

## Supplementary information

# **Catechol and 1,2,4,5-tetrahydroxybenzene functionalized cyclodiphosphazane ligands synthesis, structural studies, and transition metal complexes**

Madhusudan K. Pandey,<sup>†,a</sup> Harish S. Kunchur,<sup>†,a</sup> Guddekoppa S. Ananthnag,<sup>†,a</sup> Joel T. Mague,<sup>‡</sup>  
and Maravanji S. Balakrishna\*<sup>†</sup>

<sup>†</sup>Phosphorus Laboratory, Department of Chemistry, Indian Institute of Technology Bombay,  
Powai, Mumbai, 400076, India

<sup>‡</sup>Department of Chemistry, Tulane University, New Orleans, Louisiana, 70118, United States

---

NMR spectra of compounds <b>1-16</b>	2–26
HRMS spectra of compounds <b>1-16</b>	2–26

---

\*Corresponding author M. S. Balarkishna, E-mail [krishna@chem.iitb.ac.in](mailto:krishna@chem.iitb.ac.in) or [msb\\_krishna@iitb.ac.in](mailto:msb_krishna@iitb.ac.in)

<sup>a</sup>These authors contributed equally to this work

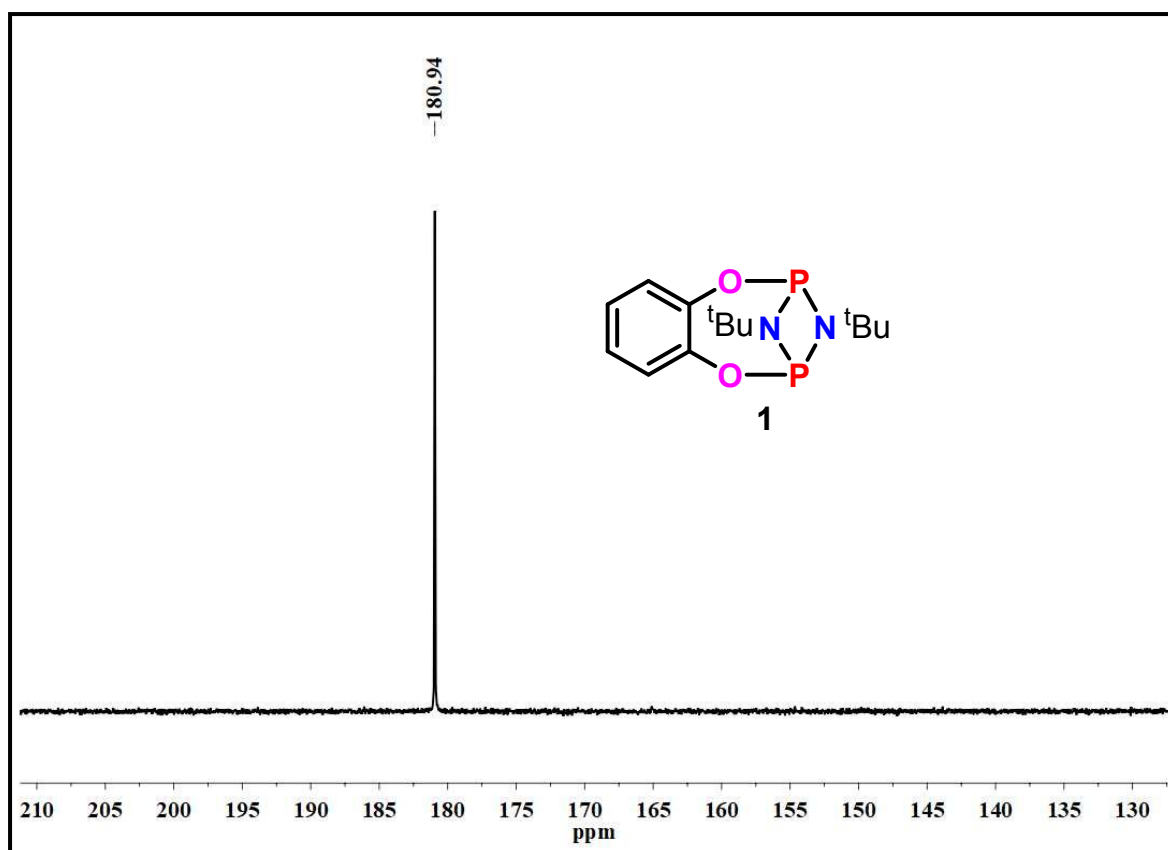


Fig. S1  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CDCl}_3$  (162 MHz)

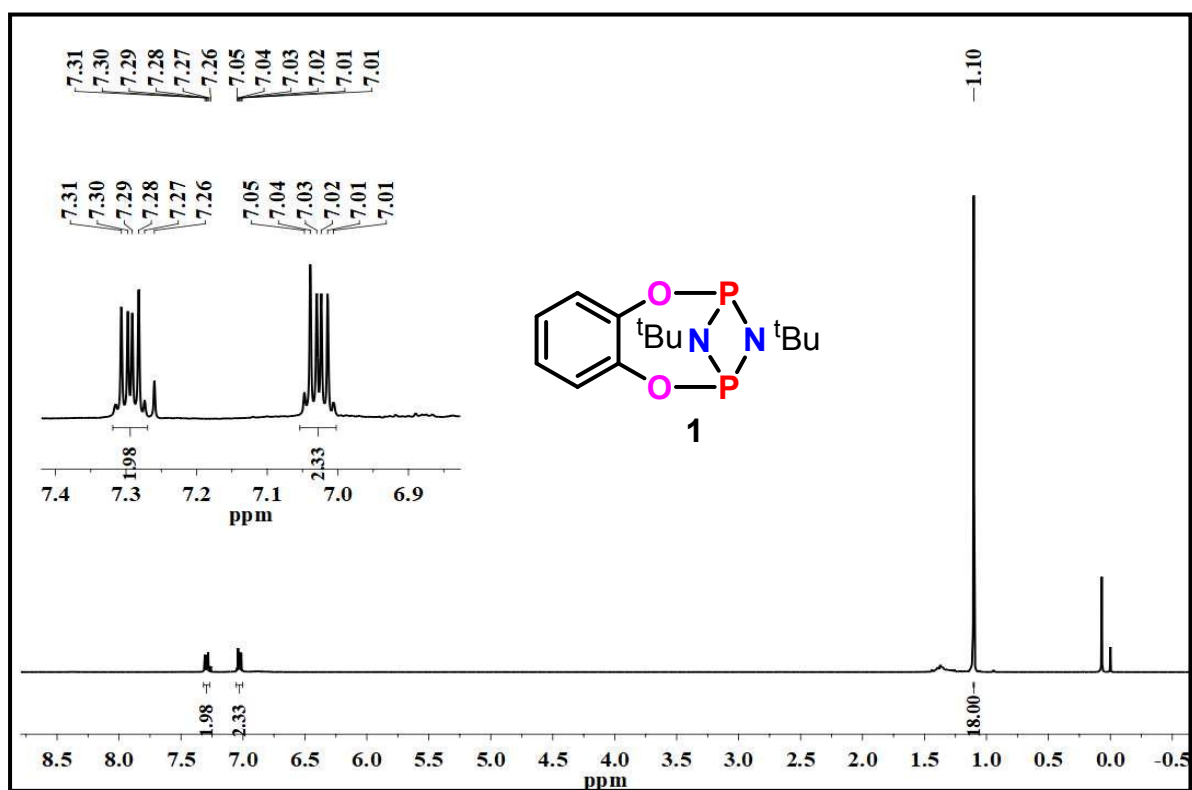


Fig. S2  $^1\text{H}$  NMR spectrum of **1** in  $\text{CDCl}_3$  (400 MHz)

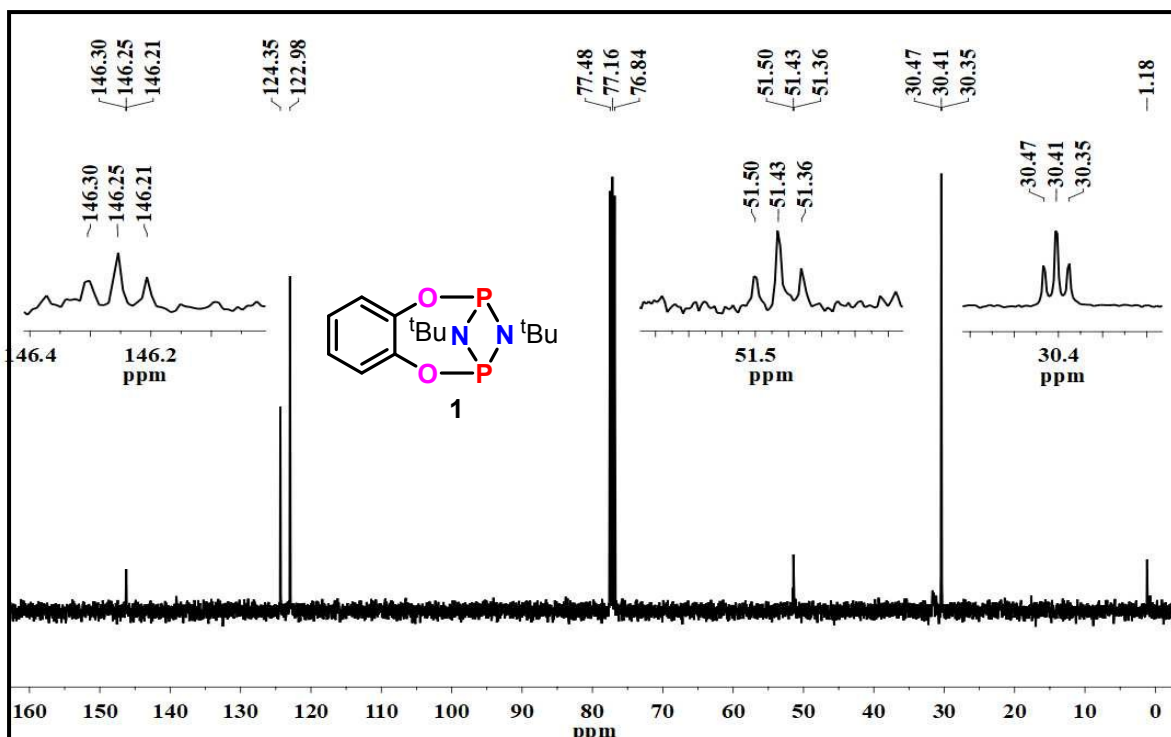


Fig. S3  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **1** in  $\text{CDCl}_3$ (101 MHz)

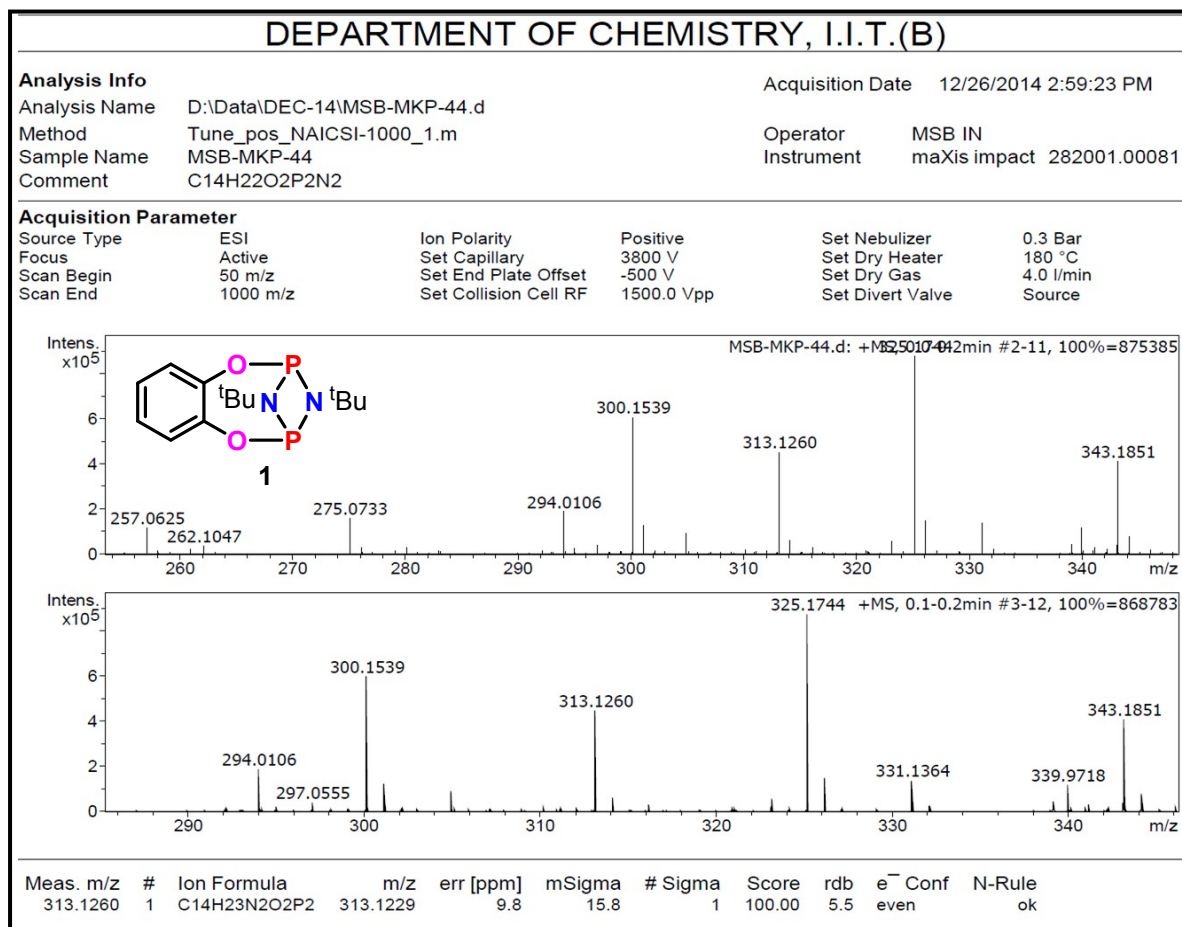


Fig. S4 HRMS spectrum of **1**

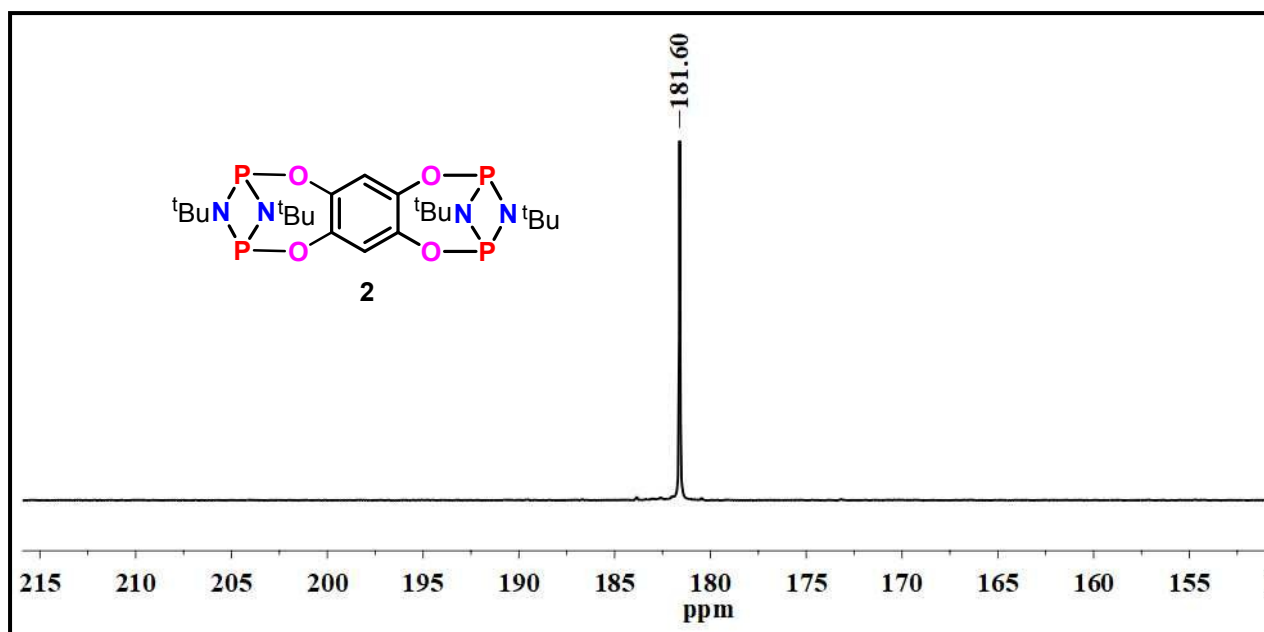


Fig. S5  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  (202 MHz)

