Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

For

Selective carbonylation of benzene to benzaldehyde using a phosphorus-nitrogen PN^3P-Rhodium (I) complex

Chunhui Zhou, Jinsong Hu, Yuan Wang, Changguang Yao, Priyanka Chakraborty, Huaifeng Li, Chao Guan, Mei-Hui Huang and Kuo-Wei Huang*

KAUST Catalysis Center and Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

E-mail: hkw@kaust.edu.sa

Table of Contents

Experimental details

General consideration

All organic reagents were purchased from commercial sources without further purification. All solvents used were dried and distilled according to known procedures to ensure purity and absence of water. CO gas was purchased from commercial sources in high pressure cylinders and used without further purification using Schlenk techniques. All reactions were carried out inside an argon atmosphere glove box or using Schlenk techniques to ensure oxygen and external water free environments. All glassware was rigorously dried. All other chemicals were commercially available and used as received. NMR spectra were recorded at 400 MHz (^{1}H), 101 MHz (^{13}C), and 162 MHz (^{31}P) using a Bruker Avance-400 NMR spectrometer, unless noted otherwise. All spectra were recorded at 25 ^{o}C, and δ values were denoted by ppm and J by Hz. ^{1}H NMR chemical shifts were referenced to the residual hydrogen signals of the deuterated solvents (7.26 ppm, $CDCl_3$; 7.16 ppm, C_6D_6; 2.50 ppm, DMSO-d_6), and the ^{13}C NMR chemical shifts were referenced to the ^{13}C signals of the deuterated solvents (77.16 ppm, $CDCl_3$; 128.06 ppm, C_6D_6; 39.52 ppm, DMSO-d_6), and to external H_3PO_4 (85%) for phosphorus chemical shifts. The HR-MS were obtained using a Finnigan MAT 95 system.

Synthesis of the PN^{3}P ligand (1)

To a dry THF (60 mL) solution of 2, 6-diaminopyridine (2.18 g, 20 mmol), the Et_3N (4.05 g, 40 mmol) was added slowly. The resulting mixture was cooled to 0 °C and stirred 30 mins, then chlorodicyclopentylphosphine (9.31 g, 40 mmol) was added to the mixture dropwise with a syringe. The ultimate reaction mixture stirred and heated at 50 °C for 24 h in the argon atmosphere. After cooling to the room temperature, the suspension was filtered in the glovebox and the brown filtrate formed. The filtrate was concentrated and recrystallized by the pentane to afford the targeted colorless solid PN^{3}P ligand **1**. Yield: 1.50 g (17%). ^{31}P {^{1}H} NMR (CD_3Cl, 162 MHz): 38.67 (s). ^{1}H NMR (CD_3Cl, 400 MHz): 7.26 (t, J = 7.9 Hz, 1H, Py H4), 6.45 (dd, J = 7.9 Hz, J = 2.0 Hz, 2H, Py H3, 5), 4.41 (d, J = 7.8 Hz, 2H, N*H*), 1.93-2.01 (m, 4H, *c*Pe-*H*), 1.82-1.88 (m, 8H, *c*Pe-*H*), 1.52-1.66 (m, 20H, *c*Pe-*H*), 1.37-1.46 (m, 4H, *c*Pe-*H*), ^{13}C NMR (CD_3Cl, 101 MHz): 159.42 (s, Py C2, 6), 139.16 (s, Py C4), 98.21 (d, J = 17.9 Hz, Py C3, 5), 39.57 (d, J = 10.1 Hz, *c*Pe-*C*), 29.13

(d, *J* = 6.1 Hz, *c*Pe-*C*), 28.98 (d, *J* = 4.8 Hz, *c*Pe-*C*), 26.67 (d, *J* = 7.6 Hz, *c*Pe-*C*), 26.22 (d, *J* = 5.4 Hz, *c*Pe-*C*). HRMS (ESI) Calcd. for $C_{25}H_{41}N_3P_2$ requires $(M+H)^+$ 446.2849, Found: 446.2845.

Syntheses of PN^{3}P pincer complexes

Reaction of ligand (1) with [Rh(COD)Cl]$_2$ to form (PN^{3}P)RhCl (2). A dry THF solution of synthesized PN^{3}P ligand **1** (10 mL, 891 mg, 2.0 mmol) was dropwise added to a stirred orange solution of $[Rh(COD)Cl]_2$ (493 mg, 1.0 mmol) in THF (10 mL). The resulting orange suspension was stirred overnight at 60 °C in the argon atmosphere. After cooling to the room temperature, the solvent was removed under vacuum, and the residue was washed with pentane three times. Complex (PN^{3}P)RhCl (**2**) was obtained as a yellowish solid. Yield: 1063 mg (91%). $^{31}P\{^1H\}$ NMR (C_6D_6, 162 MHz): 91.81 (d, *J* = 154.5 Hz, 2P). ^1H NMR (C_6D_6, 400 MHz): 6.88 (t, *J* = 7.9 Hz, 1H, Py H4), 5.51 (d, *J* = 7.9 Hz, 2H, Py H3, 5), 4.20 (s, 2H, N*H*), 2.47-2.57 (m, 4H, *c*Pe-*H*), 2.08-2.17 (m, 4H, *c*Pe-*H*), 1.88-2.02 (m, 16H, *c*Pe-*H*), 1.50-1.70 (m, 12H, *c*Pe-*H*). ^{13}C NMR (DMSO-d_6, 101 MHz): 161.65 (t, *J* = 7.9 Hz, Py C2, 6), 140.22 (s, Py C4), 97.46 (s, Py C3, 5), 38.41 (t, *J* = 14.0 Hz, *c*Pe-*C*), 29.38 (t, $J_{P\text{-}C}$ = 3.9 Hz, *c*Pe-*C*), 27.76 (s, *c*Pe-*C*), 26.47 (t, *J* = 3.2 Hz, *c*Pe-*C*), 25.58 (t, *J* = 4.8 Hz, *c*Pe-*C*). HRMS (ESI) Calcd. for $C_{25}H_{41}N_3P_2RhCl$ requires $(M)^+$ 583.1514, Found: 583.1507.

Reaction of (PN^{3}P)RhCl (2) with benzene in the presence of KN(SiMe$_3$)$_2$ to form (PN^{3}P)Rh(C$_6$H$_5$) (3). A dry benzene solution (5 mL) of $KN(SiMe_3)_2$ (42.0 mg, 0.20 mmol, 95% purity) was added to a stirred yellowish benzene suspension (5 mL) of **2** (116.8 mg, 0.20 mmol) under the argon atmosphere. A considerable amount of red solid was precipitated and consumed during 5 days at room temperature gradually, forming a homogeneous red solution. A red residue was obtained when the removing the solvent. Treating the residue with the pentane to make an extraction and filtered to remove the forming KCl in the reaction process. The ultimate extract was dried in vacuum to give 102.7 mg (Yield: 82%) of **3** as a red solid. $^{31}P\ \{^1H\}$ NMR (C_6D_6, 162 MHz): 94.22 (d, *J* = 178.2 Hz, 2P). ^1H NMR (C_6D_6, 400 MHz): 7.97 (d, *J* = 7.6 Hz, 2H, Rh-Ph), 7.27 (t, *J* = 7.4 Hz, 2H, Rh-Ph), 7.00-7.03 (m, 1H, Rh-Ph), 6.97 (d, *J* = 7.4 Hz, 1H, Py H4), 5.63 (d, *J* = 7.9 Hz, 2H, Py H3,5), 4.29 (s, 2H, N*H*), 2.00-2.08 (m, 4H, *c*Pe-*H*), 1.81-1.93 (m, 12H, *c*Pe-

H), 1.60-1.79 (m, 20H, *c*Pe-*H*). ^{13}C NMR (C_6D_6, 126 MHz): 167.61-167.81 (m, Rh-*C*), 159.73 (t, *J* = 8.3 Hz, Py C2, 6), 140.90 (s, Py C4), 96.17 (s, Py C3, 5), 133.98 (s, Ph), 125.31 (s, Ph), 119.15 (s, Ph), 39.65 (t, *J* = 10.7 Hz, *c*Pe-*C*), 29.54 (s, *c*Pe-*C*), 28.40 (t, *J* = 10.7 Hz, *c*Pe-*C*), 27.13 (s, *c*Pe-*C*). HRMS (ESI): [M-Ph+MeCN] requires 589.2071, Found: 589.1998; M = $C_{31}H_{46}N_3P_2Rh$.

