Supplementary Information

Mastering Palladium Catalyzed Cross-Coupling Reactions: The Critical Role of In Situ Pre-catalyst Reduction Design

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General Information

Commercially available reagents (reagent grade, >99%) were purchased from Sigma Aldrich, Fluorochem and TCI Chemicals and used without any further purification.

Solvents (deuterated N,N-Dimethylformamide (DMF-d_7), deuterated chloroform ($CDCl_3$), 1-(2-Hydroxyethyl)-2-pyrrolidone (HEP), Ethanol (EtOH), dichloromethane (DCM) are commercially available and solvent for reaction were used after degassing.

bis(triphenylphosphine)palladium chloride(II) $PdCl_2(PPh_3)_2$ 1,1'-Bis(diphenylphosphino)ferrocene] palladio(II)dichloride $PdCl_2$(dppf), Bis(acetonitrile)dichloropalladium(II) $PdCl_2(ACN)_2$, Bis(dibenzylideneacetone)palladium(0) $Pd(dba)_2$, triphenylphospine (PPh_3), 3-Bis(diphenylphosphino)propane (dppp) and 1,1′-Bis(diphenylphosphino)ferrocene (dppf), Dicyclohexyl(2′,6′-dimethoxy[1,1′-biphenyl]-2-yl)phosphane (SPhos), 4,5-Bis(diphenylphosphino)-9,9-dimethylxanthene (Xantphos) from FaggiEnrico (Italy).

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded on Varian 400-MR (400 MHz) (equipped with autoswitchable PFG probe) and Bruker Avance Neo 600 MHz (equipped with CryoProbe Prodigy Broadband 5mm) spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t =triplet, q = quartet, spt = septet, m = multiplet, bs = broad signal. Coupling constants *J* are given in Hz. All ^1H and ^{13}C chemical shifts are calibrated to residual protic-solvents and all ^{31}P chemical shifts are referenced to external 85% phosphoric acid (δ = 0 ppm).

HPLC-UV analysis were recorded with an Agilent 1260 InfinityLab instrument. Column: Zorbax® SB-C18; particle size 5 μm; pore size 100 Å; length 250 mm, internal diameter: 4.6 mm. Mobile phase A: H_2O, mobile phase B: ACN. Gradient (Time(min), %B): 0, 80; 25, 80; 28, 10; 30, 10; flow 0.5 mL min^{-1}column temperature 30°C; injection volume: 10 μL.

GC-MS analysis were recorded with a Hewlett-Packard 5971 spectrometer with GC injection and EI ionization at 70 eV coupled with an Agilent Technologies MSD1100 single-quadrupole mass spectrometer, reported as: m/z (rel. intensity).

High-Resolution transmission electron microscopy (HR-TEM) images were acquired on a ThermoFischer Talos F200X operated at 200 kV, which is equipped with an extreme field emission gun (FEG) electron source and Super-X Energy Dispersive X-ray Spectroscopy (EDS) system for chemical analysis.

HRMS spectra were obtained with a G2XS QTof mass spectrometer using either ESI.

Room temperature (rt) refers to the ambient temperature of the laboratory, ranging from 22 °C to 26 °C.

1. Palladium pre-catalyst reduction with PPh_3

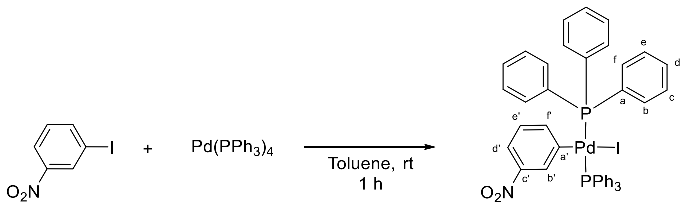
Table S1. ^{31}P NMR chemical shift in DMF-d_7 and HEP/DMF-d_7 (2:4) of palladium species with PPh_3

entry	Compound	DMF-d_7	HEP/DMF-d_7 (2:4)
1	PPh_3[a]	-4.94	-5.08
2	$Pd(OAc)_2(PPh_3)_2$	15.69	15.60
3	$3NO_2Ar(OAc)Pd(PPh_3)_2$	22.50	22.34
4	$Pd^0(PPh_3)$ [a]	23.37	23.30
5	$3NO_2ArPdI(PPh_3)_2$	24.10	24.03
6	$Pd(PPh_3)_2Cl_2$[a]	24.85	24.64
7	$OPPh_3$ [a]	26.15	27.57
8	$3NO_2ArPdI(PPh_3)$	25.10	25.40
9	$3NO_2Ar(OAc)Pd(PPh_3)TMG$	29.61	29.19
10	$Pd(PPh_3)_2Cl(CO_3^{2-})M^+$ [b]	30.58	
11	$3NO_2Ar(PdI(PPh_3)TMG$	30.86	28.32
12	$Pd(PPh_3)_2(OAc)\ (CO_3^{2-})M^+$		31.06
13	$Pd^0(PPh_3)_2$[a]	34.29	34.03

[a] See as reference [1]
[b] See as reference [2]

1.1. Synthesis of palladium species with PPh_3

Entry 5, Table S1: Oxidative addition complex $3NO_2ArPdI(PPh_3)_2$

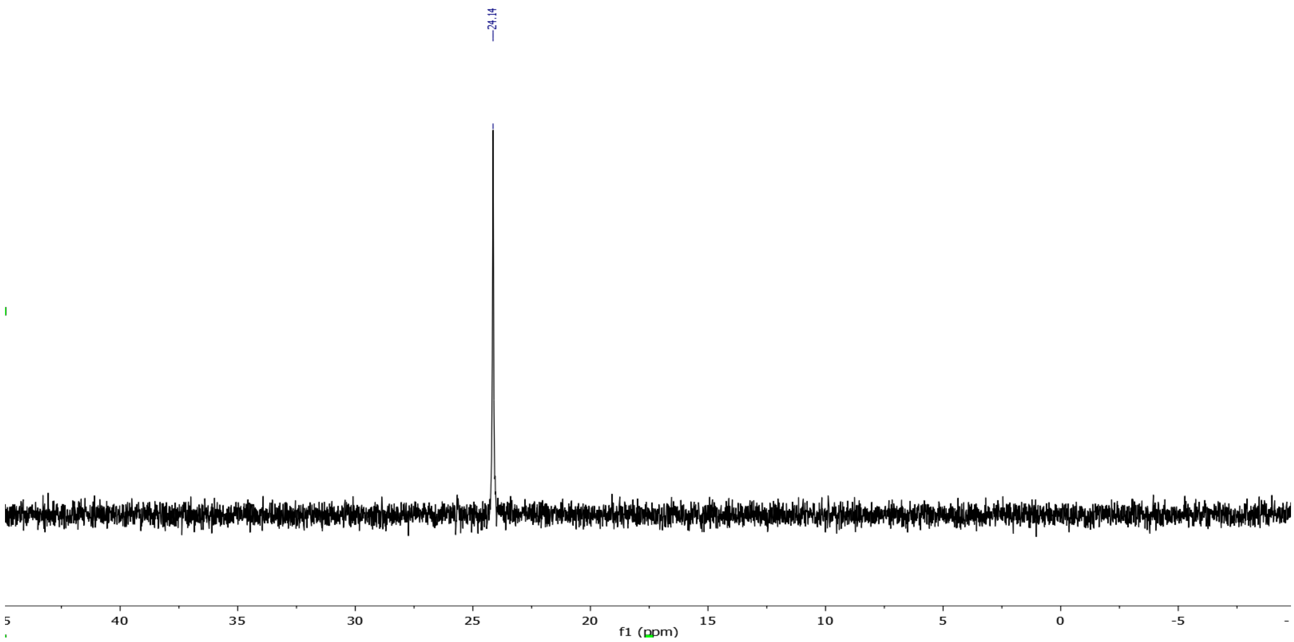


To an oven-dried 20 mL Schlenk purged under argon atmosphere, a mixture of 1-Iodo-3-nitrobenzene $3NO_2ArI$ (423 mg, 1.7 mmol, 2.46 eq) and tetrakis(triphenylphosphine)palladium(0) (798 mg, 0.69 mmol, 1 eq) was stirred in degassed toluene (13 mL), in the dark for 1 h at room temperature. The reaction mixture was filtered and the crude was washed with diethyl ether (Et_2O) to obtain the pure product (534 mg, 88%) as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55-7.50 (m, 12H, Hb-Hf); 7.33-7.29 (m, 6H, Hd); 7.26-7.22 (m, 13H, Hc-He, -Hd'); 7.15-7.11 (m, 3H, Hb'-Hc'-He')

^{13}C NMR (151.2 MHz, $CDCl_3$): δ 178.07 (s, Cd'); 143.86 (t, J=1.51 Hz, Ca'); 135.89 (t, J=4.53 Hz, Cb'-Cf'), 134.92 (t, 6.05 Hz, Cb-Cf), 131.21 (t, J=24.2 Hz, Ca), 130.40 (s, Cd), 128.00 (t, J=4.53, Cc-Ce), 120.95 (t, Cc'-Ce').

^{31}P NMR (242.4 MHz,) δ +24.14 (s) DMF-d_7 ; δ +24.02 (HEP/DMF-d_7 2/4) a)



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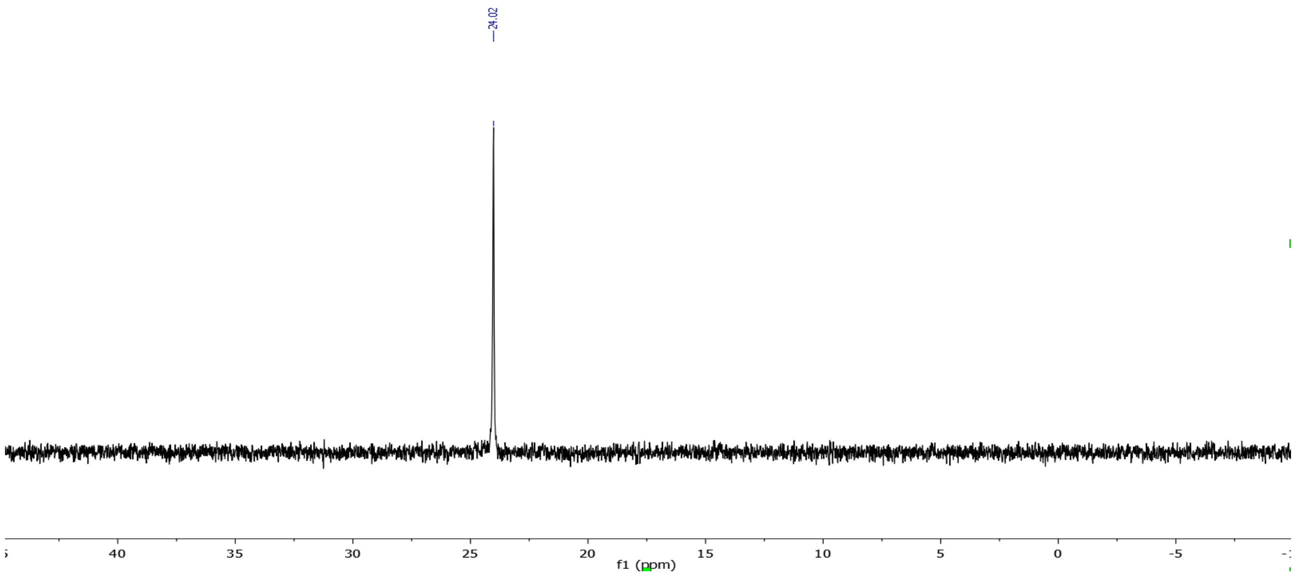
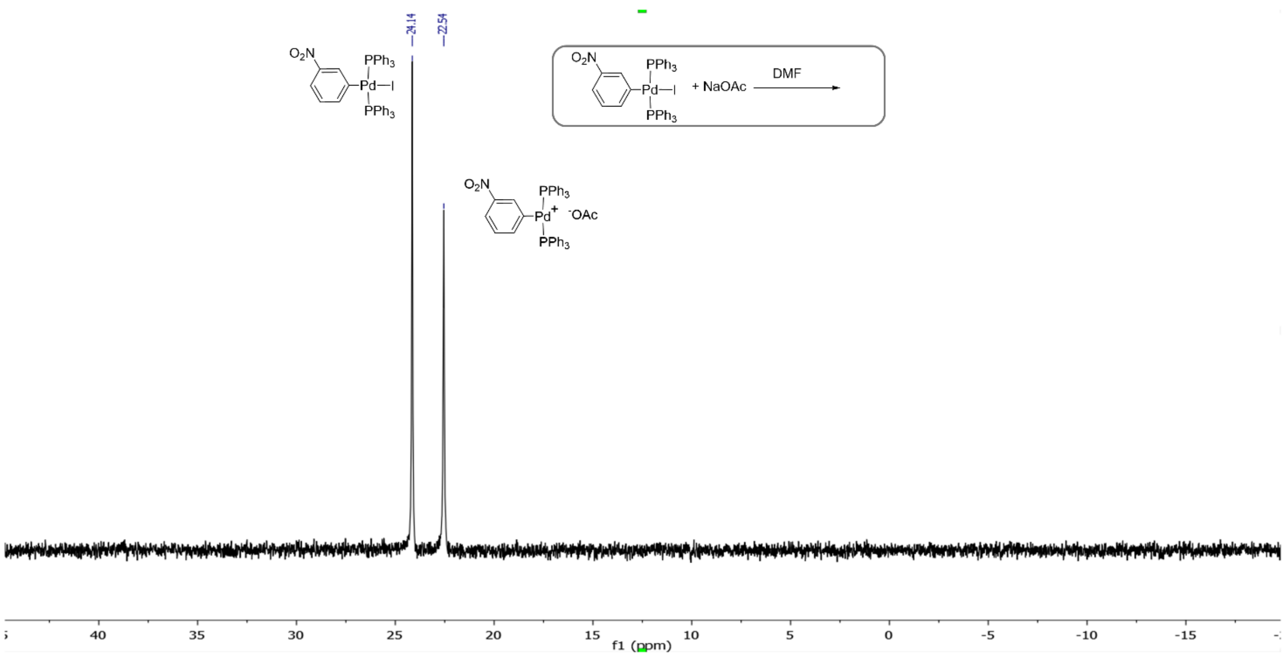


Figure S1. 31P NMR spectrum of $3NO_2ArPdI(PPh_3)_2$ in DMF-d_7 (a) and in HEP-DMF-d_7 (b) a)



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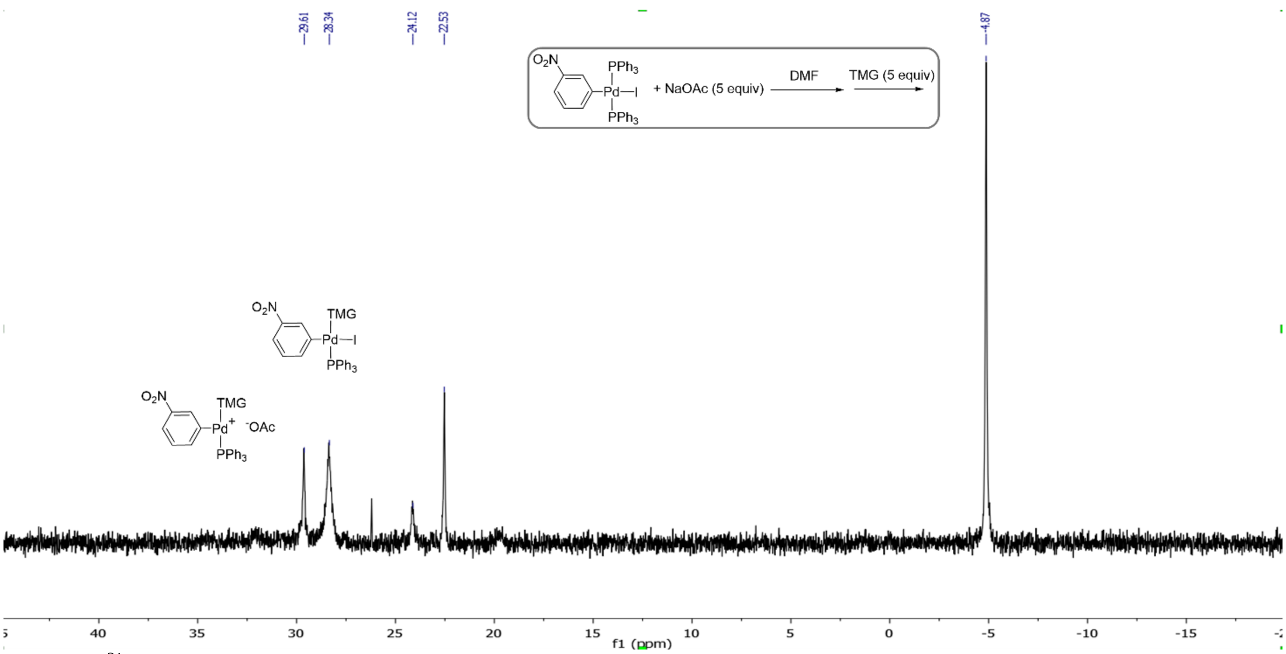


Figure S2. ^{31}P NMR spectra of $3NO_2ArPd(PPh_3)_2$ (11.40 mg, 0.013 mmol, 1 equiv) previously synthesized + NaOAc (5 mg, 0.065, 5 equiv) in DMF-d_7 (0.6 ml) (a); and after the addition of TMG (10µL, 0.065 mmol, 5 equiv) (b).

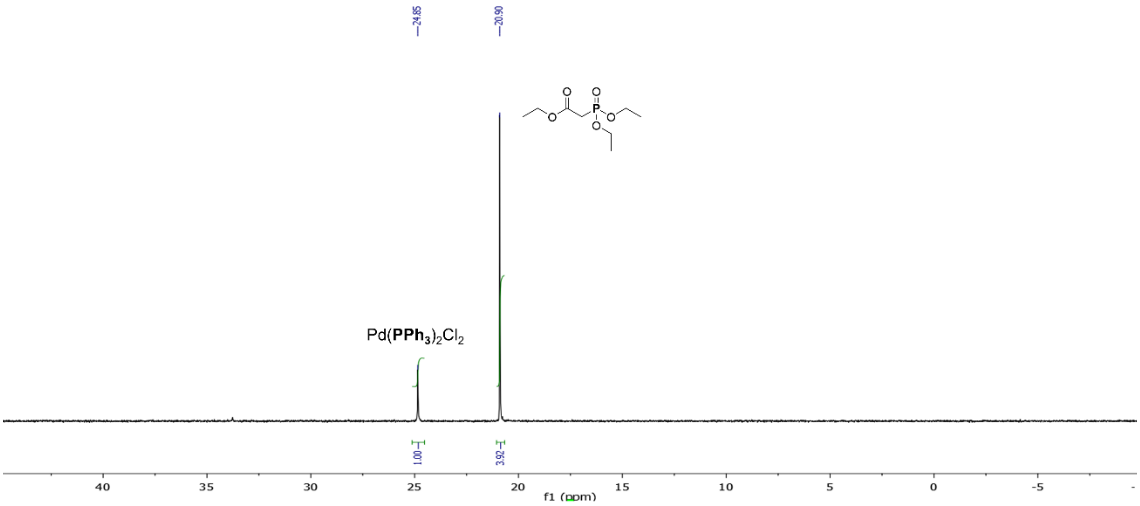
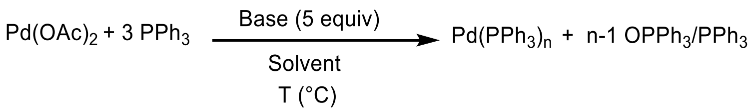


Figure S3. ^{31}P NMR spectrum of $Pd(PPh_3)_2Cl_2$ (1 equiv) and triethyl phosphonoacetate (1 equiv) as IS to know their integration ratio under the same setting used for all the experiments (d_1=1, nt=256).

1.2. $Pd(OAc)_2$

1.2.1. General Procedure 1



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(OAc)_2$ (2.91 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Triphenylphosphine (10.21 mg, 0.039 mmol, 3 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.13 mmol, 1 equiv) was added as internal standard (IS).

To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1]

Table S2. $Pd(PPh_3)_2(OAc)_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

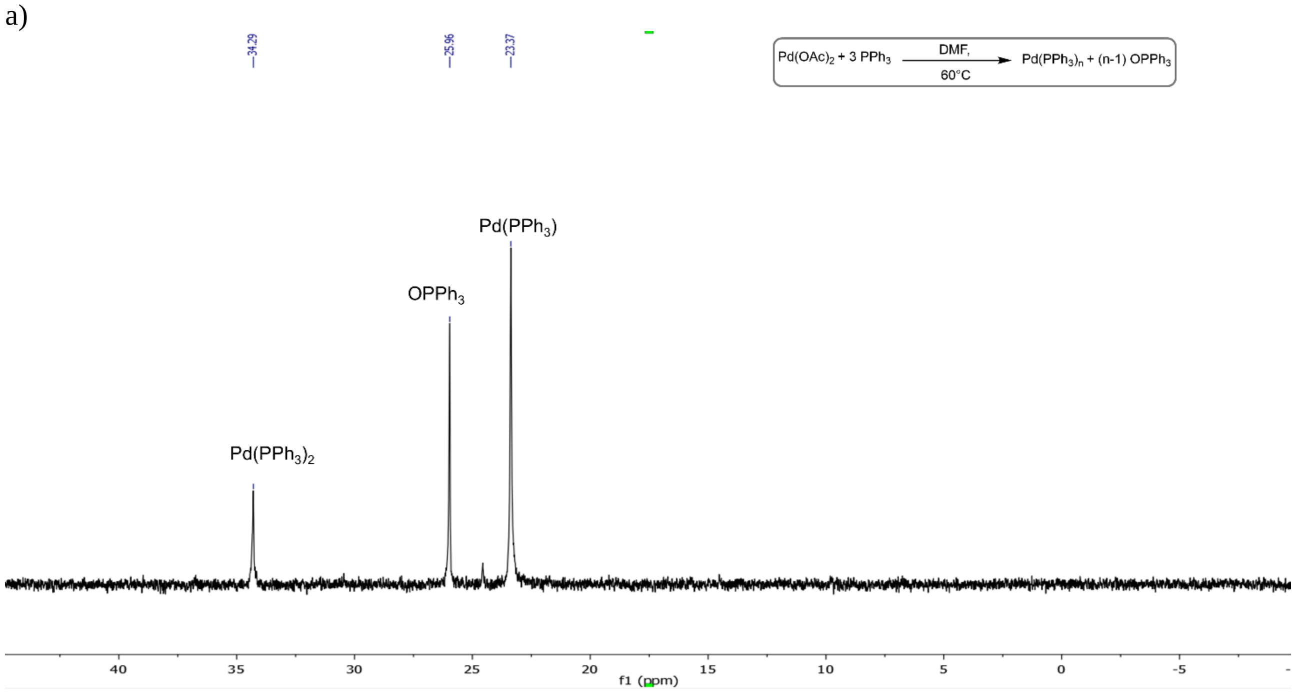
entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH[c]
1	-	DMF[d]	25	E	42/58	100/0
2	-	DMF	60	E	100/0	100/0
3	TMG	DMF	25	D/E	100/0	100/0
4	cyclohexylamine	DMF	25	D/E	100/0	100/0
5	pyrrolidine	DMF	25	D/E	100/0	100/0
6	Cs_2CO_3	DMF	25	E	43/57	100/0
7	K_2CO_3	DMF	25	E	46/54	100/0

8	TEA	DMF	25	E	42/58	100/0
9	Cs_2CO_3	DMF	60	E	100/0	100/0
10	K_2CO_3	DMF	60	E	100/0	100/0
11	TMG	DMF	60	D/E	100/0	100/0
12	TEA	DMF	80	E	100/0	100/0
13	-	DMF/HEP[e]	60	A	100/0	100/0
14	TMG	DMF/HEP	25	A/E	100/0	n.d.[d]
15	Cs_2CO_3	DMF/HEP	25	A/E	100/0	n.d.[d]
16	K_2CO_3	DMF/HEP	25	A/E	100/0	n.d.[d]
17	TEA	DMF/HEP	25	A	42/58	100/0
18	Cs_2CO_3	DMF/HEP	60	A/E	100/0	n.d.[d]
19	K_2CO_3	DMF/HEP	60	A/E	100/0	n.d.[d]
20	TMG	DMF/HEP	60	A/E	A/E	n.d.[d]

[a] The reactions were carried out according to the **General Procedure 1**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $Pd(OAc)_2(PPh_3)_2$
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

1.2.2. ^{31}P NMR spectra

Entry 2, Table S2: Completed reduction in DMF as example
a)



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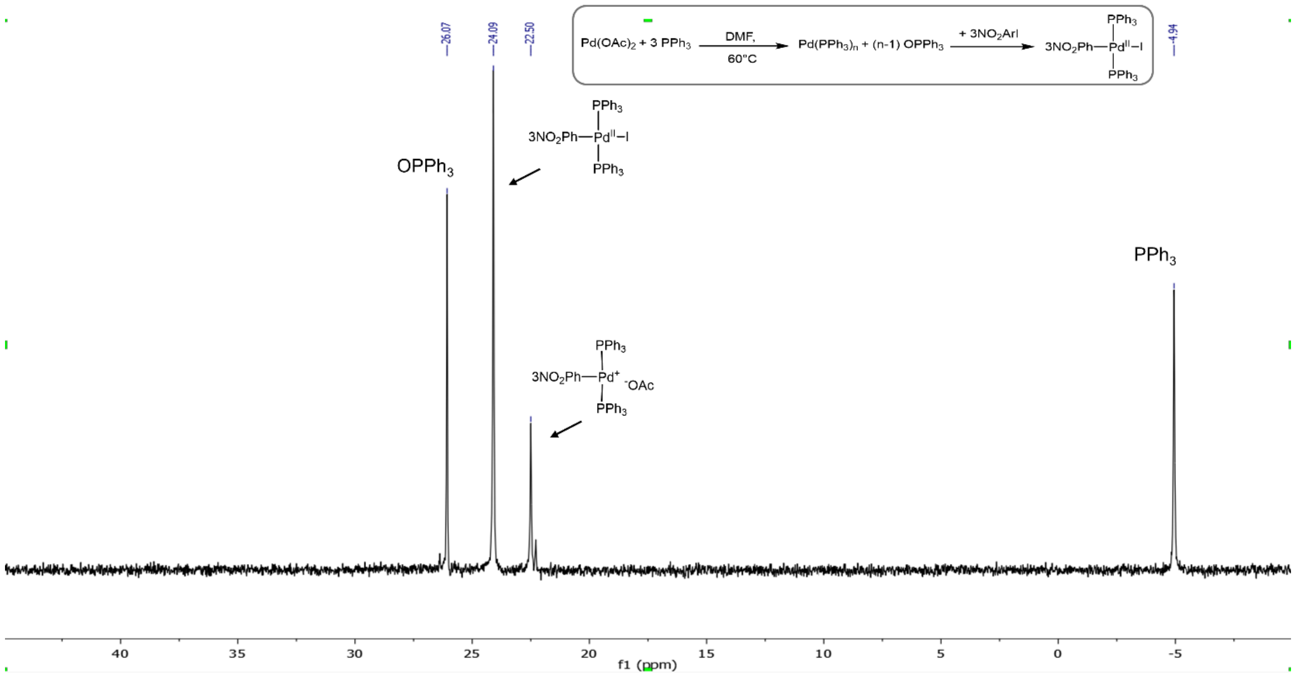
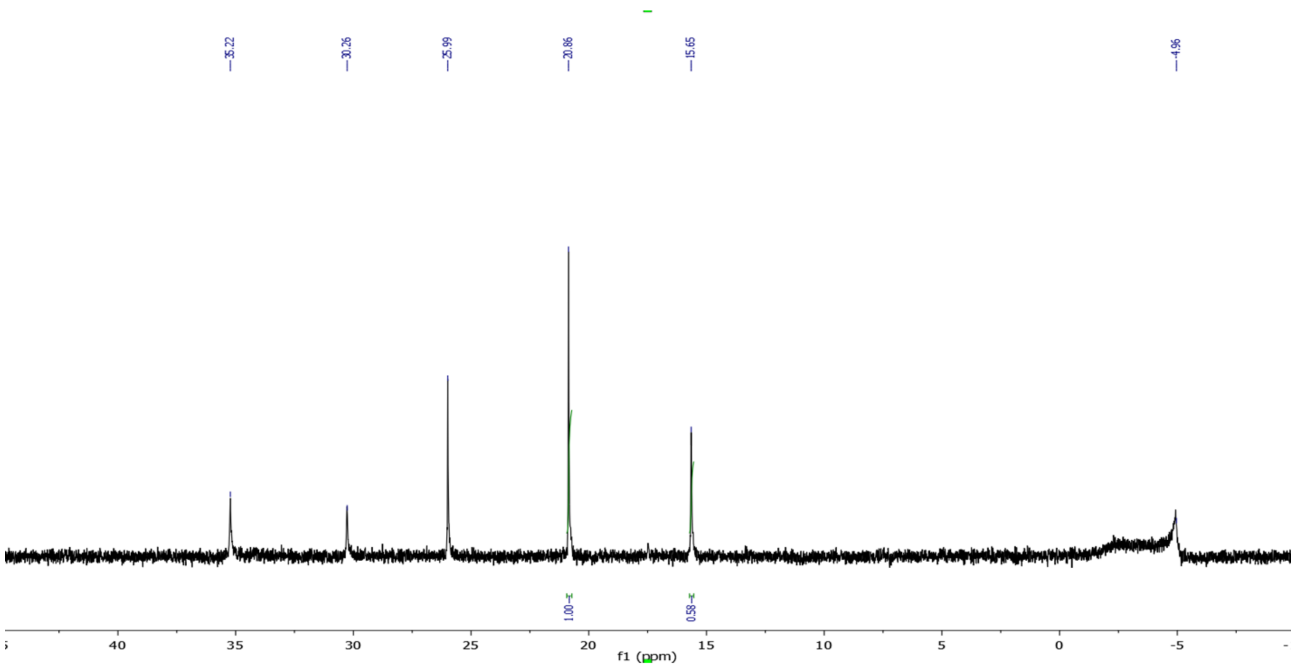


Figure S4. a) $Pd(OAc)_2 + 3PPh_3$ in DMF-d_7 at rt in 20 min b)+ $3NO_2ArI$

Other spectra

Entry 1, Table S2:

a)



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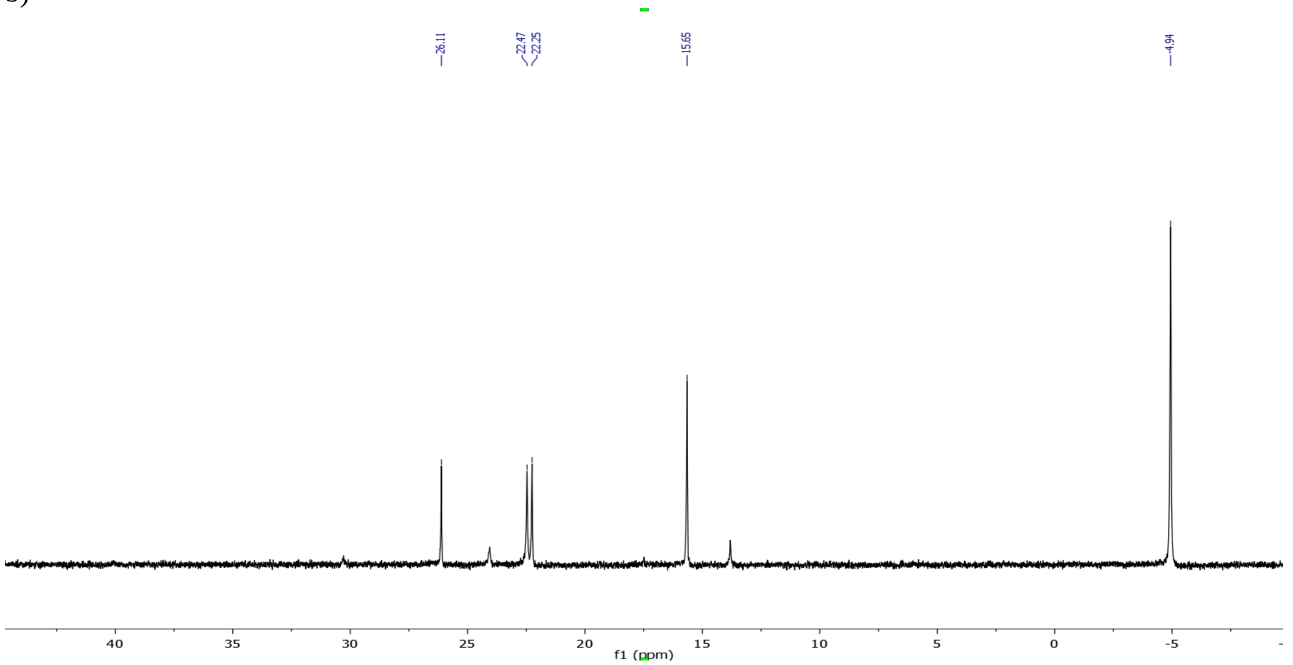
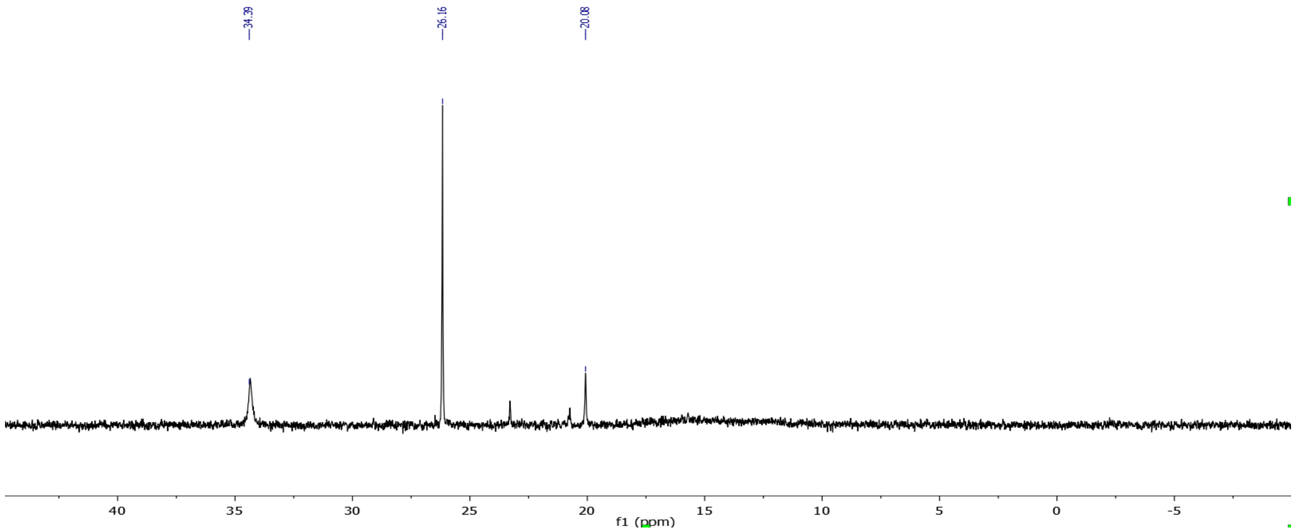


Figure S5. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) in DMF-d_7 at rt in 20 min. The peaks at 20.86 ppm and at 15.65 ppm are related to the Internal Standard (IS) and $Pd(PPh_3)_2(OAc)$; b) + $3NO_2ArI$

Entry 3, Table S2:

a)



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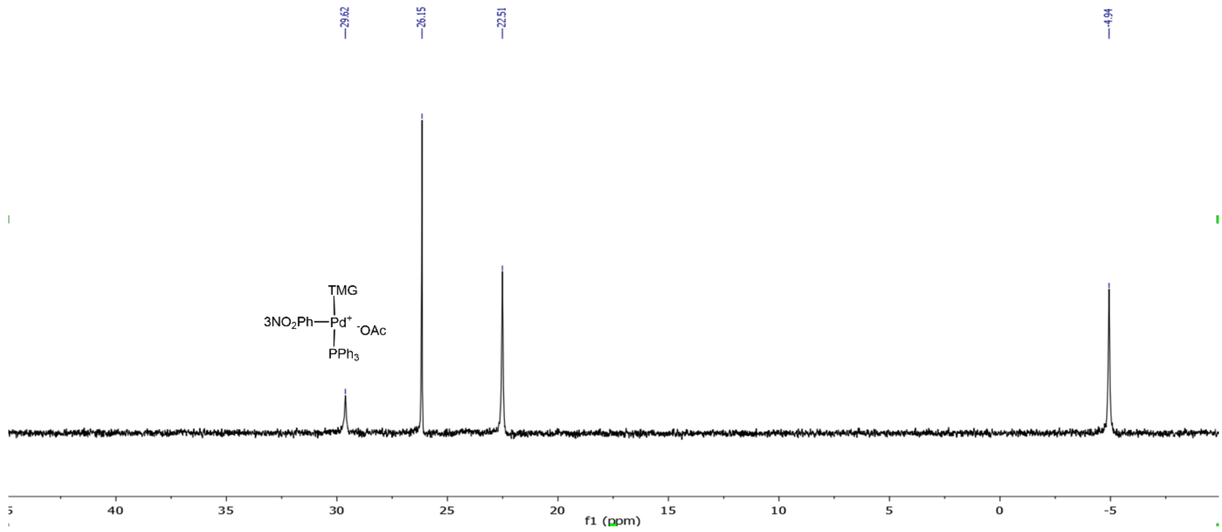
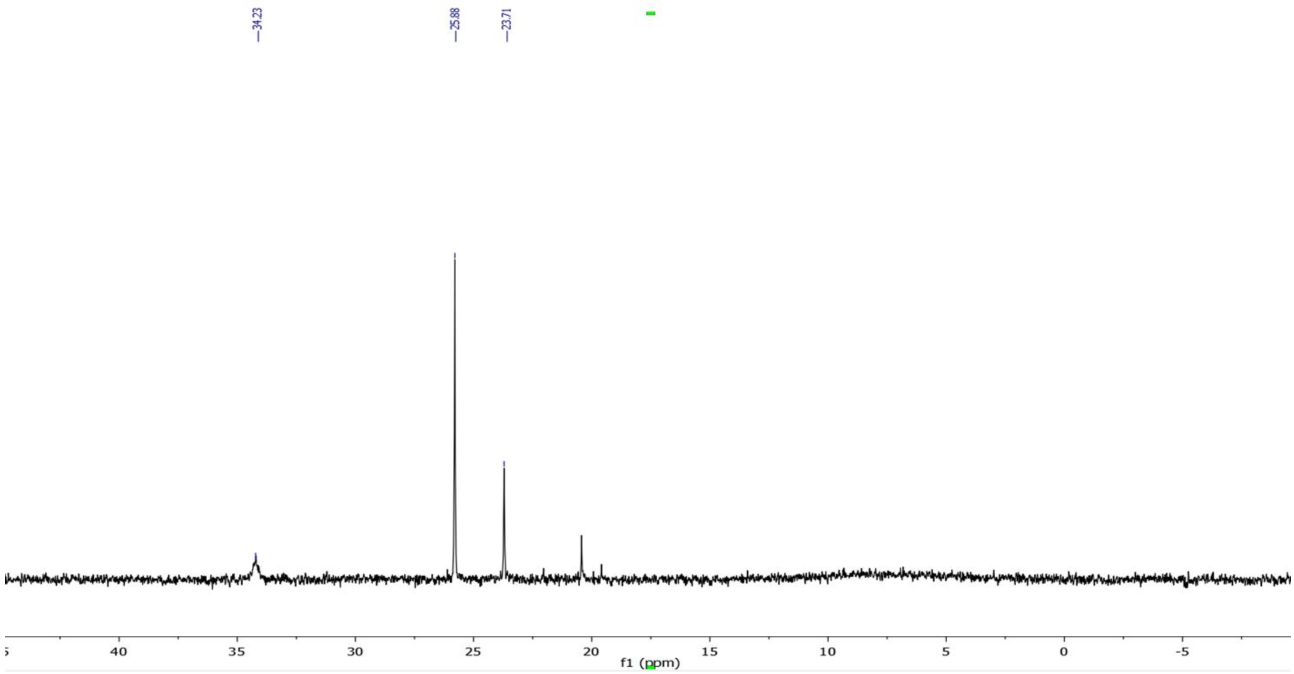


Figure S6. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min; b) + $3NO_2ArI$

Entry 4, Table S2:

a)



b)

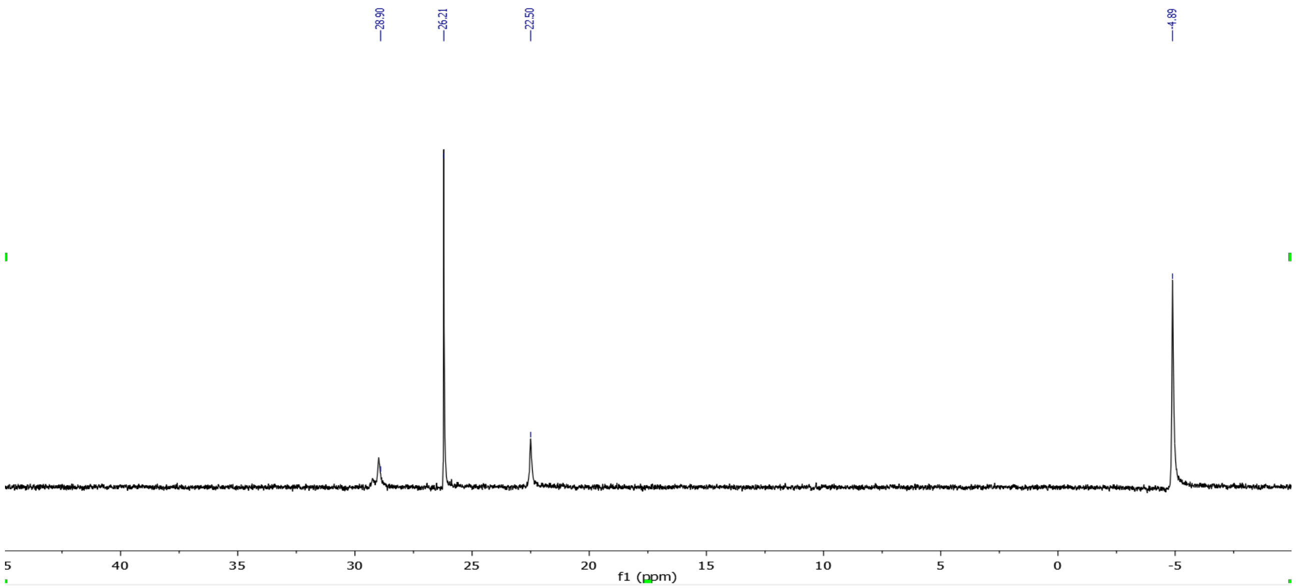
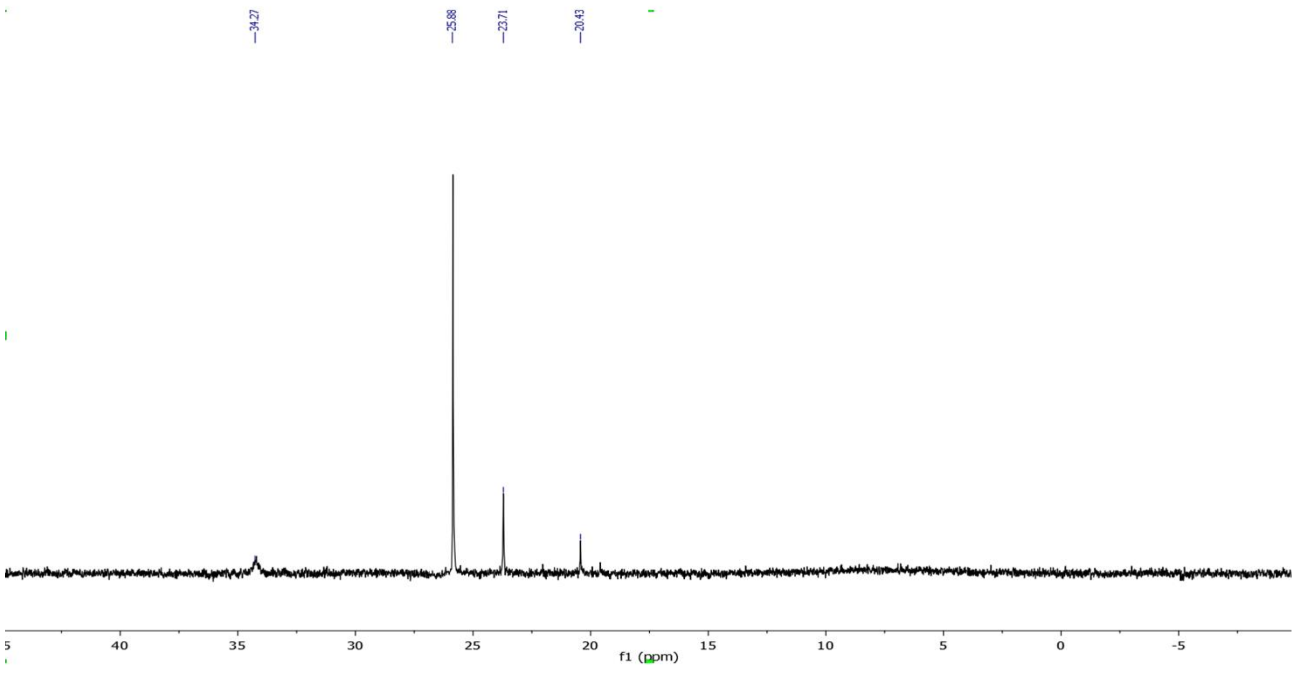


Figure S7. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + cyclohexylamine (5 equiv) in DMF-d_7 at rt in 20 min. b) + $3NO_2ArI$

Entry 5, Table S2:

a)



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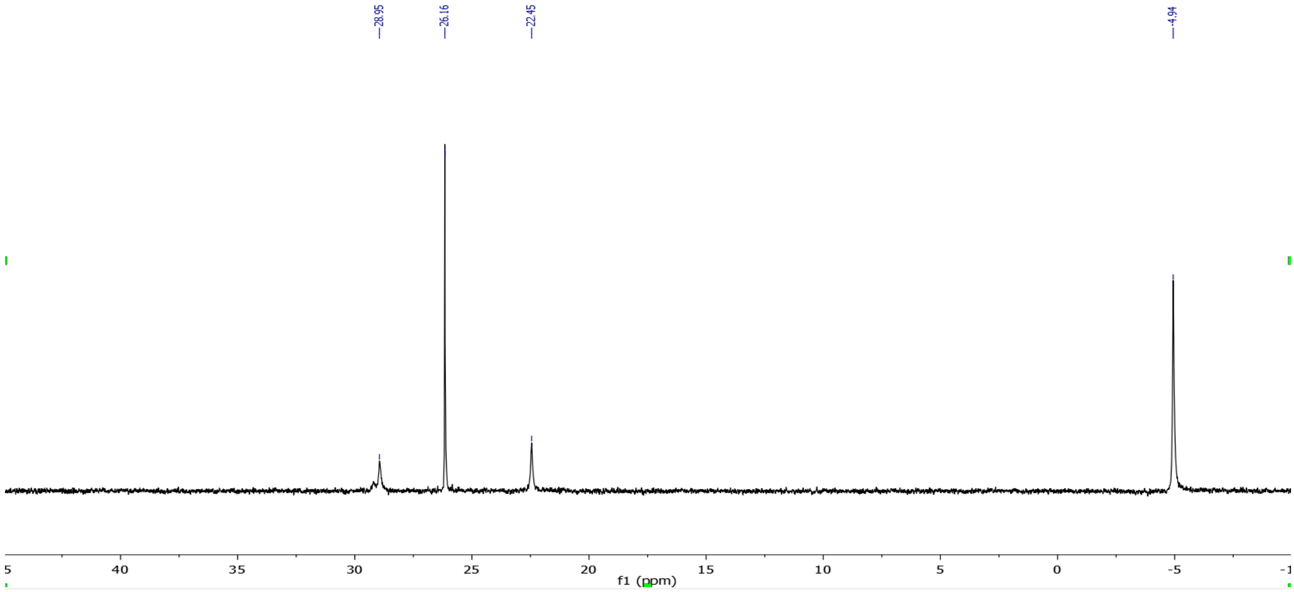
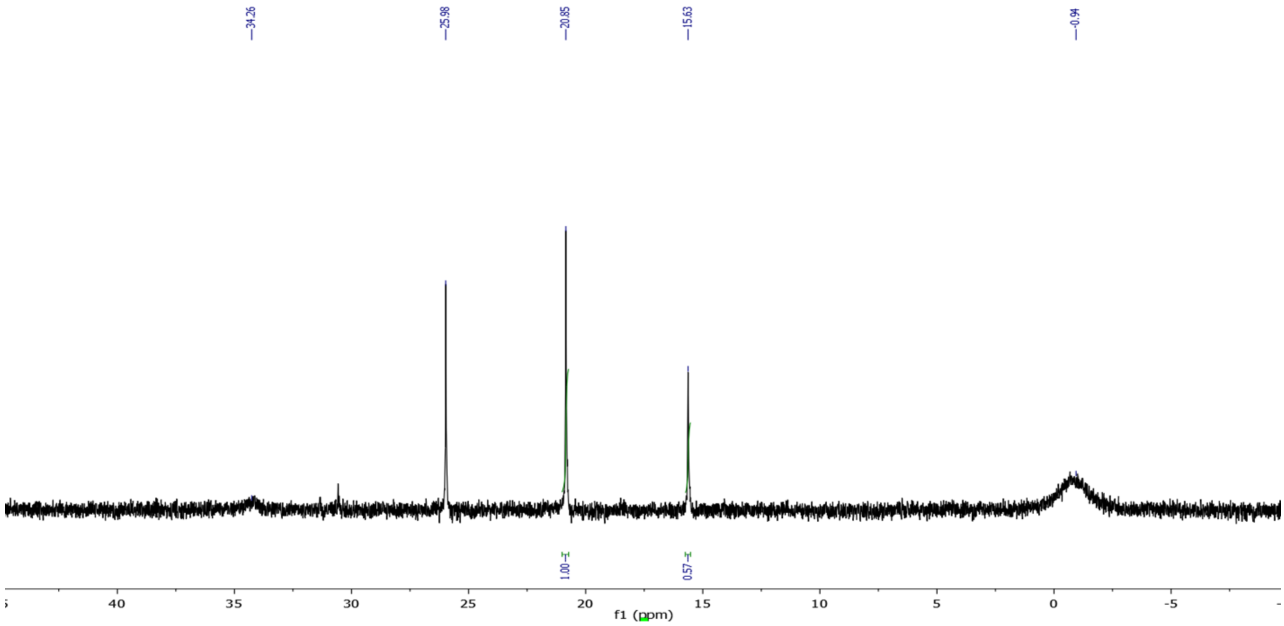


Figure S8. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + pyrrolidine (5 equiv) in DMF-d_7 at rt in 20 min. b) + $3NO_2ArI$

Entry 6, Table S2:
a)



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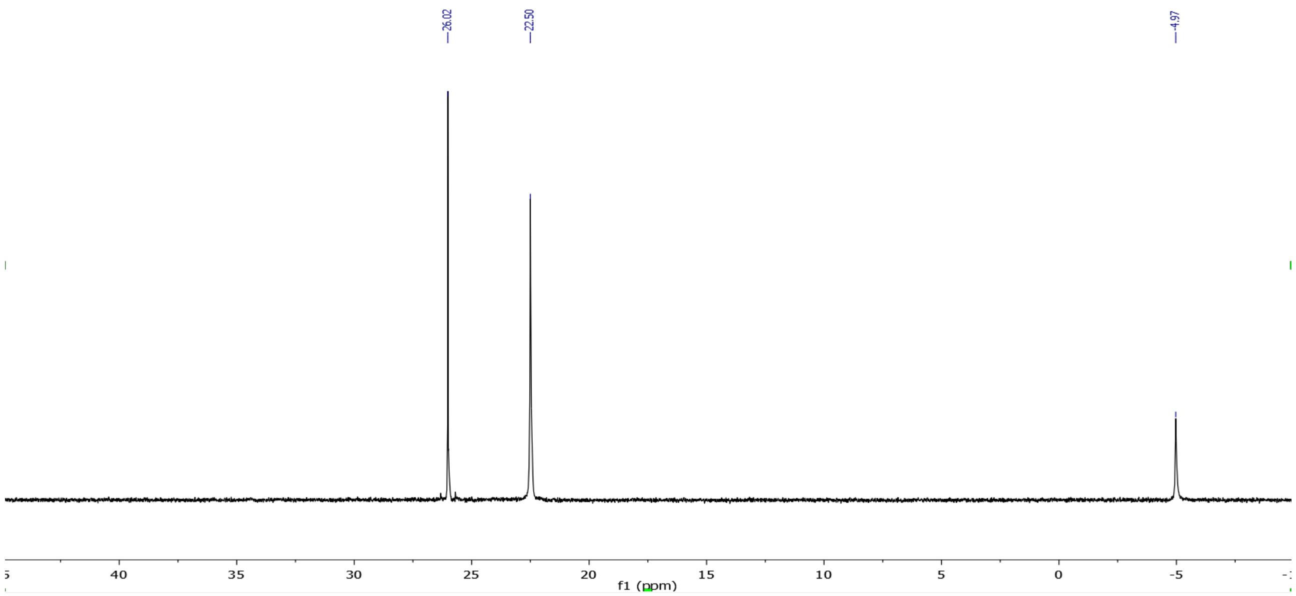
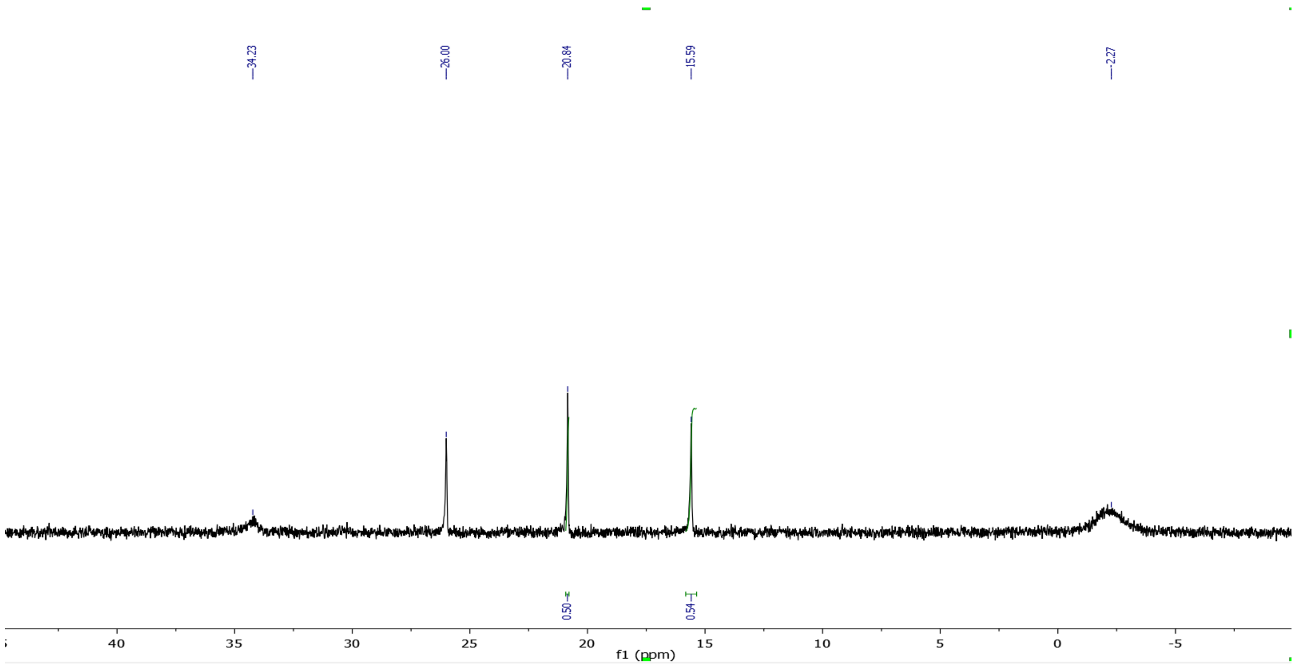


Figure S9. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at rt in 20 min. The peaks at 20.85 ppm and at 15.63 ppm are related to the IS, $Pd(PPh_3)_2(OAc)_2$. b) + $3NO_2ArI$. After the addition of the halide, the Pd(II) species sometimes disappeared, probably because the equilibrium shifted toward the formation of the oxidative addition complex, which consumed Pd(0) more rapidly.

Entry 7, Table S2:

a)



b)

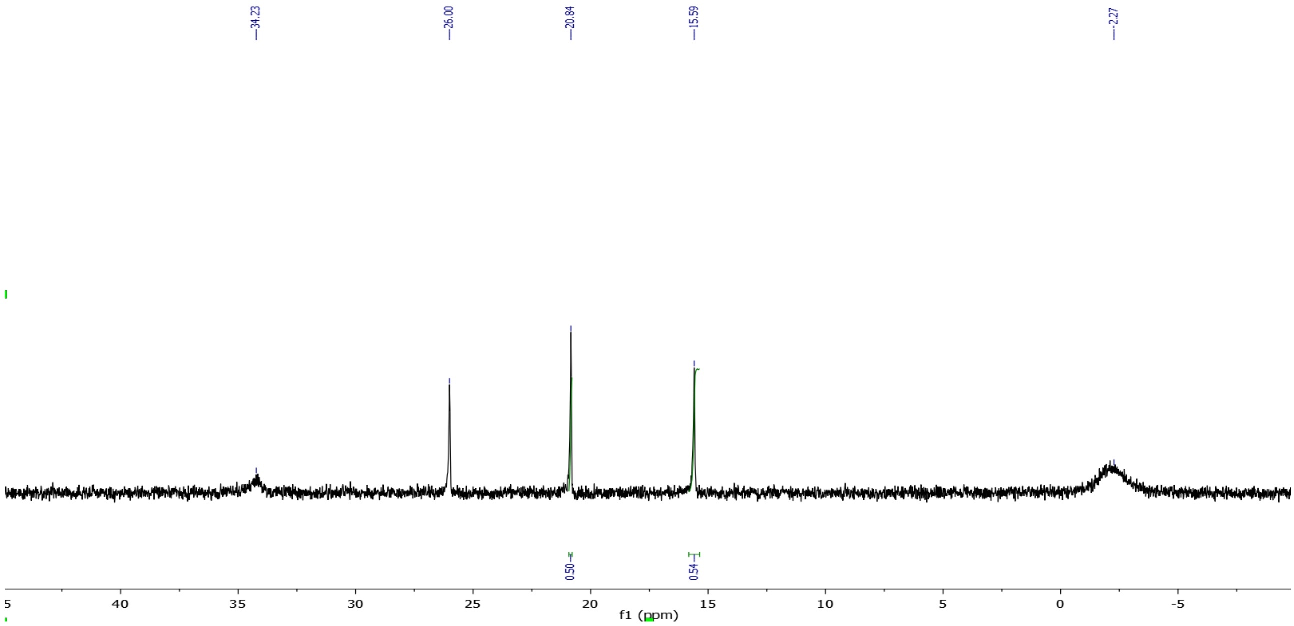


Figure S 10. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + K_2CO_3 (5 equiv) in DMF-d_7 at rt in 20 min. The peaks at 20.84 ppm and at 15.59 ppm are related to the IS, $Pd(PPh_3)_2(OAc)_2$. b) + $3NO_2ArI$. After the addition of the halide, the Pd(II) species sometimes disappeared, probably because the equilibrium shifted toward the formation of the oxidative addition complex, which consumed Pd(0) more rapidly.

Entry 8, Table S2:

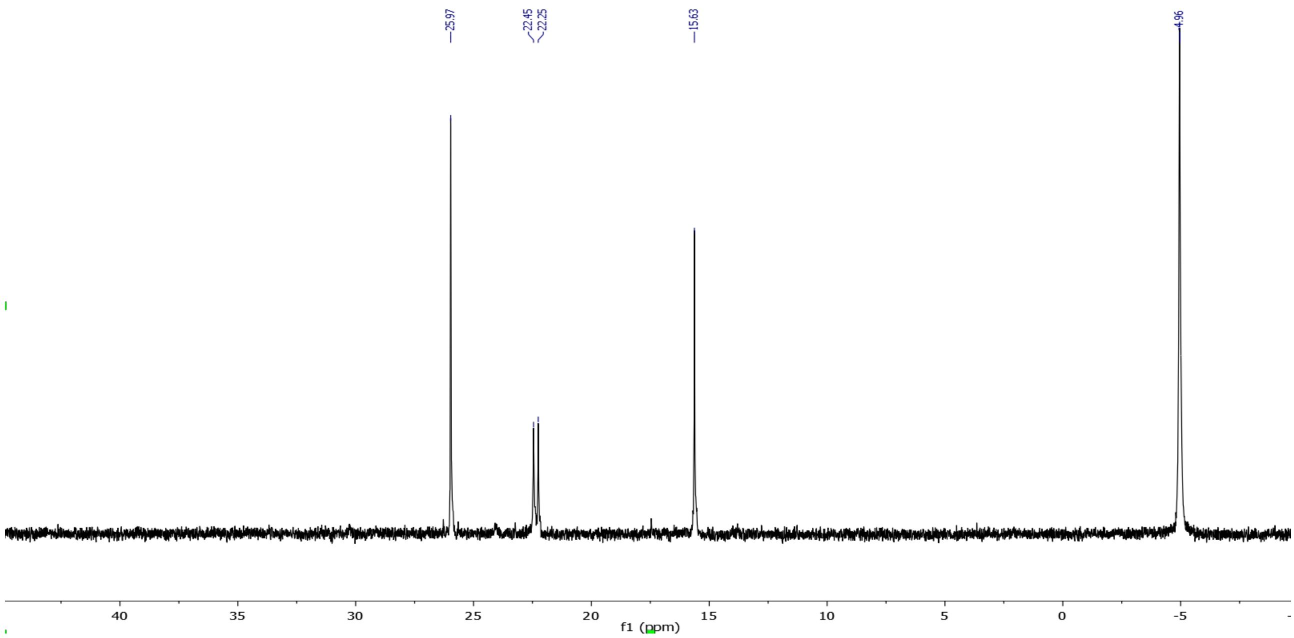
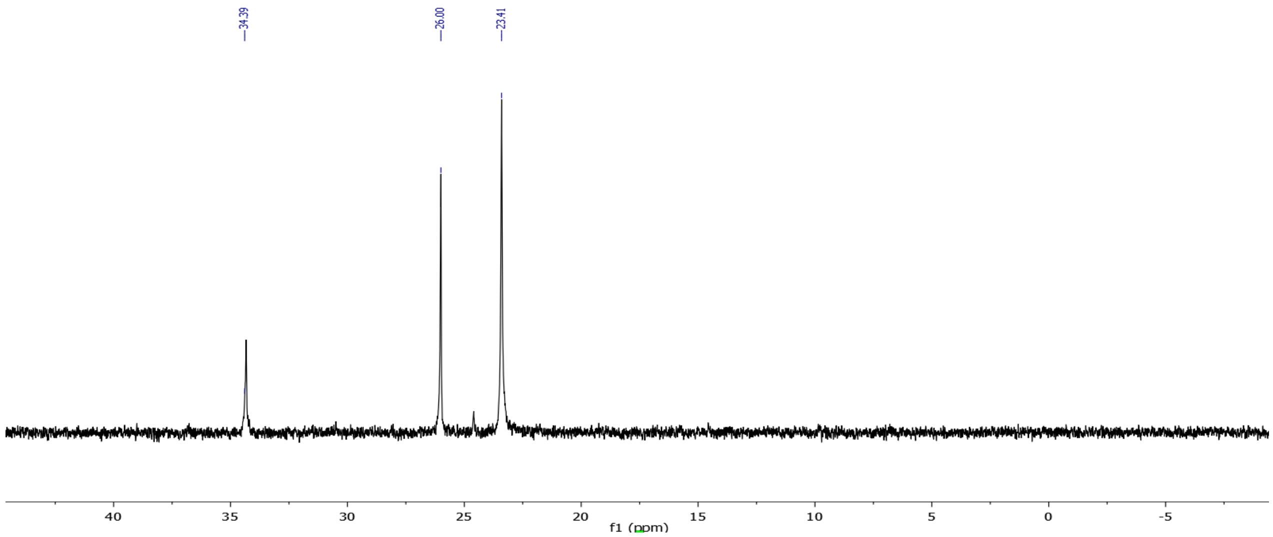


Figure S11. Figure S 12. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TEA (5 equiv) in DMF-d_7 at rt in 20 min. b) +$3NO_2ArI$

Entry 9, Table S2:

a)



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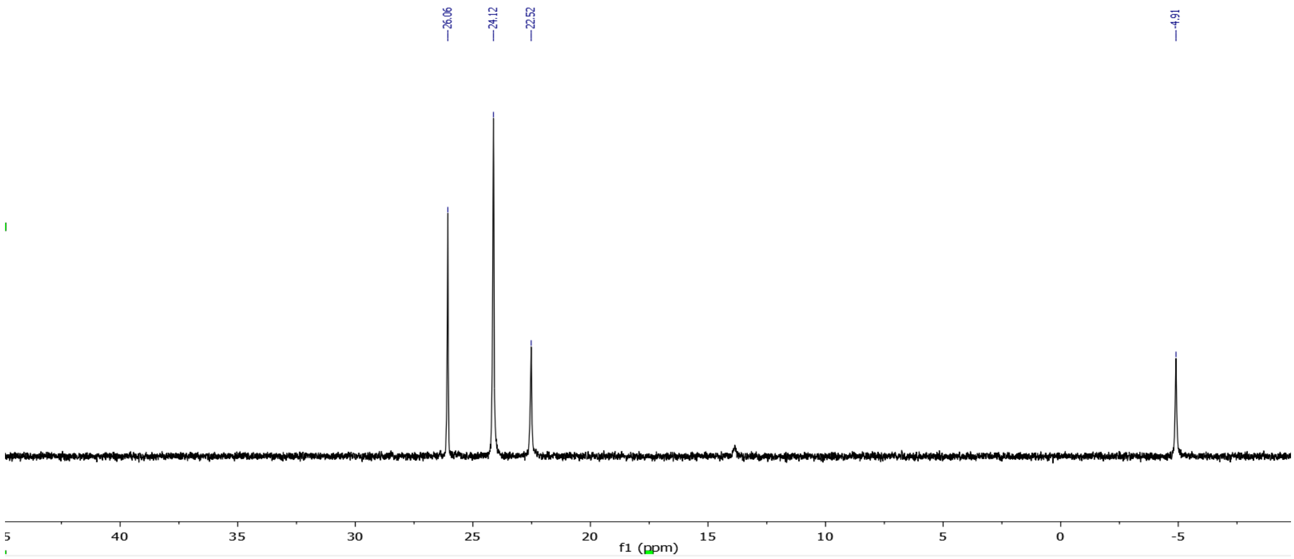
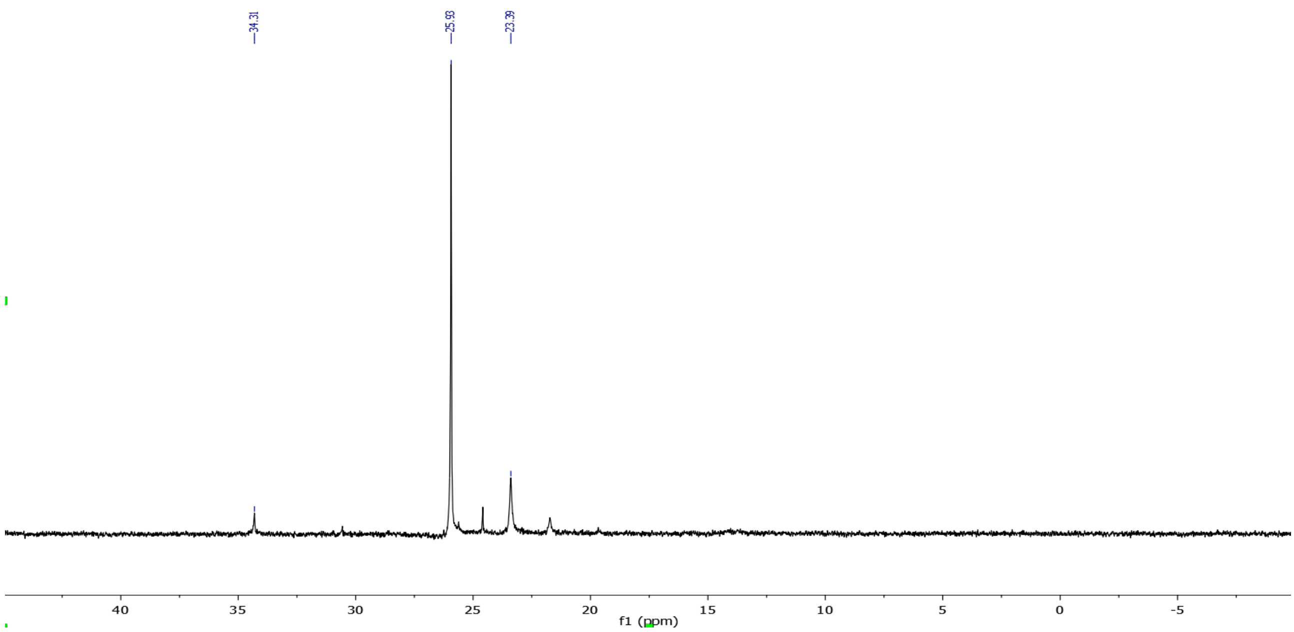


Figure S13. Figure S 14. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$.

Entry 10, Table S2:

a)



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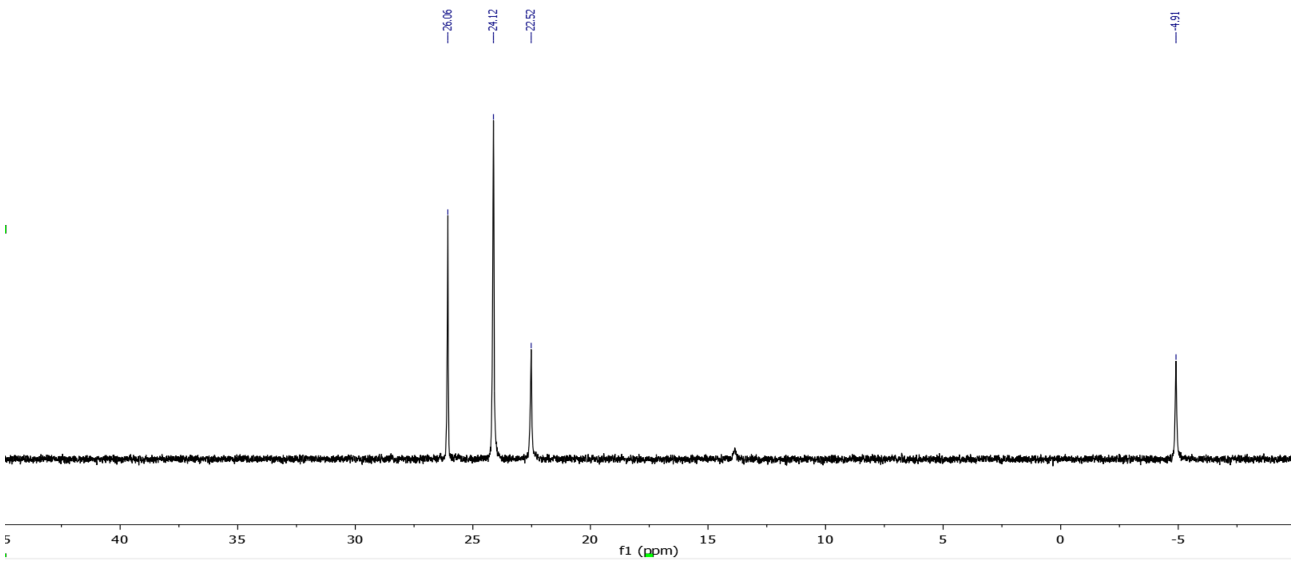
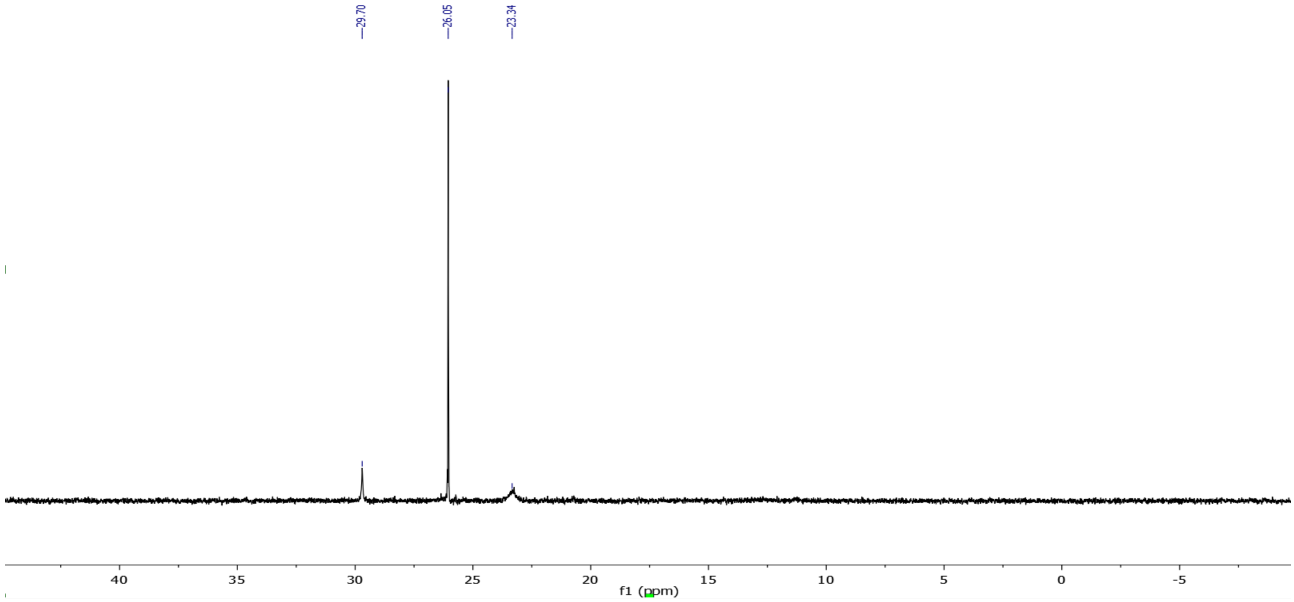


Figure S15. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + K_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + 3NO_2ArI.

Entry 11, Table S2:

a)



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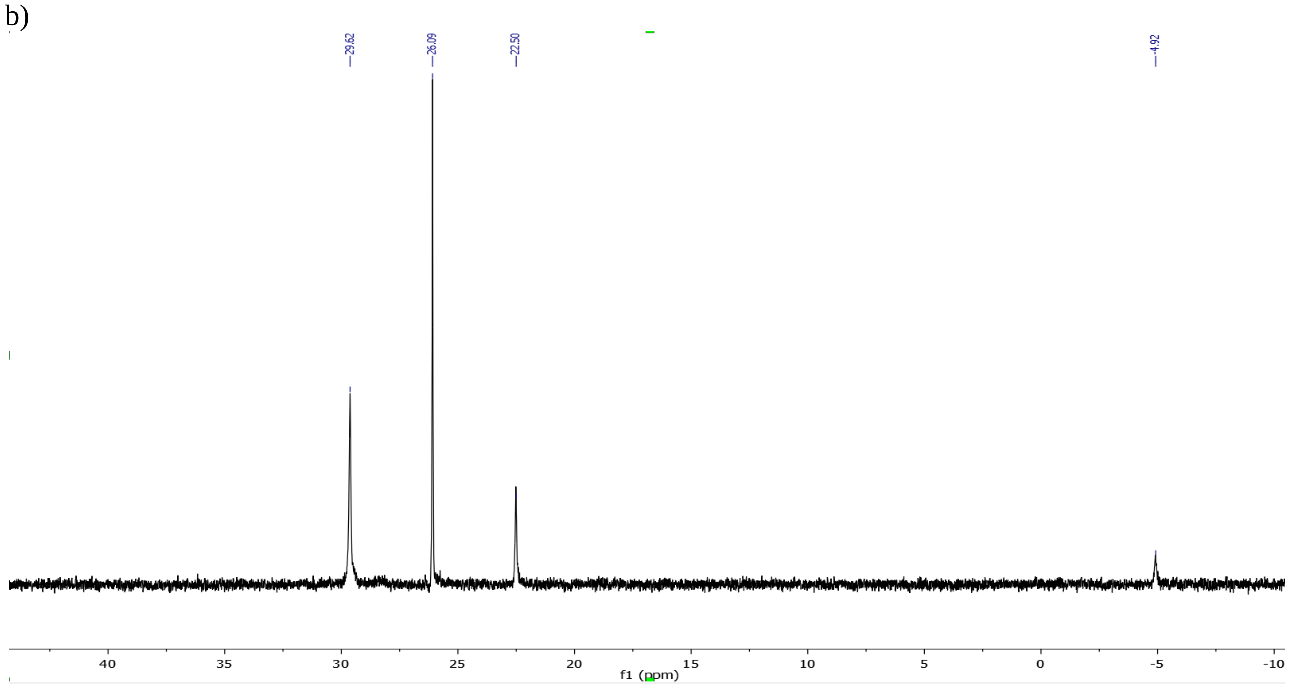
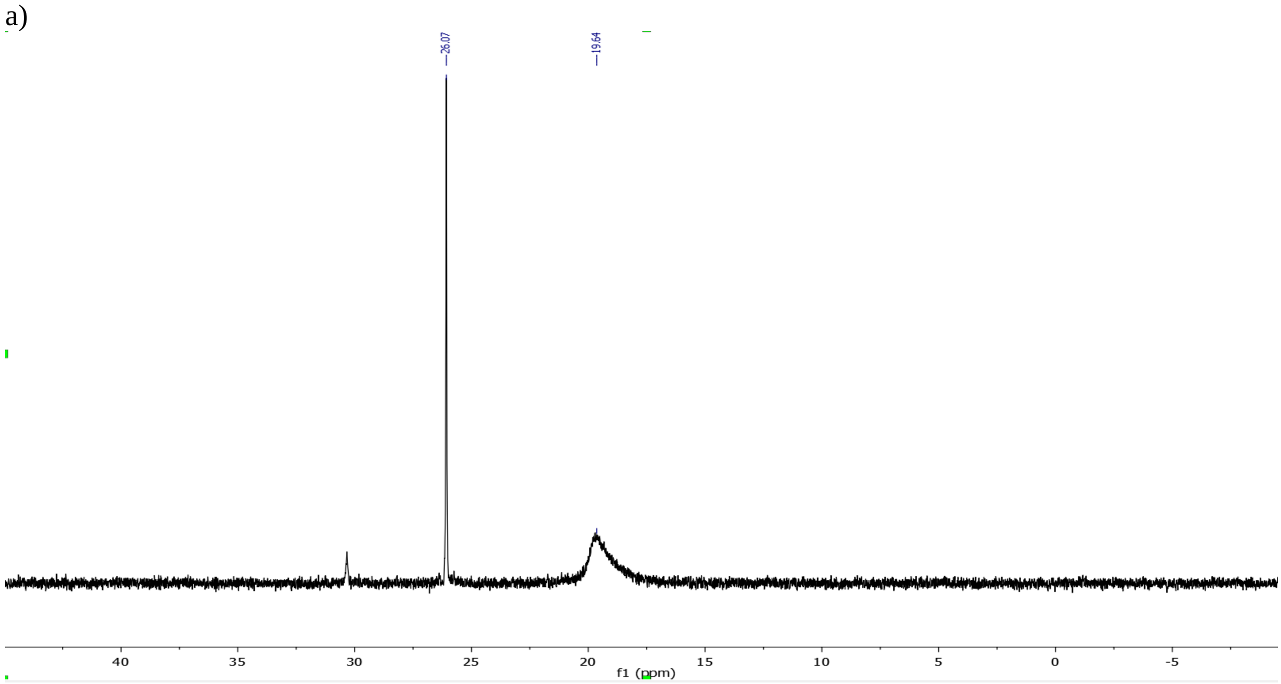


Figure S16. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TMG (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$.

Entry 12, Table S2:

a)



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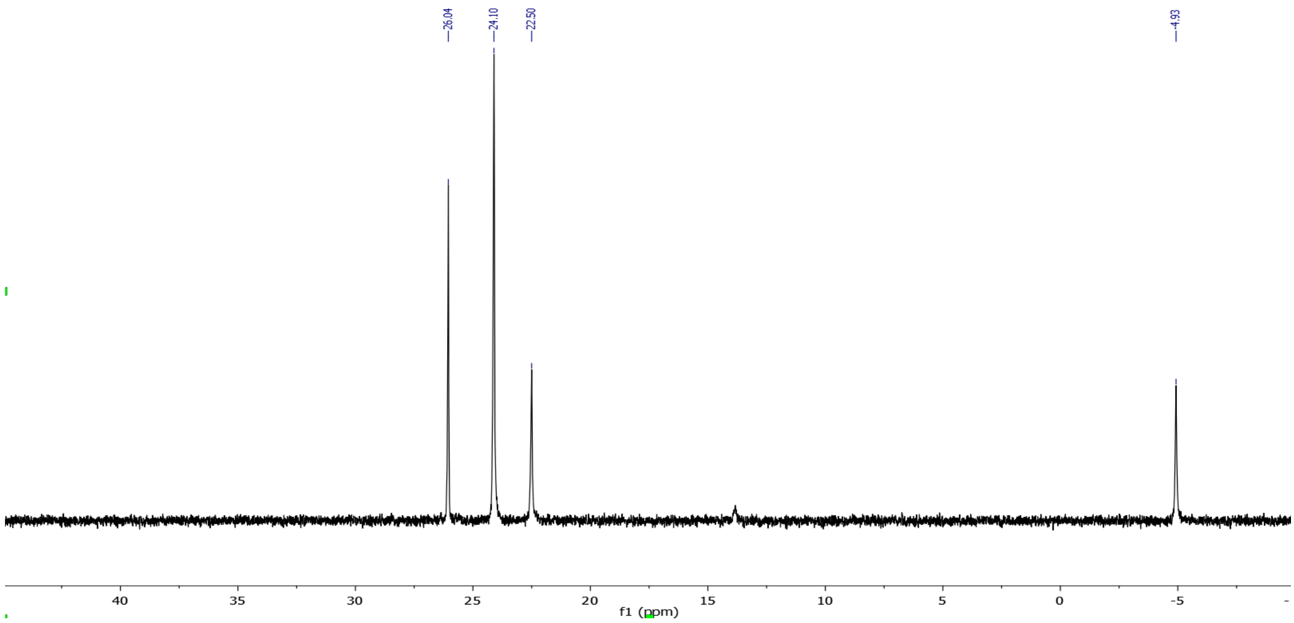
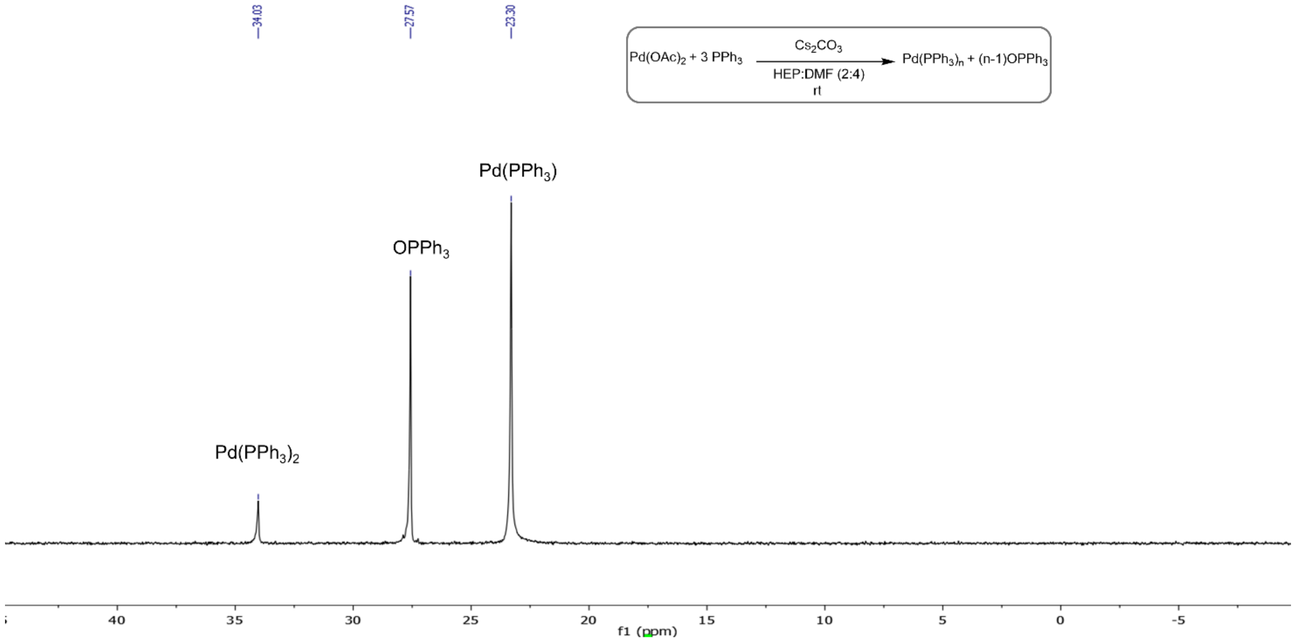


Figure S 17. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TEA (5 equiv) in DMF-d_7 at 80°C in 20 min. b) + $3NO_2ArI$.

