Electronic Supplementary Material (ESI) for Polymer Chemistry.

Controlled polymerization of isoprene promoted by a type of hemilabile X=PN^3 (X=O, S) ligand supported cobalt (II) complexes: the role of hemilabile donor on the level of control

Huafeng Chen[a], Weijing Pan[a], Kuo-Wei Huang[c], Xuequan Zhang[b], Dirong Gong[a*]

Corresponding authors: gongdirong@nbu.edu.cn

Supporting Information Content List

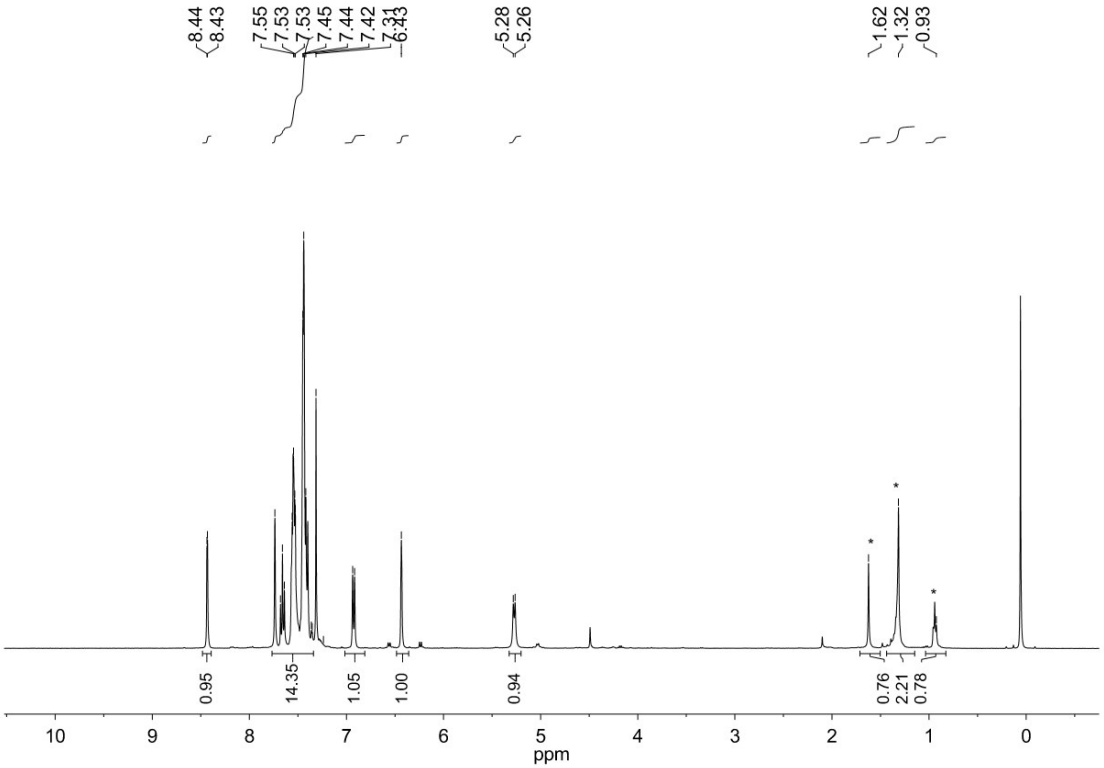

Figure 1S The ^{1}H NMR of ligand **L1(hexane included)**