Reaction of (PN^3P)Rh(C_6H_5) (3) with CO to form (PN^3P)RhCOC_6H_5 (4). To a dry benzene (10 mL) solution of complex **3** (62.5 mg, 0.1 mmol) was charged with carbon monoxide for thirty minutes at the room temperature, a deep-red solution was obtained. Then the solution was evaporated to give a red solid, and the analytically pure complex **4** was formed. Yield: 56.5 mg (86%). ^{31}P {^{1}H} NMR (C_6D_6, 162 MHz): 97.67 (d, *J* = 188.8 Hz, 2P). ^{1}H NMR (C_6D_6, 400 MHz): 8.63 (d, *J* = 7.0 Hz, 2H, Rh-Ph), 7.32 (t, *J* = 7.5 Hz, 2H, Rh-Ph), 7.15-7.18 (m, 1H, Rh-Ph), 6.98 (t, *J* = 7.9 Hz, 1H, Py H4), 5.82 (d, *J* = 7.9 Hz, 2H, Py H 3,5), 5.42 (s, 2H, N*H*), 1.98-2.06 (m, 12H, *c*Pe-*H*), 1.66-1.81 (24H, *c*Pe-*H*). ^{13}C NMR (C_6D_6, 126 MHz): 159.46 (t, *J* = 8.1 Hz, Py C2, 6), 151.64-151.48 (m, Rh*C*OPh), 139.20 (s, Py C4),135.75 (s, Ph), 129.20 (s, Ph), 128.35 (s, Ph), 127.36 (s, Ph), 96.49 (s, Py C3, 5), 40.89-41.07 (m, *c*Pe-*C*), 34.45 (s, *c*Pe-*C*), 29.75 (s, *c*Pe-*C*), 28.74 (t, *J* = 5.3 Hz, *c*Pe-*C*), 26.98 (dt, *J* = 3.8 Hz, *J*= 32.9 Hz, *c*Pe-*C*). HRMS (ESI): [M-COPh+MeCN] requires 589.2091, Found: 589.2104; M = $C_{32}H_{46}N_3OP_2Rh$.

Reaction of (PN^3P)RhCO (C_6H_5) (4) with dilute HCl to form (PN^3P)RhCl (2) and release benzaldehyde. A dilute hydrochloric acid (HCl) solution (1 mmol/mL, 0.10 mmol) was added to the THF (5 mL) solution of complex **4** (65.4 mg, 0.1 mmol) at room temperature, and a yellow solution was obtained immediately. Then the forming solution was evaporated, leaving a yellowish solid. The residue was washed with pentane and dried in the vacuum to give the 51.3 mg (Yield: 88%) of the starting complex **2** as a yellowish solid.

Single X-ray structure determination

The X-ray diffraction data of **3** and **4** were collected at the low temperature using Bruker-AXS KAPPA-APEXII CCD diffractometer with graphite-monochromated Cu-Kα radiation (λ= 1.54178

Å), and the tested crystals were epoxy-coated and mounted on the glass fiber. The structures of complexes **3** and **4** are solved by direct methods, for the non-hydrogen atoms, we used the trial structure for the locating and then they were refined anisotropically with the SHELXTL using a full-matrix least-squares procedure based on F^2 values. As to the hydrogen atoms, the positions were fixed geometrically at calculated distances and allowed to ride on the parent atoms. A semi-empirical absorption correction was applied using the SADABS program. The free solvent (benzene and THF) was squeezed (complex **4**) with PLATON during the structure refinement. The detail of the crystal data and structure refinements for complex **3** and **4** are listed in **Table S1**.

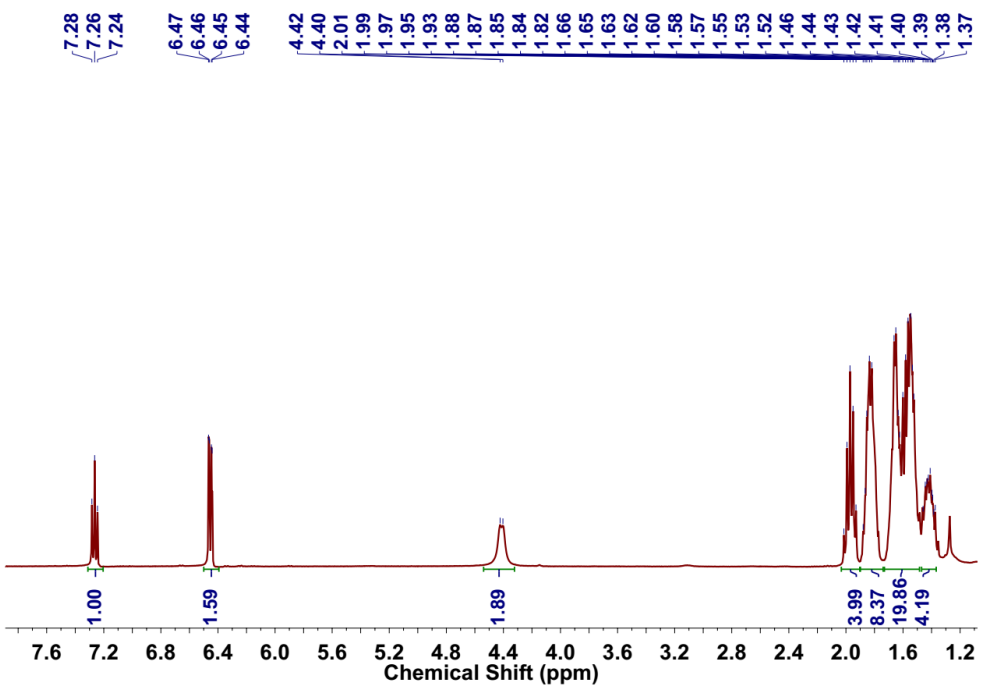

Fig. S1 ^{1}H NMR spectrum of **1** ($CDCl_3$, 400MHz)

