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Supplementary Materials for

Isolation of bis(copper) key intermediates in Cu-catalyzed azide-alkyne "click reaction"

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Published 12 June 2015, *Sci. Adv.* **1**, e1500304 (2015)
DOI: 10.1126/sciadv.1500304

This PDF file includes:

1. Experimental details

General: ^{1}H, ^{13}C NMR spectra were recorded on Bruker Avance 300, Jeol ECA 500 and Varian Inova 500 spectrometers. NMR multiplicities are abbreviated as follows: *s* = singlet, *d* = doublet, *t* = triplet, *q* = quartet, *sept* = septet, *m* = multiplet, *br* = broad signal. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (^{1}H, ^{13}C) and $CFCl_3$ (^{19}F). All spectra were obtained at 25 °C in the solvent indicated. Coupling constants *J* are given in Hz. Mass spectra were performed at the UC San Diego Mass Spectrometry Laboratory. Melting points were measured with an electrothermal MEL-TEMP apparatus. Single crystal X-ray diffraction data were collected on a Bruker Apex II-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under oil, mounted on nylon loops, and then immediately placed in a cold stream of nitrogen. Structures were solved and refined using Olex2 and SHELXTL. The CAAC and 3,3-diphenyl-1-propyne were prepared following literature procedures while all other starting materials were purchased from commercial sources.

2. Synthesis of CAAC-copper complexes

(CAAC)CuOAc:

THF (20 mL) was added to a mixture of CuOAc (1.0 g, 8.2 mmol) and CAAC (2.6 g, 8.2 mmol). The reaction mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The residue was washed with hexane (10 mL), and then was extracted with benzene (20 mL). After removal of benzene under vacuum, (CAAC)CuOAc was isolated as a white solid. Yield 73% (2.6 g). m.p. 151 ^{o}C (dec.) ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.44 (t, *J* = 7.8 Hz, 1 H, *p*-H), 7.29 (d, *J* = 7.8 Hz, 2 H, *m*-H), 2.85 (sept, *J* = 6.9 Hz, 2 H, $C\mathit{H}Me_2$), 1.99 (s, 2 H, $C\mathit{H}_2$), 1.96-1.85 (m, 2 H, $C\mathit{H}_2$), 1.85-1.66 (m, 5 H, $C\mathit{H}_2$, $COC\mathit{H}_3$), 1.34 (s, 6 H, $C\mathit{H}_3$), 1.30 (d, *J* = 6.9 Hz, 6 H, $CHC\mathit{H}_3$), 1.25 (d, *J* = 6.9 Hz, 6 H, $CHC\mathit{H}_3$), 1.08 (t, *J* = 7.5 Hz, 6 H, $C\mathit{H}_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 252.5 ($\mathit{C}_{carbene}$), 177.6 ($\mathit{C}OCH_3$), 145.5 (C_q), 135.4 (C_q) 129.8 ($\mathit{C}H_{Ar}$), 125.0 ($\mathit{C}H_{Ar}$), 81.2 (C_q), 62.9 (C_q), 42.8 ($\mathit{C}H_2$), 31.3 ($\mathit{C}H_2$), 29.5, 29.4, 27.0, 22.4, 9.7.

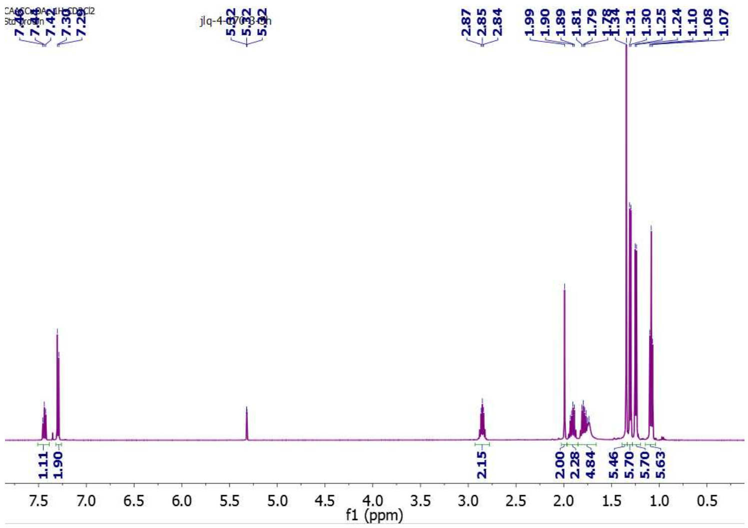


Figure S1. ^{1}H NMR of (CAAC)CuOAc in CD_2Cl_2

1H

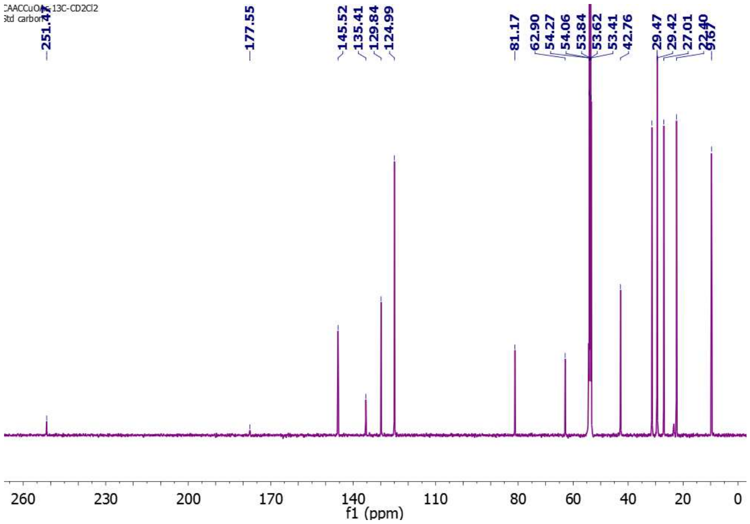


Figure S2. ^{13}C NMR of (CAAC)CuOAc in CD_2Cl_2

(CAAC)CuCl:

THF (20 mL) was added to a mixture of CuCl (1.0 g, 10.0 mmol) and CAAC (2.6 g, 8.2 mmol). The mixture was stirred overnight at room temperature. The solvent was removed under vacuum. The remaining solid was washed with hexane (10 mL), and then was extracted with benzene (20 mL). After removal of benzene under vacuum, (CAAC)CuCl was isolated as a white solid. Yield 81% (2.7 g) m.p. 207 °C (dec.). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.39 (t, *J* = 7.8 Hz, 1 H, *p*-H), 7.25 (d, *J* = 7.8 Hz, 2 H, *m*-H), 2.83 (sept, *J* = 6.9 Hz, 2 H, C*H*Me$_2$), 1.98 (s, 2 H, C*H*$_2$), 1.96-1.84 (m, 2 H, C*H*$_2$), 1.83-1.71 (m, 5 H, C*H*$_2$), 1.35 (s, 6 H, C*H*$_3$), 1.30 (d, *J* = 6.9 Hz, 6 H, CHC*H*$_3$), 1.29 (d, *J* = 6.9 Hz, 6 H, CHC*H*$_3$), 1.07 (t, *J* = 7.5 Hz, 6 H, C*H*$_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz):

δ = 250.4 ($C_{carbene}$), 145.1 (C_q), 134.6 (C_q), 129.8 (CH_{Ar}), 124.8 (CH_{Ar}), 81.1 (C_q), 62.7 (C_q), 42.5 (CH_2), 31.2 (CH_2), 29.4, 29.3, 27.4, 22.5, 9.7; HRMS (ESI-TOFMS): m/z calculated for $C_{22}H_{35}CuNCl[NH_4]^+$ 429.2092, found 429.2091.

