Electronic supplementary information

An unusually stable octanuclear σ-mesityl-bridged μ^4-oxo-copper(I) complex encapsulated by a pyrazolate-based compatmental ligand scaffold

Michael Stollenz, Christian Große and Franc Meyer*

Institut für Anorganische Chemie der Georg-August-Universität Göttingen, Tammannstraße 4, D-37077 Göttingen, Germany.
Fax: (++49)-551-393063; Tel: (++49)-551-393012;
E-mail: franc.meyer@chemie.uni-goettingen.de

Experimental procedures

General remarks:

All manipulations involving copper organic compounds were carried out by using Schlenk techniques under an atmosphere of dry argon. Glassware and NMR tubes were heat-sealed with a heat gun under vacuum. Prior to use, tetrahydrofurane, diethyl ether, toluene, and pentane were freshly distilled from sodium/benzophenone. Ethanol was dried according to the established method via sodium/diethyl phthalate.[1] Methylamine (41 wt % solution in water, Fluka) and 2-picolyl chloride hydrochloride (Acros, Aldrich) were used as purchased. Mesitylcopper was synthesised according to the known procedure.[2] Microanalysis: Analytisches Labor des Anorganisch-Chemischen Instituts der Universität Göttingen. Melting point for **1**: SRS (Stanford Research Systems) Opti Melt. Melting point for **3** was derived from a DSC-plot (Netzsch STA 409 PC Luxx®). MS-spectra: Finnigan MAT 8200 (EI) and Finnigan MAT LCQ (ESI). Values for *m*/*z* are for the most intense peak of the isotope envelope. NMR measurements were performed at 300 K on a Bruker AC 200 at 200.13 MHz (^{1}H) and on a Bruker Avance 500 at 500.13 MHz (^{1}H) and 125.77 MHz (^{13}C), respectively. The chemical shifts (in ppm) were calibrated internally to the solvent signals. Most assignments are based on a series of 2D experiments.

N-(2-Picolyl)methylamine:

Procedure according to the literature method with modifications:[3] 2-picolyl chloride hydrochloride (3.020 g, 18.4 mmol) was dissolved in ethanol (50 mL). The stirred solution was treated with a 41 wt % solution of methylamine in water (27.878 g, 368.0 mmol). After stirring at r.t. for 5 d, the volatile components were removed under reduced pressure.

The brown salty residue was re-dissolved in water (ca. 5 mL) and concentrated hydrochloric acid (40 mL). After washing with CH_2Cl_2 (3×40 mL), the aqueous phase was concentrated to dryness and extracted with CH_2Cl_2 (5×25 mL). The combined organic phase was dried over $MgSO_4$, filtered and evaporated in vacuo. The remaining brown oil was distilled from KOH to give a colourless, viscous oil (b.p. 90°C/26–28 mbar; Lit.[3]: 79–83°C/670 Pa; Lit.[4]: 78–80°C/1.34 kPa). Yield: 0.919 g (7.5 mmol, 41%). ^{1}H NMR (200.13 MHz, $CDCl_3$): $\delta = 2.17$ (s, 1 H, NH), 2.44 (s, 3 H, CH_3), 3.83 (s, 2 H, CH_2), 7.13 (dd, ^3J (H,H) = 4.8 Hz, ^3J (H,H) = 7.6 Hz, 1 H, C^5), 7.27 (d, ^3J (H,H) = 7.8 Hz, 1 H, C^3), 7.61 (dt, ^3J (H,H) = 7.6 Hz, ^4J (H,H) = 1.8 Hz, C^4), 8.52 (d, ^3J (H,H) = 4.8 Hz, C^6).

3,5-Bis(chloromethyl)-4-phenyl-1*H*-pyrazole hydrochloride:

3,5-Bis(hydroxymethyl)-4-phenyl-1*H*-pyrazole[5] (1.772 g, 8.7 mmol) was dissolved in $SOCl_2$ (20 mL) and refluxed for 1 h. The solvent was removed and the residue was dried in vacuo for 30 minutes. A beige powder was obtained in nearly quantitative yield. ^{1}H NMR (200.13 MHz, DMSO-D_6): $\delta = 4.70$ (s, 4 H, CH_2), 7.35–7.53 (m, 5 H, Ph).

3,5-Bis(chloromethyl)-1-(tetrahydropyranyl-2-yl)-4-phenyl-1*H*-pyrazole (1):

To a solution of 3,5-bis(chloromethyl)-4-phenyl-1*H*-pyrazole hydrochloride in CH_2Cl_2 (100 mL) *in situ*-prepared from 3,5-bis(hydroxymethyl)-4-phenyl-1*H*-pyrazole (1.772 g, 8.7 mmol) was added 3,4-dihydro-2*H*-pyran (2.901 g, 34.5 mmol), and the reaction mixture was stirred at r.t. for 14 h. After removal of the solvents under reduced pressure the residue was treated with an aqueous solution of $NaHCO_3$ (100 mL) and then extracted with CH_2Cl_2 (10 mL). After drying over $MgSO_4$, the filtered solution was layered with diethyl ether and stored at –32°C overnight. A precipitate formed that was separated by filtration and washed with small portions of diethyl ether. After drying for 7 h in vacuo, a colourless solid was obtained as a racemic mixture. Yield: 1.827 g (5.6 mmol, 64%). Elemental analysis calcd (%) for $C_{16}H_{18}N_2OCl_2$ (325.23): C, 59.09; H, 5.58; N, 8.61; found: C, 58.19; H, 5.53; N, 8.33; m.p.: 130–132 °C. ^{1}H NMR (500.13 MHz, $CDCl_3$): $\delta = 1.50$–1.79 (m, 3 H, CH_2, pyranyl-$H^{4,5}$), 2.05–2.16 (m, 2 H, CH_2, pyranyl-$H^{3,4}$), 2.46–2.54 (m, 1 H, CH_2, pyranyl-H^3), 3.69–3.74 (m, 1 H, CH_2, pyranyl-H^6), 4.04–4.07 (m, 1 H, CH_2, pyranyl-H^6), 4.53–4.71 (m, 4 H, CH_2, 3,5-pyrazole-CH_2), 5.55 (dd, ^3J (H,H)= 9.3 Hz, ^3J (H,H')= 9.7 Hz, 1 H, CH), 7.35–7.39, 7.43–

7.47(m, 5 H, CH, Ph). ^{13}C NMR (125.77 MHz, $CDCl_3$): δ = 22.6 (CH_2, pyranyl-C^4), 25.0 (CH_2, pyranyl-C^5), 29.4 (CH_2, pyranyl-C^3), 34.0, 37.6 (CH_2, 3,5-pyrazole-CH_2), 68.0 (CH_2, pyranyl-C^6), 85.7 (CH, pyranyl-C^2), 123.1 (C, pyrazole-$C^{3,4,5}$), 127.9 (CH, *p*-Ph), 129.0, 129.7 (CH, *o*-, *m*-Ph), 131.2 (C, *i*-Ph), 136.4, 145.9 (C, pyrazole-$C^{3,4,5}$). MS (EI): *m*/*z* (rel. intensity) = 324.1 (19) $[M]^+$, 289.1 (13) $[M - Cl]^+$, 240.0 (97) $[M - CH_2Cl - Cl]^+$, 84.0 (100) $[DHP]^+$.

***N*,*N*'-bis(2-pyridylmethyl)-*N*,*N*'-dimethyl-4-phenyl-1*H*-pyrazole-3,5-dimethanamine (2**H**):** A suspension of anhydrous Na_2CO_3 (5.309 g, 50.1 mmol), **1** (1.626 g, 5.0 mmol) and *N*-(2-picolyl)methylamine (1.231 g, 10.1 mmol) in acetonitrile (100 mL) was refluxed for 40 h, filtered and evaporated to dryness. The golden to yellow oily residue was dissolved in dry ethanol (30 mL) and treated with ethanolic HCl (40 wt.-%, 10 mL). After stirring for ½ h, diethyl ether (30 mL) was added to precipitate the hydrochloride salt as a slight brownish solid. This was separated by filtration, washed with diethylether (6×60 mL) and dried in vacuo for 1 h. Aqueous NaOH (pH 12, 80 mL) was added and the product extracted with CH_2Cl_2 (5×40 mL) and the combined organic phase dried with $MgSO_4$. Removal of the solvent yields a golden, viscous resin. Yield: 1.525 g (3.55 mmol, 71%). Elemental analysis calcd (%) for $C_{25}H_{28}N_6 \cdot 0.2\ CH_2Cl_2$ (429.52): C, 70.47; H, 6.66; N, 19.57; found: C, 70.92; H, 6.83; N, 19.61. ^{1}H NMR (500.13 MHz, C_6D_6): δ = 2.18 (s, 6 H, CH_3), 3.73, 3.76 (2x s, 8 H, CH_2), 4.33 (s, 2 H, CH_2, signal of CH_2Cl_2), 6.58–6.61 (m, 2 H, pyridyl-H^5), 7.03–7.06 (m, 2 H, pyridyl-H^4), 7.07–7.12 (m (broad), 2 H, pyridyl-H^3), 7.15–7.19 (m, 1 H, *p*-Ph), 7.30–7.33 (m, 2 H, *m*-Ph), 7.70–7.72 (m, 2 H, *o*-Ph), 8.38 (d, ^3J (H,H) = 4.6 Hz, pyridyl-H^6). ^{13}C NMR (125.77 MHz, C_6D_6): δ = 42.6 (CH_3), 52.8 (broad), 53.4 (CH_2, signal of CH_2Cl_2), 62.9 (CH_2), 120.6 (C, pyrazole-$C^{3,4,5}$), 121.8 (CH, pyridyl-C^5), 123.3 (CH, pyridyl-C^3), 126.4 (CH, *p*-Ph), 128.6 (CH, *m*-Ph), 130.5 (CH, *o*-Ph), 134.9 (C, *i*-Ph, pyridyl-C^2, pyrazole-$C^{3,4,5}$), 136.1 (CH, pyridyl-C^4), 149.2 (CH, pyridyl-C^6), 159.9 (C, *i*-Ph, pyridyl-C^2, pyrazole-$C^{3,4,5}$). One signal for a quartenary aromatic carbon atom is not observed but is likely hidden by a solvent signal or another resonance of the spectrum. MS (EI): *m*/*z* (rel. intensity) = 412 (1) $[M]^+$, 320 (100) $[M - (C_5H_4N)(CH_2)]^+$, 292 (10) $[M - (C_5H_4N)(CH_2NCH_3) + 1]^+$, 291 (6) $[M - (C_5H_4N)(CH_2NCH_3)]^+$. HRMS (ESI+ in MeOH/$NH_4OAc$): *m*/*z* calcd for $C_{25}H_{29}N_6$ $[M + H]^+$: 413.24536, found: 413.24482.

