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# Highly selective and eco-friendly dihydroisoquinoline synthesis via Cu/Co synergistic catalysis in Cu NPs@MOFs catalyst under mild conditions

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## Experimental Procedures

### Experiment

All reagents were purchased without purification.  $\text{NH}_4\text{F}$  (99.99% *aladdin*), 1,3-bis-(3,5-dicarboxyphenyl)imidazoliumchloride (99.6%  $\text{H}_4\text{LCl}$  EXTENSION.),  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.99% *aladdin*), *N,N*-diethylformamide (99%, *DEF Macklin*) 1,2,3,4-tetrahydroisoquinoline (97% *J&K*), 6-methoxy-1,2,3,4-tetrahydro-isoquinoline (97% *Bidepharm*), 8-bromo-1,2,3,4-tetrahydroisoquinoline (98% *Leyan.com*), 5-bromo-1,2,3,4-tetrahydroisoquinoline (98% *Macklin*), 7-bromo-1,2,3,4-tetrahydroisoquinoline (97% *Crgent Biotech*), 7-nitro-1,2,3,4-tetrahydroisoquinoline (97% *Adamas*), 6-bromo-1,2,3,4-tetrahydroisoquinoline (99% *Leyan.com*) 6-chloro-1,2,3,4-tetrahydroisoquinoline (95% *Adamas*), 7-methyl-1,2,3,4-tetrahydroisoquinoline (98% *Bidepharm*) acetonitrile (99%), *N,N*-dimethylformamide (97% *DMF*), Methanol (98%), Ethanol (99%) were purchased from Tianjin Damao Chemical Reagent Co., Ltd.

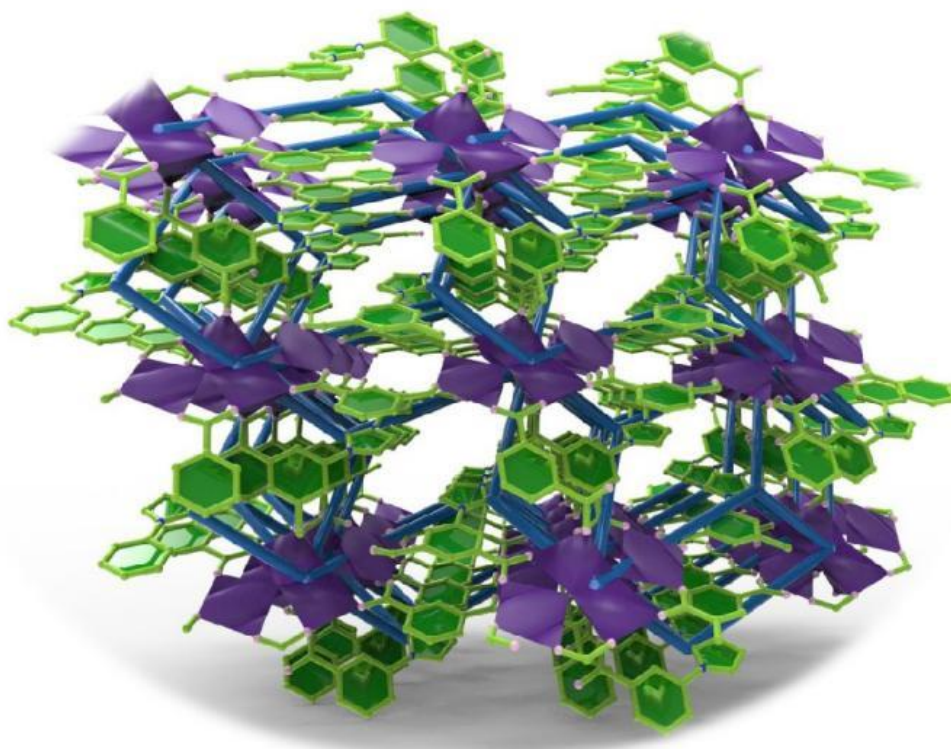


Figure S1. 3D framework 1 with *flu*-type network.

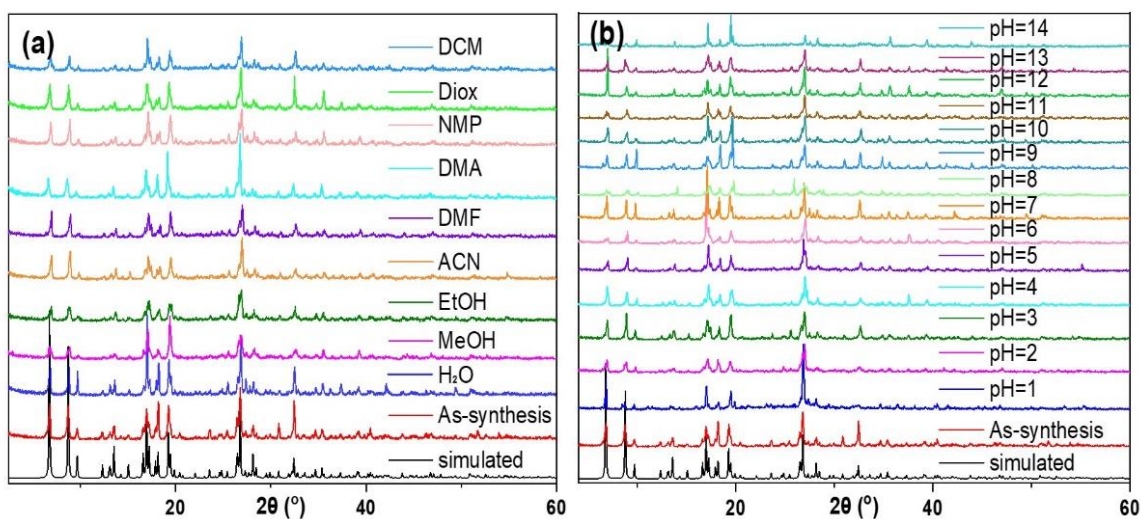


Figure S2. PXRD patterns of 1 after disposing in different solvents and water with various pH values. Typically, 20 mg 1 was

immersed in these solvents for 10 h and dried in vacuum oven over night.

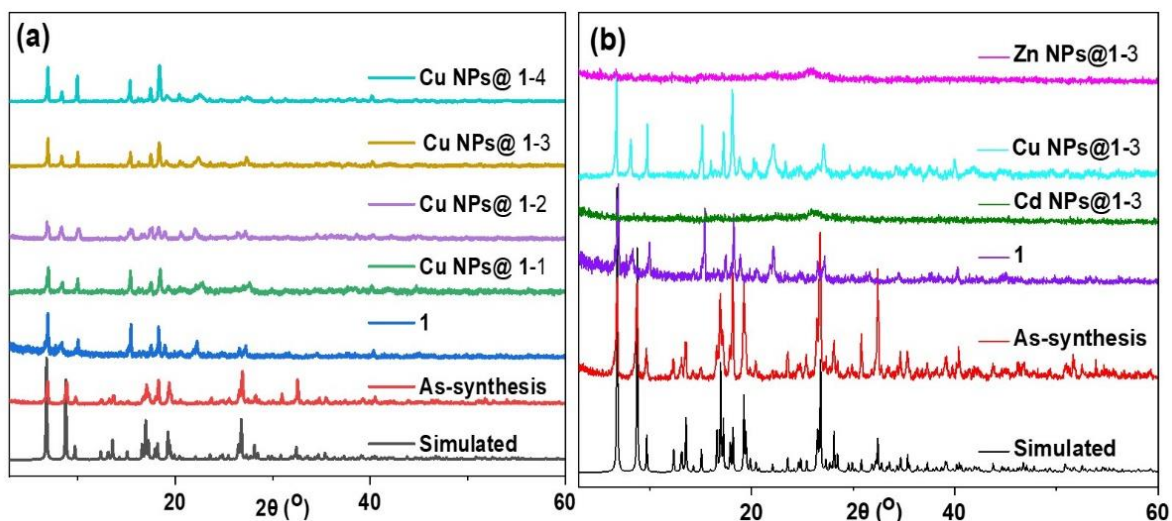


Figure S3. PXRD patterns of various amount Cu and different metal loaded on 1

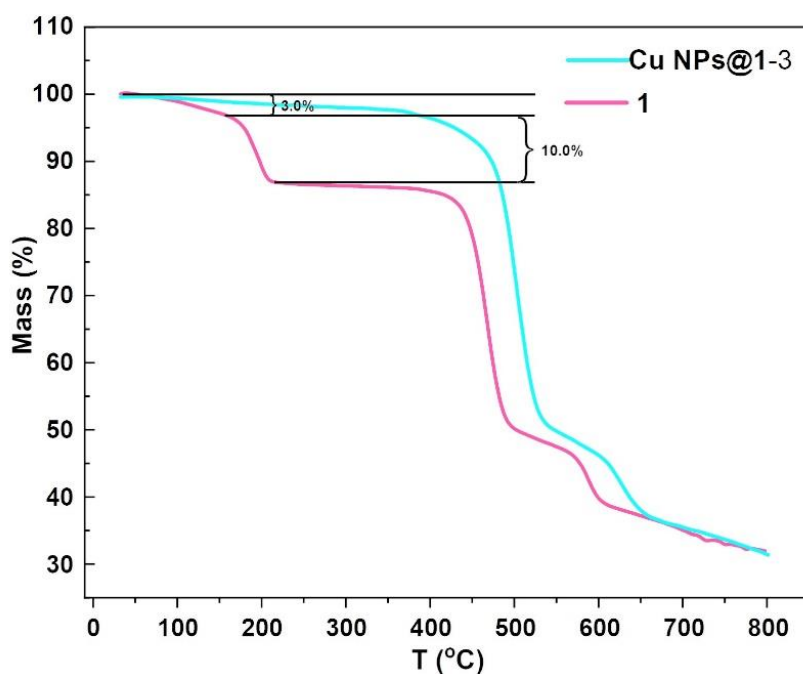


Figure S4. TGA of 1 and Cu NPs@1-3

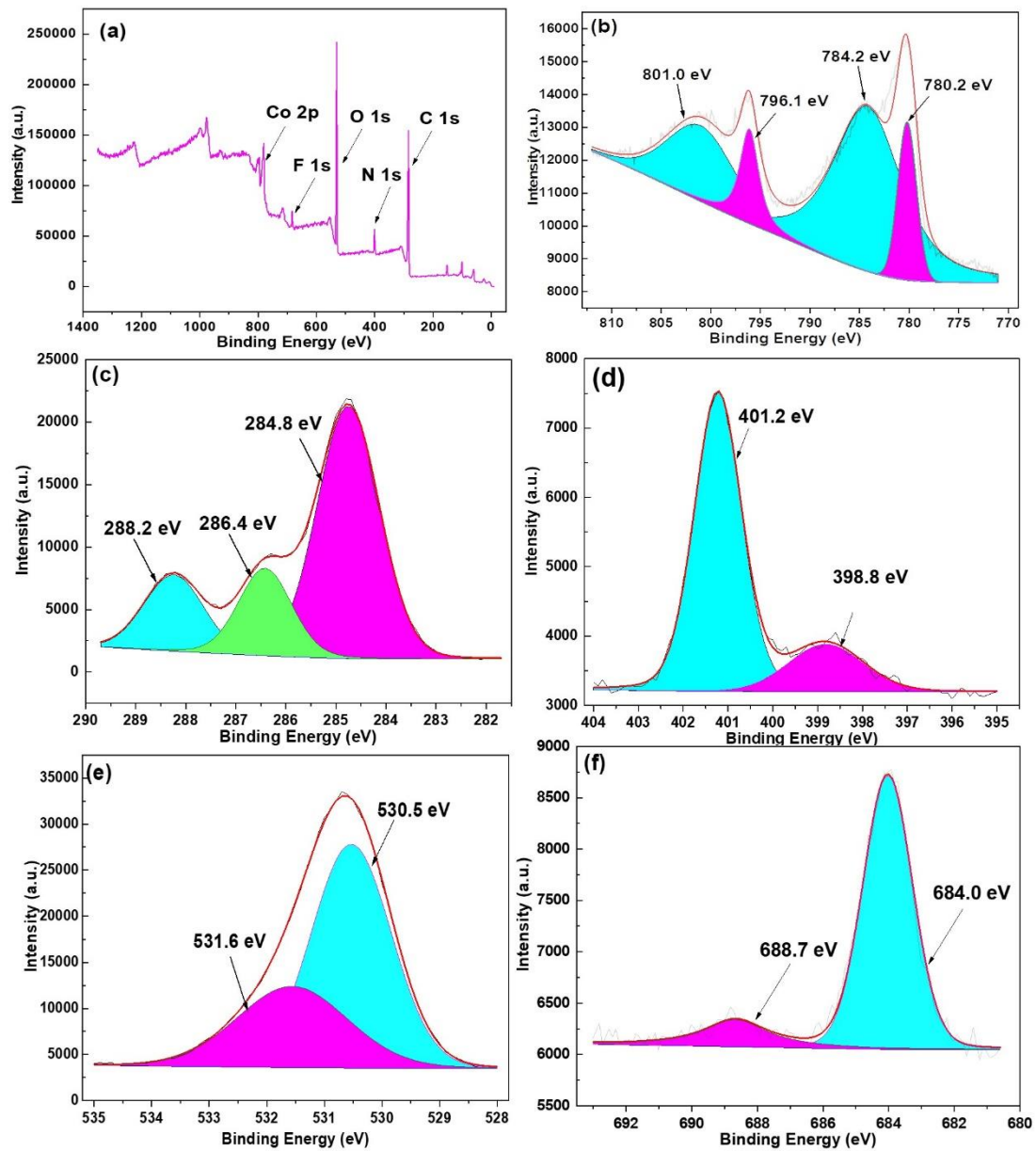


Figure S5. XPS patterns of 1, (a) XPS Survey, (b) Co 2p, (c) C 1s, (d) N 1s, (e) O 1s, (f) O 1s

