Electronic Supplementary Material (ESI) for Analyst.

C-H oxidation and chelation of a dipyrromethane mediated rapid colorimetric naked-eye Cu(II) chemosensor

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General information

^{1}H NMR (300 MHz) spectra were recorded using a Bruker-300-AVANCE II spectrometer, with chloroform-d as the solvent and tetramethylsilane (TMS) as the reference (δ = 0 ppm). The chemical shifts are expressed in δ downfield from the signal of internal TMS. Analytical thin layer chromatographic tests were carried out on aluminium sheets coated with silica gel GF provided by Merck. Column chromatography was carried out using silica gel (230–400 mesh). All yields reported are of isolated materials judged to be homogeneous using TLC, and NMR spectroscopy.

Loading of amino acid on solid support

Amino acid (1.0 mmol) and the solid support (to a total weight of 1.0 g) were taken in a mortar and pestle and hand pulverized for 2–3 min. The content was used as catalyst in DPM synthesis.

General procedure for synthesis of dipyrromethanes

A solution of aldehyde (0.50 mmol), 2,4-dimethylpyrrole (1.5 mmol, 0.16 mL) in dichloromethane (5.0 mL) was treated with glycine@support (50 μmol, 50 mg, 10 mol%) for 30 min at room temperature under N_2 atmosphere. Then, the reaction mixture was filtered, washed with dichloromethane (5 mL) and the catalyst was recovered as a residual fraction for reuse. The filtrate was concentrated by rotary evaporation under reduced pressure and the resulting mixture was purified by column chromatography to obtain 5-aryl-2,4,6,8-tetramethyldipyrromethanes. The product was characterized by ^{1}H NMR spectroscopy.

2,4,6,8-Tetramethyl-5-phenyldipyrromethane 1: (100 mg, 72% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 1.82 (s, 6H), 2.15 (s, 6H), 5.44 (s, 1H), 5.71 (d, J = 2.4 Hz, 2H), 7.14-7.34 (m, 7H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.0, 13.1, 40.6, 108.5, 115.0, 125.5, 126.1, 126.5, 128.3, 128.6, 128.7, 142.3.

5-(4-Chlorophenyl)-2,4,6,8-tetramethyl-dipyrromethane 2: (98 mg, 63% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 1.81 (s, 6H), 2.16 (s, 6H), 5.41 (s, 1H), 5.71 (d, J = 2.7 Hz, 2H), 7.08 (d, J =

8.1 Hz, 2H), 7.17 (br s, 2H), 7.27 (d, J = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.0, 13.1, 40.0, 108.7, 115.2, 125.5, 125.7, 128.8, 129.7, 132.3, 140.8.

5-(4-Methoxyphenyl)-2,4,6,8-tetramethyldipyrromethane 3: (95 mg, 62% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 1.82 (s, 6H), 2.15 (s, 6H), 3.79 (s, 3H), 5.38 (s, 1H), 5.70 (d, J = 2.4 Hz, 2H), 6.84 (d, J = 8.7 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 7.19 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 13.2, 14.8, 57.4, 109.3, 112.2, 121.4, 132.9, 143.0, 145.1, 155.1, 157.0.

2,4,6,8-Tetramethyl-5-(2-nitrophenyl)dipyrromethane 4: (113 mg, 70% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 1.75 (s, 6H), 2.16 (s, 6H), 5.69 (d, J = 2.4 Hz, 2H), 6.12 (s, 1H), 7.18 (dd, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 1H), 7.32 (br s, 2H), 7.37 (td, J_1 = 7.8 Hz, J_2 = 1.2 Hz, 2H), 7.50 (td, J_1 = 7.5 Hz, J_2 = 1.5 Hz, 2H), 7.82 (dd, J_1 = 7.8 Hz, J_2 = 1.5 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 10.9, 13.1, 36.8, 108.9, 115.7, 123.9, 124.9, 126.2, 127.5, 130.5, 132.7, 137.3, 149.3.

2,4,6,8-Tetramethyl-5-(3-nitrophenyl)dipyrromethane 5: (119 mg, 74% yield); ^{1}H NMR (300 MHz, $CDCl_3$) 1.81 (s, 6H), 2.17 (s, 6H), 5.34 (s, 1H), 5.73 (d, J = 2.4 Hz, 2H), 7.22 (br s, 2H), 7.47-7.51 (m, 2H), 8.02 (br s, 1H), 8.06-8.11 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.1, 13.1, 40.4, 109.0, 115.6, 121.8, 123.1, 124.4, 126.4, 129.5, 134.5, 144.9, 148.7.

2,4,6,8-Tetramethyl-5-(4-nitrophenyl)dipyrromethane 6: (121 mg, 75% yield) ^{1}H NMR (300 MHz, $CDCl_3$) 1.81 (s, 6H), 2.17 (s, 6H), 5.53 (s, 1H), 5.73 (d, J = 2.4 Hz, 2H), 7.23 (br s, 2H), 7.31 (d, J = 8.4 Hz, 2H), 8.15 (d, J = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 11.1, 13.0, 40.6, 108.9, 115.7, 123.9, 124.4, 126.4, 129.1, 146.7, 150.2.

Colorimetric sensor study

Metal ion solutions for sensor studies were prepared by dissolving the requisite amount of metal salts in double distilled deionised water. For colorimetric detection of copper, 200 μM DPM solutions were prepared in HPLC grade acetonitrile. Sensor studies were performed by adding 15 μM of metal ions into 3 mL of DPM solution. The colorimetric changes and the change in the UV–vis absorption spectra were followed at room temperature. The photographs were taken with a digital camera after 5 min of mixing.

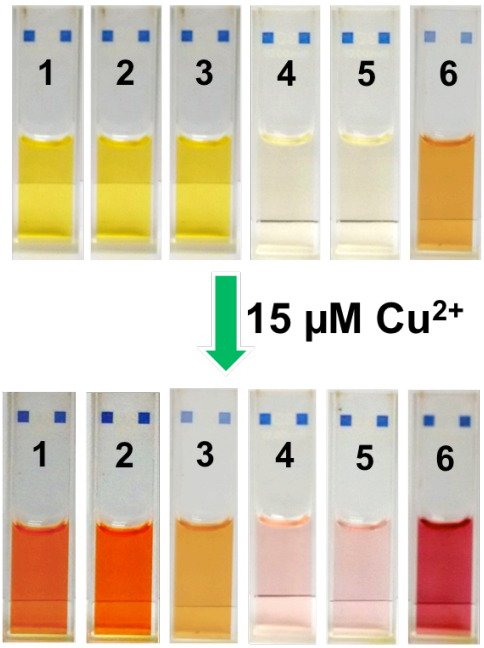


Fig. S-1: Addition of 15 μM Cu^{2+} to the synthesised dipyrromethanes 1-6

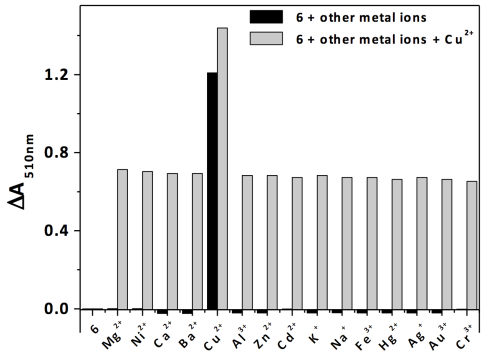


Fig. S-2: Interference study. Change in the absorbance of **6** at 510 nm in the presence of 5 μM of metal ions (black bar) and in the presence of 5 μM of metal ions + 5 μM of Cu^{2+} ions. Only Cu^{2+} produce changes in the absorbance spectra of **6**, indicating the high selectivity and specificity.

Isolation of 6-Cu complex

A solution of 2,4,6,8-tetramethyl-5-(4-nitrophenyl)dipyrromethane **6** (0.25 mmol, 81 mg) in MeCN (10 mL) was treated with an aqueous solution of $CuCl_2 \cdot 2H_2O$ (0.50 mmol, 85 mg, 1.0 mL water) and stirred for 12 h for complete complexation. Then, solvent was removed form the reaction mixture by rotary evaporation. The resulting residue was treated with dichloromethane (20 mL) and filtered. The filtrate was concentraed under reduced pressure and the resulting solid

(70 mg) was anlyzed by NMR spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$) 1.58 (br s, 12H), 6.39 (br s, 2H), 7.59 (br s, 2H), 8.36 (br s, 2H).