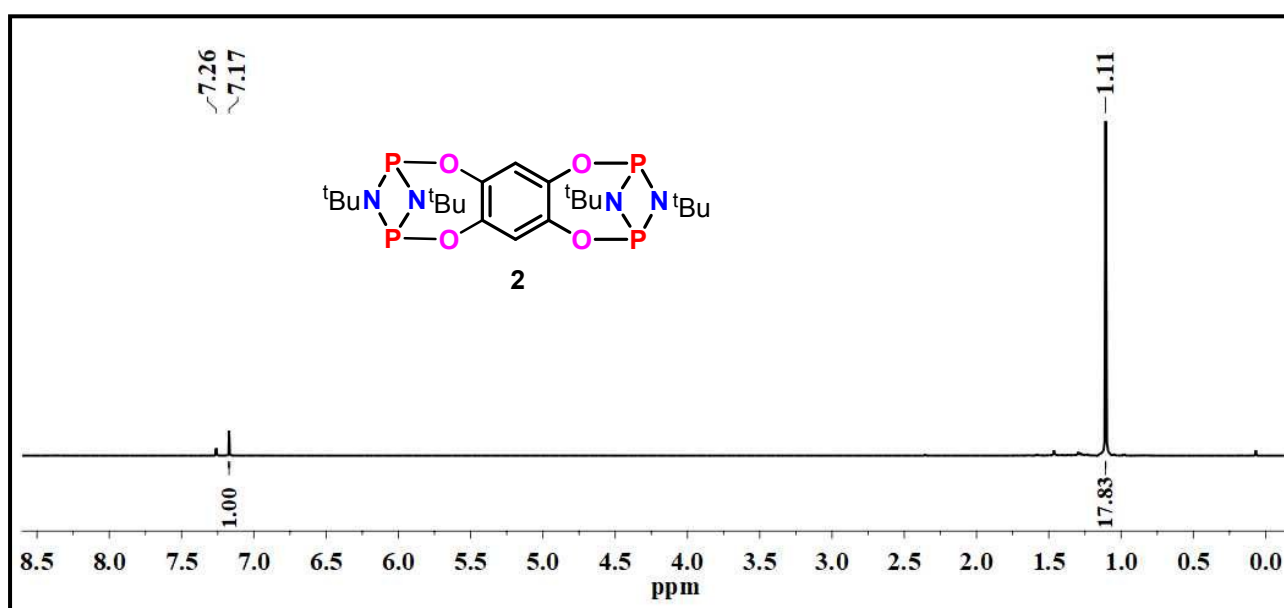


Fig. S6  $^1\text{H}$  NMR spectrum of **2** in  $\text{CDCl}_3$  (500 MHz)

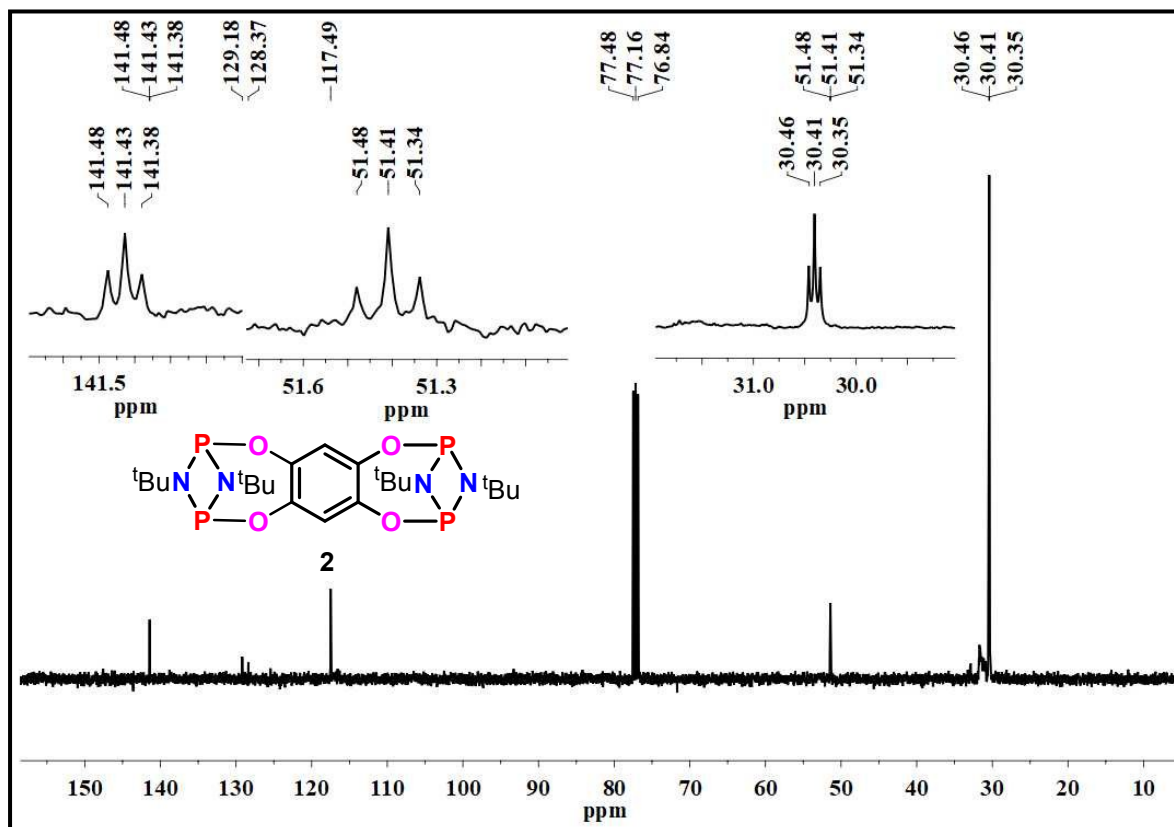


Fig. S7  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **2** in  $\text{CDCl}_3$  (126 MHz)

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

**Analysis Info**

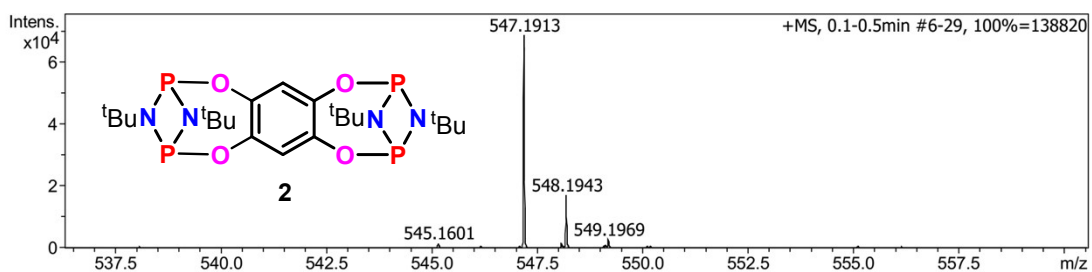
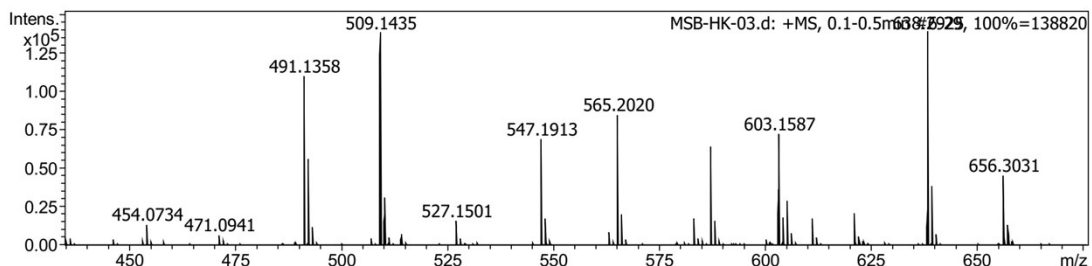
Analysis Name D:\Data\JULY-2016\MSB-HK-03.d  
 Method Tune\_pos\_NAF-1000.m  
 Sample Name MSB-HK-03  
 Comment C22H38P4O4N4

Acquisition Date 7/27/2016 1:59:52 AM

Operator RAF OUT  
 Instrument maXis impact 282001.00081

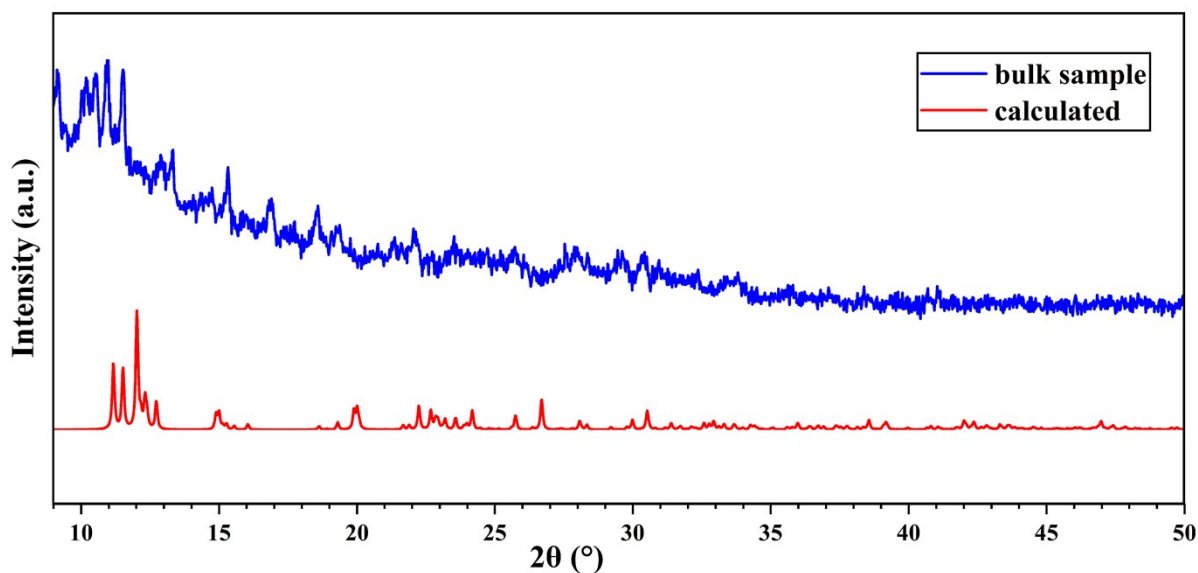
**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1000 m/z	Set Collision Cell RF	900.0 Vpp	Set Divert Valve	Source

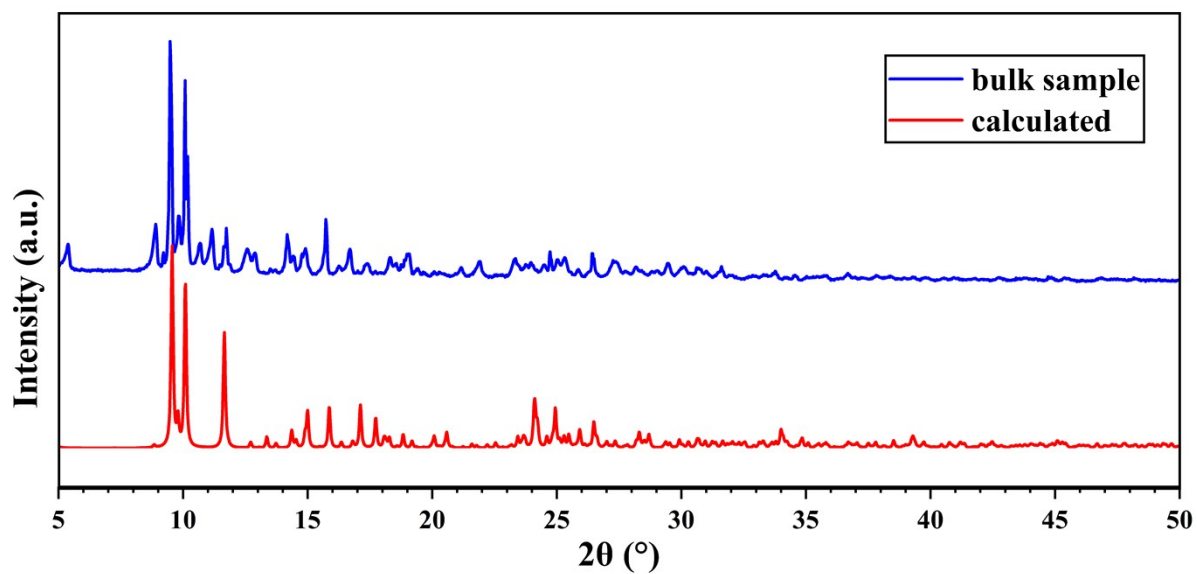


Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
547.1913	1	C22H39N4O4P4	547.1916	-0.6	6.5	1	100.00	7.5	even	ok

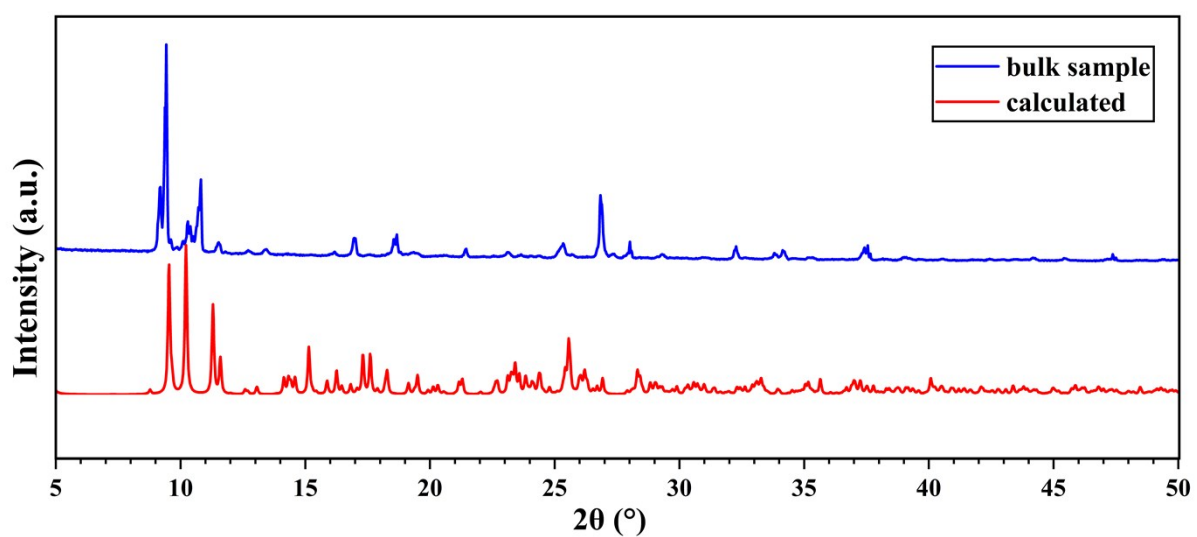
**Fig. S8** HRMS spectrum of **2**



**Fig. S9.** The powder-XRD patterns of compound **3**. Experimental in blue and simulated in red.



**Fig. S10.** The powder-XRD patterns of compound **4**. Experimental in blue and simulated in red.



**Fig. S11.** The powder-XRD patterns of compound **5**. Experimental in blue and simulated in red. (Some extra peaks observed may be due to the presence of some non-identified material).

