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Easily accessible and recyclable copper nanocatalyst for solvent free synthesis of dipyrromethanes and aromatic amines

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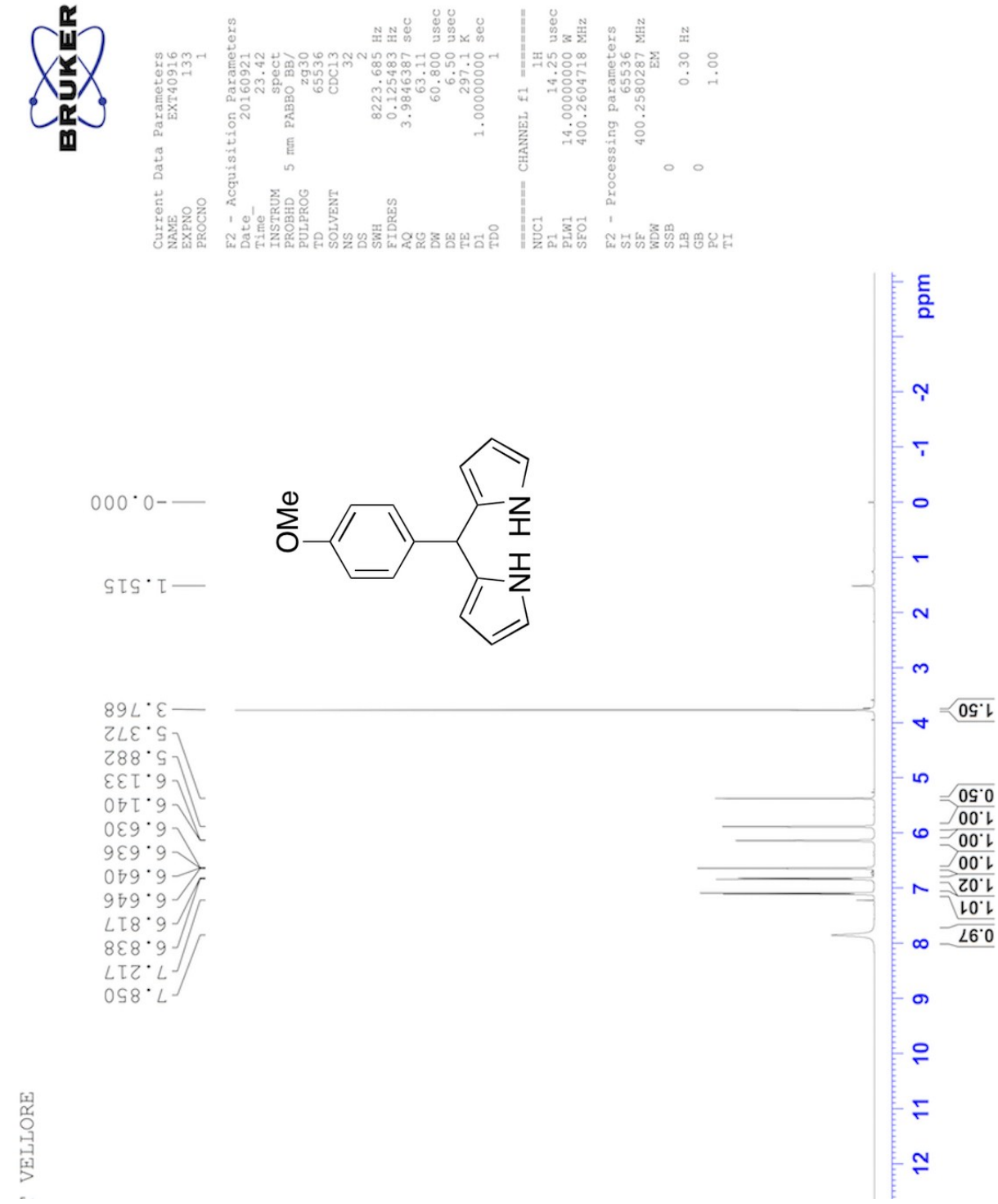

Fig. S1: ^{1}H NMR spectrum of 5-(4-methoxyphenyl)dipyrromethane: ^{1}H NMR (400 MHz, $CDCl_3$) 3.77 (s, 3H), 5.37 (s, 1H), 5.88 (s, 2H), 6.14 (d, J = 2.8 Hz, 2H), 6.40 (dd, J_1 = 4 Hz, J_2 = 2.4 Hz, 2H), 6.83 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.85 (br s, 2H).[S1]

Fig. S2: ^{13}C NMR spectrum of 5-(4-methoxyphenyl)dipyrromethane: ^{13}C NMR (100 MHz, $CDCl_3$) 43.4, 55.8, 107.3, 108.4, 114.9, 117.2, 129.7, 133.0, 134.3, 158.5.[S1]

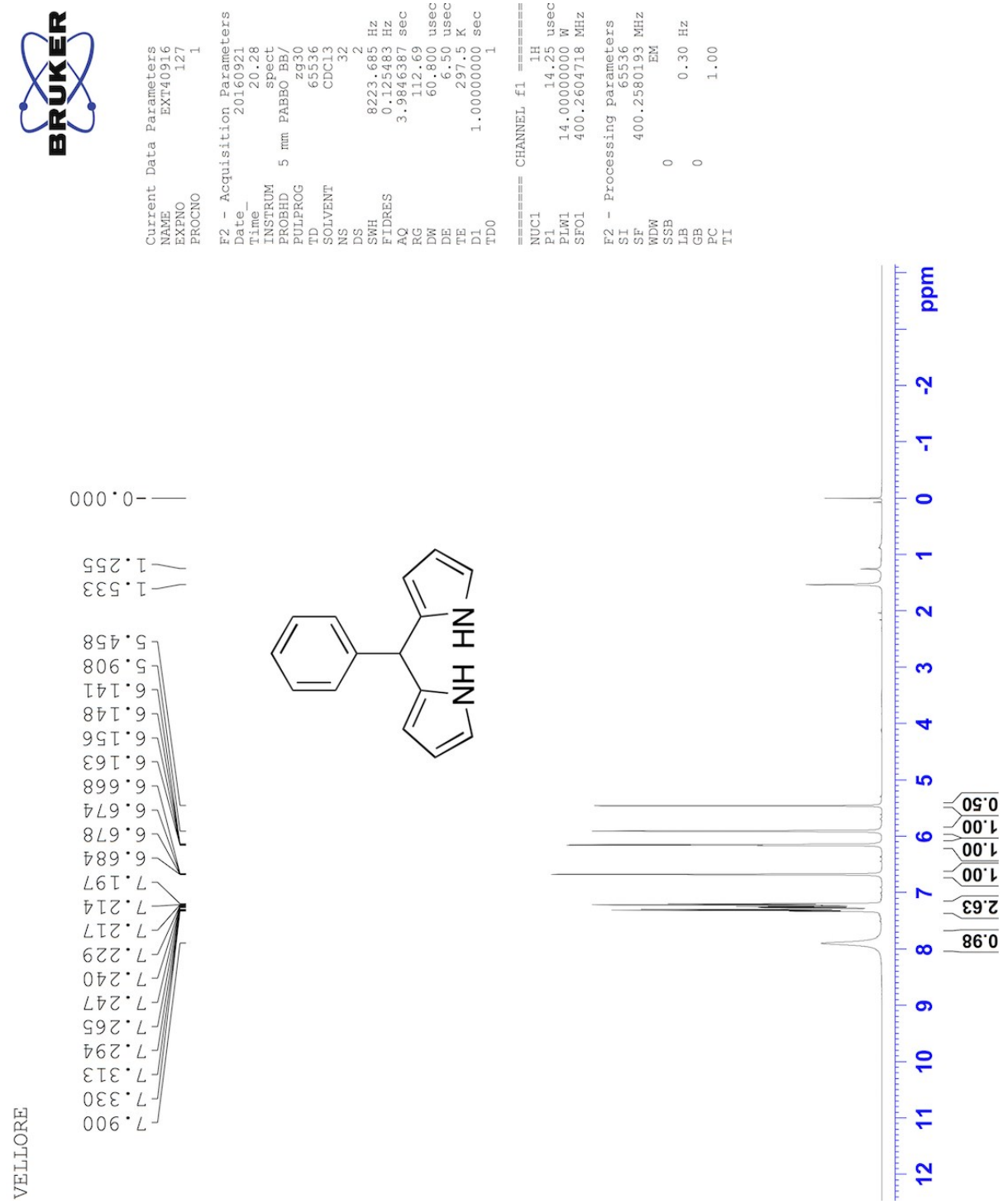

Fig. S3: ^{1}H NMR spectrum of 5-phenyldipyrromethane: ^{1}H NMR (400 MHz, $CDCl_3$) 5.46 (s, 1H), 5.91 (br s, 2H), 6.15 (dd, J_1 = 6.0 Hz, J_2 = 2.8 Hz, 2H), 6.68 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 2H), 7.20-7.29 (m, 5H), 7.90 (br s, 2H).[S1]

