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Supporting Information

CO_2 Hydrogenation by Phosphorus–Nitrogen PN^3P-Pincer Iridium Hydride Complexes: Elucidation of the Deactivation Pathway

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Electronic Supporting Information

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1 General Methods and Materials

All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. Chemicals were purchased from commercial sources and used without purification, unless otherwise noted. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent or being passed through solvent-purification columns. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz, 500 MHz or 600 MHz, spectrometer at 400 MHz and 100 MHz, 500 MHz and 125 MHz, or 600 MHz and 150 MHz, respectively. All chemical shifts were reported in δ units with references to the residual solvent resonance of the deuterated solvents for proton and carbon chemical shifts, and to external H_3PO_4 (85%) for phosphorus chemical shifts. Elemental analyses were carried out on a Flash 2000 elemental analyzer. HRMS data were performed on a Finnigan MAT 95 system. The X-ray diffraction data were collected using Bruker-AXS KAPPA-APEXII CCD diffractometer.

Safety Warning! Highly concentrated CO_2 are potentially hazardous and can undergo violent asphyxia upon high pressure. Highly concentrated H_2 are potentially flammable. The CO gas dector was used when CO is employed in the reaction process. Reactions and subsequent operations involving H_2 and CO_2 should be run behind a safety shield in fumehood. All hazardous materials should be handled in accordance with the standard procedure.

2 General Procedure for Hydrogenation of Carbon Dioxide

Catalyst (10 µmol) was dissolved in THF (10 mL), and diluted to 0.05 mmol/L. The catalyst solution (2 mL× 0.05 mol/L) and degassed KOH aqueous solution (2 mL× 0.50 mmol/L) were added to a 50 mL stainless autoclave, charged, and pressurized first by CO_2 and then by H_2 until the CO_2/H_2 ratio is 1/1. The reaction mixture was stirred at an appropriate temperature for an appropriate period of time. Sodium 3-(trimethylsilyl)-1-propanesulfonate (8.96 mg, 0.041 mmol) was added to the reaction mixture as an internal standard, and an aliquot of the mixture was dissolved in D_2O to estimate yield using the ^1H NMR spectrum. Each reaction was repeated twice to confirm the reproducibility.[1]

3 X-ray Crystallographic Studies

Crystals for X-ray analysis were obtained as described in the preparations. The crystals were manipulated in a glovebox. Data collections were performed Bruker-AXS KAPPA-APEXII CCD diffractometer (Cu Kα, λ = 1.5406 Å). Indexing was performed using APEX2 (Difference Vectors method). The determination of crystal class and unit cell parameters was carried out by the SMART program package. The raw frame data were processed using SAINT and SADABS[2] to yield the reflection data file. The structures were solved by using the SHELXTL program. Refinement was performed on F^2 anisotropically for all non-hydrogen atoms by the full-matrix least-squares method.[3-4] Hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. Platon programme (embedded in Olex-2 software)[5] has been used for squeezing the solvent peaks.[6]

4 Characterization of Compounds

4.1 Synthesis and Characterization of Compound 2b [$PN^3P^{tBu}IrH_2Cl$] and 2a [$PN^3P^{cPe}IrH_2Cl$]

Following the known synthetic route, Compound **1a** and **1b** were synthesized.[7] Compound **2b** was obtained under the reaction of **1b** (36.6 mg, 0.05 mmol) with 300 psi pressurized H_2. To the 50 mL stainless autoclave, the THF suspension of compound **1b** (36.6 mg, 0.05 mmol) was charged and pressurized by H_2 up to 300 psi. The reaction mixture was stirred at 80 °C for 12h. Then the solvent was removed under vacuum to obtain a red solid. The residue was washed with hexane (3 × 1 mL) and dried under vacuum to give compound **2b** as a red solid (23 mg, 74% yield). Single crystal of **2b** suitable for X-ray diffraction analysis was grown from THF/CH_2Cl_2 solutions at -30°C. The analogous compound **2a** was also synthesized according the same procedure. For **2b**, ^1H NMR (500 MHz, $CDCl_3$, 25 °C) δ 9.79 (br, 2H, -NH_2), 7.17 (br, 2H, -py), 6.92 (t, *J* = 10.0 Hz, 1H, -py), 1.36 (t, *J* = 10.0 Hz, 36H, -^{t}Bu), 0 (TMS) , -26.87 (br, 2H, -hydride), ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 163.9 (-py), 140.4 (-py), 99.2 (-py), 39.5 (t, *J* = 13.8 Hz, - ^{t}Bu), 28.9 (-^{t}Bu). ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ 126.18. Anal. Calc. for $C_{21}H_{43}N_3P_2IrCl$: C, 40.21; H, 6.91; N, 6.70. Found: C, 40.15; H, 7.13; N, 6.61. MS *m/z*(ESI) Calcd. for $C_{21}H_{43}N_3P_2IrCl$ requires $[M-Cl]^+$ 592.2561, Found: 592.2547. For **2a**, ^1H NMR(600 MHz, $CDCl_3$, 25 °C) δ 7.16 (t, *J* = 6.0 Hz, 1H, -py), 6.12 (d, *J* = 6.0 Hz, 2H, -py), 5.31 (br, 2H, -NH_2), 3.23 (br, 2H, -cPe), 2.35 (br, 2H , -cPe), 2.17 (br, 2H, -cPe), 2.00 (br, 2H, -cPe), 1.52–1.82 (m, 28H, -cPe), -16.93 (br, 1H, -IrH), -23.62 (br, 1H, -IrH). ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ 158.9 (t, *J* = 6.3 Hz, -py), 137.8 (-py), 96.9 (-py), 37.9 (t, *J* = 17.5 Hz, -cPe), 37.6(-cPe), 34.3 (-cPe), 26.2 (-cPe), 22.6 (-cPe). ^{31}P NMR (243 MHz, $CDCl_3$, 25 °C): δ 94.54. Anal.

Calc. for $C_{25}H_{43}N_3P_2IrCl$: C, 44.47; H, 6.42; N, 6.22. Found: C, 45.16; H, 6.67; N, 6.12. MS *m/z* (ESI) Calcd. for $C_{25}H_{43}N_3P_2IrCl$ requires $[M\text{-}Cl]^+$ 640.2561, Found: 640.2547.

4.2 Synthesis and Characterization of Compound 3b [$PN^3P^{tBu}IrH_2$]

Under argon, KO^tBu (56 mg, 0.5 mmol) was added to a suspension of **2b** (313.6 mg, 0.5 mmol) in THF (4 mL). The mixture was stirred at room temperature for 2 h. The red solid **3b**, thus obtained, was filtered and washed with cold pentane (3×3 mL), then dried under vacuum (303.1 mg, 82% yield). Single crystal of **3b** suitable for X-ray diffraction analysis was grown from THF/Et_2O solutions at -30 °C. The analogous compound **3a** was also synthesized using **2a** according the same procedure. For **3b**, ^1H NMR (600 MHz, C_6D_6, 25 °C) δ 6.92(t, *J* = 12.0 Hz, 1H, -Py), 6.83(d, *J* = 12.0 Hz, 1H, -Py), 5.21(d, *J* = 6.0 Hz, 1H, -Py) , 4.76 (s, 1H, -NH), 1.45 (d, *J* = 12.0 Hz, 18H, -^{t}Bu), 1.01 (d, *J* = 12.0 Hz, 18H, -^{t}Bu), -24.93(dd, *J* = 12.0 Hz, 2H, -IrH). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): 176.9 (d, *J* = 7.3 Hz, -Py), 162.2 (t, *J* = 7.3 Hz, -Py), 139.9 (t, *J* = 7.3 Hz, -Py), 106.1 (d, *J* = 19.3 Hz, -Py), 84.8 (d, *J*= 6.5 Hz, -Py), 38.8 (dd, J_1 = 7.0 Hz, J_2 = 28.9 Hz, -^{t}Bu), 38.2 (dd, J_1 = 4.6 Hz, J_2= 17.8 Hz, -^{t}Bu), 29.4 (d, *J* = 4.2 Hz, -^{t}Bu), 28.6 (d, *J* = 6.2 Hz, -^{t}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): δ 122.36 (d, $J_{P\text{-}P}$ = 299.2 Hz), 119.93(d, $J_{P\text{-}P}$ = 299.3 Hz). Anal. Calc. for $C_{21}H_{42}N_3P_2Ir$: C, 42.70; H, 7.17; N, 7.11. Found: C, 42.87; H, 6.93; N, 6.91. MS (ESI) Calcd. for $C_{21}H_{42}N_3P_2Ir$ requires $[M+H]^+$ 592.2556, Found: 592.2550.

