Synthesis and structural analyses of phenylethynyl-substituted tris(2-pyridylmethyl)amines and their copper(II) complexes

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Supporting Information

Data Collection Parameters for X-ray Diffraction

Compound 1.

X-ray Experimental for $C_{26}H_{22}N_4$: Crystals grew as colorless laths by slow diffusion of hexane into a dichloromethane solution of **1**. The data crystal was cut from a larger crystal and had approximate dimensions; 0.34 × 0.18 × 0.10 mm. The data were collected at −133 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 2315 frames of data were collected using ω and ϕ-scans with a scan range of 0.6 ° and a counting time of 15 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data reduction were performed using SAINT V8.27B.[1] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2013.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms were observed in a ΔF map and refined with isotropic displacement parameters.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.1069*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.191, with R(F) equal to 0.0641 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

Compound 2.

X-ray Experimental for $C_{34}H_{26}N_4$: Crystals grew as colorless needles by slow diffusion of hexane into a dichloromethane solution of **2**. The data crystal was cut from a larger crystal and had approximate dimensions; 0.40 × 0.14 × 0.12 mm. The data were collected at −140 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 559 frames of data were collected using ω and ϕ-scans with a scan range of 1.0 ° and a counting time of 120 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data reduction were performed using SAINT V8.27B.[1] The structure was solved by direct methods using Superflip[9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2013.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms were calculated in idealized positions.

There are two crystallographically unique molecules in the asymmetric unit. In one, there is disordered phenyl ring. The disorder model included one of the acetylenic carbon atoms. The disorder was modeled by assigning the variable x to the site occupancy factors for one component of the disorder. The variable (1−x) was assigned to the site occupancy factors for the alternate component. A common isotropic displacement parameter was refined for the atoms of the two components while refining x. In this way, the site occupancy for the major component consisting of atoms C7, C8, C9, C10, C11, C12 and C13 refined to 77(2)%. The geometry of the two components was restrained to be equivalent throughout the refinement process.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0465*P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.166, with R(F) equal to 0.0731 and a goodness of fit, S, = 1.03. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (9.1(8) \times 10^{-6})* F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$ where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

Compound 3.

X-ray Experimental for $C_{42}H_{30}N_4 \cdot ½CH_2Cl_2$: Crystals grew as brownish prisms by slow diffusion of hexane into a dichloromethane solution of **3**. The data crystal was cut from a larger crystal and had approximate dimensions; 0.38 × 0.21 × 0.13 mm. The data were collected on a Rigaku ACF-12 with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation ($\lambda = 0.71075$Å). A total of 564 frames of data were collected using ω-scans with a scan range of 1 ° and a counting time of 30 seconds per frame. The data were collected at −173 °C using a Rigaku XStream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[10] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[11]

A molecule of dichloromethane was disordered around a crystallographic inversion center at 0,0,0. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to these solvent molecules were removed by use of the utility SQUEEZE[12] in PLATON98.[4] Structure analysis was aided by use of the programs PLATON98 as incorporated into WinGX.[5] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0922*P)^2 + (16.0721*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.221, with R(F) equal to 0.0793 and a goodness of fit, S, = 1.04. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

Compound 4.

X-ray Experimental for ($C_{26}H_{22}N_4$)Cu(CH_3OH)·2ClO_4: Crystals grew as clusters of blue prisms by slow diffusion of diethyl ether into a methanol solution of **4**. The data crystal was cut from a larger crystal and had approximate dimensions; 0.27 × 0.12 × 0.10 mm. The data were collected on an Agilent Technologies SuperNova Dual Source diffractometer using a μ-focus MoKα radiation source (λ = 0.71073Å) with collimating mirror monochromators. A total of 591 frames of data were collected using ω-scans with a scan range of 1 ° and a counting time of 15 seconds per frame. The data were collected at 150 K using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data collection, unit cell refinement and data reduction were performed using Agilent Technologies CrysAlisPro V 1.171.37.31.[13] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2013.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms). The hydrogen atom bound to the methanolic oxygen atom, O9, was located in a ΔF map. This hydrogen atom was ultimately tied to O9 in the final refinement model.

One of the perchlorate ions was disordered over two orientations. The disorder was modeled by assigning the variable x to the site occupancy factors for one component of the disorder. The variable (1−x) was assigned to the site occupancy factors for the alternate component. The isotropic displacement parameters for the chlorine atoms and for the oxygen atoms were refined while refining the variable x. Constraints were applied so that the isotropic displacement parameters for the chlorine atoms were kept equal. Similar constraints were applied to the displacement parameters for the oxygen atoms. The geometry of the two ions was restrained to be equivalent throughout the refinement procedure. In this way, the site occupancy for the major component consisting of atoms, Cl1, O1, O2, O3 and O4 refined to 60(2)%. The atoms of this disordered ion were ultimately refined anisotropically with their displacement parameters restrained to be approximately isotropic.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0326*P)^2 + (4.3345*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.236, with R(F) equal to 0.0807 and a goodness of fit, S, = 1.05. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

Compound 5.

X-ray Experimental for $(C_{34}H_{26}N_4)Cu(CH_3CN)\cdot 2ClO_4$: Crystals grew as clusters of blue green prisms by layering diethyl ether on top of an acetonitrile solution of the Cu complex. The data crystal had approximate dimensions; 0.39 × 0.20 × 0.15 mm. The data were collected on a Rigaku AFC12 diffractometer with a Saturn 724+ CCD using a graphite monochromator with MoKα radiation (λ = 0.71073Å). A total of 1872 frames of data were collected using ω-scans with a scan range of 0.5 ° and a counting time of 25 seconds per frame. The data were collected at −120 °C using an Oxford Cryostream low temperature device. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data reduction were performed using the Rigaku Americas Corporation's Crystal Clear version 1.40.[10] The structure was solved by direct methods using SIR97[2] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms on carbon were calculated in ideal positions with isotropic displacement parameters set to 1.2xUeq of the attached atom (1.5xUeq for methyl hydrogen atoms).

One of the perchlorate anions was disordered. The disorder was modeled by assigning the variable x to the site occupancy for one component of the disordered anion and (1−x) to the site occupancy for the alternate component. The displacement parameters for the oxygen atoms of both components were constrained to be equal while refining x. A separate constraint was applied to the displacement parameters for the Cl atoms. The geometry of the two anions was restrained to be equivalent throughout the refinement process. In this way, the major component of the disorder consisting of atoms, O1, O2, O3, O4 and Cl1 had a site occupancy of 73(2)%.

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0361*P)^2 + (1.4027*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.0934, with R(F) equal to 0.0351 and a goodness of fit, S, = 1.05. Definitions used for calculating R(F), $R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

Compound 6.