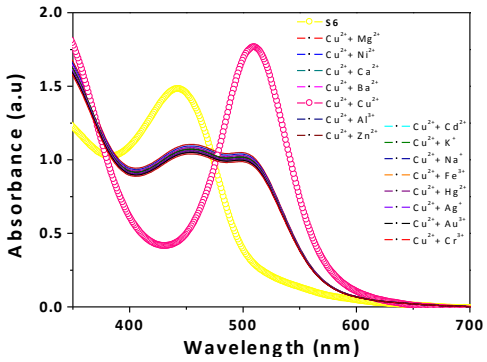


Fig. S-3: Selective sensing of Cu^{2+} ions in aCSF. Absorbance spectra of **6** measured in the prescence of mixture of 5 mM Cu^{2+} and 5 mM other metal ions. Irrespective of the presence of other metal cations **6** sense Cu^{2+} as evidenced by the absorbance peak at 510 nm.

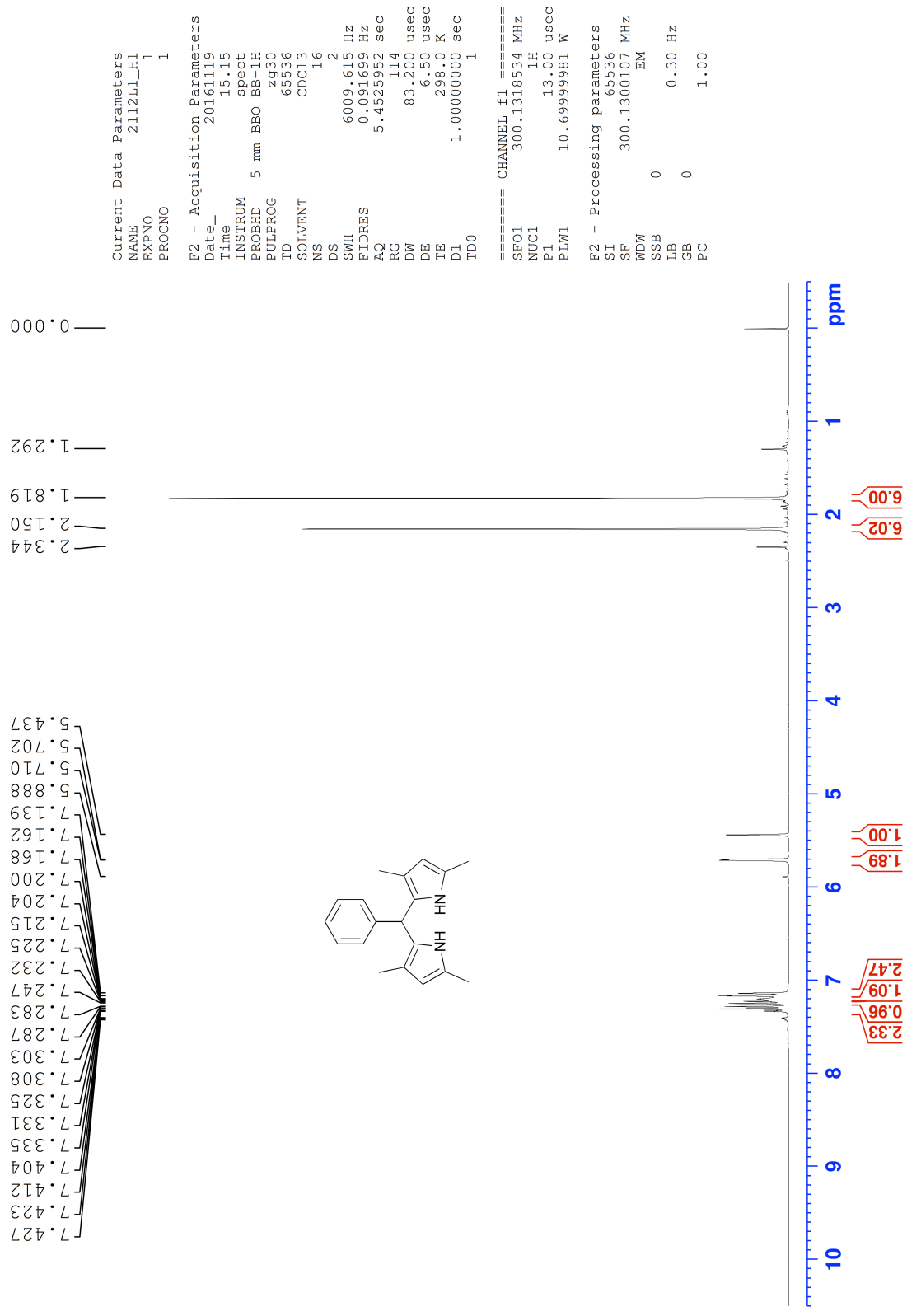
Determination of Cu^{2+} in tap water and artificial cerebrospinal fluid

In general, tap water contains a mixture of dissolved mineral matters and contributes to hardness and alkalinity. Tap water parameters used in this study were: pH -7.54; total hardness (as CaCO3 equivalent) – 168 ± 3.2 mg/L; chlorides – 68 ± 2 mg/L; total dissolved solid – 239 ± 5 mg/L. For colorimetric detection of Cu^{2+}, copper ions solutions was prepared in tap water and evaluated as describe above. For study in artificial cerebrospinal fluid, aCSF was prepared by dissolving 119 mM NaCl, 26.2 mM $NaHCO_3$, 2.5 mM KCl, 1 mM NaH_2PO_4, 1.3 mM $MgCl_2$ and 10 mM glucose. Sensor studies were performed by adding 15 μM of Cu^{2+} ions into aCSF solution and evaluated the colorimetric changes as described above.

