Supporting Information:

P-C Bond Cleavage Induced Ni(II) Complexes Bearing Rare-earth-Metal-Based Metalloligand and Reactivities Toward Isonitrile, Nitrile and Epoxide.

Peng Cui,[*, †, ‡] Xia Huang, [†] Jun Du, [†] Zeming Huang [†]

† Key Laboratory of Functionalized Molecular Solids, Ministry of Education, Anhui Laboratory of Molecule-Based Materials, College of Chemistry and Materials Science, Anhui Normal University, Wuhu, Anhui 241002, P. R. China.

‡ Key Laboratory of Organic Synthesis of Jiangsu Province, Soochow University, Suzhou 215123, P. R. China

Table of Contents:

1. Spectroscopic Data

1.1 NMR spectra

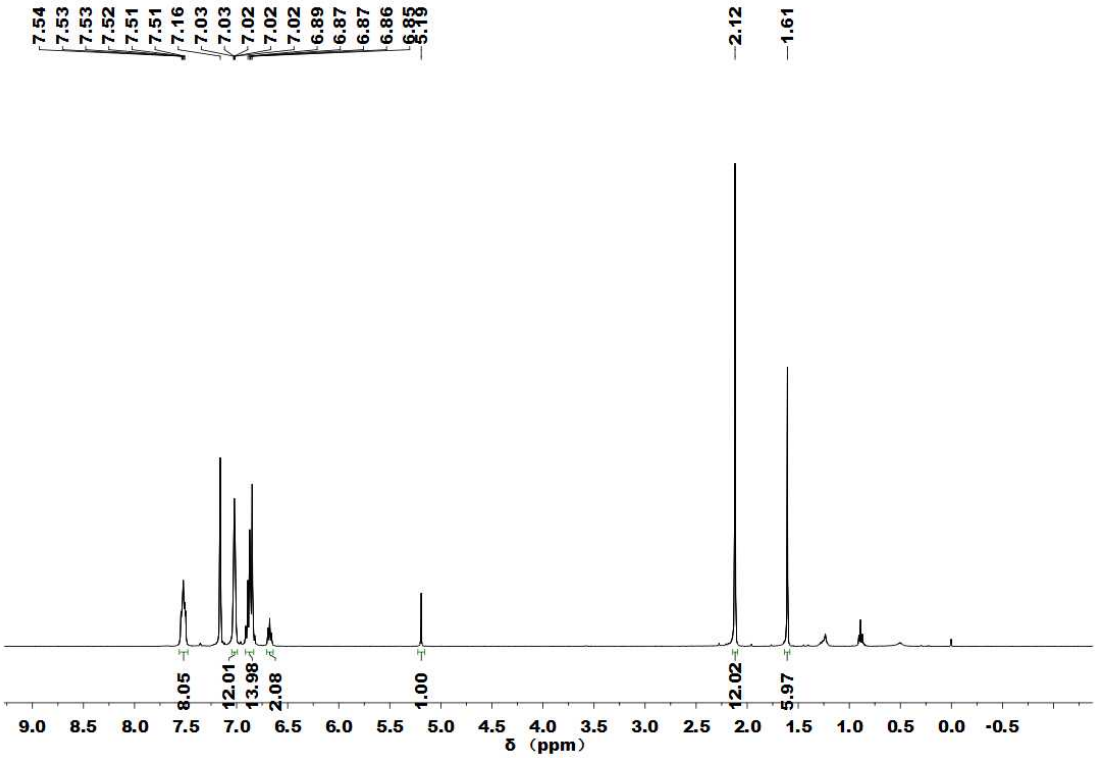

Figure S1. ^{1}H NMR spectrum of **1** in C_6D_6 at 25 °C.

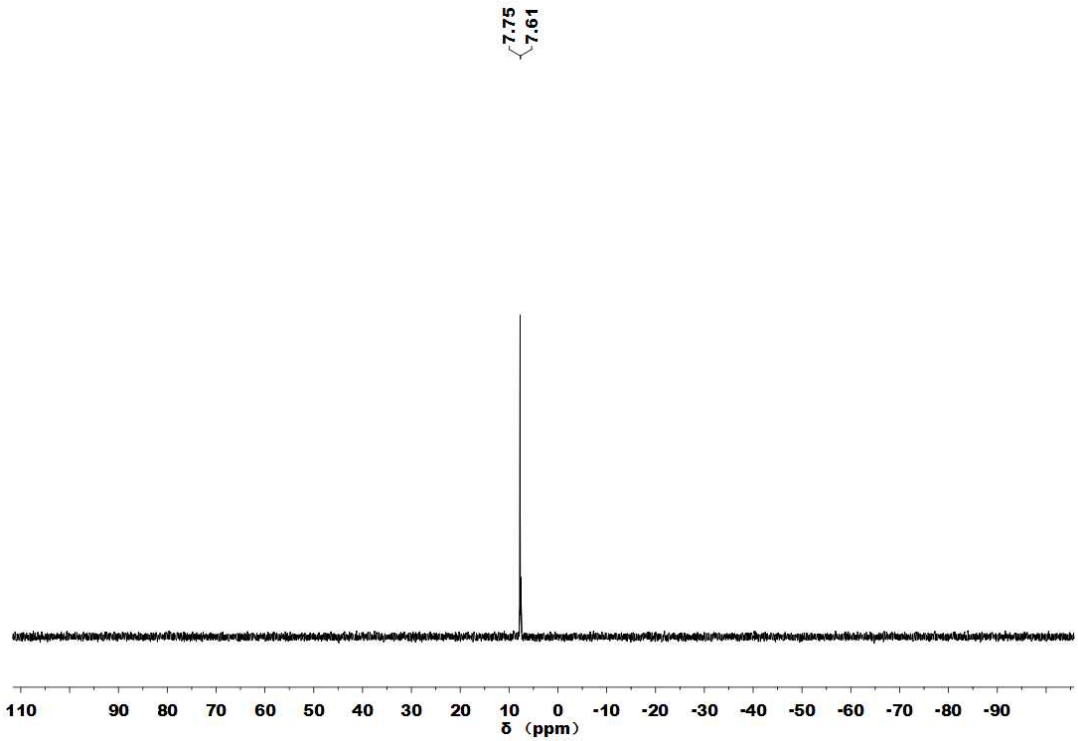

Figure S2. ^{31}P{^{1}H} NMR spectrum of **1** in C_6D_6 at 25 °C

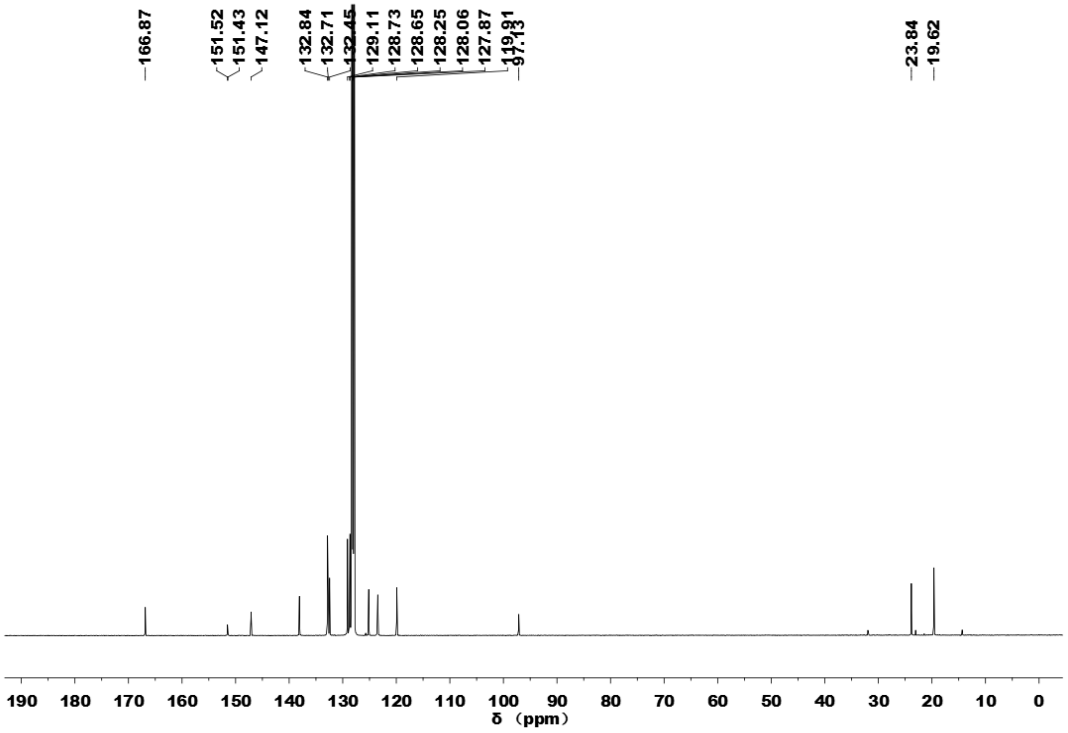

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum of **1** in C_6D_6 at 25 °C.

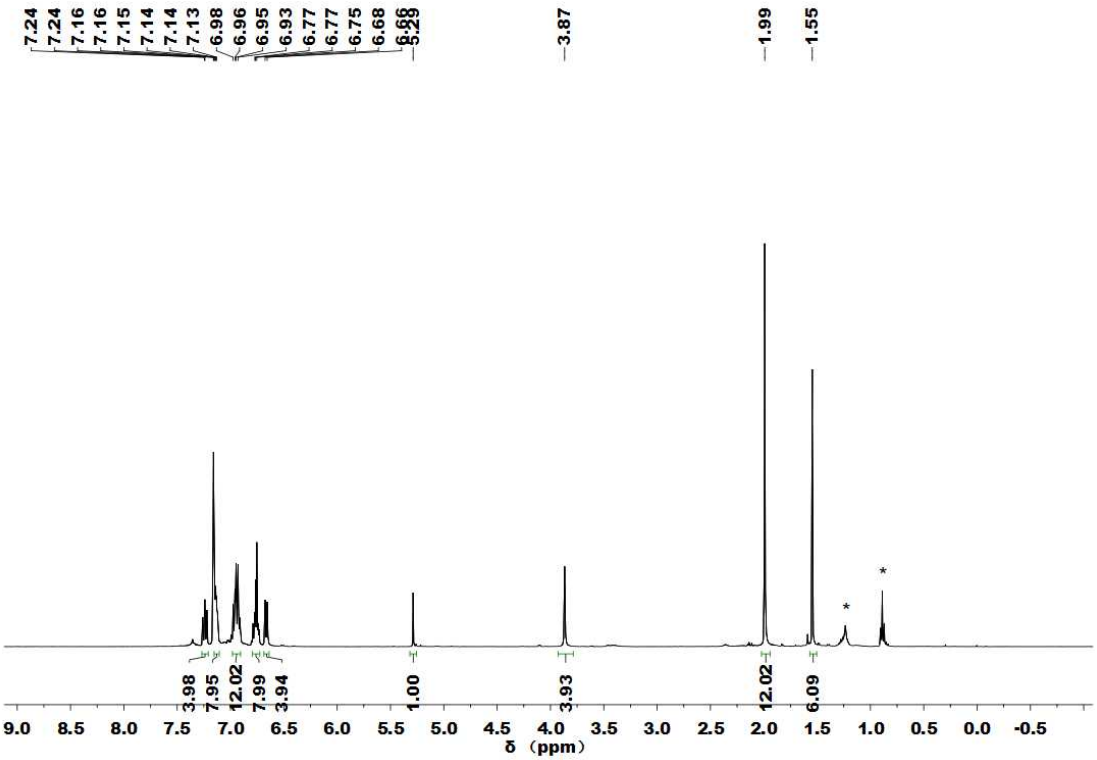

Figure S4. ^{1}H NMR spectrum of **2** in C_6D_6 at 25 °C. (* denotes small amount of hexane)

