Electronic Supplementary Material (ESI) for Dalton Transactions.

Neutral Copper(I) Complexes Featuring Phosphinesulfonate Chelates

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Computational details : All the calculations were carried out with a locally modified version of the Gaussian suite of programs,[1] using the B3PW91 hybrid density functional[2,3,4] in conjunction with the Def2tzvp[5,6.7] basis set. Semi-empirical dispersion contributions were also included in DFT computations by means of the D3BJ model of Grimme.[8,9] Solvent effects (CH_2Cl_2 or MeOH) were taken into account using the Polarizable Continuum Model (PCM).[10,11,12] Full geometry optimizations have been performed for all the compounds, checking the nature of the obtained structure by diagonalizing their Hessians.

Table S1. Comparison between computed and experimental selected bond lengths (in Å) of **Cu-1**.

	Cu-1	
	Computed	*RX*
Cu-P	2.19	2.16
Cu-O1	2.14	2.04
Cu-O2	2.06	2.10
Cu-O3	2.32	2.19
S-O3	1.46	1.46
S-O4	1.48	1.47
S-O5	1.45	1.46
Med(P-C)	1.82	1.83

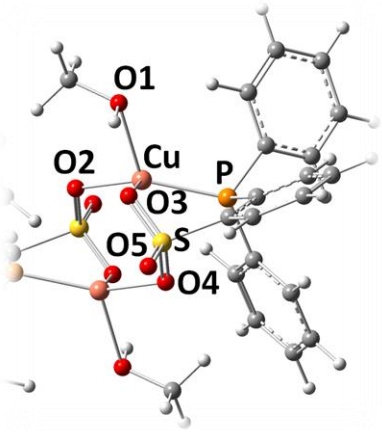
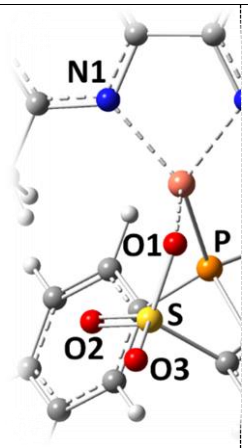
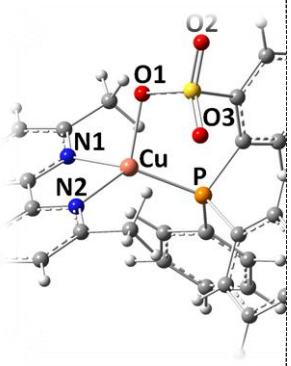
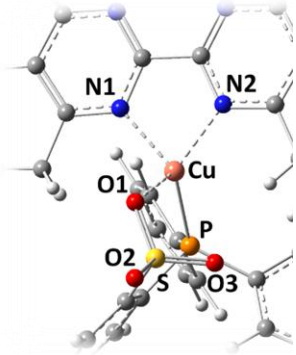


Table S2. Comparison between computed and experimental selected bond lengths (in Å) of **Cu-2**, **Cu-3** and **Cu-4**.

	Cu-2		**Cu-3**		**Cu-4**	
	Comp.	*RX*	*Comp.*	*RX*	*Comp.*	*RX*
Cu-N1	2.04	2.04	2.09	2.12	2.07	2.07
Cu-N2	2.07	2.07	2.05	2.07	2.04	2.04
Cu-P	2.18	2.17	2.18	2.18	2.18	2.18
Cu-O1	2.17	2.15	2.16	2.13	2.18	2.17
S-O1	1.48	1.47	1.48	1.48	1.48	1.47
S-O2	1.45	1.45	1.45	1.45	1.45	1.45
S-O3	1.45	1.44	1.45	1.45	1.45	1.45
Med(P-C)	1.82	1.83	1.82	1.83	1.82	1.83

In table 1 and 2 are reported selected bond lengths around the metals in compounds **Cu-1**, **Cu-2**, **Cu-3** and **Cu-4**. The first observation one can make is the relatively good reproduction of all bond length around the metals by the computations, the largest difference being in the case of the Cu-O bonds around 0.1 Å. It is also noticeable that all the bonds of the same nature have similar lengths in all compounds. The Cu-N, Cu-P and Cu-O bonds exhibit respectively lengths of ca. 2.05, 2.18 and 2.20 Å while S-O and P-C lengths around 1.45 and 1.82 Å. In Supporting Information are given the bond lengths in the ligands, which are also very similar for all compounds, and well reproduced by the computations.