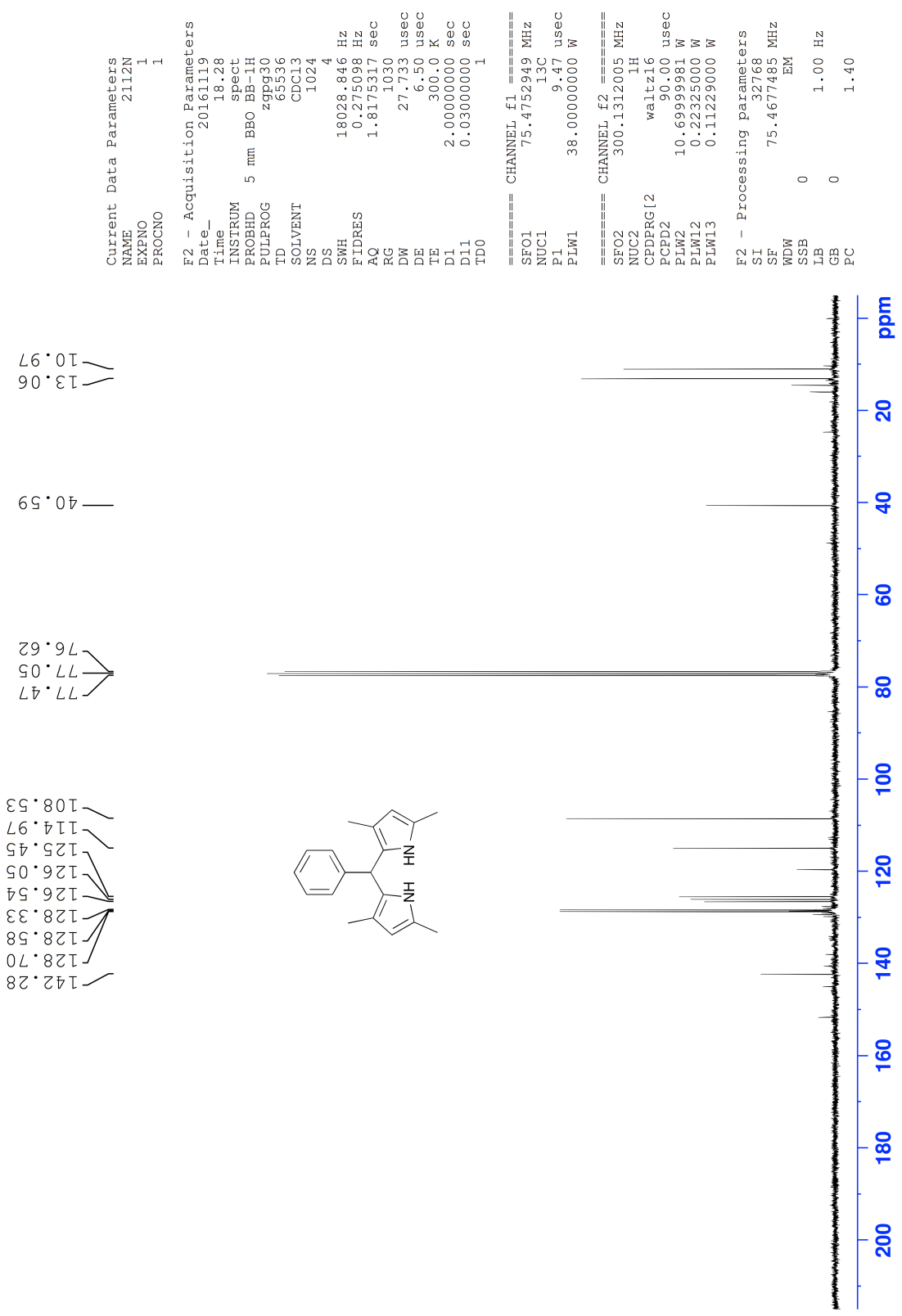
Recovery experiments

By using the above described procedure, we performed recovery experiments using tap water and aCSF spiked with 2, 4 and 6 μM of Cu^{2+} ions, respectively. The absorption measurements were performed at 510 nm. Then, using the linear regression equations, the concentration of Cu^{2+} ions in the samples was calculated. The final recovery values were determined by,

Recovery (%) = (estimated Cu^{2+} ions /added Cu^{2+} ions) × 100 (1)



^{1}H NMR spectrum of 2,4,6,8-tetramethyl-5-phenyldipyrromethane



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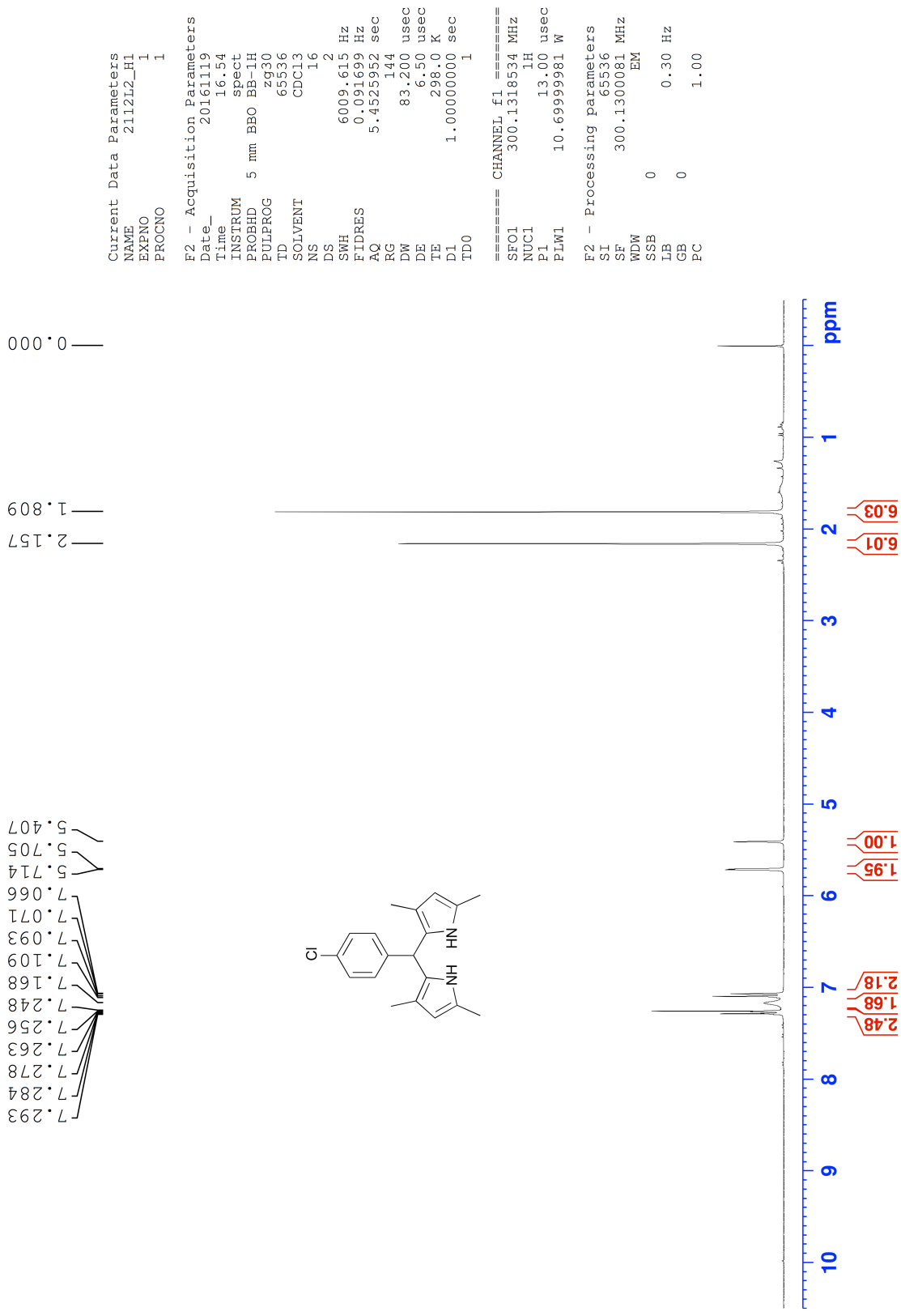
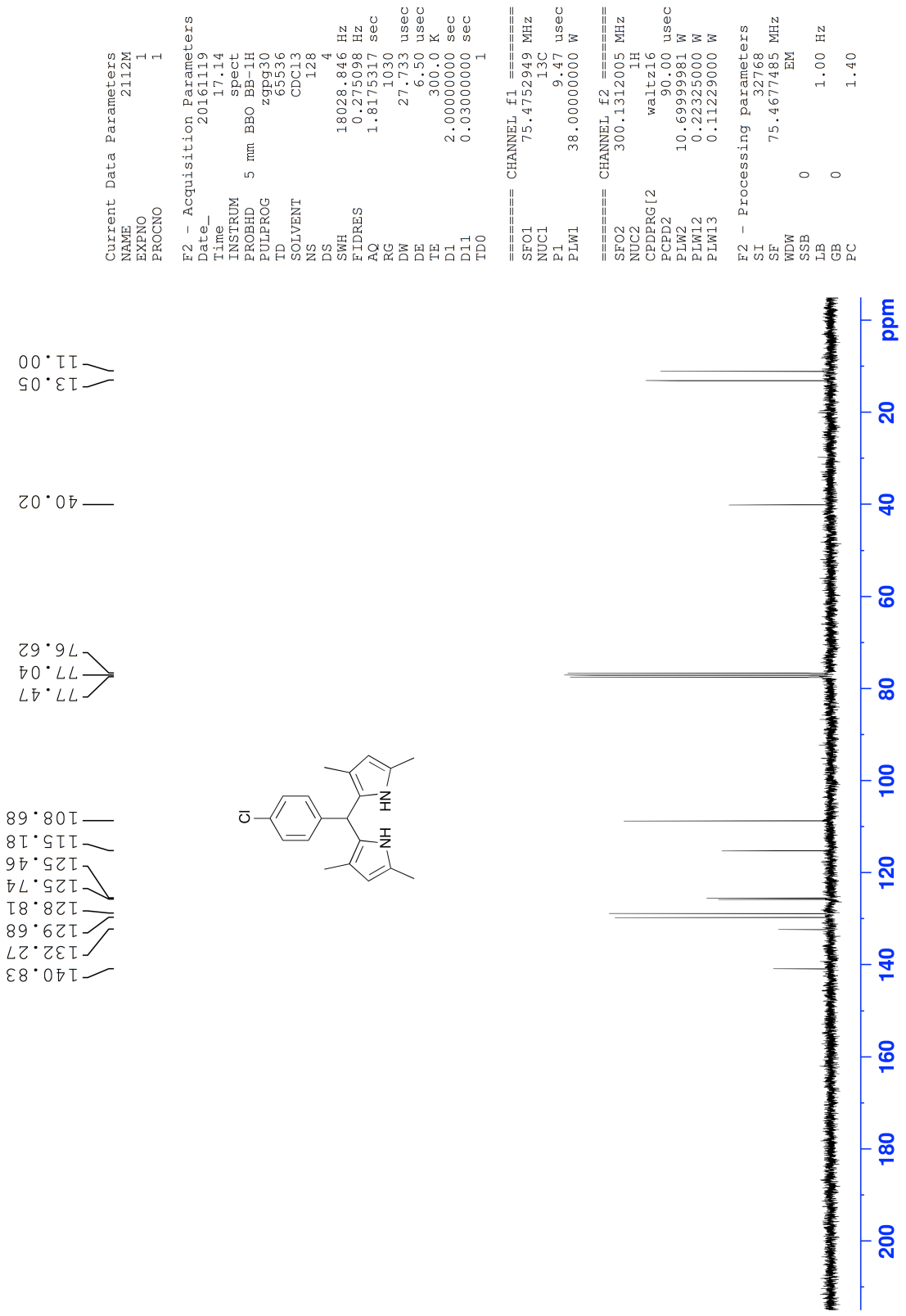