[(2)Cu_2(*μ*-Mes)$_2Cu_2$(*μ*-O)Cu_2(*μ*-Mes)$_2Cu_2$(2)] (3):

A solution of mesitylcopper (342 mg including 0.06 equivalents of toluene, determined by ^{1}H NMR, 1.82 mmol) in toluene (10 mL) was treated with a solution of **2**H (195 mg including 0.2 equivalents of CH_2Cl_2, see **2**, 0.45 mmol) in toluene (10 mL) at –78°C by means of a cannula. After stirring at r.t. overnight the solvent was concentrated to 5 mL and the reaction mixture filtered. 5 mL of toluene were added. Oxygen (dried with P_2O_5, 2.6 mL, 0.12 mmol) was slowly bubbled into the solution via a syringe. The golden orange solution immediately became dark red to brown. After stirring for 2 h the clear solution was layered with diethyl ether (10 mL) and stored for one week at –18°C. The first crop of the complex was isolated by filtration. The filtrate was concentrated to a volume of ca. 2 mL and treated with pentane (20 mL) to give more of the beige precipitate that was removed by filtration. The remaining clear solution was again concentrated to a volume of ca. 2 mL, treated with pentane (20 mL) and filtered. The unified solid fractions were washed with pentane (3×5 mL) and dried in vacuo for 14 h. A fawn to yellow powder was obtained. Yield: 358 mg (0.196 mmol, 87%). Elemental analysis calcd (%) for $C_{86}H_{98}N_{12}OCu_8$ (1824.15): C, 56.62; H, 5.42; N, 9.21; found: C, 56.41; H, 5.40; N, 9.39; m.p.: 100 °C (decomp.).^{1}H NMR (500.13 MHz, C_6D_6): δ = 1.71 (s, 6 H, *N*–CH_3), 2.15 (m, 9 H, signal of mesitylene, CH_3), 2.25 (s, 6 H, *p*-CH_3), 2.60 (s, 12 H, *o*-CH_3), 2.97 (s (broad), 4 H, CH_2), 3.49 (s, 4 H, CH_2), 6.31 (d, ^3J (H,H) = 7.6 Hz, pyridyl-C^3), 6.71–6.72 (m, 3 H, signal of mesitylene, CH), 6.77–6.80 (m, 2 H, pyridyl-C^5), 6.83 (s, 4 H, *m*-CH), 6.89 (dt, ^4J (H,H) = 1.7 Hz ^3J (H,H) = 7.6 Hz, 2 H, pyridyl-C^4), 7.09–7.12 (m, 1 H, *p*-Ph), 7.20–7.22 (m, 2 H, *o*-Ph), 7.27–7.30 (m, 2 H, *m*-Ph), 10.07 (d, ^3J (H,H) = 4.3 Hz, pyridyl-C^6). ^{13}C NMR (125.77 MHz, C_6D_6): δ = 21.3 (CH_3, signal of mesitylene), 21.6 (CH_3, *p*-CH_3), 29.7 (CH_3, *o*-CH_3), 43.2 (CH_3, *N*–CH_3), 55.7, 61.1 (CH_2), 115.2 (C, pyrazole-$C^{3,4,5}$), 122.3 (CH, pyridyl-C^3), 123.1 (CH, pyridyl-C^5), 124.5 (CH, *m*-CH), 127.4 (CH, signal of mesitylene), 128.1 (CH (masked by benzene signal), *m*-, *p*-Ph), 129.0 (CH, *o*-Ph), 135.5 (C), 135.9 (CH, pyridyl-C^4), 137.0, 137.6 (C), 137.6 (C, signal of mesitylene), 144.6 (C), 152.4 (CH, pyridyl-C^6), 153.4, 157.9 (C). MS (ESI+ in THF): *m/z* (rel. intensity) = 657.0 (24) $[(C_{25}H_{27}N_6)Cu_2Mes +1]^+$, 537.2 (100) $[(C_{25}H_{27}N_6)Cu_2]^+$.

The formation of bimesityl was determined by NMR from the residue of the pentane filtrate. The data are identical within experimental error to those of the purified product[6]:

^{1}H NMR (200.13 MHz, $CDCl_3$): δ =1.84 (s, 12 H, *o*-CH_3), 2.31 (s, 6 H, *p*-CH_3), 6.91 (s, 4 H, *m*-CH). The molar ratio between bimesityl and mesitylene was established by a sample of the pentane filtrate that was prepared in C_6D_6 under inert conditions in order to prevent hydrolyses of the present complex (expected ratio: 1:2; found ratio: ~1:2.6). ^{1}H NMR (500.13 MHz, C_6D_6): δ = 1.92 (s, 12 H, *o*-CH_3), 2.21 (s, 6 H, *p*-CH_3), 6.90 (s, 4 H, *m*-CH). The deviation from the expected ratio can be explained by the presence of traces of moisture on the surface of the glassware that are responsible for partial hydrolyses of mesityl copper and/or **3**.

---

(1) H. G. O. Becker, W. Berger, G. Domschke, E. Fanghänel, J. Faust, M. Fischer, F. Gentz, K. Gewald, R. Gluch, R. Mayer, K. Müller, D. Pavel, H. Schmidt, K. Schollberg,; K. Schwetlick, E. Seiler and G. Zeppenfeld, *Organikum*; Johann Ambrosius Barth, Leipzig; Berlin, Heidelberg, 19nd edn., 1993, pp. 668 ff.

(2) E. M. Meyer, S. Gambarotta, C. Floriani, A. Chiesi-Villa and C. Guastini, *Organometallics* 1989, **8**, 1067.

(3) E. Zára-Kaczián, G. Deák and L. György, *Acta Chim. Hung.* 1989, **126**, 441.

(4) US Pat. 2, 798, 075 (1957); *Chem Abstr.* 1958, **52**, 4494.

(5) A. Sachse, L. Penkova, G. Noel, S. Dechert, I. O. Fritsky, O. A. Varzatskii, and F. Meyer, *Synthesis*, submitted

(6) G. Cahiez, C. Chaboche, F. Mahuteau-Betzer and M. Ahr, *Org. Lett.* 2005, **7**, 1943.

Spectra

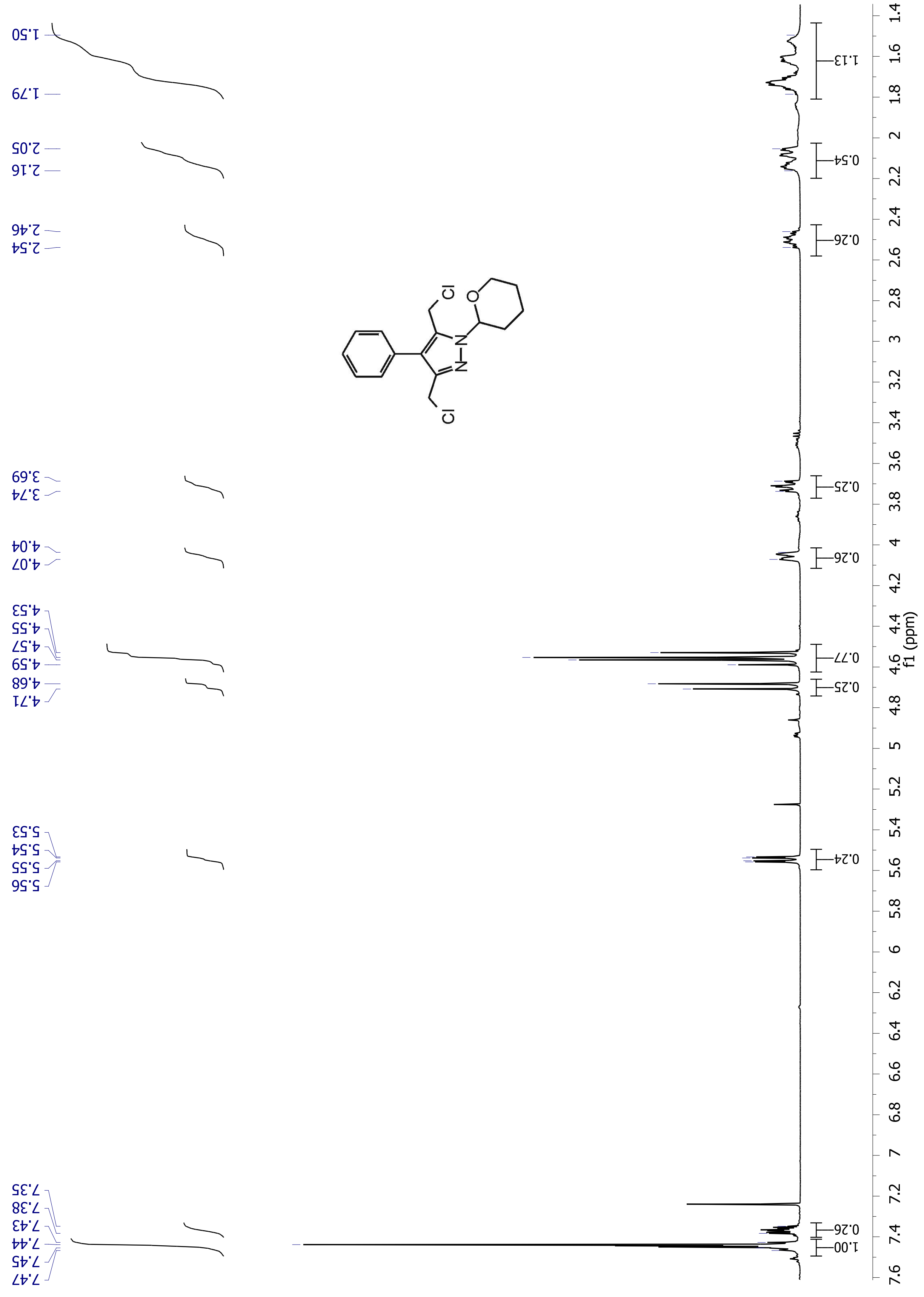

Figure S1: ^{1}H NMR spectrum of **1** in $CDCl_3$ (500.13 MHz)