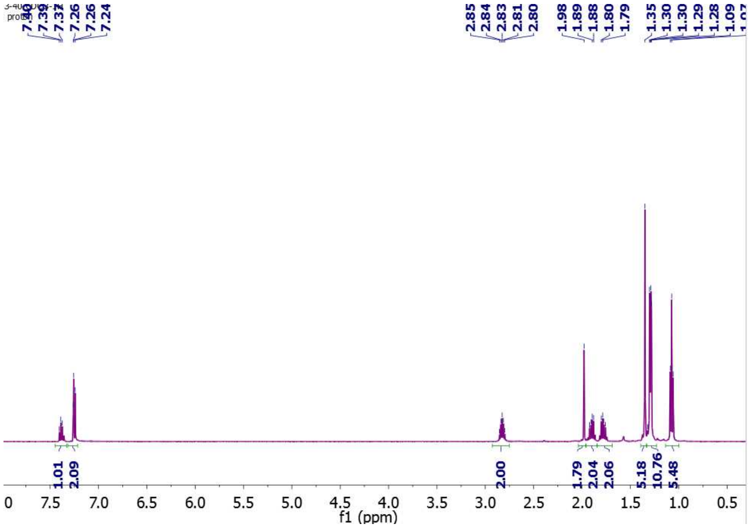


Figure S3. ^1H NMR of (CAAC)CuCl in CD_2Cl_2

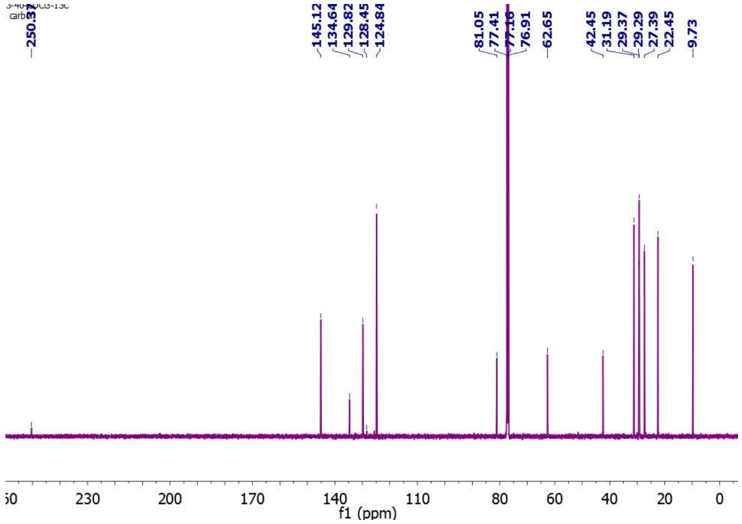


Figure S4. ^{13}C NMR of (CAAC)CuCl in CD_2Cl_2

(CAAC)CuOTf:

AgOTf (135 mg, 0.53 mmol) was added to a solution of (CAAC)CuCl (200 mg, 0.48 mmol) in methylene chloride (5 mL) and the solution was stirred in the dark for 30 minutes at room temperature. After filtration, the solvent was removed under vacuum to afford (CAAC)CuOTf as a white solid. Yield 73% (184 mg). m.p. 169 °C (dec.) ^1H NMR ($CDCl_3$, 500 MHz): δ = 7.44 (t, *J* = 7.8 Hz, 1 H, *p*-H), 7.28 (d, *J* = 7.8 Hz, 2 H, *m*-H), 2.80 (sept, *J* = 6.9 Hz, 2 H, $CHMe_2$), 2.02 (s, 2 H, CH_2), 1.96-1.82 (m, 2 H, CH_2), 1.81-1.69 (m, 2 H, CH_2), 1.38 (s, 6 H, CH_3), 1.31 (d, J = 6.9 Hz, 6 H, CHCH_3), 1.23 (d, J = 6.9 Hz, 6 H, CHCH_3), 1.08 (t, J = 7.5 Hz, 6 H, CH_3); ^{13}C NMR (CDCl$_3$, 125 MHz): δ = 248.4 ($C_{carbene}$), 144.9 (C_q), 134.5 (C_q), 130.2 (CH$_{Ar}$), 125.0 (CH$_{Ar}$), 119.5 (q, J = 318Hz, CF$_3$), 81.6 (C_q), 62.4 (C_q), 42.6 (CH$_2$), 31.0 (CH$_2$), 29.3, 29.2, 27.1, 22.4, 9.5; ^{19}F NMR (CDCl$_3$, 282 MHz): δ = -77.7.

