Supporting Information

Dinitrogen silylation catalyzed by silylene cobalt(I) and silylene iron(I) chlorides

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Table of Contents

1. **Table S1** Crystallographic data for complexes **3, 4, 6, 7**

	3	**4**	**6**	**7**
formula	$C_{38}H_{68}Cl_3CoN_4P_2Si_2$	$C_{44}H_{80}Cl_3CoN_4P_2Si_2$	$C_{38}H_{68}Cl_3FeN_4P_2Si_2$	$C_{44}H_{80}Cl_3FeN_4P_2Si_2$
Mz	864.36	948.52	861.28	945.44
crystal system	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	I2/a
a/Å	13.65400(10)	21.4451(2)	13.6644(2)	21.6307(4)
b/Å	20.1812(2)	10.29200(10)	20.2740(3)	10.3205(2)
c/Å	16.8073(2)	25.0566(3)	16.7641(2)	24.7701(5)
α/°	90	90	90	90
β/°	92.5000(10)	108.3210(10)	92.5530(10)	111.412(2)
γ/°	90	90	90	90
V [Å3]	4626.91(8)	5249.98(10)	4639.58(11)	5148.01(18)
T [K]	173.00(10)	173.00(10)	173.00(10)	173.00(10)
Z	4	4	4	4
μ[mm-1]	5.876	5.221	5.567	5.060
total reflns	40040	39439	36306	17284
unique reflns	9161	10368	9217	4515
Rint	0.0494	0.0473	0.0495	0.0605
R1[I>2σ(I)]	0.0480	0.0372	0.0499	0.0572
wR(F2) [I>2σ(I)]	0.1273	0.0944	0.1381	0.1657
R1(all data)	0.0565	0.0423	0.0577	0.0629
wR(F2) (all data)	0.1316	0.0973	0.1439	0.1710
GOF on F2	1.023	1.035	1.033	1.073

