Electronic Supplementary Information

Palladium(II) complexes supported by PBP and POCOP pincer ligands: comparison of structure, property and catalytic activity

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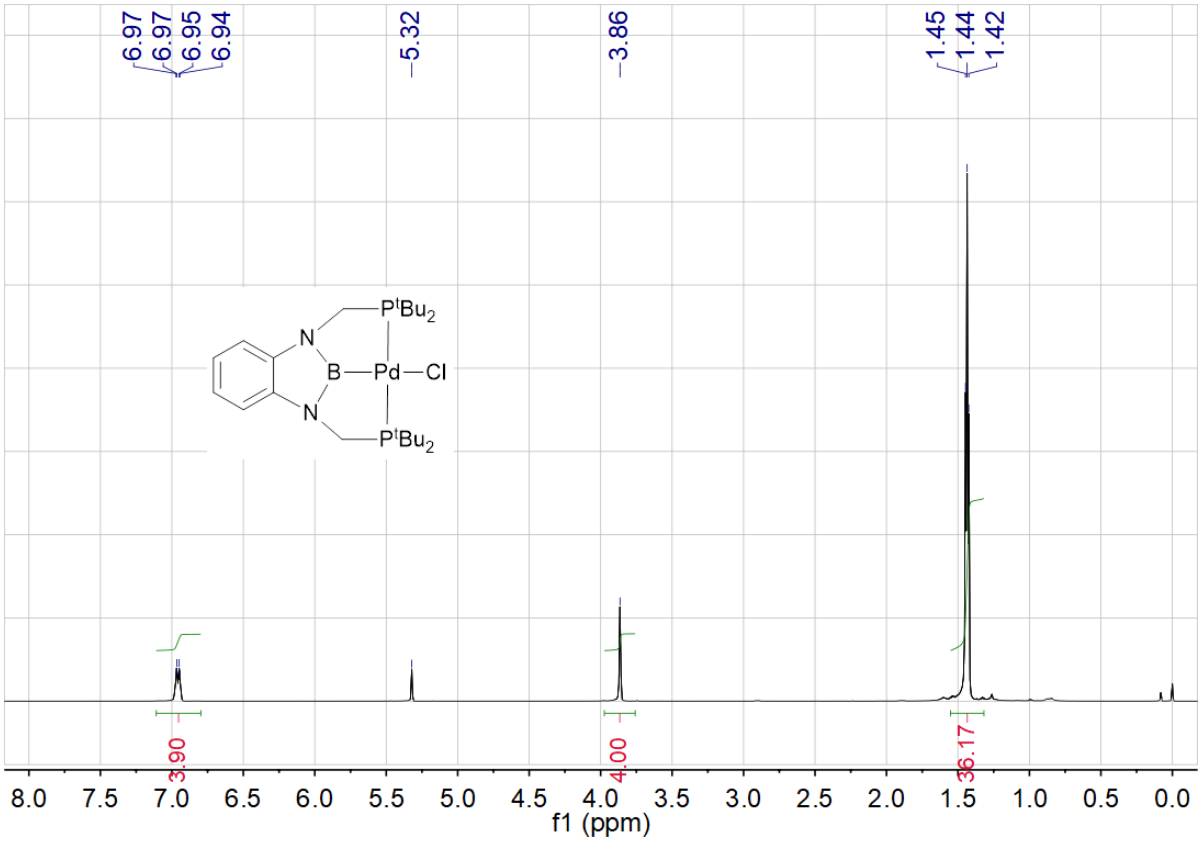

Fig. S1 ^{1}H NMR spectrum of complex **1a** (600 MHz, CD_2Cl_2)

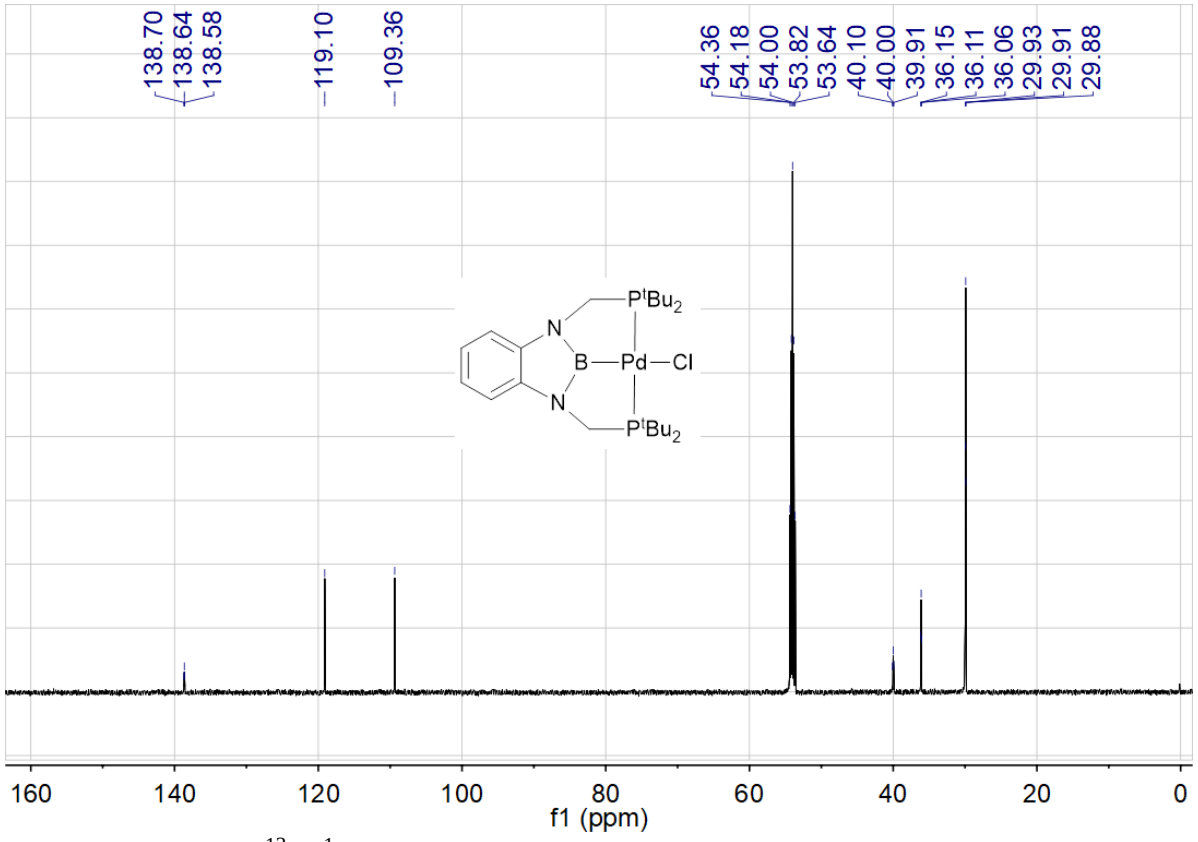

Fig. S2 $^{13}C\{^1H\}$ NMR spectrum of complex **1a** (151 MHz, CD_2Cl_2)

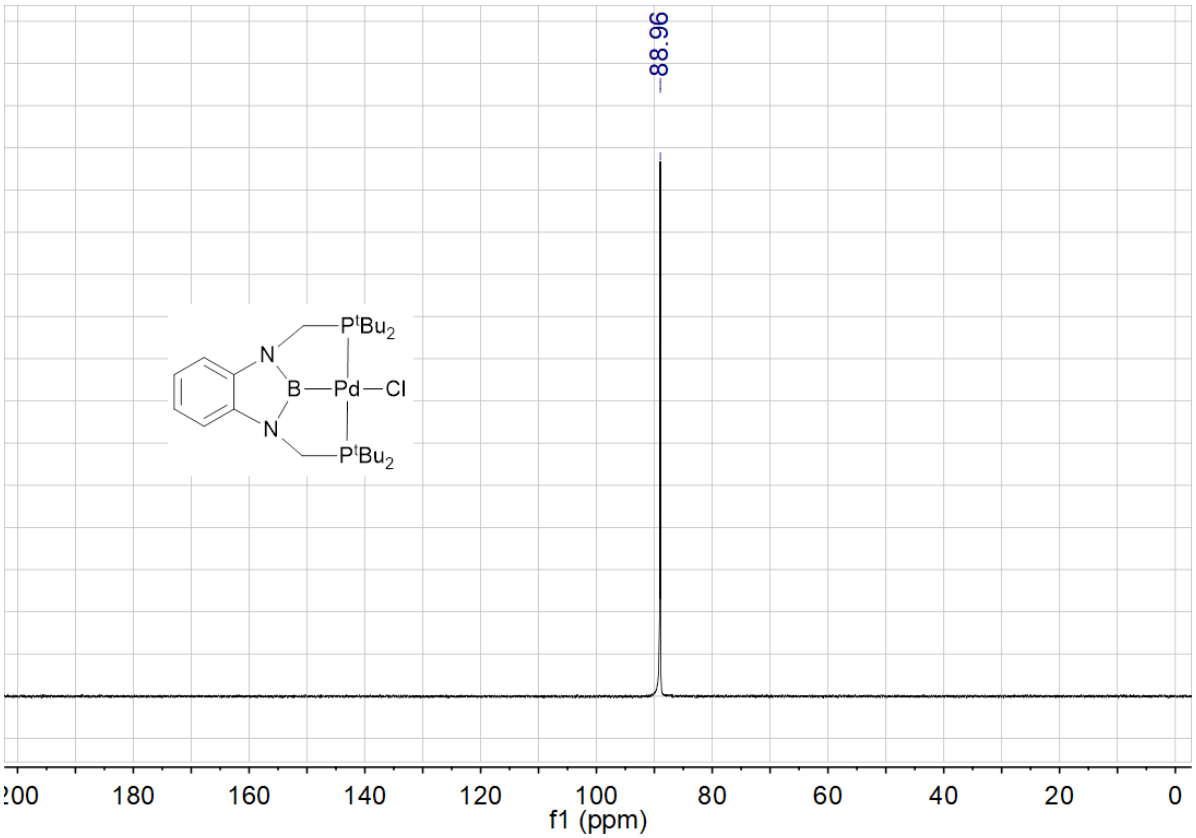

Fig. S3 $^{31}P\{^{1}H\}$ NMR spectrum of complex **1a** (162 MHz, benzene-d_6)

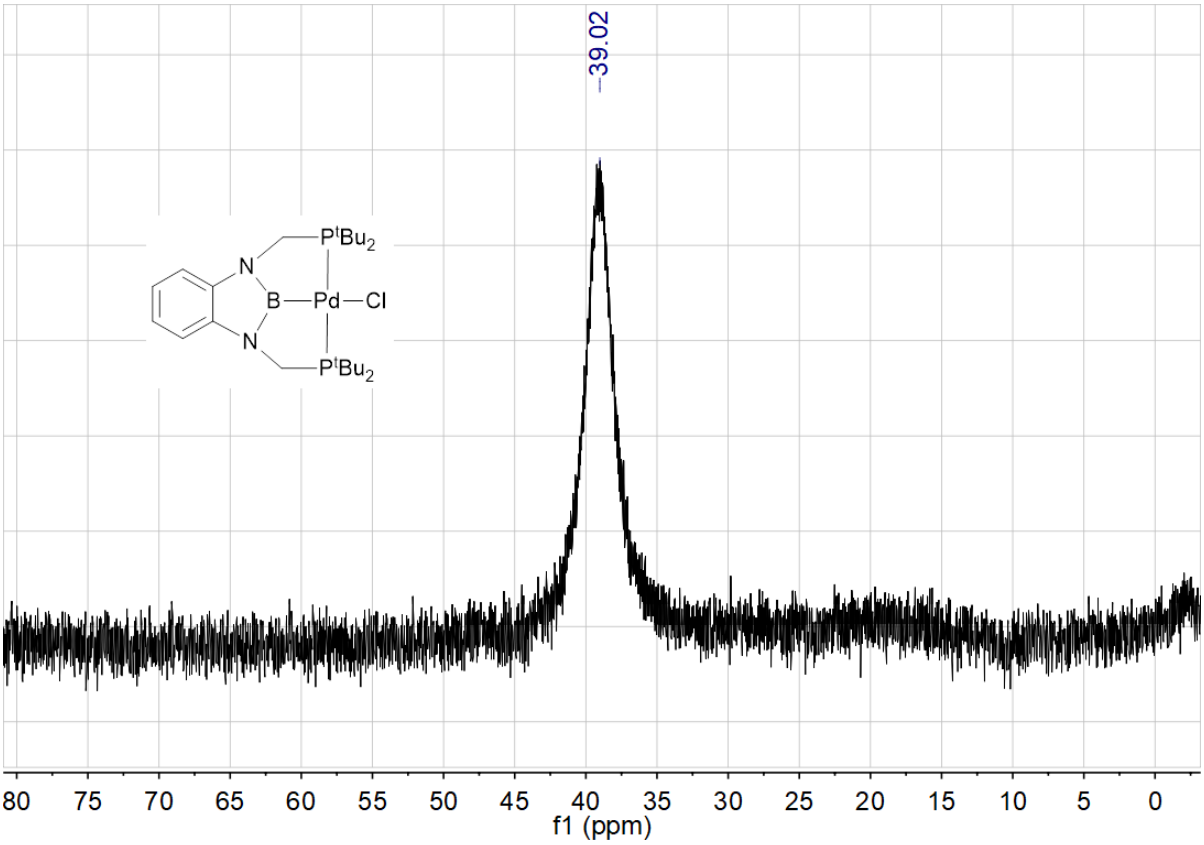

Fig. S4 ^{11}B NMR spectrum of complex **1a** (128 MHz, benzene-d_6)

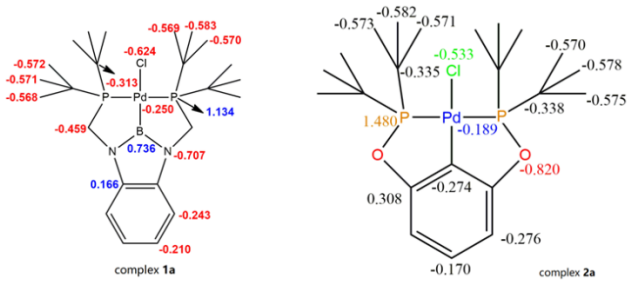

Fig. S5 Natural population analysis (NPA) results for complexes **1a** and **2a**

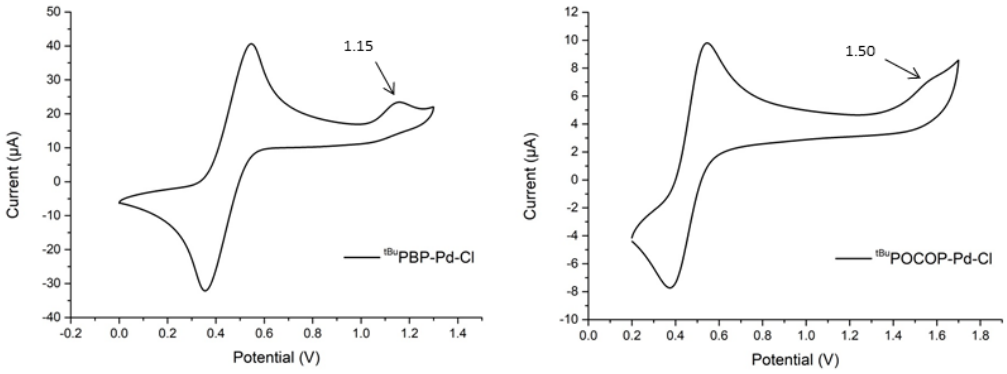

Fig. S6 Cyclic voltammograms of complexes **1a** and **2a**. Left: a mixture of **1a** and ferrocene; right: a mixture of **2a** and ferrocene. The measurements were carried out at 298 K in acetonitrile/CH_2Cl_2 (1:1) solutions containing the sample complexes (0.5 mM) and $[Bu_4N][PF_6]$ (0.1 M); scan rate: 100 mV s^{-1}; the potentials were referenced to the Fc/Fc^+.

