Supporting Information for

Copper Complexes of Anionic Nitrogen Ligands in the Amidation and Imidation of Aryl Halides

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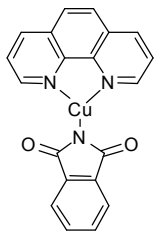
General Experimental Procedure and Reagent Availability

All manipulations were carried out under an inert atmosphere using a nitrogen-filled glovebox or standard Schlenk techniques. All glassware was oven or flame dried immediately prior to use. Tetrahydrofuran and diethyl ether were obtained as HPLC grade without inhibitors; dichloromethane, pentane, and benzene 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. Tetrahydrofuran-d_8, toluene-d_8, and C_6D_6 were dried with sodium/benzophenone ketyl and vacuum transferred prior to use. CD_2Cl_2 was dried over CaH_2 and vacuum transferred prior to use. DMSO-d_6 was stirred over CaH_2 for 24 h, distilled and stored over activated 4 Å molecular sieves. DMF-d_7 was stirred for 12 h each over three successive batches of activated 4 Å molecular sieves. Tetrabutylammonium phthalimidate[1] copper t-butoxide[2,3] ($[Cu(OtBu)]_4$), ortho-allyloxy iodobenzene[4], and 3-methyl-2,3 dihydrobenzofuran[5] were prepared using the reported procedures. All other reagents and solvents were obtained from commercial sources and used without further purification.

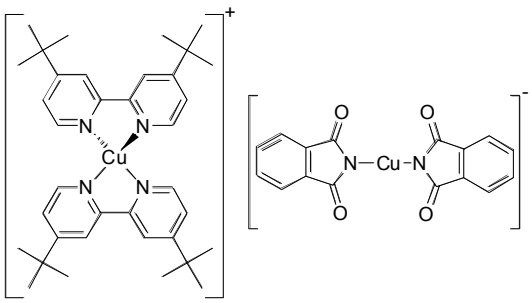
^{1}H NMR spectra were obtained at 400 or 500 MHz and recorded relative to residual protio-solvent. ^{13}C NMR spectra were obtained at 126 MHz, and chemical shifts were recorded relative to the solvent resonance. ^{31}P NMR spectra were obtained at 202 MHz and chemical shifts are reported relative to 85% H_3PO_4. ^{15}N NMR spectra were obtained at 61 MHz, and chemical shifts are reported relative to neat nitromethane.

Preparation of (phthalimidato)Cu(1,10-phenanthroline) (1a).



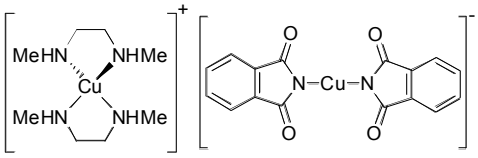
Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed $[Cu(OtBu)]_4$ (80. mg, 0.15 mmol) and 1,10-phenanthroline (106 mg, 0.582 mmol). THF (5 mL) was added, and the solution was stirred for 5 min. A solution of phthalimide (86 mg, 0.59 mmol) in 1 mL of THF was added, and the resulting solution was stirred for 20 min. After 20 min of stirring, the desired complex had precipitated from solution and was separated from the supernatant by filtration through a fine fritted funnel. The resulting residue was recrystallized by layering a 1:4 THF/DMSO solution with Et_2O at room temperature to afford 192 mg (84%) of **1a**. Single crystals suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **1a** in a 1:4 mixture of THF and DMSO. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.60 (m, 4H), 8.06 (br s, 2H), 8.30 (br s, 2H), 8.86 (d, J = 7.0 Hz, 2H), 9.05 (br s, 2H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 121.0, 125.6, 126.9, 128.9, 132.1, 136.1, 137.1, 143.0, 149.5, 179.4; Anal. Calcd for $C_{20}H_{12}CuN_3O_3$: C, 61.61; H, 3.10; N, 10.78. Found: C, 61.38; H, 2.93; N, 10.57.

Preparation of [bis(4,4'-di-tert-butyl-2,2'-bipyridine)Cu][bis(phthalimidato)Cu] (1b).



Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed $[Cu(OtBu)]_4$ (80. mg, 0.15 mmol) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (157 mg, 0.59 mmol). THF (5 mL) was added, and the solution was stirred for 10 min. A solution of phthalimide (86 mg, 0.59 mmol) in 1 mL of THF was added, and the resulting solution was stirred for 20 min. After 20 min of stirring, the solution was filtered through Celite, concentrated, layered with

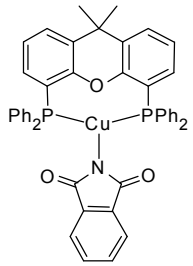
pentane, and cooled at -35 °C for 12 h. The resulting red/brown crystals were separated from the supernatant, washed with 2 x 10 mL pentane, and dried to give 252 mg (90%) of **1b**. Single crystals suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **1b** in benzene. ^{1}H NMR (500 MHz, THF-d_8) δ 1.43 (s, 18H), 7.49 (br s, 4H), 7.59 (d, J = 5.5 Hz, 2H), 8.45 (s, 2H), 8.90 (br s, 2H); ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 30.6, 36.2, 119.3, 121.6, 123.9, 131.9, 138.7, 150.7, 153.6, 163.7, 180.8; Anal. Calcd for $C_{26}H_{28}CuN_3O_2$: C, 65.32; H, 5.90; N, 8.79. Found: C, 65.29; H, 5.81; N, 8.61.



Preparation of [bis(N,N'-dimethylethylenediamine)-Cu][bis(phthalimidato)Cu] (1c).

Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed [Cu(OtBu)]$_4$ (80. mg, 0.15 mmol) and *N*,*N*′-dimethylethylenediamine (62.4 μL , 0.579 mmol). THF (5 mL) was added, and the solution was stirred for 5 min. A solution of phthalimide (86 mg, 0.59 mmol) in 1 mL of THF was added, and the resulting solution was stirred for 20 min. After 20 min of stirring, the solution was filtered through Celite, concentrated, layered with ether and cooled at -35 °C for 12 h. The resulting orange crystals were separated from the supernatant by filtration through a fine fritted funnel, washed with 2 x 10 mL pentane, and dried to give 148 mg (85%) of **1c**. Single crystals for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **1c** in dioxane. Severe positional disorder of the dmeda ligands prevented a detailed structure solution. Despite the disorder, the connectivity of the compound was clearly determined to be [(dmeda)$_2$Cu][Cu(phth)$_2$]. ^{1}H NMR (500 MHz, THF-d_8) δ 2.58 (s, 6H), 2.72 (s, 4H), 3.32 (br s, 2H), 7.47 (br s, 2H), 7.53 (br s, 2H); ^{13}C{^{1}H} NMR (126 MHz, THF-d_8) δ 38.3, 51.5, 121.5, 131.9, 138.5, 180.6; Anal. Calcd for $C_{12}H_{16}CuN_3O_3$: C, 48.39; H, 5.42; N, 14.11. Found: C, 48.17; H, 5.28; N, 13.86.

Preparation of (phthalimidato)Cu(Xantphos) (1d).



Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed [Cu(OtBu)]$_4$ (40. mg, 0.072 mmol) and Xantphos (170 mg, 0.294 mmol). THF (3 mL) was added, and the solution was stirred for 5 min. A solution of phthalimide (43 mg, 0.29 mmol) in 1 mL of THF was added, and the resulting mixture was stirred for 20 min. All volatile materials were then removed in vacuo, and the resulting residue was dissolved in a minimal amount of dichloromethane, filtered through a plug of Celite, layered with diethyl ether, and cooled at -35 °C for 12 h. The resulting light yellow crystals were separated from the supernatant, washed with 2 x 10 mL pentane, and dried to give 201 mg (87%) of **1d**. Single crystals suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **1d** in dichloromethane. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.69 (s, 6H), 6.55 (ddd, J = 7.5, 4.4, 1.1 Hz, 2H), 7.13 (t, J = 7.7 Hz, 2H), 7.21 (t, J = 7.5 Hz, 8H), 7.28 (t, J = 7.3 Hz, 4H), 7.41-7.47 (m, 8H), 7.49 (dd, J = 5.3, 2.0 Hz, 2H), 7.56 (dd, J = 5.3, 3.1 Hz, 2H), 7.59 (dd, J = 7.8, 1.1 Hz, 2H); ^{13}C{^{1}H} NMR (126 MHz, CD_2Cl_2) δ 28.2, 86.2, 120.3 (t, J = 13.5 Hz), 121.0 124.9, 127.1, 128.8 (t, J = 4.9 Hz), 130.1, 131.5, 131.9, 132.2 (t, J = 17.6 Hz), 134.1, 134.1 (t, J = 8.3 Hz), 138.1, 155.5 (t, J = 6.1 Hz), 181.4; ^{31}P{^{1}H} NMR (202 MHz, CD_2Cl_2) δ -15.5 ; Anal. Calcd for $C_{47}H_{36}CuNO_3P_2$: C, 71.61; H, 4.60; N, 1.78. Found: C, 71.29; H, 4.79; N, 1.58.

Preparation of [bis(1,10-phenanthroline)Cu][bis(pyrrolidinone)Cu] (2a).

Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed $[Cu(OtBu)]_4$ (40. mg, 0.072 mmol) and 1,10-phenanthroline (53 mg, 0.29 mmol). THF (5 mL) was added, and the solution was stirred for 5 min. A solution of pyrrolidinone (25 mg, 0.29 mmol) in 1 mL of THF was added, and the resulting solution was stirred for 20 min. After 20 min of stirring, the desired complex had partially precipitated from solution. Pentane (4 mL) was added to the solution to yield more precipitate. The solution was filtered, and the resulting solid was washed with 2 x 5 mL of pentane or diethyl ether and dried under vacuum to obtain 95 mg (98%) of **2a**. Single crystals suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **2a** in DMSO. ^{1}H NMR (500 MHz, DMF-d_7) δ 1.86 (br s, 8H), 3.24 (br s, 4H), 8.10 (br s, 4H), 8.36 (br s, 4H), 8.92 (d, J = 7.9 Hz, 4H), 9.21 (br s, 4H); ^{13}C{^{1}H} NMR (126 MHz, DMF-d_7) δ 24.9, 32.4, 51.8, 126.1 127.6, 129.8, 137.8, 144.3, 150.2, 182.7; Anal. Calcd for $C_{32}H_{28}Cu_2N_6O_2$: C, 58.62; H, 4.30; N, 12.82 . Found: C, 58.34; H, 4.02; N, 12.48.

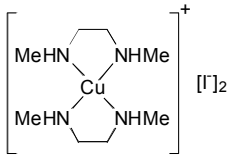
In situ generation of complex 2b.

Into a 4 mL vial, a solution of 2-pyrrolidinone (3.1 mg, 0.036 mmol) in 0.3 mL of tol-d_8 was added to a solution of $[Cu(OtBu)]_4$ (5.0 mg, 0.0092 mmol) in 0.5 mL of tol-d_8 at room temperature. The mixture was stirred for 10 min. A solution of dmeda (3.2 mg, 0.036 mmol, 1.0 equiv) in 0.2 mL tol-d_8 was added to the above mixture, and the resulting solution was stirred for 5 min. 1,3,5-trimethoxybenzene (3.4 mg, 0.020 mmol) as internal standard was added. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap. An ^{1}H NMR spectrum was acquired. (96 % NMR yield). ^{1}H NMR (400 MHz, tol-d_8) δ 0.1.70-1.74 (m, 4H), 2.14 (m, 2H), 2.23 (s, 6H), 2.39 (s, 4H), 3.29 (t, J = 6.8 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, tol-d_8) δ 25.0, 31.9, 36.9, 51.4, 52.8, 184.7.

