

Supplementary Information

Copper–complexes for Chemoselective N-arylation of Arylamines and Sulfanilamides via Chan-Evans-Lam Cross-Coupling

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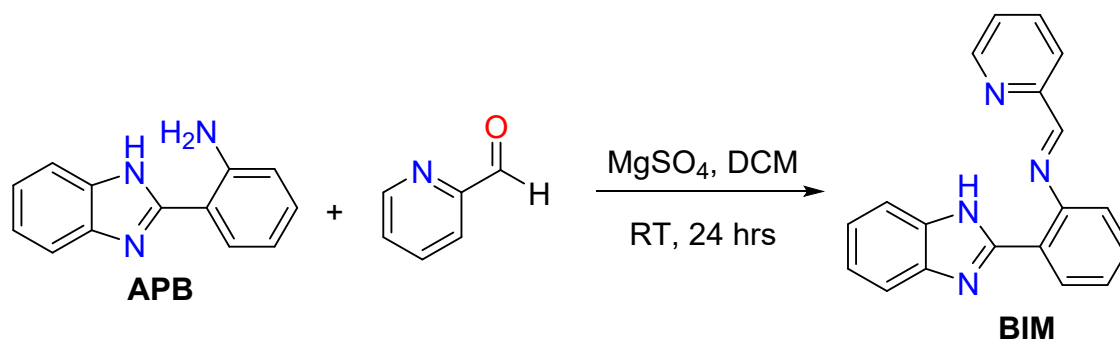
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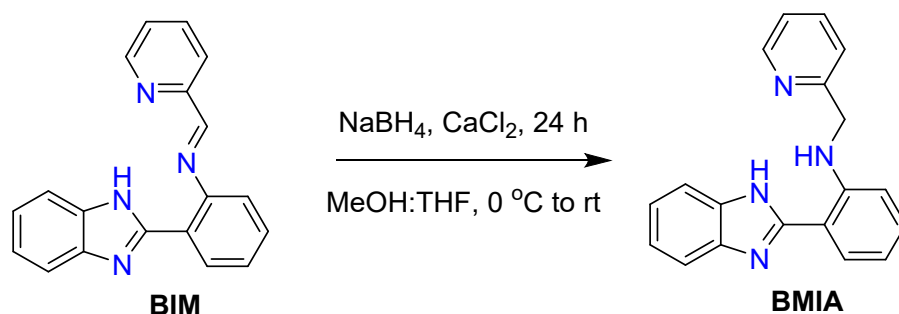
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A. Procedure for the synthesis of ligand BIM, and BIMA

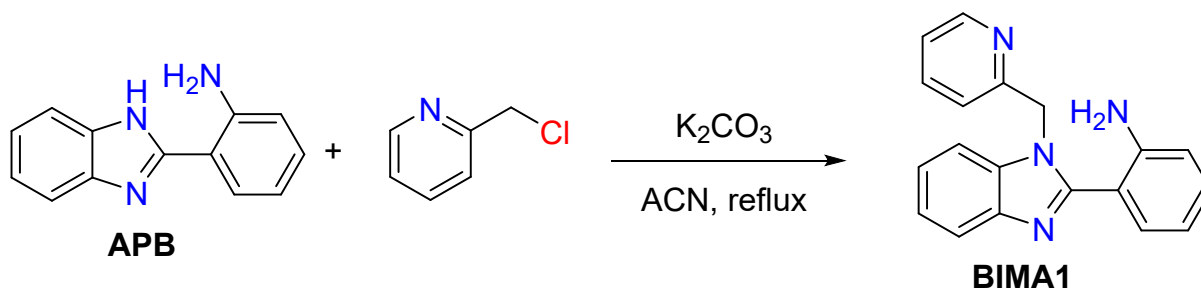


Ligand-BIM synthesis: A 25 mL round-bottom (RB) flask was charged with a magnetic stir bar, 2.0 mmol of 2-(2-aminophenyl)-1H-benzimidazole (APB), 2.2 mmol of 2-pyridine carboxaldehyde, and 10.0 mmol of MgSO_4 . This mixture was solvated in 10.0 mL of dichloromethane (DCM) and the reaction was left to stir for approximately 9 hours under an N_2 atmosphere at room temperature in a closed with a septum. After stirring, the reaction progress was monitored through TLC. Upon the completion of the precursors, the reaction mixture was filtered through celite. Evaporation of the solvent and subsequent purification by washing with DCM and n-hexane afforded the pale-yellow solid of BIM in 95% yields. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹ Yield 95% (450.0 mg), White solid, m.p. 230–232 °C; $^1\text{H NMR}$ (500 MHz, $\text{DSMO-}d_6$) δ 8.44 (d, $J = 4.4$ Hz, 1H), 7.90 (d, $J = 7.6$ Hz, 1H), 7.72 (t, $J = 7.4$ Hz, 1H), 7.69 (s, 1H), 7.64 (d, $J = 8.0$ Hz, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.30–7.09 (m, 6H), 6.84 (d, $J = 8.2$ Hz, 1H), 6.79 (t, $J = 7.2$ Hz, 1H) ppm.



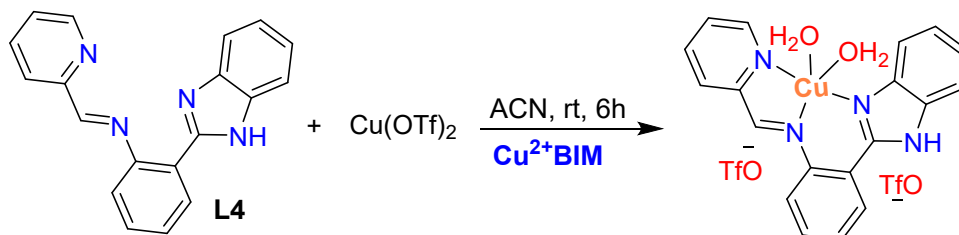
Ligand-BIMA synthesized from BIM: A 25 mL round-bottom (RB) flask was charged with a magnetic stir bar, 1.0 mmol of BIM, and 5.0 mL of 3:1 solvent (MeOH: THF) were added. The reaction mixture was stirred at 0°C temperature for 1 hour. Then, 2.5 mmol of NaBH_4 was added slowly twice at 12 hours intervals. The resulting solution was left to stir for 24 hours under

an N_2 atmosphere at rt. Upon the completion of the precursors, the reaction mixture was diluted with 20.0 mL of water and extracted with ethyl acetate and washed with 2% of NaHCO_3 and brine solution. The organic layers were evaporated under reduced pressure and subsequent purification by column chromatography on silica gel afforded the pale-yellowish product (**BIMA**, 61%) in yields. Yield 61% (180.0 mg), White solid, m.p. 254–256 °C; $R_f = 0.46$ (HX/EA = 1:2); ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ 12.8 (s, 1H), 9.83 (t, $J = 5.5$ Hz, 1H), 8.59 (d, $J = 4.5$ Hz, 1H), 7.96 (d, $J = 7.5$ Hz, 1H), 7.76 (t, $J = 7.5$ Hz, 1H), 7.70 (d, $J = 7.5$ Hz, 1H), 7.55 (d, $J = 7.5$ Hz, 1H), 7.40 (d, $J = 7.5$ Hz, 1H), 7.28–7.19 (m, 4H), 6.74 (t, $J = 8.0$ Hz, 2H), 4.68 (d, $J = 6.0$ Hz, 2H) ppm; ^{13}C NMR (125 MHz, $\text{DMSO}-d_6$) δ 159.7, 152.8, 149.6, 147.8, 143.2, 137.3, 134.0, 131.4, 128.1, 123.1, 122.6, 122.0, 121.5, 118.7, 115.6, 111.9, 111.5, 111.3, 48.7 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3340, 3325, 1615, 1545, 1360, 1210; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_4$ 301.1448; Found 301.1438.

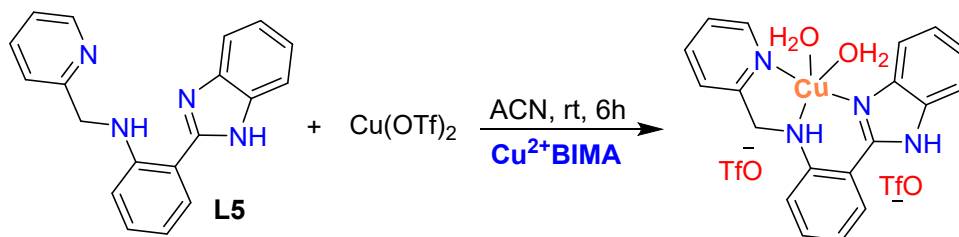


Ligand-BIMA1 synthesis: A 50 mL round-bottom (RB) flask was charged with a magnetic stir bar, 2.0 mmol of 2-(2-aminophenyl)-1H-benzimidazole (**APB**), 8.0 mmol of K_2CO_3 , and 15.0 mL of acetonitrile (ACN) were added. The resulting reaction mixture was stirred at ambient temperature for 1 hour followed by reflux. Then, 3.0 mmol of 2-(chloromethyl)pyridine hydrochloride was solvated in 5.0 mL of ACN, and the solution was added dropwise and left to stir for 24 hours under an N_2 atmosphere at refluxing. Upon the completion of the reaction time, the reaction mixture was filtered through celite. Evaporation of the solvent and subsequent purification by column chromatography on silica gel afforded the oily product of **BIMA1** in 57% yields. Yield 57% (220.0 mg), White solid, m.p. 240–242 °C; $R_f = 0.36$ (HX/EA = 1:3); ^1H NMR (500 MHz, CDCl_3) δ 8.56 (d, $J = 4.0$ Hz, 1H), 7.82 (d, $J = 8.0$ Hz, 1H), 7.54 (td, $J = 2.0, 8.0$ Hz, 1H), 7.29–7.25 (m, 1H), 7.21–7.12 (m, 5H), 6.87 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 8.4$ Hz, 1H), 6.67 (t, $J = 7.4$ Hz, 1H), 5.48 (s, 2H), 4.94 (s, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3) δ 156.0, 152.5, 149.5, 147.0, 142.7, 137.0, 135.0, 130.8, 129.6, 122.8, 122.5, 120.4, 119.3, 117.1, 116.4, 112.9, 110.3, 50.2 ppm; FT-IR (KBr) $\tilde{\nu}$ (cm^{-1}) 3410, 1920, 1675, 1540, 1320, 1250; HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{19}\text{H}_{17}\text{N}_4$ 301.1448; Found 301.1440.

B. Cu²⁺—Complexes synthesis Cu²⁺BIM & Cu²⁺BIMA



Cu²⁺BIM synthesis: A 25.0 mL round-bottom (RB) flask was equipped with a stirring bar and charged with 1.0 mmol of **BIM**, 1.0 mmol of Cu(OTf)₂, and solvated with 5.0 mL of ACN solvent. The mixture was stirred at ambient temperature for 6h, and then ACN was removed in *vacuo*. After, the precipitate was washed with methanol and *n*-hexane (1:2) to afford the Cu²⁺**BIM** in light-green color powder. Cu²⁺**BIM** could be crystallized in ACN and DCM.



Cu²⁺BIMA synthesis: A 25.0 mL round-bottom (RB) flask was equipped with a stirring bar and charged with 1.0 mmol of **BIMA**, 1.0 mmol of Cu(OTf)₂, and solvated with 5.0 mL of ACN solvent. The mixture was stirred at ambient temperature for 6h, and then ACN was removed in *vacuo*. After, the precipitate was washed with *n*-hexane to afford the Cu²⁺**BIMA** in light-green color powder.

C. FT-IR Spectra

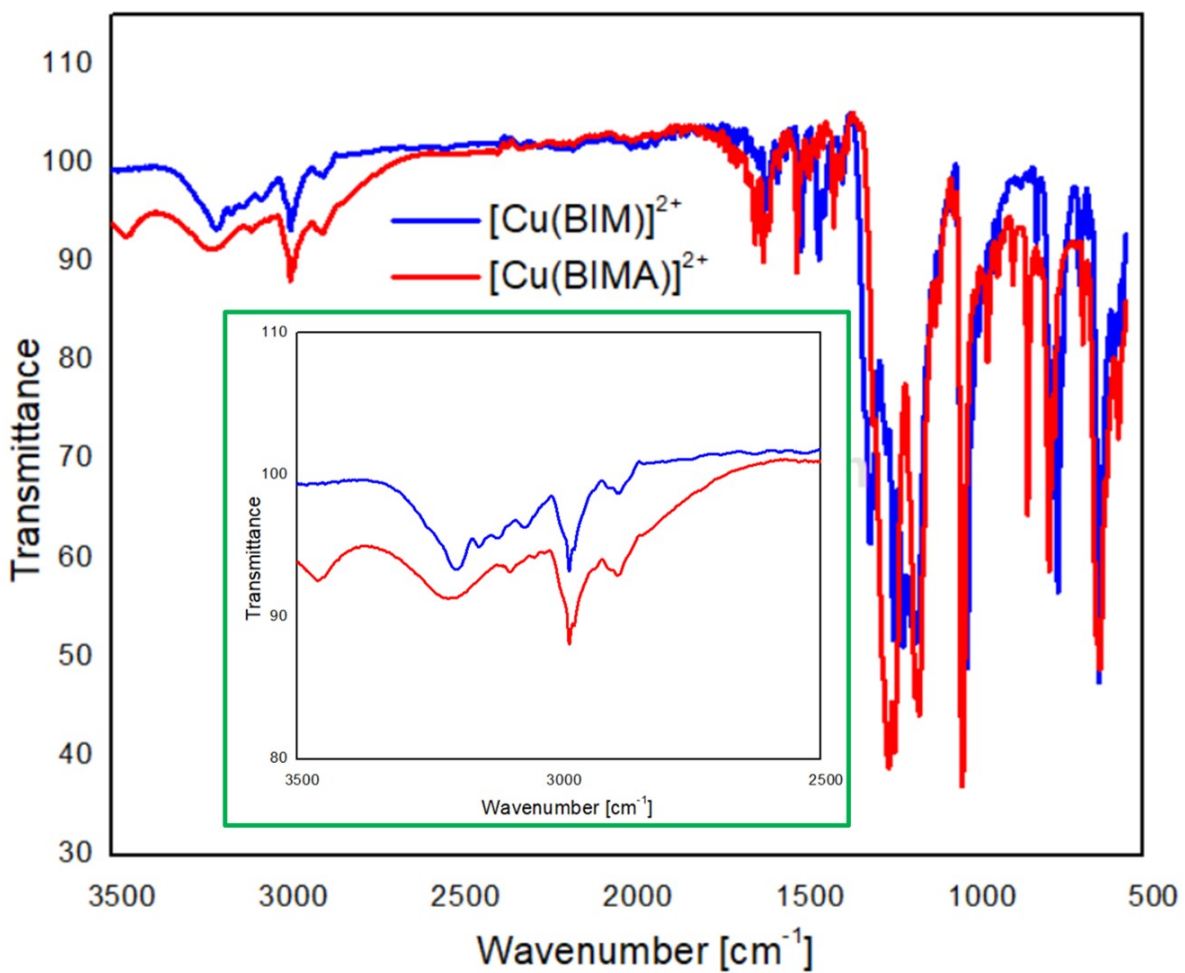
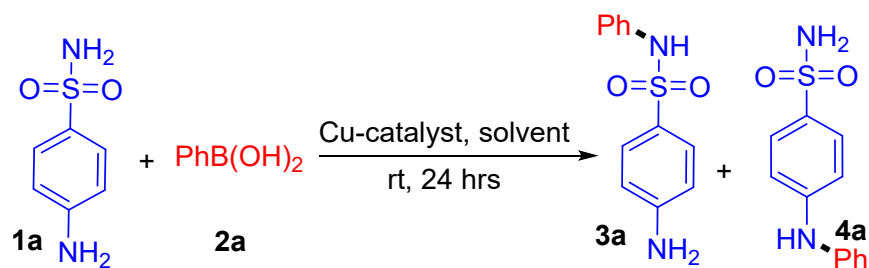


Figure S1. FT-IR comparison spectra of Cu²⁺BIM & Cu²⁺BIMA

Table S1. Copper catalyst and some solvent optimization yields for the C—N arylation of 4ABSA.