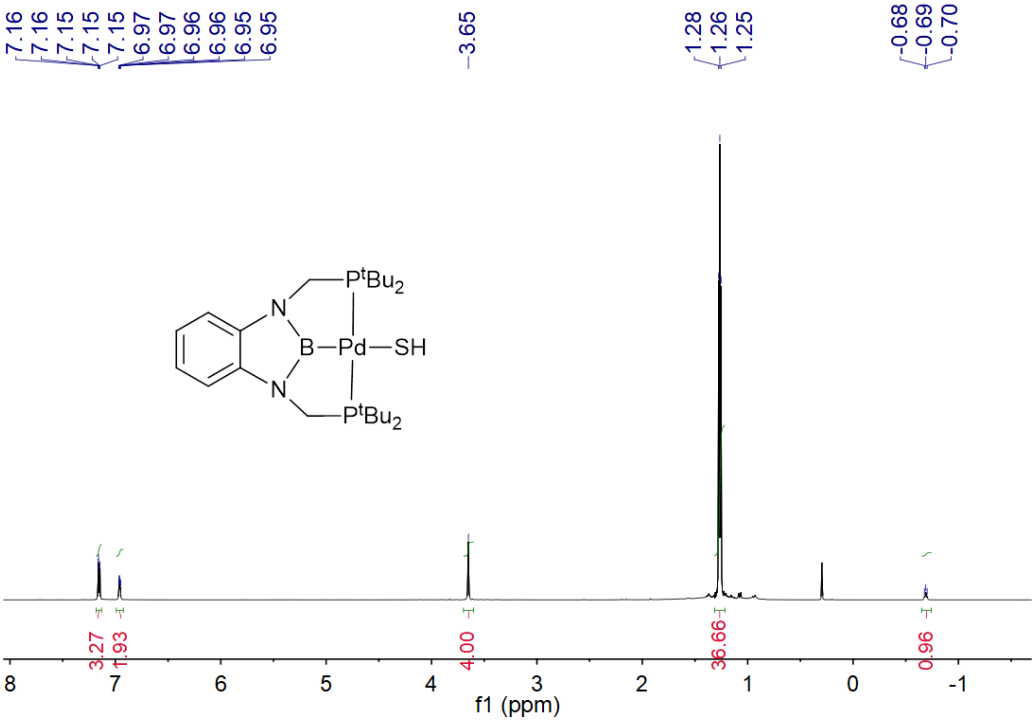

Fig. S7 ^{1}H NMR spectrum of complex **1b** (600 MHz, benzene-d_6)

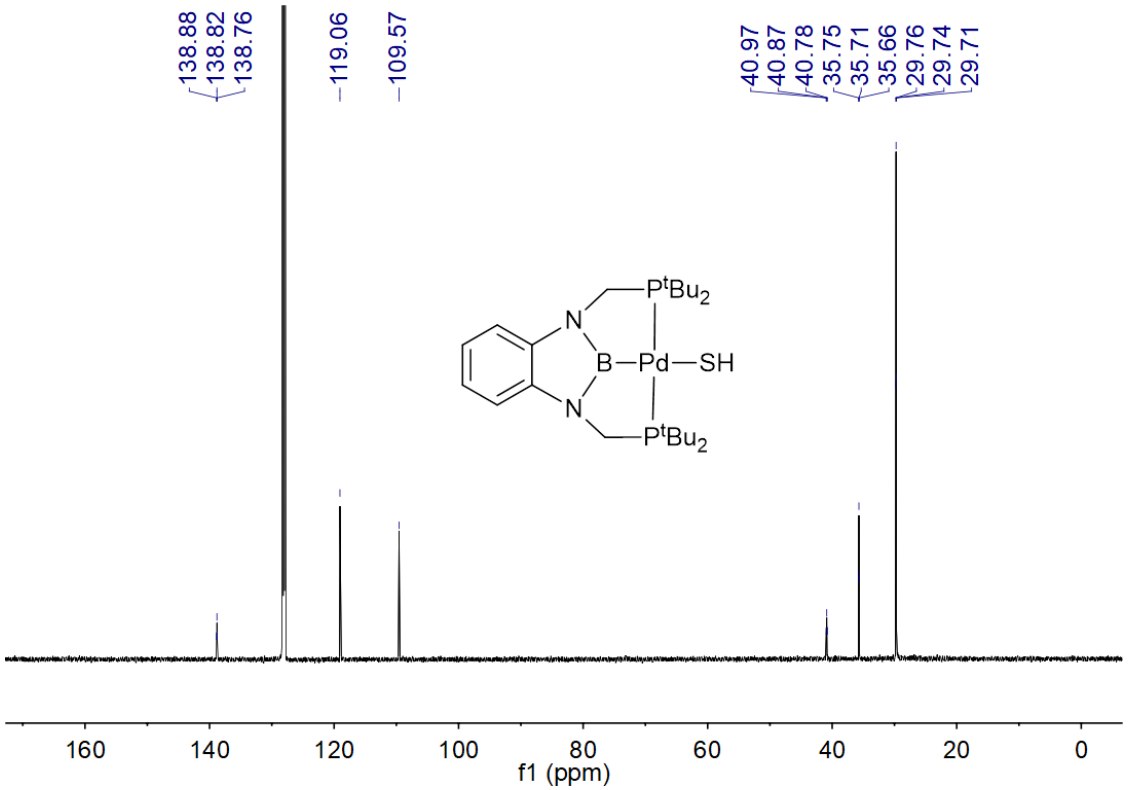

Fig. S8 $^{13}C\{^1H\}$ NMR spectrum of complex **1b** (151 MHz, benzene-d_6)

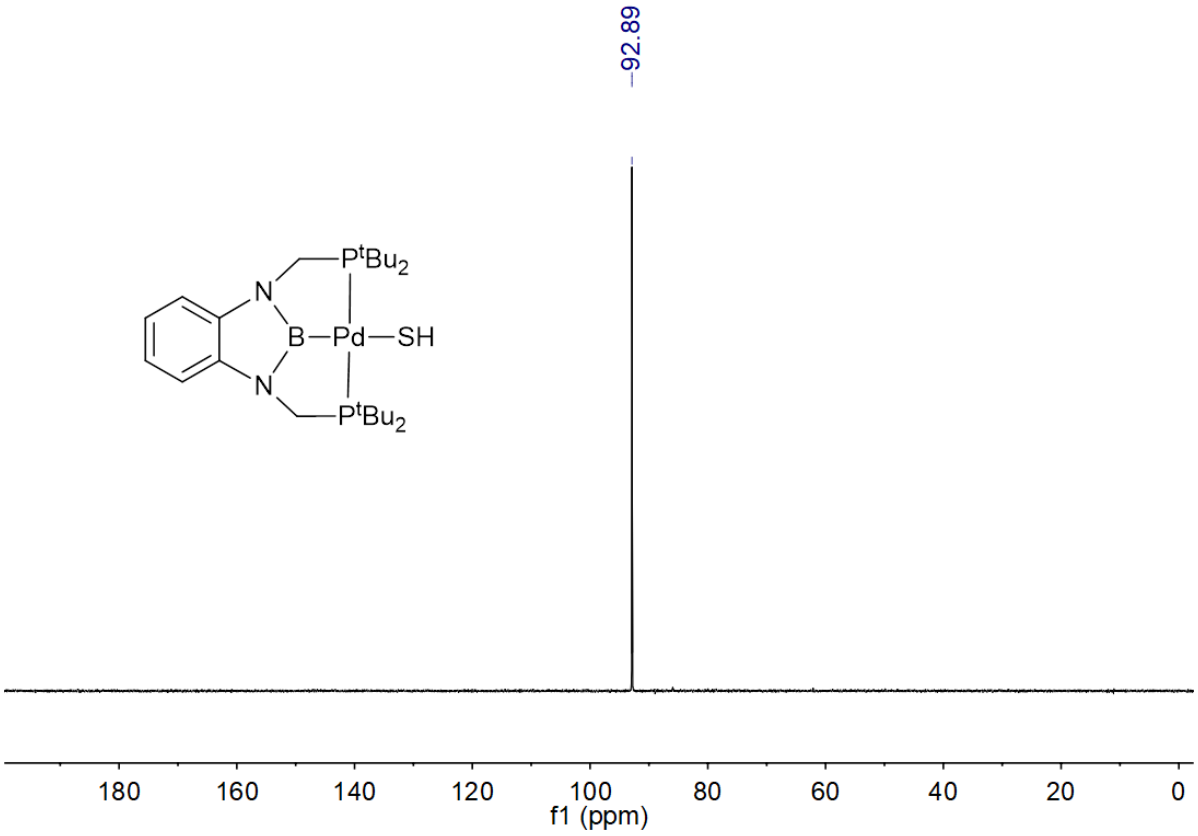

Fig. S9 $^{31}P\{^1H\}$ NMR spectrum of complex **1b** (243 MHz, benzene-d_6)

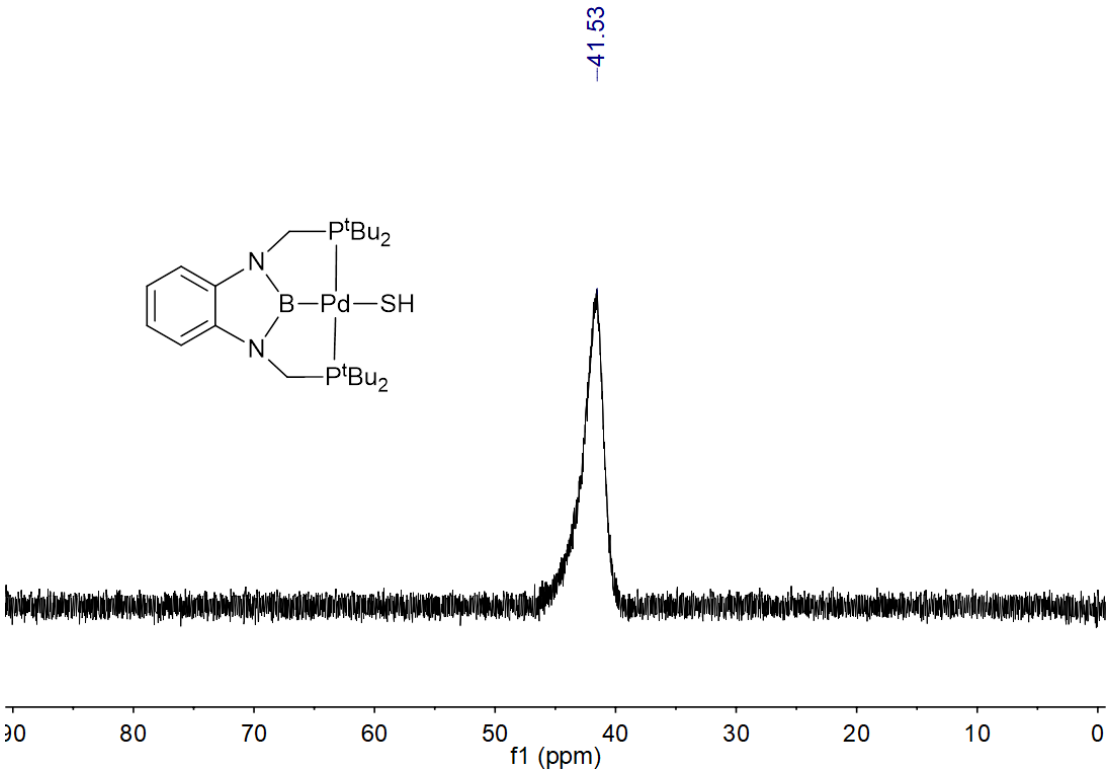

Fig. S10 ^{11}B NMR spectrum of complex **1b** (193 MHz, benzene-d_6)

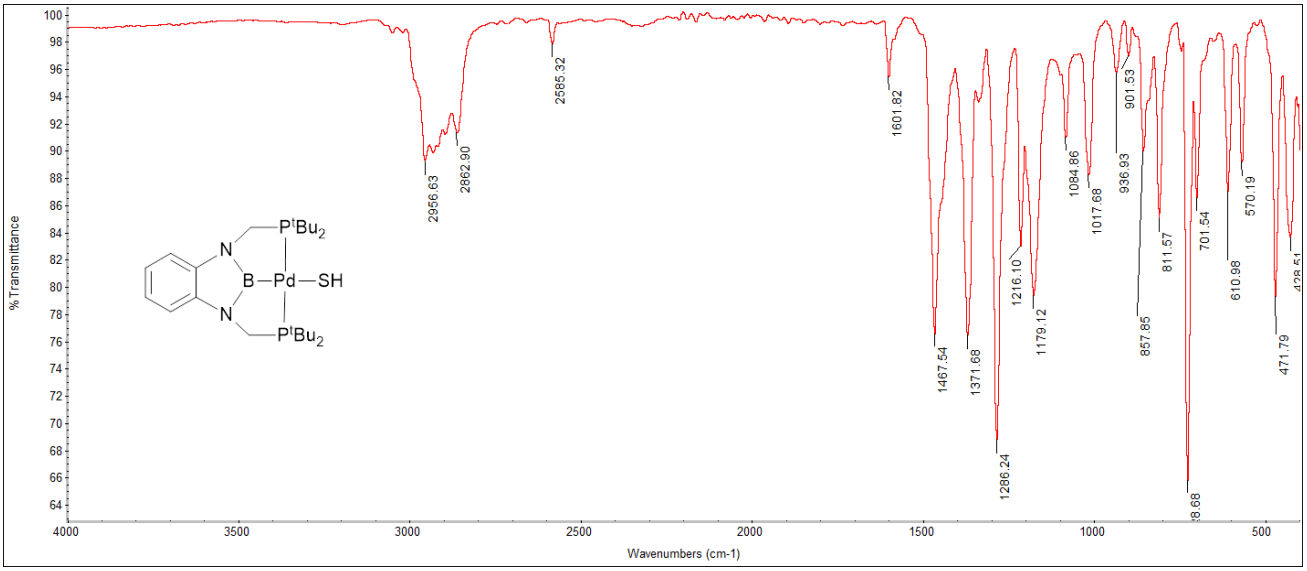

Fig. S11 FTIR spectrum of complex **1b** (KBr disc)

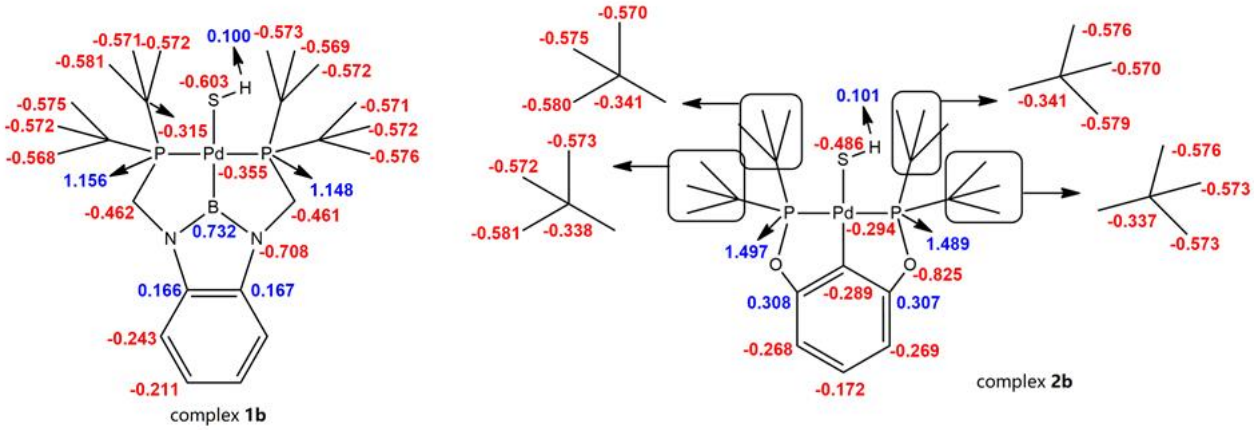

Fig. S12 Natural population analysis (NPA) results for complexes **1b** and **2b**

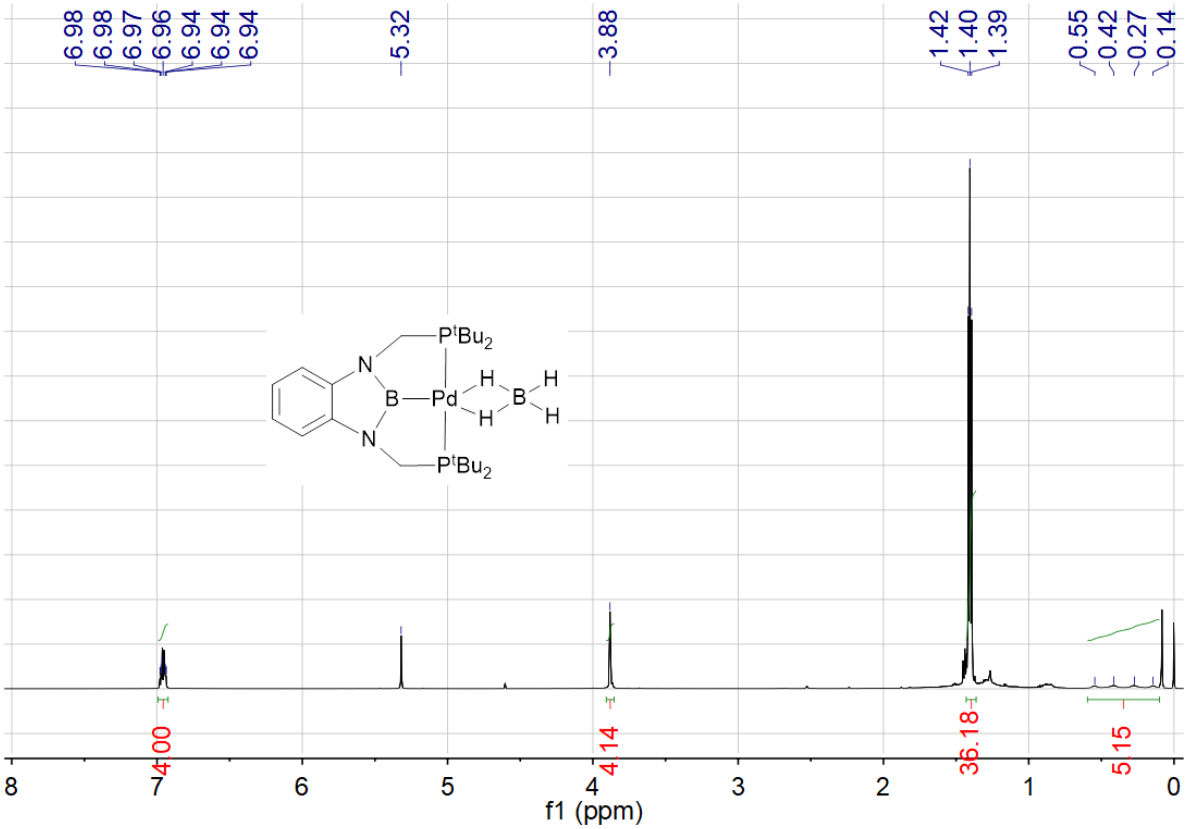

Fig. S13 ^{1}H NMR spectrum of complex **1c** (600 MHz, CD_2Cl_2)

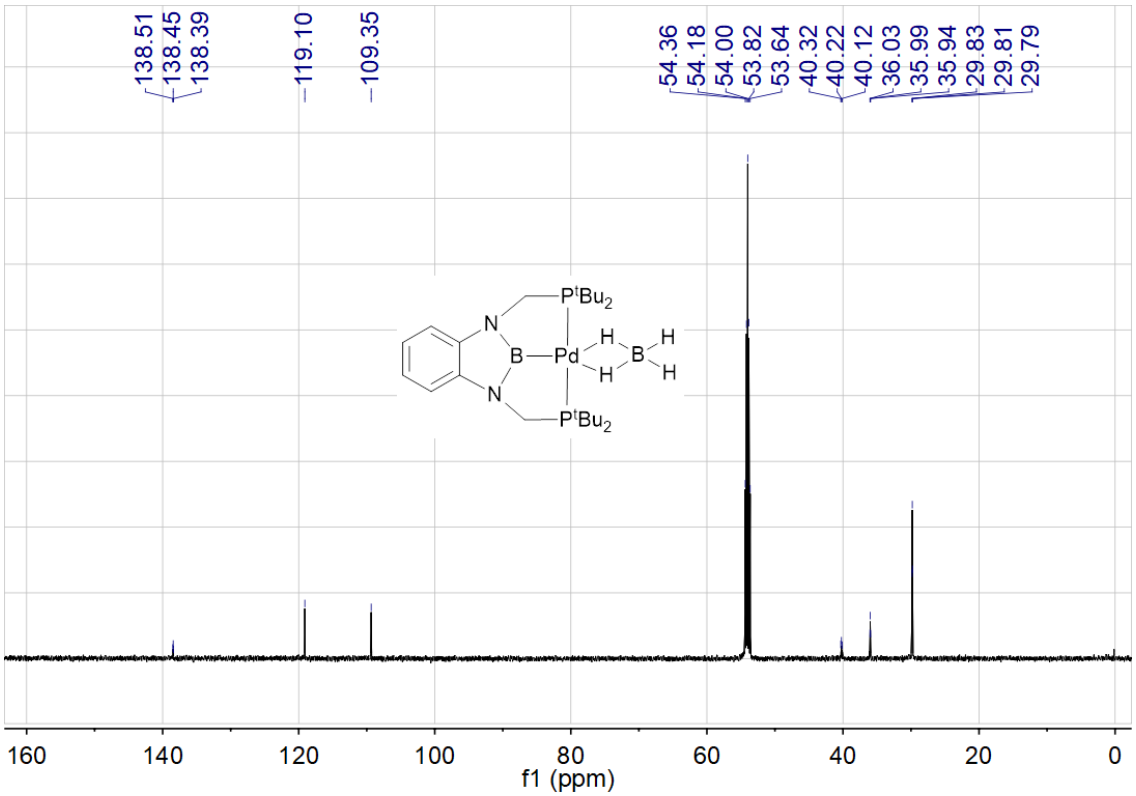

Fig. S14 $^{13}C\{^1H\}$ NMR spectrum of complex **1c** (151 MHz, CD_2Cl_2)

