

Nitrosonium Reactivity of (NHC)Copper(I) Sulfide Complexes

Abraham J. Jordan[†], Rebecca K. Walde[†], Kelly M. Schultz[‡], John Bacsa^{†§}, Joseph P. Sadighi^{†*}

[†] School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0400, United States

[‡] Department of Chemistry, Murdock Hall, Linfield College, McMinnville, OR 97128, United States

[§] X-ray Crystallography Center, Department of Chemistry, Emory University, 1515 Dickey Drive, Atlanta, Georgia 30322, United States

joseph.sadighi@chemistry.gatech.edu

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General Considerations. Unless otherwise indicated, manipulations were performed in an MBraun glovebox under an inert atmosphere of nitrogen, or in sealable glassware on a Schlenk line under an atmosphere of argon. Glassware and magnetic stir bars were dried in a ventilated oven at 160°C and were allowed to cool under vacuum. Dichloromethane (BDH), hexane (EMD Millipore Omnisolv), tetrahydrofuran (THF, EMD Millipore Omnisolv), toluene (EMD Millipore Omnisolv) were sparged with ultra-high purity argon (NexAir) for 30 minutes prior to first use, dried using an MBraun solvent purification system, transferred to Straus flasks, degassed using three freeze-pump-thaw cycles, and stored under nitrogen or argon. Anhydrous benzene (C₆H₆, EMD Millipore Drisolv) and, anhydrous pentane (EMD Millipore Drisolv, sealed under a nitrogen atmosphere) were used as received and stored in a glovebox. Tap water was purified in a Barnstead International automated still prior to use.

Benzene-*d*₆ (Cambridge Isotope Laboratories) was dried over sodium benzophenone ketyl, vacuum-transferred into oven-dried resealable flasks, and degassed by successive freeze-pump-thaw cycles. Dichloromethane-*d*₂ (Cambridge Isotope Laboratories) and acetonitrile-*d*₃ (Cambridge Isotope Laboratories) were dried over calcium hydride overnight, vacuum-transferred to an oven-dried resealable Schlenk flask, and degassed by successive freeze-pump-thaw cycles. Chloroform-*d* (Cambridge Isotope Laboratories) was used as received.

Sodium *tert*-butoxide (TCI America), copper(I) chloride (Alfa-Aesar), 2,6-diisopropylaniline (Sigma-Aldrich), *N,N*-diisopropylethylamine (Alfa-Aesar), acetic acid, (Alfa-Aesar), sodium metal (Alfa-Aesar), benzophenone (Alfa-Aesar), calcium hydride (Alfa-Aesar), 1,4-dibromobutane (Sigma-Aldrich), triethyl orthoformate (Alfa-Aesar), sodium sulfide (Alfa-Aesar), potassium hydrosulfide (Strem), 2-phenylacetic dithioperoxyanhydride (Matrix), *tert*-butyl nitrite (Sigma-Aldrich) sodium bis(trimethylsilyl)amide (NaHMDS, Sigma-Aldrich or Strem

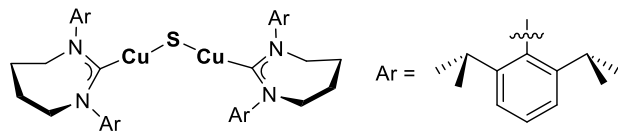
Chemicals), nitrosonium tetrafluoroborate ($\text{NO}^+ \text{BF}_4^-$, Alfa-Aesar), silver tetrafluoroborate (Alfa-Aesar), nitrogen (NexAir), and argon (both industrial and ultra-high purity grades, NexAir) were used as received. 7DippCuCl , 7DippCuOtBu (**3**),¹ and $(7\text{DippCuH})_2$ ¹ were prepared according to literature protocols and were characterized by ^1H NMR spectroscopy.

Spectroscopic Measurements. ^1H , ^{13}C , ^{11}B , ^{19}F , and ^{31}P spectra were obtained using Bruker Avance IIIHD 700 MHz, Bruker DSX 400 MHz and Varian Vx 400 MHz spectrometers. ^1H and ^{13}C NMR chemical shifts are referenced with respect to solvent signals and reported relative to tetramethylsilane. A capillary insert of α,α,α -trifluorotoluene (-63.72 ppm) was used to determine ^{19}F NMR chemical shifts. ^{31}P NMR chemical shifts were externally referenced to 85% H_3PO_4 (0.0 ppm).

Infrared spectra were collected using microcrystalline samples on a Bruker Alpha-P infrared spectrometer equipped with an attenuated total reflection (ATR) attachment. Samples were exposed to air as briefly as possible prior to data collection.

Elemental analyses were performed by Atlantic Microlab, Inc. in Norcross, Georgia.

Experimental Procedures



(7DippCu)₂S (1) 7DippCuCl (0.182 g, 0.352 mmol) and sodium sulfide (0.055 g, 0.70 mmol) were combined in a 20-mL vial, equipped with a stir bar, before THF (5 mL) was added. The mixture was allowed to stir for 24h before the THF was removed *in vacuo*. The product was extracted with C₆H₆ (3 x 3 mL) filtered through Celite and concentrated *in vacuo*. The resulting yellow solid was washed with CH₃CN (2 x 3 mL), then dried *in vacuo* to afford the title complex as a yellow solid. (0.137 g, 78% yield) ¹H NMR (700 MHz, C₆D₆): δ (ppm) 7.15 (t, t, ³J_{HH} = 7.7 Hz, 2H, *para*-CH), 7.06 (d, ³J_{HH} = 7.7 Hz, 4H, *meta*-CH), 3.29 (m, 4H, NCH₂), 3.20 (sept, ³J_{HH} = 7.0 Hz, 4H, CH(CH₃)₂), 1.62 (m, 4H, NCH₂CH₂), 1.48 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂), 1.27 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂). ¹³C{¹H} NMR (176 MHz, C₆D₆): δ (ppm) 212.6 (NCCu), 145.0 (*ortho*-C), 144.7 (*ipso*-C), 128.4 (*para*-C), 124.6 (*meta*-C), 54.1 (NCH₂), 28.9 (CH(CH₃)₂), 25.9 (CH(CH₃)₂), 25.1 (NCH₂CH₂), 24.9 (CH(CH₃)₂). IR: ν (cm⁻¹) 2958, 2927, 2864, 1486, 1427, 1384, 1361, 1320, 1299, 1286, 1177, 1105, 1057, 999, 938, 799, 721, 550, 446, 434.

Note: We have been unable to obtain satisfactory elemental analysis for **1**. The complex is extremely air-and moisture-sensitive. While NMR-silent impurities cannot be ruled out, we believe the ¹H and ¹³C NMR spectra provided reflect the purity of the sample. After addition of 1,4-dichlorobutane to a benzene solution of **1** and concentration *in vacuo*, to remove tetrahydrothiophene, and excess 1,4-dichlorobutane, the more stable 7DippCuCl complex was isolated without further purification and the elemental analysis was obtained (see p. **S16**). We reasoned that only a sufficiently pure sample of **1** would give rise to analytically pure 7DippCuCl.

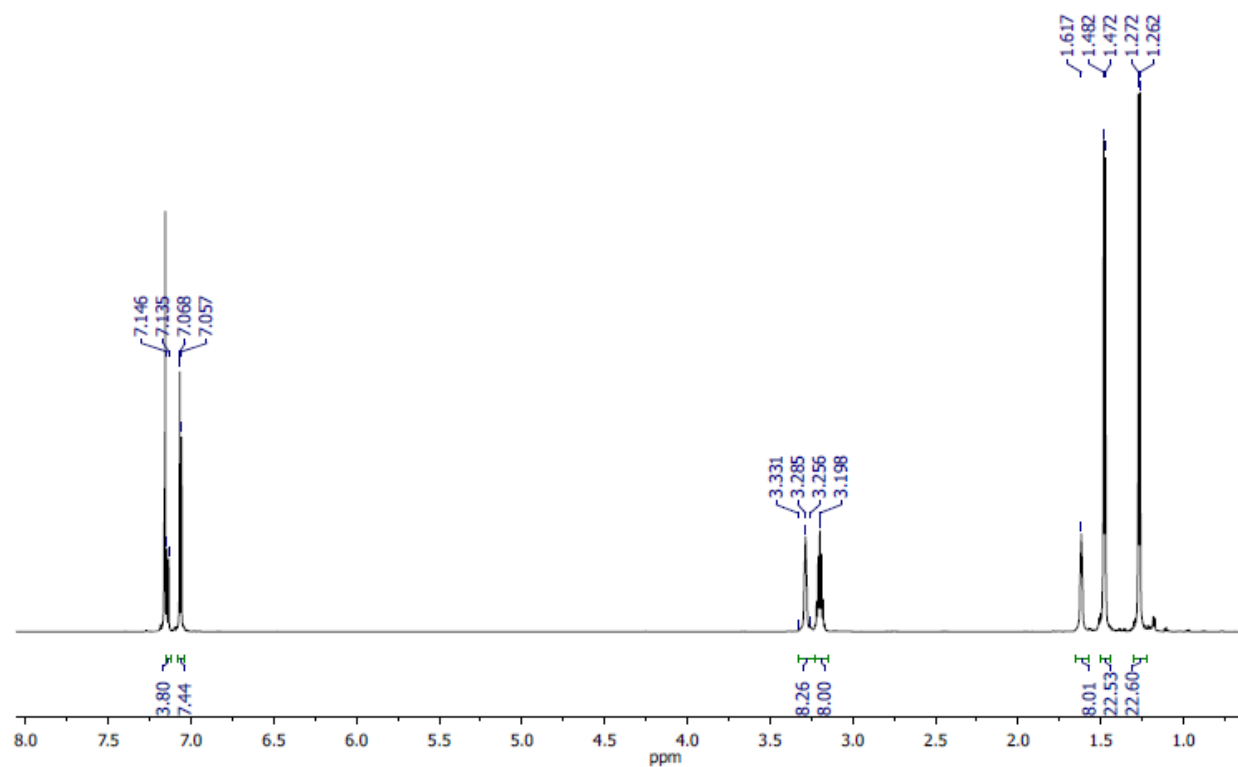


Figure S1. ¹H NMR spectrum of (7DippCu)₂S in C₆D₆.

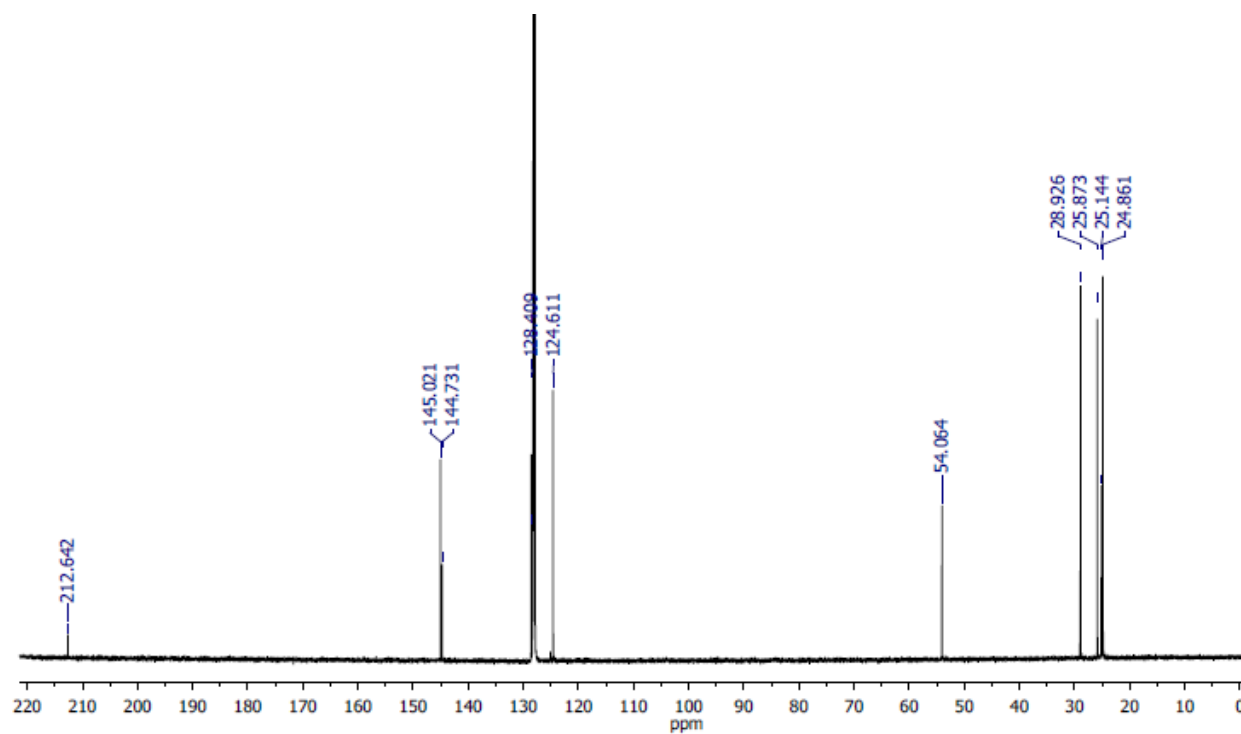
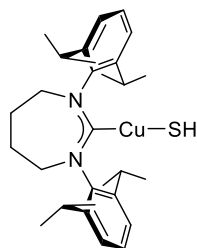


Figure S2. ¹³C NMR spectrum of (7DippCu)₂S in C₆D₆.



7DippCuSH (2) 7DippCuCl (0.202 g, 0.391 mmol) and potassium hydrosulfide (0.034 g, 0.47 mmol) were combined in a 20-mL vial, equipped with a stir bar, before MeOH (5 mL), and THF (10 mL) were added. The mixture was allowed to stir for 1h before the MeOH and THF were removed *in vacuo*. The product was extracted with CH₂Cl₂ (3 x 3 mL) filtered through Celite and concentrated *in vacuo* to afford the title complex as a colorless solid. (0.185 g, 92% yield) ¹H NMR (700 MHz, C₆D₆): δ (ppm) 7.15 (t, ³J_{HH} = 7.7 Hz, 2H, para-CH), 7.04 (d, ³J_{HH} = 7.7 Hz, 4H, meta-CH), 3.27 (m, 4H, NCH₂), 3.21 (sept, ³J_{HH} = 7.0 Hz, 4H, CH(CH₃)₂), 1.63 (m, 4H, NCH₂CH₂), 1.52 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂), 1.19 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂), -2.17 (s, 1H, Cu-SH). ¹³C{¹H} NMR (176 MHz, C₆D₆): δ (ppm) 211.4 (NCCu), 145.2 (ortho-C), 144.3 (ipso-C), 129.2 (para-C), 125.0 (meta-C), 53.4 (NCH₂), 29.0 (CH(CH₃)₂), 25.2 (NCH₂CH₂), 25.1 (CH(CH₃)₂), 24.8 (CH(CH₃)₂). IR: ν (cm⁻¹) 2960, 2938, 2865, 1494, 1447, 1385, 1362, 1323, 1309, 1190, 1177, 1095, 1033, 1000, 936, 902, 786, 552, 457. Anal. Calcd for C₂₉H₄₃CuN₂S C, 67.60; H, 8.41; N, 5.44. Found C, 67.60; H, 8.58; N, 5.40.

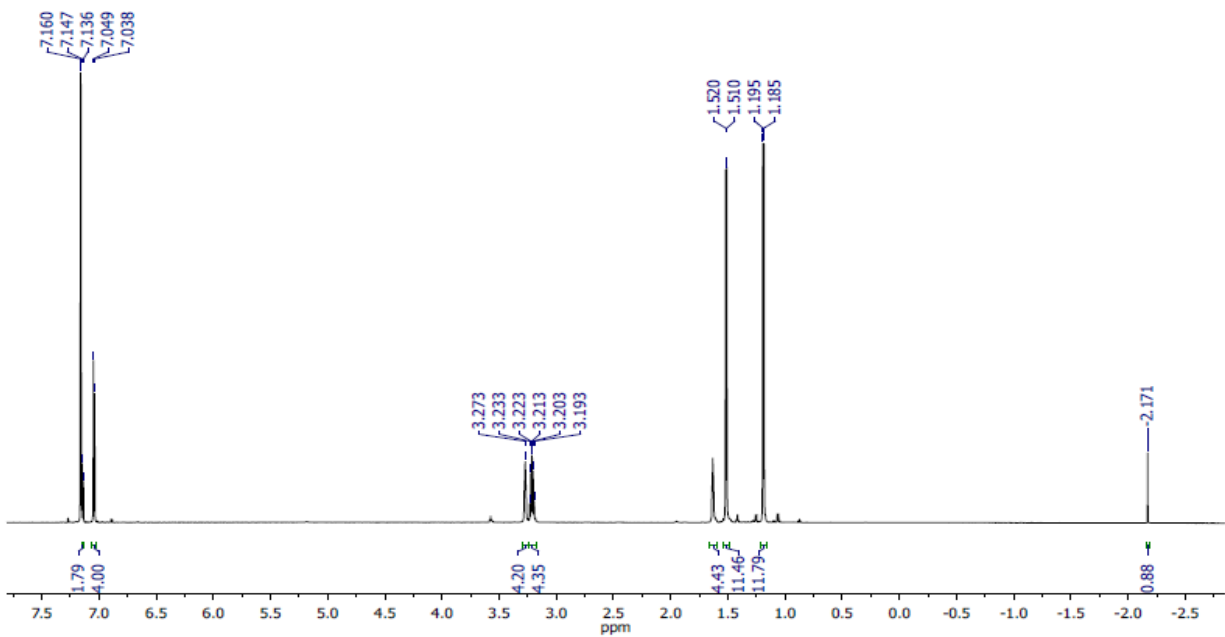


Figure S3. ¹H NMR spectrum of 7DippCuSH in C₆D₆.