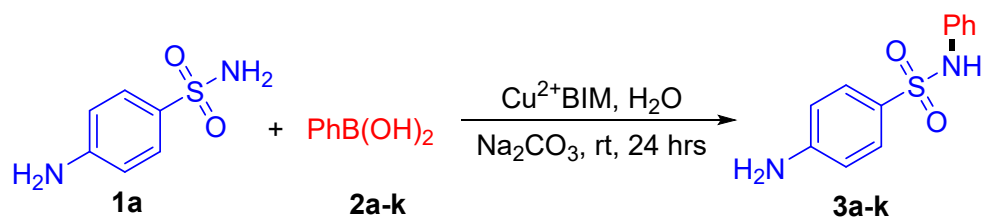


entry	catalyst	solvent	3a%	4a%
1	CuCl	DCM	ND	ND
2	CuCl ₂	DCM	ND	ND
3	CuBr	DCM	ND	ND
4	CuI	DCM	ND	ND
5	Cu(OAc) ₂	DCM	ND	<5
6	Cu(OTf) ₂	DCM	12	ND
7	Cu ²⁺ BIM	DCM	42	6
8	Cu ²⁺ BIMA	DCM	32	12
9	Cu ²⁺ BIM	CB	<15	ND
10	Cu ²⁺ BIM	DCE	28	ND
11	Cu ²⁺ BIM	DMF	25	<5
12	Cu ²⁺ BIM	D.S	ND	ND
13	Cu ²⁺ BIM	MeOH	41	ND
14	Cu ²⁺ BIM	EtOH	37	ND
15	Cu ²⁺ BIM	TFE	36	ND
16	Cu ²⁺ BIM	H ₂ O	42	ND

Reaction Conditions: 4ABSA (**1a**, 0.5 mmol), PhB(OH)_2 (**2a**, 1.5 equiv.), and Cu⁺/Cu²⁺-catalyst (10 mol%) in solvent (5.0 mL) at RT under an open-air atmosphere for 24 hours. Yields were determined using ¹H-NMR spectroscopy with mesitylene as an internal standard. Note: D.S: DMSO, THF, EtOAc, 1,4-dioxane, and toluene; ND: Not Detected

We initiated this CEL coupling process and its dependence on varying the Cu⁺ & Cu²⁺ sources with different counter-anions and ligands. Table S1, entries 1-5 sets a baseline for CEL reactivity with Cu⁺/Cu²⁺ by changing the anions such as chloride (Cl⁻), bromide (Br⁻), iodide (I⁻), and acetate (AcO⁻), where these salts performed poorly. Later, we changed to triflate (TfO⁻) showing a low conversion of 12% (Table S1, entry 6). We found that with the addition of ligand improved catalysis stability and resulted in increased amounts of product formation (Table S1, entry 7-16). Under early conditions, Cu²⁺BIM was found to catalyze arylation of the sulfonamide with a yield of 42% with good selectivity toward **3a** over **4a**. Cu²⁺BIM showed approximately 7-times the reactivity toward *N*-arylation of the sulfonamide functional group over the amino substituent. Cu²⁺BIMA showed promising reactivity, where yields of 32% of **3a** and 12% of **4a** were recorded, but lacked the selectivity afforded by the BIM system. Due to this observation the Cu²⁺BIM was selected for further optimization. When comparing Cu²⁺BIM with other solvents such as chlorobenzene (CB), dichloroethane (DCE), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), ethyl acetate (EtOAc), 1,4-dioxane, toluene, methanol (MeOH), ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and water; both methanol and water afforded comparable yields that offered a higher degree of regioselectivity than in DCM (Table S1, entries 9-16).

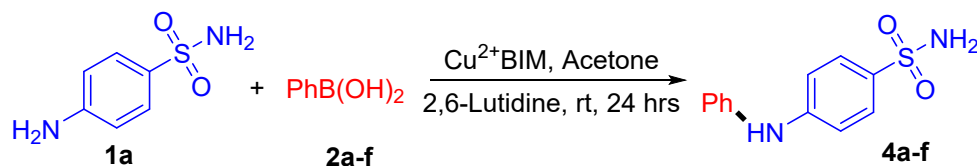
D. General procedure for chemoselectivity of sulfonamide C-N bond activation by Copper(II) catalyzed Chan-Evans-Lam cross-coupling (**3a-3k**)



A 20 mL vial was charged with a magnetic stir bar, 0.75 mmol of phenylboronic acid (**2a-2k**), 0.5 mmol of sulfonamides (**1a**), 1.0 mmol of sodium carbonate (Na₂CO₃), and 0.05 mmol of Cu²⁺BIM. This mixture was solvated in 5.0 mL of water (H₂O) and the reaction was left to stir for approximately 24 hours under an air atmosphere at room temperature. After the completion of the reaction time, the resulting reaction mixture was diluted with ethyl acetate and extracted. The

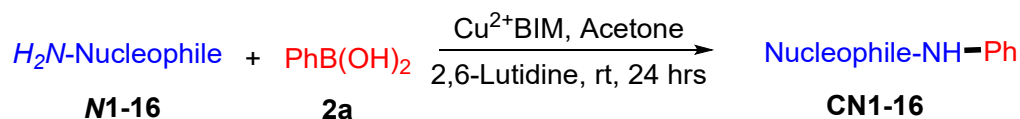
organic layers were evaporated under reduced pressure and subsequent purification by column chromatography on silica gel afforded the desired products (**3a-k**, 81-31%).

E. General procedure for chemoselectivity of aniline C-N bond activation by Copper(II) catalyzed Chan-Evans-Lam cross-coupling (**4a-f**)



A 20 mL vial was charged with a magnetic stir bar, 0.75 mmol of phenylboronic acid (**2a-2f**), 0.5 mmol of sulfonamides (**1a**), 1.0 mmol of 2,6-Lutidine, and 0.05 mmol of Cu^{2+}BIM . This mixture was solvated in 5.0 mL of acetone and the reaction was left to stir for approximately 24 hours under an air atmosphere at room temperature in a septum capped with a needle. After the completion of the reaction time, the resulting reaction mixture was filtered through celite. The organic layers were evaporated under reduced pressure and subsequent purification by column chromatography on silica gel afforded the desired products (**4a-f**, 71-51%).

F. General procedure for *N*-nucleophile involved C-N bond activation by Copper(II) catalyzed Chan-Evans-Lam cross-coupling (CN1-CN16)



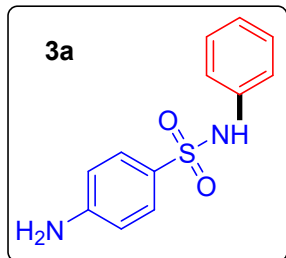
A 20 mL vial was charged with a magnetic stir bar, 0.75 mmol of phenylboronic acid (**2a**), 0.5 mmol of *N*-nucleophiles (**N1-N16**), 1.0 mmol of 2,6-Lutidine, and 0.05 mmol of Cu^{2+}BIM . This mixture was solvated in 5.0 mL of acetone and the reaction was left to stir for approximately 24 hours under an air atmosphere at room temperature in a septum capped with a needle. After the completion of the reaction time, the resulting reaction mixture was filtered through celite, washed with 1% of HCl, and extracted with ethyl acetate. The organic layers were evaporated under reduced

pressure and subsequent purification by column chromatography on silica gel afforded the desired products (CN1-CN16, 92-31%).

***N*-Nucleophiles used for the CEL cross-coupling reaction:** Aniline (N1, CAS No: 62-53-3); Carbazole (N2, CAS No: 86-74-8); 2-Aminobenzyl alcohol (N3, CAS No: 5344-90-1); 8-Aminoquinoline (N4, CAS No: 578-66-5); 2-Nitroimidazole (N5, CAS No: 527-73-1); Benzimidazole (N6, CAS No: 51-17-2); Phthalimide (N7, CAS No: 85-41-6); 2-Phenylbenzimidazole (N8, CAS No: 716-79-0); 4-Aminophenol (N9, CAS No: 123-30-8); Benzamide (N10, CAS No: 55-21-0); 1-(3-Aminopropyl)imidazole (N11, CAS No: 5036-48-6); 4-Methyl-2-phenylimidazole (N12, CAS No: 827-43-0); 1-Naphthylamine (N13, CAS No: 134-32-7); 2-Phenylimidazole (N14, CAS No: 670-96-2); Benzylamine (N15, CAS No: 100-46-9); 6-Thioguanine (N16, CAS No: 154-42-7).

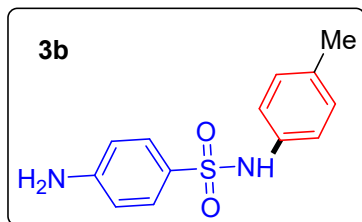
G. Spectroscopic and physical data of all compounds (3a-3k, 4a-4f, and CN1-CN16)

4-amino-*N*-phenylbenzenesulfonamide (3a)



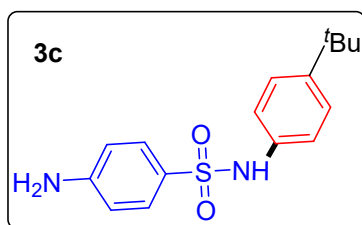
The compound **1a** (0.5 mmol, 94.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 92.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt. The reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.² Yield 78%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.82 (s, 1H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.17–7.12 (m, 2H), 7.09–7.01 (m, 2H), 6.69 (t, *J* = 7.6 Hz, 1H), 6.54 (d, *J* = 8.8 Hz, 2H), 5.95 (s, 2H) ppm.

4-amino-*N*-(*p*-tolyl)benzenesulfonamide (3b)



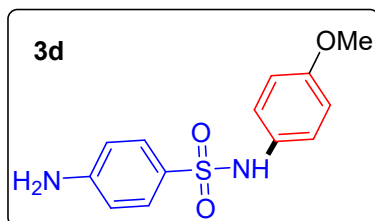
The compound **1a** (0.5 mmol, 94.0 mg), 4-tolylboronic acid (**2b**, 0.75 mmol, 100.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in H_2O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.² Yield 61%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.62 (s, 1H), 7.31 (d, $J = 8.4$ Hz, 2H), 7.02–6.92 (m, 4H), 6.50 (d, $J = 8.8$ Hz, 2H), 5.93 (s, 2H), 2.16 (s, 3H) ppm.

4-amino-*N*-(4-*tert*-butylphenyl)benzenesulfonamide (**3c**)²



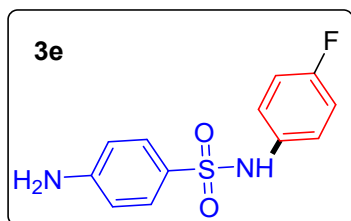
The compound **1a** (0.5 mmol, 94.0 mg), 4-*tert*-butylphenylboronic acid (**2c**, 0.75 mmol, 135.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in H_2O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra. Yield 64%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.75 (s, 1H), 7.37 (d, $J = 8.8$ Hz, 2H), 7.18 (d, $J = 8.8$ Hz, 2H), 6.98 (d, $J = 8.8$ Hz, 2H), 6.54 (d, $J = 8.8$ Hz, 2H), 5.52 (s, 2H), 1.21 (s, 9H) ppm.

4-amino-*N*-(4-methoxyphenyl)benzenesulfonamide (**3d**)



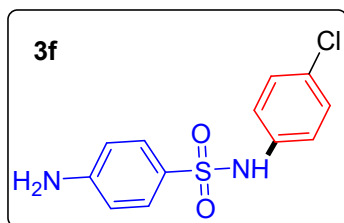
The compound **1a** (0.5 mmol, 94.0 mg), 4-methoxyphenylboronic acid (**2d**, 0.75 mmol, 112.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.³ Yield 50%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.42 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 8.8 Hz, 2H), 5.86 (s, 2H), 3.66 (s, 3H) ppm.

4-amino-*N*-(4-fluorophenyl)benzenesulfonamide (**3e**)



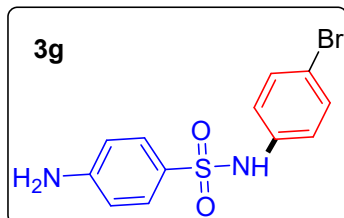
The compound **1a** (0.5 mmol, 94.0 mg), 4-fluorophenylboronic acid (**2e**, 0.75 mmol, 106.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.² Yield 50%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.79 (s, 1H), 7.31 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 7.0 Hz, 4H), 6.52 (d, *J* = 8.6 Hz, 2H), 5.98 (s, 2H) ppm.

4-amino-*N*-(4-chlorophenyl)benzenesulfonamide (**3f**)



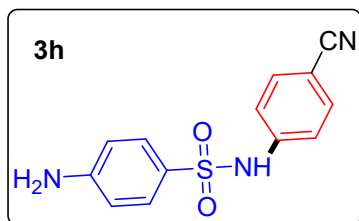
The compound **1a** (0.5 mmol, 94.0 mg), 4-chlorophenylboronic acid (**2f**, 0.75 mmol, 115.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.² Yield 59%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.98 (s, 1H), 7.45–7.33 (m, 2H), 7.31–7.27 (m, 2H), 7.05 (d, *J* = 8.8 Hz, 2H), 6.51 (d, *J* = 7.4 Hz, 2H), 5.98 (s, 2H) ppm.

4-amino-*N*-(4-bromophenyl)benzenesulfonamide (**3g**)



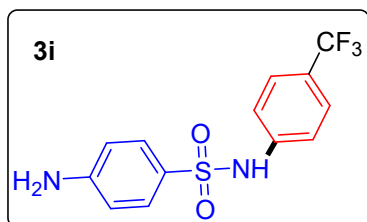
The compound **1a** (0.5 mmol, 94.0 mg), 4-bromophenylboronic acid (**2g**, 0.75 mmol, 150.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.⁴ Yield 50%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.01 (s, 1H), 7.27 (d, *J* = 9.2 Hz, 2H), 7.21 (d, *J* = 9.6 Hz, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.49 (d, *J* = 8.8 Hz, 2H), 5.97 (s, 2H) ppm.

4-amino-*N*-(4-cyanophenyl)benzenesulfonamide (**3h**)



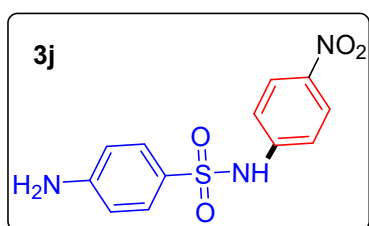
The compound **1a** (0.5 mmol, 94.0 mg), 4-cyanophenylboronic acid (**2h**, 0.75 mmol, 110.0 mg), Na₂CO₃ (1.0 mmol, 106.0 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in H₂O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.⁵ Yield 61%, Off-white solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.34 (s, 1H), 7.56–7.41 (m, 2H), 7.38–6.32 (m, 2H), 6.60–6.56 (m, 2H), 6.62 (d, *J* = 8.8 Hz, 2H), 5.51 (s, 2H) ppm.

4-amino-*N*-(4-(trifluoromethyl)phenyl)benzenesulfonamide (**3i**)



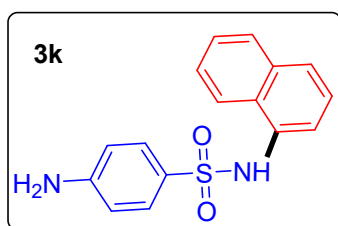
The compound **1a** (0.5 mmol, 94.0 mg), 4-(trifluoromethyl)benzeneboronic acid (**2i**, 0.75 mmol, 140.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in H_2O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.³ Yield 60%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 10.50 (s, 1H), 7.56 (d, $J = 8.8$ Hz, 2H), 7.45–7.39 (m, 2H), 7.23 (d, $J = 8.8$ Hz, 2H), 6.60–6.56 (m, 2H), 6.05 (s, 2H) ppm.

4-amino-*N*-(4-nitrophenyl)benzenesulfonamide (**3j**)



The compound **1a** (0.5 mmol, 94.0 mg), 4-nitrophenylboronic acid (**2j**, 0.75 mmol, 125.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in H_2O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.^{5,6} Yield 31%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.56 (s, 1H), 7.65–7.51 (m, 2H), 7.46 (d, $J = 8.8$ Hz, 2H), 6.75–6.61 (m, 2H), 6.57 (d, $J = 8.8$ Hz, 2H), 5.60 (s, 2H) ppm.

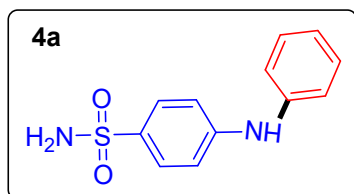
4-amino-*N*-(naphthalen-1-yl)benzenesulfonamide (**3k**)



The compound **1a** (0.5 mmol, 94.0 mg), naphthalene-1-boronic acid (**2k**, 0.75 mmol, 130.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in H_2O (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, the reaction was extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.^{7,8} Yield 34%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.72 (s, 1H), 7.81–7.76

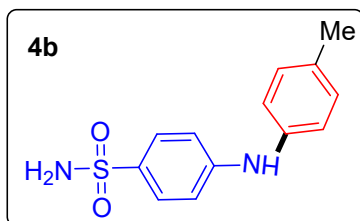
(m, 2H), 7.71 (d, $J = 8.8$ Hz, 2H), 7.54–7.30 (m, 2H), 7.15 (dd, $J = 2.0, 8.0$ Hz, 2H), 6.92 (d, $J = 5.0$ Hz, 1H), 6.80–6.67 (m, 2H), 5.61 (s, 2H) ppm.

