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Photo- and Electro-luminescence of cuprous complexes with Sterically Demanding and Hole Transmitting Diimine Ligands

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Experimental section

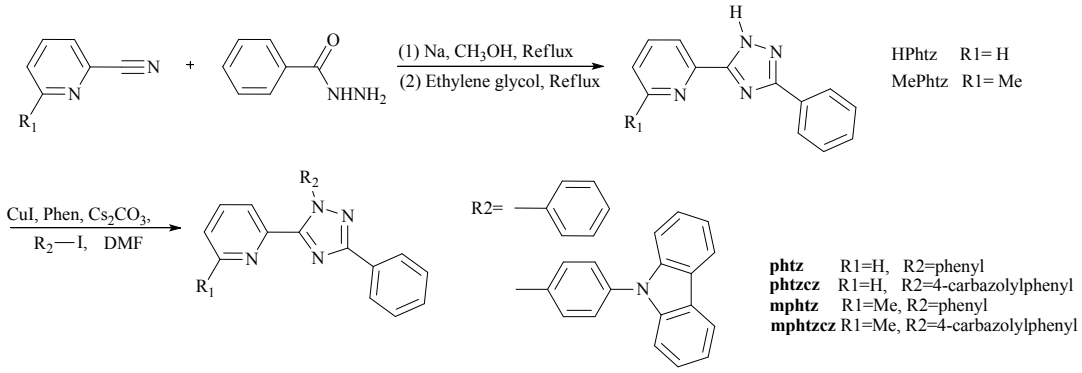


Fig. S1 The simplified synthetic route for functionalized diimine ligands.

Table S1 Crystallographic data and Structural Refinements for **1**–**4**

	1	**2**	**3**	**4**
Formula	$C_{55}H_{42}BC_{l0}CuF_4N_4OP_2$	$C_{68}H_{52}BCuF_4N_5O_{1.5}P_2$	$C_{57}H_{46}BCl_2CuF_4N_4OP_2$	$C_{68}H_{51}BCuF_4N_5OP_2$
M_r (g mol^{-1})	987.22	1175.44	1086.17	1166.43
Space group	*C*2/c	$P2_1$/c	*P*–1	$P2_1$/c
a/Å	20.846(5)	22.9549(10)	11.2117(6)	12.527(4)
b/Å	17.594(5)	21.3720(15)	11.6277(8)	20.392(6)
c/Å	29.817(7)	24.8432(9)	20.2682(12)	22.743(7)
α/°	90	90	92.924(5)	90
β/°	90.721(5)	111.602(4)	90.208(5)	101.445(5)
γ/°	90	90	102.716(5)	90
V/Å^3	10935(5)	11331.8(10)	2573.8(3)	5695(3)
Z	8	8	2	4
D_c/g cm^{-3}	1.199	1.378	1.402	1.361
μ/mm^{-1}	0.511	1.605	2.634	0.503
F(000)	4064	4856	1116	2408
total reflns	39802	43988	16781	39413
unique reflns	9524	20725	9426	10003
R_{int}	0.0332	0.0663	0.0375	0.0442
GOF	1.162	0.865	0.998	1.050
R_1 [a][$I > 2\sigma(I)$]	0.0946	0.0652	0.0757	0.0852
wR_2 [b](all data)	0.3088	0.1956	0.2241	0.2470
CCDC	1034650	1034651	1034652	1034653

[a] $R_1 = \sum(F_o - F_c) / \sum F_o$; [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table S2 Selected bond lengths (Å) and angles (°) for **1**–**4**.

1			
Cu(1)–N(4)	2.127(4)	Cu(1)–P(2)	2.2706(14)
Cu(1)–N(3)	2.156(4)	Cu(1)–P(3)	2.2967(15)
N(4)–Cu(1)–N(3)	79.27(16)	N(4)–Cu(1)–P(3)	110.32(13)
N(4)–Cu(1) –P(2)	119.13(13)	N(3)–Cu(1)–P(3)	106.36(12)
N(3)–Cu(1)–P(2)	122.64(12)	P(2)–Cu(1)–P(3)	114.12(6)
2			
Cu(1)–N(4)	2.067(3)	Cu(2)–N(8)	2.082(3)
Cu(1)–N(3)	2.110(3)	Cu(2)–N(7)	2.080(3)
Cu(1)–P(2)	2.2453(11)	Cu(2)–P(4)	2.2235(11)
Cu(1)–P(3)	2.2872(11)	Cu(2)–P(5)	2.2969(11)
N(4)–Cu(1) –N(3)	79.60(11)	N(8)–Cu(2)–N(7)	79.71(12)
N(4)–Cu(1)–P(2)	118.07(10)	N(8)–Cu(2)–P(4)	122.18(10)
N(3)–Cu(1)–P(2)	120.47(9)	N(7)–Cu(2)–P(4)	127.44(9)
N(4)–Cu(1)–P(3)	109.45(9)	N(8)–Cu(2)–P(5)	100.59(9)
N(3)–Cu(1)–P(3)	110.29(9)	N(7)–Cu(2)–P(5)	105.73(9)
P(2)–Cu(1)–P(3)	114.18(4)	P(4)–Cu(2)–P(5)	114.28(4)
3			
Cu(1)–N(4)	2.093(3)	Cu(1)–P(3)	2.2463(10)
Cu(1)–N(3)	2.117(3)	Cu(1)–P(2)	2.3010(12)
N(4)–Cu(1)–N(3)	80.70(12)	N(4)–Cu(1)–P(2)	104.62(9)
N(4)–Cu(1)–P(3)	118.79(9)	N(3)–Cu(1)–P(2)	108.68(9)
N(3)–Cu(1)–P(3)	121.78(9)	P(3)–Cu(1)–P(2)	116.29(4)
4			
Cu(1)–N(3)	2.085(4)	Cu(1)–P(2)	2.2470(14)
Cu(1)–N(4)	2.118(4)	Cu(1)–P(3)	2.3148(15)
N(3)–Cu(1)–N(4)	80.62(15)	N(3)–Cu(1)–P(3)	106.64(12)
N(3)–Cu(1)–P(2)	120.44(12)	N(4)–Cu(1)–P(3)	102.28(11)
N(4)–Cu(1)–P(2)	121.71(11)	P(2)–Cu(1)–P(3)	118.27(5)