2. IR, ^{1}H, ^{13}C and ^{29}Si NMR spectra of ligand **L3**

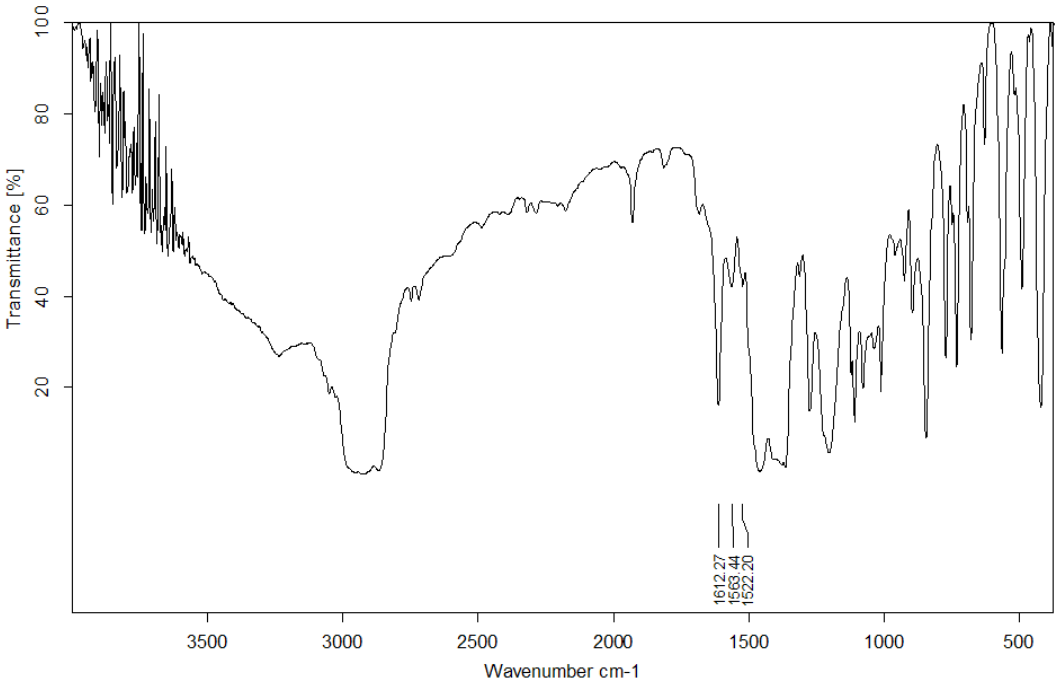

Figure S1. The IR Spectrum of ligand **L3**

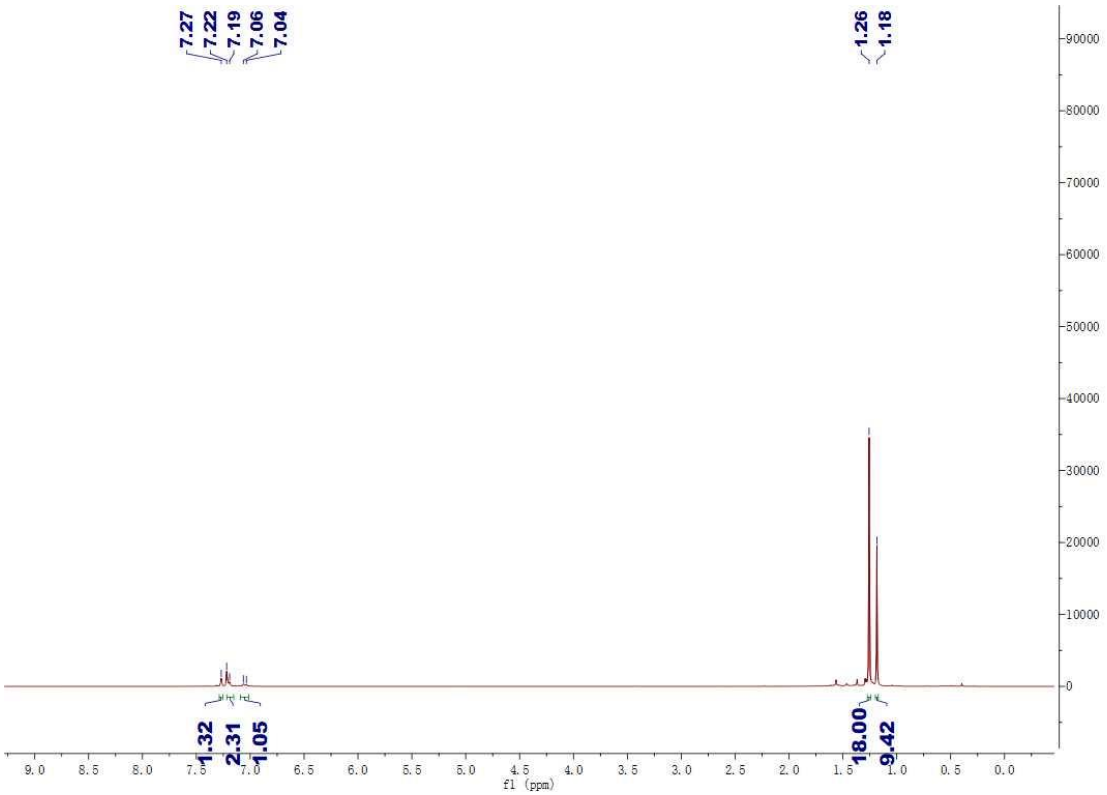

Figure S2. The ^{1}H NMR spectrum of Ligand **L3** in C_6D_6