4-(phenylamino)benzenesulfonamide (**4a**)



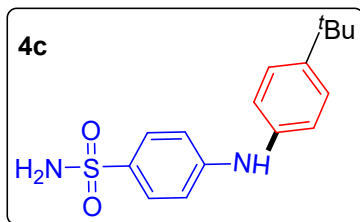
The compound **1a** (0.5 mmol, 94.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 91.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+} BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.² Yield 65%, off-white solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 8.69 (s, 1H), 7.68–7.59 (m, 2H), 7.39–7.29 (m, 2H), 7.18–7.10 (m, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 7.07 (s, 2H), 6.95 (t, $J = 7.8$ Hz, 1H) ppm.

4-(*p*-tolylamino)benzenesulfonamide (**4b**)



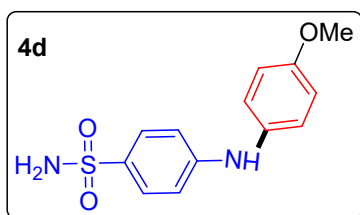
The compound **1a** (0.5 mmol, 94.0 mg), *p*-tolylboronic acid (**2b**, 0.75 mmol, 102.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+} BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.² Yield 62%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 8.58 (s, 1H), 7.67–7.56 (m, 2H), 7.13 (d, $J = 8.4$ Hz, 2H), 7.10–6.92 (m, 6H), 2.30 (s, 1H) ppm.

4-((4-(*tert*-butyl)phenyl)amino)benzenesulfonamide (**4c**)



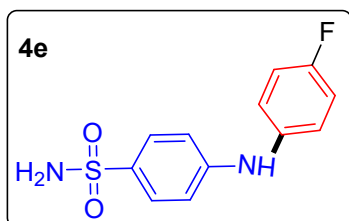
The compound **1a** (0.5 mmol, 94.0 mg), 4-*tert*-butylphenylboronic acid (**2c**, 0.75 mmol, 133.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.² Yield 51%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.60 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 7.09 (d, *J* = 8.8 Hz, 2H), 7.07–7.01 (m, 4H), 1.30 (s, 9H) ppm.

4-((4-methoxyphenyl)amino)benzenesulfonamide (**4d**)



The compound **1a** (0.5 mmol, 94.0 mg), 4-methoxyphenylboronic acid (**2d**, 0.75 mmol, 114.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.⁹ Yield 51%, White solid; ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.46 (s, 1H), 7.62–7.54 (m, 2H), 7.16 (dd, *J* = 2.0, 8.8 Hz, 2H), 6.98 (s, 2H), 6.95–6.88 (m, 4H), 3.74 (s, 3H) ppm.

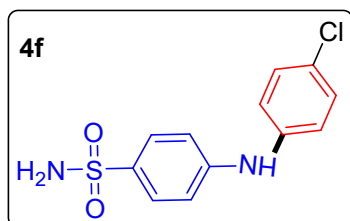
4-((4-fluorophenyl)amino)benzenesulfonamide (**4e**)



The compound **1a** (0.5 mmol, 94.0 mg), 4-fluorophenylboronic acid (**2e**, 0.75 mmol, 105.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a

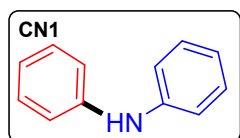
25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.² Yield 44%, Yellow solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 8.62 (s, 1H), 7.59 (d, $J = 8.8$ Hz, 2H), 7.25 (dd, $J = 2.0, 8.8$ Hz, 2H), 7.18 (dd, $J = 2.2, 8.8$ Hz, 2H), 7.08–6.94 (m, 4H) ppm.

4-((4-chlorophenyl)amino)benzenesulfonamide (**4f**)



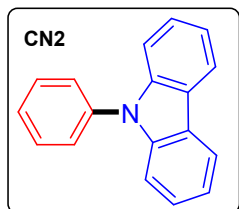
The compound **1a** (0.5 mmol, 94.0 mg), 4-chlorophenylboronic acid (**2f**, 0.75 mmol, 117.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+} BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.² Yield 51%, White solid; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 8.79 (s, 1H), 7.68 (dd, $J = 2.0, 8.8$ Hz, 2H), 7.36 (dd, $J = 2.2, 8.8$ Hz, 2H), 7.18–7.12 (m, 2H), 7.11–6.81 (m, 4H) ppm.

Diphenylamine (CN1)



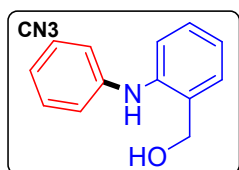
The compound **1a** (0.5 mmol, 46.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+} BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 48 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹⁰ Yield 84%, White solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.30 (t, $J = 8.0$ Hz, 4H), 7.18 (dd, $J = 2.0, 8.0$ Hz, 4H), 6.97 (tt, $J = 1.2, 7.2$ Hz, 2H), 5.69 (s, 1H) ppm.

9-phenyl-9H-carbazole (CN2)



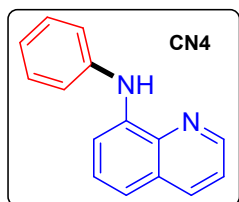
The compound **N2** (0.5 mmol, 83.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.¹¹ Yield 56%, White solid; ¹H NMR (500 MHz, CDCl₃) δ 8.10 (d, *J* = 7.8 Hz, 2H), 7.62–7.50 (m, 4H), 7.50–7.32 (m, 5H), 7.31–7.28 (m, 2H) ppm.

(2-(phenylamino)phenyl)methanol (CN3)



The compound **N3** (0.5 mmol, 61.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 36 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.¹² Yield 41%, Yellowish oil; ¹H NMR (500 MHz, CDCl₃) δ 7.41 (d, *J* = 7.8 Hz, 1H), 7.32–7.19 (m, 4H), 7.11 (dd, *J* = 1.2, 7.8 Hz, 2H), 7.04–6.85 (m, 2H), 4.73 (s, 4H) ppm.

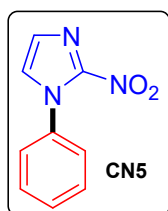
N-phenylquinolin-8-amine (CN4)



The compound **N4** (0.5 mmol, 72.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 48 h at rt, and the

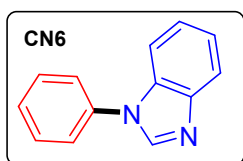
solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹³ Yield 20%, Pale-yellow solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.78–8.75 (m, 1H), 8.25 (s, 1H), 8.15 (dd, $J = 2.0, 8.4$ Hz, 1H), 7.50–7.42 (m, 1H), 7.40–7.33 (m, 6H), 7.23 (d, $J = 2.2, 8.8$ Hz, 1H), 7.07–7.01 (m, 1H) ppm.

2-nitro-1-phenyl-1H-imidazole (CN5)



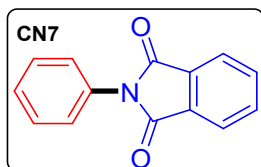
The compound **N5** (0.5 mmol, 56.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹¹ Yield 67%, White solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.58–7.45 (m, 3H), 7.38–7.29 (m, 2H), 7.27 (d, $J = 10$ Hz, 1H), 7.19 (s, 1H) ppm.

1-phenyl-1H-benzo[d]imidazole (CN6)



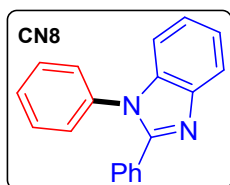
The compound **N6** (0.5 mmol, 59.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹⁴ Yield 45%, Pale-yellow solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.17 (s, 1H), 7.91–7.86 (m, 1H), 7.56–7.41 (m, 6H), 7.32–7.29 (m, 2H) ppm.

2-phenylisoindoline-1,3-dione (CN7)



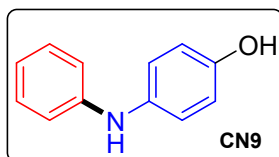
The compound **N7** (0.5 mmol, 73.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), Na_2CO_3 (1.0 mmol, 106.0 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in water (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 36 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹⁵ Yield 27%, White solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.95 (dt, $J = 2.8, 7.0$ Hz, 2H), 7.78 (dd, $J = 3.0, 5.5$ Hz, 2H), 7.50 (t, $J = 7.7$ Hz, 2H), 7.45–7.37 (m, 3H) ppm.

1,2-diphenyl-1*H*-benzo[*d*]imidazole (CN8)



The compound **N8** (0.5 mmol, 97.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 48 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹⁶ Yield 32%, White solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.89 (d, $J = 8.0$ Hz, 1H), 7.59 (d, $J = 7.2$ Hz, 2H), 7.53–7.45 (m, 3H), 7.39–7.24 (m, 8H) ppm.

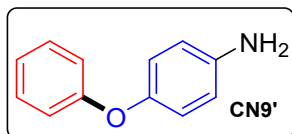
4-(phenylamino)phenol (CN9)



The compound **N9** (0.5 mmol, 54.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu^{2+}BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and $^1\text{H-NMR}$ data matches with reported spectra.¹⁷ Yield 30%, Off-white solid; $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.25–7.20 (m, 2H),

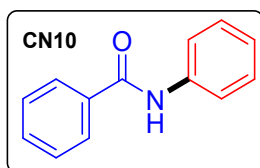
7.00 (d, $J = 8.4$ Hz, 2H), 6.92 (d, $J = 8.4$ Hz, 2H), 6.87 (t, $J = 5.6, 7.4$ Hz, 2H), 6.80 (dd, $J = 3.2, 6.8$ Hz, 2H), 5.52 (bs, 1H) ppm.

4-phenoxyaniline (CN9')



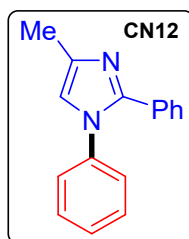
This compound is known and ¹H-NMR data matches with reported spectra.¹⁸ Yield 10%, White solid; ¹H NMR (500 MHz, CDCl₃) δ 7.26 (t, $J = 8.0$ Hz, 2H), 6.99 (t, $J = 8.0$ Hz, 1H), 6.90 (d, $J = 6.2$ Hz, 2H), 6.84 (d, $J = 8.0$ Hz, 2H), 6.65 (d, $J = 8.0$ Hz, 2H), 3.58 (s, 2H) ppm.

N-phenylbenzamide (CN10)



The compound **N10** (0.5 mmol, 60.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 48 h at rt, the reaction mixture extracted with ethyl acetate and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.¹⁹ Yield 56%, White solid; ¹H NMR (500 MHz, CDCl₃) δ 7.89 (dd, $J = 1.2, 8.4$ Hz, 3H), 7.68 (d, $J = 7.6$ Hz, 2H), 7.58–7.52 (m, 1H), 7.50 (d, $J = 7.8$ Hz, 2H), 7.41–7.30 (m, 2H), 7.15 (s, 1H) ppm.

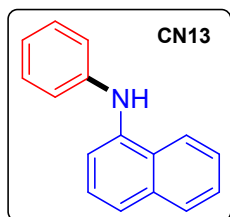
4-methyl-1,2-diphenyl-1H-imidazole (CN12)



The compound **N12** (0.5 mmol, 79.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0

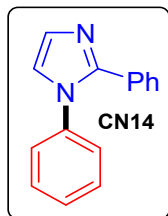
mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 36 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.²⁰ Yield 41%, Yellow oil; ¹H NMR (500 MHz, CDCl₃) δ 7.40–7.36 (m, 5H), 7.26–6.18 (m, 5H), 6.90 (s, 1H), 2.34 (s, 2H) ppm.

***N*-phenylnaphthalen-1-amine (CN13)**



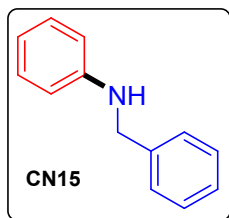
The compound **N13** (0.5 mmol, 71.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.025 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.²¹ Yield 33%, Yellowish sticky liquid; ¹H NMR (500 MHz, CDCl₃) δ 8.12–8.04 (m, 1H), 7.95–7.90 (m, 1H), 7.65 (dd, *J* = 2.0, 6.8 Hz, 1H), 7.59–7.48 (m, 2H), 7.46–7.40 (m, 2H), 7.36–7.24 (m, 2H), 7.06 (dd, *J* = 1.2, 8.6 Hz, 2H), 7.00–6.95 (m, 1H), 5.92 (bs, 1H) ppm.

1,2-diphenyl-1*H*-imidazole (CN14)



The compound **N14** (0.5 mmol, 72.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.²² Yield 40%, White solid; ¹H NMR (500 MHz, CDCl₃) δ 7.44–7.36 (m, 5H), 7.25–7.15 (m, 5H), 7.14 (d, *J* = 3.2 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H) ppm.

***N*-benzylaniline (CN15)**



The compound **N15** (0.5 mmol, 54.0 mg), phenylboronic acid (**2a**, 0.75 mmol, 93.0 mg), 2,6-Lutidine (1.0 mmol, 107.5 mg), Cu²⁺BIM (0.05 mmol, 17.0 mg) were dissolved in acetone (5.0 mL) in a 25.0 mL boiling tube. The resulting reaction mixture was stirred for 24 h at rt, and the solvent was removed under vacuum. This compound is known and ¹H-NMR data matches with reported spectra.²³ Yield 43%, Colorless sticky liquid; ¹H NMR (500 MHz, CDCl₃) δ 7.25–7.12 (m, 5H), 7.05 (t, *J* = 2.0, 8.0 Hz, 2H), 6.65 (t, *J* = 2.2, 7.8 Hz, 1H), 6.50 (d, *J* = 7.8 Hz, 2H), 4.20 (s, 2H), 3.85 (bs, 1H) ppm.

Figure S4. ¹H-NMR spectrum of compound BIMA1(CDCl₃, 500 MHz)

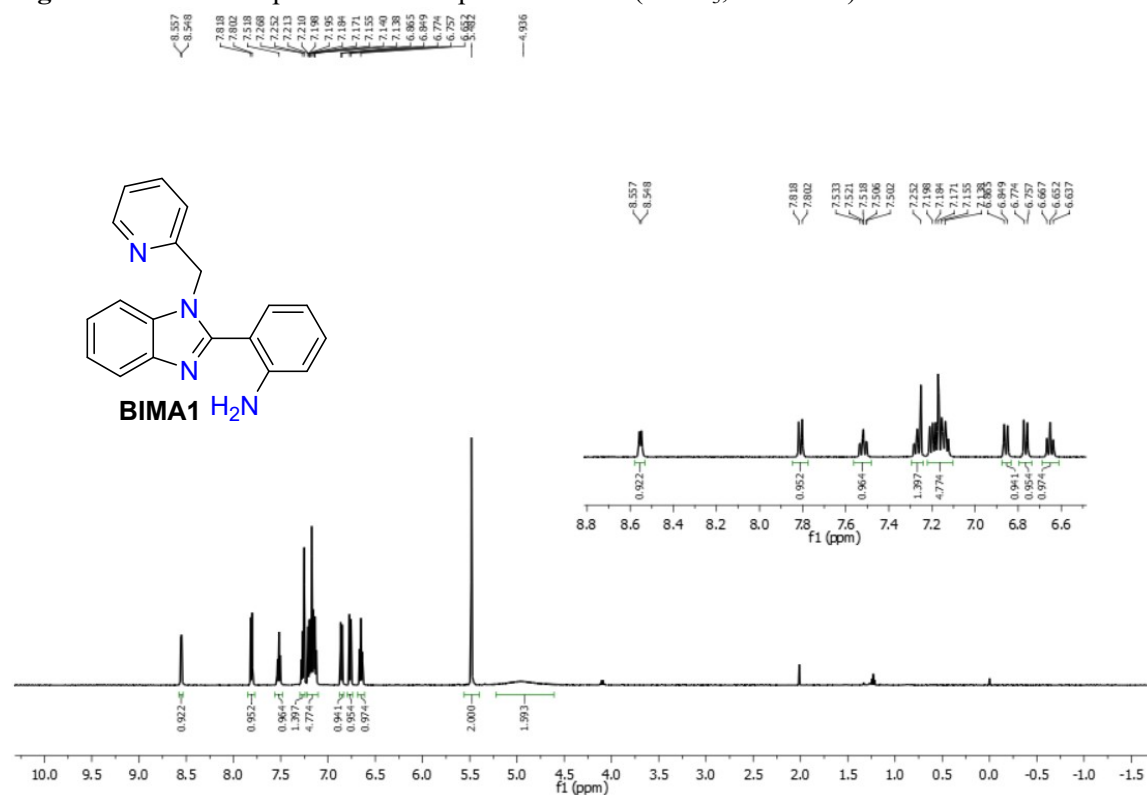


Figure S5. ¹³C-NMR spectrum of compound BIMA1(CDCl₃, 125 MHz)