Preparation of [tetra-n-butyl-ammonium][bis-(phthalimidato)Cu] (3).

Into a 20 mL scintillation vial equipped with a magnetic stirbar was placed $[Cu(OtBu)]_4$ (40. mg, 0.072 mmol) and tetrabutylammonium phthalimidate (114. mg, 0.293 mmol). THF (5 mL) was added, and the yellow solution was stirred for 5 min. A solution of phthalimide (40 mg, 0.30 mmol) in 2 mL of THF was added, and the resulting solution was stirred for 20 min. After 20 min of stirring, the solution had changed from yellow to clear. The desired complex had precipitated from solution and was separated from the supernatant. The resulting residue was washed with a 2 x 5 mL of THF, then 2 x 5 mL of pentane, and dried under vacuum to give 149 mg (85%) of **3**. In some preparations, this complex was further purified by dissolving **3** in a minumum of methylene chloride, and layering with ether. The resulting powder is washed with 2 x 10 mL of diethyl ether and dried under vacuum. ^{1}H NMR (500 MHz, DMSO-d_6) δ 0.89 (t, J = 7.4 Hz, 12H), 1.27 (br s, 8H), 1.54 (m, 8H), 3.30 (m, 8H) 7.60 (m, 8H); ^{13}C{^{1}H} NMR (126 MHz, DMSO-d_6) δ 13.4, 19.2, 23.0, 57.5 121.1, 132.3 136.1, 179.4; Anal. Calcd for $C_{32}H_{44}CuN_3O_4$: C, 64.24; H, 7.41; N, 7.02; Found: C, 64.30; H, 7.38; N, 7.06.

Isolation of complex [Cu(dmeda)$_2$][I]$_2$ (4) from the reaction of 1c and p-tolyl iodide.



A mixture of **1c** (35.2 mg, 0.120 mmol) and *p*-tolyl iodide (52.3 mg, 0.240 mmol) in 0.6 mL DMSO was stirred at room temperature for 3 h. The resulting blue mixture was filtered through a layer of Celite. To this filtrate was added 20 mL of ether, and the mixture was kept at room temperature for 30 min over which time a blue solid precipitated. The blue product was isolated by filtration and washed with diethyl ether and pentane and dried under vacuum to give 24.8 mg (0.050 mmol, 42 % yield). Single crystals suitable for X-ray diffraction were obtained by allowing diethyl ether to diffuse into a saturated solution of **4** in DMSO. ^{1}H NMR (400 MHz, DMSO-d_6): δ 3.51 (br, 4 H), 2.48 (br, overlapping with solvent), 2.35 (br, 12 H). Anal. Calcd for $C_8H_{24}CuN_4I_2$: C, 19.46; H, 4.90; N, 11.35. Found: C, 19.51; H 4.81, N 11.30.

Independent synthesis of complex [Cu(dmeda)$_2$]I$_2$ (4).

A mixture of CuI (50 mg, 0.26 mmol) and dmeda (23 mg, 0.26 mmol, 1.0 equiv) in 0.5 mL DMSO was stirred at room temperature for 20 h. The resulting blue cloudy mixture was filtered through a layer of Celite. To this filtrate was added 16 mL of ether to precipitate a blue solid. The product was washed with diethyl ether and pentane, and dried under vacuum to give 8.0 mg (0.016 mmol, 12 % yield).

Representative procedure for measuring the yield of 1a-1d and 2a with p-tolyl iodide.

Complex **1c** (8.8 mg, 0.030 mmol) and 1,3,5-trimethoxybenzene (5.0 mg, 0.030 mmol) as internal standard were weighed into a vial and dissolved in 0.7 mL of DMSO-d_6. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap. An initial ^{1}H NMR spectrum was acquired. *p*-tolyl iodide (32.7 mg, 0.15 mmol, 5.0 equiv) was then added by syringe as a DMSO-d_6 solution (0.1 mL), and the resulting mixture was left at room temperature for 2 h. A second ^{1}H NMR spectrum was acquired, and the yield of the *N*-*p*-tolyl phthalimide was calculated to be 95 %. [For reactions with **1a**, **1b**, and **1d**, the reaction mixture was transferred to an NMR tube, frozen in liquid nitrogen, sealed under vacuum, and heated at 120 °C in a temprature-controlled oil bath. The NMR tube was removed at regular intervals and ^{1}H-NMR spectra were acquired at 25 °C until the yield ceased changing. Yields ranged 92-99%.

Competition reaction of 2a and phen with p-tolyl iodide and o-tolyl iodide.

Into a small vial was placed [(phen)$_2$Cu][Cu(pyrr)$_2$] (**2a)** (7.8 mg, 0.012 mmol) and 1,10 phenanthroline (4.3 mg, 0.024 mmol). In a separate vial was placed *p*-tolyl iodide (104.8 mg, 0.4807 mmol), *o*-tolyl iodide (61.6 μL, 0.481 mmol), 2.0 mg of 1,3,5-trimethoxybenzene (as an internal standard) and 1.0 mL DMSO . The resulting DMSO solution was transferred to the vial containing **2a**. The vial was sealed with a Teflon screw cap, and the mixture was heated at 80 °C. At various time points, 0.1 mL of the reaction solution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Competition reaction of in situ generated 2b with p-tolyl iodide and o-tolyl iodide.

Into a small vial was placed [Cu(OtBu)]$_4$ (3.3 mg, 0.0060 mmol), dmeda (2.5 μL, 0.024 mmol), and pyrrolidinone (1.9 μL, 0.024 mmol), 2.0 mg of 1,3,5-trimethoxybenzene (as an internal standard) and 0.5 mL of DMSO was added. The resulting mixture is allowed to stir for 30 min.

In a separate small vial, *p*-tolyl iodide (104.8 mg, 0.4807 mmol), *o*-tolyl iodide (61.6 mg, 0.481 mmol), and 0.5 mL DMSO was added. The resulting DMSO solution was transferred to the other vial and this vial was sealed with a Teflon screw cap. The reaction mixture was stirred at 80 °C. At various time points, 0.1 mL of the solution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Competition reaction of pyrrolidinone with p-tolyl iodide and o-tolyl iodide catalyzed by CuI.

Into a small vial was placed CuI (2.4 mg, 0.012 mmol, 10 mol %), K_3PO_4 (53.0 mg, 0.250 mmol), 10.1 mg of 1,3,5-trimethoxybenzene (as an internal standard) and a teflon-coated stirbar. Into a separate vial, *p*-tolyl iodide (524.0 mg, 2.403 mmol), *o*-tolyl iodide (308 μL, 2.40 mmol), pyrrolidinone (10.2 mg, 0.120 mmol), and 0.5 mL DMSO was added. The resulting DMSO solution was transferred to the other vial and this vial was sealed with a Teflon screw cap. The reaction mixture was stirred at 80 °C. At various time points, 0.1 mL of the sol8ution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Competition reaction of pyrrolidinone with p-tolyl iodide and o-tolyl iodide catalyzed by 2a.

Into a small vial was placed $[(phen)_2Cu][Cu(pyrr)_2]$ (**2a)** (3.9 mg, 0.0059 mmol, 5 mol %), K_3PO_4 (53.0 mg, 0.250 mmol), 10.1 mg of 1,3,5-trimethoxybenzene (as an internal standard) and a teflon-coated stirbar. Into a separate small vial, *p*-tolyl iodide (524.0 mg, 2.403 mmol), *o*-tolyl iodide (308 μL, 2.40 mmol), pyrrolidinone (10.2 mg, 0.120 mmol), and 0.5 mL DMSO was added. The resulting DMSO solution was transferred to the other vial and this vial was sealed with a Teflon screw cap. The reaction mixture was stirred at 80 °C. At various time points 0.1 mL of the solution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Competition reaction of pyrrolidinone with p-tolyl iodide and o-tolyl iodide catalyzed by CuI/dmeda.

Into a small vial was placed CuI (2.4 mg, 0.012 mmol, 10 mol %), K_3PO_4 (53 mg, 0.25 mmol), 10.1 mg of 1,3,5-trimethoxybenzene (as an internal standard) and a teflon-coated stirbar. Into a separate small vial, dmeda (2.5 μL, 0.024 mmol, 20 mol %), *p*-tolyl iodide (524 mg, 2.40 mmol), *o*-tolyl iodide (308 μL, 2.40 mmol), pyrrolidinone (10.2 mg, 0.120 mmol) and 0.5 mL DMSO was added. The resulting DMSO solution was transferred to the other vial and the vial was sealed with a Teflon screw cap. The reaction mixture was stirred at 80 °C. At various time points, 0.1 mL of the solution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Procedure for the Attempted Reaction of 2a with 4-chlorobenzonitrile.

Complex **2a** (3.3 mg, 0.010 mmol) and 1,3,5-trimethoxybenzene (1.7 mg, 0.010 mmol) as internal standard were weighed into a vial and dissolved in 0.7 mL of DMSO-d_6. The contents of the vial were agitated and then transferred to an NMR tube, which was then sealed with a septum-lined screw-cap. An initial ^{1}H NMR spectrum was acquired. *4*-chlorobenzonitrile (6.9 mg, 0.050 mmol, 5.0 equiv) in DMSO-d_6 (0.1 mL) was then added by syringe, and the resulting mixture was heated at 110 °C for 2 h. A second ^{1}H NMR spectrum was acquired, and no trace of *N*-4-cyanophenyl pyrrolidinone was detected.

Procedure for the Attempted Reaction of In Situ Generated 2b with 4-chlorobenzonitrile.

Complex **2b** was generated in situ by the addition of 0.3 mL solution of 12 mg (0.022 mmol) of $[Cu(OtBu)]_4$ in toluene-d_8 to a solution of 7.5 mg (0.088 mmol) of pyrrolidinone in 0.2 mL of toluene-d_8. The resulting solution was stirred for 10 min. A solution of 7.7 mg (0.088 mmol) of dmeda in toluene-d_8 was added and the solution was stirred for and additional 5 min. This solution was transferred to a screw-capped NMR tube, and a ^{1}H-NMR spectrum was acquired. A solution of 12.5 mg (0.0909 mmol) of 4-chlorobenzonitrile and 1.7 mg of 1,3,5-trimethoxybenzene in 0.2 mL of toluene-d_8 was added. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap. The resulting mixture was heated at 110 °C for 2 h. A second ^{1}H NMR spectrum was acquired, and no trace of *N*-4-cyanophenyl pyrrolidinone was detectable.

Procedure for the Reaction of 2a with 1-bromonaphthalene.

Complex **2a** (3.3 mg, 0.010 mmol) and 1,3,5-trimethoxybenzene (1.8 mg) as internal standard were weighed into a vial and dissolved in 0.7 mL of DMSO-d_6. The contents of the vial were agitated and then transferred to an NMR tube, which was then sealed with a septum-lined screw-cap. An initial ^{1}H NMR spectrum was acquired. 1-Bromonaphthalene (10.4 mg, 0.0502 mmol, 5.0 equiv) in DMSO-d_6 (0.1 mL) was then added, and the resulting mixture was heated at 25 °C for 2 h. A second ^{1}H NMR spectrum was acquired, and the yield of *N*-1-naphthyl pyrrolidinone was determined to be 34%.

