Supporting information for:

Isolation of un Unusual [Cu_6] Nanocluster through Sequential Addition of Copper(I) to a Polynucleating Ligand

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General Experimental

All manipulations were carried out using standard Schlenk-line and glovebox techniques under an inert atmosphere of argon or dinitogen. A MBraun Labmaster glovebox was employed, operating at < 0.1 ppm O_2 and < 0.1 ppm H_2O. Solvents were dried over activated alumina from an SPS (solvent purification system) based upon the Grubbs design and degassed before use. Glassware was dried for 12 h at 120 °C prior to use. Benzene-d_6 and toluene-d_8 were stored over molecular sieves and distilled prior to use. NMR-scale reactions were conducted in J. Young's tap tubes and prepared in a glovebox. All heating mentioned was done using silicone oil baths. ^{1}H, and ^{13}C, NMR spectra were obtained on BRUKER 400 MHz or 500 MHz machines unless otherwise stated; all peak intensities are derived internal standard peak with values quoted in ppm. Data was processed using the MestReNova or Topsin software.

Chemicals were purchased from Fluorochem, Sigma Aldrich or Alfa Aeser and used without purification unless stated..

Synthesis of $[Cu_2L]_2$: In a glovebox, a suspension of **LH_2** (400 mg, 0.68 mmol) in toluene (3 mL) was added to CuMes (296 mg, 1.62 mmol, 2.4 equiv.) in a Schlenk flask. Additional toluene (17 mL) was added and the resultant suspension stirred at 80 °C for 54 h. The mixture was filtered *via* cannula and the solvent removed *in vacuo* to afford a bright red powder (350 mg, 0.24 mmol, 72%). Crystals suitable for X ray diffraction were grown by cooling a concentrated diethyl ether solution to 5 °C overnight.

^{1}H NMR (C_6D_6, 400 MHz) δ: 0.90 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 0.99 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.22 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.24 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.30 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.33 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.44 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.47 (d, 3H, $^3J_{HH}$ = 7.0 Hz, CH_3^{iPr}), 1.60 (s, 3H, CH_3^{NacNac}), 1.64 (s, 3H, CH_3^{NacNac}), 1.68 (s, 3H, CH_3^{NacNac}), 1.88 (s, 3H, CH_3^{NacNac}), 2.99 (hept, 1H, $^3J_{HH}$ = 7.0, CH^{iPr}), 3.28 (hept, 1H, $^3J_{HH}$ = 7.0, CH^{iPr}), 3.36 (hept, 1H, $^3J_{HH}$ = 7.0, CH^{iPr}), 3.58 (hept, 1H, $^3J_{HH}$ = 7.0, CH^{iPr}), 4.69 (s, 1H, CH^{NacNac}), 4.92 (s, 1H, CH^{NacNac}), 5.74 (d, 1H, $^3J_{HH}$ = 7.0, $CH^{m\,py}$), 5.82 (d, 1H, $^3J_{HH}$ = 7.0, $CH^{m\,py}$), 6.14 (t, 1H $^3J_{HH}$ = 7.0, $CH^{p\,py}$), 7.09–7.14 (m, 3H, CH^{Dipp}), 7.18–7.22 (m, 3H, CH^{Dipp}).

$^{13}C\{^1H\}$ NMR (C_6D_6, 101 MHz) δ: 23.4 (s, CH_3^{iPr}), 23.5 (s, CH_3^{iPr}), 23.9 (s, CH_3^{NacNac}), 24.0 (s, CH_3^{NacNac}), 24.2 (s, CH_3^{iPr}), 24.4 (s, CH_3^{iPr}), 24.5 (s, CH_3^{NacNac}), 24.6 (s, CH_3^{iPr}), 24.8 (s, CH_3^{NacNac}), 24.8 (s, CH_3^{iPr}), 24.9 (s, CH_3^{iPr}), 27.9 (s, CH^{iPr}), 28.0 (s, CH^{iPr}), 28.5 (s, CH^{iPr}), 28.7 (s, CH^{iPr}), 86.0 (s, $CH^{m\,py}$), 97.4 (s, CH^{NacNac}), 101.4 (s, $CH^{m\,py}$), 102.1 (s, CH^{NacNac}), 111.7 (s, $CH^{p\,py}$), 123.5 (s, C^{NacNac}), 124.0 (s, C^{NacNac}), 124.3 (s, C^{NacNac}), 124.8 (s, C^{NacNac}), 136.6 (s, $C^{Dipp/py}$), 136.3 (s, $C^{Dipp/py}$), 139.8 (s, $C^{Dipp/py}$), 139.9 (s, $C^{Dipp/py}$), 140.1 (s, $C^{Dipp/py}$), 140.5 (s, $C^{Dipp/py}$), 146.8 (s, $C^{Dipp/py}$), 149.2 (s, $C^{Dipp/py}$), 157.5 (s, $C^{Dipp/py}$), 160.4 (s, $C^{Dipp/py}$), 162.5 (s, $C^{Dipp/py}$), 162.8 (s, $C^{Dipp/py}$), 165.3 (s, $C^{Dipp/py}$), 167.6 (s, $C^{Dipp/py}$).

FT-IR (v/cm^{-1}): C–H stretches: 2959, 2924, 2866; pyridine stretches: 1568, 1508; others: 1455, 1431, 1412, 1365, 1317, 1263, 1219, 1183.

HRMS (ES): *m/z* calcd. for $C_{78}H_{102}N_{10}{}^{63}Cu_3{}^{65}Cu$ ($[M]^+$) 1432.5455, found 1432.5446.

Ligand, **L**: D_{ave} = 6.51 x 10^{-10} m^2 s^{-1} (using $\eta_{C6D6,298}$ = 6.392 x 10^{-4} m^{-1} kg s^{-1}), $\underline{r_s = 5.25\ Å}$
Cluster $[Cu_2L]_2$: D_{ave} = 4.80 x 10^{-10} m^2 s^{-1} (using $\eta_{C6D6,298}$ = 6.392 x 10^{-4} m^{-1} kg s^{-1}), $\underline{r_s = 7.11\ Å}$

λ_{max} = 377 nm (ε = 16400 M^{-1} cm^{-1}) with a shoulder at 435 nm; λ = 286 nm (ε = 16200 M^{-1} cm^{-1}).

Synthesis of [LCu$_3$I]$_2$: In a glovebox, [Cu$_2$L]$_2$ (129.2 mg, 0.0901 mmol) and CuI (42.9 mg, 0.225 mmol, 2.5 equiv.) were mixed in toluene (15 mL) in an ampoule. The mixture was heated to 80 °C for 22 h. The solution was filtered *via* a glass microfilter and the solvent removed from the resultant dark orange solution and the resultant powder was washed with pentane (6 x 1 mL) and dried *in vacuo*. The product is obtained as an analytically pure orange powder (124.7 mg, 0.0803 mmol, 89%). Crystals suitable for Xray diffraction were grown froma diethyl ether solution at –35 °C overnight.

^{1}H NMR (C$_6$D$_6$, 400 MHz) δ: 0.84 (d, $^3J_{HH}$ = 6.9 Hz, 3H, CH$_3^{iPr}$), 0.88 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_3^{iPr}$), 0.98 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_3^{iPr}$), 1.17 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_3^{iPr}$), 1.24 (d, $^3J_{HH}$ = 7.0 Hz, 3H, CH$_3^{iPr}$), 1.26 (d, $^3J_{HH}$ = 6.8 Hz, 3H, CH$_3^{iPr}$), 1.37 (d, $^3J_{HH}$ = 5.3 Hz, 3H, CH$_3^{iPr}$), 1.39 (d, $^3J_{HH}$ = 5.4 Hz, 3H, CH$_3^{iPr}$), 1.46 (s, 3H, CH$_3^{NacNac}$), 1.70 (s, 3H, CH$_3^{NacNac}$), 1.87 (s, 3H, CH$_3^{NacNac}$), 2.28 (hept, $^3J_{HH}$ = 6.7 Hz, 1H, CH^{iPr}), 2.39 (s, 3H, CH$_3^{NacNac}$), 2.96 (hept, $^3J_{HH}$ = 7.0 Hz, 1H, CH^{iPr}), 3.22 (hept, $^3J_{HH}$ = 7.0 Hz, 1H, CH^{iPr}), 3.81 (hept, $^3J_{HH}$ = 7.0 Hz, 1H, CH^{iPr}), 4.88 (s, 1H, CH^{NacNac}), 5.71 (d, $^3J_{HH}$ = 7.6 Hz, 1H, CH$^{m\text{-py}}$), 5.73 (s, 1H, CH^{NacNac}), 5.81 (d, $^3J_{HH}$ = 8.2 Hz, 1H, CH$^{m\text{-py}}$), 6.89–7.14 (m, 6H, CH$^{Dipp/p\text{-py}}$), 7.25 (dd, $^3J_{HH}$ = 1.8 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, CH$^{p\text{-Dipp}}$).

^{13}C{^{1}H} NMR (C$_6$D$_6$, 101 MHz) δ: 23.5 (s, CH$_3^{iPr}$), 23.6 (s, CH$_3^{NacNac}$), 23.9 (s, CH$_3^{iPr}$), 24.1 (s, CH$_3^{NacNac}$), 24.4 (s, CH$_3^{NacNac}$), 25.0 (s, CH$_3^{iPr}$), 25.1 (s, CH$_3^{iPr}$), 25.6 (s, CH$_3^{iPr}$), 25.9 (s, CH$_3^{iPr}$), 26.1 (s, CH$_3^{iPr}$), 26.1 (s, CH$_3^{iPr}$), 26.5 (s, CH$_3^{NacNac}$), 27.6 (s, CH^{iPr}), 27.9 (s, CH^{iPr}), 28.0 (s, CH^{iPr}), 28.2 (s, CH^{iPr}), 99.3 (s, CH^{NacNac}), 100.2 (S, CH$^{m\text{-py}}$), 104.3 (s, CH$^{m\text{-py}}$), 118.0 (s, CH^{NacNac}), 123.6 (s, CH^{Dipp}), 123.7 (s, CH^{Dipp}), 123.7 (s, CH^{Dipp}), 123.9 (s, CH^{Dipp}), 124.7 (s, CH^{Dipp}), 125.9 (s, CH^{Dipp}), 138.6 (s, C$^{m\text{-Dipp}}$), 139.0 (s, C$^{m\text{-Dipp}}$), 139.6 (s, CH$^{p\text{-py}}$), 139.8 (s, C$^{m\text{-Dipp}}$), 140.6 (s, C$^{m\text{-Dipp}}$), 144.8 (s, C$^{ipso\text{-Dipp}}$), 147.9 (s, C$^{ipso\text{-Dipp}}$), 158.1 (s, C^{NacNac}), 158.7 (s, C^{NacNac}), 161.1 (s, C$^{o\text{-py}}$), 163.5 (s, C$^{o\text{-py}}$), 166.6 (s, C^{NacNac}), 169.6 (s, C^{NacNac}).

FT-IR (v/cm^{-1}): C–H stretches: 2960, 2866; pyridine stretches: 1568, 1545, 1508; others: 1431, 1405, 1382, 1362, 1318, 1272, 1224, 1155.

Anal. calcd. for $C_{78}H_{102}Cu_6I_2N_{10}$ (found): C, 51.62 (51.70); H, 5.67 (5.49); N, 7.72 (7.81). MS (ES): *m/z* found 1815.3 ([M+H]$^+$).

Ligand, **L**: D_{ave} = 6.51 x 10^{-10} m^2 s^{-1} (using $\eta_{C6D6,298}$ = 6.392 x 10^{-4} m^{-1} kg s^{-1}), r_s = 5.25 Å.
Cluster [LCu$_3$I]$_2$: D_{ave} = 5.43 x 10^{-10} m^2 s^{-1} (using $\eta_{C6D6,298}$ = 6.392 x 10^{-4} m^{-1} kg s^{-1}), r_s = 6.29 Å.

λ_{max} = 258 nm (ε = 37000 M^{-1} cm^{-1}); λ = 421 nm (ε = 18900 M^{-1} cm^{-1}).