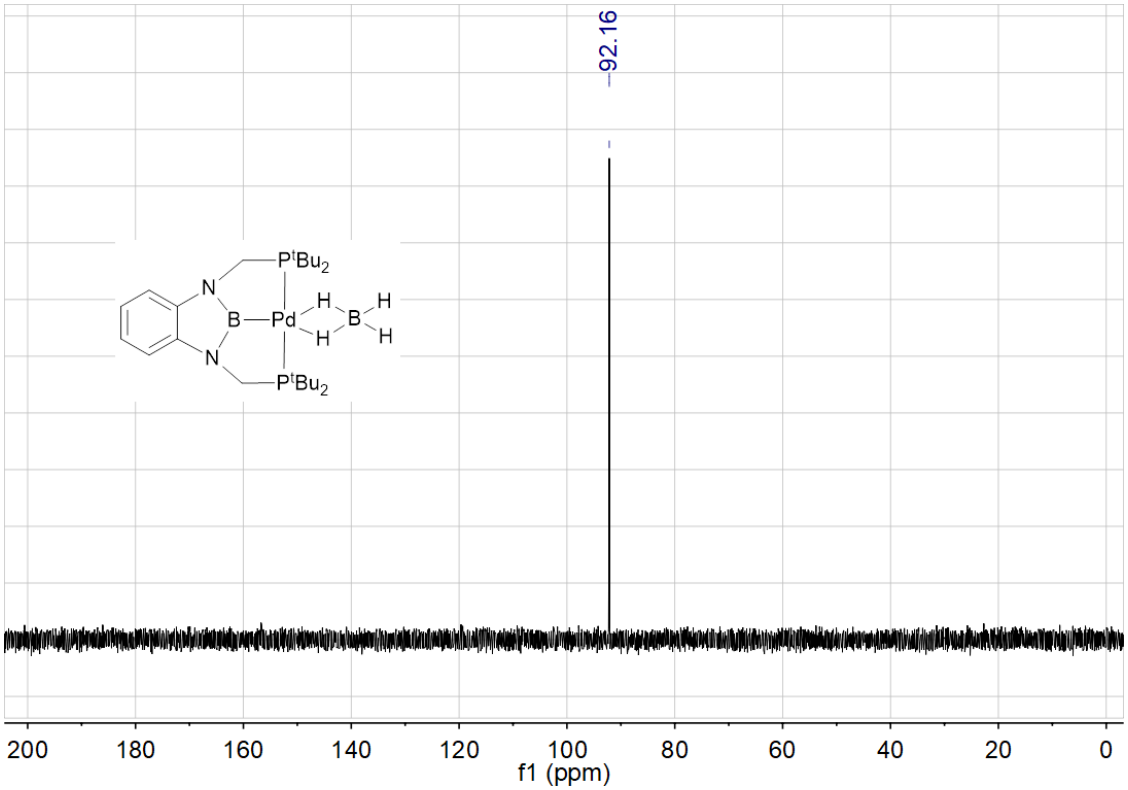

Fig. S15 $^{31}P\{^1H\}$ NMR spectrum of complex **1c** (162 MHz, benzene-d_6)

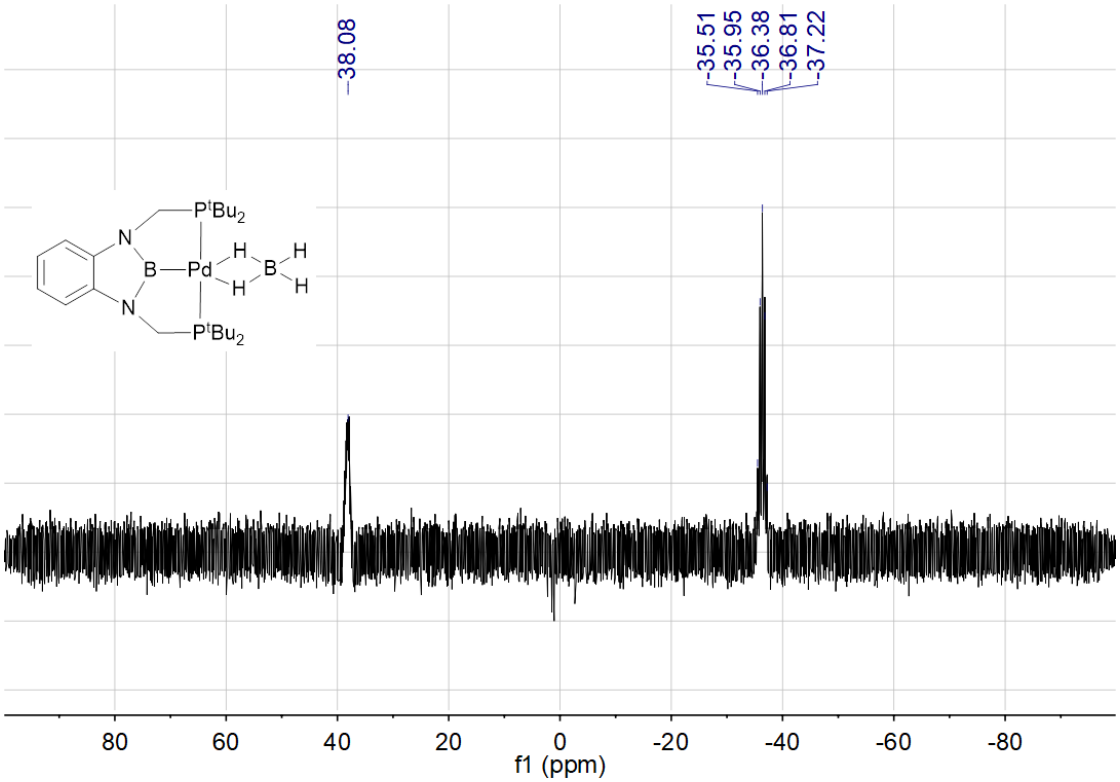

Fig. S16 ^{11}B NMR spectrum of complex **1c** (193 MHz, CD_2Cl_2)

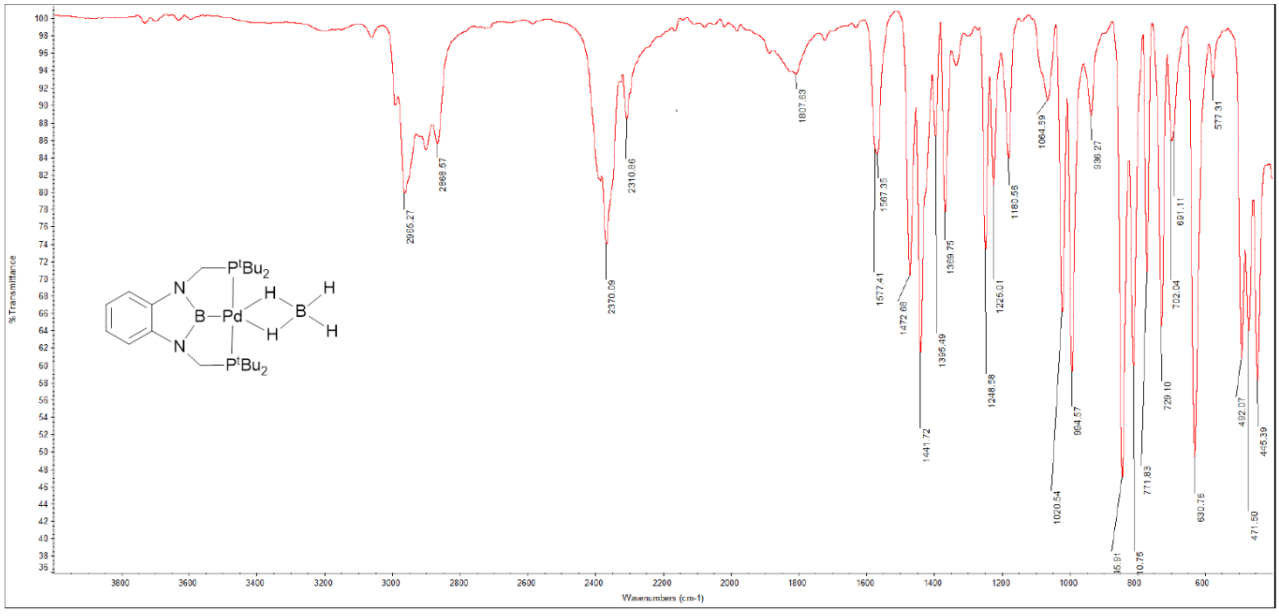

Fig. S17 FTIR spectrum of complex **1c** (KBr disc)

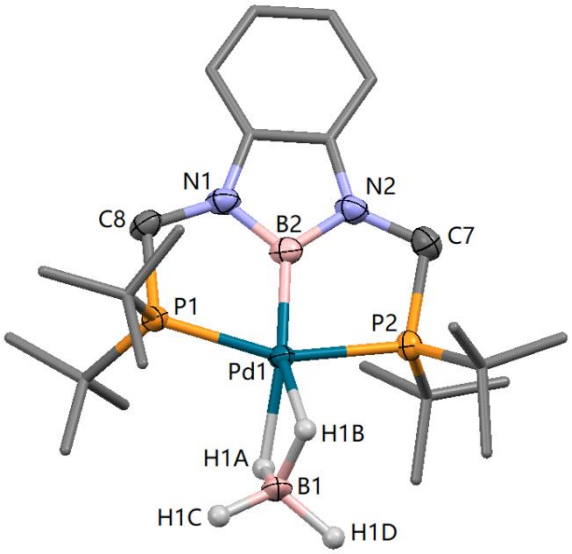

Fig. S18 The molecular image of complex **1c** (for clarity, hydrogen atoms except that attached to boron atom are omitted; the phenyl and *tert*-butyl groups are simplified). Selected bond lengths (Å) and angles (˚): Pd1-B2, 1.987(4); Pd1…B1, 2.4689(19); Pd1-P1, 2.3348(7); Pd1-P2, 2.3371(7); Pd1-H1A, 2.04(6); Pd1-H1B, 2.00(6); B1-H1A, 1.27(6); B1-H1B, 1.09(6); B1-H1C, 1.17(6); B1-H1D, 1.14(6); N1-B2-Pd1, 127.4(3); N2-B2-Pd1, 126.8(2); N1-B2-N2, 105.8(3); P1-Pd1-P2, 155.75(3).

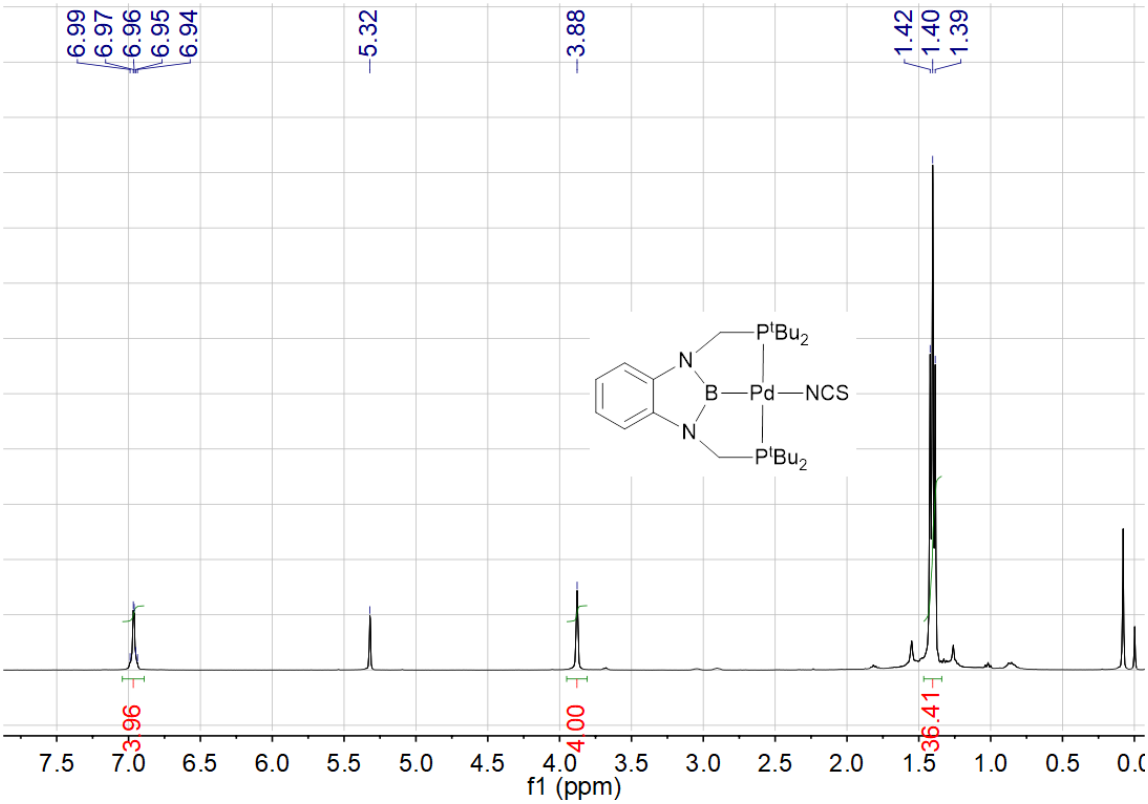

Fig. S19 ^{1}H NMR spectrum of complex **1d** (400 MHz, CD_2Cl_2)

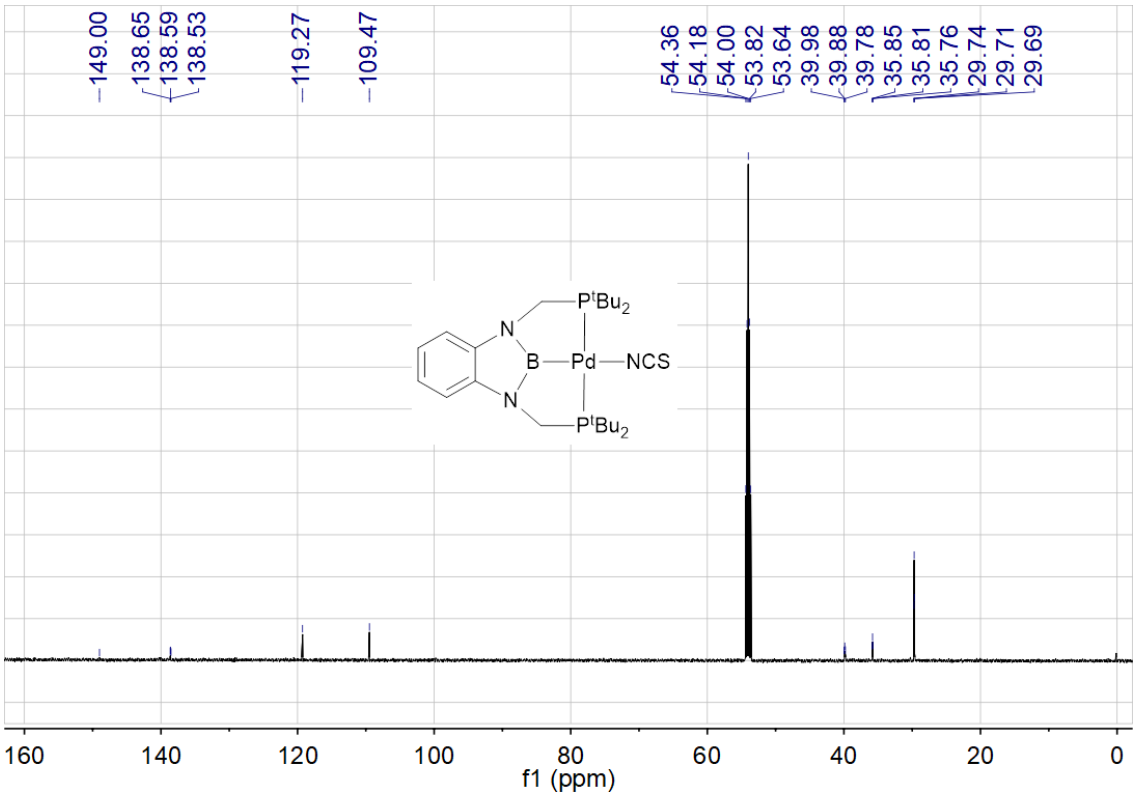

Fig. S20 $^{13}C\{^{1}H\}$ NMR spectrum of complex **1d** (151 MHz, CD_2Cl_2)