^{1}H NMR spectrum of 5-(4-chlorophenyl)-2,4,6,8-tetramethyl-dipyrromethane



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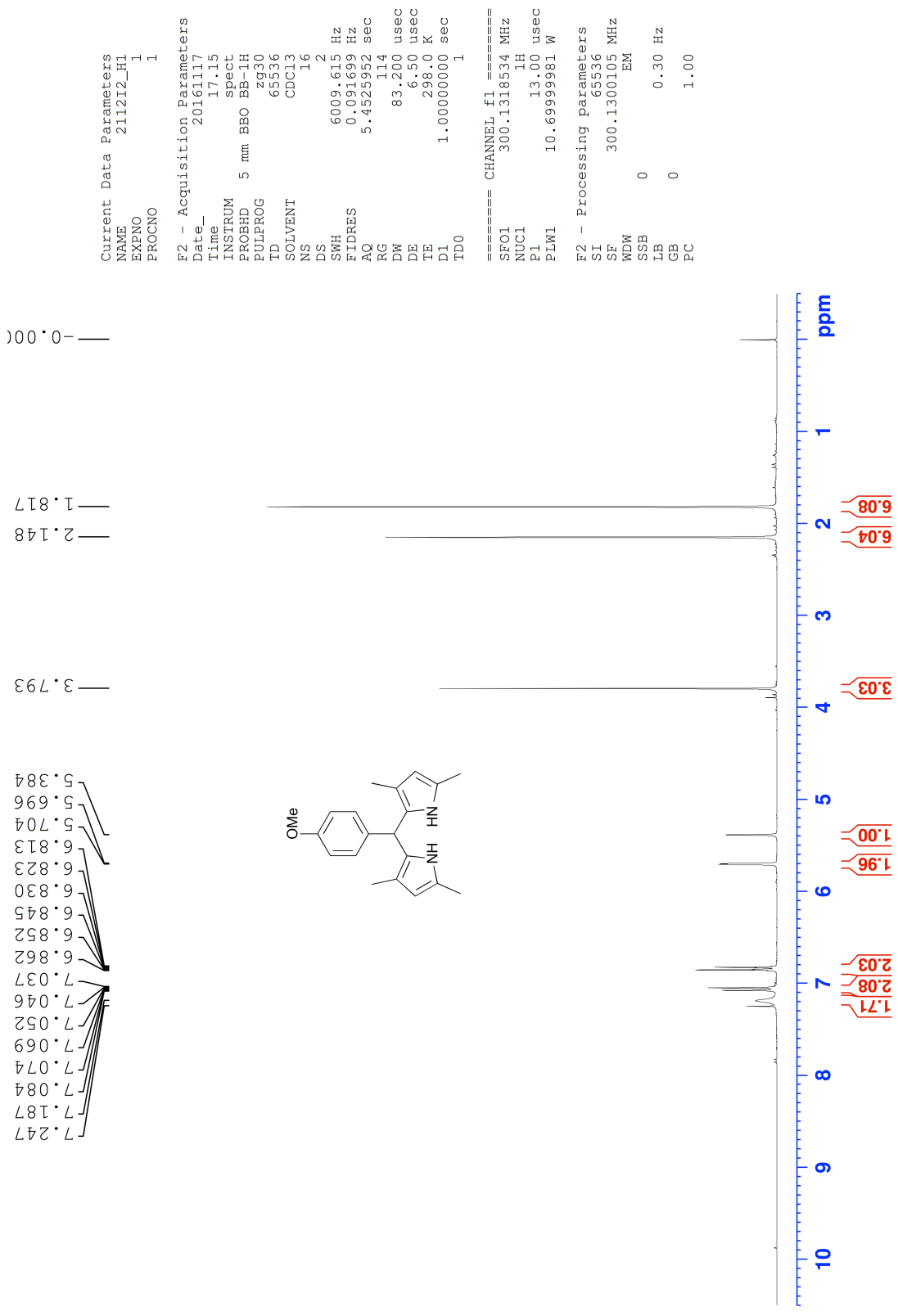
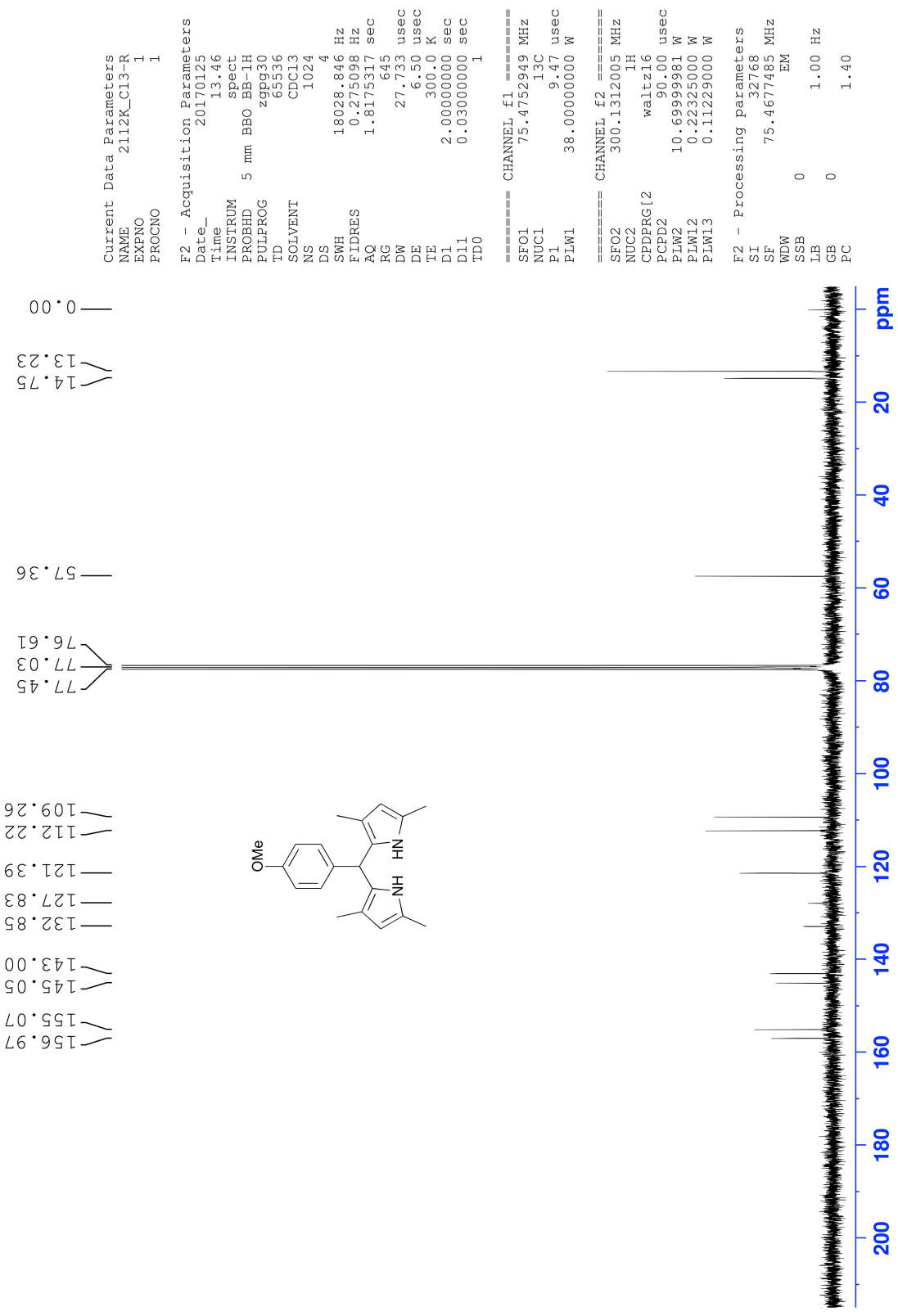