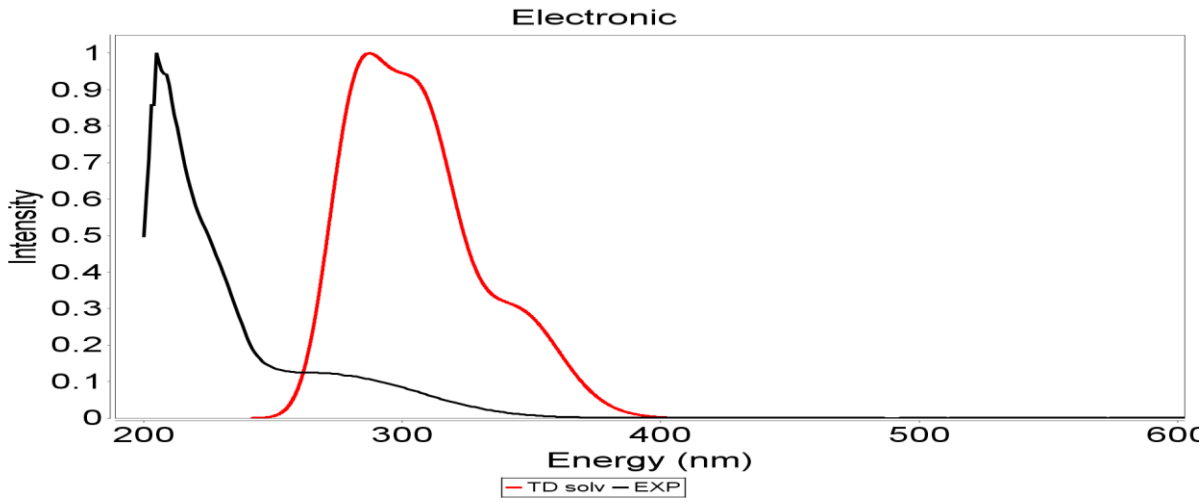


Figure S1. Experimental and calculated absorption spectra of **Cu-1**

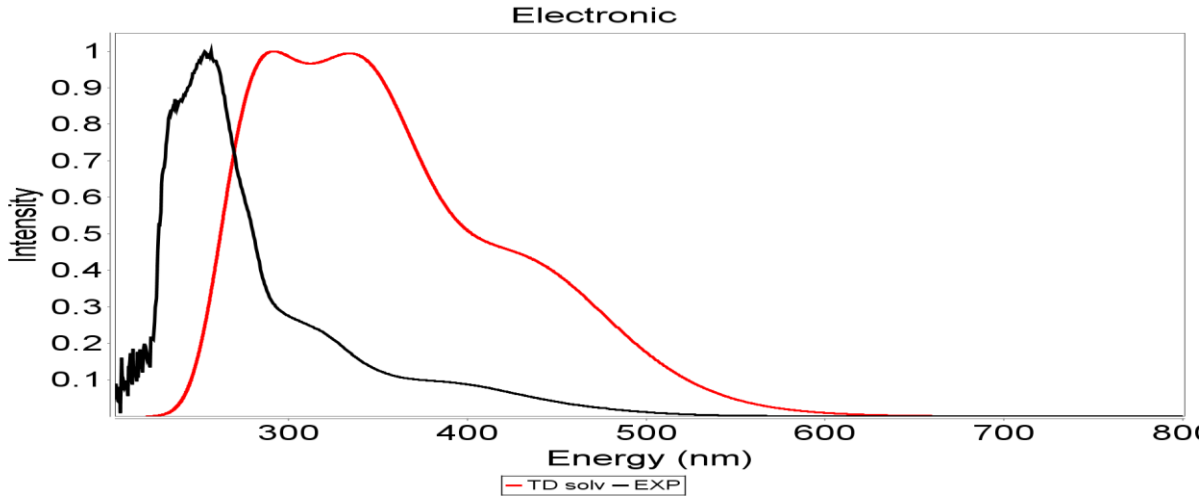


Figure S2. Experimental and calculated absorption spectra of **Cu-2**

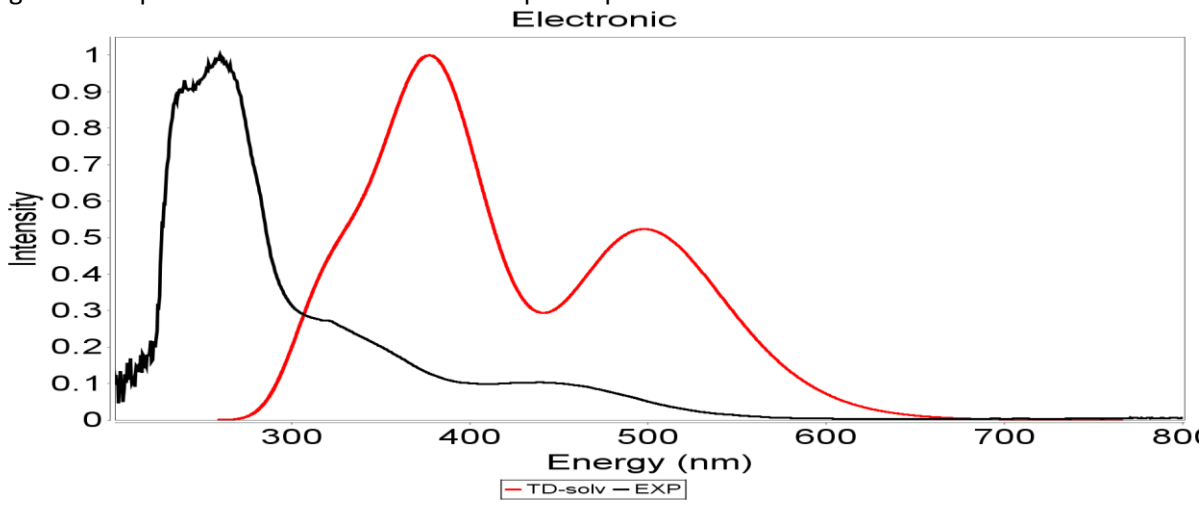


Figure S3. Experimental and calculated absorption spectra of **Cu-3**

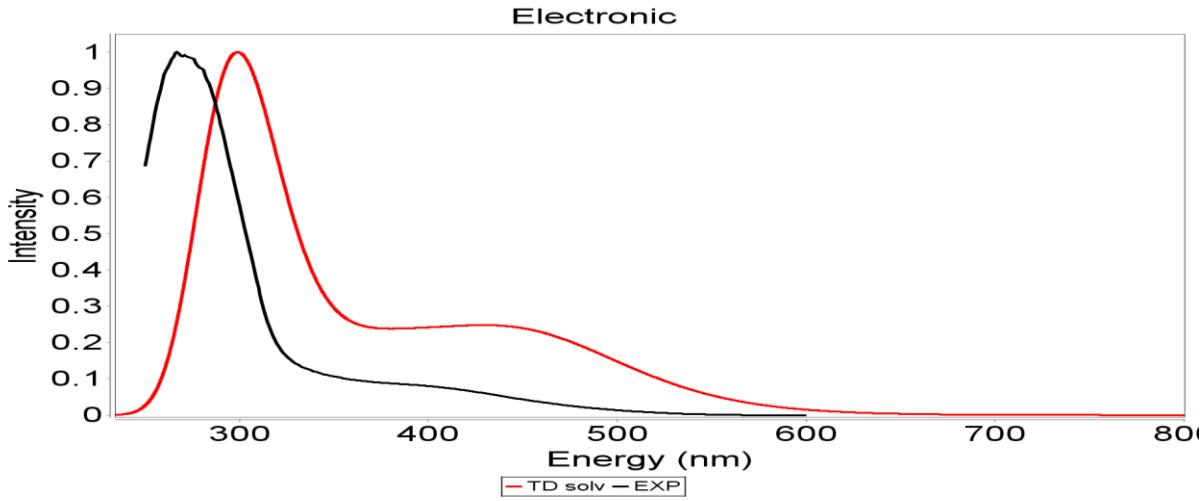


Figure S4. Experimental and calculated absorption spectra of **Cu-4**

References :

