Electronic Supplementary Information

Synthesis and characterization of copper (II) complexes with multidentate ligands as catalysts for the direct hydroxylation of benzene to phenol

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I. Characterization

1. UV–vis spectra

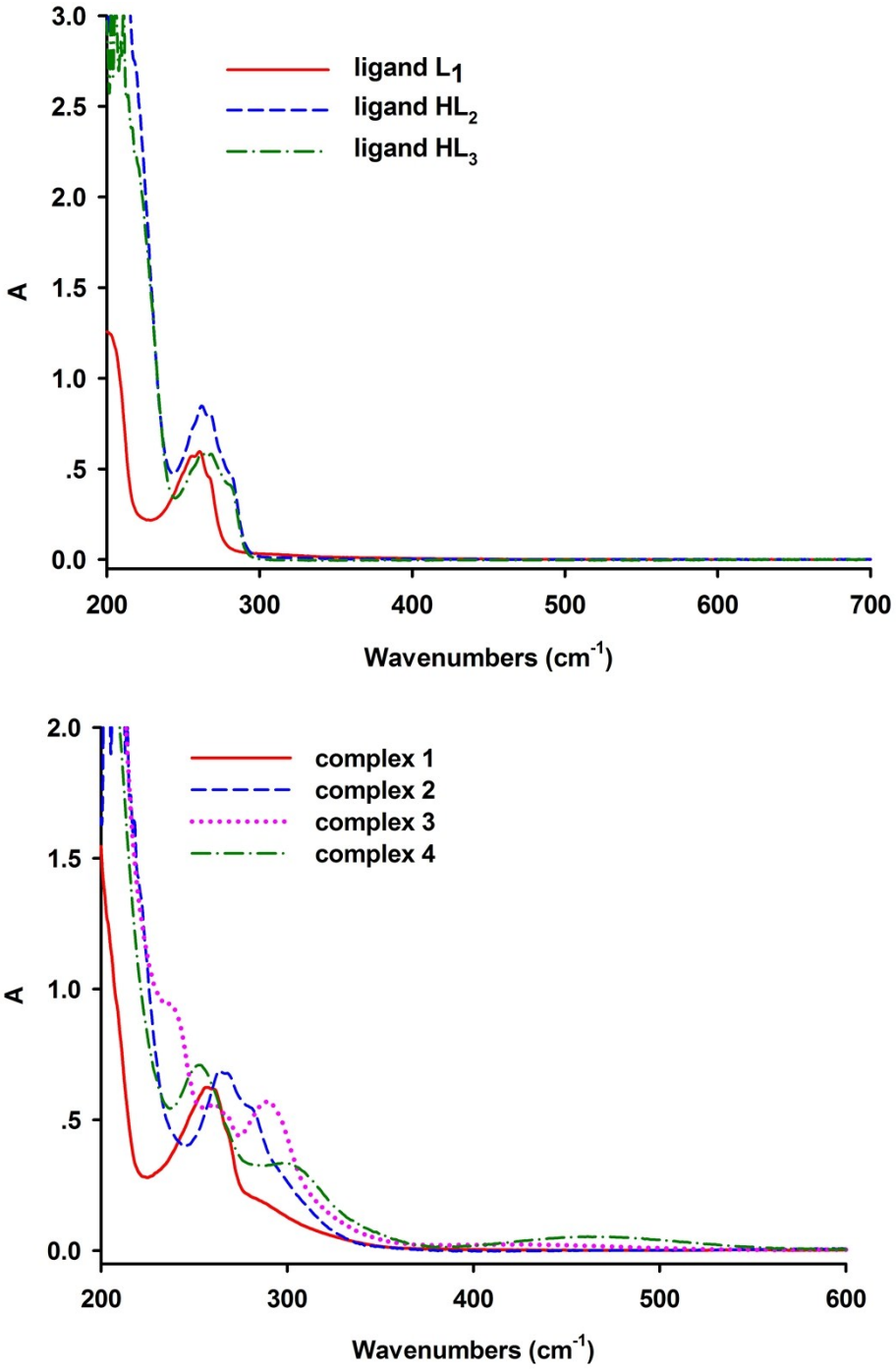


Fig. S1 UV–Vis absorption spectra of ligands $\mathbf{L_1}$, $\mathbf{HL_2}$, $\mathbf{HL_3}$ (top, solid line: ligand $\mathbf{L_1}$, dash line: ligand $\mathbf{HL_2}$, dash-dot line: ligand $\mathbf{HL_3}$) and complexes **1-4** (bottom, solid line: complex **1**, dash line: complex **2**, dot line: complex **3**, dash-dot line: complex **4**) in MeCN (1.0×10^{-5} mol L^{-1}).

