Supporting Information

Rare, Hexatomic, Boat-Shaped, Cross-Linked, Bis(iminodiphenylphosphorano)methanediide Pincer Carbon Bridged Photoluminescent Copper Clusters Capped with Methyl or Halide Bridges

Guibin Ma, Michael J. Ferguson,[#] Robert McDonald,[#] and Ronald G Cavell[*]

Chemistry Department, University of Alberta, Edmonton, Alberta, T6G 2G2, Canada

[#] X-ray Structure Determination Laboratory, University of Alberta

[*]To whom correspondence should be addressed. Telephone 780-492-5310. Fax 780-492-8231. E-mail: ron.cavell@ualberta.ca

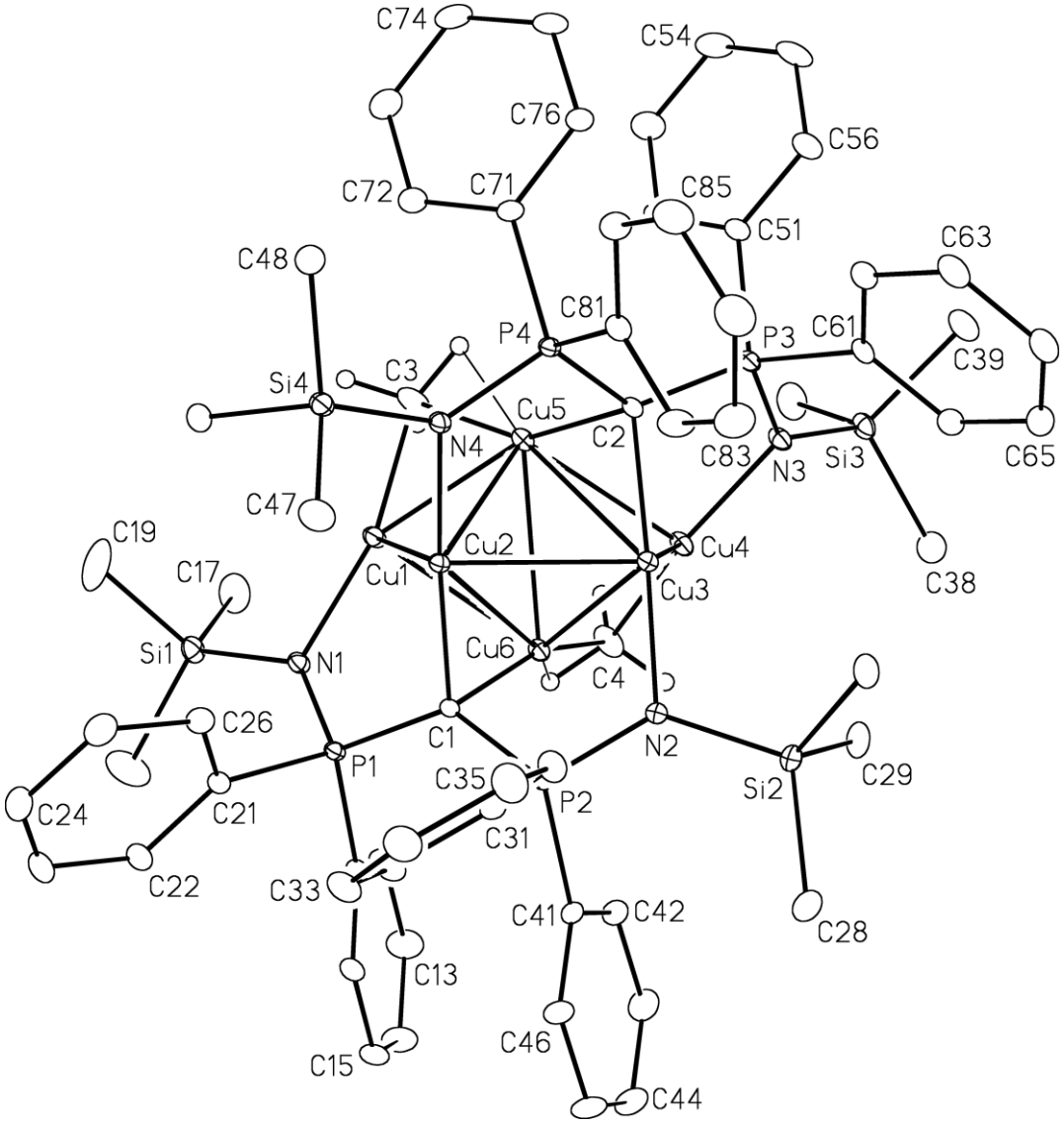


Figure S1. Perspective view of the $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**1**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms attached to C(3) and C(4) are shown with arbitrarily small thermal parameters; all other hydrogens are not shown.

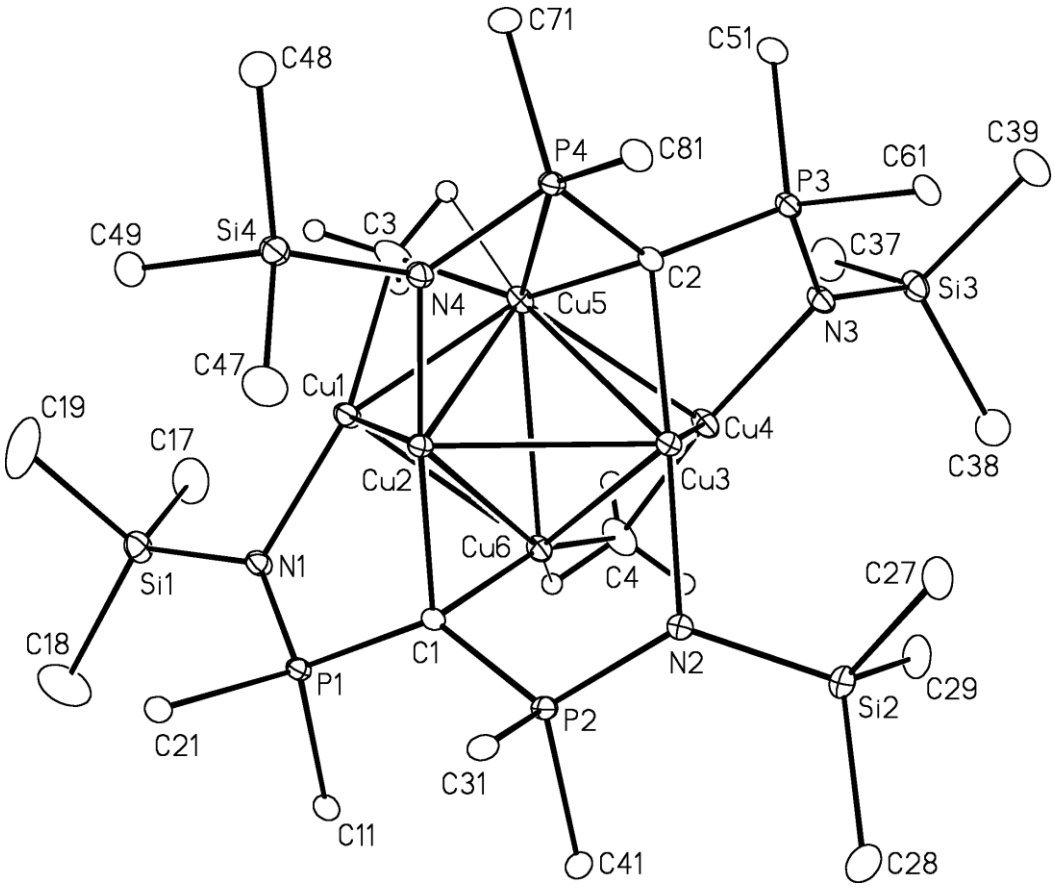


Figure S2. View of the molecule $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**1**) showing only the ipso carbons of the phosphine phenyl rings.

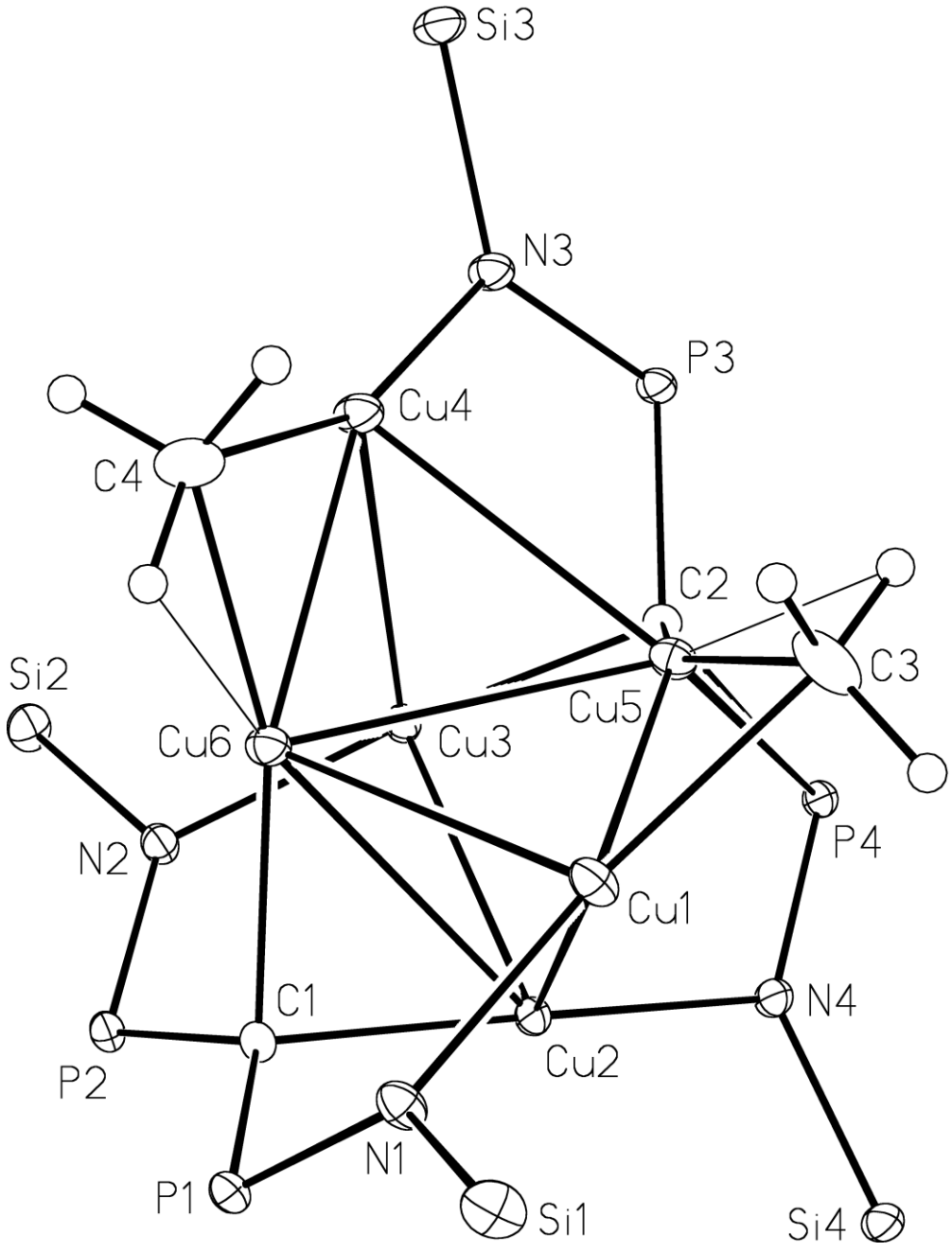


Figure S3. Alternate view of the core of the molecule $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**1**).

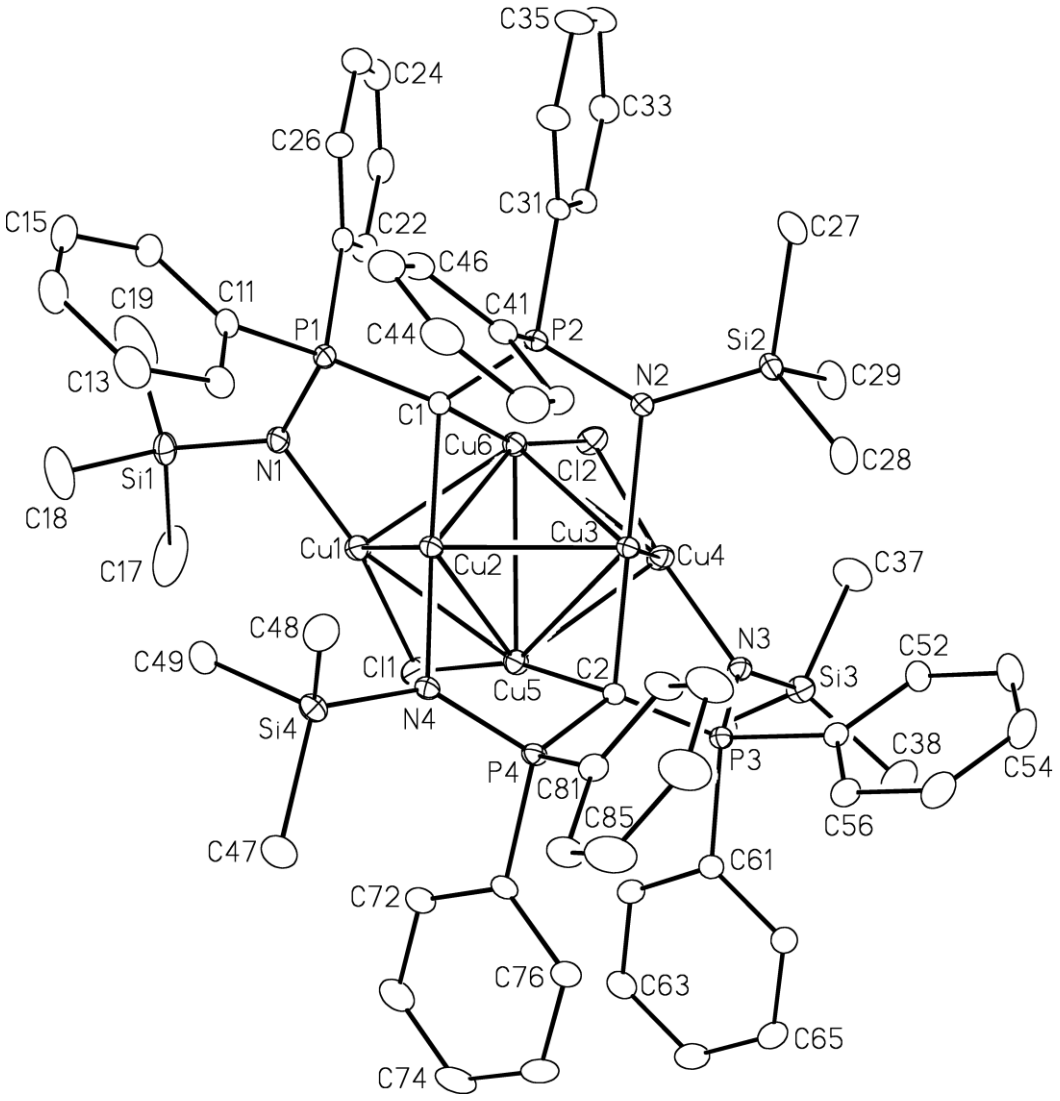


Figure S4. Perspective view of one of two crystallographically independent $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**2**) molecules (*molecule A*) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

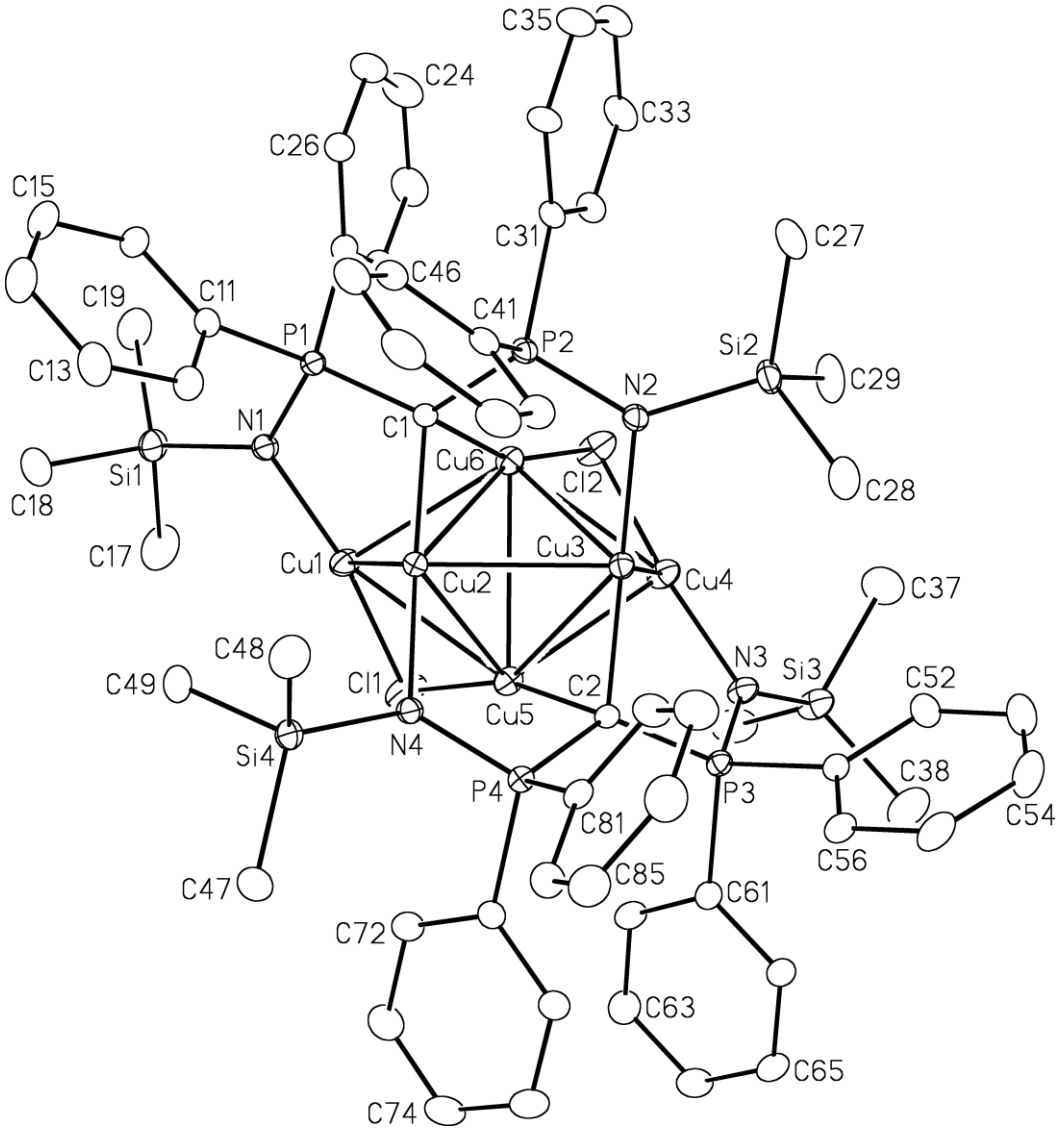


Figure S5. Perspective view of the second of two crystallographically independent $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**2**) molecules (*molecule B*) showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

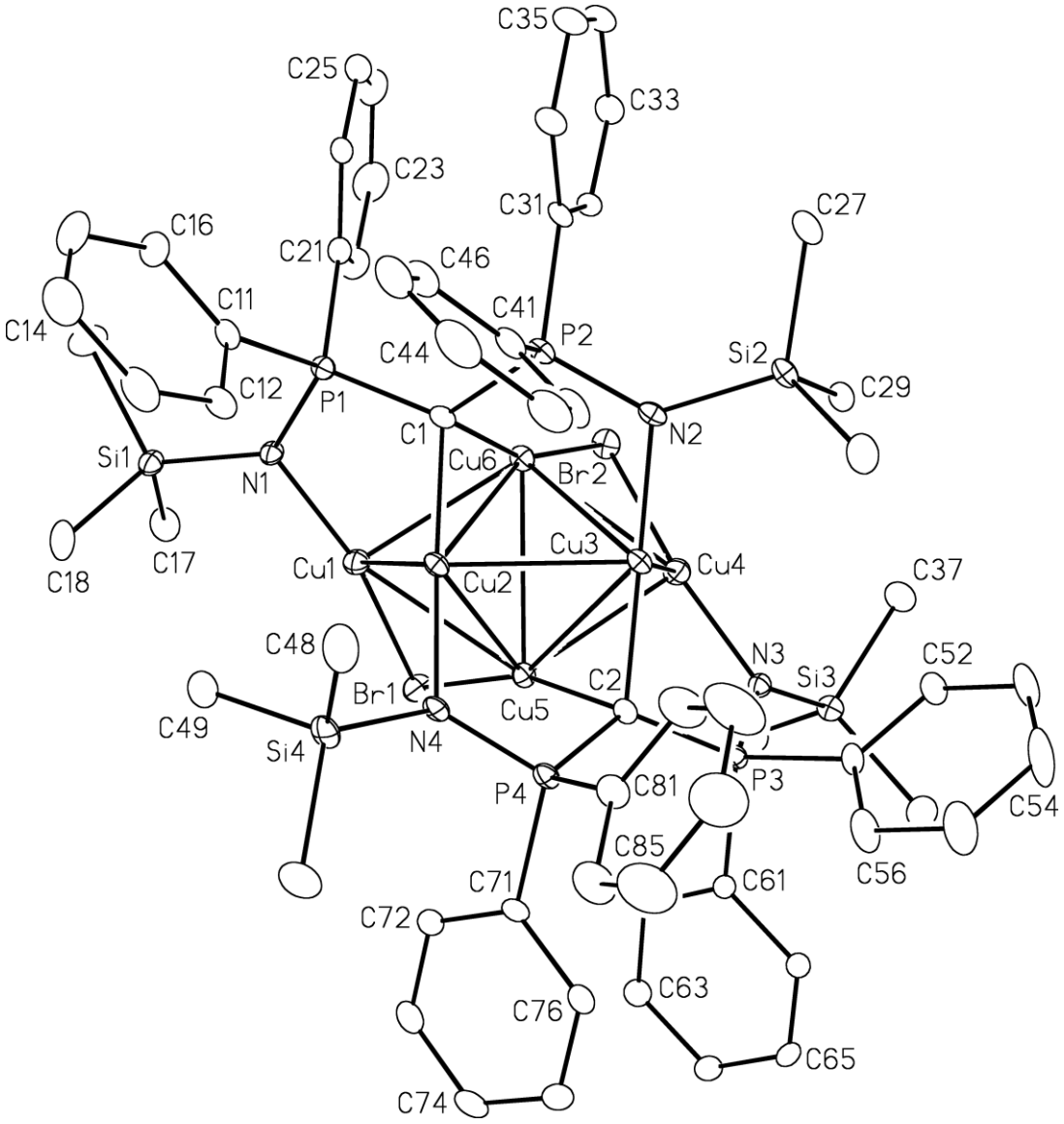


Figure S6. Perspective view of the $[Cu_6Br_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**3**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

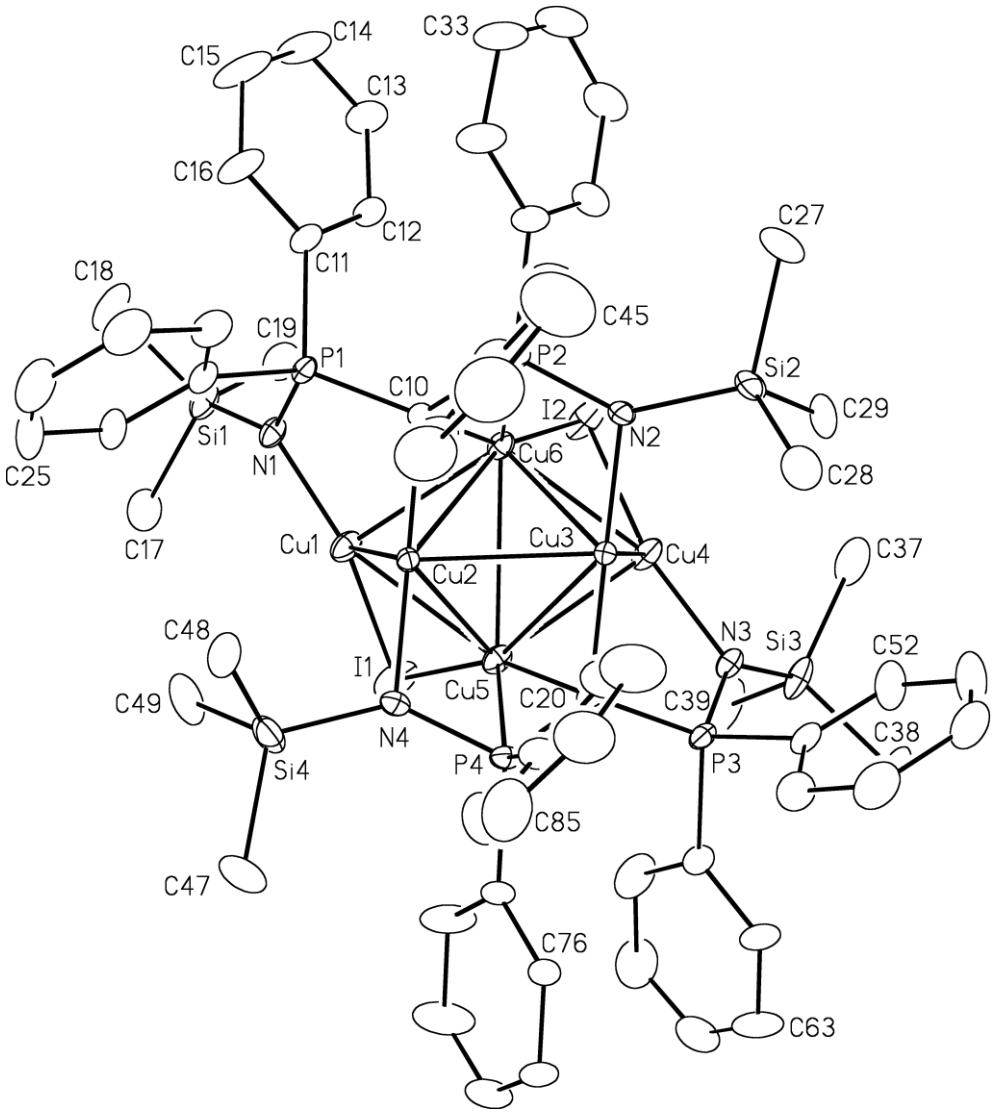


Figure S7. Perspective view of the $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**4**) molecule showing the atom labelling scheme. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown.

