Supporting Information for

Cu(I) Amido Complexes in the Ullmann Reaction. Reactions of Cu(I)-Amido Complexes with Iodoarenes with and without Autocatalysis by CuI

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Contents

1. General Information

All manipulations were carried out under an inert atmosphere using an argon-filled glovebox. All glassware was oven dried immediately prior to use. Tetrahydrofuran and diethyl ether were obtained as HPLC grade without inhibitors; pentane and toluene were obtained as ACS reagent grade. All protio solvents were degassed by purging with nitrogen for 45 min and dried with a solvent purification system containing a 1 m column of activated alumina. DMSO and DMSO-d_6 were stirred over CaH_2 for 24 h and then distilled and stored over activated 4 Å molecular sieves. CuI was dried under high vacuum at 300 °C for 24 h. Copper *t*-butoxide ($[CuO\textit{t}Bu]_4$),[1] 2-methyl-*N*,*N*-diphenylaniline (**8**),[2] *o*-allyloxyiodobenzene (**9**)[3], 3-methyl-2,3-dihydrobenzofuran (**12**),[4] [bis(1,10-phenanthroline)Cu][bis(phenoxide)Cu],[5] (phthalimidato)Cu(1,10-phenanthroline),[6] [bis(1,10-phenanthroline)Cu][bis(pyrrolidinone)Cu],[6] $[(pyrrolidinato)Cu]_4$[7] and $[phenCuI]_2$[8] were prepared using the reported procedures. $LiNPh_2$ and $KNPh_2$ were prepared by reaction of $HNPh_2$ with lithium hexamethyldisilamide (LiHMDS) or potassium hexamethyldisilamide (KHMDS) in toluene at room temperature. After stirring for 1 h, the product was separated from the supernatant by filtration through a fine fritted funnel, successively washed with toluene and pentane, and dried under vacuum to afford the corresponding salts. All other reagents and solvents were obtained from commercial sources and used without further purification.

Proton nuclear magnetic resonance spectra (^1H NMR) were recorded at 400 or 500 MHz at 20 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (benzene, δ 7.15; dimethylsulfoxide, δ 2.54). Proton-decoupled carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 100 or 126 MHz at 20 °C, unless otherwise noted. Chemical shifts are expressed in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (benzene, δ 128.6; dimethylsulfoxide, δ 40.5). Elemental analyses were obtained at the University of Illinois Urbana-Champaign Microanalysis Laboratory. Single crystal X-ray analysis was carried out at the X-ray facility at the University of Illinois Urbana-Champaign. High resolution mass spectra (HRMS) were obtained at the University of Illinois Urbana-Champaign.

2. Preparation of Cu(I)-Diphenylamido Complexes 1-5 and Compound 10

Preparation of [bis(1,10-phenanthroline)Cu][bis(diphenylamido)Cu] (1).

A solution of 1,10-phenanthroline (180 mg, 1.00 mmol) in 2 mL of THF was added to a solution of CuO*t*Bu (137 mg, 1.00 mmol) in 6 mL of THF at room temperature. The resulting reddish brown solution was stirred for 5 min. To this mixture was added a solution of $HNPh_2$ (169 mg, 1.00 mmol) in 2 mL of THF. After stirring the resulting solution at room temperature for 1 h, pentane was added to precipitate the product. The product was separated by filtration through a fine fritted funnel, washed with pentane and dried under vacuum to afford 400 mg (97%) of **1** as a reddish brown powder. ^1H NMR (500 MHz, DMSO-*d*$_6$) δ 6.36 (t, *J* = 7.0 Hz, 4H), 6.91 (t, *J* = 7.0 Hz, 8H), 7.01 (d, *J* = 8.0 Hz, 8H), 7.99-8.02 (m, 4H), 8.28 (s, 4H), 8.83 (d, *J* = 8.0 Hz, 4H), 9.00 (d, *J* = 4.5 Hz, 4H); $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-*d*$_6$) δ 115.8, 120.6, 126.7, 128.0, 129.4, 129.9, 138.2, 144.1, 150.4, 156.5; Anal. Calcd for $C_{48}H_{36}Cu_2N_6$: C, 69.97; H, 4.40; N, 10.20. Found: C, 70.19; H, 4.65; N, 10.45; Conductivity (25 ºC, 1.0 mM in DMSO) : 16.9 Ωcm^2mol^{-1}; (25 ºC, 1.0 mM in THF) : 13.7 Ωcm^2mol^{-1}. Single crystals suitable for X-ray diffraction were obtained by allowing pentane to diffuse into a solution of **1** in THF.

Preparation of [tris(1,10-phenanthroline)Li][bis(diphenylamido)Cu] (2).

Method A: A solution of 1,10-phenanthroline (270 mg, 1.50 mmol) in 2 mL of THF was added to a solution of $LiNPh_2$ (87.5 mg, 0.500 mmol) in 3 mL of THF at room temperature. The resulting reddish brown solution was stirred for 10 min. To this mixture was added a solution of $HNPh_2$ (84.6 mg, 0.500 mmol) in 1 mL of THF, followed by a solution of CuO*t*Bu (68.4 mg, 0.500 mmol) in 2 mL of THF. Partial precipitation of a golden yellow product occurred immediately. After stirring the resulting yellow suspension at room temperature for 1 h, pentane was added to precipitate the remaining product. The product was separated by filtration through a fine fritted funnel, successively washed with toluene and pentane, and dried under vacuum to afford 450 mg (95%) of **2**. ^1H NMR (500 MHz, DMSO-*d*$_6$) δ 6.43 (t, *J* = 7.0 Hz, 4H), 6.98 (t, *J* = 8.0 Hz, 8H), 7.08 (d, *J* = 7.5 Hz, 8H), 7.81-7.83 (m, 6H), 8.04 (s, 6H), 8.54 (d, *J* = 8.0 Hz, 6H), 9.14 (d, *J* = 4.0 Hz, 6H); $^{13}C\{^1H\}$ NMR (126 MHz, DMSO-*d*$_6$) δ 116.0, 120.7, 124.4, 127.7, 129.5, 129.6, 137.3, 146.5, 150.9, 156.7; Anal. Calcd for $C_{60}H_{44}CuLiN_8$: C, 76.05; H, 4.68; N, 11.83. Found: C, 75.82; H, 4.63; N, 11.46.

Method B: A solution of 1,10-phenanthroline (64.2 mg, 0.357 mmol) in 1 mL of THF was added to a solution of complex **1** (73.5 mg, 0.0890 mmol) in 2 mL of THF at room temperature followed by the addition of a solution of $LiNPh_2$ (31.2 mg, 0.178 mmol) in 1 mL of THF. Partial precipitation of a golden yellow product occurred immediately. After stirring the resulting yellow suspension at room temperature for 1 h, pentane was added to precipitate the remaining product. The product was separated by filtration through a fine fritted funnel, successively washed with toluene and pentane, and dried under vacuum to afford 156 mg (92%) of **2**.

Preparation of [tris(1,10-phenanthroline)K][bis(diphenylamido)Cu] (3).

Method A: A solution of 1,10-phenanthroline (54.0 mg, 0.300 mmol) in 1 mL of THF was added to a solution of $KNPh_2$ (20.7 mg, 0.100 mmol) in 1 mL of THF at room temperature. The resulting reddish brown solution was stirred for 10 min. To this mixture was added a solution of $HNPh_2$ (16.9 mg, 0.100 mmol) in 1 mL of THF, followed by a solution of CuO*t*Bu (13.7 mg, 0.100 mmol) in 1 mL of THF. After stirring the resulting orange-yellow solution at room temperature for 1 h, pentane was added to precipitate the product. The product was separated by filtration through a fine fritted funnel, washed with pentane and dried under vacuum to afford 80 mg (83%) of **3** as an orange-yellow powder. Single crystals suitable for X-ray diffraction were obtained by allowing pentane to diffuse into a solution of **3** in THF. ^{1}H NMR (500 MHz, DMSO-d_6) δ 6.43 (t, *J* = 7.0 Hz, 4H), 6.99 (t, *J* = 7.0 Hz, 8H), 7.09 (d, *J* = 8.5 Hz, 8H), 7.80-7.83 (m, 6H), 8.04 (s, 6H), 8.53 (d, *J* = 8.0 Hz, 6H), 9.15 (dd, *J* = 4.0, 1.0 Hz, 6H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 115.9, 120.7, 124.3, 127.7, 129.4, 129.5, 137.2, 146.5, 150.9, 156.6; Anal. Calcd for $C_{60}H_{44}CuKN_8$: C, 73.56; H, 4.53; N, 11.44. Found: C, 73.29; H, 4.50; N, 11.31.

Method B: A solution of 1,10-phenanthroline (64.2 mg, 0.337 mmol) in 1 mL of THF was added to a solution of complex **1** (73.5 mg, 0.0890 mmol) in 2 mL of THF at room temperature, followed by a solution of $KNPh_2$ (36.8 mg, 0.178 mmol) in 1 mL of THF. After stirring the resulting orange-yellow solution at room temperature for 1 h, pentane was added to precipitate the product. The product was separated by filtration through a fine fritted funnel, washed with pentane and dried under vacuum to afford 153 mg (88%) of **3** as an orange-yellow powder.

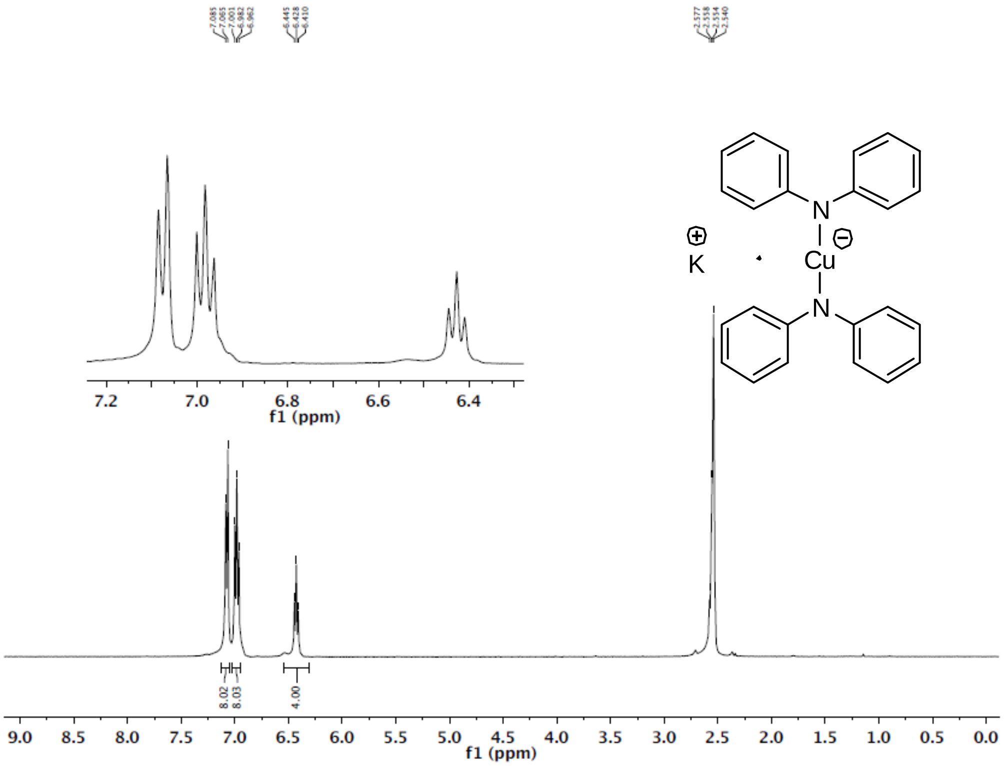
Preparation of [(18-crown-6)K][bis(diphenylamido)Cu] (4).

A solution of 18-crown-6 (132 mg, 0.500 mmol) in 1 mL of THF was added to a solution of $KNPh_2$ (104 mg, 0.500 mmol) in 2 mL of THF at room temperature. The resulting colorless solution was stirred for 10 min. To this solution was added a solution of $HNPh_2$ (85.6 mg, 0.500 mmol) in 1 mL of THF followed by a solution of CuO*t*Bu (68.5 mg, 0.500 mmol) in 1 mL of THF. After stirring the resulting solution at room temperature for 1 h, pentane was added to precipitate the product as a white powder. The product was separated by filtration through a fine fritted funnel, washed with pentane and dried under vacuum to afford 320 mg (91%) of **4**. ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.58 (s, 24H), 6.43 (t, J = 7.0 Hz, 4H), 6.98 (t, J = 7.0 Hz, 8H), 7.07 (d, J = 8.0 Hz, 8H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 70.4, 115.9, 120.6, 129.4, 156.6; Anal. Calcd for $C_{36}H_{44}CuKN_2O_6$: C, 61.47; H, 6.31; N, 3.98. Found: C, 61.52; H, 6.32; N, 4.07.

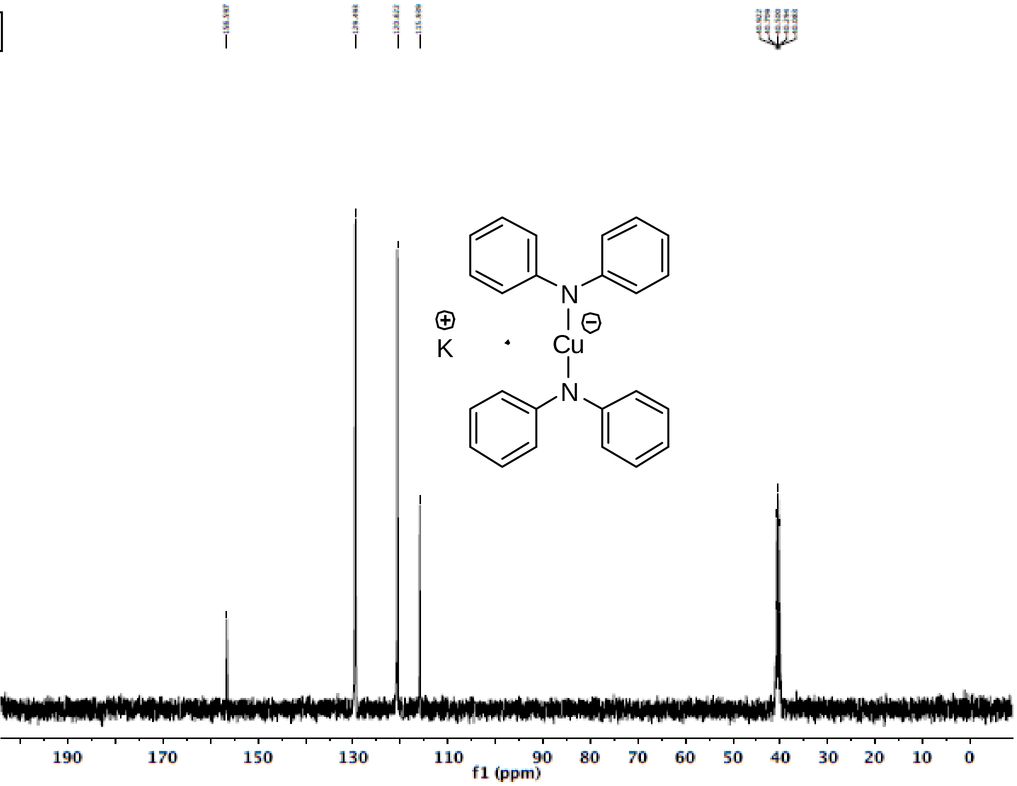
Preparation of [K][bis(diphenylamido)Cu] (5).

In a 20 mL glass scintillation vial, a solution of CuOtBu (68.5 mg, 0.500 mmol) in 1 mL of THF was added to a solution of $KNPh_2$ (104 mg, 0.500 mmol) and $HNPh_2$ (84.6 mg, 0.500 mmol) in 2 mL of THF at room temperature. After stirring the resulting solution at room temperature for 1 h, THF was removed under vacuum. The remaining sticky white solid was suspended in pentane (2 mL) and rubbed with a spatula against the wall of the vial until a white powder was formed, which was separated by filtration through a fine fritted funnel and washed with diethyl ether (1 mL × 5). The white powder was then suspended in toluene (2 mL) and stirred at room temperature for 1 h. The toluene was removed by filtration through a fine fritted funnel. The remaining white residue was further washed with toluene (2 mL × 5) and pentane (2 mL × 5) and dried under vacuum to afford 168 mg (76%) of **5** as a white powder. ^{1}H NMR (400 MHz, DMSO-d_6) δ 6.43 (t, J = 7.2 Hz, 4H), 6.98 (t, J = 7.2 Hz, 8H), 7.07 (d, J = 8.0 Hz, 8H); ^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6) δ 115.9, 120.6, 129.5, 156.6; Anal. Calcd for $C_{24}H_{20}CuKN_2$: C, 65.65; H, 4.59; N, 6.38. Found: C, 66.41; H, 4.76; N, 6.42.

^{1}H NMR



^{13}C NMR



Preparation of 2-(allyloxy)-N,N-diphenylaniline (10).