2. Electrochemistry of copper complex **3**

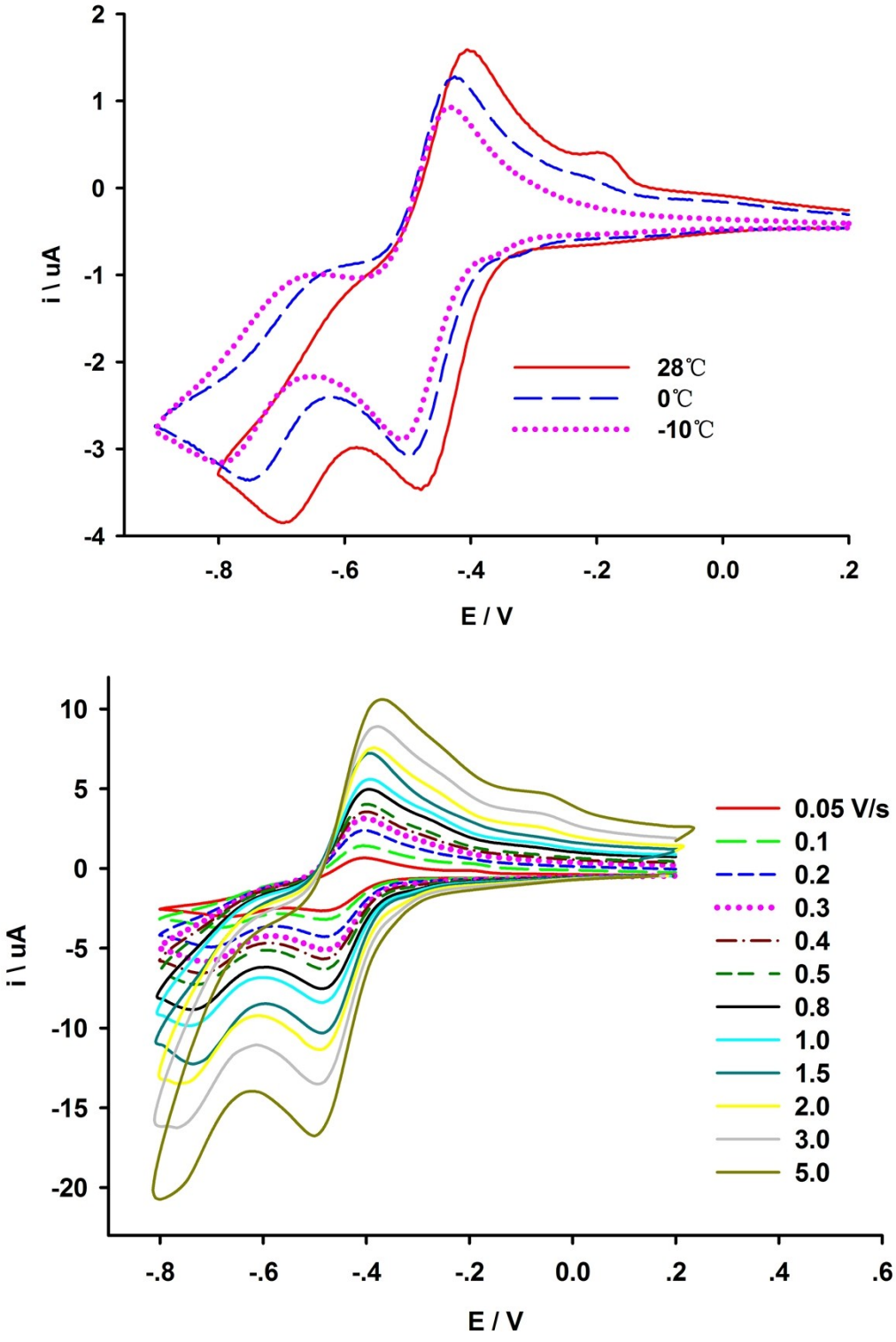


Fig. S2 Cyclic voltammograms of complex **3** (3.2 mmol L^{-1}) in the 0.1 M $[NBut_4]BF_4$–CH_3CN at different temperature (top) and at different scanning rates under Ar atmosphere (298 K) (bottom).