X-ray Experimental for $(C_{42}H_{30}N_4)Cu(CH_3CN)\cdot 2ClO_4$: Crystals grew as green prisms by layering diethyl ether on top of an acetonitrile solution of the Cu complex. The data crystal was cut from a larger crystal and had approximate dimensions; 0.38 × 0.24 × 0.18 mm. The data were collected at −120 °C on a Nonius Kappa CCD diffractometer using a Bruker AXS Apex II detector and a graphite monochromator with MoKα radiation (λ = 0.71073Å). Reduced temperatures were maintained by use of an Oxford Cryosystems 600 low-temperature device. A total of 877 frames of data were collected using ω and ϕ-scans with a scan range of 0.9 ° and a counting time of 14 seconds per frame. Details of crystal data, data collection and structure refinement are listed in Table 1 in the manuscript. Data reduction were performed using SAINT V8.27B.[1] The structure was solved by direct methods using SUPERFLIP[9] and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-2013.[3] Structure analysis was aided by use of the programs PLATON98[4] and WinGX.[5] The hydrogen atoms were calculated in idealized positions.

Data were originally collected on a C-centered monoclinic cell. The resulting space group was C2. wever, the refined structure was a suspiciously disordered complex that indicated that the symmetry was too high. The data was reworked as a primitive triclinic cell. The refinement showed some of the typical warning signs of twinning. In particular, there were many reflections with large, positive $\Delta(|F_o|^2 - |F_c|^2)$

values. The utility TwinRotMat in PLATON98[4] was used to look for possible twins. TwinRotMat suggested a possible twin with twin law, −1,0,0; 0,1,0; 0,−1,−1 about the 0,1,0 direct cell axis. Refinement resulted in a twin fraction 0.483(4). PLATON98 was used as incorporated into WinGX.[5]

The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$, was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0882{*}P)^2]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_W(F^2)$ refined to 0.207, with R(F) equal to 0.0787 and a goodness of fit, S, = 1.28. Definitions used for calculating R(F),$R_w(F^2)$ and the goodness of fit, S, are given below.[6] The data were checked for secondary extinction but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).[7] All figures were generated using SHELXTL/PC.[8]

References

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6 $R_w(F^2) = \{\Sigma w(|F_o|^2 - |F_c|^2)^2/\Sigma w(|F_o|)^4\}^{1/2}$, where w is the weight given each reflection.

$R(F) = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|\}$ for reflections with $F_o > 4(\sigma(F_o))$.

$S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(n - p)]^{1/2}$, where n is the number of reflections and p is the number of refined parameters.

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12 P. v. d. Sluis and A. L. Spek, *Acta Cryst.*, 1990, **A64**, 194.

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Figure S1. View of 1 showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

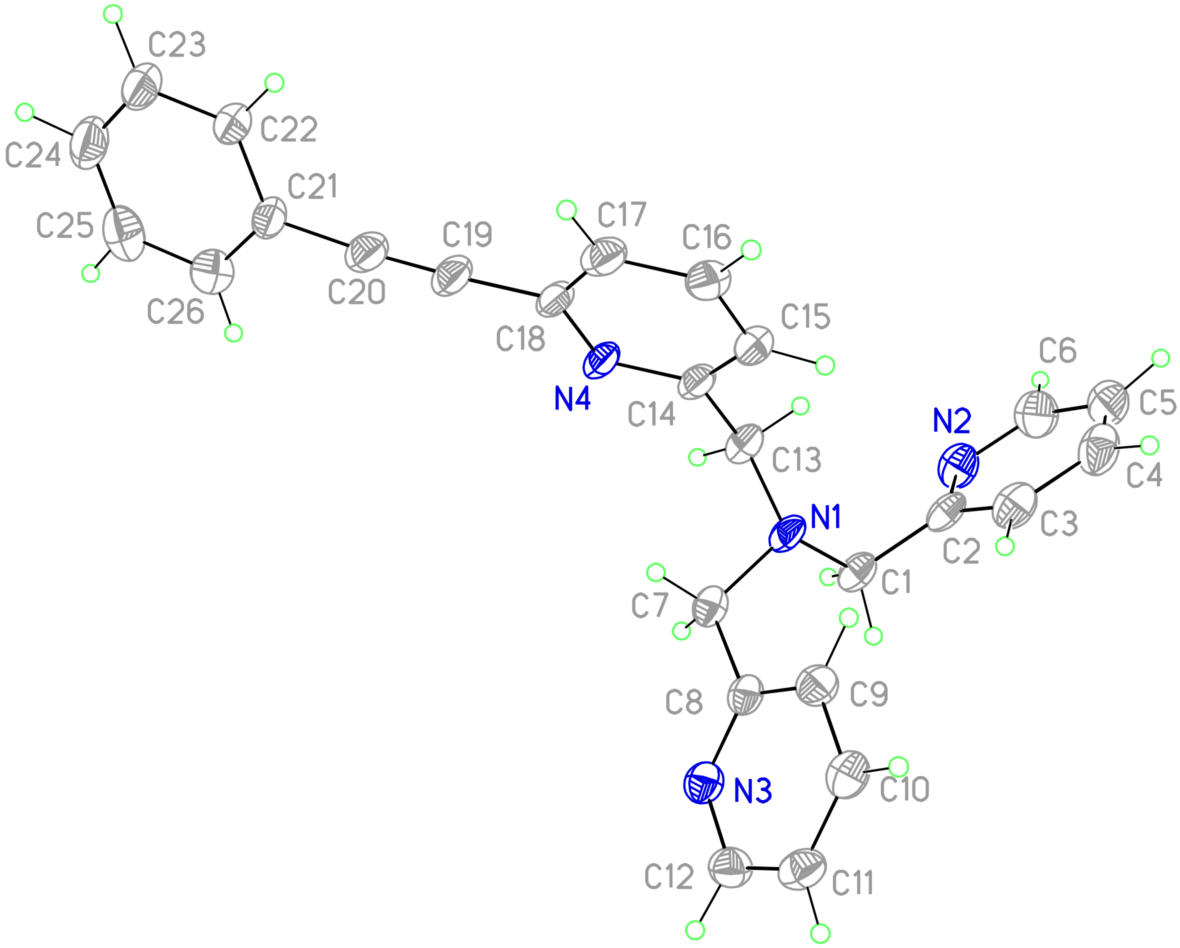


Figure S2. View of molecule 1 of **2** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level. The disordered atoms have labels appended by an A.