Procedure for the Reaction of In Situ Generated 2b with 1-bromonaphthalene.

Complex **2b** was generated in situ by the addition of 0.3 mL solution of 2.5 mg (0.0046 mmol) of $[Cu(OtBu)]_4$ in toluene-d_8 to a solution of 1.5 mg (0.018 mmol) of pyrrolidinone in 0.2 mL of toluene-d_8. The resulting solution was stirred for 10 min. A solution of 1.6 mg (0.018 mmol) of dmeda in toluene-d_8 was added, and the solution was stirred for an additional 5 min. A solution of 18.6 mg (0.0898 mmol) of 1-bromonapthalene and 2.9 mg of 1,3,5-trimethoxybenzene in 0.2 mL of toluene-d_8 was added. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap NMR tube. The resulting mixture was heated to 110 °C for 2 h. A second ^{1}H NMR spectrum was acquired, and the yield of *N*-1-naphthyl pyrrolidinone was determined to be 97%.

Procedure for the Reaction of In Situ Generated 2b with 2-bromonaphthalene.

Complex **2b** was generated in situ by the addition of 0.3 mL solution of 2.5 mg (0.0046 mmol) of $[Cu(OtBu)]_4$ in toluene-d_8 to a solution of 1.5 mg (0.018 mmol) of pyrrolidinone in 0.2 mL of toluene-d_8. The resulting solution was stirred for 10 min. A solution of 1.6 mg (0.018 mmol) of dmeda in toluene-d_8 was added, and the solution was stirred for and additional 5 min. A solution of 18.6 mg (0.0898 mmol) of 2-bromonapthalene and 1.8 mg of 1,3,5-trimethoxybenzene in 0.2 mL of toluene-d_8 was added. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap NMR tube. The resulting mixture was heated to 110 °C for 2 h. A second ^{1}H NMR spectrum was acquired, and the yield of *N*-1-naphthyl pyrrolidinone was determined to be 65%.

Procedure for attempted reaction of in situ-generated 2b with 1-naphthyl trifluoromethanesulfonate.

Complex **2b** was generated in situ by the addition of 0.3 mL solution of 25 mg (0.0045 mmol) of $[Cu(OtBu)]_4$ in toluene-d_8 to a solution of 1.6 mg (0.018 mmol) of pyrrolidinone in 0.2 mL of toluene-d_8. The resulting solution was stirred for 10 min. A solution of 1.6 mg (0.018 mmol) of dmeda in toluene-d_8 was added, and the solution was stirred for an additional 5 min. A solution of 24.9 mg (0.0901 mmol) of 1-naphthyl triflate and 1.9 mg of 1,3,5-trimethoxybenzene in 0.2 mL of toluene-d_8 was then added. The contents of the vial were agitated and transferred to an NMR tube containing a septum-lined screw-cap. A ^{1}H-NMR spectrum was acquired. The resulting mixture was then heated at 110 °C for 1 and 23 h, at which times ^{1}H NMR spectra were acquired. No *N*-1-naphthyl pyrrolidinone was detected by ^{1}H-NMR spectroscopy or GC.

Procedure for attempted reaction of 1c with p-tolyl trifluoromethanesulfonate.

Complex **1c** (4.4 mg, 0.015 mmol), *p*-tolyl trifluoromethanesulfonate (18 mg, 0.075 mmol, 5.0 equiv) and trimethoxybenzene (2.5 mg, 0.015 mmol) as internal standard were weighed into a vial and dissolved in 0.7 mL of DMSO-d_6. The contents of the vial were agitated and then transferred to an NMR tube containing a septum-lined screw-cap. An initial ^{1}H NMR spectrum was acquired. The resulting mixture was heated at 120 °C for 18 h. No *N*-*p*-tolyl phthalimide was detected by^{1}H NMR spectroscopy.

Procedure for the reaction of 2a with ortho-allyloxy iodobenzene.

Into a small vial was placed $[(phen)_2Cu][Cu(pyrr)_2]$ (**2a**) (10.0 mg, 0.0153 mmol), 7.1 mg of ortho-allyloxybenzene, 1.3 μL of 1,3-dimethoxybenzene (as an internal standard) and 0.7 mL of DMSO-d^6. The mixture was agitated and transferred to a screw-cap NMR tube. The NMR tube was heated in a silicon oil filled constant temperature bath. At various time points, the sample was removed from the oil bath, cooled by immersing in cold water, and a ^{1}H NMR spectrum was obtained at 25 °C. The final yield after 31h was 95.5 %. At the end of the reaction, 0.1 mL of the solution was withdrawn, diluted with THF, and the mixture was analyzed by GC and GC/MS. Comparison of the GC and GC/MS spectra to those of authentic sample of phenyl allyl ether and 3-methyl-2,3 dihydrobenzofuran showed that the sample contained 1.9 % yield of phenyl allyl ether.

Reaction of pyrrolidinone with ortho-allyloxy iodobenzene catalyzed by CuI/phen.

2-(allyloxy)-1-iodobenzene (31.2 mg, 0.120 mmol), 2-pyrrolidinone (9.3 μL 0.12 mmol), K_3PO_4 (53.0 mg, 0.250 mmol), CuI (2.4 mg, 0.024 mmol, 10 mol %), phen (4.3, 0.024 mmol, 20 mol %), and 10.1 mg of 1,3,5-trimethoxybenzene (as an internal standard) 0.5 mL of DMSO and a teflon-coated stir bar were added to 4mL screw-cap vial inside a nitrogen-filled glovebox. The vial was sealed by a Teflon-lined cap, removed from the glovebox and heated at 110 °C for 24 h in an oil-filled heating bath. The reaction was removed from the oil bath and allowed to cool to room temperature. At the end of the reaction, 0.1 mL of the solution was withdrawn, diluted with THF, and the mixture was analyzed by GC.

Synthesis of N-(2-allyloxy-phenyl) pyrrolidinone.

2-(allyloxy)-1-iodobenzene (135.2 mg, 0.5199 mmol), 2-pyrrolidinone (47 μL, 0.60 mmol), K_3PO_4 (225.0 mg, 1.060 mmol), CuI (10.0 mg, 0.0525 mmol, 10 mol %), N,N'-dimethylethylenediamine (12 μL, 0.11 mmol, 20 mol %), 0.5 mL of dioxane and a magnetic stir

bar were added to 4mL screw-cap vial inside a nitrogen-filled glovebox. The vial was sealed by a Teflon-lined cap, removed from the glovebox and heated at 110 °C for 24 h in an oil-filled heating bath. The reaction was removed from the oil bath and allowed to cool to room temperature. The reaction mixture was filtered through a 1 mm silica plug eluting with 5 mL of ethyl acetate. The solvents were removed on a rotary evaporator and the residue was taken up in 50 mL of ether. The ether solution was washed with 50 mL of brine and 3x50 mL of water, and the ether solution dried over Na_2SO_4. The ether solvent was removed to yield 43.1 mg (38.2 % yield) of a yellow liquid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24 (m, 2H), 6.96 (m, 2H), 6.02 (m, 1H), 5.38 (m, 1H), 5.26 (m, 1H), 4.55 (dt, J=1.5, 5.0 Hz), 3.77 (t, J=7.1 Hz, 2H), 2.54 (t, J=8.1 Hz), 2.17 (m, 2H).^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ 175.0, 153.6, 132.9, 128.6, 128.3, 127.4, 121.0, 117.1, 113.3, 69.0, 49.8, 31.1, 18.9. m/z (EIGCMS) 217.1 (M^+, 82%), 207.0 (24%), 202.1 (64%), 162.1 (100%)

Effect of added $LiBF_4$ on the reaction of 3 and p-tolyl iodide.

Complex **3** (7.2 mg, 0.012 mmol), *p*-tolyl iodide (140.0 mg, 0.6421 mmol), 2.6 mg of 1,3,5 trimethoxybenzene (as an internal standard) and 1.4 mL of DMSO-d_6 were transferred to a screw-capped vial, and the contents were agitated. A 0.7 mL portion of the solution was withdrawn with a syringe and transferred to a screw-cap vial containing $LiBF_4$ (1.2 mg, 0.013 mmol). This vial was agitated and its contents were transferred to screw-capped NMR tube. The remaining solution (without $LiBF_4$) was withdrawn by syringe and transferred to a screw-capped NMR tube. A ^{1}H-NMR spectrum was acquired for each sample. The NMR tubes were heated in a constant temperature bath filled with silicon oil at 120°C. At various time points, the samples were removed from the oil bath, cooled by immersing in cold water, and a ^{1}H NMR spectrum was obtained at 25 °C.

Effect of added KOTf on the reaction of 3 and p-tolyl iodide.

Complex **3** (3.9 mg, 0.0065 mmol), p-tolyl iodide (70.9 mg, 0.325 mmol), KOTf (3.1 mg, 0.016 mmol), 3.1 mg of 1,3,5 trimethoxybenzene (as an internal standard) and 0.7 mL of DMSO-d_6 were transferred to a screw-capped vial, and the contents were agitated. The solution was transferred to a screw-capped NMR tube. A ^{1}H-NMR spectrum was acquired. The NMR tube was heated in constant temperature bath filled with a silicon oil at 120°C. At various time points, the sample was removed from the oil bath, cooled by immersing in cold water, and ^{1}H NMR spectra were obtained at 25 °C.

Effect of added $LiBF_4$ on the reaction of 1c and p-tolyl iodide.

Complex **1c** (10.0 mg, 0.0167 mmol), p-tolyl iodide (140.5 mg, 0.6444 mmol), 2.8 mg of 1,3,5 trimethoxybenzene (as an internal standard) and 1.4 mL of DMSO-d_6 were transferred to a screw-cap vial, and the contents were agitated. A 0.7 mL portion of the solution was withdrawn by syringe and transferred to a screw-cap vial containing $LiBF_4$ (1.9 mg, 0.020 mmol). This vial was then agitated, and its contents were transferred to a screw-capped NMR tube. The remaining solution (without $LiBF_4$) was transferred to another screw-capped NMR tube. A ^{1}H-NMR spectrum was acquired for each sample. The NMR tubes were then heated in constant temperature bath filled with silicon oil at 120°C. At various time points, the samples were removed from the oil bath, cooled by immersing in cold water, and ^{1}H NMR spectra were obtained at 25 °C.

Representative Procedure for the Kinetic Experiments

Into a 1 mL volumetric flask was placed complex **1b** (8.7 mg, 0.0091 mmol) and 20-100 mg (0.092-0.459 mmol, 10-50 equiv) *p*-tolyl iodide. The solution was diluted to 1 mL by DMSO-d_6 and agitated until homogenous. A stock solution of 1,3,5-trimethoxybenzene for use as an internal standard was prepared by placing 128 mg of 1,3,5-trimethoxybenzene a 1mL volumetric flask and diluting to 1 mL by DMSO-d_6. To the DMSO solution was added 12 μL of the 1,3,5-trimethoxybenzene stock solution. The solution was transferred to an NMR tube, frozen in liquid nitrogen and sealed under vacuum. For reactions at 120.0 °C, the sample was placed into a thermostated oil bath at 120.0 °C. At fixed intervals, the sample was removed from the oil bath, cooled by immersing in cold water, and a ^{1}H NMR spectrum was obtained at 25 °C. For reactions at temperatures of 110 °C and below the data were acquired at fixed intervals as the sample was heated or cooled in the NMR spectrometer. This procedure was repeated using different initial concentrations of the copper complex **1b**, or *p*-tolyl iodide as indicated in Figures S1-S2 and Table SI-S2.

