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Supporting Information

Mechanosynthesis of polymeric and binuclear copper complexes via dehydrochlorination and its application in solvent-free C-S bond cross-coupling

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1. Crystal data and structural refinement parameters

	1-Cu	2'-Cu	2-Cu
Empirical formula	$C_{15}H_{17}Cl_5CuN_4$	$C_{19}H_{17}Cl_3CuN_4$	$C_{38}H_{38}Cl_{12}Cu_3N_8$
Formula weight	494.13	471.26	1222.78
Crystal temperature (K)	298(2)	298(2)	298(2)
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1$
Z	2	4	2
a(Å)	10.502(2)	10.1471(9)	7.8177(4)
b(Å)	10.560(3)	13.7121(12)	25.0982(14)
c(Å)	11.248(3)	14.0607(12)	12.3248(7)
α(deg)	104.664(7)	90	90
β(deg)	110.573(7)	92.858(3)	96.956(2)
γ(deg)	110.692(8)	90	90
V(Å^3)	985.9(4)	1953.9(3)	2400.5(2)
D_x(Mg.cm^{-3})	1.664	1.602	1.692
μ(mm^{-1})	1.792	1.540	2.02
F(000)	498	956	1226
R_{int}	0.0227	0.040	0.0348
No.of collected data(unique)	17315	30290	31301
No.of data with I>2σ(I)	4441	4225	7740
No.of parameters varied	234	244	551
s	1.074	1.084	1.078
R_1	0.0296	0.0521	0.0395
wR_2	0.0758	0.1018	0.0757

2. Hydrogen bonding in crystals

Table S1. Hydrogen bonds in crystal **1-Cu**. (CCDC number: 2095149)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmeyty Code
N4–H4···Cl3(i)	0.801	2.295	3.091	172.55	x-1, y-1, z-1
C1–H1···Cl1(ii)	0.930	2.844	3.521	130.72	-x+2, -y+2, -z+1
C1–H1···Cl2(iii)	0.930	2.937	3.703	140.62	-x+2, -y+2, -z+1
C4–H4···Cl2(iv)	0.970	2.867	3.754	152.40	-x+2, -y+2, -z+1
N3–H3···Cl5(v)	0.852	2.167	2.990	162.51	x, y, z

Table S2. Hydrogen bonds in crystal **2-Cu**. (CCDC number: 2095146)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmeyty Code
N1–H1···Cl1(i)	0.860	2.361	3.181	159.54	x, y, z
C6–H6···Cl8(ii)	0.969	2.837	3.678	145.60	x+1, y, z+1
C7-H7···Cl8(iii)	0.930	2.605	3.449	151.02	x+1, y, z+1
N4–H4···Cl7(iv)	0.858	0.457	3.193	144.26	x, y, z+1

Table S3. Hydrogen bonds in crystal **2'-Cu**. (CCDC number: 2094971)

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmeyty Code
C14–H14···Cl3(i)	0.971	2.762	3.509	134.26	x, -y+1/2, z-1/2
C1-H1···Cl2(ii)	0.929	2.691	3.575	159.41	-x+1, y-1/2, -z+3/2
C1–H1···Cl1(iii)	0.929	2.886	3.523	126.87	-x+1, y-1/2, -z+3/2
C8–H8···Cl1(iv)	0.969	2.794	3.655	148.41	-x+1, y-1/2, -z+3/2

3. E-factor and EcoScale

Table S4. E-factor for the C-S bond cross-coupling

Entry	Input Amount	Out Amount
1	2-bromoacetophenone 0.199 g	2-(benzo[d]thiazol-2-ylthio)-1-phenylethanone 0.2829 g
2	2-mercaptobenzothiazole 0.167 g	_
3	2'-Cu 0.00958 g	_
4	Acetonitrile 0.047 g	_
	Total 0.42258 g	Total 0.2829 g

E-Factor = (0.42258 – 0.2829)/0.2829 = 0.494

Table S5. EcoScale penalty points for the C-S bond cross-coupling

EcoScale points	Factor	Penalty
1 Yield	99%	0.5
2 Price	2-bromoacetophenone	0
	2-mercaptobenzothiazole	0
	$MgSO_4$	0
3 Safety	2-mercaptobenzothiazole (N)	5
	petroleum ether (F)	5
4 Technical setup	agate mortar	0
5 Temperature/time	room temperature, 20 min	0
6 Workup and purification	classic chromatography	10
Penalty points total		20.5

EcoScale = 100 – 20.5 = 79.5

4. Solution synthesis for C-S coupling

To a 10 mL pressure tube a stir bar, 2- bromoacetophenone (1 mmol, 199 mg), 2-mercaptobenzothiazole (1 mmol, 167 mg), 2'-Cu (1 mol%, 9.58 mg) and acetonitrile (8mL) were added into the pressure tube. The reaction was stirred at room temperature under air. Upon completion, the crude product was purified by column chromatography.