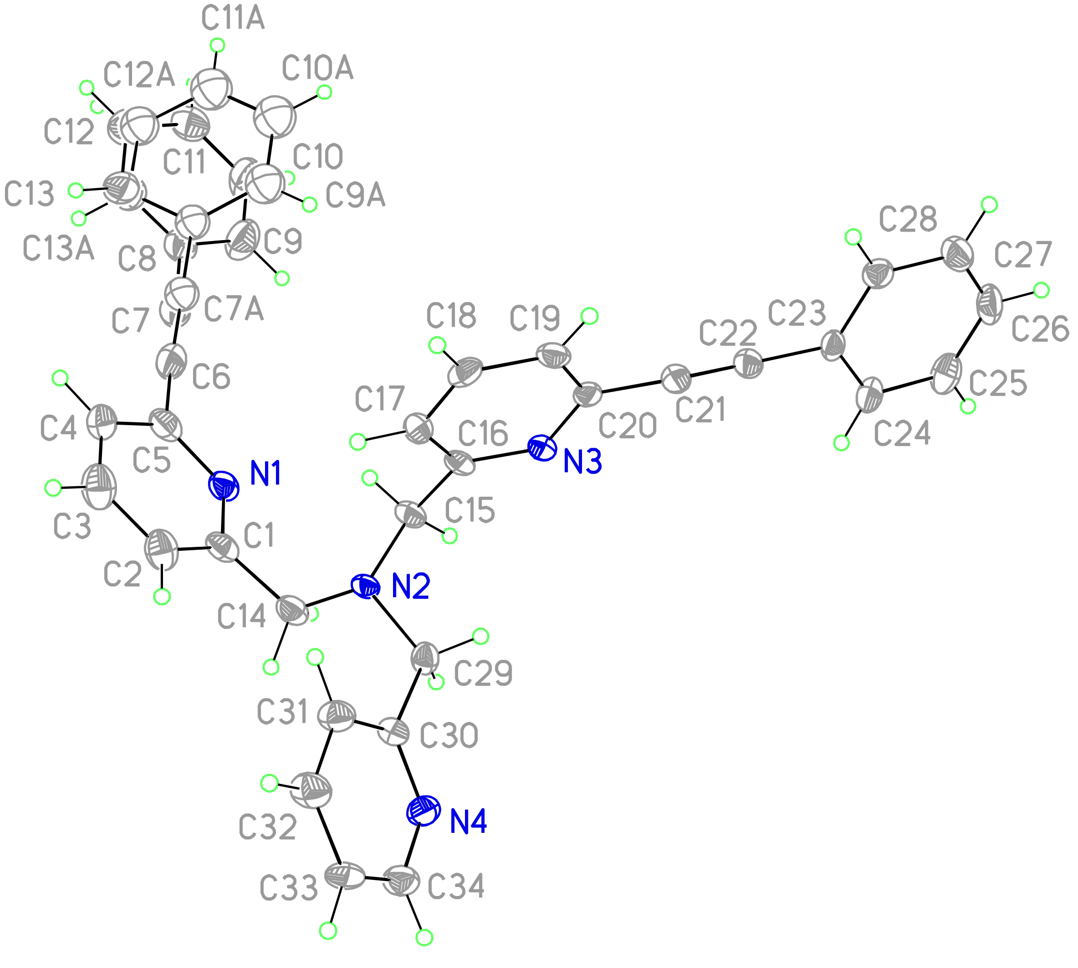


Figure S3. View of molecule 2 of **2** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

