Supporting Information for:

Binuclear β-Diketiminate Complexes of Copper(I)

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1.1	**Experimental Procedures**	**S1**
1.2	**Preparation of Starting Materials**	**S1**
1.3	***In Situ* Generation of Copper(I) Complexes**	**S5**
2	**X-ray Crystallography Data**	**S8**
3	**Multinuclear NMR Data**	**S20**

1. Experimental Procedures

For general experimental procedures see the manuscript.

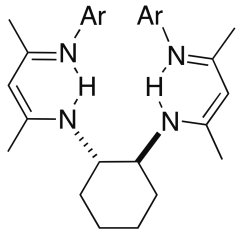
1.1 Preparation of starting materials

Synthesis of [CuO^{t}Bu]$_4$: A slurry of anhydrous CuCl (2.0g, 20.2 mmol) in THF (5 mL) was cooled to -78 ^{o}C while a solution of KO^{t}Bu (2.26 g, 20.2 mmol) in THF (10 mL) was degassed for 5 min. The KO^{t}Bu solution was added to the CuCl dropwise and the mixture allowed to stir for 30 min at -78 ^{o}C then at 25 ^{o}C for 1 h. The solvent was removed and the crude sublimed under reduced pressure (130 ^{o}-at 1 x 10 $^{-1}$ mbar) to give [CuO^{t}Bu]$_4$ as a pale yellow solid (1.8 g, 13.2 mmol, 66 %).

Synthesis of [CuMes]: To a suspension of Mg turnings (1.47 g, mmol) in THF (30 mL) was added mesityl bromide (7.5 mL, 49.0 mmol). An exothermic reaction was observed; the reaction mixture was stirred for 4h at 25 ^{o}C. The reaction mixture was transferred via filter cannula into a suspension of CuCl (5.5 g, 55.6 mmol) in THF (30 mL) at -20 ^{o}C. The reaction mixture was warmed to 25 ^{o}C and stirred overnight. 1,4-Dioxane was added and the reaction mixture stirred for 30 min. The mixture was filtered via a glass fibre, and the solids extracted with a further 20 mL of THF. The solvent was removed to give the crude product as a yellow powder. The crude product could be further purified by dissolving in toluene (50 mL), filtering and crystallization at -35 ^{o}C to give yellow crystals of CuMes (3.37 g, 18.5 mmol, 38%). 2.5:1 ratio of isomers. ^{1}H NMR (400 MHz, 298K, C_6D_6) δ 1.89 (s, 3H, *p*-Me minor), 2.01 (s, 3H, *p*-Me major), 2.92 (s, 6H, *o*-Me minor), 2.92 (s, 6H, *o*-Me major), 6.58 (s, 2H, Ar*H* minor), 6.67 (s, 2H, Ar*H* major).

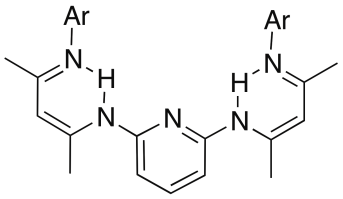
Synthesis of 2-(2,6-di-iso-propylphenyl)imido-2-penten-4-one.**[1]** To a solution of acetylacetone (20 mL, 196 mmol) and 2,6-di-iso-propylaniline (37 mL, 196 mmol) in toluene (230 mL) was added a catalytic amount of p-toluene sulphonic acid (3.7 g, 19.45 mmol, 10 mol%). The mixture was heated to a reflux (125 °C) for 7 days using the Dean-Stark apparatus. Solvent was removed *in vacuo* and red-brown residue obtained. Purification by vacuum distillation yielded *2-(2,6-di-iso-propylphenyl)imido-2-penten-4-one* as an off-white solid (21.50 g, 82.89 mmol, 42.3%), [lit.[3] 56.5%]). ^{1}H NMR ($CDCl_3$, 400 MHz, 298K): δ 12.08 (s, 1H, –N*H*), 7.30 (m, 1H, *p*-H of phenyl, $^{3}J_{H-H}$ = 8 Hz), 7.20 (d, 2H, *m*-H of phenyl, $^{3}J_{H-H}$ = 4 Hz), 5.23 (s, 1H, $CH_3C(O)CH$=), 3.05 (septet, 2H, –C*H*$(CH_3)_2$), 2.14 (s, 3H, C*H*$_3$C(O)–), 1.66 (s, 3H, –C*H*$_3$), 1.24 (d, 6H, –CH(C*H*$_3$)$_2$, $^{3}J_{H-H}$ = 8 Hz), 1.17 (d, 6H, –CH(C*H*$_3$)$_2$, $^{3}J_{H-H}$ = 8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz, 298K) δ 195.9, 163.3, 146.3, 133.5, 128.3, 123.6, 95.6, 29.1, 28.5, 24.6, 22.7, 19.2. [lit.[1] ^{1}H ($CDCl_3$, 500 MHz, 298K): 12.1 (s, 1H, –N*H*), 7.2-7.3 (3H, –C$_6$*H*$_3$(^{i}Pr)$_2$), 5.2 (s, 1H, $CH_3C(O)CH$=), 3.0 (2H, 2 –C*H*$(CH_3)_2$), 2.1 (s, 3H, C*H*$_3$C(O)–), 1.6 (s, 3H, –*CH*$_3$), 1.1-1.2 (d, 12H, 2 –CH(C*H*$_3$)$_2$); ^{13}C ($CDCl_3$, 100 MHz, 298K): 195.8, 163.3, 146.2, 133.5, 128.2, 123.5, 95.5, 29.0, 28.4, 24.5, 22.6, 19.1].

[1] X. He, Y. Yao, X. Luo, J. Zhang, Y. Liu, L. Zhang, and Q. Wu, *Organometallics*, 2003, **22**, 4952–4957



Ar = 2,6-di-iso-propylphenyl

Synthesis of ***1•H₂.*** To a colorless solution of 2-(2,6-di-iso-propylphenyl)imido-2-penten-4-one (10.0 g, 38.55 mmol) in DCM (50 mL) at 25 °C was added a solution of $[Et_3O][BF_4]$ (9.1 g, 42.60 mmol) in DCM (10 mL). The reaction mixture produced a colorless suspension that gradually dissolved over 20 minutes. The mixture was stirred for 6 h at this temperature and Et_3N (6 mL, 5.79 mmol) added, the mixture turned dark pink. The homogeneous reaction mixture was separated into two equal volumes. To a suspension of 1,2-trans-diaminocyclohexane (1.13 mL, 9.65 mmol) in Et_3N (4 mL) was added one volume of the reaction mixture (the remainder was used in the synthesis of the analogue **2•H₂**). The reaction mixture was stirred for 14 days at 25 °C. The volatiles were removed under reduced pressure and the crude recrystallized from hot n-hexane with cooling to 5 °C. The product was isolated as an off-white sold (1.73 g, 2.6 mmol, 15%). A further crop of product was isolated by trituration of the residue in acetone (440 mg, mmol, 4 %). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 0.85-0.95 (m, 2H), 1.21-1.27 (series of d, 24H), 1.21-1.27 (m, 2H), 1.32-1.40 (m, 2H), 1.65 (s, 6H), 1.80-1.90 (m, 2H), 1.91 (s, 6H), 3.05-3.15 (m, 2H), 3.12 (hept, 4H, *J* = 6.4 Hz), 4.65 (s, 2H), 7.11-7.22 (m, 6H), 11.25 (broad s, 2H, N*H*); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 19.1, 22.5, 22.7, 23.0, 23.6, 241., 24.3, 28.0, 28.2, 32.3, 57.2, 93.7, 122.9, 123.0, 123.2, 138.0, 146.9, 154.7, 166.7; Infrared (ATR cell, cm^{-1}) 2955, 2922, 1621, 1553; Mass Spec. (EI, +ve) 596 ([M]$^+$, 5%), 418, 403, 202; High-resolution mass spec. calc. for $C_{40}H_{60}N_4$ 596.4818 found 596.4793.

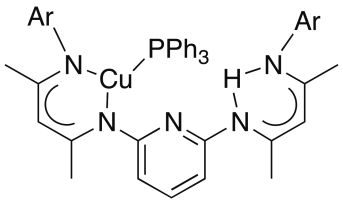


Ar = 2,6-di-iso-propylphenyl

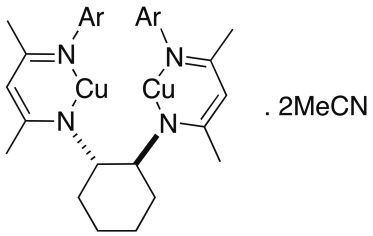
Synthesis of ***2•H₂***.[2] To a colorless solution of 2-(2,6-di-iso-propylphenyl)imido-2-penten-4-one (10.0 g, 38.55 mmol) in DCM (50 mL) at 25 °C was added a solution of $[Et_3O]BF_4$ (9.1 g, 42.60 mmol) in DCM (10 mL). The reaction mixture produced a colorless suspension that gradually dissolved over 20 minutes. The mixture was stirred for 6 h at this temperature and Et_3N (6 mL, 5.79 mmol) added, the mixture turned dark pink. The homogeneous reaction mixture was separated into two equal volumes. To a suspension of 2,6-diaminopyridine (1.05 g, 9.65 mmol) in Et_3N (4 mL) was added one volume of the reaction mixture (the remainder was used in the synthesis of the analogue **1•H₂**). After 24 h at 25 °C analysis of an aliquot by NMR showed only the mono-condensation product. The reaction mixture was heated to reflux (40 °C) for 14 days. At which point the volatiles were removed under reduced pressure. The crude product was dissolved in hot absolute ethanol (50 mL) and allowed to cool to room temperature the product was isolated as a yellow solid (2.1 g, 18%). ^{1}H NMR ($CDCl_3$, 400 MHz, 298 K) δ 1.30 (d, 12H, *J* = 6.8 Hz), 1.31 (d, 12H, *J* = 6.8 Hz), 1.71 (s, 6H), 3.17 (s, 6H), 4.93 (s, 2H), 6.25 (d, 2H, *J* = 8.0 Hz), 6.95 (t, 1H, *J* = 8.0 Hz), 7.25-7.30 (m, 6H), 13.92 (broad s, 1H, N*H*); ^{13}C NMR ($CDCl_3$, 100 MHz, 298 K) δ 21.4, 22.4, 23.8, 28.4, 99.6, 106.1, 123.1, 123.9, 138.0, 139.0, 145.4, 151.3, 154.0, 168.4.

[2] D. F. Piesik, S. Range, and S. Harder, *Organometallics*, 2008, **27**, 6178–6187.

1.3 In situ generation of copper(I) complexes



In situ generation of **[2•H•Cu(L¹)]**: In a glovebox, to a solution of the ligand (40 mg, 0.07 mmol, 1 equiv.) in C_6D_6 (0.5 mL) was added CuMes (28 mg, 0.15 mmol, 2.2 equiv.) and PPh_3 (45 mg, 0.17 mmo, 2.5 equiv.). The reaction mixture was transferred to a Youngs NMR tube and the reaction monitored by ^1H NMR spectroscopy. After 1 day at 25 °C selective formation of the monocopper product **[2•H•Cu(L¹)]**was observed by spectroscopy. *In situ* data: ^1H NMR (C_6D_6, 400 MHz, 298 K) δ 1.02 (d, 6H, *J* = 6.8 Hz), 1.26 (d, 6H, *J* = 6.8 Hz), 1.27 (d, 6H, *J* = 6.8 Hz), 1.34 (d, 6H, *J* = 7.2 Hz), 1.75 (s, 3H), 1.97 (s, 3H), 2.19 (s, 3H), 2.65 (s, 3H), 3.17 (hept, 2H, *J* = 6.8 Hz), 3.62 (hept, 2H, *J* = 6.8 Hz), 4.95 (s, 1H), 5.24 (s, 1H), 6.07 (d, 1H, *J* = 8.0 Hz), 6.16 (d, 1H, *J* = 8.0 Hz), 6.53 (t, 1H, *J* = 8.0 Hz), 7.10-7.50 (m, 21H, partially obscured by unreacted PPh_3). ^{31}P (C_6D_6, 202 MHz, 298K): +3.82.



Ar = 2,6-di-iso-propylphenyl

In situ generation of ***[1•Cu₂(NCMe)₂]*** *from [CuO^{t}Bu]*: The ligand (41 mg, 0.069 mmol) was dissolved in a 10:1 mixture of C_6D_6 to MeCN. CuO^{t}Bu was added as a solid (3 equiv.) and the mixture turned dark brown. The mixture was transferred to a J. Youngs NMR tube and the reaction monitored by ^1H NMR spectroscopy. After 30 minutes at room temperature a further 1 equiv. of CuO^{t}Bu was added, followed by 30 min then another addition of 1 equiv. of [CuO^{t}Bu]. NMR analysis after the additional of the final aliquot showed mainly the desired product **[1•Cu₂(NCMe)₂]**. ^1H NMR (C_6D_6 + MeCN, 400 MHz, 298 K) δ 1.20-1.37 (series of d, 24H, partially obscured by ^{t}Bu), 1.45-1.55 (m, 2H), 1.78 (s, 6H), 1.80-1.88 (m, 2H), 2.88 (s, 3H, unknown possibly MeCN), 2.00-2.15 (m, 4H), 2.44 (s, 6H), 3.43 (hept, 2H, *J* = 6.8 Hz), 3.52 (hept, 2H, *J* = 6.8 Hz), 4.01-4.11 (m, 2H), 4.64 (s, 2H), 7.05-7.20 (m, 6H).

In situ generation of ***[2•Cu$_2$(L^4)$_2$] (L^4=quinoline):*** **[2•Cu$_2$]$_2$** (5.8 mg, 0.00404 mmol) and quinoline (5.88 µL,, 0.0510 mmol, 12 equiv.) were dissolved in C_6D_6 (0.6 mL), showing quantitative conversion to **[2•Cu$_2$(L^4)$_2$]** by ^{1}H NMR. Attempts to isolate crystals or an analytically pure powder were unsuccessful. ^{1}H NMR (C_6D_6, 400 MHz) δ: 0.95 (br d, $^3J_{HH}$ = 6.3 Hz, 12H, CH_3^{iPr}), 1.25 (d, $^3J_{HH}$ = 6.9 Hz, 12H, CH_3^{iPr}), 1.96 (S, CH_3^{NacNac}), 2.09 (s, CH_3^{NacNac}), 3.62 (br hept, $^3J_{HH}$ = 6.7 Hz, 4H, CH^{iPr}), 5.08 (s, CH^{NacNac}), 6.39 (d, $^3J_{HH}$ = 7.7 Hz, 2H, $CH^{m\text{-py}}$), 6.72 (m, 2H, CH^{quin}), 7.12 (m, 2H, CH^{quin}), 7.31 (m, 4H, CH^{quin}), 7.46 (br d, $^3J_{HH}$ = 6.9 Hz, 2H, CH^{quin}), 8.31 (br d, $^3J_{HH}$ = 8.4 Hz, 2H, CH^{quin}), 8.70 (br s, 2H, CH^{quin}). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz) δ: 23.7–23.9 (br s x 3, $CH_3^{NacNac/iPr}$), 24.1 (s, CH_3^{NacNac}), 28.1 (s, CH^{iPr}), 95.5 (CH^{NacNac}), 112.0 (s, $CH^{m\text{-py}}$), 121.2 (s, CH^{quin}), 123.5 (S, CH), 123.6 (s, CH), 123.8 (s, CH), 124.9 (s, CH^{quin}), 126.6 (s, CH), 127.8 (s, CH), 128.4 (s, CH), 129.4 (S, CH^{quin}), 135.4 (s, CH^{quin}), 130.4 (s, CH^{quin}), 140.5 (s, C), 147.2 (s, C), 147.8 (S, C), 148.7 (S, C), 148.9 (s, C), 150.8 (s, CH^{quin}), 157.8 (s, C), 161.9 (s, C), 163.5 (s, C), 164.1 (s, C), 164.1 (s, C), 165.2 (S, C).

In situ generation of ***[2•Cu$_2$(L^5)$_2$] (L^5=hex-1-ene): [2•Cu$_2$]$_2$*** (17.0 mg, 0.0119 mmol) and hex-1-ene (17.86 µL, 0.143 mmol, 12 equiv.) were dissolved in C_6D_6 (0.6 mL), showing quantitative conversion to **[2•Cu$_2$(L^5)$_2$]** by ^{1}H NMR. Attempts to isolate crystals or an analytically pure powder were unsuccessful. ^{1}H NMR (C_6D_6, 500 MHz) δ: 0.71–0.75 (m, 6H, CH_3^{hexene}), 0.99–1.31 (m, 36H, CH_2^{hexene} and CH_3^{Dipp}), 1.80 (s, 3H, CH_3^{NacNac}), 1.81 (s, 3H, CH_3^{NacNac}), 2.07 (s, 3H, CH_3^{NacNac}), 2.09 (s, 3H, CH_3^{NacNac}), 3.10 (dd, $^2J_{HH}$ = 15.4 Hz, $^3J_{HH}$ = 5.6 Hz, CH_2^{hexene}, 2H), 3.20–3.26 (m, 2H, CH^{Dipp}), 3.30 (*pseudo* t, 2H, J_{HH} = 9.0 Hz, CH_2^{hexene}), 4.18–4.28 (m, 2H, CH^{hexene}), 5.01 (s, 1H, CH^{NacNac}), 5.02 (s, 1H, CH^{NacNac}), 6.44 (d, 1H, $^3J_{HH}$ = 3.1 Hz, *m*-$CH^{pyridine}$), 6.45 (d, 1H, $^3J_{HH}$ = 3.1 Hz, *m*-$CH^{pyridine}$), 7.09–7.15 (m, 7H, *p*-$CH^{pyridine}$ and CH^{Dipp}). $^{13}C\{^1H\}$ NMR (C_6D_6, 126 MHz) δ: 14.1 (s, CH_3^{hexene}), 22.3 (s, CH_2^{hexene}), 23.5 (s, $CH_3^{NacNac/Dipp}$), 23.9 (s, $CH_3^{NacNac/Dipp}$), 24.0 (s, $CH_3^{NacNac/Dipp}$), 24.2 (s, $CH_3^{NacNac/Dipp}$), 24.4 (s, $CH_3^{NacNac/Dipp}$), 24.6 (s, $CH_3^{NacNac/Dipp}$), 28.1 (s, CH^{iPr}), 28.2 (s, CH^{iPr}), 32.9 (s, CH_2^{hexene}), 32.9 (s, CH_2^{hexene}), 33.3 (s, CH_2^{hexene}), 33.4 (s, CH_2^{hexene}), 75.7 (s, CH_2^{hexene}-terminal), 75.8 (s, CH_2^{hexene}-terminal), 96.0 (s, CH^{NacNac}), 96.1 (s, CH^{NacNac}), 97.1 (s, CH^{hexene}), 97.3 (s, CH^{hexene}), 113.6 (s, *m*-$CH^{pyridine}$), 113.7 (s, *m*-$CH^{pyridine}$), 123.7 (s, CH^{Dipp}), 124.6 (s, CH^{iPr}), 128.4 (s, CH^{Dipp}), 137.8 (s, *p*-$CH^{pyridine}$).

In situ generation of ***[2•Cu$_2$(L^7)$_2$] (L^7 = cyclohexene):*** **[2•Cu$_2$]$_2$** (7.1 mg, 0.00495 mmol) and cyclohexene (15 µL, 0.148 mmol, 30 equiv.) were dissolved in C_6D_6 (0.6 mL), showing quantitative conversion to **[2•Cu$_2$(L^7)$_2$]** by ^{1}H NMR. Attempts to isolate crystals or an analytically pure powder were unsuccessful as a result the resonances of cyclohexene ligand could not all be resolved in the multinuclear NMR data. ^{1}H NMR (C_6D_6, 400 MHz) δ: 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH_3^{iPr}), 1.16 (d, $^3J_{HH}$ = 6.7 Hz, 12H, CH_3^{iPr}), 1.85 (s, 6H, CH_3^{NacNac}), 2.05 (s, 6H, CH_3^{NacNac}), 3.30 (hept, $^3J_{HH}$ = 6.7 Hz, 4H, CH^{iPr}), 4.48 (br s, 4H, CH^{Cyh}), 5.02 (s, 2H, CH^{NacNac}), 6.41 (d, $^3J_{HH}$ = 7.7 Hz, 2H, $CH^{m\text{-py}}$), 7.05 (t, $^3J_{HH}$ = 7.7 Hz, 1H, $CH^{p\text{-py}}$), 7.09–7.14 (m, 6H, $CH^{m\text{-}/p\text{-Dipp}}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz) δ: 23.1 (s, CH_2^{Cyh}), 23.9 (s, CH_3^{iPr}), 24.0 (s, CH_3^{NacNac}), 24.2 (s, CH_3^{NacNac}), 24.4 (s, CH_2^{Cyh}), 24.7 (s, CH_3^{iPr}), 28.1 (s, CH^{iPr}), 91.8 (s, CH^{Cyh}), 95.3 (s, CH^{NacNac}), 113.8 (s, $CH^{m\text{-py}}$), 124.5 (s, $CH^{m\text{-Dipp}}$), 128.4 (s, $CH^{p\text{-Dipp}}$), 138.0 (s, $CH^{p\text{-py}}$), 140.9 (s, C^{Dipp}), 148.1 (s, $C^{o\text{-py}}$), 162.1 (s, C^{NacNac}), 164.4 (s, C^{Dipp}), 164.7(s, C^{NacNac}).

2. Xray Crystallography Data

Table S1. Crystal Data, Data Collection and Refinement Parameters for the structures of **1·H$_2$**, **3·H$_2$**, **[1·Cu$_2$(L^1)$_2$]**, **[2·Cu$_2$(L^1)$_2$]·Et$_2$O**, **[2·Cu$_2$(L^1)$_2$]·thf**, **[3·Cu$_2$(L^1)$_2$]**, **[2·Cu$_2$(L^2)]**, **[2·Cu$_2$(L^3)$_2$]**, **[2·Cu$_2$(L^6)$_2$]** and **[2·Cu$_2$(L^8)$_2$]**.

data	1·H$_2$	3·H$_2$	[1·Cu$_2$(L^1)$_2$]	[2·Cu$_2$(L^1)$_2$]·Et$_2$O
formula	$C_{40}H_{60}N_4$	$C_{46}H_{58}N_4O$	$C_{76}H_{88}Cu_2N_4P_2$	$C_{75}H_{81}Cu_2N_5P_2$
solvent	0.75(C_6H_{14})	—	3(C_4H_8O)	$C_4H_{10}O$
formula weight	661.54	682.96	1462.83	1315.58
colour, habit	colourless	colourless	colourless	colourless
temperature / K	173	173	173	173
crystal system	monoclinic	monoclinic	triclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	P-1 (no. 2)	P-1 (no. 2)
a / Å	31.4335(10)	14.2470(12)	11.5523(3)	12.5893(3)
b / Å	16.2490(5)	9.3174(9)	16.7641(4)	17.0144(5)
c / Å	17.1849(5)	31.077(3)	20.9664(5)	18.6054(5)
α / deg	90	90	88.7166(19)	67.890(3)
β / deg	104.828(3)	92.632(8)	78.054(2)	78.6668(19)
γ / deg	90	90	85.895(2)	75.182(2)
V / Å^3	8485.1(5)	4121.0(7)	3962.18(17)	3547.01(17)
Z	8 [b]	4	2	2
D_c / g cm^{-3}	1.036	1.101	1.226	1.232
radiation used	Mo-Kα	Cu-Kα	Mo-Kα	Cu-Kα
μ / mm^{-1}	0.060	0.502	0.628	1.524
2θ max / deg	58	148	59	145
no. of unique reflns				
measured (R_{int})	18571 (0.0296)	7937 (0.0561)	18426 (0.0224)	13737 (0.0268)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	11478	4713	14649	11660
no. of variables	946	486	985	840
R_1(obs), wR_2(all) [a]	0.0658, 0.1620	0.0860, 0.3064	0.0420, 0.1139	0.0362, 0.1019

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$. [b] There are two crystallographically independent molecules.

Table S1. part 2

data	[2·Cu$_2$(L^1)$_2$]·thf	[3·Cu$_2$(L^1)$_2$]	[2·Cu$_2$(L^2)]
formula	$C_{75}H_{81}Cu_2N_5P_2$	$C_{82}H_{86}Cu_2N_4OP_2$	$C_{65}H_{75}Cu_2N_5P_2$
solvent	C_4H_8O	1.5($C_4H_{10}O$)	0.5(C_6H_{14})
formula weight	1313.57	1443.74	1158.40
colour, habit	colourless tablets	pale yellow	yellow blocks
temperature / K	173	173	173
crystal system	triclinic	triclinic	monoclinic
space group	*P*-1 (no. 2)	*P*-1 (no. 2)	$P2_1/n$ (no. 14)
***a* / Å**	12.7327(3)	12.6567(3)	14.7652(2)
***b* / Å**	16.8122(5)	13.8730(4)	17.8395(4)
***c* / Å**	18.6974(7)	24.4443(6)	23.9383(4)
α / deg	67.156(3)	90.544(2)	90
β / deg	76.696(3)	104.629(2)	98.5171(17)
γ / deg	74.461(3)	105.500(2)	90
***V* / Å^3**	3517.7(2)	3988.23(18)	6235.9(2)
Z	2	2	4
***D*$_c$ / g cm^{-3}**	1.240	1.202	1.234
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.698	0.623	0.777
2θ max / deg	57	57	59
no. of unique reflns			
measured (*R*$_{int}$)	14427 (0.0217)	15979 (0.0294)	14929 (0.0291)
obs, |*F*$_o$| > 4σ(|*F*$_o$|)	11131	11875	11853
no. of variables	840	961	739
***R*$_1$(obs), *wR*$_2$(all)** [a]	0.0383, 0.0963	0.0473, 0.1213	0.0363, 0.0905

Table S1. part 3

data	$[2{\cdot}Cu_2(L^3)_2]$	$[2{\cdot}Cu_2(L^6)_2]$	$[2{\cdot}Cu_2(L^8)_2]$
formula	$C_{49}H_{61}Cu_2N_7$	$C_{49}H_{67}Cu_2N_5$	$C_{53}H_{71}Cu_2N_5$
solvent	—	$C_4H_{10}O$	—
formula weight	875.12	927.27	905.22
colour, habit	orange blocks	pale yellow	pale yellow
temperature / K	173	173	173
crystal system	monoclinic	triclinic	triclinic
space group	*C*2 (no. 5)	*P*-1 (no. 2)	*P*-1 (no. 2)
***a* / Å**	18.3602(8)	13.1519(6)	13.4277(8)
***b* / Å**	12.4769(5)	13.7723(6)	13.8080(7)
***c* / Å**	10.1119(4)	14.9883(6)	14.3150(8)
α / deg	90	69.349(4)	99.766(4)
β / deg	103.858(5)	89.209(3)	110.966(6)
γ / deg	90	84.603(4)	92.373(4)
***V* / Å^3**	2248.98(17)	2528.63(19)	2427.4(2)
Z	2	2	2
D_c / g cm^{-3}	1.292	1.218	1.238
radiation used	Mo-Kα	Mo-Kα	Mo-Kα
μ / mm^{-1}	0.987	0.882	0.916
2θ max / deg	56	56	56
no. of unique reflns			
measured (R_{int})	3247 (0.0288)	9960 (0.0237)	14438 (0.034)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	2882	7905	8427
no. of variables	270	580	570
R_1(obs), wR_2(all) [a]	0.0406, 0.0946	0.0387, 0.0951	0.0382, 0.0724

Table 1 provides a summary of the crystallographic data for the structures of **$1{\cdot}H_2$**, **$3{\cdot}H_2$**, **$[1{\cdot}Cu_2(L^1)_2]$**, **$[2{\cdot}Cu_2(L^1)_2]{\cdot}Et_2O$**, **$[2{\cdot}Cu_2(L^1)_2]{\cdot}thf$**, **$[3{\cdot}Cu_2(L^1)_2]$**, **$[2{\cdot}Cu_2(L^2)]$**, **$[2{\cdot}Cu_2(L^3)_2]$**, **$[2{\cdot}Cu_2(L^6)_2]$** and **$[2{\cdot}Cu_2(L^8)_2]$**. Data were collected using Oxford Diffraction Xcalibur PX Ultra (**$[2{\cdot}Cu_2(L^1)_2]{\cdot}Et_2O$**), Oxford Diffraction Xcalibur 3 (**$1{\cdot}H_2$**, **$[1{\cdot}Cu_2(L^1)_2]$**, **$[2{\cdot}Cu_2(L^1)_2]{\cdot}thf$**, and **$[2{\cdot}Cu_2(L^2)]$**) Agilent Xcalibur PX Ultra A (**$3{\cdot}H_2$**) and Agilent Xcalibur 3 E (**$3{\cdot}Cu_2(L^1)_2]$**, **$[2{\cdot}Cu_2(L^3)_2]$**, **$[2{\cdot}Cu_2(L^6)_2]$** and **$[2{\cdot}Cu_2(L^8)_2]$**) diffractometers, and the structures were refined using the SHELXTL and SHELX-2013 program systems.[3] The structure of **$[2{\cdot}Cu_2(L^3)_2]$** was refined as a 2-component inversion twin [Flack parameter x = +0.21(2)]. CCDC 1511417 to 1511426.

[3] SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-2013, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

The X-ray crystal structure of $\mathbf{1{\cdot}H_2}$

The structure of $\mathbf{1{\cdot}H_2}$ was found to contain two independent molecules ($\mathbf{1{\cdot}H_2}$-A and $\mathbf{1{\cdot}H_2}$-B), and two hexane solvent sites (one in a general position and one across a centre of symmetry). Both hexane molecules were found to be disordered. For the C41-based molecule two orientations were identified of *ca*. 62 and 38% occupancy, whilst for the C51-based molecule (which sits across a centre of symmetry) two unique orientations of *ca*. 29 and 21% occupancy were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries of all four unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation of the C41-based molecule were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The four N–H hydrogen atoms on N3A, N12A, N3B and N12B were all located from Δ*F* maps and refined freely subject to an N–H distance constraint of 0.90 Å

The X-ray crystal structure of $\mathbf{3{\cdot}H_2}$

The C42-based isopropyl group in the structure of $\mathbf{3{\cdot}H_2}$ was found to be disordered. Two orientations were identified of *ca*. 81 and 19% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The N13 and N19 N–H hydrogen atoms were located from Δ*F* maps and refined freely subject to an N–H distance constraint of 0.90 Å

The X-ray crystal structure of $\mathbf{[1{\cdot}Cu_2(L^1)_2]}$

The C23 and C26-based isopropyl groups in the structure of $\mathbf{[1{\cdot}Cu_2(L^1)_2]}$ were found to be disordered, and in each case two orientations were identified, of *ca*. 88:12 and 83:17% occupancy respectively. The geometries of all four orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

All three of the included thf solvent molecules were found to be disordered, and in each case two orientations were identified, of *ca*. 87:13, 66:34 and 64:37% occupancy for the O80-, O90- and O100- based molecules respectively. The geometries of all six orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The X-ray crystal structure of [2·$Cu_2(L^1)_2$]·Et_2O

The C35-based isopropyl group in the structure of **[2·$Cu_2(L^1)_2$]·Et_2O** was found to be disordered. Two orientations were identified of *ca*. 82 and 18% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The O80-based included diethyl ether solvent molecule was found to be disordered. Two orientations were identified of *ca*. 68 and 32% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of [2·$Cu_2(L^1)_2$]·thf

The C35-based isopropyl group in the structure of **[2·$Cu_2(L^1)_2$]·thf** was found to be disordered. Two orientations were identified of *ca*. 86 and 14% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The O80-based included thf solvent molecule was found to be disordered. Two orientations were identified of *ca*. 73 and 27% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of [3·$Cu_2(L^1)_2$]

Both the O90- and O100-based included diethyl ether solvent molecules in the structure of **[3·$Cu_2(L^1)_2$]** were found to be disordered. For the O90-based molecule three orientations were identified of *ca*. 66, 20 and 14% occupancy, whilst for the O100-based molecule (which sits across a centre of symmetry) two unique orientations of *ca*. 34 and 16% occupancy were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries of all five unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation of the O90-based molecule were refined anisotropically (those of the minor occupancy orientations were refined isotropically).

The X-ray crystal structure of [2·$Cu_2(L^2)$]

The C26-based isopropyl group in the structure of **[2·$Cu_2(L^2)$]** was found to be disordered. Two orientations were identified of *ca*. 70 and 30% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The C71-based included *n*-hexane solvent molecule was found to be disordered across a centre of symmetry, and two unique orientations of *ca*. 28 and 22% occupancy were identified (with the action of the inversion centre generating two further orientations of the same occupancies). The geometries of both orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of [2·$Cu_2(L^3)_2$]

The structure of **[2·$Cu_2(L^3)_2$]** was refined as a 2-component inversion twin [Flack parameter x = +0.21(2)]. The molecule was found to have crystallographic C_2 symmetry about an axis that passes through N7 and C8.

The X-ray crystal structure of [2·$Cu_2(L^6)_2$]

The hydrogen atoms on C41, C42, C51 and C52 in the structure of **[2·$Cu_2(L^6)_2$]** were located from ΔF maps and refined freely subject to a C–H distance constraint of 1.00 Å.

The X-ray crystal structure of [2·Cu$_2$(L^8)$_2$]

The crystal of **[2·Cu$_2$(L^8)$_2$]** that was studied was found to be a two component twin in a *ca*. 73:27 ratio, with the two lattices related by the approximate twin law [–0.21 0.82 –0.40 0.79 –0.18 –0.40 –0.79 –0.82 –0.60]. The hydrogen atoms on C41, C42, C51 and C52 were located from Δ*F* maps and refined freely subject to a C–H distance constraint of 1.00 Å.

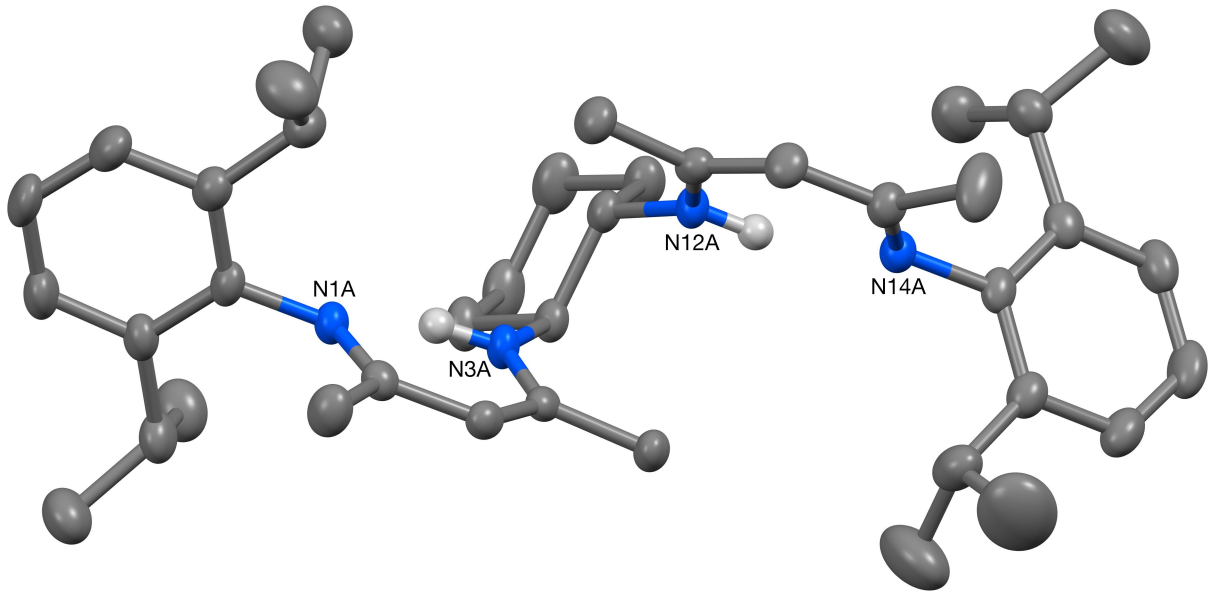


Fig. S1 The structure of one, **1·H$_2$**-A, of the two independent molecules present in the crystal of **1·H$_2$** (50% probability ellipsoids).