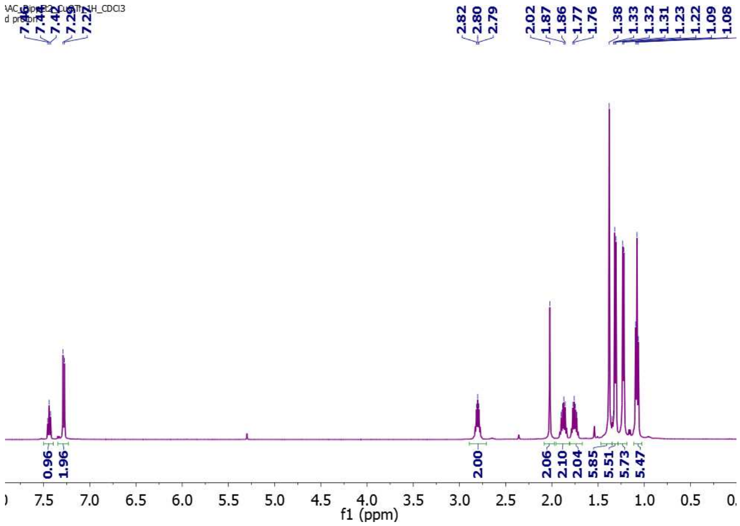


Figure S5. ^{1}H NMR of (CAAC)CuOTf in CDCl$_3$

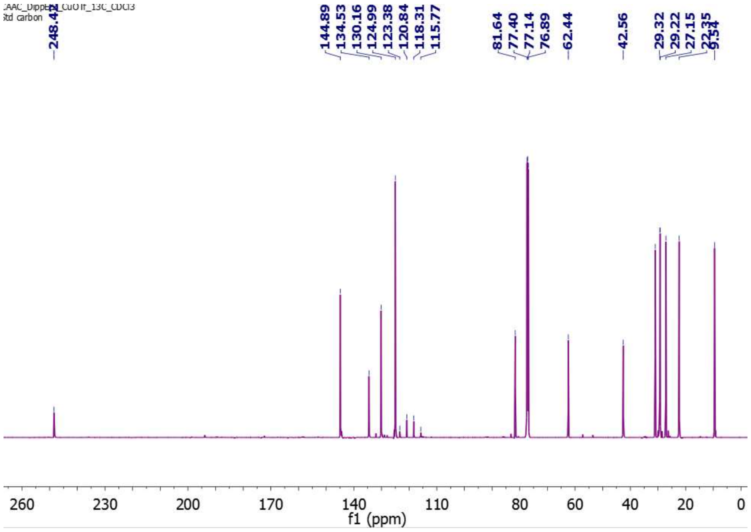


Figure S6. ^{13}C NMR of (CAAC)CuOTf in CDCl$_3$

(CAAC)CuCCPh **1_{Cu}a**:

n-BuLi (2.4 mmol, 2.5 M in hexane) was slowly added to a solution of phenyl acetylene (234 mg, 2.3 mmol) in THF (15 mL) at -78 °C. After 30 minutes a solution of (CAAC)CuOAc (1.0 g, 2.3 mmol) in THF (10 mL) was added and the mixture was stirred at ambient temperature for one hour. Volatiles were removed under vacuum and the remaining solid was extracted with benzene (3 x 10 mL). After removal of benzene under vacuum, the solid was washed with hexane (20 mL). **1_{Cu}a** was obtained as a light yellow solid. Yield 88% (970 mg). m.p. 152 °C (dec.) ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.48 (t, *J* = 7.8 Hz, 1 H, *p-H*), 7.34 (d, *J* = 7.8 Hz, 2 H, *m-H*), 7.23 (br d, *J* = 7.1 Hz, 2 H, *o-H*$_{C6H5}$), 7.14 (br t, *J* = 7.1 Hz, 2 H, *m-H*$_{C6H5}$), 7.08 (br t, *J* = 7.1 Hz, 1 H, *p-H*$_{C6H5}$), 2.88 (sept, *J* = 6.9 Hz, 2 H, C*H*Me$_2$), 1.98 (s, 2 H, C*H*$_2$), 1.96-1.87 (m, 2 H, C*H*$_2$), 1.86-1.74 (m, 2 H, C*H*$_2$), 1.39-1.30 (m, 18 H, C*H*$_3$, CHC*H*$_3$), 1.11 (t, *J* = 7.5 Hz, 6 H, C*H*$_3$); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 253.5 (*C*$_{carbene}$), 145.6 (*C*$_q$), 135.1 (*C*$_q$), 131.8 (*C*H$_{C6H5}$), 129.9 (*C*H$_{Ar}$), 128.1 (*C*H$_{C6H5}$), 127.7 (PhC*C*Cu), 125.7 (*C*H$_{Ar}$), 125.0 (*C*H$_{C6H5}$), 121.9 (*C*$_{q-C6H5}$), 106.3 (Ph*C*CCu), 81.3 (*C*$_q$), 63.3 (*C*$_q$), 42.8 (*C*H$_2$), 31.4 (*C*H$_2$), 29.5, 29.4, 27.3, 22.4, 9.9; HRMS (ESI-TOFMS): m/z calculated for $C_{30}H_{40}CuNNa^+$ 500.2349, found 500.2355.

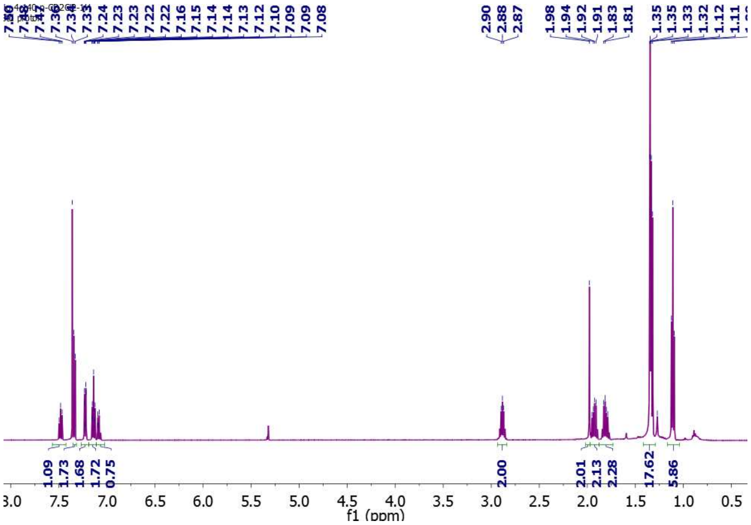


Figure S7. ^{1}H NMR of **1_{Cu}a** in CD_2Cl_2

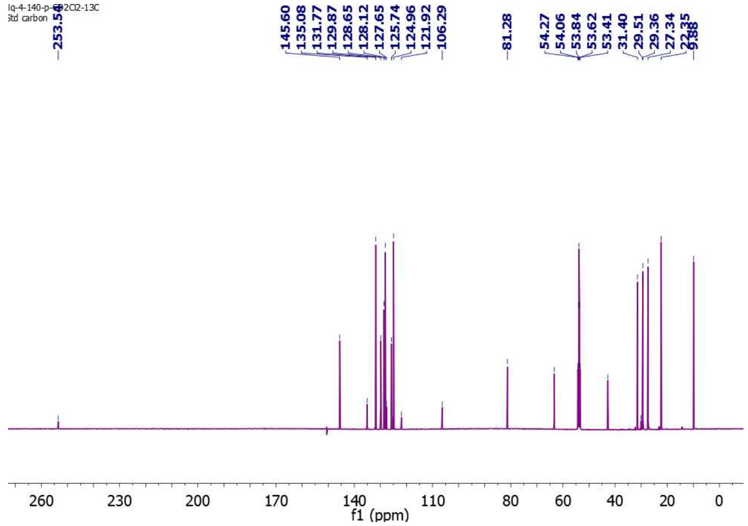


Figure S8. ^{13}C NMR of **1_{Cu}a** in CD_2Cl_2

Bis(copper) acetylide complexes **1_{Cu2}a**:

1_{Cu2}a (X=OTf):

(CAAC)CuOTf (530 mg, 1 mmol) was added to a solution of **1_{Cu}a** (480 mg, 1 mmol) in methylene chloride (20 mL). The reaction was stirred for 5 minutes at ambient temperature. After removing the solvent under vacuum, **1_{Cu2}a** was obtained as a white solid. Yield 95% (952 mg). m.p. 174 ^{o}C (dec.). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.44 (t, J = 7.8 Hz, 2 H, *p*-H), 7.26 (d, J = 7.8 Hz, 4 H, *m*-H), 7.22 (t, J = 7.6 Hz, 1 H, *p*-H), 7.04 (t, J = 7.6 Hz, 2 H, *m*-H), 6.41 (d, J = 7.6 Hz, 2 H, *o*-H), 2.82 (sept, J = 6.9 Hz, 4 H, $CHMe_2$), 2.05 (s, 4 H, CH_2), 1.96-1.83 (m, 4 H, CH_2), 1.80-1.68 (m, 4 H, CH_2), 1.38 (s, 12H, CH_3), 1.29 (d, J = 6.9 Hz, 12 H, $CHCH_3$), 1.18-1.02 (m, 24 H); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 249.4 ($C_{carbene}$), 145.3 ($C_{q\text{-}Aro}$), 134.7 ($C_{q\text{-}Aro}$), 132.0 ($CH_{\text{-}Aro}$), 130.4 ($CH_{\text{-}Aro}$), 129.4 ($CH_{\text{-}Aro}$), 128.7 ($CH_{\text{-}Aro}$), 125.4 ($CH_{\text{-}Aro}$), 122.2 ($PhCCCu_2$), 118.9 ($C_{q\text{-}Aro}$), 110.8 ($PhCCCu_2$), 82.5 (C_q), 63.1 (C_q), 42.1 (CH_2), 31.5 (CH_2), 29.4, 27.2, 22.4, 9.9; HRMS (ESI-TOFMS): m/z calculated for $C_{52}H_{75}Cu_2N_2^+$ 853.4517, found 853.4507.

1_{Cu2}a (X=BF_4):

Methylene chloride (4 mL) was added to a mixture of **1_{Cu}a** (180 mg, 0.38 mmol) and $Ph_3C^+BF_4^-$ (62 mg, 0.19 mmol). The mixture was stirred for 5 minutes at room temperature. The solvent was removed under vacuum and the remaining solid was washed with pentane (15 mL), affording **1_{Cu2}a** (X=BF_4) as a light yellow solid. Yield 93% (166 mg). Single crystals of **1_{Cu2}a** (X=BF_4) were obtained by diffusion of diethyl ether into a saturated methylene chloride solution.

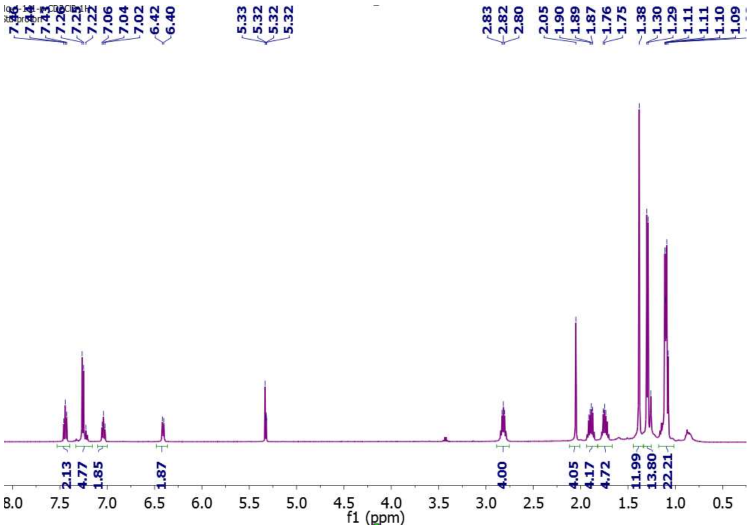


Figure S9. ^{1}H NMR of **1_{Cu2}a** in CD_2Cl_2

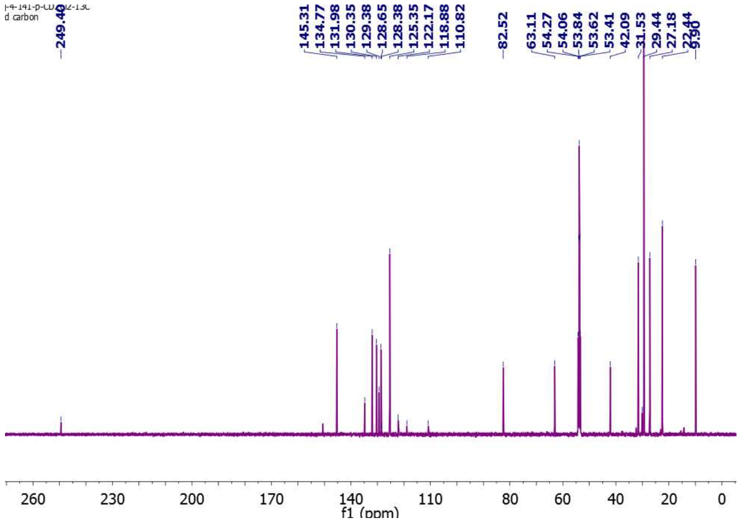


Figure S10. ^{13}C NMR of **1**$_{\mathbf{Cu2}}$**a** in CD_2Cl_2

Bis(copper) triazole complexes **2**$_{\mathbf{Cu2}}$**a** and **2**$_{\mathbf{Cu2}}$**a** (X=BF_4):

