Supporting Information

Cu(I) Coordination Polymers as the Green Heterogeneous Catalysts for Direct C-H Bonds Activation of Arylalkanes to Ketones in Water with Spatial Confinement Effect

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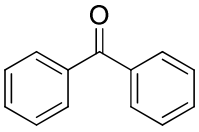
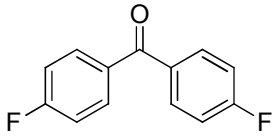
Contents

1. General Method. All reagents and solvents were commercially available and used as received without further purification. ^{1}H spectra were obtained with Bruker Avance-400 spectrometers. Chemical shifts are reported as δ (ppm) downfield with respect to an internal standard of tetramethylsilane (TMS). FT-IR spectra were recorded on a Bruker-ALPHA spectrophotometer with KBr pellets in 400-4000 cm^{-1} region. Powder X-ray diffraction (PXRD) patterns were recorded using Cu Kα1 radiation on a PANalyticalX'Pert PRO diffractometer. Atomic absorption spectrum (AAS) was performed on a Z28000 graphite-oven atomic absorption Spectrophotometer.

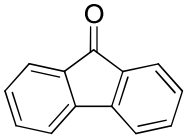
2. Synthesis



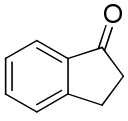
Benzophenone. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain a colorless solid 90mg (99%). This compound had been reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.76 (m, 1H), 7.64-7.55 (m, 1H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 1H) ppm.



bis(4-fluorophenyl)methanone. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain a colorless solid 101mg (93%). This compound had been reported.[2] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.85-7.79 (m, 1H), 7.21-7.13 (m, 1H) ppm.

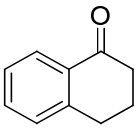


9-Fluorenone. The concentrate was purified by by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain a yellow solid 88mg (98%). This compound had been reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.63 (dt, *J* = 7.4, 0.9 Hz, 1H), 7.52-7.42 (m, 2H), 7.27 (td, *J* = 7.1, 1.6 Hz, 1H) ppm.

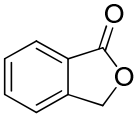


1-Indanone. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain a white solid 62 mg (96%). This

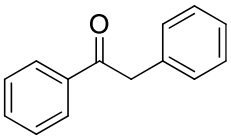
compound had been reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.76 (d, *J* = 7.7 Hz, 1H), 7.59 (td, *J* = 7.5, 1.2 Hz, 1H), 7.51-7.46 (m, 1H), 7.40-7.34 (m, 1H), 3.17-3.13 (m, 2H), 2.72-2.67 (m, 2H) ppm.



3,4-Dihydronaphthalen-1(2H)-one. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain light yellow liquid 71 mg (98%). This compound had been reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.01 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 2.98 (t, *J* = 6.0 Hz, 2H), 2.63 (t, *J* = 6.4 Hz, 2H), 2.17-2.09 (m, 2H) ppm.



isobenzofuran-1(3H)-one. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain light yellow liquid 58 mg (88%). This compound had been reported.[1] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* =7.7 Hz, 1H), 7.79-7.61 (m, 1H), 7.61-7.41 (m, 2H), 5.33 (s, 2H) ppm.



1,2-diphenylethanone. The concentrate was purified by silica gel column chromatography using petroleum ether/ethyl acetate = 10/1 as developing solvent to obtain light yellow liquid 98 mg (72%). This compound had been reported.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05-7.94 (m, 2H), 7.62-7.42 (m, 4H), 7.39-7.18 (m, 4H), 4.29 (s, 2H) ppm.