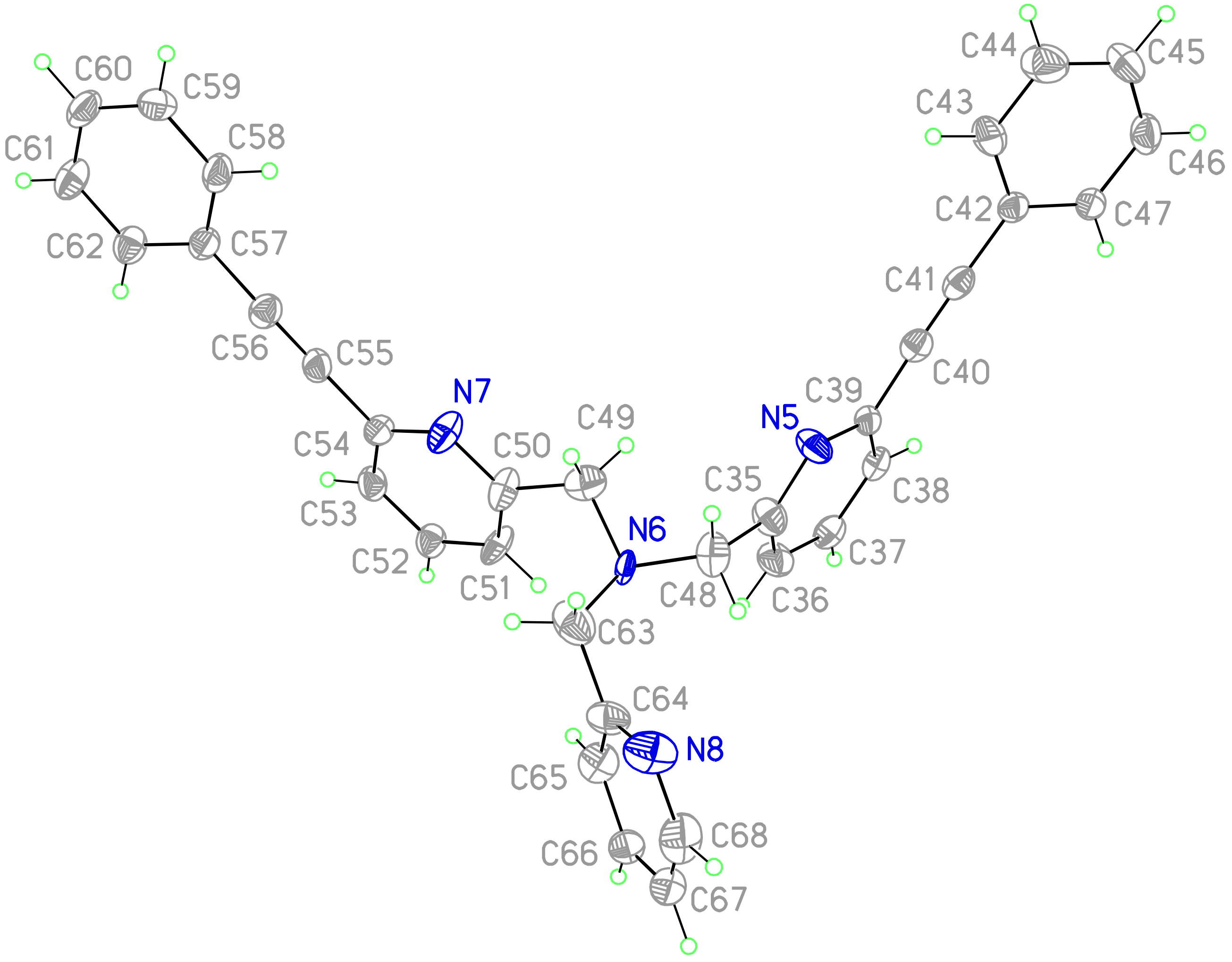


Figure 4. View of **3** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

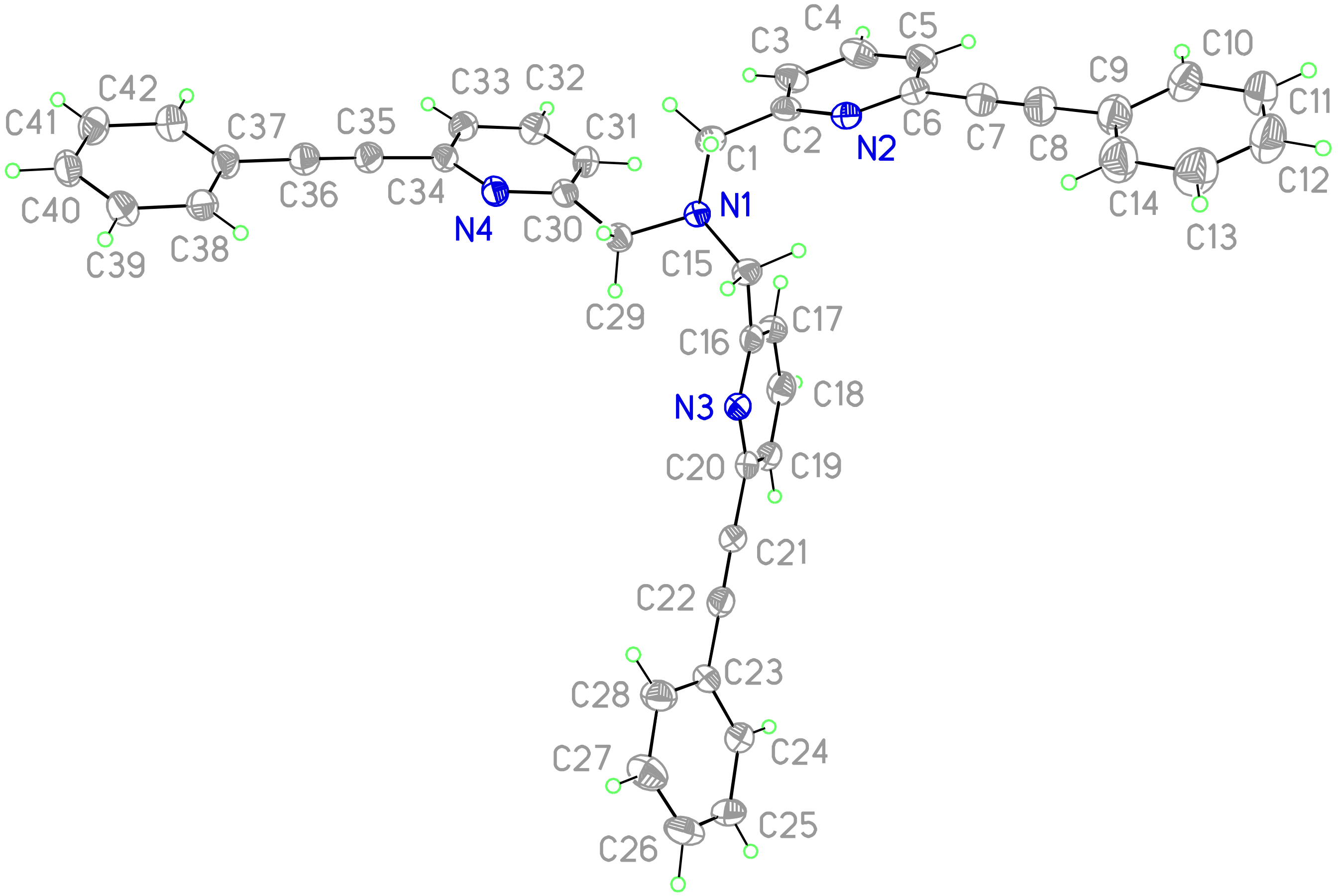


Figure S5. View of the Cu complex in **4** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 30% probability level.

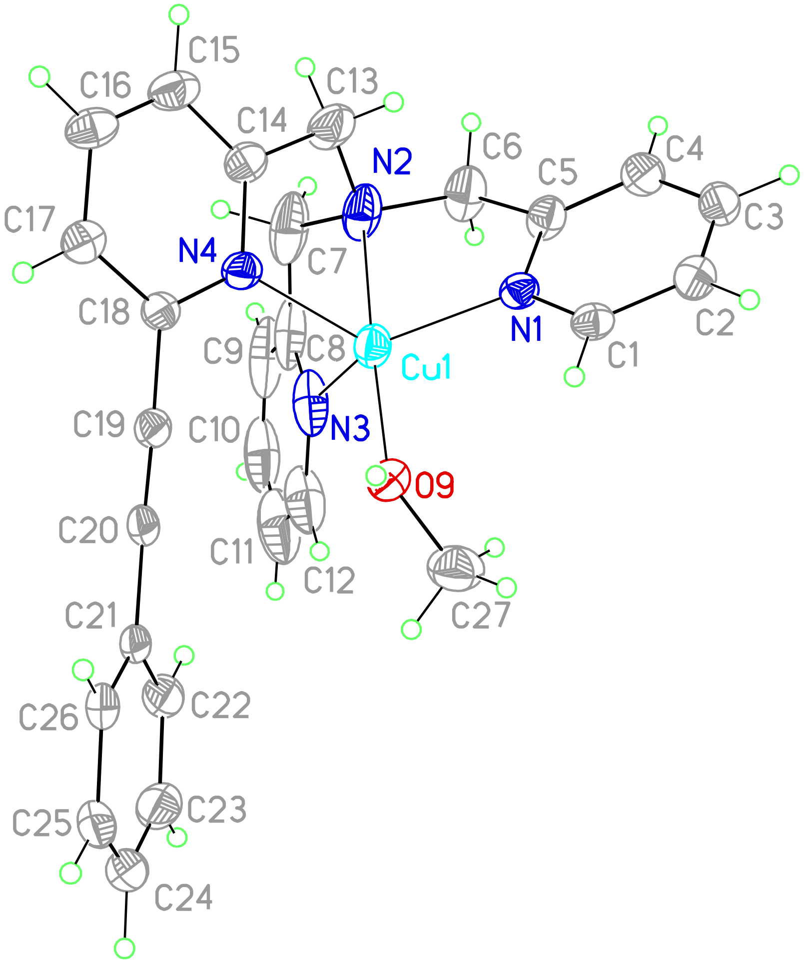


Figure S6. View of the Cu complex in **5** showing the atom labeling scheme. Displacement ellipsoids are scaled to the 50% probability level.