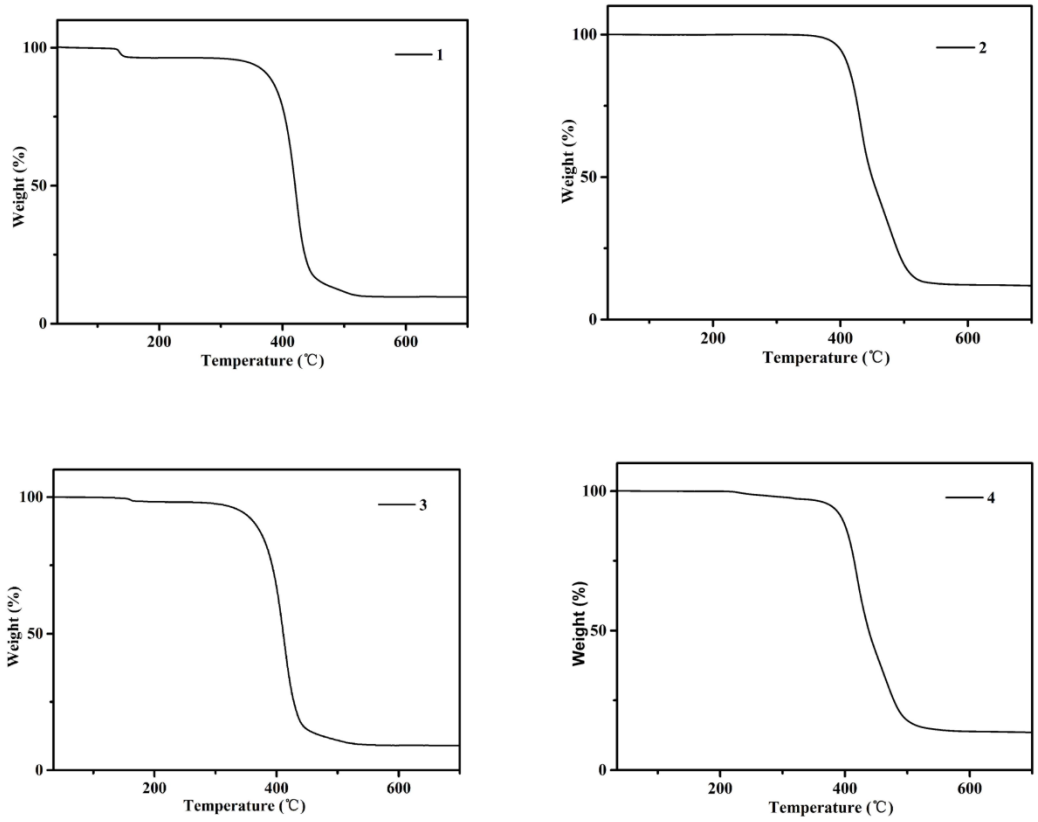


Fig. S2 TGA curves for **1**–**4.**

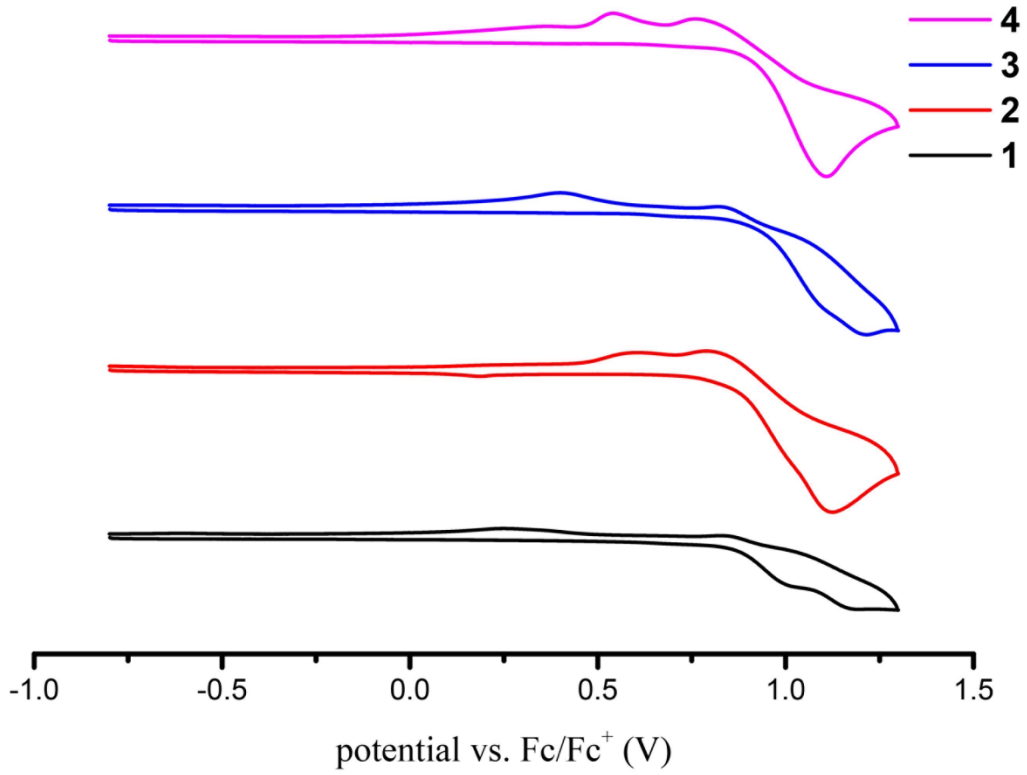


Fig. S3 Oxidation waves of **1-4** in CH_2Cl_2 solution at room temperature. Scan rate 100mVs^{-1} in 0.1M TBAP.

