

Mechanistic Studies on the Copper-Catalyzed *N*-Arylation of Amides

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Supporting Information

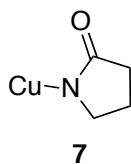
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General Information

Reagents: Copper(I) iodide (fine grey powder) was purchased from Strem Chemicals and stored in an amber vial in a dessicator. Racemic *trans*-1,2-cyclohexanediamine was purchased from Aldrich. The quality of the inorganic base K_3PO_4 is quite important. Reproducible results were obtained with K_3PO_4 available from Fluka (catalog number 04347, Riedel-de Haën product; free-flowing, fine granule of uniform size) and dried under high vacuum at 150 °C for 3 days. The dried K_3PO_4 was then stored in a nitrogen-filled glovebox. It is important to note that the particle size of K_3PO_4 is critical for reproducible kinetics, i.e., using K_3PO_4 purchased from Alfa Aesar or Aldrich (both of variable size ranging from fine powder to large chunks) led to irreproducible kinetics and in some instances complete inhibition of the reaction. 2-Pyrrolidinone (**2**) was purchased from Aldrich and distilled over 4 Å molecular sieves prior to its use. 3,5-dimethyliodobenzene (**1**) was also purchased from Aldrich and distilled from CaH_2 prior to its use. Toluene was purchased from J.T. Baker in CYCLE-TAINER solvent delivery kegs, was vigorously purged with argon for 2 h, and then purified by passing through two packed columns of neutral alumina under argon pressure. All reagents with the exception of copper(I) iodide were stored and weighed out inside a nitrogen-filled glovebox.

Analytical methods: 1H NMR and ^{13}C NMR were recorded on either a Varian 500 MHz Fourier transform NMR spectrometer with chemical shifts reported with respect to residual deuterated solvent peaks. Kinetics experiments were performed in an Omnical SuperCRC reaction calorimeter.

Experimental Section



Preparation of Copper(I)-pyrrolidinoate (7). 2-pyrrolidinone (**2**) (260 mg, 3.05 mmol) was added at ambient temperature to toluene (10 mL) containing mesitylcopper (500 mg, 2.75 mmol) inside a nitrogen-filled glovebox. The colorless mixture was allowed to stir for 15 minutes at ambient temperature prior to the removal of volatiles under high vacuum. The resulting white solid was washed with hexanes (25 mL) and dried under vacuum affording 350 mg (86 %) of an air-sensitive white solid. Iodometric analysis was performed by dissolving 250 mg in 5 mL of 6N HNO₃ and following the procedure for titration by de la Camp and Seely. ¹H NMR (C₆D₆, 500 MHz) δ 1.58 (br m, 2H), 2.04 (br m, 2H), 3.20 (br m, 2H). ¹³C NMR (C₆D₆, 125 MHz) δ 25.09, 31.37, 52.83, 185.12.

Experimental Procedure for Kinetic Studies Using Reaction Calorimetry

Reaction procedure. Reactions were performed in an Omnical SuperCRC reaction calorimeter. The instrument contains an internal magnetic stirrer and a differential scanning calorimeter (DSC), which compares the heat released or consumed in a sample vessel to an empty reference vessel. The reaction vessels were 16 mL borosilicate screw-thread vials fit with opentop black phenolic screw caps and white PTFE septa (KimbleBrand) charged with Teflon stir bars. Sample volumes did not exceed 2.5 mL. In a typical calorimetry experiment, a solution of copper iodide and diamine in toluene was added to a reaction vessel containing K₃PO₄, which was placed in the calorimeter and stirred for one hour, allowing the contents of the vessel to reach thermal equilibrium. Simultaneously, a syringe containing 3,5-dimethyliodobenzene and 2-pyrrolidinone was placed in the sample injection port of the calorimeter and was allowed to thermally equilibrate. The reaction was initiated by injecting the mixture of aryl iodide and amide into the stirred catalyst-K₃PO₄ solution. The temperature of the DSC was held constant at 363 K using the internal temperature controller in the calorimeter, ensuring that the reaction would proceed under isothermal conditions. A raw data curve was produced by measuring the heat flow from the sample vessel every fifteen seconds during the reaction. Due to the delay between the instantaneous moment heat is evolved from the reaction vessel and the time the thermophile sensor detects the heat flow, the raw data curve must be calibrated. To accomplish this calibration, a constant amount of

current was passed through a resistor in the sample chamber of the calorimeter thereby producing a known quantity of heat. This process results in a response curve, which is then transformed into a square wave allowing for the response time of the instrument to be calculated using the WinCRC software. Application of the response time to the raw data results in a “tau corrected data curve.” The tau corrected data curve is a plot of heat flow (mJ s^{-1}) versus time. The reaction rate, which is directly proportional to the heat flow (eq 1), fraction conversion (eq 2), and instantaneous concentrations of reactants/products can all be calculated from this tau corrected data curve. Conversion measured by GC analysis was compared to conversion measured by heat flow (Figure S1). Agreement between the two methods validates the use of reaction calorimetry to follow the copper-catalyzed amidation of aryl iodides.

