Electronic Supplementary Information

The mechanistic diversity of the selective aerobic oxidation of alcohols catalyzed by systems derived from CuI and a diamine ligand

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1. Experimental

1.1 General Information

Chemicals were purchased from Aladdin and Macklin and used without further purification unless otherwise stated. TEMPOH was synthesized according to a literature procedure [1]. Nuclear magnetic resonance (NMR) spectra were measured on Varian 400-MR with $CDCl_3$ as the deuterated solvent. UV-vis spectrophotometric measurements were performed on a THERMO EV201 spectrophotometer using a quartz cuvette with a path length of 1 cm. The aerobic oxidation of 1-octanol to 1-octanal at room temperature in dichloromethane with ambient air as the oxidant was monitored and quantitatively analyzed by gas chromatography (Agilent 7890) with a packed column of Restek capillary SE-54. The temperature of the GC column was set at 60 ^{o}C for 1 min and then was programmed to 165 ^{o}C at the rate of 15 ^{o}C min^{-1}. For other substrates, the products were analyzed by gas chromatograohy-mass spectrometry (Agilent 7890-5975C) with the vaporization temperature of 250 ^{o}C and the heating rate of 15 ^{o}C min^{-1}. Electrochemistry was performed at room temperature in 0.1 mol L^{-1} $[NBut_4]BF_4$ / CH_3CN under an inert atmosphere with a self-designed and gas-tightened electrochemical cell driven by Autolab 128N. A vitreous carbon disk (ϕ = 1 mm) was used as the working electrode and a platinum wire or vitreous carbon strip as the counter electrode. Ag/AgCl in dichloromethane was used as the reference electrode which is consisted of 0.45 mol L^{-1} $[NBut_4]BF_4$ plus 0.05 mol L^{-1} $[NBut_4]Cl$. The half-wave potentials of ferrocenium / ferrocene couple (Fc^+ / Fc) are 0.55 V and 0.52 V against this reference electrode in dichloromethane and CH_3CN, respectively. All the potentials in this work were quoted against the half-wave potential of this redox couple in CH_3CN. Crystallographic data of the complexes were collected on a Gemini diffractometer with graphite-monochromated Cu–Kα radiation ($\lambda = 1.54184$ Å). The crystal structures were solved using direct methods in SHELXS program and refined by full-matrix least-squares routines, based on F^2, using the SHELXL package. Details of crystal data and structure refinement for these complexes are provided in Table S2.

1.2 Synthesis of 2,6-diformylfuran (DFF)

5-hydroxymethylfurfural (2.520 g, 20 mmol), CuI (0.189 g, 1 mmol), TMEDA (0.117 g, 1 mmol) and TEMPO (156 mg, 1 mmol) were dissolved in 20 mL of dichloromethane. The reaction mixture was stirred at 25 °C for 24 h under rigorous stirring. After the end of the reaction， the solvent was removed and the crude product was purified by flash chromatography using silica gel (petroleum ether/ethyl acetate = 10/1, v/v) to give white solid (2.28 g, 92.0%). ^1H NMR ($CDCl_3$, 400 M, ppm): 9.86 (s, 2H), 7.33 (s, 2H); ^{13}C NMR ($CDCl_3$, 101 M, ppm): 179.2, 154.1, 119.3.

1.3 Synthesis of TEMPOH

The synthesis of TEMPOH was following the reported procedure.[1] TEMPO (0.5 g, 3.2 mmol) was added into a round flask charged with sodium ascorbate (1.0 g, 5.3 mmol) and H_2O (9 mL). Then the suspension was stirred vigorously at room temperature until completely decolorized with the appearance of a white precipitate. The resulting suspension was extracted with diethyl ether. Afterward, the ether extracts were washed with water and brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure to provide TEMPOH (white solid, 476 mg, 94.6%). ^1H NMR

(400 MHz, $CDCl_3$, ppm): δ 1.49 (s, 6H), 1.14 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$, ppm): δ 58.5, 39.4, 16.9.

2. Tables and figures

Table S1 Comparison of TMEDA with other bidentate ligands [a]

Entry	Ligand	Auxiliary ligand	Yield (%)[b]
1	TMEDA	NMI	72 / 70[c]
2	Pyridin-2-ylmethanamine	NMI	65 / 61[c]
3	2,2’-Bpy	/	34
4	Ethylenediamine	/	11
5	1,10-Phenanthroline	/	trace
6	Quinolin-8-ol	/	trace

[a] Reaction conditions: 1-octanol (5 mmol), bidentate ligand (0.25 mmol), CuI (0.25 mmol), auxiliary ligand (NMI, 0.25 mmol), TEMPO (0.25 mmol), MeCN (5 mL), air, 25 °C, 24 h.

[b] Yields calculated by GC analysis with biphenyl as an internal standard.

[c] No auxiliary ligand (NMI) was added.

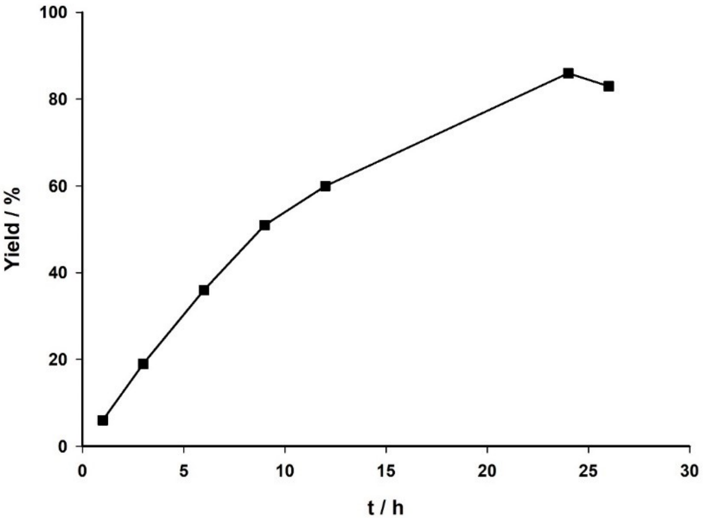


Figure S1 Effect of reaction time on the yield of product (Note: the yield decreases after 24 hours due to partial over-oxidation as a small amount of octanoic acid could be detected by GC-MS).

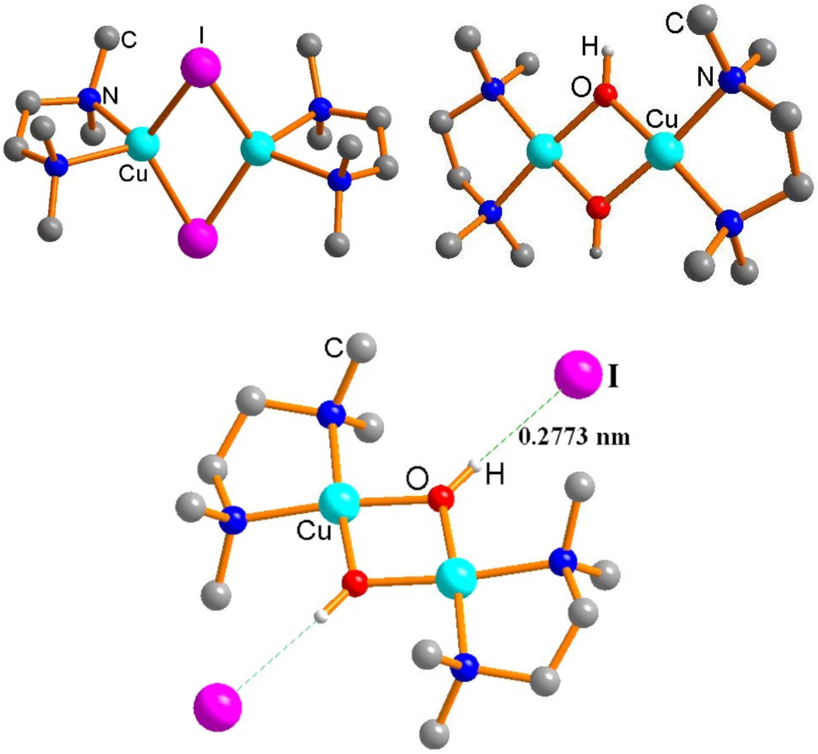


Figure S2 Crystal structures of complexes **1** (top, left) and **2** (top, right with two iodides omitted and bottom showing I···H contact of 0.2773 nm).

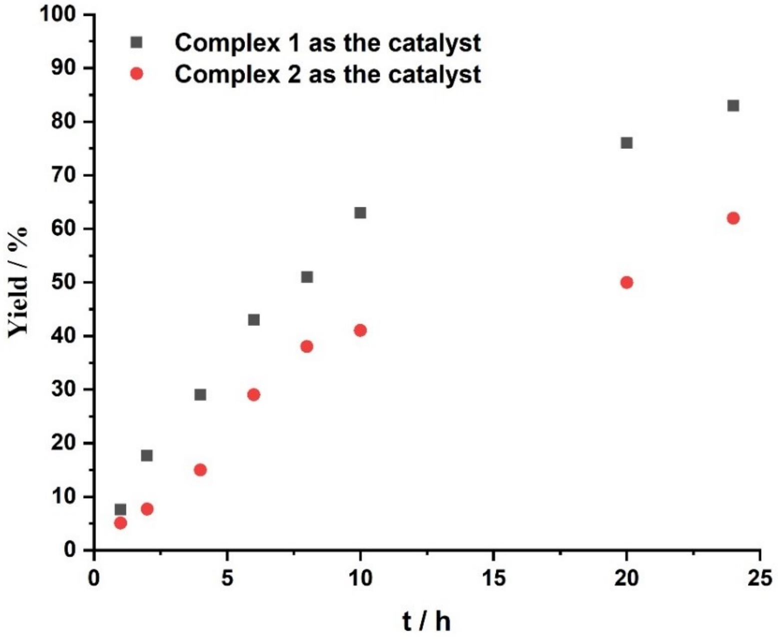


Figure S3 Comparison of the reaction yield against the time employing complexes **1** and **2** as the catalyst, respectively (Reaction conditions: 1-octanol (5 mmol), complex **1** or **2** (0.125 mmol), TEMPO (0.25 mmol, 39.1 mg), DCM (5 mL), air, 25 ^oC).

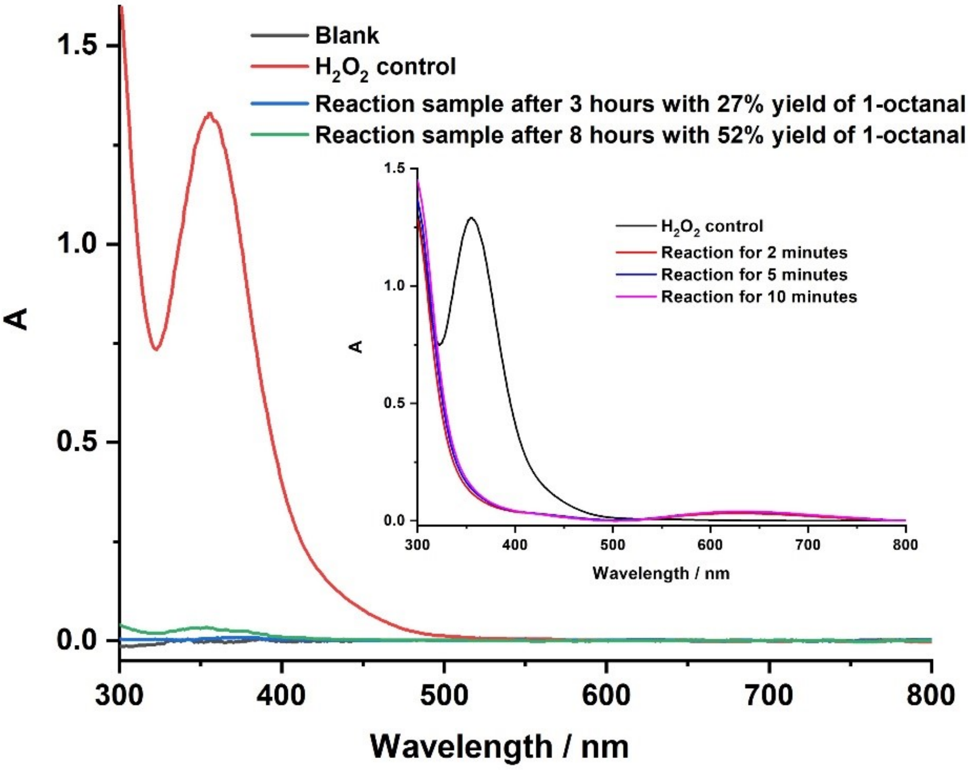


Figure S4a UV-vis spectra of the solution for detection of hydrogen peroxide with iodometric method at various stages of the catalytic reaction and the control of H_2O_2 (aq., 0.073 mmol L^{-1}). In this figure, the spectra at reaction time 3 and 8 hours, respectively, are selectively presented. Please note that the reaction solution was diluted in such a way that the concentration of H_2O_2 in the tested sample would have been 0.066 mmol L^{-1} if H_2O_2 was the sole product for O_2 in the aerobic reaction. Inset: the UV-vis spectra of H_2O_2 control and the control after being added a pseudo reaction solution at various time ($c_{(CuI)} = c_{(TMEDA)} = c_{(TEMPO)} = 0.005$ mol L^{-1}).