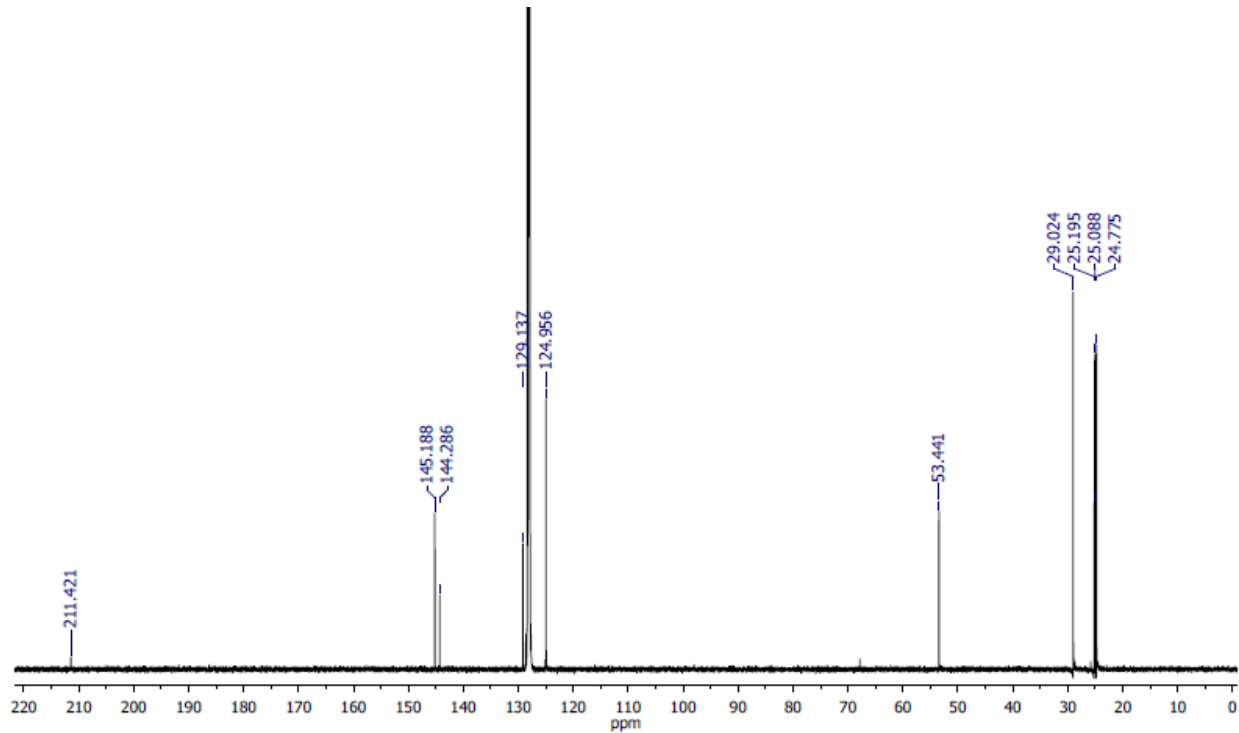
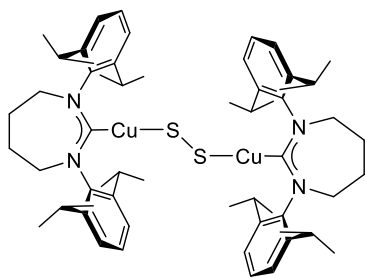


Figure S4. ¹³C NMR spectrum of 7DippCuSH in C₆D₆.



(7DippCuS)₂ (4) 7DippCuO-*t*-Bu (0.074 g, 0.13 mmol) and 2-phenylacetic dithioperxoyanhydride (0.020 g, 0.066 mmol) were combined in a 20-mL vial, equipped with a stir bar, before C₆H₆ (5 mL) were added. The mixture was allowed to stir for 1h before the C₆H₆ was removed *in vacuo*. The resulting yellow solid was washed with pentane (3 x 3 mL), the recrystallized from CH₃CN (5 mL) at -35 °C. The resulting solid was dried under *in vacuo* to afford the product as an orange solid. (0.040 g, 58% yield) ¹H NMR (700 MHz, C₆D₆): δ (ppm) 7.17 (t, ³J_{HH} = 7.7 Hz, 4H, *para*-CH), 7.07 (d, ³J_{HH} = 7.7 Hz, 8H, *meta*-CH), 3.32 (m, 8H, NCH₂), 3.23 (sept, ³J_{HH} = 7.0 Hz, 8H, CH(CH₃)₂), 1.64 (m, 8H, NCH₂CH₂), 1.54 (d, ³J_{HH} = 7.0 Hz, 24H, CH₂(CH₃)₂), 1.25 (d, ³J_{HH} = 7.0 Hz, 24H, CH₂(CH₃)₂). ¹³C{¹H} NMR (176 MHz, C₆D₆): δ (ppm) 213.9 (NCCu), 145.0 (*ortho*-C), 144.7 (*ipso*-C), 128.8 (*para*-C), 125.0 (*meta*-C), 53.6 (NCH₂), 29.1 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 25.2 (NCH₂CH₂), 25.0 (CH(CH₃)₂). IR: ν (cm⁻¹) 2957, 2926, 2865, 1498, 1446, 1385, 1363, 1312, 1290, 1222, 1096, 1055, 935, 899, 801, 756, 629, 504, 406.

Note: We have been unable to obtain satisfactory elemental analysis for **4**. The complex is extremely air-and moisture-sensitive. While NMR-silent impurities cannot be ruled out, we believe the ¹H and ¹³C NMR spectra provided reflect the purity of the sample.

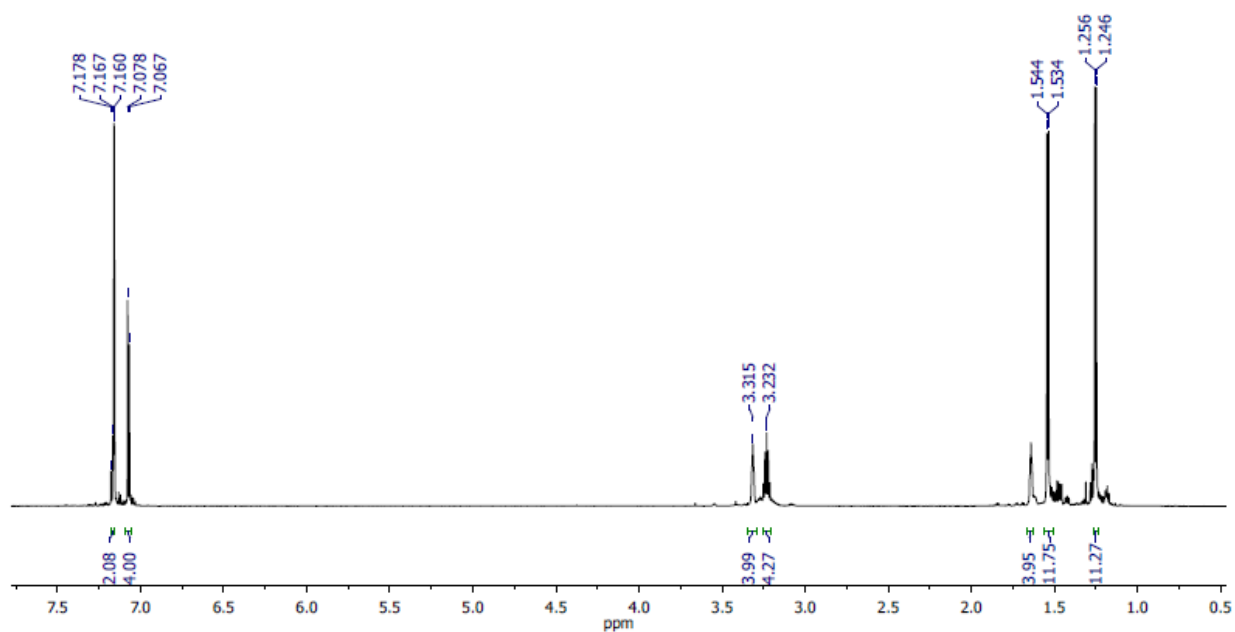


Figure S5. ¹H NMR spectrum of (7DippCuS)₂ in C₆D₆.

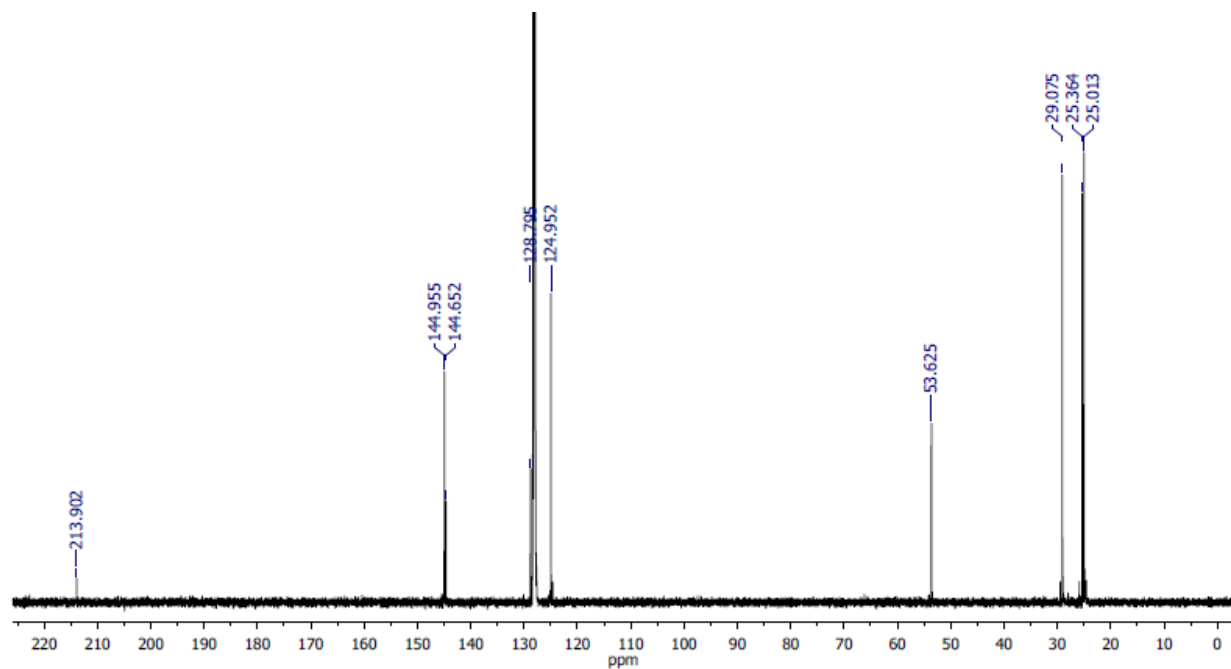
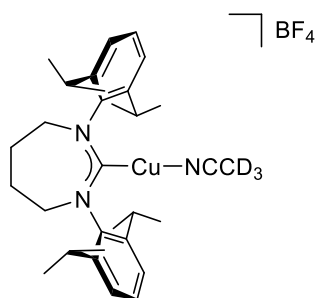


Figure S6. ¹³C NMR spectrum of (7DippCuS)₂ in C₆D₆.



7DippCu(NCCD₃)BF₄ (5) 7DippCuCl (0.059 g, 0.11 mmol) and silver tetrafluoroborate (0.022 g, 0.11 mmol) were combined in a 20-mL vial, equipped with a stir bar, before CD₃CN (0.1 mL) and DCM (3 mL) were added. The mixture was allowed to stir for 15 min, filtered through Celite, and concentrated *in vacuo*. The resulting colorless solid was dissolved in ethyl acetate (3 mL), layered with hexanes (5 mL) and placed in the freezer overnight. The resulting colorless solid was collected and dried *in vacuo* to afford the title complex. (0.051 g, 74% yield) ¹H NMR (700 MHz, CD₃CN): δ (ppm) 7.33 (t, ³J_{HH} = 7.7 Hz, 2H, para-CH), 7.26 (d, ³J_{HH} = 7.7 Hz, 4H, meta-CH), 3.98 (m, 4H, NCH₂), 3.30 (sept, ³J_{HH} = 7.0 Hz, 4H, CH(CH₃)₂), 2.29 (m, 4H, NCH₂CH₂), 1.29 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂) 1.27 (d, ³J_{HH} = 7.0 Hz, 12H, CH₂(CH₃)₂) ¹³C{¹H} NMR (176 MHz, CD₃CN): δ (ppm) 213.2 (NCCu), 146.4 (*ortho*-C), 146.2 (*ipso*-C), 129.4 (*para*-C), 125.5 (*meta*-C), 55.1 (NCH₂), 29.3 (CH(CH₃)₂), 26.0 (NCH₂CH₂), 25.1 (CH(CH₃)₂), 24.4 (CH(CH₃)₂). ¹⁹F NMR (378 MHz, CD₃CN): δ (ppm) -152.4 (4F, BF₄⁻). IR: ν (cm⁻¹) 2967, 2931, 2865, 1487, 1449, 1383, 1362, 1308, 1095, 1053, 1002, 934, 806, 790, 763, 612, 557, 518, 490.

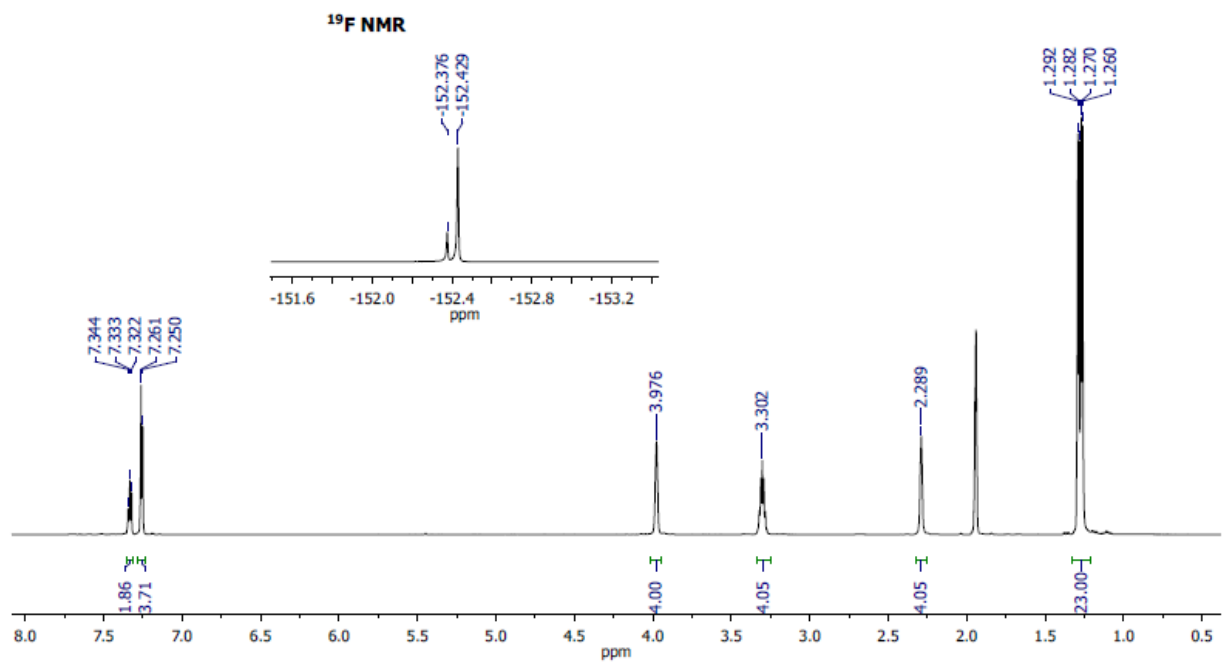


Figure S7. ¹H NMR spectrum of 7DippCu(NCCD₃)BF₄ overlaid with the BF₄⁻ resonance in ¹⁹F NMR spectrum in CD₃CN.

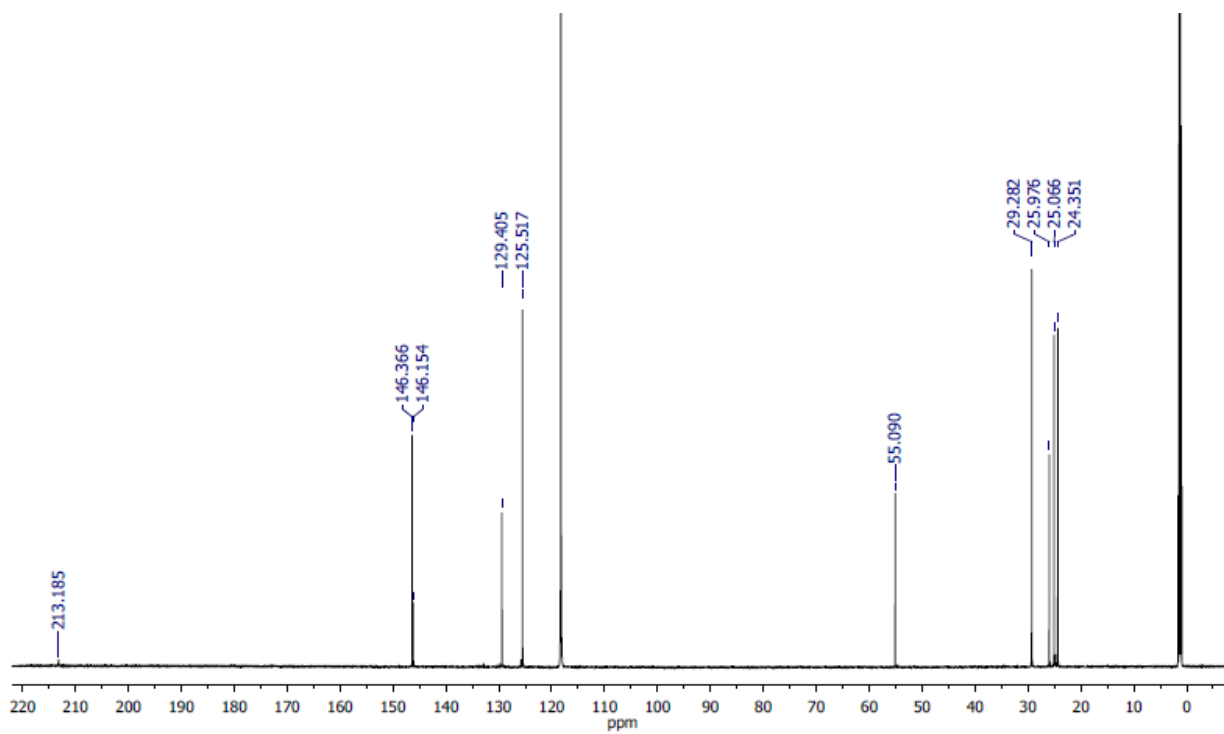
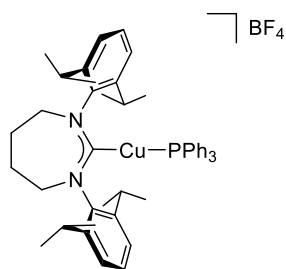


Figure S8. ¹³C NMR spectrum of 7DippCu(NCCD₃)BF₄ in CD₃CN.