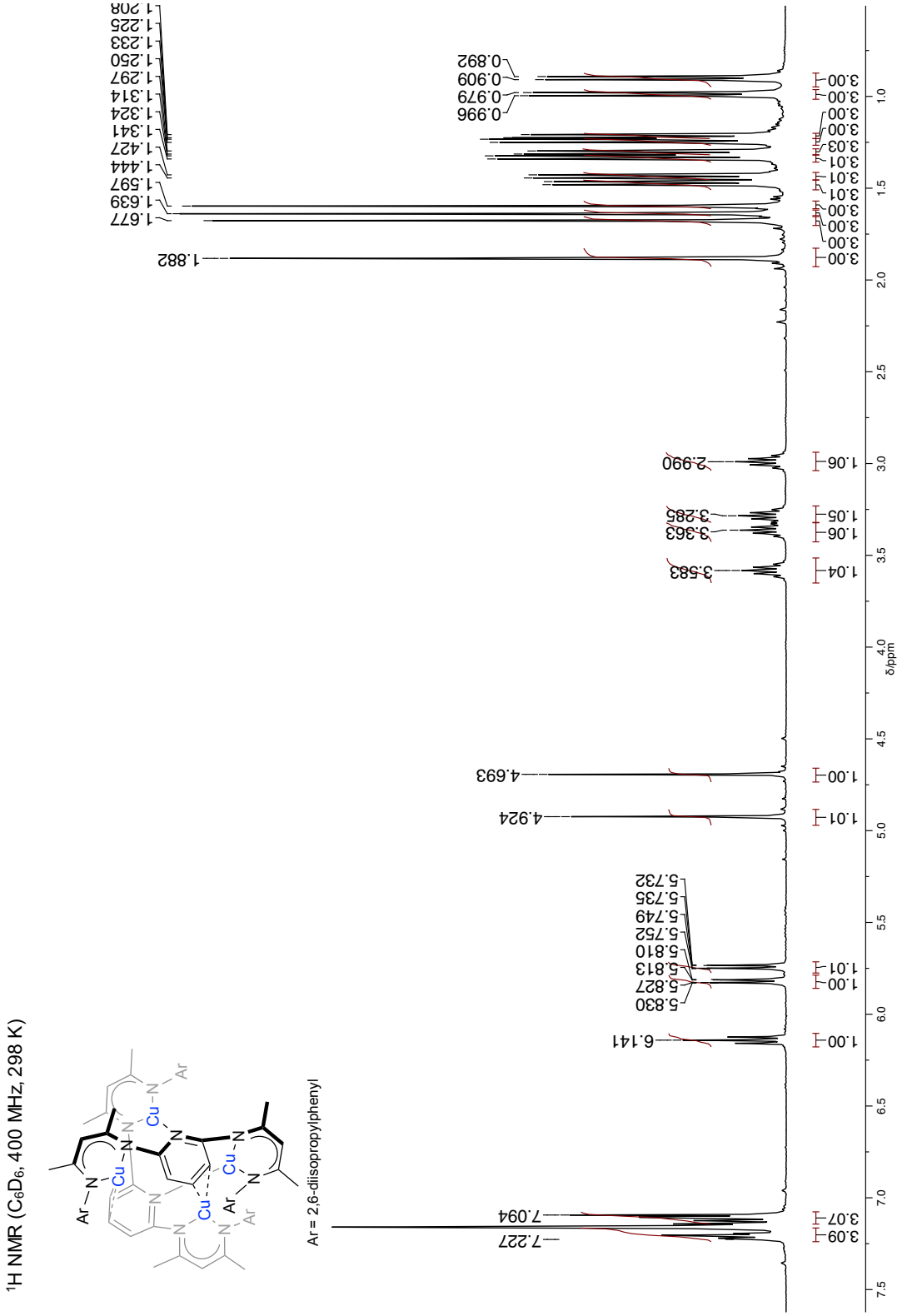

Figure S1. ^{1}H NMR spectrum $[Cu_2L]_2$ (C_6D_6, 400 MHz, 298 K)

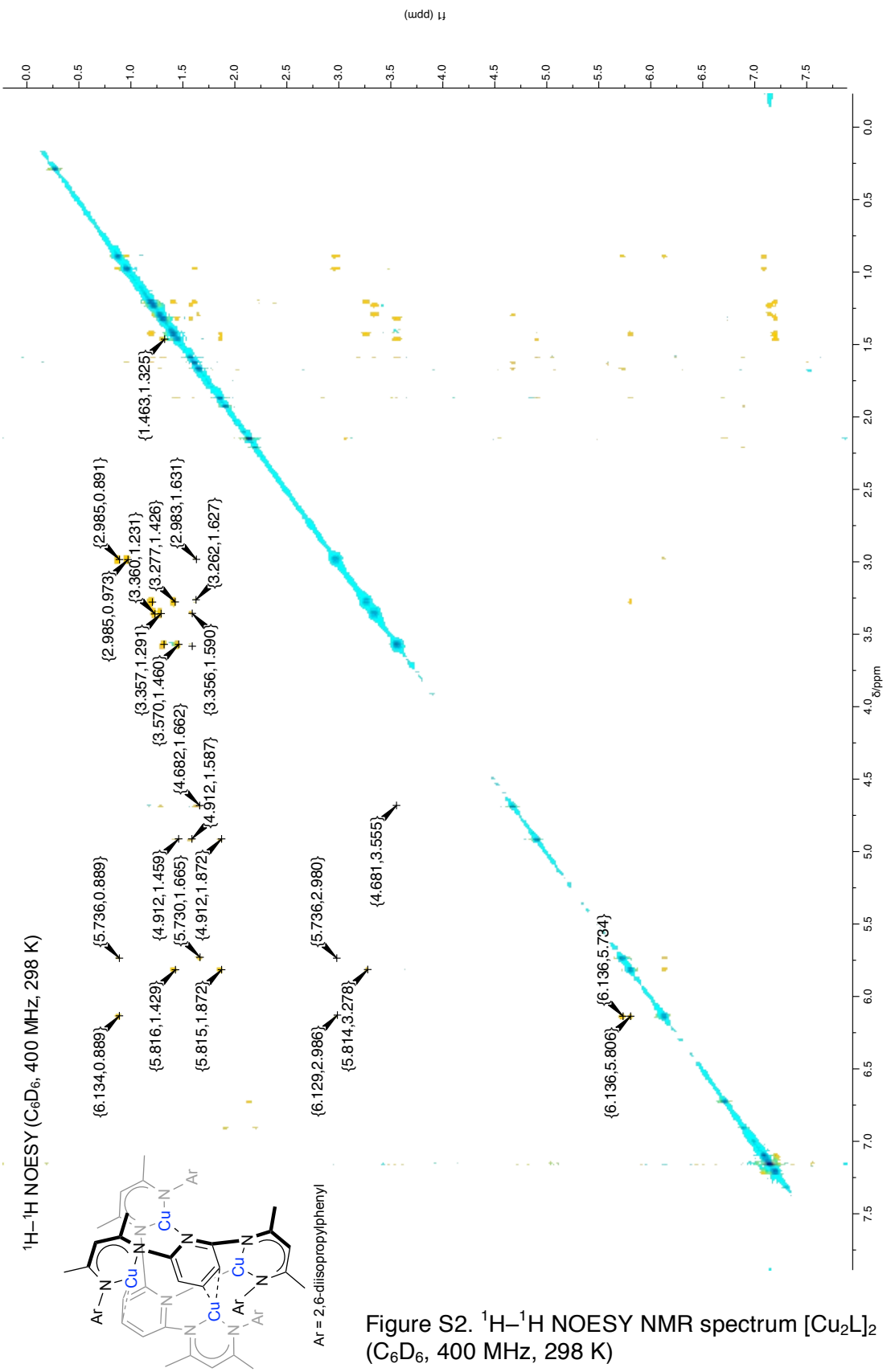

Figure S2. ^{1}H–^{1}H NOESY NMR spectrum $[Cu_2L]_2$ (C_6D_6, 400 MHz, 298 K)

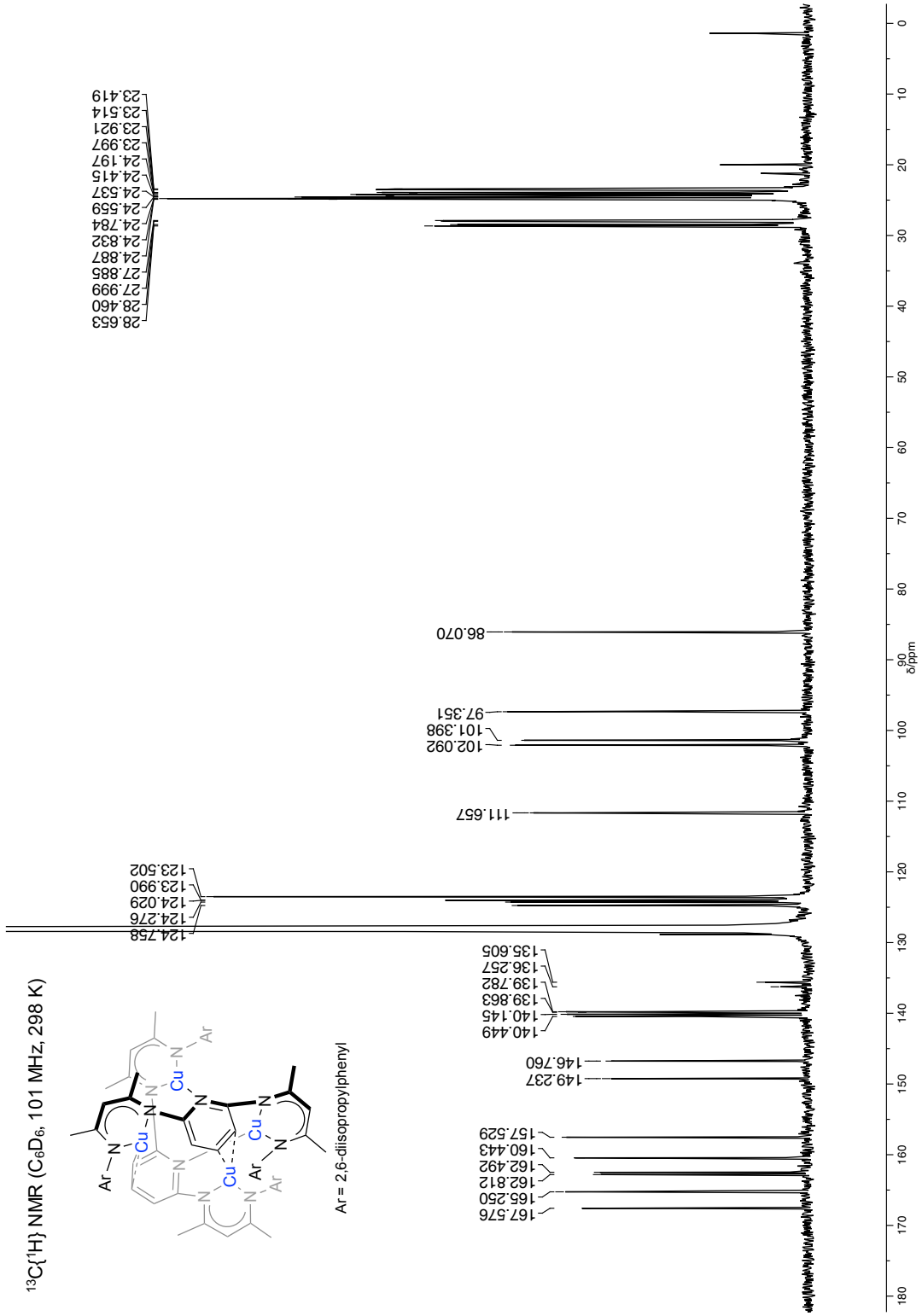

Figure S3. $^{13}C\{^{1}H\}$ NMR spectrum $[Cu_2L]_2$ (C_6D_6, 101 MHz, 298 K)

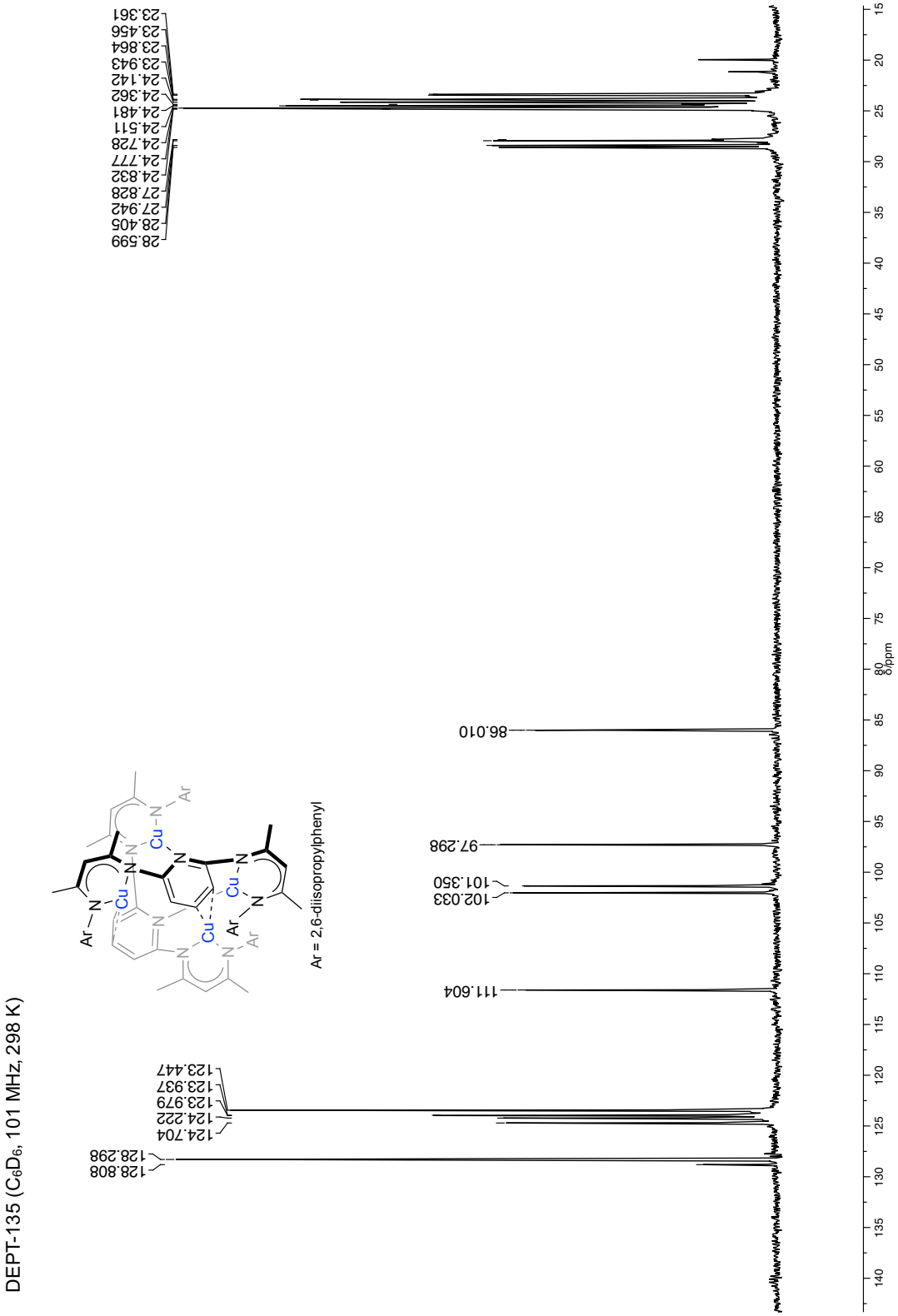

Figure S4. DEPT-135 NMR spectrum $[Cu_2L]_2$ (C_6D_6, 101 MHz, 298 K)