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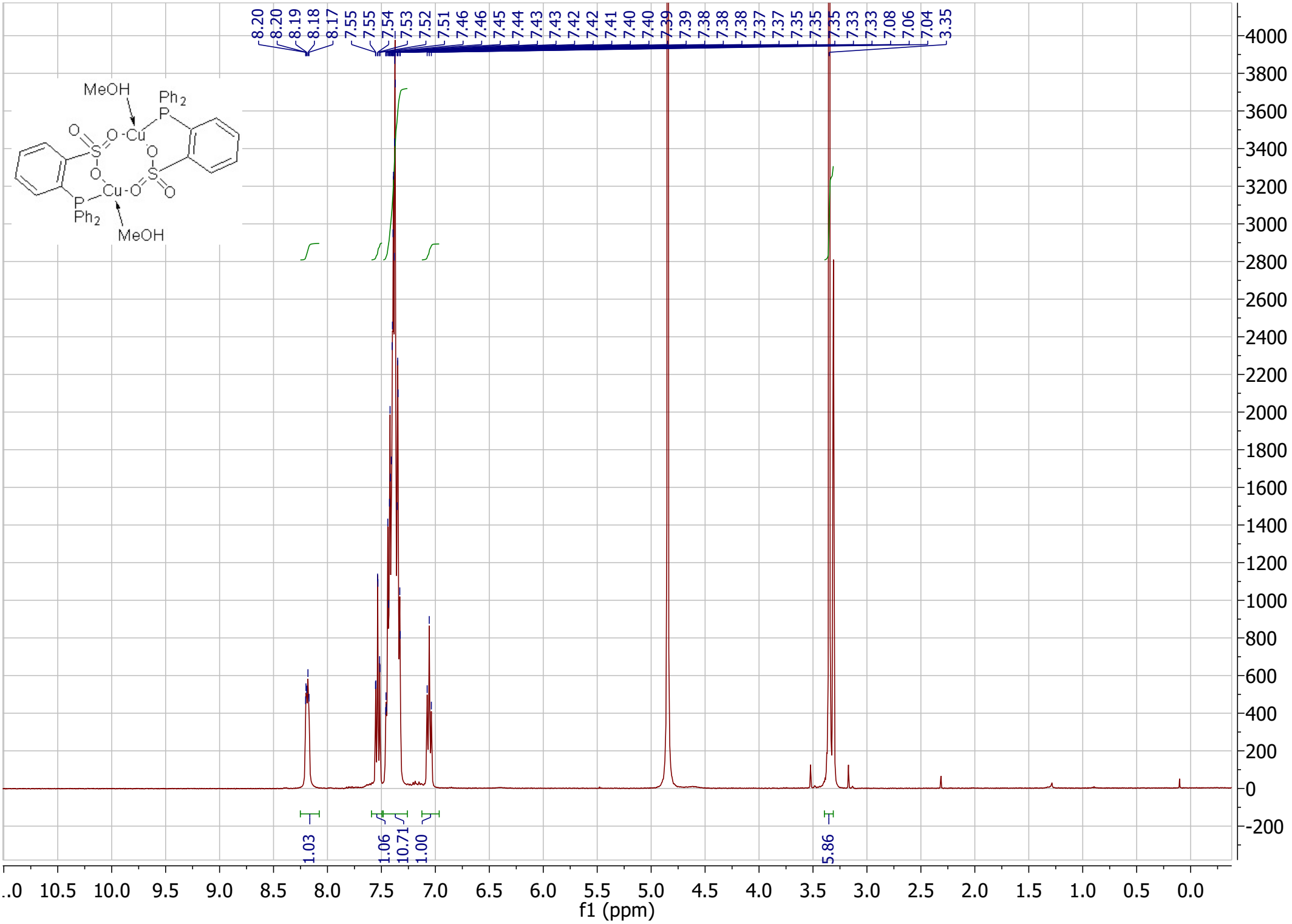
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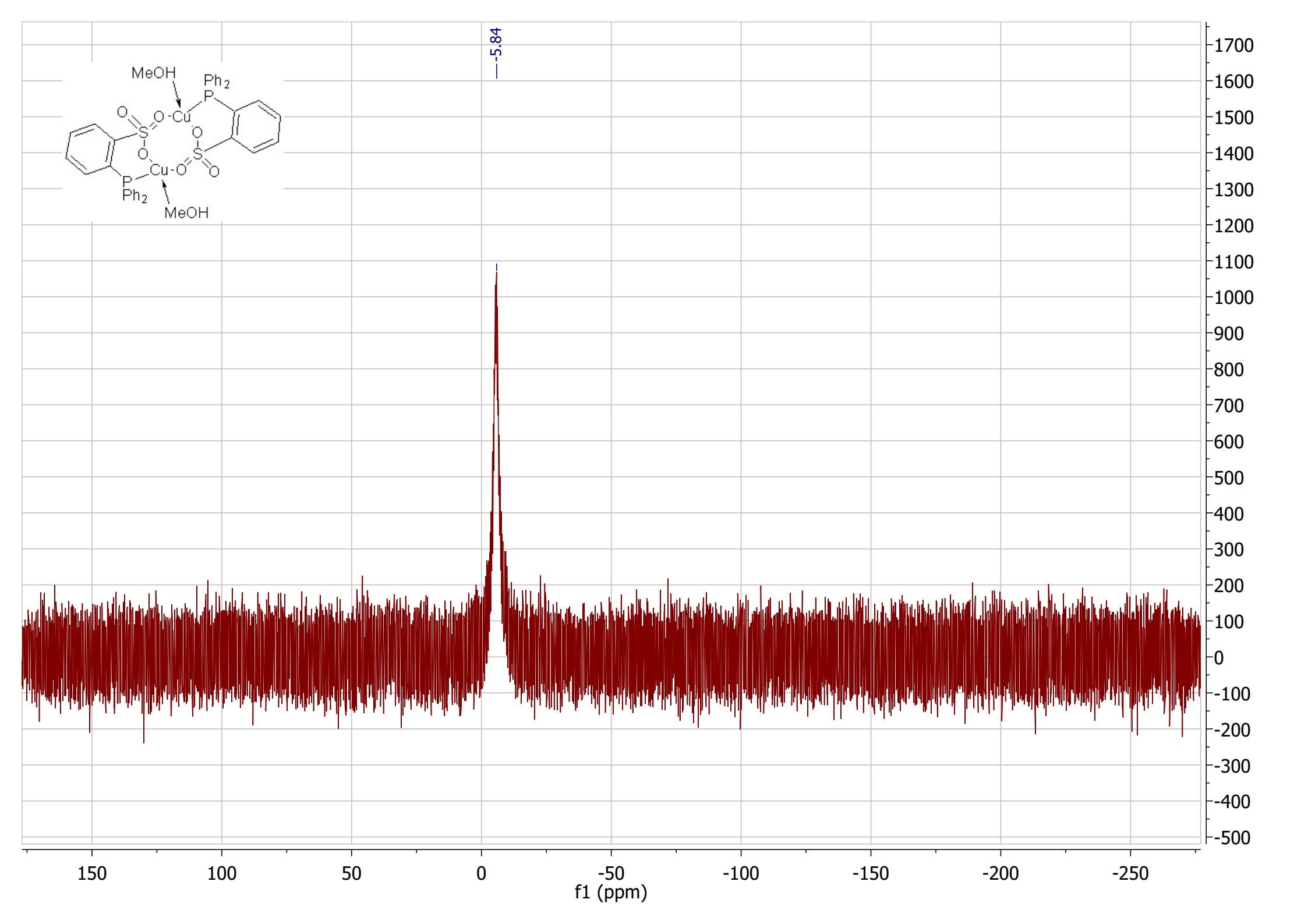