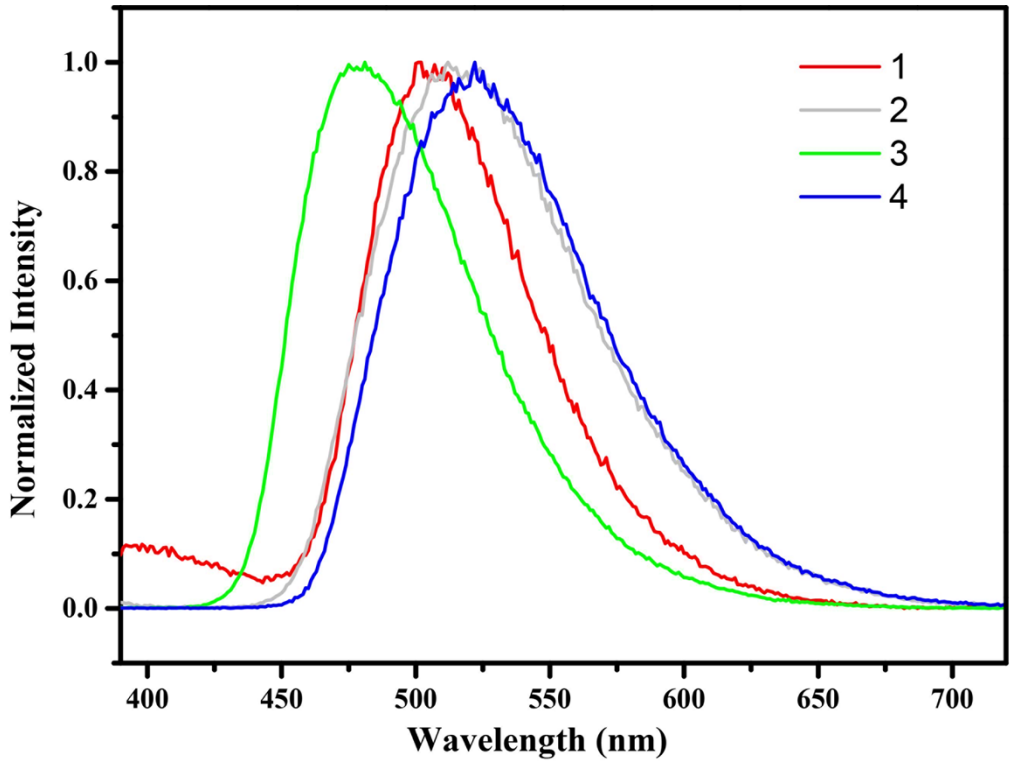


Fig. S4 Emission spectra of **1**–**4** in the solid state.

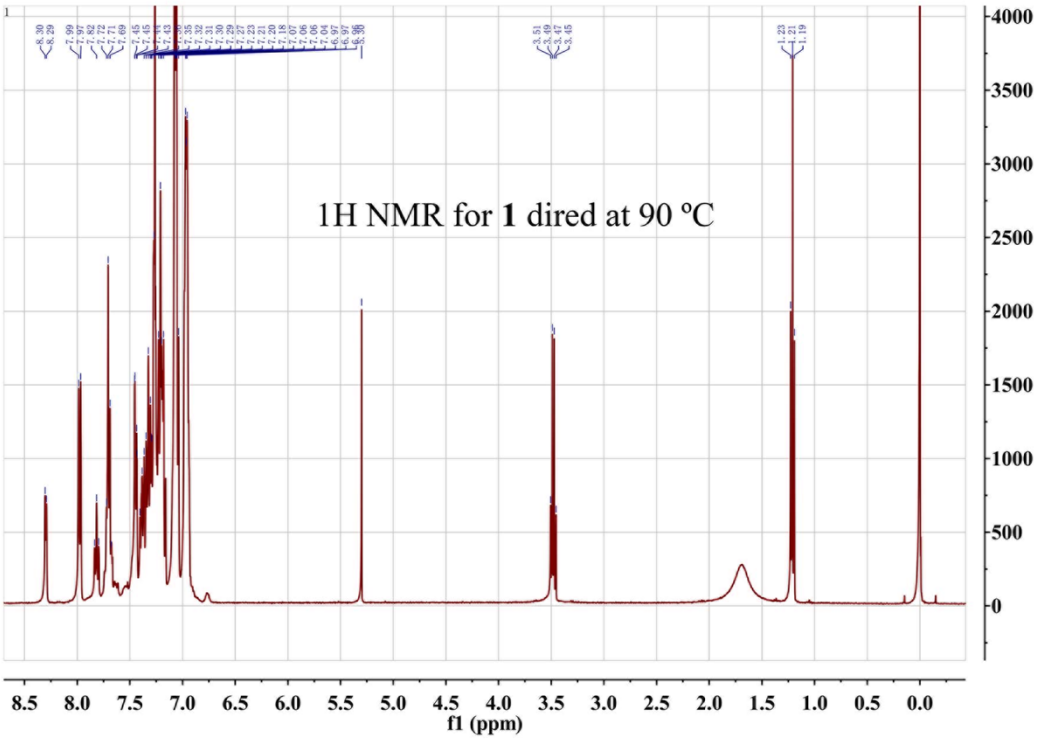
Table S3 PL properties in the crystal powder of **1**–**4**.

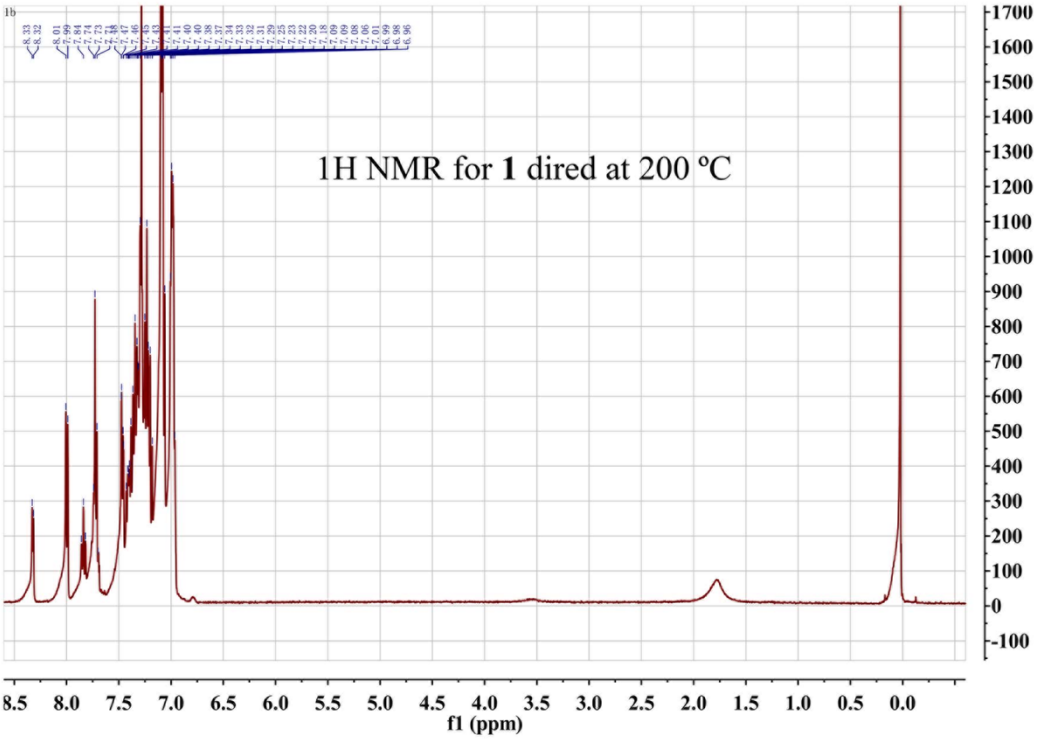
	λ_{em}(nm)	τ_{ave}(μs)	Φ(%)
1	503	25	14
2	513	12	59
3	477	26	80
4	522	17	36