Diphenylamine (169 mg, 1.00 mmol), *o*-allyloxyiodobenzene (520 mg, 2.00 mmol), CuI (190 mg, 1.00 mmol) and K_3PO_4 (636 mg, 3.00 mmol) were placed in a glass reaction vessel equipped with a vacuum adaptor. The mixture was suspended in 5 mL of toluene and heated at 130 °C for 36 h. The reaction mixture was filtered through Celite, and the solvent in the filtrate was removed under vacuum. The product **10** was purified by silica gel column chromatography with 2% ethyl acetate in hexanes as eluent to yield 270 mg (90%) of **10** as a colorless liquid. ^1H NMR (500 MHz, C_6D_6) δ 3.98-4.00 (m, 2H), 4.86 (dd, *J* = 10.5, 2.0 Hz, 1H), 4.93 (dd, *J* = 17.0, 1.5 Hz, 1H), 5.40-5.48 (m, 1H), 6.64 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.76 (dt, *J* = 7.5, 1.0 Hz, 1H), 6.80 (t, *J* = 7.5 Hz, 2H), 6.96 (dt, *J* = 7.5, 1.5 Hz, 1H), 7.04 (t, *J* = 8.5 Hz, 4H), 7.11-7.15 (m, 5H); $^{13}C\{^1H\}$ NMR (126 MHz, C_6D_6) δ 69.5, 115.3, 116.9, 122.4, 122.6, 122.9, 127.1, 129.8, 131.0, 133.8, 137.1, 149.0, 155.8; HRMS (ES-TOF) Calcd for $C_{21}H_{20}NO$ (MH^+) 302.1545, found 302.1537.

3. Reactivity Studies

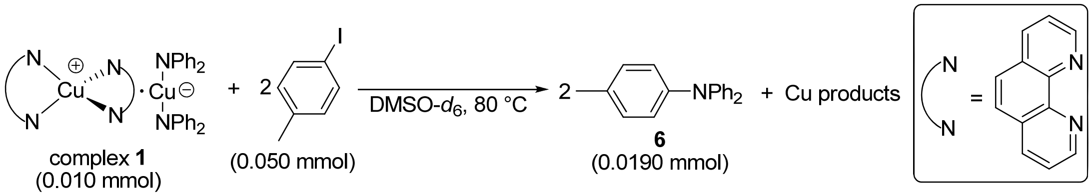
Preparation of stock solution

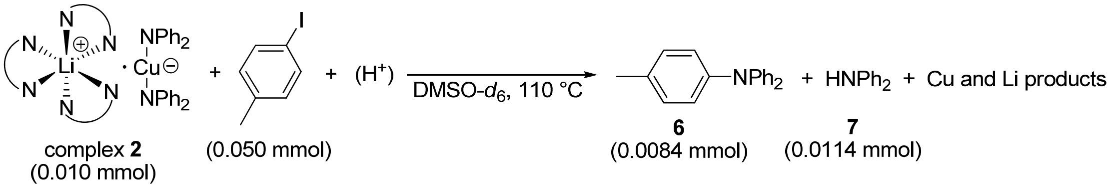
Internal standard (0.050 M): A stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was prepared by dissolving 9.5 mg of 1,4-di-*tert*-butylbenzene in DMSO-d_6 or DMSO and diluting to 1.0 mL in a volumetric flask.

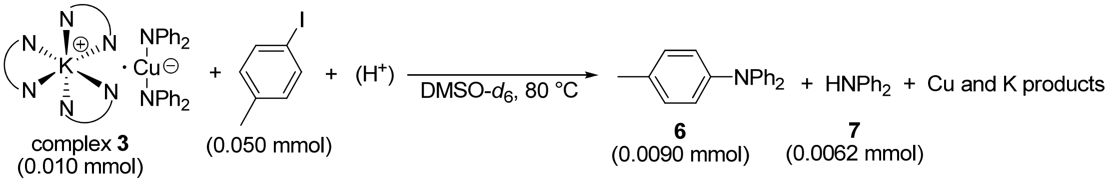
Procedure for the reactions of complexes 1-3 with p-iodotoluene.

Complexes **1**-**3** (0.010 mmol) were weighed into glass vials. In separate vials, *p*-iodotoluene (10.9 mg, 0.050 mmol) was dissolved in 1 mL DMSO-d_6 in each vial, and the solutions were added to the vials containing the complexes **1**-**3**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene in DMSO-d_6 was added to the vials. The reaction mixtures were then transferred to NMR tubes fused to J-Young valves, tightly capped, and initial ^1H NMR spectra were acquired. The reaction mixtures were heated in an oil-bath at 80 °C (complexes **1** and **3**) or 110 °C (complex **2**). The reactions were monitored by ^1H NMR every 30 min until the complexes reacted completely (1-3 h). After the reaction was complete, the reaction mixtures were then analyzed by GC to calculate the percentage yield of the product. The yields of the arylated product **6** were calculated to be 95%, 84% and 90% for complexes **1**, **2** and **3**, respectively. Molar ratios of amine **7** formed relative to the starting complexes were 1.14 and 0.62 for complexes **2** and **3**, respectively.

*Balanced chemical equations for the reactions of complexes **1-3** with p-iodotoluene*



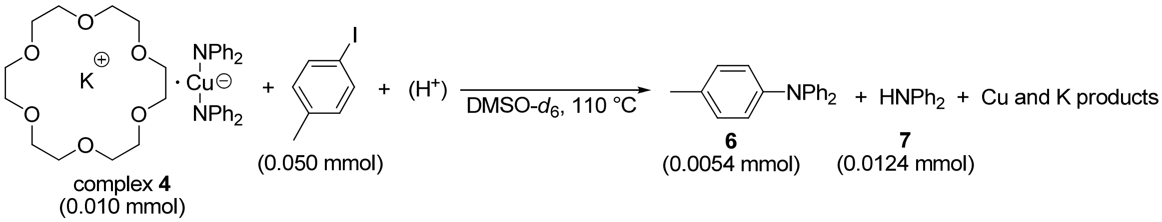


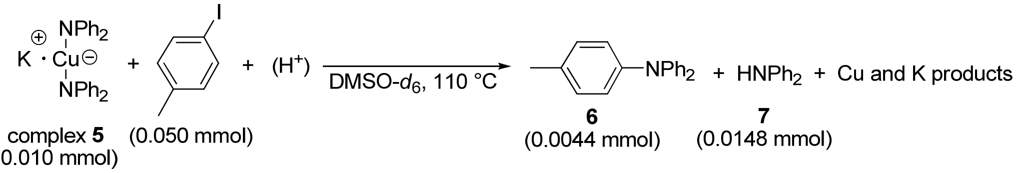


Procedure for the reactions of complexes 4 and 5 with p-iodotoluene.

Complexes **4** and **5** (0.010 mmol) were weighed into two glass vials. In two separate vials, *p*-iodotoluene (10.9 mg, 0.050 mmol) was dissolved in 1 mL of DMSO-d_6 and the solutions were added to the vials containing the complexes **4** and **5**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene in DMSO-d_6 was added to each vial, and the reaction mixtures were then heated at 110 °C. The reactions were monitored by GC until the complexes reacted completely (3 h). The yields of the arylated product **6** were calculated to be 54% and 44% for complexes **4** and **5**, respectively. Molar ratios of amine **7** formed relative to the starting complexes were 1.24 and 1.48 for complexes **4** and **5**, respectively.

*Balanced chemical equations for the reactions of complexes **4** and **5** with p-iodotoluene*





Procedure for the reactions of complexes 4 and 5 with p-iodotoluene in presence of 1,10-phenanthroline.

Complexes **4** and **5** (0.010 mmol) were weighed into two glass vials. In two separate vials, *p*-iodotoluene (10.9 mg, 0.050 mmol) and 1,10-phenanthroline (1.8 mg, 0.010 mmol) were dissolved in 1 mL of DMSO, and the solutions were added to the vials containing the complexes **4** and **5**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene in DMSO was added to each vial, and the reaction mixtures were then heated at 80 °C. The reactions were monitored by GC until the complexes reacted completely (2.5 h for **4**; 3 h for **5**). The yields of the arylated product **6** were calculated to be 100% and 56% for complexes **4** and **5**, respectively. Molar ratios of amine **7** formed relative to the starting complexes were 0.80 and 1.24 for complexes **4** and **5**, respectively.

Procedure for the attempted reactions of [(pyrrolidinato)Cu]$_4$ with iodobenzene in the absence and presence of 1,10-phenanthroline.

[(Pyrrolidinonato)Cu]$_4$ (5.4 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, iodobenzene (20.3 mg, 0.10 mmol) was dissolved in 1 mL of DMSO, and the solution was added to the vial containing the complex. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene in DMSO was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC and GC/mass spectrometry, and no *N*-phenyl pyrrolidine was observed.

A similar reaction of [(pyrrolidinonato)Cu]$_4$ (5.4 mg, 0.010 mmol) with iodobenzene (20.3 mg, 0.10 mmol) was also conducted in the presence of 1,10-phenanthroline (7.2 mg, 0.040 mmol) at 80 °C for 3 h. The reaction mixture was analyzed by GC and GC/mass spectrometry, and no *N*-phenyl pyrrolidine was observed.

4. Competition Studies

Preparation of stock solution

Internal standard (0.050 M): A stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was prepared by dissolving 9.5 mg of 1,4-di-*tert*-butylbenzene in DMSO and diluting to 1.0 mL in a volumetric flask.

Procedure for the competition reaction of complex 1 with o-iodotoluene and p-iodotoluene.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol) and *p*-iodotoluene (43.6 mg, 0.200 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **1**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C. An aliquot (100 μL) of the reaction mixture was taken at 2 min for GC analysis and, thereafter, the reaction was heated for 3 h. The reaction mixtures were analyzed by GC, and the combined yields of the arylated products **6** and **8** were calculated to be 11% and 85% for 2 min and 3 h reactions, respectively. The ratios of **6** to **8** were found to be 86:14 and 66:34 for 2 min and 3 h reactions, respectively.

Procedure for the competition reaction of complex 1 with o-iodotoluene and p-iodotoluene in presence of CuI.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (1.9 mg, 0.010 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **1**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 30 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 72%. The ratio of **6** to **8** was found to be 51:49.

Procedure for the competition reaction of complex 1 with o-iodotoluene and p-iodotoluene in presence of 1,10-phenanthroline.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and 1,10-phenanthroline (1.8 mg, 0.010 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **1**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 4 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 72%. The ratio of **6** to **8** was found to be 80:20.

Procedure for the competition reaction of complex 2 with o-iodotoluene and p-iodotoluene.

Complex **2** (9.5 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol) and *p*-iodotoluene (43.6 mg, 0.200 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **2**. 100 μL of the 0.050 M stock solution of

1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 100 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 82%. The ratio of **6** to **8** was found to be 85:15.

Procedure for the competition reaction of complex 2 with o-iodotoluene and p-iodotoluene in presence of CuI.

Complex **2** (9.5 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (7.6 mg, 0.040 mmol) were dissolved in 500 µL of DMSO, and the resulting solution was added to the vial containing **2**. 100 µL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 77% for the transformation of both amido groups in **2** in the presence of added CuI. The ratio of **6** to **8** was found to be 57:43.

Procedure for the competition reaction of complex 3 with o-iodotoluene and p-iodotoluene.

Complex **3** (9.8 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol) and *p*-iodotoluene (43.6 mg, 0.200 mmol) were dissolved in 500 µL of DMSO, and the resulting solution was added to the vial containing **3**. 100 µL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 92%. The ratio of **6** to **8** was found to be 90:10.

Procedure for the competition reaction of complex 3 with o-iodotoluene and p-iodotoluene in presence of CuI.

Complex **3** (9.8 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (7.6 mg, 0.040 mmol) were dissolved in 500 µL of DMSO, and the resulting solution was added to the vial containing **3**. 100 µL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 87% for the transformation of both amido groups in **3** in the presence of added CuI. The ratio of **6** to **8** was found to be 57:43.

Procedure for the competition reaction of complex 4 with o-iodotoluene and p-iodotoluene in presence of CuI.

Complex **4** (7.0 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (1.9 mg, 0.010 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **4**. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 89% for the transformation of both amido groups in **4** in the presence of added CuI. The ratio of **6** to **8** was found to be 53:47.

Procedure for the competition reaction of complex 5 with o-iodotoluene and p-iodotoluene in presence of CuI.

Complex **5** (4.4 mg, 0.010 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (1.9 mg, 0.010 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing **5**. 100 μL of the 0.05 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 80% for the transformation of both amido groups in **5** in the presence of added CuI. The ratio of **6** to **8** was found to be 53:47.

Procedure for the competition reaction of $KNPh_2$ with o-iodotoluene and p-iodotoluene in presence of stoichiometric amounts of CuI.

$KNPh_2$ (4.1 mg, 0.020 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol) and CuI (3.8 mg, 0.020 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing $KNPh_2$. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture was then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 54%. The ratio of **6** to **8** was found to be 53:47.

Procedure for the competition reaction of $KNPh_2$ with o-iodotoluene and p-iodotoluene in presence of stoichiometric amounts of CuI and 1,10-phenanthroline.

$KNPh_2$ (4.1 mg, 0.020 mmol) was weighed into a glass vial. In a separate vial, *o*-iodotoluene (43.6 mg, 0.200 mmol), *p*-iodotoluene (43.6 mg, 0.200 mmol), CuI (3.8 mg, 0.020 mmol) and 1,10-phenanthroline (3.6 mg, 0.020 mmol, 1 equiv, or; 10.8 mg, 0.060 mmol, 3 equiv) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing $KNPh_2$. 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the vial, and the reaction mixture then heated at 80 °C for 3 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 50% and 54% for the reactions with 1 equiv and 3 equiv of 1,10-phenanthroline, respectively. The ratio of **6** to **8** was found to be 80:20 and 82:18 for the reactions with 1 equiv and 3 equiv of 1,10-phenanthroline, respectively.

Procedure for the competition reaction of $HNPh_2$ with o-iodotoluene and p-iodotoluene catalyzed by CuI and 1,10-phenanthroline in presence of K_3PO_4 as a base.

$HNPh_2$ (16.9 mg, 0.100 mmol), 1,10-phenanthroline (1.8 mg, 0.010 mmol), K_3PO_4 (42.4 mg, 0.200 mmol) and 1,4-di-*tert*-butylbenzene (4.8 mg, 0.025 mmol) as an internal standard were placed in a glass vial. In a separate vial, *o*-iodotoluene (218 mg, 1.00 mmol), *p*-iodotoluene (218 mg, 1.00 mmol) and CuI (1.9 mg, 0.010 mmol) were dissolved in 500 μL of DMSO, and the resulting solution was added to the vial containing $HNPh_2$. The reaction mixture was then heated at 80 °C for 24 h. The reaction mixture was analyzed by GC, and the combined yield of the arylated products **6** and **8** was calculated to be 65%. The ratio of **6** to **8** was found to be 81:19.

5. Test for Aryl Radical Intermediates

Procedure for the reaction of complex 1 with o-allyloxyiodobenzene in absence of 1,10-phenanthroline.

Complex **1** (8.2 mg, 0.010 mmol), *o*-allyloxyiodobenzene (7.8 mg, 0.030 mmol) and 1,4-di-*tert*-butylbenzene (3.8 mg, 0.020 mmol) as an internal standard were placed in a 1.0 mL volumetric flask. The reaction mixture was dissolved with DMSO-d_6 and diluted to 1 mL (the final concentration of the complex **1** in the reaction mixture is 0.010 M, which is equivalent to 0.020 M concentration of the amido groups in the complex). The resulting solution was then transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 120 °C for 0.5 h. The reaction mixture was analyzed by GC by injecting 1.0 μL of the reaction mixture and GC/mass spectrometry by injecting 0.2 μL of the reaction mixture. The yield of the arylated product **10** was calculated to be 60% (0.012 M) by GC calibration. Comparison of the retention times of GC traces and GC/mass spectra to those of an authentic sample of 3-methyl-2,3-dihydrobenzofuran (**12**)[4] showed that the sample contained no detectable amount of this material. The detection limits for 3-methyl-2,3-dihydrobenzofuran (**12**) were determined to be 10 μM and 20 μM by GC and GC/mass spectrometry, respectively (*vide infra*). These detection limits correspond to 0.08% and 0.17% of the amount of **10** (60% yield, 0.012 M) formed in the present reaction.

*Determination of detection limits for 3-methyl-2,3-dihydrobenzofuran (**12**) by GC and GC/mass spectrometry*: A stock solution of 3-methyl-2,3-dihydrobenzofuran (**12**) was prepared by dissolving 6.7 mg of 3-methyl-2,3-dihydrobenzofuran (**12**) in ethyl acetate in a 5.0 mL volumetric flask and diluting to 5.0 mL (0.010 M, stock solution A). 100 μL of the stock solution A was diluted with ethyl acetate to 1.0 mL in a 1.0 mL volumetric flask (0.0010 M, stock solution B). Five different final concentrations of 3-methyl-2,3-dihydrobenzofuran (**12**), viz. 2000 μM, 200 μM, 20 μM, 10 μM, 2 μM, were prepared from stock solutions A and B in five GC vials, and analyzed by GC by injecting 1.0 μL of the reaction mixture and GC/mass spectrometry by injecting 0.2 μL of the reaction mixture. The lowest concentrations of 3-methyl-2,3-dihydrobenzofuran (**12**) detected by GC and GC/mass spectrometry were 10 μM and 20 μM, respectively.

Procedure for the reaction of complex 1 with o-allyloxyiodobenzene in presence of 1,10-phenanthroline.

Complex **1** (8.2 mg, 0.010 mmol), *o*-allyloxyiodobenzene (7.8 mg, 0.030 mmol), 1,10-phenanthroline (1.8 mg, 0.010 mmol) and 1,4-di-*tert*-butylbenzene (3.8 mg, 0.020 mmol) as an internal standard were placed in a volumetric flask. The reaction mixture was dissolved with DMSO-d_6 and diluted to 1 mL (the final concentration of the complex **1** in the reaction mixture is 0.010 M, which is equivalent to 0.020 M concentration of the amido groups in the complex). The resulting solution was then transferred to a glass vial, and the sample was then heated at 120 °C for 6 h. The reaction mixture was analyzed by GC by injecting 1.0 μL of the reaction mixture and GC/mass spectrometry by injecting 0.2 μL of the reaction mixture. The yield of the arylated product **10** was calculated to be 16% (0.0032 M) by GC calibration. Comparison of the retention times of GC traces and GC/mass spectra to those of an authentic sample of 3-methyl-2,3-dihydrobenzofuran (**12**) showed that the sample contained no detectable amount of this material.