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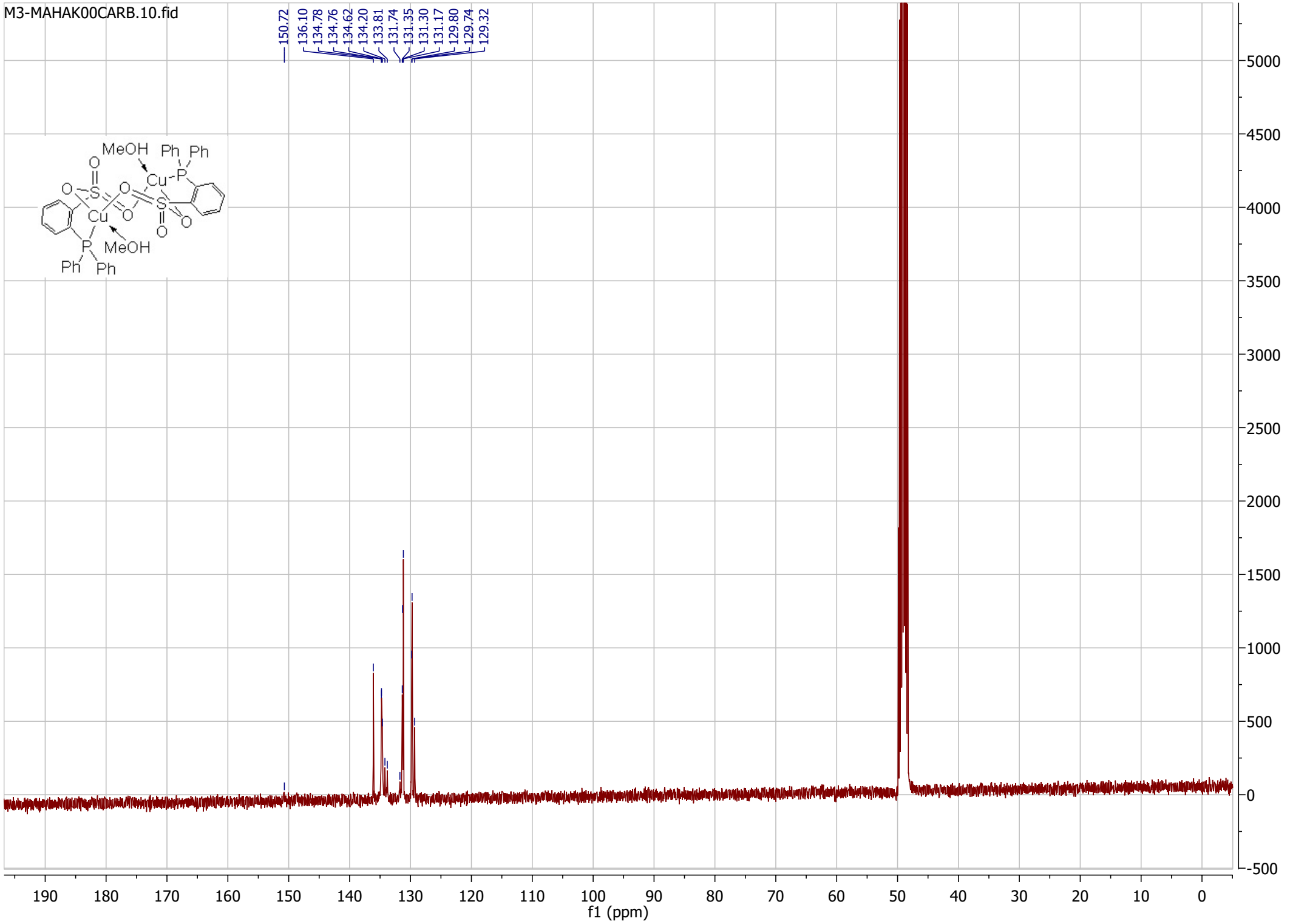
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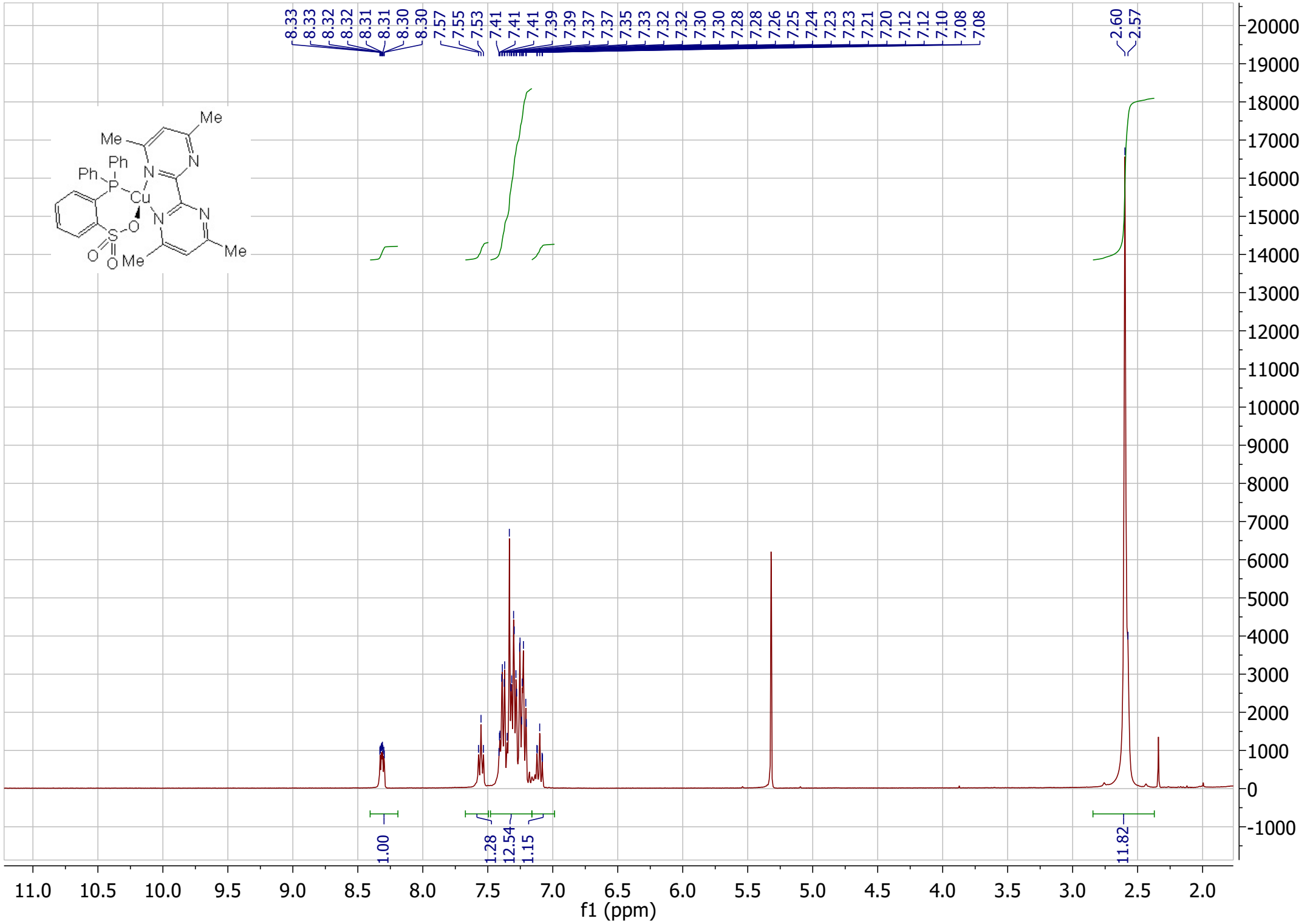
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