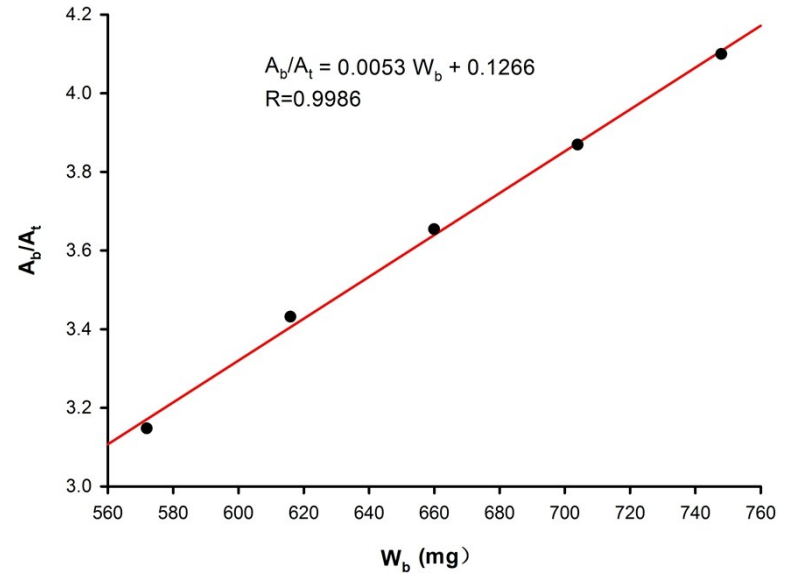
3. Conductivity

Table S1 Conductivity of complexes with different types at 10^{-3} mol L^{-1} in MeCN.

Complexes	Electrolyte type	Conductivity (μs/cm)	The expected values
$Cu\mathbf{L_1}Cl_2$	—	14.9	<25
$Cu\mathbf{HL_2}Cl_2$	—	16.2	<25
$[Cu_2(\mathbf{L_2})_2](ClO_4)_2$	2:1	>200	220-300
$[Cu\mathbf{L_3}(CH_3OH)](ClO_4)$	1:1	125.4	92-199

II. Hydroxylation of benzene

1. Internal standard method



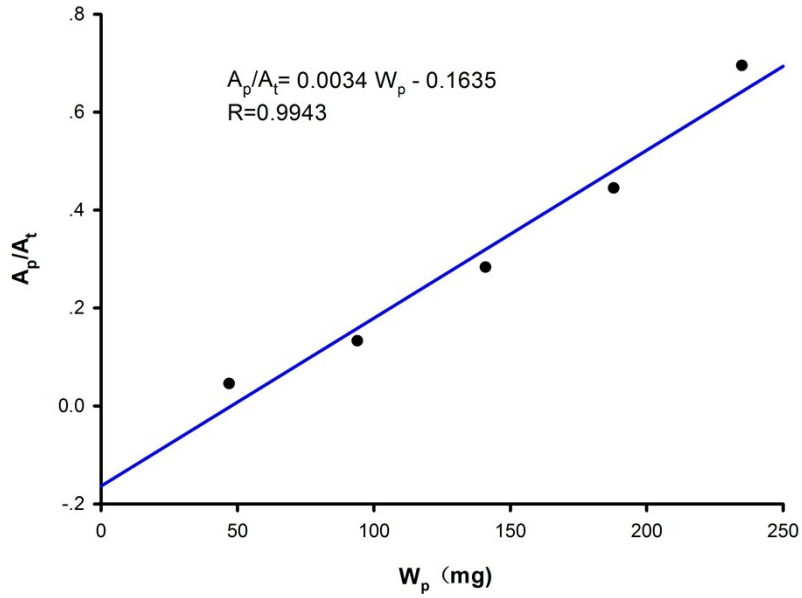


Fig. S3 The calibration curve of benzene (top) and the calibration curve of phenol (bottom).

(Note: A is designated as the chromatographic peak area; b stands for benzene, t sands for toluene and p stands for phenol; W stands for the mass of the analytes.)