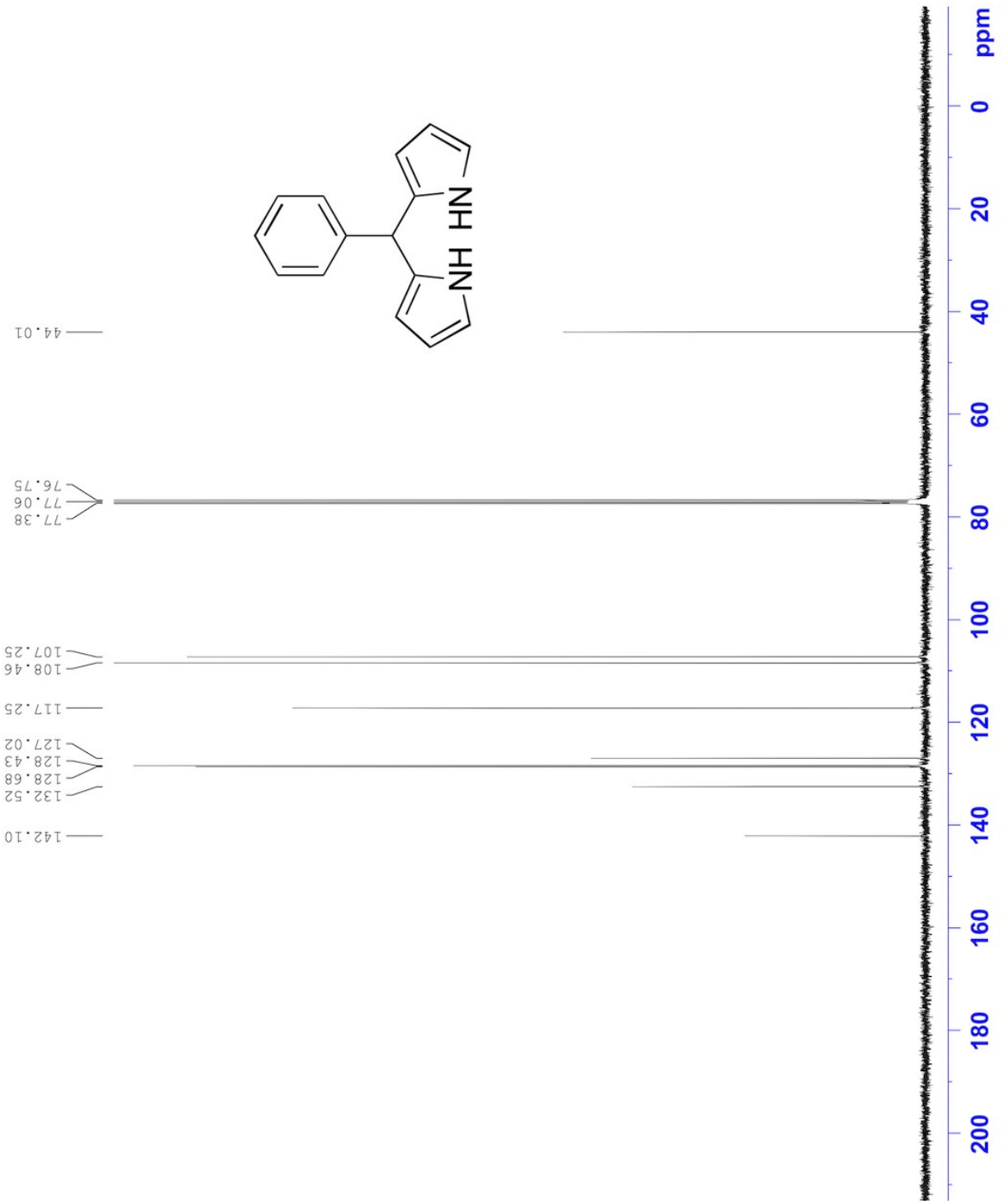

Fig. S4: ^{13}C NMR spectrum of 5-phenyldipyrromethane: ^{13}C NMR (100 MHz, $CDCl_3$) 44.0, 107.3, 108.5, 117.2, 127.0, 128.4, 128.7, 132.5, 142.1.[S1]

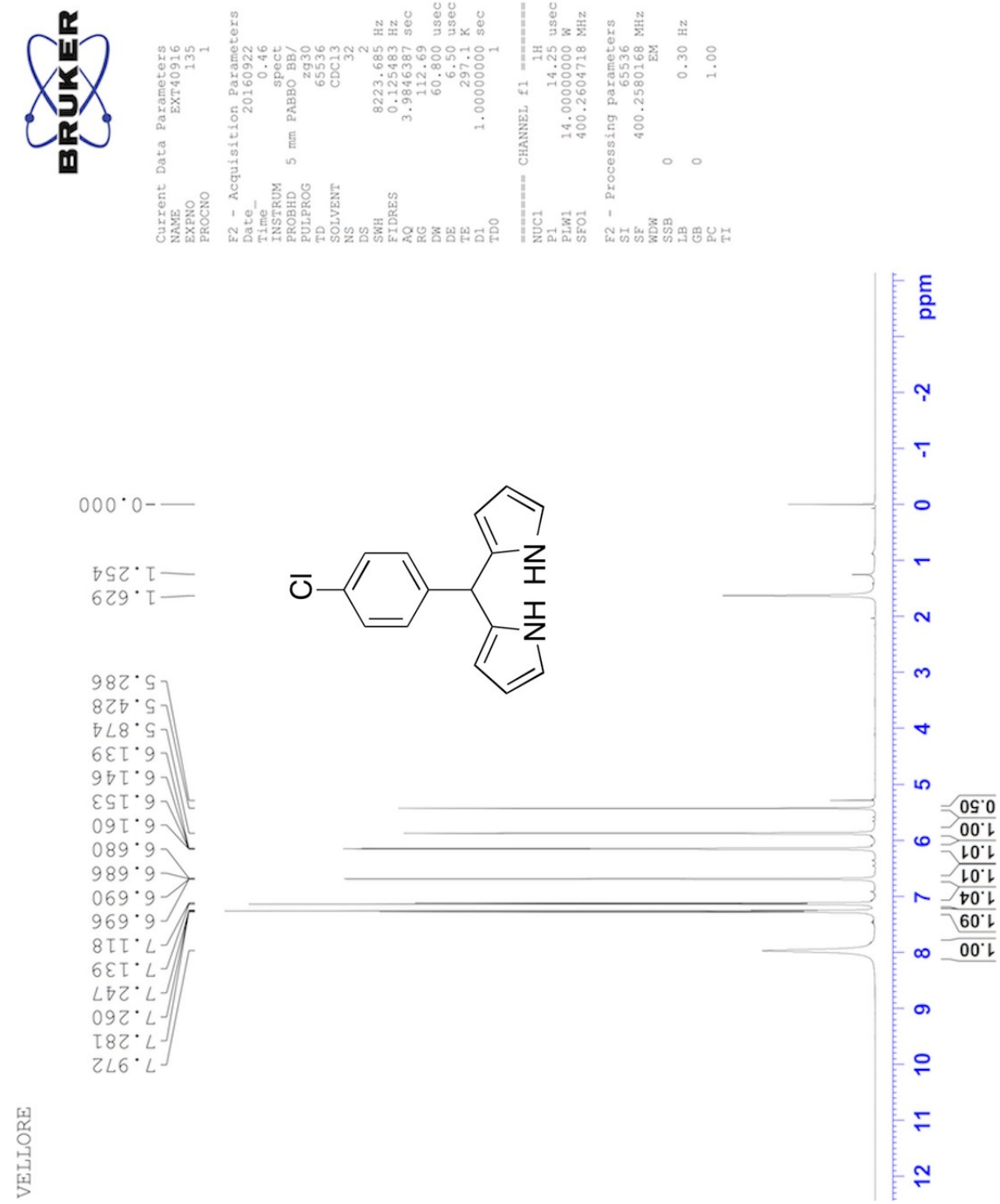

Fig. S5: ^{1}H NMR spectrum of 5-(4-chlorophenyl)dipyrromethane: ^{1}H NMR (400 MHz, $CDCl_3$) 5.43 (s, 1H), 5.87 (br s, 2H), 6.15 (dd, J_1 = 5.6 Hz, J_2 = 2.8 Hz, 2H), 6.69 (dd, J_1 = 4.0 Hz, J_2 = 2.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.4 Hz, 2H),7.97 (br s, 2H).[S2]