Benzyl azide (40.0 mg, 0.30 mmol) was added to a solution of **1**$_{\mathbf{Cu2}}$**a** (250 mg, 0.25 mmol) in methylene chloride (0.5 mL). After 1 hour, diethyl ether (15 mL) was added to induce the precipitation of the product. After filtration **2**$_{\mathbf{Cu2}}$**a** was isolated as a pale yellow solid. Yield 87% (246 mg). m.p. 175 ^{o}C (dec.). The same procedure was used for the synthesis of **2**$_{\mathbf{Cu2}}$**a** (X=BF_4), starting from **1**$_{\mathbf{Cu2}}$**a** (X=BF_4) (236 mg, 0.25 mmol), and was isolated as a pale yellow solid. Yield 83% (223 mg). m.p. 182 ^{o}C (dec.). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.48-7.38 (m, 2 H, *p*-H), 7.34-7.14 (m, 12 H), 6.82 (br, 2 H), 5.11 (s, 2 H, CH_2Ph), 2.77 (sept, J = 6.9 Hz, 4 H, C*H*Me$_2$), 2.01 (s, 2 H, CH_2), 1.96 (s, 2 H, CH_2), 1.85-1.73 (m, 2 H, CH_2), 1.73-1.61 (m, 4 H, CH_2), 1.61-1.51 (m, 2 H, CH_2), 1.34 (br, 12 H, CH_3), 1.29-1.20 (m, 12 H, CHCH_3), 1.04-0.86 (m, 24 H); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 252.7 (C_{carbene}), 249.3 (C_{carbene}), 156.7 ($C_{\text{triazolide}}$), 155.1 ($C_{\text{triazolide}}$), 145.4 (C_{q}), 145.3 (C_{q}), 136.7 (C_{qAr}), 135.2 (C_{q}), 134.8 (C_{q}), 133.3 (C_{qAr}), 130.3 ($C\text{H}_{\text{Ar}}$), 130.2 ($C\text{H}_{\text{Ar}}$), 129.1 ($C\text{H}_{\text{Ar}}$), 128.8 ($C\text{H}_{\text{Ar}}$), 128.2 ($C\text{H}_{\text{Ar}}$), 128.1 ($C_{\text{q-Ar}}$), 128.0 ($C\text{H}_{\text{Ar}}$), 127.1 ($C\text{H}_{\text{Ar}}$), 125.2 ($C\text{H}_{\text{Ar}}$), 125.1 ($C\text{H}_{\text{Ar}}$), 82.3 (C_{q}), 81.9 (C_{q}), 63.3 (C_{q}), 63.0 (C_{q}), 57.1 ($C\text{H}_2$Ph), 42.4 ($C\text{H}_2$), 31.3 ($C\text{H}_2$), 29.4, 27.0, 22.3, 9.7. HRMS (ESI-TOFMS): m/z calculated for $C_{59}H_{82}Cu_2N_5^+$ 986.5157, found 986.5161. Single crystals of **2**$_{\mathbf{Cu2}}$**a** (X=BF_4) were obtained by diffusion of hexane into a saturated methylene chloride solution.

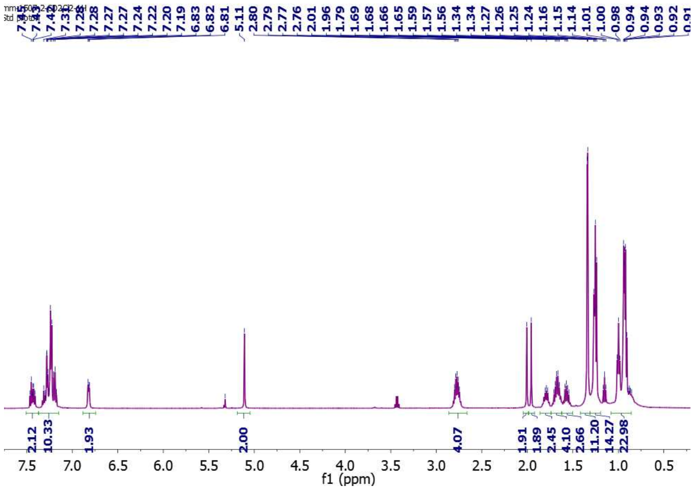


Figure S11. ^{1}H NMR of $\mathbf{2_{Cu2}a}$ in CD_2Cl_2

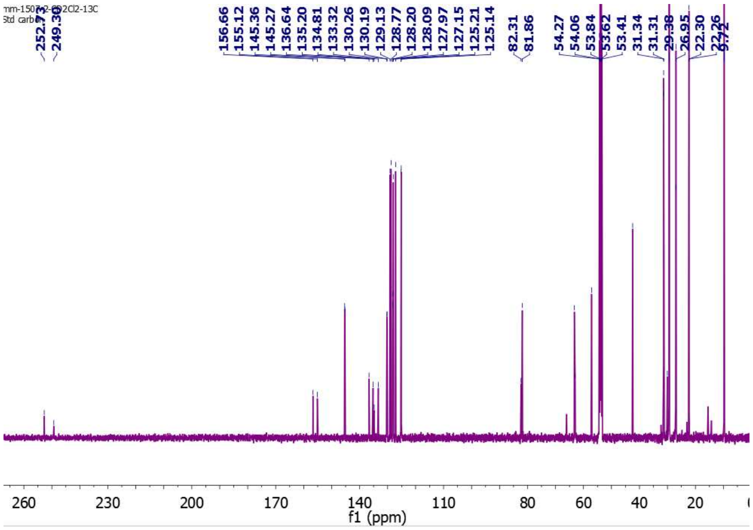


Figure S12. ^{13}C NMR of $\mathbf{2_{Cu2}a}$ in CD_2Cl_2

Bis(copper) acetylide complex $\mathbf{1_{Cu2}a}$ by proto-demetallation of $\mathbf{2_{Cu2}a}$:
Phenylacetylene (15 mg, 0.15 mmol) was added to the solution of $\mathbf{2_{Cu2}a}$ (136 mg, 0.12 mmol) in methylene chloride (5 mL). After stirring 16 hours at room temperature, the solvent was removed under vacuum. The remaining solid was washed with diethyl ether (3 x 10 mL) to remove triazole **3** and after drying $\mathbf{1_{Cu2}a}$ was obtained as a yellow solid Yield 91% (108 mg). NMR data are identical to those of a sample prepared as described above.

Bis(copper) acetylide complex $\mathbf{1_{Cu2}b}$ by proto-demetallation of $\mathbf{2_{Cu2}a}$ (X=BF_4):
3,3-Diphenyl-1-propyne (26 mg, 0.14 mmol) was added to the solution of $\mathbf{2_{Cu2}a}$ (X=BF_4) (120 mg, 0.11 mmol) in methylene chloride (5 mL). After stirring 16 hours at

