Supporting Information

Iron (Ⅲ) complexes of multidentate pyridinyl ligand: Synthesis, characterization and catalysis on the direct hydroxylation of benzene

Beibei Xu,[a] Wei Zhong,[b,c] Zhenhong Wei,[a] Hailong Wang,[b] Jian Liu,[a] Li Wu,[a] Yonggang Feng[b] and Xiaoming Liu[a,b]*

[a] Department of Chemistry, Nanchang University, Nanchang (Jiangxi 330031, China)

[b] School of Biological and Chemical Engineering, Jiaxing University (Jiaxing 314001, China)

[c] State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University (Nanjing 210093, China)

*E-mail: xiaoming.liu@mail.zjxu.edu.cn

I. UV-spectra

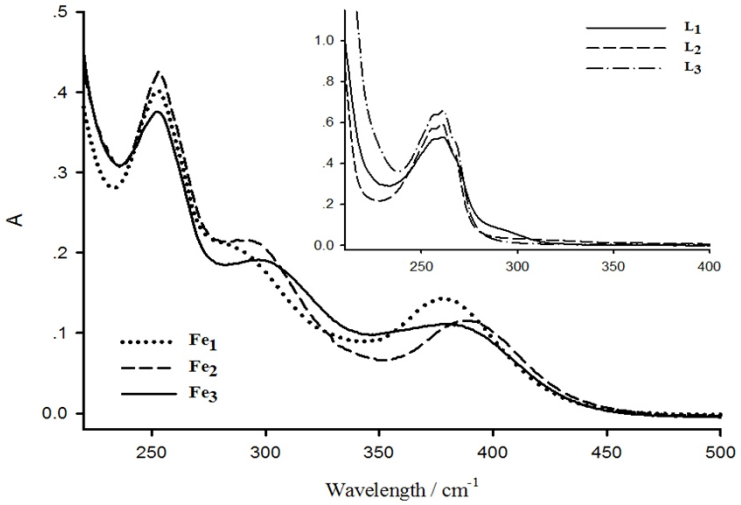


Fig. S1 UV-vis spectra of ligands $\mathbf{L_1}$–$\mathbf{L_3}$ and complexes $\mathbf{Fe_1}$–$\mathbf{Fe_3}$.

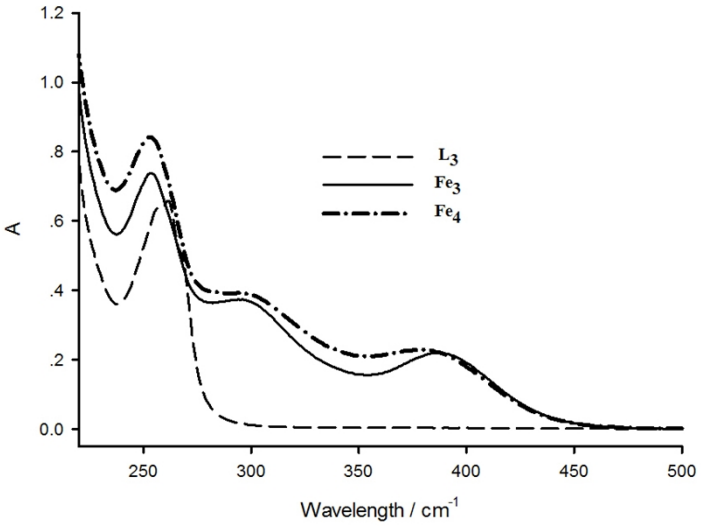


Fig. S2 UV-vis spectra of ligand $\mathbf{L_3}$ and complexes $\mathbf{Fe_3}$ and $\mathbf{Fe_4}$

II. Catalytic hydroxylation of benzene to phenol

1. Optimization of reaction conditions

The catalytic activity was assessed using benzene oxidation reaction by H_2O_2 in acetonitrile. Catalytic product analyzed by area normalization method. Reaction conditions for the catalysis were optimized using $\mathbf{Fe_2}$ as a catalyst. As shown in Table

S1, the reaction is very temperature-dependent. When the temperature is lower than 50 ℃, the reaction is hard to proceed. Raising the temperature could quickly speed up the reaction but further increasing the temperature does not improve the reaction yield. Thus, the optimal temperature and reaction time were chosen as 70 ℃ and 2h, respectively.