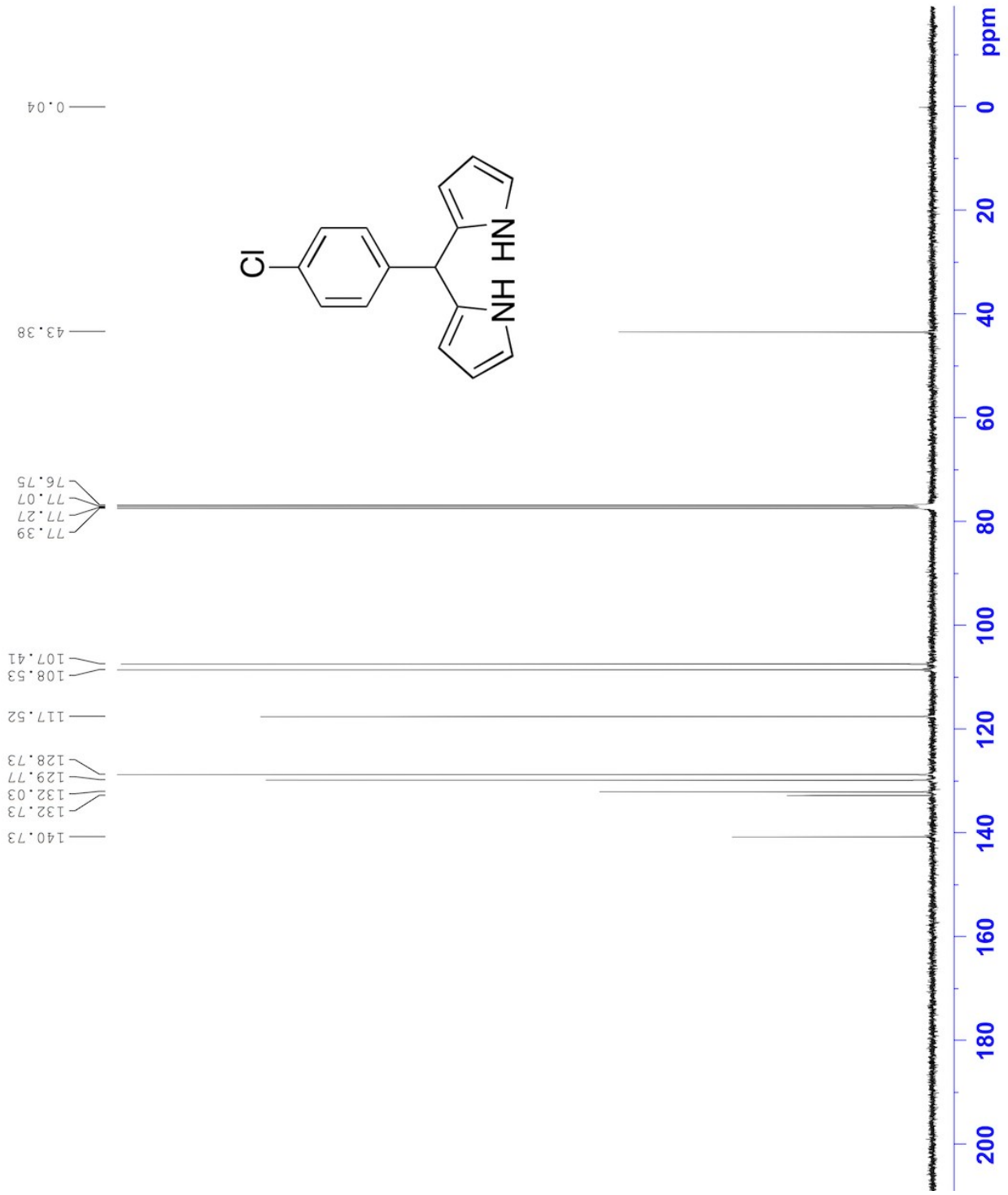

Fig. S6: ^{13}C NMR spectrum of 5-(4-chlorophenyl)dipyrromethane: ^{13}C NMR (100 MHz, $CDCl_3$) 43.4, 107.4, 108.5, 117.5, 128.7, 129.8, 132.0, 132.7, 140.7.[S2]