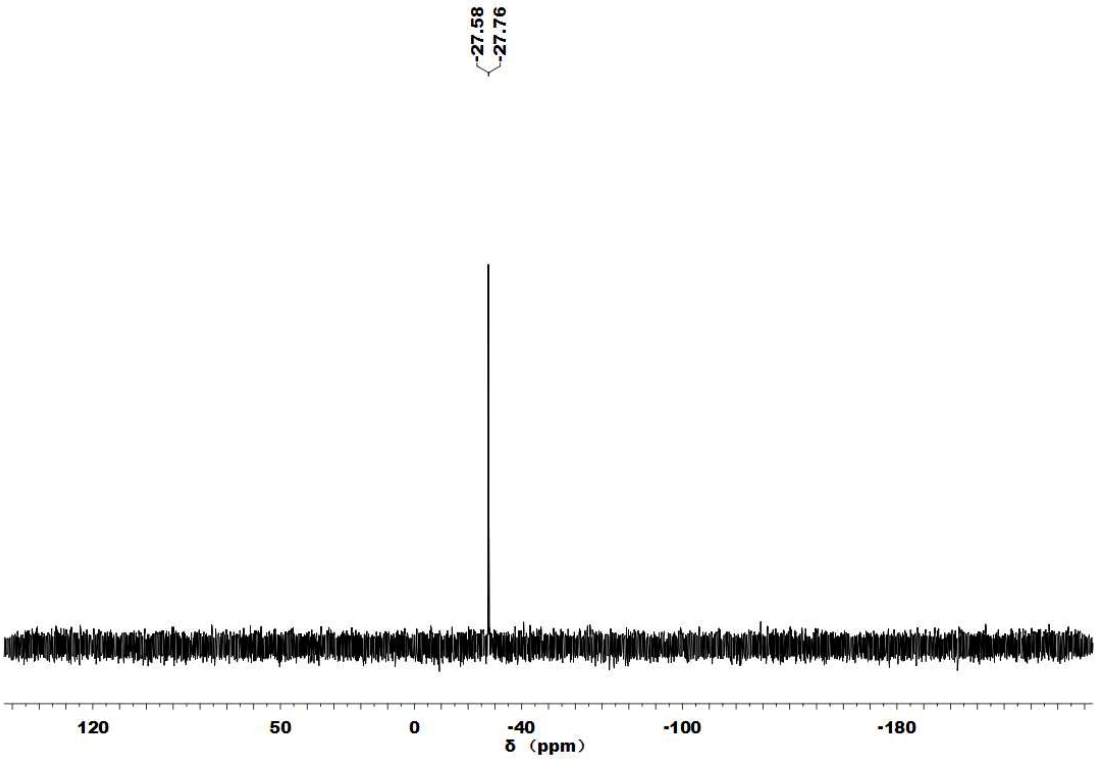

Figure S5. $^{31}P\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 25 °C.

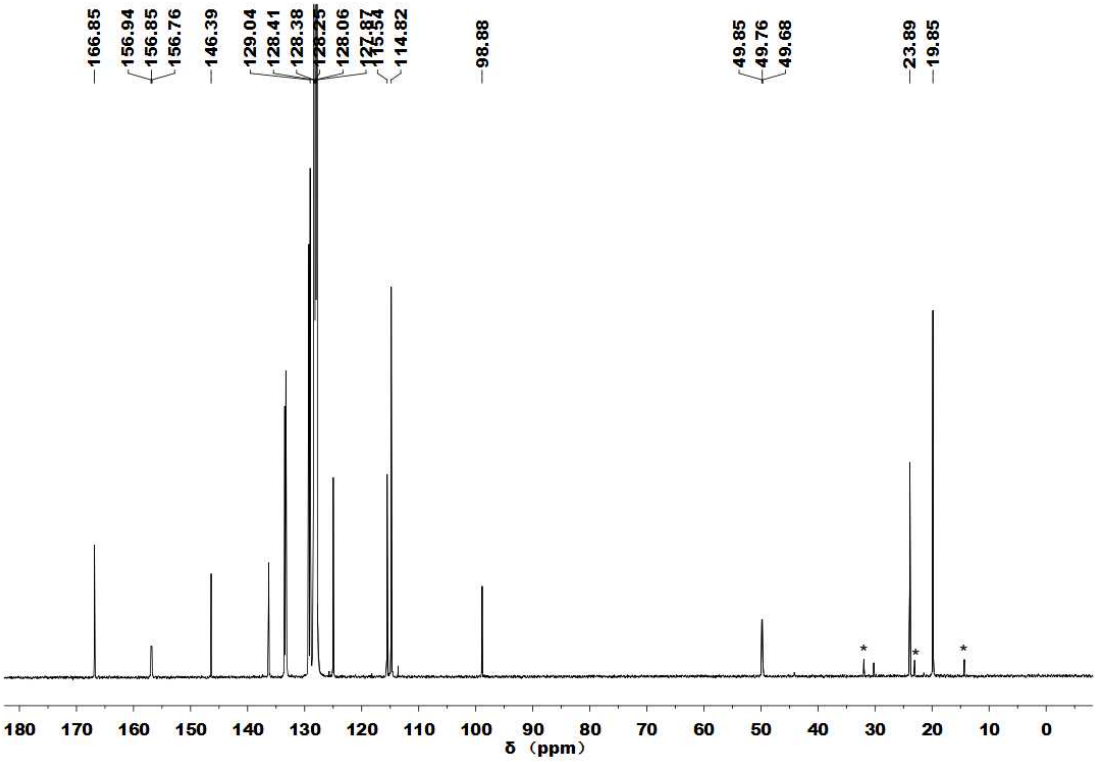

Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of **2** in C_6D_6 at 25 °C. (* denotes small amount of hexane)

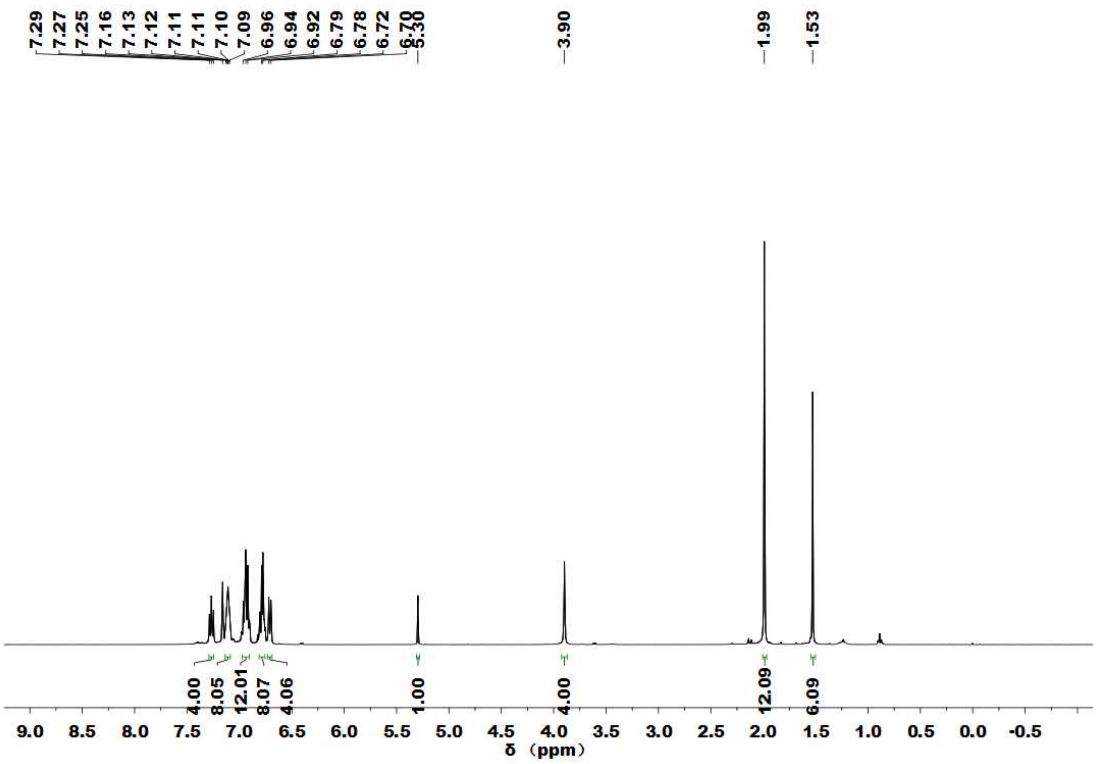

Figure S7. ^{1}H NMR spectrum of **3** in C_6D_6 at 25 °C.

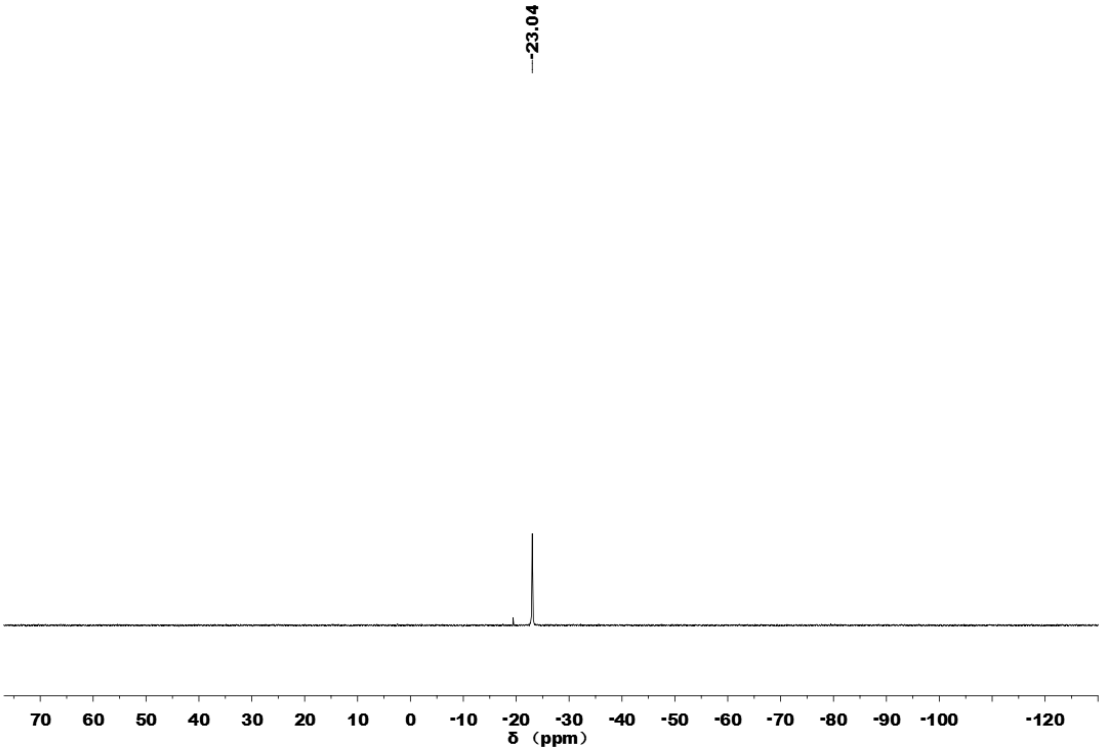

Figure S8. ^{31}P{^{1}H} NMR spectrum of **3** in C_6D_6 at 25 °C.