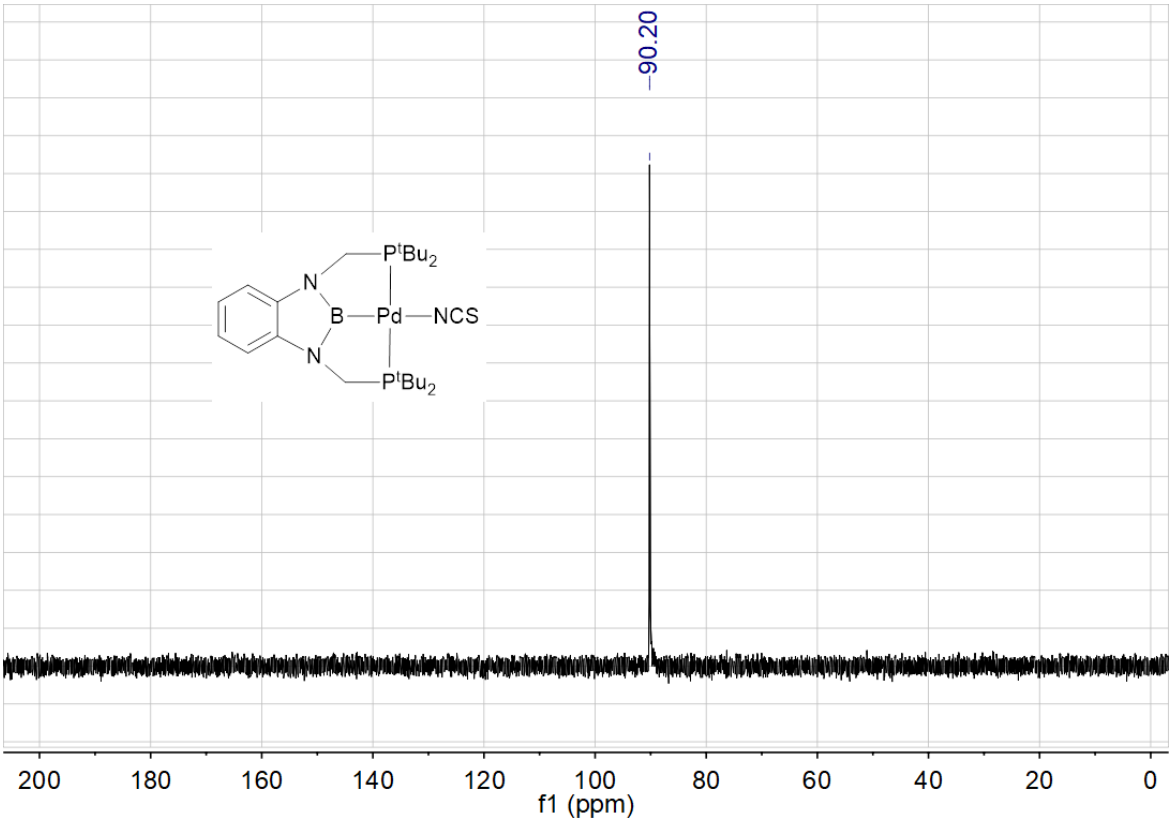

Fig. S21 $^{31}P\{^{1}H\}$ NMR spectrum of complex **1d** (162 MHz, benzene-d_6)

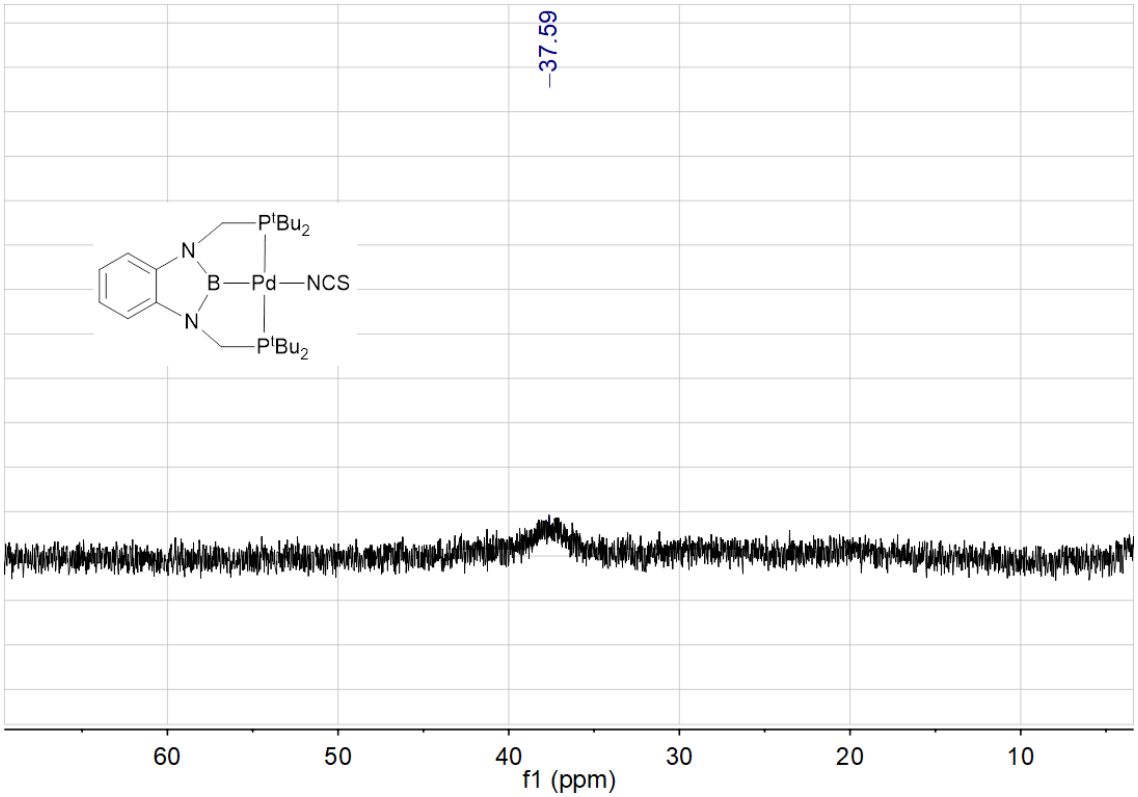

Fig. S22 ^{11}B NMR spectrum of complex **1d** (128 MHz, benzene-d_6)

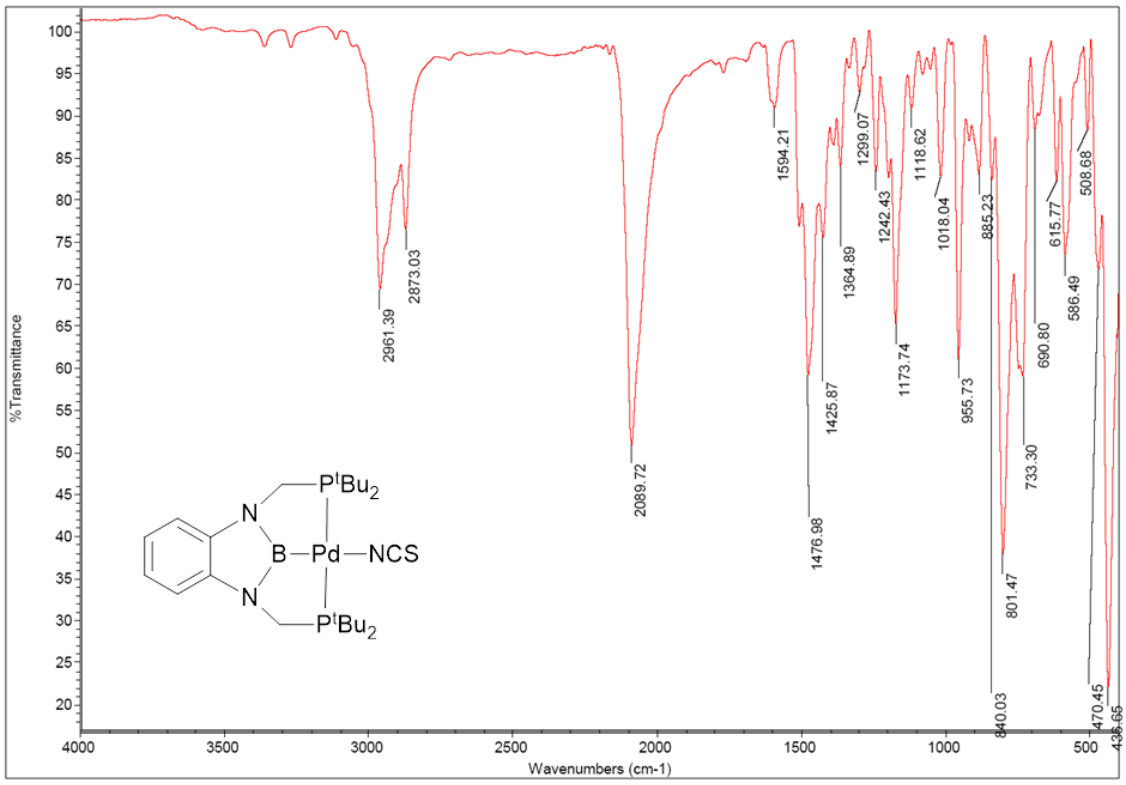

Fig. S23 FTIR spectrum of complex **1d** (KBr disc)

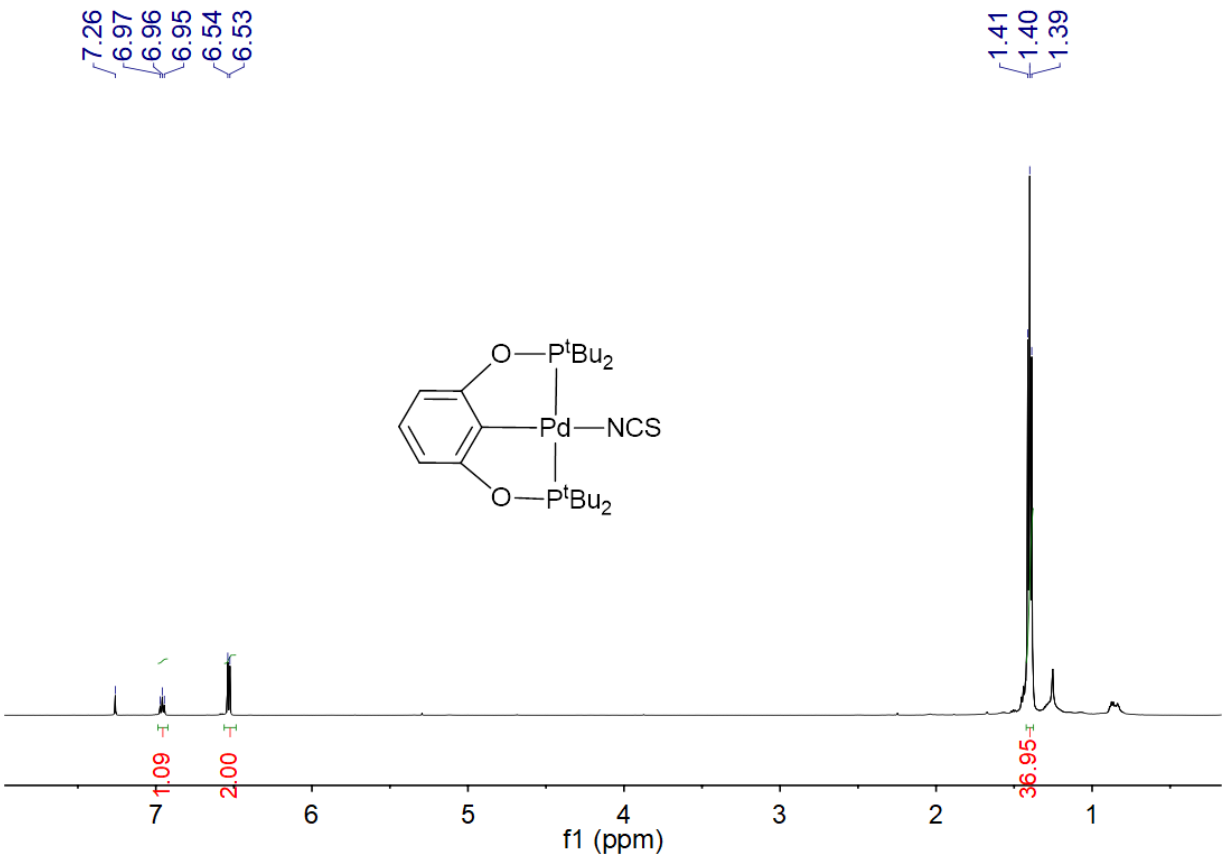

Fig. S24 ^{1}H NMR spectrum of complex **2d** (600 MHz, $CDCl_3$)

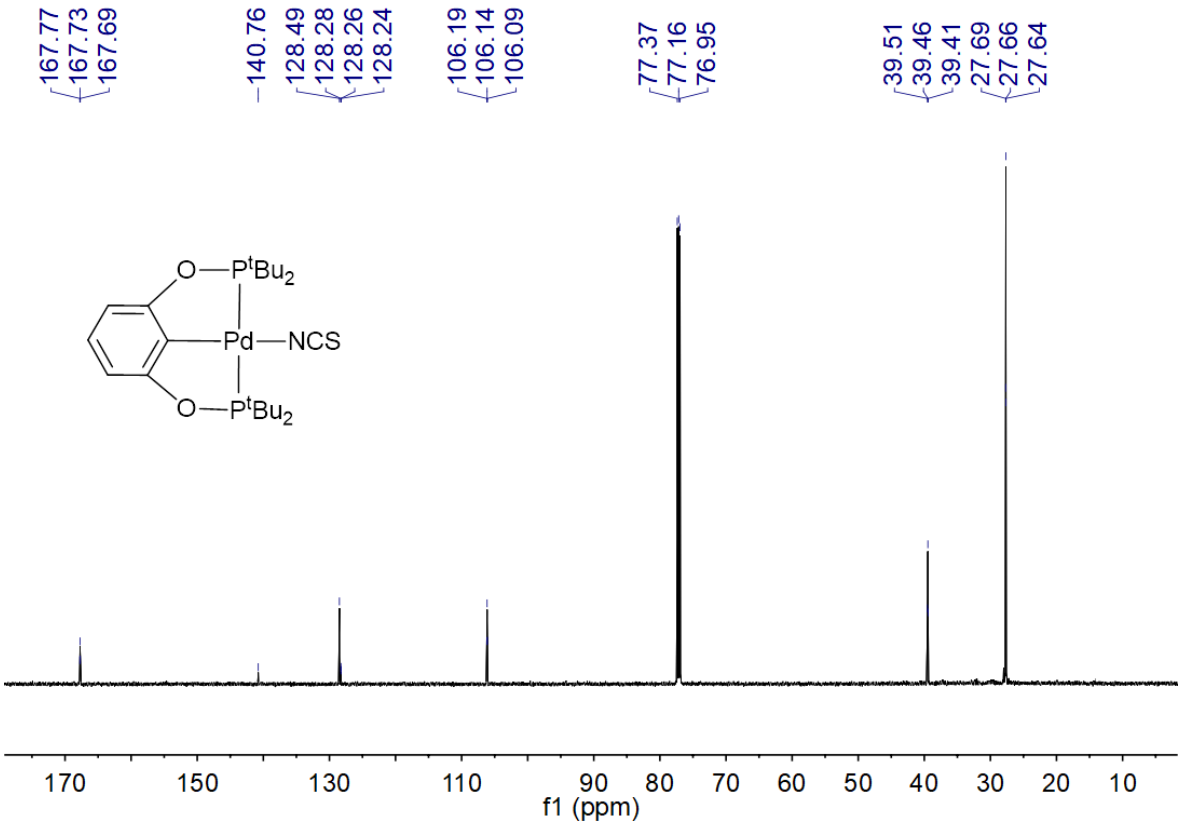

Fig. S25 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2d** (151 MHz, $CDCl_3$)

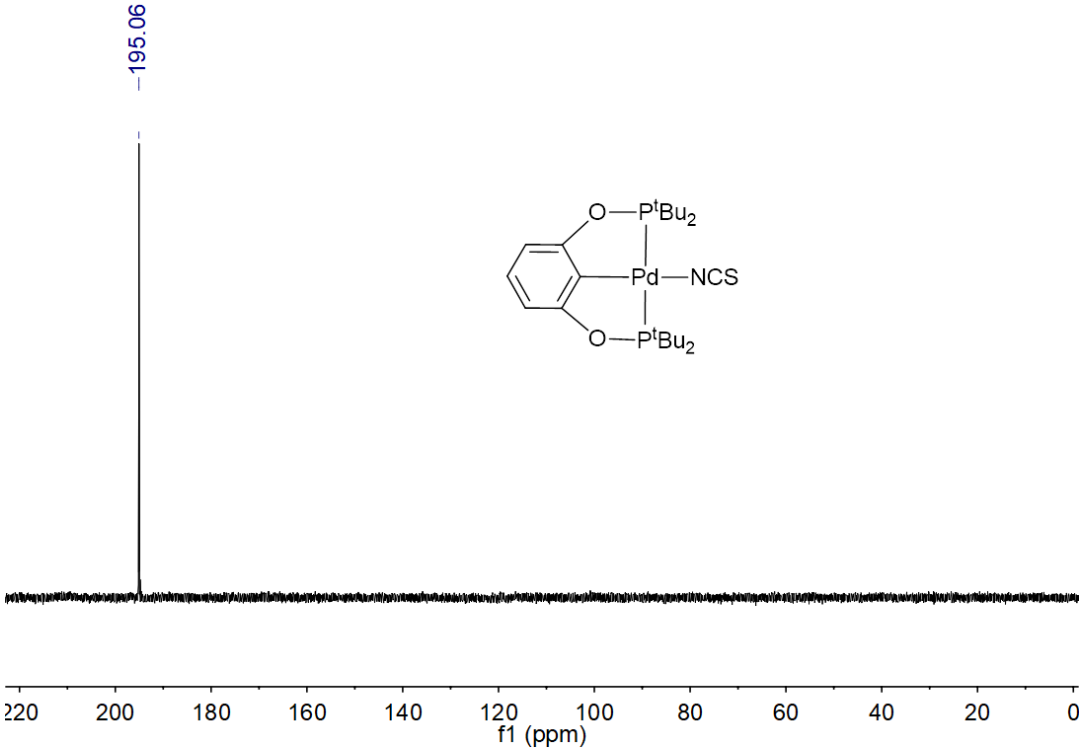

Fig. S26 $^{31}P\{^1H\}$ NMR spectrum of complex **2d** (243 MHz, $CDCl_3$)