6. Kinetic Studies

Preparation of stock solutions

p-Iodotoluene (1.00 M): A stock solution of *p*-iodotoluene was prepared by dissolving 218 mg of *p*-iodotoluene in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

Internal standard (0.050 M): A stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was prepared by dissolving 9.5 mg of 1,4-di-*tert*-butylbenzene in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

1,10-Phenanthroline (0.10 M): A stock solution of 1,10-phenanthroline was prepared by dissolving 18 mg of 1,10-phenanthroline in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

CuI (0.10 M): A 0.10 M stock solution of CuI was prepared by dissolving 19 mg of CuI in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

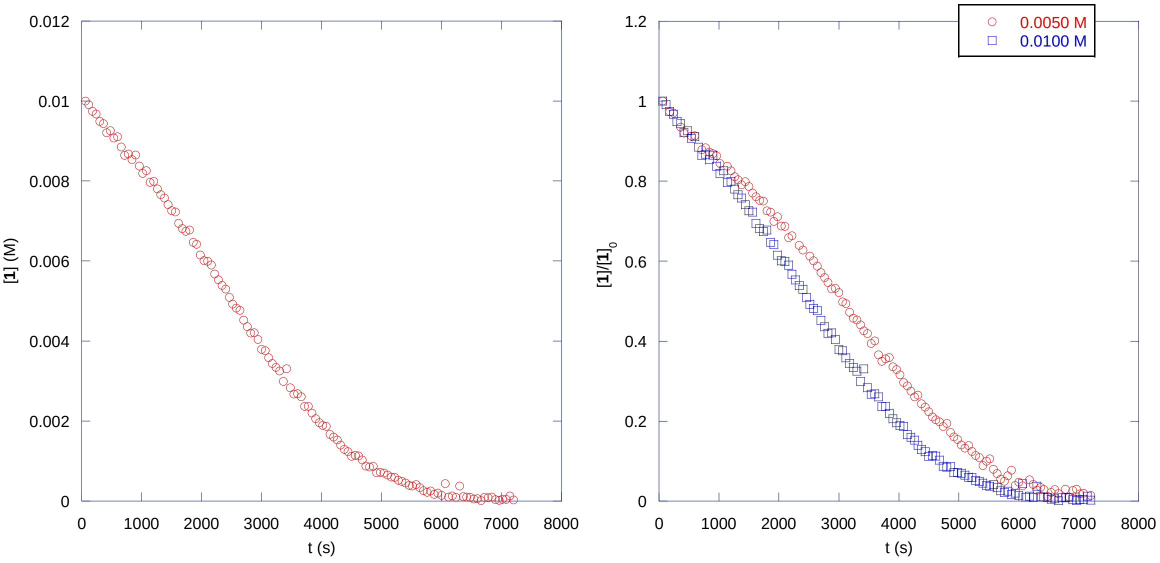
CuI (0.20 M): A 0.20 M stock solution of CuI was prepared by dissolving 38 mg of CuI in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

$[\text{phenCuI}]_2$ (0.0250 M): A stock solution of $[\text{phenCuI}]_2$ was prepared by dissolving 18.5 mg of $[\text{phenCuI}]_2$ in DMSO-d_6 and diluting the solution to 1.0 mL in a volumetric flask.

Monitoring the reaction of complex 1 with p-iodotoluene by ^{1}H NMR spectroscopy

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 200 μL of the 1.0 M stock solution of *p*-iodotoluene and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 60 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 60 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 80%.

The same reaction was conducted but with a half of the amount of complex **1** (4.1 mg, 0.0050 mmol) and the same amount of *p*-iodotoluene (0.20 M). After measurement of the reaction progress by NMR spectroscopy, the reaction mixture was analyzed by GC, and the yield of the arylated product **6** was calculated to be 58%.

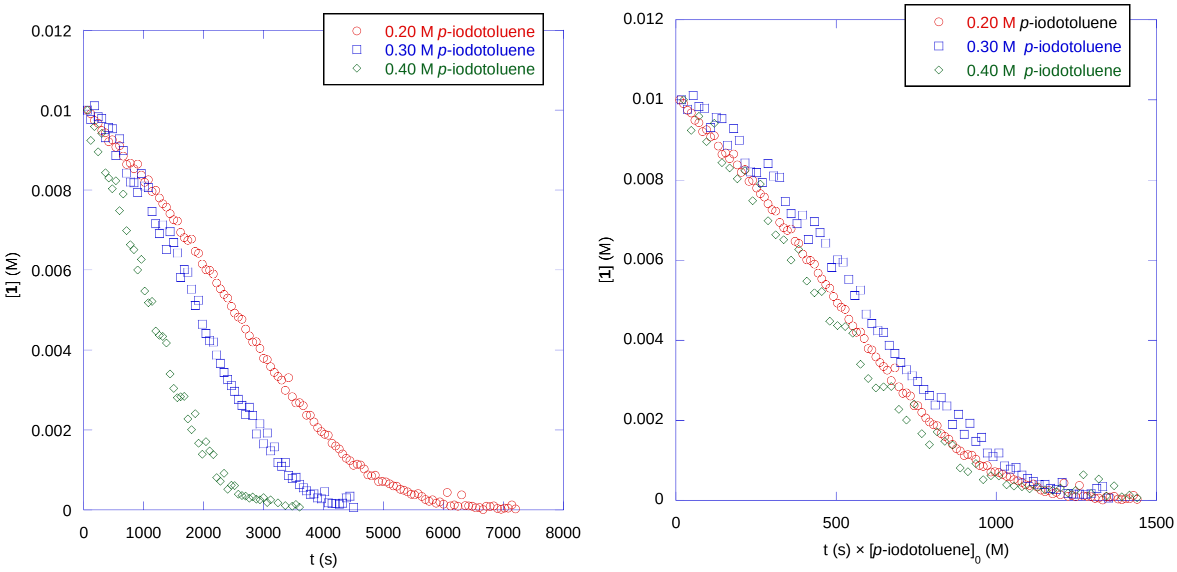


(a) (b)

Figure S1. (a) Plot of the decay of **1** from the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.20 M) in DMSO-d_6 at 60 °C. (b) Plot of normalized concentrations of the complex **1** ([**1**]/[**1**]$_0$) versus time (t) for the reaction of complex **1** (0.0050 M and 0.010 M) with *p*-iodotoluene (0.20 M) in DMSO-d_6 at 60 °C.

Determination of the dependence of rate of reaction on the concentration of p-iodotoluene for the reaction of complex 1 with p-iodotoluene.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 200-400 μL of the 1.0 M stock solution of *p*-iodotoluene and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 60 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 60 °C. The reaction mixture was then analyzed by GC, and the yields of the arylated product **6** was calculated to be 80%, 82% and 75% for reactions with 0.20 M, 0.30 M and 0.40 M concentrations of *p*-iodotoluene, respectively.



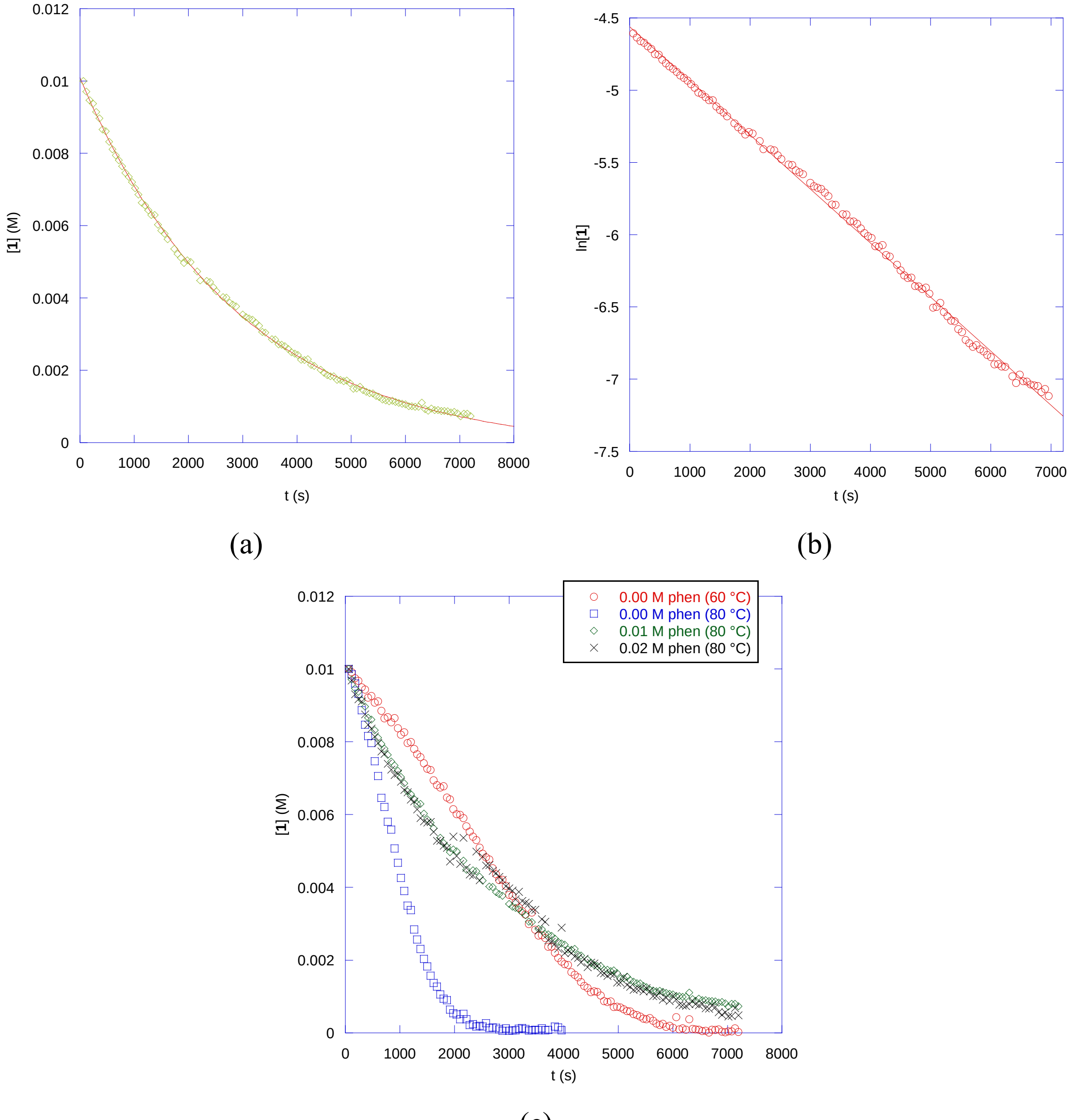
(a) (b)

Figure S2. (a) Plot of the decay of **1** for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.20 M, 0.30 M and 0.40 M) in DMSO-d_6 at 60 °C. (b) Plot of [**1**] versus a product of time (t) and the initial concentrations of *p*-iodotoluene (t × [*p*-iodotoluene]$_0$) for the reaction of complex **1** (0.010 M) with *p*-iodotoluene (0.20 M, 0.30 M and 0.40 M) in DMSO-d_6 at 60 °C.

Effect of 1,10-phenanthroline on the reaction of complex 1 with p-iodotoluene.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene, 100-200 μL of the 0.10 M stock solution of 1,10-phenanthroline and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 80 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 81% and 73% for the reactions with 0.010 M and 0.020 M concentrations of 1,10-phenanthroline. The apparent rate constants (k_{obs}) were found to be 3.6×10^{-4} s^{-1} ($t_{1/2}$: 32 min) for reactions with both 0.010 M and 0.020 M concentrations of 1,10-phenanthroline.

*Reaction of **1** with p-iodotuluene at 80 °C.* For the purpose of comparison, a reaction of **1** (0.010 M) with *p*-iodotoluene (0.10 M) was run at 80 °C in a similar manner in the absence of 1,10-phenanthroline. The yield of the arylated product **6** was calculated to be 76% yield.



(a) (b)

(c)

Figure S3. (a) Plots of the decay of **1** for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.10 M) in presence of 1,10-phenanthroline (0.010 M) in DMSO-d_6 at 80 °C. The curve for the depletion of complex **1** depicts the results of an unweighted least-square fit to y = a*exp(− b*x) ($a = 1.02 \times 10^{-2} \pm 2.69 \times 10^{-5}$, $b = 3.62 \times 10^{-4} \pm 1.44 \times 10^{-6}$, $R^2 = 0.999$). (b) Plot of ln[**1**] versus time (t) for the reaction of complex **1** (0.010 M) with *p*-iodotoluene (0.10 M) in presence of 1,10-phenanthroline (0.010 M) in DMSO-d_6 at 80 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b ($a = -3.74 \times 10^{-4}$, $b = -4.56$, $R^2 = 0.998$). (c) A comparative kinetic plot for the reaction of complex **1** (0.010 M) with *p*-iodotoluene (0.10 M) in absence (blue) and presence (light and dark green) of 1,10-phenanthroline (0.010 M and 0.020 M) in DMSO-d_6 at 80 °C and with *p*-iodotoluene (0.20 M) (red) in DMSO-d_6 at 60 °C.

Determination of the dependence of rate of reaction on the concentration of p-iodotoluene for the reaction of complex 1 with p-iodotoluene in presence of 1,10-phenanthroline.

Complex **1** (8.2 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100-400 μL of the 1.0 M stock solution of *p*-iodotoluene, 100 μL of the 0.10 M stock solution of 1,10-phenanthroline and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 80 °C. The reaction mixture was then analyzed by GC to calculate the yields of the product **6**.

Table S1. Kinetic data for the reaction of complex **1** with different concentrations of *p*-iodotoluene in presence of 1,10-phenanthroline

entry	[**1**]	[*p*-iodotoluene]	[phen]	yield (%)	k_{obs} (s^{-1})
1	0.010 M	0.10 M	0.010 M	81	3.6×10^{-4}
2	0.010 M	0.20 M	0.010 M	90	6.3×10^{-4}
3	0.010 M	0.30 M	0.010 M	88	1.0×10^{-3}
4	0.010 M	0.40 M	0.010 M	76	1.3×10^{-3}

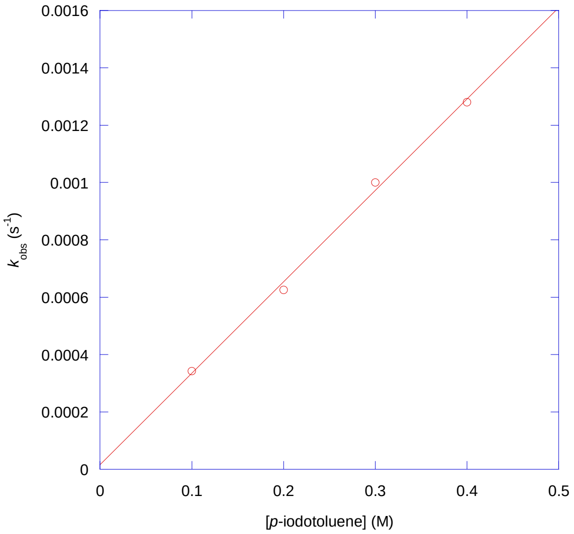


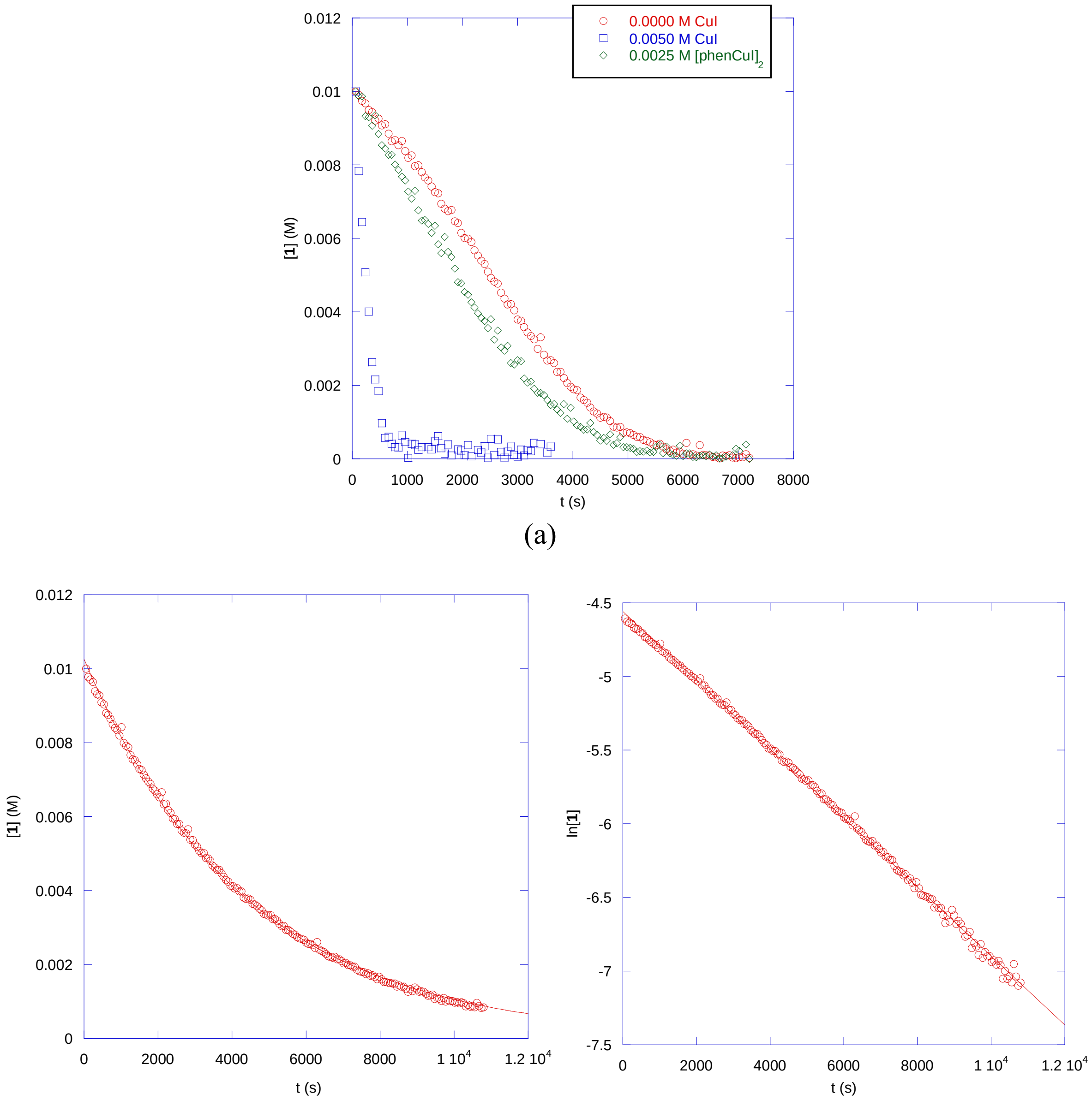
Figure S4. Plot of k_{obs} versus [*p*-iodotoluene] for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.10-0.40 M) in presence of 1,10-phenanthroline (0.010 M) in DMSO-d_6 at 80 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 3.19×10^{-3}, b = 1.55×10^{-5}, $R^2 = 0.997$).