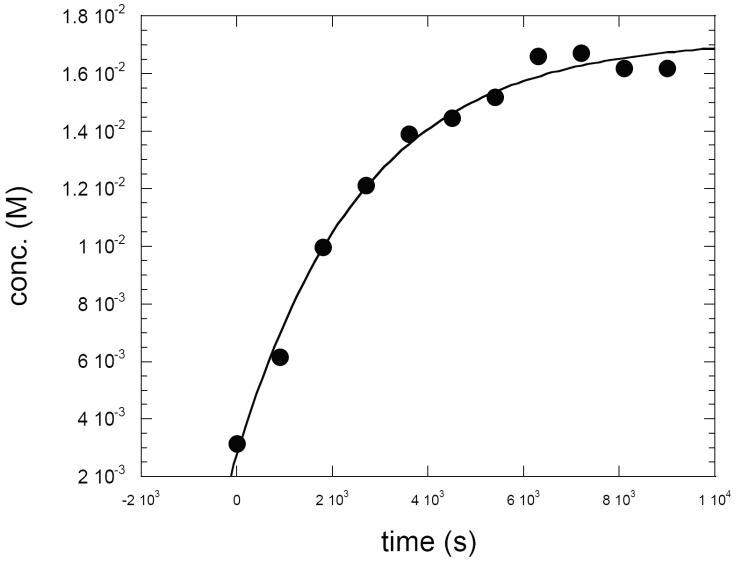


Figure S1. Representative kinetic plot for the reaction of *p*-tolyl iodide (0.565 M, 65.0 equiv) with [(dtbpy)$_2$Cu][Cu(phth)$_2$] (1b) (0.0087 M) in DMSO-d_6 at 120 °C (heating conducted in a silicon oil filled constant temperature bath). The curve for the accumulation of N-*p*-tolyl-phthalimide depicts the results of an unweighted least-square fit to y = a – b*exp(– c*x) (a = 0.0172 ± 0.0004, b = 0.0144 ± 0.0005, c = 0.000382 ± 0.00004).

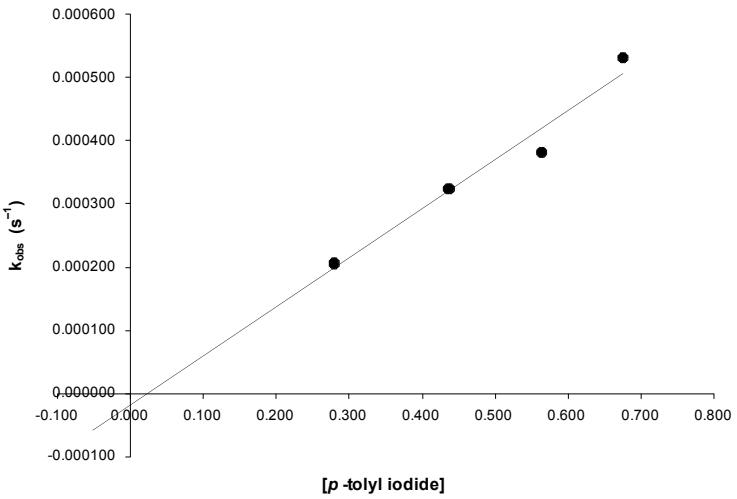


Figure S2. Plot of k_{obs} vs [*p*-tolyl iodide] for the reaction of *p*-tolyl iodide (0.279-0.675 M, 30.1-69.6 equiv) with $[(dtbpy)_2Cu][Cu(phth)_2]$ (**1b**) (~0.009 M) in DMSO-d_6 at 120 °C. The curve depicts the results of an unweighted least-square fit to y = a*x + b (a = 7.76 x 10^{-4}, b = -1.85 x 10^{-5}, R^2 = 0.961).

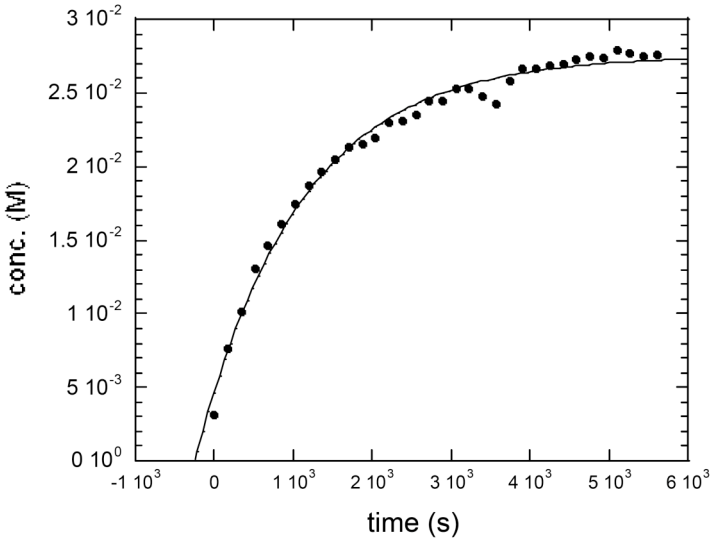


Figure S3. Representative kinetic plot for the reaction of *p*-tolyl iodide (0.0750 M, 2.0 equiv) with $[(dmeda)_2Cu][Cu(phth)_2]$ (**1c**) (0.0375 M) in DMSO-d_6 at 40 °C (Reaction monitored inside of temperature-controlled NMR probe). The curve for the accumulation of N-*p*-tolyl-phthalimide depicts the results of an unweighted least-square fit to y = a – b*exp(– c*x) (a = 0.0275 ± 0.0003, b = 0.0228 ± 0.0004, c = 0.000756 ± 0.00004).

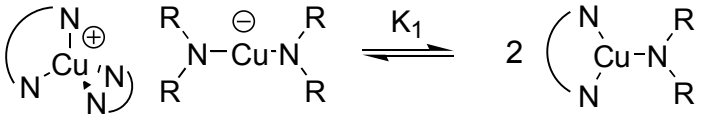
Table SI-1: Table of Kinetic Data for reactions of complex **1b** with *p*-tolyl iodide

[1b]	[ArI]	k_{obs} (s^{-1})
0.0093	0.279	0.00021
0.0087	0.565	0.00038
0.0090	0.437	0.00032
0.0097	0.675	0.00053
0.0362	0.404	0.00026
0.0363	0.460	0.00040

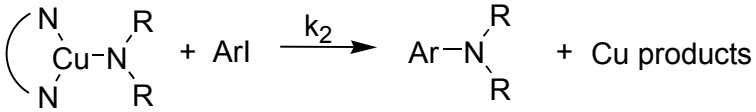
Derivation of Kinetic Rate Expressions

Scenario 1: Tight ion pair between A and B.

AB = tight ion pair



AB **C**



C

$$\text{rate} = k_2[C][ArI]$$

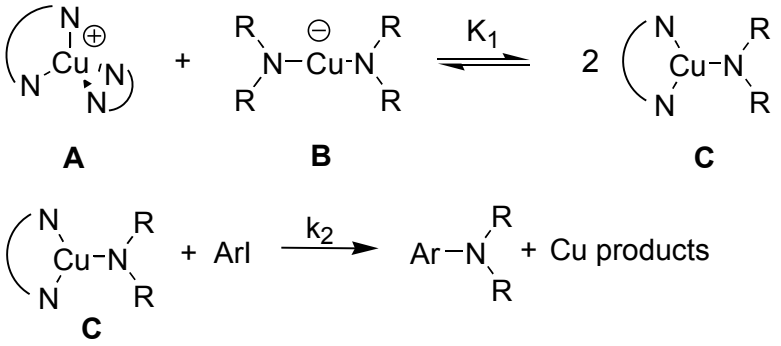
$$K_1 = \frac{[C]^2}{[AB]}$$

$$[C] = \sqrt{K_1[AB]}$$

$$\text{rate} = k_2\left(\sqrt{K_1[AB]}\right)[ArI]$$

1/2 order in Cu

Scenario 2: A and B are fully-solvent separated ions.



A **B** **C**

C

$$\text{rate} = k_2[C][ArI]$$

$$K_1 = \frac{[C]^2}{[A][B]}$$

$$[A] = [B]$$

$$[C] = \sqrt{K_1[A][B]} = \left(\sqrt{K_1}\right)[B]$$

$$\text{rate} = k_2\left(\sqrt{K_1}\right)[B][ArI]$$

1st order in Cu

Table SI-2: B3LYP Computed Energies in Hartrees

complex	ΔE	ΔG	CPCM solvation energy for toluene
(dmeda)Cu(pyrr)	-751.122737	-751.166675	0.002534
(dmeda)Cu(pyrr)(Ph)(I)	-994.053753	-994.107519	0.004335
TS C-I cleavage for (dmeda)Cu(pyrr)(Ph)(I)	-994.048811	-994.103815	0.007044
(dmeda)Cu(pyrr)(Ph)(Br)	-995.837487	-995.890192	0.003713
TS C-Br cleavage for (dmeda)Cu(pyrr)(Ph)(Br)	-995.826677	-995.879383	0.007713
$[Cu(pyrr)_2]^-$	-768.128999	-768.172412	-0.040300
$[Cu(pyrr)_2(Ph)(I)]^-$	-1011.055665	-1011.110221	-0.033211
TS C-I cleavage for $[Cu(pyrr)_2(Ph)(I)]$-	-1011.080465	-1011.102821	-0.031600
$[Cu(phth)_2]^-$	-1221.064919	-1221.114395	-0.038757
$[Cu(phth)_2(Ph)(I)]^-$	-1463.973685	-1464.034265	-0.033690
TS C-I cleavage for $[Cu(phth)_2(Ph)(I)]^-$	-1463.971487	-1464.033404	-0.032220
PhI	-242.942739	-242.973848	-0.003012
PhBr	-244.729222	-244.759498	-0.002932