7DippCu(PPh₃)BF₄ 7DippCuCl (0.067 g, 0.13 mmol), triphenylphosphine (0.034, 0.13 mmol) and silver tetrafluoroborate (0.025 g, 0.13 mmol) were combined in a 20-mL vial, equipped with a stir bar, before DCM (5 mL) was added. The mixture was allowed to stir for 15 min, filtered through Celite, before the resulting colorless solution was layered with pentane (8 mL) and placed in the freezer at $-35\text{ }^{\circ}\text{C}$ for 16h. The resulting crystals were dried *in vacuo* for 1h to afford the title complex. (0.090 g, 84 % yield) ^1H NMR (400 MHz, CD_2Cl_2): δ (ppm) 7.48-7.44 (m, 4H, dipp *para*-CH, PPh₃ *para*-CH), 7.32-7.26 (m, 10H, dipp *meta*-CH, PPh₃ *meta*-CH), 6.63-6.58 (m, PPh₃ *ortho*-CH), 4.07 (m, 4H, NCH₂), 3.27 (sept, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 4H, CH(CH₃)₂), 2.40 (m, 4H, NCH₂CH₂), 1.33 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 12H, CH₂(CH₃)₂), 1.05 (d, $^3J_{\text{HH}} = 6.8\text{ Hz}$, 12H, CH₂(CH₃)₂). $^{13}\text{C}\{^1\text{H}\}$ NMR (176 MHz CD_2Cl_2): δ (ppm) 206.1 (d, $^2J_{\text{PC}} = 60.2\text{ Hz}$, NCCu), 146.0 (dipp *ortho*-C), 143.8 (dipp *ipso*-C), 133.7 (d, $^2J_{\text{PC}} = 14.1\text{ Hz}$, PPh₃ *ortho*-C), 131.9 (d, $^4J_{\text{PC}} = 2.1\text{ Hz}$, PPh₃ *para*-C), 130.1 (*para*-C), 129.6 (d, $^3J_{\text{PC}} = 5.5\text{ Hz}$, PPh₃ *para*-C), 127.8 (d, $^1J_{\text{PC}} = 45.9\text{ Hz}$, PPh₃ *ipso*-C), 125.8 (dipp *meta*-C) 55.0 (NCH₂), 29.2 (CH(CH₃)₂), 25.5 (NCH₂CH₂), 25.2 (CH(CH₃)₂), 24.7 (CH(CH₃)₂). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CD_2Cl_2): δ (ppm) 7.7 (Cu-PPh₃). ^{19}F NMR (378 MHz, CD_2Cl_2): δ (ppm) -152.7 (4F, BF₄[−]). IR: ν (cm^{−1}) 2961, 2922, 2845, 1506, 1436, 1315, 1094, 1046, 998, 900, 807, 748, 675, 530, 506, 489, 451. Anal. Calcd for C₄₇H₅₇CuN₂BF₄P C, 67.91; H, 6.91; N, 3.37. Found C, 67.45; H, 6.73; N, 3.47.

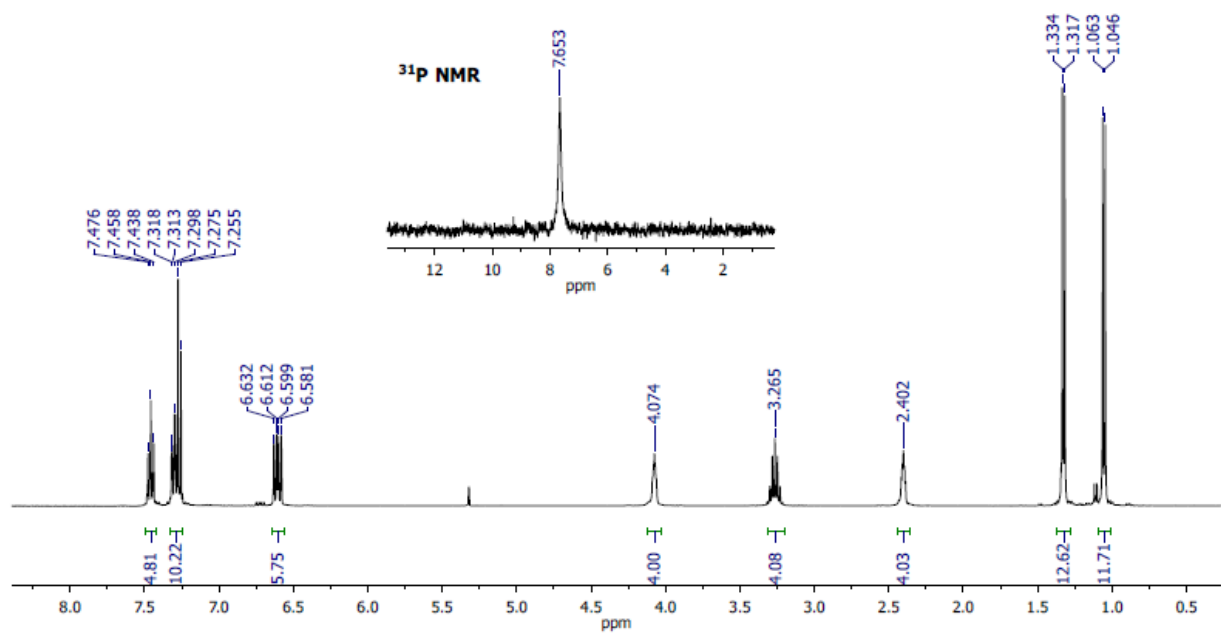


Figure S9. ^1H and ^{31}P NMR spectra of $7\text{DippCu}(\text{PPh}_3)\text{BF}_4$ in CD_2Cl_2 .

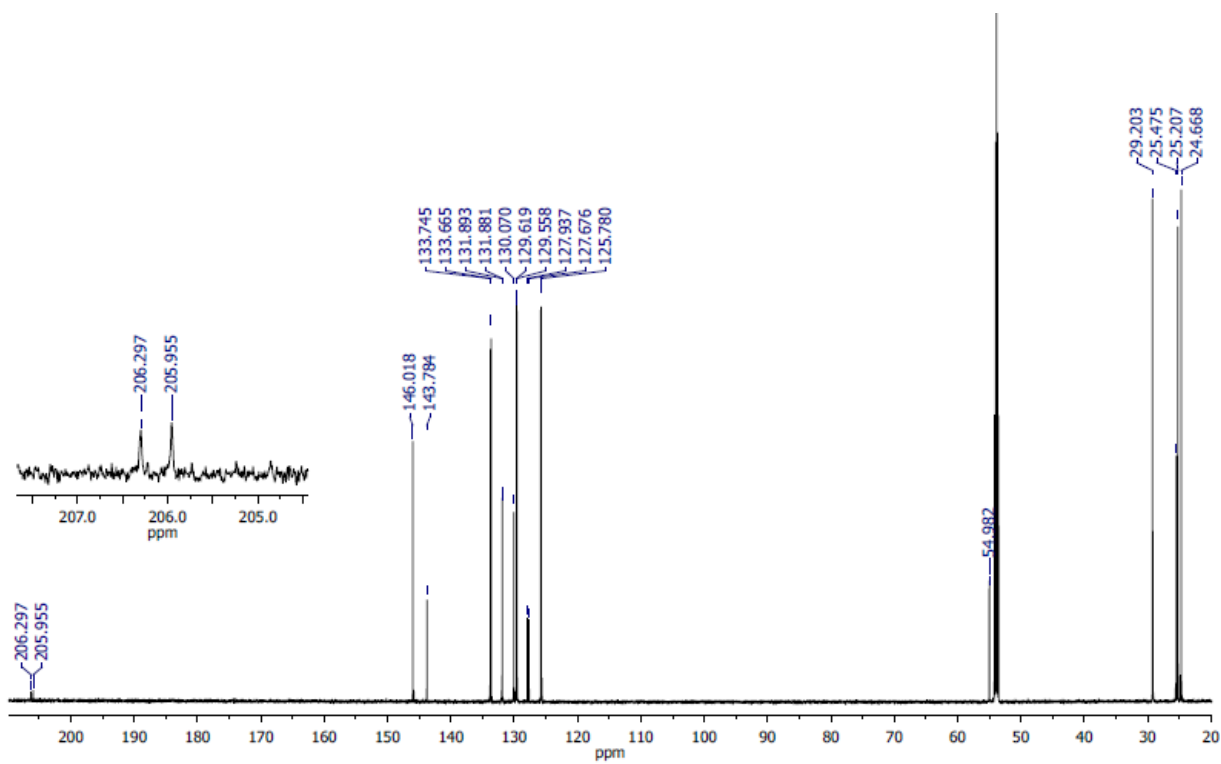
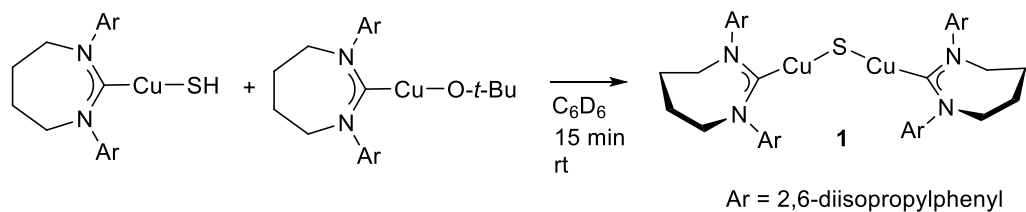


Figure S10. ^{13}C NMR spectrum of $7\text{DippCu}(\text{PPh}_3)\text{BF}_4$ in CD_2Cl_2 .

Deprotonation of **2** by **3**.



7DippCuSH (**2**, 0.013 g, 0.025 mmol) and 7DippCuO-*t*-Bu (**3**, 0.014 g, 0.025 mmol) were dissolved in C₆D₆ (0.75 mL) and mixed for 15 min before the ¹H NMR spectrum was recorded.

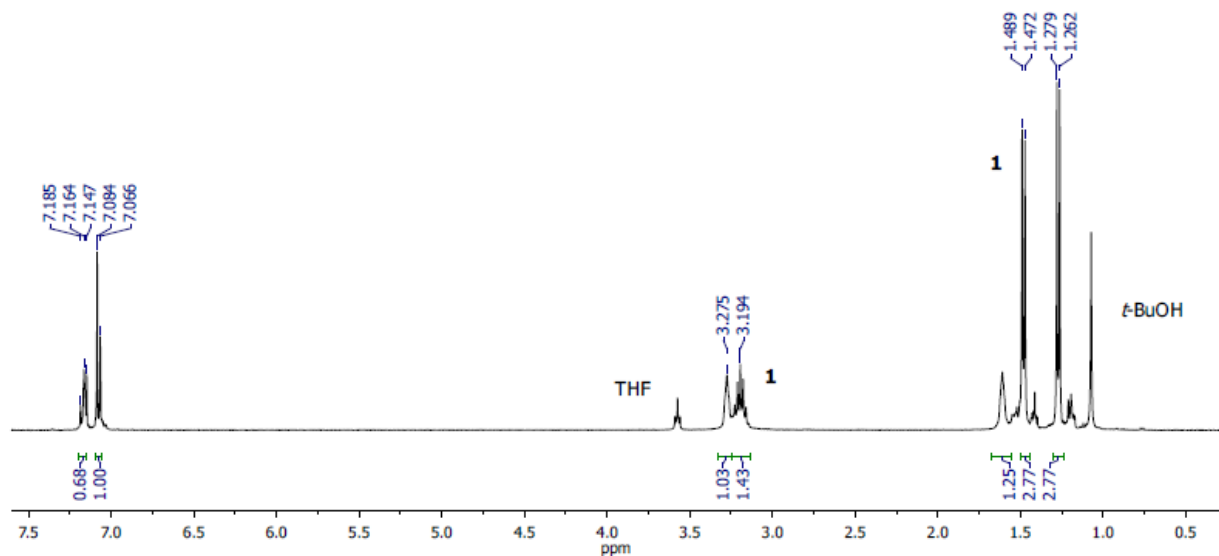
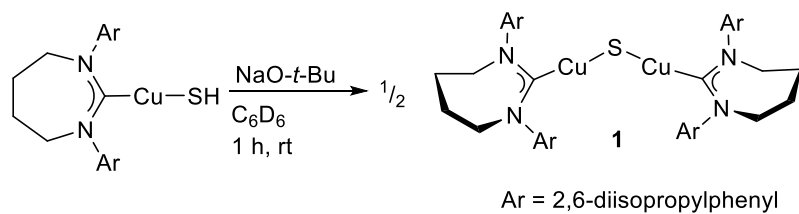


Figure S11. ¹H NMR spectrum of reaction of **2** and **3**.

Deprotonation of **2** by NaO-*t*-Bu.



7DippCuSH (**2**, 0.028 g, 0.054 mmol) and NaO-*t*-Bu (0.010 g, 0.010 mmol) were dissolved in C₆D₆ (0.75 mL) and mixed for 1 h before the ¹H NMR spectrum was recorded.

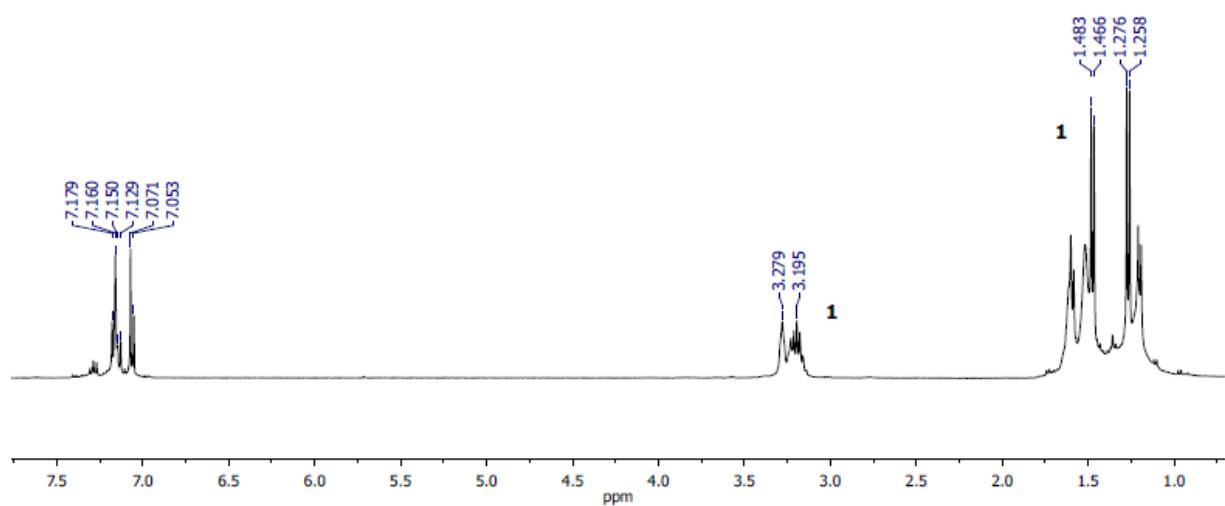
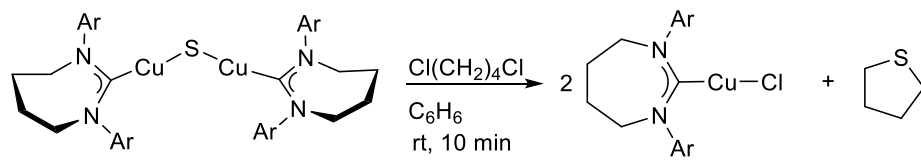


Figure S12. ¹H NMR spectrum of reaction of **2** and NaO-*t*-Bu.

Conversion of **1** to 7DippCuCl and tetrahydrothiophene for elemental analysis.

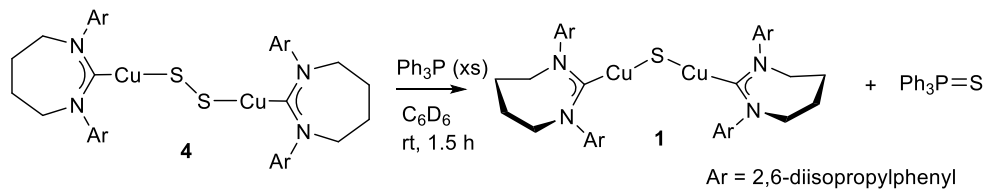


Ar = 2,6-diisopropylphenyl

1,4-Dichlorobutane (11 μ L, 0.10 mmol) was added to a solution of (7DippCu)₂S (0.020 g, 0.020 mmol) in C₆D₆ (2 mL) and mixed for 10 min. The solution was then concentrated *in vacuo* and a small amount was dissolved in CDCl₃ and the ¹H NMR spectrum was recorded. The solid was dried under vacuum for 48 h to remove the excess 1,4-dichlorobutane. Anal. Calcd for C₂₉H₄₂ClCuN₂: C, 67.29; H, 8.18; N, 5.41. Found C, 67.19; H, 8.17; N, 5.28.

Note: Hillhouse and coworkers had previously shown that the IPr*- (IPr* = 1,3-bis(2,6-(diphenylmethyl)-4-methylphenyl)imidazol-2-ylidene) supported dicopper sulfide reacts with dibromoalkanes to generate the corresponding (NHC)copper(I) bromide and cyclic thioether.²

Conversion of **4** to **1**



(7DippCuS)₂ (**4**, 0.010 g, 0.0097 mmol) was dissolved in C₆D₆ and a ¹H NMR spectrum was recorded. Triphenylphosphine (Ph₃P, 0.009 g, 0.03 mmol) was added and the ¹H and ³¹P NMR spectra were recorded after 1.5 h.

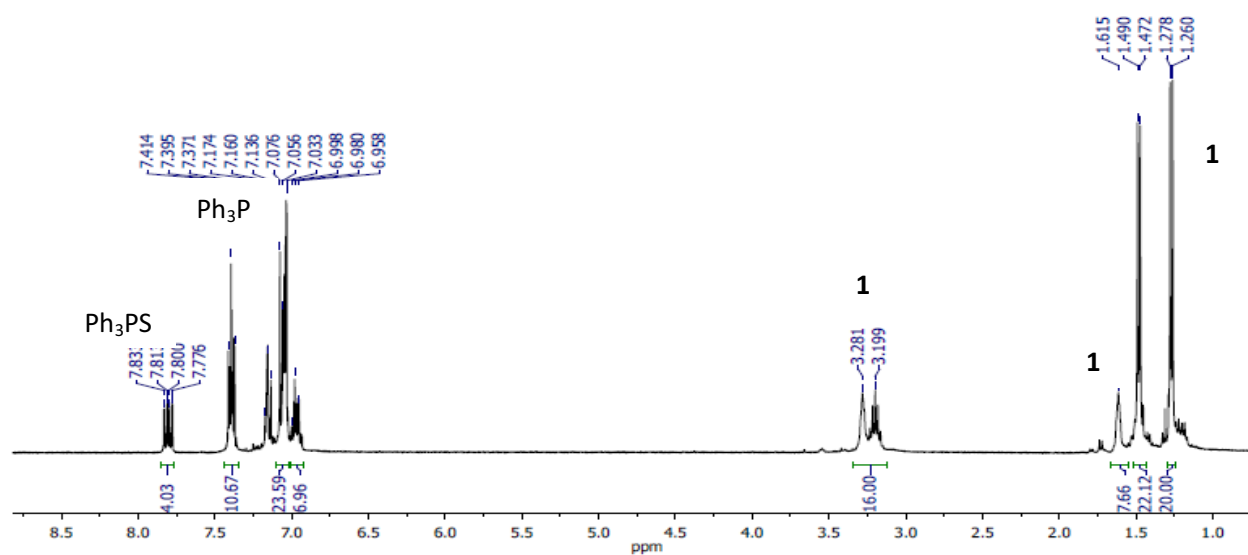


Figure S13. ¹H NMR spectrum after Ph₃P was added to **4**, generating **1** and Ph₃PS.

