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# Supplementary Information

# PEG/copper(I) halide cluster as an eco-friendly catalytic system for C-N bond formation

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**Contents**

**Table S1** Crystal data and refinement details for **L3** and **L4**.

| | **L3** | **L4** |
|---|---|---|
| Empirical formula | $C_{23}H_{24}Fe_2Te_2$ | $C_{28}H_{26}Fe_2Te_2$ |
| Formula weight | 667.32 | 729.39 |
| Crystal system | Monoclinic | Monoclinic |
| Space group | $P2_1/n$ | $C2/c$ |
| $T$ /K | 293 | 293 |
| Wavelength /Å | 0.71073 | 0.71073 |
| $a$ /Å | 5.9310(12) | 20.7280(14) |
| $b$ /Å | 10.639(2) | 7.4755(5) |
| $c$ /Å | 35.440(7) | 17.1801(10) |
| $\alpha$/° | 90.00 | 90 |
| $\beta$/° | 94.06(3) | 102.440(2) |
| $\gamma$/° | 90.00 | 90 |
| V /Å$^3$ | 2230.6(8) | 2599.6(3) |
| Z | 4 | 4 |
| $D_{calcd}$/Mg·m$^{-3}$ | 1.987 | 1.864 |
| $\mu$ /mm$^{-1}$ | 3.870 | 3.329 |
| $F$(000) | 1272 | 1400 |
| Reflections/Unique | 4471/4051 | 14137/2951 |
| Parameters/Restraints | 244/115 | 145/0 |
| $\theta$ range /° | 1.15-25.27 | 3.472-27.504 |
| $R_{int}$ | 0.0436 | 0.0189 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0755 | 0.0205 |
| $wR_2$ [$I > 2\sigma(I)$] | 0.1706 | 0.0598 |
| GOF | 1.020 | 1.167 |
| Residuals /e·Å$^{-3}$ | 1.227/-0.834 | 0.427/-0.592 |

CCDC 1823302 (**L3**) CCDC 1823303 (**L4**) contain the supplementary crystallographic data for this paper.

**Table S2** Selected bond lengths and bond angles for **L3**, **L4** and **4-8**

| | Bond length(Å) | | Bond angles (°) | |
|---|---|---|---|---|
| **L3** | Te1-C7 | 2.114(13) | C7-Te1-C11 | 97.4(5) |
| | Te1-C11 | 2.191(16) | C14-Te2-C13 | 95.6(5) |
| | Te2-C14 | 2.124(12) | C12-C13-Te2 | 113.5(11) |
| | Te2-C13 | 2.197(15) | Fe1-C7-Te1 | 124.4(6) |
| | C12-C13 | 1.466(19) | | |
| **L4** | Te1-C1 | 2.088(2) | C1-Te1-C11 | 94.56(10) |
| | Te1-C11 | 2.172(3) | Fe1-C1-Te1 | 124.49(12) |
| | C11-C12 | 1.492(4) | | |

| | Bond length (Å) | | | | Bond angles(°) | | | |
|---|---|---|---|---|---|---|---|---|
| **4** | Te1-C1 | 2.108(8) | Cu1-Br1$^{i}$ | 2.4466(14) | C1-Te1-C21 | 98.3(3) | Br1$^{i}$-Cu1-Te2$^{i}$ | 106.82(5) |
| | Te1-C21 | 2.176(9) | Cu1-Te2$^{i}$ | 2.5798(12) | C1-Te1-Cu1 | 113.1(3) | Te1-Cu1-Br1 | 90.58(4) |
| | Te1-Cu1 | 2.5579(13) | Cu1-Cu1$^{i}$ | 2.696(2) | C21-Te1-Cu1 | 105.9(2) | Te2$^{i}$-Cu1-Br1 | 99.79(4) |
| | Te2-C11 | 2.108(8) | | | C11-Te2-C23 | 93.6(3) | Br1$^{i}$-Cu1-Cu1$^{i}$ | 62.72(5) |
| | Te2-C23 | 2.177(8) | | | C11-Te2-Cu1$^{i}$ | 103.1(2) | Te1-Cu1-Cu1$^{i}$ | 112.72(6) |
| | Te2-Cu1$^{i}$ | 2.5798(12) | | | C23-Te2-Cu1$^{i}$ | 97.8(2) | Te2$^{i}$-Cu1-Cu1$^{i}$ | 115.59(6) |
| | Br1-Cu1$^{i}$ | 2.4467(14) | | | Cu1$^{i}$-Br1-Cu1 | 63.19(4) | Br1-Cu1-Cu1$^{i}$ | 54.09(4) |
| | Br1-Cu1 | 2.6847(14) | | | Br1$^{i}$-Cu1-Te1 | 114.49(5) | Te1-Cu1-Te2 | 126.64(4) |
| | | | | | | | Br1$^{i}$-Cu1-Br1 | 116.81(4) |