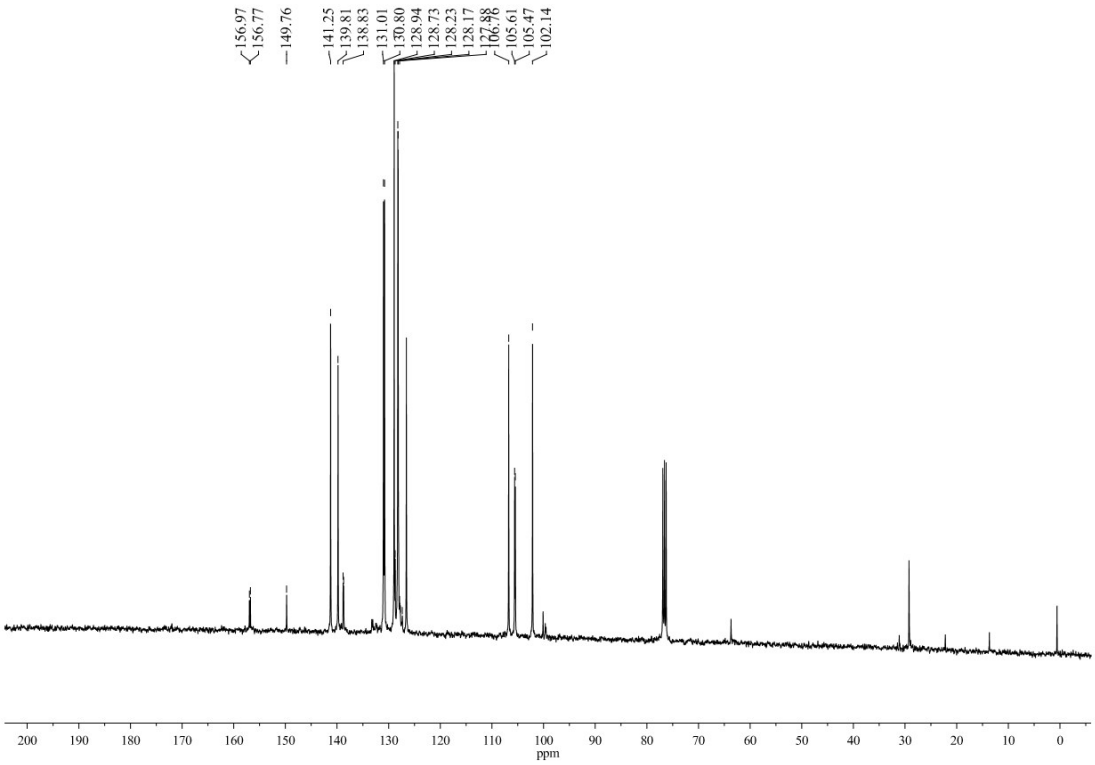

Figure 2S The ^{13}C NMR of ligand **L1**

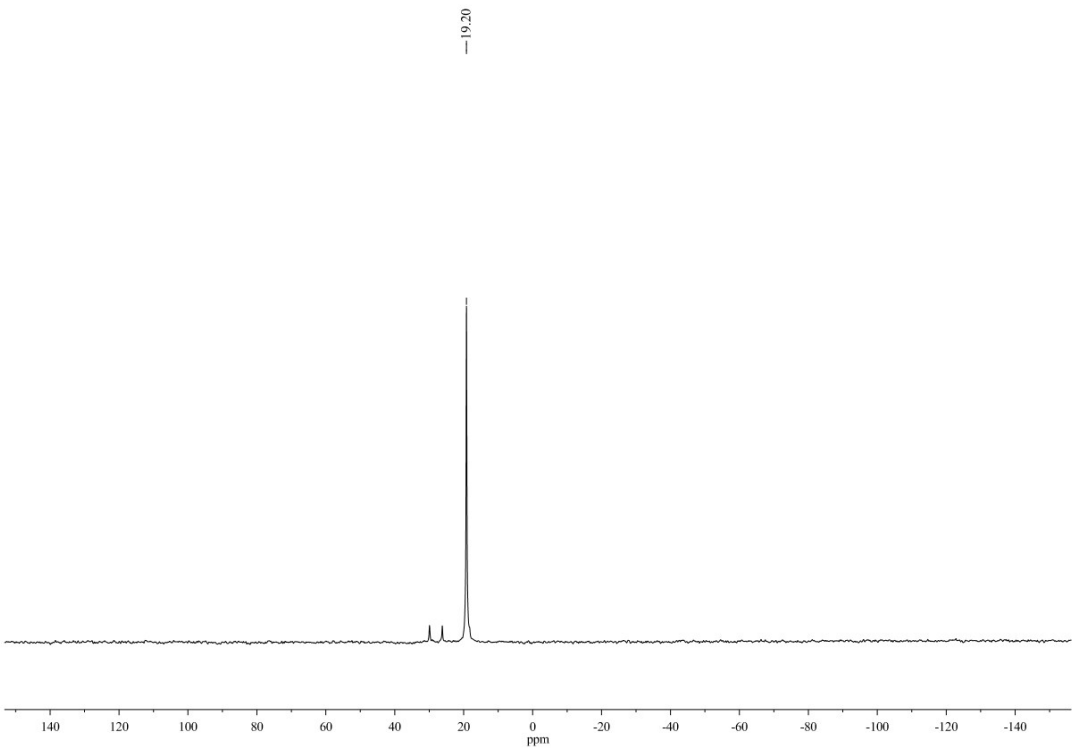

Figure 3S The ^{31}P NMR of ligand **L1**

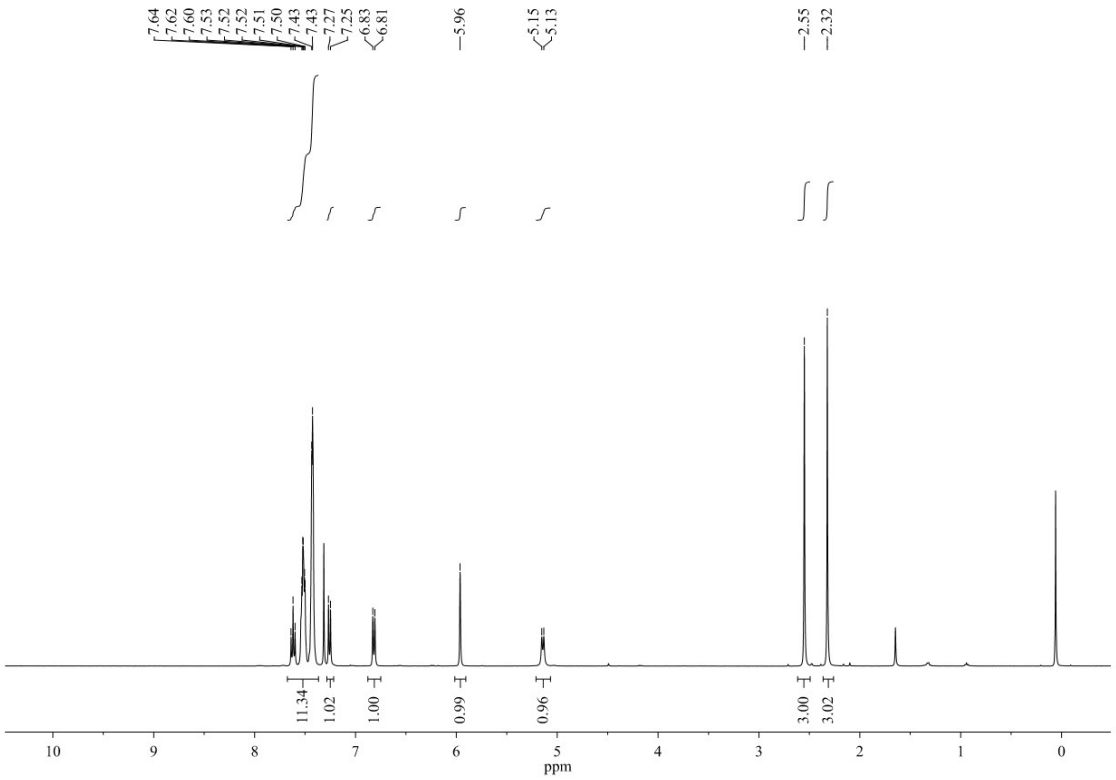

Figure 4S The ^{1}H NMR of ligand **L2**

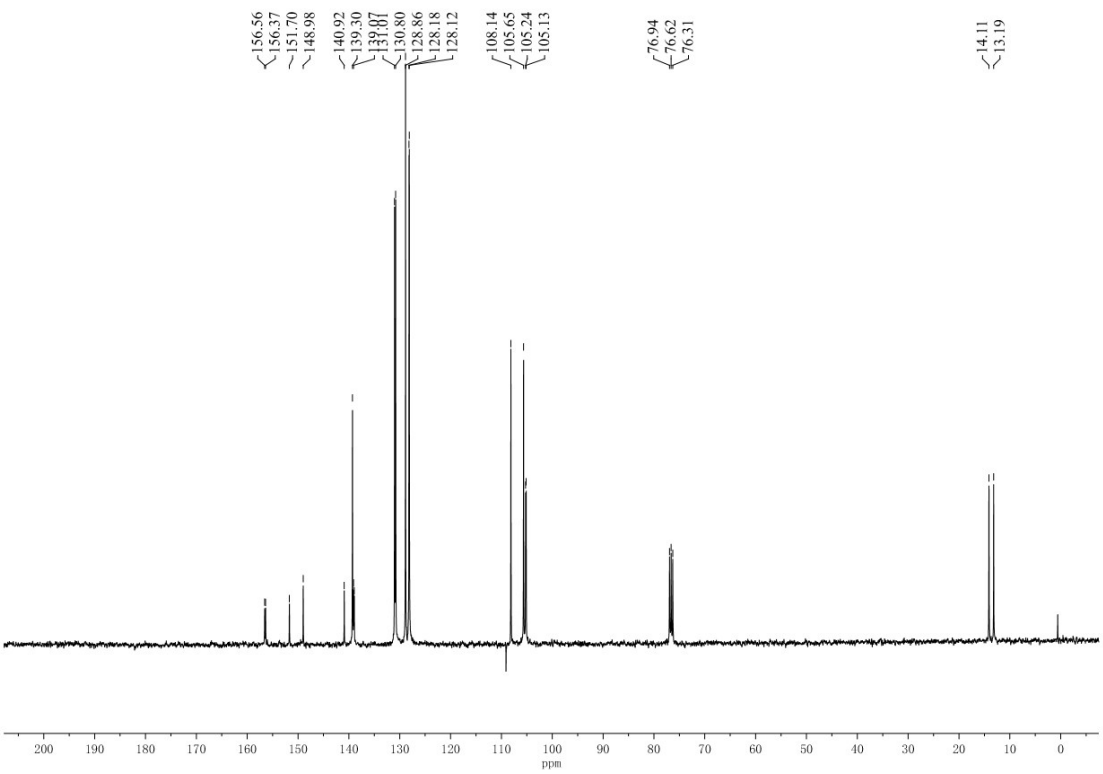

Figure 5S The ^{13}C NMR of ligand **L2**

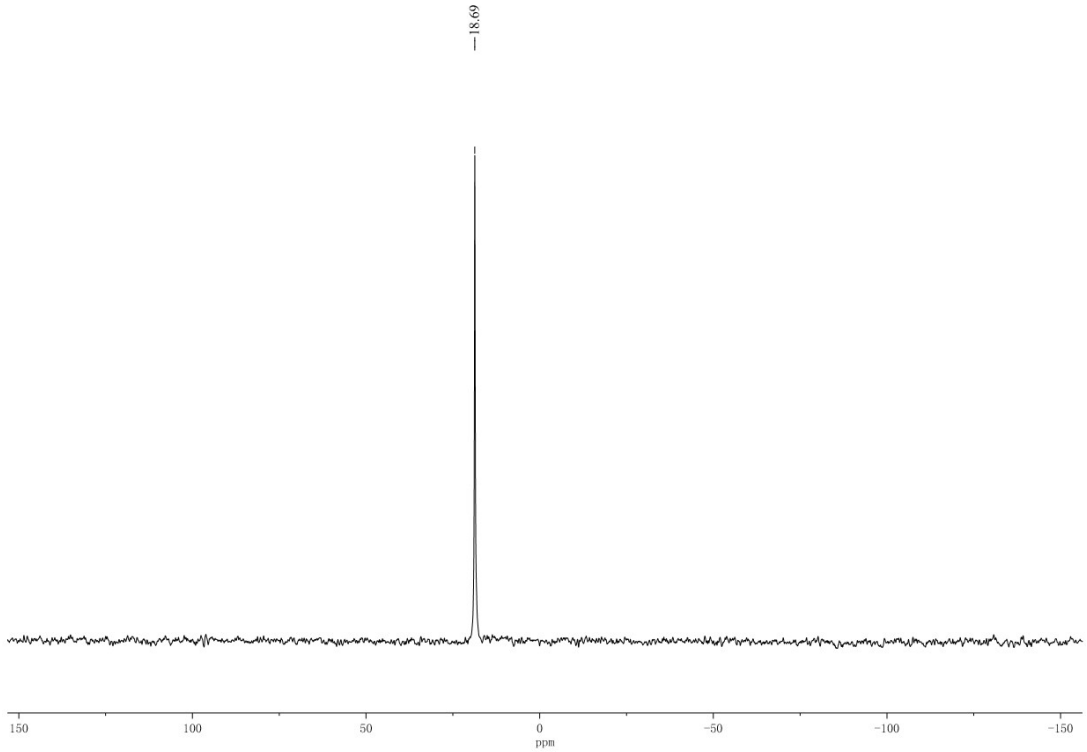

Figure 6S The ^{31}P NMR of ligand **L2**

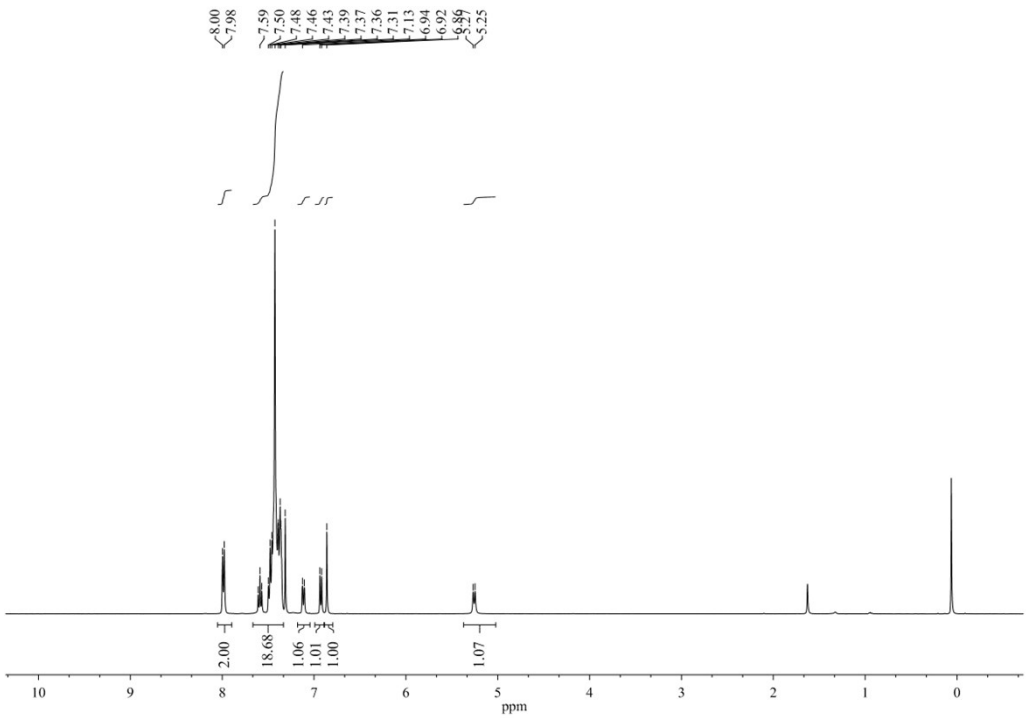