4.3 Synthesis and Characterization of Compound 4a [$PN^3P^{cPe}IrH_3$]

Compound **3a** was dissolved in THF, then the solution was transferred into the 50 mL stainless autoclave, charged, and pressurized with H_2 up to 300 psi. The reaction mixture was stirred at 80 ^oC for 12 h. The gray solid, thus obtained, was filtered and washed with pentane (3×3 mL), then dried under vacuum to give compound **4a** as a light gray solid (179 mg, 56% yield). Single crystal of **4a** suitable for X-ray diffraction analysis was grown from THF solutions at -30 °C. For **4a**, ^1H NMR (600 MHz, C_6D_6, 25 °C): δ 6.81 (t, *J* = 12.0 Hz, 1H, -Py), 5.60 (d, *J* = 12.0 Hz, 2H, -Py), 4.47 (br, 2H, $-NH_2$), 3.57 (thf), 1.40 (thf), 1.31-2.15 (m, 36H, cPe), 0 (TMS), -11.76 (dt, $J_{\text{H-H}}$ = 6.0 Hz, $J_{\text{P-H}}$ = 25.5 Hz, 2H, -IrH), -18.15 (m, $J_{\text{P-H}}$ = 12.0 Hz, 1H, -IrH), ^{13}C NMR (125 MHz, C_6D_6, 25 °C): δ 159.4 (t, *J* = 6.3 Hz, -Py), 134.7(-py), 95.3(-py), 68.2 (thf), 43.8 (t, *J* = 18.8 Hz, -cPe), 31.3 (t, *J* = 6.3 Hz, -cPe), 29.7 (-cPe), 27.8 (t, *J* = 6.0 Hz, -cPe), 26.9 (t, *J* = 3.8Hz, -cPe), 26.1(thf). ^{31}P NMR (243 MHz, C_6D_6, 25 °C): δ 114.23. Anal. Calc. for $C_{25}H_{44}N_3P_2Ir{\bullet}3THF$: C, 51.85; H, 8.00; N, 4.90. Found: C, 51.44; H, 7.82; N, 5.09. MS *m/z* (ESI) Calcd. for $C_{25}H_{44}N_3P_2Ir$ requires $[M–H]^+$ 640.2561, Found: 640.2548.

4.4 Synthesis and Characterization of Compound 4b [$PN^3P^{tBu}IrH_3$]

Following the procedure described for **4a**, compound **3b** (29.5 mg, 0.05 mmol) was also reacted with H_2 (300 psi) in THF to yield compound **4b** as a yellow solid (25.2 mg, 85% yield). For **4b**, ^1H NMR (400 MHz, C_6D_6, 25 °C): δ 6.78 (t, *J* = 8.0 Hz, 1H, -Py), 5.60 (d, *J* = 8.0 Hz, 2H, -Py), 4.89 (br, 2H, $-NH_2$), 1.42 (t, *J* = 16.0 Hz, 36H, -^{t}Bu), -10.89 (dt, $J_{\text{H-H}}$ = 4.0 Hz, $J_{\text{P-H}}$ = 17.0 Hz, 2H, -IrH), -17.36 (m, $J_{\text{P-H}}$ = 16.0 Hz, 1H, -IrH), ^{13}C NMR (100 MHz, C_6D_6, 25 ^oC): δ 159.7 (t, *J* = 6.0 Hz, -Py), 134.6 (-Py), 95.9 (-Py), 37.9 (t, *J* = 12.2 Hz, -^{t}Bu), 29.9 (-^{t}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 ^oC): δ 123.80.

Anal. Calc. for $C_{21}H_{44}N_3P_2Ir$: C, 42.55; H, 7.48; N, 7.09. Found: C, 42.88; H, 7.05; N, 6.71. MS *m/z*(ESI) Calcd. for $C_{21}H_{44}N_3P_2Ir$ requires $[M–H]^+$ 592.2561, Found: 592.2550.

4.5 Reaction of Compound 4b [$PN^3P^{tBu}IrH_3$] with CO_2 and H_2 Formation of Compound 5b [$PN^3P^{tBu}IrCO$]

A THF solution (5 mL) of **4b** (17.7 mg, 0.03 mmol) was loaded into the 50 mL stainless autoclave, charged, and pressurized with CO_2 and H_2 (1:1, 120 psi), and stirred at 140 °C for 24 hours afforded **5b** in 78% yield after recrystallization. Single crystals of **5b** suitable for X-ray diffraction analysis was grown from THF solutions at room temperature. For **5b**, ^1H NMR (400 MHz, C_6D_6, 25 °C) δ 6.83(t, *J* = 8.0 Hz, 1H, -Py), 6.74(d, *J* = 8.0 Hz, 1H, -Py) , 5.11 (d, *J* = 8.0 Hz, 1H, -Py), 4.60 (s, 1H, -NH), 1.51 (d, *J* = 12.0 Hz, 18H, -^{t}Bu), 1.04 (d, *J* = 16.0 Hz, 18H, -^{t}Bu). ^{13}C NMR (125 MHz, C_6D_6, 25 °C): 190.7 (t, *J* = 6.2 Hz,-IrCO), 176.0 (t, *J* = 8.7 Hz,-Py), 161.4 (t, *J* = 7.5 Hz, -Py), 139.0(-Py), 105.8 (d, *J* = 21.2 Hz, -Py)), 85.7 (d, *J* = 7.5 Hz, -Py), 39.9 (dd, J_1 = 6.2 Hz, J_2 = 12.5 Hz, -^{t}Bu), 39.4 (dd, J_1 = 3.7 Hz, J_2= 17.5 Hz, -^{t}Bu), 29.3 (dd, J_1 = 3.7 Hz, J_2= 25.0 Hz, -^{t}Bu), 28.5 (dd, J_1 = 3.7 Hz, J_2= 12.0 Hz, -^{t}Bu). ^{31}P NMR (162 MHz, C_6D_6, 25 °C): 119.83 (d, J_{P-P} = 252.7 Hz), 117.29 (d, J_{P-P} = 252.7 Hz). Anal. Calc. for $C_{22}H_{40}N_3P_2OIr$: C, 43.91; H, 6.87; N, 6.98. Found: C, 43.53; H, 7.13; N, 6.64. MS *m/z*(ESI) Calcd. for $C_{22}H_{40}N_3P_2OIr$ requires $[M+H]^+$ 618.2349, Found: 618.2344. IR (cm^{-1}): 1940 (ν_{CO}).