2. Optimisation of reaction conditions

Screening experiments were carried out according to Table 1 in the text. The results were demonstrated in Table S2 and Table S3. In Table S3, K_i (i = 1, 2, 3, 4) represent the sum of corresponding experimental items of level i in j column, reflecting the influence on the yield of phenol and benzene conversion when the j is at i level. $\overline{K}_i$ (i = 1, 2, 3, 4) are the average of corresponding experimental items of level i in j column. And R denotes the range among $\overline{K}_i$, reflecting the importance of the corresponding experimental items: R is higher, the corresponding factor is more important.

For the determination of optimized reaction conditions, the sums of the yield of phenol and the conversion rate of benzene for each factor at each level were calculated and listed in Table S3. As seen from R values in Table S3, it could deduce that the factors influencing the yield of phenol is in order of the amount of H_2O_2 ≈ reaction temperature > reaction time > catalyst dosage, while the order for benzene conversion is the amount of H_2O_2 > reaction temperature > catalyst dosage > reaction time. Considering that the yield of phenol is the most important index in the studies of direct hydroxylation of benzene, therefore we selected the reaction parameters on the basis of the higher yield of phenol. The effect of various parameters on the yield of phenol can be further observed by drawing plots of the sum of the yield of phenol against the factor levels (Fig. S4). As seen from Fig. S4, the parameters for achieving the maximum yield of phenol can be selected as $A_3B_4C_3D_2$, which is reaction time with 4 h, reaction temperature at 80 °C, catalyst dosage of 0.03 mmol and the amount of H_2O_2 of 1.5 mL.

Table S2 Orthogonal experimental results.

Experiment[a]	Factors				Yield of phenol / %	Benzene conversion / %
	A	B	C	D		
1	1	1	1	1	5.4	6.7
2	1	2	2	2	7.0	18.8
3	1	3	3	3	8.0	43.6
4	1	4	4	4	6.0	38.6
5	2	1	2	3	6.8	25.8
6	2	2	1	4	5.9	31.2
7	2	3	4	1	7.5	23.5
8	2	4	3	2	11.0	36.9
9	3	1	3	4	5.7	30.6
10	3	2	4	3	9.6	46.3
11	3	3	1	2	9.1	24.9
12	3	4	2	1	9.0	19.1
13	4	1	4	2	8.2	29.2
14	4	2	3	1	6.8	20.3
15	4	3	2	4	6.4	38.2
16	4	4	1	3	9.5	46.7

[a] benzene (0.9 mL, 10 mmol).

Table S3 Optimization of the results.

Entry	Yield of phenol / %				Benzene conversion / %			
	A	B	C	D	A	B	C	D
K_1	26.4	26.1	29.9	28.7	107.7	92.3	109.5	69.6
K_2	31.2	29.3	29.2	33.9	117.4	116.6	101.9	109.8
K_3	33.4	31.0	31.5	33.9	120.9	130.2	131.4	162.4
K_4	30.9	35.5	31.3	24.0	134.4	141.3	137.6	138.6
$\overline{K}_1$	6.6	6.5	7.5	7.2	26.9	23.1	27.4	17.4
$\overline{K}_2$	7.8	7.3	7.3	8.5	29.4	29.2	25.5	27.5
$\overline{K}_3$	8.4	7.8	7.9	8.5	30.2	32.6	32.9	40.6

$\overline{K}_4$	7.7	8.9	7.8	6.0	33.6	35.3	34.4	34.7
R	1.8	2.4	0.6	2.5	6.7	12.2	8.9	23.2
Factors main→minor	D≈B>A>C				D>B>C>A			
Optimal conditions	$A_3B_4C_3D_2$				$A_4B_4C_4D_3$			