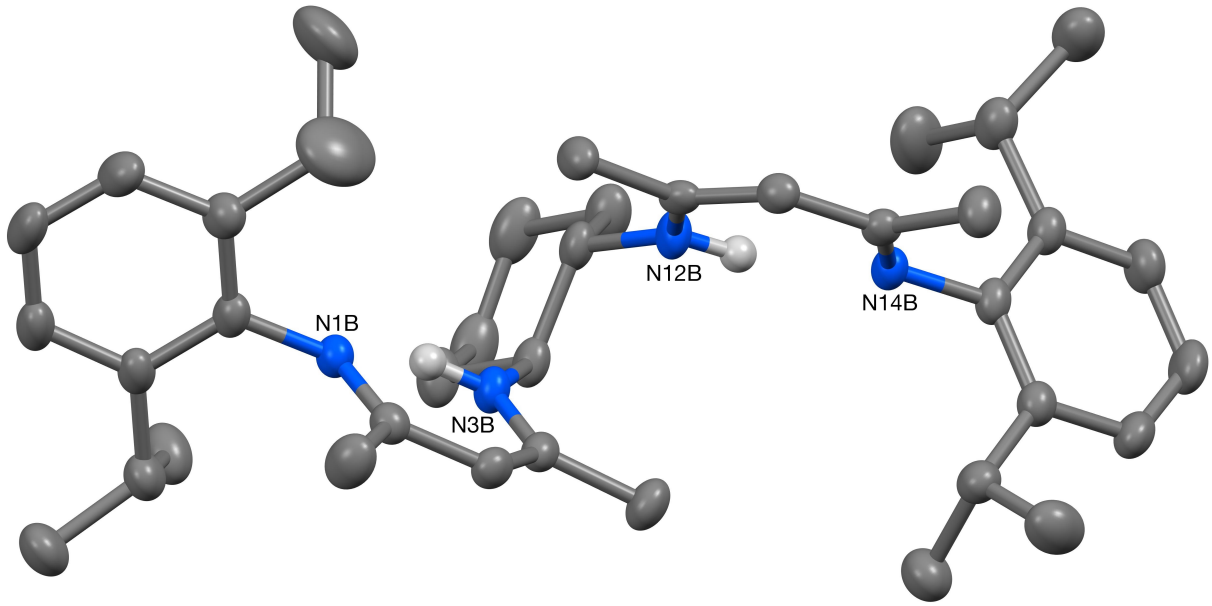


Fig. S2 The structure of one, **1·H$_2$**-B, of the two independent molecules present in the crystal of **1·H$_2$** (50% probability ellipsoids).

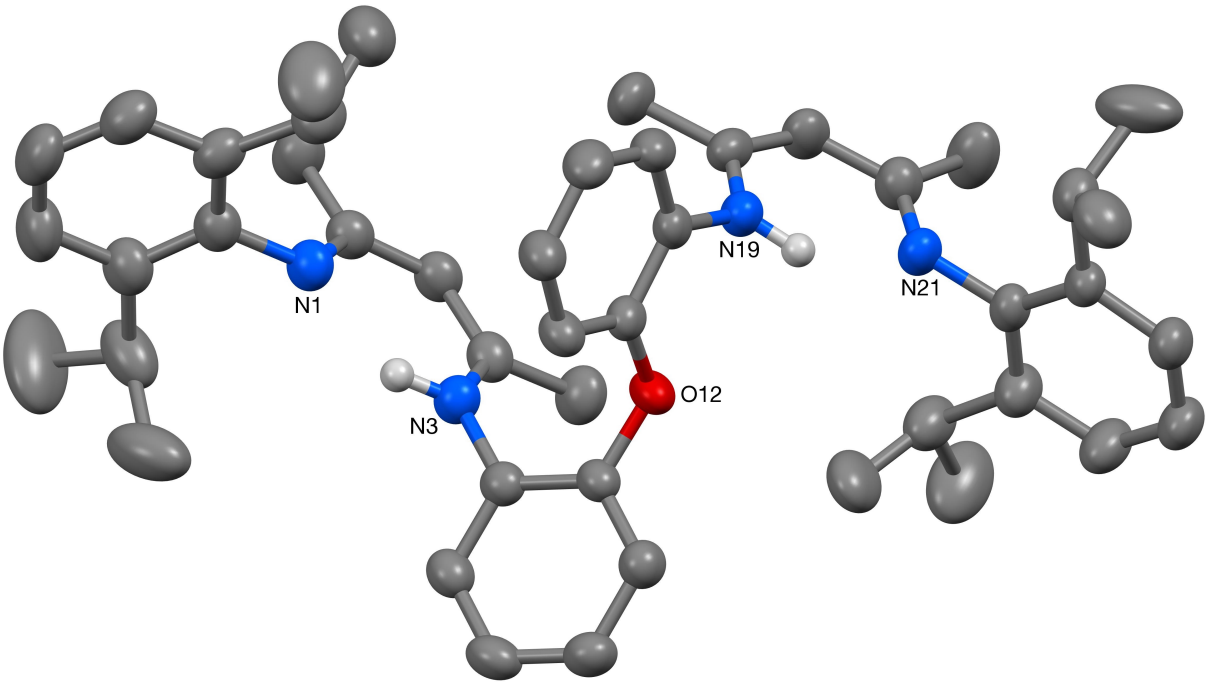


Fig. S3 The crystal structure of **3·H₂** (50% probability ellipsoids).

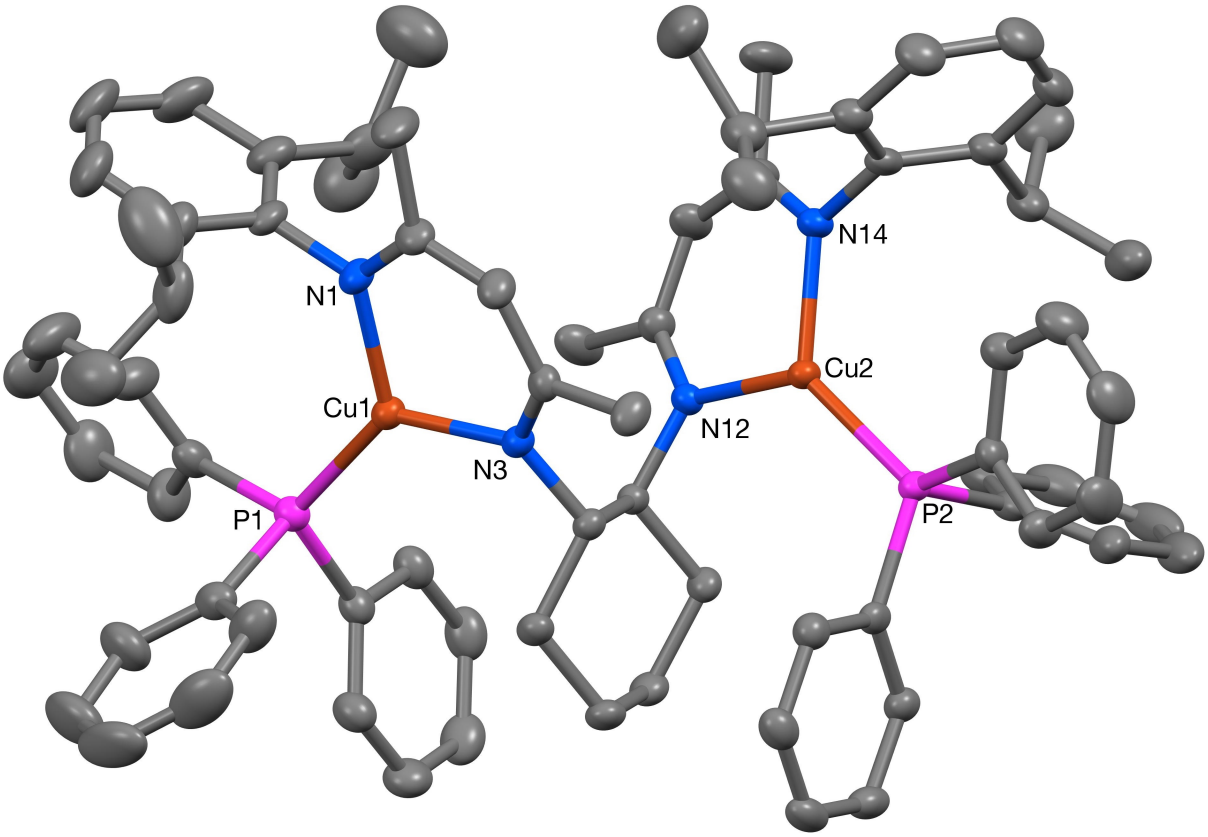


Fig. S4 The crystal structure of **[1·Cu₂(L¹)₂]** (50% probability ellipsoids).

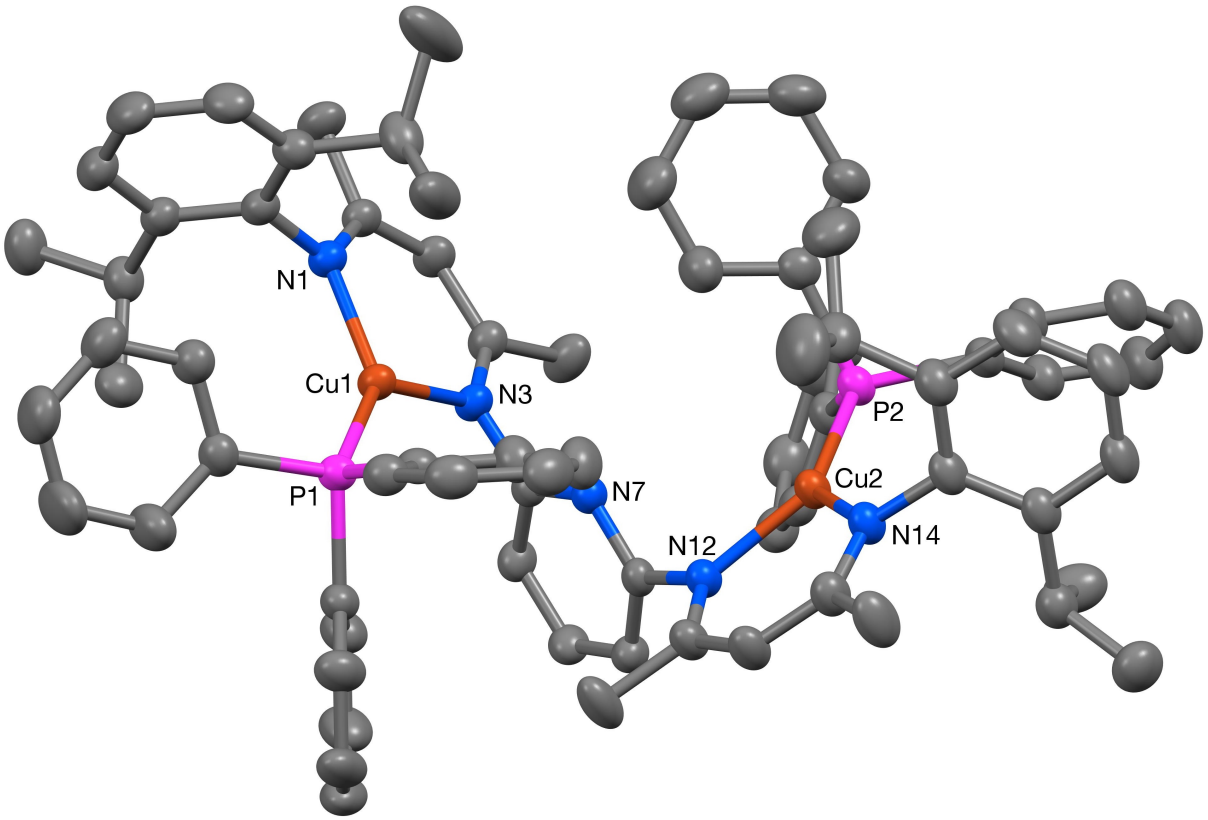


Fig. S5 The crystal structure of **[2·Cu$_2$(L^1)$_2$]·Et$_2$O** (50% probability ellipsoids).

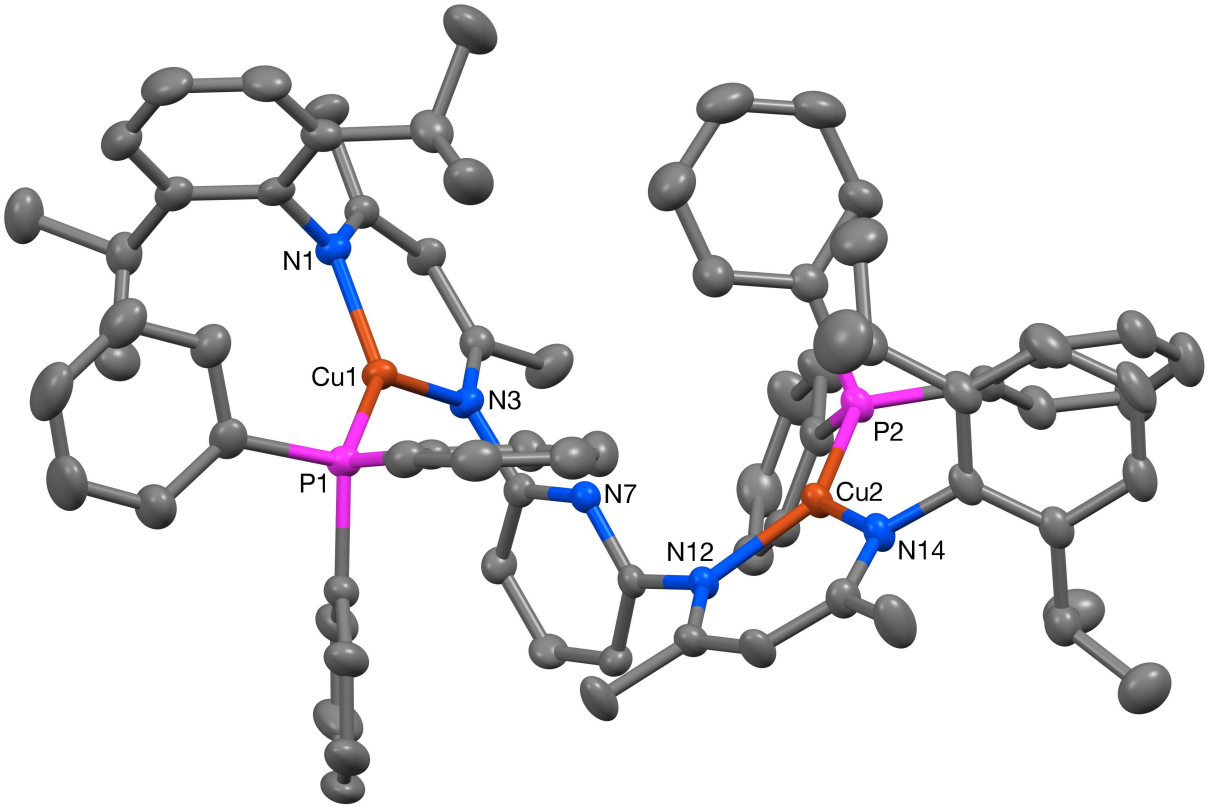


Fig. S6 The crystal structure of **[2·Cu$_2$(L^1)$_2$]·thf** (50% probability ellipsoids).

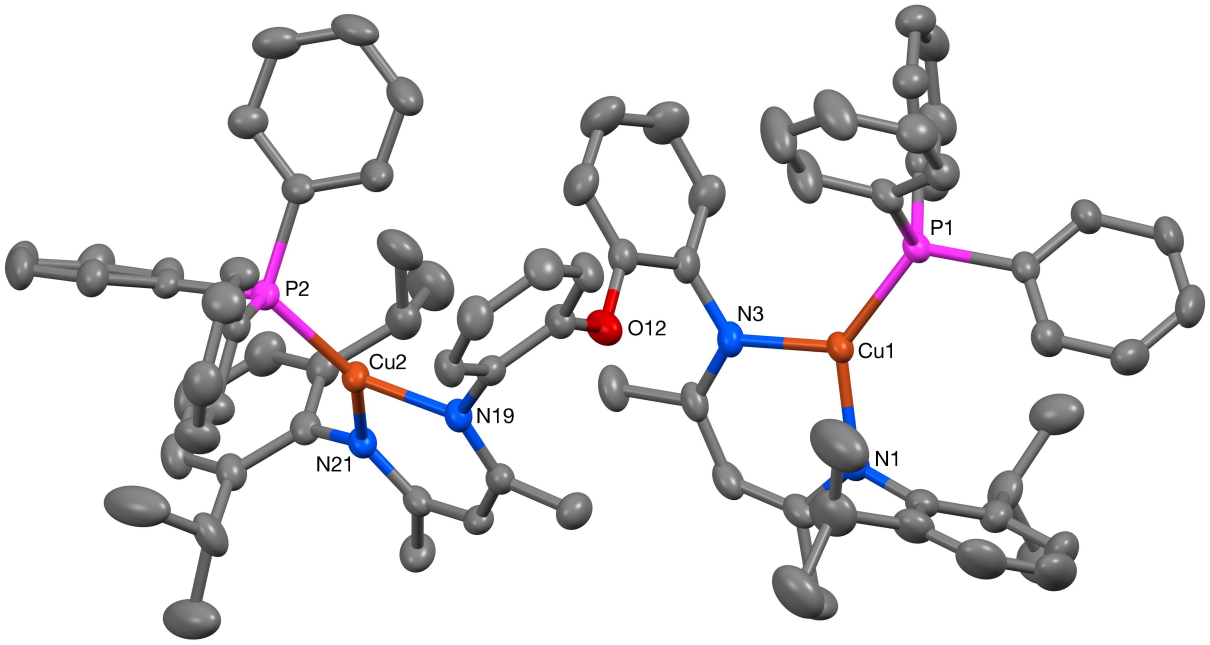


Fig. S7 The crystal structure of **[3·Cu$_2$(L^1)$_2$]** (50% probability ellipsoids).

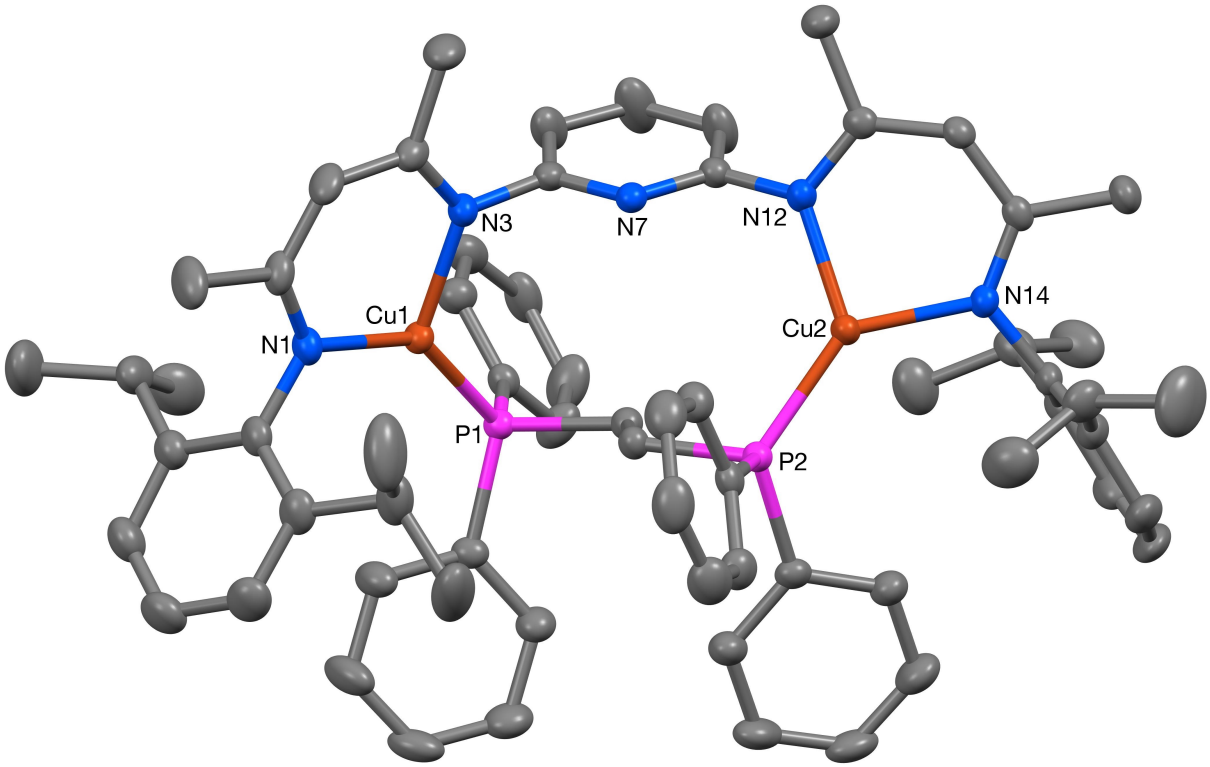


Fig. S8 The crystal structure of **[2·Cu$_2$(L^2)]** (50% probability ellipsoids).

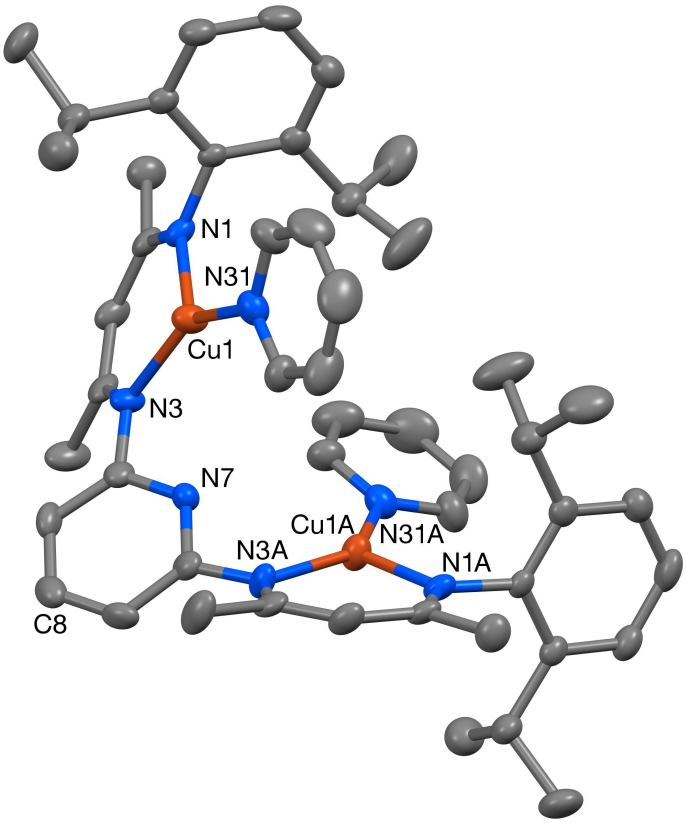


Fig. S9 The crystal structure of the C_2-symmetric complex **[2·Cu$_2$(L^3)$_2$]** (50% probability ellipsoids).

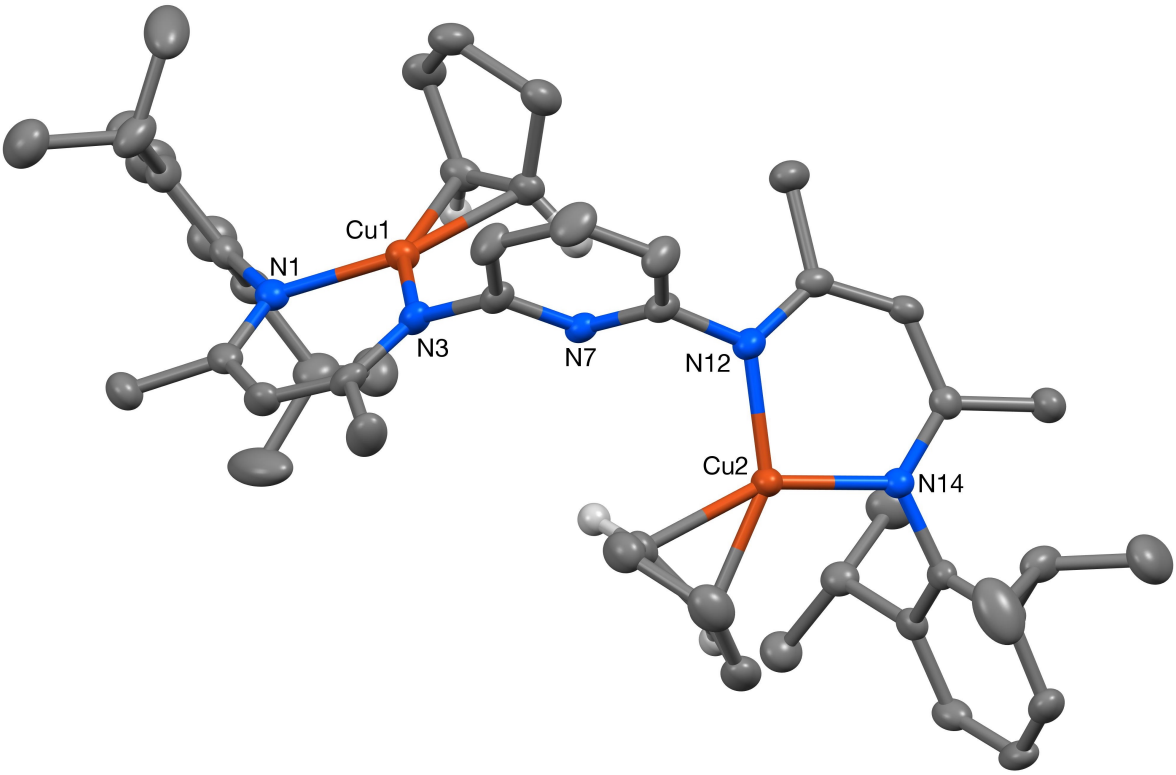


Fig. S10 The crystal structure of **[2·Cu$_2$(L^6)$_2$]** (50% probability ellipsoids).

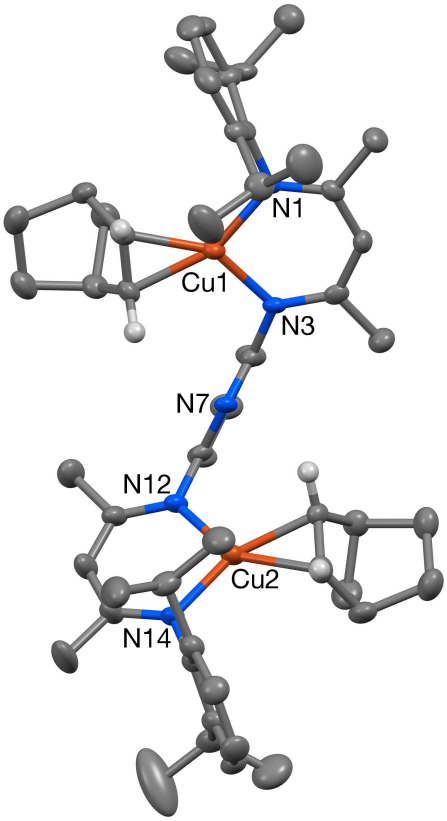
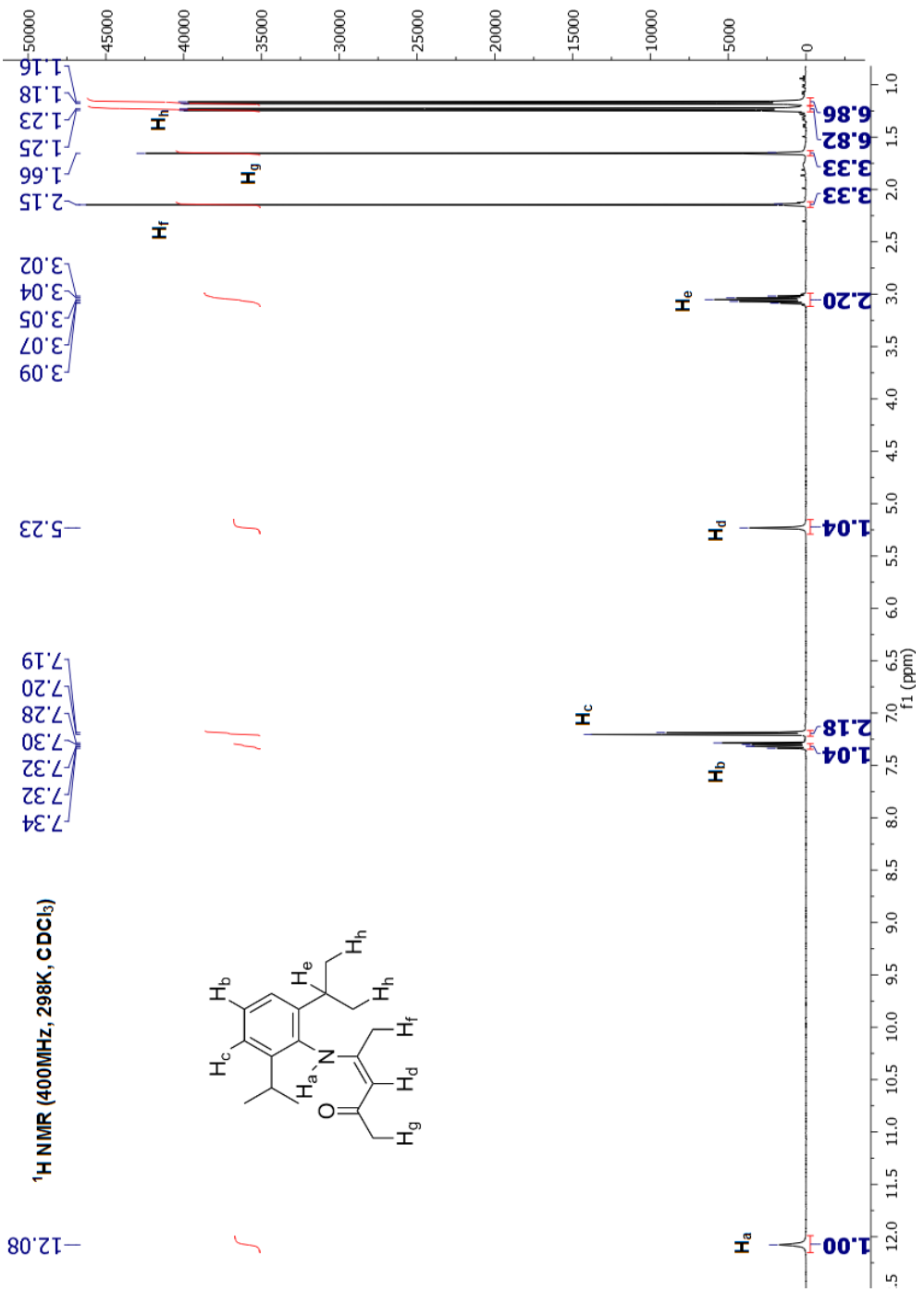
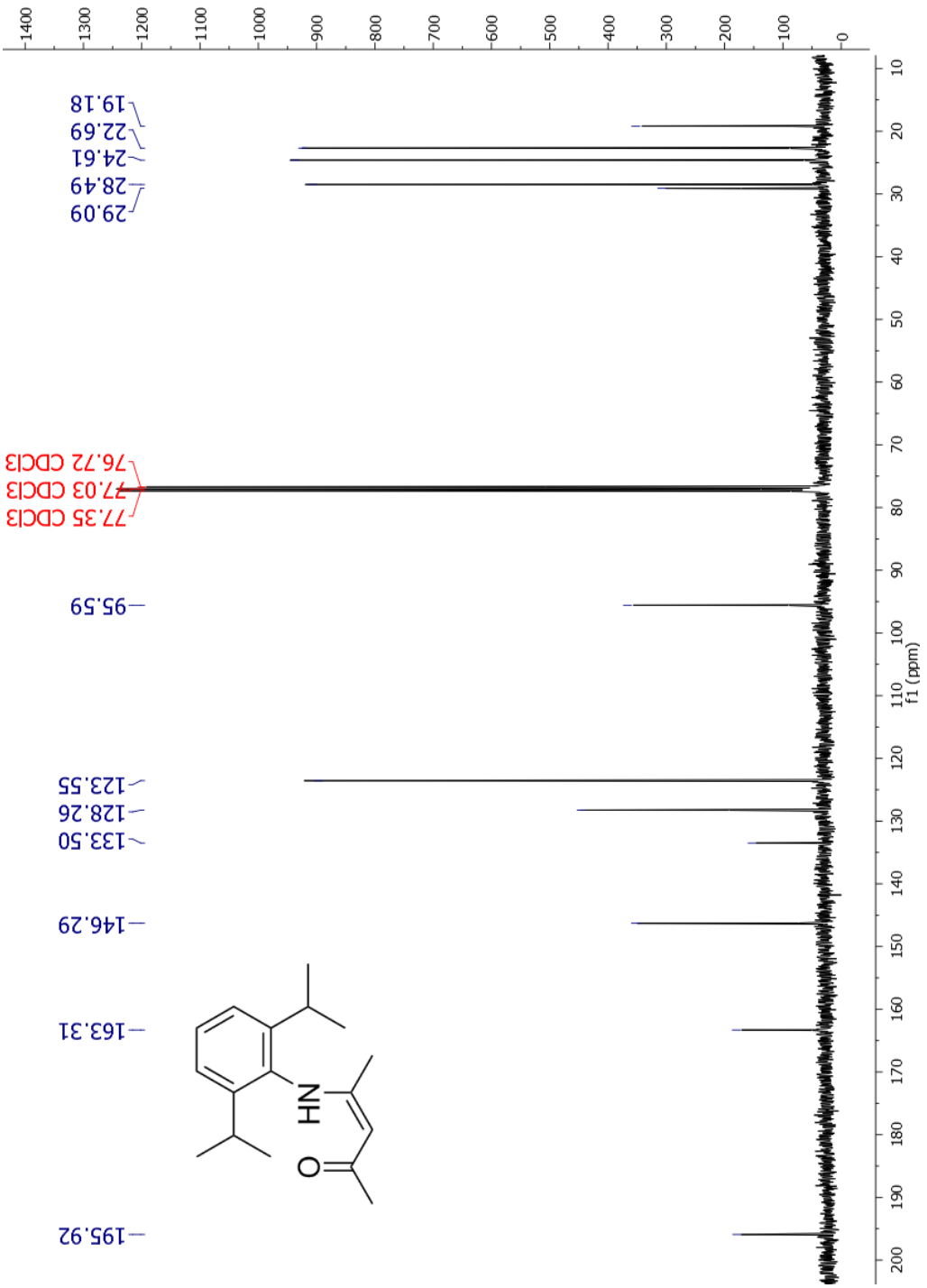
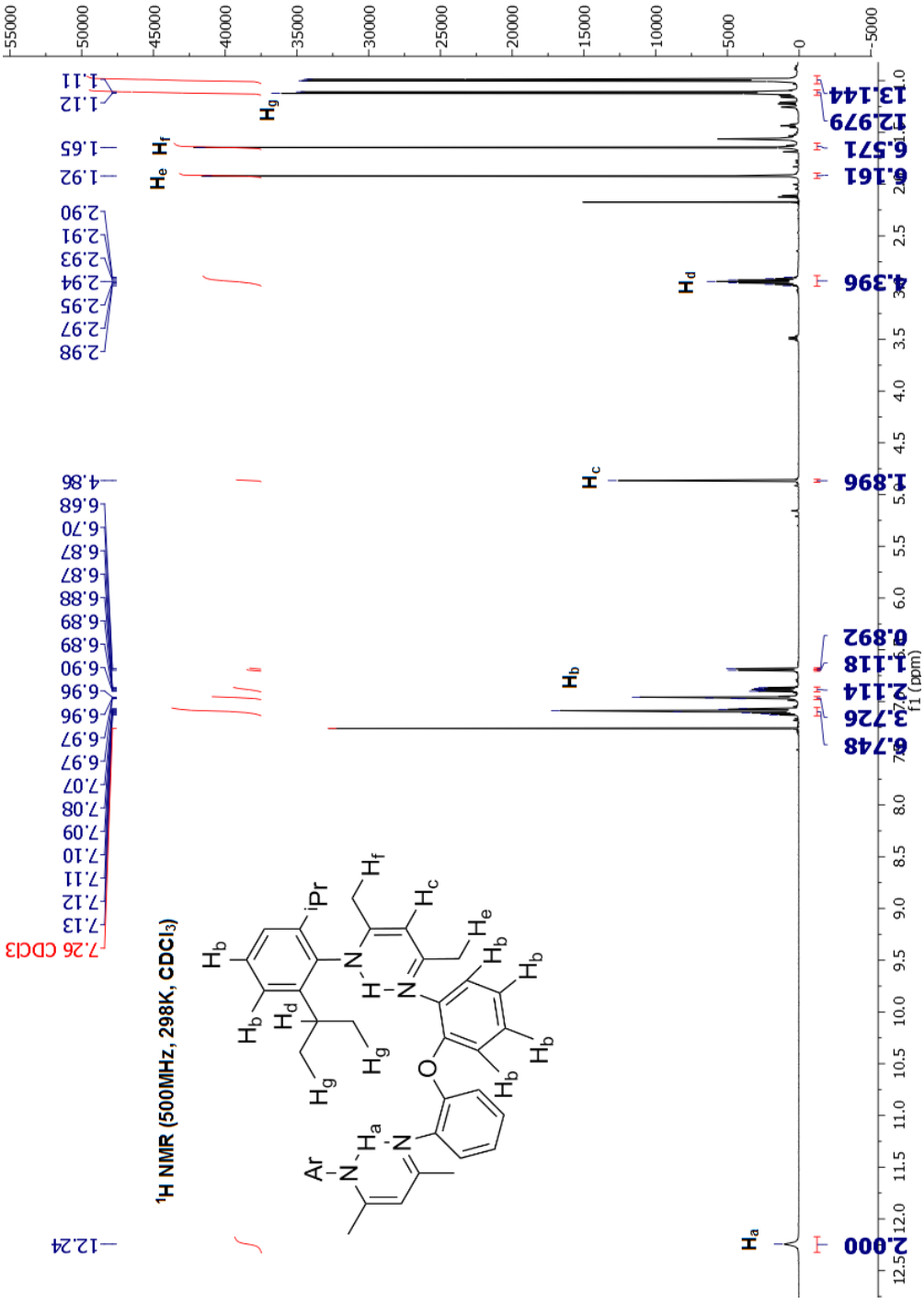