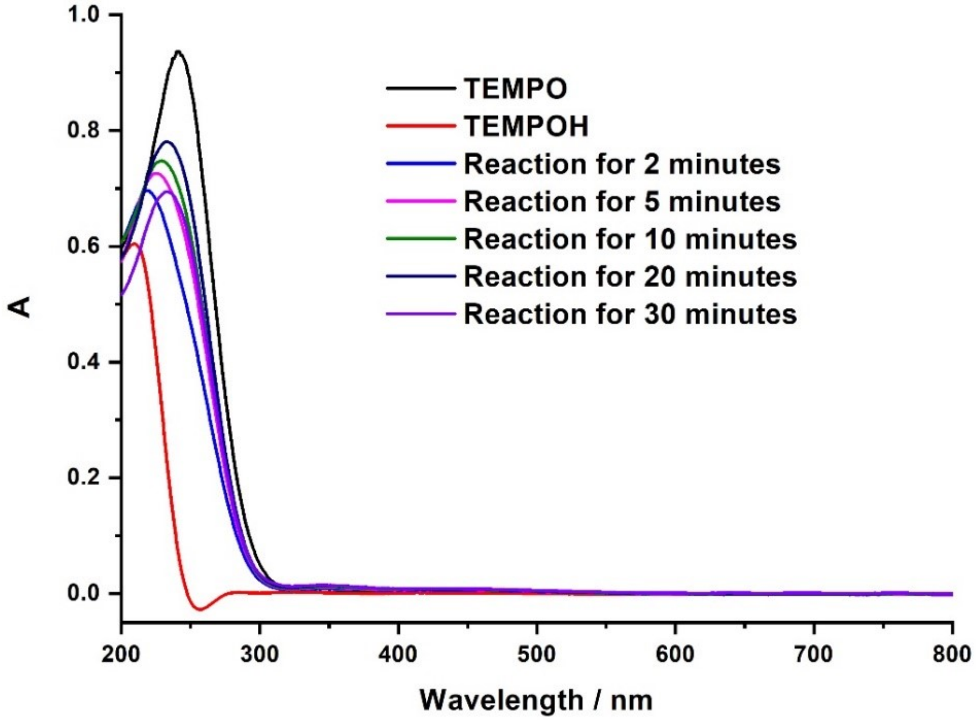


Figure S4b UV-vis spectral monitoring the conversion of TEMPOH ($c = 1.0 \times 10^{-3}$ mol L^{-1} in 3 mL of MeCN) into TEMPO oxidized by H_2O_2 ($c = 6.0 \times 10^{-2}$ mol L^{-1}, 50 μL) and the spectrum of TEMPO is in black for comparison.

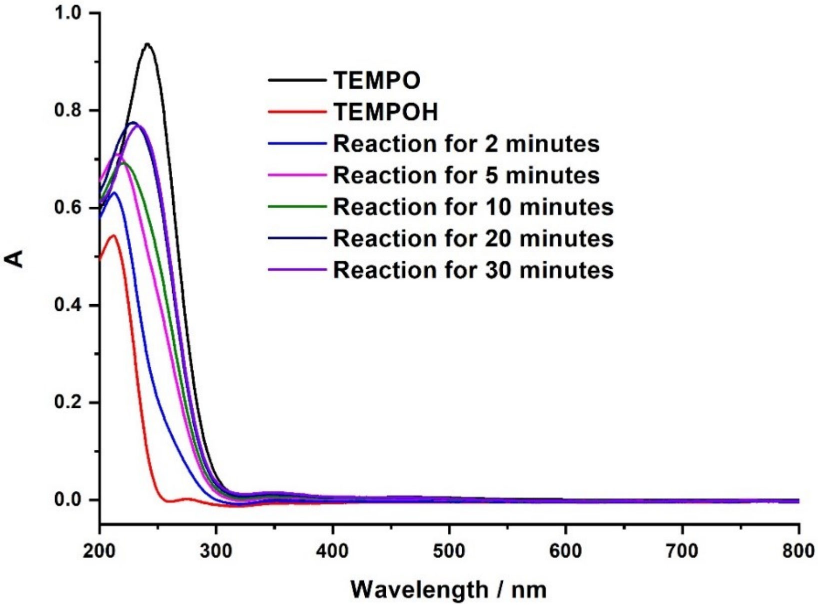


Figure S4c UV-vis spectral monitoring the conversion of TEMPOH (c = 1.0 × 10^{-3} mol L^{-1} in 3 mL of MeCN) into TEMPO oxidized by constantly bubbling O_2 through the mixture and the spectrum of TEMPO is in black for comparison.

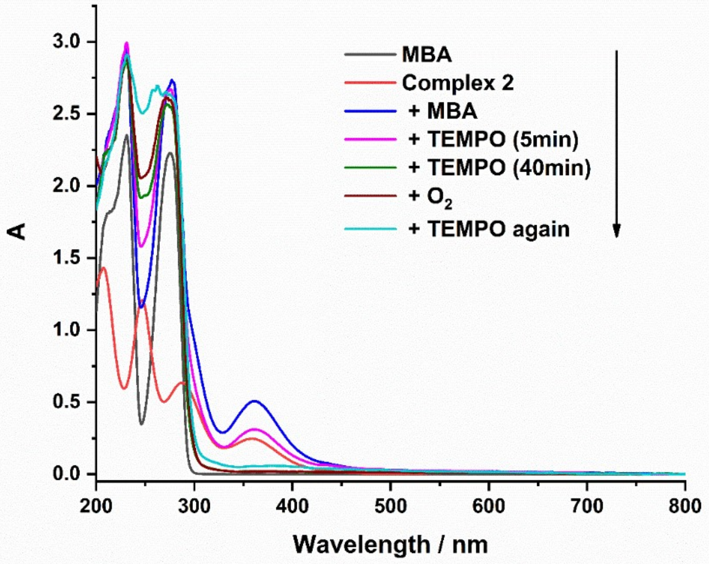


Figure S5a Stepwise monitoring the reaction catalyzed by complex **2** in MeCN upon the addition of the components in the reaction by using UV-vis spectroscopy ($c_{(\text{complex } \mathbf{2})}$ = 5.0 × 10^{-5} mol L^{-1}, $c_{(\text{TEMPO})}$ = 1.0 × 10^{-4} mol L^{-1}, $c_{(\text{MBA})}$ = 2.0 × 10^{-3} mol L^{-1}).

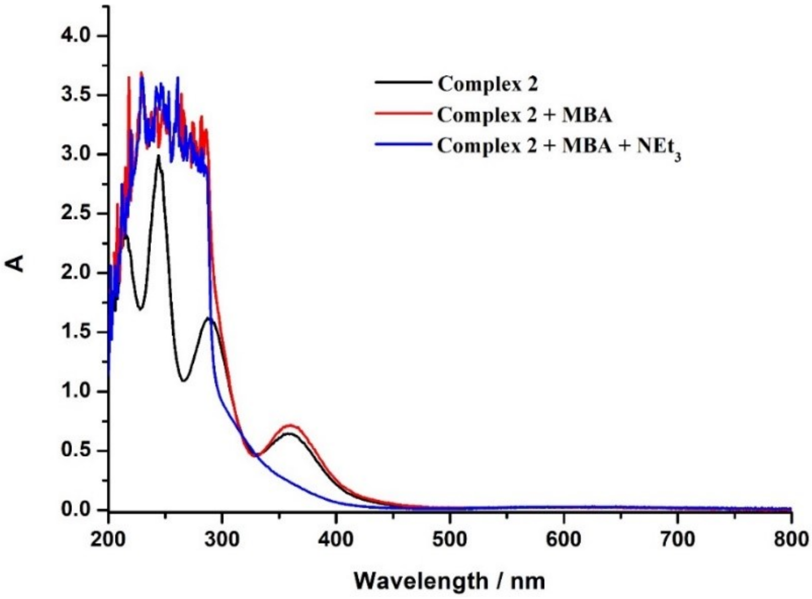
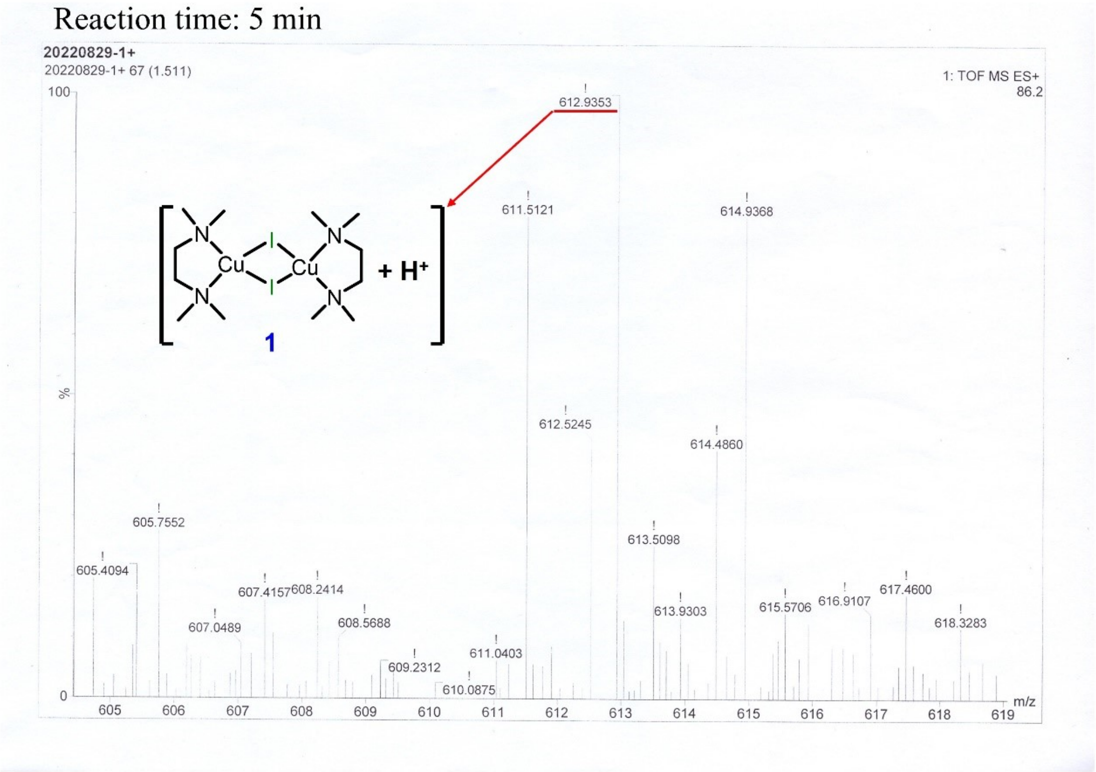


Figure S5b Stepwise monitoring of complex **2** upon the addition of the substrate using UV-vis spectroscopy (MBA = 4-Methoxybenzyl alcohol) and triethylamine (TEA or NEt$_3$) ($c_{(\text{complex } \mathbf{2})} = 1.0 \times 10^{-4}$ mol L^{-1}, $c_{(\text{MBA})} = 2.0 \times 10^{-4}$ mol L^{-1}, $c_{(\text{TEA})} = 5.0 \times 10^{-4}$ mol L^{-1}).