$$q = \Delta H_{\text{rxn}} \cdot V \cdot r \quad (1)$$

q is the reaction heat flow, ΔH_{rxn} is the heat of reaction, V is the reaction volume, and r is the reaction rate

$$\text{fractional conversion} = \frac{\int_0^t q \cdot dt}{\int_0^{t_f} q \cdot dt} \quad (2)$$

The numerator represents the area under the heat flow to any time point t and the denominator represents the total area under the heat flow curve.

Reaction rate dependence on [aryl iodide]

Since the plots for the rate dependence on the aryl iodide concentration exhibit complex rate behavior (Figure 6), they warrant further discussion. In each case (Figure 6a/6b), the data is consistent with the reciprocal rate dependence on [amide] at high and low [1,2-diamine] observed in Figure 5 and a first-order rate dependence on [aryl iodide] under all conditions. Theoretically, a first-order rate dependence on [aryl iodide] should result in overlapping rate profiles when the concentration of aryl iodide is varied while maintaining the same concentration of amide. That is, a first-order rate dependence on [aryl iodide] should afford plots that exhibit a linear relationship between the rate and [aryl iodide]. The experiments in Figure 6, however, were not performed under these pseudo-zero order conditions, thus, the stoichiometric relationship between the [amide] and [aryl iodide], i.e., $[\text{amide}] = [\text{amide}]_0 - [\text{aryl iodide}]_0 + [\text{aryl iodide}]$, plays a significant role in the reaction rate profiles.¹ ***The overall rate is higher***

with increasing [aryl iodide] because there is a first-order dependence on [aryl iodide], however, the deviation from simple first-order behavior, i.e., plots that overlap, is a result of the [amide] simultaneously changing with the [aryl iodide]. Take for example the conditions in which low 1,2-diamine concentrations are employed. According to equation 6a, the reaction rate is inversely proportional to the [amide] under these conditions. Now considering the stoichiometric relationship between [aryl iodide] and [amide], reactions performed with three different initial aryl iodide concentrations should result in higher reaction rates at each point in time when the $[\text{aryl iodide}]_t$ is the same for the three experiments. This behavior is due to the presence of lower $[\text{amide}]_t$ at any given point when using higher initial $[\text{aryl iodide}]_0$. Indeed, as shown in Figure 6a, this situation holds for the beginning of the reaction with $[\text{aryl iodide}]_0 = 0.8 \text{ M}$ and for almost the entire reactions for $[\text{aryl iodide}]_0 = 0.6$ and 0.4 M . The converse is true for the reactions performed with high [1,2-diamine]. Under these conditions, the reaction rate is directly proportional to the [amide] (eq 6b). Accordingly, when three experiments are performed at different initial $[\text{aryl iodide}]_0$, lower reaction rates should be observed at any point in time when the $[\text{aryl iodide}]_t$ is the same. This is due to the $[\text{amide}]_t$ in reactions using higher $[\text{aryl iodide}]_0$ being lower than the $[\text{amide}]_t$ when starting from lower $[\text{aryl iodide}]_0$. As shown in Figure 6b, this behavior is observed when using initial $[\text{aryl iodide}]_0$ of 0.8, 0.6 and 0.4 M. Thus, the reaction rate profiles in Figure 6 are not only consistent with the reaction rate dependencies on the [amide] observed in Figure 5, they demonstrate that the reaction rate is directly proportional to the [aryl iodide] under both high and low [1,2-diamine] conditions (eq 6c).

Reaction rate in the presence of exogenous KI

The reaction rate when 10 equivalents of KI is added relative to aryl iodide is identical to that when exogenous KI is absent, Figure S1 below.