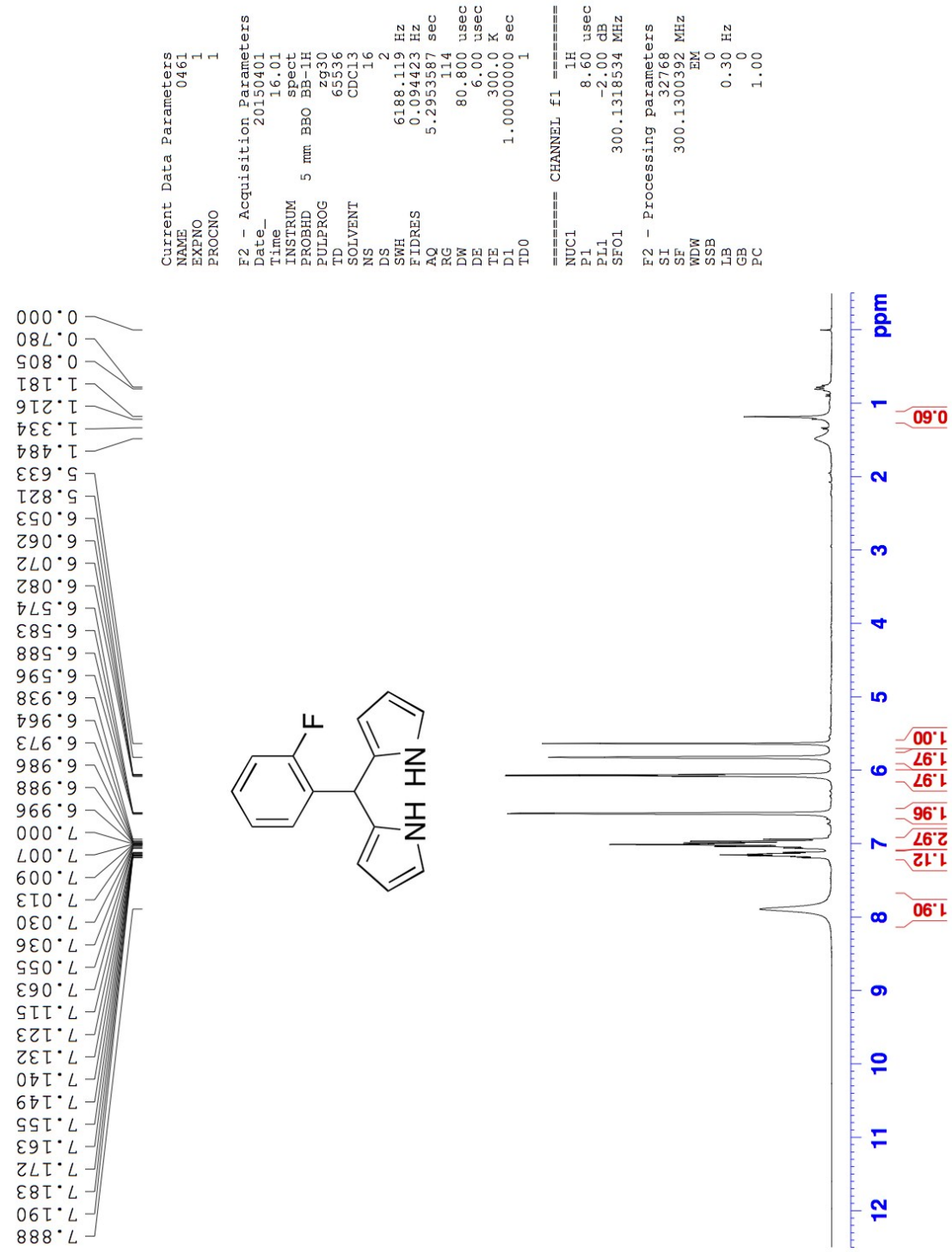

Fig. S7: ^{1}H NMR spectrum of 5-(2-fluorophenyl)dipyrromethane: ^{1}H NMR (300 MHz, $CDCl_3$) 5.63 (s, 1H), 5.82 (br s, 2H), 6.07 (dd, J_1 = 6 Hz, J_2 = 2.7 Hz, 2H), 6.59 (dd, J_1 = 3.9 Hz, J_2 = 2.7 Hz, 2H), 6.94-7.19 (m, 4H), 7.89 (br s, 2H).

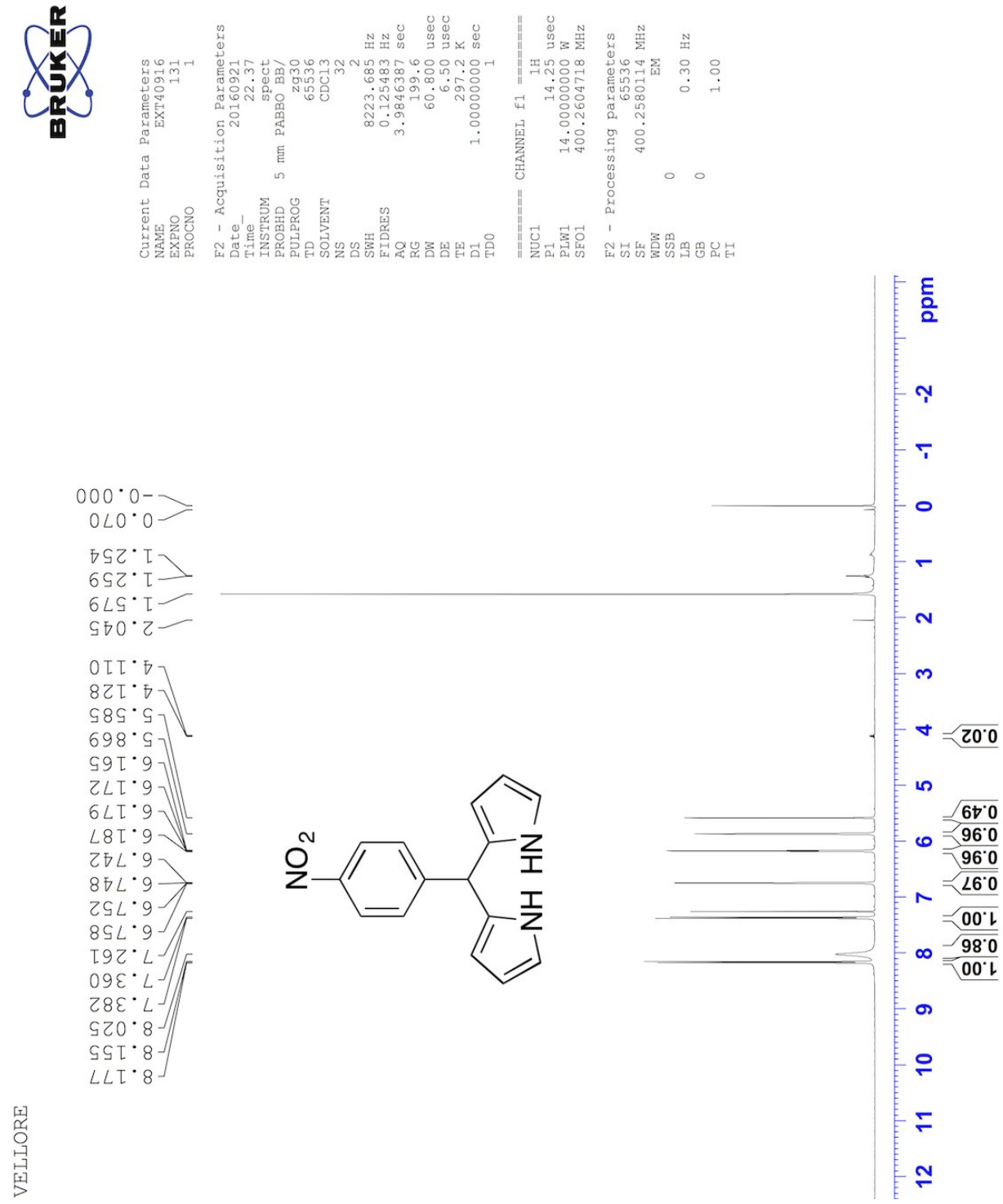

Fig. S8: ^{1}H NMR spectrum of 5-(4-nitrophenyl)dipyrromethane: ^{1}H NMR (400 MHz, $CDCl_3$) 5.52 (s, 1H), 5.80 (br s, 2H), 6.12 (dd, J_1 = 6 Hz, J_2 = 2.7 Hz, 2H), 6.68 (dd, J_1 = 4.2 Hz, J_2 = 2.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H), 7.94 (br s, 2H), 8.10 (d, J = 8.7 Hz, 2H).[S1]