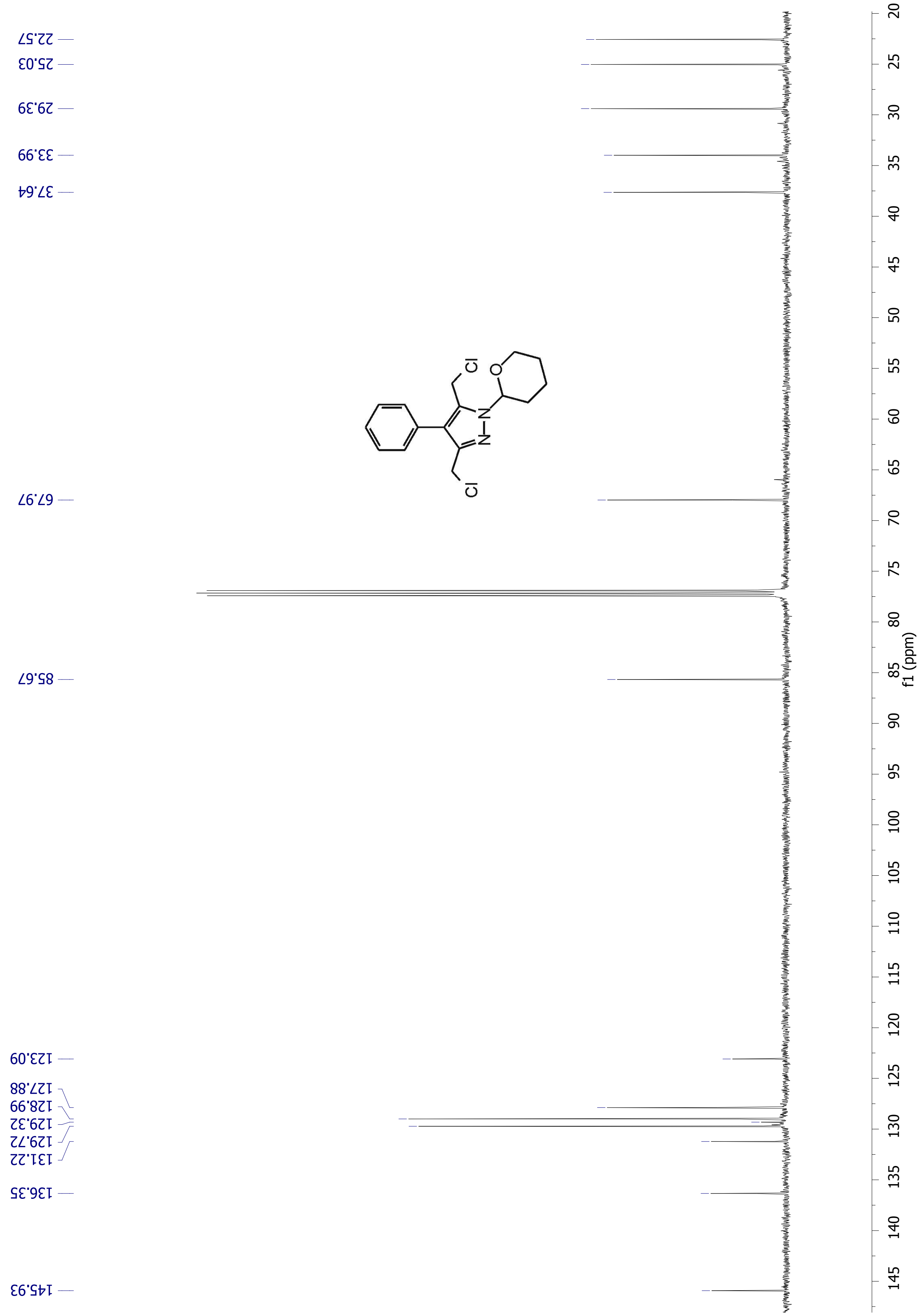

Figure S2: ^{13}C NMR spectrum of **1** in $CDCl_3$ (125.77 Hz)

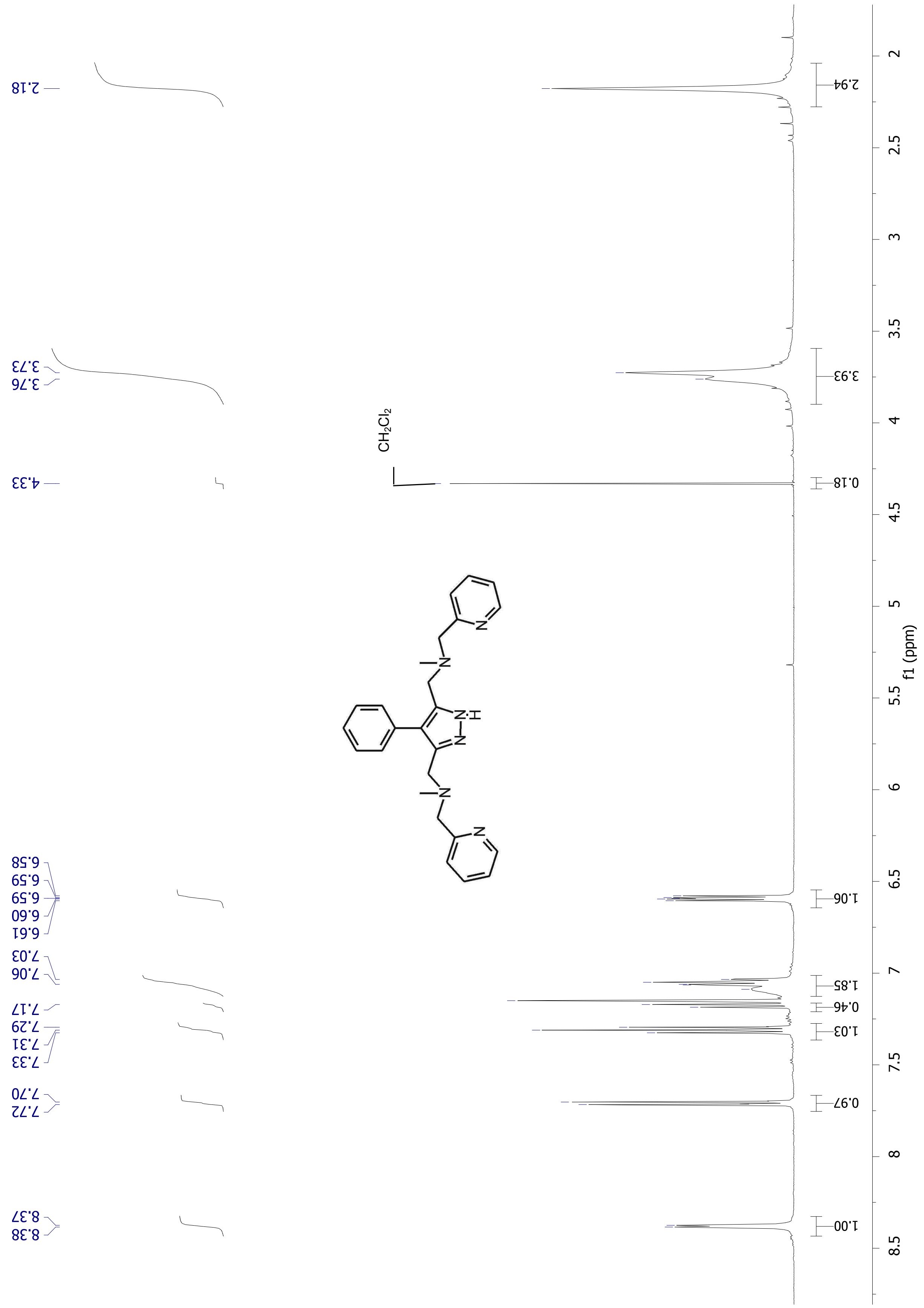

Figure S3: ^{1}H NMR spectrum of **2** in C_6D_6 (500.13 Hz)

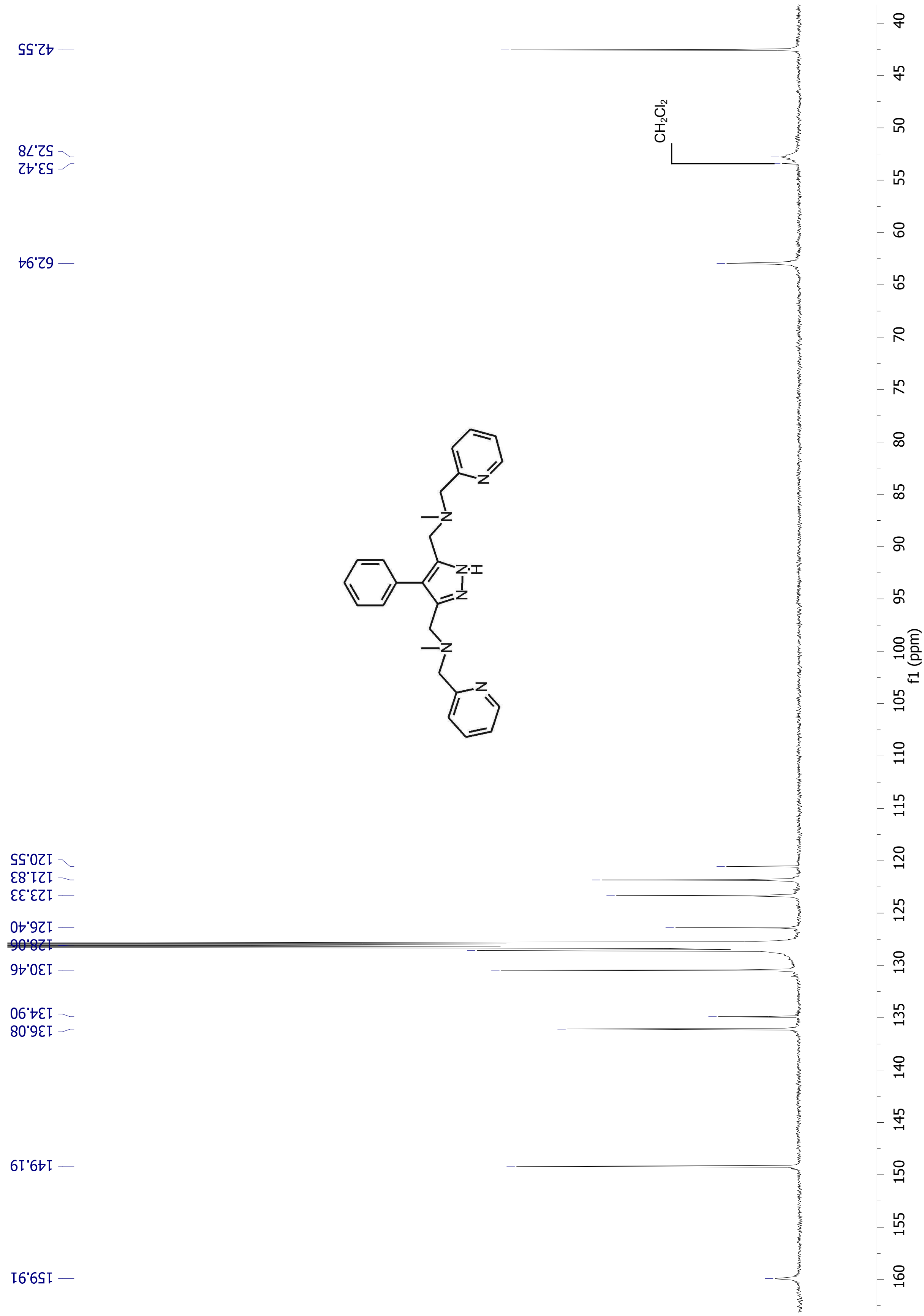

Figure S4: ^{13}C NMR spectrum of **2** in C_6D_6 (125.77 Hz)