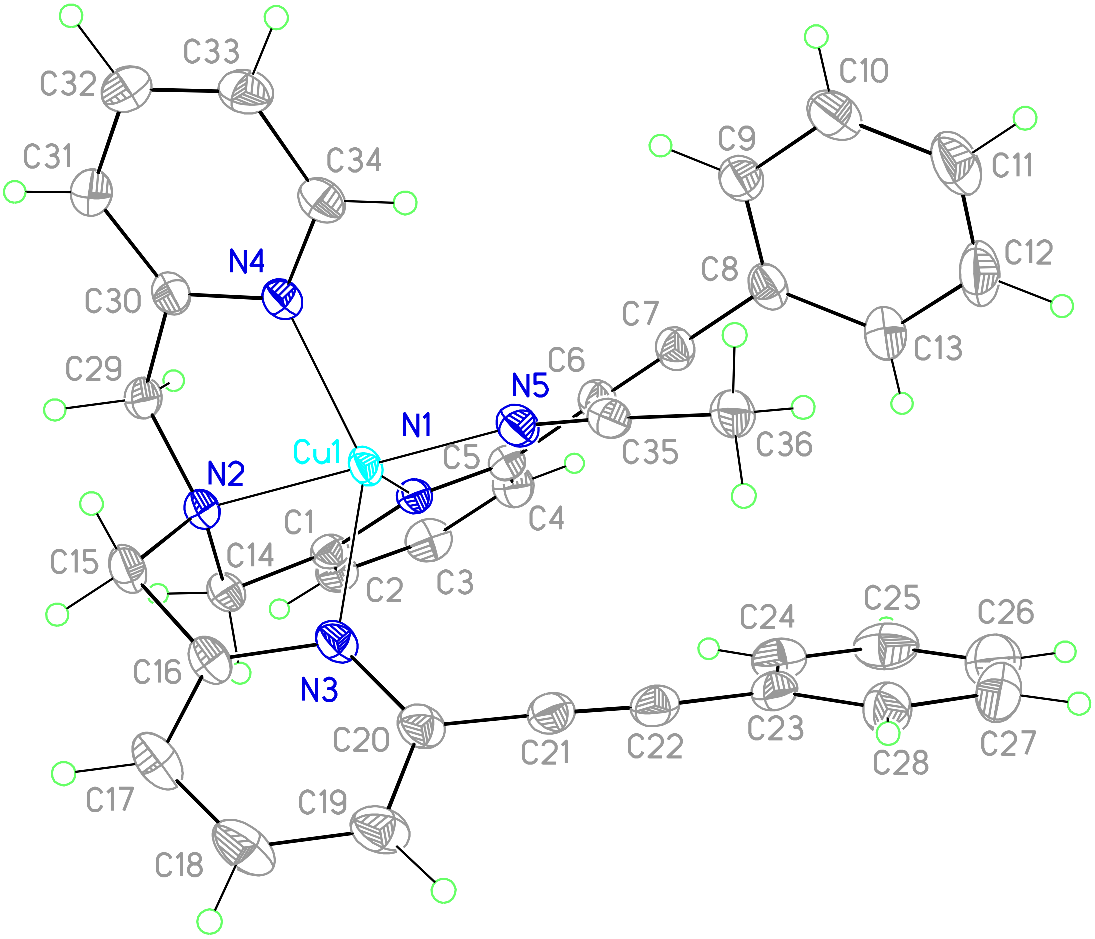
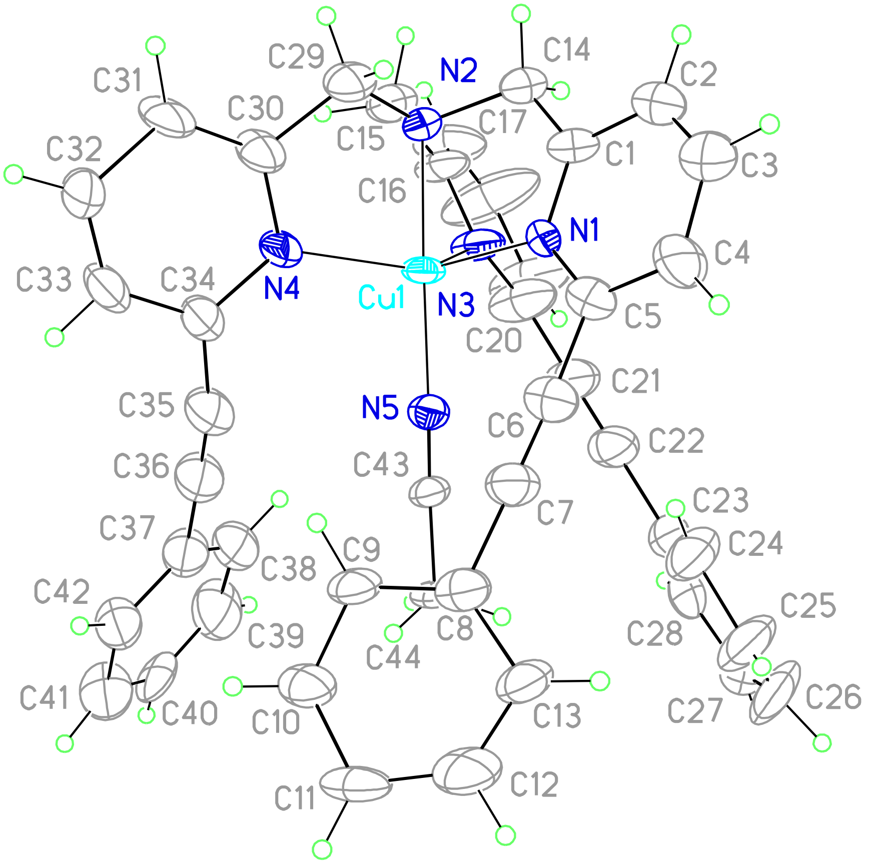


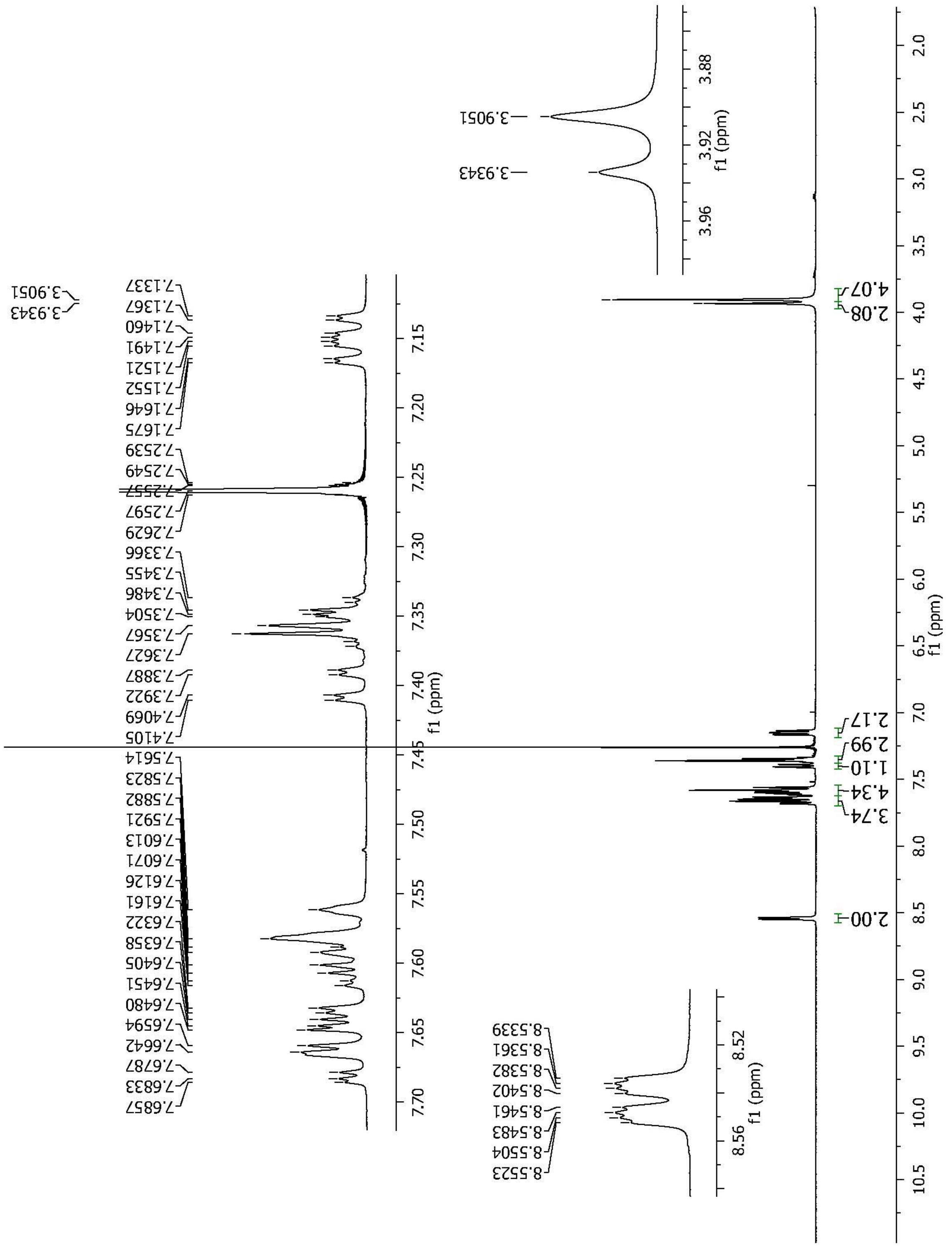
Figure S7. View of **6** showing the atom labeling scheme. Displacement ellipsoids are scaled to the