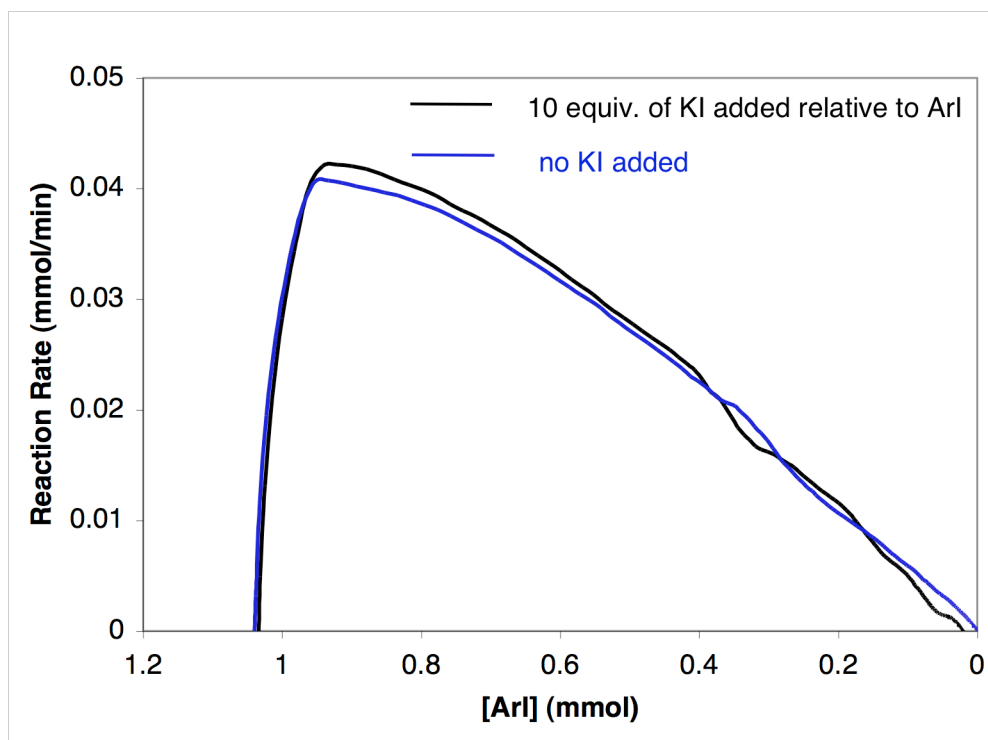


Figure S1. Reaction rate with exogenous KI. Reaction Conditions: [CuI] = 0.05 mmol, [3] = 0.1 mmol, [1]_o = 1.0 mmol, [2]_o = 2.0 mmol, [K₃PO₄]_o = 2.4 mmol, 2 mL of toluene, 90 °C.

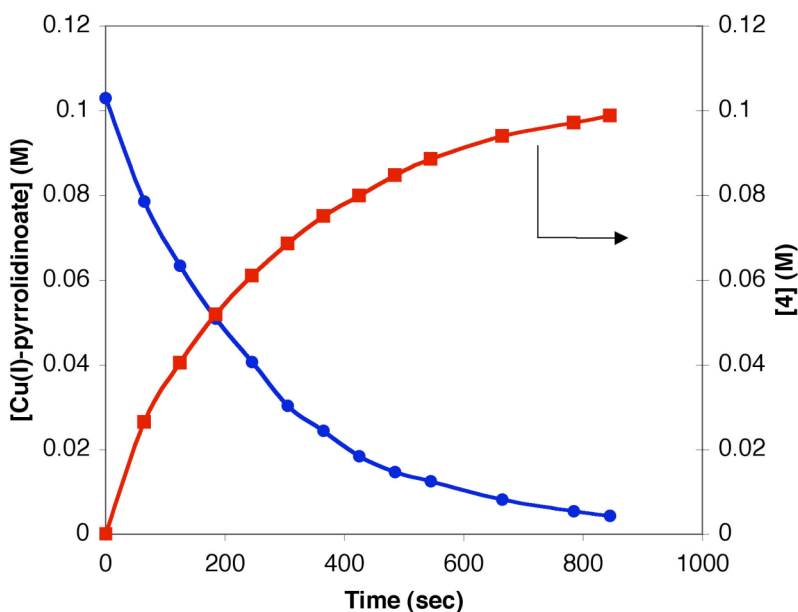
Molecular weight determination of 7 and 8 using the Signer method

In a nitrogen filled glovebox, stock solutions of the reference (DavePhos, 0.11 – 0.09 M) and the unknown (0.12 – 0.15 M) were prepared in degassed anhydrous benzene. The Signer apparatus was charged with 2.5 mL of each solution in each side arm and brought outside the glovebox. The solutions were frozen in liquid nitrogen and the apparatus evacuated under high vacuum to about 0.1 torr. The sealed apparatus under reduced pressure was then stored in dark at room temperature, and the volumes recorded every few days until the final equilibrium was attained (~ 4 weeks). The molecular weights were calculated using the formula: $G_u/M_uV_u = G_r/M_rV_r$, where G, M and V are the sample weight, molecular weight and final equilibrium volume associated with the unknown and the reference solutions. The calculated molecular weights were 517 g/mol for **7** and 267 g/mol for complex **8** respectively.