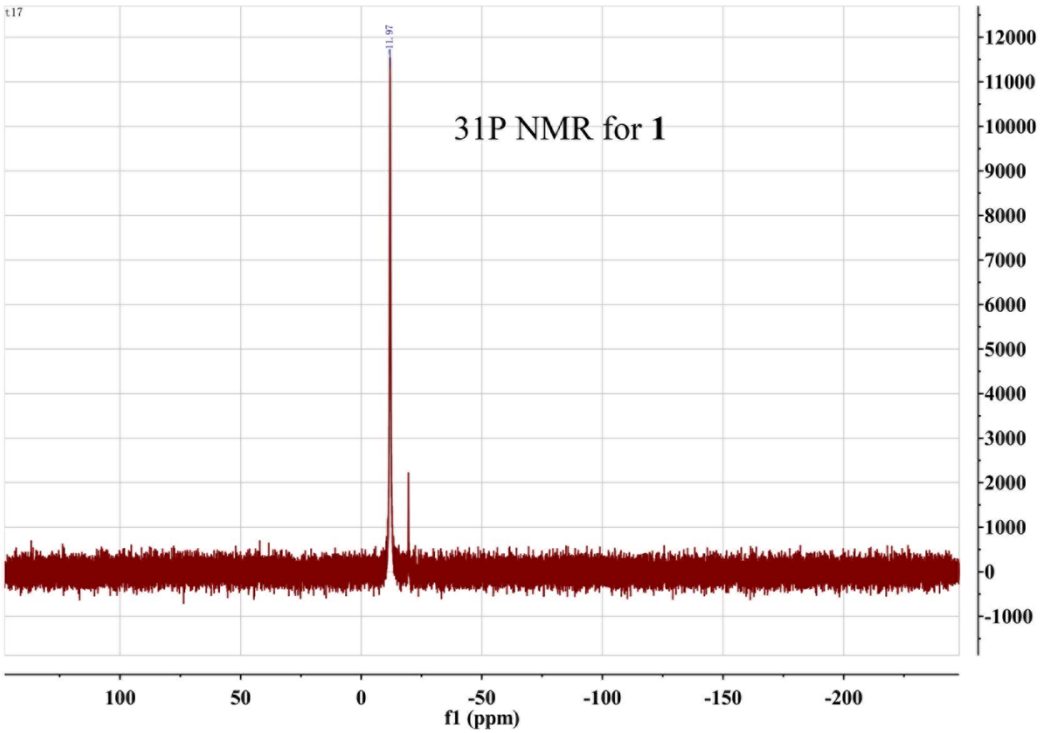
Table S4. The calculated HOMO from the oxidation curves of cyclic voltammetry, the ΔE_{gap} calculated from onset of the absorption spectra and the energy level of LUMO obtained by add the values of ΔE_{gap} to values of HOMO.

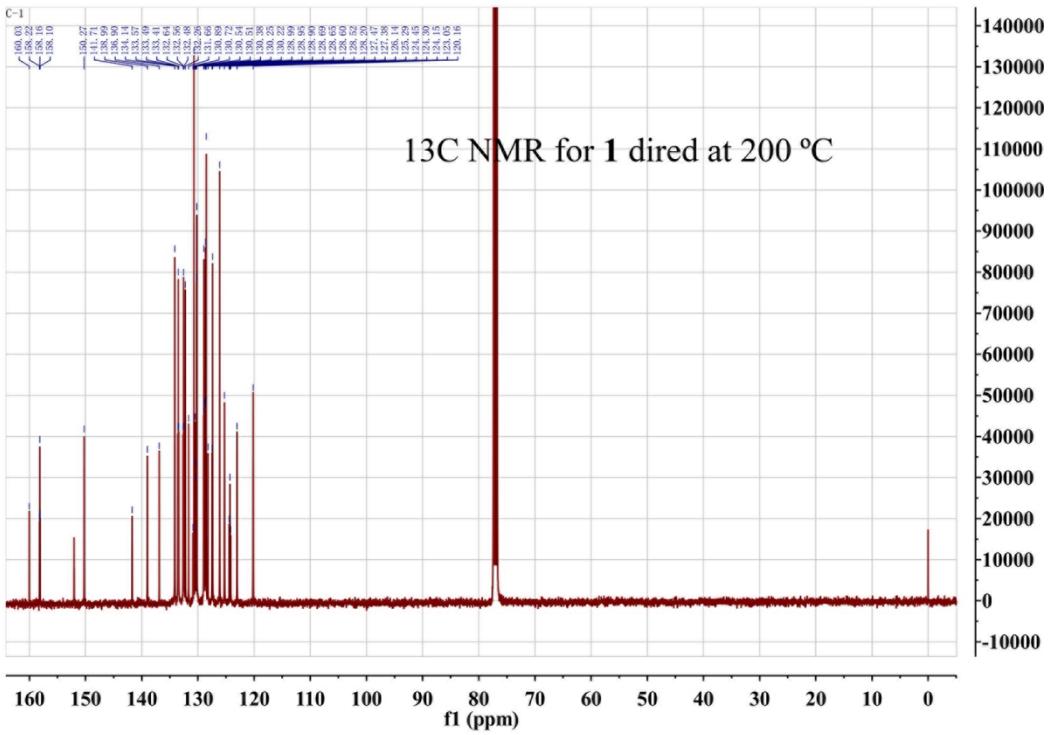
	HOMO	LUMO	ΔE_{gap}
1	-5.63ev	-2.85ev	2.78
2	-5.63ev	-2.86ev	2.77
3	-5.66ev	-2.81ev	2.85
4	-5.66ev	-2.81ev	2.85

