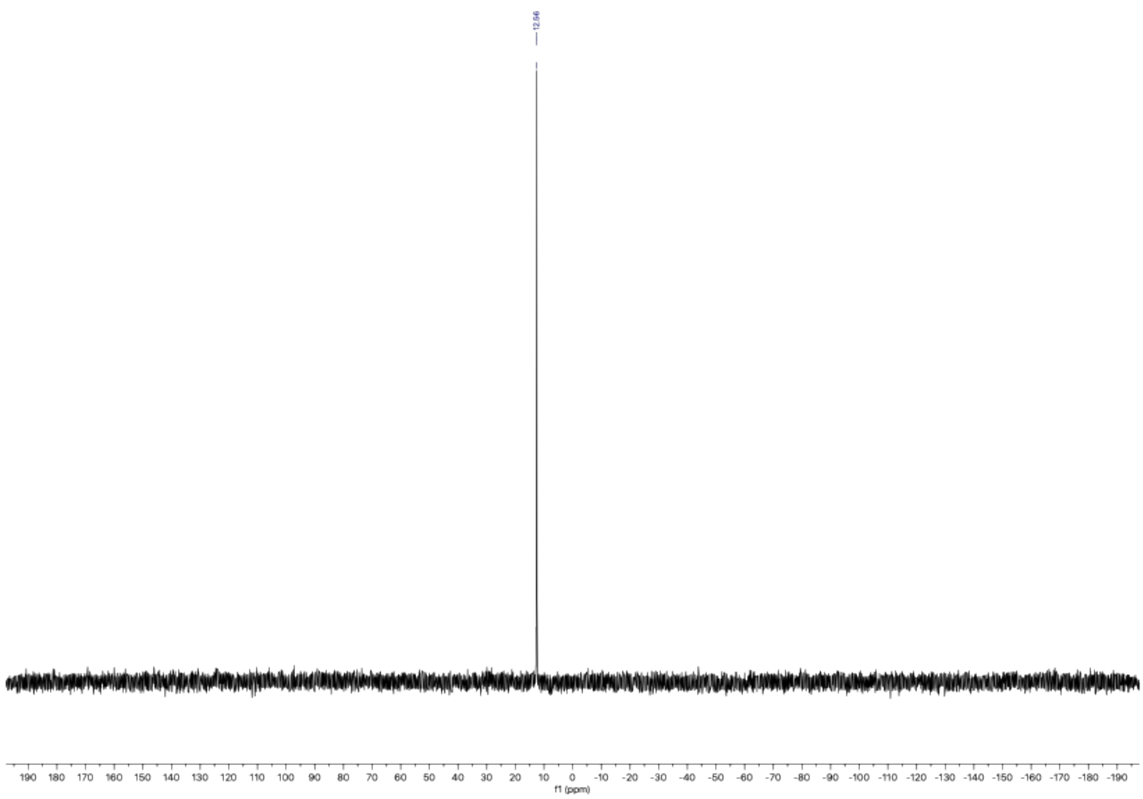


Figure S69. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppp)Cl_2]$ **(8b)** (162.0 MHz, DMSO-d_6, 298K).

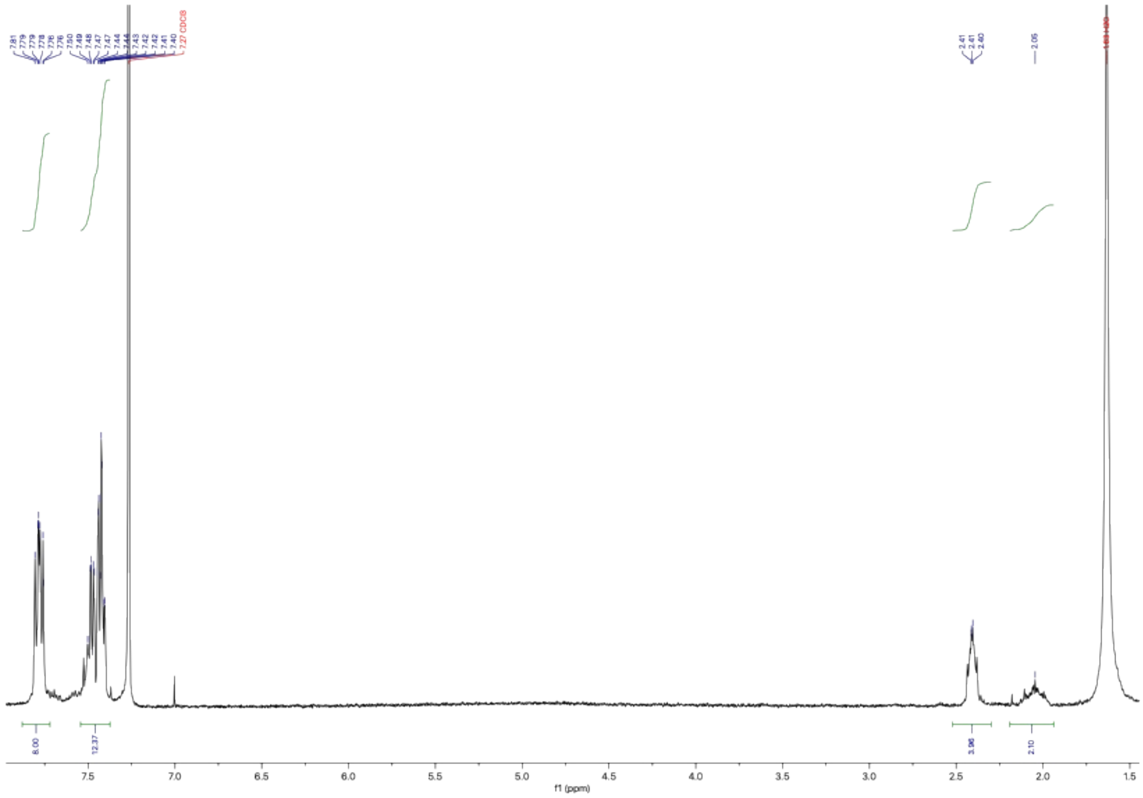


Figure S70. ^{1}H NMR spectra of $[Pd(dppp)Br_2]$ **(8c)** (400.1 MHz, $CDCl_3$, 298K).

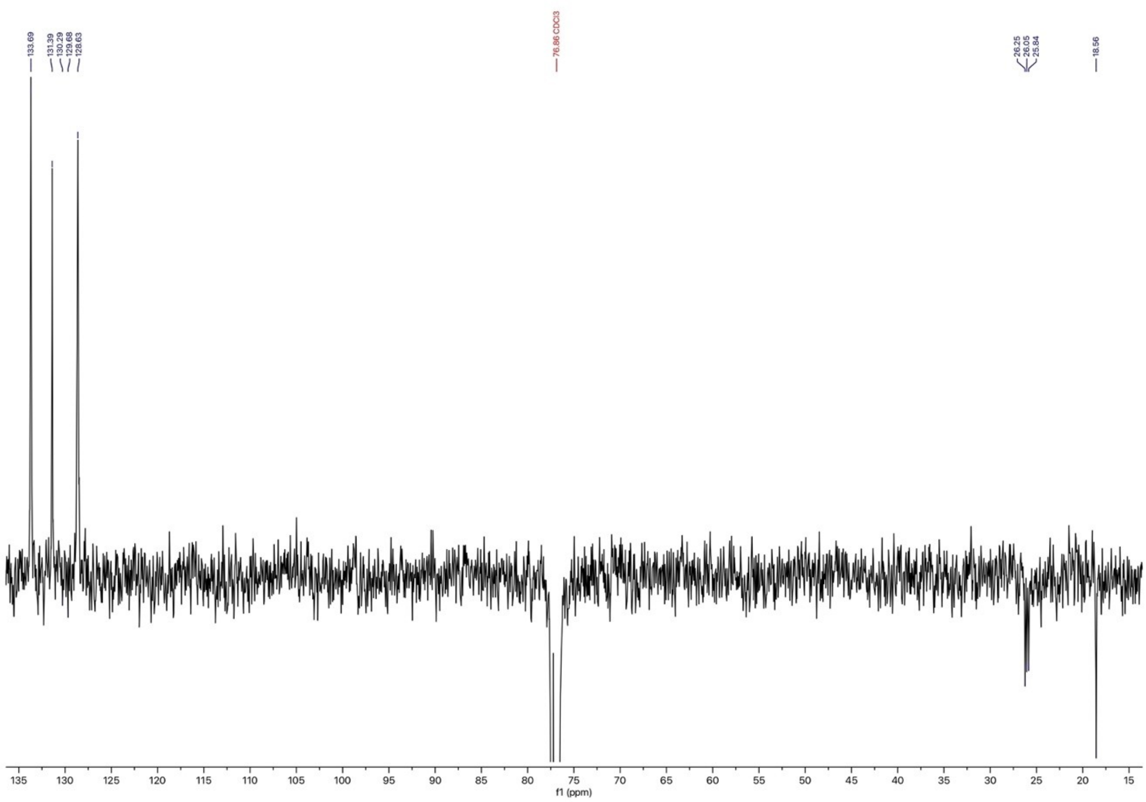


Figure S71. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppp)Br_2]$ **(8c)** (100.6 MHz, $CDCl_3$, 298K).

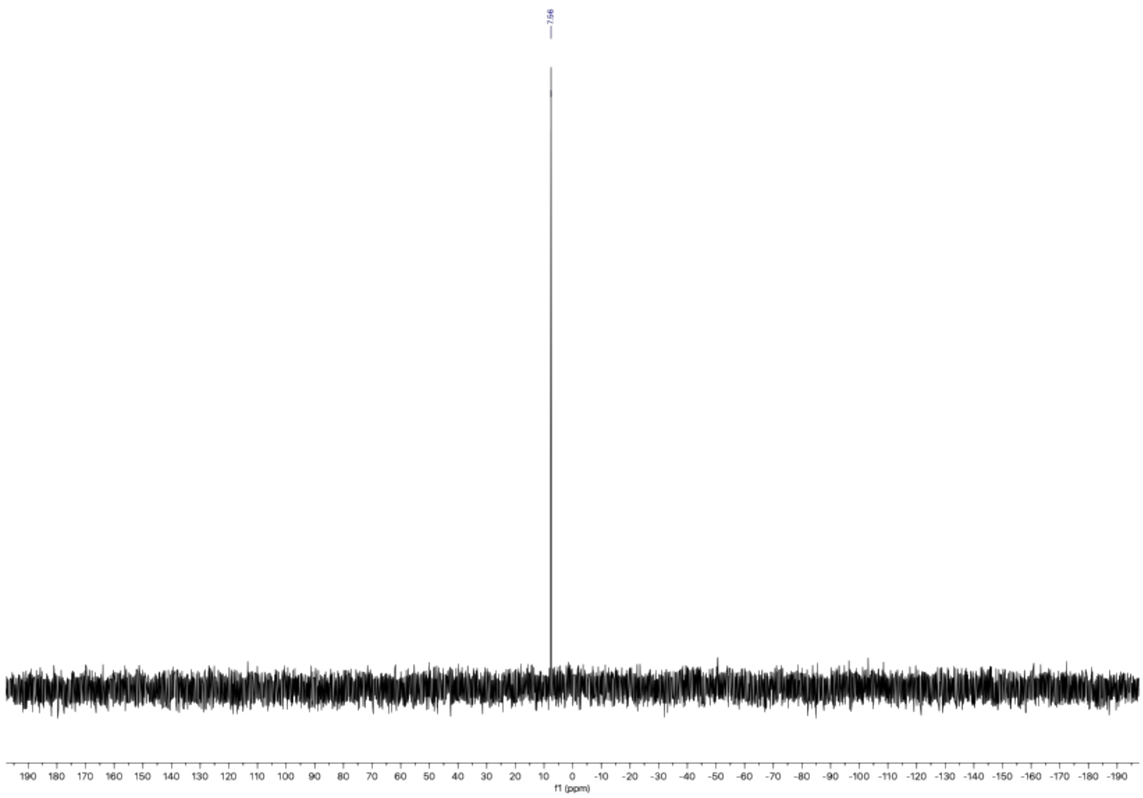


Figure S72. $^{31}P\{^1H\}$ NMR spectra of $[Pd(dppp)Br_2]$ **(8c)** (162.0 MHz, $CDCl_3$, 298K).

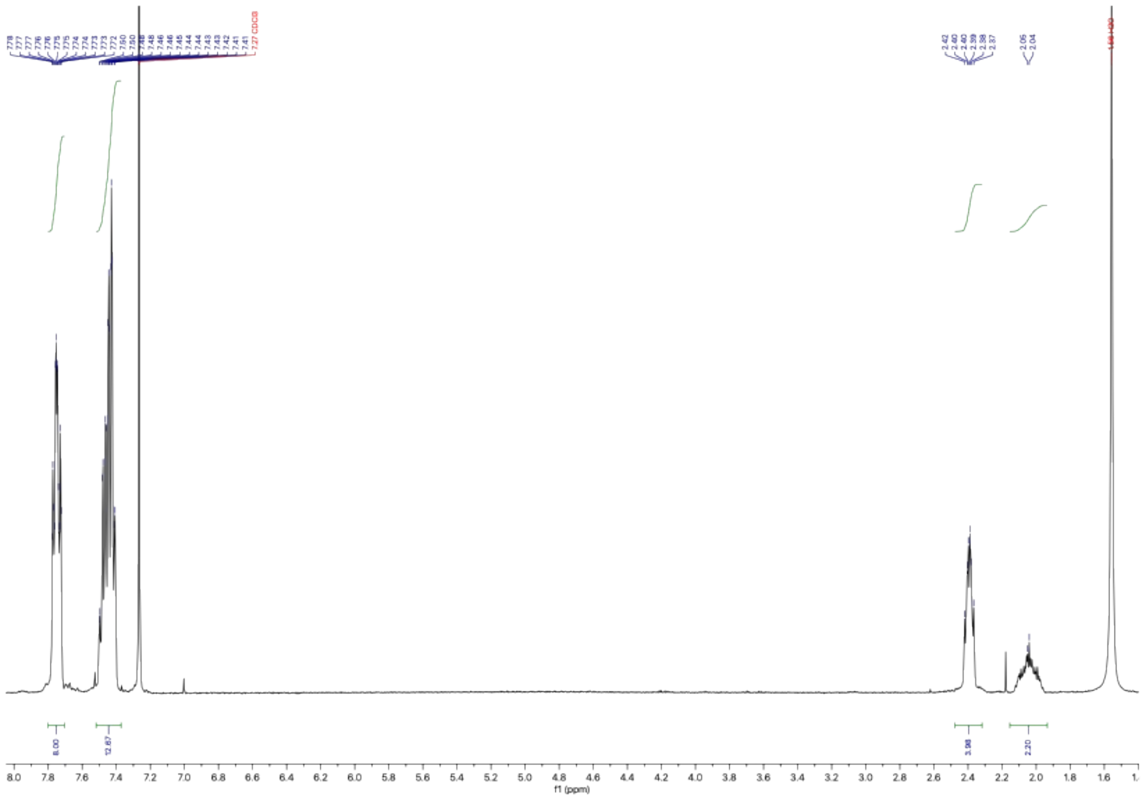


Figure S73. ^1H NMR spectra of $[Pd(dppp)I_2]$ **(8d)** (400.1 MHz, $CDCl_3$, 298K).

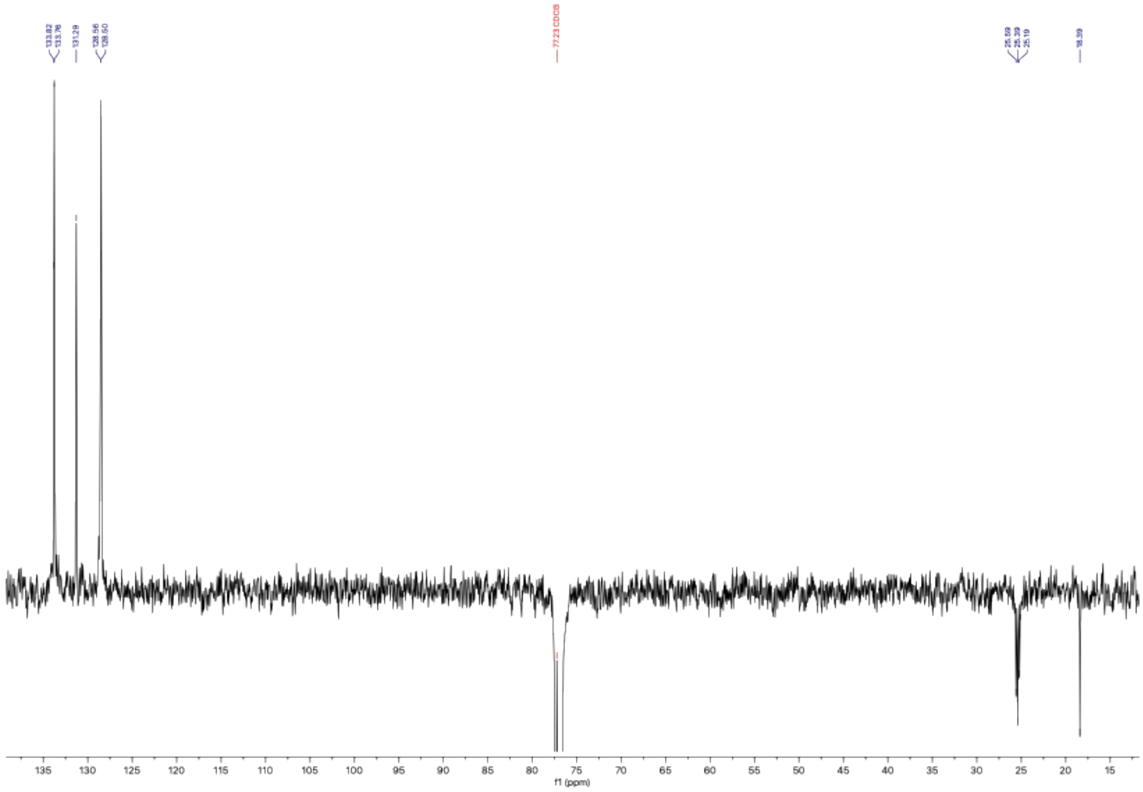


Figure S74. $^{13}C\{^1H\}$ NMR spectra of $[Pd(dppp)I_2]$ **(8d)** (100.6 MHz, $CDCl_3$, 298K).

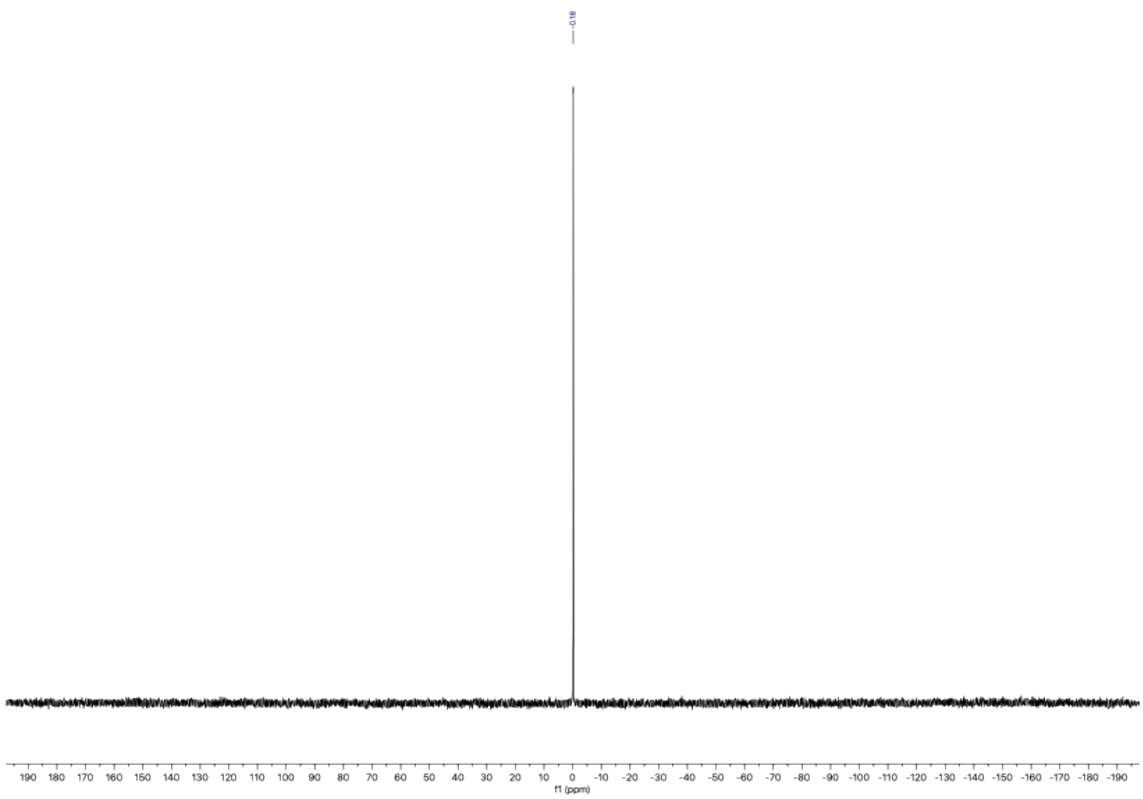


Figure S75. $^{31}P\{^1H\}$ NMR spectra of $[Pd(dppp)I_2]$ **(8d)** (162.0 MHz, $CDCl_3$, 298K).

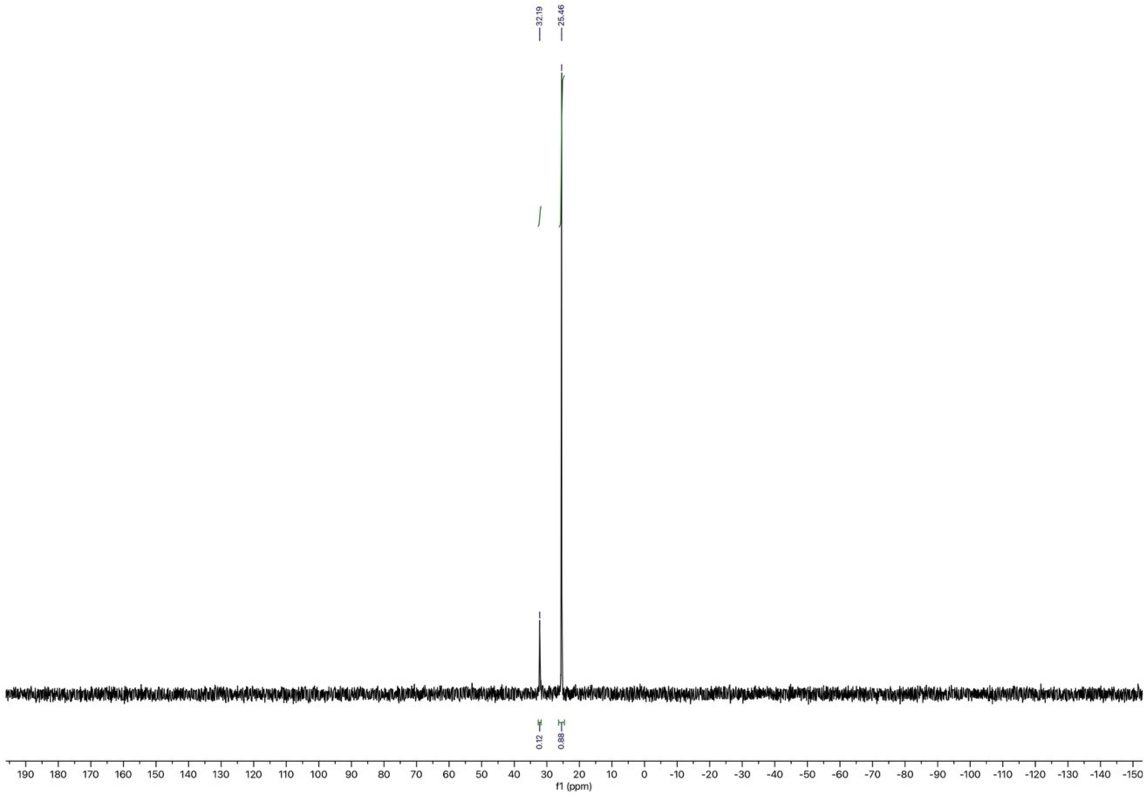


Figure S76. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppb)(OAc)_2]$ **(9a)** (162.0 MHz, $CDCl_3$, 298K).

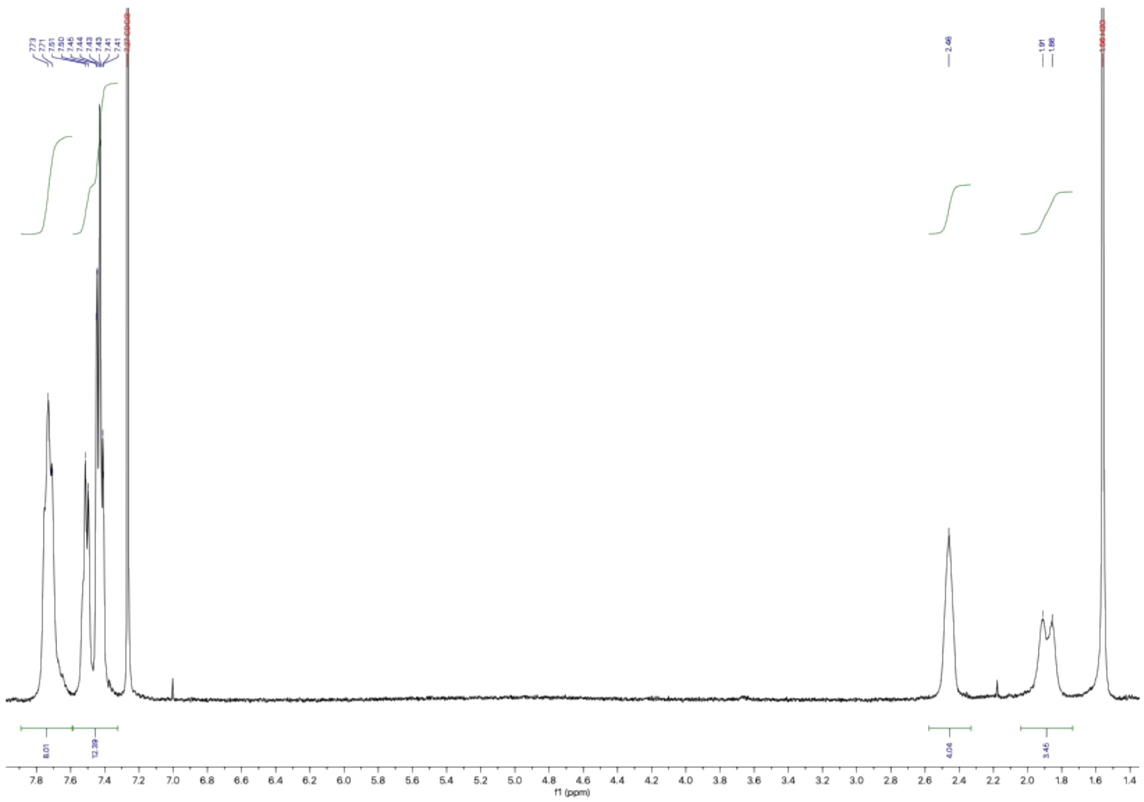


Figure S77. ^{1}H NMR spectra of $[Pd(dppb)Cl_2]$ **(9b)** (400.1 MHz, $CDCl_3$, 298K).

