Supporting Information

Direct Observation of β-Alkynyl Eliminations from Unstrained Propargylic Alkoxide Cu(I) Complexes by C-C Bond Cleavage

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General considerations

All reactions were conducted under a nitrogen atmosphere unless otherwise noted. All reagents were commercially purchased and used as received unless otherwise noted. Anhydrous solvents were purified by passage through neutral alumina using an Innovative Technology, Inc., PureSolv solvent purification system. Elemental analyses were performed by Atlantic Microlab, Inc. (Norcross, GA, USA). Multinuclear NMR spectra were acquired on a 500 MHz NMR spectrometer. Chemical shifts are reported in ppm relative to a residual solvent peak $CDCl_3$ = 7.26 ppm for ^1H NMR spectroscopy and 77.23 ppm for ^{13}C NMR spectroscopy (for C_6D_6 = 7.15 ppm). Deuterated solvents or liquid substrates/starting materials were subjected to three cycles of freeze, pump, and thaw before storing over activated 4 Å molecular sieves in the glovebox under an atmosphere of N_2. Solid substrates/starting materials were placed under vacuum before taken into the glovebox. The following chemicals were commercially purchased: copper-mesityl (CuMes) (Strem Chemicals), 1,1'-Bis(diphenylphosphino)ferrocene (dppf) (Sigma Aldrich), and *S*-2,2'-Bis(diphenylphosphino)-1,1'-binaphthyl (*S*-BINAP) (TCI America, Portland). Complexes (IPr)CuCl and the series of (IPr*R)CuCl (R = Me, OMe, Cl) were prepared from the corresponding NHC·HCl and Cu_2O in toluene at 100 ºC from published procedure.[1]

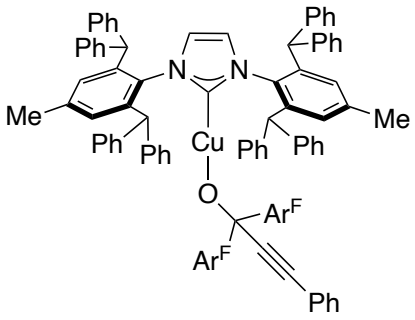
The synthesis of 1,1-bis(4-fluorophenyl)-3-phenylprop-2-yn-1-ol ($HOC(Ar^F)_2C{\equiv}CPh$) was adapted from published procedure.[2] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.65 (dd, *J* = 8.6, 5.3 Hz, 4H, Ar^F-*H*), 7.53 (dd, *J* = 7.2, 2.2 Hz, 2H, Ar-*H*), 7.38-7.37 (m, 3H, Ar-*H*), 7.06 (t, *J* = 8.5 Hz, 4H, Ar^F-*H*). **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -114.6.

1,1-Bis(4-fluorophenyl)-3-(thiophen-2-yl)-prop-2-yn-1-ol ($HOC(Ar^F)_2C{\equiv}CC_4H_4S$) was prepared according to published procedure.[3] **^{1}H NMR** (500 MHz, $CDCl_3$): δ 7.61 (dd, *J* = 8.8, 5.4 Hz, 4H, Ar-*H*), 7.34 (dd, *J* = 5.2, 1.2 Hz, 1H, Ar-*H*), 7.31 (dd, *J* = 3.7, 1.2 Hz, 2H, Ar-*H*), 7.08-7.02 (m, 5H, Ar-*H*). **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -114.4.

X-ray crystallography: Data for single crystals was collected on a Bruker KAPPA APEX III diffractometer equipped with an APEX III CCD detector using a TRIUMPH monochromator with a Mo Kα X-ray source (α = 0.71073 Å). The crystals were mounted on a cryoloop with Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. A hemisphere of data was collected using ω scans with 0.5° frame widths. Data collection and cell parameter determination were conducted using the SMART program. Integration of the data frames and final cell parameter refinement were performed using SAINT software. Absorption correction of the data was carried out using SADABS. Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.

Synthesis of (NHC)CuOC(Ar^F)$_2$C≡CPh series

A general procedure for preparing (IPr*R)CuOC(Ar^F)$_2$C≡CPh (1-Me)



Inside a nitrogen-filled glovebox, to an oven-dried 20 mL scintillation vial was added (IPr*Me)CuCl (250 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 4 mL toluene, and a small stir bar. After 0.5 h, solid HOC(Ar^F)$_2$C≡CPh (83.0 mg, 0.260 mmol) was added to the reaction mixture. After 1 h, the solution was filtered into a new oven-dried 20 mL scintillation vial by glass pipette containing Celite. All volatiles were removed by dynamic vacuum. The resulting solid was triturated with pentane (5 mL), collected on a medium porosity frit, washed with pentane (10 mL), and dried under dynamic vacuum. The product can be further recrystallized by layering of pentane over a concentrated toluene solution of **1** at 25 ºC. Yield = 80% (256 mg, 0.197 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.02 (dd, *J* = 8.5, 5.4 Hz, 4H, Ar-*H*), 7.39 (d, *J* = 7.5 Hz, 8H, Ar-*H*), 7.20-7.08 (m, 10H, Ar-*H*), 7.09 (d, *J* = 6.4 Hz, 2H, Ar-*H*), 7.03-6.93 (m, 18H, Ar-*H*), 6.94-6.88 (m, 12H, Ar-*H*), 6.85 (t, *J* = 8.7 Hz, 3H, Ar-*H*), 5.56 (s, 4H, C*H*Ph$_2$), 5.37 (s, 2H, *H*-C≡C-*H*), 1.72 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 182.4 (Cu-carbene), 161.8 (d, *J* = 242.2 Hz, Ar-F), 150.1, 143.7, 143.4, 141.3, 140.4, 135.0, 132.1, 130.35, 130.30, 129.8, 129.1, 128.6, 127.1, 126.8, 125.7, 123.4, 114.3 (d, *J* = 20.7 Hz, Ar-F), 101.4, 82.9, 77.2, 51.8 (H-*C*≡*C*-H), 21.4 (*Me*). **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -118.3. **Anal. Calcd** for $C_{90}H_{69}CuF_2N_2O$: C, 83.40; H, 5.37; N, 2.16. Found: C, 83.22; H, 5.49; N, 2.11. Single crystals for XRD measurement were obtained by layering of pentane into a saturated toluene solution of **1-Me** at 25 ºC.

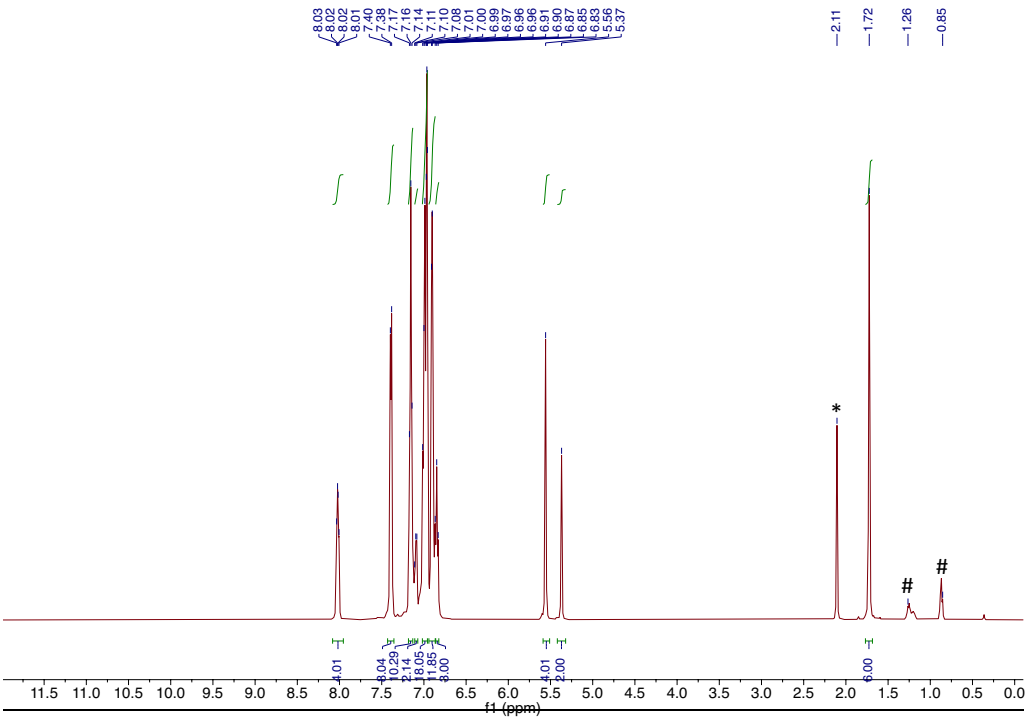


Figure S1A. ^{1}H NMR spectrum of **1-Me**.*Toluene, #pentane.

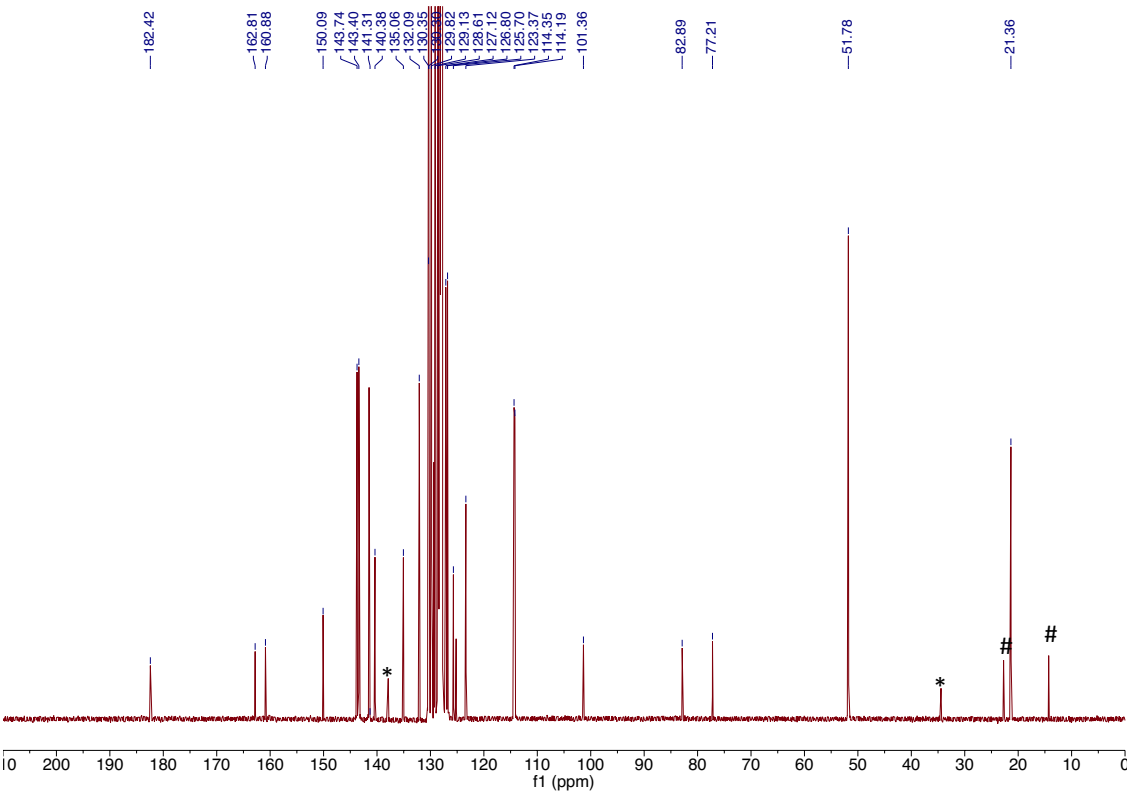


Figure S1B. $^{13}C\{^{1}H\}$ NMR spectrum of **1-Me**.*Toluene, #pentane.

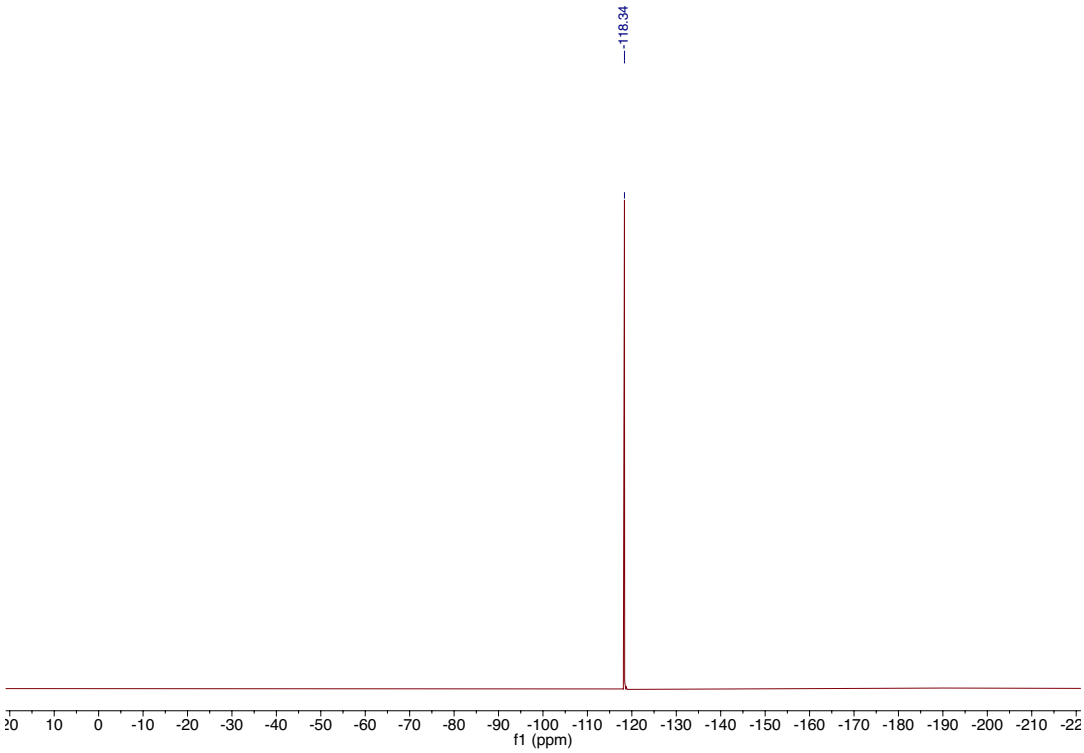
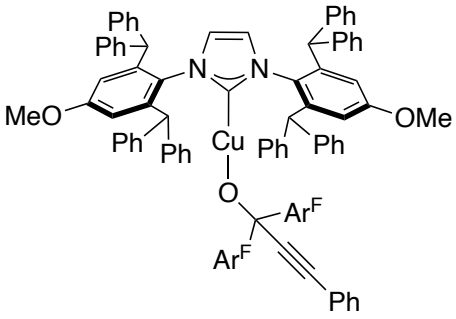


Figure S1C. $^{19}F\{^{1}H\}$ NMR spectrum of **1-Me**.

(IPr*OMe)CuOC(Ar^F)$_2$C≡CPh (1-OMe)



The titled compound was synthesized according to the general procedure for complex **1**: (IPr*OMe)CuCl (258 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 4 mL toluene, and HOC(Ar^F)$_2$C≡CPh (83.0 mg, 0.260 mmol). Yield = 75% (246 mg, 0.185 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.03 (dd, *J* = 8.4, 5.5 Hz, 4H, Ar-*H*), 7.38 (d, *J* = 7.5 Hz, 8H, Ar-*H*), 7.14 (m, 12H, Ar-*H*), 7.05 – 6.80 (m, 29H, Ar-*H*), 6.72 (s, 4H, Ar-*H*), 5.55 (s, 4H, C*H*Ph$_2$), 5.34 (s, 2H, *H*-C≡C-*H*), 3.0 (s, 6H, O*Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ-183.1 (Cu-carbene), 161.8 (d, $J_{C\text{-}F}$ = 242.3 Hz, Ar-F), 160.5, 150.0, 143.3 (d, $J_{C\text{-}F}$ = 33.9 Hz, Ar-F), 143.2, 131.9, 130.2, 129.7, 129.0, 128.6, 128.5, 128.4, 127.1, 126.7, 123.5, 114.2 (d, $J_{C\text{-}F}$ = 20.9 Hz, Ar-F) 101.3, 82.9, 77.2, 54.5, 51.9. **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -118.5. **Anal. Calcd** for $C_{90}H_{69}CuF_2N_2O_3$: C, 81.39; H, 5.24; N, 2.11. Found: C, 81.60; H, 5.38; N, 2.17. Single crystals for XRD measurement were obtained by layering of pentane into a saturated toluene solution of **1-OMe** at 25 ºC.

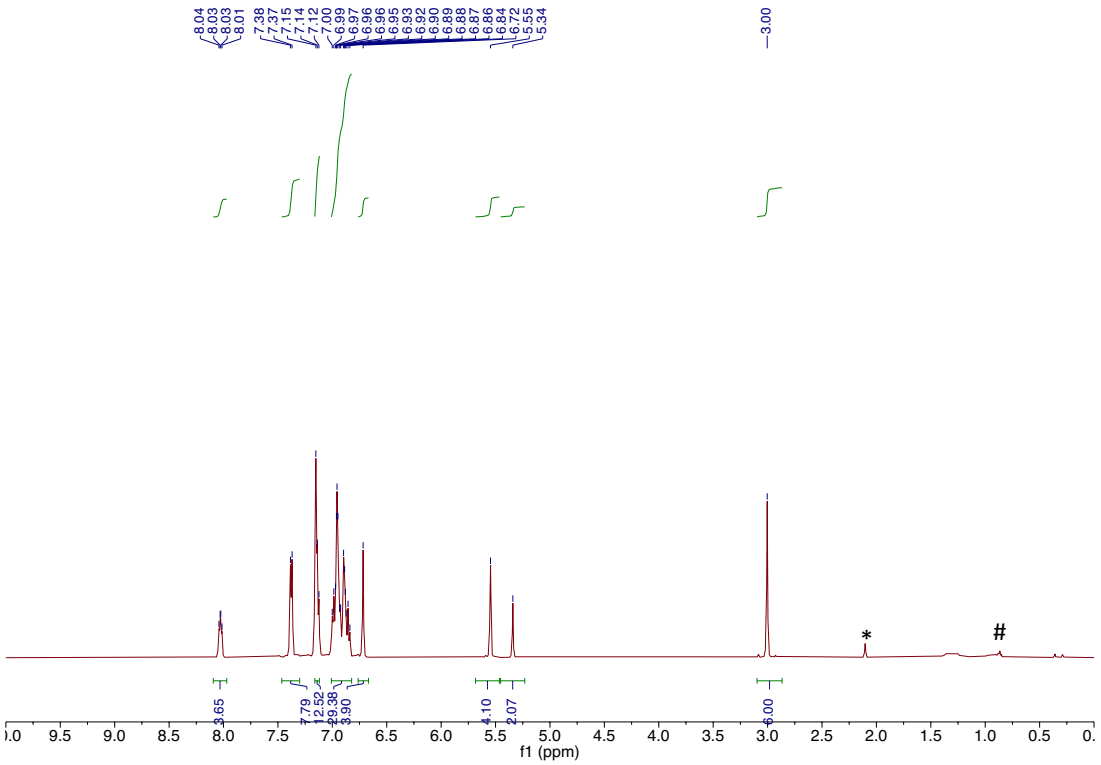


Figure S2A. ^{1}H NMR spectrum of **1-OMe**. *Toluene, #pentane.

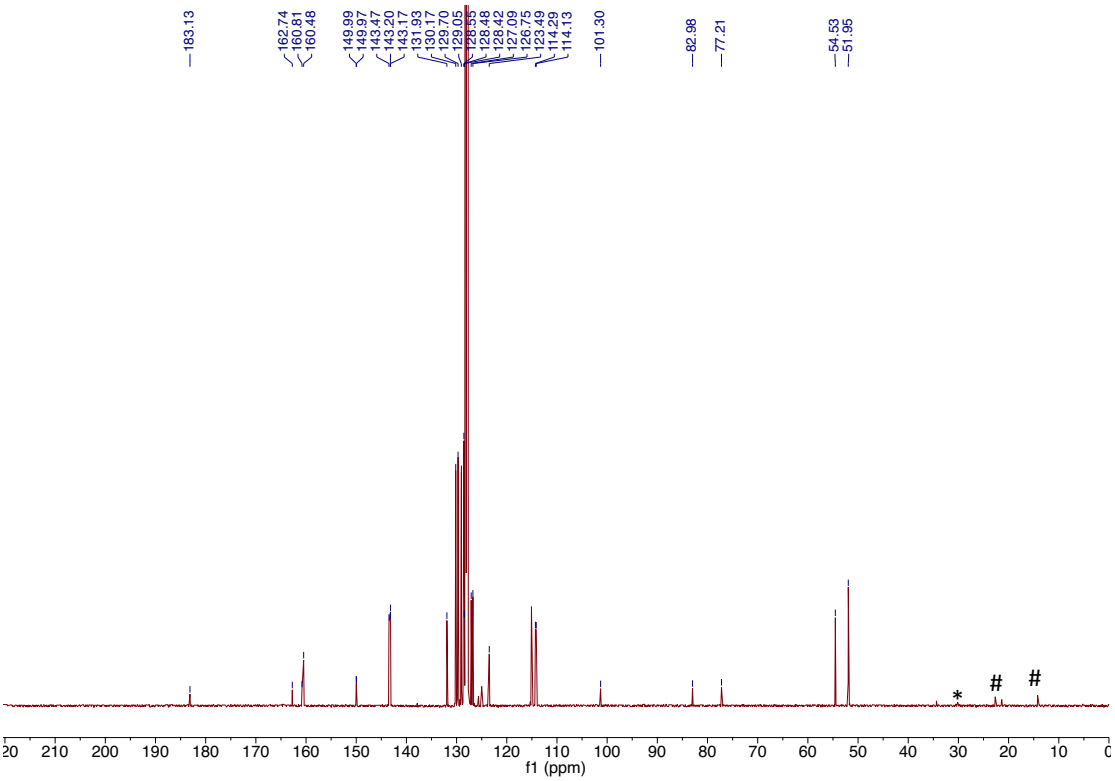
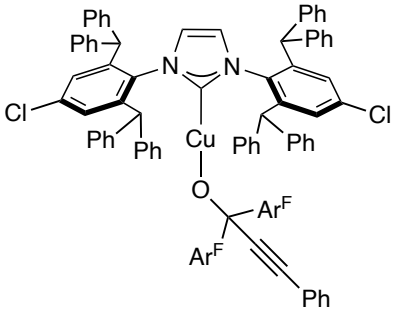


Figure S2B. $^{13}C\{^{1}H\}$ NMR spectrum of **1-OMe**. *Toluene, #pentane.

(IPr*Cl)CuOC(Ar^{F})$_2$C≡CPh (1-Cl)



The titled compound was synthesized according to the general procedure for complex **1**: (IPr*Cl)CuCl (260 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 4 mL toluene, and HOC(Ar^{F})$_2$C≡CPh (83.0 mg, 0.260 mmol). Yield = 73% (241 mg, 0.180 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.01-7.98 (m, 4H, Ar-*H*), 7.27-7.24 (m, 12H, Ar-*H*), 7.10-7.07 (m, 8H, Ar-*H*)6.98-6.88 (m, 18H, Ar-*H*), 6.94-6.88 (m, 18H, Ar-*H*), 6.73 (d, *J* = 7.4 Hz, 7H, Ar-*H*), 5.43 (s, 4H, C*H*Ph$_2$), 5.28 (s, 2H, *H*-C≡C-*H*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 183.3 (Cu-carbene), 162.6 (d, *J* = 242.0 Hz, Ar-F), 150.6, 144.8, 143.5, 142.9, 137.7.0, 136.5, 132.5, 130.7, 130.3, 130.1, 129.5, 128.2.1, 127.8, 126.4, 125.5, 124.0, 115.1 (d, *J* = 20.6 Hz, Ar-F), 101.8, 83.9, 77.9, 52.5 (H-*C*≡*C*-H), 21.4. **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -117.9. Single crystals for XRD measurement were obtained by layering of pentane into a saturated toluene solution of **1-Cl** at 25 ºC.

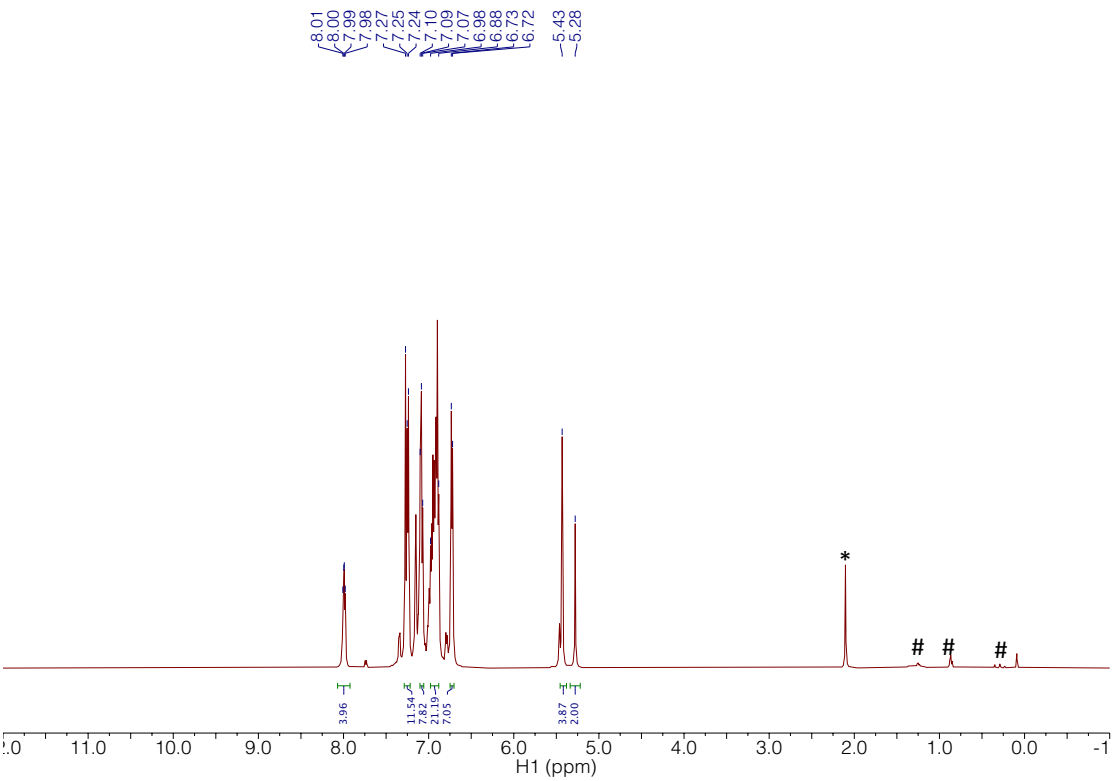


Figure S3A. ^{1}H NMR spectrum of **1-Cl**. *Toluene, #pentane.