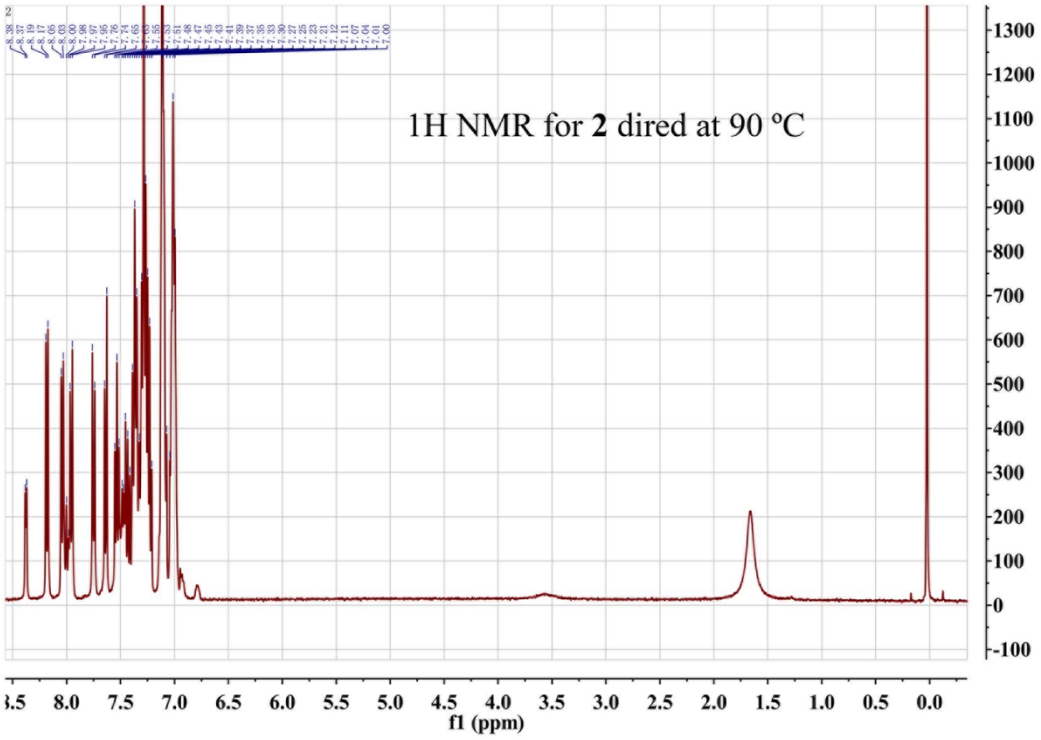
Appendix 1

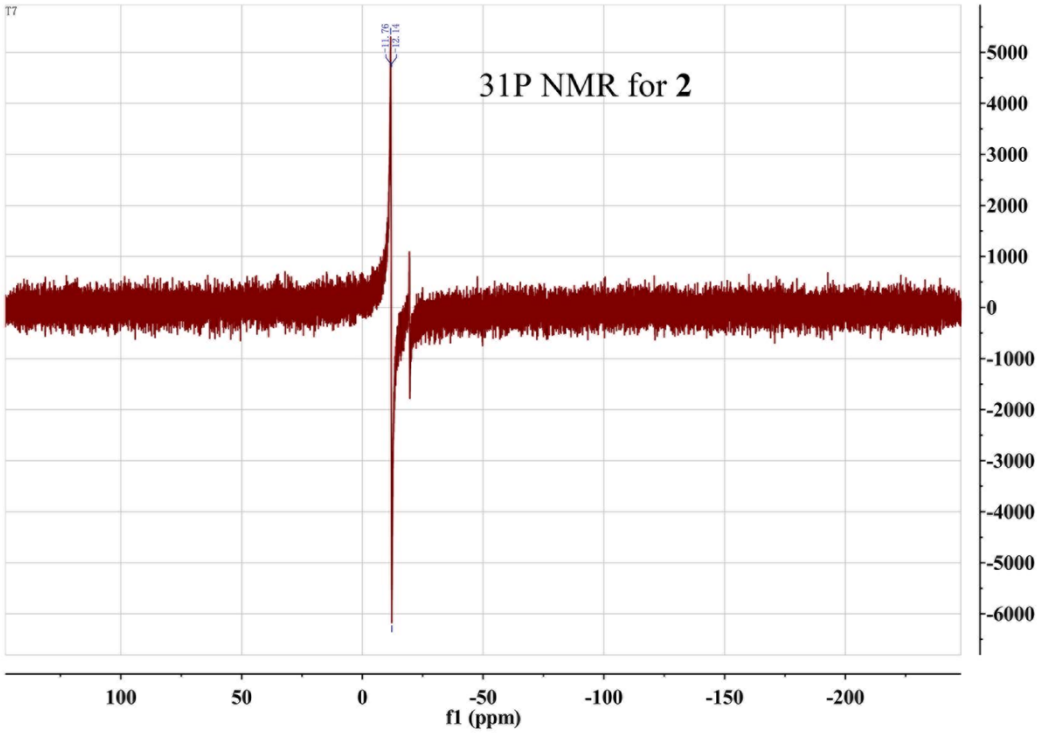

1H NMR for 1 dired at 90 ºC
f1 (ppm)

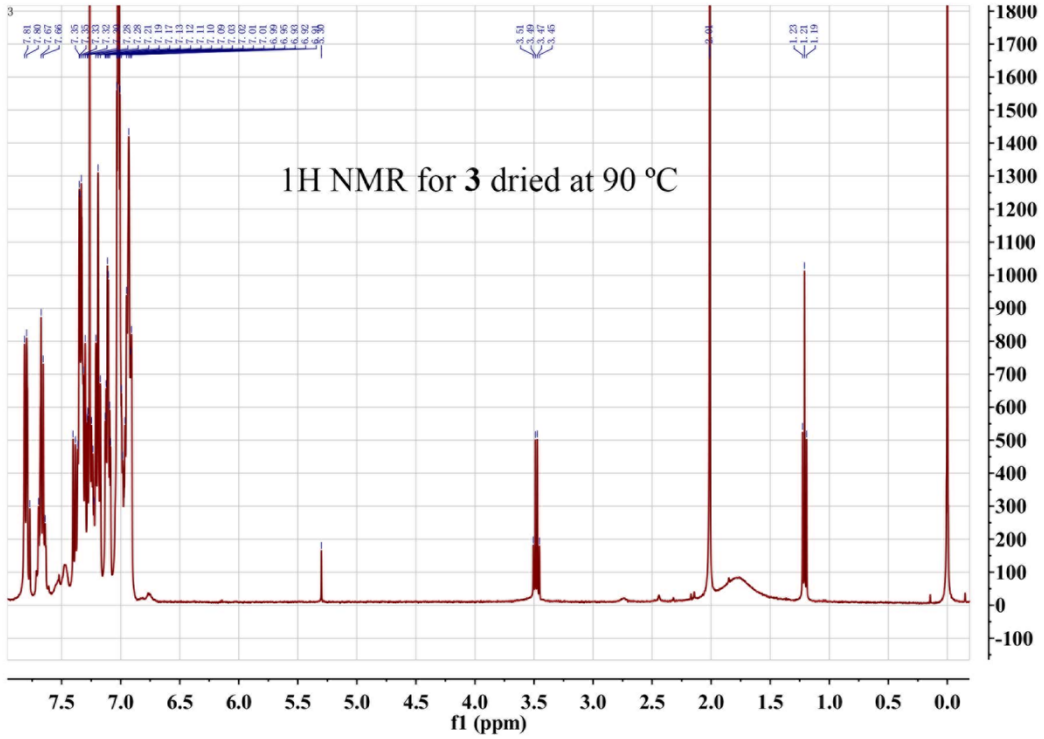

1H NMR for 1 dired at 200 ºC
f1 (ppm)