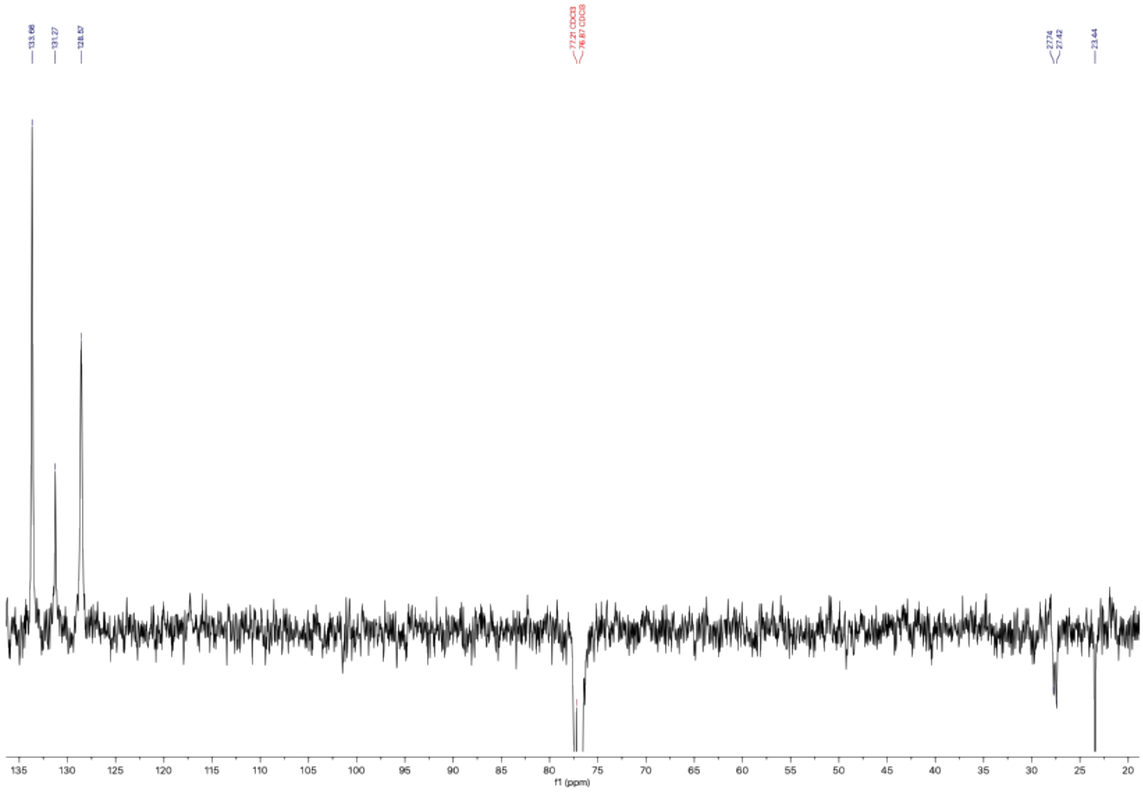


Figure S78. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppb)Cl_2]$ **(9b)** (100.6 MHz, $CDCl_3$, 298K).

Figure S79. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppb)Cl_2]$ **(9b)** (162.0 MHz, $CDCl_3$, 298K).

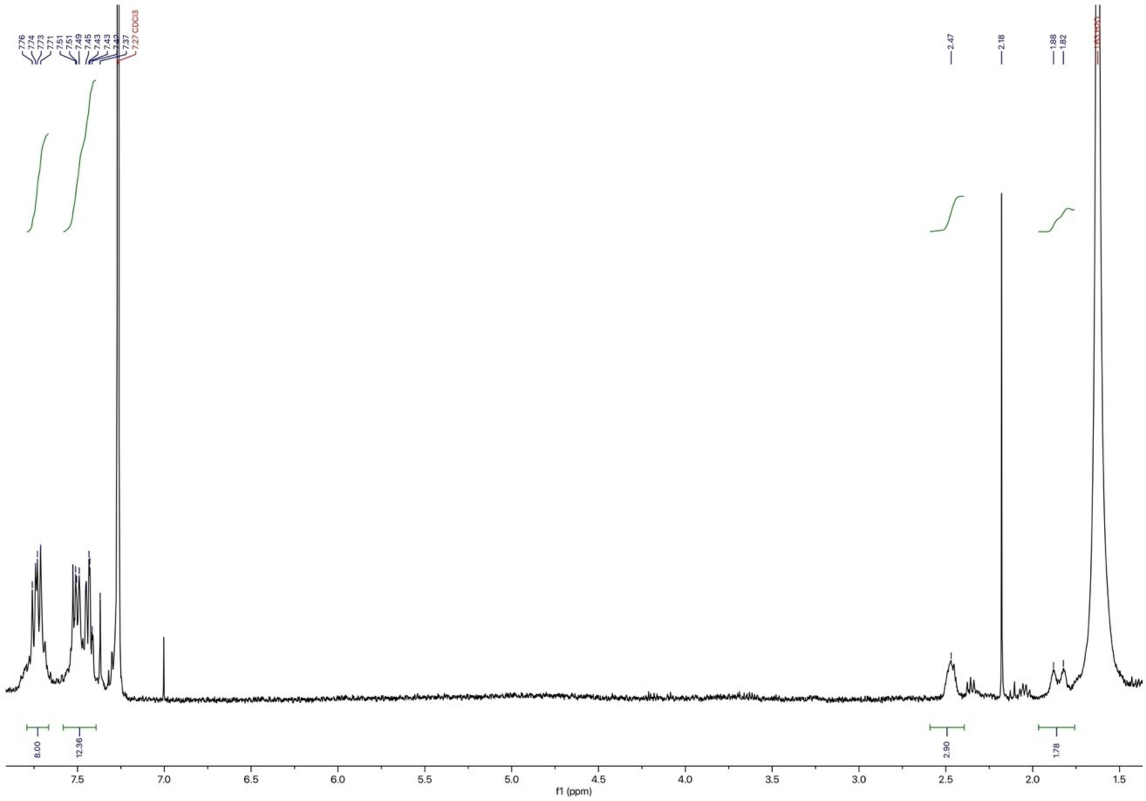


Figure S80. ^{1}H NMR spectra of $[Pd(dppb)Br_2]$ **(9c)** (400.1 MHz, $CDCl_3$, 298K).

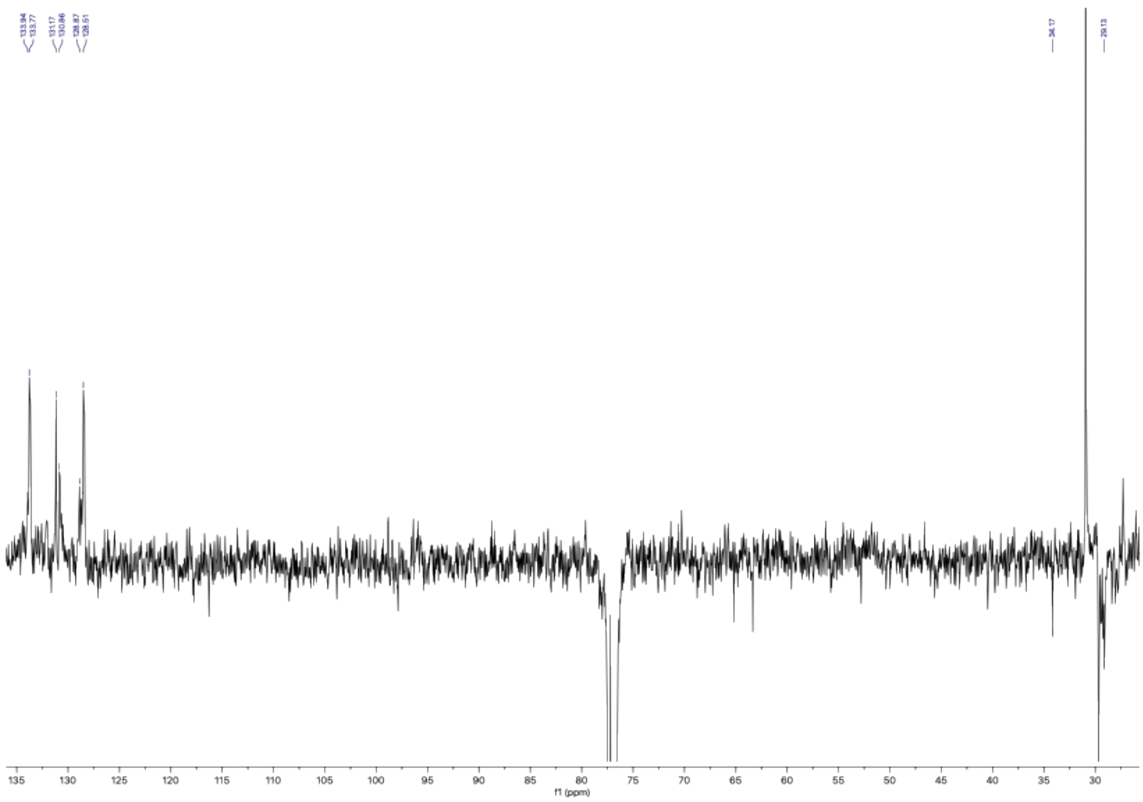


Figure S81. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppb)Br_2]$ **(9c)** (100.6 MHz, $CDCl_3$, 298K).

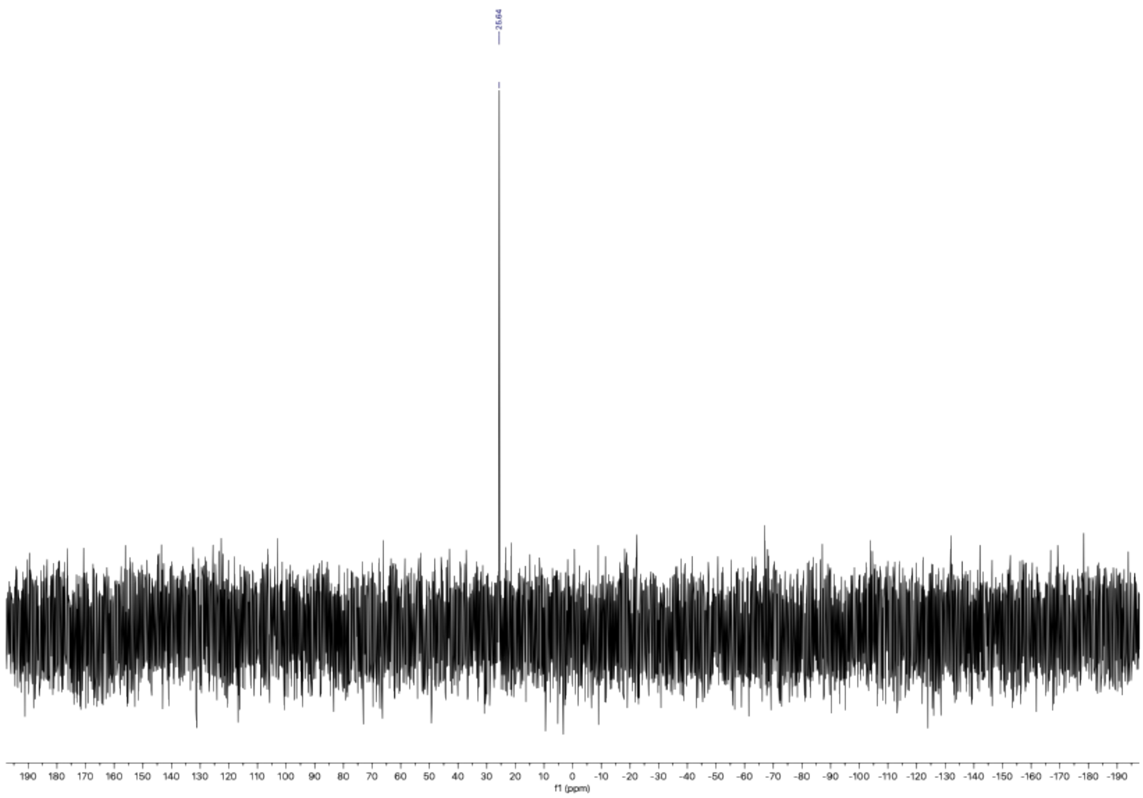


Figure S82. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd(dppb)Br_2]$ **(9c)** (162.0 MHz, $CDCl_3$, 298K).

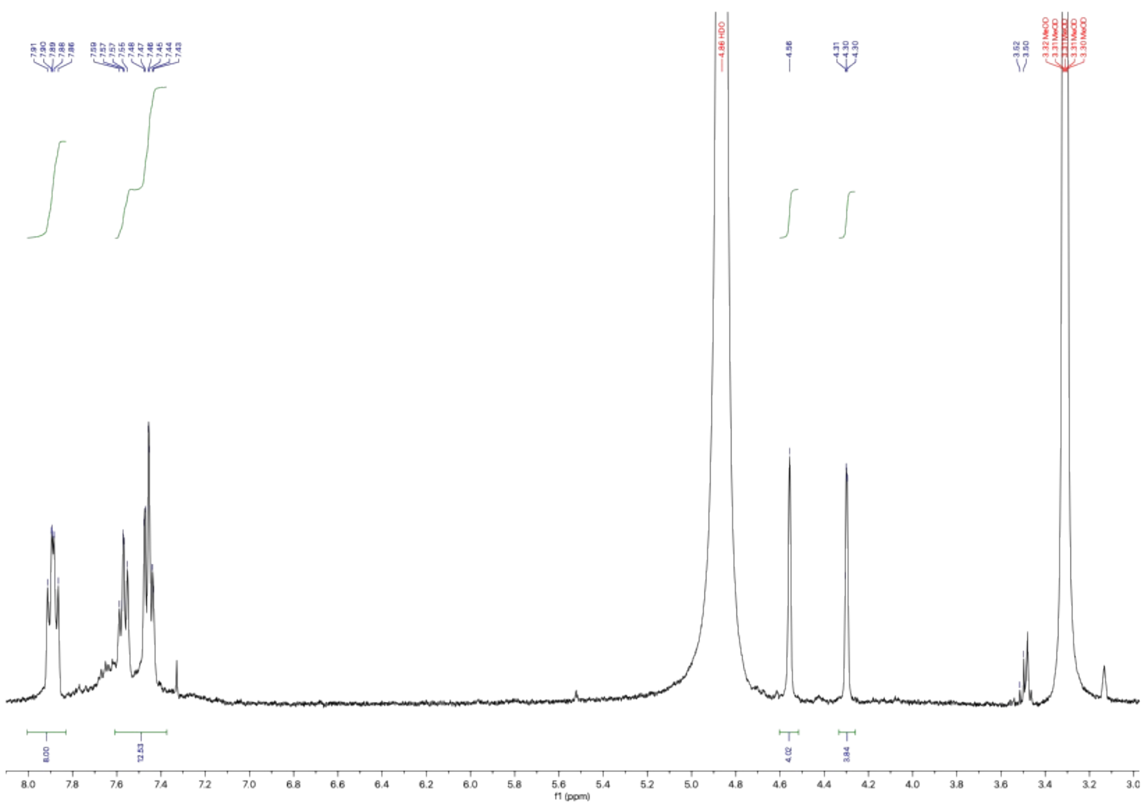


Figure S83. ^{1}H NMR spectra of $[Pd(dppf)Cl_2]$ **(10b)** (400.1 MHz, CD_3OD, 298K).

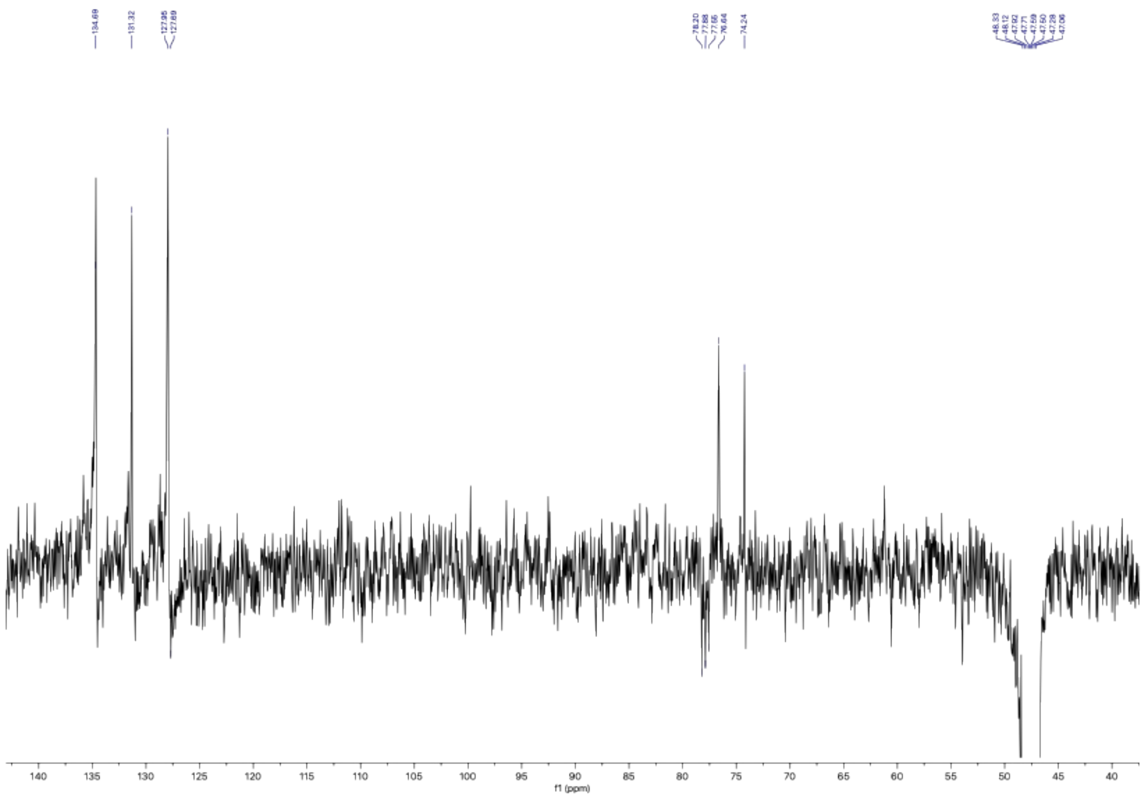


Figure S84. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(dppf)Cl_2] **(10b)** (100.6 MHz, CD_3OD, 298K).

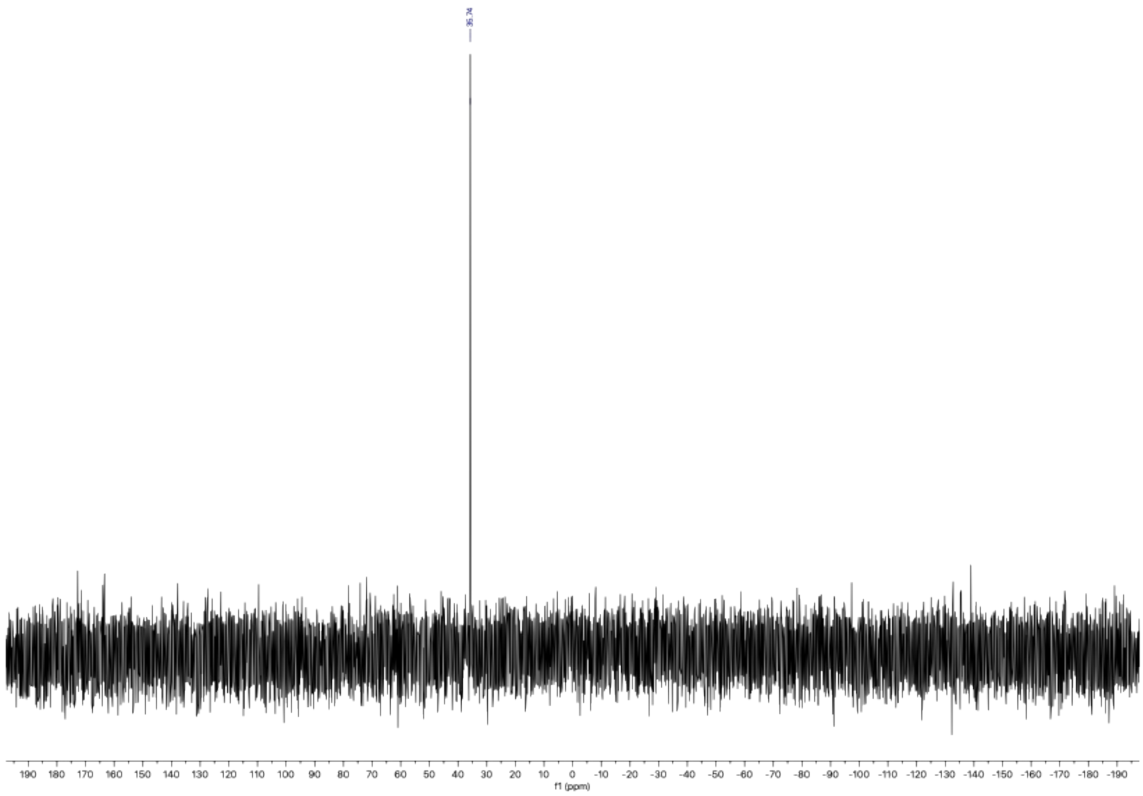


Figure S85. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(dppf)Cl_2] **(10b)** (162.0 MHz, CD_3OD, 298K).

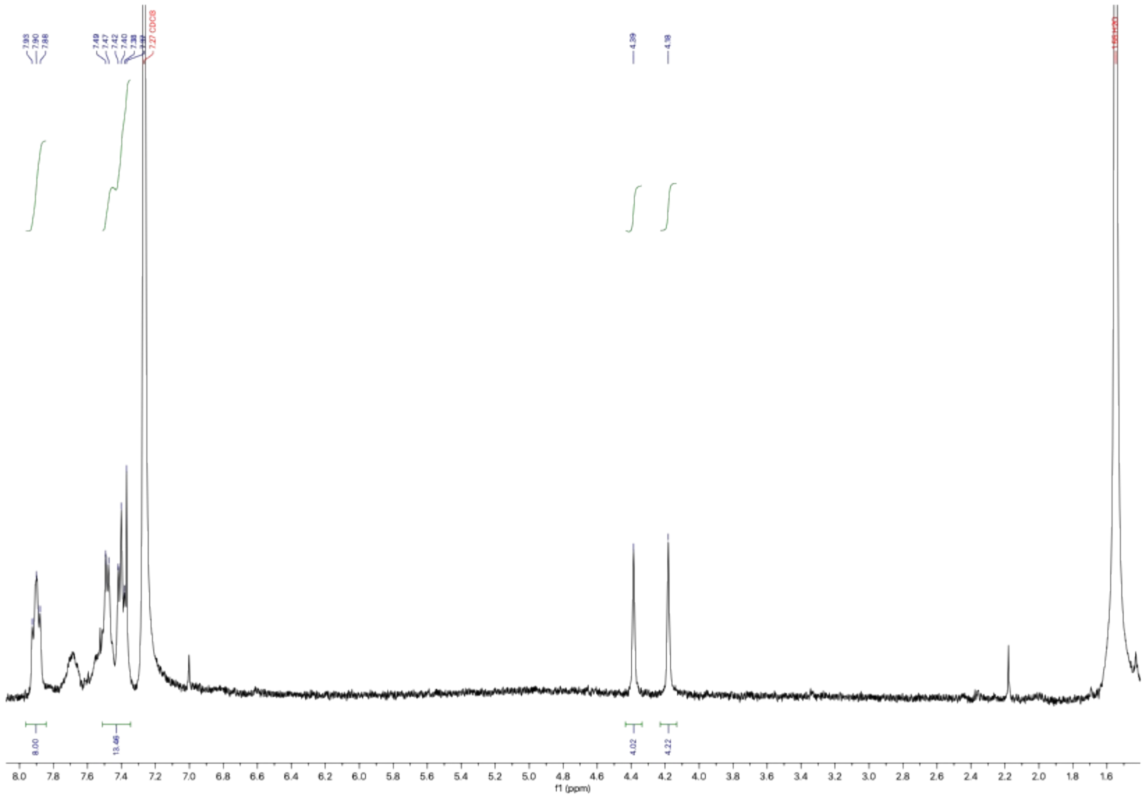


Figure S86. ^{1}H NMR spectra of $[Pd(dppf)Br_2]$ **(10c)** (400.1 MHz, $CDCl_3$, 298K).