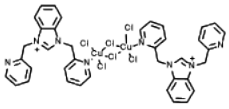
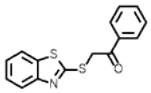
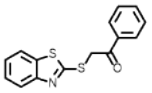
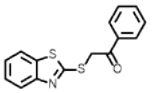
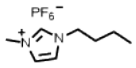
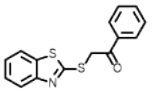
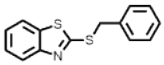
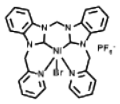
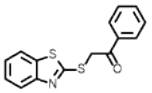
Table S6. C-S coupling with different reaction times in the solution method

Entry[a]	Time (min)	Yield(%)[b]
1	20	14
2	90	57
3	180	61
4	270	52
5	360	44
6	720	33

(a) Reaction conditions: phenacyl bromide (1a) (1 mmol), 2-mercaptobenzothiazole (2a) (1 mmol), 1.0 mol% of 2'-Cu, 20-30°C, 8 mL acetonitrile. (b) isolated yield.

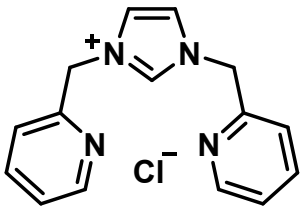
5. Comparison of data for C-S coupling

Table S7 Comparison of several reported C-S bond cross-coupling

Reference	Catalyst	Co-catalyst	Product	Reaction conditions	Yield (%)
Our Work		-		catalyst (1.0 mol%), CH_3CN (60 μL), 20-30 °C, 20 min, grinding	99
Baltaş et al[1]	C_2H_5NaO	-		catalyst (1.5 mmol), C_2H_5OH (20 mL) 20-30 °C, 48 h, solution	78
Baltaş et al[1]	C_2H_5NaO	-		catalyst (1.5 mmol), C_2H_5OH (5 mL) 120 °C, 15 min, 130W, solution	91
Zheng et al[2]		K_2CO_3		catalyst (3 mL), 50 °C, 2 h	95
Gilmour et al[3]	NaH	-		catalyst (1.5 mmol), DMF, 20-30 °C, 12 h, Ar, solution	99
Guo et al[4]		-		catalyst (1.8 mol%), CH_3OH (30 μL), 15-20 °C, 30 min, grinding	93

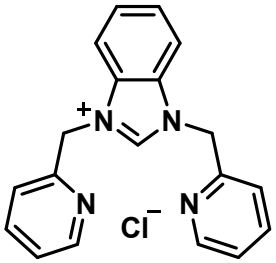
6. Analytical data of products

L1:



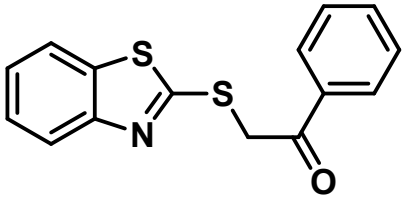
^{1}HNMR (300 MHz, DMSO): δ = 9.53 (s, 1H), 8.56 (d, J = 4.1 Hz, 2H), 8.01 – 7.76 (m, 4H), 7.47 (dt, J = 12.4, 7.9 Hz, 4H), 5.65 (s, 3H). NMR data is consistent with literature values.[5] IR(KBr): v = 1593.04 cm^{-1} (C=N), 753.28 cm^{-1} (Cl^-).

L2:



^{1}H NMR (300 MHz, $CDCl_3$) δ = 11.74 (s, 1H), 8.50 (d, J = 4.7 Hz, 2H), 7.91 – 7.67 (m, 6H), 7.52 (dd, J = 6.3, 3.1 Hz, 2H), 7.31 – 7.21 (m, 2H), 6.04 (s, 4H). NMR data is consistent with literature values.[6] IR(KBr): v = 1594.09 cm^{-1} (C=N), 753.13 cm^{-1} (Cl^-).

2-(benzo[d]thiazol-2-ylthio)-1-phenylethanone (3a): White solid, yield: 99.1%.