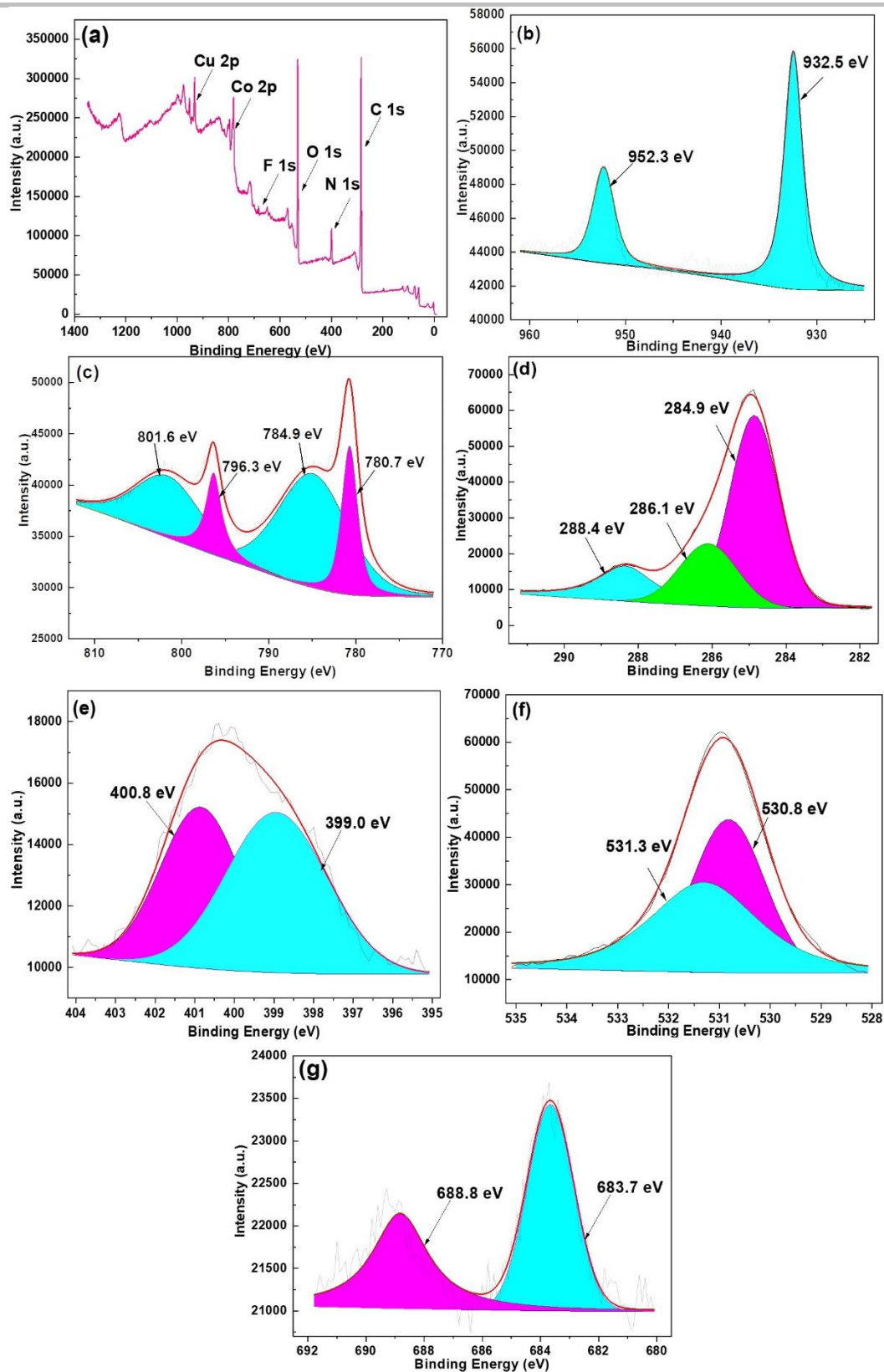
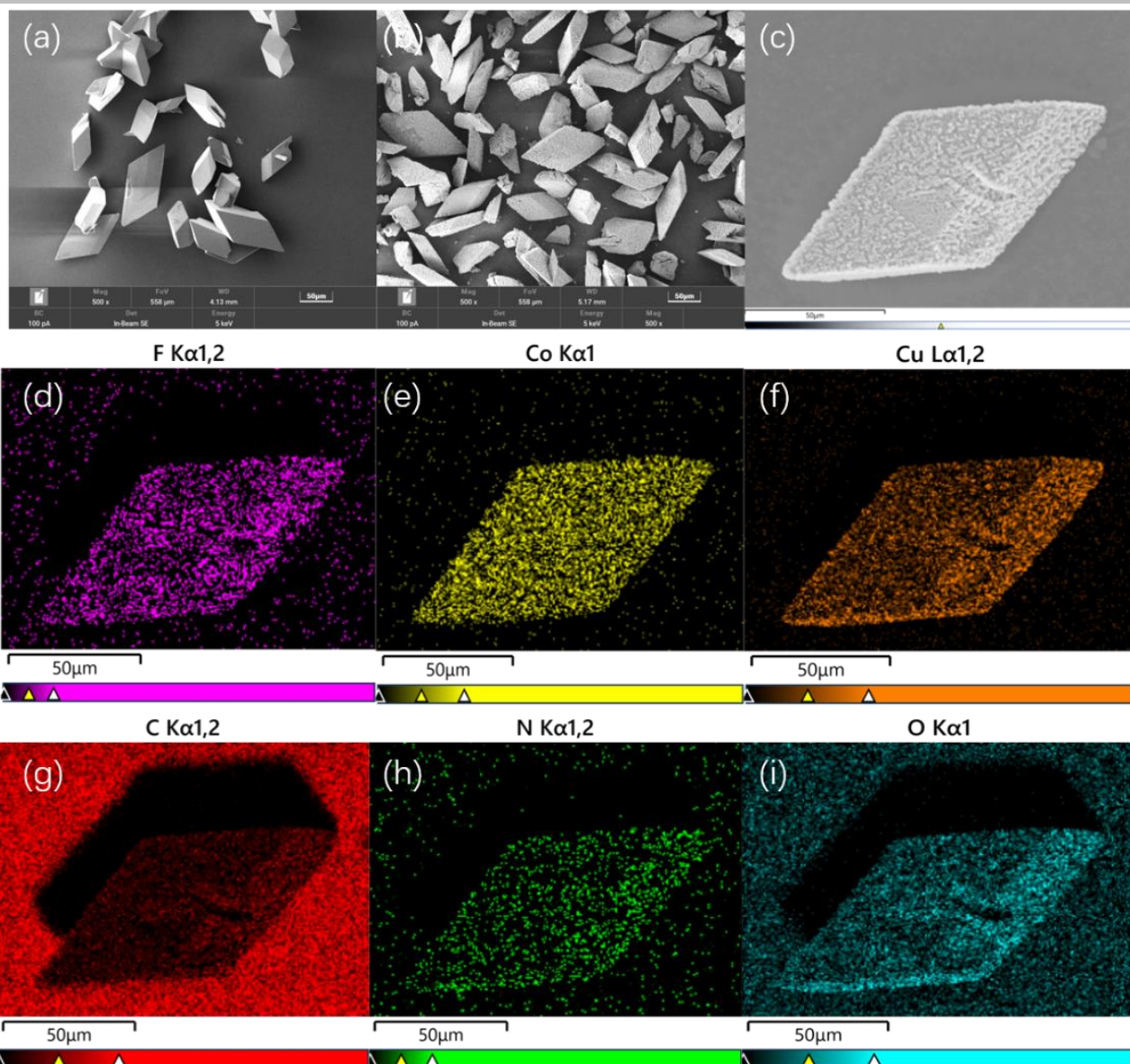


Figure S6. XPS patterns of Cu NPs@1-3, (a) XPS Survey, (b) Cu 2p, (c) Co 2p, (d) C 1s, (e) N 1s, (f) O 1s, (g) F 1s



**Figure S7.** (a) SEM of 1, (b) SEM of Cu NPs@1-3, (c) EDX Mapping patterns of Cu NPs@1-3, d (F), e (Co), f (Cu), g (C), h (N), i (O).

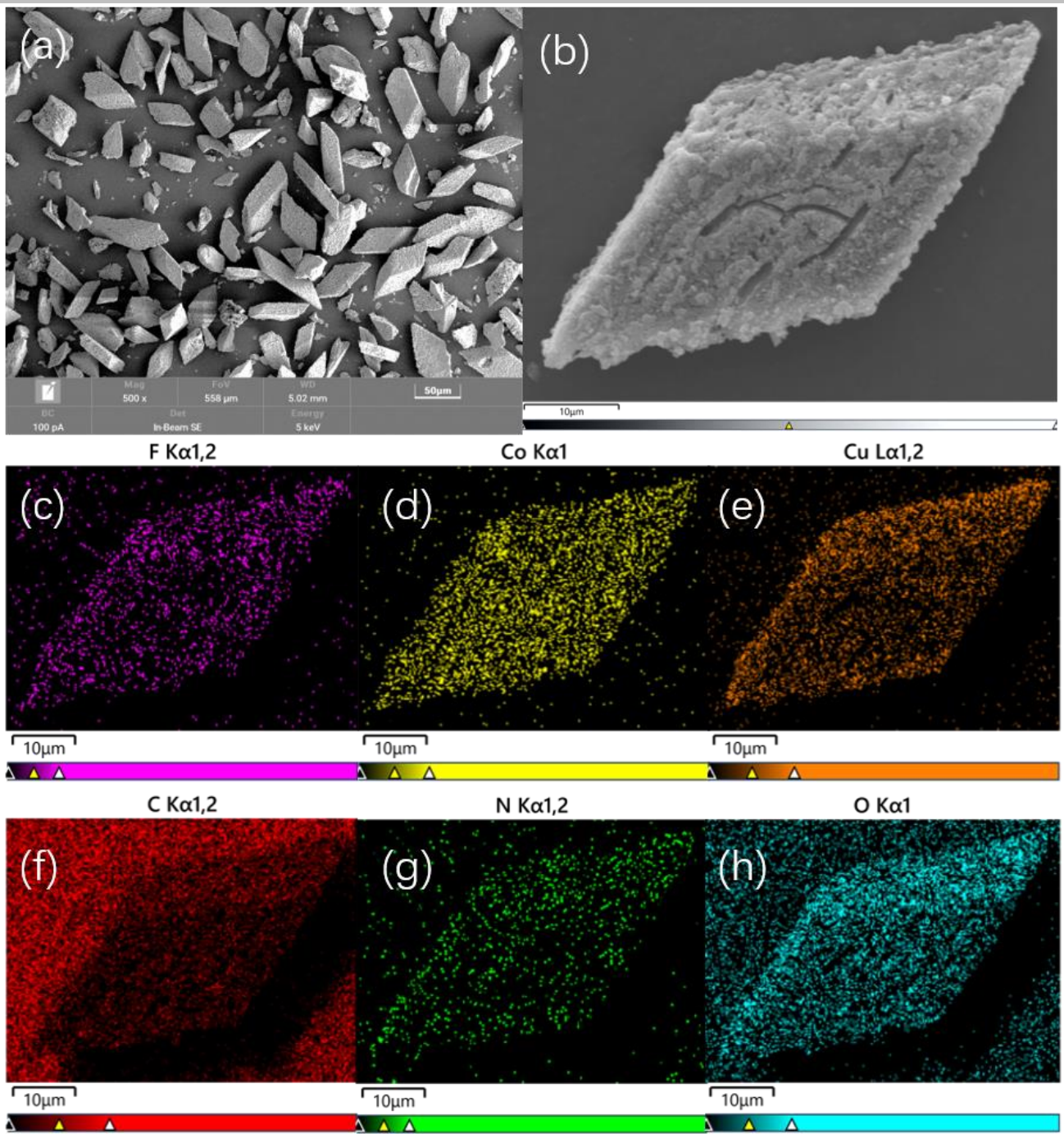
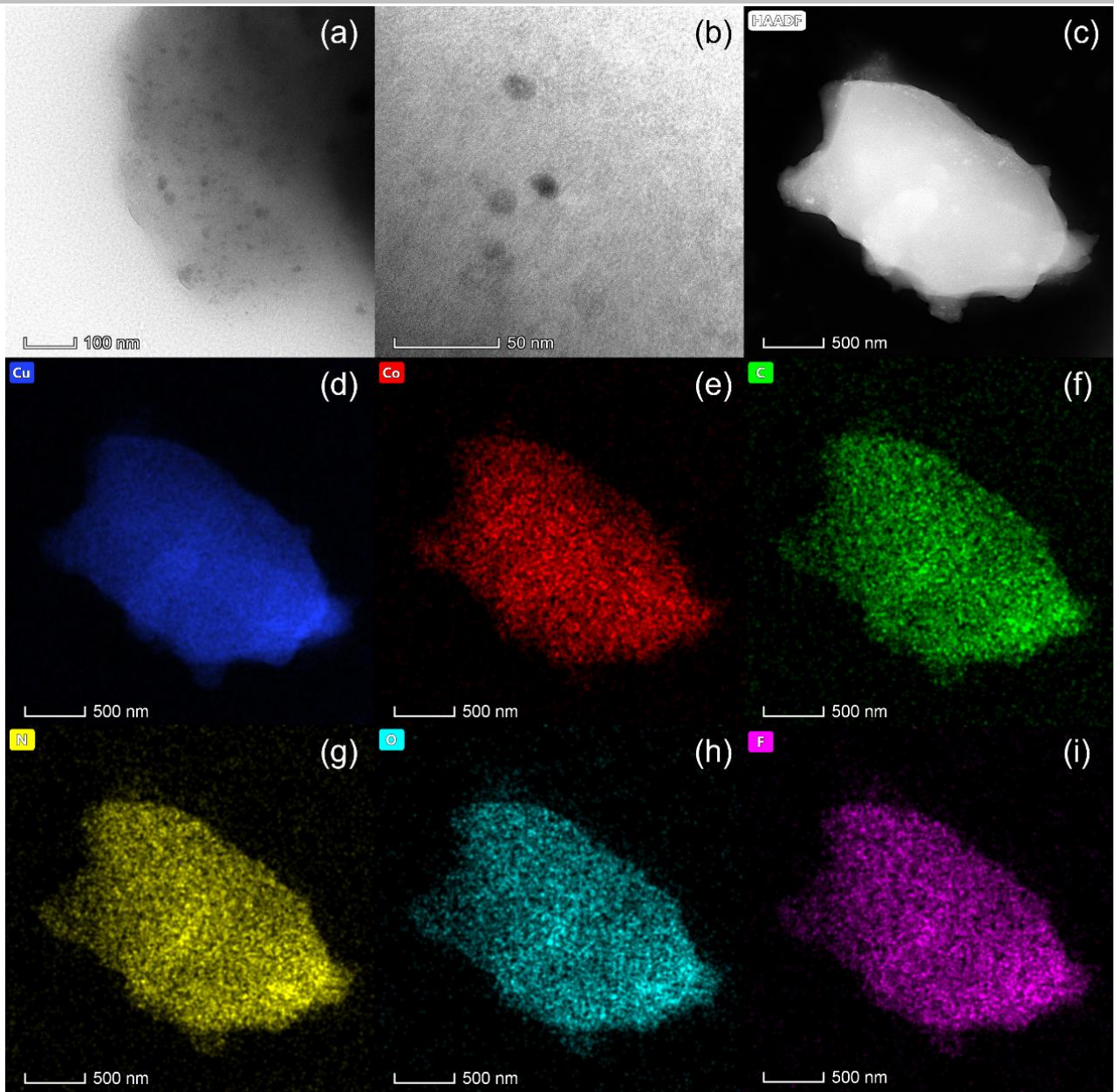
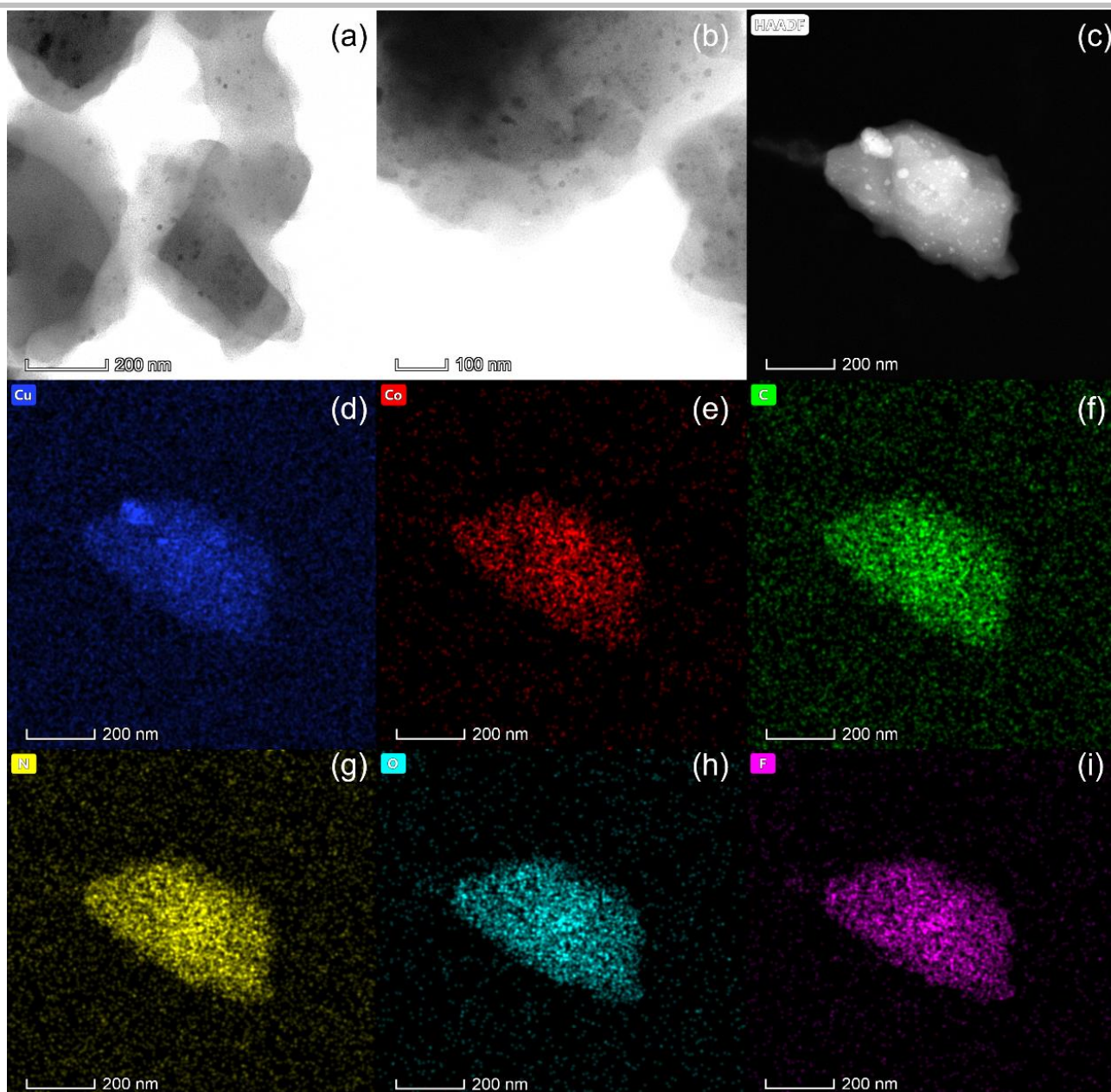