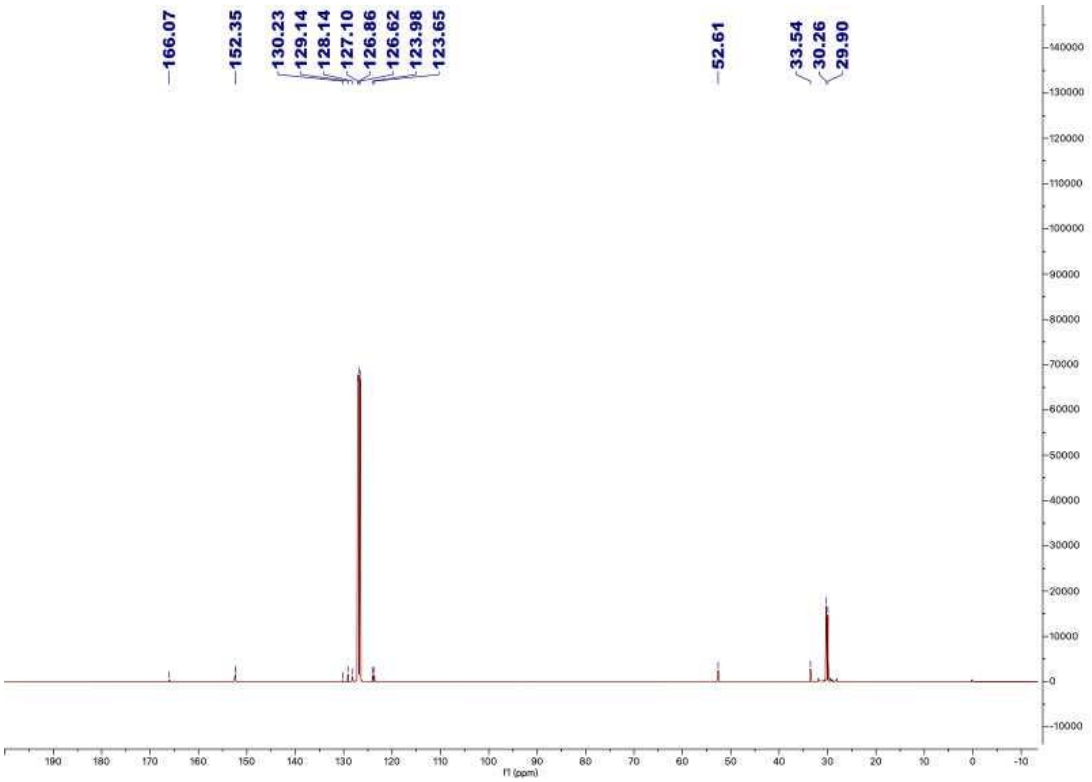

Figure S3. The ^{13}C NMR spectrum of Ligand **L3** in C_6D_6

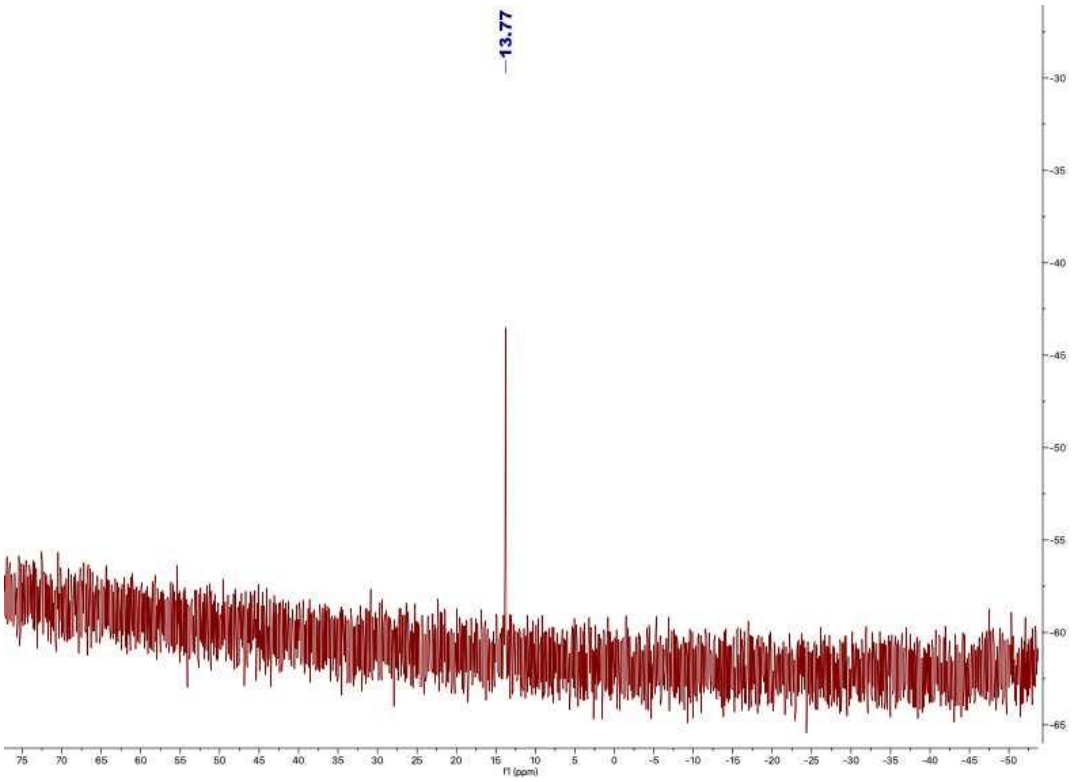

Figure S4. The ^{29}Si NMR spectrum of Ligand **L3** in C_6D_6