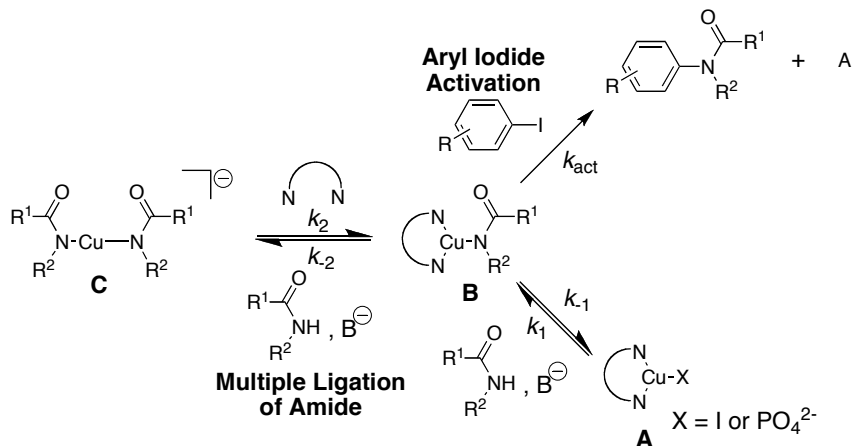
¹H NMR experiments with 7

Inside a nitrogen-filled glovebox, a volumetric flask (5 mL) was charged with **7** (76 mg, 0.51 mmol), d₈-toluene (3 mL) was then added and upon addition of **3** (76 mg, 0.52 mmol) the mixture became homogenous. Subsequently, the solution was diluted with d₈-toluene (5 mL total volume), which afforded **8** in a final concentration of 0.11 M. A NMR tube was charged with the stock solution of **8** (0.5 mL, 0.053 mmol) and diluted with d₈-toluene (0.5 mL). The tube was capped with a PTFE septum and opentop screw cap and brought outside of the glovebox and placed in a 500 MHz NMR spectrometer cooled to 273 K. Upon addition of **1** (12.3 mg, 0.053 mmol) to the NMR tube, data was collected every minute.

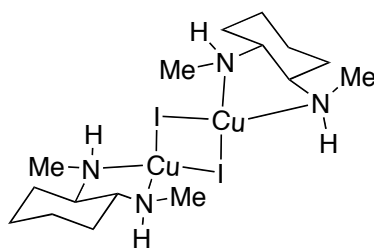
Figure S2. Representative Kinetics for the Arylation of **7** in the Presence of **3**.



Derivation of eq 9



X-ray Structure Data for (R, R, R, R)-6



(*R,R,R,R*)-**6**

Table S1. Crystal data and structure refinement for **6**.

Identification code	05063t	
Empirical formula	$C_{16}H_{36}Cu_2I_2N_4$	
Formula weight	665.32	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	$a = 8.4715(10)$ Å	$\alpha = 90^\circ$.
	$b = 7.5995(9)$ Å	$\beta = 90.054(2)^\circ$.
	$c = 36.754(4)$ Å	$\gamma = 90^\circ$.
Volume	$2366.2(5)$ Å ³	
Z	4	
Density (calculated)	1.851 Mg/m ³	
Absorption coefficient	4.412 mm ⁻¹	
F(000)	1272	
Crystal size	$0.36 \times 0.25 \times 0.17$ mm ³	
Theta range for data collection	0.55 to 28.32° .	
Index ranges	$-11 \leq h \leq 11$, $-10 \leq k \leq 10$, $-48 \leq l \leq 48$	
Reflections collected	46740	
Independent reflections	11686 [R(int) = 0.0337]	
Completeness to theta = 28.32°	99.4 %	
Absorption correction	SADABS	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	11686 / 2 / 468	
Goodness-of-fit on F ²	1.301	
Final R indices [I > 2σ(I)]	R1 = 0.0414, wR2 = 0.0962	
R indices (all data)	R1 = 0.0418, wR2 = 0.0963	
Absolute structure parameter	0.09(3)	
Largest diff. peak and hole	1.732 and -1.542 e.Å ⁻³	