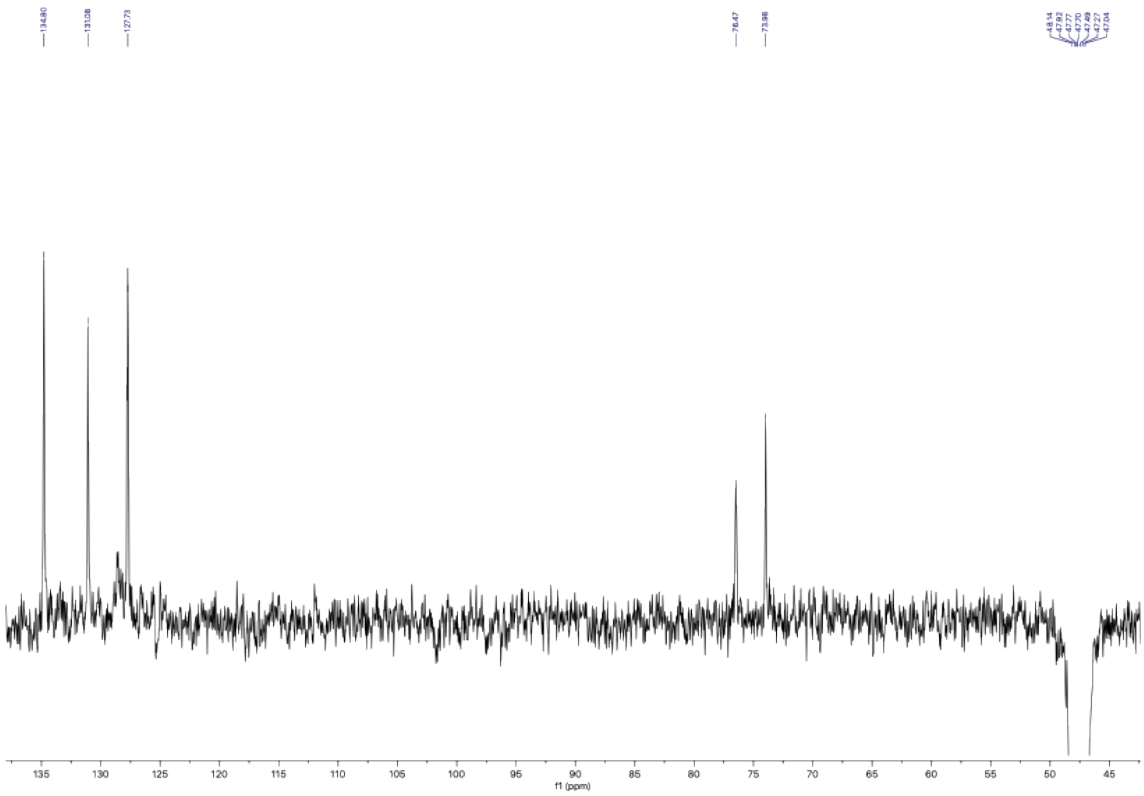


Figure S87. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd(dppf)Br_2]$ **(10c)** (100.6 MHz, CD_3OD, 298K).

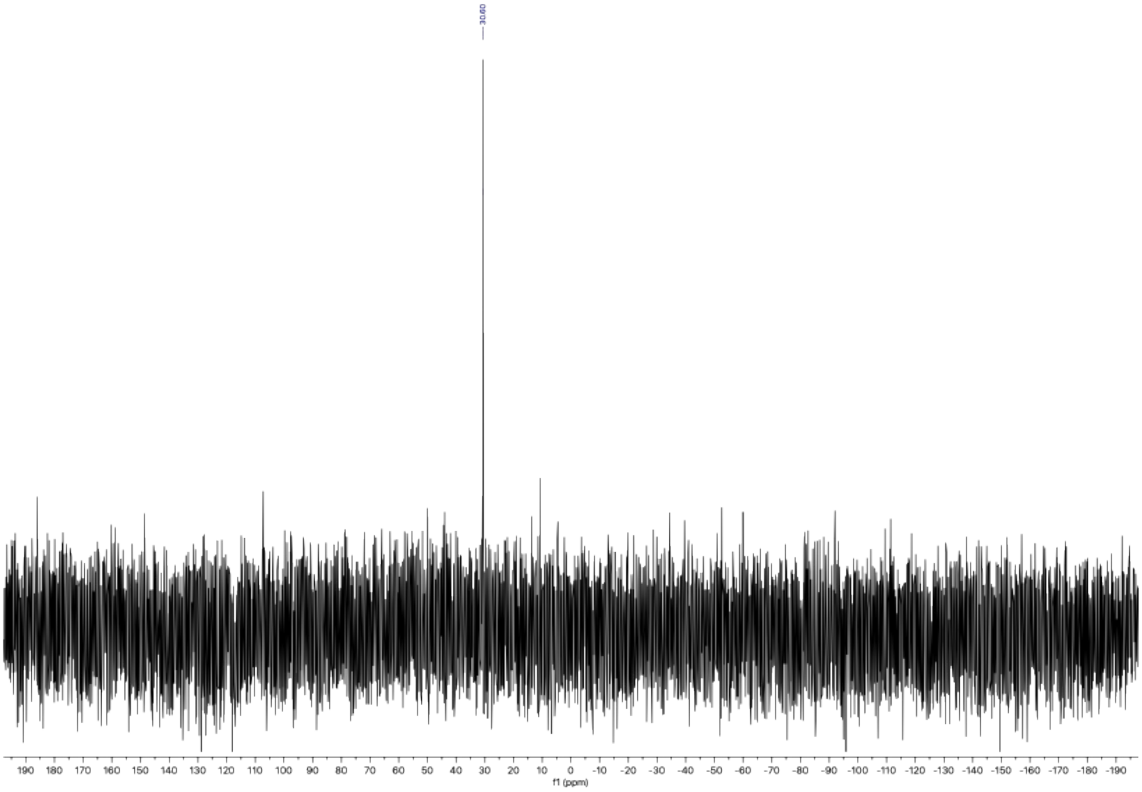


Figure S88. $^{31}P\{^1H\}$ NMR spectra of [Pd(dppf)Br_2] **(10c)** (162.0 MHz, $CDCl_3$, 298K).

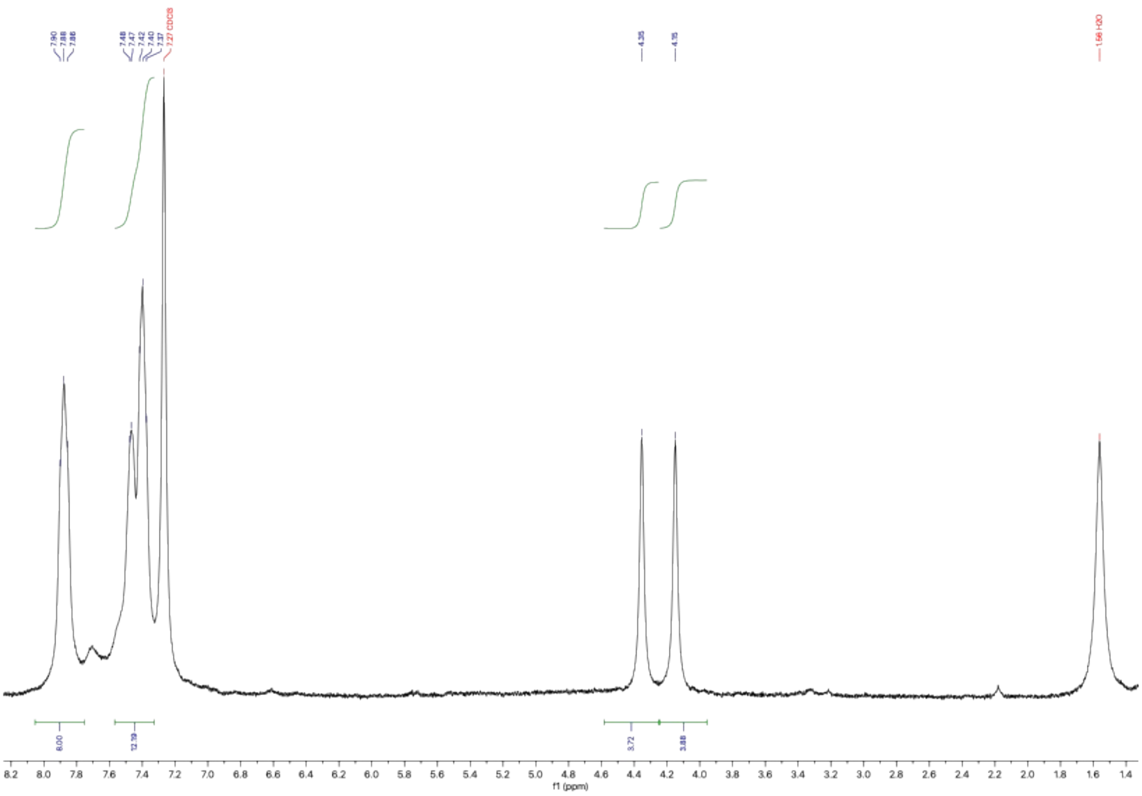


Figure S89. ^1H NMR spectra of [Pd(dppf)I_2] **(10d)** (400.1 MHz, $CDCl_3$, 298K).

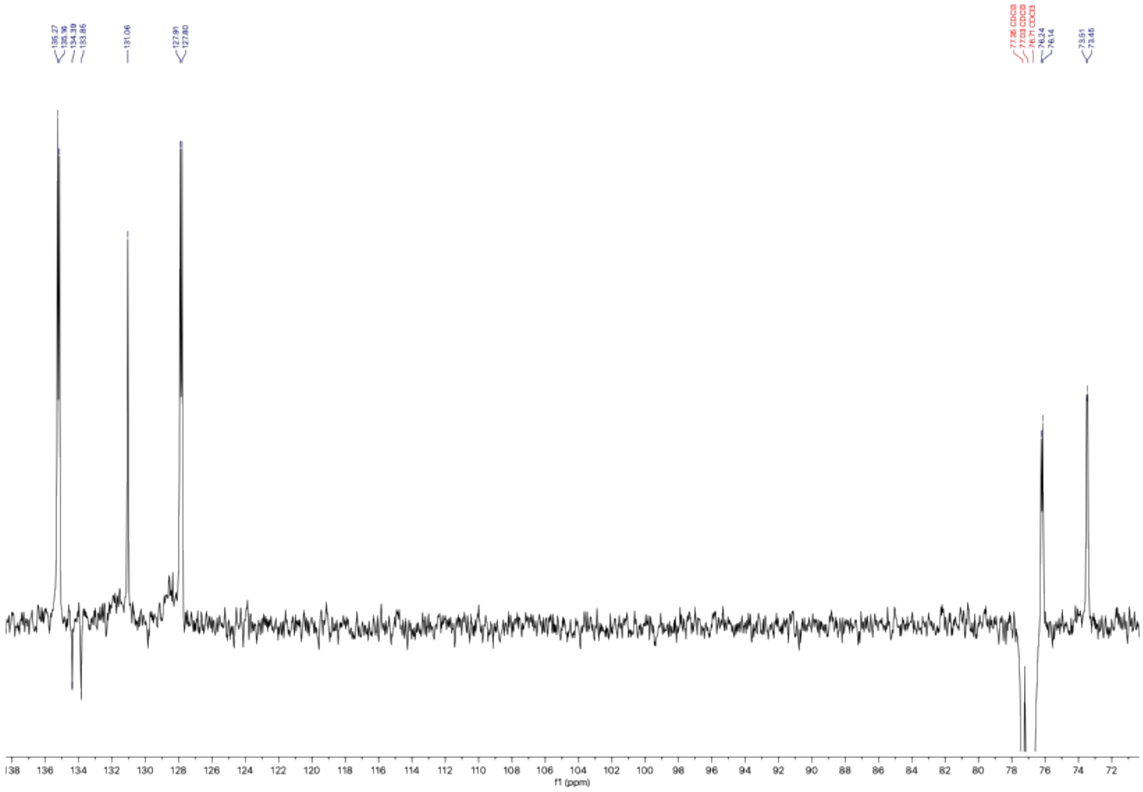


Figure S90. $^{13}C\{^1H\}$ NMR spectra of $[Pd(dppf)I_2]$ **(10d)** (100.6 MHz, $CDCl_3$, 298K).

Figure S91. $^{31}P\{^1H\}$ NMR spectra of $[Pd(dppf)I_2]$ **(10b)** (162.0 MHz, $CDCl_3$, 298K).

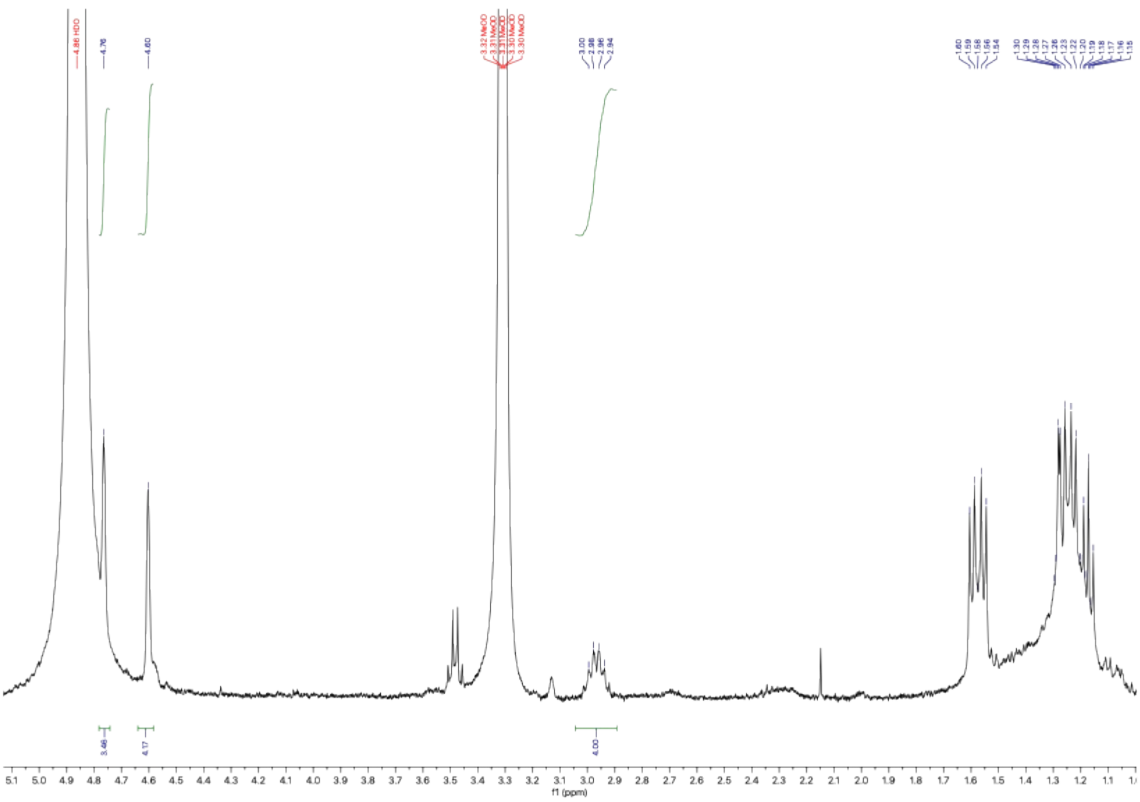


Figure S92. ^{1}H NMR spectra of [Pd(dippf)Cl_2] **(11b)** (400.1 MHz, CD_3OD, 298K).

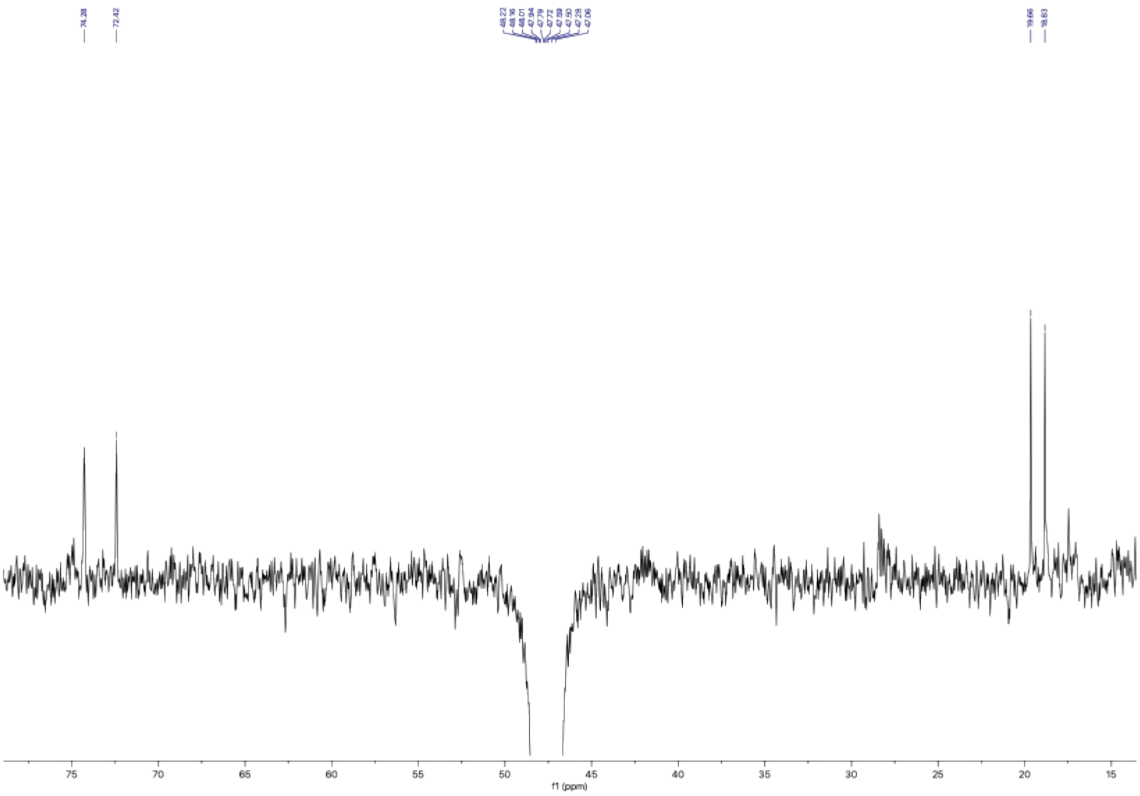


Figure S93. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(dippf)Cl_2] **(11b)** (100.6 MHz, CD_3OD, 298K).

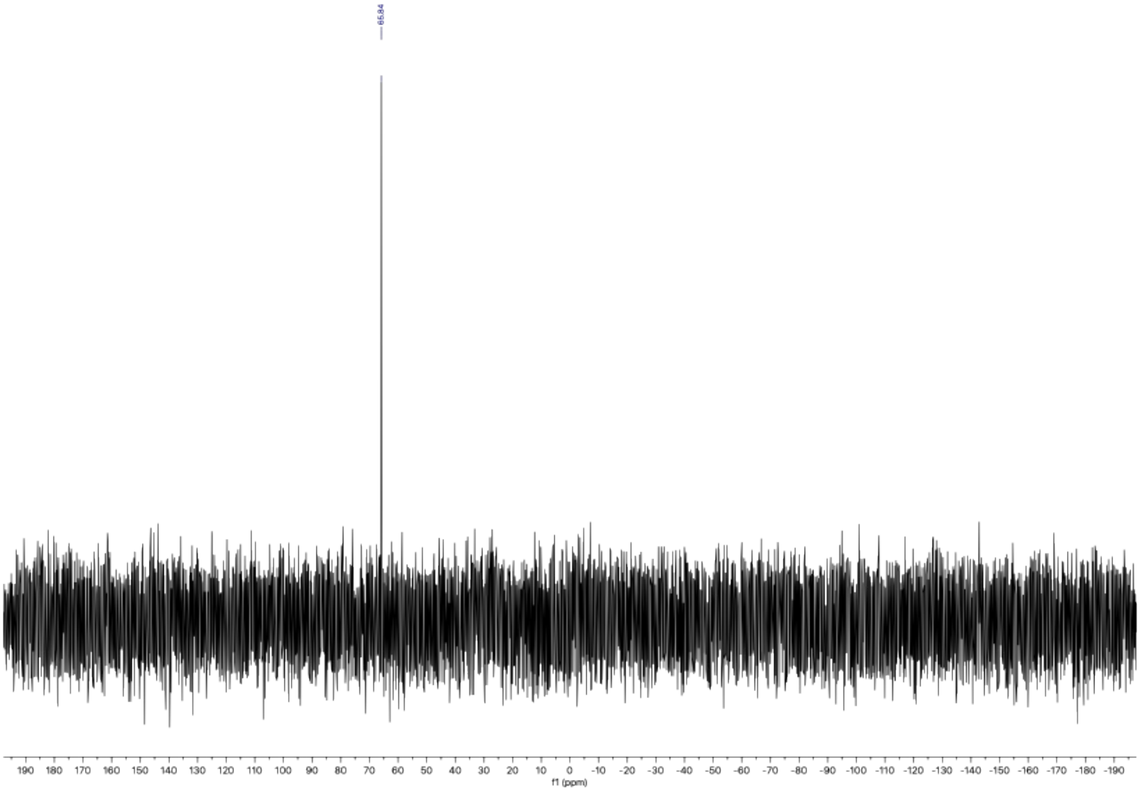


Figure S94. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(dippf)Cl_2] **(11b)** (162.0 MHz, CD_3OD, 298K).

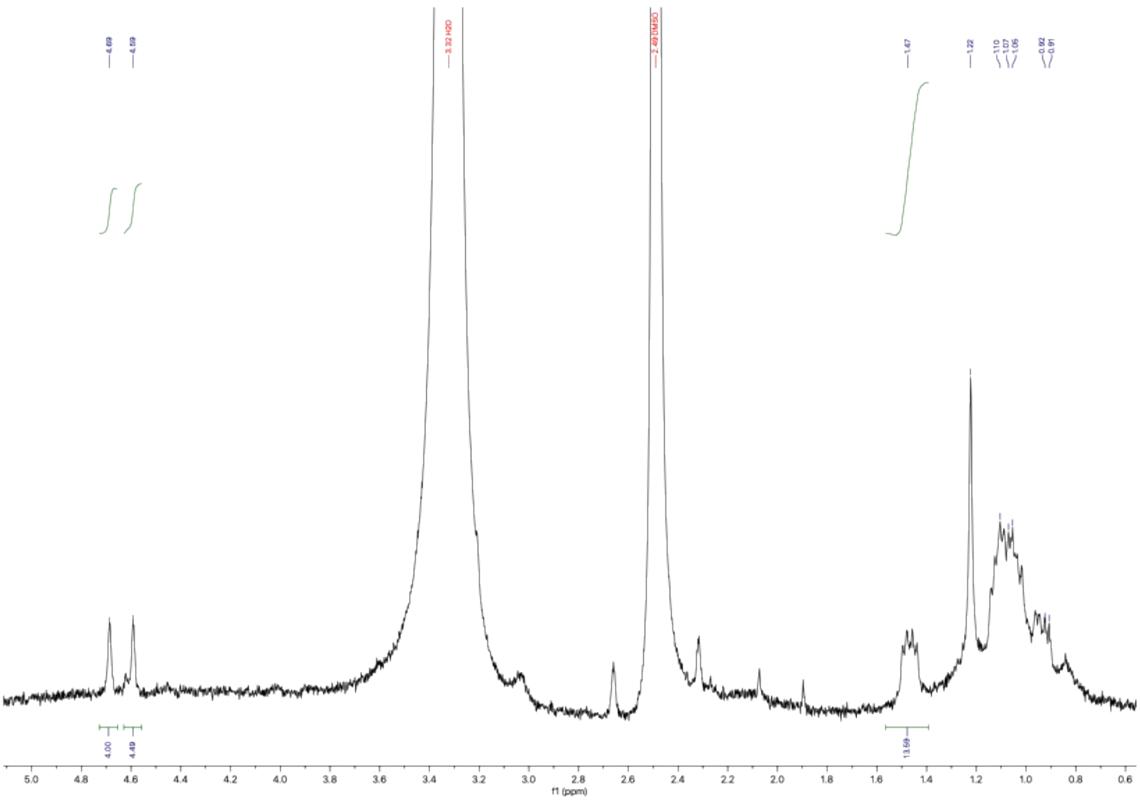


Figure S95. ^{1}H NMR spectra of [Pd(dippf)Br_2] **(11c)** (400.1 MHz, DMSO-d_6, 298K).

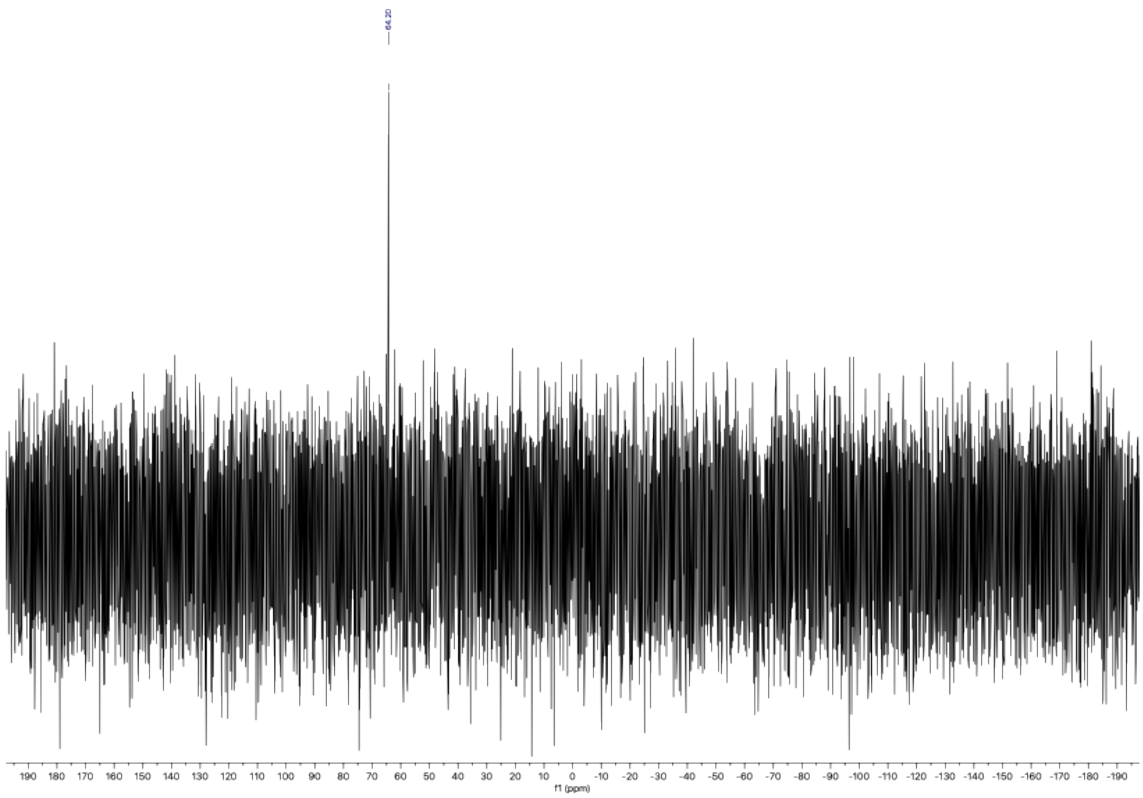


Figure S96. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(dippf)Br_2] **(11c)** (162.0 MHz, DMSO-d_6, 298K).