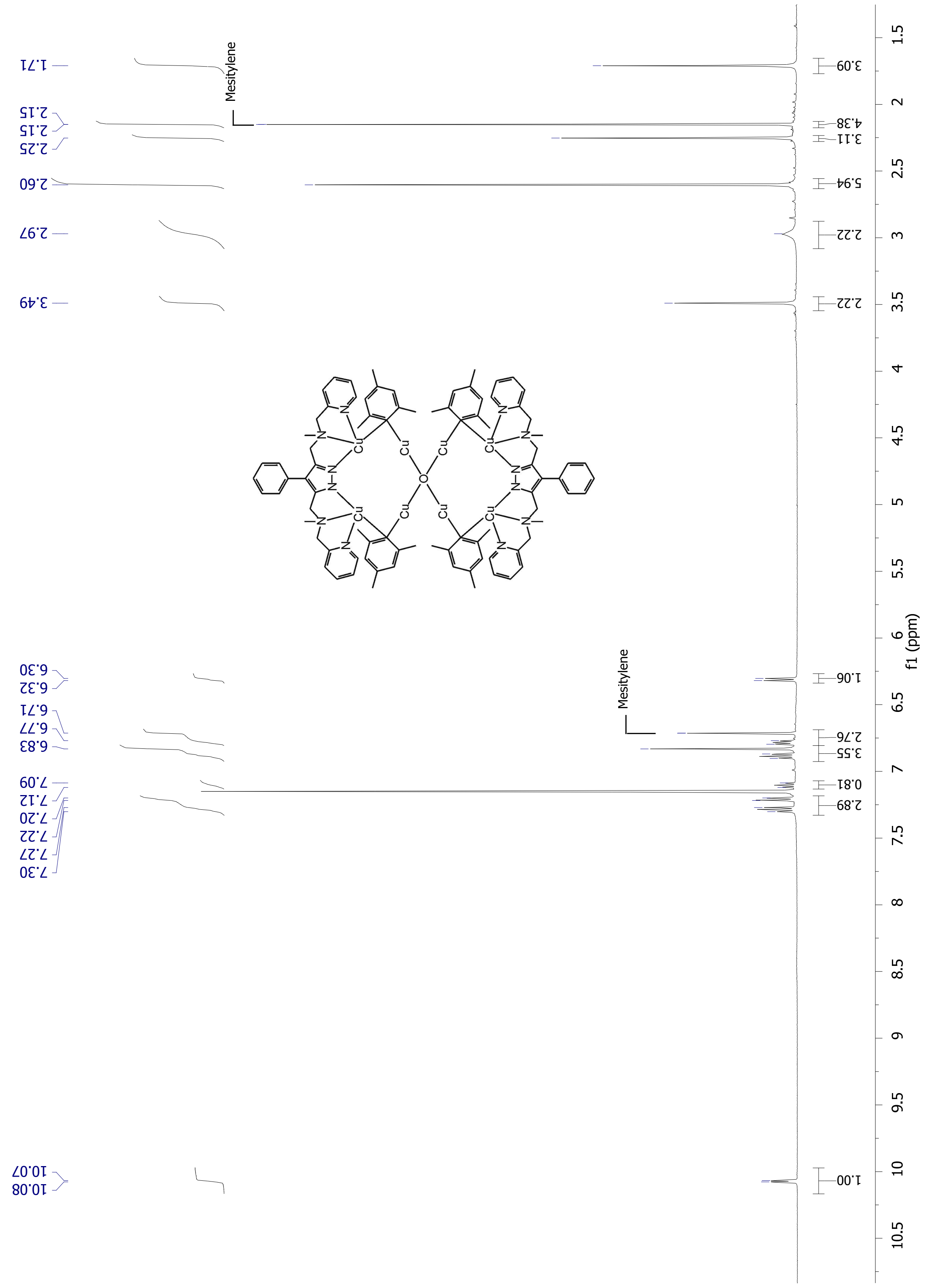

Figure S5: ^{1}H NMR spectrum of **3** in C_6D_6 (500.13 Hz)

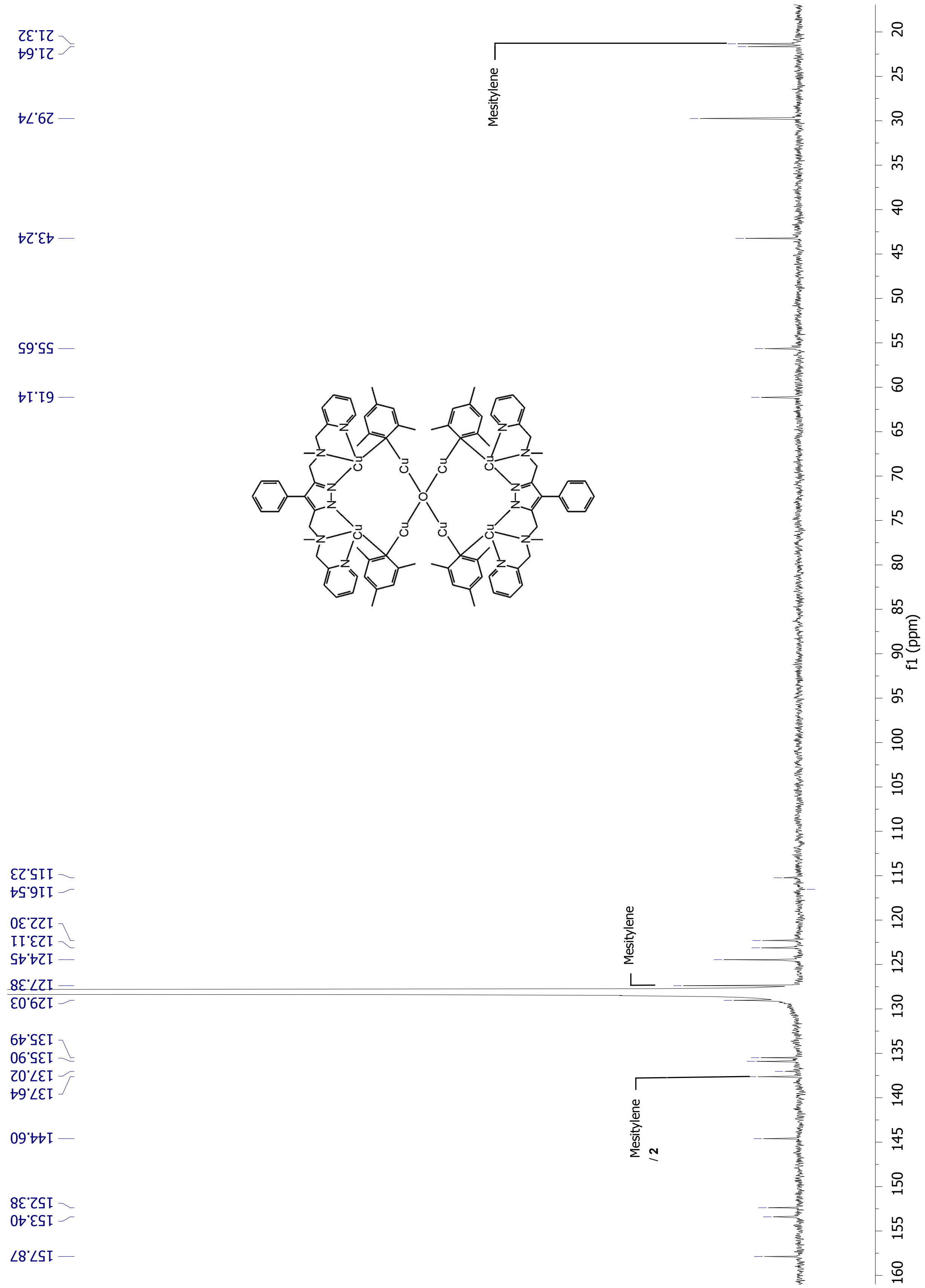

Figure S6: ^{13}C NMR spectrum of **3** in C_6D_6 (125.77 Hz)