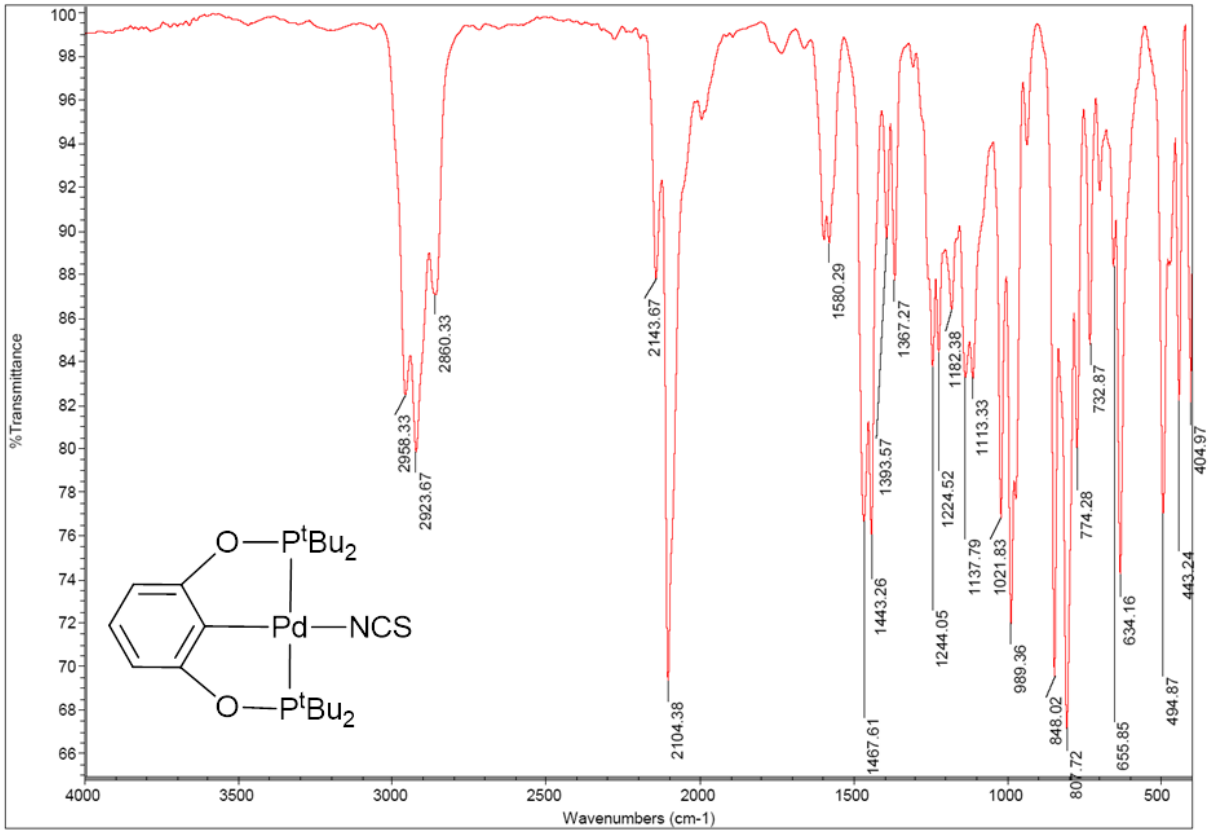

Fig. S27 FTIR spectrum of complex **2d** (KBr disc)

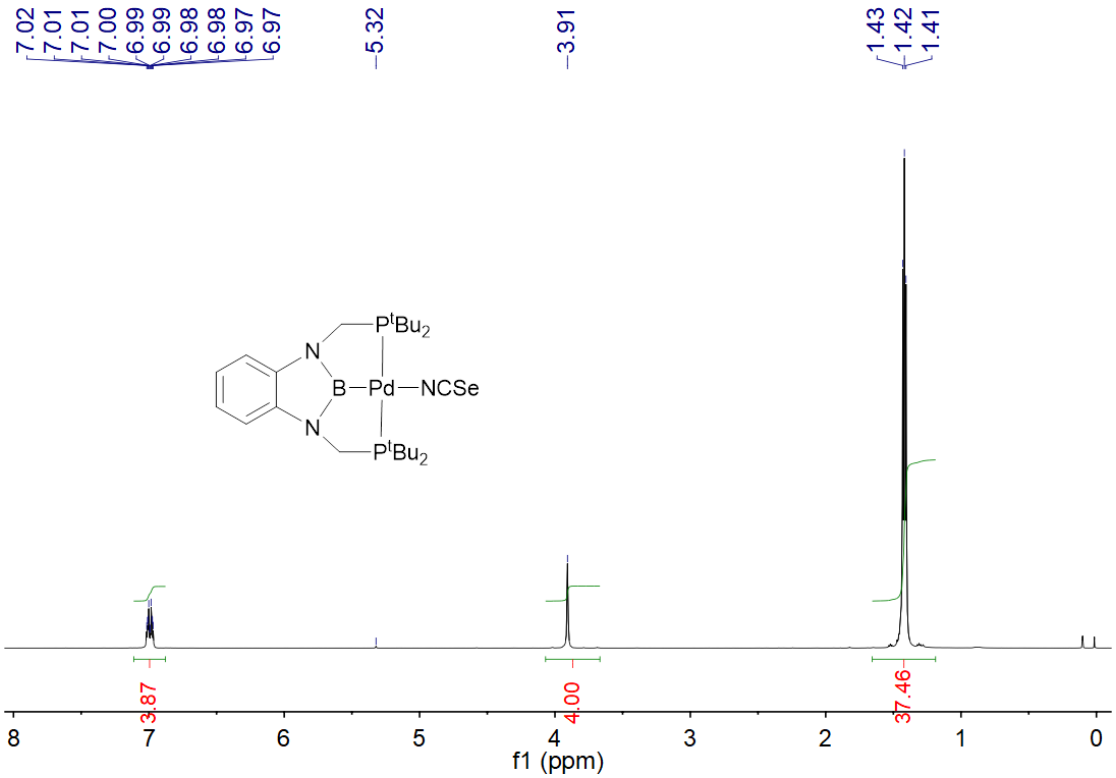

Fig. S28 ^{1}H NMR spectrum of complex **1e** (600 MHz, CD_2Cl_2)

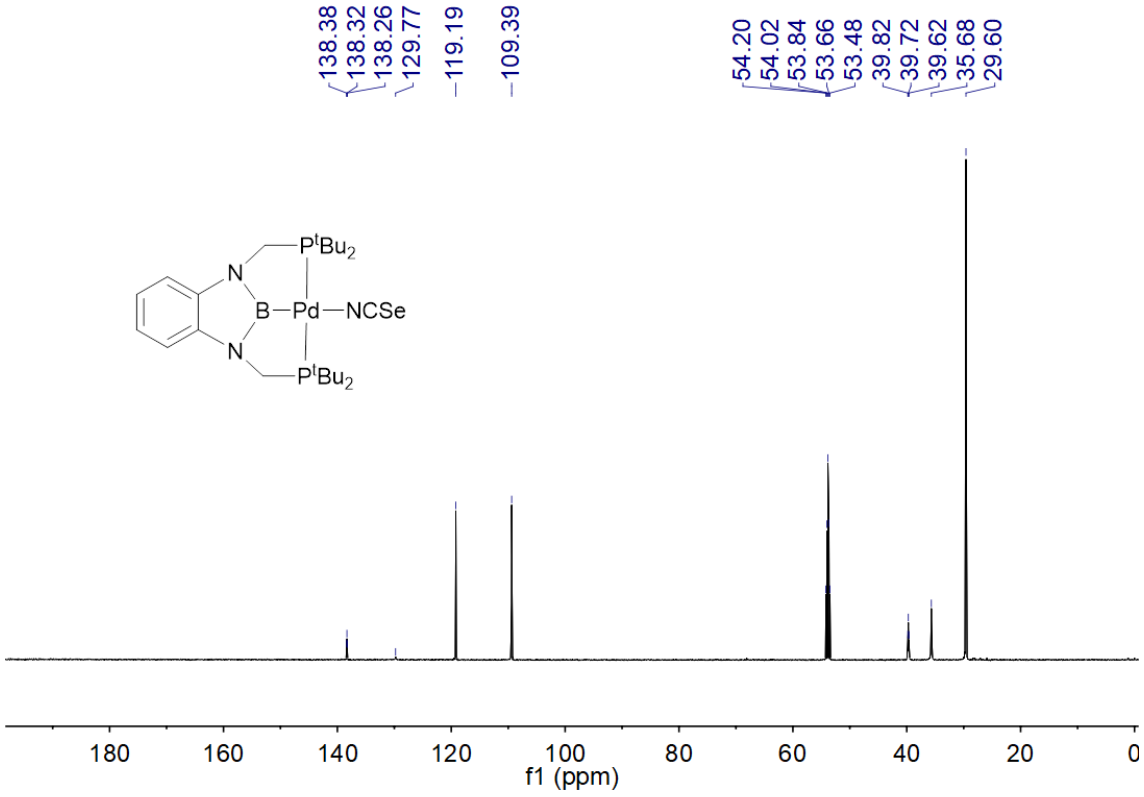

Fig. S29 ^{13}C{^{1}H} NMR spectrum of complex **1e** (151 MHz, CD_2Cl_2)

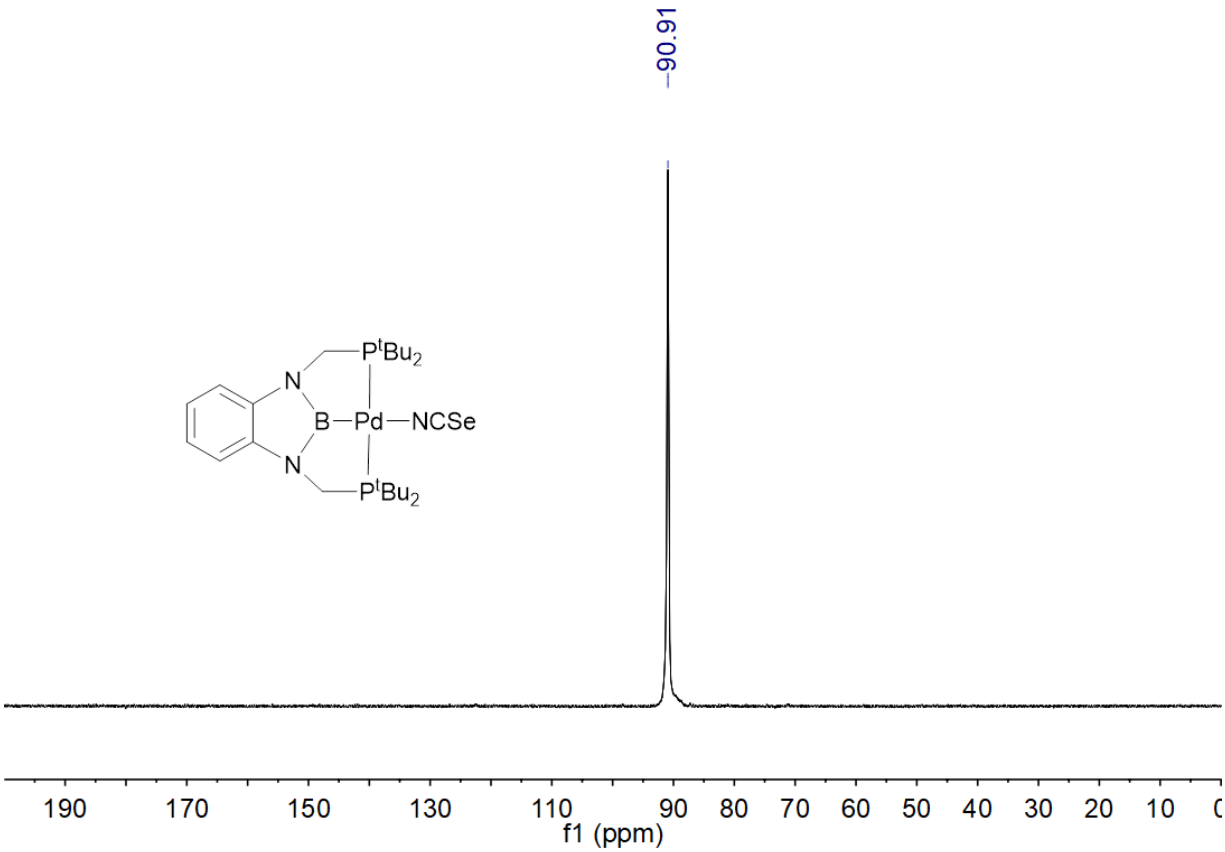

Fig. S30 $^{31}P\{^1H\}$ NMR spectrum of complex **1e** (243 MHz, CD_2Cl_2)

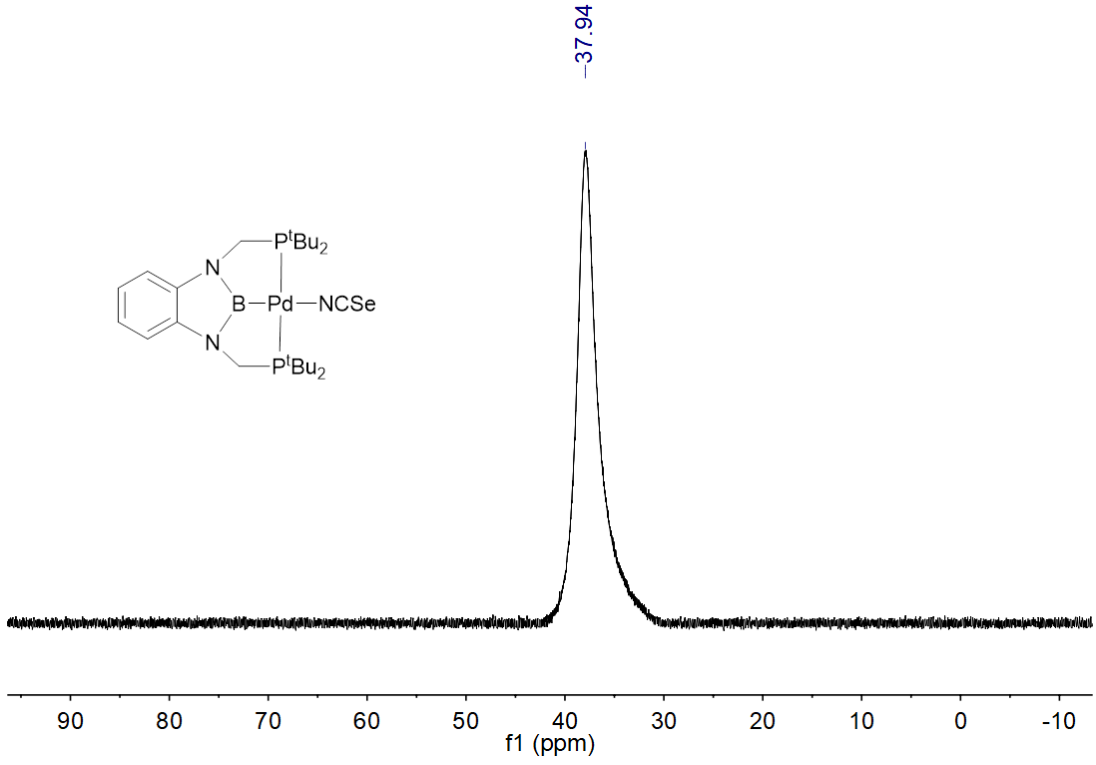

Fig. S31 ^{11}B NMR spectrum of complex **1e** (193 MHz, CD_2Cl_2)

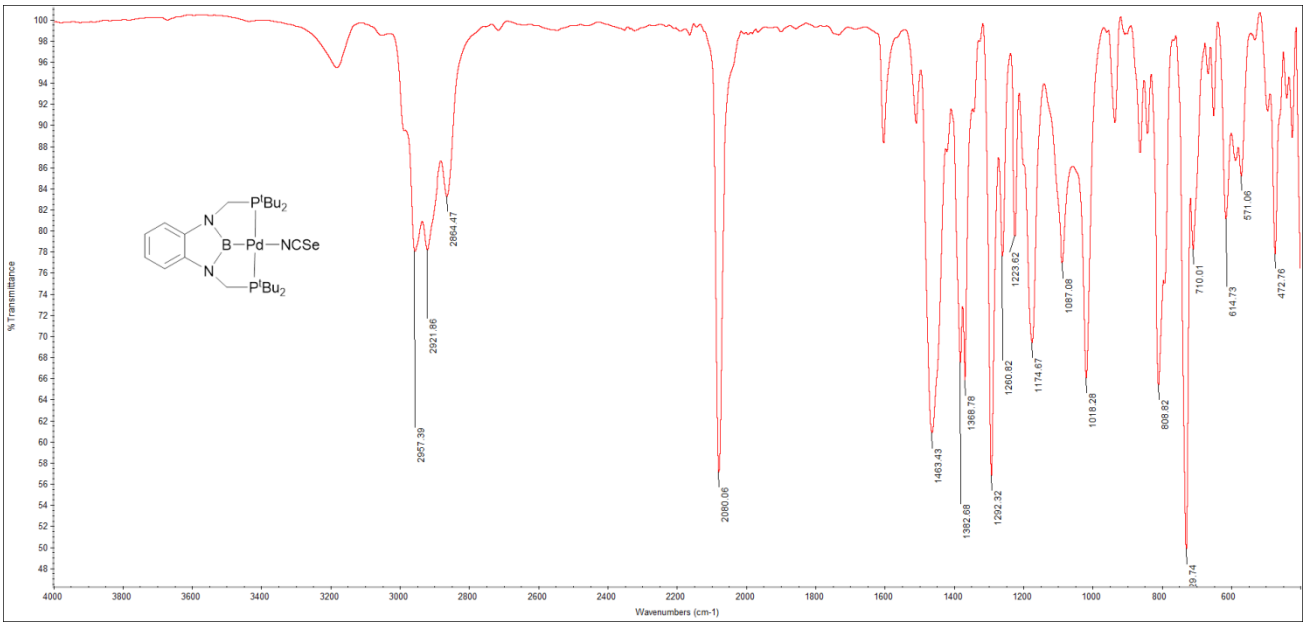

Fig. S32 FTIR spectrum of complex **1e** (KBr disc)