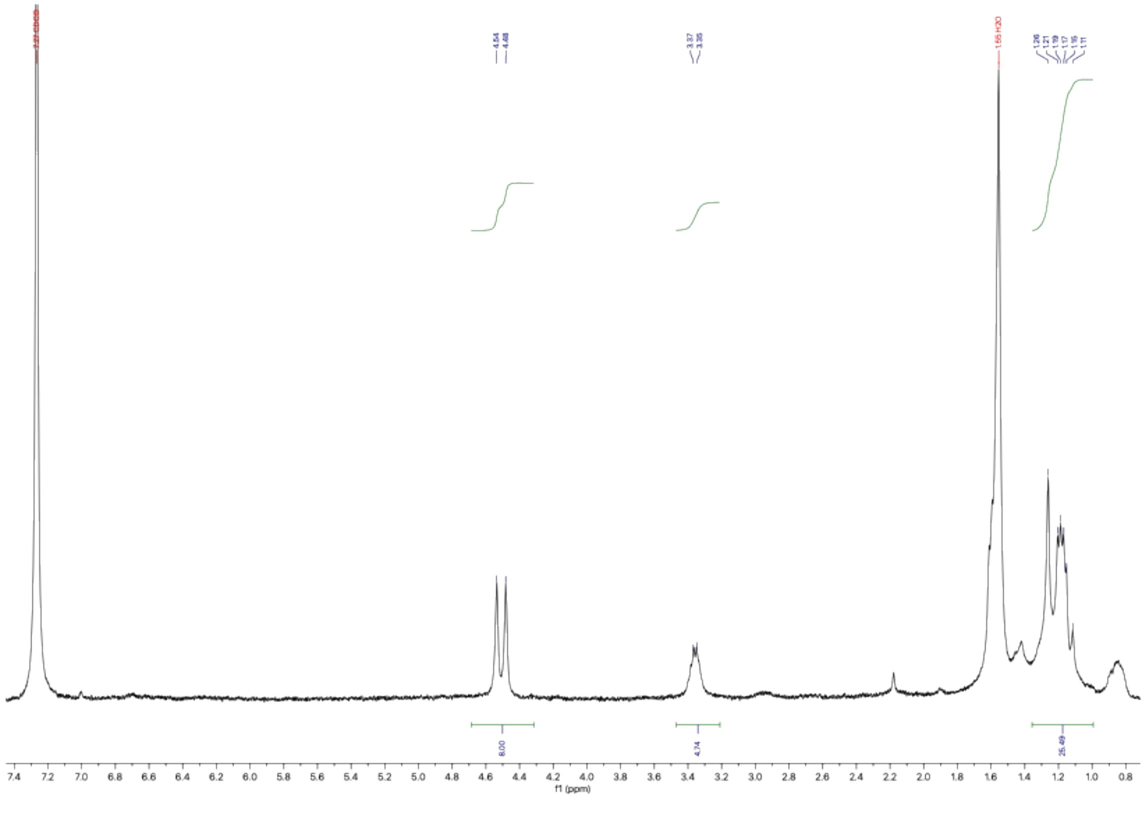


Figure S97. ^{1}H NMR spectra of [Pd(dippf)I_2] **(11d)** (400.1 MHz, $CDCl_3$, 298K).

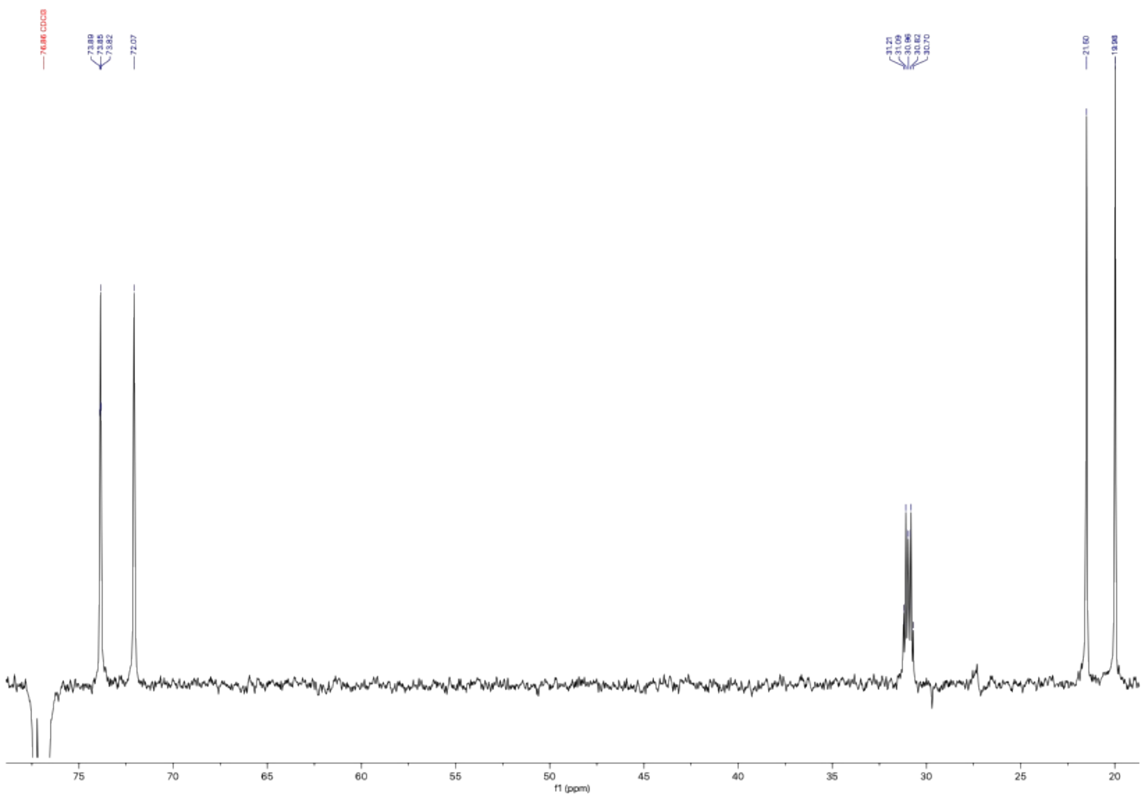


Figure S98. $^{13}C\{^{1}H\}$ NMR spectra of [Pd(dippf)I_2] **(11d)** (100.6 MHz, $CDCl_3$, 298K).

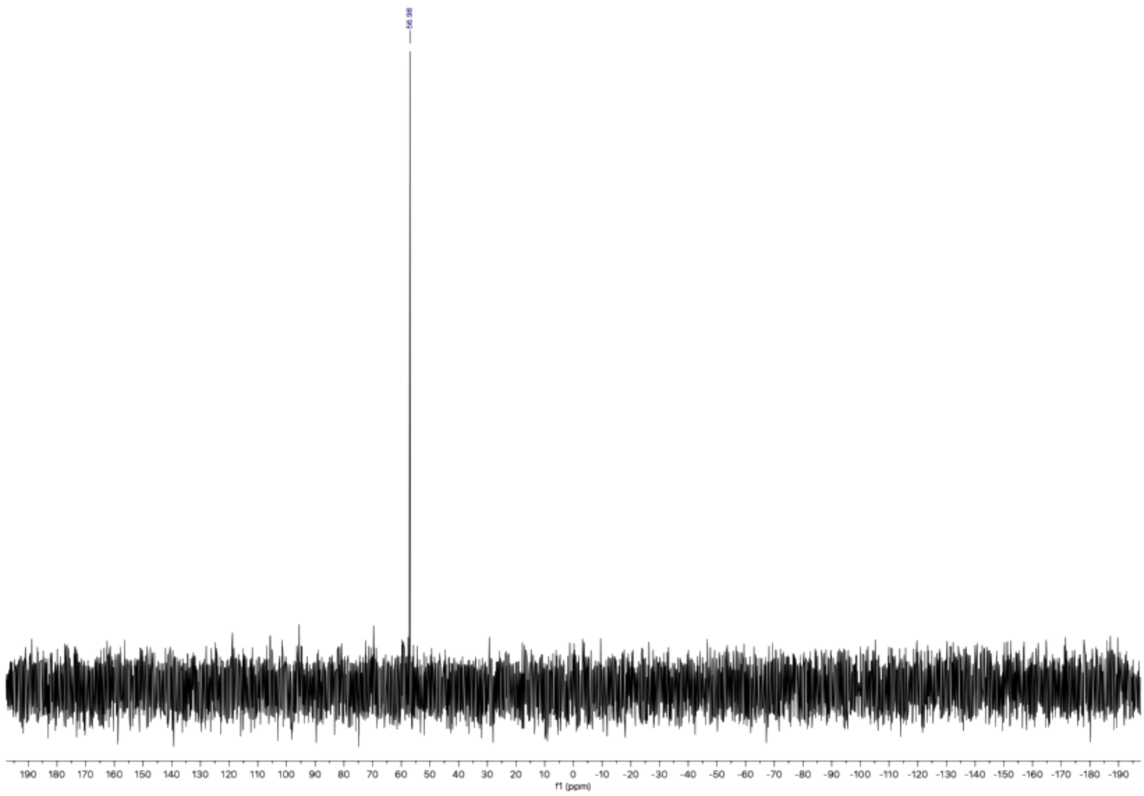


Figure S99. $^{31}P\{^{1}H\}$ NMR spectra of [Pd(dippf)I_2] **(11d)** (162.0 MHz, $CDCl_3$, 298K).

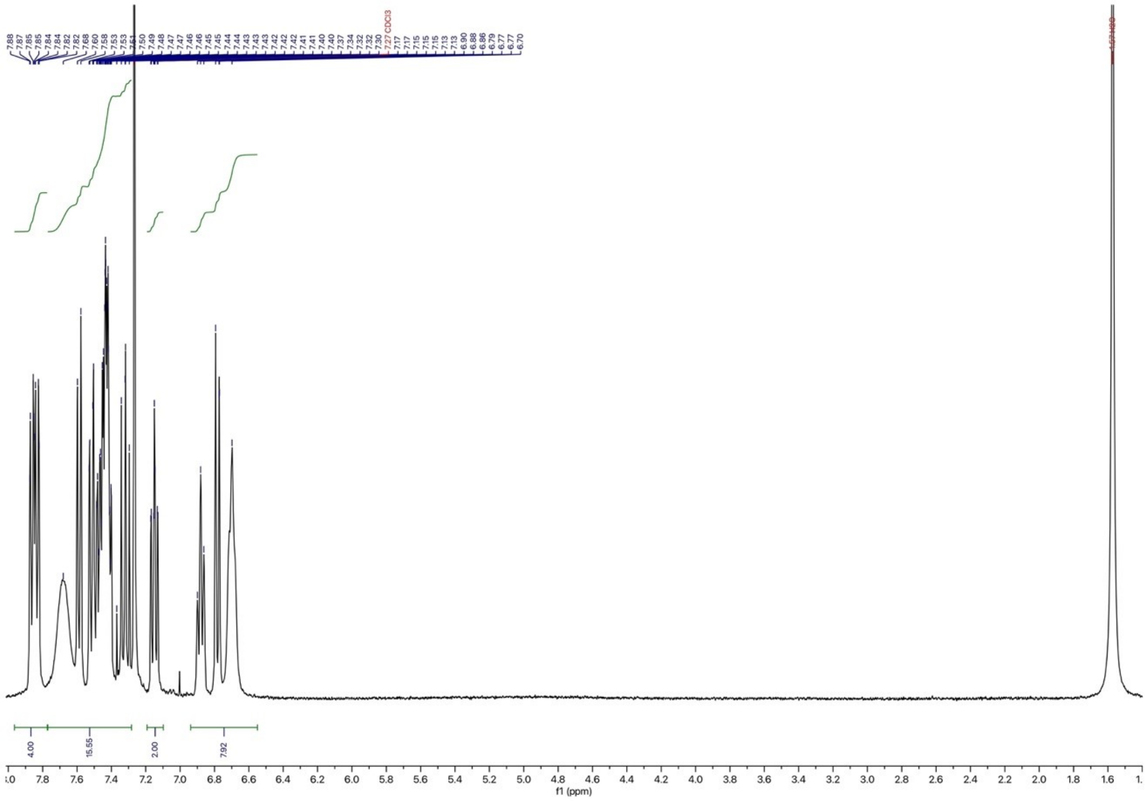


Figure S100. ^{1}H NMR spectra of $[Pd((R)\text{-BINAP})Cl_2]$ **(12b)** (400.1 MHz, $CDCl_3$, 298K).

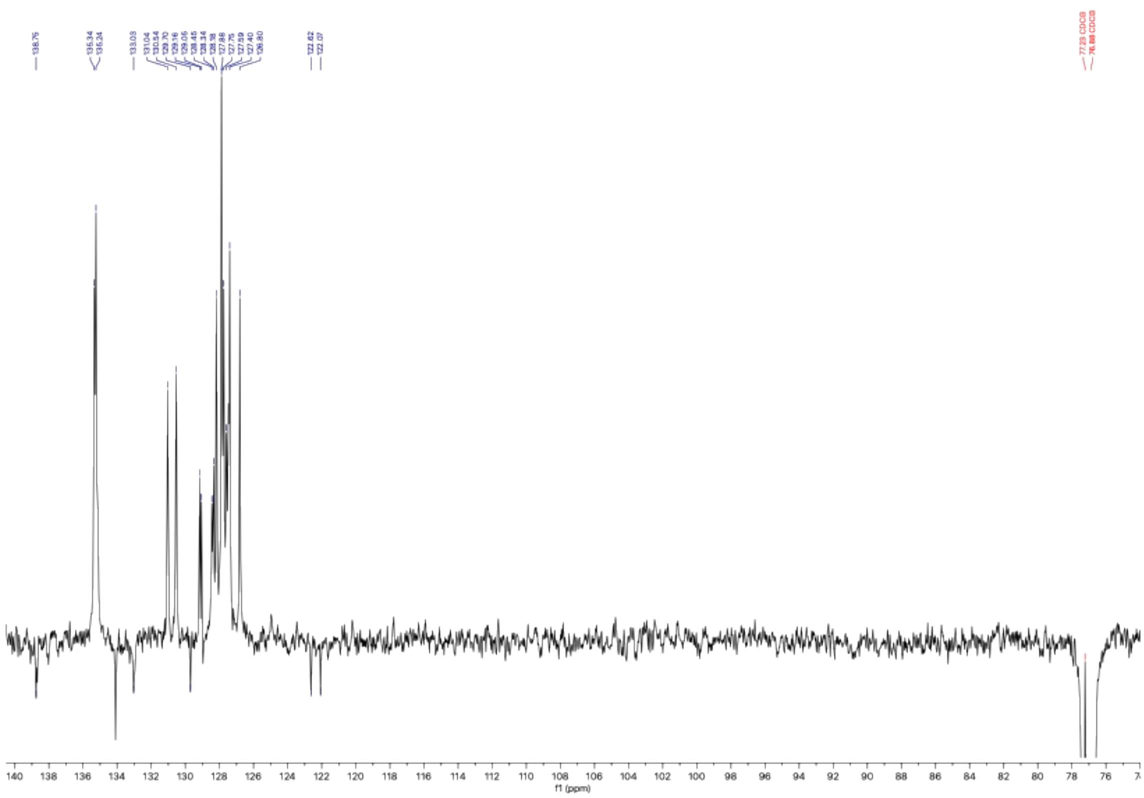


Figure S101. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd((R)\text{-BINAP})Cl_2]$ **(12b)** (100.6 MHz, $CDCl_3$, 298K).

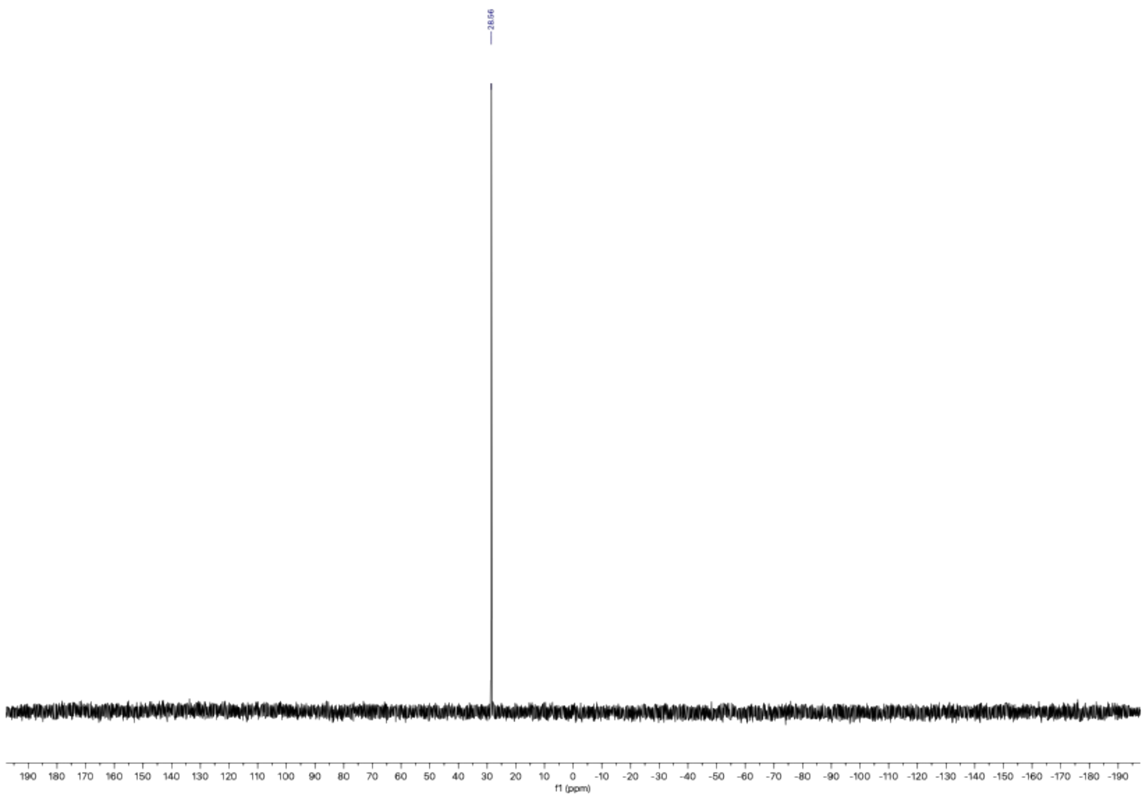


Figure S102. $^{31}P\{^{1}H\}$ NMR spectra of [Pd((*R*)-BINAP)Cl_2] **(12b)** (162.0 MHz, $CDCl_3$, 298K).

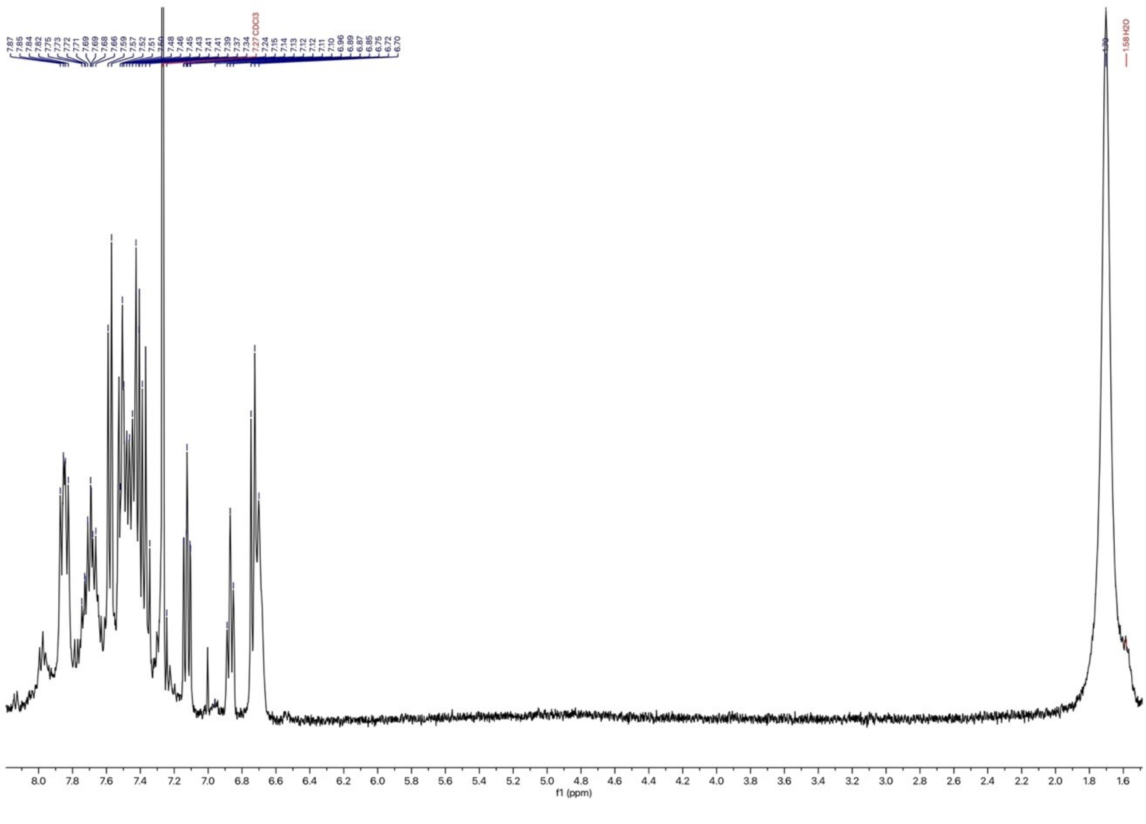


Figure S103. ^{1}H NMR spectra of [Pd((*R*)-BINAP)Br_2] **(12c)** (400.1 MHz, $CDCl_3$, 298K).

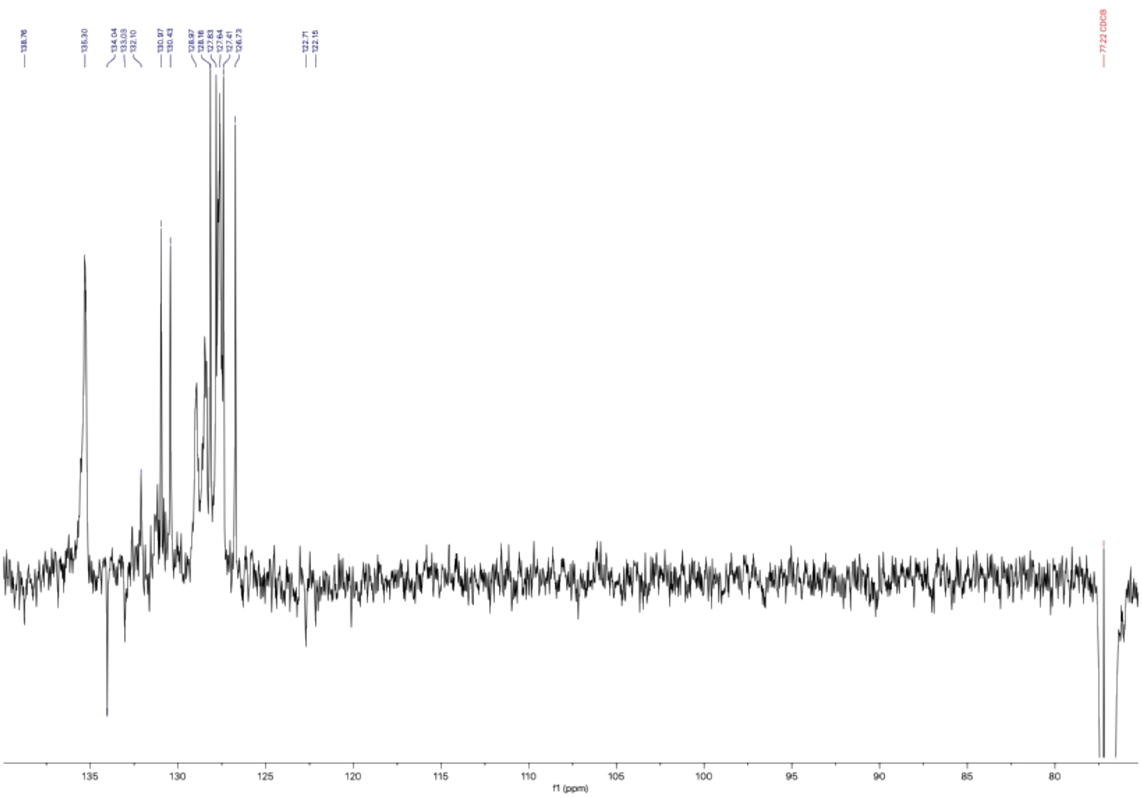


Figure S104. $^{13}C\{^{1}H\}$ NMR spectra of [Pd((*R*)-BINAP)Br$_2$] **(12c)** (100.6 MHz, $CDCl_3$, 298K).