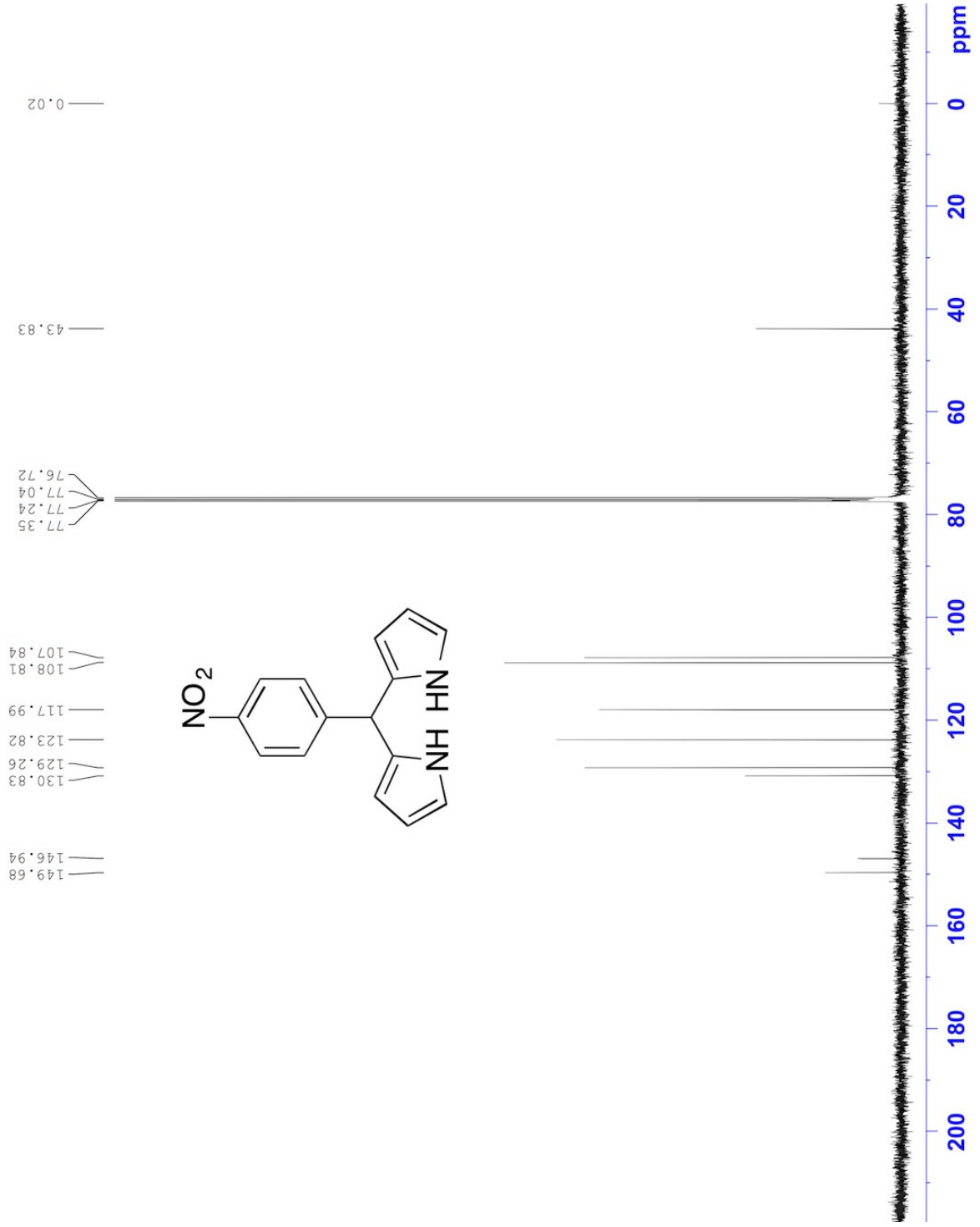

Fig. S9: ^{13}C NMR spectrum of 5-(4-nitrophenyl)dipyrromethane: ^{13}C NMR (100 MHz, $CDCl_3$) 43.4, 107.4, 108.5, 117.5, 128.7, 129.8, 132.0, 132.7, 140.7.[S1]

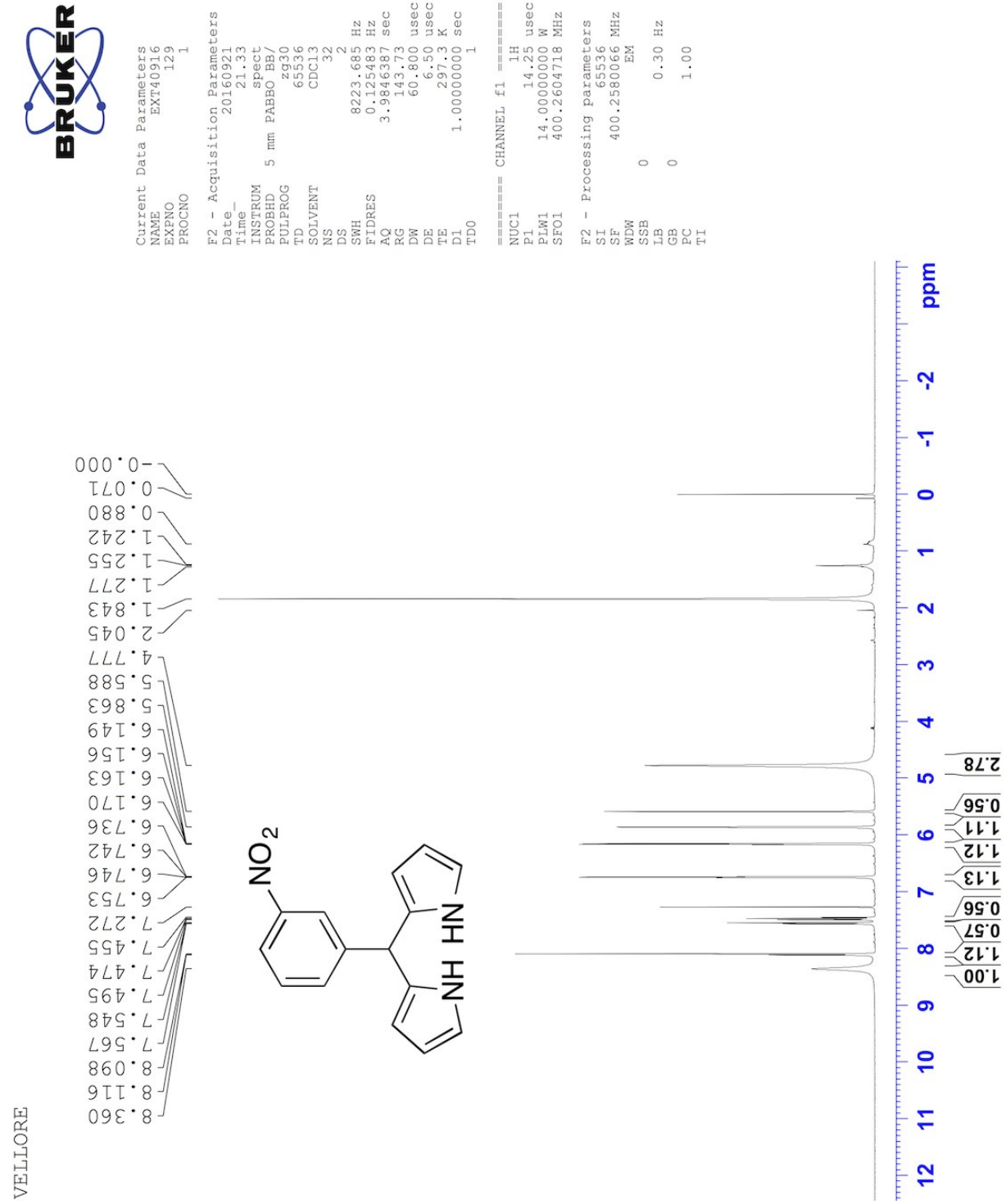

Fig. S10: ^{1}H NMR spectrum of 5-(3-nitrophenyl)dipyrromethane: ^{1}H NMR (400 MHz, $CDCl_3$) 5.59 (s, 1H), 5.87 (br s, 2H), 6.18 (dd, J_1 = 6 Hz, J_2 = 2.7 Hz, 2H), 6.76 (dd, J_1 = 3.9 Hz, J_2 = 2.7 Hz, 2H), 7.46-7.61 (m, 2H), 8.03 (br s, 2H), 8.10-8.14 (m, 2H).[S1]

Fig. S11: ^{13}C NMR spectrum of 5-(3-nitrophenyl)dipyrromethane: ^{13}C NMR (100 MHz, $CDCl_3$) 44.0, 107.3, 108.5, 117.2, 127.0, 128.4, 128.7, 132.5, 142.1.[S1]