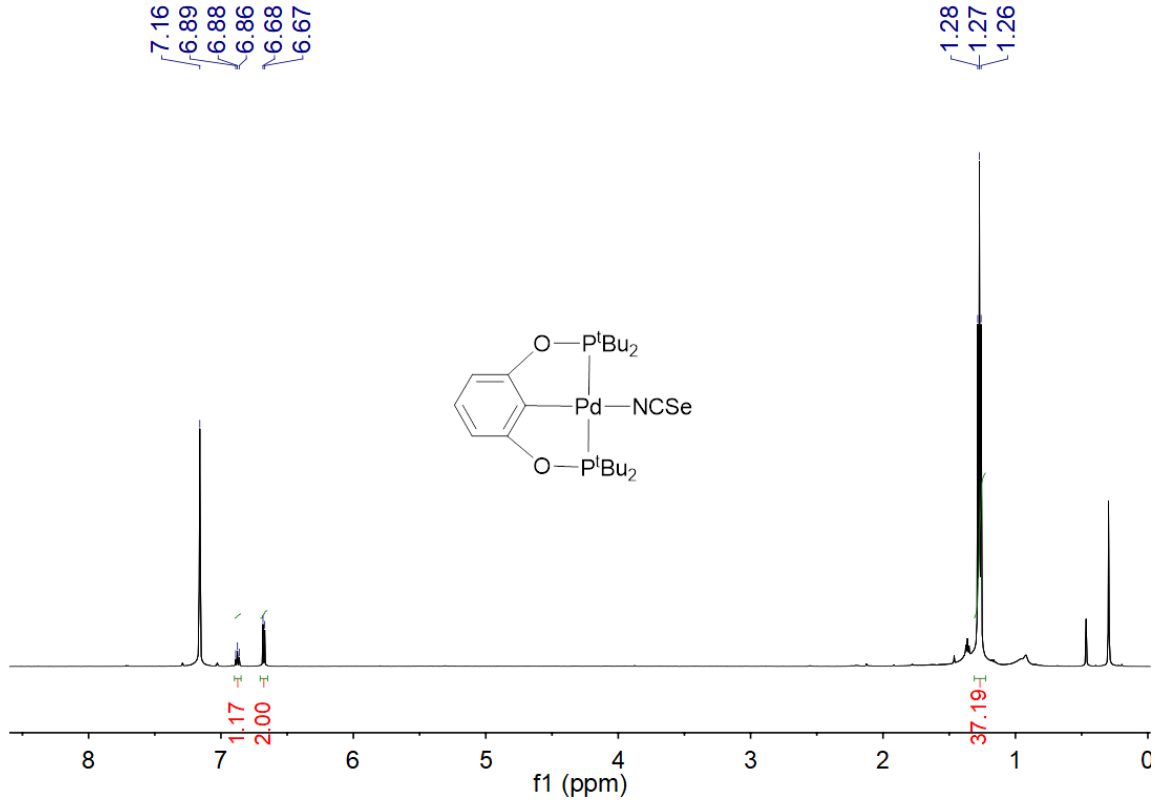

Fig. S33 ^{1}H NMR spectrum of complex **2e** (600 MHz, benzene-d_6)

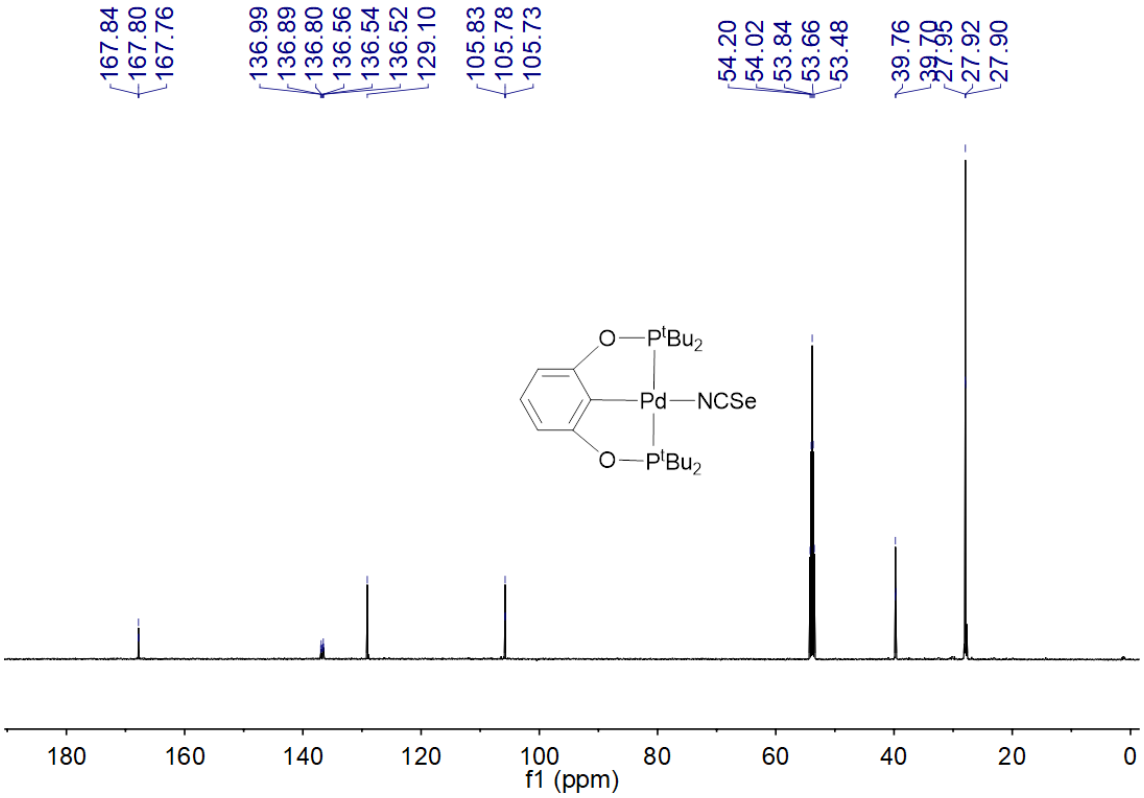

Fig. S34 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2e** (151 MHz, CD_2Cl_2)

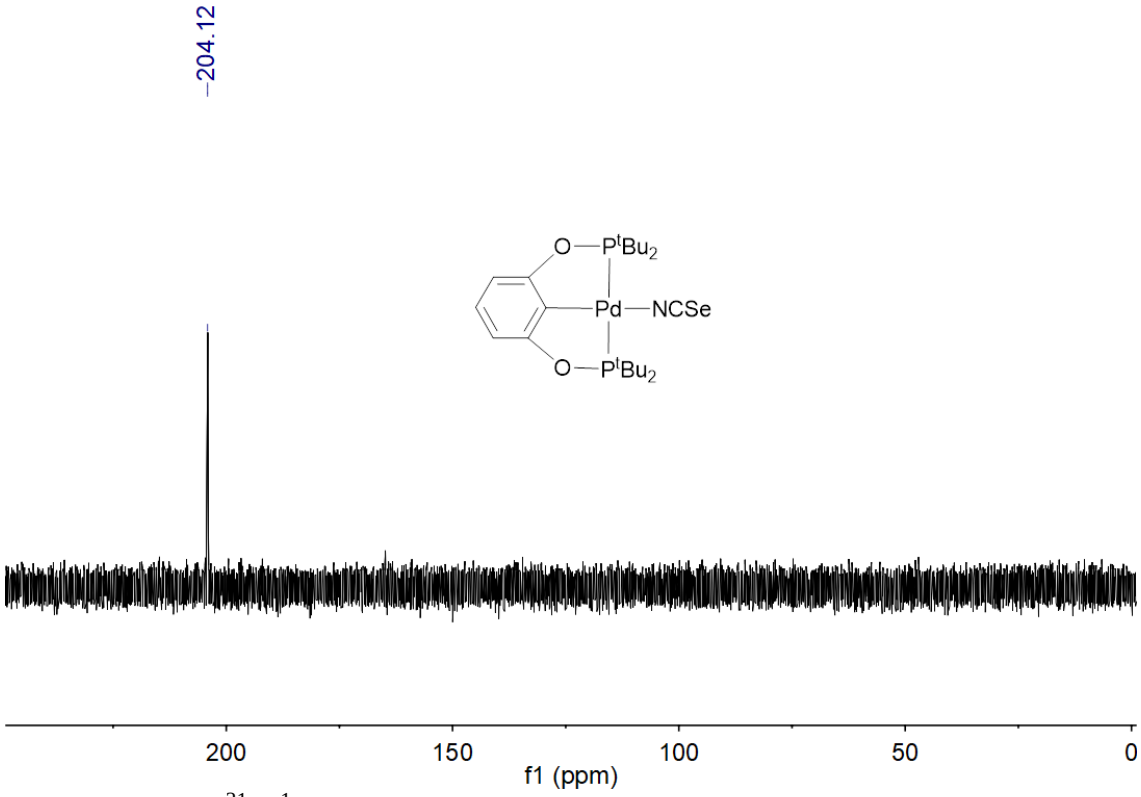

Fig. S35 $^{31}P\{^{1}H\}$ NMR spectrum of complex **2e** (243 MHz, benzene-d_6)

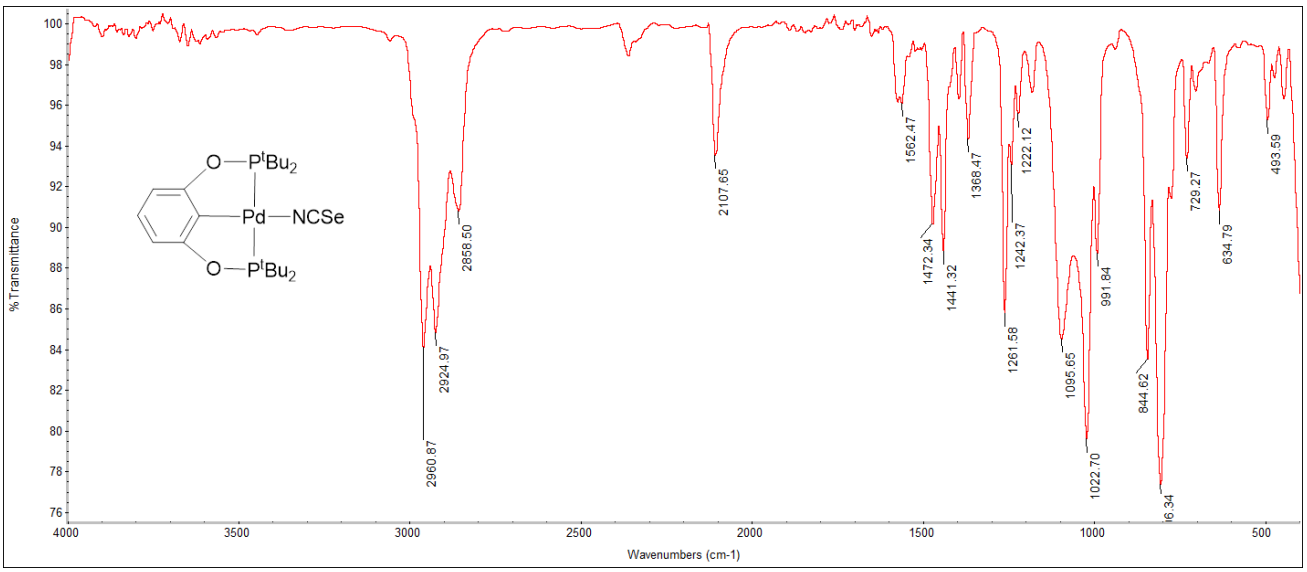

Fig. S36 FTIR spectrum of complex **2e** (KBr disc)

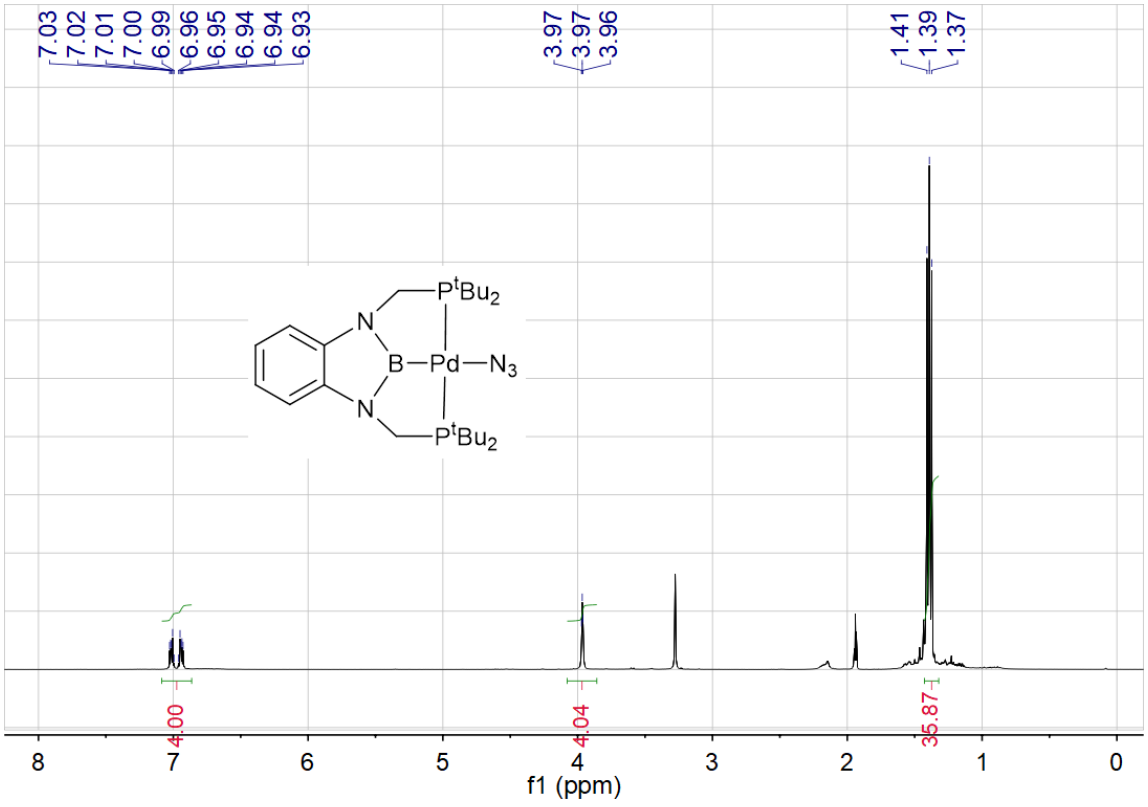

Fig. S37 ^{1}H NMR spectrum of complex **1f** (400 MHz, CD_3CN)

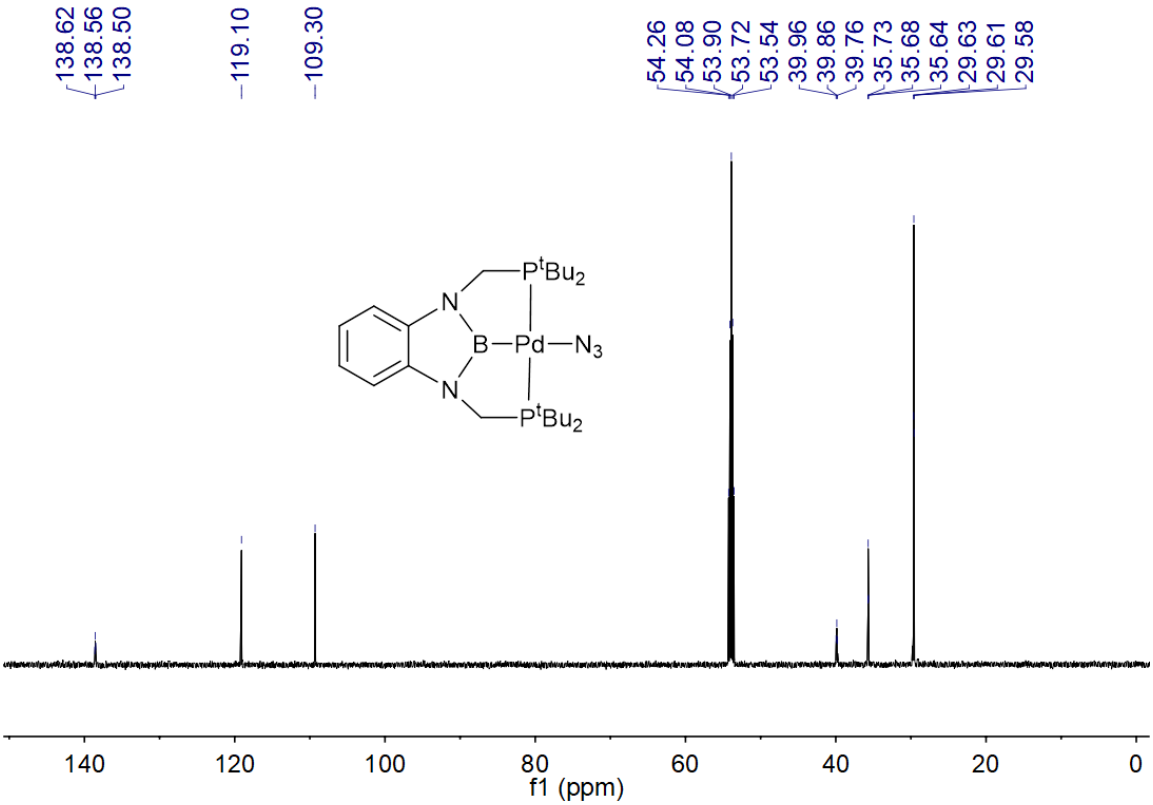

Fig. S38 $^{13}C\{^1H\}$ NMR spectrum of complex **1f** (151 MHz, CD_2Cl_2)

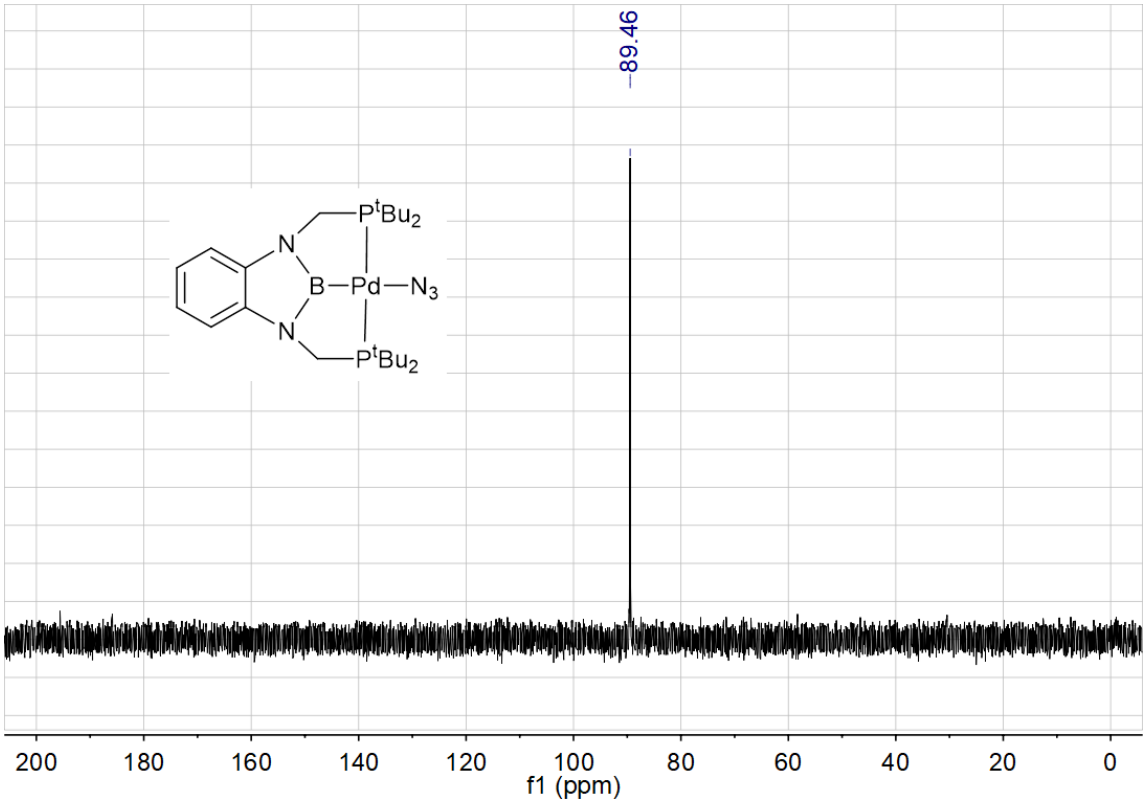

Fig. S39 $^{31}P\{^1H\}$ NMR spectrum of complex **1f** (162 MHz, benzene-d_6)