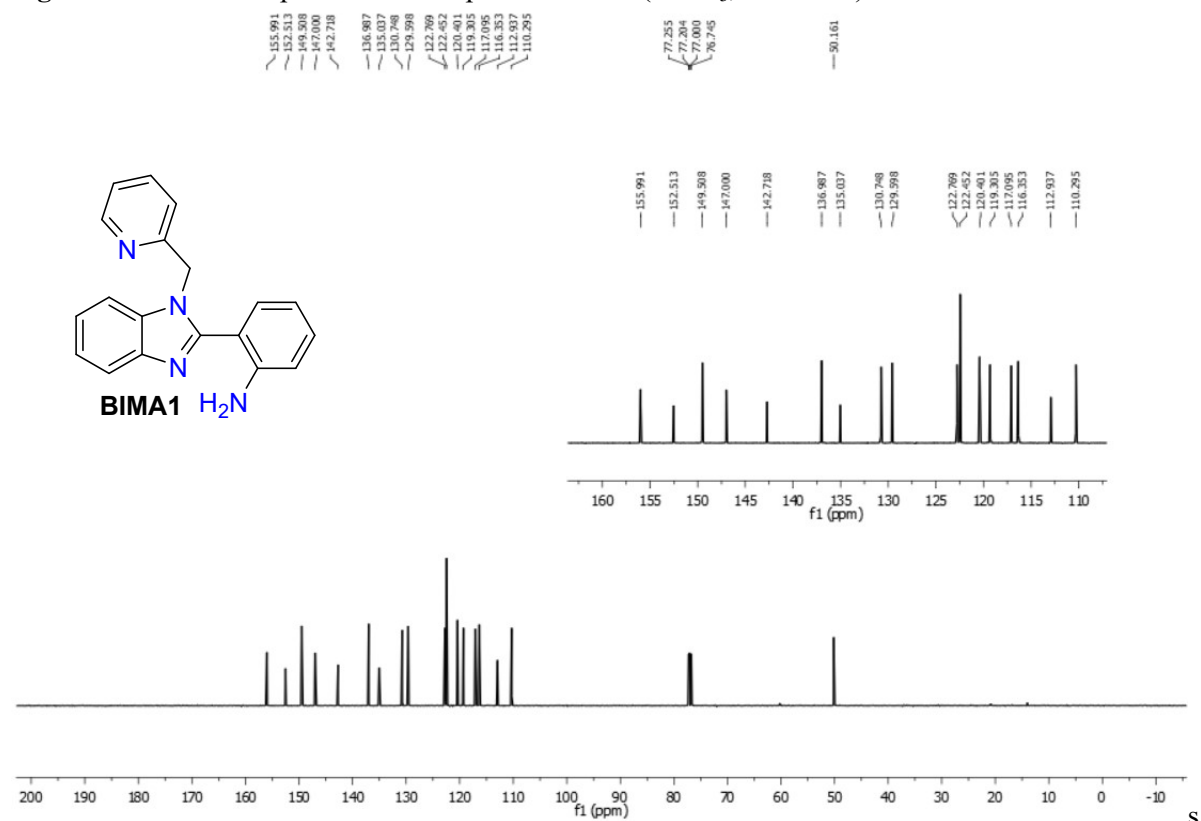
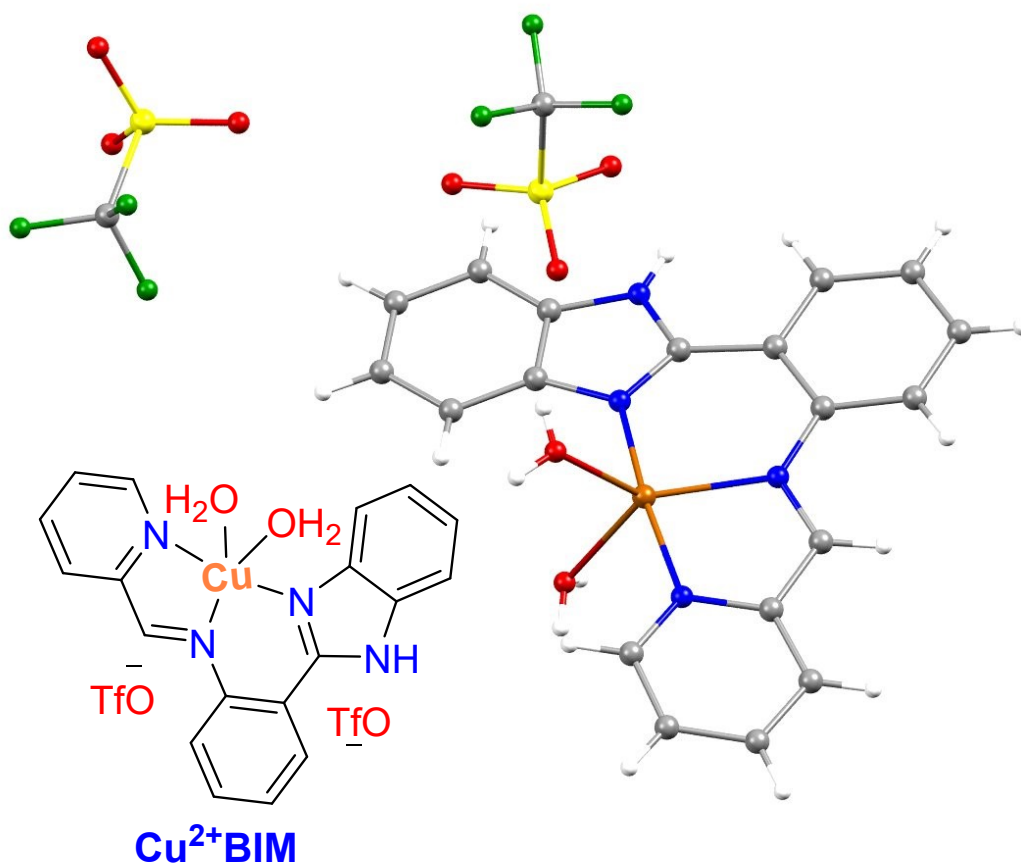


Figure S6. The solid-state structure of Cu^{2+}BIM [CCDC: 2236792]



The integration of the data using a triclinic unit cell yielded a total of 41920 reflections to a maximum θ angle of 26.48° (0.80 \AA resolution), of which 5381 were independent (average redundancy 7.790, completeness = 99.4%, $R_{\text{int}} = 2.66\%$, $R_{\text{sig}} = 1.49\%$) and 5224 (97.08%) were greater than 2σ (F^2). The final cell constants of $a = 7.8701(7) \text{ \AA}$, $b = 11.5840(11) \text{ \AA}$, $c = 14.7103(13) \text{ \AA}$, $\alpha = 100.260(3)^\circ$, $\beta = 90.700(3)^\circ$, $\gamma = 97.224(3)^\circ$, volume = $1308.4(2) \text{ \AA}^3$, are based upon the refinement of the XYZ-centroids of 842 reflections above 20σ (I) with $5.840^\circ < 2\theta < 68.29^\circ$. The final anisotropic full-matrix least-squares refinement on F^2 with 380 variables converged at $R1 = 6.10\%$, for the observed data and $wR2 = 16.17\%$ for all data. The goodness-of-fit: GOF was 1.058. The largest peak in the final difference electron density synthesis was $5.651 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-1.005 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.148 \text{ e}^-/\text{\AA}^3$. Based on the final model, the calculated density was 1.767 g/cm^3 and $F(000)$, 702 e^- .

Table S2. Sample and crystal data for Cu²⁺BIM

Identification code	Mo_D_JE_011_100K	
Chemical formula	C ₂₁ H ₁₈ CuF ₆ N ₄ O ₈ S ₂	
Formula weight	696.05 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	(0.245 x 0.493 x 0.588) mm ³	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.8701(7) Å	α = 100.260(3)°
	b = 11.5840(11) Å	β = 90.700(3)°
	c = 14.7103(13) Å	γ = 97.224(3)°
Volume	1308.4(2) Å ³	
Z	2	
Density (calculated)	1.767 g/cm ³	
Absorption coefficient	1.092 mm ⁻¹	
F(000)	702	

Table S3. Data collection and structure refinement for Cu²⁺BIM

Theta range for data collection	2.08 to 26.48°
Index ranges	-9<=h<=9, -14<=k<=14, -18<=l<=18
Reflections collected	41920
Independent reflections	5381 [R(int) = 0.0266]
Coverage of independent reflections	99.4%
Absorption correction	Multi-Scan
Max. and min. transmission	0.7760 and 0.5660
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2014/5
Refinement method	Full-matrix least-squares on F ²
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)
Function minimized	Σ w(F _o ² - F _c ²) ²

Data / restraints / parameters	5381 / 0 / 380
Goodness-of-fit on F²	1.058
Final R indices	5224 data; R1 = 0.0610, wR2 = 0.1576 I > 2σ(I)
	all data R1 = 0.0627, wR2 = 0.1617
Weighting scheme	w=1/[σ ² (F _o ²)+(0.0814P) ² +7.5894P] where P=(F _o ² +2F _c ²)/3
Extinction coefficient	0.0350(30)
Largest diff. peak and hole	5.651 and -1.005 eÅ ⁻³
R.M.S. deviation from mean	0.148 eÅ ⁻³

Table S4. Atomic coordinates and equivalent isotropic atomic displacement parameters (Å²) for Cu²⁺BIM

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x/a	y/b	z/c	U(eq)
Cu1	0.68774(6)	0.43633(4)	0.73136(3)	0.01440(19)
N1	0.8398(4)	0.5691(3)	0.8065(2)	0.0152(7)
N2	0.8669(4)	0.3411(3)	0.7730(2)	0.0118(6)
N3	0.5459(4)	0.2950(3)	0.6685(2)	0.0140(6)
N4	0.4471(4)	0.1082(3)	0.6194(2)	0.0146(6)
O1	0.6889(4)	0.5214(2)	0.61881(19)	0.0198(6)
O2	0.4713(4)	0.4919(2)	0.80329(18)	0.0156(6)
C1	0.8248(5)	0.6833(4)	0.8188(3)	0.0180(8)
C2	0.9312(5)	0.7667(4)	0.8818(3)	0.0198(8)
C3	0.0559(5)	0.7296(4)	0.9327(3)	0.0195(8)
C4	0.0729(5)	0.6097(4)	0.9193(3)	0.0181(8)
C5	0.9637(5)	0.5319(3)	0.8556(3)	0.0145(7)
C6	0.9720(5)	0.4051(3)	0.8351(3)	0.0155(8)
C7	0.8705(5)	0.2169(3)	0.7489(3)	0.0117(7)

	x/a	y/b	z/c	U(eq)
C8	0.0101(5)	0.1650(4)	0.7755(3)	0.0184(8)
C9	0.0158(5)	0.0451(4)	0.7529(3)	0.0210(8)
C10	0.8811(5)	0.9723(4)	0.7013(3)	0.0207(8)
C11	0.7439(5)	0.0223(3)	0.6726(3)	0.0162(8)
C12	0.7340(5)	0.1436(3)	0.6956(2)	0.0114(7)
C13	0.5805(5)	0.1864(3)	0.6627(2)	0.0112(7)
C14	0.3223(5)	0.1727(3)	0.5956(3)	0.0142(7)
C15	0.1630(5)	0.1353(4)	0.5496(3)	0.0160(8)
C16	0.0655(5)	0.2221(4)	0.5363(3)	0.0176(8)
C17	0.1257(5)	0.3427(4)	0.5675(3)	0.0190(8)
C18	0.2841(5)	0.3789(3)	0.6131(3)	0.0176(8)
C19	0.3821(5)	0.2915(4)	0.6268(3)	0.0140(7)
C20	0.5643(5)	0.8625(4)	0.0793(3)	0.0163(8)
O11	0.3671(4)	0.6672(3)	0.0774(2)	0.0201(6)
O12	0.6742(4)	0.6608(3)	0.0749(2)	0.0243(7)
O13	0.5198(4)	0.6947(3)	0.9379(2)	0.0232(7)
S1	0.52735(12)	0.70343(8)	0.03733(6)	0.0144(2)
F11	0.7055(3)	0.9132(2)	0.04563(18)	0.0265(6)
F12	0.5837(3)	0.8857(2)	0.17166(16)	0.0234(5)
F13	0.4321(4)	0.9141(2)	0.0565(2)	0.0290(6)
C21	0.7211(6)	0.2420(4)	0.2967(3)	0.0194(8)
O21	0.4323(4)	0.2630(3)	0.3737(2)	0.0216(6)
O22	0.6946(4)	0.3571(2)	0.46017(19)	0.0186(6)
O23	0.6242(4)	0.1428(2)	0.43387(19)	0.0158(6)
S2	0.60477(11)	0.25259(8)	0.40319(6)	0.0115(2)
F21	0.6589(5)	0.1461(3)	0.23587(19)	0.0377(7)
F22	0.8865(4)	0.2346(3)	0.3137(2)	0.0341(7)
F23	0.7135(4)	0.3360(2)	0.25786(18)	0.0316(7)

Table S5. Bond lengths (Å) for Cu²⁺BIM

Cu1-N3	1.938(3)	Cu1-N1	1.980(3)
Cu1-N2	2.047(3)	Cu1-O1	2.072(3)
Cu1-O2	2.124(3)	N1-C1	1.323(5)
N1-C5	1.363(5)	N2-C6	1.286(5)
N2-C7	1.423(5)	N3-C13	1.309(5)
N3-C19	1.414(5)	N4-C13	1.366(5)
N4-C14	1.384(5)	N4-H4	0.880000
O1-H11W	0.689(3)	O1-H12W	0.794(3)
O2-H22W	0.732(3)	O2-H21W	0.638(3)
C1-C2	1.397(6)	C1-H1	0.950000
C2-C3	1.382(6)	C2-H2	0.950000
C3-C4	1.391(6)	C3-H3	0.950000
C4-C5	1.384(6)	C4-H4A	0.950000
C5-C6	1.456(5)	C6-H6	0.950000
C7-C8	1.400(5)	C7-C12	1.416(5)
C8-C9	1.376(6)	C8-H8	0.950000
C9-C10	1.392(6)	C9-H9	0.950000
C10-C11	1.383(6)	C10-H10	0.950000
C11-C12	1.398(5)	C11-H11	0.950000
C12-C13	1.470(5)	C14-C19	1.390(5)
C14-C15	1.398(5)	C15-C16	1.377(6)
C15-H15	0.950000	C16-C17	1.410(6)
C16-H16	0.950000	C17-C18	1.388(6)
C17-H17	0.950000	C18-C19	1.388(6)

C18-H18	0.950000	C20-F13	1.331(5)
C20-F11	1.333(5)	C20-F12	1.341(5)
C20-S1	1.821(4)	O11-S1	1.445(3)
O12-S1	1.453(3)	O13-S1	1.448(3)
C21-F23	1.323(5)	C21-F21	1.332(5)
C21-F22	1.339(5)	C21-S2	1.817(4)
O21-S2	1.447(3)	O22-S2	1.441(3)
O23-S2	1.448(3)		

Table S6. Bond angles (°) for Cu²⁺BIM

N3-Cu1-N1	173.12(14)	N3-Cu1-N2	92.57(13)
N1-Cu1-N2	81.73(14)	N3-Cu1-O1	94.21(13)
N1-Cu1-O1	92.38(13)	N2-Cu1-O1	128.98(13)
N3-Cu1-O2	89.75(13)	N1-Cu1-O2	90.75(12)
N2-Cu1-O2	128.06(12)	O1-Cu1-O2	102.50(11)
C1-N1-C5	119.2(3)	C1-N1-Cu1	127.8(3)
C5-N1-Cu1	112.7(3)	C6-N2-C7	120.7(3)
C6-N2-Cu1	111.6(3)	C7-N2-Cu1	127.2(2)
C13-N3-C19	108.5(3)	C13-N3-Cu1	125.8(3)
C19-N3-Cu1	125.5(3)	C13-N4-C14	107.9(3)
C13-N4-H4	126.000000	C14-N4-H4	126.000000
Cu1-O1-H11W	117.0(3)	Cu1-O1-H12W	129.3(3)
H11W-O1-H12W	107.3(4)	Cu1-O2-H22W	115.1(3)
Cu1-O2-H21W	105.1(3)	H22W-O2-H21W	115.6(4)
N1-C1-C2	121.8(4)	N1-C1-H1	119.100000
C2-C1-H1	119.100000	C3-C2-C1	119.4(4)
C3-C2-H2	120.300000	C1-C2-H2	120.300000