3. IR, ^{31}P NMR spectra of complexes **3**, **4**, **6**, **7**

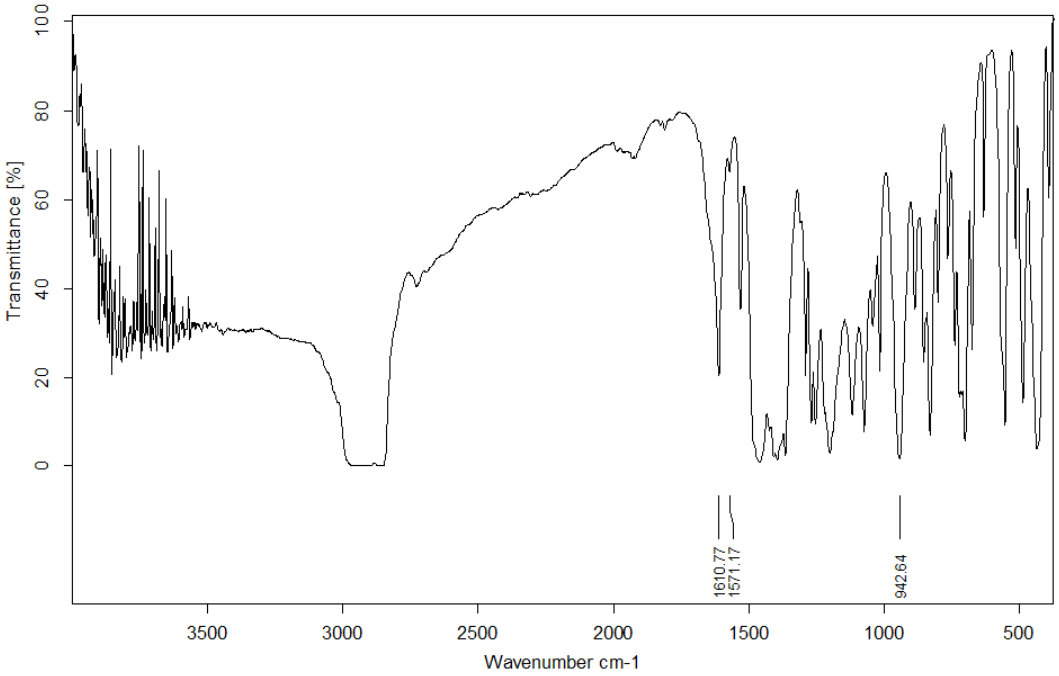

Figure S5. The IR Spectrum of complex **3**

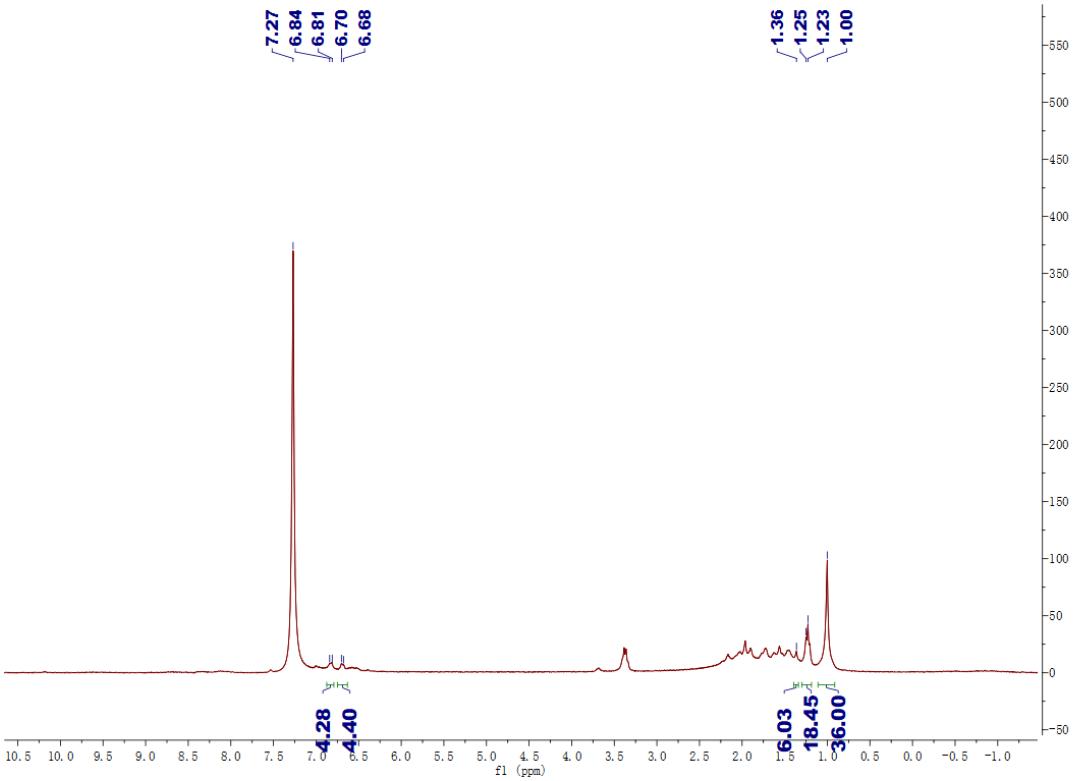

Figure S6. The ^{1}H NMR spectrum of complex **3** in C_6D_6