^{1}H NMR spectrum of 5-(4-methoxyphenyl)-2,4,6,8-tetramethyldipyrromethane



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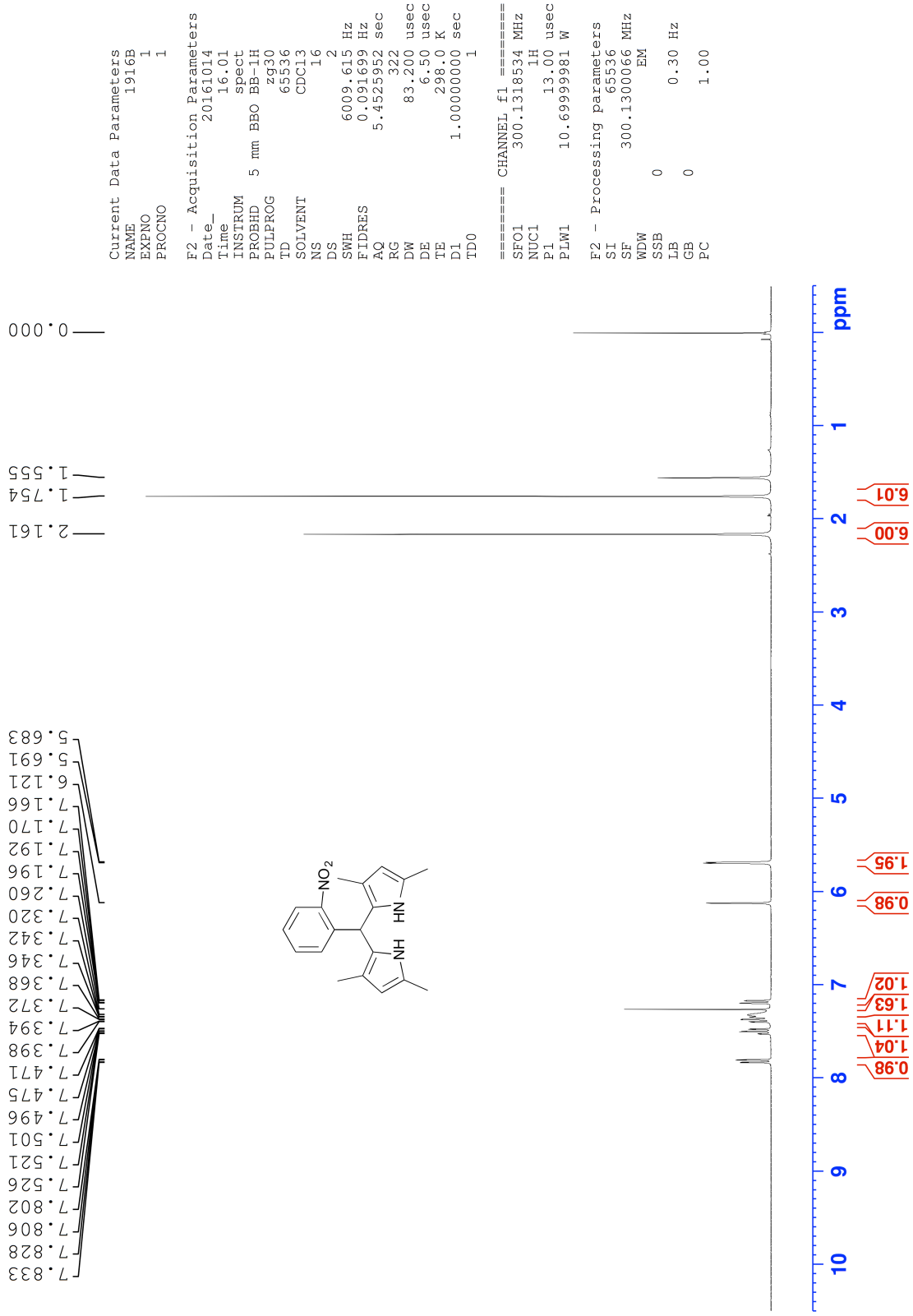

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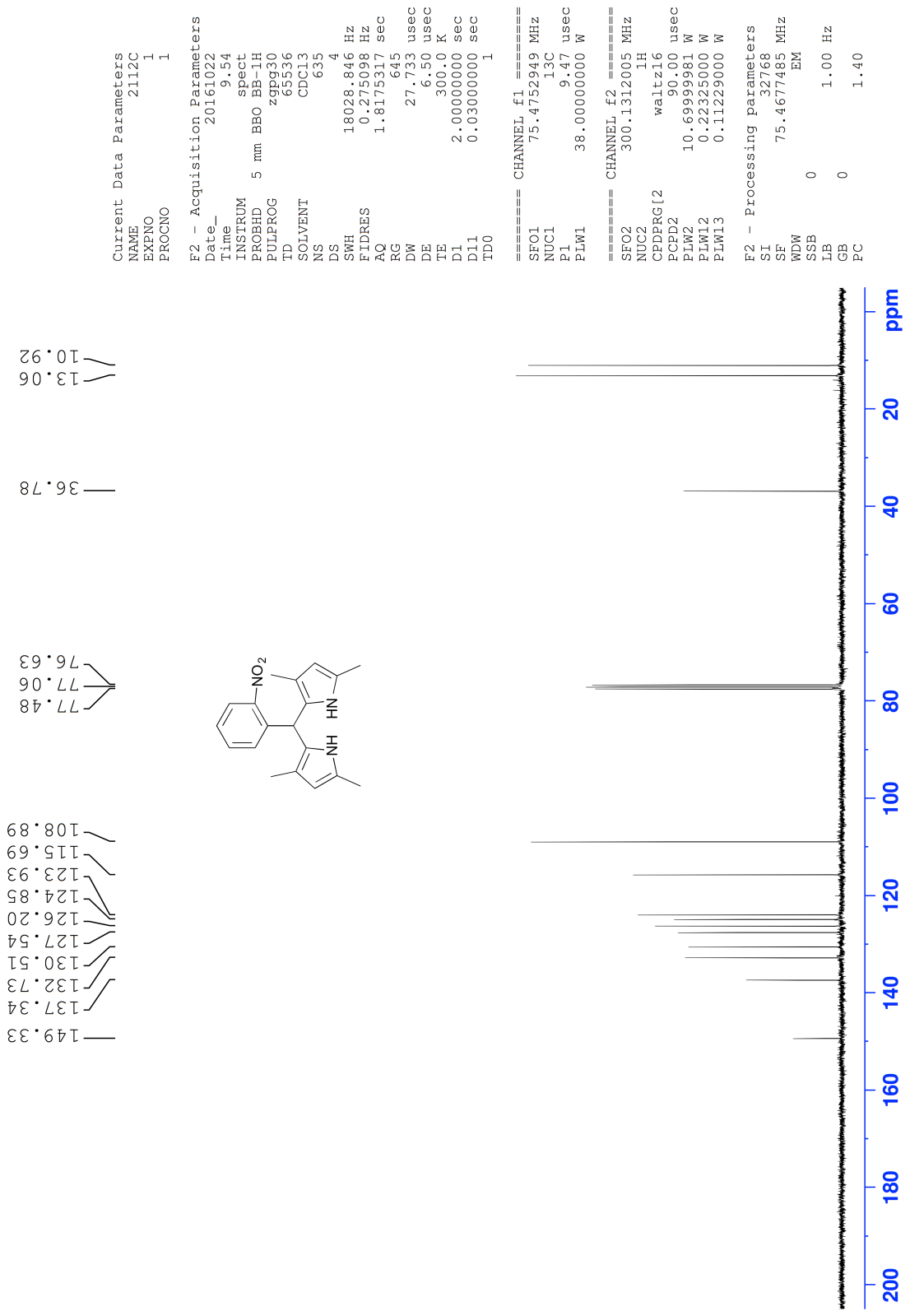