^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.09 (d, J = 7.5 Hz, 2H), 7.81 (d, J = 8.1 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.62 (d, J = 7.5 Hz, 1H), 7.52 (t, J = 7.7 Hz, 2H), 7.40 (s, 1H), 7.29 (t, J = 7.6 Hz, 1H), 4.98 (s, 2H).^{13}C NMR (75 MHz, $CDCl_3$) δ = 192.75 (s), 165.10 (s), 152.69 (s), 135.31 (d, J = 4.6 Hz), 133.69 (s), 128.53 (d, J = 18.2 Hz), 125.89 (s), 124.25 (s), 121.33 (s), 120.94 (s), 40.92 (s). NMR data is consistent with literature values.[7] IR (KBr): v = 1597.43 cm^{-1} (C=O).

7. Spectra of products

Figure S1. ^{1}**H NMR** spectrum of **L1**

L1:

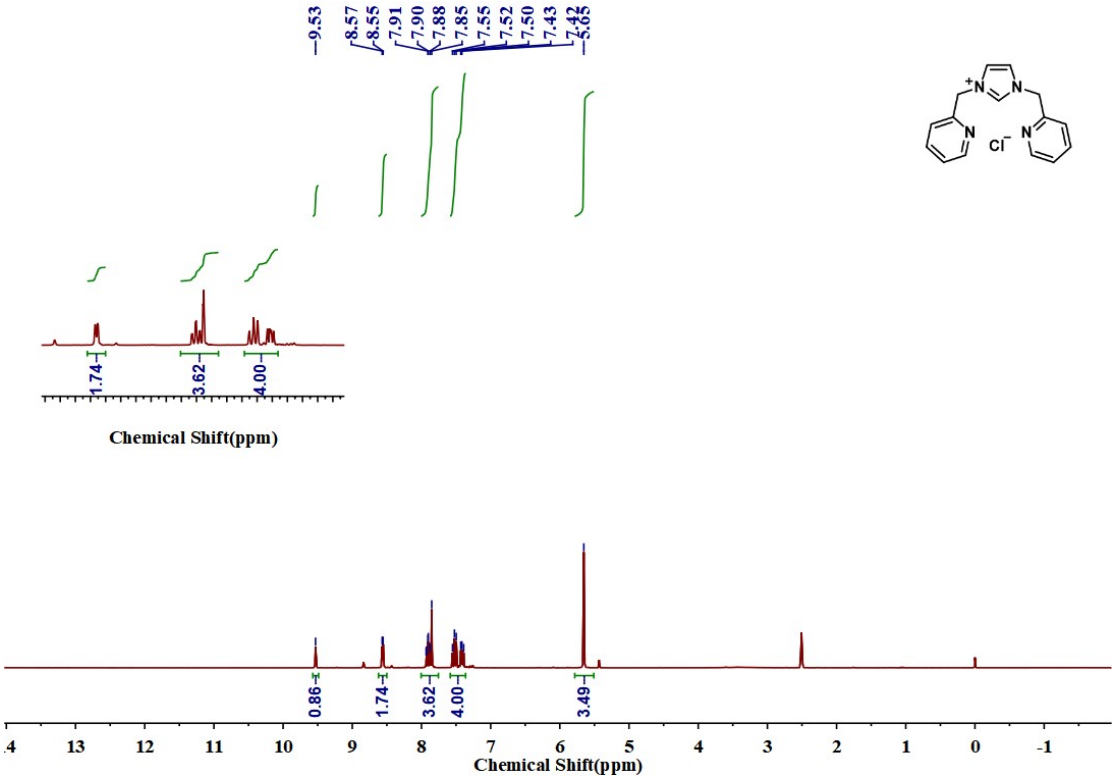


Figure S2. **^{1}H NMR** spectrum of **L2**

L2:

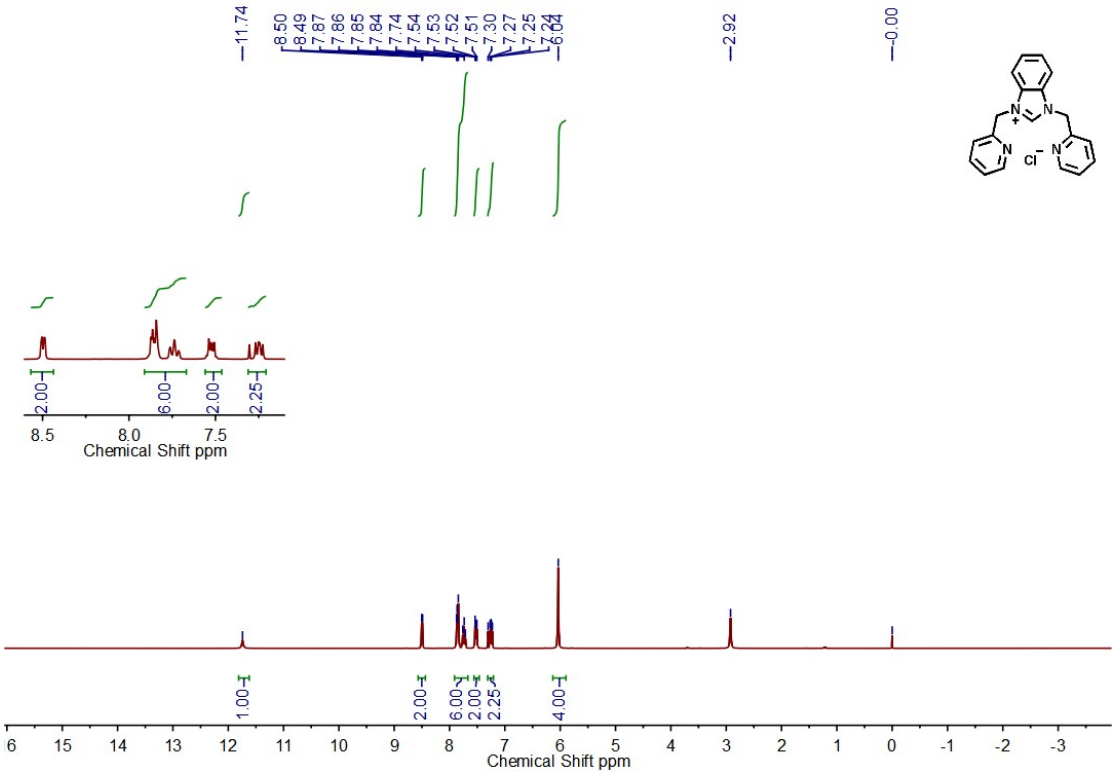


Figure S3. **^{1}H NMR** and **^{13}C NM**R spectrum of **3a**

2-(benzo[d]thiazol-2-ylthio)-1-phenylethanone (3a):