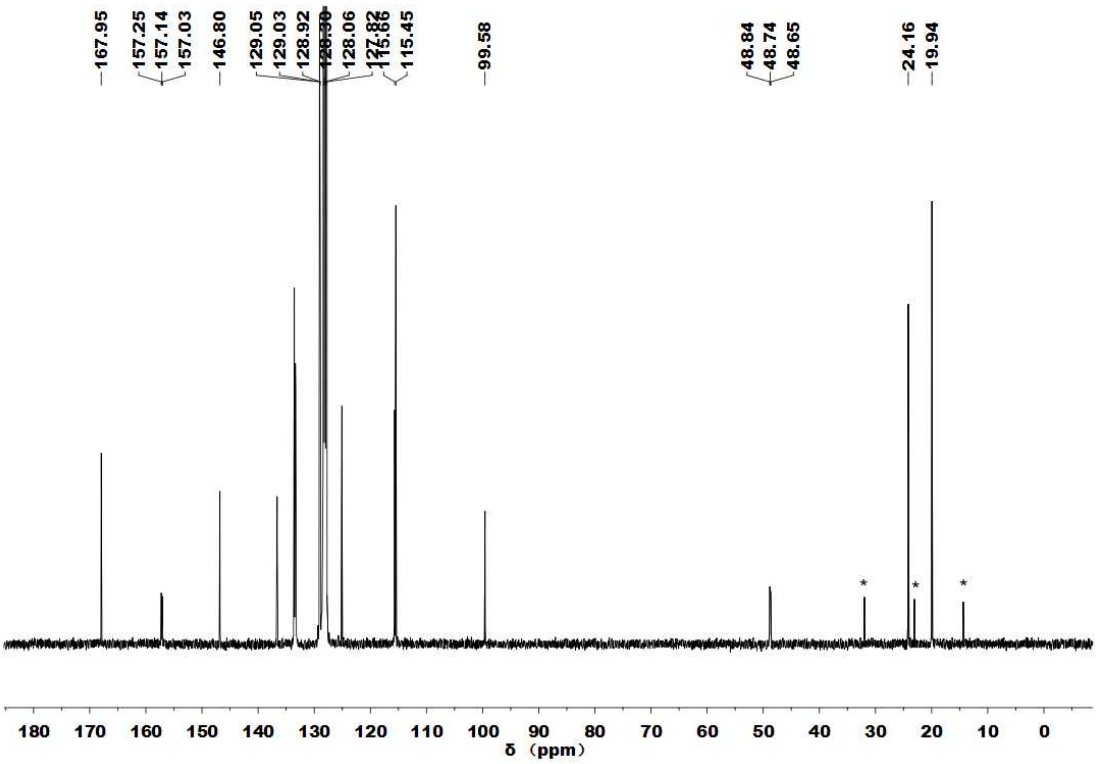

Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **3** in C_6D_6 at 25 °C. (* denotes small amount of hexane)

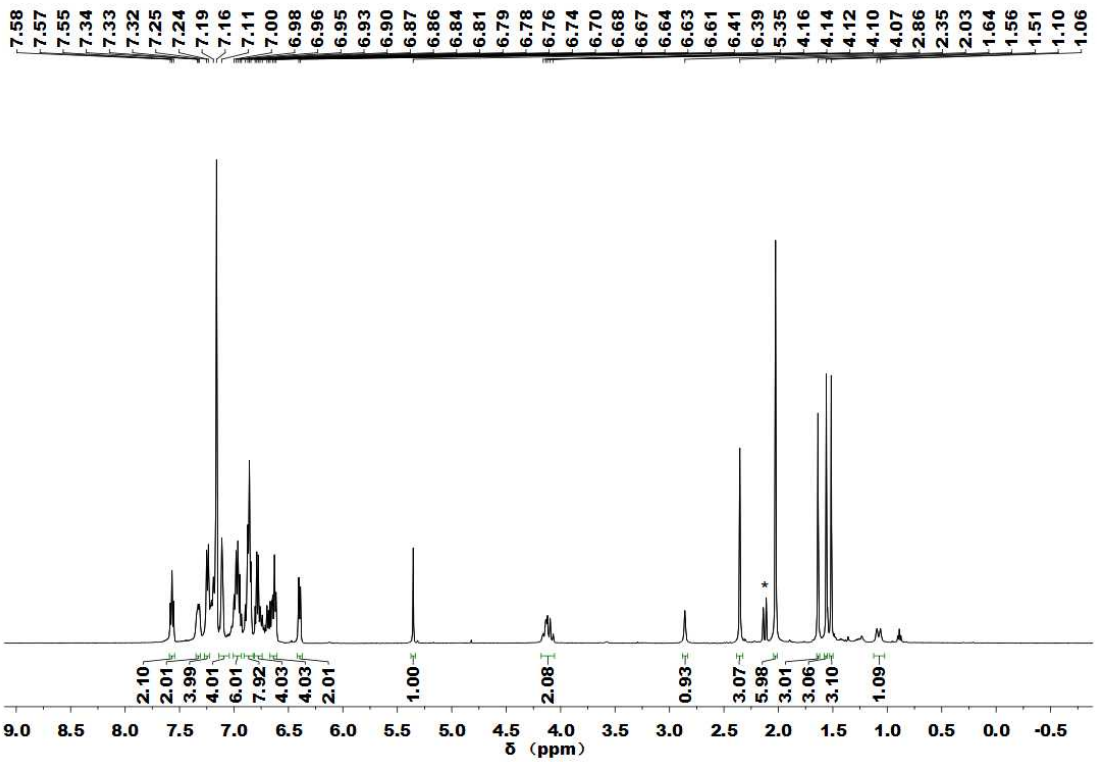

Figure S10. ^{1}H NMR spectrum of **4** in C_6D_6 at 25 °C. (* denotes small amount of toluene)

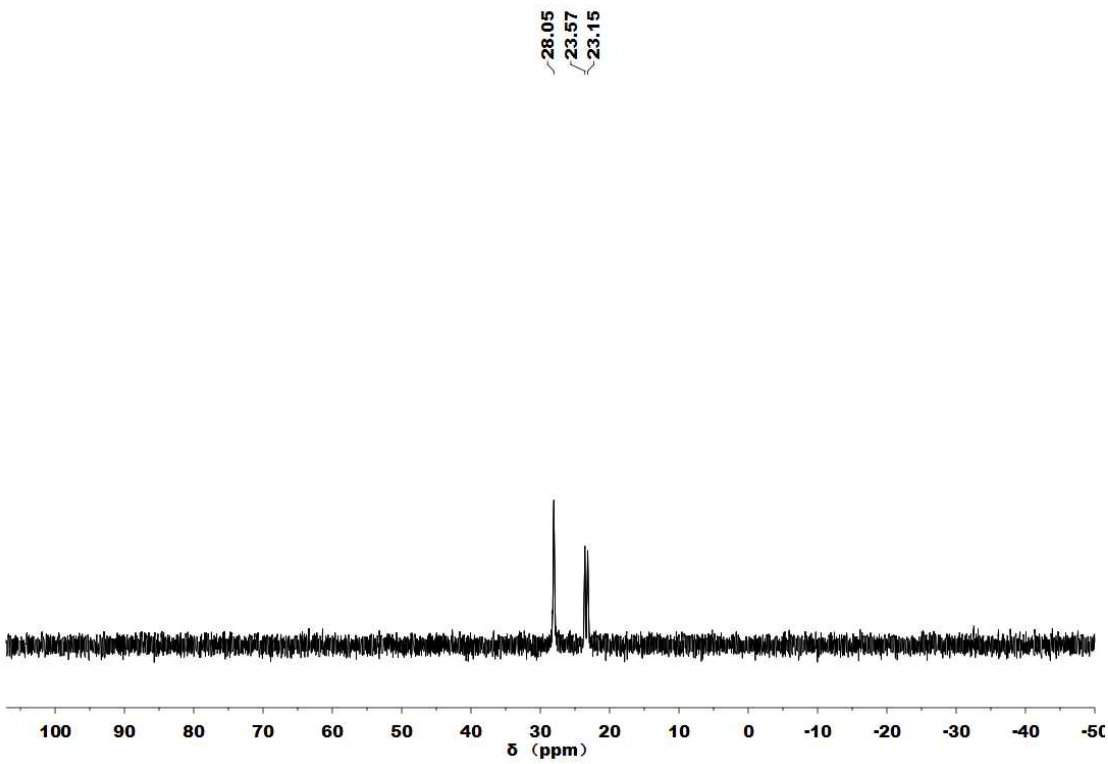

Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of **4** in C_6D_6 at 25 °C.

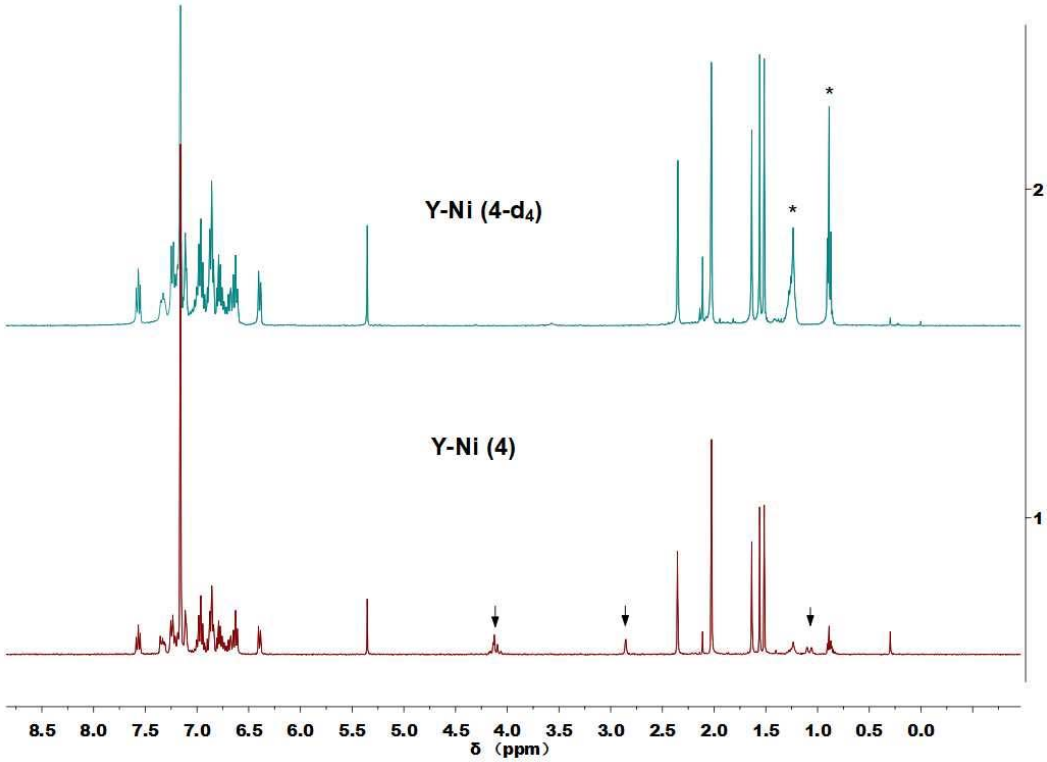

Figure S12. Stacked ^{1}H NMR spectra of **4** and **4-*d₄*** in C_6D_6 at 25 °C. (* denotes small amount of hexane)