3. Crystal Data Collection and Refinement. **Crystal Data Collection and Refinement**. The data of the **1-3** were collected on a Rigaku Saturn 724 CCD diffractomer (Mo-*K*α, λ = 0.71073 Å) at temperature of 20 ± 1 °C. Absorption corrections were applied by using numerical program. The data were corrected for Lorentz and polarization effects. The structures were solved by direct methods and refined with a full-matrix least-squares technique based on F^2 with the SHELXL-97 crystallographic software package.[4] The hydrogen atoms were placed at calculated positions and refined as riding atoms with isotropic displacement parameters. Crystallographic data for **1-3** have been deposited at the Cambridge Crystallographic Data Centre with CCDC reference numbers 988513, 988512, and 1565786.

Table S1. Crystallographic data and structure refinement details for complex **1-3.**

Complex	**1**	**2**	**3**
Formula	$C_{24}H_{18}CuIN_6O_3$	$C_{26}H_{21}BrCuN_7O_3$	$C_{24}H_{18}CuClN_6O_3$
F_w	628.88	622.95	537.43 g
Temp. (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	Triclinic	orthorhombic
Space group	*C*2/*c*	*P*$\bar{1}$	*Pbca*
a (Å)	32.013(6)	9.002 (18)	6.997 (14)
b (Å)	7.894 (16)	11.618(2)	25.358(5)
c (Å)	20.331(4)	12.591(3)	25.482(5)
α(°)	90	97.81(3)	90
β(°)	119.22(3)	103.15(3)	90
γ(°)	90	93.34(3)	90
V (Å^3)	4484.0(16)	1265.0(4)	4521.2 (155)
Z	8	2	8
$D_{calcd.}$(g·cm^{-3})	1.863	1.636	1.578
Reflections collected /unique	18044 / 5342	14223 / 5917	17390 / 4184
μ (mm^{-1})	2.393	2.487	1.125
F(000)	2480	628	2192
θ (°)	2.30-27.90	1.68-27.84	0.9254-0.87
GOF on F^2	1.126	1.135	1.158
R_1(I>2sigma(I))[a]	0.0632	0.0652	0.0997
wR_2(I>2sigma(I))[b]	0.1108	0.1437	0.2434

[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 Distances (Å) and Angles (deg) for **1-3.**

Complex **1**			
Cu(1)-N(1)	1.979(4)	C(12)-N(4)-Cu(1)#2	122.9(3)
Cu(1)-N(4)#1	1.998(4)	C(15)-N(4)-Cu(1)#2	119.6(3)
Cu(1)-I(1)	2.5602(9)	C(4)-N(1)-Cu(1)	123.6(3)
N(1)-Cu(1)-N(4)#1	126.48(17)	C(1)-N(1)-Cu(1)	119.3(3)
N(1)-Cu(1)-I(1)	120.57(12)	C(15)-N(4)-Cu(1)#2	119.6(3)
N(4)#1-Cu(1)-I(1)	109.56(12)	C(4)-N(1)-Cu(1)	123.6(3)

#1=-x+2, y-1, -z+3/2; #2=-x+2, y+1, -z+3/2

Complex **2**			
Cu(1)-N(4)#1	2.042(4)	N(4)#1-Cu(1)-N(1)	119.20(16)
Cu(1)-N(1)	2.047(4)	N(4)#1-Cu(1)-N(6)#2	106.77(17)
Cu(1)-N(6)#2	2.097(5)	N(1)-Cu(1)-N(6)#2	109.05(17)
Cu(1)-Br(1)	2.5025(11)	N(4)#1-Cu(1)-Br(1)	107.23(12)
N(4)-Cu(1)#3	2.042(4)	N(1)-Cu(1)-Br(1)	112.70(13)
N(6)-Cu(1)#4	2.097(5)	N(6)#2-Cu(1)-Br(1)	100.05(13)
C(10)-N(4)-Cu(1)#3	123.2(3)	C(23)-N(1)-Cu(1)	118.4(3)
C(9)-N(4)-Cu(1)#3	118.2(3)	C(24)-N(1)-Cu(1)	123.8(3)
C(16)-N(6)-Cu(1)#4	122.4(3)	C(19)-N(2)-C(20)	125.9(4)
C(15)-N(6)-Cu(1)#4	120.4(4)		

#1=x+1, y-1, z; #2=x, y-1, z-1; #3=x-1, y+1, z; #4 x, y+1, z+1.