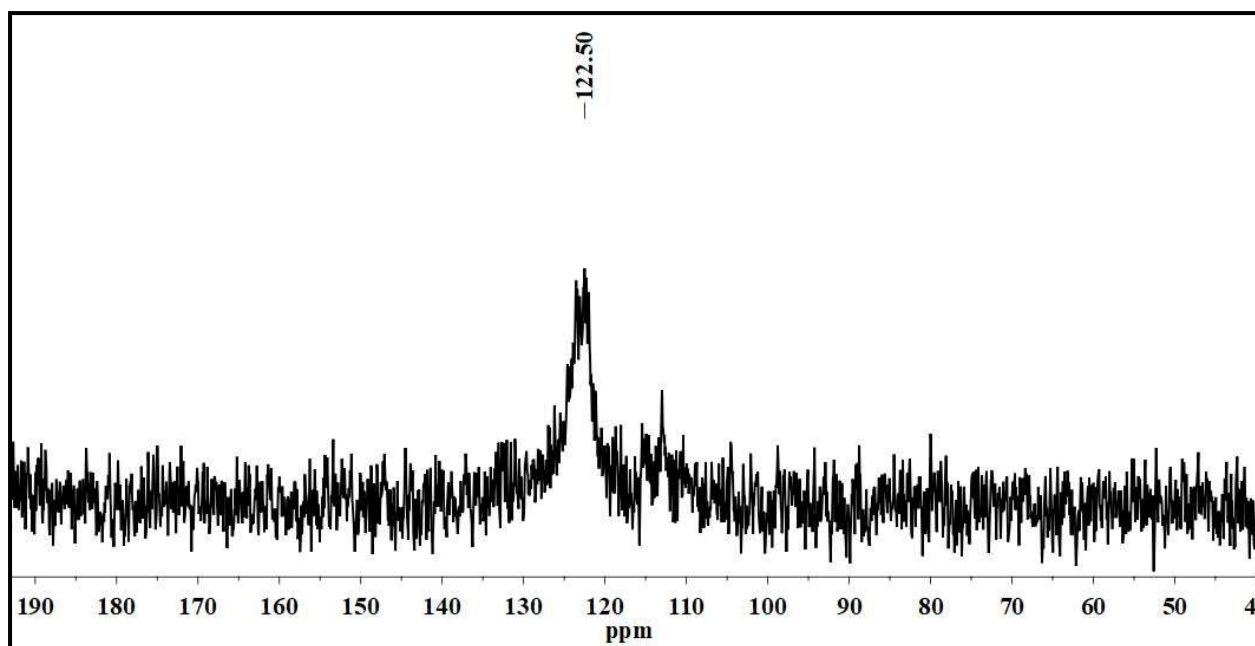


Fig. S12  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **6** in  $\text{CDCl}_3$  (162 MHz)

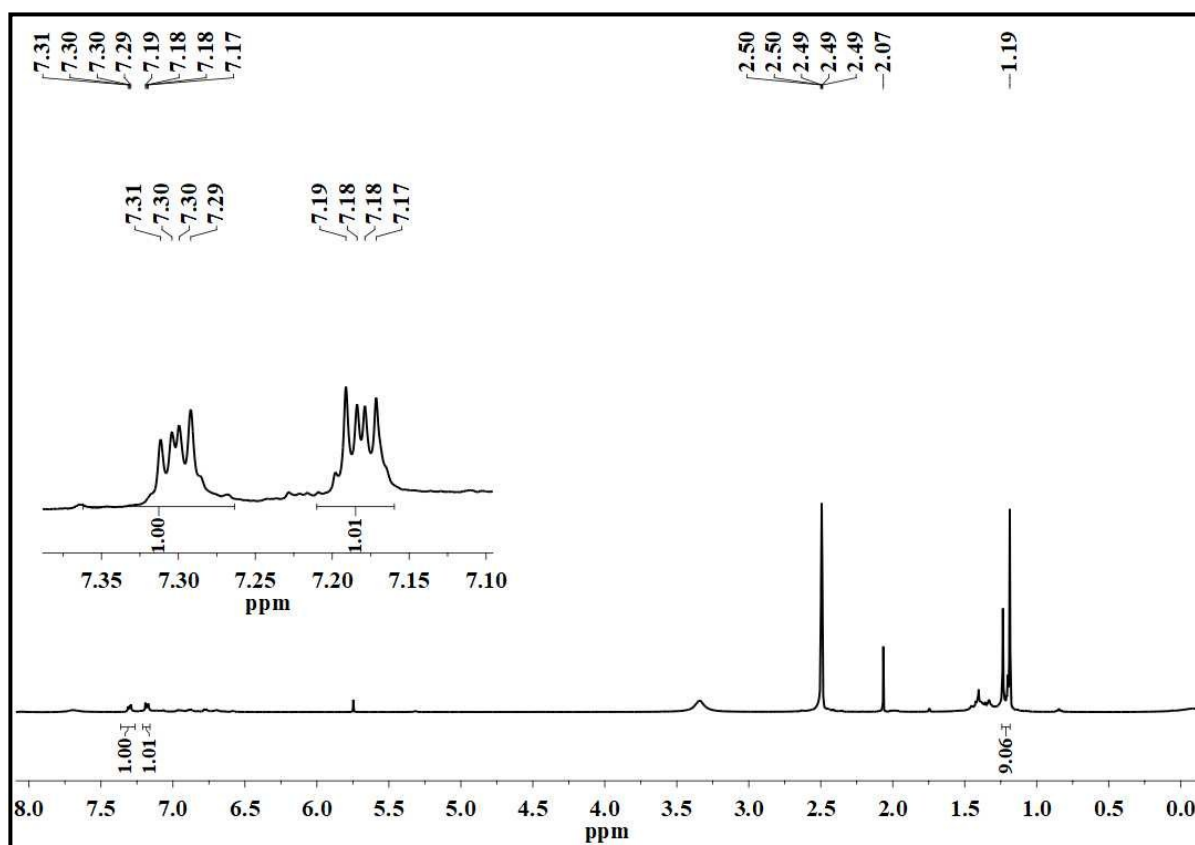
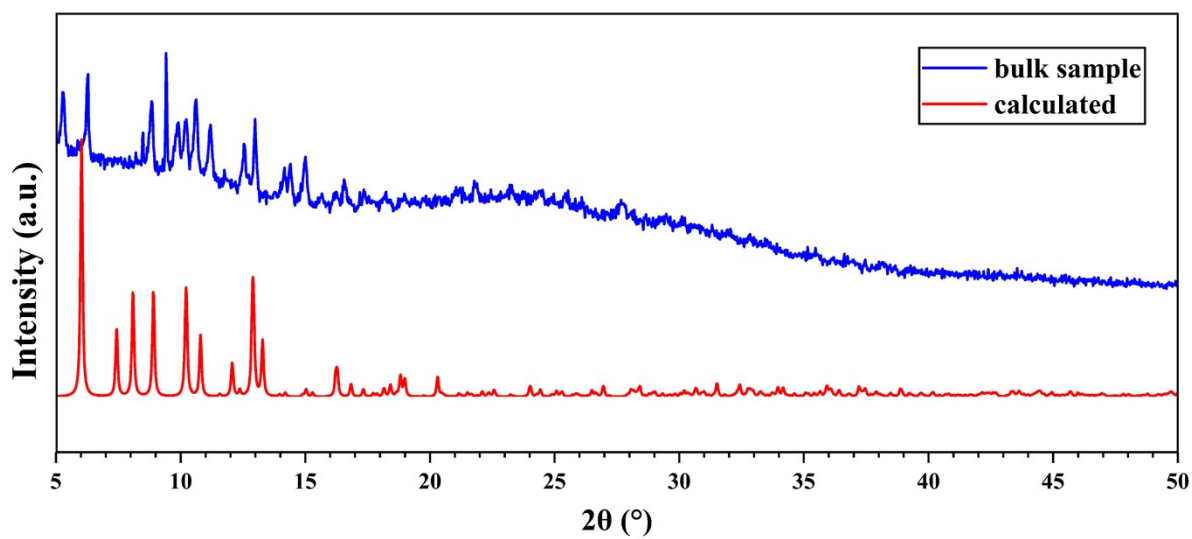
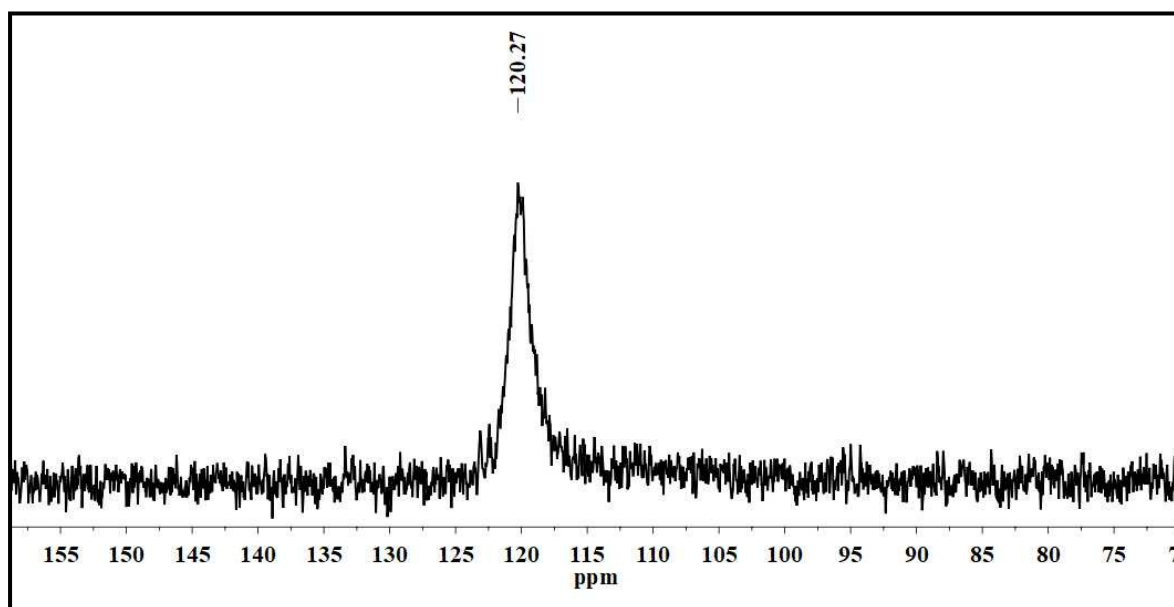


Fig. S13  $^1\text{H}$  NMR spectrum of **6** in  $\text{CDCl}_3$  (500 MHz)

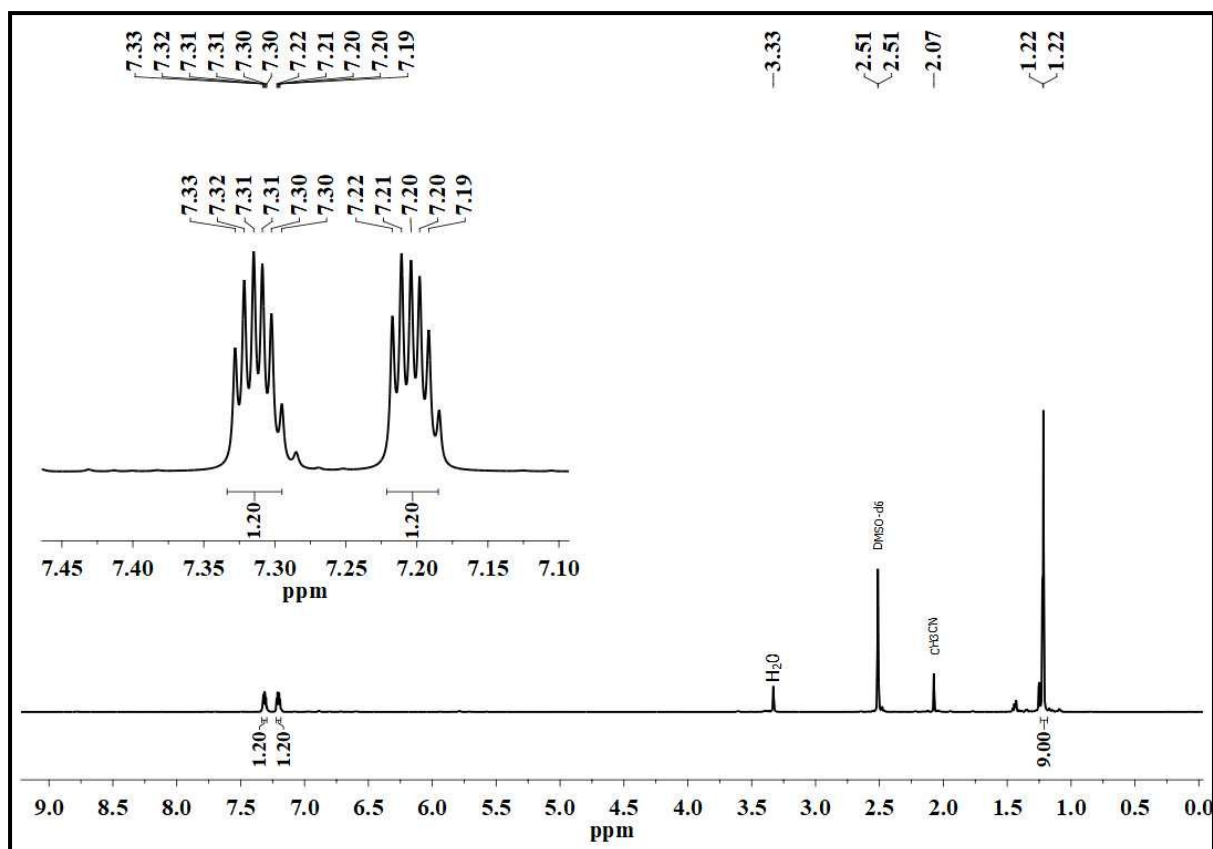




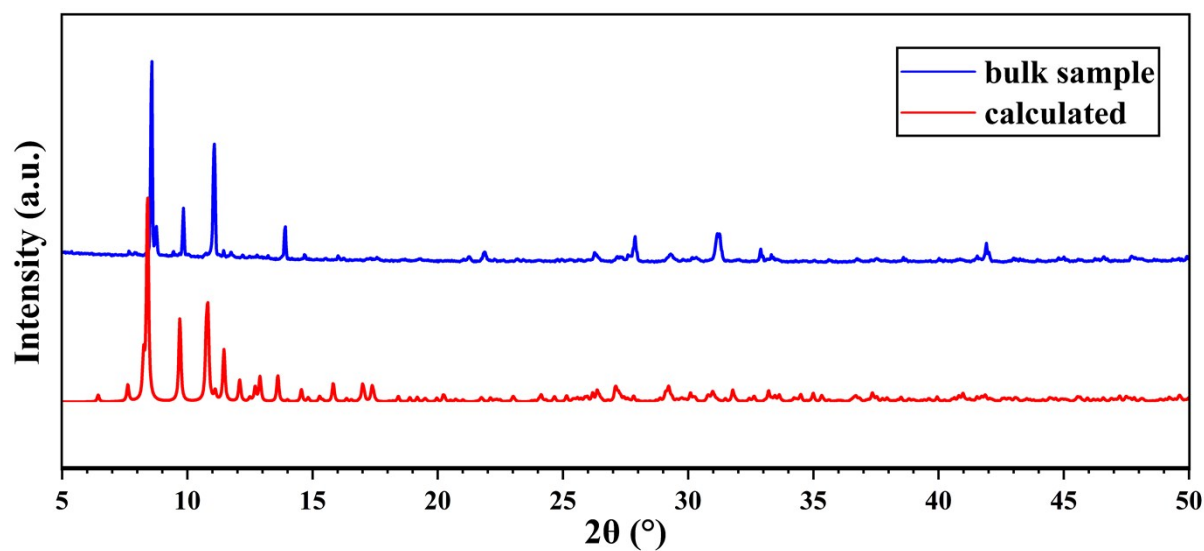
**Fig. S14.** The powder-XRD patterns of compound **6**. Experimental in blue and simulated in red.