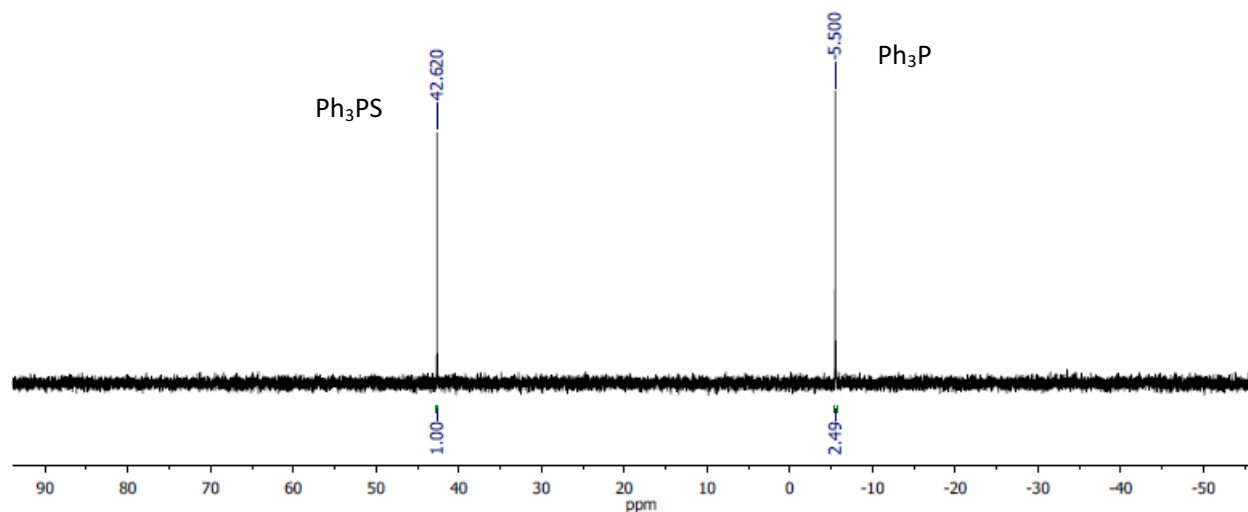
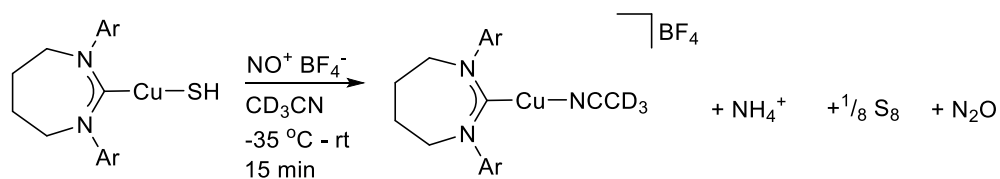


Figure S14. ³¹P NMR spectrum after Ph₃P was added to **4**.

Nitrosonium reactivity of **2**.



NO^+BF_4^- (0.007 g, 0.060 mmol) was added to a solution of 7DippCuSH (0.030 g, 0.060 mmol) in CD_3CN (1 mL) at -35°C . The mixture was allowed to warm to room temperature with stirring before the ^1H NMR spectrum was recorded.

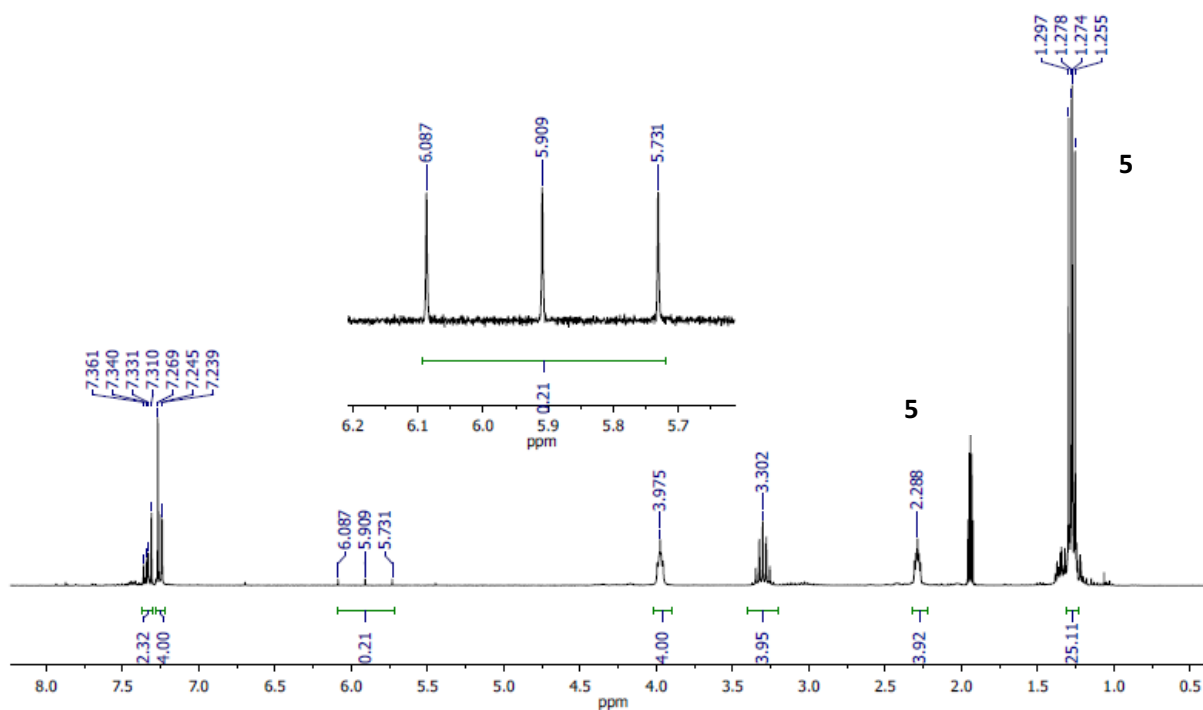


Figure S15. ^1H NMR spectrum following addition of NO^+BF_4^- to **2**, resulting in **5** in CD_3CN .

Nitrosonium reactivity of **2** (cont'd)

Triphenylphosphine (0.016 g, 0.060 mmol) was added and the ^1H and ^{31}P NMR spectra were recorded after 15 min.

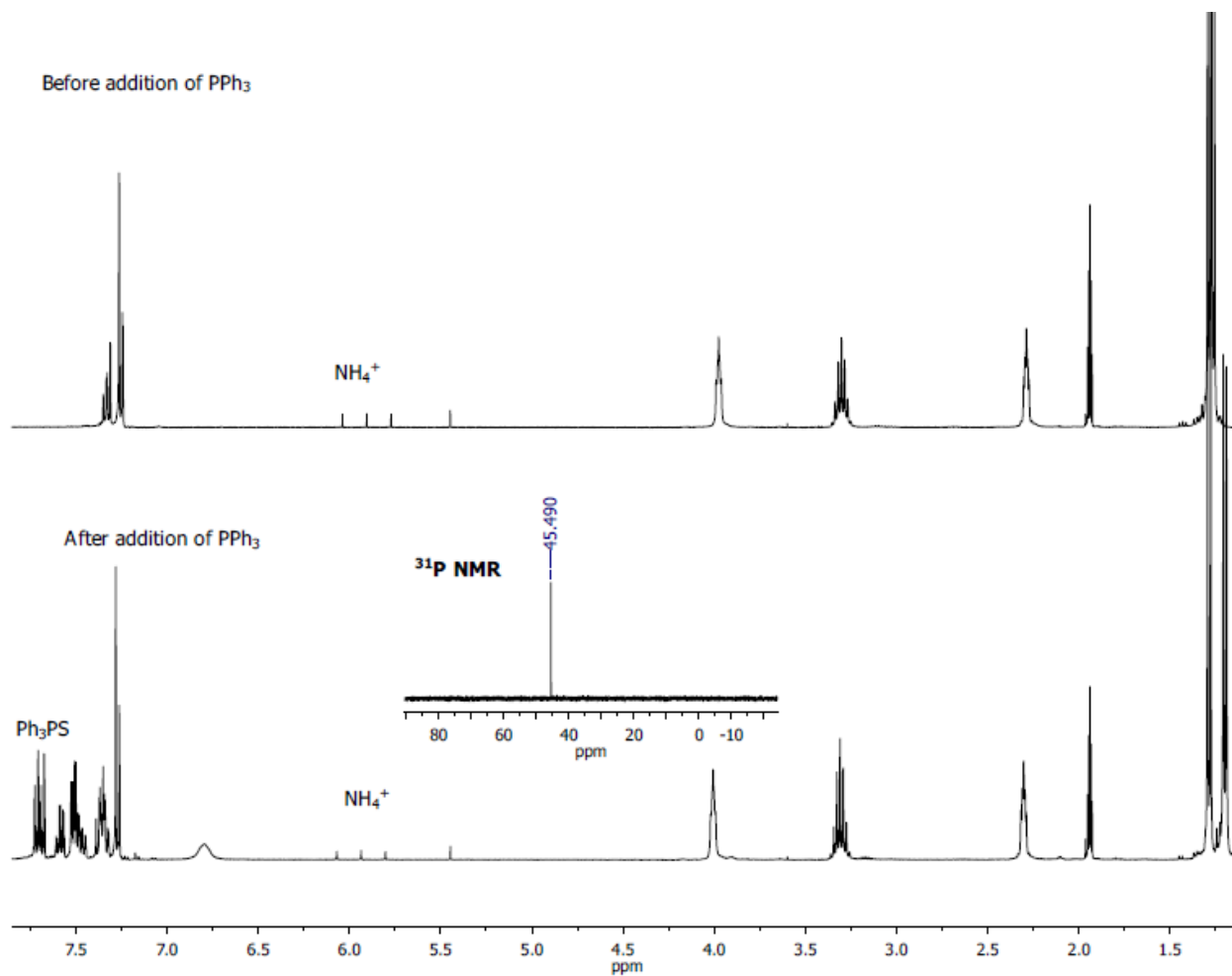


Figure S16. ^1H and ^{31}P spectrum following addition of Ph_3P in CD_3CN .

GC-MS detection of N₂O.

Selected ion recording (SIR) of m/z 44 (N₂O) was performed on a 50 μ L sample of the reaction headspace. As a control set up, to rule out CO₂ (m/z 44), SIR was also performed on a 50 μ L sample of the headspace of a vial prepared in the glovebox with just solvent added. The headspace analysis of a reaction of NO⁺ (0.007 g, 0.06 mmol) with 7DippCuSH (0.030 g, 0.060 mmol) showed an integration of the m/z 44 peak to be 15 times that of the headspace analysis of the control set up.

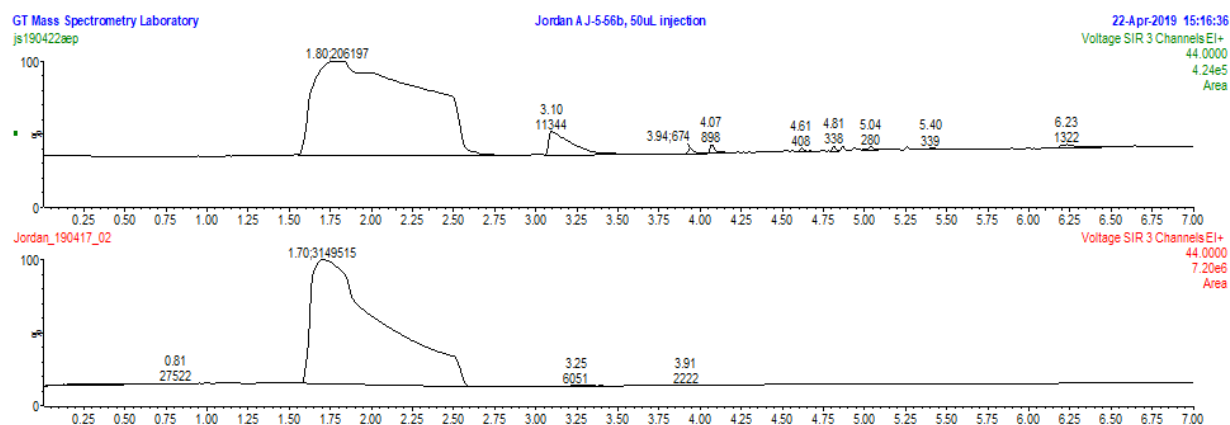
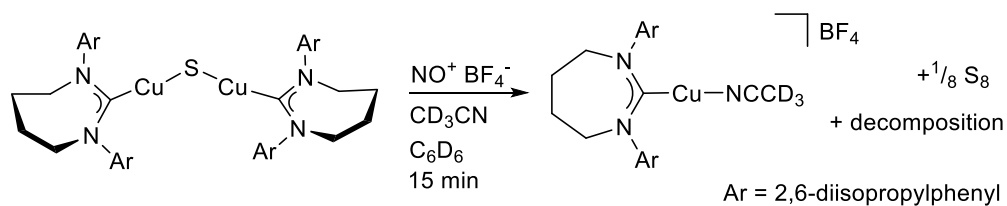


Figure S17. GC-MS SIR headspace analysis of the control set up (top) and the reaction of 7DippCuSH with NO⁺ (bottom).

Nitrosonium Reactivity of **1**



NO⁺BF₄⁻ (0.003 g, 0.026 mmol) was added to a solution of (7DippCu)₂S (0.025 g, 0.025 mmol) in CD₃CN (0.5 mL) and C₆D₆ (0.5 mL) at room temperature. The mixture was allowed to stir for 15 min, filtered through celite to remove deposited Cu⁰, and concentrated *in vacuo*. The resulting solid was dried for 2 h under vacuum. (0.015 g, 93% of **5** + S). The solid was taken up in CD₃CN (0.6 mL) before the ¹H NMR spectrum was recorded.

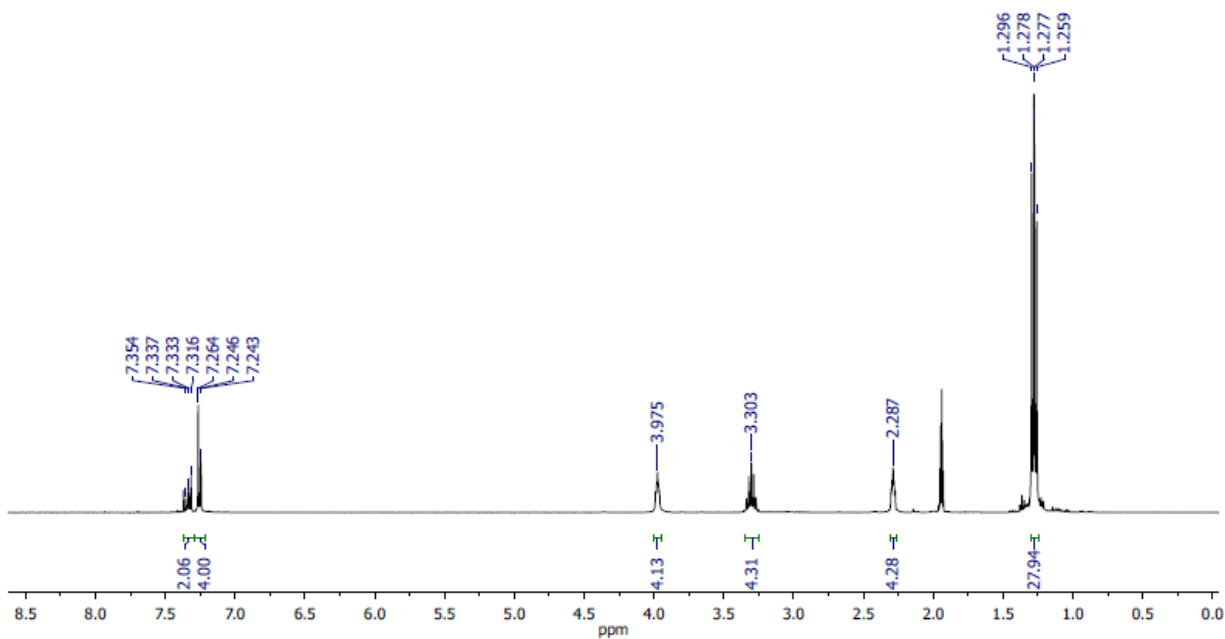


Figure S18. ¹H NMR spectrum of **1** in CD₃CN after reaction with NO⁺BF₄⁻.

Nitrosonium Reactivity of **1** (cont'd)

Triphenylphosphine (0.013 g, 0.050 mmol) was then added, and the solution was reanalyzed by NMR spectroscopy.