Figure 7S The ^{1}H NMR of ligand **L3**

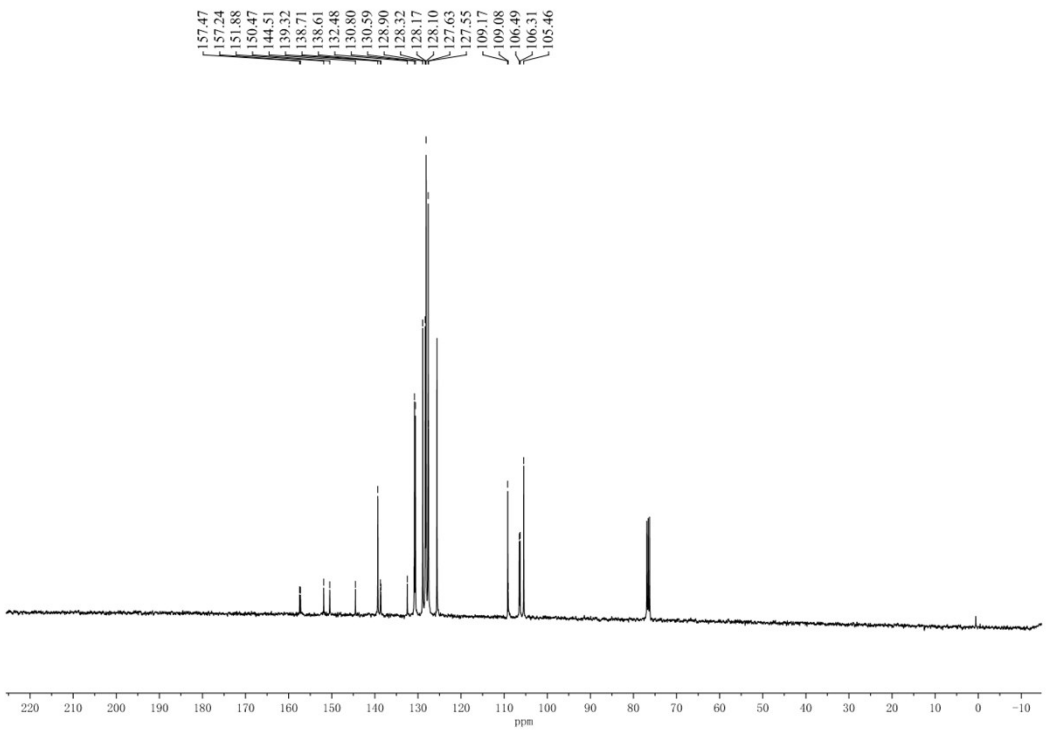

Figure 8S The ^{13}C NMR of ligand **L3**

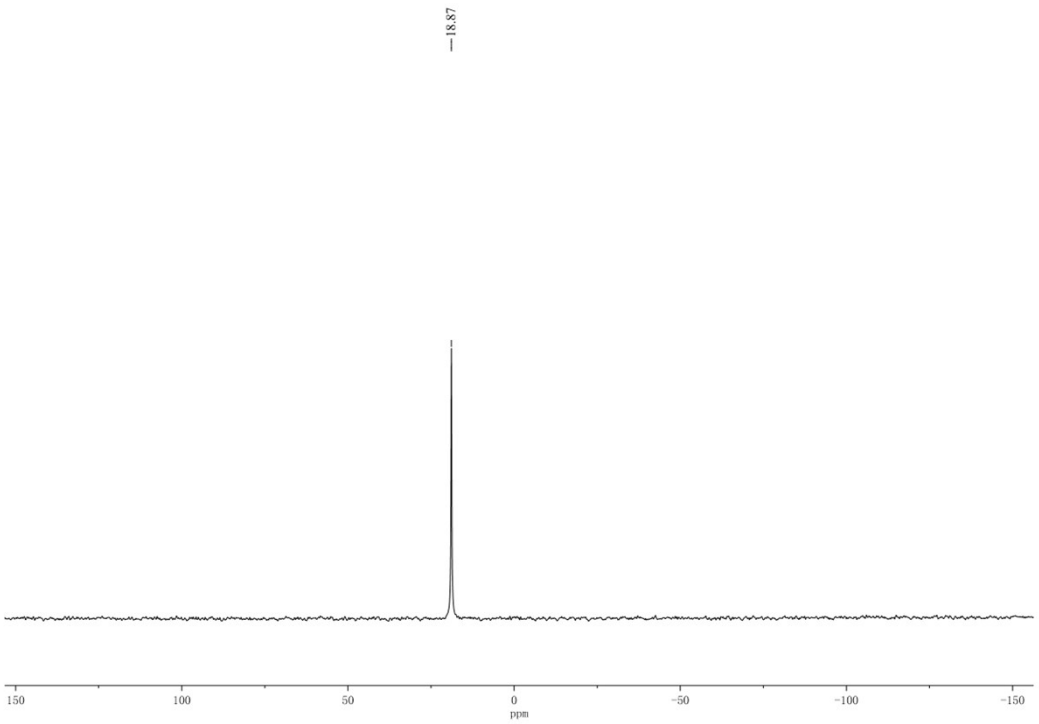

Figure 9S The ^{31}P NMR of ligand **L3**

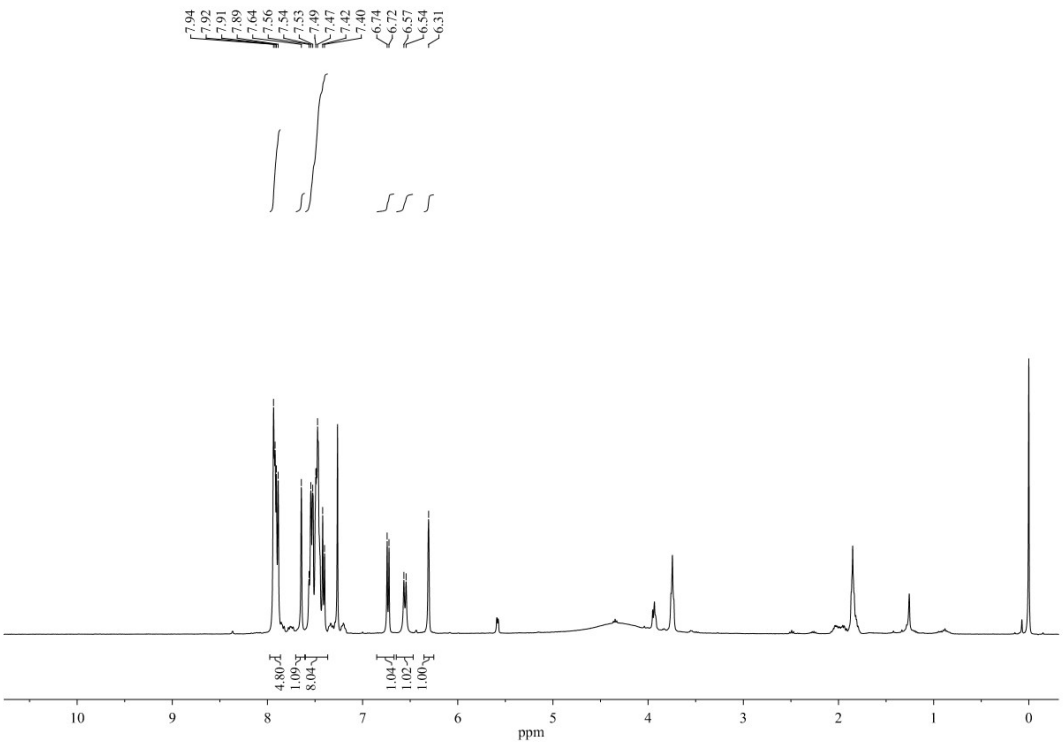

Figure 10S The ^{1}H NMR of ligand **L4 (trace THF included)**

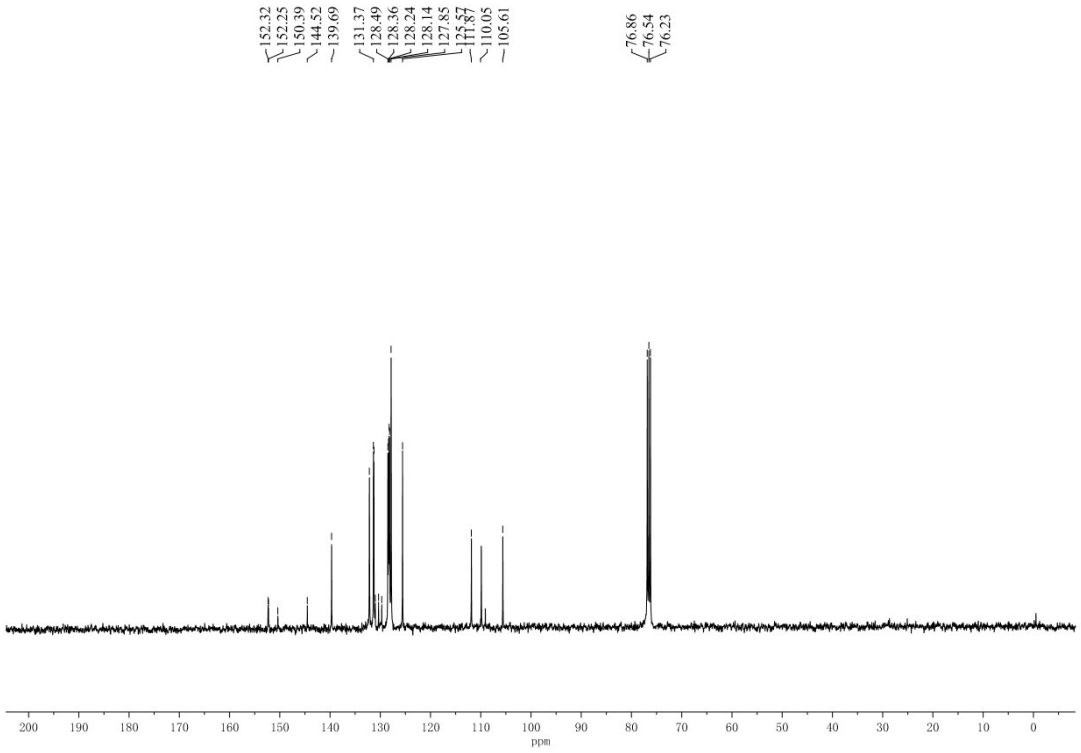

Figure 11S The ^{13}C NMR of ligand **L4**

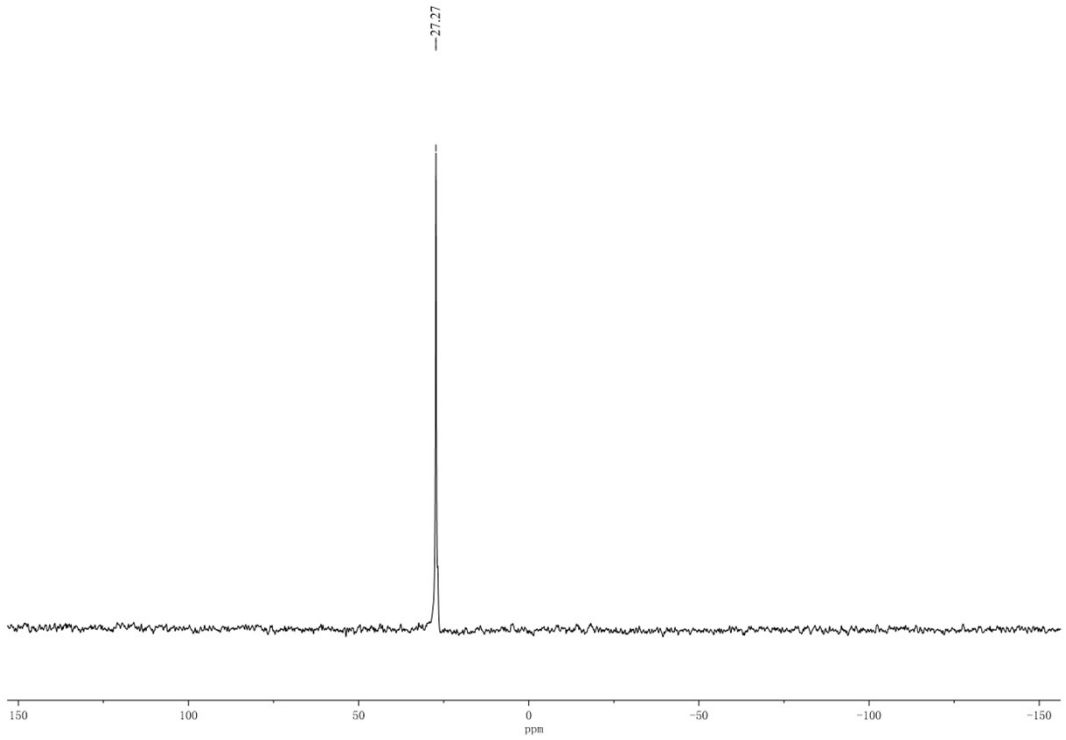

Figure 12S The ^{31}P NMR of ligand **L4**