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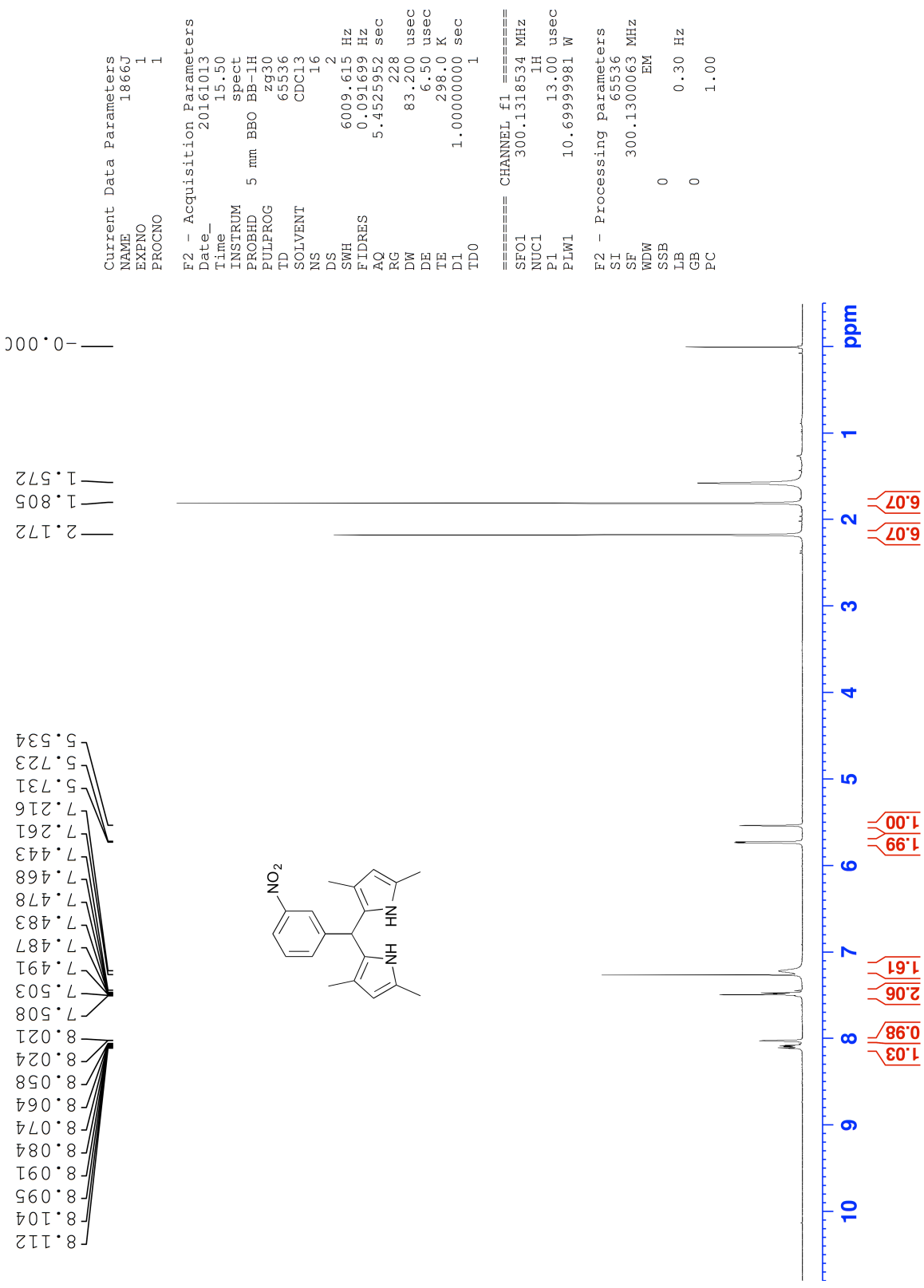

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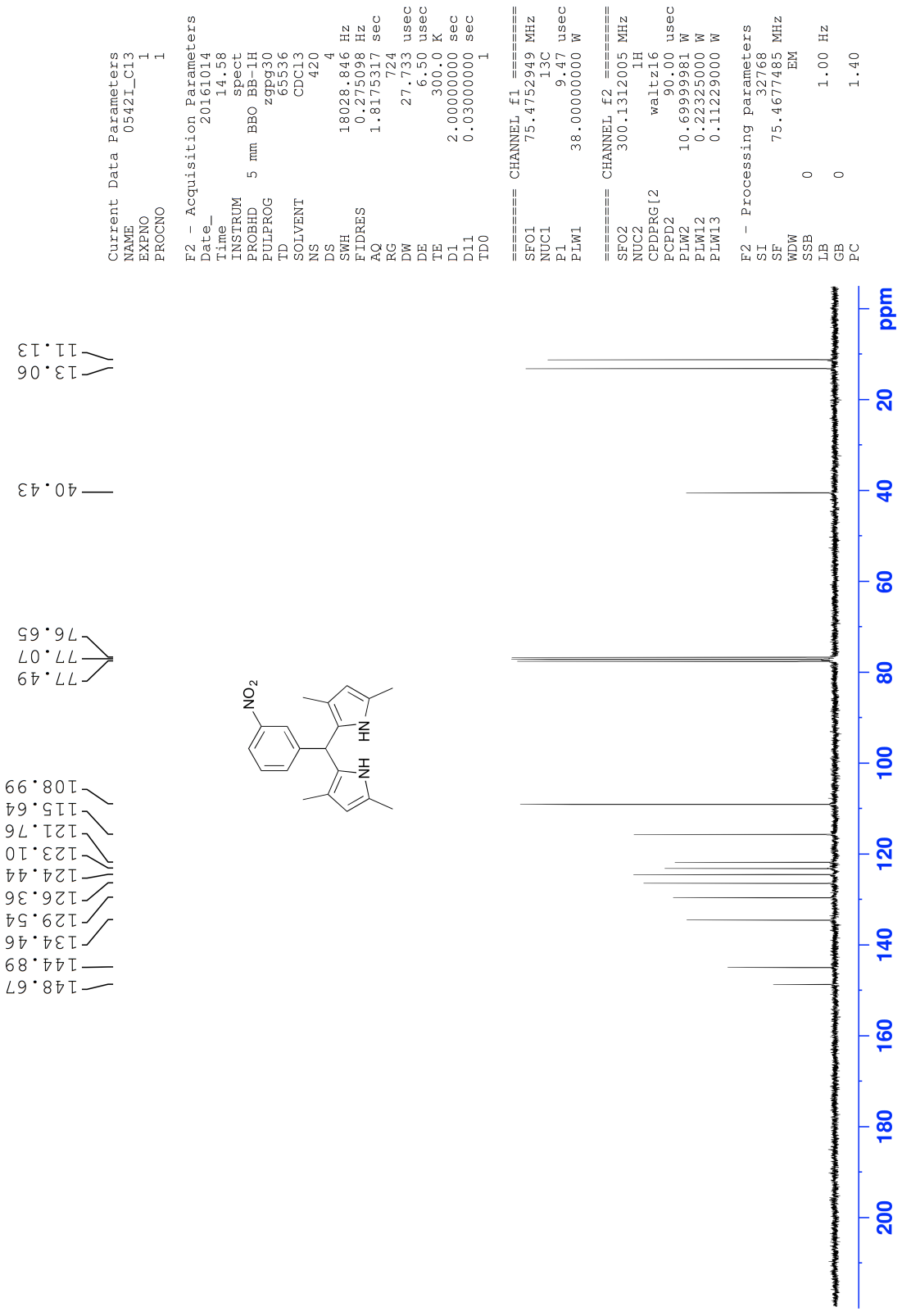