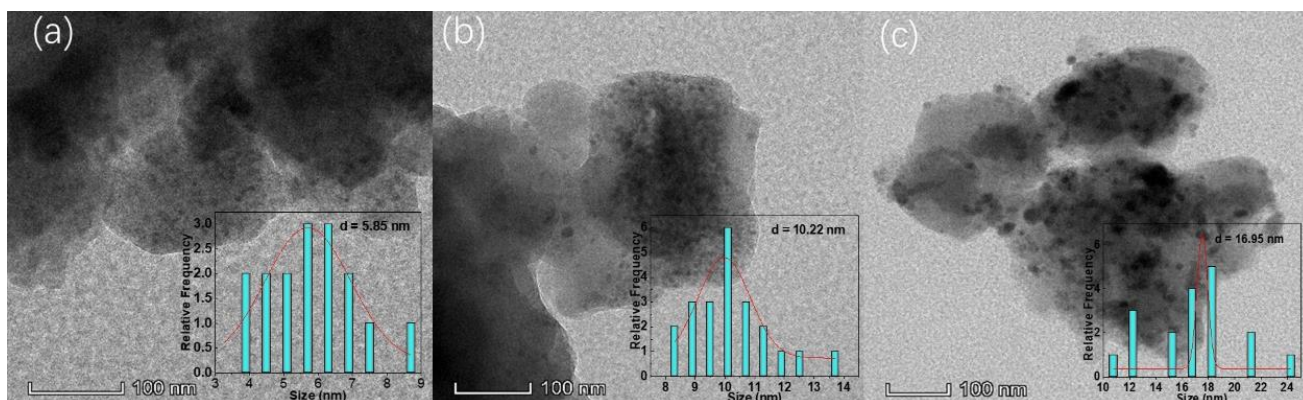
Figure S8. (a) SEM of used Cu NPs@1-3, (b) EDX Mapping patterns of used Cu NPs@1-3, c (F), d (Co), e (Cu), f (C), g (N), h (O).



**Figure S9.** (a), (b) HR-TEM of Cu NPs@1-3, (c) EDX Mapping patterns of Cu NPs@1-3, d (Cu), e (Co), f (C), g (N), h (O), i (F).



**Figure S10.** (a), (b) HR-TEM of used Cu NPs@1-3, (c) EDX Mapping patterns of used Cu NPs@1-3, d (Cu), e (Co), f (C) g (N), h (O), i (F).



**Figure S11.** (a), HR-TEM of Cu NPs@1-1, (b) HR-TEM of Cu NPs@1-2, (c) HR-TEM of Cu NPs@1-4.

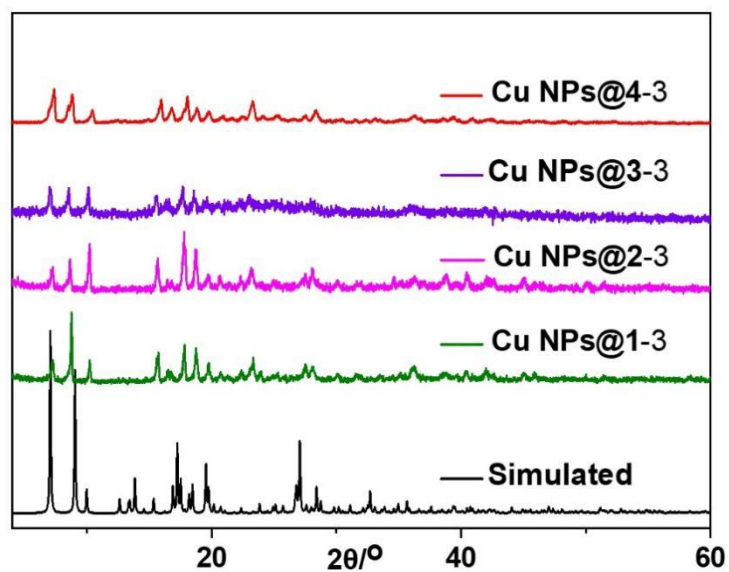


Figure S12 PXRD patterns of Cu NPs@1-3, Cu NPs@2-3, Cu NPs@3-3, Cu NPs@4-3.

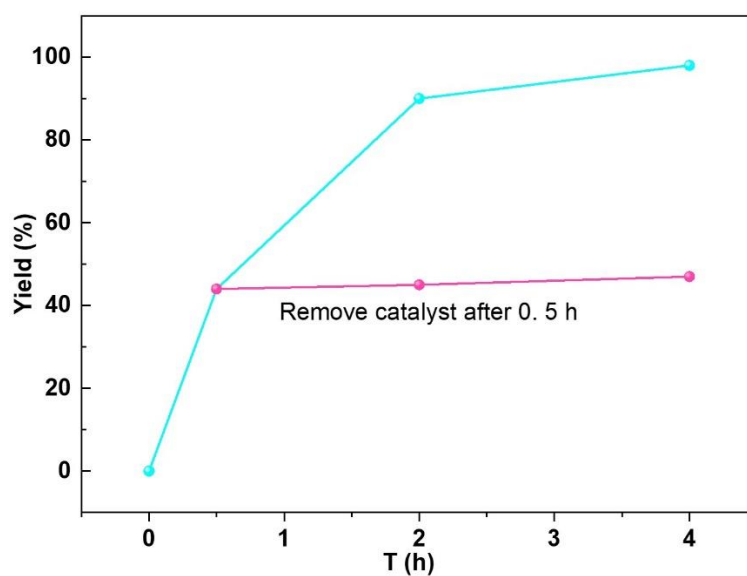


Figure S13. Catalytic filtration experiments for DHIQ synthesis.

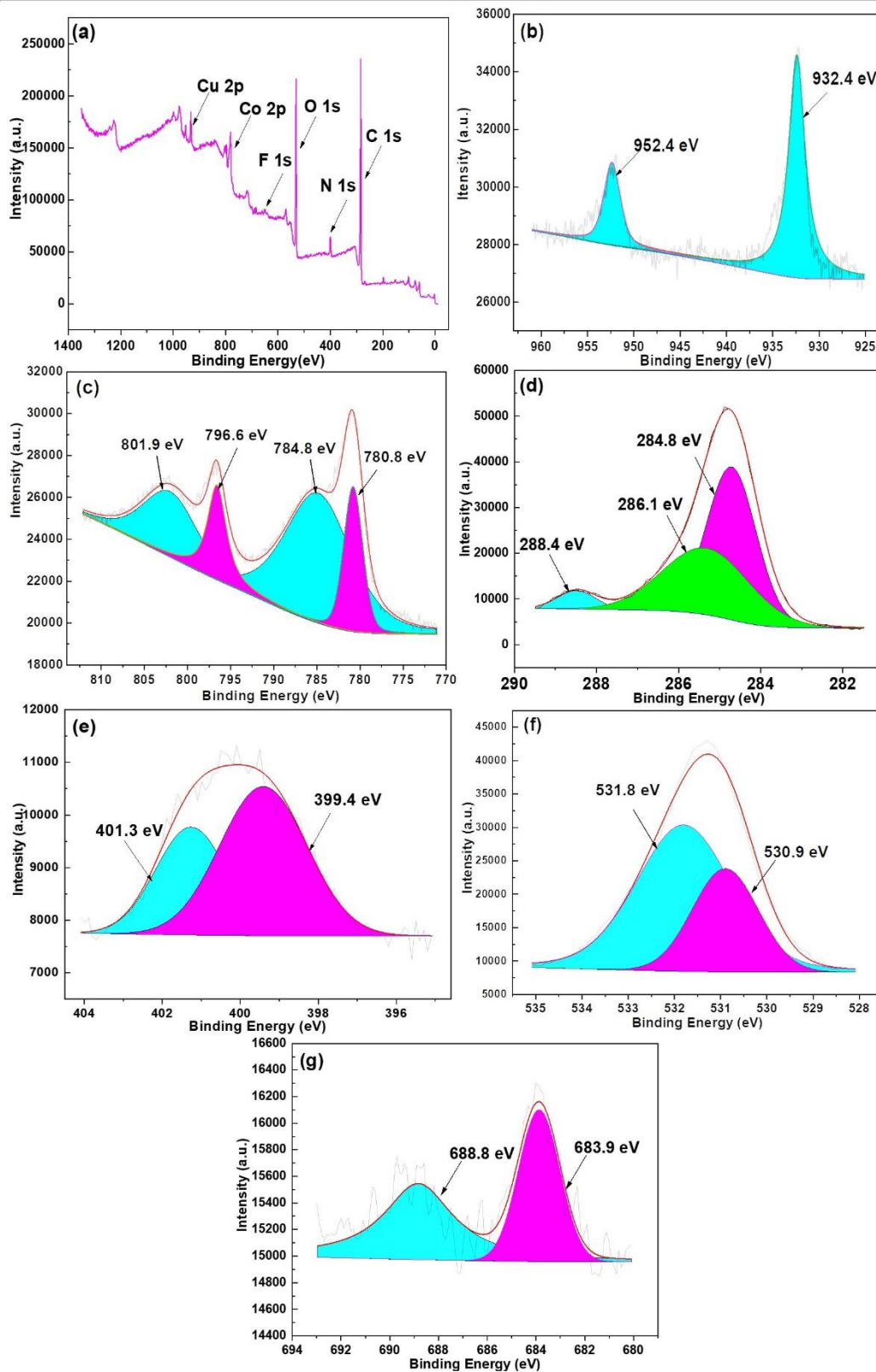


Figure S14. XPS patterns of used Cu NPs@1-3, (a) XPS Survey, (b) Cu 2p, (c) Co 2p, (d) C 1s, (e) N 1s, (f) O 1s, (g) F 1s