DFT-Optimized Geometries

(dmeda)Cu(pyrr)

```
REMARK   4 dmed COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1      -0.231  -0.745   0.237  1.00  0.00
CU2+
HETATM    2  N2  RES NRES1      -1.083   1.403   0.313  1.00  0.00
N
HETATM    3  N3  RES NRES1      -2.202  -1.263  -0.058  1.00  0.00
N
HETATM    4  N4  RES NRES1       1.663  -0.585   0.123  1.00  0.00
N1-
HETATM    5  C5  RES NRES1      -2.331   1.207  -0.406  1.00  0.00
C
HETATM    6  C6  RES NRES1      -3.048  -0.050   0.119  1.00  0.00
C
HETATM    7  C7  RES NRES1       2.163   0.550  -0.404  1.00  0.00
C
HETATM    8  C8  RES NRES1       2.729  -1.553   0.383  1.00  0.00
C
HETATM    9  C9  RES NRES1       3.695   0.456  -0.507  1.00  0.00
C
HETATM   10  C10 RES NRES1       4.037  -0.727   0.406  1.00  0.00
C
HETATM   11  O11 RES NRES1       1.518   1.546  -0.789  1.00  0.00
O1-
HETATM   12  C12 RES NRES1      -1.161   2.221   1.518  1.00  0.00
C
HETATM   13 3H1  RES NRES1      -0.286   1.689  -0.273  1.00  0.00
H
HETATM   14 4H1  RES NRES1      -2.461  -1.939   0.656  1.00  0.00
H
HETATM   15  C15 RES NRES1      -2.395  -1.911  -1.376  1.00  0.00
C
HETATM   16 6H1  RES NRES1      -3.020   2.066  -0.320  1.00  0.00
H
HETATM   17 7H1  RES NRES1      -2.110   1.084  -1.474  1.00  0.00
H
HETATM   18 8H1  RES NRES1      -4.023  -0.182  -0.375  1.00  0.00
H
HETATM   19 9H1  RES NRES1      -3.232   0.068   1.193  1.00  0.00
H
HETATM   20 0H2  RES NRES1      -0.152   2.340   1.924  1.00  0.00
H
HETATM   21 1H2  RES NRES1      -1.582   3.226   1.332  1.00  0.00
H
HETATM   22 2H2  RES NRES1      -1.778   1.739   2.288  1.00  0.00
H
HETATM   23 3H2  RES NRES1      -3.450  -2.164  -1.559  1.00  0.00
H
HETATM   24 4H2  RES NRES1      -2.054  -1.240  -2.170  1.00  0.00
H
```

```
HETATM   25 5H2  RES NRES1      -1.790  -2.821  -1.422  1.00  0.00
H
HETATM   26 6H2  RES NRES1       2.558  -2.088   1.326  1.00  0.00
H
HETATM   27 7H2  RES NRES1       2.766  -2.319  -0.413  1.00  0.00
H
HETATM   28 8H2  RES NRES1       3.958   0.261  -1.557  1.00  0.00
H
HETATM   29 9H2  RES NRES1       4.160   1.406  -0.227  1.00  0.00
H
HETATM   30 0H3  RES NRES1       4.229  -0.369   1.425  1.00  0.00
H
HETATM   31 1H3  RES NRES1       4.911  -1.305   0.086  1.00  0.00
H
TER      32      RES NRES1
END
```

(dmeda)Cu(pyrr)(Ph)(I)

```
REMARK   4 Cu_2 COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.061  -1.111  -0.027  1.00  0.00
CU2+
HETATM    2  I2  RES NRES1      -0.014  -3.712  -0.120  1.00  0.00
I1-
HETATM    3  C3  RES NRES1      -1.884  -1.110   0.056  1.00  0.00
C1-
HETATM    4  N4  RES NRES1      -0.195   0.790   0.032  1.00  0.00
N1-
HETATM    5  N5  RES NRES1       2.008  -1.041  -0.050  1.00  0.00
N1-
HETATM    6  C6  RES NRES1      -2.527  -1.313   1.276  1.00  0.00
C
HETATM    7  C7  RES NRES1      -2.616  -0.869  -1.108  1.00  0.00
C
HETATM    8  C8  RES NRES1      -0.352   1.662   1.184  1.00  0.00
C
HETATM    9  C9  RES NRES1       2.884  -1.326  -1.178  1.00  0.00
C
HETATM   10 0H1  RES NRES1      -1.955  -1.506   2.181  1.00  0.00
H
HETATM   11 1H1  RES NRES1      -2.102  -0.660  -2.043  1.00  0.00
H
HETATM   12  C12 RES NRES1       2.665  -0.477   0.976  1.00  0.00
C
HETATM   13  C13 RES NRES1      -0.088   1.431  -1.142  1.00  0.00
C
HETATM   14  C14 RES NRES1      -4.014  -0.865  -1.047  1.00  0.00
C
HETATM   15  C15 RES NRES1      -4.674  -1.080   0.167  1.00  0.00
C
HETATM   16  C16 RES NRES1      -3.928  -1.297   1.328  1.00  0.00
C
HETATM   17 7H1  RES NRES1      -4.589  -0.685  -1.955  1.00  0.00
H
```

```
HETATM   18 8H1  RES NRES1      -5.762  -1.076   0.209  1.00  0.00
H
HETATM   19 9H1  RES NRES1      -4.431  -1.467   2.279  1.00  0.00
H
HETATM   20  O20 RES NRES1       0.042   0.912  -2.257  1.00  0.00
O1-
HETATM   21  C21 RES NRES1      -0.126   2.946  -0.859  1.00  0.00
C
HETATM   22  C22 RES NRES1      -0.727   3.029   0.554  1.00  0.00
C
HETATM   23  C23 RES NRES1       4.164  -0.370   0.618  1.00  0.00
C
HETATM   24  C24 RES NRES1       4.308  -1.331  -0.567  1.00  0.00
C
HETATM   25  O25 RES NRES1       2.182  -0.082   2.048  1.00  0.00
O1-
HETATM   26 6H2  RES NRES1       4.539  -2.340  -0.201  1.00  0.00
H
HETATM   27 7H2  RES NRES1       5.084  -1.051  -1.291  1.00  0.00
H
HETATM   28 8H2  RES NRES1       4.372   0.671   0.329  1.00  0.00
H
HETATM   29 9H2  RES NRES1       4.792  -0.606   1.484  1.00  0.00
H
HETATM   30 0H3  RES NRES1       2.626  -2.287  -1.641  1.00  0.00
H
HETATM   31 1H3  RES NRES1       2.788  -0.549  -1.957  1.00  0.00
H
HETATM   32 2H3  RES NRES1      -1.141   1.289   1.852  1.00  0.00
H
HETATM   33 3H3  RES NRES1       0.582   1.696   1.761  1.00  0.00
H
HETATM   34 4H3  RES NRES1      -1.819   3.113   0.485  1.00  0.00
H
HETATM   35 5H3  RES NRES1      -0.362   3.877   1.146  1.00  0.00
H
HETATM   36 6H3  RES NRES1       0.906   3.323  -0.889  1.00  0.00
H
HETATM   37 7H3  RES NRES1      -0.697   3.471  -1.632  1.00  0.00
H
TER      38      RES NRES1
END
```

TS for C-I cleavage from (dmeda)Cu(pyrr)(Ph)(I)

```
REMARK   4 TS_C COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.123  -0.381  -0.154  1.00  0.00
CU2+
HETATM    2  N2  RES NRES1       0.769  -2.310  -1.084  1.00  0.00
N
HETATM    3  N3  RES NRES1       0.403  -1.621   1.743  1.00  0.00
N
HETATM    4  N4  RES NRES1      -1.825  -0.807  -0.484  1.00  0.00
N1-
HETATM    5  C5  RES NRES1       1.328  -3.133  -0.001  1.00  0.00
C
```

```
HETATM    6  C6  RES NRES1       0.462  -3.006   1.255  1.00  0.00
C
HETATM    7  C7  RES NRES1      -2.669  -1.041   0.540  1.00  0.00
C
HETATM    8  C8  RES NRES1      -2.577  -0.451  -1.687  1.00  0.00
C
HETATM    9  C9  RES NRES1      -4.129  -0.950   0.068  1.00  0.00
C
HETATM   10  C10 RES NRES1      -4.005  -0.999  -1.459  1.00  0.00
C
HETATM   11  O11 RES NRES1      -2.359  -1.295   1.721  1.00  0.00
O1-
HETATM   12  I12 RES NRES1       2.297   1.038  -0.312  1.00  0.00
I
HETATM   13  C13 RES NRES1      -0.032   1.684   0.070  1.00  0.00
C1-
HETATM   14  C14 RES NRES1      -0.357   2.013   1.391  1.00  0.00
C
HETATM   15  C15 RES NRES1      -1.321   2.998   1.622  1.00  0.00
C
HETATM   16  C16 RES NRES1      -1.913   3.678   0.554  1.00  0.00
C
HETATM   17  C17 RES NRES1      -1.539   3.371  -0.758  1.00  0.00
C
HETATM   18  C18 RES NRES1      -0.582   2.385  -1.011  1.00  0.00
C
HETATM   19 9H1  RES NRES1       0.113   1.503   2.225  1.00  0.00
H
HETATM   20 0H2  RES NRES1      -1.600   3.236   2.646  1.00  0.00
H
HETATM   21 1H2  RES NRES1      -2.650   4.454   0.743  1.00  0.00
H
HETATM   22 2H2  RES NRES1      -1.983   3.906  -1.594  1.00  0.00
H
HETATM   23 3H2  RES NRES1      -0.277   2.165  -2.029  1.00  0.00
H
HETATM   24  C24 RES NRES1       1.572  -2.334  -2.311  1.00  0.00
C
HETATM   25 5H2  RES NRES1      -0.180  -2.623  -1.283  1.00  0.00
H
HETATM   26 6H2  RES NRES1      -0.566  -1.442   2.051  1.00  0.00
H
HETATM   27  C27 RES NRES1       1.387  -1.318   2.781  1.00  0.00
C
HETATM   28 8H2  RES NRES1       1.413  -4.194  -0.295  1.00  0.00
H
HETATM   29 9H2  RES NRES1       2.345  -2.770   0.201  1.00  0.00
H
HETATM   30 0H3  RES NRES1       0.839  -3.696   2.027  1.00  0.00
H
HETATM   31 1H3  RES NRES1      -0.565  -3.313   1.021  1.00  0.00
H
HETATM   32 2H3  RES NRES1       1.231  -0.300   3.152  1.00  0.00
H
HETATM   33 3H3  RES NRES1       1.327  -2.009   3.639  1.00  0.00
H
```

```
HETATM   34 4H3  RES NRES1       2.405  -1.365   2.375  1.00  0.00
H
HETATM   35 5H3  RES NRES1       1.054  -1.776  -3.097  1.00  0.00
H
HETATM   36 6H3  RES NRES1       2.534  -1.843  -2.125  1.00  0.00
H
HETATM   37 7H3  RES NRES1       1.767  -3.357  -2.673  1.00  0.00
H
HETATM   38 8H3  RES NRES1      -4.736  -1.745   0.512  1.00  0.00
H
HETATM   39 9H3  RES NRES1      -4.539   0.009   0.417  1.00  0.00
H
HETATM   40 0H4  RES NRES1      -4.771  -0.427  -1.994  1.00  0.00
H
HETATM   41 1H4  RES NRES1      -4.062  -2.039  -1.806  1.00  0.00
H
HETATM   42 2H4  RES NRES1      -2.601   0.645  -1.826  1.00  0.00
H
HETATM   43 3H4  RES NRES1      -2.109  -0.871  -2.590  1.00  0.00
H
TER      44      RES NRES1
END
```