**Fig. S15**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** in  $\text{CDCl}_3$  (162 MHz)



**Fig. S16**  $^1\text{H}$  NMR spectrum of **7** in  $\text{CDCl}_3$  (500 MHz)



**Fig. S17.** The powder-XRD patterns of compound **7**. Experimental in blue and simulated in red.

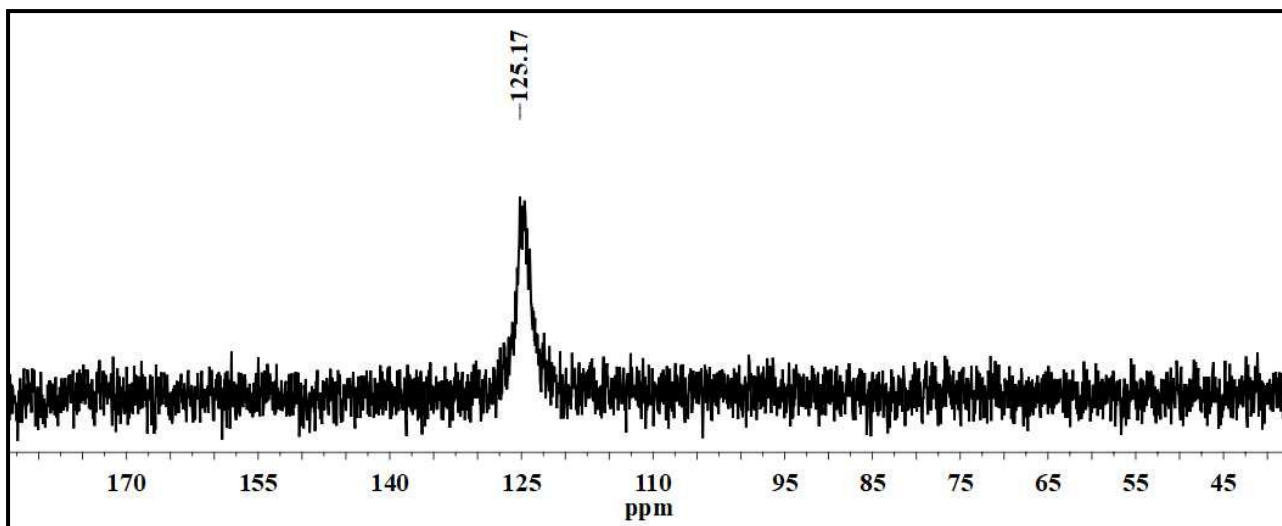


Fig. S18  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **8** in  $\text{CDCl}_3$  (162 MHz)

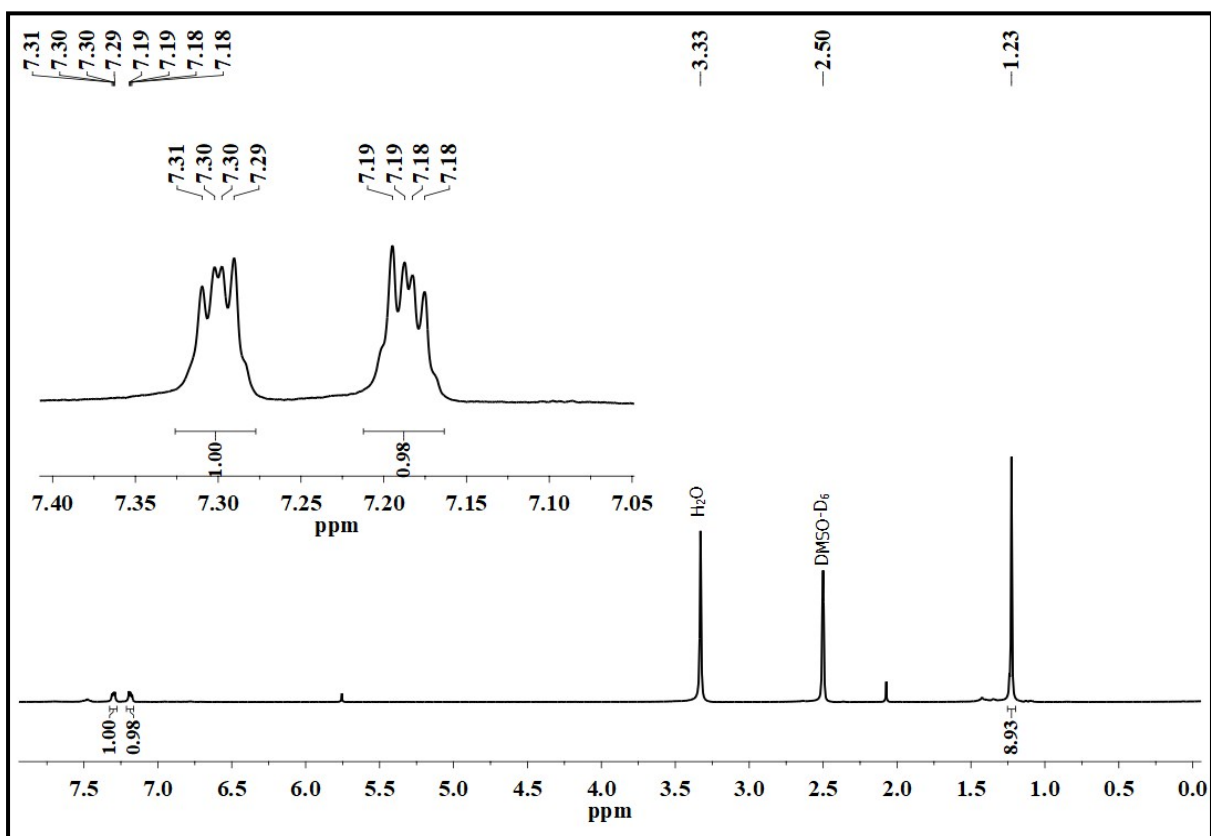
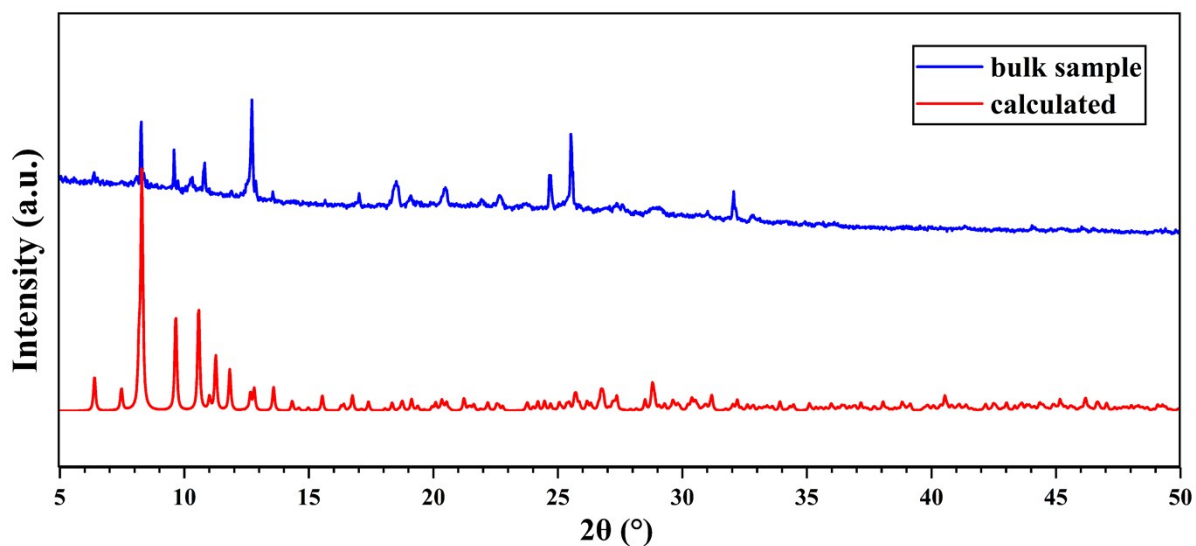
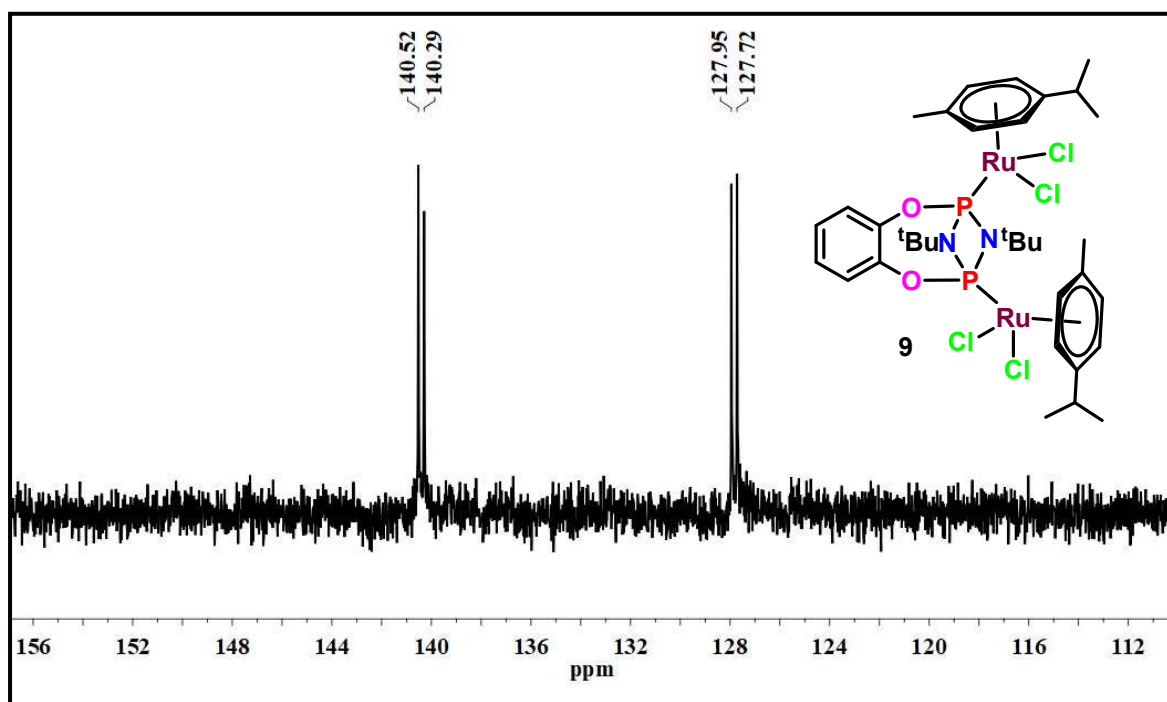


Fig. S19  $^1\text{H}$  NMR spectrum of **8** in  $\text{CDCl}_3$  (500 MHz)



**Fig. S20.** The powder-XRD patterns of compound **8**. Experimental in black and simulated in red. (Some extra peaks observed may be due to the presence of some non-identified material).



**Fig. S21**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **9** in  $\text{CDCl}_3$  (202 MHz)

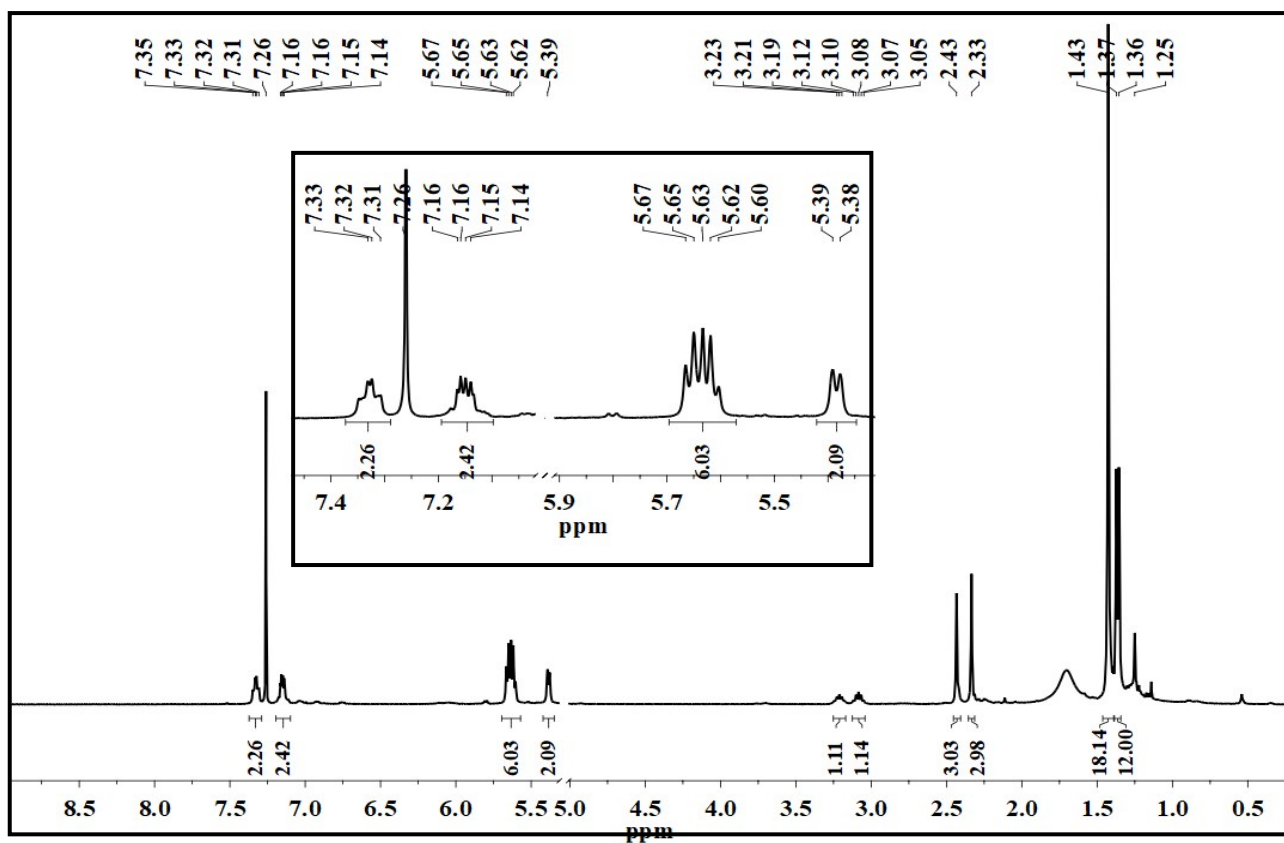


Fig. S22  $^1\text{H}$  NMR spectrum of **9** in  $\text{CDCl}_3$  (400 MHz)