(i)-x, 1-y, -z

| | Bond length(Å) | | Bond angles(°) | | | |
|---|---|---|---|---|---|---|
| **5** | Te1-C1 | 2.094(3) | C1-Te1-C21 | 94.99(14) | I1-Cu1-Te2 | 117.39(2) |
| | Te1-C21 | 2.158(4) | C1-Te1-Cu1 | 109.77(10) | Te2-Cu1-I1$^{i}$ | 86.597(16) |
| | Te1-Cu1 | 2.5774(6) | C21-Te1-Cu1 | 92.18(9) | I1-Cu1-Cu1$^{i}$ | 62.585(18) |
| | Te2-Cu1 | 2.6801(6) | Cu1-I1-Cu1$^{i}$ | 62.402(18) | Te1-Cu1-Cu1$^{i}$ | 136.88(3) |
| | I1-Cu1 | 2.5486(5) | I1-Cu1-Te1 | 125.35(2) | Te2-Cu1-Cu1$^{i}$ | 111.46(3) |
| | I1-Cu1$^{i}$ | 2.7614(6) | I1-Cu1-I1$^{i}$ | 117.599(2) | Cu1$^{i}$-Cu1-I1$^{i}$ | 55.014(18) |
| | Cu1-Cu1$^{i}$ | 2.7568(10) | Te1-Cu1-I1$^{i}$ | 101.224(19) | Te1-Cu1-Te2 | 100.881(17) |

(i)1-x, -y, 1-z

| | Bond length(Å) | | Bond angles(°) | | | |
|---|---|---|---|---|---|---|
| **6** | Te1-C1 | 2.104(5) | C1-Te1-C21 | 96.0(2) | Te1-Cu1-Te2 | 126.61(3) |
| | Te1-C21 | 2.180(5) | C1-Te1-Cu1 | 108.50(14) | $Br1^{i}$-Cu1-$Cu1^{i}$ | 54.80(3) |
| | Te1-Cu1 | 2.5509(7) | C21-Te1-Cu1 | 97.54(13) | Br1-Cu1-$Cu1^{i}$ | 54.63(2) |
| | Br1-$Cu1^{i}$ | 2.5133(9) | $Cu1^{i}$-Br1-Cu1 | 70.57(3) | Te1-Cu1-$Cu1^{i}$ | 127.83(4) |
| | Br1-Cu1 | 2.5187(8) | $Br1^{i}$-Cu1-Br1 | 109.43(3) | Te2-Cu1-$Cu1^{i}$ | 105.13(3) |
| | Cu1-$Br1^{i}$ | 2.5133(9) | $Br1^{i}$-Cu1-Te1 | 116.52(3) | | |
| | Cu1-Te2 | 2.5892(7) | Br1-Cu1-Te1 | 105.20(3) | | |
| | Cu1-$Cu1^{i}$ | 2.9069(14) | $Br1^{i}$-Cu1-Te2 | 97.77(3) | | |
| | | | Br1-Cu1-Te2 | 99.57(3) | | |

(i)2-x, -y, -z

| | Bond length (Å) | | Bond angles(°) | | | |
|---|---|---|---|---|---|---|
| **7** | Te1-C1 | 2.102(5) | C1-Te1-$C21^{i}$ | 95.4(2) | $I1^{ii}$-Cu1-I1 | 113.92(2) |
| | Te1-$C21^{i}$ | 2.184(5) | C1-Te1-Cu1 | 110.65(16) | Te1-Cu1-$Cu1^{ii}$ | 128.41(3) |
| | Te1-Cu1 | 2.5777(6) | $C21^{i}$-Te1-Cu1 | 98.05(13) | Te2-Cu1-$Cu1^{ii}$ | 106.00(3) |
| | I1-$Cu1^{ii}$ | 2.6634(7) | $Cu1^{ii}$-I1-Cu1 | 66.08(2) | $I1^{ii}$-Cu1-$Cu1^{ii}$ | 57.07(2) |
| | I1-Cu1 | 2.6700(7) | Te1-Cu1-$I1^{ii}$ | 115.60(2) | I1-Cu1-$Cu1^{ii}$ | 56.85(2) |
| | Cu1-$I1^{ii}$ | 2.6635(7) | Te1-Cu1-Te2 | 125.18(3) | | |
| | Cu1-Te2 | 2.6195(6) | Te2-Cu1-$I1^{ii}$ | 97.73(2) | | |
| | Cu1-$Cu1^{ii}$ | 2.9079(13) | Te1-Cu1-I1 | 104.22(2) | | |
| | | | Te2-Cu1-I1 | 99.56(2) | | |