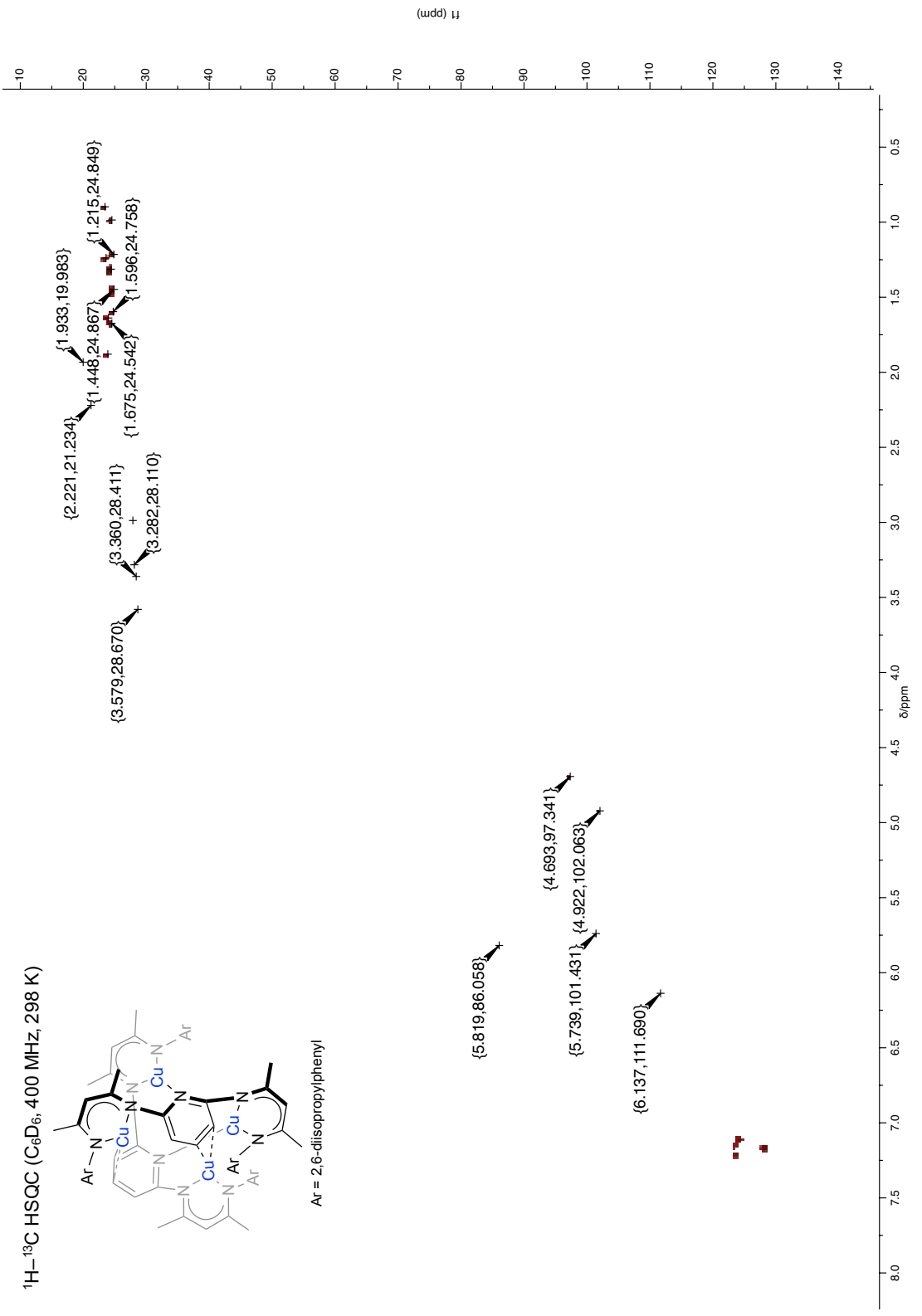

Figure S5. ^{1}H–^{13}C HSQC NMR spectrum $[Cu_2L]_2$ (C_6D_6, 400 MHz, 298 K)

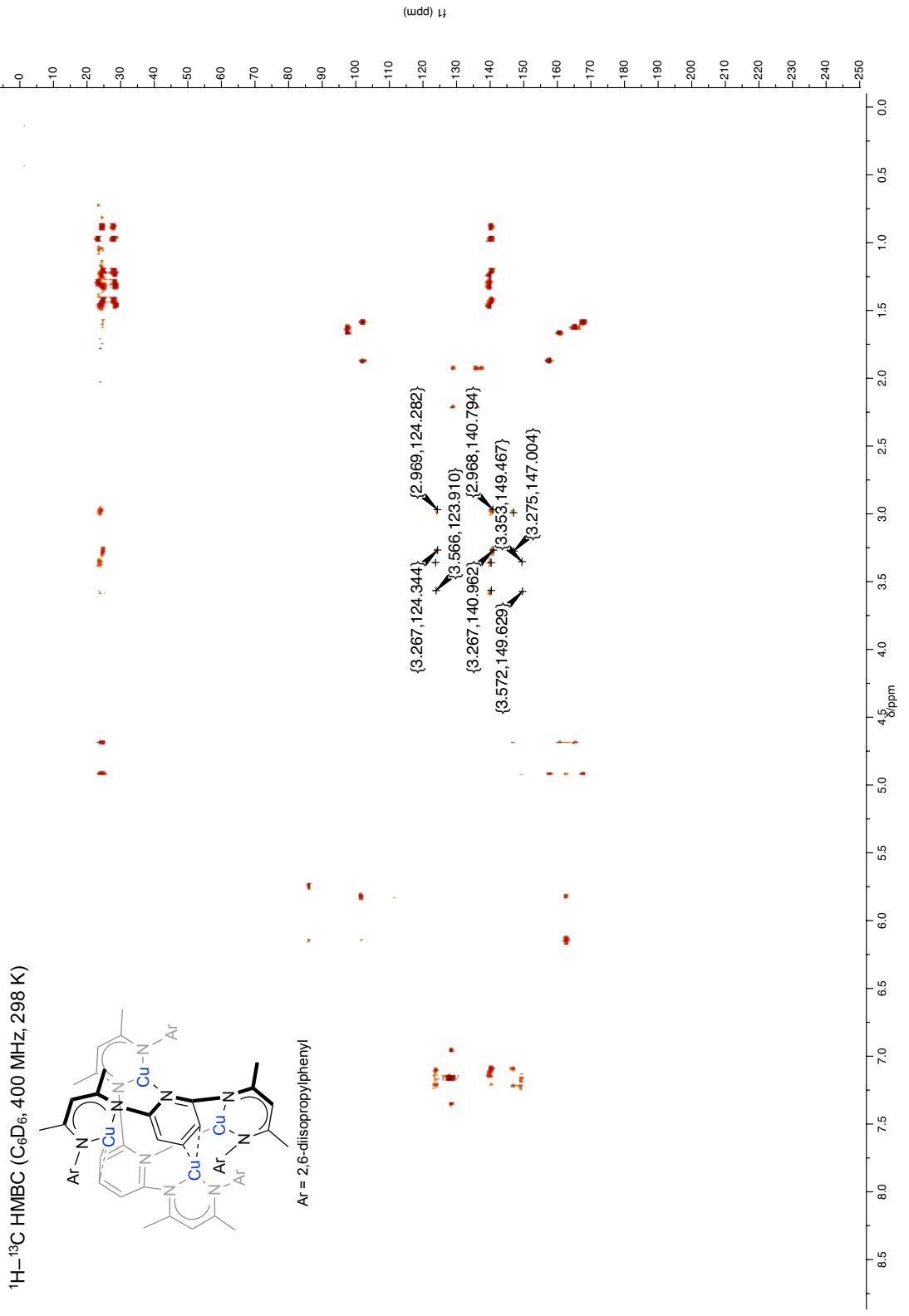

Figure S6. $^{1}H–^{13}C$ HMBC NMR spectrum $[Cu_2L]_2$ (C_6D_6, 400 MHz, 298 K)

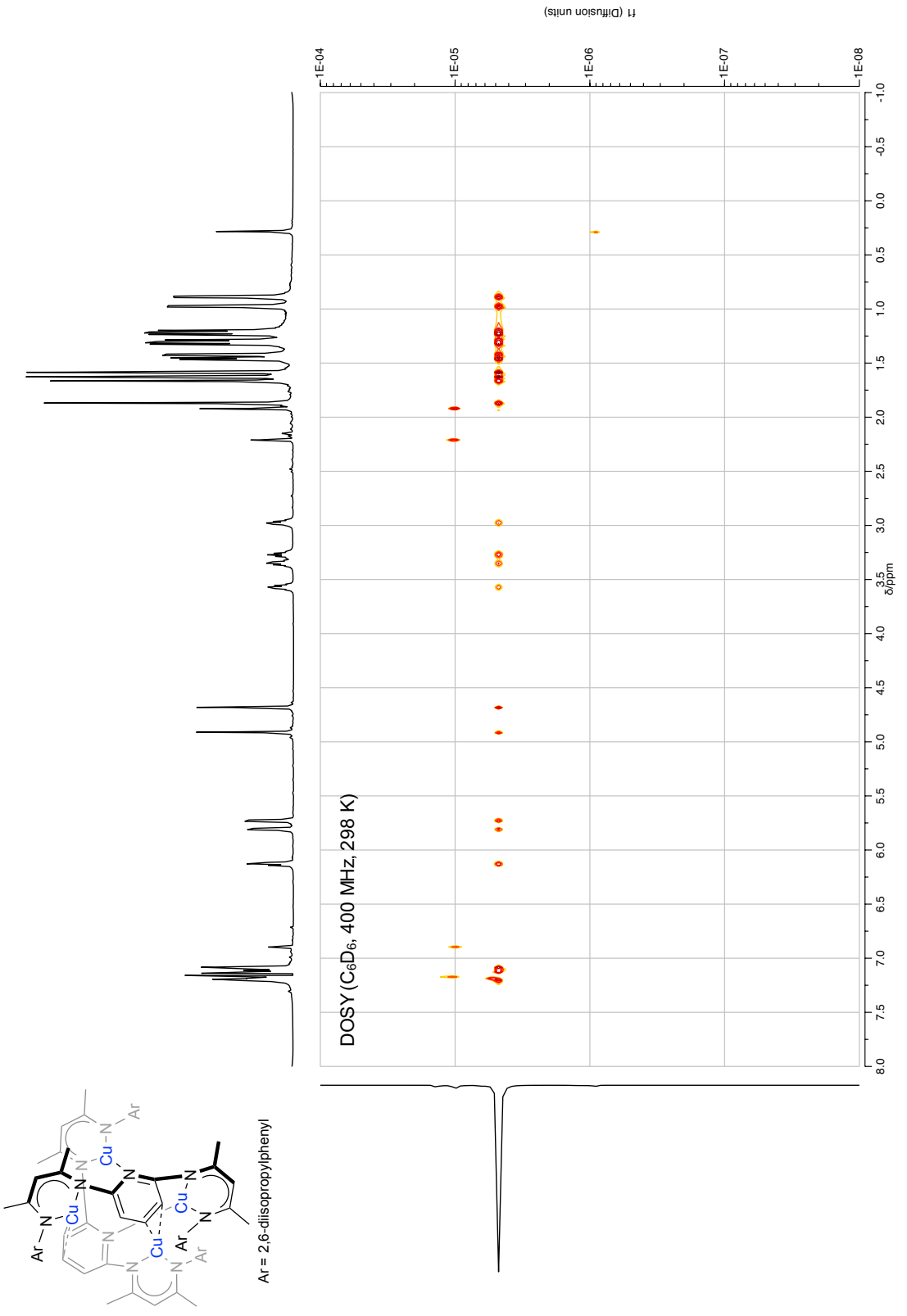

Figure S7. DOSY NMR spectrum $[Cu_2L]_2$ (C_6D_6, 400 MHz, 298 K)