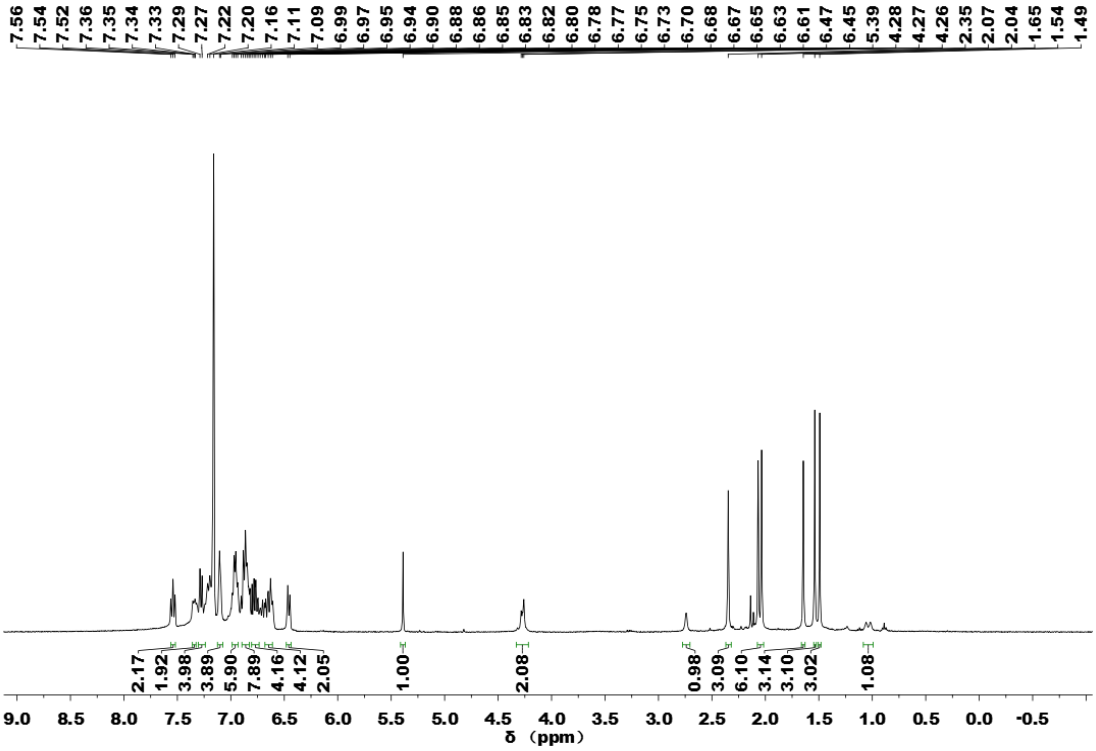

Figure S13. ^{1}H NMR spectrum of **5** in C_6D_6 at 25 °C.

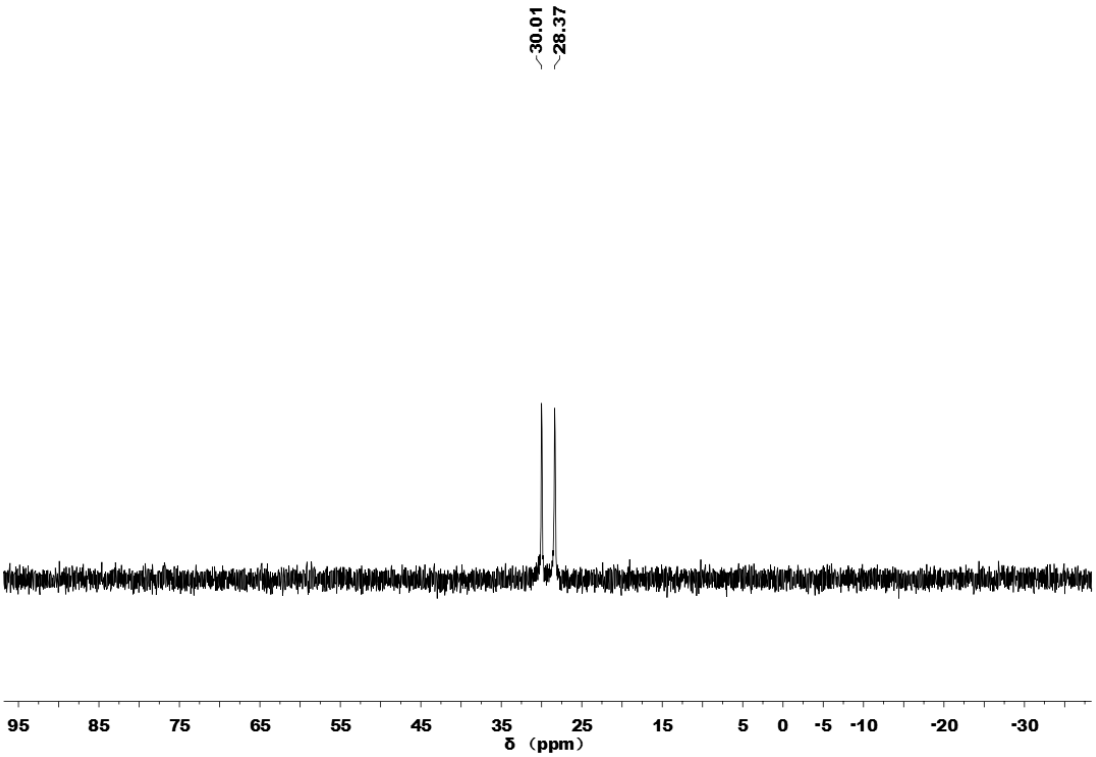

Figure S14. ^{31}P{^{1}H} NMR spectrum of **5** in C_6D_6 at 25 °C.

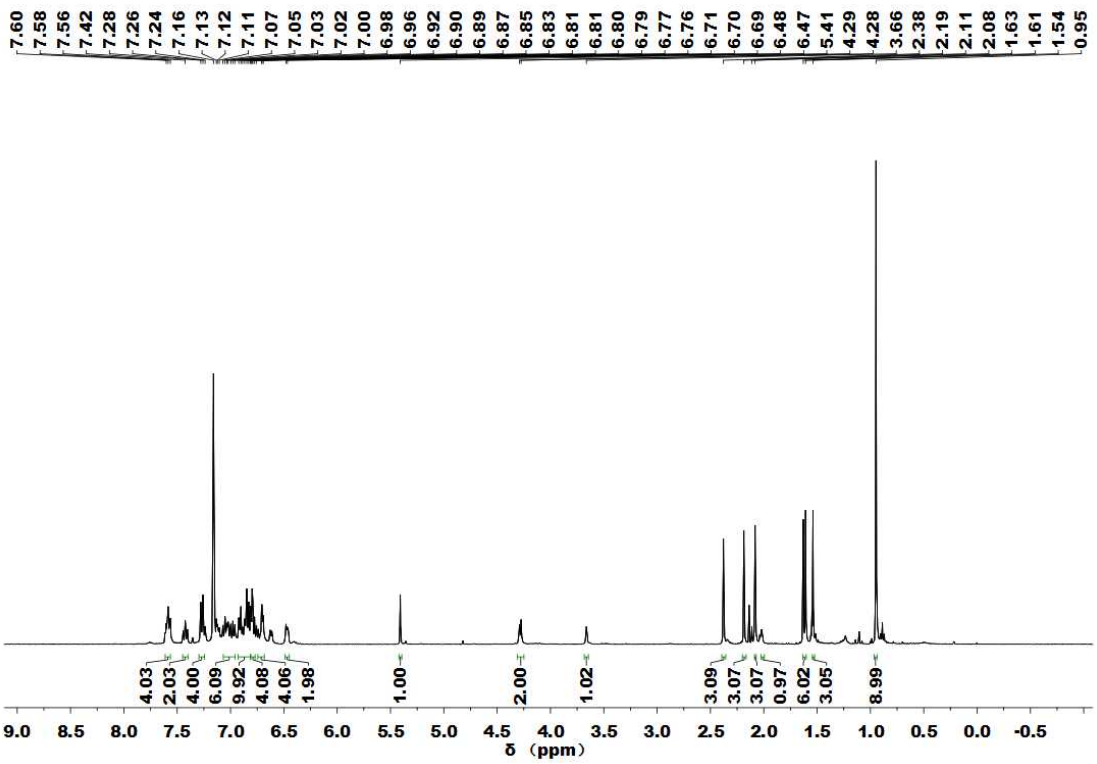

Figure S15. ^{1}H NMR spectrum of **6** in C_6D_6 at 25 °C.

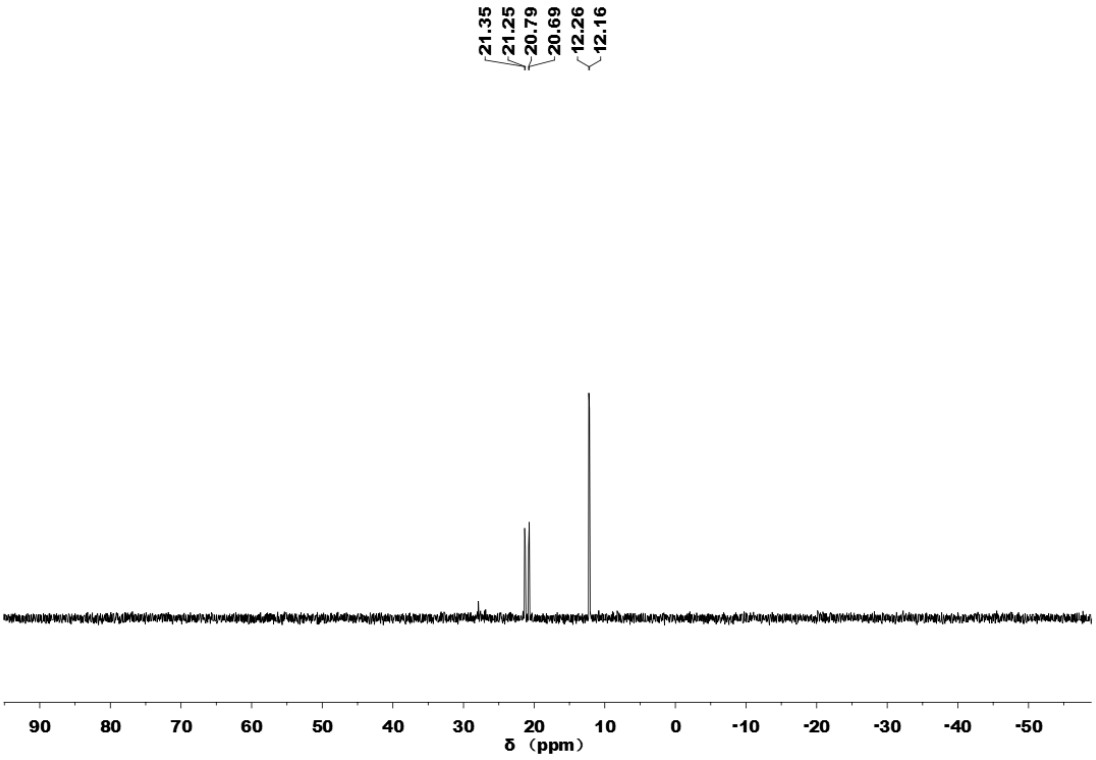

Figure S16. ^{31}P{^{1}H} NMR spectrum of **6** in C_6D_6 at 25 °C.