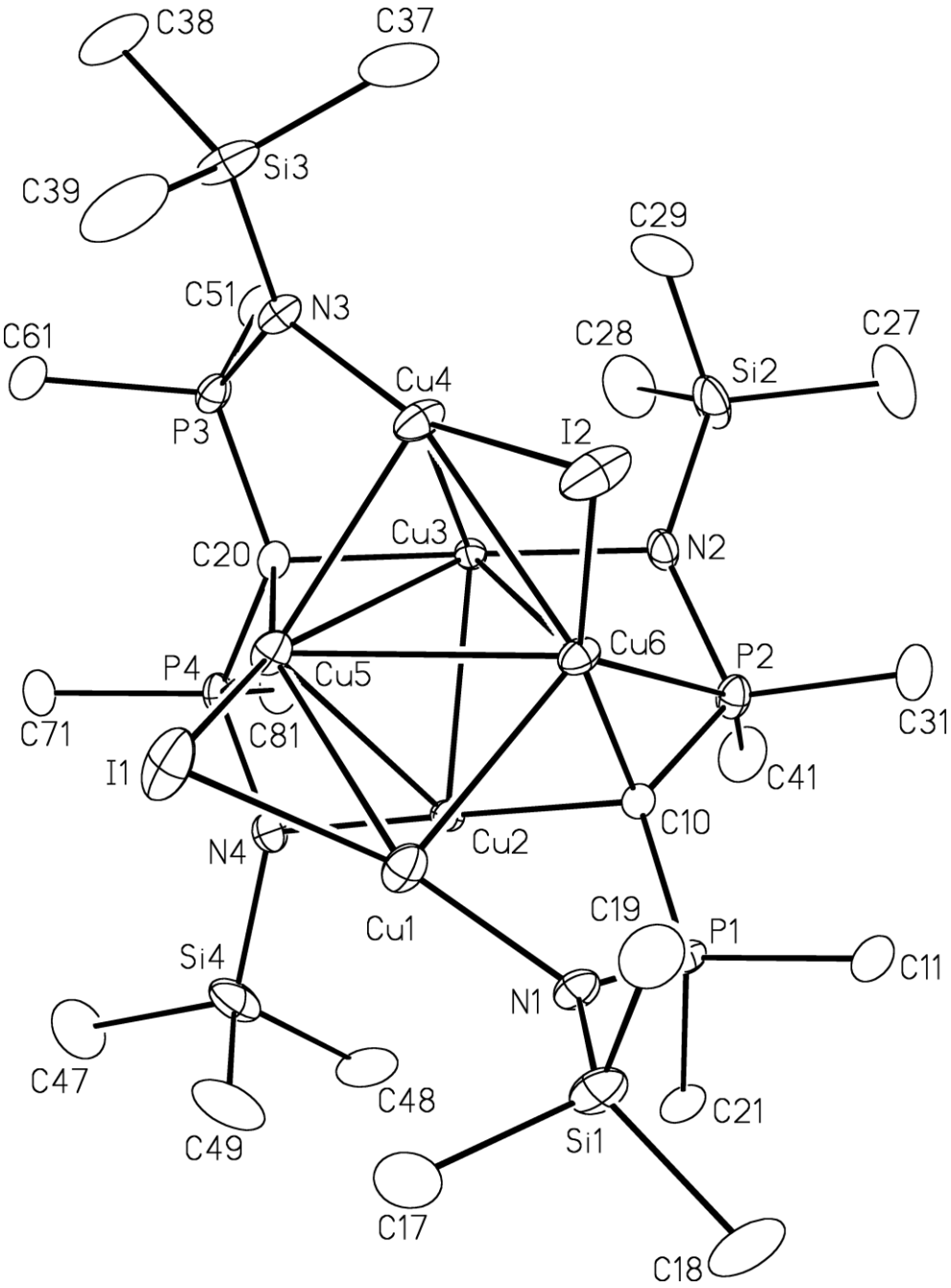


Figure S8. Alternate view of the core of the molecule $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**4**)

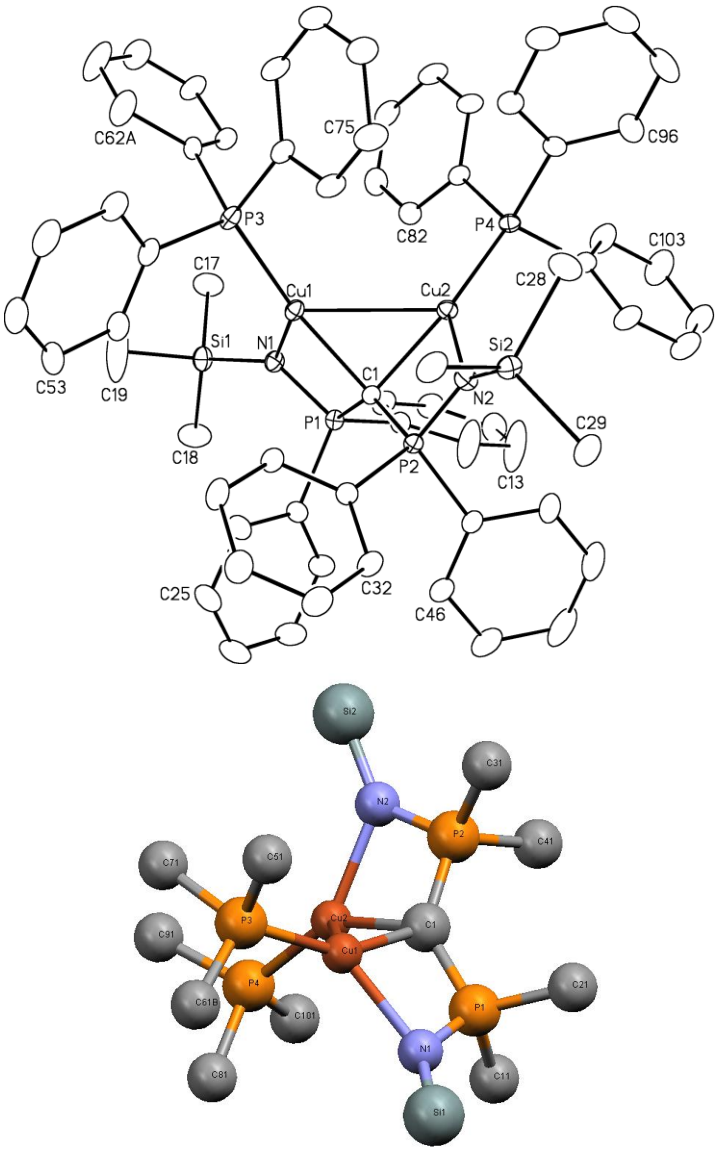


Figure S9. Perspective view of the [{(PhP$_3$)Cu}$_2${C(Ph$_2$PNSiMe$_3$)$_2$}] (**6**) molecule showing the atom labelling scheme. Only the major orientation of the disordered phenyl group (C61A to C66A) is shown. Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are not shown. The core structure is shown below the molecular view.

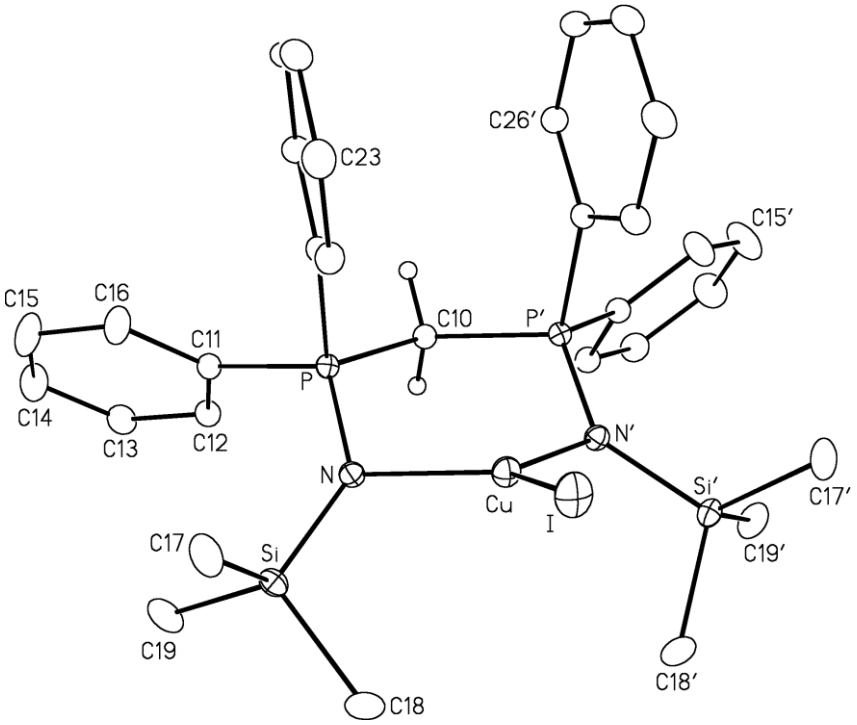


Figure S10. Perspective view of the [{$CH_2(PPh_2{=}NSiMe_3)_2$}CuI] (**7**) molecule showing the atom labelling scheme. Primed atoms are related to unprimed ones by the mirror plane located at (x, $^1/_4$, z). Non-hydrogen atoms are represented by Gaussian ellipsoids at the 20% probability level. Hydrogen atoms are shown with arbitrarily small thermal parameters for the methylene group, and are not shown for the methyl and phenyl groups.

Figure S11. The Mass Spectrum of $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**1**)

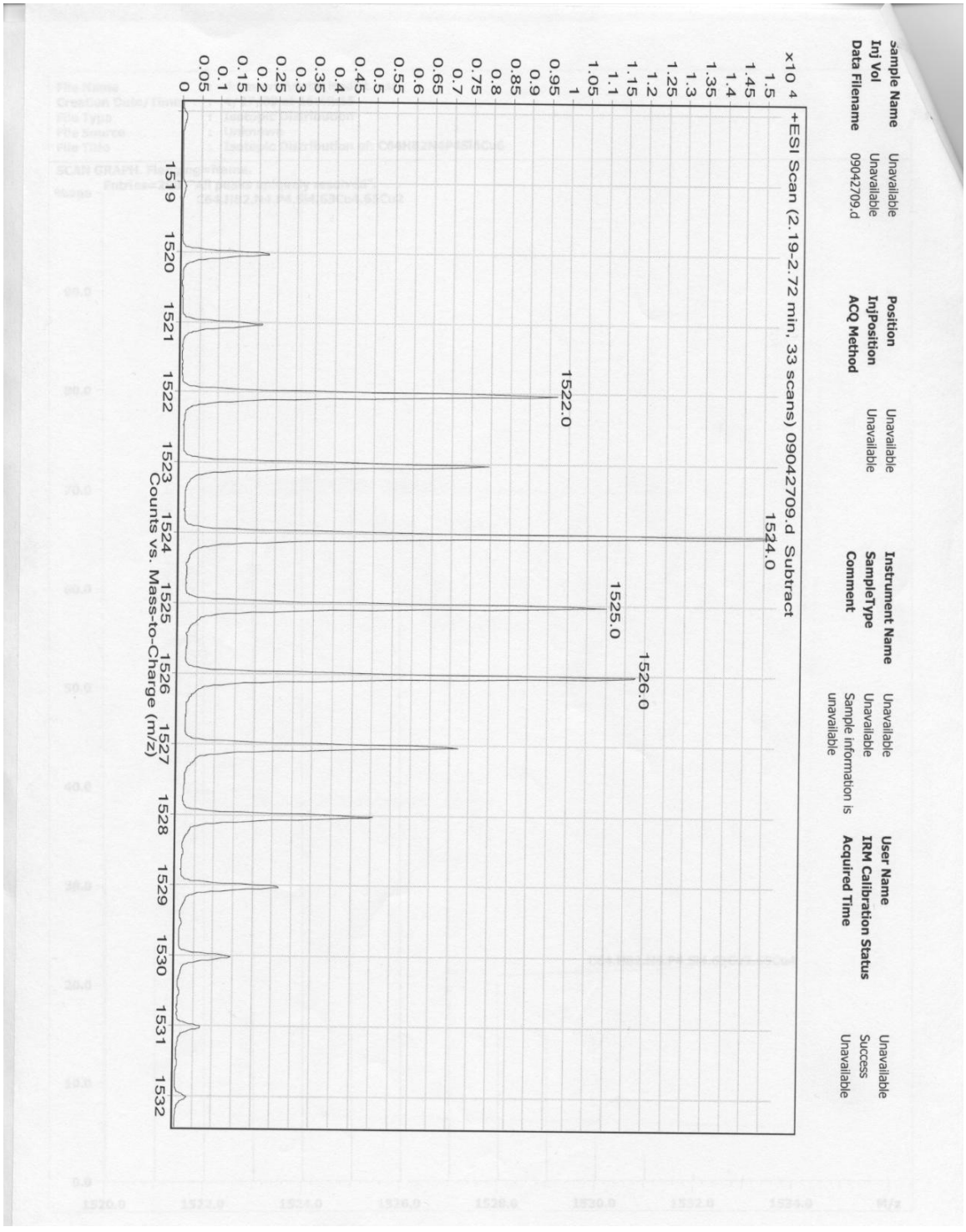


Figure S12. Simulation of the Mass Spectrum of $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**1**)

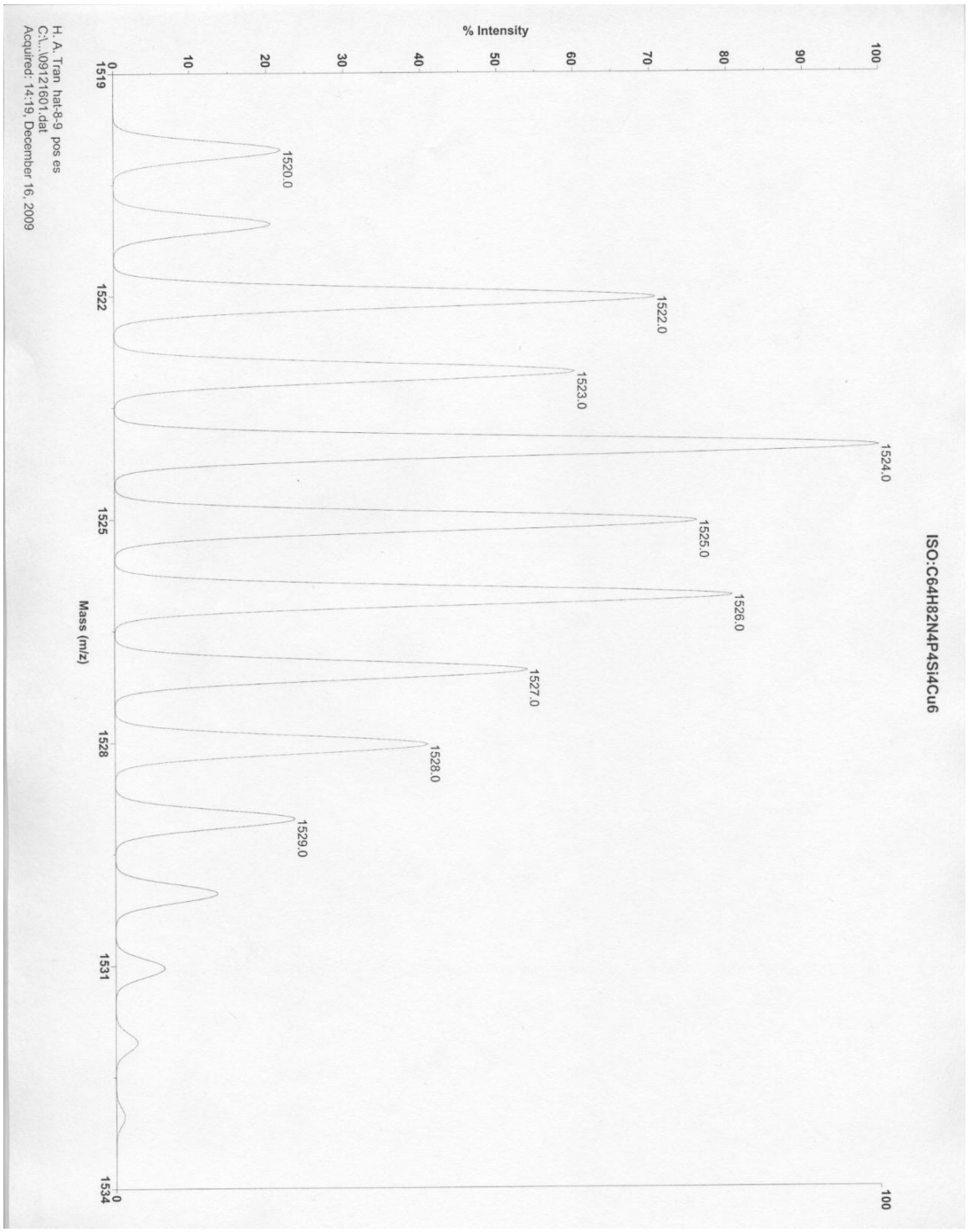


Figure S13. The Mass Spectrum of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**)

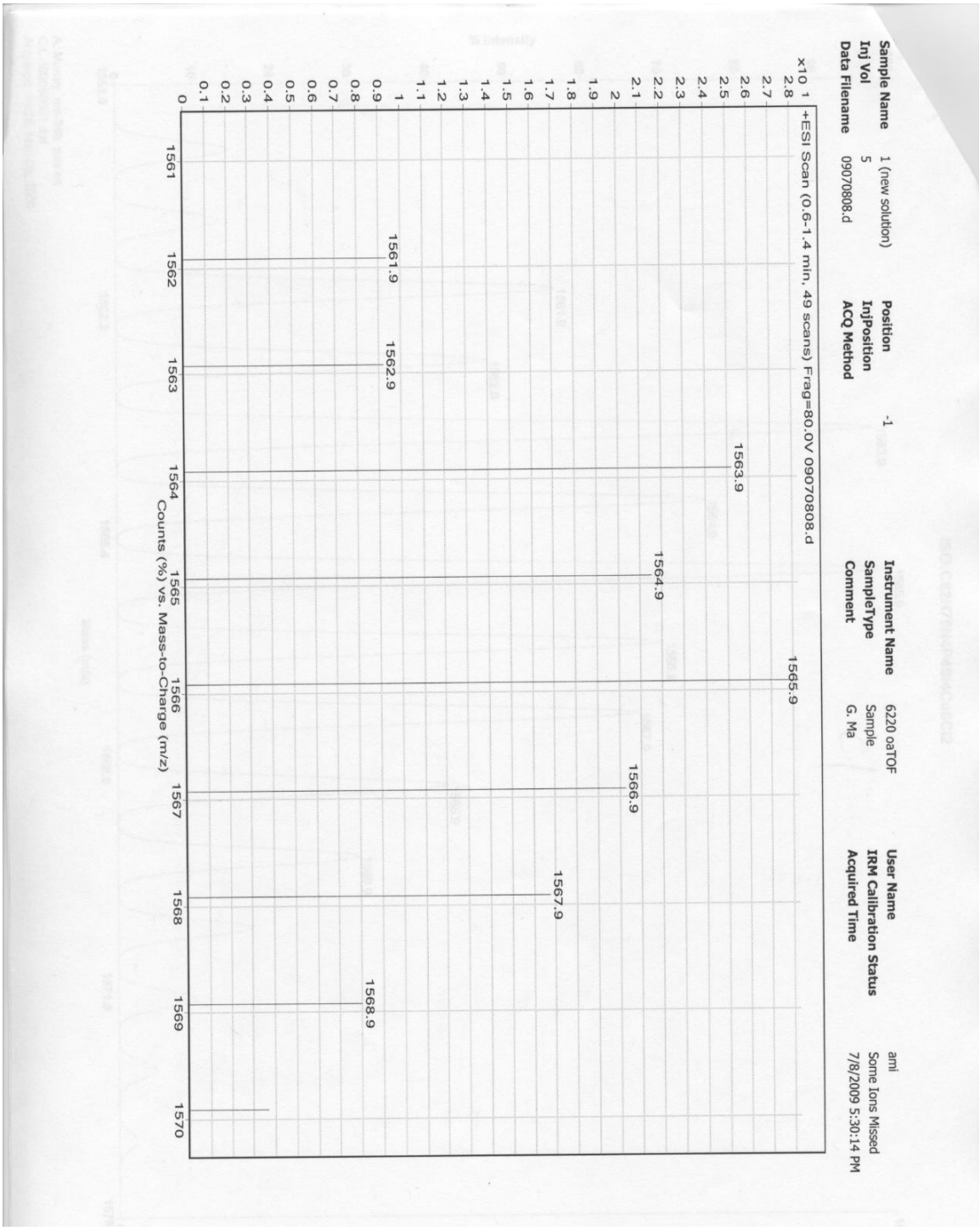


Figure S14. The Simulated Mass Spectrum of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**)

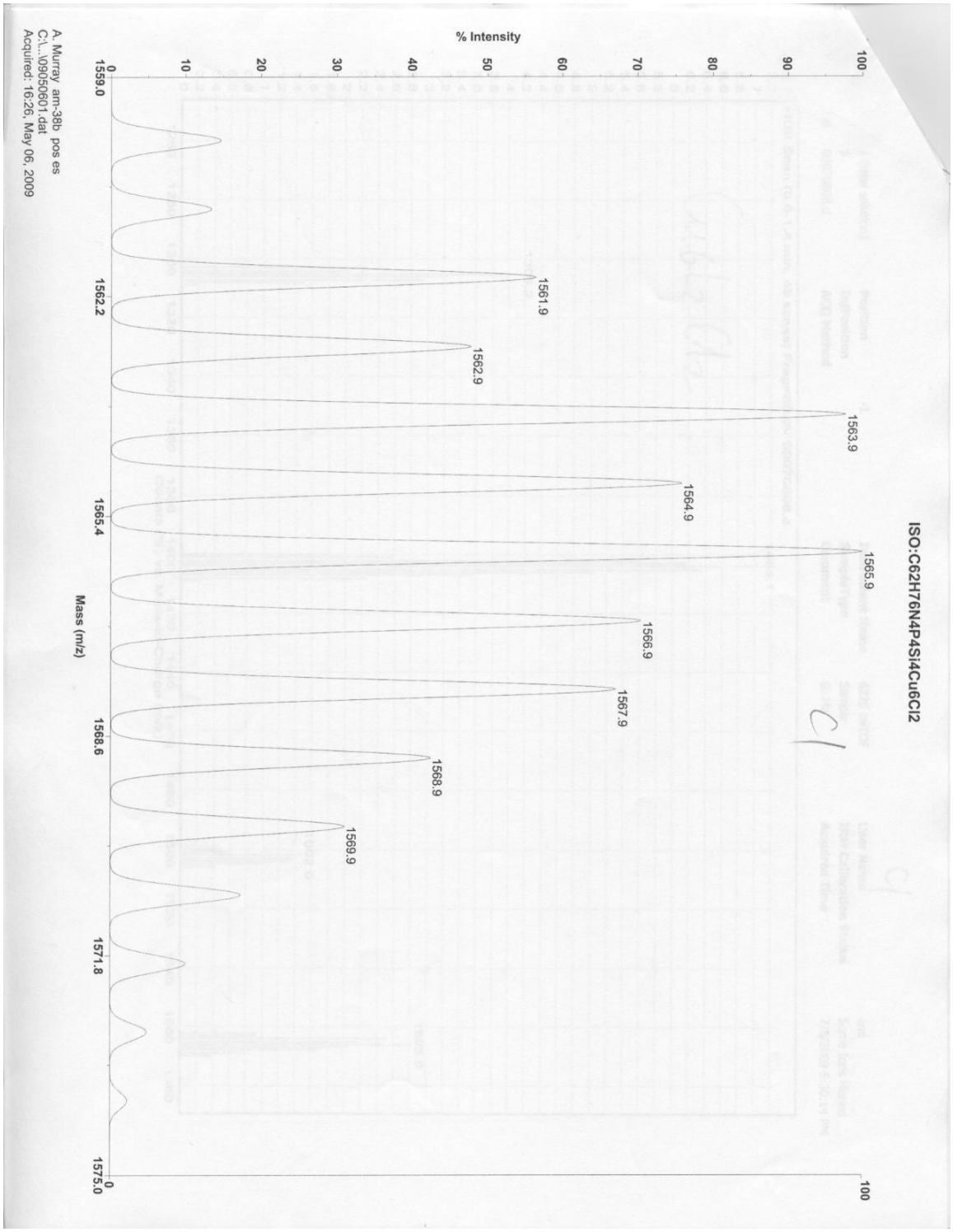


Figure S15. The Mass Spectrum of $[Cu_6Br_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**3**)

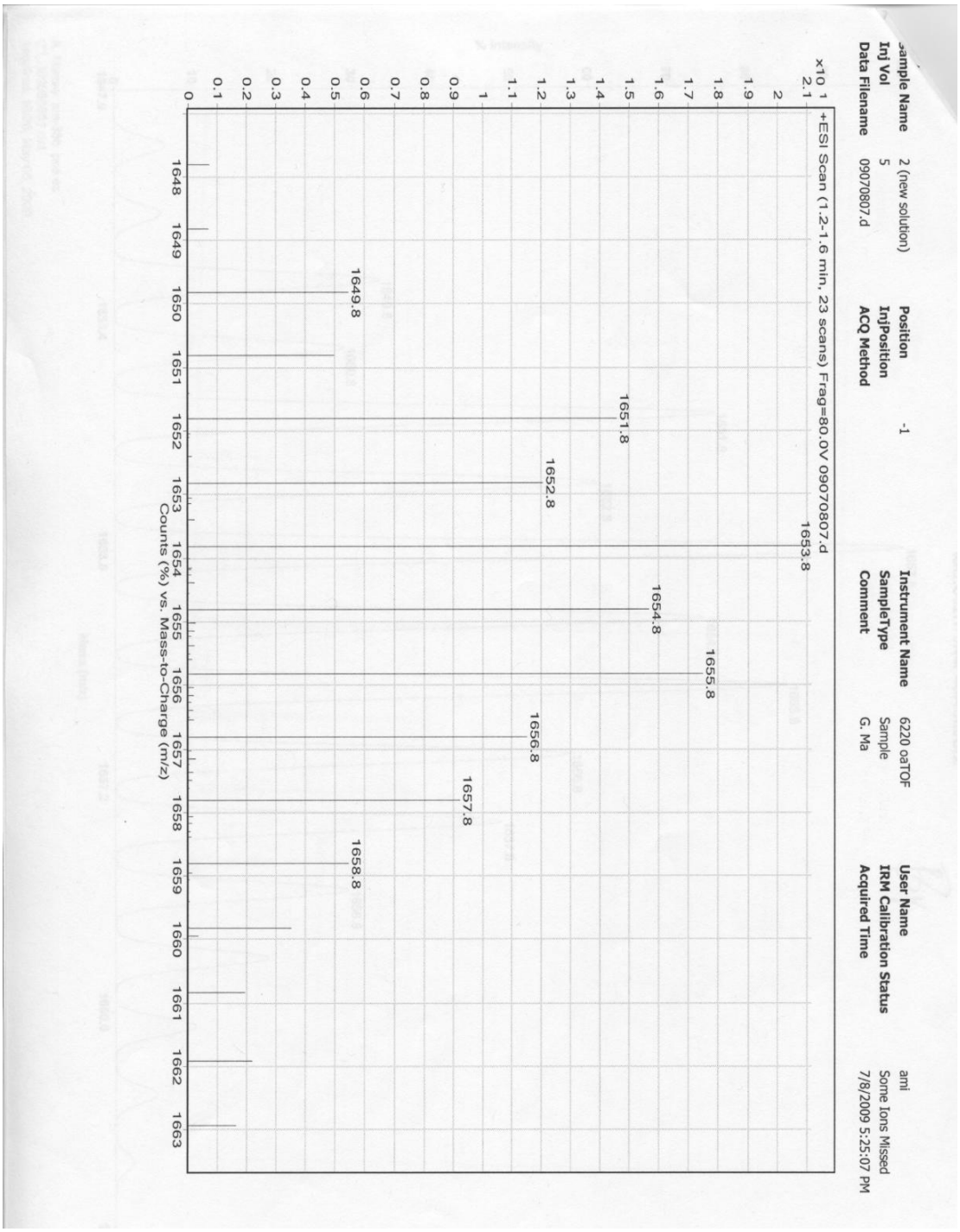


Figure S16. Simulation of the Mass Spectrum of $[Cu_6Br_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**3**)