Table S2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	$U(\text{eq})$
I(1)	6198(1)	7387(1)	1510(1)	20(1)
I(2)	3795(1)	3015(1)	835(1)	25(1)
Cu(1)	4168(1)	6428(1)	1040(1)	20(1)
Cu(2)	5481(1)	3932(1)	1369(1)	21(1)
C(1)	3487(8)	2556(12)	2007(2)	25(2)
N(1)	7572(7)	2464(9)	1449(2)	21(1)
N(2)	5071(7)	3276(8)	1925(2)	16(1)
I(4)	-1198(1)	6556(1)	6510(1)	20(1)
I(3)	1205(1)	10927(1)	5835(1)	24(1)
Cu(5)	-481(1)	10011(1)	6369(1)	21(1)
Cu(7)	831(1)	7515(1)	6039(1)	19(1)
N(6)	-70(7)	10668(8)	6924(2)	16(1)
N(5)	-2572(7)	11492(9)	6449(2)	20(1)
N(7)	972(7)	6031(8)	5557(2)	17(1)
C(23)	-1381(8)	11810(10)	7053(2)	16(1)
C(6)	6384(8)	2130(10)	2054(2)	16(1)
N(8)	1731(8)	7092(9)	1088(2)	20(1)
N(3)	4029(7)	7914(8)	556(2)	16(1)
C(2)	1163(10)	7639(14)	1448(3)	30(2)
N(9)	3264(8)	6857(8)	6088(2)	19(1)
C(16)	3839(10)	6312(14)	6452(2)	31(2)
C(24)	-2905(7)	11391(9)	6840(2)	16(1)
C(14)	2664(8)	6045(9)	5452(2)	15(1)
C(20)	3091(10)	4828(10)	5138(2)	24(2)
C(7)	7906(7)	2554(9)	1841(2)	16(1)
C(4)	1352(8)	8350(10)	791(2)	18(1)
C(12)	8879(11)	3076(14)	1217(2)	33(2)
C(15)	3650(9)	5580(9)	5792(2)	18(1)
C(21)	-3876(11)	10838(14)	6216(2)	36(2)
C(13)	-91(9)	6712(11)	5267(2)	24(2)
C(19)	4850(10)	4754(11)	5058(2)	24(2)
C(22)	1506(8)	11386(12)	7009(2)	24(2)
C(5)	2339(8)	7897(9)	452(2)	15(1)

C(3)	5094(9)	7236(11)	267(2)	24(2)
C(17)	5412(9)	5501(10)	5708(2)	25(2)
C(10)	9529(9)	1532(13)	2377(2)	30(2)
C(8)	6665(8)	2270(11)	2465(2)	21(1)
C(11)	9233(8)	1320(10)	1966(2)	23(2)
C(18)	5770(10)	4210(10)	5397(3)	29(2)
C(9)	8031(10)	1119(12)	2592(2)	31(2)
C(32)	-1668(8)	11673(11)	7466(2)	20(1)
C(25)	1922(10)	9123(10)	140(2)	24(2)
C(26)	147(10)	9179(11)	59(2)	26(2)
C(28)	-408(9)	8444(10)	710(2)	26(2)
C(29)	-4529(9)	12424(13)	7378(2)	30(2)
C(30)	-4236(8)	12628(10)	6965(2)	23(2)
C(27)	-778(10)	9727(11)	396(3)	29(2)
C(31)	-3035(10)	12830(12)	7590(2)	30(2)

Table S3. Bond lengths [Å] and angles [°] for **6**.

I(1)-Cu(1)	2.5450(10)
I(1)-Cu(2)	2.7439(11)
I(2)-Cu(2)	2.5253(11)
I(2)-Cu(1)	2.7192(11)
Cu(1)-N(3)	2.110(6)
Cu(1)-N(8)	2.133(7)
Cu(1)-Cu(2)	2.5094(13)
Cu(2)-N(1)	2.114(7)
Cu(2)-N(2)	2.133(6)
C(1)-N(2)	1.480(9)
N(1)-C(7)	1.469(9)
N(1)-C(12)	1.473(10)
N(2)-C(6)	1.489(9)
I(4)-Cu(7)	2.5468(10)
I(4)-Cu(5)	2.7445(11)
I(3)-Cu(5)	2.5274(11)
I(3)-Cu(7)	2.7185(11)
Cu(5)-N(5)	2.119(7)
Cu(5)-N(6)	2.127(6)
Cu(5)-Cu(7)	2.5106(13)
Cu(7)-N(7)	2.106(6)
Cu(7)-N(9)	2.129(7)
N(6)-C(22)	1.476(9)
N(6)-C(23)	1.488(9)
N(5)-C(24)	1.468(9)
N(5)-C(21)	1.483(10)
N(7)-C(14)	1.484(9)
N(7)-C(13)	1.488(9)
C(23)-C(32)	1.539(10)
C(23)-C(24)	1.542(9)
C(6)-C(8)	1.535(10)
C(6)-C(7)	1.544(9)
N(8)-C(2)	1.468(11)
N(8)-C(4)	1.486(10)
N(3)-C(5)	1.481(9)
N(3)-C(3)	1.486(9)

N(9)-C(16)	1.482(10)
N(9)-C(15)	1.494(10)
C(24)-C(30)	1.538(10)
C(14)-C(20)	1.523(10)
C(14)-C(15)	1.543(10)
C(20)-C(19)	1.519(11)
C(7)-C(11)	1.535(10)
C(4)-C(28)	1.522(10)
C(4)-C(5)	1.540(10)
C(15)-C(17)	1.526(10)
C(19)-C(18)	1.525(13)
C(5)-C(25)	1.519(10)
C(17)-C(18)	1.539(12)
C(10)-C(9)	1.528(12)
C(10)-C(11)	1.539(12)
C(8)-C(9)	1.523(11)
C(32)-C(31)	1.524(10)
C(25)-C(26)	1.533(11)
C(26)-C(27)	1.524(13)
C(28)-C(27)	1.542(12)
C(29)-C(31)	1.518(12)
C(29)-C(30)	1.544(12)