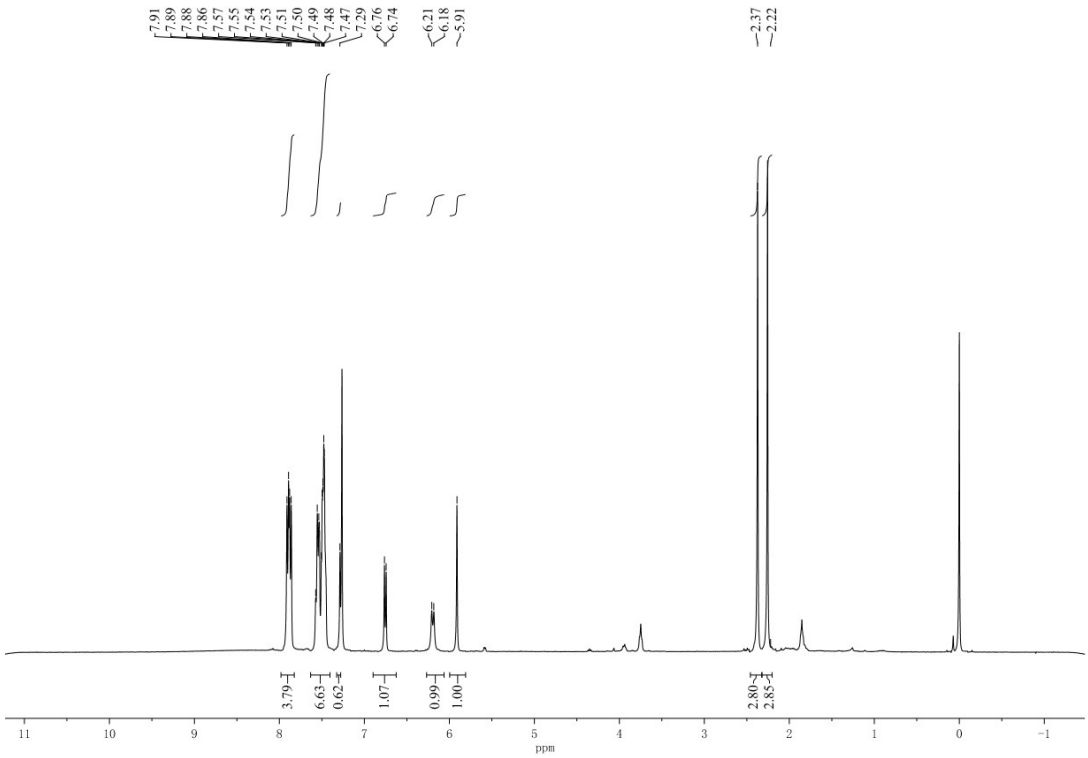

Figure 13S The ^{1}H NMR of ligand **L5 (trace THF included)**

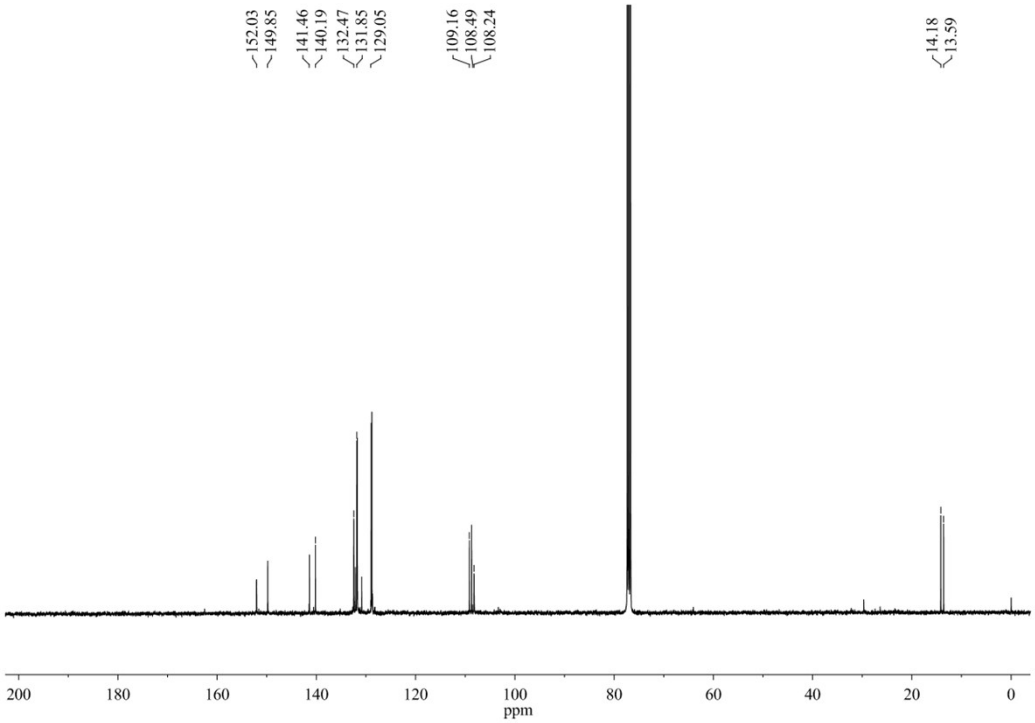

Figure 14S The ^{13}C NMR of ligand **L5**

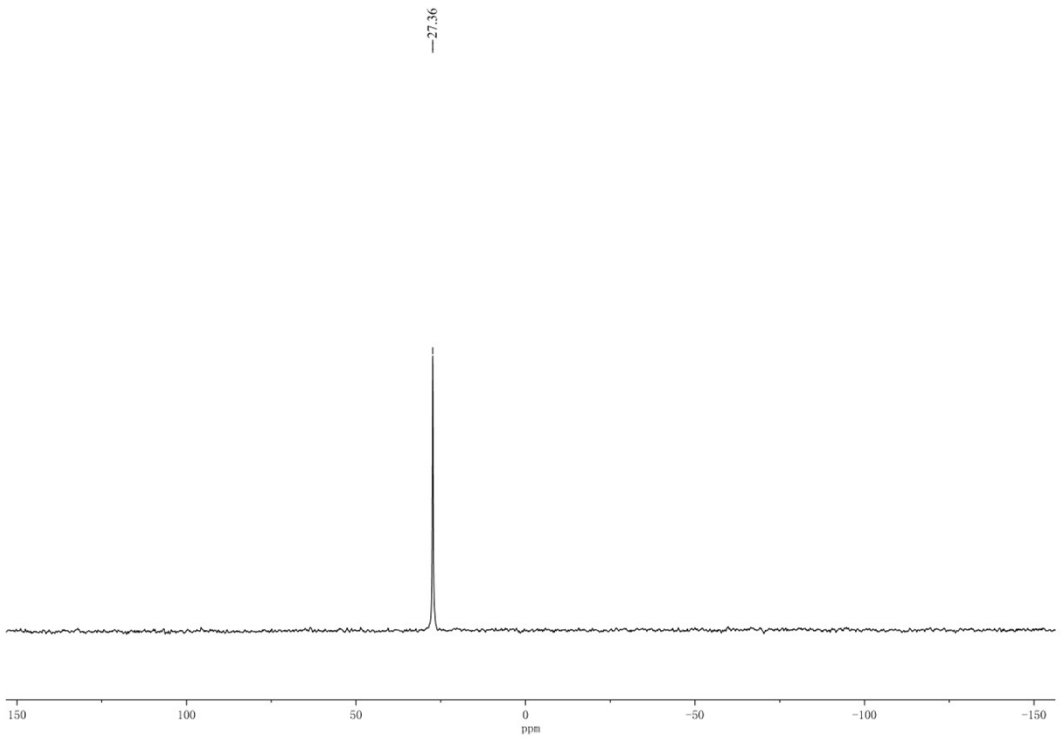

Figure 15S The ^{31}P NMR of ligand **L5**

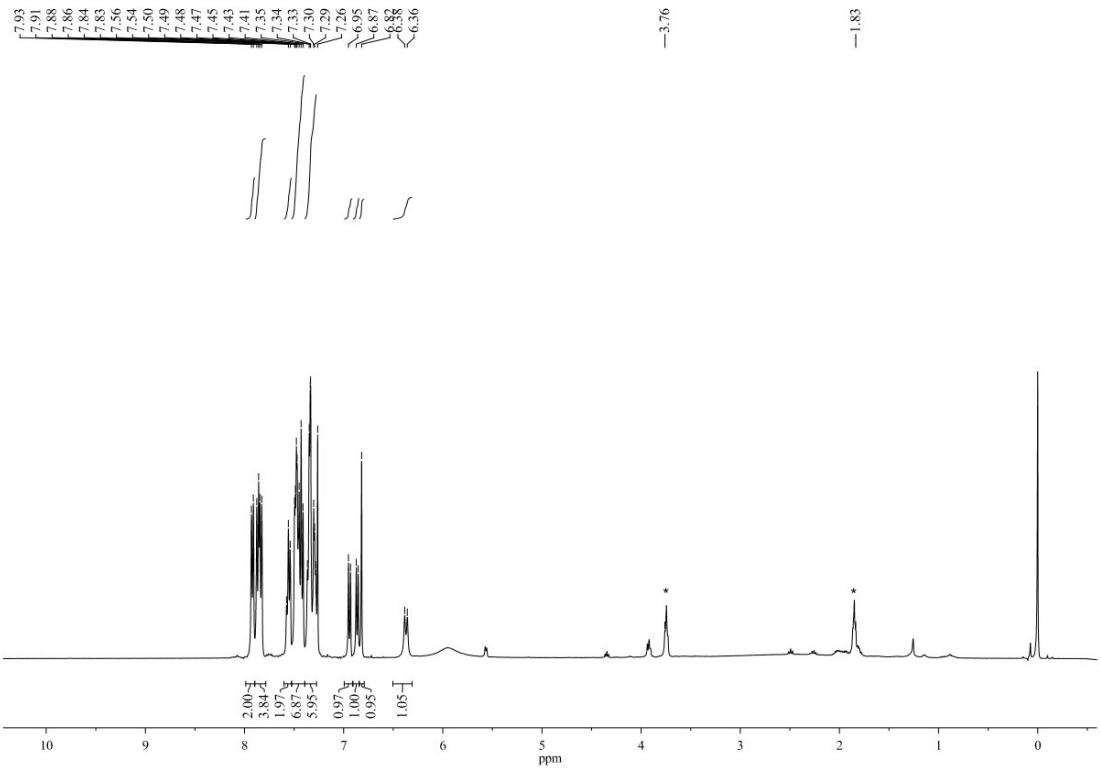

Figure 16S The ^{1}H NMR of ligand **L6 (THF included)**

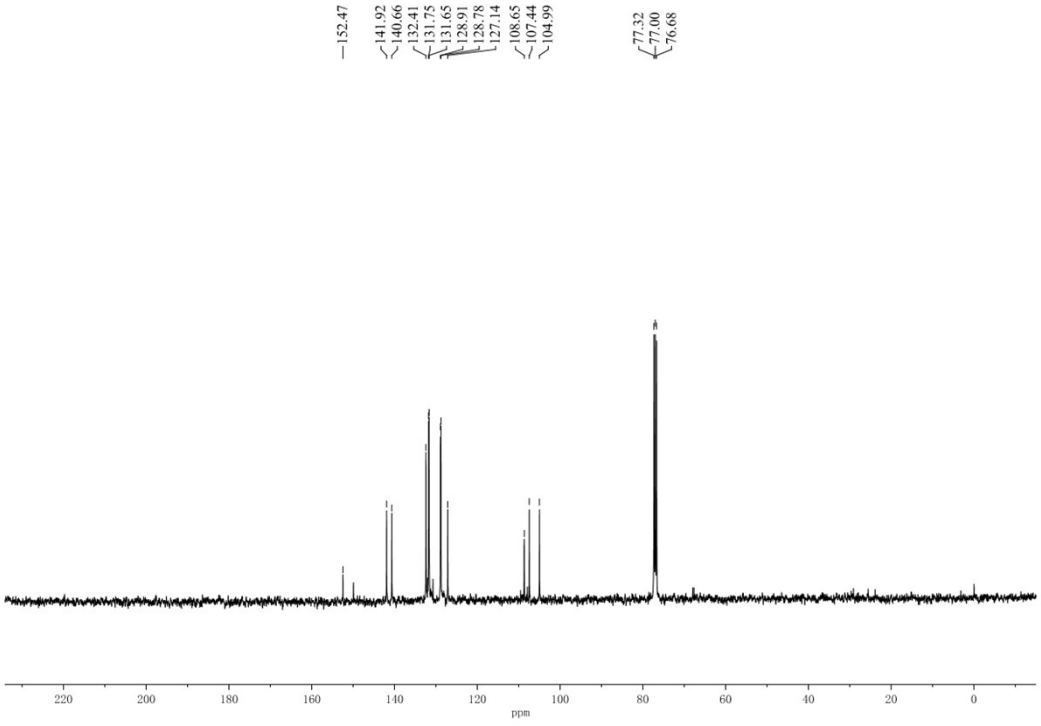

Figure 17S The ^{13}C NMR of ligand **L6**