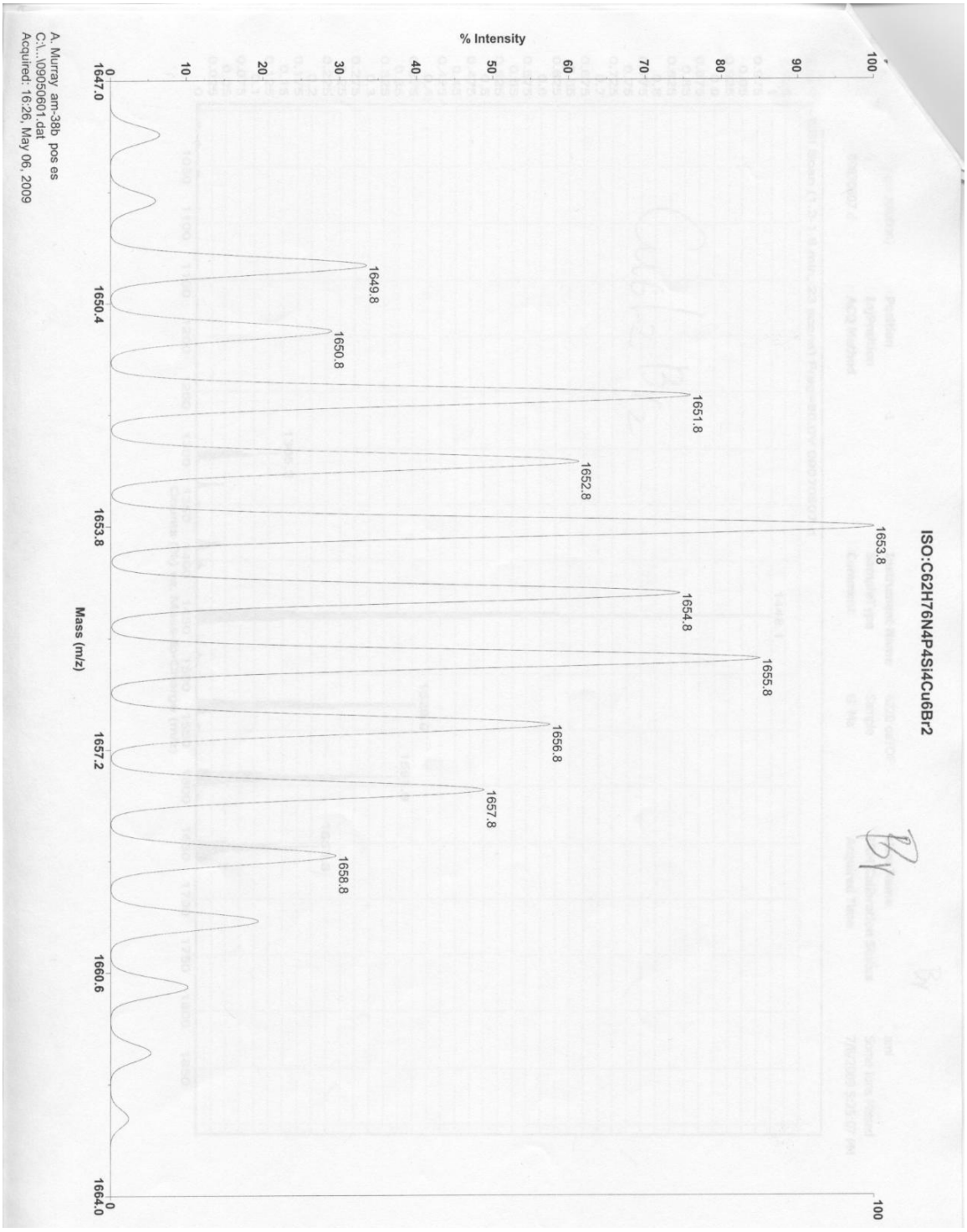


Figure S17. The Mass Spectrum of $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**4**)

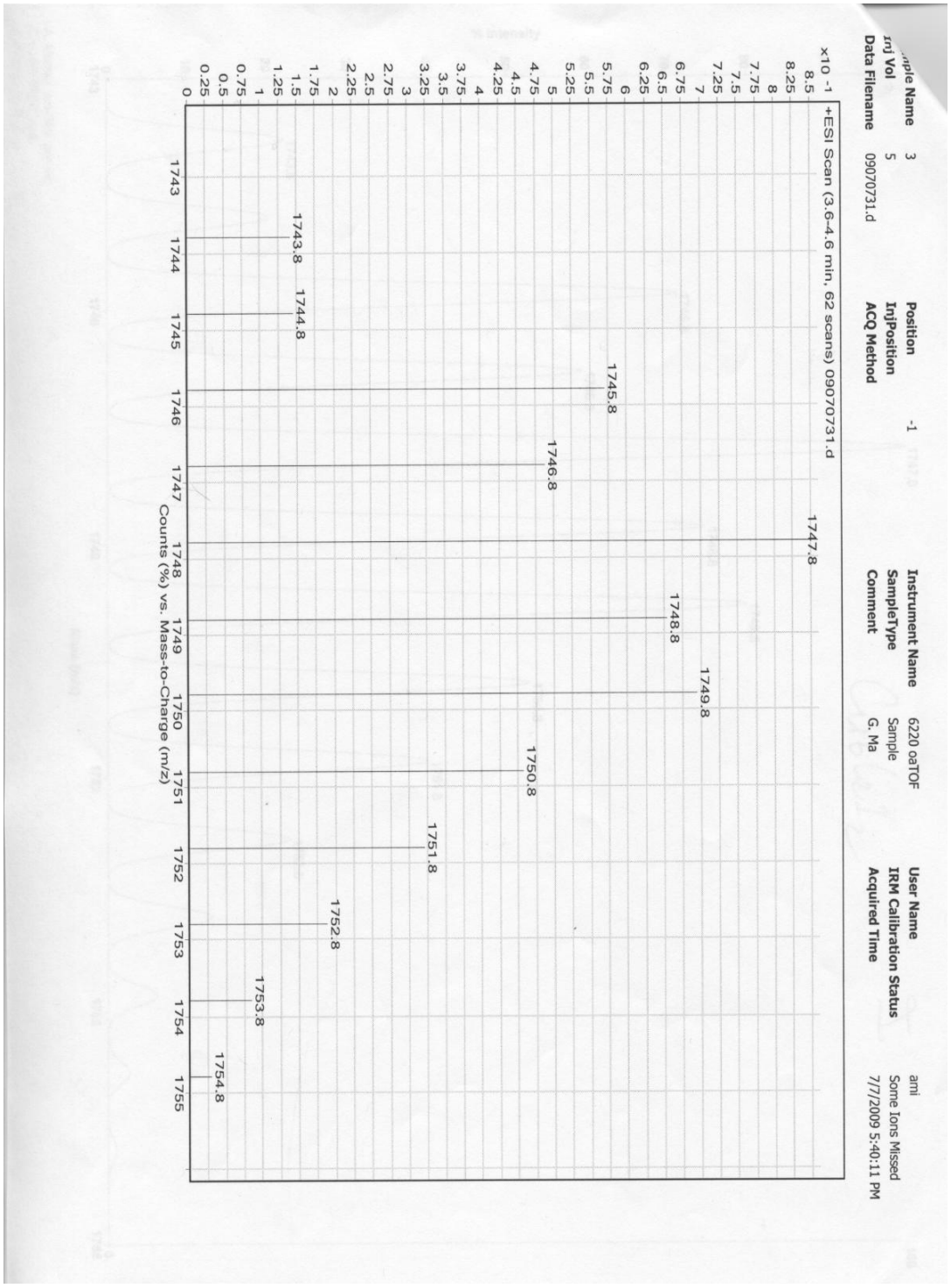


Figure S18. Simulation of the Mass Spectrum of $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**4**)

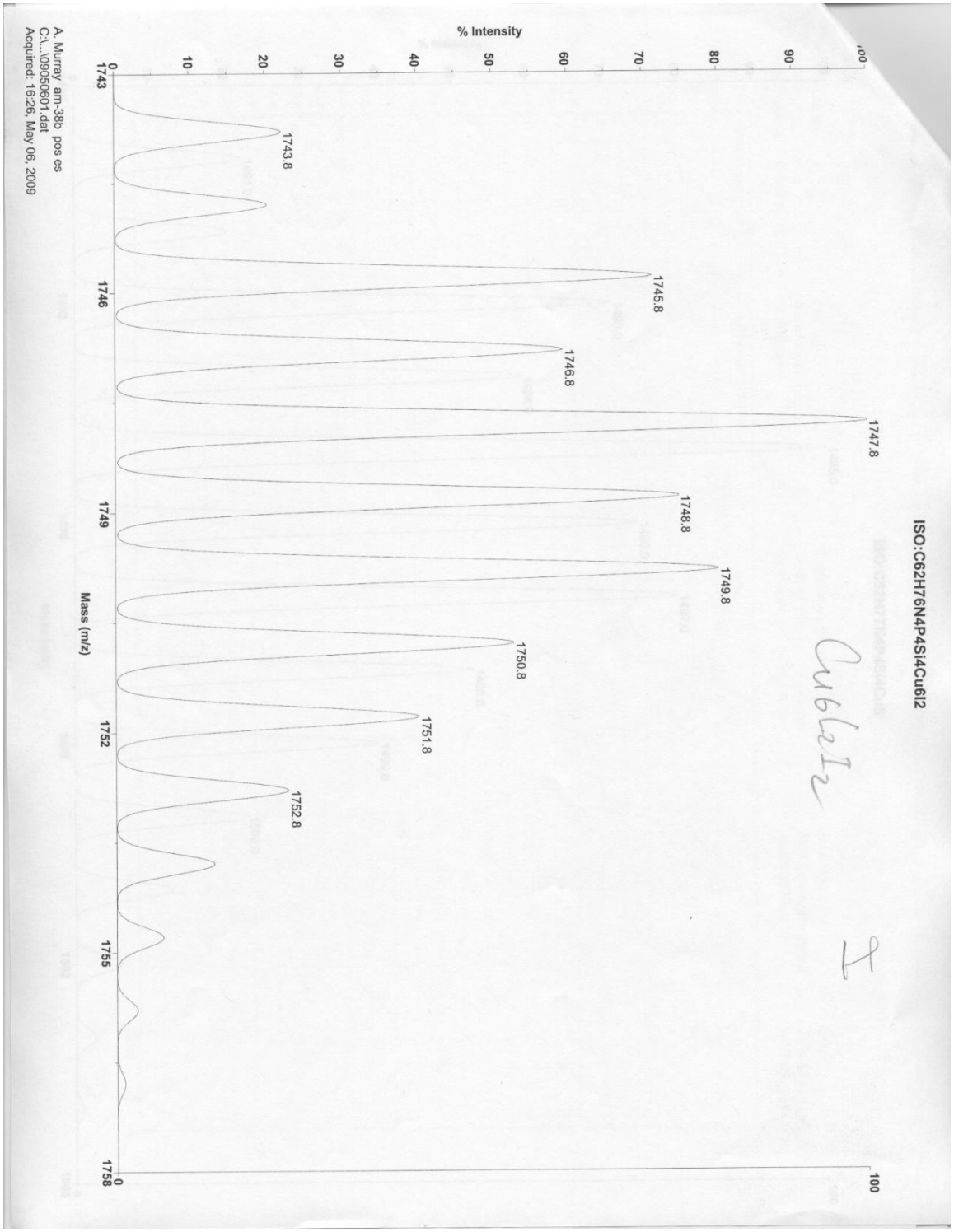


Figure S19. TGA of $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**1**)

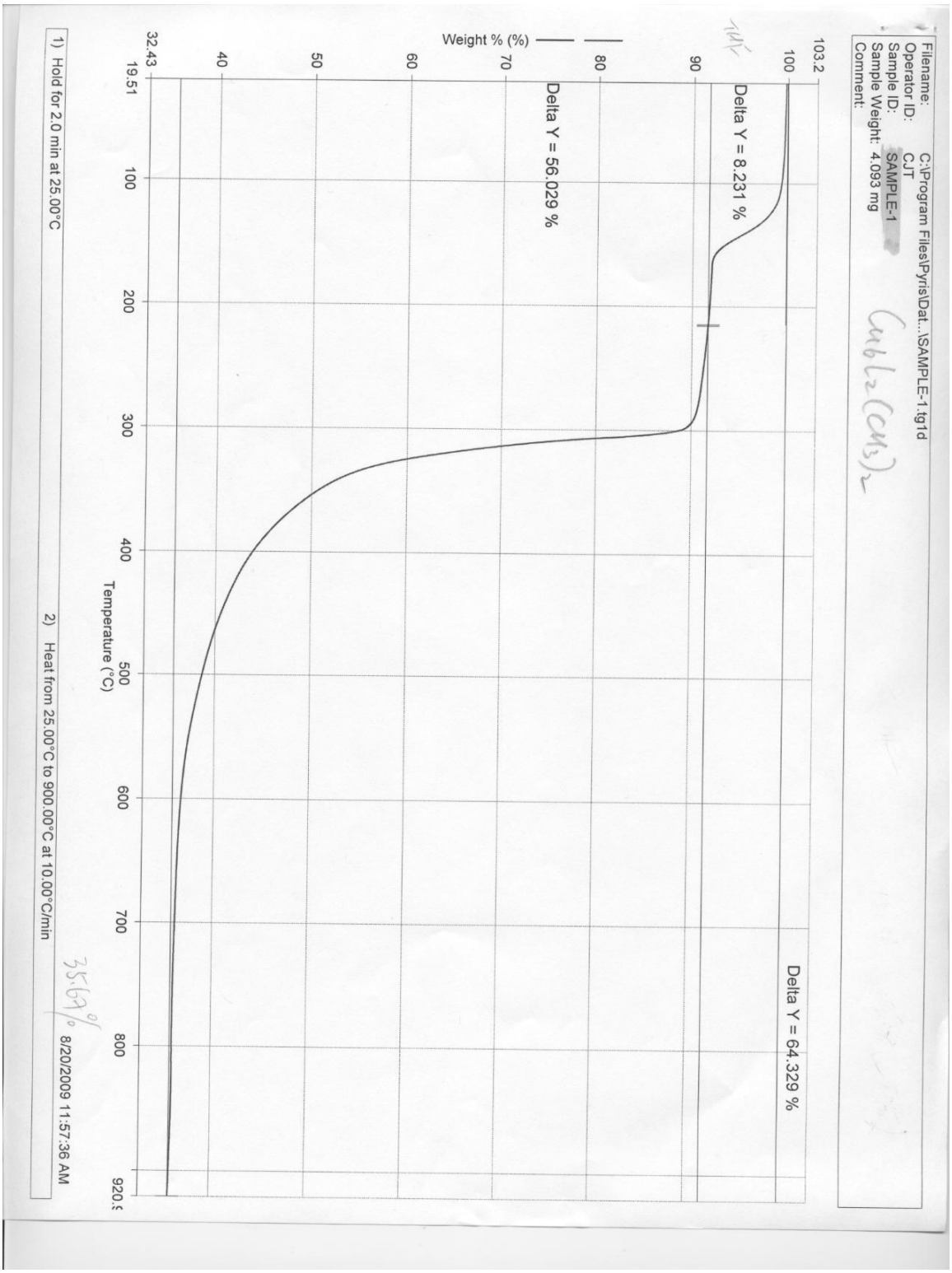


Figure S20. TGA of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**)

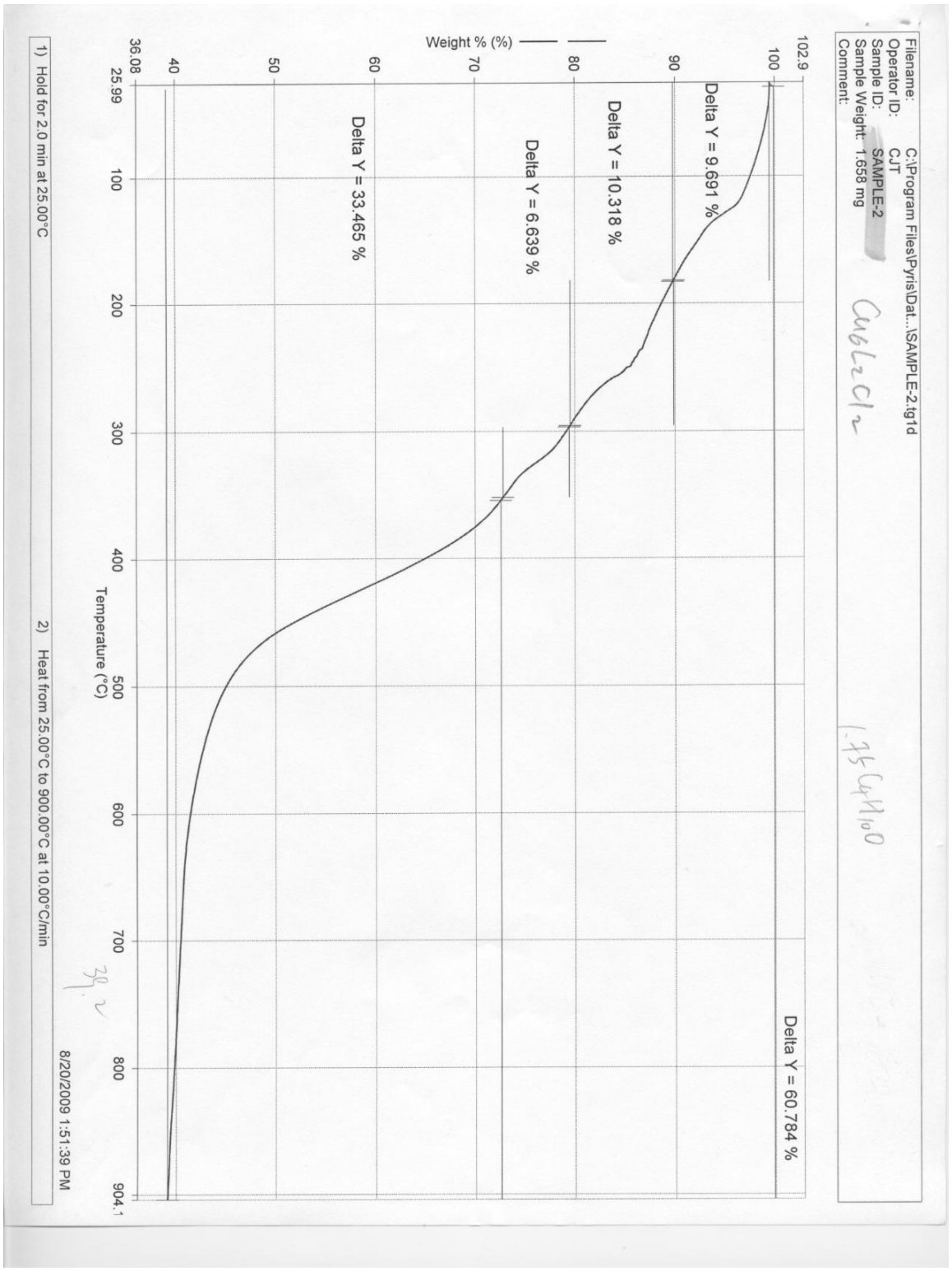


Figure S21. TGA of $[Cu_6Br_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**3**)

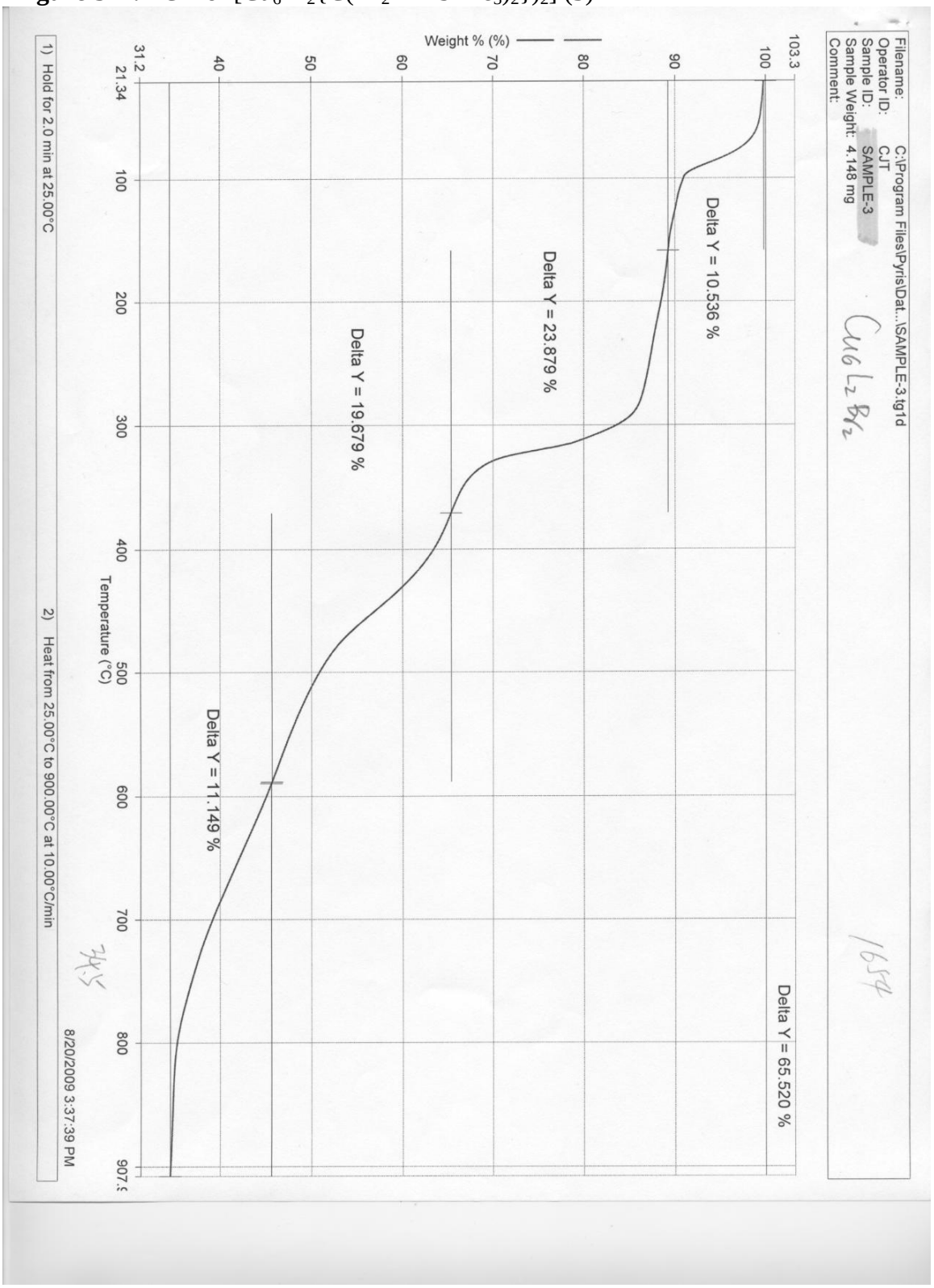


Figure S22. TGA of $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**4**)

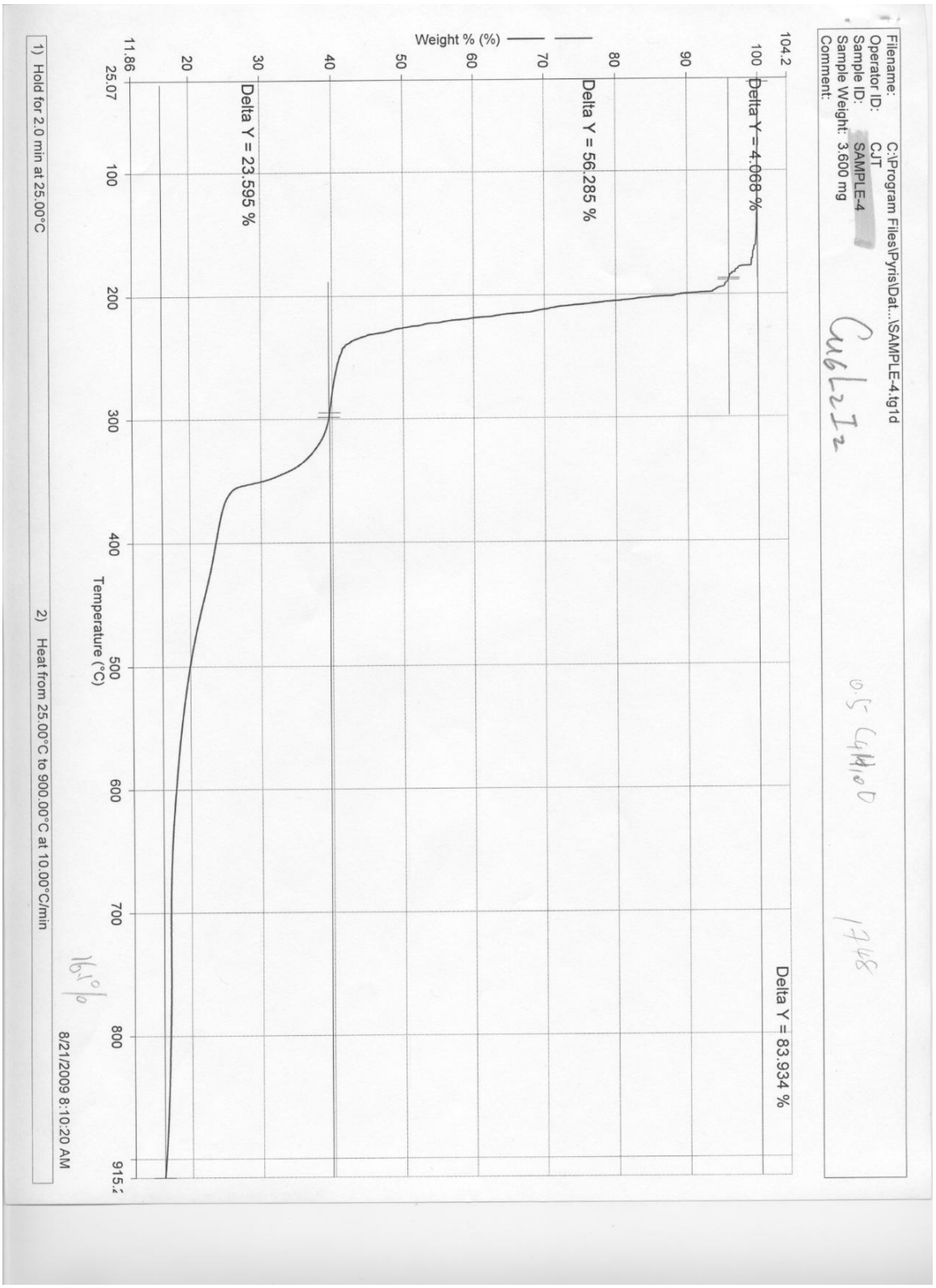


Figure S23. ^{31}P NMR of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**) in THF-d_8