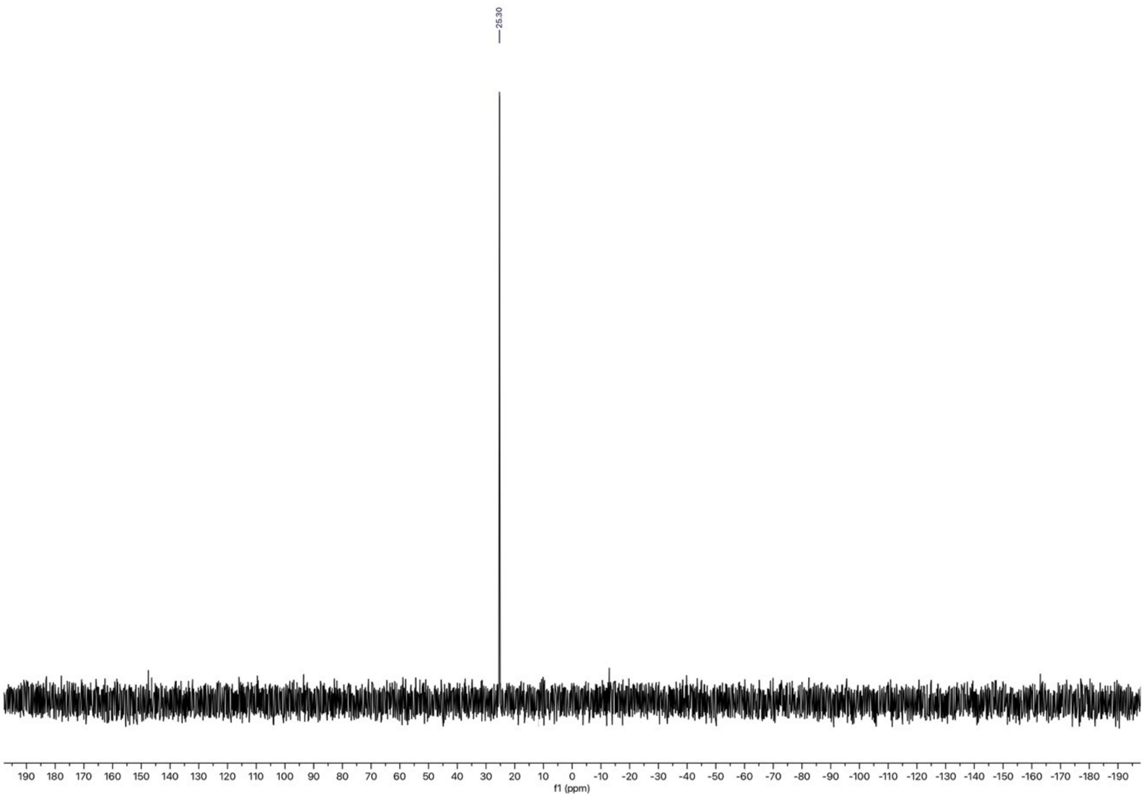


Figure S105. $^{31}P\{^{1}H\}$ NMR spectra of [Pd((*R*)-BINAP)Br$_2$] **(12c)** (162.0 MHz, $CDCl_3$, 298K).

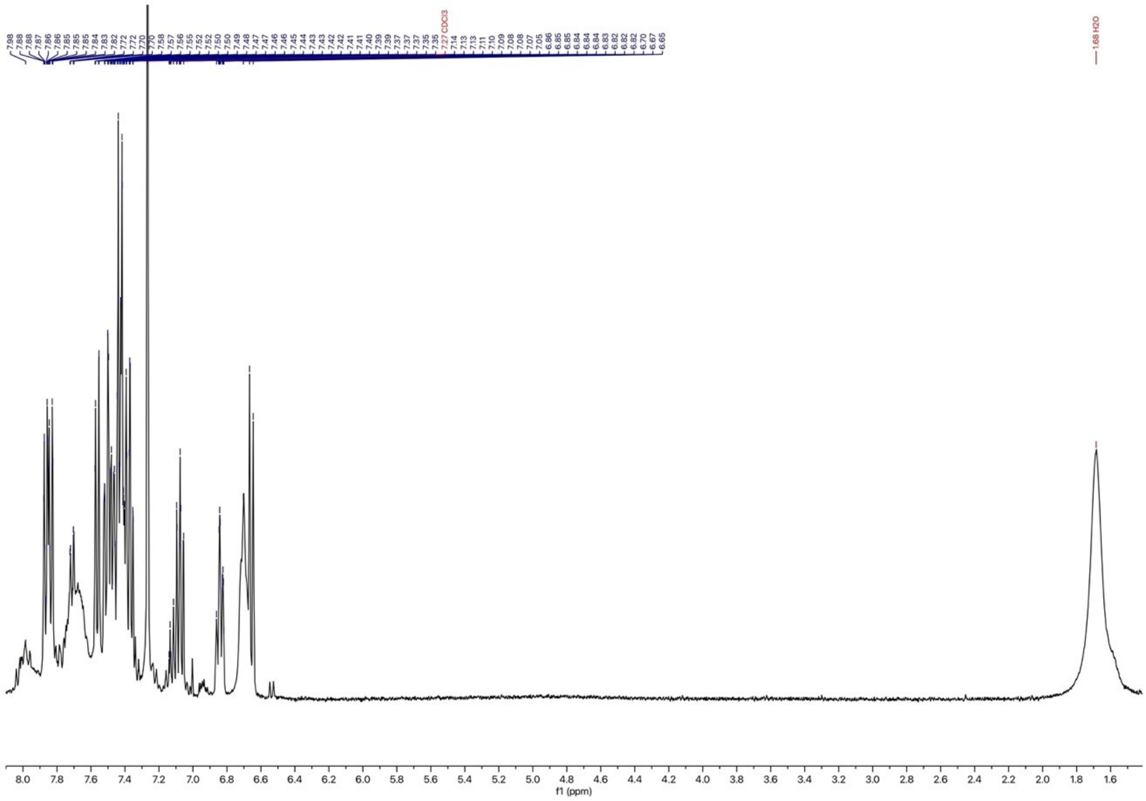


Figure S106. ^{1}H NMR spectra of $[Pd((R)\text{-BINAP})I_2]$ **(12d)** (400.1 MHz, $CDCl_3$, 298K).

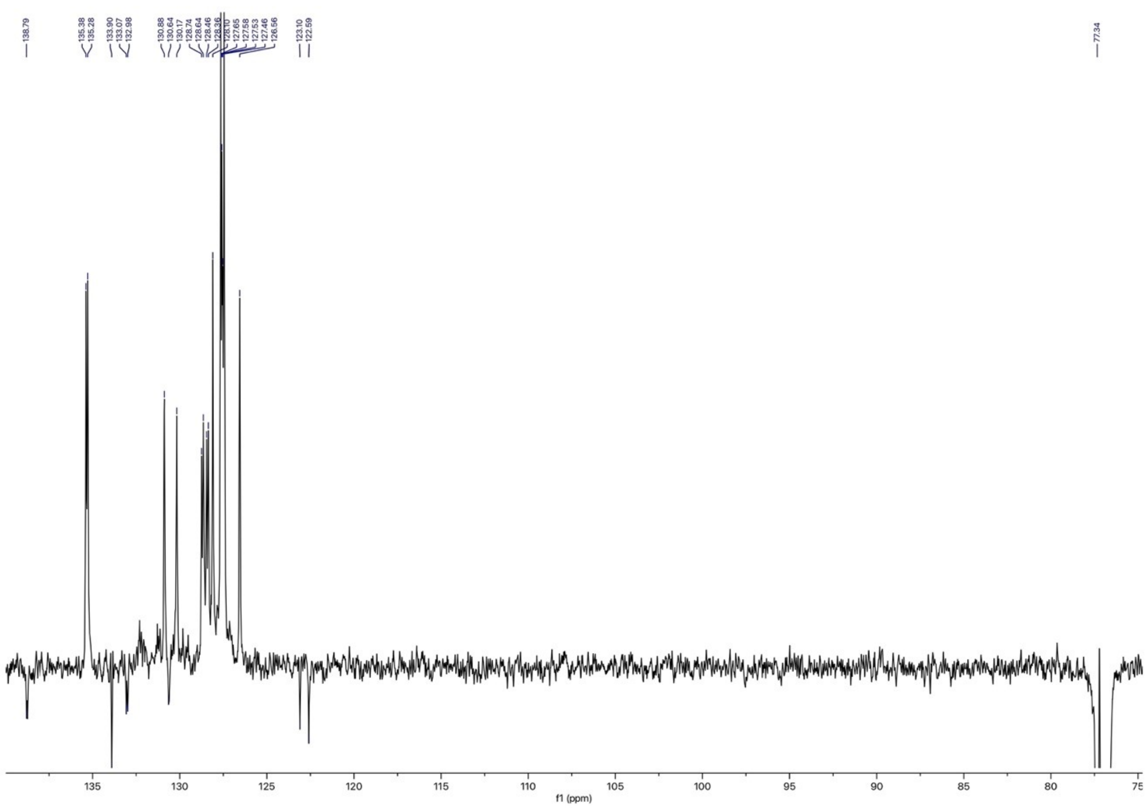


Figure S107. $^{13}C\{^{1}H\}$ NMR spectra of $[Pd((R)\text{-BINAP})I_2]$ **(12d)** (100.6 MHz, $CDCl_3$, 298K).

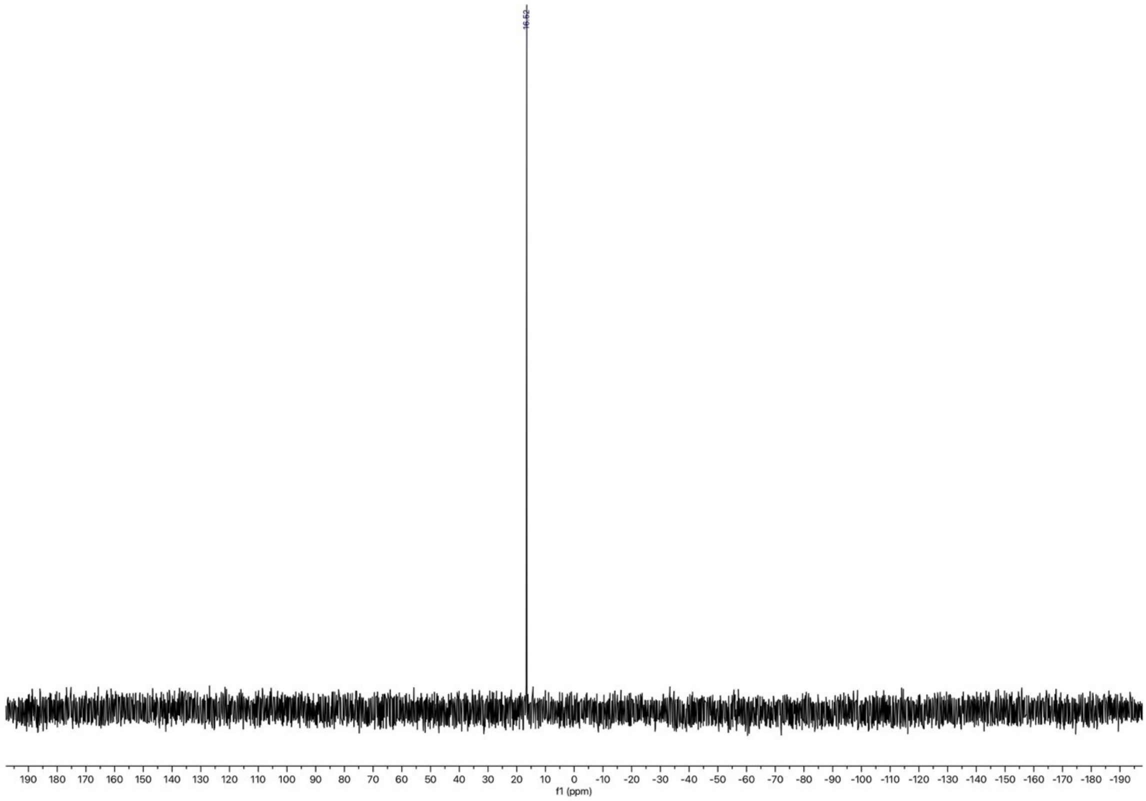


Figure S108. $^{31}P\{^{1}H\}$ NMR spectra of $[Pd((R)\text{-BINAP})I_2]$ **(12d)** (162.0 MHz, $CDCl_3$, 298K).

Part 5. NMR's tests spectra's

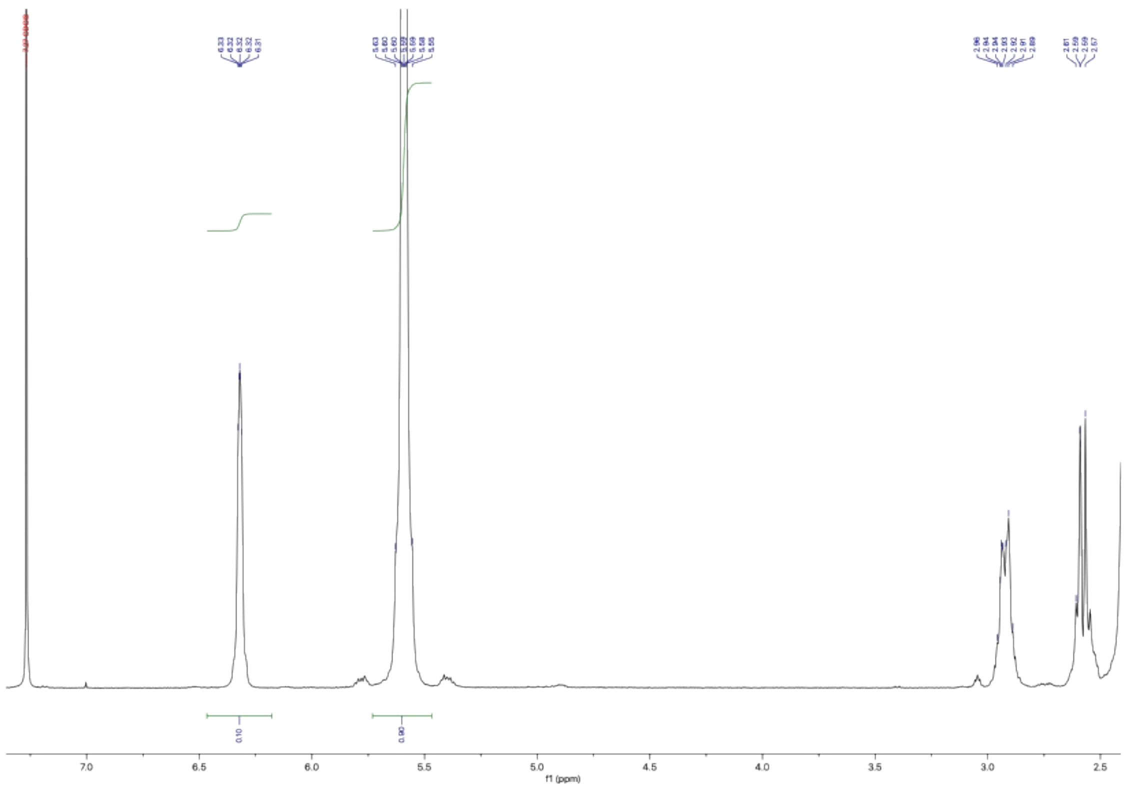


Figure S109. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 20 minutes (400.1 MHz, $CDCl_3$, 298K).

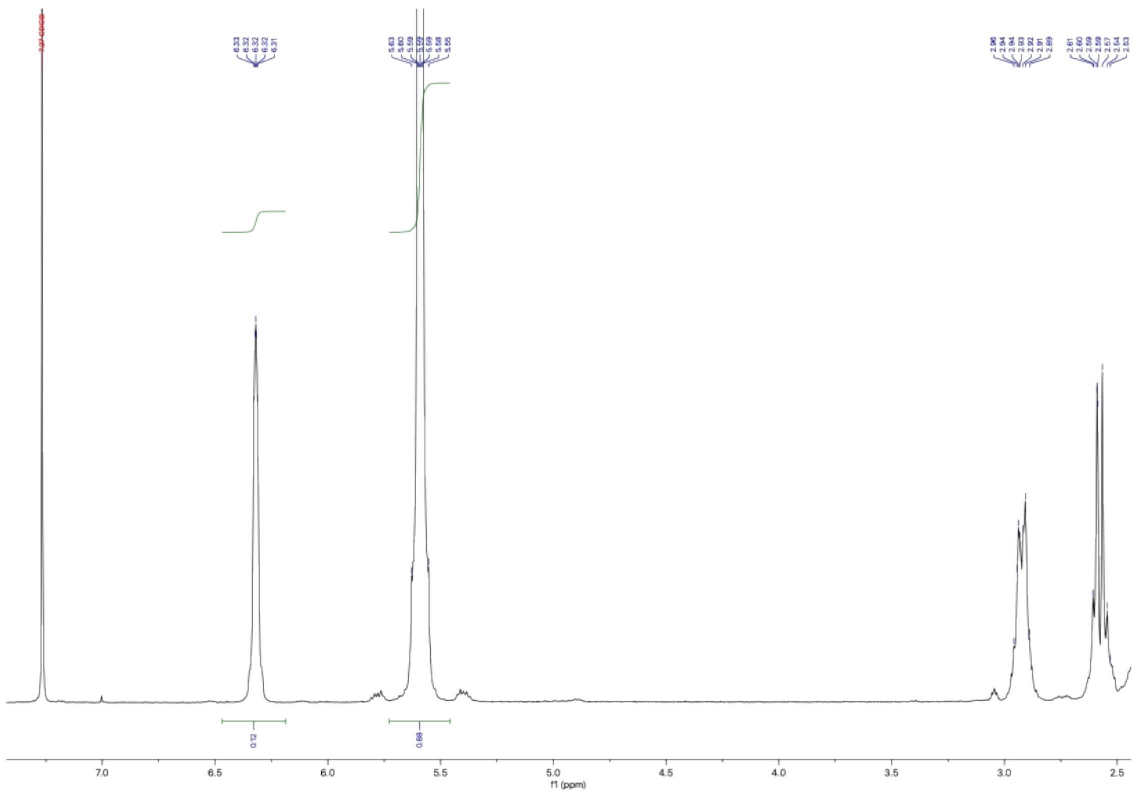


Figure S110. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 4.30 hours (400.1 MHz, $CDCl_3$, 298K).

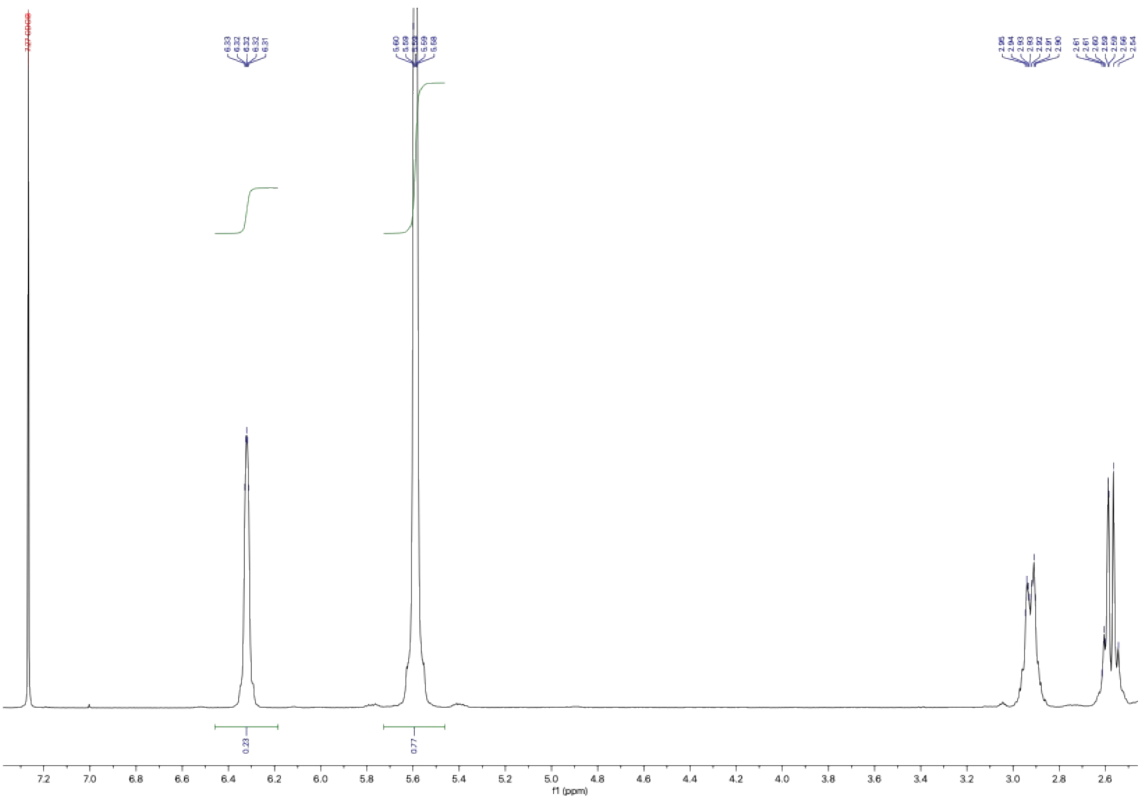


Figure S111. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 28 hours (400.1 MHz, $CDCl_3$, 298K).

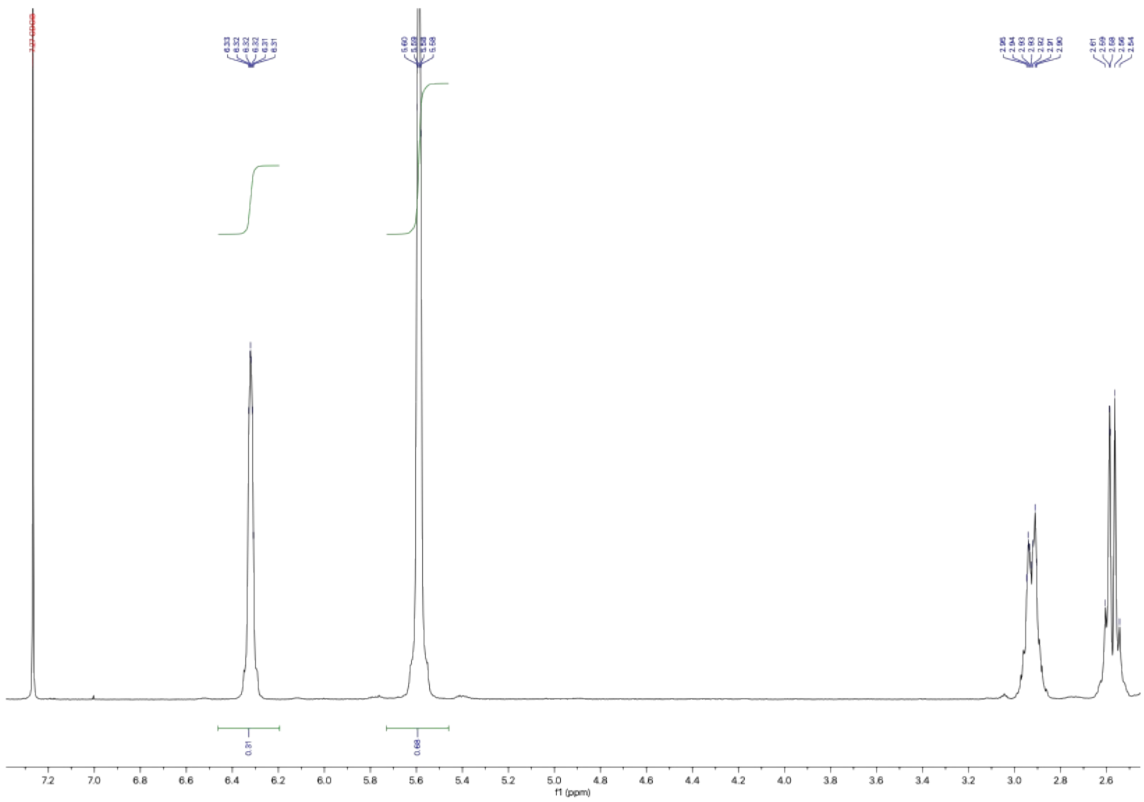


Figure S112. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 52 hours (400.1 MHz, $CDCl_3$, 298K).

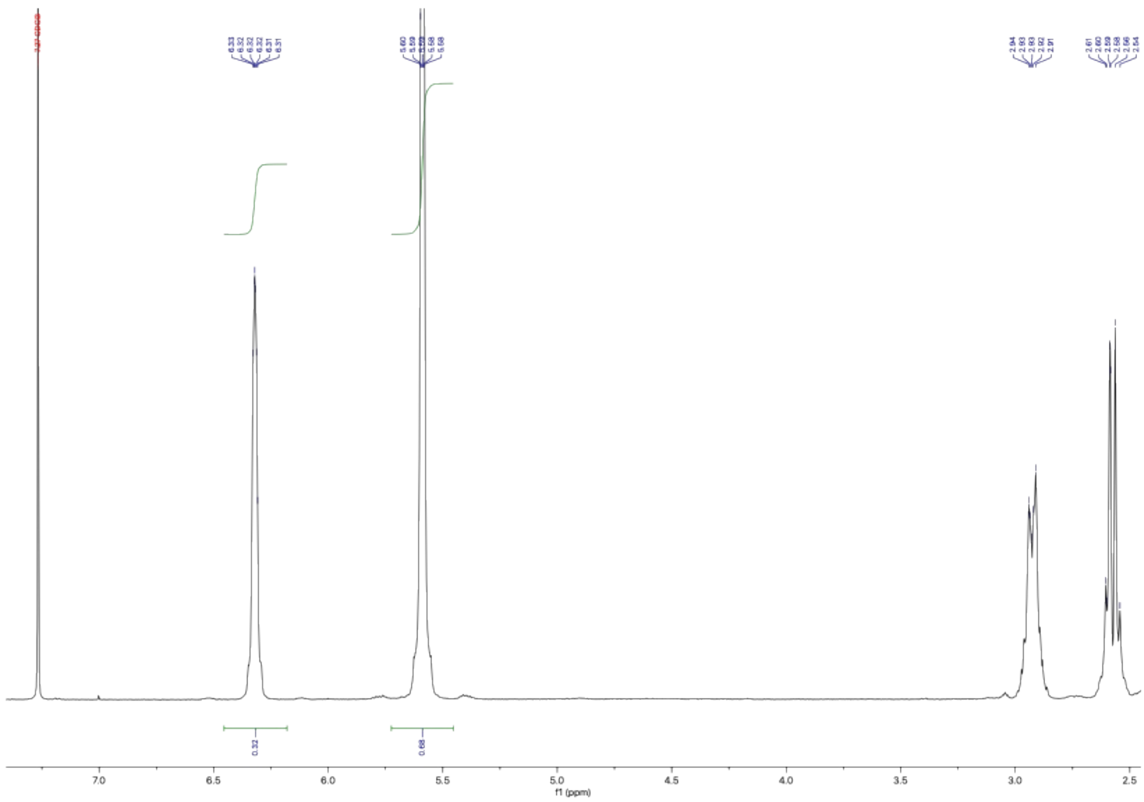


Figure S113. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 72 hours (400.1 MHz, $CDCl_3$, 298K).