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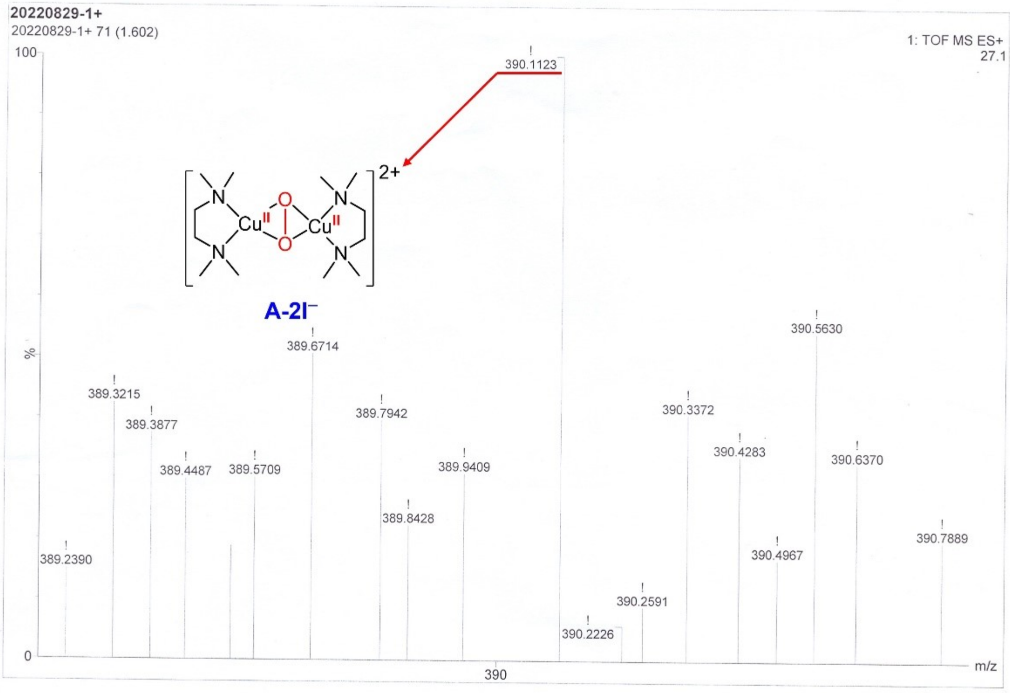

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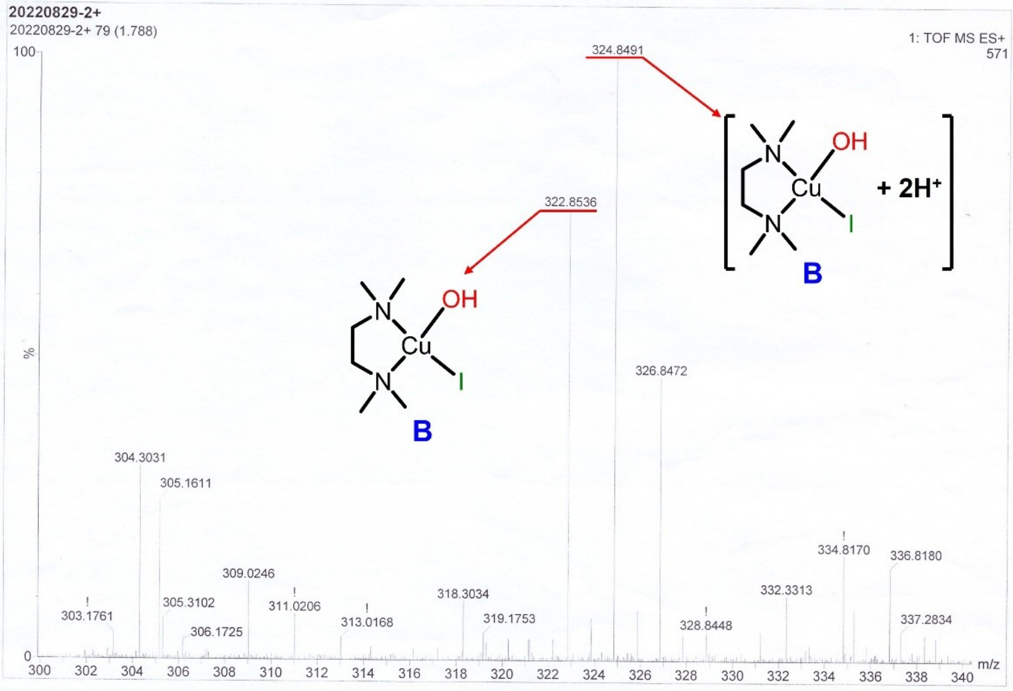

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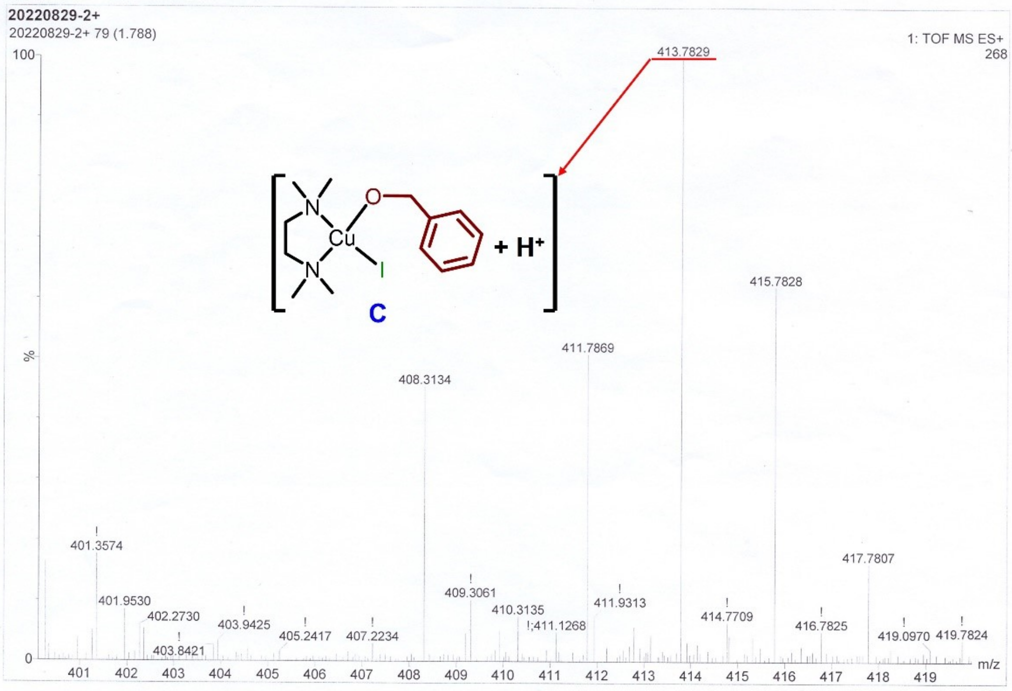

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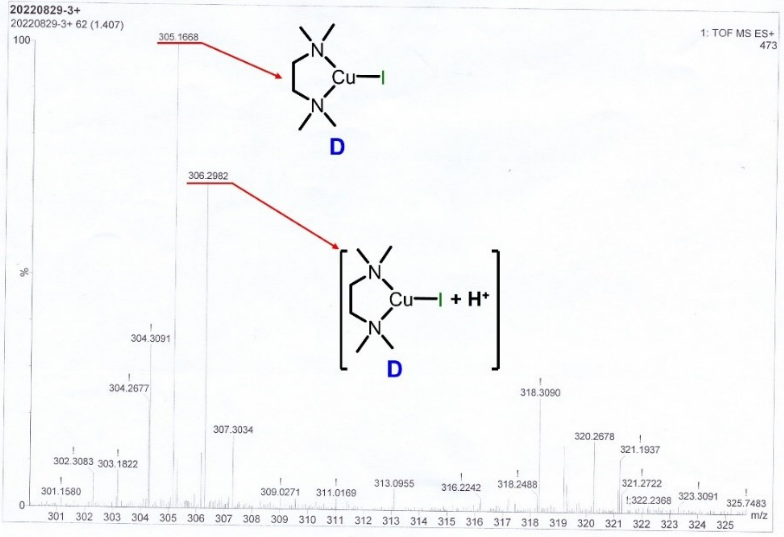
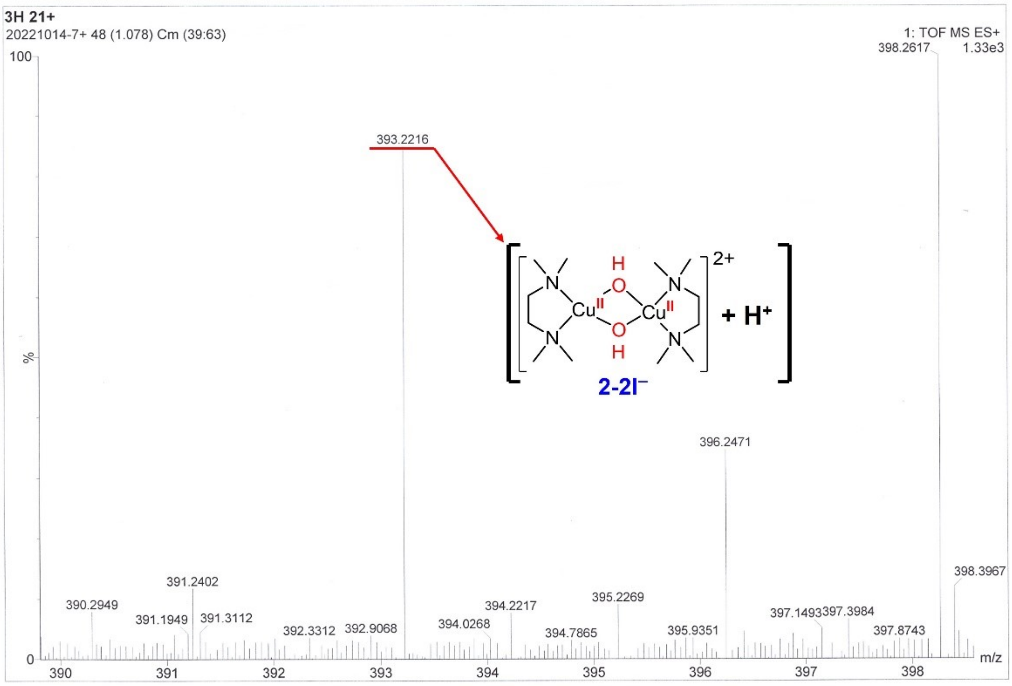


Figure S6 Tandem ESI-MS monitoring of the reaction catalyzed by CuI/TMEDA/TEMPO system with benzyl alcohol as the substrate. Reaction conditions: benzyl alcohol (5 mmol), CuI (0.25 mmol), TMEDA (0.25 mmol), TEMPO (0.25 mmol), DCM (5 mL), air, 25 °C.

Reaction time: 3 h



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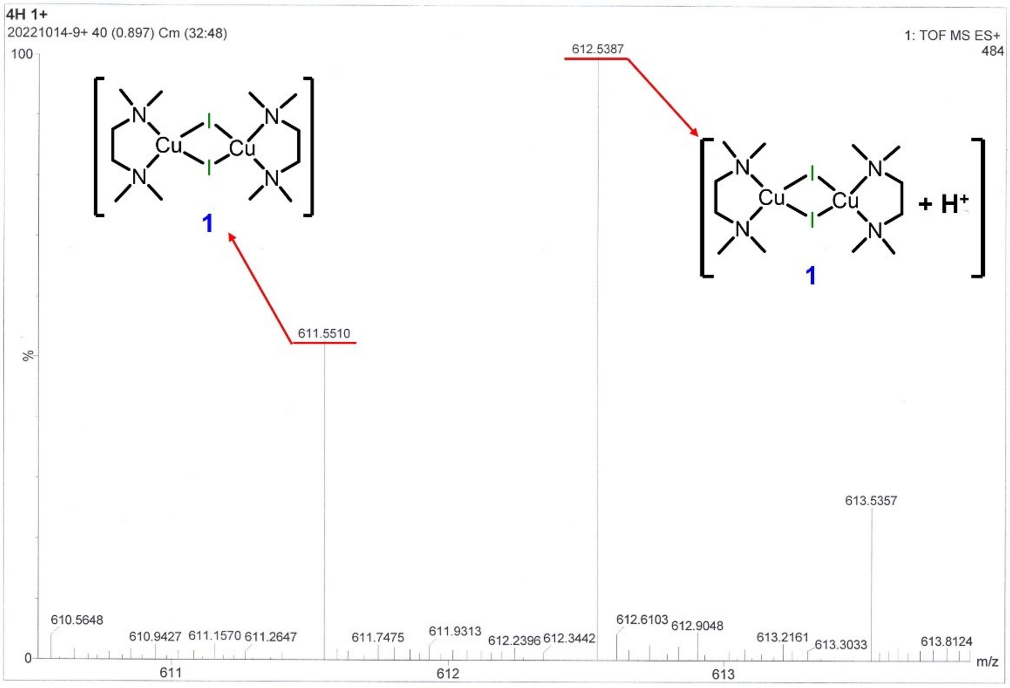