Table S1 Conversion rate and selectivity for the benzene oxidation.

T / ℃	1h	2h	4h	6h
40	3.8[a] ± 1	6.5 ± 0.8	9.2 ± 1	10 ± 1
	(78.9)[b]	(89.5)	(97.5)	(> 99)
50	5.7 ± 1	6.8 ± 1	9.3 ± 1	11.6 ± 1
	(70.1)	(88.2)	(96.5)	(95.2)
60	7.2 ± 0.8	20 ± 1	19 ± 2	18 ± 1
	(> 99)	(> 99)	(> 99)	(> 99)
70	18 ± 2	21 ± 1	20 ± 3	18 ± 1
	(> 99)	(> 99)	(> 99)	(> 99)
80	20 ± 1	22 ± 2	21 ± 2	18 ±1
	(> 99)	(> 99)	(> 99)	(> 99)
90	20 ± 2	23 ± 2	20 ± 2	19 ± 1
	(> 99)	(> 99)	(> 99)	(> 99)

[a] Selectivity is placed in Conversion percentage of benzene was calculated according to the formula Area (phenol) / [Area (substrate + products)] × 100%.

[b] Selectivity percentage of phenol was calculated according to the formula Area (phenol) / [Area (products)] × 100%.

2. Internal standard method

The Standard curve results are as following:

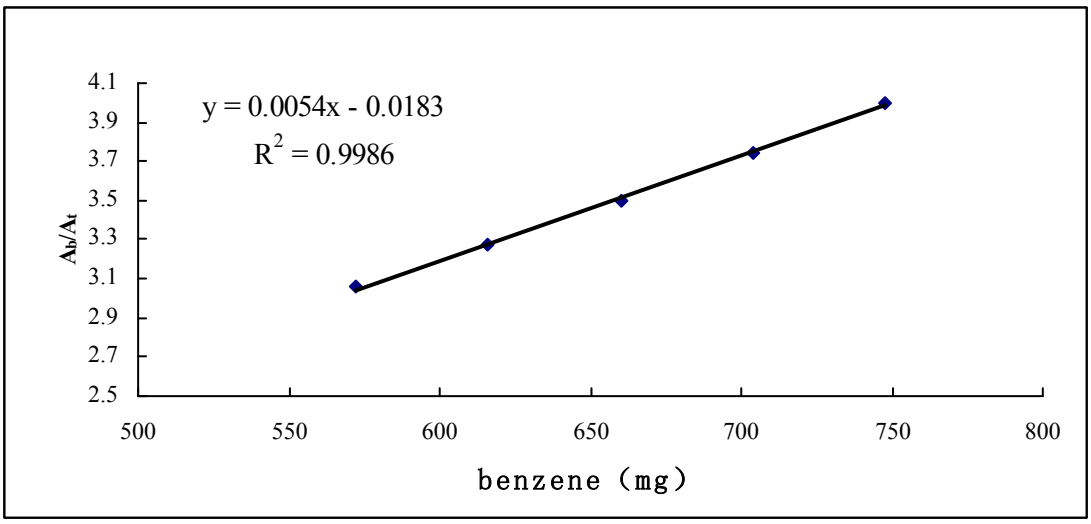


Fig. S3 The standard cave of the mass ration of benzene to area ration (A_b / A_t)[a]

[a] A is designated as the chromatographic peak area; b stands for benzene and t for toluene.