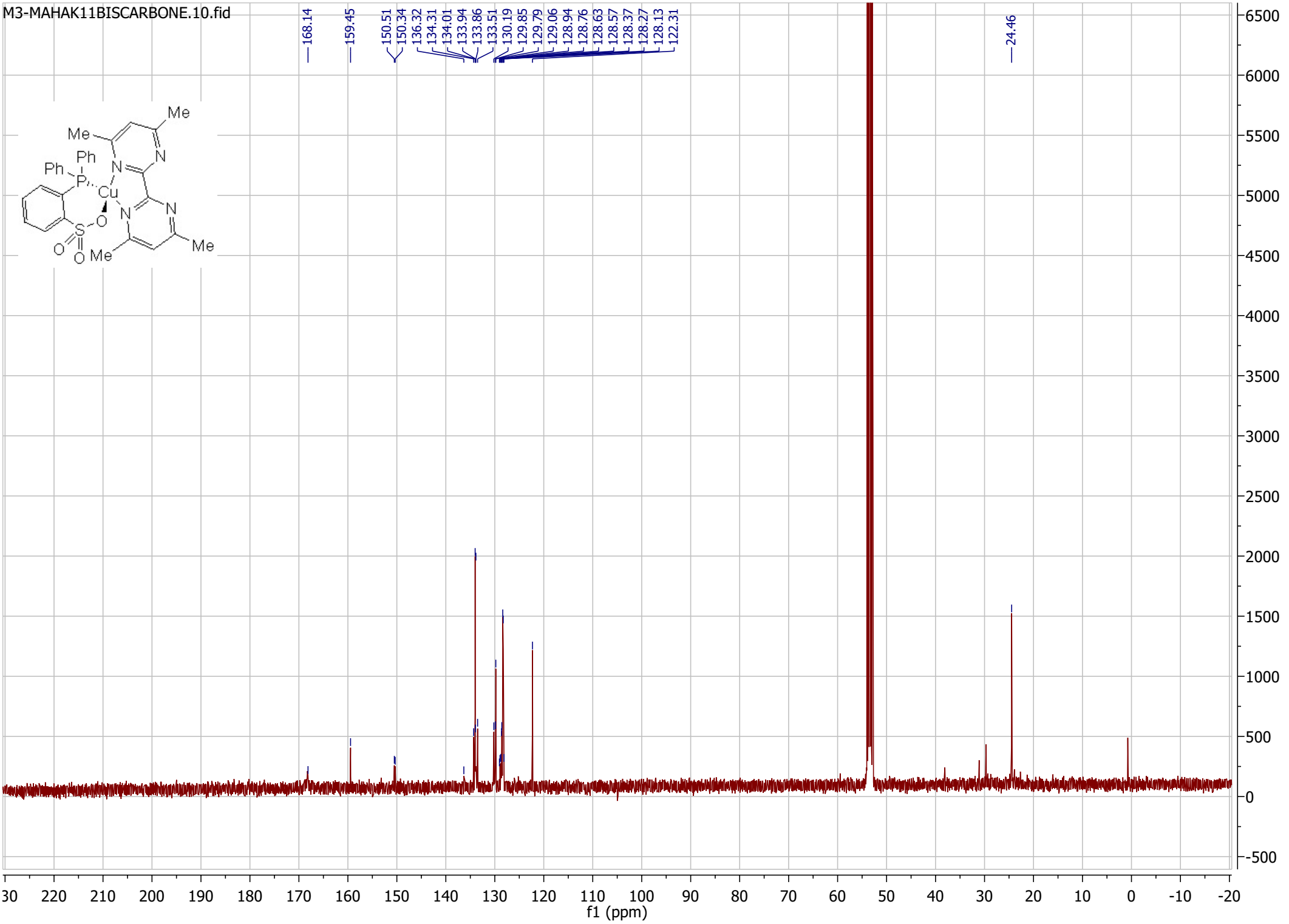
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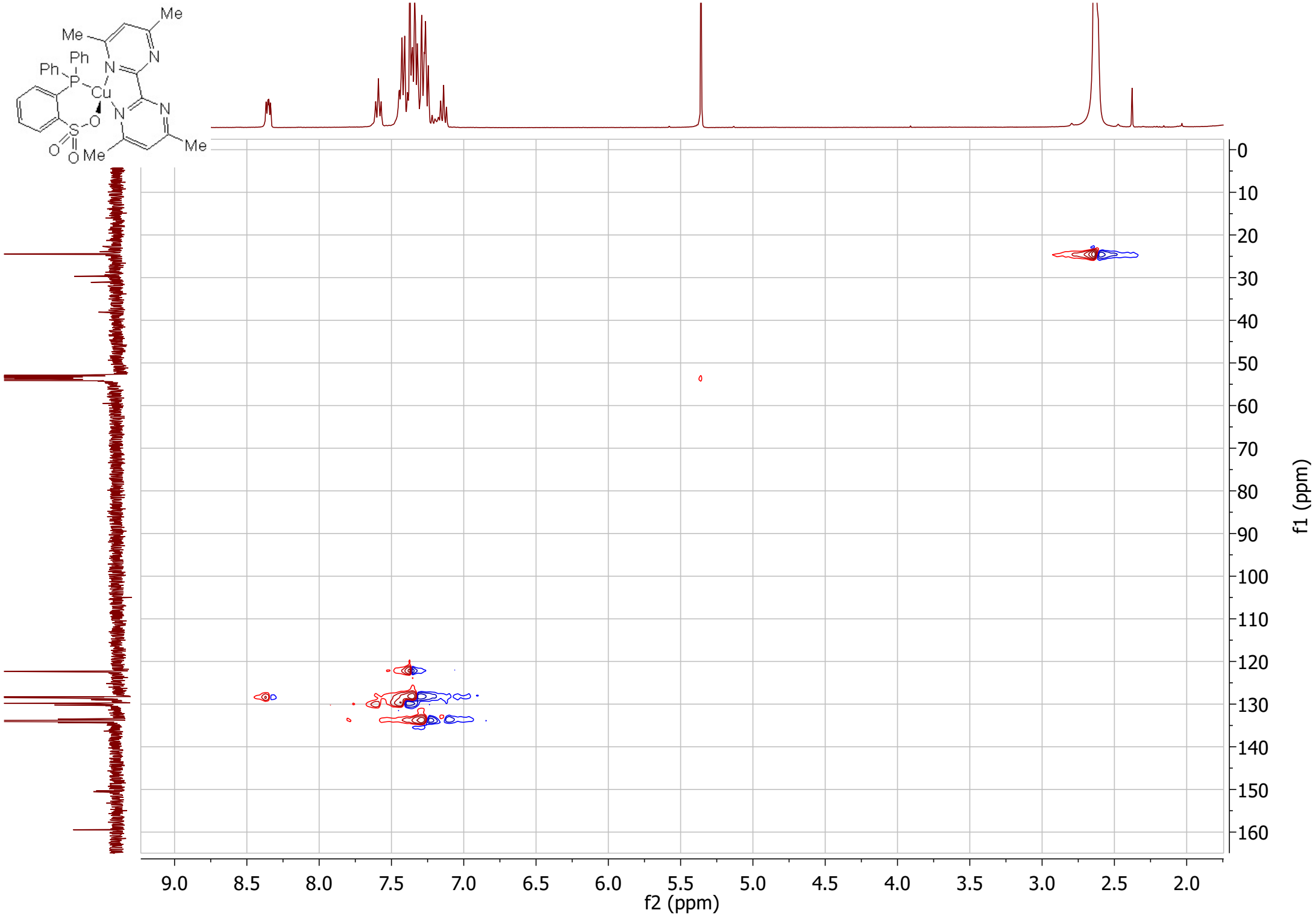
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