room temperature, the solvent was removed under vacuum. The remaining solid was washed with diethyl ether (3 x 10 mL) to remove triazole **3** and after drying $\mathbf{1_{Cu2}b}$ (X=BF_4) was obtained as a yellow solid. Yield 87% (100 mg). m.p. 185 ^{o}C (dec.). ^{1}H NMR (CD_2Cl_2, 500 MHz): δ = 7.56 (t, *J* = 7.8 Hz, 2 H, *p*-H), 7.32 (d, *J* = 7.8 Hz, 4 H, *m*-H), 7.22 (t, *J* = 7.6 Hz, 1 H, *p*-H), 7.24-7.06 (m, 6 H, H_{Ar}), 6.84 (d, *J* = 6.2 Hz, 4 H, H_{Ar}), 3.43 (br, 1 H, C*H*CC), 2.80 (sept, *J* = 6.9 Hz, 4 H, C*H*Me$_2$), 2.04 (s, 4 H, CH_2), 1.89-1.77 (m, 4 H, CH_2), 1.75-1.62 (m, 4 H, CH_2), 1.40 (s, 12H, CH_3), 1.29 (d, *J* = 6.9 Hz, 12 H, CHCH_3), 1.12-0.98 (m, 24 H); ^{13}C NMR (CD_2Cl_2, 125 MHz): δ = 249.9 ($C_{carbene}$), 145.6 (C_q), 141.1 (C*C*Cu$_2$), 135.0 (C_q), 130.4 (*C*H$_{Ar}$), 128.8 (*C*H$_{C6H5}$), 127.3 (*C*H$_{C6H5}$), 125.5 (*C*H$_{Ar}$), 120.1 ($C_{q\text{-}C6H5}$),, 109.0 (*C*CCu$_2$), 82.3 (C_q), 62.8 (C_q), 46.5 (*C*HCC), 42.5 (*C*H$_2$), 31.4 (*C*H$_2$), 29.5, 29.4, 27.1, 22.6, 9.9; HRMS (ESI-TOFMS): m/z calculated for $C_{59}H_{81}Cu_2N_2^+$ 943.4986, found 943.5004. Single crystals of $\mathbf{1_{Cu2}b}$ (X=BF_4) were obtained by diffusion of diethyl ether into a saturated methylene chloride solution.

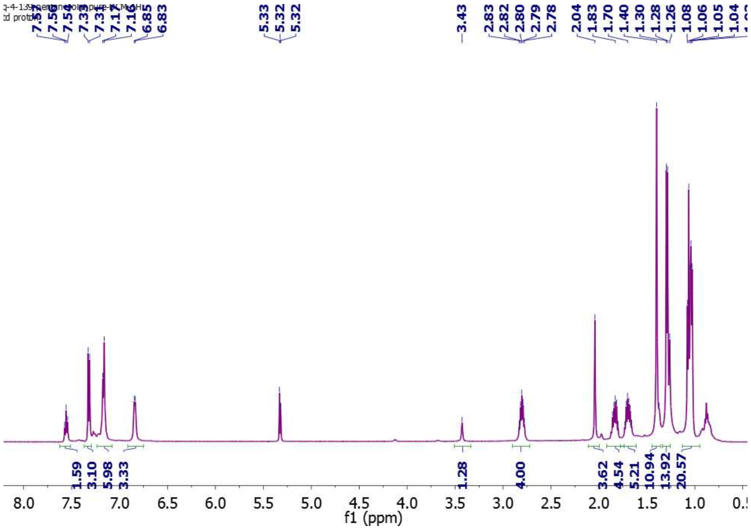


Figure S13. ^{1}H NMR of $\mathbf{1_{Cu2}b}$ in CD_2Cl_2

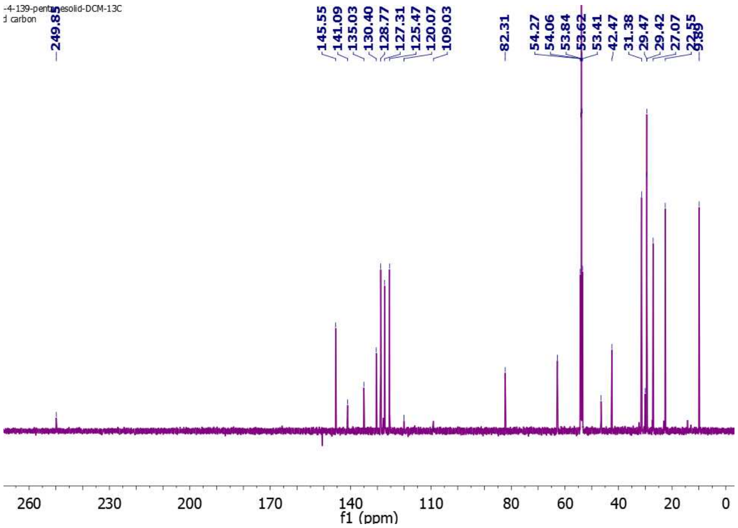


Figure S14. ^{13}C NMR of $\mathbf{1_{Cu2}b}$ in CD_2Cl_2

Mono(copper) triazole complex $\mathbf{2_{Cu}a}$:

Benzyl azide (68.2 mg, 0.51 mmol) was added to a solution of $\mathbf{1_{Cu}a}$ (200 mg, 0.42 mmol) in methylene chloride (0.5 mL). After 15 hours, diethyl ether (15 mL) was added to induce the precipitation of the product. After filtration, the residue was washed with pentane (10 mL) to afford $\mathbf{2_{Cu}a}$ as a pale yellow solid. Yield 61% (156 mg). m.p. 155 ^{o}C (dec.) ^{1}H NMR (CD_2Cl_2, 300 MHz): δ = 7.78 (br d, J = 7.5 Hz, 2 H), 7.48 (t, J = 7.8 Hz, 1 H, *p*-H), 7.35-7.07 (m, 8 H), 6.84 (br, d, J = 7.5 Hz, 2 H), 5.21 (s, 2 H, CH_2Ph), 2.87 (sept, J = 6.9 Hz, 2 H, C*H*Me$_2$), 1.99 (s, 2 H, CH_2), 1.89-1.63 (m, 4 H, CH_2), 1.37 (s, 6 H, CH_3), 1.27 (d, J = 6.9 Hz, 6 H, CHCH_3), 1.07 (d, J = 6.9 Hz, 6 H, CHCH_3), 1.00 (t, J = 7.5 Hz, 6 H, CH$_2$CH_3); ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz): δ = 254.0 ($C_{carbene}$), 156.1 ($C_{triazolide}$), 152.8 ($C_{triazolide}$), 145.7 (C_q), 139.2, 136.7 (C_{qAr}), 135.4 (C_q), 130.2 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 127.2 (CH_{Ar}), 126.8, 126.3, 125.8, 125.3 (CH_{Ar}), 81.6 (C_q), 63.5 (C_q), 55.9 (CH_2Ph), 42.4 (CH_2), 31.6 (CH_2), 29.5, 27.0, 22.5, 9.8; HRMS (ESI-TOFMS): m/z calculated for $C_{37}H_{48}CuN_4^+$ 611.3169, found 611.3166.