(i)-0.5+x, 1.5-y, 0.5+z
(ii)2-x, 1-y, -1-z

| | Bond length (Å) | | Bond angles(°) | | | |
|---|---|---|---|---|---|---|
| **8** | I1-Cu1 | 2.6408(18) | Cu1-I1-$Cu1^{i}$ | 79.90(3) | Te2-Cu1-$I1^{i}$ | 114.79(2) |
| | I1-$Cu^{i}$ | 2.765(3) | C1-Te1-C21 | 95.03(16) | Te1-Cu1-$I1^{i}$ | 92.32(4) |
| | Te1-C1 | 2.106(4) | C1-Te1-Cu1 | 120.38(10) | I1-Cu1-$I1^{i}$ | 100.10(3) |
| | Te1-C21 | 2.183(4) | C21-Te1-Cu1 | 102.89(12) | | |
| | Te1-Cu1 | 2.586(2) | Te2-Cu1-Te1 | 117.13(3) | | |
| | Cu1-Te2 | 2.567(2) | Te2-Cu1-I1 | 116.97(6) | | |
| | Cu1-$I1^{i}$ | 2.765(3) | Te1-Cu1-I1 | 111.61(6) | | |

(i)1-x, -y, 1-z

**Table S3** Cyclic voltammetric data (mV).

| | $E_{1/2}$[a] | $\Delta E_{1/2}$[a] |
|---|---|---|
| **L3** | 401/299 | - |
| **4** | 604 | 203 |
| **5** | 352 | -49 |

[a] $E_{1/2}$ values are the half-wave potential of the ferrocenyl group and are quoted relative to $FcH/[FcH]^+$.