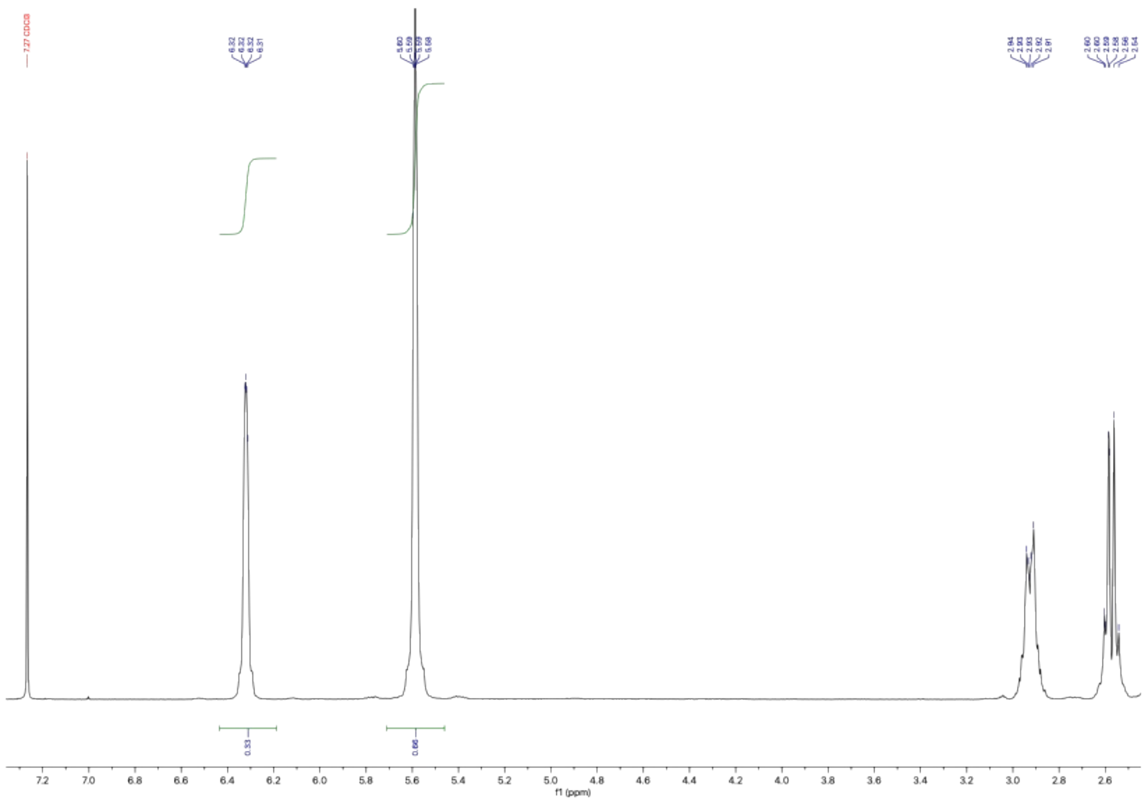


Figure S114. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with COD (1:1) **(1a)**, after 1 week (400.1 MHz, $CDCl_3$, 298K).

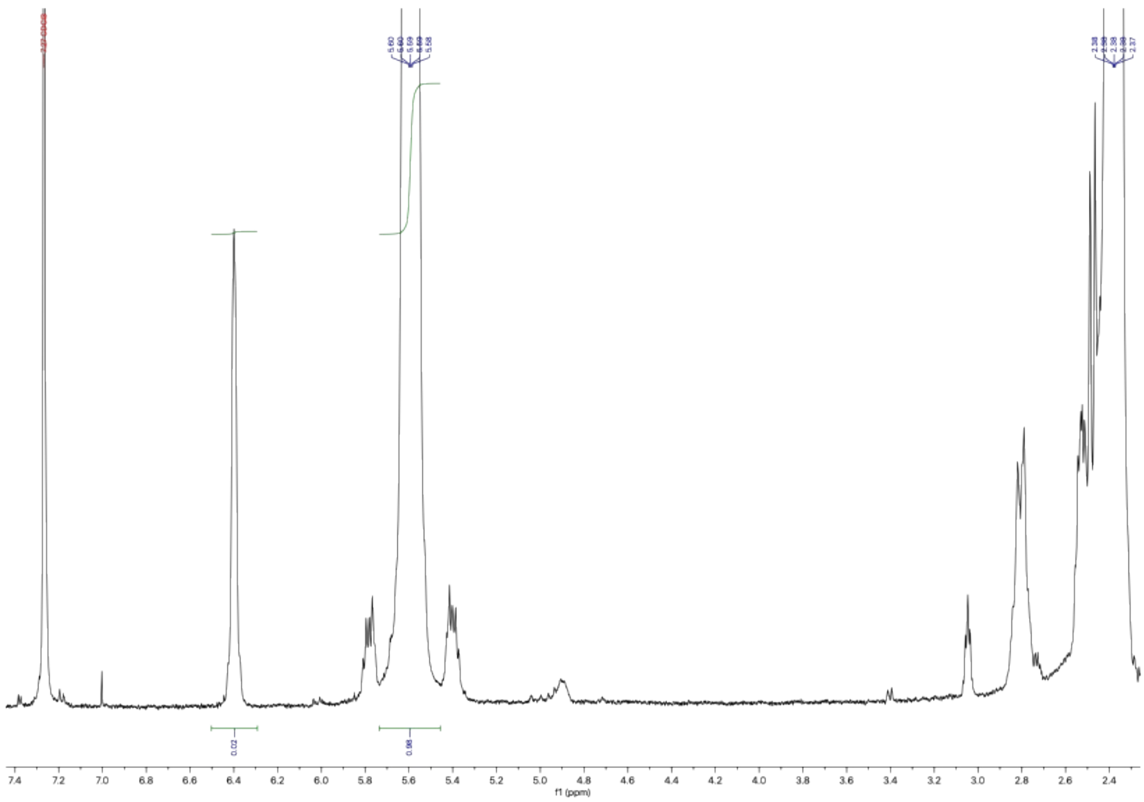


Figure S115. ^1H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 20 minutes (400.1 MHz, $CDCl_3$, 298K).

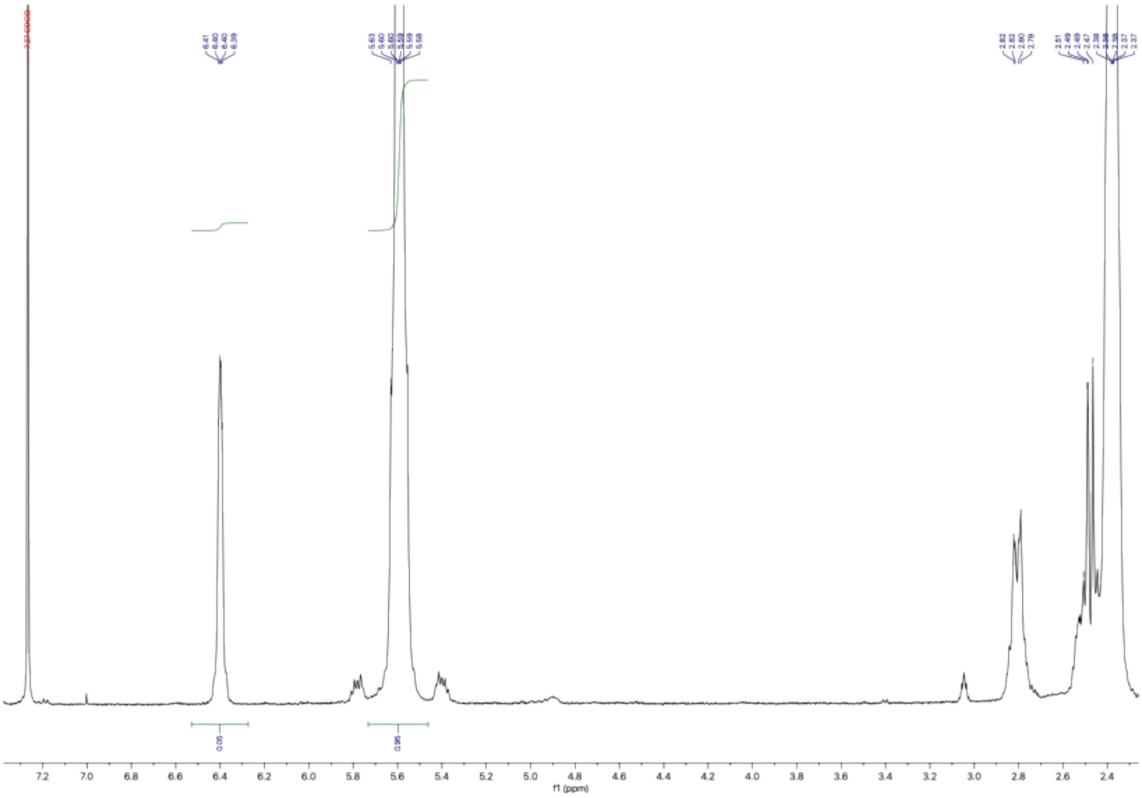


Figure S116. ^1H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 4.30 hours (400.1 MHz, $CDCl_3$, 298K).

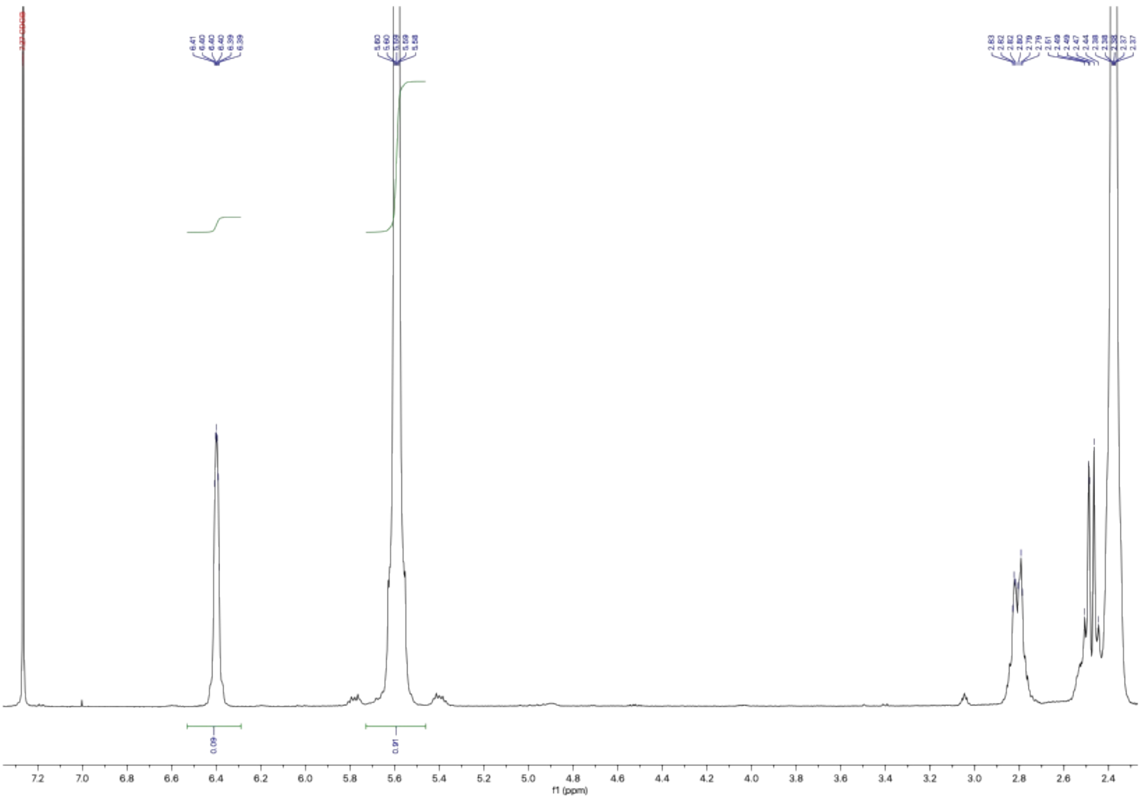


Figure S117. [1]H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 28 hours (400.1 MHz, $CDCl_3$, 298K).

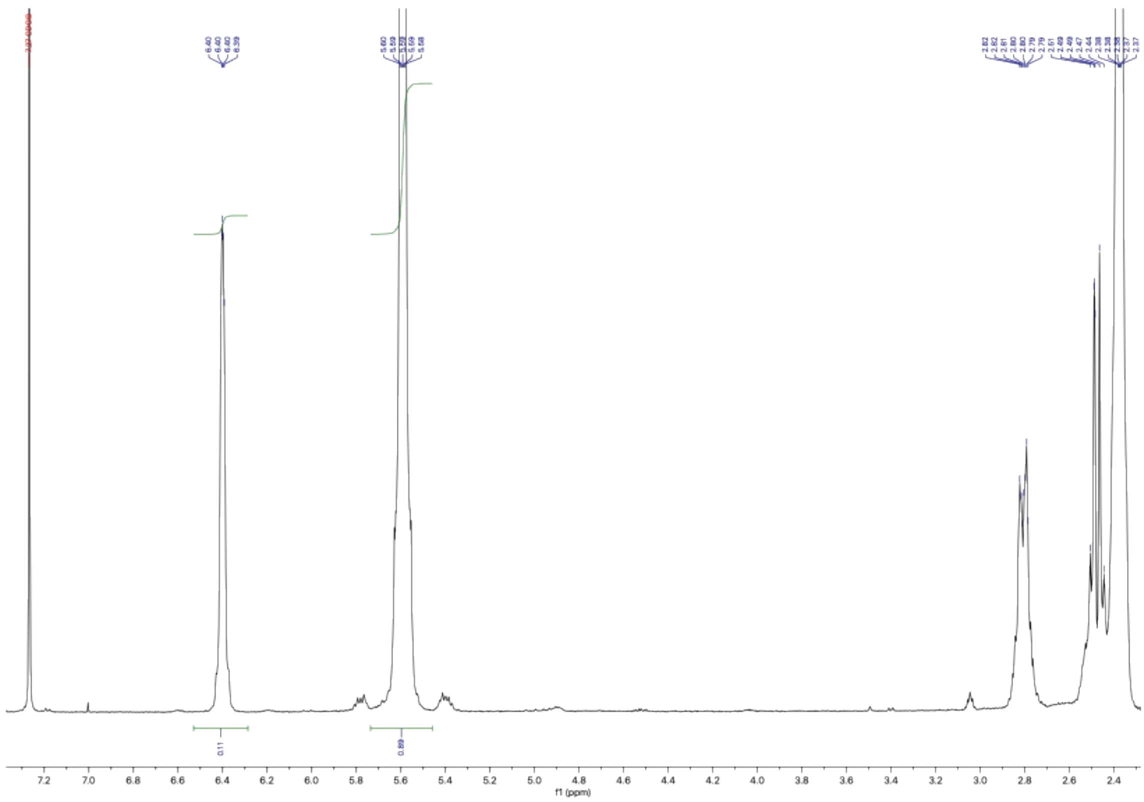


Figure S118. [1]H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 52 hours (400.1 MHz, $CDCl_3$, 298K).

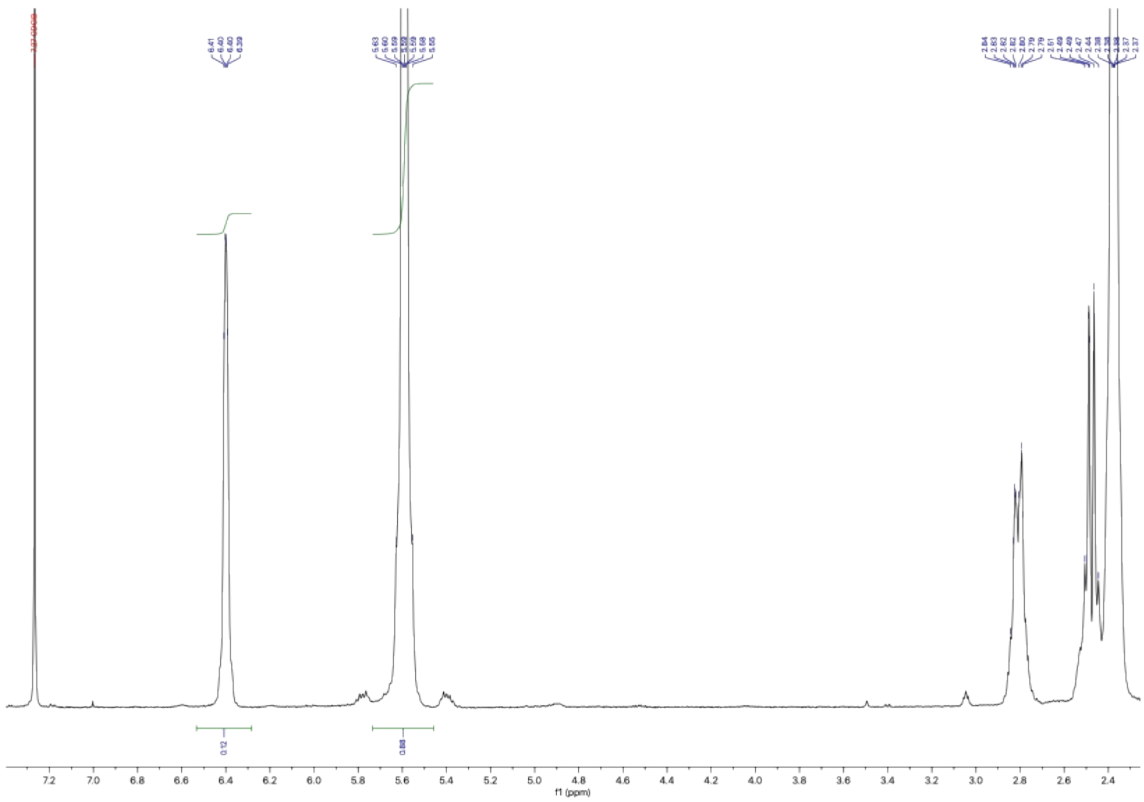


Figure S119. ^{1}H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 76 hours (400.1 MHz, $CDCl_3$, 298K).

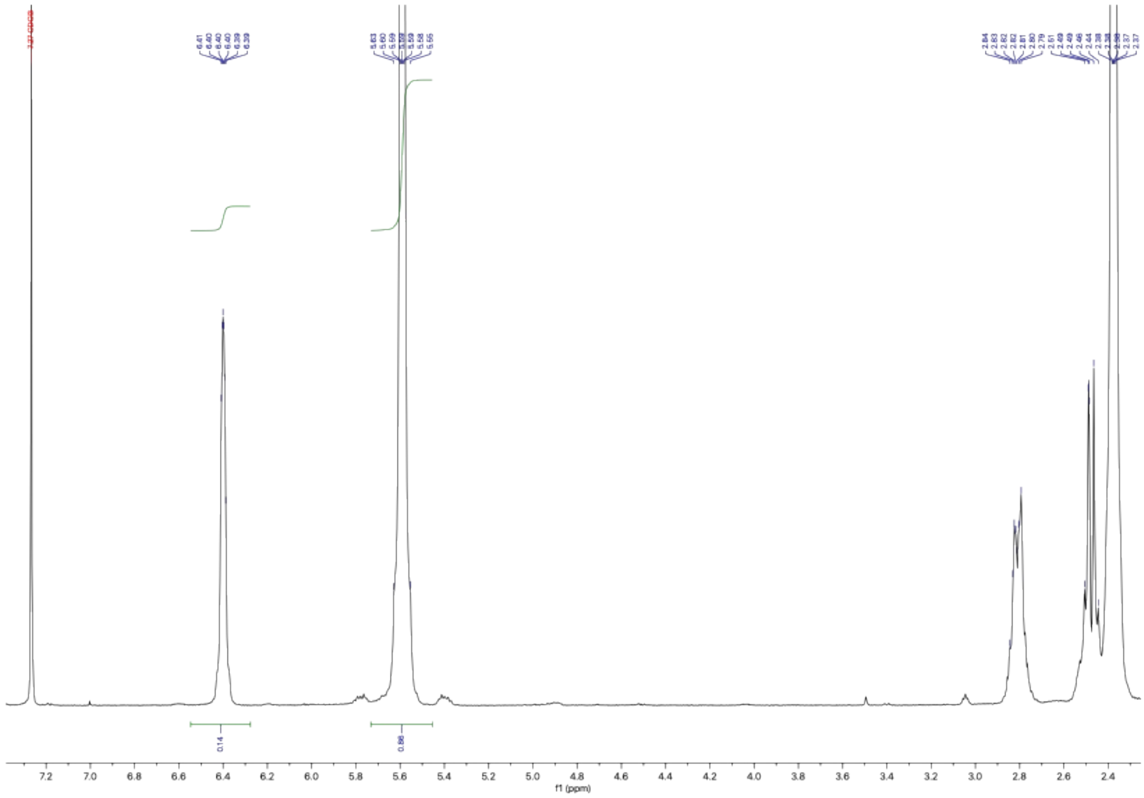


Figure S120. ^{1}H NMR spectra of tube reaction $Na_2[PdBr_4]$ with COD (1:1) **(1b)**, after 1 week (400.1 MHz, $CDCl_3$, 298K).

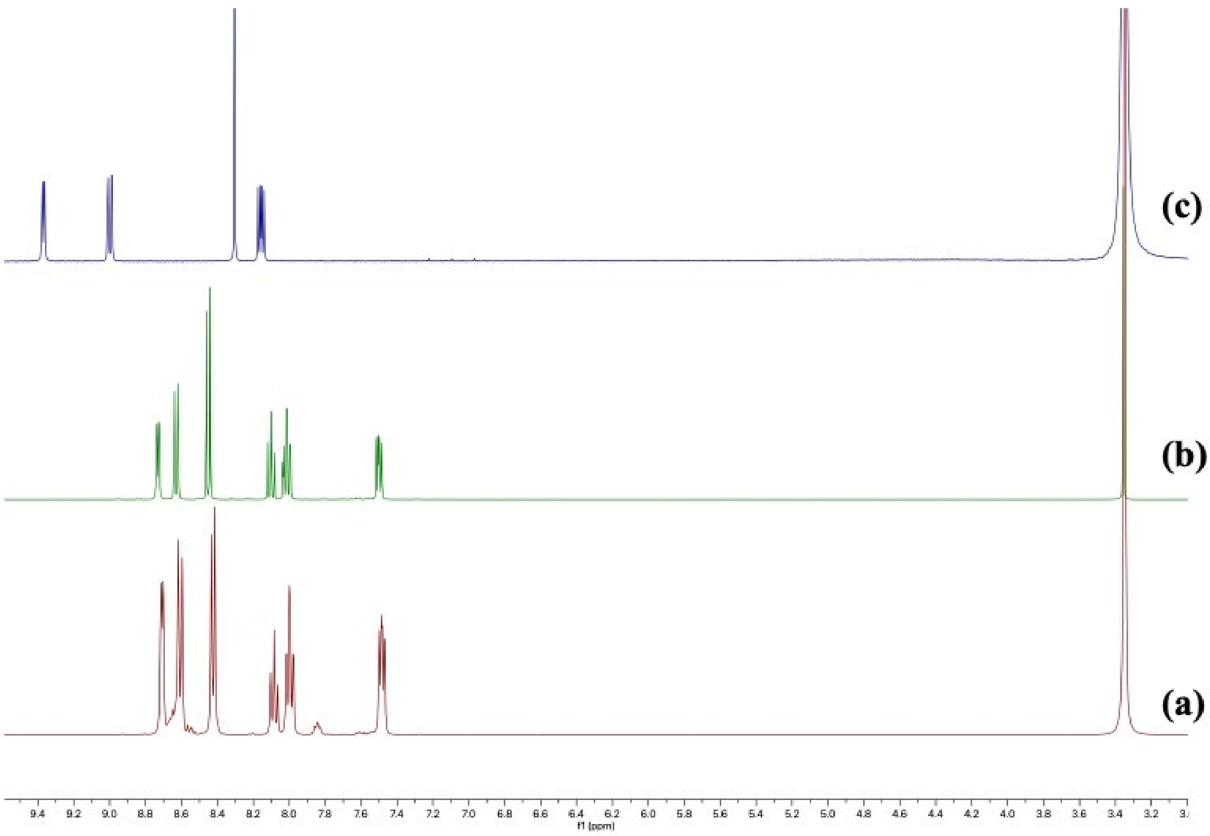


Figure S121. ^{1}H NMR (400.1 MHz, DMSO-d_6, 298K) spectra of: (a) tube reaction of $Na_2[PdCl_4]$ with terpy (1:1) after 6 hours, (b) free terpy, (c) [Pd(terpy)Cl]Cl **(3b)**.