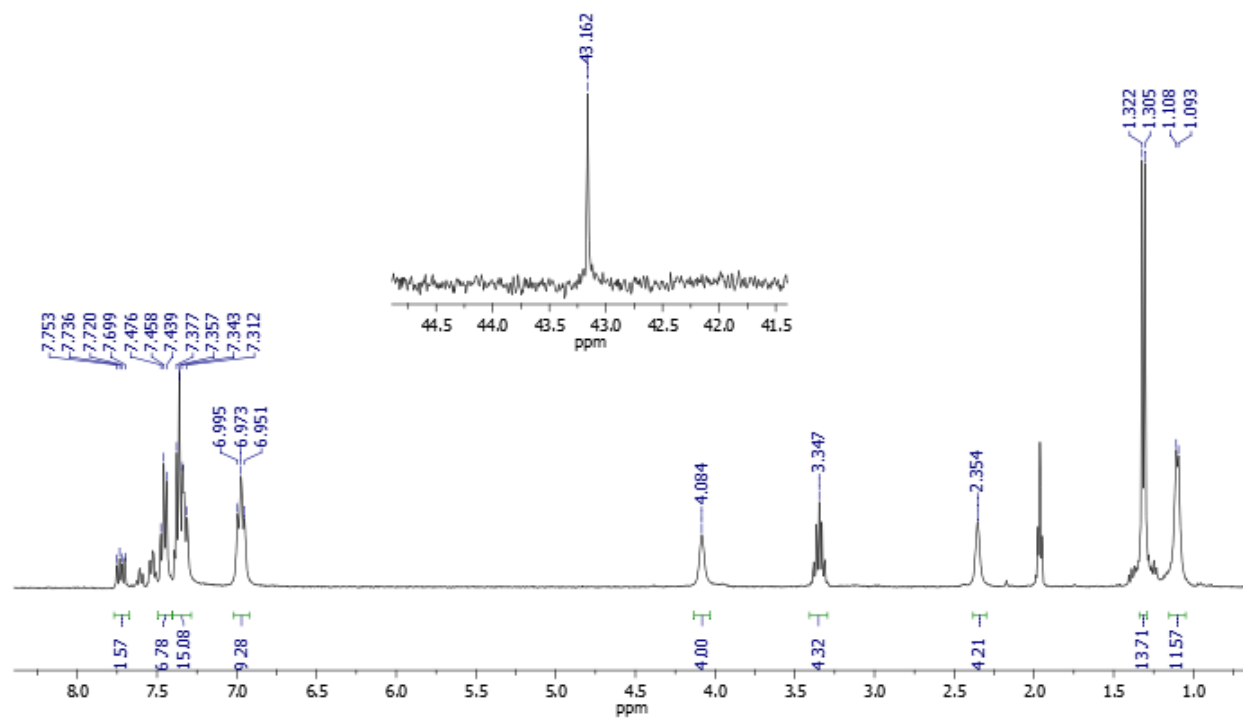
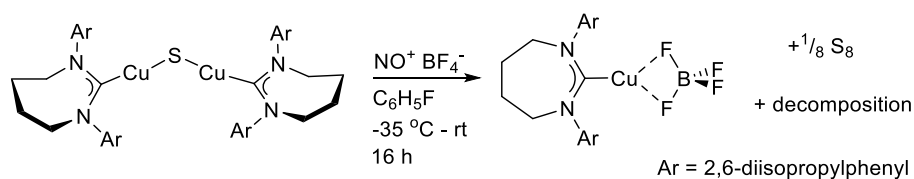


Figure S19. ^1H and ^{31}P NMR spectra following addition of Ph_3P , resulting in $\text{Ph}_3\text{P}=\text{S}$ in CD_3CN .

Nitrosonium Reactivity of **1** in C₆H₅F



A solution of (7DippCu)₂S (0.050 g, 0.050 mmol) in C₆H₅F (2 mL) was slowly added to solid NO⁺BF₄[−] (0.006 g, 0.052 mmol) at −40 °C. The mixture was allowed to stir at −40 °C for 4h before it was allowed to warm to room temperature while stirring for an additional 12h. The resulting mixture was filtered through Celite to remove the precipitate and concentrated *in vacuo*. The resulting colorless solid was taken up in CD₂Cl₂ and analyzed by NMR spectroscopy.

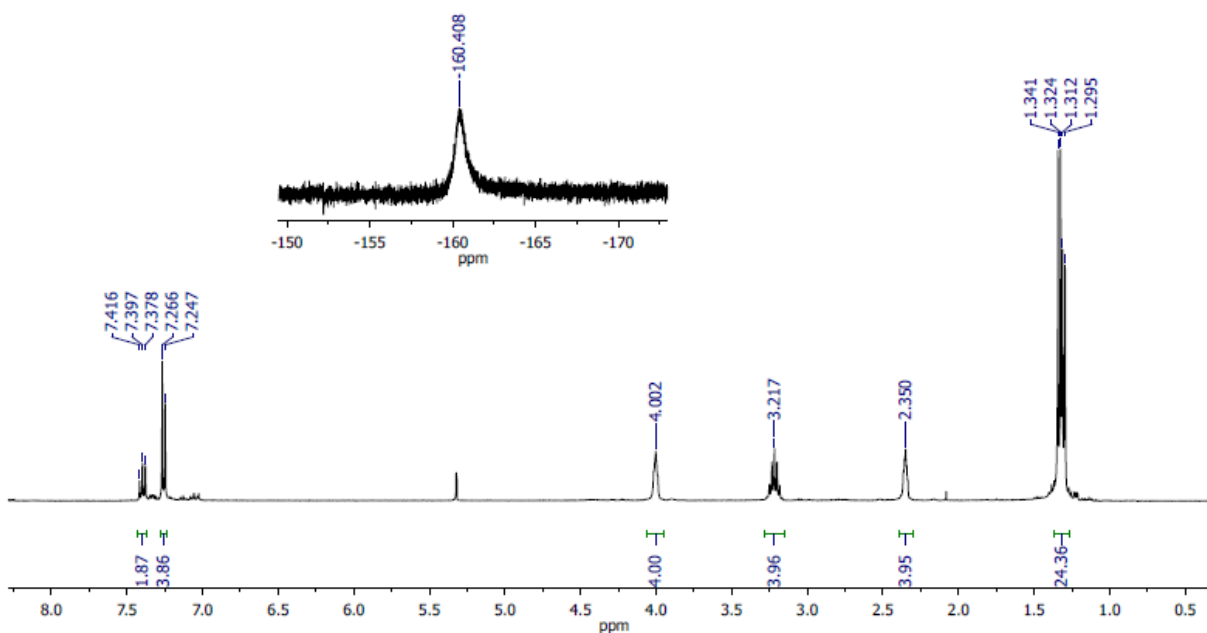
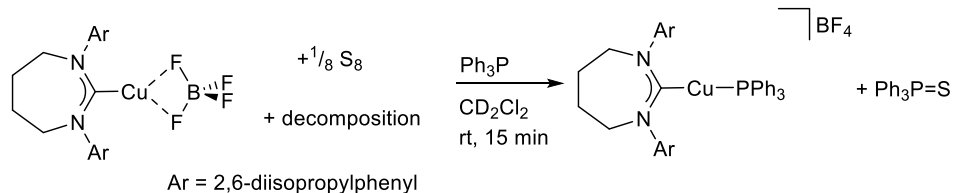


Figure S20. ¹H NMR spectrum of **1** after reaction with NO⁺BF₄[−] with ¹⁹F NMR spectra overlaid in CD₂Cl₂.

Nitrosonium Reactivity of **1** in C₆H₅F (cont'd)



Triphenylphosphine (0.026 g, 0.100 mmol) was then added, and the solution was reanalyzed by NMR spectroscopy.

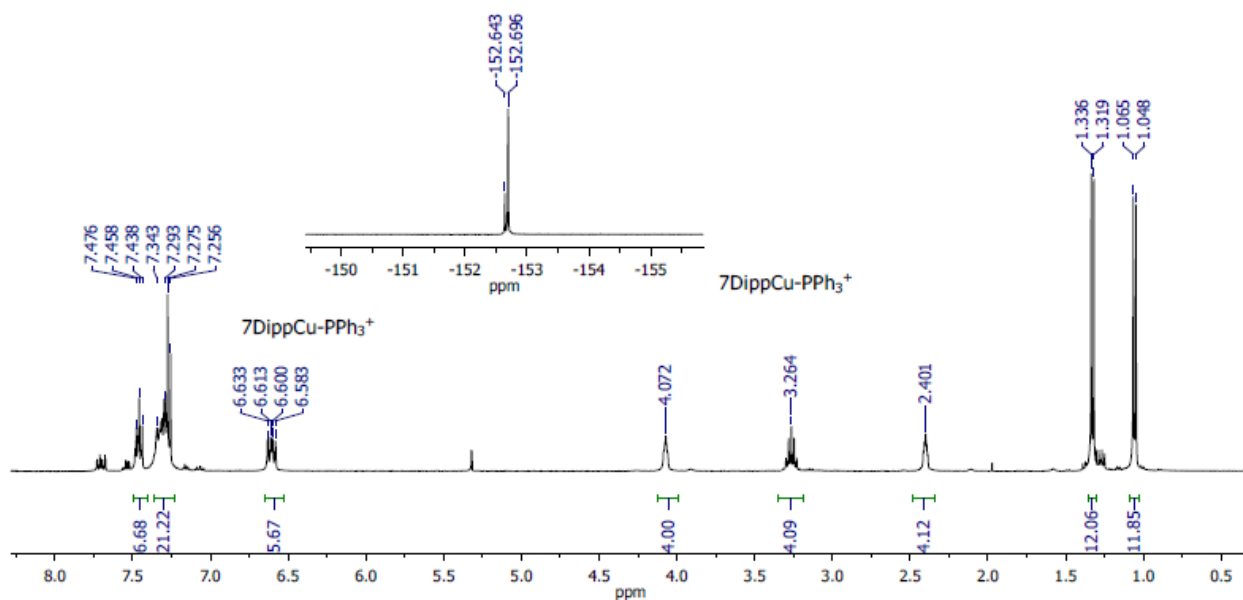


Figure S21. ¹H spectrum following addition of PPh₃ with the ¹⁹F NMR spectrum overlaid in CD₂Cl₂.

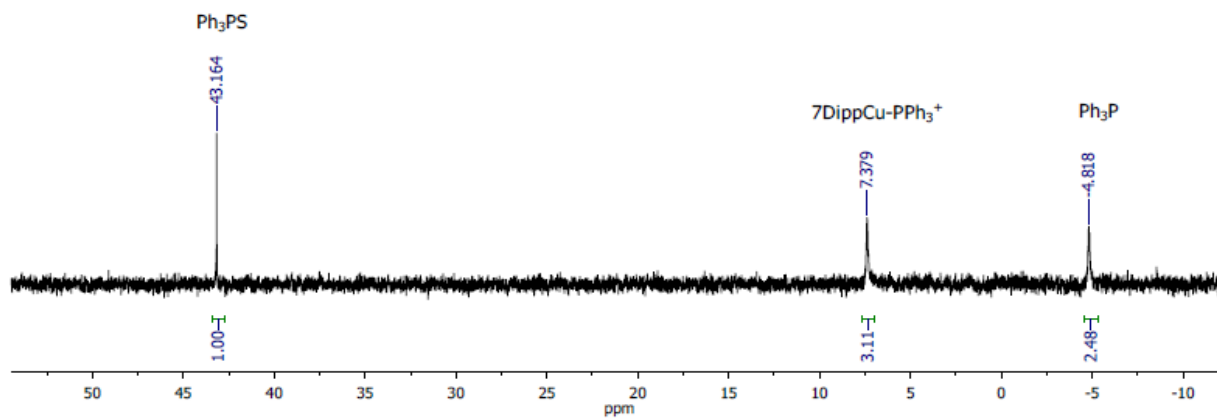
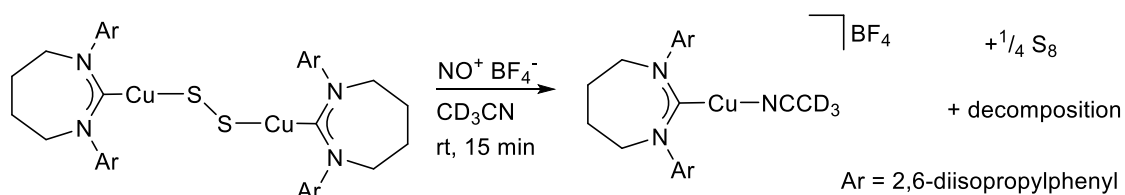


Figure S22. ³¹P spectrum following addition of PPh₃ in CD₂Cl₂.

Nitrosonium Reactivity of **4**



NO^+BF_4^- (0.004 g, 0.034 mmol) was added to a solution of $(7\text{DippCuS})_2$ (0.035 g, 0.034 mmol) in CD_3CN (1 mL) at room temperature. The mixture was allowed to stir for 15 min before the ^1H NMR spectrum was recorded.

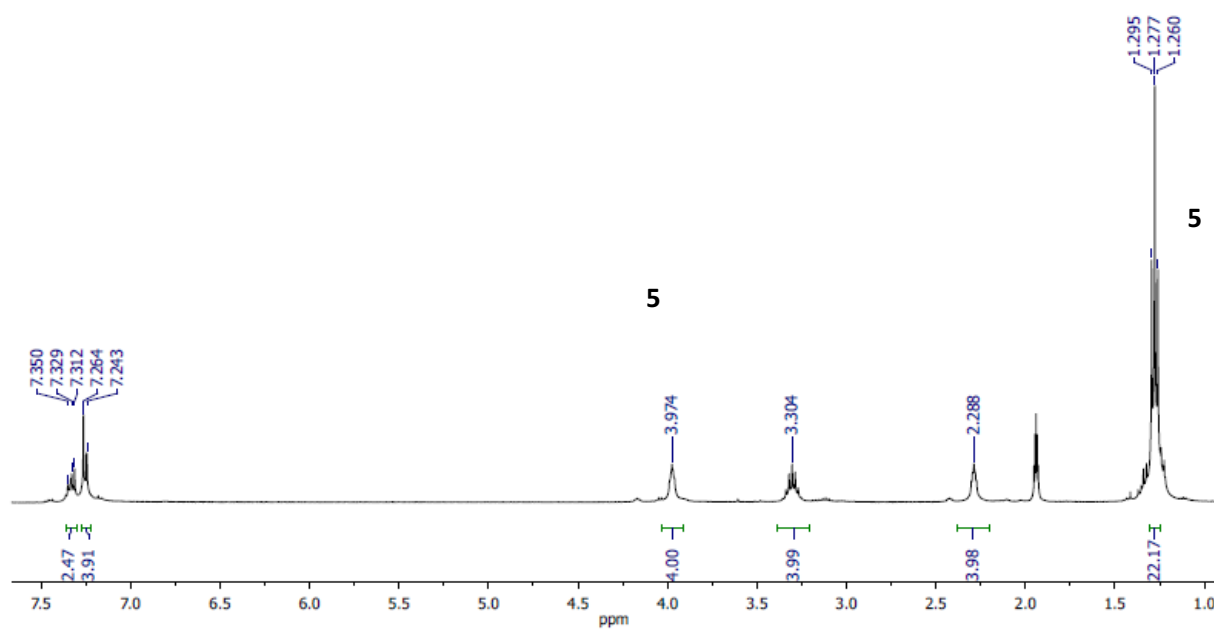


Figure S23. ^1H NMR spectrum following addition of NO^+BF_4^- to **4**, resulting in **5** in CD_3CN .

Nitrosonium Reactivity of **4** (cont'd)

Triphenylphosphine (0.026 g, 0.099 mmol) was added and the ^1H and ^{31}P NMR spectra were recorded after 15 min.

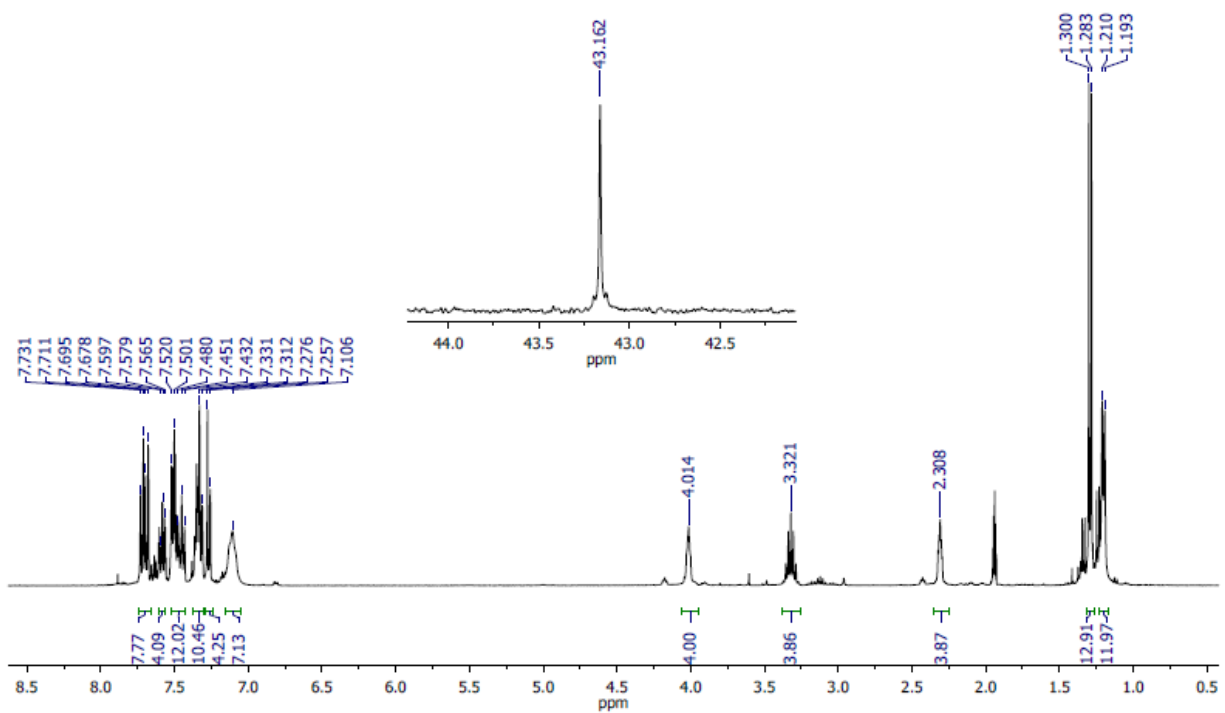
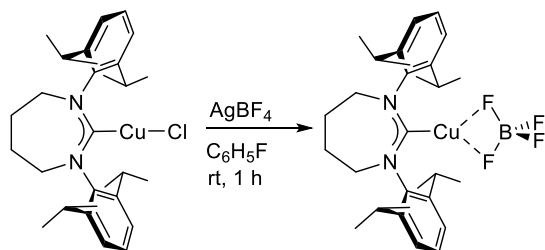


Figure S24. ^1H and ^{31}P NMR spectra following addition of Ph_3P , resulting in $\text{Ph}_3\text{P}=\text{S}$ in CD_3CN .