Entry 15, Table S2**:** Completed reduction in HEP/DMF as example

a)



b)

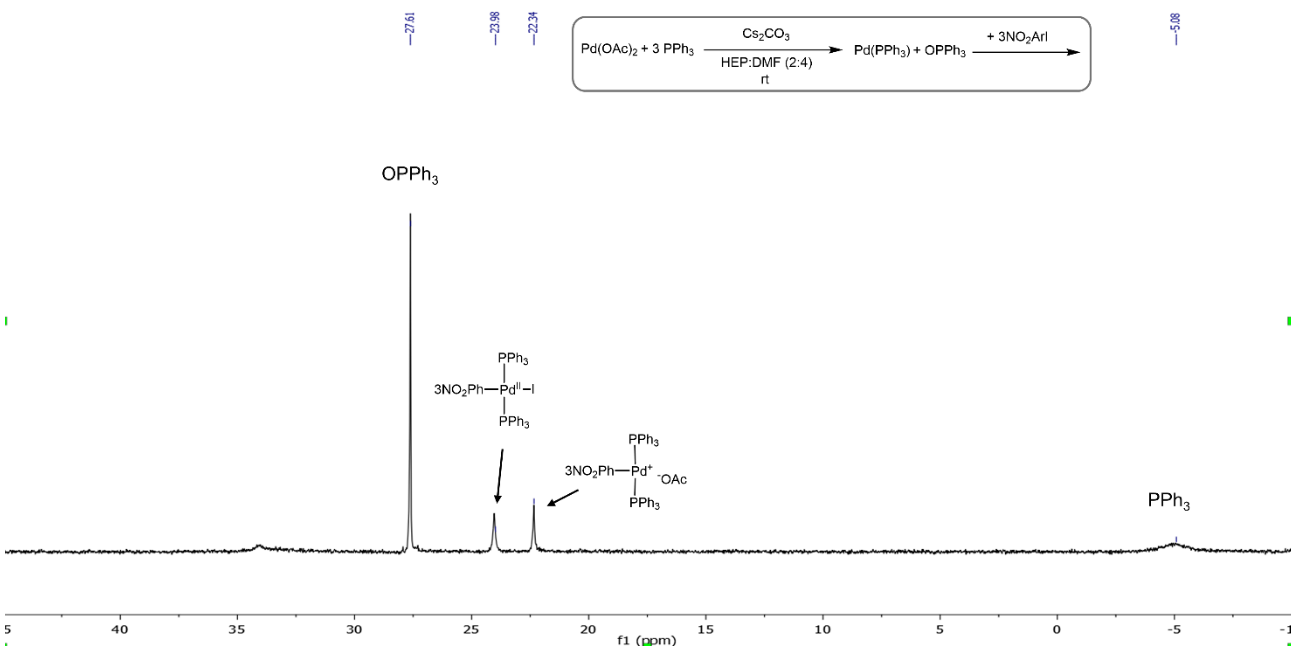
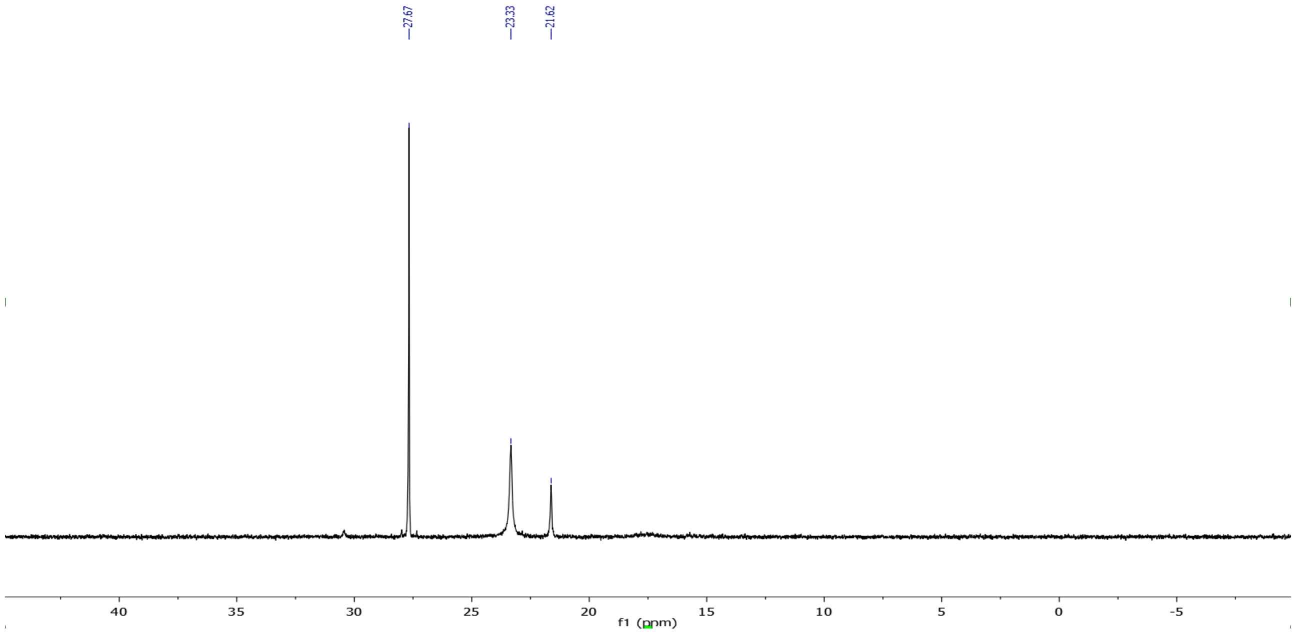


Figure S18. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + Cs_2CO_3 in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$

Other spectra

Entry 13, Table S2:

a)



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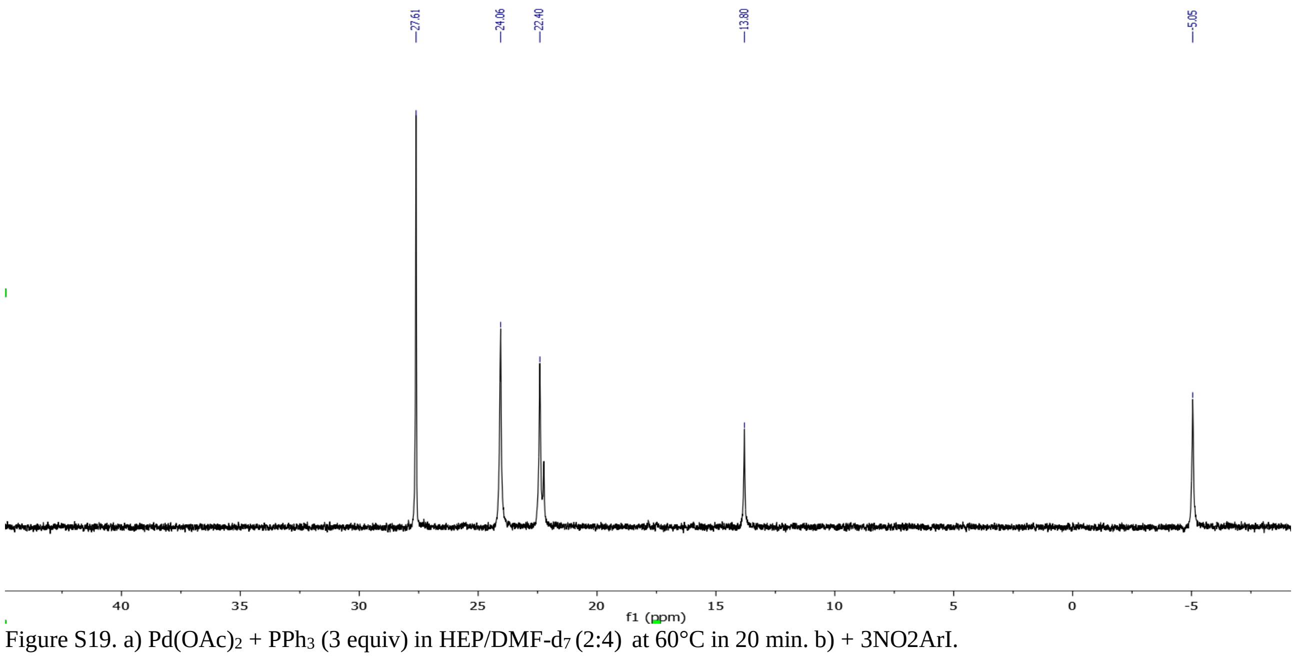
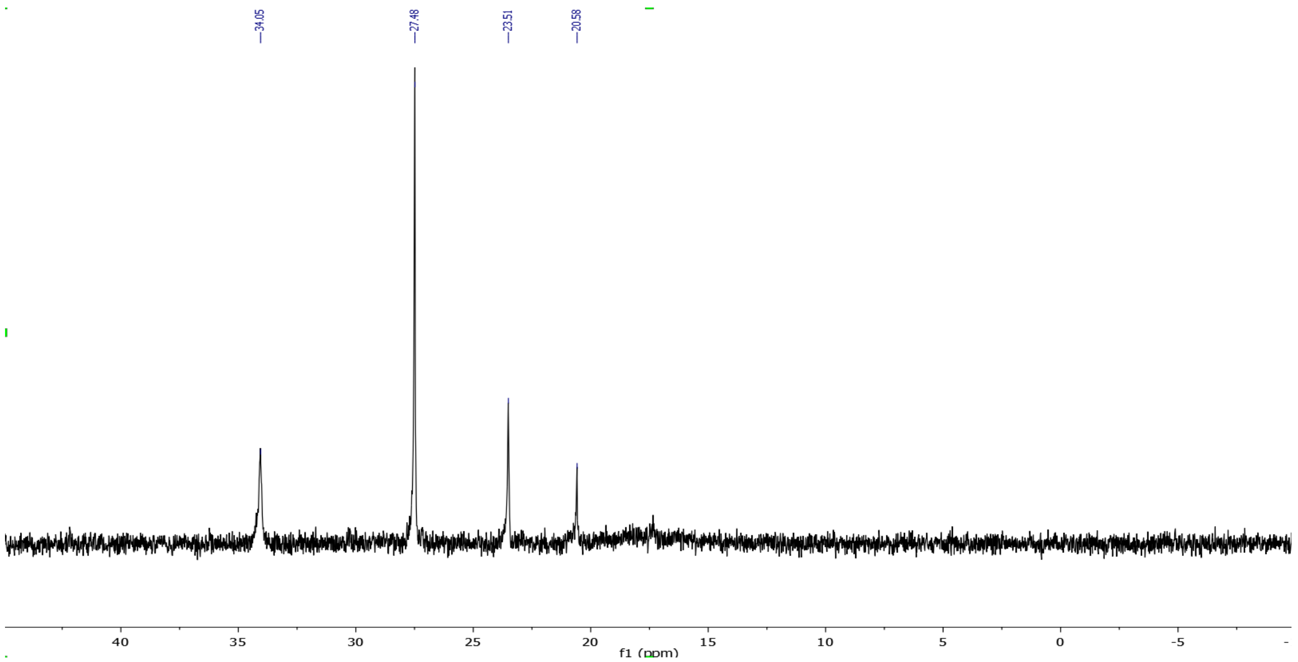


Figure S19. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + 3NO2ArI.

Entry 14, Table S2:
a)



b)

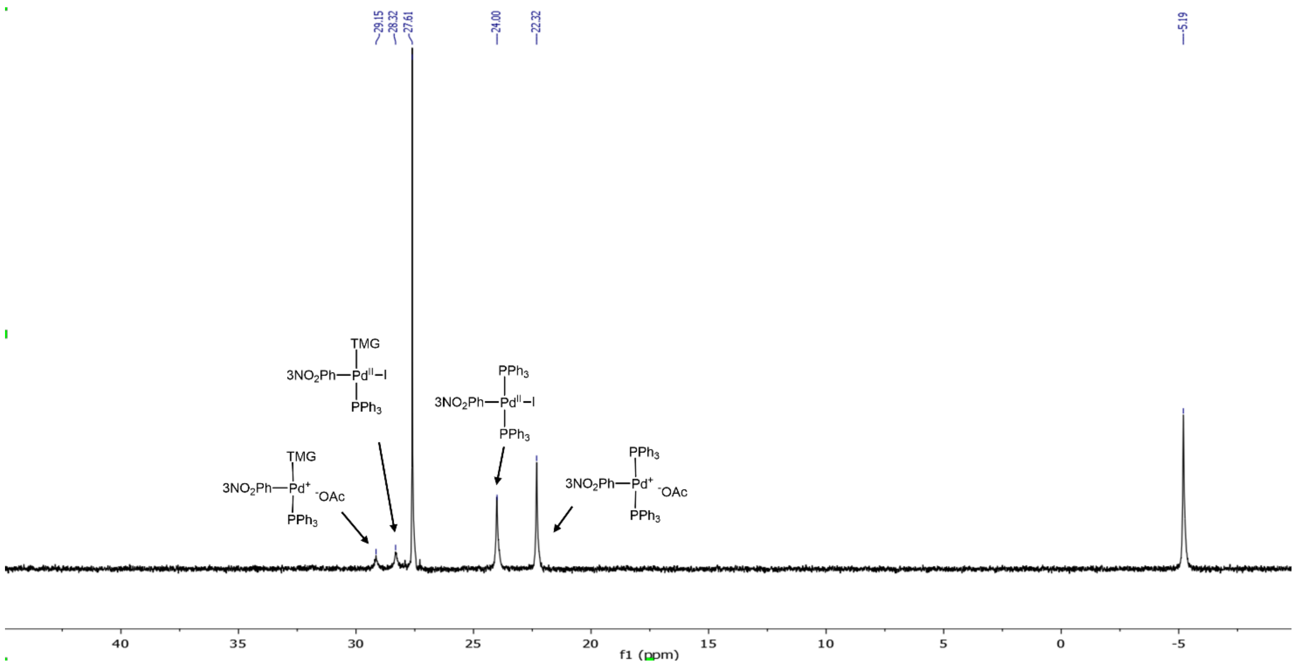


Figure S20. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TMG (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$.

Entry 16, Table S2:

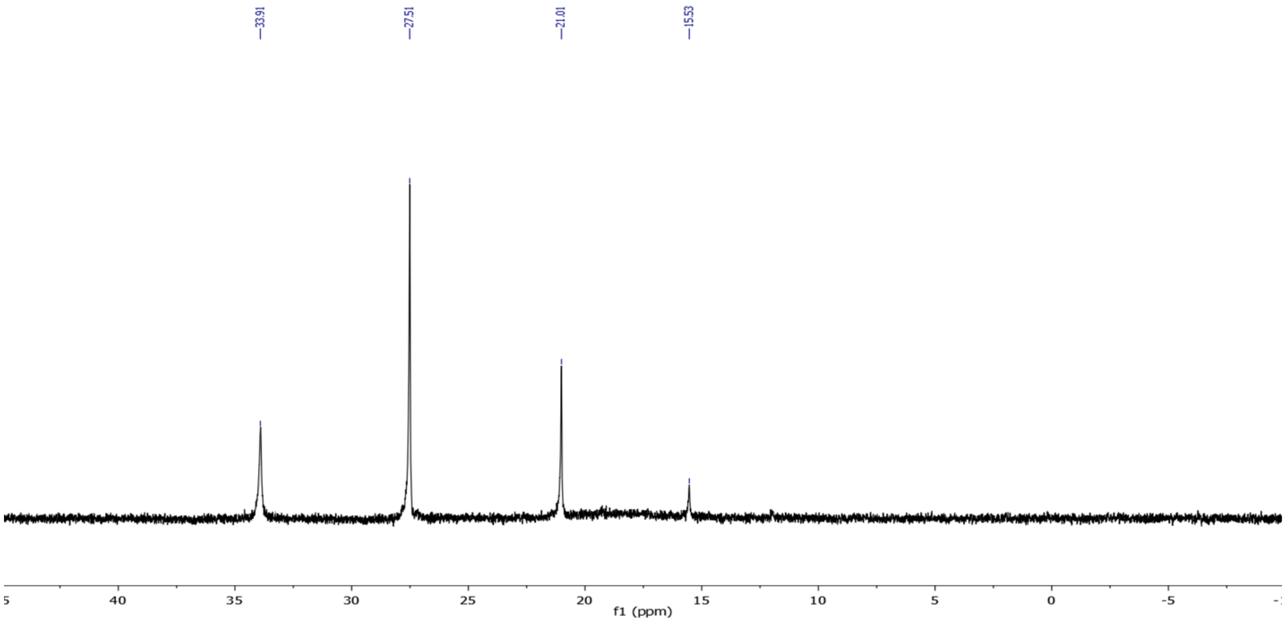
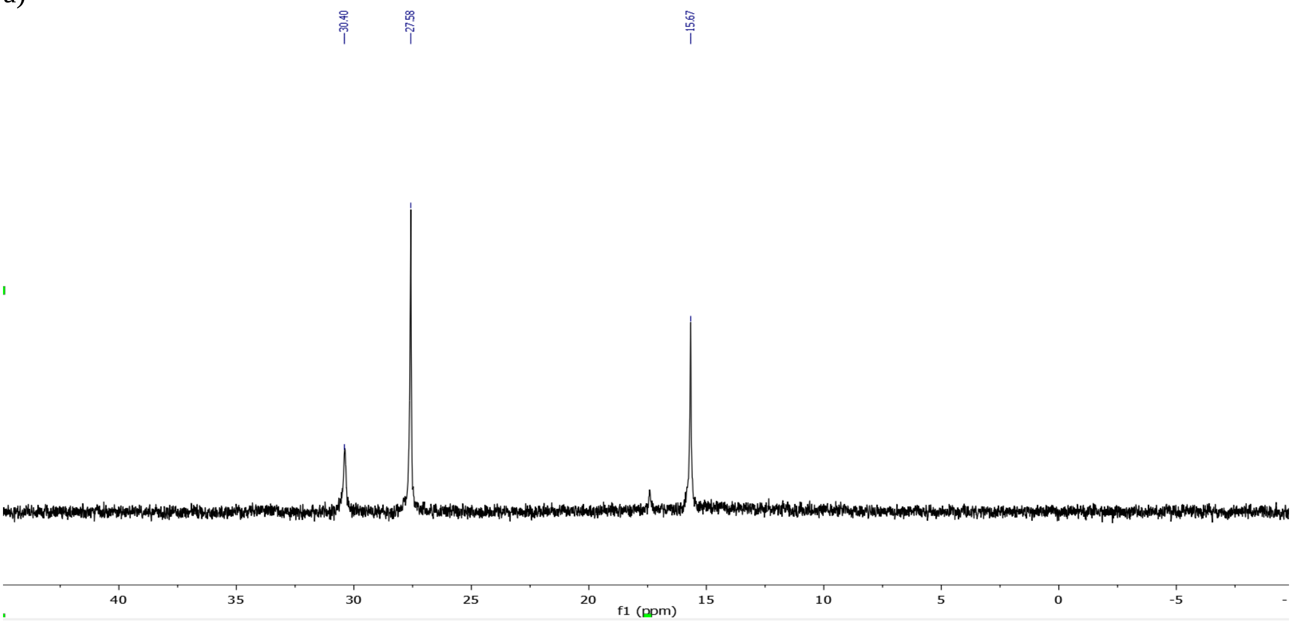


Figure S21. $Pd(OAc)_2$ + PPh_3 (3 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min

Entry 17, Table S2:
a)



b)

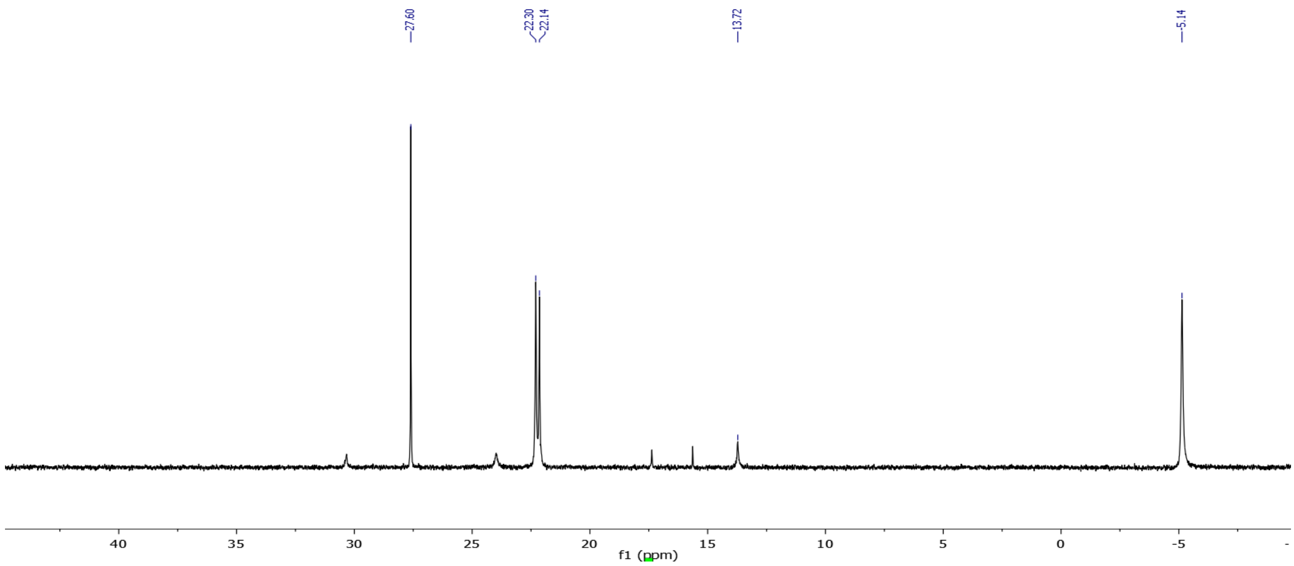
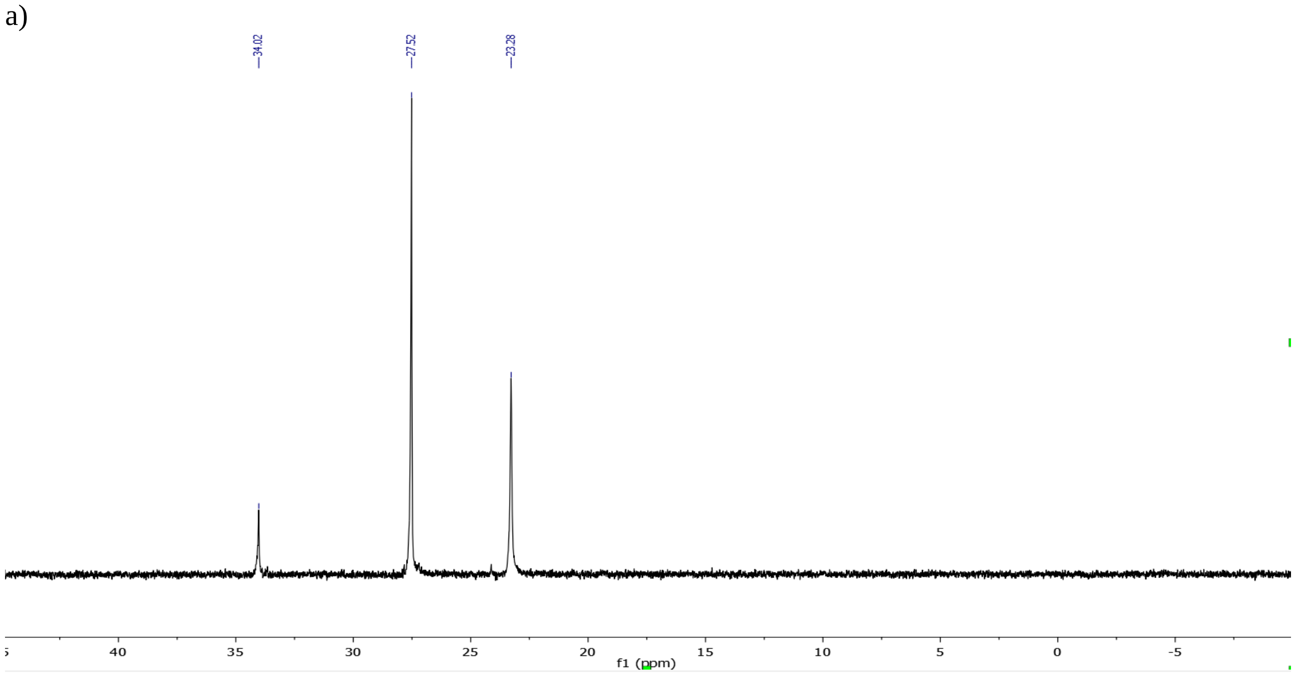


Figure S22. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TEA (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$.

Entry 18, Table S2:

a)



b)

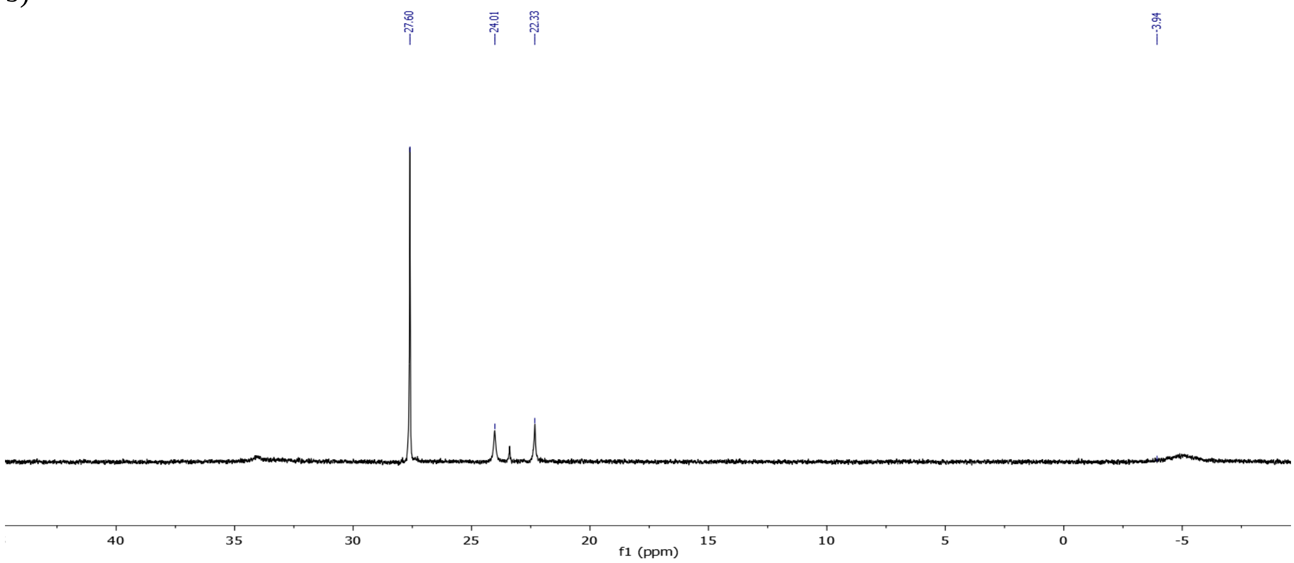
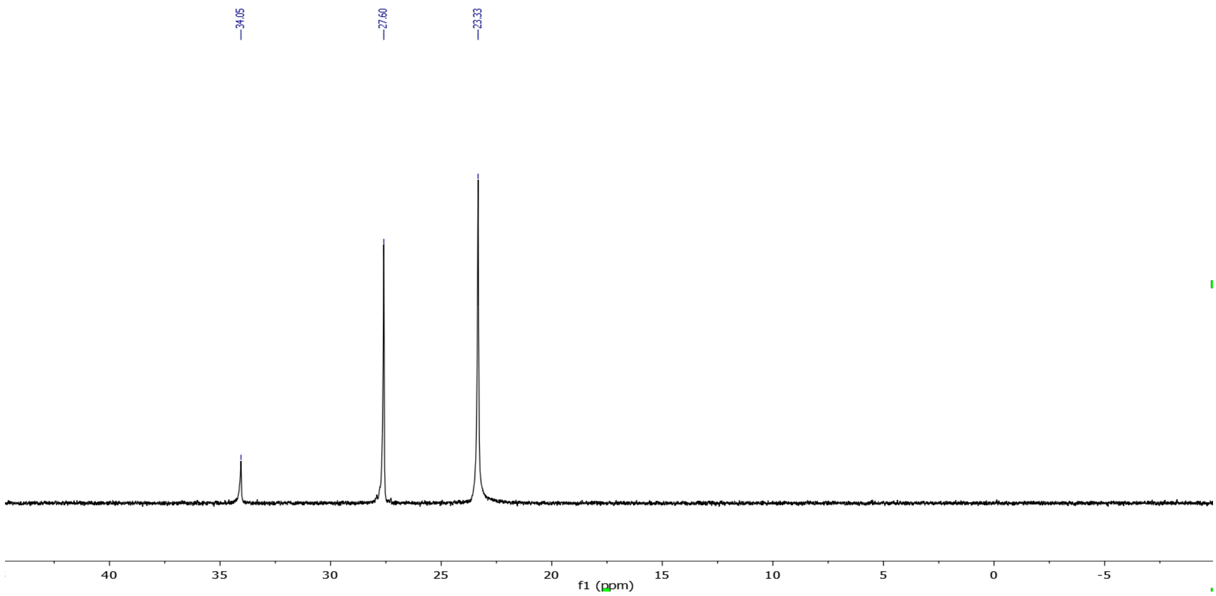


Figure S23. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$.

Entry 19, Table S2:

a)



b)

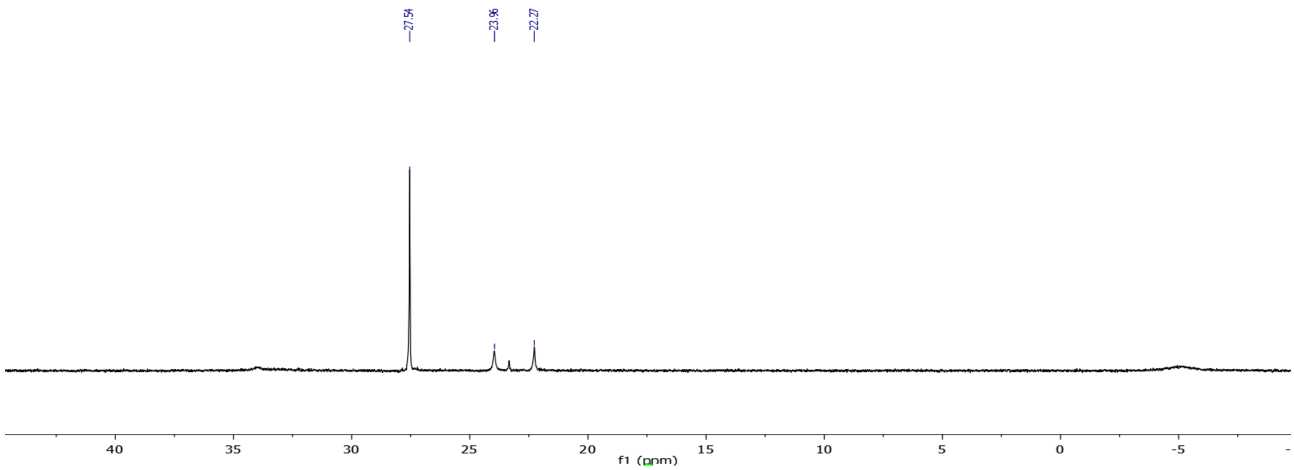
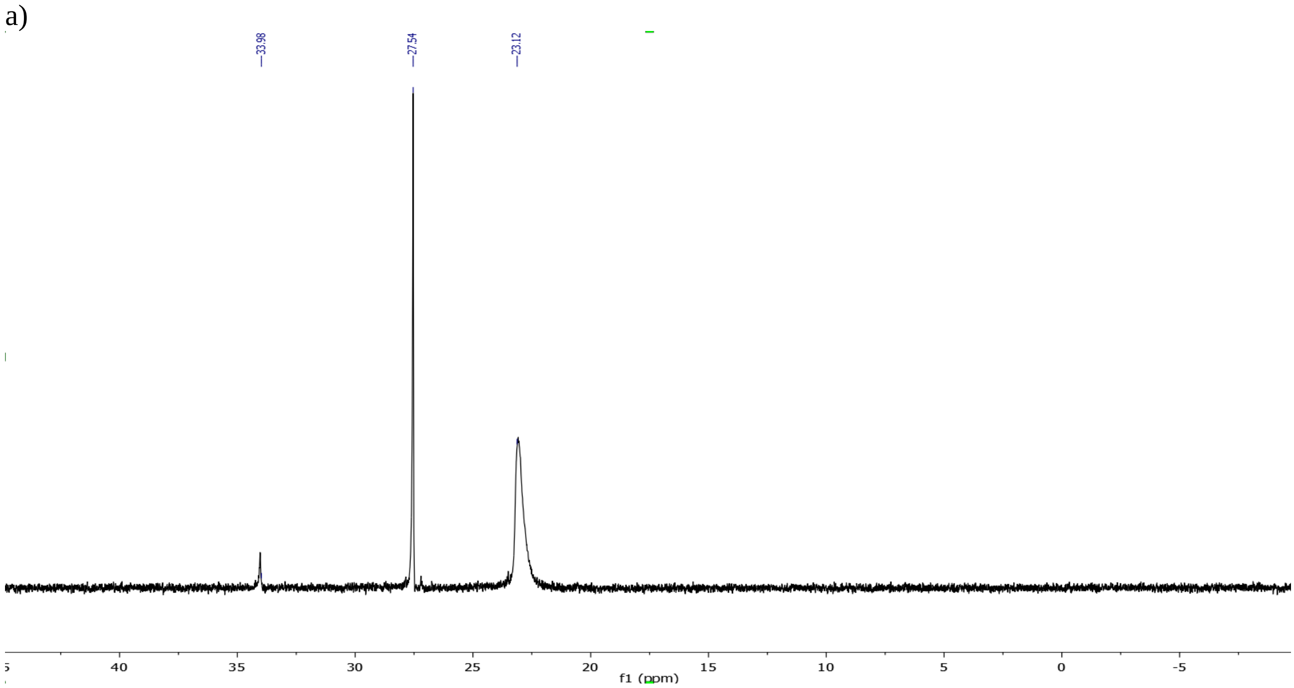


Figure S24. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$.

Entry 20, Table S2:

a)



b)

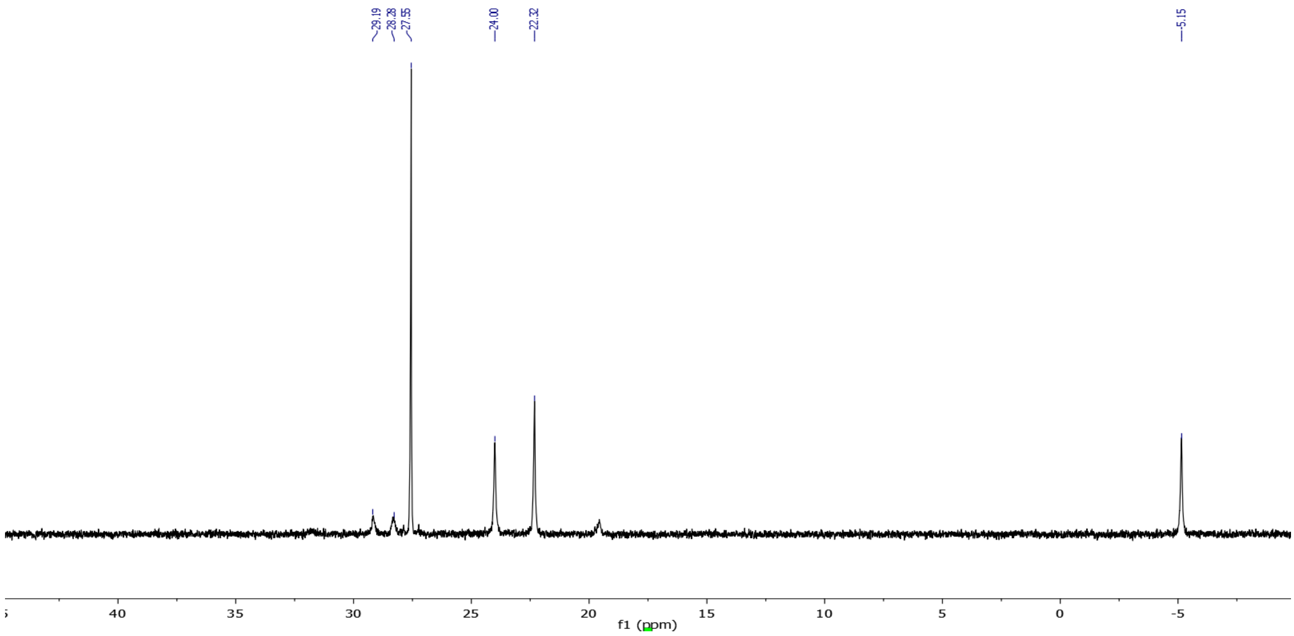


Figure S25. a) $Pd(OAc)_2$ + PPh_3 (3 equiv) + TMG (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$.

1.3. $PdCl_2$

1.3.1. General Procedure 2

$$Pd(PPh_3)_2Cl_2 + PPh_3 \xrightarrow[\text{Solvent, T (°C)}]{\text{Base (5 equiv)}} Pd(PPh_3)_n + \text{n-1 } OPPh_3/PPh_3$$

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(PPh_3)_2Cl_2$ (9.12 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Triphenylphosphine (3.41 mg, 0.013 mmol, 1 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.013 mmol, 1 equiv) was added as internal standard (IS).
To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1]

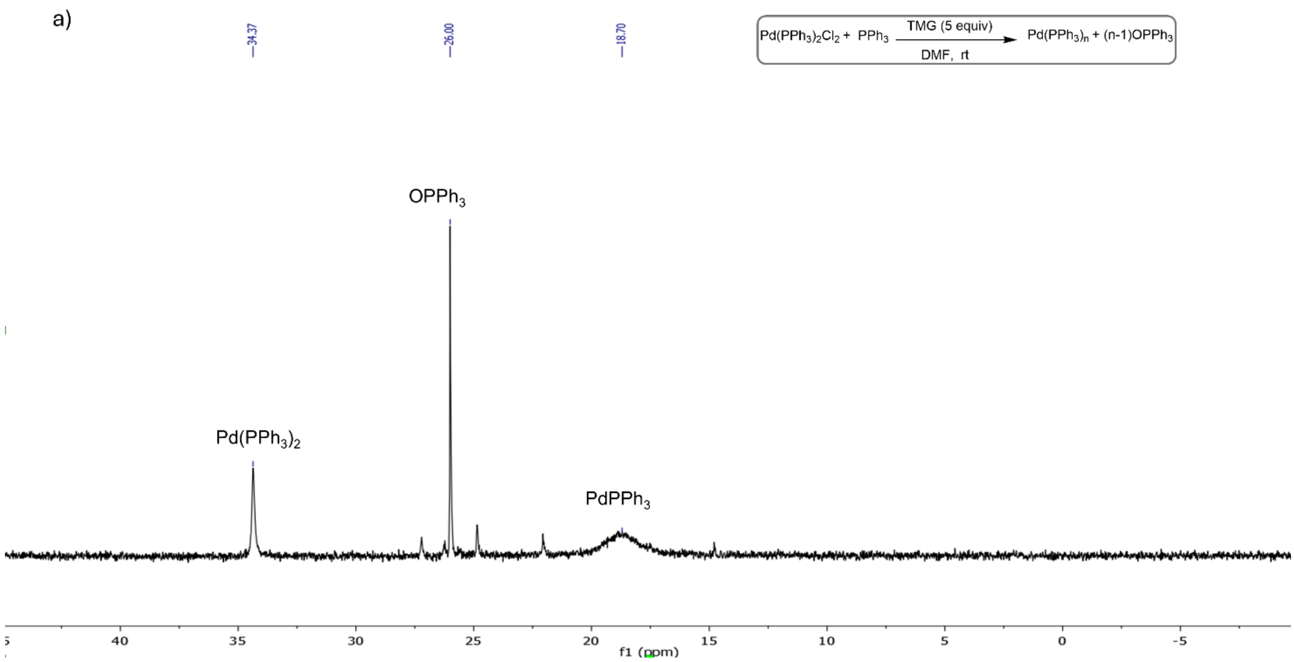
Table S3. $Pd(PPh_3)_2Cl_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

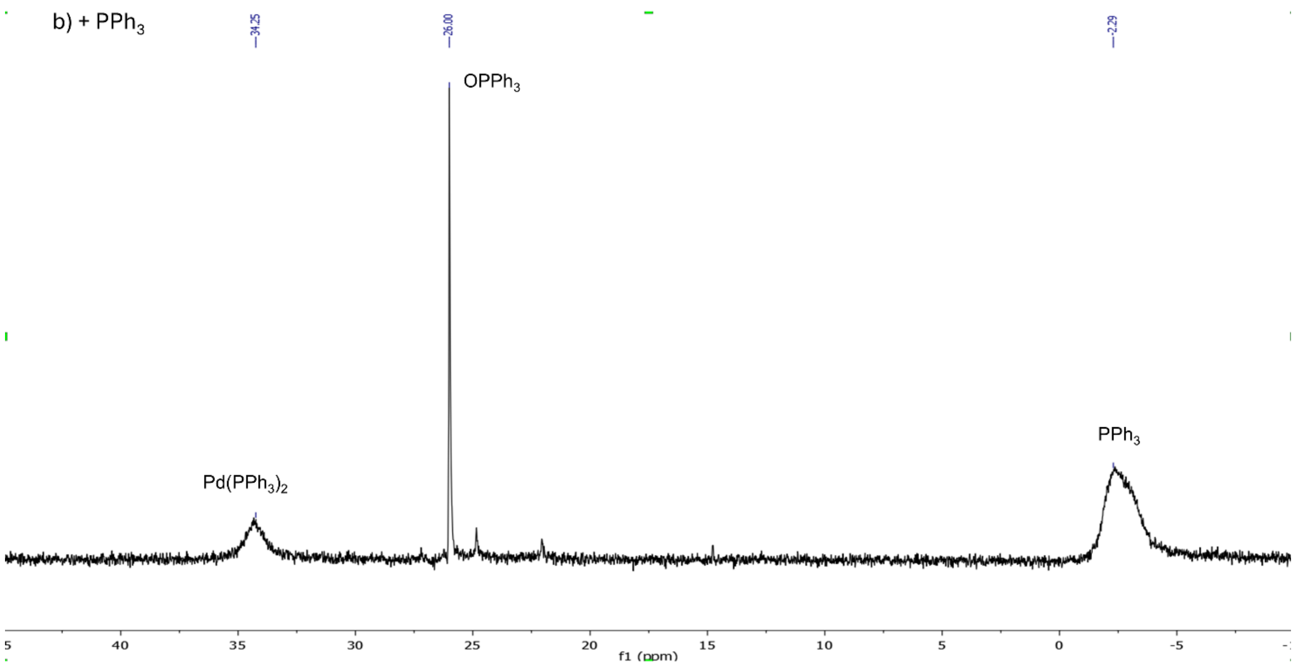
entry	Base	Solvent	T(°C)	Mech	Pd^0/Pd^{2+} [b]	P/OH[c]
1	-	DMF[d]	60	-	0/100	
2	TMG	DMF	25	D	100/0	100/0
3	cyclohexylamine	DMF	25	D	100/0	100/0
4	Pyrrolidine	DMF	25	D	100/0	100/0
5	Cs_2CO_3	DMF	25	-	0/100	-
6	TEA	DMF	25	-	0/100	-
7	Cs_2CO_3	DMF	60	E	34/66	100/0
8	K_2CO_3	DMF	60	E	12/88	100/0
9	TEA	DMF	80	-	0/100	-
10	Cs_2CO_3	DMF/HEP[e]	25	A	100/00	0/100
11	K_2CO_3	DMF/HEP	25	A	28/72	0/100
12	TMG	DMF/HEP	25	A+D	100/0	n.d.[d]
13	TEA	DMF/HEP	25	-	0/100	-
14	Cs_2CO_3	DMF/HEP	60	A+D	100/0	n.d.[d]
15	K_2CO_3	DMF/HEP	60	A+D	100/0	n.d.[d]

[a] The reactions were carried out according to the **General Procedure 2**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $PdCl_2(PPh_3)_2$
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

1.3.2. ^{31}P NMR spectra

Entry 2, Table S3: Completed reduction in DMF as example





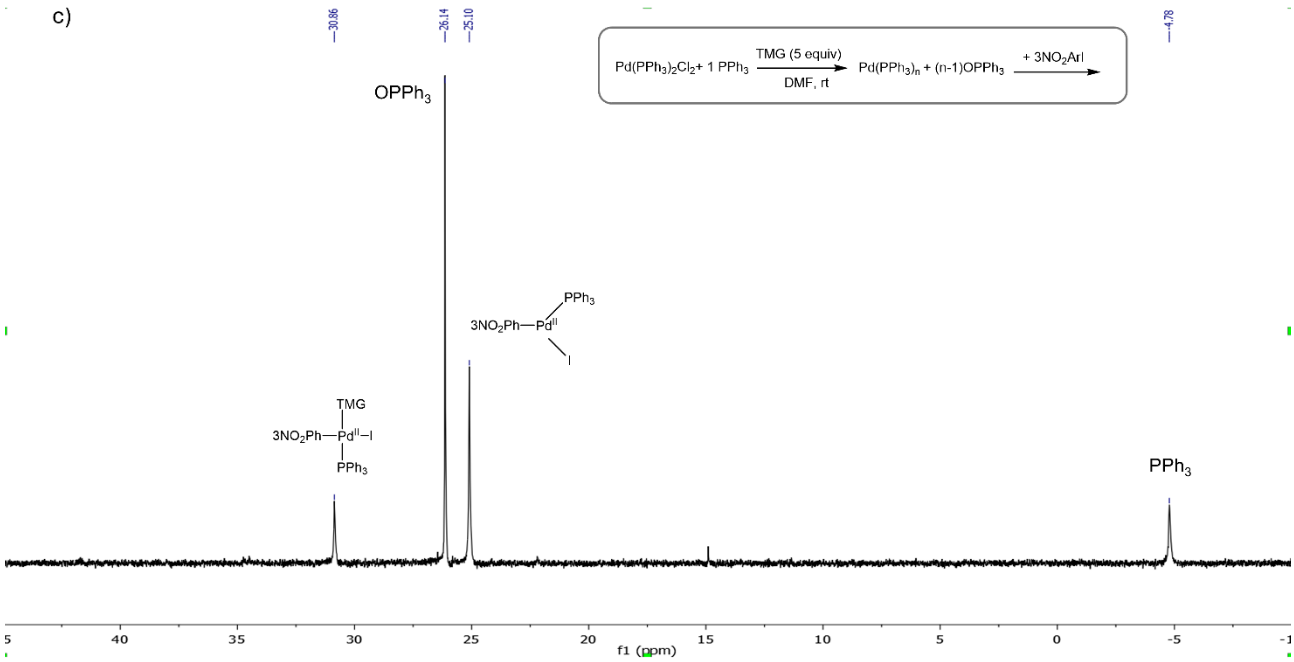


Figure S26. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min. The resonance at 18.70 ppm has been assigned to a Pd(0) specie and this was confirmed by adding PPh_3. After the addition, the peak at +18.70 disappeared (NMR spectrum b) + $3NO_2ArI$

Other spectra

Entries 1 and 6, Table S3:

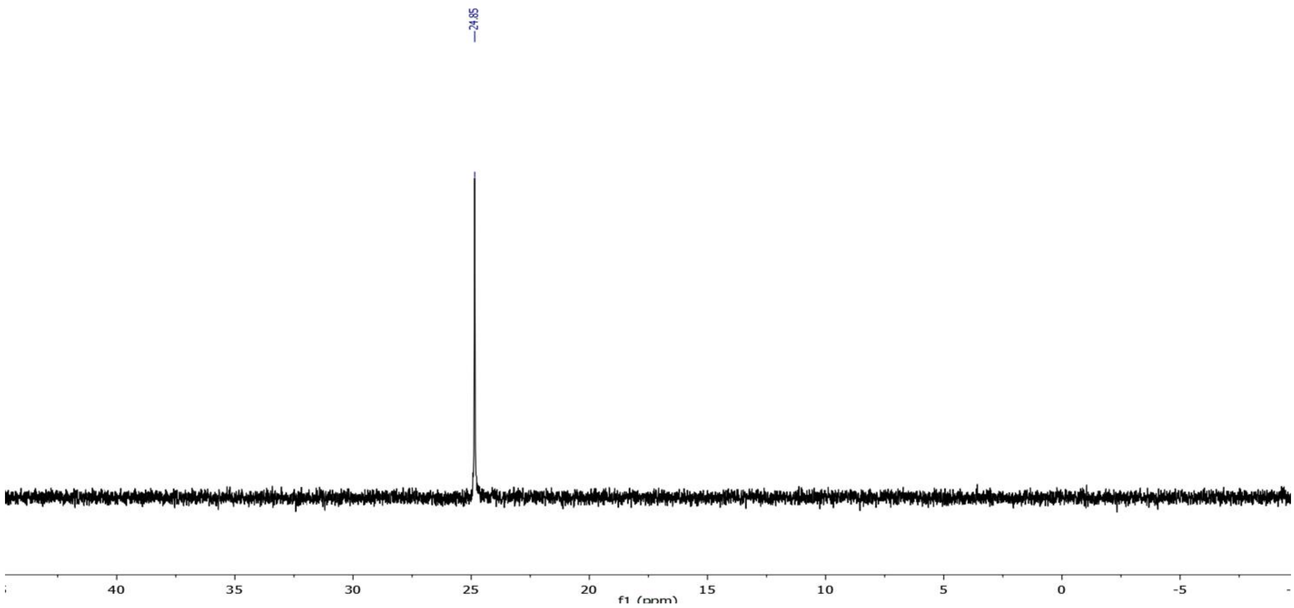
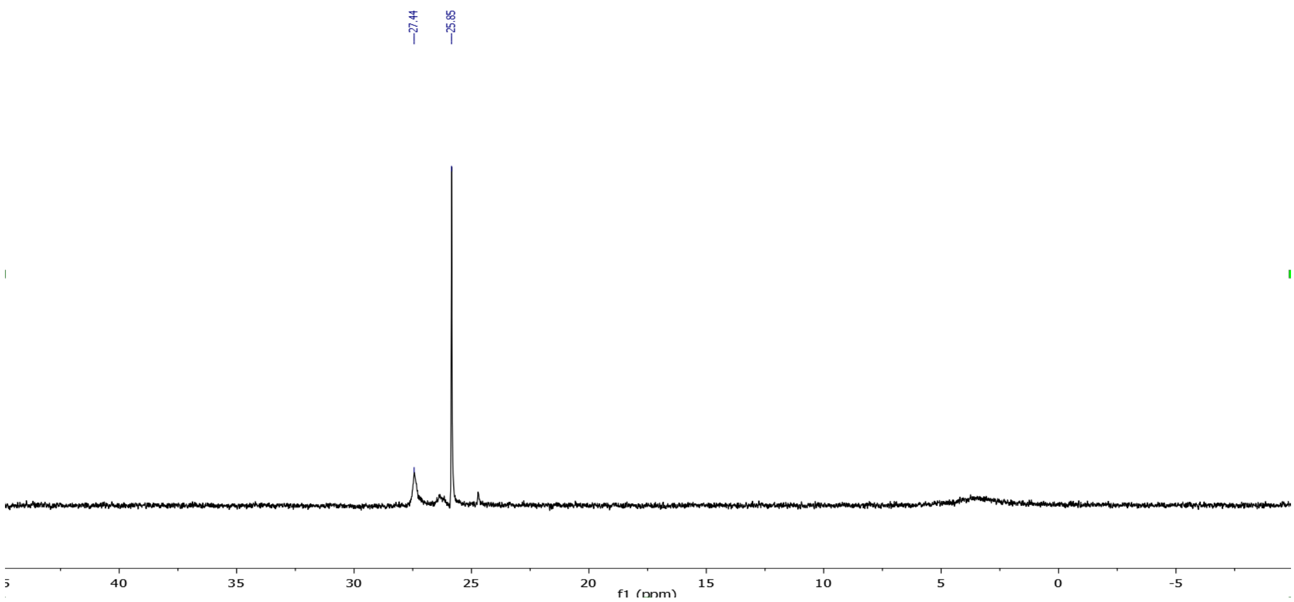


Figure S27. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) in DMF-d_7 at 60°C in 20 min

Entry 3, Table S3:

a)



b)

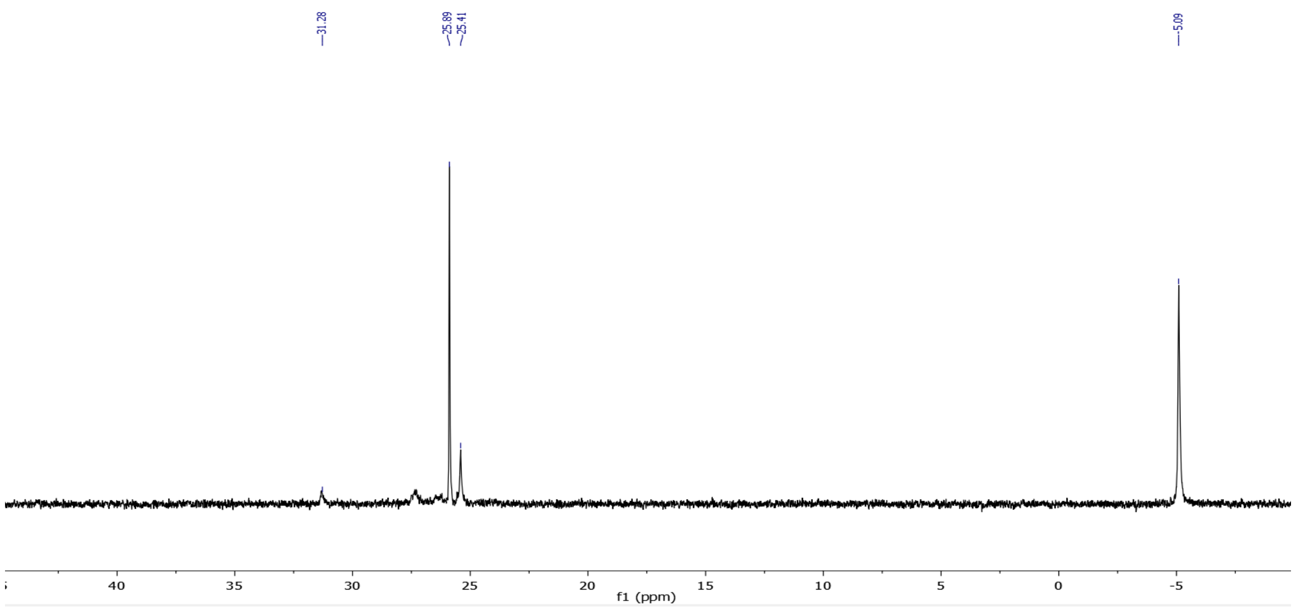
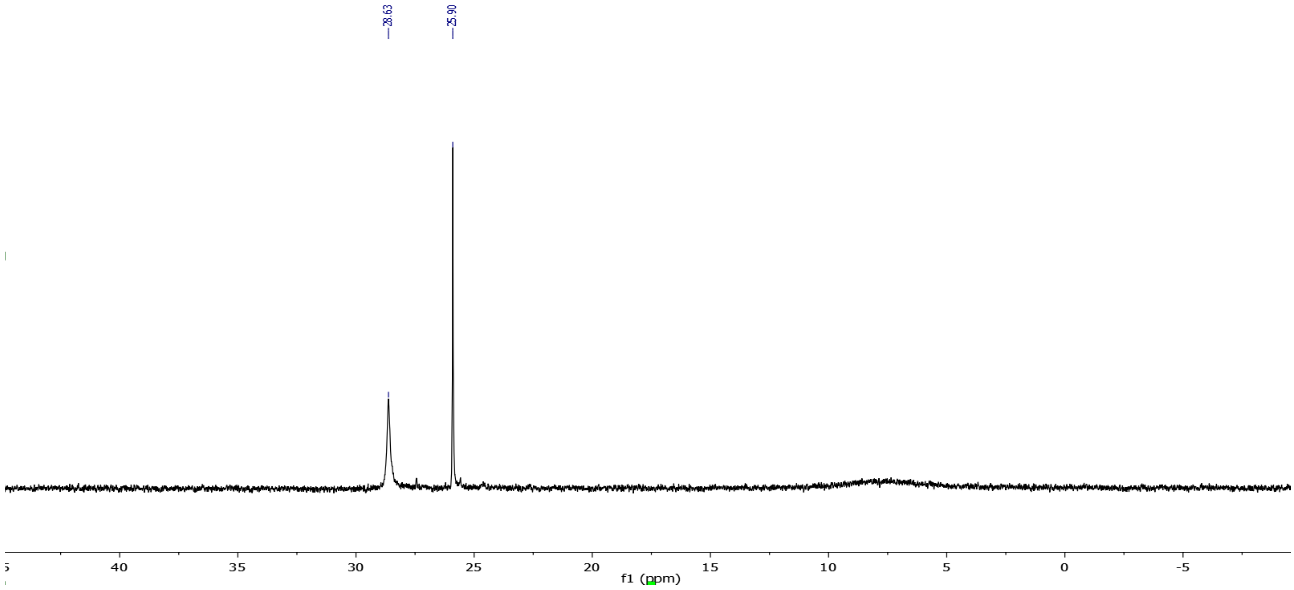


Figure S28. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + Cyclohexylamine (5 equiv) in DMF-d_7 at rt in 20 min. b) +NO_2ArI

Entry 4, Table S3:

a)



b)

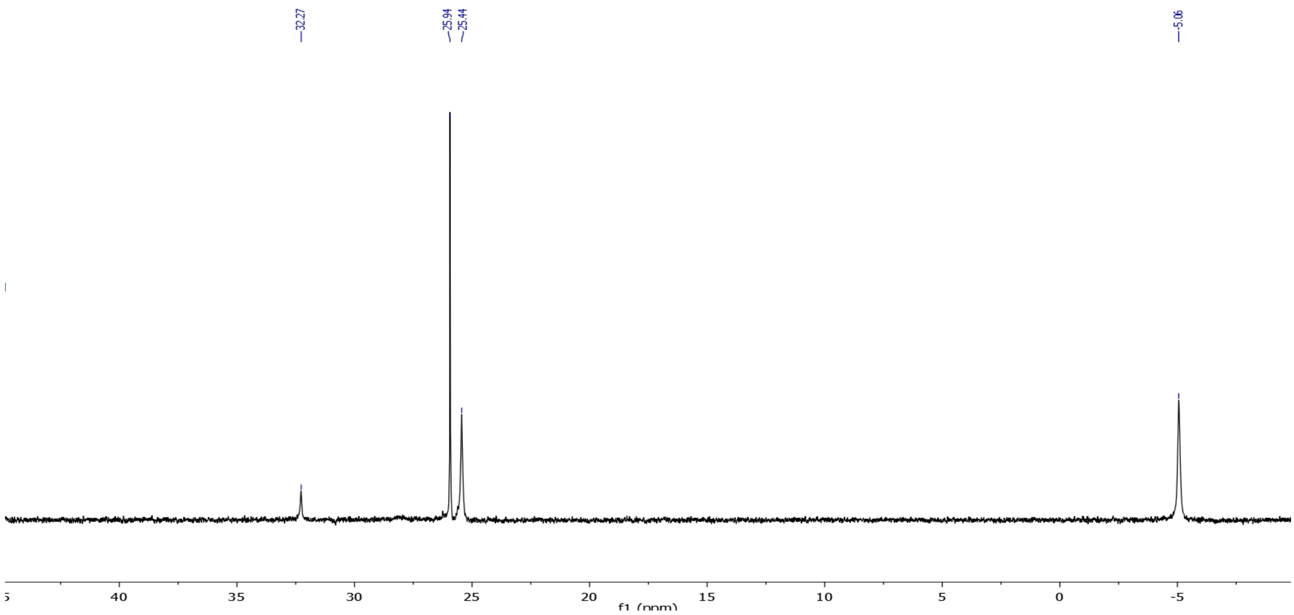
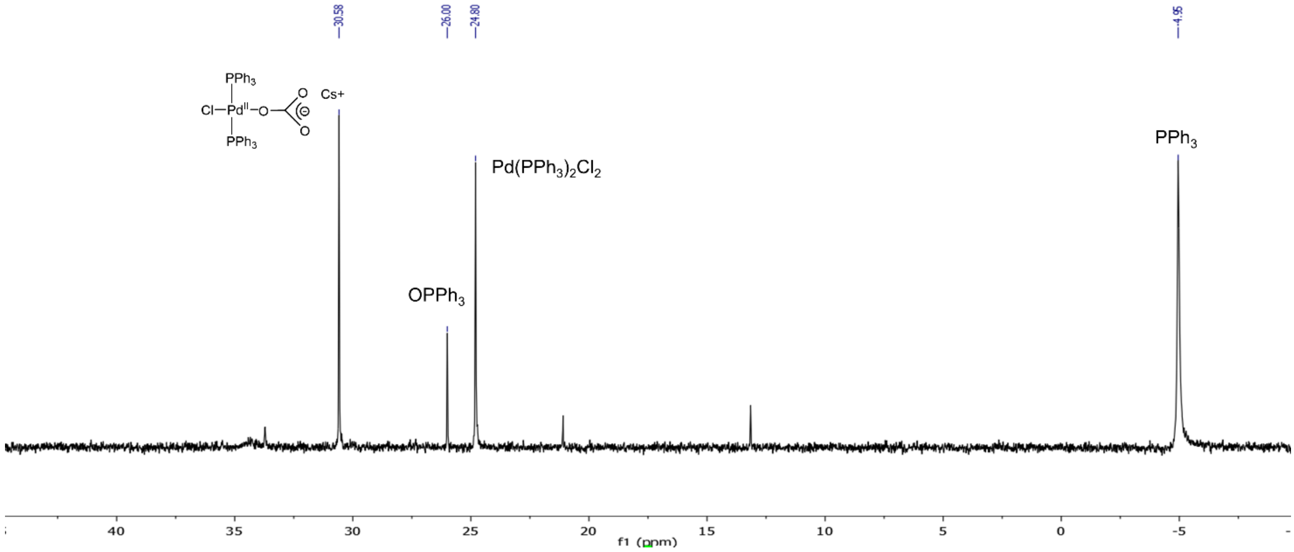


Figure S29. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + pyrrolidine (5 equiv) in DMF-d_7 at rt in 20 min. b) +NO_2ArI

Entry 5, Table S3:

a)



b)

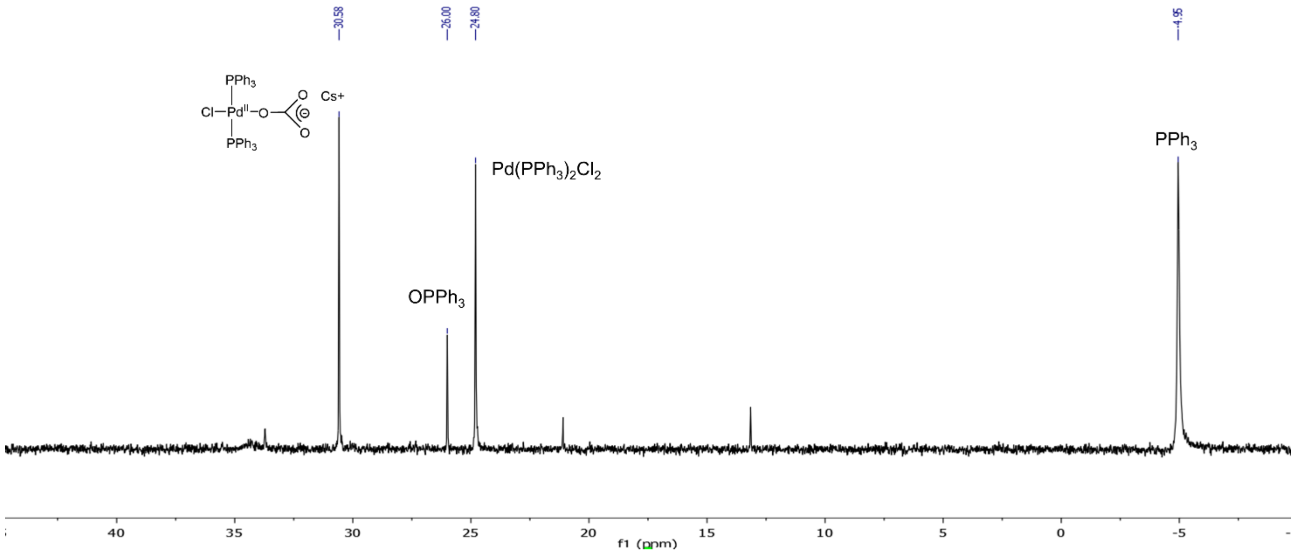


Figure S30. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at rt in 20 min. b) +NO_2ArI

Entry 7, Table S3

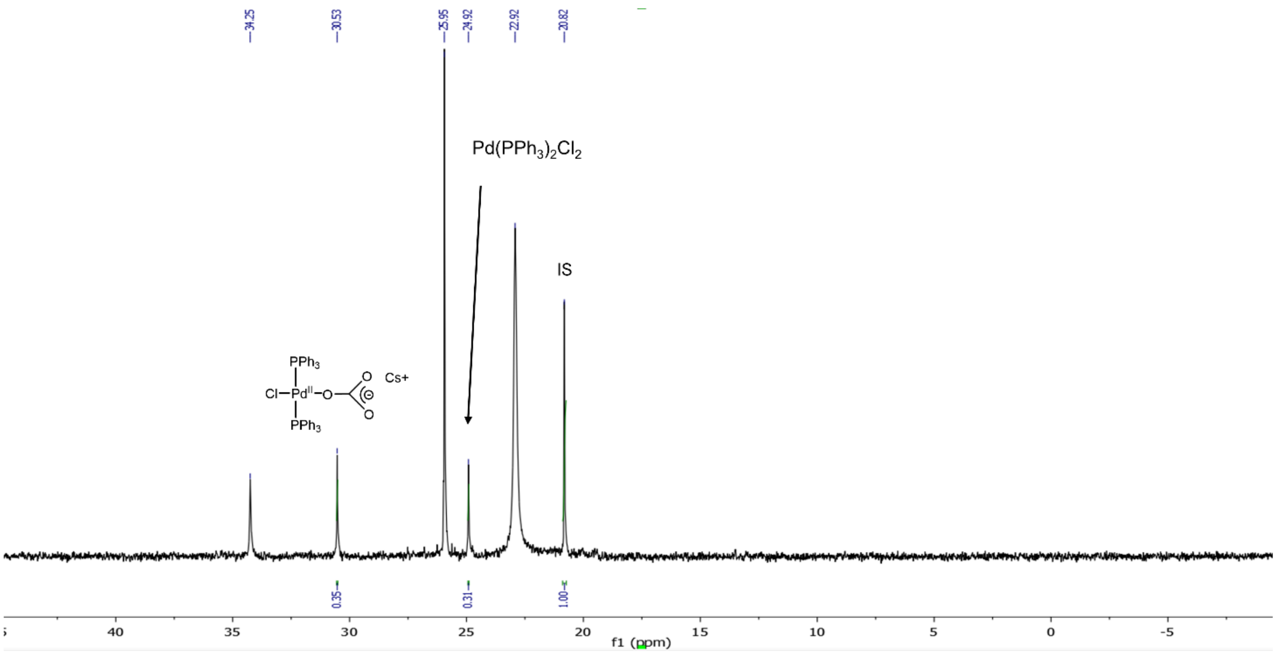


Figure S31. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. The peaks at 20.86, 24.96 and 30.57 ppm are related to the IS, $Pd(PPh_3)_2Cl_2$ and $Cs(CO_3)Pd(PPh_3)_2Cl$ respectively.

Entry 8, Table S3:

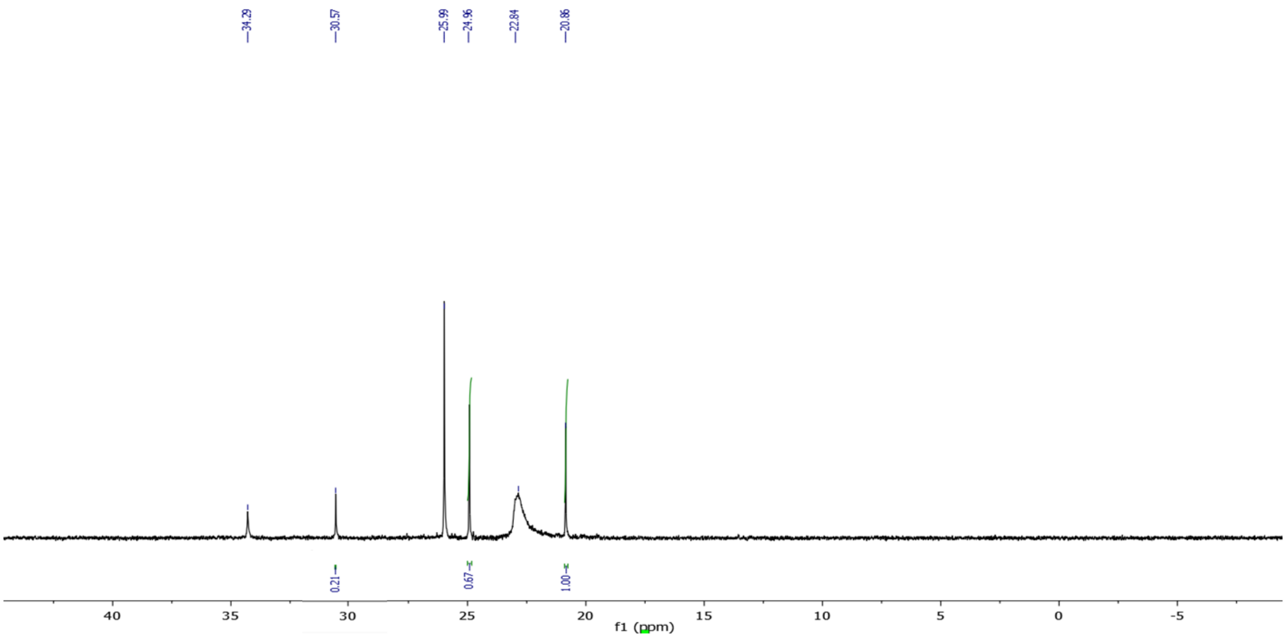


Figure S32. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + K_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. The peaks at 20.86, 24.96 and 30.57 ppm are related to the IS, $Pd(PPh_3)_2Cl_2$ and $K(CO_3)Pd(PPh_3)_2Cl$ respectively.

Entry 9, Table S3:

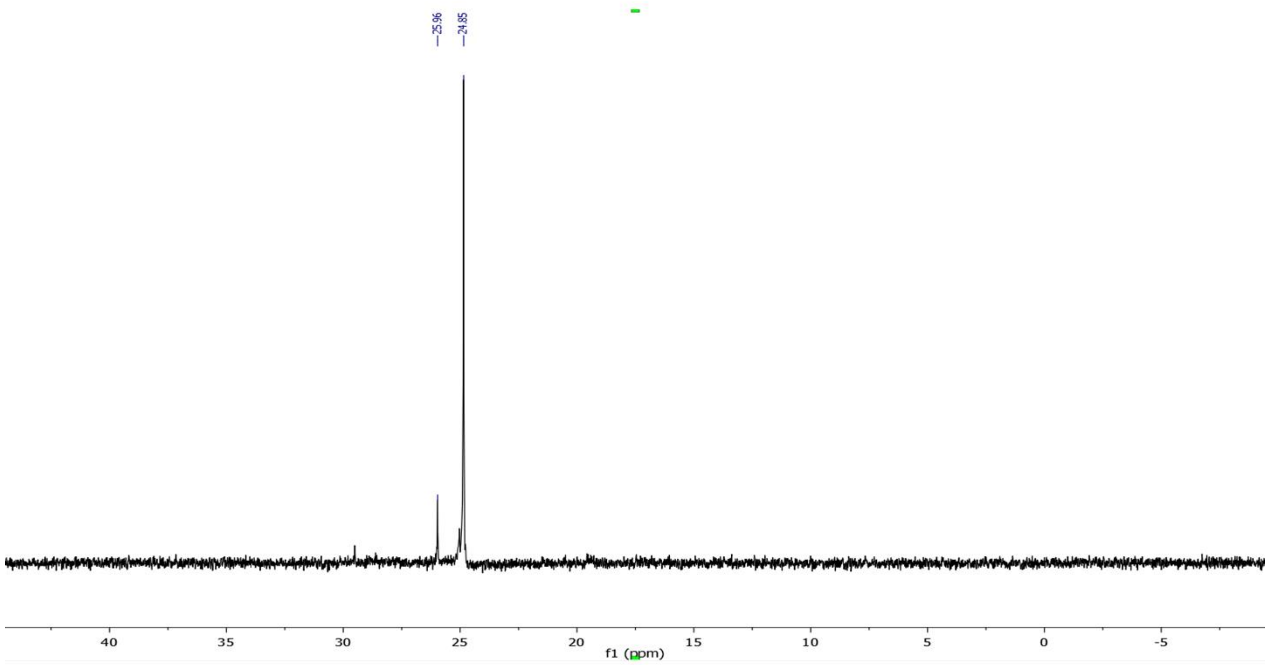
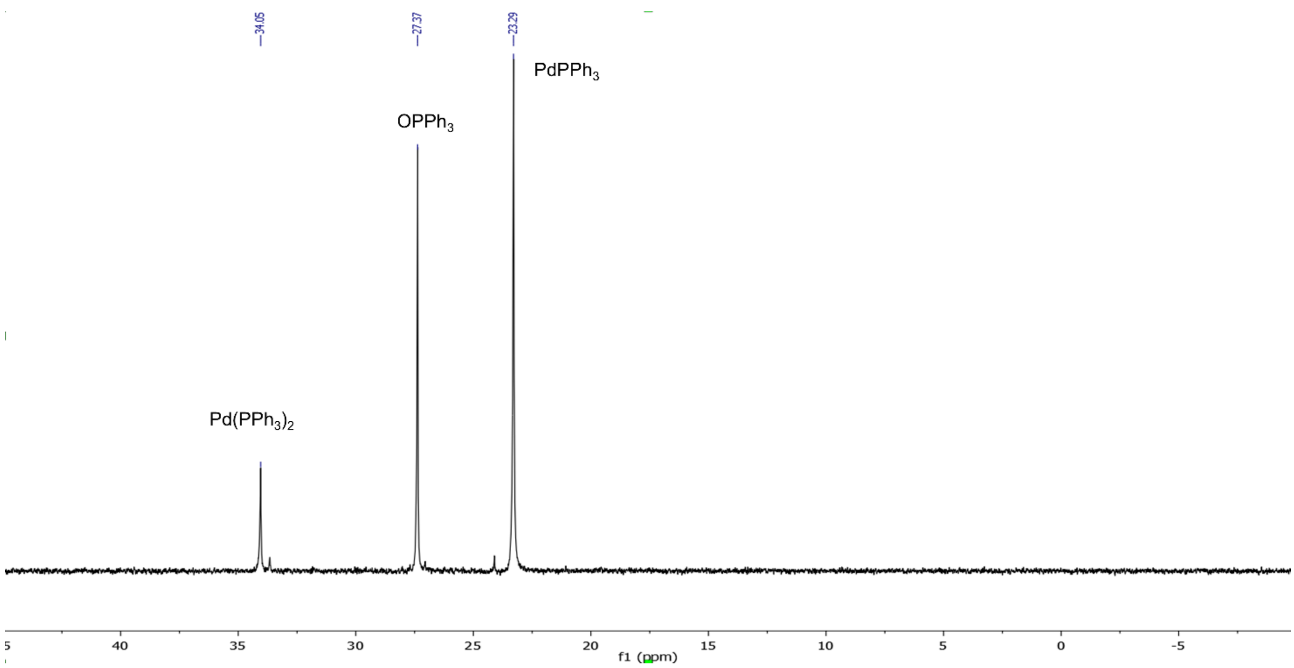


Figure S33. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + TEA (5 equiv) in DMF-d_7 at 80°C in 20 min

Entry 10, Table S3: Completed reduction in HEP/DMF as example
a)



b)

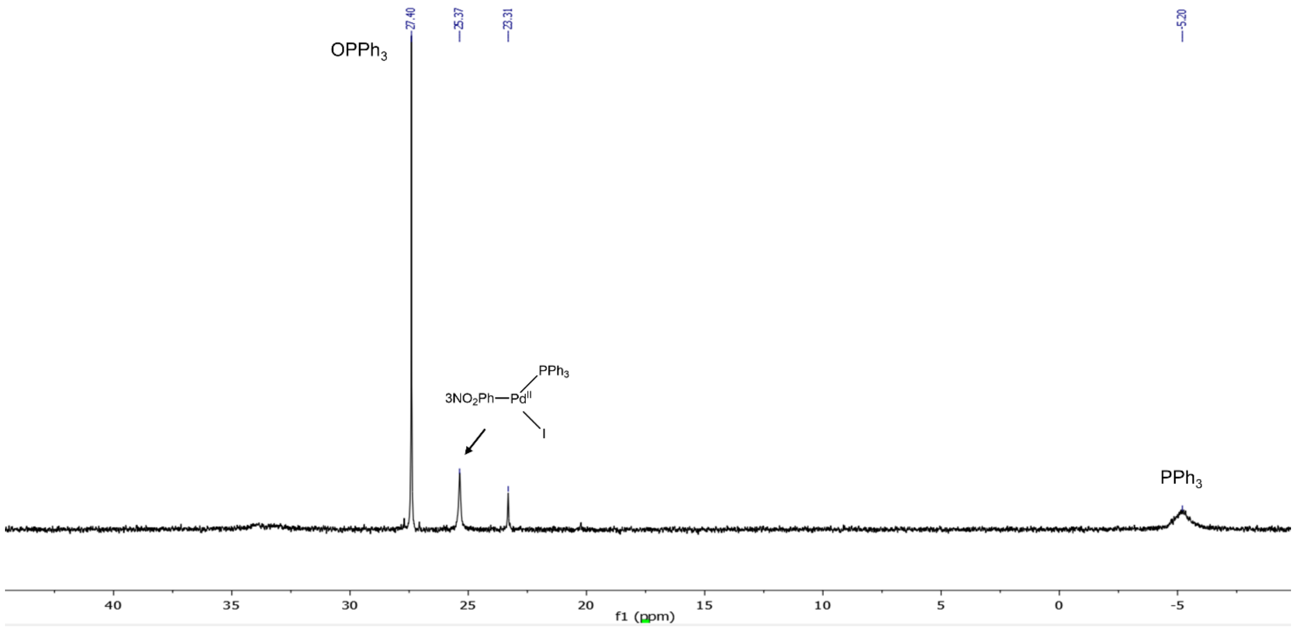


Figure S34. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$

Other spectra

Entry 11, Table S3:

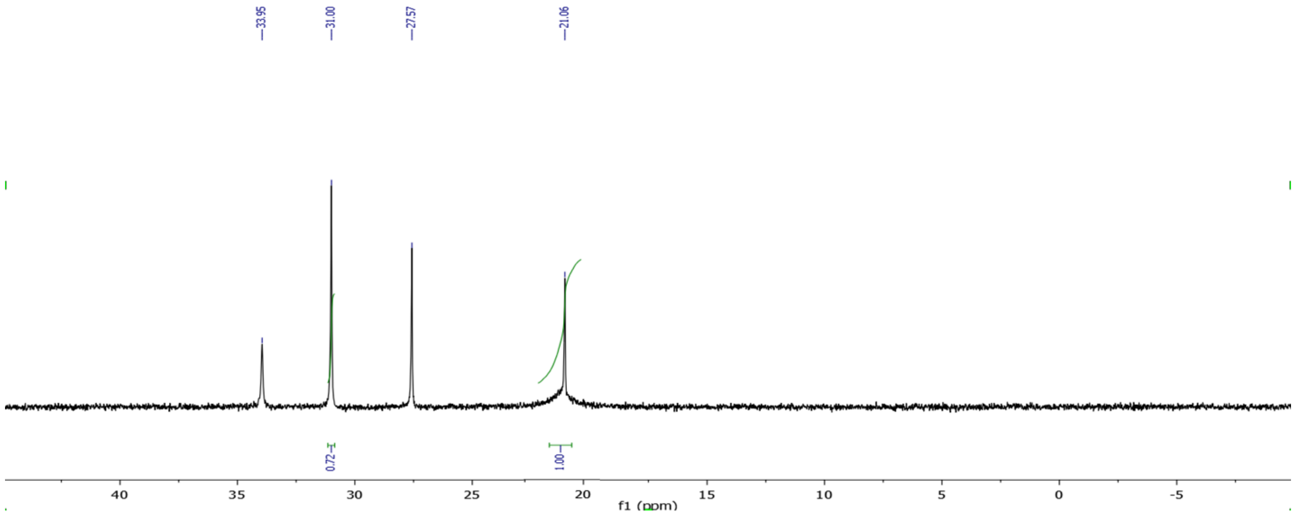
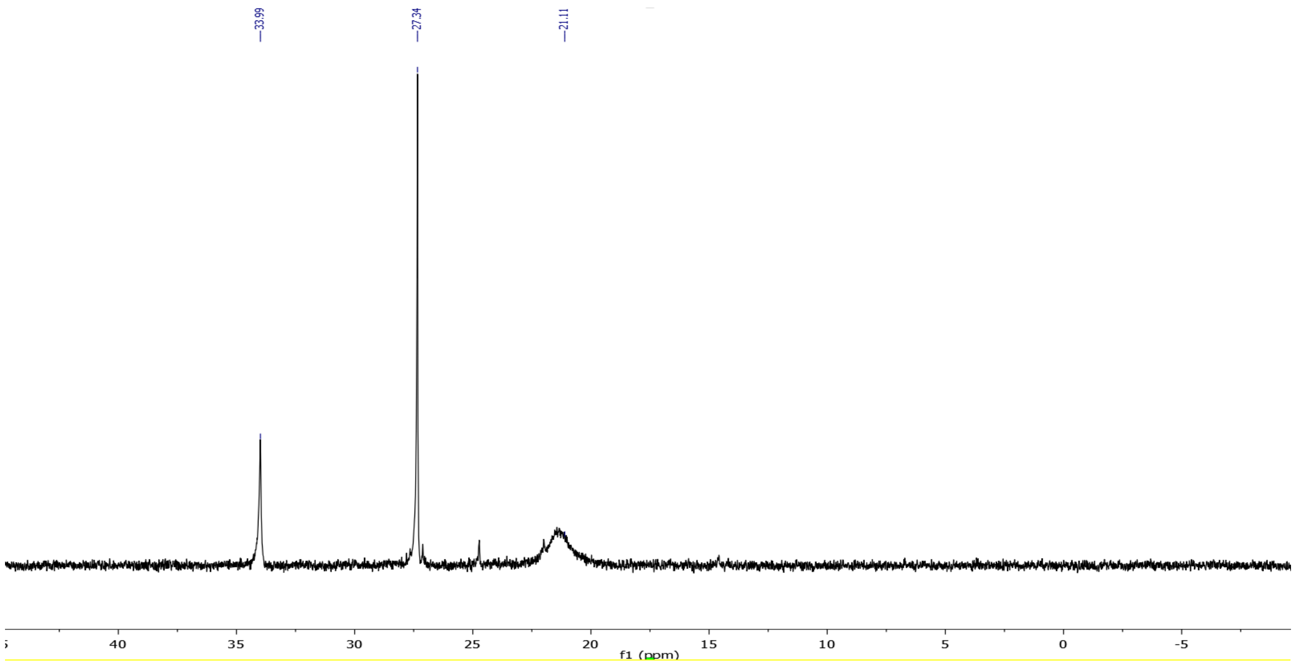


Figure S35. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (4:2) at 60°C in 20 min. The peaks at 21.06 and 31 ppm are related to the IS, and $K(CO_3)Pd(PPh_3)_2Cl$ respectively.

Entry 12, Table S3:

a)



b)

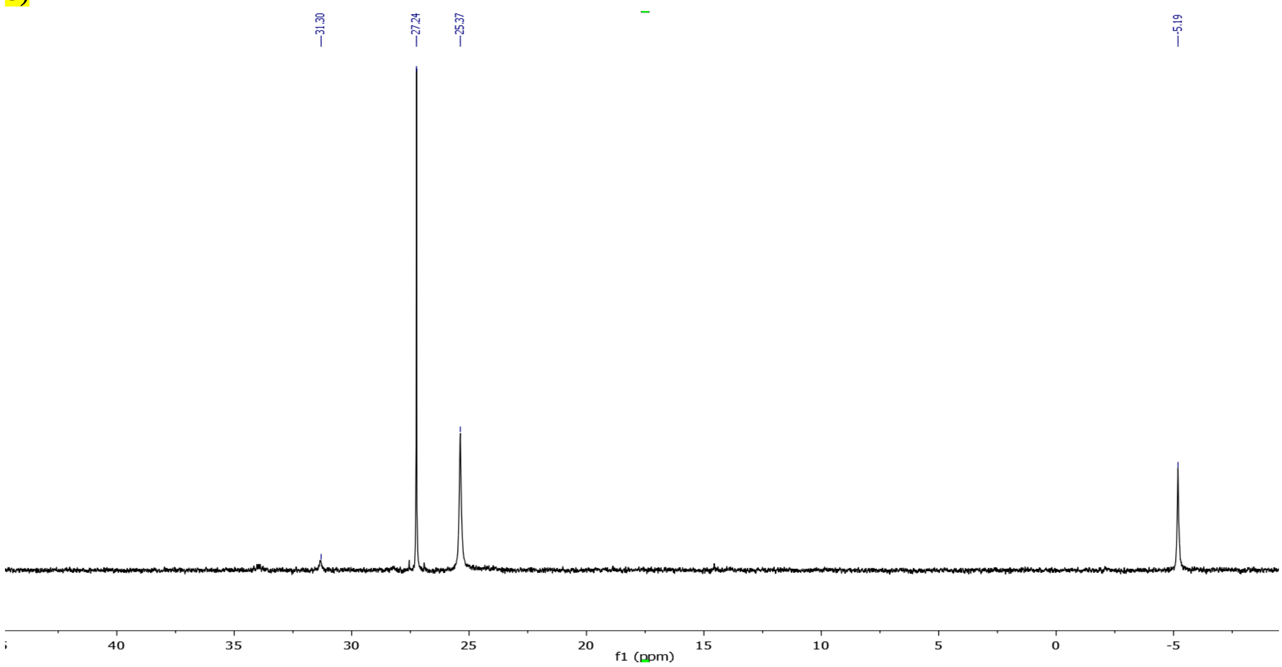


Figure S36. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + TMG(5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$

Entry 13, Table S3:

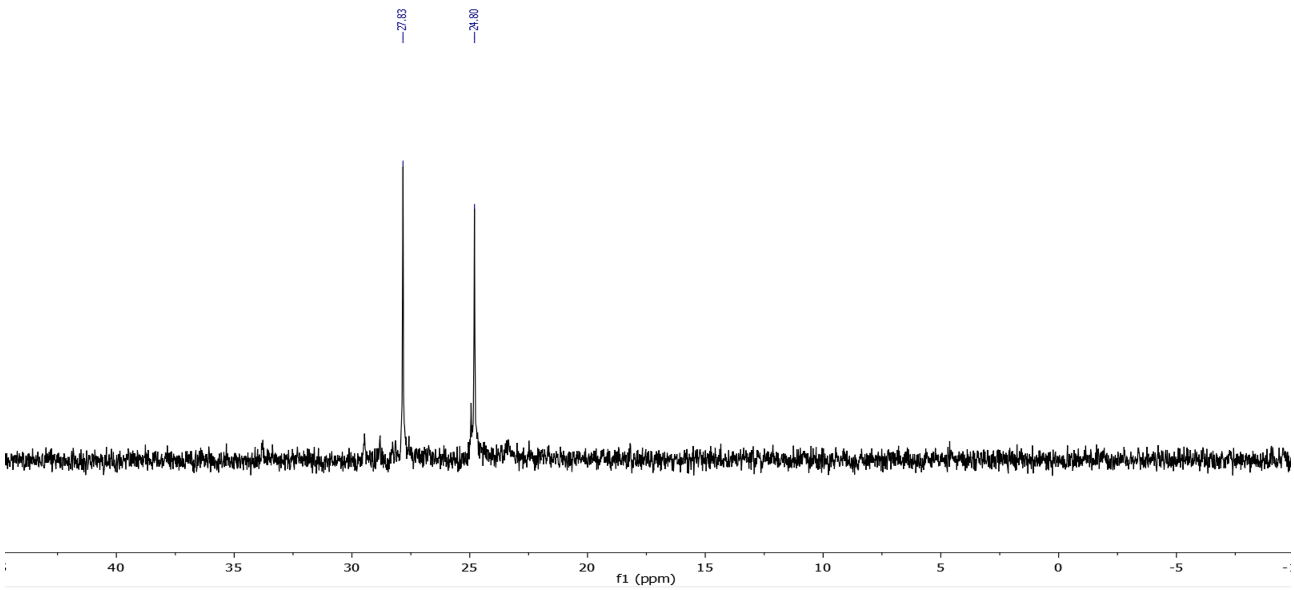
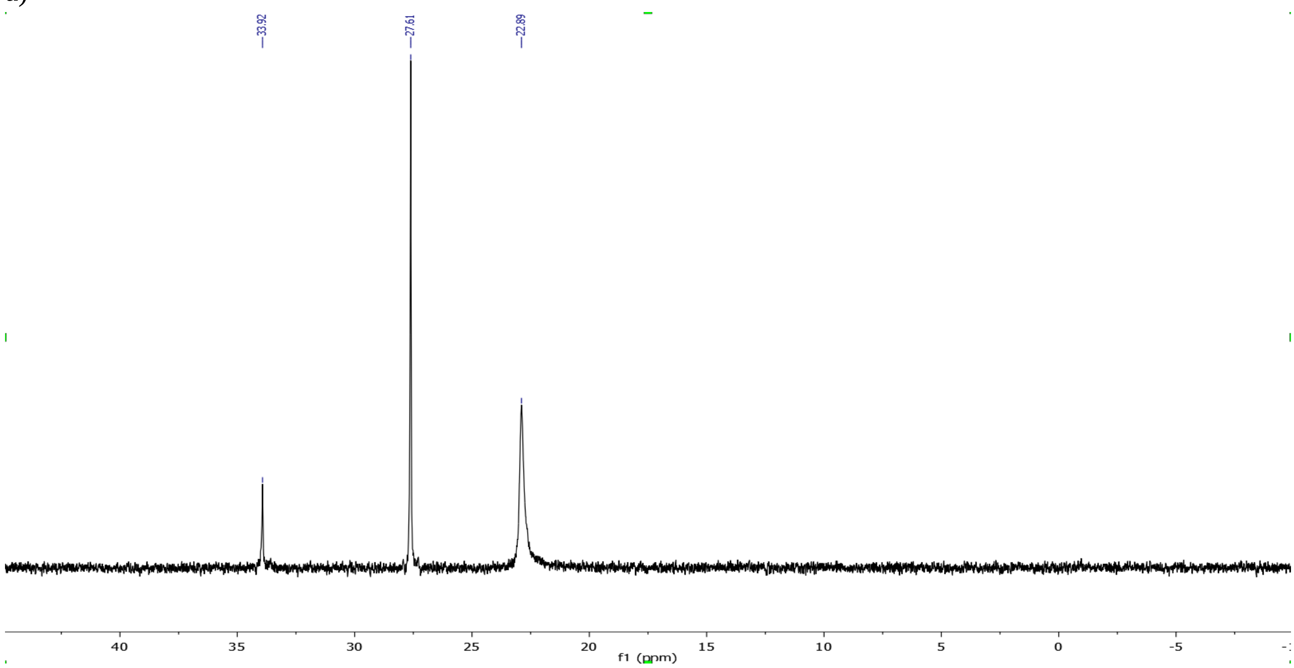


Figure S37. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + TEA(5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min.