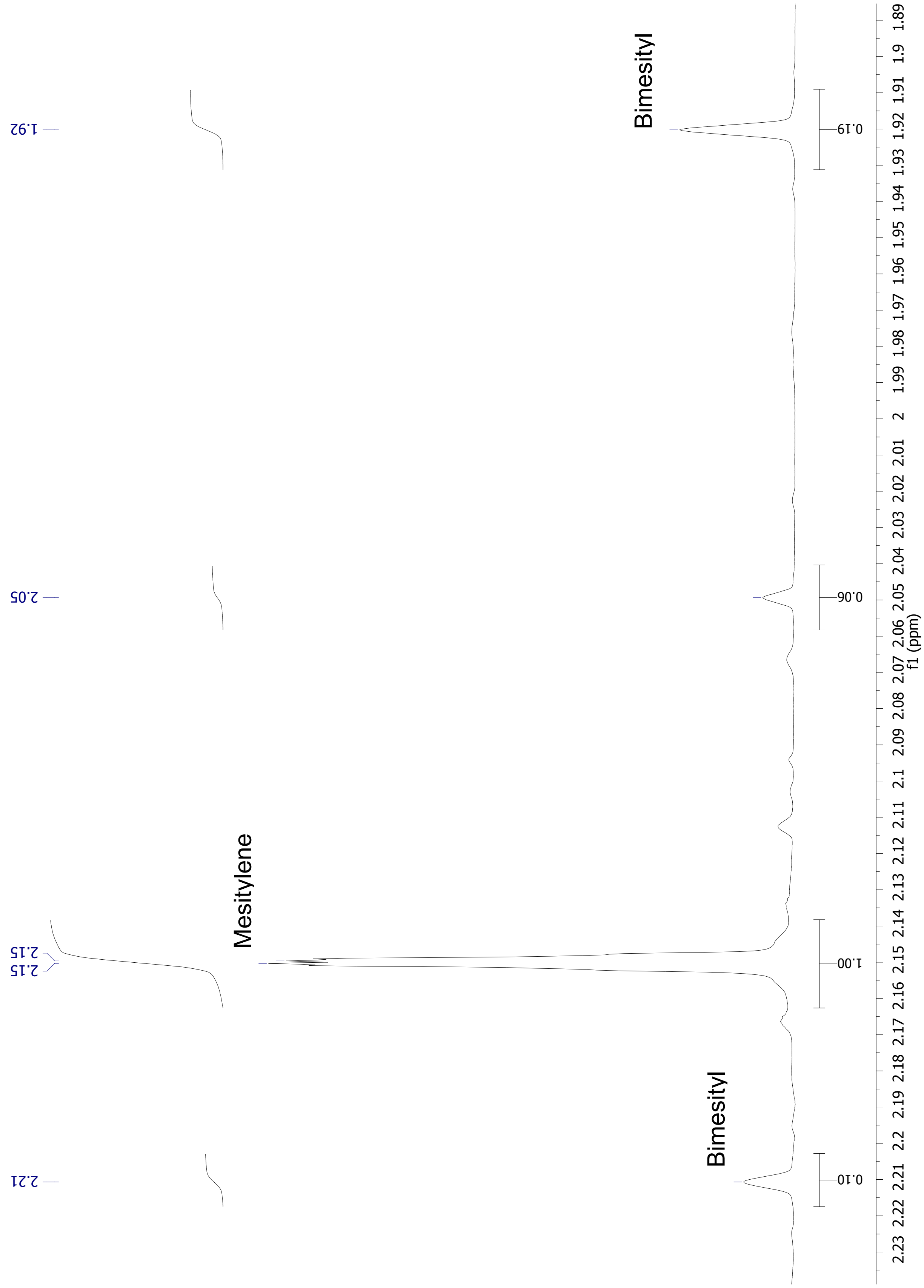

Figure S7: ^{1}H NMR spectrum of the residue of the pentane filtrate in C_6D_6 (500.13 Hz, selected region)

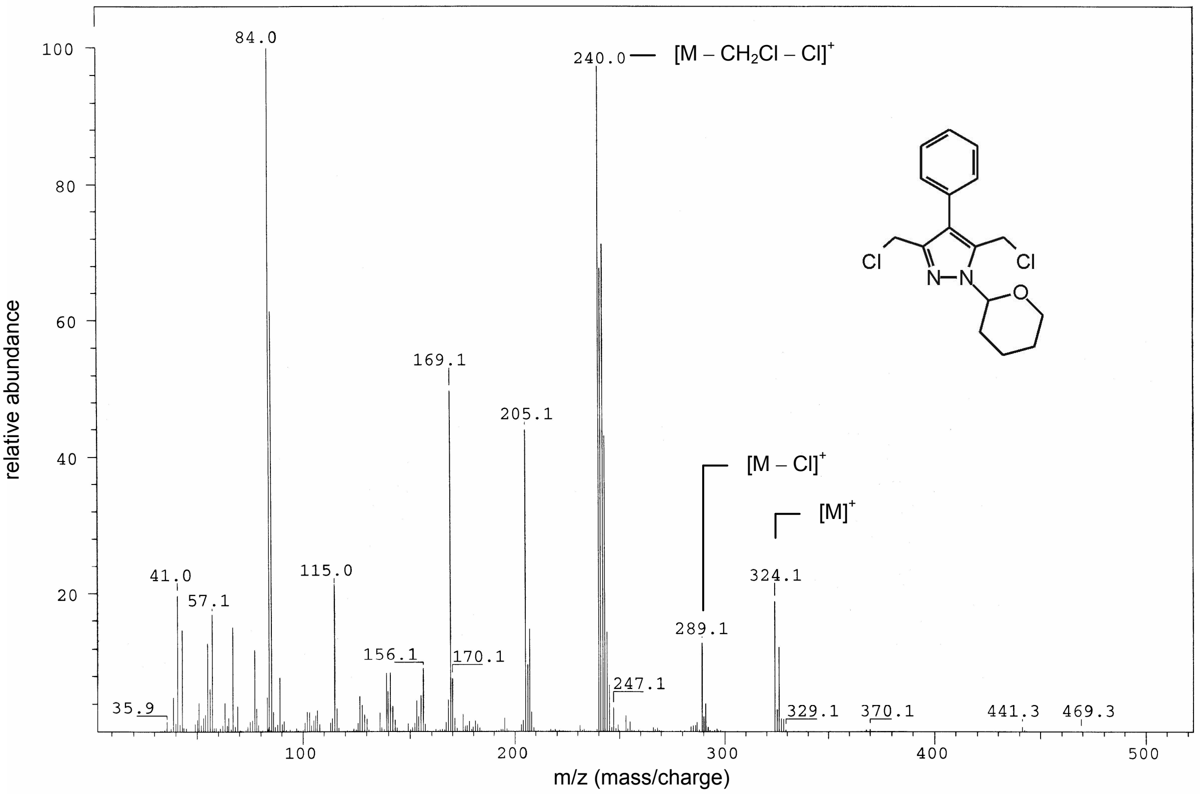

Figure S8: EI mass spectrum of **1**

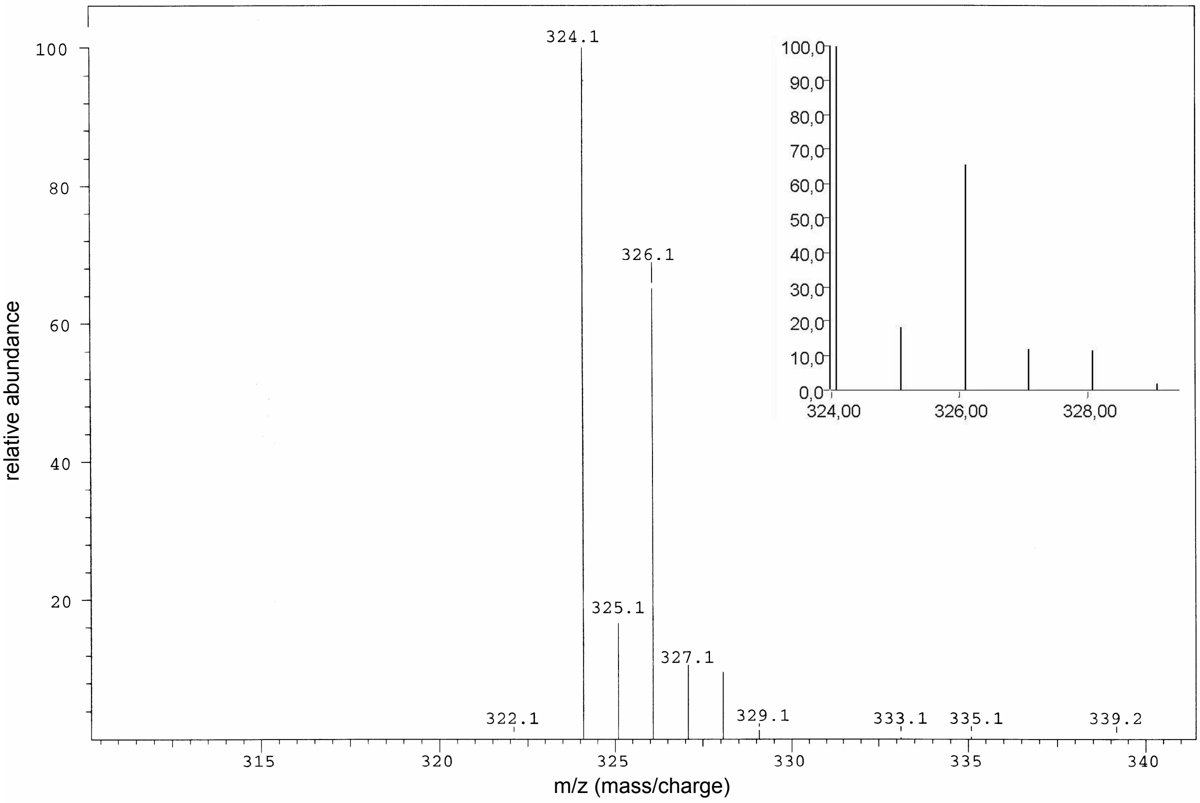

Figure S9: EI mass spectrum of **1** (selected region of the molecular peak; inset shows the simulated isotope pattern)