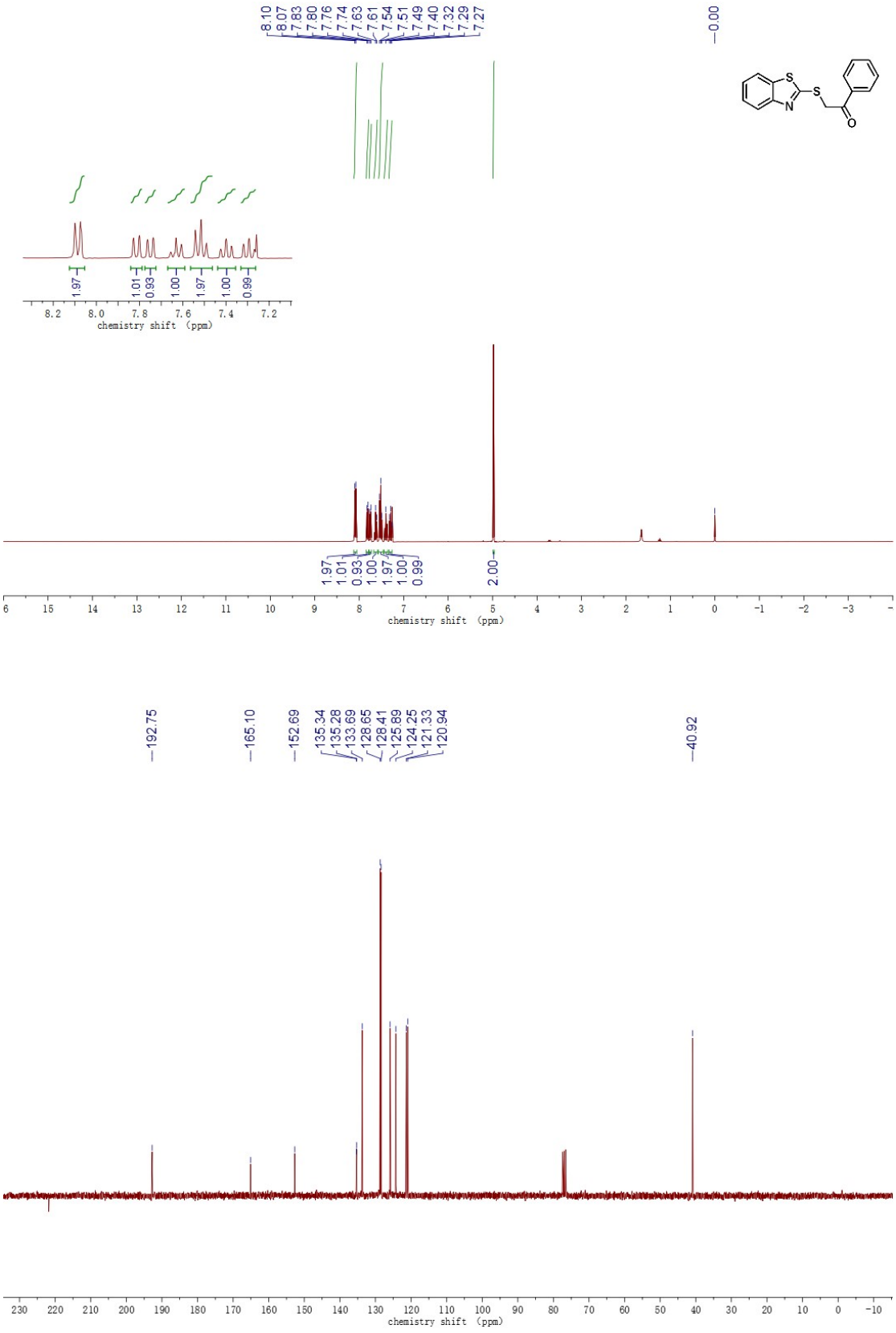


Figure S4. Neat **FT-IR** spectrum of **L1**

L1:

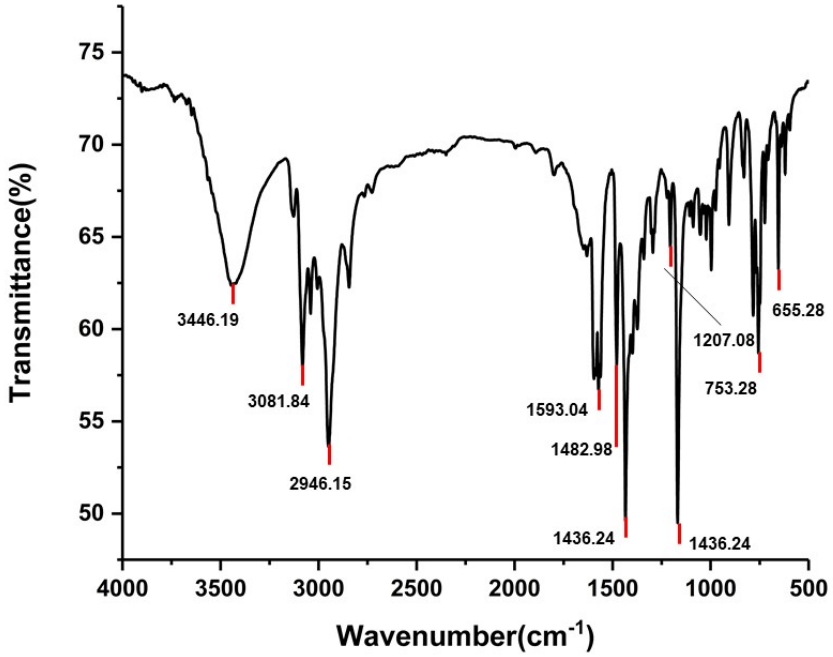
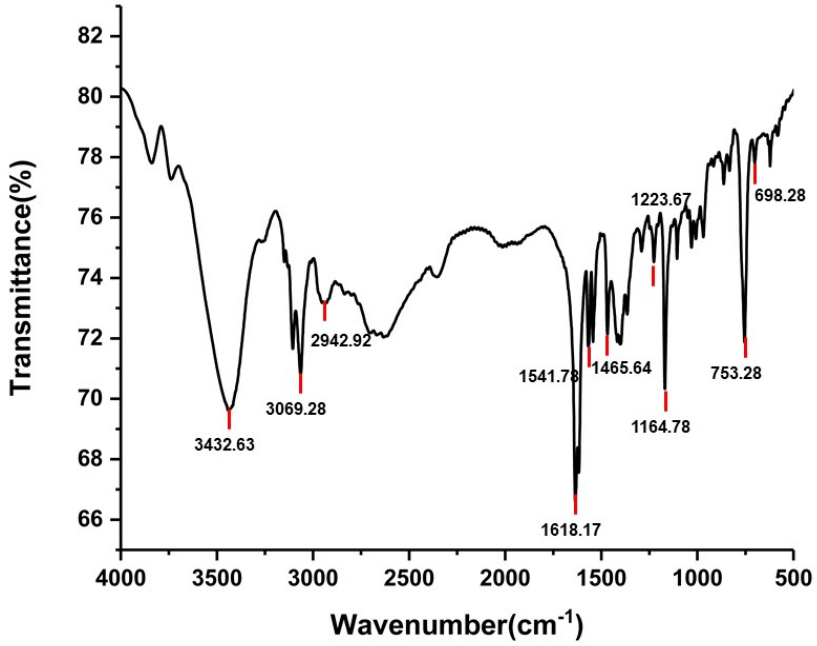