Entry 14, Table S3:

a)



b)

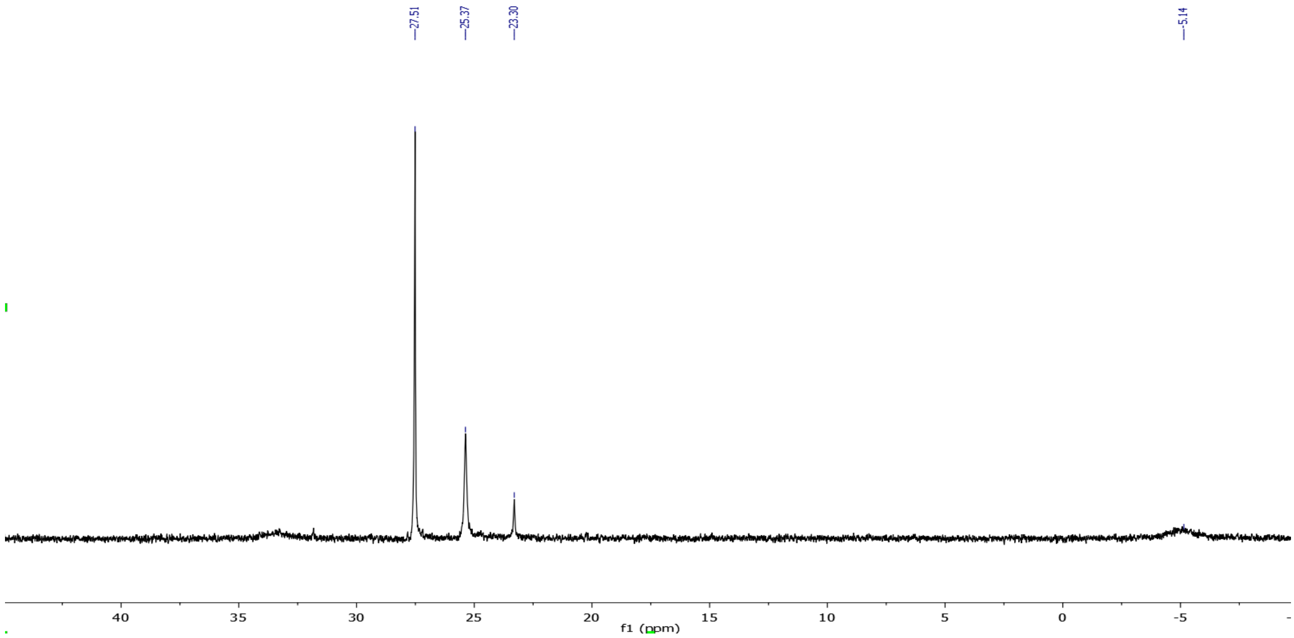
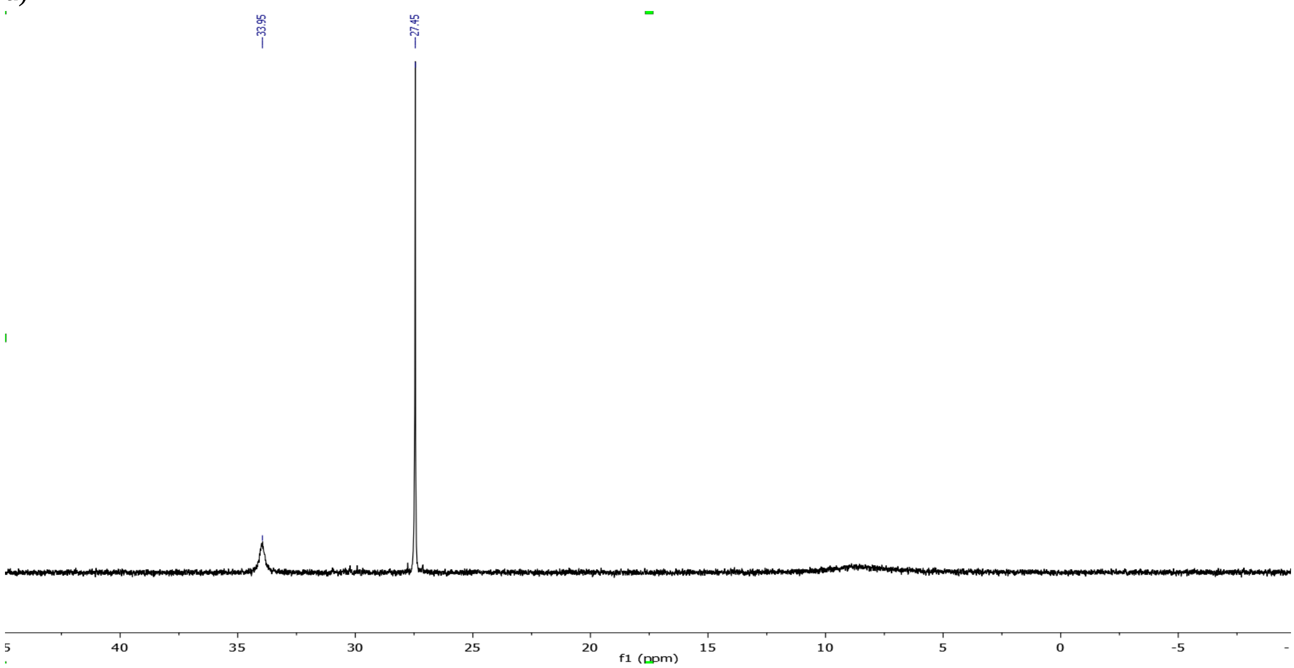


Figure S38. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60° in 20 min. b) + $3NO_2ArI$

Entry 15, Table S3:

a)



b)

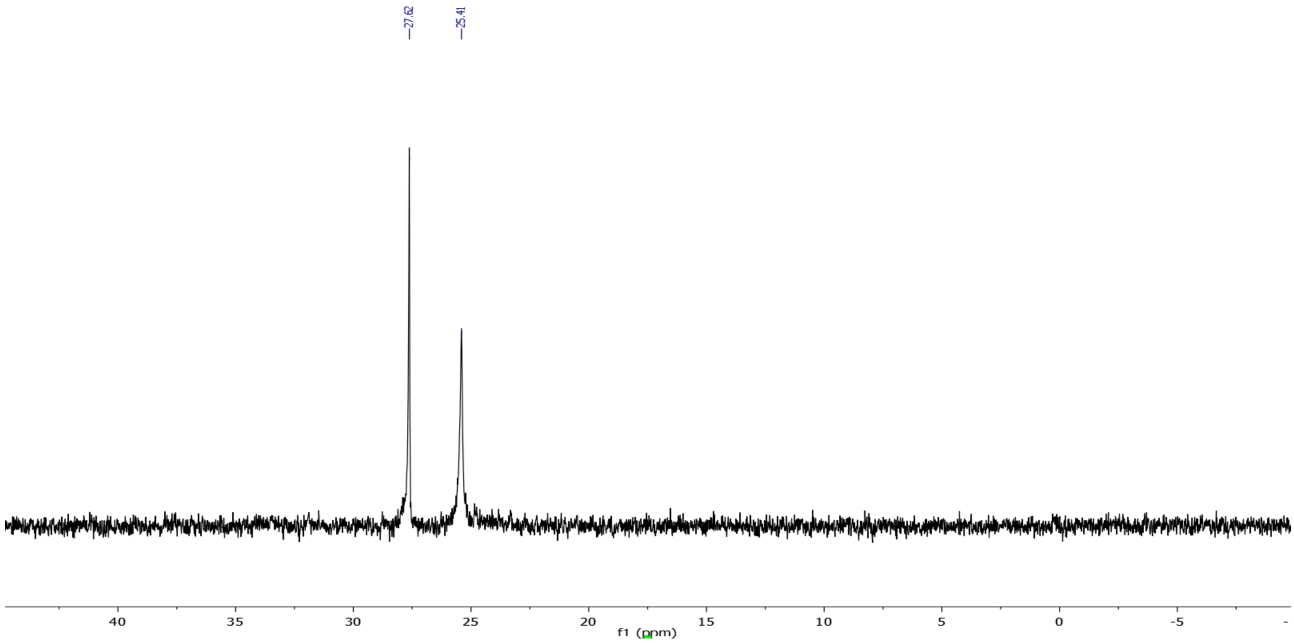


Figure S39. $Pd(PPh_3)_2Cl_2$ + PPh_3 (1 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60 °C in 20 min. b) + $3NO_2ArI$

2. Palladium pre-catalyst reduction with SPhos

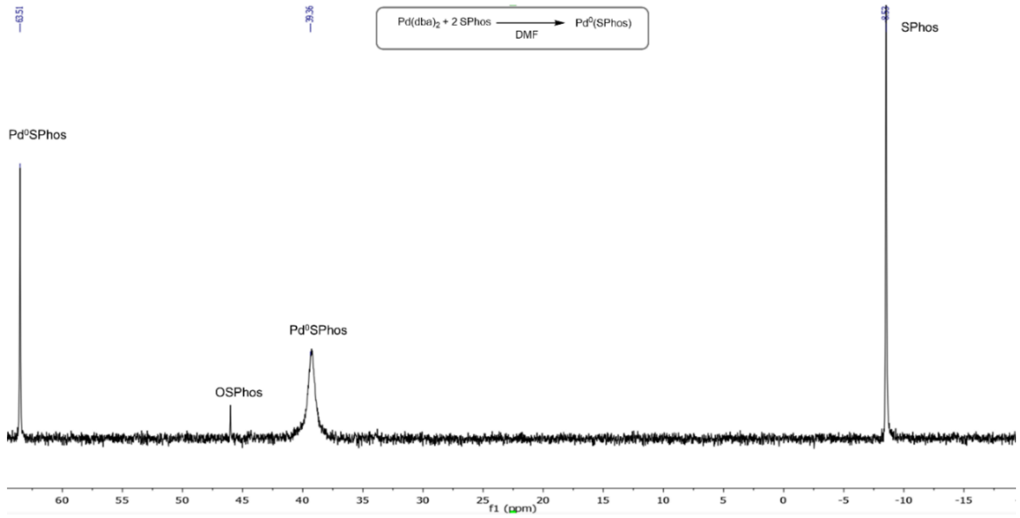
Table S4. ^{31}P NMR chemical shift in DMF-d_7 and HEP/DMF-d_7 (2:4) of palladium species with SPhos

entry	Compound	DMF-d_7	HEP/DMF-d_7 (2:4)
1	SPhos	-8.58	-8.72
2	$3NO_2ArPd(SPhos)I$	33.46	33.28
3	$Pd^0(SPhos)^a$	39.18	39.30
4	$Pd(SPhos)_2Cl_2$	44.33	44.27
5	$Pd(SPhos)_2(OAc)_2$	46.01	48.50
6	OSPhos	46.03	48.30
7	$3NO_2ArPd(SPhos)(CsCO_3)$	51	48.83
8	$Pd^0(SPhos)^a$	63.50	63.30

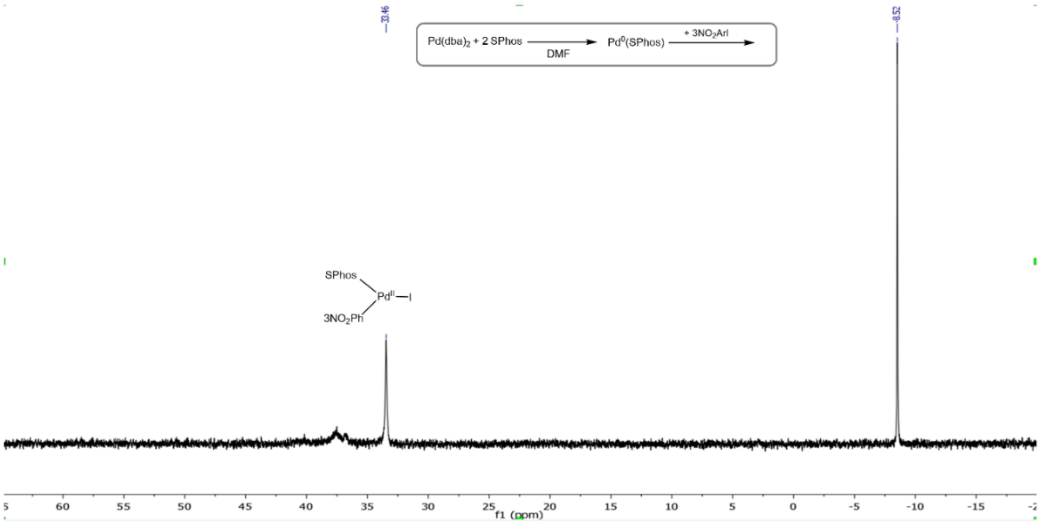
[a] Pd^0SPhos can exist in different conformations, according to the literature [3]

2.1. Synthesis of palladium species with Sphos

a)



b)



c)

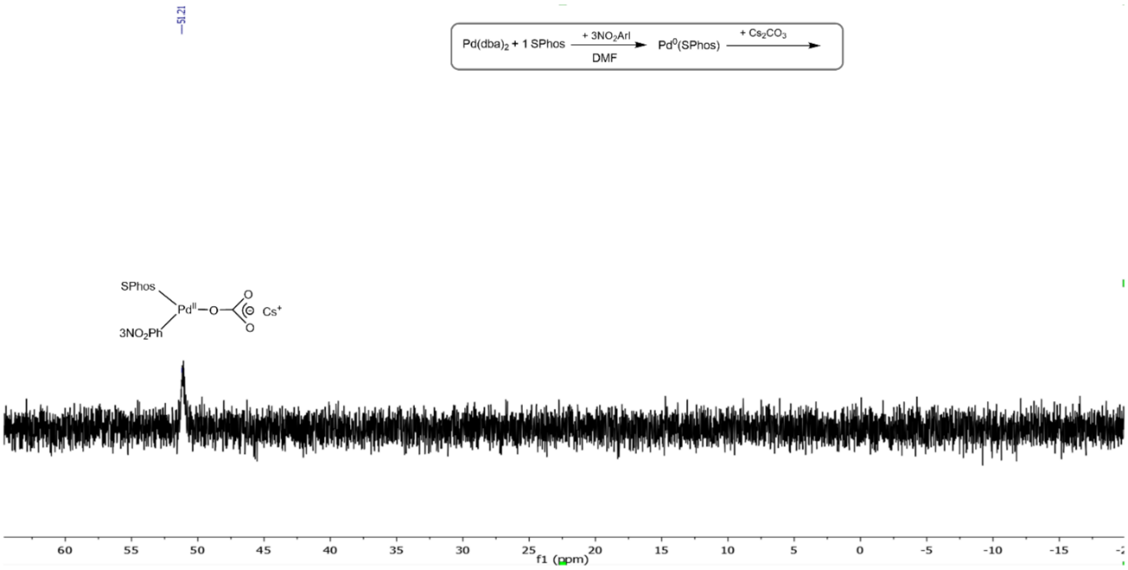
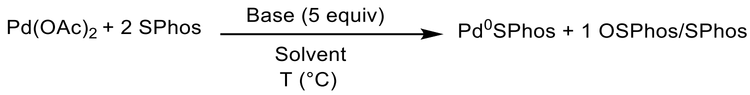


Figure S40. a) $Pd(dba)_2$ (11.9 mg, 0.013 mmol, 1 equiv), SPhos (10.67 mg, 0.026, 2 equiv) in DMF (0.6 ml). b) + $3NO_2ArI$ (16.17 mg, 0.065 mmol, 5 equiv); c) $Pd(dba)_2$ (11.9 mg, 0.013 mmol, 1 equiv), SPhos (5.40 mg, 0.013, 1 equiv) in DMF (0.6 ml) + $3NO_2ArI$ (16.17 mg, 0.065 mmol, 5 equiv) + Cs_2CO_3 (21.37 mg, 0.065 mmol, 5equiv)

2.2. $Pd(OAc)_2$

2.2.1. General Procedure 1



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(OAc)_2$ (2.91 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). SPhos (10.67 mg, 0.026 mmol, 2 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.0065 mmol, 0.5 eq) was added as internal standard (IS).
To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex.

Table S5. $Pd(SPhos)_2(OAc)_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	25	-	0/100	-
2	-	DMF	60	E	29/71	100/0
3	TMG	DMF	25	-	0/100	-
4	Cs_2CO_3	DMF	25	E	71/29	100/0
5	K_2CO_3	DMF	25	E	54/46	100/0
6	TMG	DMF	60	E	15/85	100/0
7	K_2CO_3	DMF	60	E	100/0	100/0
8	TEA	DMF	80	E	25/75	100/0
9	Cs_2CO_3	DMF/HEP[e]	25	A/E	100/0	42/58
10	K_2CO_3	DMF/HEP	25	A	100/0	0/100
11	TMG	DMF/HEP	60	A/E	31/69	n.d.[d]

[a] The reactions were carried out according to the **General Procedure 1**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and Pd^0SPhos
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

2.2.2. ^{31}P NMR spectra

Entry 1, Table S51.

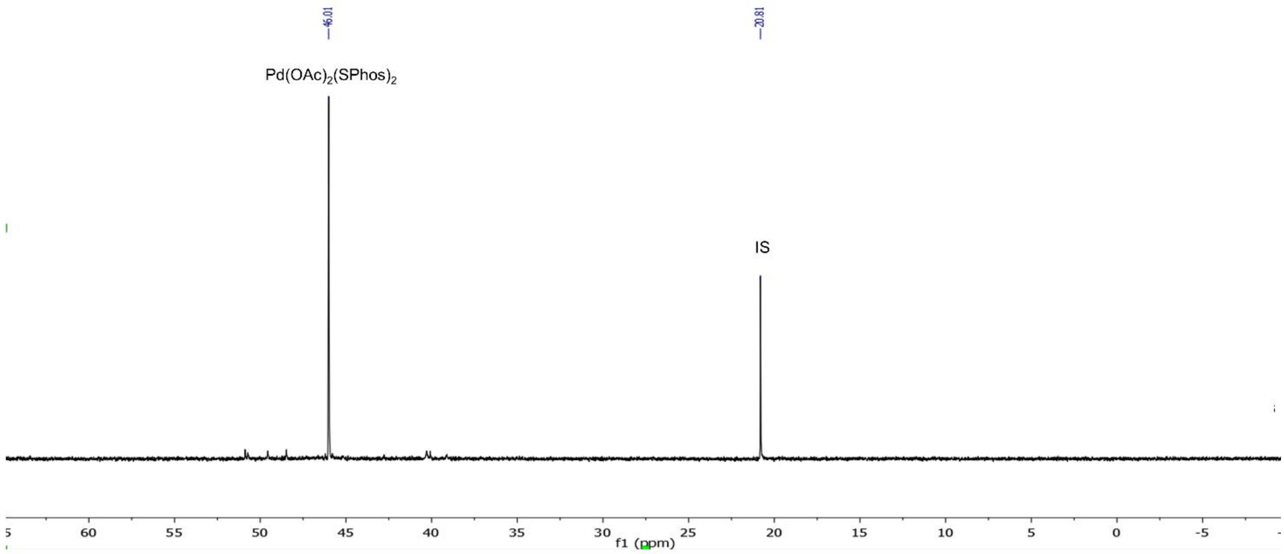


Figure S41. $Pd(OAc)_2$ +SPhos (2 equiv) in DMF-d_7 at rt in 20 min. The peak at 20.81 ppm is related to the internal standard.

Entry 2, Table S5:

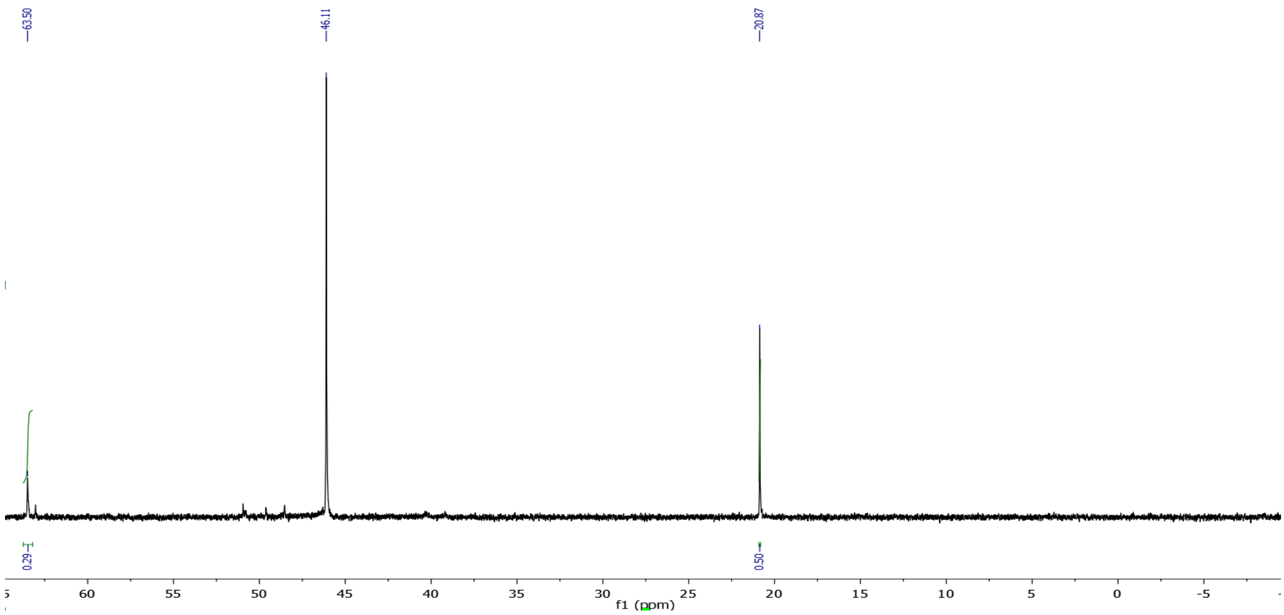


Figure S42. $Pd(OAc)_2$ +SPhos (2 equiv) in DMF-d_7 at 60°C in 20 min. The peaks at 20.87 ppm and at 63.50 ppm are related to the IS and Pd^0(SPhos) respectively.

Entry 3, Table S5:

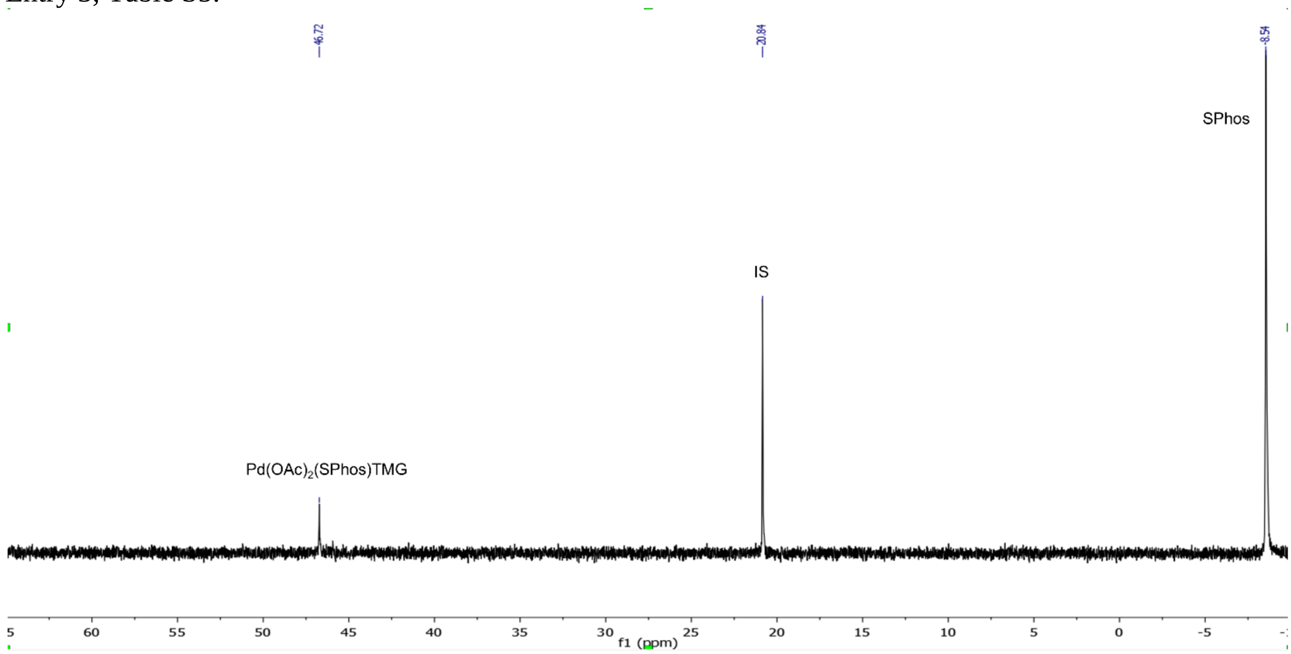


Figure S43. $Pd(OAc)_2$ +SPhos (2 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min.

Entry 4, Table S5:

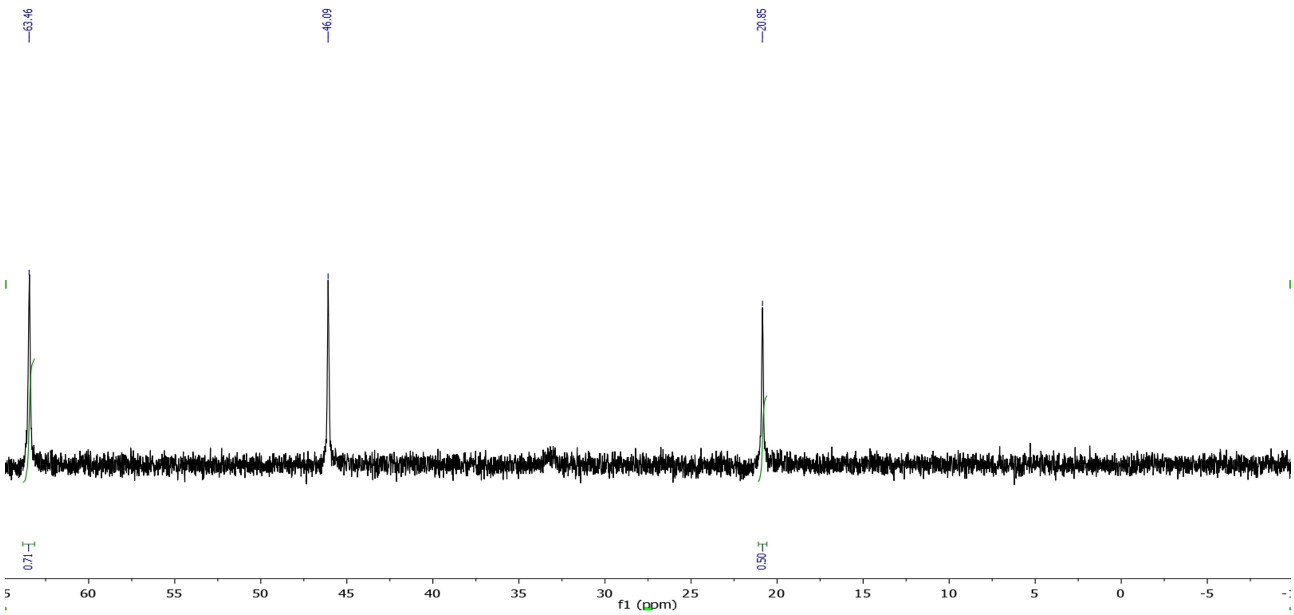


Figure S44. $Pd(OAc)_2$ +SPhos (2 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at rt in 20 min.

Entry 5, Table S5:

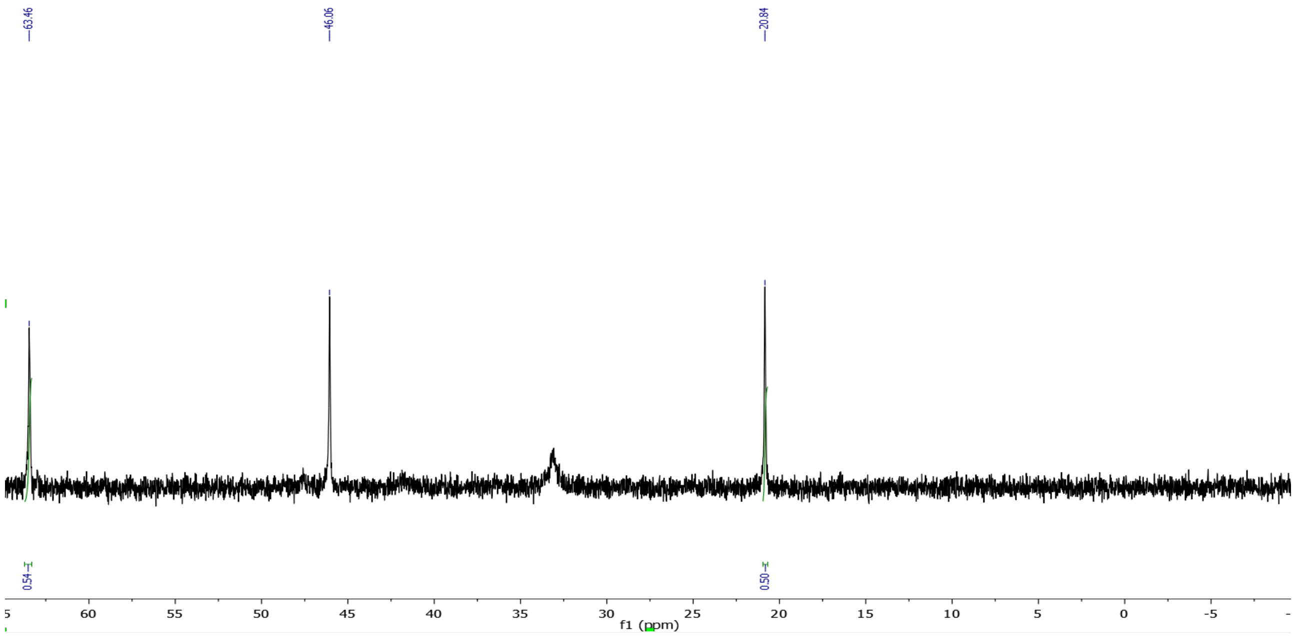


Figure S45. Pd(OAc)$_2$ +SPhos (2 equiv) + K_2CO_3 (5 equiv) in DMF-d$_7$ at rt in 20 min. The peaks at 20.84 ppm and at 63.46 ppm are related to the IS and Pd^0(SPhos) respectively.

Entry 6, Table S5:

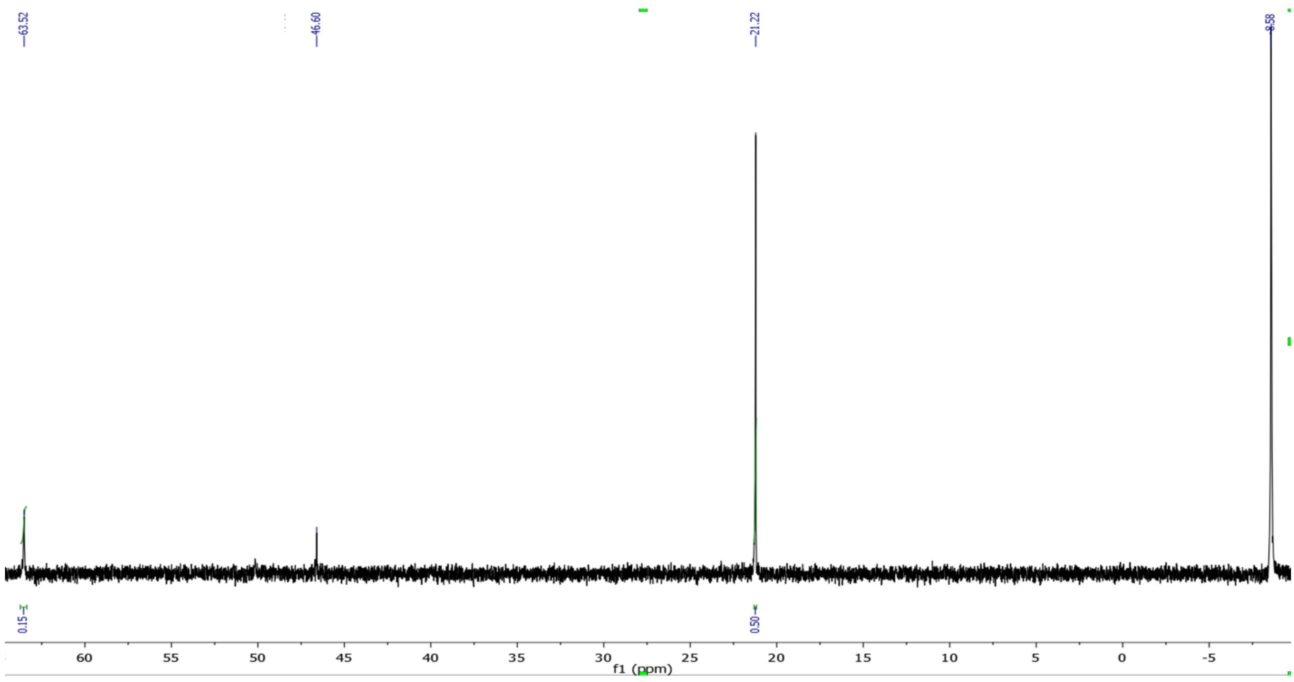


Figure S46. Pd(OAc)$_2$ +SPhos (2 equiv) + TMG (5 equiv) in DMF-d$_7$ at 60°C in 20 min. The peaks at 21.22 ppm and at 63.52 ppm are related to the IS and Pd^0(SPhos) respectively.

Entry 7, Table S5:

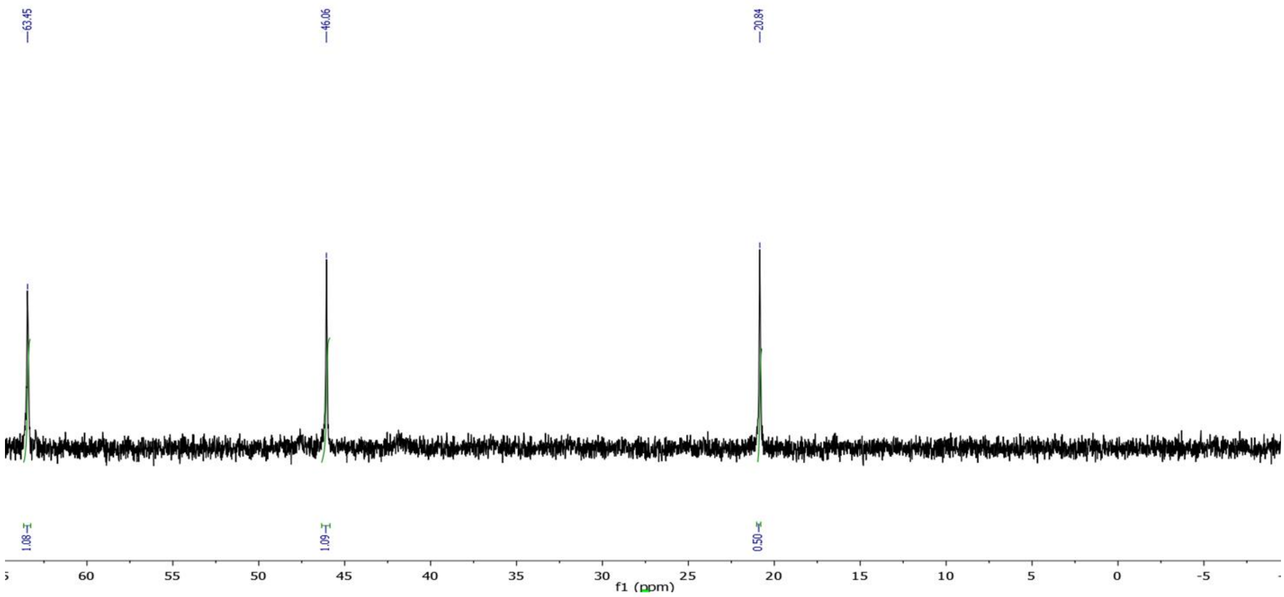


Figure S47. Pd(OAc)$_2$ +SPhos (2 equiv) + K_2CO_3 (5 equiv) in DMF-d$_7$ at rt in 20 min. The peaks at 20.84 ppm and at 63.45 ppm are related to the IS and Pd^0(SPhos) respectively.

Entry 8, Table S5:

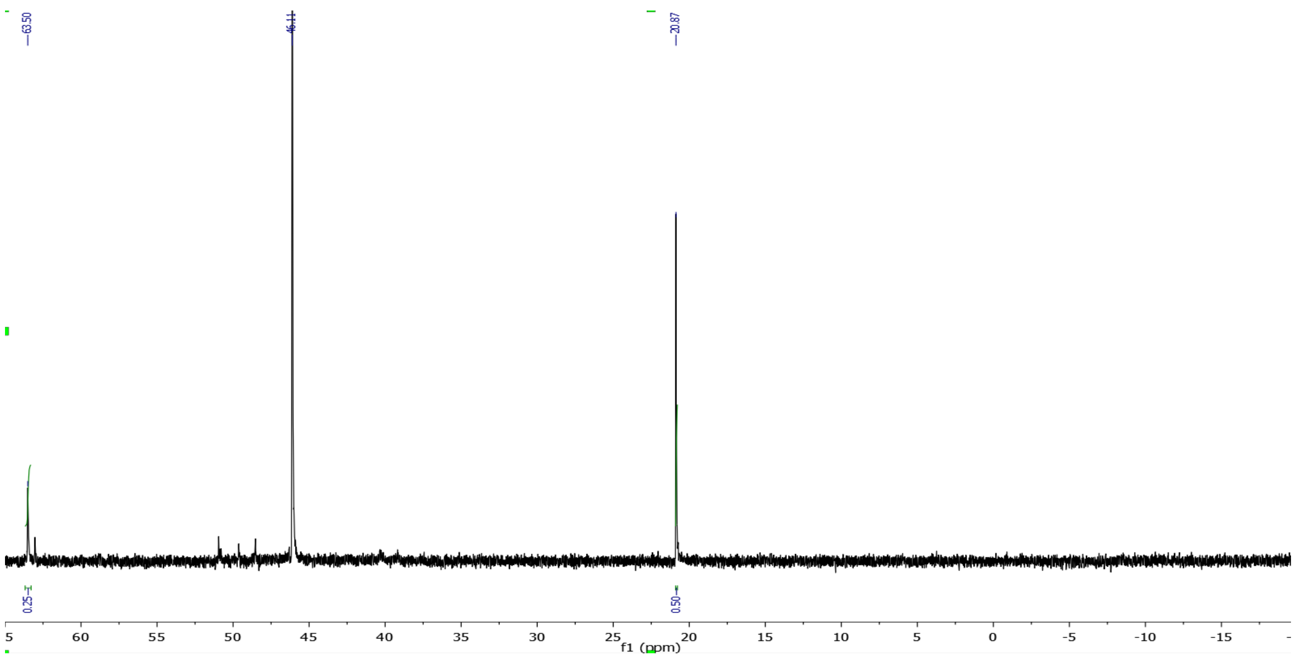
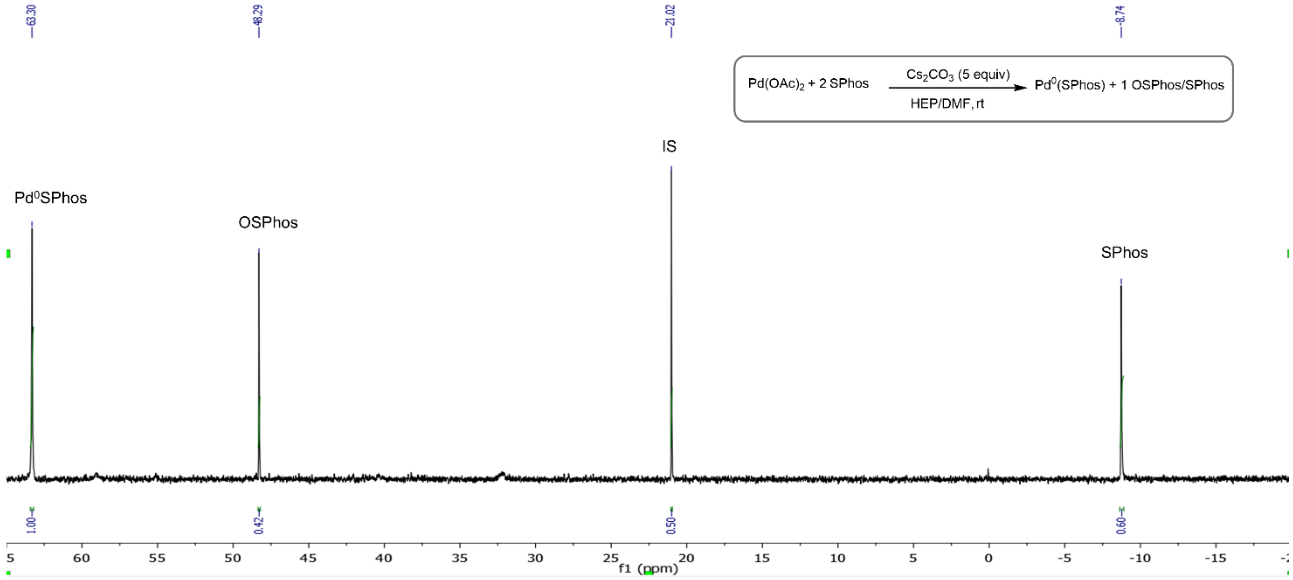


Figure S48. Pd(OAc)$_2$ +SPhos (2 equiv) + TEA (5 equiv) in DMF-d$_7$ at 80°C in 20 min. The peaks at 20.87 ppm and at 63.50 ppm are related to the IS and Pd^0(SPhos) respectively.

Entry 9, Table S5: Completed reduction in HEP/DMF-d_7 as example

a)



b)

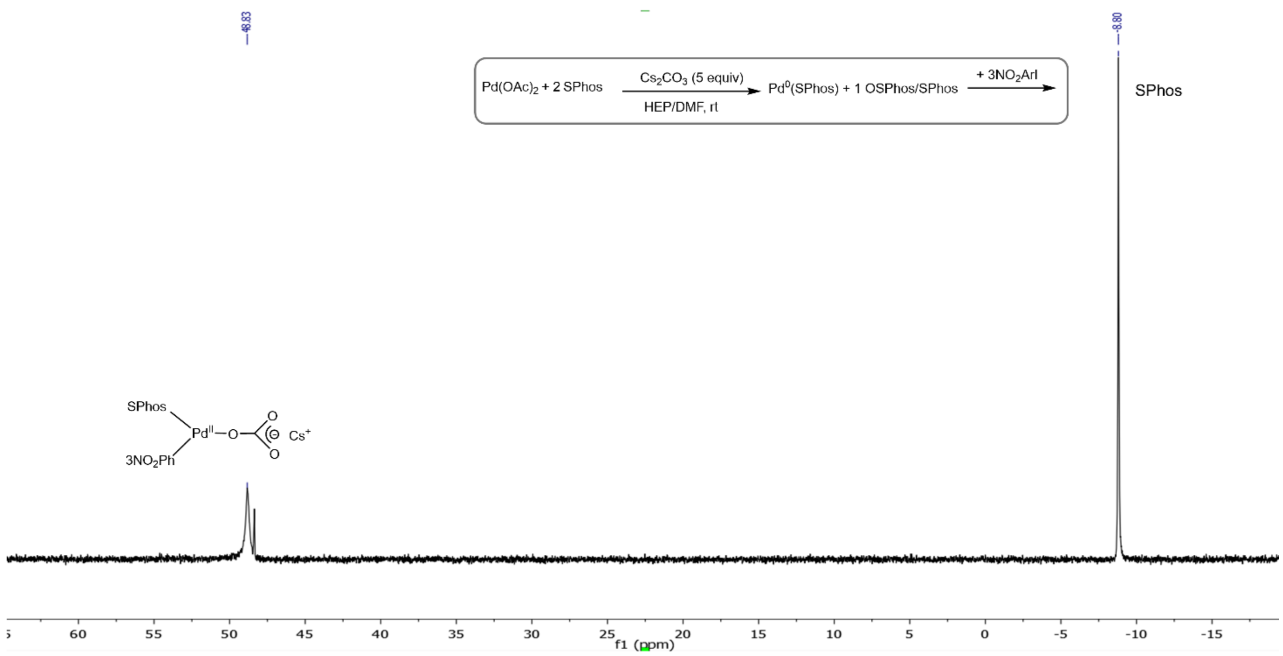


Figure S49. $Pd(OAc)_2$ +SPhos (2 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (4:2) at rt in 20 min b) +$3NO_2ArI$.

Entry 10, Table S5:

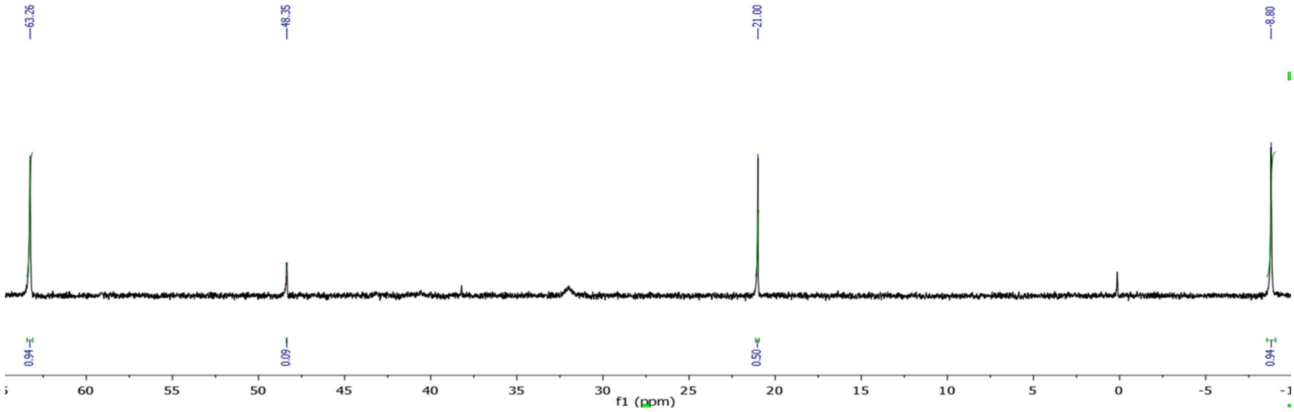


Figure S50. $Pd(OAc)_2$ +SPhos (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (4:2) at 60°C in 20 min

Entry 11, Table S5:

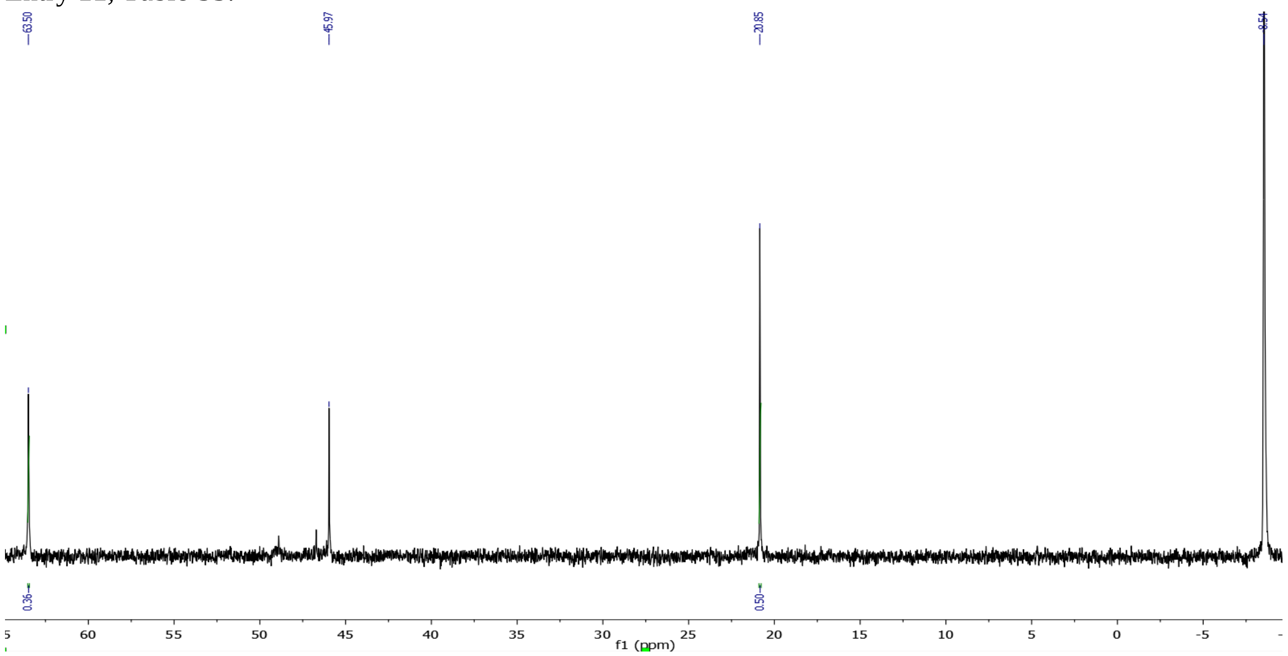
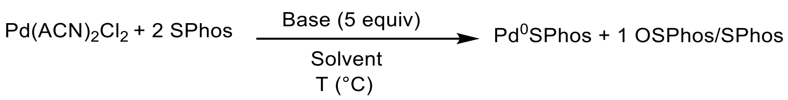


Figure S51. $Pd(OAc)_2$ +SPhos (2 equiv) + TMG (5 equiv) in HEP/DMF-d_7 (4:2) at 60°C in 20 min

2.3. $PdCl_2$

2.3.1. General Procedure 2



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(ACN)_2Cl_2$ (3.37 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). SPhos (10.67 mg, 0.026 mmol, 2 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature

and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.0065 mmol, 0.5 equiv) was added as internal standard (IS).
To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex.

Table S6. $Pd(SPhos)_2Cl_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	60	-	0/100	-
2	TMG	DMF	60	-	0/100	-
3	Cs_2CO_3	DMF	60	-	0/100	-
4	K_2CO_3	DMF	60	-	0/100	
5	TEA	DMF	80	-	0/100	-
6	Cs_2CO_3	DMF/HEP[e]	25	A	56/44	0/100
7	Cs_2CO_3	DMF/HEP	60	A	100/0	0/100
8	K_2CO_3	DMF/HEP	60	A	100/0	0/100
9	TMG	DMF/HEP	60	A	15/85	0/100

[a] The reactions were carried out according to the **General Procedure 2**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and Pd^0SPhos
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

2.3.2. ^{31}P NMR spectra

Entries 1-5, Table S6:

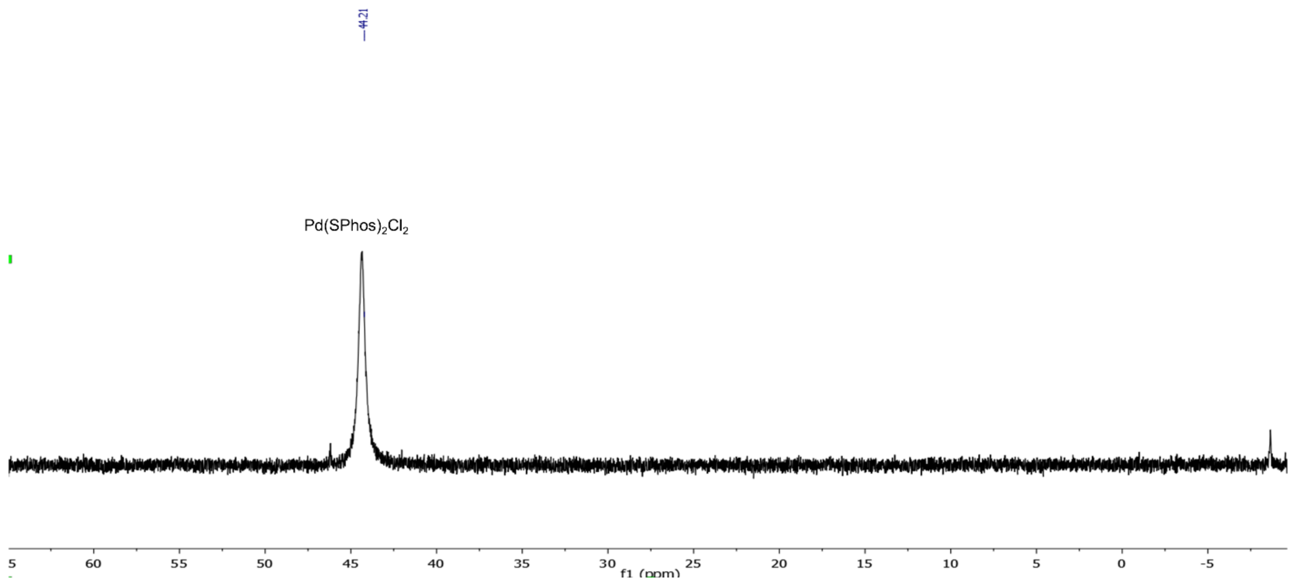
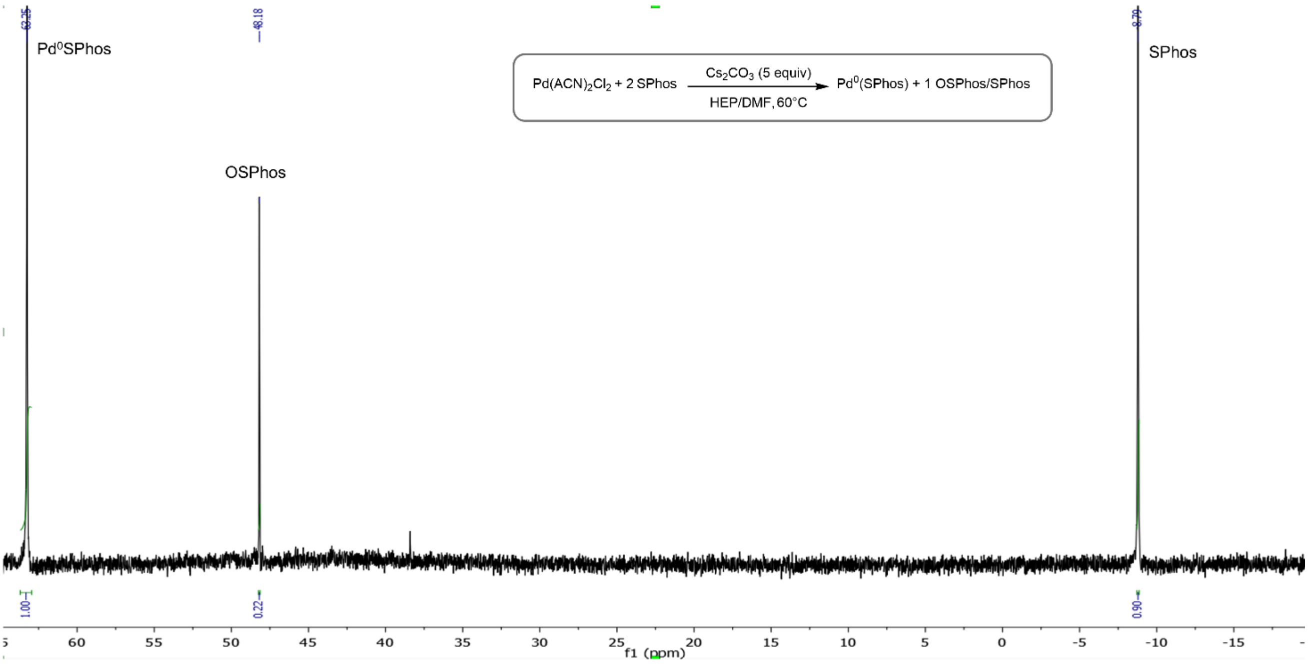


Figure S52. $Pd(ACN)_2Cl_2$ + SPhos (2 equiv) + TMG (5 equiv) at rt and 60°C, + Cs_2CO_3 (5 equiv) at 60°C, + TEA at 80°C in DMF-d_7 in 20 min

Entry 7, Table S6: Completed reduction in HEP/DMF-d_7 as example

a)



b)

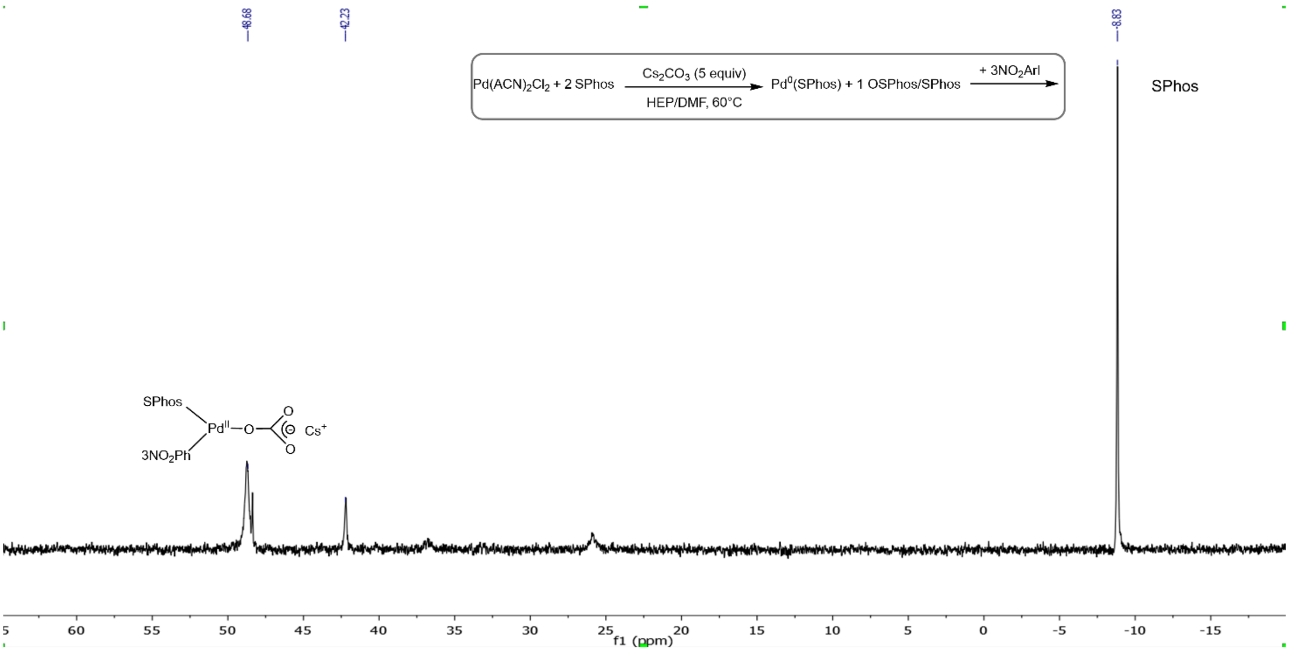


Figure S53. $Pd(ACN)_2Cl_2$ + SPhos (2 equiv) + Cs_2CO_3 (5 equiv) at 60°C in HEP/DMF-d_7 in 20 min. b) + $3NO_2ArI$

Other spectra

Entry 6, Table S6:

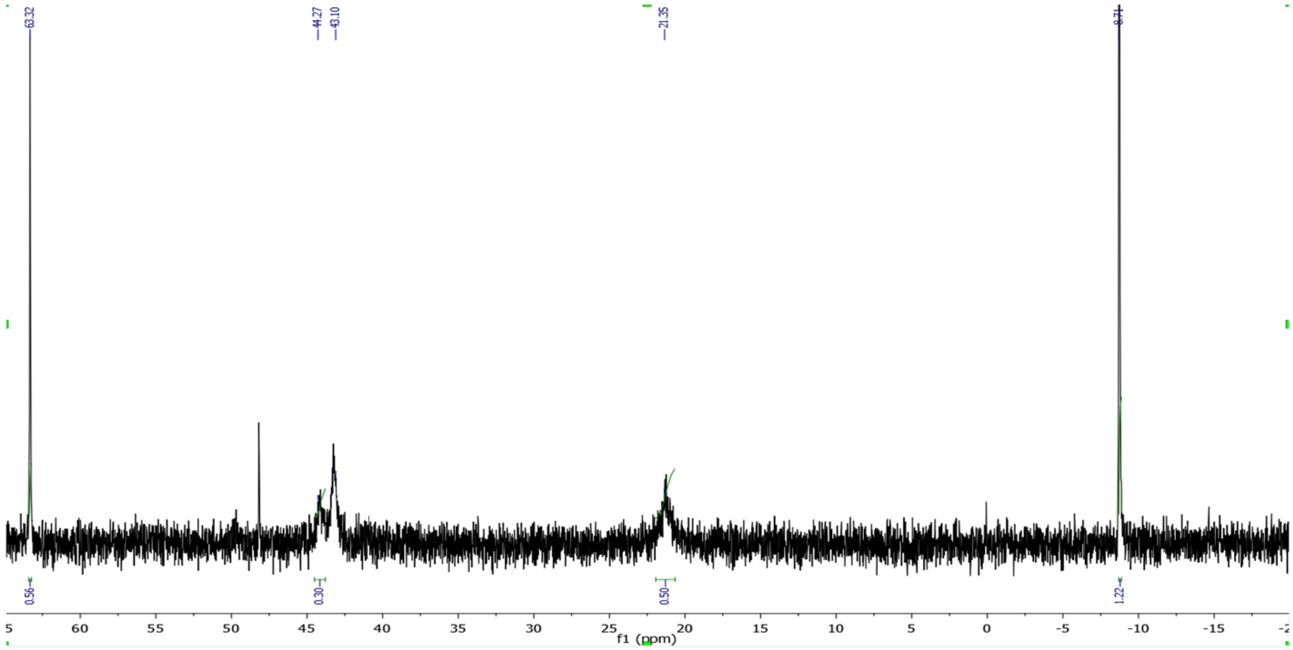


Figure S54. $PdCl_2(SPhos)_2$ + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 at rt. The peaks at 21.35 ppm and at 44.27 ppm are related to the IS and $PdCl_2(SPhos)_2$ respectively. The peak of the IS was broad in this condition.

Entry 8, Table S6:

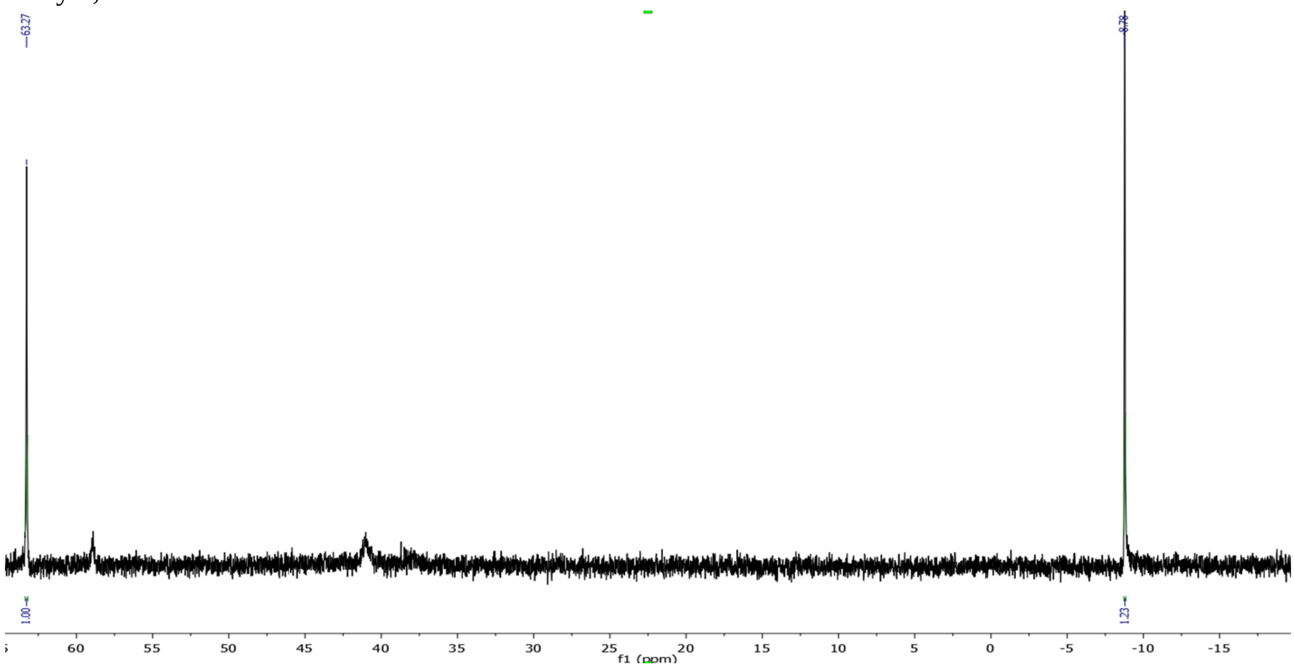


Figure S55. $PdCl_2(SPhos)_2$ + K_2CO_3 (5 equiv) in HEP/DMF-d_7 at 60°C.

Entry 9, Table S6:

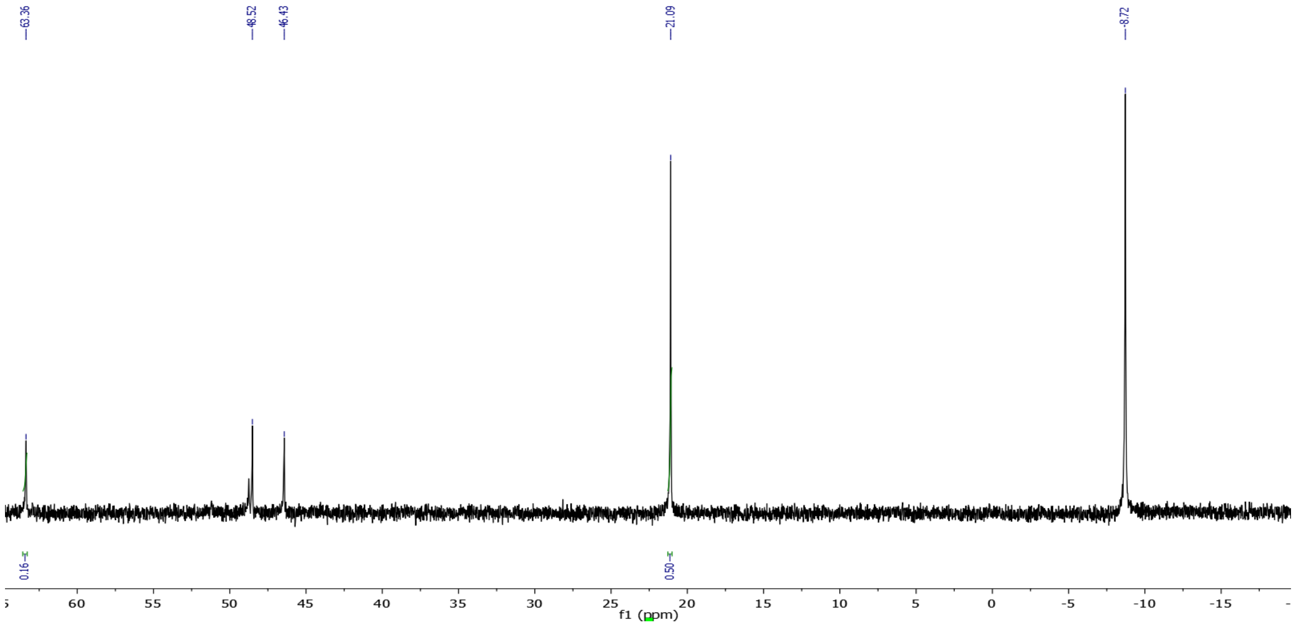


Figure S56. $PdCl_2(SPhos)_2$ + TMG (5 equiv) in HEP/DMF-d_7 at 60°C. The peaks at 21.09 ppm and at 63.36 ppm are related to the IS and Pd(SPhos) respectively.

3. Palladium pre-catalyst reduction with Xantphos

Table S7. ^{31}P NMR chemical shift in DMF-d_7 and HEP/DMF-d_7 (2:4) of palladium species with Xantphos

entry	Compound	DMF-d_7	HEP/DMF-d_7 (2:4)
1	Xantphos	-17.79	-18.03
2	Xantphos(O)[a]	-21.83; 25	-
3	$3NO_2ArPd^{II}$Xantphos(O) [b]	9.42; 25.02	10.22
4	$3NO_2$ArPdIXantphos	11.00	10.24
5	Pd^0Xantphos(O)	41.57; 17.08	41.54; 17.03
6	Pd^0Xantphos	19.39	19.18
7	$PdCl_2$Xantphos	22.70	22.13
8	$XantphosO_2$	27.56	28.60

[a] Xantphos(O) is the label for the Xantphos Mono-Oxide
[b] According to the literature[4]

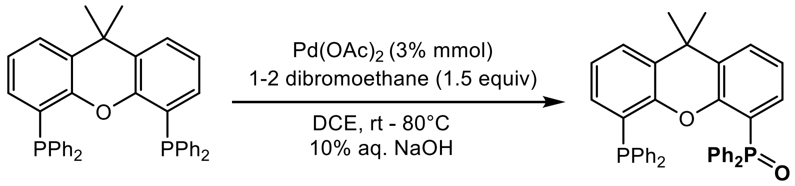
As the pre-catalyst $Pd(OAc)_2$Xantphos is not soluble in DMF-d_7, we used THF-d_8 instead of DMF

Table S8. ^{31}P NMR chemical shift in THF-d_7 and HEP/THF-d_8 (2:4) of palladium species with Xantphos

entry	Compound	THF-d_8	HEP/THF-d_8 (2:4)
1	Xantphos(O)	-21.5; 23.16	-21.70; 28.41
2	$3NO_2ArPdIXantphos$	10.87	10.79
3	$3NO_2ArPd^{II}Xantphos(O)$ [b]	11.62; 40.38	11.75, 40.65
4	$Pd^0Xantphos$	18.86	18.80
5	$Pd^0Xantphos(O)$	20.22; 39.53	-
6	$Pd(OAc)_2Xantphos$	25.51	-
7	OXantphos	-	29

3.1. Synthesis of palladium species with Xantphos and Reference for ^{31}P NMR

Entry 2, Table S7: Xantphos(O)



To an oven-dried 20 mL Schlenk purged under argon atmosphere, $Pd(OAc)_2$ (3.4 mg, 0.015 mmol, 0.03 equiv), xantphos (289.3 mg, 0.5 mmol, 1 equiv), 1,2-dibromoethane (65µL, 0.75 mmol, 1.5 equiv), 10% NaOH aq. solution (2 mL) were added in 1.5 mL of degassed 1,2-dicloroethane (DCE).
The result mixture was allowed to stir at 20°C for 12 hours, then warmed to 50°C for 5 hours, and at 80°C for 2 hours. Then, the result mixture was diluted with water (5 mL), extracted with DCM (3 x 5 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed by rotary evaporator and the crude material was purified by silica gel chromatography (DCM/EtOAc 100/0 to 60:40) to yield desired product as a pale yellow solid (30 mg, 17% yield)[5].

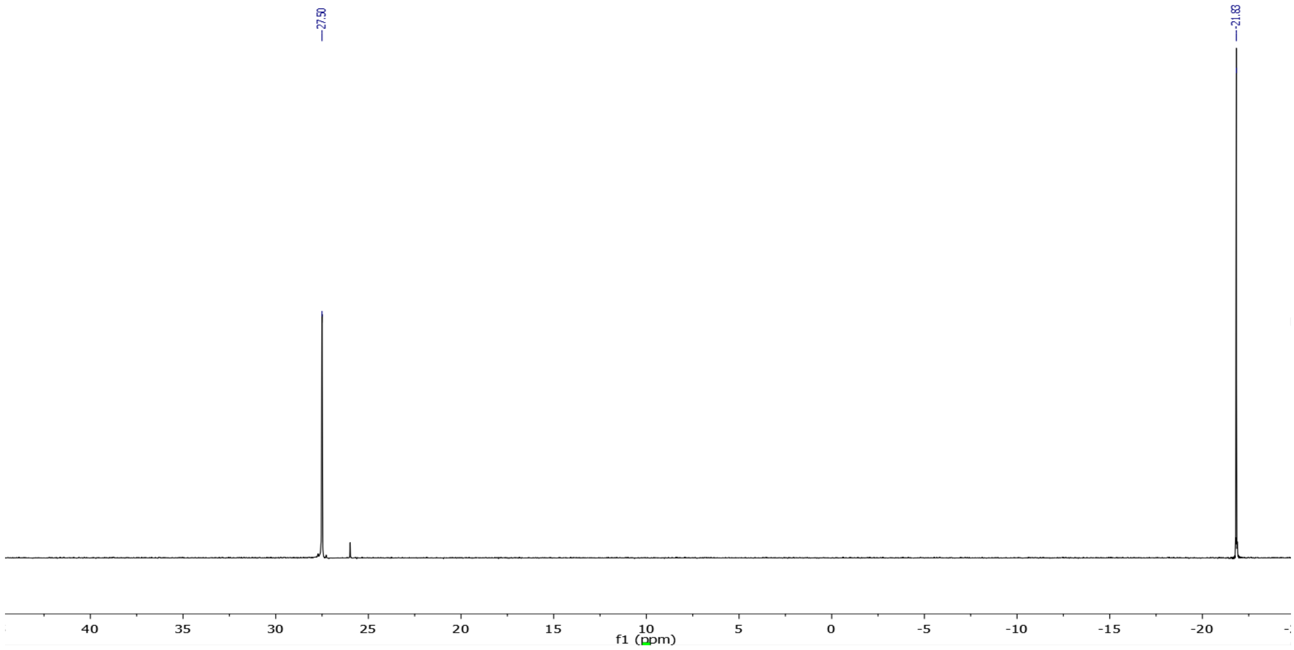
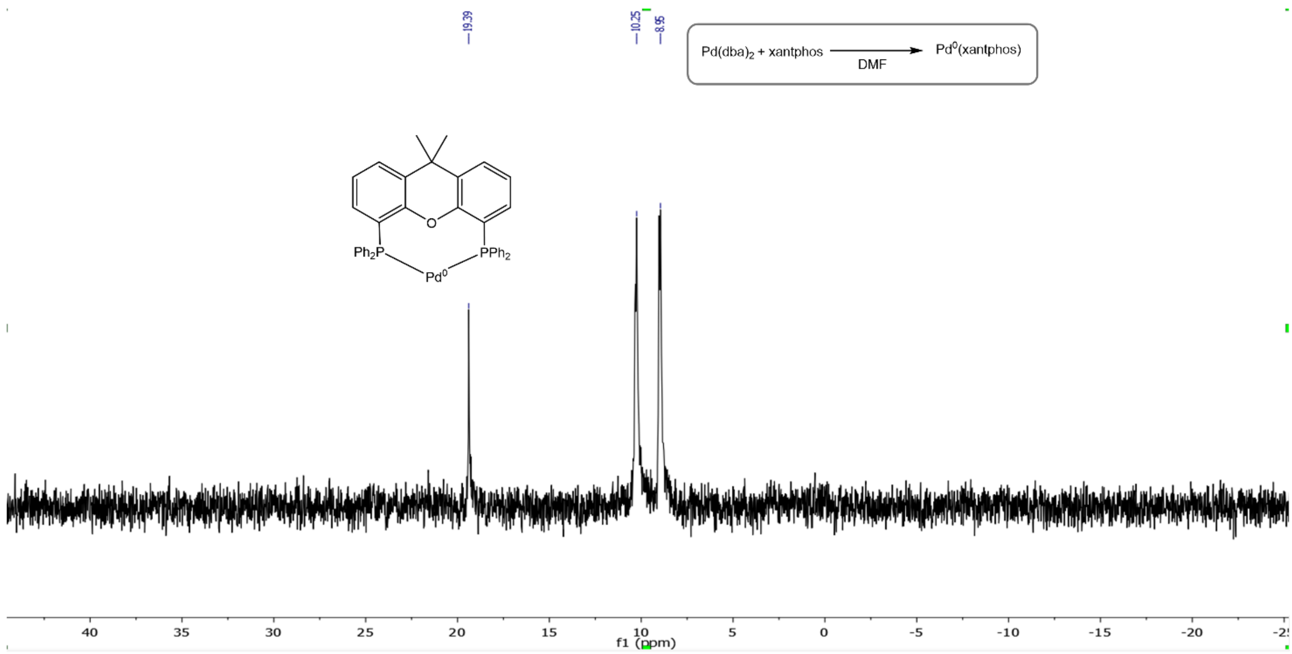


Figure S57. ^{31}P NNM spectrum of Xantphos(O) in DMF-d_7

Entry 4-5, Table S7: Pd^0(Xantphos) and $3NO_2$ArPdIXantphos

a)



b)

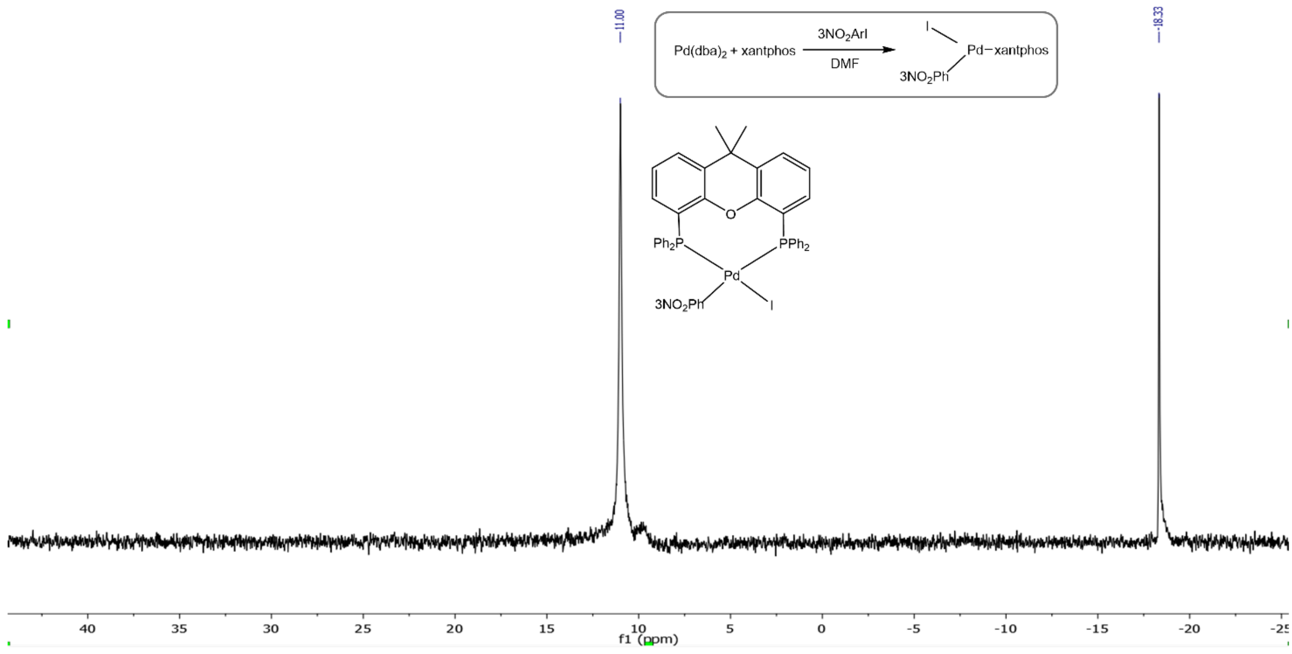


Figure S58 a) $Pd(dba)_2$ (11.9 mg, 0.013 mmol, 1 equiv), xantphos (6.94 mg, 0.013, 1 equiv) in DMF-d_7. The peaks at 10.25, 8.95 ppm are related to the dba coordinated to the Pd compound[6,7] ; b) +$3NO_2$ArI (16.18 mg, 0.065, 5 equiv) in DMF-d_7

Entry 5, Table S8:

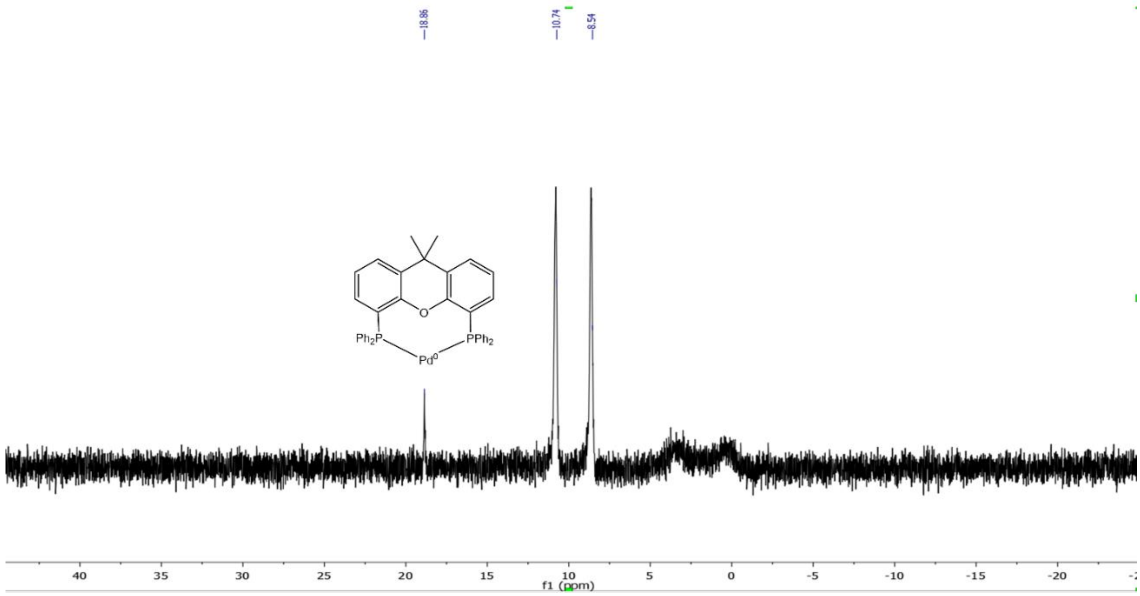
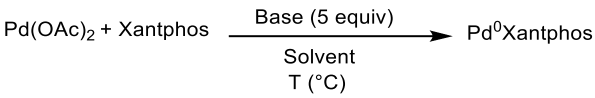


Figure S59. Pd(dba)$_2$ (11.9 mg, 0.013 mmol, 1 equiv), xantphos (6.94 mg, 0.013, 1 equiv) in THF-d$_8$. The peaks at 10.74, 8.54 ppm are related to the dba coordinated to the Pd compound[6]

3.2. Pd(OAc)$_2$

3.2.1. General Procedure 1



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst Pd(OAc)$_2$ (2.91 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Xantphos (7.52 mg, 0.013 mmol, 1 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis.
To further demonstrate that the formation of Pd(0) specie occurred, 3NO$_2$ArI (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex.