Cu(1)-I(1)-Cu(2)	56.50(3)
Cu(2)-I(2)-Cu(1)	57.03(3)
N(3)-Cu(1)-N(8)	83.7(2)
N(3)-Cu(1)-Cu(2)	146.65(17)
N(8)-Cu(1)-Cu(2)	124.55(17)
N(3)-Cu(1)-I(1)	117.20(17)
N(8)-Cu(1)-I(1)	121.90(18)
Cu(2)-Cu(1)-I(1)	65.76(3)
N(3)-Cu(1)-I(2)	105.70(18)
N(8)-Cu(1)-I(2)	97.87(18)
Cu(2)-Cu(1)-I(2)	57.59(3)
I(1)-Cu(1)-I(2)	122.66(4)
N(1)-Cu(2)-N(2)	83.1(2)
N(1)-Cu(2)-Cu(1)	146.85(18)
N(2)-Cu(2)-Cu(1)	124.51(16)

N(1)-Cu(2)-I(2)	115.81(17)
N(2)-Cu(2)-I(2)	126.01(17)
Cu(1)-Cu(2)-I(2)	65.38(3)
N(1)-Cu(2)-I(1)	107.09(18)
N(2)-Cu(2)-I(1)	94.49(17)
Cu(1)-Cu(2)-I(1)	57.75(3)
I(2)-Cu(2)-I(1)	122.44(4)
C(7)-N(1)-C(12)	114.0(6)
C(7)-N(1)-Cu(2)	105.8(4)
C(12)-N(1)-Cu(2)	112.5(6)
C(1)-N(2)-C(6)	113.4(6)
C(1)-N(2)-Cu(2)	115.4(5)
C(6)-N(2)-Cu(2)	108.6(4)
Cu(7)-I(4)-Cu(5)	56.50(3)
Cu(5)-I(3)-Cu(7)	57.04(3)
N(5)-Cu(5)-N(6)	83.0(2)
N(5)-Cu(5)-Cu(7)	147.00(18)
N(6)-Cu(5)-Cu(7)	124.57(16)
N(5)-Cu(5)-I(3)	115.76(17)
N(6)-Cu(5)-I(3)	126.00(17)
Cu(7)-Cu(5)-I(3)	65.31(3)
N(5)-Cu(5)-I(4)	107.27(18)
N(6)-Cu(5)-I(4)	94.53(17)
Cu(7)-Cu(5)-I(4)	57.77(3)
I(3)-Cu(5)-I(4)	122.41(4)
N(7)-Cu(7)-N(9)	83.6(2)
N(7)-Cu(7)-Cu(5)	146.79(18)
N(9)-Cu(7)-Cu(5)	124.49(17)
N(7)-Cu(7)-I(4)	117.28(18)
N(9)-Cu(7)-I(4)	121.98(18)
Cu(5)-Cu(7)-I(4)	65.73(3)
N(7)-Cu(7)-I(3)	105.71(18)
N(9)-Cu(7)-I(3)	97.72(18)
Cu(5)-Cu(7)-I(3)	57.64(3)
I(4)-Cu(7)-I(3)	122.68(4)
C(22)-N(6)-C(23)	113.0(6)
C(22)-N(6)-Cu(5)	116.0(5)
C(23)-N(6)-Cu(5)	108.8(4)

C(24)-N(5)-C(21)	113.9(6)
C(24)-N(5)-Cu(5)	105.6(4)
C(21)-N(5)-Cu(5)	111.3(6)
C(14)-N(7)-C(13)	113.3(6)
C(14)-N(7)-Cu(7)	105.6(4)
C(13)-N(7)-Cu(7)	112.5(5)
N(6)-C(23)-C(32)	113.2(6)
N(6)-C(23)-C(24)	110.0(6)
C(32)-C(23)-C(24)	110.6(5)
N(2)-C(6)-C(8)	112.8(6)
N(2)-C(6)-C(7)	109.9(6)
C(8)-C(6)-C(7)	110.9(6)
C(2)-N(8)-C(4)	114.2(6)
C(2)-N(8)-Cu(1)	117.4(5)
C(4)-N(8)-Cu(1)	107.4(4)
C(5)-N(3)-C(3)	113.6(6)
C(5)-N(3)-Cu(1)	105.3(4)
C(3)-N(3)-Cu(1)	112.6(5)
C(16)-N(9)-C(15)	113.8(6)
C(16)-N(9)-Cu(7)	117.3(5)
C(15)-N(9)-Cu(7)	107.7(4)
N(5)-C(24)-C(30)	113.7(6)
N(5)-C(24)-C(23)	108.9(5)
C(30)-C(24)-C(23)	109.6(6)
N(7)-C(14)-C(20)	115.0(6)
N(7)-C(14)-C(15)	108.1(6)
C(20)-C(14)-C(15)	110.2(6)
C(19)-C(20)-C(14)	113.7(7)
N(1)-C(7)-C(11)	114.0(6)
N(1)-C(7)-C(6)	109.1(5)
C(11)-C(7)-C(6)	109.4(6)
N(8)-C(4)-C(28)	112.7(6)
N(8)-C(4)-C(5)	109.5(6)
C(28)-C(4)-C(5)	112.5(6)
N(9)-C(15)-C(17)	112.7(6)
N(9)-C(15)-C(14)	108.8(6)
C(17)-C(15)-C(14)	112.0(6)
C(20)-C(19)-C(18)	110.7(7)