Effects of CuI and [phenCuI]$_2$ on the reaction of complex 1 with p-iodotoluene.

Effect of CuI. Complex **1** (9.1 mg, 0.011 mmol) and *p*-iodotoluene (48.4 mg, 0.222 mmol) were weighed into a 1.0 mL volumetric flask. 111 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the flask containing **1**, and the solution was then diluted to 1.0 mL. 900 μL of this reaction solution was transferred to a screw-capped NMR tube and 50 μL of DMSO-d_6 was added to it. An initial ^{1}H NMR spectrum was acquired at 20 °C. 50 μL of the 0.10 M stock solution of CuI was then added to the reaction mixture, and the resulting solution was heated at 60 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 60 °C. The reaction mixture was then analyzed by GC and the yield of the arylated product **6** was calculated to be 82%.

Effect of [phenCuI]$_2$. Complex **1** (8.2 mg, 0.010 mmol) and *p*-iodotoluene (43.6 mg, 0.200 mmol) were weighed into a 1.0 mL volumetric flask. 100 μL of the 0.0250 M stock solution of [phenCuI]$_2$ and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the solution was then heated at 60 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 60 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 88%.

*Reaction of **1** with p-iodotoluene in presence of CuI at 30 °C.* Complex **1** (9.1 mg, 0.011 mmol) and *p*-iodotoluene (48.4 mg, 0.222 mmol) was weighed into a 1.0 mL volumetric flask. 111 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard was added to the flask containing **1**, and the solution was then diluted to 1.0 mL. 900 μL of this reaction solution was transferred to a screw-capped NMR tube and 25 μL of DMSO-d_6 was added to it. An initial ^{1}H NMR spectrum was acquired at 20 °C. 75 μL of 0.10 M stock solution of CuI was then added to the reaction mixture, and the resulting solution was heated at 30 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 30 °C. The reaction mixture was then analyzed by GC and the yield of the arylated product **6** was calculated to be 80%.



(a)

(b)

(c)

Figure S5. (a) Plots of the decay of **1** from the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.20 M) in the absence (red) and presence (blue) of CuI (0.0050 M) and in the presence of [phenCuI]$_2$ (0.0025 M) (green) in DMSO-d_6 at 60 °C. (b) Plot of the decay of **1** from the reaction of complex **1** (0.010 M) with *p*-iodotoluene (0.20 M) in presence of CuI (0.0075 M) in DMSO-d_6 at 30 °C. The curve for the depletion of complex **1** depicts the results of an unweighted least-square fit to y = a*exp(− b*x) ($a = 1.03 \times 10^{-2} \pm 1.80 \times 10^{-5}$, $b = 2.27 \times 10^{-4} \pm 5.99 \times 10^{-7}$, $R^2 = 0.999$). (c) Plot of ln[**1**] versus time (t) for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.20 M) in presence of CuI (0.0075 M) in DMSO-d_6 at 30 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b ($a = -2.34 \times 10^{-4}$, $b = -4.56$, $R^2 = 0.999$).

Determination of the dependence of rate of reaction on the concentration of CuI for the reaction of complex 1 with p-iodotoluene.

Complex **1** (9.1 mg, 0.011 mmol) and *p*-iodotoluene (48.4 mg, 0.222 mmol) was weighed into a 1.0 mL volumetric flask. 111 µL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. 900 µL of this reaction solution was transferred to a screw-capped NMR tube and 0-50 µL of DMSO-d_6 was added to it. An initial ^{1}H NMR spectrum was acquired at 20 °C. 50-100 µL of the 0.20 M stock solution of CuI was then added to the reaction mixture, and resulting solution was heated at 30 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 30 °C. The reaction mixture was then analyzed by GC to calculate the yields of the product **6**.

Table S2. Kinetic data for the reaction of complex **1** with *p*-iodotoluene in presence of different concentrations of CuI

entry	[**1**]	[*p*-iodotoluene]	[CuI]	yield (%)	k_{obs} (s^{-1})
1	0.010 M	0.20 M	0.0050 M	83	1.2×10^{-4}
2	0.010 M	0.20 M	0.0075 M	80	2.3×10^{-4}
3	0.010 M	0.20 M	0.0100 M	83	3.1×10^{-3}
4	0.010 M	0.20 M	0.0150 M	85	4.3×10^{-3}
5	0.010 M	0.20 M	0.0200 M	87	5.9×10^{-3}

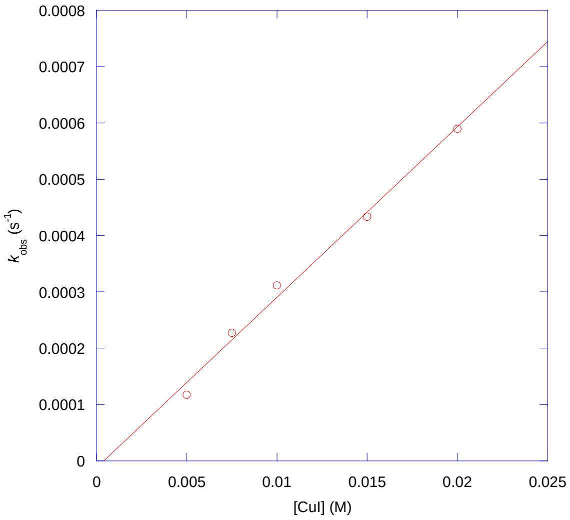


Figure S6. Plot of k_{obs} versus [CuI] for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.20 M) in presence of CuI (0.0050-0.0100 M) in DMSO-d_6 at 30 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 3.03×10^{-2}, b = -1.23×10^{-5}, R^2 = 0.991).

Determination of the dependence of rate of reaction on the concentration of p-iodotoluene for the reaction of complex 1 with p-iodotoluene in presence of CuI.

Complex **1** (9.1 mg, 0.011 mmol) and *p*-iodotoluene (24.2-96.9 mg, 0.111-0.444 mmol) was weighed into a 1.0 mL volumetric flask. 111 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **1**. The solution was then diluted to 1.0 mL. 900 μL of this reaction solution was transferred to a screw-capped NMR tube and an initial ^{1}H NMR spectrum was acquired at 20 °C. 100 μL of the 0.10 M stock solution of CuI was then added to the reaction mixture, and the resulting solution was heated at 30 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 30 °C. The reaction mixture was then analyzed by GC to calculate the yields of the product **6**.

Table S3. Kinetic data for the reaction of complex **1** with different concentrations of *p*-iodotoluene in presence of CuI

entry	[**1**]	[*p*-iodotoluene]	[CuI]	yield (%)	k_{obs} (s^{-1})
1	0.010 M	0.10 M	0.010 M	86	1.7×10^{-4}
2	0.010 M	0.20 M	0.010 M	83	3.1×10^{-4}
3	0.010 M	0.30 M	0.010 M	87	4.9×10^{-4}
4	0.010 M	0.40 M	0.010 M	81	6.4×10^{-4}

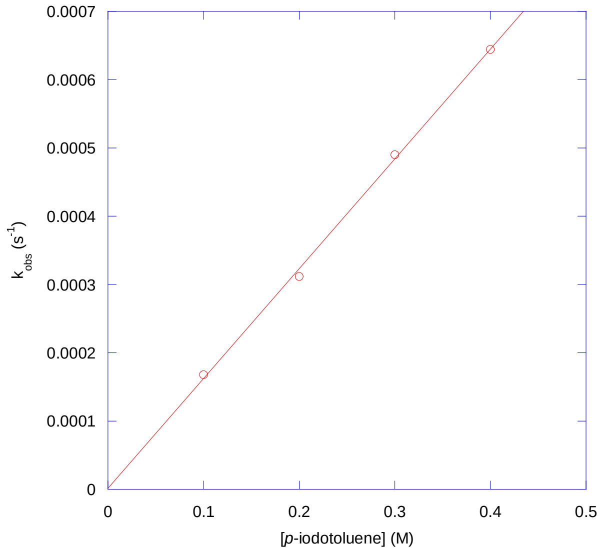


Figure S7. Plot of k_{obs} versus [*p*-idotoluene] for the reaction of phen-ligated complex **1** (0.010 M) with *p*-iodotoluene (0.10-0.40 M) in presence of CuI (0.010 M) in DMSO-d_6 at 30 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 1.61×10^{-2}, b = 1.49×10^{-6}, R^2 = 0.999).

Monitoring the reaction of cuprate 2 with p-iodotoluene by ^{1}H NMR.

Cuprate **2** (9.5 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **2**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 100 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 100 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 106%. The yield of free amine **7** was calculated to be 94%.

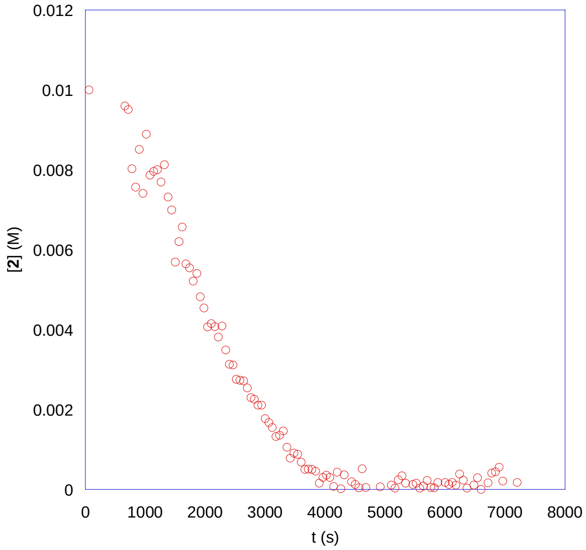
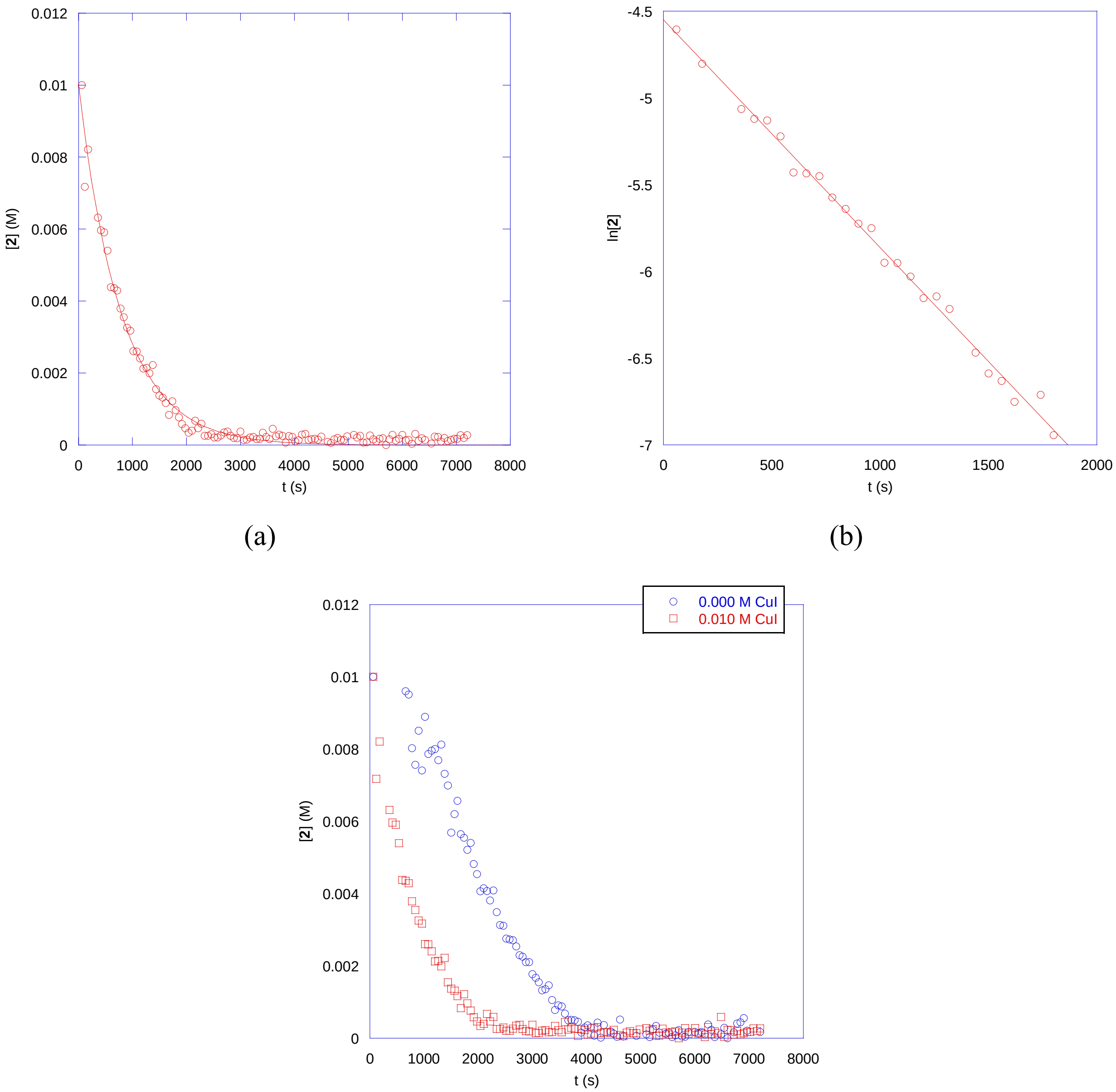


Figure S8. Kinetic plot for the reaction of cuprate **2** (0.010 M) with *p*-iodotoluene (0.20 M) in DMSO-d_6 at 100 °C.

Effect of CuI on the reaction of cuprate 2 with p-iodotoluene.

Cuprate **2** (9.5 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene, 100 μL of the 0.10 M stock solution of CuI and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **2**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 100 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 100 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 49% for the transformation of both amido groups in **2** in the presence of added CuI. The yield of the free amine **7** was calculated to be 40%.



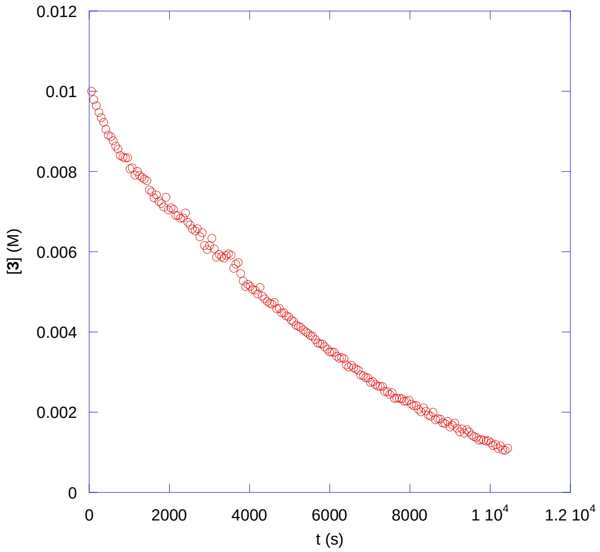
(a) (b)

(c)

Figure S9. (a) Plot of the decay of cuprate **2** (0.010 M) from the reaction of cuprate **2** with *p*-iodotoluene (0.10 M) in the presence of CuI (0.010 M) in DMSO-d_6 at 100 °C. The curve for the depletion of cuprate **2** depicts the results of an unweighted least-square fit to y = a*exp(− b*x) (a = $1.00 \times 10^{-2} \pm 1.54 \times 10^{-4}$, b = $1.27 \times 10^{-3} \pm 2.47 \times 10^{-5}$, $R^2 = 0.984$). (b) Plot of ln[**1**] versus time (t) for the reaction of cuprate **2** (0.010 M) with *p*-iodotoluene (0.10 M) in presence of CuI (0.010 M) in DMSO-d_6 at 100 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = -1.31×10^{-3}, b = − 4.55, $R^2 = 0.994$). (c) A comparative kinetic plot for the reaction of cuprate **2** (0.010 M) with *p*-iodotoluene (0.10 M) in absence (blue) or presence (red) of CuI (0.010 M) in DMSO-d_6 at 100 °C.