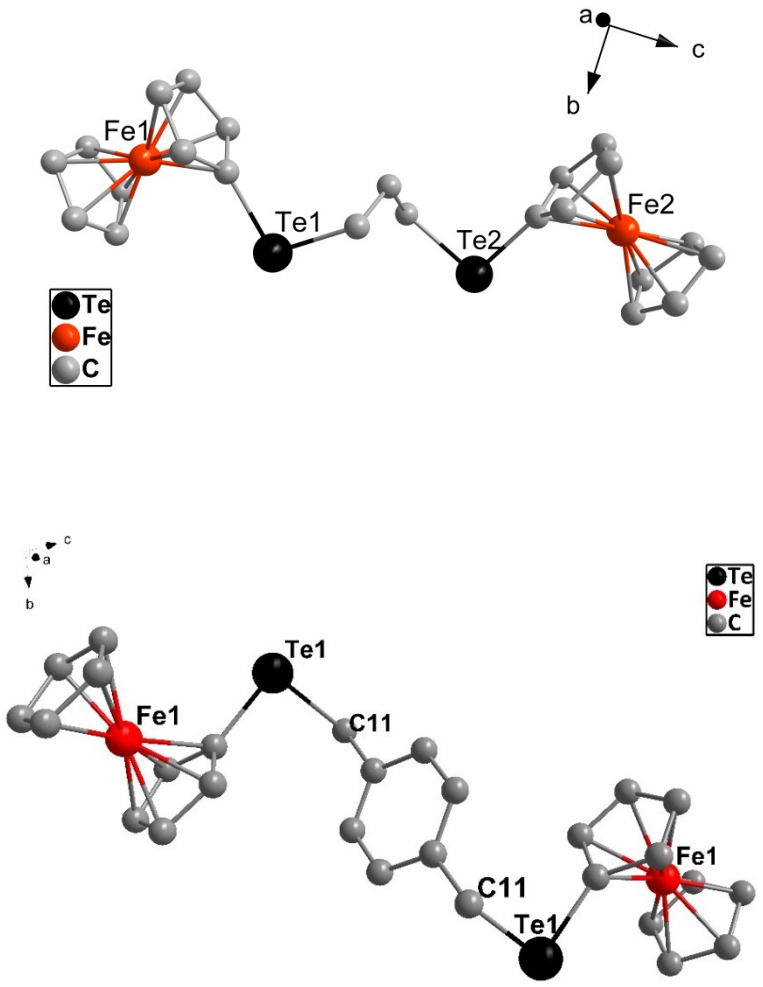


**Fig. S1** The molecular structures of **L3** and **L4.**

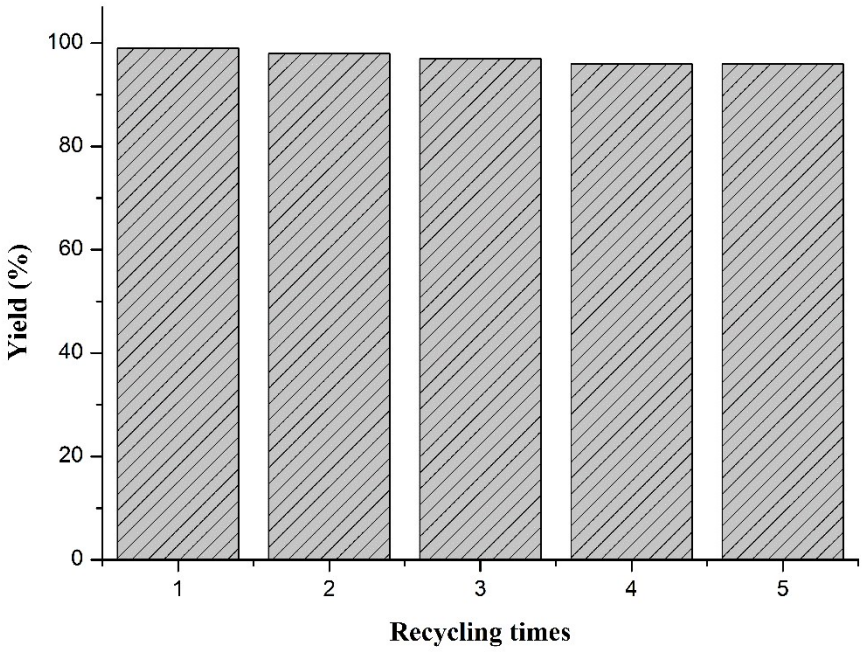


**Fig. S2.** Recycle of PEG-400/**5** catalytic system.

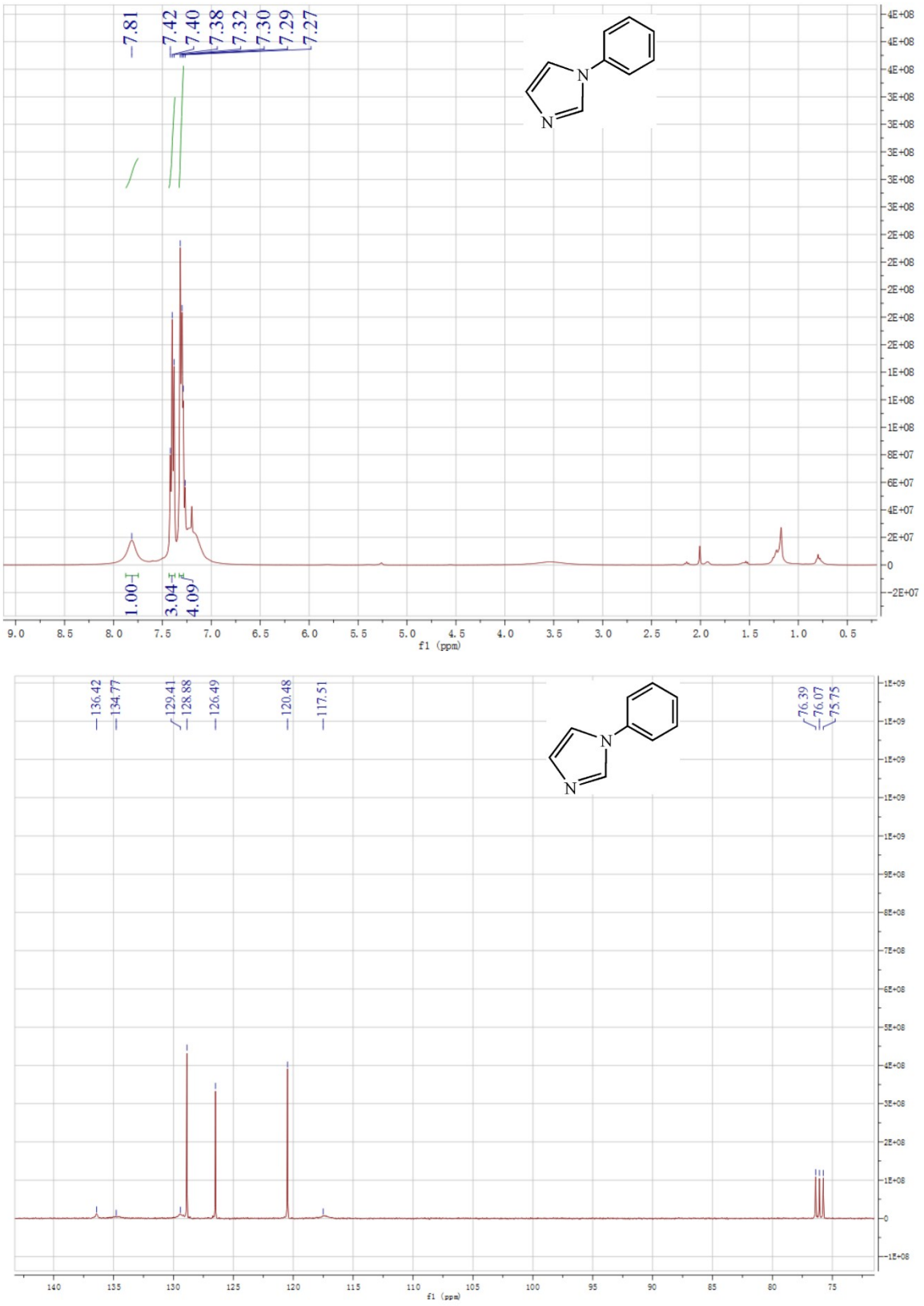