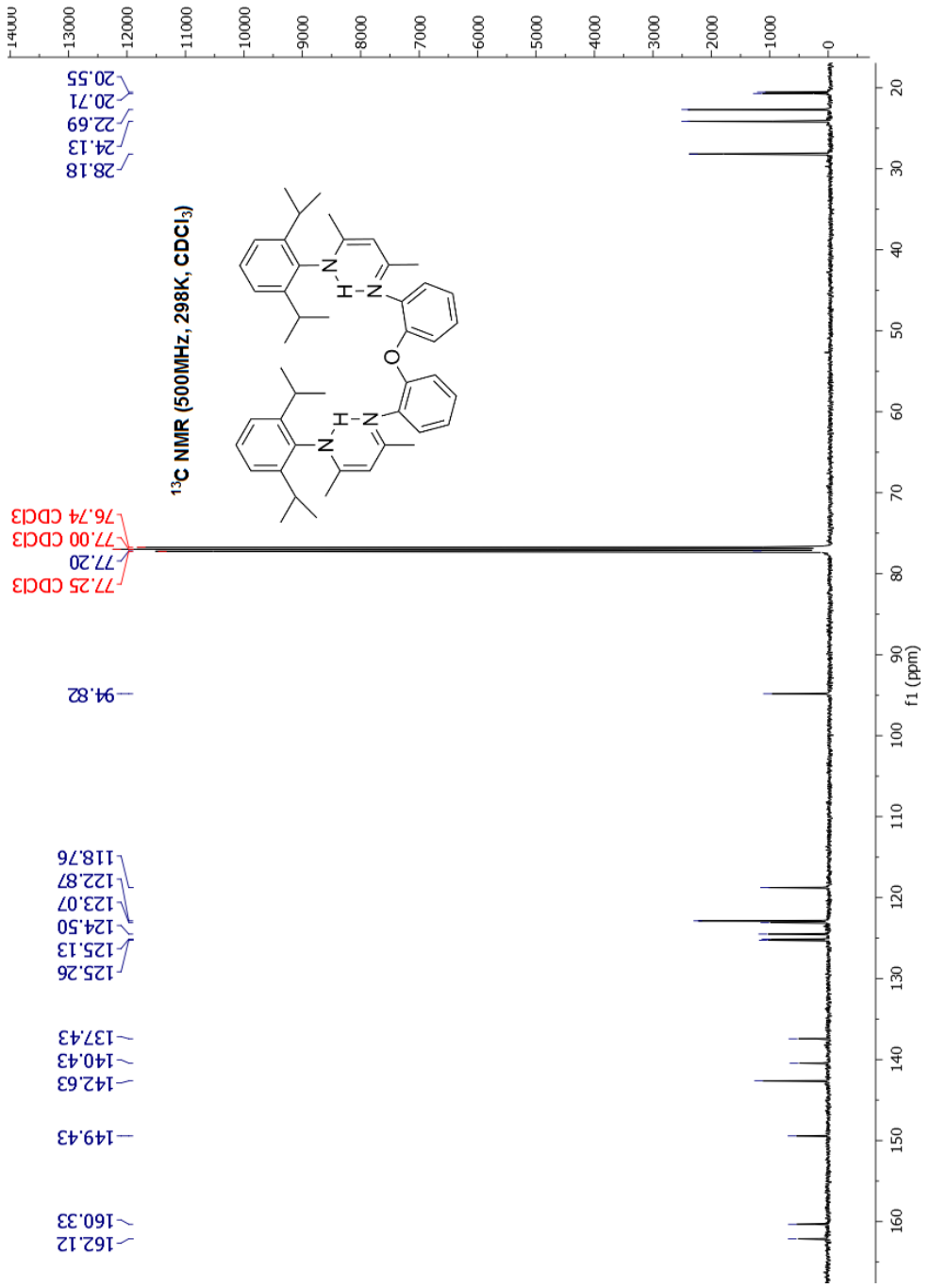
Fig. S11 The crystal structure of **[2·Cu$_2$(L^8)$_2$]** (50% probability ellipsoids).

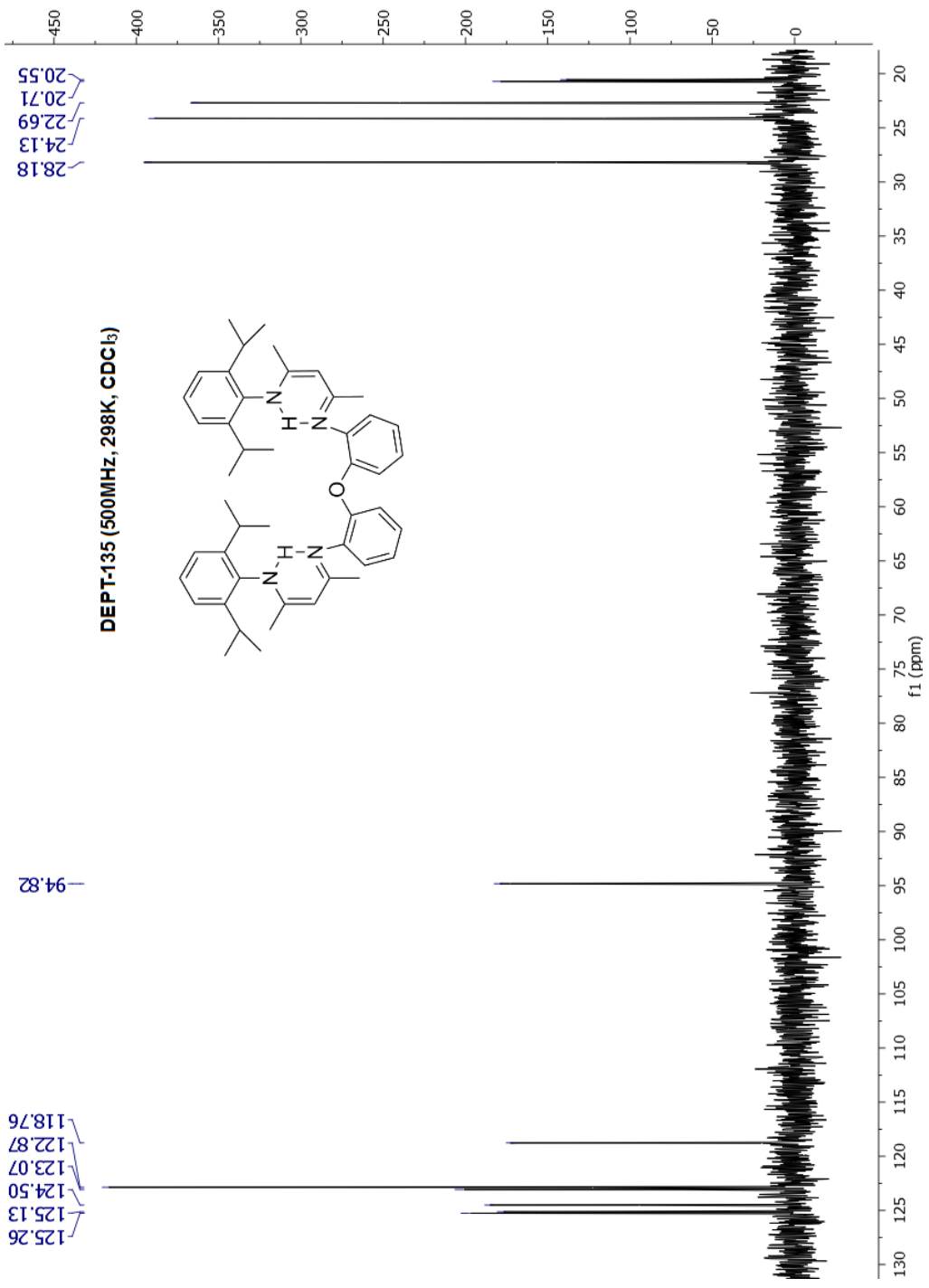
3. Multinuclear NMR data

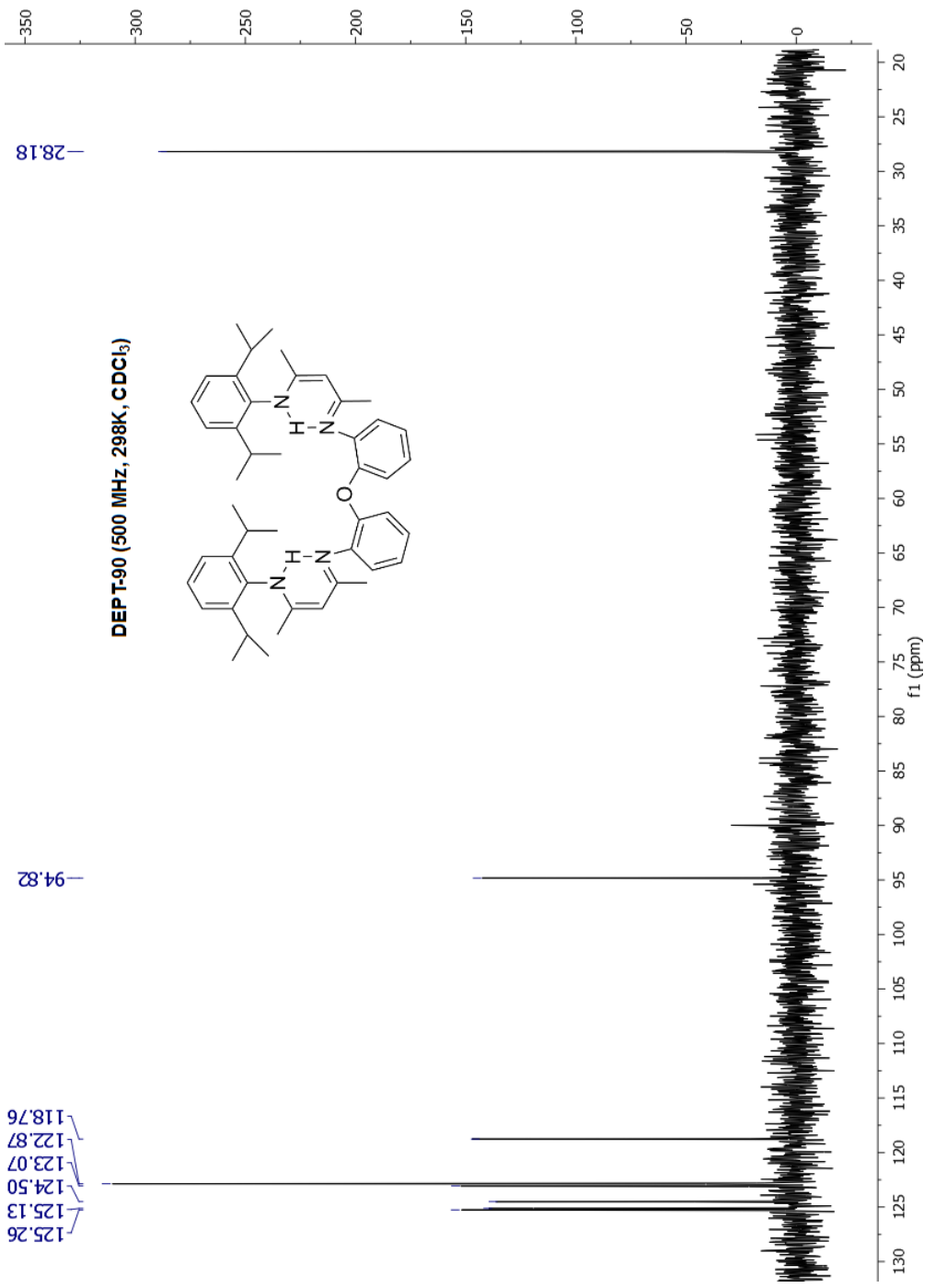


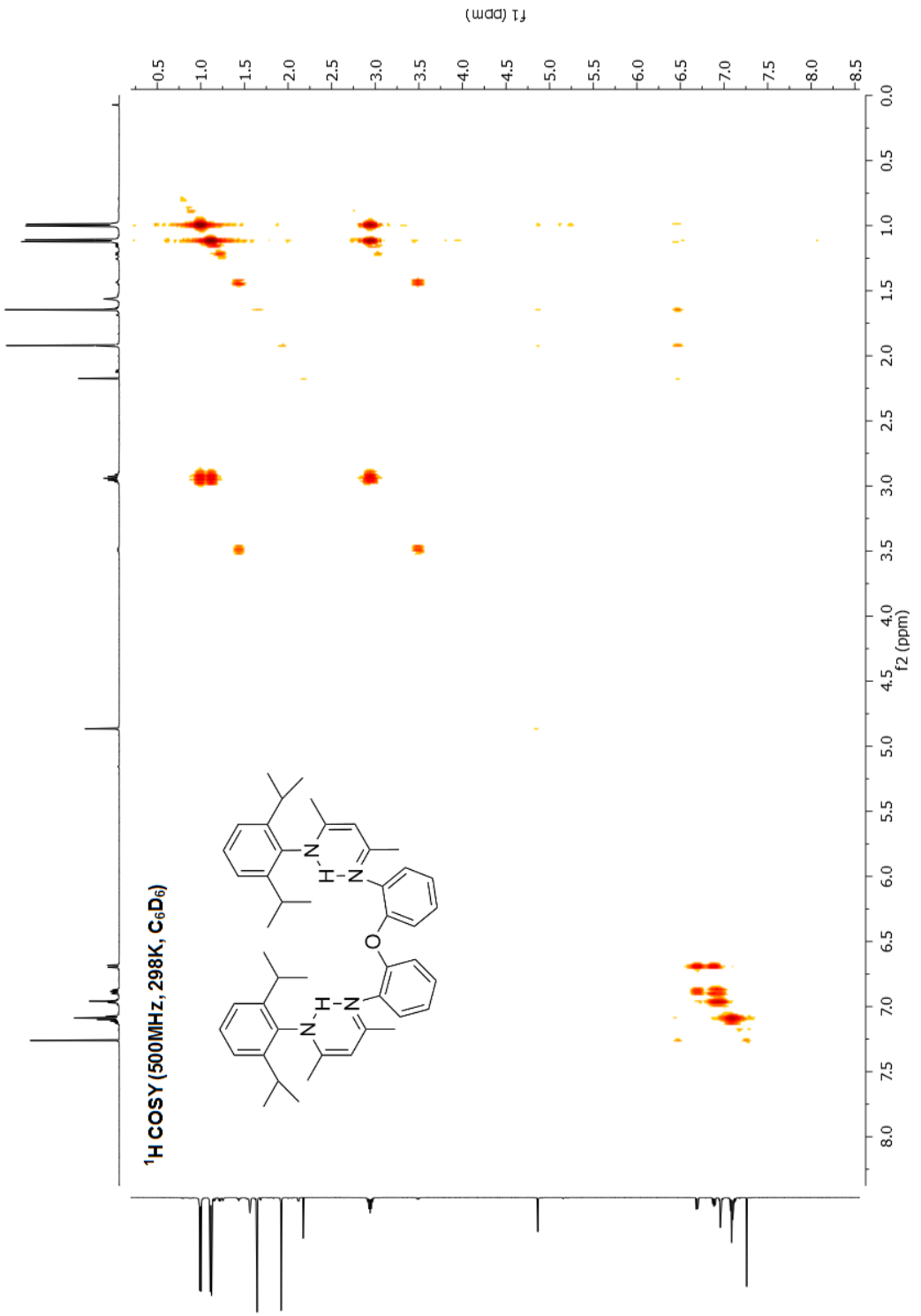

19.18
22.69
24.61
28.49
29.09
76.72 CDCl3
77.03 CDCl3
77.35 CDCl3
95.59
123.55
128.26
133.50
146.29
163.31
195.92
NH
O
f1 (ppm)

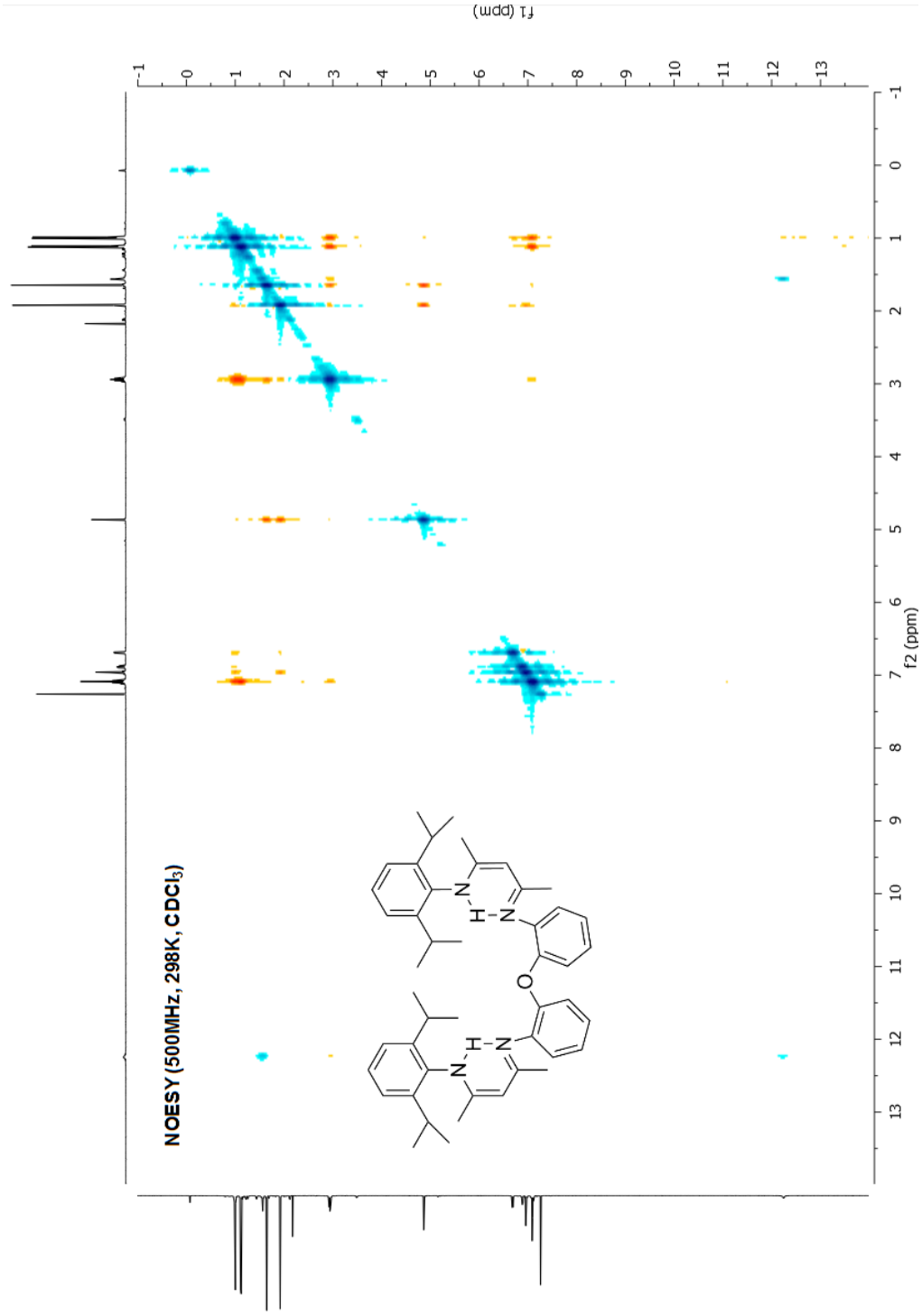

^{1}H NMR (500MHz, 298K, CDCl$_3$)
7.26 CDCl3
H_a
H_b
H_c
H_d
H_e
H_f
H_g
2.000
6.748
3.726
2.114
1.118
0.892
1.896
4.396
6.161
6.571
12.979
13.144
f1 (ppm)

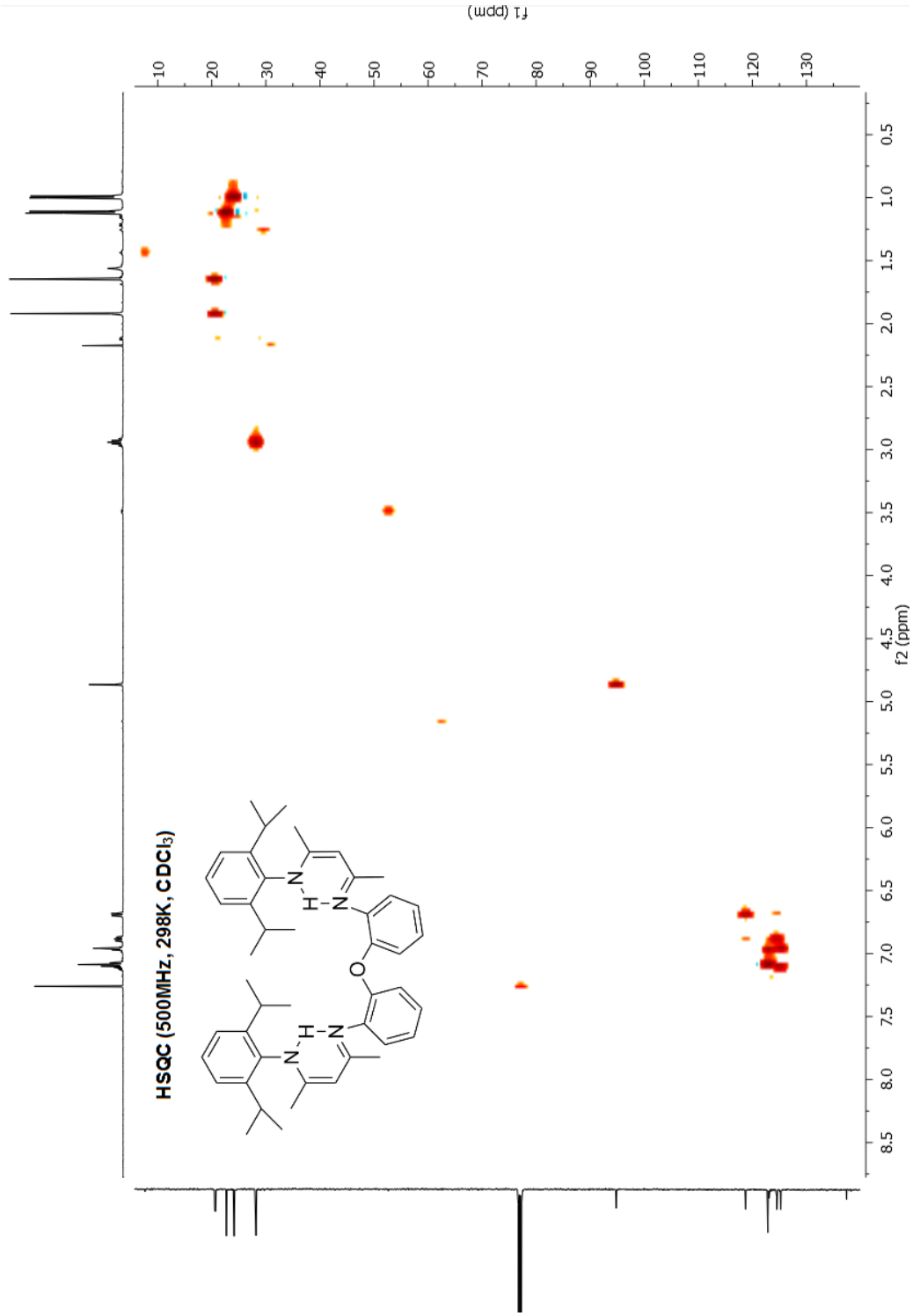

13C NMR (500MHz, 298K, CDCl3)
20.55
20.71
22.69
24.13
28.18
76.74 CDCl3
77.00 CDCl3
77.20
77.25 CDCl3
94.82
118.76
122.87
123.07
124.50
125.13
125.26
137.43
140.43
142.63
149.43
160.33
162.12
f1 (ppm)

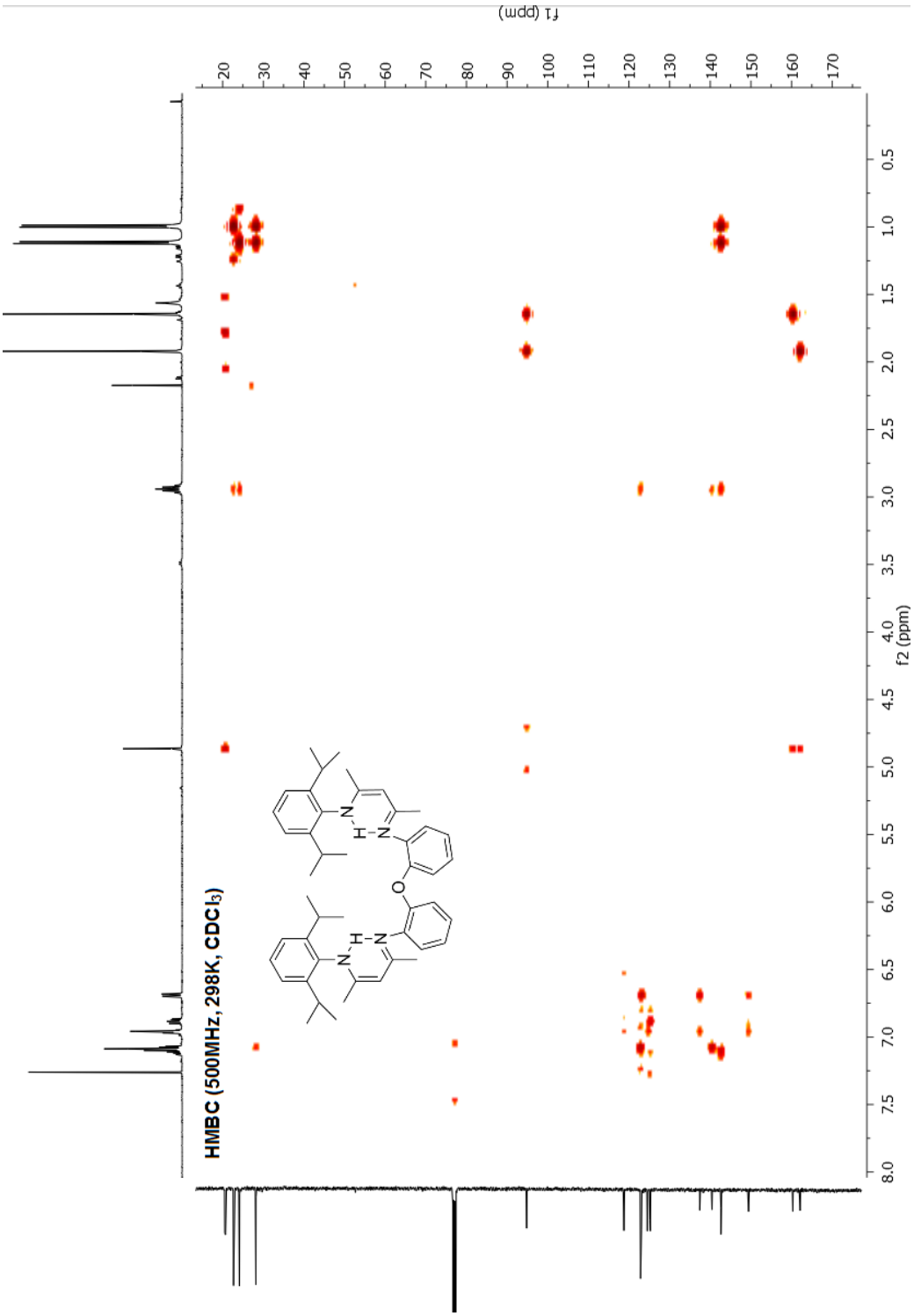

DEPT-135 (500MHz, 298K, CDCl3)
20.55
20.71
22.69
24.13
28.18
94.82
118.76
122.87
123.07
124.50
125.13
125.26
f1 (ppm)

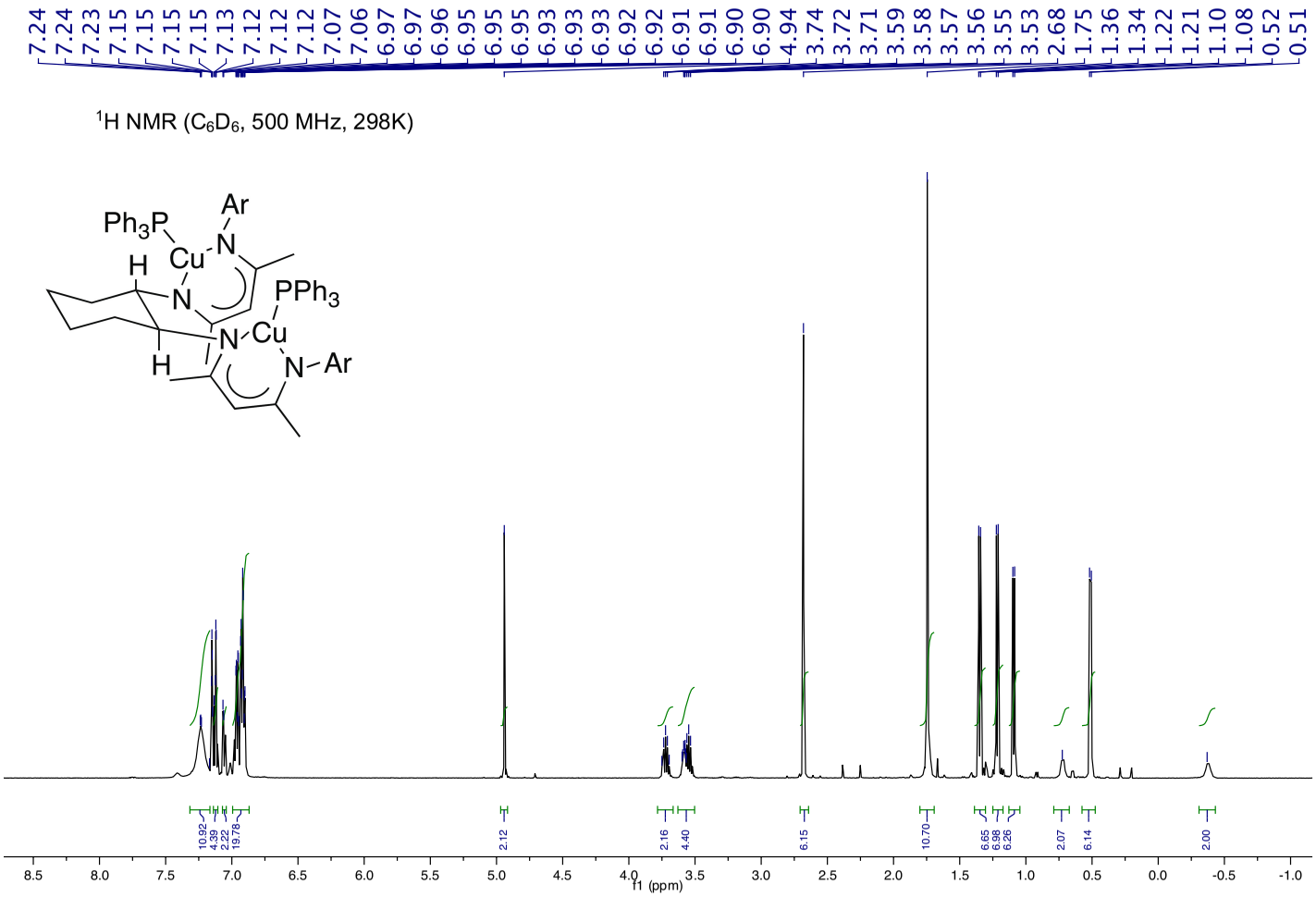

DEPT-90 (500 MHz, 298K, CDCl3)
28.18
94.82
125.26
125.13
124.50
123.07
122.87
118.76
f1 (ppm)


^{1}H COSY (500MHz, 298K, C_6D_6)
f2 (ppm)
f1 (ppm)

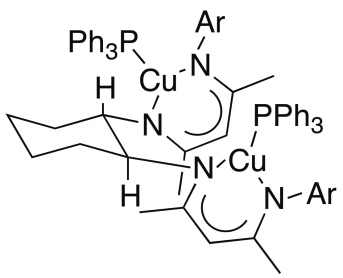

NOESY (500MHz, 298K, CDCl3)
f1 (ppm)
f2 (ppm)