Table S9 Pd (OAc)$_2$Xantphos reduction in 20 min in THF-d$_8$ and HEP/THF-d$_8$[a]

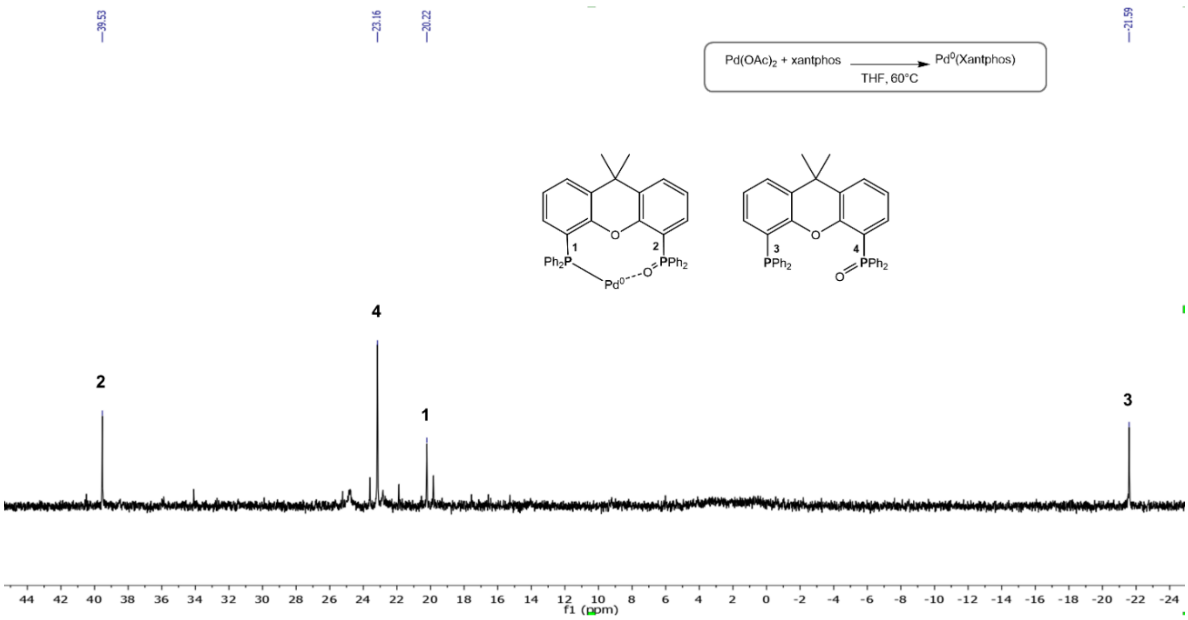
entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	THF[d]	25	-	0/100	-
2	-	THF	60	E	100/0	100/0
3	TMG	THF	60	-	100/0	-
4	Cs_2CO_3	THF	25	E	40/60	100/0
5	K_2CO_3	THF	25	-	0/100	-
6	K_2CO_3	THF/HEP[e]	25	A	100/0	0/100
7	Cs_2CO_3	THF/HEP	25	A	100/0	47/53

[a] The reactions were carried out according to the **General Procedure 1**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and Pd(OAc)$_2$Xantphos
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of THF-d$_8$
[e] The solvent is a mixture of HEP 200µL and THF-d$_8$ 400µL

3.2.2. ^{31}P NMR spectra

Entry 2, Table S9: Completed reduction in THF as example

a)



b)

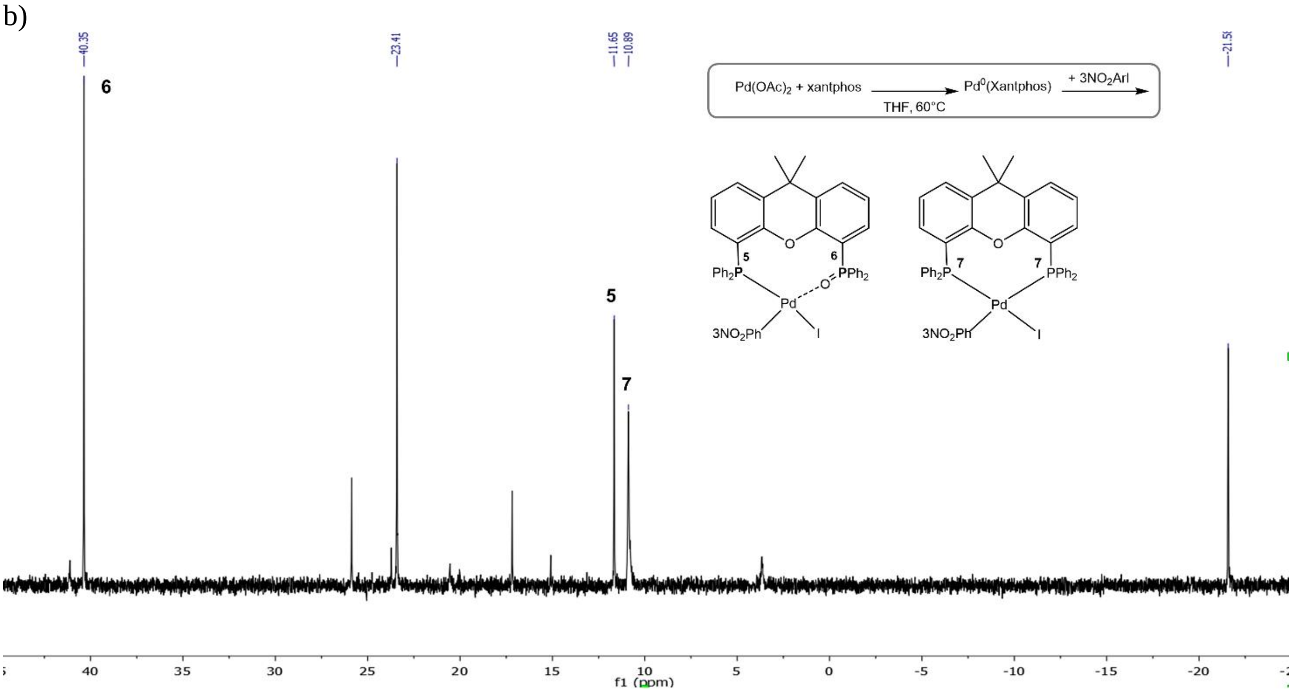


Figure S60. Pd(OAc)$_2$ + xantphos (1 equiv) in THF-d$_8$ at 60°C in 20 min; b) + 3NO$_2$ArI

Entry 1, Table S9:

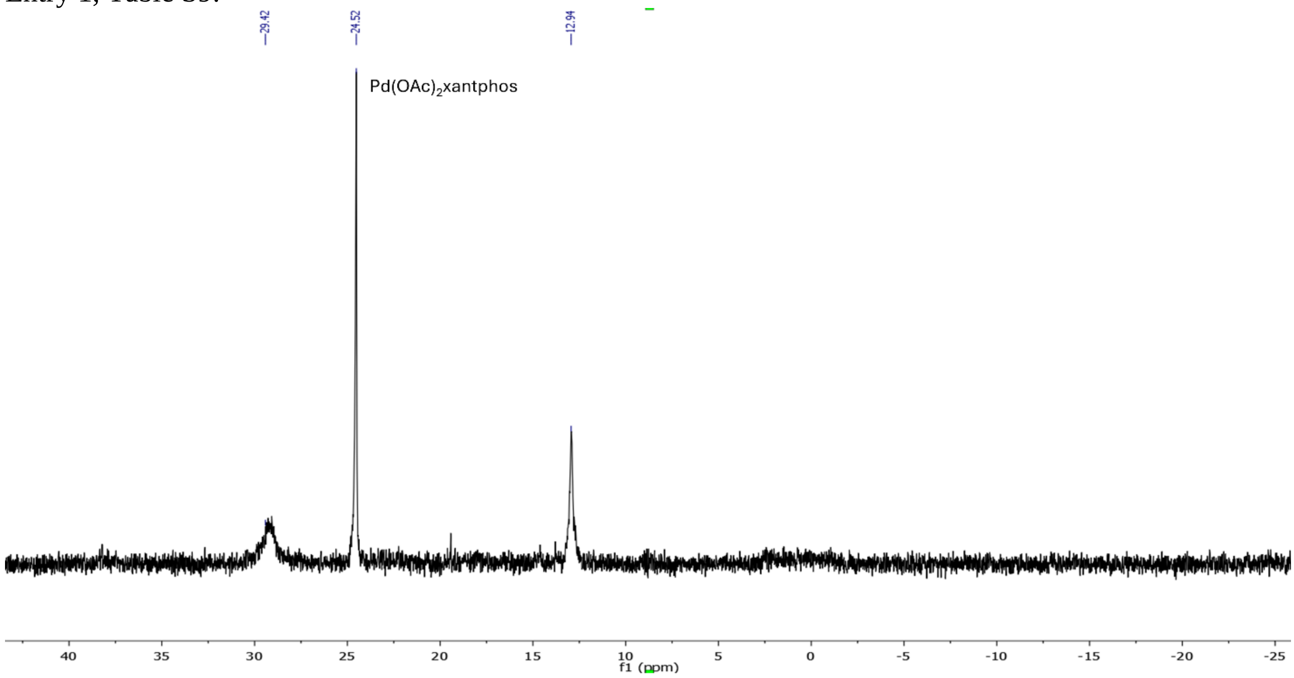


Figure S61. $Pd(OAc)_2$ + xantphos (1 equiv) in THF-d_8 at rt in 20 min.

Entry 3, Table S9:

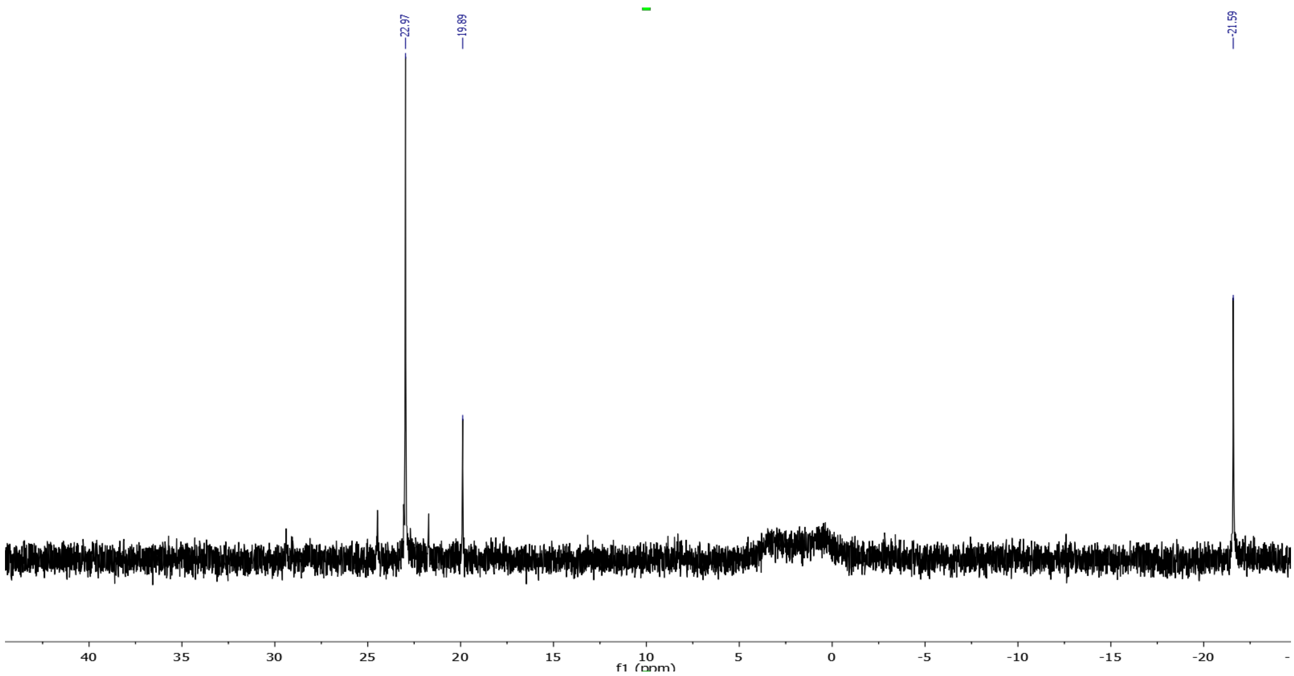


Figure S62. $Pd(OAc)_2$ + xantphos (1 equiv) + TMG (5 equiv) in THF-d_8 at 60°C in 20 min. It is reasonable to assume that the pre-catalyst complex is not stable in the presence of TMG (as with dppp, see below)

Entry 4, Table S9:

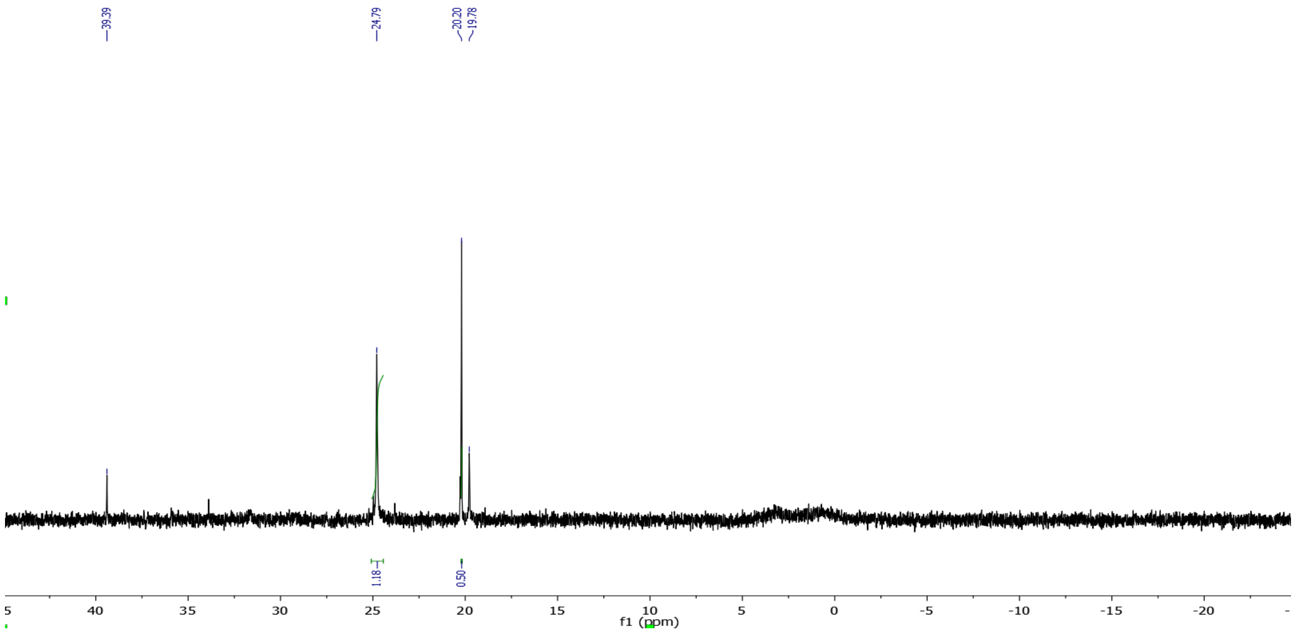


Figure S 63. $Pd(OAc)_2$ + xantphos (1 equiv) + Cs_2CO_3 (5 equiv) in THF-d_8 at 25°C in 20 min

Entry 5, Table S9:

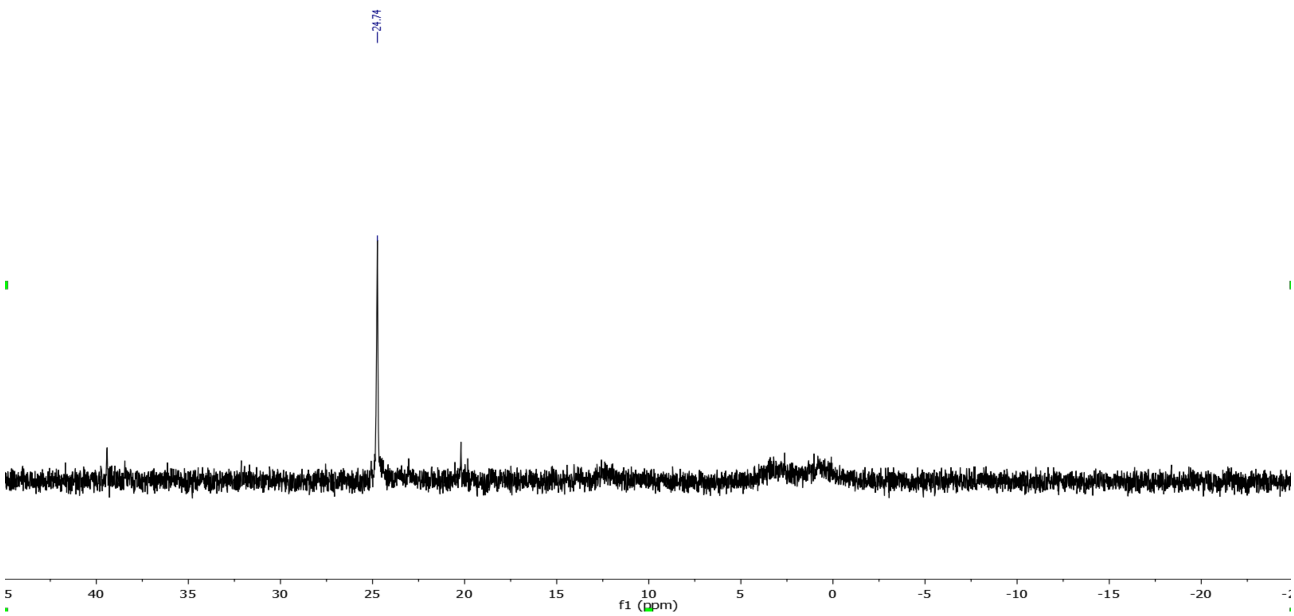
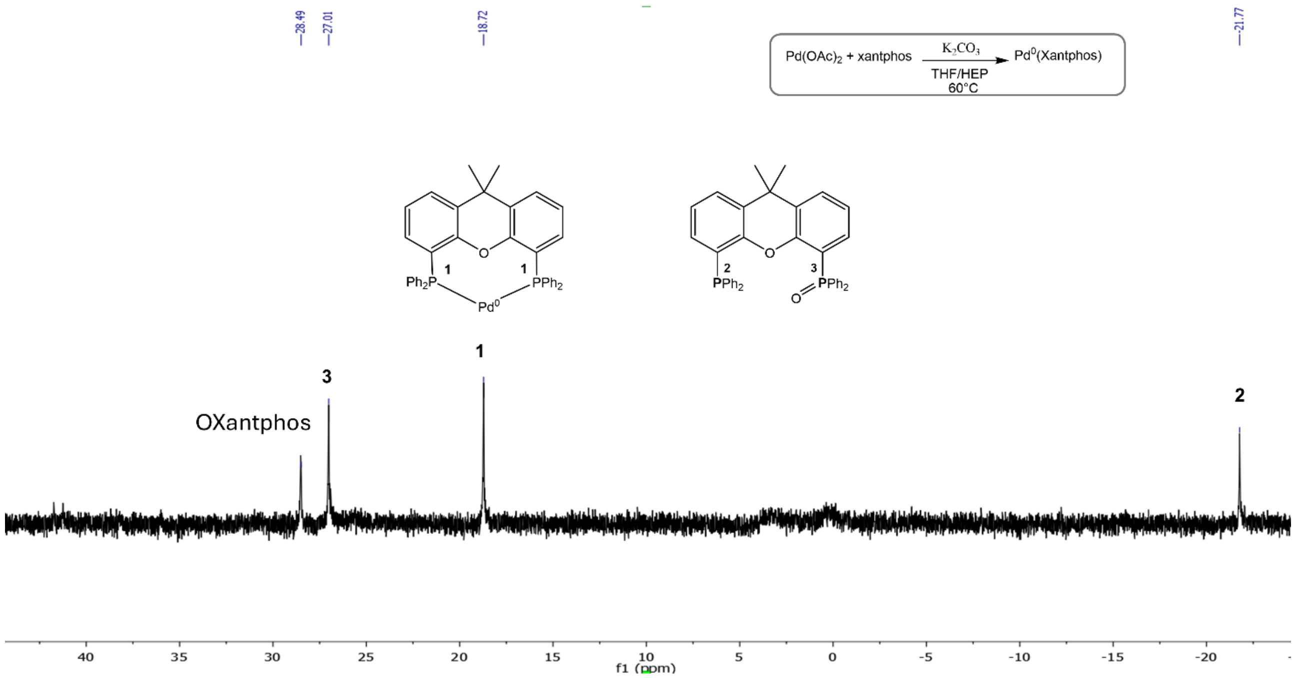


Figure S64. $Pd(OAc)_2$ + xantphos (1 equiv) + K_2CO_3 (5 equiv) in THF-d_8 at 25°C in 20 min

Entry 6, Table S9: Completed reduction in HEP/THF as example

a)



b)

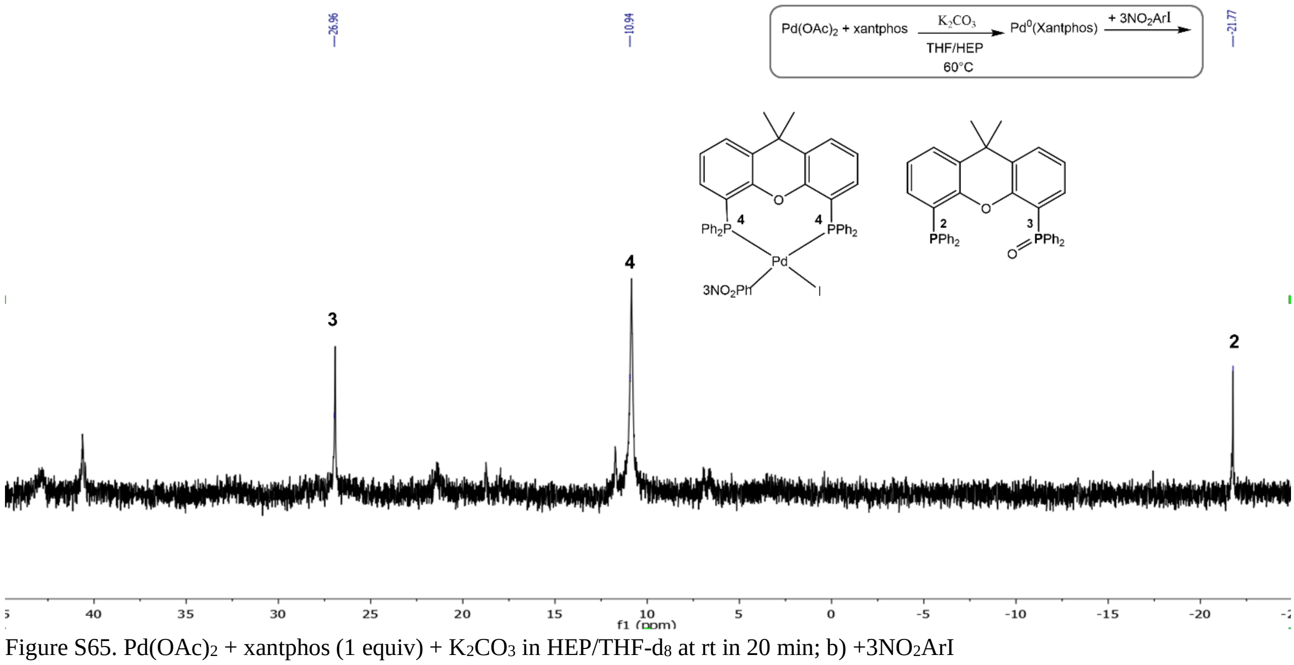
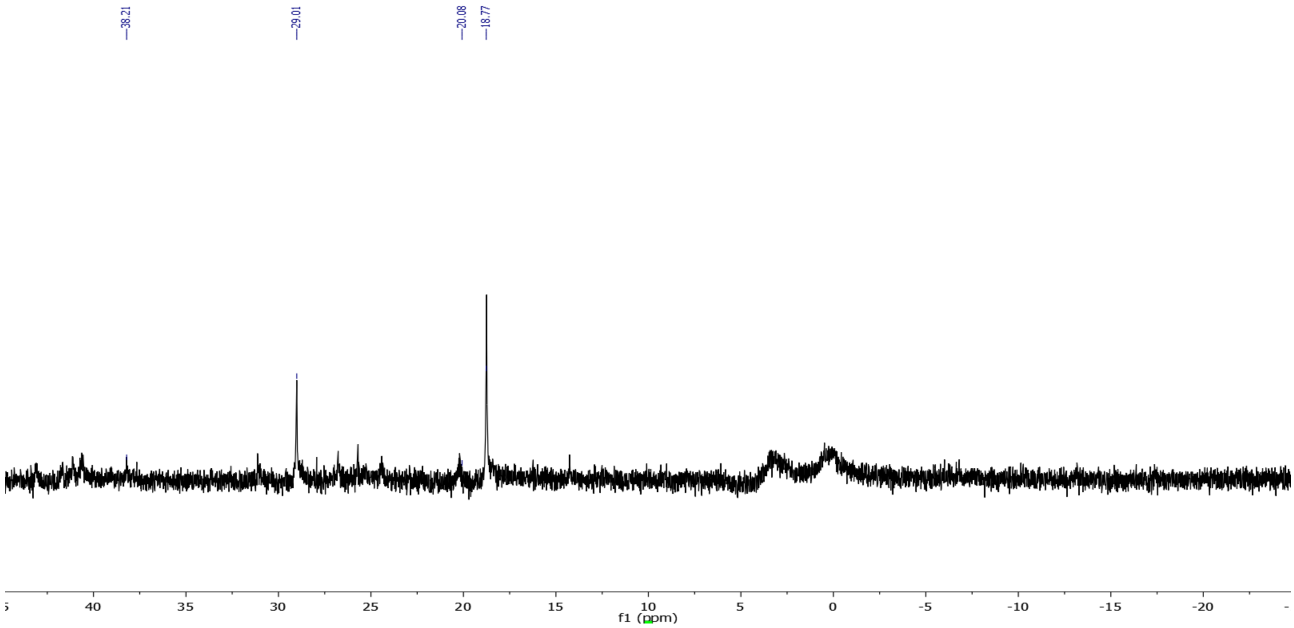


Figure S65. $Pd(OAc)_2$ + xantphos (1 equiv) + K_2CO_3 in HEP/THF-d_8 at rt in 20 min; b) +$3NO_2ArI$

Entry 7, Table S9:

a)



b)

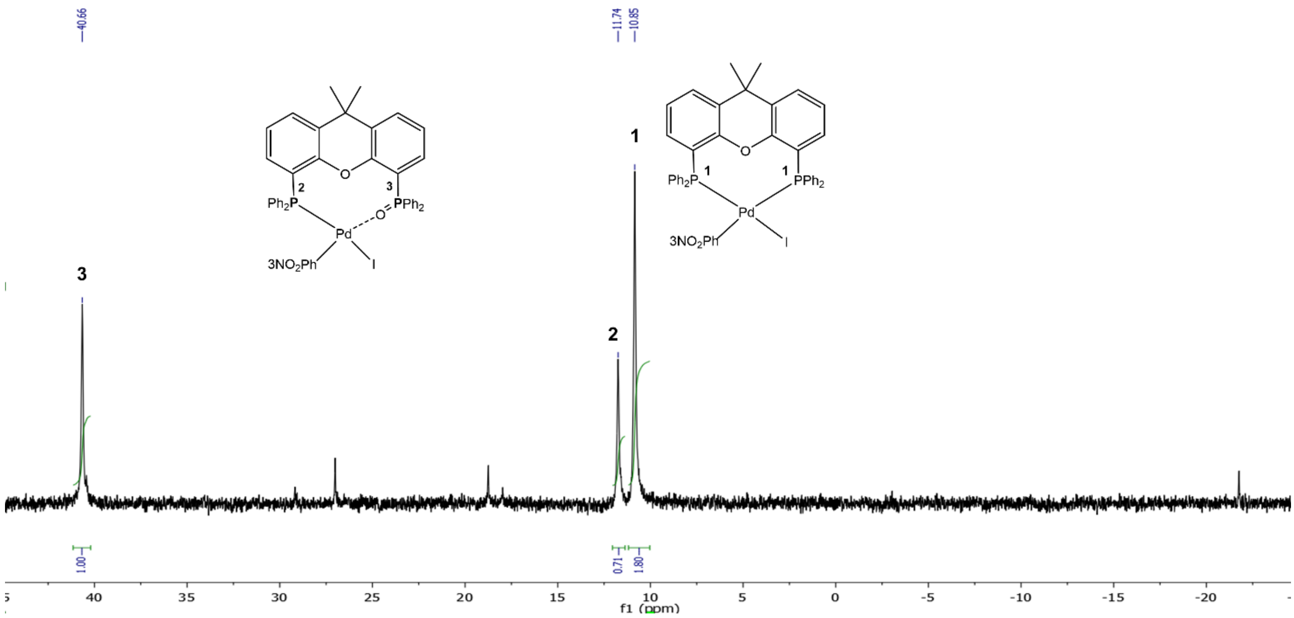
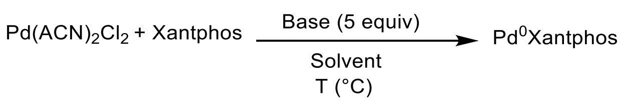


Figure S66. $Pd(OAc)_2$ + xantphos (1 equiv) +Cs_2CO_3 in HEP/THF-d_8 at rt in 20 min; b) +$3NO_2ArI$. The signals became clear after the addition of aryl halide

3.3. $PdCl_2$

3.3.1 General Procedure 2



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(ACN)_2Cl_2$ (3.37 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Xantphos (7.52 mg, 0.013 mmol, 1

equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis.
To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex.

Table S10. Pd(Xantphos)Cl_2 reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

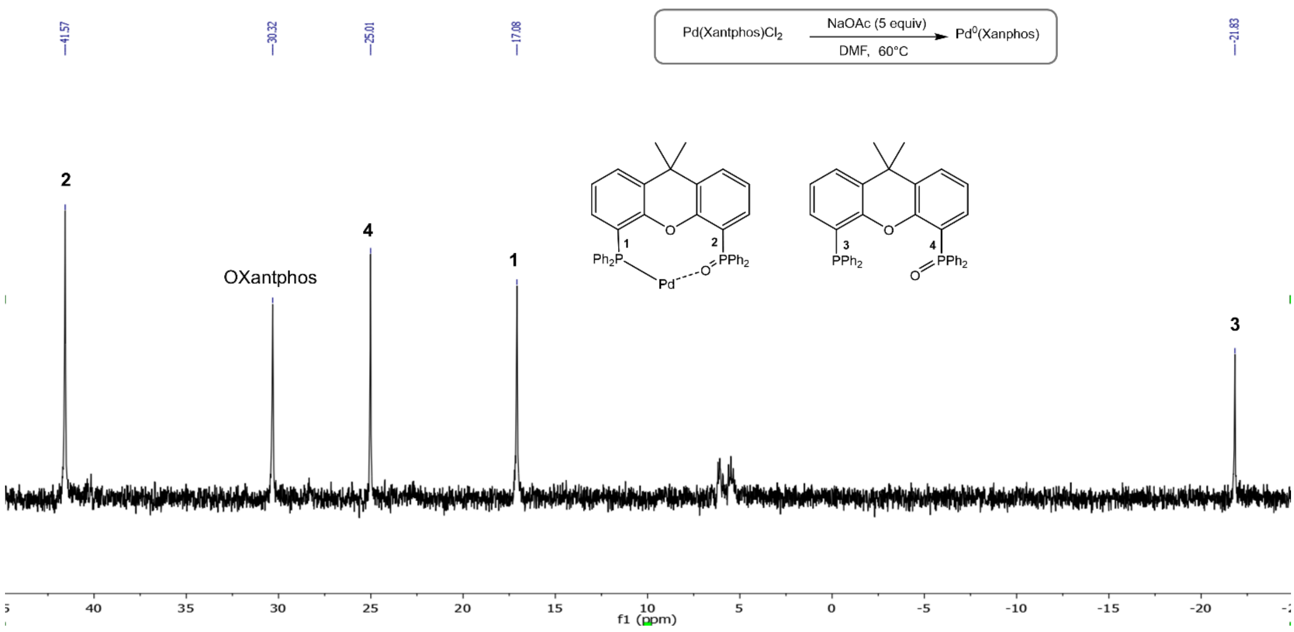
entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	60	-	0/100	-
2	TEA	DMF	80	-	0/100	-
3	TMG	DMF	60	-	0/100	-
4	Cs_2CO_3	DMF	60	-	0/100	-
5	K_2CO_3	DMF	60	-	0/100	-
6	NaOAc	DMF	60	E	100/0	-
7	Cs_2CO_3	DMF/HEP[e]	25	-	0/100	-
8	K_2CO_3	DMF/HEP	25	-	0/100	-
9	Cs_2CO_3	DMF/HEP	60	A	100/0	0/100
10	K_2CO_3	DMF/HEP	60	A	100/0	0/100

[a] The reactions were carried out according to the **General Procedure 2**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $PdCl_2$(Xantphos)
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

3.3.2. ^{31}P NMR spectra

Entry 6, Table S10: Completed reduction in DMF as example

a)



b)

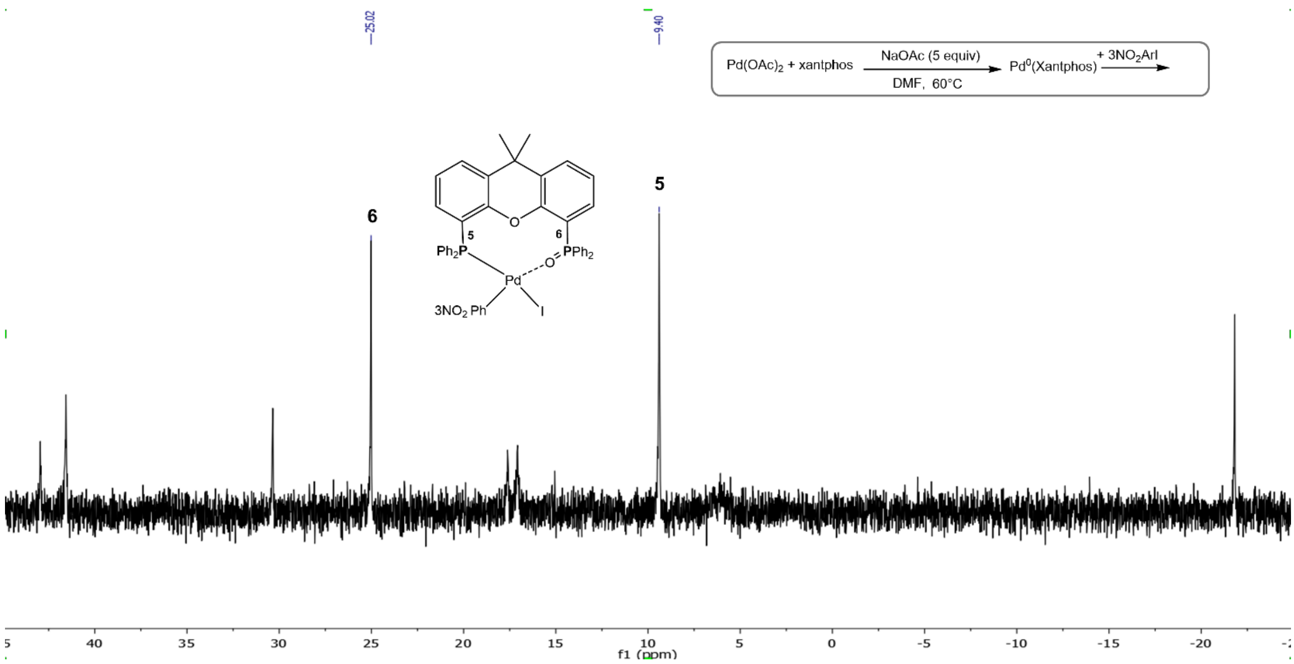


Figure S67. Pd(ACN)$_2$Cl$_2$ + xantphos (1 equiv) + NaOAc (5 equiv) in DMF-d$_7$ at 60°C in 20 min[4]. b) +3NO$_2$ArI

Other spectra

Entries 1-3, Table S10:

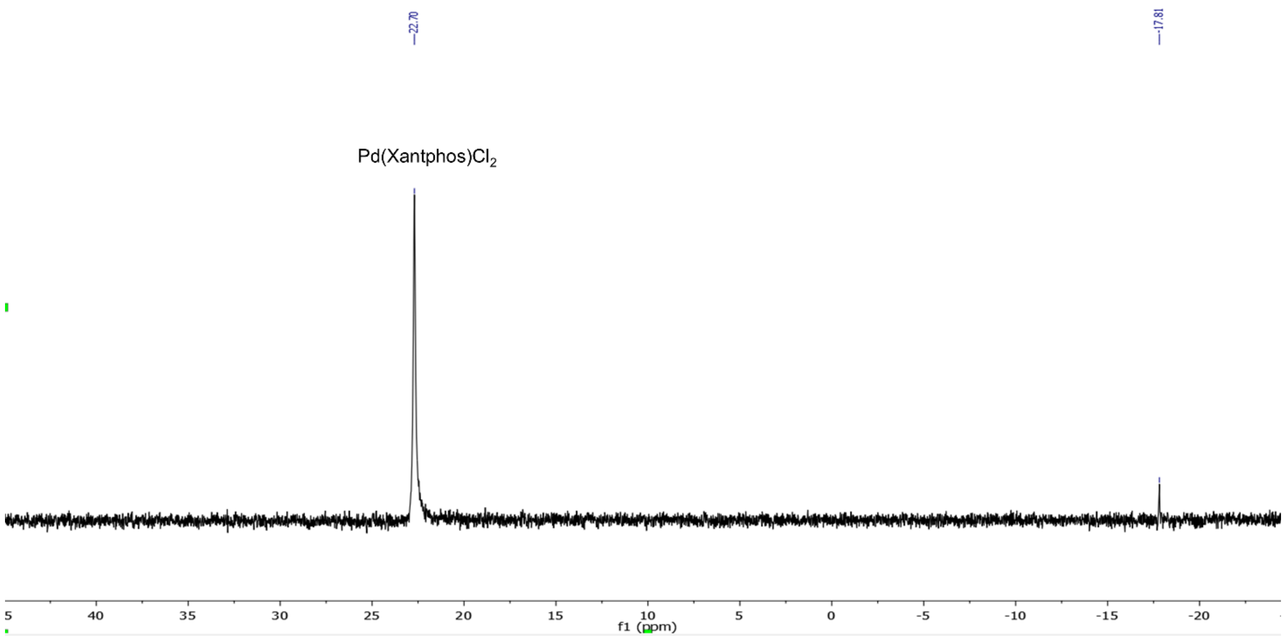


Figure S68. Pd(ACN)$_2$Cl$_2$ + xantphos (1 equiv); Pd(OAc)$_2$ + xantphos (1 equiv) + TMG (5 equiv) at 60°C and + TEA (5 equiv) at 80°C in DMF-d$_7$ in 20 min.

Entries 4 and 5, Table S10:

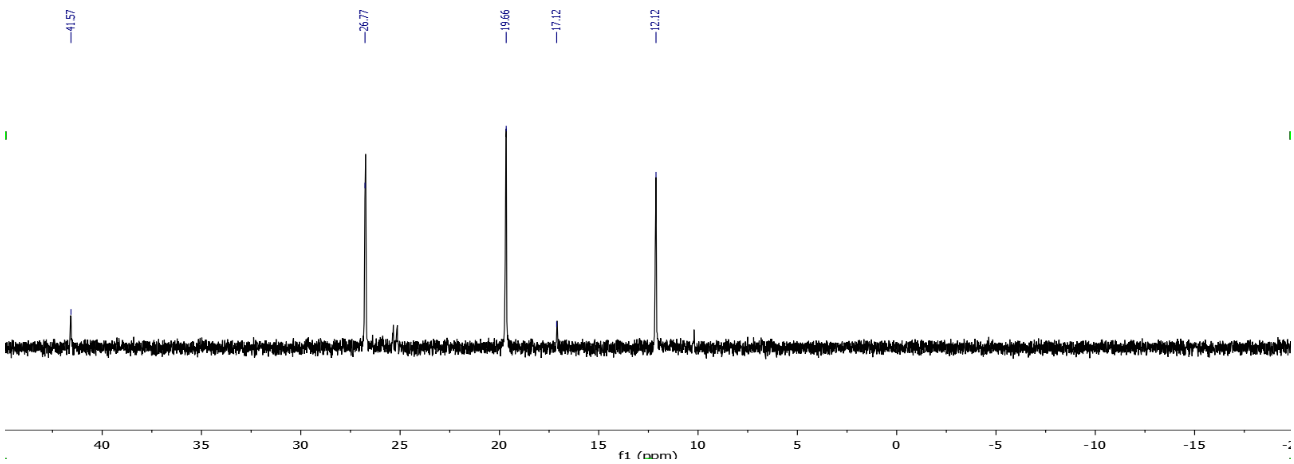
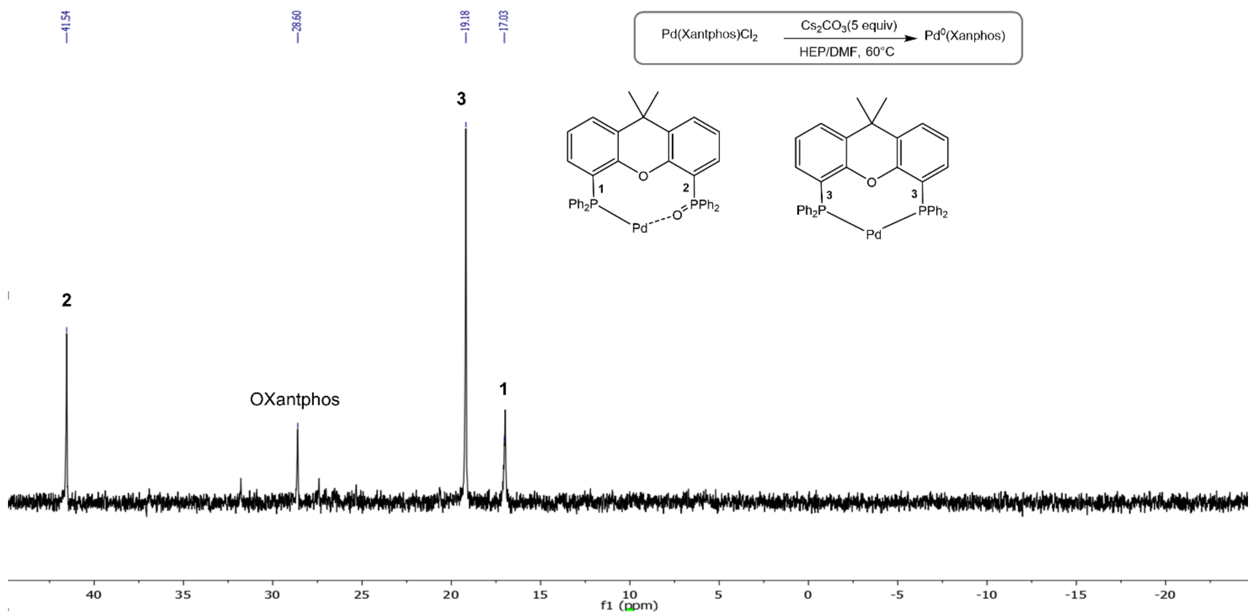


Figure S69. a) Pd(ACN)$_2$Cl$_2$ + Xantphos (1 equiv) + Cs_2CO_3 and K_2CO_3 (5 equiv) in DMF-d$_7$ at 60°C. The reduction occurred in traces (41.57 ppm, 17.12 ppm). Since the spectrum was the same after the addition of the aryl halide, the species 26.77, 19.66, 12.12 ppm are considered to be different species of palladium(II).

Entry 9, Table S10: Completed reduction in HEP/DMF as example

a)



b)

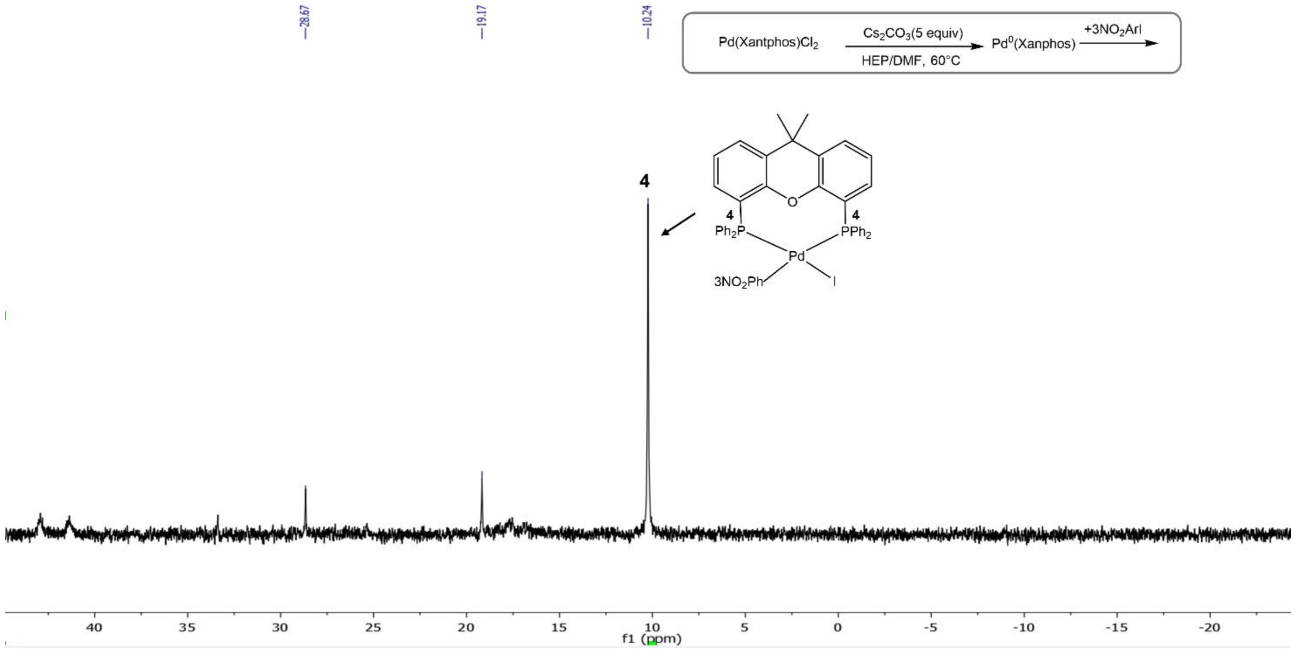


Figure S70. a) $Pd(ACN)_2Cl_2$ + xantphos (1 equiv) + Cs_2CO_3 (5 equiv) at 60°C in HEP/DMF-d_7 (2:4) in 20 min; b) +$3NO_2ArI$

Other spectra

Entry 7-8, Table S10:

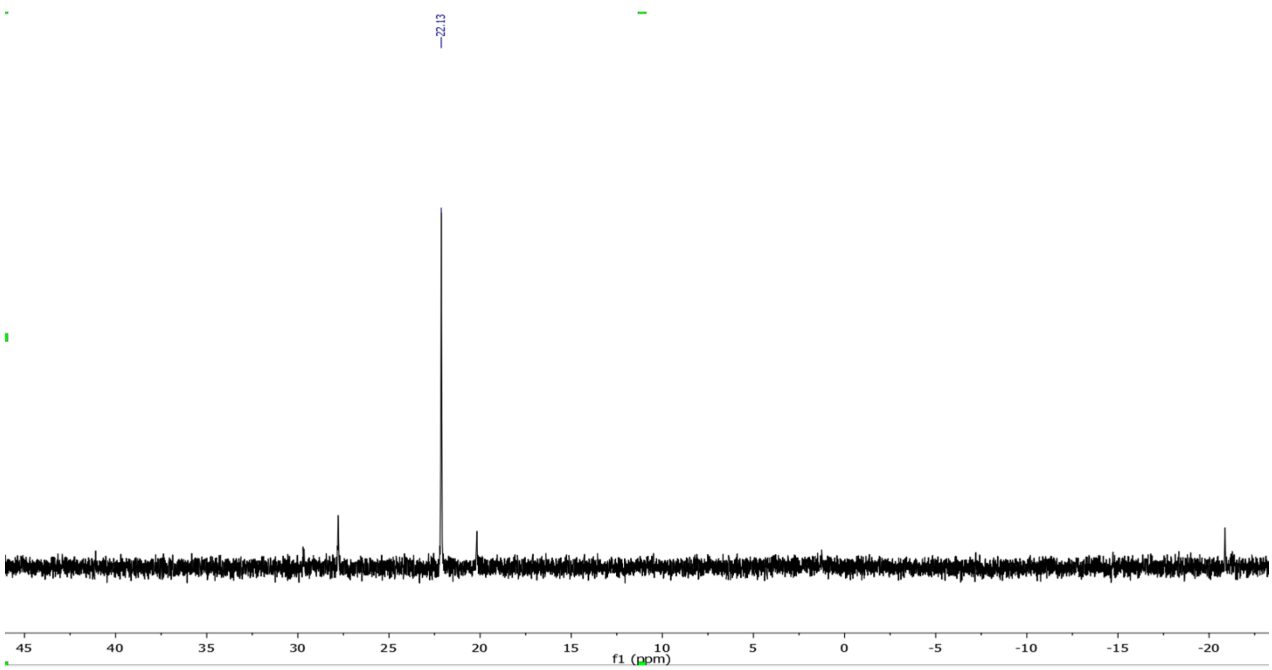
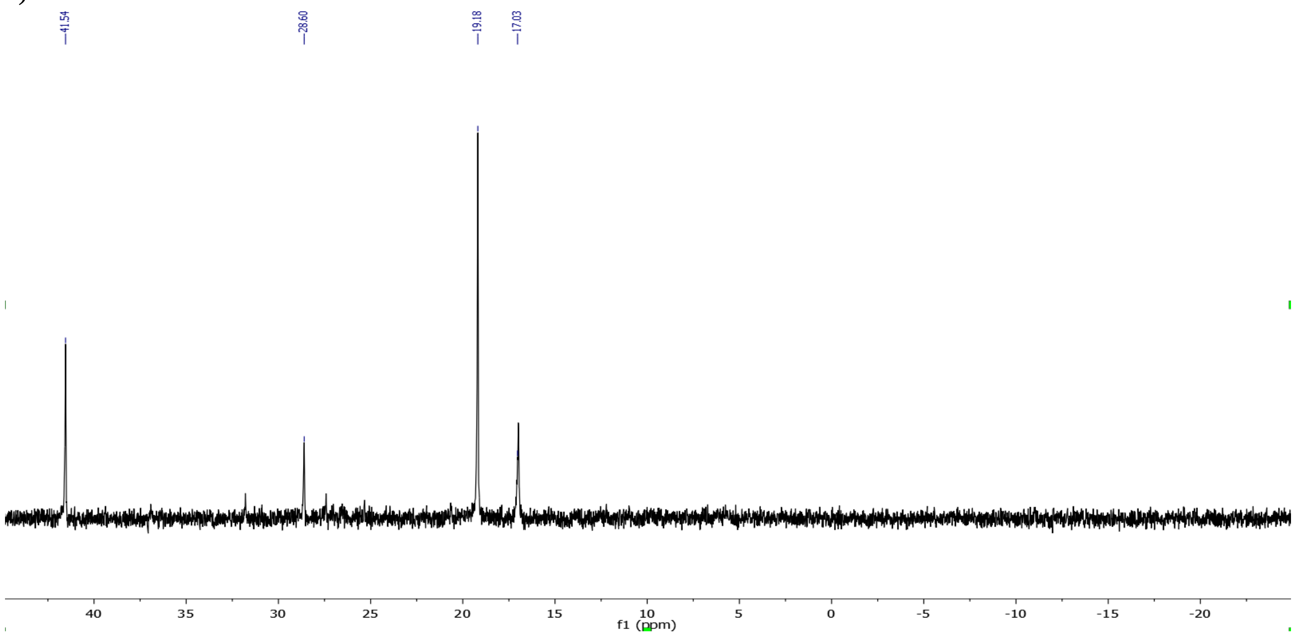


Figure S71. $Pd(ACN)_2Cl_2$ + xantphos (1 equiv) + Cs_2CO_3 and K_2CO_3 (5 equiv) at rt in 20 min.

Entry 11, Table S10:

a)



b)

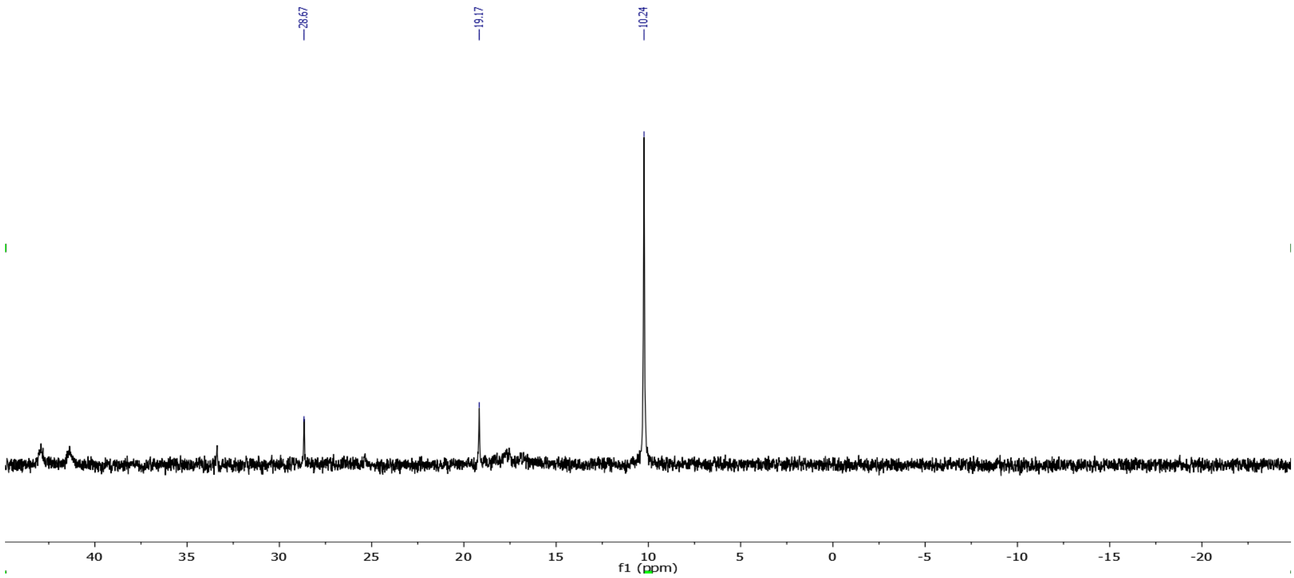


Figure S72. $Pd(ACN)_2Cl_2$ + xantphos (1 equiv) + K_2CO_3 (5 equiv) at 60°C in HEP/DMF-d_7 (2:4) in 20 min; b) + $3NO_2ArI$

4. Palladium pre-catalyst reduction with DPPF

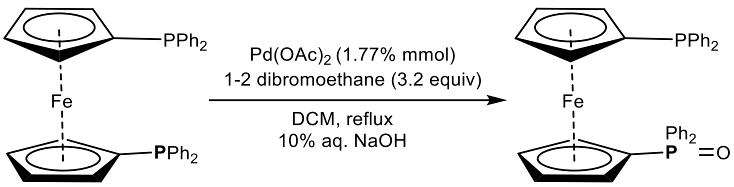
Table S11. ^{31}P NMR chemical shift in DMF-d_7 and HEP/DMF-d_7 (2:4) of palladium species with dppf

entry	Compound	DMF-d_7	HEP/DMF-d_7 (2:4)
1	dppf	-17.12	-17.16
2	dppf(O)[a]	-17.43; 25.95	-17.58; 27.30
3	$Pd^0(dppf)_2$[b]	6.91	6.83
4	$Pd^0(dppf)$	33.83	34.25
5	Pd^0dppf(O)dppf	9.3 (m); 16.60 (m)	9.18 (m); 16.56 (m)
6	$3NO_2ArPd(dppf)I$	13.01(d); 32.69 (d)	12.83(d); 32.72 (d)
7	$dppfO_2$ [c]	26.04	27.76
8	$Pd(OAc)_2(dppf)$	31.66	32.18
9	$Pd^0(dppf)$	33.83	34.25
10	$PdCl_2(dppf)$	34.94	34.97

[a] dppf(O) is the label for the dppf Mono-Oxide
[b] according to the literature[8]

4.1. Synthesis of palladium species with dppf and Reference for ^{31}P NMR

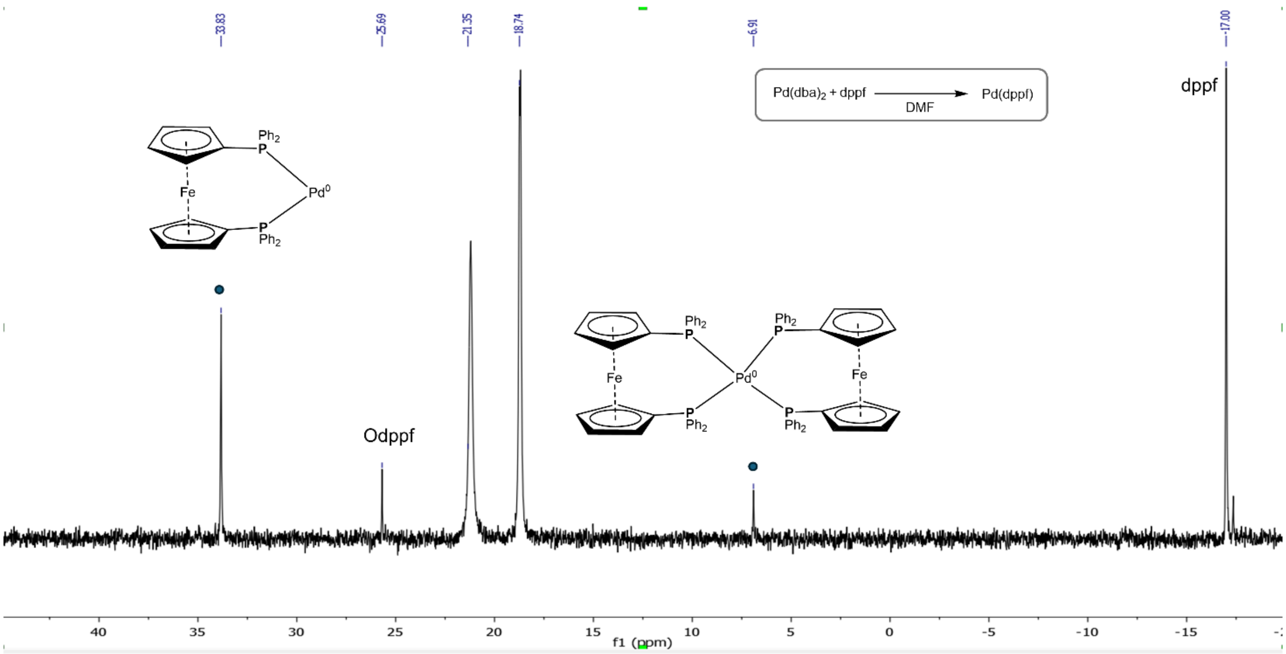
Entry 2, Table S11: dppf(O)



To an oven-dried 20 mL Schlenk purged under argon atmosphere, $Pd(OAc)_2$ (1.5 mg, 0.006 mmol, 0.00177 equiv), dppf (196 mg, 0.36 mmol, 1 equiv), 1,2-dibromoethane (100 µL, 1.15 mmol, 3.2 equiv), 10% NaOH aq (500 µL) were added in degassed DCM (1.2 mL). The resulting mixture was refluxed with vigorous stirring for 17 h. Then, the result mixture was diluted with water (5 mL), extracted with DCM (3 x 5 mL), the combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed by rotary evaporator and the crude material was purified by silica gel chromatography (DCM/EtOAc 100/0 to 50:50) to yield desired product as an orange solid (60 mg, 30% yield)[9].
^{31}P NMR (DMF-d_7): -17.43 (s); 25.95 (s)

Entries 3-9, Table S11: Pd^0(dppf) and $3NO_2ArPd$(dppf)I

a)



b)

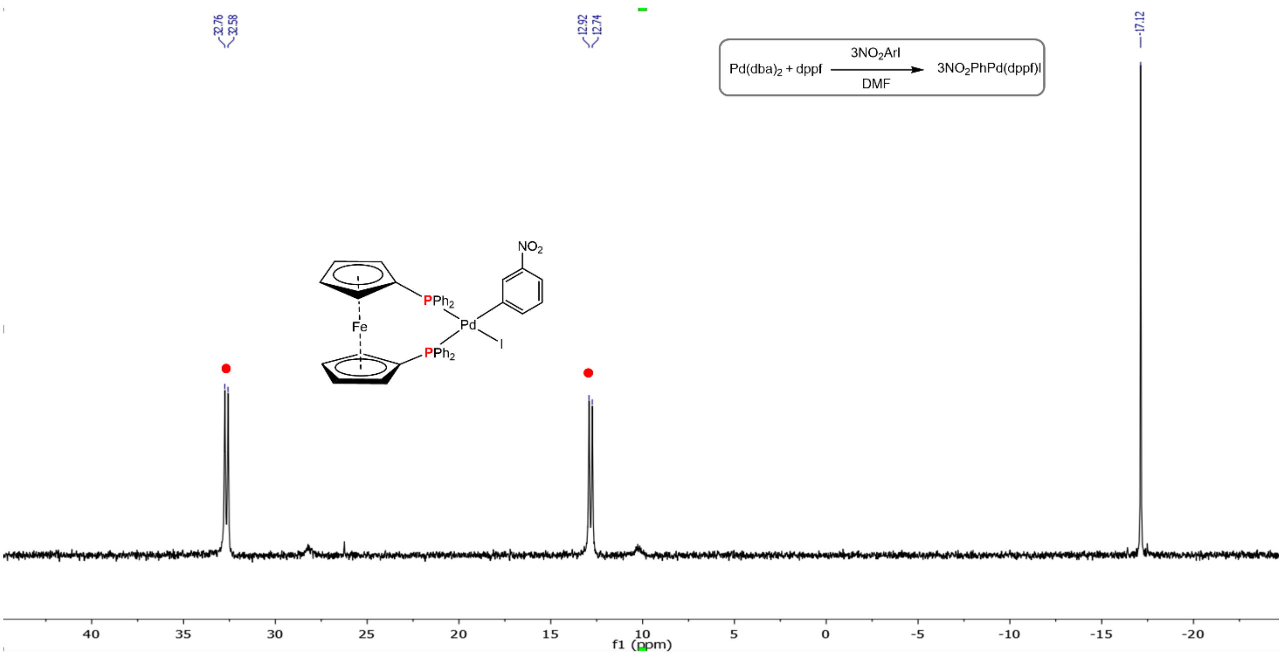


Figure S73. a) $Pd(dba)_2$ (11.9 mg, 0.013 mmol, 1 equiv), dppf (7.5 mg, 0.013, 1 equiv) in DMF-d_7. The peaks at 10.25, 8.95 ppm are related to the dba coordinated to the Pd compound[6,7] b) +$3NO_2ArI$ (16.18 mg, 0.065, 5 equiv) in DMF-d_7

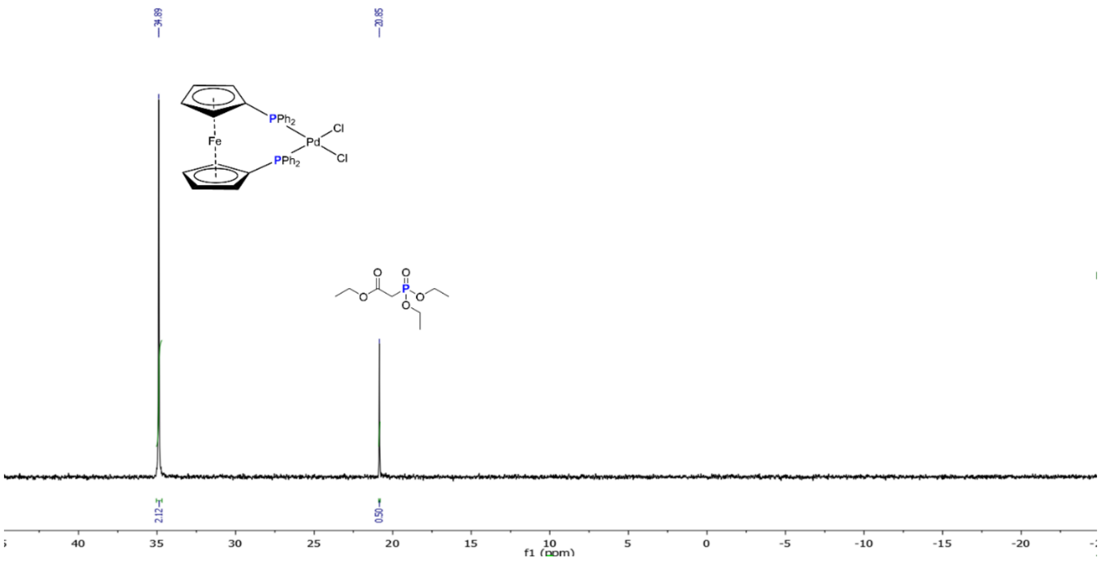
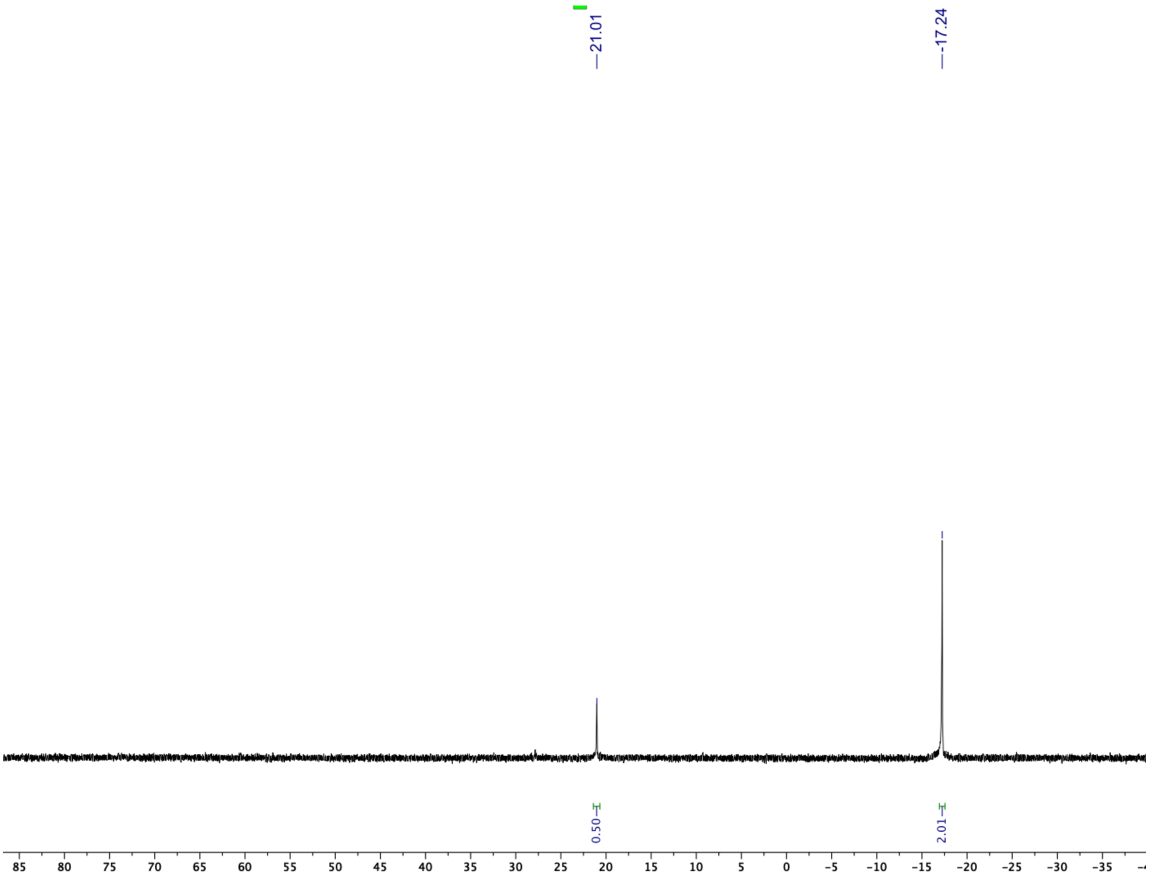


Figure S74. ^{31}P NMR spectrum of Pddppf (1 equiv) and triethyl phosphonoacetate (0.5 equiv) as IS to know their integration ratio under the same setting used for all the experiments (d_1=1, nt=256).

a)



b)

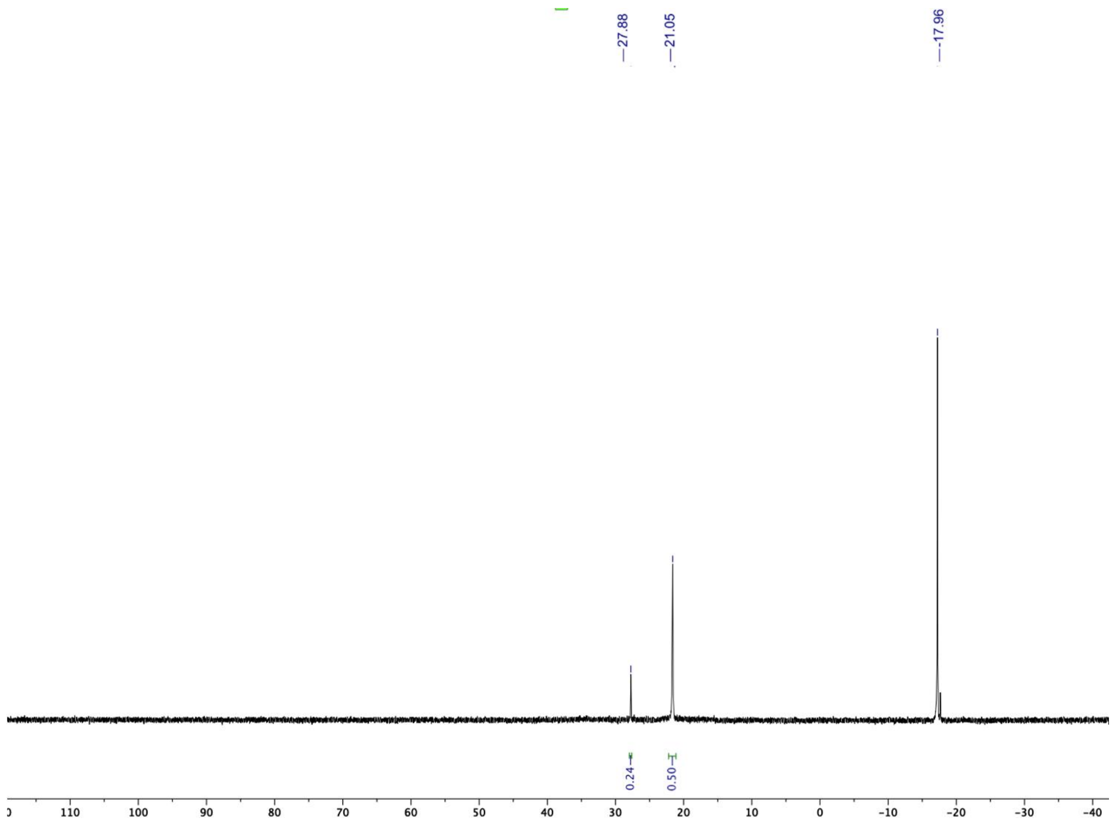
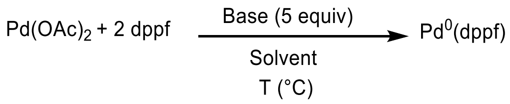


Figure S75. a) dppf in DMF/HEP at 60°C: No dppf oxidation. b) dppf in DMF/HEP in the presence of Cs_2CO_3 (5 equiv) at 60°C: partial oxidation of dppf producing dppf(O) at 27.88 ppm. Triethyl phosphonoacetate (0.5 equiv) as internal standard at 21.05 ppm.

4.2. $Pd(OAc)_2$

4.2.1. General Procedure 1



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(OAc)_2$ (2.91 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Dppf (14.41 mg, 0.026 mmol, 2 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.0065 mmol, 0.5 eq) was added as internal standard (IS).
To further demonstrate that the formation of Pd(0) specie occurred, the $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1].

Table S12 Pd(dppf)$(OAc)_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

entry	Base	Solvent	T(°C)	Mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	25	E	20/80	100/0
2	TMG	DMF	25	D	100/0	100/0
3	-	DMF	60	E	100/0	100/0
4	TMG	DMF	60	D/E	100/0	100/0
5	Cs_2CO_3	DMF	60	E	100/0	100/0
6	K_2CO_3	DMF	60	E	100/0	100/0
7	Cs_2CO_3	DMF/HEP[e]	25	A/E	100/0	45/55
8	K_2CO_3	DMF/HEP	25	A	100/0	0/100

[a] The reactions were carried out according to the **General Procedure 1**

[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $Pd(OAc)_2$dppf

[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.

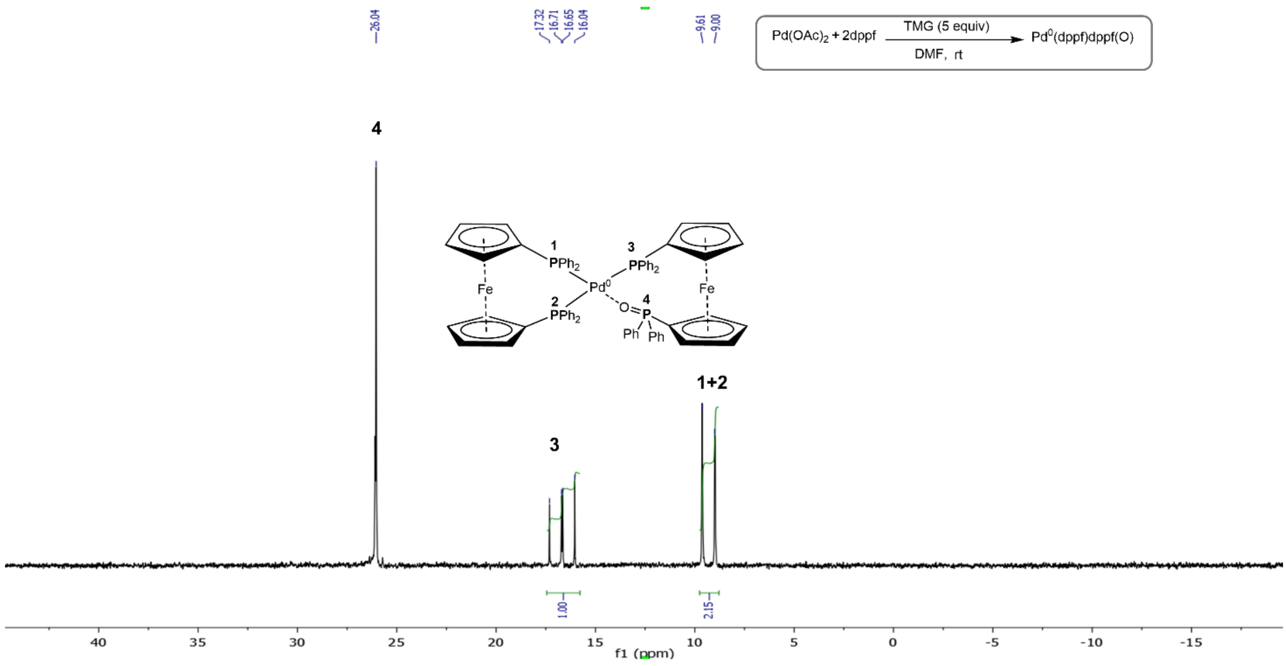
[d] 600µL of DMF-d_7

[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

4.2.2. ^{31}P NMR spectra

Entry 2, Table S12: Completed reduction in DMF as example

a)



b)

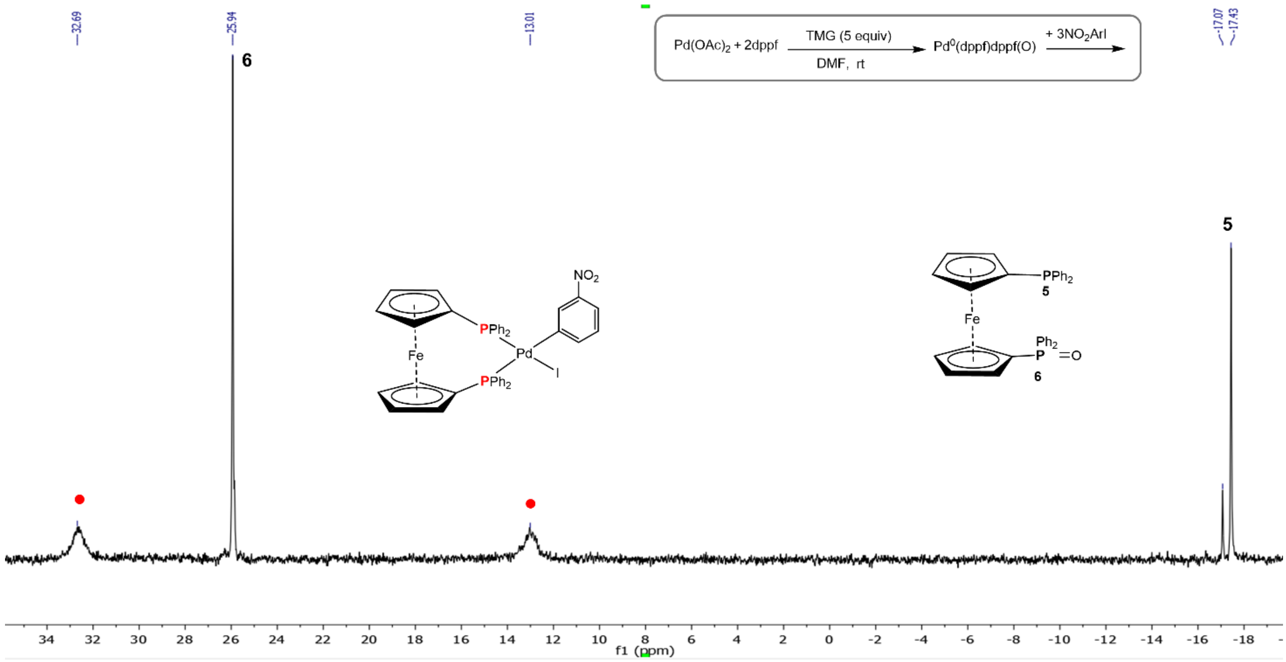
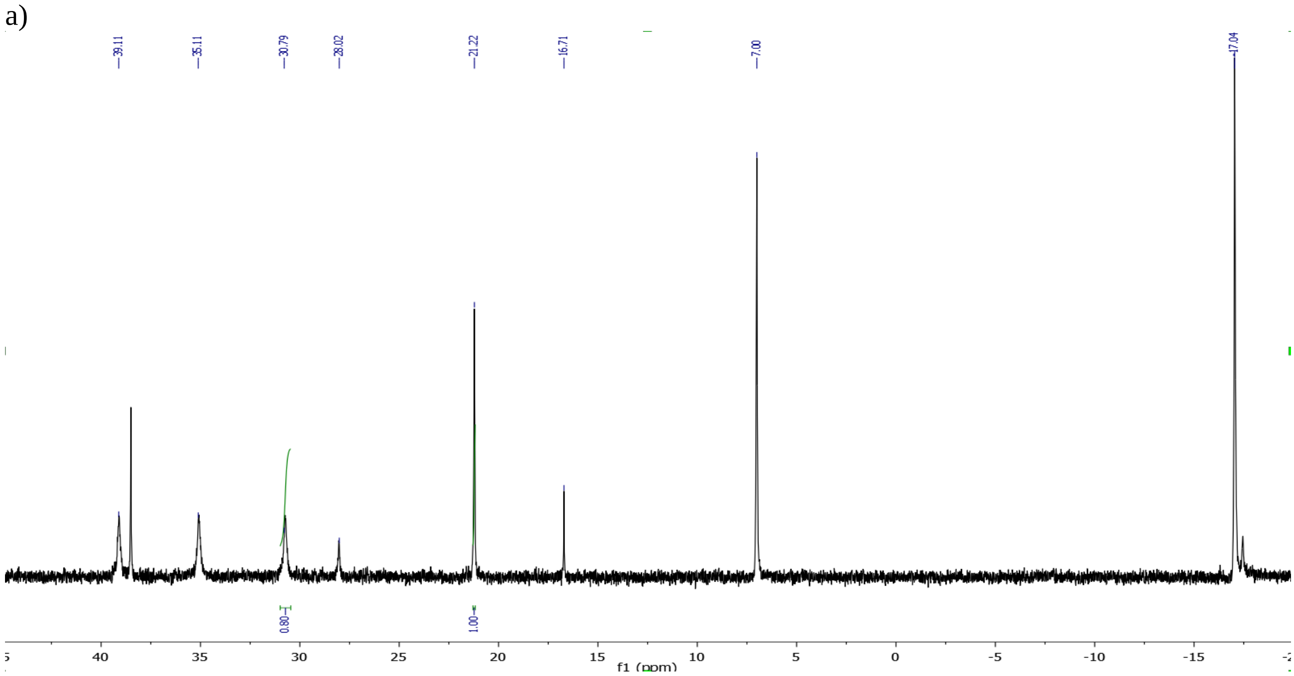


Figure S76. $Pd(OAc)_2$ + dppf (2 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min. b) +$3NO_2ArI$

Other spectra

Entry 1, Table S12:

a)



b)

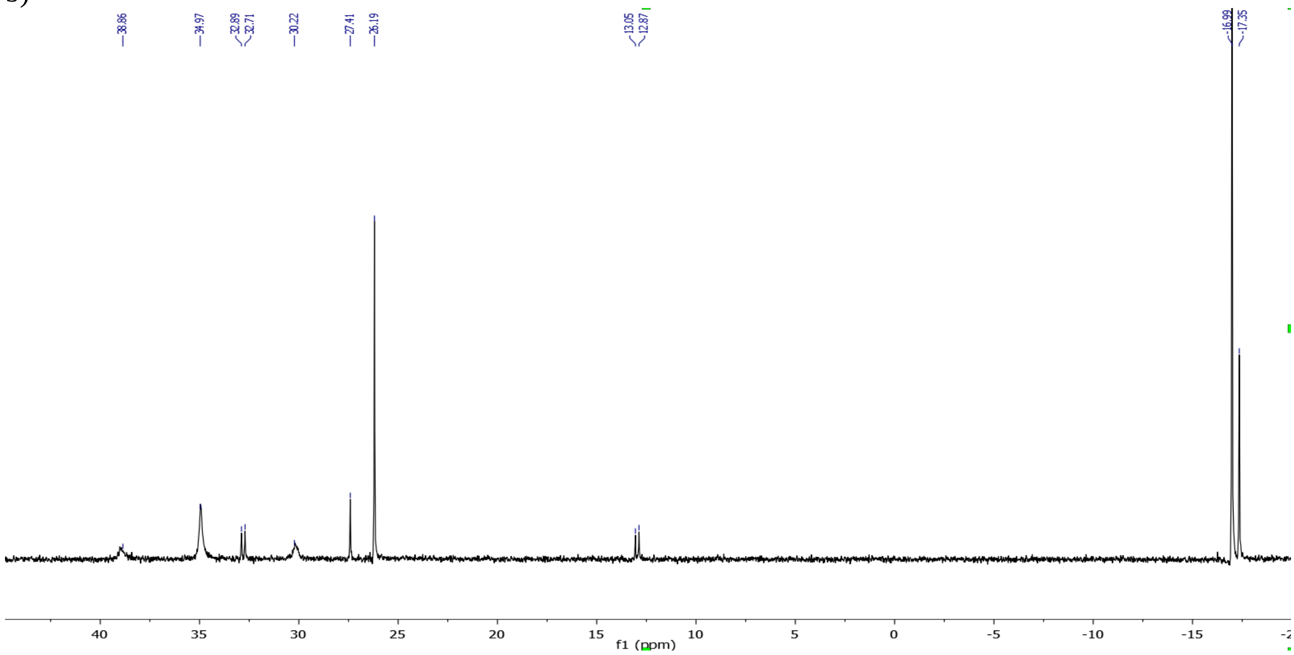
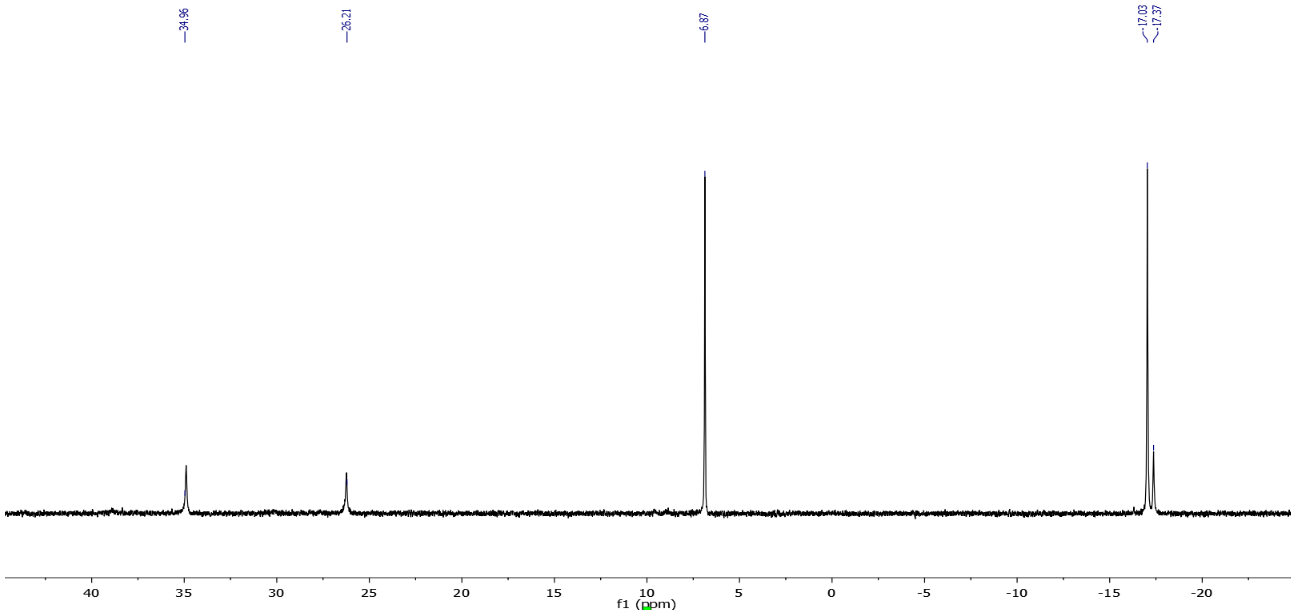


Figure S77. $Pd(OAc)_2$ + dppf (2 equiv) + in DMF-d_7 at rt in 20 min. The peaks at 21.22 ppm and at 30.79 ppm are related to the IS and $Pd(dppf)(OAc)_2$ respectively. b) + $3NO_2ArI$

Entry 3, Table S12:

a)



b)

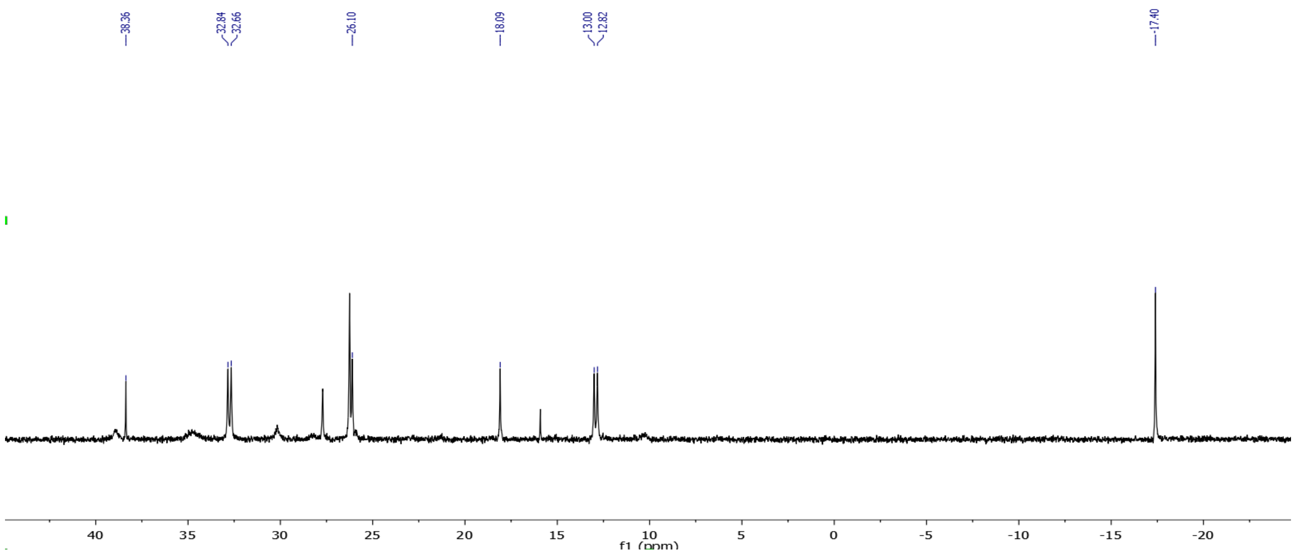
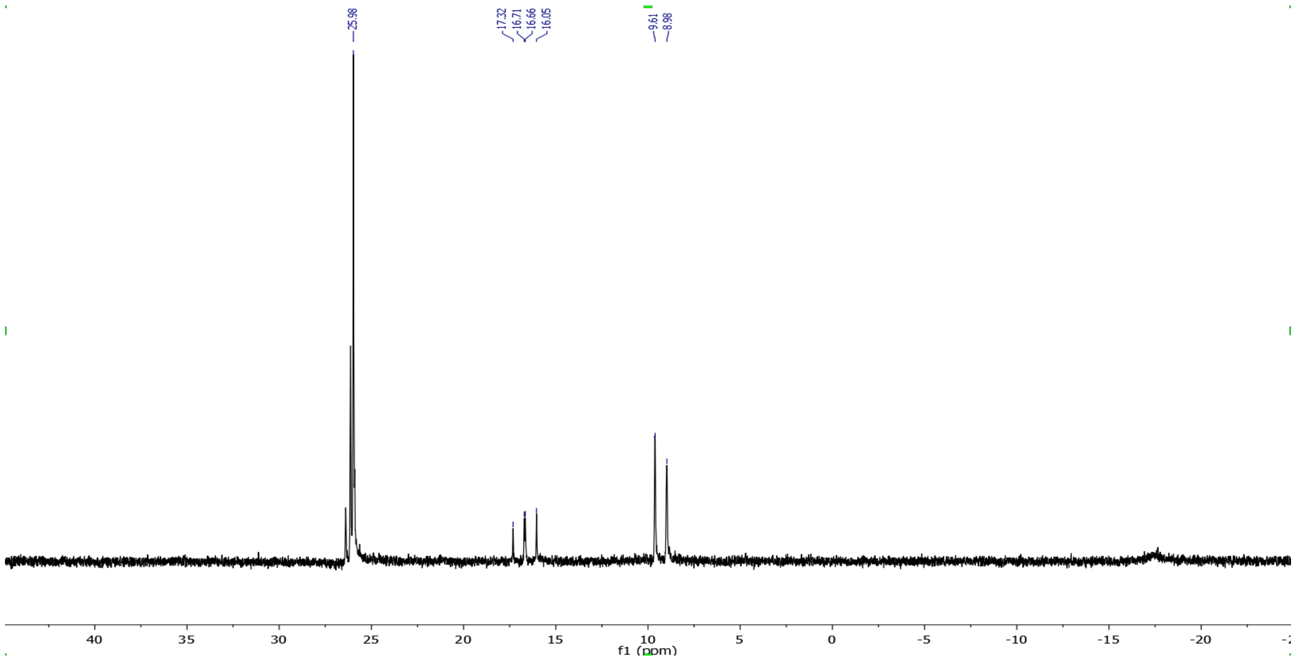