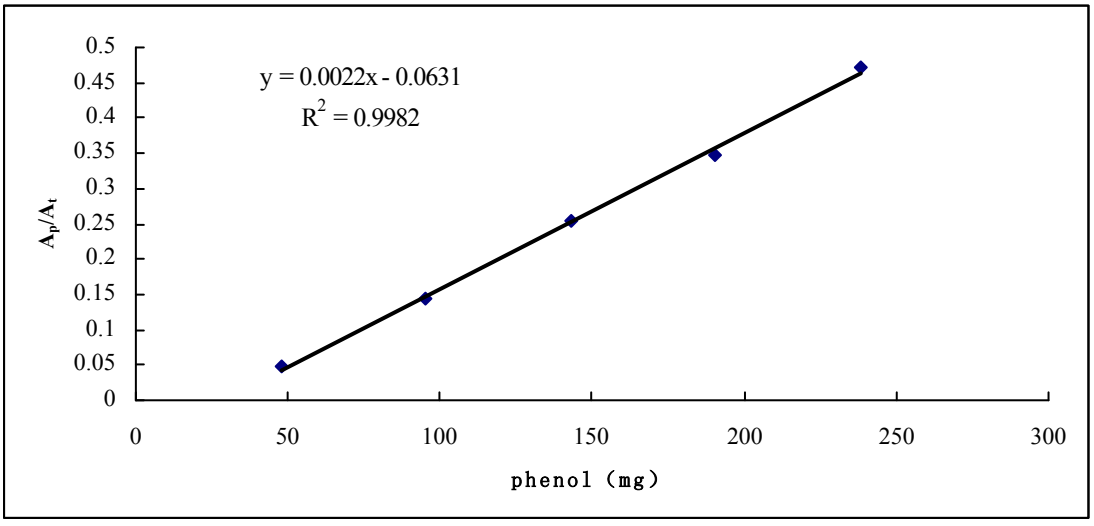


Fig. S4 The standard cave of the mass ration of phenol to area ration (A_p/A_t)[a]

[a] A is designated as the chromatographic peak area; p stands for phenol and t for toluene.

Table S2 Oxidation of benzene with **Fe_1-Fe_4** under different amount of hydrogen peroxide.

	Conversion[a]	Selectivity[b]	Yield[c]	TON[d]	TOF/h^{-1} [e]

Fe_1	V_{H2O2}=1.2mL	42.0%	26.8%	11.2%	56	28
	V_{H2O2}=2mL	49.5%	26.5%	13.1%	65	33
Fe_2	V_{H2O2}=1.2mL	37.7%	52.9%	19.9%	100	50
	V_{H2O2}=2mL	42.3%	44.5%	18.8%	94	47
Fe_3	V_{H2O2}=1.2mL	35.2%	34.7%	12.2%	61	30
	V_{H2O2}=2mL	39.3%	34.4%	13.5%	68	34
Fe_4	V_{H2O2}=1.2mL	31.5%	41.2%	13.0%	65	32
	V_{H2O2}=2mL	37.6%	34.6%	13.0%	65	32

a. Conversion of benzene = $\frac{\text{Benzene -Unreacted benzene(mole)}}{\text{Benzene(mole}}$

b. Selectivity of phenol = $\frac{\text{Phenol(mole)}}{\text{Benzene-Unreacted benzene(mole)}}$