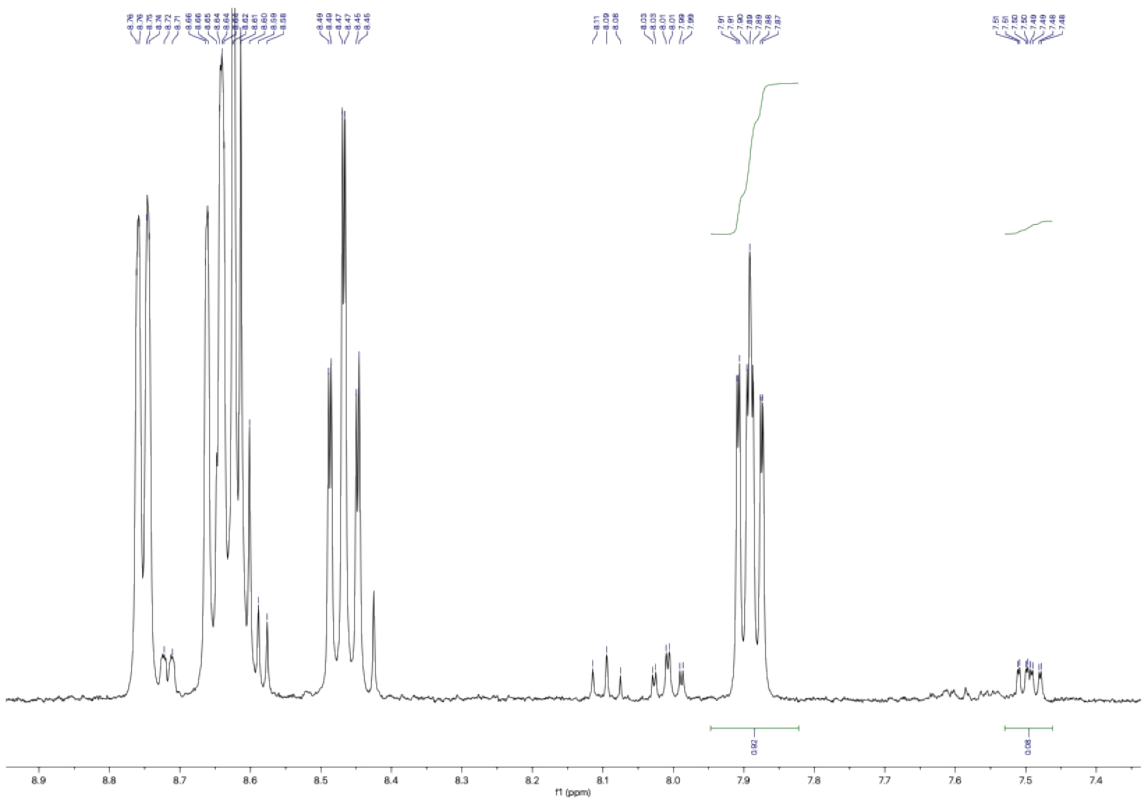


Figure S122. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 5 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

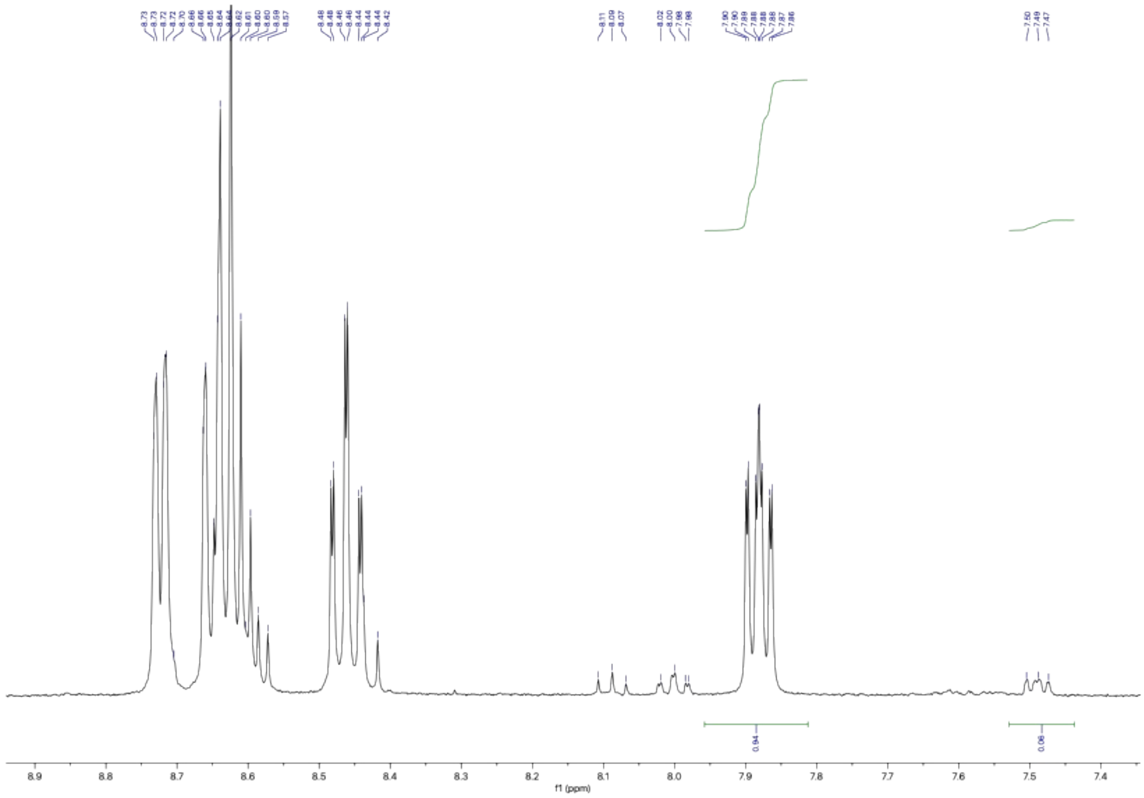


Figure S123. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 10 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

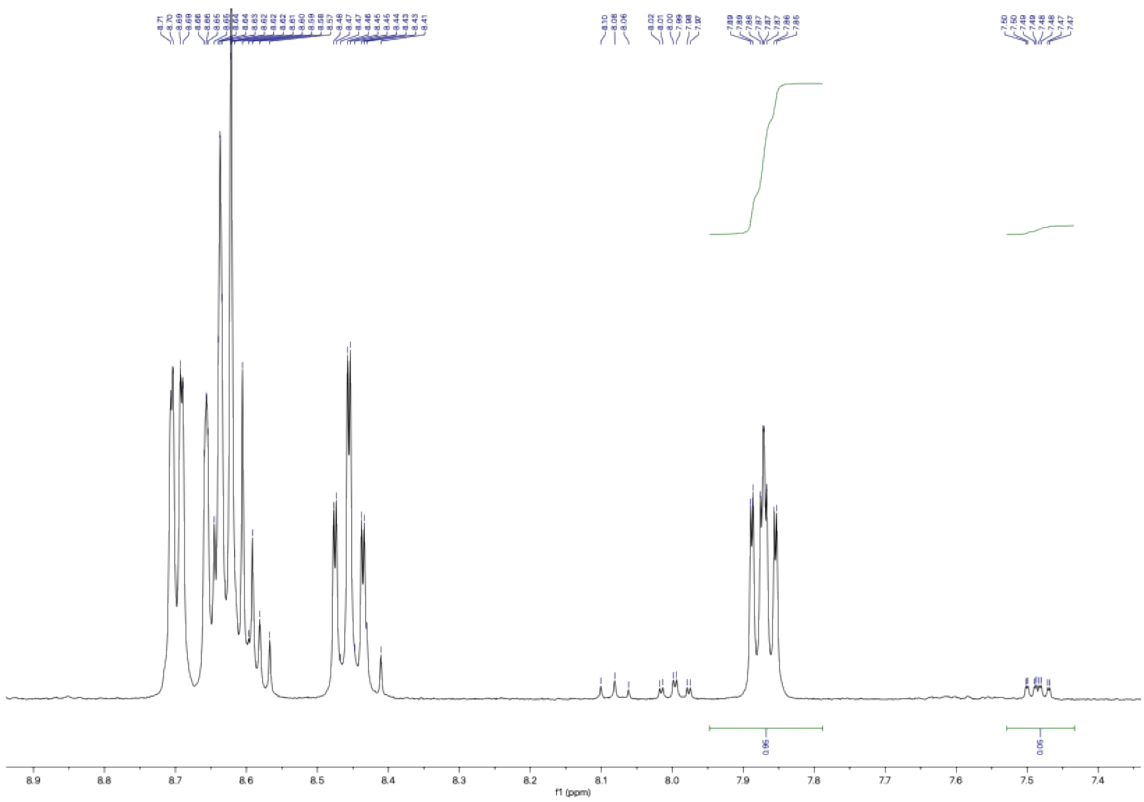


Figure S124. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 15 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

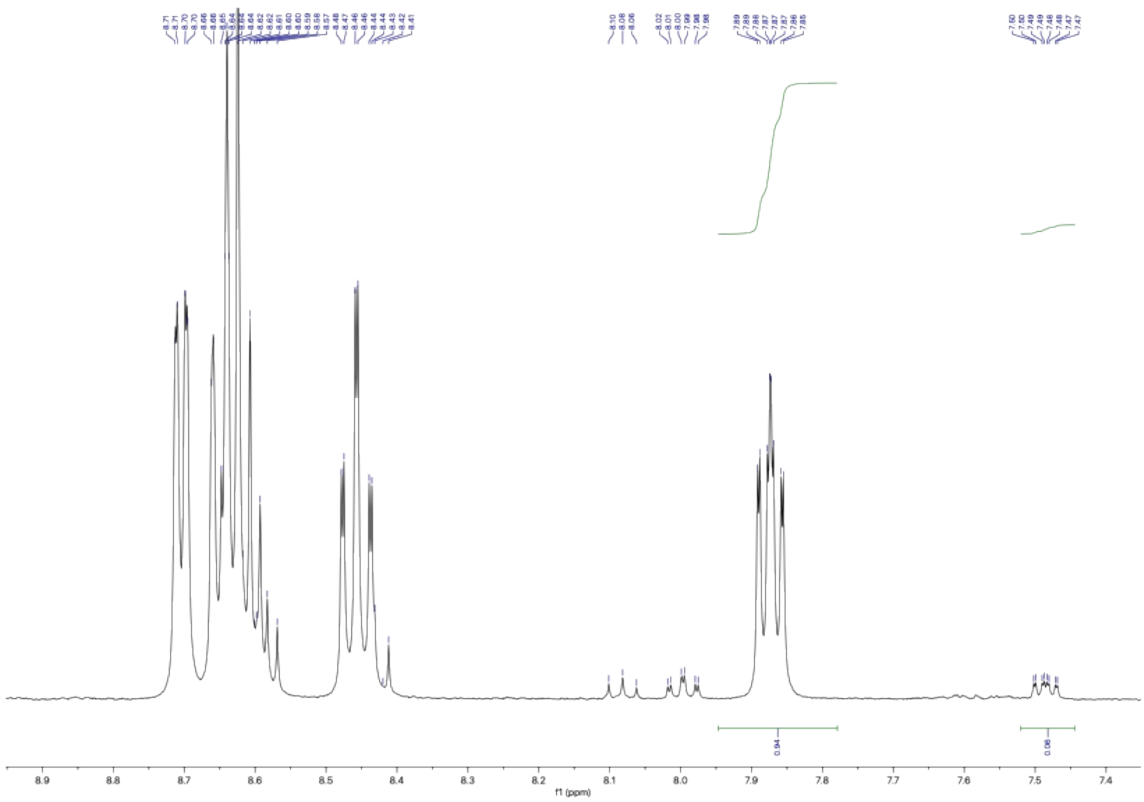


Figure S125. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 30 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

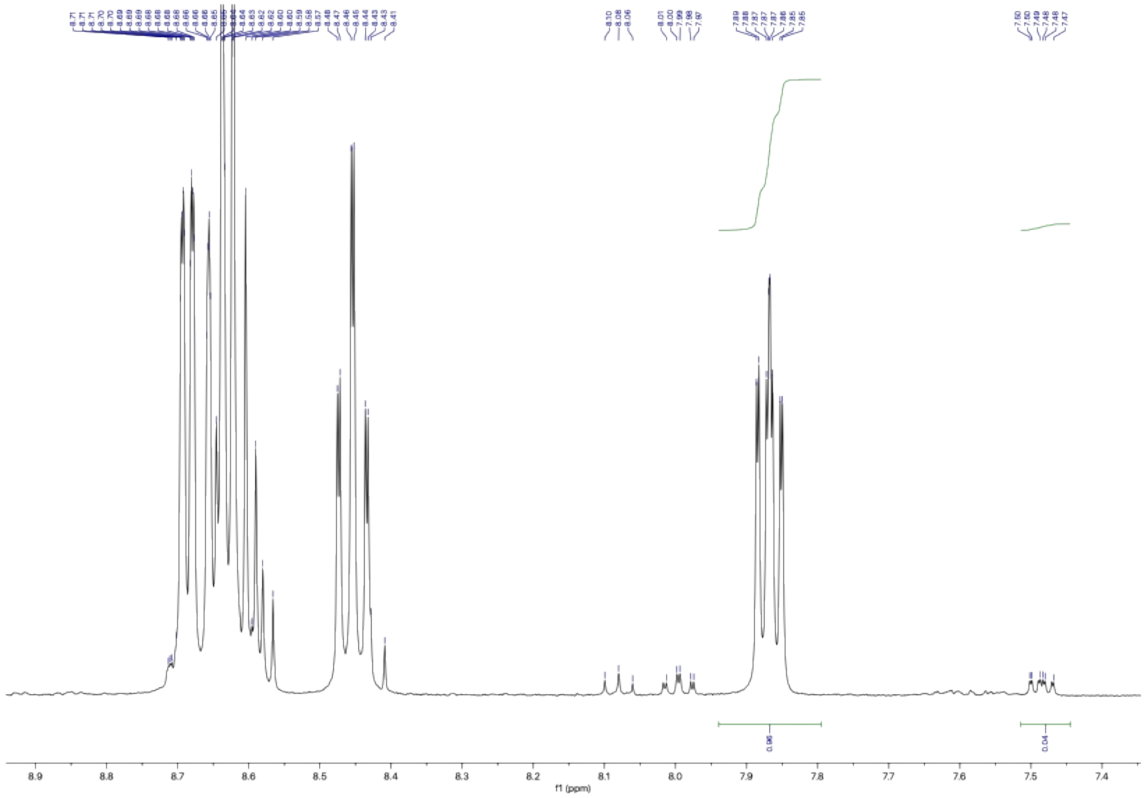


Figure S126. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 60 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

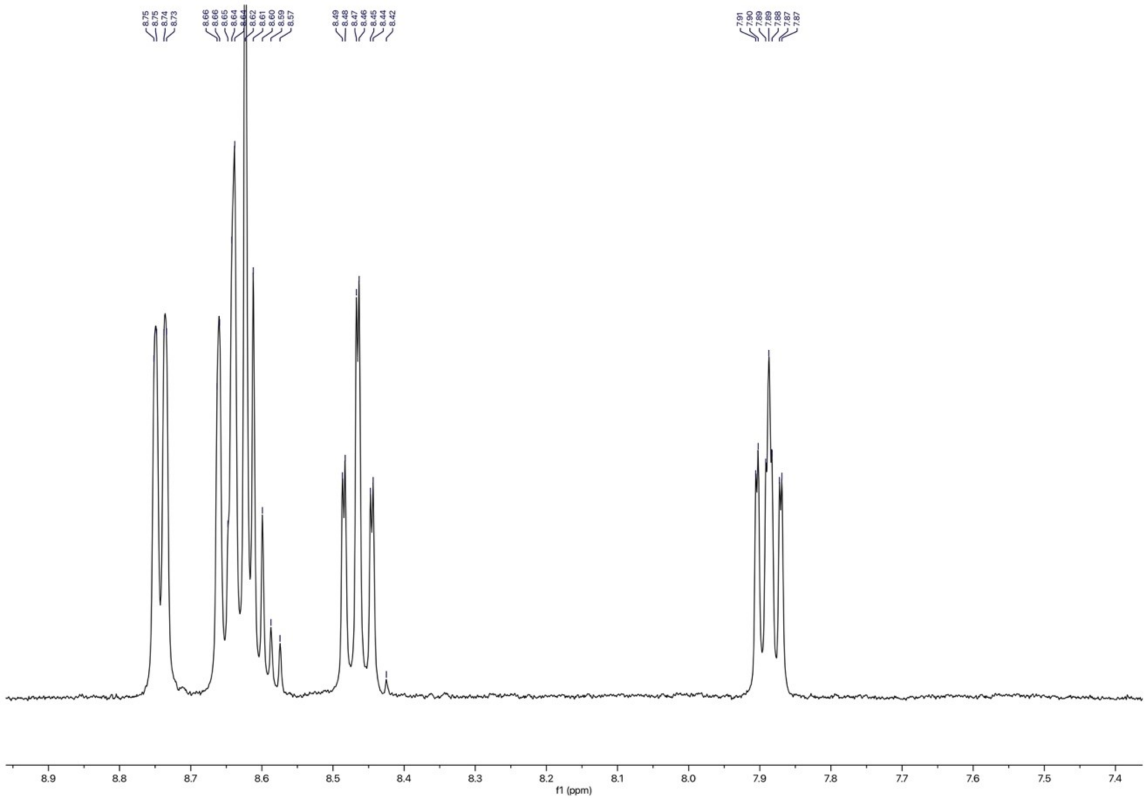


Figure S127. ^{1}H NMR spectra of tube reaction $PdCl_2$ with terpy (1:1) **(3b)**, after 75 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

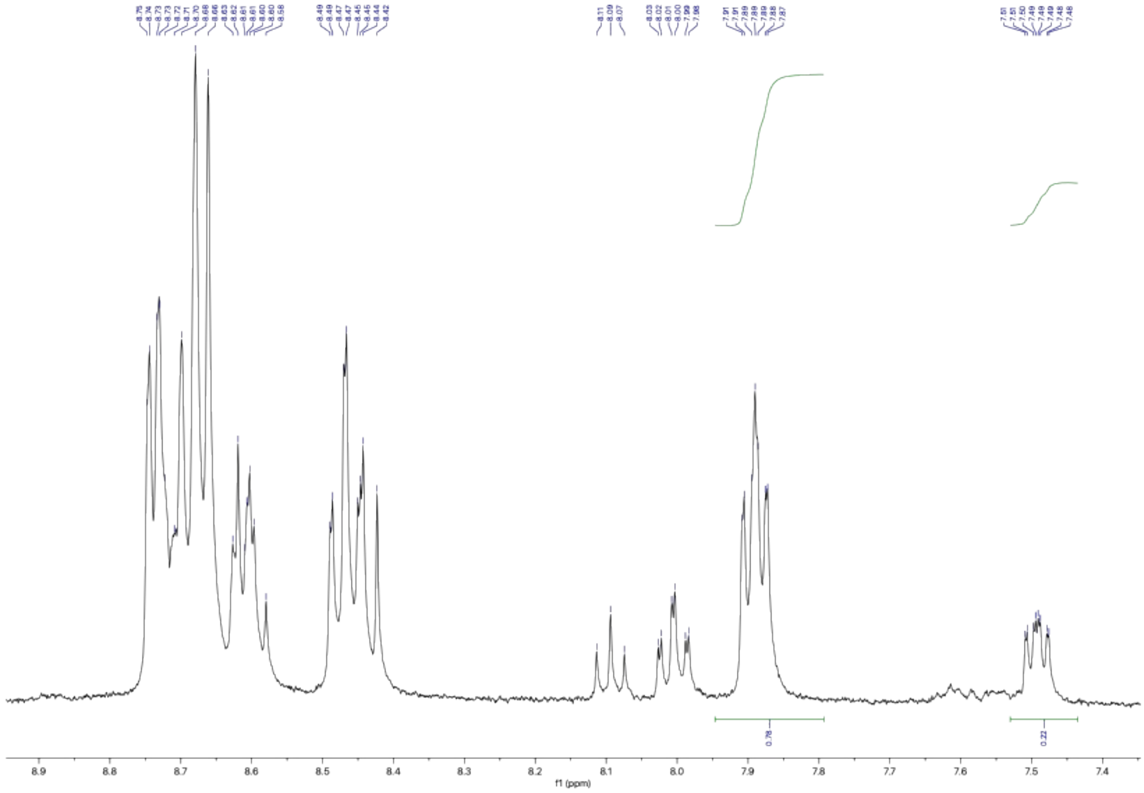


Figure S128. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 5 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

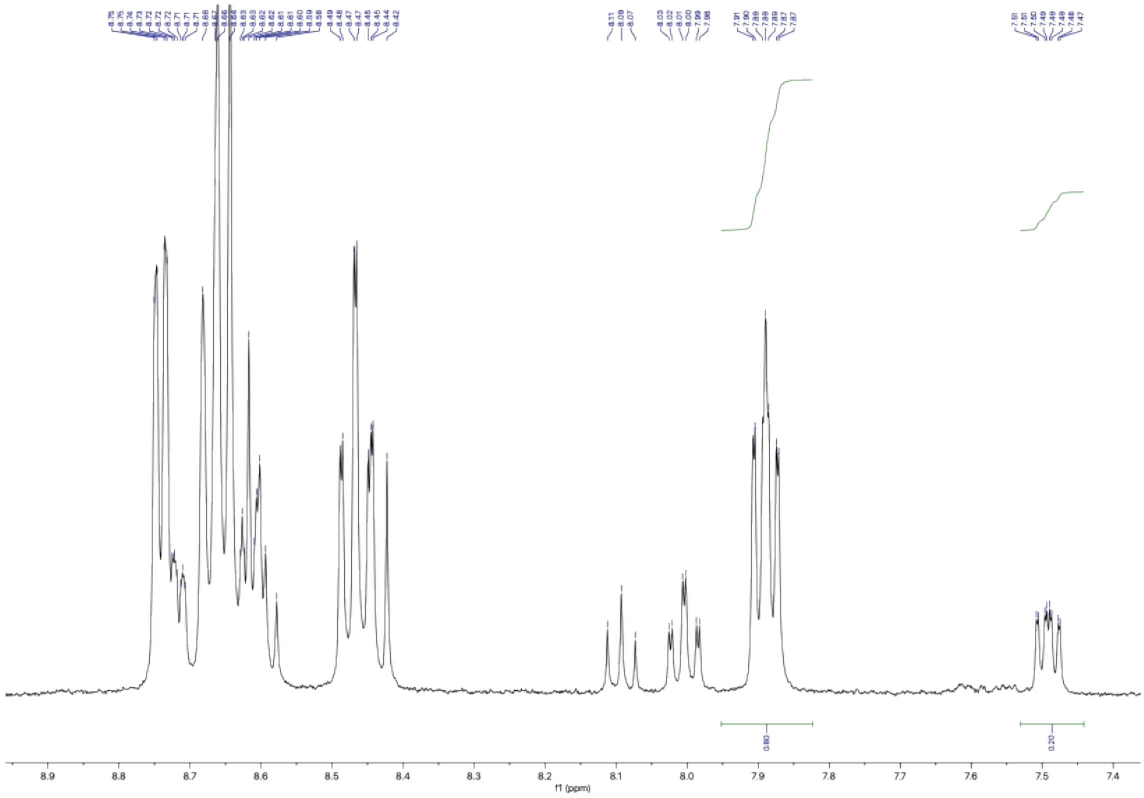


Figure S129. [1]H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 10 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

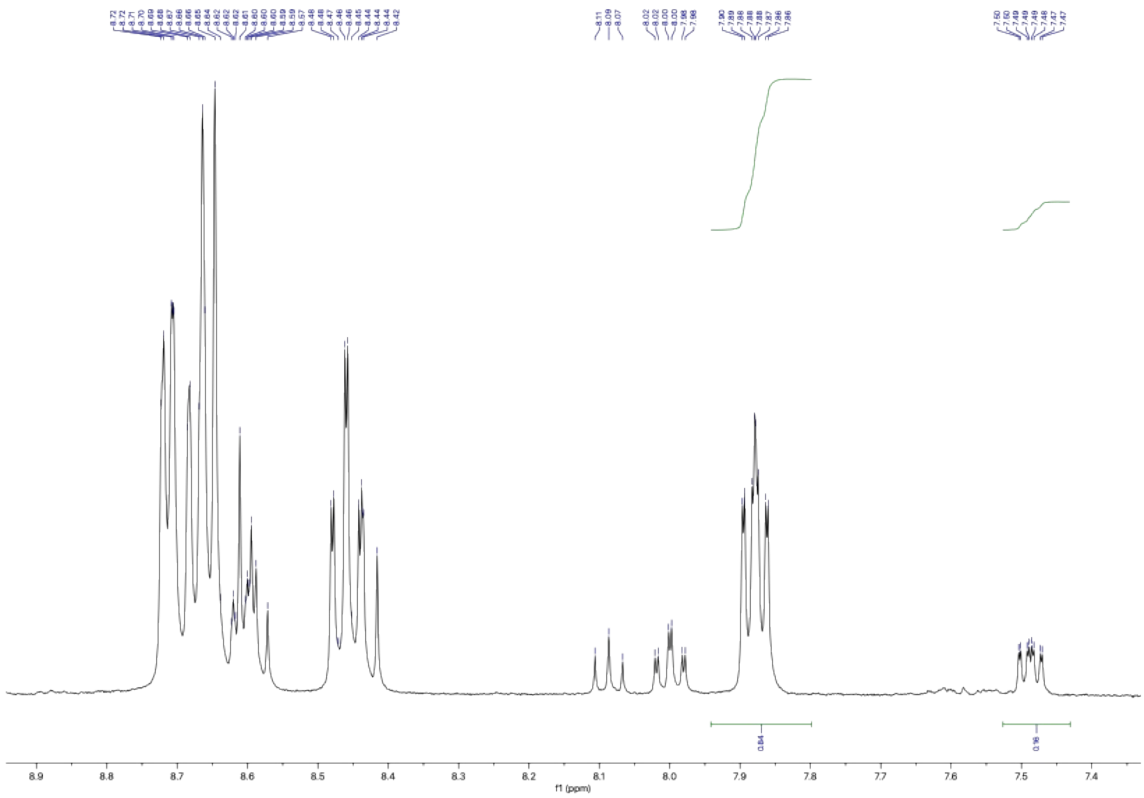


Figure S130. [1]H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 15 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