N(3)-C(5)-C(25)	114.4(6)
N(3)-C(5)-C(4)	108.4(6)
C(25)-C(5)-C(4)	110.4(6)
C(15)-C(17)-C(18)	111.6(6)
C(9)-C(10)-C(11)	110.5(7)
C(9)-C(8)-C(6)	112.2(6)
C(7)-C(11)-C(10)	110.5(6)
C(19)-C(18)-C(17)	109.5(6)
C(8)-C(9)-C(10)	110.8(7)
C(31)-C(32)-C(23)	112.2(6)
C(5)-C(25)-C(26)	113.0(7)
C(27)-C(26)-C(25)	110.8(7)
C(4)-C(28)-C(27)	112.1(6)
C(31)-C(29)-C(30)	110.4(7)
C(24)-C(30)-C(29)	110.5(6)
C(26)-C(27)-C(28)	109.3(6)
C(29)-C(31)-C(32)	111.2(7)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**. The anisotropic displacement factor exponent takes the form: $-2\sigma^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
I(1)	23(1)	14(1)	22(1)	-3(1)	0(1)	-6(1)
I(2)	37(1)	13(1)	24(1)	-3(1)	-6(1)	-5(1)
Cu(1)	21(1)	17(1)	21(1)	1(1)	-1(1)	0(1)
Cu(2)	25(1)	19(1)	19(1)	1(1)	-2(1)	0(1)
C(1)	9(3)	32(4)	35(4)	1(3)	3(3)	-6(3)
N(1)	22(3)	19(3)	21(3)	-7(3)	6(2)	-6(3)
N(2)	11(3)	18(3)	21(3)	-3(2)	2(2)	5(2)
I(4)	23(1)	14(1)	22(1)	3(1)	0(1)	-6(1)
I(3)	37(1)	13(1)	24(1)	3(1)	6(1)	-5(1)
Cu(5)	25(1)	20(1)	19(1)	-1(1)	2(1)	0(1)
Cu(7)	21(1)	17(1)	20(1)	-1(1)	1(1)	0(1)
N(6)	10(3)	17(3)	20(3)	4(2)	-2(2)	4(2)
N(5)	17(3)	24(3)	20(3)	8(3)	-5(2)	-6(3)
N(7)	16(3)	11(3)	23(3)	-1(2)	0(2)	-3(2)
C(23)	13(3)	15(3)	19(3)	0(3)	1(2)	-1(2)
C(6)	13(3)	17(3)	19(3)	-1(3)	-1(2)	-2(2)
N(8)	25(3)	16(3)	17(3)	-1(2)	5(2)	-10(3)
N(3)	14(3)	9(3)	25(3)	1(2)	0(2)	-2(2)
C(2)	24(4)	30(5)	37(5)	-4(4)	0(3)	5(3)
N(9)	24(3)	16(3)	19(3)	1(2)	-7(2)	-10(2)
C(16)	28(4)	36(6)	29(4)	5(4)	0(3)	3(4)
C(24)	7(3)	13(3)	28(4)	1(3)	-4(2)	-2(2)
C(14)	21(3)	8(3)	17(3)	3(2)	0(2)	0(2)
C(20)	33(4)	11(3)	27(4)	1(3)	0(3)	6(3)
C(7)	8(3)	12(3)	29(4)	1(3)	4(2)	0(2)
C(4)	18(3)	14(4)	22(4)	-1(3)	3(3)	-3(3)
C(12)	35(5)	38(5)	25(4)	-4(4)	14(3)	-6(4)
C(15)	23(4)	10(3)	20(4)	1(3)	-2(3)	-5(3)
C(21)	38(5)	44(5)	26(4)	7(4)	-16(4)	-13(4)
C(13)	25(4)	19(4)	29(4)	1(3)	-9(3)	-2(3)
C(19)	25(4)	13(4)	35(5)	-3(3)	9(3)	2(3)
C(22)	10(3)	30(4)	32(4)	-4(3)	-2(3)	-4(3)
C(5)	20(3)	7(3)	19(3)	-3(2)	-1(2)	0(2)