5 Reference

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6 NMR spectra

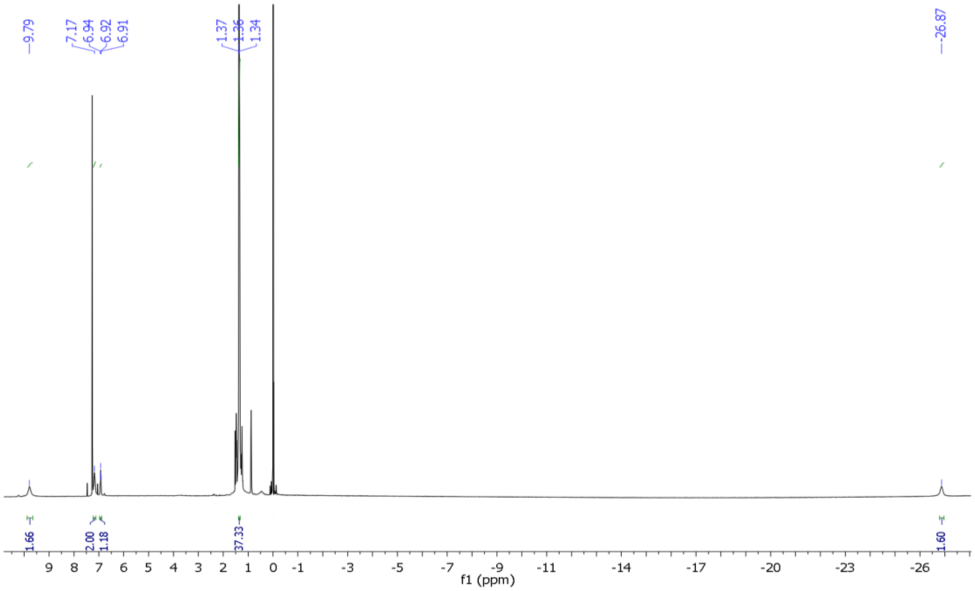

Fig. 1. ^{1}H NMR spectrum of **2b** [PN^{3}P^{tBu}IrH$_2$Cl] (500 MHz, CDCl$_3$, 25 °C).

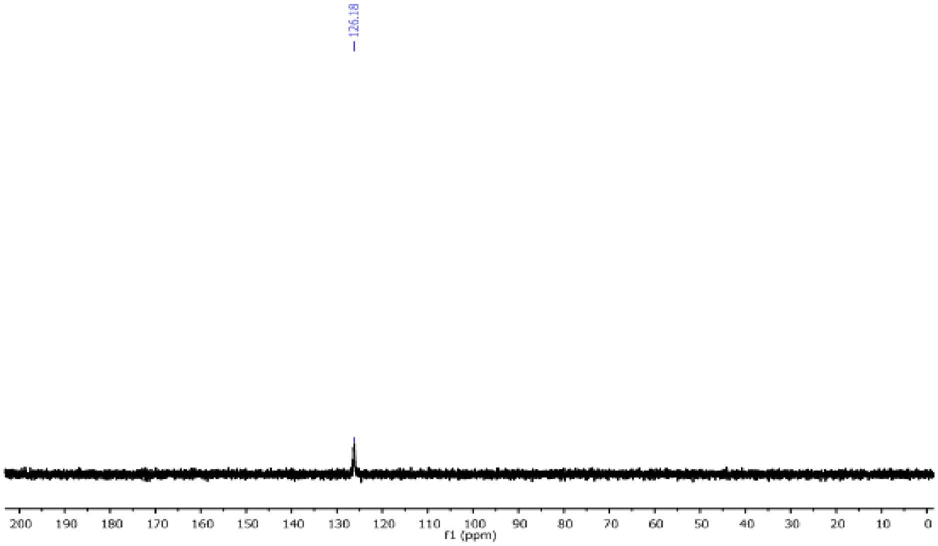

Fig. 2. ^{31}P NMR spectrum of **2b** [PN^{3}P^{tBu}IrH$_2$Cl] (243 MHz, CDCl$_3$, 25 °C).

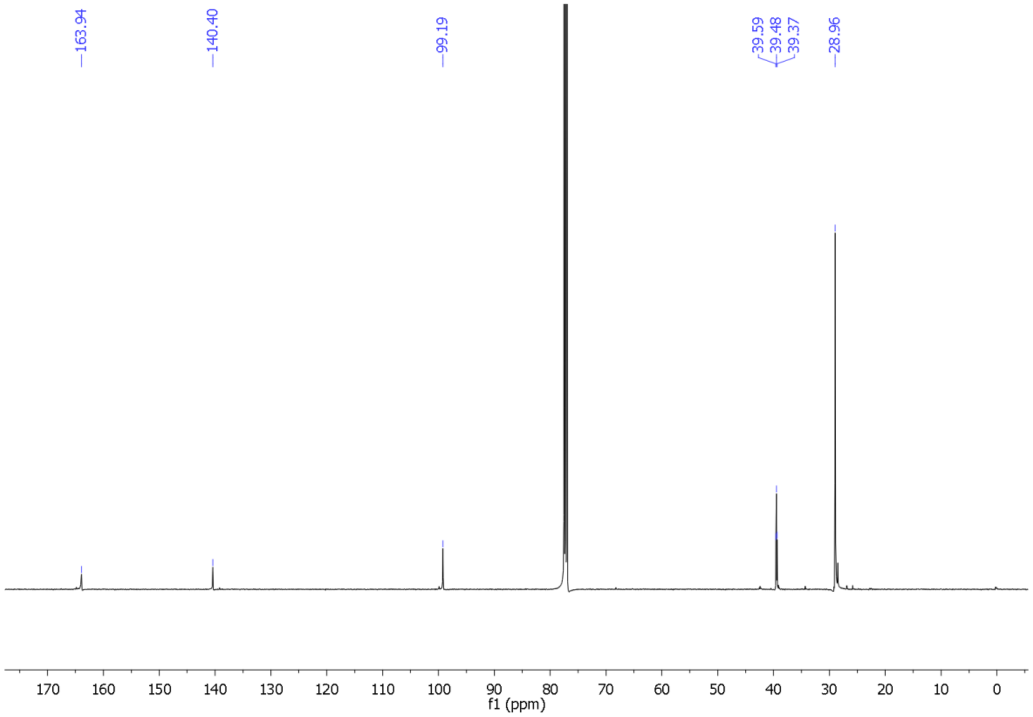

Fig. 3. ^{13}C NMR spectrum of **2b** [PN^{3}P^{tBu}IrH$_2$Cl] (125 MHz, CDCl$_3$, 25 °C).

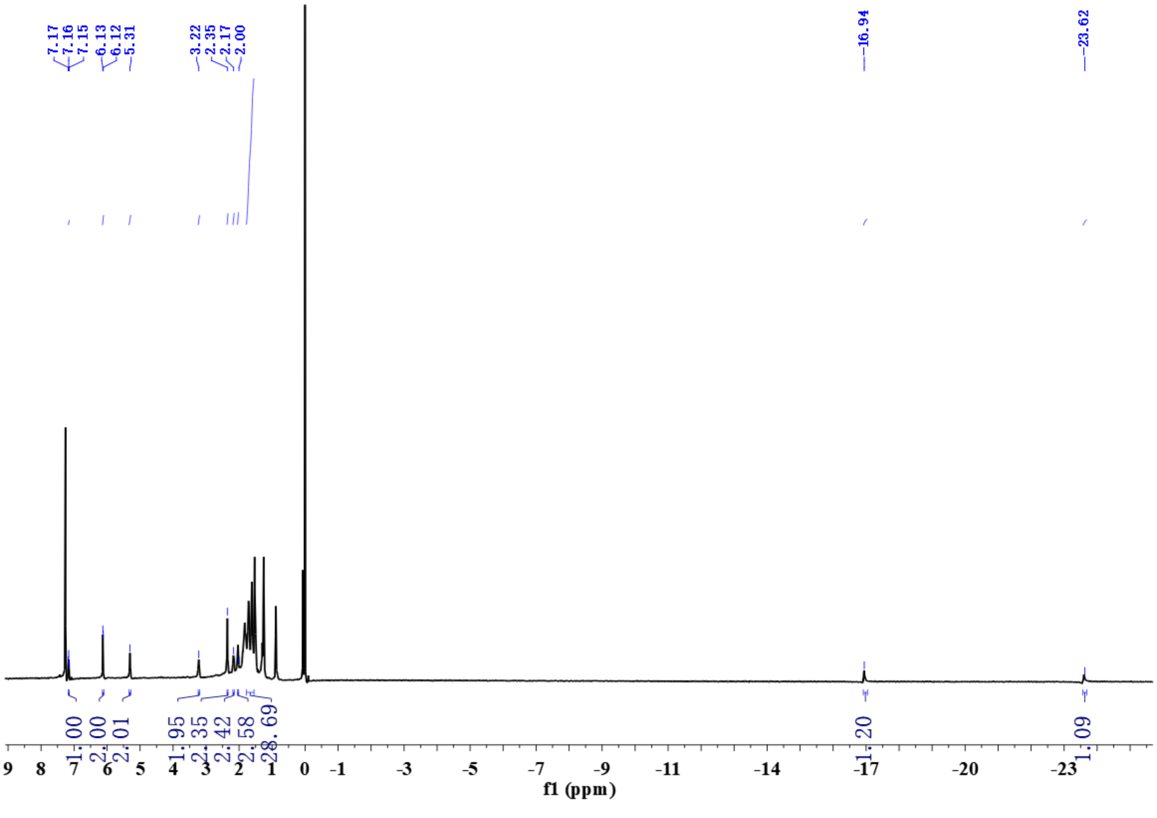

Fig. 4. ^{1}H NMR spectrum of **2a** [PN^{3}P^{cPe}IrH$_2$Cl] (600 MHz, CDCl$_3$, 25 °C).