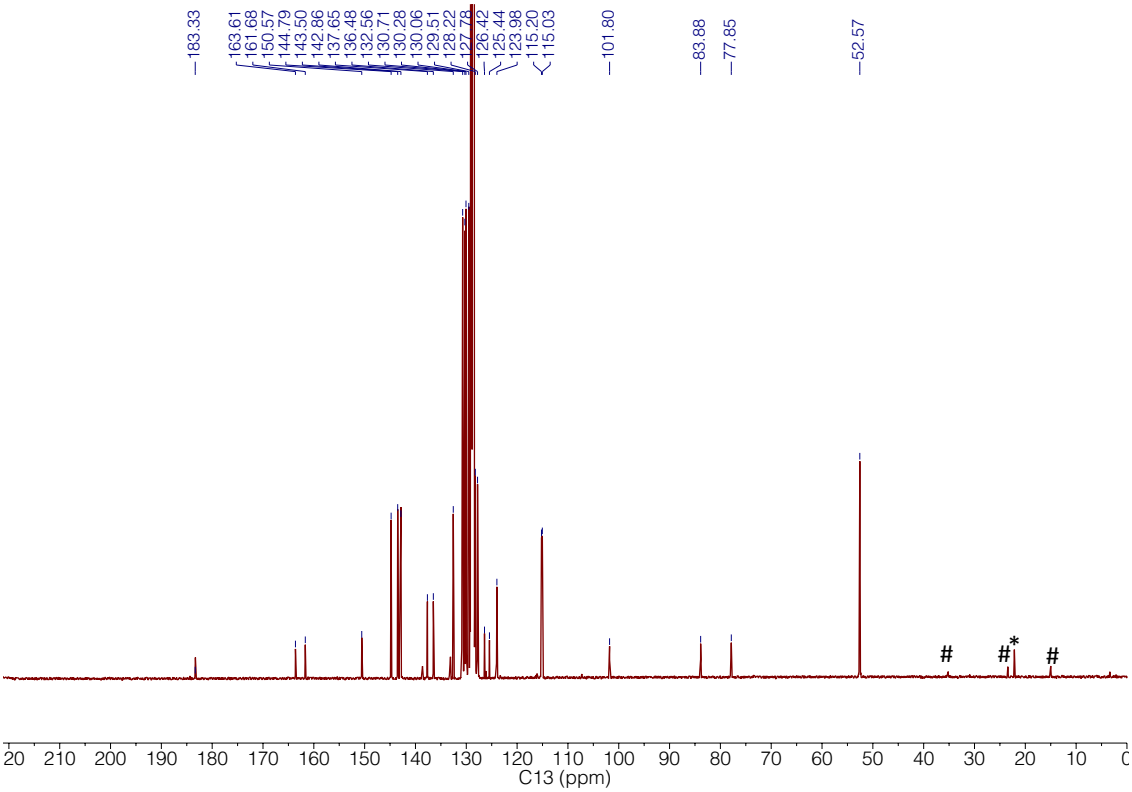


Figure S3B. ^{13}C NMR spectrum of **1-Cl**. *Toluene, #pentane.

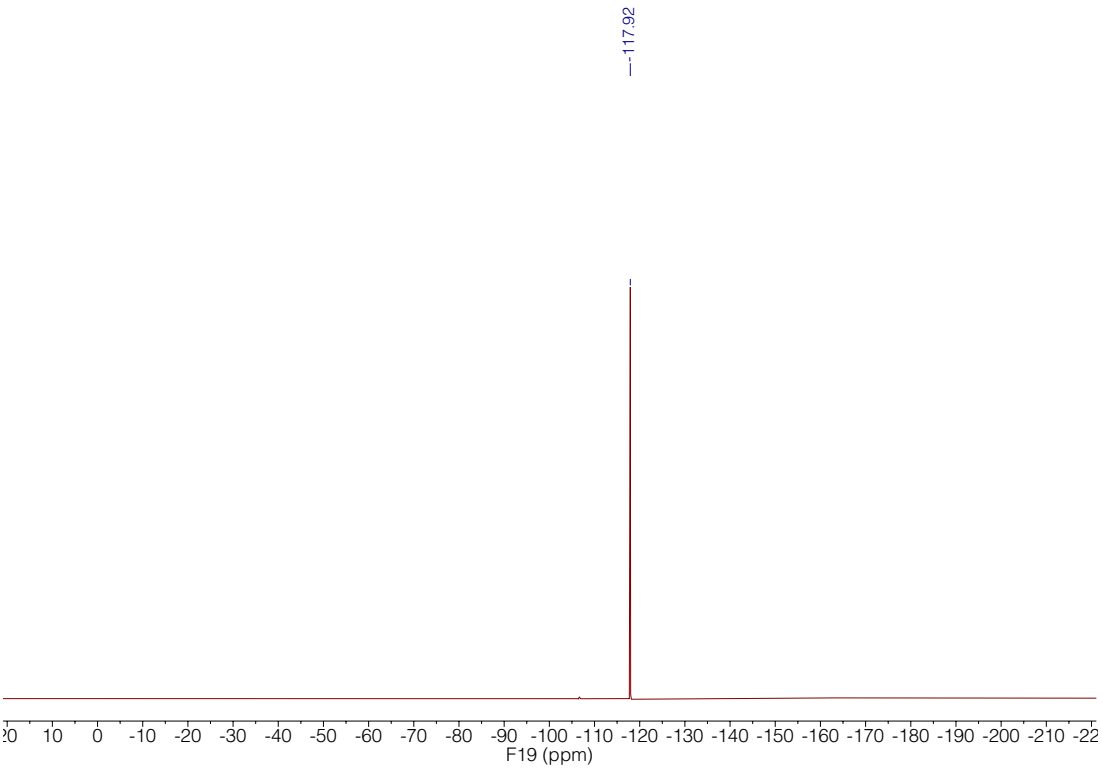
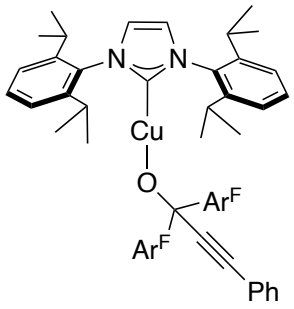


Figure S3C. $^{19}F\{^{1}H\}$ NMR spectrum of **1-Cl**.

(IPr)CuOC(Ar^{F})$_2$C≡CPh (3)



Inside a nitrogen-filled glovebox, to an oven-dried 20 mL scintillation vial was added (IPr)CuCl (120 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 10 mL toluene, and a small stir bar. After 0.5 h, the reaction mixture was filtered into a new oven-dried 20 mL scintillation by a glass pipette containing Celite. To the colorless filtrate was added solid HOC(Ar^{F})$_2$C≡CPh (83.0 mg, 0.260 mmol). After 1.5 h, the white precipitate was collected on a 25 mL medium porous glass frit, washed with pentane (3 mL), and dried under dynamic vacuum. Yield = 65% (124 mg, 0.160 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.76 (d, *J* = 3.2 Hz, 4H, Ar-*H*), 7.30 (d, *J* = 7.1 Hz, 2H, Ar-*H*), 7.20 (m, 2H, Ar-*H*), 7.04-6.97 (m, 7H, Ar-*H*), 6.71 (t, *J* = 8.4 Hz, 4H, Ar-*H*), 6.16 (s, 2H, *H*-C=C-*H*), 2.44 (septet, *J* = 6.85 Hz, 4H, C*H*(Me)$_2$), 1.25 (d, *J* = 6.9 Hz, 12H, CH(*Me*)$_2$), 1.25 (d, *J* = 6.6 Hz, 12H, CH(*Me*)$_2$). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 182.4 (Cu-carbene), 161.6 (d, $J_{C\text{-}F}$ = 241.7 Hz), 149.8, 145.5, 134.9, 132.1, 130.6, 127.2, 125.6, 124.2, 122.5, 114.0 (d, *J* = 20.9 Hz), 101.1, 82.8, 76.9, 28.9 (*C*HMe$_2$), 24.9 (CH*Me*$_2$), 23.6 (CH*Me*$_2$). **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -119.0.

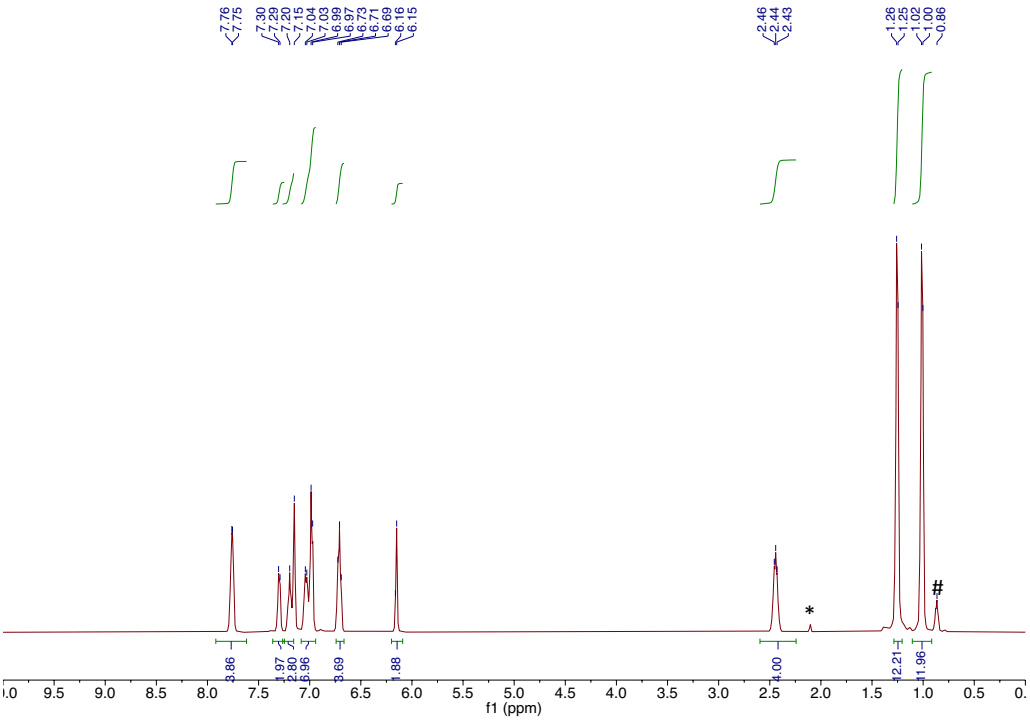


Figure S4A. ^{1}H NMR spectrum of **3**. *Toluene, #pentane.

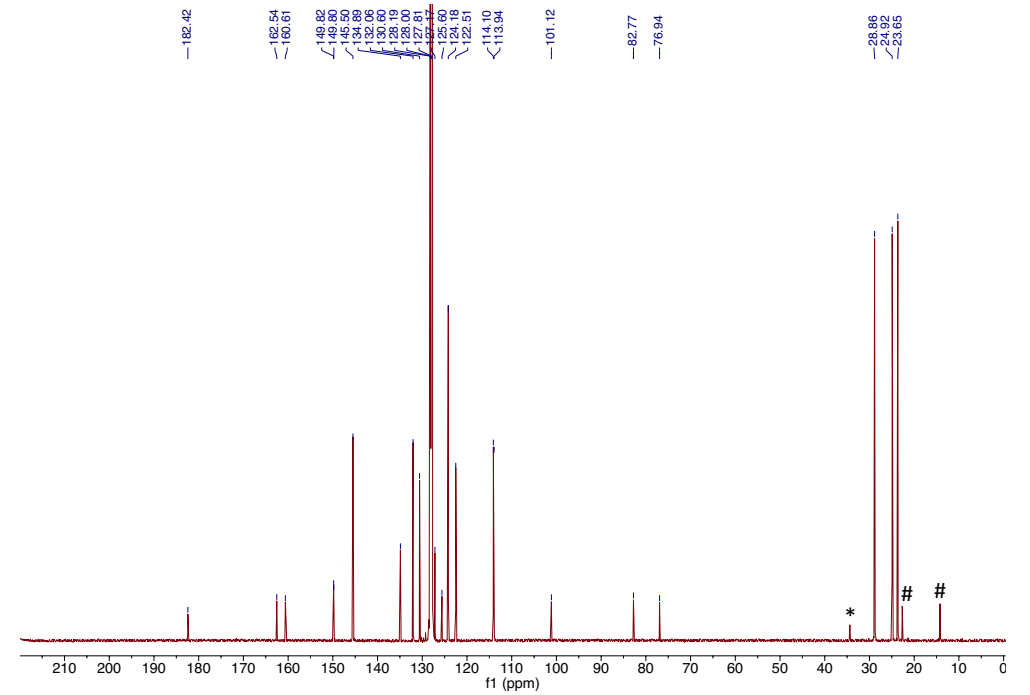


Figure S4B. $^{13}C\{^{1}H\}$ NMR spectrum of **3**. *Toluene, #pentane.

β-Alkynyl eliminations of (NHC)CuOC(Ar^F)$_2$C≡CPh series

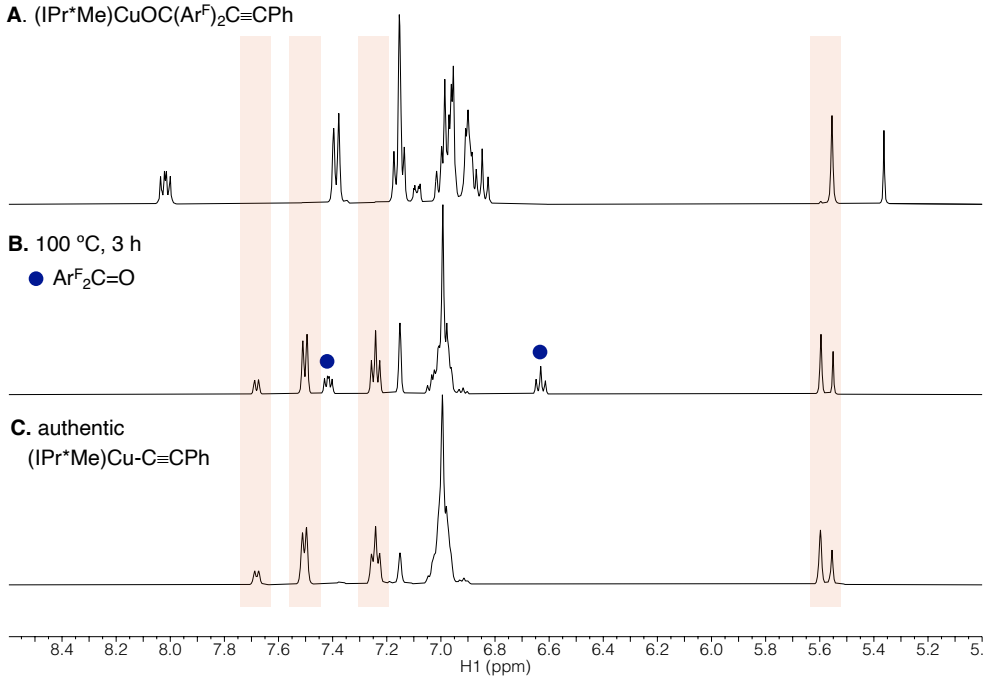


Figure S5A. ^{1}H NMR spectra for the conversion of **1-Me** to (IPr*Me)CuC≡CPh (**2-Me**) and Ar^F_2C=O at 100 ºC for 3 h.

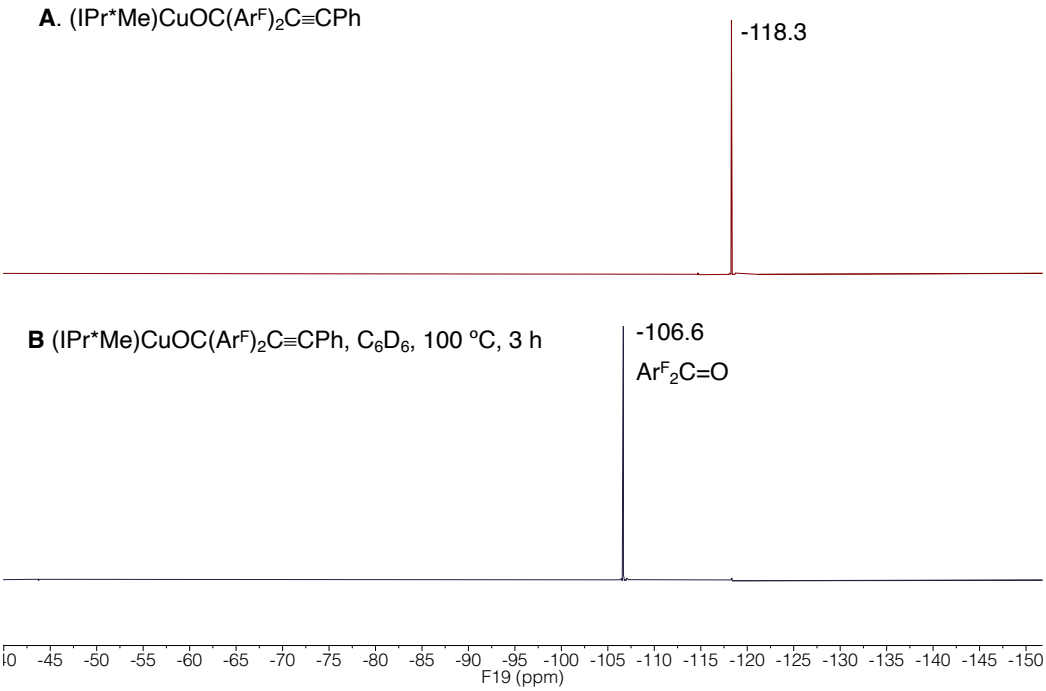


Figure S5B. $^{19}F\{^1H\}$ NMR spectra of **1-Me** at 100 ºC for 3 h showing Ar^F_2C=O formation.

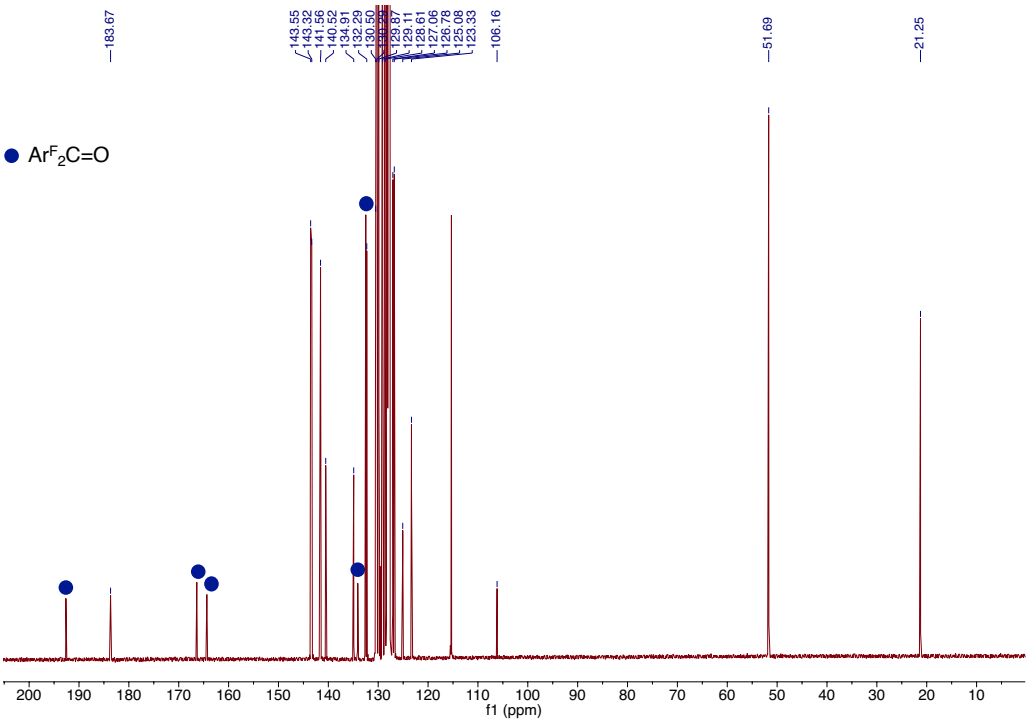


Figure S5C. $^{13}C\{^{1}H\}$ NMR spectrum of **1-Me** at 100 ºC for 3 h.

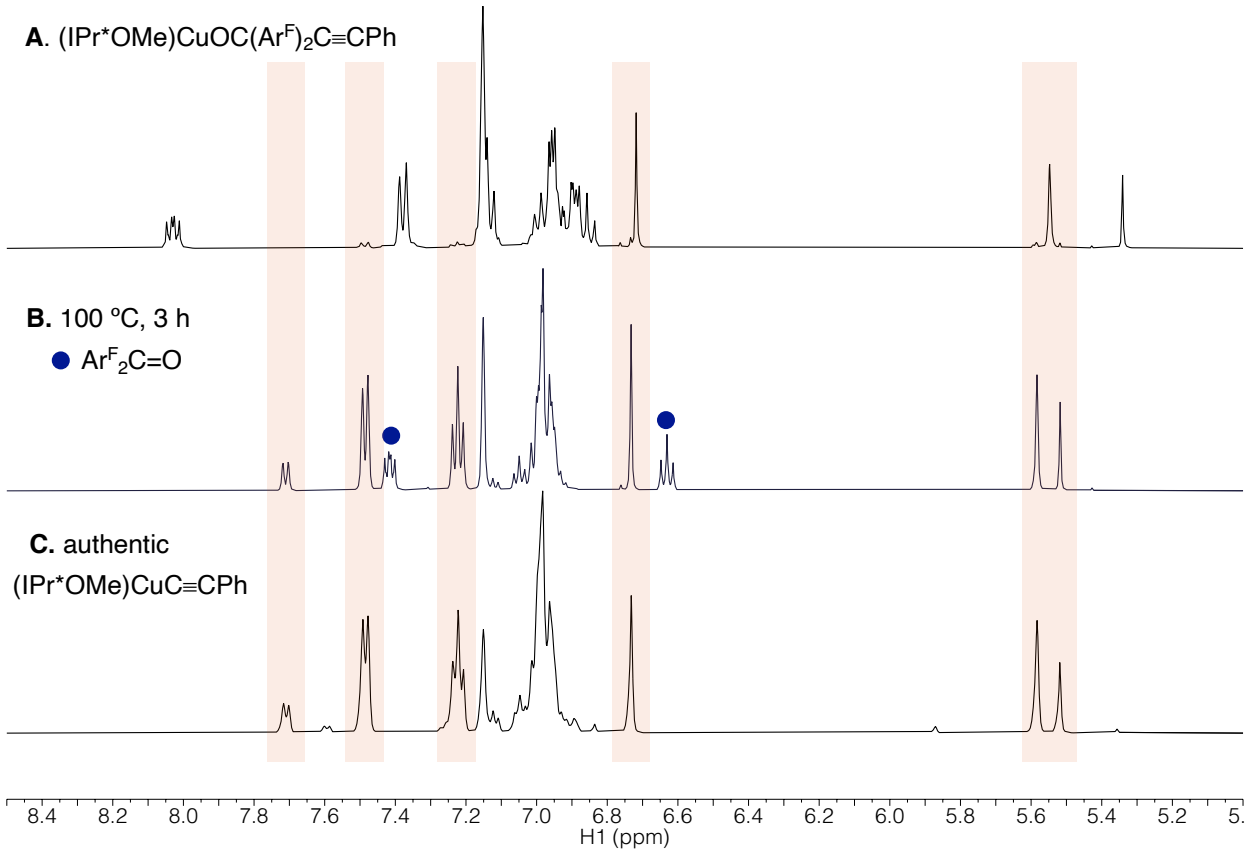


Figure S6. ^{1}H NMR spectra of (IPr*OMe)CuOC(Ar^{F})$_2$C≡CPh (**1-OMe**) at 100 ºC for 3 h.