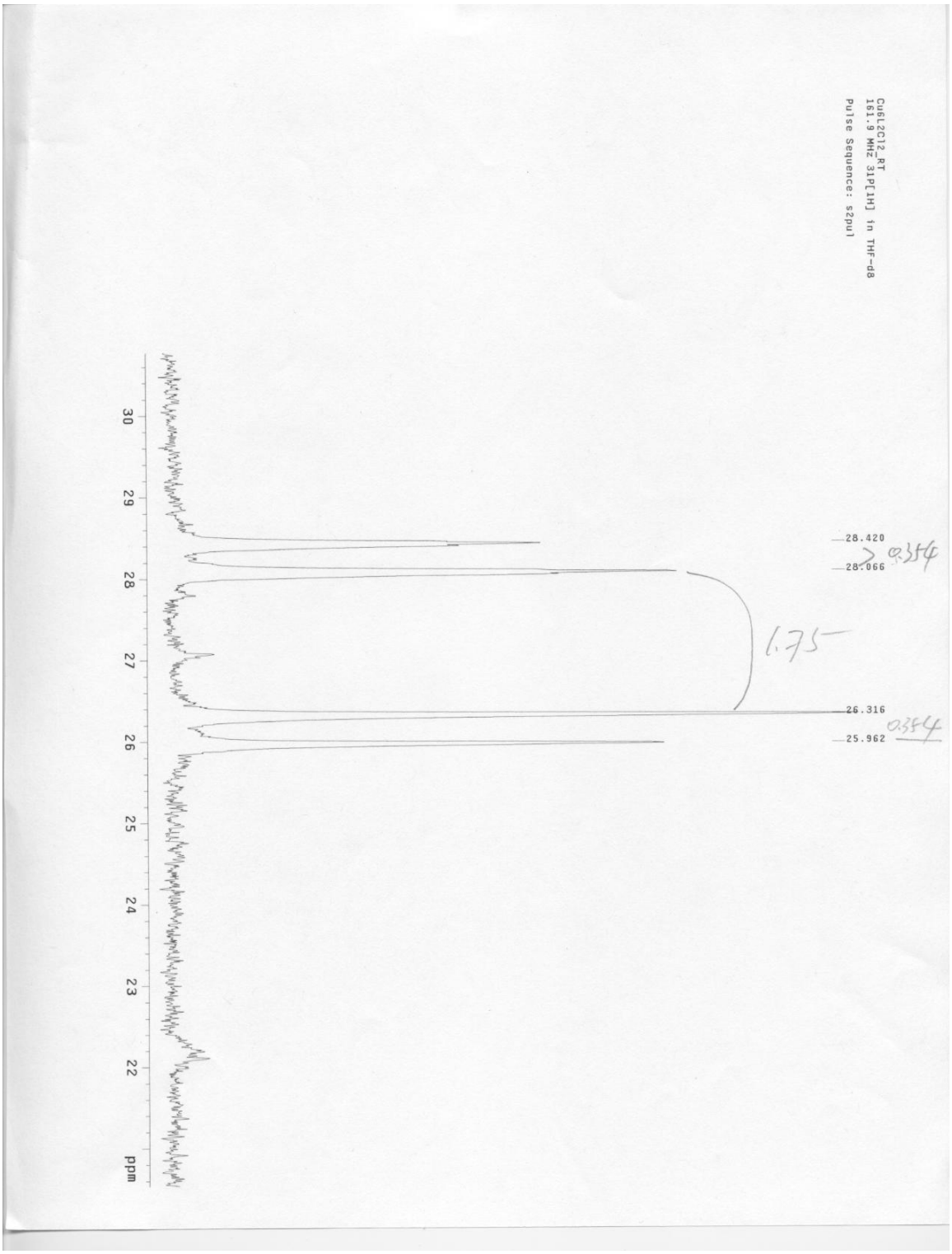


Figure S24. ^{31}P NMR of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**) in THF-d_8 following addition of a 2-fold molar ratio of Bu^tONa after 3 hours.

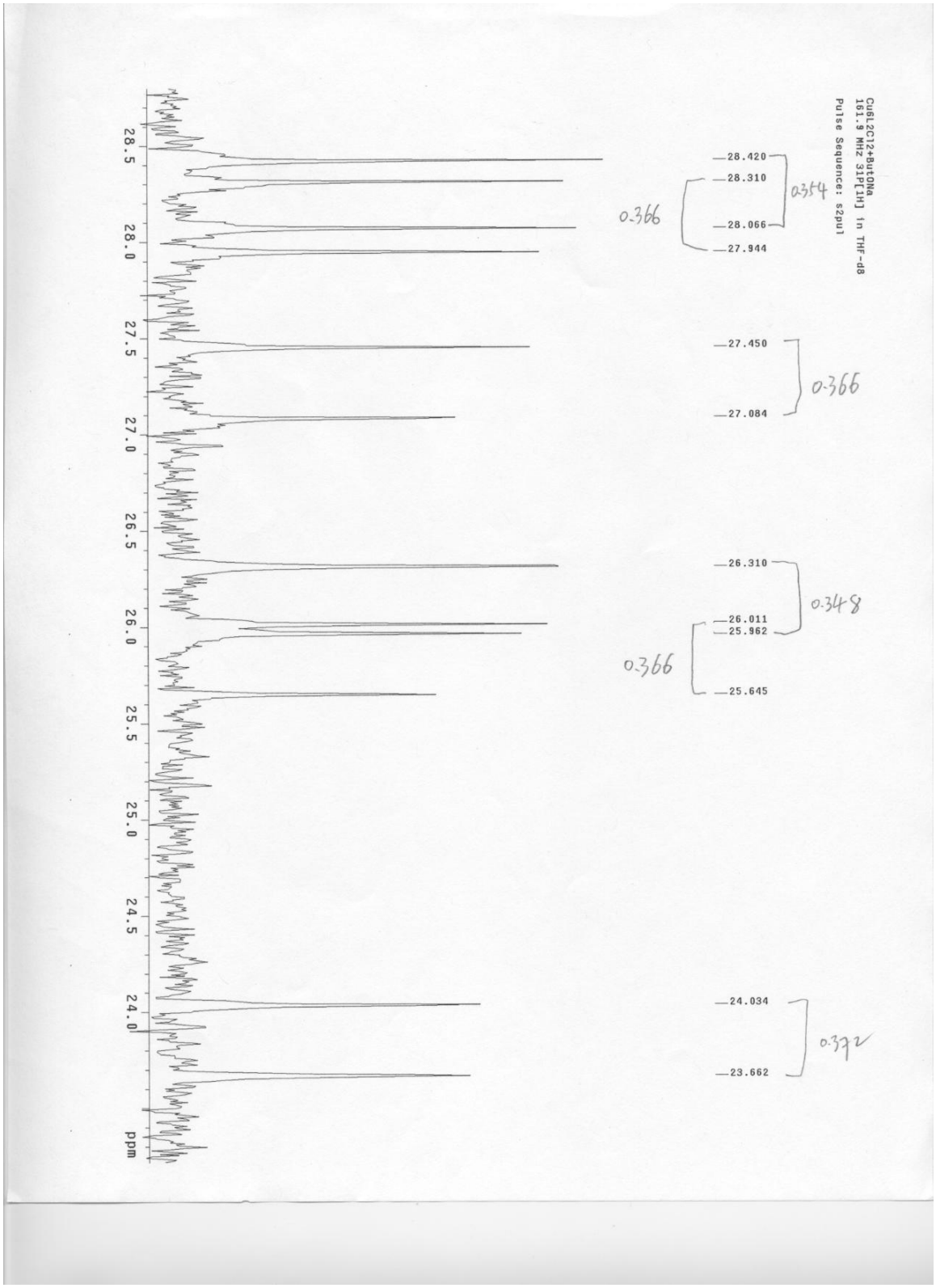


Figure S25. ^{31}P NMR of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**2**) in THF-d_8 following addition of a 2-fold molar ratio of Bu^tONa after two days.

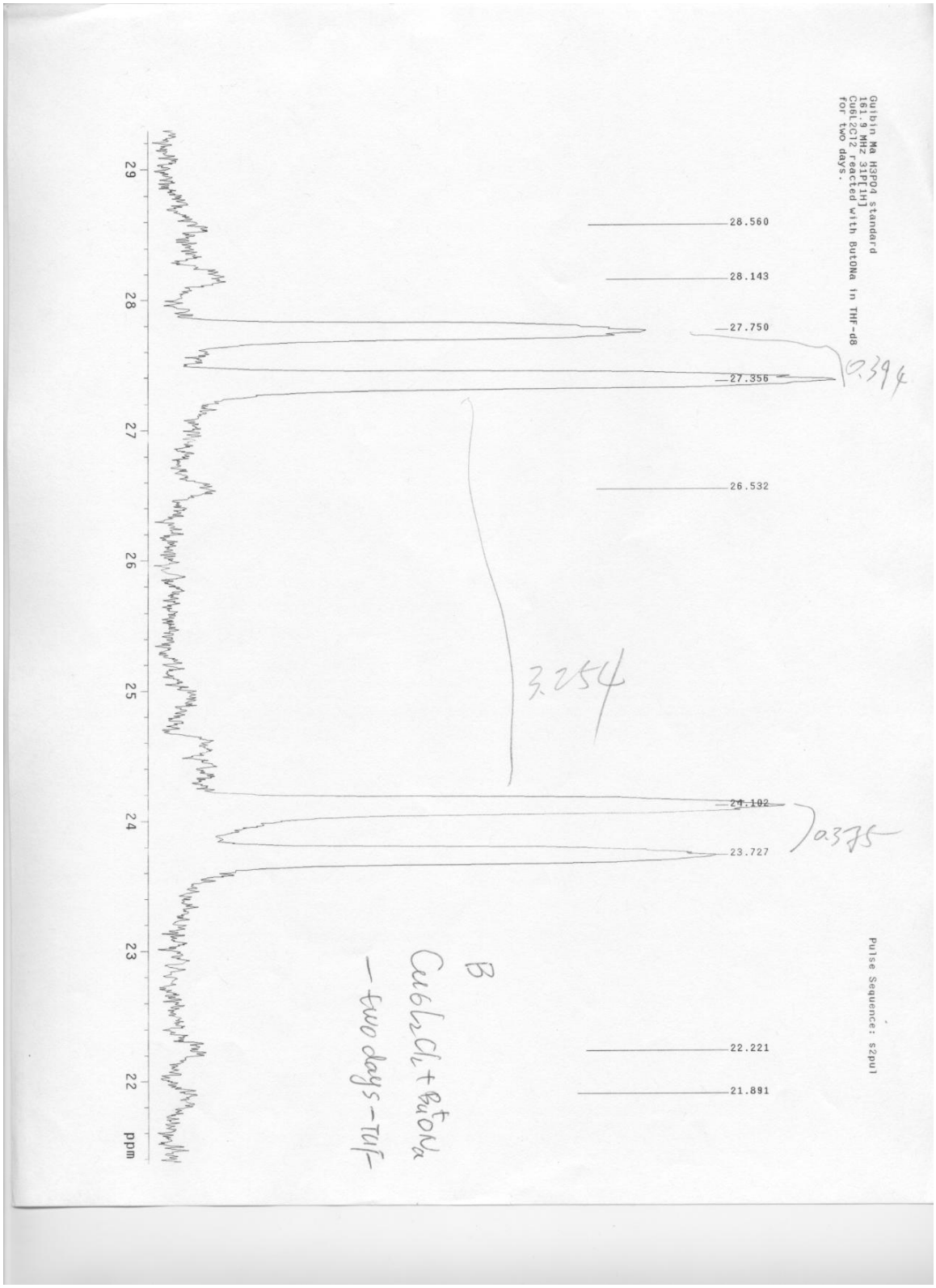


Figure 26. Simulated (top) and measured (bottom) ^{31}P NMR of $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**1**).

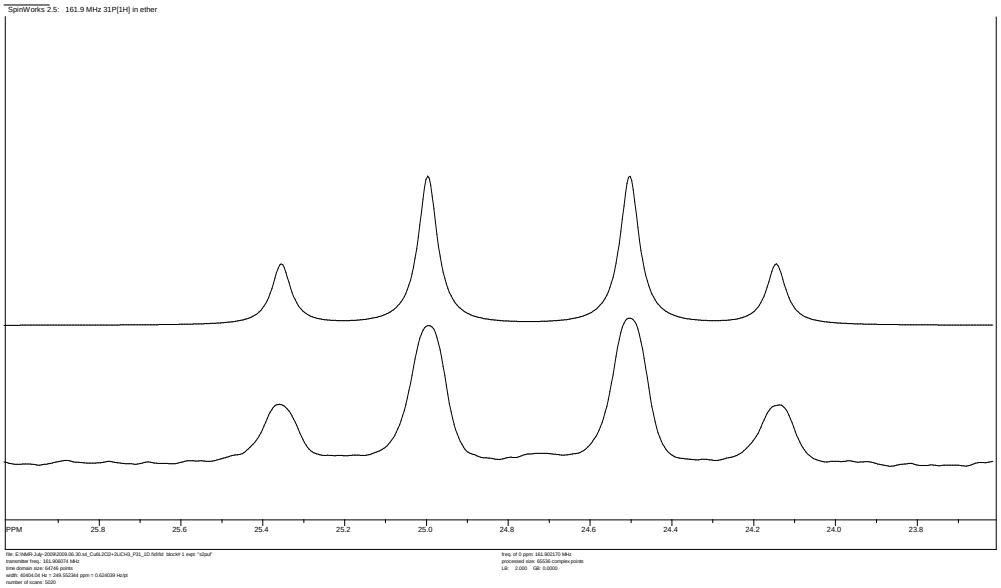


Figure 27. Simulated (top) and measured (bottom) ^{31}P NMR of $[Cu_6Cl_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**2**).

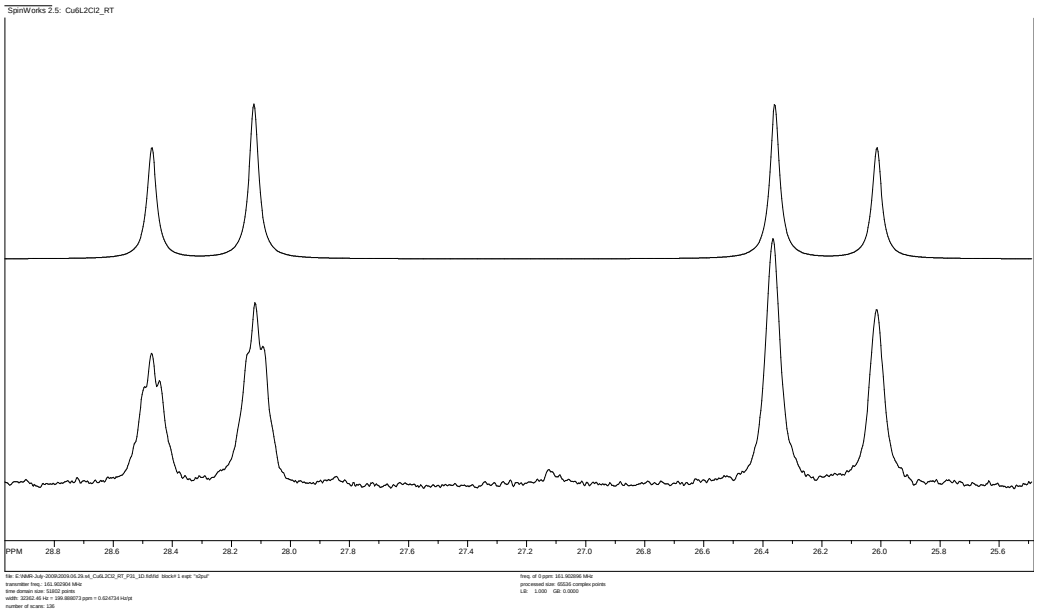


Figure 28. Simulated (top) and measured (bottom) ^{31}P NMR of $[Cu_6Br_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**3**).

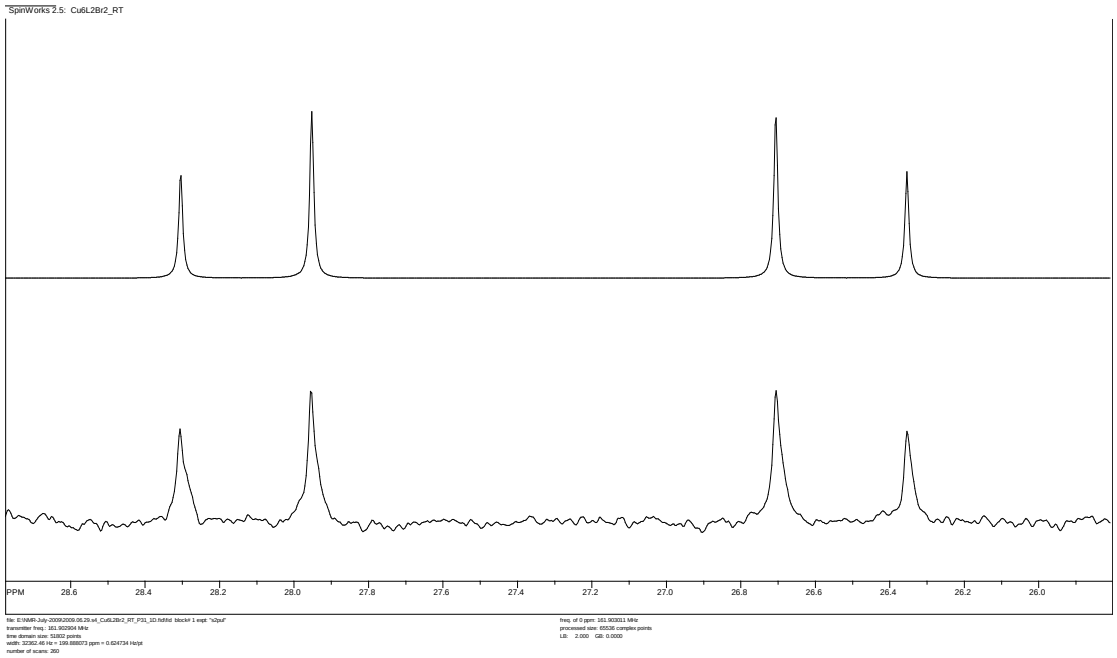


Figure 29. Simulated (top) and measured (bottom) ^{31}P NMR of $[Cu_6I_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**4**).

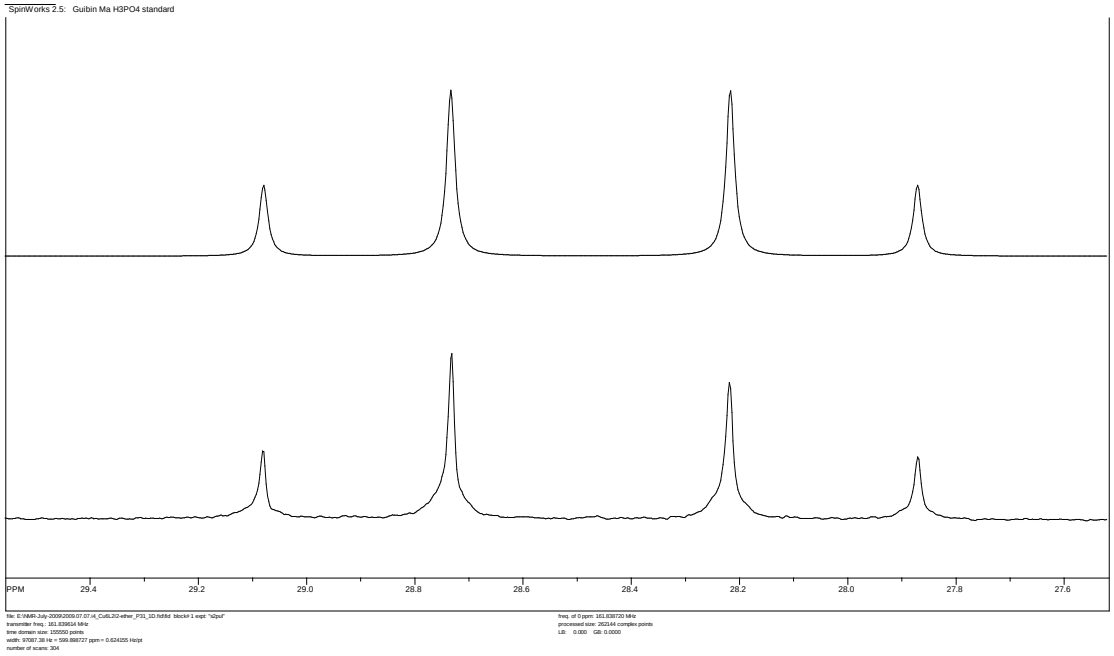


Figure 30. Simulated (top) and measured (bottom) ^{31}P NMR of $[Cu_6(OBu^t)_2\{C(Ph_2P{=}NSiMe_3)_2\})_2]$ (**5**).

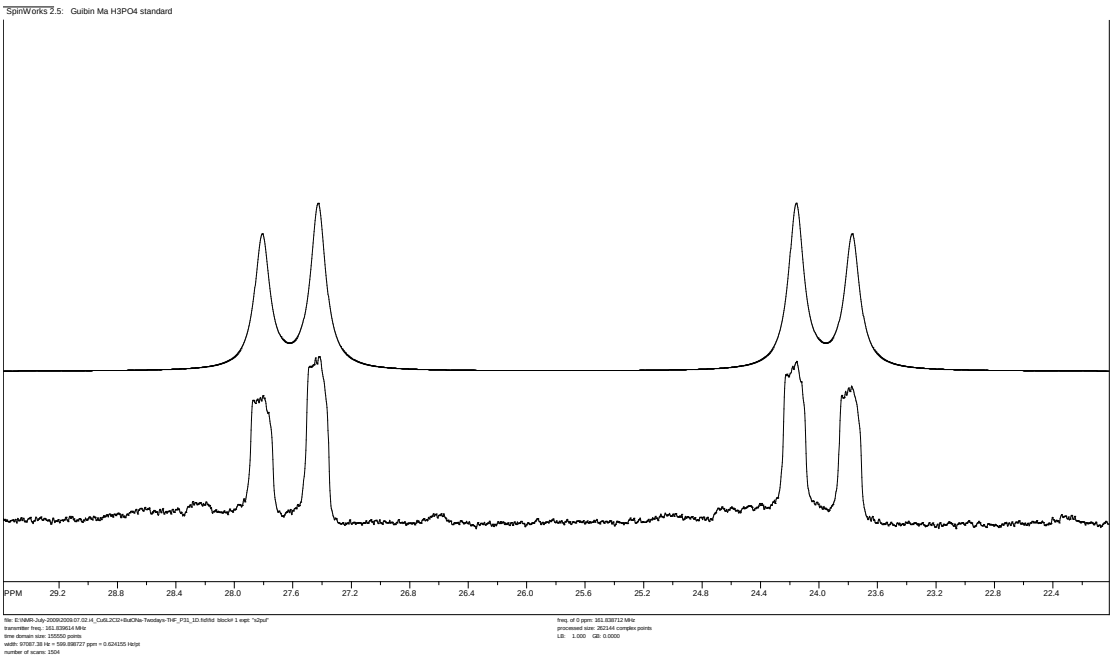
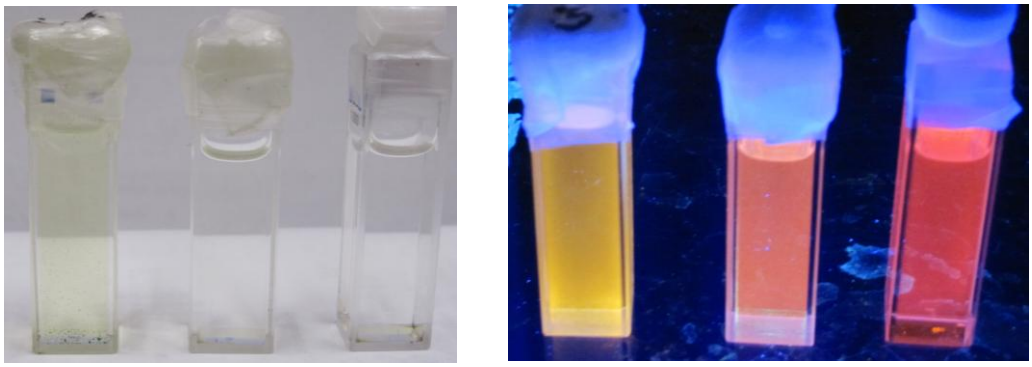


Figure S31: Color images of compounds of **1**, **2** and **4** under two different conditions; (a) without UV-light irradiation and (b) under UV-light irradiation in toluene



(a) **1** **2** **4**
Without UV-light irradiation

(b) **1** **2** 4
Under UV-light irradiation

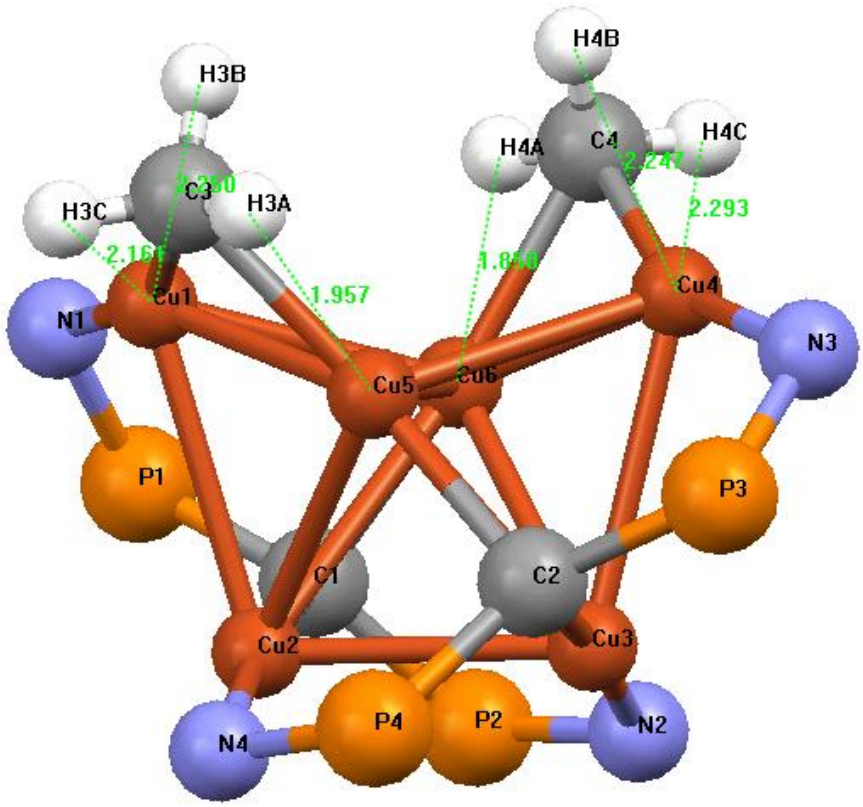


Figure S32. Diagram of core structure of $[Cu_6(CH_3)_2\{C(Ph_2P{=}NSiMe_3)_2\}_2]$ (**1**) showing (green lines) interactions between methyl protons and copper(I).