c. Yield of phenol = $\frac{\text{Phenol(mole)}}{\text{Benzene(mole)}}$

d. TON = $\frac{\text{Phenol(mole)}}{\text{Catalyst(mole)}}$

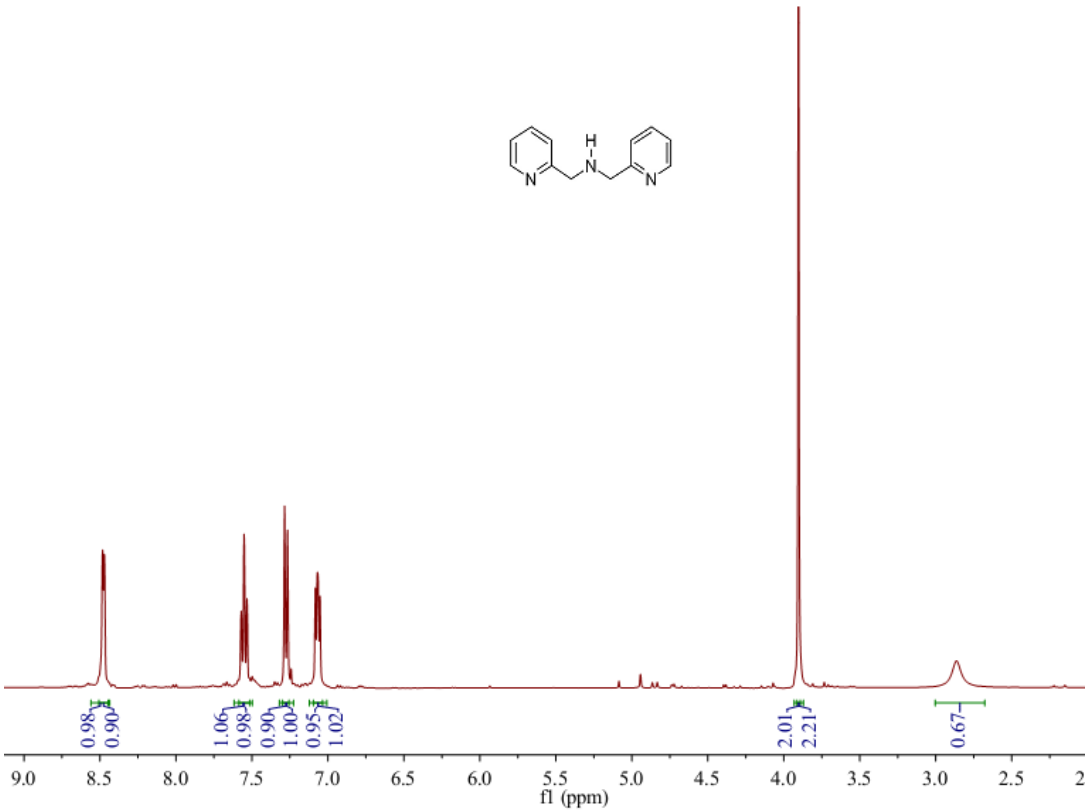
e. TOF = $\frac{\text{TON}}{\text{hours}}$