**Fig. S3** $^{1}H$ and $^{13}C$ NMR spectra of N-(4-phenyl)imidazole.

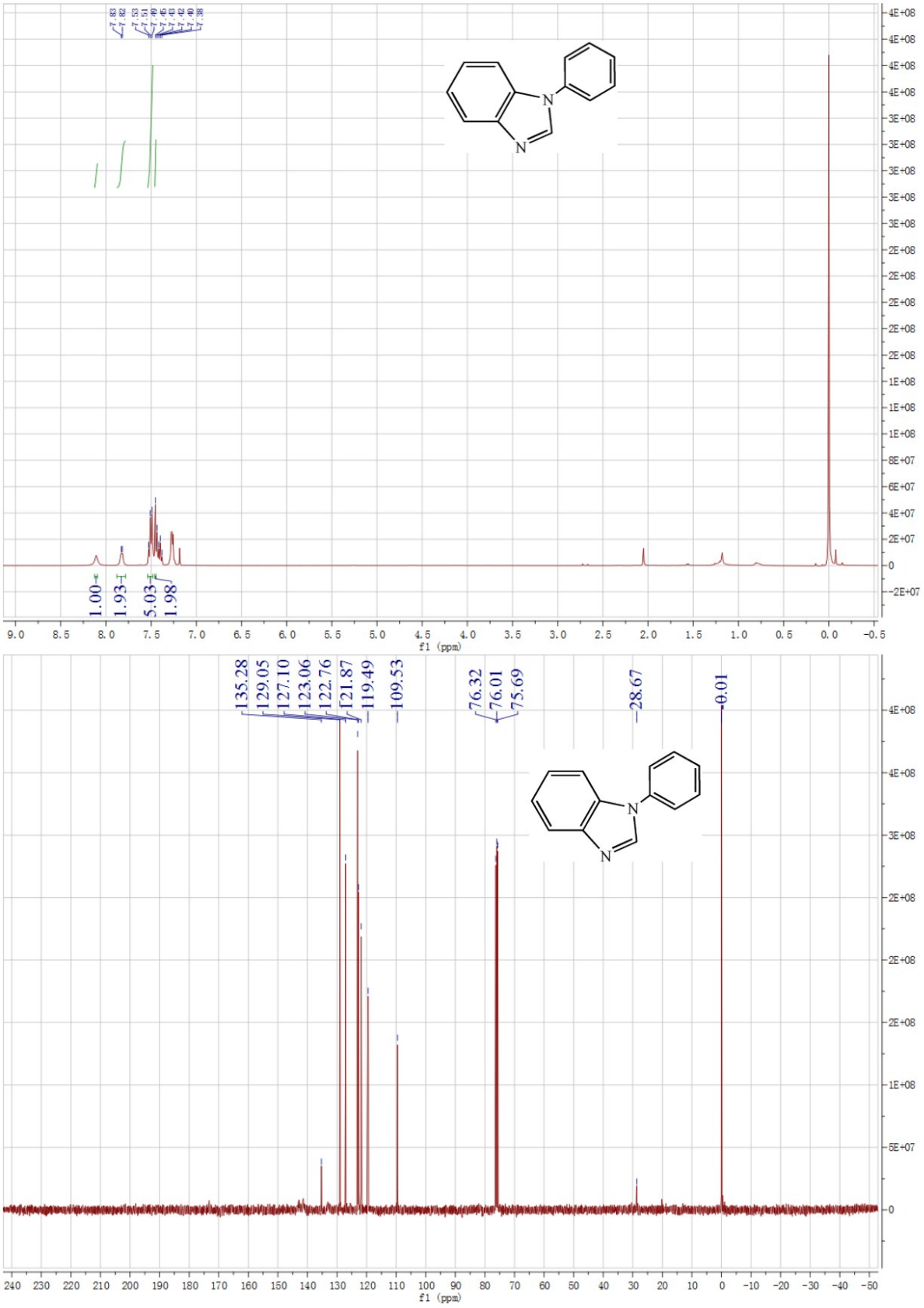


**Fig. S4** $^{1}H$ and $^{13}C$ NMR spectra of N-(4-phenyl)benzimidazole.

N-(4-phenyl)4-methyimidazole