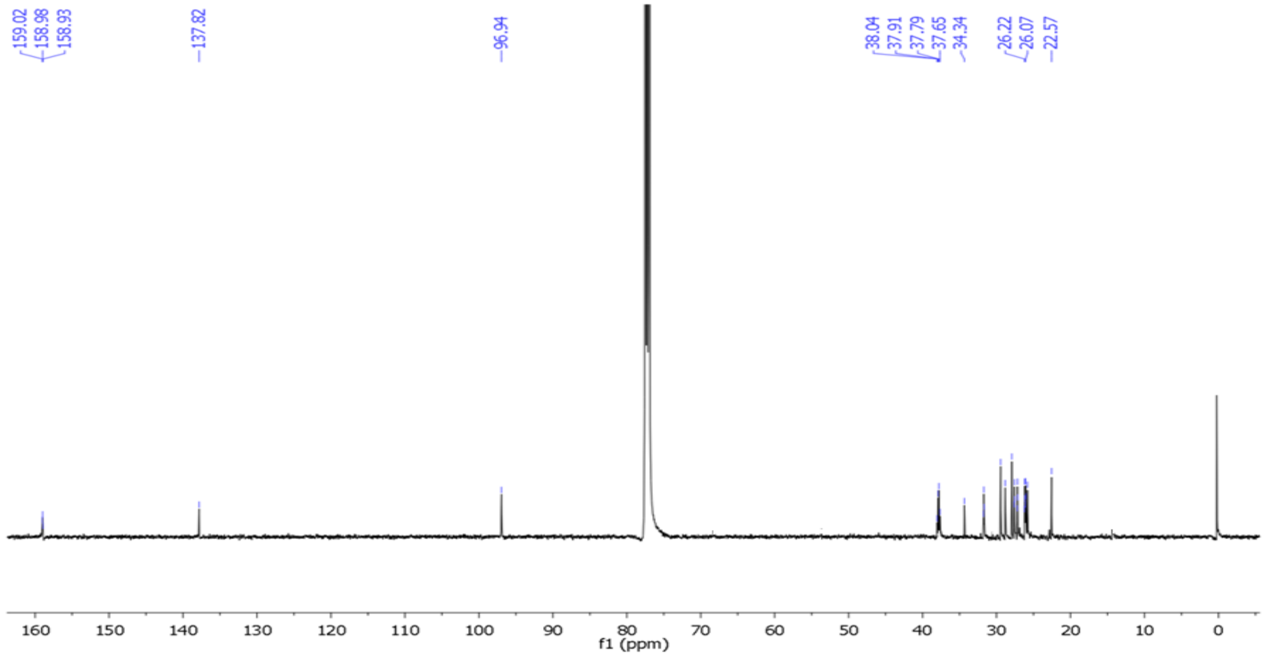

Fig. 5. ^{13}C NMR spectrum of **2a** [PN^{3}P^{cPe}IrH$_2$Cl] (125 MHz, CDCl$_3$, 25 °C).

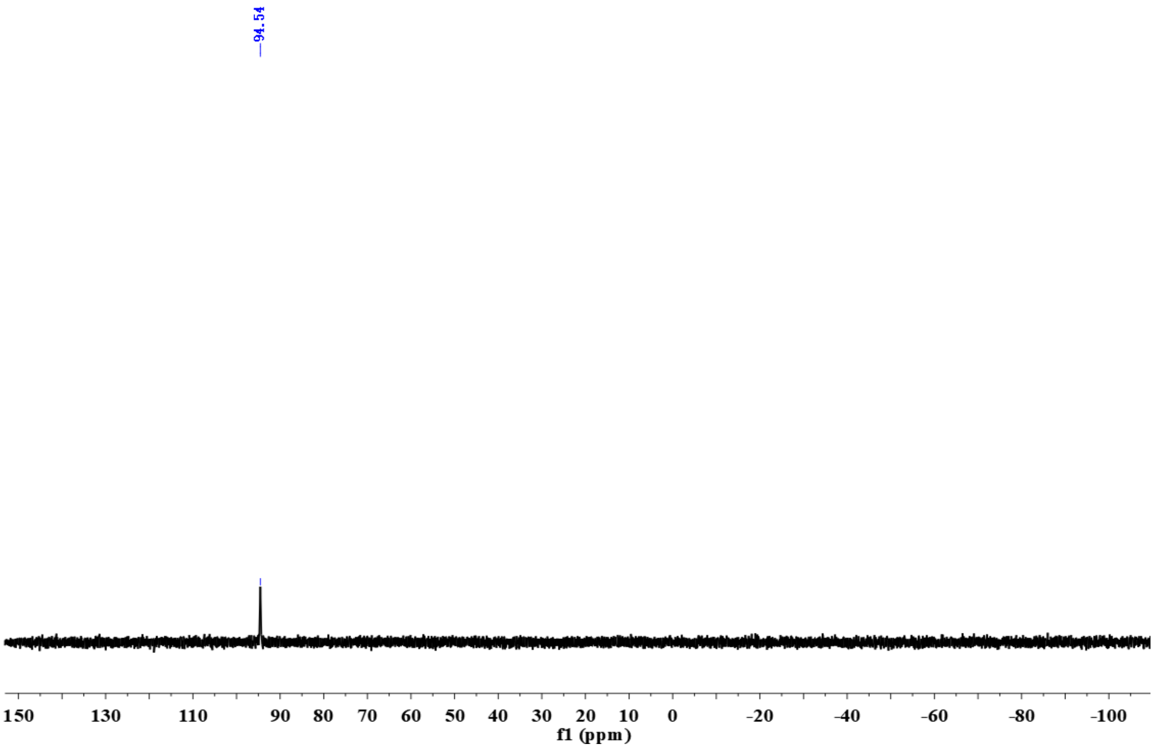

Fig. 6. ^{31}P NMR spectrum of **2a** [PN^{3}P^{cPe}IrH$_2$Cl] (243 MHz, CDCl$_3$, 25 °C).