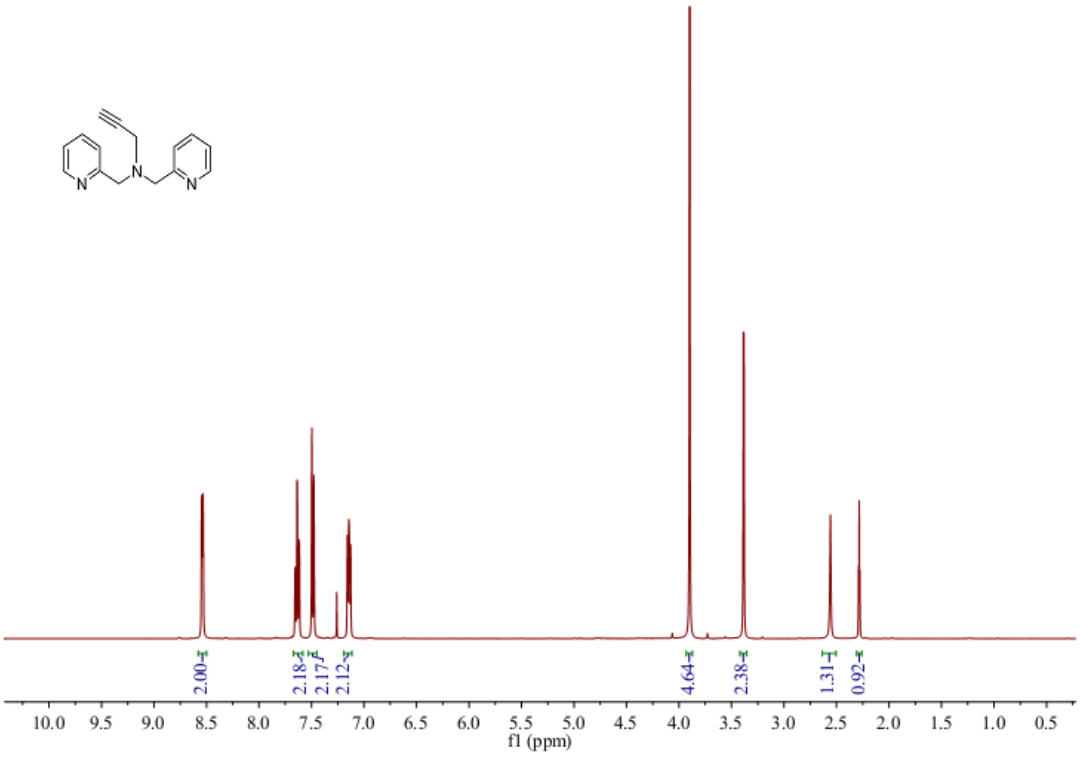
Table S3 The effect of concentration of catalyst employing complex **Fe_2**[a].

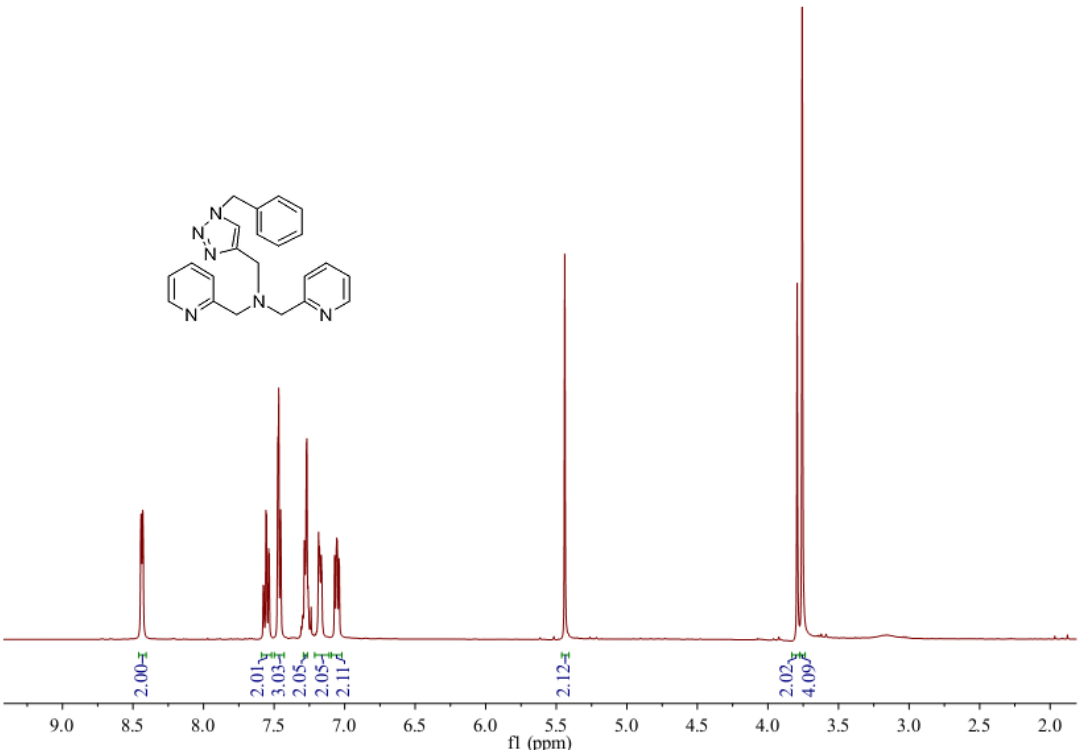
n_c/n_b	Conversion	Selectivity	Yield	TON	TOF/h^{-1}
1‰	35.4%	36.4%	12.9%	129	64
2‰	37.7%	52.9%	19.9%	100	50
3‰	38.6%	51.1%	19.7%	66	33
4‰	42.8%	35.9%	15.3%	38	19
5‰	36.5%	34.0%	12.4%	25	12