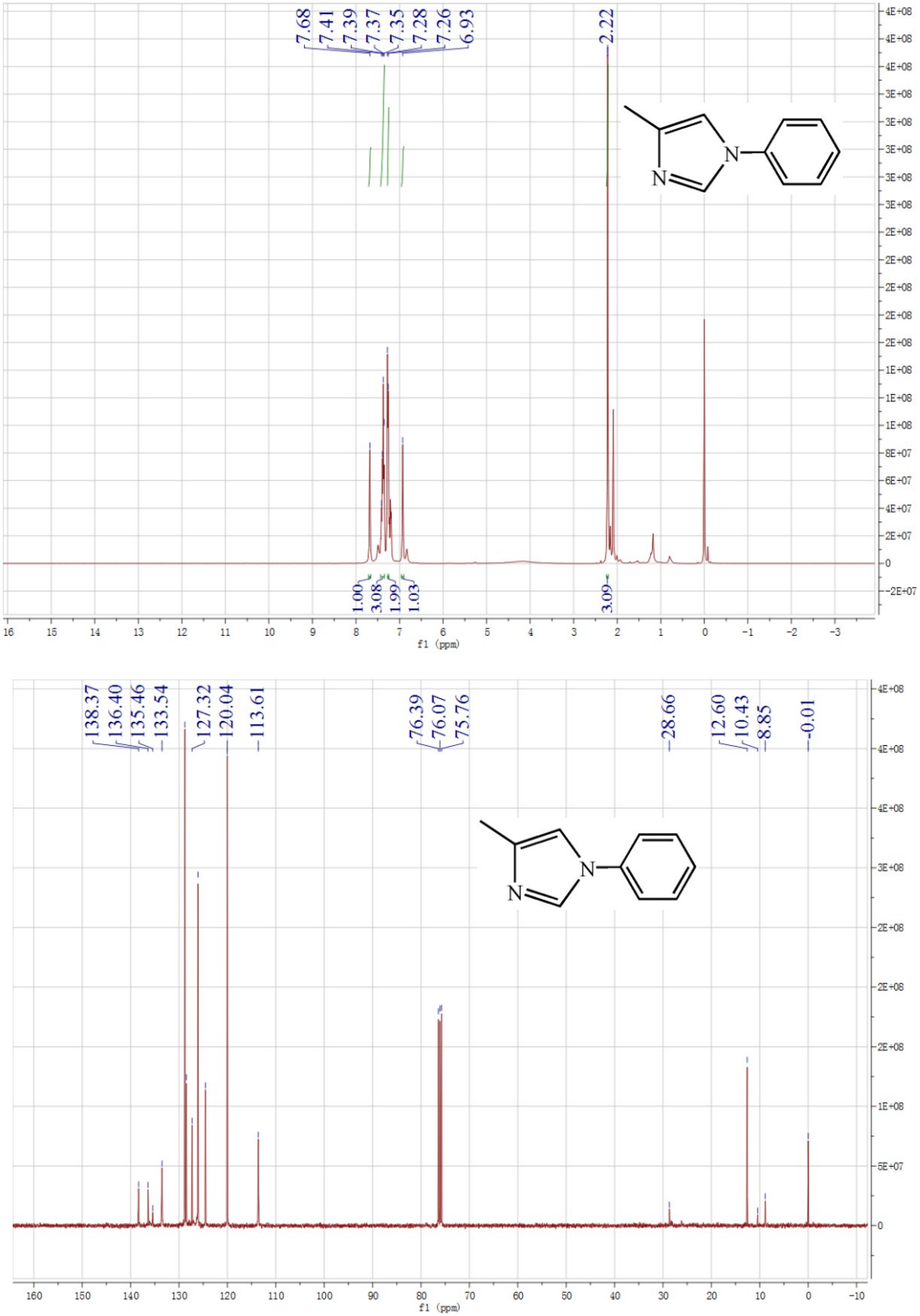


**Fig. S5** $^{1}H$ and $^{13}C$ NMR spectra of N-(4-phenyl)-4-methyimidazole.

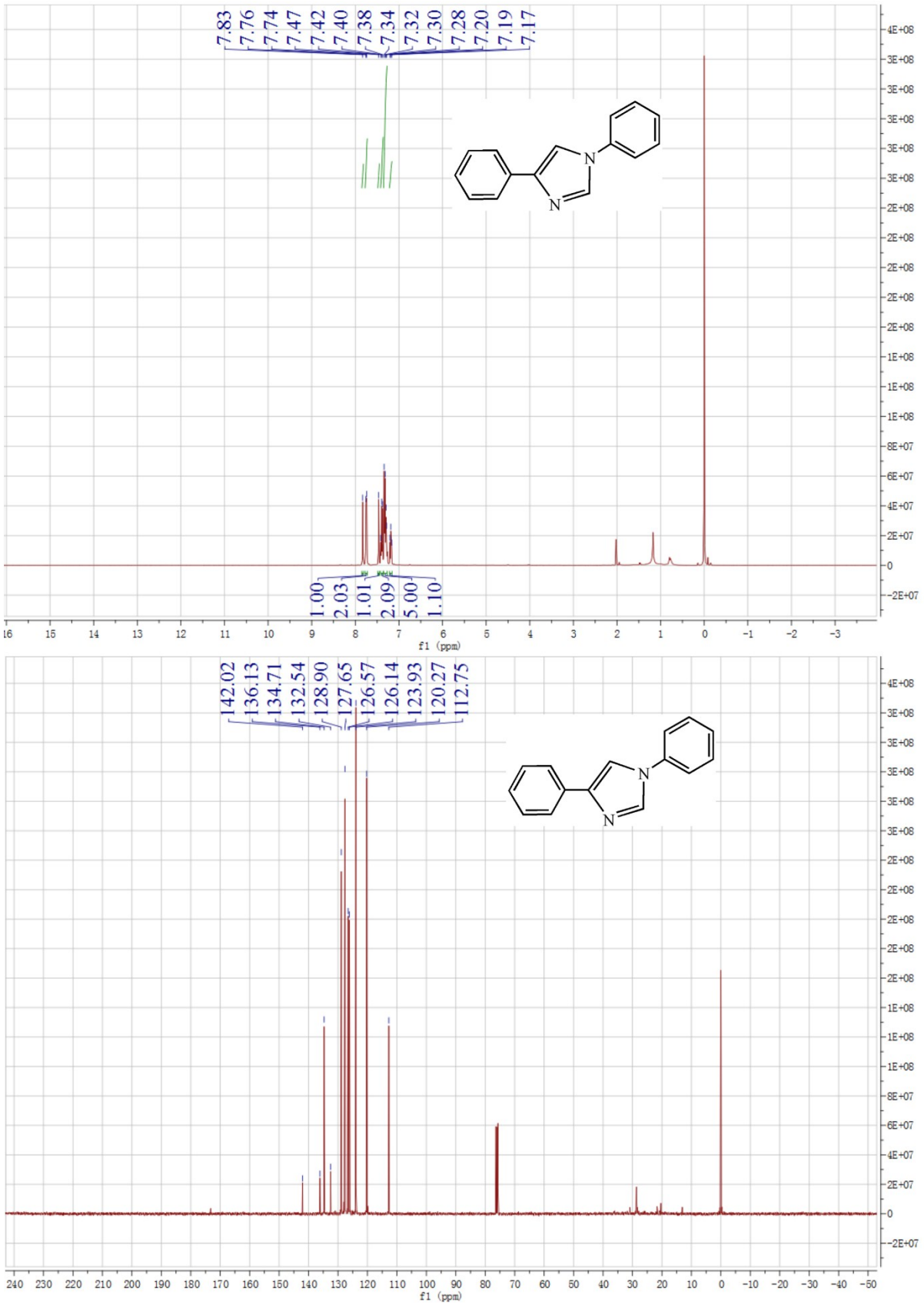


**Fig. S6** $^{1}H$ and $^{13}C$ NMR spectra of N-(4-phenyl)-4-phenylimidazole.