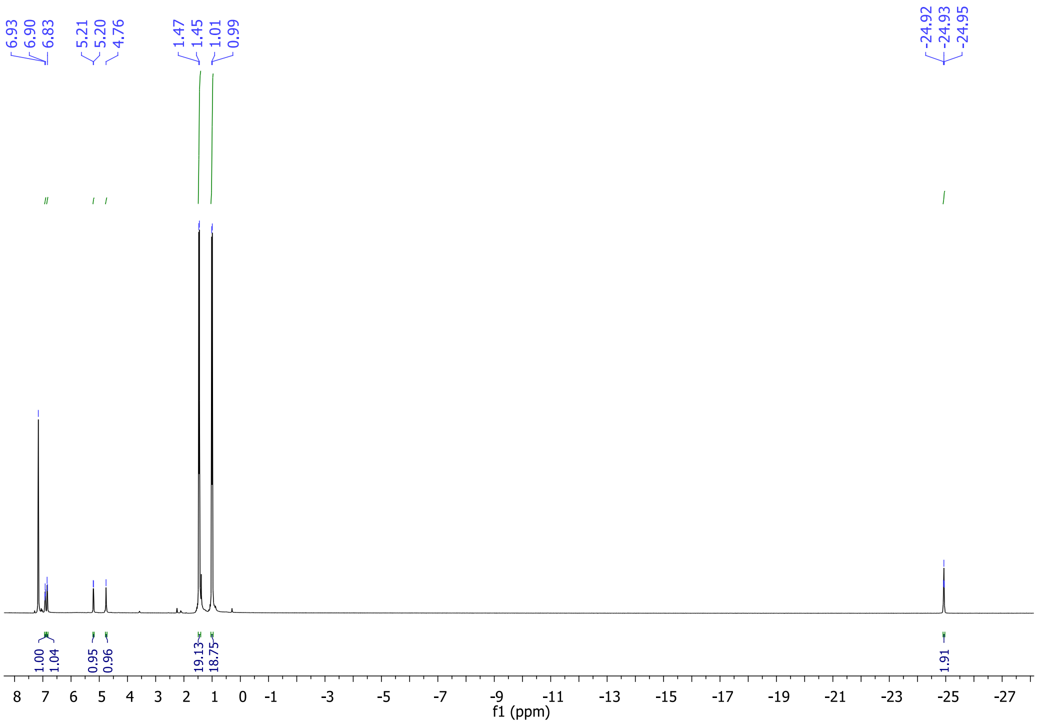

Fig. 7. ^{1}H NMR spectrum of **3b** [PN^{3}P^{tBu}IrH$_2$] (600 MHz, C$_6$D$_6$, 25 °C).

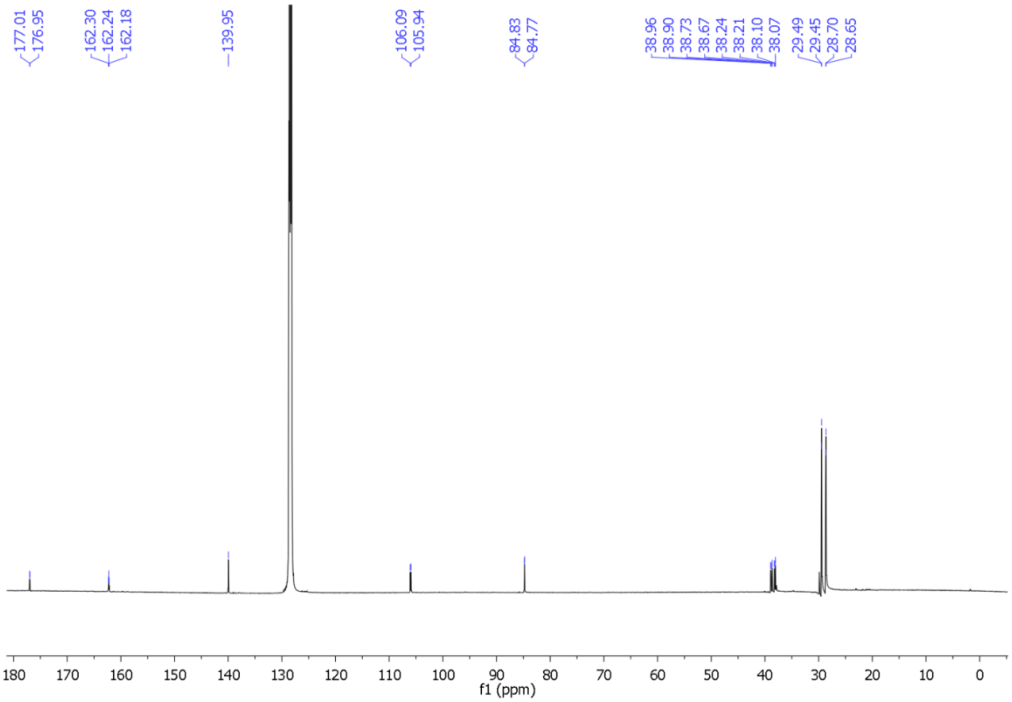

Fig. 8. ^{13}C NMR spectrum of **3b** [PN^{3}P^{tBu}IrH$_2$] (125 MHz, C$_6$D$_6$, 25 °C).

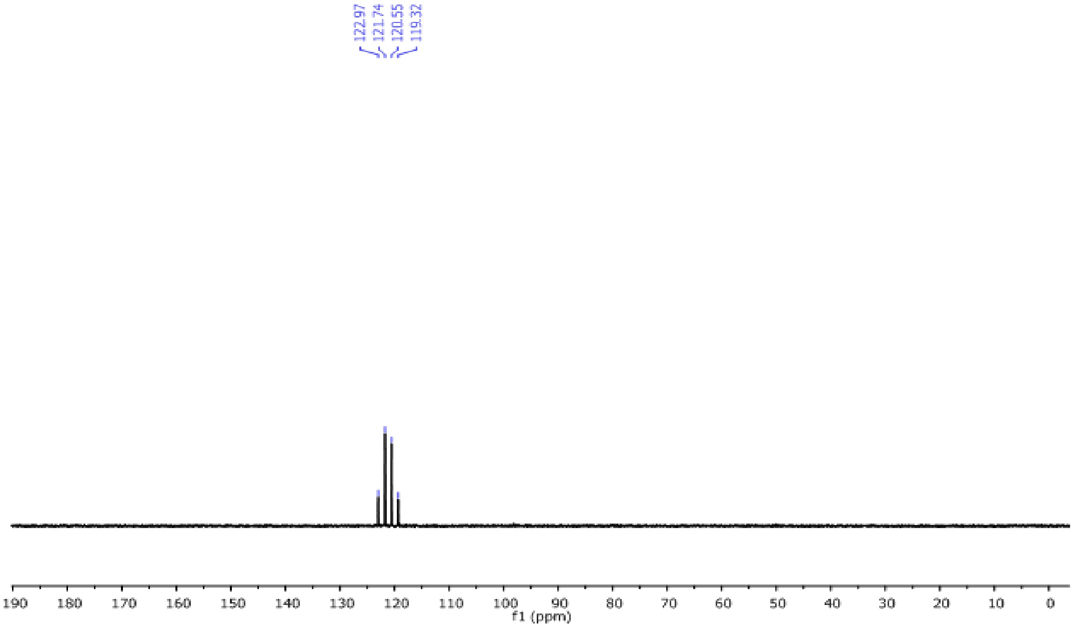

Fig. 9. ^{31}P NMR spectrum of **3b** [PN^{3}P^{tBu}IrH$_2$] (162 MHz, C$_6$D$_6$, 25 °C).