Table S1. Crystallographic Experimental Details for Compound **1**

formula	$C_{72}H_{98}Cu_6N_4O_2P_4Si_4$
formula weight	1669.02
crystal dimensions (mm)	0.37 × 0.27 × 0.23
crystal system	orthorhombic
space group	*Pbca* (No. 61)
unit cell parameters[a]	
a (Å)	22.8100 (15)
b (Å)	24.5879 (16)
c (Å)	27.1406 (18)
V (Å^3)	15221.8 (17)
Z	8
ρ_{calcd} (g cm^{-3})	1.457
μ (mm^{-1})	1.839
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.4°) (10 s exposures)
data collection 2θ limit (deg)	52.80
total data collected	117669 (-28 ≤ *h* ≤ 28, -30 ≤ *k* ≤ 30, -33 ≤ *l* ≤ 33)
independent reflections	15594 (R_{int} = 0.0495)
number of observed reflections (*NO*)	12598 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6792–0.5494
data/restraints/parameters	15594 / 0 / 829
goodness-of-fit (*S*)[d]	1.016 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[e]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0279
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0709
largest difference peak and hole	0.640 and –0.471 e Å^{-3}

[a]Obtained from least-squares refinement of 9930 reflections with 4.48° < 2θ < 52.36°.

[b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker.

[c]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122.

[d]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (*n* = number of data; *p* = number of parameters varied; **Table**

S1 (Continued)

$w = [\sigma^2(F_o^2) + (0.0310P)^2 + 13.8644P]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3)$.

[e] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S2. Crystallographic Experimental Details Compound **2**

formula	$C_{69}H_{93.50}Cl_2Cu_6N_4O_{1.75}P_4Si_4$
formula weight	1695.36
crystal dimensions (mm)	0.45 × 0.21 × 0.06
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell parameters[a]	
a (Å)	14.4174 (5)
b (Å)	21.7660 (7)
c (Å)	25.8932 (8)
α (deg)	100.5122 (4)
β (deg)	98.6051 (4)
γ (deg)	97.5673 (4)
V (Å^3)	7792.9 (4)
Z	4
ρ_{calcd} (g cm^{-3})	1.445
μ (mm^{-1})	1.863
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	53.16
total data collected	63501 ($-18 \le h \le 18$, $-27 \le k \le 27$, $-32 \le l \le 32$)
independent reflections	32339 (R_{int} = 0.0356)
number of observed reflections (*NO*)	23223 [$F_o^2 \ge 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.8900–0.4877
data/restraints/parameters	32339 [$F_o^2 \ge -3\sigma(F_o^2)$] / 20[d] / 1657
goodness-of-fit (S)[e]	1.010 [$F_o^2 \ge -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \ge 2\sigma(F_o^2)$]	0.0366

Table S2 (Continued)

wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0997
largest difference peak and hole	0.726 and –0.553 e Å^{-3}

[a]Obtained from least-squares refinement of 9869 reflections with 4.42° < 2θ < 51.98°. [b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. [c]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122. [d]Two of the solvent diethylether molecules had the following restraints applied during refinement: C–C, 1.530(4) Å; C–O, 1.430(4) Å; C···O, 2.420(4) Å; C···C, 2.340(4) Å. The anisotropic displacement parameter for oxygen atom O4S (in the half-occupancy solvent diethylether molecule) was restrained to approximate isotropic behavior by use of the *SHELXL* instruction **ISOR** during refinement. [e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0510P)^2]^{-1}$ where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$). [f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S3. Crystallographic Experimental Details Compound **3**

formula	$C_{62}H_{76}Br_2Cu_6N_4P_4Si_4$
formula weight	1654.57
crystal dimensions (mm)	0.25 × 0.24 × 0.14
crystal system	orthorhombic
space group	$P2_12_12_1$ (No. 19)
unit cell parameters[a]	
a (Å)	16.0037 (9)
b (Å)	19.4167 (11)
c (Å)	22.5945 (12)
V (Å^3)	7021.0 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.565
μ (mm^{-1})	3.122
B. Data Collection and Refinement Conditions	
diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.4°) (10 s exposures)
data collection 2θ limit (deg)	55.08
total data collected	61719 (-20 ≤ h ≤ 20, -25 ≤ k ≤ 25, -29 ≤ l ≤ 29)
independent reflections	16121 (R_{int} = 0.0546)

Table S3 (Continued)

number of observed reflections (*NO*)	13648 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	Patterson/structure expansion (*DIRDIF–2008*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[d])
absorption correction method	Gaussian integration (face-indexed)
range of transmission factors	0.6655–0.5079
data/restraints/parameters	16121 [$F_o^2 \geq -3\sigma(F_o^2)$] / 0 / 739
Flack absolute structure parameter[e]	0.003(5)
goodness-of-fit (*S*)[f]	1.024 [$F_o^2 \geq -3\sigma(F_o^2)$]
final *R* indices[g]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0348
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.0796
largest difference peak and hole	1.966 and –0.681 e Å^{-3}

[a]Obtained from least-squares refinement of 6303 reflections with 4.42° < 2θ < 36.98°. [b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. [c]Beurskens, P. T.; Beurskens, G.; de Gelder, R.; Smits, J. M. M; Garcia-Granda, S.; Gould, R. O. (2008). The *DIRDIF-2008* program system. Crystallography Laboratory, Radboud University Nijmegen, The Netherlands. [d]Sheldrick, G. M. *Acta Crystallogr*. **2008**, *A64*, 112–122. [e]Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876–881; Flack, H. D.; Bernardinelli, G. *Acta Crystallogr*. **1999**, *A55*, 908–915; Flack, H. D.; Bernardinelli, G. *J. Appl. Cryst*. **2000**, *33*, 1143–1148. The Flack parameter will refine to a value near zero if the structure is in the correct configuration and will refine to a value near one for the inverted configuration. [f]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0392P)^2]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). [g]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S4. Crystallographic Experimental Details Compound **4**

formula	$C_{64}H_{81}Cu_6I_2N_4O_{0.50}P_4Si_4$
formula weight	1785.61
crystal dimensions (mm)	0.33 × 0.31 × 0.25
crystal system	monoclinic
space group	$P2_1/n$ (an alternate setting of $P2_1/c$ [No. 14])
unit cell parameters[a]	
a (Å)	14.6629 (8)
b (Å)	23.1444 (12)
c (Å)	21.4145 (11)

Table S4 (Continued)

β (deg)	99.6880 (10)
V (Å^3)	7163.7 (7)
Z	4
ρ_{calcd} (g cm^{-3})	1.656
μ (mm^{-1})	2.809

B. Data Collection and Refinement Conditions

diffractometer	Bruker D8/APEX II CCD[b]
radiation (λ [Å])	graphite-monochromated Mo Kα (0.71073)
temperature (°C)	–100
scan type	ω scans (0.3°) (20 s exposures)
data collection 2θ limit (deg)	55.06
total data collected	62625 (-19 ≤ h ≤ 19, -30 ≤ k ≤ 29, -27 ≤ l ≤ 27)
independent reflections	16410 (R_{int} = 0.0238)
number of observed reflections (*NO*)	13756 [$F_o^2 \geq 2\sigma(F_o^2)$]
structure solution method	direct methods (*SHELXS–97*[c])
refinement method	full-matrix least-squares on F^2 (*SHELXL–97*[c])
absorption correction method	multi-scan (*SADABS*)
range of transmission factors	0.4981–0.4263
data/restraints/parameters	16410 [$F_o^2 \geq -3\sigma(F_o^2)$] /7[d] / 758
goodness-of-fit (S)[e]	1.025 [$F_o^2 \geq -3\sigma(F_o^2)$]
final R indices[f]	
R_1 [$F_o^2 \geq 2\sigma(F_o^2)$]	0.0485
wR_2 [$F_o^2 \geq -3\sigma(F_o^2)$]	0.1331
largest difference peak and hole	3.480 and –2.196 e Å^{-3}

[a]Obtained from least-squares refinement of 9677 reflections with 4.50° < 2θ < 54.72°. [b]Programs for diffractometer operation, data collection, data reduction and absorption correction were those supplied by Bruker. [c]Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112–122. [d]The partially occupied/disordered diethylether solvent molecule had the following distances restrains applied during refinement: O–C, 1.43(1) Å; C–C, 1.53(1) Å; C2S···C3S, 2.34(1) Å; C1S···O1S and C4S···O1S, 2.42(1) Å. [e]$S = [\Sigma w(F_o^2 - F_c^2)^2/(n-p)]^{1/2}$ (n = number of data; p = number of parameters varied; $w = [\sigma^2(F_o^2) + (0.0608P)^2 + 26.9806P]^{-1}$ where $P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). [f]$R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^4)]^{1/2}$.

Table S5. ^{31}P NMR Chemical Shifts and Spin-Spin Coupling Constants

Compounds	P_A (ppm)	P_B (ppm)	J_{A-B} (Hz.)	Solvent
$Cu_6L_2(CH_3)_2$ (**1**)	25.14	24.33	58	Toluene
$Cu_6L_2(Cl)_2$ (**2**)	28.24	26.17	56	THF
$Cu_6L_2(Br)_2$ (**3**)	28.10	26.59	57	THF
$Cu_6L_2(I)_2$ (**4**)	28.95	28.08	56	THF
$Cu_6L_2(OBu^t)_2$ (**5**)	27.58	23.95	62	THF

L = $[C\{Ph_2P{=}NSi(CH_3)_3\}_2^{2-}]$

Table S6. Selected Bond Distances for Compound **1**.

Cu(1)	Cu(2)	2.7546(4)
Cu(1)	Cu(5)	2.4047(4)
Cu(1)	Cu(6)	2.6128(4)
Cu(1)	N(1)	1.9077(18)
Cu(1)	C(3)	1.979(2)
Cu(2)	Cu(3)	2.5649(4)
Cu(2)	Cu(5)	2.6502(4)
Cu(2)	Cu(6)	2.7732(4)
Cu(2)	N(4)	1.9325(18)
Cu(2)	C(1)	1.961(2)
Cu(3)	Cu(4)	2.7496(4)
Cu(3)	Cu(5)	2.7785(4)
Cu(3)	Cu(6)	2.7046(4)
Cu(3)	N(2)	1.9249(18)
Cu(3)	C(2)	1.953(2)
Cu(4)	Cu(5)	2.6512(4)
Cu(4)	Cu(6)	2.4000(4)
Cu(4)	N(3)	1.9178(18)
Cu(4)	C(4)	1.992(2)
Cu(5)	Cu(6)	2.7472(4)
Cu(5)	C(2)	1.992(2)
Cu(5)	C(3)	2.057(3)
Cu(6)	C(1)	1.993(2)
Cu(6)	C(4)	2.047(3)

Table S7. Selected Interatomic Angles (deg) for Compound **1**

Cu(2)	Cu(1)	Cu(5)	61.374(10)
Cu(2)	Cu(1)	Cu(6)	62.155(10)
Cu(2)	Cu(1)	N(1)	91.48(6)
Cu(2)	Cu(1)	C(3)	109.59(8)
Cu(5)	Cu(1)	Cu(6)	66.244(12)
Cu(5)	Cu(1)	N(1)	147.53(6)
Cu(5)	Cu(1)	C(3)	54.95(8)
Cu(6)	Cu(1)	N(1)	85.98(6)
Cu(6)	Cu(1)	C(3)	110.94(9)
N(1)	Cu(1)	C(3)	157.30(9)
Cu(1)	Cu(2)	Cu(3)	105.540(12)
Cu(1)	Cu(2)	Cu(5)	52.795(10)
Cu(1)	Cu(2)	Cu(6)	56.413(10)
Cu(1)	Cu(2)	N(4)	109.79(6)
Cu(1)	Cu(2)	C(1)	77.81(6)
Cu(3)	Cu(2)	Cu(5)	64.363(10)
Cu(3)	Cu(2)	Cu(6)	60.733(10)
Cu(3)	Cu(2)	N(4)	90.48(6)
Cu(3)	Cu(2)	C(1)	85.87(6)
Cu(5)	Cu(2)	Cu(6)	60.818(11)
Cu(5)	Cu(2)	N(4)	78.31(6)
Cu(5)	Cu(2)	C(1)	106.11(6)
Cu(6)	Cu(2)	N(4)	136.82(6)
Cu(6)	Cu(2)	C(1)	45.92(6)
N(4)	Cu(2)	C(1)	172.25(8)
Cu(2)	Cu(3)	Cu(4)	104.647(12)
Cu(2)	Cu(3)	Cu(5)	59.307(10)
Cu(2)	Cu(3)	Cu(6)	63.444(10)
Cu(2)	Cu(3)	N(2)	91.50(6)
Cu(2)	Cu(3)	C(2)	85.81(6)
Cu(4)	Cu(3)	Cu(5)	57.313(11)
Cu(4)	Cu(3)	Cu(6)	52.203(10)
Cu(4)	Cu(3)	N(2)	108.02(6)
Cu(4)	Cu(3)	C(2)	77.75(6)
Cu(5)	Cu(3)	Cu(6)	60.119(10)
Cu(5)	Cu(3)	N(2)	136.23(6)
Cu(5)	Cu(3)	C(2)	45.80(6)
Cu(6)	Cu(3)	N(2)	78.27(6)
Cu(6)	Cu(3)	C(2)	105.07(6)
N(2)	Cu(3)	C(2)	174.12(9)
Cu(3)	Cu(4)	Cu(5)	61.892(10)

Table S7 (continued)

Cu(3)	Cu(4)	Cu(6)	62.933(11)
Cu(3)	Cu(4)	N(3)	85.47(6)
Cu(3)	Cu(4)	C(4)	116.00(8)
Cu(5)	Cu(4)	Cu(6)	65.676(12)
Cu(5)	Cu(4)	N(3)	92.82(6)
Cu(5)	Cu(4)	C(4)	101.01(8)
Cu(6)	Cu(4)	N(3)	147.24(6)
Cu(6)	Cu(4)	C(4)	54.62(7)
N(3)	Cu(4)	C(4)	158.11(9)
Cu(1)	Cu(5)	Cu(2)	65.831(11)
Cu(1)	Cu(5)	Cu(3)	109.447(13)
Cu(1)	Cu(5)	Cu(4)	104.475(14)
Cu(1)	Cu(5)	Cu(6)	60.514(11)
Cu(1)	Cu(5)	C(2)	148.40(6)
Cu(1)	Cu(5)	C(3)	51.95(7)
Cu(2)	Cu(5)	Cu(3)	56.330(10)
Cu(2)	Cu(5)	Cu(4)	105.069(13)
Cu(2)	Cu(5)	Cu(6)	61.805(10)
Cu(2)	Cu(5)	C(2)	82.75(6)
Cu(2)	Cu(5)	C(3)	110.98(7)
Cu(3)	Cu(5)	Cu(4)	60.795(11)
Cu(3)	Cu(5)	Cu(6)	58.606(10)
Cu(3)	Cu(5)	C(2)	44.65(6)
Cu(3)	Cu(5)	C(3)	160.94(7)
Cu(4)	Cu(5)	Cu(6)	52.756(10)
Cu(4)	Cu(5)	C(2)	79.62(6)
Cu(4)	Cu(5)	C(3)	115.73(9)
Cu(6)	Cu(5)	C(2)	102.44(6)
Cu(6)	Cu(5)	C(3)	103.60(7)
C(2)	Cu(5)	C(3)	153.92(10)
Cu(1)	Cu(6)	Cu(2)	61.433(11)
Cu(1)	Cu(6)	Cu(3)	105.642(13)
Cu(1)	Cu(6)	Cu(4)	105.788(14)
Cu(1)	Cu(6)	Cu(5)	53.242(10)
Cu(1)	Cu(6)	C(1)	80.91(6)
Cu(1)	Cu(6)	C(4)	103.16(9)
Cu(2)	Cu(6)	Cu(3)	55.823(10)
Cu(2)	Cu(6)	Cu(4)	108.641(13)
Cu(2)	Cu(6)	Cu(5)	57.377(10)
Cu(2)	Cu(6)	C(1)	44.98(6)
Cu(2)	Cu(6)	C(4)	153.83(8)

Table S7 (continued)

Cu(3)	Cu(6)	Cu(4)	64.864(11)
Cu(3)	Cu(6)	Cu(5)	61.275(10)
Cu(3)	Cu(6)	C(1)	81.54(6)
Cu(3)	Cu(6)	C(4)	115.82(7)
Cu(4)	Cu(6)	Cu(5)	61.568(11)
Cu(4)	Cu(6)	C(1)	146.37(6)
Cu(4)	Cu(6)	C(4)	52.49(7)
Cu(5)	Cu(6)	C(1)	101.77(6)
Cu(5)	Cu(6)	C(4)	96.51(8)
Cu(2)	C(1)	Cu(6)	89.09(8)
Cu(2)	C(1)	P(1)	114.51(11)
Cu(2)	C(1)	P(2)	106.75(10)
Cu(6)	C(1)	P(1)	105.76(10)
Cu(6)	C(1)	P(2)	102.41(10)
P(1)	C(1)	P(2)	129.63(12)
Cu(3)	C(2)	Cu(5)	89.55(8)
Cu(3)	C(2)	P(3)	109.09(11)
Cu(3)	C(2)	P(4)	109.56(11)
Cu(5)	C(2)	P(3)	112.32(11)
Cu(5)	C(2)	P(4)	99.19(10)
P(3)	C(2)	P(4)	129.51(12)
Cu(1)	C(3)	Cu(5)	73.10(8)
Cu(4)	C(4)	Cu(6)	72.89(8)

Table S8. Selected Bond Distances for Compound **2**.

(a) within molecule A

Cu(1)	Cu(2)	2.8289(5)
Cu(1)	Cu(5)	2.7326(6)
Cu(1)	Cu(6)	2.6113(6)
Cu(1)	Cl(1)	2.1543(10)
Cu(1)	N(1)	1.896(3)
Cu(2)	Cu(3)	2.5782(5)
Cu(2)	Cu(5)	2.7491(6)
Cu(2)	Cu(6)	2.7643(5)
Cu(2)	N(4)	1.927(2)
Cu(2)	C(1)	1.951(3)
Cu(3)	Cu(4)	2.7820(5)
Cu(3)	Cu(5)	2.7425(5)
Cu(3)	Cu(6)	2.7640(5)
Cu(3)	N(2)	1.912(2)
Cu(3)	C(2)	1.945(3)
Cu(4)	Cu(5)	2.6379(6)
Cu(4)	Cu(6)	2.6738(6)
Cu(4)	Cl(2)	2.1491(9)
Cu(4)	N(3)	1.897(2)
Cu(5)	Cu(6)	2.9458(5)
Cu(5)	Cl(1)	2.1635(9)
Cu(5)	C(2)	1.969(3)
Cu(6)	Cl(2)	2.1829(9)
Cu(6)	C(1)	1.967(3)
P(1)	N(1)	1.614(3)
P(1)	C(1)	1.749(3)
P(1)	C(11)	1.829(3)
P(1)	C(21)	1.835(3)
P(2)	N(2)	1.613(3)
P(2)	C(1)	1.750(3)
P(2)	C(31)	1.822(3)
P(2)	C(41)	1.822(3)
P(3)	N(3)	1.608(3)
P(3)	C(2)	1.745(3)
P(3)	C(51)	1.829(3)
P(3)	C(61)	1.815(3)
P(4)	N(4)	1.615(3)
P(4)	C(2)	1.744(3)
P(4)	C(71)	1.825(3)

Table S8 (continued)

(b) within molecule B

Cu(1)	Cu(2)	2.8317(6)
Cu(1)	Cu(5)	2.7429(6)
Cu(1)	Cu(6)	2.6264(6)
Cu(1)	Cl(1)	2.1447(10)
Cu(1)	N(1)	1.893(3)
Cu(2)	Cu(3)	2.5982(5)
Cu(2)	Cu(5)	2.7593(5)
Cu(2)	Cu(6)	2.7301(5)
Cu(2)	N(4)	1.928(3)
Cu(2)	C(1)	1.954(3)
Cu(3)	Cu(4)	2.7688(5)
Cu(3)	Cu(5)	2.7397(5)
Cu(3)	Cu(6)	2.7059(5)
Cu(3)	N(2)	1.917(3)
Cu(3)	C(2)	1.945(3)
Cu(4)	Cu(5)	2.6510(6)
Cu(4)	Cu(6)	2.6624(6)
Cu(4)	Cl(2)	2.1489(10)
Cu(4)	N(3)	1.891(3)
Cu(5)	Cu(6)	2.8840(6)
Cu(5)	Cl(1)	2.1659(10)
Cu(5)	C(2)	1.967(3)
Cu(6)	Cl(2)	2.1703(9)
Cu(6)	C(1)	1.966(3)
P(1)	N(1)	1.614(3)
P(1)	C(1)	1.740(3)

Table S9. Selected Interatomic Angles (deg) for Compound **2**

(a) within molecule A

Cu(2)	Cu(1)	Cu(5)	59.218(14)
Cu(2)	Cu(1)	Cu(6)	60.922(14)
Cu(2)	Cu(1)	Cl(1)	107.82(3)
Cu(2)	Cu(1)	N(1)	85.49(8)
Cu(5)	Cu(1)	Cu(6)	66.860(15)
Cu(5)	Cu(1)	Cl(1)	50.89(3)
Cu(5)	Cu(1)	N(1)	143.59(8)
Cu(6)	Cu(1)	Cl(1)	102.46(3)
Cu(6)	Cu(1)	N(1)	89.30(8)
Cl(1)	Cu(1)	N(1)	165.32(8)
Cu(1)	Cu(2)	Cu(3)	106.353(17)
Cu(1)	Cu(2)	Cu(5)	58.645(14)
Cu(1)	Cu(2)	Cu(6)	55.649(13)
Cu(1)	Cu(2)	N(4)	108.92(8)
Cu(1)	Cu(2)	C(1)	77.51(9)
Cu(3)	Cu(2)	Cu(5)	61.872(14)
Cu(3)	Cu(2)	Cu(6)	62.195(14)
Cu(3)	Cu(2)	N(4)	93.05(8)
Cu(3)	Cu(2)	C(1)	85.82(9)
Cu(5)	Cu(2)	Cu(6)	64.592(14)
Cu(5)	Cu(2)	N(4)	75.04(8)
Cu(5)	Cu(2)	C(1)	109.85(9)
Cu(6)	Cu(2)	N(4)	138.97(8)
Cu(6)	Cu(2)	C(1)	45.36(9)
N(4)	Cu(2)	C(1)	173.51(12)
Cu(2)	Cu(3)	Cu(4)	106.757(17)
Cu(2)	Cu(3)	Cu(5)	62.128(14)
Cu(2)	Cu(3)	Cu(6)	62.208(14)
Cu(2)	Cu(3)	N(2)	93.50(8)
Cu(2)	Cu(3)	C(2)	85.77(9)
Cu(4)	Cu(3)	Cu(5)	57.039(14)
Cu(4)	Cu(3)	Cu(6)	57.645(13)
Cu(4)	Cu(3)	N(2)	106.54(7)
Cu(4)	Cu(3)	C(2)	79.82(9)
Cu(5)	Cu(3)	Cu(6)	64.682(14)
Cu(5)	Cu(3)	N(2)	138.79(7)
Cu(5)	Cu(3)	C(2)	45.87(8)
Cu(6)	Cu(3)	N(2)	74.70(7)
Cu(6)	Cu(3)	C(2)	110.46(9)

Table S9 (continued)

(b) within molecule B

Cu(2)	Cu(1)	Cu(5)	59.312(14)
Cu(2)	Cu(1)	Cu(6)	59.883(14)
Cu(2)	Cu(1)	Cl(1)	107.22(3)
Cu(2)	Cu(1)	N(1)	87.39(8)
Cu(5)	Cu(1)	Cu(6)	64.933(16)
Cu(5)	Cu(1)	Cl(1)	50.82(3)
Cu(5)	Cu(1)	N(1)	144.63(8)
Cu(6)	Cu(1)	Cl(1)	102.43(4)
Cu(6)	Cu(1)	N(1)	89.14(8)
Cl(1)	Cu(1)	N(1)	164.54(8)
Cu(1)	Cu(2)	Cu(3)	106.360(17)
Cu(1)	Cu(2)	Cu(5)	58.741(14)
Cu(1)	Cu(2)	Cu(6)	56.323(14)
Cu(1)	Cu(2)	N(4)	108.64(8)
Cu(1)	Cu(2)	C(1)	77.20(9)
Cu(3)	Cu(2)	Cu(5)	61.423(14)
Cu(3)	Cu(2)	Cu(6)	60.980(14)
Cu(3)	Cu(2)	N(4)	92.67(8)
Cu(3)	Cu(2)	C(1)	85.94(9)
Cu(5)	Cu(2)	Cu(6)	63.384(14)
Cu(5)	Cu(2)	N(4)	74.89(7)
Cu(5)	Cu(2)	C(1)	109.25(9)
Cu(6)	Cu(2)	N(4)	137.46(7)
Cu(6)	Cu(2)	C(1)	46.05(9)
N(4)	Cu(2)	C(1)	174.14(12)
Cu(2)	Cu(3)	Cu(4)	107.619(18)
Cu(2)	Cu(3)	Cu(5)	62.188(14)
Cu(2)	Cu(3)	Cu(6)	61.917(14)
Cu(2)	Cu(3)	N(2)	93.21(8)
Cu(2)	Cu(3)	C(2)	85.97(9)
Cu(4)	Cu(3)	Cu(5)	57.533(15)
Cu(4)	Cu(3)	Cu(6)	58.184(14)
Cu(4)	Cu(3)	N(2)	105.82(8)
Cu(4)	Cu(3)	C(2)	79.54(9)
Cu(5)	Cu(3)	Cu(6)	63.954(15)
Cu(5)	Cu(3)	N(2)	137.91(8)
Cu(5)	Cu(3)	C(2)	45.87(9)
Cu(6)	Cu(3)	N(2)	74.47(8)
Cu(6)	Cu(3)	C(2)	109.72(9)

Table S10. Selected Bond Distances for Compound **3**.