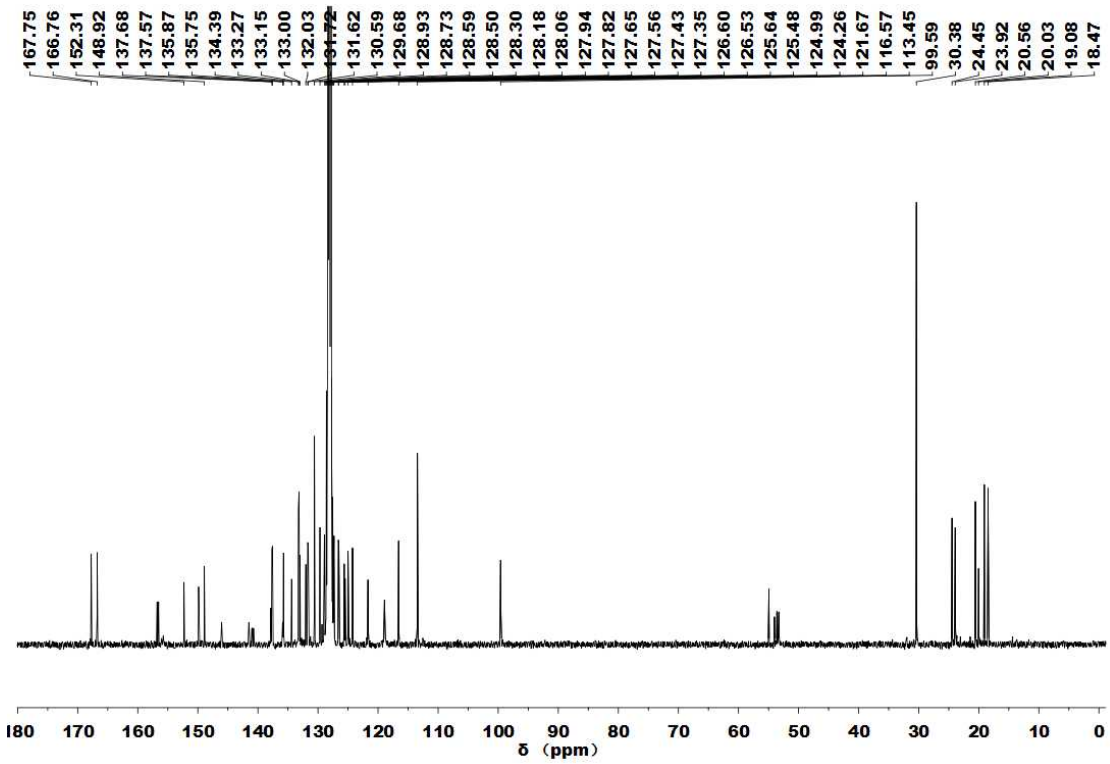

Figure S17. $^{13}C\{^{1}H\}$ NMR spectrum of **6** in C_6D_6 at 25 °C.

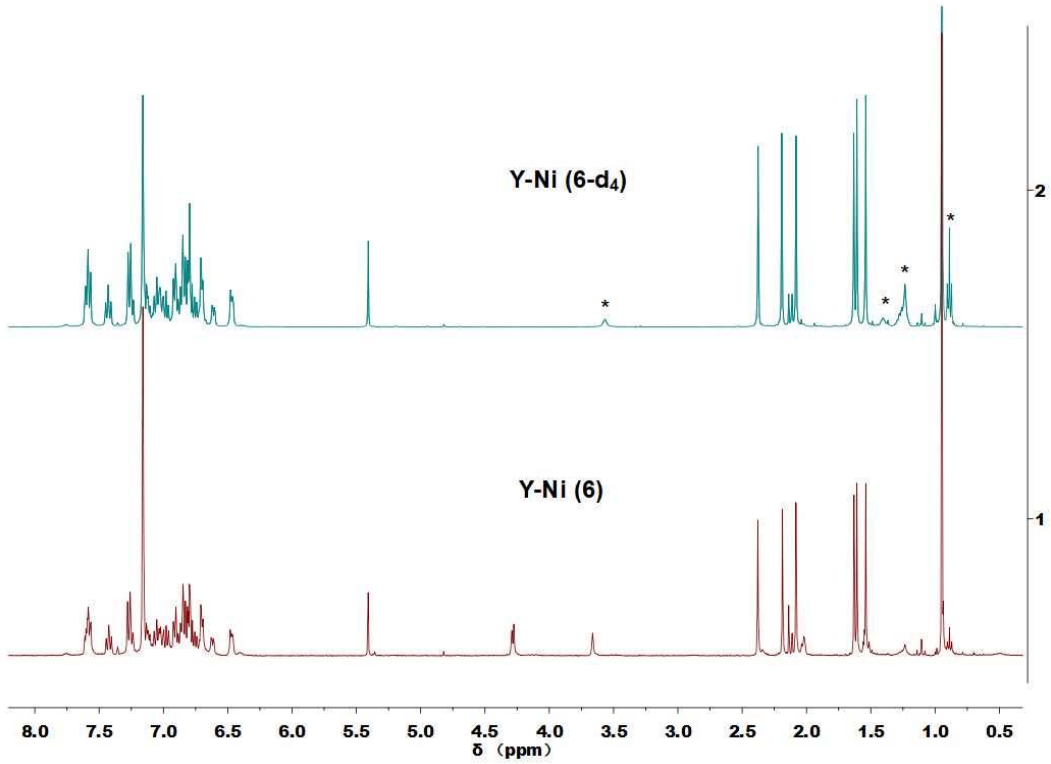

Figure S18. Stacked ^{1}H NMR spectra of **6** and **6-*d₄*** in C_6D_6 at 25 °C. (*denotes small amount of THF and hexane)

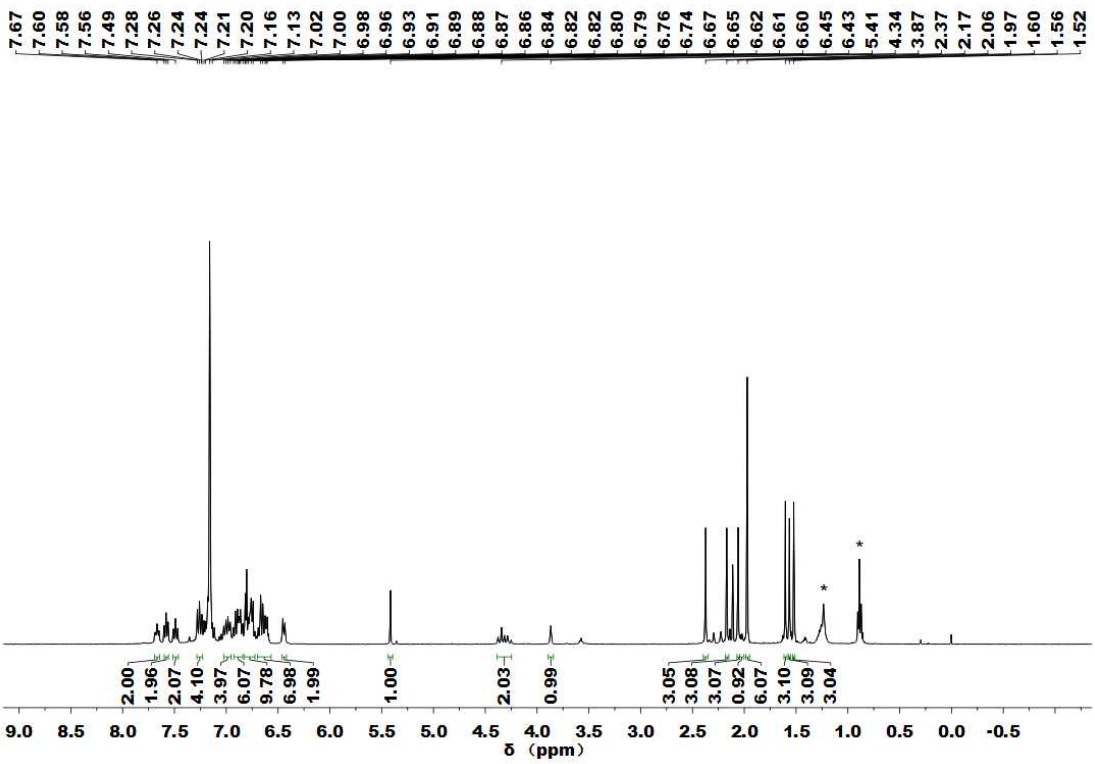

Figure S19. ^{1}H NMR spectrum of **7** in C_6D_6 at 25 °C. (* denotes small amount of hexane)

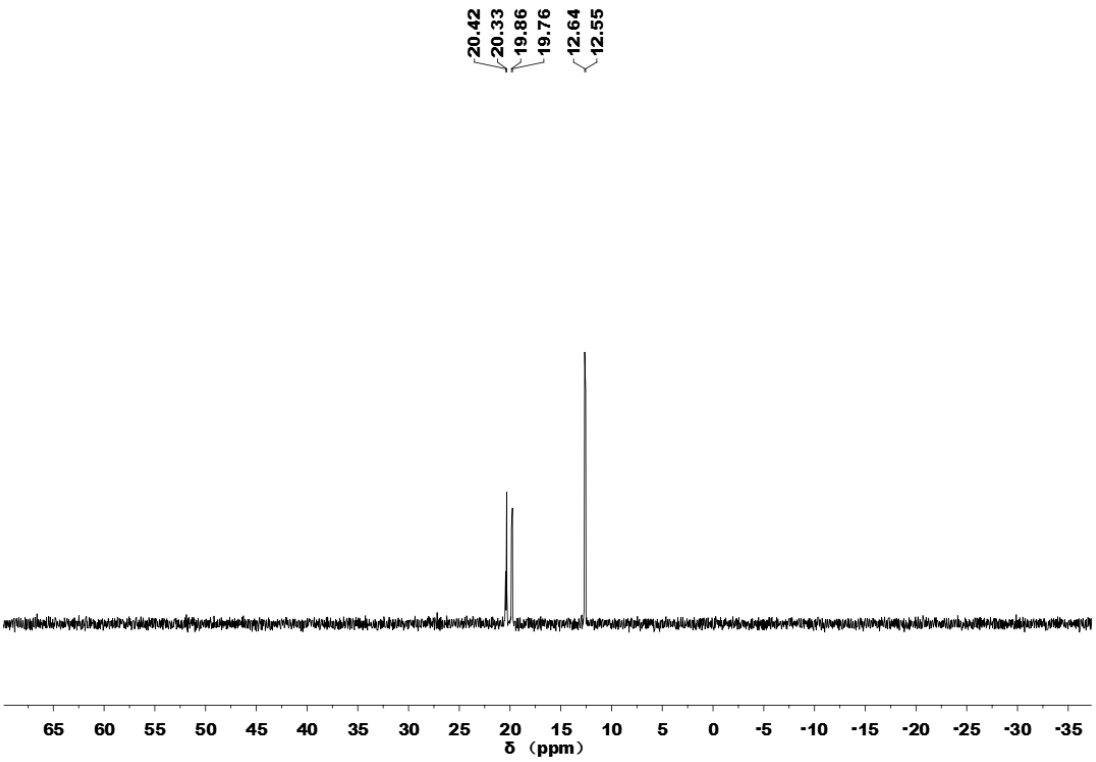

Figure S20. ^{31}P{^{1}H} NMR spectrum of **7** in C_6D_6 at 25 °C.