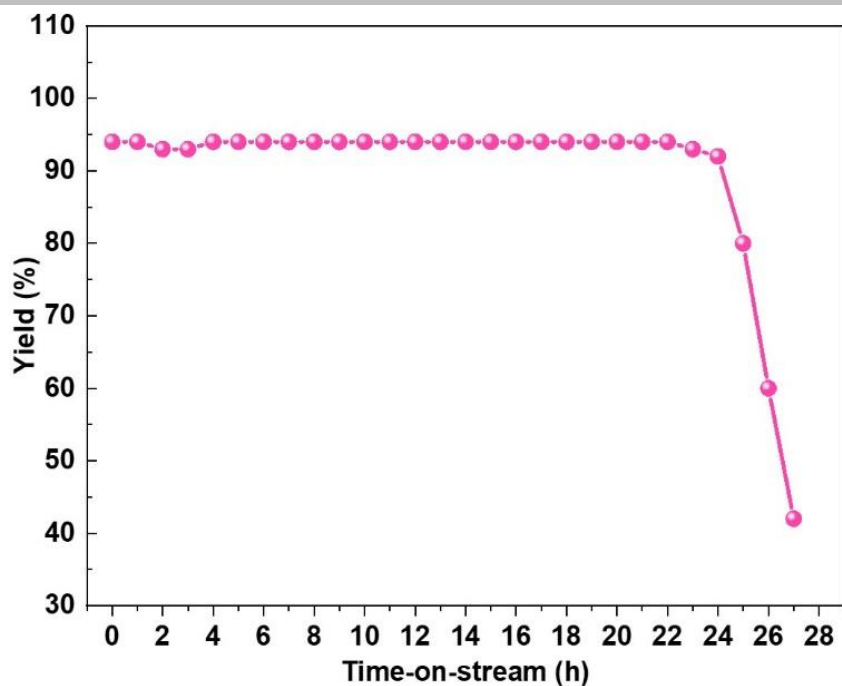


Figure S15. The lifetime of Cu NPs@1-3

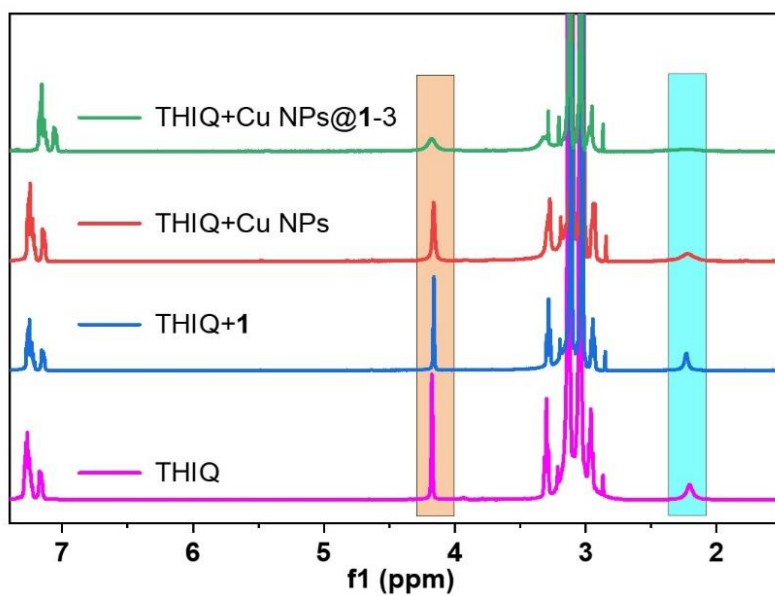


Figure S16. <sup>1</sup>H NMR the mixture with various components in the system

Table S1. Crystal data and structure refinements for 1 and 4

Compounds	1	4
Formula	C <sub>19</sub> H <sub>17</sub> Co <sub>2</sub> FN <sub>2</sub> O <sub>12</sub>	C <sub>19</sub> H <sub>17</sub> Ni <sub>2</sub> FN <sub>2</sub> O <sub>12</sub>
$F_w$	602.19	601.75
$T$ (K)	120	120
Cryst syst	triclinic	triclinic
Space group	<i>P</i> -1	<i>P</i> -1
$a$ (Å)	7.5302(4)	7.4276(7)
$b$ (Å)	10.7759(7)	10.6059(7)
$c$ (Å)	13.7913(5)	13.7520(10)
$\alpha$ (°)	73.258(5)	73.912(6)
$\beta$ (°)	76.676(4)	76.946(8)
$\gamma$ (°)	74.755(5)	75.709(8)
$Z$	2	2
Reflections collected	10304	11022
$R_{(int)}$	0.0375	0.0507
Goodness-of-fit on $F^2$	1.050	1.034
Final $R$ indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0416$ , $wR_2 = 0.0755$	$R_1 = 0.0449$ , $wR_2 = 0.1138$
Final $R$ indexes [all data]	$R_1 = 0.0616$ , $wR_2 = 0.0905$	$R_1 = 0.0552$ , $wR_2 = 0.1261$
CCDC	2312632	2312633

**Table S2** Comparison of the oxidation of 1,2,3,4-tetrahydroisoquinoline over different catalysts.

Team	Conditions	additive	Temp./( $^{\circ}$ C)	Time/(h)	Yield(%)	TOF/(1/h)	Ref.
Saini	1,2,3,4-tetrahydroisoquinoline (3.0 mmol), FeBr <sub>2</sub> (5 mol%), O <sub>2</sub> balloon, chlorobenzene (2 ml),	none	110	6	92	3.1	1
Angelici	1,2,3,4-tetrahydroisoquinoline (0.20 mmol), toluene (5 mL), gold powder, (1.0 g), O <sub>2</sub> (1.0 L).	none	100	24	87	0.0014	2
Ogawa	1,2,3,4-tetrahydroisoquinoline (1.5 mmol), VO(Hhpic) <sub>2</sub> (0.03 mmol), acetonitrile (6 mL), O <sub>2</sub> (0.1MPa)	none	120	18	78	2.2	3
Yamamoto	1,2,3,4-tetrahydroisoquinoline (0.5 mmol), O <sub>2</sub> (1 atm), dioxane (1 mL), Au <sub>90</sub> Ag <sub>10</sub> NPore (5 mol%)	none	80	24	58	0.5	4
Blechert	1,2,3,4-tetrahydroisoquinoline (0.6 mmol), mpg-C <sub>3</sub> N <sub>4</sub> catalyst (50 mg), CH <sub>3</sub> CN (10 mL), O <sub>2</sub> (0.5 MPa).	none	80	4.5	82	0.3	5
Mondal	1,2,3,4-tetrahydroisoquinoline (1.83 mmol), Cu-1 nanocatalyst (0.3619 mol % of Cu), O <sub>2</sub> (1 balloon),	none	100	14	99	19.5	6
Cheng	1,2,3,4-tetrahydroisoquinoline (0.2 mmol), <i>o</i> -Q4 (10 mol%), CH <sub>3</sub> CN (1mL), O <sub>2</sub>	none	60	48	80	0.17	7
Taketoshi	1,2,3,4-tetrahydroisoquinoline (0.15 mmol), Ru catalyst (5 mol%), CD <sub>3</sub> OD (1 mL), O <sub>2</sub> (1 atm)	K <sub>2</sub> CO <sub>3</sub>	reflux	24	57	0.475	8
Wendlandt	1,2,3,4-tetrahydroisoquinoline (0.130 mmol), 1,10-phenanthroline-5,6-dione (phd) (5% mmol), MeCN (0.5 mL), O <sub>2</sub> atmosphere	ZnI <sub>2</sub> (2.5%)	rt	24	75	0.625	9
Liu	1,2,3,4-tetrahydroisoquinoline (0.5 mmol), <i>o</i> -xylene (2 mL), 0.1 MPa N <sub>2</sub> , 140 $^{\circ}$ C, 36 h.	KOrBu	140	36	86	0.0080	10
Zhang	1,2,3,4-tetrahydroisoquinoline (0.20 mmol), GO (30 mg), EtoAc (1.5 mL),	Na <sub>2</sub> CO <sub>3</sub>	120	24	74	0.00021	11
This work	1,2,3,4-tetrahydroisoquinoline (1.5 mmol), 0.025g Cu NPs@1-3, O <sub>2</sub> (1 balloon), DMF(0.5 mL)	none	90	4	92	22.1	-

The TOF value was calculated as below:

$$\text{TOF} = \frac{\text{TON}}{\text{Time}} = \frac{n(\text{product})}{n(\text{catalyst}) \times \text{Time}} = \frac{1.5 \times 0.92}{0.0156 \times 4} = 22.1 \text{ h}^{-1}$$

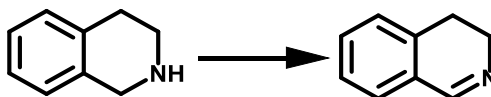
1.5 mmol THIQ was completely conversion to produce 1.5 mmol DHIQ.

The yield of DHIQ was 92% under optimized reaction.

$n(\text{catalyst})$  was calculated by ICP-OES measurement.

**Table S3.** ICP measurement results of Leakage after reaction.

Cu NPs@1-3	Cu (%)	Co (%)
Leakage for oxydehydrogenation of THIQ	0.65%	0.61%

**Table S4.** Synthesis of DHIQ from THIQ under various conditions. <sup>a</sup>

Entry	Catalyst	Solvent	Yield. (%) <sup>g</sup>
1	None	DMF	38
2	4.0 wt% Cu	DMF	52
3	<b>1</b>	DMF	35
4	4.0 wt% Cu+1	DMF	59
5	Cu NPs@1-3	DMF	98
6 <sup>b</sup>	Cu NPs@1-3	DMF	85
7 <sup>c</sup>	Cu NPs@1-3	DMF	57
8	Zn NPs@1-3	DMF	60
9	Cd NPs@1-3	DMF	65
10	4.0 wt% Cu NPs@ZIF-67	DMF	77
11	4.0 wt% Cu NPs@ZIF-8	DMF	49

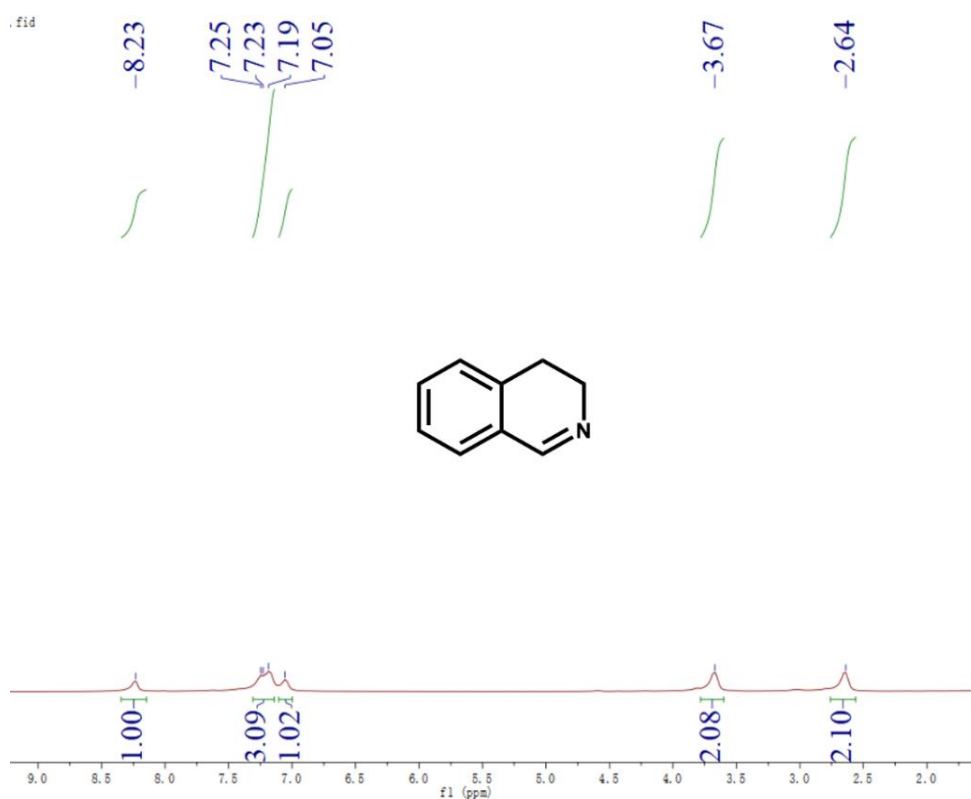
12	4.0 wt% Cu NPs@MIL-68(In)	DMF	40
13 <sup>d</sup>	Cu NPs@1-3	DMF	94
14 <sup>e</sup>	Cu NPs@1-3	DMF	96
15 <sup>f</sup>	Cu NPs@1-3	DMF	-

<sup>a</sup> Reaction Conditions: 1,2,3,4-Tetrahydroisoquinoline (1 mmol); catalyst (25 mg); O<sub>2</sub> (1 balloon); Time (4 h); Temperature (90 °C), DMF (1 mL). <sup>b</sup> without glucose in the preparation of catalyst. <sup>c</sup> In Ar. atmosphere. <sup>d</sup> In air for 10 h. <sup>e</sup> Reaction Conditions: 1,2,3,4-Tetrahydroisoquinoline (10 mmol); catalyst (0.25 g); O<sub>2</sub> (1 balloon); Time (10 h); Temperature (90 °C). <sup>f</sup> the substrate was replaced by 3,4-dihydroisoquinoline, <sup>g</sup> the Yield of DHIQ was obtained by GC with internal standard of 1,3-dichlorobenzene.