Br(1)	Cu(1)	2.2658(6)
Br(1)	Cu(5)	2.3077(6)
Br(2)	Cu(4)	2.2647(6)
Br(2)	Cu(6)	2.3187(6)
Cu(1)	Cu(2)	2.8031(7)
Cu(1)	Cu(5)	2.7254(7)
Cu(1)	Cu(6)	2.6288(7)
Cu(1)	N(1)	1.905(3)
Cu(2)	Cu(3)	2.5853(6)
Cu(2)	Cu(5)	2.7414(6)
Cu(2)	Cu(6)	2.7629(6)
Cu(2)	N(4)	1.924(3)
Cu(2)	C(1)	1.944(4)
Cu(3)	Cu(4)	2.7894(7)
Cu(3)	Cu(5)	2.7300(6)
Cu(3)	Cu(6)	2.7214(6)
Cu(3)	N(2)	1.925(3)
Cu(3)	C(2)	1.948(4)
Cu(4)	Cu(5)	2.6472(7)
Cu(4)	Cu(6)	2.7109(7)
Cu(4)	N(3)	1.907(3)
Cu(5)	Cu(6)	2.8557(7)
Cu(5)	C(2)	1.974(4)
Cu(6)	C(1)	1.981(4)
P(1)	N(1)	1.606(3)
P(1)	C(1)	1.752(4)
P(1)	C(11)	1.834(4)
P(1)	C(21)	1.824(4)
P(2)	N(2)	1.612(3)
P(2)	C(1)	1.755(4)
P(2)	C(31)	1.827(4)

Table S11. Selected Interatomic Angles (deg) for Compound **3.**

Cu(1)	Br(1)	Cu(5)	73.15(2)
Cu(4)	Br(2)	Cu(6)	72.51(2)
Br(1)	Cu(1)	Cu(2)	111.29(2)
Br(1)	Cu(1)	Cu(5)	54.134(17)
Br(1)	Cu(1)	Cu(6)	101.73(2)
Br(1)	Cu(1)	N(1)	161.61(9)
Cu(2)	Cu(1)	Cu(5)	59.433(17)
Cu(2)	Cu(1)	Cu(6)	61.047(17)
Cu(2)	Cu(1)	N(1)	86.12(9)
Cu(5)	Cu(1)	Cu(6)	64.436(18)
Cu(5)	Cu(1)	N(1)	144.23(9)
Cu(6)	Cu(1)	N(1)	91.75(9)
Cu(1)	Cu(2)	Cu(3)	107.01(2)
Cu(1)	Cu(2)	Cu(5)	58.874(16)
Cu(1)	Cu(2)	Cu(6)	56.361(16)
Cu(1)	Cu(2)	N(4)	110.57(9)
Cu(1)	Cu(2)	C(1)	76.79(11)
Cu(3)	Cu(2)	Cu(5)	61.579(17)
Cu(3)	Cu(2)	Cu(6)	61.065(17)
Cu(3)	Cu(2)	N(4)	92.88(9)
Cu(3)	Cu(2)	C(1)	85.51(11)
Cu(5)	Cu(2)	Cu(6)	62.505(17)
Cu(5)	Cu(2)	N(4)	77.24(9)
Cu(5)	Cu(2)	C(1)	108.13(11)
Cu(6)	Cu(2)	N(4)	138.73(9)
Cu(6)	Cu(2)	C(1)	45.80(11)
N(4)	Cu(2)	C(1)	172.60(15)
Cu(2)	Cu(3)	Cu(4)	108.64(2)
Cu(2)	Cu(3)	Cu(5)	62.025(17)
Cu(2)	Cu(3)	Cu(6)	62.689(17)
Cu(2)	Cu(3)	N(2)	93.57(9)
Cu(2)	Cu(3)	C(2)	85.27(11)
Cu(4)	Cu(3)	Cu(5)	57.309(16)
Cu(4)	Cu(3)	Cu(6)	58.919(17)
Cu(4)	Cu(3)	N(2)	106.32(9)
Cu(4)	Cu(3)	C(2)	78.90(11)
Cu(5)	Cu(3)	Cu(6)	63.183(17)
Cu(5)	Cu(3)	N(2)	137.15(9)
Cu(5)	Cu(3)	C(2)	46.27(10)
Cu(6)	Cu(3)	N(2)	74.49(9)
Cu(6)	Cu(3)	C(2)	109.36(11)
N(2)	Cu(3)	C(2)	174.73(14)
Br(2)	Cu(4)	Cu(3)	110.55(2)
Br(2)	Cu(4)	Cu(5)	104.98(2)

Table S 11 (continued)

Br(2)	Cu(4)	Cu(6)	54.665(18)
Br(2)	Cu(4)	N(3)	161.56(10)
Cu(3)	Cu(4)	Cu(5)	60.216(17)
Cu(3)	Cu(4)	Cu(6)	59.288(17)
Cu(3)	Cu(4)	N(3)	87.31(9)
Cu(5)	Cu(4)	Cu(6)	64.401(18)
Cu(5)	Cu(4)	N(3)	87.62(9)
Cu(6)	Cu(4)	N(3)	143.65(9)
Br(1)	Cu(5)	Cu(1)	52.718(17)
Br(1)	Cu(5)	Cu(2)	112.11(2)
Br(1)	Cu(5)	Cu(3)	152.55(2)
Br(1)	Cu(5)	Cu(4)	104.82(2)
Br(1)	Cu(5)	Cu(6)	94.29(2)
Br(1)	Cu(5)	C(2)	161.72(11)
Cu(1)	Cu(5)	Cu(2)	61.694(17)
Cu(1)	Cu(5)	Cu(3)	105.20(2)
Cu(1)	Cu(5)	Cu(4)	106.39(2)
Cu(1)	Cu(5)	Cu(6)	56.142(17)
Cu(1)	Cu(5)	C(2)	142.26(11)
Cu(2)	Cu(5)	Cu(3)	56.396(16)
Cu(2)	Cu(5)	Cu(4)	108.28(2)
Cu(2)	Cu(5)	Cu(6)	59.117(16)
Cu(2)	Cu(5)	C(2)	80.64(11)
Cu(3)	Cu(5)	Cu(4)	62.475(18)
Cu(3)	Cu(5)	Cu(6)	58.261(16)
Cu(3)	Cu(5)	C(2)	45.51(11)
Cu(4)	Cu(5)	Cu(6)	58.881(17)
Cu(4)	Cu(5)	C(2)	82.20(11)
Cu(6)	Cu(5)	C(2)	103.69(11)
Br(2)	Cu(6)	Cu(1)	109.05(2)
Br(2)	Cu(6)	Cu(2)	155.66(2)
Br(2)	Cu(6)	Cu(3)	111.19(2)
Br(2)	Cu(6)	Cu(4)	52.825(17)
Br(2)	Cu(6)	Cu(5)	97.39(2)
Br(2)	Cu(6)	C(1)	159.62(11)
Cu(1)	Cu(6)	Cu(2)	62.592(18)
Cu(1)	Cu(6)	Cu(3)	108.19(2)
Cu(1)	Cu(6)	Cu(4)	107.34(2)
Cu(1)	Cu(6)	Cu(5)	59.422(17)
Cu(1)	Cu(6)	C(1)	80.67(11)
Cu(2)	Cu(6)	Cu(3)	56.246(16)

Table S12. Selected Bond Distances for Compound **4**.

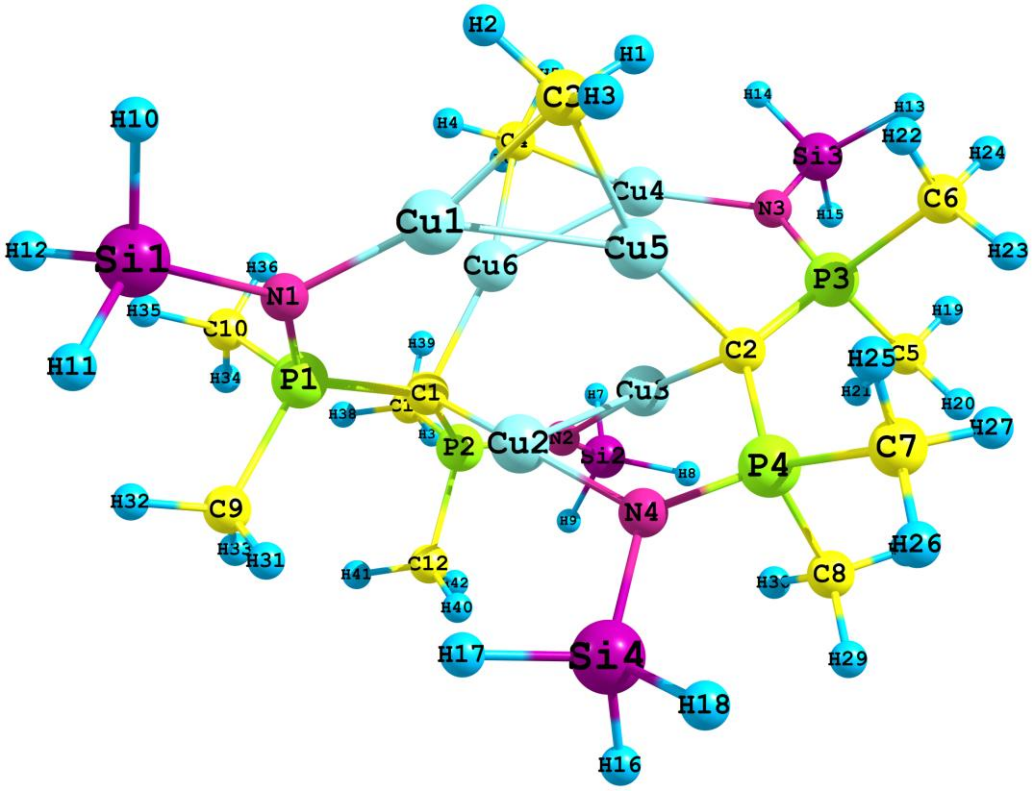
I(1)	Cu(1)	2.4531(7)
I(1)	Cu(5)	2.4716(6)
I(2)	Cu(4)	2.4559(6)
I(2)	Cu(6)	2.4770(6)
Cu(1)	Cu(2)	2.6983(7)
Cu(1)	Cu(5)	2.6630(8)
Cu(1)	Cu(6)	2.6306(8)
Cu(1)	N(1)	1.920(4)
Cu(2)	Cu(3)	2.6052(6)
Cu(2)	Cu(5)	2.6704(7)
Cu(2)	Cu(6)	2.7373(7)
Cu(2)	N(4)	1.924(3)
Cu(2)	C(10)	1.942(4)
Cu(3)	Cu(4)	2.6805(7)
Cu(3)	Cu(5)	2.7583(7)
Cu(3)	Cu(6)	2.6849(7)
Cu(3)	N(2)	1.912(3)
Cu(3)	C(20)	1.944(4)
Cu(4)	Cu(5)	2.6391(9)
Cu(4)	Cu(6)	2.6480(7)
Cu(4)	N(3)	1.920(3)
Cu(5)	Cu(6)	2.9318(8)
Cu(5)	C(20)	1.983(4)
Cu(6)	C(10)	1.989(4)
P(1)	N(1)	1.602(4)
P(1)	C(10)	1.742(4)
P(1)	C(11)	1.822(4)
P(1)	C(21)	1.825(4)
P(2)	N(2)	1.615(4)
P(2)	C(10)	1.746(4)
P(2)	C(31)	1.859(5)
P(2)	C(41)	1.791(5)
P(3)	N(3)	1.614(4)
P(3)	C(20)	1.748(4)
P(3)	C(51)	1.826(5)
P(3)	C(61)	1.814(5)
P(4)	N(4)	1.612(4)

Table S13. Selected Interatomic Angles (deg) for Compound **4.**

I(2)	Cu(6)	C(10)	159.13(11)
Cu(1)	Cu(6)	Cu(2)	60.31(2)
Cu(1)	Cu(6)	Cu(3)	106.95(2)
Cu(1)	Cu(6)	Cu(4)	104.67(3)
Cu(1)	Cu(6)	Cu(5)	56.898(19)
Cu(1)	Cu(6)	C(10)	81.84(11)
Cu(2)	Cu(6)	Cu(3)	57.421(17)
Cu(2)	Cu(6)	Cu(4)	103.76(2)
Cu(2)	Cu(6)	Cu(5)	56.078(18)
Cu(2)	Cu(6)	C(10)	45.16(11)
Cu(3)	Cu(6)	Cu(4)	60.343(19)
Cu(3)	Cu(6)	Cu(5)	58.629(17)
Cu(3)	Cu(6)	C(10)	80.28(10)
Cu(4)	Cu(6)	Cu(5)	56.18(2)
Cu(4)	Cu(6)	C(10)	140.42(11)
Cu(5)	Cu(6)	C(10)	101.21(11)
N(1)	P(1)	C(10)	109.08(18)
N(1)	P(1)	C(11)	109.2(2)
N(1)	P(1)	C(21)	109.3(2)
C(10)	P(1)	C(11)	113.5(2)
C(10)	P(1)	C(21)	112.28(19)
C(11)	P(1)	C(21)	103.4(2)
N(2)	P(2)	C(10)	108.34(18)
N(2)	P(2)	C(31)	107.5(2)
N(2)	P(2)	C(41)	106.8(3)
C(10)	P(2)	C(31)	111.8(2)
C(10)	P(2)	C(41)	115.5(3)
C(31)	P(2)	C(41)	106.5(3)
N(3)	P(3)	C(20)	109.03(18)
N(3)	P(3)	C(51)	109.8(2)
N(3)	P(3)	C(61)	108.2(2)
C(20)	P(3)	C(51)	110.4(2)
C(20)	P(3)	C(61)	114.4(2)
C(51)	P(3)	C(61)	104.9(2)
N(4)	P(4)	C(20)	107.94(18)
N(4)	P(4)	C(71)	110.9(2)
N(4)	P(4)	C(81)	107.1(2)
C(20)	P(4)	C(71)	111.1(2)
C(20)	P(4)	C(81)	115.2(2)
C(71)	P(4)	C(81)	104.5(2)

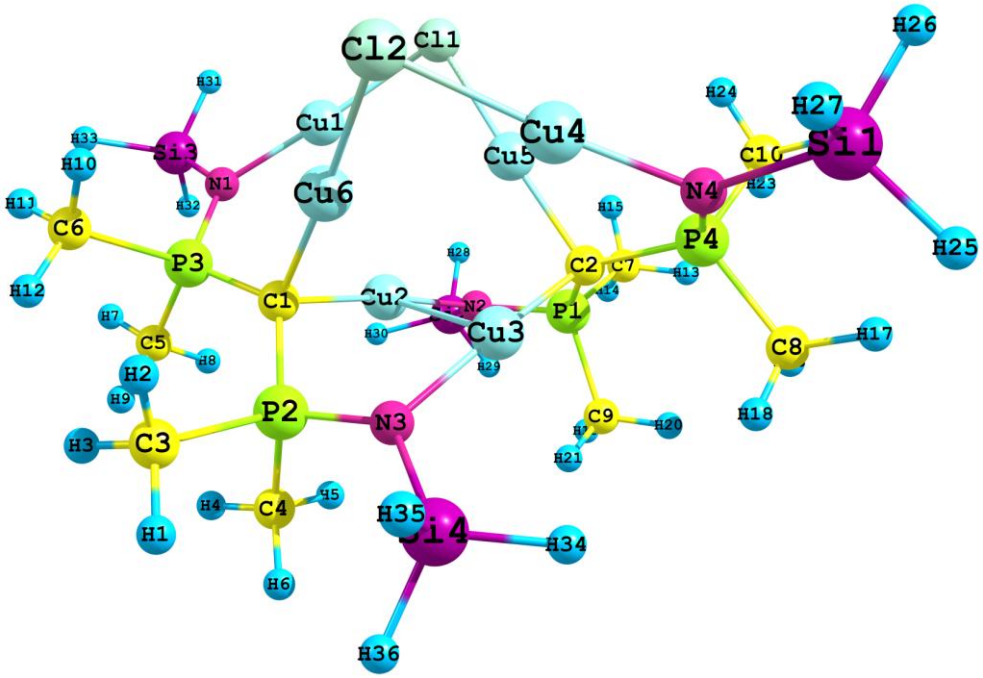
END of Table S13

Figure S33: OPT Structures for Model Compounds **1-4:**



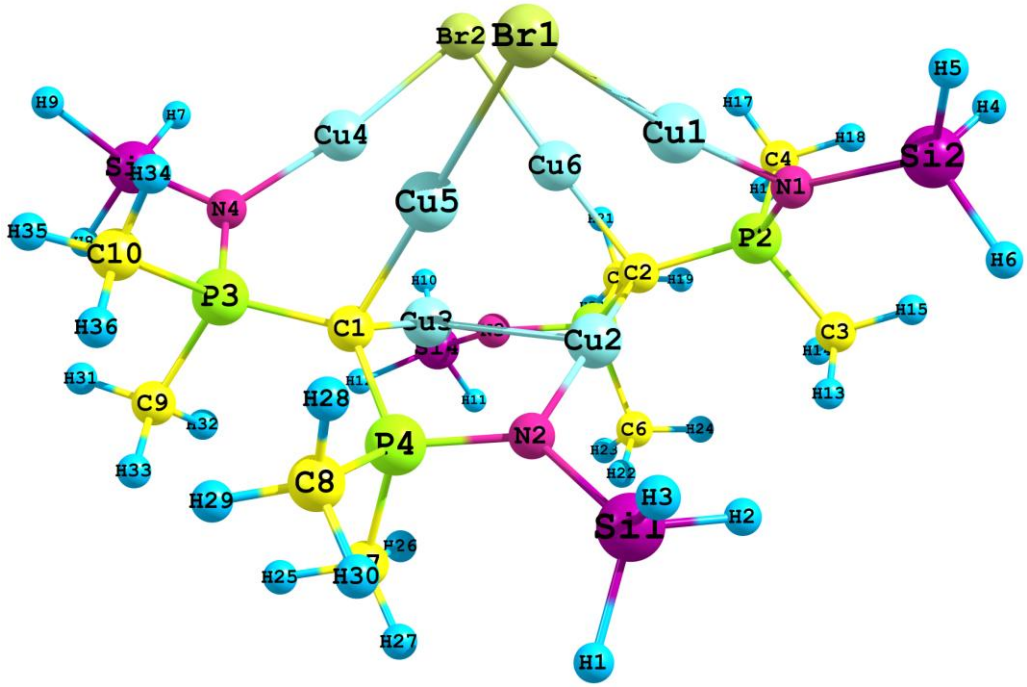
Compound 1

Figure S33 (continued): OPT Structures for Model Compounds **1**-**4:**

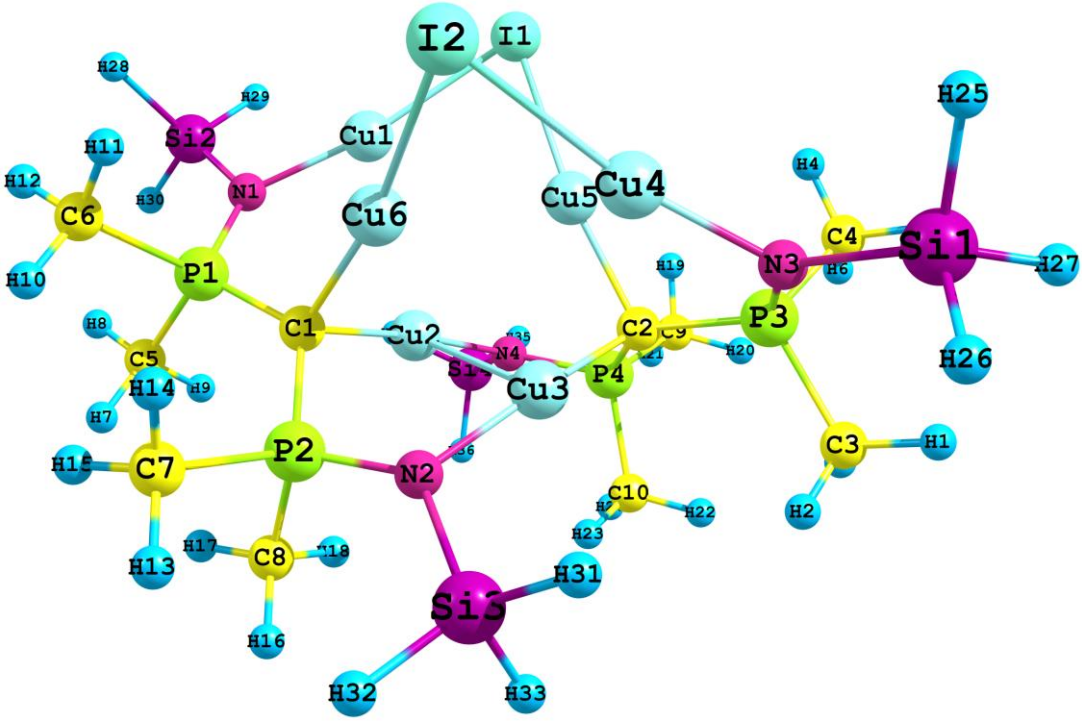


Compound 2

Figure S33 (continued): OPT Structures for Model Compounds **1-4:**

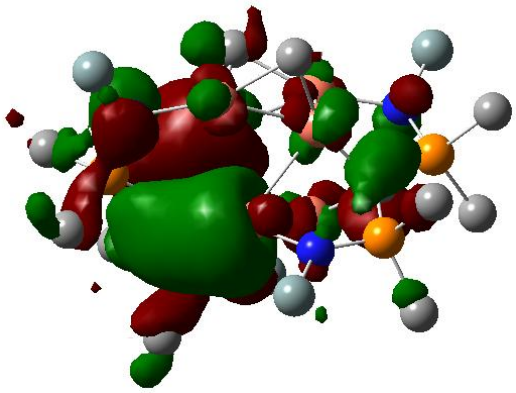


Compound 3

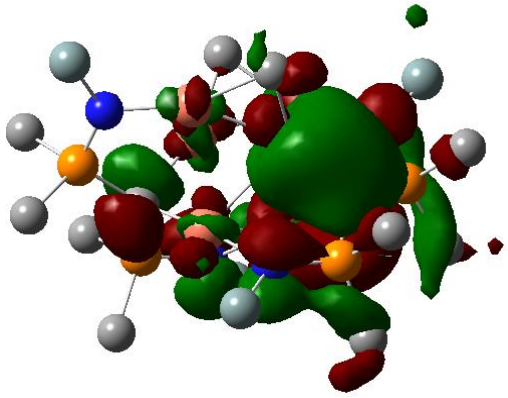


Compound 4

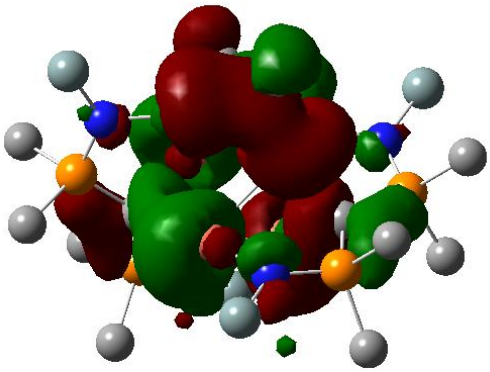
Figure S34: Calculated DFT MO for Model Compound **1**.