Generation of 7DippCuBF₄



7DippCuBF₄ 7DippCuCl (0.092 g, 0.18 mmol) and silver tetrafluoroborate (0.035 g, 0.18 mmol) were combined in a 20-mL vial, equipped with a stirbar, before C₆H₅F (5 mL) was added. The mixture was allowed to stir for 1h, filtered through Celite, and concentrated *in vacuo* to afford the product as a colorless solid (0.090 g, 89%). ¹H NMR (400 MHz, CD₂Cl₂): δ (ppm) 7.43 (t, ³J_{HH} = 7.6 Hz, 2H, *para*-CH), 7.25 (d, ³J_{HH} = 7.6 Hz, 4H, *meta*-CH), 4.00 (m, 4H, NCH₂), 3.21 (sept, ³J_{HH} = 6.8 Hz, 4H, CH(CH₃)₂), 2.35 (m, 4H, NCH₂CH₂), 1.33 (d, ³J_{HH} = 6.8 Hz, 12H, CH₂(CH₃)₂), 1.29 (d, ³J_{HH} = 6.8 Hz, 12H, CH₂(CH₃)₂). ¹³C {¹H} NMR (176 MHz CD₂Cl₂): δ (ppm) 145.4 (*ortho*-C), 144.3 (*ipso*-C), 129.6 (*para*-C), 125.4 (*meta*-C), 54.4 (NCH₂), 29.2 (CH(CH₃)₂), 25.5 (NCH₂CH₂), 24.8 (CH(CH₃)₂). ¹¹B NMR (128 MHz, CD₂Cl₂): δ (ppm) -1.8 (br s, 1B, BF₄⁻). ¹⁹F NMR (378 MHz, CD₂Cl₂): δ (ppm) -161.9 (br s, 4F, BF₄⁻).

Note: The carbene-*C* resonance could not be resolved despite prolonged acquisition time. We suggest the signal is broadened by coupling to the BF₄⁻. The complex is extremely air- and moisture-sensitive. A small amount of HOBf₃⁻ (1:1:1:1 quartet, under 5%)³ is typically observed in the ¹⁹F NMR spectrum (see below) but continues to grow in over time. In the solid-state, decomposition is observed within 24h at room temperature while under an inert atmosphere.

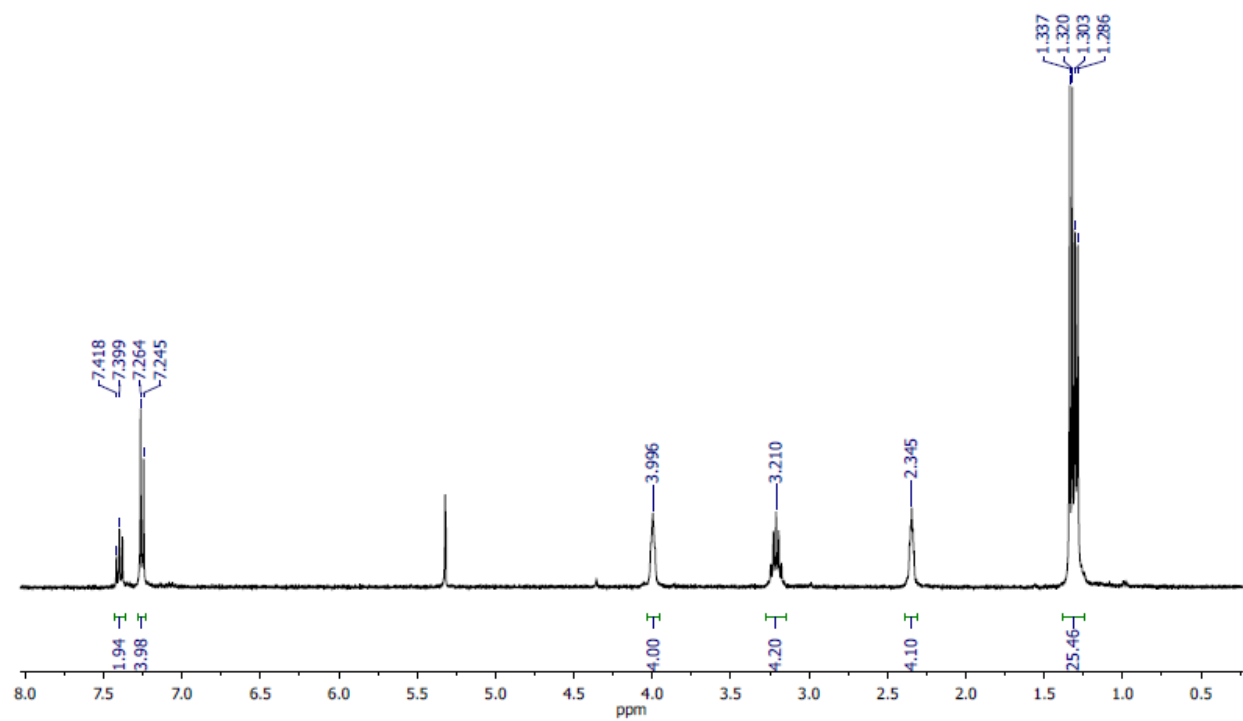


Figure S25. ¹H NMR spectrum of 7DippCuBF₄ in CD₂Cl₂.

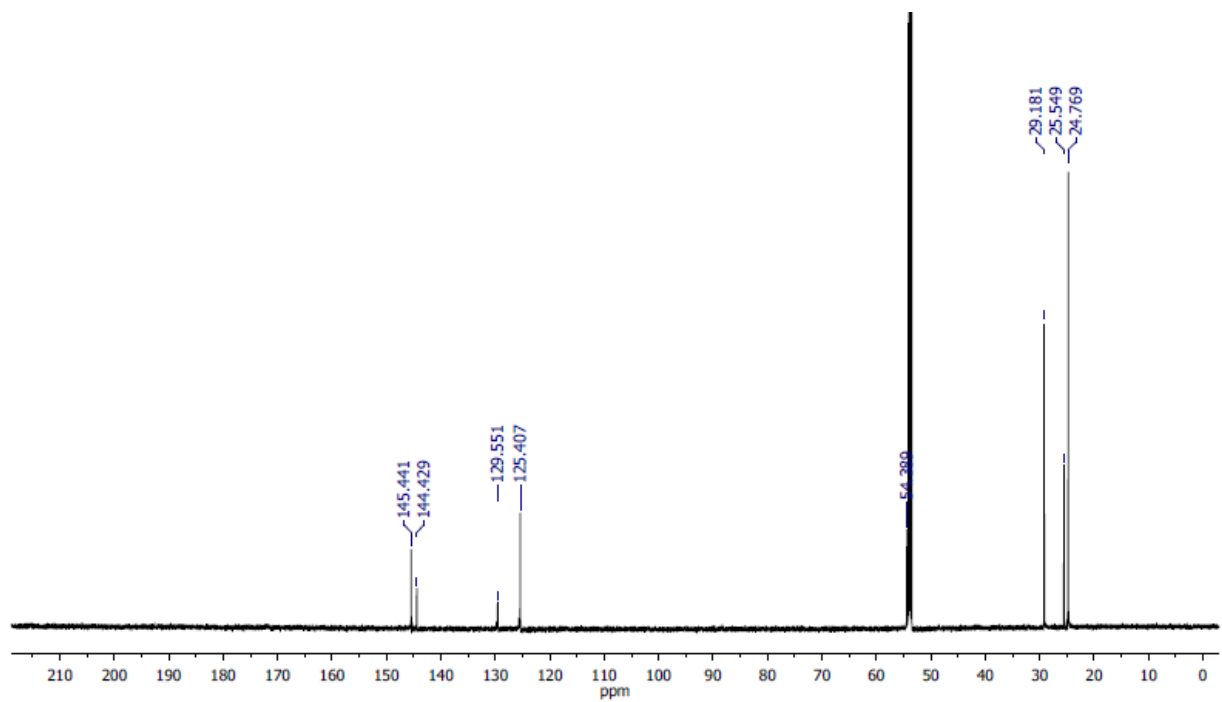


Figure S26. ¹³C NMR spectrum of 7DippCuBF₄ in CD₂Cl₂.

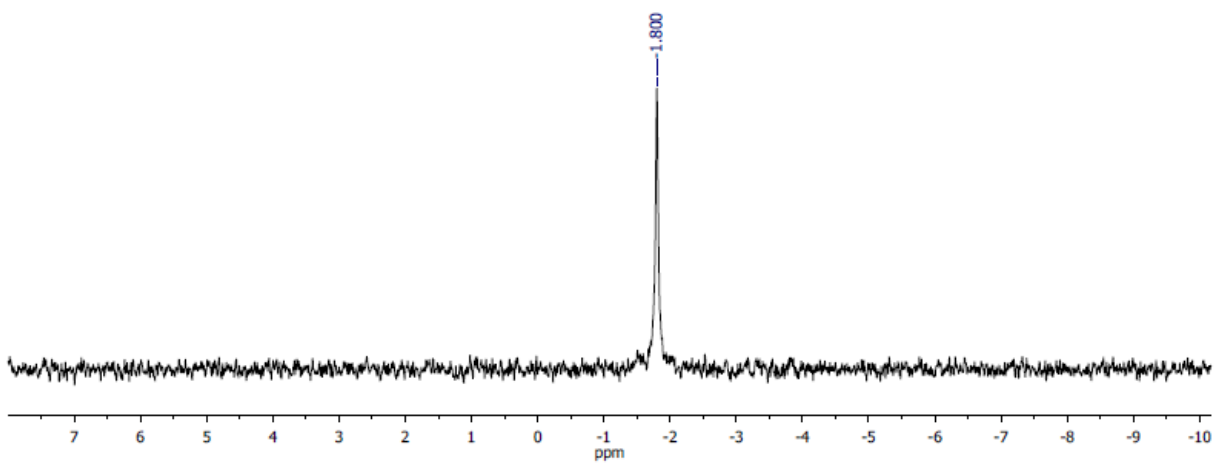


Figure S27. ^{11}B NMR spectrum of 7DippCuBF₄ in CD₂Cl₂.

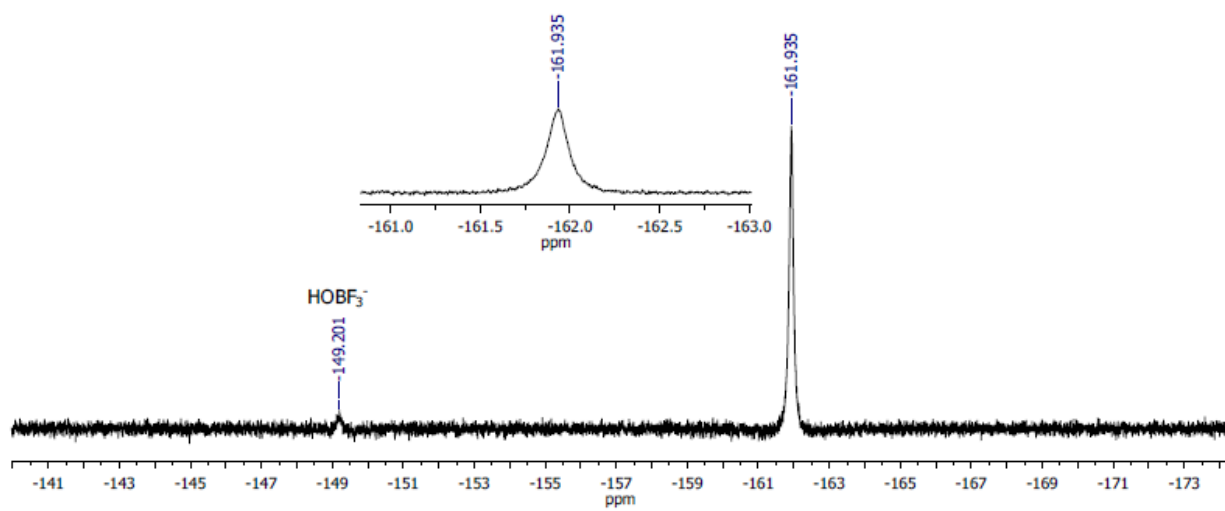
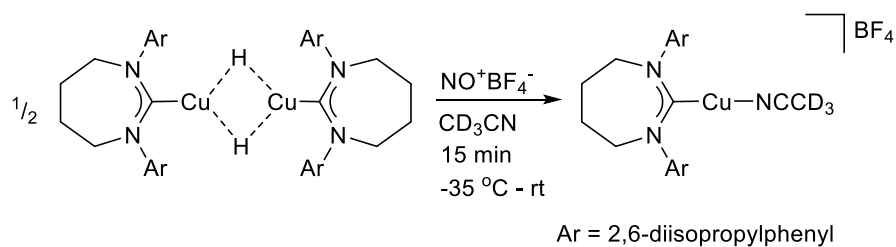


Figure S28. ^{19}F NMR spectrum of 7DippCuBF₄ in CD₂Cl₂.

Nitrosonium Reactivity of (7DippCuH)₂



(7DippCuH)₂ (0.015 g, 0.016 mmol) and NO⁺BF₄[−] (0.04 g, 0.034 mmol) were dissolved in CD₃CN (0.75 mL) at −35 °C and mixed for 15 min, then allowed to warm to room temperature, before the ¹H NMR spectrum was recorded.

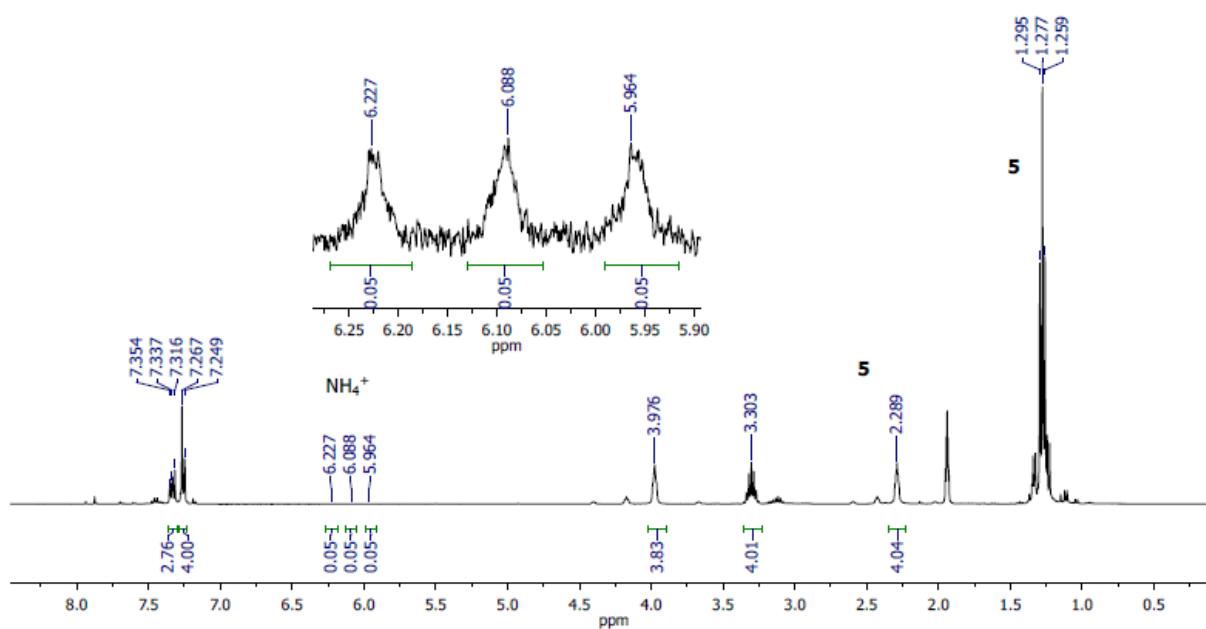
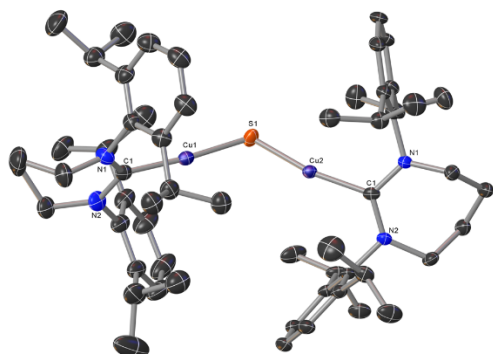


Figure S29. ¹H NMR spectrum following addition of NO⁺BF₄[−] to (7DippCuH)₂.

X-ray Diffraction Studies.

Compound **1**



Experimental Single crystals of $C_{188}H_{273}Cu_6N_{19}S_3$ **1** were obtained from acetonitrile. A suitable crystal was selected, and the crystal was mounted on a loop with paratone oil on a Bruker D8 Venture diffractometer. The crystal was kept at 100(2) K during data collection. Using Olex2,⁴ the structure was solved with the ShelXT⁵ structure solution program using Intrinsic Phasing and refined with the ShelXL⁶ refinement package using Least Squares minimization.

Crystal Data for $C_{188}H_{273}Cu_6N_{19}S_3$ ($M = 3276.75$ g/mol): monoclinic, space group P2/n (no. 13), $a = 24.8277(13)$ Å, $b = 12.3758(7)$ Å, $c = 62.737(3)$ Å, $\beta = 97.108(3)^\circ$, $V = 19128.6(17)$ Å³, $Z = 4$, $T = 100(2)$ K, $\mu(\text{CuK}\alpha) = 1.424$ mm⁻¹, $D_{\text{calc}} = 1.138$ g/cm³, 142144 reflections measured ($5.218^\circ \leq 2\theta \leq 130.166^\circ$), 32605 unique ($R_{\text{int}} = 0.0744$, $R_{\text{sigma}} = 0.0549$) which were used in all calculations. The final R_1 was 0.0655 ($I > 2\sigma(I)$) and wR_2 was 0.1751 (all data).

Table S1 Crystal data and structure refinement for 1.