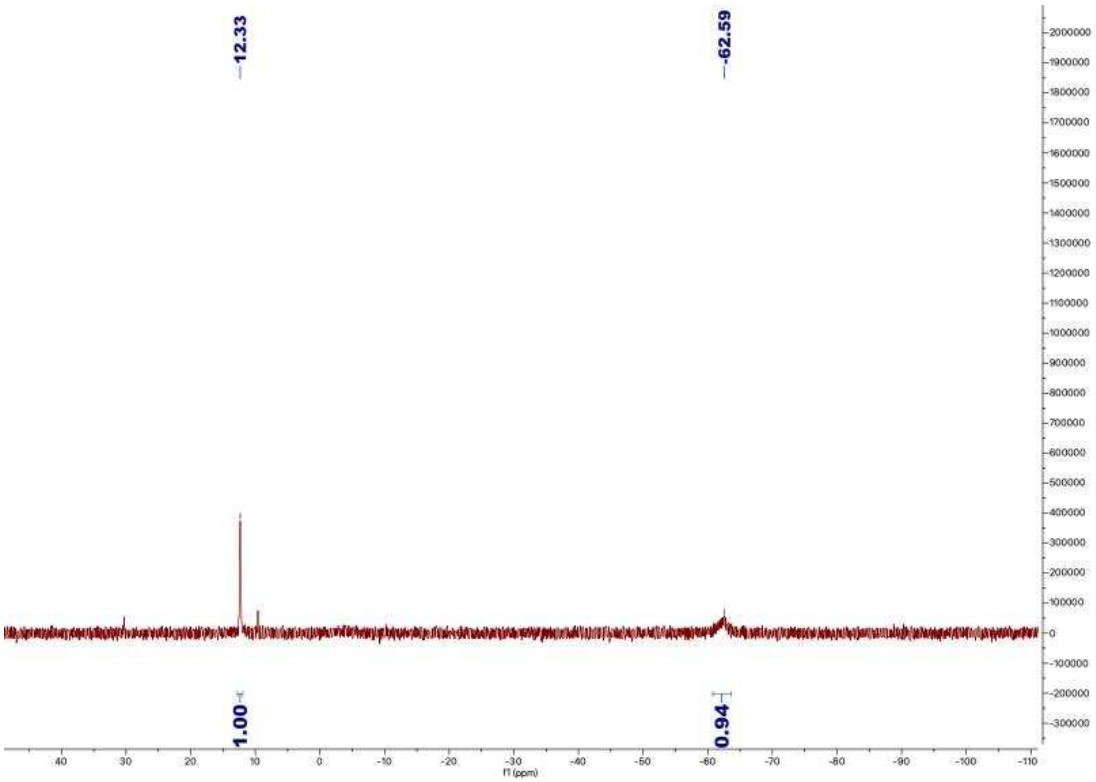

Figure S7. The ^{31}P NMR spectrum of complex **3** in C_6D_6

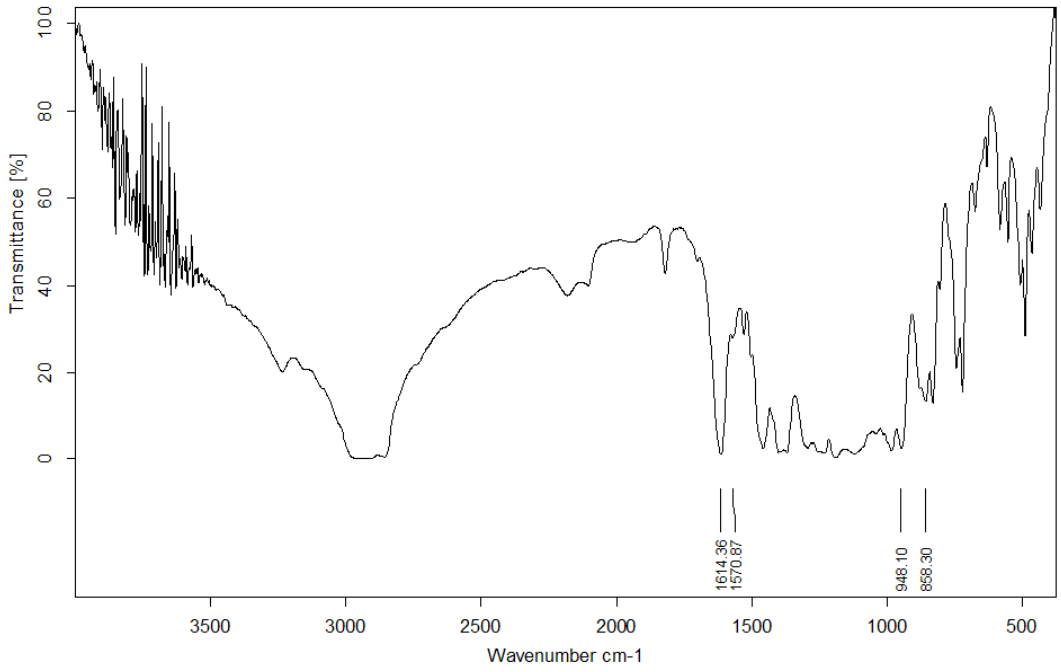

Figure S8. The IR Spectrum of complex **4**