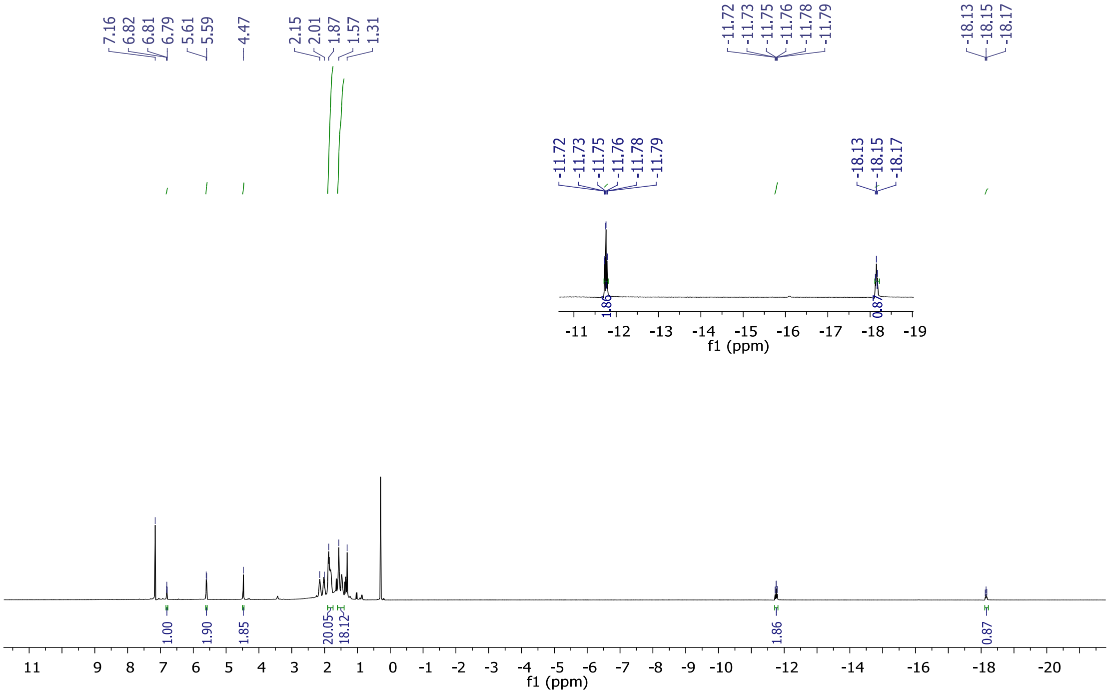

Fig. 10. ^{1}H NMR spectrum of **4a** [PN^{3}P^{cPe}IrH$_3$] (600 MHz, C$_6$D$_6$, 25 °C).

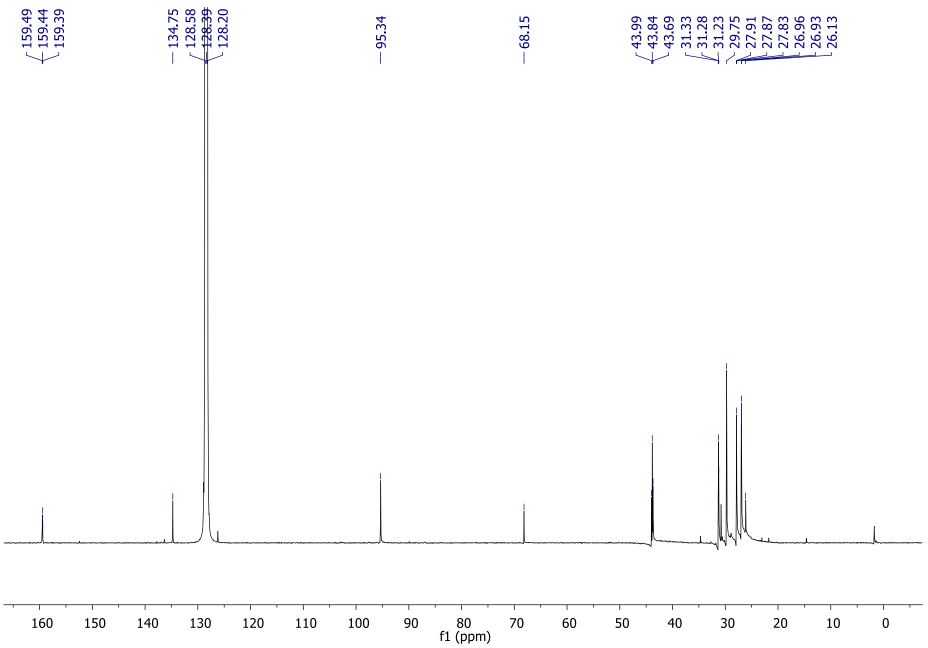

Fig. 11. ^{13}C NMR spectrum of **4a** [PN^{3}P^{cPe}IrH$_3$] (125MHz, C_6D_6, 25 °C).

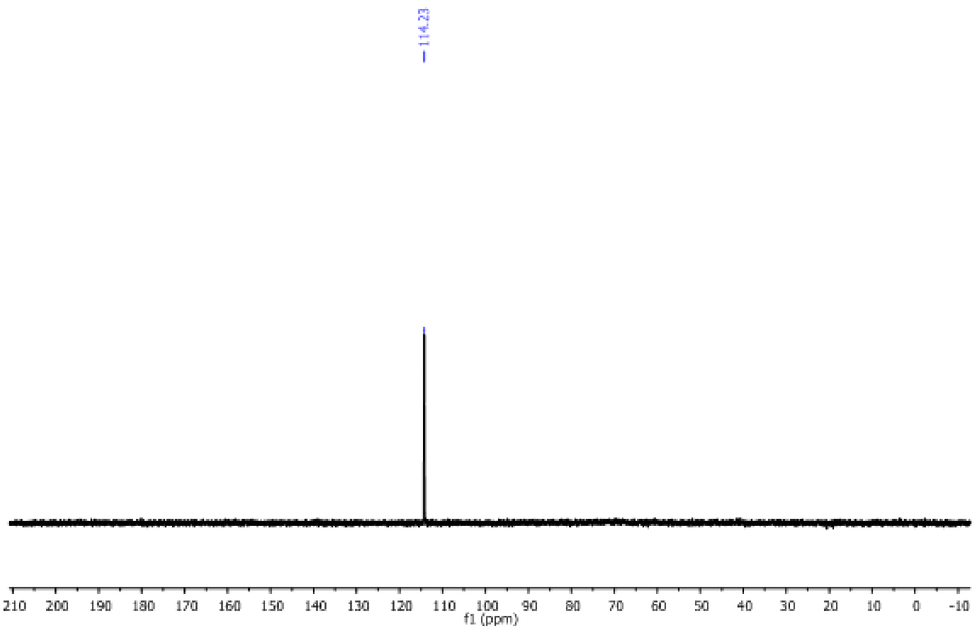

Fig. 12. ^{31}P NMR spectrum of **4a** [PN^{3}P^{cPe}IrH$_3$] (243 MHz, C_6D_6, 25 °C).

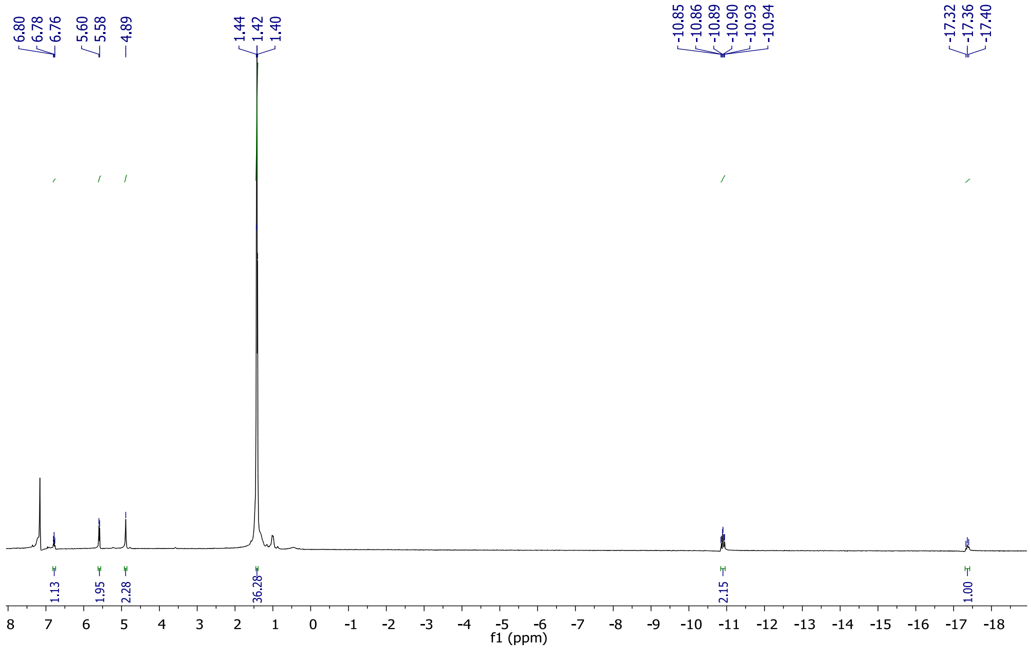

Fig. 13. ^{1}H NMR spectrum of **4b** [PN^{3}P^{tBu}IrH$_3$] (400 MHz, C_6D_6, 25 °C).