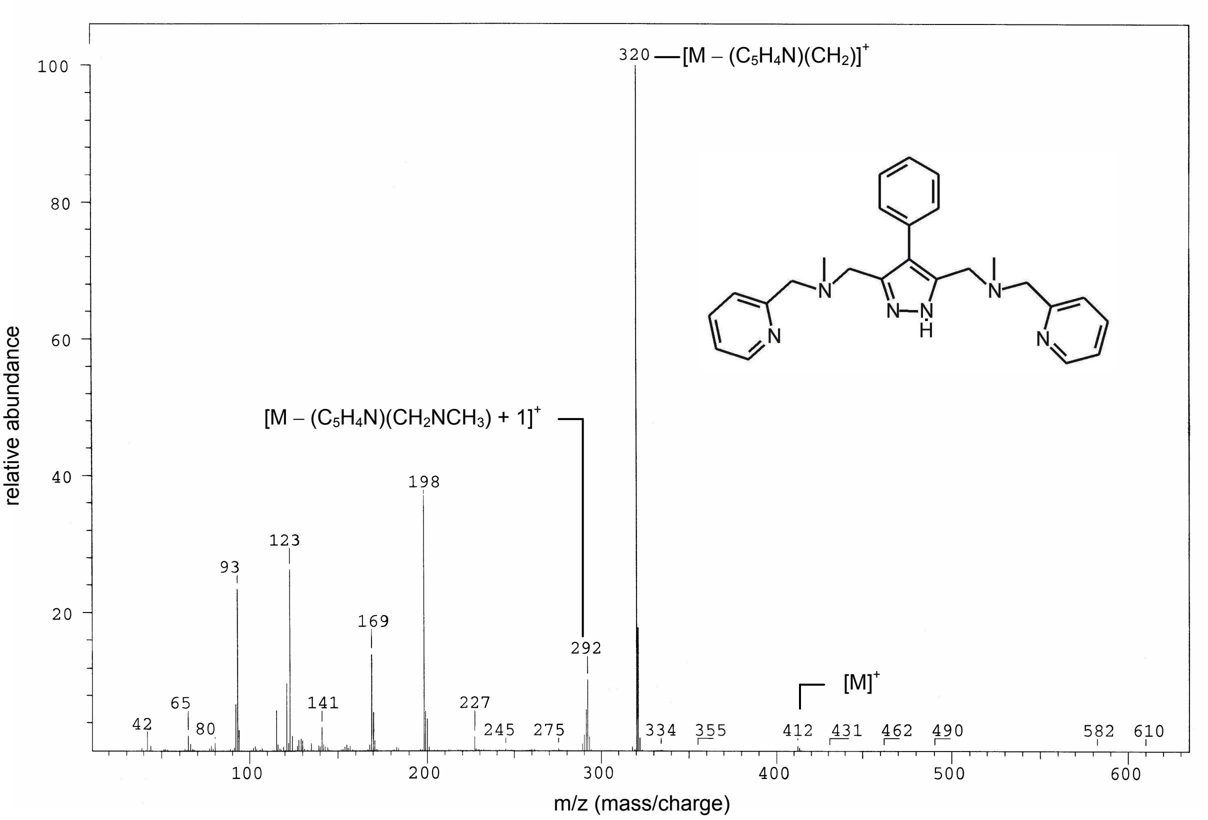

Figure S10: EI mass spectrum of **2**

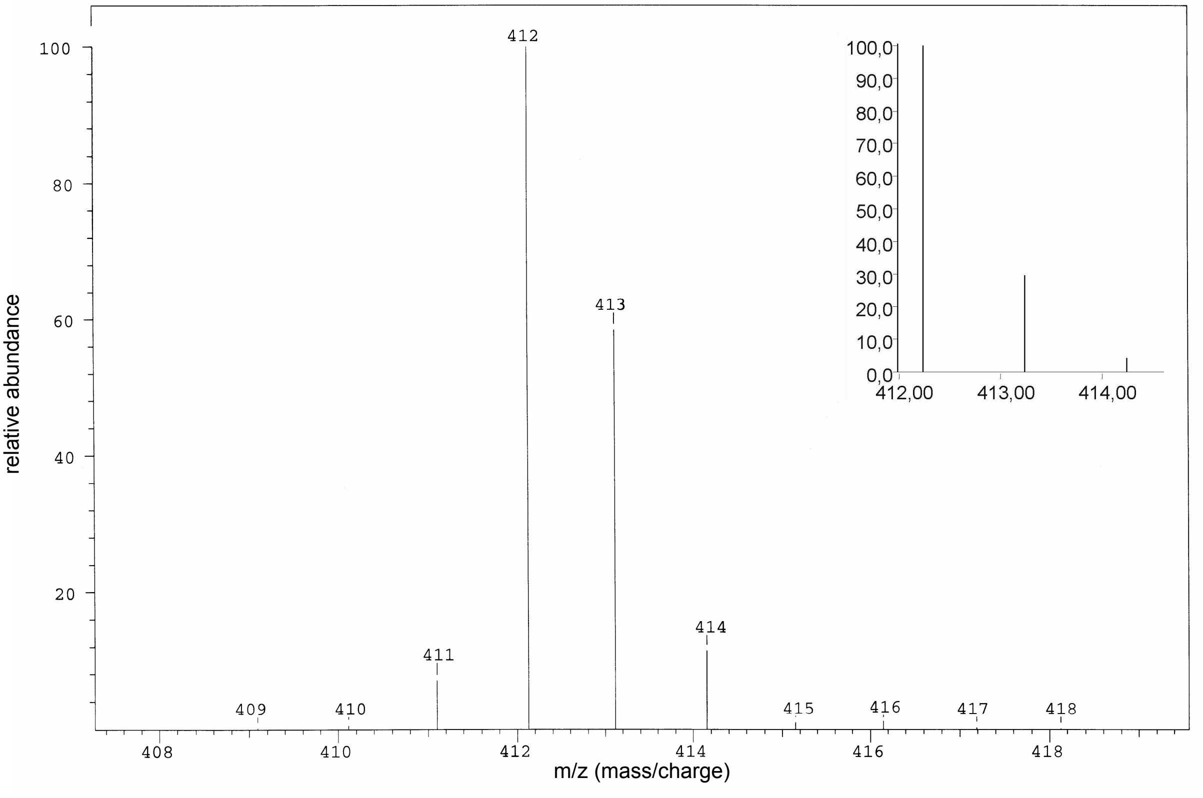

Figure S11: EI mass spectrum of **2** (selected region of the molecular peak; inset shows the simulated isotope pattern)

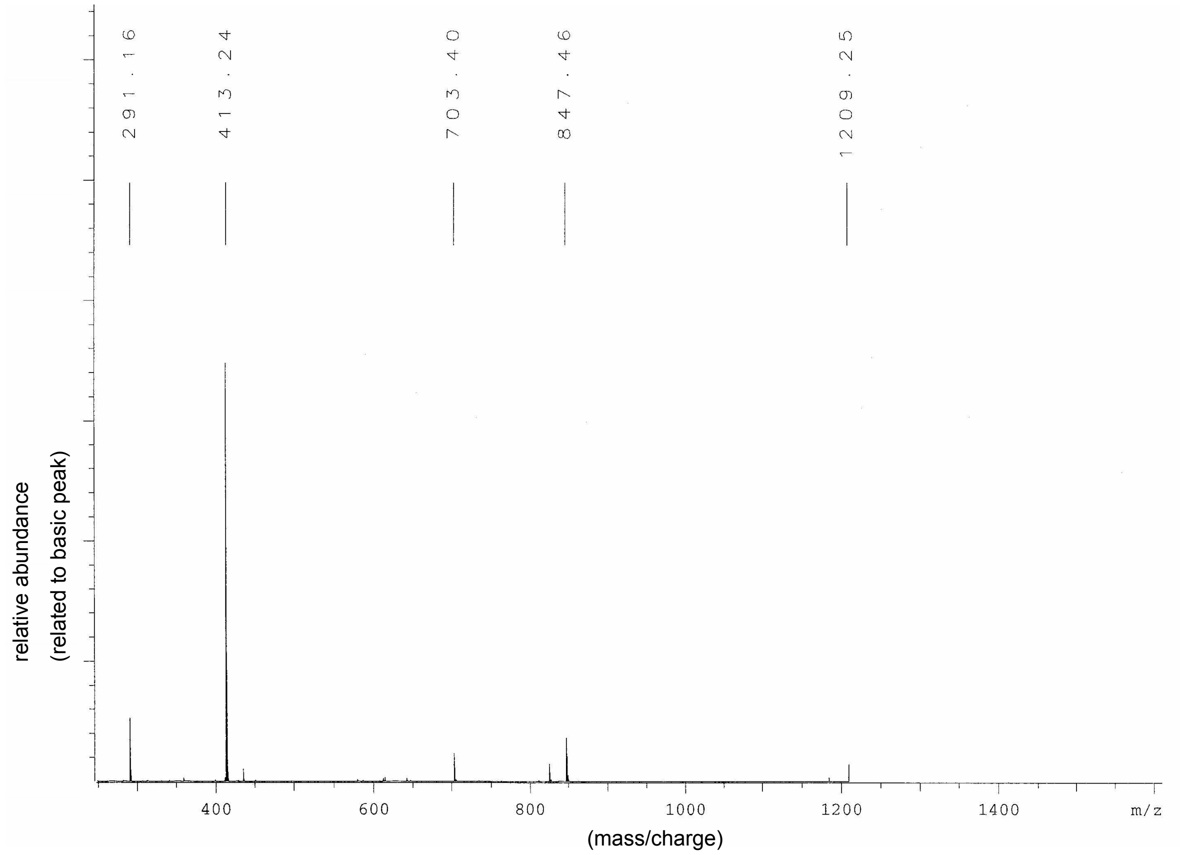

Figure S12: HRESI(+) mass spectrum of **2** in MeOH/NH_4OAc

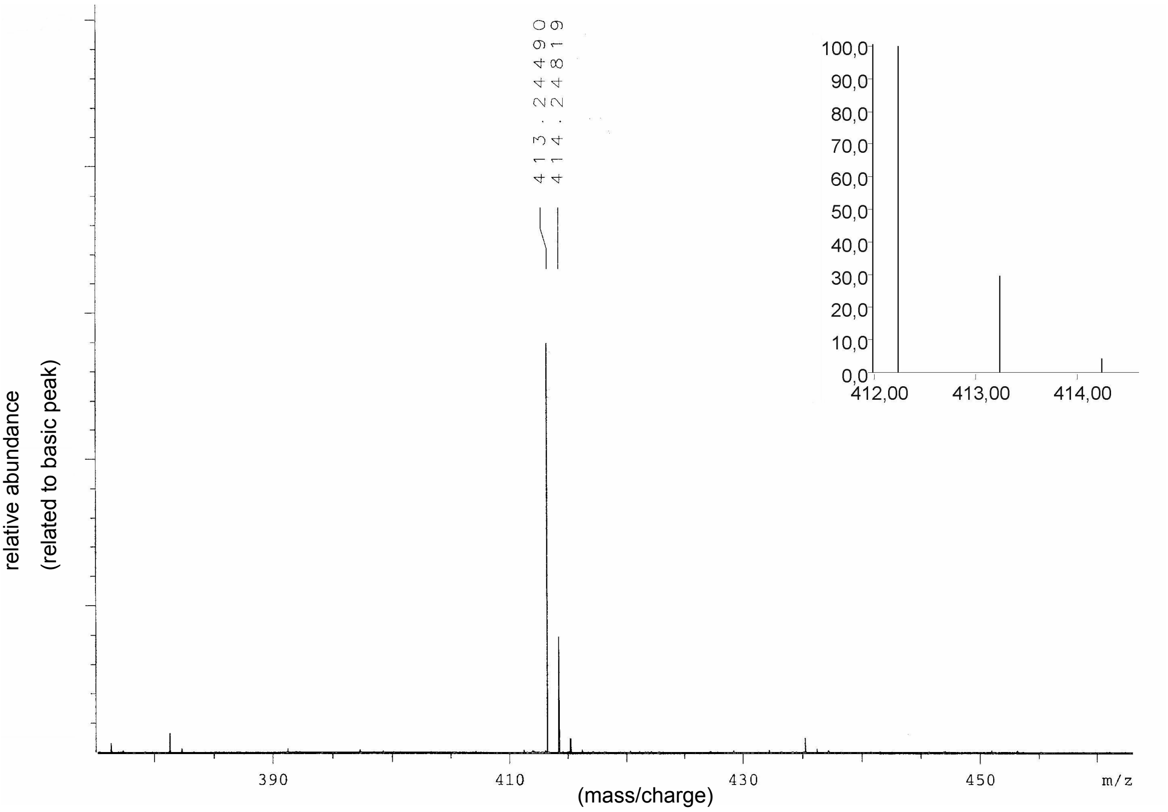

Figure S13: HRESI(+) mass spectrum of **2** in MeOH/NH_4OAc (selected region of the molecular peak; inset shows the simulated isotope pattern)