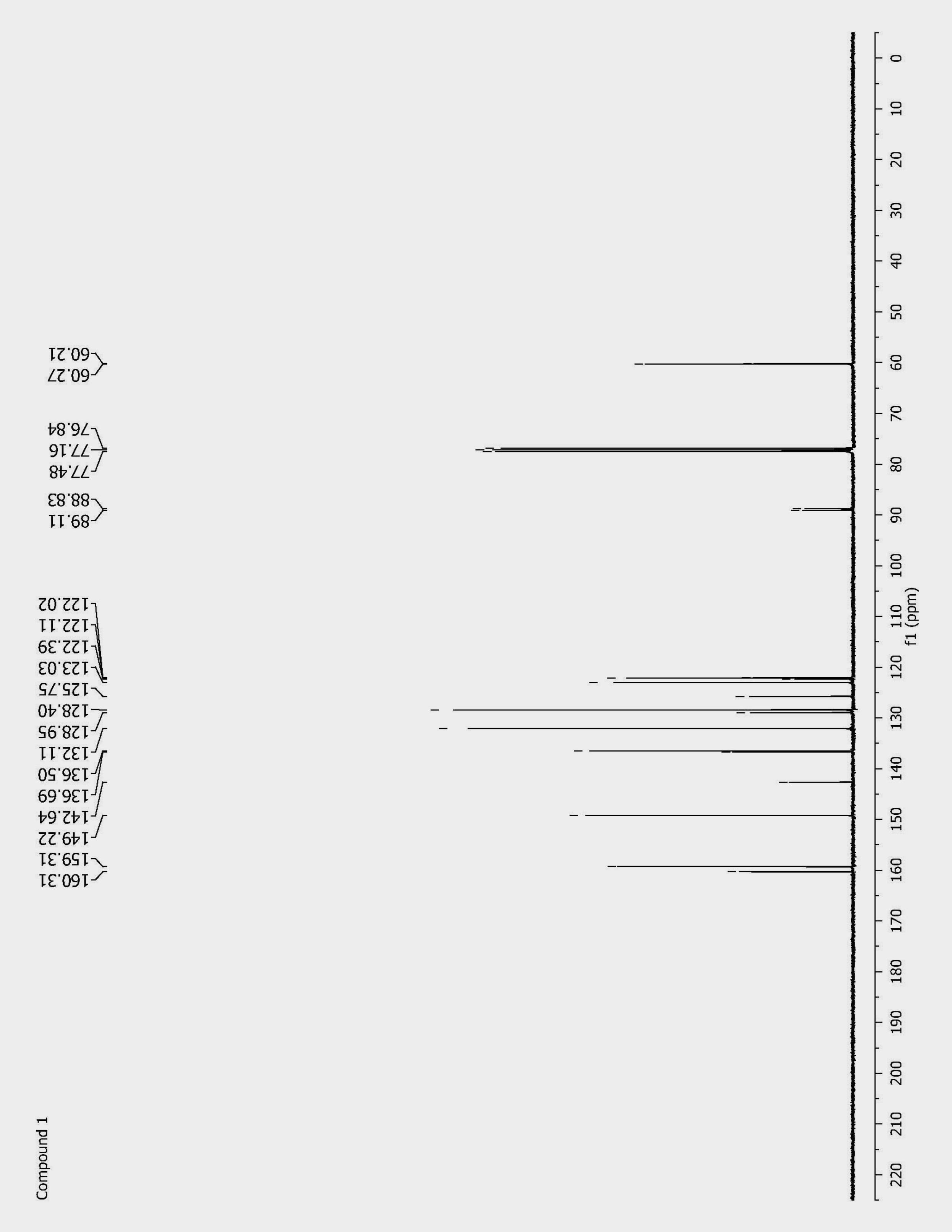
50% probability level.

NMR Spectra of Compound 1–3.