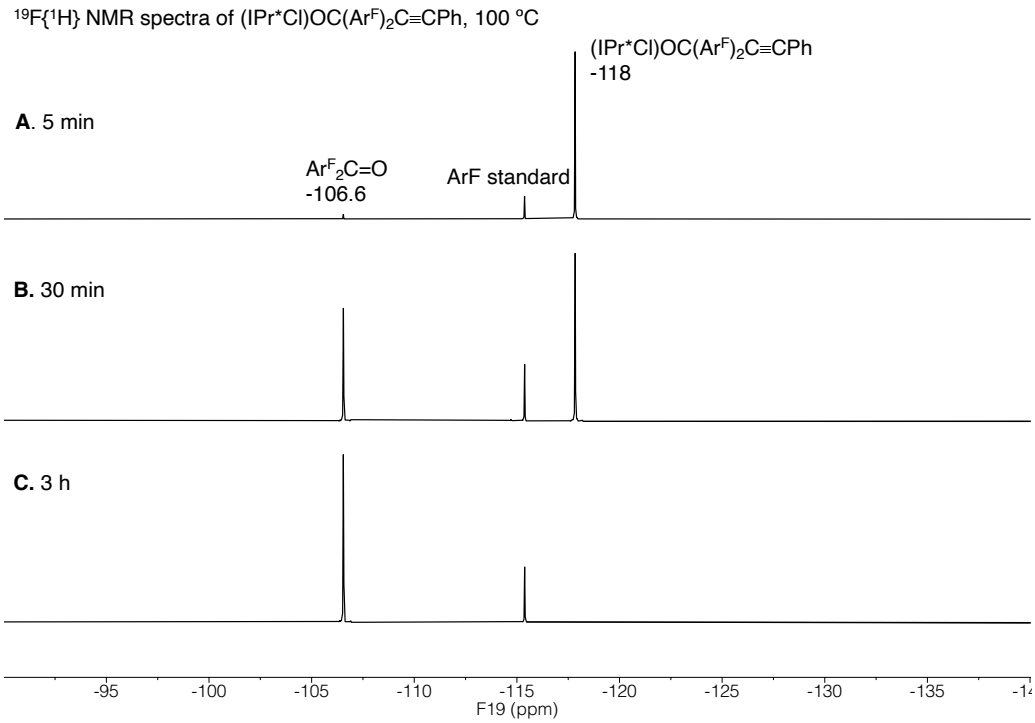


Figure S7. $^{19}F\{^{1}H\}$ NMR spectra of (IPr*Cl)CuOC(Ar^F)$_2$C≡CPh (**1-Cl**) at 100 ºC for 3 h.

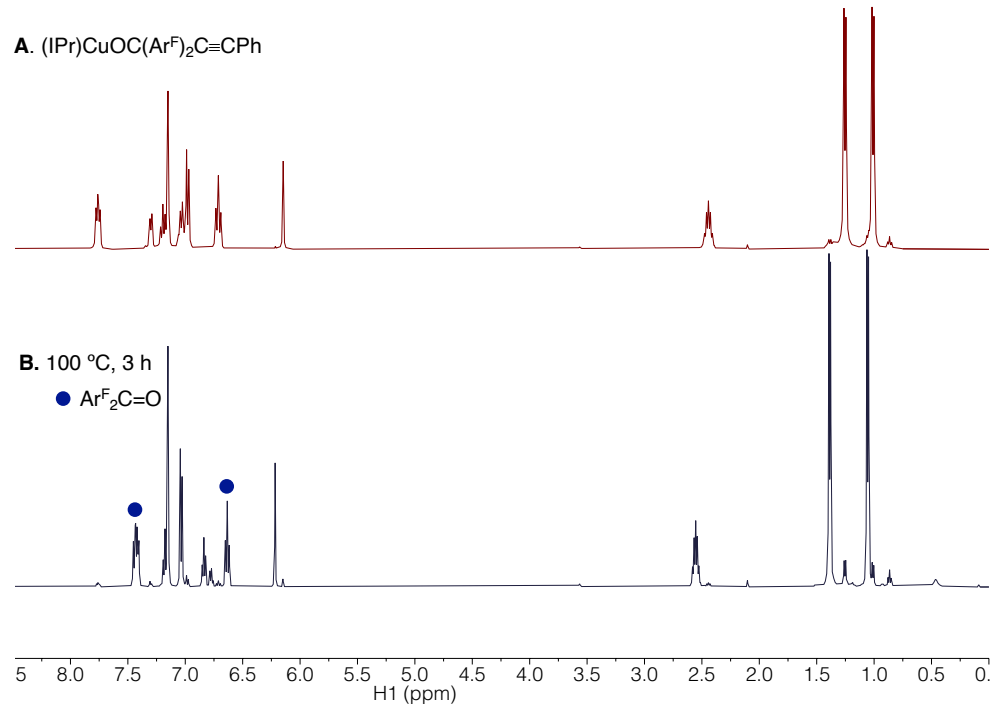
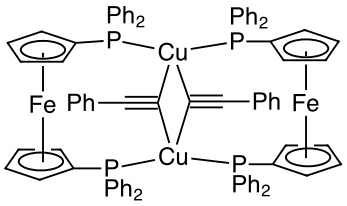


Figure S8. ^{1}H NMR spectra of (IPr)CuOC(Ar^F)$_2$C≡CPh (**3**) at 25 ºC (A) and at 100 ºC for 3 h (B). The resonances of the resulting (IPr)CuC≡CPh are consistent with those reported in the literature.[4]

β-Alkynyl eliminations of (L)CuCuOC(Ar^F)$_2$C≡CPh complexes (L = dppf, *S*-BINAP)

Formation of [(μ-dppf)CuC≡CPh]$_2$ (4)



Inside a nitrogen-filled glovebox, to oven-dried 4 mL scintillation vial was added dppf (15.2 mg, 0.0273 mmol) and C_6D_6 (750 μL) to give a yellow solution. This solution was added to an oven-dried 4 mL scintillation vial containing Cu-mesityl (5.00 mg, 0.0273 mmol) and a small stir bar. After 0.5 h, this yellow mixture was added to solid HOC(Ar^F)$_2$C≡CPh (9.18 mg mg, 0.0286 mmol) in an oven-dried 4 mL scintillation vial. The resulting golden mixture was transferred to a J. Young NMR tube, removed from the glovebox, and analyzed by ^{1}H, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR spectroscopy. The reaction progress was monitored over 3 h at 25 ºC.

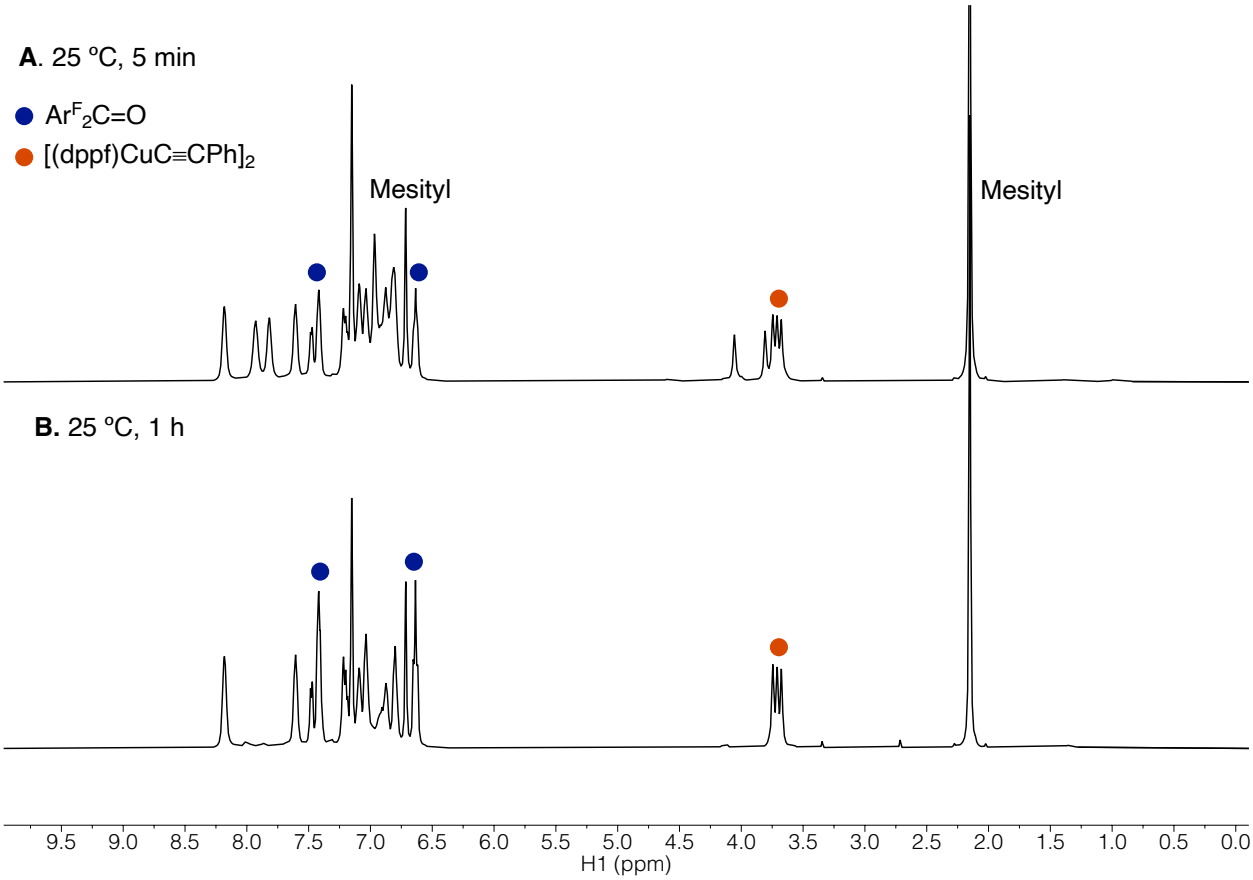


Figure S9A. ^{1}H NMR spectra for the reaction of dppf, CuMes, and HOC(Ar^F)$_2$C≡CPh at 25 ºC for 5 min and 1 h, showing the formation of [(μ-dppf)CuC≡CPh]$_2$ (**4**) and Ar$^F_2$C=O.

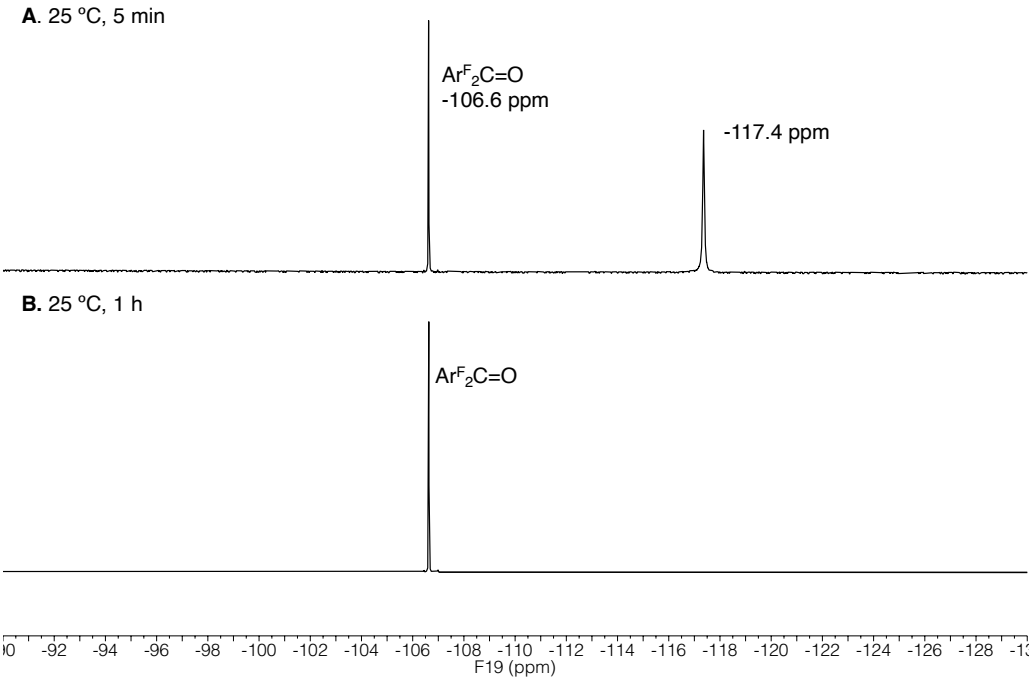


Figure S9B. $^{19}F\{^{1}H\}$ NMR spectra for the reaction of dppf, CuMes, and $HOC(Ar^F)_2C{\equiv}CPh$ at 25 °C for 5 min and 1 h, showing the formation of $Ar^F{}_2C{=}O$ from proposed (dppf)Cu $OC(Ar^F)_2C{\equiv}CPh$.

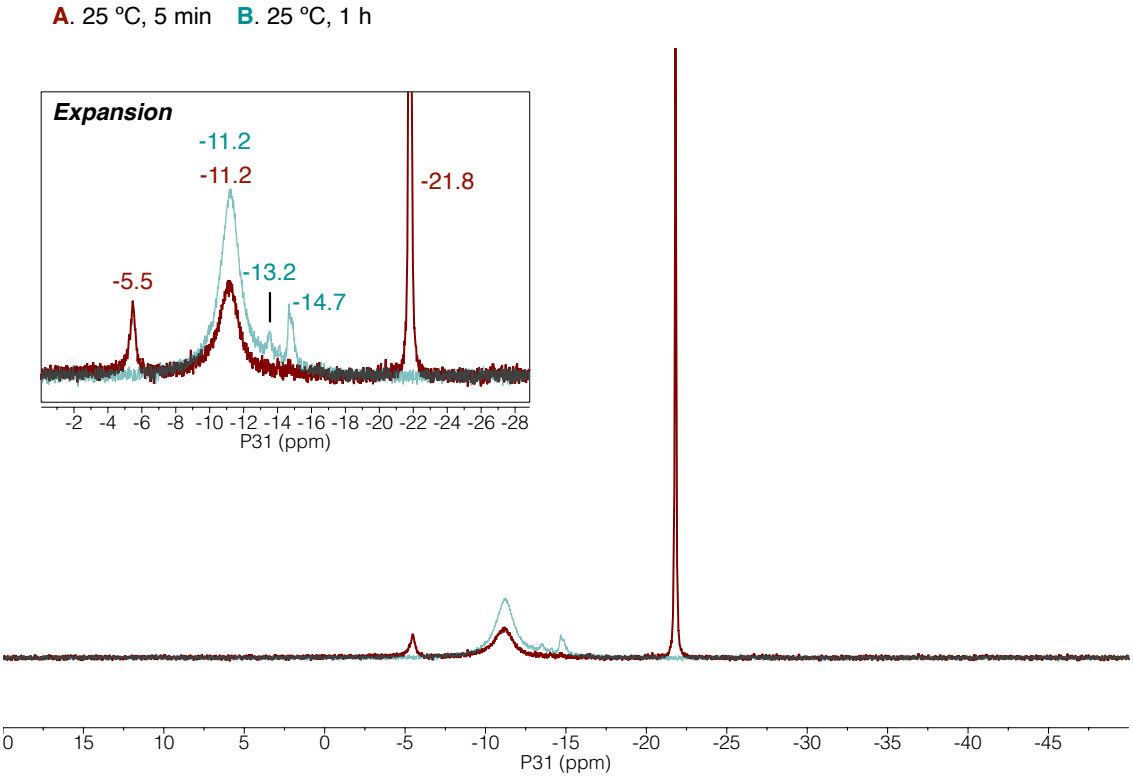


Figure S9C. $^{31}P\{^{1}H\}$ NMR spectral overlay for the reaction of dppf, CuMes, and $HOC(Ar^F)_2C{\equiv}CPh$ at 25 °C for 5 min and 1 h, showing the formation of **4**.

Preparative-scale isolation of [(μ-dppf)CuC≡CPh]$_2$ (4): Inside a nitrogen-filled glovebox, to an oven-dried 20 mL scintillation vial was added Cu-mesityl (50 mg, 0.273 mmol), a small stir bar, and toluene (0.5 mL). In a separate oven-dried 4 mL scintillation vial was added dppf (152 mg, 0.273 mmol) and toluene (3 mL), which was added to the Cu-mesityl solution to give a golden reaction mixture. After 1 h, a 2 mL toluene solution of HOC(Ar^F)$_2$C≡CPh (87.5 mg, 0.273 mmol) was added to give an orange-yellow mixture. After 3 h, all volatiles were removed by dynamic vacuum. The resulting yellow solids were dissolved in THF (5 mL) and filtered through a glass pipette containing Celite into a new 20 mL scintillation vial. The resulting THF solution was layered with pentane (15 mL). After 48 h at room temperature, the mother liquor was decanted, the yellow-orange solid was rinsed with pentane, the pentane was decanted, and the solid was dried under dynamic vacuum. Yield = 60% (124 mg, 0.0819 mmol). **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.18 (br s, 6H, Ar-*H*), 7.61 (br s, 6H, Ar-*H*), 7.48 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 7.22-7.18 (m, 8H, Ar-*H*), 7.09 (d, *J* = 6.9 Hz, 8H, Ar-*H*), 7.03 (t, *J* = 7.6 Hz, 10H, Ar-*H*), 6.88-6.66 (m, 4H, Ar-*H*), 6.80 (t, *J* = 7.6 Hz, 8H, Ar-*H*), 3.74 (s, 4H, C_5H_4), 3.71 (s, 4H, C_5H_4), 3.68 (s, 4H, C_5H_4). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): δ -11.1. The ^{1}H, ^{31}P{^{1}H} NMR spectroscopic data is consistent with those reported in the literature for complex **4**.[5] Single crystals for XRD measurement were obtained by layering of 10 mL of pentane over a saturated THF solution of **4** at 25 ºC.

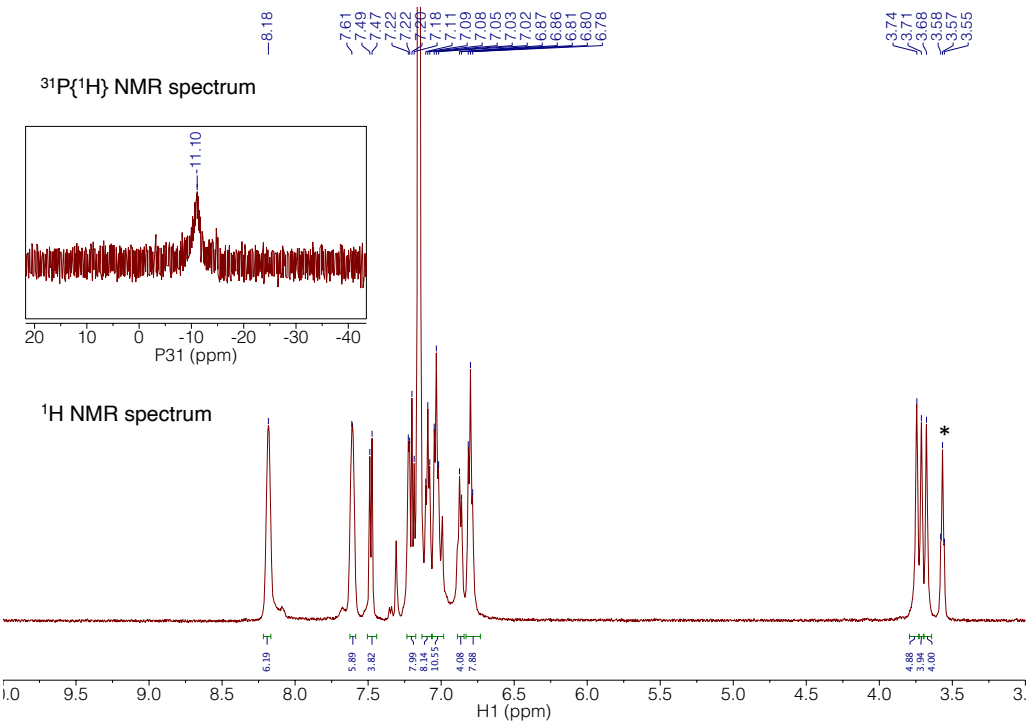
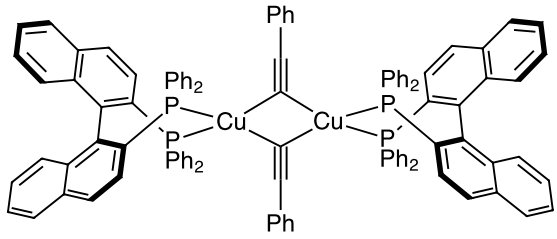


Figure S10. ^{1}H and ^{31}P{^{1}H} spectrum of isolated **4**. *THF residue in the crystalline product.

Formation of [(*S*-BINAP)CuC≡CPh]$_2$ (5)



Inside a nitrogen-filled glovebox, to oven-dried 4 mL scintillation vial was added *S*-BINAP (17.0 mg, 0.0273 mmol) and C_6D_6 (750 μL) to give a colorless solution. This solution was added to an oven-dried 4 mL scintillation vial containing Cu-mesityl (5.00 mg, 0.0273 mmol) and a small stir bar. After 1 h, this yellow mixture was added to solid HOC(Ar^F)$_2$C≡CPh (9.18 mg, 0.0286 mmol) in an oven-dried 4 mL scintillation vial. The resulting yellow mixture was transferred to a J. Young NMR tube, removed from the glovebox, and analyzed by ^{1}H, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR spectroscopy. The reaction progress was monitored over 2 h at room temperature to give a bright golden solution. After completion, the yellow crystalline product of [(*S*-BINAP)CuC≡CPh]$_2$ was isolated by slow diffusion of pentane into the C_6D_6 reaction mixture at room temperature for 48 h. Yield = 52% (24.0 mg, 0.0152 mmol). **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.72 (br s, 8H, Ar-*H*), 8.09 (broad resonance, 6H, Ar-*H*), 7.66 (m, 4H, Ar-*H*), 7.55 (d, *J* = 7.6 Hz, 4H, Ar-*H*), 7.23-7.19 (m, 8H, Ar-*H*), 7.13-7.10 (m, 10H, Ar-*H*), 7.03 (t, *J* = 7.5 Hz, 4H, Ar-*H*), 6.83 (t, *J* = 7.7 Hz, 4H, Ar-*H*), 6.72 (t, *J* = 7.7 Hz, 8H, Ar-*H*), 6.66 (t, *J* = 7.4 Hz, 4H, Ar-*H*), 6.49 (t, *J* = 7.4 Hz, 4H, Ar-*H*), 6.39 (br s, 10H, Ar-*H*). **^{31}P{^{1}H} NMR** (202 MHz, C_6D_6): δ -3.5. A closely related analogue of [(*R*-BINAP)CuC≡C(C_6H_5-*p*-Me]$_2$ has been reported: G. Hattori, K. Sakata, H. Matsuzawa, Y. Tanabe, Y. Miyake and Y. Nishibayashi, *J. Am. Chem. Soc.*, 2010, *132*, 10592-10608.

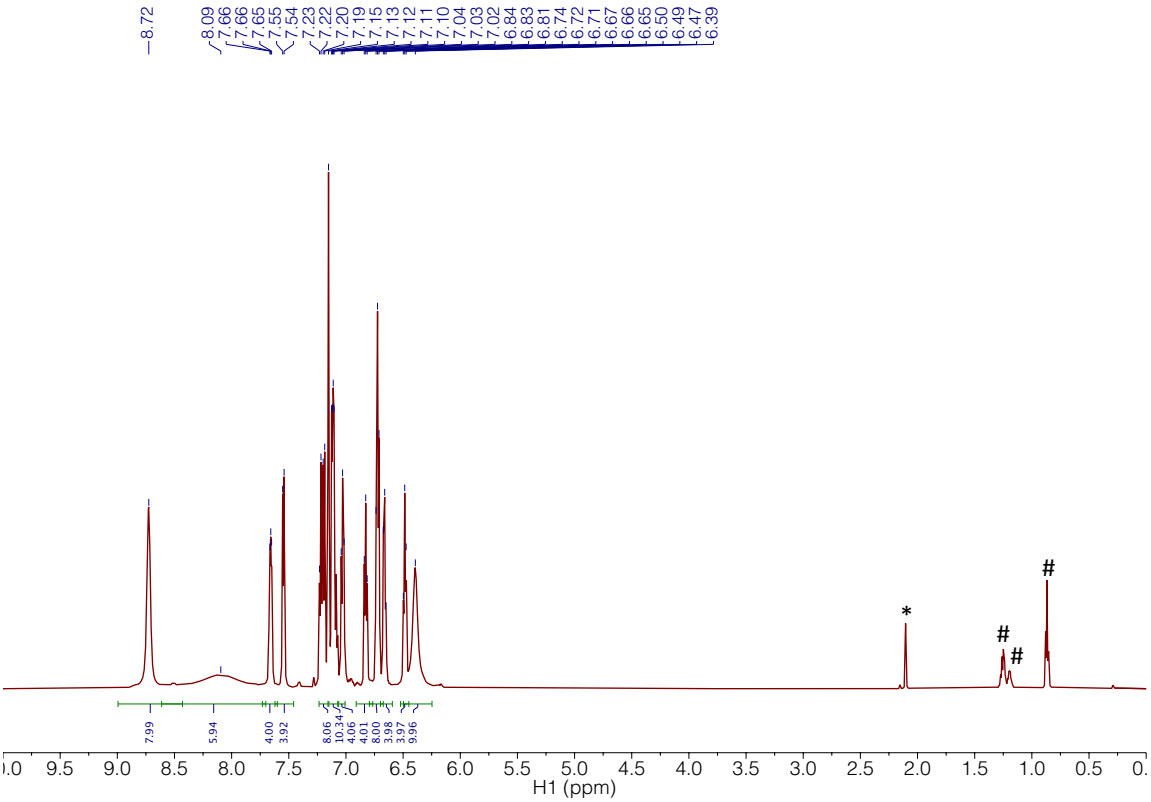


Figure S11A. ^{1}H NMR spectrum of **5**. *Toluene, #pentane.