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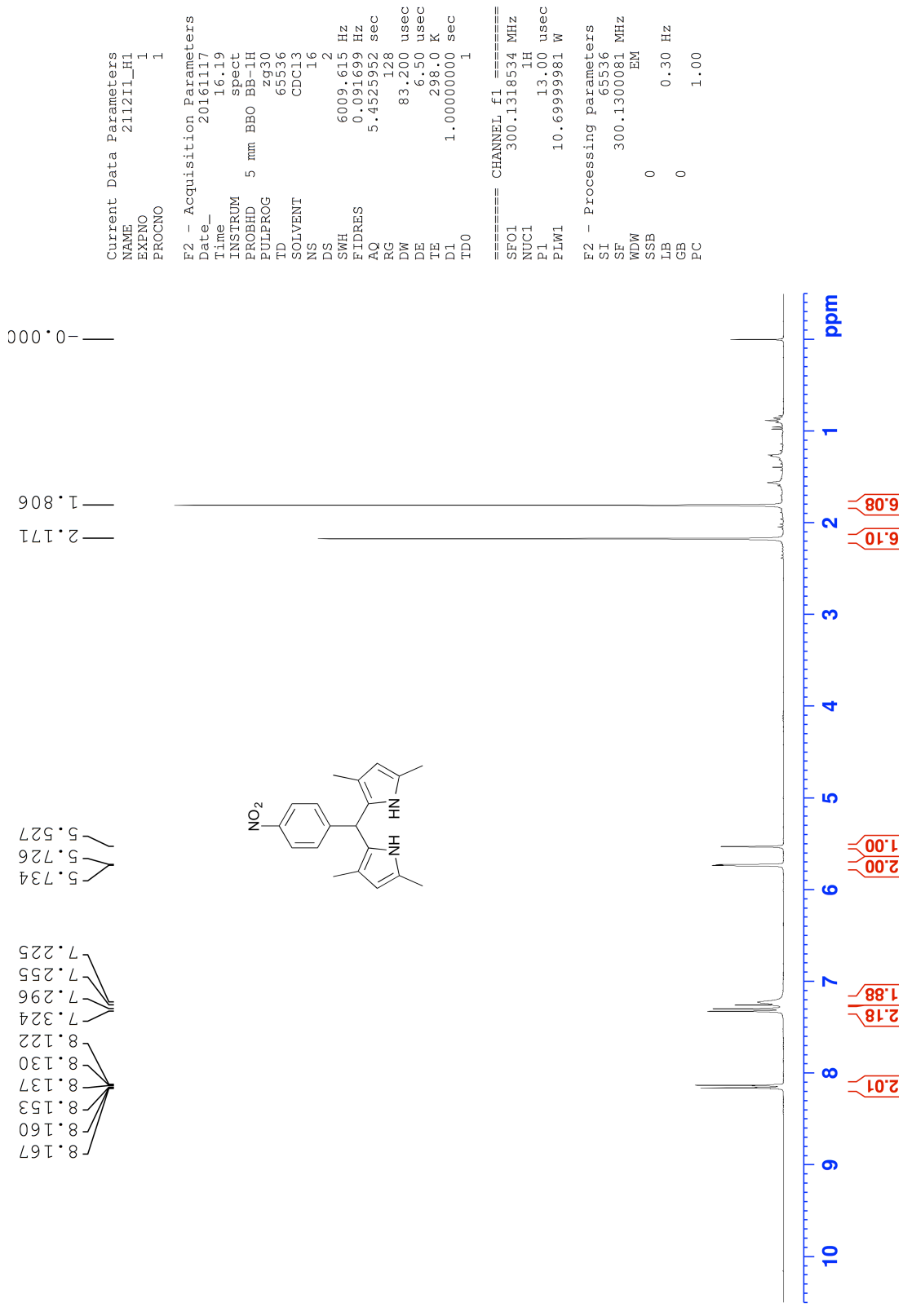

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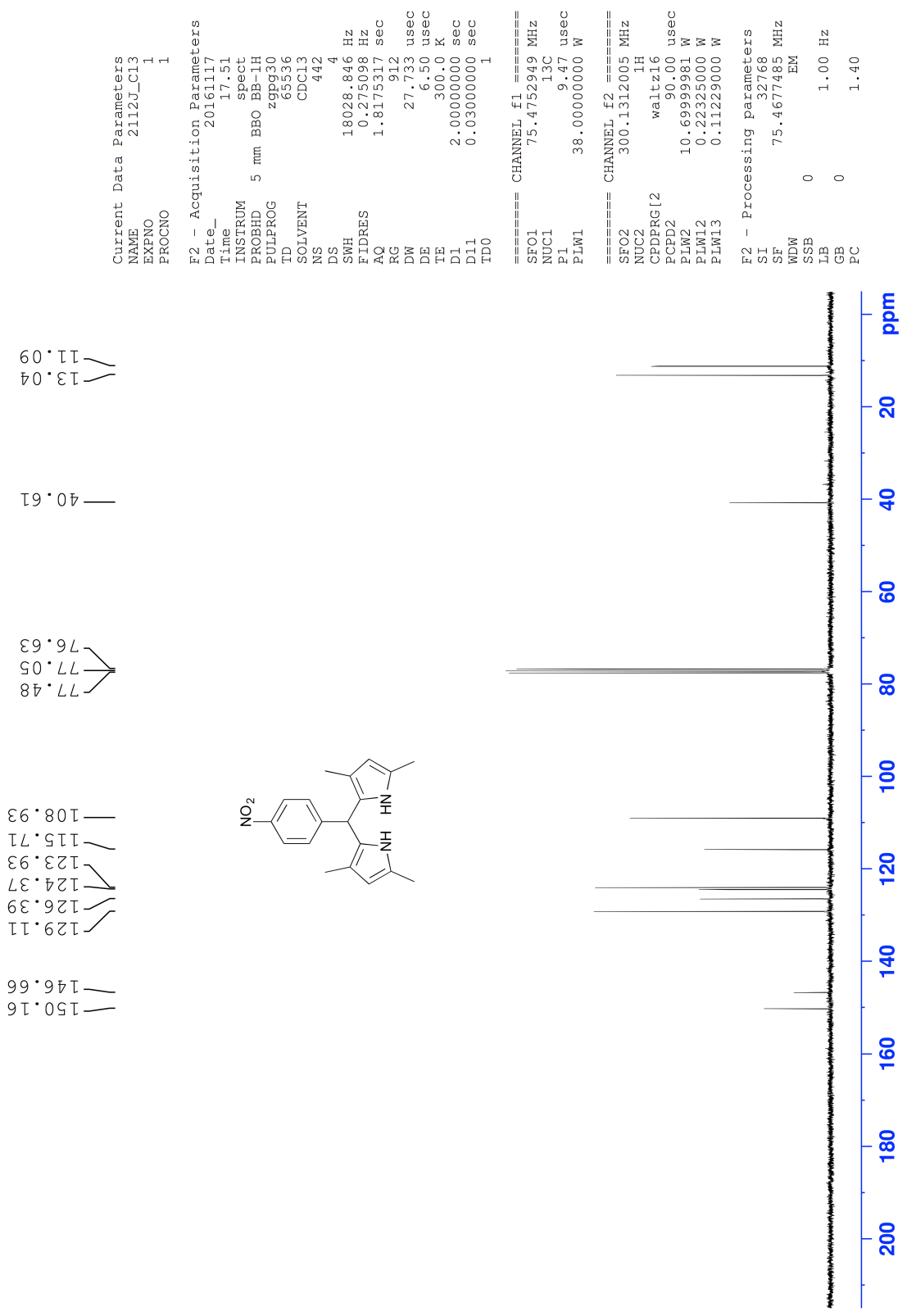