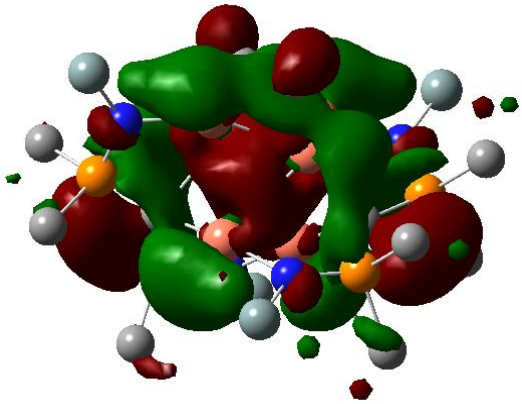
MO-184



MO-185

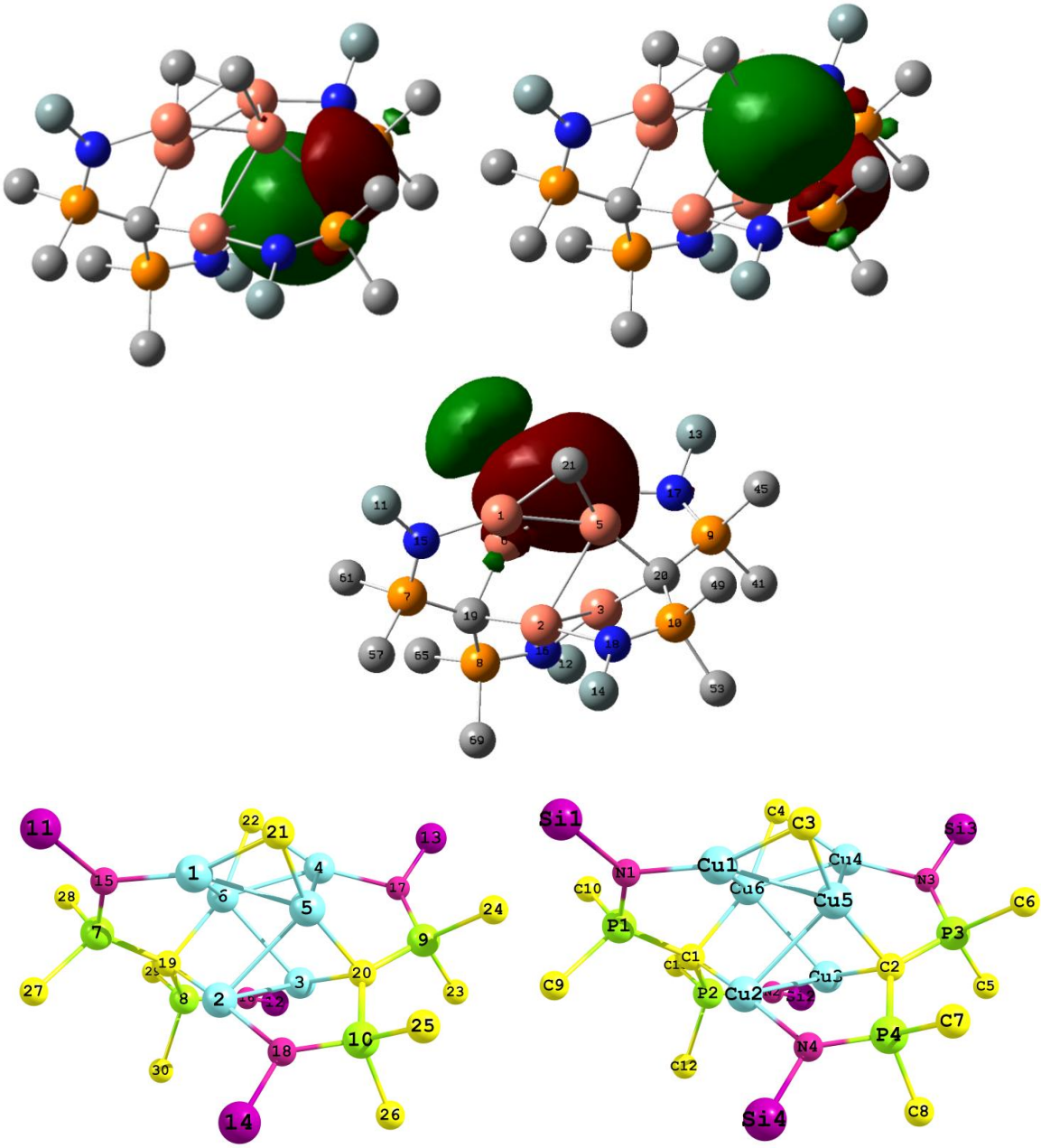


MO-186 (HOMO)



MO-187 (LUMO)

Figure S35: Calculated DFT NBO for Model Compound **1**.



NBO Components for Model Compound **1** as shown in **Figure S35**.

(Occupancy) Bond orbital/ Coefficients/ Hybrids (Compound 1)

---

2. (1.80196) BD (1)Cu 2 - C 19
(12.27%) 0.3503*Cu 2 s(90.80%)p 0.00(0.21%)d 0.10(8.99%)
0.0022 0.9528 0.0065 -0.0045 -0.0159
-0.0049 -0.0047 -0.0416 -0.0086 -0.0010
-0.0027 0.0008 0.2334 0.0080 0.0688
0.0033 0.0973 0.0000 -0.0707 -0.0078
-0.1266 -0.0081
(87.73%) 0.9366* C 19 s(25.60%)p 2.91(74.40%)d 0.00(0.00%)
0.0002 0.5058 -0.0111 0.5579 -0.0142
0.6568 -0.0110 -0.0315 0.0006 -0.0041
0.0033 0.0028 -0.0007 0.0031

3. (1.82082) BD (1)Cu 3 - C 20
(12.07%) 0.3475*Cu 3 s(90.75%)p 0.00(0.19%)d 0.10(9.05%)
-0.0026 -0.9526 -0.0066 -0.0042 -0.0251
0.0003 -0.0051 -0.0321 -0.0058 0.0019
0.0136 0.0018 -0.2119 -0.0078 0.1099
0.0083 0.1472 0.0052 0.0620 0.0016
0.0884 0.0082
(87.93%) 0.9377* C 20 s(15.84%)p 5.31(84.16%)d 0.00(0.00%)
-0.0003 -0.3979 0.0084 0.4233 -0.0092
0.7127 -0.0120 -0.3927 0.0048 0.0048
0.0002 0.0011 0.0008 -0.0025

4. (1.77679) BD (1)Cu 4 - C 22
(16.41%) 0.4051*Cu 4 s(89.85%)p 0.01(0.92%)d 0.10(9.24%)
-0.0042 0.9475 -0.0275 -0.0009 -0.0753
0.0305 -0.0034 0.0239 0.0201 -0.0054
0.0255 0.0304 0.1240 0.0030 0.1751
0.0036 0.0576 0.0042 0.1869 0.0261
-0.0846 -0.0146

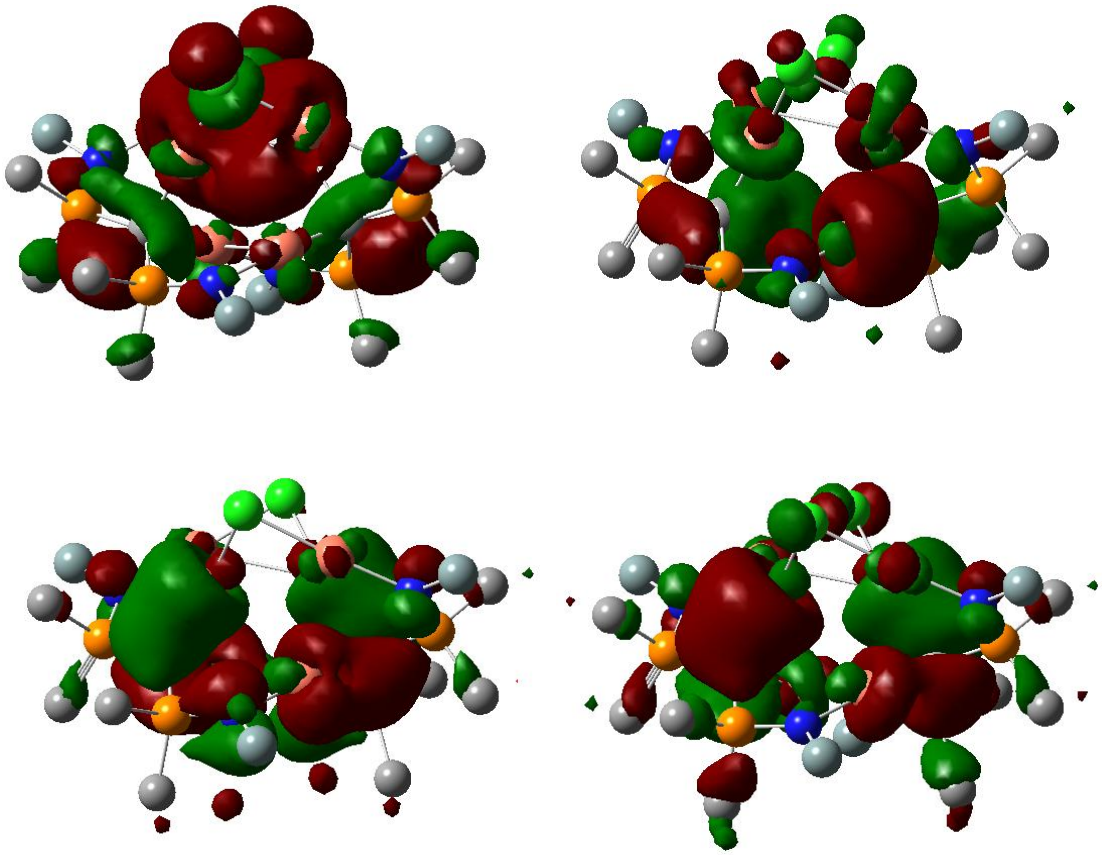
NBO for Compound **1** (continued)

(83.59%) 0.9143* C 22 s(17.27%)p 4.79(82.73%)d 0.00(0.00%)
0.0015 0.4134 -0.0428 0.4038 -0.0317
0.4248 -0.0356 0.6912 -0.0614 -0.0016
-0.0026 0.0026 0.0022 0.0008

5. (1.80942) BD (1)Cu 5 - C 20
(11.75%) 0.3428*Cu 5 s(92.77%)p 0.01(0.52%)d 0.07(6.70%)
-0.0019 -0.9630 0.0165 -0.0048 -0.0540
-0.0080 0.0016 0.0092 0.0072 -0.0039
-0.0452 -0.0064 0.0737 -0.0020 -0.1993
-0.0099 0.1070 -0.0055 -0.0540 -0.0045
-0.0856 -0.0061
(88.25%) 0.9394* C 20 s(13.42%)p 6.45(86.57%)d 0.00(0.01%)
-0.0002 -0.3661 0.0133 0.5461 -0.0115
-0.1192 0.0025 0.7437 -0.0082 0.0037
0.0035 0.0048 0.0033 -0.0005

Figure S36: Calculated DFT MO for Model Compound **2**.

(Model for $[Cu_6L_2Cl_2]$)

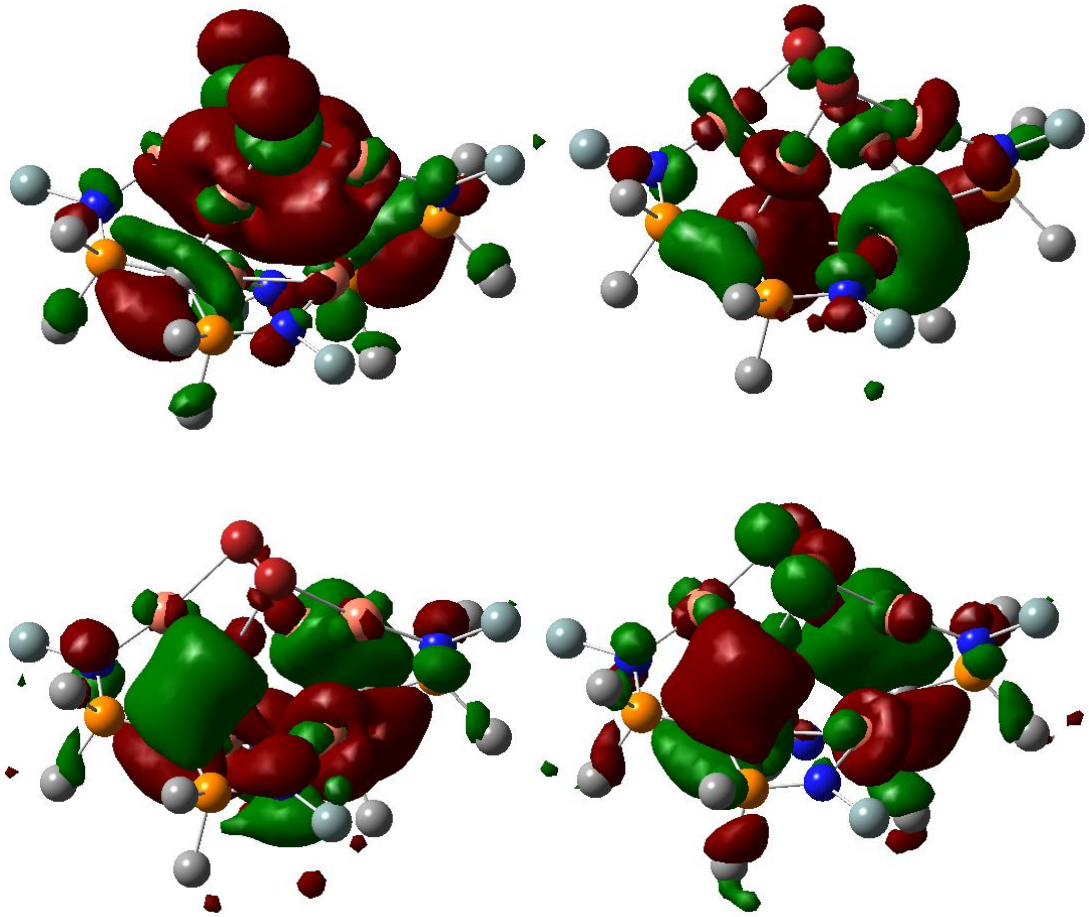


LUMO
MO-183

HOMO (Top)
MO-182 (Bottom)

Figure S37: Calculated DFT MO for Model Compound **3**.

(Model for $[Cu_6L_2Br_2]$)

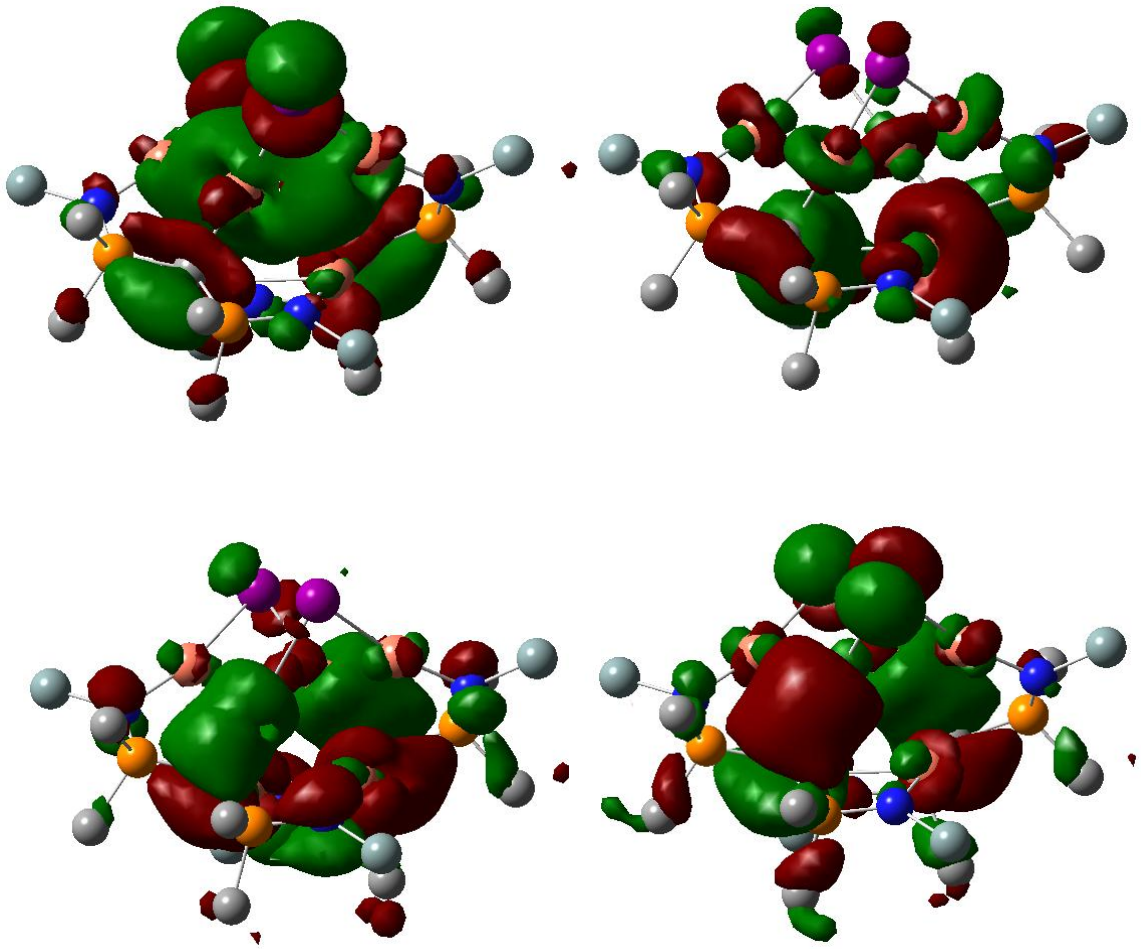


LUMO
MO-183

HOMO (top)
MO-182 (bottom)

Figure S38: Calculated DFT MO for Model Compound **4**.

(Model for $[Cu_6L_2I_2]$))

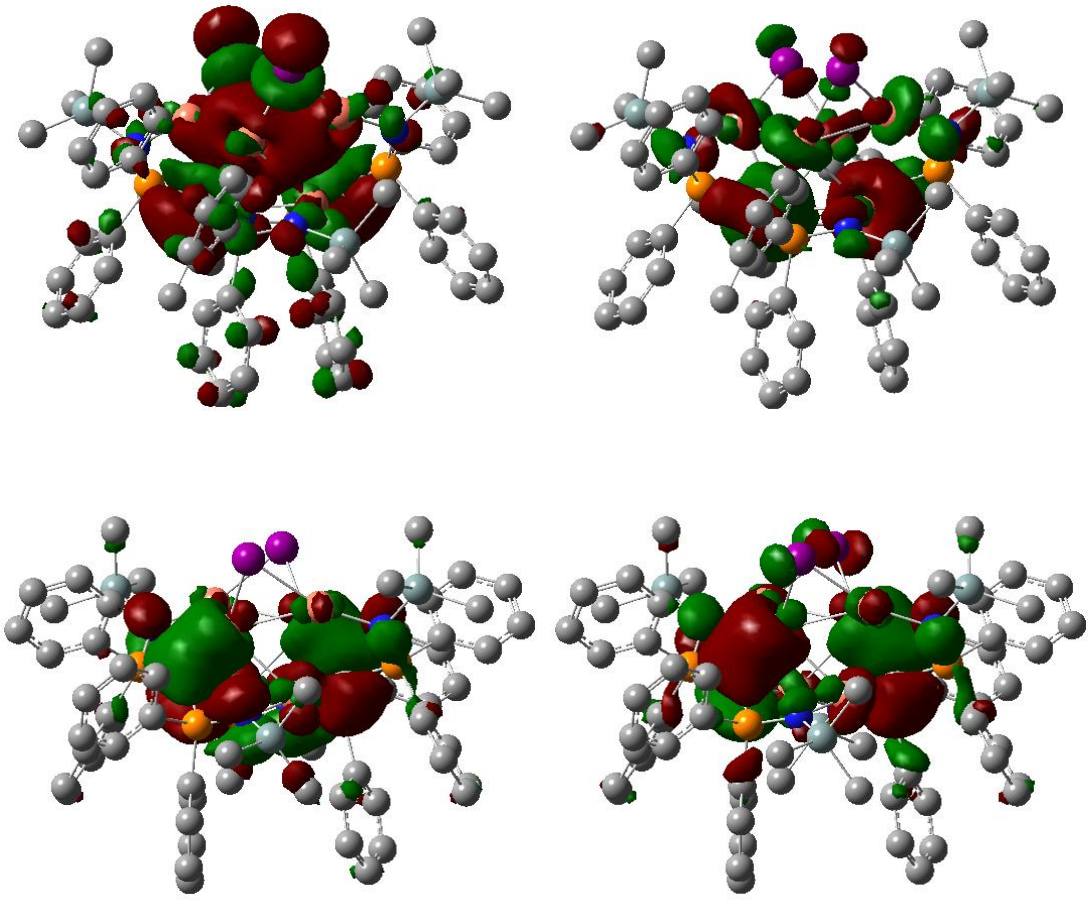


LUMO
MO-183

HOMO
MO-182

Figure S38 (continued): Calculated DFT MO for Compound **4**.

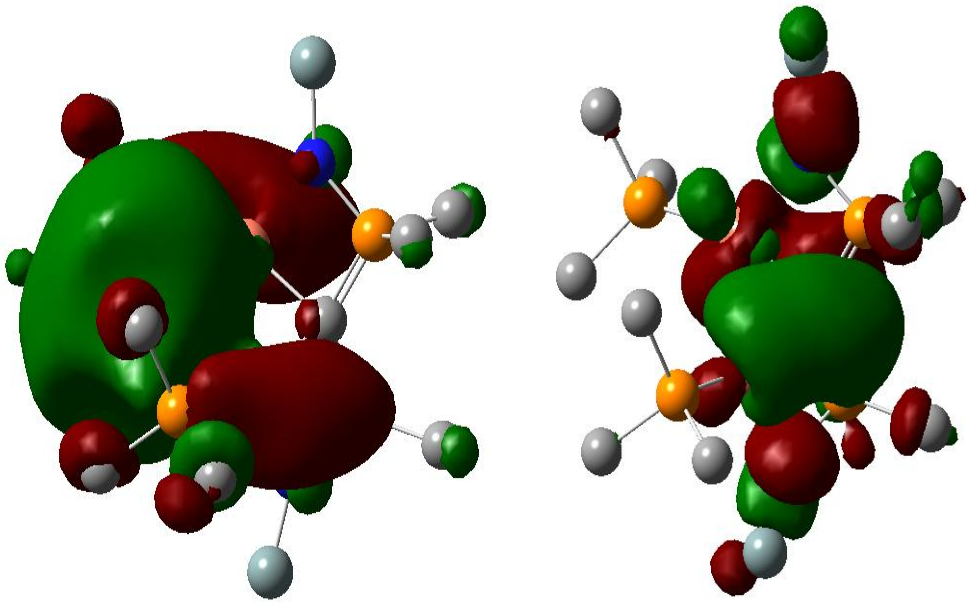
([$Cu_6L_2I_2$] Full molecule with phenyl groups attached to phosphorus.)



LUMO
MO-359

HOMO
MO-358

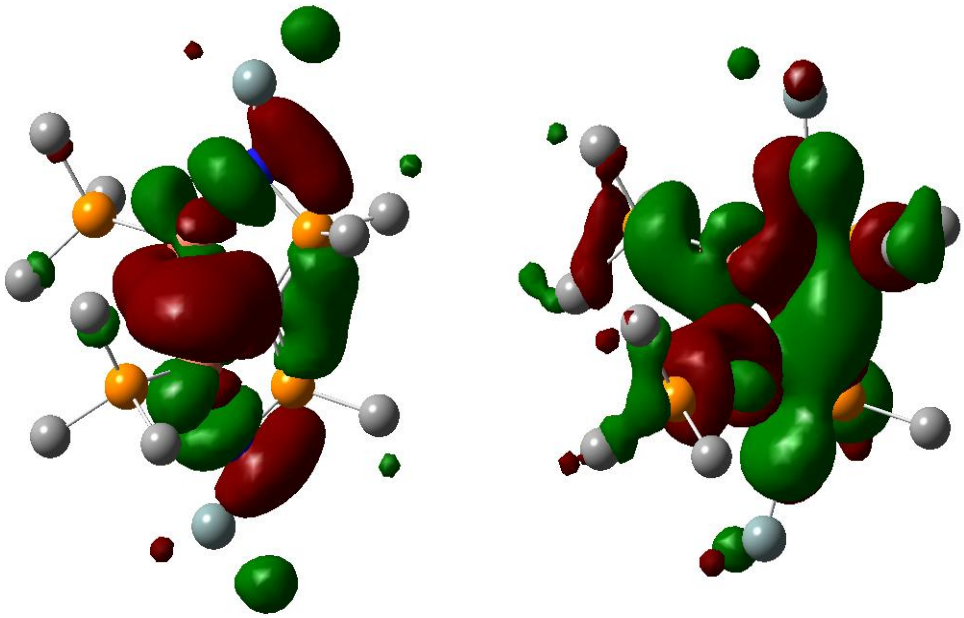
Figure S39: Calculated DFT MO and Coefficients for Model Complex **6.**



LUMO

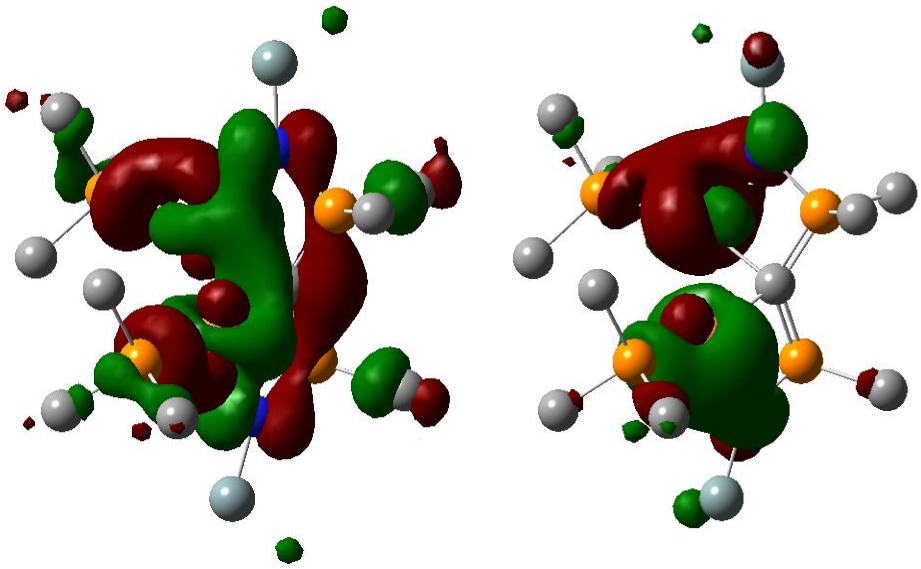
1 Cu:	3s (-0.156)
	$5p_z$ (0.103)
	$7D_0$ (0.101)
	$7D_{+2}$ (0.185)
	$7D_{-2}$ (0.249)
2 Cu:	3s (0.149)
	$5p_z$ (0.107)
	$7D_0$ (-0.115)
	$7D_{+2}$ (-0.148)
	$7D_{-2}$ (0.271)
5 N:	3s (-0.166)
	$4p_z$ (-0.180)
	$5p_z$ (-0.147)
6 C:	$4p_x$ (0.339)
	$4p_z$ (0.262)
	$5p_x$ (0.304)
	$5p_z$ (0.159)
9 N:	3s (0.159)
	$4p_z$ (-0.179)
	$5p_z$ (-0.145)

Figure S39 (Continued, part 2)