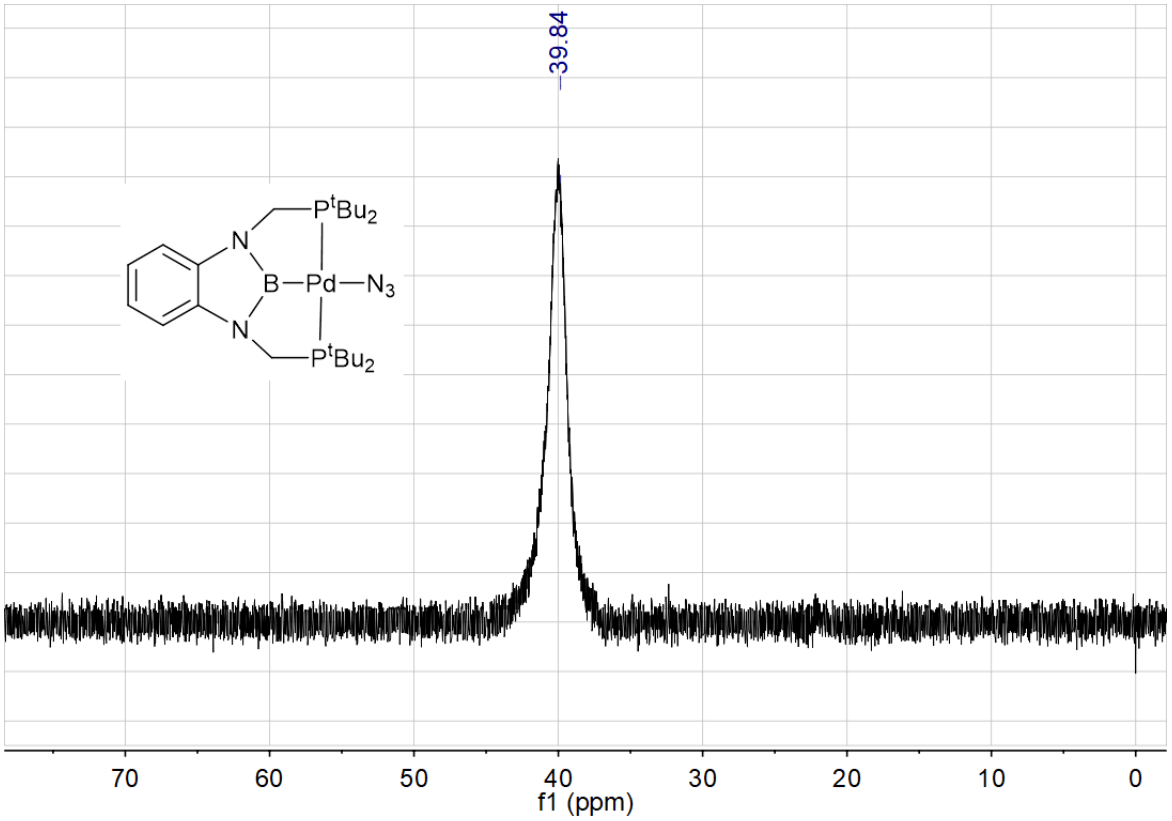

Fig. S40 ^{11}B NMR spectrum of complex **1f** (193 MHz, benzene-d_6)

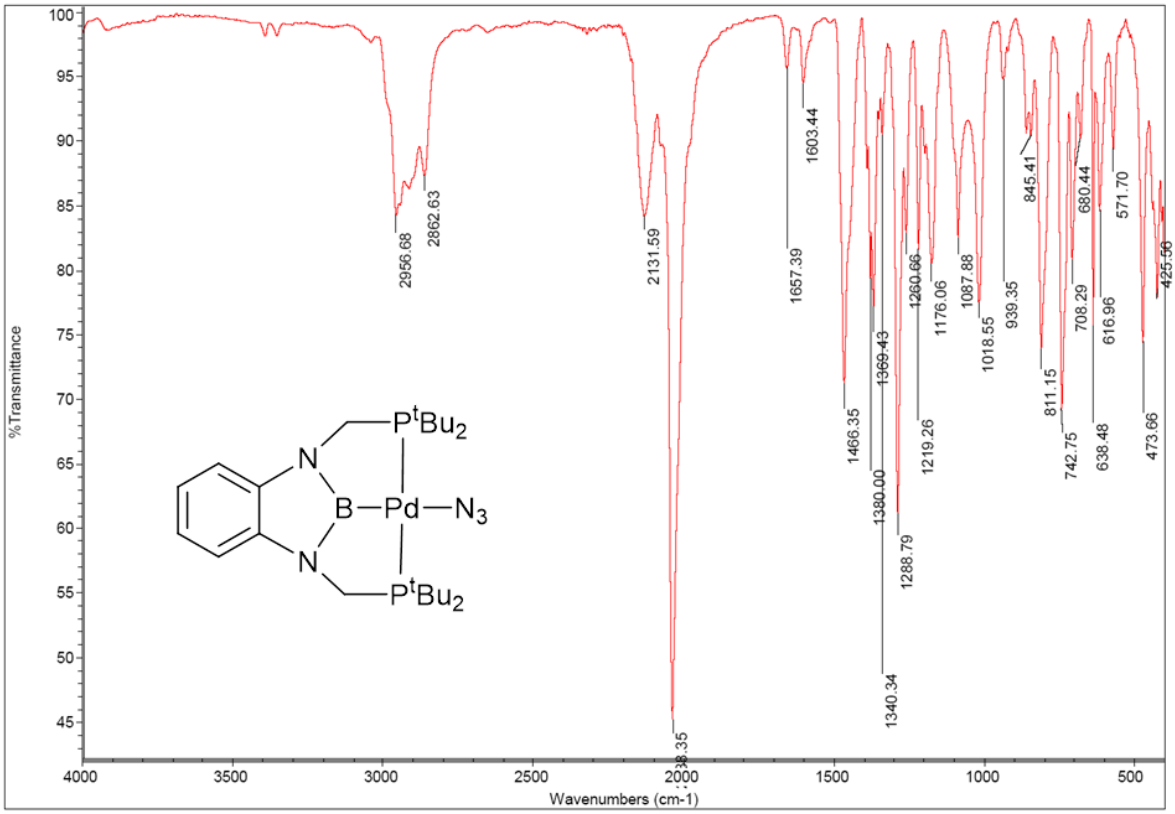

Fig. S41 FTIR spectrum of complex **1f** (KBr disc)

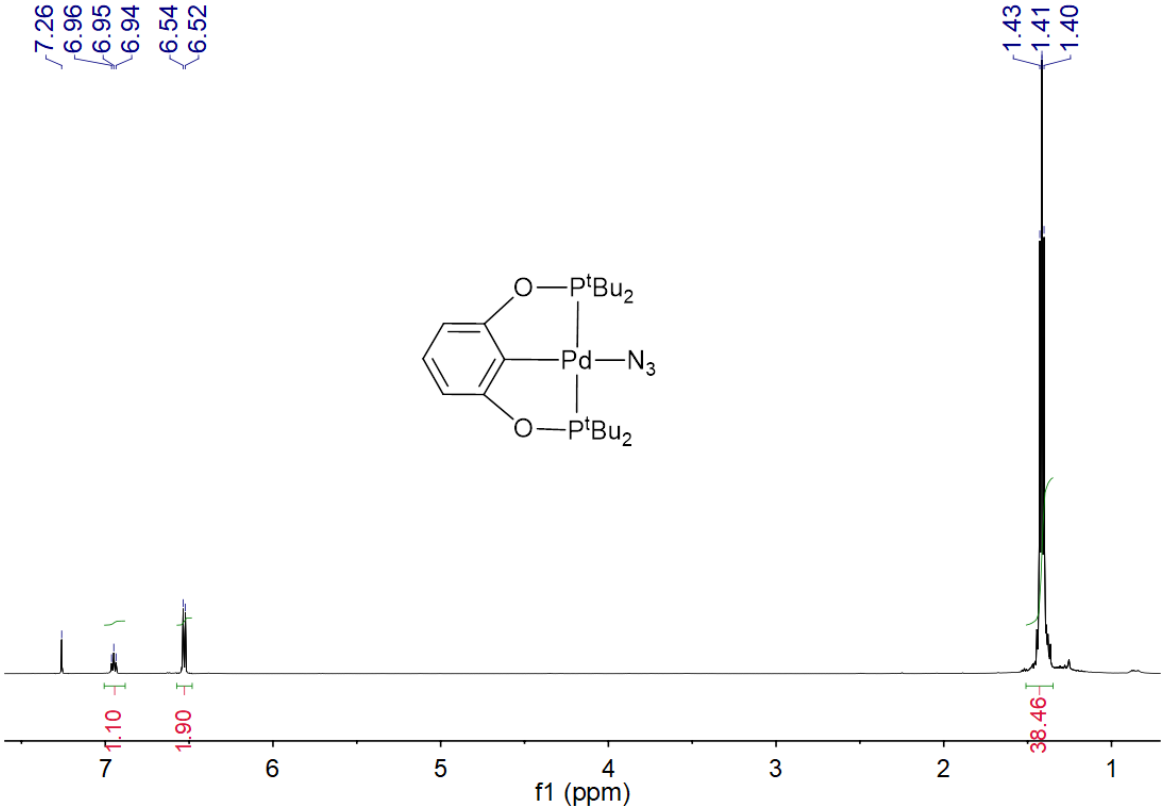

Fig. S42 ^{1}H NMR spectrum of complex **2f** (600 MHz, $CDCl_3$)

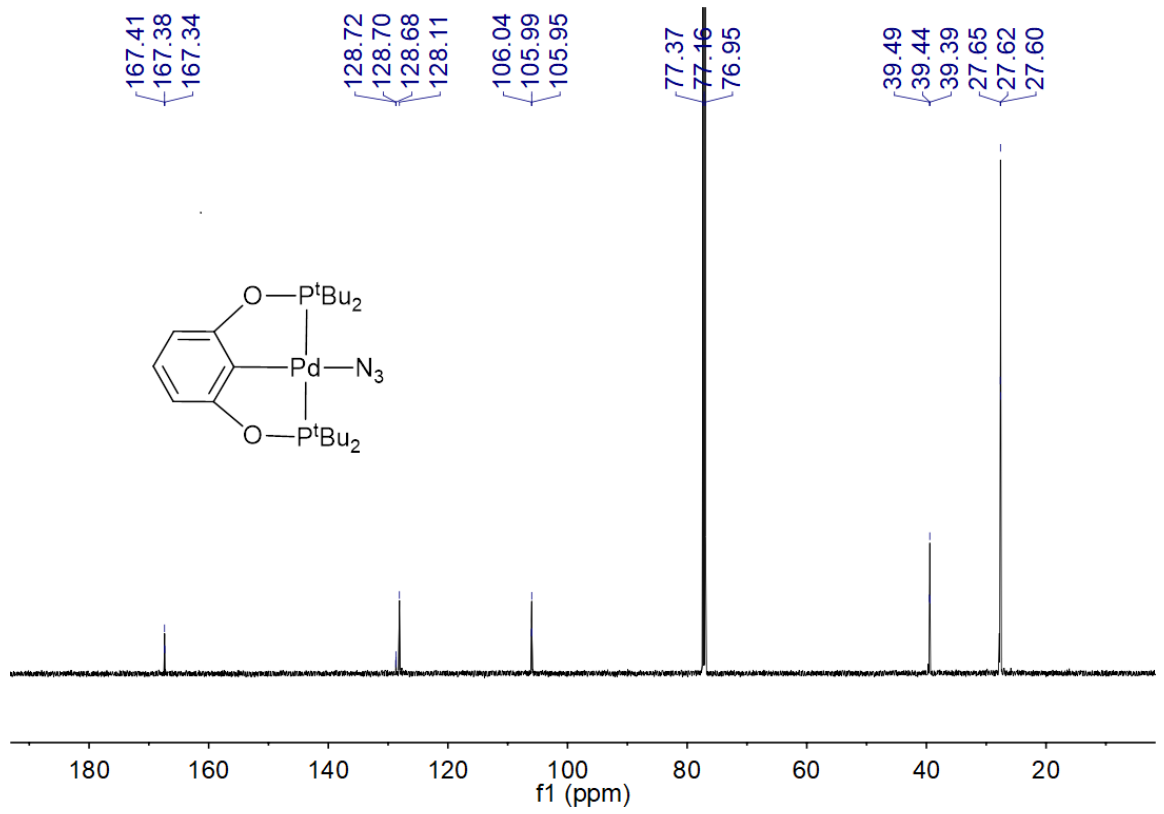

Fig. S43 $^{13}C\{^{1}H\}$ NMR spectrum of complex **2f** (151 MHz, $CDCl_3$)

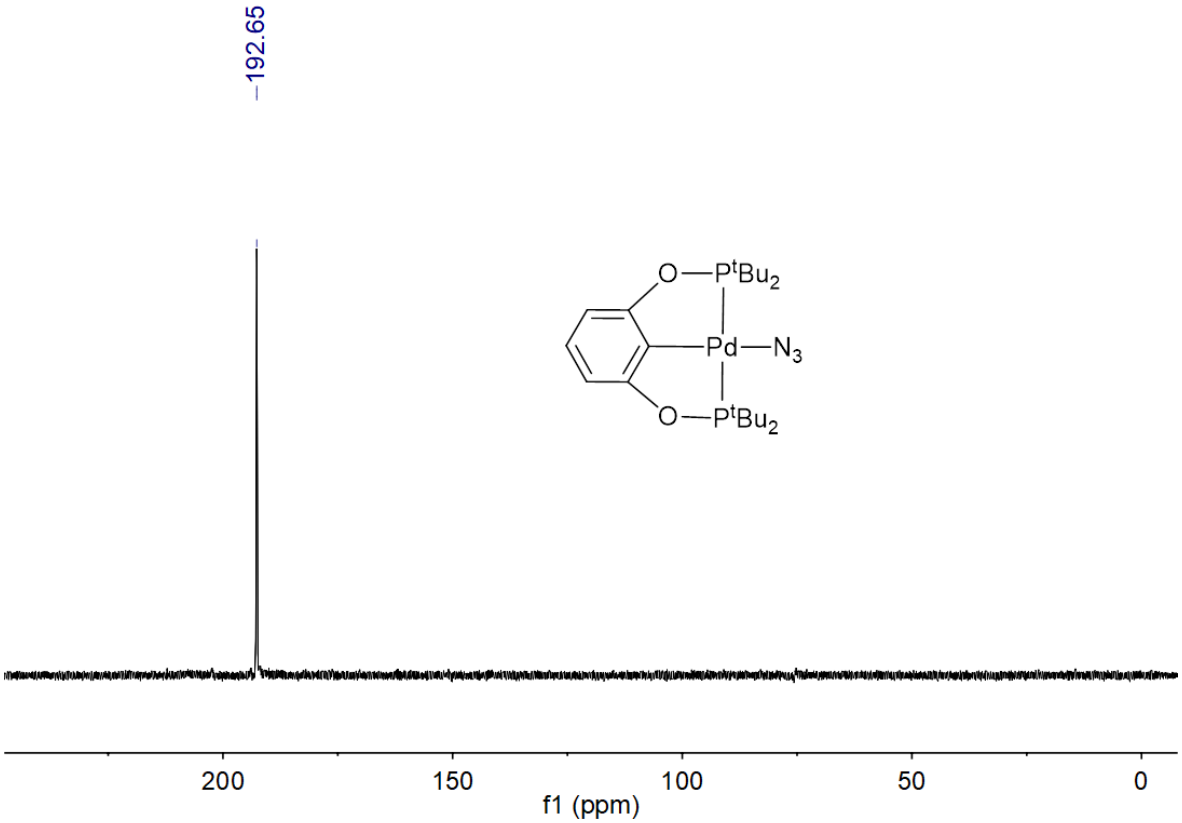

Fig. S44 $^{31}P\{^{1}H\}$ NMR spectrum of complex **2f** (243 MHz, $CDCl_3$)

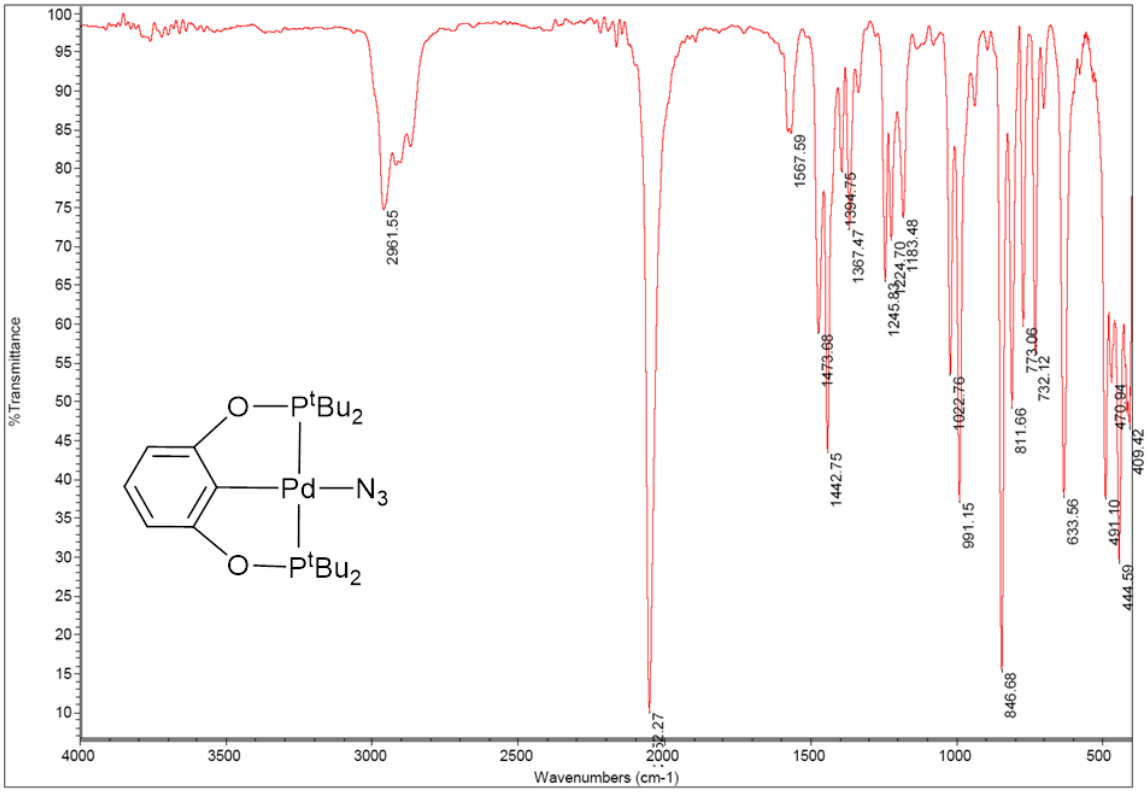

Fig. S45 FTIR spectrum of complex **2f** (KBr disc)