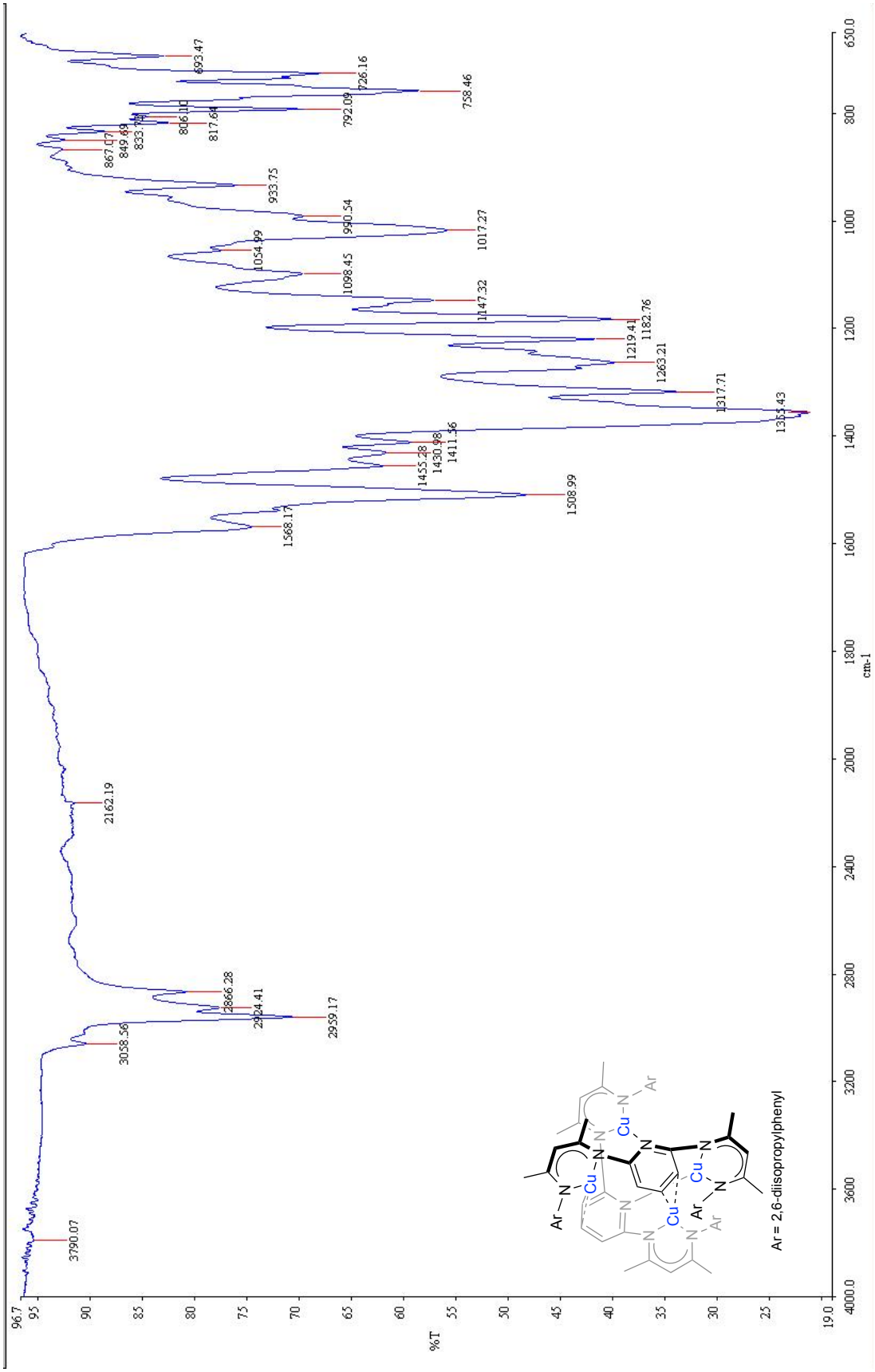

Figure S8. Solid-state FT-IR spectrum $[Cu_2L]_2$

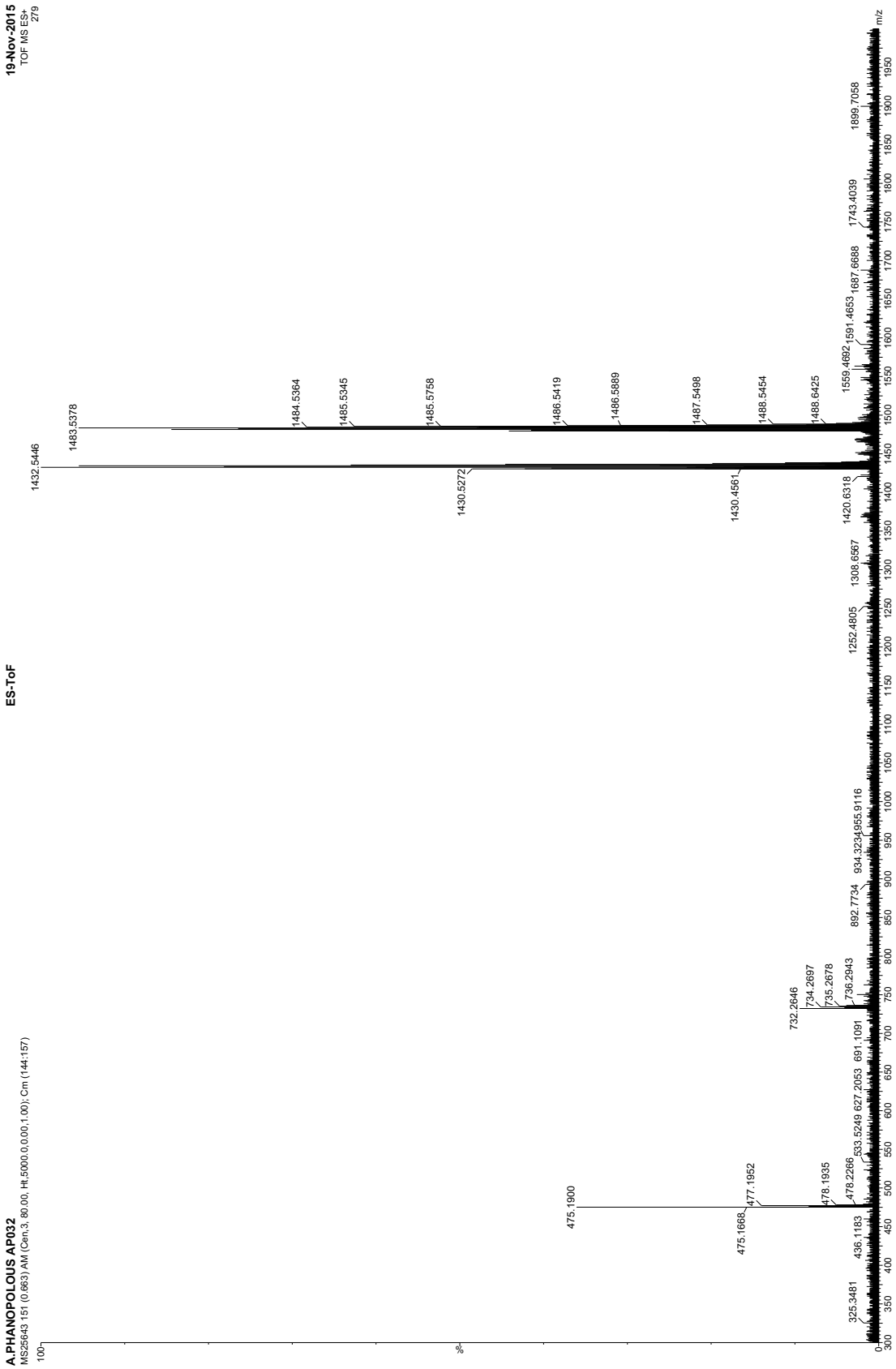

Figure S9. High-resolution mass spectrum $[Cu_2L]_2$ (+ve, ES, Et_2O)