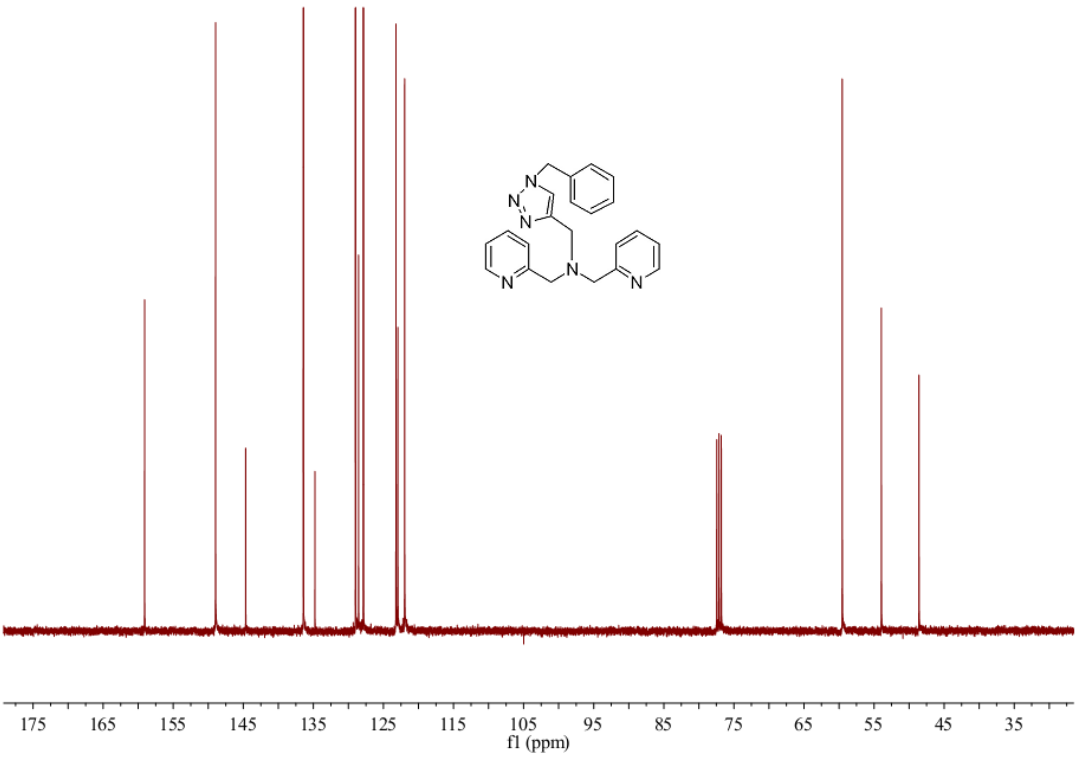
a. Reactions conditions: benzene (0.9 mL, 10 mmol), H_2O_2 (1.2 mL, 12 mmol), acetonitrile as solvent (3.8 mL), temp = 70 ℃, time = 2h.

III NMR copies of ligands






2.00
2.01
3.03
2.05
2.05
2.11
2.12
2.02
4.09
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)


175
165
155
145
135
125
115
105
95
85
75
65
55
45
35
f1 (ppm)