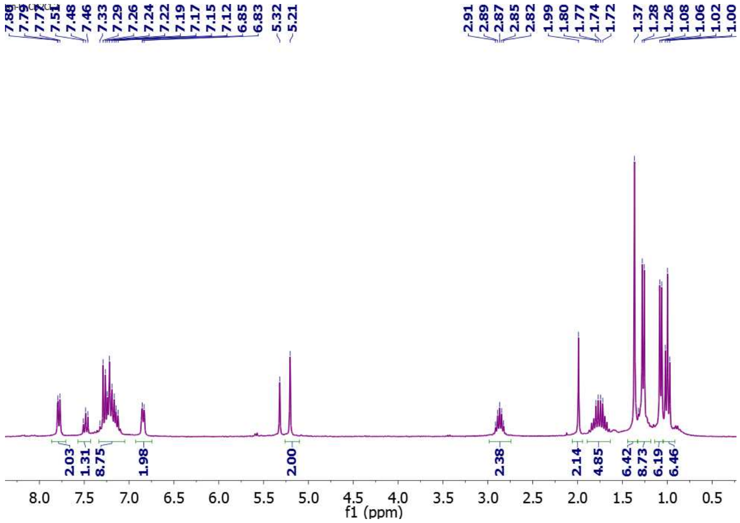


Figure S15. ^{1}H NMR of $\mathbf{2_{Cu}a}$ in CD_2Cl_2

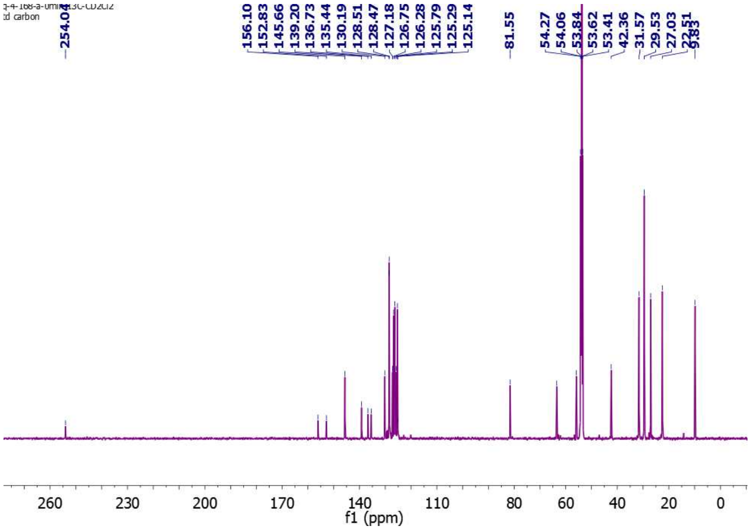


Figure S16. ^{13}C NMR of $\mathbf{2_{Cu}a}$ in CD_2Cl_2

Mono(copper) acetylide complex $\mathbf{1_{Cu}a}$ by proto-demetallation of $\mathbf{2_{Cu}a}$: Phenylacetylene (27 µL, 0.25 mmol) was added to the solution of $\mathbf{2_{Cu}a}$ (15.3 mg, 0.025 mmol) in methylene chloride (0.4 mL). After stirring for 4.5 hours at room temperature, the solvent was removed under vacuum. The remaining solid was washed with pentane (10 mL) to remove triazole **3** and after drying $\mathbf{1_{Cu}a}$ was obtained as a yellow solid in 73% yield. NMR data are identical to those of a sample prepared as described above.

3. Kinetic Experiments

Annulation reaction of benzyl azide and complexes $\mathbf{1_{Cu2}a}$ and $\mathbf{1_{Cu}a}$:
In a NMR tube, benzyl azide (0.3 mmol) was added to a solution of $\mathbf{1_{Cu2}a}$ (0.015 mmol) in CD_2Cl_2 (0.5 mL) and 1,2-dibromoethane (0.06 mmol) as internal standard. The reaction was monitored by ^1H NMR (Blue). The same procedure was used for the reaction involving $\mathbf{1_{Cu}a}$ (0.015 mmol, red).

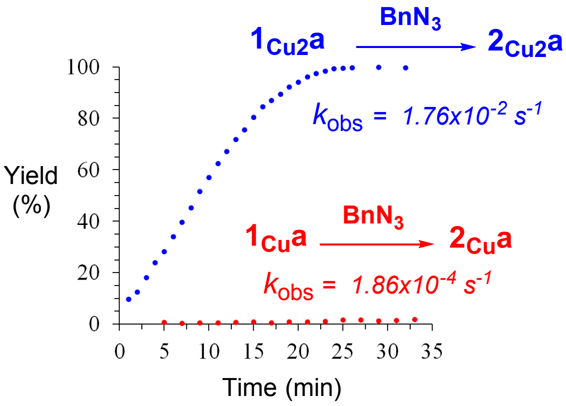


Figure S17. Evolution of the annulation reaction monitored by ^1H NMR

Proto-demetallation of complexes $\mathbf{2_{Cu2}a}$ and $\mathbf{2_{Cu}a}$:
In a NMR tube, phenylacetylene (0.3 mmol) was added to a solution of $\mathbf{2_{Cu2}a}$ (0.015 mmol) in CD_2Cl_2 (0.5 mL) with 1,2-dibromoethane (0.06 mmol) as internal standard. The reaction was monitored by ^1H NMR (Blue). The same procedure was used for the reaction involving $\mathbf{2_{Cu}a}$ (0.015 mmol, red).