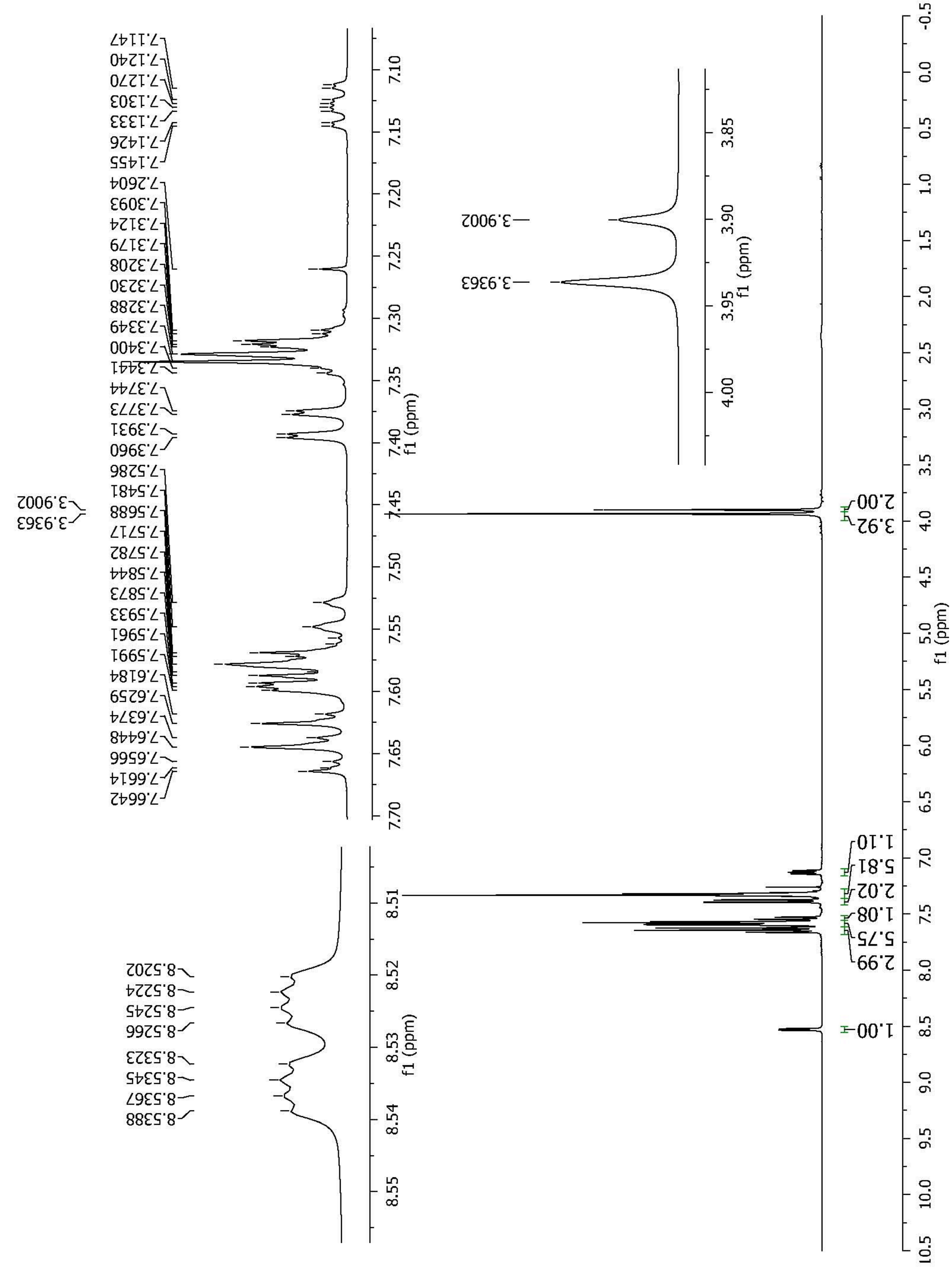
^{1}H NMR of Compound **1** ($CDCl_3$, 400 MHz)



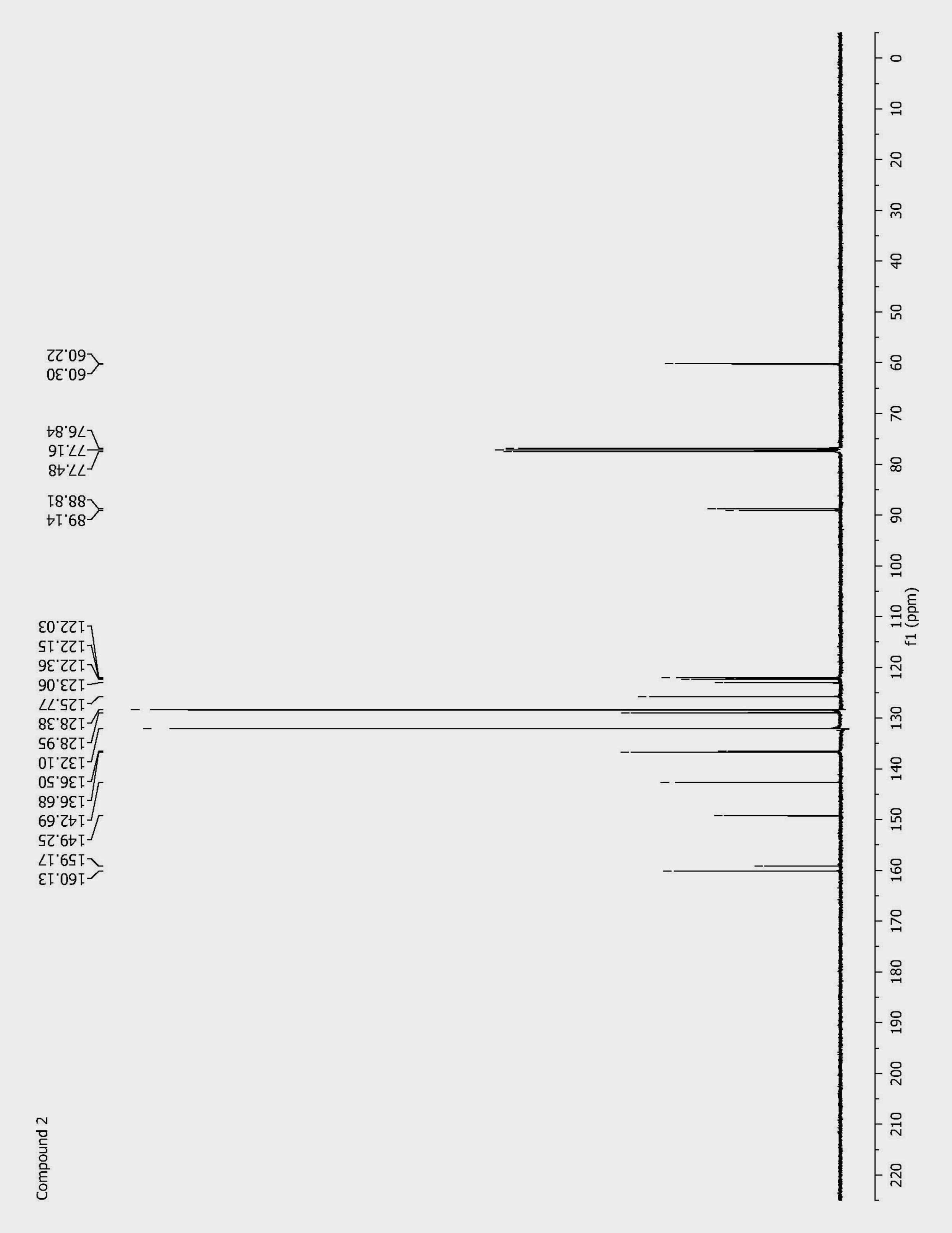
^{13}C NMR of Compound **1** ($CDCl_3$, 100 MHz)