C2-C3-C4	119.0(4)	C2-C3-H3	120.500000
C4-C3-H3	120.500000	C5-C4-C3	118.6(4)
C5-C4-H4A	120.700000	C3-C4-H4A	120.700000
N1-C5-C4	122.0(4)	N1-C5-C6	114.8(3)
C4-C5-C6	123.2(4)	N2-C6-C5	118.1(4)
N2-C6-H6	120.900000	C5-C6-H6	120.900000
C8-C7-C12	118.6(3)	C8-C7-N2	121.0(3)
C12-C7-N2	120.4(3)	C9-C8-C7	121.8(4)
C9-C8-H8	119.100000	C7-C8-H8	119.100000
C8-C9-C10	119.9(4)	C8-C9-H9	120.100000
C10-C9-H9	120.100000	C11-C10-C9	119.2(4)
C11-C10-H10	120.400000	C9-C10-H10	120.400000
C10-C11-C12	122.1(4)	C10-C11-H11	119.000000
C12-C11-H11	119.000000	C11-C12-C7	118.4(3)
C11-C12-C13	117.3(3)	C7-C12-C13	124.3(3)
N3-C13-N4	110.2(3)	N3-C13-C12	129.4(3)
N4-C13-C12	120.4(3)	N4-C14-C19	107.0(3)
N4-C14-C15	130.6(4)	C19-C14-C15	122.4(4)
C16-C15-C14	116.9(4)	C16-C15-H15	121.500000
C14-C15-H15	121.500000	C15-C16-C17	120.9(4)
C15-C16-H16	119.500000	C17-C16-H16	119.500000
C18-C17-C16	121.7(4)	C18-C17-H17	119.200000
C16-C17-H17	119.200000	C17-C18-C19	117.4(4)
C17-C18-H18	121.300000	C19-C18-H18	121.300000
C18-C19-C14	120.6(3)	C18-C19-N3	133.0(4)
C14-C19-N3	106.4(3)	F13-C20-F11	108.4(3)
F13-C20-F12	107.6(3)	F11-C20-F12	107.2(3)
F13-C20-S1	110.9(3)	F11-C20-S1	112.1(3)
F12-C20-S1	110.4(3)	O11-S1-O13	115.02(18)

O11-S1-O12	113.85(19)	O13-S1-O12	115.7(2)
O11-S1-C20	103.37(18)	O13-S1-C20	102.97(18)
O12-S1-C20	103.58(18)	F23-C21-F21	108.3(3)
F23-C21-F22	107.8(4)	F21-C21-F22	107.5(3)
F23-C21-S2	111.4(3)	F21-C21-S2	111.4(3)
F22-C21-S2	110.3(3)	O22-S2-O21	115.23(18)
O22-S2-O23	114.84(17)	O21-S2-O23	114.75(17)
O22-S2-C21	102.83(19)	O21-S2-C21	103.4(2)
O23-S2-C21	103.41(17)		

Table S7. Torsion angles ($^{\circ}$) for Cu²⁺BIM

C5-N1-C1-C2	-0.9(6)	Cu1-N1-C1-C2	173.0(3)
N1-C1-C2-C3	0.1(6)	C1-C2-C3-C4	0.4(6)
C2-C3-C4-C5	-0.2(6)	C1-N1-C5-C4	1.2(6)
Cu1-N1-C5-C4	-173.6(3)	C1-N1-C5-C6	-178.5(3)
Cu1-N1-C5-C6	6.7(4)	C3-C4-C5-N1	-0.6(6)
C3-C4-C5-C6	179.0(4)	C7-N2-C6-C5	179.0(3)
Cu1-N2-C6-C5	-8.3(4)	N1-C5-C6-N2	1.3(5)
C4-C5-C6-N2	-178.4(4)	C6-N2-C7-C8	-14.7(5)
Cu1-N2-C7-C8	173.8(3)	C6-N2-C7-C12	166.8(3)
Cu1-N2-C7-C12	-4.8(5)	C12-C7-C8-C9	-1.5(6)
N2-C7-C8-C9	179.9(4)	C7-C8-C9-C10	0.9(7)
C8-C9-C10-C11	0.7(7)	C9-C10-C11-C12	-1.5(6)
C10-C11-C12-C7	0.9(6)	C10-C11-C12-C13	-178.8(4)
C8-C7-C12-C11	0.7(5)	N2-C7-C12-C11	179.2(3)
C8-C7-C12-C13	-179.7(4)	N2-C7-C12-C13	-1.1(5)
C19-N3-C13-N4	-0.4(4)	Cu1-N3-C13-N4	175.5(2)

C19-N3-C13-C12	180.0(3)	Cu1-N3-C13-C12	-4.2(6)
C14-N4-C13-N3	0.9(4)	C14-N4-C13-C12	-179.4(3)
C11-C12-C13-N3	-174.2(4)	C7-C12-C13-N3	6.1(6)
C11-C12-C13-N4	6.1(5)	C7-C12-C13-N4	-173.5(3)
C13-N4-C14-C19	-1.0(4)	C13-N4-C14-C15	179.3(4)
N4-C14-C15-C16	179.6(4)	C19-C14-C15-C16	0.0(6)
C14-C15-C16-C17	0.3(6)	C15-C16-C17-C18	-0.4(6)
C16-C17-C18-C19	0.2(6)	C17-C18-C19-C14	0.1(6)
C17-C18-C19-N3	179.2(4)	N4-C14-C19-C18	-179.9(3)
C15-C14-C19-C18	-0.2(6)	N4-C14-C19-N3	0.8(4)
C15-C14-C19-N3	-179.5(3)	C13-N3-C19-C18	-179.5(4)
Cu1-N3-C19-C18	4.6(6)	C13-N3-C19-C14	-0.3(4)
Cu1-N3-C19-C14	-176.2(3)	F13-C20-S1-O11	-56.0(3)
F11-C20-S1-O11	-177.3(3)	F12-C20-S1-O11	63.2(3)
F13-C20-S1-O13	64.1(3)	F11-C20-S1-O13	-57.3(3)
F12-C20-S1-O13	-176.7(3)	F13-C20-S1-O12	-175.0(3)
F11-C20-S1-O12	63.7(3)	F12-C20-S1-O12	-55.8(3)
F23-C21-S2-O22	-61.4(4)	F21-C21-S2-O22	177.6(3)
F22-C21-S2-O22	58.3(3)	F23-C21-S2-O21	58.8(4)
F21-C21-S2-O21	-62.2(3)	F22-C21-S2-O21	178.5(3)
F23-C21-S2-O23	178.8(3)	F21-C21-S2-O23	57.8(3)
F22-C21-S2-O23	-61.5(3)		

Table S8. Anisotropic atomic displacement parameters (\AA^2) for Cu^{2+} BIM

The anisotropic atomic displacement factor exponent takes the

*form: $-2\pi^2 [h^2 a^{*2} U_{11} + \dots + 2 h k a^* b^* U_{12}]$*

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cu1	0.0131(3)	0.0107(3)	0.0180(3)	0.00047(18)	-0.00472(18)	-0.00029(17)
N1	0.0126(15)	0.0181(16)	0.0132(15)	0.0013(12)	-0.0004(12)	-0.0024(12)
N2	0.0105(14)	0.0127(15)	0.0127(15)	0.0028(12)	0.0011(11)	0.0025(11)
N3	0.0141(15)	0.0109(15)	0.0162(15)	0.0009(12)	-0.0038(12)	0.0012(12)
N4	0.0135(15)	0.0158(16)	0.0149(15)	0.0041(12)	-0.0011(12)	0.0018(12)
O1	0.0379(17)	0.0107(13)	0.0114(13)	0.0019(10)	0.0014(12)	0.0049(12)
O2	0.0195(14)	0.0140(13)	0.0130(13)	-0.0002(10)	0.0006(10)	0.0045(11)
C1	0.0156(18)	0.0189(19)	0.0201(19)	0.0048(15)	0.0021(15)	0.0020(15)
C2	0.022(2)	0.0143(18)	0.022(2)	0.0003(15)	0.0061(16)	0.0015(15)
C3	0.0177(19)	0.0181(19)	0.0177(19)	-0.0050(15)	0.0026(15)	-0.0049(15)
C4	0.0145(18)	0.021(2)	0.0164(18)	-0.0016(15)	-0.0006(15)	0.0010(15)
C5	0.0148(18)	0.0150(18)	0.0122(17)	0.0005(14)	0.0036(14)	-0.0004(14)
C6	0.0166(18)	0.0166(19)	0.0134(18)	0.0020(14)	0.0042(14)	0.0035(15)
C7	0.0102(16)	0.0117(17)	0.0132(17)	0.0023(13)	0.0011(13)	0.0016(13)
C8	0.0133(18)	0.0165(19)	0.024(2)	0.0003(15)	-0.0050(15)	0.0031(15)
C9	0.0156(19)	0.020(2)	0.028(2)	0.0044(17)	-0.0058(16)	0.0074(16)
C10	0.020(2)	0.0126(18)	0.030(2)	0.0021(16)	-0.0011(17)	0.0050(15)
C11	0.0129(18)	0.0133(18)	0.0214(19)	0.0009(15)	-0.0028(15)	0.0016(14)
C12	0.0086(16)	0.0131(17)	0.0126(16)	0.0029(13)	-0.0001(13)	0.0011(13)
C13	0.0100(16)	0.0150(17)	0.0100(16)	0.0044(13)	0.0025(13)	0.0040(13)
C14	0.0118(17)	0.0193(19)	0.0121(17)	0.0050(14)	-0.0003(14)	0.0016(14)
C15	0.0141(18)	0.0169(18)	0.0157(18)	0.0023(14)	-0.0028(14)	-0.0020(15)
C16	0.0123(18)	0.023(2)	0.0171(18)	0.0041(15)	-0.0064(14)	0.0004(15)
C17	0.021(2)	0.019(2)	0.0184(19)	0.0049(16)	-0.0014(16)	0.0073(16)
C18	0.022(2)	0.0129(18)	0.0165(18)	0.0008(14)	-0.0005(15)	-0.0022(15)
C19	0.0081(16)	0.0206(19)	0.0108(16)	0.0000(14)	-0.0031(13)	-0.0038(14)
C20	0.0154(18)	0.0190(19)	0.0145(18)	0.0030(14)	0.0007(14)	0.0019(15)
O11	0.0180(14)	0.0240(15)	0.0173(14)	0.0053(11)	0.0000(11)	-0.0027(11)
O12	0.0173(15)	0.0213(15)	0.0341(17)	0.0022(13)	-0.0063(13)	0.0059(12)
O13	0.0270(16)	0.0266(16)	0.0123(14)	-0.0029(11)	0.0013(12)	-0.0016(13)
S1	0.0143(5)	0.0154(5)	0.0124(4)	-0.0001(3)	-0.0016(3)	0.0013(3)
F11	0.0258(13)	0.0248(13)	0.0271(13)	0.0058(11)	0.0066(11)	-0.0058(10)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
F12	0.0275(13)	0.0254(13)	0.0134(11)	-0.0034(9)	0.0007(10)	-0.0014(10)
F13	0.0275(14)	0.0226(13)	0.0388(16)	0.0061(11)	-0.0057(12)	0.0105(11)
C21	0.029(2)	0.0170(19)	0.0149(18)	0.0038(15)	0.0055(16)	0.0137(16)
O21	0.0147(14)	0.0159(14)	0.0349(17)	0.0040(12)	-0.0012(12)	0.0057(11)
O22	0.0272(16)	0.0095(13)	0.0160(13)	-0.0030(10)	0.0010(11)	-0.0013(11)
O23	0.0200(14)	0.0088(12)	0.0186(14)	0.0042(10)	-0.0023(11)	-0.0003(10)
S2	0.0146(5)	0.0077(4)	0.0118(4)	0.0003(3)	0.0013(3)	0.0024(3)
F21	0.066(2)	0.0255(14)	0.0187(13)	-0.0104(11)	0.0009(13)	0.0140(14)
F22	0.0258(14)	0.0467(18)	0.0380(16)	0.0177(14)	0.0160(12)	0.0208(13)
F23	0.0549(18)	0.0269(14)	0.0214(13)	0.0145(11)	0.0143(12)	0.0217(13)

Table S9. Hydrogen atomic coordinates and isotropic atomic displacement parameters (\AA^2) for Cu^{2+} BIM

	x/a	y/b	z/c	$U(\text{eq})$
H4	0.4415	0.0306	0.6086	0.018000
H1	0.7395	0.7092	0.7839	0.022000
H2	0.9179	0.8483	0.8896	0.024000
H3	1.1288	0.7851	0.9761	0.023000
H4A	1.1578	0.5819	0.9532	0.022000
H6	1.0527	0.3706	0.8668	0.019000
H8	1.1035	0.2139	0.8100	0.022000
H9	1.1114	0.0120	0.7725	0.025000
H10	0.8834	-0.1107	0.6860	0.025000

	x/a	y/b	z/c	U(eq)
H11	0.6536	-0.0274	0.6361	0.019000
H15	0.1238	0.0538	0.5286	0.019000
H16	-0.0438	0.2003	0.5057	0.021000
H17	0.0561	0.4008	0.5571	0.023000
H18	0.3238	0.4603	0.6341	0.021000
H11W	0.6697	0.4863	0.5760	0.038000
H12W	0.6650	0.5853	0.6160	0.038000
H22W	0.4875	0.5488	0.8348	0.038000
H21W	0.4406	0.4481	0.8215	0.038000

Computational output data for Cu²⁺BIM

Table S10. Cartesian coordinates for Cu²⁺BIM (angstroms)

atom		x	y	z
Cu1	1	-0.5580662	-0.6763629	-0.3253296
N1	2	-2.5859122	-0.9589293	-0.1116355
N2	3	-1.1084366	1.2195968	0.2296194
N3	4	1.3724416	-0.1802497	-0.2250015
N4	5	3.1226147	0.9901018	0.4997509
H4	6	3.6684845	1.7760540	0.8664898
O1	7	-0.4553130	-1.8834563	-2.1558287
O2	8	-0.2816331	-2.4653674	1.0260700
C1	9	-3.3440017	-2.0066011	-0.4649532
H1	10	-2.8535066	-2.8039459	-1.0404187
C2	11	-4.7077914	-2.0880909	-0.1327218
H2	12	-5.2931070	-2.9610921	-0.4518516
C3	13	-5.2902338	-1.0513963	0.6020087
H3	14	-6.3529605	-1.0894230	0.8810295
C4	15	-4.5035968	0.0517564	0.9575739
H4	16	-4.9352387	0.9005694	1.5055608
C5	17	-3.1588323	0.0788637	0.5676678
C6	18	-2.3068581	1.2398733	0.7433954
H6	19	-2.7002323	2.1377288	1.2514123
C7	20	-0.3466616	2.3747021	0.0324442
C8	21	-1.0007626	3.6006806	-0.2243293
H8	22	-2.0939912	3.6246170	-0.3123387
C9	23	-0.2723858	4.7684357	-0.4185648
H9	24	-0.7937949	5.7143334	-0.6134330
C10	25	1.1314812	4.7244525	-0.4002029
H10	26	1.7126175	5.6359398	-0.5858975
C11	27	1.7917759	3.5109413	-0.2005235
H11	28	2.8861081	3.4966052	-0.2771714
C12	29	1.0795844	2.3110032	0.0043965
C13	30	1.8121542	1.0540881	0.1136635
C14	31	3.5587612	-0.3248664	0.4215591
C15	32	4.7922752	-0.9250773	0.6929890
H15	33	5.6557141	-0.3492162	1.0508617
C16	34	4.8824303	-2.2983652	0.4564386
H16	35	5.8330757	-2.8121793	0.6492202
C17	36	3.7843508	-3.0423626	-0.0396470
H17	37	3.9081559	-4.1179281	-0.2217893
C18	38	2.5546467	-2.4405646	-0.3016448
H18	39	1.7060528	-3.0271368	-0.6757158
C19	40	2.4391419	-1.0603007	-0.0520329

H19	41	0.0797421	-1.5130256	-2.8888475
H12	42	-0.3291436	-2.8545406	-2.1914187
H22	43	-1.0509336	-2.7757074	1.5465948
H21	44	0.4617651	-2.4104307	1.6646211