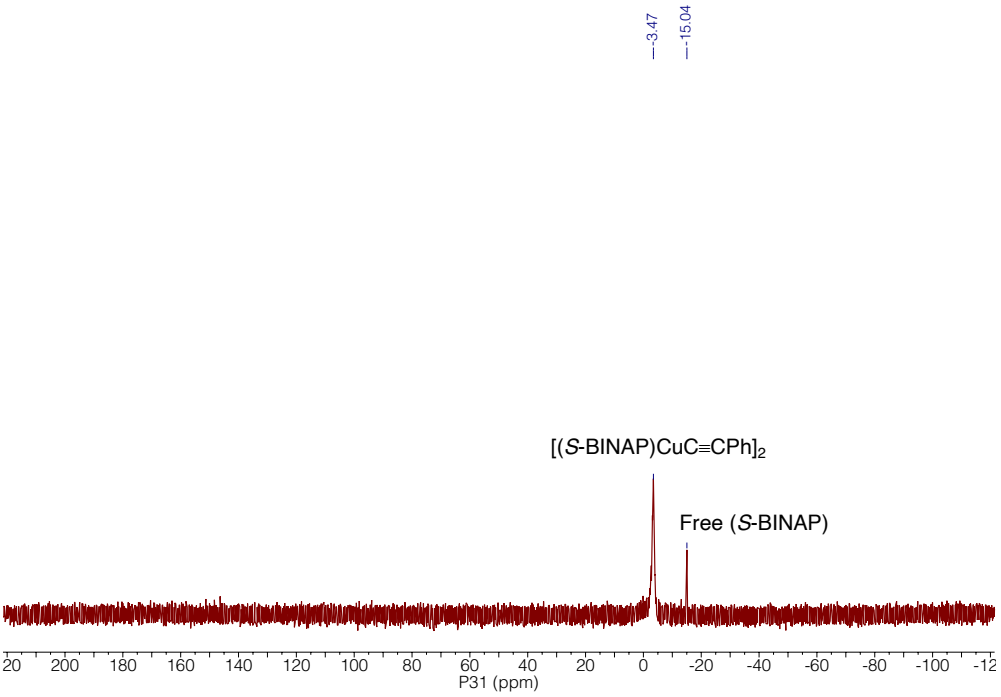


Figure S11B. $^{31}P\{^{1}H\}$ NMR spectrum of **5**.

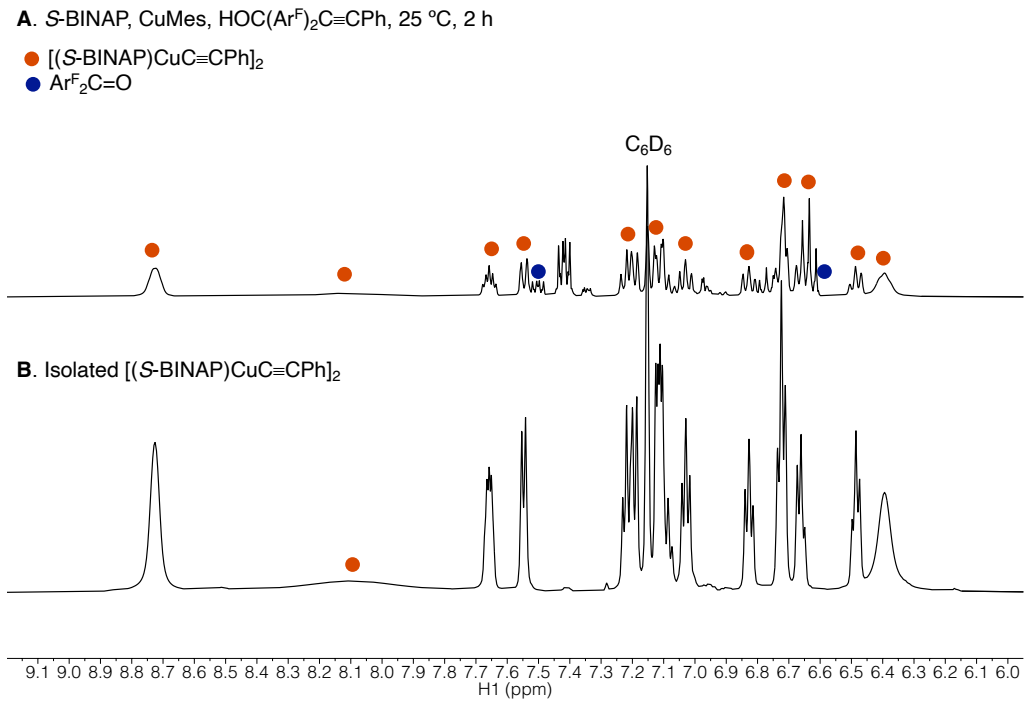


Figure S12A. ^{1}H NMR spectra for the reaction of *S*-BINAP, CuMes, and $HOC(Ar^{F})_2C{\equiv}CPh$ at 25 ºC for 2 h to form **5** and $Ar^{F}_2C{=}O$ and isolated **5**.

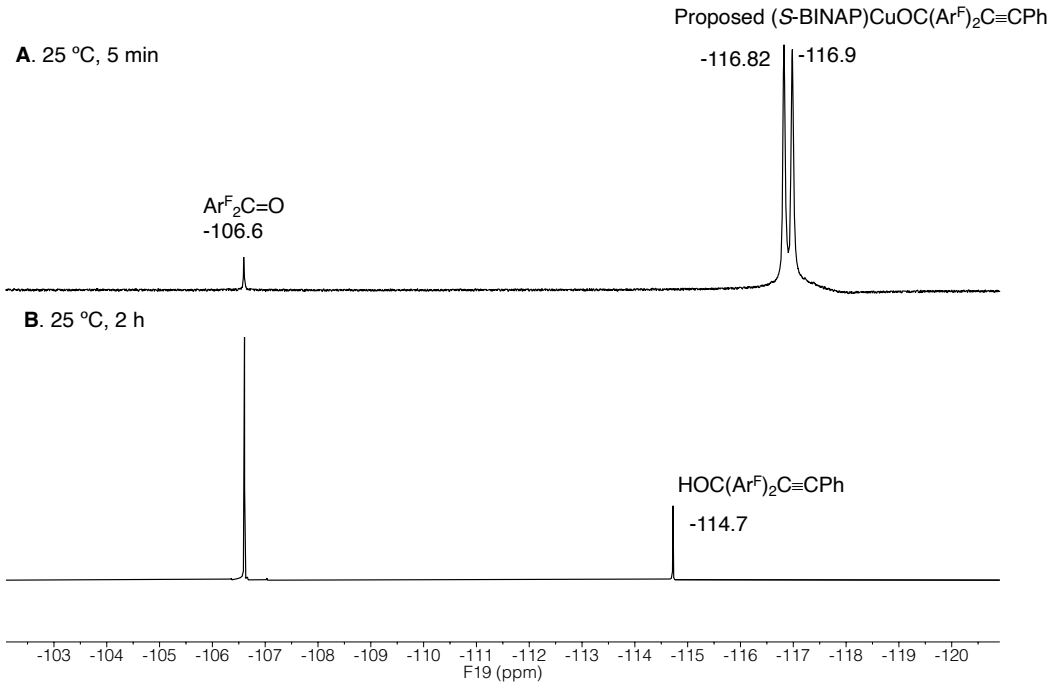


Figure S12B. $^{19}F\{^{1}H\}$ NMR spectra for the reaction of *S*-BINAP, CuMes, and $HOC(Ar^F)_2C{\equiv}CPh$ at 25 °C for 2 h, showing the formation of $Ar^F{}_2C{=}O$. Excess $HOC(Ar^F)_2C{\equiv}CPh$ is observed at the end of the reaction, which is not observed during the reaction plausibly because of rapid exchange or interaction with the propargylic alkoxide species.

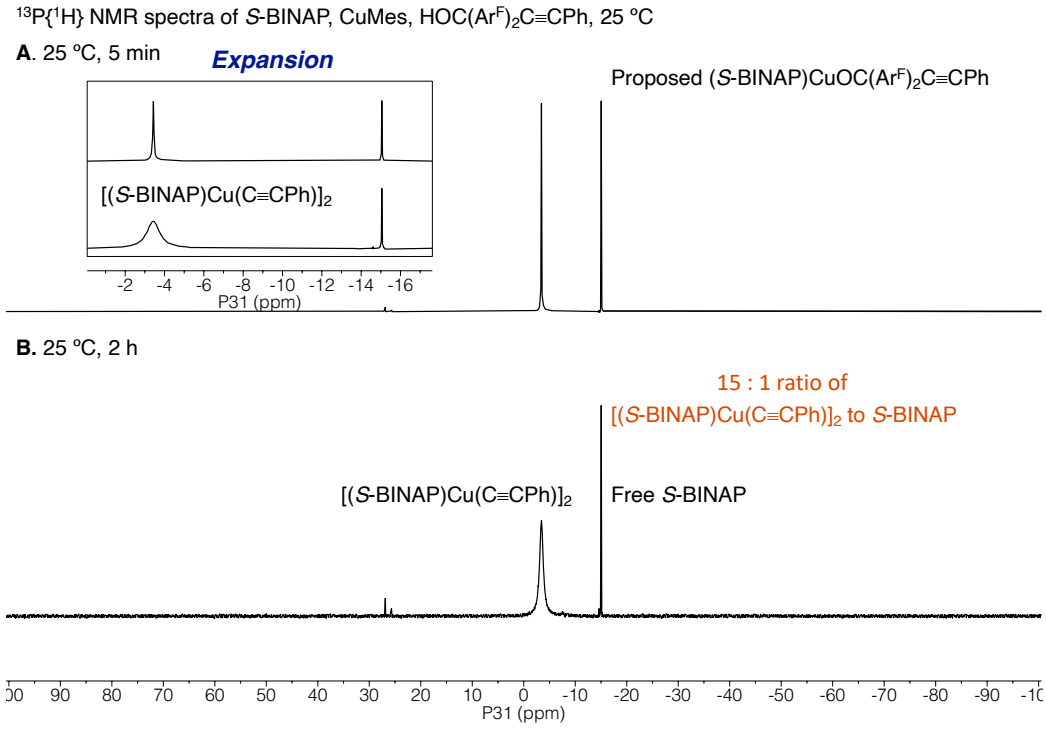
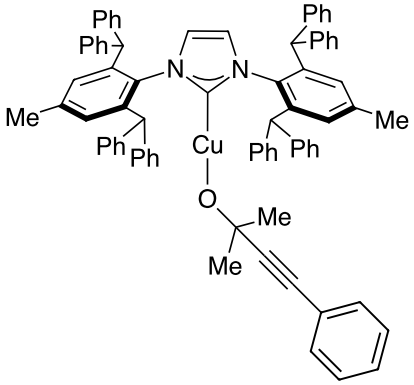


Figure S12C. $^{31}P\{^{1}H\}$ NMR spectra for the reaction of *S*-BINAP, CuMes, and $HOC(Ar^F)_2C{\equiv}CPh$ at 25 °C for 2 h, showing the formation of **5**. There appears to be incidental overlap of $^{13}P\{^{1}H\}$ NMR resonances for the proposed $(S\text{-BINAP})CuOC(Ar^F)_2C{\equiv}CPh$ and free *S*-BINAP ligand.

Scope of β-alkynyl eliminations of propargyl alkoxide (IPr*Me)Cu complexes

(IPr*Me)CuOCMe$_2$C≡CPh (6a)



The titled compound was synthesized according to the general procedure for complex **1**: (IPr*Me)CuCl (250 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 4 mL toluene, and HOC(Me)$_2$C≡CPh (42.0 mg, 0.260 mmol). Yield = 40% (112 mg, 0.0988 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.51-7.49 (m, 8H, Ar-H), 7.26 (t, *J* = 7.8 Hz, 8H, Ar-*H*), 7.02-6.95 (m, 33H, Ar-*H*), 5.62 (s, 4H, C*H*Ph$_2$), 5.43 (s, 2H, *H*-C=C-*H*), 1.81 (s, 6H, *Me*), 1.71 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 183.0 (Cu-carbene), 143.4, 143.1, 141.3, 140.0, 134.9, 131.7, 130.03, 130.01, 129.5, 128.8, 128.2, 127.9, 126.8, 126.4, 122.7, 103.7, 77.9, 67.8, 51.6 (H-*C*=*C*-H), 37.9 (*Me*), 20.9 (*Me*).

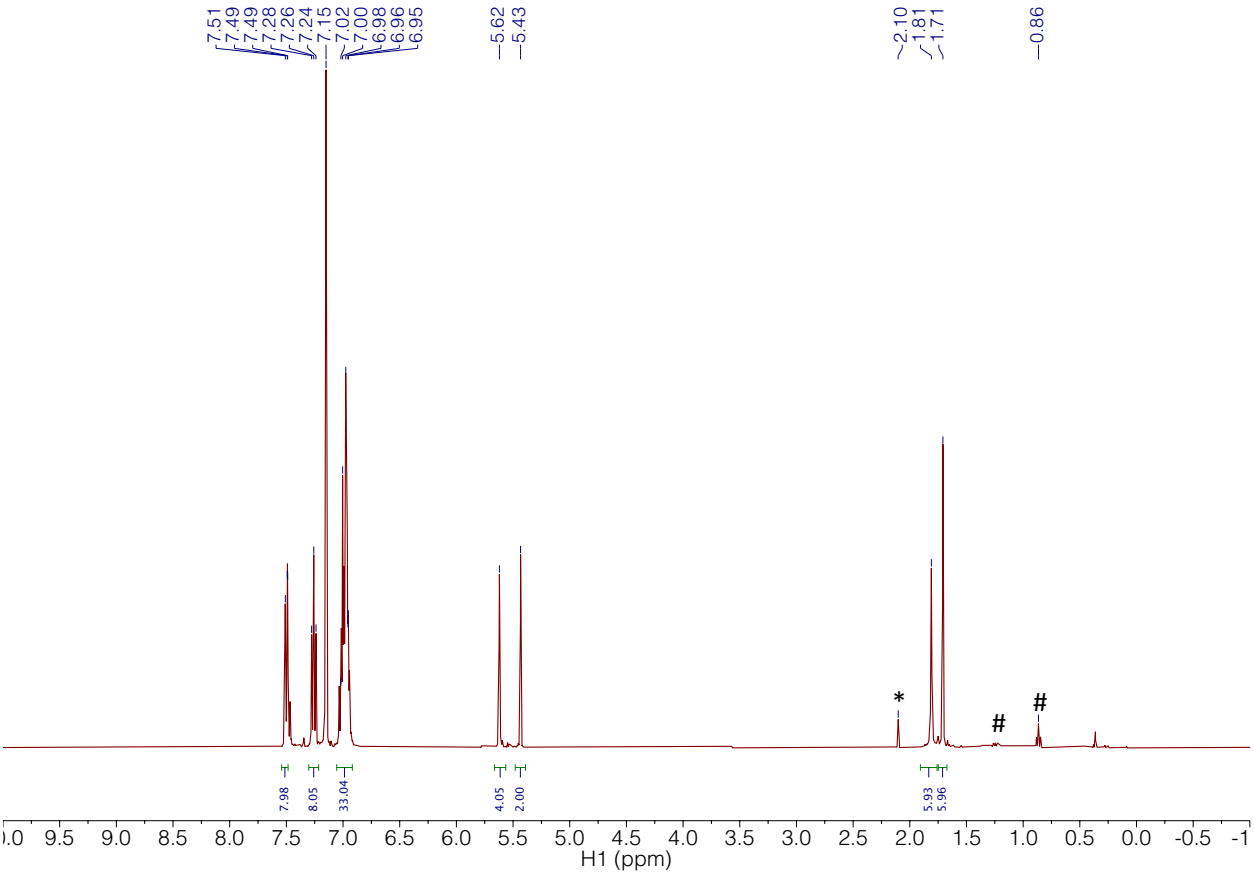


Figure S13A. ^{1}H NMR spectrum of **6a**. *Toluene, #pentane.

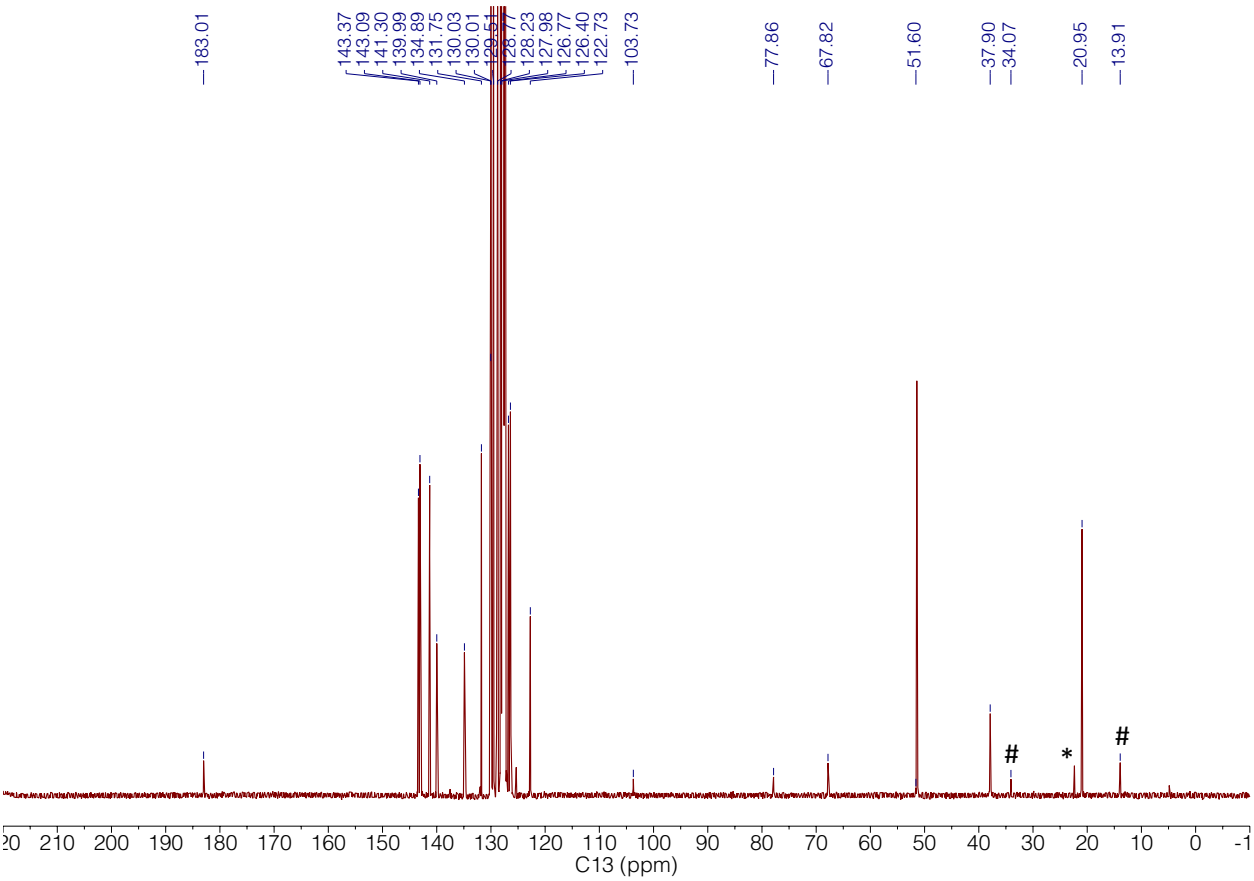


Figure S13B. $^{13}C\{^{1}H\}$ NMR spectrum of **6a.** *Toluene, #pentane.

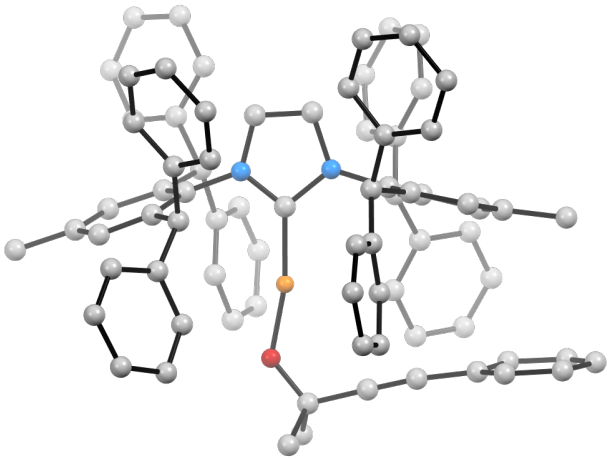


Figure S14. A ball-and-stick display for the connectivity scXRD structure of **6a**. a = 11.22, b = 22.12, c = 24.56, α, γ = 90 °, β = 91.55 °, V = 6096.87 Å^3, monoclinic $P2_1/c$. Single crystals for XRD measurement were obtained by layering of pentane on top a saturated toluene solution of **6a** at 25 ºC.

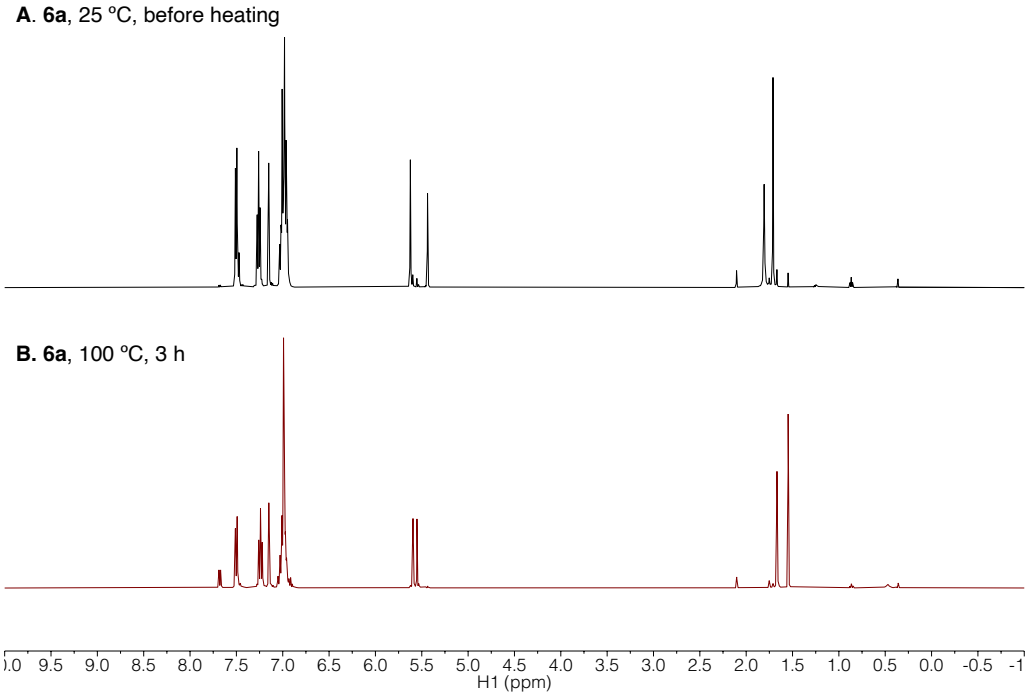
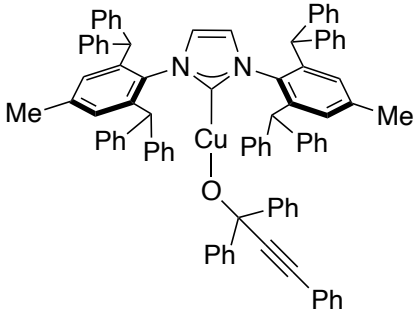


Figure S15. ^{1}H NMR spectra of **6a** at 100 ºC for 3 h to produce **1-Me** and acetone.

(IPr*Me)CuOC(Ph)$_2$C≡CPh (6b)



Inside a nitrogen-filled glovebox, to an oven-dried 20 mL scintillation vial was added (IPr*Me)CuCl (500 mg, 0.494 mmol), NaHMDS (96.0 mg, 0.520 mmol), 5 mL toluene, and a small stir bar. After 0.5 h, solid 1,1,3-triphenylprop-2-yn-1-ol (HOCPh$_2$C≡Ph) (148 mg, 0.520 mmol) was added to the reaction mixture. After 1 h, the solution was filtered into a new oven-dried 20 mL scintillation vial by a glass pipette containing Celite. The colorless solution was layered with 10 mL pentane. The colorless crystals were collected on a glass frit and dried under dynamic vacuum. Yield = 73% (454 mg, 0.361 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.24 (d, *J* = 7.7 Hz, 4H, Ar-*H*), 7.43 (d, *J* = 7.6 Hz, 8H, Ar-*H*), 7.21-7.17 (m, 10H, Ar-*H*), 7.09 – 7.03 (m, 4H, Ar-*H*, 7.03 – 6.95 (m, 20H, Ar-*H*), 6.92-6.90 (m, 8H, Ar-*H*), 6.87-6.84 (m, 3H, Ar-*H*), 5.60 (s, 4H, C*H*Ph$_2$), 5.40 (s, 2H, *H*-C=C-*H*), 1.69 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (101 MHz, 25 ºC, C_6D_6): δ 182.4 (Cu-carbene), 154.0, 143.4, 143.1, 141.1, 139.8, 134.7, 131.8, 130.0, 129.5, 128.8, 128.2, 126.7, 126.5, 126.4, 125.4, 125.2, 122.9, 101.8 (C≡C), 82.3 (C≡C), 77.7 (C-O), 51.4 (H-C=C-H), 21.0 (Me). IR (Nujol, KBr): v 3143 w, 3081 m, 3026 m, 3066 m, 2212 w (C≡C), 1950 w, 1890 w, 1809 w, 1597 s, 1500 s, 1446 s, 1377 m, 1260 m, 1155 m, 1104 m, 1077 m 1029 m, cm^{-1}. **Anal. Calcd** for $C_{90}H_{71}CuN_2O$: C, 85.78; H, 5.68; N, 2.22. Found: C, 84.52; H, 5.59; N, 2.32. Single crystals for XRD measurement were obtained by layering of pentane into a saturated toluene solution of **6b** at 25 ºC.