## DEPARTMENT OF CHEMISTRY, I.I.T.(B)

### Analysis Info

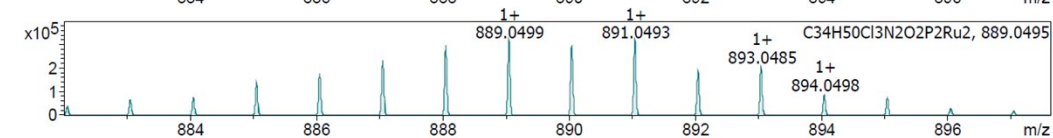
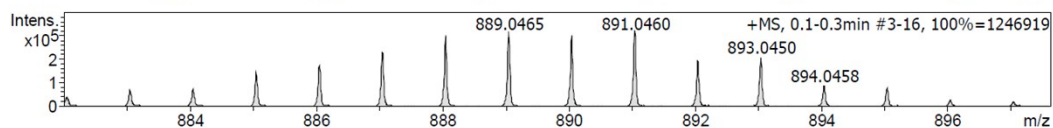
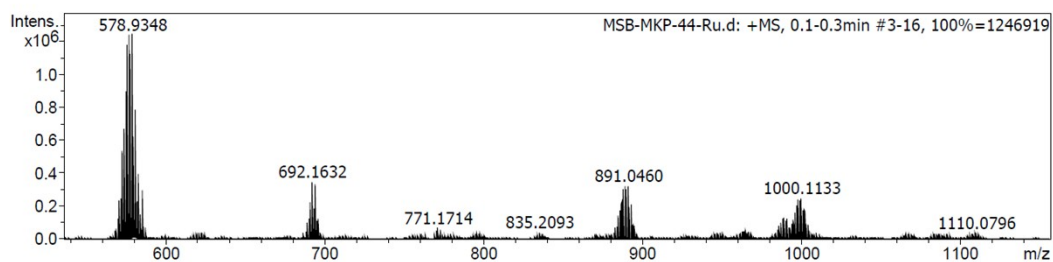
Analysis Name D:\Data\JUN-2018\MSB-MKP-44-Ru.d  
 Method Tune\_pos\_NAICSI-2000A.m  
 Sample Name MSB-MKP-44-Ru  
 Comment C34H50O2P2N2Ru2Cl4

Acquisition Date 6/26/2018 12:03:42 PM

Operator INN out  
 Instrument maXis impact 282001.00081

### Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	2100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
891.0460	1	C34H50Cl3N2O2P2Ru2	889.0499	-3.7	12.2	1	100.00	11.5	even	ok

**Fig. S23** HRMS spectrum of **9**

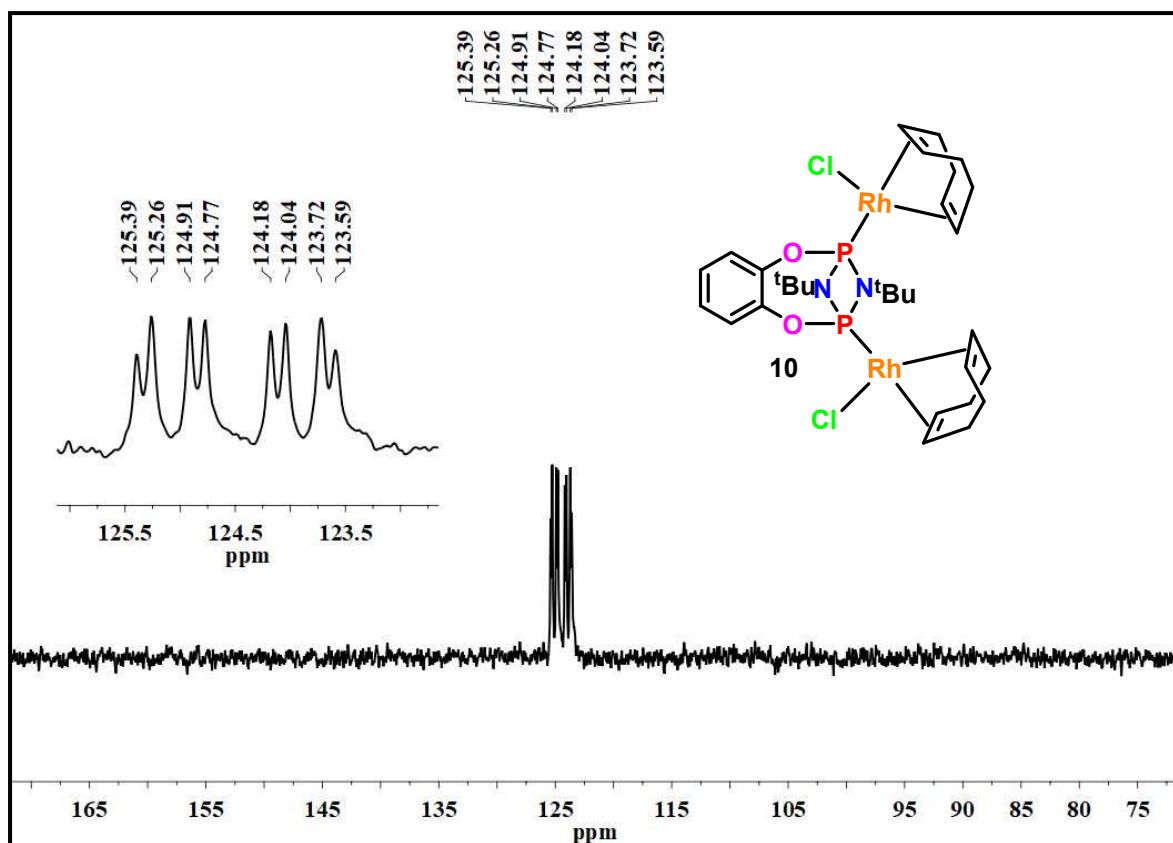


Fig. S24  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **10** in  $\text{CDCl}_3$  (202 MHz)

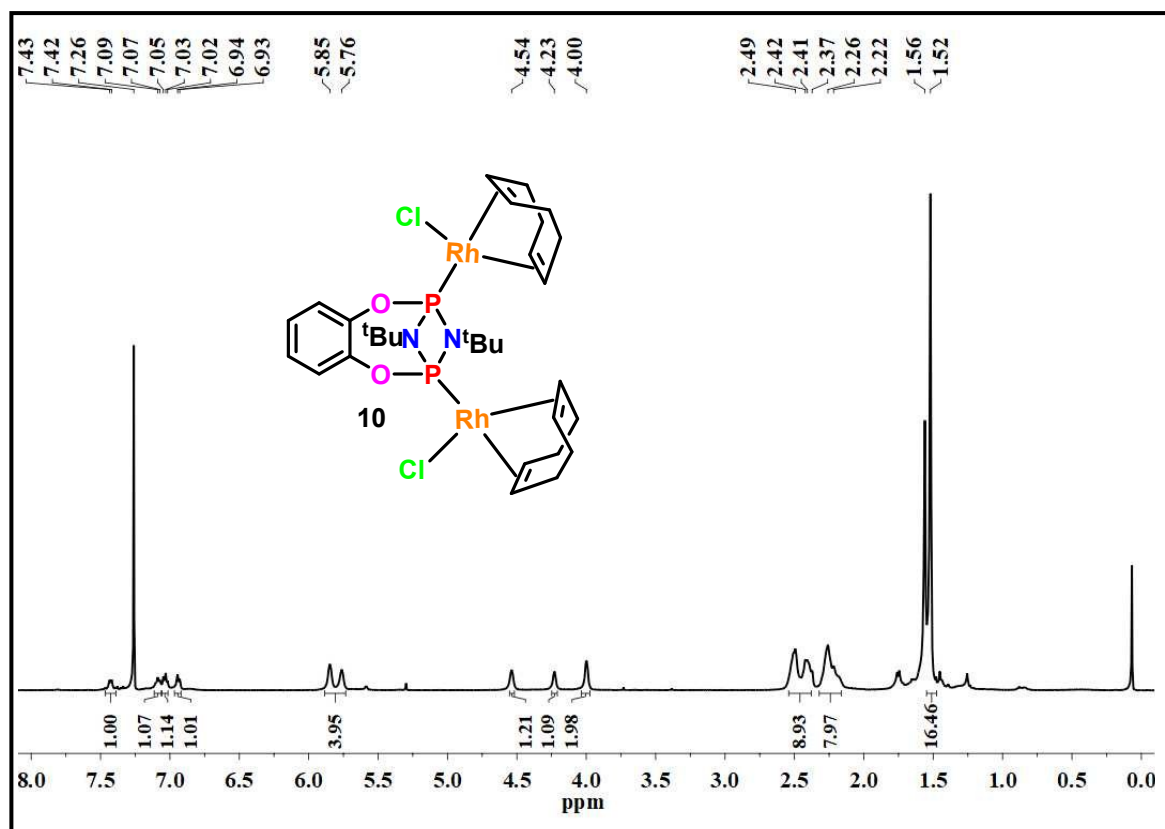


Fig. S25  $^1\text{H}$  NMR spectrum of **10** in  $\text{CDCl}_3$  (500 MHz)

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

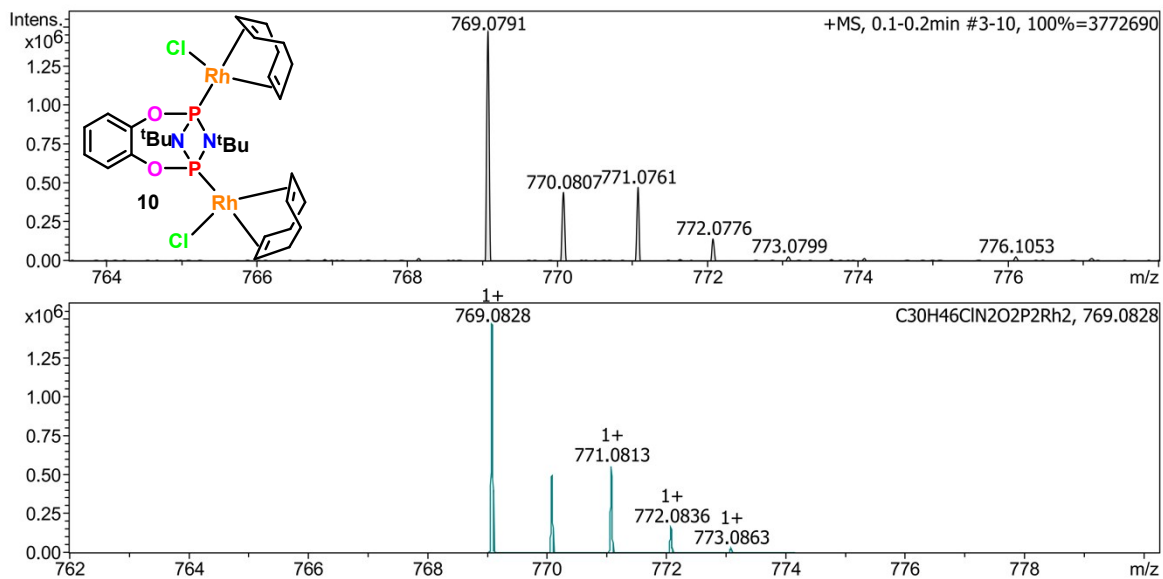
Analysis Info

Analysis Name D:\Data\SEP-2018\MSB-MKP-44-Rh.d  
 Method Tune\_pos\_NAICSI-1500B.m  
 Sample Name MSB-MKP-44-Rh  
 Comment C30H46O2P2N2Rh2Cl2

Acquisition Date 9/24/2018 11:25:58 AM  
 Operator MSB IN  
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type ESI Ion Polarity Positive Set Nebulizer 0.3 Bar  
 Focus Active Set Capillary 4500 V Set Dry Heater 180 °C  
 Scan Begin 50 m/z Set End Plate Offset -500 V Set Dry Gas 4.0 l/min  
 Scan End 1500 m/z Set Collision Cell RF 1800.0 Vpp Set Divert Valve Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
769.0791	1	C30H46ClN2O2P2Rh2	769.0828	4.8	34.3	1	100.00	10.5	even	ok

Fig. S26 HRMS spectrum of 10

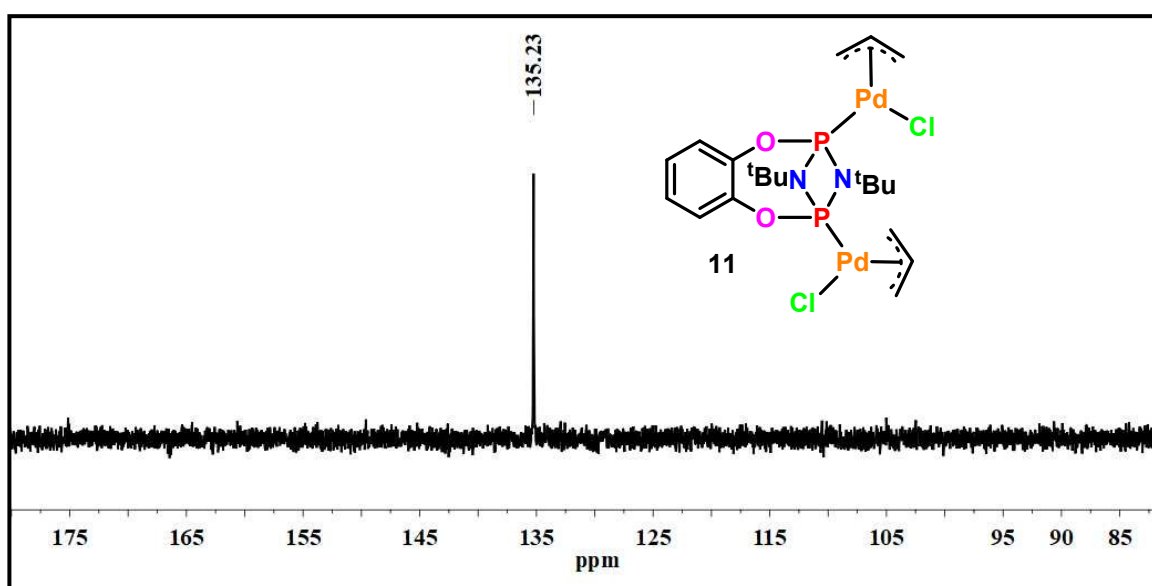


Fig. S27 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 11 in CDCl<sub>3</sub>(202 MHz)