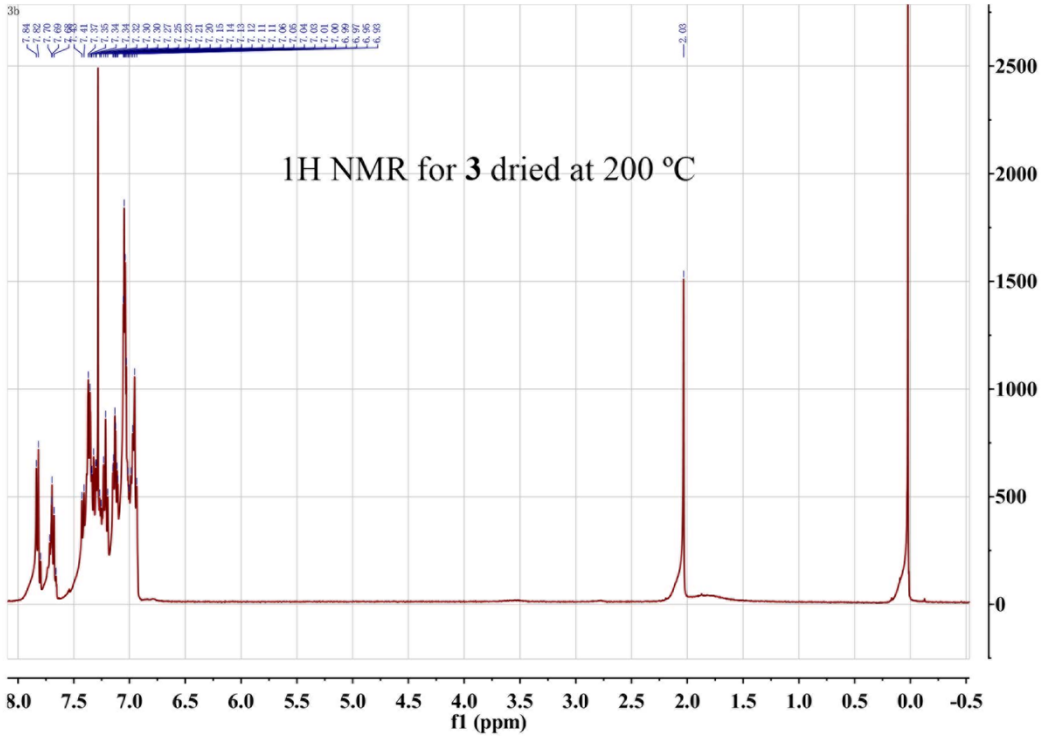

t17
11.97
31P NMR for 1
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
100
50
0
-50
-100
-150
-200
f1 (ppm)

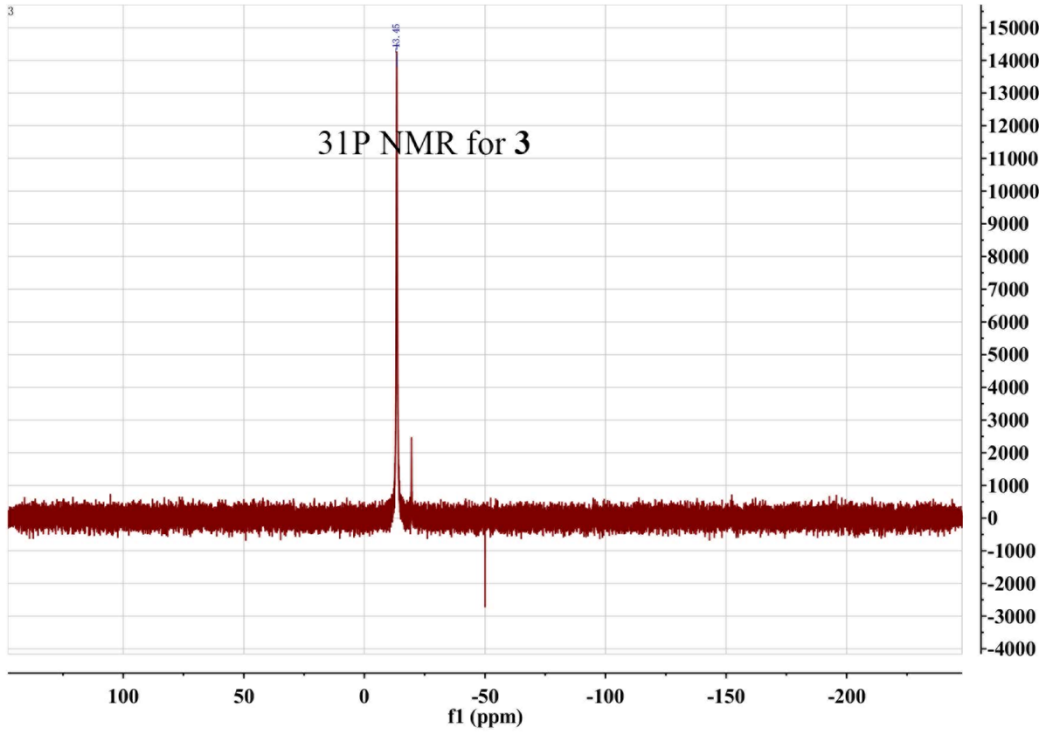

C-1
13C NMR for 1 dired at 200 ºC
140000
130000
120000
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
-10000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