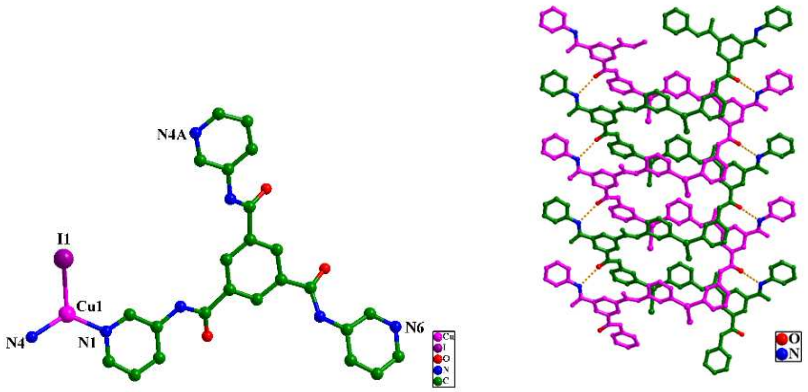
Complex **3**			
Cu(1)-N(4)#1	1.948(6)	N(4)#1-Cu(1)-N(1)	119.6(3)
Cu(1)-N(1)	1.970(5)	N(4)#1-Cu(1)-N(6)#2	118.4(2)
Cu(1)-N(6)#2	2.012(6)	N(1)-Cu(1)-N(6)#2	120.7(2)
N(4)-Cu(1)#3	1.948(6)	C(5)-N(1)-C(1)	118.4(6)
N(6)-Cu(1)#4	2.012(6)	C(5)-N(1)-Cu(1)	119.7(5)
C(14)-N(4)-Cu(1)#3	115.4(5)	C(1)-N(1)-Cu(1)	121.6(5)
C(18)-N(4)-Cu(1)#3	126.6(5)	C(6)-N(2)-C(4)	126.7(5)
C(24)-N(6)-Cu(1)#4	126.3(5)	C(21)-N(6)-Cu(1)#4	116.0(4)

#1=x,-y+1/2, z+1/2; #2=-x+5/2,-y+1, z+1/2; #3=x,-y+1/2, z-1/2; #4=-x+5/2,-y+1, z-1/2.

Table S3. Hydrogen Bonds of complexes **1-3**.

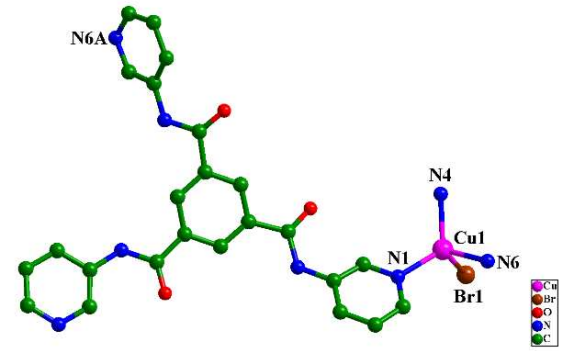
Complex	D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	<(D-H···A) (deg)
1	N(5)-H(5A) ···O(2)#2	0.86	2.15	2.983(5)	162.1
2	N(3)-H(3) ···Br(1)#1	0.86	2.76	3.578(4)	160.2
3	N(2)-H(2A)···Cl(1)#1	0.86	2.50	3.234(5)	143.4
	N(3)-H(3A)···Cl(1)#2	0.86	2.50	3.326(5)	161.3
	N(5)-H(5A)···Cl(1)#2	0.86	2.53	3.333(5)	156.2
Symmetry codes: #1= -x+2,-y+1,-z; #2= x,y-1,z.					