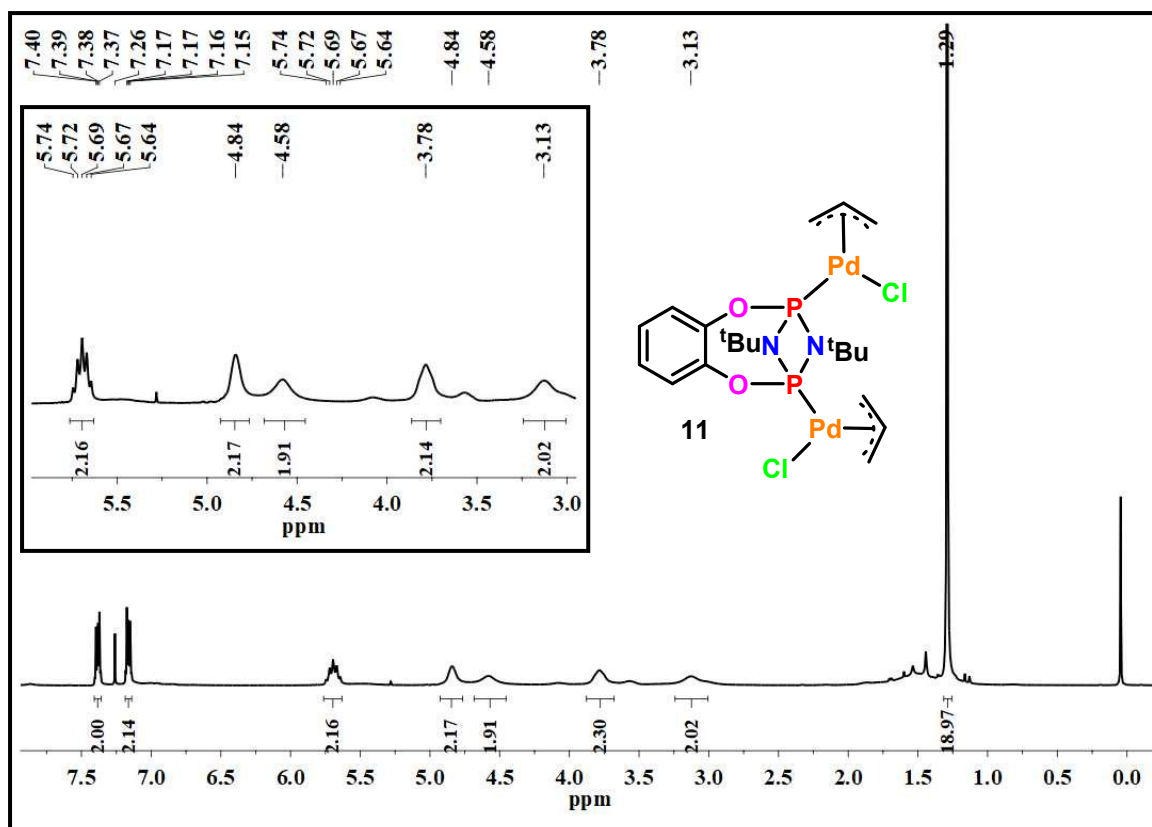


Fig. S28  $^1\text{H}$  NMR spectrum of **11** in  $\text{CDCl}_3$  (400 MHz)

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

Analysis Info

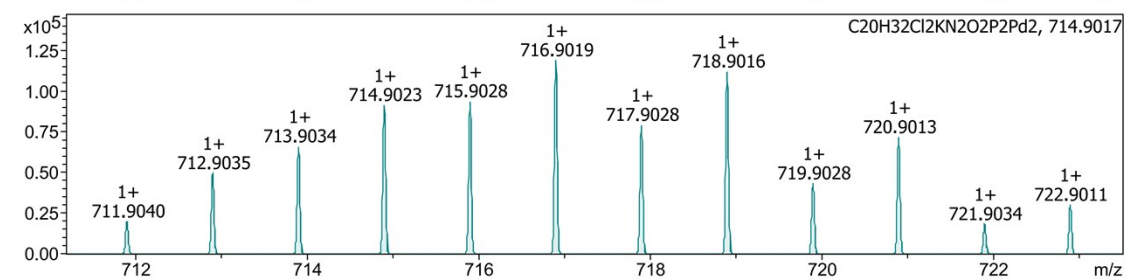
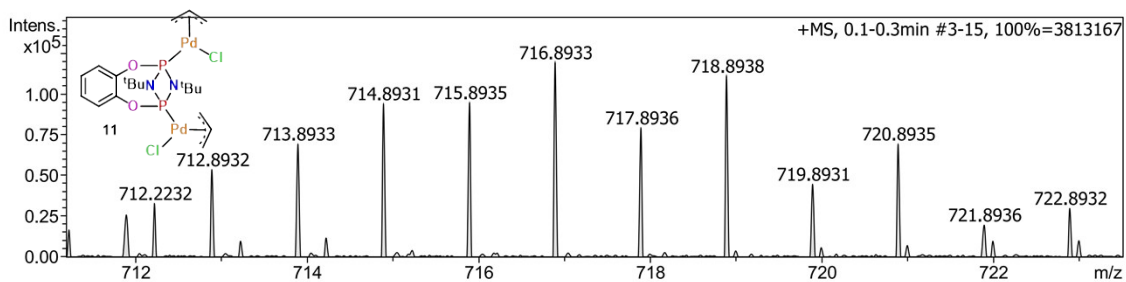
Analysis Name D:\Data\JUN-2018\MSB-MKP-44-Pd.d  
 Method Tune\_pos\_NAICSI-2000A.m  
 Sample Name MSB-MKP-44-Pd  
 Comment C20H32O2P2N2Pd2Cl2

Acquisition Date 6/26/2018 11:53:27 AM

Operator INN out  
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2000 m/z	Set Collision Cell RF	2100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
716.8933	1	C20H32Cl2KN2O2P2Pd2	714.9023	-12.0	19.9	1	100.00	5.5	even	ok

Fig. S29 HRMS spectrum of 11

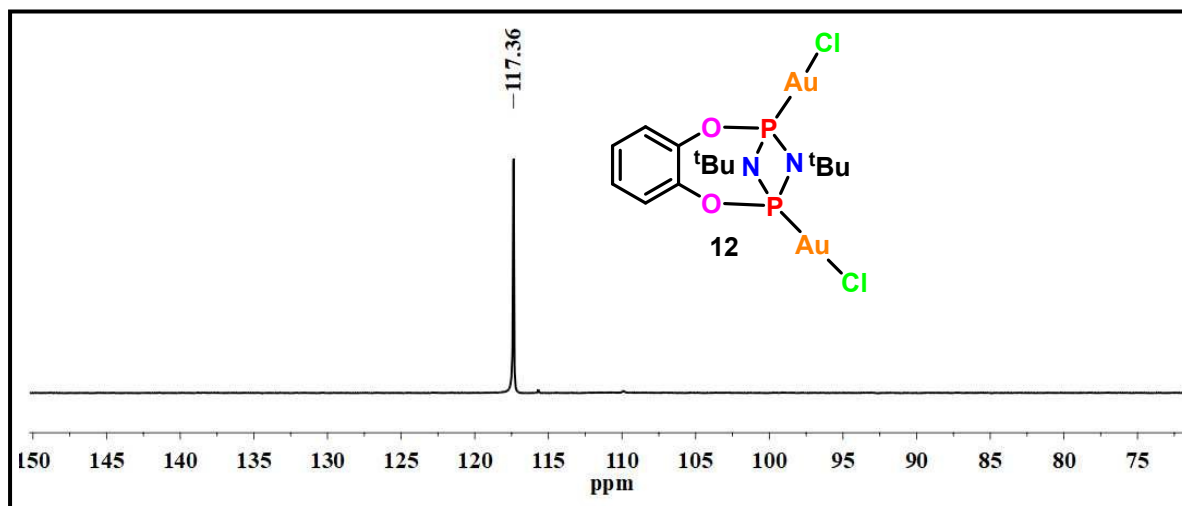


Fig. S30 <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of 12 in CDCl<sub>3</sub>(202 MHz)

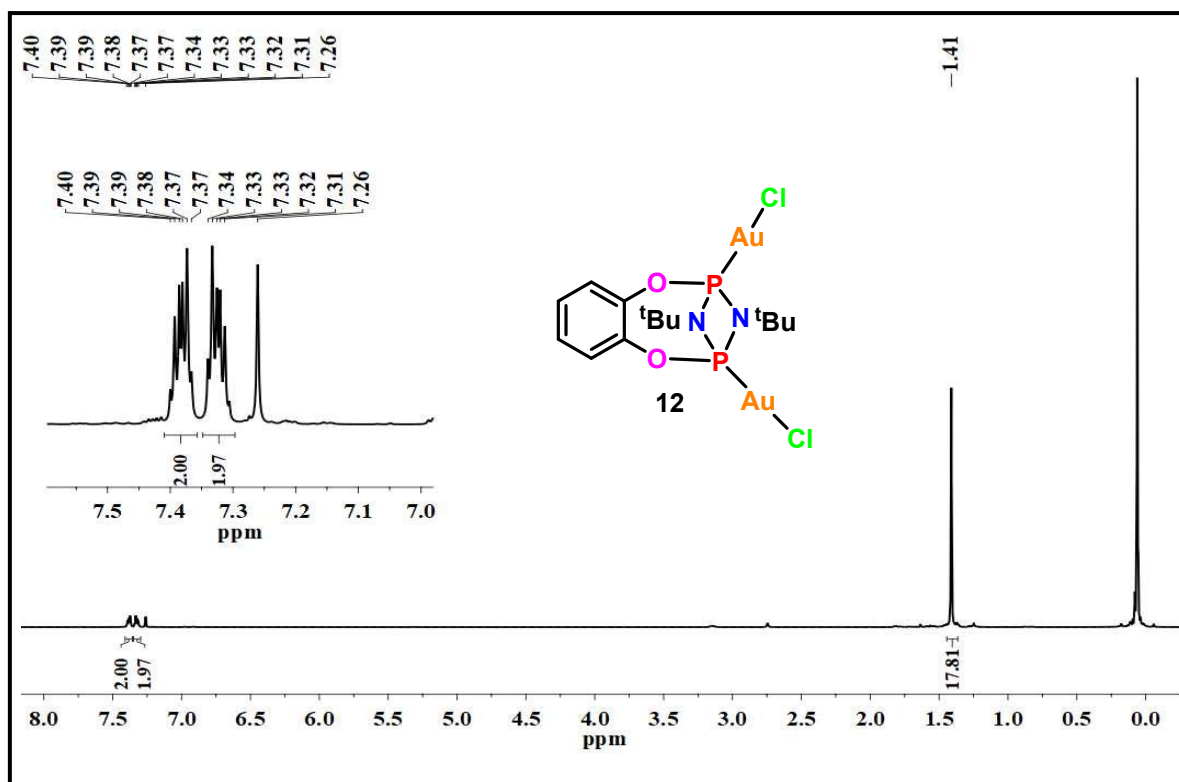


Fig. S31 <sup>1</sup>H NMR spectrum of **12** in CDCl<sub>3</sub>(500 MHz)

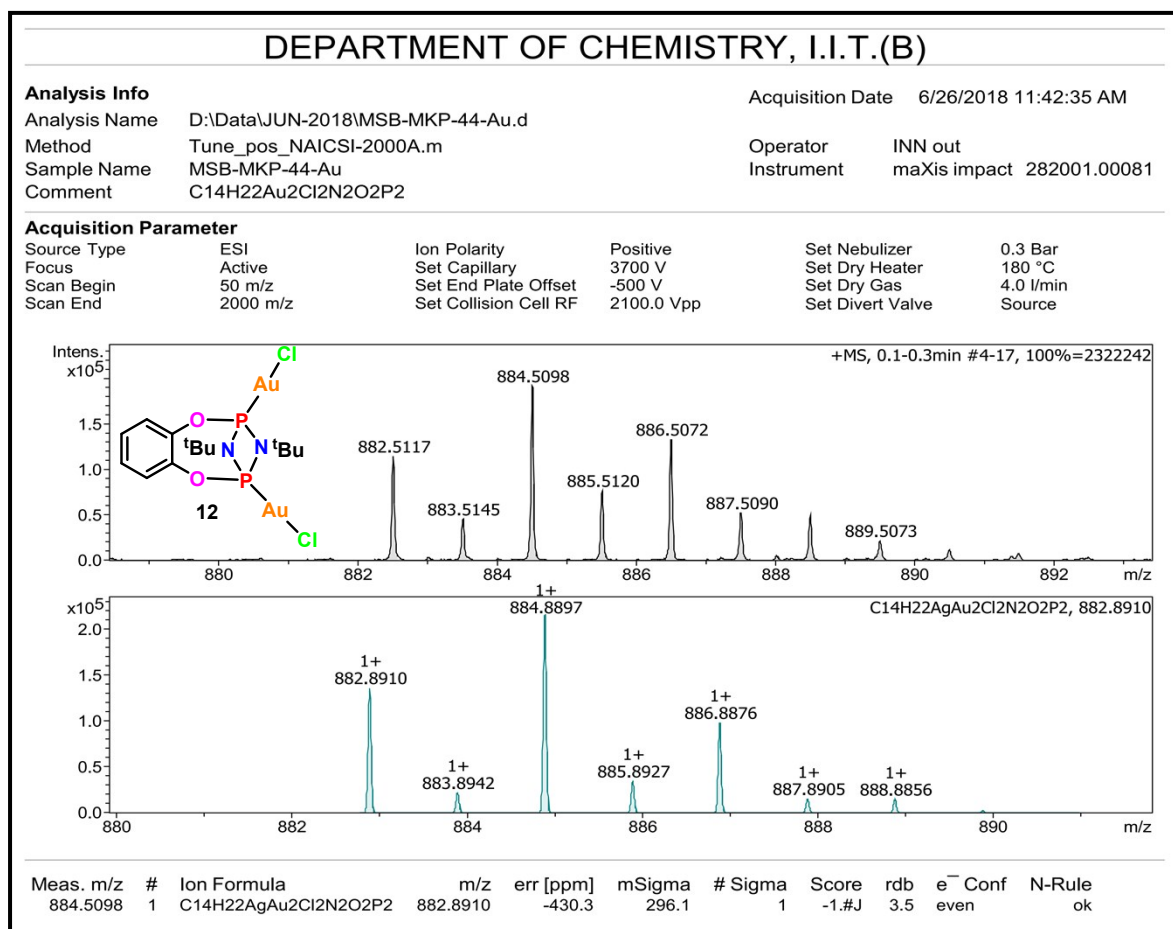


Fig. S32 HRMS spectrum of **12**

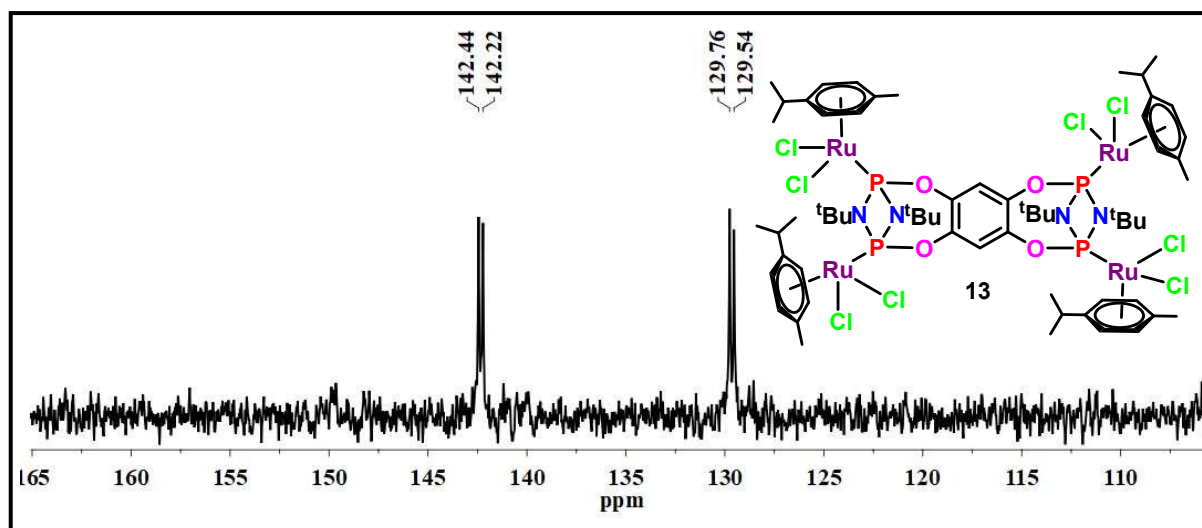


Fig. S33  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **13** in  $\text{CDCl}_3$ (202 MHz)