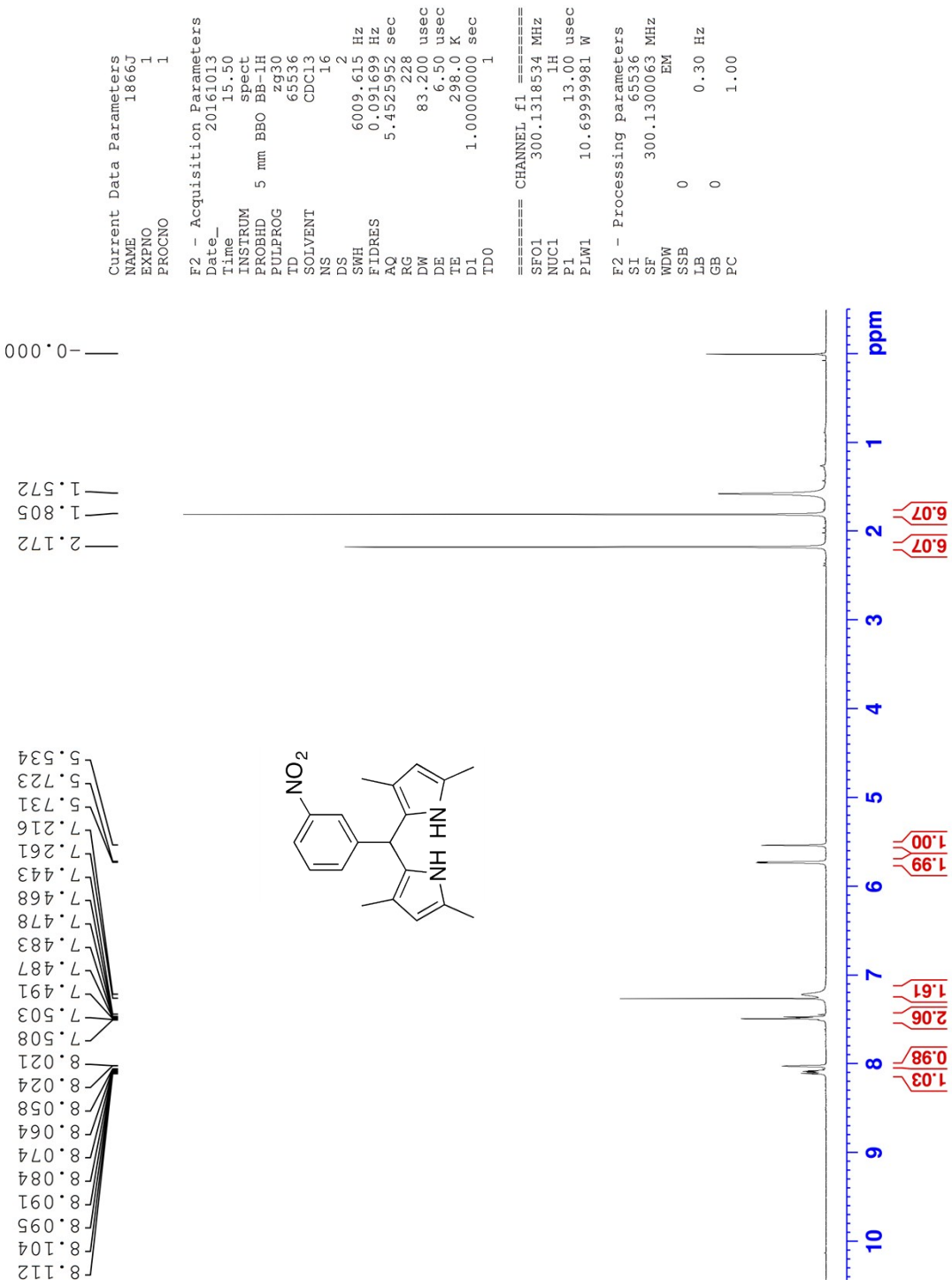

Fig. S12: ^{1}H NMR spectrum of 5,5'-((3-nitrophenyl)methylene)bis(2,4-dimethyl-1*H*-pyrrole): ^{1}H NMR (300 MHz, $CDCl_3$) 1.81 (s, 6H), 2.17 (s, 6H), 5.53 (s, 1H), 5.73 (d, J = 2.4 Hz, 2H), 7.22 (br s, 2H), 7.47-7.51 (m, 2H), 8.02 (br s, 1H), 8.06-8.11 (m, 1H).

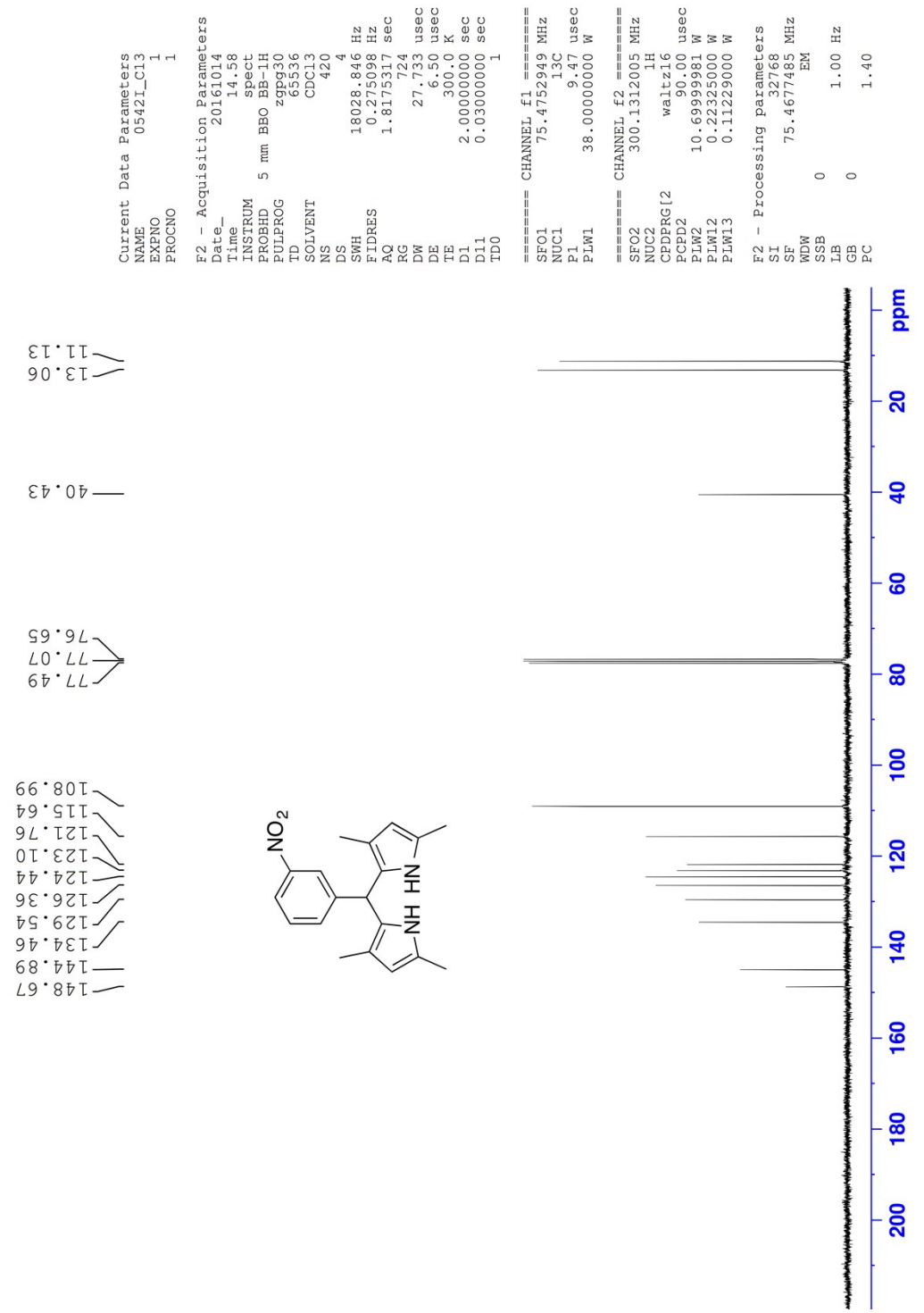

Fig. S13: ^{13}C NMR spectrum of 5,5'-((3-nitrophenyl)methylene)bis(2,4-dimethyl-1*H*-pyrrole): ^{13}C NMR (75 MHz, $CDCl_3$) 11.1, 13.1, 40.4, 109.0, 115.6, 121.8, 123.1, 124.4, 126.4, 129.5, 134.5, 144.9, 148.7.