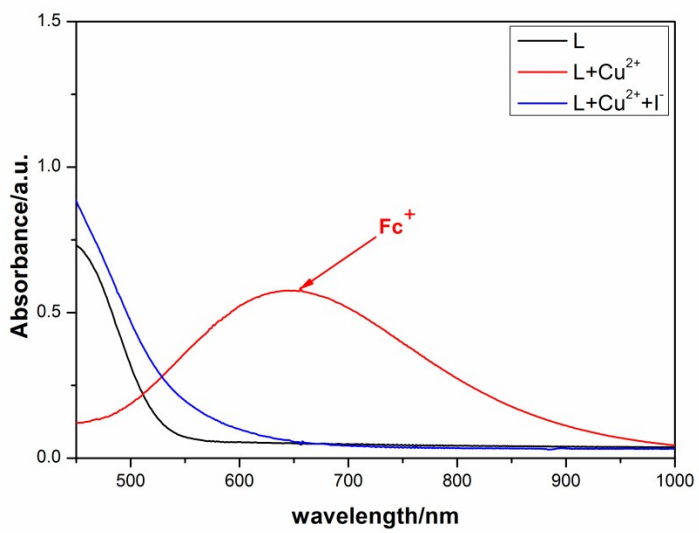


**Fig. S7** UV-Vis spectra of free **L3** ($1\times10^{-4}$ mol/L), and successive addition of $Cu(ClO_4)_2{\cdot}6H_2O$ (red line) and KI (blue line) in methanol solution.