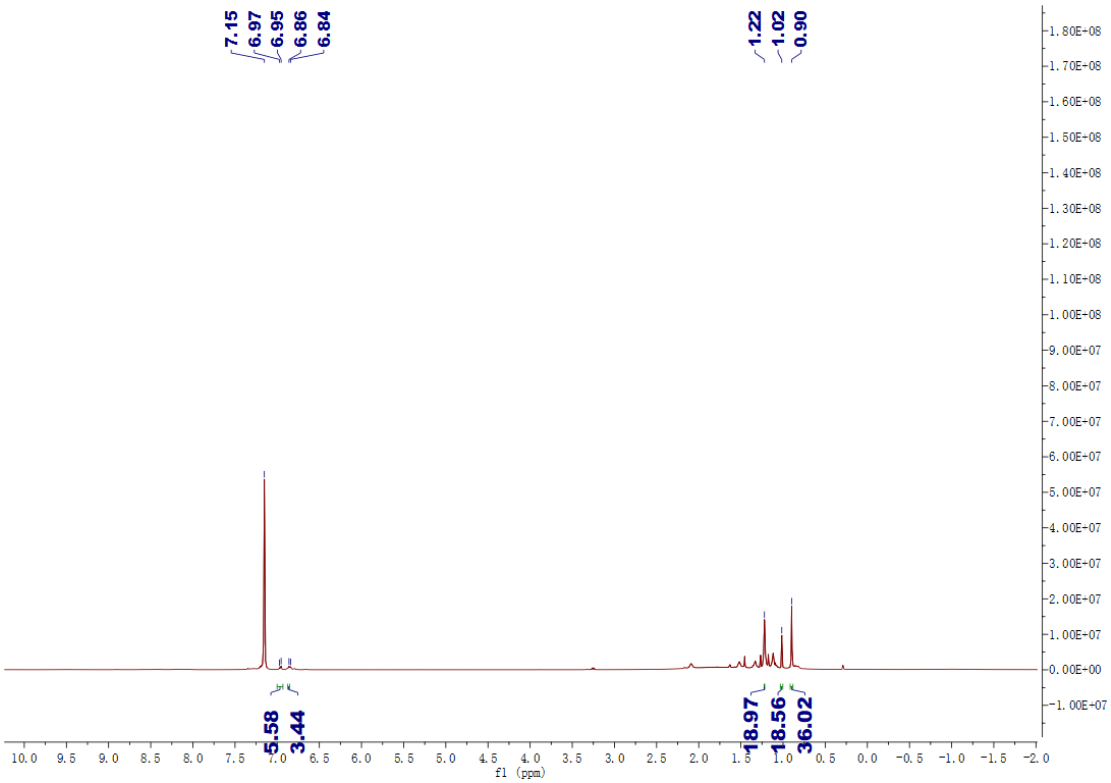

Figure S9. The ^{1}H NMR spectrum of complex **4** in C_6D_6

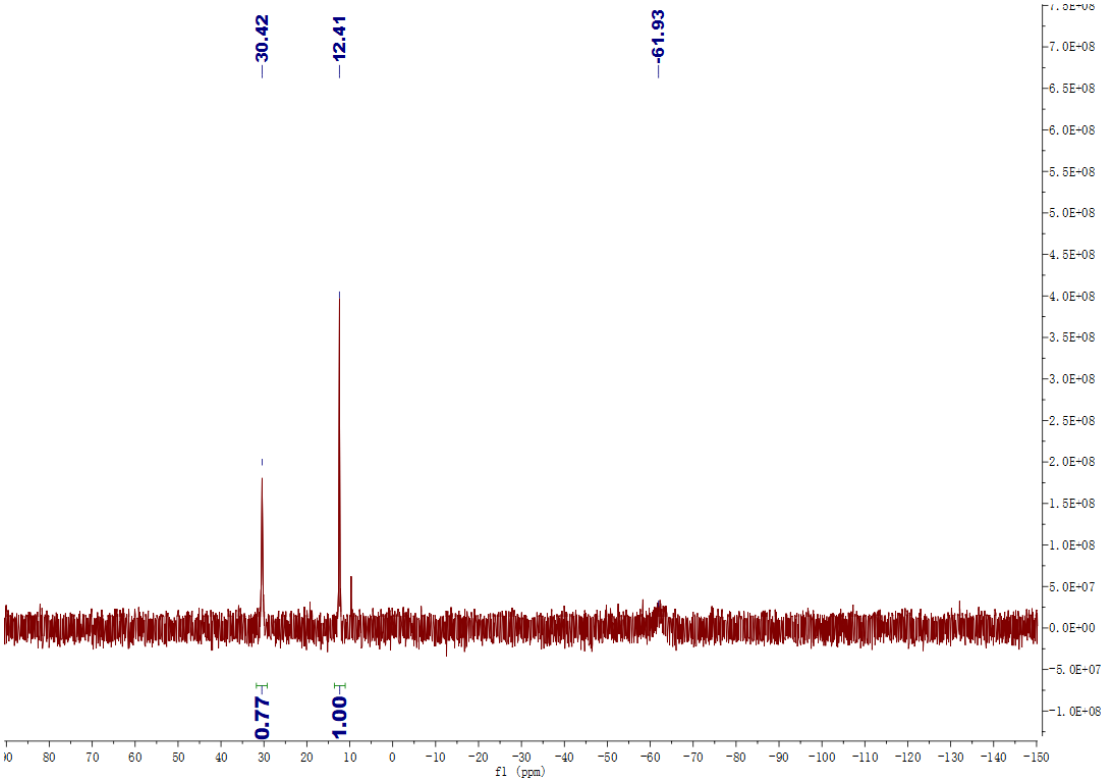

Figure S10. The ^{31}P NMR spectrum of complex **4** in C_6D_6

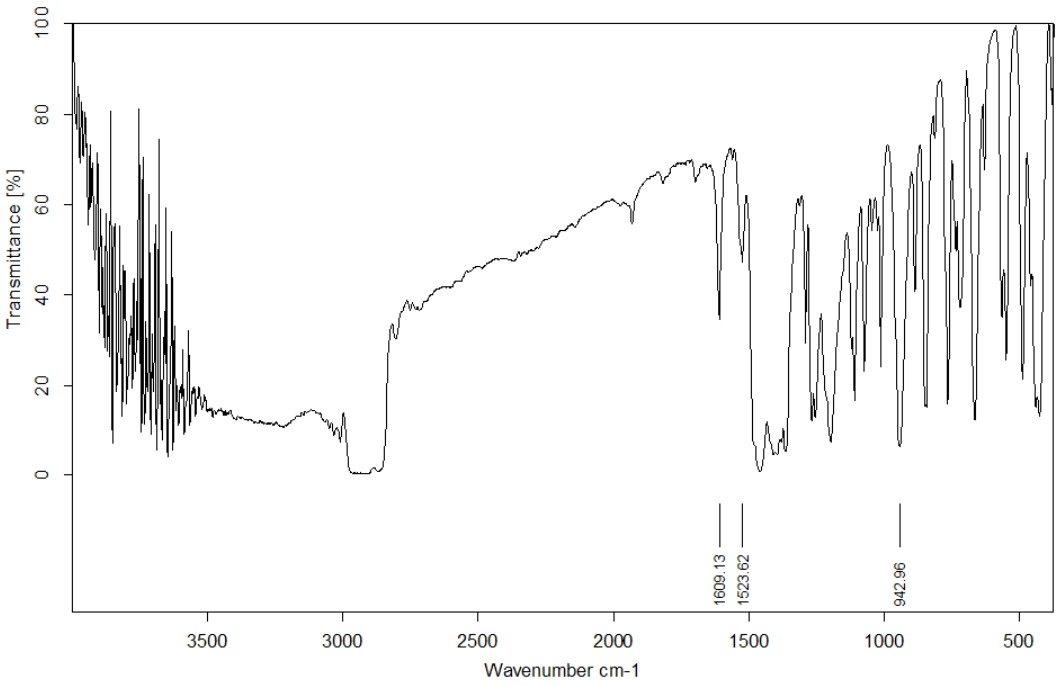