Table S11. Condensed population analysis for Cu²⁺BIM

			alpha	beta	charge	spin
1	1	Cu1	1s	1.000	1.000	2.000 0.000
2	1	Cu1	2s	1.000	1.000	2.000 0.000
3	1	Cu1	3s	0.998	0.999	1.997 -0.001
4	1	Cu1	4s	0.181	0.177	0.358 0.005
5	1	Cu1	2p	3.000	3.000	6.000 0.000
6	1	Cu1	3p	2.995	2.996	5.992 -0.001
7	1	Cu1	4p	0.255	0.253	0.508 0.003
8	1	Cu1	3d	5.026	4.571	9.597 0.456
9	2	N1	1s	1.000	1.000	2.000 0.000
10	2	N1	2s	0.786	0.770	1.557 0.016
11	2	N1	2p	1.903	1.827	3.730 0.076
12	2	N1	3d	0.031	0.030	0.061 0.000
13	3	N2	1s	1.000	1.000	2.000 -0.000
14	3	N2	2s	0.783	0.762	1.545 0.021
15	3	N2	2p	1.906	1.789	3.695 0.117
16	3	N2	3d	0.031	0.031	0.062 0.000
17	4	N3	1s	1.000	1.000	2.000 0.000
18	4	N3	2s	0.796	0.779	1.575 0.017
19	4	N3	2p	1.929	1.846	3.775 0.083
20	4	N3	3d	0.030	0.030	0.060 0.001
21	5	N4	1s	1.000	1.000	2.000 0.000
22	5	N4	2s	0.720	0.719	1.439 0.000
23	5	N4	2p	1.917	1.918	3.835 -0.001
24	5	N4	3d	0.029	0.029	0.058 0.000
25	6	H4	1s	0.328	0.328	0.656 0.000
26	6	H4	2p	0.023	0.023	0.046 0.000
27	7	O1	1s	1.000	1.000	2.000 0.000
28	7	O1	2s	0.844	0.843	1.687 0.002
29	7	O1	2p	2.417	2.397	4.814 0.020
30	7	O1	3d	0.011	0.011	0.022 0.000
31	8	O2	1s	1.000	1.000	2.000 0.000
32	8	O2	2s	0.846	0.845	1.691 0.001
33	8	O2	2p	2.413	2.401	4.814 0.013
34	8	O2	3d	0.011	0.011	0.023 0.000
35	9	C1	1s	1.000	1.000	2.000 0.000
36	9	C1	2s	0.607	0.607	1.214 -0.000
37	9	C1	2p	1.340	1.344	2.683 -0.004
38	9	C1	3d	0.035	0.034	0.069 0.001

39	10	H1	1s	0.399	0.394	0.793	0.004
40	10	H1	2p	0.013	0.013	0.026	0.000
41	11	C2	1s	1.000	1.000	2.000	0.000
42	11	C2	2s	0.620	0.620	1.240	0.001
43	11	C2	2p	1.417	1.411	2.828	0.005
44	11	C2	3d	0.024	0.024	0.048	0.000
45	12	H2	1s	0.379	0.378	0.757	0.001
46	12	H2	2p	0.013	0.013	0.027	0.000
47	13	C3	1s	1.000	1.000	2.000	0.000
48	13	C3	2s	0.619	0.620	1.239	-0.000
49	13	C3	2p	1.392	1.396	2.788	-0.004
50	13	C3	3d	0.025	0.025	0.050	0.000
51	14	H3	1s	0.380	0.379	0.759	0.000
52	14	H3	2p	0.013	0.013	0.027	0.000
53	15	C4	1s	1.000	1.000	2.000	0.000
54	15	C4	2s	0.630	0.630	1.260	-0.000
55	15	C4	2p	1.413	1.413	2.826	0.000
56	15	C4	3d	0.024	0.024	0.049	0.000
57	16	H4	1s	0.384	0.383	0.767	0.002
58	16	H4	2p	0.014	0.014	0.027	0.000
59	17	C5	1s	1.000	1.000	2.000	0.000
60	17	C5	2s	0.592	0.592	1.184	0.000
61	17	C5	2p	1.256	1.253	2.509	0.004
62	17	C5	3d	0.042	0.041	0.083	0.001
63	18	C6	1s	1.000	1.000	2.000	0.000
64	18	C6	2s	0.623	0.624	1.247	-0.001
65	18	C6	2p	1.323	1.334	2.657	-0.011
66	18	C6	3d	0.036	0.034	0.071	0.002
67	19	H6	1s	0.391	0.379	0.770	0.013
68	19	H6	2p	0.014	0.014	0.028	0.000
69	20	C7	1s	1.000	1.000	2.000	0.000
70	20	C7	2s	0.604	0.604	1.207	-0.000
71	20	C7	2p	1.273	1.258	2.531	0.015
72	20	C7	3d	0.041	0.039	0.081	0.002
73	21	C8	1s	1.000	1.000	2.000	0.000
74	21	C8	2s	0.623	0.622	1.245	0.001
75	21	C8	2p	1.435	1.424	2.859	0.011
76	21	C8	3d	0.025	0.025	0.049	0.000
77	22	H8	1s	0.396	0.396	0.792	-0.000
78	22	H8	2p	0.014	0.014	0.028	0.000
79	23	C9	1s	1.000	1.000	2.000	0.000
80	23	C9	2s	0.617	0.617	1.233	0.000
81	23	C9	2p	1.412	1.406	2.818	0.006
82	23	C9	3d	0.025	0.025	0.050	0.000
83	24	H9	1s	0.387	0.386	0.773	0.001
84	24	H9	2p	0.014	0.014	0.027	0.000

85 25	C10	1s	1.000	1.000	2.000	0.000
86 25	C10	2s	0.617	0.616	1.232	0.001
87 25	C10	2p	1.422	1.396	2.818	0.025
88 25	C10	3d	0.025	0.025	0.050	0.000
89 26	H10	1s	0.385	0.386	0.772	-0.001
90 26	H10	2p	0.014	0.013	0.027	0.000
91 27	C11	1s	1.000	1.000	2.000	0.000
92 27	C11	2s	0.622	0.623	1.245	-0.001
93 27	C11	2p	1.419	1.425	2.844	-0.006
94 27	C11	3d	0.025	0.025	0.050	0.000
95 28	H11	1s	0.401	0.401	0.802	0.000
96 28	H11	2p	0.014	0.014	0.028	0.000
97 29	C12	1s	1.000	1.000	1.999	0.000
98 29	C12	2s	0.636	0.635	1.271	0.001
99 29	C12	2p	1.344	1.318	2.663	0.026
100 29	C12	3d	0.031	0.031	0.062	0.000
101 30	C13	1s	1.000	1.000	2.000	0.000
102 30	C13	2s	0.579	0.578	1.158	0.001
103 30	C13	2p	1.201	1.194	2.396	0.007
104 30	C13	3d	0.053	0.051	0.104	0.001
105 31	C14	1s	1.000	1.000	2.000	0.000
106 31	C14	2s	0.589	0.588	1.177	0.001
107 31	C14	2p	1.292	1.276	2.568	0.015
108 31	C14	3d	0.041	0.041	0.083	0.000
109 32	C15	1s	1.000	1.000	2.000	0.000
110 32	C15	2s	0.621	0.621	1.242	-0.000
111 32	C15	2p	1.421	1.421	2.842	-0.001
112 32	C15	3d	0.025	0.024	0.049	0.000
113 33	H15	1s	0.396	0.395	0.791	0.001
114 33	H15	2p	0.014	0.014	0.028	0.000
115 34	C16	1s	1.000	1.000	2.000	0.000
116 34	C16	2s	0.617	0.616	1.233	0.001
117 34	C16	2p	1.436	1.410	2.846	0.026
118 34	C16	3d	0.025	0.025	0.050	0.000
119 35	H16	1s	0.389	0.390	0.779	-0.001
120 35	H16	2p	0.014	0.013	0.027	0.000
121 36	C17	1s	1.000	1.000	2.000	0.000
122 36	C17	2s	0.613	0.613	1.226	-0.000
123 36	C17	2p	1.421	1.422	2.843	-0.000
124 36	C17	3d	0.025	0.025	0.050	0.000
125 37	H17	1s	0.394	0.394	0.787	0.000
126 37	H17	2p	0.014	0.014	0.027	0.000
127 38	C18	1s	1.000	1.000	2.000	0.000
128 38	C18	2s	0.623	0.623	1.247	0.000
129 38	C18	2p	1.435	1.426	2.862	0.009
130 38	C18	3d	0.025	0.025	0.049	0.000

131 39	H18	1s	0.421	0.421	0.843	0.000
132 39	H18	2p	0.014	0.014	0.028	0.000
133 40	C19	1s	1.000	1.000	2.000	0.000
134 40	C19	2s	0.597	0.597	1.194	0.000
135 40	C19	2p	1.300	1.288	2.588	0.012
136 40	C19	3d	0.042	0.041	0.083	0.001
137 41	H19	1s	0.295	0.294	0.589	0.001
138 41	H19	2p	0.031	0.031	0.062	0.000
139 42	H12	1s	0.300	0.300	0.599	0.000
140 42	H12	2p	0.031	0.031	0.062	0.000
141 43	H22	1s	0.301	0.301	0.602	0.001
142 43	H22	2p	0.031	0.031	0.063	0.000
143 44	H21	1s	0.296	0.296	0.592	0.000
144 44	H21	2p	0.031	0.031	0.062	0.000

Computational output data for Cu²⁺BIMA

Table S12. Cartesian coordinates for Cu²⁺BIMA (angstroms)

atom		x	y	z
Cu1	1	0.5626500	-0.7184851	-0.1209832
N1	2	2.5527944	-0.9714771	-0.0570114
N3	3	-1.3210784	-0.2228154	-0.0463763
N4	4	-3.1856877	0.9595743	0.0960628
H4	5	-3.8243713	1.7571812	0.1260508
O1	6	0.3866772	-2.1787597	-1.8625790
O2	7	0.3638227	-2.3158119	1.4086820
C1	8	3.2268374	-2.0999343	-0.3693470
H1	9	2.6349657	-2.9379063	-0.7576403
C2	10	4.6136997	-2.1796772	-0.2299204
H2	11	5.1359788	-3.1041536	-0.5091998
C3	12	5.3110611	-1.0631083	0.2477134
H3	13	6.4025880	-1.0974253	0.3636475
C4	14	4.6078103	0.1088550	0.5477002
H4	15	5.1339079	1.0086175	0.8939681
C5	16	3.2206200	0.1273308	0.3800913
C7	17	0.2913250	2.4435475	-0.2075641
C8	18	0.8722586	3.7166720	-0.3031447
H8	19	1.9512744	3.8163818	-0.4858644
C9	20	0.1046008	4.8770655	-0.1937382
H9	21	0.5840644	5.8609751	-0.2705327
C10	22	-1.2734095	4.7653064	0.0091738
H10	23	-1.8970402	5.6636069	0.1024933

C11	24	-1.8602819	3.5046684	0.0710182
H11	25	-2.9464947	3.4684224	0.2210236
C12	26	-1.1095434	2.3097286	-0.0407336
C13	27	-1.8237297	1.0302390	0.0008121
C14	28	-3.5860197	-0.3656052	0.1210033
C15	29	-4.8530174	-0.9555399	0.1997118
H15	30	-5.7714873	-0.3585988	0.2711029
C16	31	-4.8938414	-2.3482565	0.1829174
H16	32	-5.8651186	-2.8591190	0.2376217
C17	33	-3.7118606	-3.1187801	0.0881956
H17	34	-3.7918623	-4.2124796	0.0758190
C18	35	-2.4496139	-2.5258894	0.0150254
H18	36	-1.5472725	-3.1470164	-0.0494516
C19	37	-2.3915635	-1.1209512	0.0249394
H19	38	-0.0559292	-1.8837813	-2.6852727
H12	39	0.0811623	-3.1002568	-1.7259682
H22	40	1.0963738	-2.4812292	2.0381924
H21	41	-0.4630647	-2.3234009	1.9391108
N2	42	1.1934109	1.2929058	-0.3187222
H23	43	1.5557985	1.2549187	-1.2909149
C6	44	2.3644259	1.3427656	0.6159030
H7	45	1.9709528	1.3755055	1.6511057
H13	46	2.9603453	2.2642232	0.4692597

Table S13. Condensed population analysis for **Cu²⁺BIMA**

			alpha	beta	charge	spin	
1	1	Cu1	1s	1.000	1.000	2.000	0.000
2	1	Cu1	2s	1.000	1.000	2.000	0.000
3	1	Cu1	3s	0.998	0.999	1.997	-0.001
4	1	Cu1	4s	0.204	0.185	0.389	0.019
5	1	Cu1	2p	3.000	3.000	6.000	0.000
6	1	Cu1	3p	2.995	2.996	5.991	-0.002
7	1	Cu1	4p	0.256	0.255	0.510	0.001
8	1	Cu1	3d	5.032	4.549	9.581	0.483
9	2	N1	1s	1.000	1.000	2.000	0.000
10	2	N1	2s	0.781	0.764	1.544	0.017
11	2	N1	2p	1.919	1.827	3.746	0.092
12	2	N1	3d	0.031	0.031	0.061	0.000
13	3	N3	1s	1.000	1.000	2.000	0.000
14	3	N3	2s	0.793	0.773	1.567	0.020
15	3	N3	2p	1.945	1.861	3.806	0.084
16	3	N3	3d	0.030	0.030	0.060	0.000
17	4	N4	1s	1.000	1.000	2.000	0.000
18	4	N4	2s	0.718	0.717	1.435	0.001
19	4	N4	2p	1.918	1.916	3.835	0.002

20	4	N4	3d	0.029	0.029	0.058	0.000
21	5	H4	1s	0.332	0.331	0.663	0.001
22	5	H4	2p	0.024	0.024	0.047	0.000
23	6	O1	1s	1.000	1.000	2.000	0.000
24	6	O1	2s	0.847	0.846	1.693	0.001
25	6	O1	2p	2.418	2.400	4.817	0.018
26	6	O1	3d	0.011	0.011	0.022	0.000
27	7	O2	1s	1.000	1.000	2.000	0.000
28	7	O2	2s	0.845	0.842	1.686	0.003
29	7	O2	2p	2.420	2.396	4.816	0.024
30	7	O2	3d	0.011	0.011	0.022	0.000
31	8	C1	1s	1.000	1.000	2.000	0.000
32	8	C1	2s	0.605	0.605	1.209	-0.000
33	8	C1	2p	1.337	1.340	2.677	-0.003
34	8	C1	3d	0.035	0.033	0.068	0.002
35	9	H1	1s	0.398	0.394	0.793	0.004
36	9	H1	2p	0.013	0.013	0.027	0.000
37	10	C2	1s	1.000	1.000	2.000	0.000
38	10	C2	2s	0.618	0.618	1.236	0.001
39	10	C2	2p	1.422	1.414	2.836	0.008
40	10	C2	3d	0.024	0.024	0.048	0.000
41	11	H2	1s	0.382	0.380	0.762	0.001
42	11	H2	2p	0.014	0.014	0.027	0.000
43	12	C3	1s	1.000	1.000	2.000	0.000
44	12	C3	2s	0.619	0.620	1.239	-0.000
45	12	C3	2p	1.392	1.396	2.788	-0.004
46	12	C3	3d	0.025	0.025	0.051	0.000
47	13	H3	1s	0.382	0.381	0.763	0.001
48	13	H3	2p	0.013	0.013	0.027	0.000
49	14	C4	1s	1.000	1.000	1.999	0.000
50	14	C4	2s	0.623	0.623	1.247	0.000
51	14	C4	2p	1.420	1.415	2.835	0.005
52	14	C4	3d	0.024	0.024	0.048	0.000
53	15	H4	1s	0.387	0.385	0.771	0.002
54	15	H4	2p	0.014	0.014	0.027	0.000
55	16	C5	1s	1.000	1.000	2.000	0.000
56	16	C5	2s	0.594	0.594	1.188	-0.000
57	16	C5	2p	1.267	1.268	2.535	-0.000
58	16	C5	3d	0.042	0.040	0.082	0.001
59	17	C7	1s	1.000	1.000	2.000	0.000
60	17	C7	2s	0.603	0.604	1.207	-0.001
61	17	C7	2p	1.282	1.283	2.564	-0.001
62	17	C7	3d	0.038	0.037	0.075	0.002
63	18	C8	1s	1.000	1.000	2.000	0.000
64	18	C8	2s	0.619	0.618	1.237	0.001
65	18	C8	2p	1.432	1.424	2.856	0.008