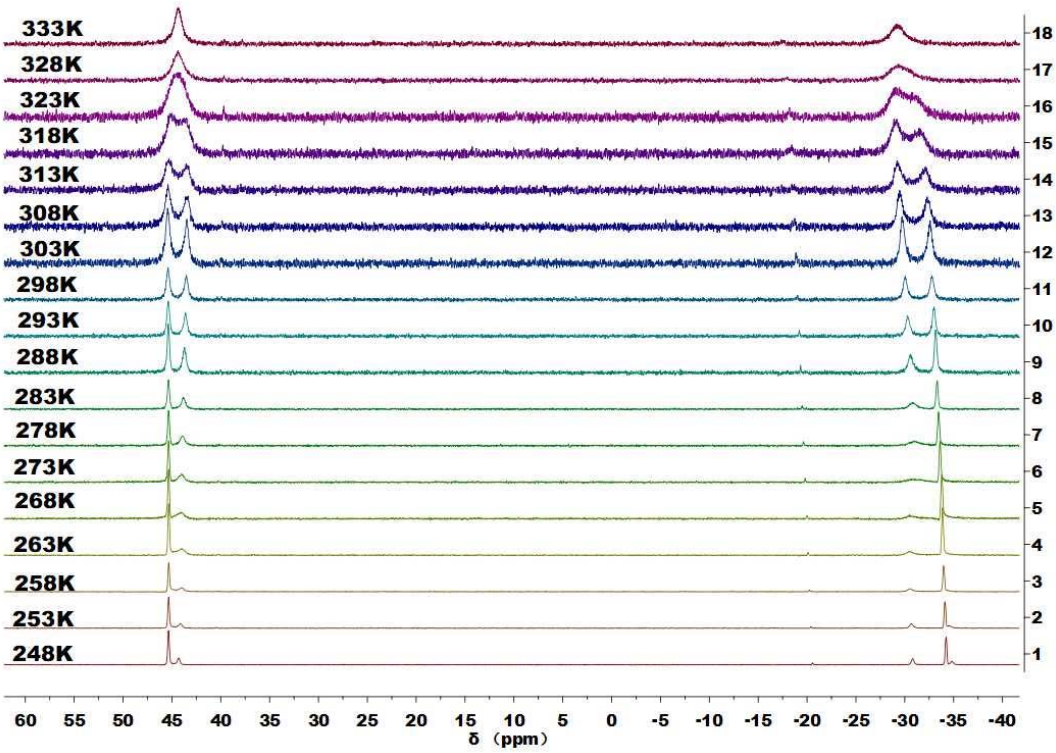

Figure S21. VT-^{31}P{^{1}H} NMR spectra of **8** in toluene-d_8 at various temperature (248-333K).

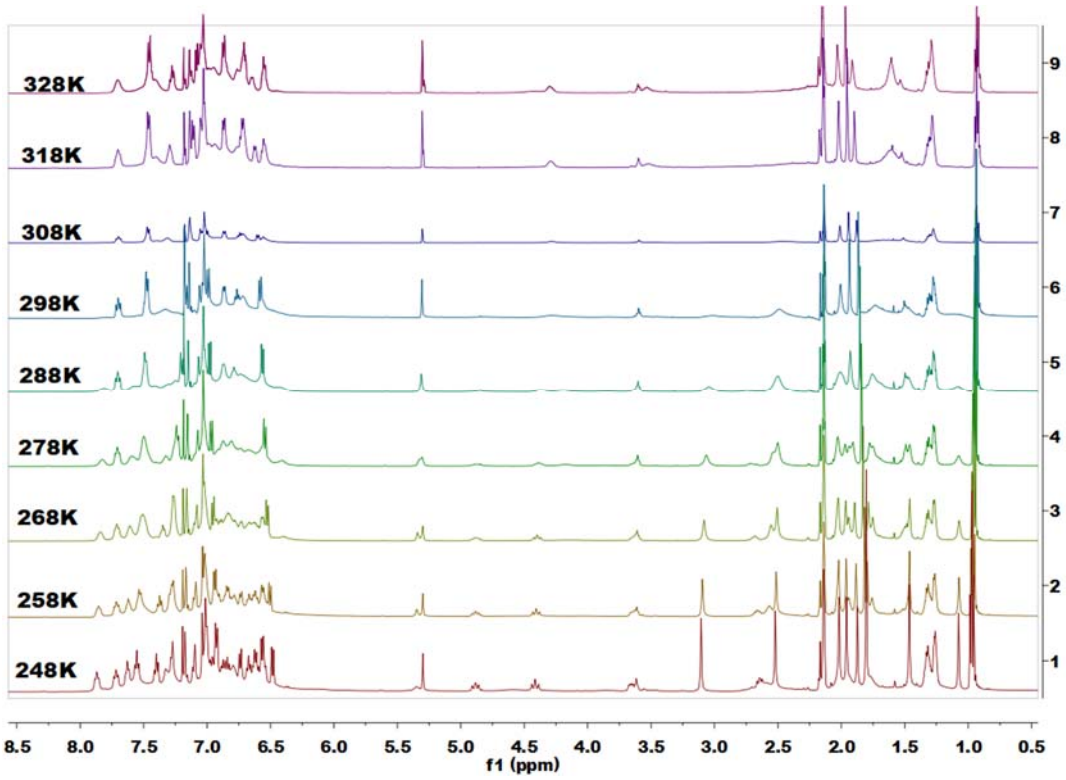

Figure S22. VT-^{1}H NMR spectra of **8** in toluene-d_8 at various temperature (248-328K).

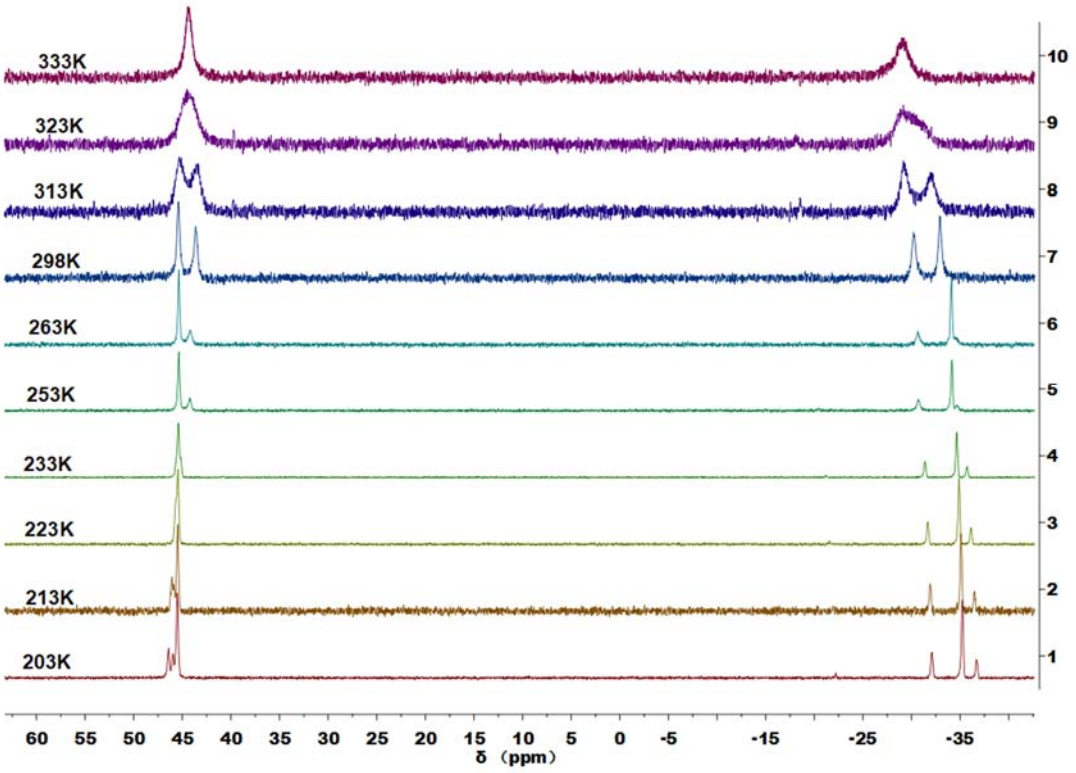

Figure S23. VT-$^{31}P\{^{1}H\}$ NMR spectra of **8** in toluene-d_8 at various temperature (203-333K).

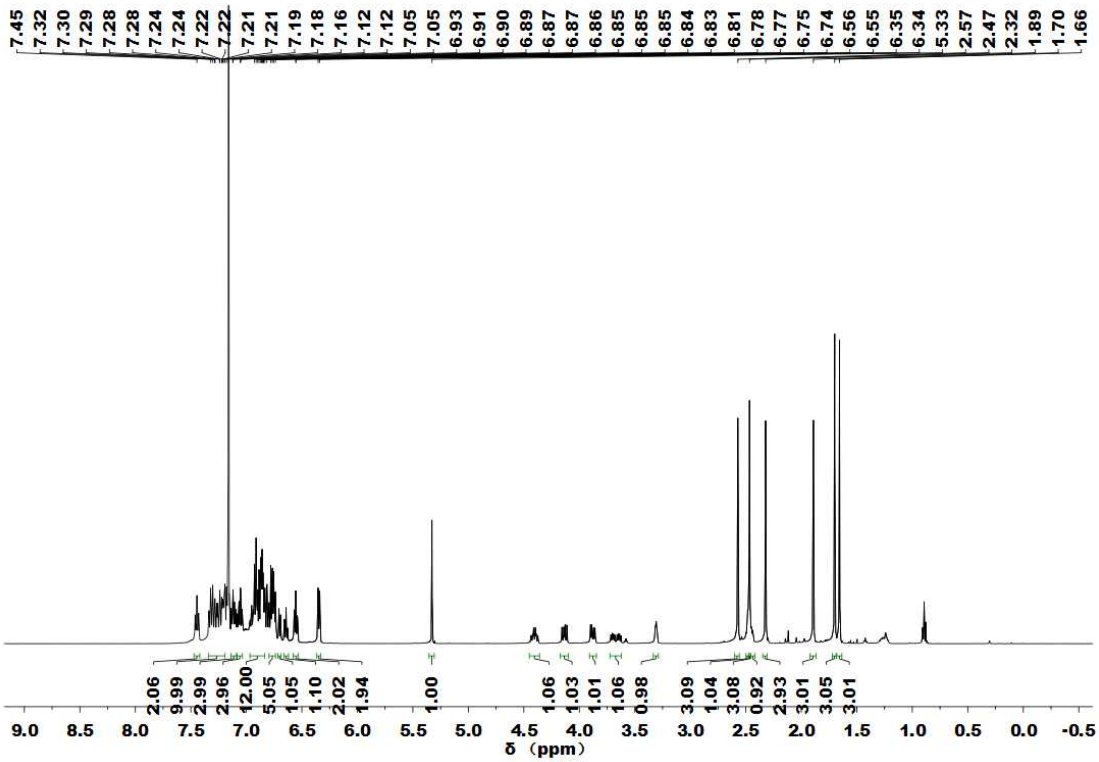

Figure S24. ^{1}H NMR spectrum of **9** in C_6D_6 at 25 °C.