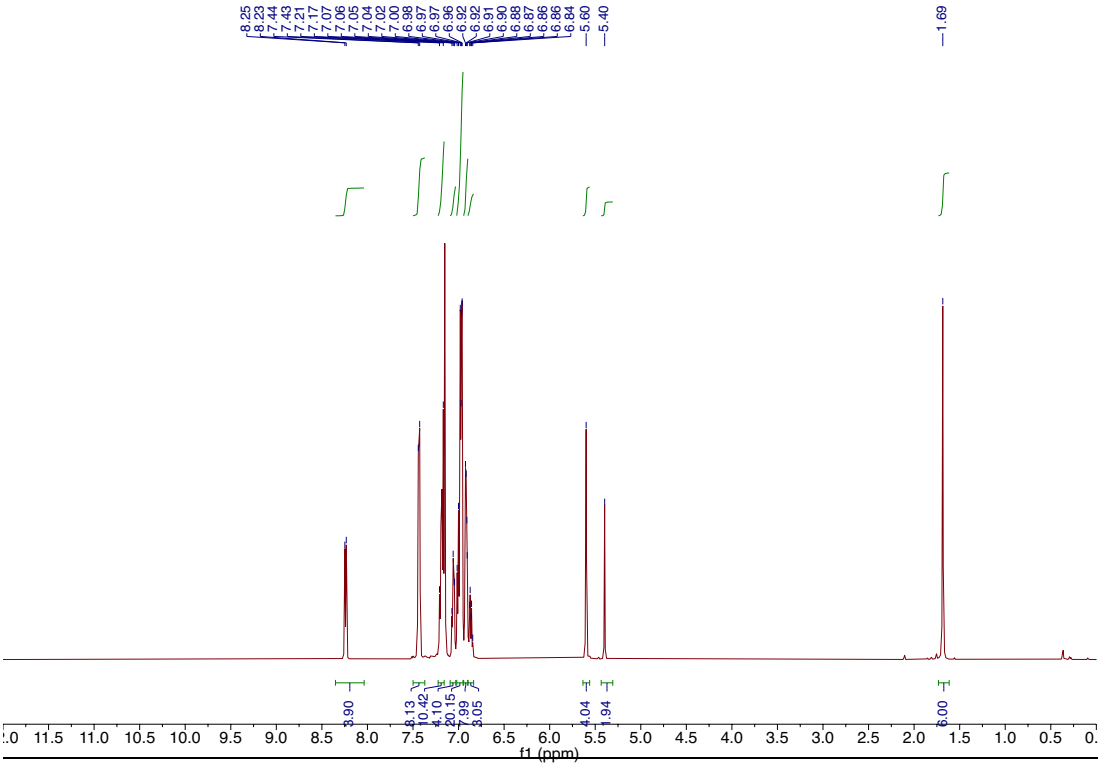


Figure S16A. ^{1}H NMR spectrum of **6b**.

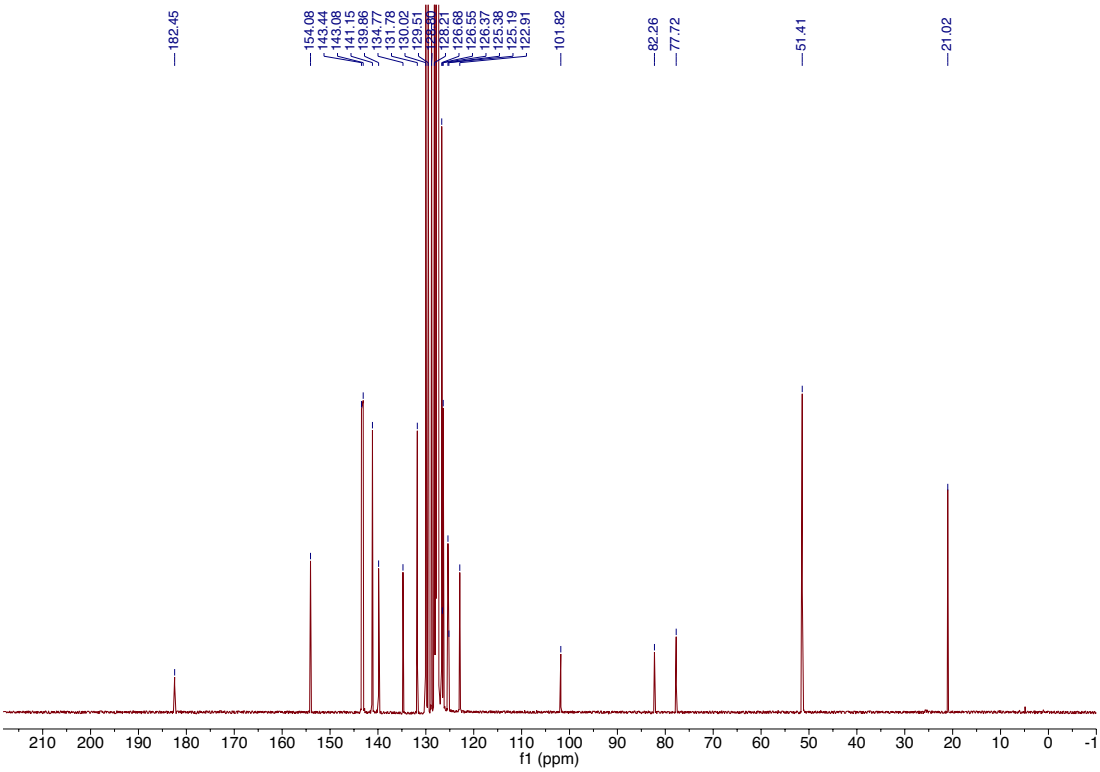


Figure S16B. $^{13}C\{^{1}H\}$ NMR spectrum of **6b**.

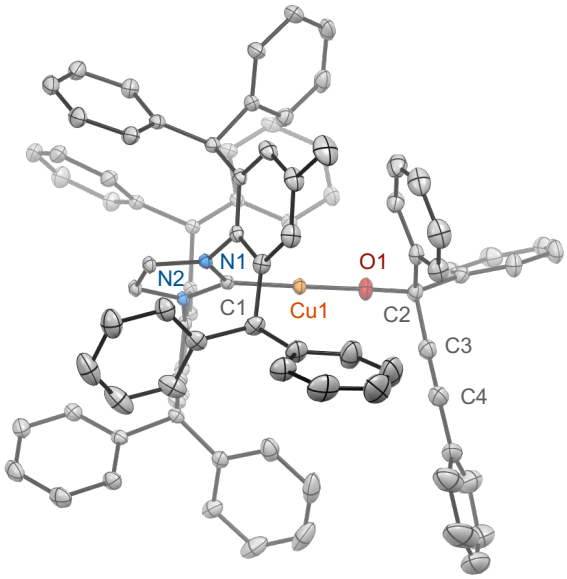


Figure S17. scXRD structure of **6b** is shown at 50% probability thermal ellipsoid. All hydrogen atoms, solvents are omitted.

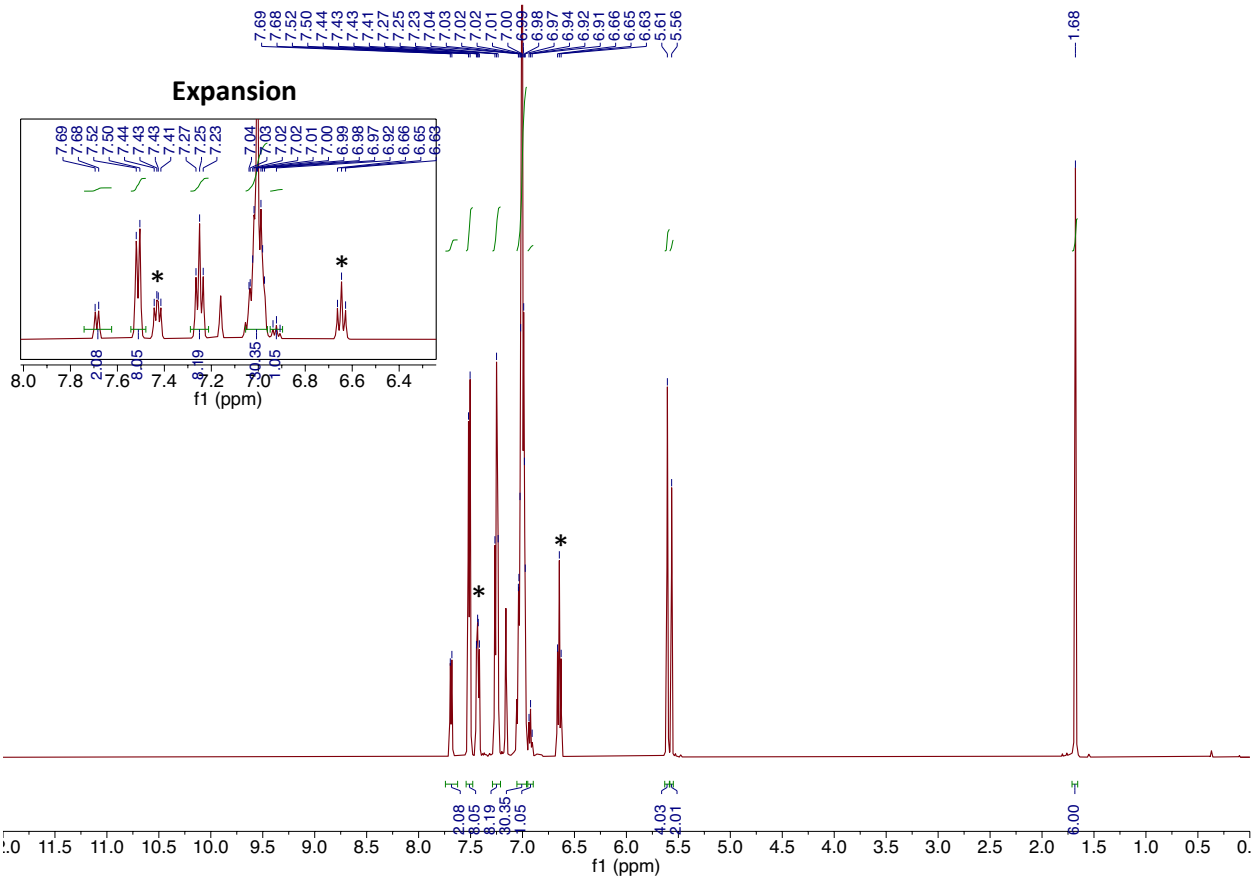
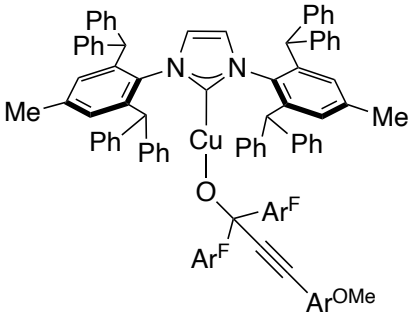


Figure S18. ^{1}H NMR spectrum of **6b** at 100 °C for 3 h to produce **1-Me** and *Ph_2C=O.

(IPr*Me)CuN(SiMe$_3$)$_2$

Inside a nitrogen-filled glovebox, to an oven-dried 20 mL scintillation vial was added (IPr*Me)CuCl (1.00 g, 0.988 mmol), NaHMDS (192 mg, 1.04 mmol), 15 mL toluene, and a small stir bar. After 1.5 h, the solution was filtered into a new oven-dried 20 mL scintillation vial by a glass pipette containing Celite. All volatiles were removed by dynamic vacuum. The resulting white solid was triturated with pentane (10 mL), collected on a medium porosity frit, and dried under dynamic vacuum. Yield = 84% (944 mg, 0.830 mmol). **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.63-7.60 (m, 8H, Ar-H), 7.28 (m, 8H, Ar-*H*), 7.05 (m, 4H, Ar-*H*), 7.02-6.99 (m, 6H, Ar-*H*) 6.90-6.89 (m, 18H, Ar-*H*), 5.88 (s, 4H, C*H*Ph$_2$), 5.38 (s, 2H, *H*-C=C-*H*), 1.81 (s, 6H, *Me*), 0.25 (s, 18H, Si*Me*$_3$).

(IPr*Me)CuOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe) (7a): Thermolysis of (IPr*Me)CuN(SiMe$_3$)$_2$ and HOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe) to product (IPr*Me)CuC≡C$_6$H$_4$-*p*-OMe) (**7b**)



Inside a nitrogen-filled glovebox, to an oven-dried 4 mL scintillation vial was added 1,3,5-trimethoxybenzene (3.0 mg), HOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe) (9.10 mg, 0.0260 mmol), (IPr*Me)CuN(SiMe$_3$)$_2$ (28.0 mg, 0.0247 mmol), and 750 μL C_6D_6. The resulting colorless solution was transferred to a J. Young NMR tube, removed from the glovebox, and analyzed by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy at 25 ºC. The J. Young NMR tube was placed in a preheated oil bath at 100 ºC for 3 h and analyzed by ^{1}H and ^{19}F{^{1}H} NMR spectroscopy.

Spectroscopic characterization of *in situ* (IPr*Me)CuOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe). **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 8.06-8.03 (4H, *ortho* C-H to aryl C-F), 5.57 (s, 4H, C*H*Ph$_2$), 5.38 (s, 2H, *H*-C=C-*H*), 3.19 (s, 3H, O*Me*), 1.67 (s, 6H, *Me*). **^{19}F{^{1}H} NMR** (470 MHz, 25 ºC, C_6D_6): δ -118.5. The ^{19}F{^{1}H} NMR resonance of free HOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe) is at -114.9 ppm.

After 3 h at 100 ºC, complete consumption of **7a** and formation of **7b** was evidenced by loss of 8.06-8.03 (4H, *ortho* C-H to aryl C-F), and the downfield shifts of 5.62 (s, 4H, C*H*Ph$_2$), 5.56 (s, 2H, *H*-C=C-*H*) in the ^{1}H NMR spectrum. The ^{19}F{^{1}H} NMR spectrum shows Ar$^F_2$C=O formation at -106.6 ppm and excess HOC(Ar^F)$_2$C≡C(C$_6$H$_4$-*p*-OMe) at -114.9 ppm. **7b** was verified by comparing the ^{1}H NMR spectrum of the reaction mixture to that of authentic (IPr*Me)Cu-C≡C(C$_6$H$_4$-*p*-OMe), which was independently synthesized from the reaction of (IPr*Me)CuCl, NaHMDS, HC≡C(C$_6$H$_4$-*p*-OMe) on page S35.

Reactions of HOC(C≡CPh)(C$_6$H$_4$-*p*-NMe$_2$)(-CH=CHPh)

The thermolysis of (IPr*Me)CuN(SiMe$_3$)$_2$ and HOC(C≡CPh)(C$_6$H$_4$-*p*-NMe$_2$)(-CH=CHPh) to form (IPr*Me)CuC≡CPh) (**2-Me**) was performed identically to that of **7a** to **7b**: (IPr*Me)CuN(SiMe$_3$)$_2$ (28.0 mg, 0.0247 mmol), HOC(C≡CPh)(C$_6$H$_4$-*p*-NMe$_2$)(-CH=CHPh) (9.20 mg, 0.0260 mmol), and 750 μL C_6D_6. The reactions of dppf/CuMes or *S*-BINAP/CuMes with HOC(C≡CPh)(C$_6$H$_4$-*p*-NMe$_2$)(-CH=CHPh) to form **4** or **5**, respectively, were performed identically to the reactions of dppf/CuMes or *S*-BINAP/CuMes with HOC(Ar^F)$_2$C≡CPh on page S13-S18.

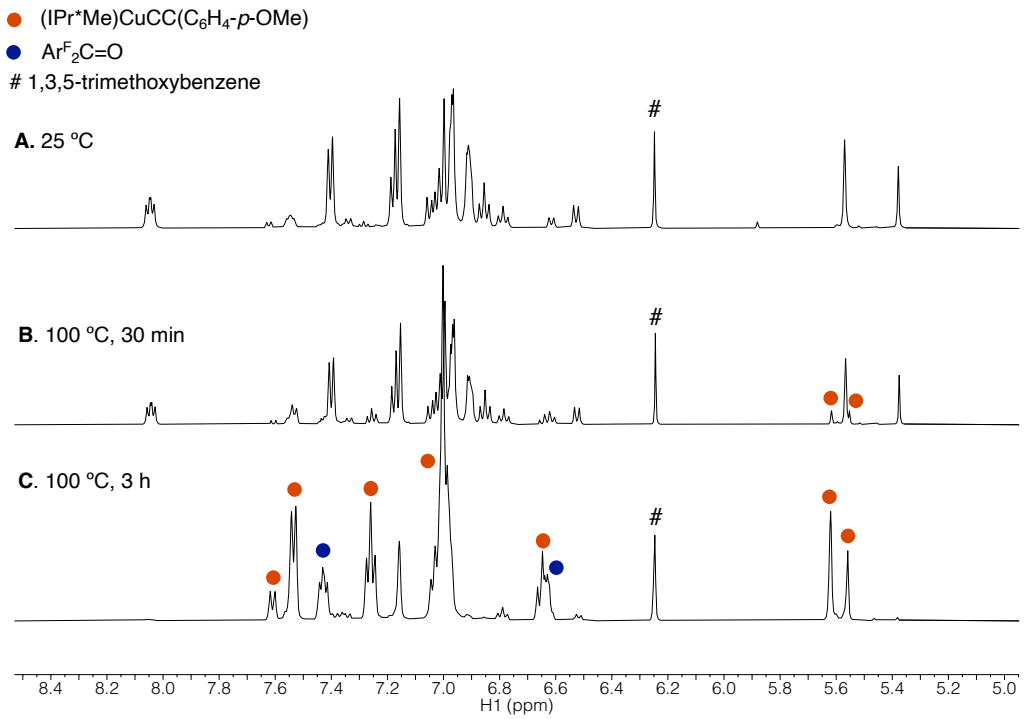


Figure S19A. ^{1}H NMR spectra of *in situ* generated **7a** at 100 °C for 3 h to produce **7b** and $Ar^{F}_{2}C=O$.

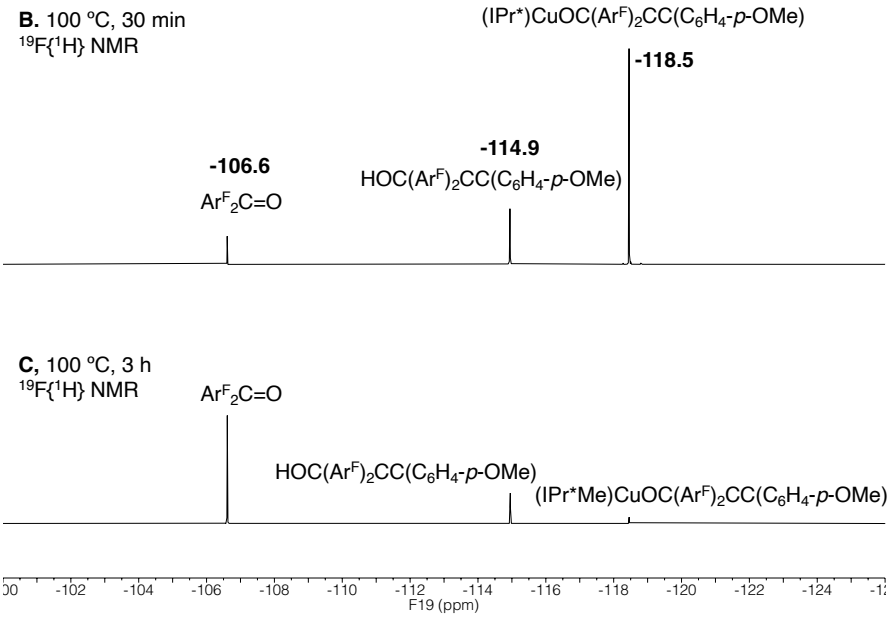
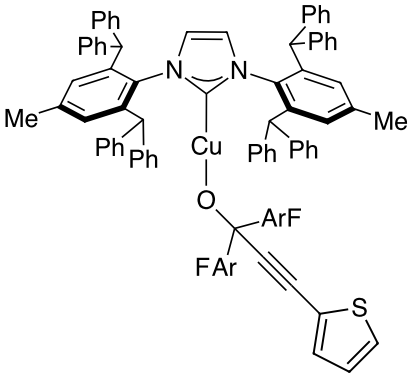


Figure S19B. ^{19}F{^{1}H} NMR spectra for *in situ* generated **7a** in C_6D_6 at 100 °C to produce **7b** and $Ar^{F}_{2}C=O$.

(IPr*Me)CuOC(Ar^F)$_2$C≡C(C$_4$H$_3$S) (8a)



The titled compound was synthesized according to the general procedure for complex **1**: (IPr*Me)CuCl (250 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 4 mL toluene, and HOC(Ar^F)$_2$C≡C(C$_4$H$_3$S) (85.0 mg, 0.260 mmol). Yield = 67% (215 mg, 0.165 mmol), tan solid. **^{1}H NMR** (500 MHz, 25 ºC, C$_6$D$_6$): δ 7.97 (dd, *J* = 8.7, 5.8 Hz, 4H, Ar-H), 7.37 (d, *J* = 7.4 Hz, 8H, Ar-*H*), 7.19-7.15 (m, 10H, Ar-*H*), 7.03 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.99-6.96 (m, 16H, Ar-*H*), 6.92-6.89 (m, 8H, Ar-*H*), 6.80 (t, *J* = 8.8 Hz, 4H, Ar-*H*), 6.67 (dd, *J* = 3.5, 1.2 Hz, 1H, Ar-*H*), , 6.47 (dd, *J* = 5.2, 3.6 Hz, 1H, Ar-*H*), 5.54 (s, 4H, C*H*Ph$_2$), 5.38 (s, 2H, *H*-C=C-*H*), 1.72 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C$_6$D$_6$): δ 181.9 (Cu-carbene), 161.5 (d, *J* = 242.7 Hz, Ar-F), 149.3, 143.4, 142.9, 141.1, 140.0, 134.7, 132.1, 130.9, 130.0, 129.9, 128.8, 128.2, 126.8, 126.4, 125.5, 125.3, 113.9 (d, *J* = 20.9 Hz, Ar-F), 104.7, 77.2, 75.9, 51.4 (H-*C*≡*C*-H), 21.0 (*Me*). Single crystals for XRD measurement were obtained by layering of pentane into a saturated toluene solution of **8a** at 25 ºC.

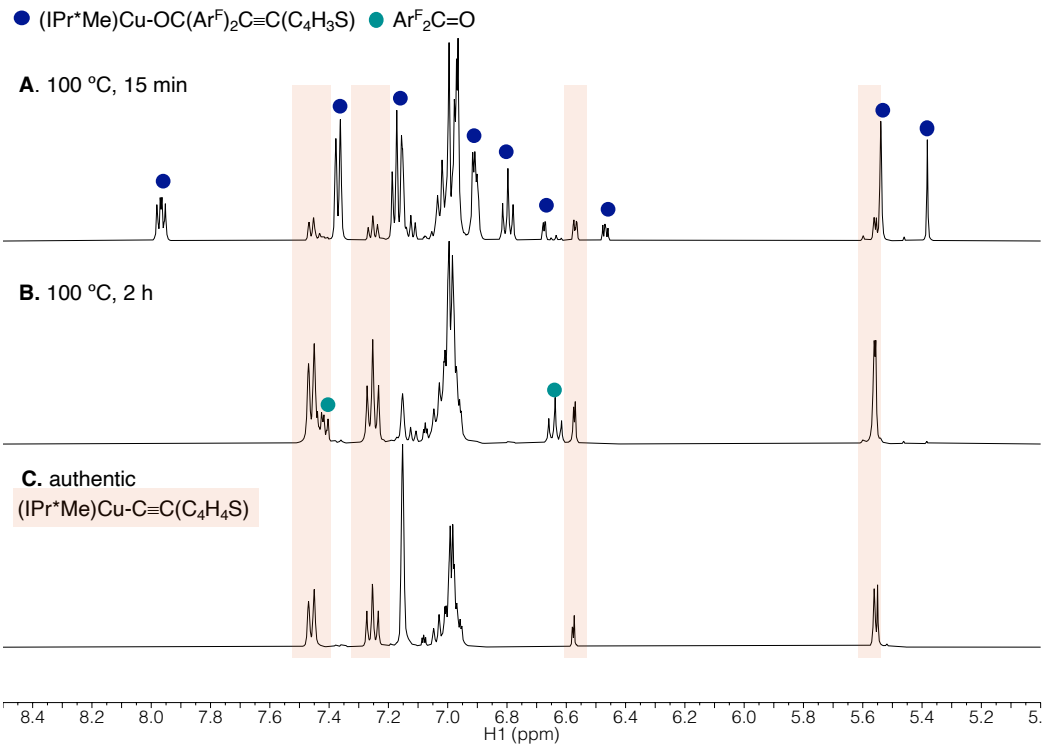
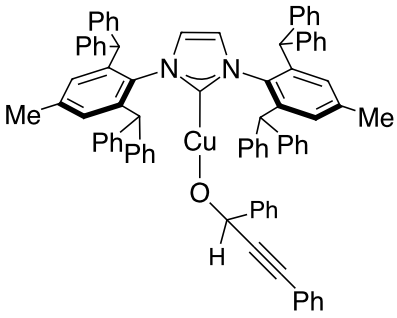


Figure S20. ^{1}H NMR spectra of **8a** in C$_6$D$_6$ at 100 ºC for 2 h to produce (IPr*Me)CuC≡C(C$_4$H$_3$S) (**8b**) and Ar^F$_2$C=O.