66	18	C8	3d	0.025	0.025	0.050	0.000
67	19	H8	1s	0.403	0.404	0.807	-0.001
68	19	H8	2p	0.014	0.014	0.028	0.000
69	20	C9	1s	1.000	1.000	2.000	0.000
70	20	C9	2s	0.616	0.616	1.232	0.000
71	20	C9	2p	1.411	1.411	2.822	0.001
72	20	C9	3d	0.025	0.025	0.050	0.000
73	21	H9	1s	0.389	0.388	0.777	0.002
74	21	H9	2p	0.013	0.013	0.027	0.000
75	22	C10	1s	1.000	1.000	2.000	0.000
76	22	C10	2s	0.613	0.613	1.227	0.000
77	22	C10	2p	1.413	1.412	2.825	0.001
78	22	C10	3d	0.025	0.025	0.050	0.000
79	23	H10	1s	0.388	0.388	0.776	0.000
80	23	H10	2p	0.013	0.013	0.027	0.000
81	24	C11	1s	1.000	1.000	2.000	0.000
82	24	C11	2s	0.622	0.622	1.243	-0.000
83	24	C11	2p	1.420	1.421	2.841	-0.001
84	24	C11	3d	0.025	0.025	0.050	0.000
85	25	H11	1s	0.415	0.415	0.831	0.000
86	25	H11	2p	0.014	0.014	0.028	0.000
87	26	C12	1s	1.000	1.000	2.000	0.000
88	26	C12	2s	0.635	0.635	1.270	0.000
89	26	C12	2p	1.319	1.314	2.633	0.004
90	26	C12	3d	0.031	0.031	0.062	0.000
91	27	C13	1s	1.000	1.000	2.000	0.000
92	27	C13	2s	0.581	0.580	1.161	0.001
93	27	C13	2p	1.188	1.192	2.380	-0.004
94	27	C13	3d	0.052	0.051	0.104	0.001
95	28	C14	1s	1.000	1.000	2.000	0.000
96	28	C14	2s	0.589	0.588	1.176	0.001
97	28	C14	2p	1.289	1.284	2.573	0.005
98	28	C14	3d	0.042	0.042	0.083	0.000
99	29	C15	1s	1.000	1.000	2.000	0.000
100	29	C15	2s	0.621	0.621	1.241	0.000
101	29	C15	2p	1.422	1.422	2.844	0.001
102	29	C15	3d	0.025	0.025	0.049	0.000
103	30	H15	1s	0.397	0.395	0.792	0.001
104	30	H15	2p	0.014	0.014	0.028	0.000
105	31	C16	1s	1.000	1.000	2.000	0.000
106	31	C16	2s	0.615	0.615	1.230	0.000
107	31	C16	2p	1.425	1.425	2.851	0.000
108	31	C16	3d	0.025	0.025	0.050	0.000
109	32	H16	1s	0.390	0.390	0.781	0.000
110	32	H16	2p	0.013	0.013	0.027	0.000
111	33	C17	1s	1.000	1.000	2.000	0.000

112 33	C17	2s	0.612	0.612	1.224	0.000
113 33	C17	2p	1.421	1.421	2.842	-0.000
114 33	C17	3d	0.025	0.025	0.050	0.000
115 34	H17	1s	0.395	0.395	0.791	0.000
116 34	H17	2p	0.014	0.014	0.027	0.000
117 35	C18	1s	1.000	1.000	2.000	0.000
118 35	C18	2s	0.624	0.624	1.249	0.000
119 35	C18	2p	1.449	1.449	2.897	0.000
120 35	C18	3d	0.025	0.025	0.049	0.000
121 36	H18	1s	0.424	0.423	0.847	0.001
122 36	H18	2p	0.014	0.014	0.028	0.000
123 37	C19	1s	1.000	1.000	2.000	0.000
124 37	C19	2s	0.596	0.596	1.192	0.000
125 37	C19	2p	1.285	1.283	2.568	0.002
126 37	C19	3d	0.041	0.040	0.082	0.001
127 38	H19	1s	0.297	0.297	0.594	0.001
128 38	H19	2p	0.031	0.031	0.062	0.000
129 39	H12	1s	0.301	0.300	0.601	0.000
130 39	H12	2p	0.031	0.031	0.062	0.000
131 40	H22	1s	0.299	0.296	0.595	0.002
132 40	H22	2p	0.031	0.031	0.062	0.000
133 41	H21	1s	0.294	0.293	0.588	0.001
134 41	H21	2p	0.031	0.031	0.062	0.000
135 42	N2	1s	1.000	1.000	2.000	-0.000
136 42	N2	2s	0.776	0.756	1.532	0.019
137 42	N2	2p	2.048	1.891	3.939	0.157
138 42	N2	3d	0.029	0.029	0.058	0.000
139 43	H23	1s	0.314	0.316	0.630	-0.002
140 43	H23	2p	0.021	0.020	0.041	0.001
141 44	C6	1s	1.000	1.000	2.000	0.000
142 44	C6	2s	0.610	0.611	1.220	-0.001
143 44	C6	2p	1.454	1.453	2.907	0.000
144 44	C6	3d	0.031	0.030	0.060	0.001
145 45	H7	1s	0.369	0.365	0.734	0.003
146 45	H7	2p	0.012	0.012	0.024	0.000
147 46	H13	1s	0.388	0.379	0.767	0.009
148 46	H13	2p	0.013	0.013	0.026	0.000

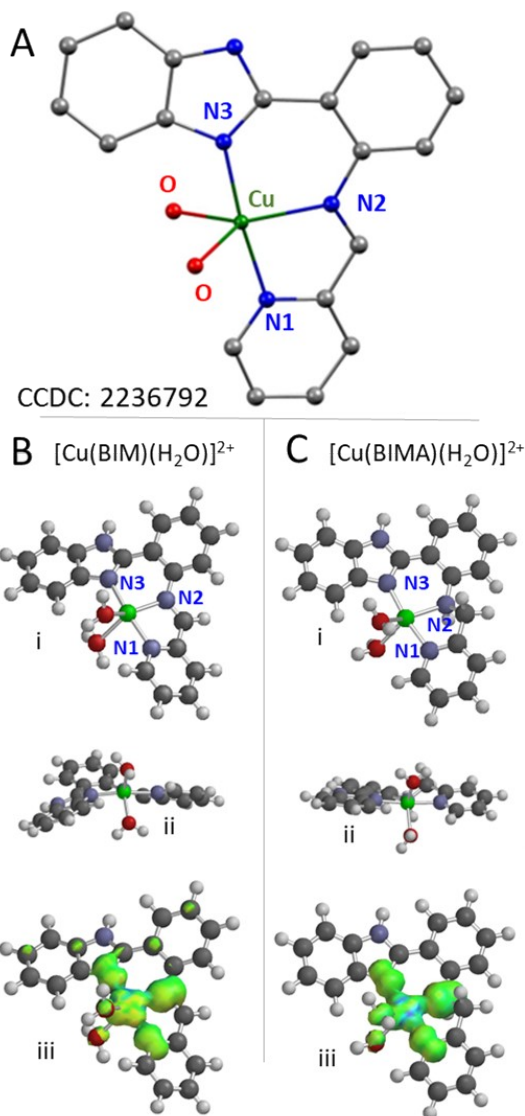


Figure S7. (A) Crystal structures of copper complex Cu^{2+}BIM shown as ADP plot. Triflate ions and H-atoms are removed for clarity. (B and C) DFT optimized, gas-phase structures of Cu^{2+}BIM (B, i) and $\text{Cu}^{2+}\text{BIMA}$ (C, i). Selected bond lengths and angles are reported in Table 1. In both panels the ii structures are rotated images looking down the Cu—N2 axis as a means of demonstrating the ring strain in Cu^{2+}BIM and the relaxed structure in $\text{Cu}^{2+}\text{BIMA}$. Finally, iii structures showcase the calculated spin density delocalized in these complexes (shown in green).

Gas phase structures for both Cu^{2+}BIM and $\text{Cu}^{2+}\text{BIMA}$ have been optimized computationally using DFT methods to give some insight into the coordination modes of these ligand complexes. Models using pBP/DN* and pBP/DN** converged to structures shown in Figure S7B and S7C. The DFT optimized structure of Cu^{2+}BIM shows structural similarity to the X-ray defined structure reported in Figure 2 and S7A. The 5-member chelate ring, which contains both Cu—N1 and Cu—N2 shows similar ~ 2.05 Å bond lengths and a slightly stronger Cu—N3 bond (~ 2.00 Å). Interestingly, the BIM ligand in $\text{Cu}^{2+}\text{BIMA}$ shows a planar configuration (Figure S7Bi and S7Bii). We associate this little twisted planar with overall ring strain from the 5- and 6-member chelate

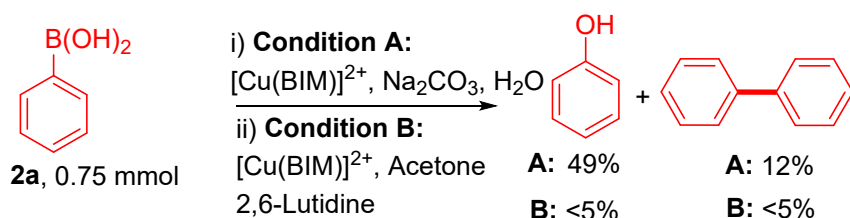
rings binding the copper(II) to this primarily sp^2 hybridized ligand. The DFT optimized model for $\text{Cu}^{2+}\text{BIMA}$ shows a planar coordination mode, where some of the ring strain appears to be relieved through the flexibility of the sp^3 hybridized methylene and secondary amine in the ligand backbone. There is more asymmetry in the Cu—N bonds, where the Cu—pyridine (Cu—N1) and Cu—benzimidazole (Cu—N3) are ~ 2.0 Å and the Cu—N2 bond distance is a long 2.12 Å.

Table S13. Select bond lengths and angles for X-ray crystallographically characterized and DFT-optimized copper complexes.

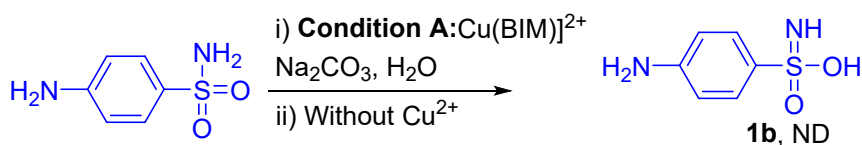
	Cu^{2+}BIM	Cu^{2+}BIM	$\text{Cu}^{2+}\text{BIMA}$
Sample:	X-ray Structure	Theoretical model	Theoretical model
Cu—N1 (Å)	1.980(3)	2.06	2.01
Cu—N2 (Å)	2.047(3)	2.05	2.12
Cu—N3 (Å)	1.938(3)	2.00	1.95
Cu—OH ₂ (Å)	2.072(3)	2.20	2.22
	2.124(3)	2.26	2.28
N1-Cu-N2 (o)	81.73(14)	80.47	80.06
N2-Cu-N3 (o)	92.57(13)	90.93	92.86
N1-Cu-N3 (o)	173.12(14)	169.04	171.49

K. Scheme S1: Control experiments

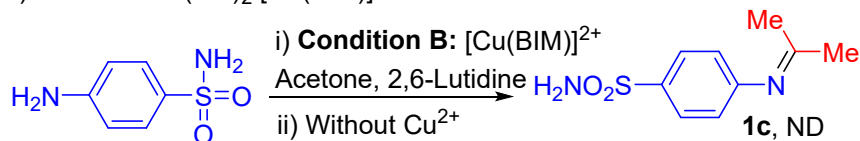
a) Without sulfanilamide



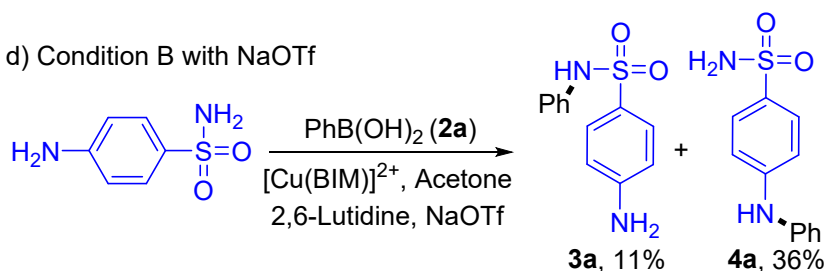
b) Without $\text{PhB}(\text{OH})_2/[\text{Cu}(\text{BIM})]^{2+}$



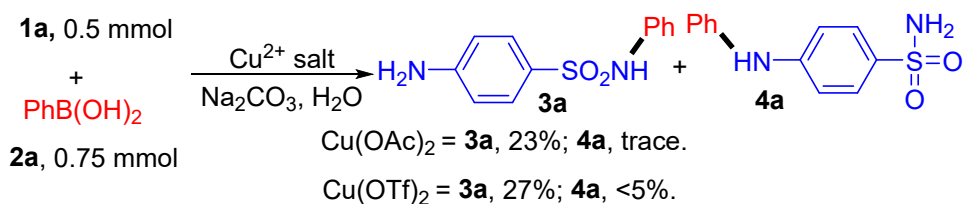
c) Without $\text{PhB}(\text{OH})_2/[\text{Cu}(\text{BIM})]^{2+}$



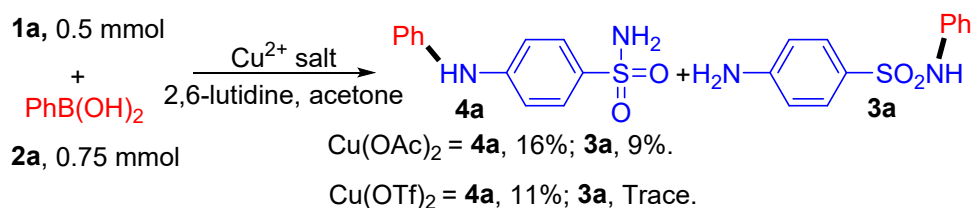
d) Condition B with NaOTf



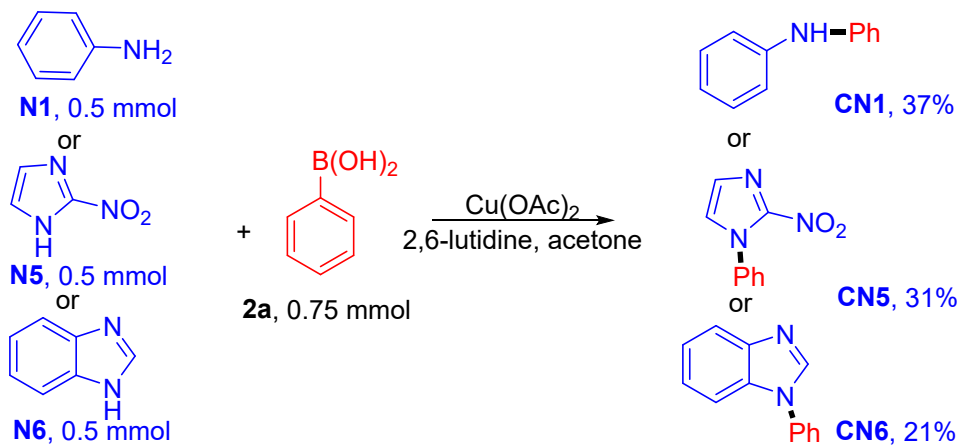
e) Cu^{2+} (0.05 mmol) source without BIM ligand in $\text{Na}_2\text{CO}_3/\text{H}_2\text{O}$



f) Cu^{2+} (0.05 mmol) source without BIM ligand in 2,6-lutidine/acetone

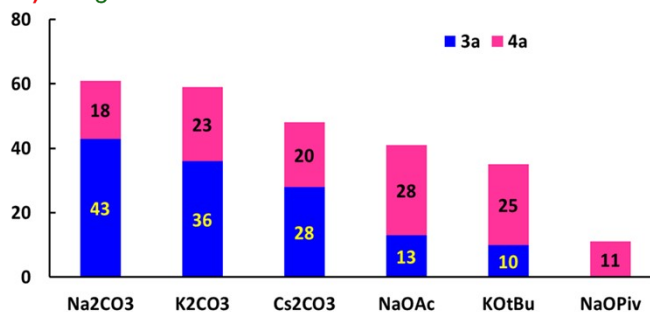


g) Cu^{2+} (0.05 mmol) source without BIM ligand in conditions A and B



L Base effects on % conversion

a) Inorganic bases in acetone solvent



b) Organic bases in a water solvent

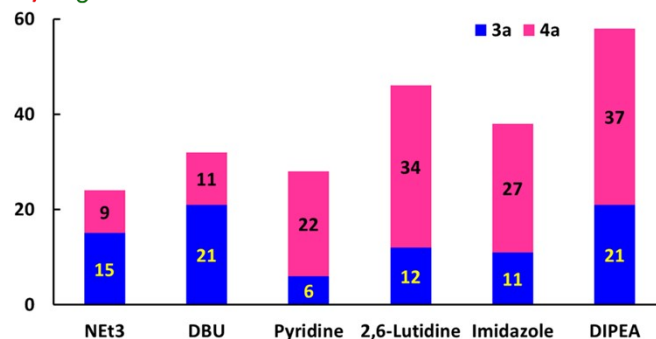


Figure S8. Base effects on % conversion for the *N*-arylation of 4ABSA (**1a**, 0.5 mmol) with PhB(OH)₂ (**2a**, 0.75 mmol), base (1.0 mmol), Cu²⁺BIM (0.05 mmol), and solvent (5.0 mL) at RT under open air atmosphere for 24 hours. Yields were determined using ¹H-NMR spectroscopy with mesitylene as an internal standard. **a)** the reaction condition for sulfonamide *N*-activation with inorganic bases in acetone solvent and **b)** the reaction condition for the arylamine *N*-activation with organic bases in water.

M. Powder X-ray diffraction (PXRD) analysis

Powder X-ray diffraction (PXRD) analysis for the Cu^{2+}BIM fitted with the LeBail profile fitting.