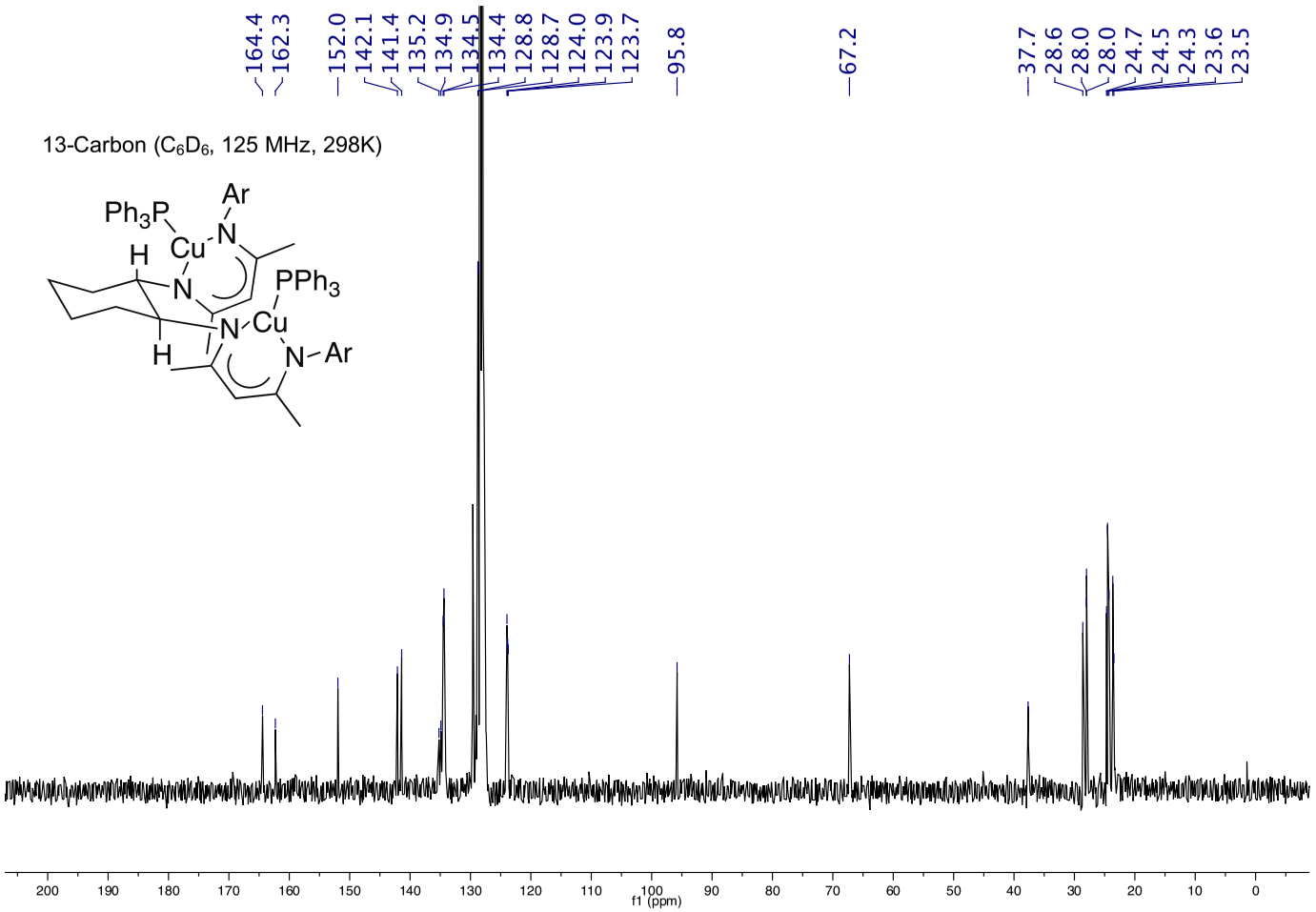

HSQC (500MHz, 298K, CDCl3)
f1 (ppm)
f2 (ppm)

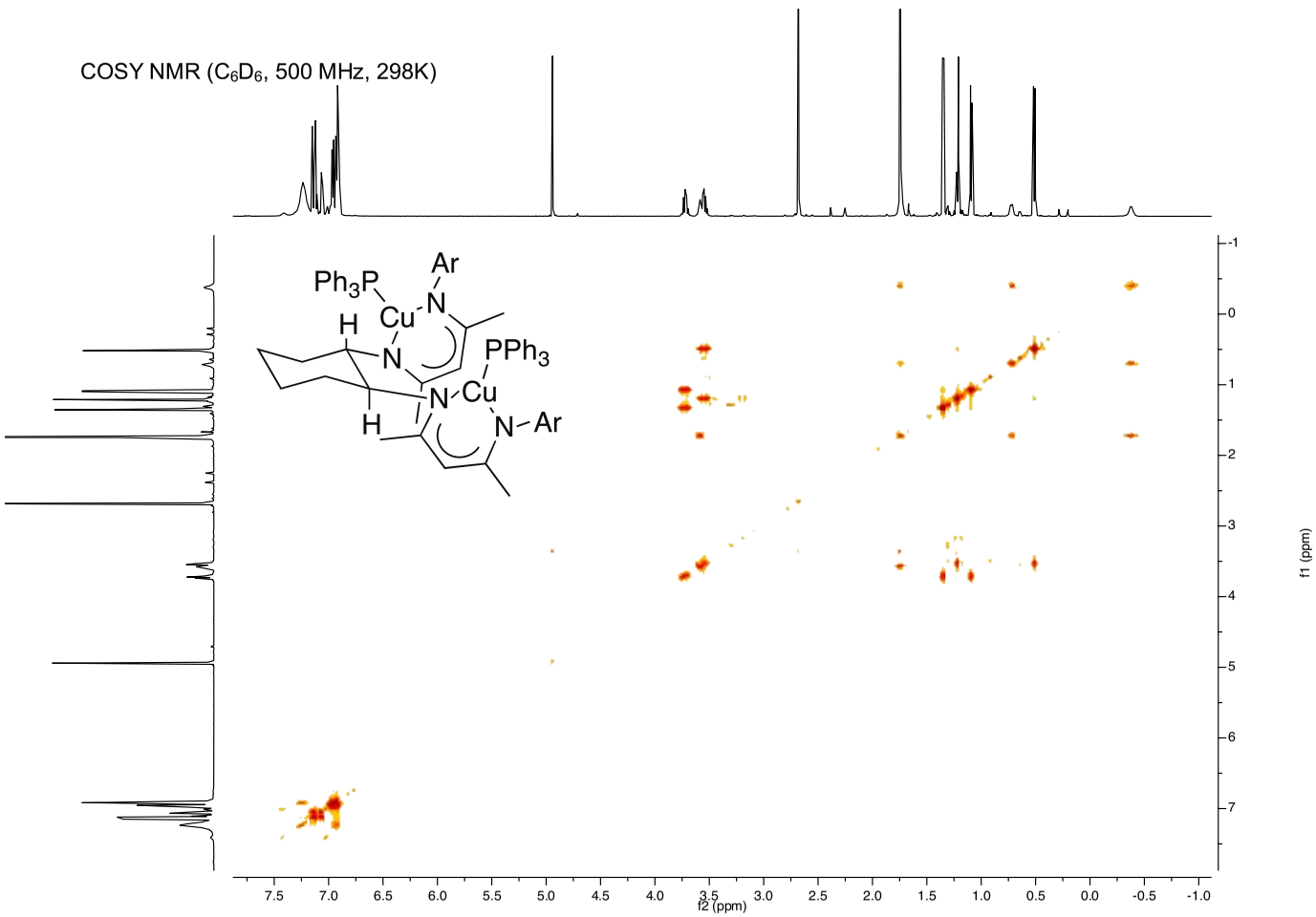

HMBC (500MHz, 298K, CDCl3)
f1 (ppm)
f2 (ppm)


7.24 7.24 7.23 7.15 7.15 7.15 7.15 7.13 7.12 7.12 7.12 7.07 7.06 6.97 6.97 6.96 6.95 6.95 6.95 6.93 6.93 6.93 6.92 6.92 6.91 6.91 6.90 6.90 4.94 3.74 3.72 3.71 3.59 3.58 3.57 3.56 3.55 3.53 2.68 1.75 1.36 1.34 1.22 1.21 1.10 1.08 0.52 0.51
1H NMR (C6D6, 500 MHz, 298K)
Ar
Ph3P
N
Cu
H
N
PPh3
N
Cu
H
N
Ar
10.92
4.39
2.22
19.78
2.12
2.16
4.40
6.15
10.70
6.66
6.68
6.26
2.07
6.14
2.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

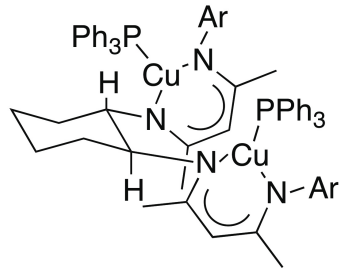
31P NMR (C_6D_6, 202 MHz, 298K)

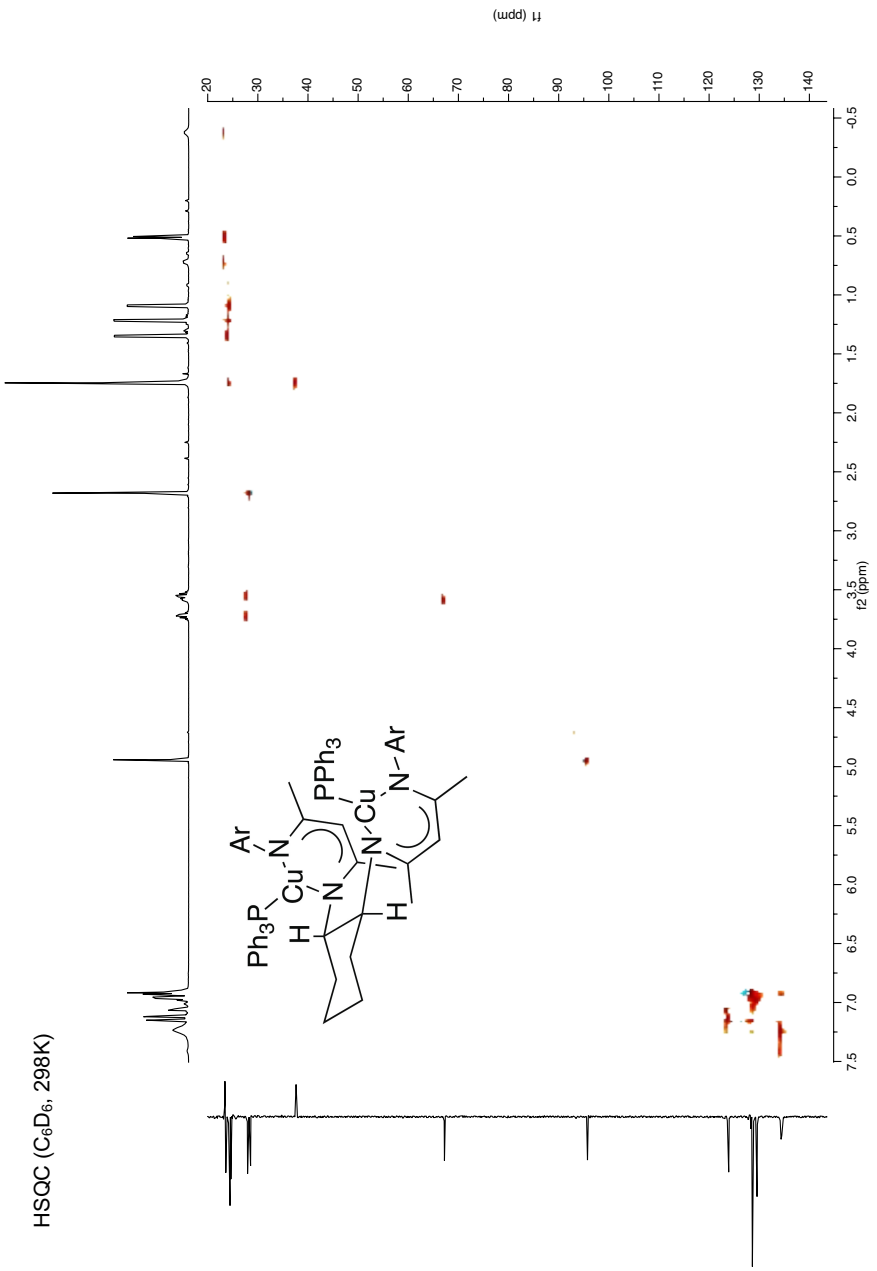


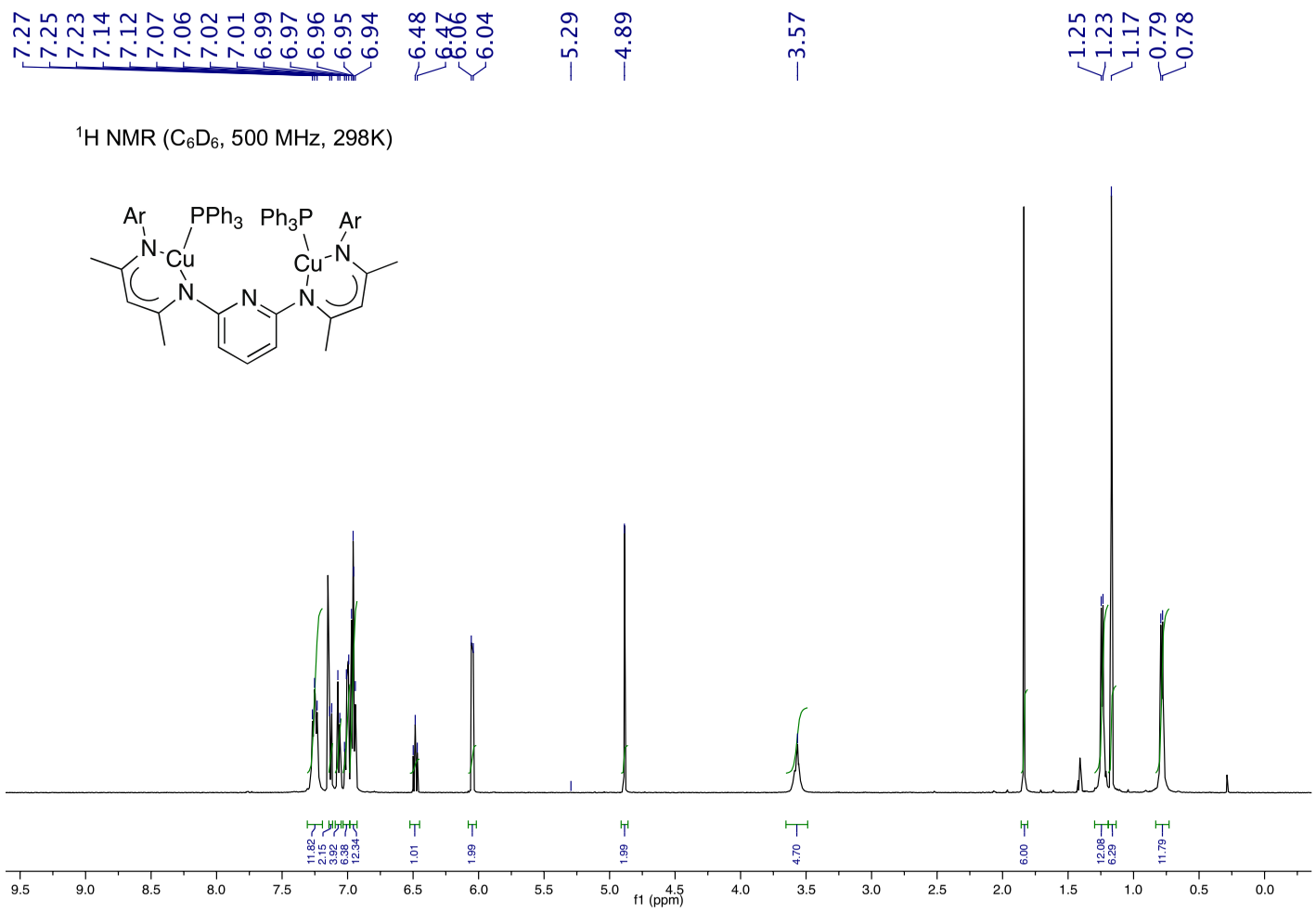

164.4
162.3
152.0
142.1
141.4
135.2
134.9
134.5
134.4
128.8
128.7
124.0
123.9
123.7
95.8
67.2
37.7
28.6
28.0
28.0
24.7
24.5
24.3
23.6
23.5
13-Carbon (C6D6, 125 MHz, 298K)
Ph3P
Ar
N
Cu
H
N
PPh3
N
Cu
H
N
Ar
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


COSY NMR (C_6D_6, 500 MHz, 298K)
Ph3P
Cu
H
N
Ar
PPh3
Cu
N
H
N
Ar
f2 (ppm)
f1 (ppm)

Dept-135 (C_6D_6, 125 MHz, 298K)

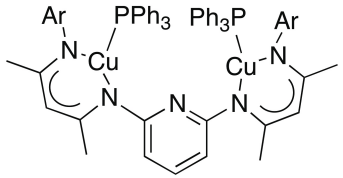


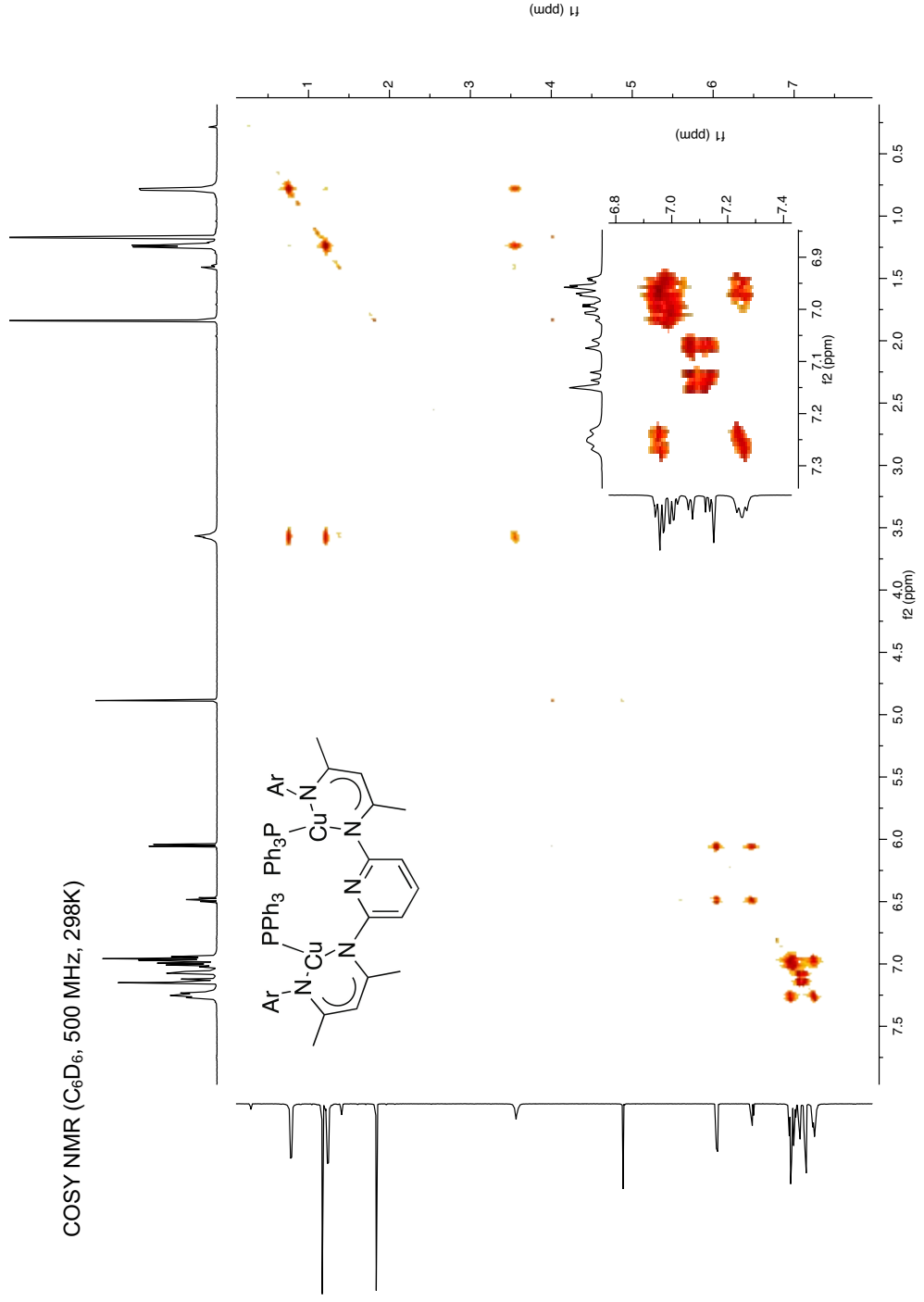

HSQC (C_6D_6, 298K)
f1 (ppm)
f2 (ppm)
Ar
N
Cu
PPh3
N
Cu
N
Ar
Ph3P
H
H

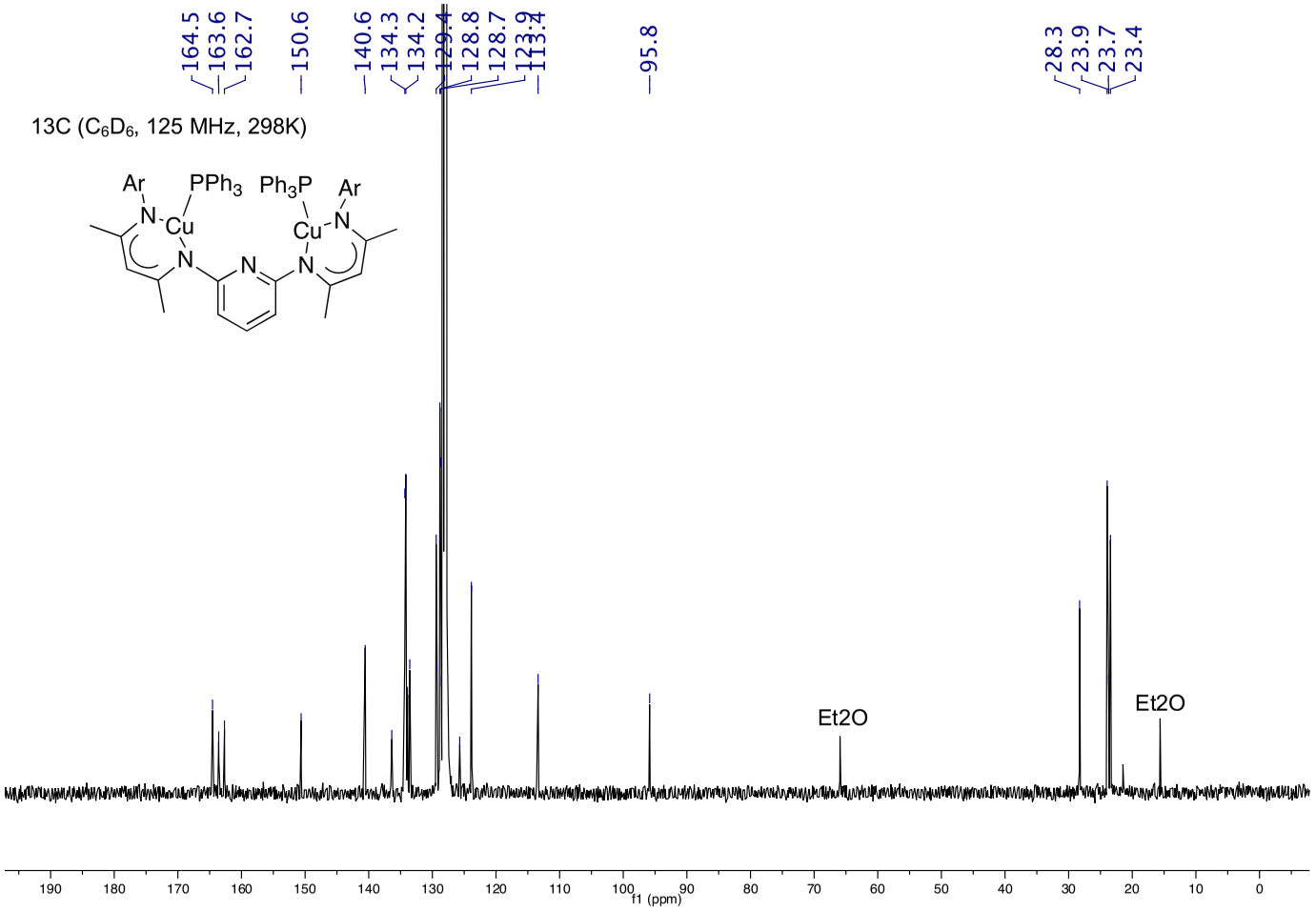


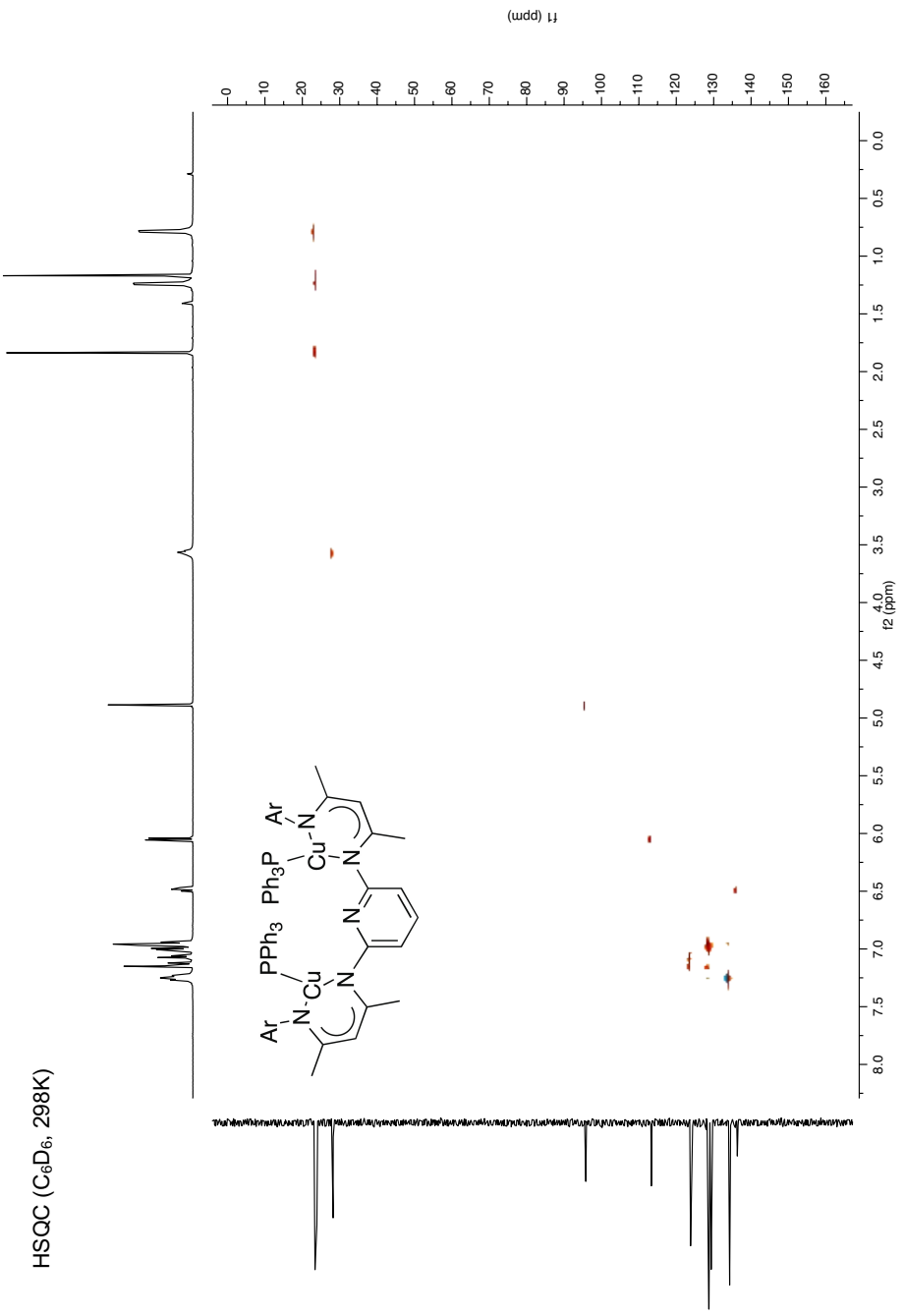
^{1}H NMR (C_6D_6, 500 MHz, 298K)

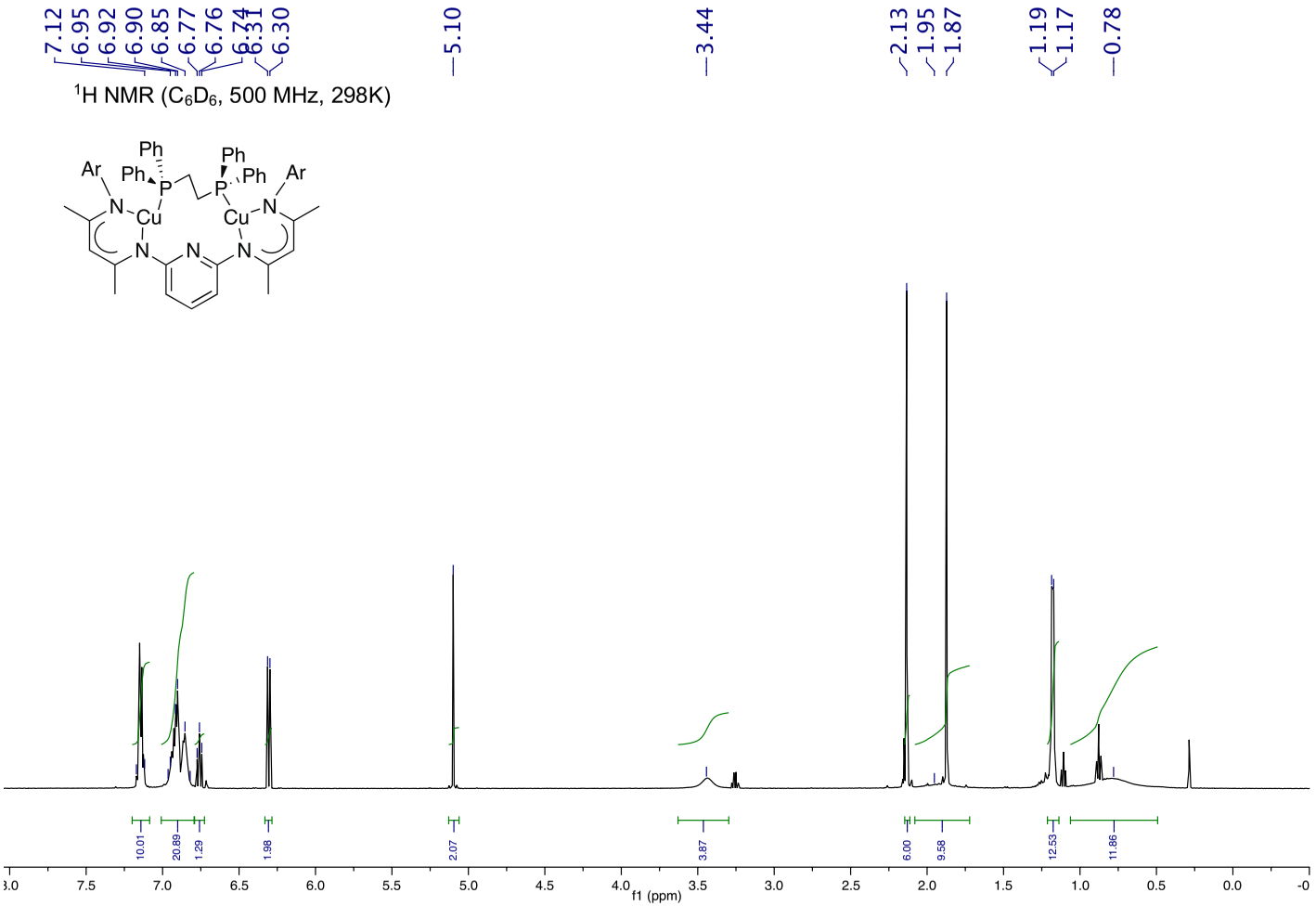
^{1}H NMR (C_6D_6, 500 MHz, 298K)



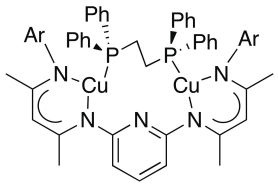

COSY NMR (C_6D_6, 500 MHz, 298K)
f1 (ppm)
f2 (ppm)
Ar
N
Cu
PPh3
Ph3P

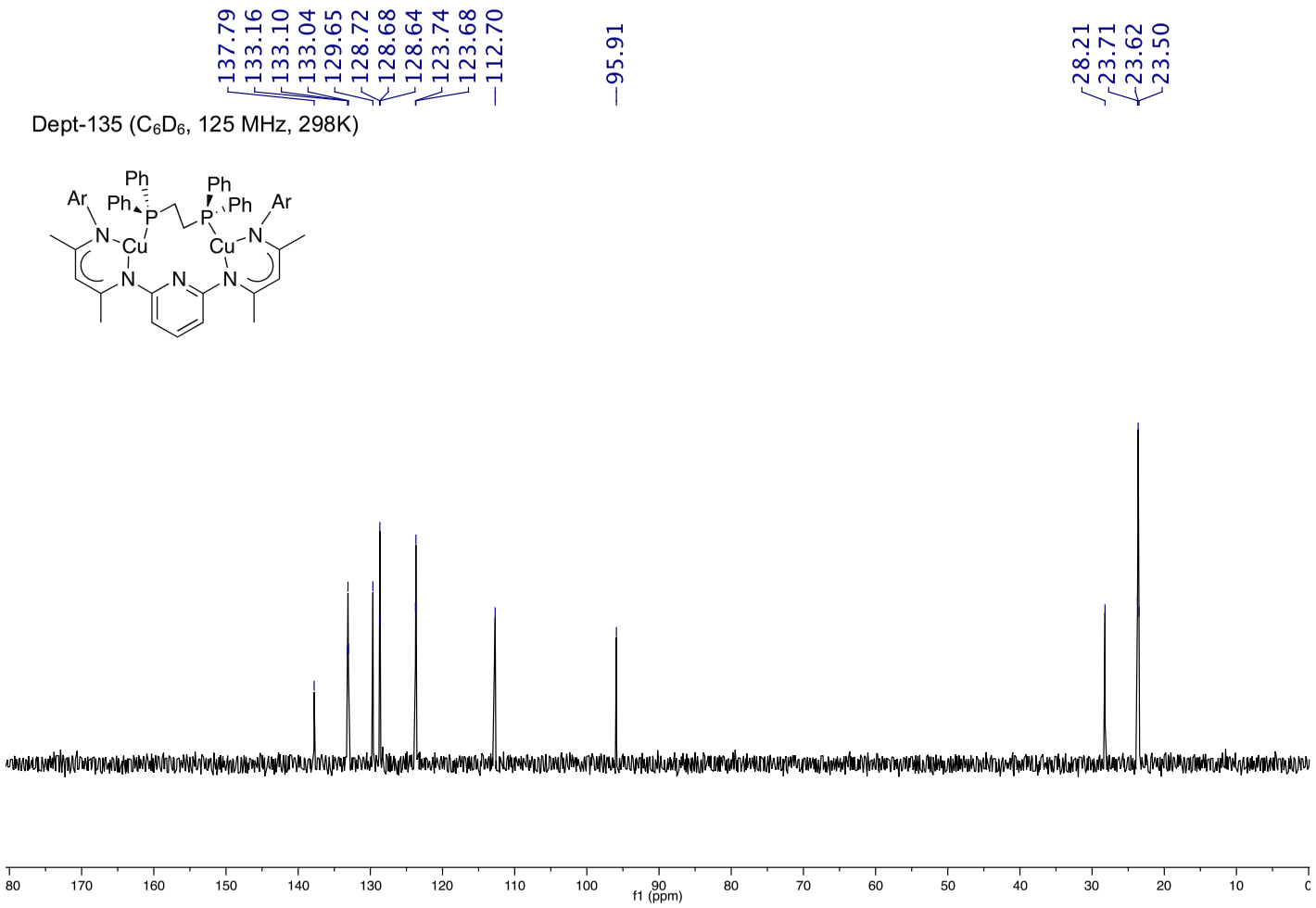

164.5
163.6
162.7
150.6
140.6
134.3
134.2
129.4
128.8
128.7
123.9
113.4
95.8
28.3
23.9
23.7
23.4
13C (C_6D_6, 125 MHz, 298K)
Ar
PPh3
Ph3P
Ar
N
Cu
N
N
Cu
N
Et2O
Et2O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HSQC (C_6D_6, 298K)
f1 (ppm)
f2 (ppm)
Ar
PPh3
Ph3P
Cu
N