4. Additional structure figures of Cu-complexes

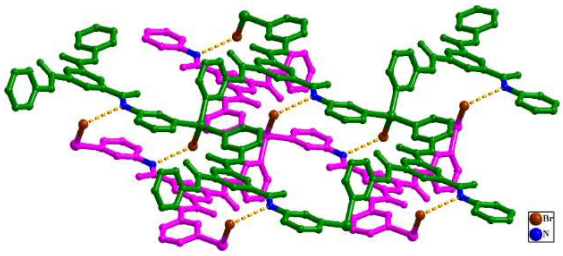


a **b**

Figure S1. (a) Coordination environments of the Cu(I) ions in **1**. Hydrogen atoms are omitted for clarity; (b) Intermolecular hydrogen bonding interactions in **1**.



a



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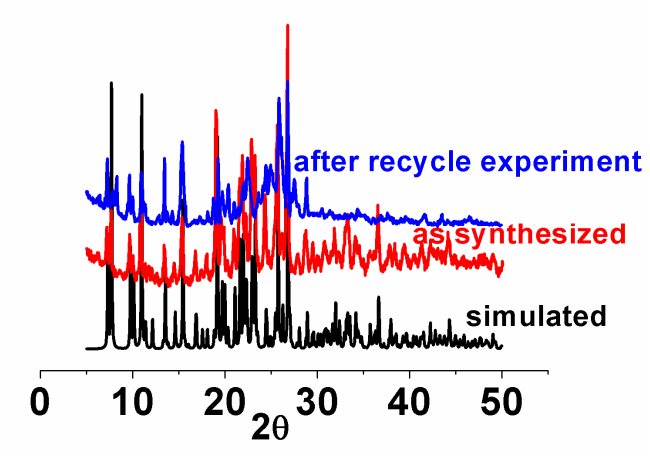

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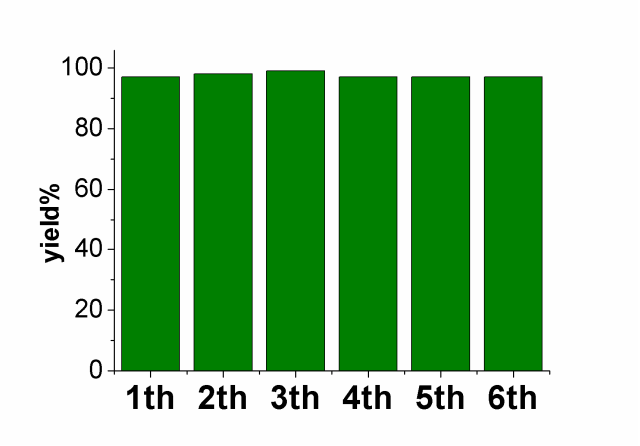
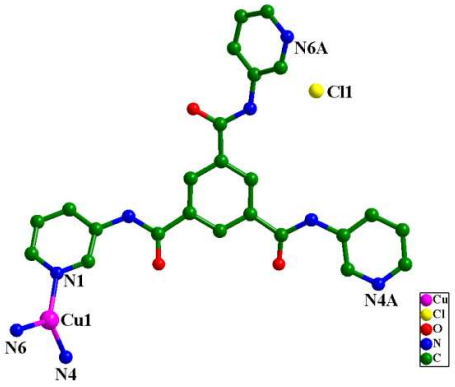


d

Figure S2. (a) Coordination environments of the Cu(I) ions in **2**. Hydrogen atoms are omitted for clarity; (b) Intermolecular hydrogen bonding interactions in **2**; (c) Recycling test for the conversion of alkanes into ketones with **2**; (d) Comparison of the PXRD patterns of **2** before and after recycles experiments.