Selectivity of β-alkynyl and β-hydrogen eliminations of LCuOC(H)(Ph)C≡CPh (L = IPr*Me, dppf)

(IPr*Me)CuOC(H)(Ph)C≡CPh (9)



The titled compound was synthesized according to the general procedure for complex **1**. (IPr*Me)CuCl (250 mg, 0.247 mmol), NaHMDS (48.0 mg, 0.260 mmol), 5 mL toluene, and HOC(H)(Ph)C≡CPh (51.5 μL, 0.272 mmol) was added by glass syringe. Yield = 52% (152 mg, 0.128 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.94 (br s,, 4H, Ar-*H*), 7.41 (d, *J* = 7.7 Hz, 8H, Ar-*H*), 7.38 (m, 1H, Ar-*H*), 7.29 – 7.27 (m, 2H, Ar-*H*), 7.22 – 7.18 (m, 8H, Ar-*H*), 7.08 (t, *J* = 7.2 Hz, 2H, Ar-*H*), 7.00 – 6.94 (m, 26H, Ar-*H*), 6.91-6.90 (m, 4H, Ar-*H*), 6.47 (br s, 1H, Ar-*H*), 5.57 (s, 4H, C*H*Ph$_2$), 5.52 (s, 1H, OC*H*Ph), 5.49 (s, 2H, *H*-C=C-*H*), 1.71 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, C_6D_6): δ 182.4 (Cu-carbene), 150.1, 143.4, 142.9, 141.2, 140.0, 134.8, 131.8, 130.1, 129.9, 129.5, 128.8, 128.3, 126.7, 126.6, 126.4, 122.9, 99.1, 81.5, 69.5, 51.4, 20.9. Single crystals for XRD measurement were obtained by slow diffusion of pentane into a saturated toluene solution of **9** at 25 ºC.

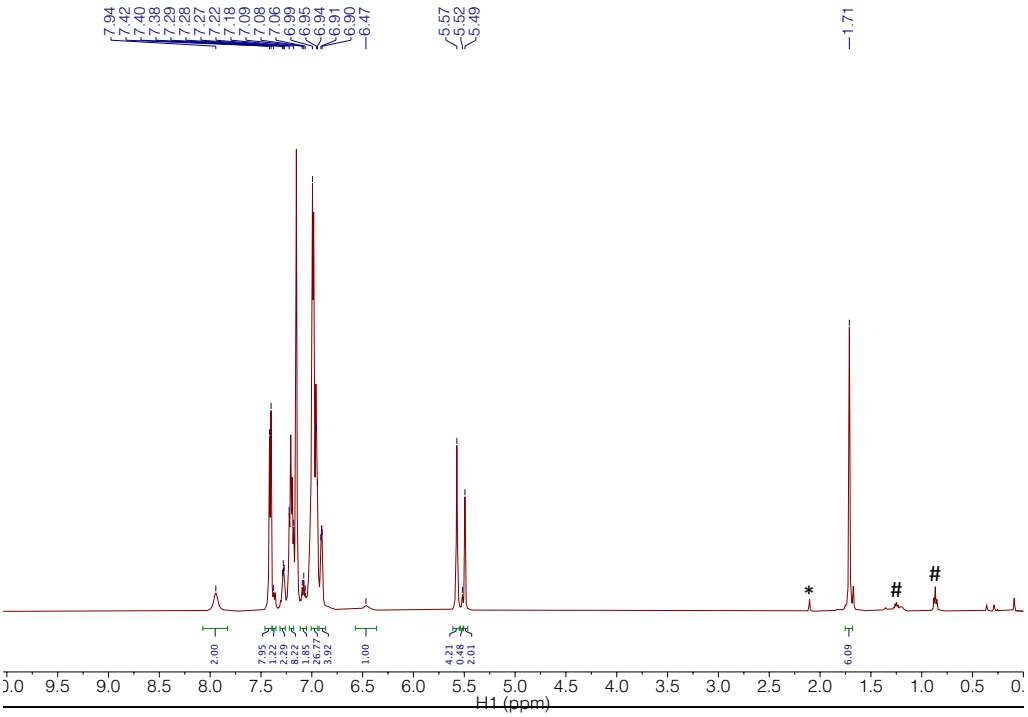


Figure S21A. ^{1}H NMR spectrum of **9**. *Toluene, #pentane.

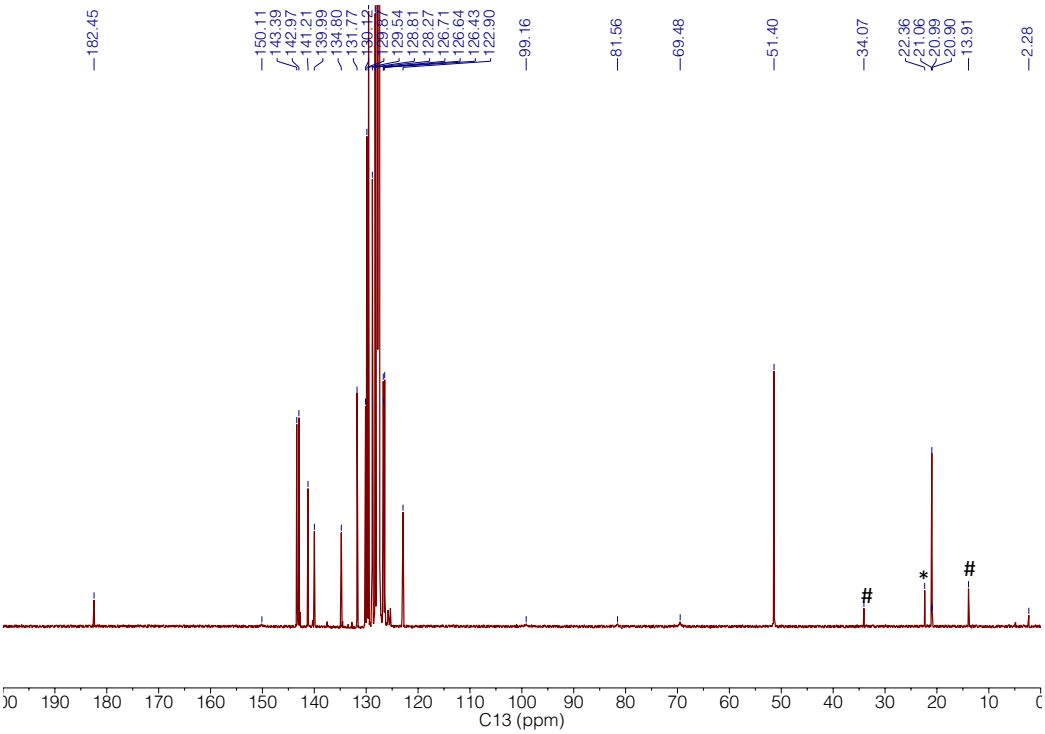


Figure S21B. $^{13}C\{^{1}H\}$ NMR spectrum of **9**. *toluene, #pentane.

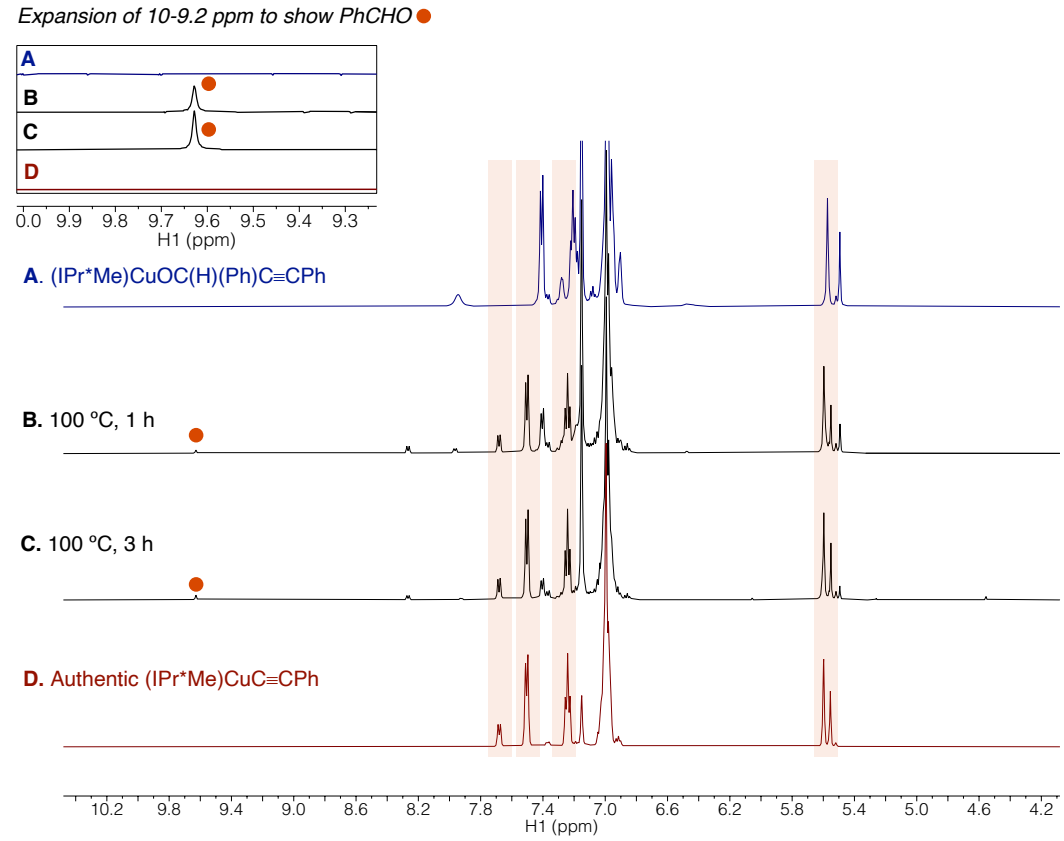


Figure S22. ^{1}H NMR spectra of (IPr*Me)CuOC(H)(Ph)C≡CPh (**9**) in C_6D_6 at 25 °C and at 100 °C for 1 h and 3 h to produce **2-Me** and PhCHO (9.63 ppm).

Formation of [(μ-dppf)CuC≡CPh]$_2$ (4) from reaction of dppf, CuMes, HOC(H)(Ph)C≡CPh

Inside a nitrogen-filled glovebox, to oven-dried 4 mL scintillation vial was added dppf (15.2 mg, 0.0273 mmol) and C_6D_6 (750 μL) to give a yellow solution. This solution was added to an oven-dried 4 mL scintillation vial containing Cu-mesityl (5.00 mg, 0.0273 mmol) and a small stir bar. After 0.5 h, this yellow C_6D_6 solution was added to solid HOC(H)(Ph)C≡CPh (5.14 μL, 0.0286 mmol) in an oven-dried 4 mL scintillation vial. The resulting yellow mixture was transferred to a J. Young NMR tube, removed from the glovebox, and analyzed by ^{1}H, ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR spectroscopy over 1 h at 25 ºC.

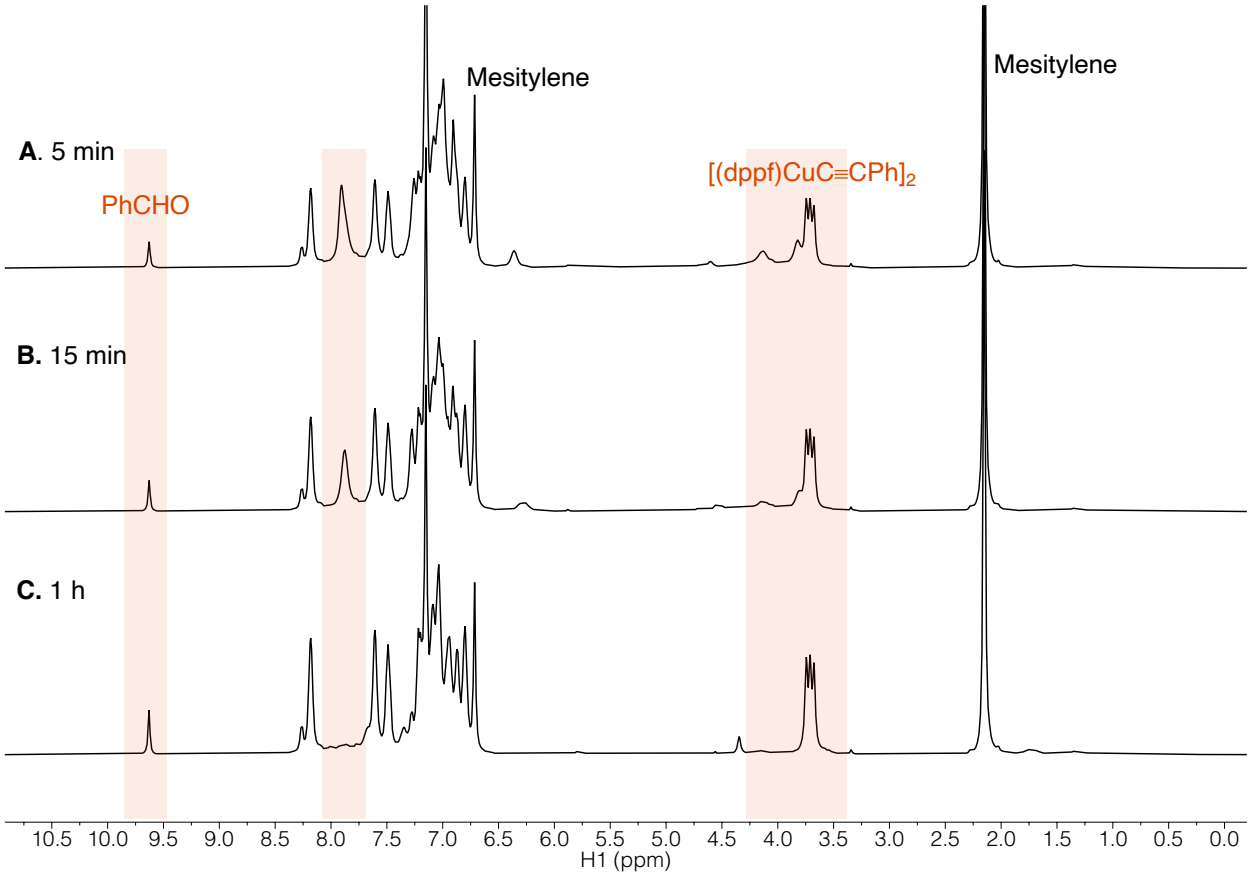


Figure S23A. ^{1}H NMR spectra for the reaction of dppf, CuMes, and HOC(H)(Ph)C≡CPh in C_6D_6 at 25 ºC for 1 h to product **4** and PhCHO.

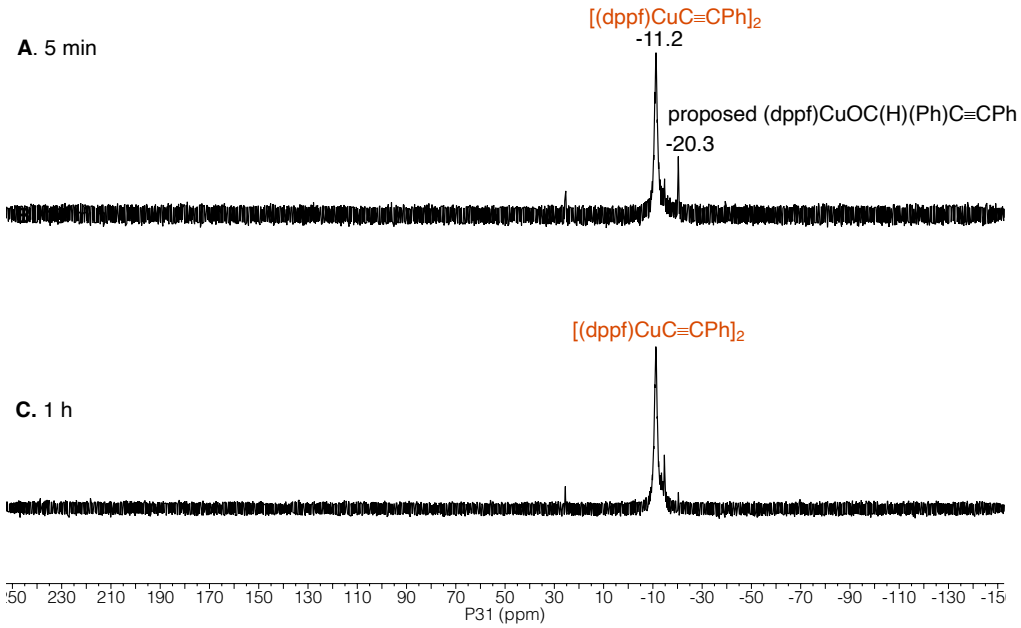
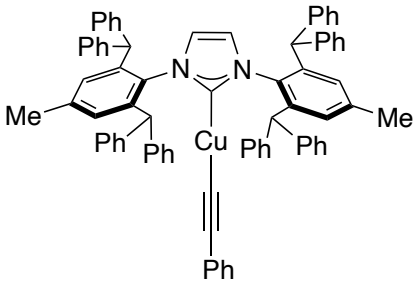


Figure S23B. $^{13}P\{^{1}H\}$ NMR spectra for the reaction of dppf, CuMes, and HOC(H)(Ph)C≡CPh in C_6D_6 at 25 ºC for 1 h to generate **4**.

General procedure for the independent synthesis of Cu-alkynyl complexes

(IPr*Me)CuC≡CPh (2-Me)



The synthesis of (IPr*R)Cu-alkynyl (R = Me, OMe, Cl) complexes was adapted from published procedure.[4] Inside a hood equipped with a Schlenk manifold, under flowing N_2, to a 50 mL Schlenk tube was added a medium stir bar, (IPr*Me)CuCl (250 mg, 0.247 mmol), phenylacetylene (30.0 μL, 0.272 mmol) was added by micro-syringe, freshly grounded 3.0 equiv. K_2CO_3 (102 mg, 0.740 mmol), and absolute EtOH (5 mL). The suspension was heated at 50 ºC. After 12 h, the suspension was concentrated to dryness under dynamic vacuum. The Schlenk tube was taken into the glovebox and 5 mL of anhydrous toluene was added. The resulting colorless solution was filtered through a fiberglass-containing glass pipette top with Celite into oven-dried 20 mL scintillation vial. The toluene solution was layered with 10 mL of pentane to give colorless microcrystalline material. The mother liquor was decanted, and the colorless microcrystalline solid was rinsed with 5 mL of pentane, decanted, and dried under dynamic vacuum. Yield = 68% (180 mg, 0.167 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.69 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.51 (d, *J* = 7.7 Hz, 8H, Ar-*H*), 7.25 (t, *J* = 7.7 Hz, 8H, Ar-*H*), 7.04-6.97 (m, 30H, Ar-*H*), 6.92 (t, *J* = 7.5 Hz, 1H), 6.92 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 5.61 (s, 4H, C*H*Ph$_2$), 5.56 (s, 2H, *H*-C=C-*H*), 1.68 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 183.7 (Cu-carbene), 143.5, 143.3, 141.5, 140.5, 134.9, 132.3, 130.5, 130.3, 129.9, 129.1, 128.6, 128.3, 127.1, 126.8, 125.1, 123.3, 106.2, 51.9 (H-C=C-H), 21.3 (Me). The ^{1}H, ^{13}C NMR data is consistent with published NMR data for **2-Me**.[4]

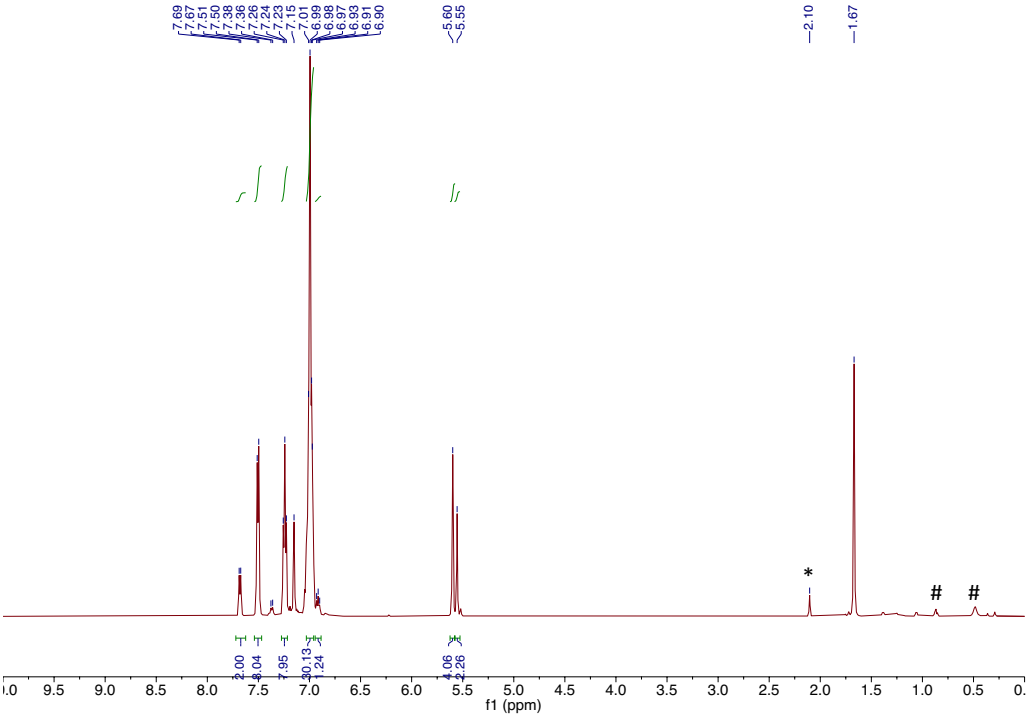


Figure S24A. ^{1}H NMR spectrum of **2-Me**.*Toluene, #pentane.

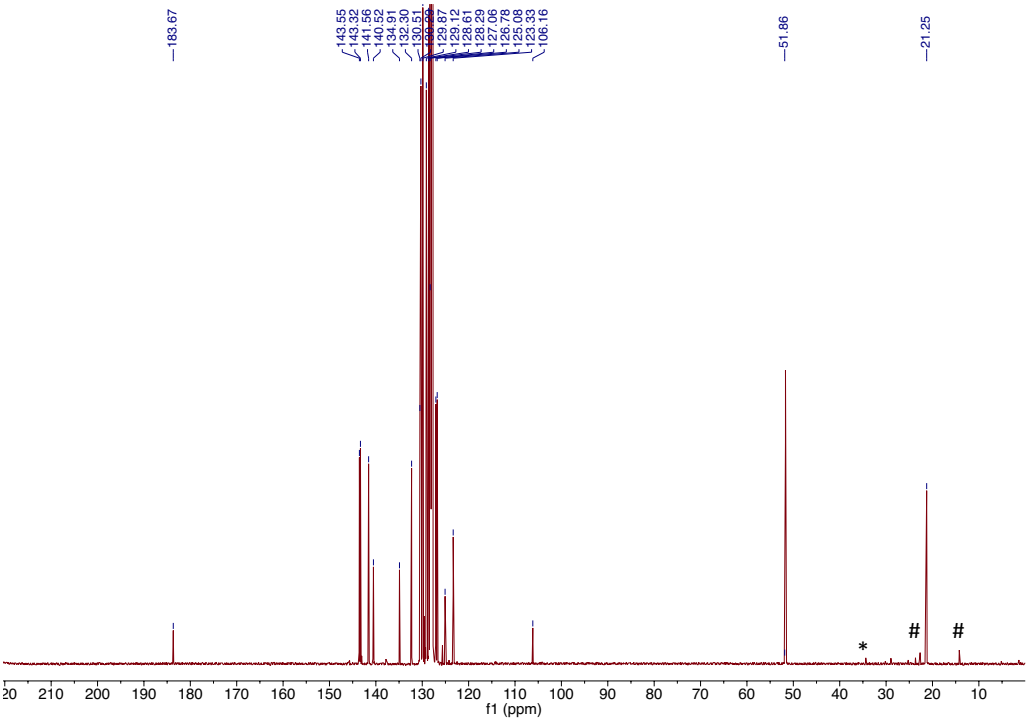
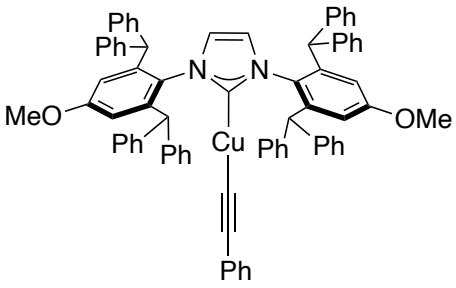


Figure S24B. $^{13}C\{^{1}H\}$ NMR spectrum of **2-Me**.*Toluene, #pentane.