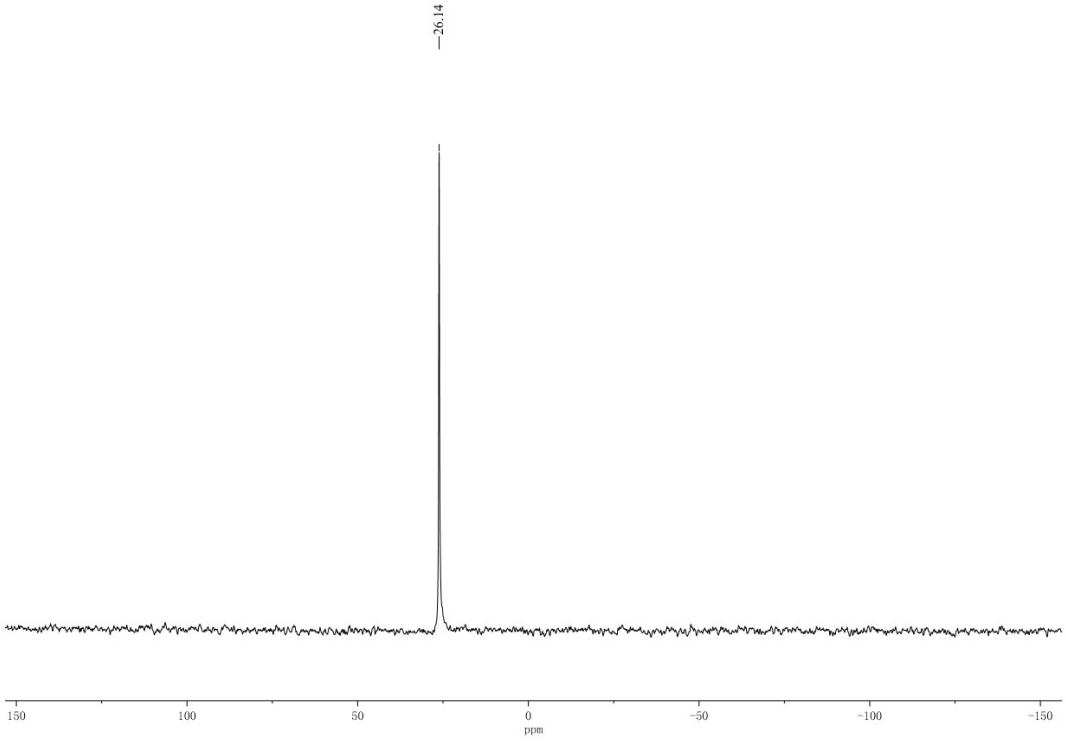

Figure 18S The ^{31}P NMR of ligand **L6**

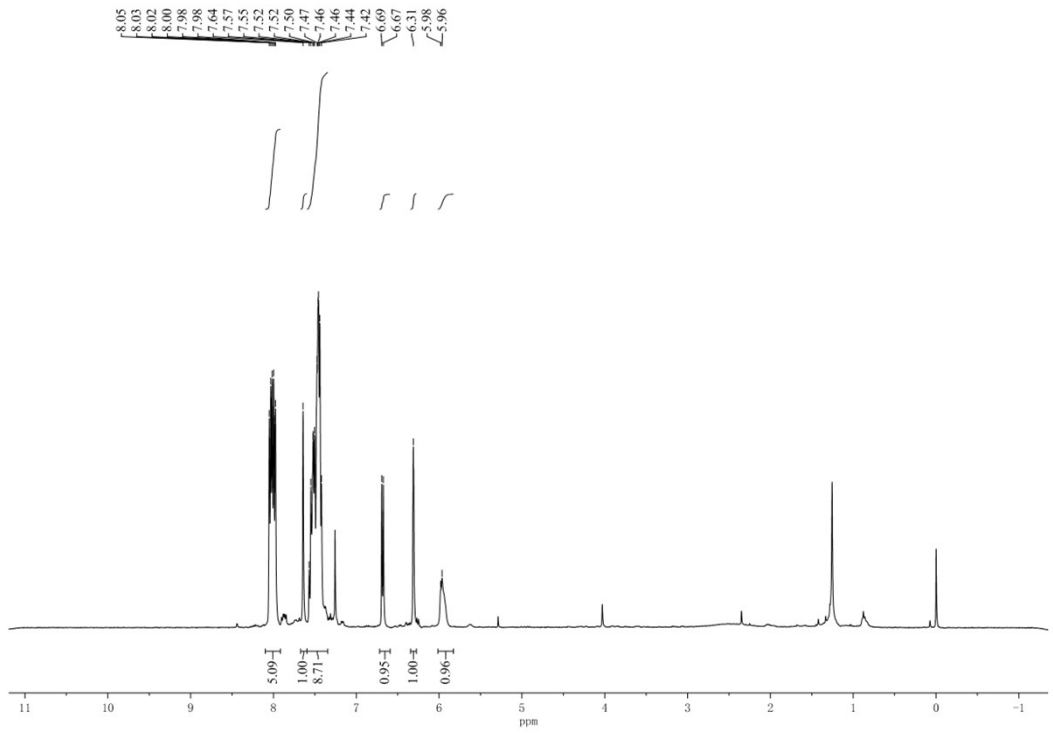

Figure 19S The ^{1}H NMR of ligand **L7**

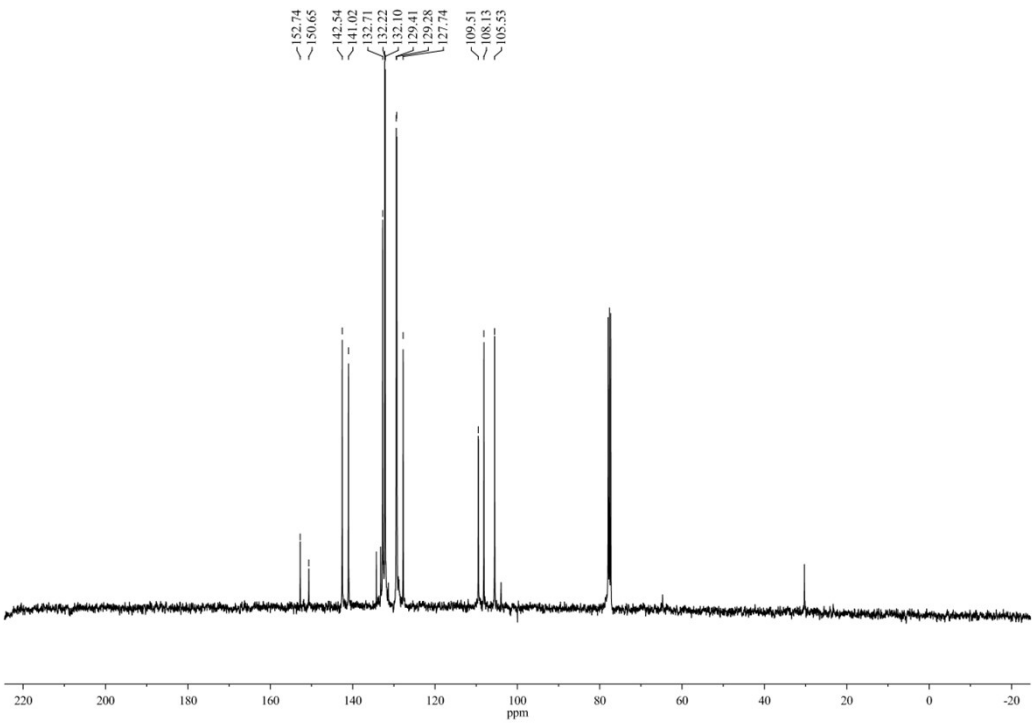

Figure 20S The ^{13}C NMR of ligand **L7**

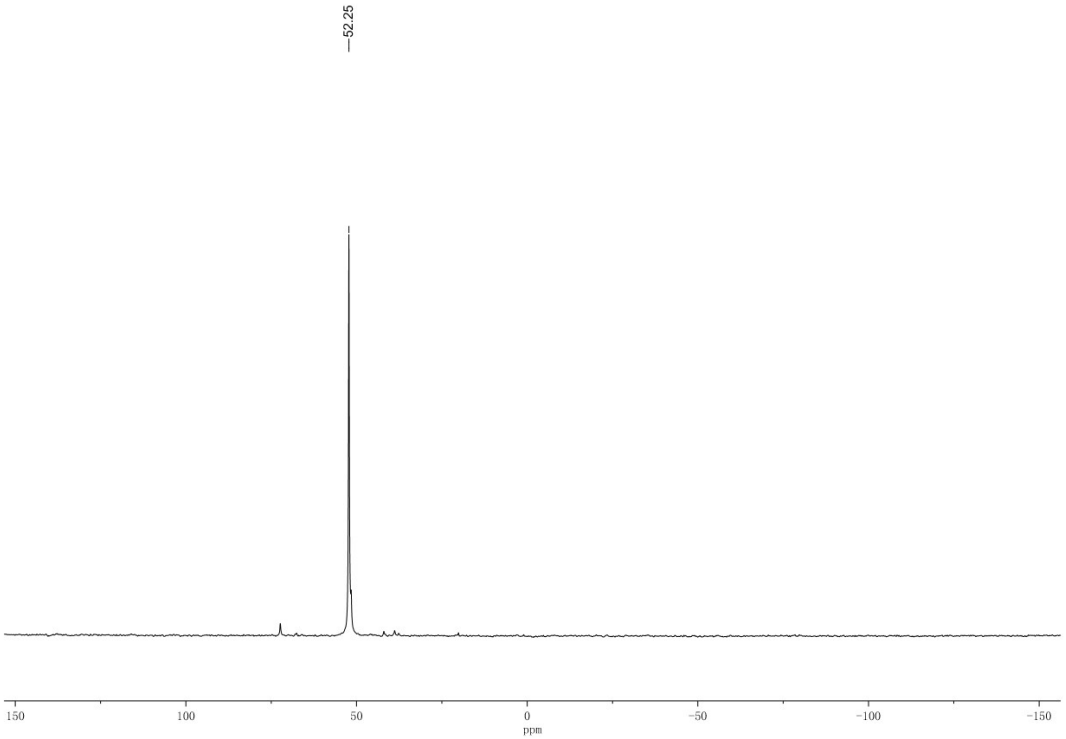

Figure 21S The ^{31}P NMR of ligand **L7**

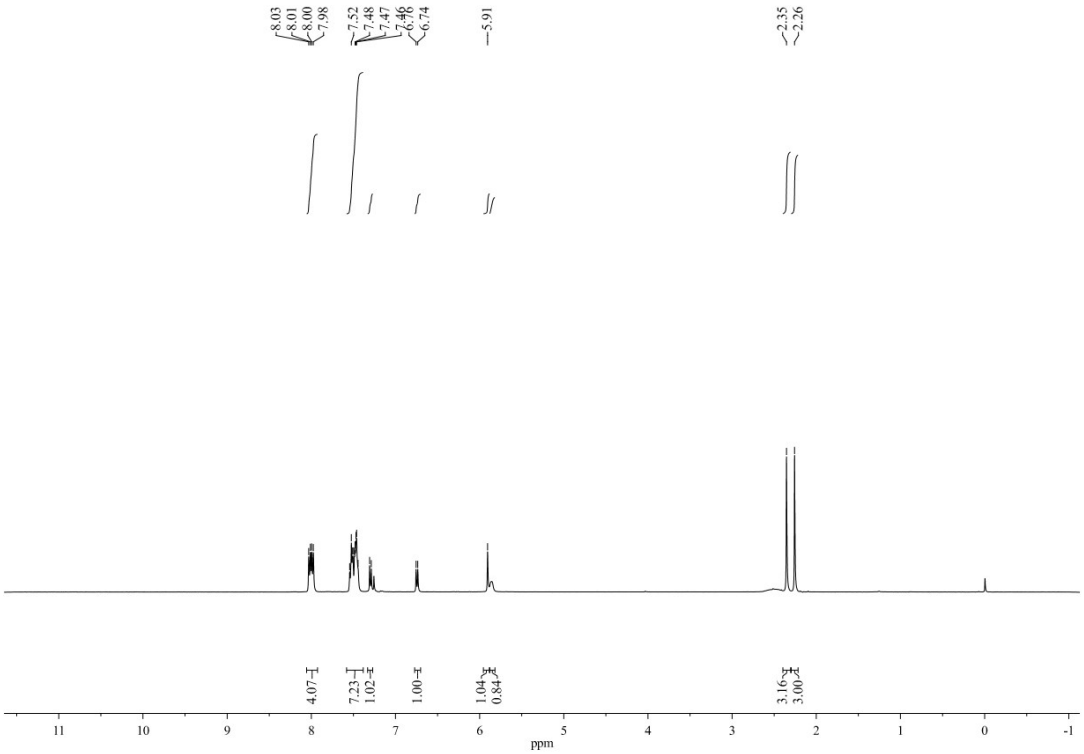

Figure 22S The ^{1}H NMR of ligand **L8**

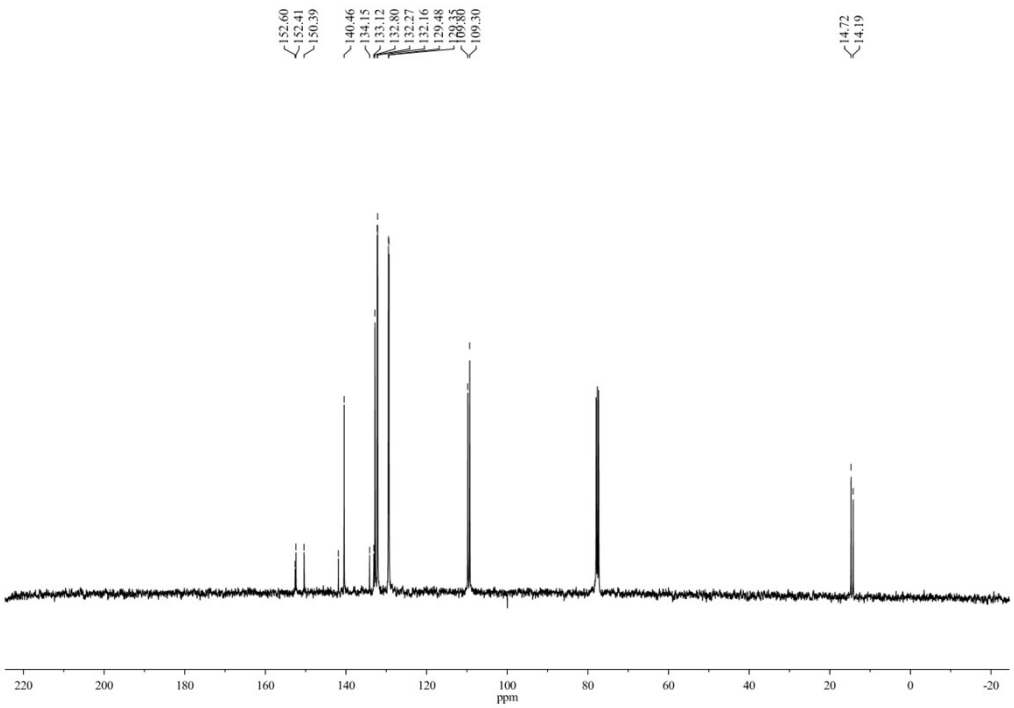

Figure 23S The ^{13}C NMR of ligand **L8**