C(3)	22(3)	18(3)	31(4)	1(3)	8(3)	-1(3)
C(17)	18(4)	16(4)	41(5)	-5(3)	-5(3)	3(3)
C(10)	23(4)	28(4)	39(5)	0(4)	-10(3)	8(3)
C(8)	17(3)	26(4)	20(3)	-2(3)	5(3)	6(3)
C(11)	11(3)	17(4)	42(5)	-4(3)	0(3)	4(3)
C(18)	21(4)	13(3)	52(5)	0(3)	6(3)	6(3)
C(9)	28(4)	29(5)	36(5)	3(4)	-3(3)	2(3)
C(32)	12(3)	26(4)	22(3)	3(3)	-5(2)	5(3)
C(25)	37(4)	12(3)	24(4)	1(3)	1(3)	2(3)
C(26)	24(4)	16(4)	37(5)	5(3)	-10(3)	1(3)
C(28)	17(4)	18(4)	43(5)	5(3)	6(3)	2(3)
C(29)	19(3)	28(4)	44(5)	-1(4)	13(3)	5(3)
C(30)	12(3)	18(4)	40(4)	5(3)	-1(3)	4(3)
C(27)	20(4)	16(4)	52(5)	1(4)	-7(3)	6(3)
C(31)	27(4)	28(4)	35(4)	-7(3)	4(3)	2(3)

Table S5. Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **6**.

	x	y	z	U(eq)
H(1A)	3318	1478	1866	37
H(1B)	2681	3426	1941	37
H(1C)	3413	2288	2267	37
H(99)	7420(110)	1290(40)	1420(30)	31
H(23)	-1087	13057	6998	19
H(6)	6089	884	1999	20
H(2A)	1698	8727	1521	45
H(2B)	1391	6712	1626	45
H(2C)	22	7842	1438	45
H(16A)	3332	5203	6522	46
H(16B)	3578	7224	6630	46
H(16C)	4986	6149	6444	46
H(24)	-3224	10156	6899	19
H(14)	2943	7273	5379	18
H(20A)	2716	3626	5196	29
H(20B)	2530	5227	4917	29
H(7)	8225	3788	1900	20
H(4)	1689	9545	875	21
H(12A)	9143	4294	1280	49
H(12B)	8561	3015	961	49
H(12C)	9805	2325	1256	49
H(15)	3315	4384	5876	21
H(21A)	-4164	9643	6291	54
H(21B)	-3533	10824	5961	54
H(21C)	-4793	11614	6241	54
H(13A)	231	7907	5200	36
H(13B)	-1180	6731	5357	36
H(13C)	-26	5945	5053	36
H(19A)	5216	5924	4976	29
H(19B)	5049	3899	4861	29
H(22A)	1687	12453	6866	36
H(22B)	2314	10509	6950	36

H(22C)	1562	11673	7269	36
H(5)	2062	6672	376	18
H(3A)	4766	6046	197	35
H(3B)	6180	7206	358	35
H(3C)	5037	8011	54	35
H(17A)	5992	5129	5929	30
H(17B)	5788	6690	5641	30
H(10A)	10386	728	2454	36
H(10B)	9869	2753	2429	36
H(8A)	6891	3511	2529	26
H(8B)	5692	1915	2595	26
H(11A)	10213	1593	1831	28
H(11B)	8938	86	1913	28
H(18A)	6916	4215	5344	35
H(18B)	5466	3003	5470	35
H(9A)	7750	-135	2558	37
H(9B)	8225	1322	2854	37
H(32A)	-1898	10434	7529	24
H(32B)	-697	12027	7597	24
H(25A)	2489	8735	-81	29
H(25B)	2289	10325	200	29
H(26A)	-58	10024	-140	31
H(26B)	-211	8002	-22	31
H(59A)	-976	8830	931	31
H(62B)	-795	7256	644	31
H(29A)	-5381	13234	7454	36
H(29B)	-4874	11205	7431	36
H(30A)	-5216	12350	6830	28
H(30B)	-3943	13861	6911	28
H(27A)	-1924	9709	342	35
H(27B)	-483	10939	467	35
H(31A)	-3228	12634	7853	36
H(31B)	-2752	14083	7556	36
H(61)	1210(80)	6280(110)	1030(19)	0(17)
H(65)	5120(80)	4350(100)	2045(19)	0(16)
H(66)	-160(80)	9740(100)	7062(19)	0(16)
H(67)	3760(90)	7740(110)	6030(20)	4(18)
H(64)	4260(100)	8890(120)	610(20)	10(20)

H(68)

640(90)

5100(120)

5610(20)

6(18)

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