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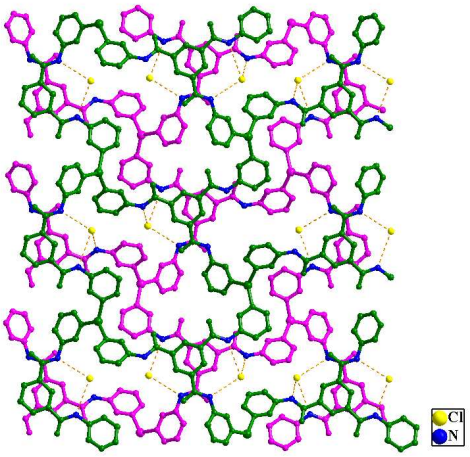

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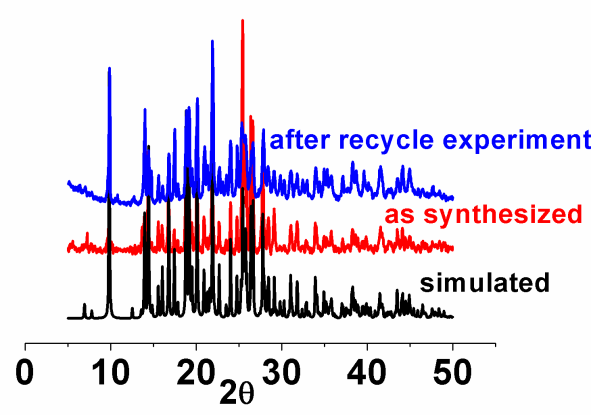