**Table S5.** the influence of the oxidation of 1,2,3,4-tetrahydroisoquinoline over the catalyst with different mole ratios (Co : Ni). <sup>a</sup>

Catalyst	ICP (Co:Ni)	Yield (%) <sup>b</sup>
Cu NPs@1-3	1:0	95
Cu NPs@2-3	39.9:6.3	88
Cu NPs@3-3	16.4:10.5	72
Cu NPs@4-3	0:1	59

<sup>a</sup> Reaction Conditions: 1,2,3,4-Tetrahydroisoquinoline (1 mmol); catalyst (25 mg); O<sub>2</sub> (1 balloon); Time (4 h); Temperature (90 °C), DMF (1 mL). <sup>b</sup> the Yield of DHIQ was obtained by GC with internal standard of 1,3-dichlorobenzene.



**Figure S17.** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.23 (s, 1H), 7.25 - 7.19 (d, 3H), 7.05 (s, 1H), 3.67 (s, 2H), 2.64 (s, 2H).

GPF-0520-1.1.fid  
C13CPD

-159.27  
135.24  
130.00  
127.42  
126.36  
126.14  
126.02  
-46.30  
-23.96

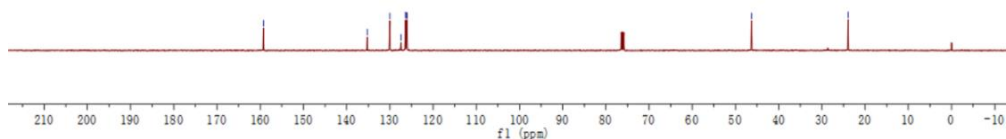
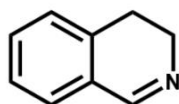


Figure S18. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.27(s), 135.24(s), 130.00(s), 127.42(s), 126.36(s), 126.14(s), 126.02(s), 46.30(s), 23.96(s).  
gpd-0525-6-xiu-1.1.fid  
PROTON

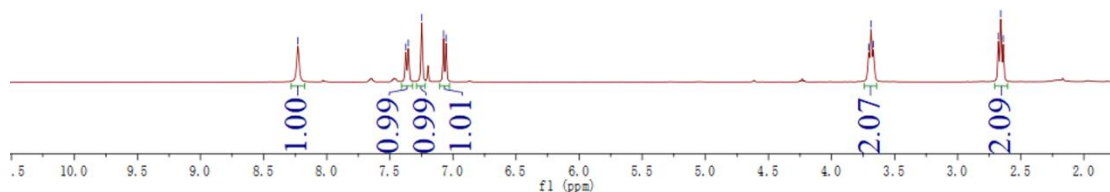
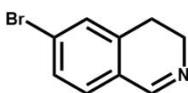
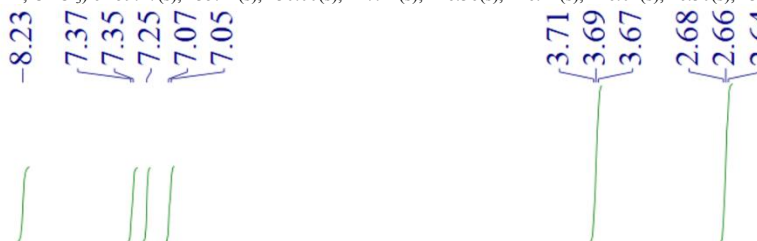


Figure S19. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.23 (s, 1H), 7.37 - 7.35 (d, 1H), 7.25 (s, 1H), 7.07 - 7.05 (d, 1H), 3.71 - 3.67 (t, 2H), 2.68 - 2.64 (t, 2H).

spd-0525-6-xiu-1. 2. fid  
C13CPD

-158.27  
137.28  
129.55  
129.25  
127.53  
126.12  
124.08

-45.96

-23.72

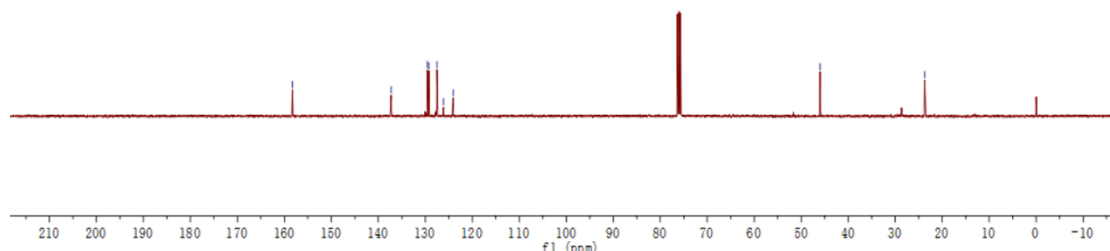
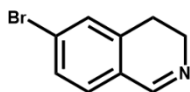


Figure S20. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.27(s), 137.28(s), 129.55(s), 129.25(s), 127.53(s), 126.12(s), 124.08(s), 45.96(s), 23.72(s).  
GFF-0527-5-XIU. 1. fid  
PROTON

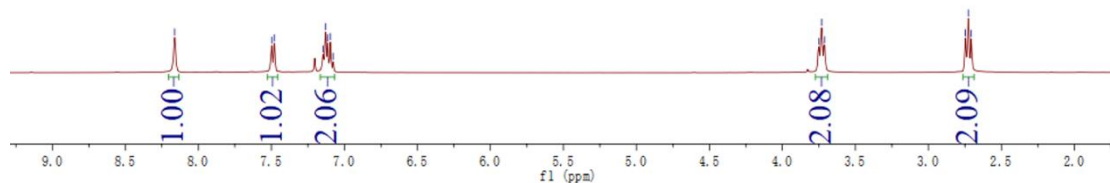
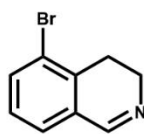
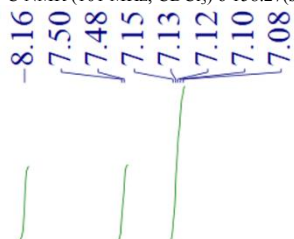


Figure S21. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.50 - 7.48 (d 1H), 7.15 - 7.08 (m, 2H), 3.75 - 3.71 (t, 2H), 2.75 - 2.71 (t, 2H).

-159.42  
136.09  
134.83  
130.22  
128.34  
126.39  
123.77

-47.33

-24.55

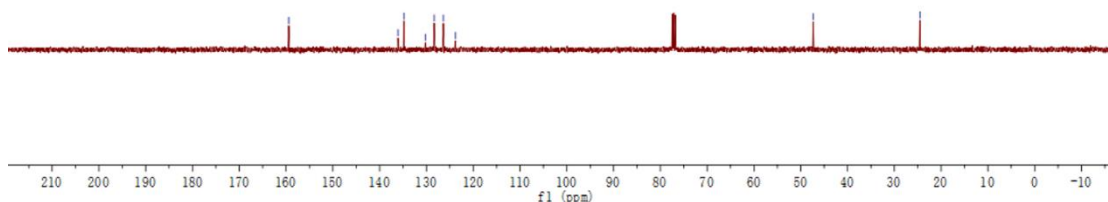
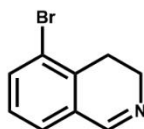


Figure S22. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.42 (s), 136.09 (s), 134.83 (s), 130.22 (s), 128.34 (s), 126.39 (s), 123.77 (s), 47.33 (s), 24.55 (s).  
7-溴-3,4-二氢异喹啉/基谱  
PROTON

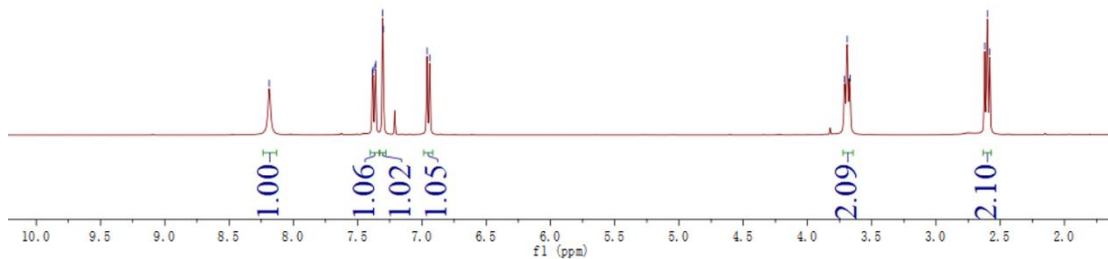
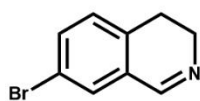
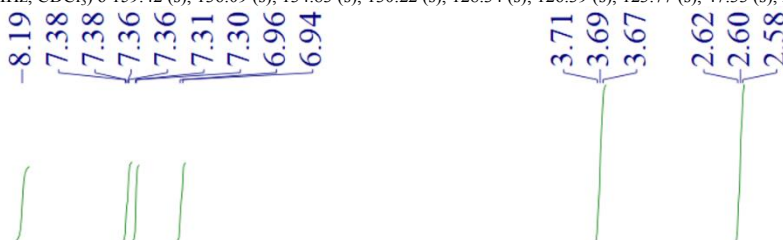


Figure S23. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.38 - 7.36 (dd, 1H), 7.31 - 7.30 (d, 1H), 6.96 - 6.94 (d, 1H), 3.71 - 3.67 (t, 2H), 2.62 - 2.58 (t, 2H).

7-溴-3,4-二氢异喹啉/杂质  
C13CPD

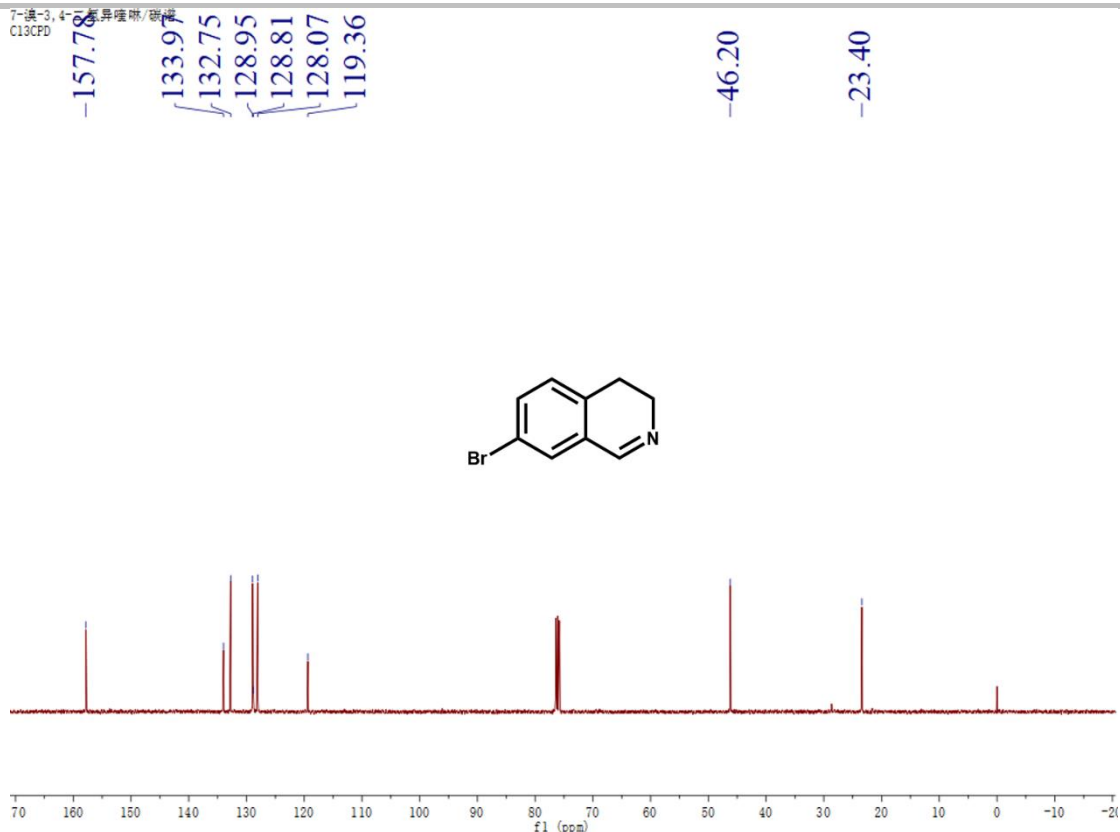


Figure S24.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  157.78z (s), 133.97 (s), 132.75 (s), 128.95 (s), 128.81 (s), 128.07 (s), 119.36 (s), 46.20 (s), 23.40 (s).