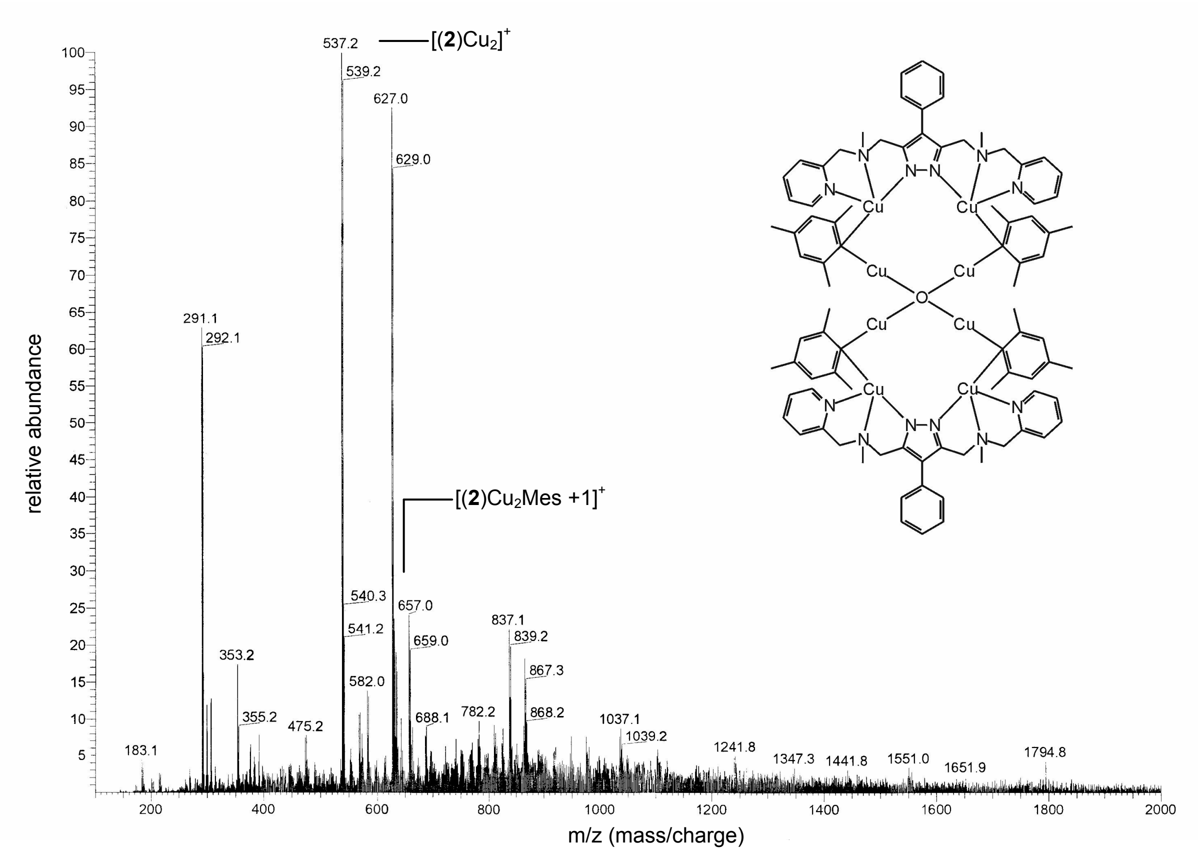

Figure S14: ESI(+) mass spectrum of **3** in THF

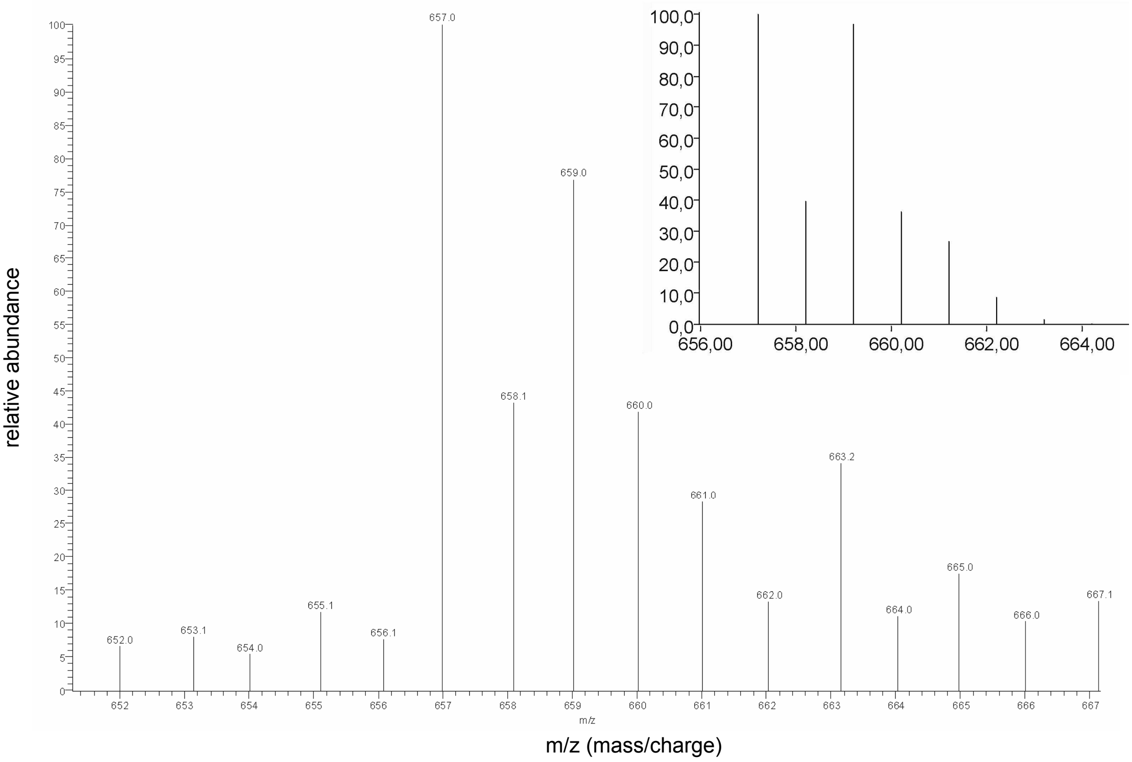

Figure S15: ESI(+) mass spectrum of **3** in THF (selected region of the fragment $[(\mathbf{2})Cu_2Mes +1]^+$; inset shows the simulated isotope pattern)

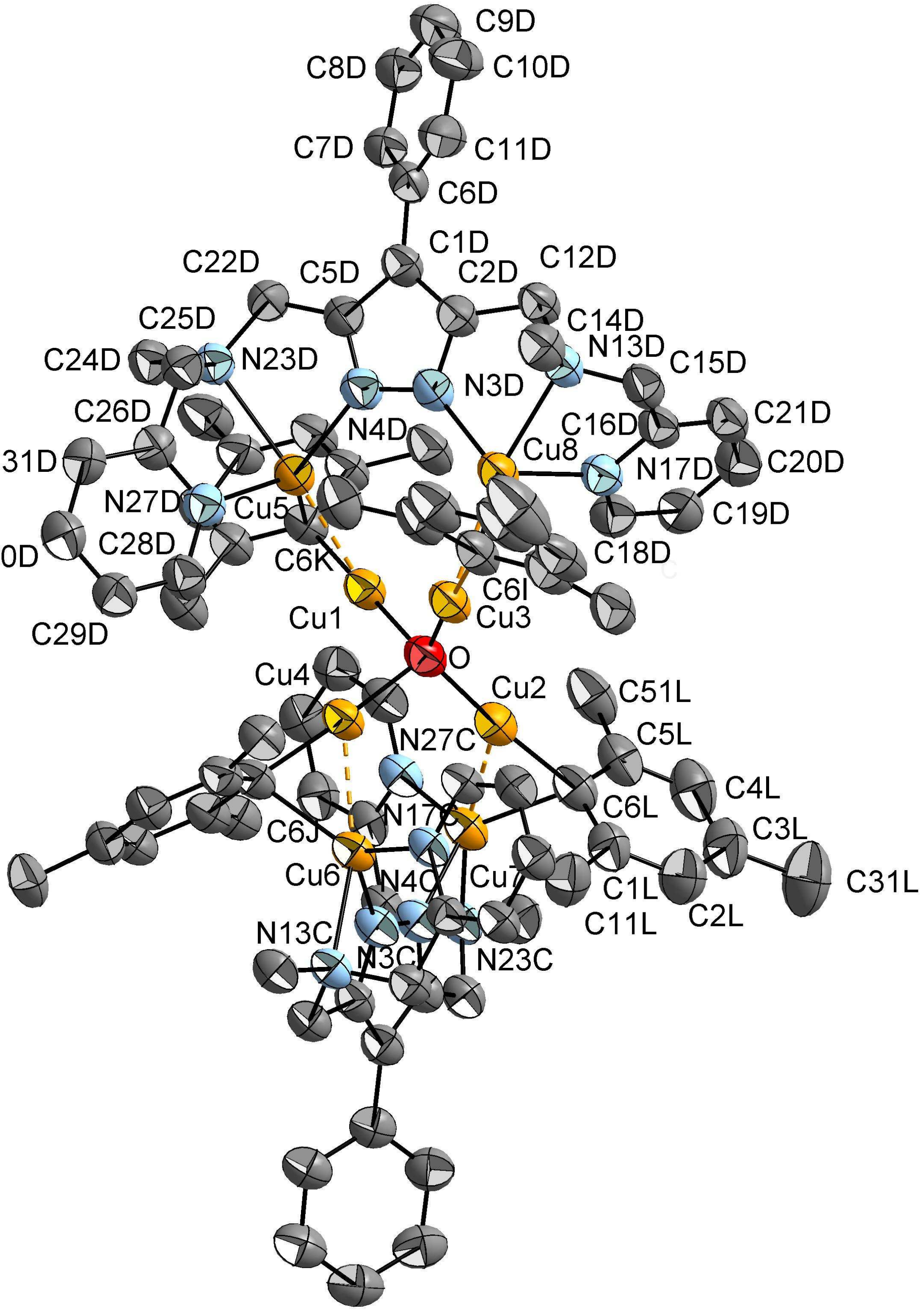

Figure S16: Molecular structure in the solid state of one (**A**) of the two independent molecules present in the single crystals of **3** with the corresponding atom labels. Hydrogen atoms are omitted for clarity. Anisotropic displacement ellipsoids are of 50% probability.