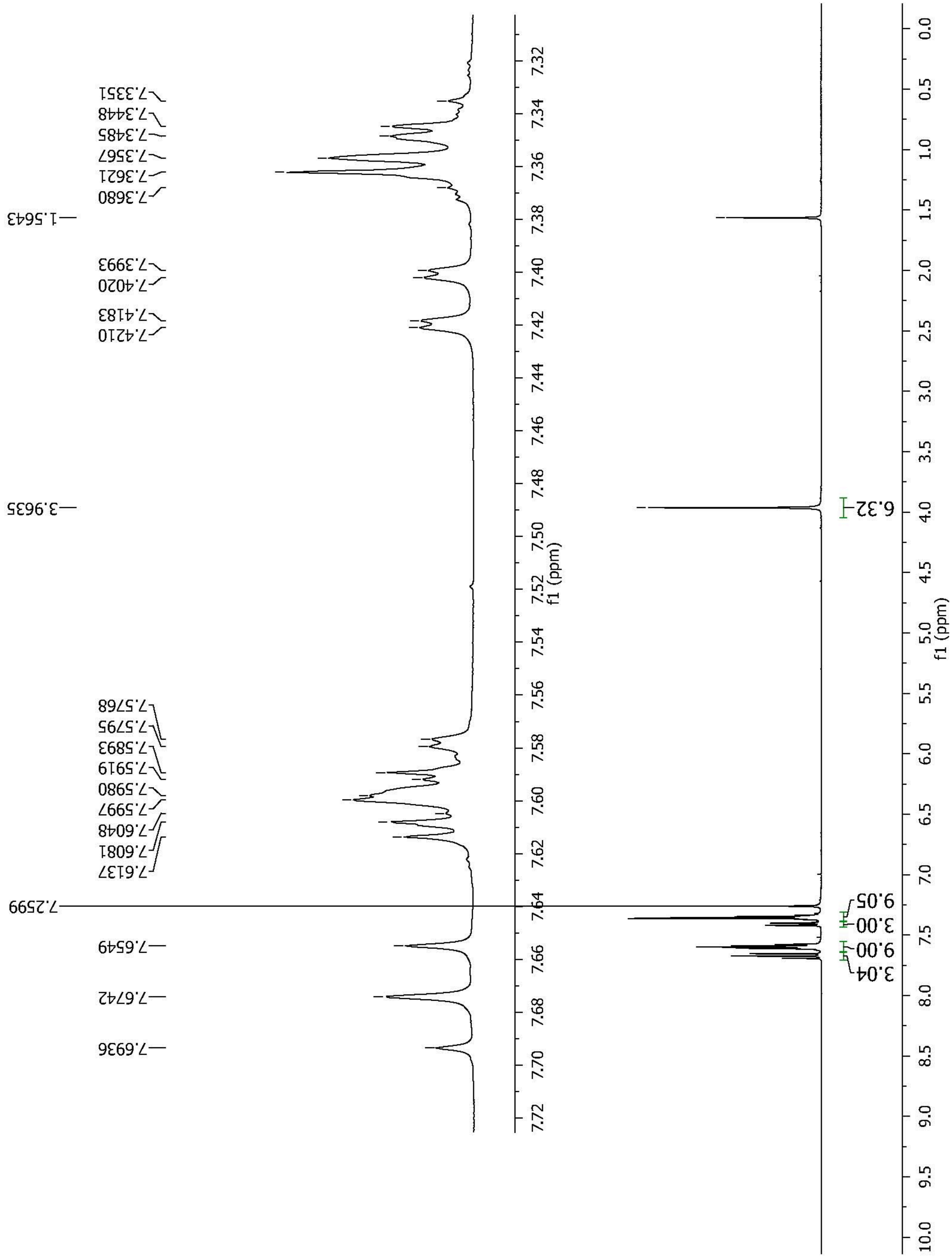
^{1}H NMR of Compound **2** ($CDCl_3$, 400 MHz)



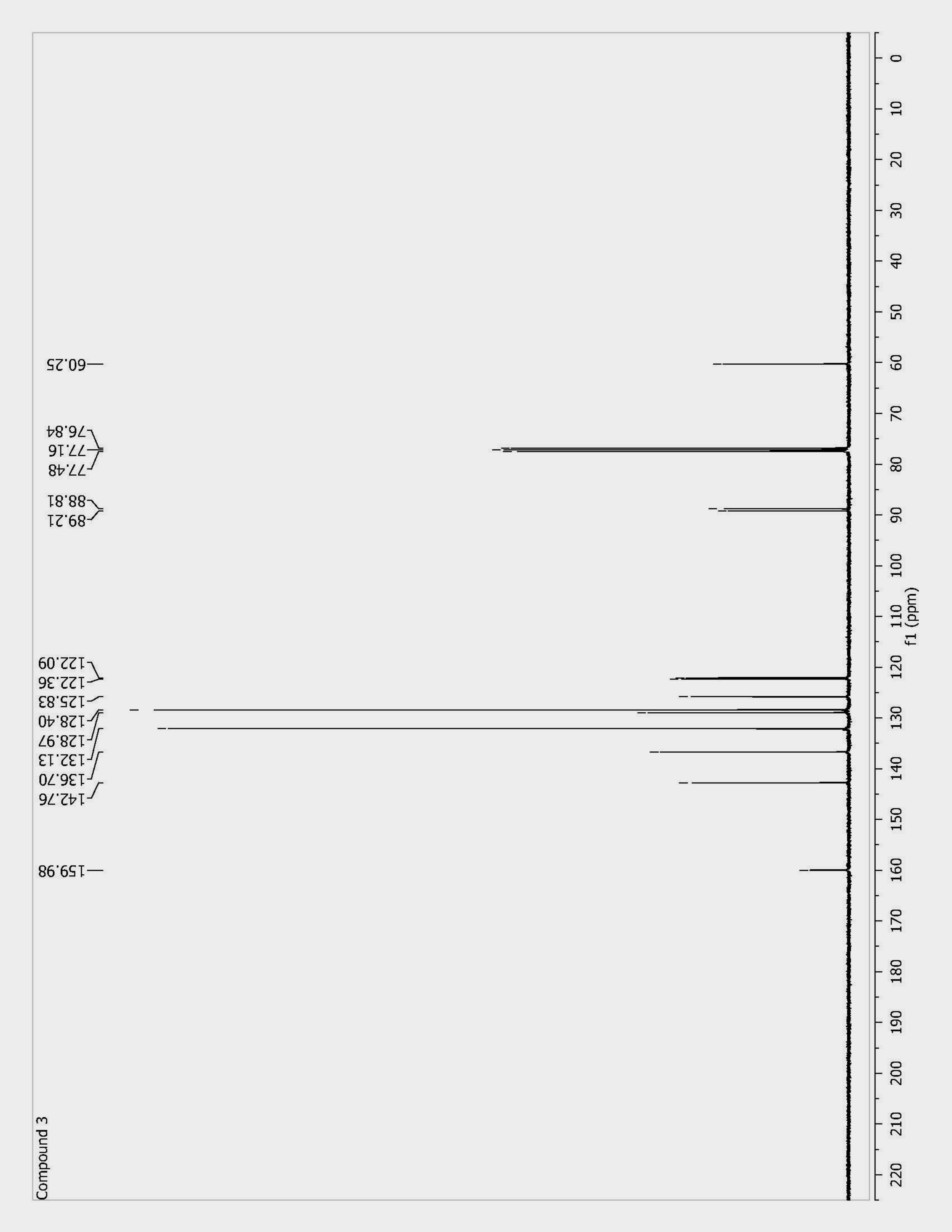
^{13}C NMR of Compound **2** ($CDCl_3$, 100 MHz)



^{1}H NMR of Compound **3** ($CDCl_3$, 400 MHz)



^{13}C NMR of Compound **3** ($CDCl_3$, 100 MHz)


Compound 3
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142.76
136.70
132.13
128.97
128.40
125.83
122.36
122.09
89.21
88.81
77.48
77.16
76.84
60.25
f1 (ppm)
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