Monitoring the reaction of cuprate 3 with p-iodotoluene by ^{1}H NMR.

Cuprate **3** (9.8 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene, and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **3**, and the resulting solution was diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 80 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 90%. The yield of free amine **7** was calculated to be 62%.



(a) (b)

Figure S10. (a) Plot of the decay of **3** from the reaction of cuprate **3** (0.010 M) with *p*-iodotoluene (0.10 M) in DMSO-d_6 at 80 °C.

Determination of the dependence of rate of reaction on the concentration of p-iodotoluene for the reaction of cuprate 3 with p-iodotoluene.

Cuprate **3** (9.8 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100-300 μL of the 1.0 M stock solution of *p*-iodotoluene and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **3**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 80 °C. The reaction mixture was then analyzed by GC, and the yields of the arylated product **6** were calculated to be 90%, 100% and 92%, respectively for reactions with 0.10 M, 0.20 M and 0.30 M concentrations of *p*-iodotoluene.

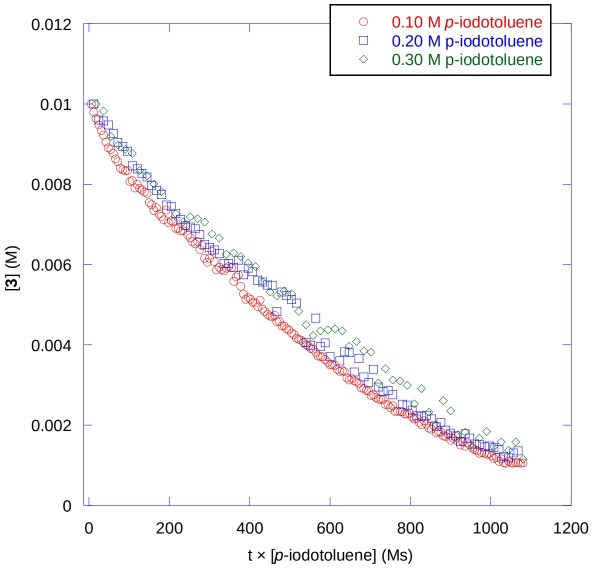
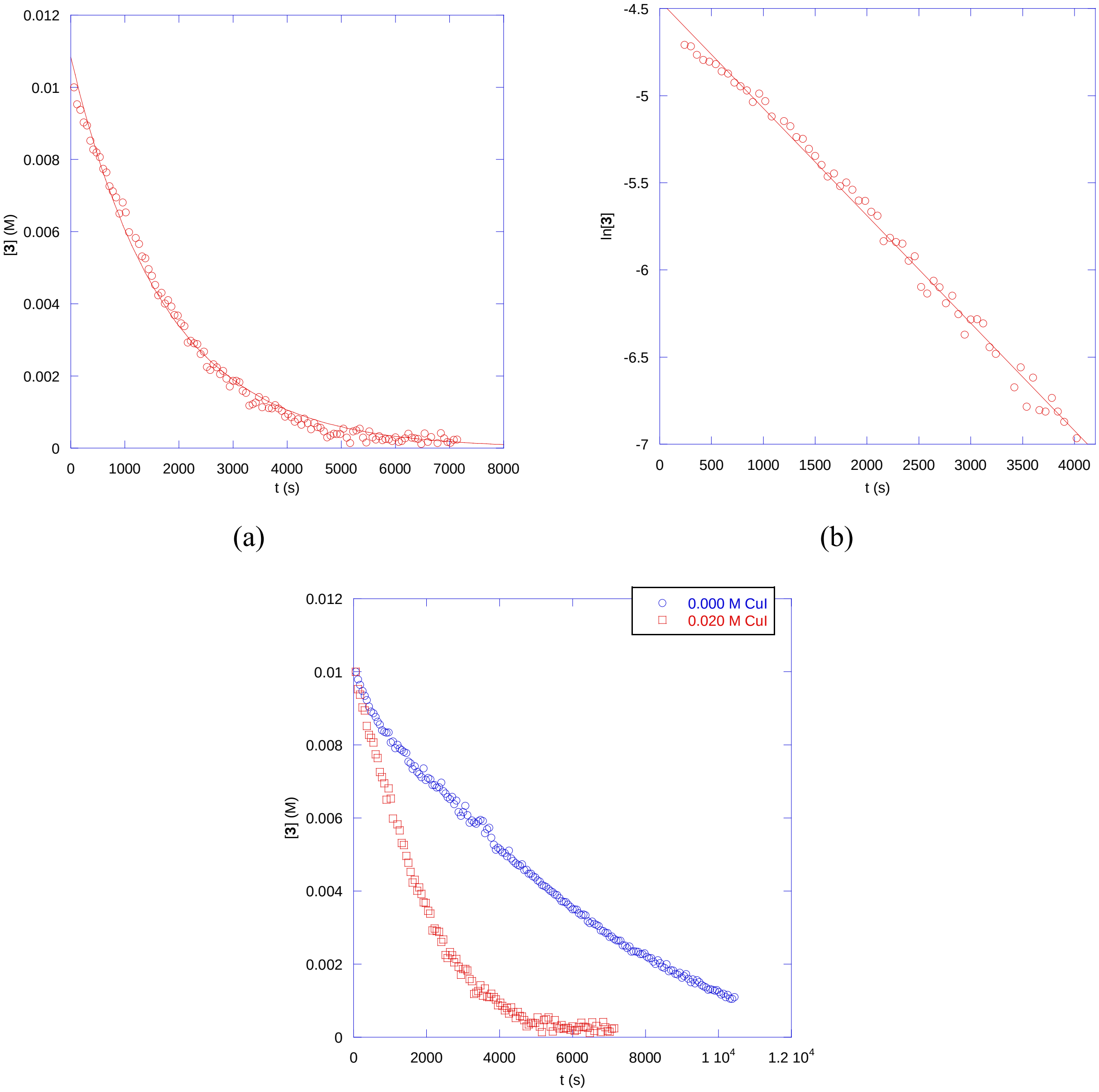


Figure S11. Plot of [**3**] versus a product of time (t) and the initial concentrations of *p*-iodotoluene (t × [*p*-iodotoluene]$_0$) for the reaction of complex **1** (0.010 M) with *p*-iodotoluene (0.10-0.30 M) in DMSO-d_6 at 80 °C.

Effect of CuI on the reaction of cuprate 3 with p-iodotoluene.

Cuprate **3** (9.8 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene, 100 μL of the 0.20 M stock solution of CuI and 100 μL of the 0.050 M stock solution of 1,4-di-*tert*-butylbenzene as an internal standard were added to the flask containing **3**. The solution was then diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 80 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 80 °C. The reaction mixture was then analyzed by GC, and the yield of the arylated product **6** was calculated to be 73% for the transformation of both amido groups in **2** in the presence of added CuI. The yield of the free amine **7** was calculated to be 14%.



(a)

(b)

(c)

Figure 12. (a) Plots of the decay of **3** from the reaction of cuprate **3** (0.010 M) with *p*-iodotoluene (0.10 M) in presence of CuI (0.020 M) in DMSO-d_6 at 80 °C. The curve for the depletion of cuprate **3** depicts the results of an unweighted least-square fit to y = a*exp(− b*x) ($a = 1.08 \times 10^{-2} \pm 8.46 \times 10^{-5}$, $b = 5.81 \times 10^{-4} \pm 6.33 \times 10^{-6}$, $R^2 = 0.994$). (b) Plot of ln[**1**] versus time (t) for the reaction of cuprate **3** (0.010 M) with *p*-iodotoluene (0.10 M) in presence of CuI (0.020 M) in DMSO-d_6 at 80 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b ($a = -6.16 \times 10^{-4}$, $b = -4.46$, $R^2 = 0.993$). (c) A comparative kinetic plot for the reaction of cuprate **3** (0.010 M) with *p*-iodotoluene (0.10 M) in absence (blue) and presence (red) of CuI (0.020 M) in DMSO-d_6 at 80 °C.

Effect of CuI on the reaction of [bis(1,10-phenanthroline)Cu][bis(phenoxide)Cu] with p-iodotoluene.

[Bis(1,10-phenanthroline)Cu][bis(phenoxide)Cu] (6.7 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. A 0.10 M stock solution of 1,3,5-trimethoxybenzene as an internal standard was prepared by dissolving 16.8 mg of 1,3,5-trimethoxybenzene in DMSO, and diluting the resulting solution to 1.0 mL in a volumetric flask. 100 μL of the 1.0 M stock solution of *p*-iodotoluene, 100 μL of the 0.10 M stock solution of 1,3,5-trimethoxybenzene and 100 μL of the 0.10 M stock solution of CuI were added to the flask containing the complex and diluted to 1.0 mL. The reaction solution was transferred to a vial and heated at 80 °C. Aliquots (100 μL) of the reaction mixture were analyzed by GC at 0.5 h, 1 h, 2 h and 4 h. A control reaction was also run in the absence of CuI for comparison. No rate enhancement was observed in presence of CuI. The reaction mixtures were then analyzed by GC, and the yields of the arylated product were calculated to be 66% and 64% for reactions run in absence and presence of CuI, respectively.

Effect of CuI on the reaction of (phthalimidato)Cu(1,10-phenanthroline) with p-iodotoluene.

(Phthalimidato)Cu(1,10-phenanthroline) (7.8 mg, 0.020 mmol) was weighed into a 1.0 mL volumetric flask. A 0.10 M stock solution of 1,3,5-trimethoxybenzene as an internal standard was prepared by dissolving 16.8 mg of 1,3,5-trimethoxybenzene in DMSO-d_6, and diluting the resulting solution to 1.0 mL in a volumetric flask. 250 μL of the 1.0 M stock solution of *p*-iodotoluene, 100 μL of the 0.10 M stock solution of 1,3,5-trimethoxybenzene and 100 μL of the 0.10 M stock solution of CuI were added to the flask containing the complex, and the resulting solution was diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C, and the sample was then heated at 120 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 120 °C. A control reaction was also run in the absence of CuI for comparison. No rate enhancement was observed in the presence of CuI. The reaction mixtures were then analyzed by GC, and the yields of the arylated product were calculated to be 77% and 68% for reactions run in absence and presence of CuI, respectively.

Effect of CuI on the reaction of [bis(1,10-phenanthroline)Cu][bis(pyrrolidinone)Cu] with p-iodotoluene.

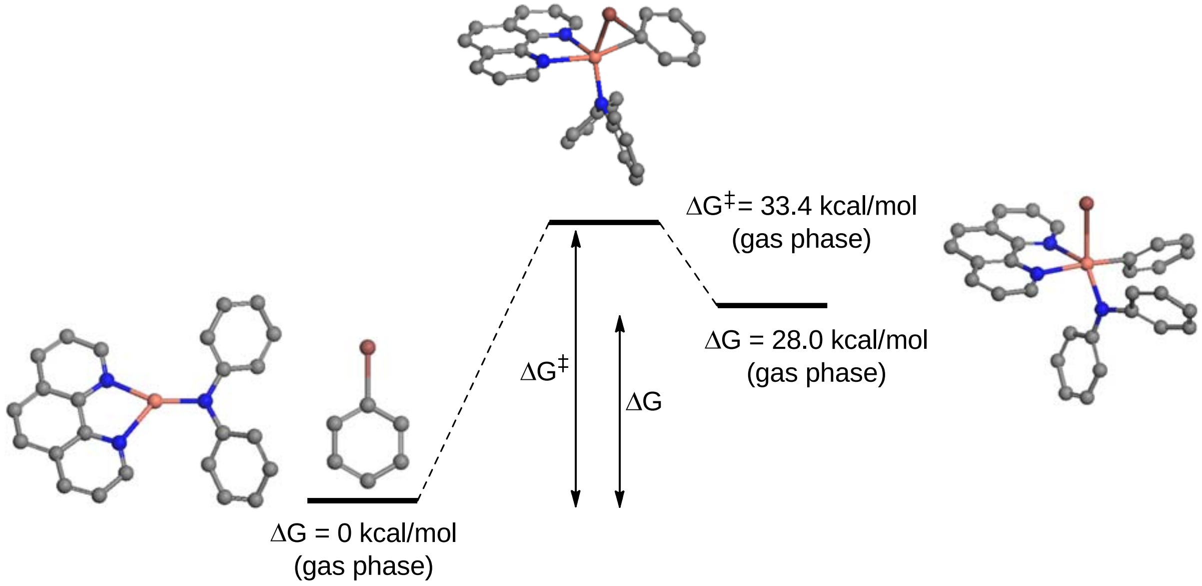
[Bis(1,10-phenanthroline)Cu][bis(pyrrolidinone)Cu] (7.6 mg, 0.010 mmol) was weighed into a 1.0 mL volumetric flask. A 0.10 M stock solution of 1,3,5-trimethoxybenzene as an internal standard was prepared by dissolving 16.8 mg of 1,3,5-trimethoxybenzene in DMSO-d_6, and diluting the resulting solution to 1.0 mL in a volumetric flask. 100 µL of the 1.0 M stock solution of *p*-iodotoluene, 100 µL of the 0.10 M stock solution of 1,3,5-trimethoxybenzene and 100 µL of the 0.10 M stock solution of CuI were added to the flask containing the complex, and the resulting solution was diluted to 1.0 mL. The reaction solution was transferred to an NMR tube fused to a J-Young valve. An initial ^{1}H NMR spectrum was acquired at 20 °C and, the sample was then heated at 120 °C in the NMR spectrometer. ^{1}H NMR spectra were acquired at fixed intervals at 120 °C. A control reaction was also run in the absence of CuI for comparison. No rate enhancement was observed in the presence of CuI. The reaction mixtures were then analyzed by GC, and the yields of the arylated product were calculated to be 82% and 90% for reactions run in absence and presence of CuI, respectively.

7. DFT Calculations

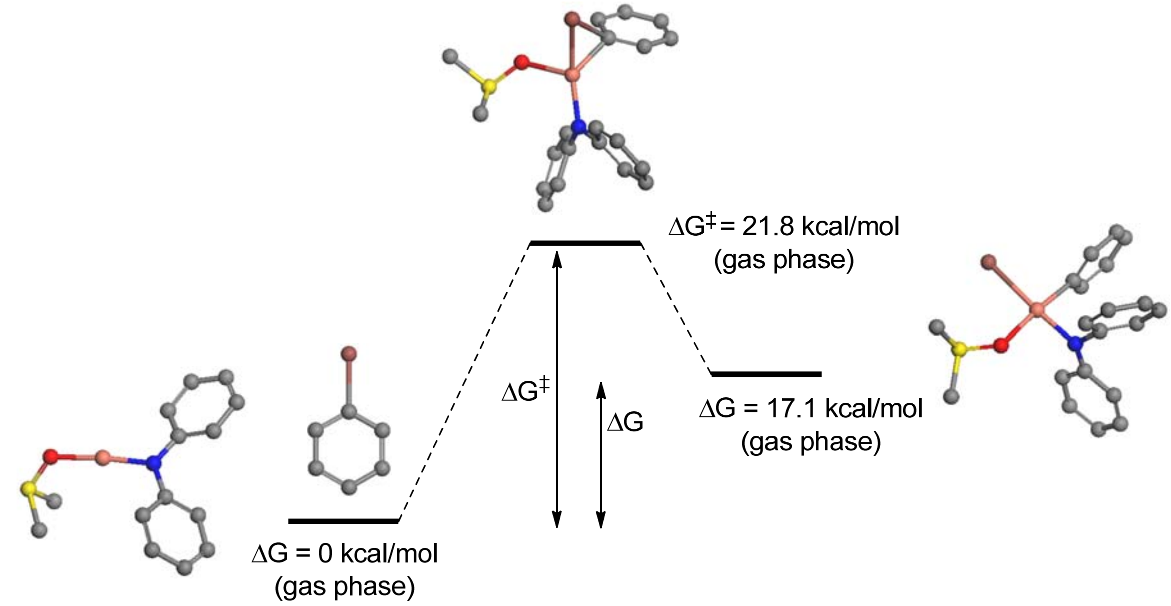
DFT analysis of the oxidative addition of PhI to (DMSO)Cu(I)(NPh$_2$) and (phen)Cu(I)(NPh$_2$).

All DFT calculations were performed using a hybrid functional [the three-parameter exchange functional of Becke (B3)[9] and the correlation functional of Lee, Yang, and Parr (LYP)[10]] (B3LYP) as implemented in Gaussian 09.[11] The effective core potential and associated triple ζ basis sets of Hay and Wadt (LANL2TZ) were utilized for the copper and iodine atoms.[12] For the copper atom, an f polarization function[13] was added to the basis set. For iodine, the basis set was augmented by d polarization function. The 6-311G** basis set was utilized for all other atoms.[13,14] Unless otherwise noted, all geometries are fully optimized and confirmed as minima or n-order saddle points by analytical frequency calculations at the same level.