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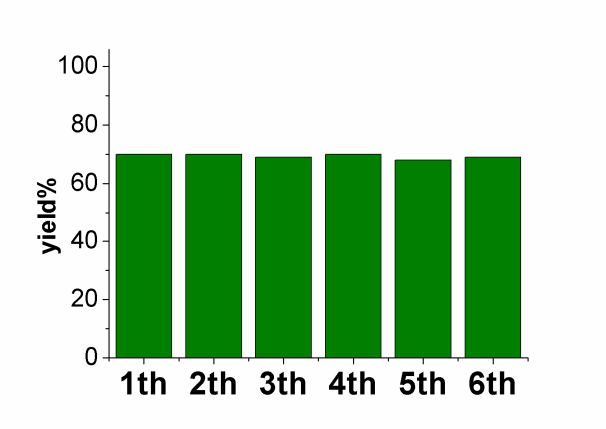
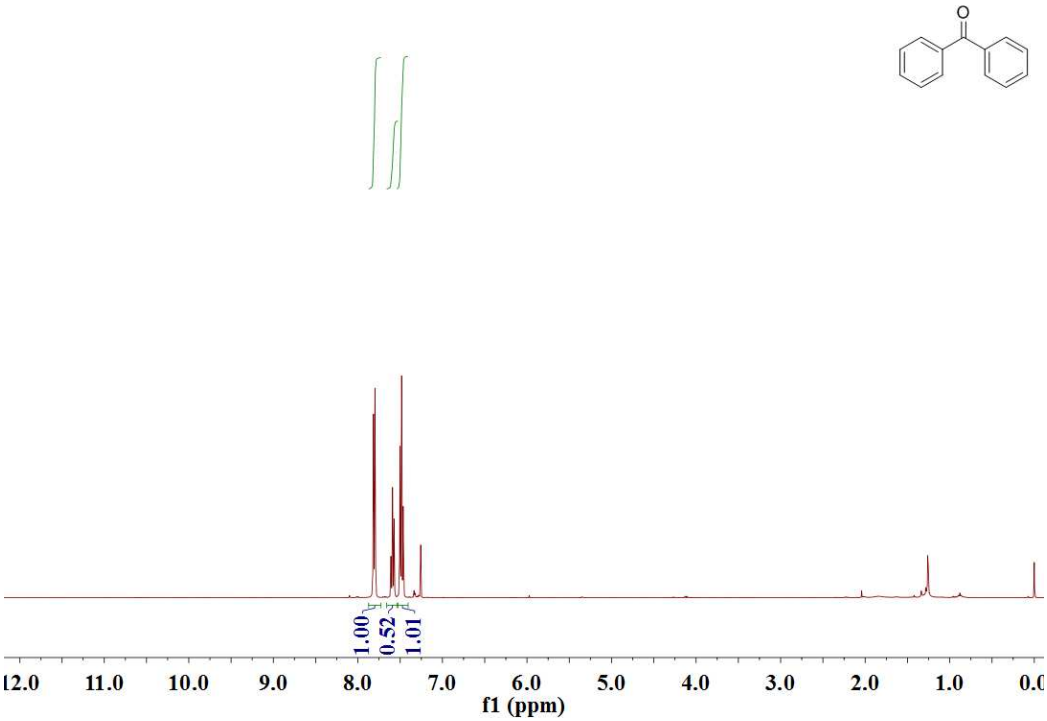
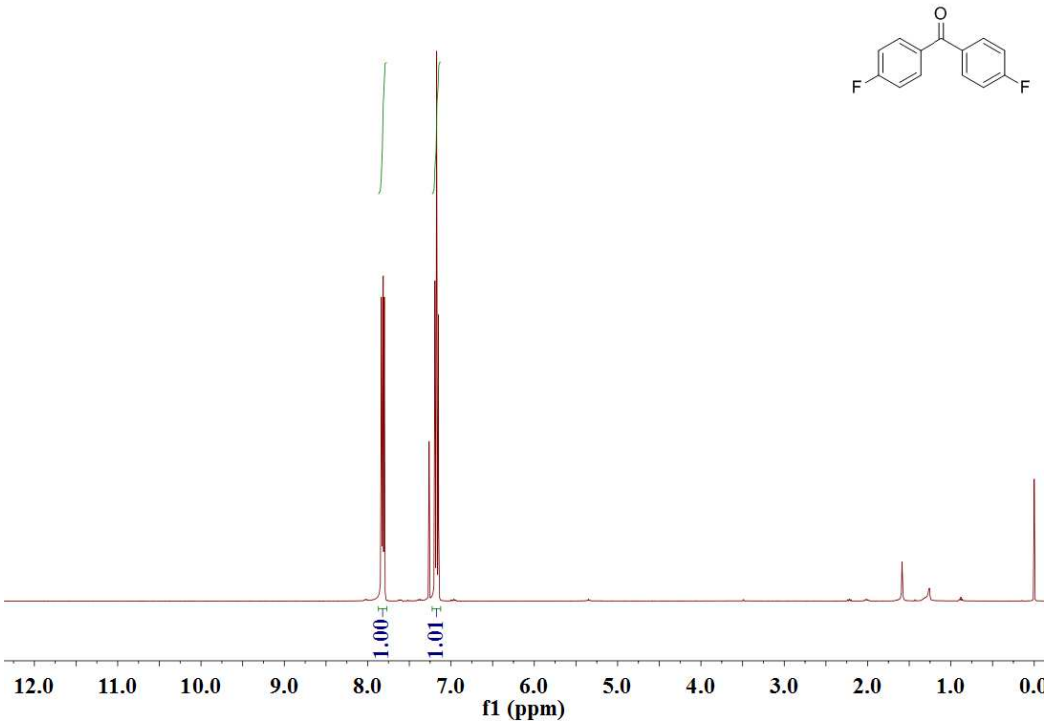