Figure S78. Pd(OAc)$_2$ + dppf (2 equiv) + in DMF-d$_7$ at 60°C in 20 min. The peaks at 21.22 ppm and at 30.79 ppm are related to the IS and Pd(dppf)(OAc)$_2$ respectively. b) + 3NO$_2$ArI

Entry 4, Table S12:

a)



b)

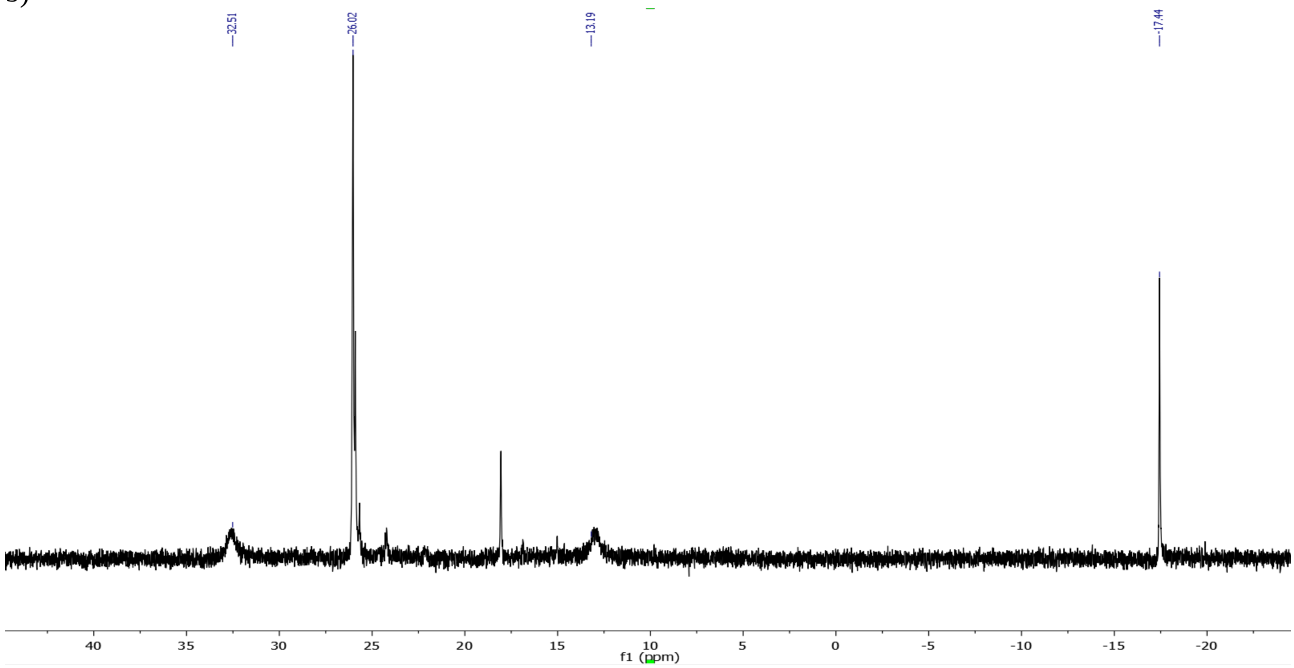
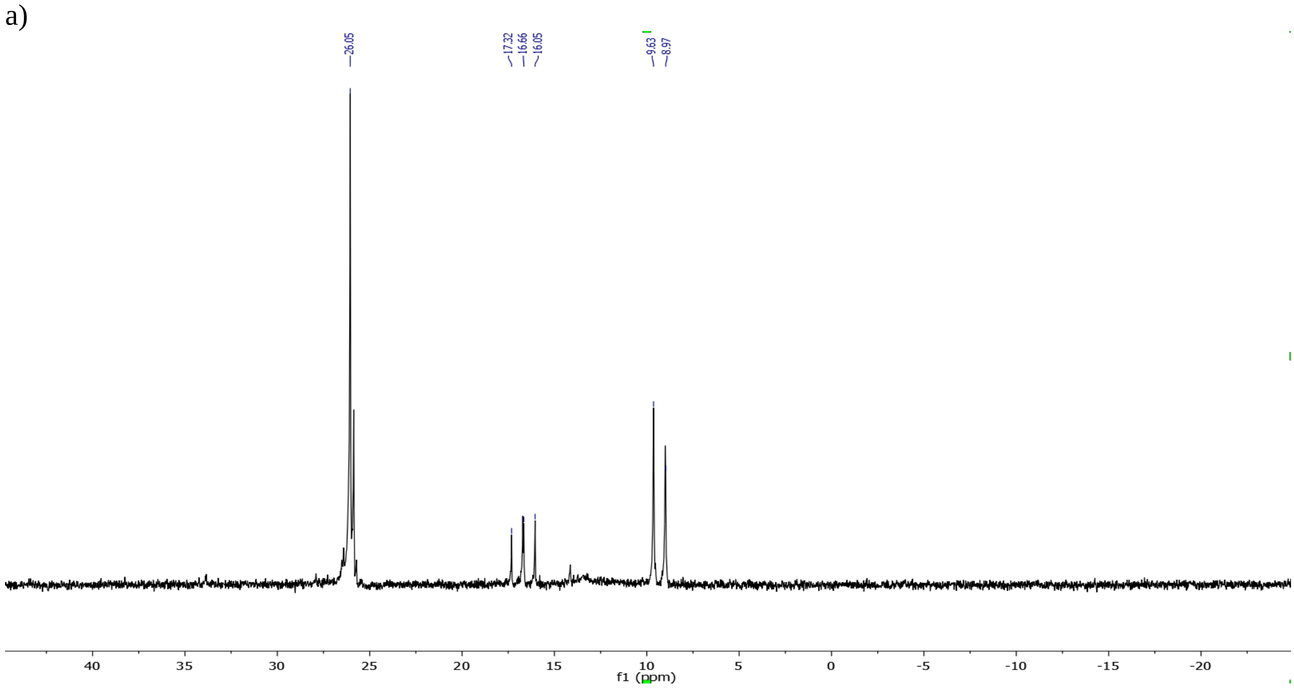


Figure S79. $Pd(OAc)_2$ + dppf (2 equiv) + TMG (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$

Entry 5, Table S12:

a)



b)

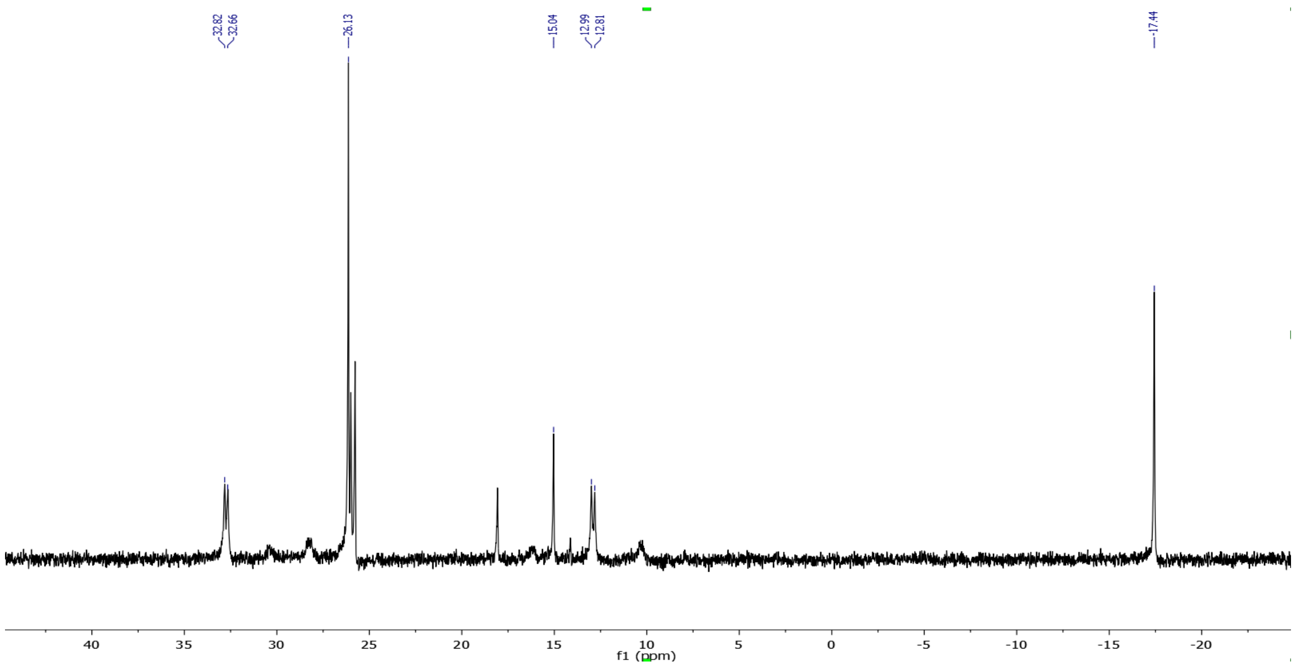
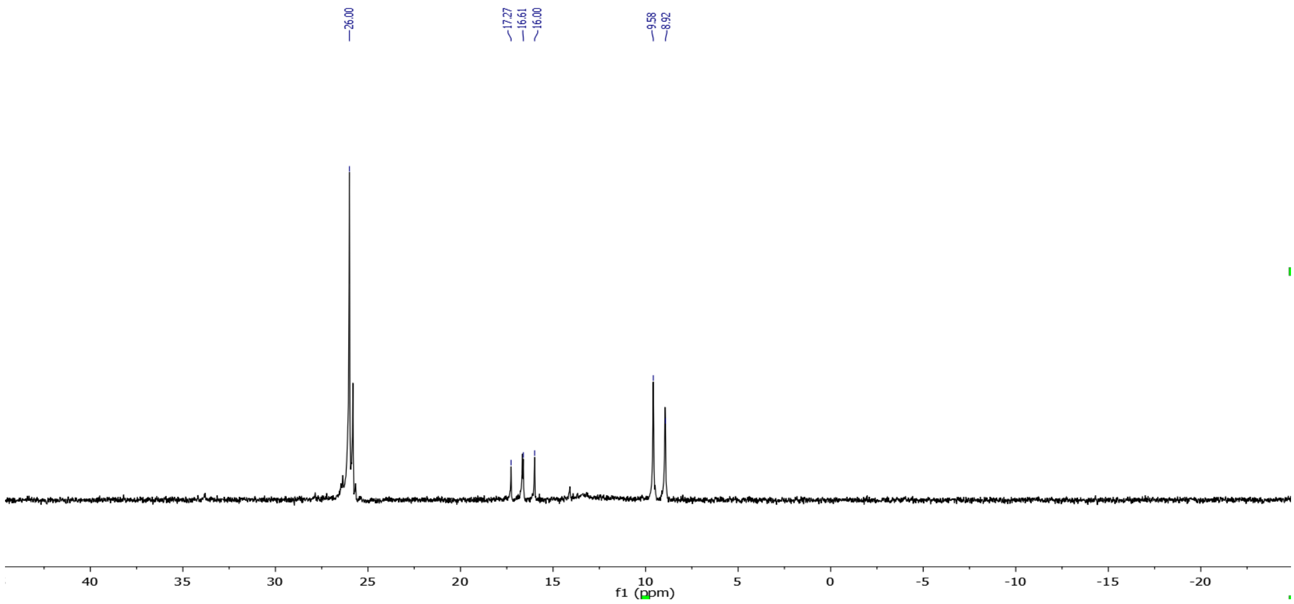


Figure S80. Pd(OAc)$_2$ + dppf (2 equiv) + Cs_2CO_3 (5 equiv) in DMF-d$_7$ at 60°C in 20 min. b) + 3NO$_2$ArI

Entry 6, Table S12:

a)



b)

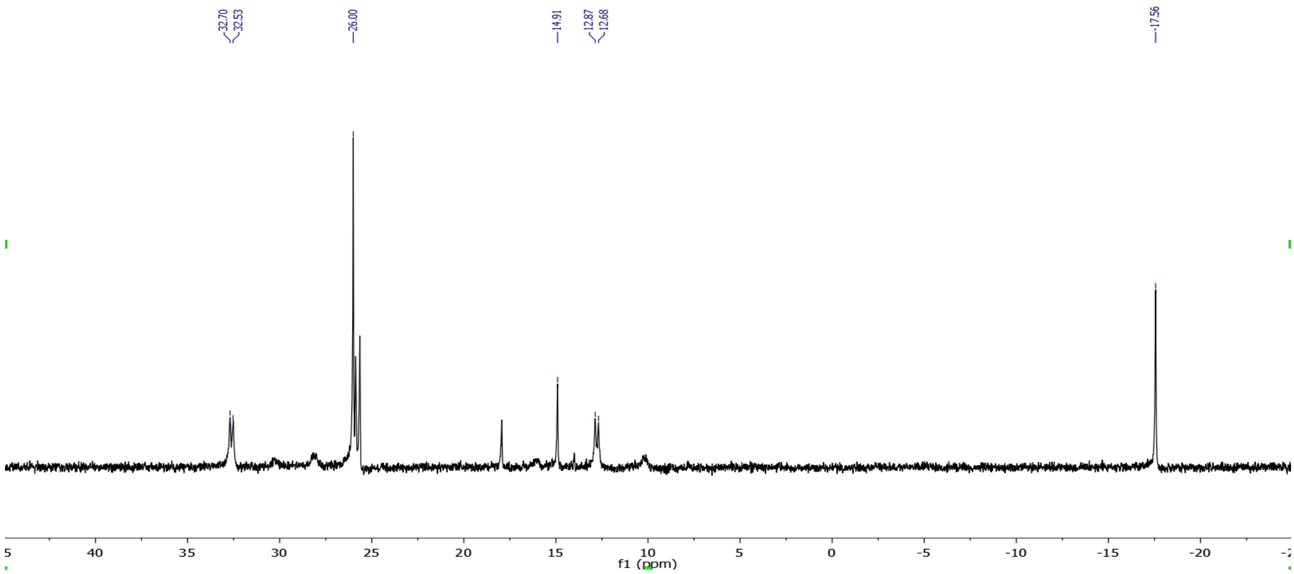
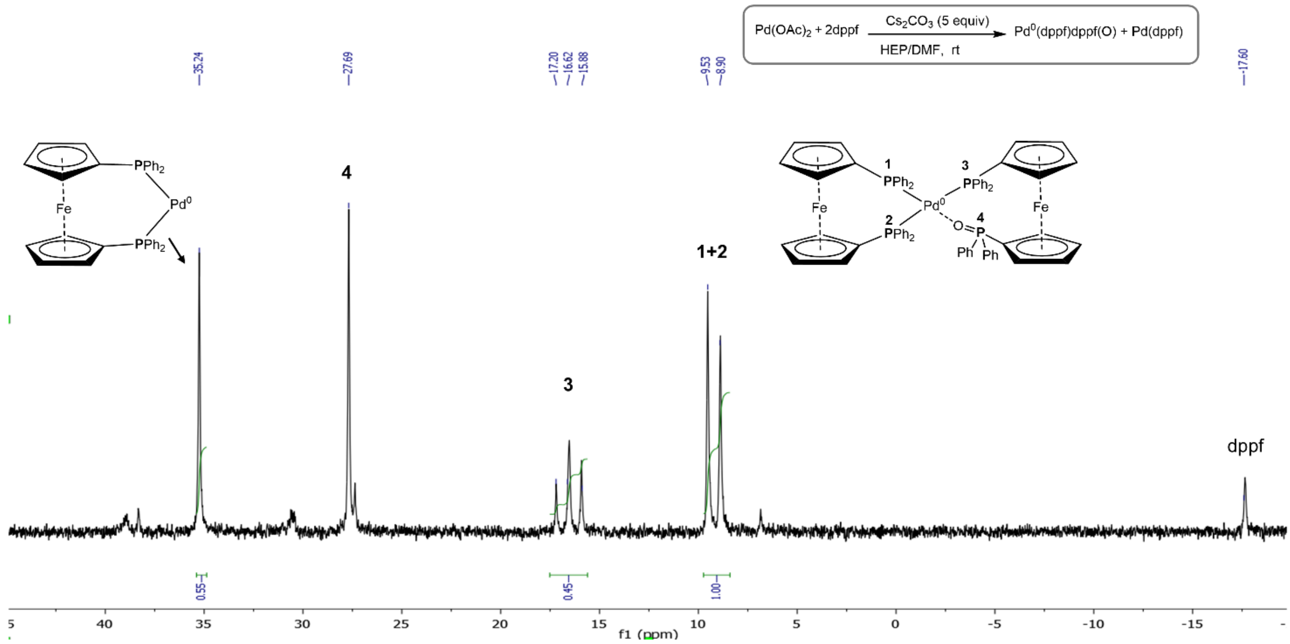


Figure S81. $Pd(OAc)_2$ + dppf (2 equiv) + K_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$

Entry 7, Table S12: Completed reduction in HEP/DMF as example:

a)



b)

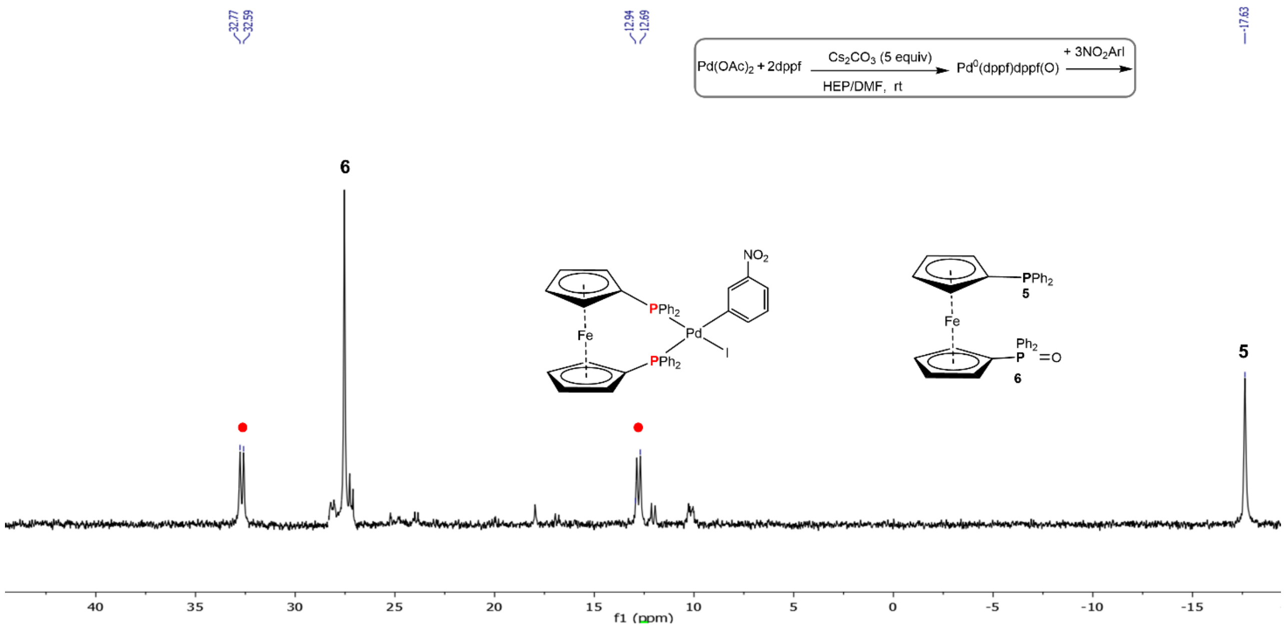


Figure S82. $Pd(OAc)_2$ + dppf (2 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$

Other spectra

Entry 8, Table S12:

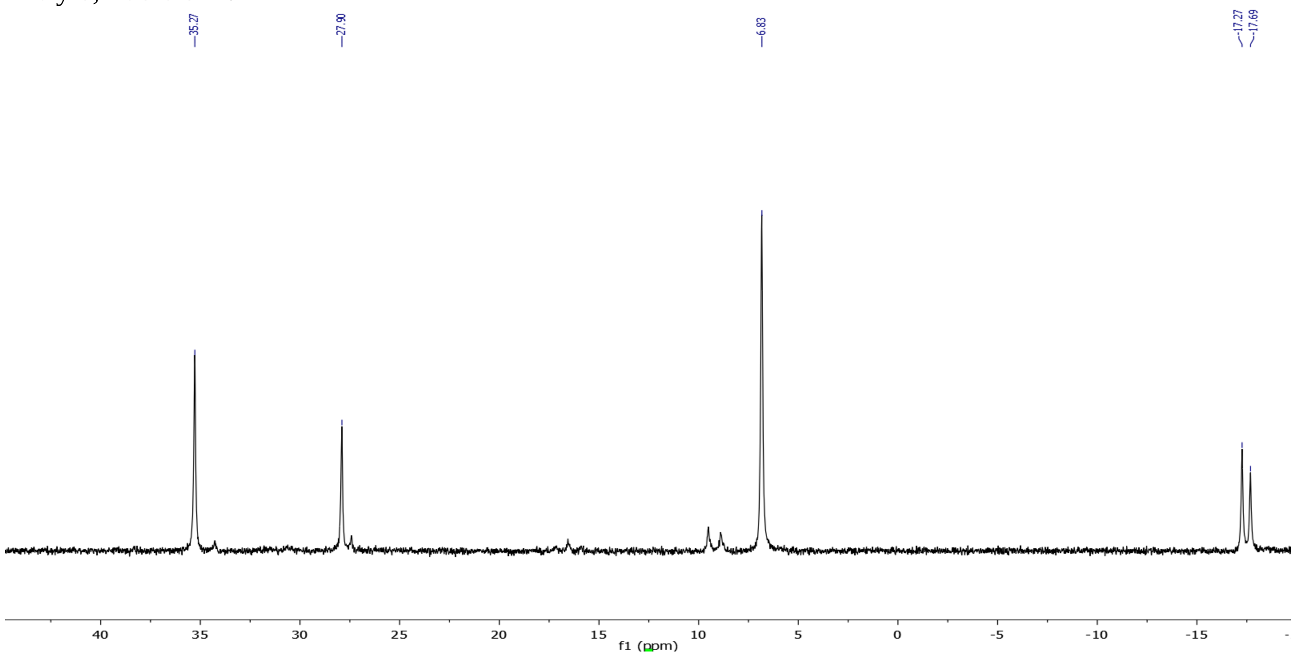


Figure S83. $Pd(OAc)_2$ + dppf (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min.

4.3. $PdCl_2$

4.3.1. General Procedure 2

$$Pd(dppf)Cl_2 + \text{dppf} \xrightarrow[\text{Solvent, T (°C)}]{\text{Base (5 equiv)}} Pd^0(\text{dppf})$$

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(dppf)Cl_2\ CH_2Cl_2$(10.61 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Dppf (7.20 mg, 0.013 mmol, 1 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.0065 mmol, 0.5 eq) was added as internal standard (IS).
To further demonstrate that the formation of Pd(0) specie occurred, the $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1].

Table S13. $Pd(dppf)Cl_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

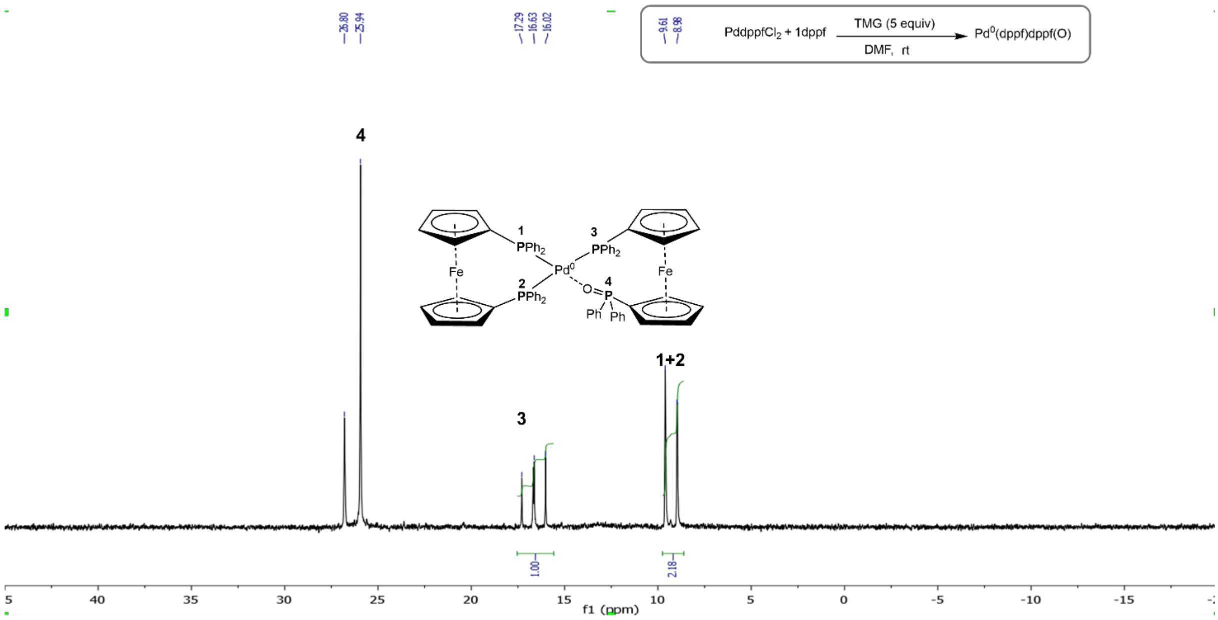
entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	25	-	0/100	-
2	TMG	DMF	25	D	100/0	100/0
3	Cs_2CO_3	DMF	25		39/61	100/0
4	-	DMF	60	-	0/100	-
5	Cs_2CO_3	DMF	60	E	100/0	100/0
6	K_2CO_3	DMF	60	E	100/0	100/0
7	TMG	DMF	60	E	100/0	100/0
8	TEA	DMF	80	-	0/100	-
9	TMG	DMF/HEP[e]	25	A/D	100/0	91/9
10	Cs_2CO_3	DMF/HEP	25	A/E	100/0	30/70
11	K_2CO_3	DMF/HEP	25	A	100/0	0/100
12	TMG	DMF/HEP	60	D	100/0	100/0
13	Cs_2CO_3	DMF/HEP	60	A/E	100/0	81/19
14	K_2CO_3	DMF/HEP	60	A/E	100/0	78/22

[a] The reactions were carried out according to the **General Procedure 2**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $Pd(dppf)Cl_2$
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

4.3.2. ^{31}P NMR spectra

Entry 2, Table S13: Completed reduction in DMF as example

a)



b)

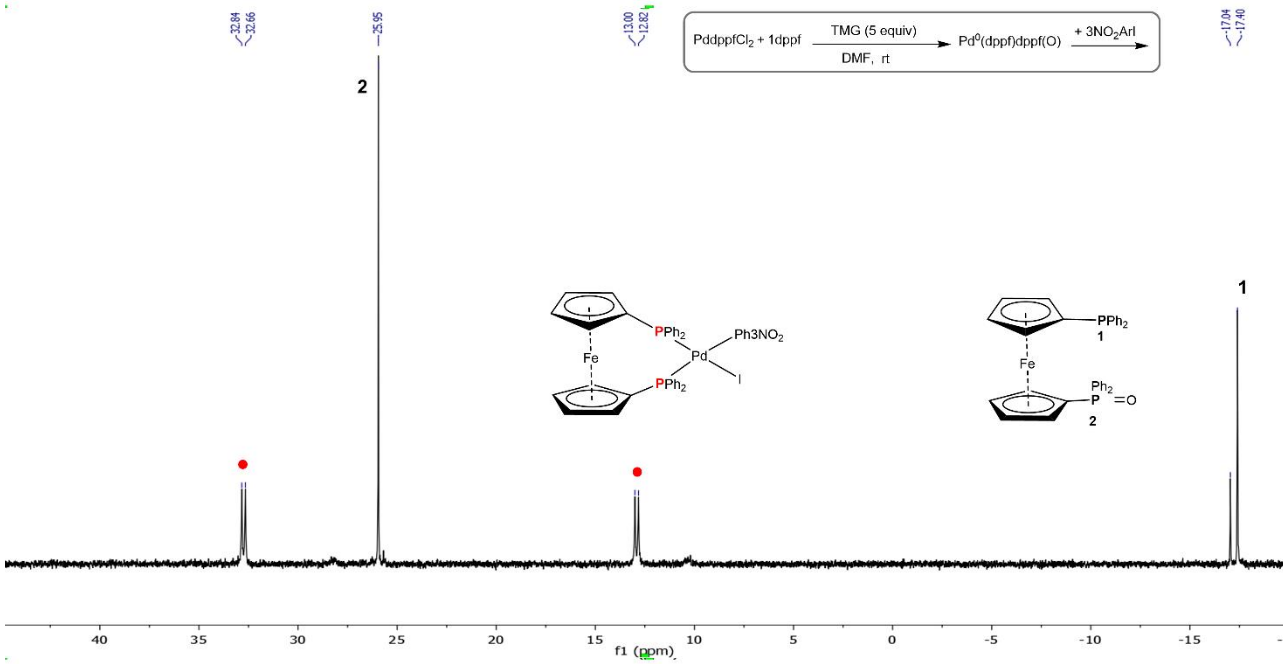


Figure S84. Pd(dppf)Cl_2 + dppf (1 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min. b) +3NO_2ArI

Other spectra

Entry 3, Table S13:

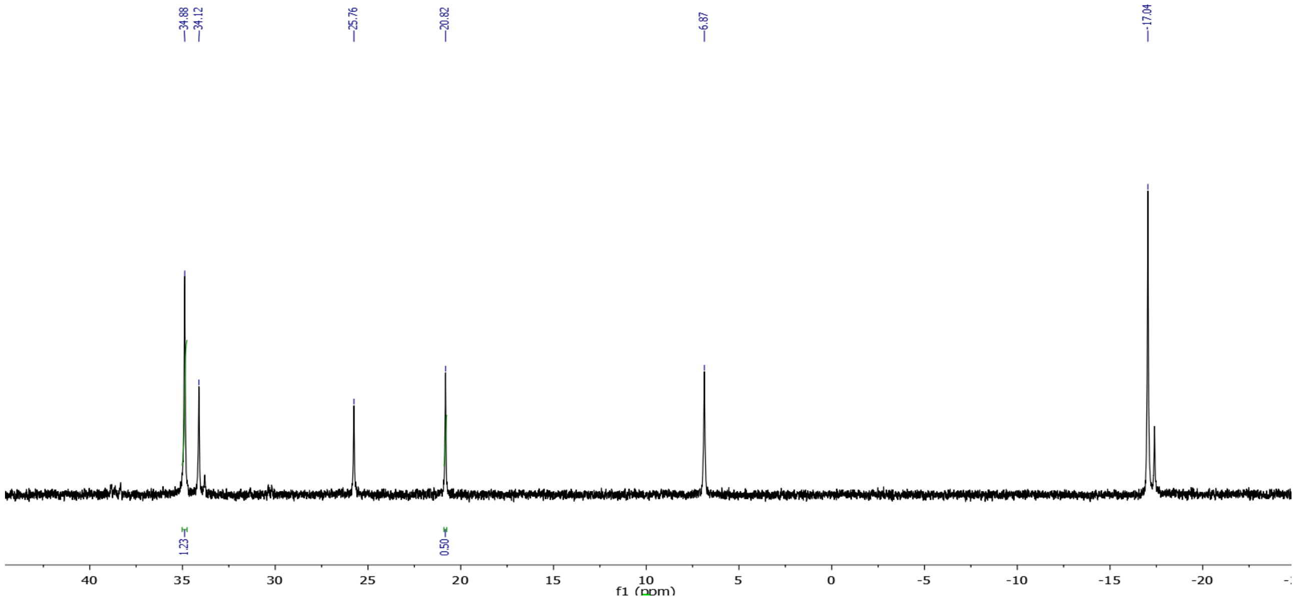


Figure S85. Pd(dppf)Cl_2 + dppf (1 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at rt in 20 min. The peaks at 20.82 ppm and at 34.88 ppm are related to the IS and Pd(dppf)Cl_2 respectively.

Entries 1 and 4 Table S13:

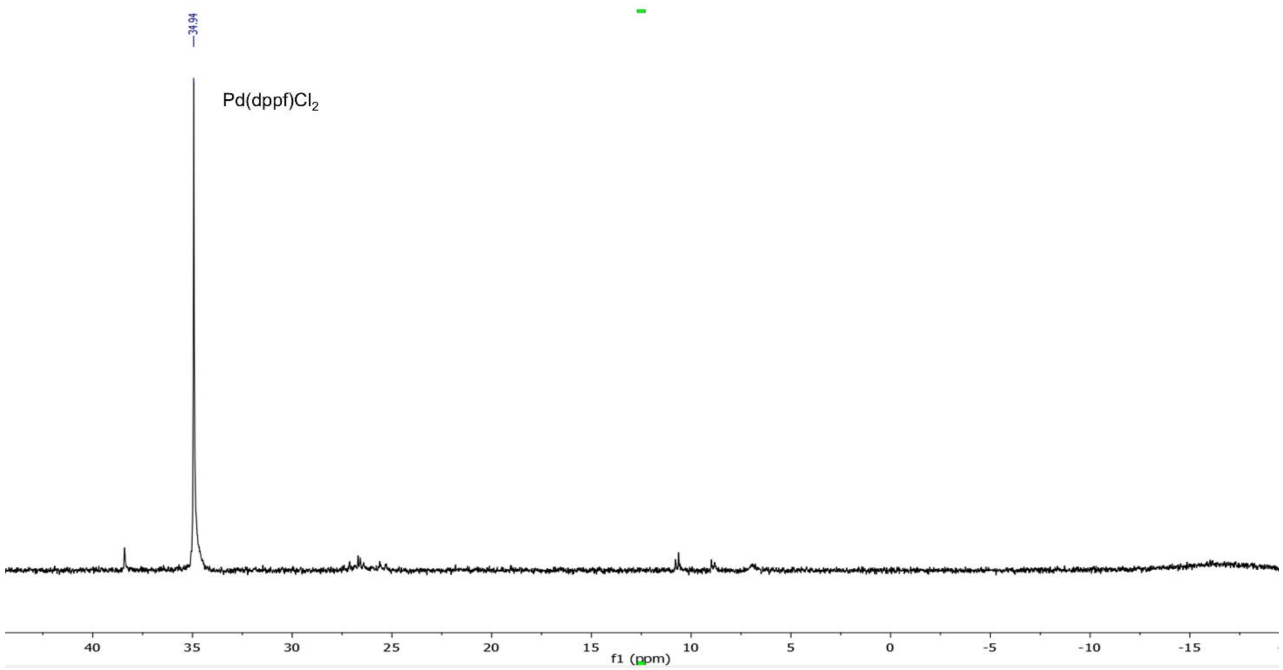
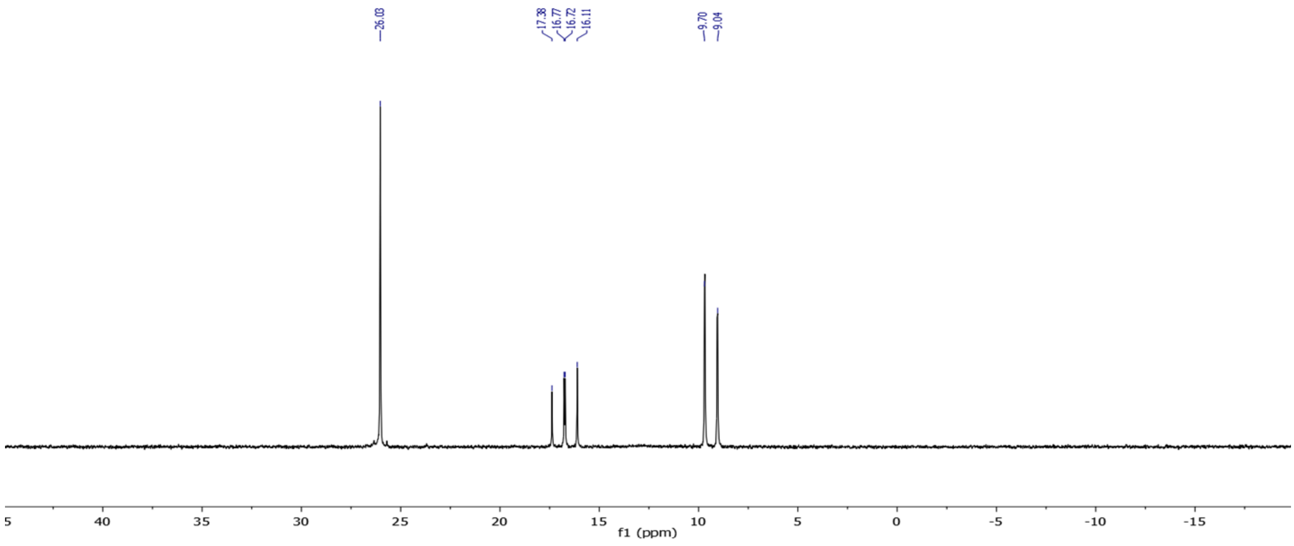


Figure S86. Pd(dppf)Cl_2 + dppf (1 equiv) at rt and at 60°C.

Entry 5, Table S13:

a)



b)

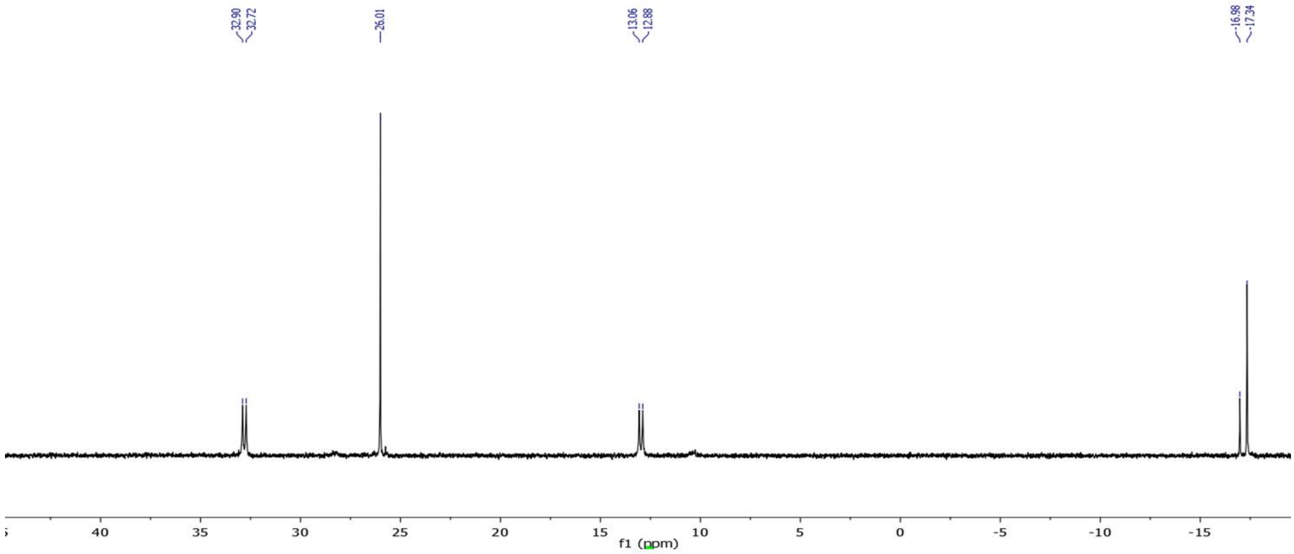
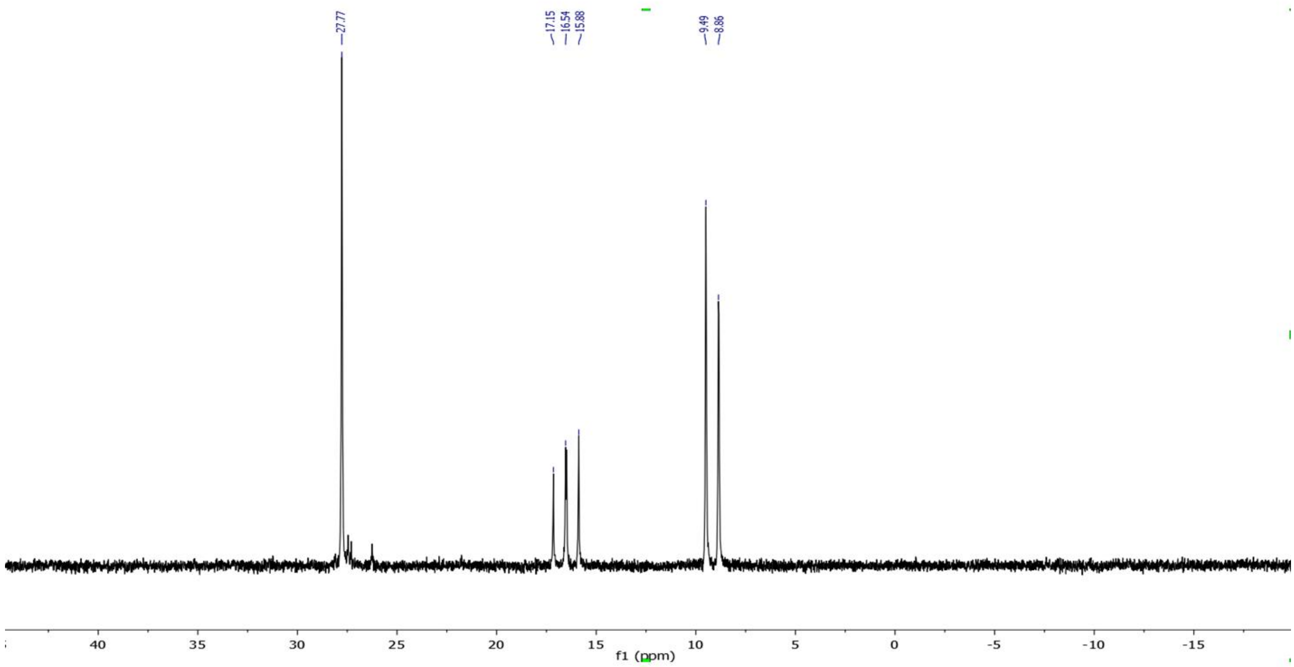


Figure S87. $Pd(dppf)Cl_2$ + dppf (1 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) +3NO_2ArI

Entry 6, Table S13:

a)



b)

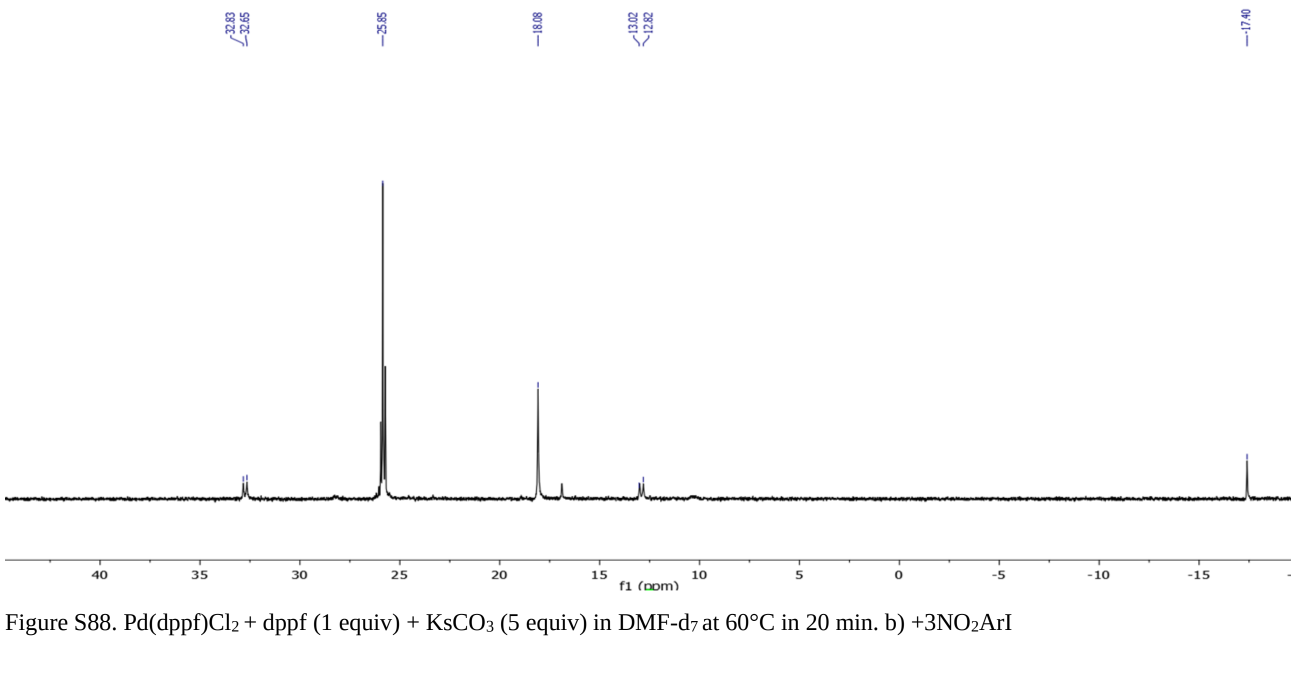
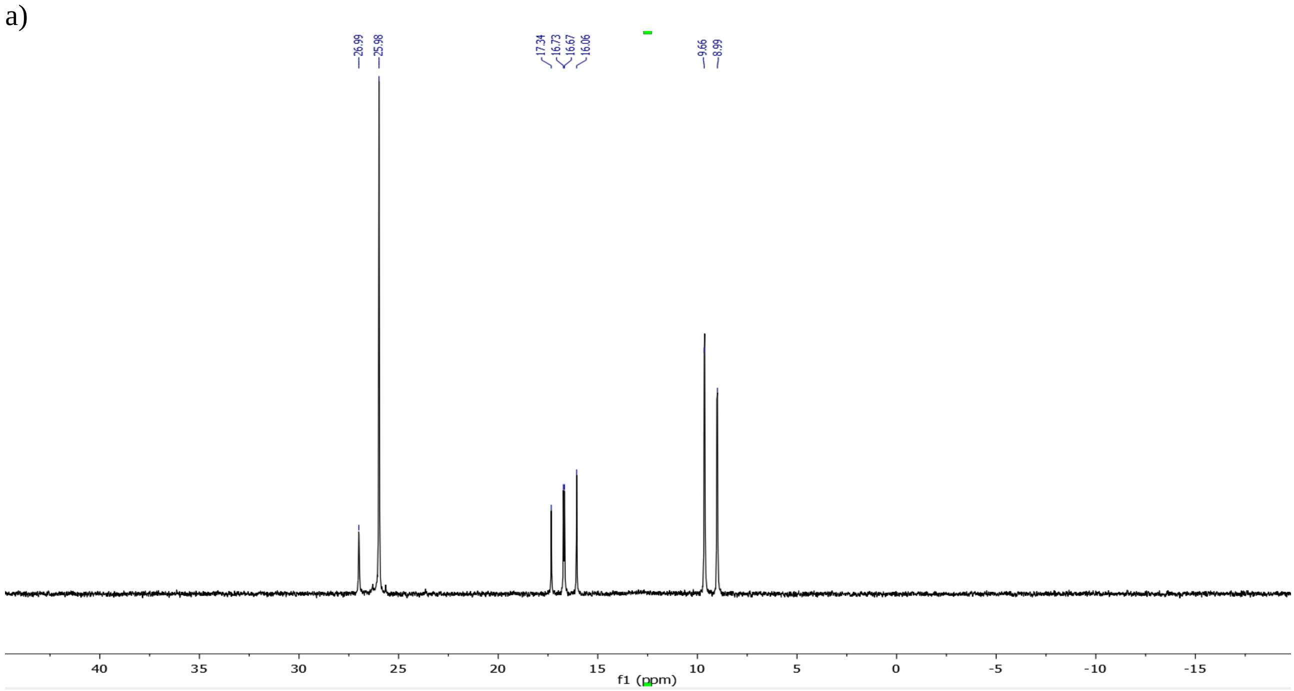


Figure S88. $Pd(dppf)Cl_2$ + dppf (1 equiv) + $KsCO_3$ (5 equiv) in DMF-d_7 at 60°C in 20 min. b) +3NO_2ArI

Entry 7, Table S13:

a)



b)

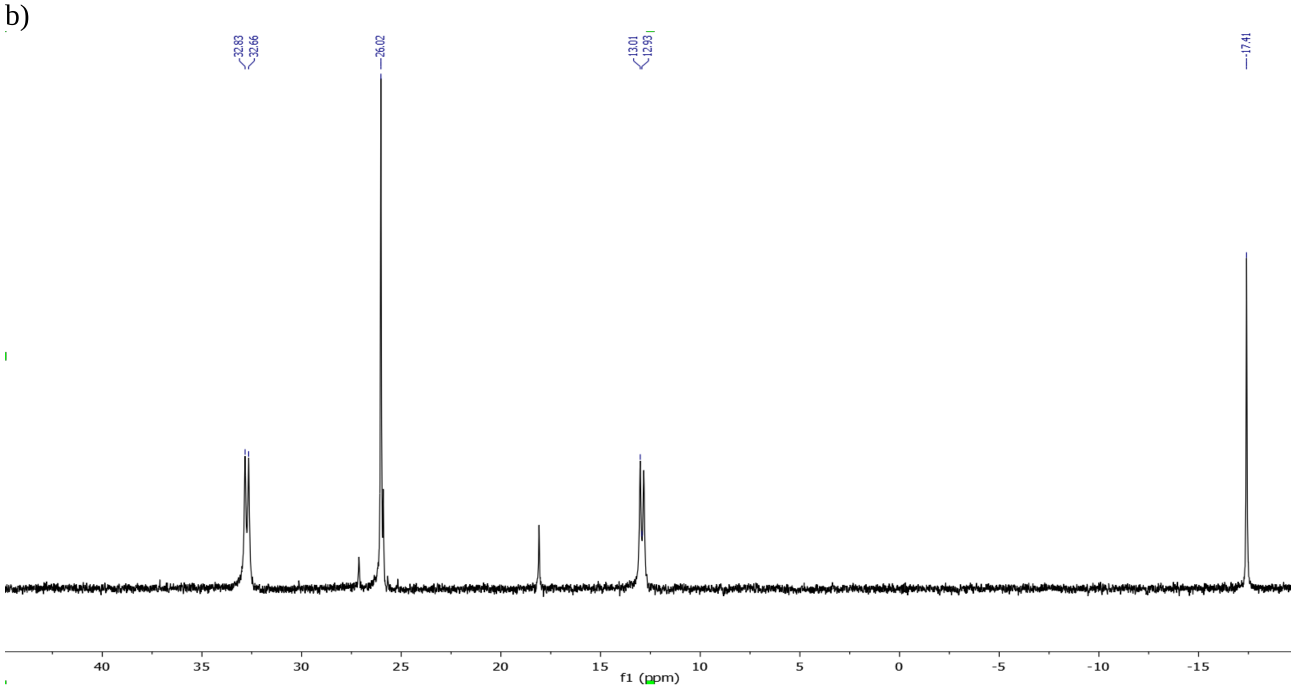


Figure S89. Pd(dppf)Cl_2 + dppf (1 equiv) + TMG (5 equiv) in DMF-d_7 at 60°C in 20 min. b) +3NO_2ArI

Entry 8, Table S13:

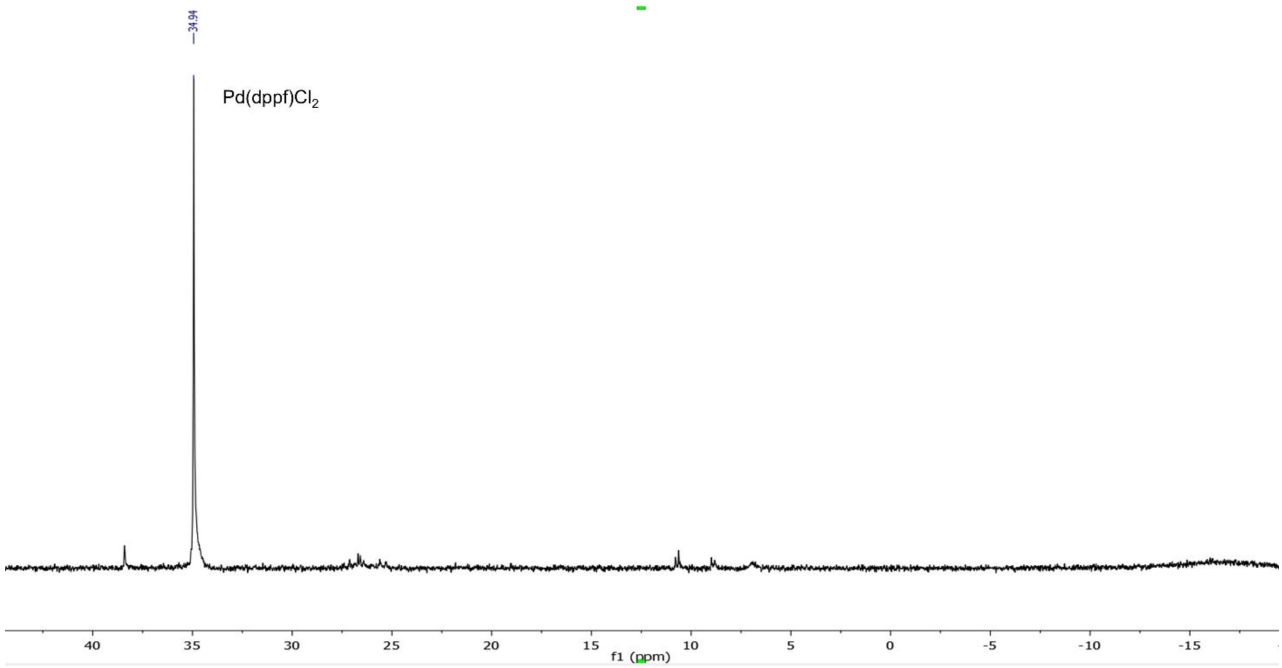
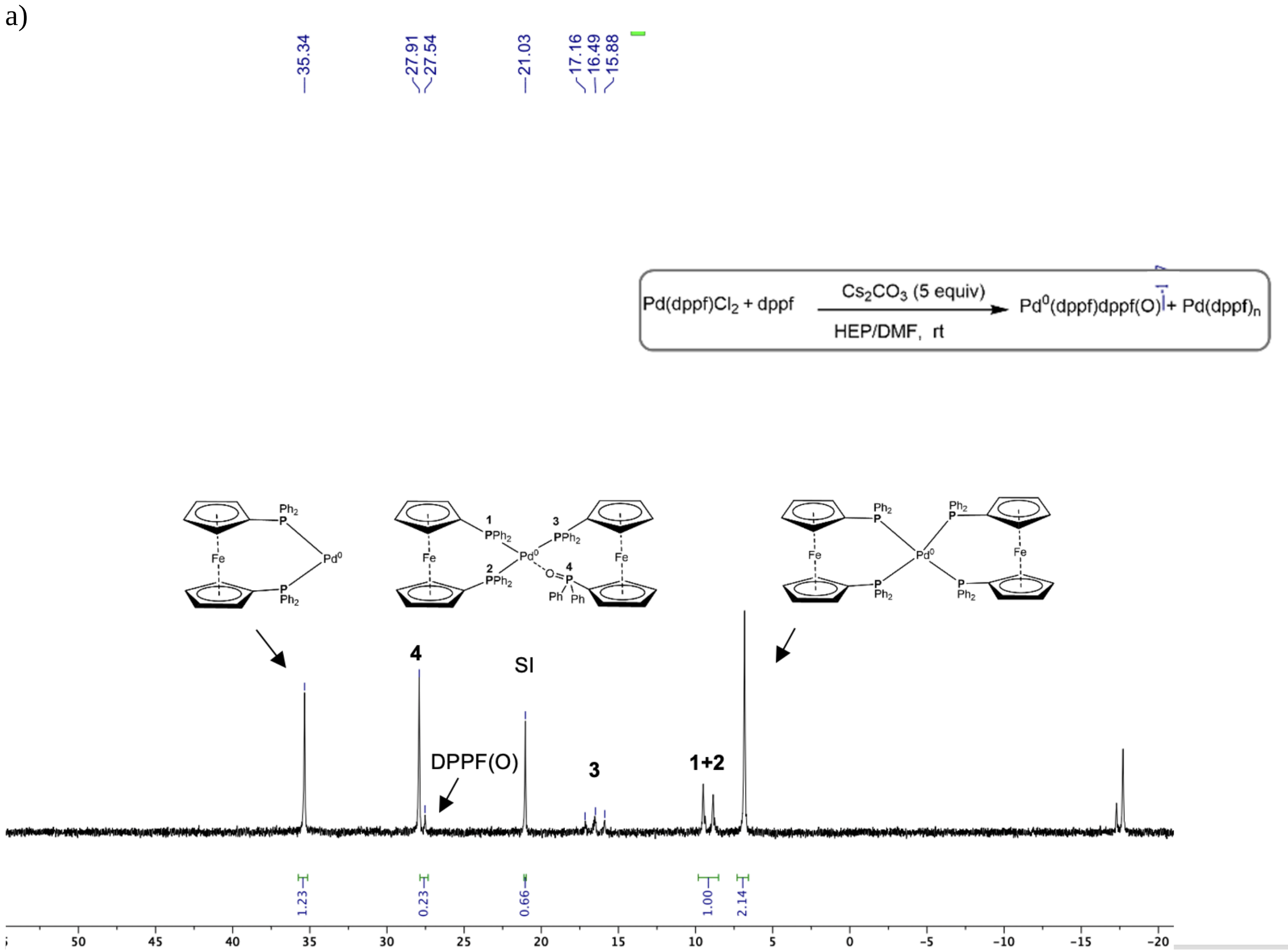


Figure S90. Pd(dppf)Cl$_2$ + dppf (1 equiv) + TEA (5 equiv) in DMF-d$_7$ at 80°C in 20 min.

Entry 10, Table S13: Completed reduction in HEP/DMF as example

a)



b)

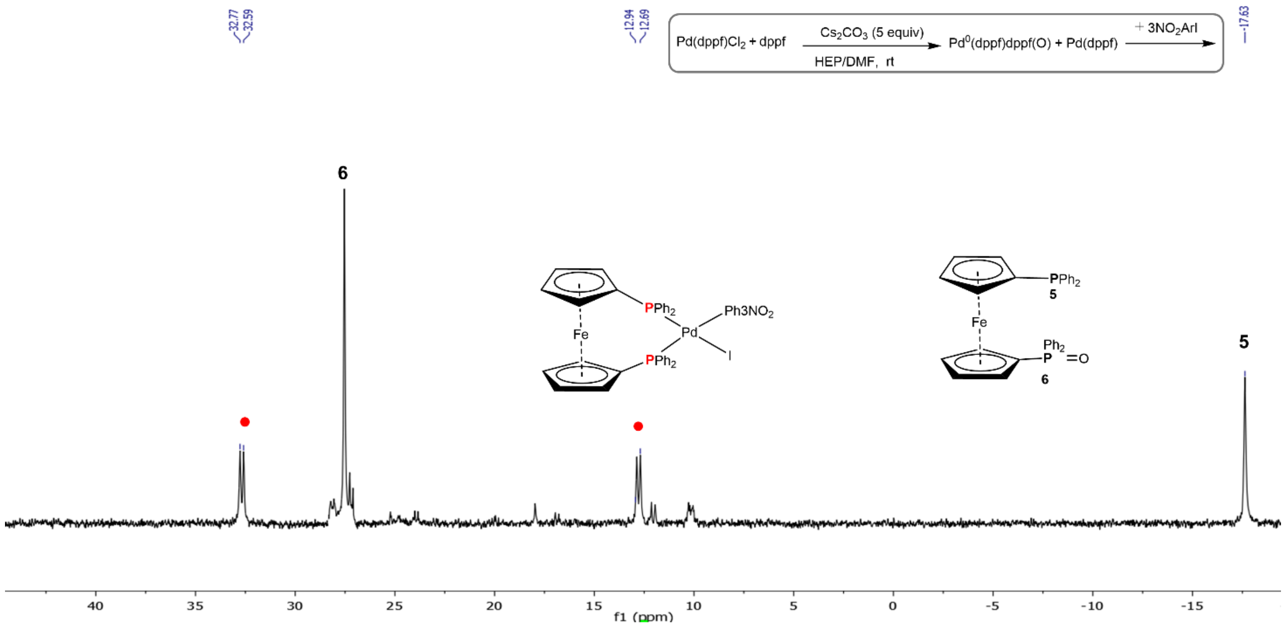


Figure S91. Pd(dppf)Cl_2 + dppf (1 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) +3NO_2ArI

Other spectra

Entry 9, Table S13:

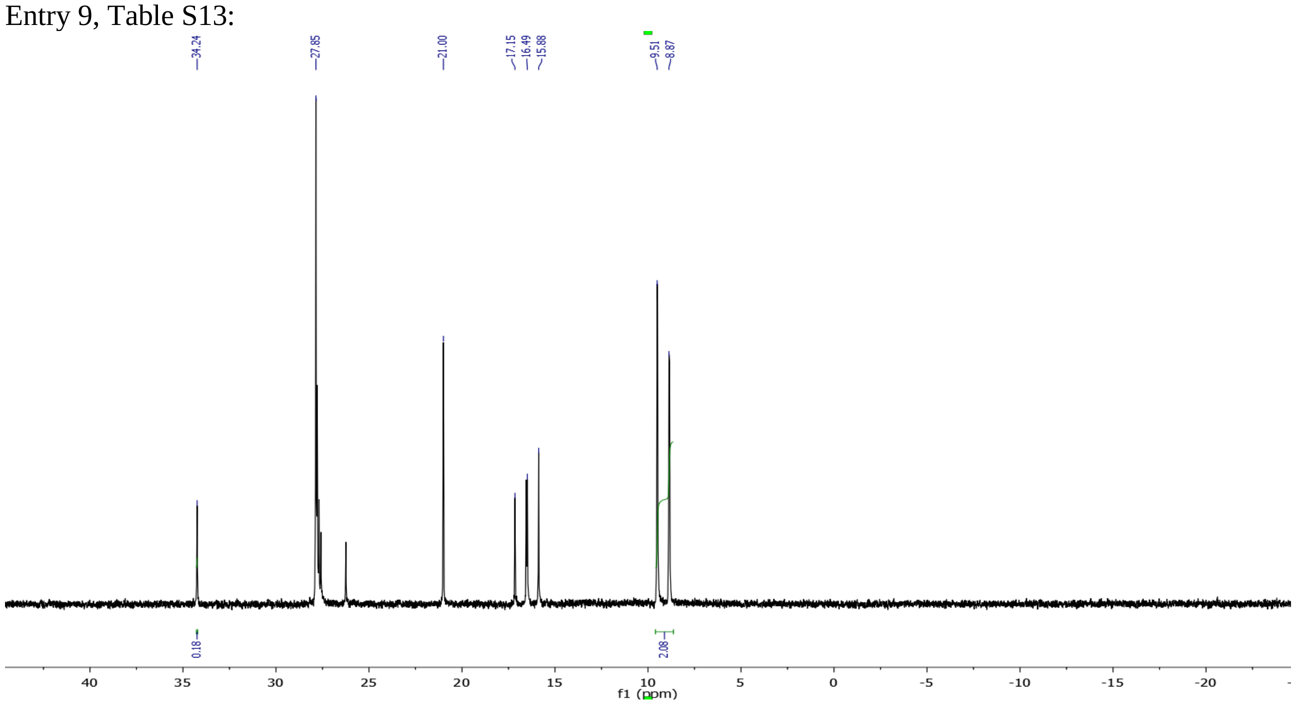


Figure S92. Pd(dppf)Cl_2 + dppf (1 equiv) + TMG (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min

Entry 11, Table S13:

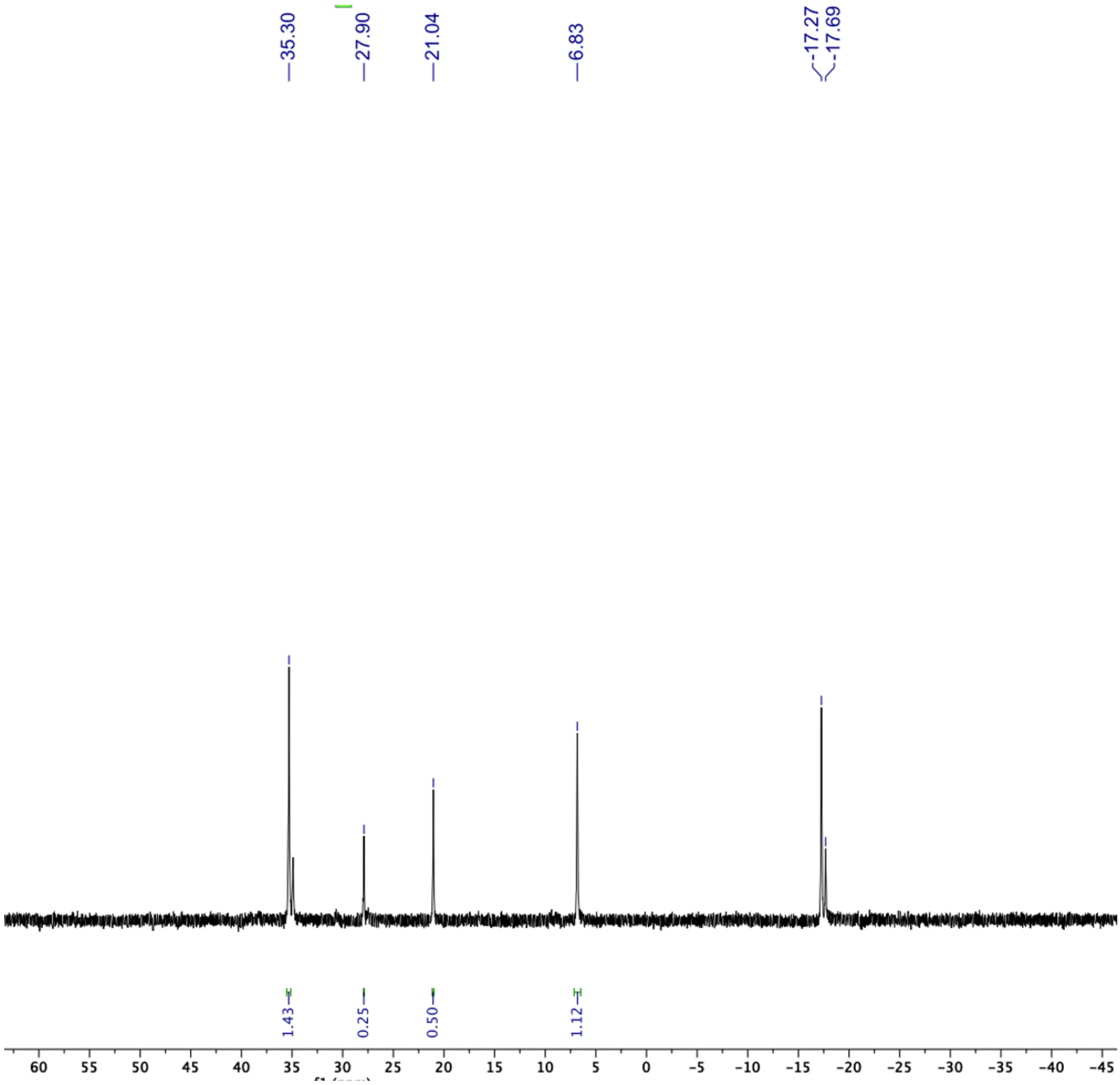


Figure S93. $Pd(dppf)Cl_2$ + dppf (1 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min

Entry 12, Table S13:

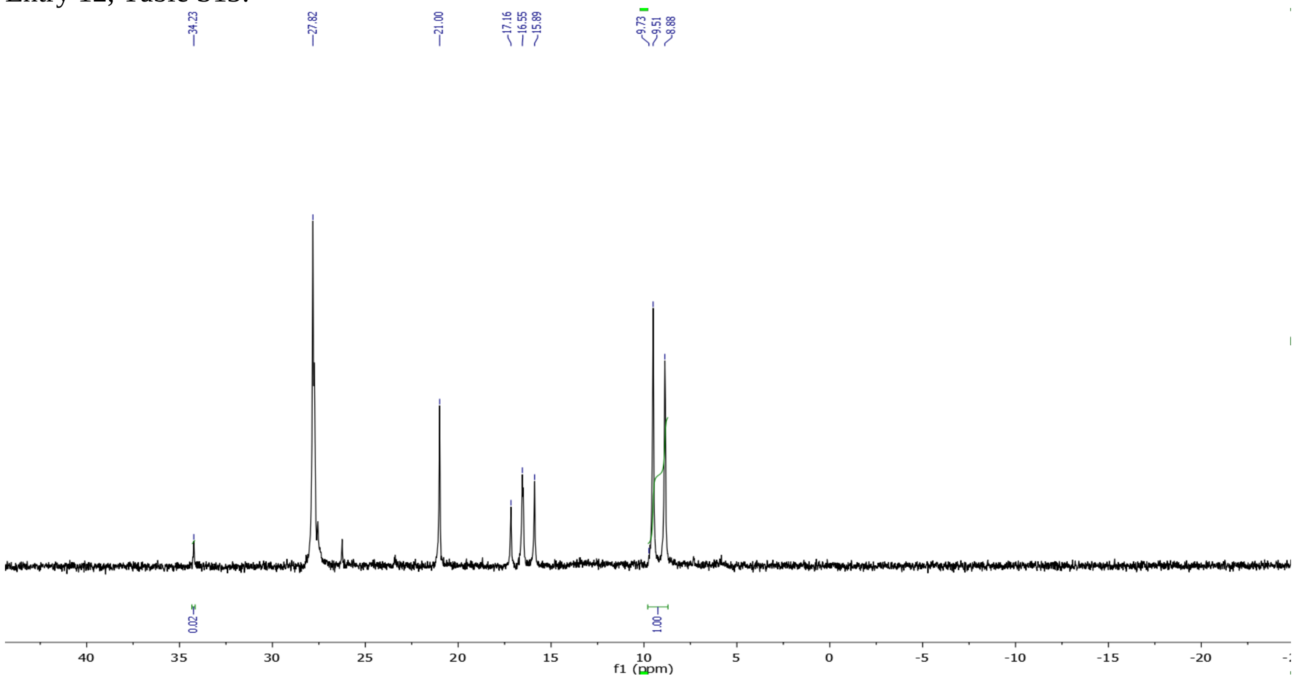


Figure S94. Pd(dppf)Cl_2 + dppf (1 equiv) + TMG (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min

Entry 13, Table S13:

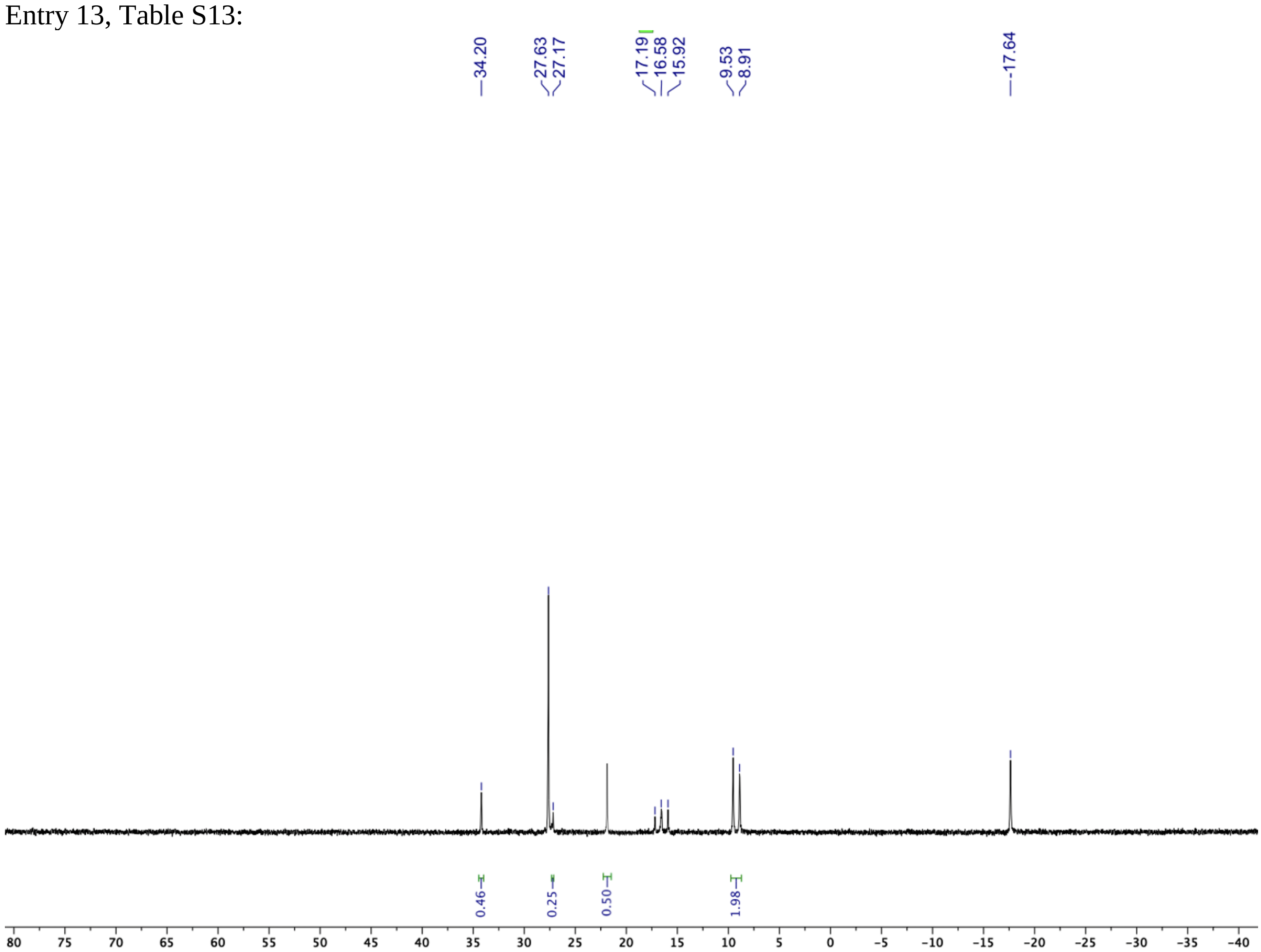


Figure S95. Pd(dppf)Cl_2 + dppf (1 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min

Entry 14, Table S13:

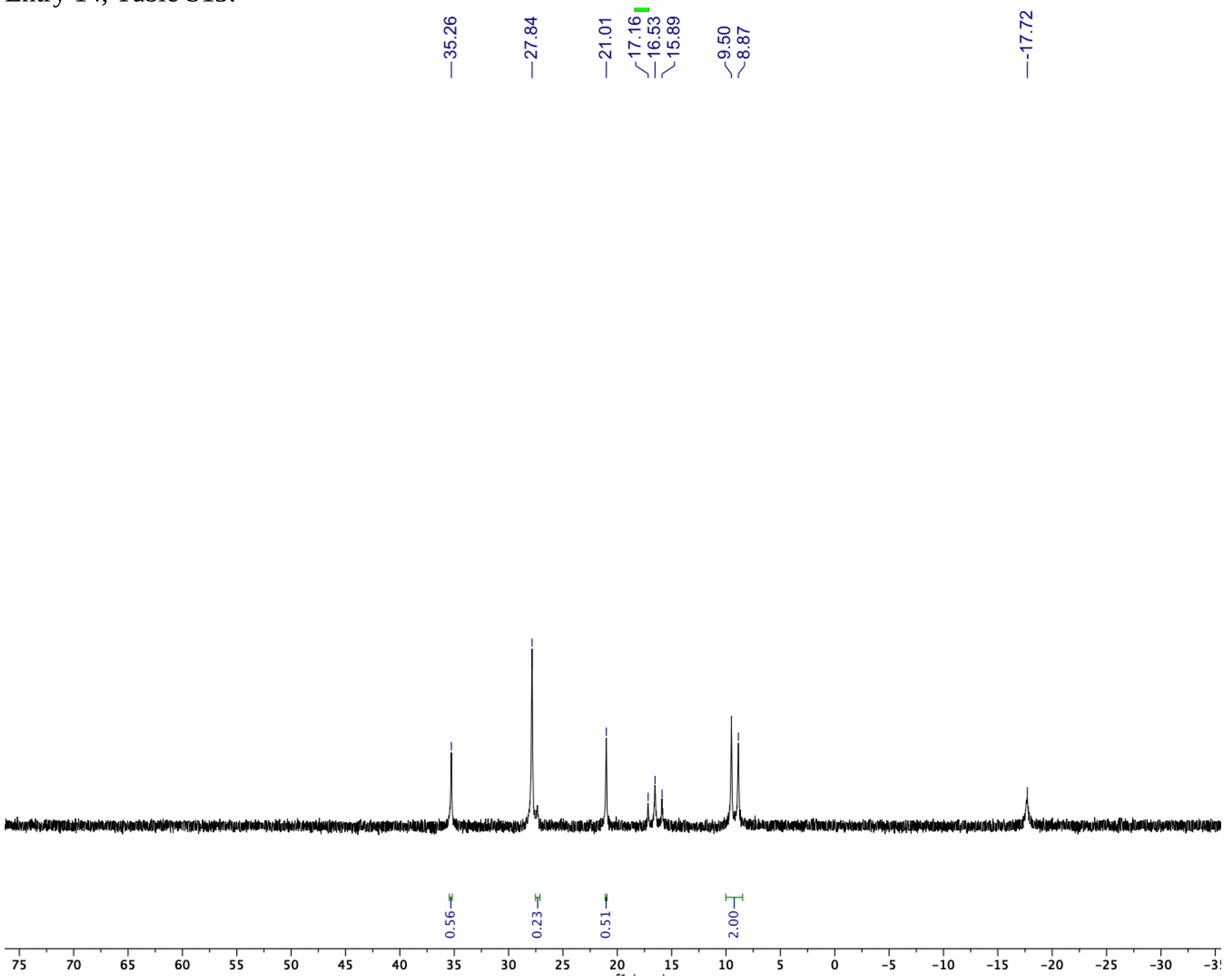


Figure S96. Pd(dppf)Cl_2 + dppf (1 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min

5. Palladium pre-catalyst reduction with DPPP

entry	Compound	DMF-d_7	HEP/DMF-d_7 (2:4)
1	dppp	-16.94	-17.01
2	dppp(O)[a,b]	-16.88; 30	-16.96; 31.71
3	Pd^0(dppp)[b]	4.64	4.55
4	$Pd(OAc)_2$(dppp)[b]	11.31	11.44
5	Pd^0dppp(O)	12.37; 30.12	12.53; 31.60
6	Pd(dppp)Cl_2	13.11	13.25
7	dpppO_2[b]	30.58	31.83

[a] dppp(O) is the label for the dppp Mono-Oxide
[b] According to the literature[9]

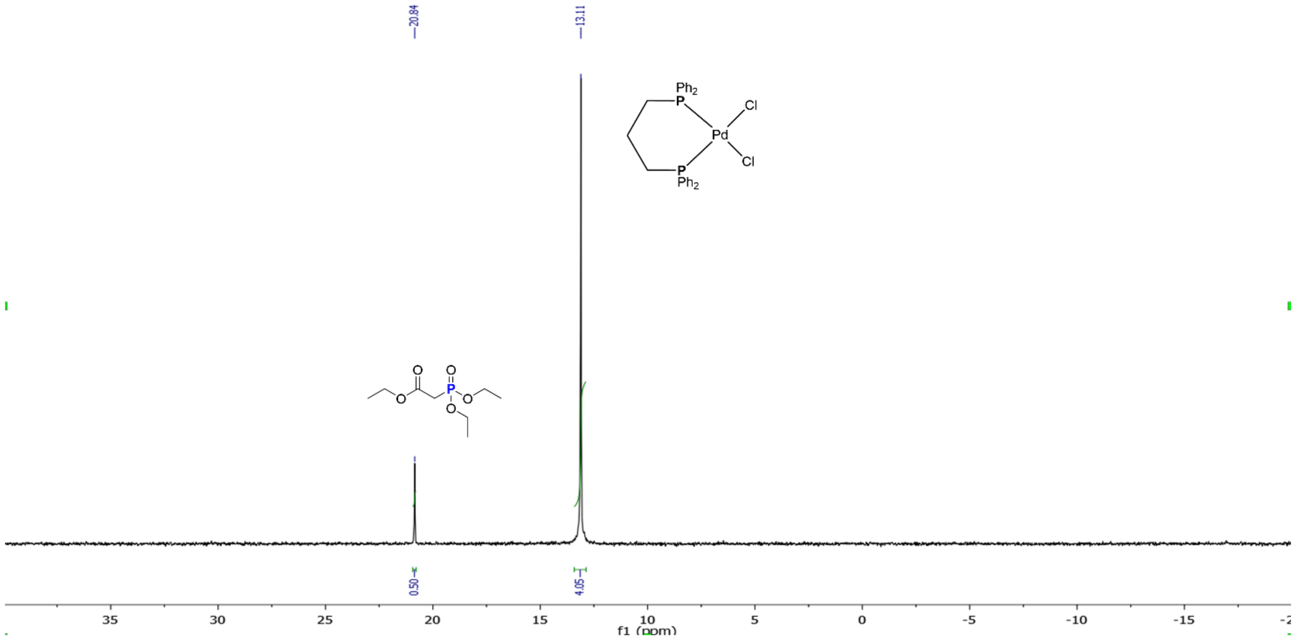
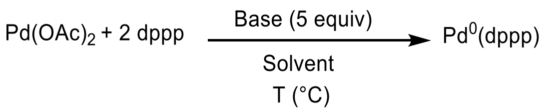


Figure S97. ^{31}P NMR spectrum of Pd(dppp)Cl_2 (1 equiv) and triethyl phosphonoacetate (0.5 equiv) as IS to know their integration ratio under the same setting used for all the experiments (d_1=1, nt=256).

5.1. $Pd(OAc)_2$

5.1.1. General Procedure 1



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(OAc)_2$ (2.91 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Dppp (10.71 mg, 0.026 mmol, 2 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, the triethyl phosphonoacetate (0.0065 mmol, 0.5 eq) was added as internal standard (IS).

To further demonstrate that the formation of Pd(0) specie occurred, the $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1]

Table S14. $Pd(dppp)(OAc)_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+} [b]	P/OH [c]
1	-	DMF[d]	25	E	11/89	100/0
2	TMG	DMF	25	-	0/100	-
3	Cs_2CO_3	DMF	25	E	23/77	100/0
4	-	DMF	60	E	100/0	100/0
5	Cs_2CO_3	DMF	60	E	100/0	100/0
6	K_2CO_3	DMF	60	E	100/0	100/0
7	Cs_2CO_3	DMF/HEP[e]	25	A /E	100/0	n.d.[d]
8	K_2CO_3	DMF/HEP	25	A /E	100/0	n.d.[d]
9	Cs_2CO_3	DMF/HEP	60	A /E	100/0	n.d.[d]
10	K_2CO_3	DMF/HEP	60	A /E	100/0	n.d.[d]

[a] The reactions were carried out according to the **General Procedure 1**

[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and $Pd(OAc)_2(dppp)$

[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.