Figure S5. Neat **FT-IR** spectrum of **1-Cu**

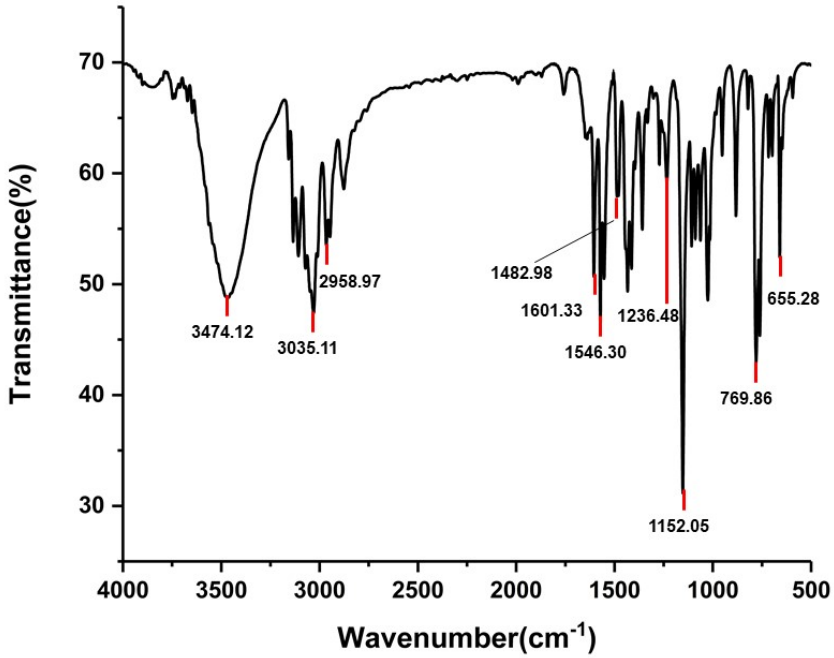
1-Cu:



IR(KBr): v = 1618.17 cm^{-1} (C=N), 753.28 cm^{-1} (Cl^-).

Figure S6. Neat **FT-IR** spectrum of **1'-Cu**

1'-Cu:



IR(KBr): v = 1546.30 cm^{-1} (C=N), 769.86 cm^{-1} (Cl^-).

Figure S7. Neat **FT-IR** spectrum of **L2**

L2:

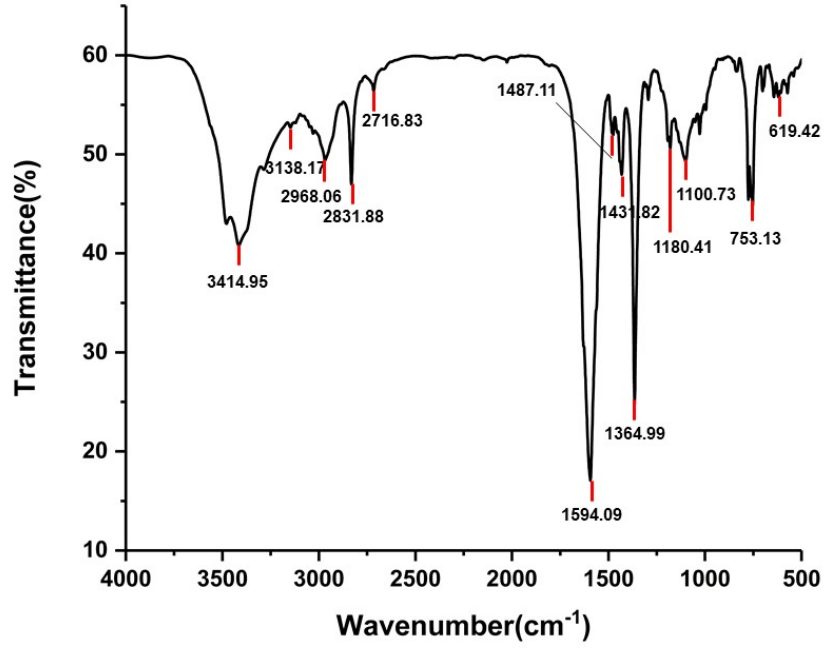
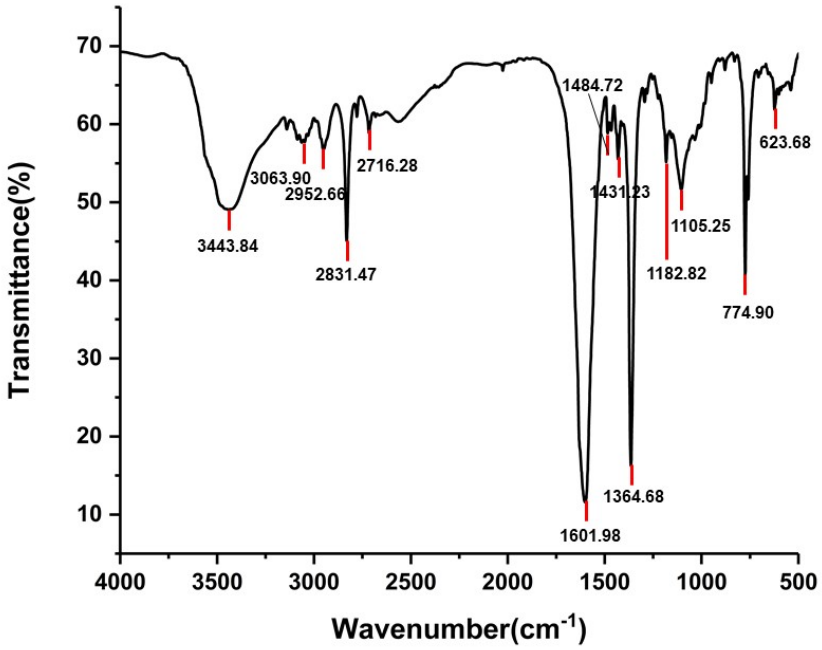


Figure S8. Neat **FT-IR** spectrum of **2-Cu**

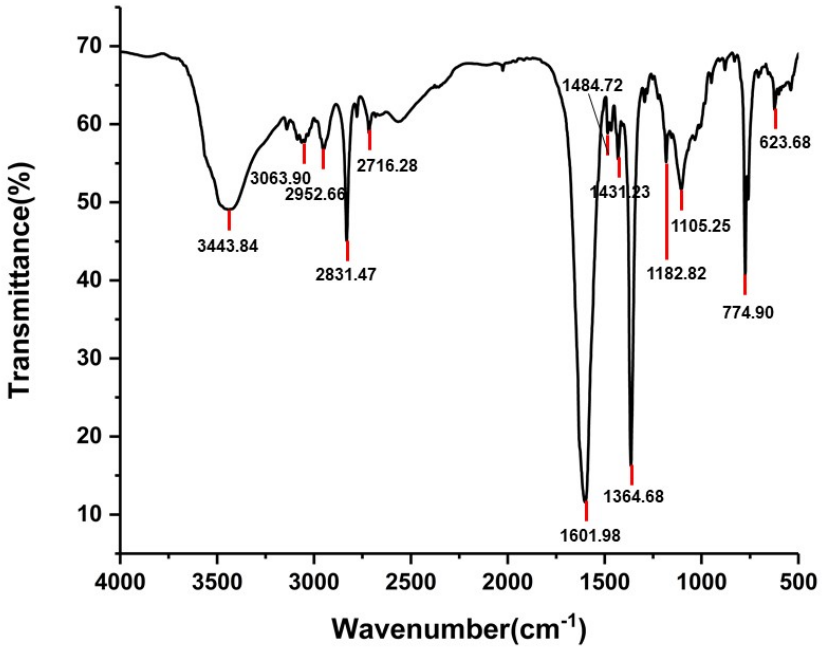
2-Cu:



IR(KBr): v = 1601.98 cm^{-1} (C=N), 774.90 cm^{-1} (Cl^-).