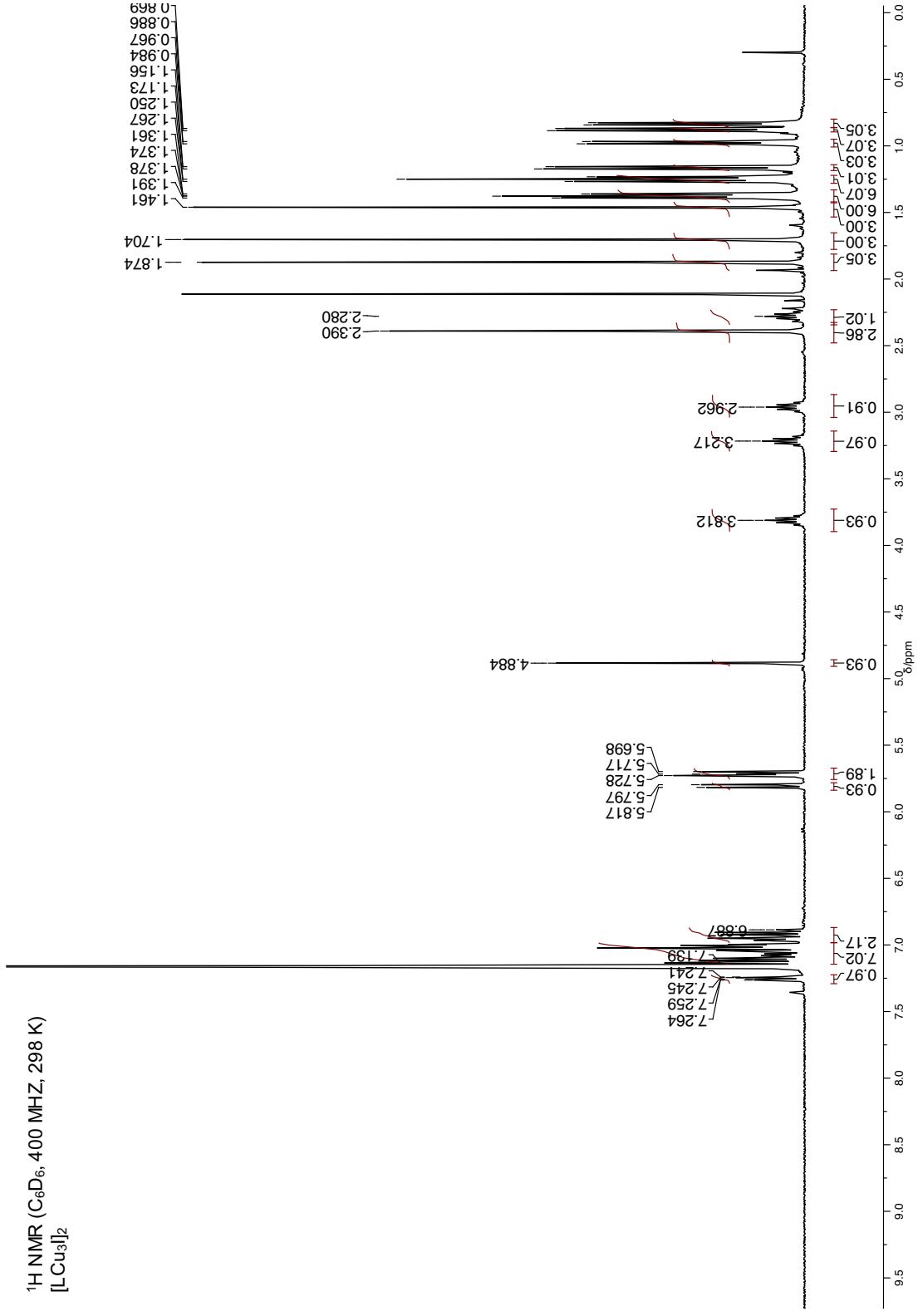

Figure S10. ^{1}H NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

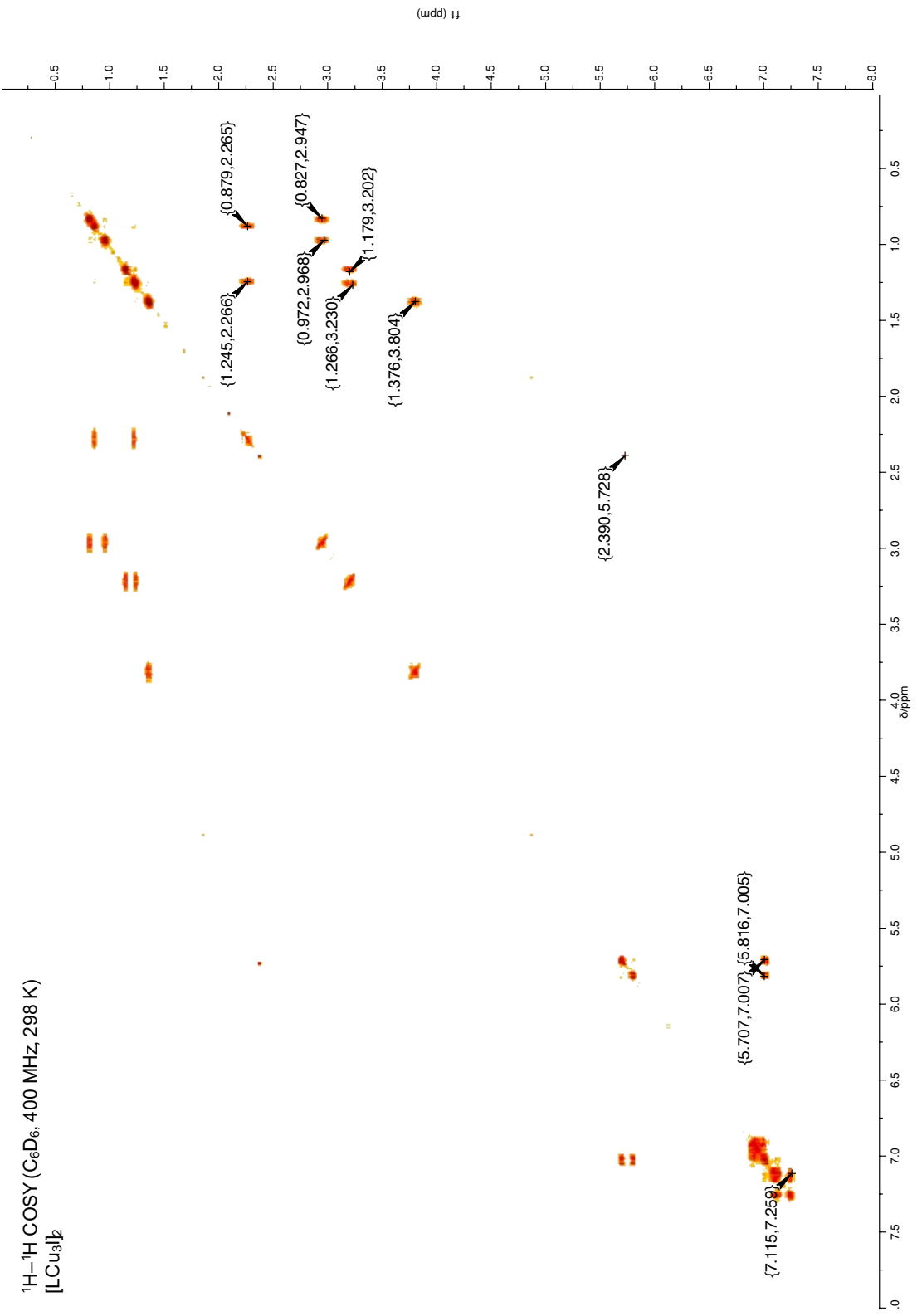

Figure S11. ^{1}H–^{1}H COSY NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

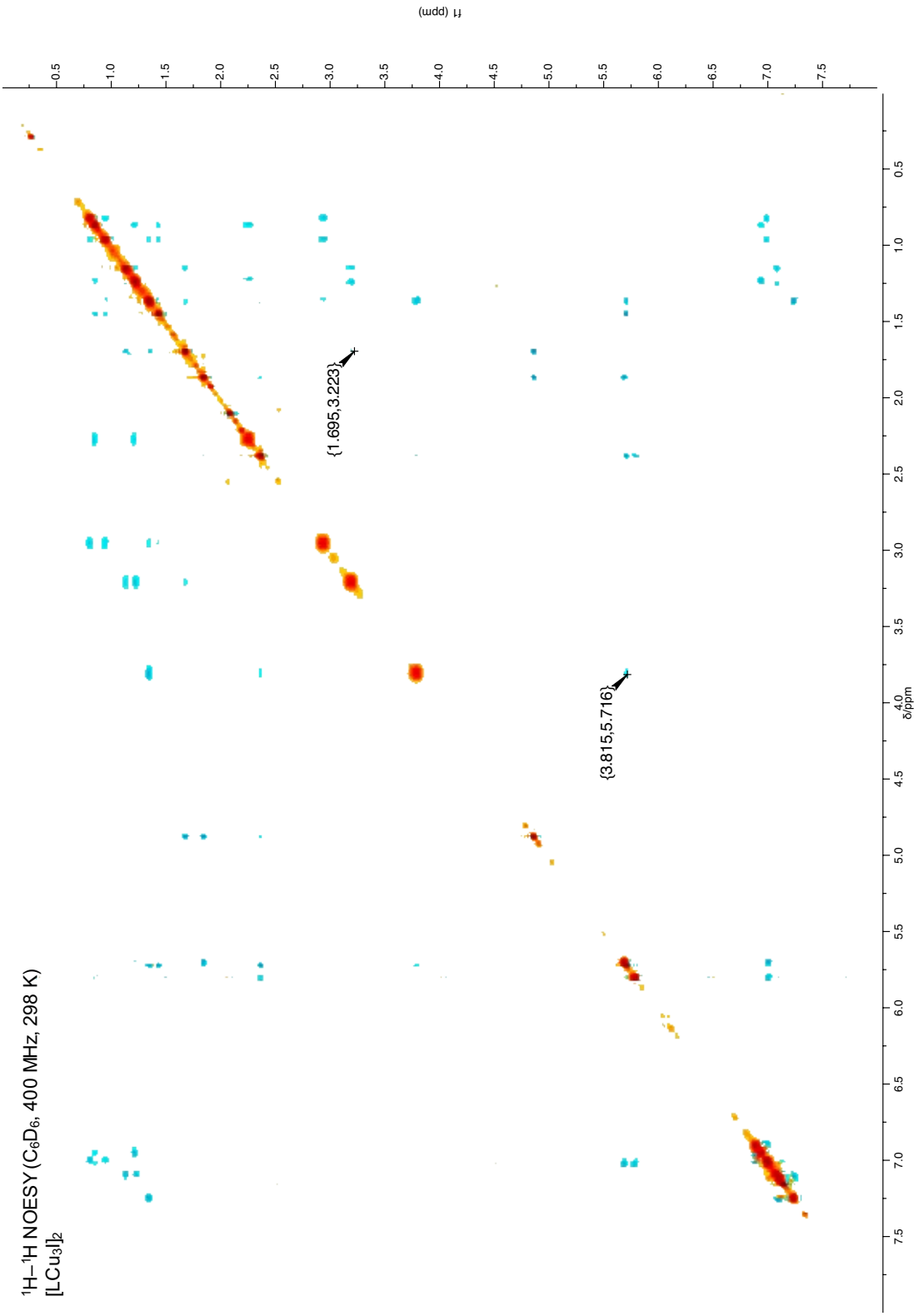

Figure S12. ^{1}H–^{1}H NOESY NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

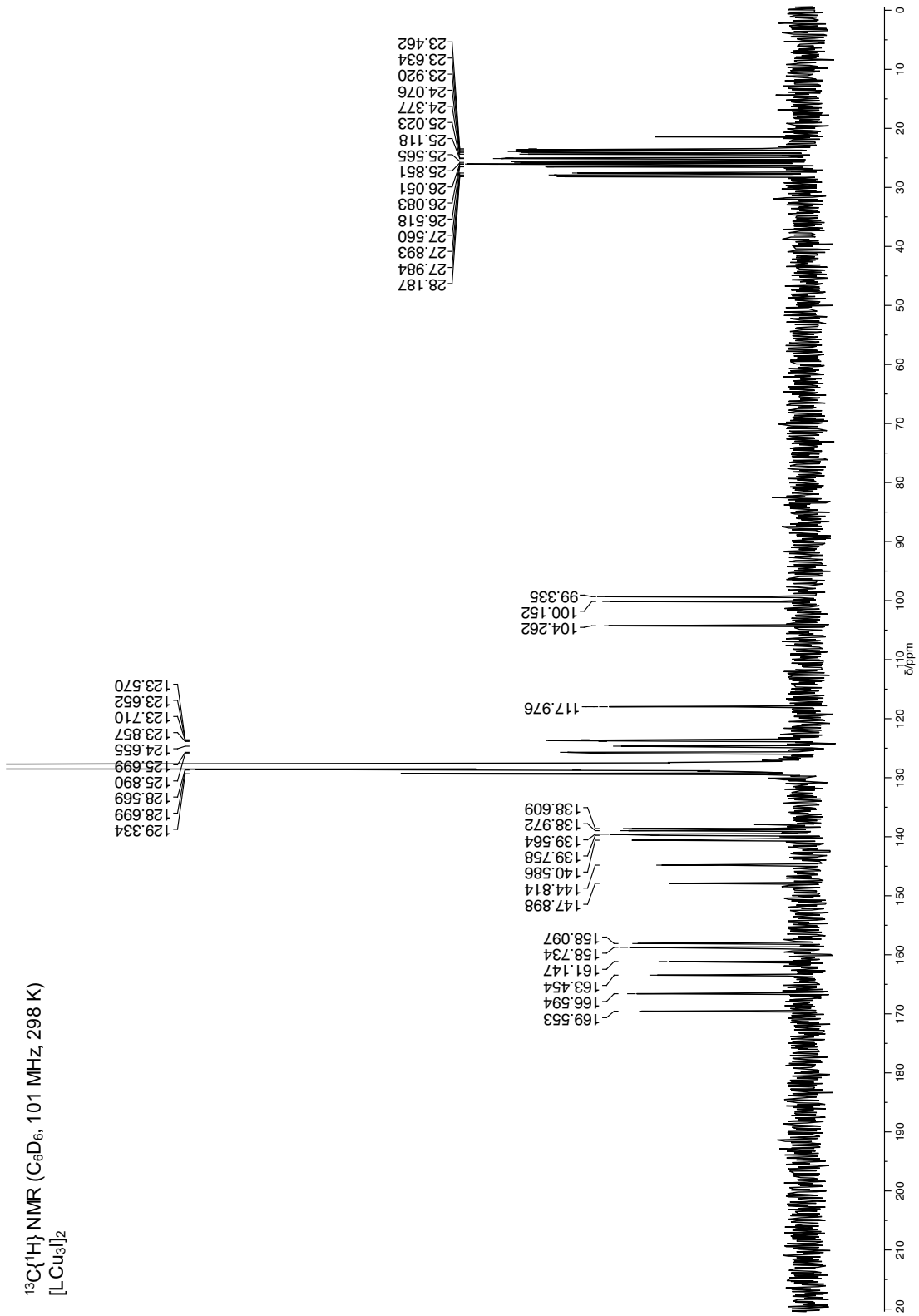

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum $[LCu_3I]_2$ (C_6D_6, 101 MHz, 298 K)

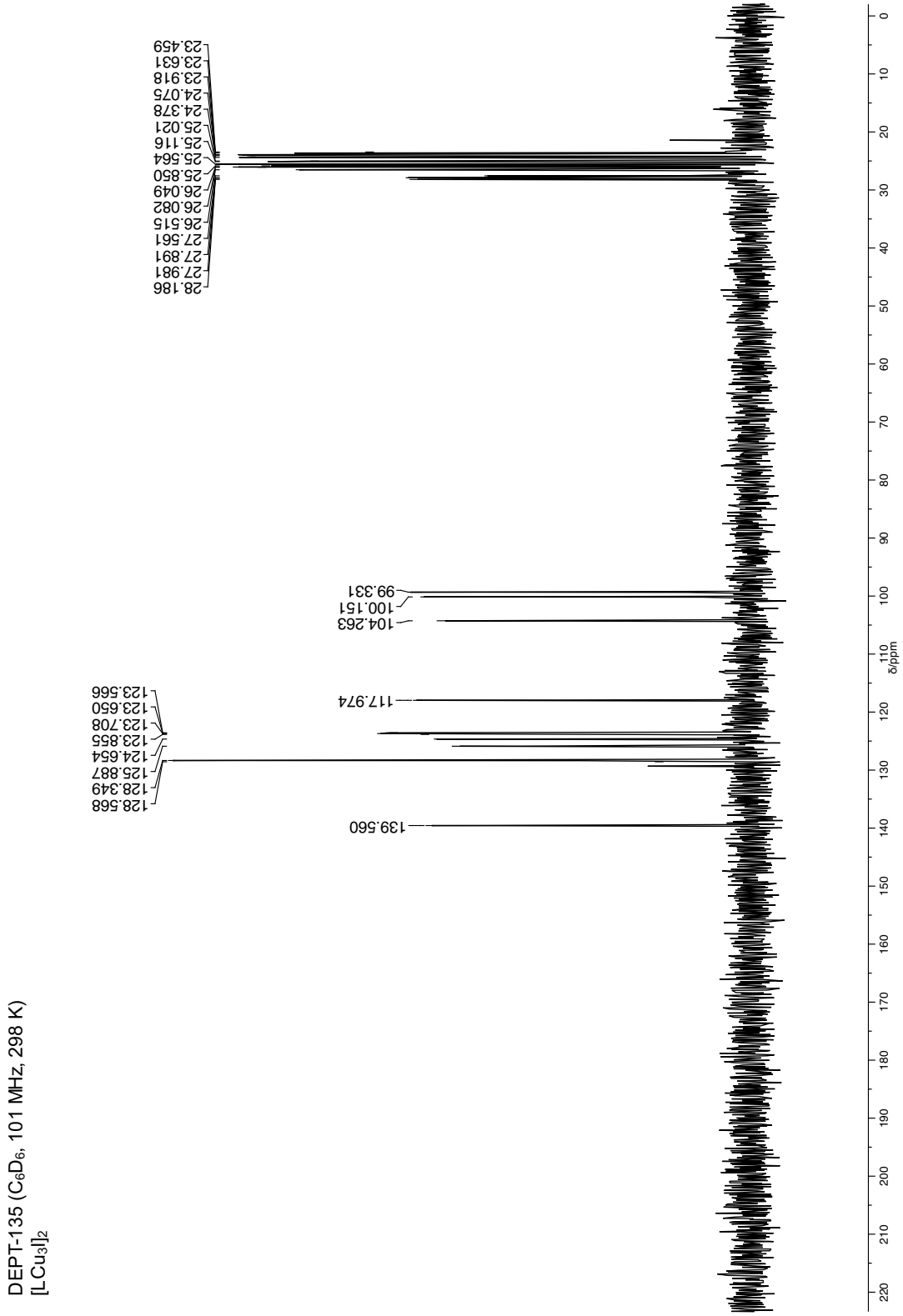

Figure S14. DEPT-135 NMR spectrum $[LCu_3I]_2$ (C_6D_6, 101 MHz, 298 K)