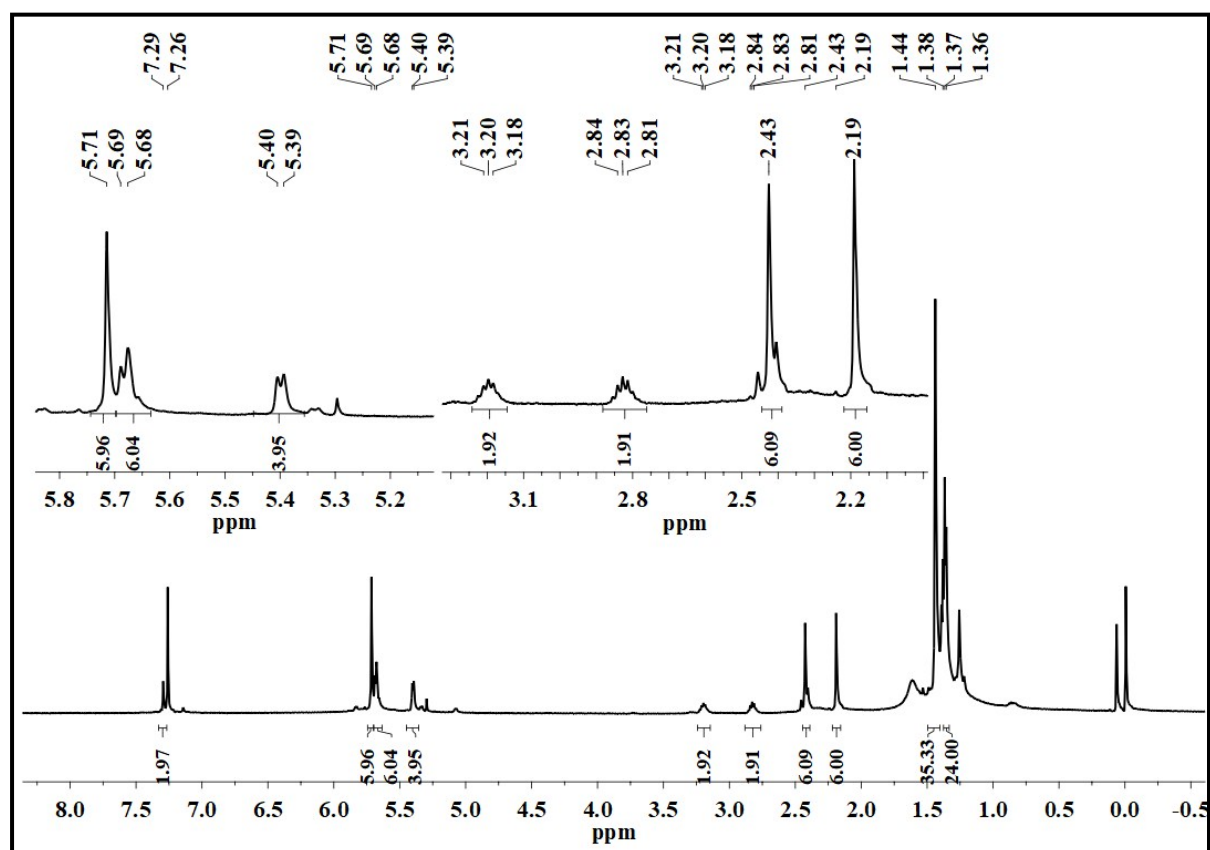


Fig. S34  $^1\text{H}$  NMR spectrum of **13** in  $\text{CDCl}_3$ (500 MHz)

DEPARTMENT OF CHEMISTRY, I.I.T.(B)

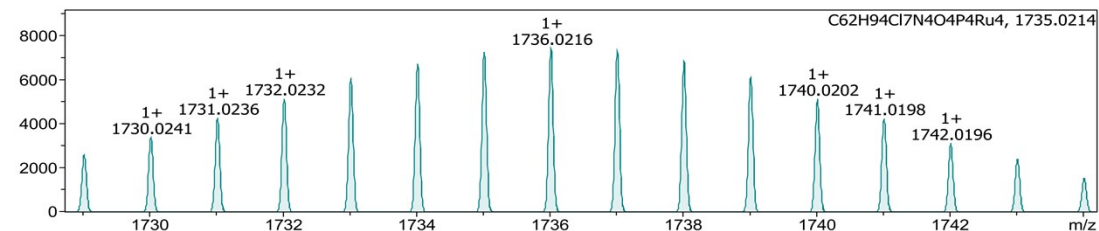
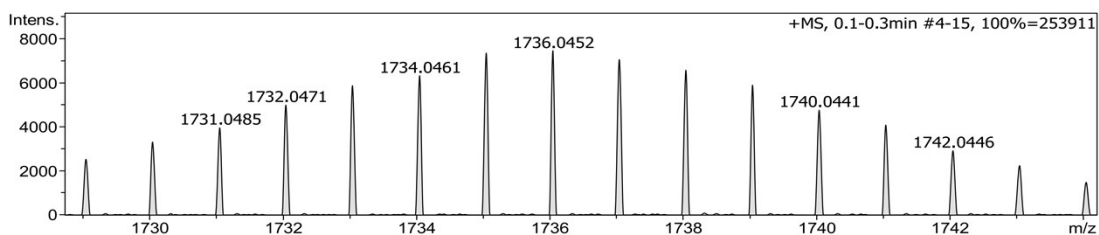
Analysis Info

Analysis Name D:\Data\NOV-2016\MSB-HK-11.d  
 Method Tune\_pos\_NAICSI-2500.m  
 Sample Name MSB-HK-11  
 Comment C62H94N4P4O4Ru4Cl4

Acquisition Date 11/28/2016 4:53:34 PM  
 Operator MSB IN  
 Instrument maXis impact 282001.00081

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	3700 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	2500 m/z	Set Collision Cell RF	2100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# Sigma	Score	rdb	e <sup>-</sup> Conf	N-Rule
1736.0452	1	C62H94Cl7N4O4P4Ru4	1735.0220	13.6	23.9	1	100.00	18.5	even	ok

Fig. S35 HRMS spectrum of 13

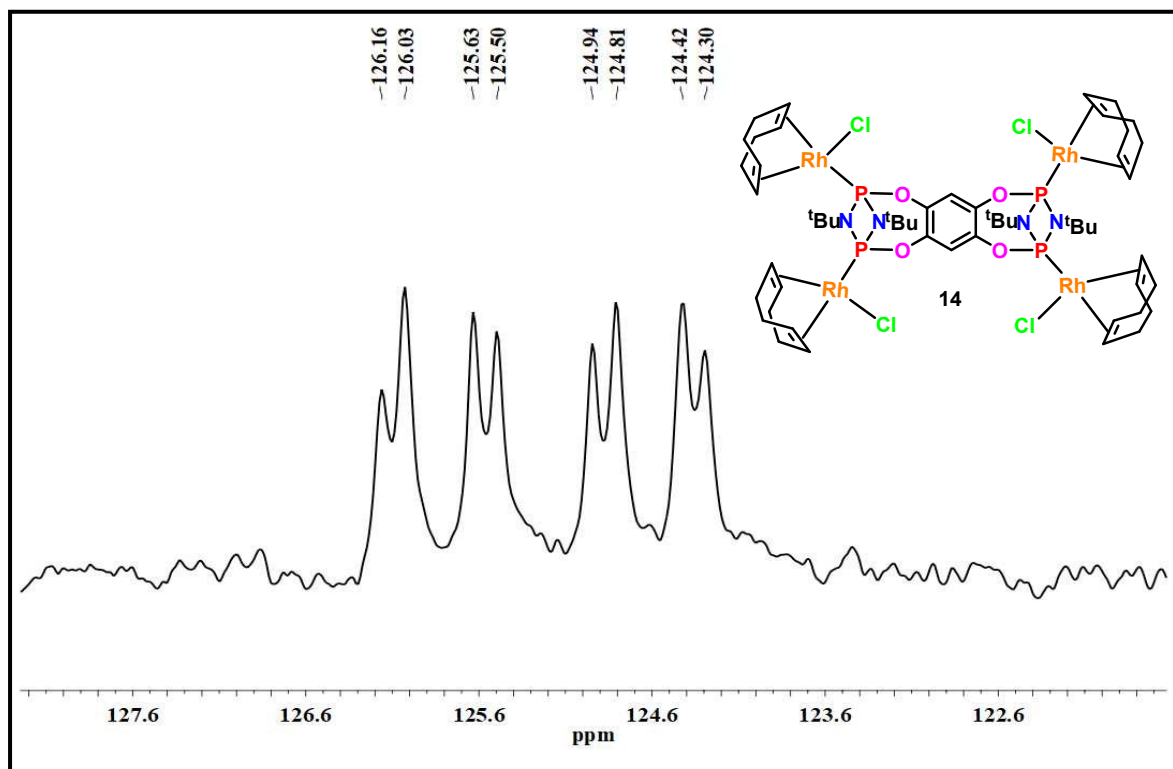


Fig. S36  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of 14 in  $\text{CDCl}_3$  (202 MHz)

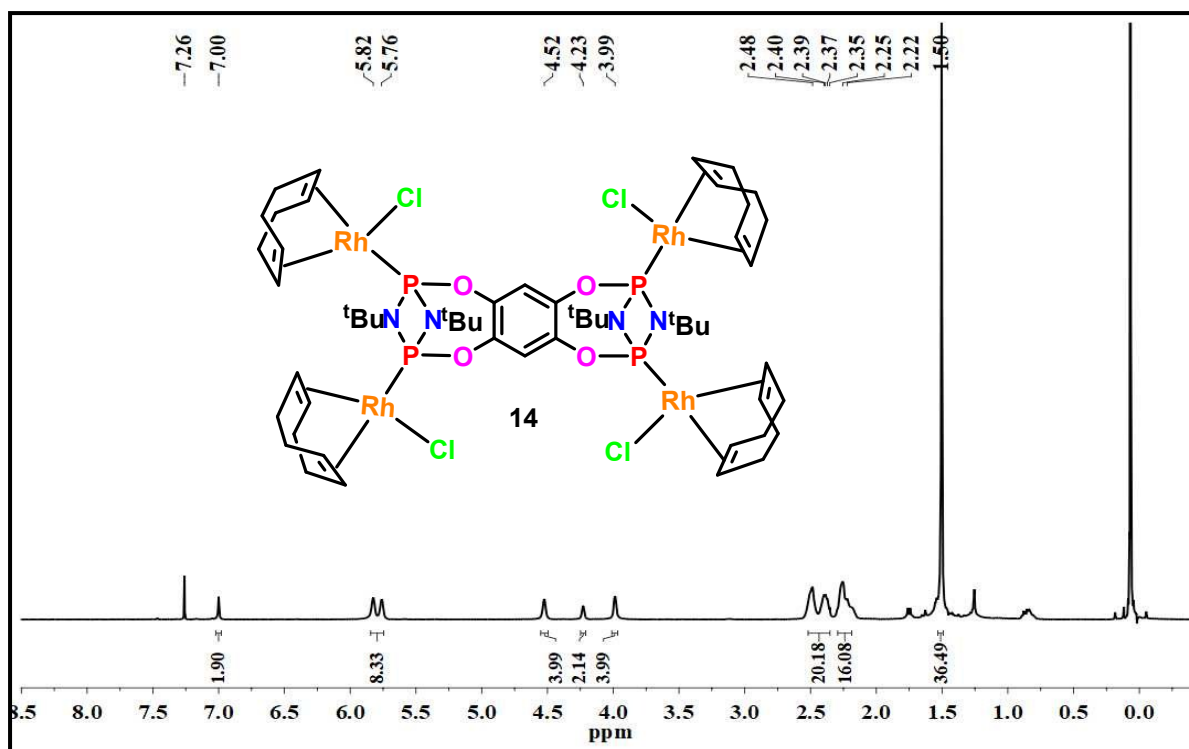


Fig. S37  $^1\text{H}$  NMR spectrum of **14** in  $\text{CDCl}_3$  (500 MHz)