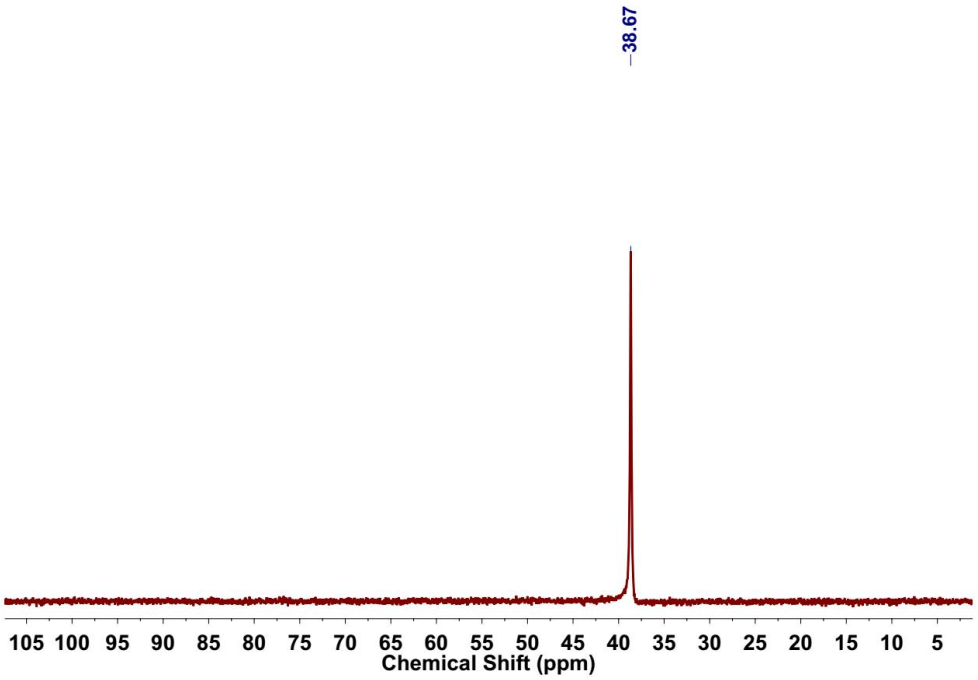

Fig. S2 ^{31}P NMR spectrum of **1** ($CDCl_3$, 162MHz)

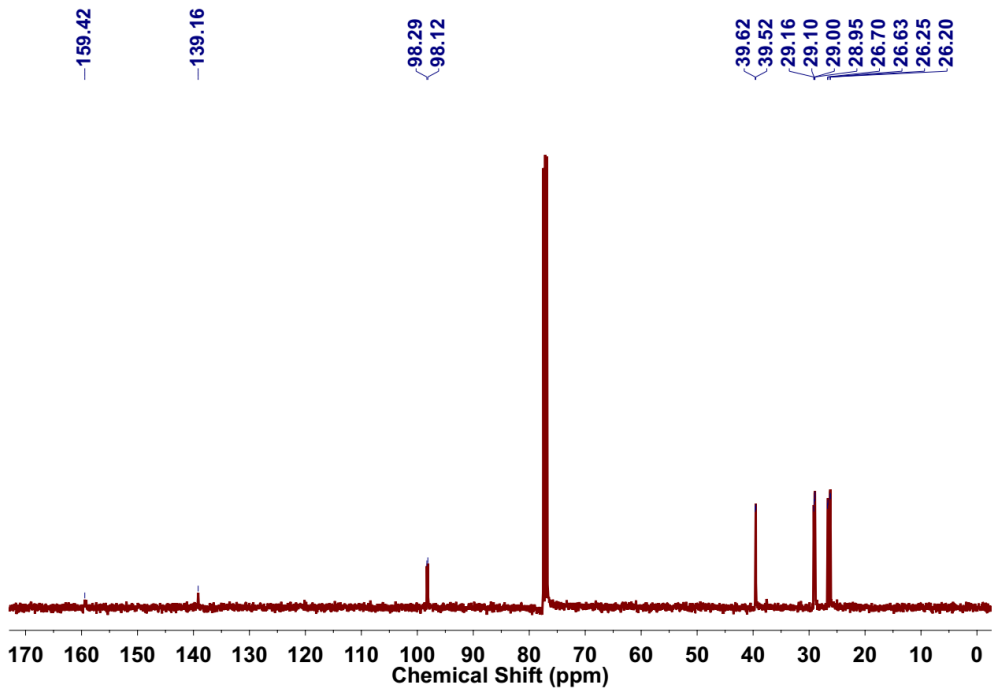

Fig. S3 ^{13}C NMR spectrum of **1** ($CDCl_3$, 101 MHz)

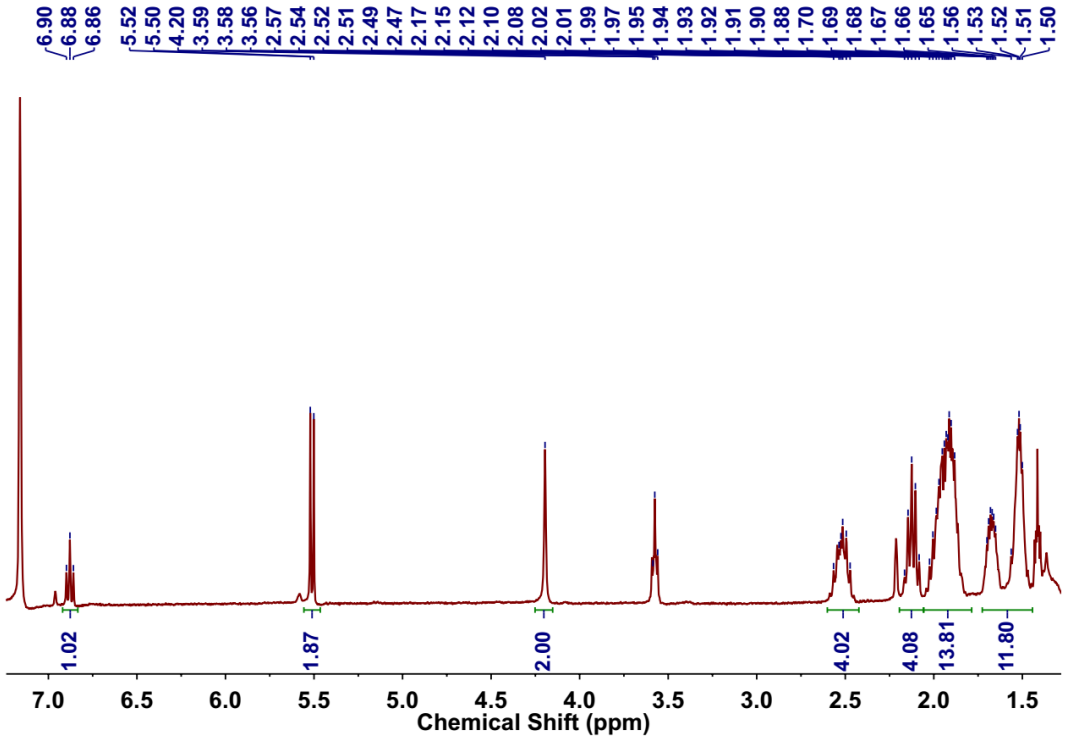

Fig. S4 ^{1}H NMR spectrum of **2** (C_6D_6, 400MHz)