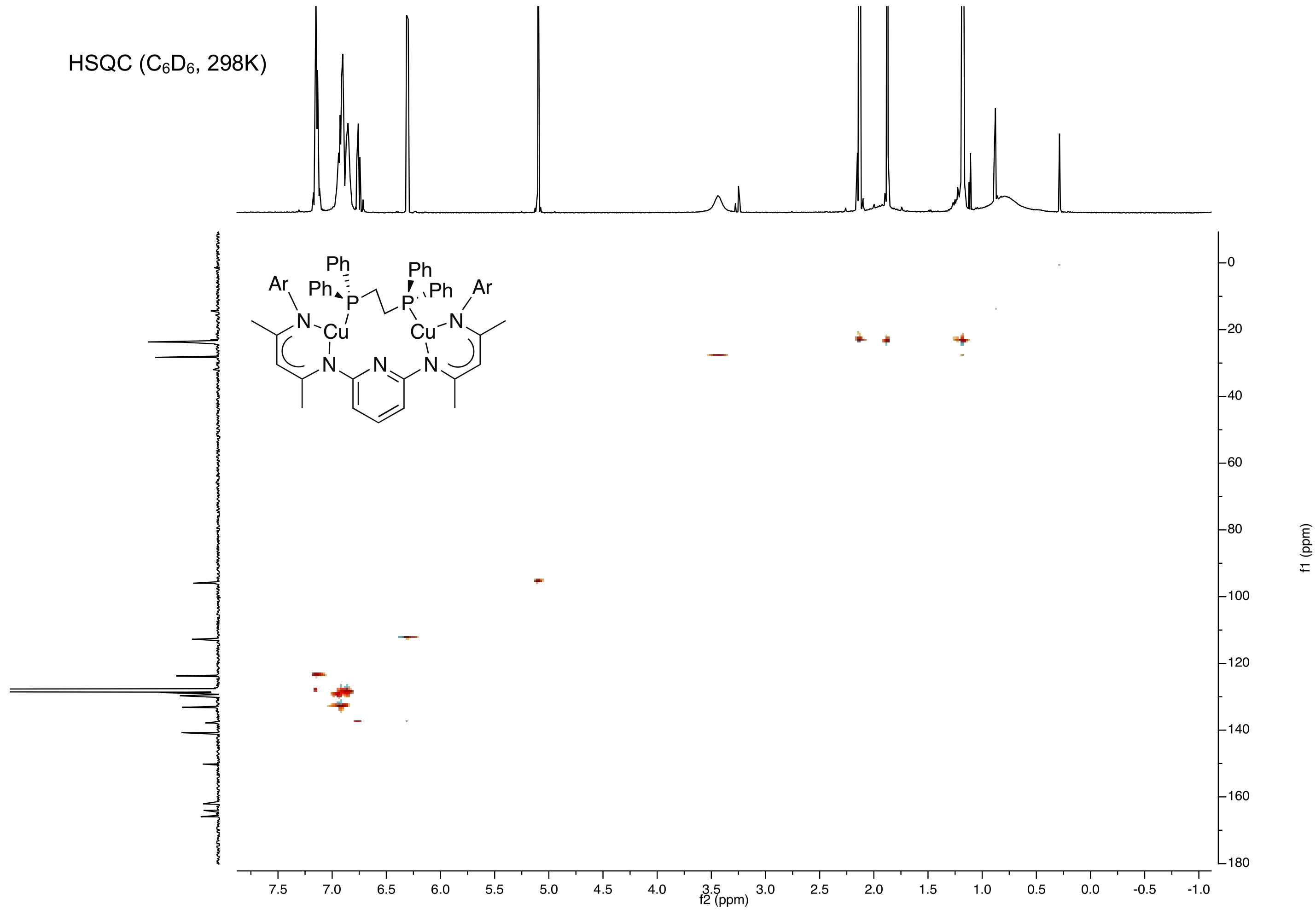

7.12
6.95
6.92
6.90
6.85
6.77
6.76
6.74
6.31
6.30
5.10
3.44
2.13
1.95
1.87
1.19
1.17
0.78
1H NMR (C6D6, 500 MHz, 298K)
Ph
Ar
Ph
P
P
Ph
Ph
Ar
N
Cu
Cu
N
N
N
N
10.01
20.89
1.29
1.98
2.07
3.87
6.00
9.58
12.53
11.86
f1 (ppm)

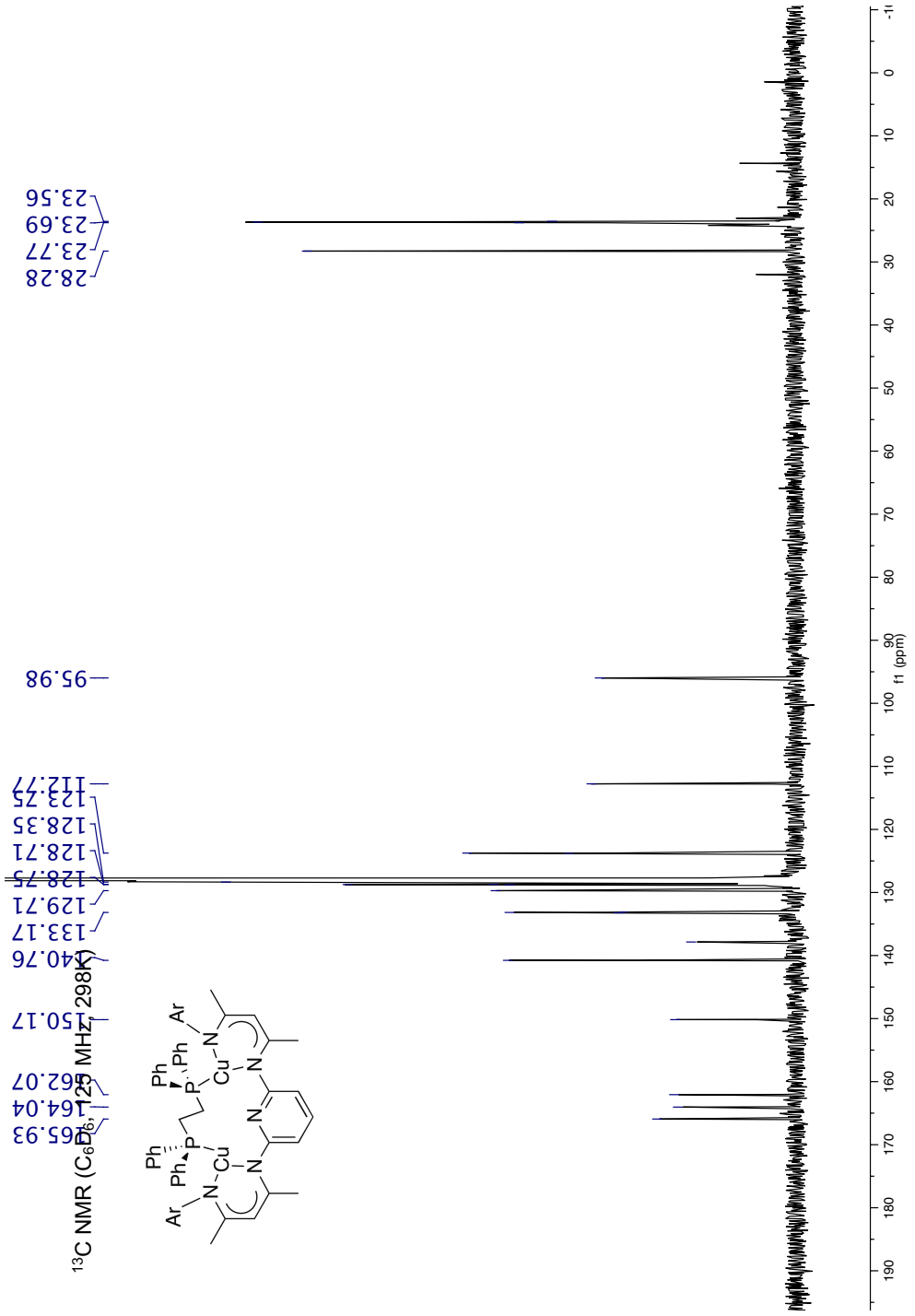
31P NMR (C_6D_6, 202 MHz, 298K)



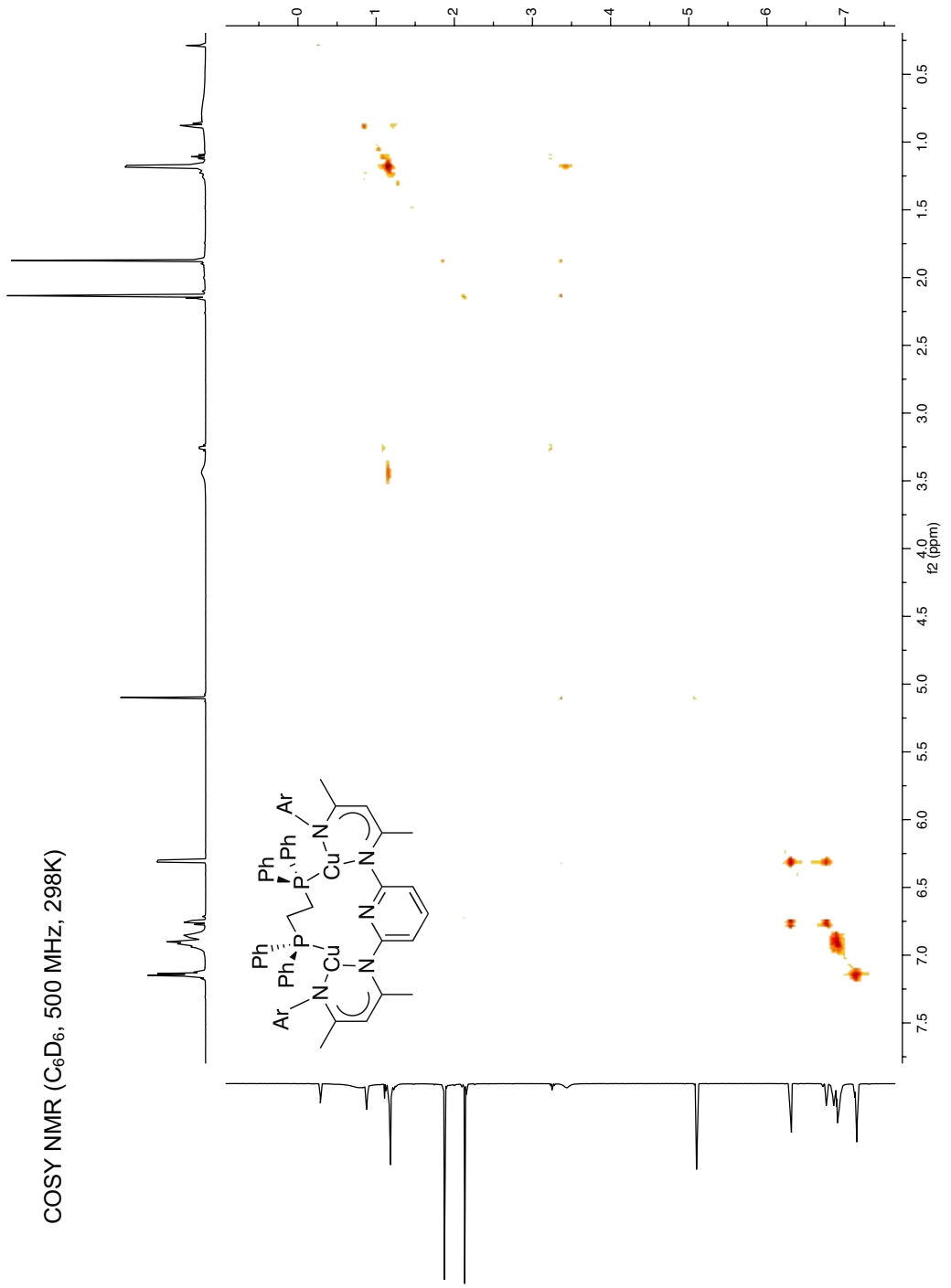

137.79
133.16
133.10
133.04
129.65
128.72
128.68
128.64
123.74
123.68
112.70
95.91
28.21
23.71
23.62
23.50
Dept-135 (C_6D_6, 125 MHz, 298K)
Ph
Ph
P
P
Ph
Ph
Ar
Ar
N
Cu
Cu
N
N
N
N
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

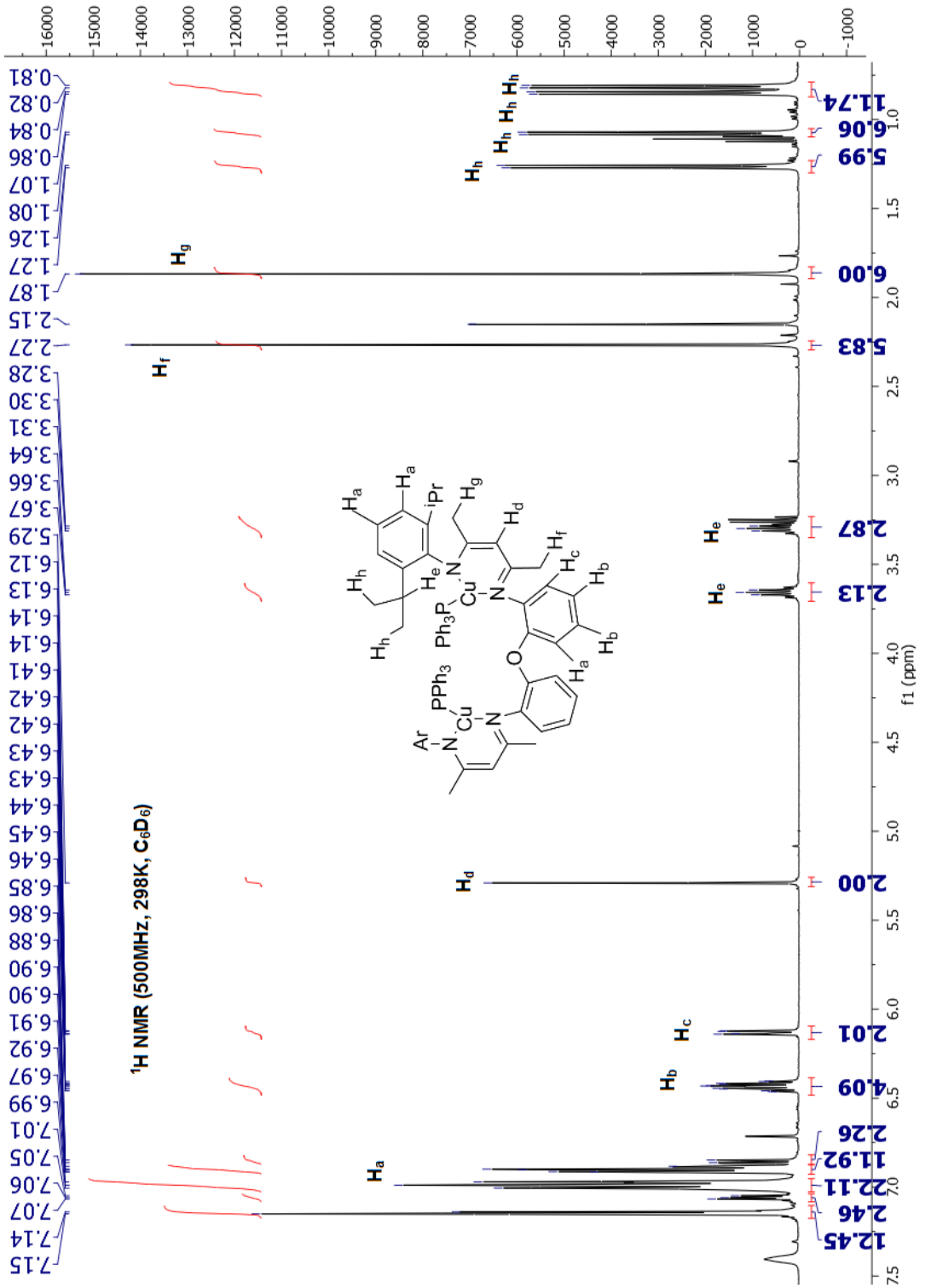
HSQC (C_6D_6, 298K)

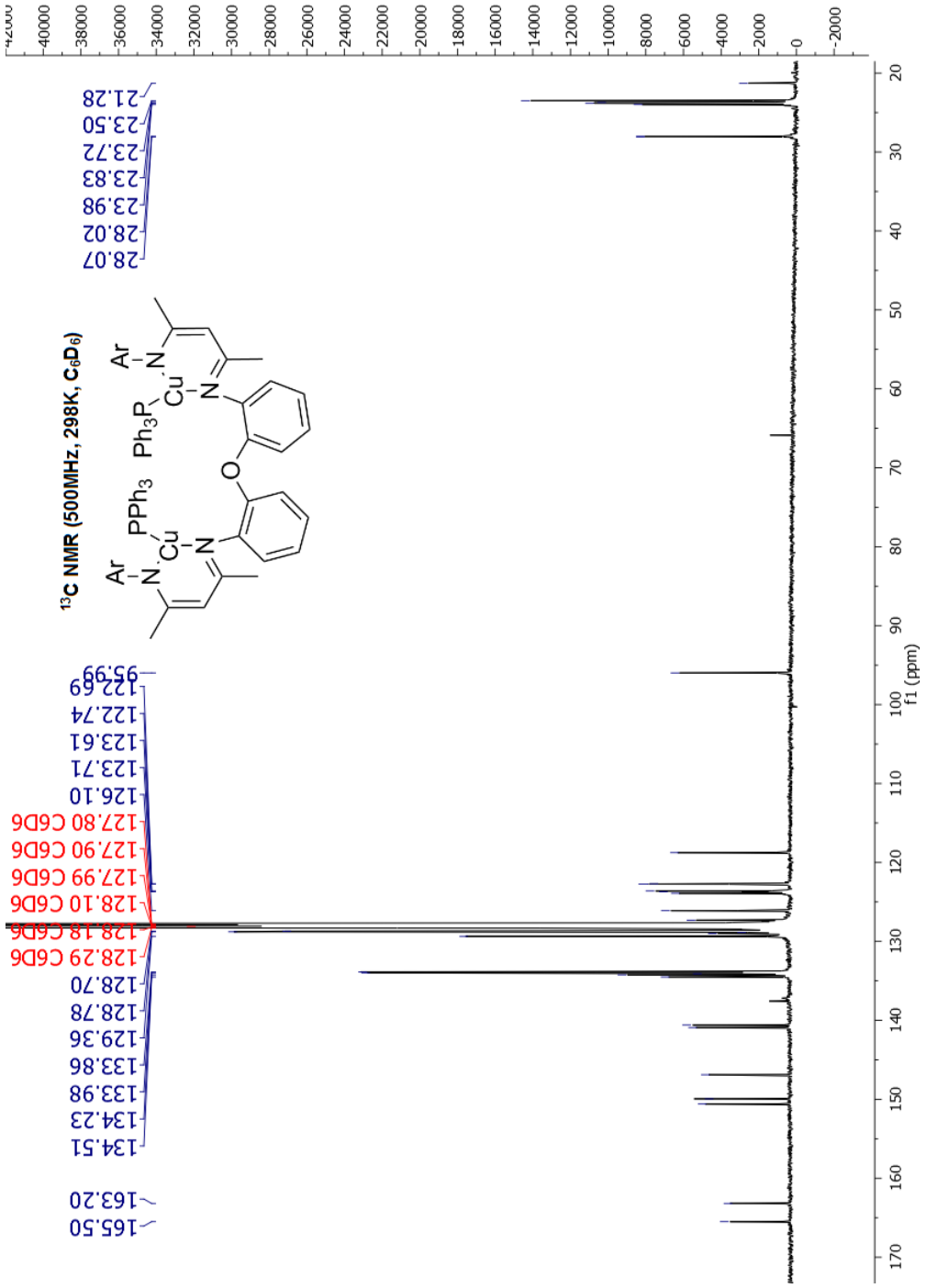


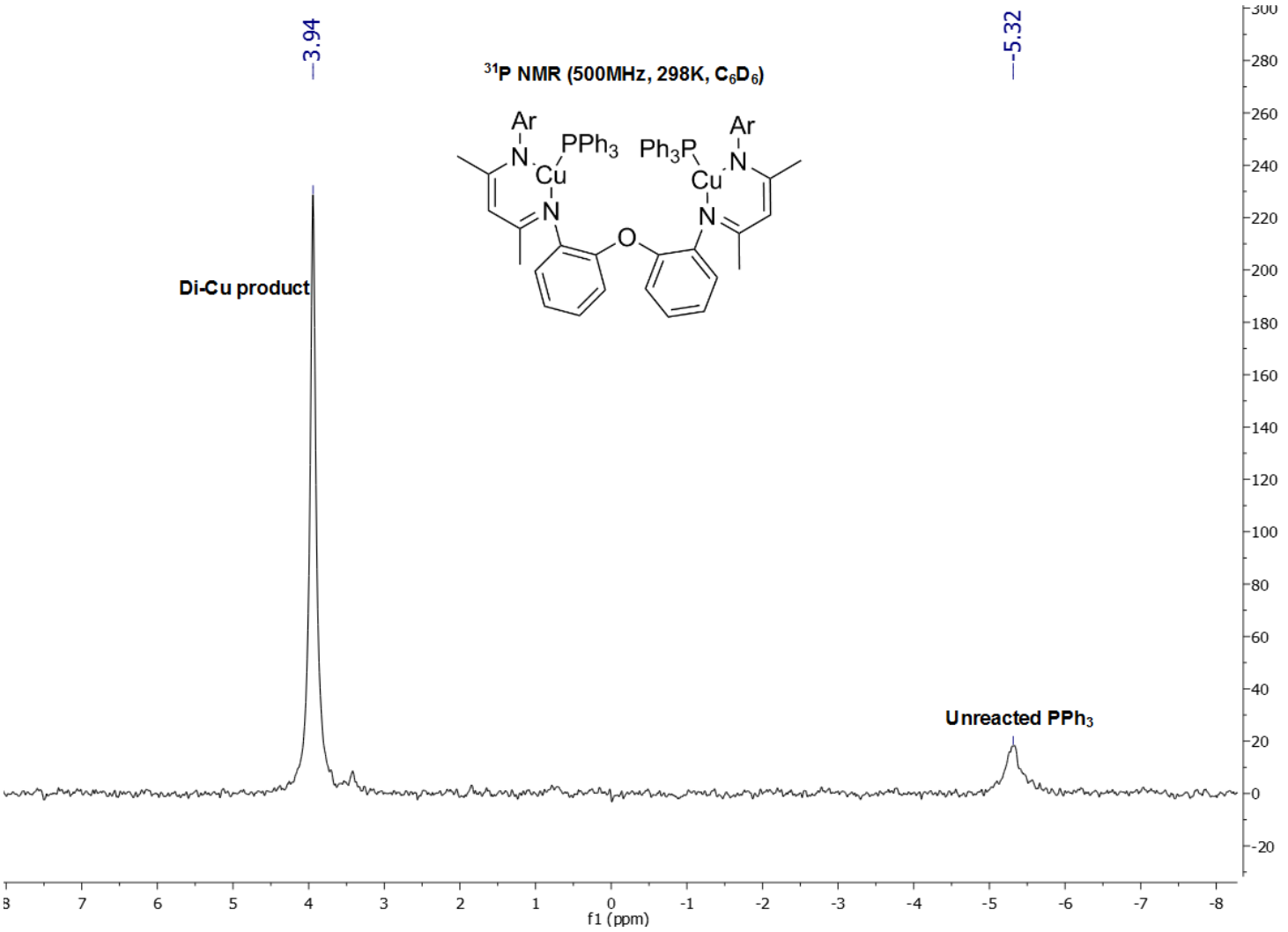

^{13}C NMR (C_6D_6, 125 MHz, 298K)
165.93
164.04
162.07
150.17
140.76
133.17
129.71
128.75
128.71
128.35
123.75
112.77
95.98
28.28
23.77
23.69
23.56
f1 (ppm)

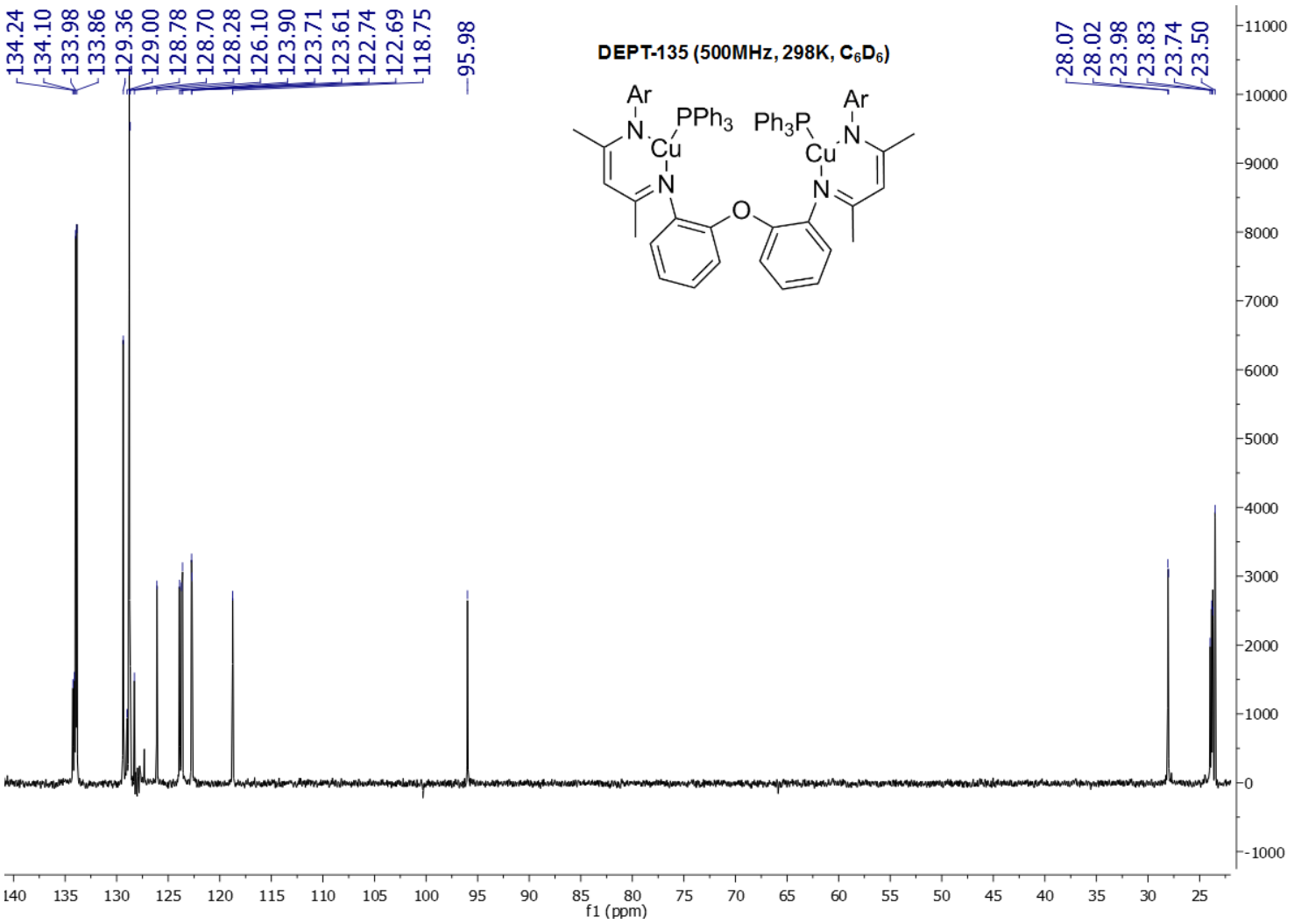
COSY NMR (C_6D_6, 500 MHz, 298K)

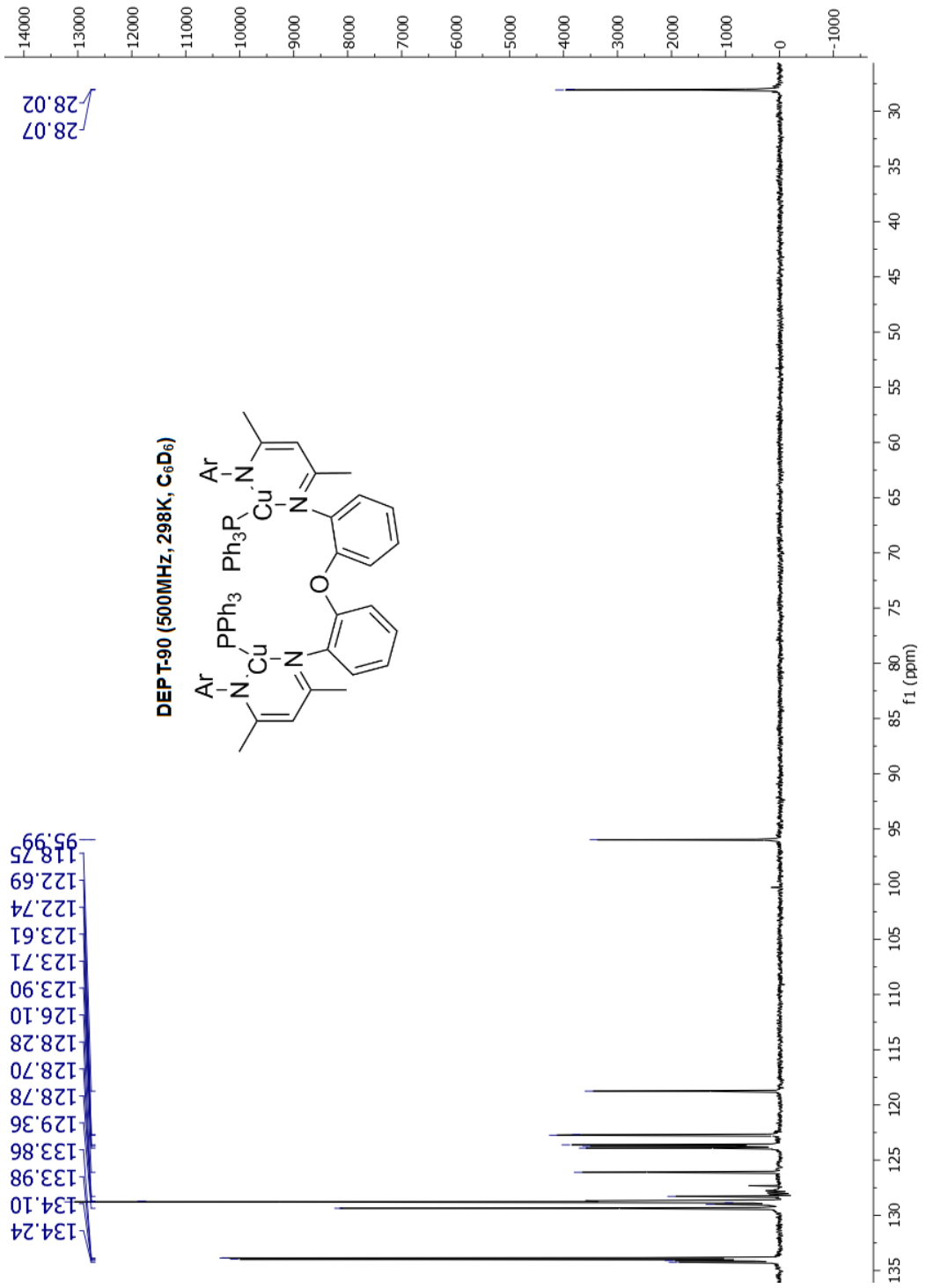


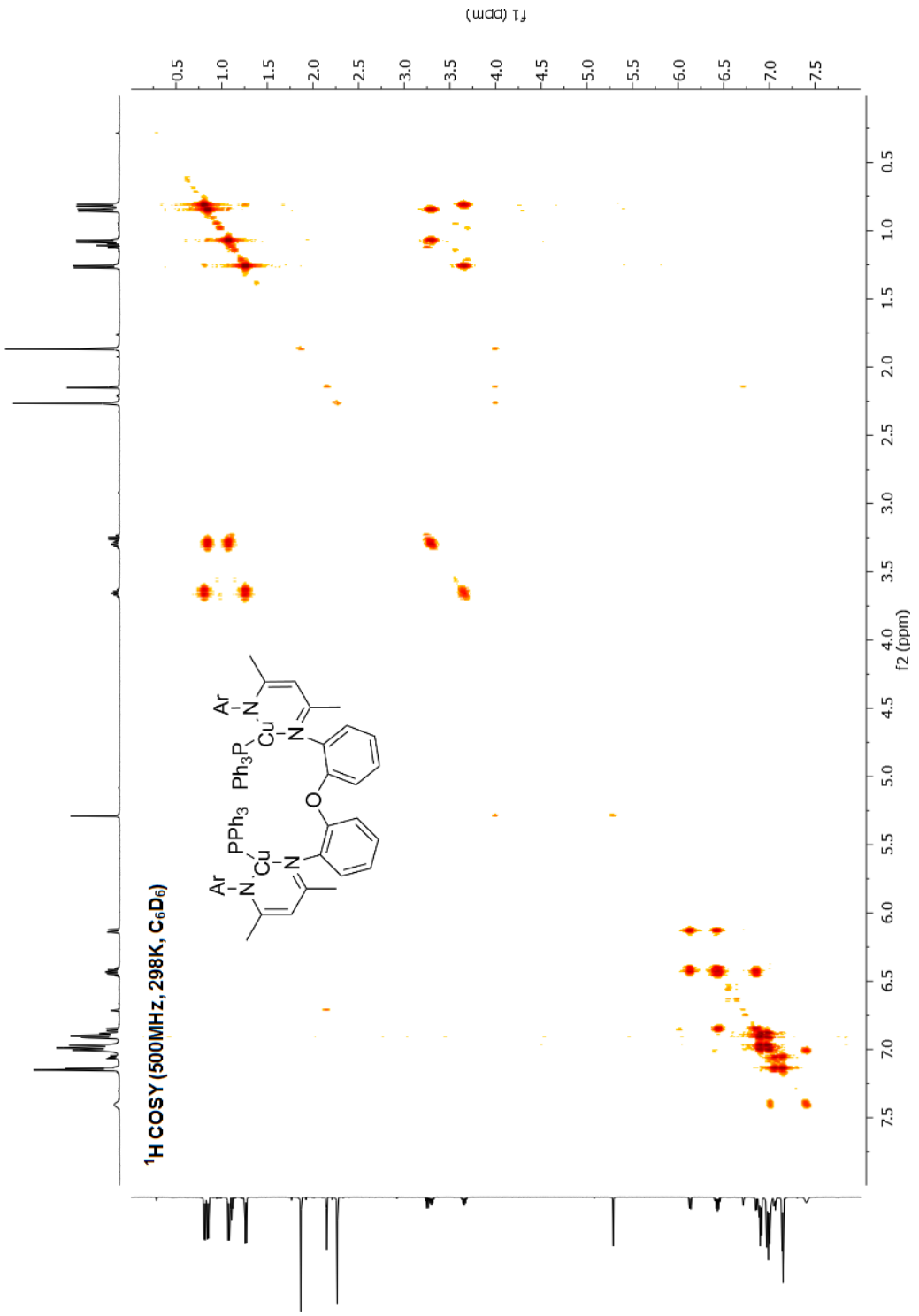

^{1}H NMR (500MHz, 298K, C_6D_6)
H_a
H_b
H_c
H_d
H_e
H_f
H_g
H_h
12.45
2.46
22.11
11.92
2.26
4.09
2.01
2.00
2.13
2.87
5.83
6.00
5.99
6.06
11.74
f1 (ppm)