Figure S9. Neat **FT-IR** spectrum of **2'-Cu**

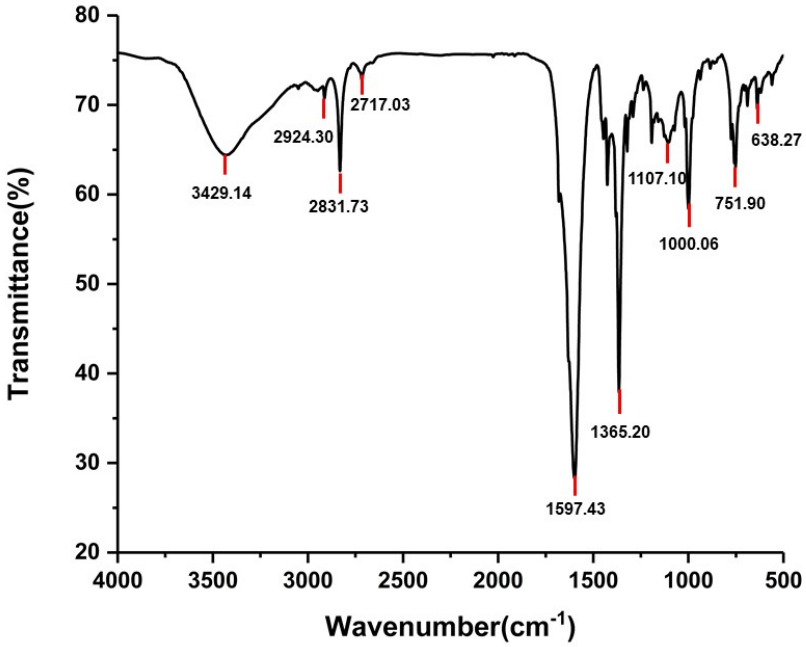
2'-Cu



IR(KBr): v = 1601.98 cm^{-1} (C=N), 774.90 cm^{-1} (Cl^-).

Figure S10. Neat **FT-IR** spectrum of **3a**

2-(benzo[d]thiazol-2-ylthio)-1-phenylethanone (3a):



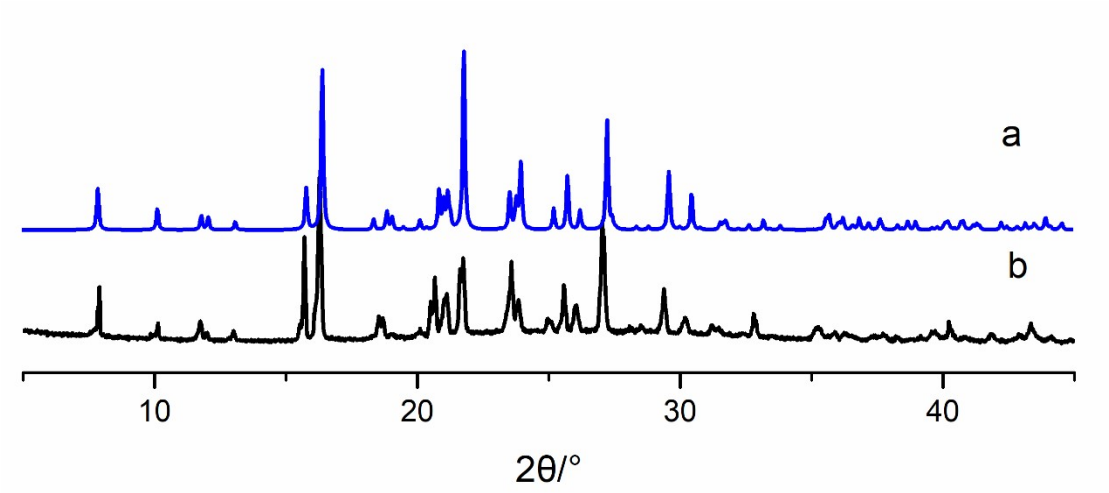


Figure S11. Comparison PXRD patterns of crystal **3a**: (a) Simulated PXRD from single crystal **3a** (CSDcode: PUFGED and PUFGED01)[8-9]; (b) Recrystallization PXRD spectrum of **3a**.

References

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