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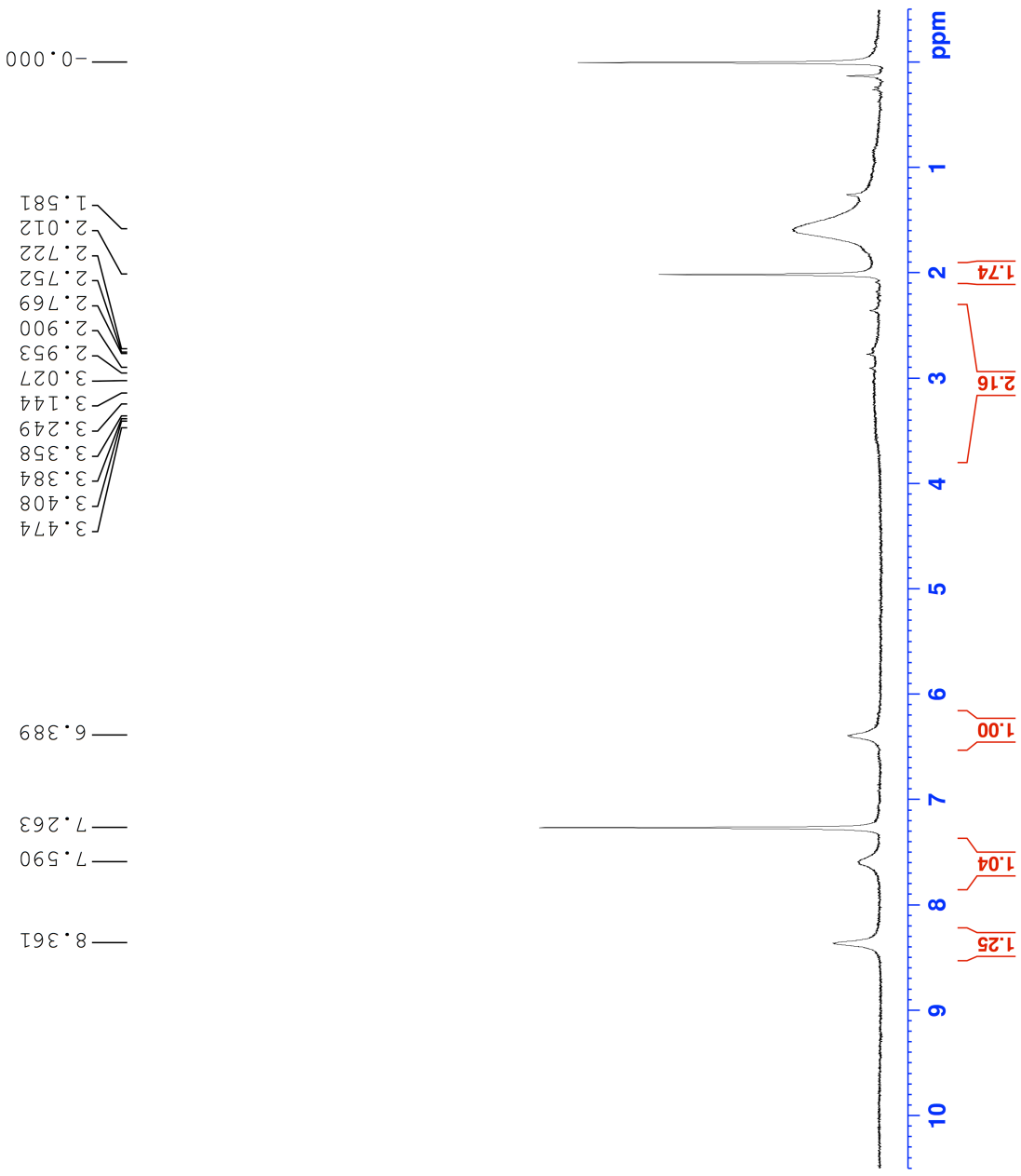
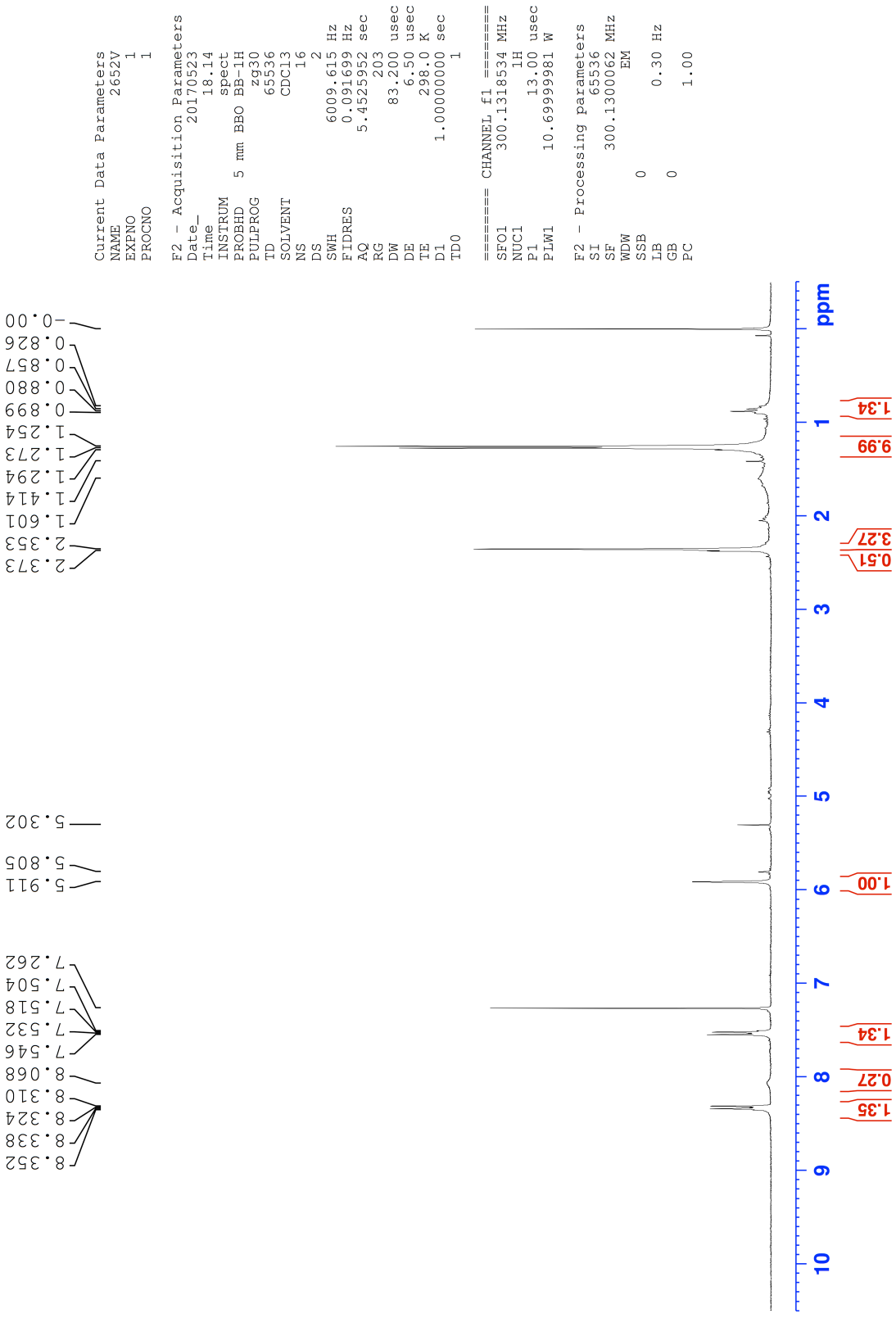


^{1}H NMR spectrum of 6-Cu complex



^{1}H NMR spectrum of 6D obtained by decomplexation of 6-Cu