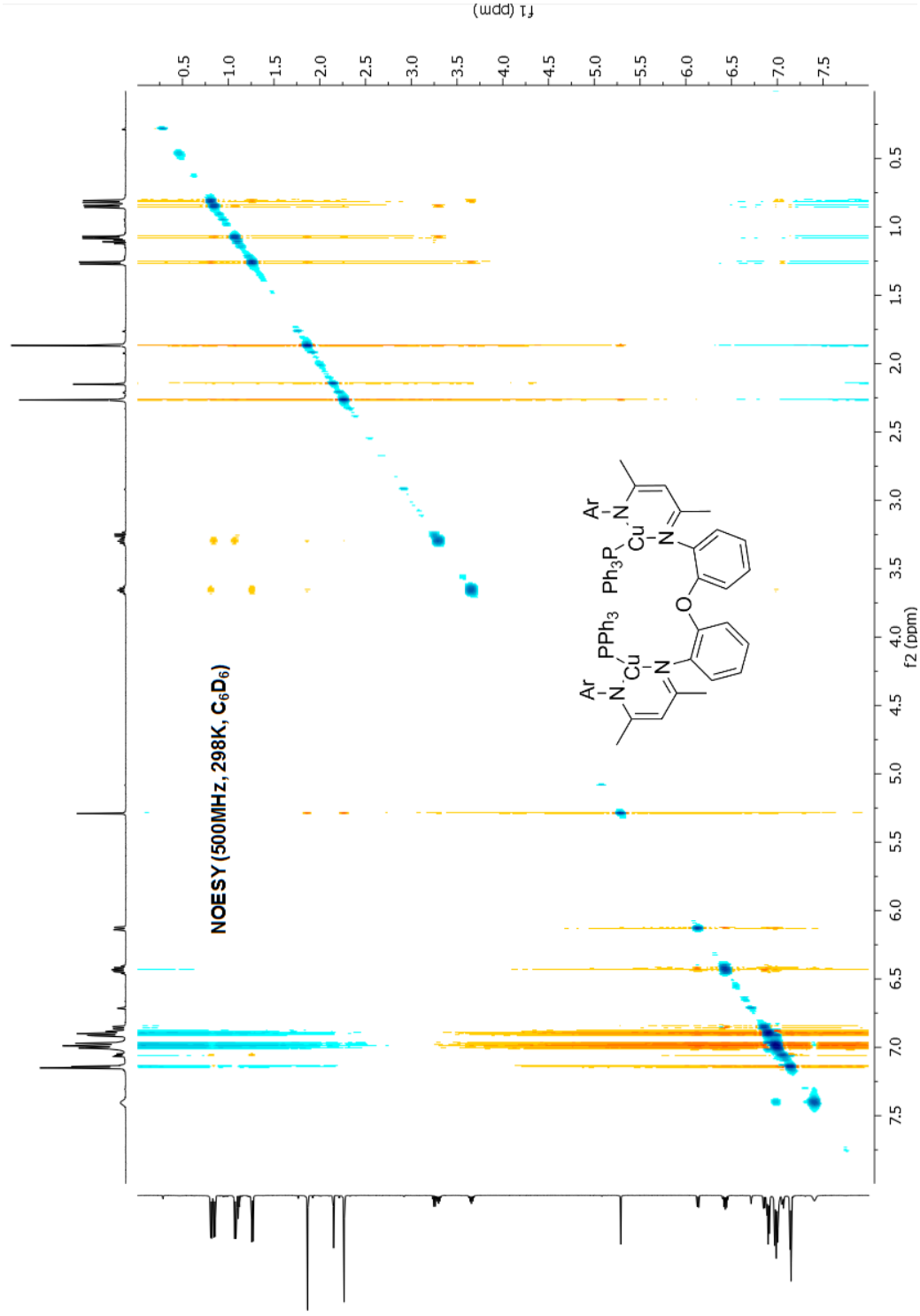

13C NMR (500MHz, 298K, C6D6)
Ar
N
Cu
PPh3
Ph3P
O
21.28
23.50
23.72
23.83
23.98
28.02
28.07
95.99
122.69
122.74
123.61
123.71
126.10
127.80 C6D6
127.90 C6D6
127.99 C6D6
128.10 C6D6
128.18 C6D6
128.29 C6D6
128.70
128.78
129.36
133.86
133.98
134.23
134.51
163.20
165.50
f1 (ppm)

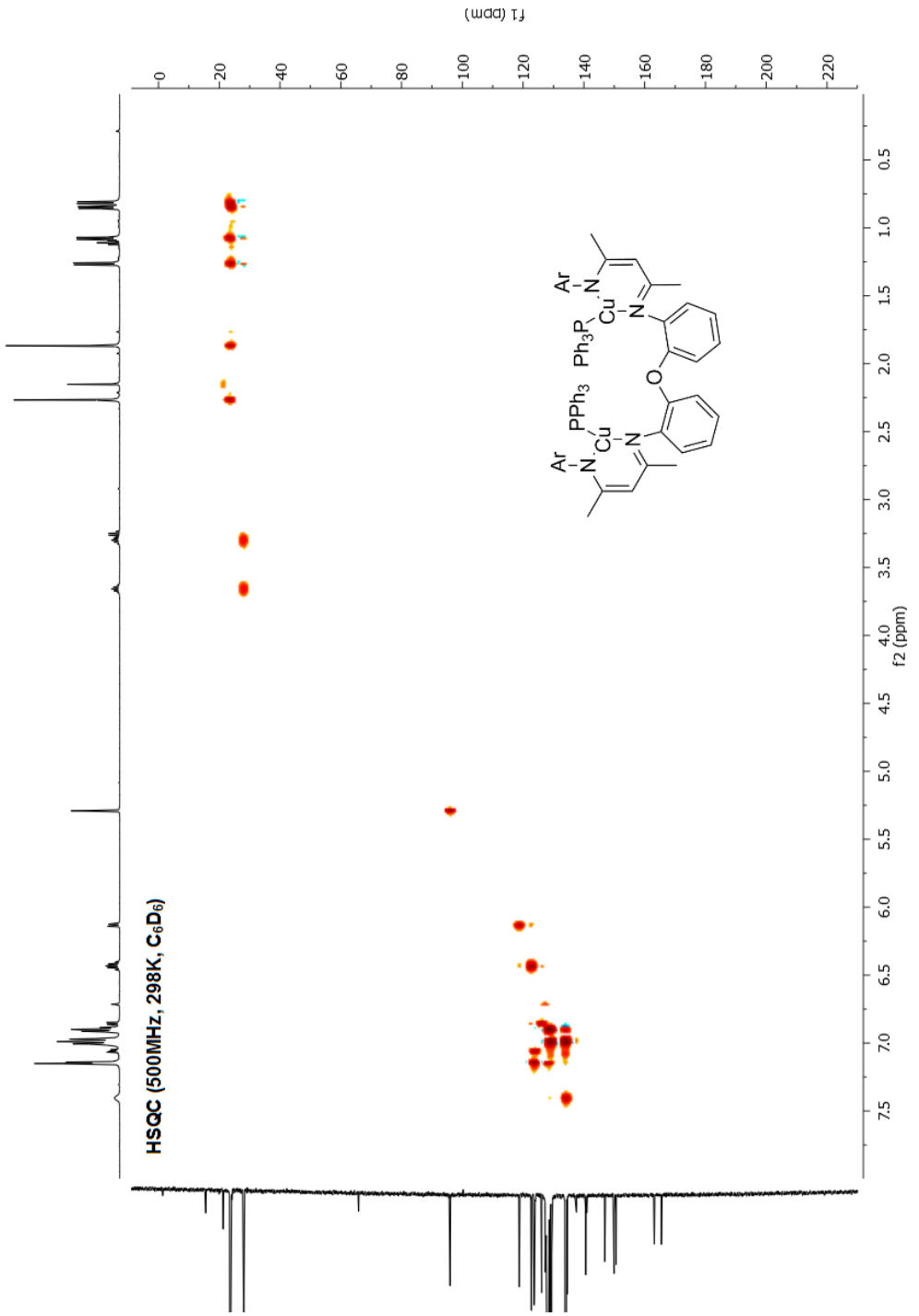

3.94
-5.32
31P NMR (500MHz, 298K, C6D6)
Ar
PPh3
Ph3P
Ar
Cu
Cu
N
N
N
O
Di-Cu product
Unreacted PPh3
f1 (ppm)

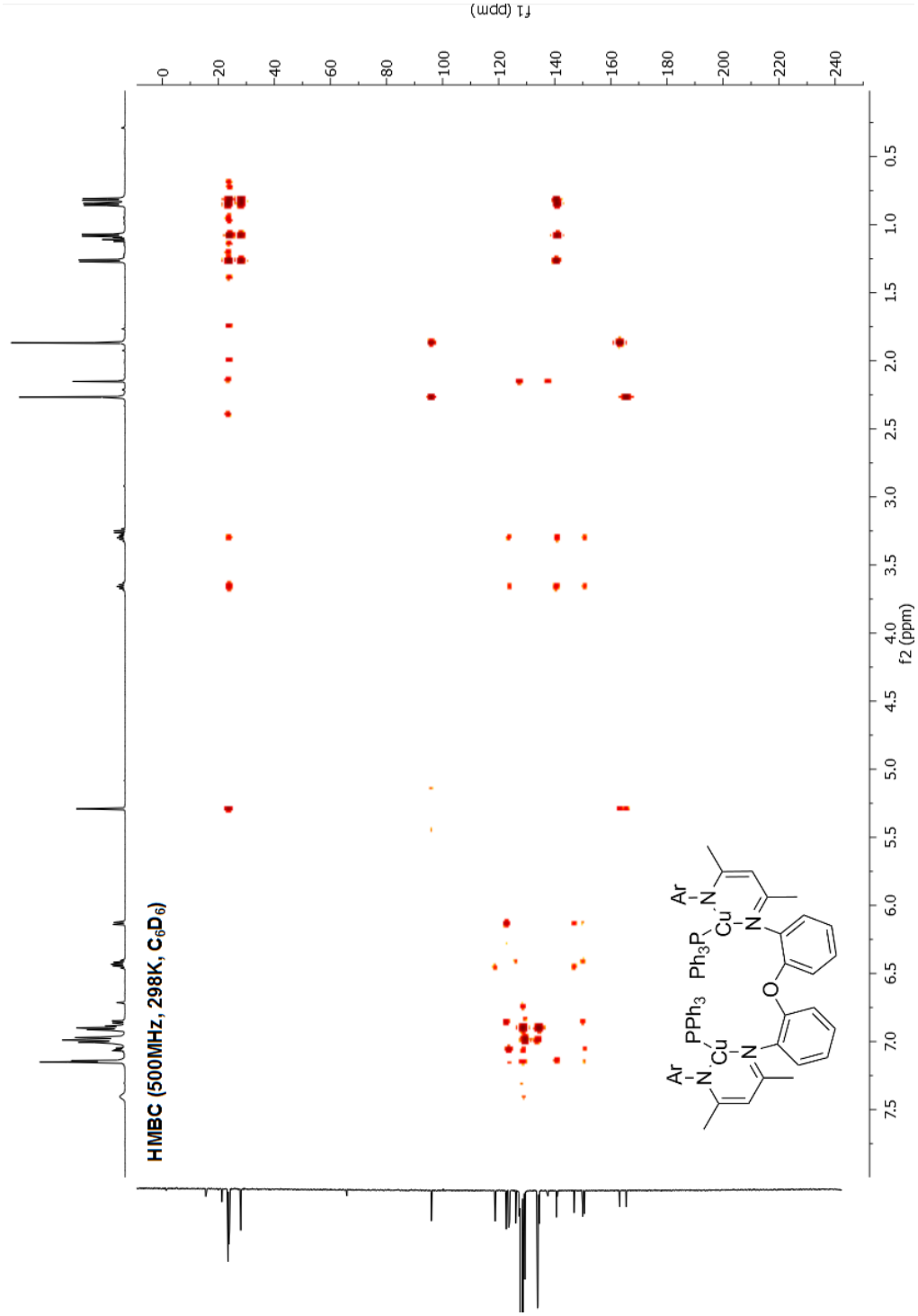

DEPT-135 (500MHz, 298K, C6D6)
134.24
134.10
133.98
133.86
129.36
129.00
128.78
128.70
128.28
126.10
123.90
123.71
123.61
122.74
122.69
118.75
95.98
28.07
28.02
23.98
23.83
23.74
23.50
Ar
PPh3
Ph3P
Cu
N
O
f1 (ppm)


DEPT-90 (500MHz, 298K, C6D6)
Ar
N
Cu
PPh3
Ph3P
O
28.07
28.02
95.99
118.75
122.69
122.74
123.61
123.71
123.90
126.10
128.28
128.70
128.78
129.36
133.86
133.98
134.10
134.24
f1 (ppm)

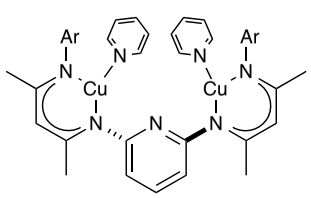

^{1}H COSY (500MHz, 298K, C_6D_6)
f2 (ppm)
f1 (ppm)
Ar
N
Cu
PPh3
Ph3P
O


NOESY (500MHz, 298K, C6D6)
f1 (ppm)
f2 (ppm)
Ar
N
Cu
N
Ph3P
PPh3
O


HSQC (500MHz, 298K, C6D6)
f1 (ppm)
f2 (ppm)
Ar
N
Cu
PPh3
Ph3P
O

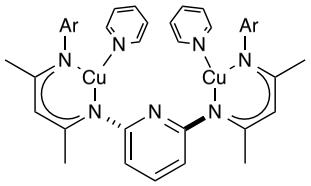

HMBC (500MHz, 298K, C6D6)
f1 (ppm)
f2 (ppm)
Ar
N
Cu
Ph3P
PPh3
O

^{1}H NMR (C_6D_6, 500 MHz, 298 K)



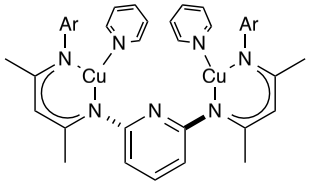
Ar = 2,6-diisopropylamine

$^{1}H–^{1}H$ COSY (C_6D_6, 500 MHz, 298 K)



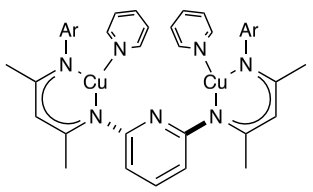
Ar = 2,6-diisopropylamine

NOESY (C_6D_6, 500 MHz, 298 K)



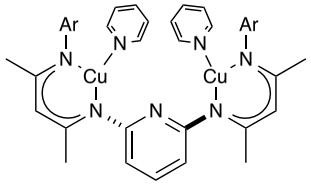
Ar = 2,6-diisopropylamine

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 298 K)



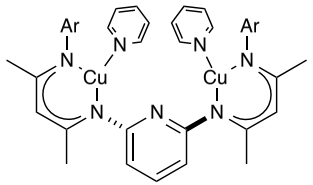
Ar = 2,6-diisopropylamine

DEPT-135 (C_6D_6, 126 MHz, 298 K)



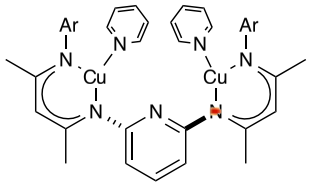
Ar = 2,6-diisopropylamine

$^{1}H–^{13}C$ HSQC (C_6D_6, 500 MHz, 298 K)

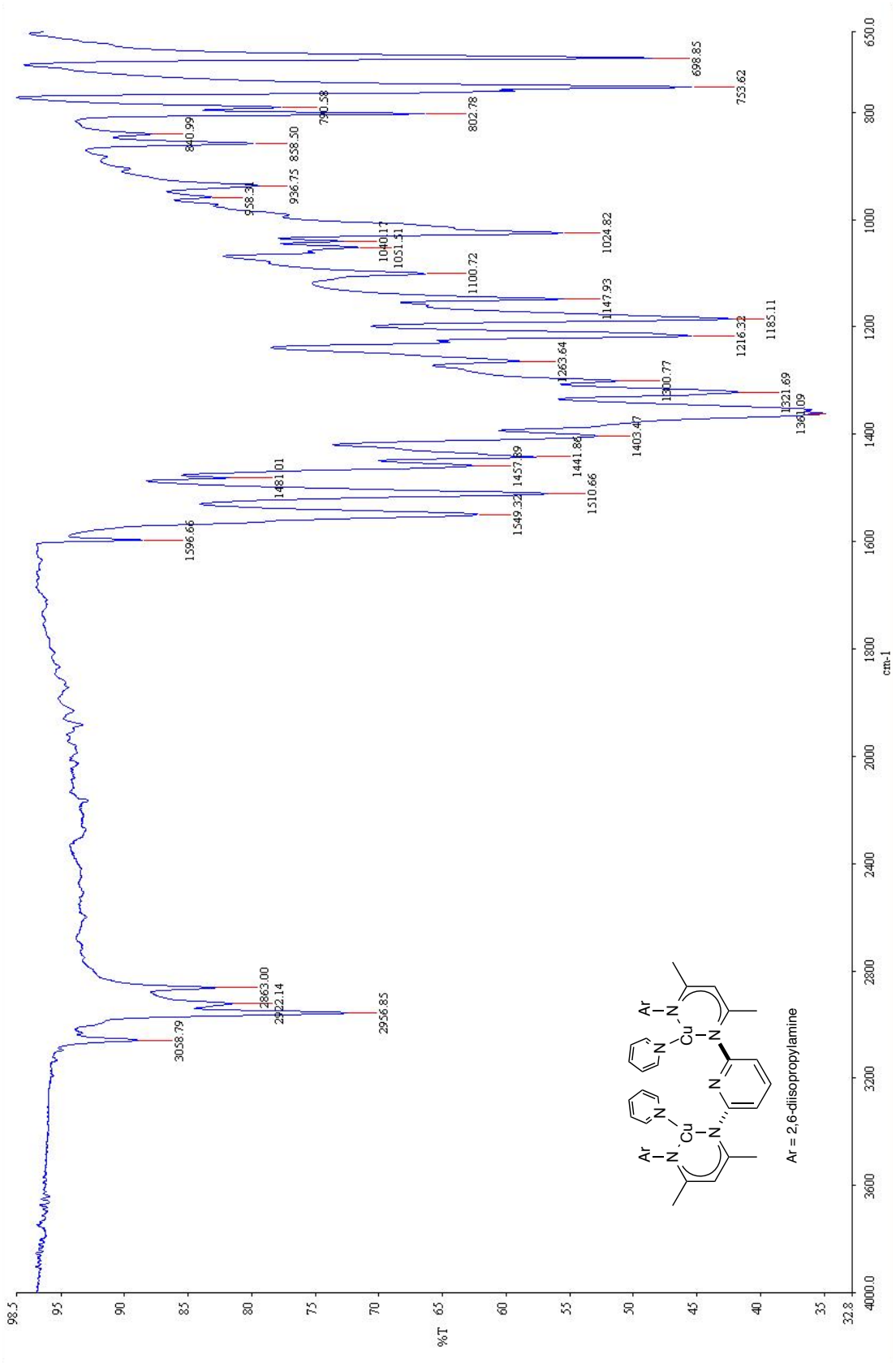


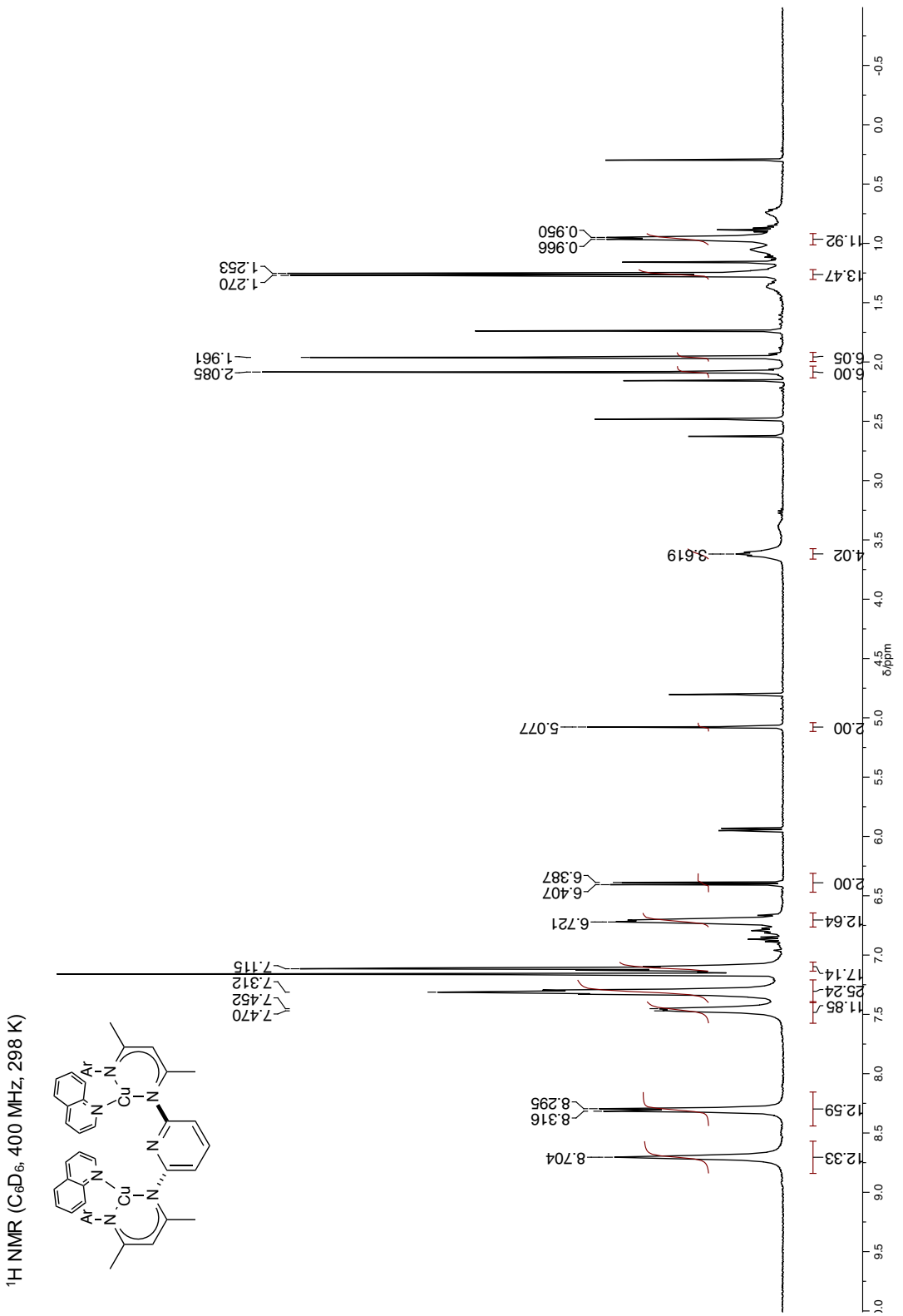
Ar = 2,6-diisopropylamine

$^{1}H–^{13}C$ HMBC (C_6D_6, 500 MHz, 298 K)

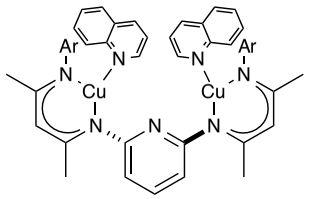


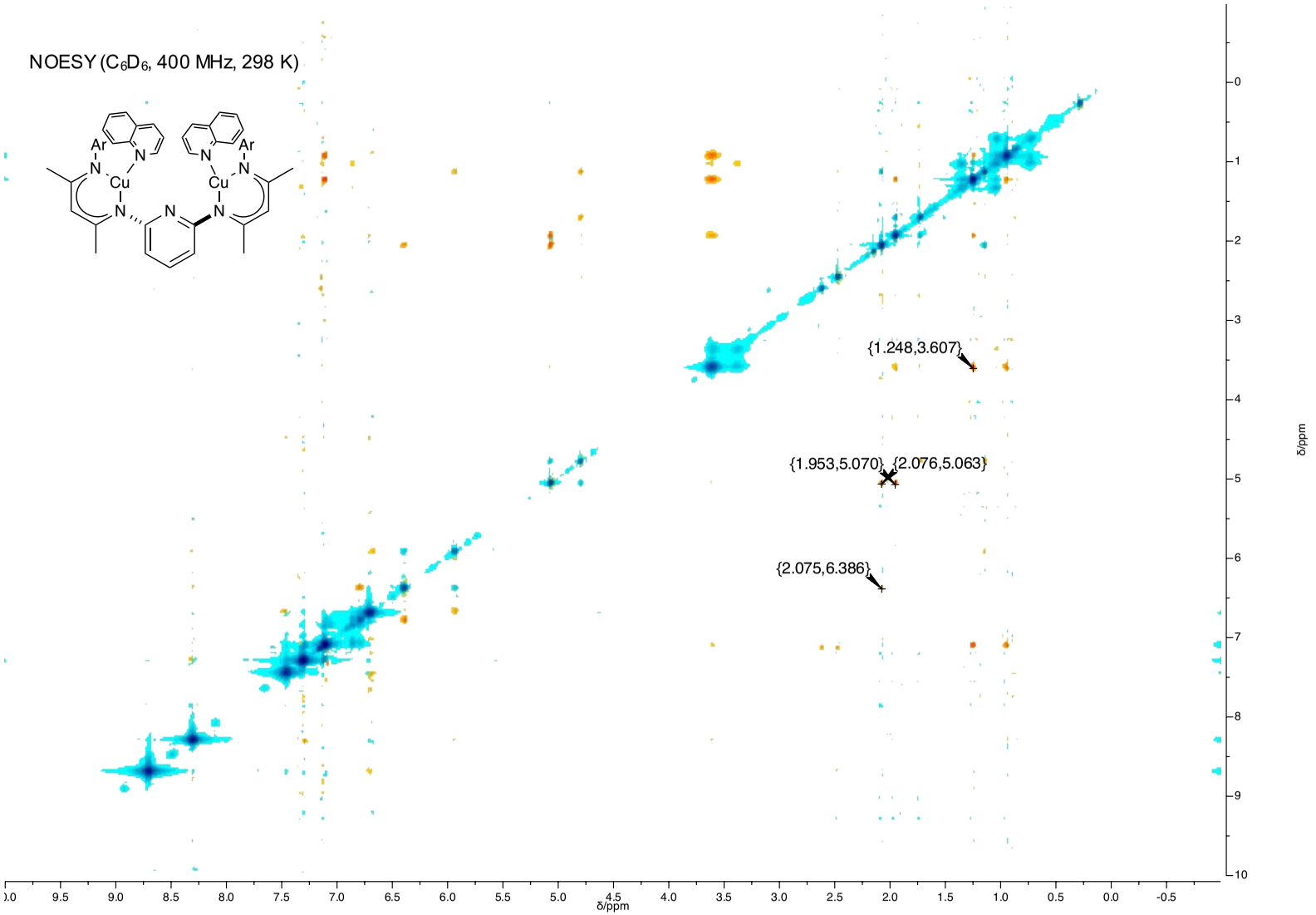
Ar = 2,6-diisopropylamine

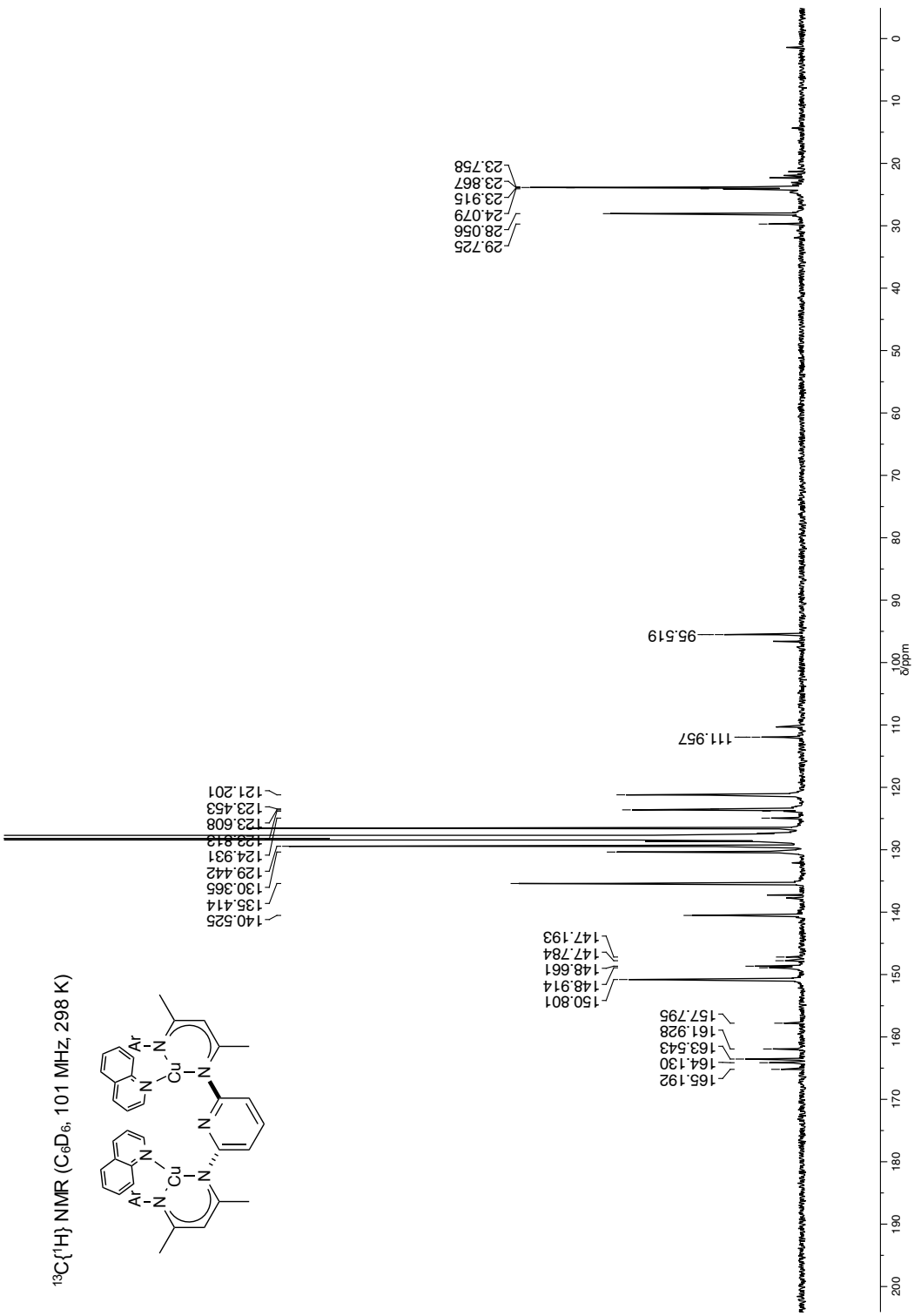

%T
cm-1
Ar = 2,6-diisopropylamine

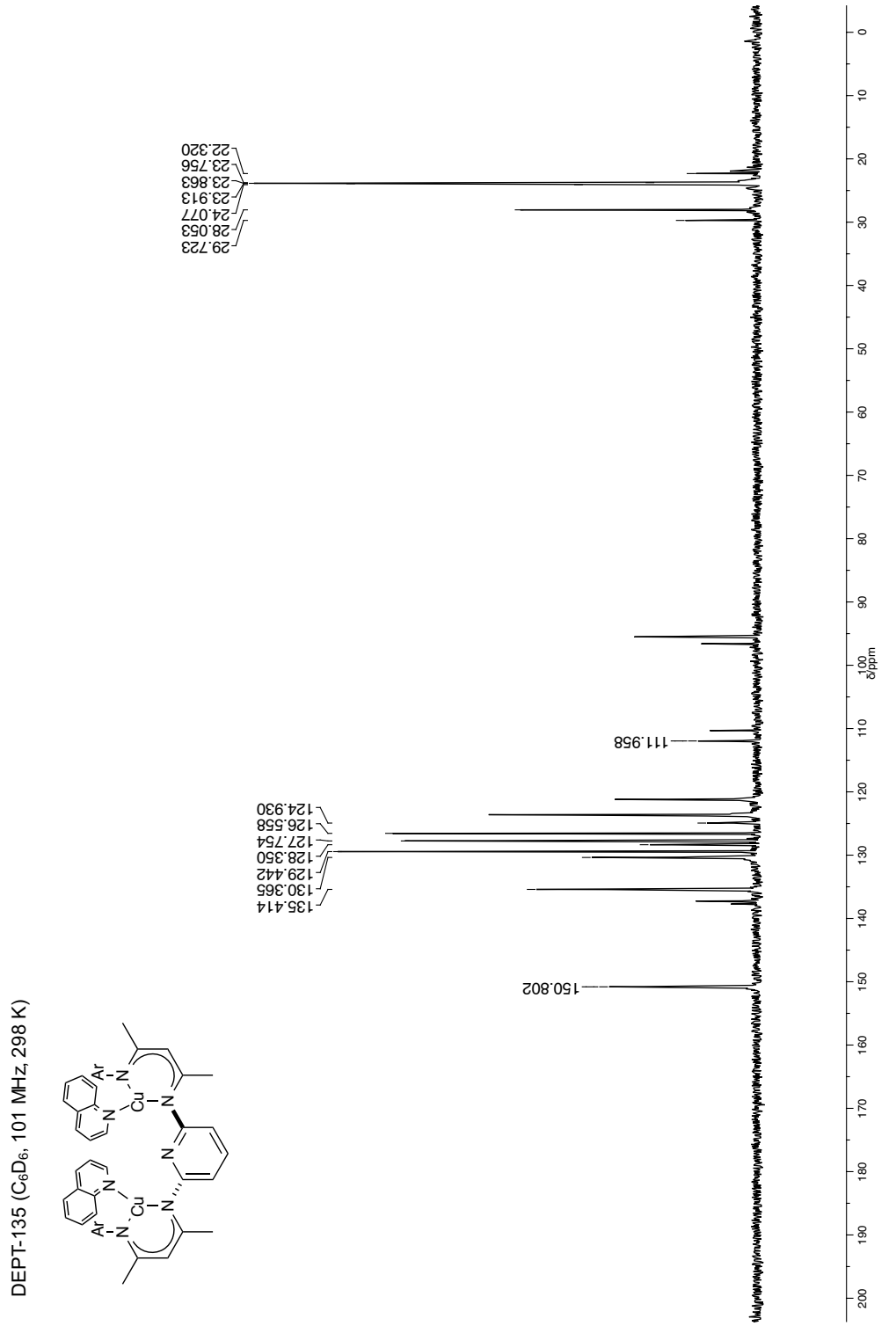

^{1}H NMR (C_6D_6, 400 MHz, 298 K)
8.704
8.316
8.295
7.470
7.452
7.312
7.115
6.721
6.407
6.387
5.077
3.619
2.085
1.961
1.270
1.253
0.966
0.950
12.33
12.59
11.85
25.24
17.14
12.64
2.00
2.00
4.02
6.00
6.05
13.47
11.92
δ/ppm