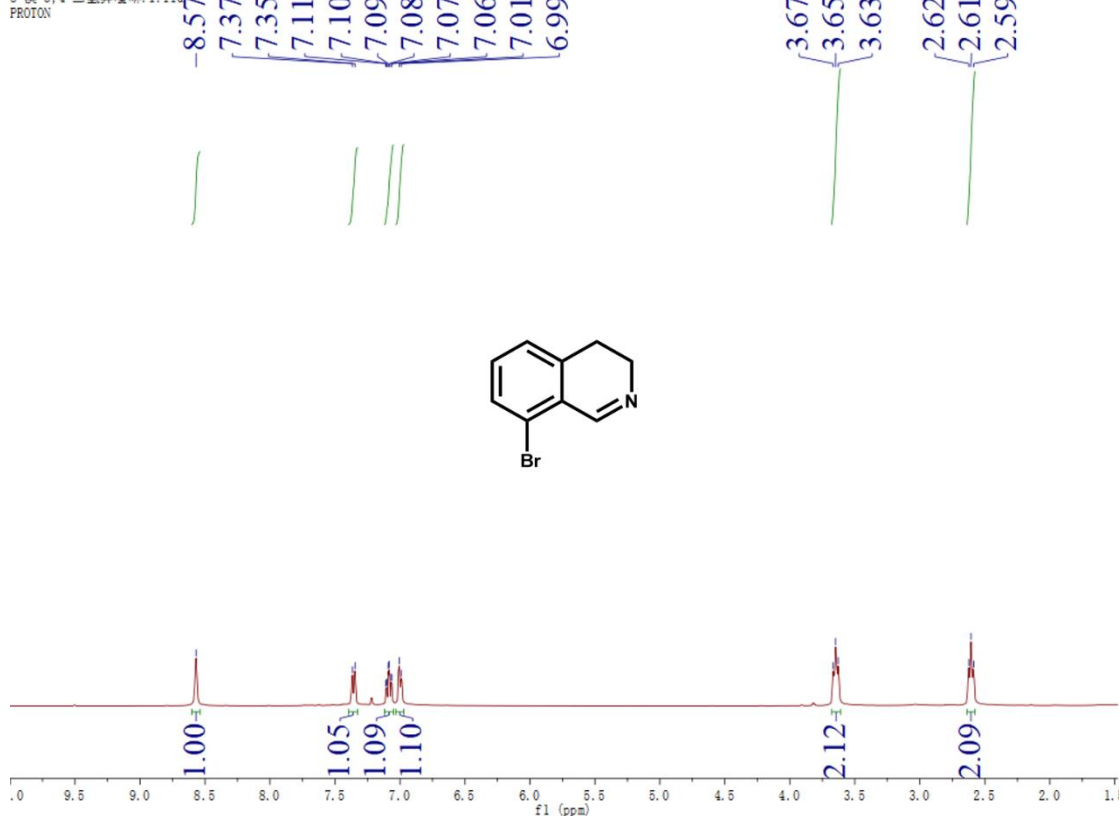
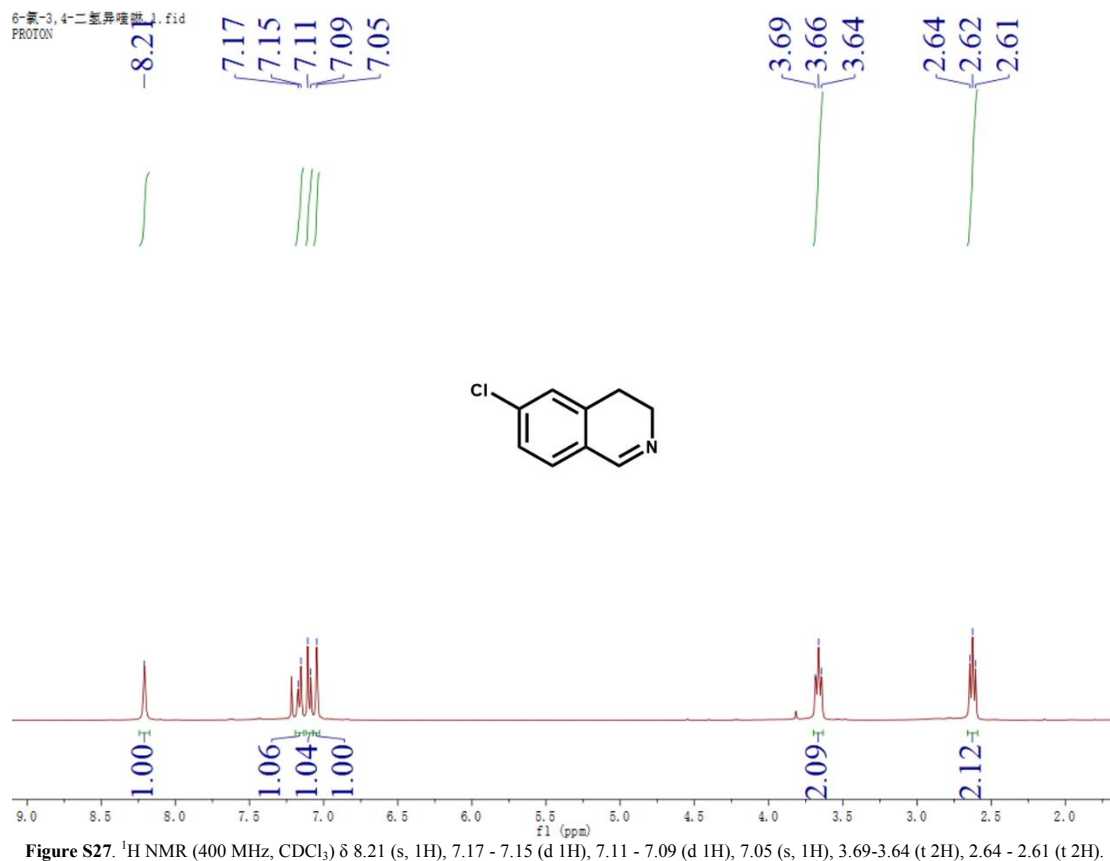
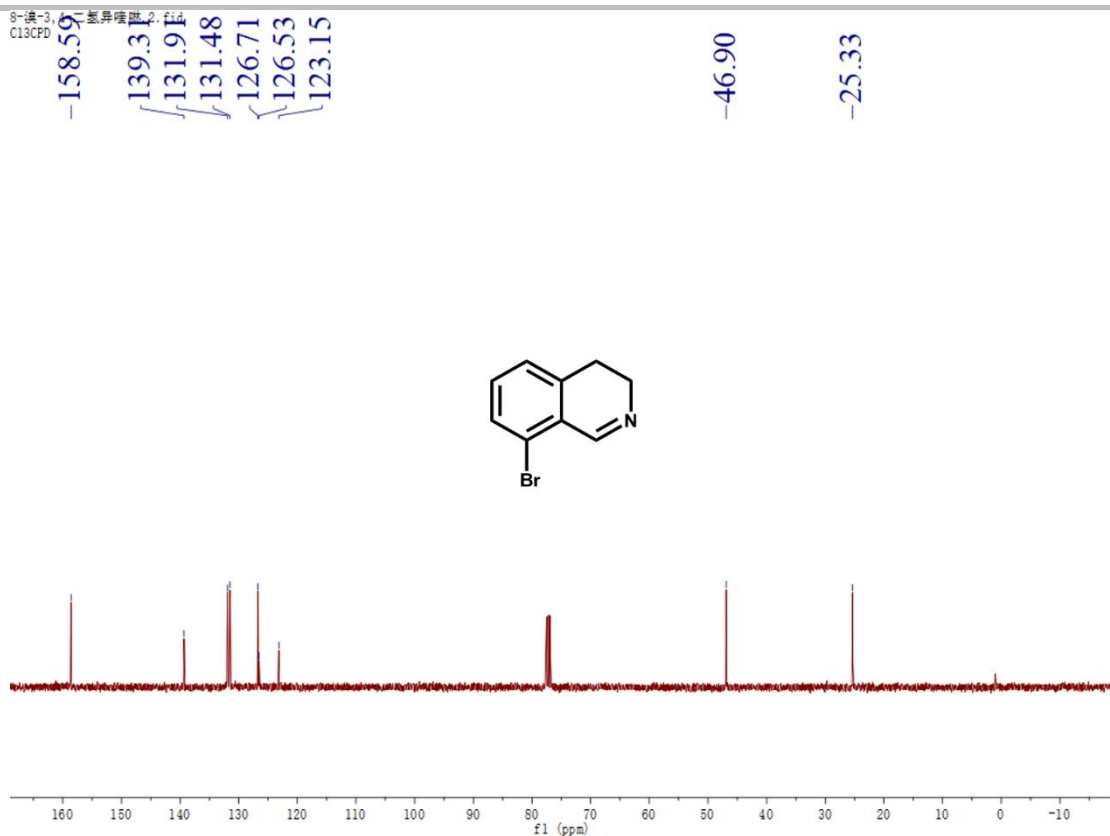


Figure S25.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.57 (s, 1H), 7.37 - 7.35 (d, 1H), 7.11 - 7.06 (tt, 1H), 7.01 - 6.99 (d, 1H), 3.67 - 3.63 (t, 2H), 2.62 - 2.56 (t, 2H).



6-氯-3,4-二氢喹啉, 1.fid  
 C13CPD  
 -159.12  
 138.10  
 136.58  
 128.35  
 127.62  
 127.24  
 126.76

-46.95

-24.84

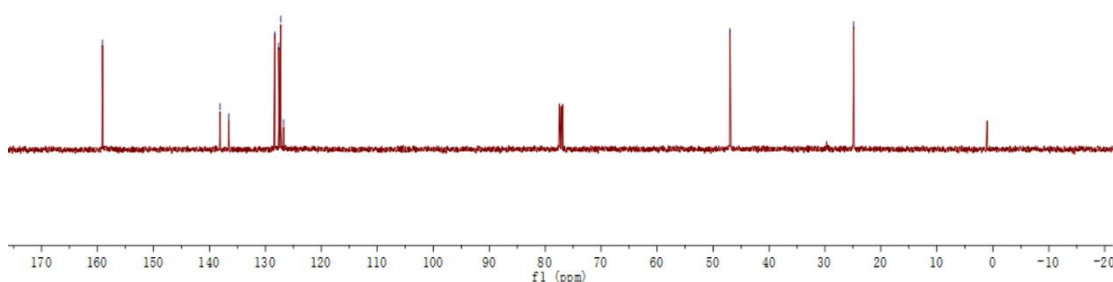
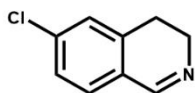


Figure S28. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.12 (s), 138.10 (s), 136.58 (s), 128.35 (s), 127.62 (s), 127.24 (s), 126.76 (s), 46.95 (s), 24.84 (s).

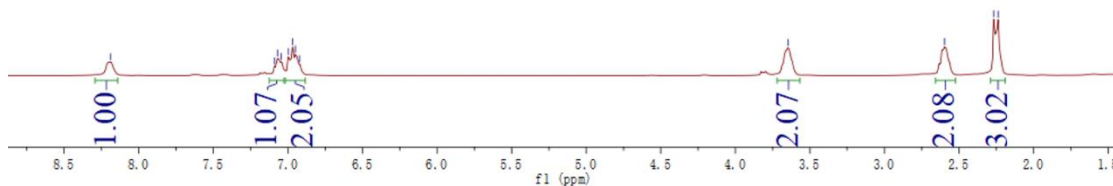
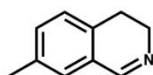
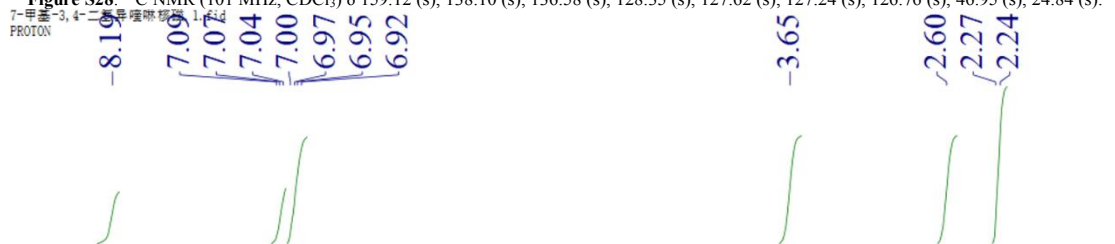


Figure S29. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.09 - 7.04 (t, 1H), 7.00 - 6.92 (m, 2H), 3.65 (s, 2H), 2.60 (s, 1H), 2.27 - 2.24 (d, 3H).

7-甲基-3,4-二氢异喹啉核磁. 2.fid  
C13CPD

-160.54  
136.68  
133.31  
131.68  
128.41  
127.84  
127.25

-47.63

24.70  
21.05

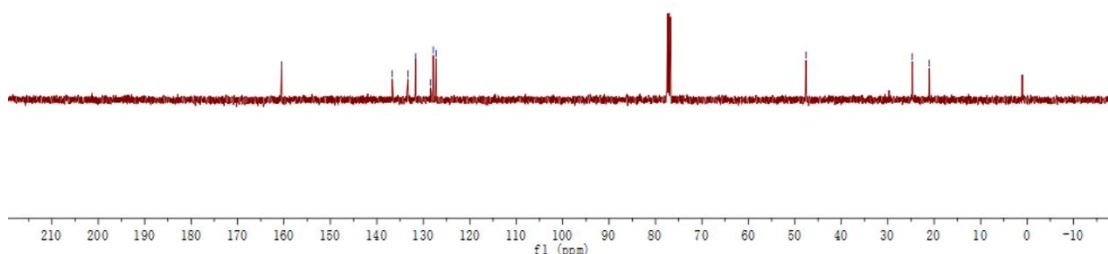
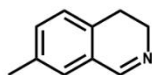


Figure S30. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.54 (s), 136.68 (s), 133.31 (s), 131.68 (s), 128.41 (s), 127.84 (s), 127.25 (s), 47.63 (s), 24.73 (s), 21.05 (s).

6-甲氧基-3,4-二氢异喹啉. 1.fid  
PROTON

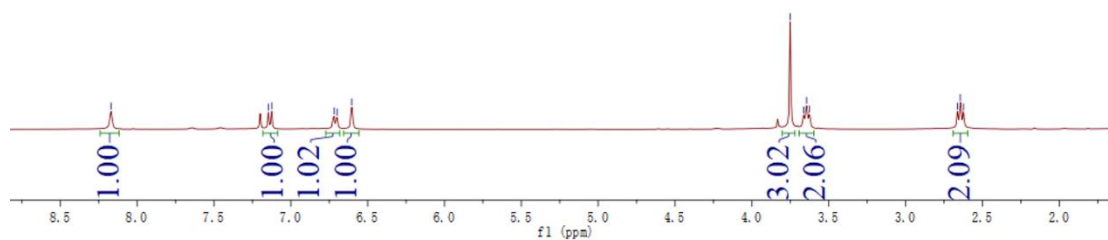
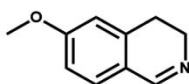


Figure S31. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.15 - 7.12 (d, 1H), 6.72 - 6.70 (d, 1H), 6.60 (s, 1H), 3.75 (s, 3H), 3.66 - 3.63 (t, 2H), 2.66 - 2.62 (t, 2H).