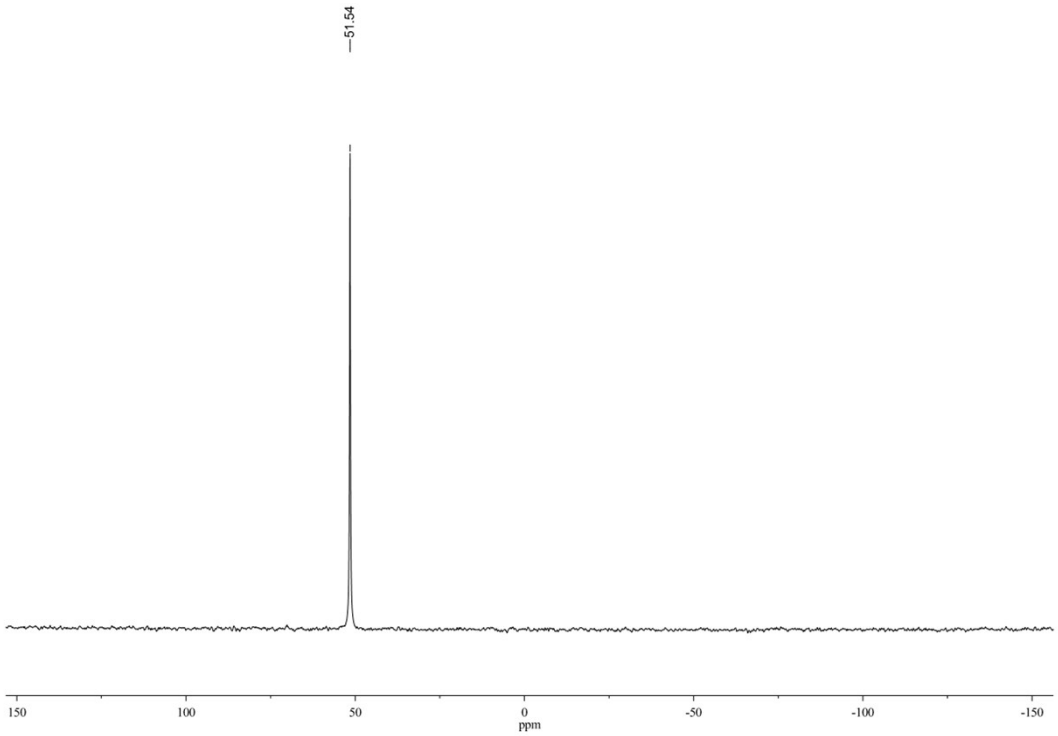

Figure 24S The ^{31}P NMR of ligand **L8**

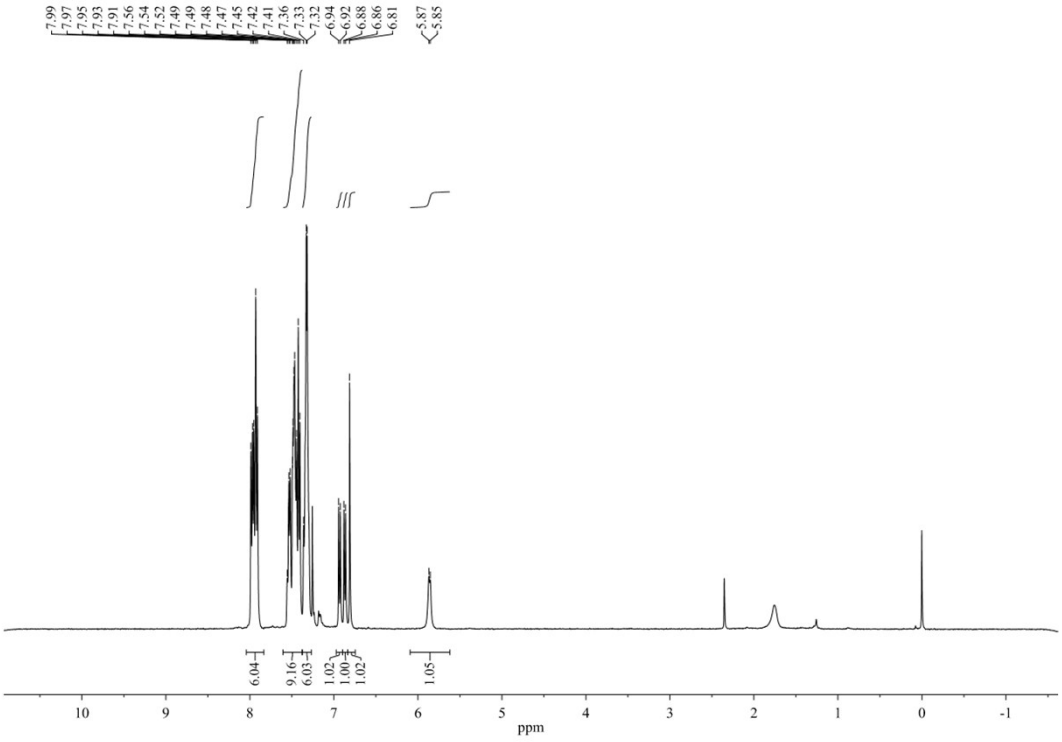

Figure 25S The ^{1}H NMR of ligand **L9**

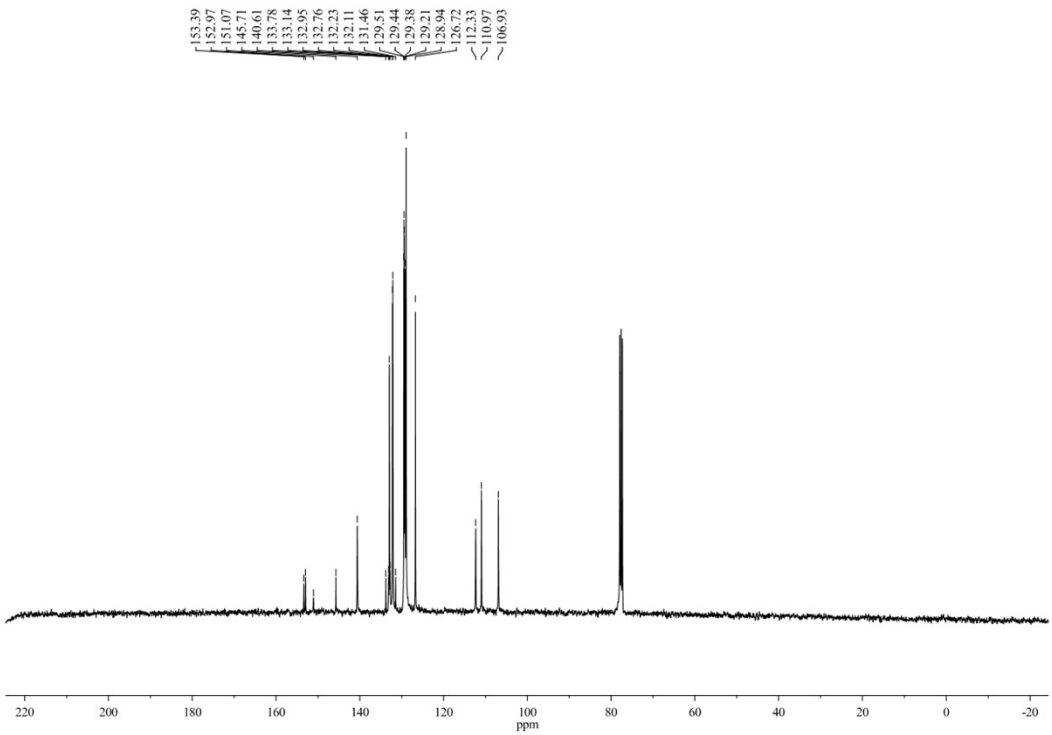

Figure 26S The ^{13}C NMR of ligand **L9**

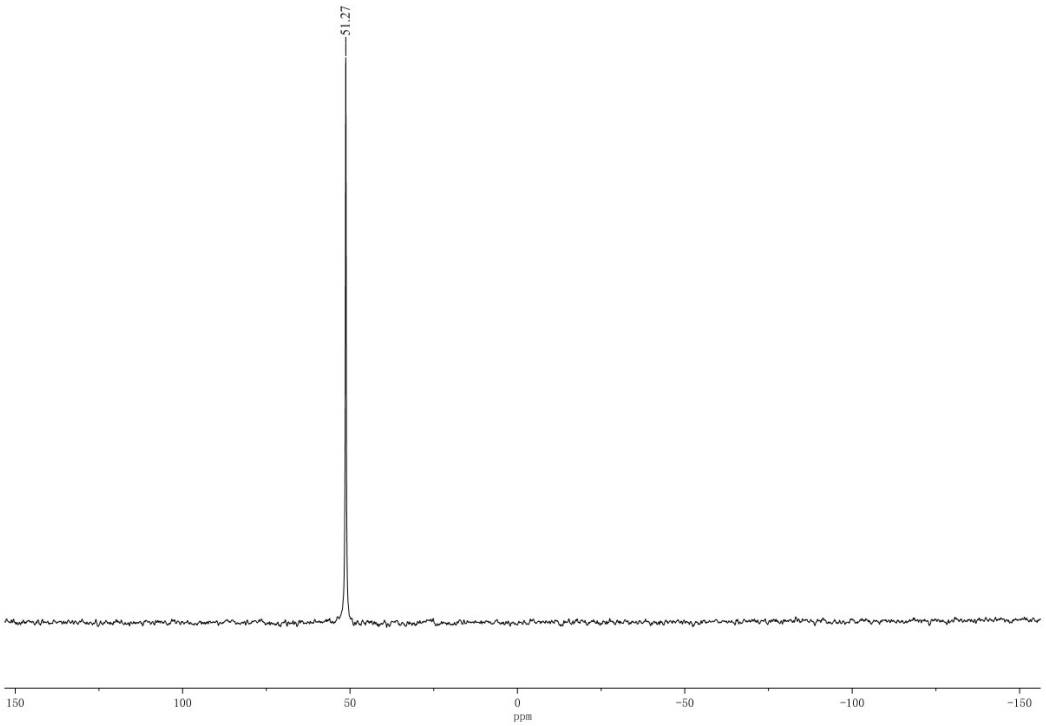

Figure 27S The ^{31}P NMR of ligand **L9**

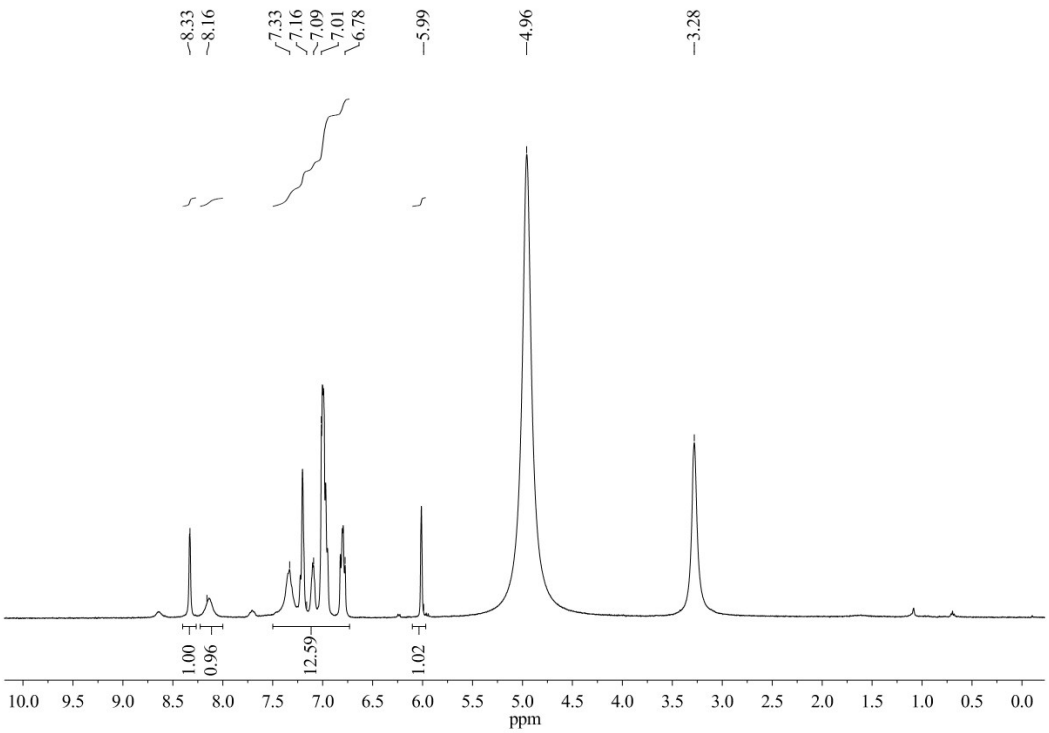

Figure 28S The ^{1}H NMR of complex **Co1**

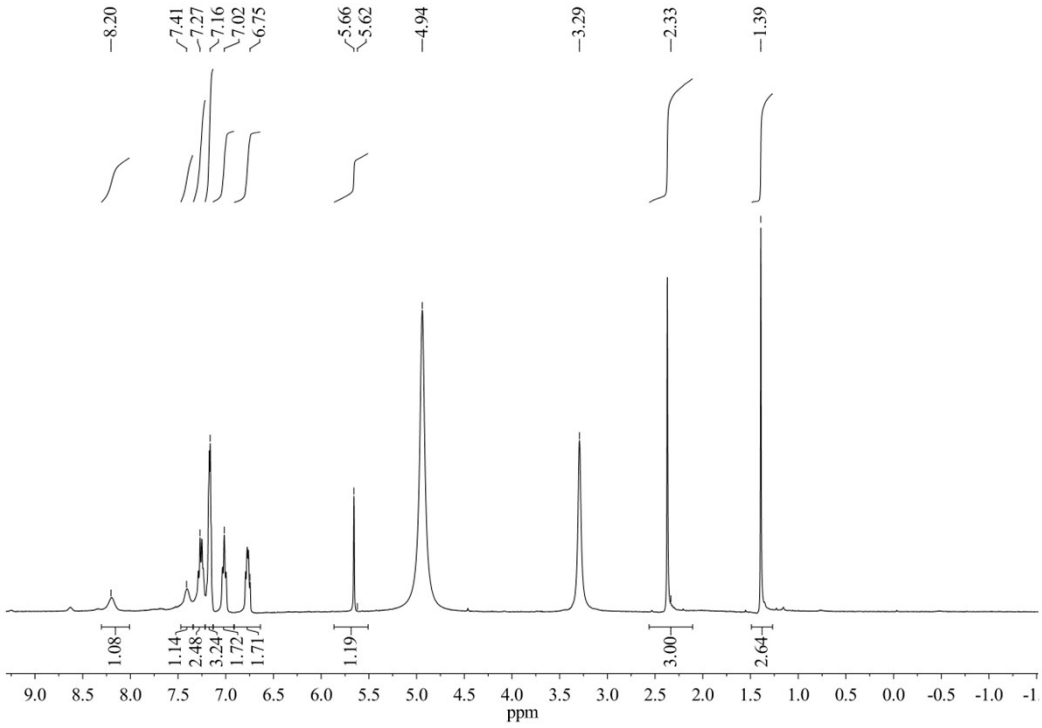