(IPr*OMe)CuC≡CPh (2-OMe)



The titled complex was synthesized according to the general procedure for complex **2-Me**: (IPr*OMe)CuCl (258 mg, 0.247 mmol), phenylacetylene (30.0 μL, 0.272 mmol), freshly grounded 3.0 equiv. K_2CO_3 (102 mg, 0.740 mmol), and absolute EtOH (5 mL). Yield = 83% (227, 0.205 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.71 (d, *J* = 7.5 Hz, 2H, Ar-*H*), 7.48 (d, *J* = 7.6 Hz, 8H, Ar-*H*), 7.22 (t, *J* = 7.7 Hz, 8H, Ar-*H*), 7.12 (t, *J* = 7.4 Hz, 1H, Ar-*H*) 7.06-6.93 (m, 26H, Ar-*H*), 6.92 (s 3H, Ar-*H*), 5.58 (s, 4H, C*H*Ph_2), 5.52 (s, 2H, *H*-C=C-*H*), 2.93 (s, 6H, O*Me*). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ 184.4 (Cu-carbene), 160.6, 143.4, 143.3, 143.1, 132.3, 130.2, 129.8, 129.1, 128.6, 127.1, 126.8, 125.6, 123.5, 115.3, 106.2, 54.5, 51.9. Single crystals for XRD measurement were obtained by layering of pentane over a concentrated toluene solution of **2-OMe** at 25 ºC.

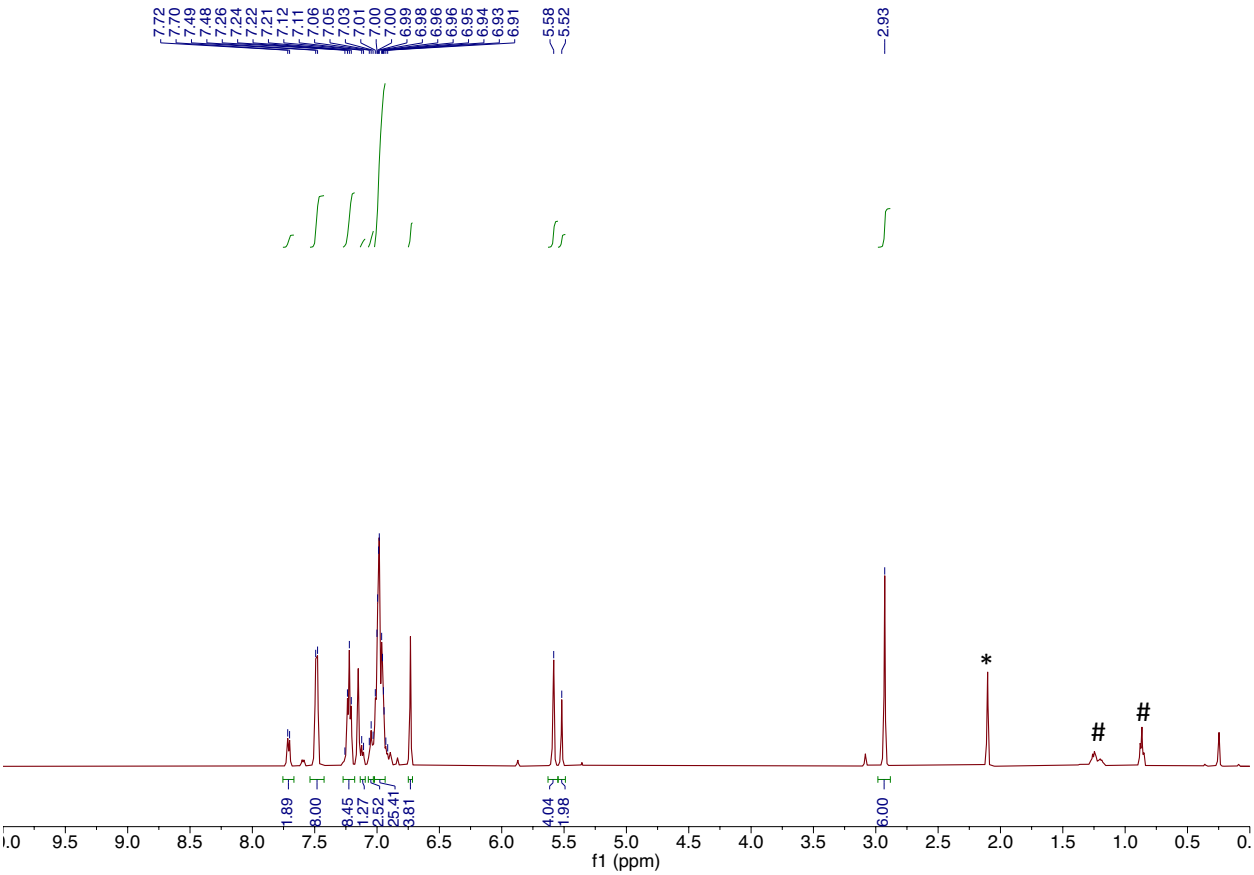


Figure S25A. ^{1}H NMR spectrum of **2-OMe**. *Toluene, #pentane.

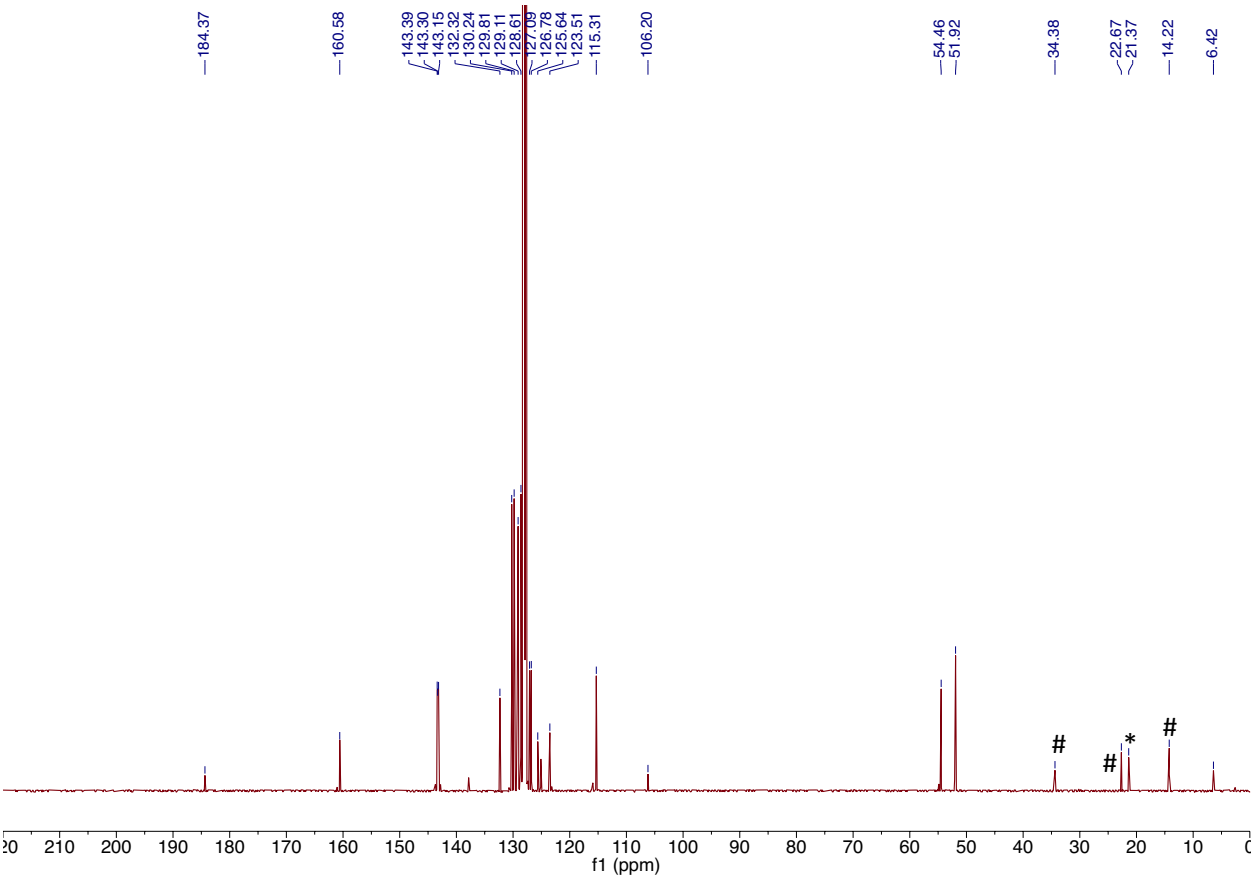
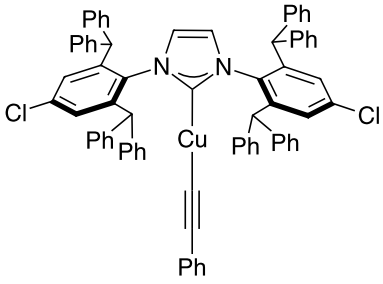


Figure S25B. $^{13}C\{^{1}H\}$ NMR spectrum of **2-OMe**. *Toluene, #pentane.

(IPr*Cl)CuC≡CPh (2-Cl)



The titled complex was synthesized according to the general procedure for complex **2-Me**: (IPr*Cl)CuCl (260 mg, 0.247 mmol), phenylacetylene (30.0 μL, 0.272 mmol), freshly grounded 3.0 equiv. K_2CO_3 (102 mg, 0.740 mmol), and EtOH (5 mL). Yield = 73% (202 mg, 0.180 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.61 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 7.21 (d, *J* = 7.7 Hz, 8H, Ar-*H*), 7.03-7.02 (m, 11H, Ar-*H*), 6.94 (t, *J* = 7.6 Hz, 2H, Ar-*H*), 6.83-6.80 (m, 18H, Ar-*H*), 6.66 (d, *J* = 7.1 Hz, 8H, Ar-*H*), 5.34 (s, 2H, *H*-C≡C-*H*), 5.33 (s, 4H, C*H*Ph_2). **^{13}C{^{1}H} NMR** (151 MHz, C_6D_6): δ 183.7 (Cu-carbene), 144.1, 142.6, 142.1, 137.1, 135.7, 132.4, 130.2, 130.0, 129.7, 129.4, 128.9, 128.3, 127.5, 127.1, 125.4, 123.3, 122.6, 106.5, 51.8. Single crystals for XRD measurement were obtained by slow diffusion of pentane into a concentrated THF solution of **2-Cl** at 25 ºC.

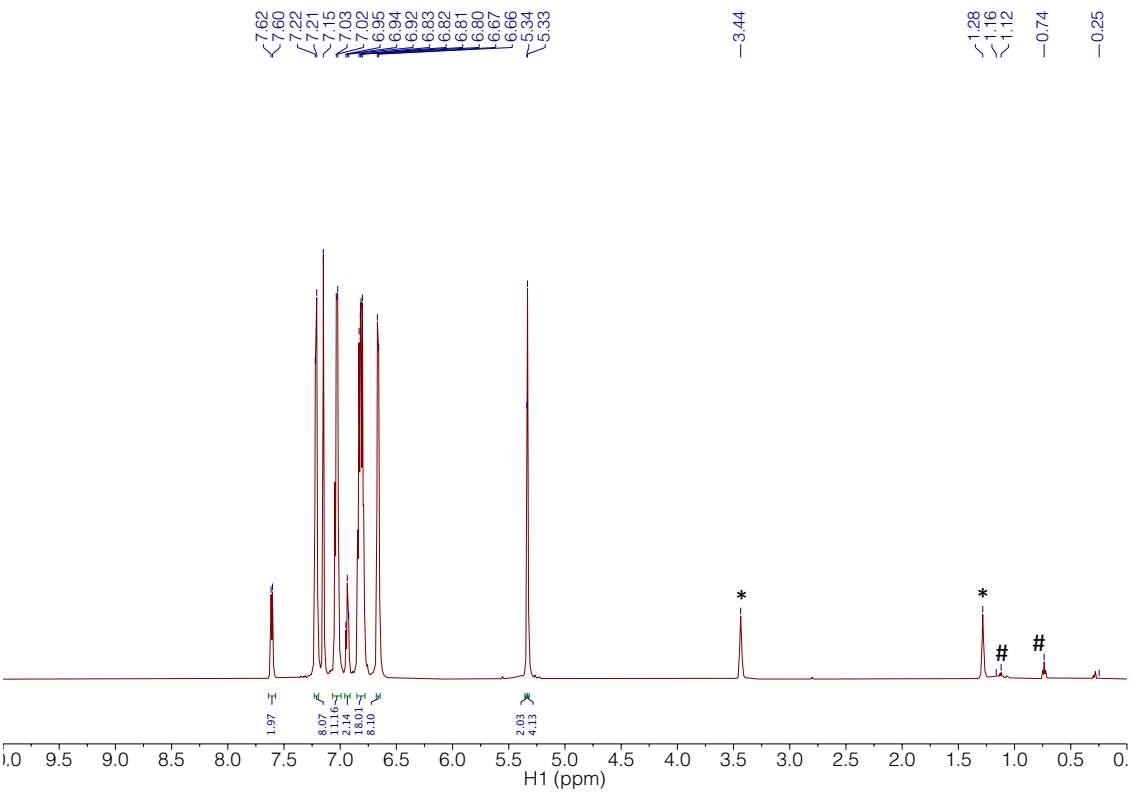


Figure S26A. ^{1}H NMR spectrum of **2-Cl**. *THF, #pentane.

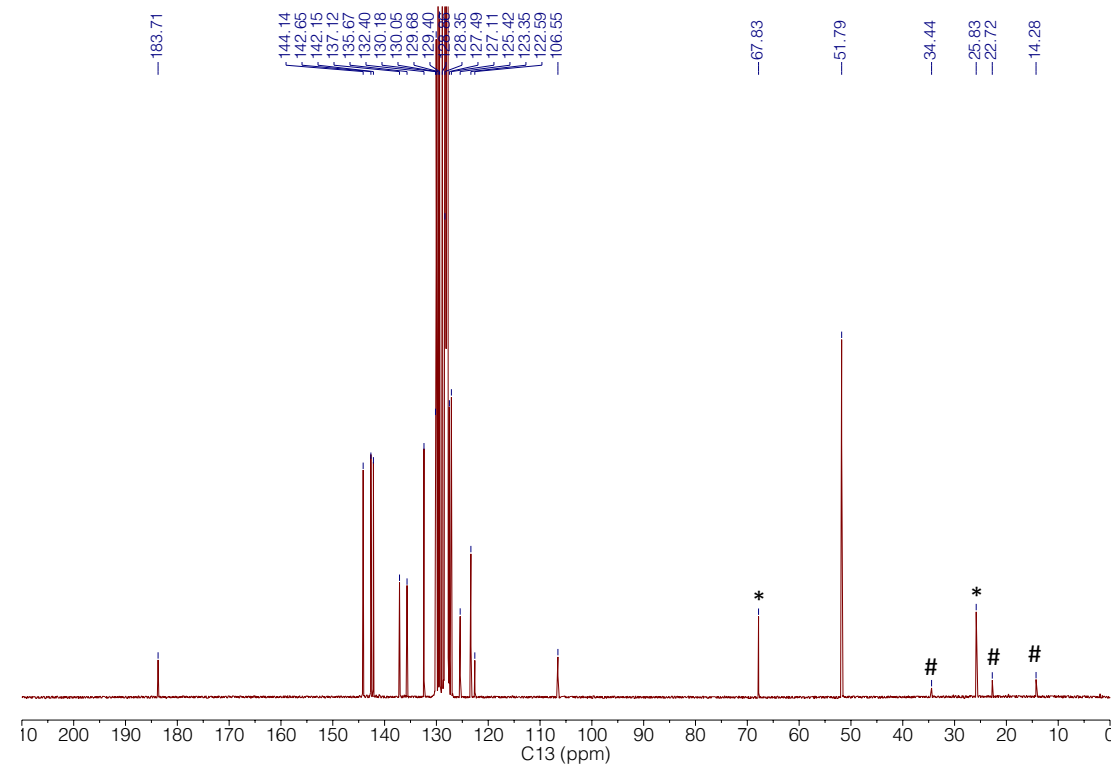
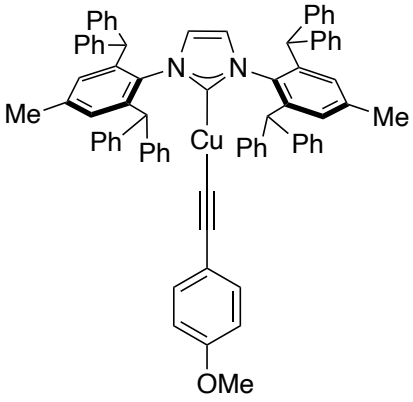


Figure S26B. ^{13}C{^{1}H} NMR spectrum of **2-Cl**. *THF, #pentane.

(IPr*Me)CuC≡C(C_6H_4-*p*-OMe) (7b)



The titled complex was synthesized according to the general procedure for complex **2-Me**: (IPr*Me)CuCl (250 mg, 0.247 mmol), 4-methoxyphenyl acetylene (34.4, 0.272 mmol), freshly grounded 3.0 equiv. K_2CO_3 (102 mg, 0.740 mmol), and EtOH (5 mL). Yield = 66% (180 mg, 0.162 mmol), colorless solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.61 (d, *J* = 8.1 Hz, 2H, Ar-*H*), 7.53 (d, *J* = 7.4 Hz, 8H, Ar-*H*), 7.37 (d, *J* = 7.5 Hz, 2H, Ar-*H*) 7.26 (t, *J* = 7.5 Hz, 8H, Ar-*H*), 7.07 – 6.86 (m, 26H, Ar-*H*), 6.63 (d, *J* = 8.2 Hz, 2H, Ar-*H*), 5.62 (s, 4H, C*H*Ph_2), 5.55 (s, 2H, *H*-C=C-*H*), 3.19 (s, 3H, O*Me*), 1.67 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (125 MHz, C_6D_6): δ 183.8 (Cu-carbene), 157.8, 143.6, 143.4, 141.6, 140.5, 134.9, 133.4, 130.5, 130.3, 129.9, 129.1, 128.60, 127.0, 126.7, 125.6, 123.3, 113.8, 105.7, 54.5, 51.7, 21.2. The ^{1}H, ^{13}C NMR data is consistent with the published NMR data for **7b**.[4] Single crystals for XRD measurement were obtained by layering of pentane over a concentrated toluene solution of the complex at 25 ºC.

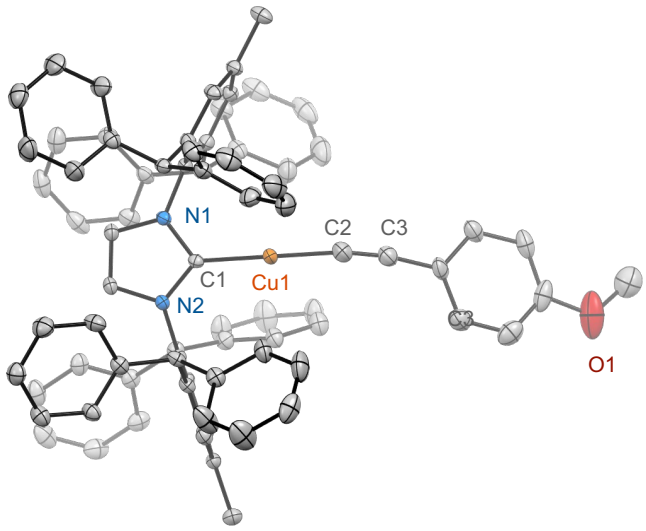
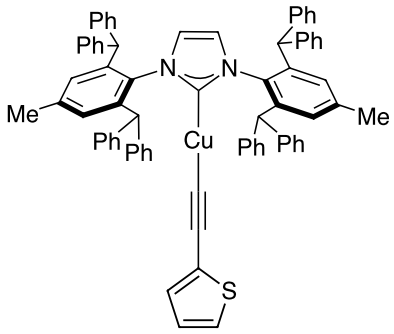


Figure S27. scXRD structure of **7b** is shown at 50% probability thermal ellipsoid. All hydrogen atoms, solvents are omitted. The scXRD structure of **7b** has also been reported.[4]

(IPr*Me)CuC≡C(C_4H_3S) (8b)



The titled complex was synthesized according to the general procedure for complex **2-Me**: (IPr*Me)CuCl (250 mg, 0.247 mmol), 2-thiophene acetylene (27.0 μL, 0.272 mmol), freshly grounded K_2CO_3 (102 mg, 0.740 mmol), and absolute EtOH (5 mL). Yield = 56% (150 mg, 0.138 mmol), faint yellow solid. **^{1}H NMR** (500 MHz, 25 ºC, C_6D_6): δ 7.46 (d, *J* = 7.7 Hz, 8H, Ar-*H*), 6.80 (t, *J* = 7.8 Hz, 8H, Ar-*H*), 7.10-7.07 (m, 1H, Ar-*H*), 7.05-6.95 (m, 29H, Ar-*H*), 6.58 (br s, 1H, Ar-*H*), 6.57 (br s, 1H, Ar-*H*), 5.56 (s, 4H, C*H*Ph_2), 5.55 (s, 2H, *H*-C≡C-*H*), 1.66 (s, 6H, *Me*). **^{13}C{^{1}H} NMR** (126 MHz, 25 ºC, C_6D_6): δ 183.1 (Cu-carbene), 143.3, 142.9, 141.2, 140.3, 134.5, 130.2, 129.9, 129.5, 128.8, 128.3, 127.9, 126.8, 126.5, 126.2, 123.0, 122.4, 113.9, 97.4, 51.4 (H-*C*≡*C*-H), 20.9 (*Me*). Single crystals for XRD measurement were obtained by layering of pentane over a concentrated toluene solution of **8b** at 25 ºC.

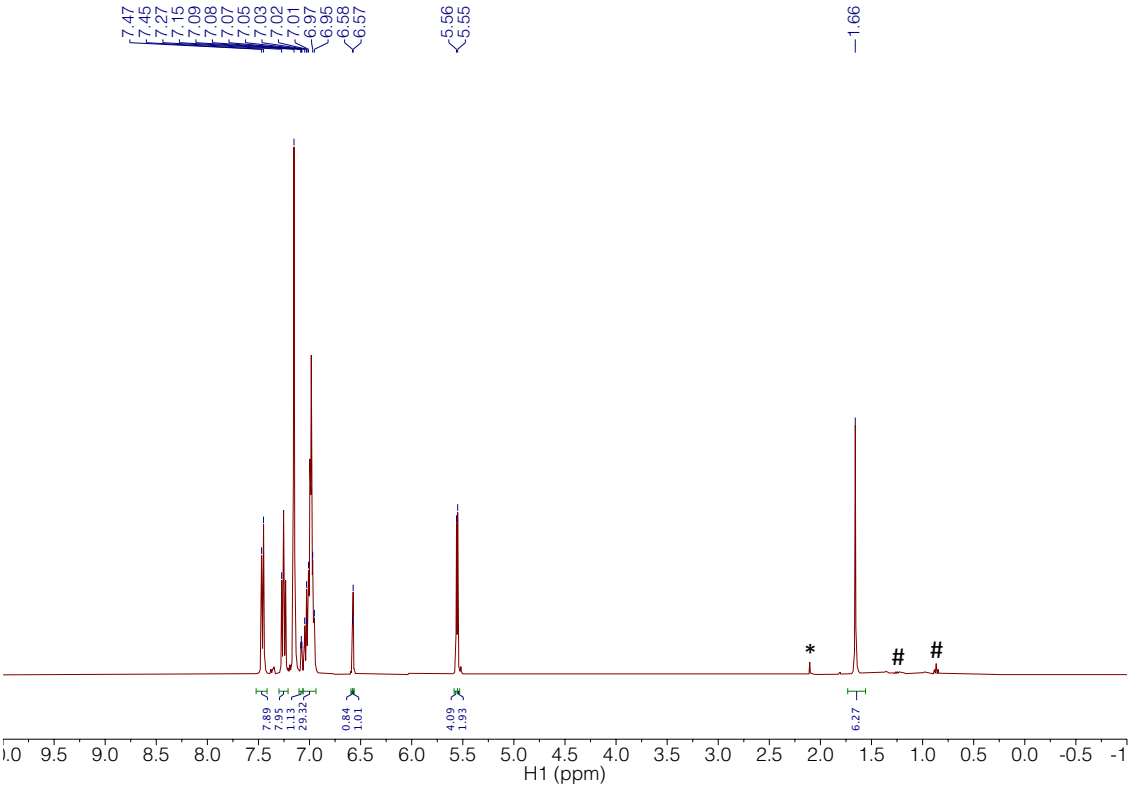


Figure S28A. ^{1}H NMR of **8b**. *Toluene, #pentane.

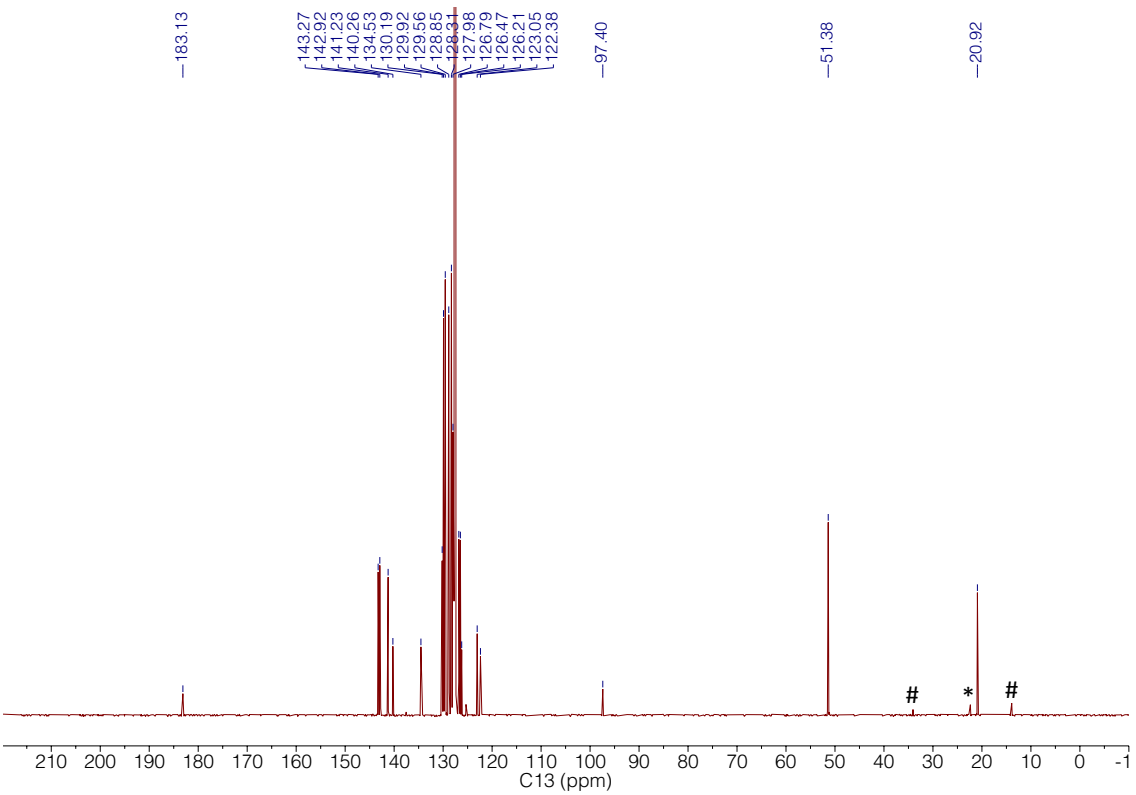


Figure S28B. $^{13}C\{^{1}H\}$ NMR of **8b**. *Toluene, #pentane.