6-甲氧基-3,4-二氢异喹啉, 2. fid  
C13CPD

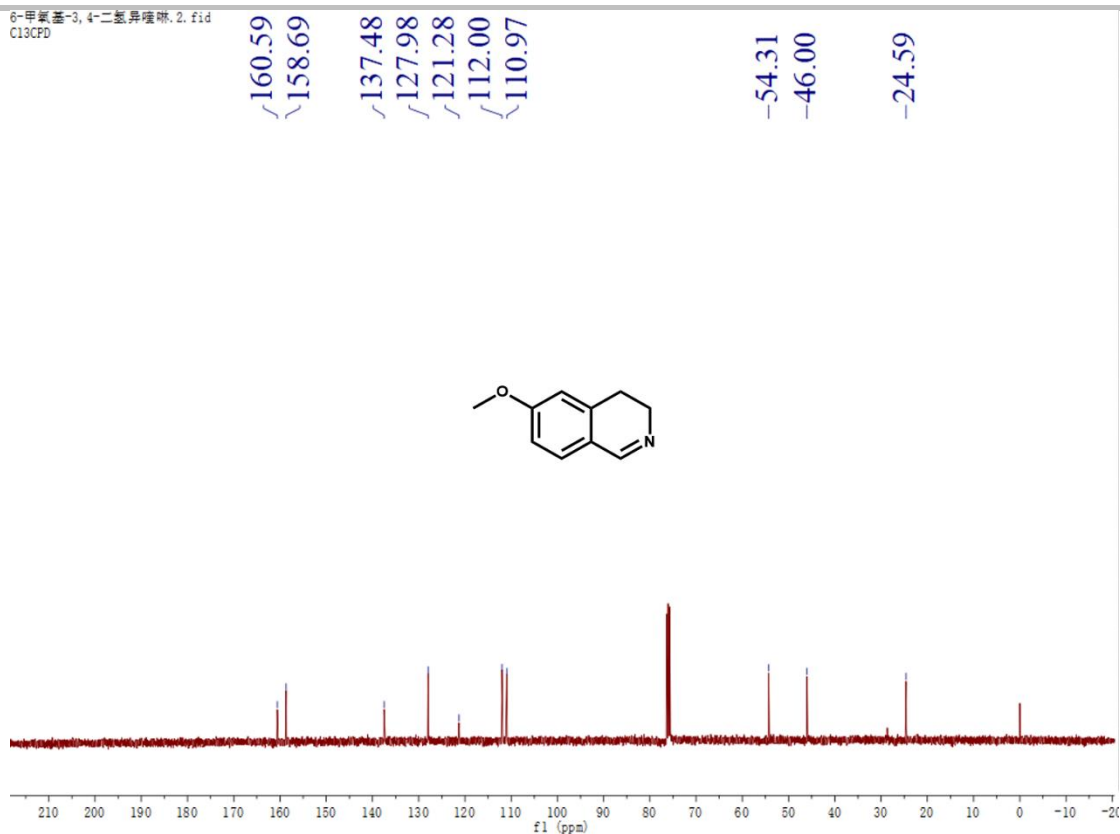


Figure S32.  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  160.59 (s), 158.69 (s), 137.48 (s), 127.98 (s), 121.28 (s), 112.00 (s), 110.97 (s), 54.31 (s), 46.00 (s), 24.59 (s).

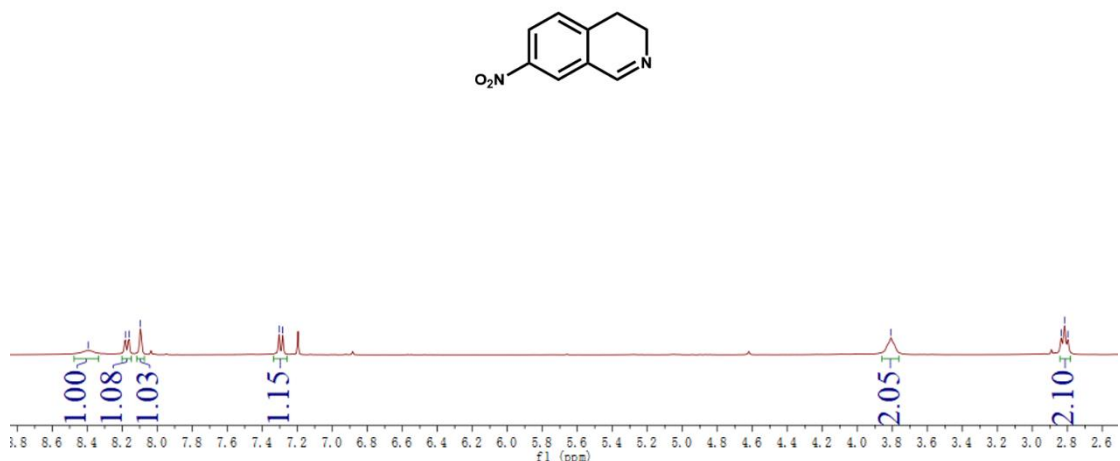
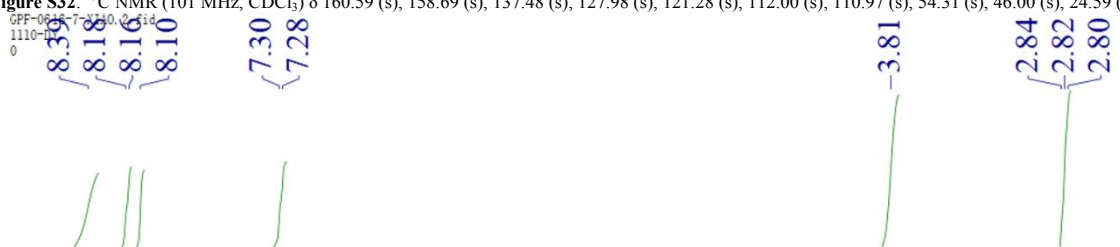


Figure S33.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.39 (s, 1H), 8.18-8.16 (d, 1H), 8.10 (d 1H), 7.30 - 7.28 (d 1H), 3.881 (s, 2H), 2.84 - 2.80 (t 2H).

7-硝基-3,4-二氢异喹啉  
C13CPD

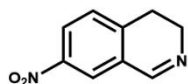
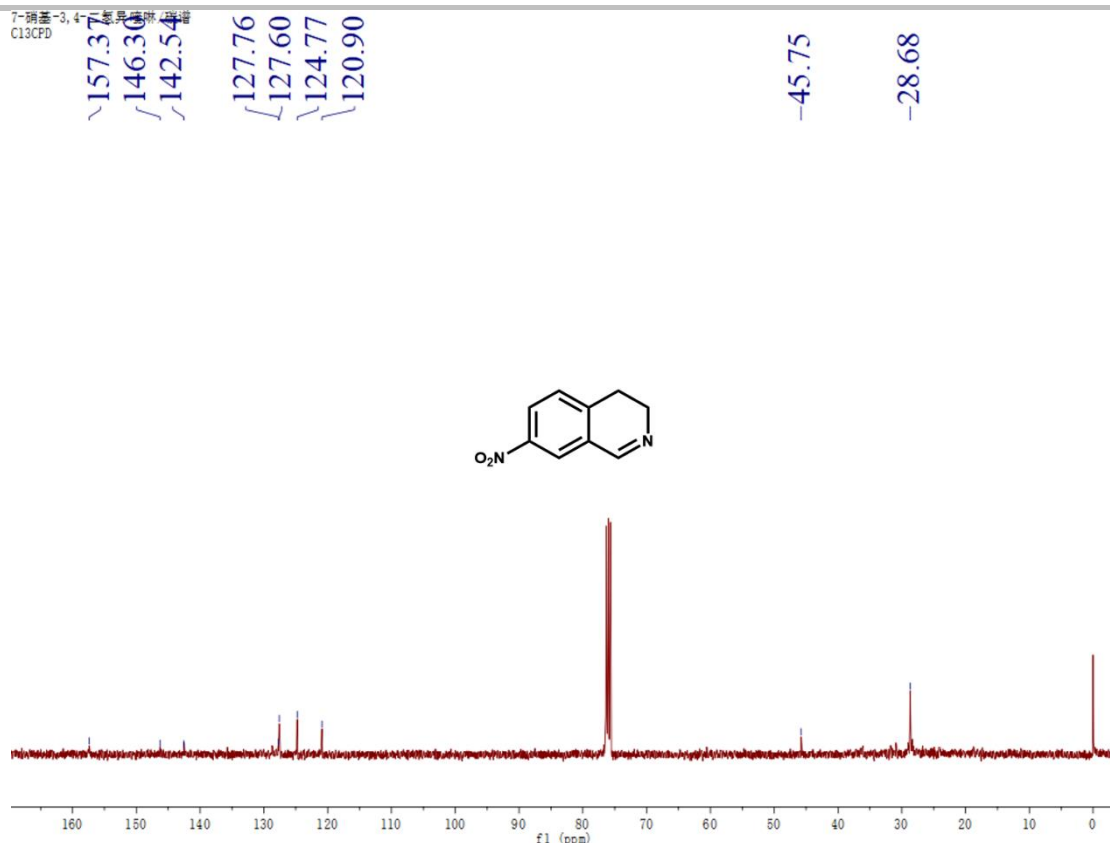


Figure S34. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 157.37 (s), 146.30 (s), 142.54 (s), 127.76 (s), 127.60 (s), 124.77 (s), 120.90(s), 45.75 (s), 28.68 (s).

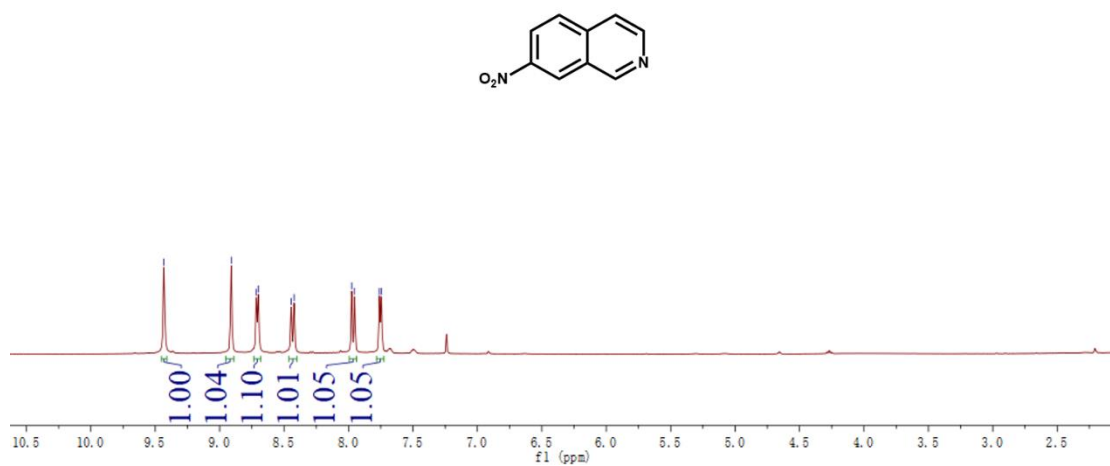
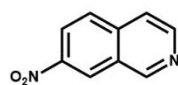
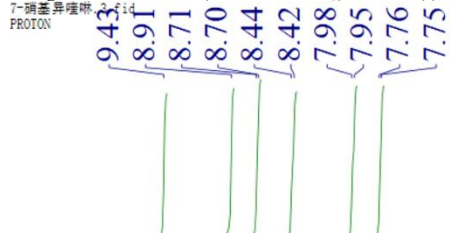


Figure S35. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.43 (s, 1H), 8.91 (s 1H), 8.71 - 8.70 (d 1H), 8.44 - 8.42 (d 1H), 7.98 - 7.95 (d 1H) 7.76 - 7.75 (d 1H).

7-硝基异喹啉  
C13CPD

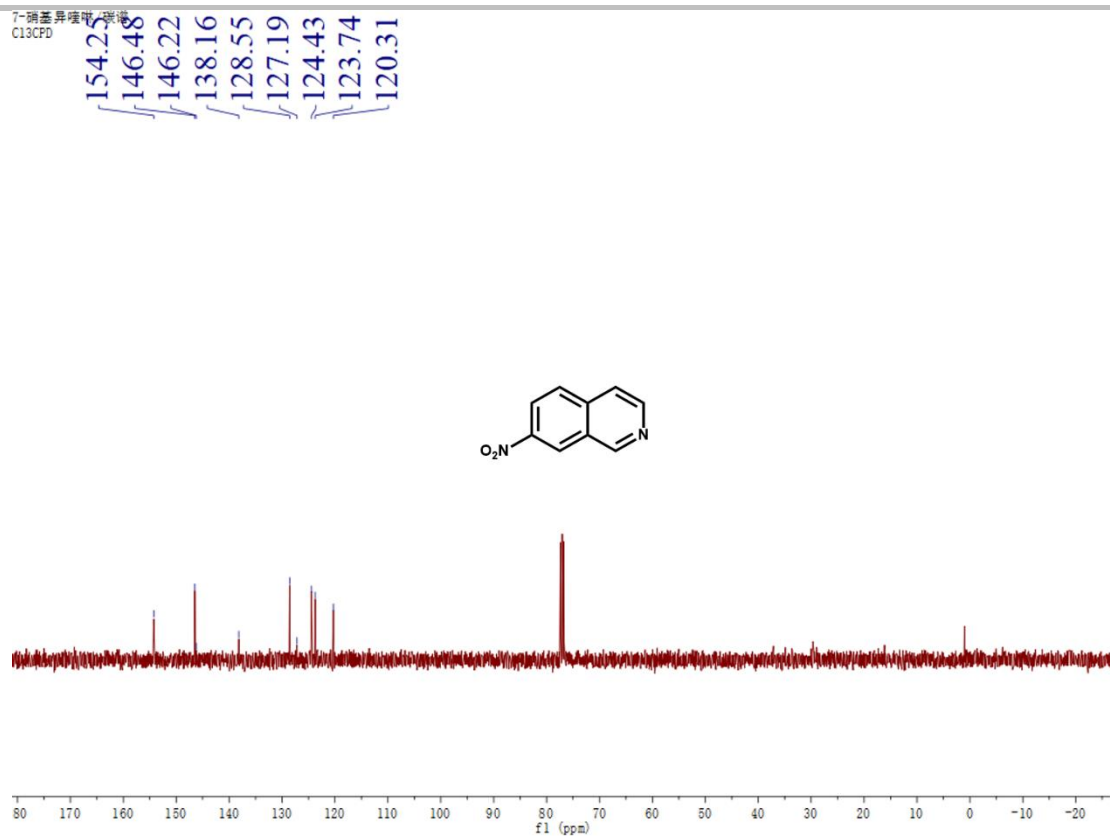


Figure S36. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 154.25 (s), 146.48 (s), 146.22 (s), 138.16 (s), 128.55 (s), 127.19 (s), 124.43 (s), 123.74 (s), 120.31 (s).  
GPF-6, 7-OCH<sub>3</sub>-DMF, 1.fid  
PROTON