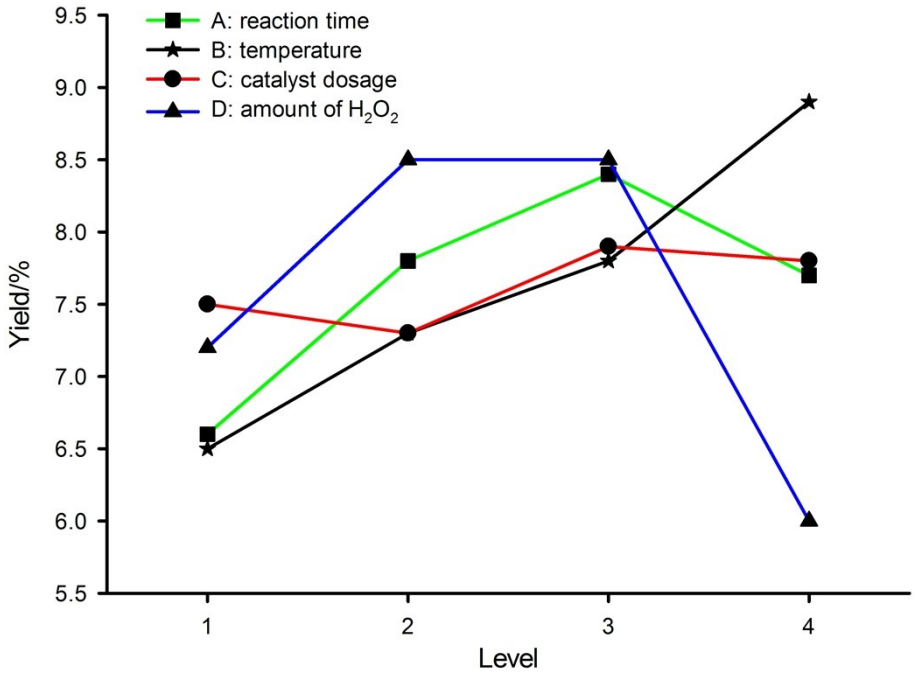


Fig. S4 The effect of reaction parameters (reaction time (■), reaction temperature (★), catalyst dosage (●), and Amount of H_2O_2 (▲)) on the reaction yield. Levels were showed in Table 1.