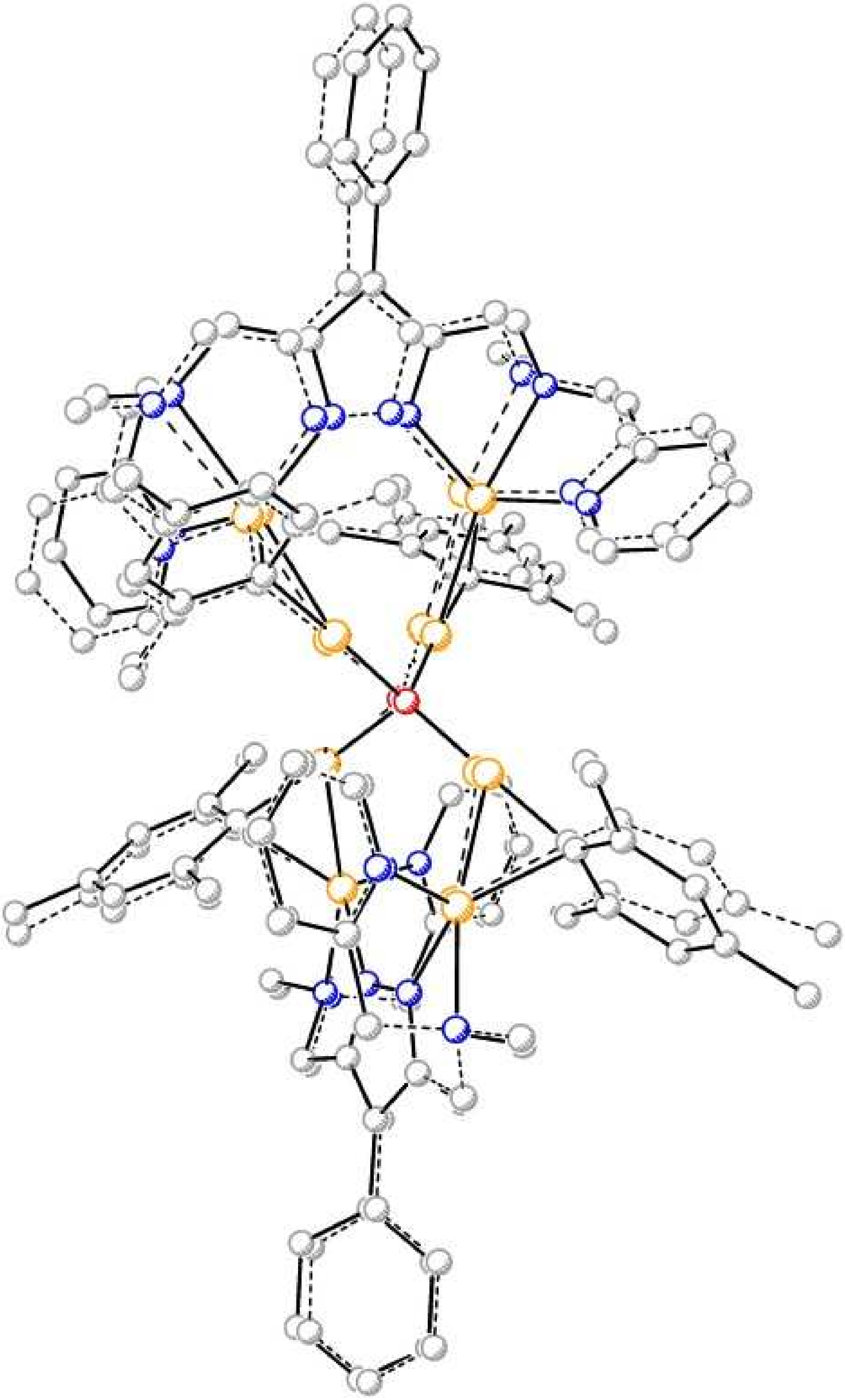

Figure S17: Overlay of both independent molecules (**A** and **B**) present in the single crystals of **3**.

Table 1: Selected bond distances (in Å) of **3** (left: **A**, right: **B**) including the corresponding labels with respect to the both overlaid independent molecules depicted in **Fig. S17**.

Cu1–O1	1.854(5)	Cu4’–O1’	1.851(5)
Cu2–O1	1.848(5)	Cu2’–O1’	1.836(4)
Cu3–O1	1.843(5)	Cu1’–O1’	1.862(4)
Cu4–O1	1.860(4)	Cu3’–O1’	1.853(5)
Cu1–C6K	1.924(7)	Cu4’–C6E	1.936(8)
Cu2–C6L	1.913(8)	Cu2’–C6F	1.920(7)
Cu3–C6I	1.924(7)	Cu1’–C6H	1.930(6)
Cu4–C6J	1.918(6)	Cu3’–C6G	1.919(7)
Cu5–C6K	2.115(7)	Cu7’–C6E	2.175(6)
Cu6–C6J	2.149(7)	Cu6’–C6G	2.133(7)
Cu7–C6L	2.157(7)	Cu8’–C6F	2.104(7)
Cu8–C6I	2.104(7)	Cu5’–C6H	2.149(7)
Cu1–Cu5	2.4481(15)	Cu4’–Cu7’	2.4409(14)
Cu2–Cu7	2.4243(14)	Cu2’–Cu8’	2.4073(13)
Cu3–Cu8	2.4064(13)	Cu1’–Cu5’	2.4358(13)
Cu4–Cu6	2.4357(13)	Cu3’–Cu6’	2.4501(15)
Cu5–N4D	1.986(5)	Cu7’–N4A	1.997(5)
Cu5–N23D	2.387(5)	Cu7’–N23A	2.347(6)
Cu5–N27D	2.039(5)	Cu7’–N27A	2.064(6)
Cu6–N3C	1.982(6)	Cu6’–N4B	2.005(5)
Cu6–N13C	2.323(5)	Cu6’–N23B	2.355(6)
Cu6–N17C	2.072(5)	Cu6’–N27B	2.050(6)
Cu7–N4C	2.018(5)	Cu8’–N3B	1.958(6)
Cu7–N23C	2.370(5)	Cu8’–N13B	2.297(5)
Cu7–N27C	2.082(6)	Cu8’–N17B	2.085(6)
Cu8–N3D	1.962(6)	Cu5’–N3A	1.991(6)
Cu8–N13D	2.323(5)	Cu5’–N13A	2.317(5)
Cu8–N17D	2.090(6)	Cu5’–N17A	2.062(5)

Table 2: Selected bond angles (in °) of **3** (left: **A**, right: **B**) including the corresponding labels with respect to the both overlaid independent molecules depicted in **Fig. S17**.

Cu1–O1–Cu2	124.6(3)	Cu4’–O1’–Cu2’	112.8(2)
Cu1–O1–Cu3	104.2(2)	Cu4’–O1’–Cu1’	106.1(2)
Cu1–O1–Cu4	94.75(19)	Cu4’–O1’–Cu3’	131.9(3)
Cu3–O1–Cu4	105.2(2)	Cu1’–O1’–Cu3’	94.7(2)
O1–Cu1–C6K	174.0(3)	O1’–Cu4’–C6E	176.8(3)
O1–Cu3–C6I	175.3(3)	O1’–Cu1’–C6H	175.8(3)
O1–Cu4–C6J	176.4(3)	O1’–Cu3’–C6G	170.4(3)
O1–Cu2–C6L	175.6(2)	O1’–Cu2’–C6F	175.0(3)
Cu1–C6K–Cu5	74.5(2)	Cu4’–C6E–Cu7’	72.6(2)
Cu3–C6I–Cu8	73.2(2)	Cu1’–C6H–Cu5’	73.1(2)
Cu2–C6L–Cu7	72.8(3)	Cu2’–C6F–Cu8’	73.3(3)
Cu4–C6J–Cu6	73.3(2)	Cu3’–C6G–Cu6’	74.2(2)
N4D–Cu5–N23D	76.2(2)	N4A–Cu7’–N23A	76.2(2)
N4D–Cu5–N27D	117.8(2)	N4A–Cu7’–N27A	116.6(2)
N3C–Cu6–N13C	77.4(2)	N4B–Cu6’–N23B	76.2(2)
N3C–Cu6–N17C	117.4(2)	N4B–Cu6’–N27B	115.0(2)
N4C–Cu7–N23C	75.3(2)	N3B–Cu8’–N13B	78.8(2)
N4C–Cu7–N27C	116.2(2)	N3B–Cu8’–N17B	110.6(2)
N3D–Cu8–N13D	79.0(2)	N3A–Cu5’–N13A	76.81(19)
N3D–Cu8–N17D	108.7(2)	N3A–Cu5’–N17A	117.2(2)
Cu1–Cu5–N23D	157.31(14)	Cu4’–Cu7’–N23A	165.97(13)
Cu2–Cu7–N23C	167.75(12)	Cu2’–Cu8’–N13B	159.59(14)
Cu3–Cu8–N13D	159.95(15)	Cu1’–Cu5’–N13A	164.00(15)
Cu4–Cu6–N13C	163.72(14)	Cu3’–Cu6’–N23B	157.82(15)