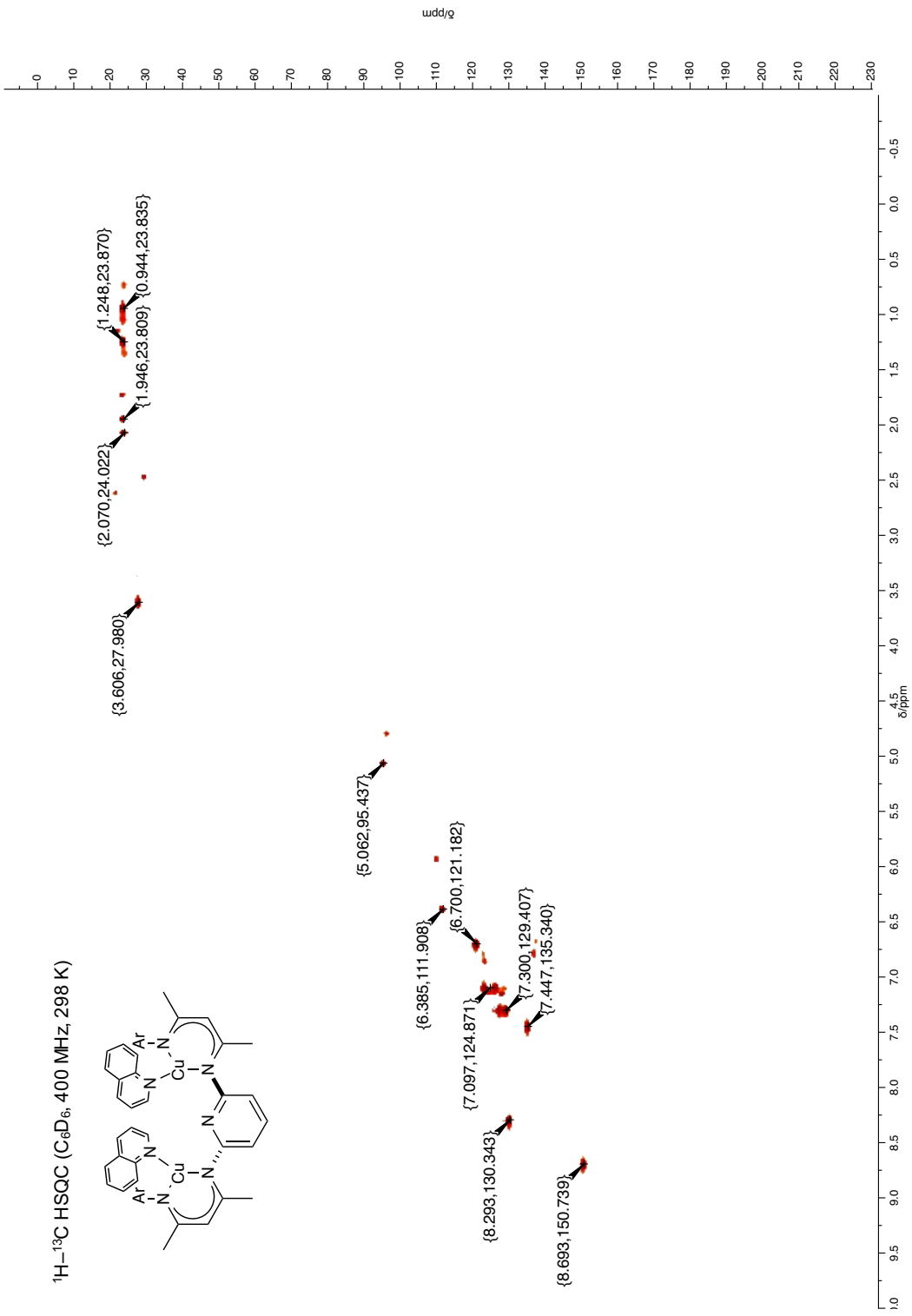
^{1}H–^{1}H COSY (C_6D_6, 400 MHz, 298 K)

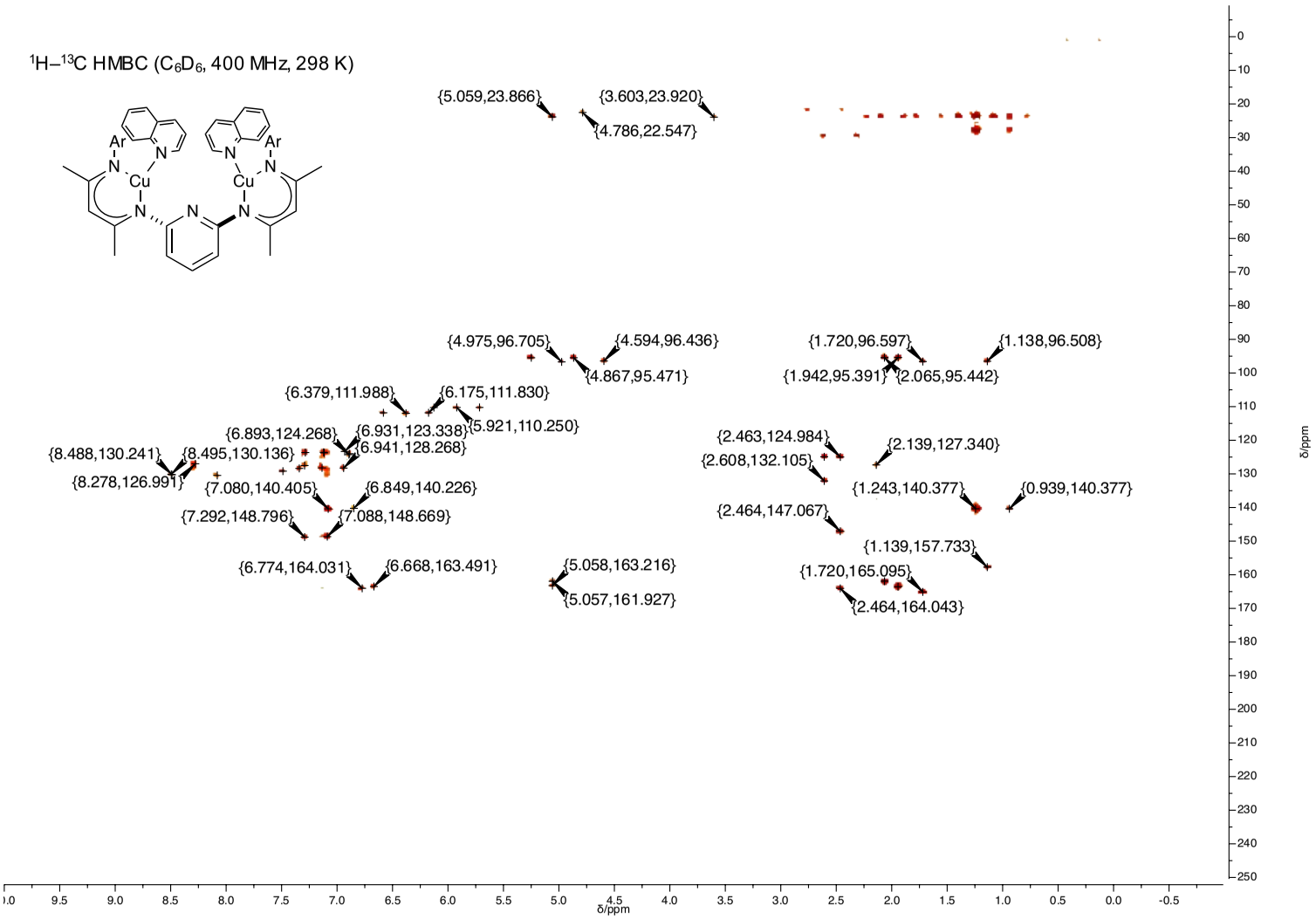


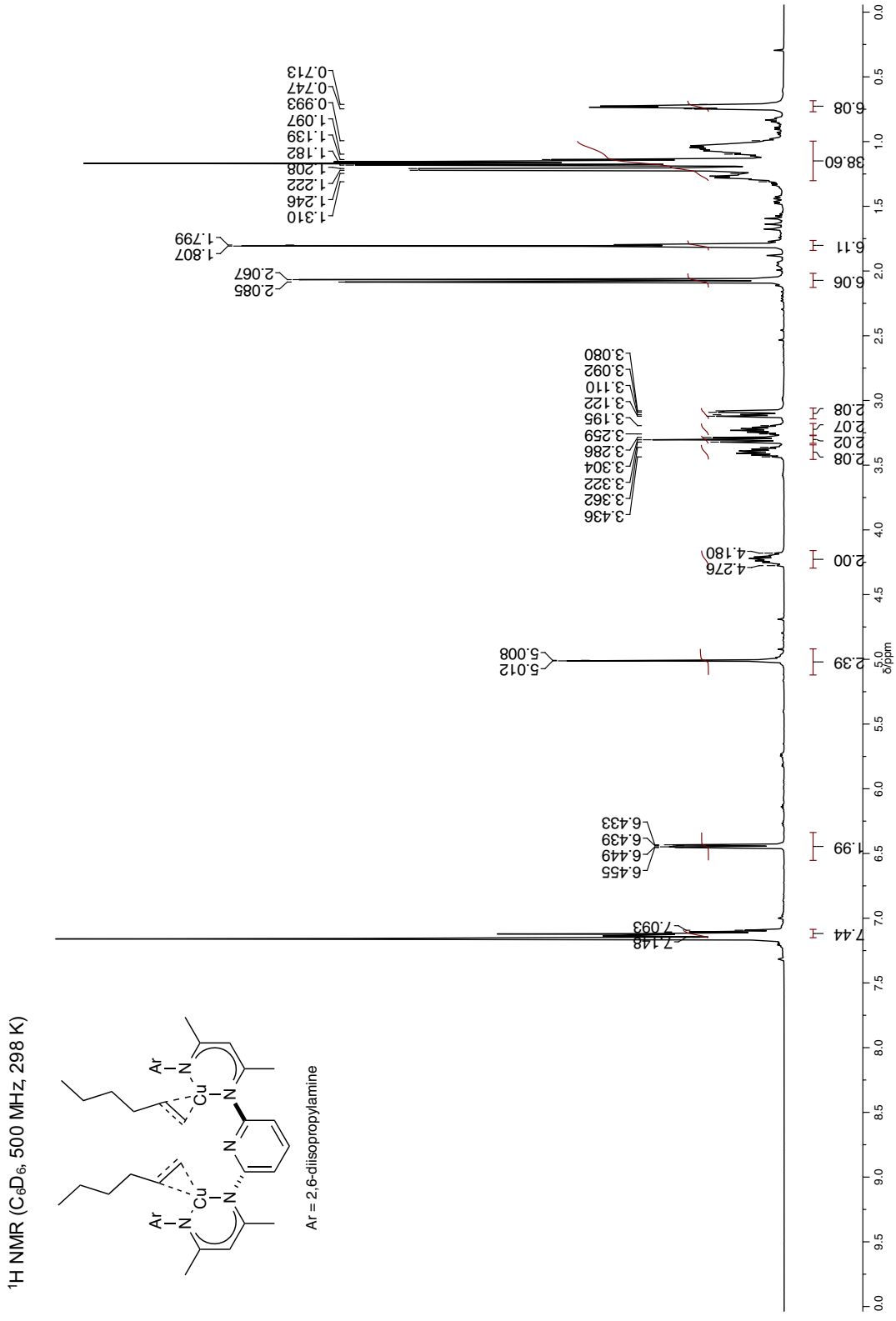

NOESY (C_6D_6, 400 MHz, 298 K)
{1.248,3.607}
{1.953,5.070}
{2.076,5.063}
{2.075,6.386}
δ/ppm
δ/ppm

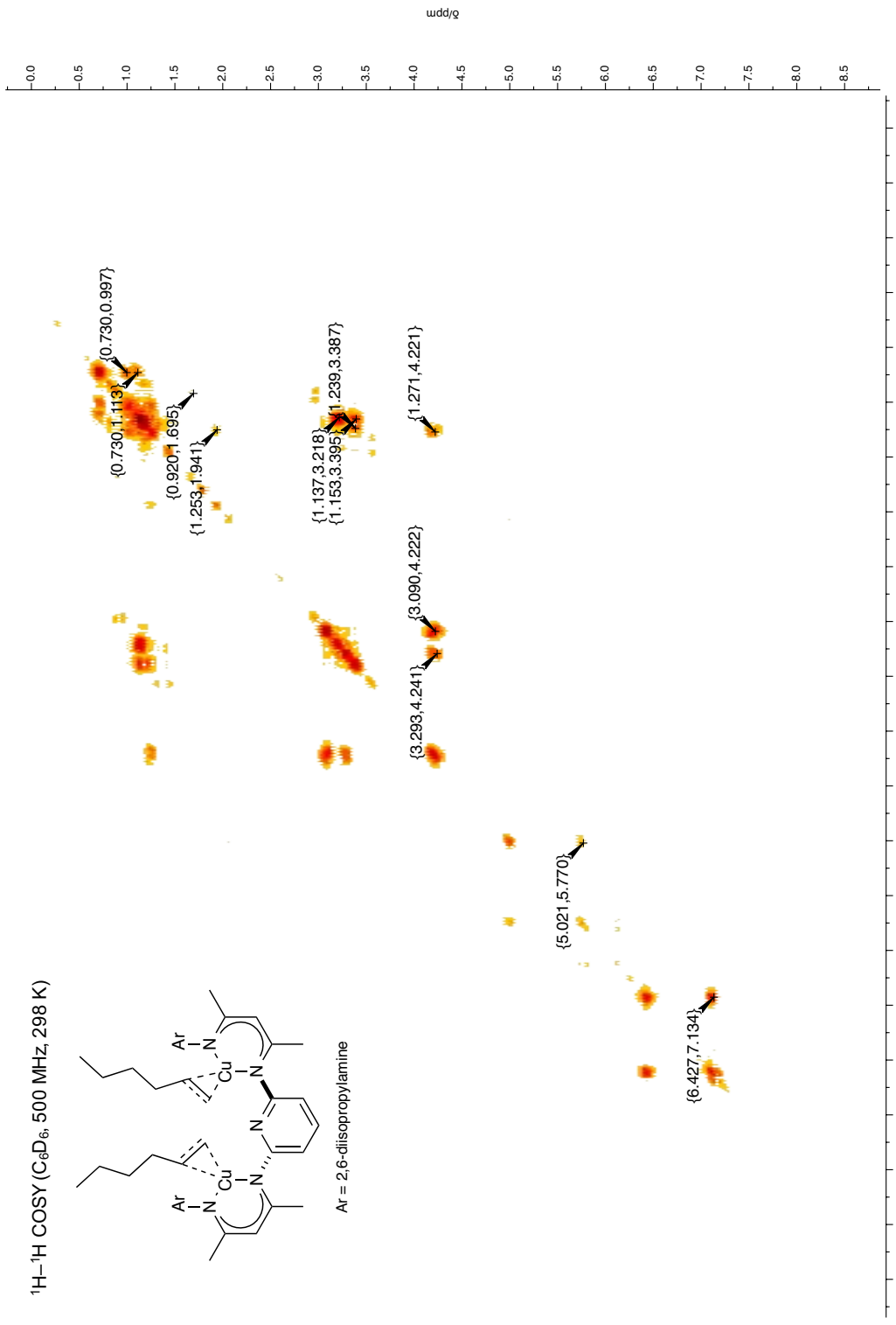

$^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz, 298 K)
Ar
N
Cu
N
N
Ar
N
Cu
N
N
165.192
164.130
163.543
161.928
157.795
150.801
148.914
148.661
147.784
147.193
140.525
135.414
130.365
129.442
124.931
123.608
123.453
121.201
111.957
95.519
29.725
28.056
24.079
23.915
23.867
23.758
δ/ppm

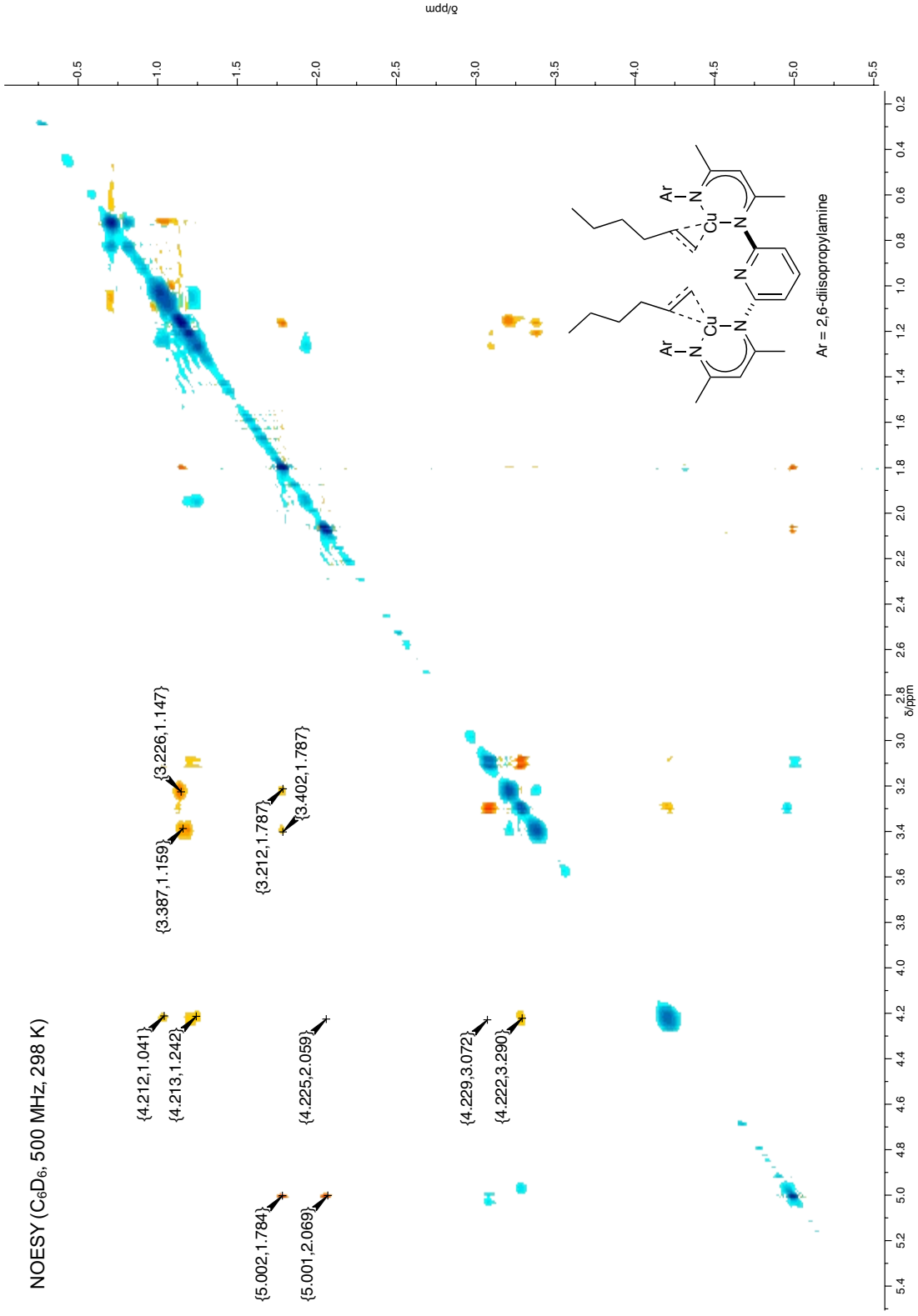

DEPT-135 (C_6D_6, 101 MHz, 298 K)
Ar
N
Cu
N
N
N
Ar
N
Cu
N
150.802
135.414
130.365
129.442
128.350
127.754
126.558
124.930
111.958
29.723
28.053
24.077
23.913
23.863
23.756
22.320
δ/ppm

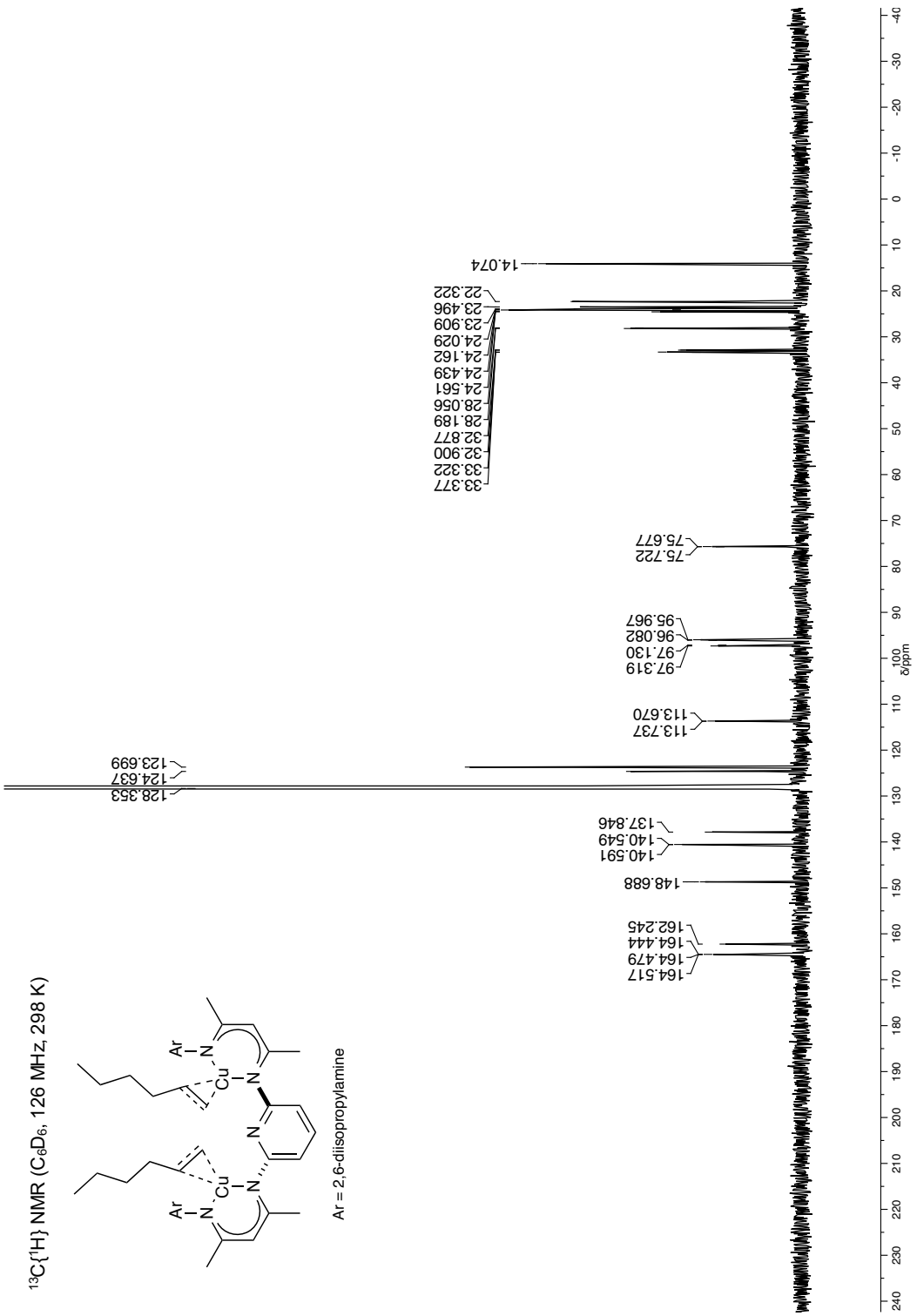

^{1}H–^{13}C HSQC (C_6D_6, 400 MHz, 298 K)
{1.248,23.870}
{0.944,23.835}
{1.946,23.809}
{2.070,24.022}
{3.606,27.980}
{5.062,95.437}
{6.385,111.908}
{6.700,121.182}
{7.097,124.871}
{7.300,129.407}
{7.447,135.340}
{8.293,130.343}
{8.693,150.739}
δ/ppm
δ/ppm

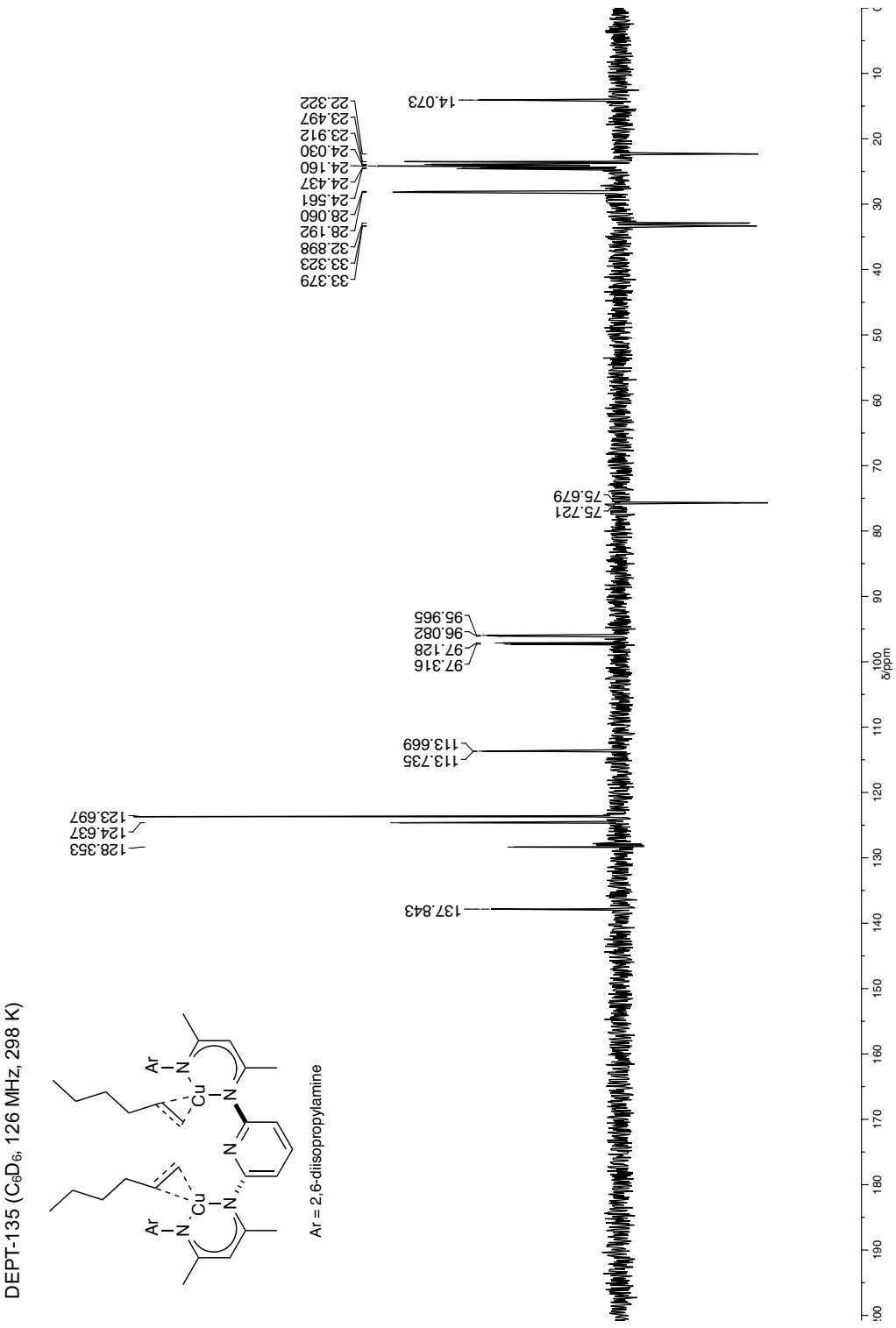

^{1}H–^{13}C HMBC (C_6D_6, 400 MHz, 298 K)
{5.059,23.866}
{3.603,23.920}
{4.786,22.547}
{4.975,96.705}
{4.594,96.436}
{4.867,95.471}
{1.720,96.597}
{1.138,96.508}
{1.942,95.391}
{2.065,95.442}
{6.379,111.988}
{6.175,111.830}
{5.921,110.250}
{6.893,124.268}
{6.931,123.338}
{6.941,128.268}
{8.488,130.241}
{8.495,130.136}
{8.278,126.991}
{7.080,140.405}
{6.849,140.226}
{7.292,148.796}
{7.088,148.669}
{6.774,164.031}
{6.668,163.491}
{5.058,163.216}
{5.057,161.927}
{2.463,124.984}
{2.139,127.340}
{2.608,132.105}
{1.243,140.377}
{0.939,140.377}
{2.464,147.067}
{1.139,157.733}
{1.720,165.095}
{2.464,164.043}
δ/ppm
δ/ppm


^{1}H NMR (C_6D_6, 500 MHz, 298 K)
Ar = 2,6-diisopropylamine
δ/ppm

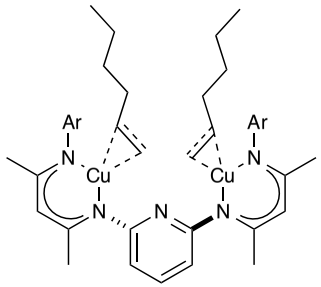

^{1}H–^{1}H COSY (C_6D_6, 500 MHz, 298 K)
Ar = 2,6-diisopropylamine
{0.730,0.997}
{0.730,1.113}
{0.920,1.695}
{1.253,1.941}
{1.137,3.218}
{1.153,3.395}
{1.239,3.387}
{1.271,4.221}
{3.090,4.222}
{3.293,4.241}
{5.021,5.770}
{6.427,7.134}
δ/ppm


NOESY (C_6D_6, 500 MHz, 298 K)
{4.212,1.041}
{4.213,1.242}
{3.387,1.159}
{3.226,1.147}
{3.212,1.787}
{3.402,1.787}
{4.225,2.059}
{5.002,1.784}
{5.001,2.069}
{4.229,3.072}
{4.222,3.290}
δ/ppm
δ/ppm
Ar = 2,6-diisopropylamine

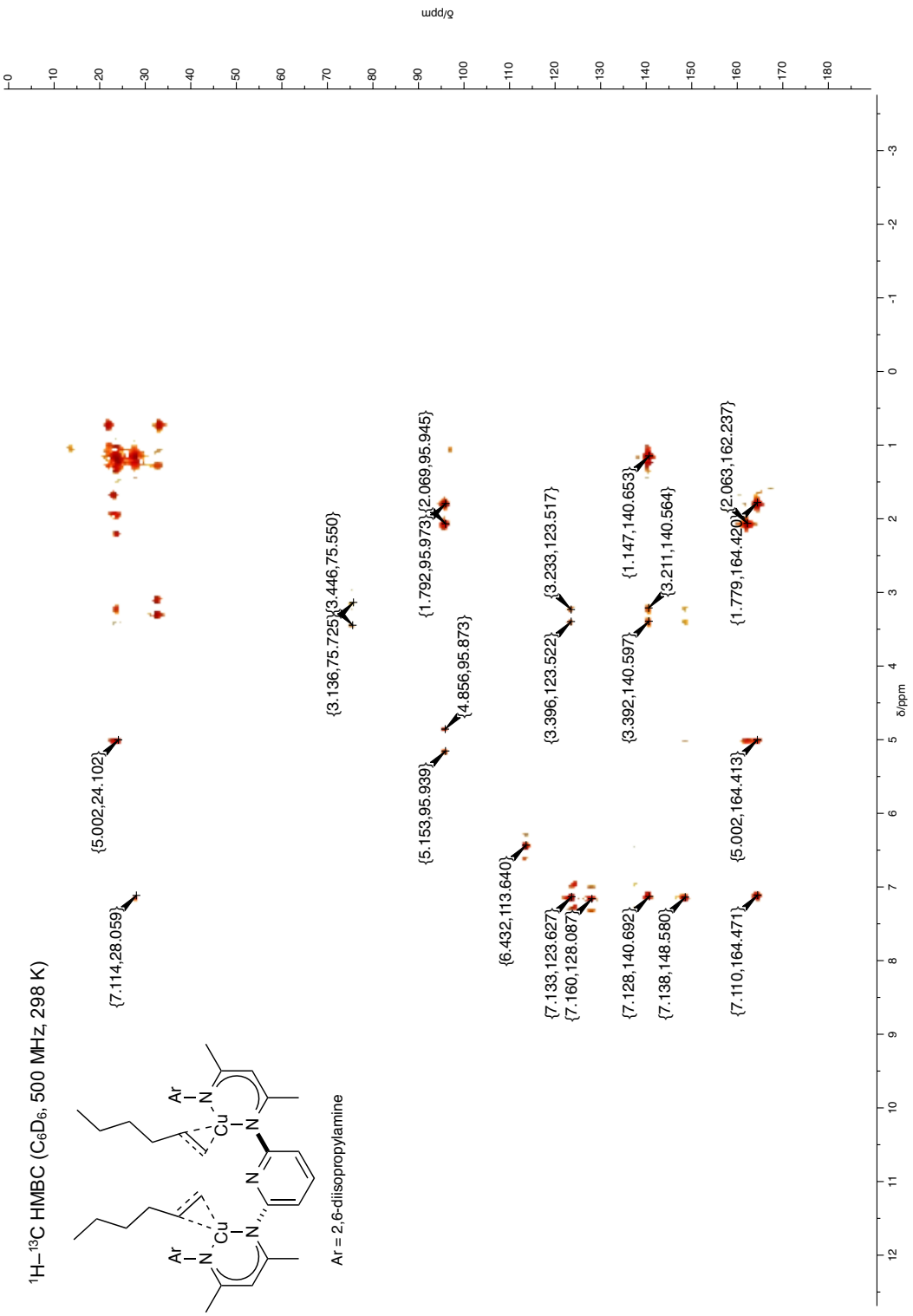

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 126 MHz, 298 K)
Ar = 2,6-diisopropylamine
Ar
N
Cu
N
N
Ar
N
Cu
N
14.074
22.322
23.496
23.909
24.029
24.162
24.439
24.561
28.056
28.189
32.877
32.900
33.322
33.377
75.677
75.722
95.967
96.082
97.130
97.319
113.670
113.737
123.699
124.637
128.353
137.846
140.549
140.591
148.688
162.245
164.444
164.479
164.517
δ/ppm