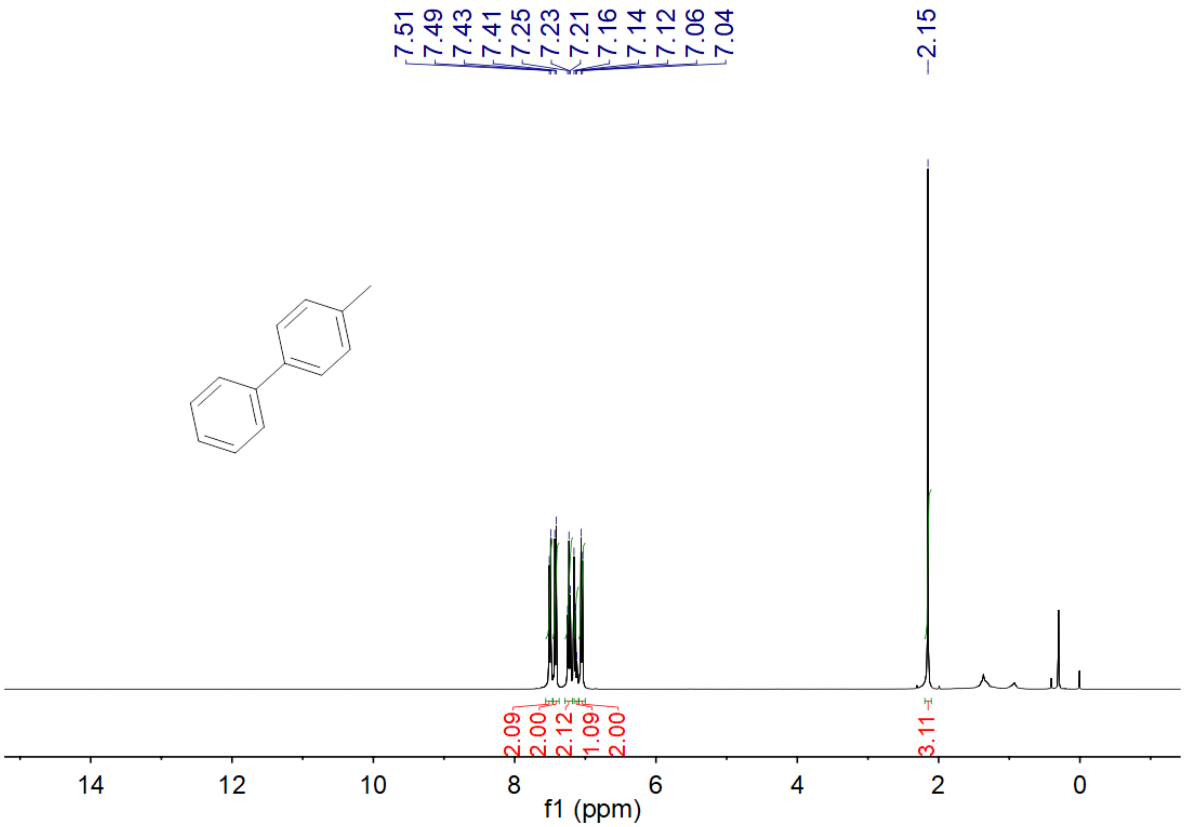

Fig. S46 ^{1}H NMR spectrum of the cross-coupling product (400 MHz, C_6D_6)

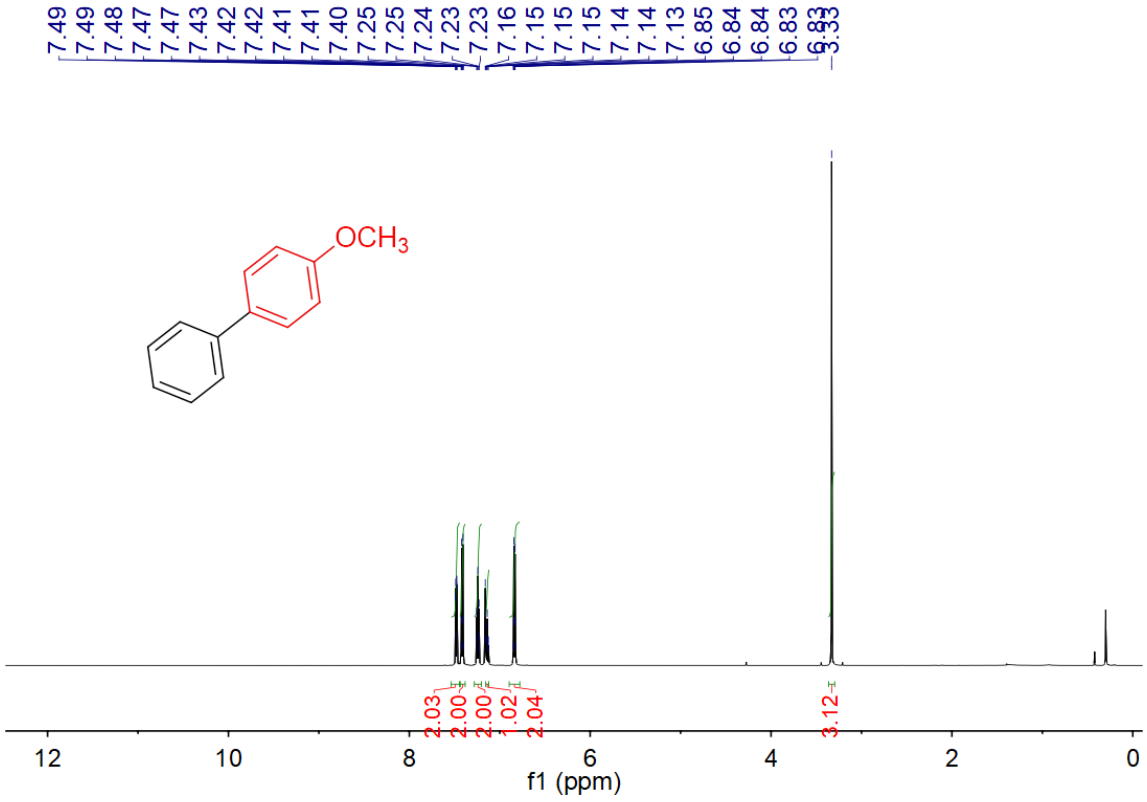

Fig. S47 ^{1}H NMR spectrum of the cross-coupling product (600 MHz, C_6D_6)

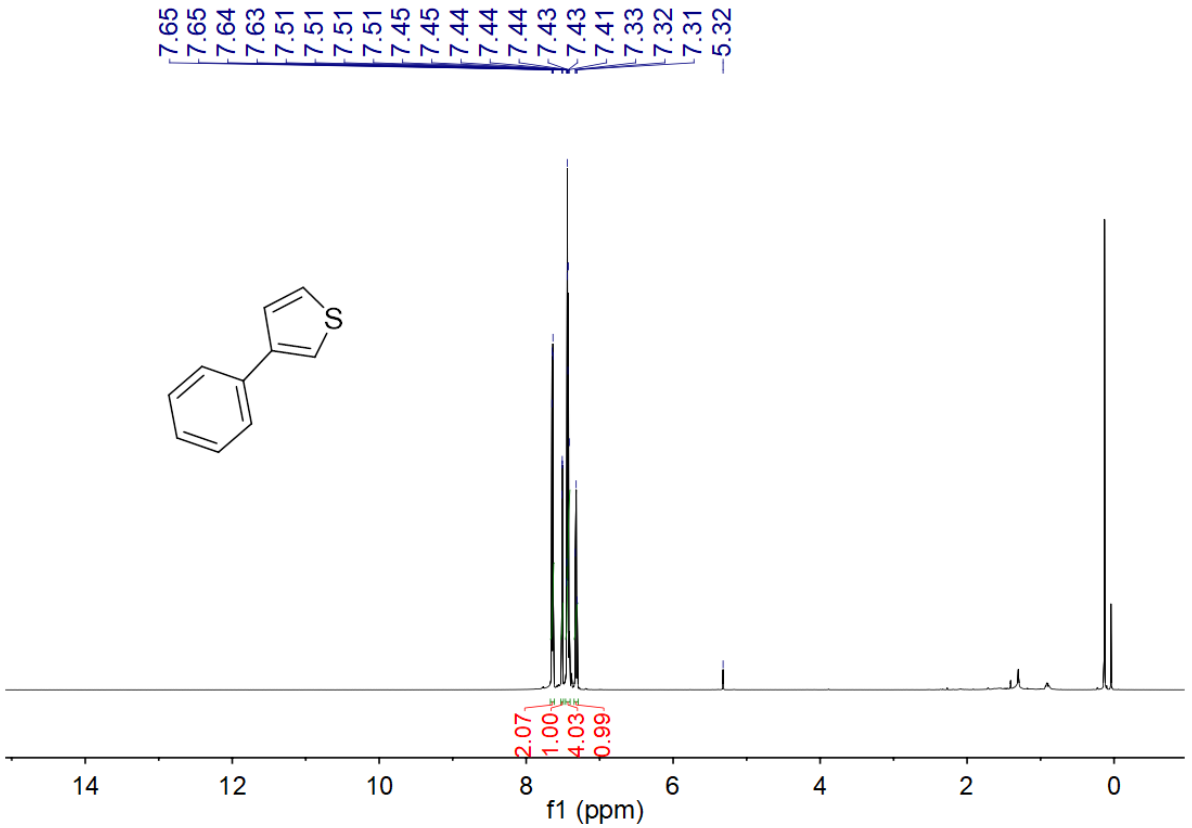

Fig. S48 ^{1}H NMR spectrum of the cross-coupling product (600 MHz, CD_2Cl_2)

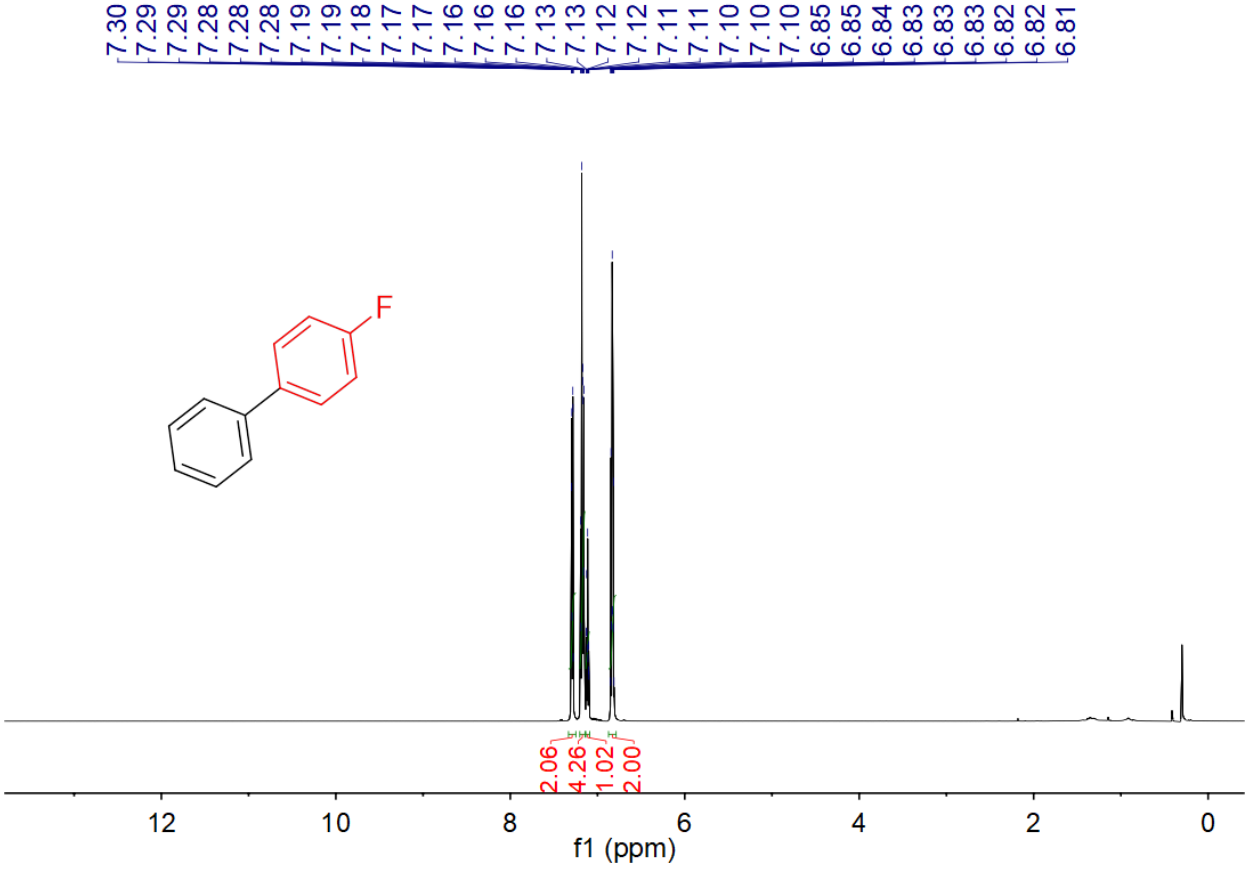

Fig. S49 ^{1}H NMR spectrum of the cross-coupling product (600 MHz, C_6D_6)

Table S1. Summary of crystal data and structure refinement for complexes **1a** and **1b**

Complex	**1a**·0.5(C_6H_{14})·(CH_2Cl_2)	**1b**·2(C_6H_6)
Empirical formula	$C_{24}H_{44}BClN_2P_2Pd$·0.5(C_6H_{14})·(CH_2Cl_2)	$C_{24}H_{45}BN_2P_2PdS$·2(C_6H_6)
Formula weight	703.22	729.04
Temp, K	289	170
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
a, Å	8.1561(2)	15.2903(3)
b, Å	30.3997(7)	17.5028(3)
c, Å	14.3424(3)	15.0487(3)
α (°)	90	90
β (°)	93.997(2)	107.062(2)
γ (°)	90	90
Volume, Å^3	3547.45(14)	3850.13(13)
Z	4	4
d_{calc}, g cm^{-3}	1.317	1.258
λ, Å	0.71073	1.54184
μ, mm^{-1}	0.859	5.360
No. of data collected	35003	17318
No. of unique data	8576	7351
R_{int}	0.0428	0.0284
Goodness-of-fit on F^2	1.128	1.024
R_1, wR_2 ($I > 2\sigma(I)$)	0.0605, 0.1235	0.0460, 0.1216
R_1, wR_2 (all data)	0.0824, 0.1326	0.0544, 0.1278

Table S2. Summary of crystal data and structure refinement for complexes **1d**, **1e** and **1f**

Complex	**1d**	**1e**	**1f**
Empirical formula	$C_{24}H_{44}BN_3P_2PdS$	$C_{25}H_{44}BN_3P_2PdSe$	$C_{24}H_{44}BN_5P_2Pd$
Formula weight	597.84	644.74	581.79
Temp, K	150	150	295
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	P-1	Cc	$P2_1/n$
a, Å	7.9460(2)	16.8528(2)	12.2561(3)
b, Å	16.5470(4)	16.7026(2)	16.6838(3)
c, Å	23.1657(6)	21.5950(2)	14.5569(3)
α (°)	71.489(2)	90	90
β (°)	86.395(2)	100.309(1)	105.454(2)
γ (°)	86.289(2)	90	90
Volume, $Å^3$	2879.36(13)	5980.55(12)	2868.95(11)
Z	4	8	4
d_{calc}, g cm^{-3}	1.379	1.432	1.347
λ, Å	1.54184	1.54184	1.54184
μ, mm^{-1}	7.053	7.531	6.421
No. of data collected	26389	13545	12824
No. of unique data	11158	8551	5445
R_{int}	0.0412	0.0218	0.0215
Goodness-of-fit on F^2	1.135	1.062	1.063
R_1, wR_2 ($I > 2\sigma(I)$)	0.0353, 0.0889	0.0349, 0.0971	0.0318, 0.0813
R_1, wR_2 (all data)	0.0489, 0.0952	0.0355, 0.0979	0.0350, 0.0841

Table S3. Summary of crystal data and structure refinement for complexes **2d**, **2e** and **2f**

Complex	**2d**	**2e**	**2f**
Empirical formula	$C_{23}H_{39}NO_2P_2PdS$	$C_{23}H_{39}NO_2P_2PdSe$	$C_{22}H_{39}N_3O_2P_2Pd$
Formula weight	561.95	608.85	545.90
Temp, K	150	170	170
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	I2/a	I2/a	P-1
a, Å	25.0749(3)	25.1910(3)	8.4289(2)
b, Å	8.1279(1)	8.1720(1)	11.8643(3)
c, Å	26.3766(4)	26.5788(4)	13.2820(4)
α (°)	90	90	99.726(2)
β (°)	103.032(1)	103.098(2)	95.763(2)
γ (°)	90	90	102.906(2)
Volume, Å^3	5237.26(12)	5329.19(13)	1262.82(6)
Z	8	8	2
d_{calc}, g cm^{-3}	1.425	1.518	1.436
λ, Å	1.54184	1.54184	1.54184
μ, mm^{-1}	7.760	8.457	7.300
No. of data collected	13254	11096	14092
No. of unique data	5045	5077	4863
R_{int}	0.0284	0.0244	0.0299
Goodness-of-fit on F^2	1.146	1.070	1.067
R_1, wR_2 ($I > 2\sigma(I)$)	0.0305, 0.0747	0.0285, 0.0734	0.0253, 0.0612
R_1, wR_2 (all data)	0.0361, 0.0774	0.0308, 0.0747	0.0271, 0.0620