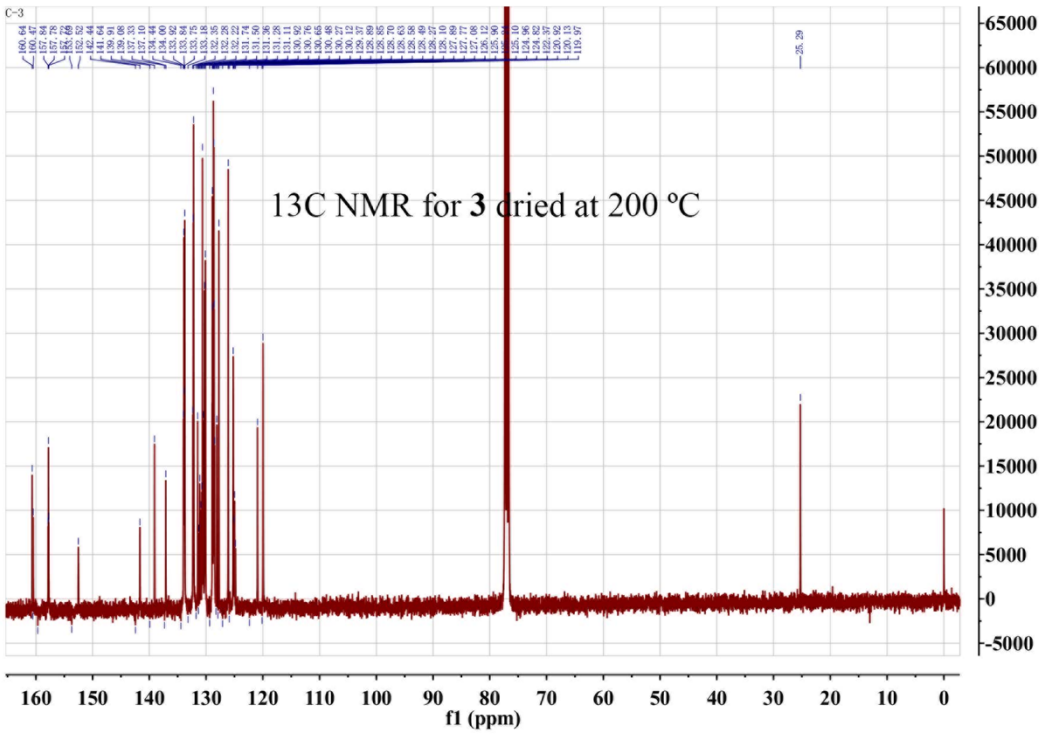

1H NMR for 2 dired at 90 ℃
f1 (ppm)

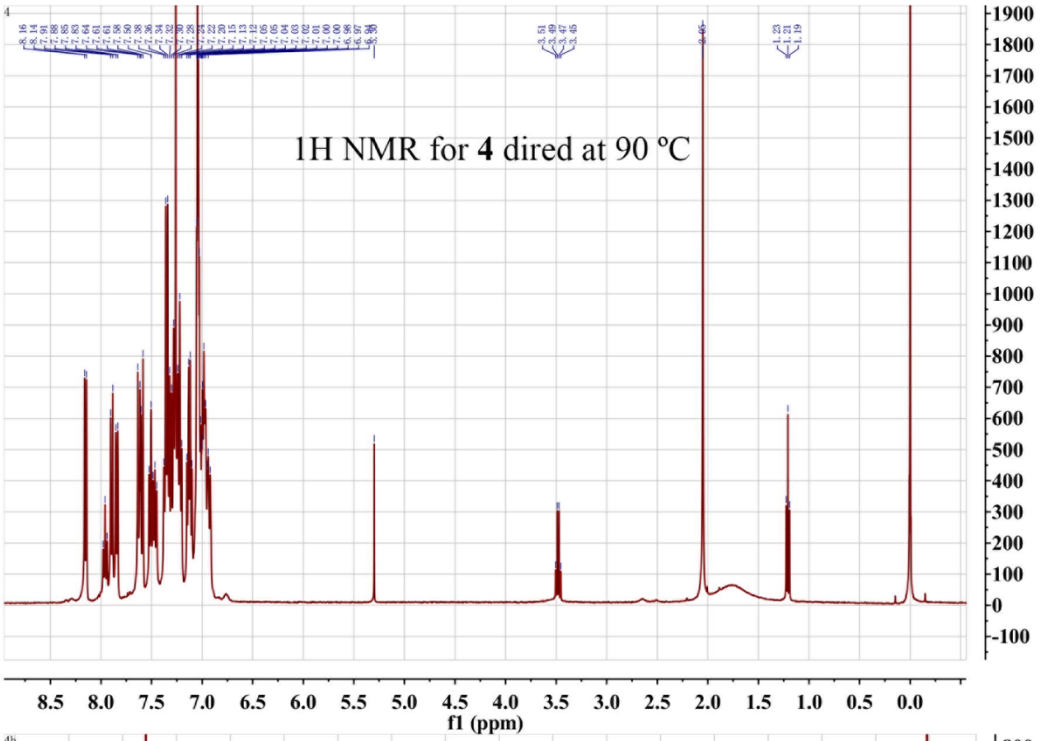

31P NMR for 2
f1 (ppm)

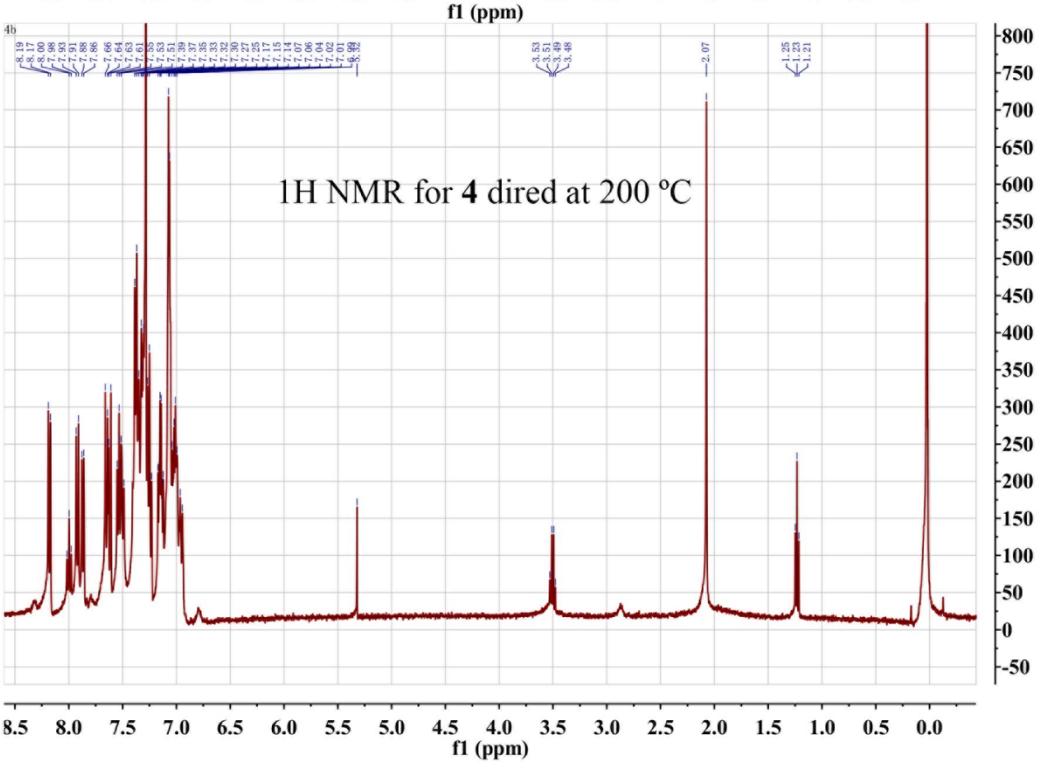

1H NMR for 3 dried at 90 ºC
f1 (ppm)