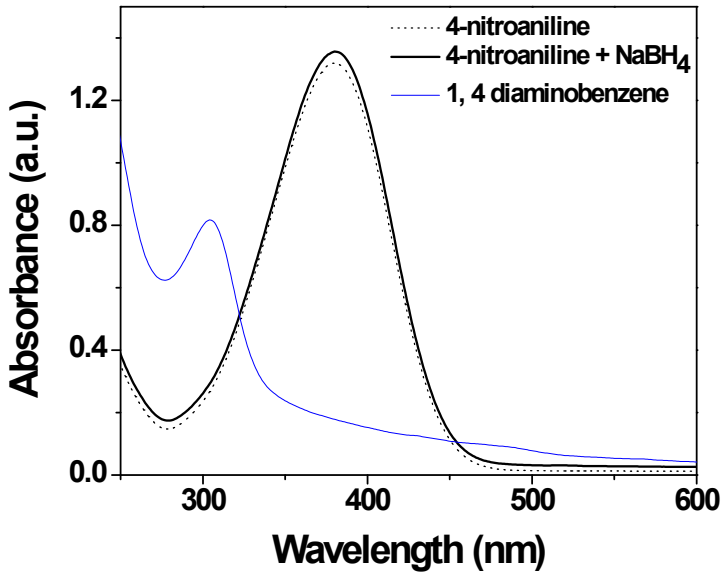

Fig. S14: UV-vis spectrum of 4-nitroaniline and its reduction product

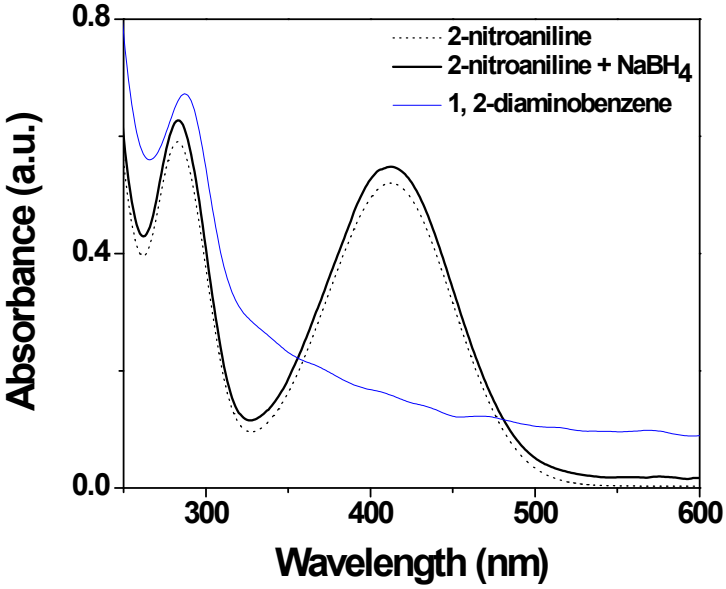

Fig. S15: UV-vis spectrum of 2-nitroaniline and its reduction product

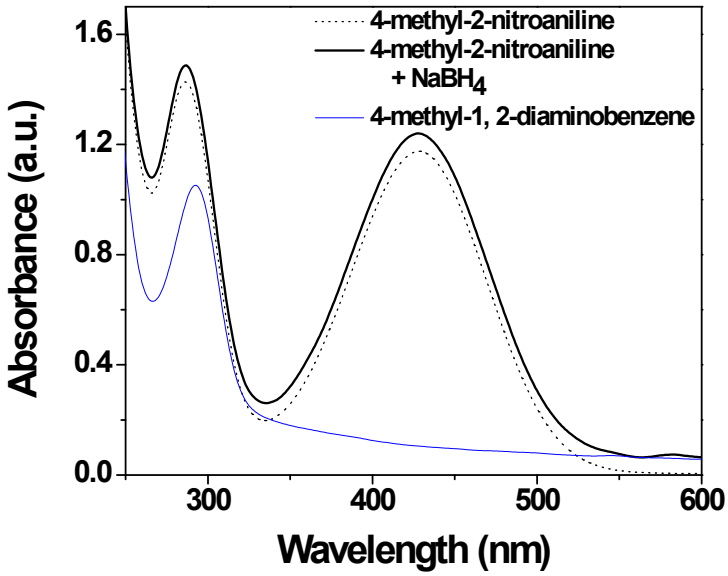

Fig. S16: UV-vis spectrum of 4-methyl-2-nitroaniline and its reduction product

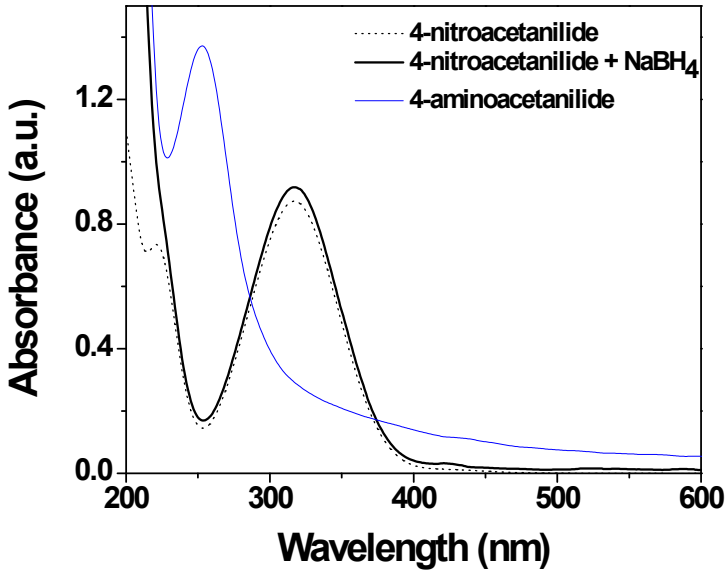

Fig. S17: UV-vis spectrum of 4-nitroacetanilide and its reduction product

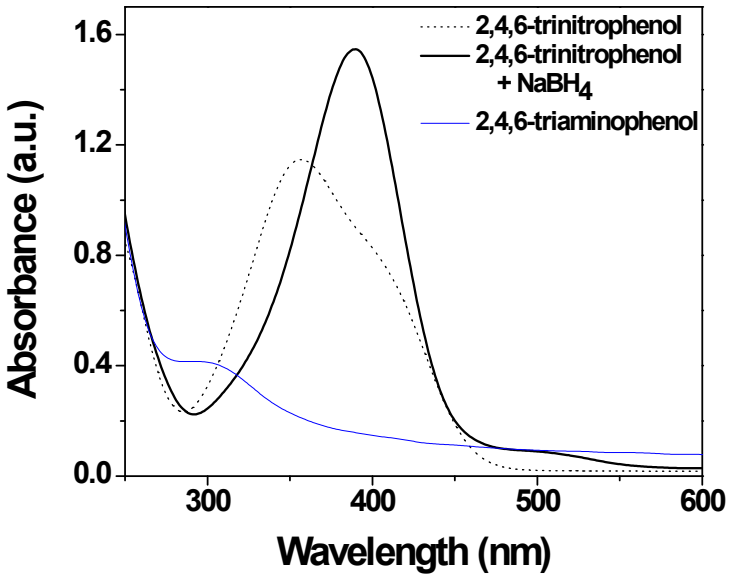

Fig. S18: UV-vis spectrum of 2,4,6-trinitrophenol and its reduction product

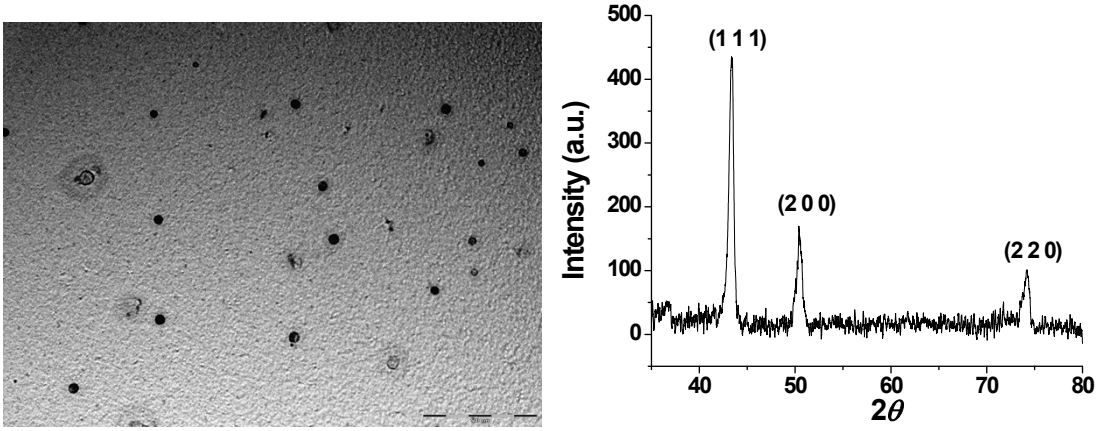

Fig. S19: (A) TEM image and (B) PXRD of CuNPs after the reaction. It is clear from the micrograph and XRD that the NPs morphology and crystallinity is unchanged after participating in the reaction as a catalyst.