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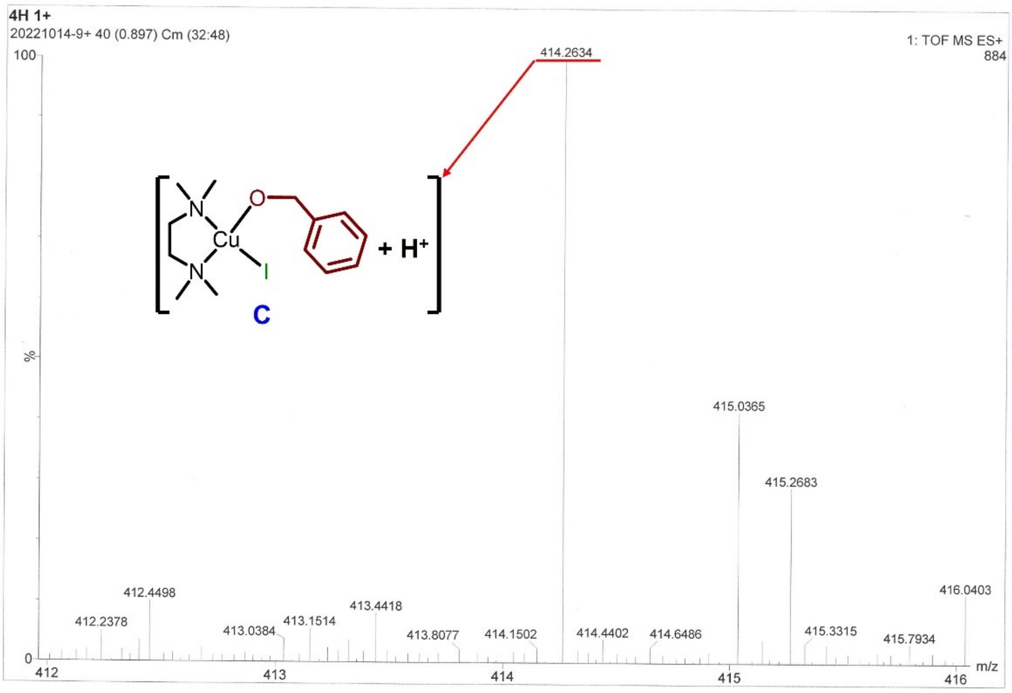
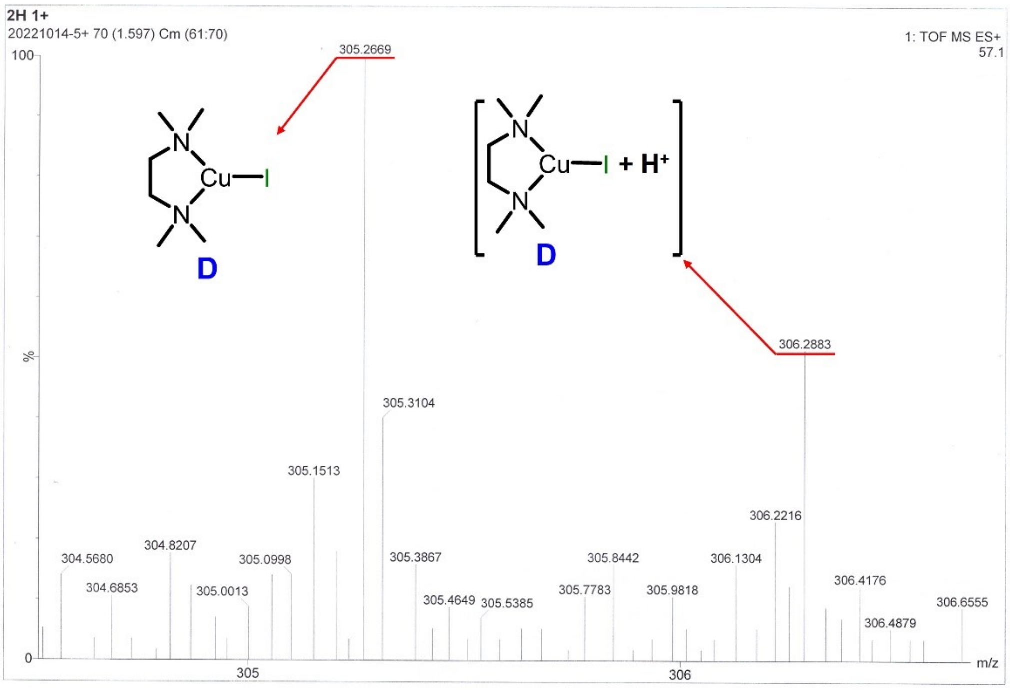
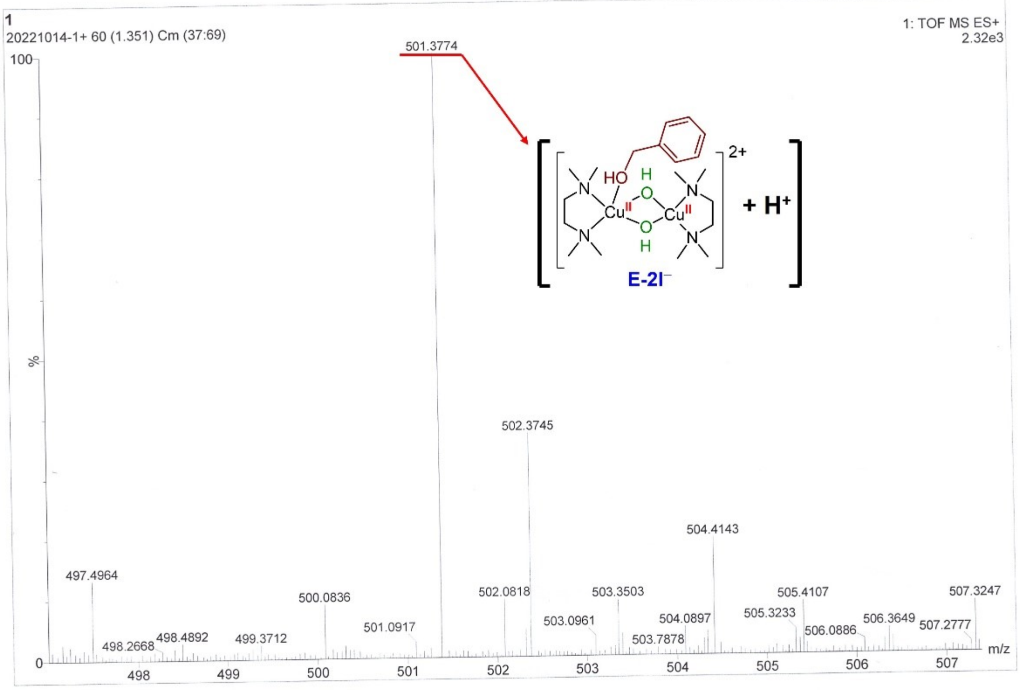


Reaction time: 2 h



Reaction time: 0.5 h



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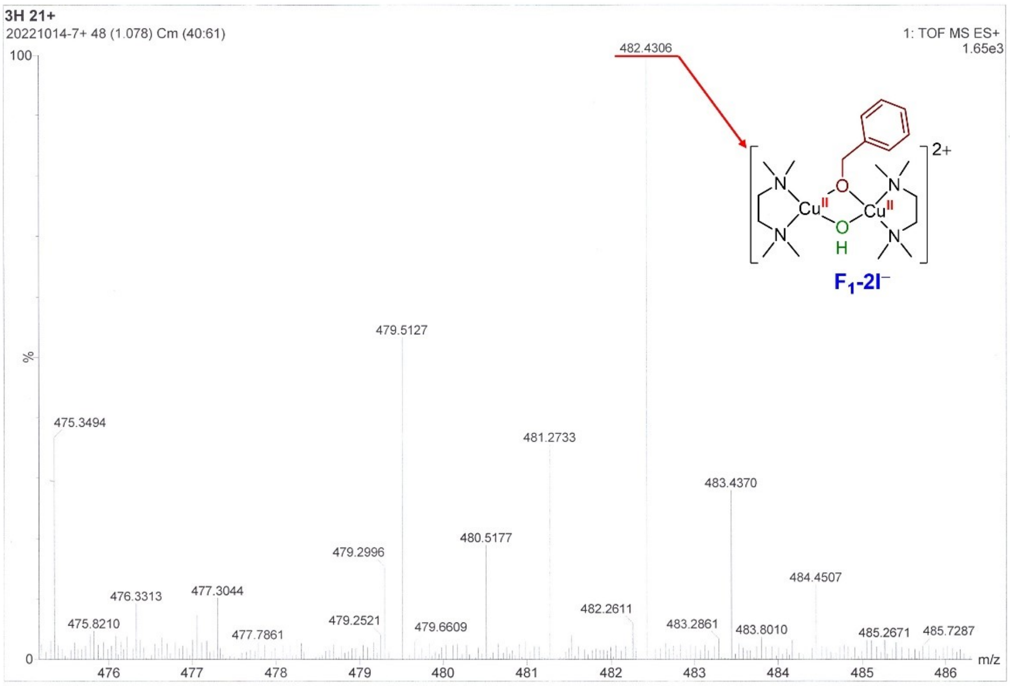

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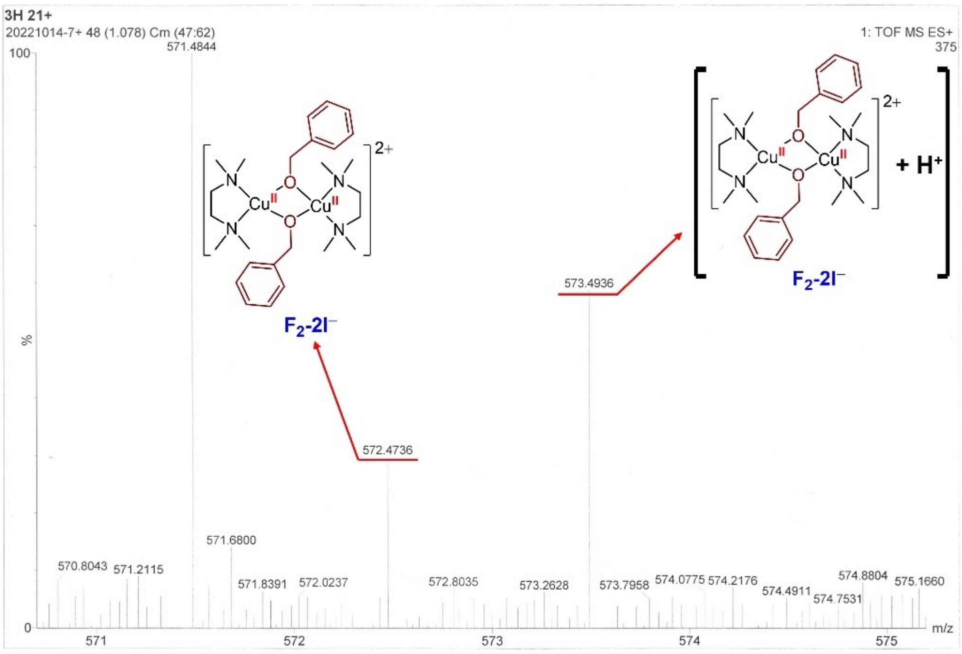

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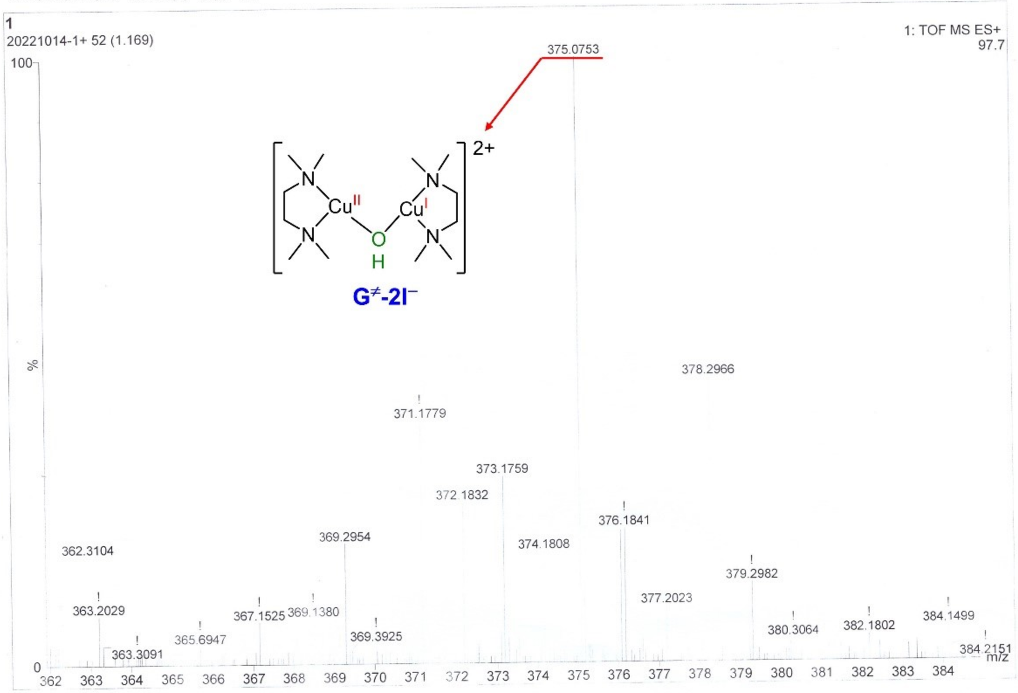