Figure S11. The IR Spectrum of complex **6**

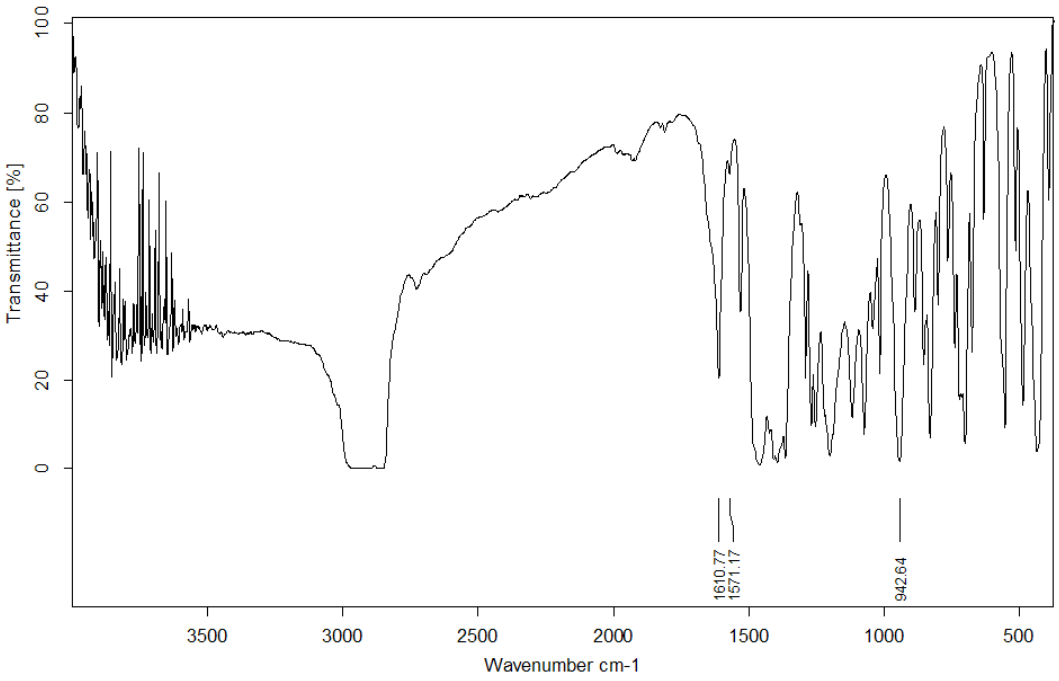

Figure S12. The IR Spectrum of complex **7**

4. The IR spectra of mechanism study

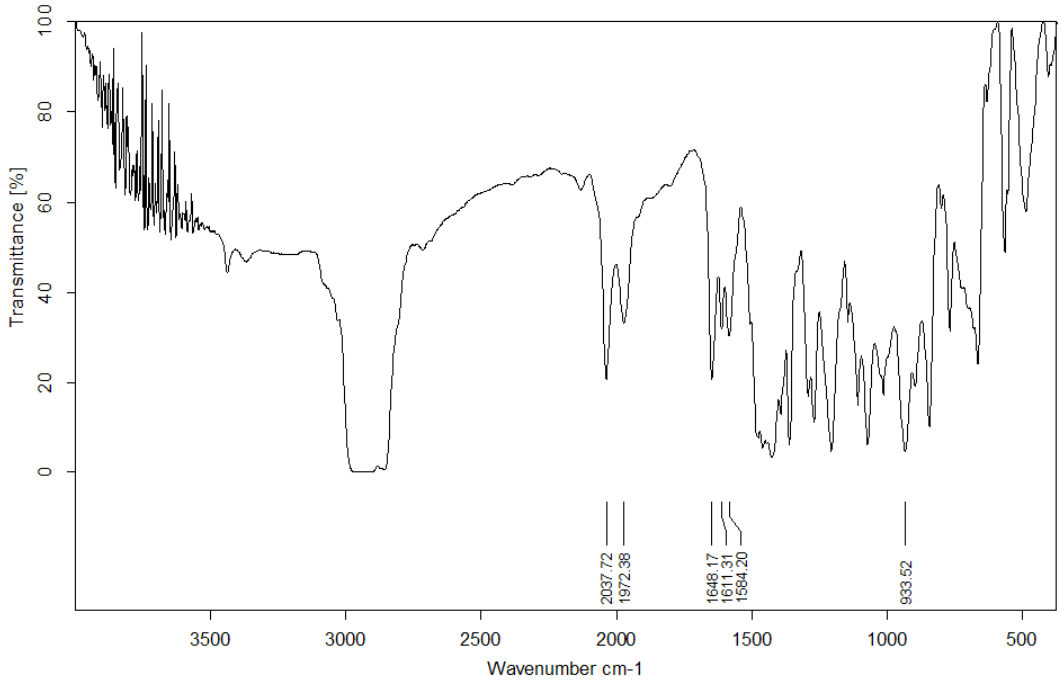