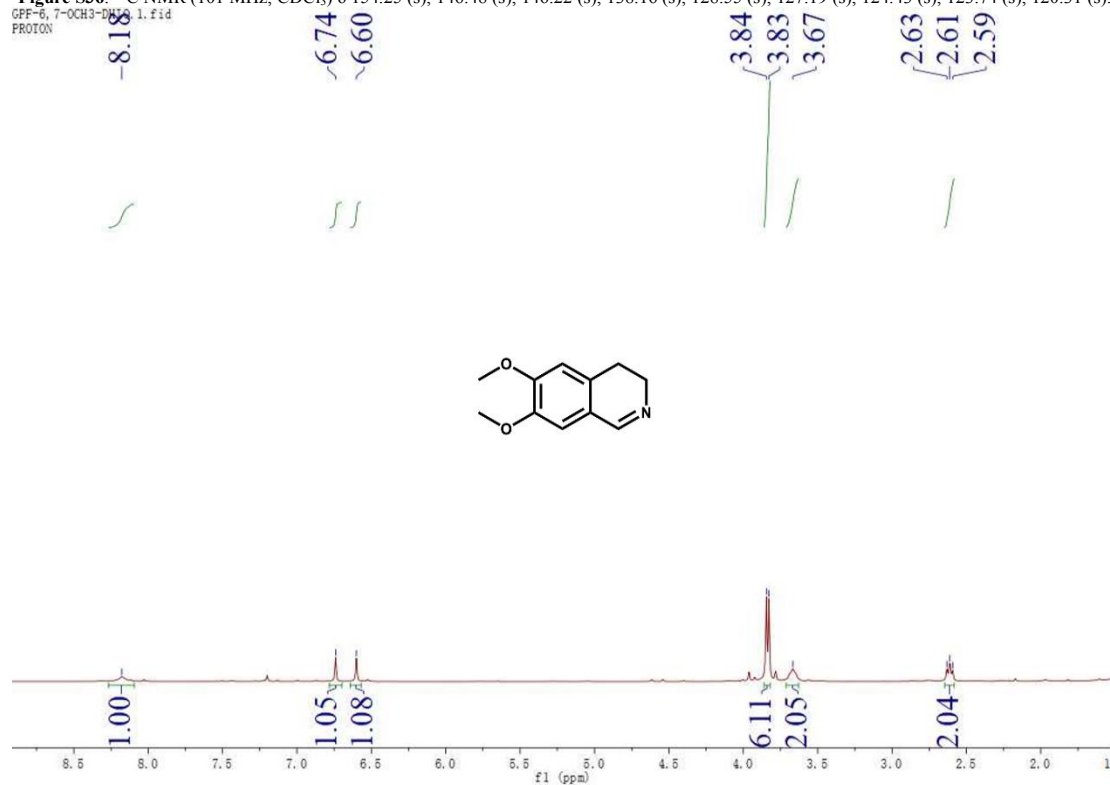


Figure S37. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.18 (s, 1H), 6.74 (s, 1H), 6.60 (s, 1H), 3.84 - 3.83 (d, 6H), 3.67 (s, 2H), 2.63 - 2.59 (t, 2H).

GPF-6, 7-och2-dhiq-chun-20230419.2. fig  
C13CPD

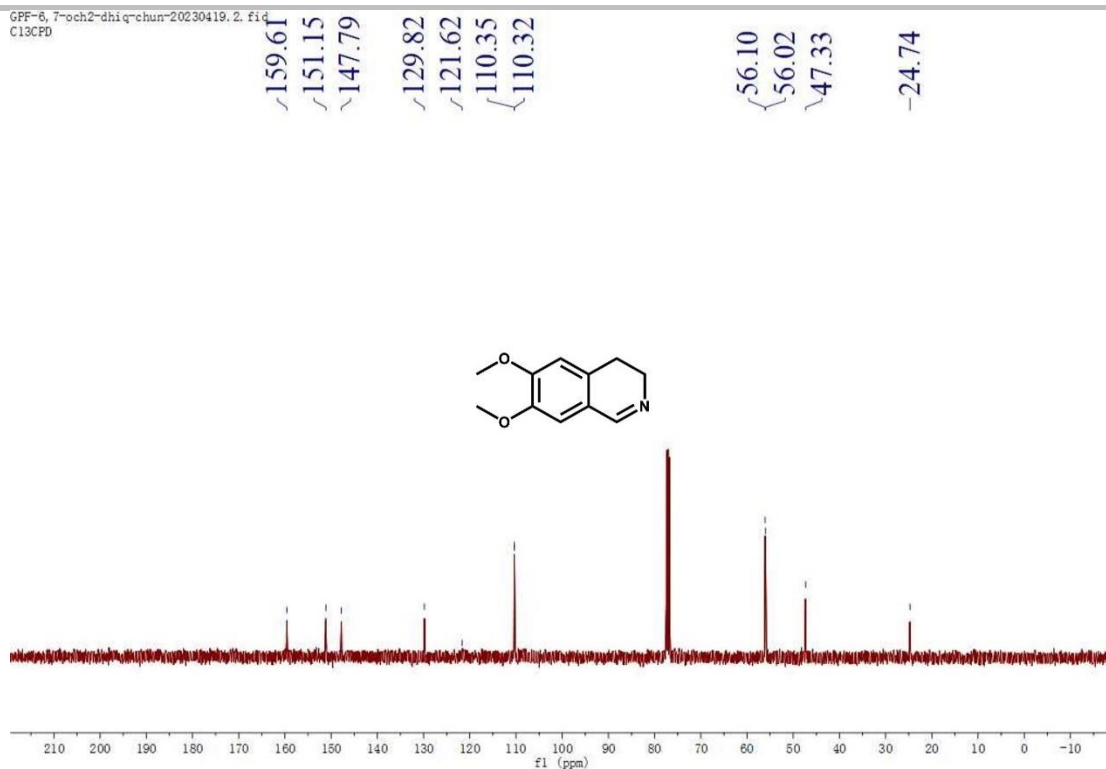


Figure S38. <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 159.61(s), 151.15 (s), 147.79 (s), 129.82 (s), 121.62(s), 110.35 (s), 110.32 (s), 56.10 (s), 56.02 (s), 47.33 (s), 24.74 (s).

GPF-BA-10H-20230214\_1. fig  
PROTON

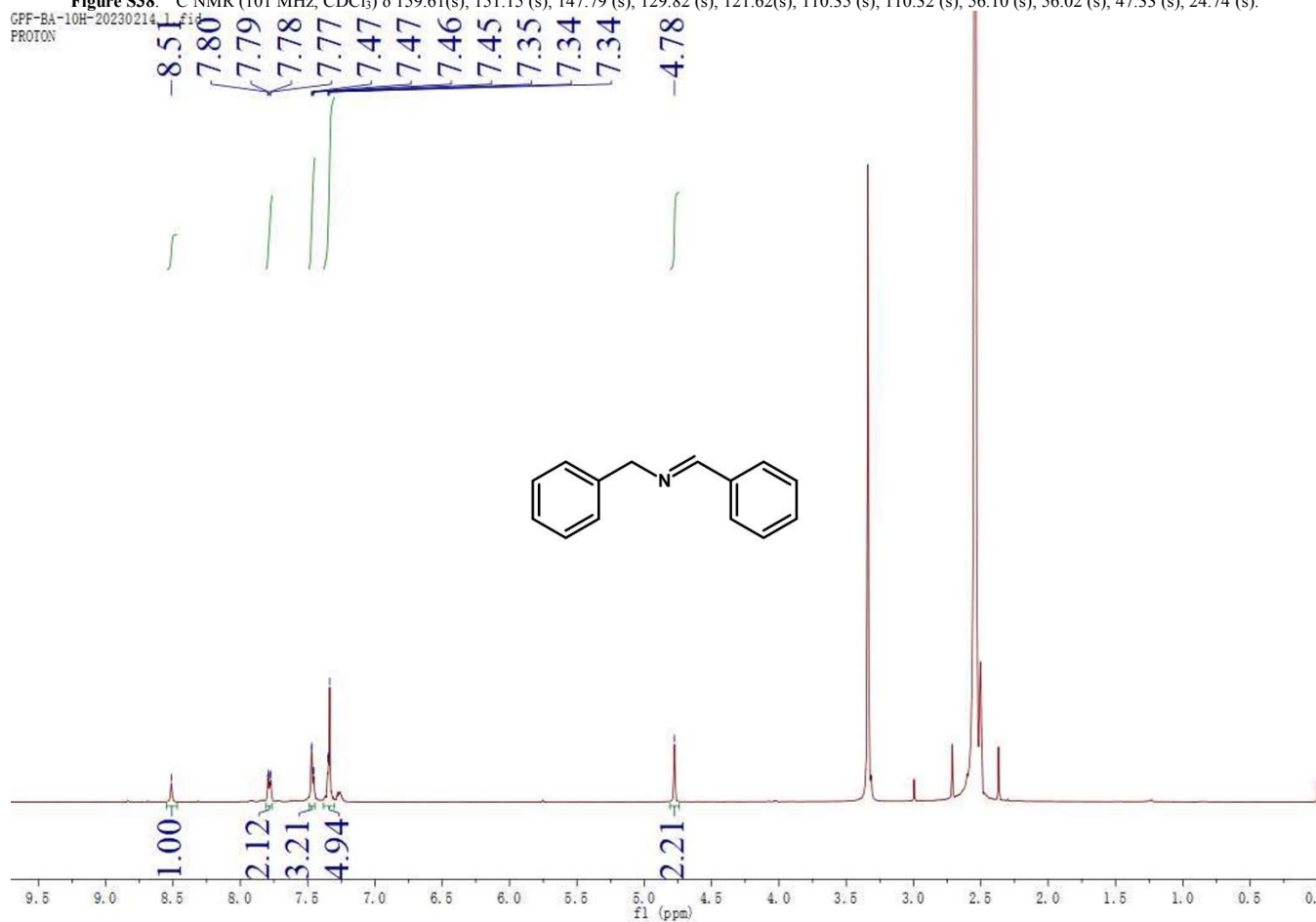


Figure S39. <sup>1</sup>H NMR (400 MHz, DMSO-d<sub>6</sub>) δ= 8.51 (s, 1H), 7.80-7.77 (m, 2H), 7.47-7.45 (m, 3H), 7.35-7.34 (t, 5H), 4.78 (s, 2H).

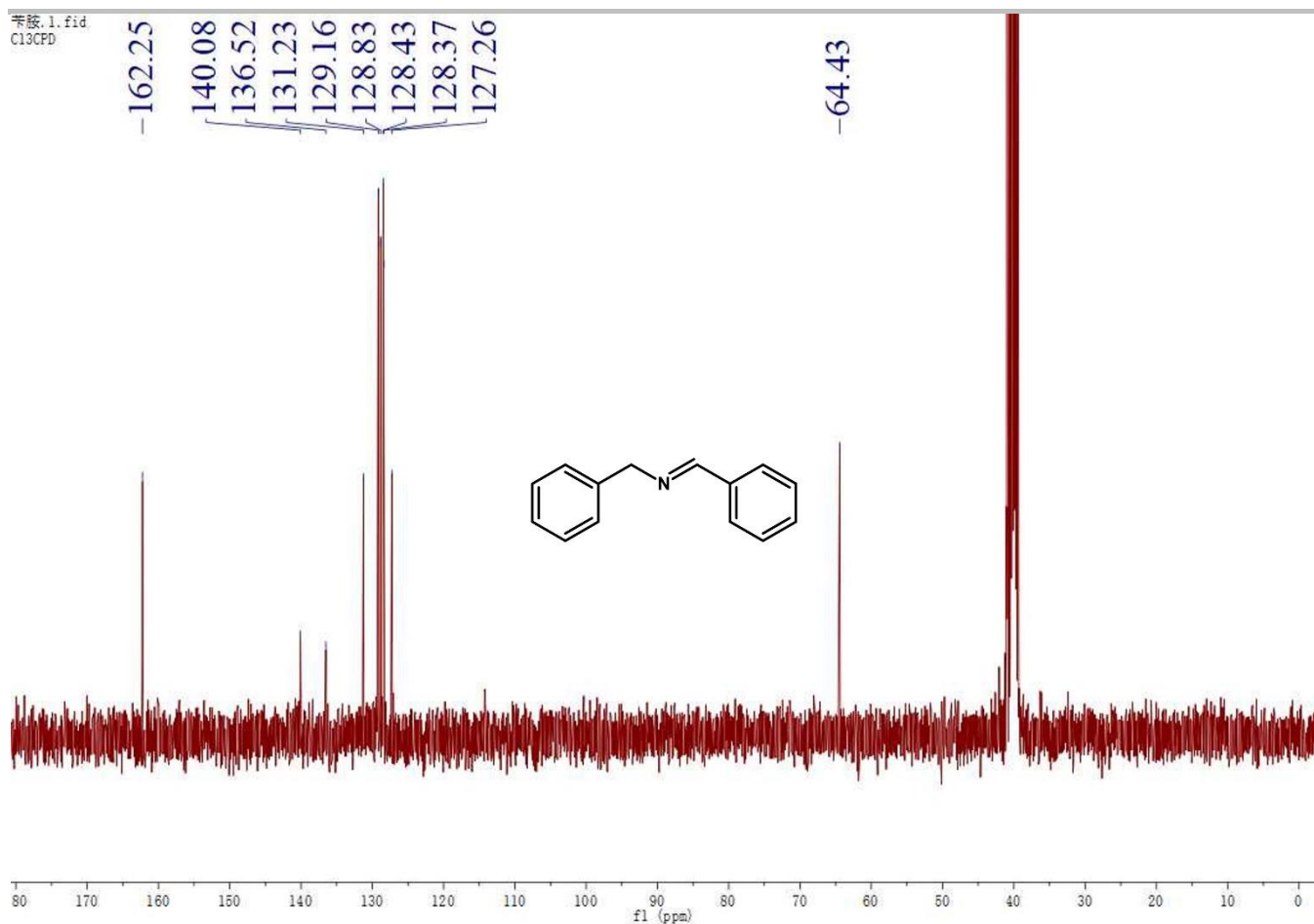


Figure S40.  $^{13}\text{C}$  NMR (101 MHz, DMSO- $d_6$ )  $\delta$ = 162.25, 140.08, 136.52, 131.23, 129.16, 128.83, 128.43, 128.37, 127.26, 64.43.

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