Energy profile for oxidative addition of PhI to (Phen)Cu(I)(NPh$_2$)



Energy profile for oxidative addition of PhI to (DMSO)Cu(I)(NPh$_2$)



B3LYP computed energies in Hartrees

Complex	E	G
PhI	-242.993551	-243.032134
(Phen)Cu(I)(NPh$_2$)	-1285.768484	-1285.847135
(Phen)Cu(III)(NPh$_2$)(Ph)(I)	-1528.738475	-1528.834709
(Phen)Cu(NPh$_2$)(PhI)-TS	-1528.729281	-1528.826088
(DMSO)Cu(I)(NPh$_2$)	-879.275211	-879.346042
(DMSO)Cu(III)(NPh$_2$)(Ph)(I)	-1122.260218	-1122.350875
(DMSO)Cu(NPh$_2$)(PhI)-TS	-1122.252042	-1122.343393

Energy-minimized geometries computed using DFT

PhI

C	-1.034996	0.165877	0.060421
C	0.169285	-0.43291	0.427174
C	1.346135	-0.125763	-0.251441
C	1.318868	0.786038	-1.303916
C	0.122364	1.39306	-1.682405
C	-1.046979	1.076022	-0.99442
I	-2.870813	1.992171	-1.560479
H	-1.947678	-0.074994	0.589922
H	0.181208	-1.141351	1.247809
H	2.2793	-0.594673	0.038074
H	2.230222	1.03143	-1.837479
H	0.104722	2.10127	-2.500637

(Phen)Cu(I)(NPh$_2$)

C	1.565317	-0.297166	-0.246377
N	1.945487	0.91939	-0.721129
C	2.988146	0.978935	-1.548934
C	3.707629	-0.155361	-1.94789
C	3.326073	-1.396323	-1.479342
C	2.225597	-1.495821	-0.604694

C	0.438044	-0.344471	0.651014
C	-0.011475	-1.592144	1.145587
C	0.677346	-2.789168	0.758727
C	1.749836	-2.742288	-0.075453
N	-0.144678	0.830331	0.980851
C	-1.193281	0.813911	1.790872
C	-1.722615	-0.374277	2.324448
C	-1.128227	-1.577465	2.005994
Cu	0.886235	2.50255	-0.087266
N	0.427639	4.343764	-0.024116
C	-0.332608	4.819353	1.042103
C	-1.338791	5.80338	0.904037
C	-2.125964	6.185003	1.983158
C	-1.953484	5.608184	3.242908
C	-0.963939	4.638495	3.400527
C	-0.165618	4.256886	2.327008
C	0.823488	5.196002	-1.052499
C	1.103087	6.568939	-0.863443
C	1.567493	7.360215	-1.907214
C	1.777046	6.827898	-3.179873
C	1.50712	5.47524	-3.386421
C	1.035803	4.678776	-2.349852
H	3.255727	1.964771	-1.910557
H	4.547606	-0.041979	-2.621428
H	3.859312	-2.292646	-1.77622
H	0.32512	-3.738248	1.147751
H	2.265324	-3.652925	-0.359882
H	-1.623365	1.779089	2.037398
H	-2.582366	-0.328948	2.981233
H	-1.50775	-2.510475	2.408473
H	-1.508569	6.249827	-0.068062
H	-2.895619	6.936173	1.834861
H	-2.569891	5.913098	4.08071
H	-0.795976	4.187994	4.374193
H	0.622708	3.523596	2.464821
H	0.973455	7.003646	0.11996
H	1.781086	8.407832	-1.718616
H	2.138577	7.451663	-3.989167
H	1.649339	5.037825	-4.369979
H	0.801986	3.633114	-2.527545

(Phen)Cu(III)(NPh$_2$)(Ph)(I)

C	-4.444982	-0.824244	2.251539
C	-4.234732	-0.086099	1.068525
C	-2.897399	0.064647	0.628042
N	-1.842064	-0.433454	1.309447
C	-2.07214	-1.130548	2.409353
C	-3.363604	-1.356247	2.91768
C	-5.299697	0.504216	0.311903
C	-5.045483	1.204888	-0.824276
C	-3.706585	1.35811	-1.314105
C	-2.633781	0.772551	-0.600741
N	-1.354327	0.84885	-1.035278
C	-1.086488	1.532151	-2.136631
C	-2.082065	2.16164	-2.899195
C	-3.394594	2.064183	-2.493869
Cu	0.14594	-0.284738	-0.051879
N	1.491727	1.132932	-0.341126
C	1.405472	2.319136	0.388773
C	2.282007	3.407776	0.162816
C	2.092338	4.625145	0.802914
C	1.041782	4.812044	1.700761
C	0.169343	3.751484	1.934248
C	0.342217	2.531351	1.291482
C	1.408074	-1.102546	1.204397
C	1.337145	-0.655485	2.517757
C	2.167814	-1.230875	3.487374
C	3.064892	-2.23324	3.133718
C	3.138786	-2.654543	1.807116
C	2.314066	-2.087471	0.833739
I	-0.556165	-2.51368	-1.308637
C	2.735545	0.710502	-0.849114
C	2.755971	0.047609	-2.088983
C	3.951514	-0.403604	-2.637453
C	5.153917	-0.210709	-1.960115
C	5.144666	0.423455	-0.716641
C	3.953099	0.869136	-0.160308
H	-5.454694	-0.969267	2.620287
H	-1.200103	-1.531415	2.914938
H	-3.489463	-1.937935	3.822323
H	-6.316922	0.381448	0.667162
H	-5.8558	1.653535	-1.3881
H	-0.040565	1.583657	-2.414788

H	-1.806319	2.704155	-3.794448
H	-4.191068	2.524448	-3.068468
H	3.091048	3.301379	-0.546951
H	2.776177	5.440599	0.591542
H	0.906085	5.76221	2.203621
H	-0.656966	3.870228	2.62736
H	-0.350581	1.723088	1.486584
H	0.674639	0.152292	2.804623
H	2.116818	-0.874238	4.511141
H	3.709946	-2.677266	3.883845
H	3.834193	-3.436413	1.520578
H	2.376411	-2.427361	-0.190798
H	1.820937	-0.118614	-2.610272
H	3.941235	-0.909314	-3.596543
H	6.086129	-0.560779	-2.388539
H	6.07111	0.553875	-0.16796
H	3.952296	1.329339	0.819604

(Phen)Cu(NPh$_2$)(PhI) (Transition State)

C	4.247045	0.507458	-2.209204
C	4.104701	0.140565	-0.855647
C	2.795351	-0.129818	-0.385303
N	1.705827	-0.05798	-1.184993
C	1.872542	0.311181	-2.444867
C	3.127883	0.601897	-3.004376
C	5.217337	0.049011	0.043993
C	5.03617	-0.273691	1.350864
C	3.725814	-0.53289	1.870728
C	2.603772	-0.470364	1.007448
N	1.345543	-0.70253	1.439137
C	1.149632	-0.986783	2.716589
C	2.195948	-1.067021	3.650585
C	3.486368	-0.844396	3.224751
Cu	-0.26163	-0.452063	-0.080795
N	-0.931196	1.317036	0.565473
C	-0.411504	2.46858	-0.054948
C	0.337127	3.414557	0.671015
C	0.90332	4.51909	0.043099
C	0.74537	4.713502	-1.330035
C	0.004128	3.788443	-2.0619
C	-0.570546	2.684294	-1.434646
C	-1.705704	-1.101405	-1.432176

C	-1.243978	-1.177013	-2.748643
C	-2.045776	-0.680572	-3.777908
C	-3.305894	-0.158385	-3.498615
C	-3.772422	-0.143083	-2.181966
C	-2.990255	-0.637972	-1.143945
I	-0.935294	-3.001276	-0.097998
C	-1.95602	1.440978	1.467108
C	-2.405404	0.303655	2.192694
C	-3.442614	0.38124	3.11293
C	-4.091201	1.590527	3.364427
C	-3.677893	2.719295	2.653613
C	-2.649081	2.655997	1.724161
H	5.23391	0.722325	-2.604733
H	0.973729	0.388221	-3.045098
H	3.196251	0.898989	-4.043286
H	6.210388	0.252919	-0.341087
H	5.882124	-0.333138	2.026789
H	0.1233	-1.155083	3.021752
H	1.974688	-1.301337	4.68426
H	4.319978	-0.900165	3.916512
H	0.465105	3.265651	1.737485
H	1.476811	5.231133	0.628207
H	1.187521	5.574993	-1.817911
H	-0.141835	3.933353	-3.12796
H	-1.168222	1.980786	-2.003313
H	-0.28568	-1.627183	-2.969888
H	-1.686047	-0.726457	-4.80043
C	-0.643866252	1.435235129	-0.311754833
C	-0.697327272	1.462189392	-0.318044787
C	-0.750788291	1.489143655	-0.32433474

(DMSO)Cu(I)(NPh_2) (O-bound DMSO)

Cu	0.086651	0.496065	0.658909
N	0.5993	-0.289325	-0.954486
C	1.709406	0.178351	-1.657515
C	2.452032	-0.617539	-2.557179
C	3.587856	-0.121622	-3.186863
C	4.04025	1.175165	-2.944993
C	3.32689	1.970797	-2.049406
C	2.184491	1.486476	-1.424764
C	-0.232657	-1.287193	-1.464252
C	-0.88574	-2.171188	-0.576474

C	-1.797114	-3.120489	-1.027746
C	-2.085034	-3.240376	-2.38618
C	-1.439493	-2.384877	-3.280623
C	-0.535397	-1.427028	-2.837403
O	-0.602765	1.294296	2.260287
S	-2.096857	1.703021	2.469298
C	-2.550489	2.709591	1.012126
C	-3.082324	0.213614	2.081088
H	2.142466	-1.638345	-2.742575
H	4.135588	-0.766774	-3.866676
H	4.928249	1.553804	-3.437504
H	3.65682	2.983563	-1.84056
H	1.63152	2.122946	-0.739021
H	-0.636494	-2.113463	0.479237
H	-2.268681	-3.786814	-0.311887
H	-2.787073	-3.985792	-2.741109
H	-1.652231	-2.455332	-4.34281
H	-0.066219	-0.762155	-3.551843
H	-3.615679	2.942876	1.064148
H	-2.30382	2.154666	0.105572
H	-1.963568	3.625519	1.069083
H	-2.862554	-0.517464	2.858288
H	-2.787078	-0.171547	1.103331
H	-4.141182	0.478301	2.106392

(DMSO)Cu(III)(NPh_2)(Ph)(I) (O-bound DMSO)

Cu	0.923628	-0.462747	0.581085
N	1.909164	0.080575	-0.981177
C	1.986063	-0.786687	-2.061021
C	2.614165	-0.446479	-3.281802
C	2.766493	-1.385949	-4.29429
C	2.294845	-2.689035	-4.148849
C	1.679382	-3.044338	-2.948581
C	1.53271	-2.118806	-1.925374
I	-0.436022	-1.007295	2.684039
C	-0.688944	0.227915	-0.275935
C	2.076422	1.468018	-1.131911
C	2.816008	2.144919	-0.145892
C	2.994106	3.522732	-0.209654
C	2.437437	4.255221	-1.257373
C	1.68927	3.596701	-2.233825
C	1.49904	2.221353	-2.170515

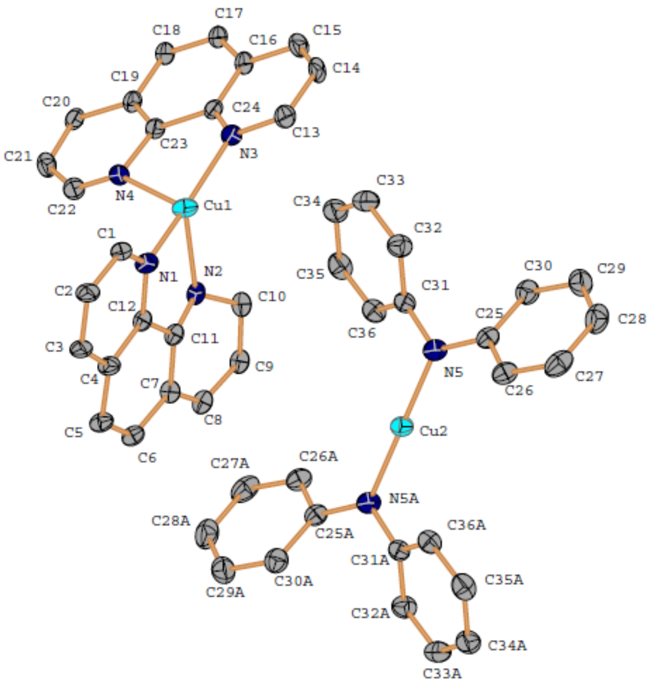
O	2.696592	-1.232078	1.328853
S	2.861392	-2.379286	2.381274
H	3.015837	0.548205	-3.416843
H	3.265582	-1.090544	-5.211329
H	2.408459	-3.412031	-4.947758
H	1.308707	-4.053926	-2.805506
H	1.065477	-2.426893	-0.995767
H	3.259613	1.559517	0.651287
H	3.575913	4.025057	0.555472
H	2.579466	5.328635	-1.310028
H	1.234626	4.161711	-3.040268
H	0.888732	1.722238	-2.912374
C	-1.471017	-0.604933	-1.060097
C	-2.632187	-0.089643	-1.643922
C	-2.996807	1.23748	-1.43351
C	-2.19711	2.056928	-0.640133
C	-1.032837	1.553687	-0.055447
H	-1.199484	-1.638298	-1.235198
H	-3.24607	-0.735303	-2.262919
H	-3.900829	1.631237	-1.884357
H	-2.474227	3.091127	-0.465885
H	-0.419594	2.199338	0.561807
C	4.497696	-3.055471	1.929694
C	3.340381	-1.536679	3.930837
H	4.79952	-3.797853	2.670699
H	5.213468	-2.236108	1.867213
H	4.379632	-3.523735	0.9534
H	2.450486	-1.013142	4.276343
H	4.144044	-0.833273	3.711785
H	3.650461	-2.284081	4.663619

(DMSO)Cu(NPh_2)(PhI) (O-bound DMSO) (Transition State)

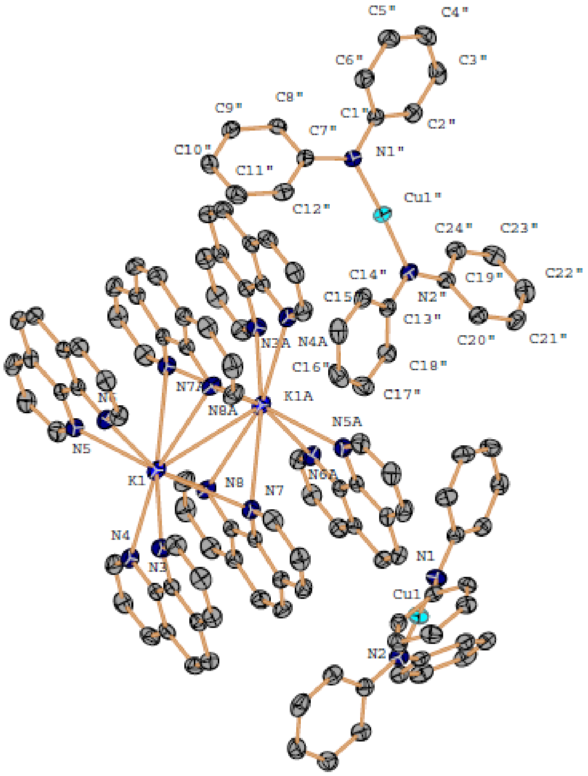
Cu	-0.37445	0.510138	0.471561
N	1.310123	0.463801	-0.470019
C	1.748164	-0.689095	-1.128781
C	3.11831	-0.994322	-1.297574
C	3.521106	-2.189172	-1.881782
C	2.582911	-3.125673	-2.318769
C	1.227923	-2.840698	-2.159064
C	0.815156	-1.645567	-1.578653
I	-1.734519	1.878126	2.148604

C	-2.136815	1.105622	-0.242255
C	1.983703	1.672273	-0.676022
C	1.988822	2.64592	0.344814
C	2.592216	3.884129	0.160269
C	3.216089	4.198107	-1.046529
C	3.216802	3.248936	-2.069228
C	2.61211	2.010128	-1.895221
O	-0.706973	-1.460196	1.410526
S	0.308518	-2.583409	1.745416
H	3.862717	-0.284901	-0.956305
H	4.581353	-2.393326	-1.991649
H	2.902375	-4.053672	-2.778475
H	0.480373	-3.54816	-2.502703
H	-0.241787	-1.42772	-1.478093
H	1.517261	2.407077	1.291512
H	2.580094	4.606248	0.969985
H	3.68946	5.162631	-1.18878
H	3.683933	3.480151	-3.021088
H	2.605716	1.296867	-2.709988
C	-3.056124	0.061769	-0.348164
C	-3.879019	0.014848	-1.473841
C	-3.810211	1.016009	-2.44139
C	-2.911538	2.072711	-2.292249
C	-2.078801	2.139162	-1.176848
H	-3.105606	-0.705982	0.412273
H	-4.581117	-0.804464	-1.584196
H	-4.46401	0.980028	-3.305168
H	-2.857586	2.854459	-3.041861
H	-1.38804	2.963339	-1.051527
C	1.796213	-1.74421	2.407682
C	-0.31101	-3.262696	3.331486
H	2.509935	-2.502458	2.734945
H	1.501299	-1.090712	3.229171
H	2.210588	-1.161467	1.586363
H	-1.252863	-3.764109	3.111879
H	-0.477261	-2.436676	4.022993
H	0.411185	-3.979042	3.727593