3. Mechanistic considerations

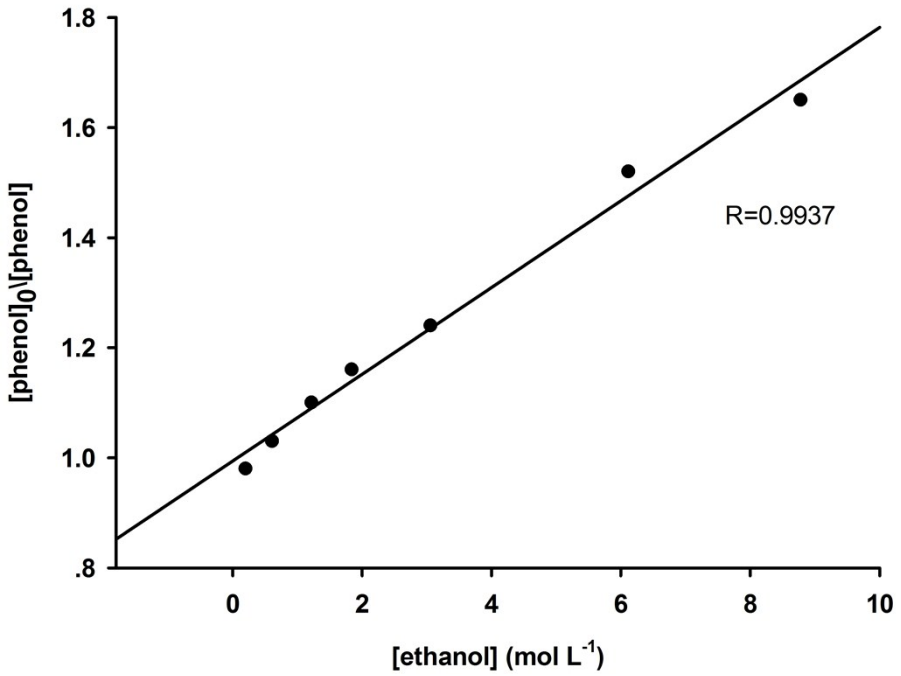
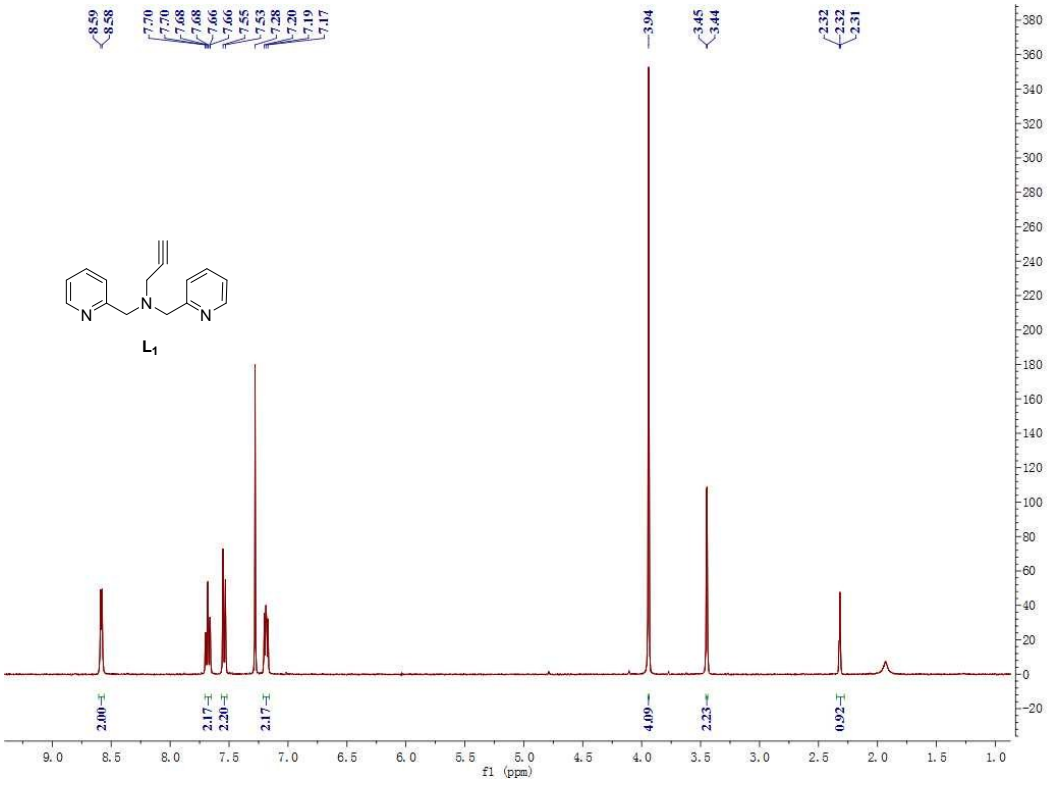
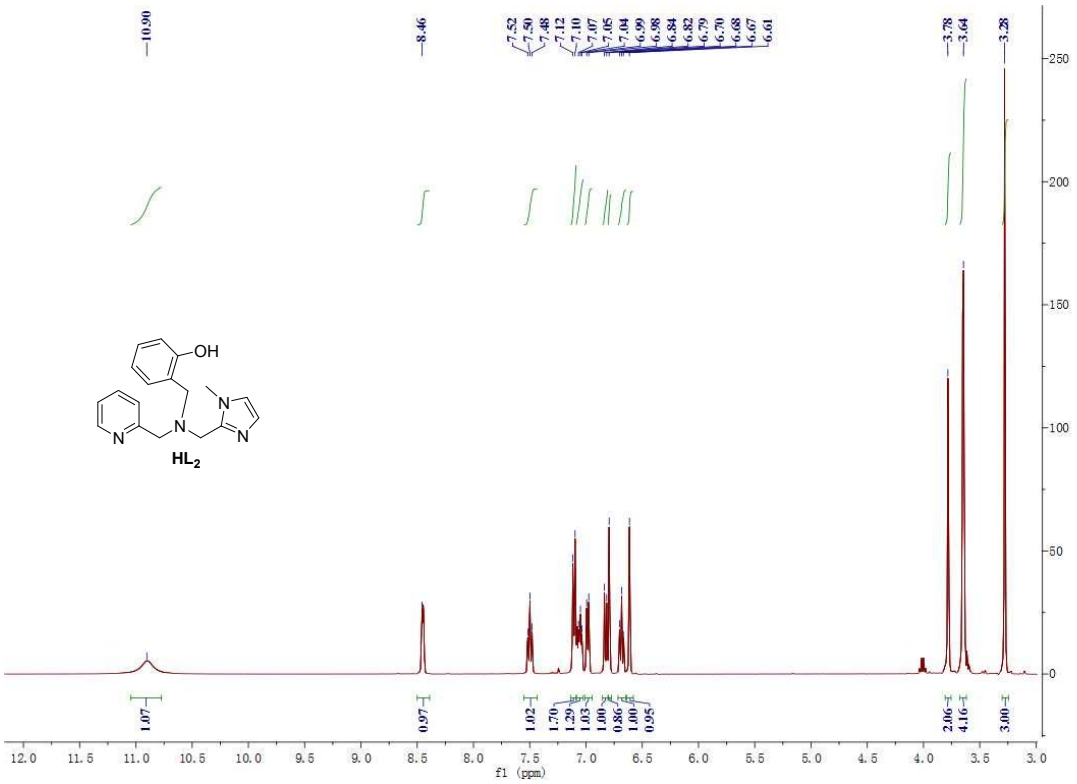