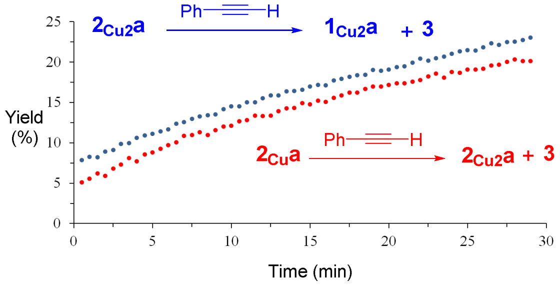


Figure S18. Evolution of the protodemetallation reaction monitored by ^1H NMR

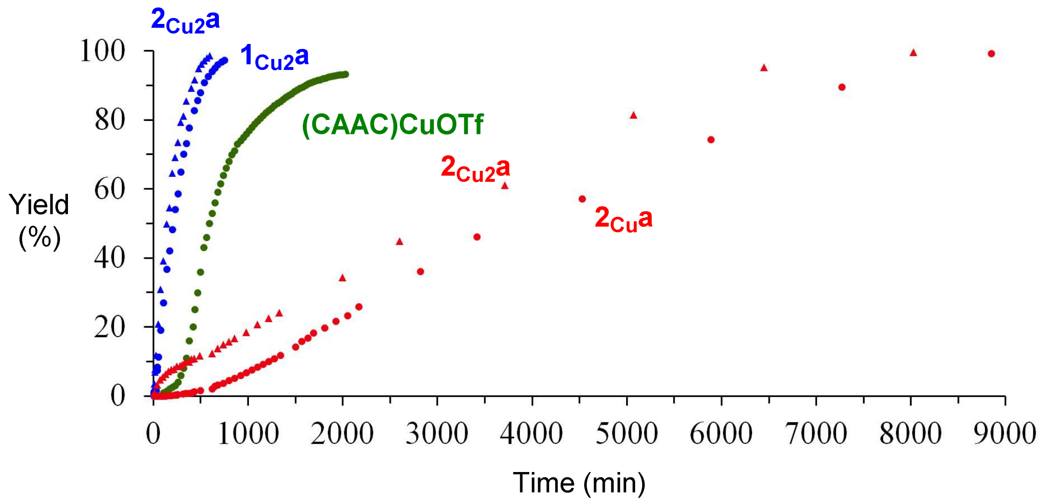


Figure S19. Evolution of the catalytic reaction between benzyl azide and phenyl acetylene monitored by ^{1}H NMR

In NMR tube, a CD_2Cl_2 solution (0.5 mL) of phenylacetylene (0.3 mmol), benzylazide (0.3 mmol), and 1,2-dibromoethane (0.06 mmol) as internal standard was added to the copper catalyst (**2$_{Cu2}$a**, **1$_{Cu2}$a**, (CAAC)CuOTf, **2$_{Cu}$a** and **1$_{Cu}$a**) (0.015 mmol). The reaction was monitored by ^{1}H NMR.

4. X-Ray Diffraction Details

Bis(copper) acetylide complex $\mathbf{1_{Cu2}a}$:

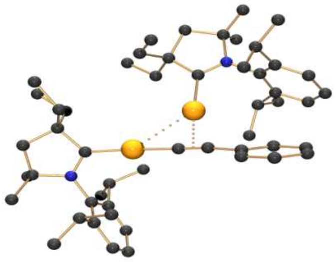


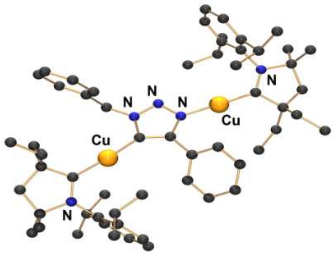
Table S1. Crystal data and structure refinement for $\mathbf{1_{Cu2}a}$.

Identification code	$\mathbf{1_{Cu2}a}$ (CCDC # 1042483)	
Empirical formula	C53 H75 Cu2 F3 N2 O3 S	
Molecular formula	C52 H75 Cu2 N2, C F3 O3 S	
Formula weight	1004.29	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 9.3364(9) Å	α= 90°.
	b = 31.672(3) Å	β= 97.3090(10)°.
	c = 17.7655(17) Å	γ = 90°.
Volume	5210.6(9) Å^3	
Z	4	
Density (calculated)	1.280 Mg/m^3	
Absorption coefficient	0.909 mm^{-1}	
F(000)	2128	
Crystal size	0.215 x 0.122 x 0.104 mm^3	
Crystal color, habit	Yellow Block	
Theta range for data collection	1.286 to 26.433°.	
Index ranges	-11<=h<=11, -39<=k<=39, -22<=l<=22	
Reflections collected	78788	
Independent reflections	10713 [R(int) = 0.0464]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0656	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10713 / 2 / 607	
Goodness-of-fit on F^2	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0325, wR2 = 0.0741	
R indices (all data)	R1 = 0.0444, wR2 = 0.0803	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.424 and -0.272 e.Å^{-3}	

Bis(copper) triazole complex $\mathbf{2_{Cu2}a}$ (X = BF4):

Table S2. Crystal data and structure refinement for $\mathbf{2_{Cu2}a}$ (X = BF4).

Identification code	$\mathbf{2_{Cu2}a}$ (X = BF4) (CCDC # 1042484)	
Empirical formula	C59 H82 B Cu2 F4 N5	
Molecular formula	C59 H82 Cu2 N5, B F4	
Formula weight	1075.18	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 9.365(2) Å	α = 98.164(5)°.
	b = 15.912(3) Å	β = 97.065(5)°.
	c = 19.408(4) Å	γ = 96.941(5)°.
Volume	2812.9(10) Å^3	
Z	2	
Density (calculated)	1.269 Mg/m^3	
Absorption coefficient	0.811 mm^{-1}	
F(000)	1140	
Crystal size	0.113 x 0.035 x 0.021 mm^3	
Crystal color, habit	Yellow Needle	
Theta range for data collection	1.071 to 25.642°.	
Index ranges	-11<=h<=11, -19<=k<=19, -23<=l<=23	
Reflections collected	44855	
Independent reflections	10442 [R(int) = 0.0619]	
Completeness to theta = 25.000°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0613 and 0.0340	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	10442 / 0 / 656	
Goodness-of-fit on F^2	1.132	
Final R indices [I>2sigma(I)]	R1 = 0.0780, wR2 = 0.1933	
R indices (all data)	R1 = 0.1110, wR2 = 0.2132	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.446 and -1.191 e.Å^{-3}	



Bis(copper) triazole complex $\mathbf{1_{Cu2}b}$ (X = BF4):

Table S3. Crystal data and structure refinement for $\mathbf{1_{Cu2}b}$ (X = BF4).

Identification code	$\mathbf{1_{Cu2}b}$ (X = BF4) (CCDC # 1042482)	
Empirical formula	C60.50 H84 B Cl3 Cu2 F4 N2	
Molecular formula	C59 H81 Cu2 N2, B F4, 1.5(C H2 Cl2),	
Formula weight	1159.53	
Temperature	100.0 K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 11.9729(9) Å	α= 85.829(2)°.
	b = 18.9530(15) Å	β = 77.985(2)°.
	c = 27.613(2) Å	γ = 77.201(2)°.
Volume	5974.0(8) Å^3	
Z	4	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.897 mm^{-1}	
F(000)	2444	
Crystal size	0.255 x 0.247 x 0.153 mm^3	
Crystal color, habit	Yellow Block	
Theta range for data collection	1.102 to 24.999°.	
Index ranges	-13<=h<=14, -22<=k<=22, -32<=l<=29	
Reflections collected	81431	
Independent reflections	20999 [R(int) = 0.0419]	
Completeness to theta = 24.999°	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.0932 and 0.0665	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	20999 / 346 / 1517	
Goodness-of-fit on F^2	1.023	
Final R indices [I>2sigma(I)]	R1 = 0.0861, wR2 = 0.2427	
R indices (all data)	R1 = 0.1113, wR2 = 0.2642	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.082 and -1.193 e.Å^{-3}