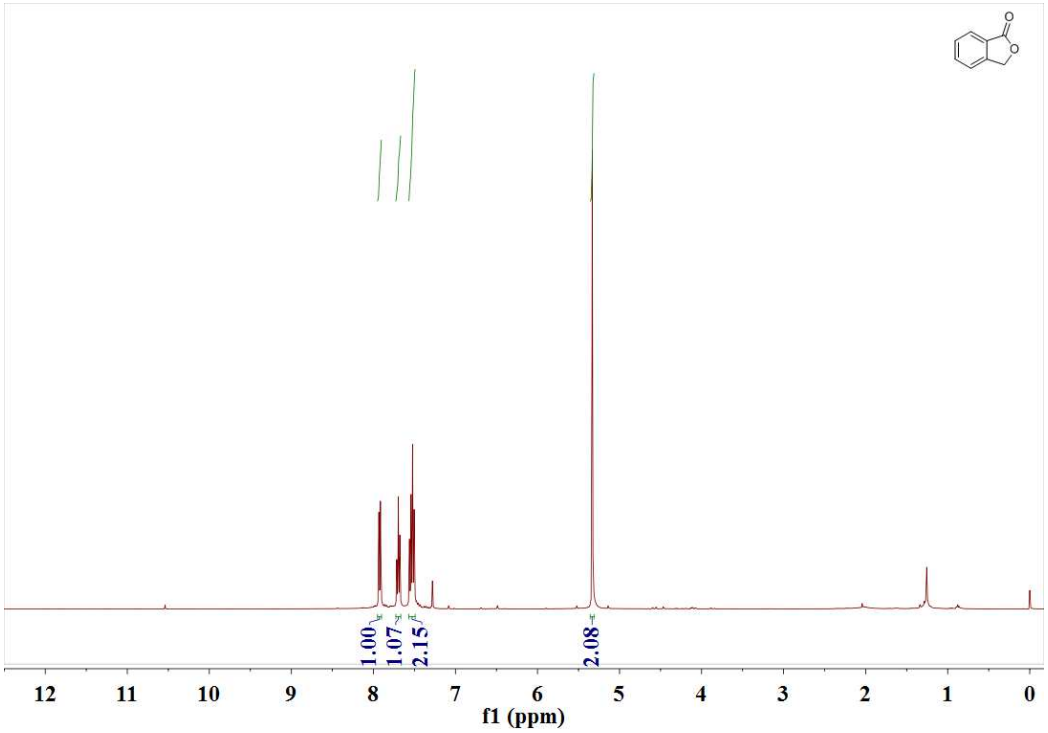
d

Figure S3. (a) Coordination environments of the Cu(I) ions in **3**. Hydrogen atoms are omitted for clarity; (b) Intermolecular hydrogen bonding interactions in **3**; (c) Recycling test for the conversion of alkanes into ketones with **3**; (d) Comparison of the PXRD patterns of **3** before and after recycles experiments.