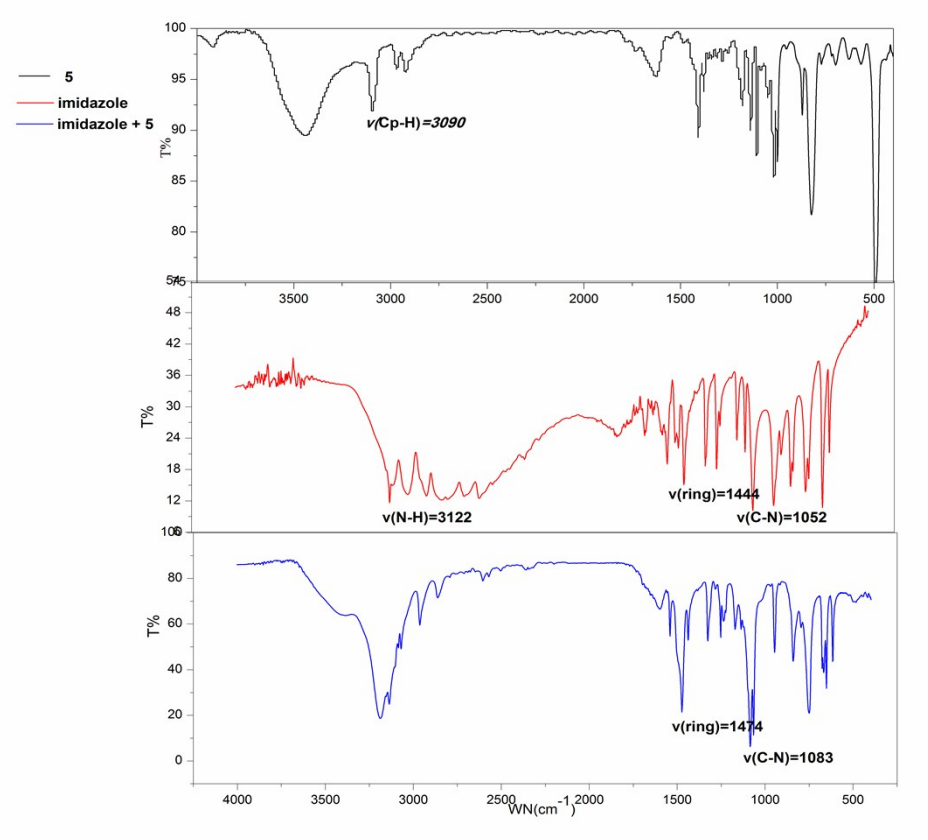


**Fig. S8** Infrared spectrum of **5 (**black line**)**, imidazole (red line) and intermediates (**5i,** blue line)

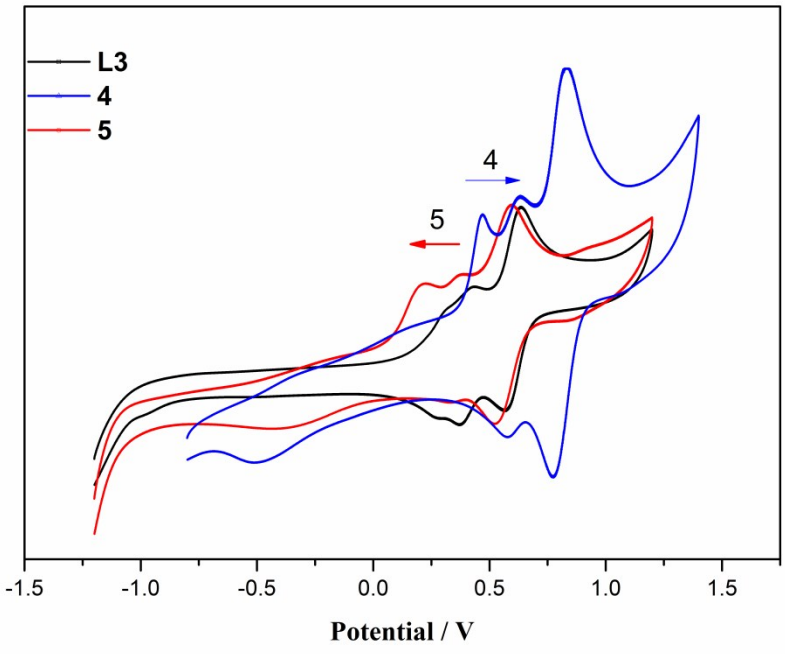


**Fig. S9** Cyclic voltammetric of **L3**, **4** and **5**