Figure 29S The ^{1}H NMR of complex **Co2**

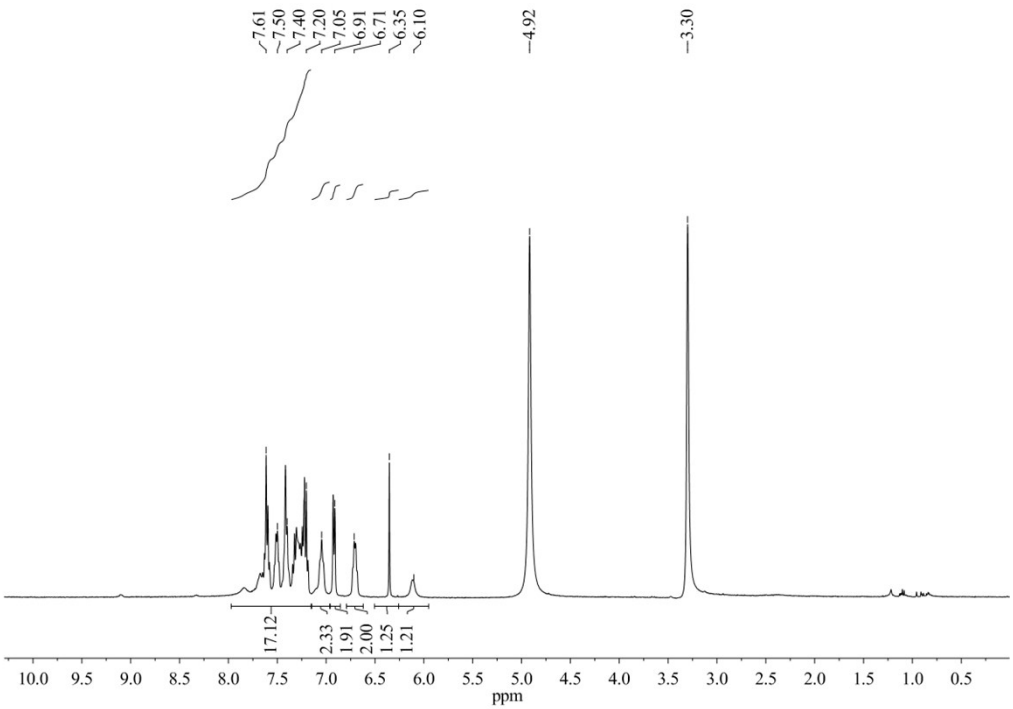

Figure 30S The ^{1}H NMR of complex **Co3**

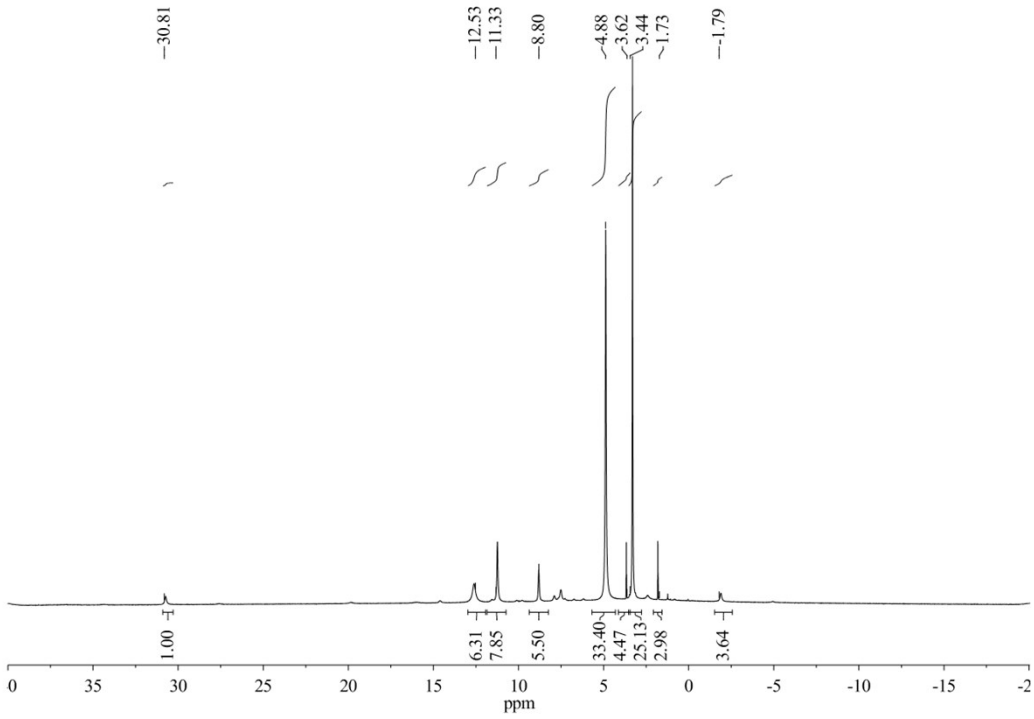

Figure 31S The ^{1}H NMR of complex **Co4**

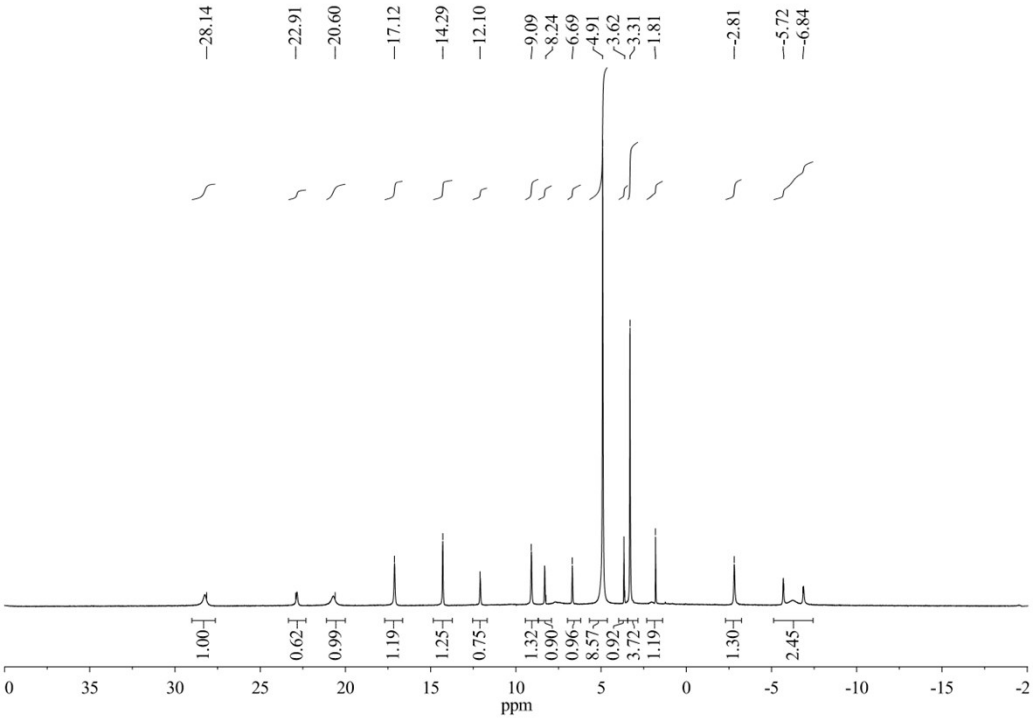

Figure 32S The ^{1}H NMR of complex **Co5**

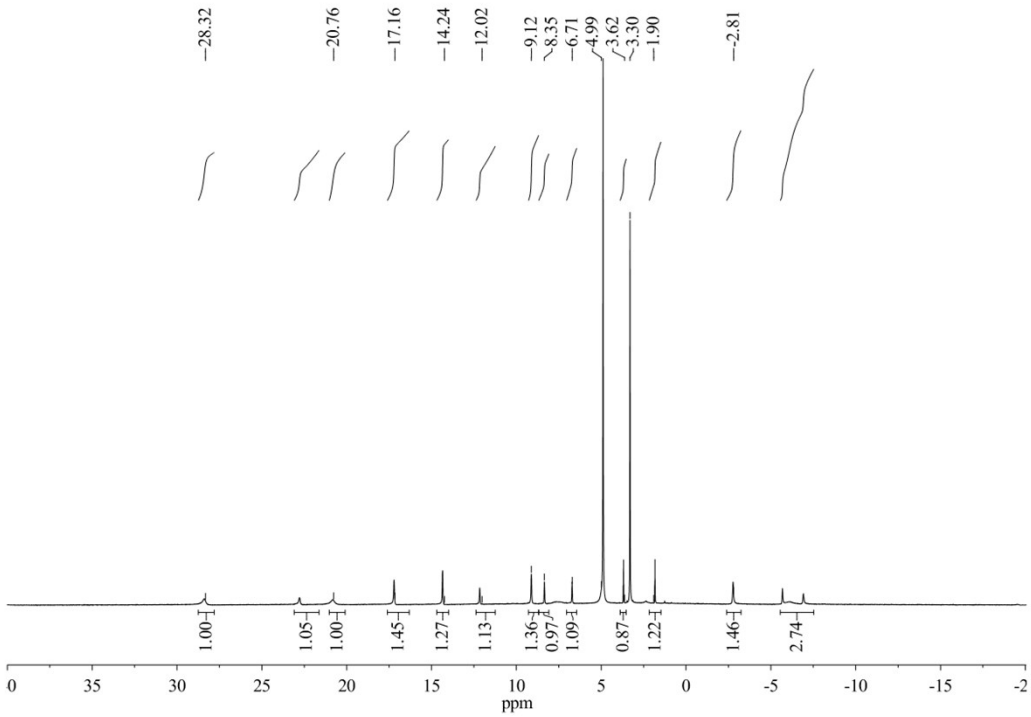

Figure 33S The ^{1}H NMR of complex **Co6**

Table S1 Crystal data and structure refinements of complexes **Co2, Co4, Co4-DMF** and **Co7**