5. Spectral copies of ^{1}H NMR of compounds obtained in this study.



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10
9
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7
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4
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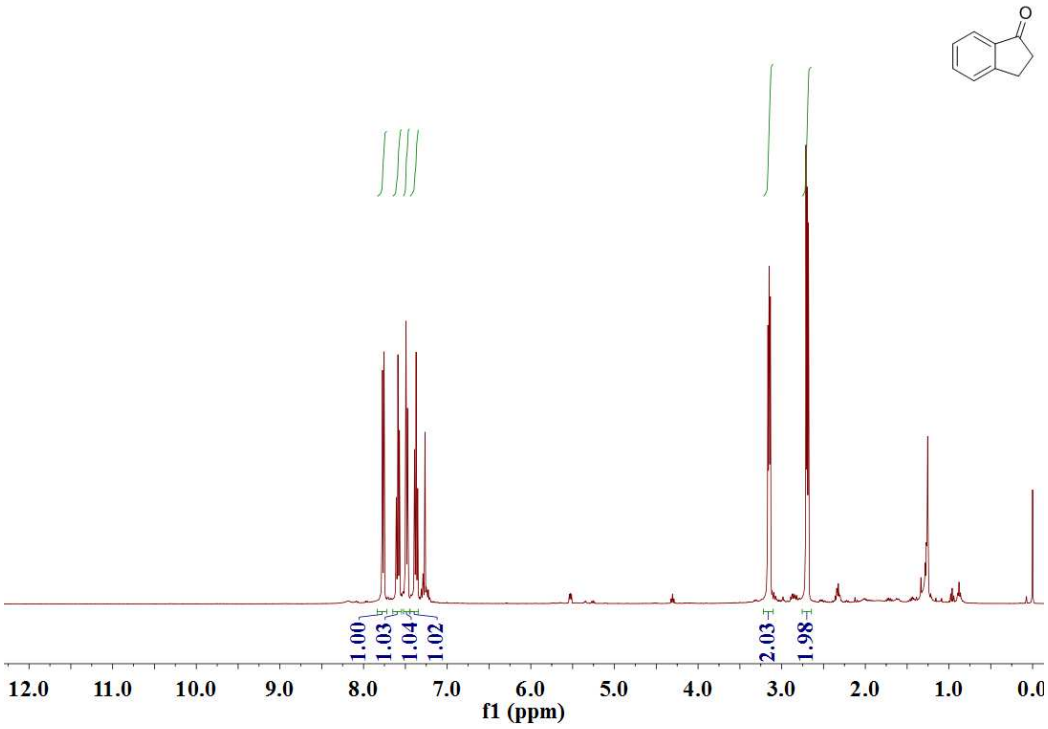
f1 (ppm)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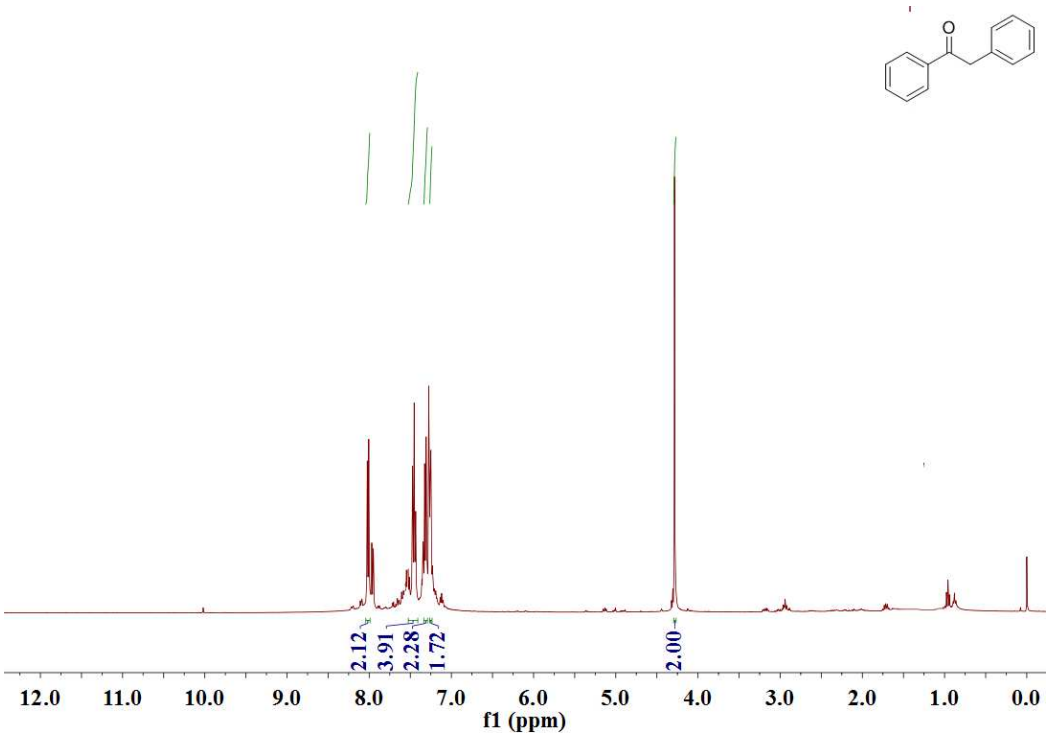
f1 (ppm)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9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

7. References.

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