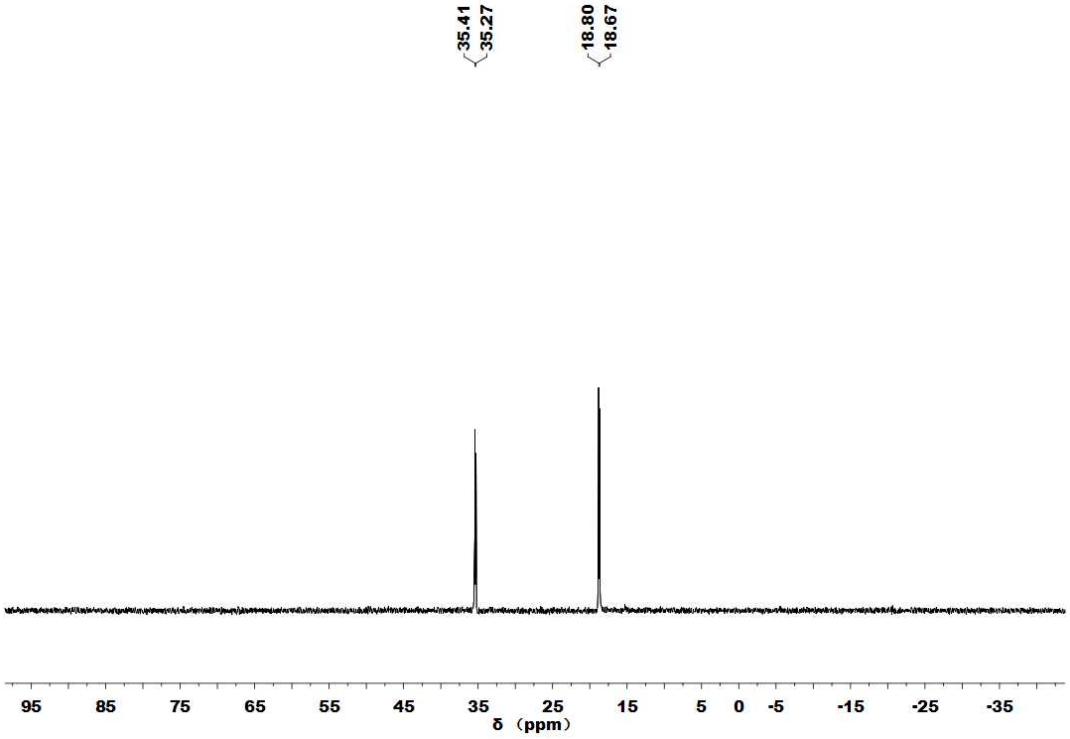

Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of **9** in C_6D_6 at 25 °C.

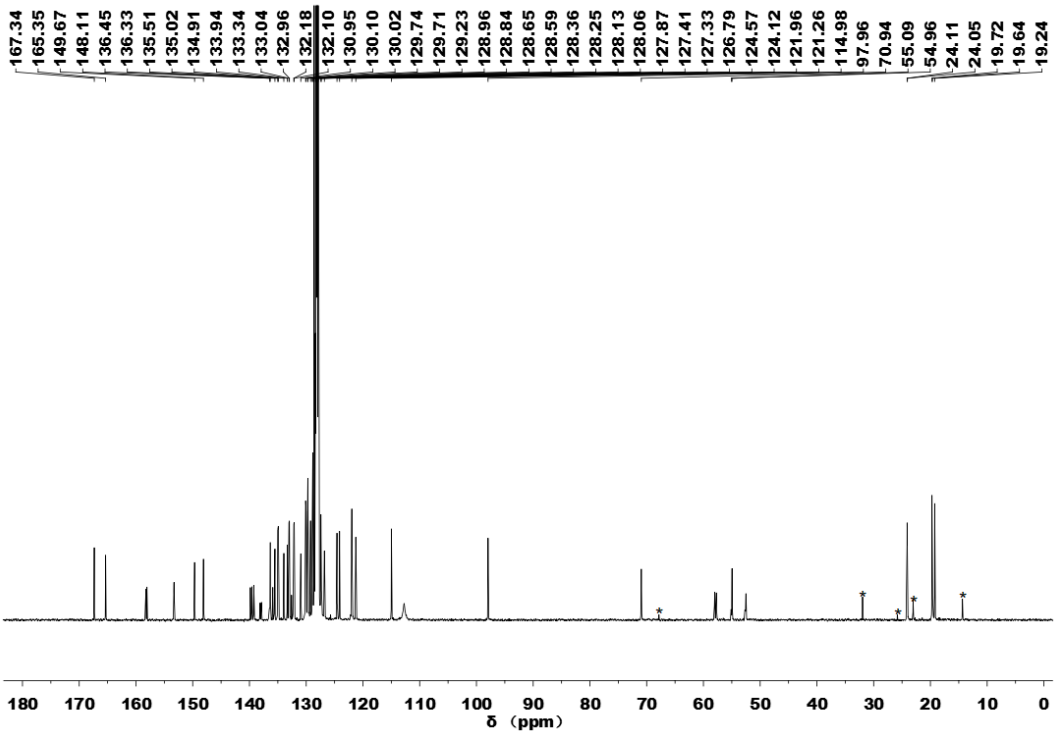

Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of **9** in C_6D_6 at 25 °C. (* denotes small amount of THF and hexane)

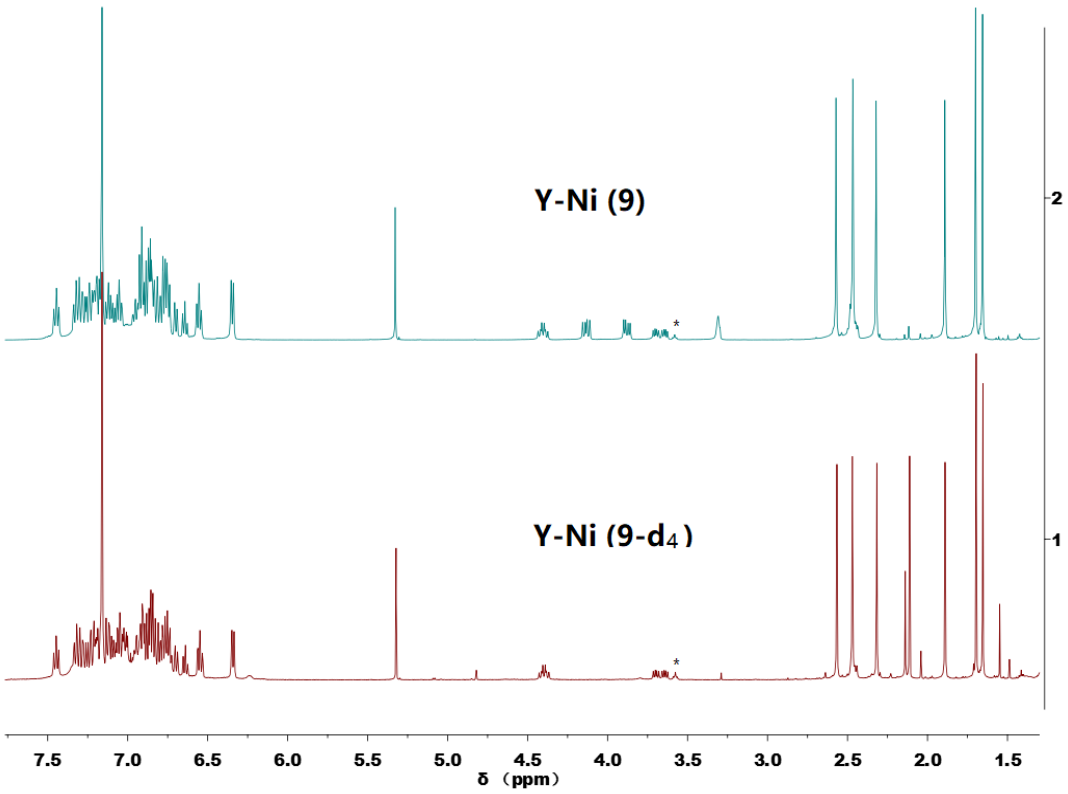

Figure S27. Stacked ^{1}H NMR spectra of **9** and **9-*d₄*** in C_6D_6 at 25 °C. (*denotes small amount of THF)

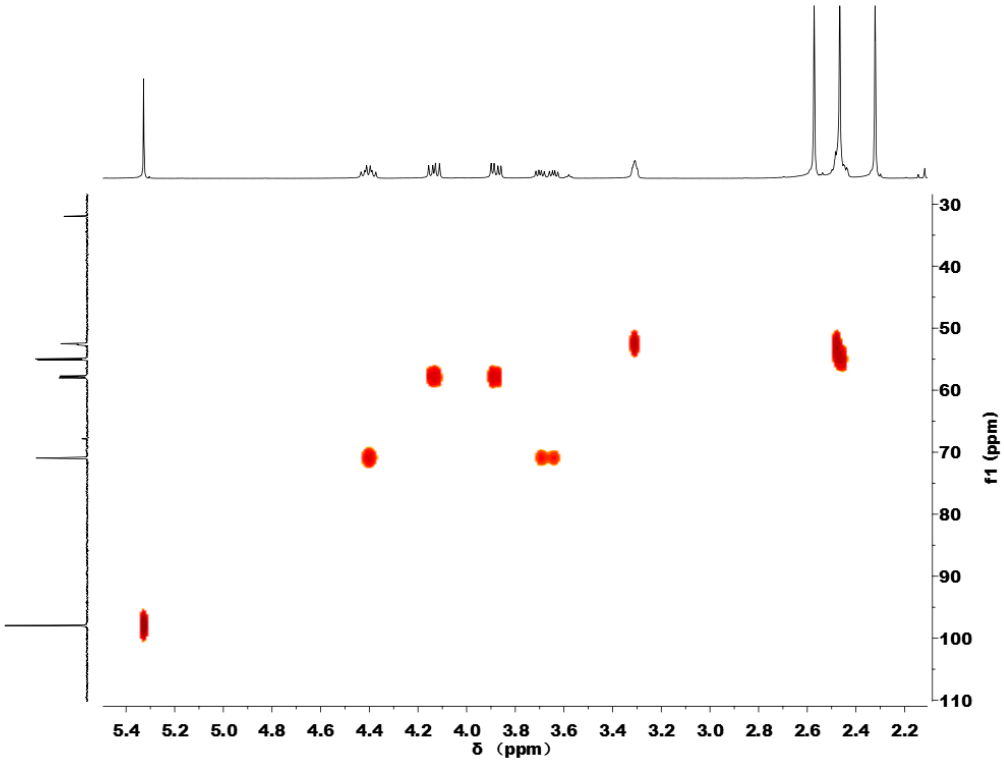

Figure S28. HSQC spectrum of **9**

1.2. IR Spectra

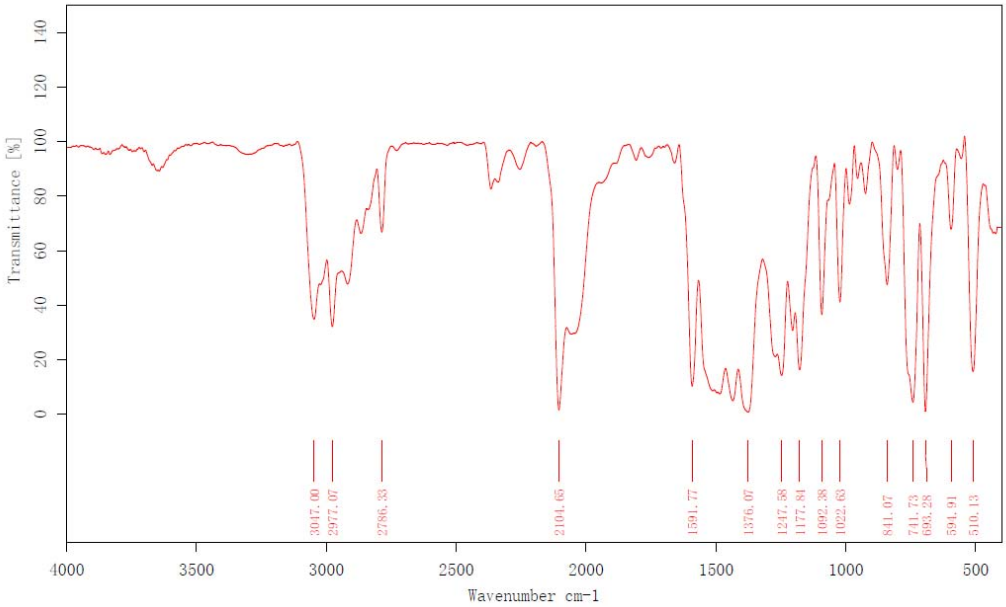

Figure S29. IR spectrum of solid **6**.