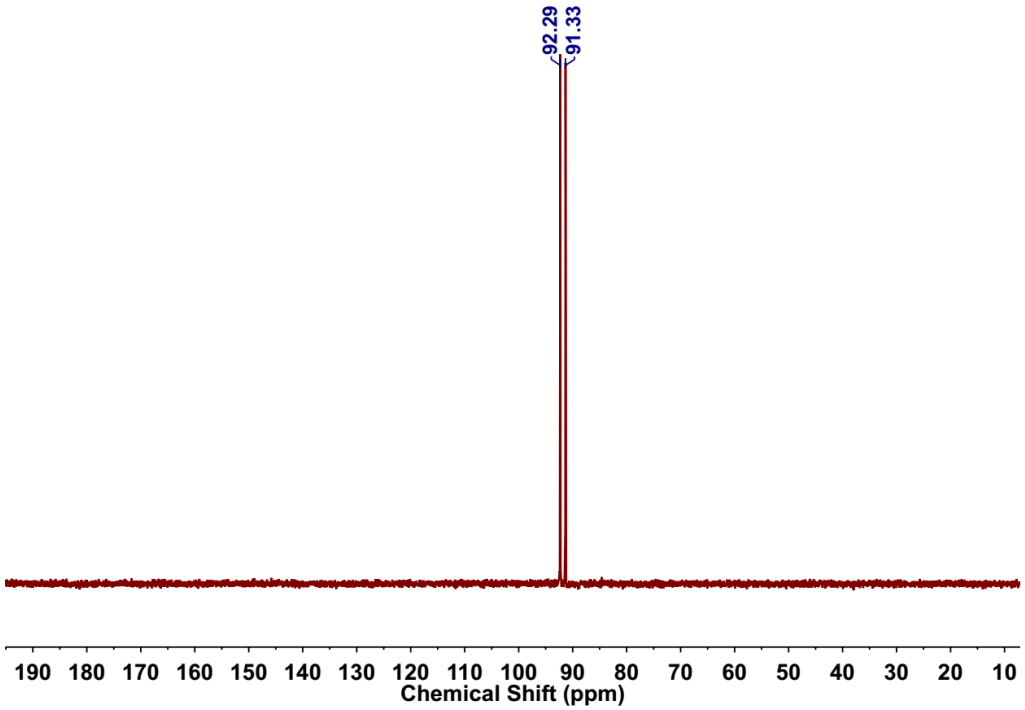

Fig. S5 ^{31}P NMR spectrum of **2** (C_6D_6, 162MHz)

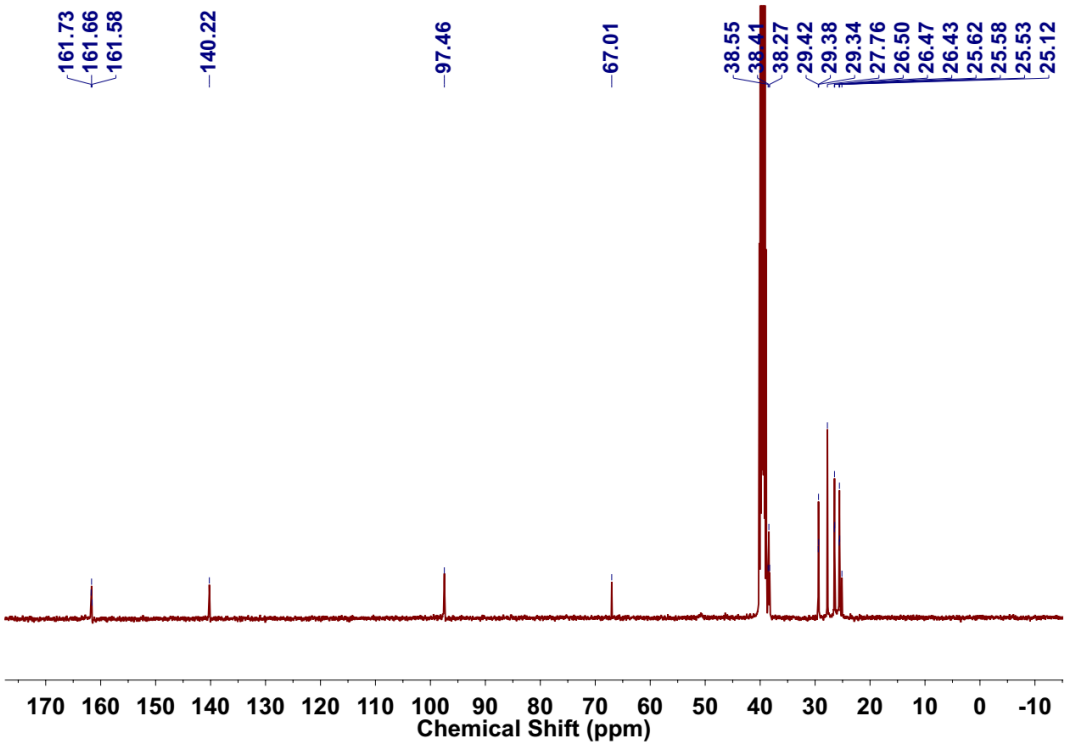

Fig. S6 ^{13}C NMR spectrum of **2** (DMSO-d_6, 101MHz)

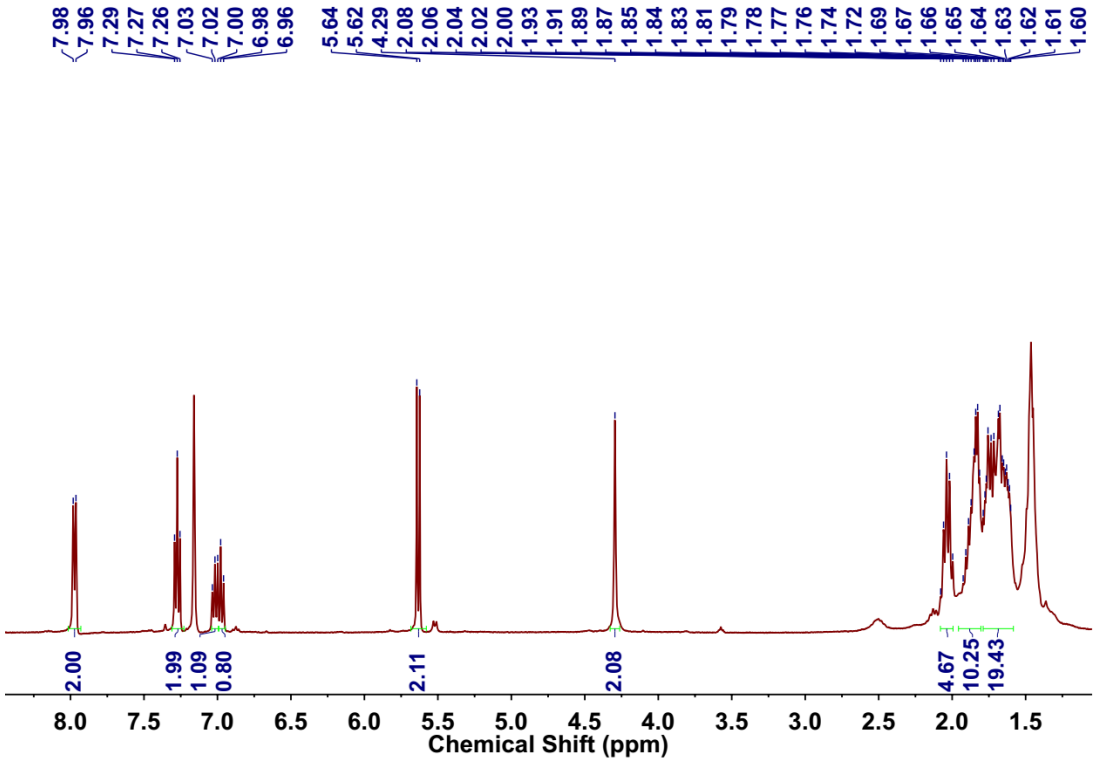

Fig. S7 ^{1}H NMR spectrum of **3** (C_6D_6, 400MHz)