8. Crystal Structure for Complex 1



9. Crystal Structure for Complex 3



10. Table of Bond Lengths and Angles for Complexes 1 and 3

Bond lengths [Å] and angles [°] for complex **1**.		Bond lengths [Å] and angles [°] for complex **3**.	
Cu(1)-N(3)	1.982(7)	Cu(1)-N(1)	1.860(2)
Cu(1)-N(1)	1.985(7)	Cu(1)-N(2)	1.879(2)
Cu(1)-N(4)	2.122(12)	N(1)-C(1)	1.398(3)
Cu(1)-N(2)	2.141(12)	N(1)-C(7)	1.405(3)
N(1)-C(1)	1.323(11)	N(2)-C(19)	1.389(3)
N(1)-C(12)	1.371(12)	N(2)-C(13)	1.392(3)
N(2)-C(11)	1.18(2)	C(1)-C(2)	1.398(4)
N(2)-C(10)	1.51(2)	C(1)-C(6)	1.409(4)
C(1)-C(2)	1.394(11)	C(2)-C(3)	1.389(4)
C(1)-H(1)	0.9500	C(2)-H(2)	0.9500
C(2)-C(3)	1.353(12)	C(3)-C(4)	1.378(4)
C(2)-H(2)	0.9500	C(3)-H(3)	0.9500
C(3)-C(4)	1.446(14)	C(4)-C(5)	1.383(4)
C(3)-H(3)	0.9500	C(4)-H(4)	0.9500
C(4)-C(12)	1.409(10)	C(5)-C(6)	1.381(4)
C(4)-C(5)	1.427(13)	C(5)-H(5)	0.9500
C(5)-C(6)	1.362(16)	C(6)-H(6)	0.9500
C(5)-H(5)	0.9500	C(7)-C(12)	1.402(4)
C(6)-C(7)	1.433(16)	C(7)-C(8)	1.406(4)
C(6)-H(6)	0.9500	C(8)-C(9)	1.379(4)
C(7)-C(8)	1.38(2)	C(8)-H(8)	0.9500
C(7)-C(11)	1.404(14)	C(9)-C(10)	1.382(4)
C(8)-C(9)	1.34(2)	C(9)-H(9)	0.9500
C(8)-H(8)	0.9500	C(10)-C(11)	1.378(4)
C(9)-C(10)	1.42(2)	C(10)-H(10)	0.9500
C(9)-H(9)	0.9500	C(11)-C(12)	1.384(4)
C(10)-H(10)	0.9500	C(11)-H(11)	0.9500
C(11)-C(12)	1.421(17)	C(12)-H(12)	0.9500
N(3)-C(13)	1.352(11)	C(13)-C(14)	1.403(4)
N(3)-C(24)	1.363(11)	C(13)-C(18)	1.409(4)
N(4)-C(22)	1.16(2)	C(14)-C(15)	1.379(4)
N(4)-C(23)	1.54(2)	C(14)-H(14)	0.9500
C(13)-C(14)	1.383(12)	C(15)-C(16)	1.389(4)

C(13)-H(13)	0.9500	C(15)-H(15)	0.9500
C(14)-C(15)	1.357(11)	C(16)-C(17)	1.382(4)
C(14)-H(14)	0.9500	C(16)-H(16)	0.9500
C(15)-C(16)	1.400(12)	C(17)-C(18)	1.377(4)
C(15)-H(15)	0.9500	C(17)-H(17)	0.9500
C(16)-C(24)	1.407(10)	C(18)-H(18)	0.9500
C(16)-C(17)	1.421(12)	C(19)-C(24)	1.407(4)
C(17)-C(18)	1.325(14)	C(19)-C(20)	1.414(4)
C(17)-H(17)	0.9500	C(20)-C(21)	1.379(4)
C(18)-C(19)	1.435(15)	C(20)-H(20)	0.9500
C(18)-H(18)	0.9500	C(21)-C(22)	1.385(4)
C(19)-C(23)	1.396(14)	C(21)-H(21)	0.9500
C(19)-C(20)	1.412(18)	C(22)-C(23)	1.389(4)
C(20)-C(21)	1.42(2)	C(22)-H(22)	0.9500
C(20)-H(20)	0.9500	C(23)-C(24)	1.383(4)
C(21)-C(22)	1.38(2)	C(23)-H(23)	0.9500
C(21)-H(21)	0.9500	C(24)-H(24)	0.9500
C(22)-H(22)	0.9500	K(1)-N(6)	2.806(2)
C(23)-C(24)	1.466(16)	K(1)-N(5)	2.810(2)
Cu(1A)-N(3A)	1.975(7)	K(1)-N(3)	2.826(2)
Cu(1A)-N(1A)	1.988(8)	K(1)-N(4)	2.859(2)
Cu(1A)-N(4A)	2.122(13)	K(1)-N(8)	2.916(2)
Cu(1A)-N(2A)	2.146(13)	K(1)-N(7)	3.018(2)
N(1A)-C(1A)	1.326(10)	K(1)-N(8)#1	3.101(2)
N(1A)-C(12A)	1.369(11)	K(1)-N(7)#1	3.408(2)
N(2A)-C(11A)	1.18(2)	N(3)-C(25)	1.322(4)
N(2A)-C(10A)	1.51(2)	N(3)-C(36)	1.360(3)
C(1A)-C(2A)	1.391(10)	N(4)-C(34)	1.321(3)
C(1A)-H(1A)	0.9500	N(4)-C(35)	1.355(3)
C(2A)-C(3A)	1.353(12)	N(5)-C(37)	1.326(3)
C(2A)-H(2A)	0.9500	N(5)-C(48)	1.360(3)
C(3A)-C(4A)	1.445(14)	N(6)-C(46)	1.320(3)
C(3A)-H(3A)	0.9500	N(6)-C(47)	1.359(3)
C(4A)-C(12A)	1.410(10)	N(7)-C(49)	1.324(3)
C(4A)-C(5A)	1.426(12)	N(7)-C(60)	1.356(3)
C(5A)-C(6A)	1.356(14)	N(7)-K(1)#1	3.408(2)
C(5A)-H(5A)	0.9500	N(8)-C(58)	1.320(4)

C(6A)-C(7A)	1.437(16)	N(8)-C(59)	1.361(3)
C(6A)-H(6A)	0.9500	N(8)-K(1)#1	3.101(2)
C(7A)-C(8A)	1.382(19)	C(25)-C(26)	1.393(4)
C(7A)-C(11A)	1.400(14)	C(25)-H(25)	0.9500
C(8A)-C(9A)	1.34(2)	C(26)-C(27)	1.361(4)
C(8A)-H(8A)	0.9500	C(26)-H(26)	0.9500
C(9A)-C(10A)	1.42(2)	C(27)-C(28)	1.403(4)
C(9A)-H(9A)	0.9500	C(27)-H(27)	0.9500
C(10A)-H(10A)	0.9500	C(28)-C(36)	1.413(4)
C(11A)-C(12A)	1.424(16)	C(28)-C(29)	1.434(4)
N(3A)-C(13A)	1.354(11)	C(29)-C(30)	1.346(4)
N(3A)-C(24A)	1.359(10)	C(29)-H(29)	0.9500
N(4A)-C(22A)	1.16(2)	C(30)-C(31)	1.430(4)
N(4A)-C(23A)	1.54(2)	C(30)-H(30)	0.9500
C(13A)-C(14A)	1.381(11)	C(31)-C(35)	1.409(3)
C(13A)-H(13A)	0.9500	C(31)-C(32)	1.410(4)
C(14A)-C(15A)	1.356(11)	C(32)-C(33)	1.364(4)
C(14A)-H(14A)	0.9500	C(32)-H(32)	0.9500
C(15A)-C(16A)	1.399(12)	C(33)-C(34)	1.393(4)
C(15A)-H(15A)	0.9500	C(33)-H(33)	0.9500
C(16A)-C(24A)	1.408(10)	C(34)-H(34)	0.9500
C(16A)-C(17A)	1.423(11)	C(35)-C(36)	1.449(4)
C(17A)-C(18A)	1.324(13)	C(37)-C(38)	1.390(4)
C(17A)-H(17A)	0.9500	C(37)-H(37)	0.9500
C(18A)-C(19A)	1.437(15)	C(38)-C(39)	1.368(4)
C(18A)-H(18A)	0.9500	C(38)-H(38)	0.9500
C(19A)-C(23A)	1.396(13)	C(39)-C(40)	1.404(4)
C(19A)-C(20A)	1.411(17)	C(39)-H(39)	0.9500
C(20A)-C(21A)	1.42(2)	C(40)-C(48)	1.411(4)
C(20A)-H(20A)	0.9500	C(40)-C(41)	1.427(4)
C(21A)-C(22A)	1.38(2)	C(41)-C(42)	1.342(4)
C(21A)-H(21A)	0.9500	C(41)-H(41)	0.9500
C(22A)-H(22A)	0.9500	C(42)-C(43)	1.431(4)
C(23A)-C(24A)	1.465(15)	C(42)-H(42)	0.9500
Cu(2)-N(5)#1	1.8659(15)	C(43)-C(44)	1.401(4)
Cu(2)-N(5)	1.8659(15)	C(43)-C(47)	1.414(3)
N(5)-C(25)	1.390(2)	C(44)-C(45)	1.363(4)

N(5)-C(31)	1.400(2)
C(25)-C(30)	1.400(3)
C(25)-C(26)	1.403(3)
C(26)-C(27)	1.387(3)
C(26)-H(26)	0.9500
C(27)-C(28)	1.371(3)
C(27)-H(27)	0.9500
C(28)-C(29)	1.391(3)
C(28)-H(28)	0.9500
C(29)-C(30)	1.378(3)
C(29)-H(29)	0.9500
C(30)-H(30)	0.9500
C(31)-C(36)	1.400(3)
C(31)-C(32)	1.401(3)
C(32)-C(33)	1.382(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.384(3)
C(33)-H(33)	0.9500
C(34)-C(35)	1.380(3)
C(34)-H(34)	0.9500
C(35)-C(36)	1.381(3)
C(35)-H(35)	0.9500
C(36)-H(36)	0.9500

N(3)-Cu(1)-N(1)	152.1(4)
N(3)-Cu(1)-N(4)	86.3(6)
N(1)-Cu(1)-N(4)	109.3(7)
N(3)-Cu(1)-N(2)	125.3(7)
N(1)-Cu(1)-N(2)	77.0(6)
N(4)-Cu(1)-N(2)	96.8(4)
C(1)-N(1)-C(12)	117.6(8)
C(1)-N(1)-Cu(1)	129.4(8)
C(12)-N(1)-Cu(1)	112.7(7)
C(11)-N(2)-C(10)	119.6(15)
C(11)-N(2)-Cu(1)	116.4(12)
C(10)-N(2)-Cu(1)	122.2(12)
N(1)-C(1)-C(2)	123.6(10)

C(44)-H(44)	0.9500
C(45)-C(46)	1.398(4)
C(45)-H(45)	0.9500
C(46)-H(46)	0.9500
C(47)-C(48)	1.451(4)
C(49)-C(50)	1.397(4)
C(49)-H(49)	0.9500
C(50)-C(51)	1.361(4)
C(50)-H(50)	0.9500
C(51)-C(52)	1.401(4)
C(51)-H(51)	0.9500
C(52)-C(53)	1.425(4)
C(52)-C(60)	1.426(4)
C(53)-C(54)	1.340(4)
C(53)-H(53)	0.9500
C(54)-C(55)	1.429(4)
C(54)-H(54)	0.9500
C(55)-C(56)	1.396(4)
C(55)-C(59)	1.408(3)
C(56)-C(57)	1.359(4)
C(56)-H(56)	0.9500
C(57)-C(58)	1.397(4)
C(57)-H(57)	0.9500
C(58)-H(58)	0.9500
C(59)-C(60)	1.449(4)

N(1)-Cu(1)-N(2)	176.45(10)
C(1)-N(1)-C(7)	118.5(2)
C(1)-N(1)-Cu(1)	122.30(17)
C(7)-N(1)-Cu(1)	119.04(17)
C(19)-N(2)-C(13)	120.9(2)
C(19)-N(2)-Cu(1)	121.22(17)
C(13)-N(2)-Cu(1)	117.70(17)
N(1)-C(1)-C(2)	120.7(2)
N(1)-C(1)-C(6)	122.7(2)
C(2)-C(1)-C(6)	116.5(2)
C(3)-C(2)-C(1)	121.4(3)

N(1)-C(1)-H(1)	118.2	C(3)-C(2)-H(2)	119.3
C(2)-C(1)-H(1)	118.2	C(1)-C(2)-H(2)	119.3
C(3)-C(2)-C(1)	119.5(10)	C(4)-C(3)-C(2)	120.7(3)
C(3)-C(2)-H(2)	120.3	C(4)-C(3)-H(3)	119.6
C(1)-C(2)-H(2)	120.3	C(2)-C(3)-H(3)	119.6
C(2)-C(3)-C(4)	120.2(9)	C(3)-C(4)-C(5)	119.2(3)
C(2)-C(3)-H(3)	119.9	C(3)-C(4)-H(4)	120.4
C(4)-C(3)-H(3)	119.9	C(5)-C(4)-H(4)	120.4
C(12)-C(4)-C(5)	119.6(11)	C(6)-C(5)-C(4)	120.2(3)
C(12)-C(4)-C(3)	115.4(10)	C(6)-C(5)-H(5)	119.9
C(5)-C(4)-C(3)	124.9(10)	C(4)-C(5)-H(5)	119.9
C(6)-C(5)-C(4)	120.6(10)	C(5)-C(6)-C(1)	121.9(3)
C(6)-C(5)-H(5)	119.7	C(5)-C(6)-H(6)	119.1
C(4)-C(5)-H(5)	119.7	C(1)-C(6)-H(6)	119.1
C(5)-C(6)-C(7)	120.7(11)	C(12)-C(7)-N(1)	120.3(2)
C(5)-C(6)-H(6)	119.7	C(12)-C(7)-C(8)	116.7(2)
C(7)-C(6)-H(6)	119.7	N(1)-C(7)-C(8)	122.8(2)
C(8)-C(7)-C(11)	117.6(13)	C(9)-C(8)-C(7)	121.3(2)
C(8)-C(7)-C(6)	123.6(13)	C(9)-C(8)-H(8)	119.3
C(11)-C(7)-C(6)	118.8(13)	C(7)-C(8)-H(8)	119.3
C(9)-C(8)-C(7)	122.6(17)	C(8)-C(9)-C(10)	121.0(3)
C(9)-C(8)-H(8)	118.7	C(8)-C(9)-H(9)	119.5
C(7)-C(8)-H(8)	118.7	C(10)-C(9)-H(9)	119.5
C(8)-C(9)-C(10)	117.3(18)	C(11)-C(10)-C(9)	118.7(3)
C(8)-C(9)-H(9)	121.4	C(11)-C(10)-H(10)	120.6
C(10)-C(9)-H(9)	121.4	C(9)-C(10)-H(10)	120.6
C(9)-C(10)-N(2)	116.0(17)	C(10)-C(11)-C(12)	121.0(3)
C(9)-C(10)-H(10)	122.0	C(10)-C(11)-H(11)	119.5
N(2)-C(10)-H(10)	122.0	C(12)-C(11)-H(11)	119.5
N(2)-C(11)-C(7)	122.7(15)	C(11)-C(12)-C(7)	121.3(3)
N(2)-C(11)-C(12)	115.5(12)	C(11)-C(12)-H(12)	119.4
C(7)-C(11)-C(12)	120.9(11)	C(7)-C(12)-H(12)	119.4
N(1)-C(12)-C(4)	123.6(10)	N(2)-C(13)-C(14)	119.2(2)
N(1)-C(12)-C(11)	117.5(8)	N(2)-C(13)-C(18)	124.9(2)
C(4)-C(12)-C(11)	118.8(10)	C(14)-C(13)-C(18)	115.7(3)
C(13)-N(3)-C(24)	115.8(8)	C(15)-C(14)-C(13)	122.2(3)
C(13)-N(3)-Cu(1)	129.5(9)	C(15)-C(14)-H(14)	118.9

C(24)-N(3)-Cu(1)	112.6(8)	C(13)-C(14)-H(14)	118.9
C(22)-N(4)-C(23)	114.3(15)	C(14)-C(15)-C(16)	121.0(3)
C(22)-N(4)-Cu(1)	140.8(17)	C(14)-C(15)-H(15)	119.5
C(23)-N(4)-Cu(1)	101.6(9)	C(16)-C(15)-H(15)	119.5
N(3)-C(13)-C(14)	122.8(10)	C(17)-C(16)-C(15)	117.8(3)
N(3)-C(13)-H(13)	118.6	C(17)-C(16)-H(16)	121.1
C(14)-C(13)-H(13)	118.6	C(15)-C(16)-H(16)	121.1
C(15)-C(14)-C(13)	120.3(10)	C(18)-C(17)-C(16)	121.6(3)
C(15)-C(14)-H(14)	119.9	C(18)-C(17)-H(17)	119.2
C(13)-C(14)-H(14)	119.9	C(16)-C(17)-H(17)	119.2
C(14)-C(15)-C(16)	119.9(9)	C(17)-C(18)-C(13)	121.7(3)
C(14)-C(15)-H(15)	120.0	C(17)-C(18)-H(18)	119.1
C(16)-C(15)-H(15)	120.0	C(13)-C(18)-H(18)	119.1
C(15)-C(16)-C(24)	116.1(9)	N(2)-C(19)-C(24)	120.0(2)
C(15)-C(16)-C(17)	124.8(9)	N(2)-C(19)-C(20)	124.2(2)
C(24)-C(16)-C(17)	119.0(9)	C(24)-C(19)-C(20)	115.7(2)
C(18)-C(17)-C(16)	122.8(10)	C(21)-C(20)-C(19)	121.7(3)
C(18)-C(17)-H(17)	118.6	C(21)-C(20)-H(20)	119.2
C(16)-C(17)-H(17)	118.6	C(19)-C(20)-H(20)	119.2
C(17)-C(18)-C(19)	120.6(10)	C(20)-C(21)-C(22)	121.6(3)
C(17)-C(18)-H(18)	119.7	C(20)-C(21)-H(21)	119.2
C(19)-C(18)-H(18)	119.7	C(22)-C(21)-H(21)	119.2
C(23)-C(19)-C(20)	117.2(13)	C(21)-C(22)-C(23)	117.8(3)
C(23)-C(19)-C(18)	119.5(12)	C(21)-C(22)-H(22)	121.1
C(20)-C(19)-C(18)	123.0(11)	C(23)-C(22)-H(22)	121.1
C(19)-C(20)-C(21)	116.1(15)	C(24)-C(23)-C(22)	121.2(3)
C(19)-C(20)-H(20)	121.9	C(24)-C(23)-H(23)	119.4
C(21)-C(20)-H(20)	121.9	C(22)-C(23)-H(23)	119.4
C(22)-C(21)-C(20)	121.3(17)	C(23)-C(24)-C(19)	122.0(3)
C(22)-C(21)-H(21)	119.3	C(23)-C(24)-H(24)	119.0
C(20)-C(21)-H(21)	119.3	C(19)-C(24)-H(24)	119.0
N(4)-C(22)-C(21)	129(2)	N(6)-K(1)-N(5)	59.04(6)
N(4)-C(22)-H(22)	115.7	N(6)-K(1)-N(3)	94.27(6)
C(21)-C(22)-H(22)	115.7	N(5)-K(1)-N(3)	124.09(7)
C(19)-C(23)-C(24)	119.4(10)	N(6)-K(1)-N(4)	123.75(7)
C(19)-C(23)-N(4)	122.1(12)	N(5)-K(1)-N(4)	94.85(6)
C(24)-C(23)-N(4)	118.4(10)	N(3)-K(1)-N(4)	58.11(6)