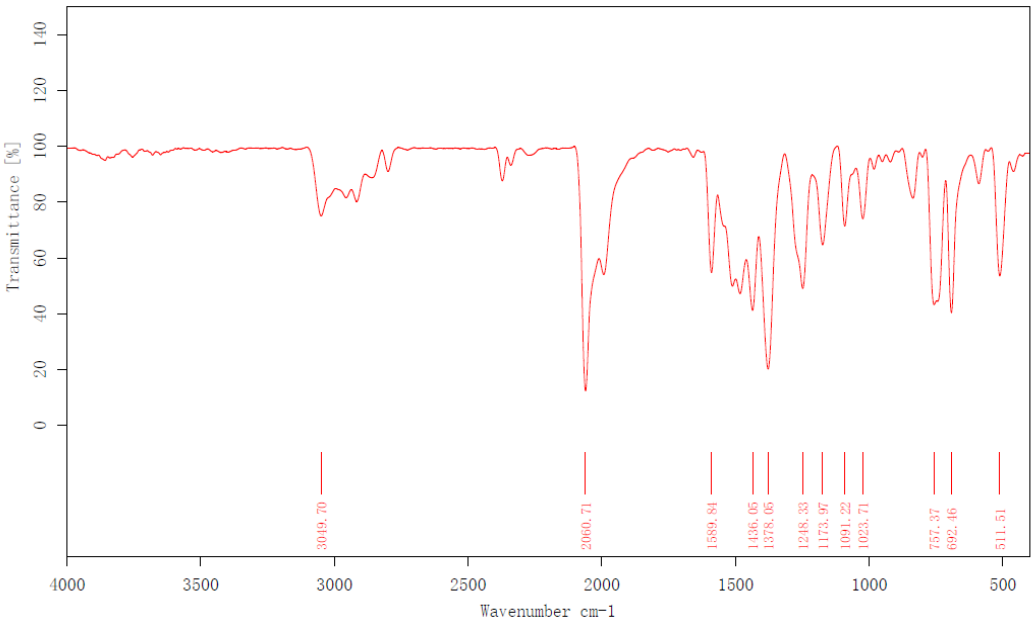

Figure S30. IR spectrum of solid **7**.

2. X-ray Crystallography

X-ray Crystallography. Diffraction was performed on a Bruker SMART APEX II CCD area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) and Bruker Platon II area detector diffractometer using graphite-monochromated Mo *Kα* radiation (λ = 0.71073 Å) for complexes, φ and ω scan technique. An empirical absorption correction was applied using the SADABS program.[1] All structures were solved by direct methods, completed by subsequent difference Fourier syntheses, and refined anisotropically for all non-hydrogen atoms by full-matrix least-squares calculations based on F^2 using the SHELXTL program package[2] and Olex 2 program[4].The hydrogen atom coordinates were calculated with SHELXTL by using an appropriate riding model with varied thermal parameters. The residual electron densities of solvent were squeezed by using PLATON.[3] All crystal structural pictures drawn by Olex 2 program.[4] Crystal parameters and refinement results are given in Table S1-S2.

Table S1. Crystallographic and Refinement Data [a,b] for **1**, **2, 4, 5**

	1	**2**	**4**	**5**
formula	$C_{57}H_{55}N_4P_2Y$	$C_{59}H_{59}N_4P_2Y$	$C_{59}H_{59}N_4P_2NiY$	$C_{59}H_{59}N_4P_2NiLu$
Fw, g·mol^{-1}	946.90	974.95	1033.66	1119.72
cryst size, mm	0.22 x 0.21 x 0.2	0.21 x 0.2 x 0.18	0.21 x 0.19 x 0.18	0.22 x 0.20 x 0.19
cryst. syst.	triclinic	monoclinic	triclinic	triclinic
space group	P -1	P 1 21/n 1	P -1	P -1
T, K	273(2)	273(2)	273(2)	300(2)
a, Å	12.168(2)	13.7148(8)	12.1820(5)	12.2096(6)
b, Å	12.969(2)	19.1621(13)	12.4634(5)	12.4762(7)
c, Å	17.303(3)	20.6907(13)	19.2026(7)	19.1394(10)
α, °	84.336(6)	90	82.367(2)	82.165(2)
β, °	72.086(6)	108.426(2)	76.584(2)	76.565(2)
γ, °	73.669(6)	90	64.7460(10)	64.391(2)
V, Å^3	2493.1(8)	5158.8(6)	2563.01(18)	2555.0(2)
Z	2	4	2	2
D_{calcd}, Kg·m^{-3}	1.261	1.255	1.339	1.455
F(000)	988.0	2040.0	1076.0	1140.0
μ, mm^{-1}	1.275	1.234	1.598	2.394
θ range /°	2.949 - 25.039	2.971 - 27.815	2.888 - 27.564	2.899 - 27.537
refns collected	8659	207071	132946	71865
indep reflns (R_{int})	8659	11995 (0.0718)	11820 (0.0594)	11738 (0.0501)
reflns obsd [$I > 2\sigma(I)$]	7609	8848	9315	9914
data/restrnts/params	8659 / 1216 / 488	11995 / 1284 / 601	11820 / 1323 / 610	11738 / 1308 / 610
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.1224, 0.3296	0.0545, 0.1376	0.0440, 0.1076	0.0319, 0.0624
*R*1, *wR*2 (all data)	0.1324, 0.3345	0.0832, 0.1608	0.0644, 0.1197	0.0466, 0.0681
GOF on F2	1.125	1.083	1.047	1.037
$\Delta\rho_{max, min}$, e·Å^{-3}	2.274, -1.933	0.721, -0.418	0.644, -0.657	0.849, -0.801

[a]$R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b]$wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

Table S2. Crystallographic and Refinement Data [a,b] for **6-9**

	6	**7**	**8**	**9**
formula	$C_{64}H_{68}N_5P_2NiY$	$C_{68}H_{68}N_5NiP_2Y$	$C_{75}H_{73}N_6NiP_2Y$	$C_{67}H_{67}N_4NiOP_2Y{\cdot}C_7H_8$
Fw, g·mol^{-1}	1116.79	1164.83	1267.95	1245.94
cryst size, mm	0.22 x 0.21 x 0.2	0.22 x 0.21 x 0.2	0.22 x 0.21 x 0.2	0.22 x 0.21 x 0.2
cryst. syst.	monoclinic	triclinic	monoclinic	triclinic
space group	P 1 21/n 1	P -1	P 1 21/c 1	P -1
T, K	273(2)	273(2)	273(2)	293(2)
a, Å	12.2206(19)	12.443(4)	14.384(3)	14.533(5)
b, Å	22.319(4)	12.656(4)	20.649(4)	15.248(5)
c, Å	21.549(3)	23.095(9)	21.706(4)	16.887(6)
α, °	90	82.321(11)	90	86.604(4)
β, °	97.461(5)	82.700(11)	92.10(3)	80.637(4)
□, °	90	64.088(10)	90	62.662(4)
V, Å^3	5827.8(16)	3232(2)	6443(2)	3279.5(19)
Z	4	2	4	2
D_{calcd}, Kg·m^{-3}	1.273	1.197	1.307	1.262
F(000)	2336.0	1216.0	2648	1304
μ, mm^{-1}	1.412	1.275	1.286	1.262
θ range /°	2.851 -24.998	2.830 - 24.999	2.985 - 28.722	1.504 - 25.064
refns collected	101045	205675	148216	11330
indep reflns (R_{int})	10248 (0.1993)	11357 (0.1649)	15008 (0.0853)	11330
reflns obsd [$I > 2\sigma(I)$]	6408	7778	10320	7895
data/restrnts/params	10248/1425/631	11357/1519/702	15008/1764/774	11330/1618/720
*R*1, *wR*2 ($I > 2\sigma(I)$)	0.1107, 0.2722	0.0647, 0.1344	0.0588, 0.1377	0.1265, 0.3446
*R*1, *wR*2 (all data)	0.1737, 0.3210	0.1081, 0.1638	0.0958, 0.1573	0.1639, 0.3628
GOF on F2	1.126	1.056	1.013	1.084
$\Delta\rho_{max,\ min}$, e·Å^{-3}	0.953, -0.748	0.425, -0.601	0.476, -0.451	1.704, -1.355

[a] $R1 = \Sigma|F_o| - |F_c|/\Sigma|F_o|$. [b] $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$.

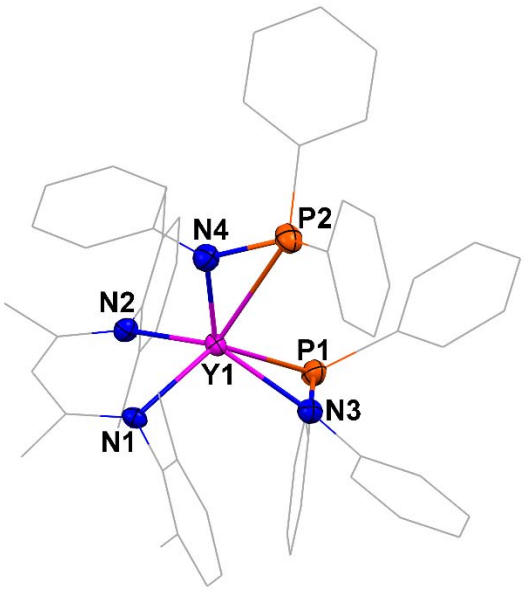

Figure S31. Molecular structure of **1** at the 30% thermal ellipsoids probability.

Hydrogen atoms were omitted for clarity.

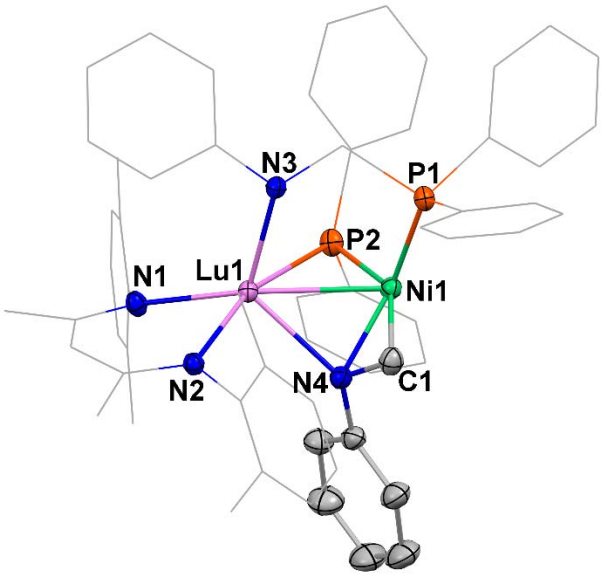

Figure S32. Molecular structure of **5** at the 30% thermal ellipsoids probability.

Hydrogen atoms were omitted for clarity.

3. References

1. Sheldrick G. M. *SADABS: Program for Empirical Absorption Correction of Area Detector Data*; University of Göttingen: Germany (**1996**).
2. Sheldrick G. M. *SHELXT*-Integrated space-group and crystalstructure determination. *Acta Cryst.* **A71**, 3-8 (**2015**).
3. Spek A. L. *PLATON* SQUEEZE: a tool for the calculation of the disordered solvent contribution to the calculated structure factors. *Acta Cryst*. **C71**, 9-18 (**2015**).
4. Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. and Puschmann, H. *J. Appl. Crystallogr.* **2009**, 42, 339-341.