Identification code	Cu2S_L
Empirical formula	C ₁₈₈ H ₂₇₃ Cu ₆ N ₁₉ S ₃
Formula weight	3276.75
Temperature/K	100(2)
Crystal system	monoclinic
Space group	P2/n
a/Å	24.8277(13)
b/Å	12.3758(7)
c/Å	62.737(3)
α/°	90
β/°	97.108(3)
γ/°	90
Volume/Å ³	19128.6(17)
Z	4
ρ _{calc} /cm ³	1.138
μ/mm ⁻¹	1.424
F(000)	7023.0
Crystal size/mm ³	0.257 × 0.228 × 0.146
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.218 to 130.166
Index ranges	-26 ≤ h ≤ 29, -14 ≤ k ≤ 14, -73 ≤ l ≤ 73
Reflections collected	142144
Independent reflections	32605 [R _{int} = 0.0744, R _{sigma} = 0.0549]
Data/restraints/parameters	32605/2766/2000
Goodness-of-fit on F ²	1.027
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0655, wR ₂ = 0.1647
Final R indexes [all data]	R ₁ = 0.0828, wR ₂ = 0.1751
Largest diff. peak/hole / e Å ⁻³	2.72/-1.27

Table S2 Bond Lengths (Å) for 1

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cu1	Cu2	3.5816(7)	C27_10	C29_10	1.530(3)
Cu1	S1	2.1115(11)	N1_11	C1_11	1.345(2)
Cu1	C1_8	1.912(3)	N1_11	C2_11	1.479(2)
Cu2	S1	2.1236(10)	N1_11	C6_11	1.453(2)
Cu2	C1_9	1.916(2)	N2_11	C1_11	1.347(2)
Cu3	Cu4	3.4751(7)	N2_11	C5_11	1.484(2)
Cu3	S2	2.1171(10)	N2_11	C18_11	1.451(2)
Cu3	C1_10	1.909(2)	C2_11	C3_11	1.513(3)
Cu4	S2	2.1081(11)	C3_11	C4_11	1.531(3)

Cu4	C1_11	1.892(3)	C4_11	C5_11	1.520(3)
Cu5	Cu5 ¹	3.5959(10)	C6_11	C7_11	1.398(3)
Cu5	S3	2.1128(10)	C6_11	C11_11	1.404(2)
Cu5	C1_13	1.900(2)	C7_11	C8_11	1.393(3)
Cu6	Cu6 ²	3.6774(11)	C7_11	C12_11	1.522(3)
Cu6	S4	2.1159(10)	C8_11	C9_11	1.394(3)
Cu6	C1_12	1.904(2)	C9_11	C10_11	1.374(3)
N1_8	C1_8	1.344(2)	C10_11	C11_11	1.393(3)
N1_8	C2_8	1.479(2)	C11_11	C15_11	1.519(3)
N1_8	C6_8	1.454(2)	C12_11	C13_11	1.532(3)
N2_8	C1_8	1.350(2)	C12_11	C14_11	1.530(3)
N2_8	C5_8	1.485(2)	C15_11	C16_11	1.526(3)
N2_8	C18_8	1.451(2)	C15_11	C17_11	1.542(3)
C2_8	C3_8	1.512(3)	C18_11	C19_11	1.398(2)
C3_8	C4_8	1.531(3)	C18_11	C23_11	1.401(2)
C4_8	C5_8	1.519(3)	C19_11	C20_11	1.401(3)
C6_8	C7_8	1.398(3)	C19_11	C24_11	1.516(2)
C6_8	C11_8	1.404(2)	C20_11	C21_11	1.384(3)
C7_8	C8_8	1.394(3)	C21_11	C22_11	1.385(3)
C7_8	C12_8	1.521(3)	C22_11	C23_11	1.395(3)
C8_8	C9_8	1.393(3)	C23_11	C27_11	1.527(3)
C9_8	C10_8	1.374(3)	C24_11	C25_11	1.528(3)
C10_8	C11_8	1.393(3)	C24_11	C26_11	1.534(3)
C11_8	C15_8	1.519(3)	C27_11	C28_11	1.527(3)
C12_8	C13_8	1.532(3)	C27_11	C29_11	1.528(3)
C12_8	C14_8	1.530(3)	N1_12	C1_12	1.344(2)
C15_8	C16_8	1.527(3)	N1_12	C2_12	1.476(2)
C15_8	C17_8	1.541(3)	N1_12	C6_12	1.456(2)
C18_8	C19_8	1.398(3)	N2_12	C1_12	1.348(2)
C18_8	C23_8	1.400(2)	N2_12	C5_12	1.486(2)
C19_8	C20_8	1.401(3)	N2_12	C18_12	1.448(2)
C19_8	C24_8	1.518(2)	C2_12	C3_12	1.511(3)
C20_8	C21_8	1.383(3)	C3_12	C4_12	1.532(3)
C21_8	C22_8	1.385(3)	C4_12	C5_12	1.520(3)
C22_8	C23_8	1.395(3)	C6_12	C7_12	1.397(3)
C23_8	C27_8	1.527(3)	C6_12	C11_12	1.403(2)
C24_8	C25_8	1.529(3)	C7_12	C8_12	1.393(3)
C24_8	C26_8	1.534(3)	C7_12	C12_12	1.520(3)
C27_8	C28_8	1.530(3)	C8_12	C9_12	1.393(3)
C27_8	C29_8	1.531(3)	C9_12	C10_12	1.373(3)
N1_9	C1_9	1.346(2)	C10_12	C11_12	1.393(3)
N1_9	C2_9	1.481(2)	C11_12	C15_12	1.518(3)
N1_9	C6_9	1.454(2)	C12_12	C13_12	1.531(3)
N2_9	C1_9	1.349(2)	C12_12	C14_12	1.529(3)
N2_9	C5_9	1.484(2)	C15_12	C16_12	1.527(3)
N2_9	C18_9	1.452(2)	C15_12	C17_12	1.543(3)
C2_9	C3_9	1.514(3)	C18_12	C19_12	1.400(3)
C3_9	C4_9	1.532(3)	C18_12	C23_12	1.400(2)
C4_9	C5_9	1.518(3)	C19_12	C20_12	1.401(3)

C6_9	C7_9	1.399(3)	C19_12 C24_12	1.517(3)
C6_9	C11_9	1.403(2)	C20_12 C21_12	1.383(3)
C7_9	C8_9	1.393(2)	C21_12 C22_12	1.385(3)
C7_9	C12_9	1.521(3)	C22_12 C23_12	1.396(3)
C8_9	C9_9	1.393(3)	C23_12 C27_12	1.527(3)
C9_9	C10_9	1.374(3)	C24_12 C25_12	1.529(3)
C10_9	C11_9	1.393(3)	C24_12 C26_12	1.534(3)
C11_9	C15_9	1.519(3)	C27_12 C28_12	1.529(3)
C12_9	C13_9	1.531(3)	C27_12 C29_12	1.532(3)
C12_9	C14_9	1.530(3)	N1_13 C1_13	1.344(2)
C15_9	C16_9	1.527(3)	N1_13 C2_13	1.479(2)
C15_9	C17_9	1.543(3)	N1_13 C6_13	1.453(2)
C18_9	C19_9	1.398(2)	N2_13 C1_13	1.349(2)
C18_9	C23_9	1.401(2)	N2_13 C5_13	1.484(2)
C19_9	C20_9	1.402(3)	N2_13 C18_13	1.450(2)
C19_9	C24_9	1.517(2)	C2_13 C3_13	1.512(3)
C20_9	C21_9	1.383(3)	C3_13 C4_13	1.531(3)
C21_9	C22_9	1.385(3)	C4_13 C5_13	1.518(3)
C22_9	C23_9	1.394(3)	C6_13 C7_13	1.399(3)
C23_9	C27_9	1.525(3)	C6_13 C11_13	1.404(2)
C24_9	C25_9	1.530(3)	C7_13 C8_13	1.394(3)
C24_9	C26_9	1.535(3)	C7_13 C12_13	1.520(3)
C27_9	C28_9	1.528(3)	C8_13 C9_13	1.393(3)
C27_9	C29_9	1.530(3)	C9_13 C10_13	1.374(3)
N1_10	C1_10	1.346(2)	C10_13 C11_13	1.393(3)
N1_10	C2_10	1.481(2)	C11_13 C15_13	1.520(3)
N1_10	C6_10	1.453(2)	C12_13 C13_13	1.533(3)
N2_10	C1_10	1.349(2)	C12_13 C14_13	1.531(3)
N2_10	C5_10	1.485(2)	C15_13 C16_13	1.527(3)
N2_10	C18_10	1.451(2)	C15_13 C17_13	1.543(3)
C2_10	C3_10	1.512(3)	C18_13 C19_13	1.397(3)
C3_10	C4_10	1.533(3)	C18_13 C23_13	1.401(2)
C4_10	C5_10	1.519(3)	C19_13 C20_13	1.402(3)
C6_10	C7_10	1.398(3)	C19_13 C24_13	1.517(3)
C6_10	C11_10	1.403(2)	C20_13 C21_13	1.383(3)
C7_10	C8_10	1.393(3)	C21_13 C22_13	1.385(3)
C7_10	C12_10	1.521(3)	C22_13 C23_13	1.395(3)
C8_10	C9_10	1.394(3)	C23_13 C27_13	1.526(3)
C9_10	C10_10	1.374(3)	C24_13 C25_13	1.529(3)
C10_10	C11_10	1.393(3)	C24_13 C26_13	1.536(3)
C11_10	C15_10	1.519(3)	C27_13 C28_13	1.529(3)
C12_10	C13_10	1.532(3)	C27_13 C29_13	1.530(3)
C12_10	C14_10	1.529(3)	N1S_2 C2S_2	1.128(3)
C15_10	C16_10	1.527(3)	C2S_2 C3S_2	1.440(3)
C15_10	C17_10	1.542(3)	N1S_3 C2S_3	1.128(3)
C18_10	C19_10	1.398(2)	C2S_3 C3S_3	1.441(3)
C18_10	C23_10	1.399(2)	N1S_4 C2S_4	1.128(3)
C19_10	C20_10	1.401(3)	C2S_4 C3S_4	1.440(3)
C19_10	C24_10	1.517(2)	N1S_5 C2S_5	1.128(3)

C20_10 C21_10	1.383(3)	C2S_5 C3S_5	1.440(3)
C21_10 C22_10	1.385(3)	N1S_6 C2S_6	1.129(3)
C22_10 C23_10	1.396(3)	C2S_6 C3S_6	1.439(3)
C23_10 C27_10	1.526(3)	N1S_7 C2S_7	1.128(3)
C24_10 C25_10	1.529(3)	C2S_7 C3S_7	1.441(3)
C24_10 C26_10	1.536(3)	N1S_1 C2S_1	1.129(3)
C27_10 C28_10	1.528(3)	C2S_1 C3S_1	1.441(3)

Table S3 Bond Angles (deg) for **1**

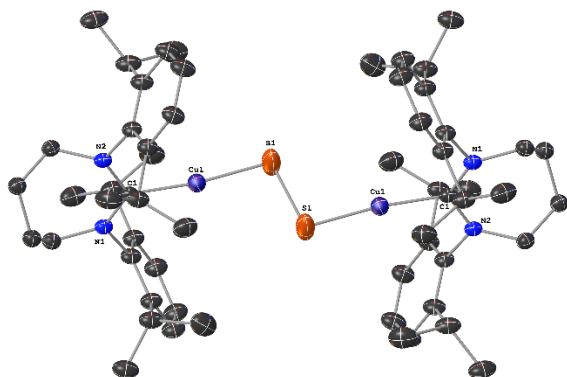
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
S1	Cu1	Cu2	32.36(3)	C22_10	C23_10	C27_10	119.62(19)
C1_8	Cu1	Cu2	154.64(10)	C19_10	C24_10	C25_10	111.8(2)
C1_8	Cu1	S1	172.83(10)	C19_10	C24_10	C26_10	110.98(19)
S1	Cu2	Cu1	32.15(3)	C25_10	C24_10	C26_10	109.8(2)
C1_9	Cu2	Cu1	163.25(8)	C23_10	C27_10	C28_10	110.7(2)
C1_9	Cu2	S1	164.29(9)	C23_10	C27_10	C29_10	111.8(2)
S2	Cu3	Cu4	34.58(3)	C28_10	C27_10	C29_10	110.9(2)
C1_10	Cu3	Cu4	161.23(8)	C1_11	N1_11	C2_11	125.3(2)
C1_10	Cu3	S2	163.95(9)	C1_11	N1_11	C6_11	117.61(19)
S2	Cu4	Cu3	34.75(3)	C6_11	N1_11	C2_11	115.60(19)
C1_11	Cu4	Cu3	156.32(9)	C1_11	N2_11	C5_11	129.56(19)
C1_11	Cu4	S2	168.61(10)	C1_11	N2_11	C18_11	117.00(19)
S3	Cu5	Cu5 ¹	31.68(4)	C18_11	N2_11	C5_11	113.40(18)
C1_13	Cu5	Cu5 ¹	160.01(9)	N1_11	C1_11	Cu4	119.86(16)
C1_13	Cu5	S3	168.27(10)	N1_11	C1_11	N2_11	118.3(2)
S4	Cu6	Cu6 ²	29.66(4)	N2_11	C1_11	Cu4	121.62(17)
C1_12	Cu6	Cu6 ²	161.01(9)	N1_11	C2_11	C3_11	113.5(2)
C1_12	Cu6	S4	168.98(11)	C2_11	C3_11	C4_11	111.4(2)
Cu1	S1	Cu2	115.49(4)	C5_11	C4_11	C3_11	112.1(2)
Cu4	S2	Cu3	110.67(4)	N2_11	C5_11	C4_11	113.7(2)
Cu5 ¹	S3	Cu5	116.63(8)	C7_11	C6_11	N1_11	118.69(18)
Cu6	S4	Cu6 ²	120.68(8)	C7_11	C6_11	C11_11	122.30(18)
C1_8	N1_8	C2_8	125.7(2)	C11_11	C6_11	N1_11	118.99(19)
C1_8	N1_8	C6_8	118.22(19)	C6_11	C7_11	C12_11	122.82(19)
C6_8	N1_8	C2_8	115.26(19)	C8_11	C7_11	C6_11	117.73(19)
C1_8	N2_8	C5_8	129.18(19)	C8_11	C7_11	C12_11	119.4(2)
C1_8	N2_8	C18_8	116.62(19)	C7_11	C8_11	C9_11	120.8(2)
C18_8	N2_8	C5_8	113.46(19)	C10_11	C9_11	C8_11	120.2(2)
N1_8	C1_8	Cu1	122.19(16)	C9_11	C10_11	C11_11	121.2(2)
N1_8	C1_8	N2_8	117.8(2)	C6_11	C11_11	C15_11	122.2(2)
N2_8	C1_8	Cu1	120.01(16)	C10_11	C11_11	C6_11	117.7(2)
N1_8	C2_8	C3_8	114.1(2)	C10_11	C11_11	C15_11	120.0(2)
C2_8	C3_8	C4_8	111.2(2)	C7_11	C12_11	C13_11	112.0(2)
C5_8	C4_8	C3_8	112.2(2)	C7_11	C12_11	C14_11	110.3(2)
N2_8	C5_8	C4_8	114.6(2)	C14_11	C12_11	C13_11	110.5(2)
C7_8	C6_8	N1_8	118.47(18)	C11_11	C15_11	C16_11	111.8(2)
C7_8	C6_8	C11_8	122.28(18)	C11_11	C15_11	C17_11	110.9(2)
C11_8	C6_8	N1_8	119.22(19)	C16_11	C15_11	C17_11	110.9(2)

C6_8	C7_8	C12_8	122.29(19)	C19_11	C18_11	N2_11	119.24(18)
C8_8	C7_8	C6_8	118.07(19)	C19_11	C18_11	C23_11	122.92(18)
C8_8	C7_8	C12_8	119.6(2)	C23_11	C18_11	N2_11	117.77(19)
C9_8	C8_8	C7_8	120.4(2)	C18_11	C19_11	C20_11	117.20(19)
C10_8	C9_8	C8_8	120.3(2)	C18_11	C19_11	C24_11	122.94(19)
C9_8	C10_8	C11_8	121.5(2)	C20_11	C19_11	C24_11	119.9(2)
C6_8	C11_8	C15_8	122.5(2)	C21_11	C20_11	C19_11	120.8(2)
C10_8	C11_8	C6_8	117.4(2)	C20_11	C21_11	C22_11	120.7(2)
C10_8	C11_8	C15_8	120.1(2)	C21_11	C22_11	C23_11	120.5(2)
C7_8	C12_8	C13_8	111.6(2)	C18_11	C23_11	C27_11	121.54(19)
C7_8	C12_8	C14_8	110.5(2)	C22_11	C23_11	C18_11	117.71(19)
C14_8	C12_8	C13_8	110.7(2)	C22_11	C23_11	C27_11	120.47(19)
C11_8	C15_8	C16_8	111.5(2)	C19_11	C24_11	C25_11	112.5(2)
C11_8	C15_8	C17_8	111.4(2)	C19_11	C24_11	C26_11	111.7(2)
C16_8	C15_8	C17_8	111.0(2)	C25_11	C24_11	C26_11	110.0(2)
C19_8	C18_8	N2_8	118.62(18)	C23_11	C27_11	C28_11	110.5(2)
C19_8	C18_8	C23_8	122.69(19)	C23_11	C27_11	C29_11	112.3(2)
C23_8	C18_8	N2_8	118.69(19)	C28_11	C27_11	C29_11	111.1(2)
C18_8	C19_8	C20_8	117.57(19)	C1_12	N1_12	C2_12	128.63(18)
C18_8	C19_8	C24_8	122.59(19)	C1_12	N1_12	C6_12	116.54(19)
C20_8	C19_8	C24_8	119.8(2)	C6_12	N1_12	C2_12	114.64(18)
C21_8	C20_8	C19_8	120.6(2)	C1_12	N2_12	C5_12	126.73(19)
C20_8	C21_8	C22_8	120.6(2)	C1_12	N2_12	C18_12	118.43(19)
C21_8	C22_8	C23_8	120.8(2)	C18_12	N2_12	C5_12	114.22(18)
C18_8	C23_8	C27_8	121.8(2)	N1_12	C1_12	Cu6	120.95(15)
C22_8	C23_8	C18_8	117.7(2)	N1_12	C1_12	N2_12	118.11(19)
C22_8	C23_8	C27_8	120.3(2)	N2_12	C1_12	Cu6	120.90(16)
C19_8	C24_8	C25_8	111.7(2)	N1_12	C2_12	C3_12	115.2(2)
C19_8	C24_8	C26_8	111.6(2)	C2_12	C3_12	C4_12	111.6(2)
C25_8	C24_8	C26_8	110.0(2)	C5_12	C4_12	C3_12	112.09(19)
C23_8	C27_8	C28_8	111.3(2)	N2_12	C5_12	C4_12	113.6(2)
C23_8	C27_8	C29_8	111.4(2)	C7_12	C6_12	N1_12	118.05(19)
C28_8	C27_8	C29_8	110.0(2)	C7_12	C6_12	C11_12	122.73(18)
C1_9	N1_9	C2_9	124.90(18)	C11_12	C6_12	N1_12	119.20(19)
C1_9	N1_9	C6_9	118.38(18)	C6_12	C7_12	C12_12	122.21(19)
C6_9	N1_9	C2_9	115.15(18)	C8_12	C7_12	C6_12	117.76(19)
C1_9	N2_9	C5_9	129.36(18)	C8_12	C7_12	C12_12	120.0(2)
C1_9	N2_9	C18_9	117.35(18)	C9_12	C8_12	C7_12	120.4(2)
C18_9	N2_9	C5_9	113.23(17)	C10_12	C9_12	C8_12	120.6(2)
N1_9	C1_9	Cu2	118.24(14)	C9_12	C10_12	C11_12	121.3(2)
N1_9	C1_9	N2_9	117.74(19)	C6_12	C11_12	C15_12	122.73(19)
N2_9	C1_9	Cu2	123.59(16)	C10_12	C11_12	C6_12	117.2(2)
N1_9	C2_9	C3_9	113.5(2)	C10_12	C11_12	C15_12	120.0(2)
C2_9	C3_9	C4_9	110.95(19)	C7_12	C12_12	C13_12	111.7(2)
C5_9	C4_9	C3_9	112.4(2)	C7_12	C12_12	C14_12	110.4(2)
N2_9	C5_9	C4_9	114.71(19)	C14_12	C12_12	C13_12	111.1(2)
C7_9	C6_9	N1_9	118.22(18)	C11_12	C15_12	C16_12	111.5(2)
C7_9	C6_9	C11_9	122.19(18)	C11_12	C15_12	C17_12	111.3(2)
C11_9	C6_9	N1_9	119.50(18)	C16_12	C15_12	C17_12	110.5(2)