Figure S13. The IR Spectrum of stoichiometric reaction of **2** and KC_8 at -30℃ for 6 h in THF.

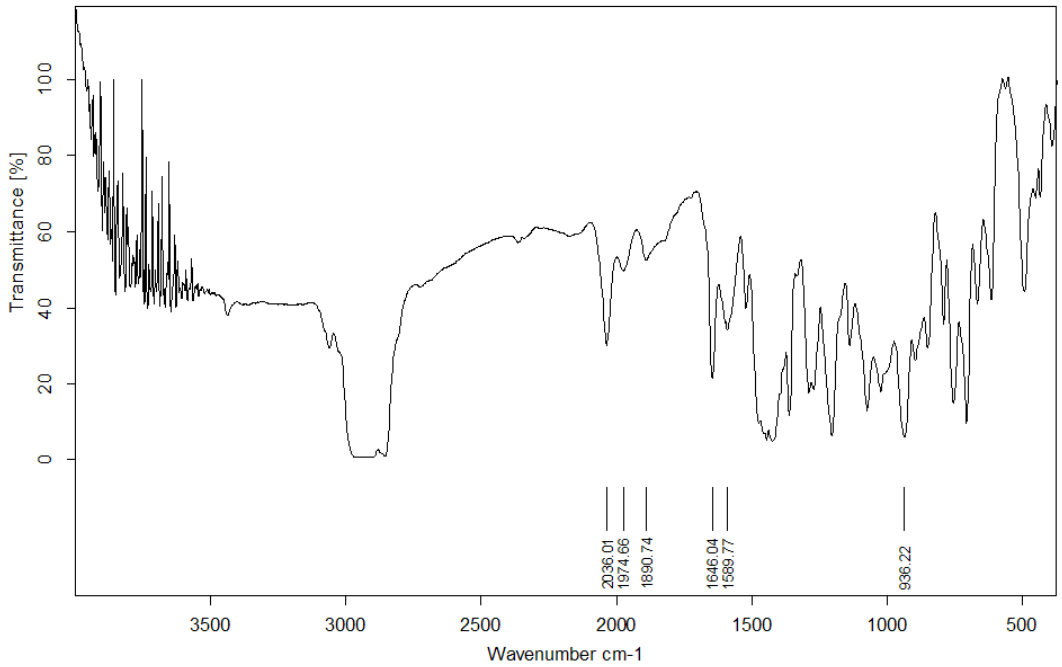

Figure S14. The IR Spectrum of stoichiometric reaction of **5** and KC_8 at 25℃ for 10 h in THF.