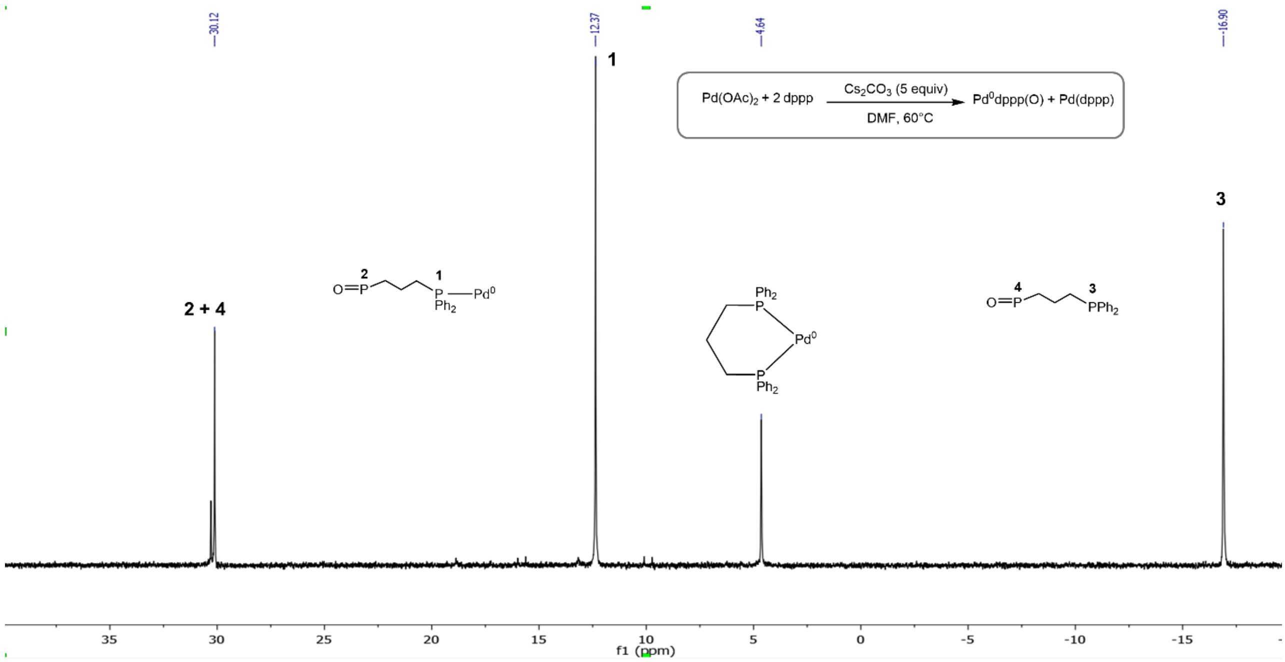
[d] 600µL of DMF-d_7

[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

5.1.2. ^{31}P NMR spectra

Entry 5, Table S14: Completed reduction in DMF as example

a)



b)

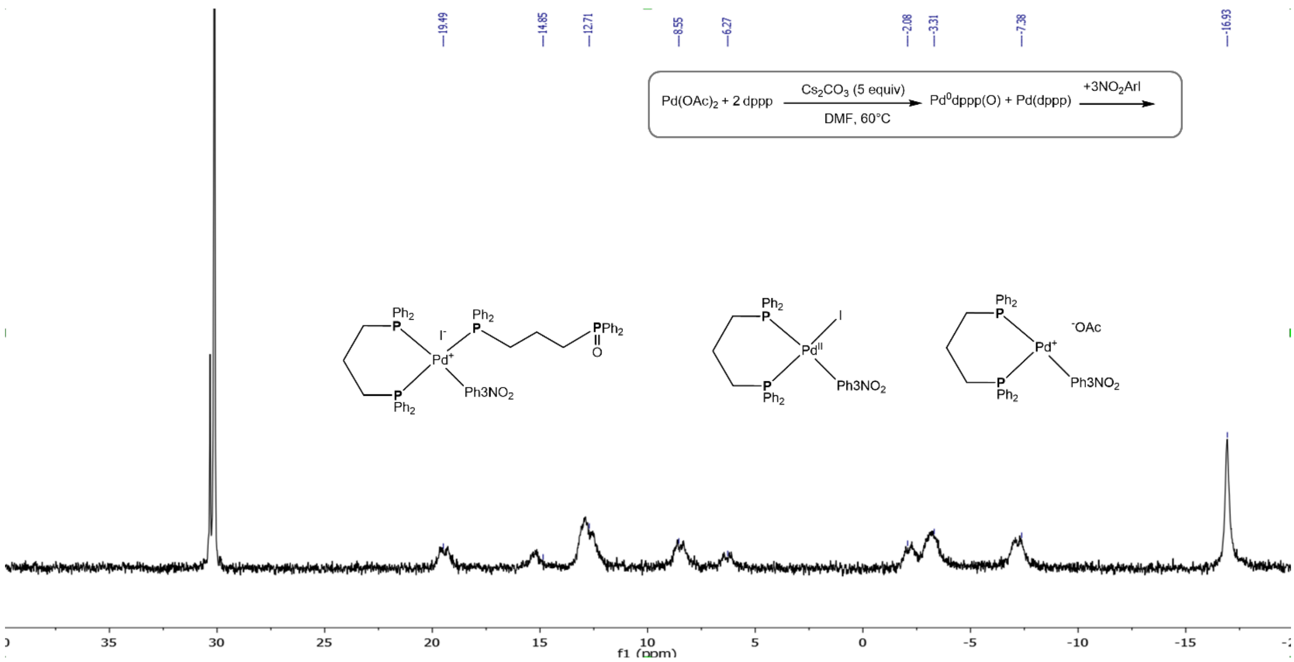


Figure S98. a) $Pd(OAc)_2$ + dppp (2 equiv) + Cs_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$. The Pd(0) species potentially involved are shown in Figure a). All peaks in the first figure disappeared, and the possible oxidative addition complexes involved are depicted in Figure b), according to the literature[10]. After the addition of the aryl halide, the spectrum usually showed poor quality and broad signals.

Other spectra

Entry 1, Table S14. $Pd(dppp)(OAc)_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

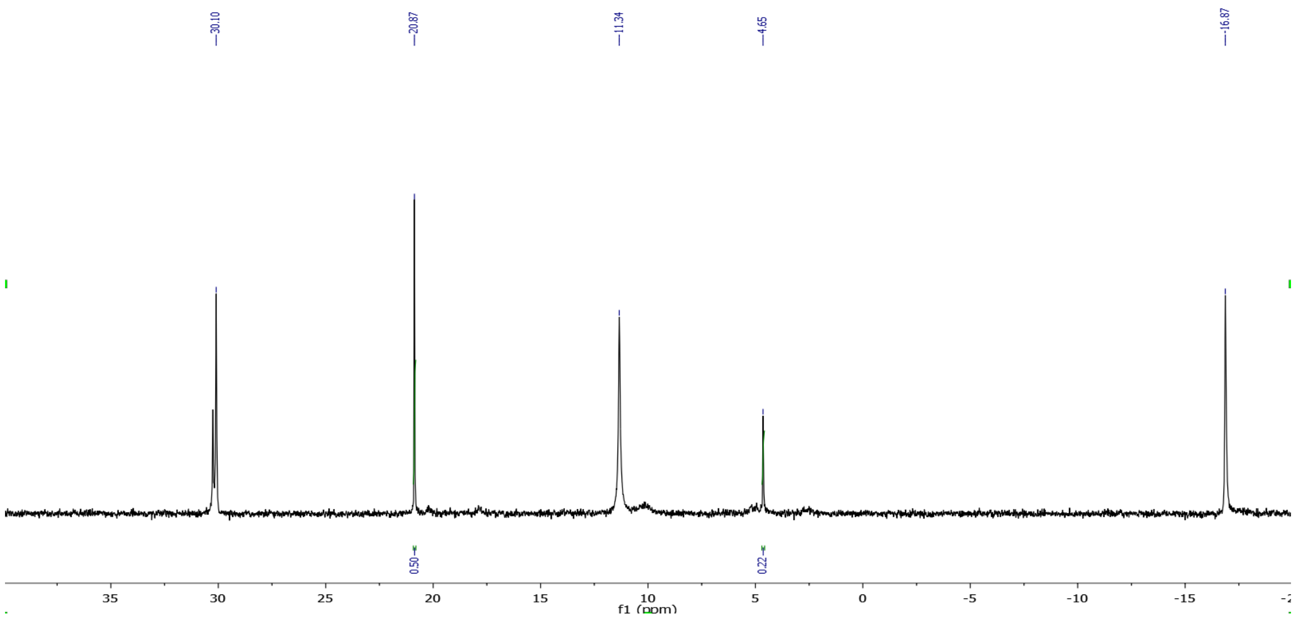
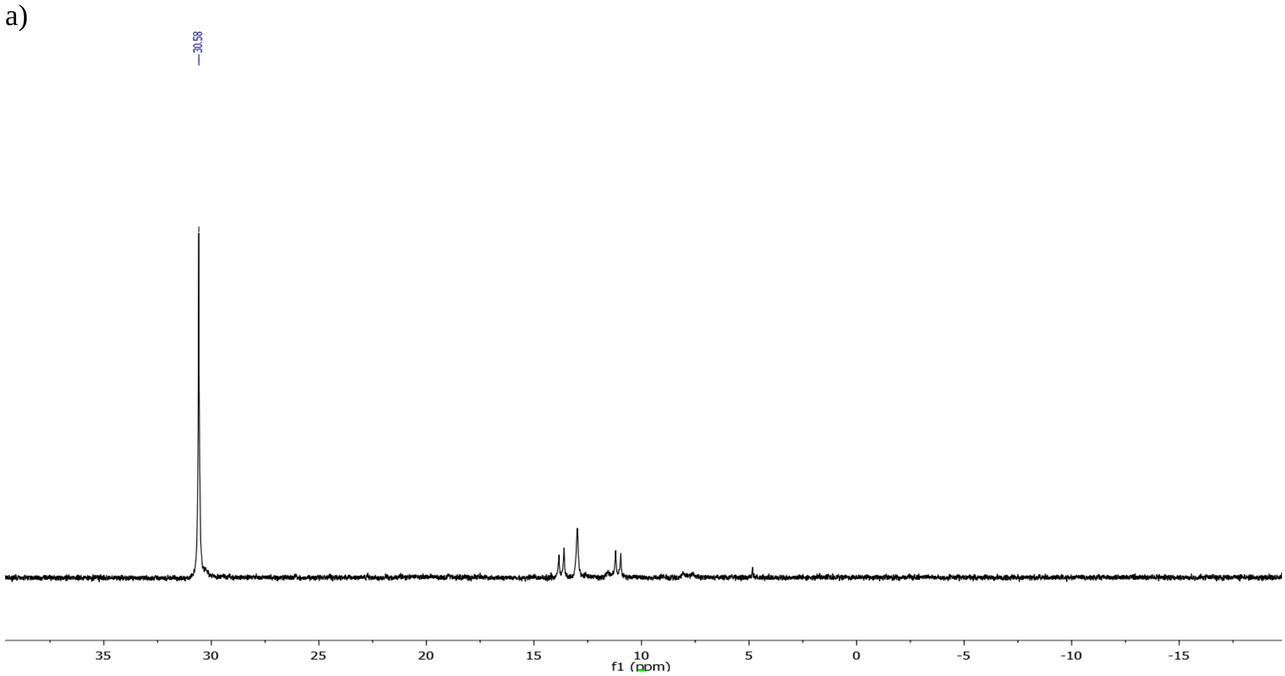


Figure S99. $Pd(OAc)_2$ + dppp (2 equiv) + in DMF-d_7 at rt in 20 min. The peaks at 20.87 ppm and at 4.85 ppm are related to the IS and Pd^0(dppp) respectively.

Entry 2, Table S14:

a)



b)

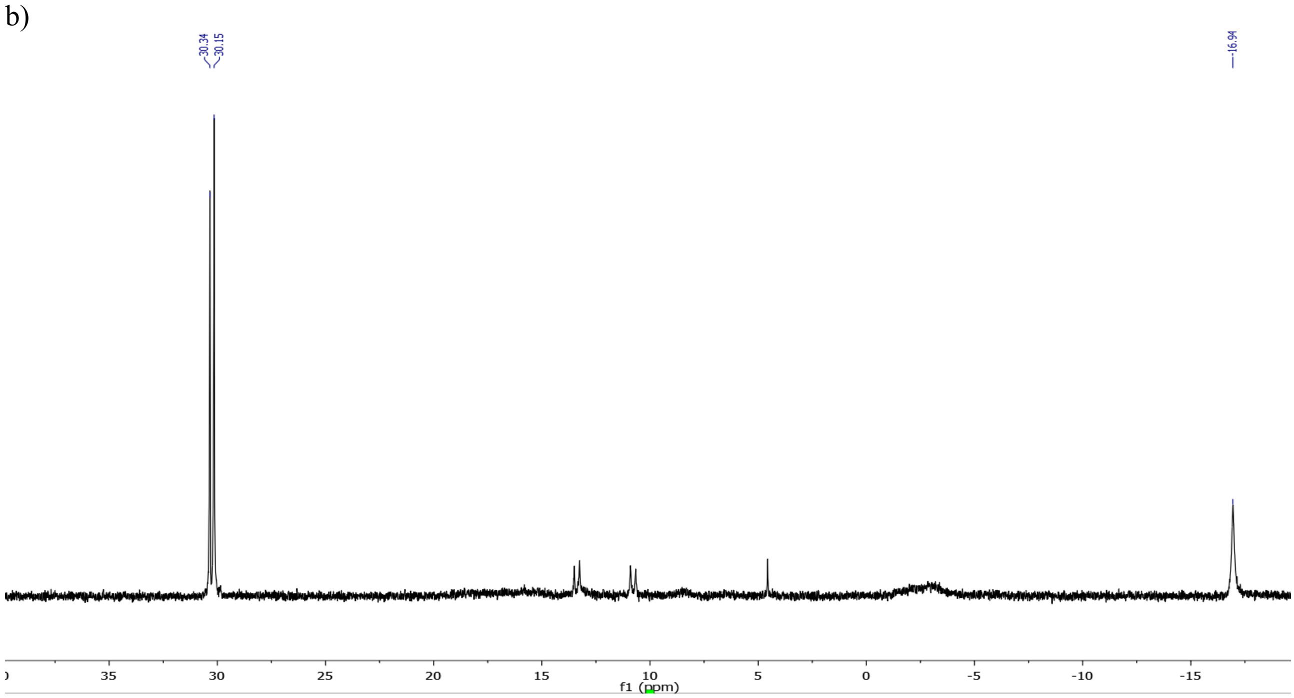


Figure S100. $Pd(OAc)_2$ + dppp (2 equiv) + TMG (5 equiv) in DMF-d_7 at rt in 20 min. b) + $3NO_2ArI$ (5 equiv). Is reasonable to assume that the Pd specie with TMG is unstable

Entry 3, Table S14:

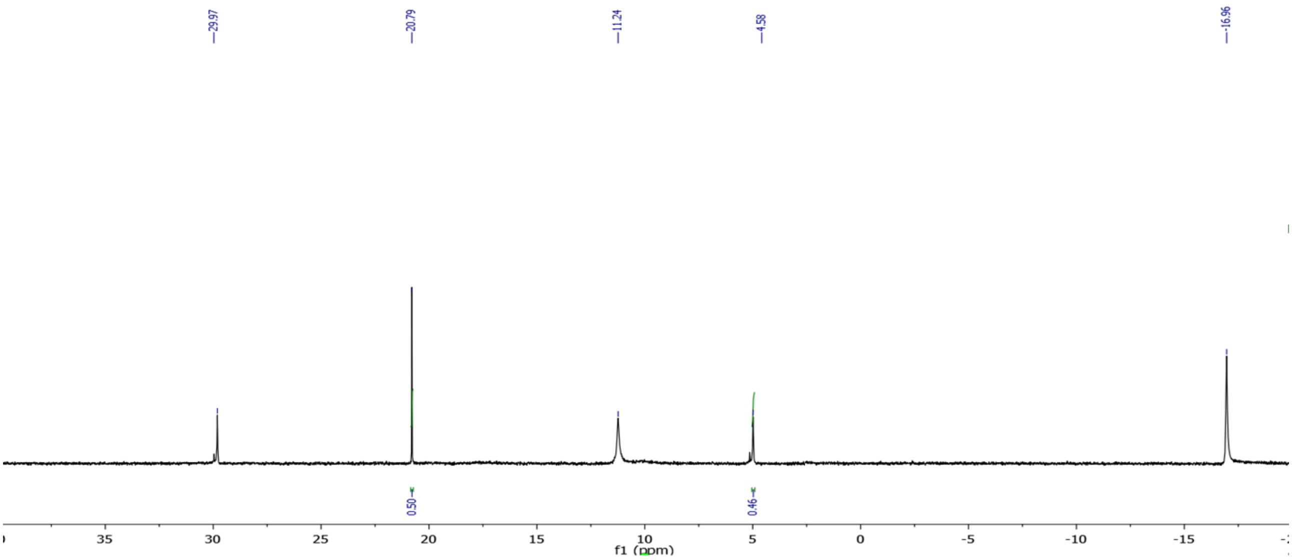


Figure S101. $Pd(OAc)_2$ + dppp (2 equiv) + K_2CO_3(5 equiv) in DMF-d_7 at rt in 20 min. The peaks at 20.79 ppm and at 4.58 ppm are related to the IS and Pd^0(dppp) respectively.

Entry 4, Table S14:

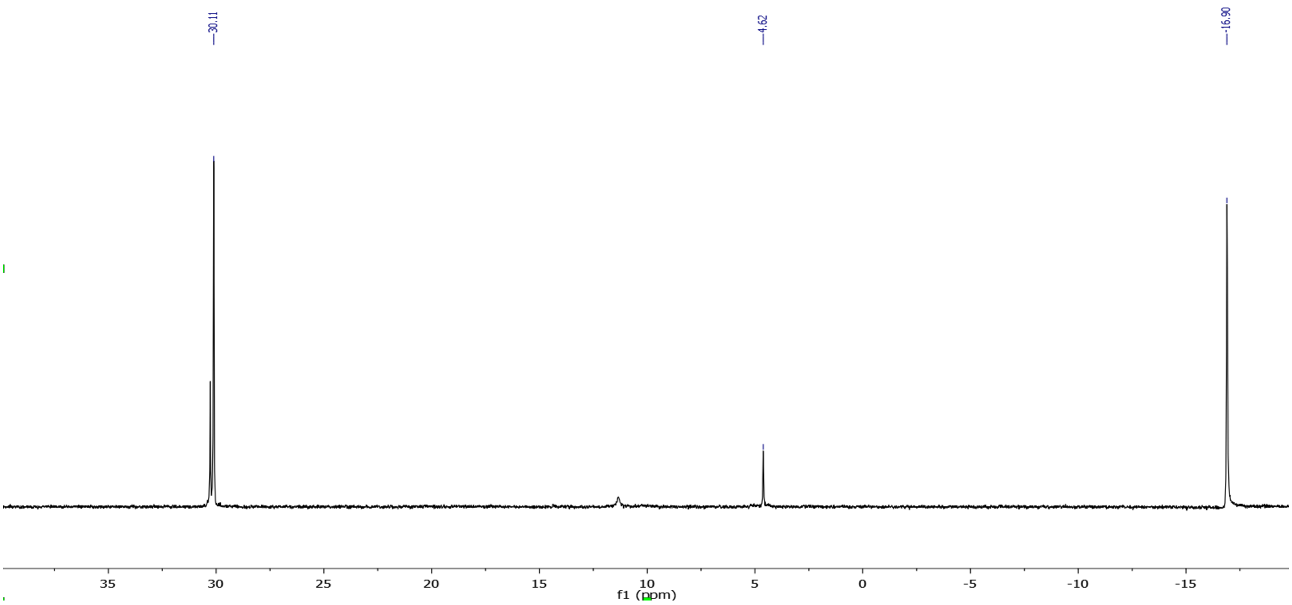
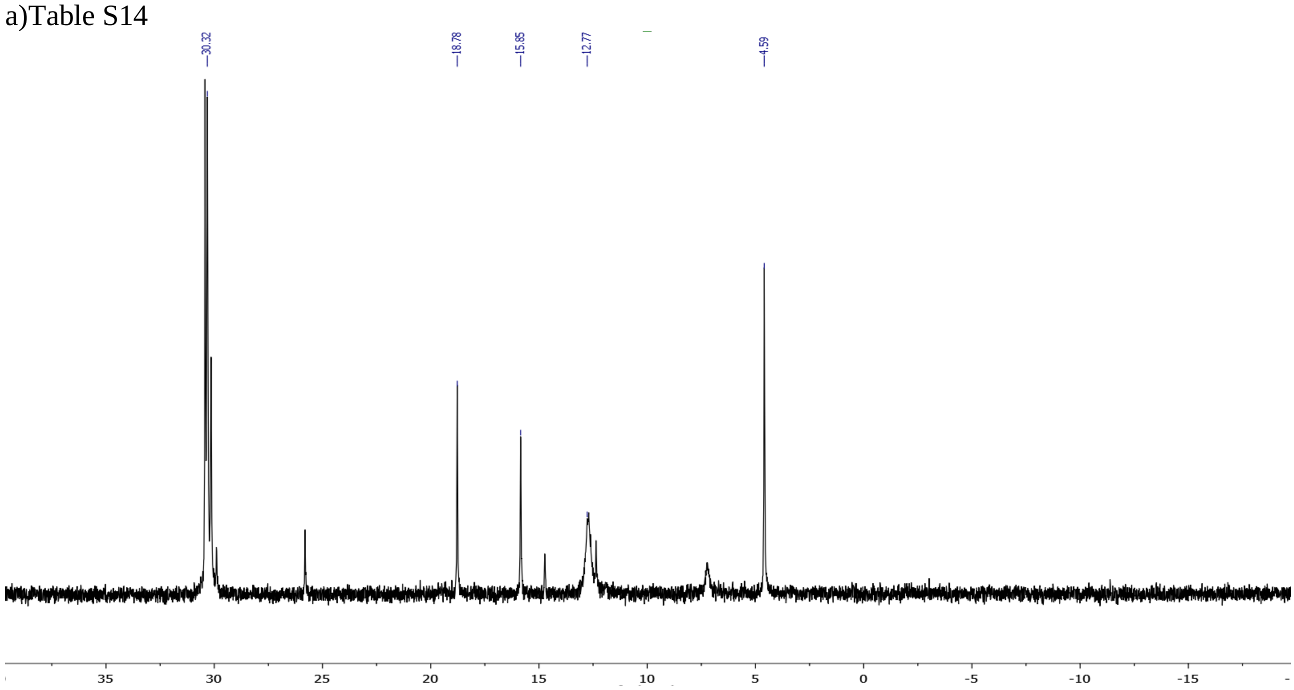


Figure S102. $Pd(OAc)_2$ + dppp (2 equiv) in DMF-d_7 at 60°C in 20 min.

Entry 6, Table S14:

a)Table S14



b)

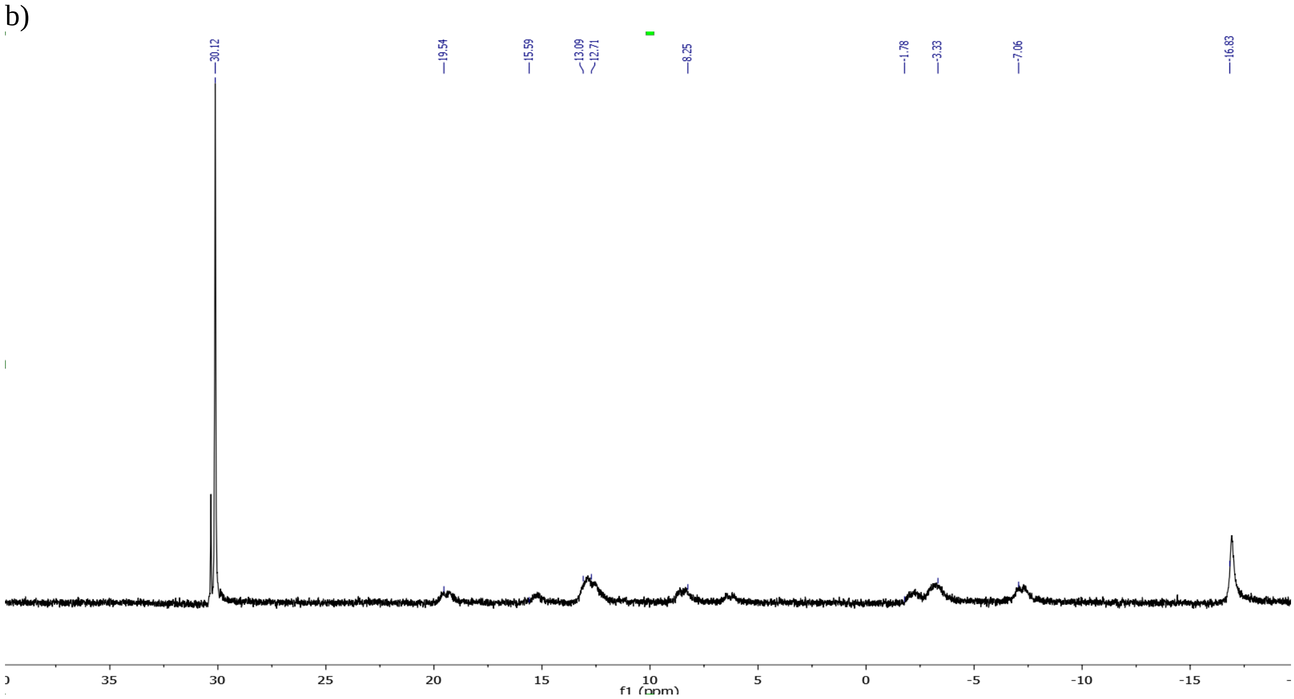
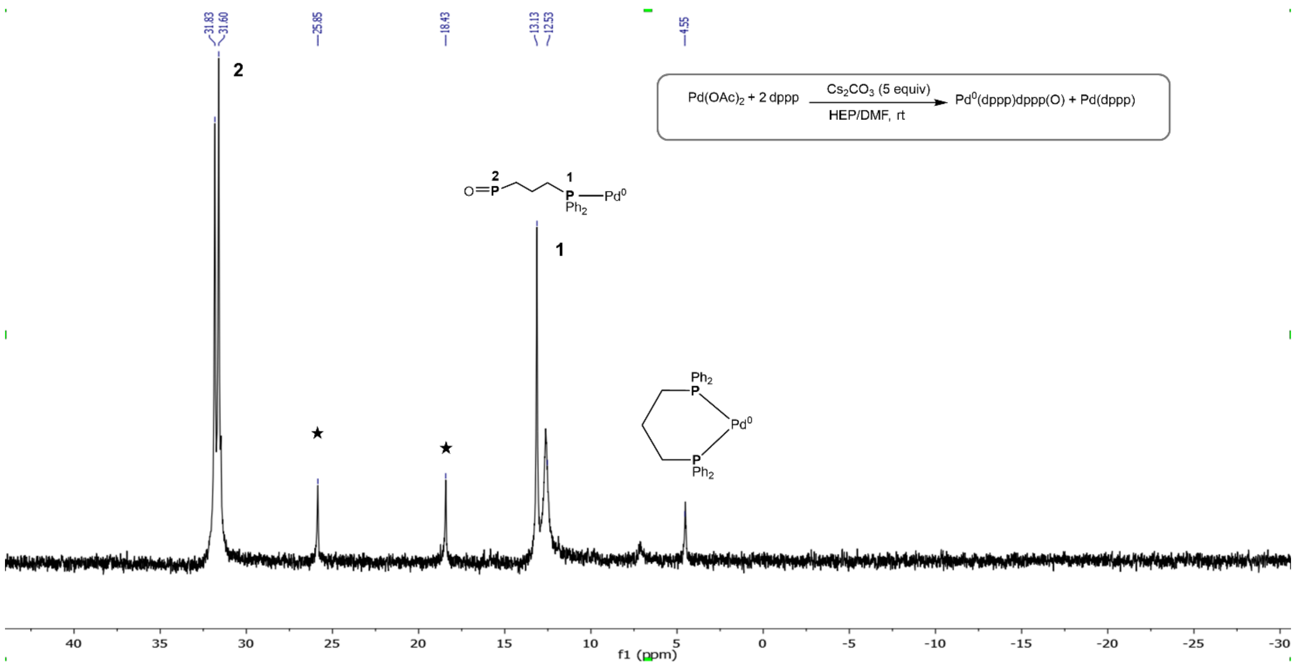


Figure S103. a) $Pd(OAc)_2$ + dppp (2 equiv) + K_2CO_3 (5 equiv) in DMF-d_7 at 60°C in 20 min. b) + $3NO_2ArI$.. After the addition of the aryl halide, the spectrum usually showed poor quality and broad signals.

Entry 7, Table S14: Completed reduction in HEP/DMF as example

a)



b)

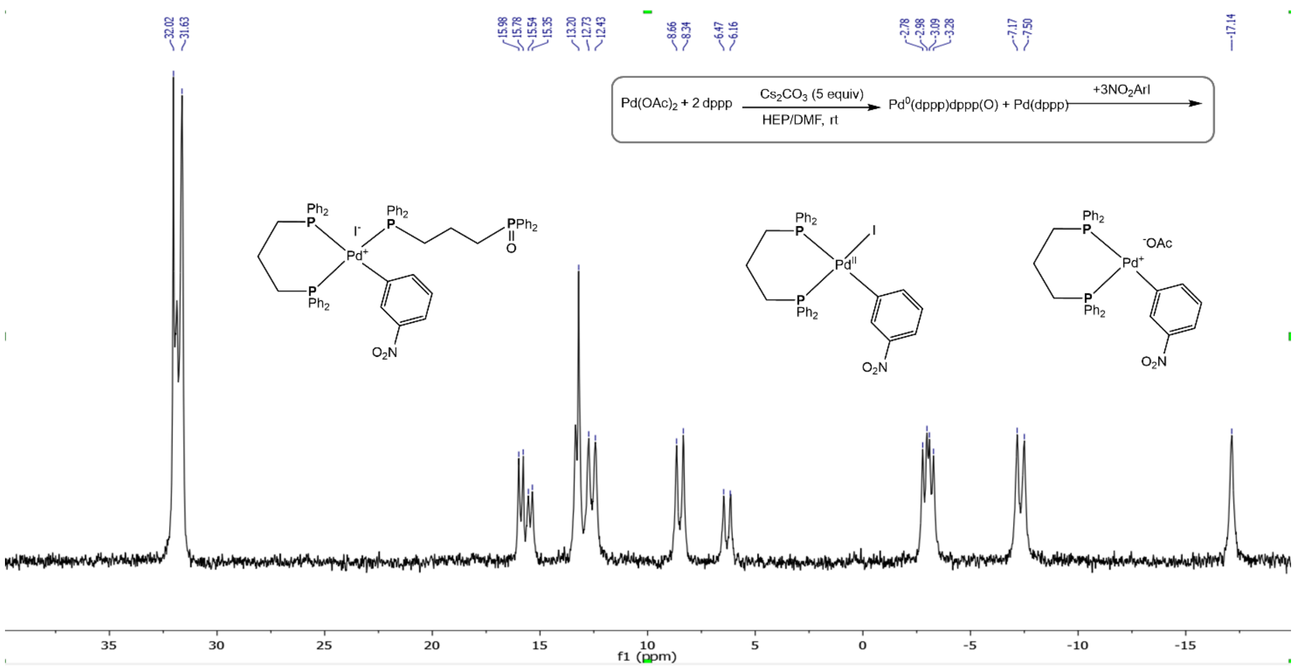
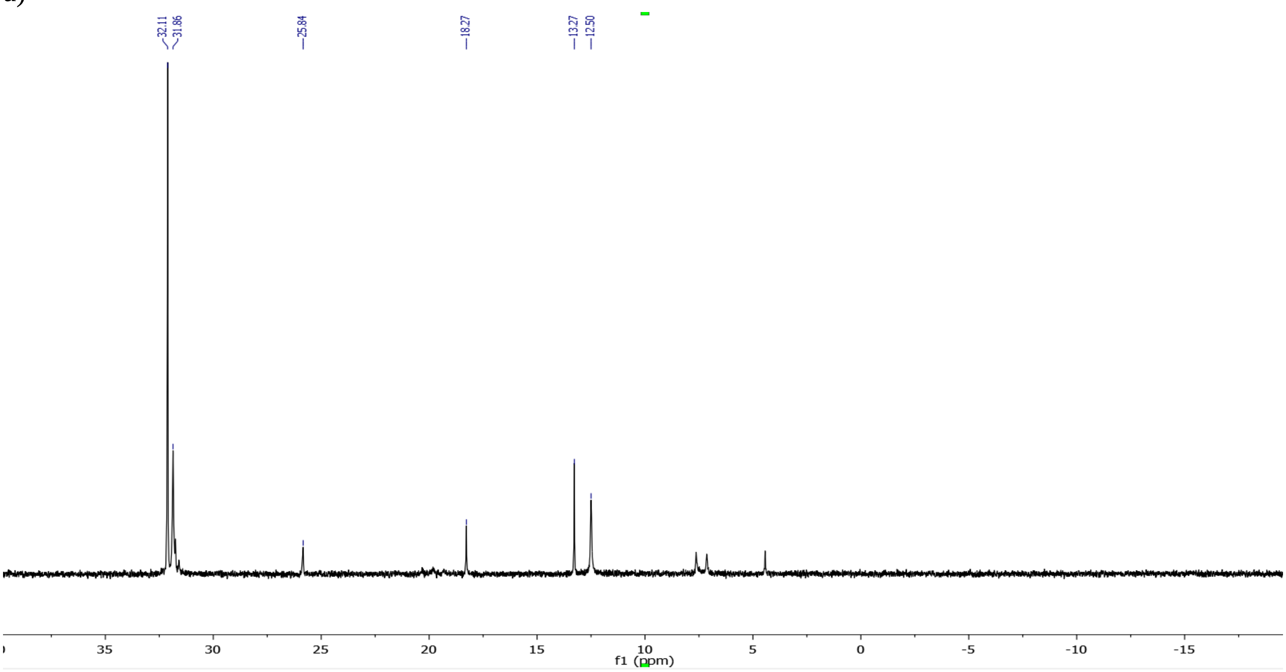


Figure S104. a) $Pd(OAc)_2$ + dppp (2 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$. The Pd(0) species potentially involved are shown in Figure a) (The labelled peaks at at 25.85 ppm and 18.43 ppm, disappeared after the aryl halide addition, It is reasonable to assume that these are some Pd(0) species). All peaks in the first figure disappeared, and the possible oxidative addition complexes involved are depicted in Figure b), according to the literature[10]

Other spectra

Entry 8, Table S14:

a)



b)

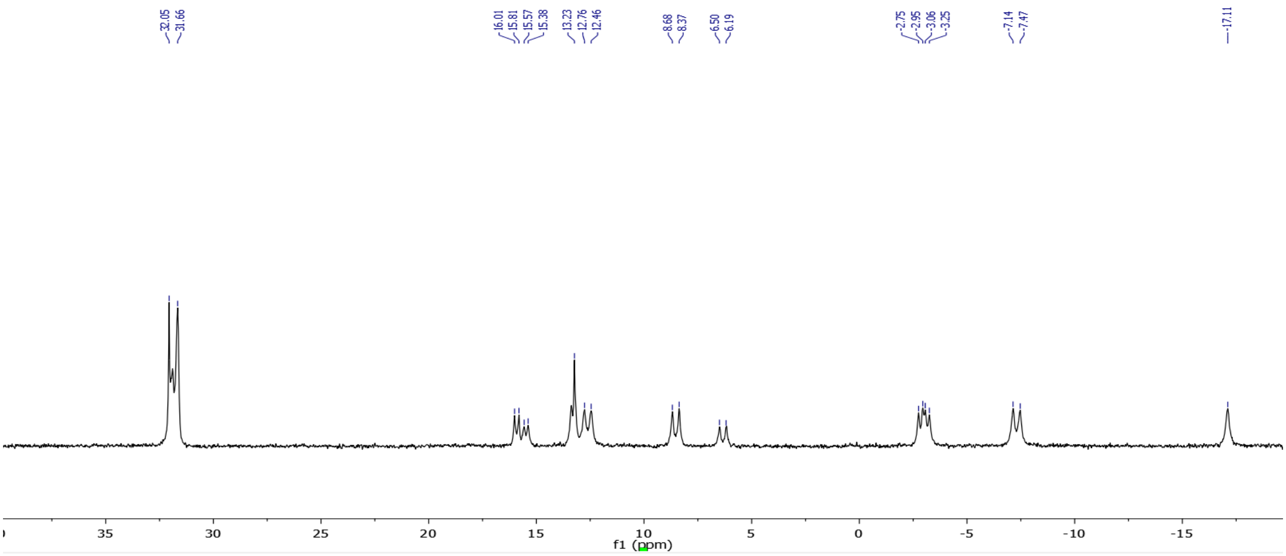
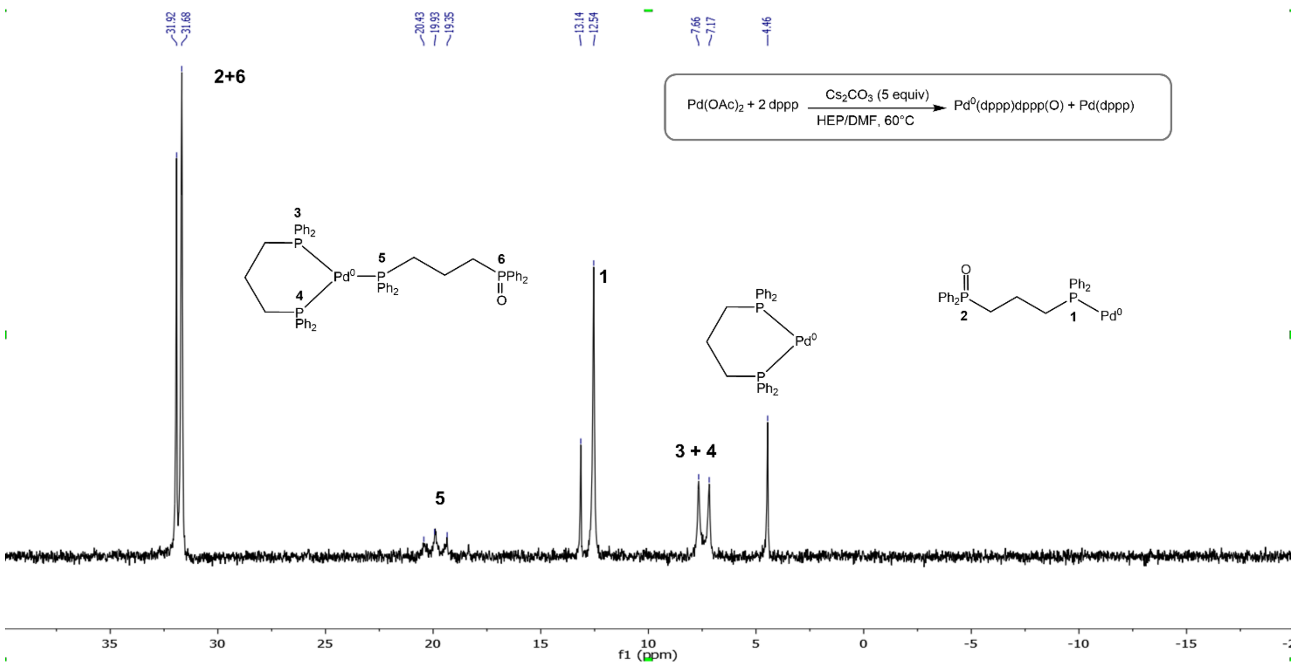


Figure S105. a) $Pd(OAc)_2$ + dppp (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. + $3NO_2ArI$

Entry 9, Table S14:

a)



b)

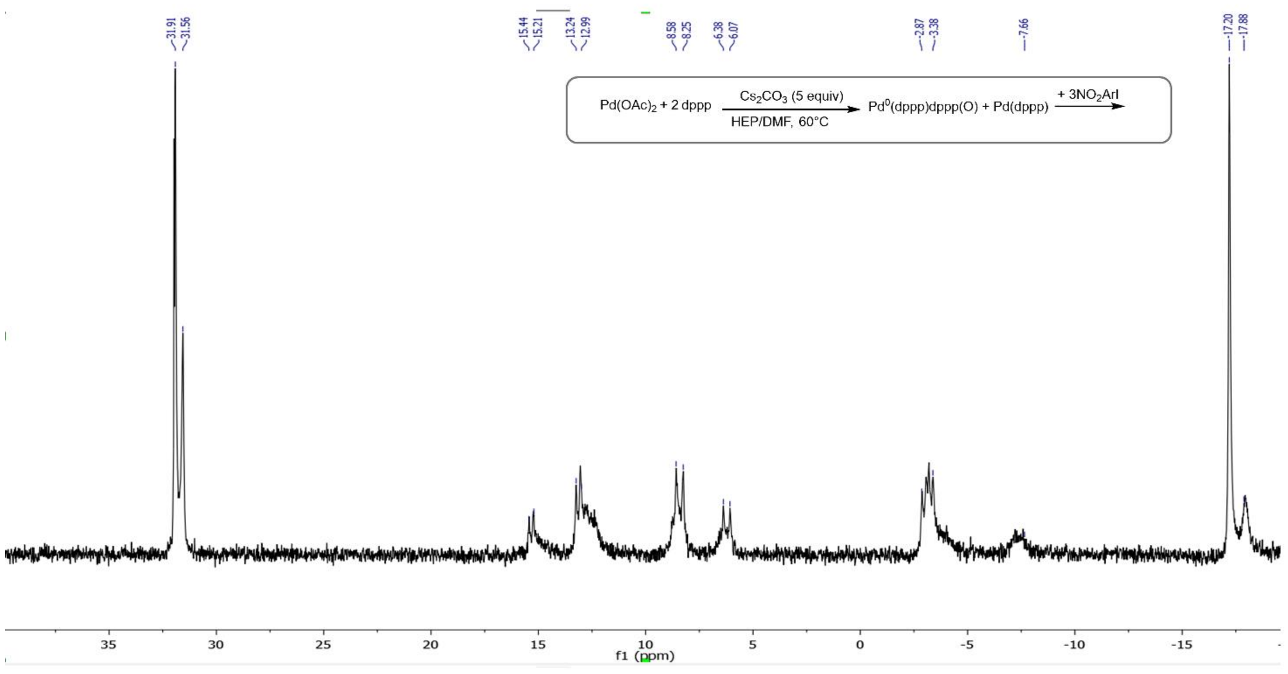
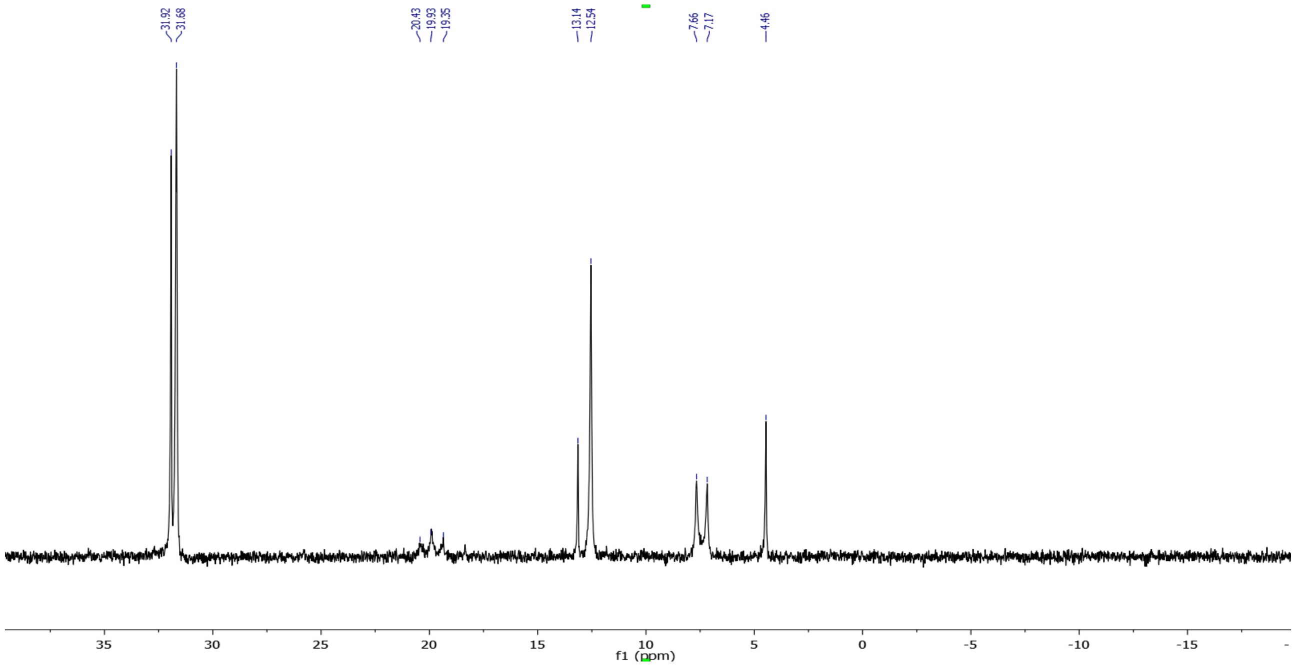


Figure S106. a) $Pd(OAc)_2$ + dppp (2 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$

Entry 10, Table S14:

a)



b)

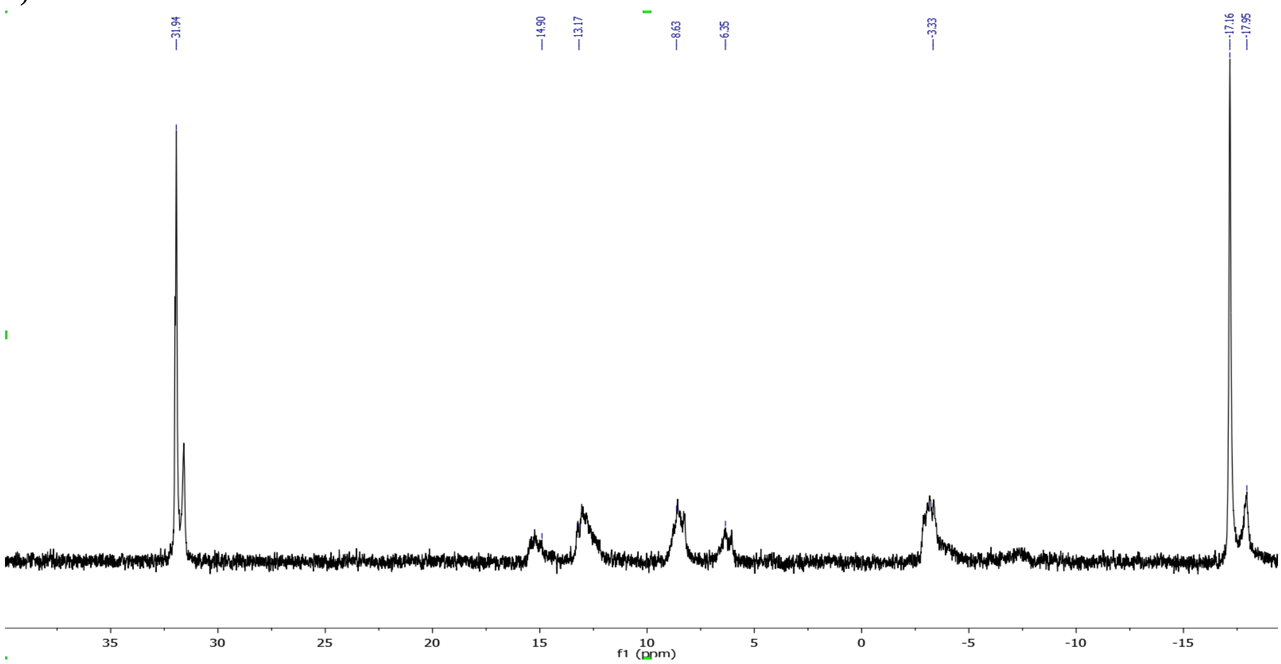


Figure S107. a) $Pd(OAc)_2$ + dppp (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$

5.2. $PdCl_2$

5.2.1. General Procedure 2

$$Pd(ACN)_2Cl_2 + 2dppp \xrightarrow[\text{Solvent, T (°C)}]{\text{Base (5 equiv)}} Pd^0(dppp)$$

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $Pd(ACN)_2Cl_2$ (3.41 mg, 0.013 mmol, 1 equiv) was dissolved in the degassed solvent (0.6 mL). Dppp (10.71 mg, 0.026 mmol, 2 equiv) and base (0.065 mmol, 5 equiv) were added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis.

To further demonstrate that the formation of Pd(0) specie occurred, $3NO_2ArI$ (16.2 mg, 0.065 mmol, 5 equiv) was added to detect the formation of the oxidative addition (OA) complex. The OA complex was previously synthesized according to the literature[1]

Table S15 $Pd(dppp)Cl_2$ reduction in 20 min in DMF-d_7 and HEP/DMF-d_7[a]

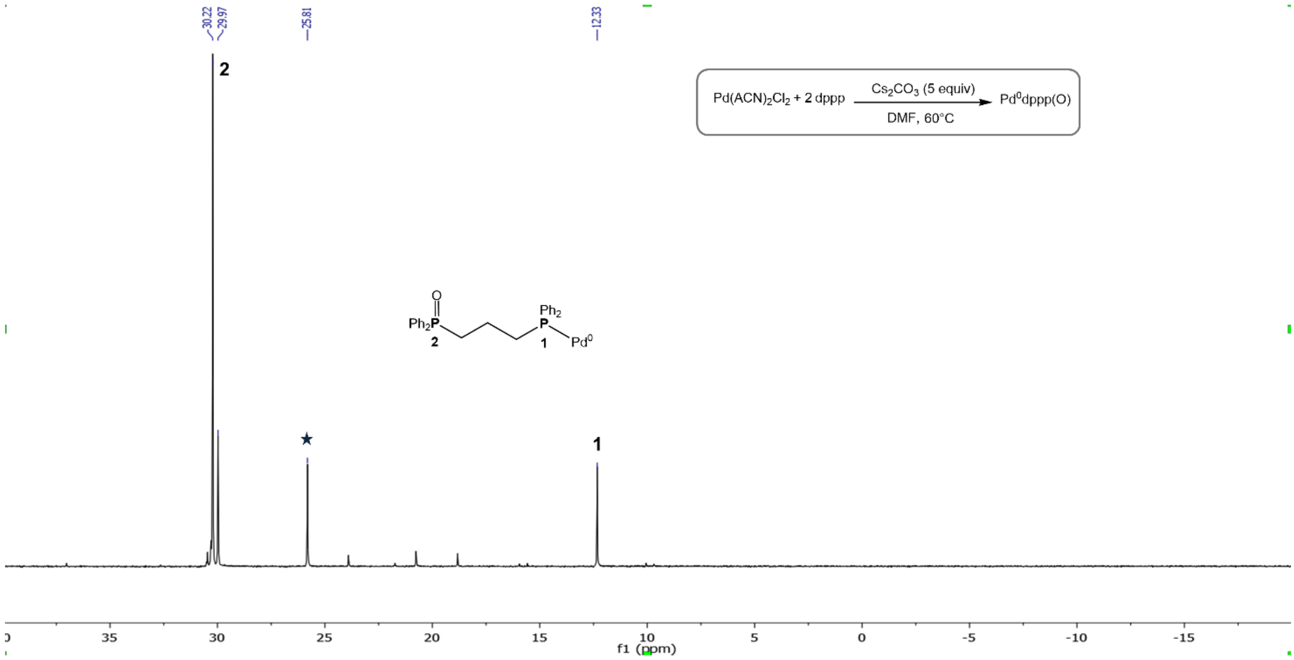
entry	Base	Solvent	T(°C)	mech	Pd^0/Pd^{2+}[b]	P/OH [c]
1	-	DMF[d]	25	-	0/100	-
2	-	DMF	60	-	0/100	-
3	Cs_2CO_3	DMF	25	-	0/100	-
4	K_2CO_3	DMF	25	-	0/100	-
5	TMG	DMG	60	-	0/100	-
6	Cs_2CO_3	DMF	60	E	100/0	100/0
7	K_2CO_3	DMF	60	E	100/0	100/0
8	Cs_2CO_3	DMF/HEP[e]	25	A	100/0	0/100
9	K_2CO_3	DMF/HEP	25	A	55/45	0/100
10	Cs_2CO_3	DMF/HEP	60	A/E	100/0	n.d.[d]
11	K_2CO_3	DMF/HEP	60	A/E	100/0	n.d.[d]

[a] The reactions were carried out according to the **General Procedure 2**
[b] The conversion was calculated by ^{31}P NMR comparing the signals of the IS signal and Pd (dppp)Cl_2
[c] P/OH represents the ratio between the oxidation of phosphine (P) or alcohol (OH) to form Pd(0) and n,d, means not determined.
[d] 600µL of DMF-d_7
[e] The solvent is a mixture of HEP 200µL and DMF-d_7 400µL

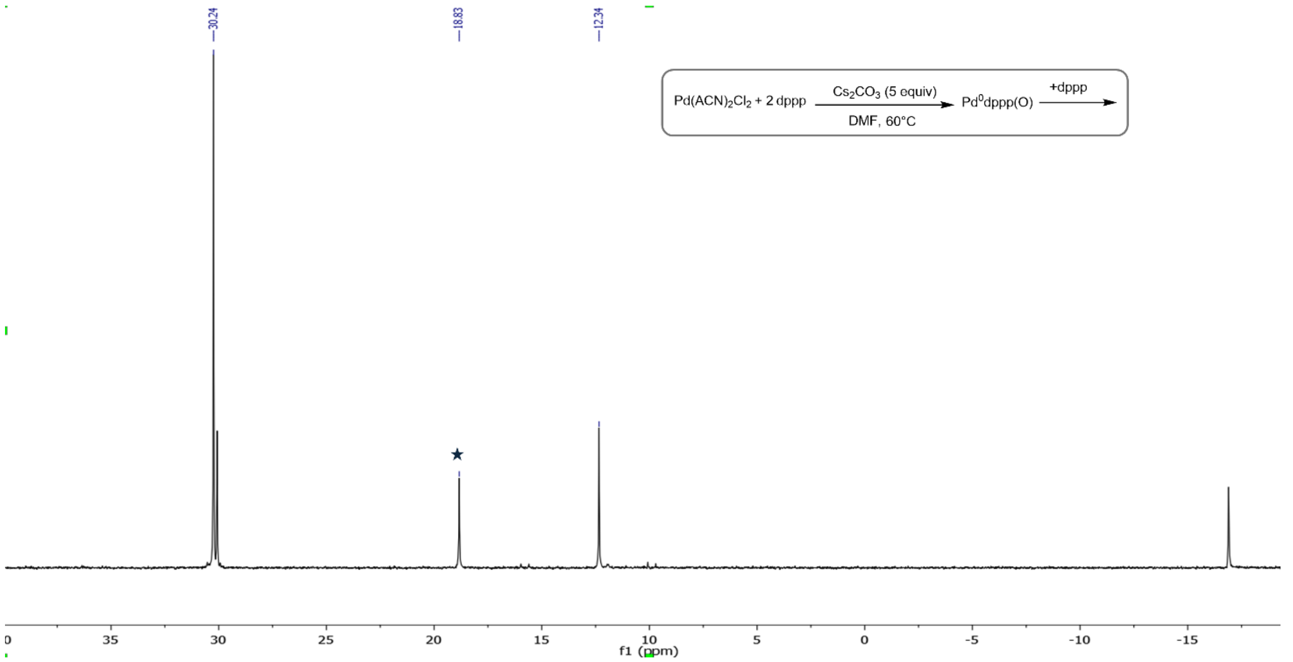
5.2.2. ^{31}P NMR spectra

Entry 6, Table S15 Completed reduction in DMF

a)



b)



c)

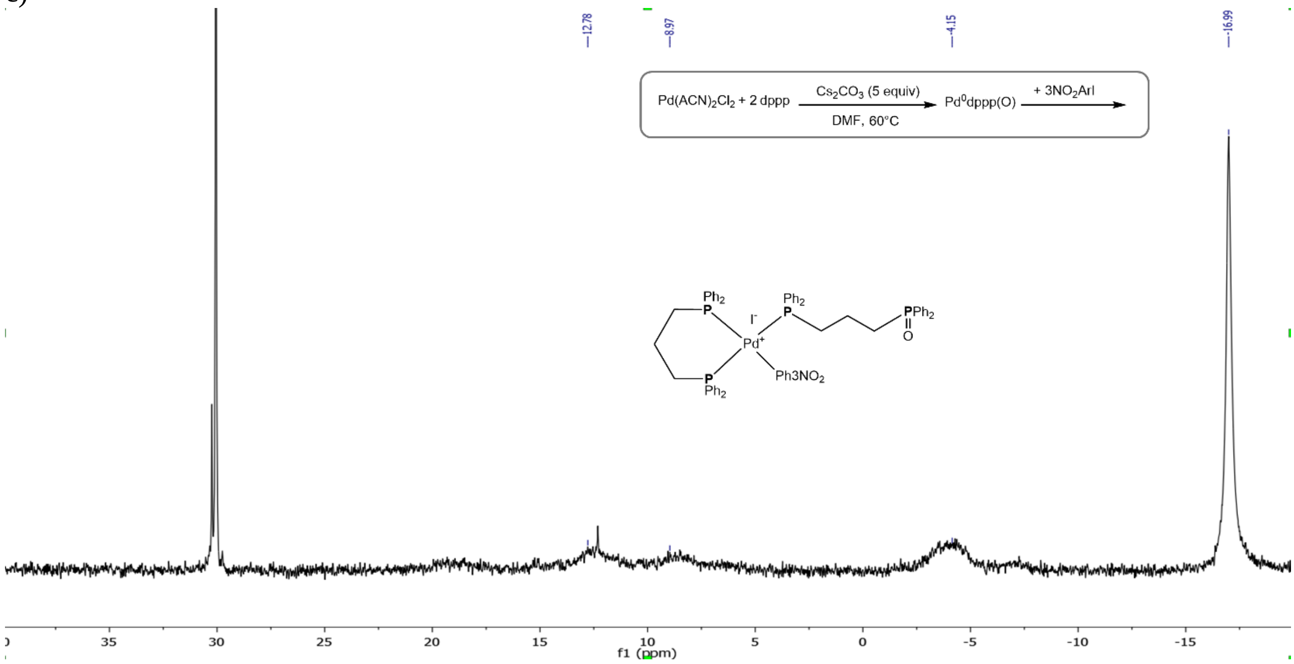


Figure S108. a) Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) + Cs_2CO_3 (5 equiv) in DMF-d$_7$ at 60°C in 20 min. b) + 1equiv dppp. After the addition of the ligand, the peak at 25.81 ppm disappeared and the peak at 18.83 ppm appeared. Since both of them disappeared after the addition of the aryl halide, they are probably Pd(0) species in equilibrium. c) + 3NO$_2$ArI. Although the resolution of the ^{31}P NMR spectra is often poor after the aryl halide addition, the Pd(0) species have distinctly disappeared. According to the literature[10], the complex reported in figure above, is supposed to be the OA complex

Other spectra

Entries 1-5, Table S15:

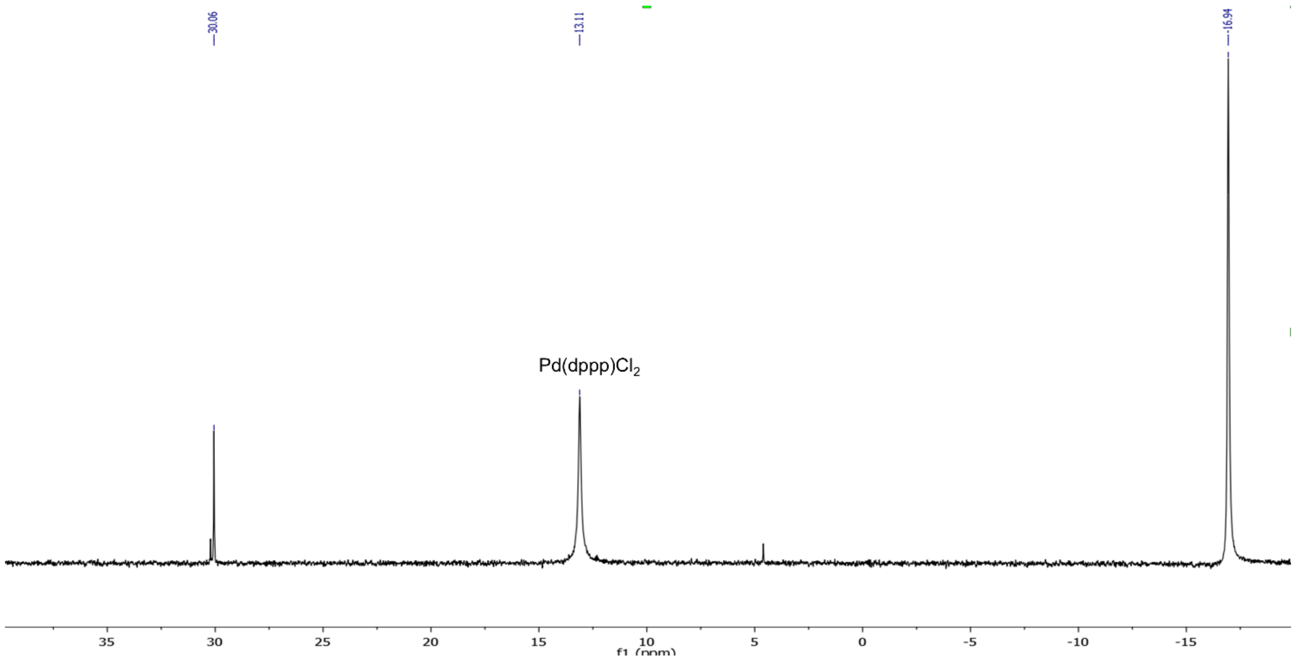
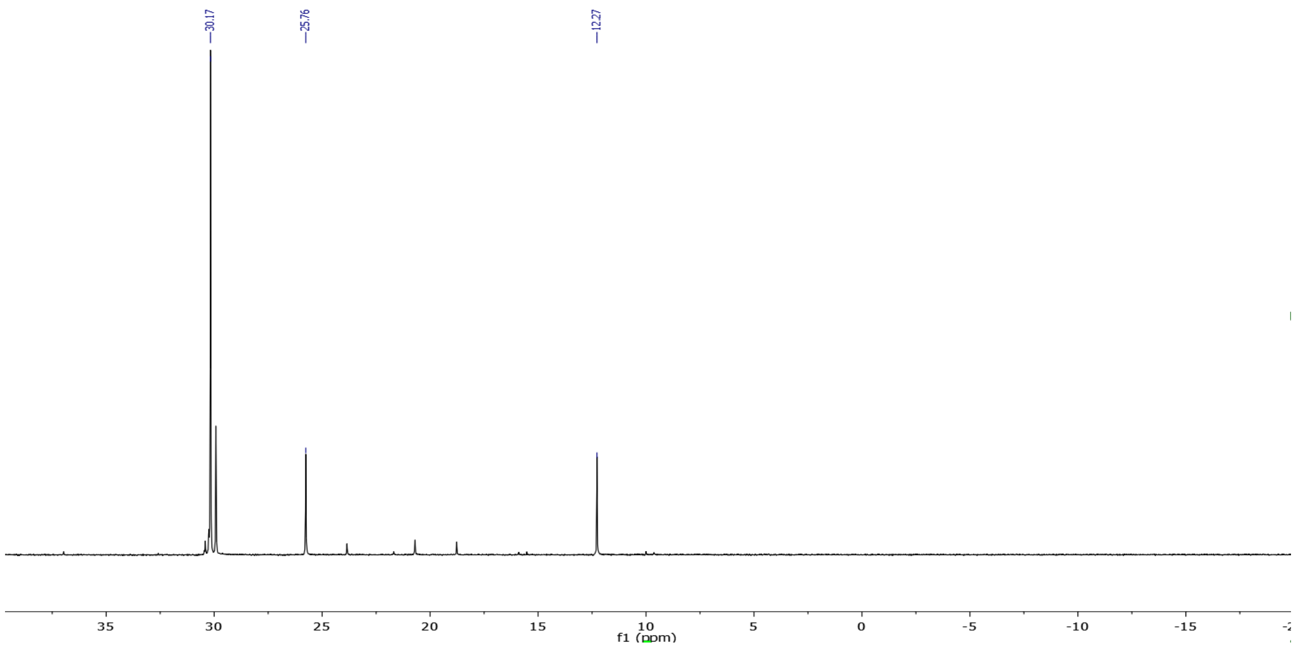


Figure S109. Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) in DMF-d$_7$ at rt and 60°C, Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) + Cs_2CO_3, K_2CO_3 (5 equiv) in DMF-d$_7$ at rt, Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) + TMG (5 equiv) at 60°C in DMF-d$_7$ in 20 min.

Entry 7, Table S15:

a)



b)

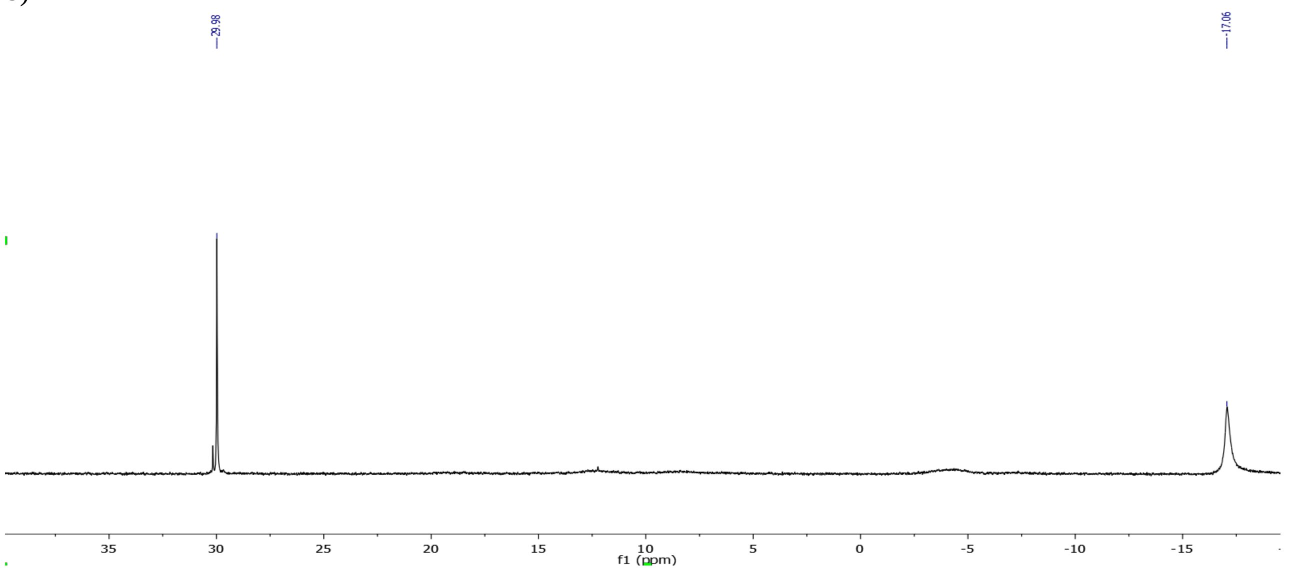
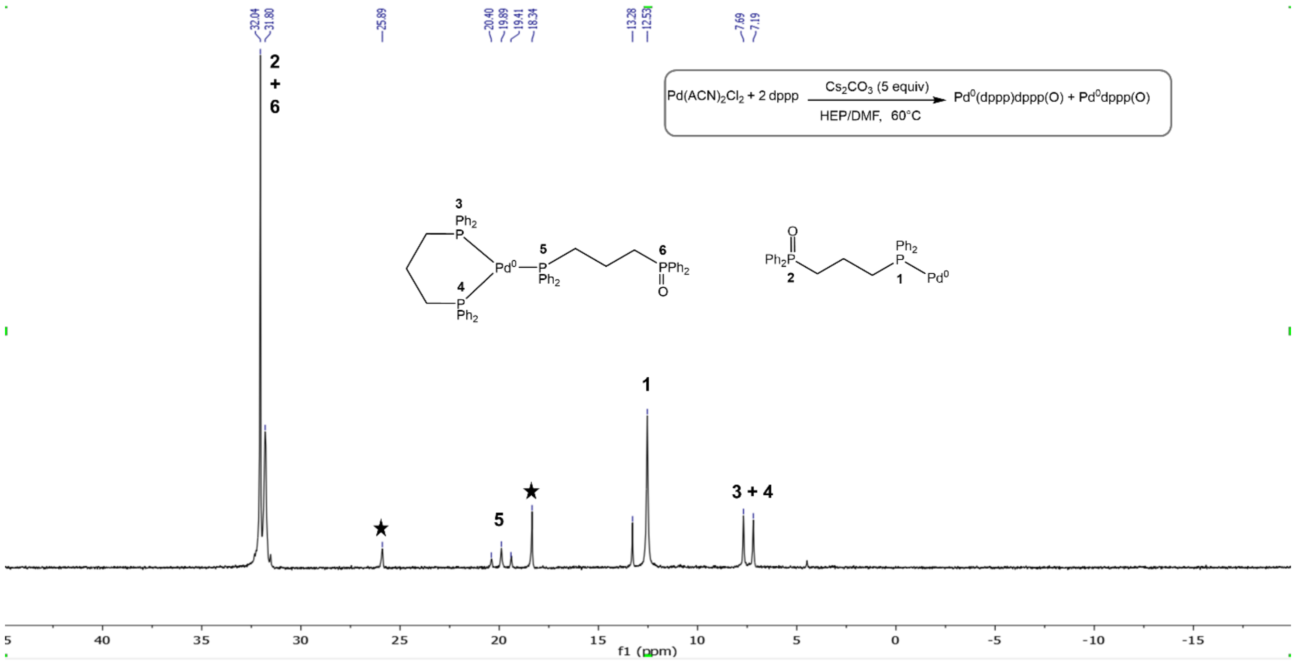


Figure S110. $Pd(ACN)_2Cl_2$ + dppp (2 equiv) + K_2CO_3 in DMF-d_7 at 60°C in 20 min. b) +3NO_2ArI. After the addition of the aryl halide, the spectrum usually showed poor quality and broad signals.

Entry 10, Table S15: Completed reduction in HEP/DMF as example

a)



b)

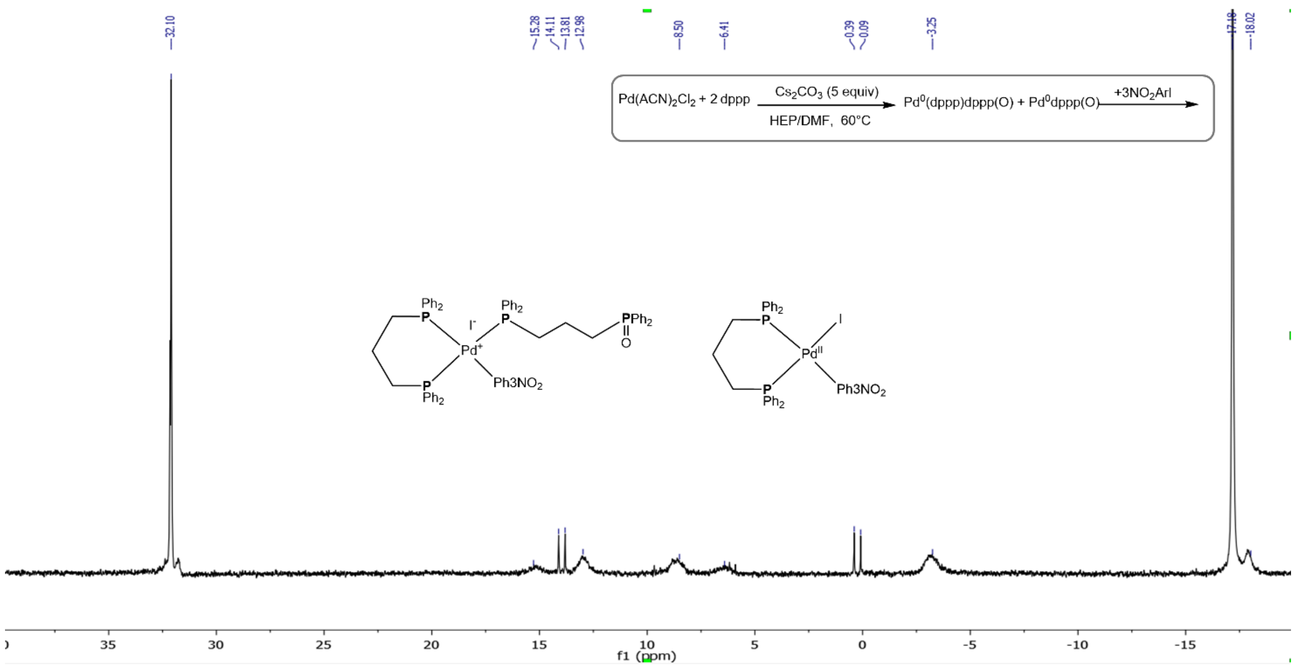
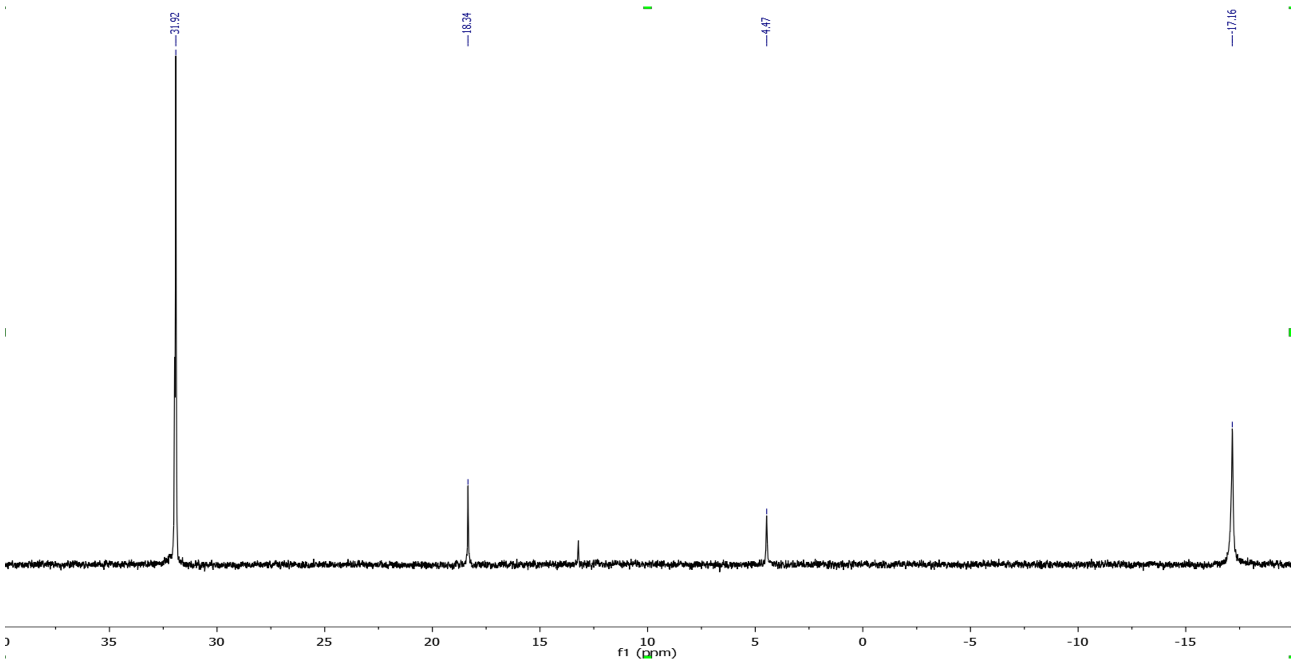


Figure S111. a) Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) + Cs$_2$CO$_3$ (5 equiv) in HEP/DMF-d$_7$ (2:4) at 60°C in 20 min. b) + 3NO$_2$ArI. The Pd(0) species potentially involved are shown in Figure a) (For the labeled peaks at 25.89 ppm and 18.34 ppm see Figure S108). All peaks in the first figure disappeared, and the possible oxidative addition complexes involved are depicted in Figure b), according to the literature[10].

Entry 8, Table S15:

a)



b)

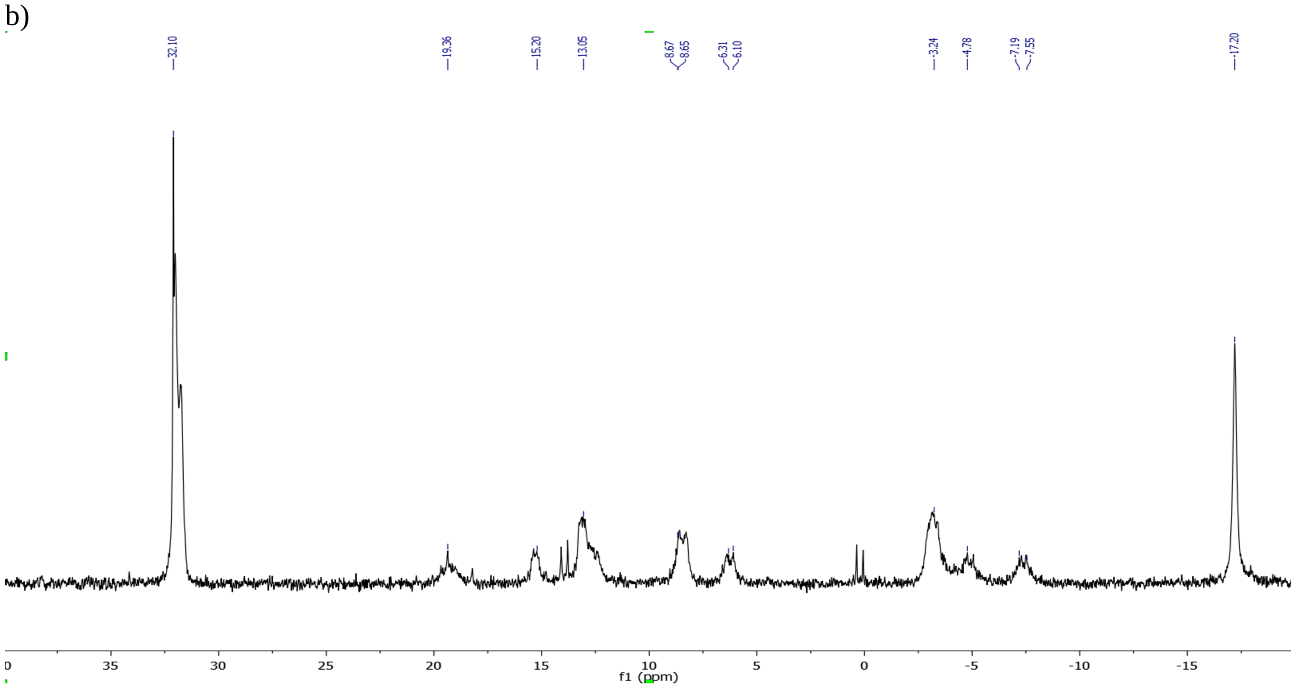


Figure S112. a) $Pd(ACN)_2Cl_2$ + dppp (2 equiv) + Cs_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at rt in 20 min. b) + $3NO_2ArI$. After the addition of the aryl halide, the spectrum usually showed poor quality and broad signals.

Entry 9, Table S15:

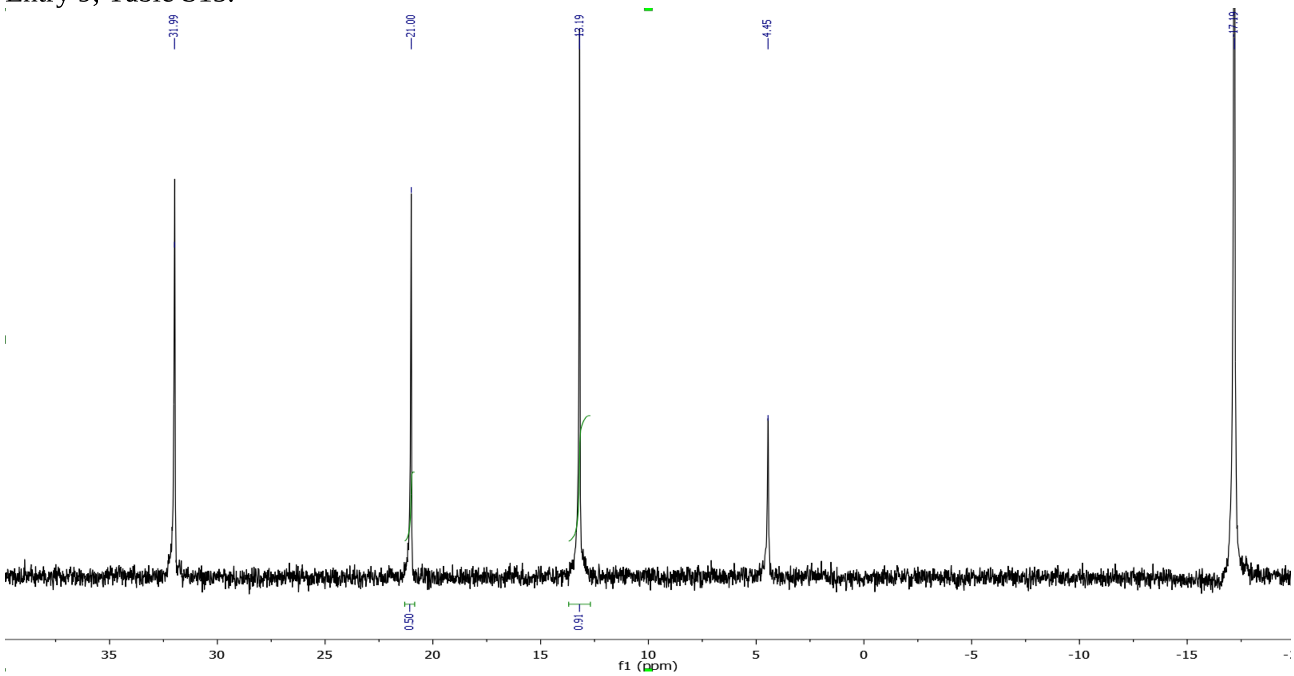
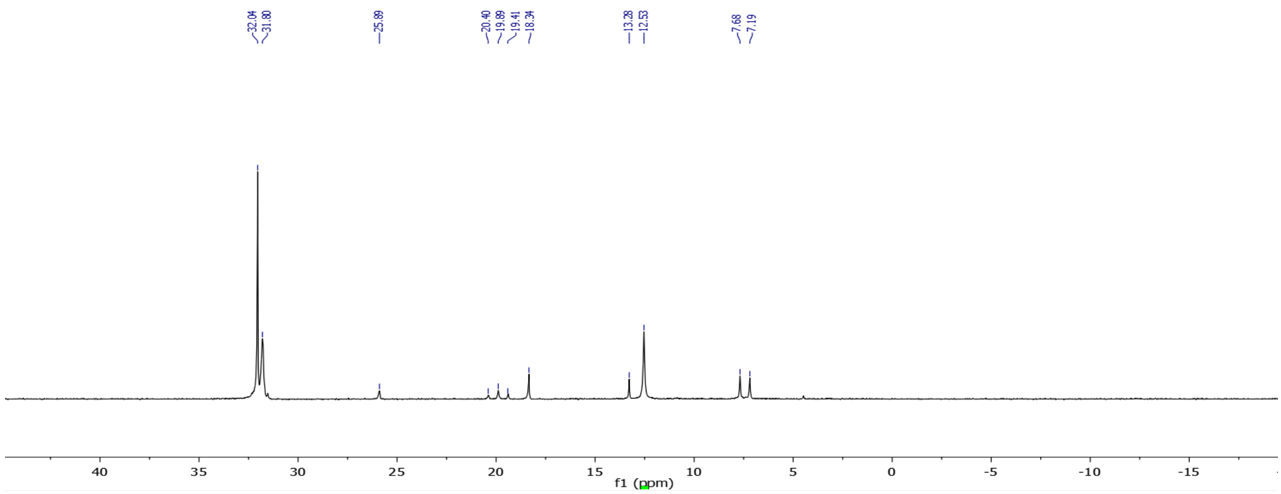


Figure S113. Pd(ACN)$_2$Cl$_2$ + dppp (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d$_7$ at rt in 20 min. The peaks at 21 ppm and at 13.19 ppm are related to the IS and Pd(dppp)Cl$_2$ respectively.

Entry 10, Table S15:

a)



b)

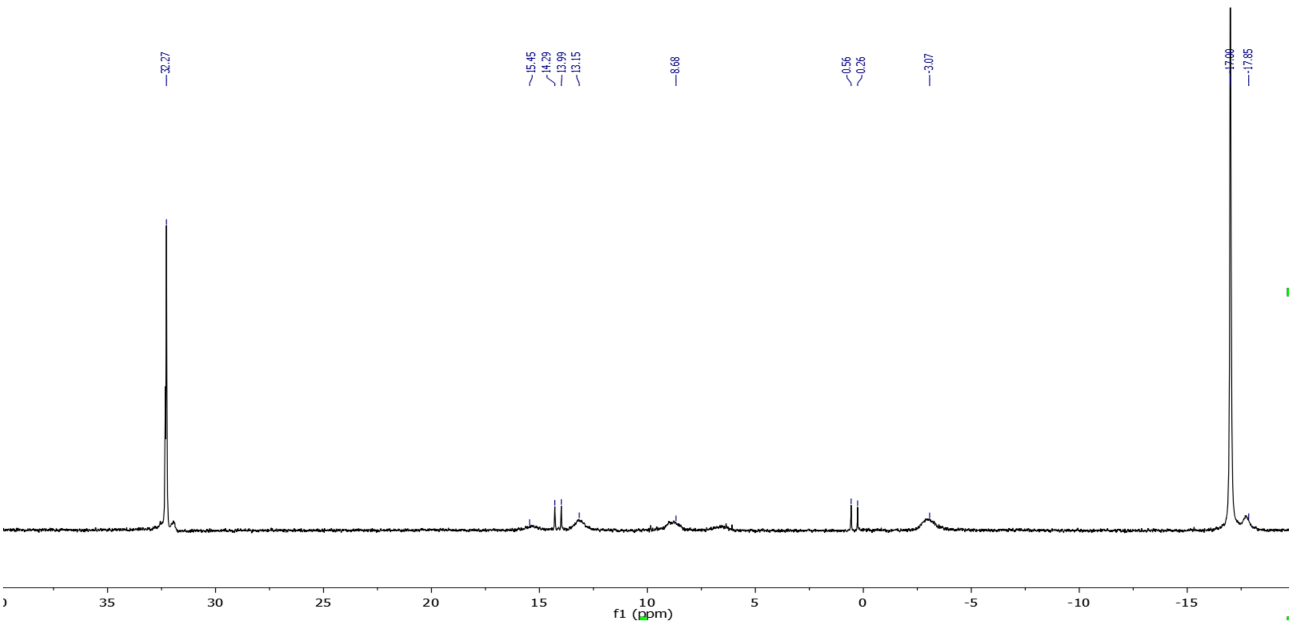


Figure S114. a) $Pd(ACN)_2Cl_2$ + dppp (2 equiv) + K_2CO_3 (5 equiv) in HEP/DMF-d_7 (2:4) at 60°C in 20 min. b) + $3NO_2ArI$. After the addition of the aryl halide, the spectrum usually showed poor quality and broad signals.

6. Investigation of the possible Pd-NPs

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2$(ddpf) (14.6 mg, 0.02 mmol, 1 equiv) was dissolved in degassed DMF (0.5 µL), followed by the addition TMG (65 µL from a stock solution of 0.66 M, 0.04 mmol, 2 equiv). After 30 min of stirring at 60°C, the solution was maintained under inert atmosphere, transferred into a falcon with silicon septum and centrifugated. The particles obtained were isolated by taking the supernatant and analyzed by TEM.
The analysis showed the formation of palladium nanoparticles.

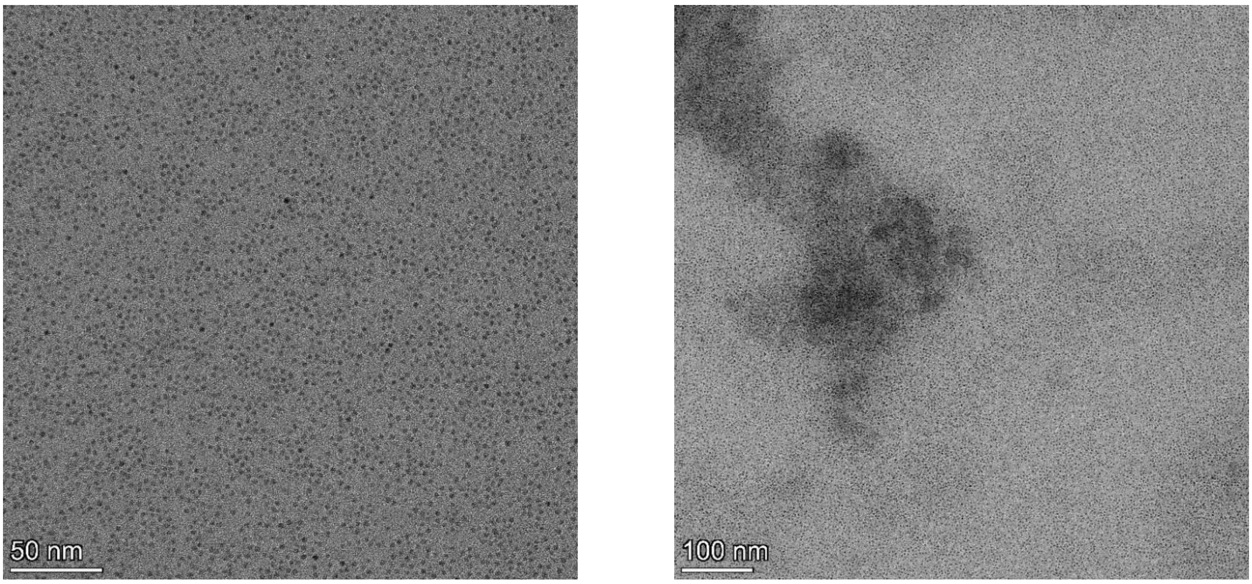


Figure S115. TEM images of $PdCl_2$(dppf) reduction with TMG (5 equiv) in DMF at 60°C.