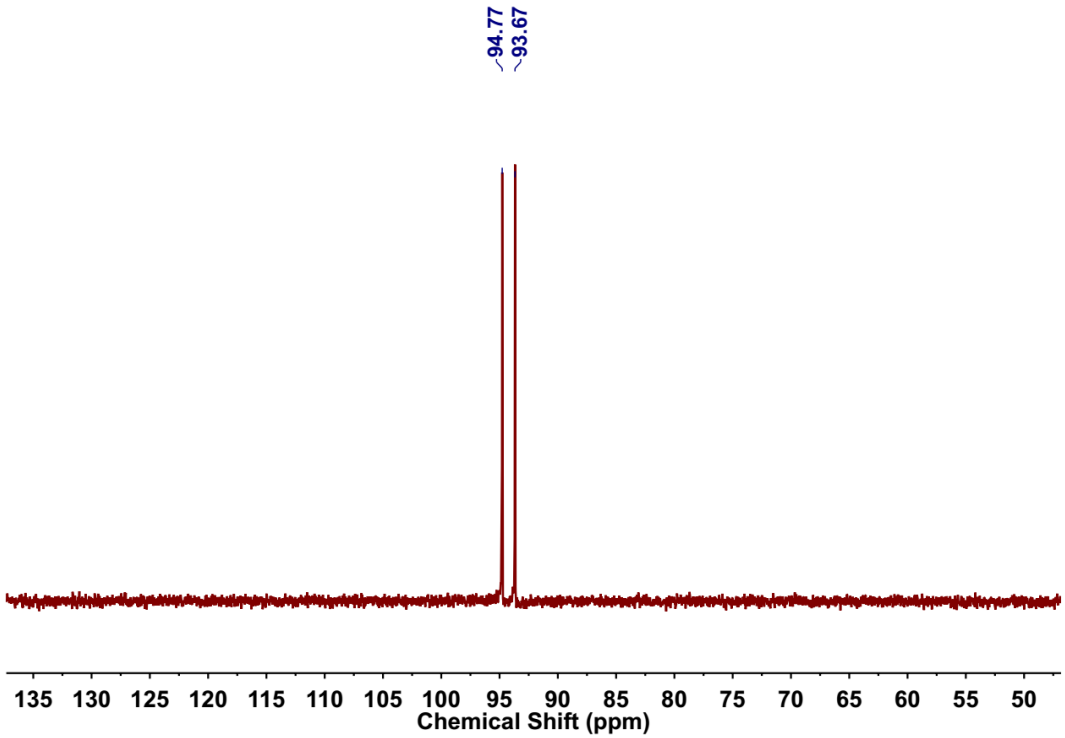

Fig. S8 ^{31}P NMR spectrum of **3** (C_6D_6, 162MHz)

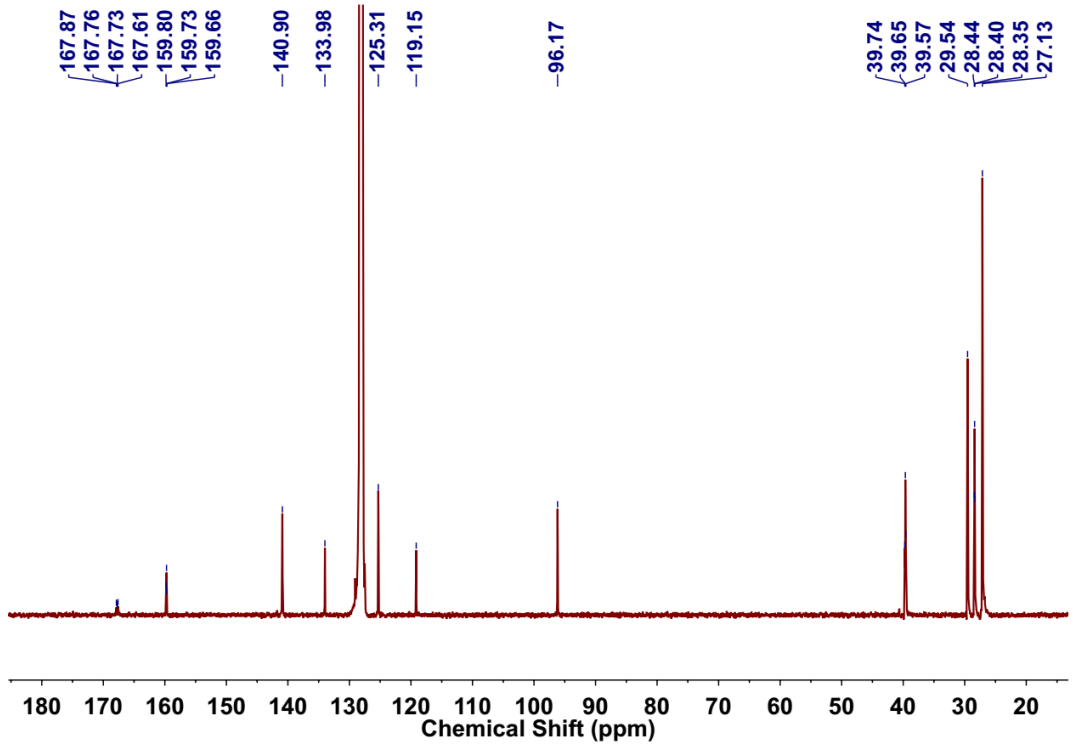

Fig. S9 ^{13}C NMR spectrum of **3** (C_6D_6, 126 MHz)

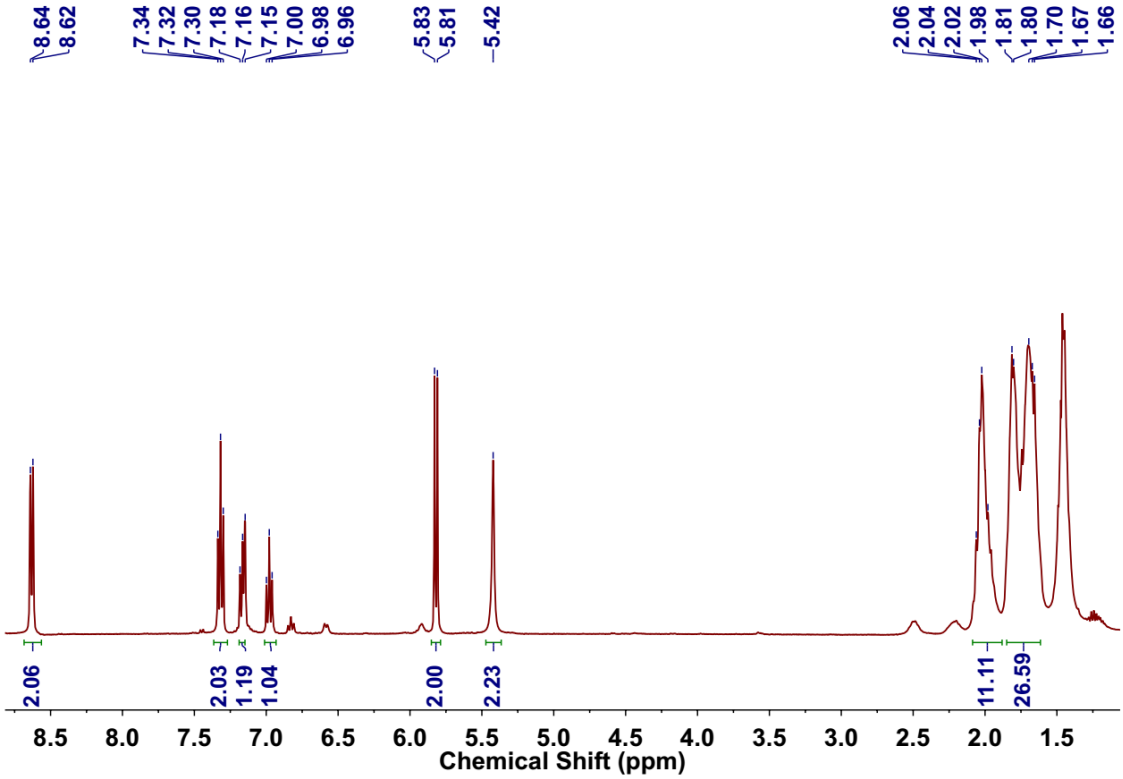

Fig. S10 ^{1}H NMR spectrum of **4** (C_6D_6, 400MHz)