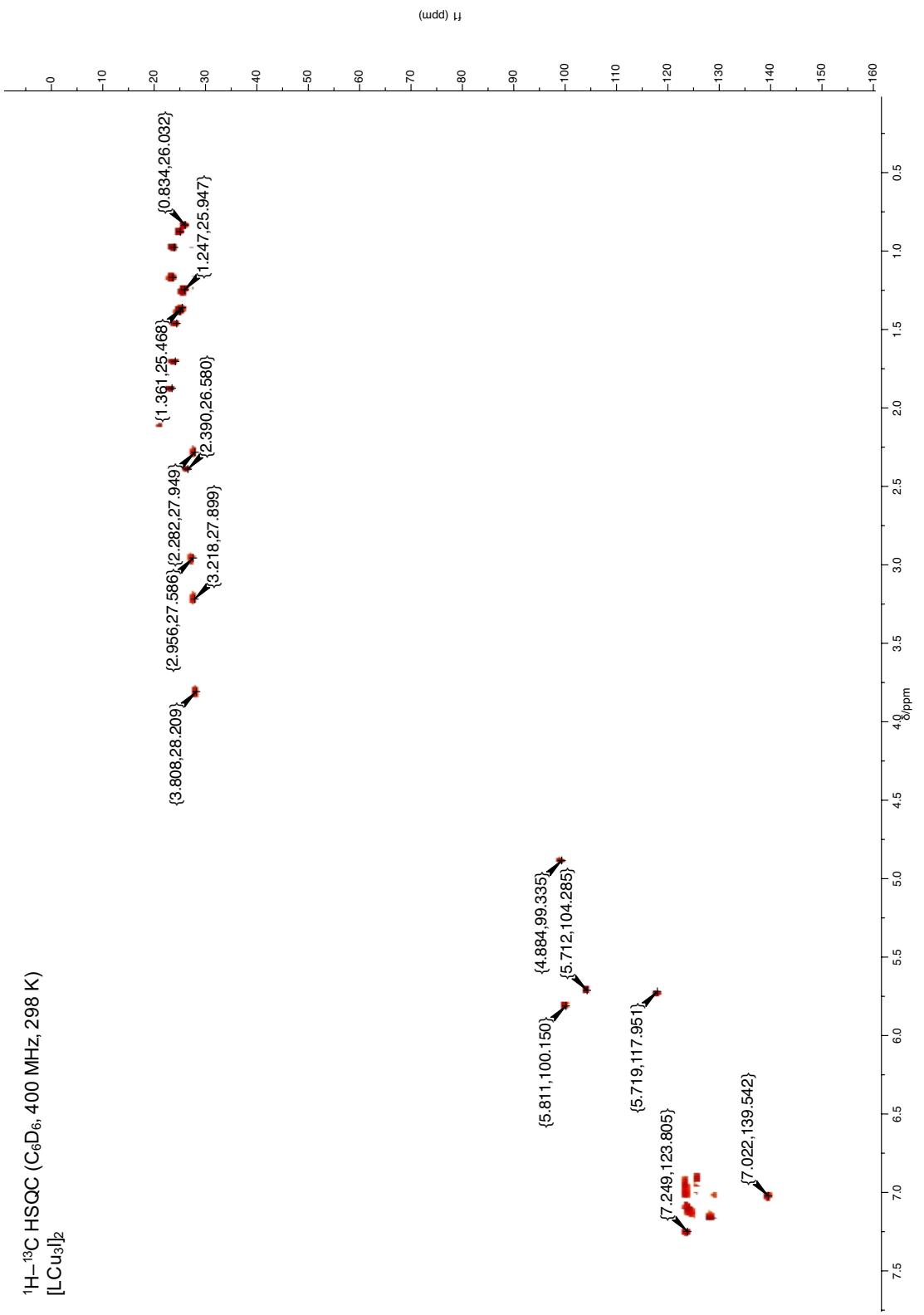

Figure S15. $^{1}H–^{13}C$ HSQC NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

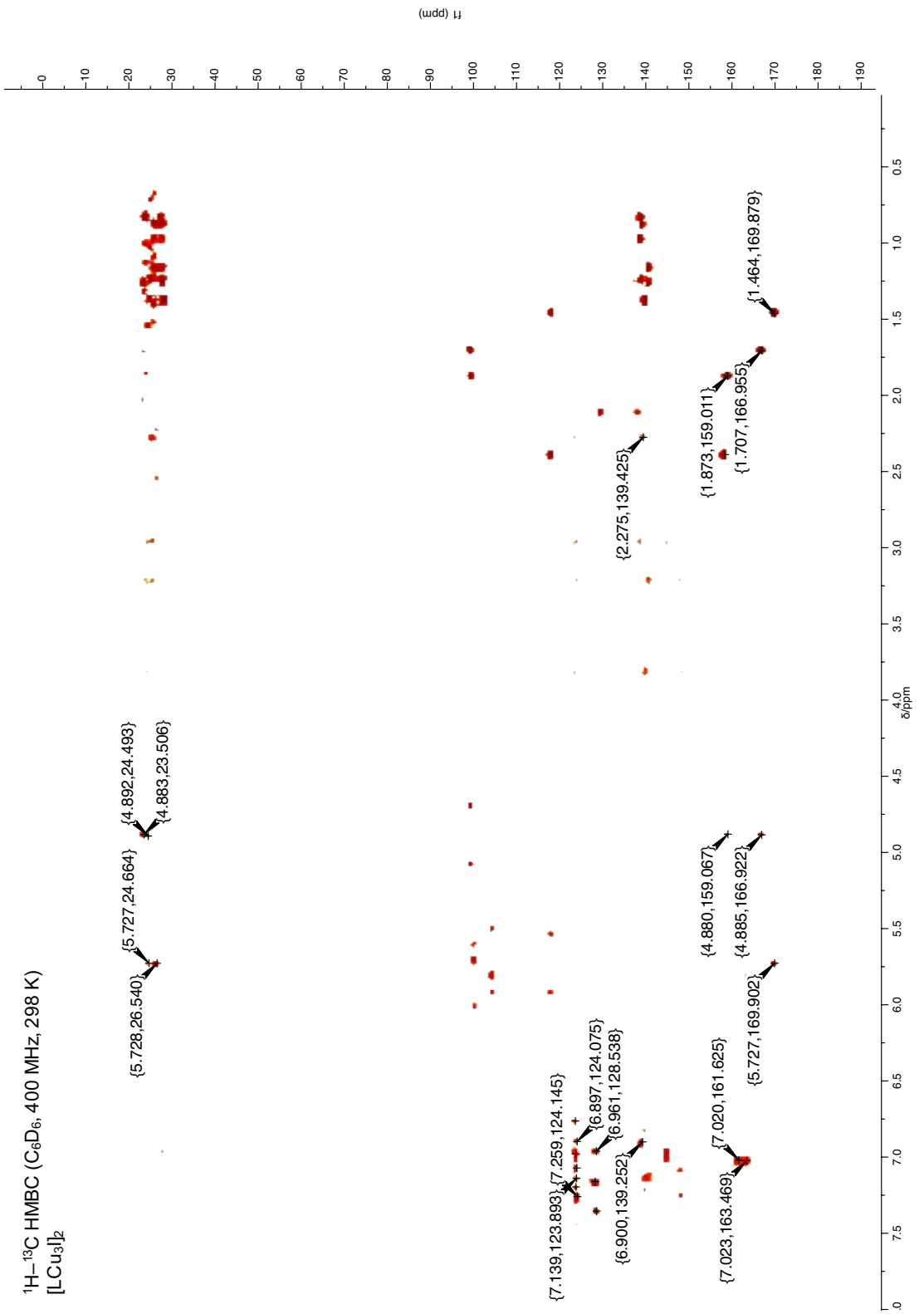

Figure S16. ^{1}H–^{13}C HMBC NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

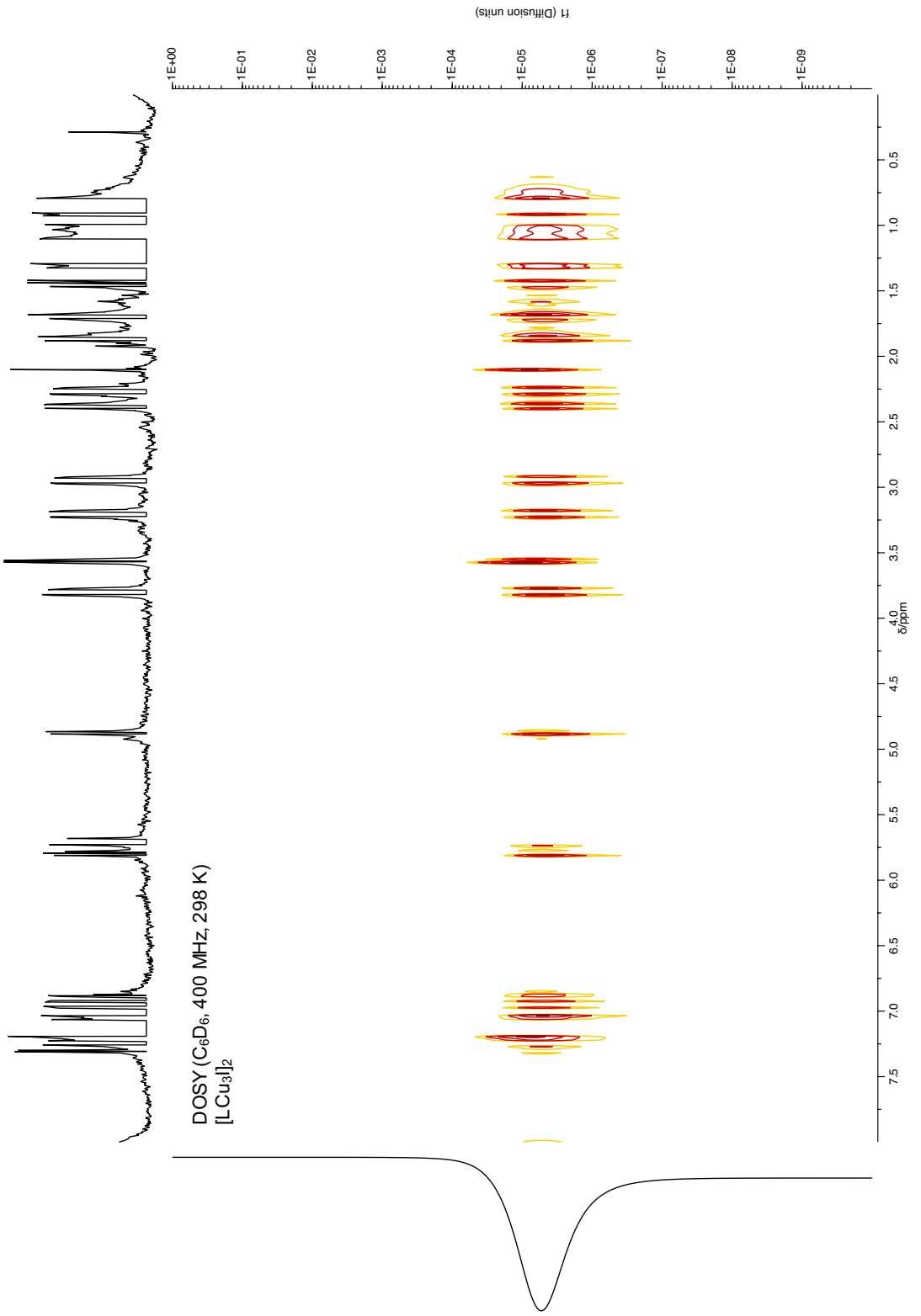

Figure S17. DOSY NMR spectrum $[LCu_3I]_2$ (C_6D_6, 400 MHz, 298 K)