(dmeda)Cu(pyrr)(Ph)(Br)

```
REMARK   4 dmed COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1      -0.392   0.012  -0.232  1.00  0.00
CU2+
HETATM    2  N2  RES NRES1      -2.036   1.261  -0.810  1.00  0.00
N
HETATM    3  N3  RES NRES1      -1.306   0.520   1.893  1.00  0.00
N
HETATM    4  N4  RES NRES1       0.834   1.511  -0.456  1.00  0.00
N1-
HETATM    5  C5  RES NRES1      -3.026   1.278   0.285  1.00  0.00
C
HETATM    6  C6  RES NRES1      -2.314   1.549   1.612  1.00  0.00
C
HETATM    7  C7  RES NRES1       1.409   2.159   0.596  1.00  0.00
C
HETATM    8  C8  RES NRES1       1.606   1.721  -1.686  1.00  0.00
C
HETATM    9  C9  RES NRES1       2.569   3.021   0.086  1.00  0.00
C
HETATM   10  C10 RES NRES1       2.367   3.042  -1.434  1.00  0.00
C
HETATM   11  O11 RES NRES1       1.071   2.087   1.782  1.00  0.00
O1-
HETATM   12 BR12 RES NRES1      -1.563  -2.052  -0.651  1.00  0.00
BR1-
HETATM   13  C13 RES NRES1       1.246  -1.019   0.033  1.00  0.00
C1-
 HETATM   14  C14 RES NRES1       1.768  -1.089   1.317  1.00  0.00
C
HETATM   15  C15 RES NRES1       2.923  -1.858   1.525  1.00  0.00
C
```

```
HETATM   16  C16 RES NRES1       3.534  -2.521   0.460  1.00  0.00
C
HETATM   17  C17 RES NRES1       2.994  -2.420  -0.824  1.00  0.00
C
HETATM   18  C18 RES NRES1       1.836  -1.663  -1.050  1.00  0.00
C
HETATM   19 9H1  RES NRES1       1.327  -0.538   2.140  1.00  0.00
H
HETATM   20 0H2  RES NRES1       3.344  -1.920   2.526  1.00  0.00
H
HETATM   21 1H2  RES NRES1       4.429  -3.116   0.629  1.00  0.00
H
HETATM   22 2H2  RES NRES1       3.456  -2.944  -1.658  1.00  0.00
H
HETATM   23 3H2  RES NRES1       1.399  -1.621  -2.042  1.00  0.00
H
HETATM   24  C24 RES NRES1      -2.635   1.017  -2.133  1.00  0.00
C
HETATM   25 5H2  RES NRES1      -1.541   2.152  -0.822  1.00  0.00
H
HETATM   26 6H2  RES NRES1      -0.477   0.977   2.276  1.00  0.00
H
HETATM   27  C27 RES NRES1      -1.781  -0.575   2.742  1.00  0.00
C
HETATM   28 8H2  RES NRES1      -3.803   2.038   0.104  1.00  0.00
H
HETATM   29 9H2  RES NRES1      -3.510   0.295   0.301  1.00  0.00
H
HETATM   30 0H3  RES NRES1      -3.063   1.629   2.417  1.00  0.00
H
HETATM   31 1H3  RES NRES1      -1.799   2.517   1.555  1.00  0.00
H
HETATM   32 2H3  RES NRES1      -0.959  -1.273   2.927  1.00  0.00
H
HETATM   33 3H3  RES NRES1      -2.172  -0.222   3.710  1.00  0.00
H
HETATM   34 4H3  RES NRES1      -2.568  -1.135   2.227  1.00  0.00
H
HETATM   35 5H3  RES NRES1      -1.863   1.107  -2.903  1.00  0.00
H
HETATM   36 6H3  RES NRES1      -3.030  -0.002  -2.161  1.00  0.00
H
HETATM   37 7H3  RES NRES1      -3.443   1.730  -2.353  1.00  0.00
H
HETATM   38 8H3  RES NRES1       2.569   4.003   0.570  1.00  0.00
H
HETATM   39 9H3  RES NRES1       3.502   2.513   0.369  1.00  0.00
H
HETATM   40 0H4  RES NRES1       3.297   3.102  -2.008  1.00  0.00
H
HETATM   41 1H4  RES NRES1       1.739   3.894  -1.720  1.00  0.00
H
HETATM   42 2H4  RES NRES1       2.308   0.890  -1.855  1.00  0.00
H
HETATM   43 3H4  RES NRES1       0.944   1.774  -2.560  1.00  0.00
H
TER      44      RES NRES1
```

```
END
```

TS for C-Br cleavage from (dmeda)Cu(pyrr)(Ph)(Br)

```
REMARK   4 TS_C COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1      -0.415  -0.017  -0.230  1.00  0.00
CU2+
HETATM    2  N2  RES NRES1      -2.201   0.958  -1.161  1.00  0.00
N
HETATM    3  N3  RES NRES1      -1.570   0.534   1.674  1.00  0.00
N
HETATM    4  N4  RES NRES1       0.712   1.628  -0.402  1.00  0.00
N1-
HETATM    5  C5  RES NRES1      -3.216   1.078  -0.103  1.00  0.00
C
HETATM    6  C6  RES NRES1      -2.556   1.517   1.207  1.00  0.00
C
HETATM    7  C7  RES NRES1       1.113   2.312   0.690  1.00  0.00
C
HETATM    8  C8  RES NRES1       1.579   1.933  -1.540  1.00  0.00
C
HETATM    9  C9  RES NRES1       2.273   3.256   0.335  1.00  0.00
C
HETATM   10  C10 RES NRES1       2.245   3.287  -1.197  1.00  0.00
C
HETATM   11  O11 RES NRES1       0.646   2.221   1.842  1.00  0.00
O1-
HETATM   12 BR12 RES NRES1      -0.937  -2.373  -0.504  1.00  0.00
BR
HETATM   13  C13 RES NRES1       1.098  -1.410  -0.015  1.00  0.00
C1-
HETATM   14  C14 RES NRES1       1.503  -1.534   1.317  1.00  0.00
C
HETATM   15  C15 RES NRES1       2.866  -1.685   1.585  1.00  0.00
C
HETATM   16  C16 RES NRES1       3.793  -1.764   0.542  1.00  0.00
C
HETATM   17  C17 RES NRES1       3.355  -1.693  -0.783  1.00  0.00
C
HETATM   18  C18 RES NRES1       1.998  -1.534  -1.076  1.00  0.00
C
HETATM   19 9H1  RES NRES1       0.784  -1.492   2.127  1.00  0.00
H
HETATM   20 0H2  RES NRES1       3.196  -1.749   2.620  1.00  0.00
H
HETATM   21 1H2  RES NRES1       4.849  -1.900   0.761  1.00  0.00
H
HETATM   22 2H2  RES NRES1       4.068  -1.772  -1.602  1.00  0.00
H
HETATM   23 3H2  RES NRES1       1.653  -1.506  -2.105  1.00  0.00
H
HETATM   24  C24 RES NRES1      -2.732   0.442  -2.427  1.00  0.00
C
HETATM   25 5H2  RES NRES1      -1.768   1.868  -1.309  1.00  0.00
H
HETATM   26 6H2  RES NRES1      -0.771   1.055   2.066  1.00  0.00
H
```

```
HETATM   27  C27 RES NRES1      -2.117  -0.451   2.605  1.00  0.00
C
HETATM   28 8H2  RES NRES1      -4.016   1.786  -0.381  1.00  0.00
H
HETATM   29 9H2  RES NRES1      -3.683   0.092   0.021  1.00  0.00
H
HETATM   30 0H3  RES NRES1      -3.337   1.708   1.962  1.00  0.00
H
HETATM   31 1H3  RES NRES1      -2.023   2.464   1.047  1.00  0.00
H
HETATM   32 2H3  RES NRES1      -1.314  -1.095   2.977  1.00  0.00
H
HETATM   33 3H3  RES NRES1      -2.614   0.014   3.473  1.00  0.00
H
HETATM   34 4H3  RES NRES1      -2.843  -1.098   2.099  1.00  0.00
H
HETATM   35 5H3  RES NRES1      -1.950   0.482  -3.193  1.00  0.00
H
HETATM   36 6H3  RES NRES1      -3.023  -0.606  -2.297  1.00  0.00
H
HETATM   37 7H3  RES NRES1      -3.607   1.007  -2.786  1.00  0.00
H
HETATM   38 8H3  RES NRES1       2.152   4.228   0.823  1.00  0.00
H
HETATM   39 9H3  RES NRES1       3.200   2.809   0.721  1.00  0.00
H
HETATM   40 0H4  RES NRES1       3.229   3.405  -1.664  1.00  0.00
H
HETATM   41 1H4  RES NRES1       1.609   4.111  -1.546  1.00  0.00
H
HETATM   42 2H4  RES NRES1       2.343   1.148  -1.673  1.00  0.00
H
HETATM   43 3H4  RES NRES1       1.005   1.977  -2.477  1.00  0.00
H
TER      44      RES NRES1
END
```

$[Cu(pyrr)_2]^-$

```
REMARK   4 Cu_2 COMPLIES WITH FORMAT V. 2.0
HETATM    1  C1  RES NRES1      -0.011   0.076   2.867  1.00  0.00
C
HETATM    2  C2  RES NRES1       0.911  -0.024   4.111  1.00  0.00
C
HETATM    3 3H   RES NRES1       0.826  -1.040   4.525  1.00  0.00
H
HETATM    4 4H   RES NRES1       0.586   0.674   4.890  1.00  0.00
H
HETATM    5  C5  RES NRES1       2.304   0.244   3.537  1.00  0.00
C
HETATM    6 6H   RES NRES1       3.123  -0.263   4.064  1.00  0.00
H
HETATM    7 7H   RES NRES1       2.513   1.322   3.555  1.00  0.00
H
HETATM    8  C8  RES NRES1       2.144  -0.226   2.071  1.00  0.00
C
```

```
HETATM    9 9H   RES NRES1       2.800   0.324   1.382  1.00  0.00
H
HETATM   10 0H1  RES NRES1       2.426  -1.294   1.981  1.00  0.00
H
HETATM   11  N11 RES NRES1       0.737  -0.018   1.745  1.00  0.00
N1-
HETATM   12  O12 RES NRES1      -1.237   0.207   2.949  1.00  0.00
O1-
HETATM   13 CU13 RES NRES1       0.000   0.000   0.000  1.00  0.00
CU2+
HETATM   14  C14 RES NRES1       0.011  -0.076  -2.867  1.00  0.00
C
HETATM   15  C15 RES NRES1      -0.911   0.024  -4.111  1.00  0.00
C
HETATM   16 6H1  RES NRES1      -0.826   1.040  -4.525  1.00  0.00
H
HETATM   17 7H1  RES NRES1      -0.586  -0.674  -4.890  1.00  0.00
H
HETATM   18  C18 RES NRES1      -2.304  -0.244  -3.537  1.00  0.00
C
HETATM   19 9H1  RES NRES1      -3.123   0.263  -4.064  1.00  0.00
H
HETATM   20 0H2  RES NRES1      -2.513  -1.322  -3.555  1.00  0.00
H
HETATM   21  C21 RES NRES1      -2.144   0.226  -2.071  1.00  0.00
C
HETATM   22 2H2  RES NRES1      -2.800  -0.324  -1.382  1.00  0.00
H
HETATM   23 3H2  RES NRES1      -2.426   1.294  -1.981  1.00  0.00
H
HETATM   24  N24 RES NRES1      -0.737   0.018  -1.745  1.00  0.00
N1-
HETATM   25  O25 RES NRES1       1.237  -0.207  -2.949  1.00  0.00
O1-
TER      26      RES NRES1
END
```