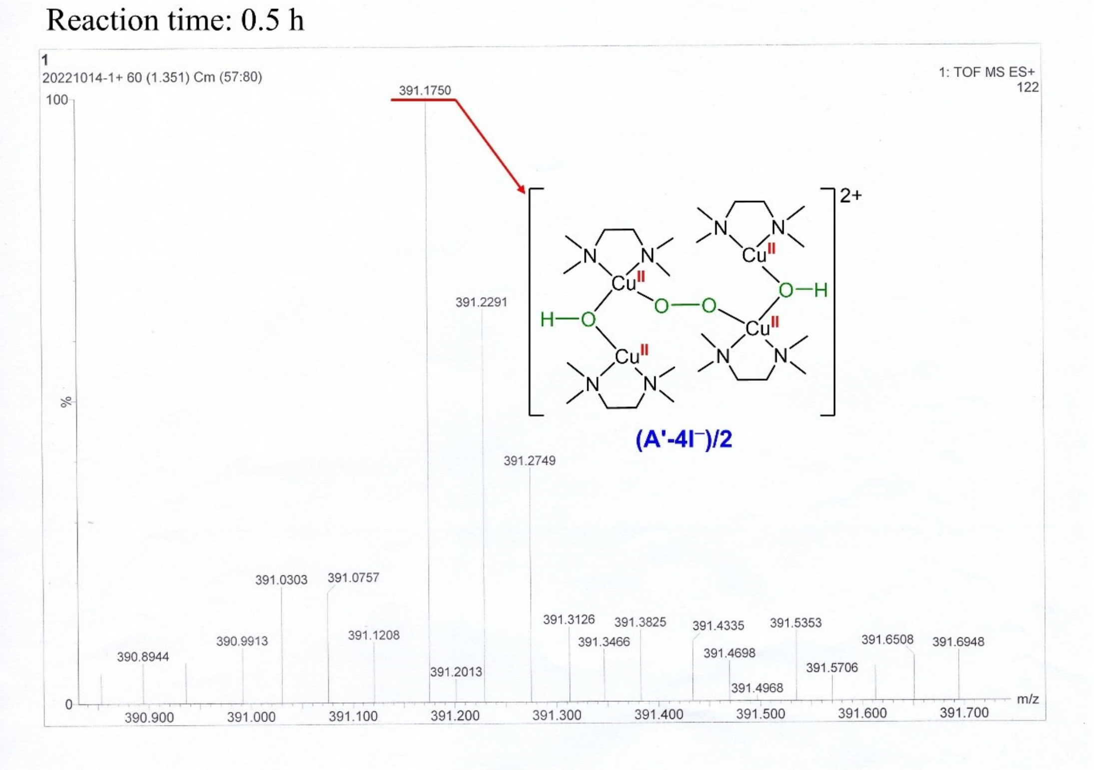
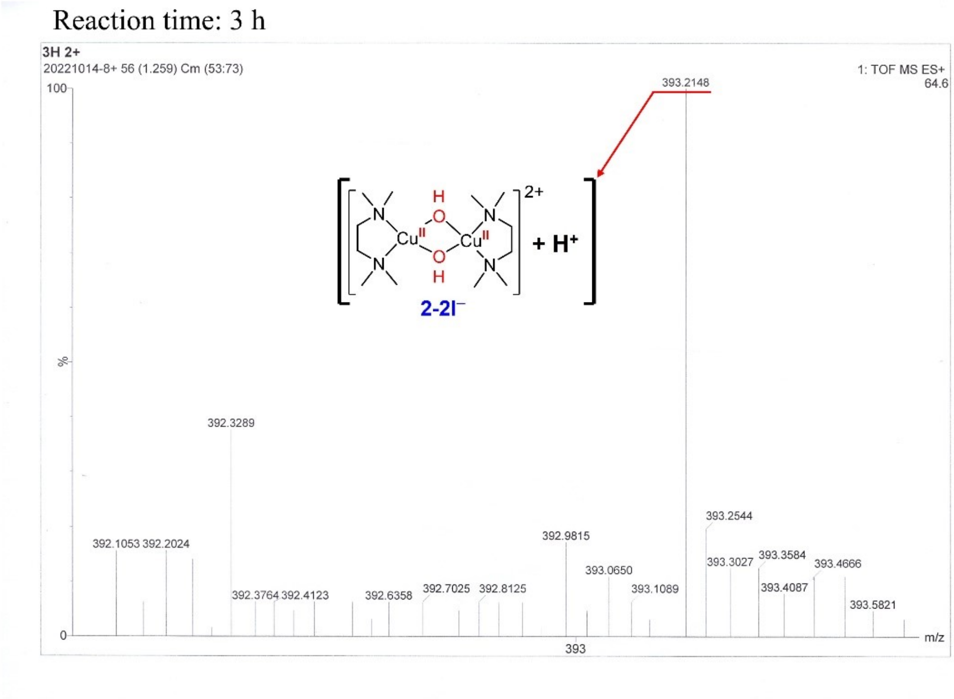
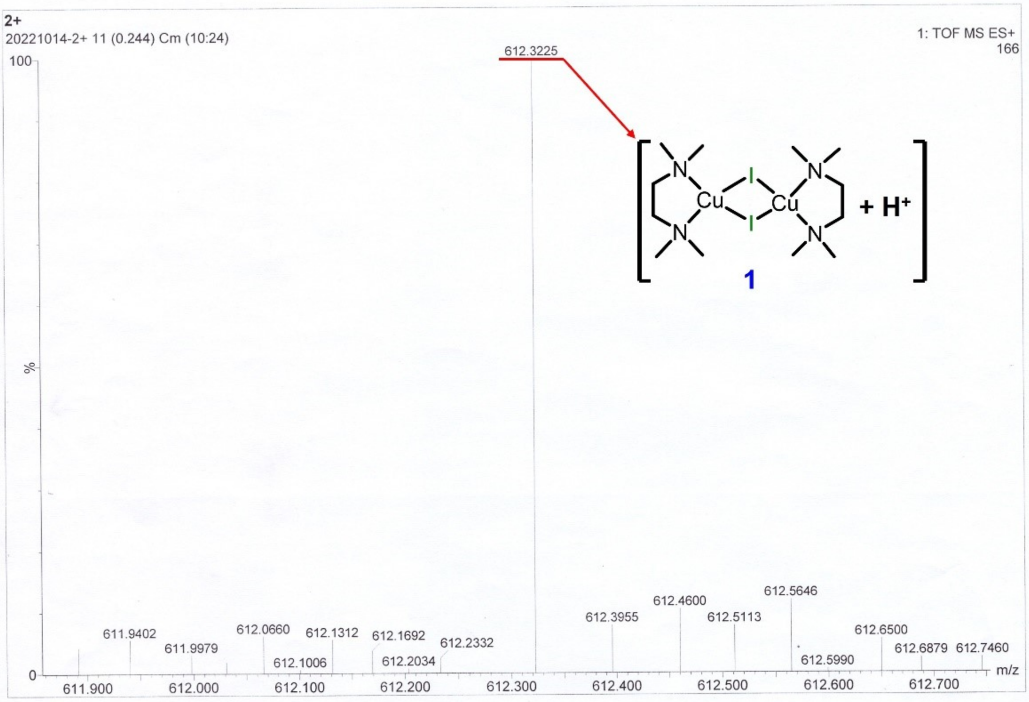


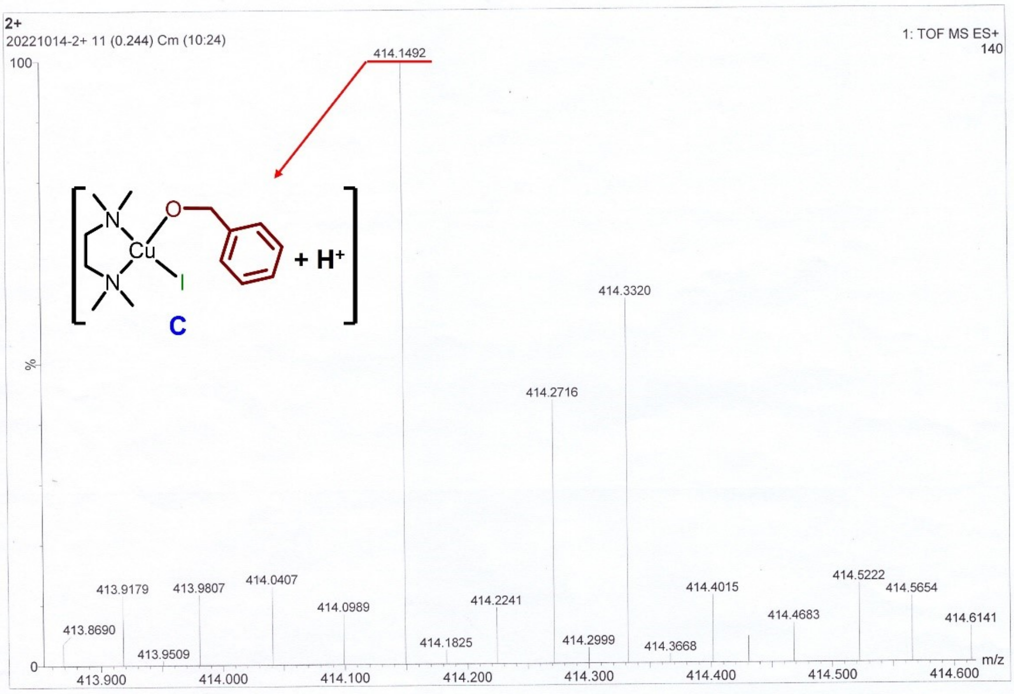
Figure S7 Tandem ESI-MS monitoring of the reaction catalyzed by complex **2**/TEMPO system with benzyl alcohol as the substrate. Reaction conditions: benzyl alcohol (5 mmol), complex **2** (0.125 mmol), TEMPO (0.25 mmol), DCM (5 mL), air, 25 ^{o}C.