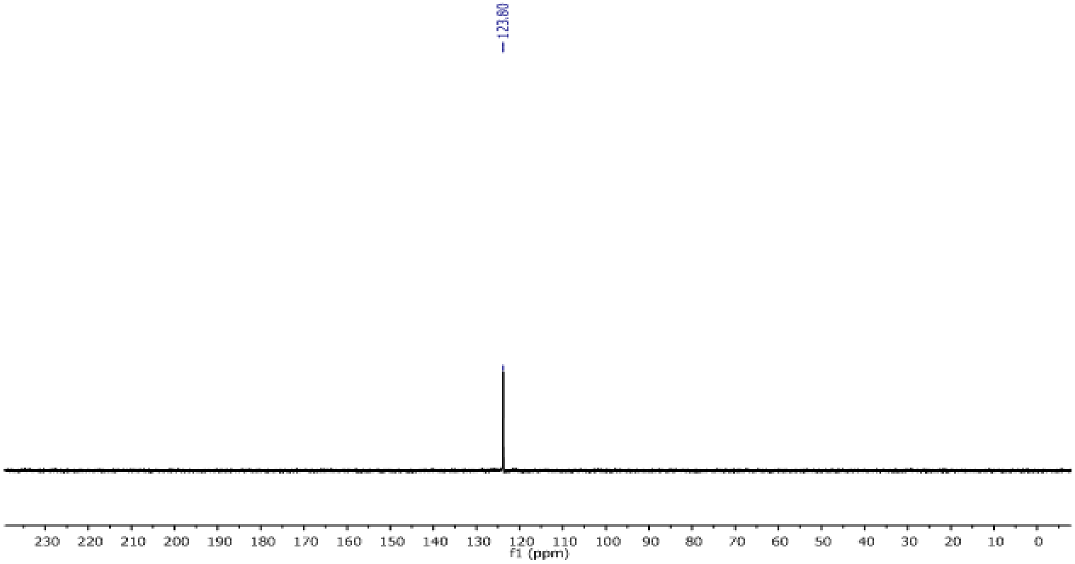

Fig. 14. ^{31}P NMR spectrum of **4b** [PN^{3}P^{tBu}IrH$_3$] (162 MHz, C_6D_6, 25 °C).

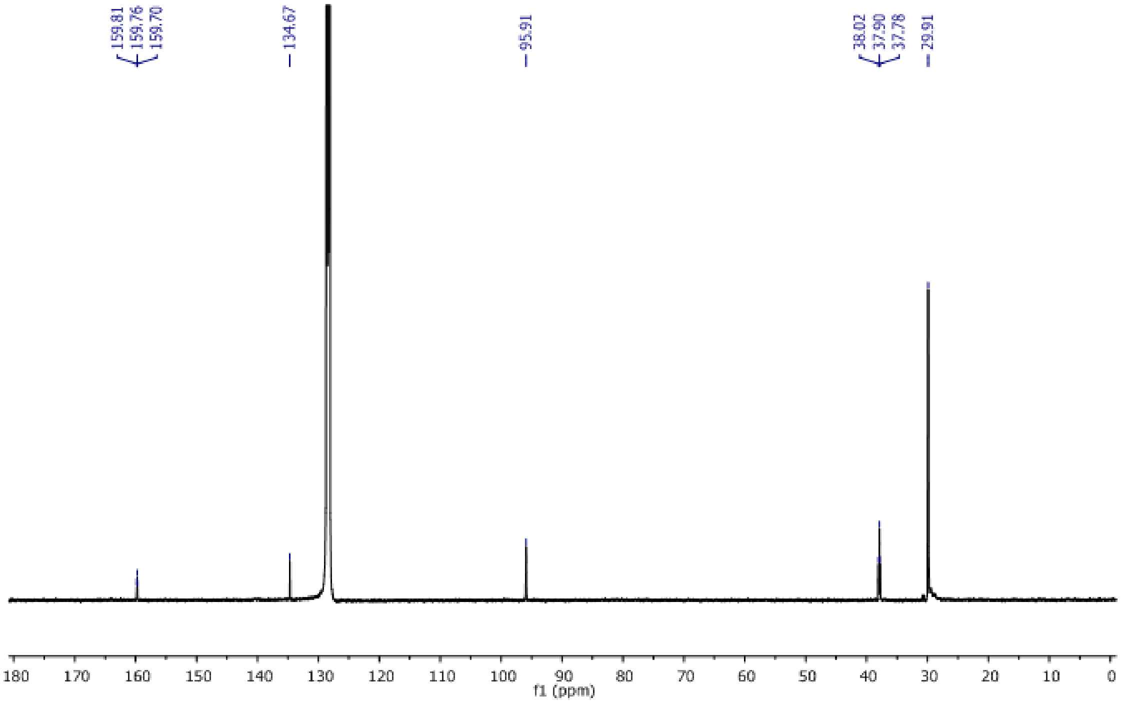

Fig. 15. ^{13}C NMR spectrum of **4b** [PN^{3}P^{tBu}IrH$_3$] (100MHz, C_6D_6, 25 °C).

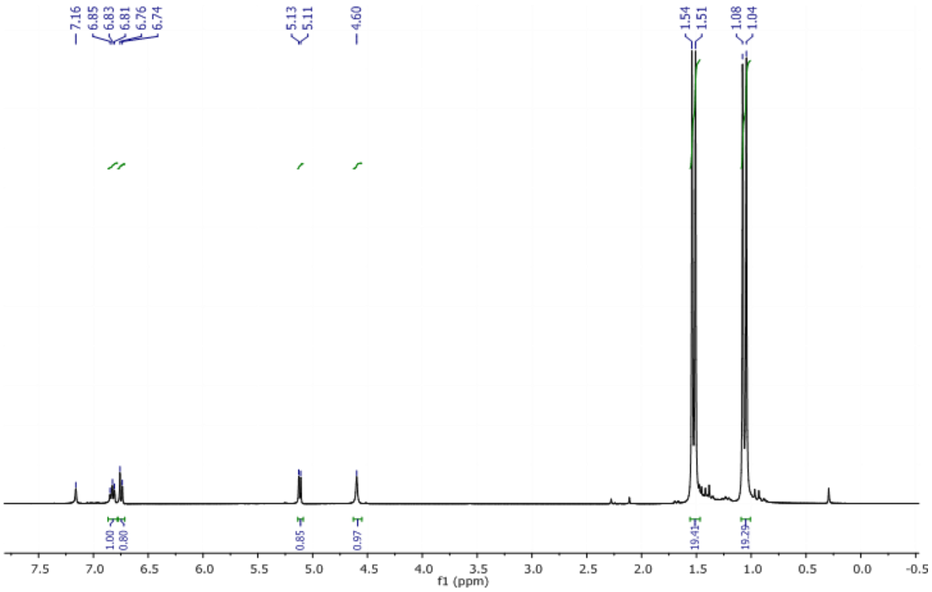

Fig. 16. ^1H NMR spectrum of **5b** [PN^{3}P^{tBu}IrCO] (I) complex (400 MHz, C_6D_6, 25 °C).