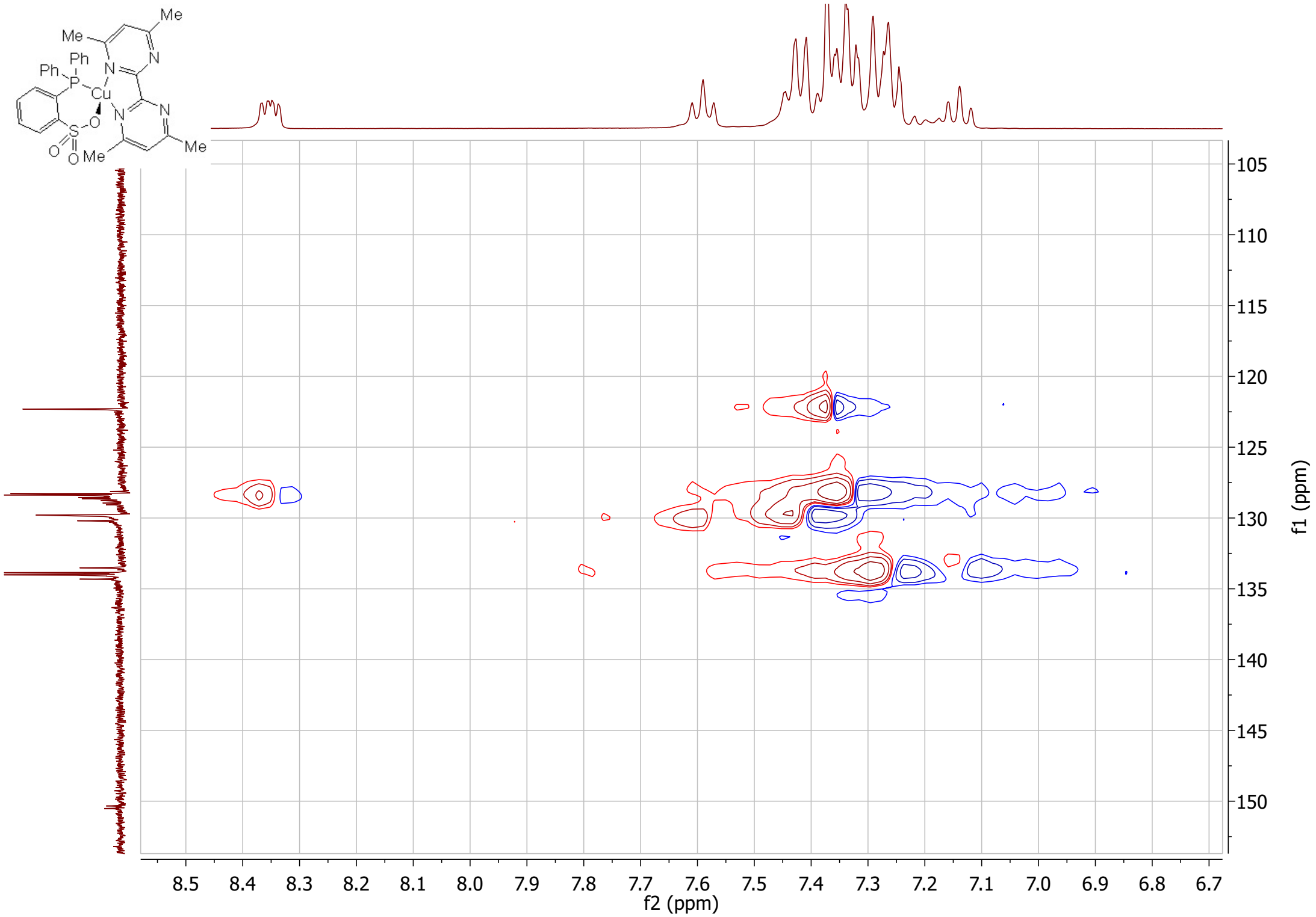
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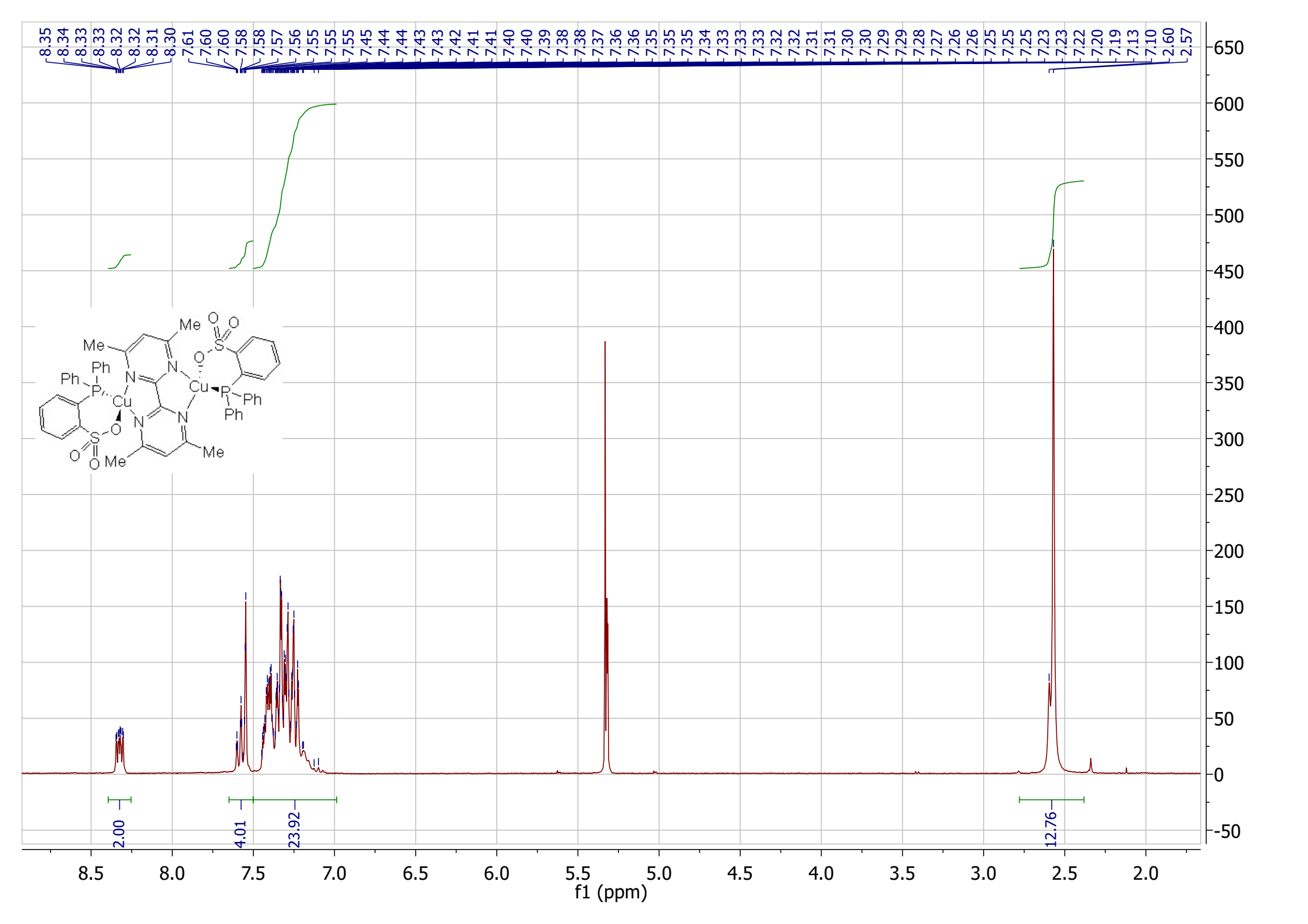
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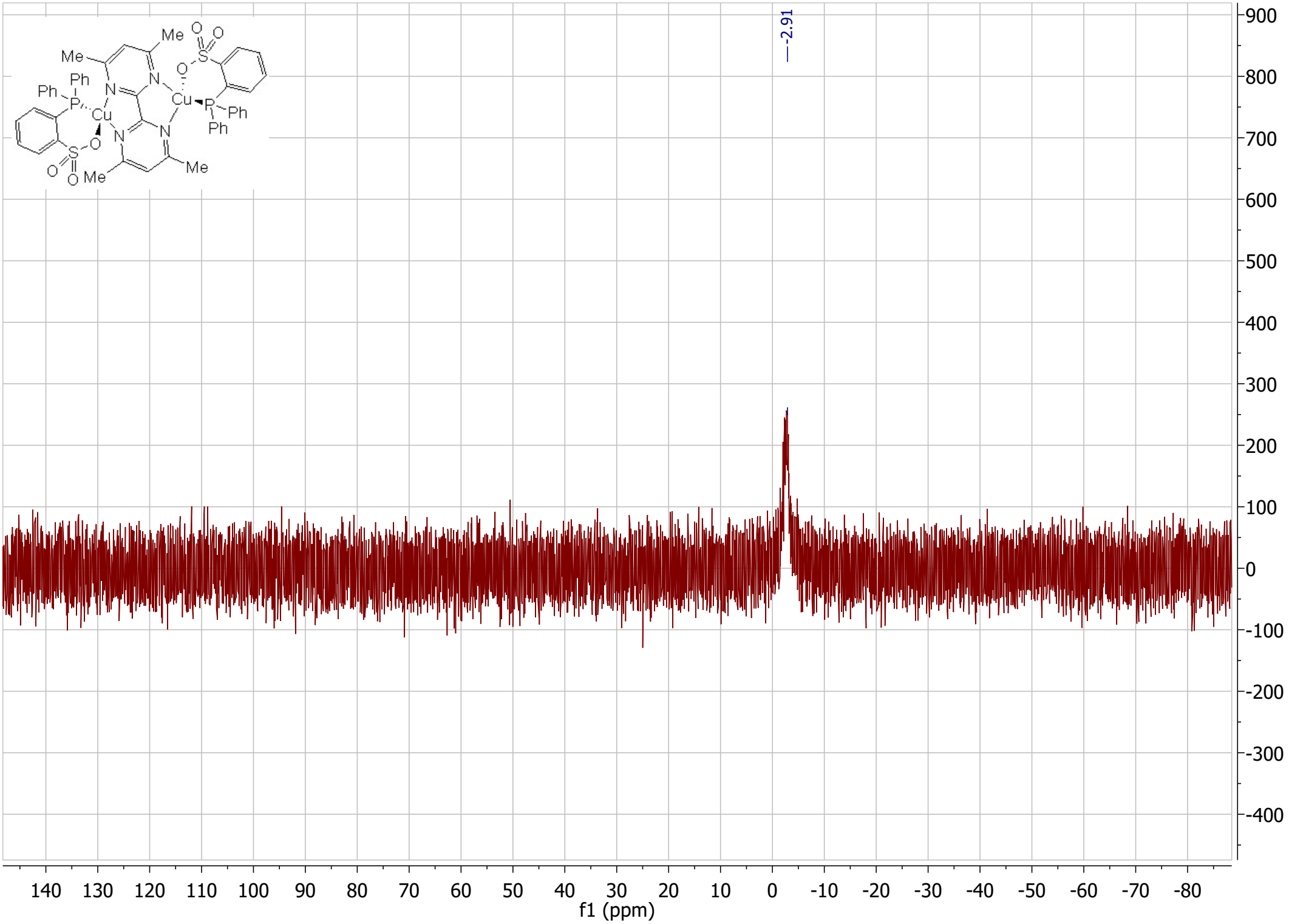