Fig. S5 Effects of ethanol concentration on the formation of phenol ($[phenol]_0$ and [phenol] represent phenol produced without and with added ethanol and [ethanol] is initial concentration of ethanol)

III. NMR copies of ligands

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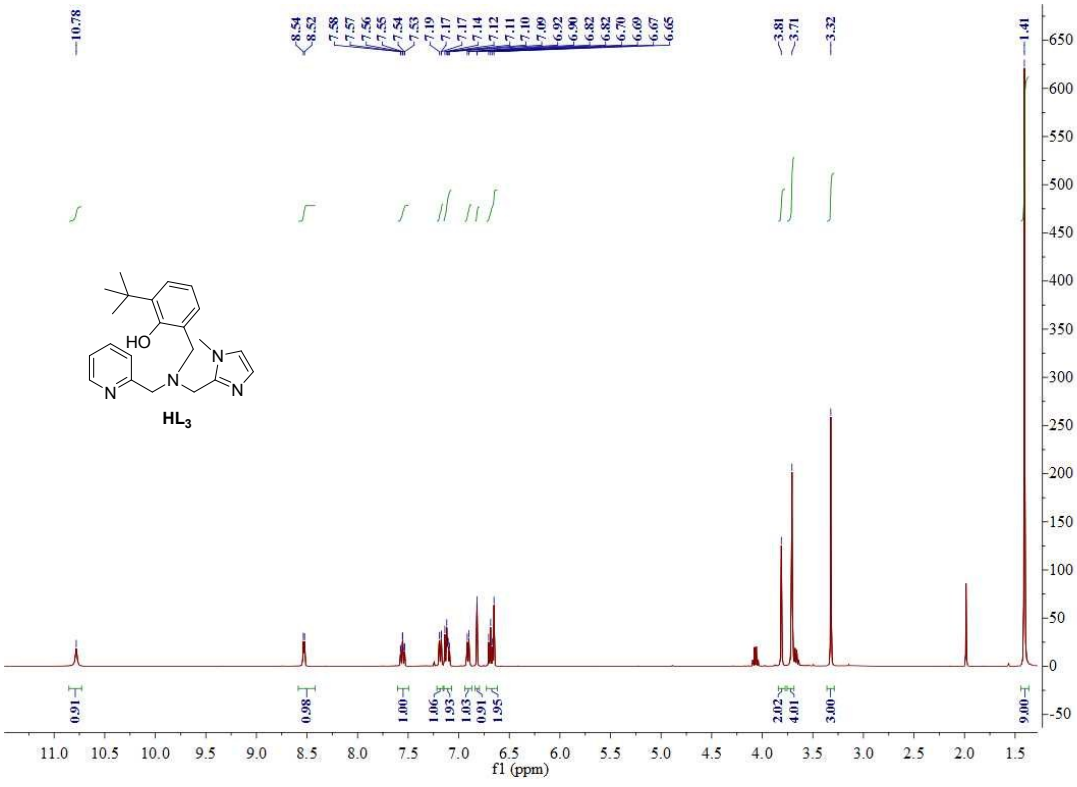
7.52
7.50
7.48
7.12
7.10
7.07
7.05
7.04
6.99
6.98
6.84
6.82
6.79
6.70
6.68
6.67
6.61
3.78
3.64
3.28
OH
N
N
N
HL2
1.07
0.97
1.02
1.70
1.29
1.03
1.00
0.86
1.00
0.95
2.06
4.16
3.00
f1 (ppm)


10.78
8.54
8.52
7.58
7.57
7.56
7.55
7.54
7.53
7.19
7.17
7.17
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7.12
7.11
7.10
7.09
6.92
6.90
6.82
6.70
6.69
6.67
6.65
3.81
3.71
3.32
1.41
HO
N
N
N
HL3
0.91
0.98
1.00
1.06
1.93
1.03
0.91
1.95
2.02
4.01
3.00
9.00
f1 (ppm)