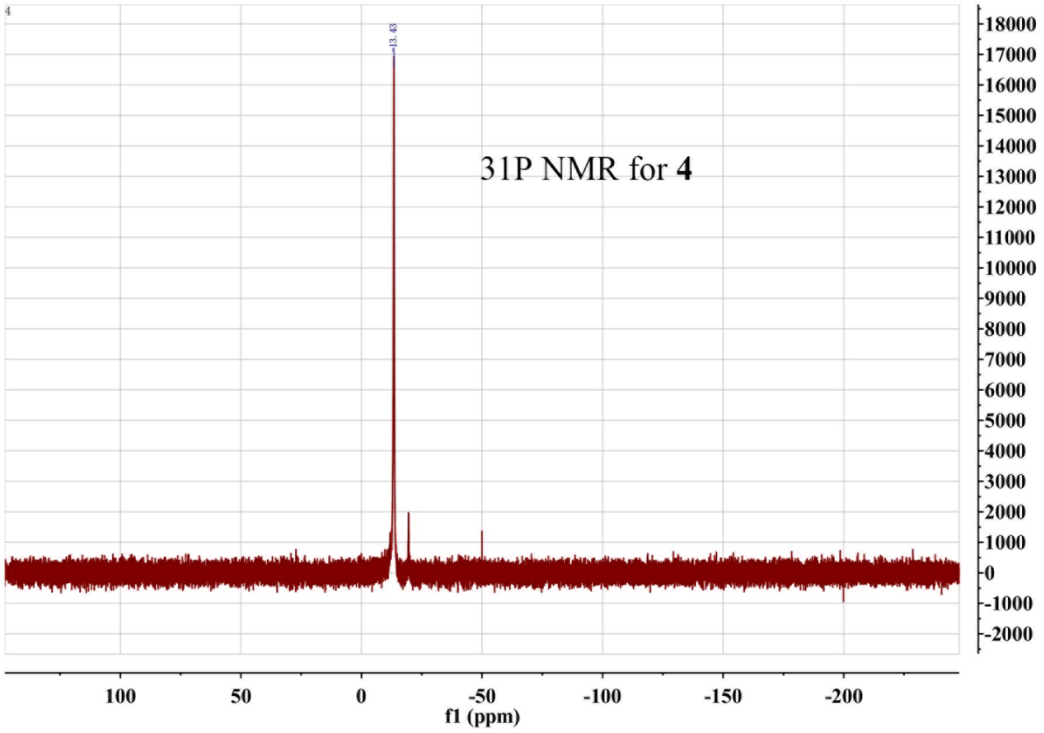

1H NMR for 3 dried at 200 ºC
f1 (ppm)

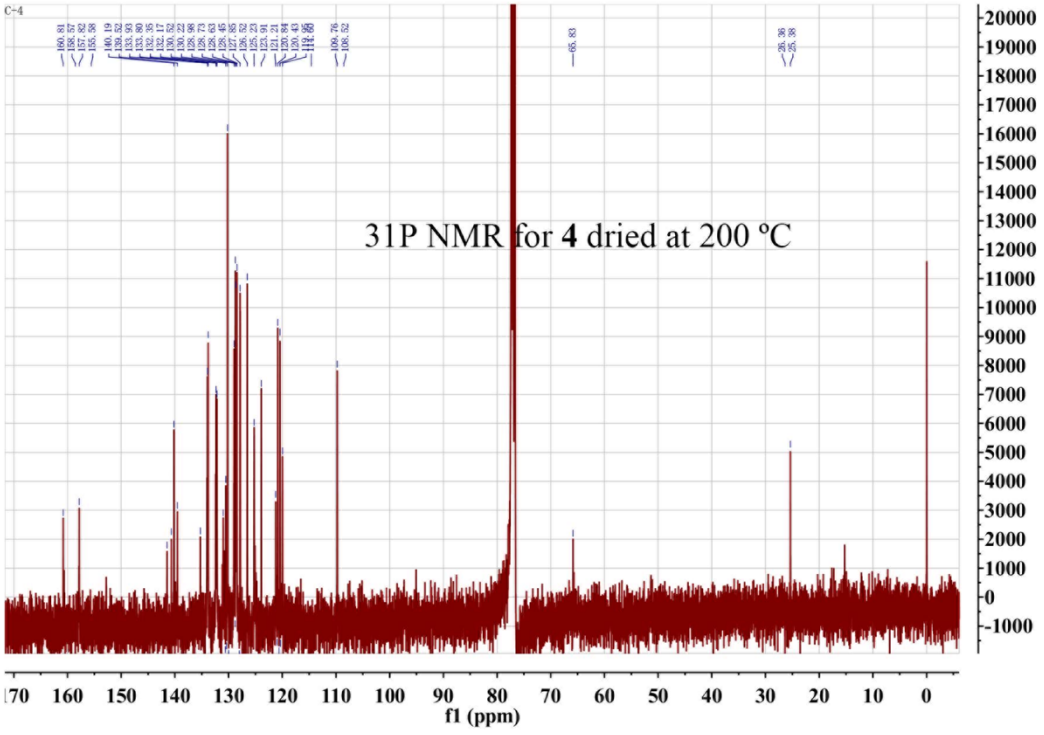

31P NMR for 3
43.45
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
-3000
-4000
100
50
0
-50
-100
-150
-200
f1 (ppm)


13C NMR for 3 dried at 200 ℃
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


1H NMR for 4 dired at 90 ℃
f1 (ppm)


1H NMR for 4 dired at 200 ℃
f1 (ppm)


31P NMR for 4
13.43
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
100
50
0
-50
-100
-150
-200
f1 (ppm)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65.83
26.36
25.38
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)