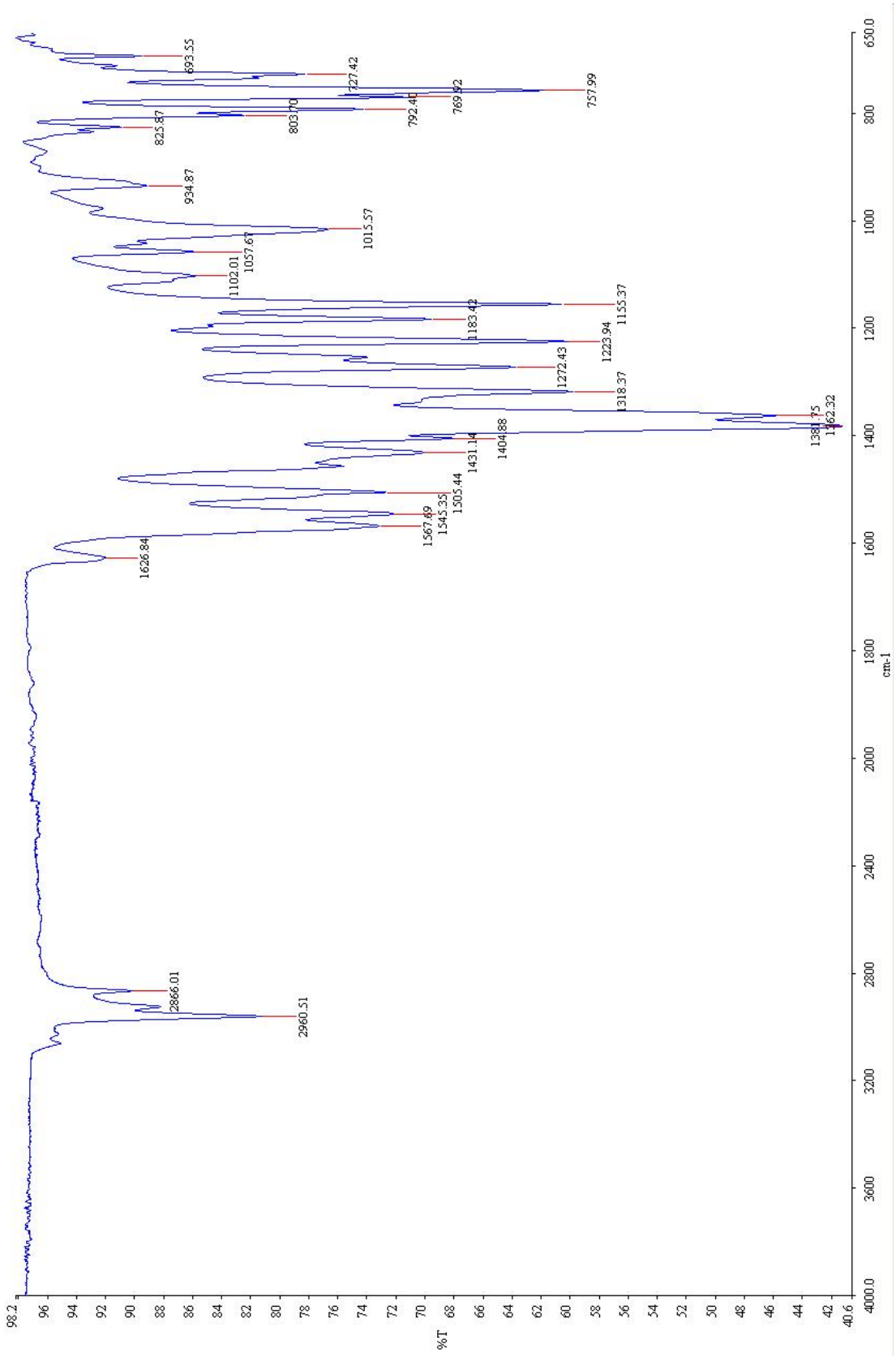

Figure S18. Solid-state FT-IR spectrum $[LCu_3I]_2$

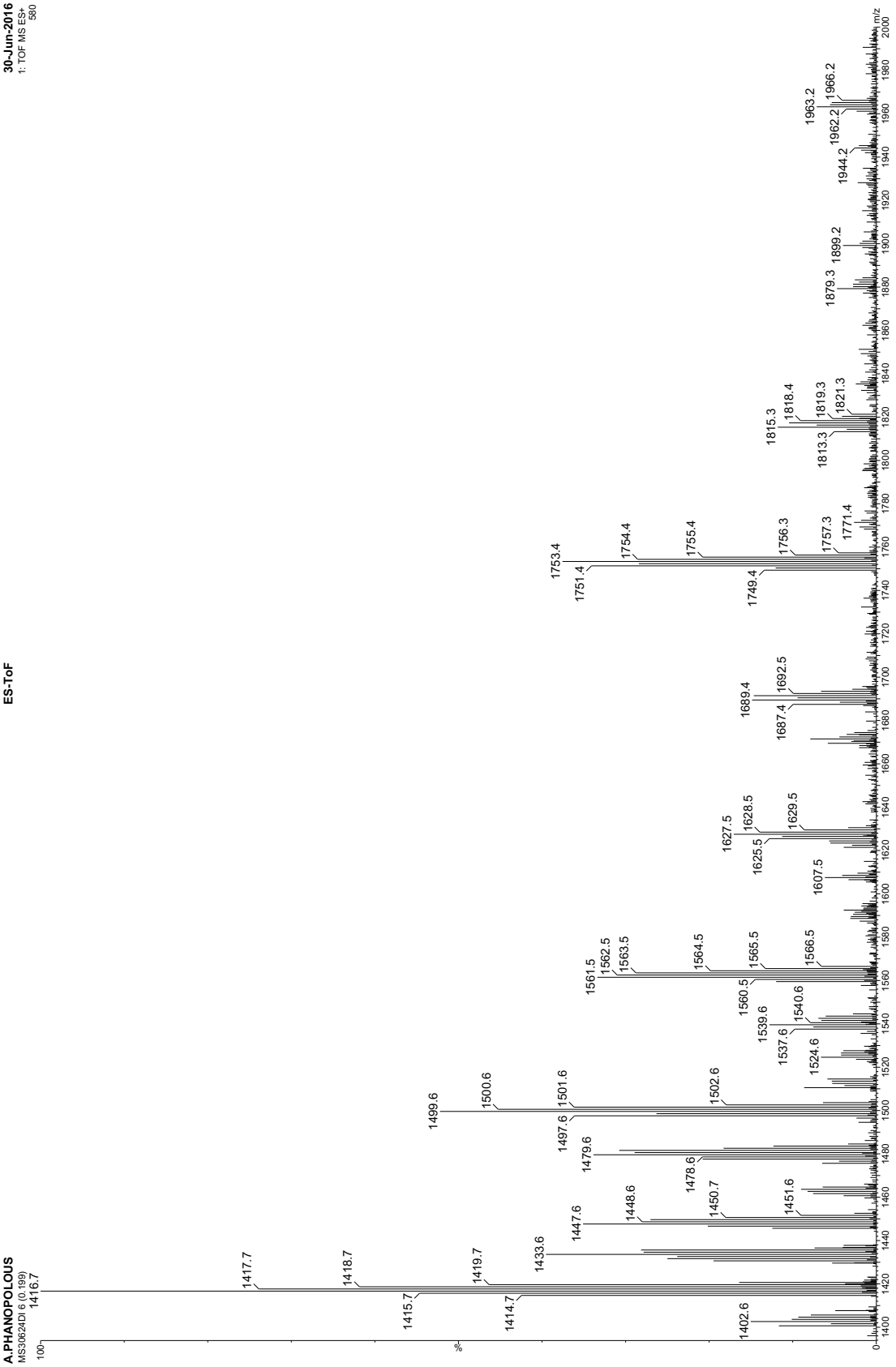

Figure S19. Mass spectrum $[LCu_3I]_2$ (+ve, ES, Et_2O)

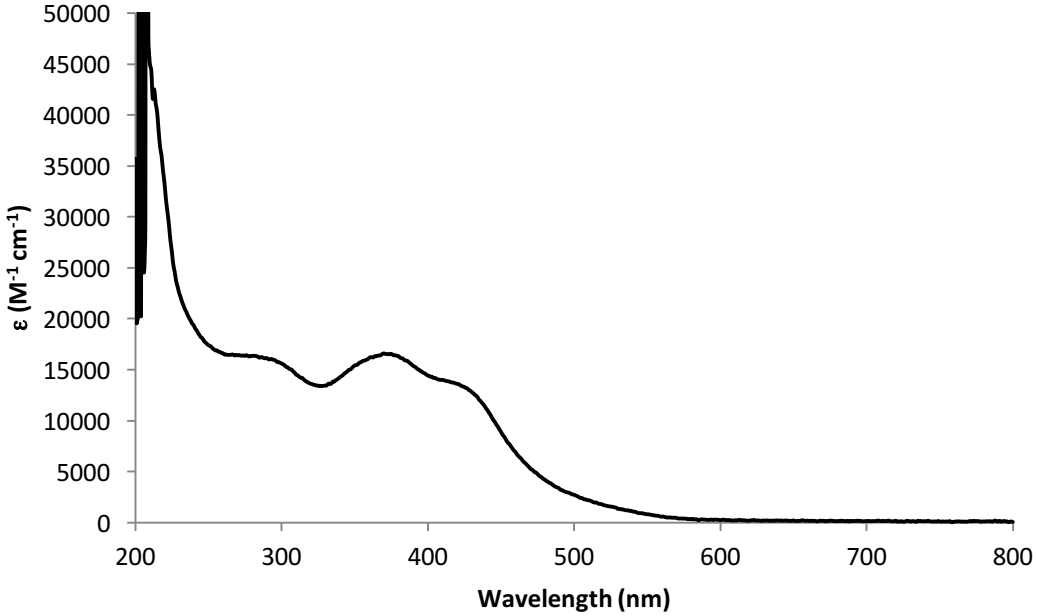

Figure S20. UV-vis spectrum of $[Cu_2L]_2$

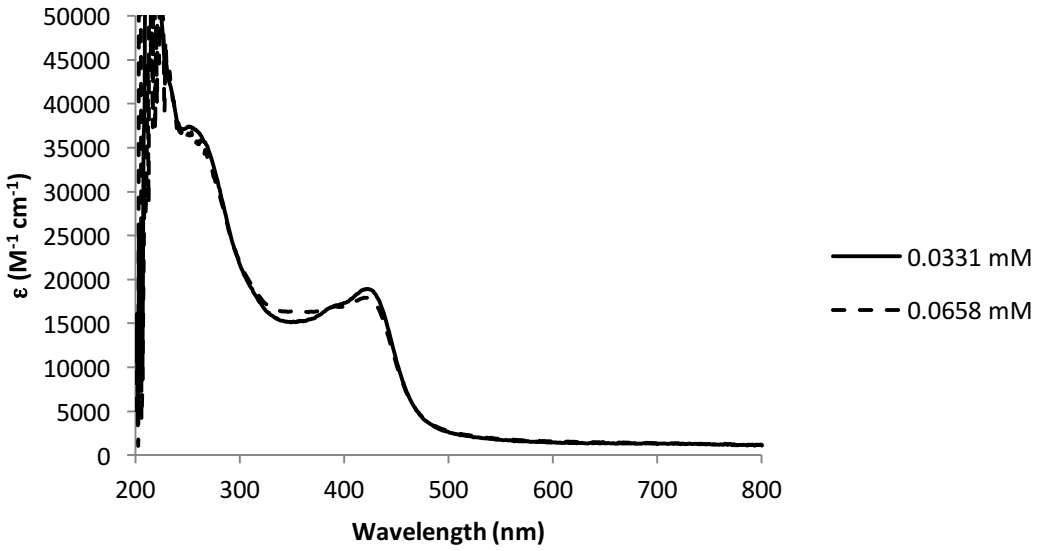

Figure S21. UV-vis spectrum of $[LCu_3I]_2$

The X-ray crystal structure of $[LCu_3I]_2$-I

Crystal data for **$[LCu_3I]_2$-I**: $C_{78}H_{102}Cu_6I_2N_{10}\cdot1.5(C_4H_{10}O)$, M = 1925.91, orthorhombic, *Pna*2$_1$ (no. 33), a = 26.7700(5), b = 15.1245(3), c = 22.5140(4) Å, V = 9115.6(3) Å^3, Z = 4, D_c = 1.403 g cm^{-3}, μ(Mo-Kα) = 2.099 mm^{-1}, T = 173 K, dark orange blocks, Agilent Xcalibur 3E diffractometer; 13046 independent measured reflections (R_{int} = 0.0213), F^2 refinement,[1] R_1(obs) = 0.0345, wR_2(all) = 0.0854, 11563 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 50°], 978 parameters. The absolute structure of **$[LCu_3I]_2$-I** was determined by use of the Flack parameter [x = +0.072(16)]. CCDC 1500849.

The O95-based included diethylether solvent molecule in the structure of **$[LCu_3I]_2$-I** was found to be disordered. Two orientations were identified of *ca*. 35 and 15% occupancy, the total site occupancy being set at 50% based on comparison of the thermal parameters with the rest of the structure (in particular the other solvent molecule) and to give a simple round number. 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 $[LCu_3I]_2$-II

Crystal data for **$[LCu_3I]_2$-II**: $C_{78}H_{102}Cu_6I_2N_{10}\cdot1.5(C_4H_{10}O)$, M = 1925.91, orthorhombic, *Pna*2$_1$ (no. 33), a = 26.7510(3), b = 15.13554(18), c = 22.5819(3) Å, V = 9143.2(2) Å^3, Z = 4, D_c = 1.399 g cm^{-3}, μ(Cu-Kα) = 7.176 mm^{-1}, T = 173 K, orange plates, Agilent Xcalibur PX Ultra A diffractometer; 13490 independent measured reflections (R_{int} = 0.0462), F^2 refinement,[1] R_1(obs) = 0.0420, wR_2(all) = 0.1059, 11889 independent observed absorption-corrected reflections [$|F_o| > 4\sigma(|F_o|)$, $2\theta_{full}$ = 135°], 982 parameters. The structure of **$[LCu_3I]_2$-II** was refined as a 2-component inversion twin [Flack parameter x = 0.346(5)]. CCDC 1500850.