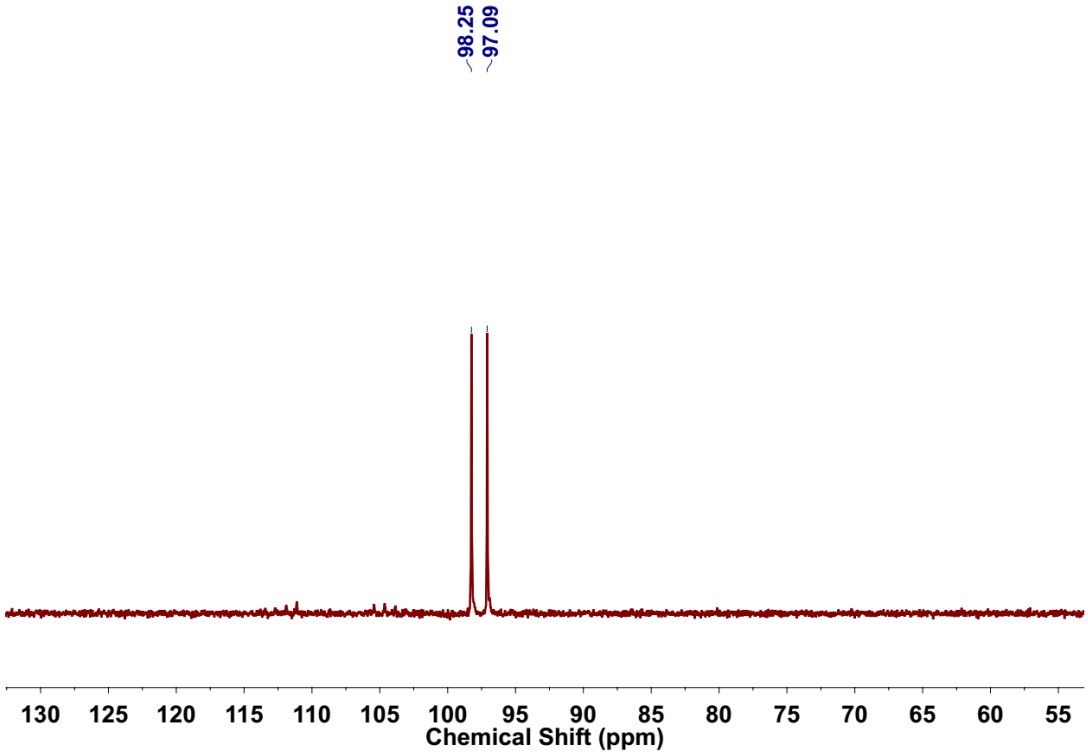

Fig. S11 ^{31}P NMR spectrum of **4** (C_6D_6, 162MHz)

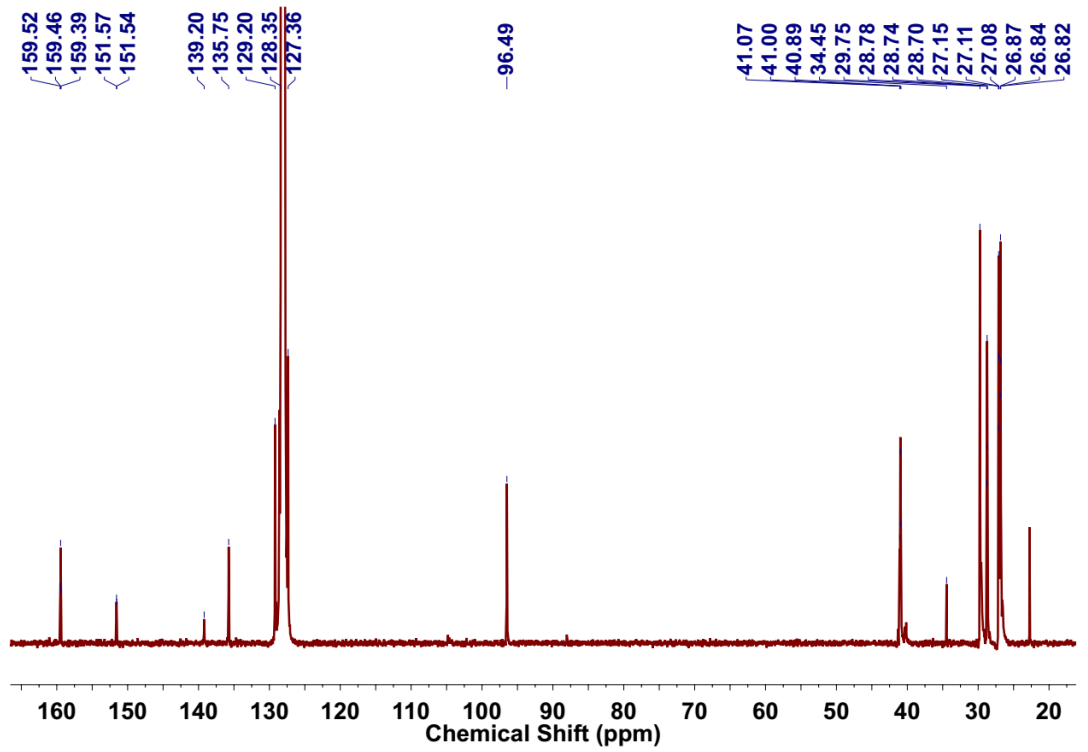

Fig. S12 ^{13}C NMR spectrum of **4** (C_6D_6, 126 MHz)

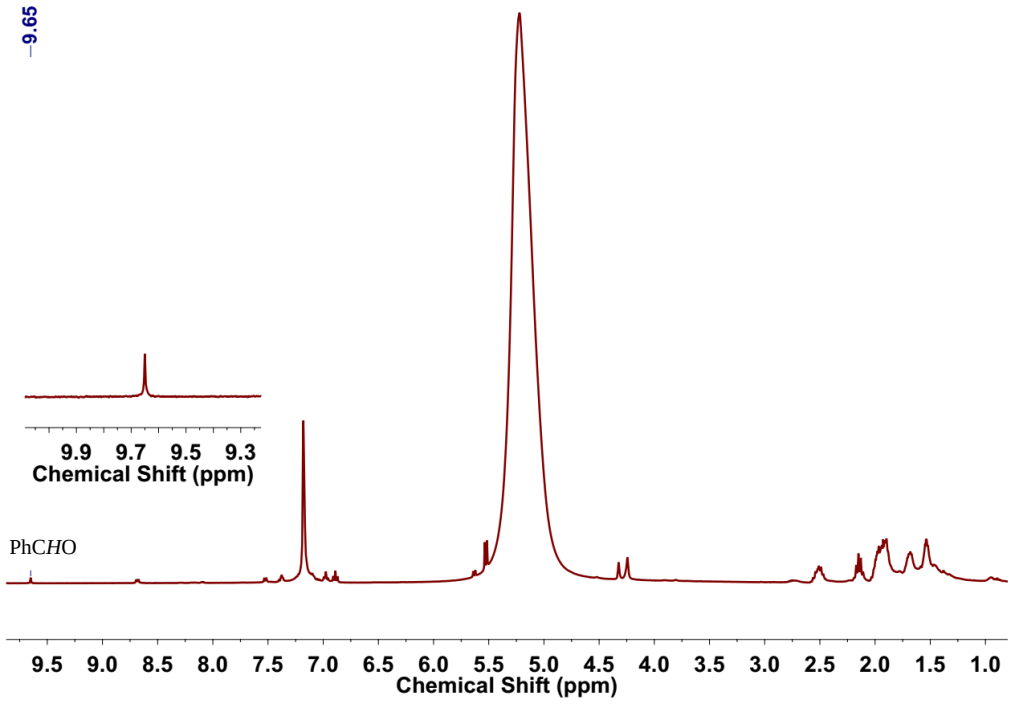

Fig. S13 ^{1}H NMR spectrum of **4** with HCl (C_6D_6, 400MHz)