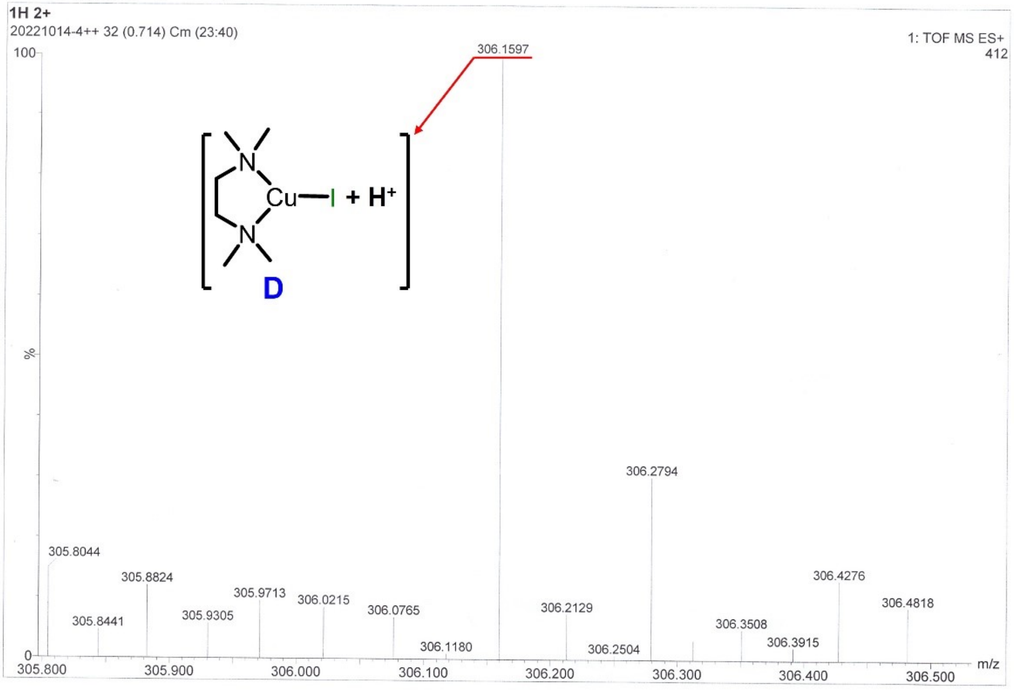
Reaction time: 0.5 h



Reaction time: 0.5 h



Reaction time: 1 h



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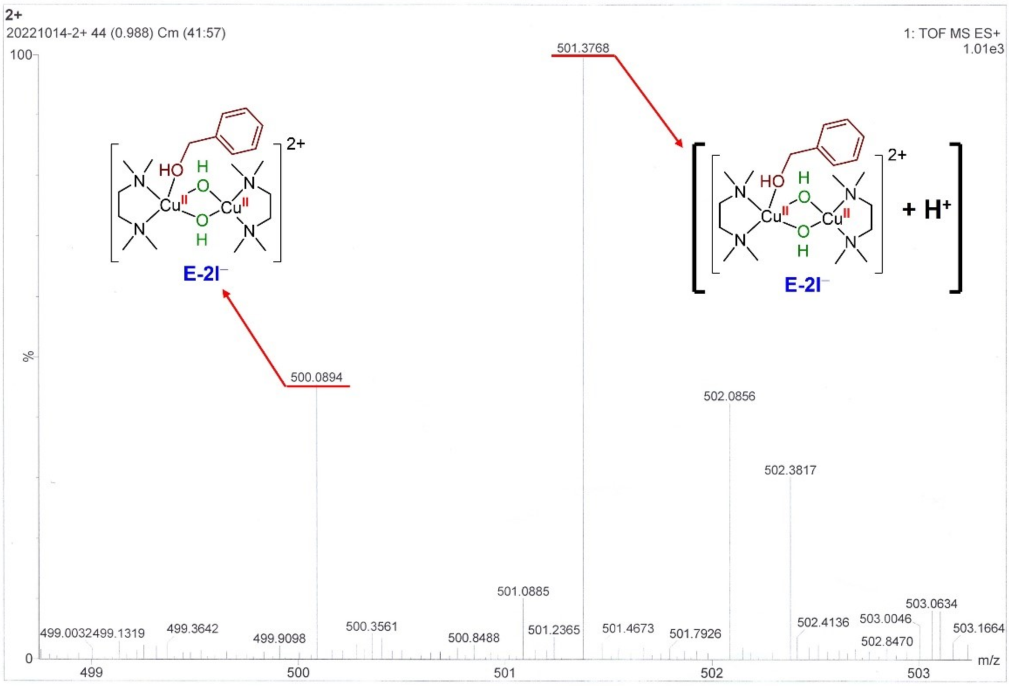
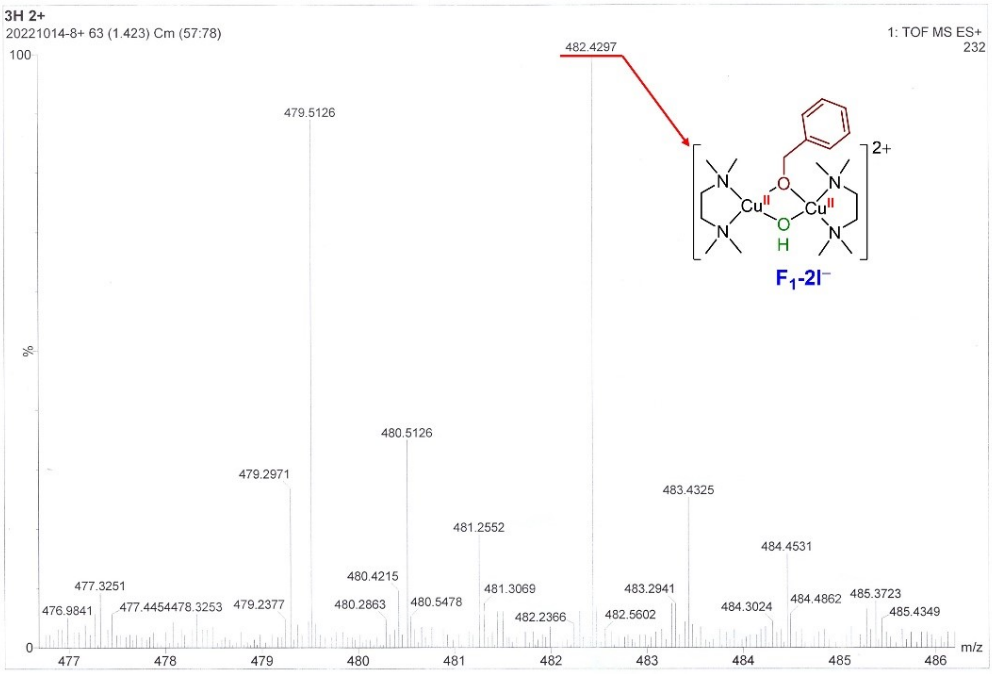


Reaction time: 3 h



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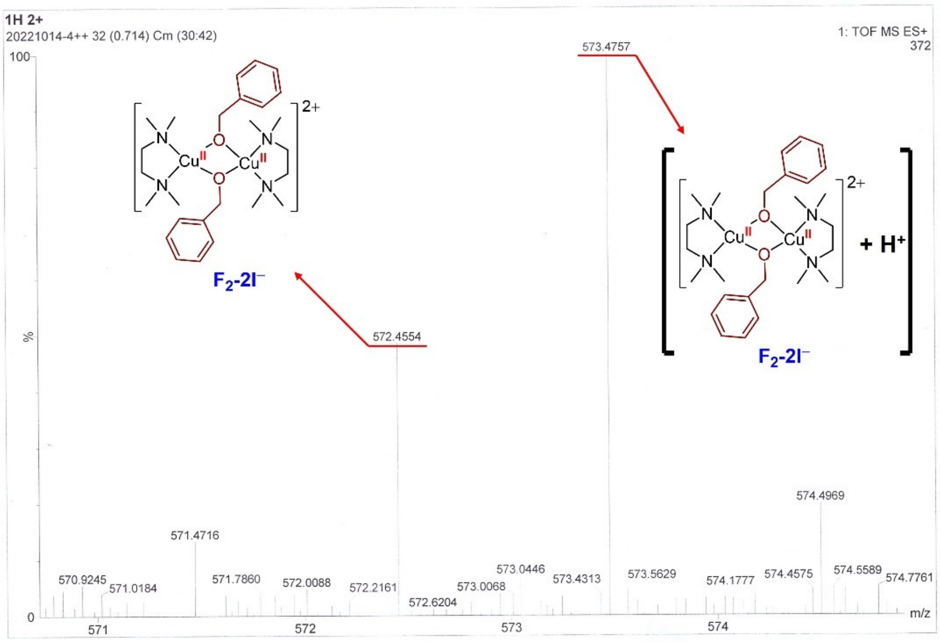


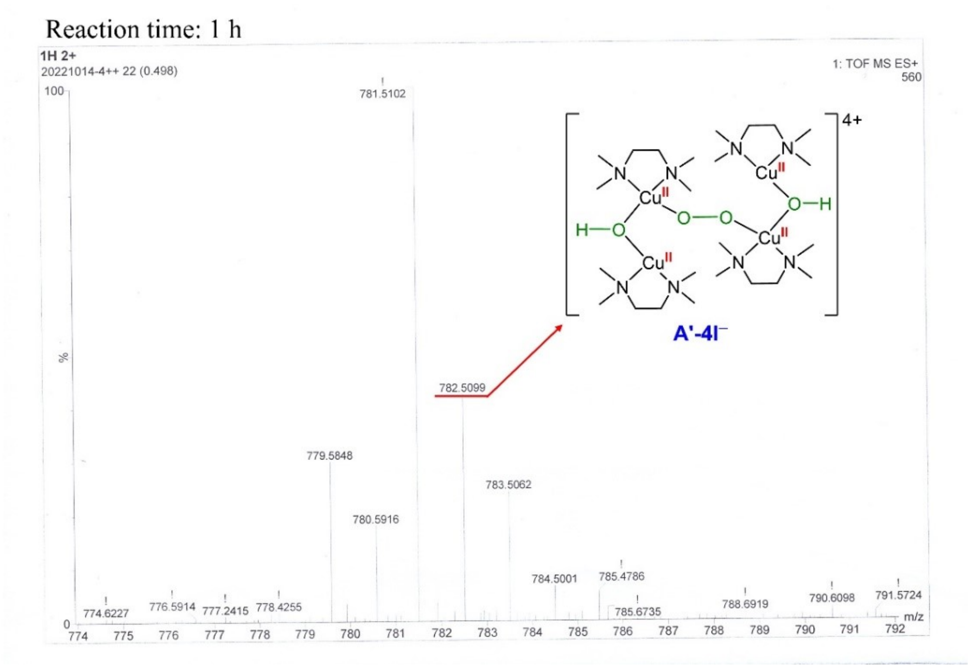


Figure S8 Tandem ESI-MS monitoring of the reaction catalyzed by complex **2**/TEMPO system with added KI and benzyl alcohol as the substrate. Reaction conditions: benzyl alcohol (5 mmol), complex **2** (0.125 mmol), KI (0.50 mmol), TEMPO (0.25 mmol), DCM (5 mL), air, 25 °C.

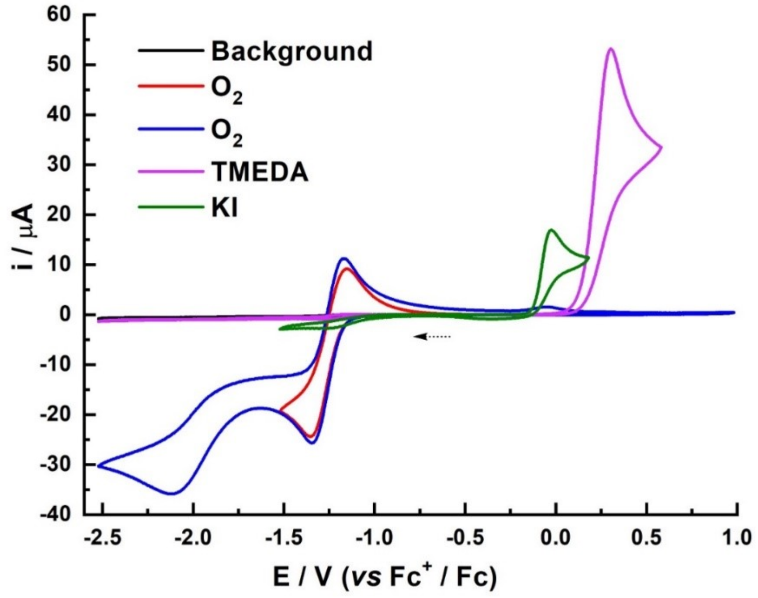


Figure S9 Cyclic voltammograms of O_2 (bubbling O_2 into the solution), TMEDA (5.0×10^{-3} mol L^{-1}) and KI (5.0×10^{-3} mol L^{-1}) in 0.10 mol L^{-1} $[NBut_4]BF_4$ / MeCN (starting potential = −0.50 V, scanning rate = 0.1 V s^{-1}, 298 K).