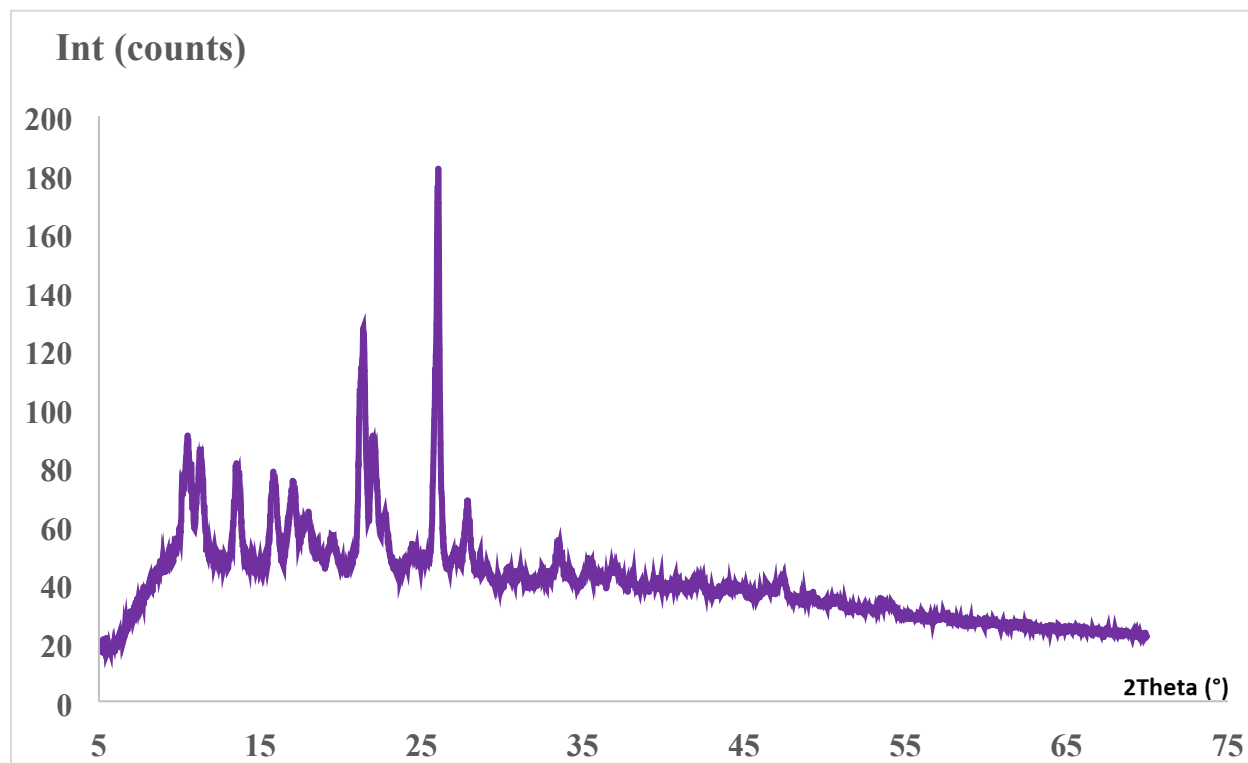


Figure S9. Cu^{2+}BIM powder XRD pattern measured.

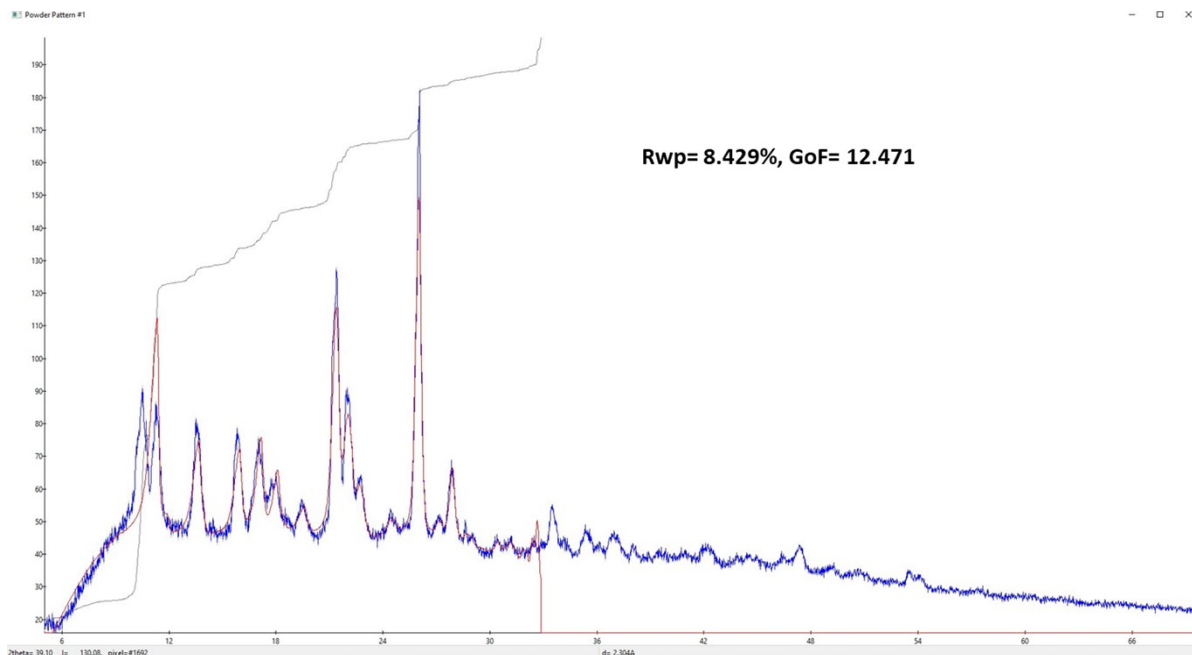
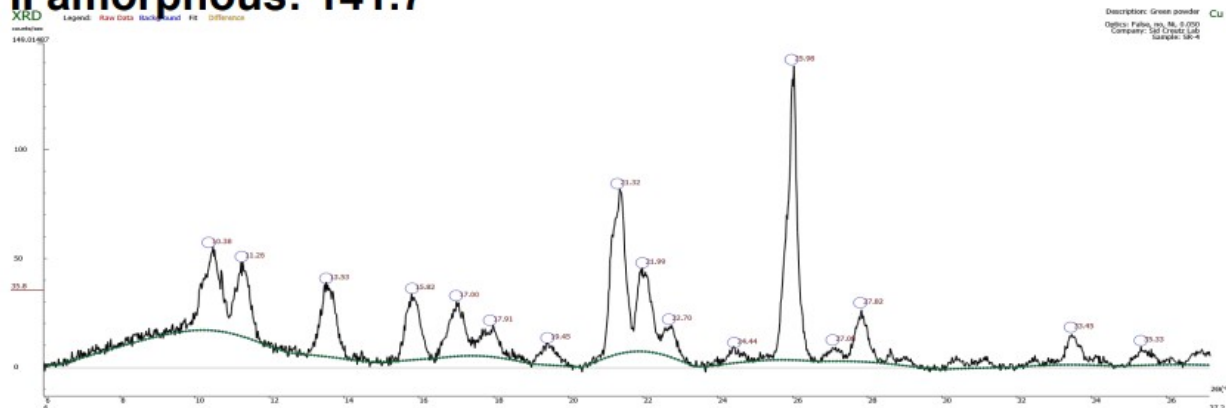


Figure S10. Cu^{2+}BIM LeBail refinement fitting profile of PXRD and single-XRD [Blue-measured and Red – stimulated].

Powder sample:	Single crystal:
Symmetry_space_group_name_H-M 'P -1 '	Symmetry_space_group_name_H-M 'P -1 '
a = 7.7922 Å	a = 7.8701 Å
b = 11.3394 Å	b = 11.5840 Å
c = 14.4604 Å	c = 14.7103 Å
α = 99.8853 °	α = 100.260 °
β = 104.070 °	β = 90.700 °
γ = 97.3408 °	γ = 97.224 °
volume = 1201.59 Å ³	volume = 1308.4 Å ³

CRYSTALLINITY REPORT

% crystallinity: 66.31
% amorphous: 33.69
|| crystallinity: 278.9
|| amorphous: 141.7



Sample

File: 22_08_16_0001_SR-4.xml

Figure S11. Crystallinity report for the Cu²⁺BIM complex.

Sample Information:

Description: Green powder

Sample: SR-4

Company: Sid Creutz Lab

Job Number: 004

Notes:

Experimental Conditions:

Scan Type: Coupled

2 start (°): 5.00

2 end (°): 70.00

(step size, °): 0.02

Dwell (sec): 2

Source Soller Slit: No

Divergence Slit: 1.00 mm

Anti-Scatter Slit: no mm

Diffacted-Beam Soller Slit: No

Receiving Slit: 0.050 mm

Spinner: False

Wavelength: 1.540593

V: 30.00 kV

C: 20.00 mA

Powder X-ray diffraction (PXRD) analysis for the Cu²⁺BIMA

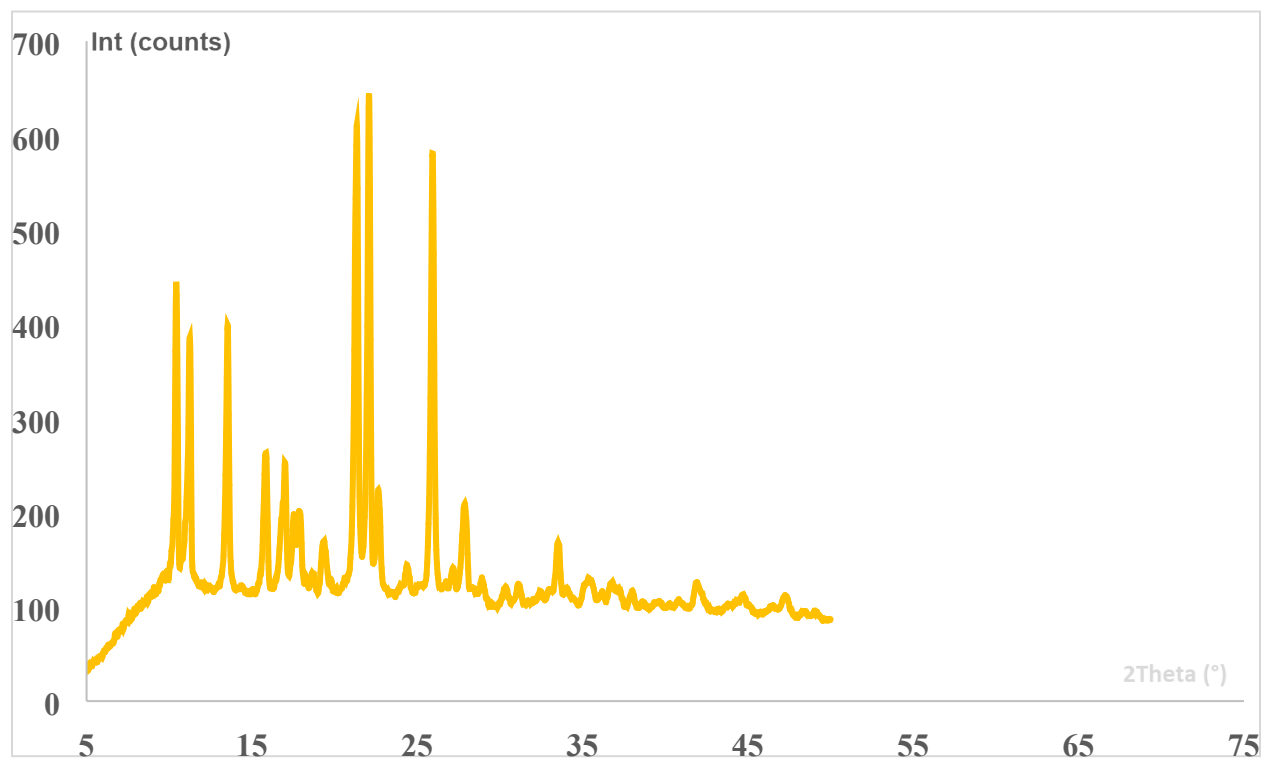


Figure S12. Cu²⁺-complex, Cu²⁺BIMA powder XRD pattern measured.

M. Elemental analysis data for Cu²⁺BIM & Cu²⁺BIMA

	C	H	N	S
Cu²⁺BIM	37.98	2.409	8.45	9.946
Cu²⁺BIMA	39.06	2.413	8.71	9.872

ESI-High-resolution mass spectrometry data for the Cu²⁺BIM and Cu²⁺BIMA

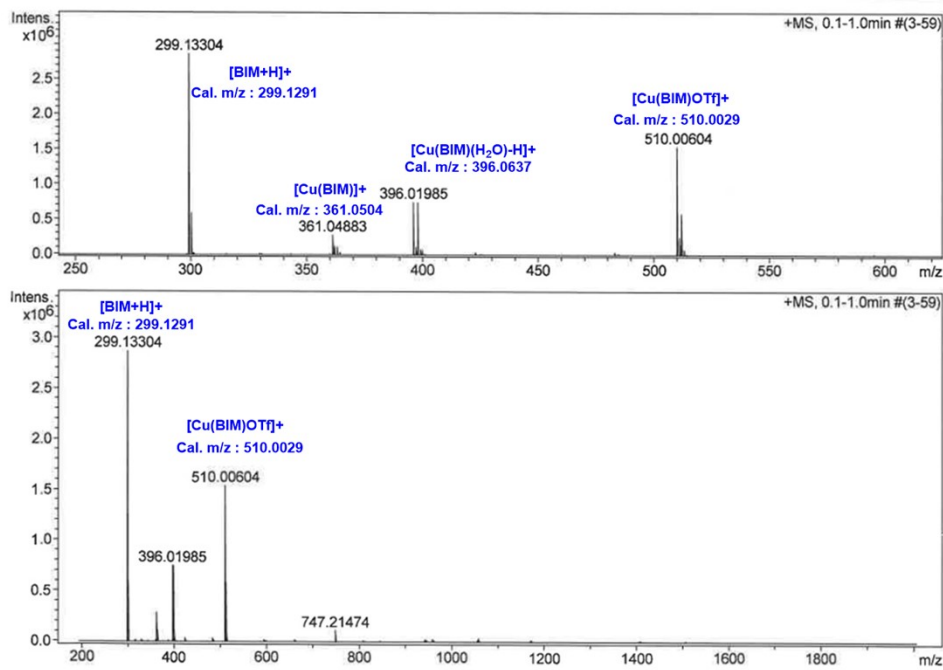


Figure S13. ESI-HRMS spectrum of Cu²⁺BIM complex

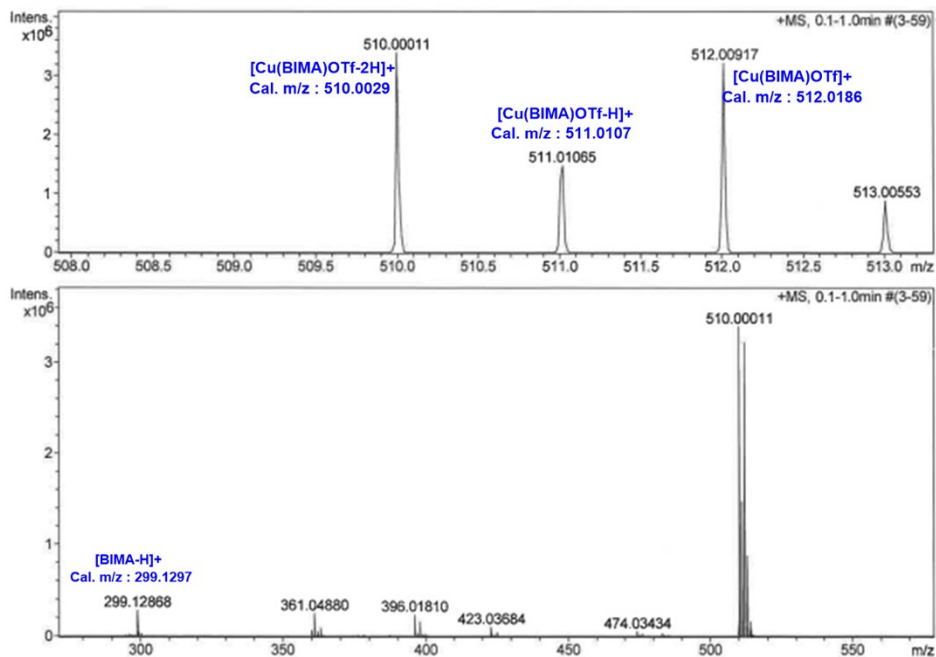


Figure S14. ESI-HRMS spectrum of Cu²⁺BIMA complex

N. References:

- (1) Saluja, P.; Kaur, N.; Singh, N.; Jang, D. O. Benzimidazole-Based Fluorescent Sensors for Cr³⁺ and Their Resultant Complexes for Sensing HSO₄⁻ and F⁻. *Tetrahedron* **2012**, *68* (41), 8551–8556. <https://doi.org/10.1016/j.tet.2012.08.022>.
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