	Co2	**Co4**	**Co4+DMF**	**Co7**
Formula	$C_{48}H_{52}Cl_4Co_2N_8OP_2$	$C_{20}H_{17}Cl_2CoN_4OP$	$C_{20}H_{17}Cl_2CoN_4OP$, C_3H_7NO	$C_{44}H_{42}Cl_4Co_2N_8P_2S_2$
Molecular weight	1078.48	490.18	563.27	1068.58
Crystal system	tetragonal	monoclinic	triclinic	monoclinic
Space group	P212121	P 1 21/n 1	P 1	P 1 21/n 1
a (Å)	15.231(2)	9.8667(9)	7.881(2)	9.4650(10)
b (Å)	15.231	12.3170(11)	8.610(2)	15.7090(16)
c (Å)	20.271(3)	17.6260(15)	10.582(3)	16.2919(16)
α (deg)	90.00	90.00	101.612(3)	90.00
β (deg)	90.00	100.7850(10)	110.925(2)	106.147(2)
γ (deg)	90.00	90.00	103.559(2)	90.00
V (Å^3)	4702.4(9)	2104.2(3)	619.0(3)	2326.8(4)
Z	4	4	1	2
D_{calcd} (Mg/m^3)	1.523	1.547	1.511	1.525
Absorp coeff (mm^{-1})	1.048	1.165	1.005	1.144
F(000)	2835	996	289	1092
Crystal size (mm)	0.15×0.15×0.15	0.2×0.2×0.2	0.2×0.2×0.2	0.2×0.2×0.2
θ Range (deg)	1.67 to 27.42	2.03 to 25.01	2.56 to 27.49	2.59 to 27.14
No. of reflns collected	27124	10489	4268	13806
No. of indep reflns	10405 (R_{int}= 0.0390)	3703 (R_{int}= 0.0244)	3528 (R_{int}= 0.0279)	5257 (R_{int}= 0.0488)
No. of data/ restraint/params	10405/0/596	3703/0/262	3528/0/281	5257/0/282
GOF on F^2	1.033	1.084	1.093	0.995
R_1(I>2sigma(I))	0.0450	0.0258	0.0309	0.0412
wR_2	0.1213	0.0686	0.0822	0.0931

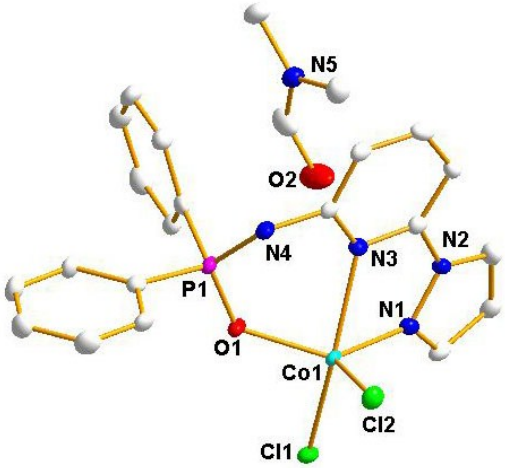

Figure 34S Drawing of complex **Co4-DMF**, Hydrogen atoms are omitted for clarity. Selected bond length (Å) and angles (°): Co1-Cl1 2.3184(10), Co1-Cl2 2.3110(11), Co1-N1 2.057(3), Co1-N3 2.302(3), Co1-O1 1.996(3), Cl2-Co1-Cl1 105.05(4), N1 Co1-Cl1-94.21(9), N1-Co1 Cl2 113.90(10), N1-Co1-N3 73.20(12), N3-Co1-Cl1 161.96(8), N3-Co1-Cl2 92.05(9), O1-Co1-Cl1 95.71(7), O1-Co1-Cl2 108.79(9), O1-Co1-N1 131.68(13), O1-Co1-N3 83.90(11).

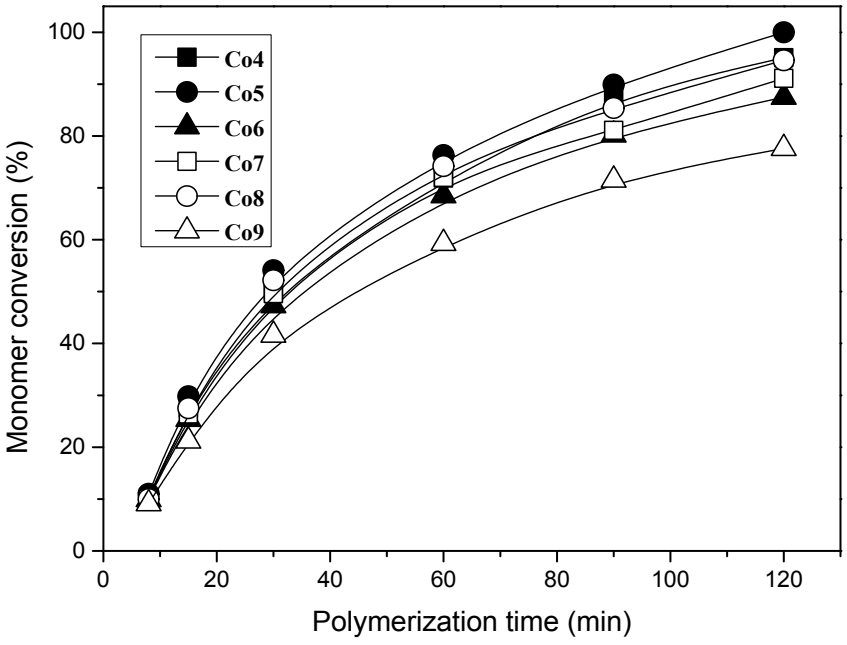

Figure 35S The polymer yield against polymerization time for **Co4-Co9**

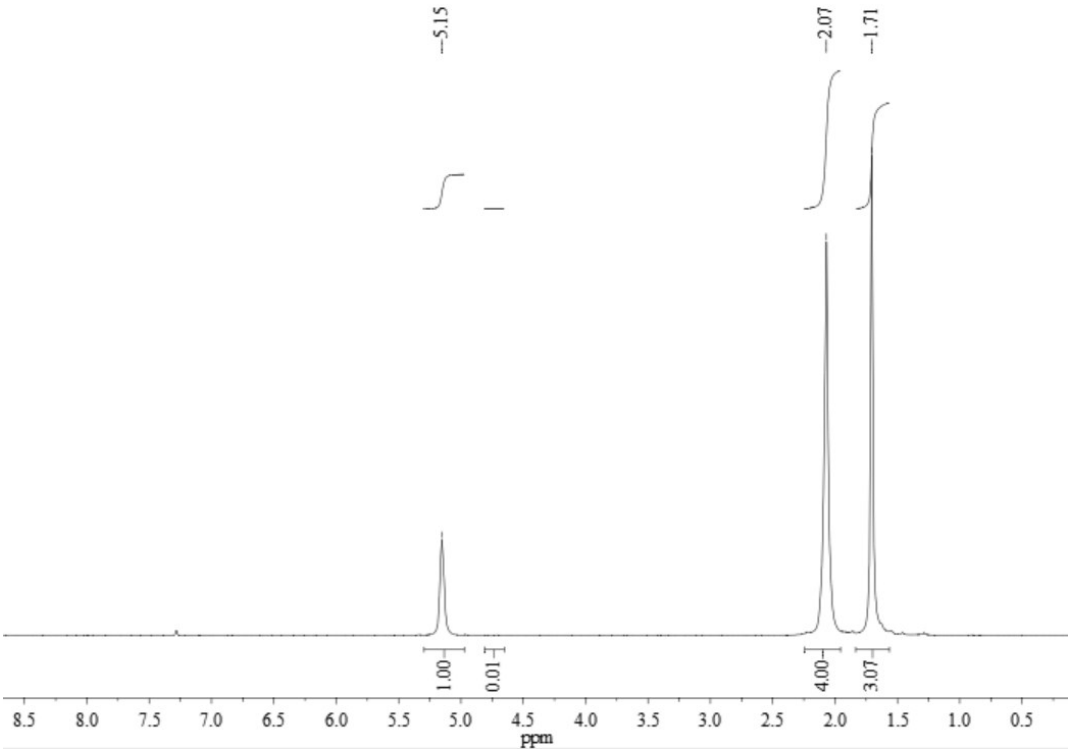

Figure 36S The [1]HNMR of polyisoprene obtained from **Co1**/$AlEt_2Cl$ (run 3, table 1)

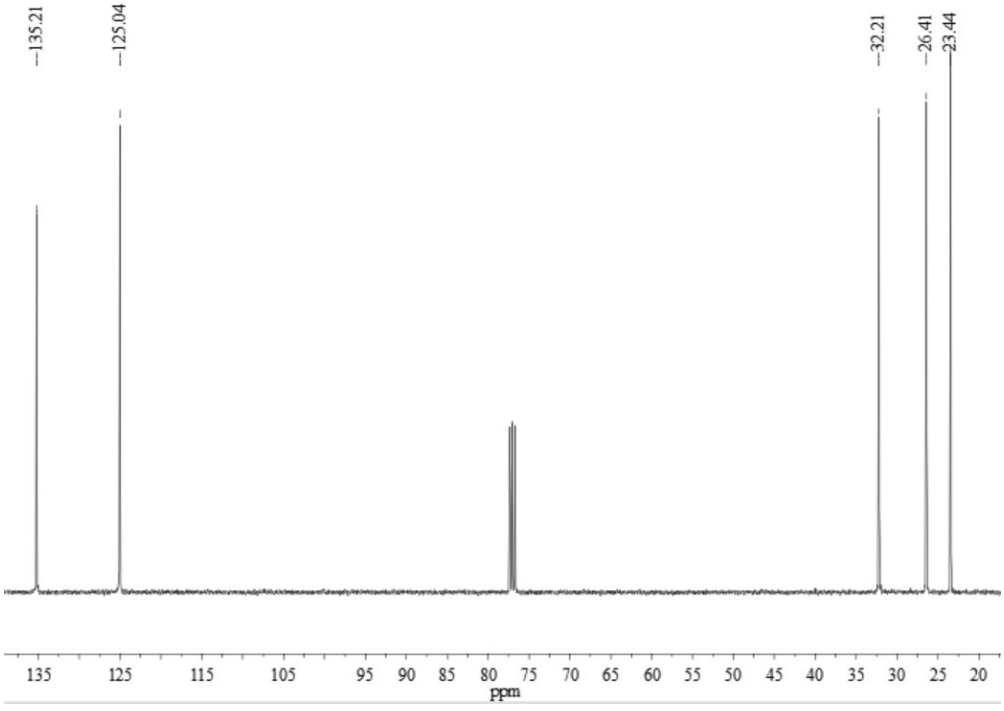

Figure 37S The [13]CNMR of polyisoprene obtained from **Co1**/$AlEt_2Cl$ (run 3, table 1)