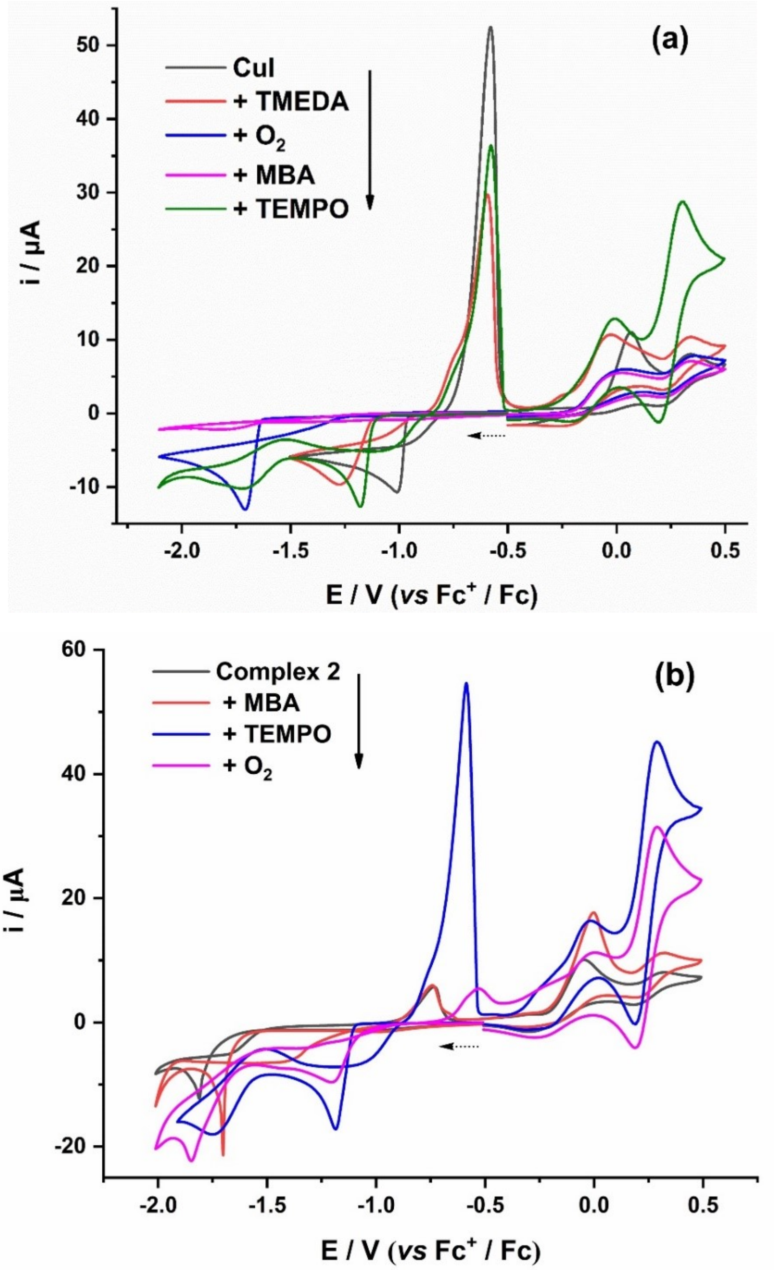


Figure S10 Cyclic voltammograms of the catalyst systems in 0.10 mol L^{-1} $[NBut_4]BF_4$ / CH_3CN (starting potential = –0.50 V, scanning rate = 0.1 V s^{-1}, 298 K, and the arrow indicating the sweeping direction), (a) CuI (5.0×10^{-3} mol L^{-1}) upon successive addition of the ligand (5.0×10^{-3} mol L^{-1}), O_2, MBA (0.10 mol L^{-1}) and TEMPO (5.0×10^{-3} mol L^{-1}); (b) Complex **2** (2.5×10^{-3} mol L^{-1}) upon successive addition of MBA (0.10 mol L^{-1}) and TEMPO (5.0×10^{-3} mol L^{-1}) and then O_2.

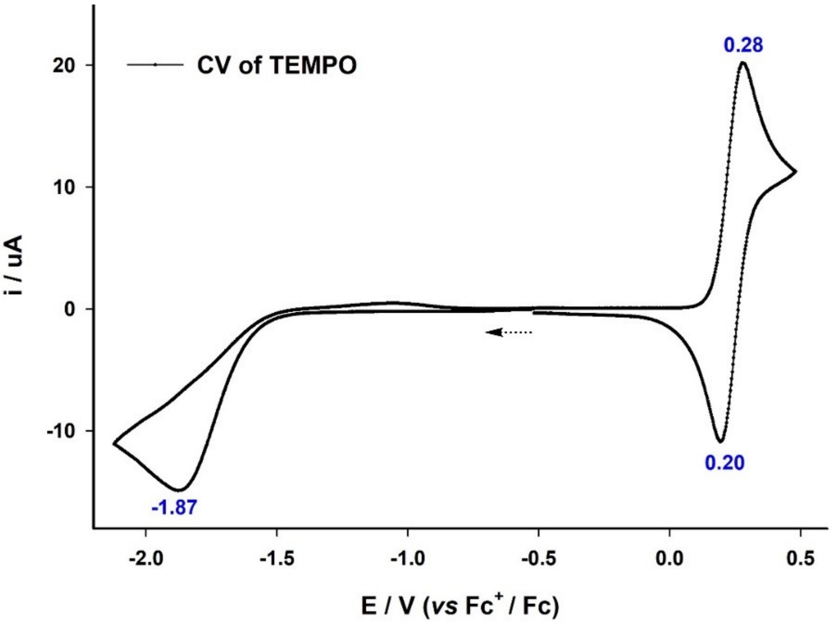


Figure S11 Cyclic voltammogram of TEMPO in 0.1 mol L^{-1} $[NBut_4]BF_4$ / CH_3CN ($c_{(TEMPO)} = 5.0 \times 10^{-3}$ mol L^{-1}, starting potential = –0.50 V, scan rate = 0.1 V s^{-1}, 298 K).

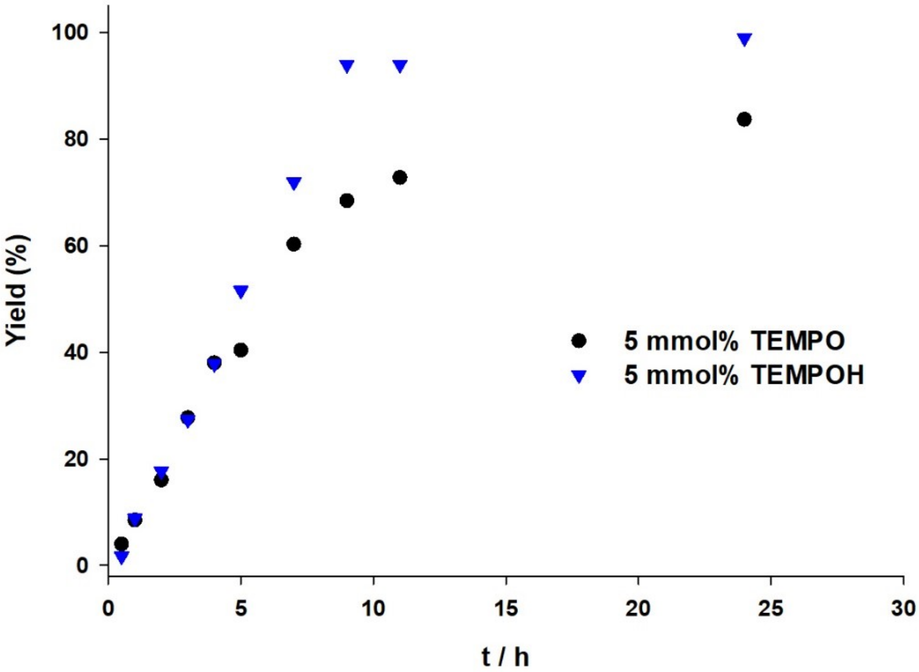


Figure S12 Comparison for the effect of TEMPO and TEMPOH on the catalysis.

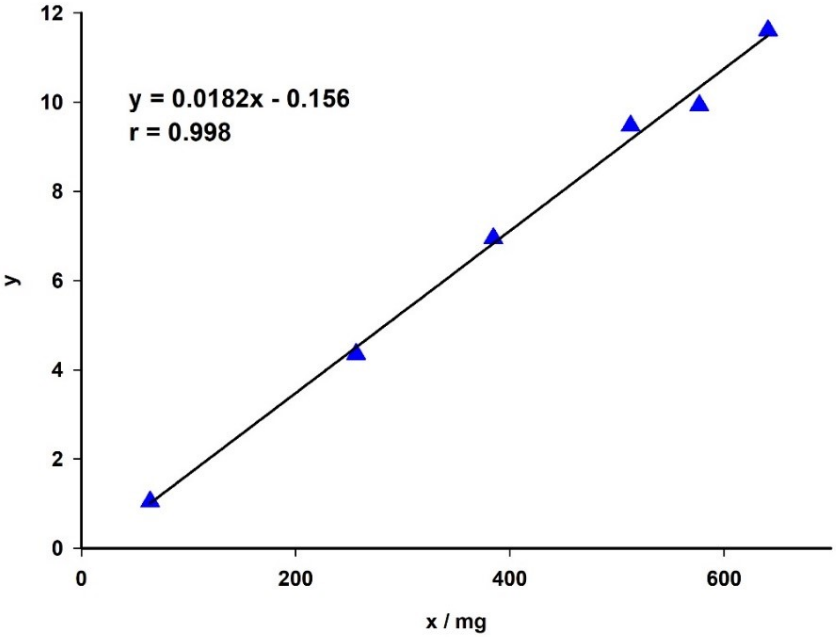
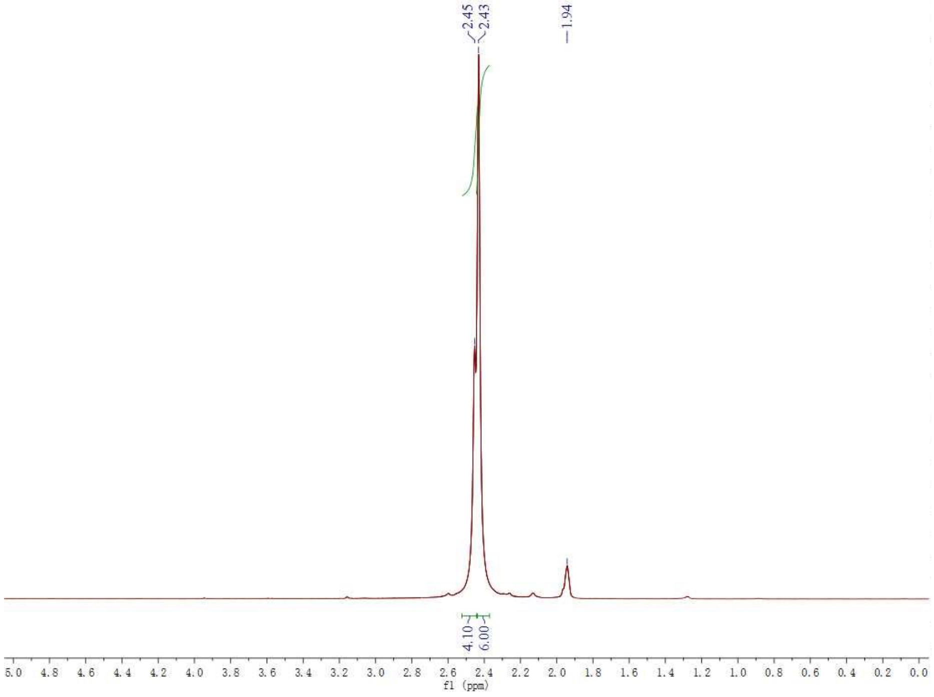


Figure S13 The calibration curve of 1-octanal using biphenyl as the internal standard.



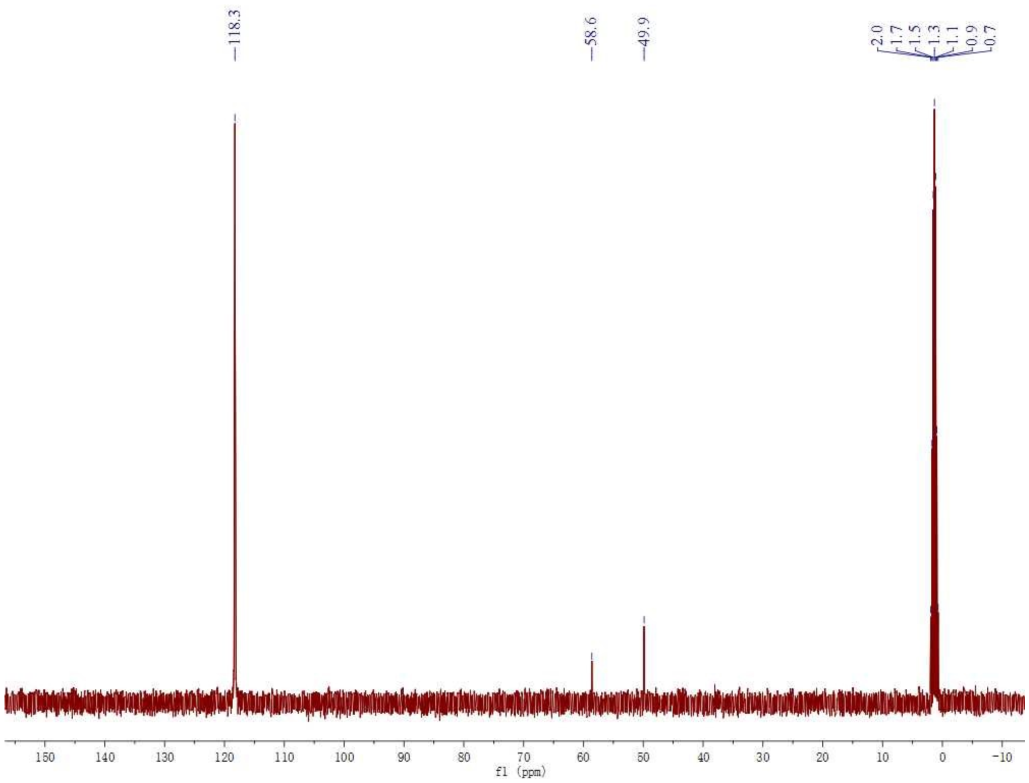
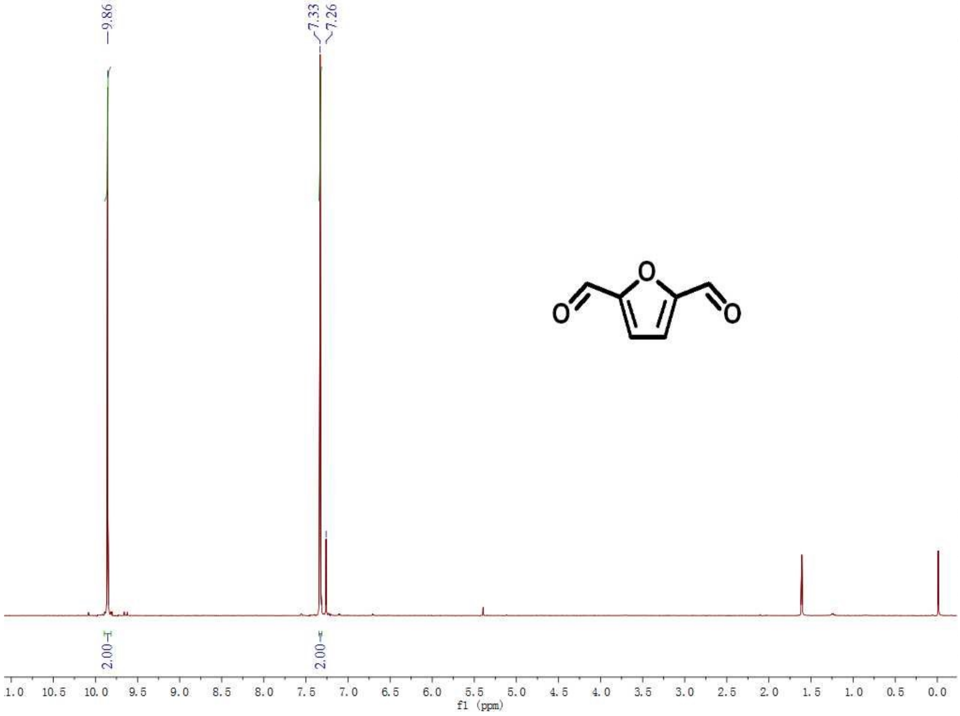