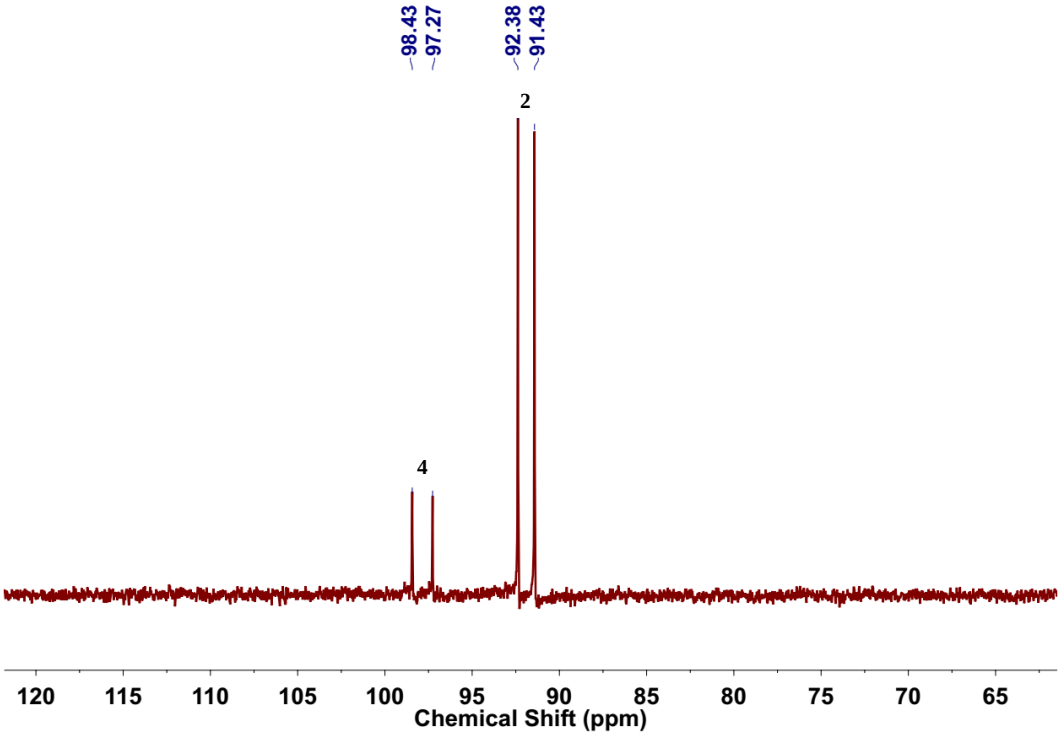

Fig. S14 ^{1}P NMR spectrum of **4** with HCl (C_6D_6, 162MHz)

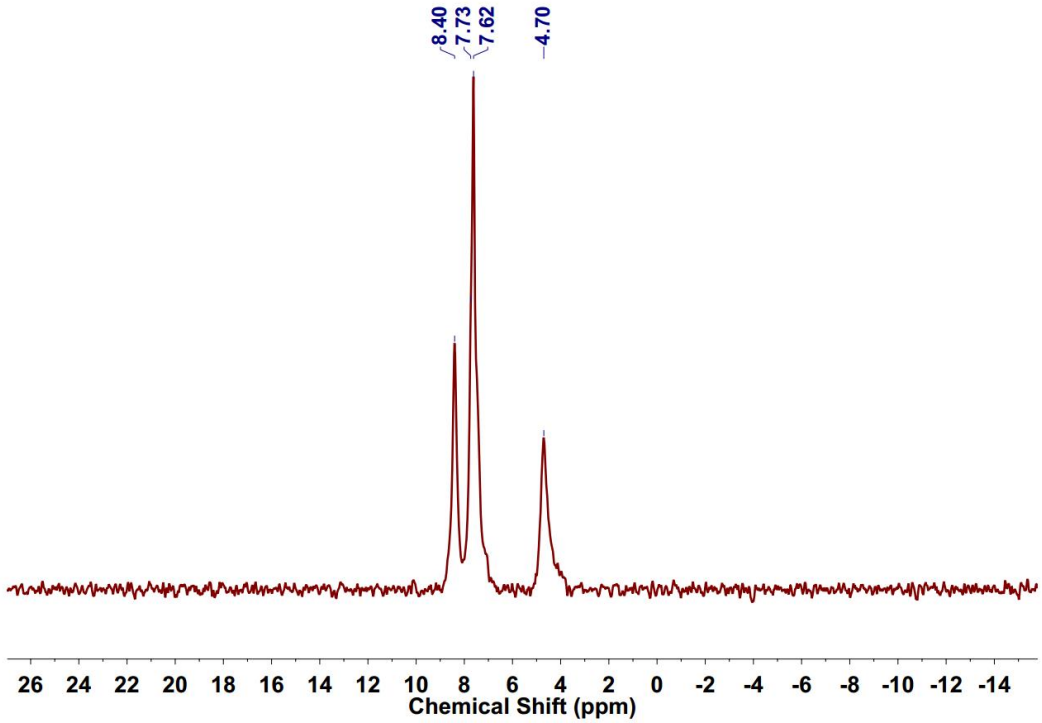

Fig. S15 ^{2}H NMR spectrum of **2** with C_6D_6 (benzene, 600MHz, 1024 scan times)