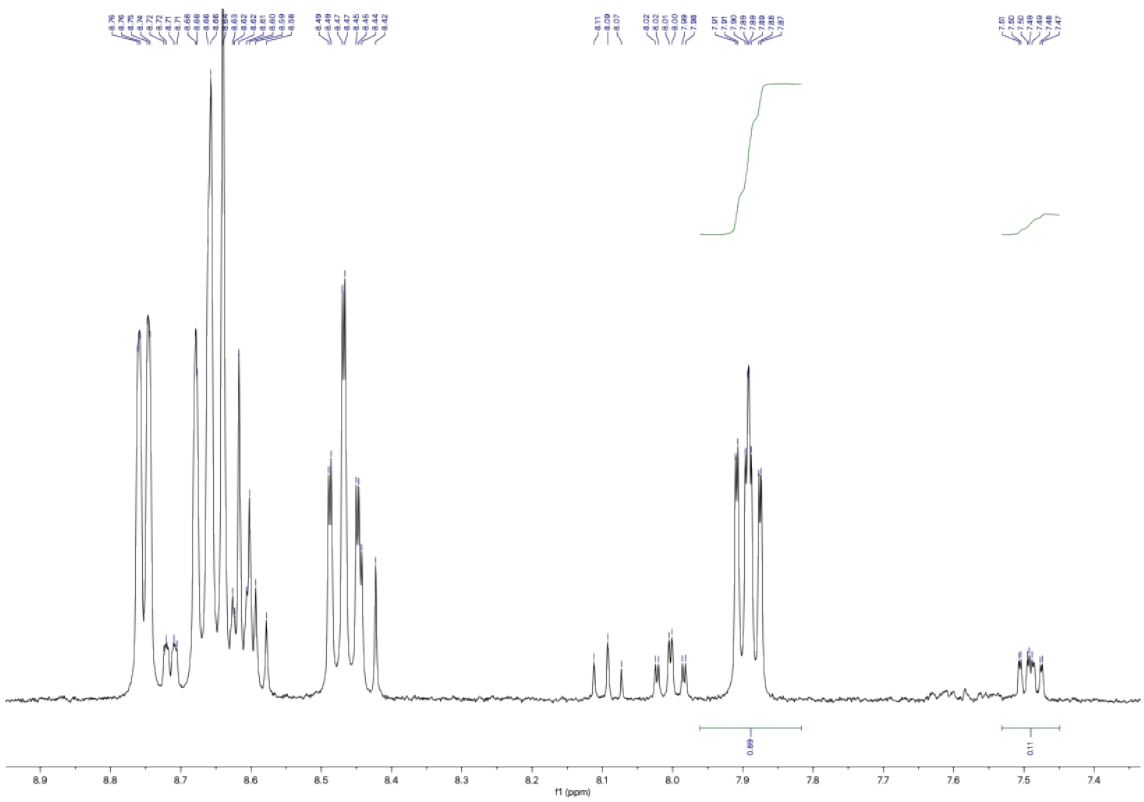


Figure S131. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 30 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

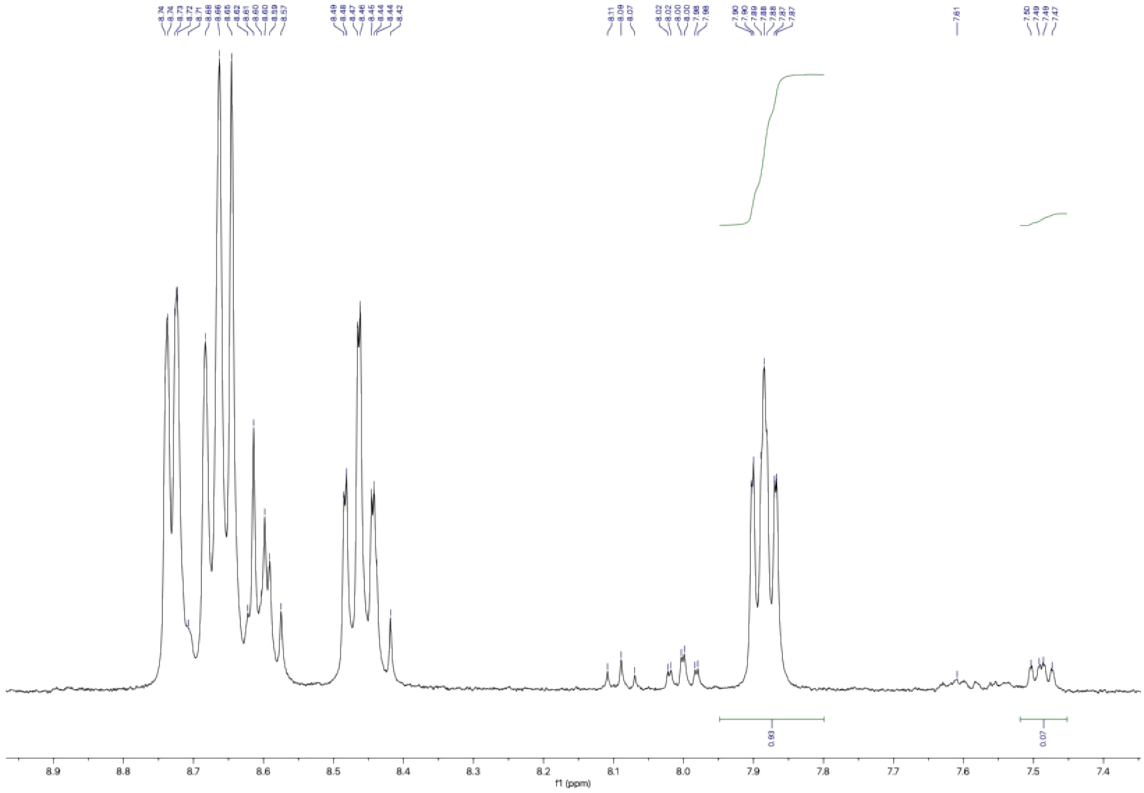


Figure S132. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 40 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

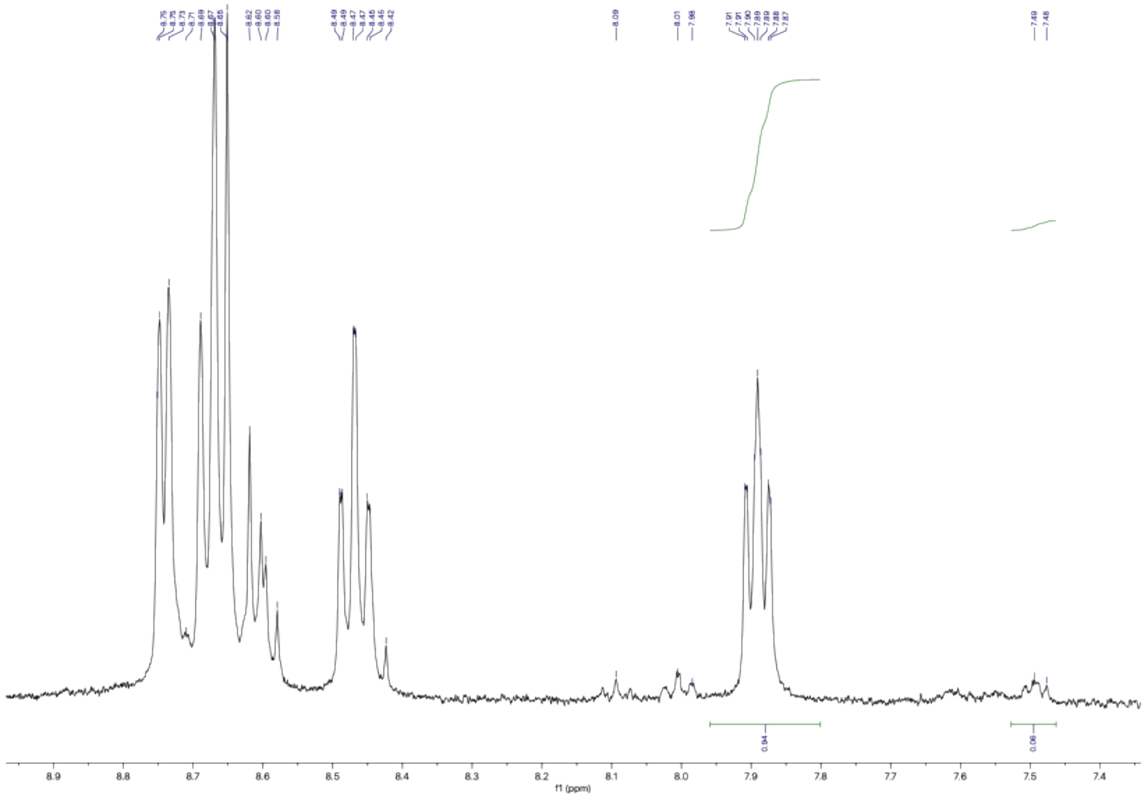


Figure S133. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 50 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

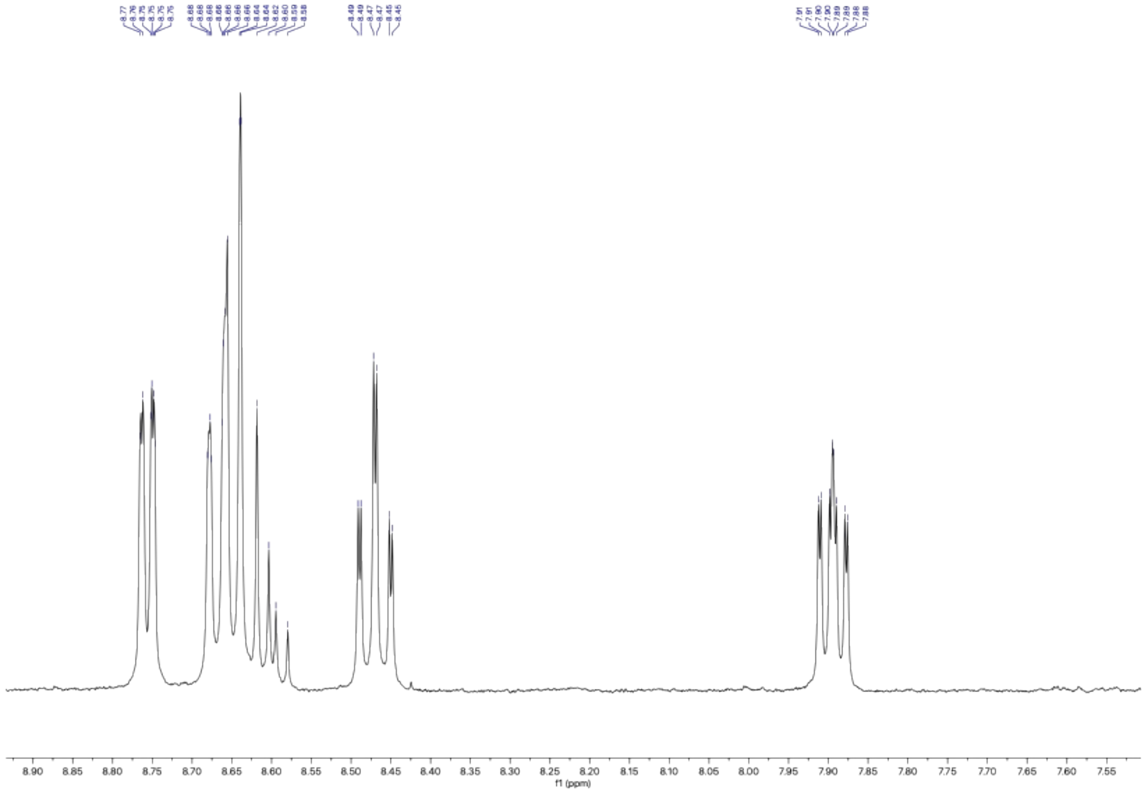


Figure S134. ^{1}H NMR spectra of tube reaction $Na_2[PdCl_4]$ with terpy (1:1) **(3b)**, after 60 minutes of milling (400.1 MHz, DMSO-d_6, 298K).

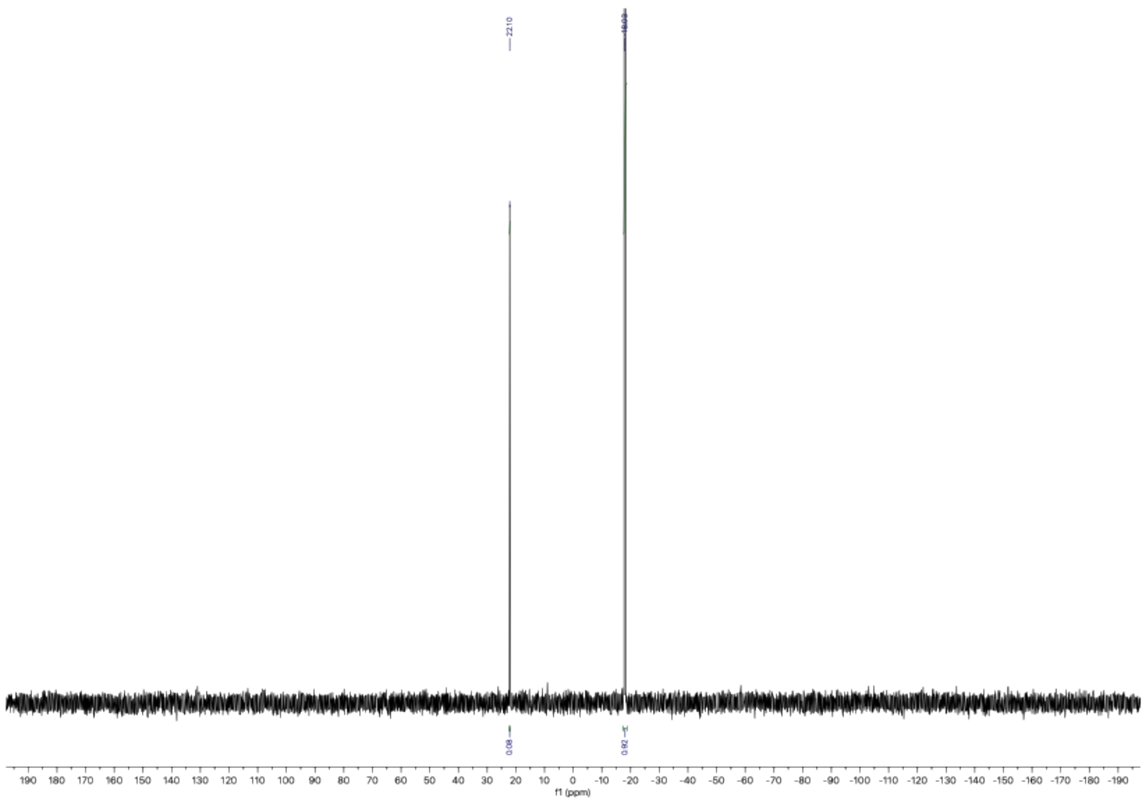


Figure S135. $^{31}P\{^{1}H\}$ NMR spectra of tube reaction $Na_2[PdCl_4]$ with Xantphos **(5b)** (1:1), after 15 minutes (162.0 MHz, $CDCl_3$, 298K).

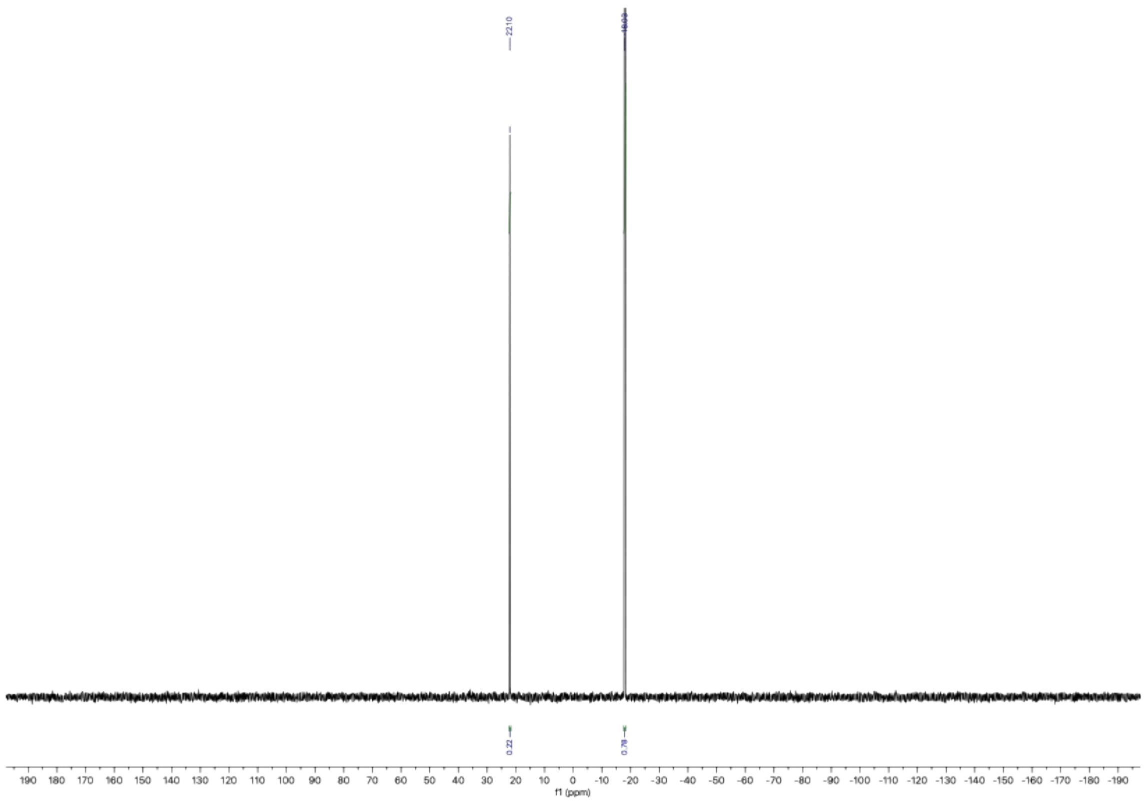


Figure S136. $^{31}P\{^{1}H\}$ NMR spectra of tube reaction $Na_2[PdCl_4]$ with Xantphos **(5b)** (1:1), after 1.15 hours (162.0 MHz, $CDCl_3$, 298K).

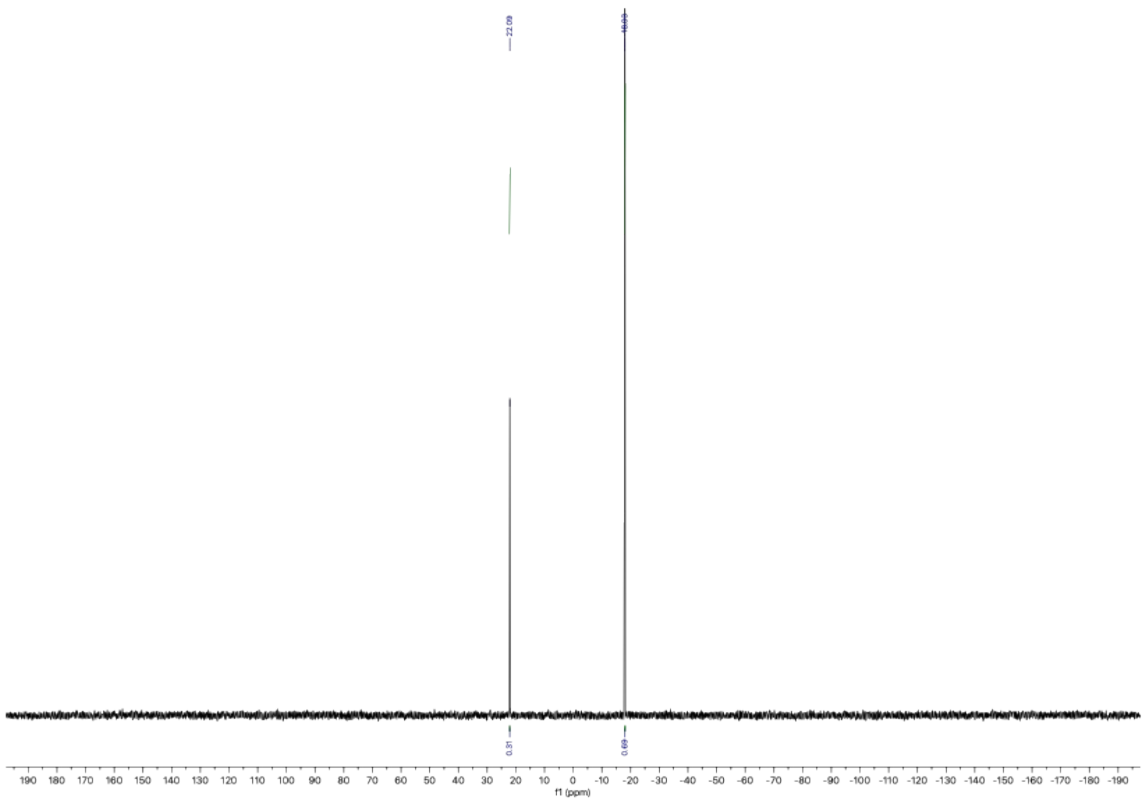


Figure S137. $^{31}P\{^{1}H\}$ NMR spectra of tube reaction $Na_2[PdCl_4]$ with Xantphos **(5b)** (1:1), after 1 day (162.0 MHz, $CDCl_3$, 298K).

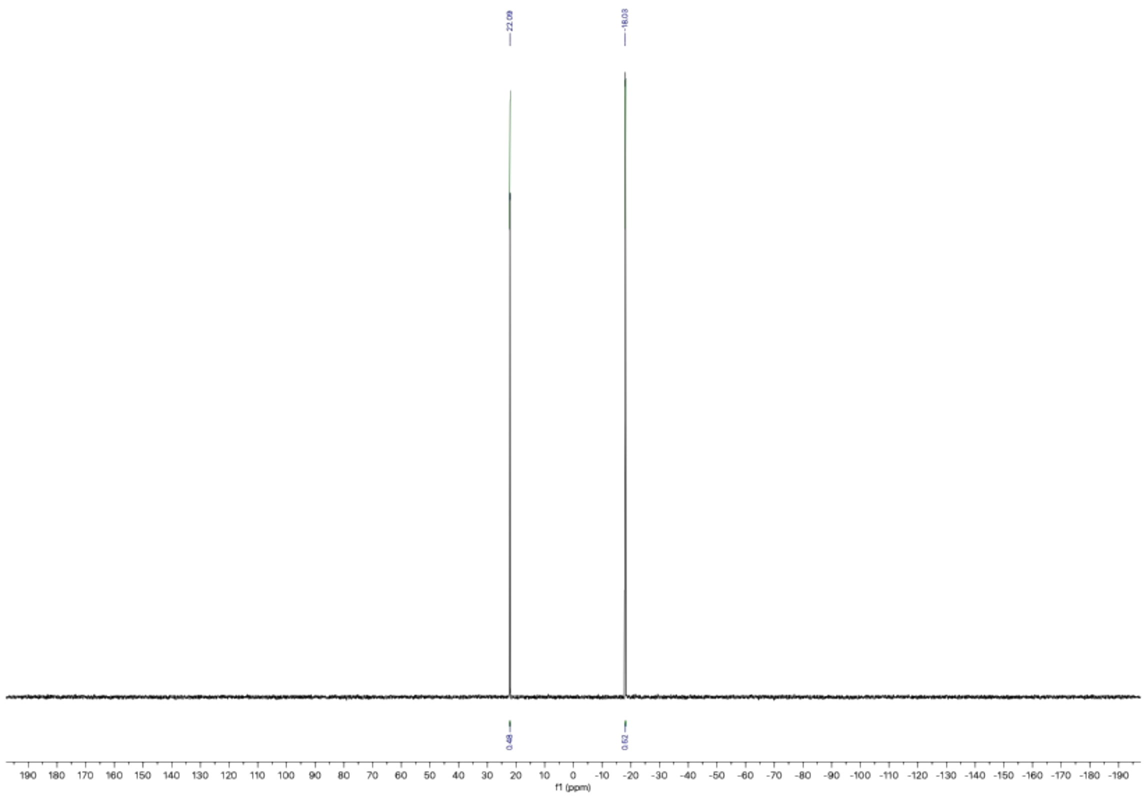


Figure S138. $^{31}P\{^{1}H\}$ NMR spectra of tube reaction $Na_2[PdCl_4]$ with Xantphos **(5b)** (1:1), after 2 days (162.0 MHz, $CDCl_3$, 298K).

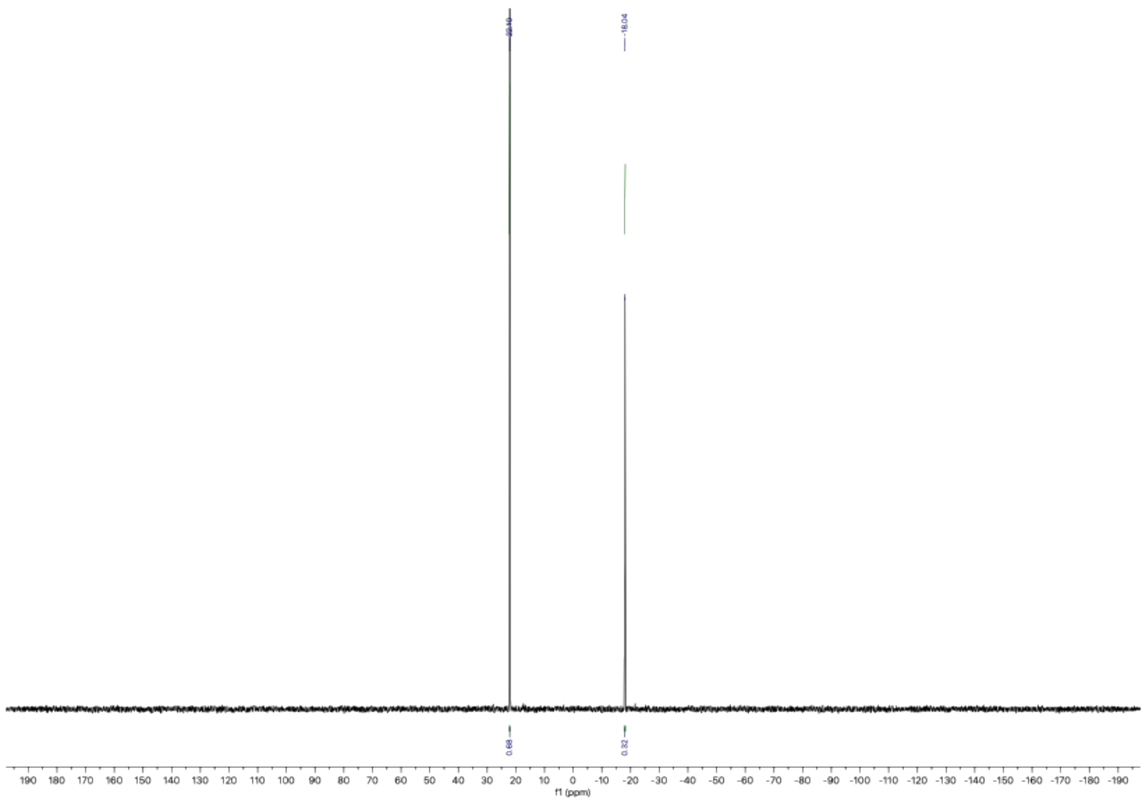


Figure S139. $^{31}P\{^1H\}$ NMR spectra of tube reaction $Na_2[PdCl_4]$ with Xantphos **(5b)** (1:1), after 6 days (162.0 MHz, $CDCl_3$, 298K).