Figure S14 ^{1}H NMR and ^{13}C NMR spectra of complex **1** in CD_3CN solution.



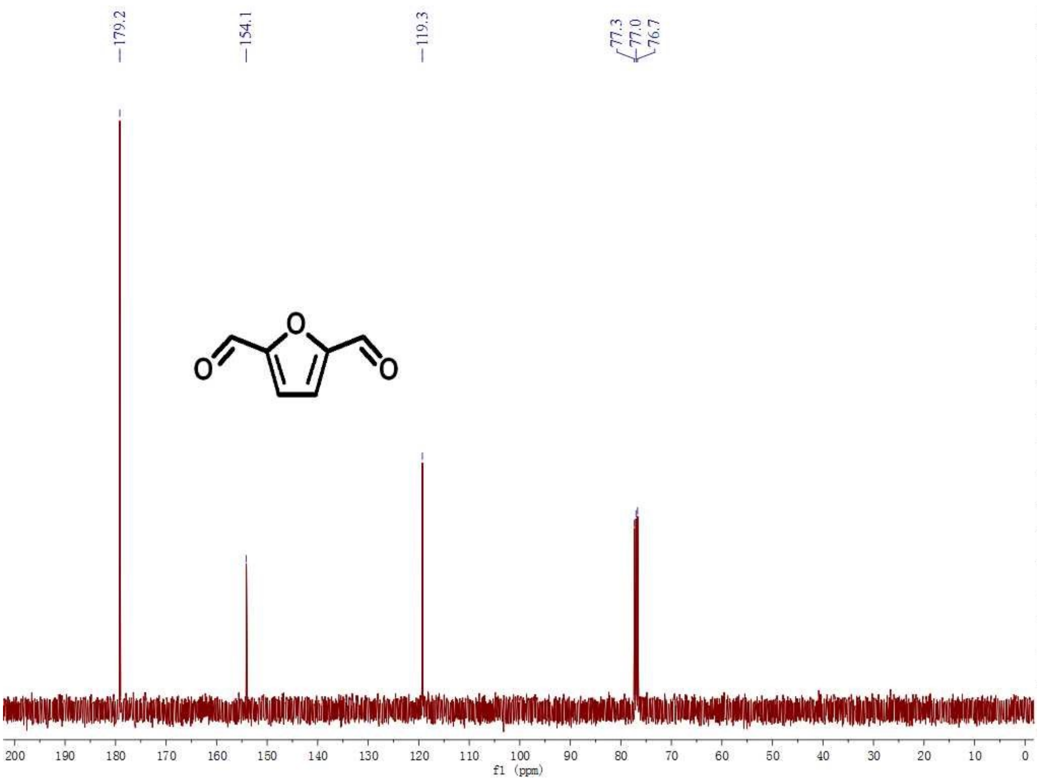
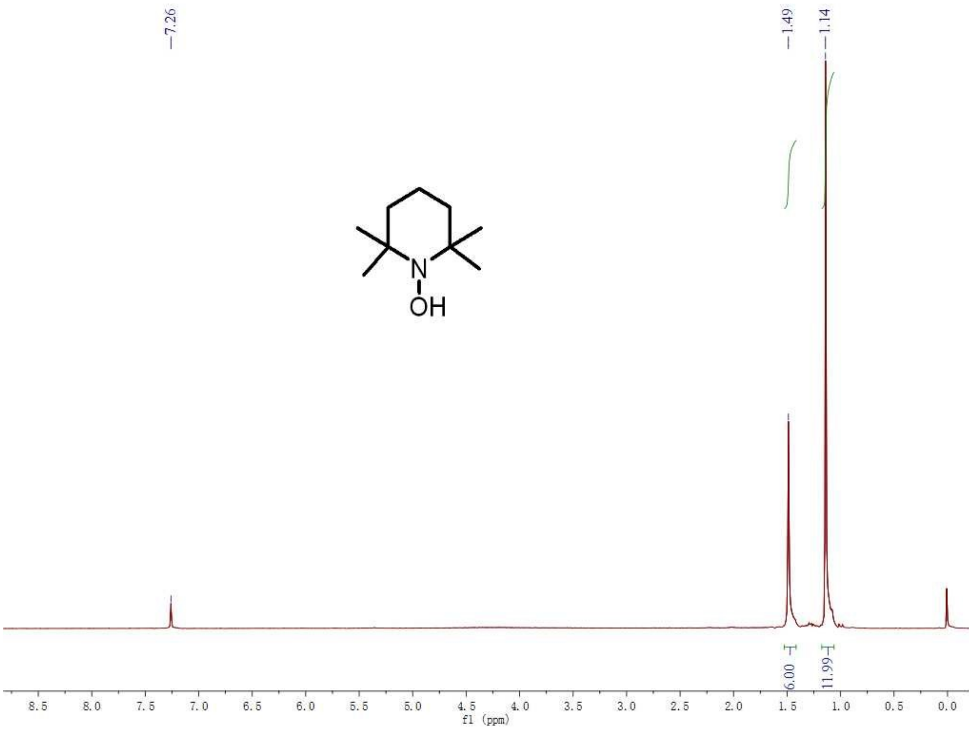


Figure S15 ^{1}H NMR and ^{13}C NMR spectra of 2,6-diformylfuran in $CDCl_3$ solution.



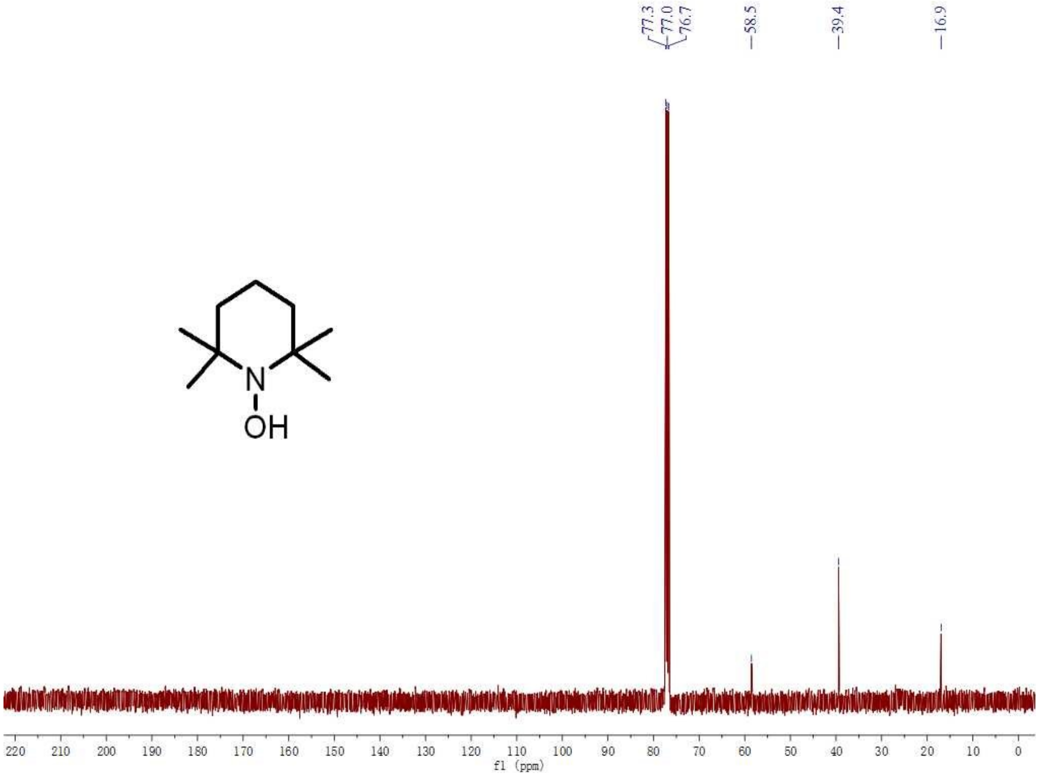


Figure S16 ^{1}H NMR and ^{13}C NMR spectra of TEMPOH in $CDCl_3$ solution.

Table S2 Crystallographic details for complexes **1** and **2**

Complex	**1**	**2**
Chemical formula	$C_{12}H_{32}Cu_2I_2N_4$	$C_{12}H_{34}Cu_2I_2N_4O_2$
CCDC number	/	2168446
Formula weight	613.30	647.31
Crystal size (mm)	0.29 × 0.21 × 0.17	0.47 × 0.33 × 0.25
Temperature (K)	293(2)	293(2)
Radiation	1.54184	1.54184
Crystal system	Monoclinic	Monoclinic
Space group	P21/c	P21/n
a (Å)	12.3749(5)	7.2810(4)
b (Å)	12.1265(4)	14.5330(7)
c (Å)	15.3714(8)	11.0519(6)
α (°)	90	90
β (°)	109.140(5)	103.619(5)
γ (°)	90	90
V (Å^3)	2179.19(16)	1136.56(10)
Z	4	2

$\rho_{(calc)}$ (g/cm^3)	1.869	1.891
F (000)	1184	628
Absorp.coeff. (mm^{-1})	24.620	23.710
θ range (deg)	3.78 to 72.26	5.12 to 72.11
Reflns collected	7775 (R_{int} = 0.1415)	3736 (R_{int} = 0.0360)
Indep. reflns	4211	2170
Refns obs. [$I > 2\sigma(I)$]	2898	1975
Data/restr/paras	4211/0/189	2170/0/104
GOF	1.383	1.033
R_1/wR_2 [$I > 2\sigma(I)$]	0.1513/0.3689	0.0418/0.1069
R_1/wR_2 (all data)	0.1727/0.4054	0.0459/0.1120
Large peak and hole (e/Å^3)	5.881/–7.465	1.220/–1.190

Table S3 The addition of H_2O to affect the catalysis [a]

Entry	MeCN:H_2O (v/v)	Yield (%)[b]
1	MeCN	70
2	98:2	46
3	95:5	40
4	90:10	32
5	80:20	15

[a] Reaction conditions: 1-octanol (651 mg, 5 mmol), CuI (47.2 mg, 0.25 mmol), TMEDA (29.0 mg, 0.25 mmol), TEMPO (39.1 mg, 0.25 mmol), solvent (5 mL), air, 25 °C, 24 h.

[b] Yields calculated by GC analysis with biphenyl as an internal standard.

Reference

1. Y. Zhu, L. Li, Z. Shen. *Chem. Eur. J.* 2015, **21**, 13246–13252.