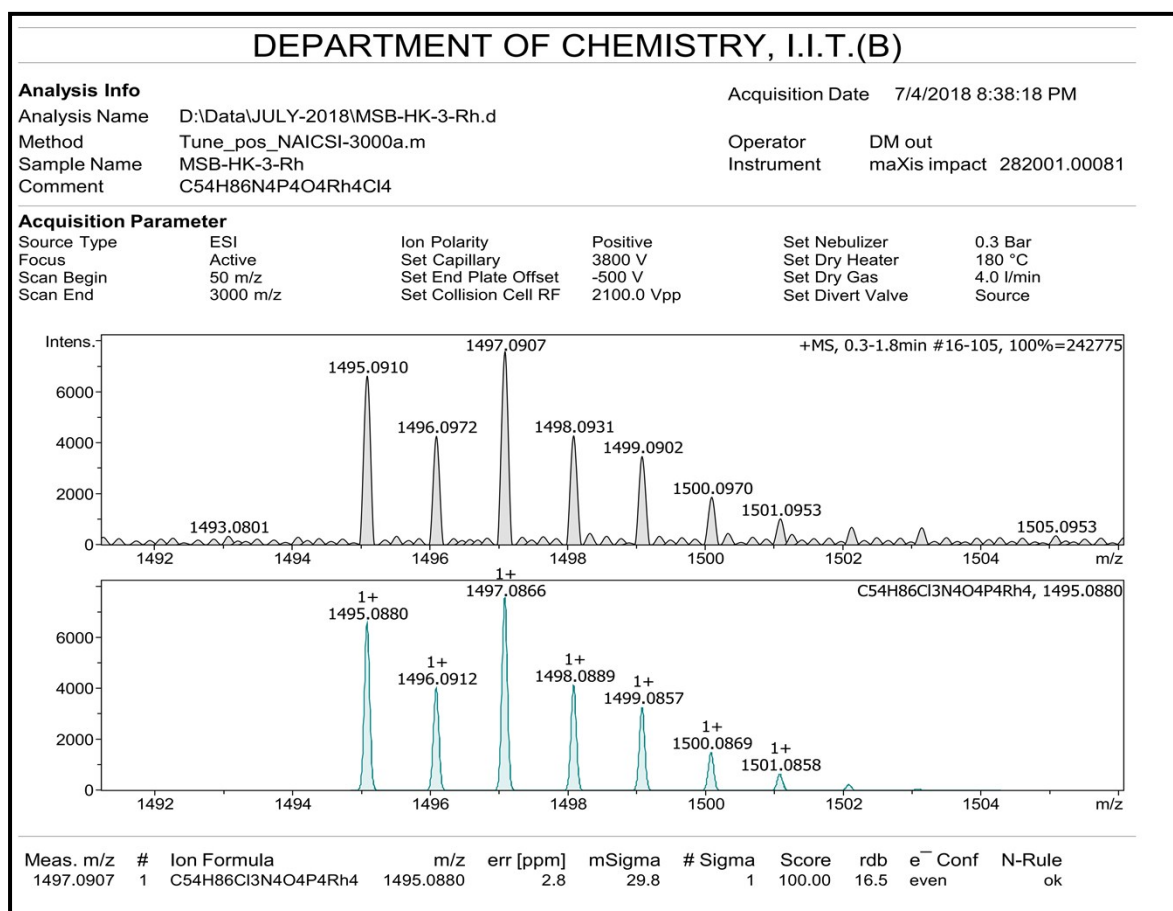


Fig. S38 HRMS spectrum of **14**

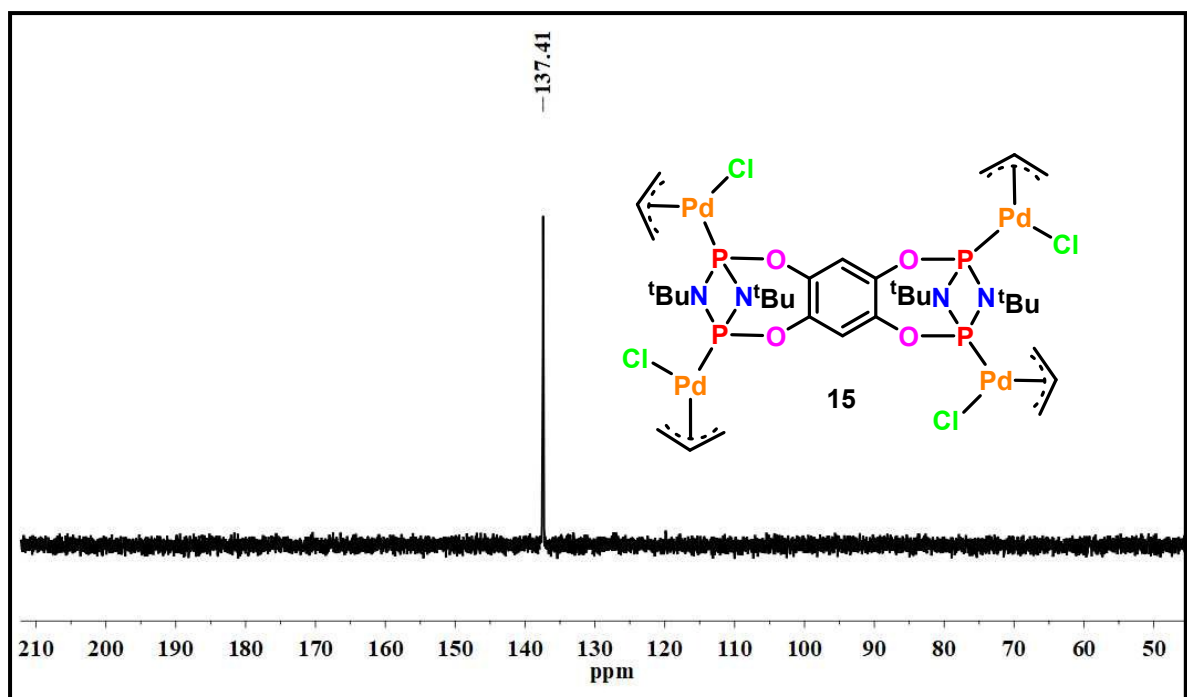


Fig. S39  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **15** in  $\text{CDCl}_3$  (202 MHz)

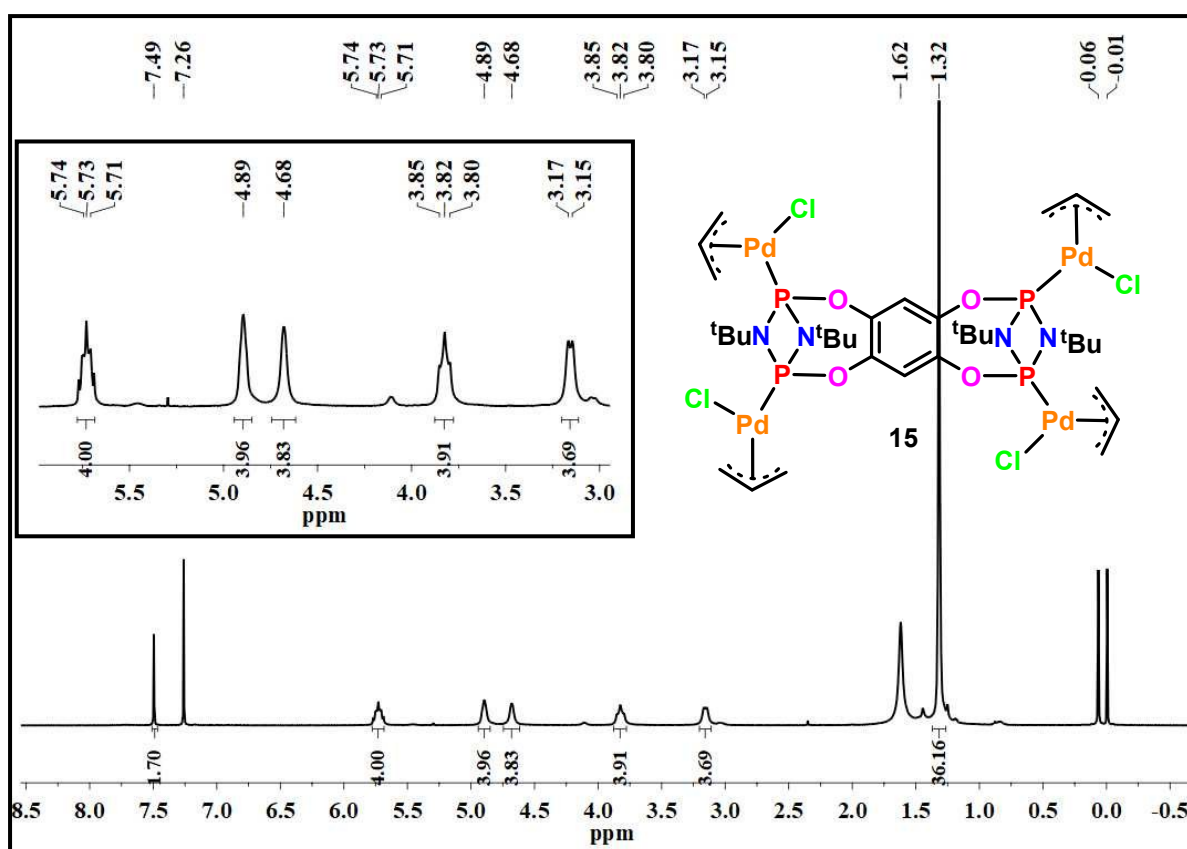
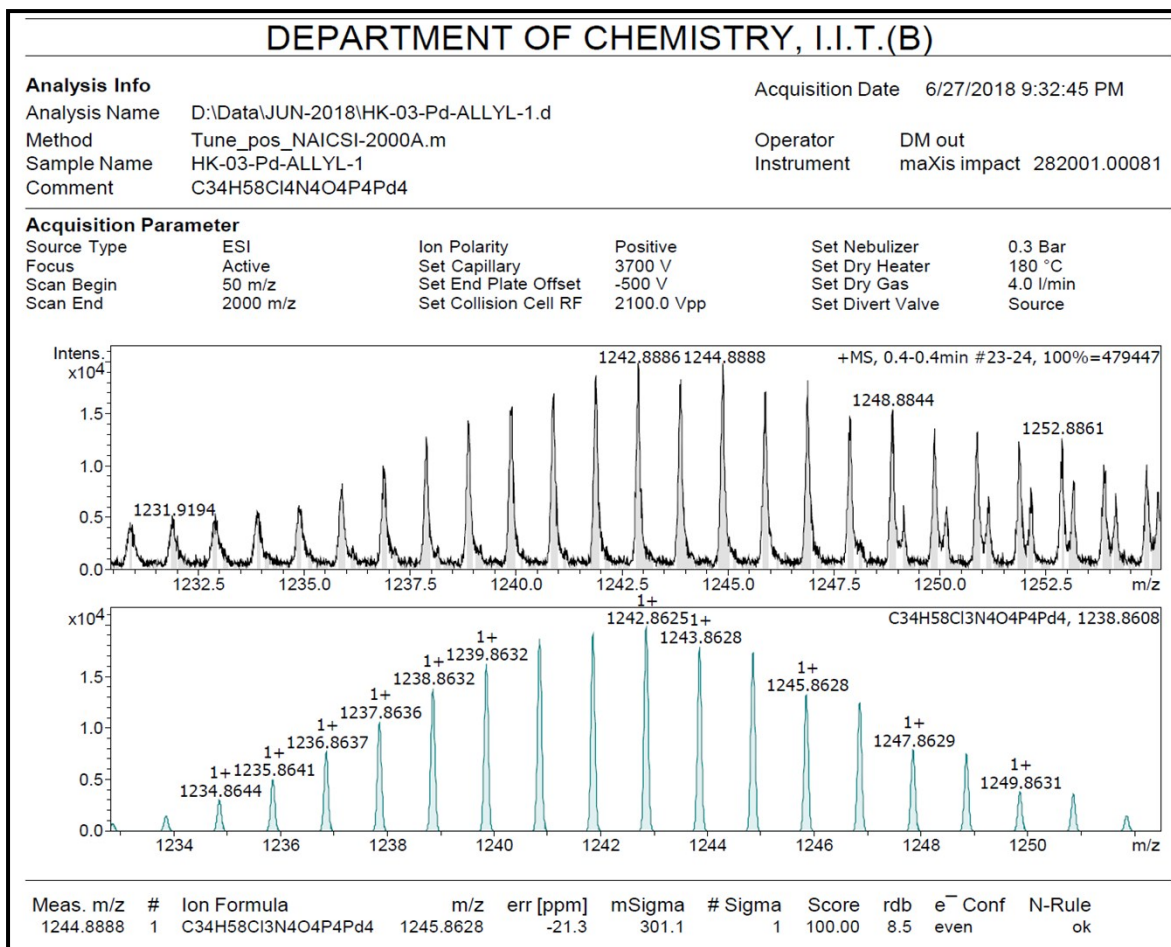
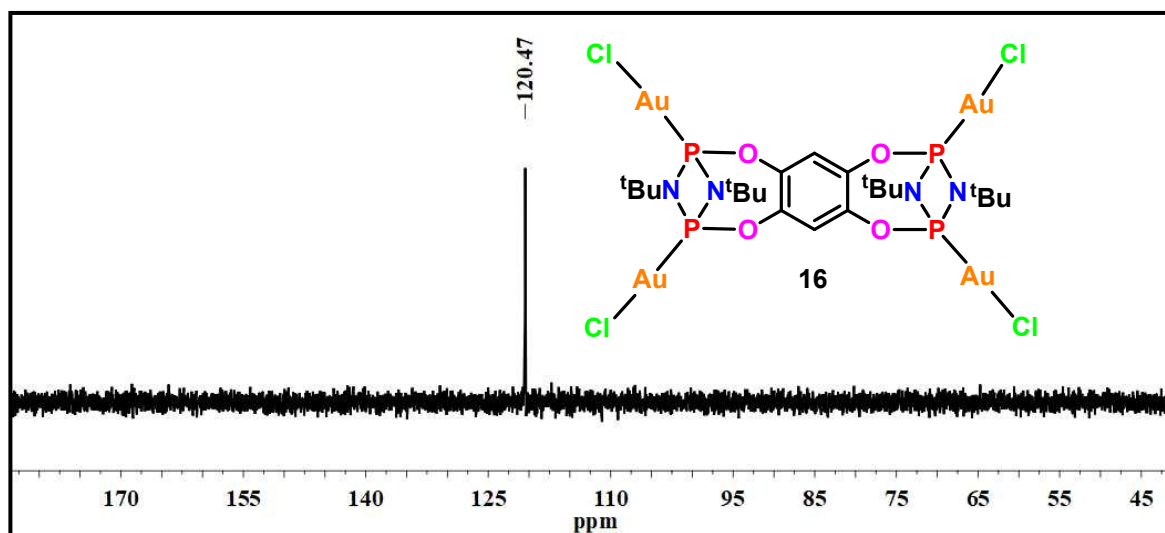


Fig. S40  $^1\text{H}$  NMR spectrum of **15** in  $\text{CDCl}_3$  (500 MHz)

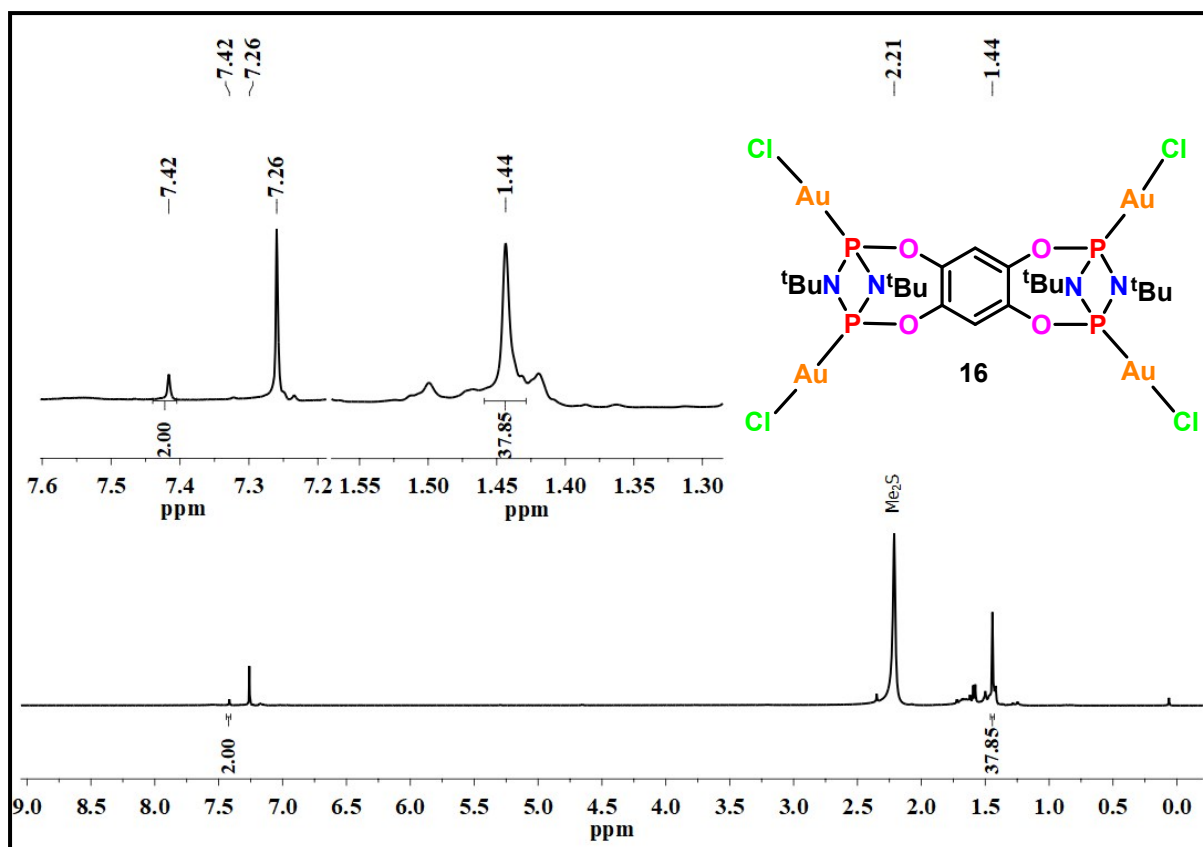


**Fig. S41** HRMS spectrum of **15**



**Fig. S42**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **16** in  $\text{CDCl}_3$  (202 MHz)





**Fig. S43**  $^1\text{H}$  NMR spectrum of **16** in  $\text{CDCl}_3$  (500 MHz)