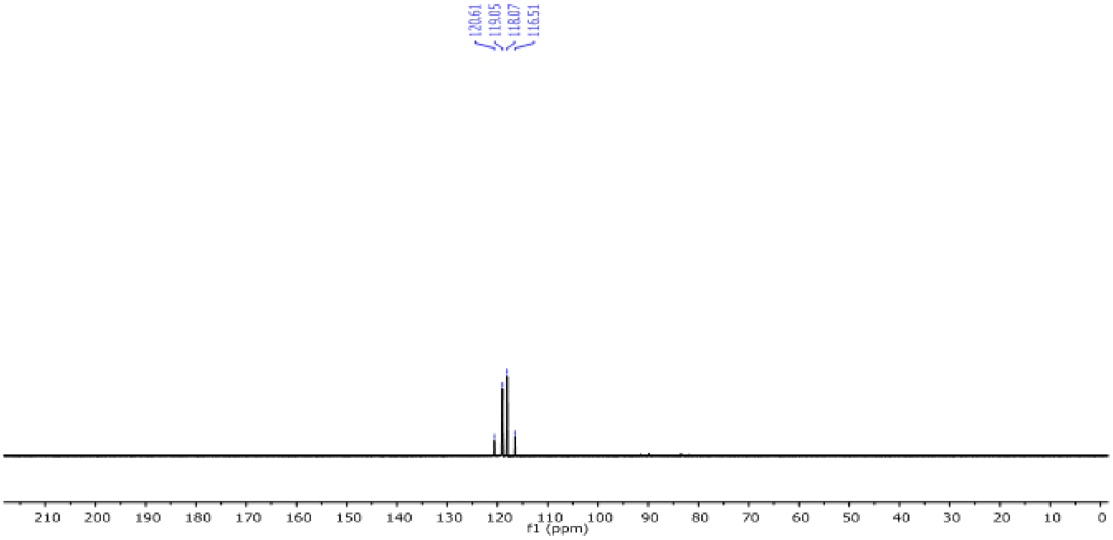

Fig. 17. ^{31}P NMR spectrum of **5b** $[PN^3P^{tBu}IrCO]$ (I) complex (162 MHz, C_6D_6, 25 °C).

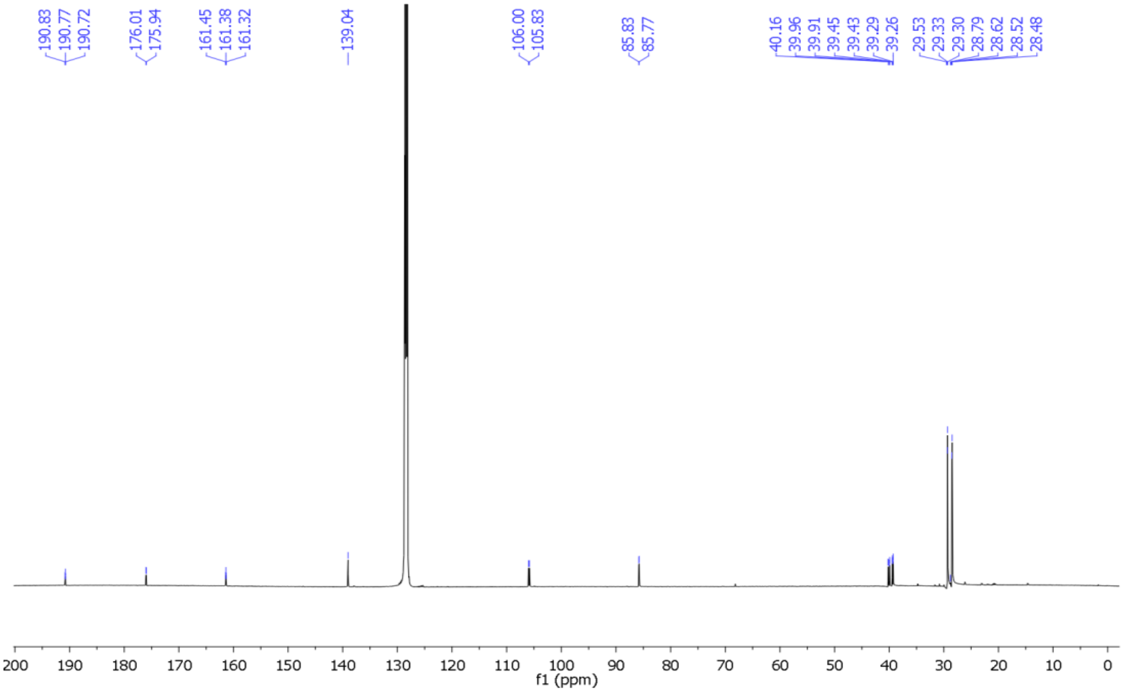

Fig. 18. ^{13}C NMR spectrum of **5b** $[PN^3P^{tBu}IrCO]$ (I) complex (125 MHz, C_6D_6, 25 °C).

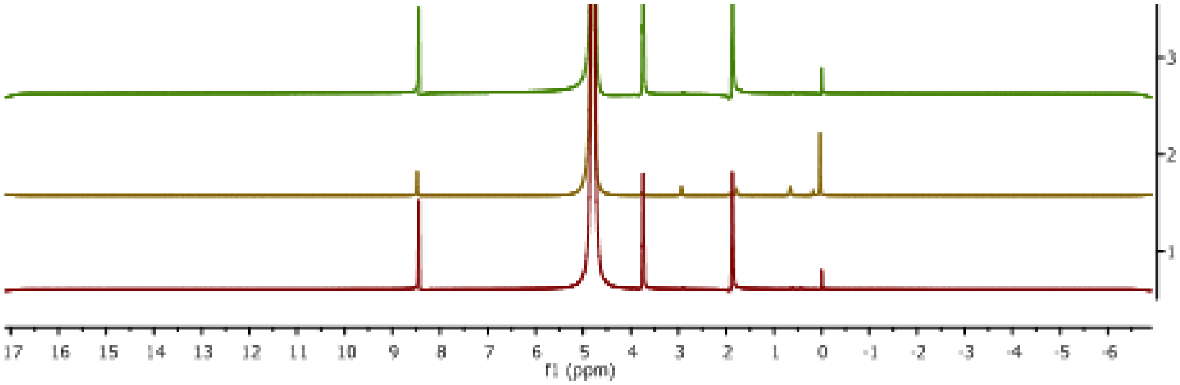

Fig. **19.** Selected ^{1}H NMR spectrum of hydrogenation reaction mixture in D_2O (green line 3 represent entry 4 in table 1; brown line 2 represent entry 1 in table 1; red line 1 represent entry 5 I table 1) (400 MHz, 25 °C)

STable1. Crystallographic Data for Iridium Complexes 2b, 3b, 4a and 5b.

Entry	**2b**	**4a**	**3b**	**5b**
Formula	$C_{21}H_{43}ClN_3IrP_2$	$C_{25}H_{44}N_3P_2Ir\cdot 3(C_4H_8O)$	$C_{21}H_{42}N_3IrP_2$	$C_{22}H_{40}N_3IrP_2O$
Formula weight	627.21	857.13	590.75	616.74
Crystal system	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	P–1	P2(1)/c	C2/c	C2/c
a (Å)	14.7189(5)	10.1942(8)	30.0076(19)	44.5757(9)
b (Å)	14.7186(5)	18.8062(14)	12.9046(7)	8.2230 (10)
c (Å)	18.2416(6)	21.1584(16)	26.2920(14)	33.2828(7)
α (deg)	72.7870(10)	90	90	90
β (deg)	72.0540(10)	102.736(2)	99.263(4)	108.629(2)
γ (deg)	61.3420(10)	90	90	90
V (Å^3)	3246.69(19)	3956.6(5)	10048.4(10)	11560.5(4)
Z	2	4	8	16
D_{calcd} (g/cm^3)	1.282	1.076	1.458	3.427
radiation (λ), Å	Cu K (1.54178)	Cu K (1.54178)	Cu K (1.54178)	Cu K (1.5406)
2θ range (^{o})	2.59 to 64.75	3.18 to 72.49	2.98 to 79.48	3.33 to 25.00
μ (mm^{-1})	9.713	7.578	11.555	4.746
F(000)	1254	1752	4112	10400
reflns_number_total	10376	7838	69898	80147
Reflns no gt	8847	7707	8919	10148
R(int)	0.0379	0.0504	0.0736	0.0567
GOF	1.019	1.149	0.925	0.933
R_1 [I> 2σ(I)]	0.0348	0.0303	0.0652	0.0360
wR_2 [I> 2σ(I)]	0.1097	0.1246	0.1606	0.0933
R_1 [all data]	0.0421	0.0307	0.0708	0.0399
wR_2 [all data]	0.1315	0.1246	0.1655	0.0959