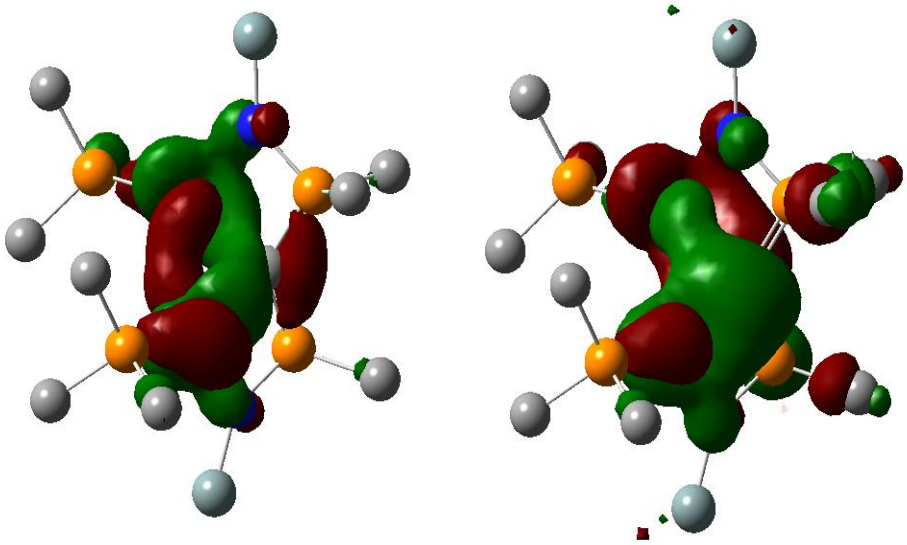
1 Cu:	2s (0.084)	1 Cu:	$7D_{+1}$ (0.342)
	$5p_x$ (-0.105)		$7D_{-1}$ (-0.166)
	$7D_0$ (0.198)		$7D_{-2}$ (-0.181)
	$7D_{+1}$ (-0.246)		$8D_{+1}$ (0.114)
	$7D_{-2}$ (0.271)	2 Cu:	$7D_{+1}$ (-0.341)
2 Cu:	2s (0.092)		$7D_{-1}$ (-0.124)
	$5p_x$ (0.100)		$7D_{-2}$ (-0.155)
	$7D_0$ (0.223)		$8D_{+1}$ (-0.114)
	$7D_{+1}$ (-0.277)	3 P:	2s (-0.156)
	$7D_{-2}$ (-0.254)	4 P:	2s (-0.100)
3 P:	$4p_x$ (0.144)	5 N:	$4p_z$ (0.168)
5 N:	3s (-0.150)		$5p_z$ (0.120)
	$4p_x$ (0.126)	6 C:	$4p_x$ (0.114)
	$4p_y$ (0.153)		$4p_z$ (0.222)
	$5p_x$ (0.104)		$5p_x$ (0.137)
	$5p_y$ (0.091)	7 P:	2s (0.156)
6 C:	3s (0.363)	9 N:	$4p_z$ (0.176)
	$4p_y$ (-0.196)		$5p_z$ (0.126)
7 P:	$4p_x$ (-0.142)		
9 N:	3s (-0.155)		
	$4p_x$ (0.113)		
	$4p_y$ (-0.168)		
	$5p_x$ (0.096)		
	$5p_y$ (0.102)		

Figure S39 (Continued, part 3)



1 Cu:	$7D_{+1}$ (-0.267)	1 Cu:	2s (0.110)
	$7D_{+2}$ (0.388)		$7D_{+1}$ (0.212)
	$7D_{-2}$ (-0.155)		$7D_{-1}$ (0.437)
	$8D_{+2}$ (0.129)		$7D_{+2}$ (0.259)
2 Cu:	$7D_{+1}$ (-0.295)		$8D_{-1}$ (0.141)
	$7D_{+2}$ (0.356)		$8D_{+2}$ (0.081)
	$7D_{-2}$ (0.101)		$8D_{-2}$ (0.018)
	$8D_{+2}$ (0.119)	2 Cu:	2s (-0.091)
4 P:	$4p_y$ (0.142)		$7D_{+1}$ (-0.131)
5 N:	$4p_y$ (0.141)		$7D_{-1}$ (0.440
6 C:	$4p_y$ (0.221)		$7D_{+2}$ (-0.261)
	$5p_y$ (0.176)		$7D_{-2}$ (0.119)
8 P:	2s (0.102)		$8D_{-1}$ (0.143)
	$4p_y$ (0.127)		$8D_{+2}$ (-0.082)
9 N:	$4p_y$ (0.145)		$8D_{-2}$ (0.035)
		5 N:	$4p_z$ (0.121)
			$5p_z$ (0.065)
		9 N:	$4p_z$ (0.120)
			$5p_z$ (0.064)

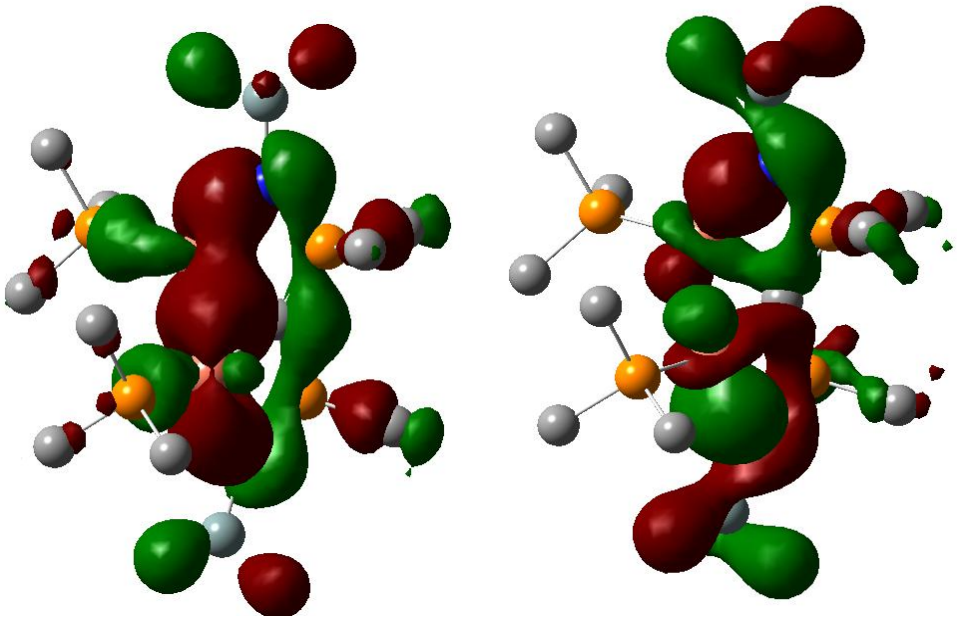
Figure S39 (Continued, part 4)



1 Cu:	$7D_0$ (0.232)
	$7D_{+1}$ (0.404)
	$7D_{+2}$ (0.268)
	$7D_{-2}$ (0.203)
	$8D_0$ (0.110)
	$8D_{+1}$ (0.129)
2 Cu:	$7D_0$ (0.174)
	$7D_{+1}$ (0.403)
	$7D_{+2}$ (0.225)
	$7D_{-2}$ (-0.317)
	$8D_{+1}$ (0.129)
	$8D_{-2}$ (-0.105)
6 C:	$4p_y$ (0.116)
	$5p_y$ (0.048)

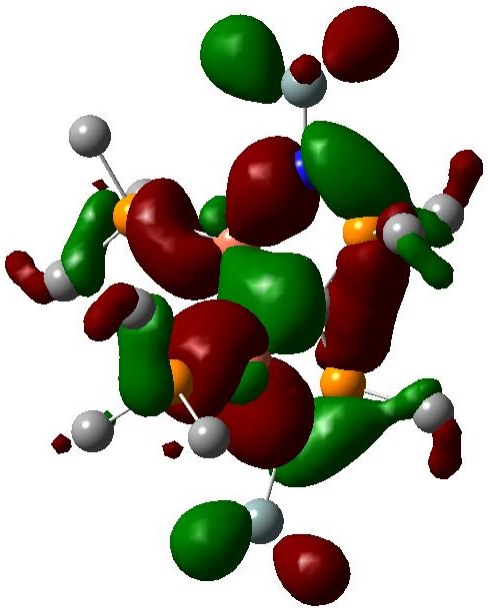
1 Cu:	$7D_0$ (-0.332)
	$7D_{+1}$ (-0.293)
	$7D_{-1}$ (0.197)
	$7D_{+2}$ (-0.178)
	$8D_0$ (0.110)
	$8D_{+1}$ (-0.096)
	$8D_{-1}$ (0.064)
2 Cu:	$7D_0$ (0.335)
	$7D_{+1}$ (0.318)
	$7D_{-1}$ (0.110)
	$7D_{+2}$ (0.147)
	$7D_{-2}$ (-0.130)
	$8D_0$ (0.111)
	$8D_{+1}$ (0.104)
	$8D_{-1}$ (0.035)
	$8D_{+2}$ (0.048)
	$8D_{-2}$ (0.041)
6 C:	$4p_x$ (0.159)
	$4p_z$ (0.156)

Figure S39 (Continued, part 5)



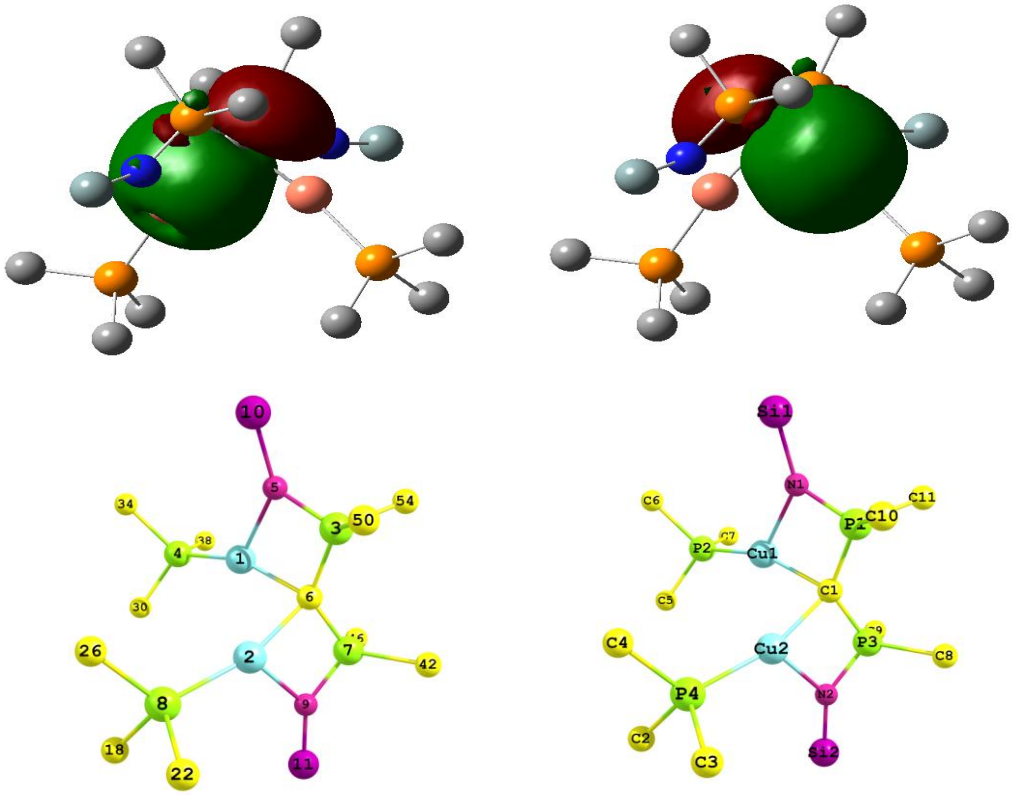
1 Cu:	$7D_0$ (-0.104)	1 Cu:	$7D_0$ (0.109)
	$7D_{+2}$ (0.359)		$7D_{+1}$ (-0.248)
	$8D_{+2}$ (0.114)		$7D_{-1}$ (-0.146)
2 Cu:	$7D_{+1}$ (-0.094)		$7D_{+2}$ (0.119)
	$7D_{+2}$ (0.366)		$7D_{-2}$ (0.199)
	$8D_{+2}$ (0.117)	2 Cu:	$7D_0$ (-0.150)
3 P:	$3p_y$ (0.061)		$7D_{+1}$ (0.254)
4 P:	2s (-0.074)		$7D_{-1}$ (-0.161)
	$3p_y$ (-0.061)		$7D_{+2}$ (0.201)
5 N:	$4p_y$ (-0.174)	5 N:	$4p_y$ (-0.181)
	$4p_z$ (0.125)		$4p_z$ (0.185)
	$5p_y$ (-0.111)		$5p_y$ (-0.114)
6 C:	$4p_y$ (-0.203)		$5p_z$ (0.124)
	$5p_y$ (-0.165)	6 C:	$4p_x$ (-0.124)
7 P:	$3p_y$ (0.060)		$5p_x$ (-0.094)
8 P:	2s (-0.071)	9 N:	$4p_y$ (0.176)
	$3p_y$ (-0.056)		$4p_z$ (0.208)
9 N:	$4p_y$ (-0.167)		$5p_y$ (0.111)
	$4p_z$ (-0.142)		$5p_z$ (0.139)
	$5p_y$ (-0.106)		

Figure S39 (Continued, part 6)



1 Cu:	$7D_0$ (0.145)
	$7D_{+1}$ (-0.165)
	$7D_{-1}$ (-0.133)
	$7D_{+2}$ (-0.136)
	$7D_{-2}$ (0.248)
2 Cu:	$7D_0$ (0.151)
	$7D_{+1}$ (-0.146)
	$7D_{-1}$ (0.138)
	$7D_{+2}$ (-0.180)
	$7D_{-2}$ (-0.170)
3 P:	$3p_x$ (-0.103)
	$4p_x$ (-0.084)
5 N:	$4p_y$ (-0.152)
	$4p_z$ (0.120)
	$5p_y$ (-0.084)
6 C:	3s (-0.229)
	$4p_y$ (0.222)
7 P:	$3p_x$ (0.098)
	$4p_x$ (0.077)
9 N:	$4p_y$ (-0.132)
	$4p_z$ (-0.121)

Figure S40: Calculated DFT NBO and MO Coefficients for Model Complex **6.**



NBO-77 NBO-78

$[Cu_2L(PPh_3)_2]$

1. (1.81732) BD (1)Cu 1 - C 6
(7.46%) 0.2731*Cu 1 s(93.58%)p 0.02(1.95%)d 0.05(4.47%)
-0.0027 -0.9664 0.0435 0.0048 0.0681
-0.0240 -0.0034 0.0158 -0.0035 -0.0012
-0.1181 -0.0047 0.1517 -0.0081 -0.0074
-0.0045 0.1111 0.0217 0.0490 0.0214
0.0763 -0.0055
(92.54%) 0.9620* C 6 s(18.39%)p 4.44(81.61%)
0.0001 -0.4286 0.0142 -0.4830 0.0134
0.6128 -0.0228 -0.4545 0.0071

2. (1.82246) BD (1)Cu 2 - C 6
(8.02%) 0.2832*Cu 2 s(93.41%)p 0.02(1.79%)d 0.05(4.80%)
-0.0029 -0.9657 0.0376 -0.0049 -0.0520
0.0212 -0.0028 0.0198 -0.0111 0.0011
0.1187 0.0096 -0.1681 0.0018 -0.0354
-0.0072 -0.1132 -0.0191 0.0030 0.0203
0.0696 -0.0061
(91.98%) 0.9591* C 6 s(19.50%)p 4.13(80.50%)
0.0001 -0.4414 0.0130 0.5486 -0.0156
0.4979 -0.0193 0.5054 -0.0085

Figure S41 . Calculated DFT MO for Complex (**7**); LUMO (left) and HOMO (right).

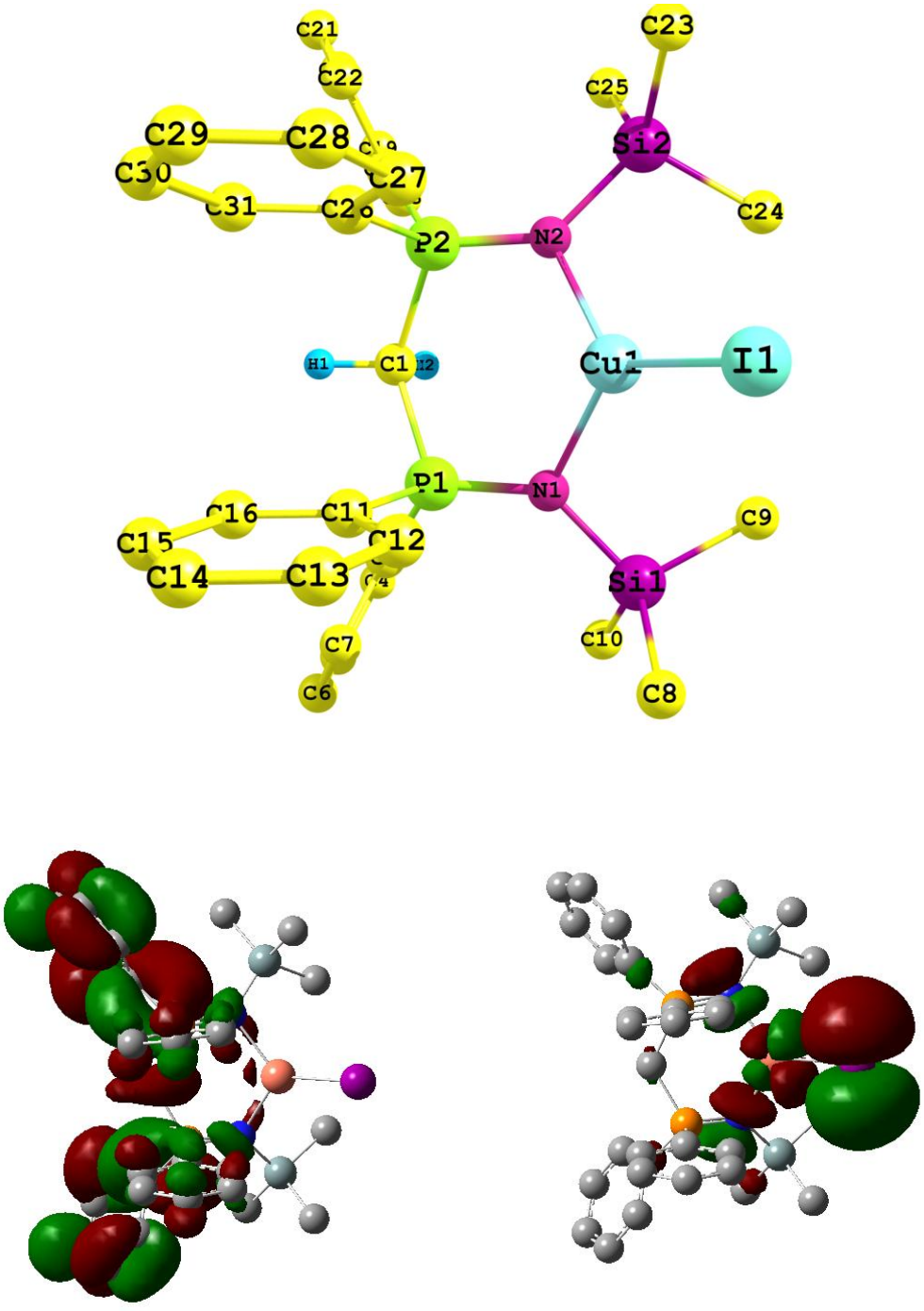
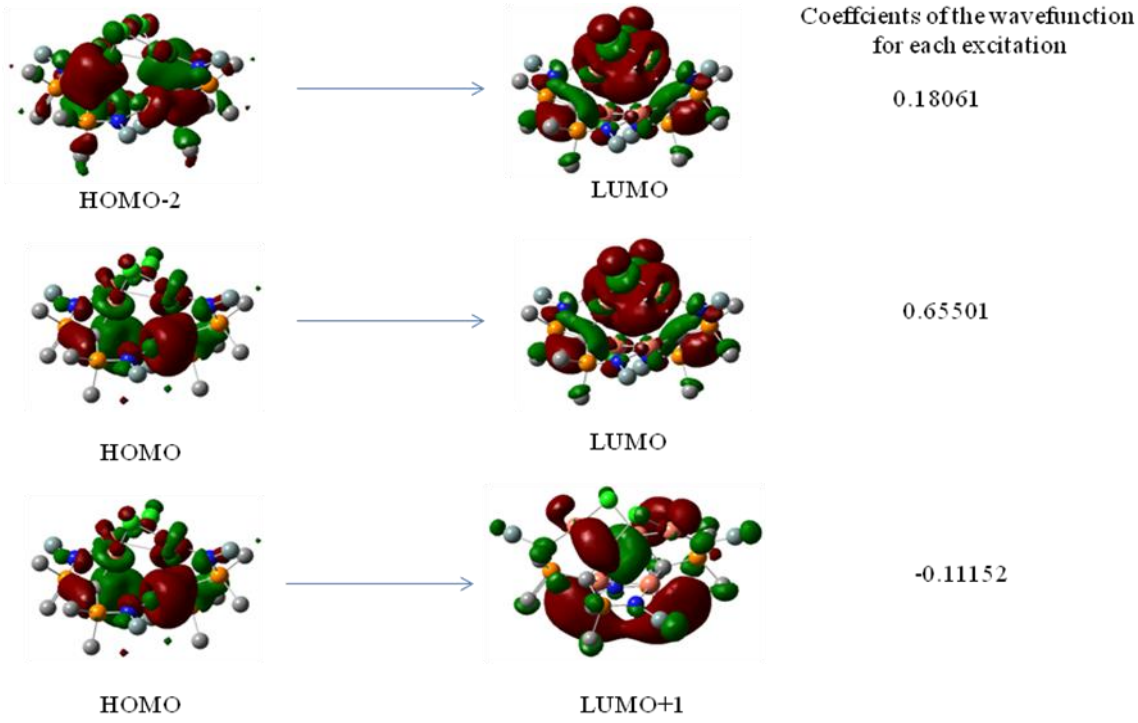
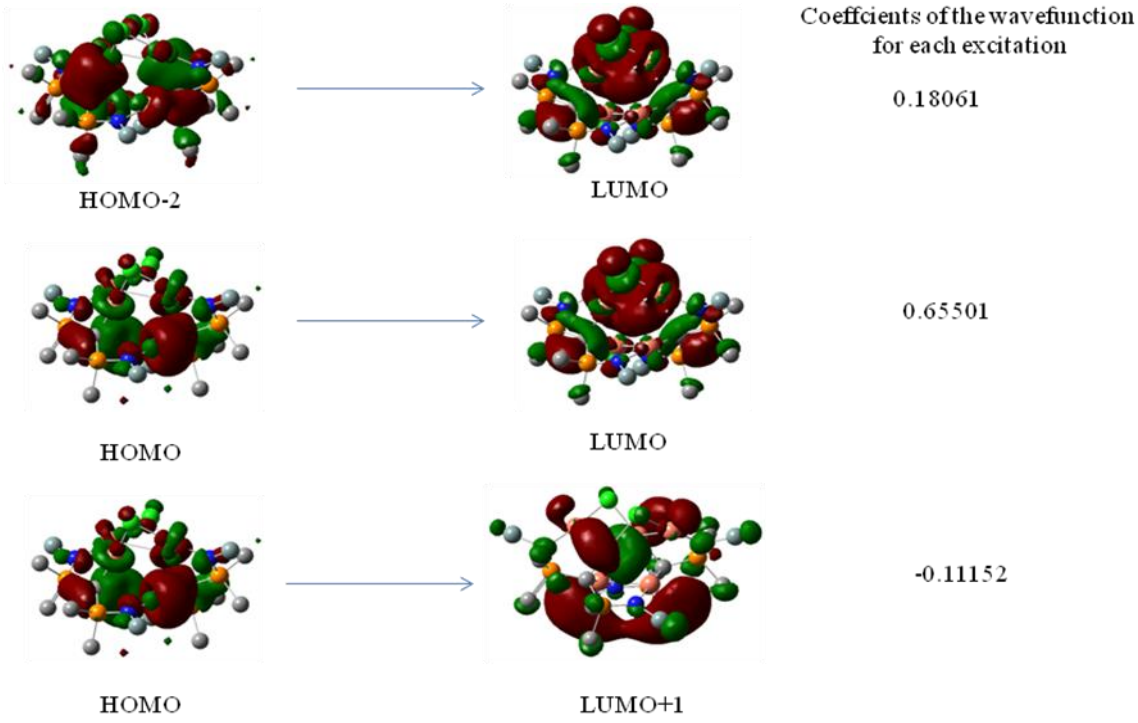


Figure S42. Orbital excitation contribution to two allowed excited states of chloride cluster **2**



Excited state 1: 3.5957 eV 344.81 nm f=0.0116 (f is Oscillator strength)



Excited state 1: 3.5957 eV 344.81 nm f=0.0116 (f is Oscillator strength)

TD-DFT calculated excited states for cluster 2

Excited states from <AA,BB:AA,BB> singles matrix:
****

1PDM for each excited state written to RWF 633
Ground to excited state Transition electric dipole moments (Au):

state	X	Y	Z	Osc.
1	0.1584	-0.3272	-0.0079	0.0116
2	-0.0038	0.0057	-0.0052	0.0000
3	-0.3155	0.4501	0.0003	0.0286

Ground to excited state transition velocity dipole Moments (Au):

state	X	Y	Z	Osc.
1	-0.0323	0.0501	0.0012	0.0180
2	0.0009	-0.0010	-0.0090	0.0004
3	0.0477	-0.0780	0.0002	0.0393

Ground to excited state transition magnetic dipole Moments (Au):

state	X	Y	Z
1	-0.1555	0.3822	-0.0131
2	0.0109	-0.0054	-0.0526
3	-0.7671	-0.4484	0.0159

<0|del|b> * <b|rxdel|0> (Au), Rotatory Strengths (R) in
cgs (10**-40 erg-esu-cm/Gauss)

state	X	Y	Z	R(velocity)
1	0.0050	0.0192	0.0000	43.1090
2	0.0000	0.0000	0.0005	0.8434
3	-0.0366	0.0350	0.0000	-2.6280

<0|r|b> * <b|rxdel|0> (Au), Rotatory Strengths (R) in
cgs (10**-40 erg-esu-cm/Gauss)

state	X	Y	Z	R(length)
1	-0.0246	-0.1251	0.0001	35.2625
2	0.0000	0.0000	0.0003	-0.0476
3	0.2420	-0.2019	0.0000	-9.4639

<0|del|b> * <b|r|0> (Au)

state	X	Y	Z	Osc.(frdel)
1	-0.0051	-0.0164	0.0000	0.0144
2	0.0000	0.0000	0.0000	0.0000
3	-0.0150	-0.0351	0.0000	0.0334

Ground to excited state transition densities written to RWF 633

Excitation energies and oscillator strengths:

Excited State 1: Singlet-A 3.5957 eV 344.81 nm f=0.0116
182 ->185 0.18061
184 ->185 0.65501
184 ->186 -0.11152

This state for optimization and/or second-order correction.
Total Energy, E(RPA) = -4352.32424736
Copying the excited state density for this state as the 1-particle RhoCI density.

Excited State	2:	Singlet-A	3.7362 eV	331.85 nm f=0.0000
183 ->185		0.67528		

Excited State	3:	Singlet-A	3.8580 eV	321.37 nm f=0.0286
182 ->185		0.63878		
183 ->187		0.11233		
184 ->185		-0.17079		

Reference 22 - Full Gaussian citation:

(a) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery Jr, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Menucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Rega, N.; Salvador, P.; Dannenberg, J. J.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Revision C02 Gaussian, Inc., Pittsburgh PA,* **2004**.

END of Supporting Information