C6_9	C7_9	C12_9	122.34(18)	C19_12	C18_12	N2_12	118.90(19)
C8_9	C7_9	C6_9	118.05(19)	C23_12	C18_12	N2_12	118.63(19)
C8_9	C7_9	C12_9	119.59(19)	C23_12	C18_12	C19_12	122.25(19)
C9_9	C8_9	C7_9	120.5(2)	C18_12	C19_12	C20_12	117.6(2)
C10_9	C9_9	C8_9	120.2(2)	C18_12	C19_12	C24_12	122.59(19)
C9_9	C10_9	C11_9	121.5(2)	C20_12	C19_12	C24_12	119.5(2)
C6_9	C11_9	C15_9	122.68(18)	C21_12	C20_12	C19_12	120.9(2)
C10_9	C11_9	C6_9	117.41(19)	C20_12	C21_12	C22_12	120.3(2)
C10_9	C11_9	C15_9	119.89(19)	C21_12	C22_12	C23_12	120.7(2)
C7_9	C12_9	C13_9	112.0(2)	C18_12	C23_12	C27_12	122.3(2)
C7_9	C12_9	C14_9	110.0(2)	C22_12	C23_12	C18_12	118.0(2)
C14_9	C12_9	C13_9	110.7(2)	C22_12	C23_12	C27_12	119.6(2)
C11_9	C15_9	C16_9	111.8(2)	C19_12	C24_12	C25_12	111.3(2)
C11_9	C15_9	C17_9	111.1(2)	C19_12	C24_12	C26_12	111.8(2)
C16_9	C15_9	C17_9	110.5(2)	C25_12	C24_12	C26_12	110.1(2)
C19_9	C18_9	N2_9	119.15(18)	C23_12	C27_12	C28_12	110.7(2)
C19_9	C18_9	C23_9	122.60(18)	C23_12	C27_12	C29_12	111.5(2)
C23_9	C18_9	N2_9	117.98(18)	C28_12	C27_12	C29_12	110.7(2)
C18_9	C19_9	C20_9	117.46(19)	C1_13	N1_13	C2_13	125.74(19)
C18_9	C19_9	C24_9	123.16(19)	C1_13	N1_13	C6_13	118.13(18)
C20_9	C19_9	C24_9	119.37(19)	C6_13	N1_13	C2_13	115.25(18)
C21_9	C20_9	C19_9	120.9(2)	C1_13	N2_13	C5_13	129.43(18)
C20_9	C21_9	C22_9	120.5(2)	C1_13	N2_13	C18_13	116.95(19)
C21_9	C22_9	C23_9	120.8(2)	C18_13	N2_13	C5_13	113.41(18)
C18_9	C23_9	C27_9	122.13(19)	N1_13	C1_13	Cu5	119.60(15)
C22_9	C23_9	C18_9	117.75(19)	N1_13	C1_13	N2_13	117.66(19)
C22_9	C23_9	C27_9	120.12(19)	N2_13	C1_13	Cu5	122.74(15)
C19_9	C24_9	C25_9	111.6(2)	N1_13	C2_13	C3_13	113.7(2)
C19_9	C24_9	C26_9	111.3(2)	C2_13	C3_13	C4_13	111.06(19)
C25_9	C24_9	C26_9	109.8(2)	C5_13	C4_13	C3_13	112.5(2)
C23_9	C27_9	C28_9	111.0(2)	N2_13	C5_13	C4_13	114.5(2)
C23_9	C27_9	C29_9	112.2(2)	C7_13	C6_13	N1_13	118.56(18)
C28_9	C27_9	C29_9	110.5(2)	C7_13	C6_13	C11_13	122.25(18)
C1_10	N1_10	C2_10	124.89(18)	C11_13	C6_13	N1_13	119.04(19)
C1_10	N1_10	C6_10	118.17(18)	C6_13	C7_13	C12_13	122.71(19)
C6_10	N1_10	C2_10	115.20(18)	C8_13	C7_13	C6_13	117.91(19)
C1_10	N2_10	C5_10	129.37(18)	C8_13	C7_13	C12_13	119.32(19)
C1_10	N2_10	C18_10	117.29(18)	C9_13	C8_13	C7_13	120.6(2)
C18_10	N2_10	C5_10	113.25(17)	C10_13	C9_13	C8_13	120.3(2)
N1_10	C1_10	Cu3	117.79(14)	C9_13	C10_13	C11_13	121.3(2)
N1_10	C1_10	N2_10	117.73(19)	C6_13	C11_13	C15_13	122.39(19)
N2_10	C1_10	Cu3	124.01(16)	C10_13	C11_13	C6_13	117.59(19)
N1_10	C2_10	C3_10	113.5(2)	C10_13	C11_13	C15_13	119.78(19)
C2_10	C3_10	C4_10	110.90(19)	C7_13	C12_13	C13_13	112.0(2)
C5_10	C4_10	C3_10	111.9(2)	C7_13	C12_13	C14_13	110.2(2)
N2_10	C5_10	C4_10	114.32(19)	C14_13	C12_13	C13_13	110.6(2)
C7_10	C6_10	N1_10	118.57(18)	C11_13	C15_13	C16_13	112.0(2)
C7_10	C6_10	C11_10	121.98(18)	C11_13	C15_13	C17_13	110.7(2)
C11_10	C6_10	N1_10	119.45(19)	C16_13	C15_13	C17_13	110.8(2)

C6_10	C7_10	C12_10	122.36(19)	C19_13	C18_13	N2_13	119.38(19)
C8_10	C7_10	C6_10	118.08(19)	C19_13	C18_13	C23_13	122.52(18)
C8_10	C7_10	C12_10	119.5(2)	C23_13	C18_13	N2_13	118.03(19)
C7_10	C8_10	C9_10	120.6(2)	C18_13	C19_13	C20_13	117.58(19)
C10_10	C9_10	C8_10	120.1(2)	C18_13	C19_13	C24_13	123.23(19)
C9_10	C10_10	C11_10	121.4(2)	C20_13	C19_13	C24_13	119.2(2)
C6_10	C11_10	C15_10	122.91(19)	C21_13	C20_13	C19_13	120.7(2)
C10_10	C11_10	C6_10	117.6(2)	C20_13	C21_13	C22_13	120.7(2)
C10_10	C11_10	C15_10	119.51(19)	C21_13	C22_13	C23_13	120.5(2)
C7_10	C12_10	C13_10	111.6(2)	C18_13	C23_13	C27_13	121.8(2)
C7_10	C12_10	C14_10	110.3(2)	C22_13	C23_13	C18_13	117.9(2)
C14_10	C12_10	C13_10	110.9(2)	C22_13	C23_13	C27_13	120.1(2)
C11_10	C15_10	C16_10	111.7(2)	C19_13	C24_13	C25_13	111.6(2)
C11_10	C15_10	C17_10	110.9(2)	C19_13	C24_13	C26_13	111.2(2)
C16_10	C15_10	C17_10	110.4(2)	C25_13	C24_13	C26_13	109.9(2)
C19_10	C18_10	N2_10	119.04(18)	C23_13	C27_13	C28_13	110.4(2)
C19_10	C18_10	C23_10	122.36(18)	C23_13	C27_13	C29_13	112.3(2)
C23_10	C18_10	N2_10	118.43(18)	C28_13	C27_13	C29_13	110.7(2)
C18_10	C19_10	C20_10	117.69(19)	N1S_2	C2S_2	C3S_2	177.8(6)
C18_10	C19_10	C24_10	122.91(19)	N1S_3	C2S_3	C3S_3	179.3(6)
C20_10	C19_10	C24_10	119.39(19)	N1S_4	C2S_4	C3S_4	178.7(6)
C21_10	C20_10	C19_10	120.8(2)	N1S_5	C2S_5	C3S_5	178.0(6)
C20_10	C21_10	C22_10	120.5(2)	N1S_6	C2S_6	C3S_6	177.4(9)
C21_10	C22_10	C23_10	120.7(2)	N1S_7	C2S_7	C3S_7	179.8(8)
C18_10	C23_10	C27_10	122.36(19)	N1S_1	C2S_1	C3S_1	179.1(7)
C22_10	C23_10	C18_10	118.00(19)				

Compound 4



Experimental. Single yellow plate-shaped crystals of **4** were chosen from the sample. A suitable crystal $0.39 \times 0.28 \times 0.13 \text{ mm}^3$ was selected and mounted on a loop with paratone oil on a Bruker D8 VENTURE diffractometer. The crystal was kept at $T = 100(2) \text{ K}$ during data collection. The structure was solved with the ShelXT⁵ structure solution program using the Intrinsic Phasing solution method and by using Olex2⁴ as the graphical interface. The model was refined with version 2018/3 of ShelXL⁷ using Least Squares minimization.

Crystal Data. $\text{C}_{58}\text{H}_{84}\text{Cu}_2\text{N}_4\text{S}_2$, $M_r = 1028.53$, monoclinic, $P2_1/n$ (No. 14), $a = 12.3238(9) \text{ \AA}$, $b = 23.592(2) \text{ \AA}$, $c = 12.3896(11) \text{ \AA}$, $\beta = 91.999(3)^\circ$, $\alpha = \gamma = 90^\circ$, $V = 3600.0(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 2$, $Z' = 0.5$, $\mu(\text{MoK}\alpha) = 0.679 \text{ mm}^{-1}$, 62264 reflections measured, 8228 unique ($R_{\text{int}} = 0.0389$) which were used in all calculations. The final wR_2 was 0.2052 (all data) and R_1 was 0.0649 ($I > 2\sigma(I)$).

Table S4. Crystal Data for **1**.

Compound	4
Formula	C ₅₈ H ₈₄ Cu ₂ N ₄ S ₂
$D_{calc.}/\text{g cm}^{-3}$	0.949
μ/mm^{-1}	0.679
Formula Weight	1028.53
Colour	yellow
Shape	plate
Size/mm ³	0.39×0.28×0.13
T/K	100(2)
Crystal System	monoclinic
Space Group	$P2_1/n$
$a/\text{\AA}$	12.3238(9)
$b/\text{\AA}$	23.592(2)
$c/\text{\AA}$	12.3896(11)
$\alpha/^\circ$	90
$\beta/^\circ$	91.999(3)
$\gamma/^\circ$	90
$V/\text{\AA}^3$	3600.0(5)
Z	2
Z'	0.5
Wavelength/ \AA	0.710730
Radiation type	MoK α
$\Theta_{min}/^\circ$	2.291
$\Theta_{max}/^\circ$	27.482
Measured Refl.	62264
Independent Refl.	8228
Reflections with $I > 2(I)$	7203
R_{int}	0.0389
Parameters	322
Restraints	302
Largest Peak	1.183
Deepest Hole	-0.628
GooF	1.036
wR_2 (all data)	0.2052
wR_2	0.1992
R_1 (all data)	0.0704
R_1	0.0649

Table S5. Bond Length (\AA) for **4**

Atom	Atom	Length/ \AA
C2	C3	1.401(3)
C2	C10	1.396(4)
C2	N1_1	1.456(3)
C2	N1_2	1.454(3)
C3	C4	1.509(4)
C3	C7	1.396(4)
C4	C5	1.527(4)
C4	C6	1.516(4)
C7	C8	1.385(4)
C8	C9	1.383(4)
C9	C10	1.407(4)
C10	C11	1.517(4)
C11	C12	1.523(4)
C11	C13	1.546(5)
C18	C19	1.409(3)
C18	C26	1.393(4)
C18	N2_1	1.454(3)
C18	N2_2	1.458(3)
C19	C20	1.521(4)
C19	C23	1.389(4)
C20	C21	1.525(4)
C20	C22	1.523(4)
C23	C24	1.384(4)
C24	C25	1.396(4)
C25	C26	1.393(4)
C26	C27	1.522(4)
C27	C28	1.529(4)
C27	C29	1.526(5)
S1	S1 ¹	2.119(2)
S1	Cu1_1	2.1315(10)
S1	Cu1_2	2.1315(10)
Cu1_1	C1_1	1.899(2)
N1_1	C1_1	1.345(3)
N1_1	C14_1	1.487(3)
N2_1	C1_1	1.357(3)
N2_1	C17_1	1.475(3)
C14_1	C15_1	1.501(4)
C15_1	C16_1	1.543(4)
C16_1	C17_1	1.507(4)
Cu1_2	C1_2	1.899(2)
N1_2	C1_2	1.345(3)
N1_2	C14_2	1.487(3)
N2_2	C1_2	1.357(3)
N2_2	C17_2	1.475(3)
C14_2	C15_2	1.501(4)
C15_2	C16_2	1.543(4)
C16_2	C17_2	1.507(4)

Table S6. Bond Angle (deg) for **4**

Atom	Atom	Atom	Angle/°
C3	C2	N1_1	122.6(3)
C3	C2	N1_2	116.3(3)
C10	C2	C3	122.0(2)
C10	C2	N1_1	115.3(3)
C10	C2	N1_2	121.6(3)
C2	C3	C4	122.8(2)
C7	C3	C2	117.9(2)
C7	C3	C4	119.3(2)
C3	C4	C5	110.5(2)
C3	C4	C6	111.3(3)
C6	C4	C5	112.1(3)
C8	C7	C3	121.4(3)
C9	C8	C7	119.8(3)
C8	C9	C10	121.0(3)
C2	C10	C9	117.9(2)
C2	C10	C11	122.8(2)
C9	C10	C11	119.3(2)
C10	C11	C12	111.4(2)
C10	C11	C13	111.1(3)
C12	C11	C13	109.7(3)
C19	C18	N2_1	114.5(3)
C19	C18	N2_2	120.7(2)
C26	C18	C19	122.0(2)
C26	C18	N2_1	123.4(3)
C26	C18	N2_2	117.3(2)
C18	C19	C20	122.6(2)
C23	C19	C18	117.7(2)
C23	C19	C20	119.7(2)
C19	C20	C21	111.1(3)
C19	C20	C22	110.9(2)
C22	C20	C21	111.0(3)
C24	C23	C19	121.5(3)
C23	C24	C25	119.8(3)
C26	C25	C24	120.6(3)
C18	C26	C25	118.4(2)

Atom	Atom	Atom	Angle/°
C18	C26	C27	122.8(2)
C25	C26	C27	118.8(2)
C26	C27	C28	111.7(2)
C26	C27	C29	111.2(3)
C29	C27	C28	111.1(3)
S1 ¹	S1	Cu1_1	99.66(6)
S1 ¹	S1	Cu1_2	99.66(6)
C1_1	Cu1_1	S1	171.87(12)
C2	N1_1	C14_1	115.3(2)
C1_1	N1_1	C2	115.6(2)
C1_1	N1_1	C14_1	129.05(19)
C18	N2_1	C17_1	115.1(2)
C1_1	N2_1	C18	116.97(18)
C1_1	N2_1	C17_1	127.70(19)
N1_1	C1_1	Cu1_1	123.14(16)
N1_1	C1_1	N2_1	117.8(2)
N2_1	C1_1	Cu1_1	117.60(15)
N1_1	C14_1	C15_1	113.67(19)
C14_1	C15_1	C16_1	112.3(2)
C17_1	C16_1	C15_1	111.9(2)
N2_1	C17_1	C16_1	114.13(18)
C1_2	Cu1_2	S1	173.60(9)
C2	N1_2	C14_2	113.21(19)
C1_2	N1_2	C2	117.48(19)
C1_2	N1_2	C14_2	129.07(19)
C18	N2_2	C17_2	117.1(2)
C1_2	N2_2	C18	114.91(19)
C1_2	N2_2	C17_2	127.68(19)
N1_2	C1_2	Cu1_2	123.15(16)
N1_2	C1_2	N2_2	117.8(2)
N2_2	C1_2	Cu1_2	117.60(15)
N1_2	C14_2	C15_2	113.68(19)
C14_2	C15_2	C16_2	112.3(2)
C17_2	C16_2	C15_2	111.9(2)
N2_2	C17_2	C16_2	114.12(18)

References

- (1) Jordan, A. J.; Wyss, C. M.; Bacsá, J.; Sadighi, J. P. Synthesis and Reactivity of New Copper(I) Hydride Dimers. *Organometallics* **2016**, *35*, 613-616.
- (2) Zhai, J.; Filatov, A. S.; Hillhouse, G. L.; Hopkins, M. D. Synthesis, structure, and reactions of a copper-sulfido cluster comprised of the parent Cu₂S unit: {(NHC)Cu}₂(μ-S). *Chem. Sci.* **2016**, *7*, 589-595.
- (3) Hartman, J. S.; Shoemaker, J. A. W.; Janzen, A. F.; Ragoona, P. J.; Szerminski, W. R. The coordination chemistry of (py)₂BF₂⁺ and related difluoroboron cations. *J. Fluorine Chem.* **2003**, *119*, 125-139.
- (4) Dolomanov, O.V., Bourhis, L. J., Gildea, R. J, Howard, J. A. K. & Puschmann, H. *J. Appl. Cryst.* **2009**, *42*, 339-341.
- (5) Sheldrick, G.M. *Acta Cryst.* **2015** A71, 3-8.
- (6) Sheldrick, G.M. *Acta Cryst.* **2015** C71, 3-8.
- (7) Sheldrick, G.M. *Acta Cryst.* **2015** C27, 3-8.