N(3)-C(24)-C(16)	124.7(10)	N(6)-K(1)-N(8)	157.93(7)
N(3)-C(24)-C(23)	116.5(8)	N(5)-K(1)-N(8)	107.18(6)
C(16)-C(24)-C(23)	118.6(9)	N(3)-K(1)-N(8)	107.77(6)
N(3A)-Cu(1A)-N(1A)	150.8(5)	N(4)-K(1)-N(8)	71.54(7)
N(3A)-Cu(1A)-N(4A)	86.9(6)	N(6)-K(1)-N(7)	135.72(6)
N(1A)-Cu(1A)-N(4A)	109.2(7)	N(5)-K(1)-N(7)	161.99(6)
N(3A)-Cu(1A)-N(2A)	126.9(7)	N(3)-K(1)-N(7)	70.09(7)
N(1A)-Cu(1A)-N(2A)	76.7(5)	N(4)-K(1)-N(7)	83.66(6)
N(4A)-Cu(1A)-N(2A)	96.5(4)	N(8)-K(1)-N(7)	55.28(6)
C(1A)-N(1A)-C(12A)	117.6(7)	N(6)-K(1)-N(8)#1	69.95(6)
C(1A)-N(1A)-Cu(1A)	129.3(7)	N(5)-K(1)-N(8)#1	99.73(6)
C(12A)-N(1A)-Cu(1A)	112.2(6)	N(3)-K(1)-N(8)#1	116.77(6)
C(11A)-N(2A)-C(10A)	119.8(15)	N(4)-K(1)-N(8)#1	164.14(6)
C(11A)-N(2A)-Cu(1A)	115.3(11)	N(8)-K(1)-N(8)#1	98.00(6)
C(10A)-N(2A)-Cu(1A)	121.7(13)	N(7)-K(1)-N(8)#1	80.54(6)
N(1A)-C(1A)-C(2A)	123.4(9)	N(6)-K(1)-N(7)#1	81.19(6)
N(1A)-C(1A)-H(1A)	118.3	N(5)-K(1)-N(7)#1	64.16(6)
C(2A)-C(1A)-H(1A)	118.3	N(3)-K(1)-N(7)#1	166.56(6)
C(3A)-C(2A)-C(1A)	119.9(9)	N(4)-K(1)-N(7)#1	134.61(6)
C(3A)-C(2A)-H(2A)	120.0	N(8)-K(1)-N(7)#1	77.03(6)
C(1A)-C(2A)-H(2A)	120.0	N(7)-K(1)-N(7)#1	104.41(5)
C(2A)-C(3A)-C(4A)	119.7(9)	N(8)#1-K(1)-N(7)#1	49.79(6)
C(2A)-C(3A)-H(3A)	120.1	N(6)-K(1)-K(1)#1	114.51(5)
C(4A)-C(3A)-H(3A)	120.1	N(5)-K(1)-K(1)#1	110.53(5)
C(12A)-C(4A)-C(5A)	119.7(9)	N(3)-K(1)-K(1)#1	125.37(5)
C(12A)-C(4A)-C(3A)	115.5(9)	N(4)-K(1)-K(1)#1	121.44(5)
C(5A)-C(4A)-C(3A)	124.5(9)	N(8)-K(1)-K(1)#1	51.03(5)
C(6A)-C(5A)-C(4A)	121.4(9)	N(7)-K(1)-K(1)#1	56.67(5)
C(6A)-C(5A)-H(5A)	119.3	N(8)#1-K(1)-K(1)#1	46.97(4)
C(4A)-C(5A)-H(5A)	119.3	N(7)#1-K(1)-K(1)#1	47.74(4)
C(5A)-C(6A)-C(7A)	120.0(10)	C(25)-N(3)-C(36)	117.3(2)
C(5A)-C(6A)-H(6A)	120.0	C(25)-N(3)-K(1)	120.78(18)
C(7A)-C(6A)-H(6A)	120.0	C(36)-N(3)-K(1)	113.53(16)
C(8A)-C(7A)-C(11A)	118.5(13)	C(34)-N(4)-C(35)	117.6(2)
C(8A)-C(7A)-C(6A)	122.0(12)	C(34)-N(4)-K(1)	121.83(18)
C(11A)-C(7A)-C(6A)	119.1(11)	C(35)-N(4)-K(1)	112.09(16)
C(9A)-C(8A)-C(7A)	122.3(15)	C(37)-N(5)-C(48)	117.3(2)

C(9A)-C(8A)-H(8A)	118.8
C(7A)-C(8A)-H(8A)	118.8
C(8A)-C(9A)-C(10A)	117.1(18)
C(8A)-C(9A)-H(9A)	121.4
C(10A)-C(9A)-H(9A)	121.4
C(9A)-C(10A)-N(2A)	117.3(18)
C(9A)-C(10A)-H(10A)	121.3
N(2A)-C(10A)-H(10A)	121.3
N(2A)-C(11A)-C(7A)	123.8(14)
N(2A)-C(11A)-C(12A)	115.2(11)
C(7A)-C(11A)-C(12A)	120.9(10)
N(1A)-C(12A)-C(4A)	123.6(9)
N(1A)-C(12A)-C(11A)	117.7(7)
C(4A)-C(12A)-C(11A)	118.6(9)
C(13A)-N(3A)-C(24A)	116.1(7)
C(13A)-N(3A)-Cu(1A)	130.1(7)
C(24A)-N(3A)-Cu(1A)	113.8(7)
C(22A)-N(4A)-C(23A)	114.3(15)
C(22A)-N(4A)-Cu(1A)	141.3(17)
C(23A)-N(4A)-Cu(1A)	102.3(9)
N(3A)-C(13A)-C(14A)	122.5(8)
N(3A)-C(13A)-H(13A)	118.8
C(14A)-C(13A)-H(13A)	118.8
C(15A)-C(14A)-C(13A)	120.2(9)
C(15A)-C(14A)-H(14A)	119.9
C(13A)-C(14A)-H(14A)	119.9
C(14A)-C(15A)-C(16A)	120.2(8)
C(14A)-C(15A)-H(15A)	119.9
C(16A)-C(15A)-H(15A)	119.9
C(15A)-C(16A)-C(24A)	116.0(9)
C(15A)-C(16A)-C(17A)	124.7(8)
C(24A)-C(16A)-C(17A)	119.3(9)
C(18A)-C(17A)-C(16A)	122.9(9)
C(18A)-C(17A)-H(17A)	118.6
C(16A)-C(17A)-H(17A)	118.6
C(17A)-C(18A)-C(19A)	120.1(9)
C(17A)-C(18A)-H(18A)	119.9
C(37)-N(5)-K(1)	122.18(17)
C(48)-N(5)-K(1)	117.29(16)
C(46)-N(6)-C(47)	117.7(2)
C(46)-N(6)-K(1)	121.52(17)
C(47)-N(6)-K(1)	116.92(15)
C(49)-N(7)-C(60)	117.3(2)
C(49)-N(7)-K(1)	120.83(17)
C(60)-N(7)-K(1)	110.19(15)
C(49)-N(7)-K(1)#1	121.41(18)
C(60)-N(7)-K(1)#1	103.78(15)
K(1)-N(7)-K(1)#1	75.59(5)
C(58)-N(8)-C(59)	117.2(2)
C(58)-N(8)-K(1)	115.81(18)
C(59)-N(8)-K(1)	113.02(16)
C(58)-N(8)-K(1)#1	111.13(18)
C(59)-N(8)-K(1)#1	112.45(16)
K(1)-N(8)-K(1)#1	82.00(6)
N(3)-C(25)-C(26)	124.7(3)
N(3)-C(25)-H(25)	117.6
C(26)-C(25)-H(25)	117.6
C(27)-C(26)-C(25)	118.3(3)
C(27)-C(26)-H(26)	120.8
C(25)-C(26)-H(26)	120.8
C(26)-C(27)-C(28)	119.6(3)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(27)-C(28)-C(36)	118.1(2)
C(27)-C(28)-C(29)	122.3(3)
C(36)-C(28)-C(29)	119.6(2)
C(30)-C(29)-C(28)	120.9(3)
C(30)-C(29)-H(29)	119.5
C(28)-C(29)-H(29)	119.5
C(29)-C(30)-C(31)	121.0(2)
C(29)-C(30)-H(30)	119.5
C(31)-C(30)-H(30)	119.5
C(35)-C(31)-C(32)	118.0(2)
C(35)-C(31)-C(30)	120.3(2)

C(19A)-C(18A)-H(18A)	119.9
C(23A)-C(19A)-C(20A)	117.3(12)
C(23A)-C(19A)-C(18A)	119.8(11)
C(20A)-C(19A)-C(18A)	122.7(10)
C(19A)-C(20A)-C(21A)	115.8(15)
C(19A)-C(20A)-H(20A)	122.1
C(21A)-C(20A)-H(20A)	122.1
C(22A)-C(21A)-C(20A)	121.6(18)
C(22A)-C(21A)-H(21A)	119.2
C(20A)-C(21A)-H(21A)	119.2
N(4A)-C(22A)-C(21A)	128(2)
N(4A)-C(22A)-H(22A)	115.8
C(21A)-C(22A)-H(22A)	115.8
C(19A)-C(23A)-C(24A)	119.4(9)
C(19A)-C(23A)-N(4A)	122.1(12)
C(24A)-C(23A)-N(4A)	118.3(9)
N(3A)-C(24A)-C(16A)	124.4(9)
N(3A)-C(24A)-C(23A)	117.2(7)
C(16A)-C(24A)-C(23A)	118.2(8)
N(5)#1-Cu(2)-N(5)	180.0
C(25)-N(5)-C(31)	118.32(15)
C(25)-N(5)-Cu(2)	123.25(12)
C(31)-N(5)-Cu(2)	118.41(12)
N(5)-C(25)-C(30)	123.01(17)
N(5)-C(25)-C(26)	120.33(17)
C(30)-C(25)-C(26)	116.61(18)
C(27)-C(26)-C(25)	121.2(2)
C(27)-C(26)-H(26)	119.4
C(25)-C(26)-H(26)	119.4
C(28)-C(27)-C(26)	121.2(2)
C(28)-C(27)-H(27)	119.4
C(26)-C(27)-H(27)	119.4
C(27)-C(28)-C(29)	118.6(2)
C(27)-C(28)-H(28)	120.7
C(29)-C(28)-H(28)	120.7
C(30)-C(29)-C(28)	120.7(2)
C(30)-C(29)-H(29)	119.6
C(32)-C(31)-C(30)	121.7(2)
C(33)-C(32)-C(31)	119.1(2)
C(33)-C(32)-H(32)	120.4
C(31)-C(32)-H(32)	120.4
C(32)-C(33)-C(34)	118.6(3)
C(32)-C(33)-H(33)	120.7
C(34)-C(33)-H(33)	120.7
N(4)-C(34)-C(33)	124.4(3)
N(4)-C(34)-H(34)	117.8
C(33)-C(34)-H(34)	117.8
N(4)-C(35)-C(31)	122.2(2)
N(4)-C(35)-C(36)	119.1(2)
C(31)-C(35)-C(36)	118.7(2)
N(3)-C(36)-C(28)	121.9(2)
N(3)-C(36)-C(35)	118.6(2)
C(28)-C(36)-C(35)	119.4(2)
N(5)-C(37)-C(38)	124.6(3)
N(5)-C(37)-H(37)	117.7
C(38)-C(37)-H(37)	117.7
C(39)-C(38)-C(37)	118.3(3)
C(39)-C(38)-H(38)	120.8
C(37)-C(38)-H(38)	120.8
C(38)-C(39)-C(40)	119.7(3)
C(38)-C(39)-H(39)	120.1
C(40)-C(39)-H(39)	120.1
C(39)-C(40)-C(48)	117.7(2)
C(39)-C(40)-C(41)	121.9(2)
C(48)-C(40)-C(41)	120.4(2)
C(42)-C(41)-C(40)	120.6(3)
C(42)-C(41)-H(41)	119.7
C(40)-C(41)-H(41)	119.7
C(41)-C(42)-C(43)	121.5(2)
C(41)-C(42)-H(42)	119.3
C(43)-C(42)-H(42)	119.3
C(44)-C(43)-C(47)	117.8(2)
C(44)-C(43)-C(42)	122.6(2)
C(47)-C(43)-C(42)	119.6(2)

C(28)-C(29)-H(29)	119.6
C(29)-C(30)-C(25)	121.71(19)
C(29)-C(30)-H(30)	119.1
C(25)-C(30)-H(30)	119.1
C(36)-C(31)-N(5)	120.40(17)
C(36)-C(31)-C(32)	116.69(17)
N(5)-C(31)-C(32)	122.76(17)
C(33)-C(32)-C(31)	121.28(18)
C(33)-C(32)-H(32)	119.4
C(31)-C(32)-H(32)	119.4
C(32)-C(33)-C(34)	120.87(19)
C(32)-C(33)-H(33)	119.6
C(34)-C(33)-H(33)	119.6
C(35)-C(34)-C(33)	118.81(19)
C(35)-C(34)-H(34)	120.6
C(33)-C(34)-H(34)	120.6
C(34)-C(35)-C(36)	120.53(19)
C(34)-C(35)-H(35)	119.7
C(36)-C(35)-H(35)	119.7
C(35)-C(36)-C(31)	121.81(18)
C(35)-C(36)-H(36)	119.1
C(31)-C(36)-H(36)	119.1
C(45)-C(44)-C(43)	120.2(2)
C(45)-C(44)-H(44)	119.9
C(43)-C(44)-H(44)	119.9
C(44)-C(45)-C(46)	117.7(3)
C(44)-C(45)-H(45)	121.1
C(46)-C(45)-H(45)	121.1
N(6)-C(46)-C(45)	124.7(3)
N(6)-C(46)-H(46)	117.7
C(45)-C(46)-H(46)	117.7
N(6)-C(47)-C(43)	121.8(2)
N(6)-C(47)-C(48)	119.1(2)
C(43)-C(47)-C(48)	119.0(2)
N(5)-C(48)-C(40)	122.4(2)
N(5)-C(48)-C(47)	118.8(2)
C(40)-C(48)-C(47)	118.8(2)
N(7)-C(49)-C(50)	124.5(3)
N(7)-C(49)-H(49)	117.7
C(50)-C(49)-H(49)	117.7
C(51)-C(50)-C(49)	118.4(3)
C(51)-C(50)-H(50)	120.8
C(49)-C(50)-H(50)	120.8
C(50)-C(51)-C(52)	119.9(3)
C(50)-C(51)-H(51)	120.0
C(52)-C(51)-H(51)	120.0
C(51)-C(52)-C(53)	123.0(2)
C(51)-C(52)-C(60)	117.5(2)
C(53)-C(52)-C(60)	119.5(2)
C(54)-C(53)-C(52)	121.5(2)
C(54)-C(53)-H(53)	119.2
C(52)-C(53)-H(53)	119.2
C(53)-C(54)-C(55)	121.1(2)
C(53)-C(54)-H(54)	119.5
C(55)-C(54)-H(54)	119.5
C(56)-C(55)-C(59)	117.6(2)
C(56)-C(55)-C(54)	122.5(2)
C(59)-C(55)-C(54)	119.9(2)
C(57)-C(56)-C(55)	120.5(3)

		C(57)-C(56)-H(56)	119.8
		C(55)-C(56)-H(56)	119.8
		C(56)-C(57)-C(58)	117.8(3)
		C(56)-C(57)-H(57)	121.1
		C(58)-C(57)-H(57)	121.1
		N(8)-C(58)-C(57)	124.6(3)
		N(8)-C(58)-H(58)	117.7
		C(57)-C(58)-H(58)	117.7
		N(8)-C(59)-C(55)	122.3(2)
		N(8)-C(59)-C(60)	118.4(2)
		C(55)-C(59)-C(60)	119.3(2)
		N(7)-C(60)-C(52)	122.3(2)
		N(7)-C(60)-C(59)	119.0(2)
		C(52)-C(60)-C(59)	118.7(2)

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