To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2$(ddpf) (14.6 mg, 0.02 mmol, 1 equiv) and dppf (11.08 mg, 0.02 mmol, 1 equiv) were dissolved in degassed DMF (0.5 µL), followed by the addition TMG (65 µL from a stock solution of 0.66 M, 0.04 mmol, 2 equiv). After 30 min of stirring at

60°C, the solution was maintained under inert atmosphere, transferred into a falcon with silicon septum and centrifugated. The particles obtained were isolated by taking the supernatant and analyzed by TEM.
The analysis did not show the formation of palladium nanoparticles.

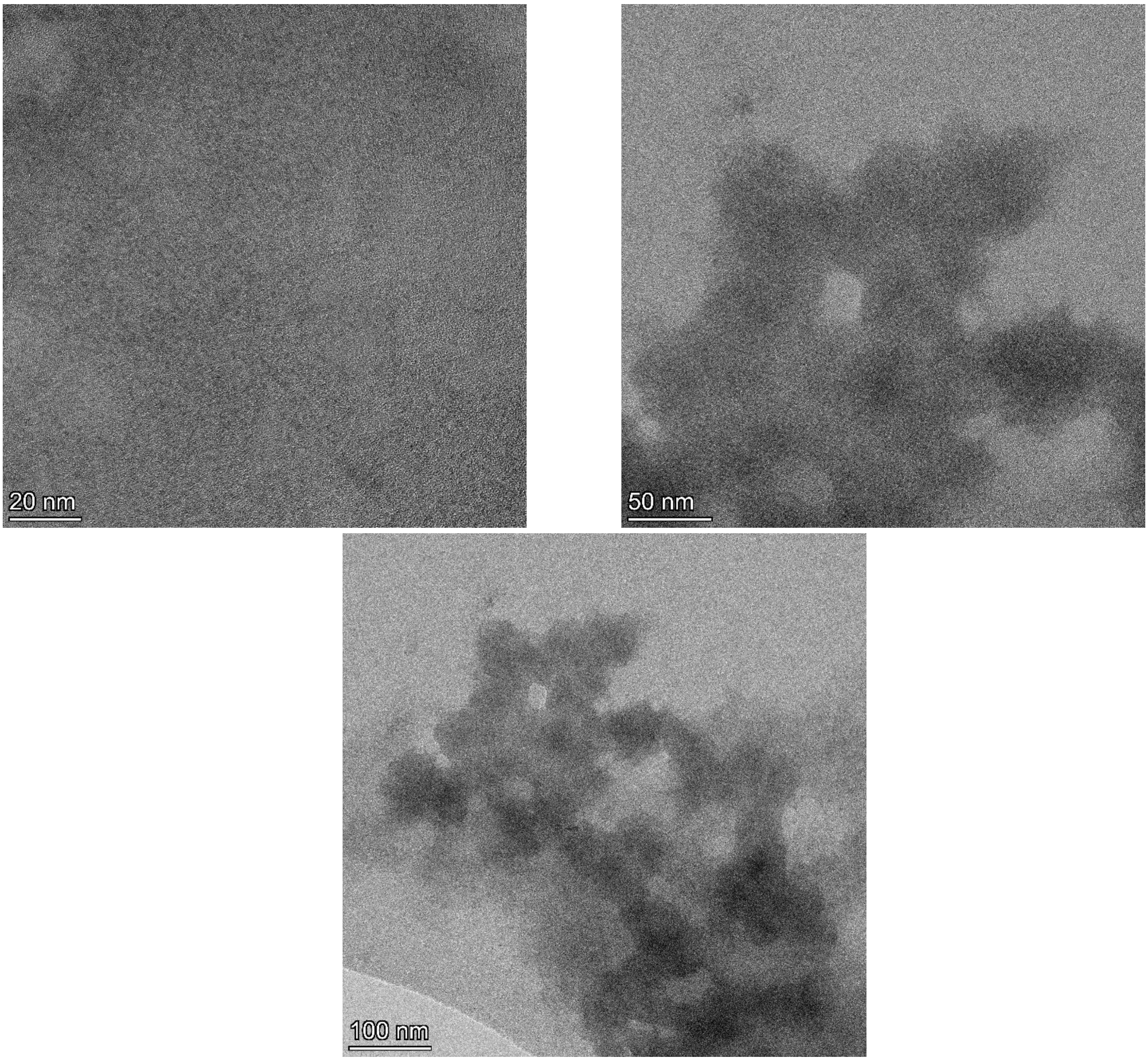
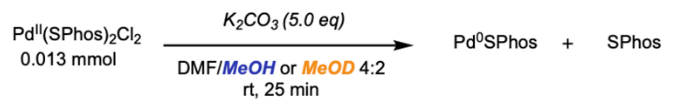


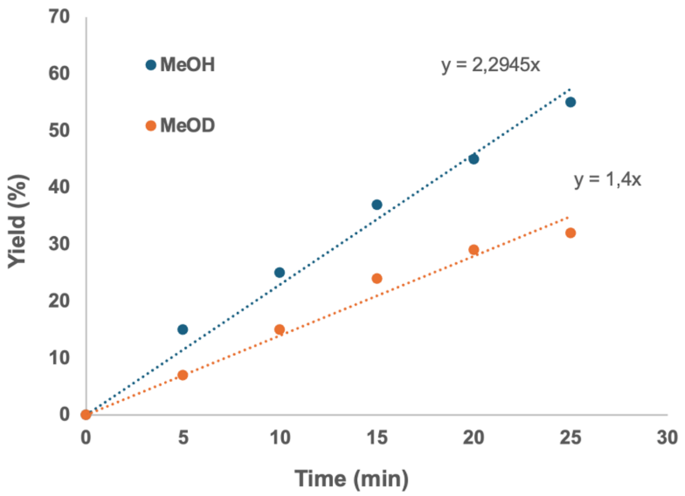
Figure S116. TEM images of $PdCl_2$(dppf) reduction with dppf (1 equiv) and TMG (5 equiv) in DMF at 60°C.

7. Kinetic Isotope Effect (KIE)

The reaction was performed in an 20 mL Schlenk purged under argon atmosphere. $Pd(ACN)_2Cl_2$ (39.37 mg, 0.152 mmol, 1 equiv), SPhos (128.80 mg, 0.304 mmol, 2 equiv) and Cs_2CO_3 (248 mg, 0.72 mmol, 5 equiv) were dissolved in 3.2 ml MeOH/D and 1.6 ml DMF-d_7. The reaction was let at room temperature and monitored by ^{31}P NMR spectroscopy at intervals of 5 minutes for 25 minutes. The triphenylphosphine oxide (0.5 equiv) was used as internal standard.

Chart S1. Kinetic isotope effect of Pd(SPhos)$_2$Cl$_2$ reduction in methanol





$$\text{KIE} = \frac{K_H}{K_D} = \frac{2.2945}{1.4} = 1.64$$

MeOH

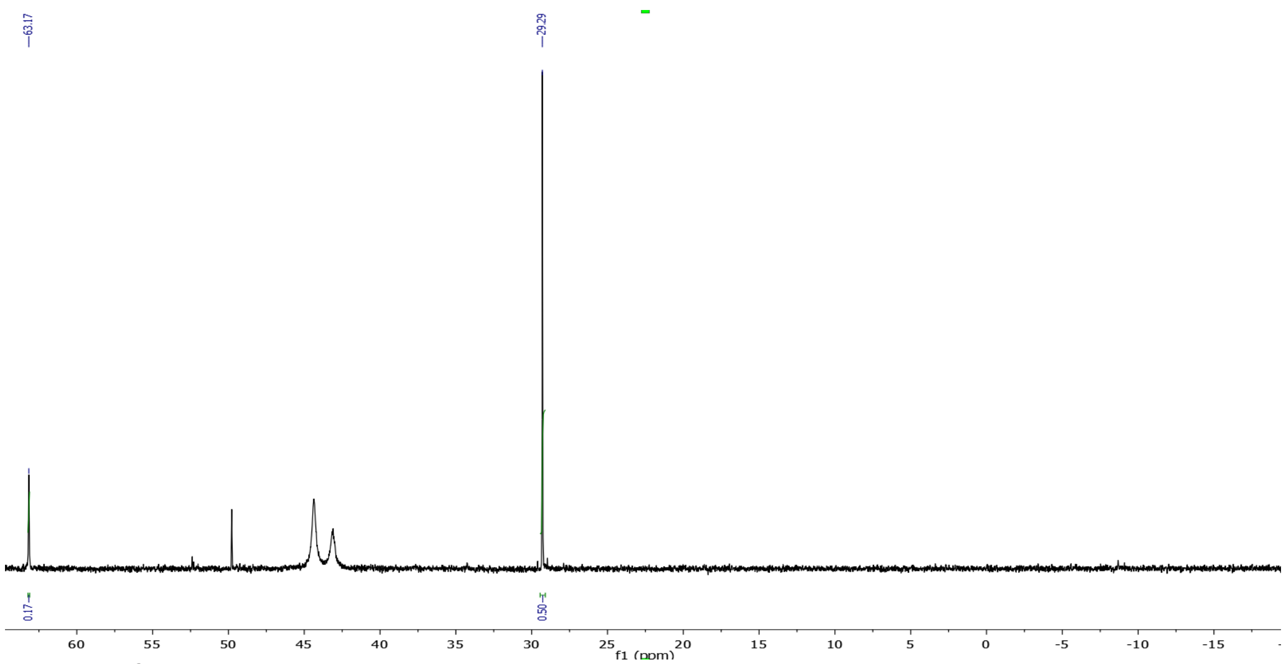


Figure S117. ^{31}P NMR spectrum of Pd(SPhos)$_2$Cl$_2$ in MeOH at rt after 5 min

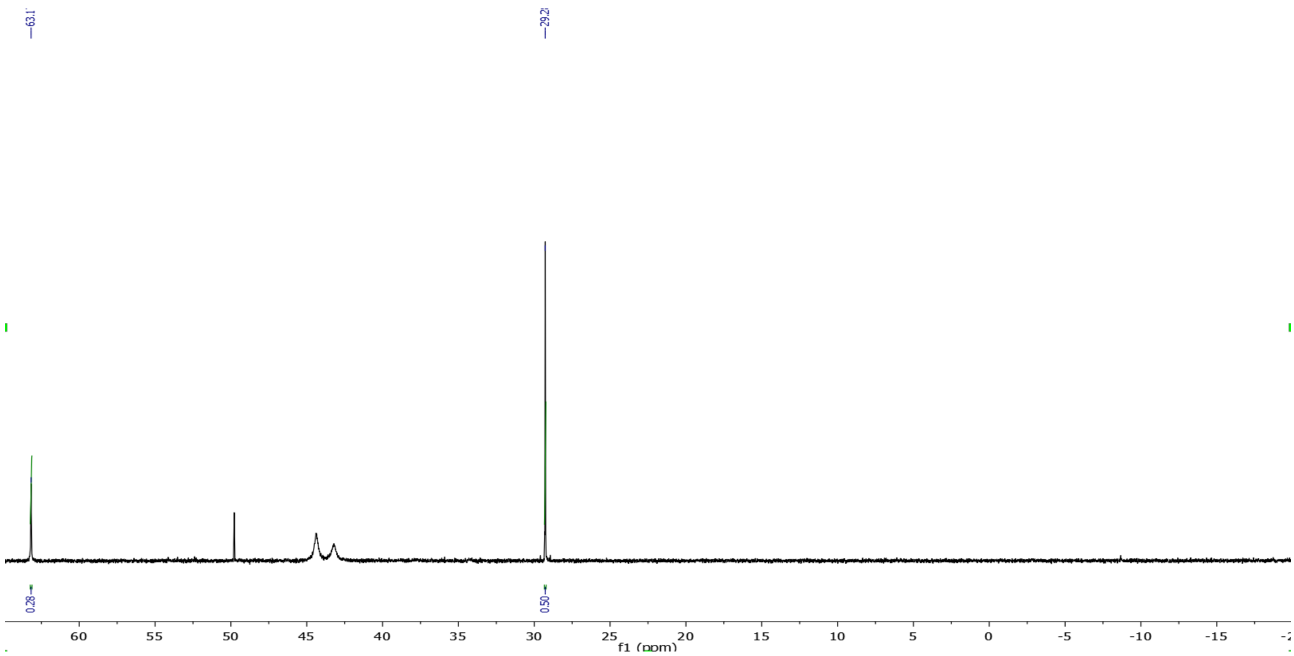


Figure S118. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOH at rt after 10 min

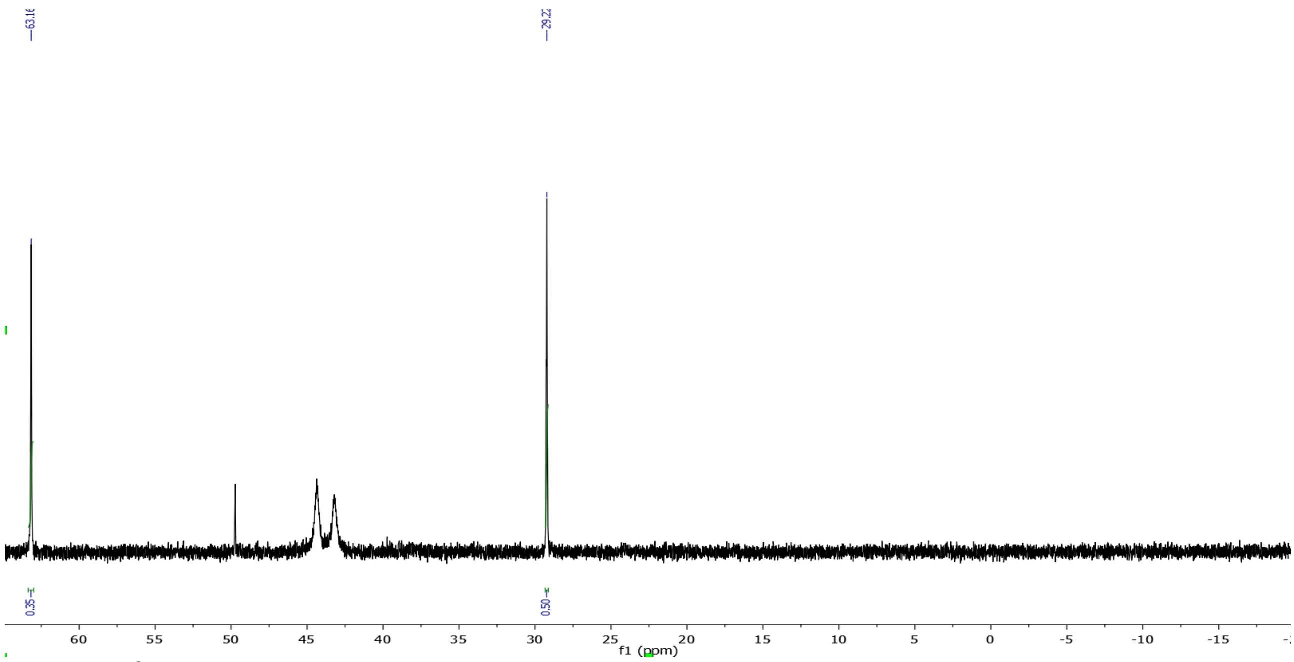


Figure S119. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOH at rt after 15 min

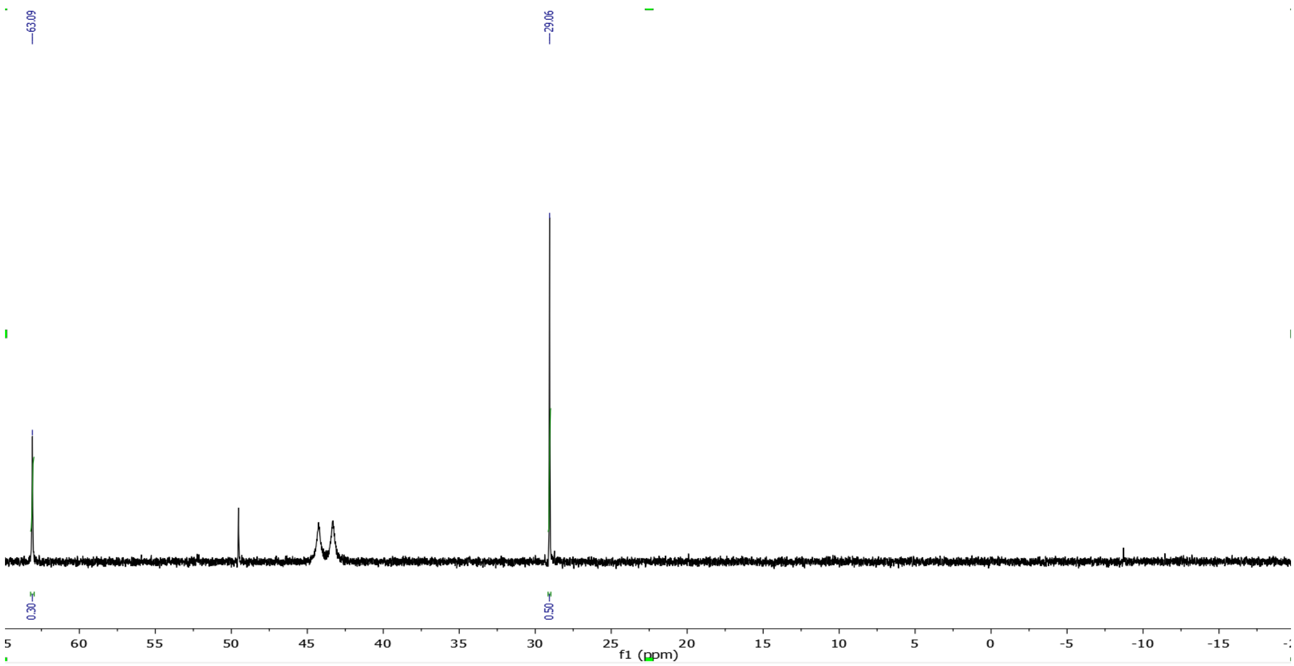


Figure S120. [31]P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOH at rt after 20 min

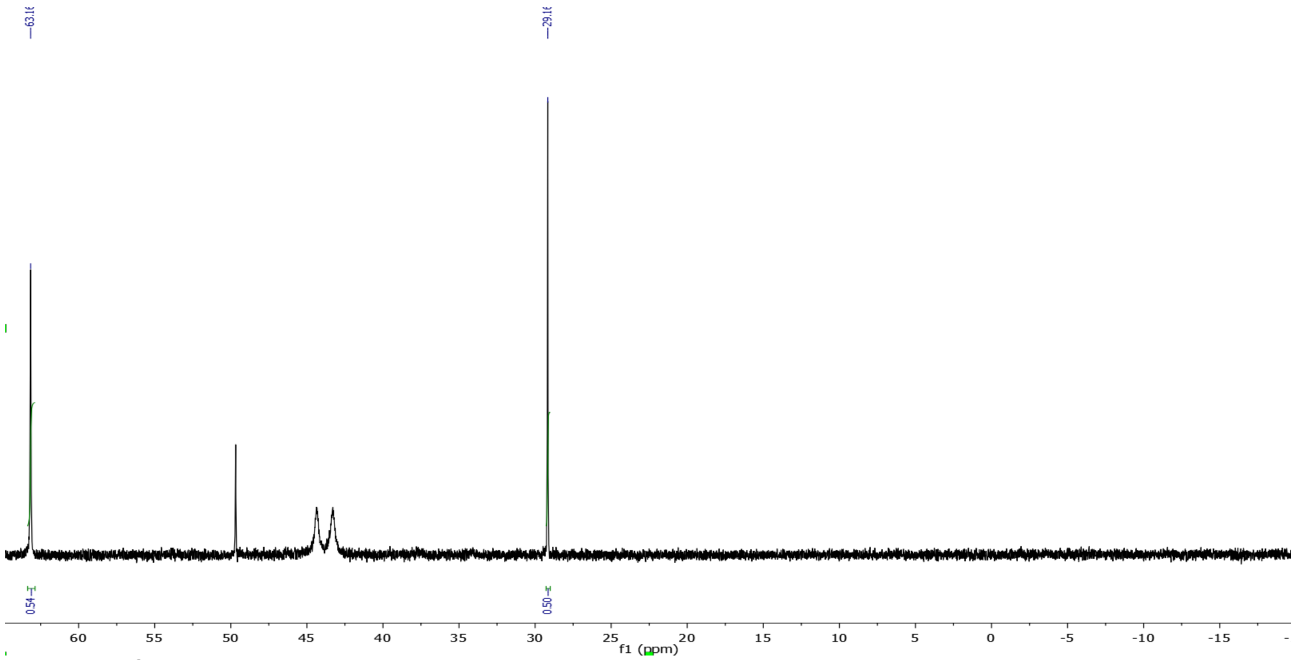


Figure S121. [31]P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOH at rt after 25 min

MeOD

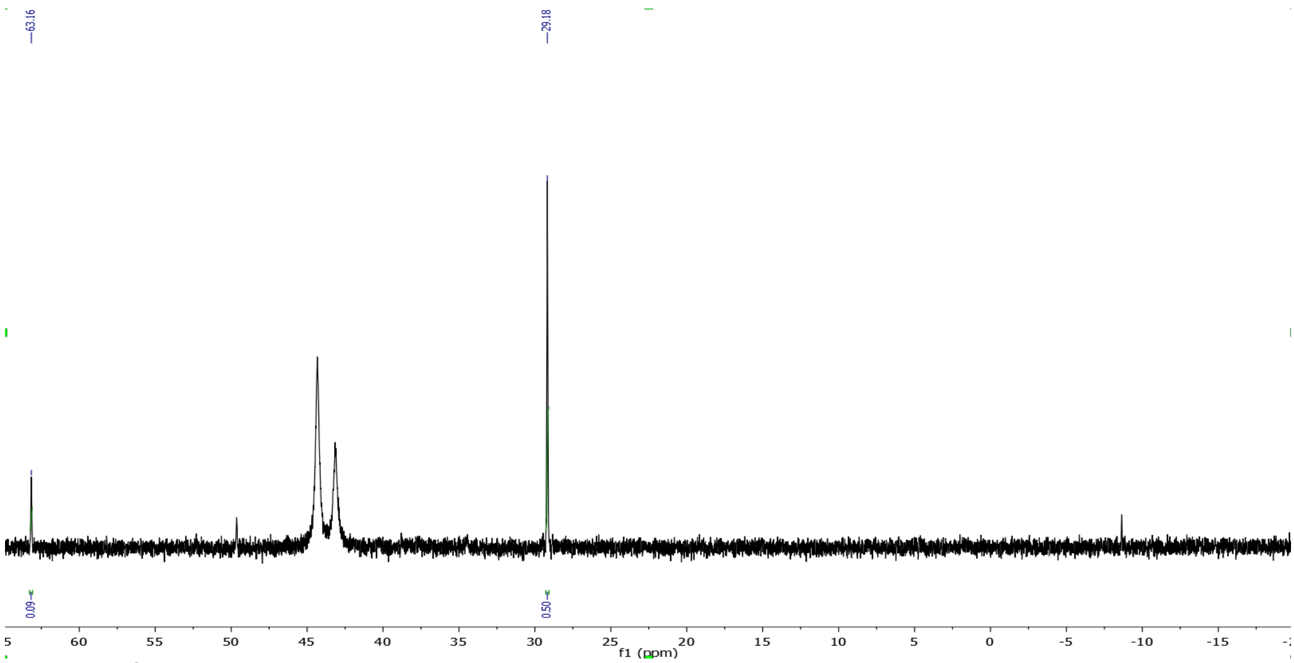


Figure S122. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOD at rt after 5 min

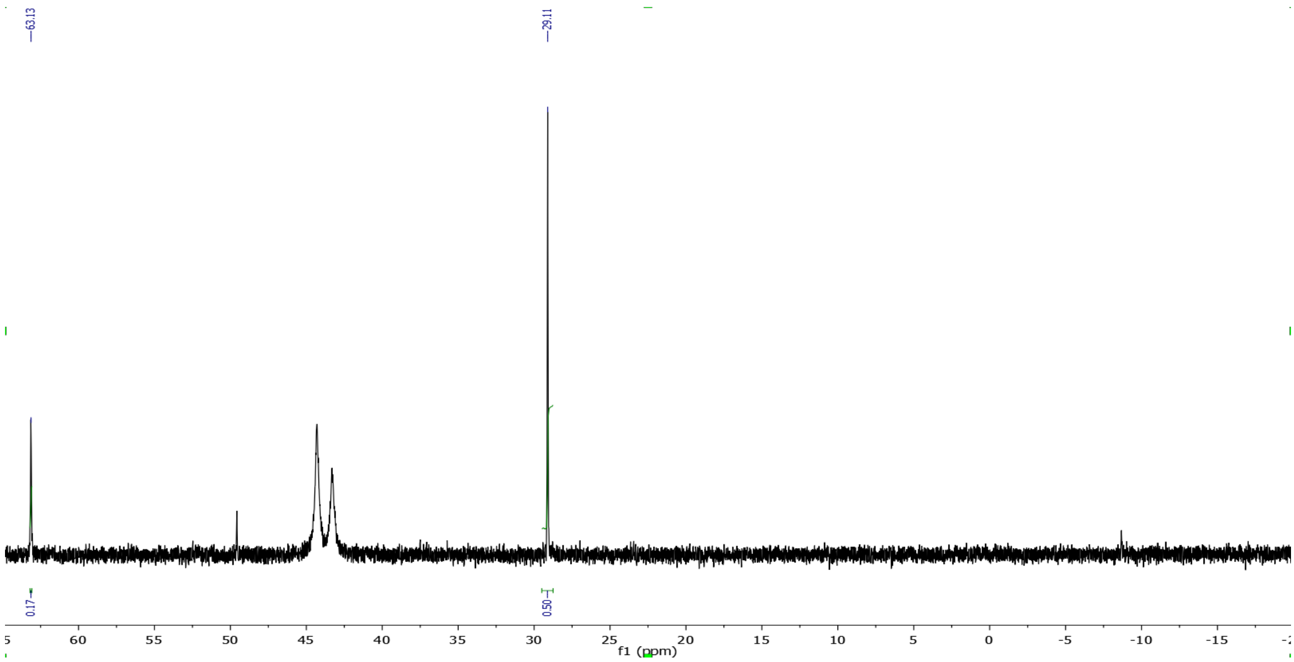


Figure S123. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOD at rt after 10 min

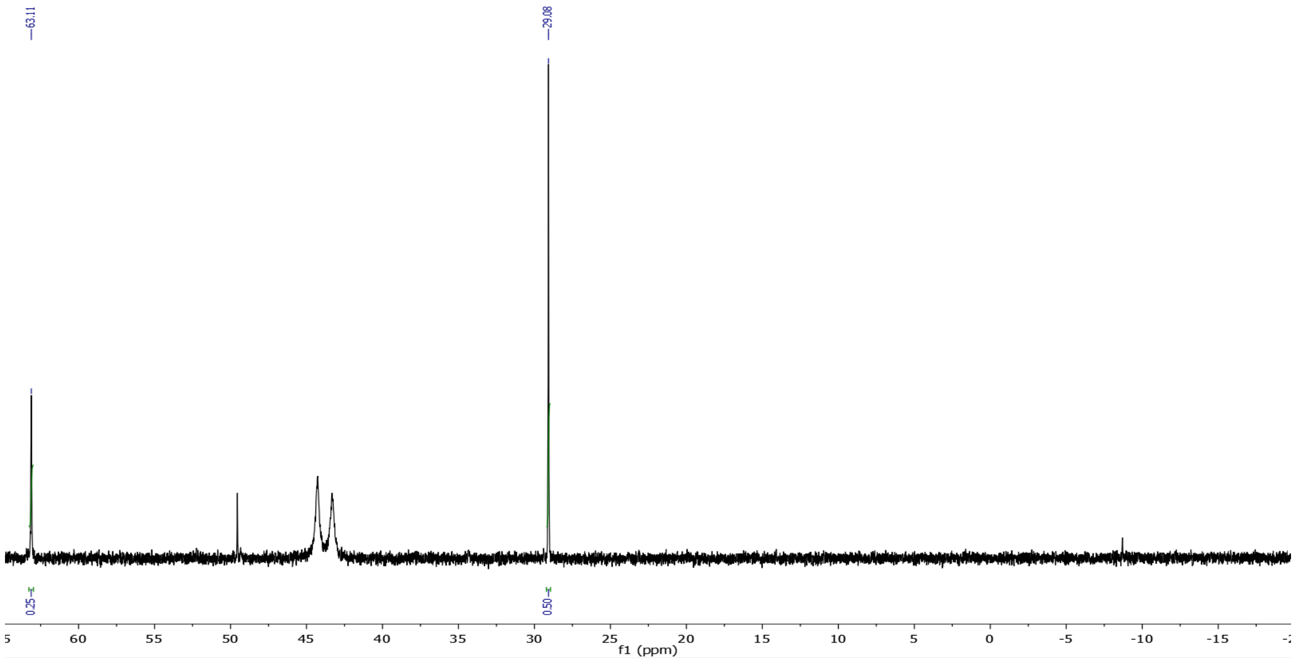


Figure S124. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOD at rt after 15 min

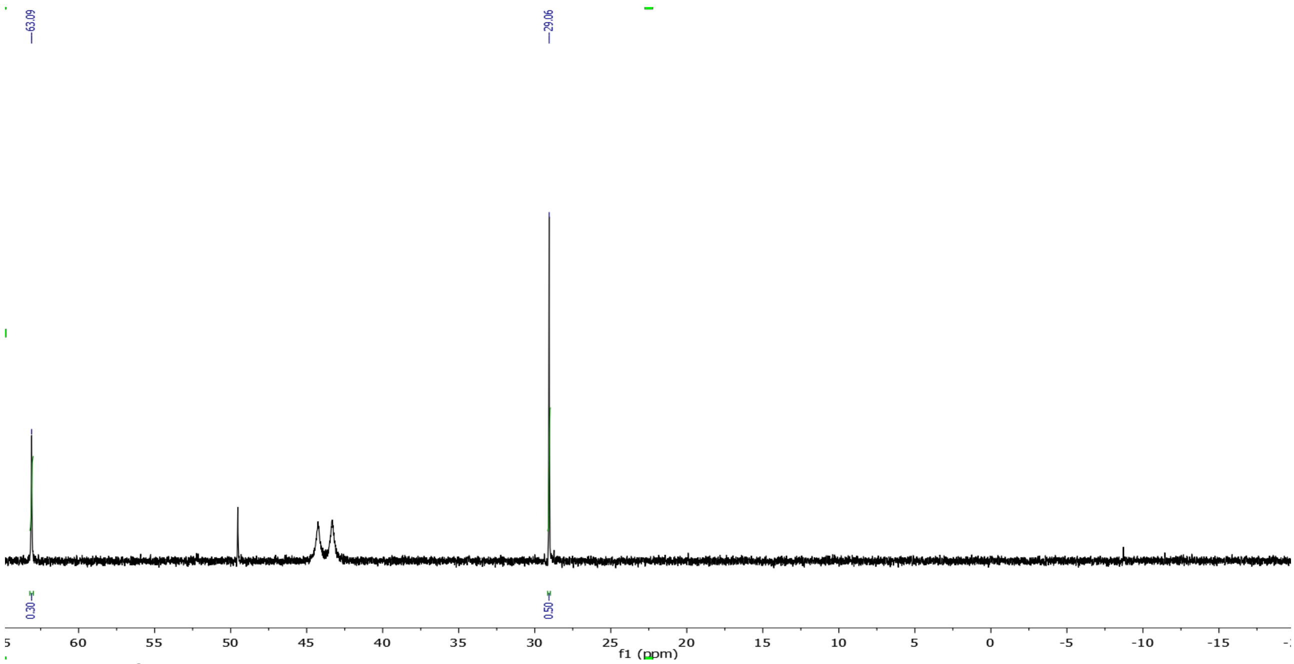


Figure S125. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOD at rt after 20 min

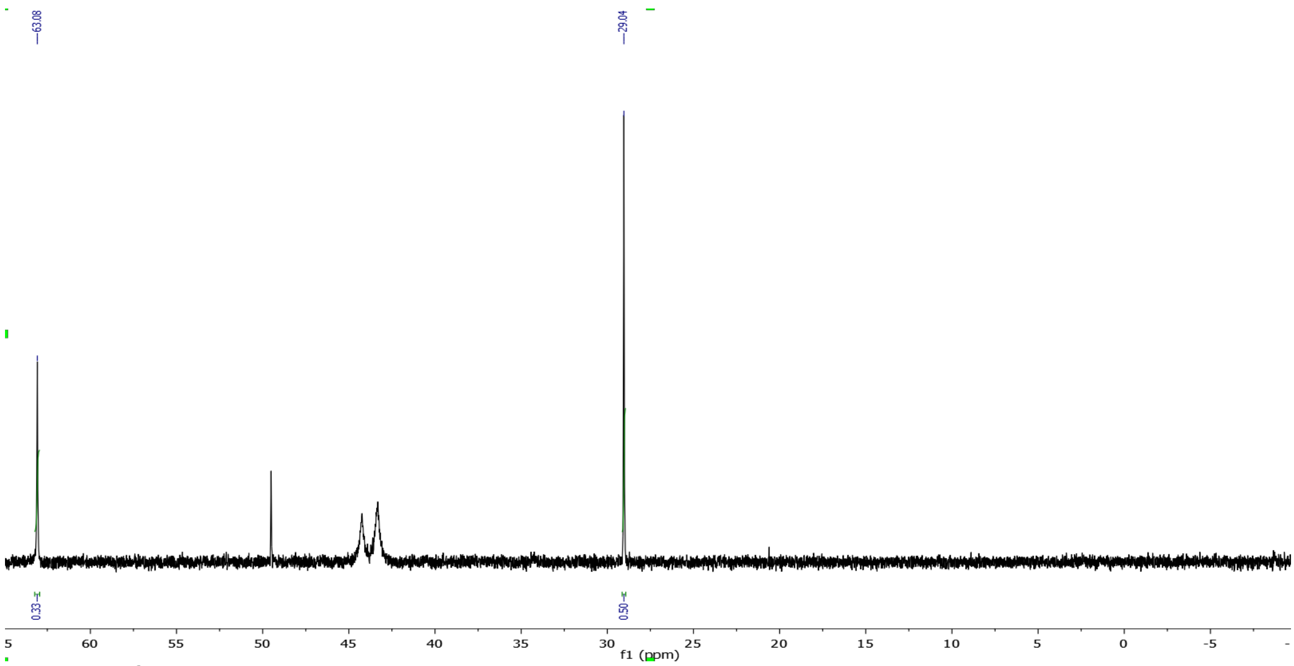
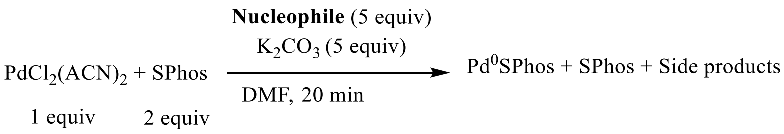


Figure S126. ^{31}P NMR spectrum of $Pd(SPhos)_2Cl_2$ in MeOD at rt after 25 min.

8. Pd reduction with different nucleophiles



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (3.4 mg, 0.013 mmol, 1 equiv), the ligand SPhos (10.7 mg, 0.026 mmol, 2 equiv) and K_2CO_3 (9.0 mg, 0.065 mmol, 5 equiv) were dissolved in degassed DMF (0.6 mL). The nucleophile (0.065 mmol, 5 equiv) of the selected reaction was then added. The reaction was stirred for 20 minutes at the desired temperature and analyzed by ^{31}P NMR analysis to evaluate the formation of the Pd^0 complex.

Table S16. Pd Reduction with nucluophiles in Mizoroky-Heck, Stille, Suzukt-Miyaura and Heck-Cassar-Sonogashira reactions

Entry	Reactant	T°C	Reaction	Pd(0)/Pd(II)
1	-	25	-	0/100
2	Styrene	25	MH	0/100
3	Styrene	60	MH	0/100
4	$PhSnBu_3$	25	Stille	0/100
5	$PhSnBu_3$	60	Stille	0/100
6	$PhB(OH)_2$	25	SM	0/100
7	$PhB(OH)_2$	60	SM	100/0
8	PhC≡CH	25	HCS	0/100
9	PhC≡CH	60	HCS	100/0

Entry 1, Table S16:

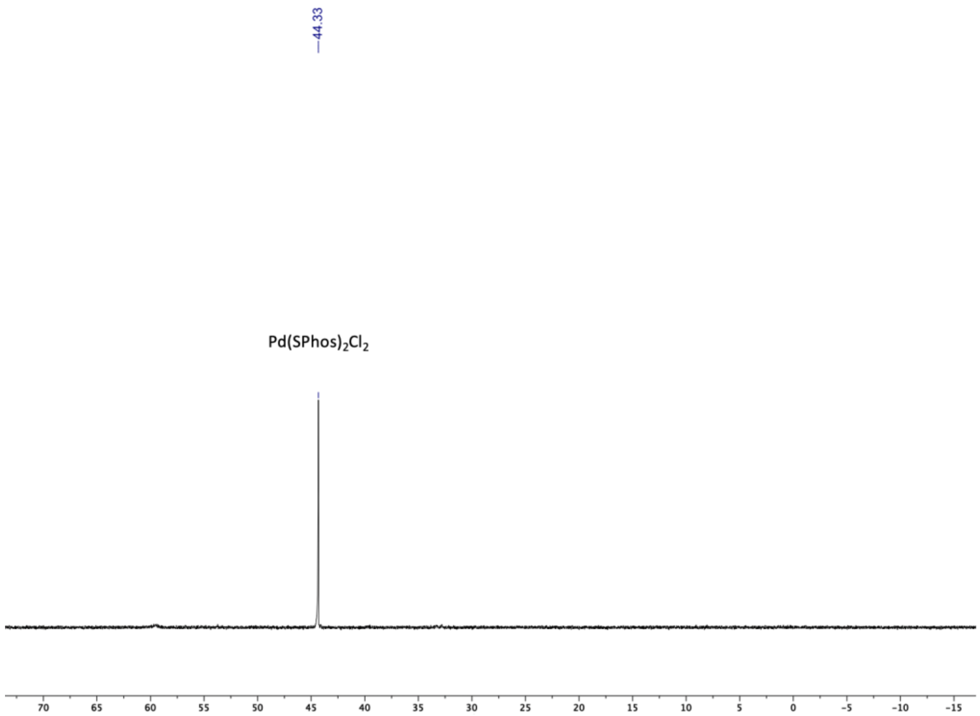


Figure S127. $PdCl_2(ACN)_2$ and SPhos in DMF-d_7 at rt in 20 min

Entry 2, Table S16:

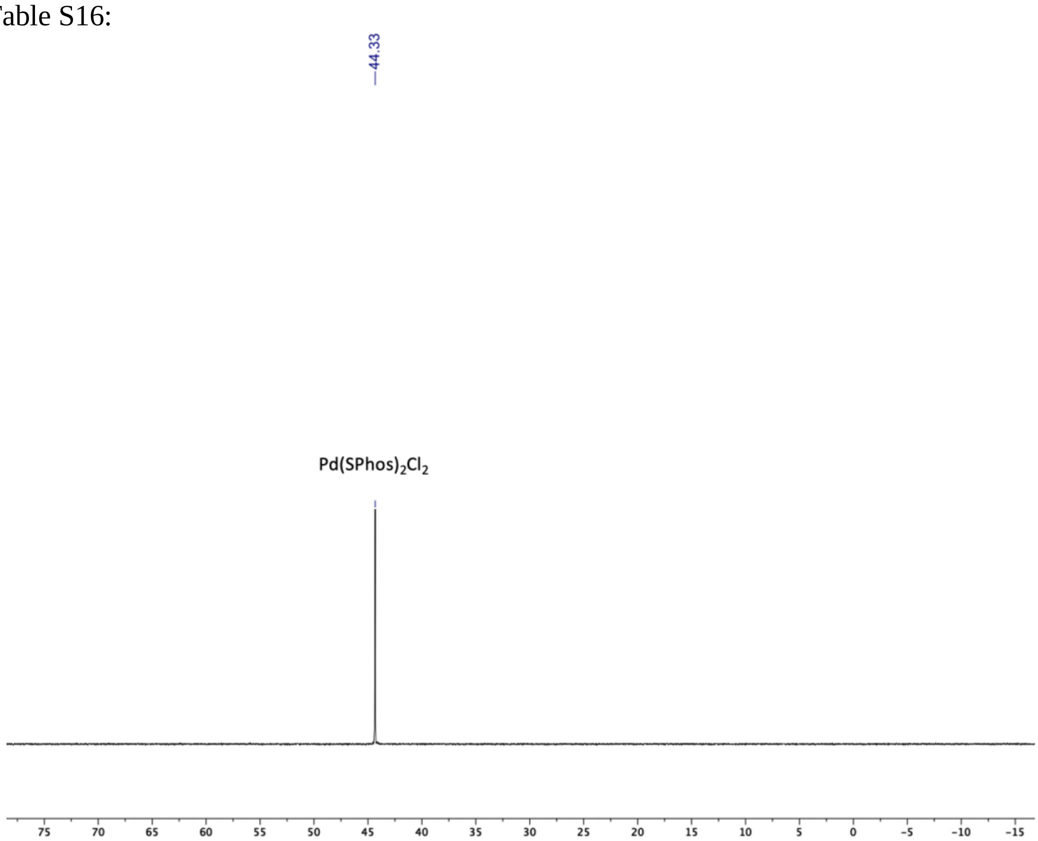


Figure S128. $PdCl_2(ACN)_2$, SPhos and styrene in DMF-d_7 at rt in 20 min

Entry 3, Table S16:

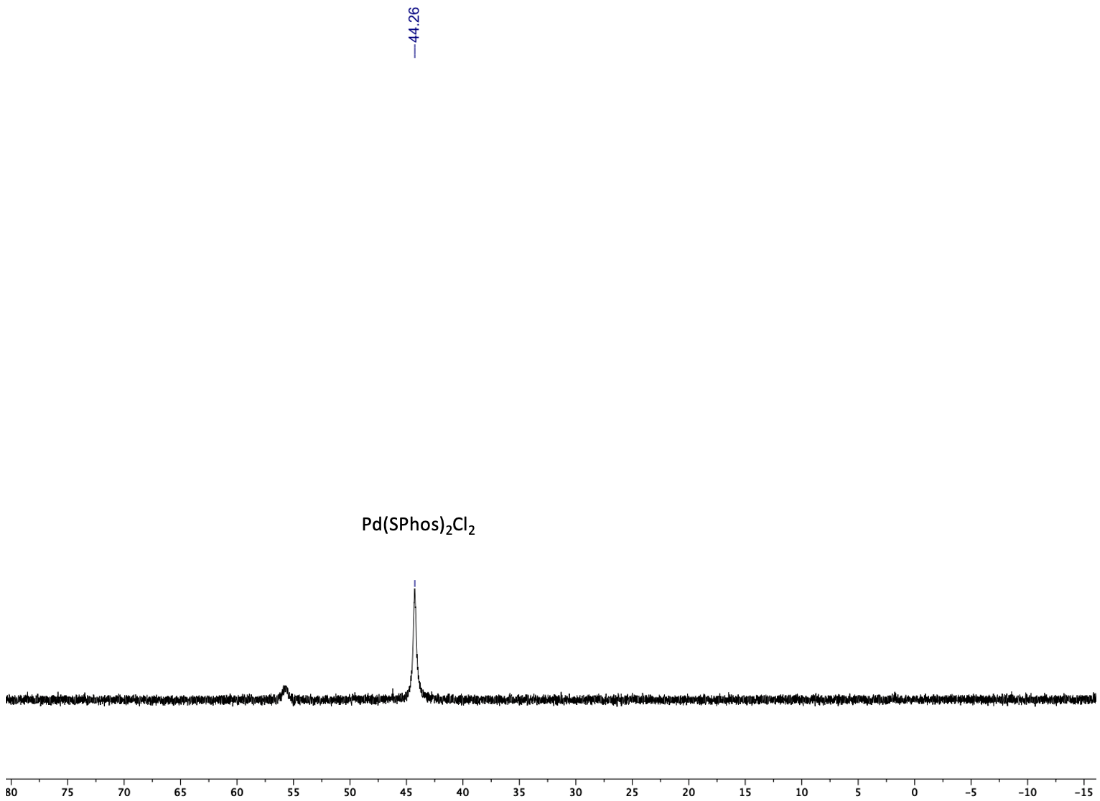


Figure S129. $PdCl_2(ACN)_2$, SPhos and styrene in DMF-d_7 at 60°C in 20 min

Entry 4, Table S16:

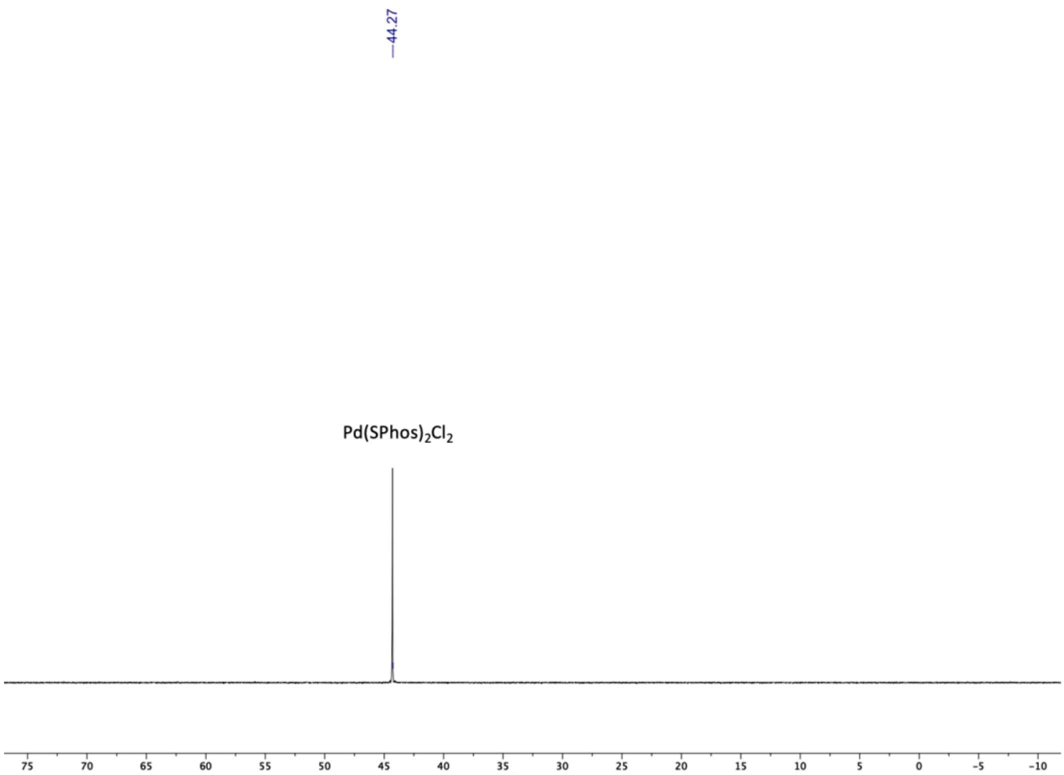


Figure S130. $PdCl_2(ACN)_2$, SPhos and $PhSnBu_3$ in DMF-d_7 at rt in 20 min

Entry 5, Table S16

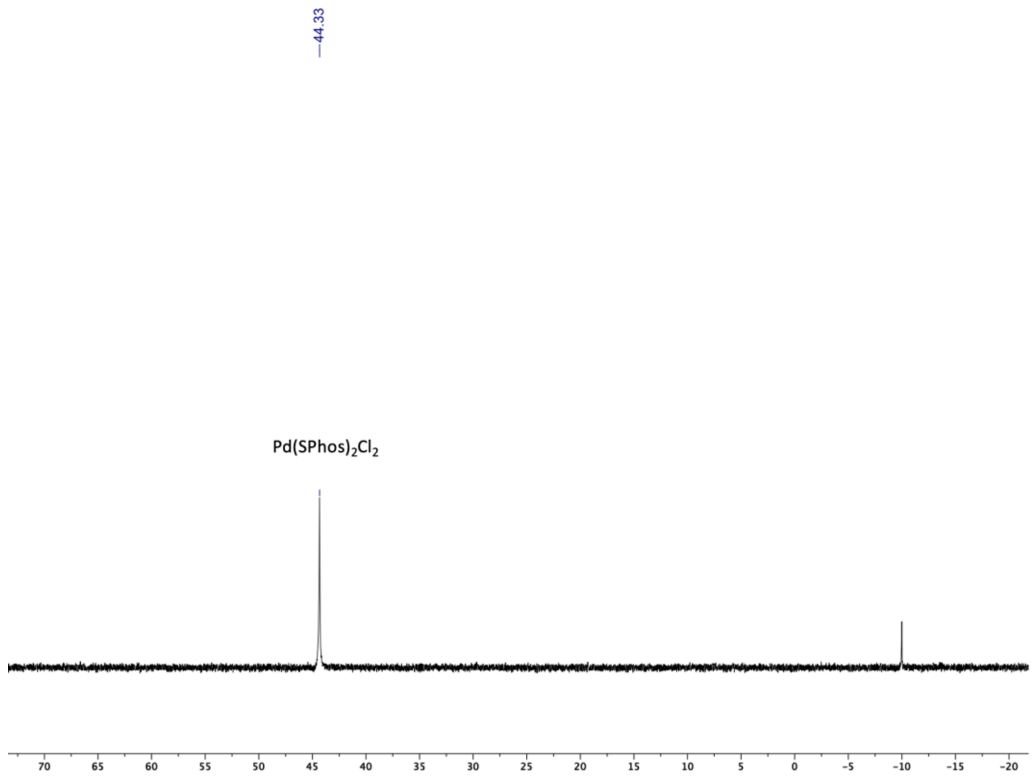


Figure S131. $PdCl_2(ACN)_2$, SPhos and $PhSnBu_3$ in DMF-d_7 at 60°C in 20 min

Entry 6, Table S16:

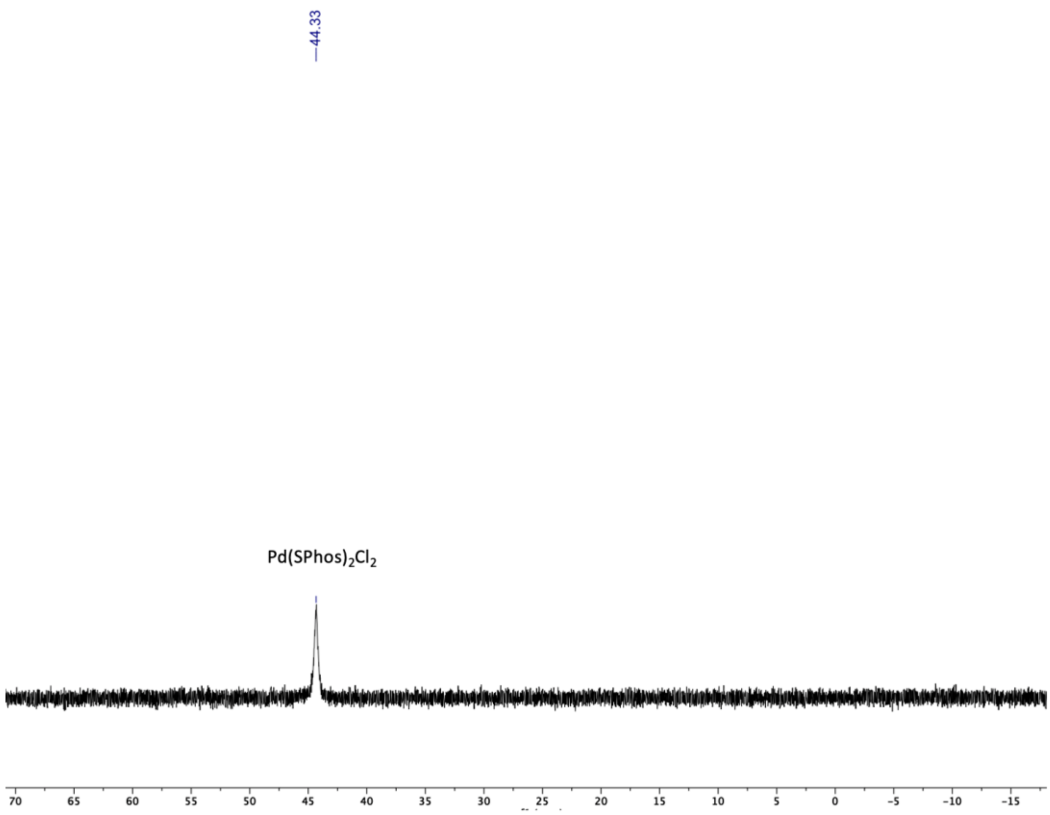


Figure S132. $PdCl_2(ACN)_2$, SPhos and $PhB(OH)_2$ in DMF-d_7 at rt in 20 min

Entry 7, Table S16:

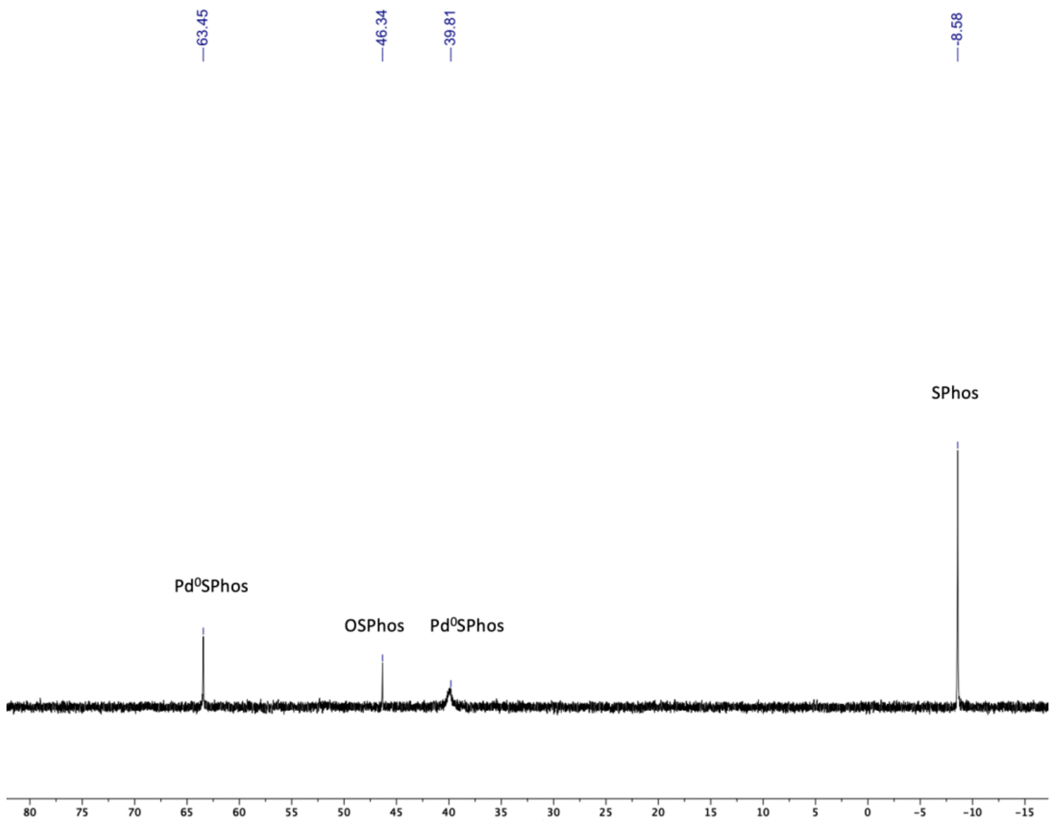


Figure S133. $PdCl_2(ACN)_2$, SPhos and $PhB(OH)_2$ in DMF-d_7 at 60°C in 20 min

Entry 8, Table S16:

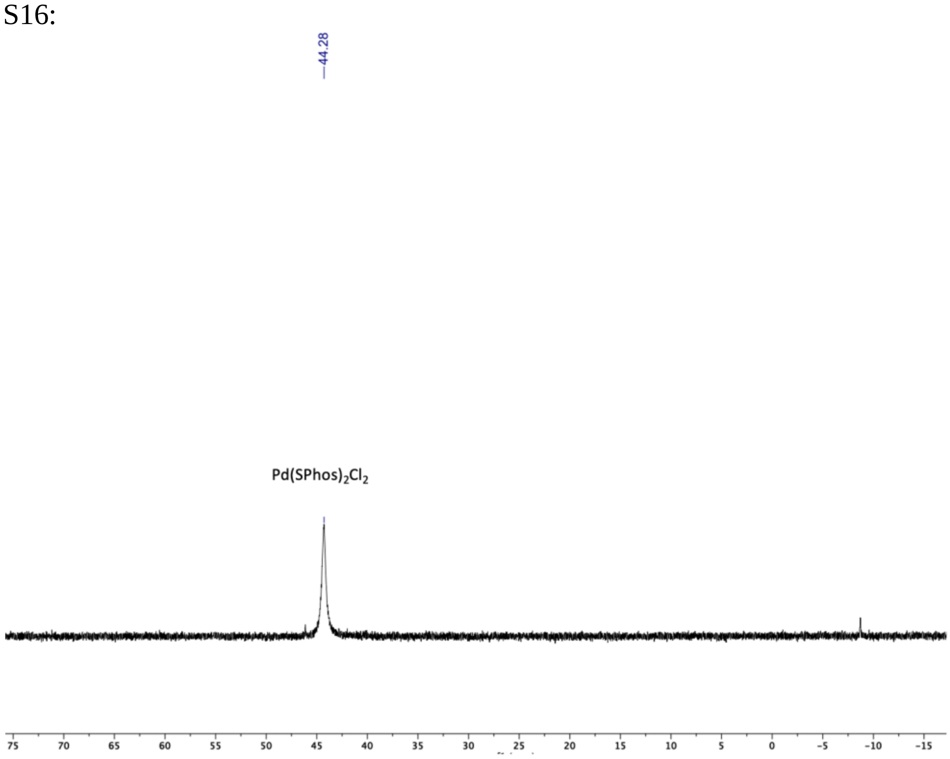


Figure S134. $PdCl_2(ACN)_2$, SPhos and PhC≡CH in DMF-d_7 at rt in 20 min

Entry 9, Table S16

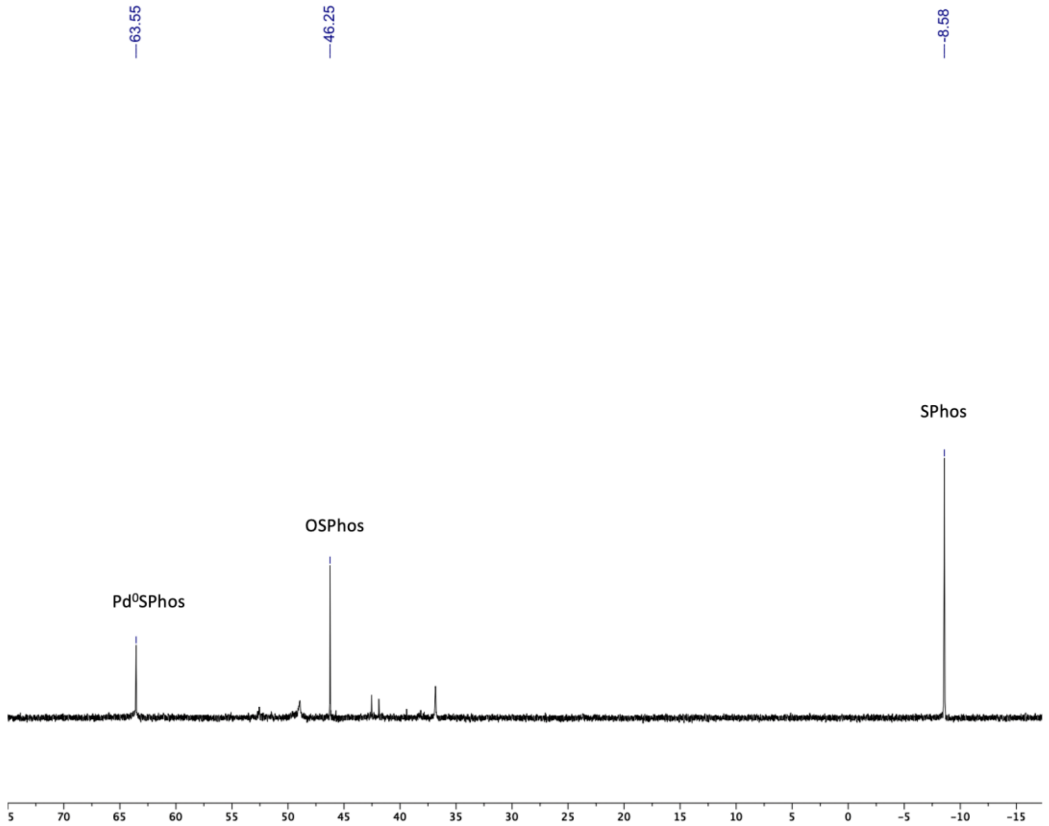
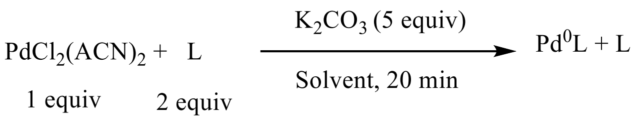


Figure S135. $PdCl_2(ACN)_2$, SPhos and PhC≡CH in DMF-d_7 at 60°C in 20 min

9. Pd reduction with different ligands and solvents



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (3.4 mg, 0.013 mmol, 1 equiv), the selected ligand (0.026 mmol, 2 equiv) and K_2CO_3 (9.0 mg, 0.065 mmol, 5 equiv) were dissolved in the degassed solvent mixture (0.6 mL). The reaction was stirred for 20 minutes at 60°C and analyzed by ^{31}P NMR analysis. To calculate the conversion of the uncompleted reduction, triphenylphosphine oxide (0.0065 mmol, 0.5 equiv) was added as internal standard (IS).

Table S17. $PdCl_2(SPhos)_2$ reduction in green solvent with different ligands

Entry	Ligand	Base	Solvent	Pd(0)/Pd(II)
1	SPhos	K_2CO_3	Anisole/EtOH 4/2	100/0
2	SPhos	K_2CO_3	CPME/EtOH 4/2	100/0
3	SPhos	K_2CO_3	MeTHF/EtOH 4/2	100/0
4	SPhos	K_2CO_3	Anisole/MeOH 4/2	100/0
5	SPhos	K_2CO_3	Anisole/HEP 4/2	100/0
6	RuPhos	K_2CO_3	Anisole/EtOH 4/2	100/0
7	XPhos	K_2CO_3	Toluene/EtOH 4/2	100/0
8	SPhos	PYR	Anisole/EtOH 4/2	25/0
9	SPhos	TMG	Anisole/EtOH 4/2	28/0
10	sSPhos	K_2CO_3	HEP/H_2O 8/2	100/0
11	sSPhos	K_2CO_3	EtOH/H_2O 8/2	100/0
12	sSPhos	PYR	EtOH/H_2O 8/2	52/0
13	sSPhos	K_2CO_3	IPA/H_2O 8/2	0/100

Entry 1, Table S17:

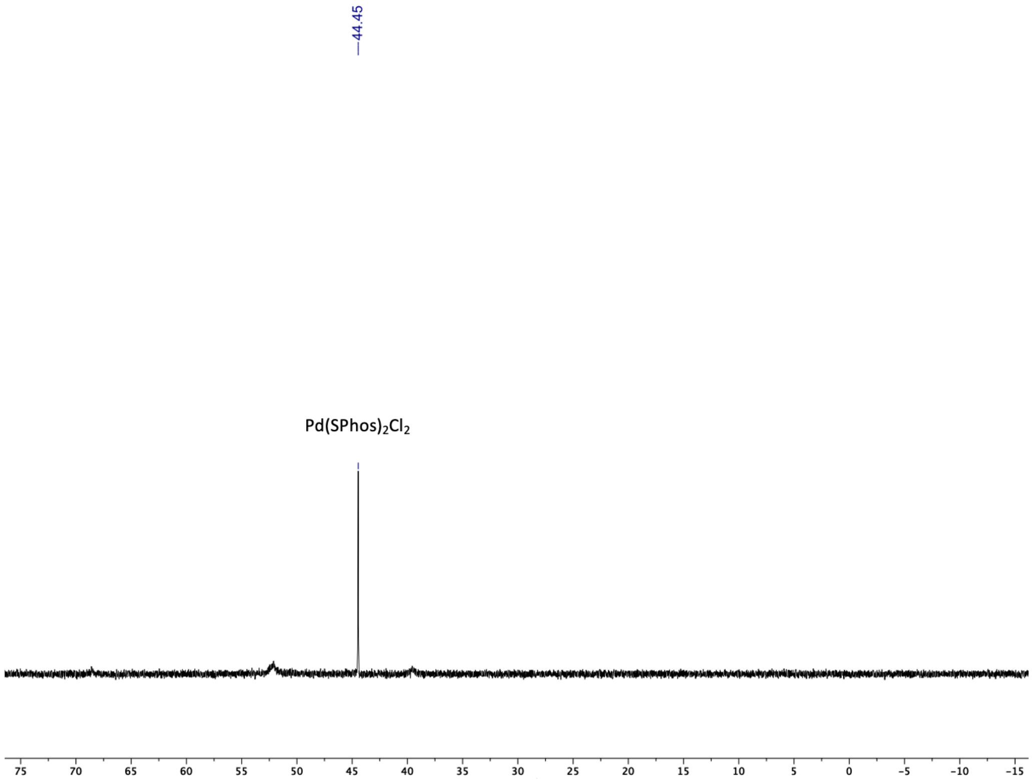


Figure S136. $PdCl_2(ACN)_2$ and SPhos exchange in Anisole/EtOH 4/2

Entry 1, Table S17:

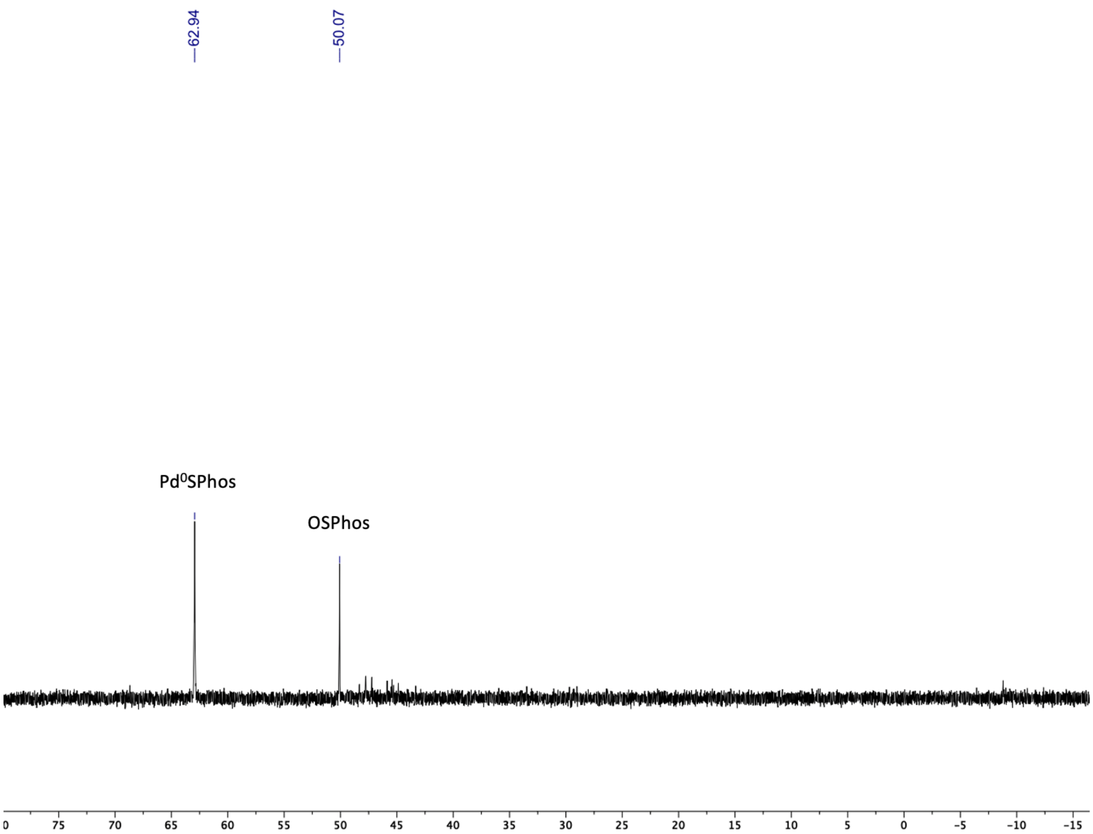


Figure S137. $PdCl_2(ACN)_2$ and SPhos in Anisole/EtOH 4/2 at 60°C in 20 min

Entry 2, Table S17:

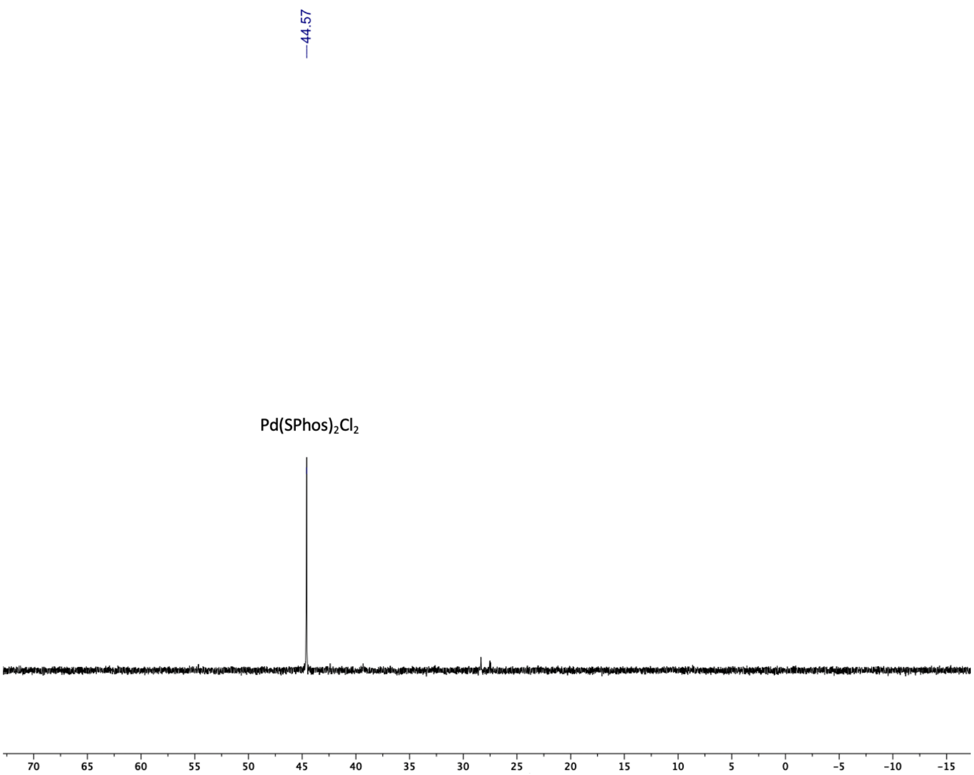


Figure S138. $PdCl_2(ACN)_2$ and SPhos exchange in CPME/EtOH 4/2

Entry 2, Table S17:

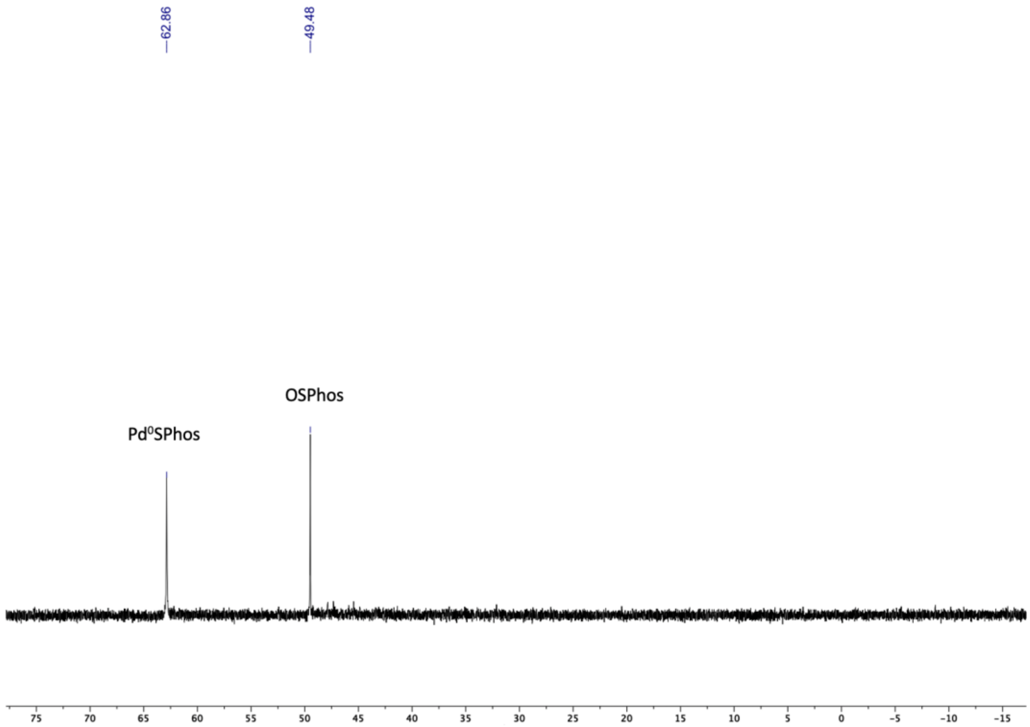


Figure S139. $PdCl_2(ACN)_2$ and SPhos in CPME/EtOH 4/2 at 60°C in 20 min

Entry 3, Table S17:

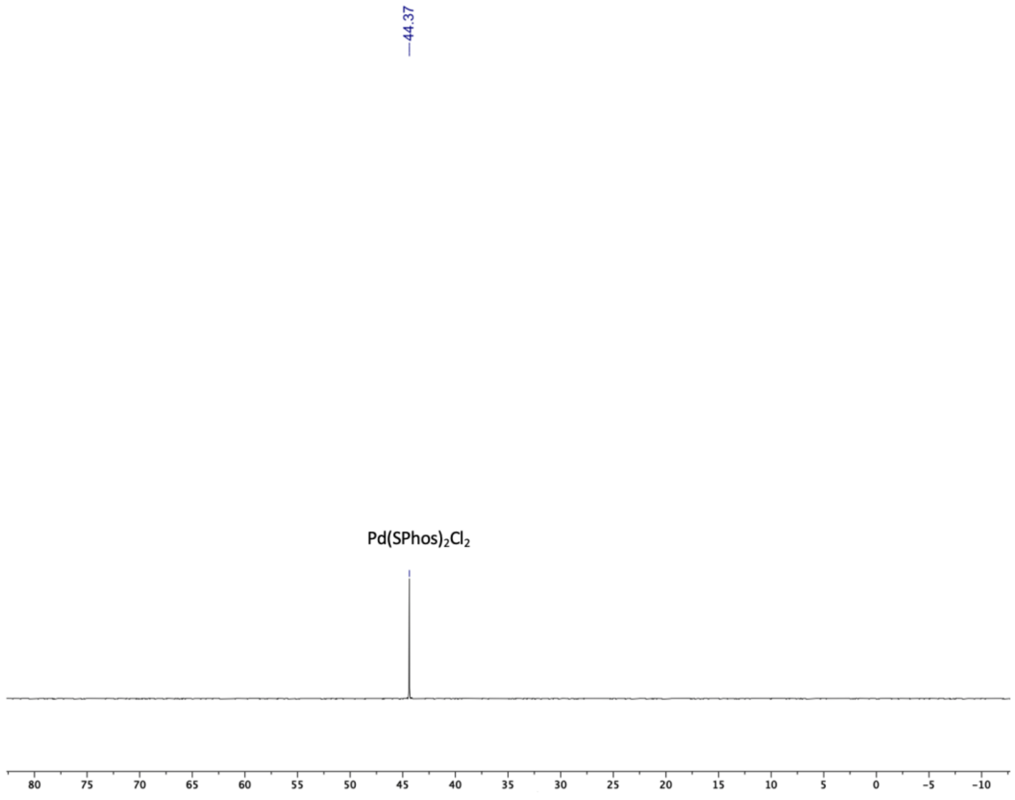


Figure S140. $PdCl_2(ACN)_2$ and SPhos exchange in MeTHF/EtOH 4/2

Entry 3, Table S17:

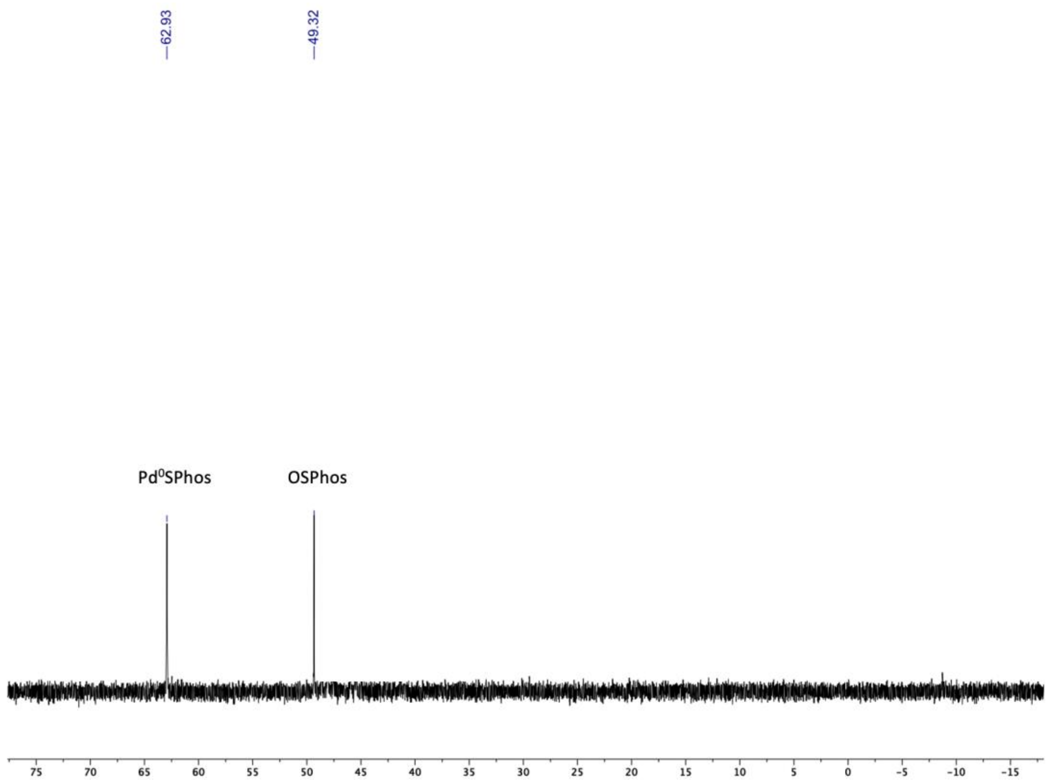


Figure S141. $PdCl_2(ACN)_2$ and SPhos in MeTHF/EtOH 4/2 at 60°C in 20 min

Entry 4, Table S17:

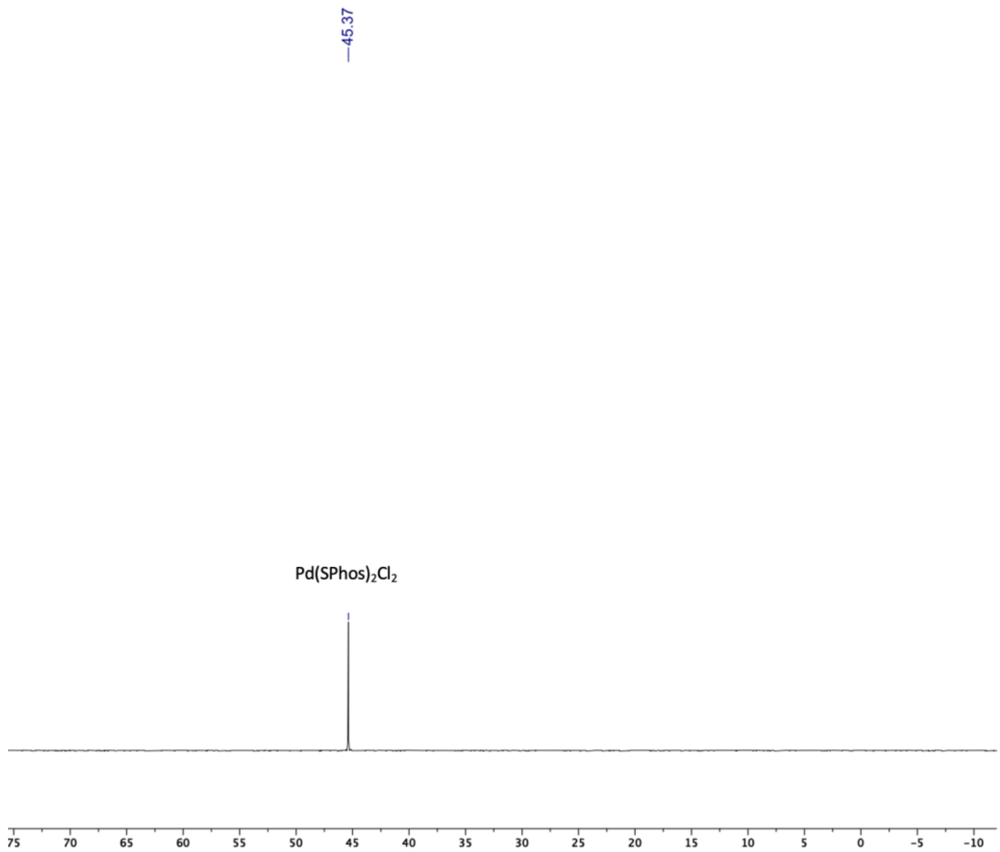


Figure S142. $PdCl_2(ACN)_2$ and SPhos exchange in Anisole/MeOH 4/2 at 60°C

Entry 4, Table S17:

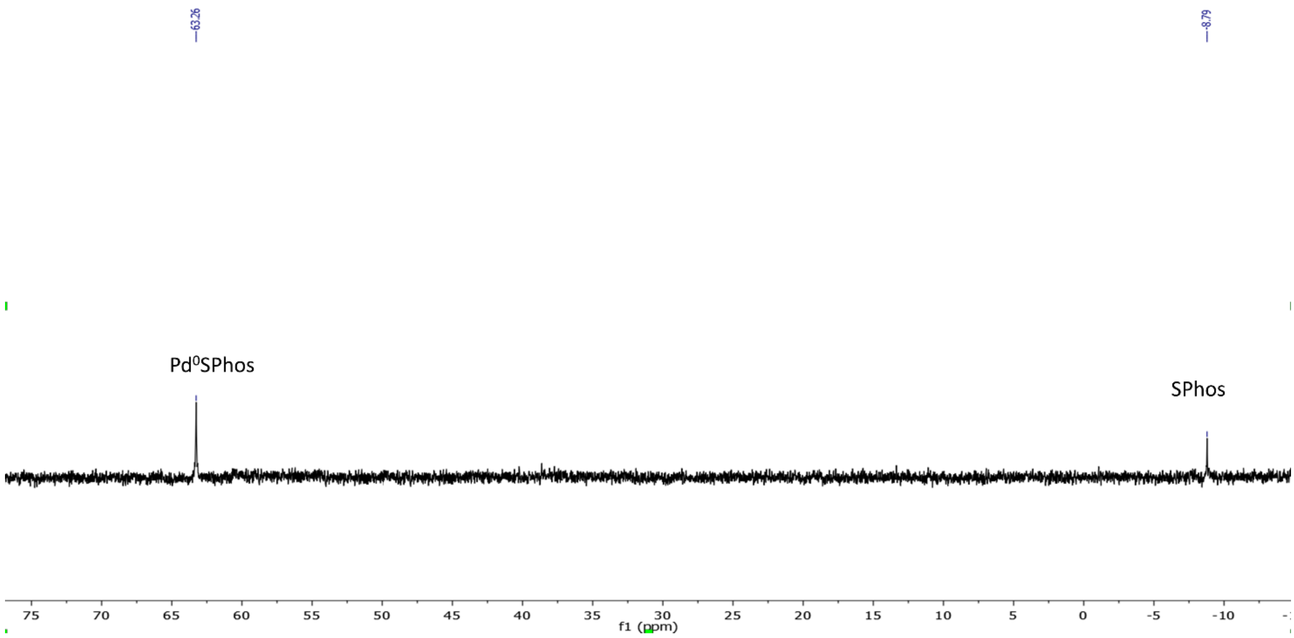


Figure S143. $PdCl_2(ACN)_2$ and SPhos in Anisole/MeOH 4/2 at 60°C in 20 min

Entry 5, Table S17:

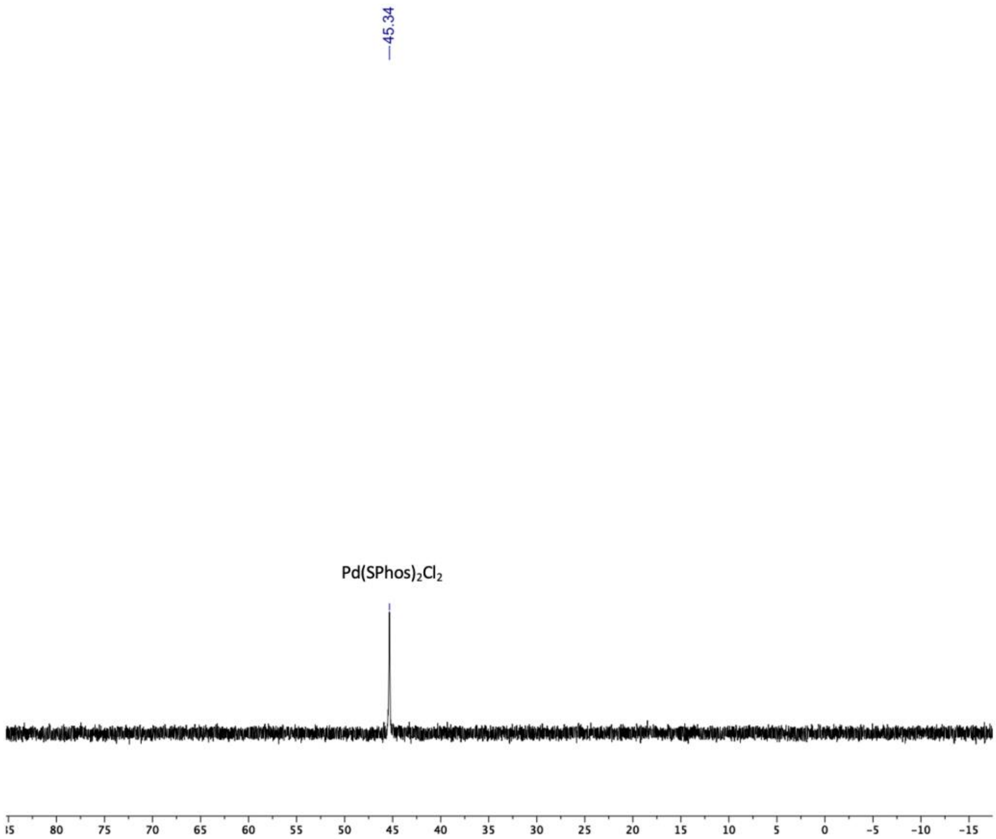


Figure S144. $PdCl_2(ACN)_2$ and SPhos exchange in Anisole/HEP 4/2

Entry 5, Table S17:

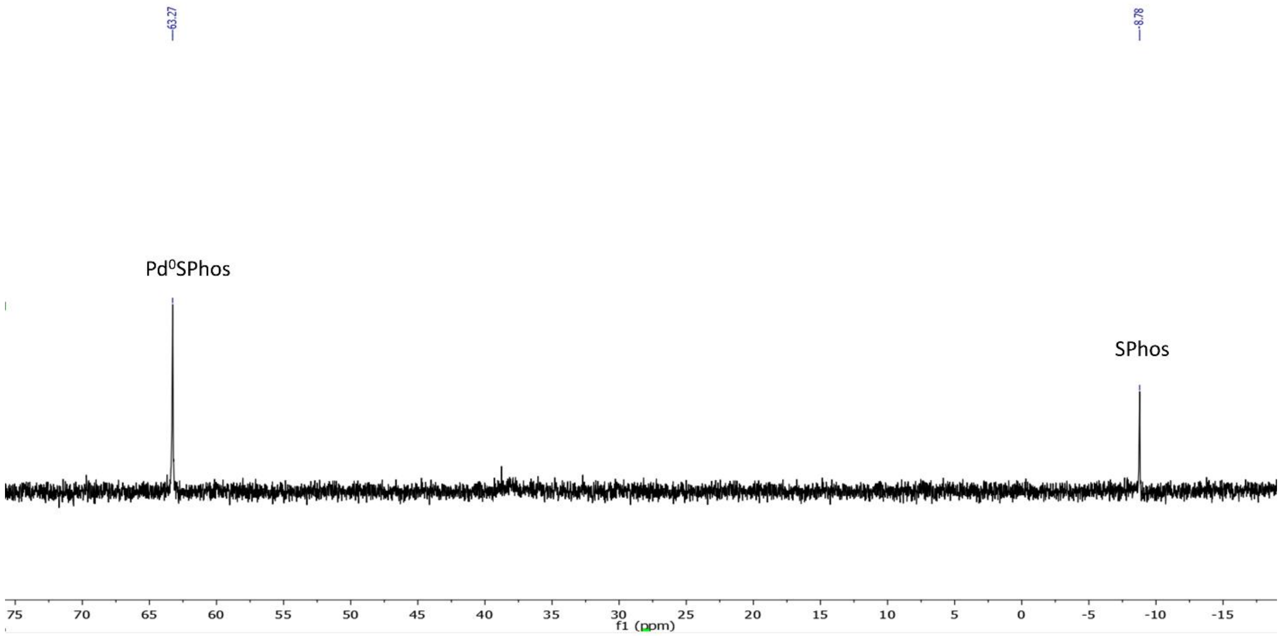


Figure S145. $PdCl_2(ACN)_2$ and SPhos in Anisole/HEP 4/2 at 60°C in 20 min

Entry 6, Table S17:

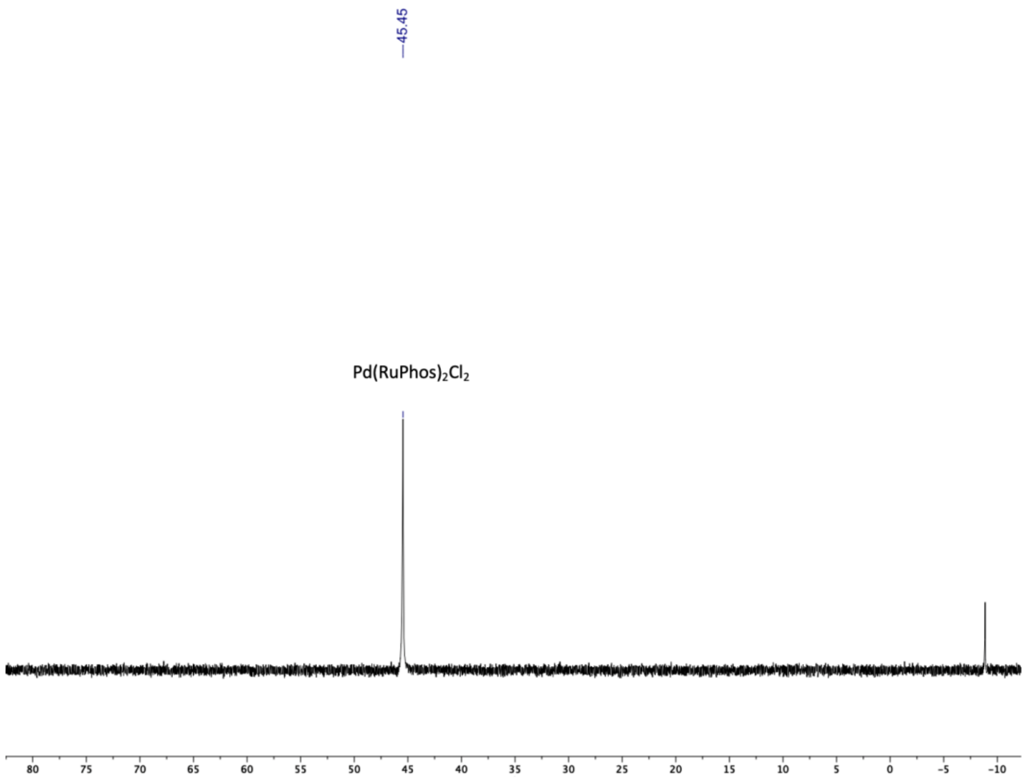


Figure S146. $PdCl_2(ACN)_2$ and RuPhos exchange in Anisole/EtOH 4/2

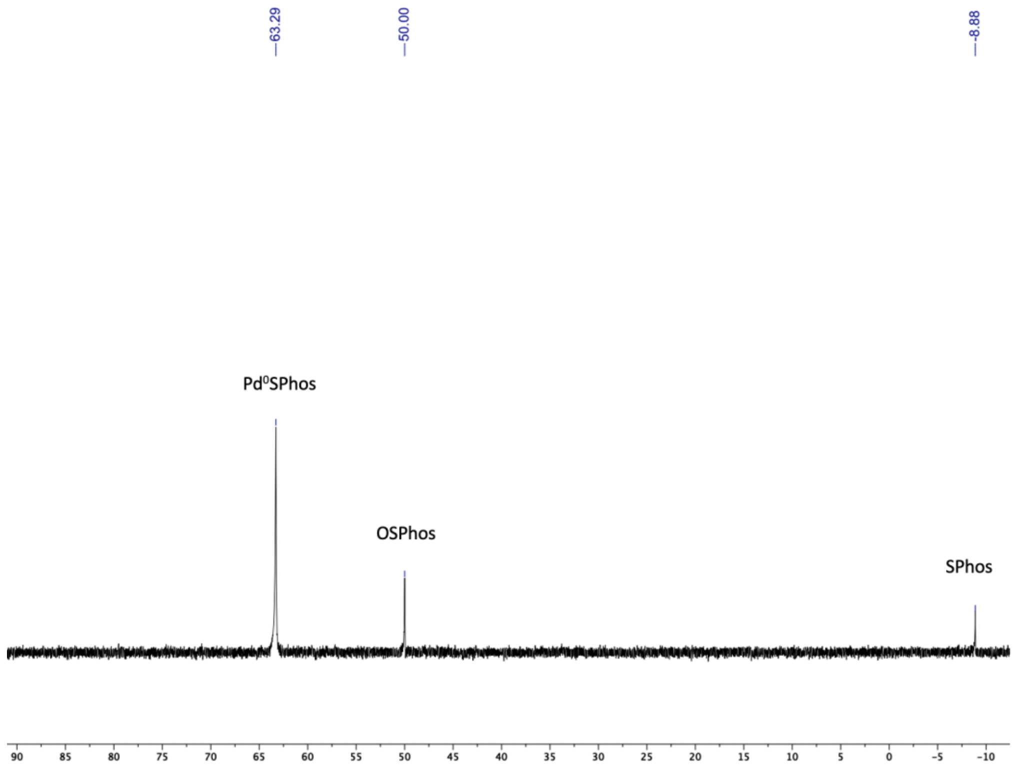


Figure S147. $PdCl_2(ACN)_2$ and RuPhos in Anisole/EtOH 4/2 at 60°C in 20 min

Entry 7, Table S17:

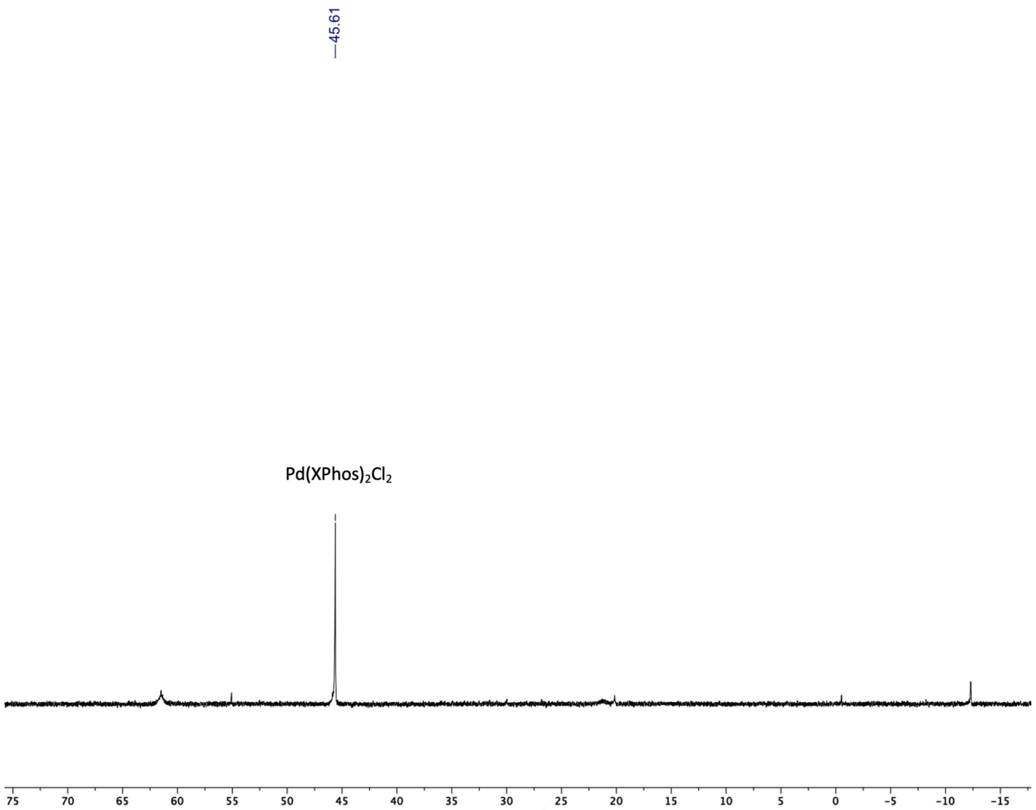


Figure S148. $PdCl_2(ACN)_2$ and XPhos exchange in Anisole/HEP 4/2

Entry 7, Table S17:

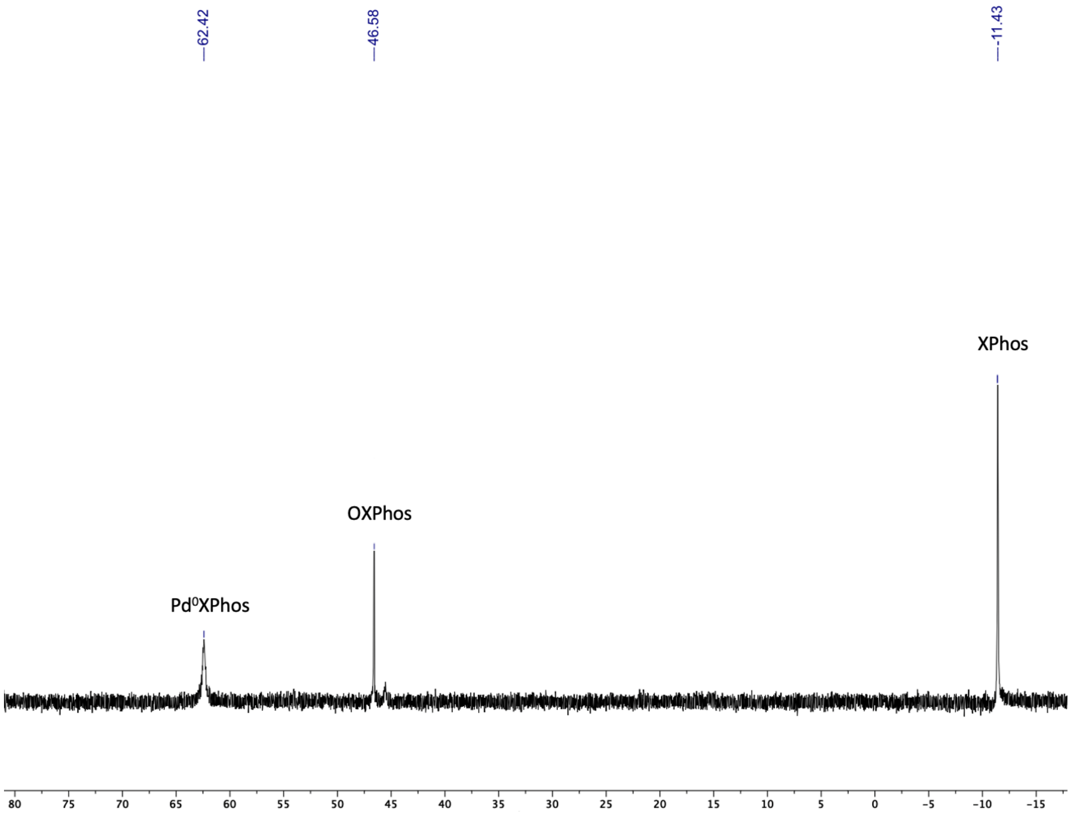


Figure S149. $PdCl_2(ACN)_2$ and XPhos in Anisole/EtOH 4/2 at 60°C in 20 min

Entry 8, Table S17:

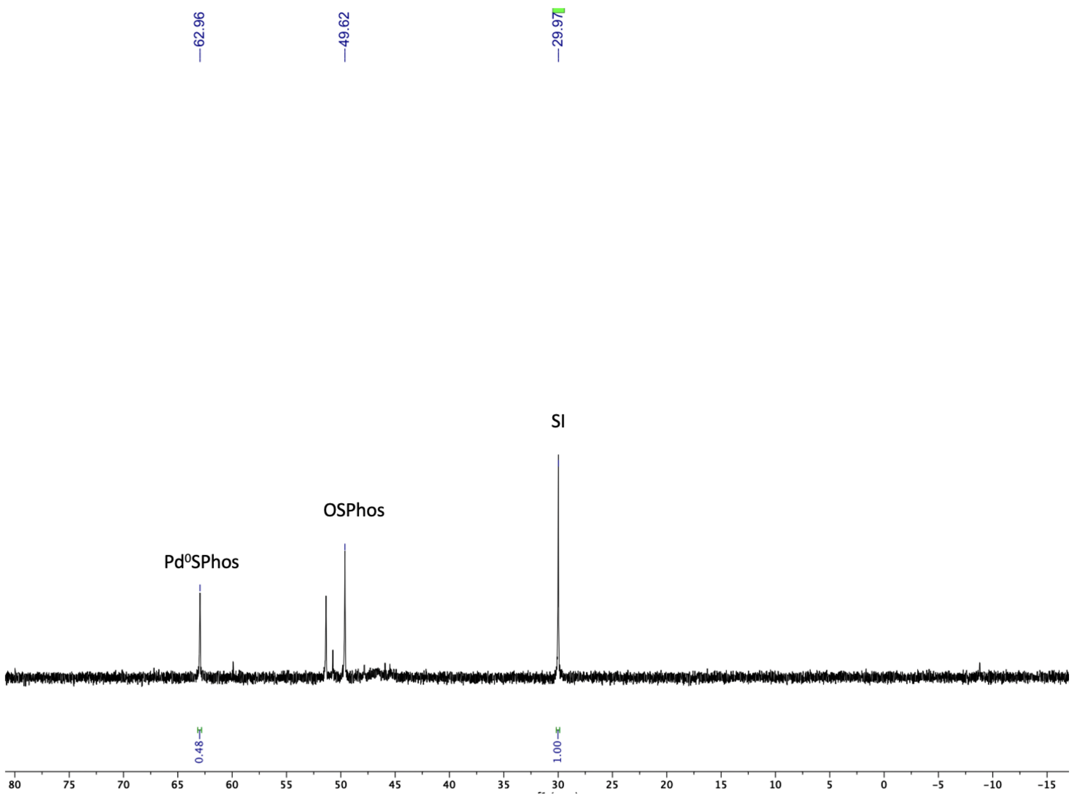


Figure S150. $PdCl_2(ACN)_2$ and SPhos with PYR in Anisole/EtOH 4/2 at 60°C in 20 min

Entry 9, Table S17:

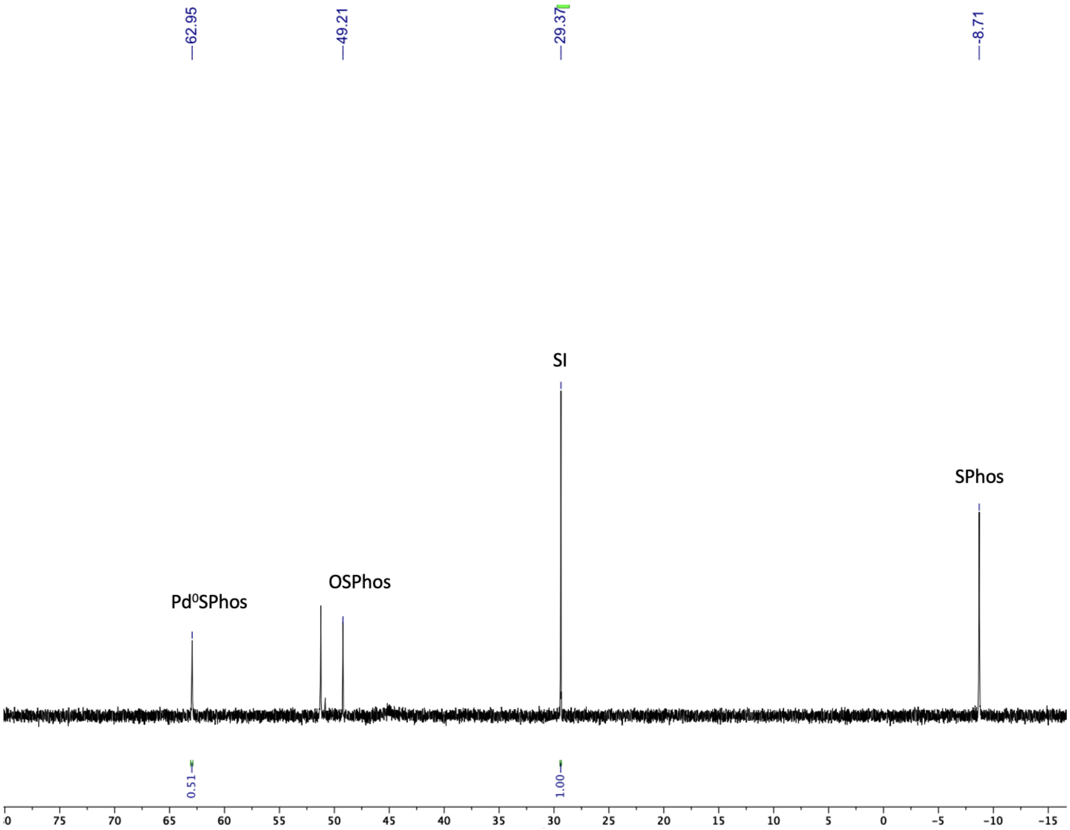


Figure S151. $PdCl_2(ACN)_2$ and SPhos with TMG in Anisole/EtOH 4/2 at 60°C in 20 min

Entry 10, Table S17:

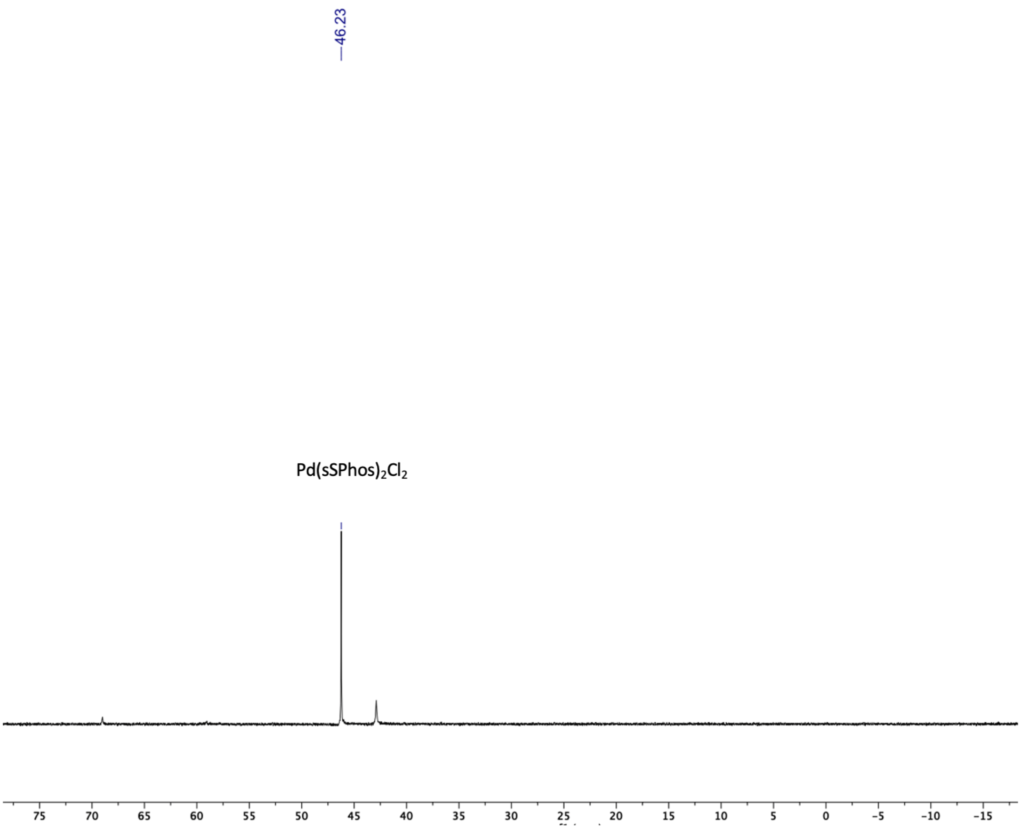


Figure S152. $PdCl_2(ACN)_2$ and sSPhos exchange in HEP/H_2O 8/2

Entry 10, Table S17:

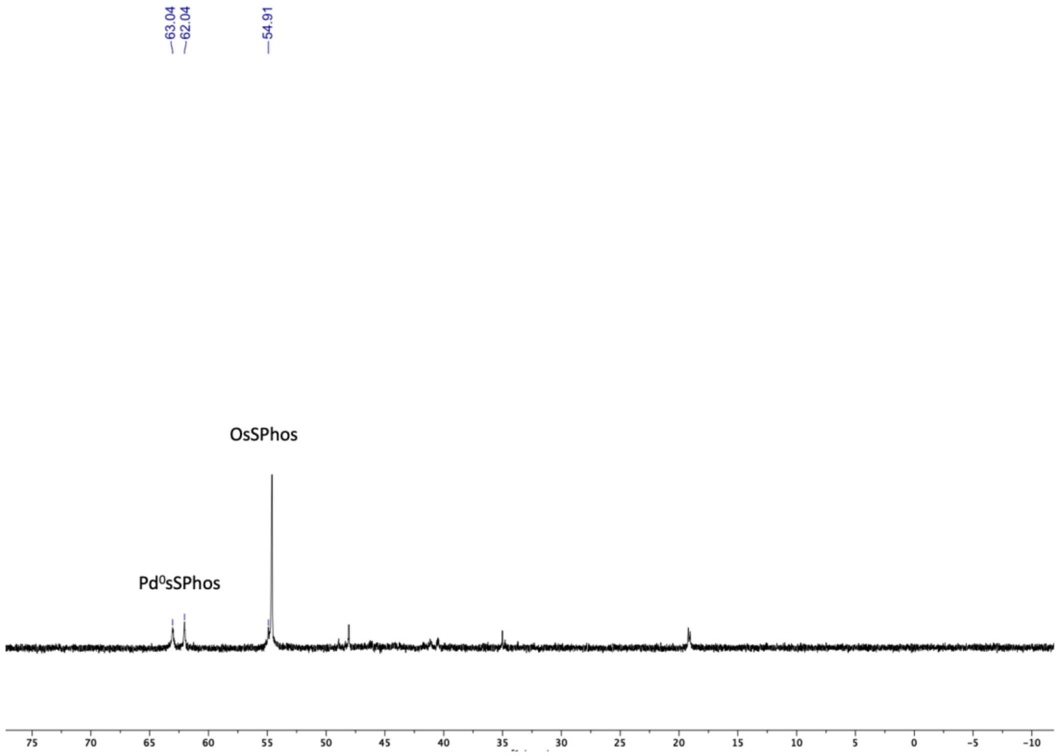


Figure S153. $PdCl_2(ACN)_2$ and sSPhos in HEP/H_2O 8/2 at 60°C in 20 min

Entry 11, Table S17:

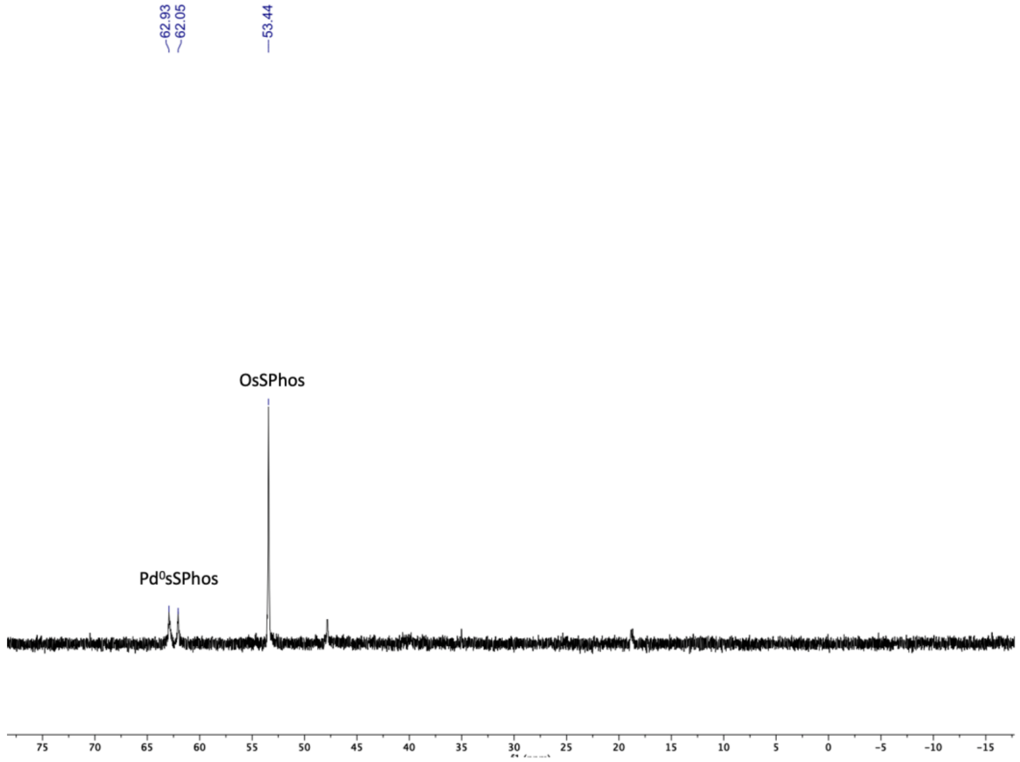


Figure S154. $PdCl_2(ACN)_2$ and sSPhos in EtOH/H_2O 8/2 at 60°C in 20 min

Entry 12, Table S17:

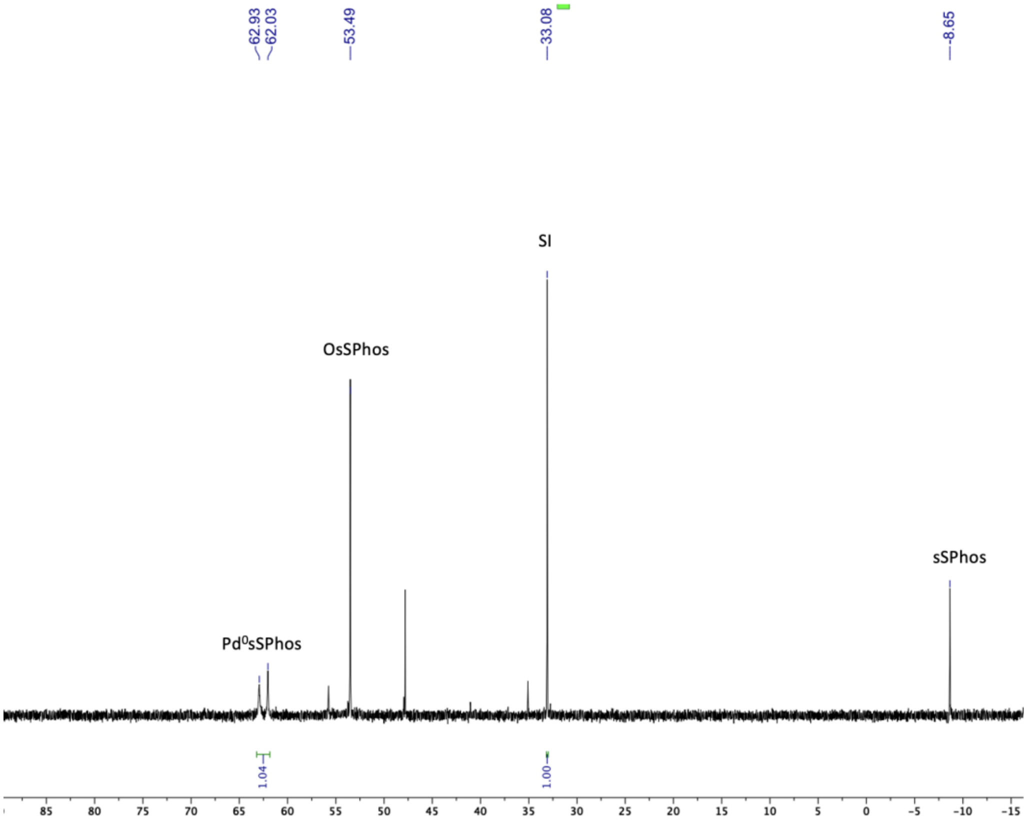


Figure S155. $PdCl_2(ACN)_2$ and sSPhos with PYR in EtOH/H_2O 8/2 at 60°C in 20 min

Entry 13, Table S17:

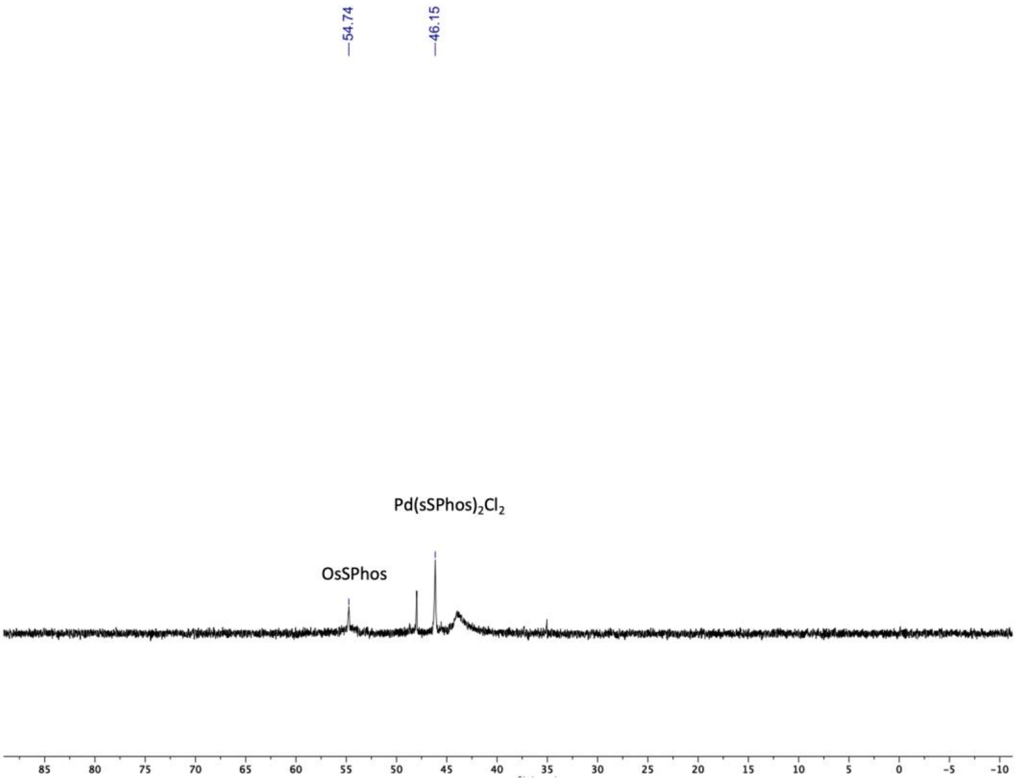
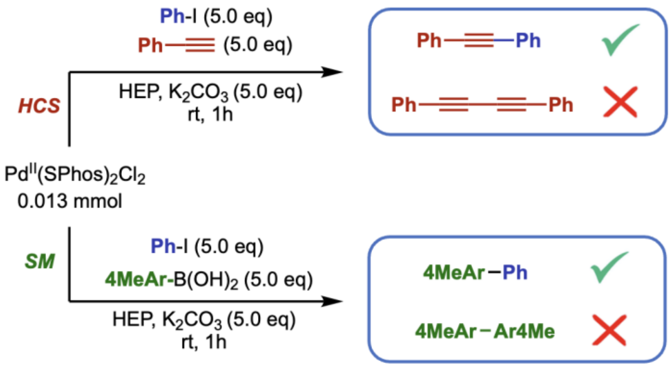


Figure S156. $PdCl_2(ACN)_2$ and sSPhos with K_2CO_3 in IPA/H_2O 8/2 at 60°C in 20 min

10. Selectivity Studies



To an oven-dried 20 mL Schlenk purged under argon atmosphere, the pre-catalyst $PdCl_2(ACN)_2$ (3.4 mg, 0.013 mmol, 1 equiv), the ligand SPhos (10.7 mg, 0.026 mmol, 2 equiv) and K_2CO_3 (9.0 mg, 0.065 mmol, 5 equiv) were dissolved in degassed HEP (0.6 mL). The Ph-I (0.065 mmol, 5 equiv) and the nucleophile ($4MePhB(OH)_2$ for the SM and PhC≡CH for the HC) were added to the solution. The reaction was stirred for 1h at rt and analyzed by HPLC to evaluate the formation of the desired product or the side products.

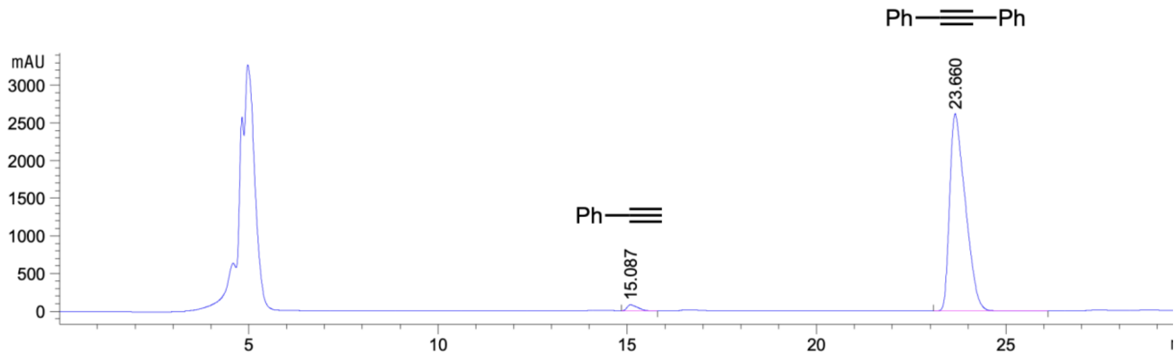


Figure S157. HC cross-coupling reaction: only the desired product was the detected at 23.660 min.

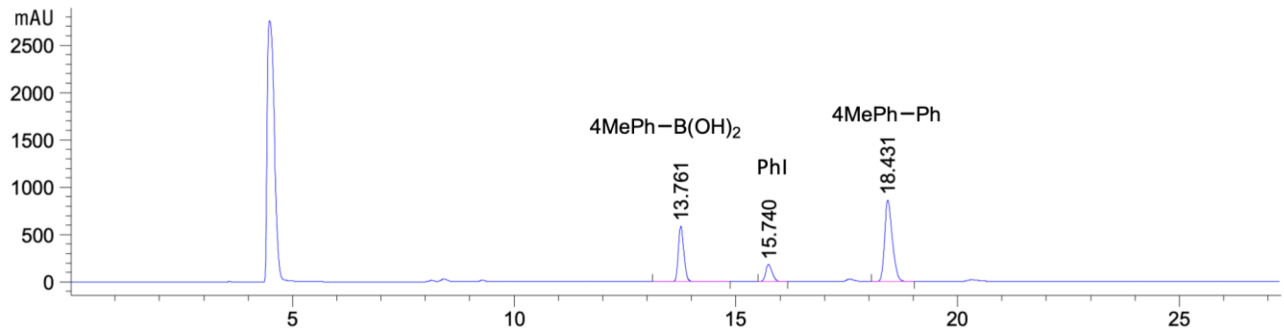


Figure S158. SM cross-coupling reaction: only the desired product was the detected at 18.431

11. DFT calculations

DFT calculations were conducted at CINECA, through the Italian SuperComputing Resource Allocation – ISCRA, using the Gaussian 16 software package[11]. Geometry optimizations for all reported structures were performed with the dispersion corrected B3LYP-D3 functional with a mixed basis set of LANL2DZ for Pd and 6-31G(d) (for other atoms)[12]. Frequency calculations were performed on all optimized structures to ensure that each local minimum lacked imaginary frequencies and that each transition state contained exactly one imaginary frequency. Solvation in DMF were introduced through single point calculations at optimized gas-phase geometries for all the minima and transition state using def2-TZVP for all atoms and the SMD implicit solvation model[13]. The reported Gibbs free energies were corrected considering the thermal correction computed at 298.15 K.

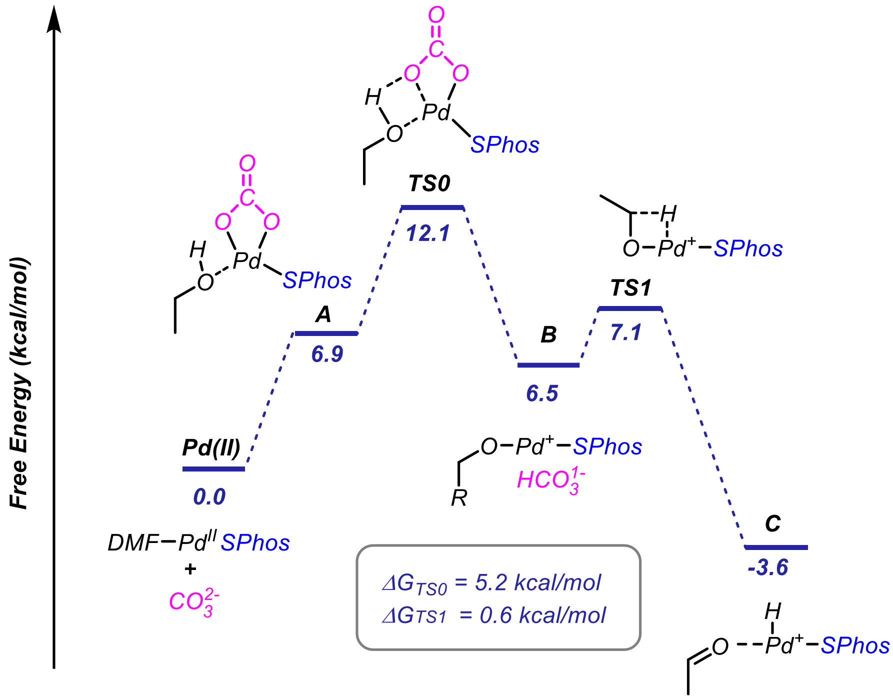


Figure S159. DFT-calculation-computed reaction profile and solution-state Gibbs free energies (ΔG_{DMF}, kcal mol^{-1}) B3LYP/DEF2-TZVP level of theory at 298 K for stationary points of Mechanism A with Pyridine

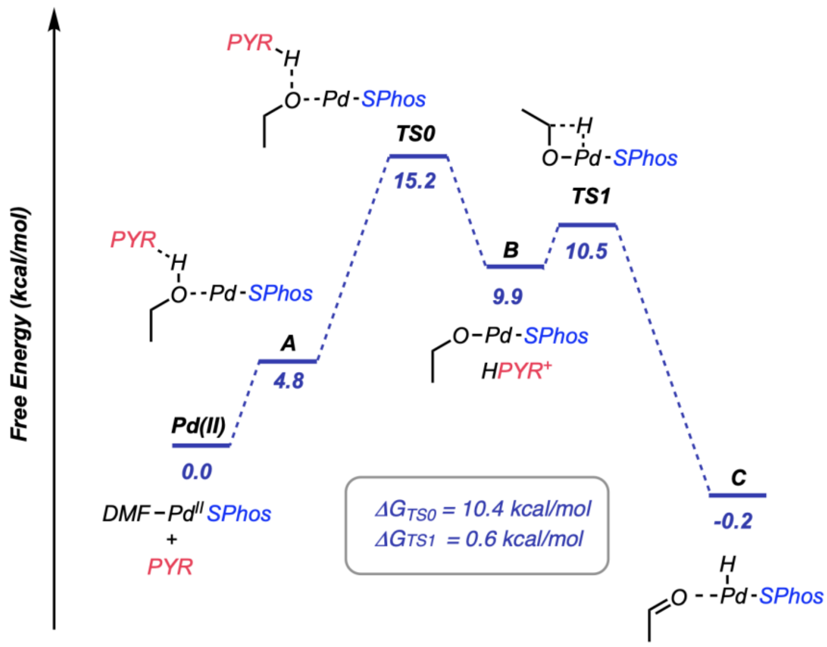


Figure S160. DFT-calculation-computed reaction profile and solution-state Gibbs free energies (ΔG_{DMF}, kcal mol^{-1}) B3LYP/DEF2-TZVP level of theory at 298 K for stationary points of Mechanism A with Carbonate.

Cartesian Coordinates (Å) of Optimized Structures

DMF

E (DMF) = -248.555079

C	5.45972551	-2.89352624	0.00000000
O	4.83818651	-3.97006224	0.00000000
N	6.82590251	-2.84708924	0.00000000
H	4.95541551	-1.89974524	0.00001900
C	7.61708553	-4.08601193	0.00000149
H	7.38251723	-4.65899949	-0.87267427
H	8.65927492	-3.84365378	-0.00194528
H	7.38535928	-4.65718304	0.87462513
C	7.54358083	-1.56418715	-0.00018782
H	8.16263296	-1.50168610	0.87031093
H	8.15317994	-1.49665371	-0.87695926
H	6.83732103	-0.76040892	0.00594816

Pyridine

E (DMF) = -212.578652

C	1.16089000	-0.44787100	0.17369500
C	-1.16000200	-0.44997800	0.17380500
H	0.00196100	-2.14812900	-0.08624700
C	0.77787200	1.02977300	-0.05755600
H	2.07745400	-0.74129800	-0.34898100
H	1.31984400	-0.62469800	1.25487200
C	-0.77980800	1.02830300	-0.05772200
H	-1.31843500	-0.62689900	1.25506400
H	-2.07615100	-0.74521100	-0.34858900
H	1.19902400	1.67958800	0.71473300
H	1.15936900	1.37537700	-1.02223500
H	-1.20237400	1.67751300	0.71430500
H	-1.16174100	1.37296900	-1.02257100
N	0.00104800	-1.16865400	-0.35766900

PyridineH^{+}

E (DMF) = -213.040097

C	-0.33320800	-1.23879400	0.14384400
C	-0.33448900	1.23854000	-0.14347800
H	-1.85796700	0.08813900	0.81219100
C	1.05129400	-0.72529900	-0.25258500
H	-0.73333600	-2.04087600	-0.47671200
H	-0.37569300	-1.53685800	1.19277100
C	1.05067500	0.72627600	0.25240200
H	-0.73529300	2.03976600	0.47774500
H	-0.37750600	1.53737300	-1.19216400

H	1.83739000	-1.33442800	0.19794400
H	1.17970000	-0.76073900	-1.33937700
H	1.17937600	0.76174300	1.33916100
H	1.83604100	1.33621300	-0.19829600
N	-1.24304200	-0.00064100	-0.00017400
H	-1.85704900	-0.09018100	-0.81315000

EtOH

E (DMF) = -155.063892

C	0.08744800	0.55092400	-0.00000900
H	1.98471600	0.08229800	-0.00006600
C	-1.22085000	-0.22308500	0.00004400
H	0.13504800	1.20468900	0.88710500
H	0.13498700	1.20467500	-0.88713600
H	-2.07642800	0.45976900	0.00007200
H	-1.28238800	-0.86209400	-0.88587800
H	-1.28232200	-0.86208400	0.88597800
O	1.14835000	-0.39928600	-0.00003600

PdII + Pyridine

E (DMF) = -2092.551529

H	-3.82241300	2.21004600	-2.47553600
H	-3.61889200	2.84421300	-0.11523200
H	-0.45256500	-1.00284700	5.14937300
C	-2.86768800	2.06842100	-1.97691700
C	-2.76496900	2.42125900	-0.62751500
H	-1.89927300	-1.32190000	4.20606400
H	-1.21017100	1.09716800	4.04512100
C	-0.84173900	-1.04596000	4.12419300
H	1.22074300	0.82153100	4.32512000
H	-1.93714500	1.33939700	-3.77309300
H	1.87146300	-1.75227200	4.16419000
H	-0.16245800	-3.09165900	3.80698300
C	-0.68844800	0.32899600	3.46423200
C	-1.80185400	1.56340200	-2.72343500
C	-1.53899900	2.26333900	0.01517000
C	0.78796000	0.72116100	3.32173500
C	-0.07693300	-2.11054700	3.32873900
H	0.88177000	1.69990600	2.84412600
C	1.40803300	-1.74848500	3.16964100
H	-1.15890800	0.31746500	2.46816600
H	-0.07493900	-0.06170100	-4.34108400
C	-0.55496300	1.43657300	-2.10914900
C	-0.38452200	1.70518400	-0.68343700
H	-0.54385500	-2.19772900	2.34048300
C	1.63807600	-0.34026500	2.58200200
H	1.94470000	-2.51173000	2.59493600
P	1.50787800	-0.19214400	0.71901400
H	2.18867100	-2.30992300	0.11073600
H	0.20711300	1.67087000	-4.72350200

H	4.07862600	-1.52694700	1.65463300
C	0.55688700	0.81085900	-4.14534500
O	0.57593300	1.11721000	-2.73861900
H	5.01691500	0.45296600	0.45630600
H	2.69651600	-0.07928200	2.72288100
C	2.71713500	-1.37083500	-0.06909400
H	1.59089700	0.58778600	-4.40265100
C	0.94604600	2.29454600	-0.27199600
C	4.12744900	-1.53287000	0.56071100
C	1.90702200	1.55572900	0.41826800
C	5.19193800	-0.54780500	0.05289000
H	6.16702100	-0.86484100	0.43659600
H	3.52912200	0.87534300	-1.69735400
H	0.44330900	4.22158600	-1.09944500
H	4.44745000	-2.54683400	0.28646900
H	1.80617600	-0.90201100	-1.99958600
C	1.18616100	3.64635600	-0.55398500
C	2.79207900	-1.16335800	-1.60356000
C	3.83261700	-0.12176600	-2.03628000
C	3.07080000	2.18147400	0.89253500
C	5.21982900	-0.46718700	-1.47908700
H	5.95592200	0.27580900	-1.80103900
H	3.79544200	1.63008400	1.47968700
H	3.06475600	-2.13243900	-2.04151100
C	2.36209400	4.25543400	-0.12360700
H	3.86260800	-0.08478800	-3.13117200
H	5.54613400	-1.43153700	-1.89137300
C	3.29861400	3.52645700	0.61723300
H	2.54180300	5.30199900	-0.34753400
H	4.20118700	4.00682600	0.98045100
Pd	-0.60455200	-0.48327900	-0.14276000
O	-1.28545100	2.63169600	1.27219100
C	-2.31360000	3.26049700	2.05634000
H	-2.64939700	4.18744000	1.58238400
H	-3.16058300	2.58185500	2.20235600
H	-1.85055600	3.48219000	3.01607800
C	-3.67427500	-0.46600500	0.19954700
O	-2.75420400	-0.68587200	-0.62967200
N	-4.96751300	-0.51575400	-0.09312300
H	-3.44774900	-0.21505700	1.24402500
C	-5.99559900	-0.29215200	0.92708200
H	-6.62705700	0.55334200	0.63925200
H	-6.62322400	-1.18253900	1.02444200
H	-5.53117600	-0.08006500	1.89205300
C	-5.43635000	-0.82447400	-1.44712700
H	-6.11316400	-0.03432700	-1.78454800
H	-4.58234000	-0.89216100	-2.11829100
H	-5.97990600	-1.77388300	-1.44365600
C	-1.26942300	-3.07792300	-1.58786800
C	0.08608600	-3.77667200	0.23090300
H	-1.69351800	-2.73273500	0.40858800
C	0.04125100	-3.53459900	-2.21660000
H	-1.75810700	-2.24592100	-2.09222100
H	-1.98384600	-3.90960300	-1.52707500
C	0.76152500	-4.27874200	-1.06867000
H	-0.49021500	-4.57734100	0.70563100

H	0.78124100	-3.39605700	0.97491200
H	-0.12645700	-4.16754700	-3.09027600
H	0.61927200	-2.66521400	-2.53965900
H	0.63238900	-5.35951400	-1.15773200
H	1.83677900	-4.08705300	-1.07536900
N	-0.86999200	-2.69165700	-0.18799500

PdII + CO_3^{2-}

E (DMF) = **-** 2144.186698

H	-2.54368400	4.10441600	0.60479300
H	-2.52682600	2.35392400	2.33349000
H	-1.42549500	-4.59747200	1.93574400
C	-1.67081500	3.46726200	0.70661700
C	-1.66489400	2.49427900	1.69805500
H	-2.74885000	-3.53152800	1.48637600
H	-1.34122900	-2.49116500	3.27654800
C	-1.65864300	-3.63553900	1.45463200
H	0.81909600	-3.54627400	2.75614100
H	-0.66973200	4.39690500	-0.95549800
H	0.63465300	-4.79044800	0.39731400
H	-1.61416500	-4.49110900	-0.54677300
C	-0.99361400	-2.49598400	2.23661100
C	-0.60650000	3.64265300	-0.18328400
C	-0.54583400	1.65711100	1.82161900
C	0.53574600	-2.63003200	2.21875500
C	-1.15857200	-3.65934300	0.00365800
H	0.99696400	-1.79498600	2.75641300
C	0.37009400	-3.81504600	-0.03574400
H	-1.29864300	-1.53701900	1.80629900
H	0.66258800	3.33549400	-2.68436100
C	0.49424600	2.79579700	-0.09249500
C	0.54623100	1.74907600	0.89113000
H	-1.45840300	-2.74033000	-0.51383600
C	1.12252500	-2.74539900	0.79100900
H	0.72611200	-3.83711300	-1.07073800
P	1.22416600	-1.08184700	-0.05060200
H	1.12844800	-1.89978800	-2.20498900
H	1.42345700	4.72511000	-1.84462300
H	3.07077900	-3.24648500	-1.18143100
C	1.51219700	3.65563000	-2.07031400
O	1.59539000	2.87556500	-0.87869000
H	4.64371700	-1.42852900	-0.50450000
H	2.17077600	-3.06103800	0.87842100
C	1.99264800	-1.41441000	-1.73206700
H	2.44484600	3.47636300	-2.60544100
C	1.88657400	1.21068700	1.32470900
C	3.20209000	-2.37216300	-1.82806900
C	2.31448500	-0.09743700	1.04427600

C	4.56152600	-1.70608900	-1.55913100
H	5.36131700	-2.43047200	-1.75476000
H	3.60194300	0.90791500	-1.17150800
H	2.36983300	3.05523200	2.31629700
H	3.20917700	-2.76057500	-2.85648500
H	1.43529300	0.59624100	-2.37310800
C	2.69832100	2.04064000	2.11076800
C	2.25470100	-0.11223700	-2.52821900
C	3.60369900	0.54234400	-2.20416100
C	3.50031900	-0.57750500	1.62062900
C	4.75930900	-0.44554800	-2.41199600
H	5.71851900	0.02653700	-2.16881800
H	3.80913300	-1.60415500	1.45337700
H	2.23880600	-0.38006500	-3.59374300
C	3.89692200	1.57134800	2.64163400
H	3.74095100	1.42181900	-2.84487000
H	4.80620700	-0.72858600	-3.47355400
C	4.29148200	0.25032600	2.41238200
H	4.51286700	2.22700600	3.25011300
H	5.21048300	-0.13092000	2.84749300
Pd	-0.56898200	0.26222700	-0.49572000
O	-0.35644100	0.77253900	2.82012200
C	-1.39351000	0.59009900	3.79456400
H	-1.58789100	1.52763000	4.32925100
H	-2.30132900	0.21723700	3.31663900
H	-0.99953400	-0.14925900	4.49237200
C	-2.34519300	0.22696200	-2.24923000
O	-2.10916800	1.25626600	-1.45267200
O	-1.53037400	-0.79963500	-1.95484400
O	-3.19299500	0.19051900	-3.13136200
C	-3.87846000	-0.81460000	0.57494300
O	-3.33718500	-0.11677700	1.43572400
N	-4.73911300	-0.38651200	-0.36858900
H	-3.68979800	-1.89924400	0.50530400
C	-5.05488100	1.02851400	-0.51429500
H	-4.78801200	1.34999000	-1.52393700
H	-6.12457800	1.19625600	-0.33527300
H	-4.46163100	1.58809700	0.20654800
C	-5.30406400	-1.29815900	-1.35357400
H	-6.40005800	-1.26999300	-1.31131200
H	-4.96039700	-1.01769800	-2.35287400
H	-4.97386600	-2.31834200	-1.14092200

IntA (PYR)

E (DMF) = -1999.052698

H	2.00832200	4.00035500	1.79707000
H	2.03418300	3.74291700	-0.64669900
H	2.14624500	-2.25108200	-3.95567900
C	1.19610700	3.46125200	1.31821300
C	1.22954600	3.30318000	-0.07295600
H	3.25845300	-1.44656300	-2.86930000
H	1.62035000	0.16901600	-3.87800000
C	2.20440100	-1.72977900	-2.99194200
H	-0.31125300	-1.33797700	-4.15792900
H	0.15665000	3.17922000	3.18427900
H	0.12647000	-3.63409000	-2.90408700
H	2.35802900	-3.59803400	-1.88580300
C	1.32144900	-0.47595100	-3.04496800
C	0.15053100	2.98548900	2.12009700
C	0.17179800	2.62984300	-0.70257700
C	-0.16232800	-0.83830200	-3.19291300
C	1.76228900	-2.67837400	-1.86768900
H	-0.77897300	0.06513700	-3.20998200
C	0.27719100	-3.04869100	-1.98834600
H	1.45378200	0.11434100	-2.12586300
H	-1.35728400	1.52682500	4.08497100
C	-0.91577600	2.31150300	1.51046000
C	-0.86968200	1.99864500	0.09141800
H	1.92238400	-2.20659600	-0.89428700
C	-0.65146200	-1.82095600	-2.10296100
H	-0.02335600	-3.70138500	-1.16260500
P	-1.07365000	-0.94615500	-0.51127900
H	-0.61804100	-2.70694500	0.90880300
H	-2.12312700	3.13098200	3.81426100
H	-2.37360700	-3.65199400	-0.70638600
C	-2.14762700	2.06869600	3.55547000
O	-2.01440100	1.88901700	2.13116500
H	-4.31736600	-2.11652600	-0.35099900
H	-1.65127400	-2.17764100	-2.39106800
C	-1.58433500	-2.20875400	0.75942000
H	-3.11965700	1.64880000	3.80615200
C	-2.13893100	1.59185300	-0.60245800
C	-2.60332100	-3.28842200	0.30047000
C	-2.35315900	0.26176400	-0.98616600
C	-4.07662700	-2.86638900	0.40815600
H	-4.70376600	-3.73711400	0.19149600
H	-3.63849000	-0.29657900	1.44011600
H	-2.93024600	3.59494700	-0.61889600
H	-2.43756000	-4.14296600	0.96947000
H	-1.35334500	-0.72050700	2.35193200
C	-3.09287000	2.56442300	-0.91989400
C	-2.00846400	-1.56433600	2.10388900
C	-3.47916800	-1.12612200	2.13878800
C	-3.48690000	-0.08063800	-1.74015800
C	-4.41062700	-2.29439000	1.79156000
H	-5.45508400	-1.96911500	1.81988700
H	-3.64485800	-1.09788000	-2.08069100
H	-1.84707000	-2.32553500	2.87805900
C	-4.23781400	2.21541500	-1.63403500
H	-3.70903600	-0.74303000	3.13900200
H	-4.30563900	-3.08141000	2.55020100

C	-4.42800200	0.89604600	-2.05654400
H	-4.97438300	2.97438200	-1.87697000
H	-5.30761600	0.62921900	-2.63309900
Pd	0.52641600	0.31429500	0.49209600
O	1.92154000	-1.03955000	1.06827000
C	1.76967600	-1.87496900	2.22007300
H	0.74350400	-1.81009200	2.60117800
H	2.41770500	-1.48907900	3.02219700
C	2.12053300	-3.32426300	1.90507800
H	3.15615300	-3.41706100	1.55937200
H	2.01288700	-3.95046600	2.79604200
H	1.47118400	-3.72615900	1.12091300
H	3.26782600	-1.07497500	0.43919200
O	0.02206200	2.50084800	-2.02171600
C	0.99430800	3.08300300	-2.90948300
H	1.97729300	2.62520000	-2.75893700
H	0.63518500	2.86352900	-3.91332600
H	1.05083600	4.16556100	-2.76403400
C	4.37576000	0.36231500	-0.64168500
C	5.29659000	-1.04069600	1.13455700
H	4.39250400	-1.75318300	-0.66043500
C	4.72811300	1.26135200	0.54101900
H	3.42807400	0.58885900	-1.13328900
H	5.17529700	0.33799600	-1.38699800
C	5.76182800	0.42077400	1.31535900
H	6.10577400	-1.71655400	0.85612200
H	4.79172500	-1.44345500	2.01401600
H	5.12251100	2.22745000	0.21976500
H	3.83284100	1.43839200	1.14816900
H	6.75591100	0.55413200	0.88017700
H	5.82442400	0.69542700	2.36970400
N	4.27319400	-0.99194400	0.00833300

IntA (CO_3^{2-})

E (DMF) = -2050.684506

H	2.93850600	-3.74363300	1.01562900
H	3.33318200	-1.57860900	2.10661100
H	1.49894800	5.39267800	-0.53070000
C	2.09434100	-3.09896100	1.23889000
C	2.32204300	-1.88580700	1.87522800
H	2.92940000	4.36814400	-0.37834400
H	1.52929800	4.35614400	1.71681300
C	1.83594300	4.34897500	-0.43436400
H	-0.69198200	4.65677800	0.72045700
H	0.65306100	-4.48756000	0.43380200
H	-0.55930800	4.42653700	-1.93777200
H	1.76267500	4.03578900	-2.58615600
C	1.25547500	3.74178200	0.85001100
C	0.80611700	-3.50799000	0.87005500
C	1.23521100	-1.03136900	2.12767900
C	-0.27152900	3.64155800	0.77791400
C	1.39616500	3.55397200	-1.67141600
H	-0.66507300	3.19731500	1.69638300

C	-0.13286100	3.42905500	-1.75859600
H	1.69085200	2.75211000	1.00447500
H	-1.36570000	-4.17770700	-0.81426000
C	-0.27775700	-2.65950300	1.15585800
C	-0.07100100	-1.39904500	1.73842800
H	1.85336300	2.56208600	-1.62676000
C	-0.79946800	2.88966700	-0.46702600
H	-0.41027600	2.81933800	-2.62678500
P	-0.74836000	1.01165000	-0.37563900
H	-1.17731400	0.38175500	-2.58895700
H	-1.55195300	-5.05223500	0.73743800
H	-2.67591200	2.43385000	-2.37404300
C	-1.85778100	-4.16599000	0.16752900
O	-1.57990500	-2.96494200	0.87146400
H	-4.15644600	1.75800100	-0.45102600
H	-1.87226200	3.10336600	-0.54121900
C	-1.91343200	0.45684600	-1.77934300
H	-2.93897500	-4.18343900	0.02500300
C	-1.21853100	-0.48995700	2.03241400
C	-3.03107200	1.40454700	-2.27548000
C	-1.56942500	0.62753500	1.24237500
C	-4.32689700	1.35415800	-1.45373600
H	-5.07772700	1.99948900	-1.92529500
H	-3.58783400	-0.74221700	0.29246900
H	-1.68499000	-1.63573800	3.78081000
H	-3.26921500	1.07666700	-3.29819400
H	-1.73427700	-1.60966800	-1.10410500
C	-1.96084400	-0.76706900	3.19121300
C	-2.48331700	-0.96669200	-1.56023100
C	-3.78544500	-1.01304600	-0.74798800
C	-2.61946600	1.45332300	1.68599700
C	-4.85497400	-0.08201200	-1.33324200
H	-5.76104400	-0.10358700	-0.71639800
H	-2.88888800	2.33588300	1.11884800
H	-2.68021600	-1.38355300	-2.55872500
C	-3.01659300	0.04299700	3.59556900
H	-4.15333700	-2.04637800	-0.73028400
H	-5.14411600	-0.44086200	-2.33198000
C	-3.33908600	1.17221700	2.84282600
H	-3.57314300	-0.19658100	4.49685900
H	-4.14582200	1.83090900	3.15042000
Pd	1.30755200	-0.04662500	-0.83611700
O	0.49381300	-1.84873300	-1.82041300
C	1.27466000	-2.27031800	-2.97231200
H	2.33943700	-2.18120900	-2.73703600
H	1.03191600	-1.54827600	-3.75564400
C	0.88699100	-3.68366400	-3.37512300
H	-0.18460000	-3.74817300	-3.58724900
H	1.43981400	-3.98592700	-4.27029200
H	1.12916500	-4.39560400	-2.57782700
O	1.33734100	0.17478200	2.72685500
C	2.62453100	0.62413900	3.16644300
H	3.32141700	0.71865700	2.33091000
H	2.44856300	1.60752400	3.60351500
H	3.02774900	-0.04951600	3.93290900
C	3.69322500	0.25875800	-0.24083100

O	4.82095100	0.36210800	0.20585500
O	2.69326600	1.10381400	0.07491000
O	3.24091900	-0.69645700	-1.04217900
H	0.67867100	-2.46575900	-1.08273000

TS0 (PYR)

E (DMF) = -1999.036104

H	3.10233100	-3.42821400	0.26809000
H	3.20881900	-1.56587300	1.86105900
H	1.40792200	4.66121100	-0.07278400
C	2.20238800	-2.84998100	0.45606800
C	2.27722400	-1.77992400	1.35503900
H	2.44291200	3.29698000	-0.46316900
H	1.62653600	3.22823800	1.93126300
C	1.41548200	3.57153200	-0.20441900
H	-0.61838800	4.18848400	1.73448500
H	1.02072600	-4.10483100	-0.82864200
H	-1.03634500	4.66375700	-0.80060100
H	0.76545900	3.71544800	-2.28613800
C	0.99304800	2.89178100	1.10392400
C	1.02325600	-3.23766800	-0.18212400
C	1.12858800	-1.04113800	1.61839500
C	-0.48293900	3.13569800	1.45899600
C	0.46204700	3.23214200	-1.35253100
H	-0.76374800	2.54549500	2.33726600
C	-0.98747500	3.58529500	-0.99584800
H	1.16199600	1.80696100	1.01377300
H	-0.99394800	-3.95147200	-2.11430400
C	-0.14452900	-2.51912100	0.06582100
C	-0.12773000	-1.31160600	0.90137100
H	0.53379400	2.12551800	-1.58085300
C	-1.44962300	2.85812800	0.28448800
H	-1.66317600	3.40489600	-1.83590000
P	-1.65747100	1.03884400	-0.05799800
H	-2.14256400	1.34195400	-2.30891800
H	-1.19760500	-4.92811700	-0.61979900
H	-3.95430900	2.67855400	-1.09148800
C	-1.53359200	-4.04300100	-1.16689600
O	-1.35559500	-2.85666200	-0.36491200
H	-4.98670100	0.91210300	0.36293000
H	-2.45599300	3.19921600	0.56285600
C	-2.77709600	0.87102400	-1.54491200
H	-2.60398500	-4.10279800	-1.35251400
C	-1.38485600	-0.99486200	1.68985000
C	-4.10886000	1.66561300	-1.47777500
C	-2.15078500	0.14800600	1.43127000

C	-5.22256000	0.94287600	-0.70574800
H	-6.14700600	1.52134100	-0.80040700
H	-3.80239900	-1.43401200	-0.13518700
H	-1.15260700	-2.71624300	2.96874000
H	-4.42736600	1.78956300	-2.52105000
H	-2.08818800	-1.16788200	-1.94129700
C	-1.73499800	-1.82294500	2.76183400
C	-3.01945700	-0.59496400	-1.97741900
C	-4.12493100	-1.29325100	-1.17318100
C	-3.21314500	0.50755100	2.27321700
C	-5.43241900	-0.48977900	-1.21531600
H	-6.20357600	-0.98933600	-0.62095600
H	-3.78016600	1.41526800	2.09510900
H	-3.32048700	-0.55466500	-3.03226300
C	-2.81532800	-1.48848100	3.57805700
H	-4.28734500	-2.29412100	-1.58796600
H	-5.80442900	-0.45677100	-2.24785700
C	-3.54166100	-0.31463100	3.34818200
H	-3.08082300	-2.13443300	4.40874700
H	-4.36327600	-0.04534600	4.00360300
Pd	0.31936700	0.15986600	-0.71004700
O	2.14979300	-0.55502600	-1.59885700
C	2.19376200	-0.89372700	-3.00234700
H	2.89196500	-1.72969400	-3.12942100
H	2.58065300	-0.03948900	-3.57354100
C	0.81571200	-1.28222700	-3.50937500
H	0.11019700	-0.44338000	-3.44149500
H	0.86913600	-1.57782500	-4.56122100
H	0.41485300	-2.12289700	-2.93605100
O	1.02464200	-0.08630300	2.54360400
C	2.13750600	0.19465100	3.41510600
H	2.98714000	0.58397800	2.84771200
H	1.77551700	0.95258100	4.10739400
H	2.42834000	-0.70520100	3.96466000
C	4.48750400	1.24782000	0.26866300
C	5.40370500	-0.69087900	-0.83569800
H	4.78491800	1.03452900	-1.76362700
C	5.57920500	0.60822200	1.15852800
H	3.49911800	1.22572700	0.73780700
H	4.71639900	2.29084200	0.03486600
C	6.44373900	-0.19257100	0.16998600
H	5.81113600	-0.98591600	-1.80521500
H	4.84418200	-1.54237600	-0.42984100
H	6.14527000	1.35599000	1.71792900
H	5.12796100	-0.07240700	1.89036700
H	7.16646800	0.46206800	-0.32928600
H	7.00063400	-1.00314400	0.64566400
N	4.44751000	0.44734600	-1.00390300

H	3.07084100	-0.10573700	-1.33297600

TS0 (CO_3^{2-})

E (DMF) = -2050.676177

H	2.59063100	-4.23818300	1.18669600
H	2.65979200	-2.29381000	2.68476300
H	1.48633500	5.06875900	1.46657800
C	1.75748500	-3.54282800	1.19256200
C	1.80320200	-2.44915900	2.04376300
H	2.82893100	4.14056500	0.77717300
H	1.82400900	3.03002300	2.79979200
C	1.74671400	4.13914400	0.93754400
H	-0.53313100	3.66976200	2.55449200
H	0.70036700	-4.62546900	-0.33638200
H	-0.86303800	4.88131300	0.25445600
H	1.25230600	5.02099400	-0.98219700
C	1.35885700	2.93721700	1.81077600
C	0.68393900	-3.77027900	0.32537200
C	0.73041000	-1.53972600	2.05469400
C	-0.16196000	2.80575800	1.98544900
C	1.03251500	4.10543200	-0.42037300
H	-0.40685100	1.91278300	2.57185300
C	-0.48528500	3.97867300	-0.24901100
H	1.76158000	2.02309300	1.36845500
H	-0.65615900	-3.90041900	-2.15542400
C	-0.36880100	-2.86394800	0.30638100
C	-0.37105200	-1.69919500	1.14888500
H	1.41803500	3.26909300	-1.00782400
C	-0.92964700	2.79584400	0.64145100
H	-0.98351000	3.95285200	-1.22320800
P	-0.93793700	1.07924000	-0.12909900
H	-0.75827100	1.98887300	-2.22956500
H	-1.47134100	-5.00979900	-1.00821600
H	-3.01578600	2.88821800	-1.33772900
C	-1.49639400	-4.01071600	-1.45964500
O	-1.47330200	-2.99049200	-0.46608400
H	-4.29225600	0.78400300	-0.96308700
H	-1.99324800	2.94504300	0.86503400
C	-1.56298200	1.33086600	-1.87614700
H	-2.43525400	-3.87735900	-1.99670900
C	-1.69897100	-1.06144800	1.46986300
C	-2.91527600	2.06482600	-2.05330900
C	-2.11019200	0.18477900	0.96845700
C	-4.14945400	1.14873700	-1.98452500
H	-5.04166800	1.73443500	-2.23644100
H	-2.78599600	-1.23854800	-1.57537700
H	-2.22891000	-2.73068900	2.71448000
H	-2.89033600	2.53347000	-3.04707700
H	-0.58556700	-0.50441000	-2.52301000
C	-2.55029900	-1.76546300	2.33429500
C	-1.50200800	0.05319900	-2.74375800
C	-2.73748300	-0.84301000	-2.59616100
C	-3.34520000	0.71702100	1.37458800

C	-4.01897200	-0.06351900	-2.91489600
H	-4.89949400	-0.70921100	-2.81552400
H	-3.66304400	1.69037400	1.01571300
H	-1.42641200	0.37909700	-3.79065200
C	-3.78288600	-1.24094800	2.71168300
H	-2.63842500	-1.70648500	-3.26531800
H	-3.99011000	0.27453500	-3.96081700
C	-4.18100800	0.00991400	2.23403100
H	-4.42681300	-1.80003700	3.38407400
H	-5.13542600	0.43344300	2.53196300
Pd	0.90411700	-0.23702700	-0.19516500
O	2.58710100	-1.77766400	-1.03906700
C	2.88686900	-1.62094000	-2.43559200
H	2.42476700	-0.69978900	-2.81256300
H	2.42369600	-2.47554100	-2.94287800
C	4.39018700	-1.58419700	-2.68135400
H	4.87046400	-2.48804000	-2.29229600
H	4.60220900	-1.50836600	-3.75343800
H	4.83105900	-0.71257800	-2.18646300
O	0.63137200	-0.51491100	2.92840600
C	1.85227200	-0.01470600	3.50134400
H	2.58362600	0.18540900	2.71062100
H	1.57729500	0.91334200	4.00085900
H	2.25534200	-0.71687200	4.23980100
H	3.12914500	-1.11101000	-0.52855100
C	3.11020300	1.23665800	-0.66030900
O	3.86198700	2.12257500	-1.05398300
O	1.87843900	1.15166600	-1.26068700
O	3.32345800	0.34805900	0.26162500

IntB (CO_3^{2-})

E (DMF) = -2050.685088

H	-1.34784600	-4.82979900	1.17073800
H	0.19212500	-3.60838000	2.63747300
H	4.89222000	2.03388100	1.45024300
C	-1.37955000	-3.74497100	1.18363300
C	-0.50635200	-3.06041900	2.02039000
H	4.99269000	0.55578500	0.47565100
H	3.65086200	0.25277900	2.59589600
C	4.31144200	1.33299000	0.83153900
H	2.59905900	2.47528800	2.77079900
H	-2.98158500	-3.66633300	-0.24857600
H	3.15275100	3.86087100	0.70551900
H	4.53484400	2.59462600	-0.91858600
C	3.20960300	0.70129400	1.69743500
C	-2.31036000	-3.09031400	0.37334100
C	-0.53109900	-1.66211800	2.02861700
C	2.14012700	1.72379600	2.11288400
C	3.73089200	2.08380700	-0.37657600
H	1.34033400	1.24526400	2.68651200
C	2.67746600	3.10574500	0.06166300
H	2.73907500	-0.11921500	1.14618800

H	-3.59507700	-2.18906600	-1.99141900
C	-2.32262400	-1.70168800	0.35121500
C	-1.39698800	-0.92970800	1.13955000
H	3.29934100	1.35992300	-1.07309200
C	1.54644600	2.48590200	0.90644600
H	2.27637800	3.65851800	-0.79456000
P	0.28162600	1.41516800	-0.00226600
H	1.17472200	2.30997700	-1.94661000
H	-4.80473300	-2.25371400	-0.66978400
H	-0.18909200	4.24387100	-0.92120700
C	-4.12004300	-1.60496100	-1.22914400
O	-3.19990900	-0.95374600	-0.35571400
H	-2.46481200	3.23769600	-0.79752600
H	0.93258000	3.30683900	1.29422700
C	0.11301100	2.21263600	-1.69613600
H	-4.68471200	-0.80447600	-1.70754500
C	-1.82541400	0.46611900	1.52766900
C	-0.54481600	3.61070500	-1.74328500
C	-1.18707400	1.63339200	1.08171100
C	-2.08438800	3.57106100	-1.76713000
H	-2.46589700	4.58794800	-1.91965500
H	-2.33755100	0.78702700	-1.74056500
H	-3.40947000	-0.33386400	2.74137200
H	-0.19604600	4.09466900	-2.66628800
H	-0.04529400	0.29215100	-2.70912500
C	-2.91827400	0.57342300	2.40172600
C	-0.49878300	1.28475700	-2.76800100
C	-2.02743500	1.22187500	-2.69821500
C	-1.63825200	2.88271000	1.54117200
C	-2.62643100	2.62715100	-2.85071900
H	-3.72120600	2.59137200	-2.79723000
H	-1.14679400	3.79230000	1.21155500
H	-0.20746500	1.69673200	-3.74509500
C	-3.36928700	1.81554900	2.83610600
H	-2.40543200	0.55519700	-3.48319800
H	-2.37154400	3.02134900	-3.84499300
C	-2.72446200	2.97810600	2.40528100
H	-4.21557000	1.87844100	3.51380000
H	-3.06577900	3.95234400	2.74211200
Pd	0.41391000	-0.87057600	-0.32540300
O	0.51827600	-2.87442900	-0.80011300
C	0.47964200	-3.16402300	-2.18448000
H	0.79732400	-4.21187600	-2.30961600
H	1.20145200	-2.54567600	-2.73998700
C	-0.90595900	-2.98203400	-2.80615300
H	-1.24706100	-1.94749100	-2.68013900
H	-0.88315000	-3.20594000	-3.87916400
H	-1.63532000	-3.64401800	-2.32955300
O	0.18379600	-0.90218100	2.88752400
C	1.28834400	-1.50743900	3.56614000
H	1.97904900	-1.96239300	2.84835800
H	1.79059400	-0.69564100	4.09112400
H	0.94730800	-2.25454300	4.29159200
C	3.17551200	-1.24826700	-1.23443100
O	2.05382500	-0.58491300	-1.52312900
O	4.26484700	-0.84522800	-1.60648200

O	3.05840100	-2.37667200	-0.50366500
H	2.10120500	-2.68653700	-0.51795700

IntB

E (DMF) = - 1786.004466

H	4.48587400	-2.65791800	-0.24090100
H	4.31075700	-0.91114700	1.47057200
H	0.76230300	5.20862100	0.97860900
C	3.50127400	-2.30947000	0.05427500
C	3.41060200	-1.31390500	1.02694500
H	2.04799000	4.55599300	-0.02846800
H	1.86574000	3.34839500	2.17510600
C	1.06868600	4.32363400	0.40448600
H	-0.55136600	3.53398100	2.57565300
H	2.50995600	-3.65946700	-1.29307400
H	-1.71223200	4.54022700	0.44862900
H	-0.06728600	4.96111500	-1.33709700
C	1.17747300	3.12199900	1.35320500
C	2.38137800	-2.88377600	-0.55064600
C	2.14864100	-0.85951400	1.41390700
C	-0.18771500	2.72149500	1.93324500
C	0.04116600	4.07102400	-0.70831200
H	-0.08577800	1.83710100	2.57008300
C	-1.32812500	3.68804900	-0.12762900
H	1.61234200	2.26671500	0.81558100
H	0.47279900	-3.60064300	-2.54575900
C	1.11278600	-2.43950600	-0.18227500
C	0.94551900	-1.36129200	0.77392900
H	0.40531400	3.27071600	-1.36523600
C	-1.26658900	2.49112400	0.84688800
H	-2.05713400	3.51546600	-0.92589600
P	-1.05517500	0.81987600	0.03419700
H	-1.94021800	1.54081200	-1.97091400
H	0.51043200	-4.86815800	-1.27702300
H	-3.86435600	1.87994900	-0.29888900
C	-0.00973200	-3.97407000	-1.63585300
O	-0.04356100	-2.95863200	-0.62564600
H	-4.25987300	-0.44103900	0.53406900
H	-2.24102900	2.40502600	1.34467400
C	-2.31767500	0.72243100	-1.34218200
H	-1.05195300	-4.21305900	-1.84111100
C	-0.32816700	-1.32603500	1.58700100
C	-3.79386900	1.03606200	-0.99446900
C	-1.32663400	-0.35999600	1.39829500
C	-4.59562700	-0.16717300	-0.46979100
H	-5.64780600	0.12360500	-0.37821500
H	-2.53198400	-2.04862100	-0.61117600
H	0.29688200	-3.02365500	2.75384100
H	-4.26167800	1.37913600	-1.92702100
H	-1.14190100	-0.84911800	-2.31022300
C	-0.47308800	-2.27088600	2.61156400
C	-2.19605300	-0.58086000	-2.17011300

C	-2.97585300	-1.75834800	-1.57062900
C	-2.42092100	-0.30549700	2.27556900
C	-4.45361900	-1.39352500	-1.38020500
H	-5.00548400	-2.23970100	-0.95725800
H	-3.17299700	0.46863600	2.16635400
H	-2.59889400	-0.36413900	-3.16856100
C	-1.58146000	-2.23739100	3.45406400
H	-2.88248100	-2.62393500	-2.23661500
H	-4.90417900	-1.18053000	-2.35951200
C	-2.55124000	-1.24284700	3.29642000
H	-1.68109900	-2.97434500	4.24477800
H	-3.40304100	-1.19812300	3.96745900
Pd	1.00984700	0.24353300	-0.79801700
O	2.78067000	-0.00750300	-1.81742700
C	2.33609700	0.94694300	-2.64007800
H	2.86198400	1.91581100	-2.56444500
H	1.20367300	1.33385100	-2.18002800
C	2.00335600	0.54281500	-4.07187000
H	1.38068800	-0.35482900	-4.07886000
H	1.49287400	1.34856100	-4.60778100
H	2.94050800	0.32086500	-4.59220100
O	1.91952700	0.01888600	2.40376200
C	3.03458700	0.63816500	3.05784400
H	3.63837200	1.20552600	2.34197000
H	2.60057200	1.31565600	3.79187400
H	3.65410200	-0.10789900	3.56584200

TS1

E (DMF) = - 1786.0037

H	3.51493500	-3.81040300	-0.63310300
H	3.82452000	-2.24959400	1.23394400
H	2.10954500	4.66210400	1.36721200
C	2.66383600	-3.23601900	-0.28142800
C	2.84873800	-2.34908900	0.77857400
H	3.18232000	3.80028700	0.27307300
H	2.67219800	2.46164900	2.34592100
C	2.17350100	3.79135000	0.70068400
H	0.39154200	3.25160800	2.81270800
H	1.33962100	-4.12260200	-1.72360200
H	-0.45862000	4.73053700	0.81009300
H	1.25941100	4.88156300	-0.94395400
C	1.95255200	2.51330200	1.52134000
C	1.43005100	-3.41792700	-0.90829300
C	1.75758300	-1.60642300	1.23775700
C	0.52708300	2.43711500	2.08930500
C	1.12452400	3.93389600	-0.41164800
H	0.38516900	1.50090400	2.63814000
C	-0.30288400	3.86634100	0.15075400
H	2.14240500	1.63238700	0.89110000

H	-0.60220700	-3.38867300	-2.91055700
C	0.33010200	-2.68345800	-0.46262300
C	0.46605500	-1.70758500	0.59421000
H	1.26897500	3.13844600	-1.15195000
C	-0.56862700	2.60922200	1.00876100
H	-1.04229600	3.96571400	-0.65049600
P	-0.82811200	1.02228300	0.05291900
H	-1.47227400	2.12310200	-1.86795100
H	-0.91327600	-4.73552600	-1.76714400
H	-3.22578100	2.84873000	-0.13078000
C	-1.16846200	-3.70289400	-2.02684300
O	-0.92460800	-2.81985900	-0.92569000
H	-4.26578300	0.67297900	0.51936700
H	-1.53094000	2.74538900	1.51847000
C	-2.06540200	1.39476500	-1.29807100
H	-2.23618600	-3.62844400	-2.22679500
C	-0.74997100	-1.36851300	1.42163300
C	-3.39422000	2.08010800	-0.89354700
C	-1.42600900	-0.14342700	1.32389600
C	-4.50575800	1.11290800	-0.45231700
H	-5.43291400	1.68054600	-0.31730500
H	-3.05684300	-1.25545800	-0.78606200
H	-0.65214400	-3.26009200	2.44253800
H	-3.74296100	2.61795500	-1.78532500
H	-1.37782300	-0.36046200	-2.40799700
C	-1.17160600	-2.30899100	2.37124100
C	-2.31368700	0.18159800	-2.22812500
C	-3.39725500	-0.77289800	-1.70965700
C	-2.46608600	0.15342000	2.21903400
C	-4.71250400	-0.02361600	-1.46142500
H	-5.48270700	-0.71185800	-1.09731900
H	-2.96338200	1.11683300	2.18296900
H	-2.63429600	0.58385500	-3.19840200
C	-2.23072700	-2.02535300	3.22967100
H	-3.54969900	-1.57126400	-2.44500500
H	-5.08065800	0.38827100	-2.41129700
C	-2.87073700	-0.78439400	3.16467600
H	-2.54570000	-2.76293400	3.96112600
H	-3.67961600	-0.54905600	3.84892800
Pd	0.99909800	-0.02213500	-0.85353100
O	2.68420100	-0.62373800	-1.94590700
C	2.58083500	0.53550200	-2.53758400
H	2.19548900	0.53437200	-3.57263600
C	3.60004100	1.62050600	-2.23869700
H	3.26855800	2.59727700	-2.60056500
H	3.80504100	1.67169400	-1.16749300
H	4.52712500	1.35702400	-2.76019400
O	1.78253700	-0.78637800	2.30438900

C	3.02706800	-0.55379600	2.97402700
H	3.42276300	-1.48081200	3.40158200
H	3.76046700	-0.11207300	2.29096400
H	2.79970900	0.15003500	3.77365800
H	1.37422400	1.13586000	-2.00139300

IntC

E (DMF) = -1786.02079

H	3.88201400	-3.21033500	-0.19251700
H	3.78357000	-1.54834200	1.62634800
H	1.28310600	4.97993000	1.06773300
C	2.92007500	-2.80454800	0.10864500
C	2.87037600	-1.87193900	1.14421200
H	2.54144100	4.17345100	0.13916700
H	2.00712400	2.94171200	2.26860800
C	1.50480500	4.07965100	0.47939300
H	-0.38380000	3.50429500	2.48169800
H	1.83799300	-3.97063000	-1.33915000
H	-1.23750500	4.68379900	0.27081500
H	0.61939400	4.92950300	-1.31301900
C	1.35059900	2.86078100	1.39587900
C	1.76558900	-3.24309800	-0.54099200
C	1.62079200	-1.38010800	1.55084500
C	-0.09981800	2.65178200	1.85184000
C	0.55094100	4.01082500	-0.72122800
H	-0.17730100	1.75502000	2.47397400
C	-0.90461700	3.79413400	-0.28001100
H	1.72749100	1.94323900	0.88075400
H	-0.14333900	-3.75234800	-2.58531800
C	0.52060000	-2.75814000	-0.11384600
C	0.43485100	-1.83289600	0.94100100
H	0.86477200	3.19226800	-1.38721600
C	-1.09929200	2.59274100	0.67301400
H	-1.56301300	3.71754900	-1.15107700
P	-0.99378200	0.90844500	-0.15398400
H	-1.56623300	1.66205900	-2.25430100
H	-0.25915200	-5.04466500	-1.35019200
H	-3.55612500	2.35912800	-0.76419400
C	-0.68616500	-4.09613300	-1.69601400
O	-0.67085300	-3.11212800	-0.66497000
H	-4.46119800	0.17165500	0.02058400
H	-2.11497900	2.64342500	1.07974000
C	-2.12486800	0.93946700	-1.64481300
H	-1.73599800	-4.24185300	-1.94921700
C	-0.88943900	-1.42250500	1.49715300
C	-3.55810100	1.50288000	-1.44788900
C	-1.57702800	-0.23973200	1.15226600
C	-4.61759100	0.47321700	-1.01810800
H	-5.60308200	0.95023600	-1.05966300
H	-2.90900600	-1.73000200	-0.89487000
H	-0.91370500	-3.17538400	2.73024700
H	-3.85470000	1.90619000	-2.42525800

H	-1.15555600	-0.84999500	-2.44785500
C	-1.44272200	-2.26259900	2.47558800
C	-2.15222900	-0.39584000	-2.42697400
C	-3.18575100	-1.40072400	-1.90263300
C	-2.75660800	0.09168400	1.84530300
C	-4.58939800	-0.78369200	-1.89537700
H	-5.32613200	-1.50879900	-1.53349900
H	-3.28073500	1.01382500	1.62160100
H	-2.40120200	-0.14613000	-3.46696900
C	-2.62950600	-1.94130900	3.12738700
H	-3.16585800	-2.29220900	-2.53967500
H	-4.87894100	-0.52511000	-2.92352000
C	-3.28384600	-0.74756900	2.82119200
H	-3.03243400	-2.61014900	3.88148200
H	-4.19795200	-0.47005200	3.33635000
Pd	1.18804200	0.68252300	-0.73142900
O	3.27312700	0.56131700	-1.32401700
C	5.28817600	-0.44272100	-2.12150700
H	5.67346900	-1.36958200	-1.67824400
H	5.49433800	-0.50615000	-3.19751500
H	5.79152100	0.42325000	-1.68969800
O	1.44721800	-0.44730300	2.53204600
C	2.59079000	0.00838500	3.24945000
H	3.29702900	0.52736600	2.58877800
H	2.21358300	0.70868300	3.99520900
H	3.10316000	-0.81802300	3.75515000
C	3.81703000	-0.37670800	-1.90594800
H	3.20589500	-1.20986700	-2.28512500
H	0.62702600	-0.27645900	-1.76609200

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