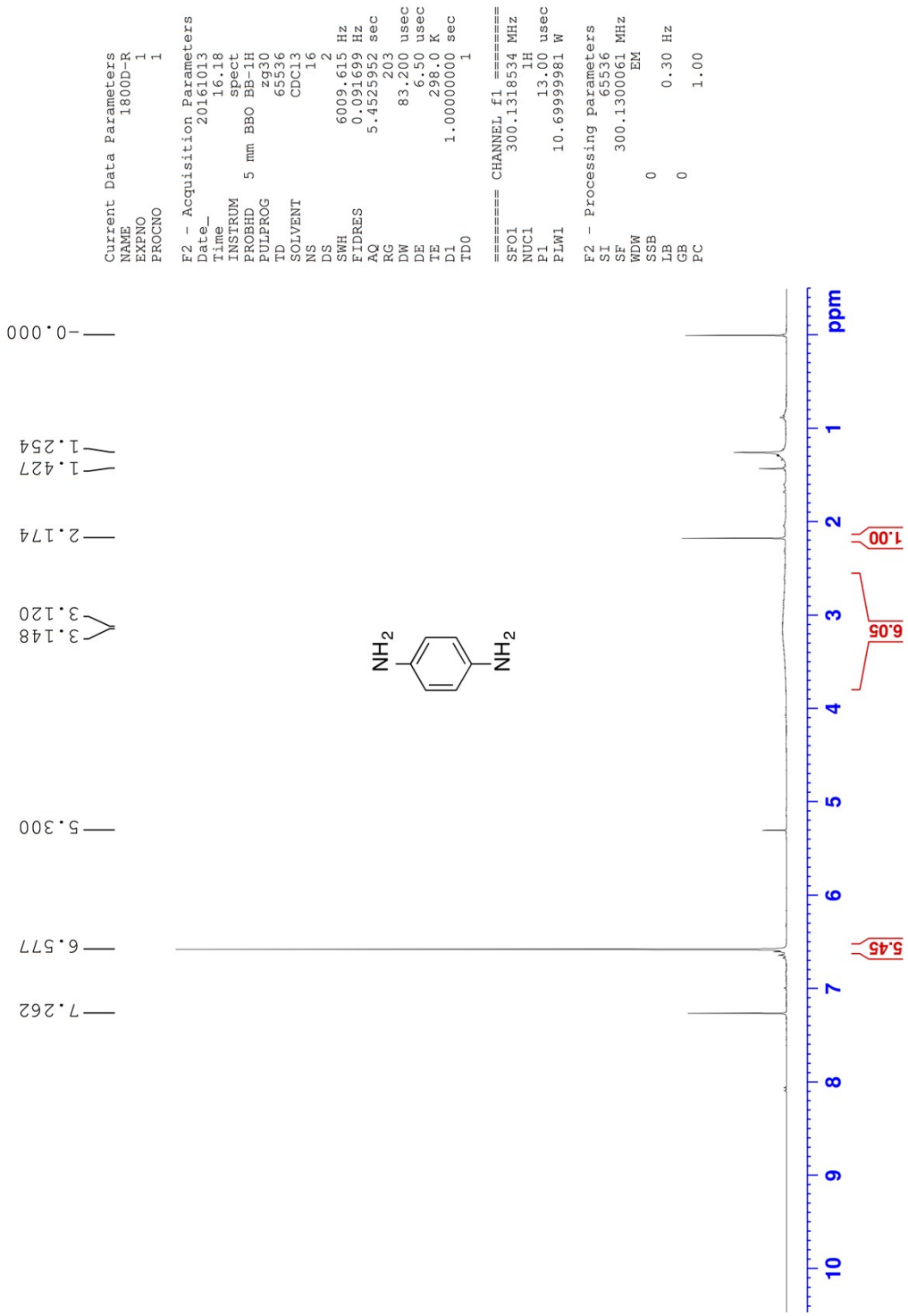

Fig. S20: ^{1}H NMR spectrum of p-phenylene diamine (crude): ^{1}H NMR (300 MHz, $CDCl_3$) 3.15 (br s, 4H), 6.58 (s, 4H).

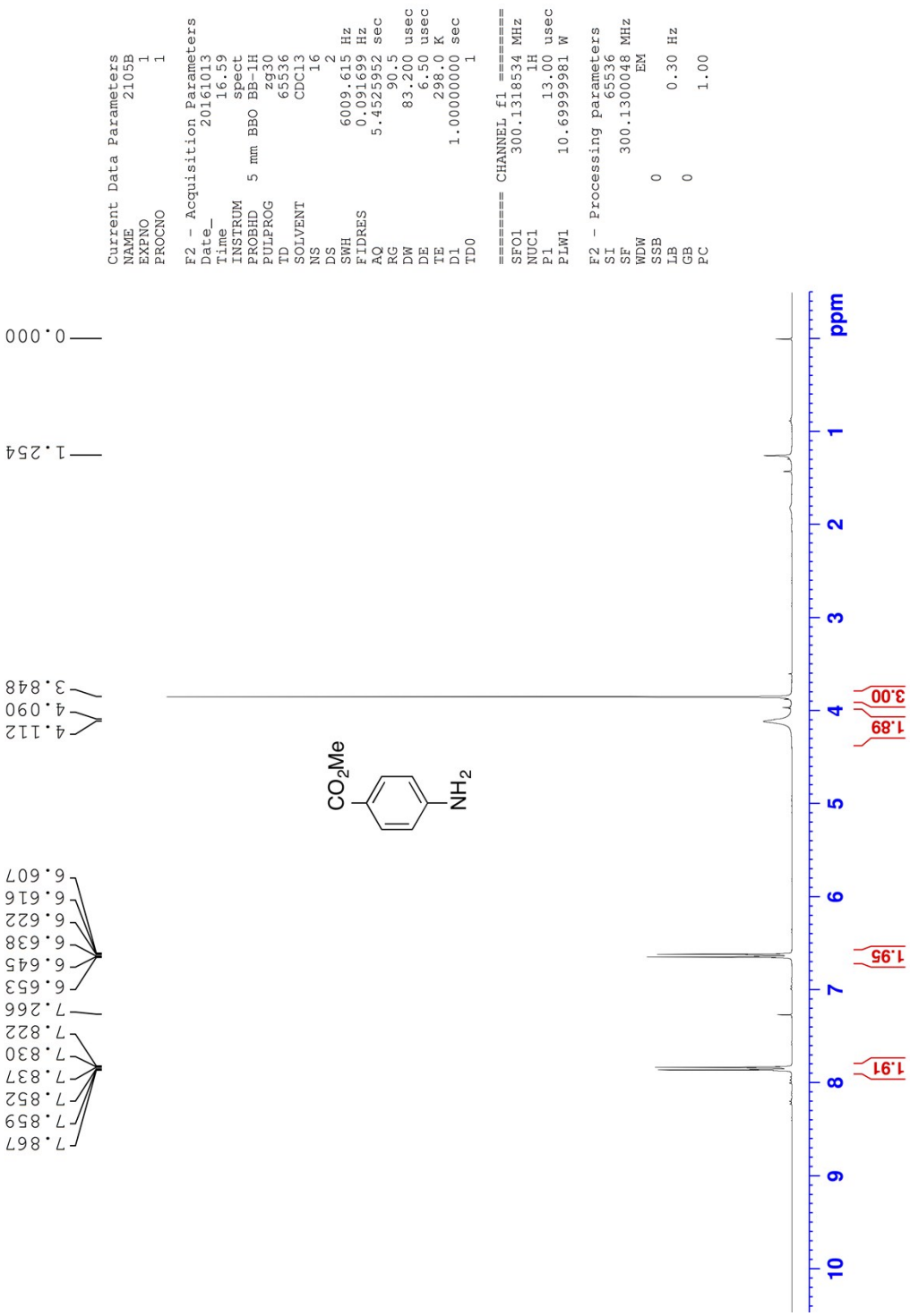

Fig. S21: ^{1}H NMR spectrum of methyl 4-aminobenzoate (crude): ^{1}H NMR (300 MHz, $CDCl_3$) 3.85 (s, 3H), 4.09 (br s, 2H), 6.63 (d, J = 9.0 Hz, 2H), 7.84 (d, J = 9.0 Hz, 2H).[S3]

References:

S1. K. Singh, S. Behal and M. S. Hundal *Tetrahedron* 2005, **61**, 6614–6622.

S2. K. Singh, S. Sharma and A. Sharma *J. Mol. Cat. A: Chemical* 2011, **347**, 34–3.

S3. H. Yang, Y. Li, M. Jiang, J. Wang and H. Fu *Chem. Eur. J.* 2011, **17**, 5652-5660.