UV-vis kinetics, Eyring analysis, ligand effect for (IPr*R)CuOC(Ar^{F})$_2$C≡CPh thermolysis

The UV-vis samples of (IPr*R)CuOC(Ar^{F})$_2$C≡CPh (R = Me **1-Me**, OMe **1-OMe**, Cl **1-Cl**) and (IPr)CuOC(Ar^{F})$_2$C≡CPh (**3**) for kinetic measurements were prepared inside a nitrogen-filled glovebox. To an oven-dried 20 mL scintillation vial was added the corresponding propargylic alkoxide complex (37.6 mmol) and 5 mL of toluene leading to a soluble, colorless solution. This solution was transferred to a 10 mL volumetric flask and diluted with toluene to the 10 mL mark. From this stock solution, an aliquot of 2.5 mL was transferred to a Starna 10 mm UV-vis cuvette equipped with a Teflon screwcap. The sealed UV-vis cuvette was removed from the glovebox for kinetic measurements.

UV-vis kinetic measurements were performed at 60-100 °C using the scanning kinetic function (285 nm – 600 nm) on a Cary 60 UV-vis spectrophotometer equipped with a Peltier temperature-controlled cuvette holder. The progress of the elimination reaction was monitored at 355 nm corresponding to Ar$^{F}_2$C=O formation for 5-6 half-lives. The nonlinear regression fit of the UV-vis kinetic data was performed by applying the exponential growth equation of f = y0+a*(1-exp(-b*x)) in SigmaPlot 14. All UV-vis kinetic measurements were performed in duplicate or triplicate as noted.

T (ºC)	Run 1 k_{obs} (s^{-1})	Run 2 k_{obs} (s^{-1})
60	1.1×10^{-5}	1.1×10^{-5}
70	3.5×10^{-5}	3.2×10^{-5}
80	1.0×10^{-4}	9.8×10^{-5}
90	2.5×10^{-4}	2.6×10^{-4}
100	6.2×10^{-4}	6.5×10^{-4}

Table S1. Summary of variable temperature UV-vis kinetic data for the β-alkynyl elimination of (IPr*Me)CuOC(Ar^F)$_2$C≡CPh (3.8 mM, toluene) at 60-100 ºC.

Ligand	Run 1 k_{obs} (x 10^{-4} s^{-1})	Run 2 k_{obs} (x 10^{-4} s^{-1})	Run 3 k_{obs} (x 10^{-4} s^{-1})
IPr*Me	2.5	2.6	
IPr*OMe	3.5	3.4	
IPr*Cl	6.0	5.7	5.8
IPr	2.4	2.4	2.2

Table S2. Summary of UV-vis kinetic data for the β-alkynyl elimination of 3.8 mM (L)CuOC(Ar^F)$_2$C≡CPh (L = IPr*Me, IPr*OMe, IPr*Cl, IPr) in toluene at 90 ºC.

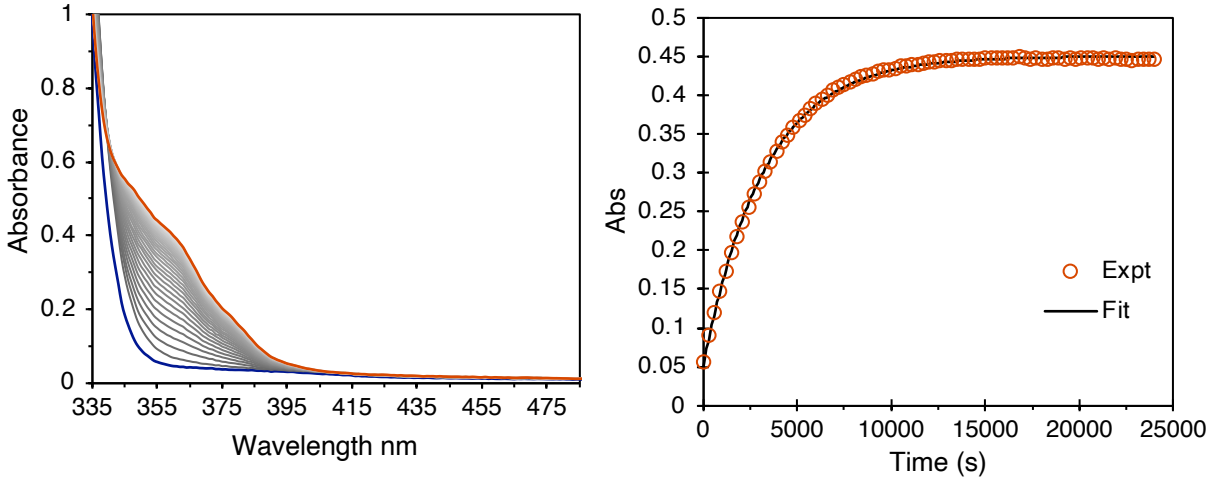


Figure S29A. UV-vis kinetic data of (IPr*Me)CuOC(Ar^F)$_2$)C≡CPh at 90 ºC as monitored by the formation of Ar^F_2C=O at 355 nm.

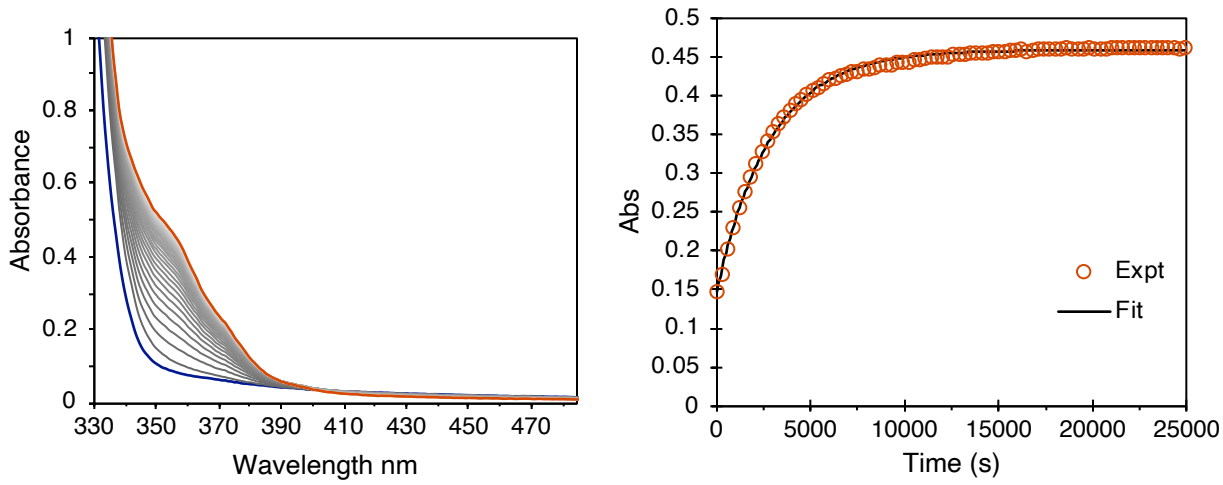


Figure S29B. UV-vis kinetic data of (IPr*OMe)CuOC(Ar^F)$_2$)C≡CPh at 90 ºC as monitored by the formation of Ar$^F{}_2$C=O at 355 nm.

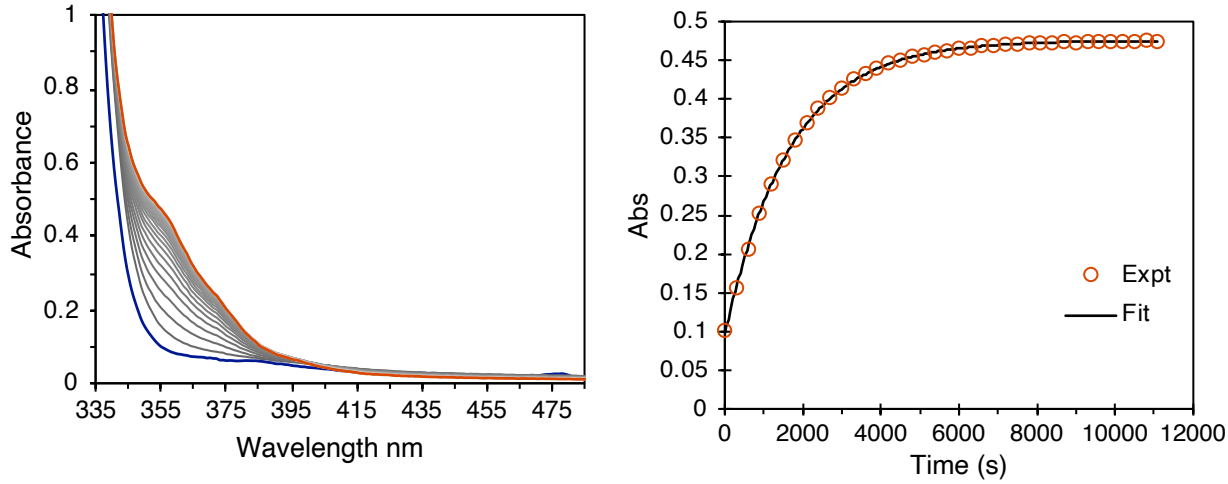


Figure S29C. UV-vis kinetic data of (IPr*Cl)CuOC(Ar^F)$_2$)C≡CPh at 90 ºC as monitored by the formation of Ar$^F{}_2$C=O at 355 nm.

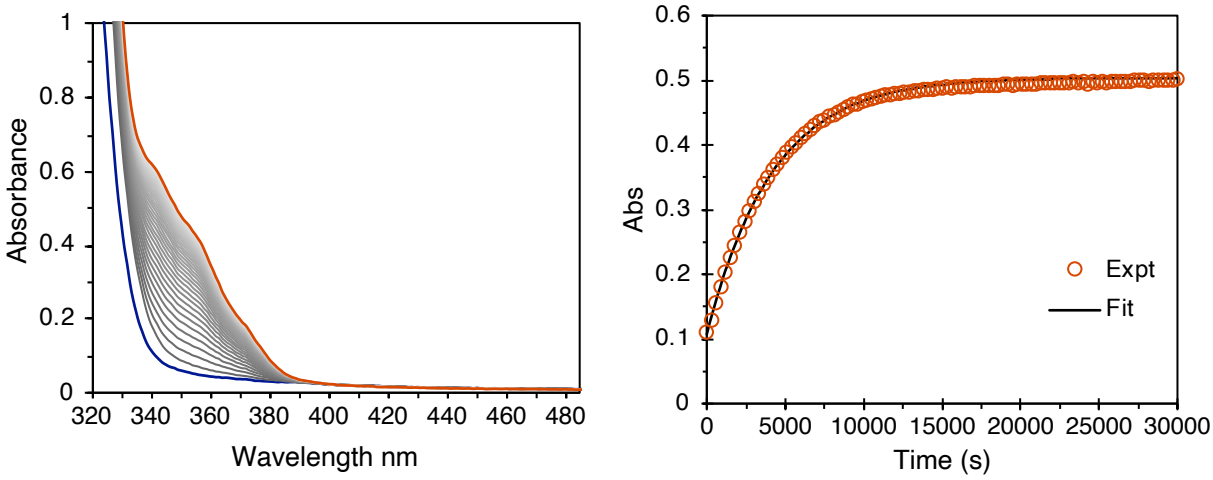


Figure S29D. UV-vis kinetic data of (IPr)CuOC(Ar^F)$_2$)C≡CPh at 90 ºC as monitored by the formation of Ar$^F{}_2$C=O at 355 nm.

Solid-state β-alkynyl elimination of (IPr*Me)CuOC(ArF)$_2$C≡CPh by thermolysis

Inside a nitrogen-filled glovebox, to oven-dried 4 mL scintillation vial was weighted 50 mg of (IPr*Me)CuOC(Ar^F)$_2$)C≡CPh. The solid was transferred to a 25 mL Schlenk tube, N_2 was evacuated by dynamic vacuum, and removed from the glovebox to a preheated oil bath at 100 ºC. At the time intervals of 3 h, 6 h, and 9 h, the Schlenk tube was returned to the glovebox. After reaching room temperature, a solid aliquot was collected and dissolved in 700 μL C_6D_6 for ^{1}H and ^{19}F{^{1}H} NMR spectroscopic analysis.

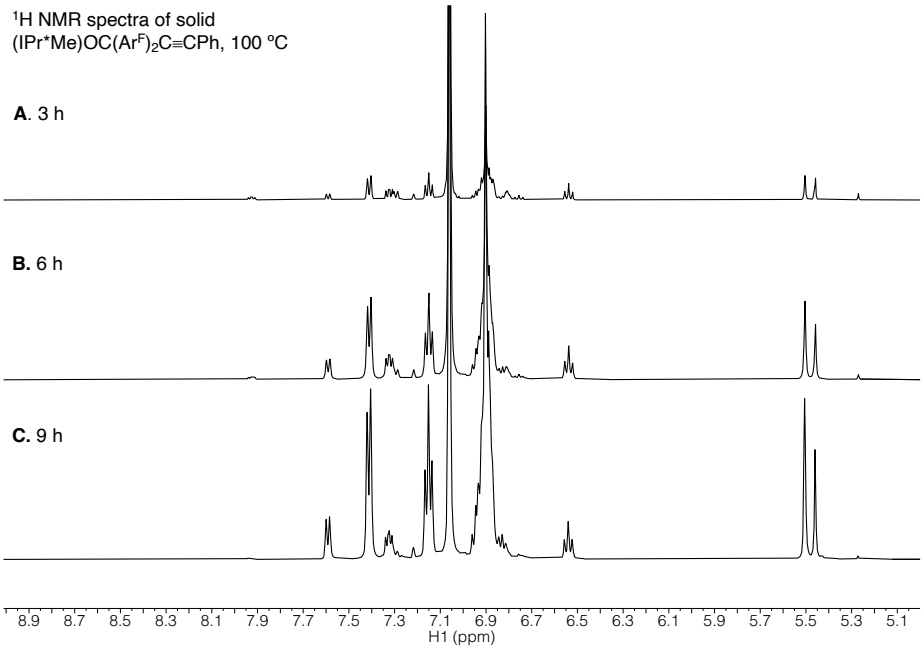


Figure S30A. ^{1}H NMR spectra of solid (IPr*Me)CuOC(Ar^F)$_2$)C≡CPh **1-Me** at 100 ºC for 3 h, 6 h, and 9 h to produce (IPr*Me)CuC≡CPh **2-Me** and Ar$^F{}_2$C=O.

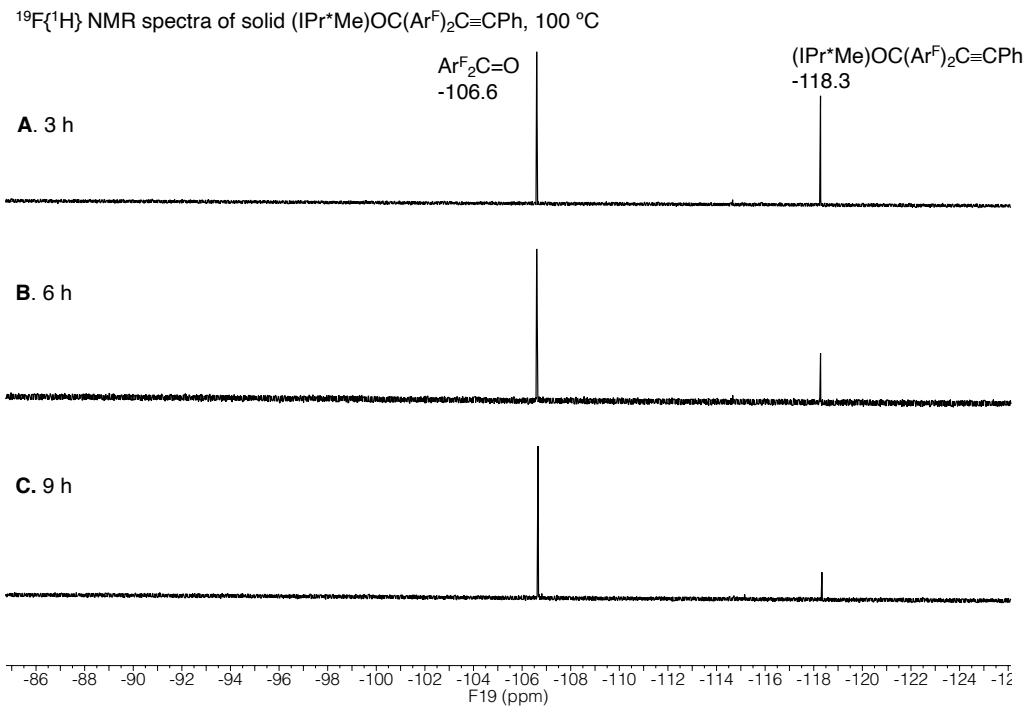
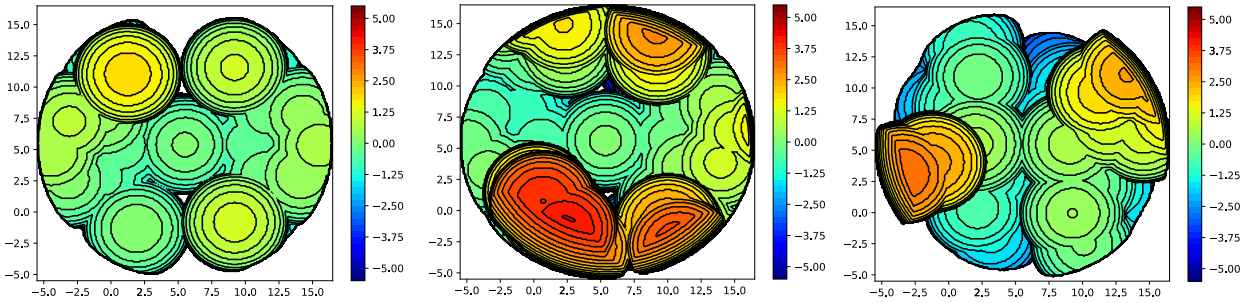


Figure S30B. $^{19}F\{^{1}H\}$ NMR spectra of solid **1-Me** at 100 °C for 3 h, 6 h, and 9 h, showing the consumption of **1-Me** and formation of $Ar^F{}_2C{=}O$.

%Volume buried calculations

$\%V_{Bur}$ calculations were performed on the SCXRD structure of (IPr*Me)CuOC(Ar^F)$_2$)C≡CPh **1-Me** and DFT-optimized structures of (IPr)CuOC(Ar^F)$_2$)C≡CPh and (*S*-BINAP)CuOC(Ar^F)$_2$)C≡CPh by SambVca 2.19 (https://www.molnac.unisa.it/OMtools/sambvca2.1/index.html) using a 5.5 Å sphere radius and H atoms omitted.



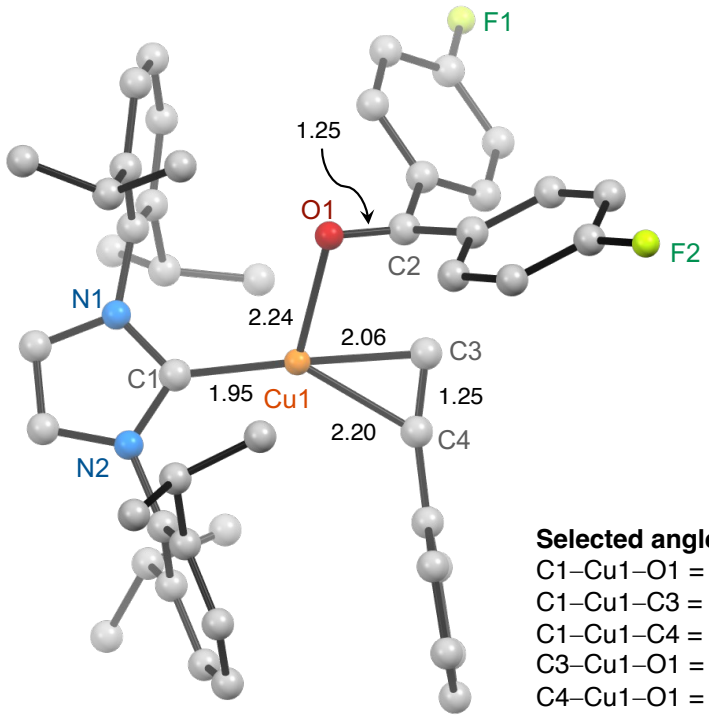
(IPr)CuOCAr$^F{}_2$CCPh (IPr*Me)CuOCAr$^F{}_2$CCPh (*S*-BINAP)CuOCAr$^F{}_2$CCPh

Complex	(IPr)CuOCAr$^{F}_{2}$CCPh	(IPr*Me)CuOCAr$^{F}_{2}$CCPh	(*S*-BINAP)CuOCAr$^{F}_{2}$CCPh
Final %V_{Bur}	46.3	63.6	50.2
Quadrant %V_{Bur}			
SW	46.5	78.1	53.7
NW	46.2	48.4	45.6
NE	46.5	61.1	52.9
SE	46.2	66.8	48.8

Figure S31. Summary of %V_{Bur} (r = 5.5 Å) and quadrant %V_{Bur} for the supporting ligands of IPr, IPr*Me, and *S*-BINAP for the corresponding propargylic alkoxide Cu(I) complexes. The calculated %V_{Bur} values for IPr and IPr*Me in complexes of (IPr)CuCl (CCDC # 234224) and (IPr*Me)CuCl[1] are identical.

Computational methods

ωB97X-D3[6] functional with the def2-SVP basis set[7] in ORCA 6.0[8–16] was used to optimize structures and calculate thermostatistical corrections. The electronic energy was recalculated using the def2-TZVP basis set.[7] For solvated energies, the SMD model of benzene was used.[17] The grid scheme DEFGRID3 and the RIJCOSX approximation were used. All structures converged to zero gradient, but some had small extra imaginary frequencies. For the free energy calculation, all wavenumbers below 100 cm^{-1} were set to 100 cm^{-1}, including extra imaginary frequencies.



Selected angles (°)
C1–Cu1–O1 = 106.45
C1–Cu1–C3 = 172.95
C1–Cu1–C4 = 143.31
C3–Cu1–O1 = 76.53
C4–Cu1–O1 = 107.16

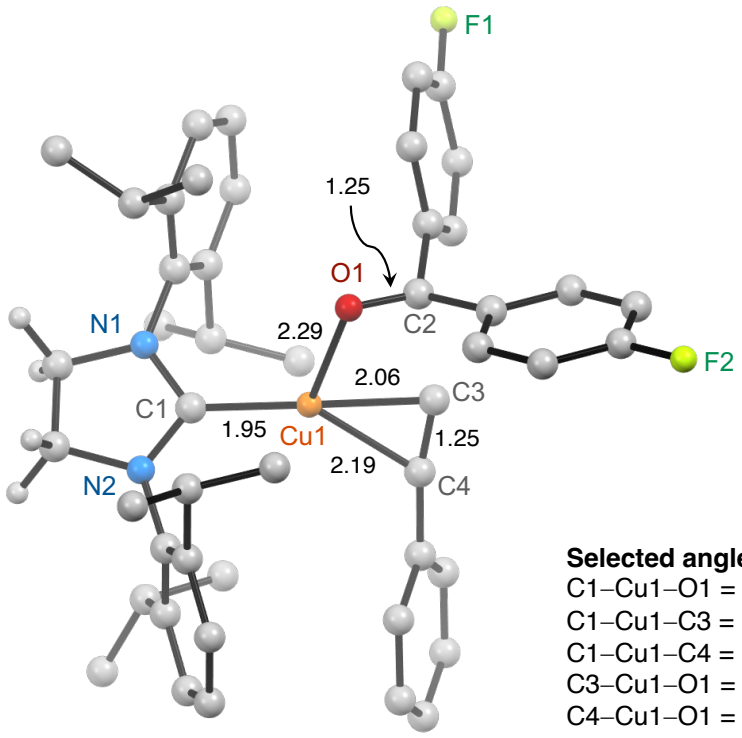


Figure S32. The transition-state structures depicting the C-C bond cleavage of (IPr)CuOC(Ar^F)$_2$)C≡CPh (top) and (SIPr)CuOC(Ar^F)$_2$)C≡CPh (bottom). Selected bond distances (Å) and angles (°) are shown.

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