The occupancy of the O95-based included diethylether solvent molecule in the structure of **$[LCu_3I]_2$-II** was set at 50% based on comparison of the thermal parameters with the rest of the structure (in particular the other solvent molecule) and to give a simple round number.

The X-ray crystal structure of $[LCu_2]_2$

Crystal data for **$[LCu_2]_2$**: $C_{86}H_{122}Cu_4N_{10}O_2$, M = 1582.18, monoclinic (no. 14), a = 26.8050(6), b = 11.3607(4), c = 27.7024(7) Å, β = 98.596(2), V = 8341.3(4) Å^3, Z = 4, D_c = 1.260 g cm^{-3}, μ = 0.972 mm^{-1}, T = 300 K, dark red needles, synchrotron X-ray irradiation wavelength = 0.6889, 16339 independent measured reflections (R_{int} = 0.0841), F^2 refinement,[2] R_1(obs) = 0.0515, wR_2(all) = 0.1333. CCDC 1527701.

The O2-based included diethylether solvent molecule in the structure of **$[LCu_2]_2$** was found to be disordered. Two orientations were identified of *ca*. 40 and 60% occupancy to give a simple round number. The geometries of both orientations were optimized and all of the atoms were refined isotropically.

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[1] SHELXTL, Bruker AXS, Madison, WI; (b) SHELX-2014/7, G.M. Sheldrick, *Acta Cryst.*, 2015, **C71**, 3-8.

[2] The structure was solved with olex.solve and refined with olex2.refine: O. V. Dolomanov, L. J.Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: A complete structure solution, refinement and analysis program *J. Appl. Cryst.,* 2009, **42**, 339-341.

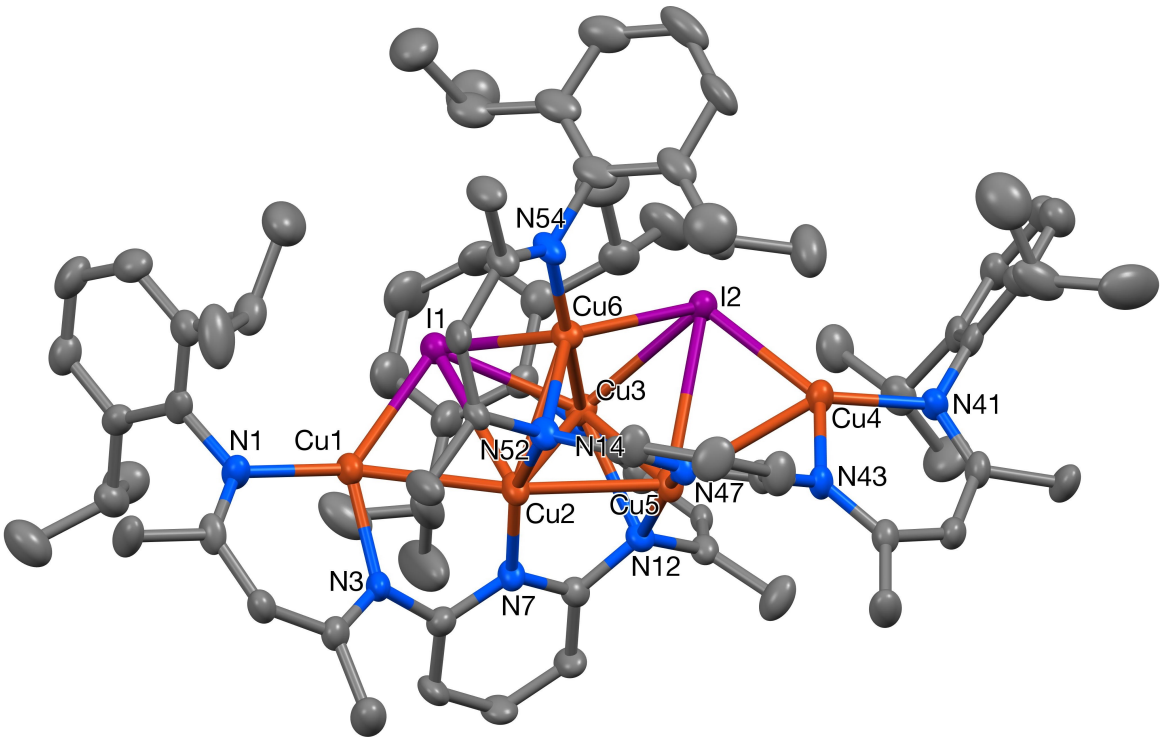

Figure. S22 The crystal structure of **[LCu$_3$I]$_2$-I** (50% probability ellipsoids).

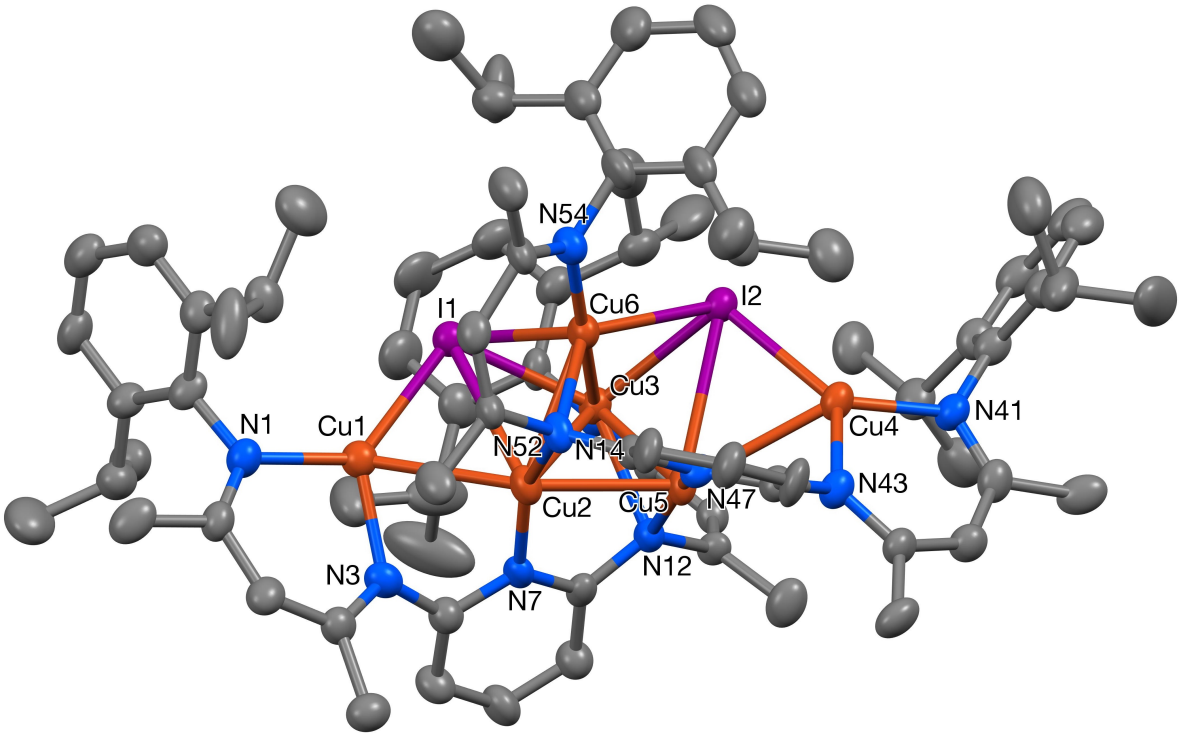

Figure. S23 The crystal structure of **[LCu$_3$I]$_2$-II** (50% probability ellipsoids).

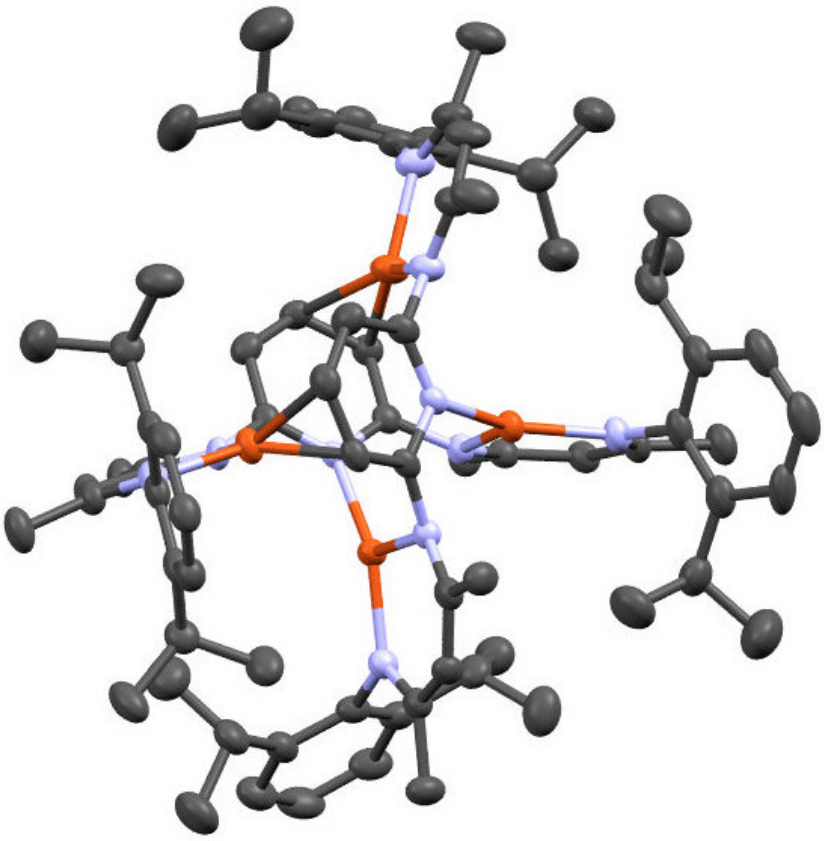

Figure. S24 The crystal structure of **[LCu$_2$]$_2$** (50% probability ellipsoids).

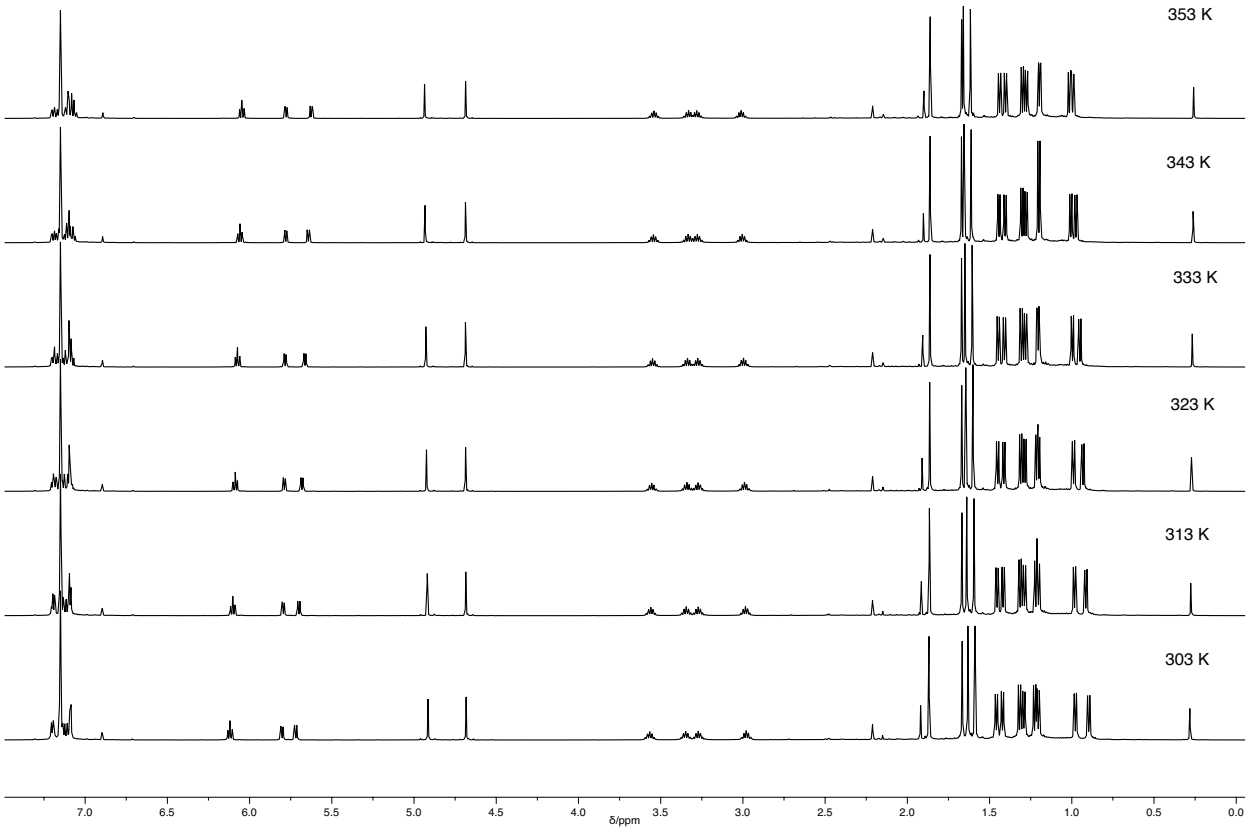

Figure. S25 Variable Temperature ^{1}H NMR data on **1** in C_6D_6 solution from 303 to 353 K.