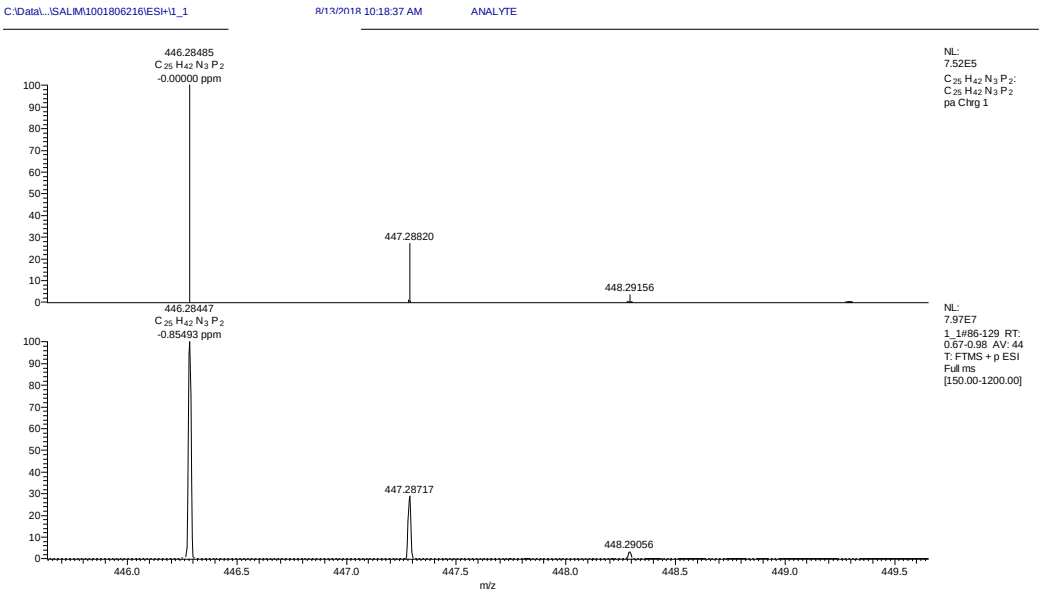

Fig. S16 HRMS spectrum of ligand **1**

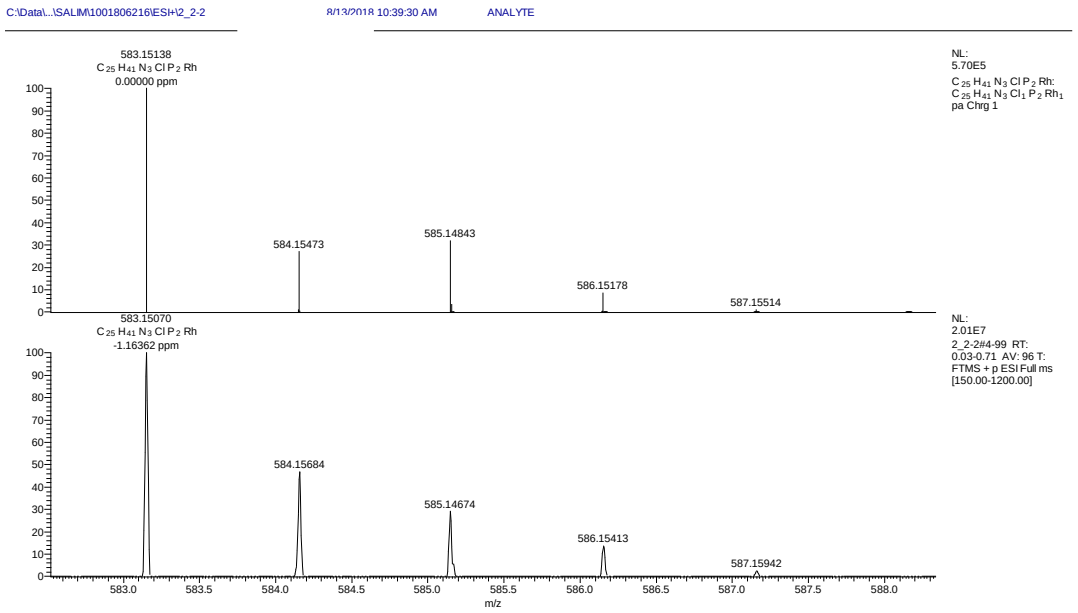

Fig. S17 HRMS spectrum of complex **2**

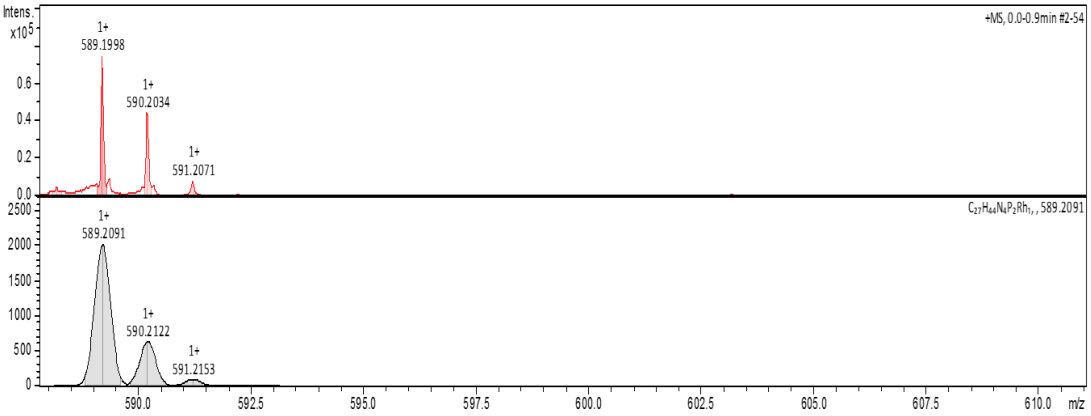

Fig. S18 HRMS spectrum of complex **3**

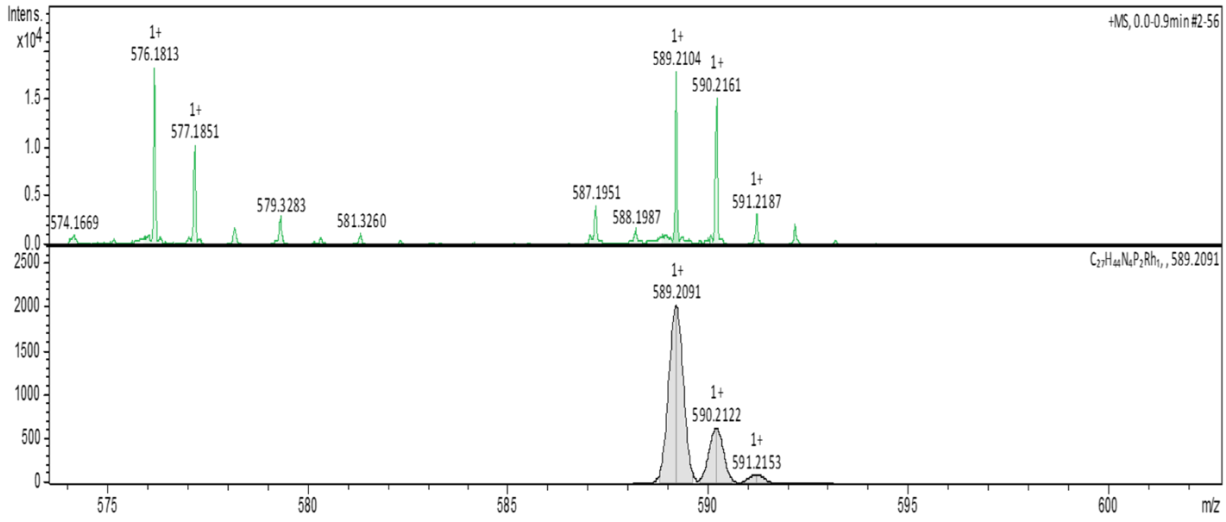

Fig. S19 HRMS spectrum of complex **4**

Table 1 crystal data and structure refinements for the complex **3** and **4**

identification code	complex **3**	complex **4**
empirical formula	$C_{31}H_{44}N_3P_2Rh$	$C_{92}H_{120}N_6O_3P_4Rh_2$
formula weight	623.54	1687.64
temperature (K)	230	200
wavelength (Å)	1.54178	1.54178
crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$	$C2/c$
a (Å)	10.9778(7)	29.2408(9)
b (Å)	16.1480(10)	13.8295(4)
c (Å)	17.5888(11)	25.4214(7)
α (deg)	90	90
β (deg)	106.2308(16)	120.9250(10)
γ (deg)	90	90
Z	4	4
V (Å^3)	2993.7(3)	8818.6(5)
D_{calcd} (g cm^{-3})	1.383	1.271
μ (mm^{-1})	5.798	4.101
F (000)	1304	3552
theta min-max (deg)	4.3, 66.9	3.5, 72.2
total uniq. Data	20033, 5214	79256, 8674
R(int)	0.043	0.030
observed data [$I > 2\sigma(I)$]	5064	8302
R_1, wR_2 ($I > 2\sigma(I)$)	0.0339, 0.0937	0.0276, 0.0763
S	1.05	1.01

$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$, where $w = 1/[\sigma^2(F_o^2)+(aP)^2 + bP]$, $P = (F_o^2 + 2F_c^2)/3$.