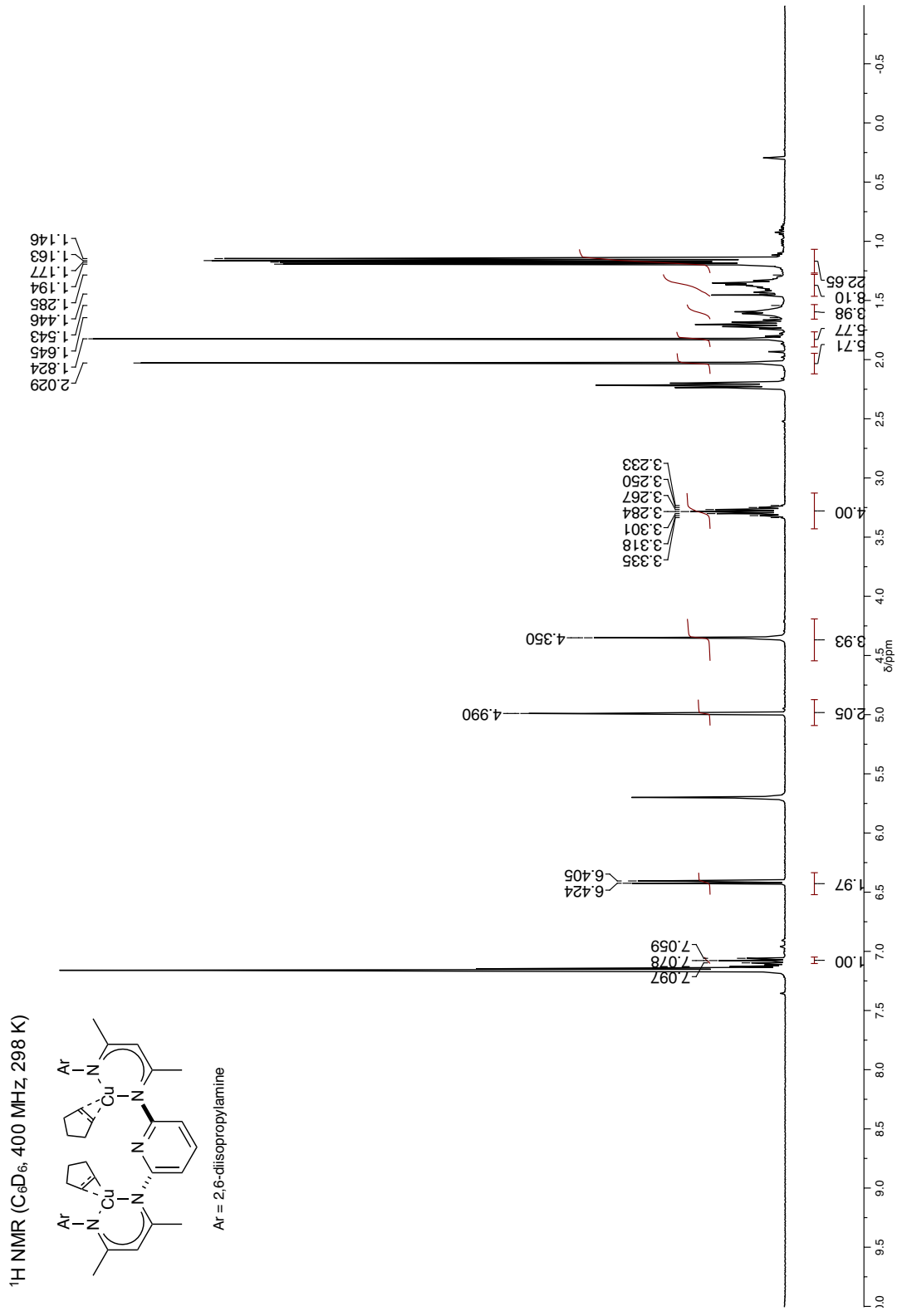

DEPT-135 (C_6D_6, 126 MHz, 298 K)
Ar = 2,6-diisopropylamine
δ/ppm

$^{1}H–^{13}C$ HSQC (C_6D_6, 500 MHz, 298 K)

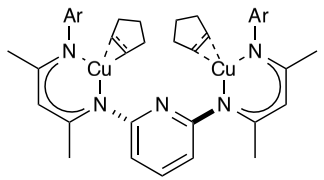


Ar = 2,6-diisopropylamine


^{1}H–^{13}C HMBC (C_6D_6, 500 MHz, 298 K)
Ar = 2,6-diisopropylamine
{7.114,28.059}
{5.002,24.102}
{3.136,75.725}{3.446,75.550}
{1.792,95.973}{2.069,95.945}
{4.856,95.873}
{5.153,95.939}
{6.432,113.640}
{3.396,123.522}
{3.233,123.517}
{7.133,123.627}
{7.160,128.087}
{3.392,140.597}
{1.147,140.653}
{3.211,140.564}
{7.128,140.692}
{7.138,148.580}
{5.002,164.413}
{1.779,164.420}
{2.063,162.237}
{7.110,164.471}
δ/ppm
δ/ppm

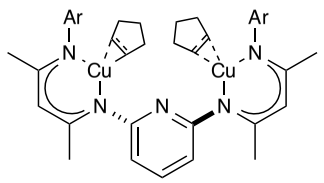

^{1}H NMR (C_6D_6, 400 MHz, 298 K)
Ar = 2,6-diisopropylamine
7.097
7.078
7.059
6.424
6.405
4.990
4.350
3.335
3.318
3.301
3.284
3.267
3.250
3.233
2.029
1.824
1.645
1.543
1.446
1.285
1.194
1.177
1.163
1.146
1.00
1.97
2.05
3.93
4.00
5.71
5.77
3.98
3.10
22.65
δ/ppm

$^{1}H–^{1}H$ COSY (C_6D_6, 400 MHz, 298 K)



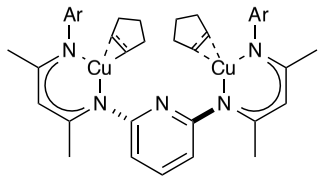
Ar = 2,6-diisopropylamine

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 101 MHz, 298 K)

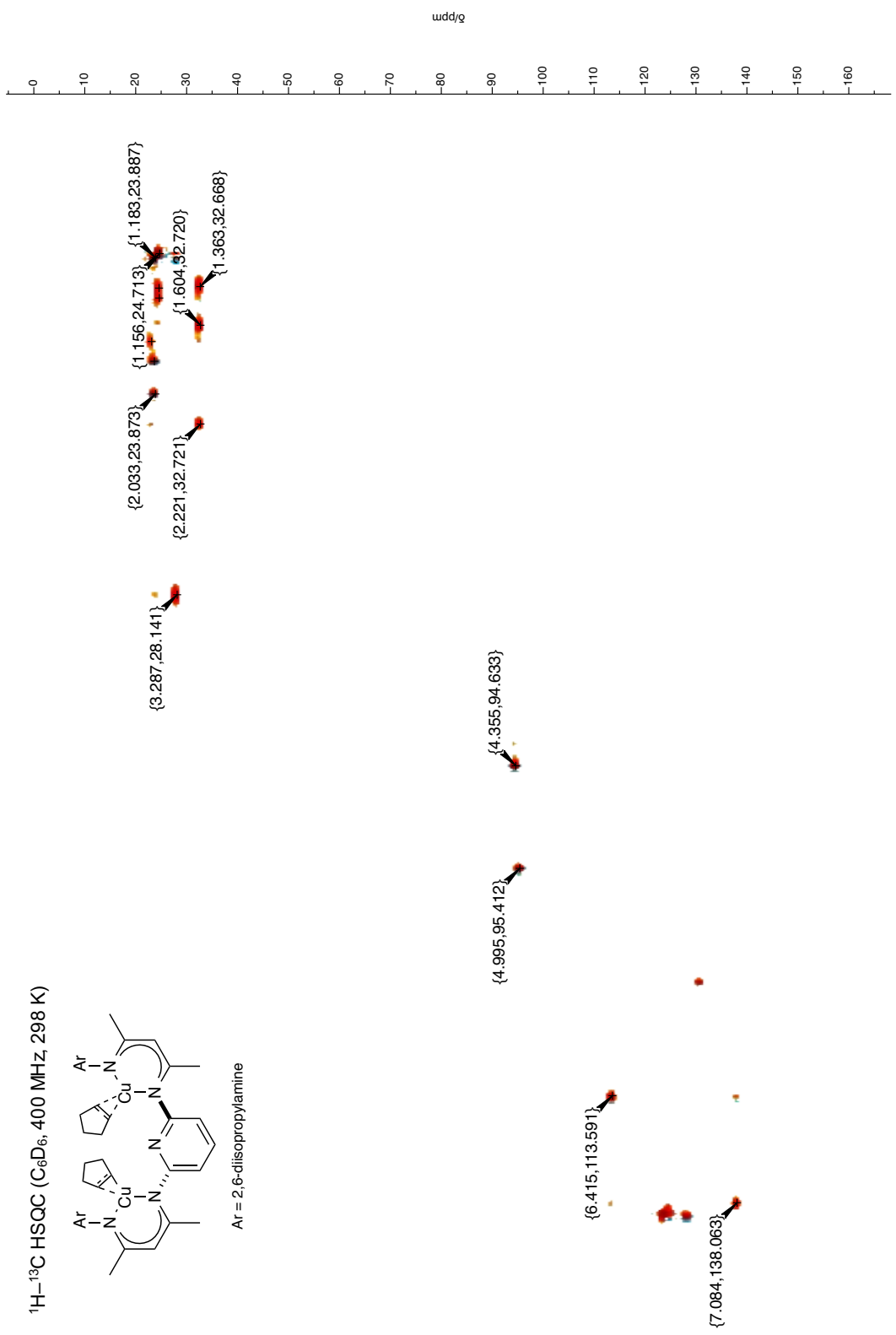


Ar = 2,6-diisopropylamine

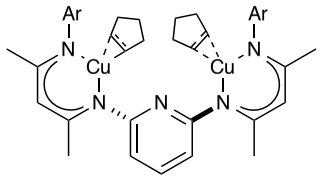
DEPT-135 (C_6D_6, 101 MHz, 298 K)



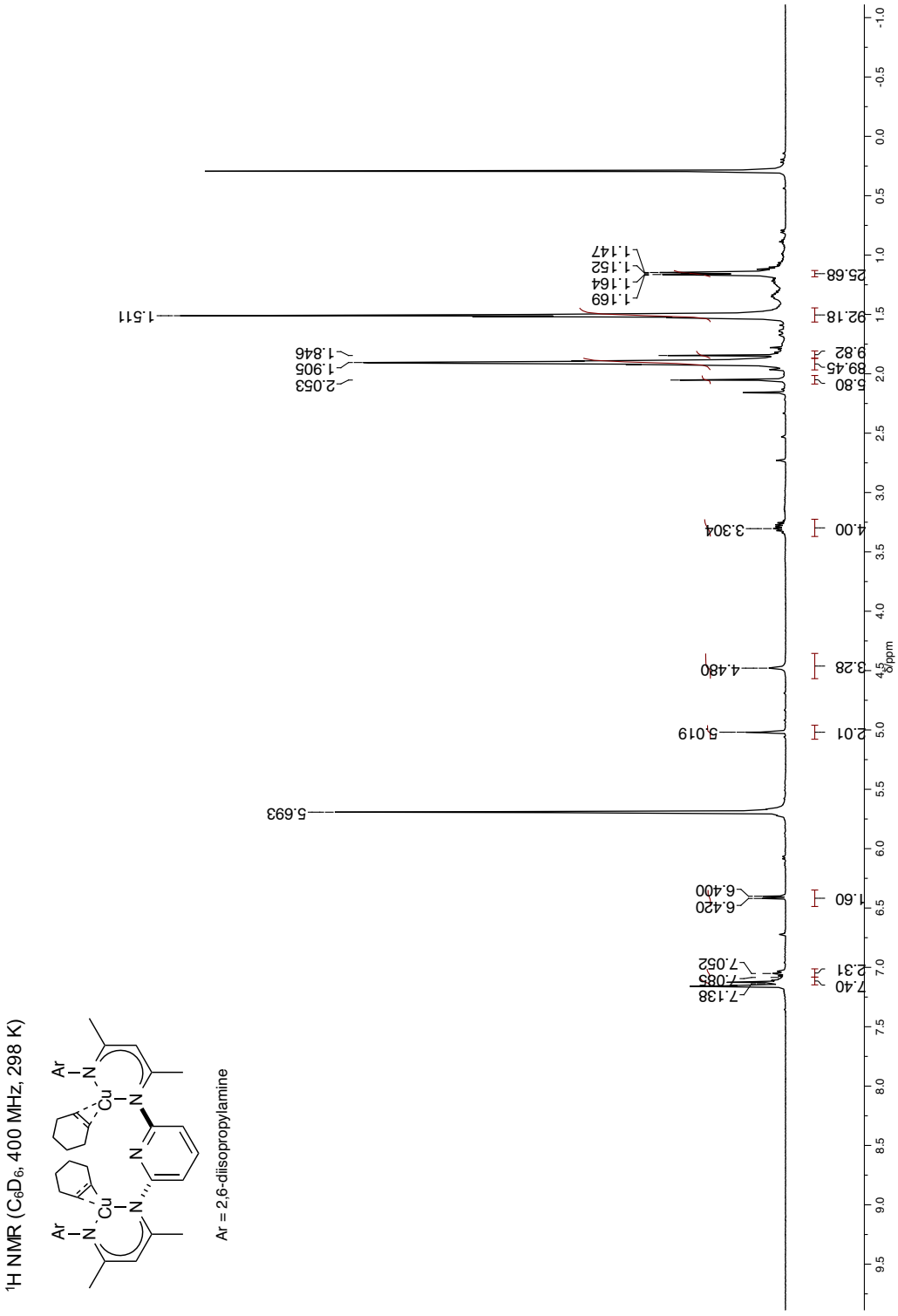
Ar = 2,6-diisopropylamine


^{1}H–^{13}C HSQC (C_6D_6, 400 MHz, 298 K)
Ar = 2,6-diisopropylamine
{1.183,23.887}
{1.156,24.713}
{1.604,32.720}
{1.363,32.668}
{2.033,23.873}
{2.221,32.721}
{3.287,28.141}
{4.355,94.633}
{4.995,95.412}
{6.415,113.591}
{7.084,138.063}
δ/ppm
δ/ppm

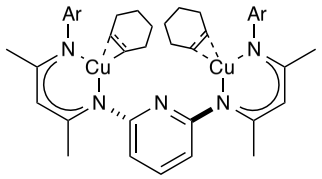
$^{1}H–^{13}C$ HMBC (C_6D_6, 400 MHz, 298 K)



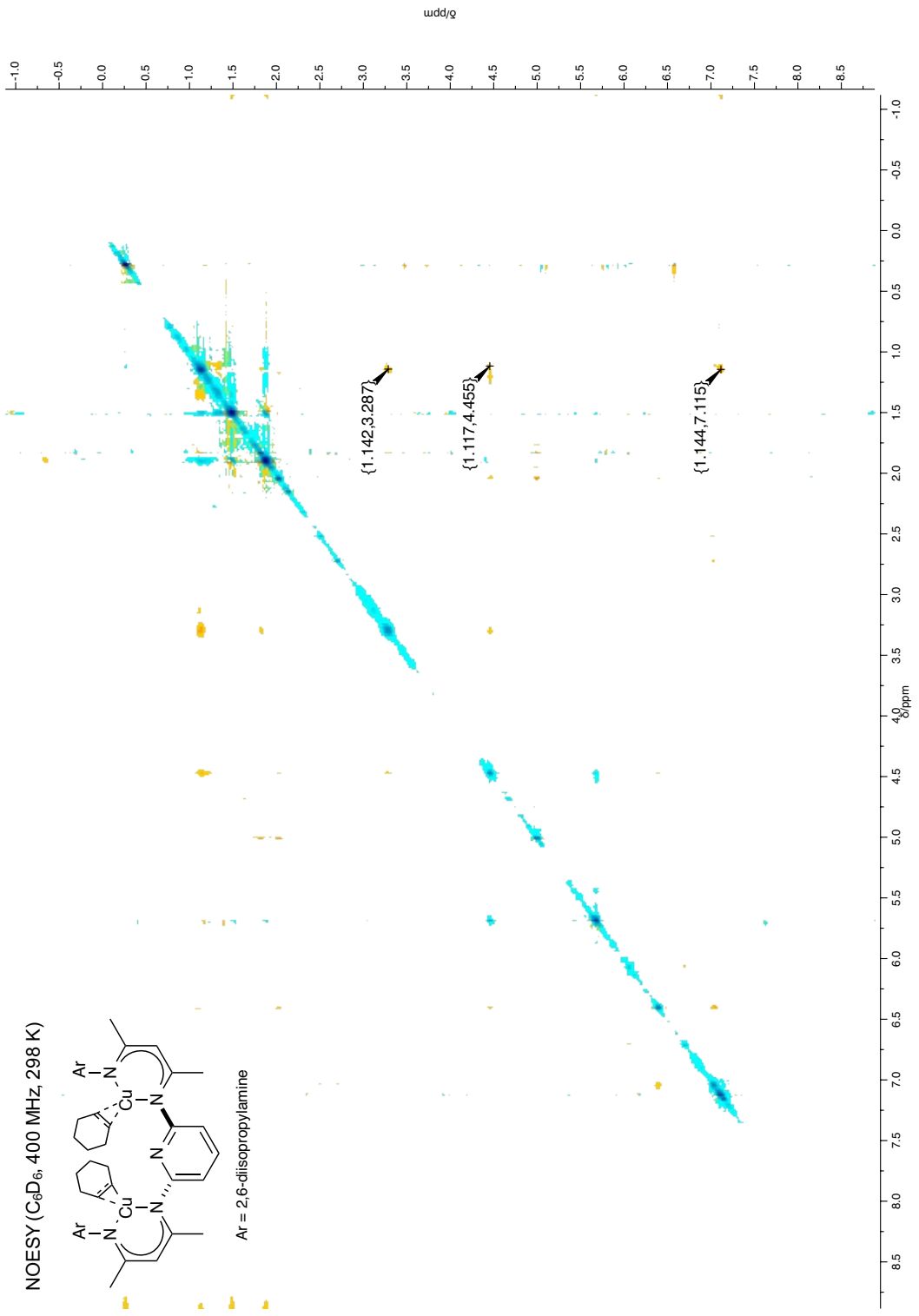
Ar = 2,6-diisopropylamine

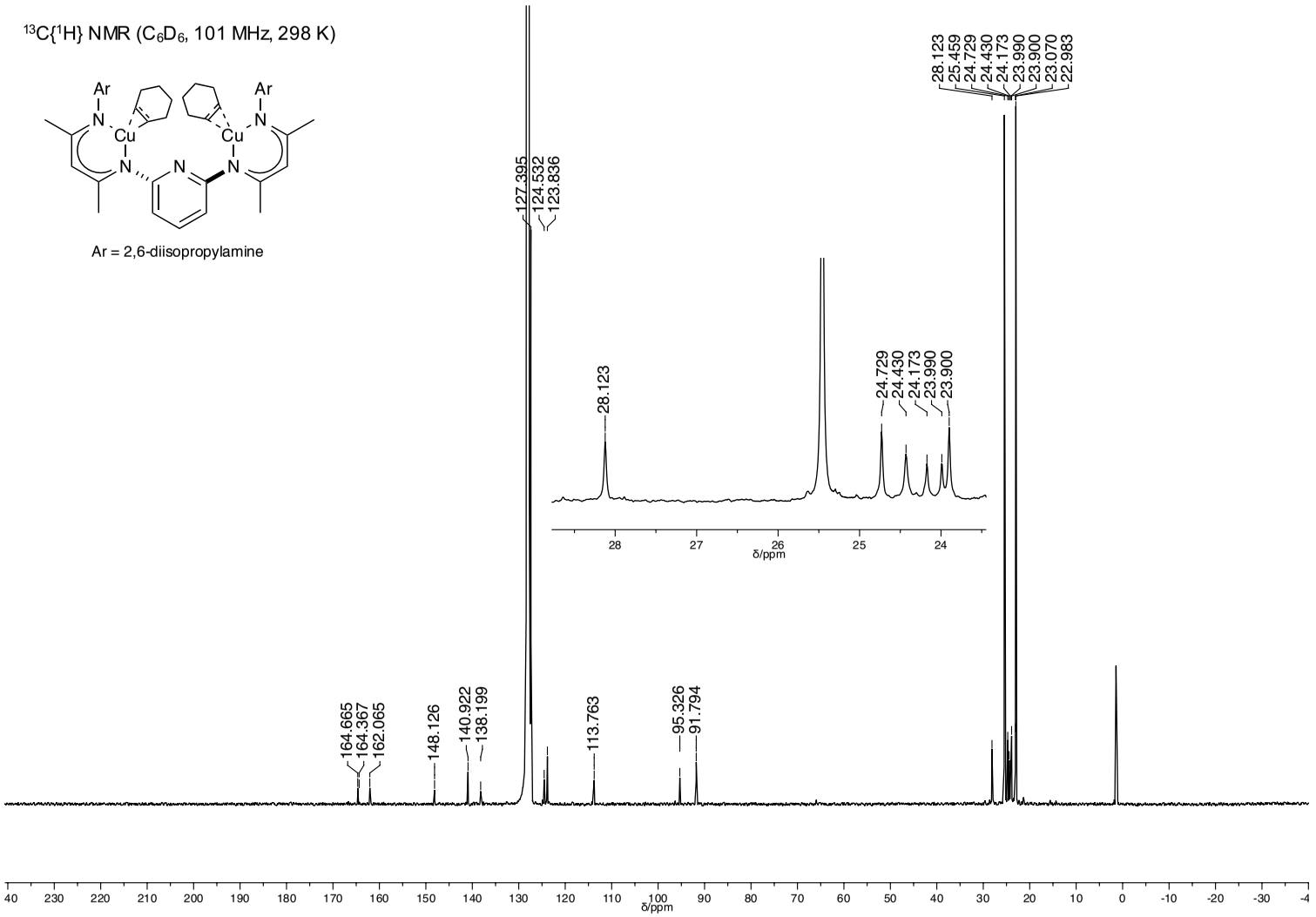

^{1}H NMR (C_6D_6, 400 MHz, 298 K)
Ar = 2,6-diisopropylamine
7.138
7.085
7.052
6.420
6.400
5.693
5.019
4.480
3.304
2.053
1.905
1.846
1.511
1.169
1.164
1.152
1.147
7.40
2.31
1.60
2.01
3.28
4.00
5.80
9.82
89.45
92.18
25.68
ppm

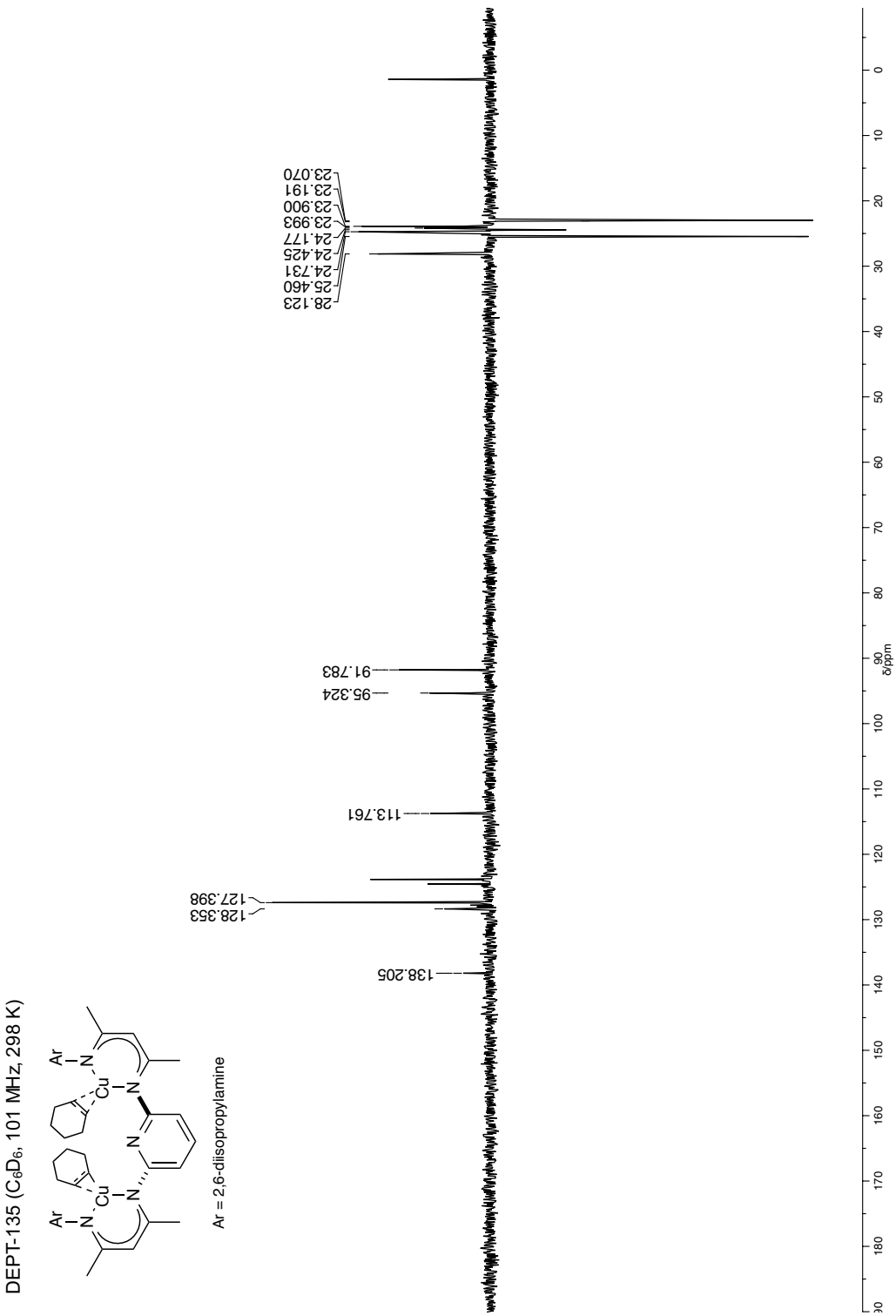
$^{1}H–^{1}H$ COSY (C_6D_6, 400 MHz, 298 K)



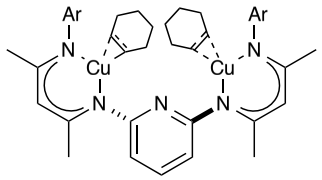
Ar = 2,6-diisopropylamine


NOESY (C_6D_6, 400 MHz, 298 K)
Ar = 2,6-diisopropylamine
{1.142,3.287}
{1.117,4.455}
{1.144,7.115}
δ/ppm

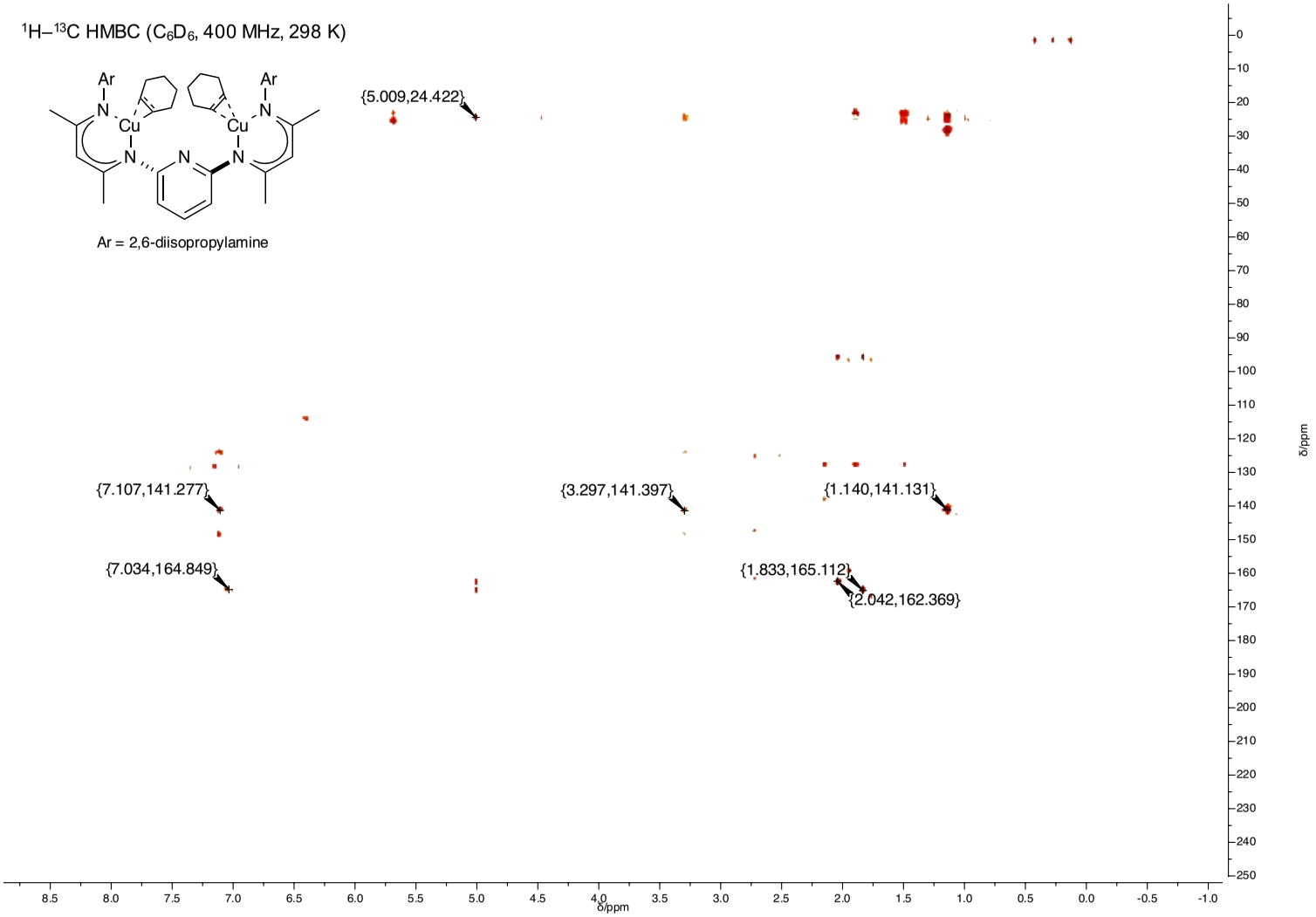

13C{1H} NMR (C6D6, 101 MHz, 298 K)
Ar = 2,6-diisopropylamine
28.123
25.459
24.729
24.430
24.173
23.990
23.900
23.070
22.983
127.395
124.532
123.836
164.665
164.367
162.065
148.126
140.922
138.199
113.763
95.326
91.794
δ/ppm

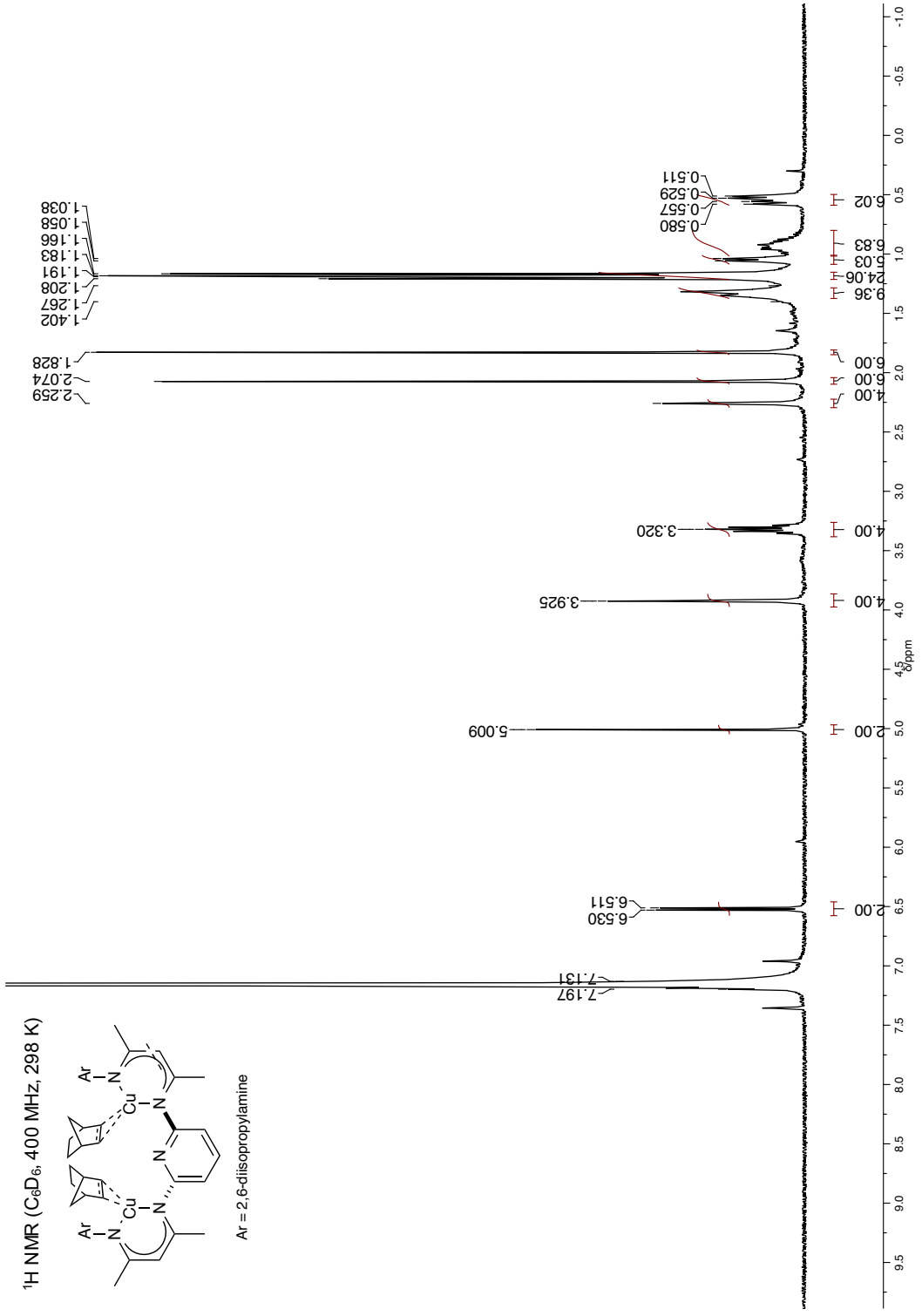

DEPT-135 (C_6D_6, 101 MHz, 298 K)
Ar = 2,6-diisopropylamine
138.205
128.353
127.398
113.761
95.324
91.783
28.123
25.460
24.731
24.425
24.177
23.993
23.900
23.191
23.070
δ/ppm

$^{1}H-^{13}C$ HSQC (C_6D_6, 400 MHz, 298 K)

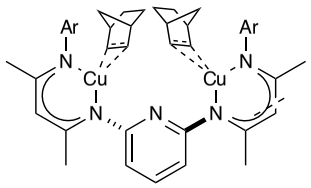


Ar = 2,6-diisopropylamine


^{1}H–^{13}C HMBC (C_6D_6, 400 MHz, 298 K)
Ar
N
Cu
Cu
N
N
N
Ar
Ar = 2,6-diisopropylamine
{5.009,24.422}
{7.107,141.277}
{7.034,164.849}
{3.297,141.397}
{1.140,141.131}
{1.833,165.112}
{2.042,162.369}
δ/ppm
δ/ppm

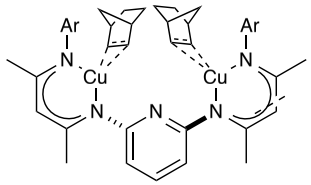

^{1}H NMR (C_6D_6, 400 MHz, 298 K)
Ar = 2,6-diisopropylamine
7.197
7.131
6.530
6.511
5.009
3.925
3.320
2.259
2.074
1.828
1.402
1.267
1.208
1.191
1.183
1.166
1.058
1.038
0.580
0.557
0.529
0.511
2.00
2.00
4.00
4.00
2.00
6.00
6.00
4.00
9.36
24.06
5.03
6.83
6.02
δ/ppm

$^{1}H–^{1}H$ COSY (C_6D_6, 400 MHz, 298 K)



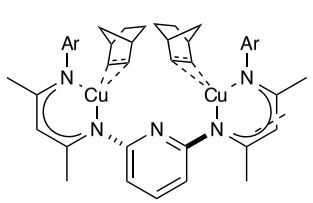
Ar = 2,6-diisopropylamine

$^{13}C\{^{1}H\}$ NMR (C_6D_6, 101 MHz, 298 K)



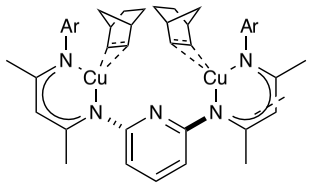
Ar = 2,6-diisopropylamine

DEPT-135 (C_6D_6, 101 MHz, 298 K)



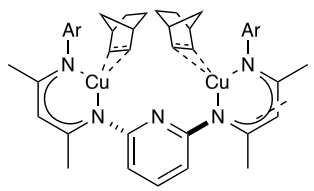
Ar = 2,6-diisopropylamine

$^{1}H–^{13}C$ HSQC (C_6D_6, 400 MHz, 298 K)



Ar = 2,6-diisopropylamine

$^{1}H–^{13}C$ HMBC (C_6D_6, 400 MHz, 298 K)



Ar = 2,6-diisopropylamine