$[Cu(pyrr)_2(Ph)(I)]^-$

```
REMARK   4 Cu_2 COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.095  -0.057   0.007  1.00  0.00
CU2+
HETATM    2  I2  RES NRES1       0.020  -2.657  -0.085  1.00  0.00
I1-
HETATM    3  C3  RES NRES1      -1.851  -0.055   0.090  1.00  0.00
C1-
HETATM    4  N4  RES NRES1      -0.162   1.845   0.066  1.00  0.00
N1-
HETATM    5  N5  RES NRES1       2.042   0.014  -0.016  1.00  0.00
N1-
HETATM    6  C6  RES NRES1      -2.494  -0.259   1.311  1.00  0.00
C
HETATM    7  C7  RES NRES1      -2.583   0.186  -1.074  1.00  0.00
C
HETATM    8  C8  RES NRES1      -0.318   2.717   1.219  1.00  0.00
C
```

```
HETATM    9  C9  RES NRES1       2.917  -0.271  -1.144  1.00  0.00
C
HETATM   10 0H1  RES NRES1      -1.921  -0.451   2.215  1.00  0.00
H
HETATM   11 1H1  RES NRES1      -2.069   0.394  -2.009  1.00  0.00
H
HETATM   12  C12 RES NRES1       2.698   0.578   1.011  1.00  0.00
C
HETATM   13  C13 RES NRES1      -0.055   2.485  -1.108  1.00  0.00
C
HETATM   14  C14 RES NRES1      -3.981   0.189  -1.013  1.00  0.00
C
HETATM   15  C15 RES NRES1      -4.640  -0.025   0.201  1.00  0.00
C
HETATM   16  C16 RES NRES1      -3.894  -0.242   1.362  1.00  0.00
C
HETATM   17 7H1  RES NRES1      -4.556   0.370  -1.921  1.00  0.00
H
HETATM   18 8H1  RES NRES1      -5.728  -0.021   0.243  1.00  0.00
H
HETATM   19 9H1  RES NRES1      -4.398  -0.412   2.313  1.00  0.00
H
HETATM   20  O20 RES NRES1       0.075   1.967  -2.223  1.00  0.00
O1-
HETATM   21  C21 RES NRES1      -0.093   4.001  -0.825  1.00  0.00
C
HETATM   22  C22 RES NRES1      -0.694   4.084   0.588  1.00  0.00
C
HETATM   23  C23 RES NRES1       4.198   0.685   0.652  1.00  0.00
C
HETATM   24  C24 RES NRES1       4.341  -0.277  -0.533  1.00  0.00
C
HETATM   25  O25 RES NRES1       2.216   0.973   2.082  1.00  0.00
O1-
HETATM   26 6H2  RES NRES1       4.573  -1.285  -0.166  1.00  0.00
H
HETATM   27 7H2  RES NRES1       5.118   0.004  -1.257  1.00  0.00
H
HETATM   28 8H2  RES NRES1       4.405   1.726   0.363  1.00  0.00
H
HETATM   29 9H2  RES NRES1       4.825   0.449   1.518  1.00  0.00
H
HETATM   30 0H3  RES NRES1       2.659  -1.232  -1.607  1.00  0.00
H
HETATM   31 1H3  RES NRES1       2.822   0.506  -1.923  1.00  0.00
H
HETATM   32 2H3  RES NRES1      -1.107   2.344   1.886  1.00  0.00
H
HETATM   33 3H3  RES NRES1       0.616   2.751   1.795  1.00  0.00
H
HETATM   34 4H3  RES NRES1      -1.786   4.168   0.519  1.00  0.00
H
HETATM   35 5H3  RES NRES1      -0.328   4.932   1.180  1.00  0.00
H
HETATM   36 6H3  RES NRES1       0.939   4.378  -0.855  1.00  0.00
H
```

```
HETATM   37 7H3  RES NRES1      -0.664   4.526  -1.598  1.00  0.00
H
TER      38      RES NRES1
END
```

TS for C-I cleavage from $[Cu(pyrr)_2(Ph)(I)]^-$

```
REMARK   4 TS_C COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.005  -0.604  -0.187  1.00  0.00
CU2+
HETATM    2  I2  RES NRES1       0.673  -2.918  -1.139  1.00  0.00
I1-
HETATM    3  C3  RES NRES1      -1.066  -2.135   0.552  1.00  0.00
C1-
HETATM    4  N4  RES NRES1      -1.440   0.760  -0.112  1.00  0.00
N1-
HETATM    5  N5  RES NRES1       1.726   0.404  -0.164  1.00  0.00
N1-
HETATM    6  C6  RES NRES1      -0.590  -2.262   1.868  1.00  0.00
C
HETATM    7  C7  RES NRES1      -2.391  -2.429   0.195  1.00  0.00
C
HETATM    8  C8  RES NRES1      -1.497   1.821   0.786  1.00  0.00
C
HETATM    9  C9  RES NRES1       2.199   1.417  -0.990  1.00  0.00
C
HETATM   10 0H1  RES NRES1       0.459  -2.037   2.106  1.00  0.00
H
HETATM   11 1H1  RES NRES1      -2.729  -2.300  -0.837  1.00  0.00
H
HETATM   12  C12 RES NRES1       2.603   0.180   0.883  1.00  0.00
C
HETATM   13  C13 RES NRES1      -2.500   0.812  -1.004  1.00  0.00
C
HETATM   14  C14 RES NRES1      -3.278  -2.806   1.214  1.00  0.00
C
HETATM   15  C15 RES NRES1      -2.843  -2.908   2.548  1.00  0.00
C
HETATM   16  C16 RES NRES1      -1.508  -2.626   2.872  1.00  0.00
C
HETATM   17 7H1  RES NRES1      -4.326  -3.010   0.959  1.00  0.00
H
HETATM   18 8H1  RES NRES1      -3.545  -3.213   3.332  1.00  0.00
H
HETATM   19 9H1  RES NRES1      -1.159  -2.701   3.909  1.00  0.00
H
HETATM   20  O21 RES NRES1      -0.727   2.047   1.721  1.00  0.00
O1-
HETATM   21  C22 RES NRES1      -3.321   2.039  -0.674  1.00  0.00
C
HETATM   22  C23 RES NRES1      -2.705   2.658   0.421  1.00  0.00
C
HETATM   23  C26 RES NRES1       3.770   1.126   0.728  1.00  0.00
C
HETATM   24  C27 RES NRES1       3.522   1.887  -0.422  1.00  0.00
C
```

```
HETATM   25  O29 RES NRES1       1.660   1.860  -2.006  1.00  0.00
O1-
HETATM   26 4H4  RES NRES1      -3.300   2.696   1.162  1.00  0.00
H
HETATM   27 5H4  RES NRES1      -2.430   3.536   0.183  1.00  0.00
H
HETATM   28 6H4  RES NRES1      -3.336   2.621  -1.425  1.00  0.00
H
HETATM   29 7H4  RES NRES1      -4.207   1.784  -0.446  1.00  0.00
H
HETATM   30 8H4  RES NRES1      -2.165   0.868  -1.891  1.00  0.00
H
HETATM   31 9H4  RES NRES1      -3.036   0.033  -0.912  1.00  0.00
H
HETATM   32 0H5  RES NRES1       2.159   0.339   1.708  1.00  0.00
H
HETATM   33 1H5  RES NRES1       2.912  -0.718   0.855  1.00  0.00
H
HETATM   34 2H5  RES NRES1       3.830   1.684   1.495  1.00  0.00
H
HETATM   35 3H5  RES NRES1       4.575   0.633   0.622  1.00  0.00
H
HETATM   36 4H5  RES NRES1       4.208   1.755  -1.066  1.00  0.00
H
HETATM   37 5H5  RES NRES1       3.466   2.808  -0.195  1.00  0.00
H
TER      38      RES NRES1
END
```

$[Cu(phth)_2]^-$

```
REMARK   4 Cu_2 COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.002  -0.358   0.029  1.00  0.00
CU2+
HETATM    2  N2  RES NRES1      -0.006  -0.203   1.928  1.00  0.00
N1-
HETATM    3  C3  RES NRES1       0.871   0.579   2.662  1.00  0.00
C
HETATM    4  C4  RES NRES1       0.524   0.416   4.123  1.00  0.00
C
HETATM    5  C5  RES NRES1      -0.554  -0.462   4.190  1.00  0.00
C
HETATM    6  C6  RES NRES1      -0.889  -0.857   2.771  1.00  0.00
C
HETATM    7  O7  RES NRES1      -1.789  -1.620   2.449  1.00  0.00
O1-
HETATM    8  O8  RES NRES1       1.771   1.283   2.229  1.00  0.00
O1-
HETATM    9  C9  RES NRES1       1.081   0.969   5.268  1.00  0.00
C
HETATM   10  C10 RES NRES1      -1.121  -0.825   5.404  1.00  0.00
C
HETATM   11  N11 RES NRES1       0.009  -0.512  -1.870  1.00  0.00
N1-
```

```
HETATM   12  C12 RES NRES1      -0.708   0.299  -2.734  1.00  0.00
C
HETATM   13  C13 RES NRES1      -0.425  -0.161  -4.144  1.00  0.00
C
HETATM   14  C14 RES NRES1       0.456  -1.235  -4.052  1.00  0.00
C
HETATM   15  C15 RES NRES1       0.732  -1.455  -2.583  1.00  0.00
C
HETATM   16  O16 RES NRES1       1.464  -2.322  -2.129  1.00  0.00
O1-
HETATM   17  O17 RES NRES1      -1.447   1.225  -2.433  1.00  0.00
O1-
HETATM   18  C18 RES NRES1      -0.881   0.300  -5.371  1.00  0.00
C
HETATM   19  C19 RES NRES1       0.920  -1.892  -5.184  1.00  0.00
C
HETATM   20 0H2  RES NRES1      -1.570   1.140  -5.427  1.00  0.00
H
HETATM   21 1H2  RES NRES1       1.608  -2.730  -5.095  1.00  0.00
H
HETATM   22 2H2  RES NRES1       1.923   1.654   5.200  1.00  0.00
H
HETATM   23 3H2  RES NRES1      -1.962  -1.513   5.439  1.00  0.00
H
HETATM   24  C24 RES NRES1       0.467  -1.437  -6.431  1.00  0.00
C
HETATM   25  C25 RES NRES1      -0.422  -0.356  -6.524  1.00  0.00
C
HETATM   26 6H2  RES NRES1       0.807  -1.927  -7.342  1.00  0.00
H
HETATM   27 7H2  RES NRES1      -0.757  -0.023  -7.505  1.00  0.00
H
HETATM   28  C28 RES NRES1      -0.567  -0.274   6.570  1.00  0.00
C
HETATM   29  C29 RES NRES1       0.519   0.611   6.503  1.00  0.00
C
HETATM   30 0H3  RES NRES1      -0.984  -0.534   7.542  1.00  0.00
H
HETATM   31 1H3  RES NRES1       0.928   1.023   7.424  1.00  0.00
H
TER      32      RES NRES1
END
```