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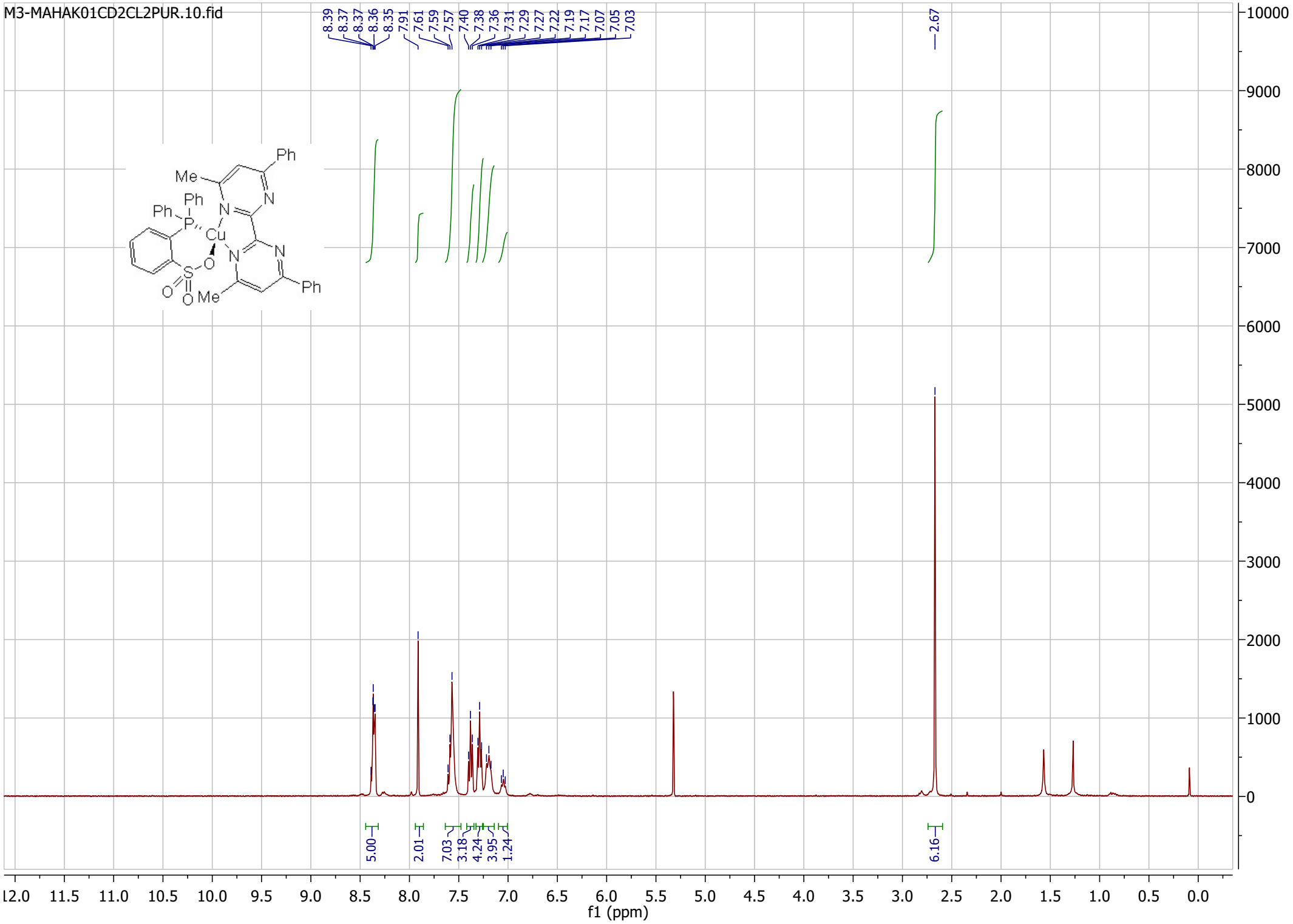
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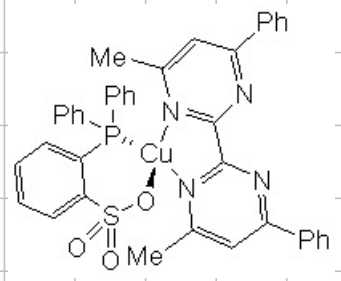