$[Cu(phth)_2(Ph)(I)]^-$

```
REMARK   4 Cu_2 COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.727  -0.075   0.000  1.00  0.00
CU2+
HETATM    2  I2  RES NRES1       3.016   1.087   0.000  1.00  0.00
I1-
HETATM    3  C3  RES NRES1       1.761  -1.731   0.000  1.00  0.00
C1-
HETATM    4  N4  RES NRES1      -0.818  -1.256   0.000  1.00  0.00
N1-
HETATM    5  N5  RES NRES1      -0.284   1.621   0.000  1.00  0.00
N1-
```

```
HETATM    6  C6  RES NRES1       2.065  -2.333   1.218  1.00  0.00
C
HETATM    7  C7  RES NRES1       2.065  -2.333  -1.218  1.00  0.00
C
HETATM    8  C8  RES NRES1      -1.407  -1.765   1.146  1.00  0.00
C
HETATM    9  C9  RES NRES1      -0.650   2.312  -1.140  1.00  0.00
C
HETATM   10 0H1  RES NRES1       1.795  -1.860   2.157  1.00  0.00
H
HETATM   11 1H1  RES NRES1       1.795  -1.860  -2.157  1.00  0.00
H
HETATM   12  C12 RES NRES1      -0.650   2.312   1.140  1.00  0.00
C
HETATM   13  C13 RES NRES1      -1.407  -1.765  -1.146  1.00  0.00
C
HETATM   14  C14 RES NRES1       2.713  -3.575  -1.209  1.00  0.00
C
HETATM   15  C15 RES NRES1       3.041  -4.195   0.000  1.00  0.00
C
HETATM   16  C16 RES NRES1       2.713  -3.575   1.209  1.00  0.00
C
HETATM   17 7H1  RES NRES1       2.958  -4.055  -2.155  1.00  0.00
H
HETATM   18 8H1  RES NRES1       3.547  -5.158   0.000  1.00  0.00
H
HETATM   19 9H1  RES NRES1       2.958  -4.055   2.155  1.00  0.00
H
HETATM   20  O20 RES NRES1      -1.045  -1.588  -2.296  1.00  0.00
O1-
HETATM   21  O21 RES NRES1      -1.045  -1.588   2.296  1.00  0.00
O1-
HETATM   22  C22 RES NRES1      -2.571  -2.614  -0.697  1.00  0.00
C
HETATM   23  C23 RES NRES1      -2.571  -2.614   0.697  1.00  0.00
C
HETATM   24  C24 RES NRES1      -3.518  -3.323  -1.423  1.00  0.00
C
HETATM   25  C25 RES NRES1      -3.518  -3.323   1.423  1.00  0.00
C
HETATM   26  C26 RES NRES1      -1.357   3.571   0.696  1.00  0.00
C
HETATM   27  C27 RES NRES1      -1.357   3.571  -0.696  1.00  0.00
C
HETATM   28  O28 RES NRES1      -0.443   1.983   2.297  1.00  0.00
O1-
HETATM   29  O29 RES NRES1      -0.443   1.983  -2.297  1.00  0.00
O1-
HETATM   30  C30 RES NRES1      -1.933   4.605  -1.422  1.00  0.00
C
HETATM   31  C31 RES NRES1      -1.933   4.605   1.422  1.00  0.00
C
HETATM   32 2H3  RES NRES1      -3.503  -3.316  -2.510  1.00  0.00
H
HETATM   33 3H3  RES NRES1      -3.503  -3.316   2.510  1.00  0.00
H
```

```
HETATM   34 4H3  RES NRES1      -1.923   4.592  -2.510  1.00  0.00
H
HETATM   35 5H3  RES NRES1      -1.923   4.592   2.510  1.00  0.00
H
HETATM   36  C36 RES NRES1      -4.484  -4.039  -0.701  1.00  0.00
C
HETATM   37  C37 RES NRES1      -4.484  -4.039   0.701  1.00  0.00
C
HETATM   38 8H3  RES NRES1      -5.246  -4.606  -1.234  1.00  0.00
H
HETATM   39 9H3  RES NRES1      -5.246  -4.606   1.234  1.00  0.00
H
HETATM   40  C40 RES NRES1      -2.520   5.656  -0.701  1.00  0.00
C
HETATM   41  C41 RES NRES1      -2.520   5.656   0.701  1.00  0.00
C
HETATM   42 2H4  RES NRES1      -2.982   6.485  -1.234  1.00  0.00
H
HETATM   43 3H4  RES NRES1      -2.982   6.485   1.234  1.00  0.00
H
TER      44      RES NRES1
END
```

TS for C-I cleavage from $[Cu(phth)_2(Ph)(I)]^-$

```
REMARK   4 TS_C COMPLIES WITH FORMAT V. 2.0
HETATM    1 CU1  RES NRES1       0.005  -0.604  -0.187  1.00  0.00
CU2+
HETATM    2  I2  RES NRES1       0.673  -2.918  -1.139  1.00  0.00
I1-
HETATM    3  C3  RES NRES1      -1.066  -2.135   0.552  1.00  0.00
C1-
HETATM    4  N4  RES NRES1      -1.440   0.760  -0.112  1.00  0.00
N1-
HETATM    5  N5  RES NRES1       1.726   0.404  -0.164  1.00  0.00
N1-
HETATM    6  C6  RES NRES1      -0.590  -2.262   1.868  1.00  0.00
C
HETATM    7  C7  RES NRES1      -2.391  -2.429   0.195  1.00  0.00
C
HETATM    8  C8  RES NRES1      -1.497   1.821   0.786  1.00  0.00
C
HETATM    9  C9  RES NRES1       2.199   1.417  -0.990  1.00  0.00
C
HETATM   10 0H1  RES NRES1       0.459  -2.037   2.106  1.00  0.00
H
HETATM   11 1H1  RES NRES1      -2.729  -2.300  -0.837  1.00  0.00
H
HETATM   12  C12 RES NRES1       2.603   0.180   0.883  1.00  0.00
C
HETATM   13  C13 RES NRES1      -2.500   0.812  -1.004  1.00  0.00
C
HETATM   14  C14 RES NRES1      -3.278  -2.806   1.214  1.00  0.00
C
HETATM   15  C15 RES NRES1      -2.843  -2.908   2.548  1.00  0.00
C
```

```
HETATM   16  C16 RES NRES1      -1.508  -2.626   2.872  1.00  0.00
C
HETATM   17 7H1  RES NRES1      -4.326  -3.010   0.959  1.00  0.00
H
HETATM   18 8H1  RES NRES1      -3.545  -3.213   3.332  1.00  0.00
H
HETATM   19 9H1  RES NRES1      -1.159  -2.701   3.909  1.00  0.00
H
HETATM   20  O20 RES NRES1      -2.748   0.003  -1.906  1.00  0.00
O1-
HETATM   21  O21 RES NRES1      -0.727   2.047   1.721  1.00  0.00
O1-
HETATM   22  C22 RES NRES1      -3.321   2.039  -0.674  1.00  0.00
C
HETATM   23  C23 RES NRES1      -2.705   2.658   0.421  1.00  0.00
C
HETATM   24  C24 RES NRES1      -4.476   2.564  -1.252  1.00  0.00
C
HETATM   25  C25 RES NRES1      -3.222   3.825   0.984  1.00  0.00
C
HETATM   26  C26 RES NRES1       3.770   1.126   0.728  1.00  0.00
C
HETATM   27  C27 RES NRES1       3.522   1.887  -0.422  1.00  0.00
C
HETATM   28  O28 RES NRES1       2.466  -0.651   1.793  1.00  0.00
O1-
HETATM   29  O29 RES NRES1       1.660   1.860  -2.006  1.00  0.00
O1-
HETATM   30  C30 RES NRES1       4.416   2.865  -0.856  1.00  0.00
C
HETATM   31  C31 RES NRES1       4.922   1.315   1.490  1.00  0.00
C
HETATM   32 2H3  RES NRES1      -4.946   2.068  -2.110  1.00  0.00
H
HETATM   33 3H3  RES NRES1      -2.728   4.295   1.842  1.00  0.00
H
HETATM   34 4H3  RES NRES1       4.205   3.451  -1.758  1.00  0.00
H
HETATM   35 5H3  RES NRES1       5.103   0.713   2.388  1.00  0.00
H
HETATM   36  C36 RES NRES1      -5.007   3.744  -0.694  1.00  0.00
C
HETATM   37  C37 RES NRES1      -4.389   4.365   0.408  1.00  0.00
C
HETATM   38 8H3  RES NRES1      -5.914   4.188  -1.122  1.00  0.00
H
HETATM   39 9H3  RES NRES1      -4.825   5.284   0.820  1.00  0.00
H
HETATM   40  C40 RES NRES1       5.584   3.066  -0.094  1.00  0.00
C
HETATM   41  C41 RES NRES1       5.834   2.302   1.063  1.00  0.00
C
HETATM   42 2H4  RES NRES1       6.312   3.827  -0.401  1.00  0.00
H
HETATM   43 3H4  RES NRES1       6.751   2.480   1.637  1.00  0.00
H
TER      44      RES NRES1
```

```
END
```

PhI

```
REMARK    4 PhI  COMPLIES WITH FORMAT V. 2.0
HETATM    1  C1  UNK     0       0.000   0.000  -0.564  1.00  0.00
C
HETATM    2  I2  UNK     0       0.000   0.000   1.557  1.00  0.00
I
HETATM    3  C3  UNK     0       0.000   1.217  -1.252  1.00  0.00
C
HETATM    4 4H   UNK     0       0.000   2.157  -0.709  1.00  0.00
H
HETATM    5  C5  UNK     0       0.000   1.208  -2.649  1.00  0.00
C
HETATM    6 6H   UNK     0       0.000   2.153  -3.187  1.00  0.00
H
HETATM    7  C7  UNK     0       0.000   0.000  -3.350  1.00  0.00
C
HETATM    8 8H   UNK     0       0.000   0.000  -4.438  1.00  0.00
H
HETATM    9  C9  UNK     0       0.000  -1.208  -2.649  1.00  0.00
C
HETATM   10 0H1  UNK     0       0.000  -2.153  -3.187  1.00  0.00
H
HETATM   11  C11 UNK     0       0.000  -1.217  -1.252  1.00  0.00
C
HETATM   12 2H1  UNK     0       0.000  -2.157  -0.709  1.00  0.00
H
TER      13      UNK     0
END
```

PhBr

```
REMARK    4 PhBr COMPLIES WITH FORMAT V. 2.0
HETATM    1  C1  UNK     0       0.000   1.217  -0.792  1.00  0.00
C
HETATM    2 2H   UNK     0       0.000   2.154  -0.242  1.00  0.00
H
HETATM    3  C3  UNK     0       0.000   0.000  -0.109  1.00  0.00
C
HETATM    4 BR4  UNK     0       0.000   0.000   1.819  1.00  0.00
BR
HETATM    5  C5  UNK     0       0.000  -1.217  -0.792  1.00  0.00
C
HETATM    6 6H   UNK     0       0.000  -2.154  -0.242  1.00  0.00
H
HETATM    7  C7  UNK     0       0.000  -1.208  -2.189  1.00  0.00
C
HETATM    8 8H   UNK     0       0.000  -2.154  -2.727  1.00  0.00
H
HETATM    9  C9  UNK     0       0.000   0.000  -2.890  1.00  0.00
C
HETATM   10 0H1  UNK     0       0.000   0.000  -3.977  1.00  0.00
H
HETATM   11  C11 UNK     0       0.000   1.208  -2.189  1.00  0.00
C
```

```
HETATM   12 2H1  UNK     0       0.000   2.154  -2.727  1.00  0.00
H
TER      13      UNK     0
END
```

Computational Details.

All DFT calculations were performed using a hybrid functional [the three-parameter exchange functional of Becke (B3)[6] and the correlation functional of Lee, Yang, and Parr (LYP)[7]] (B3LYP) as implemented in Gaussian 03.[8] The copper atom uses the effective core potential and associated basis set of Hay and Wadt (LANL2DZ)[9,10] in which the two outermost p functions were replaced by reoptimized 4p functions as suggested by Couty and Hall[11] and an f polarization function[12] was added. For iodine and phosphorus, the basis set was augmented by a diffuse p function and d polarization function.[13] All other atoms use the 6-31G(d',p') basis set.[14-16] 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. The toluene solvent was modeled using the Conductor-like Polarizable Continuum Model (CPCM) as implemented in Gaussian 03.[17,18]

Full Citation for Reference 60.

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