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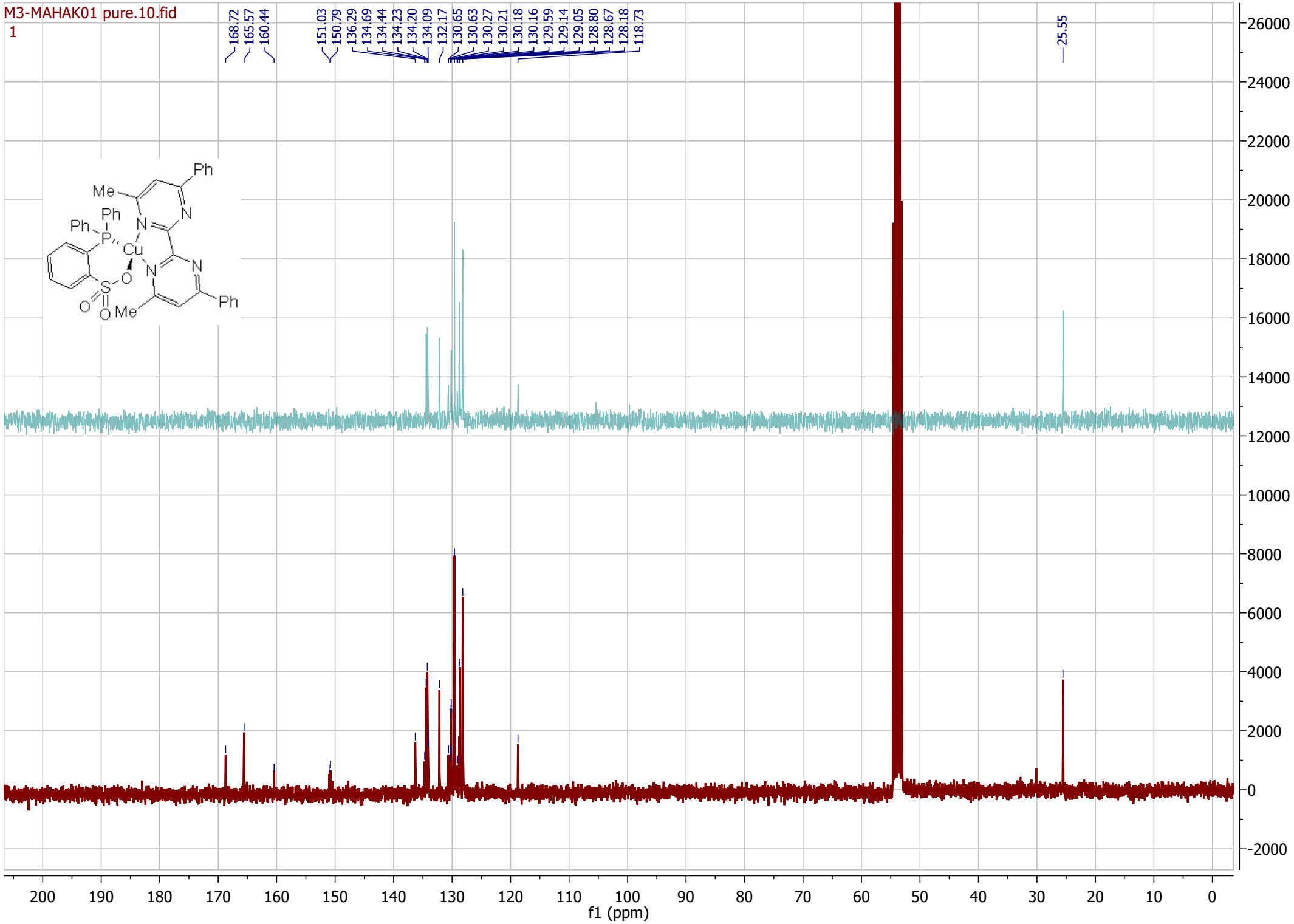
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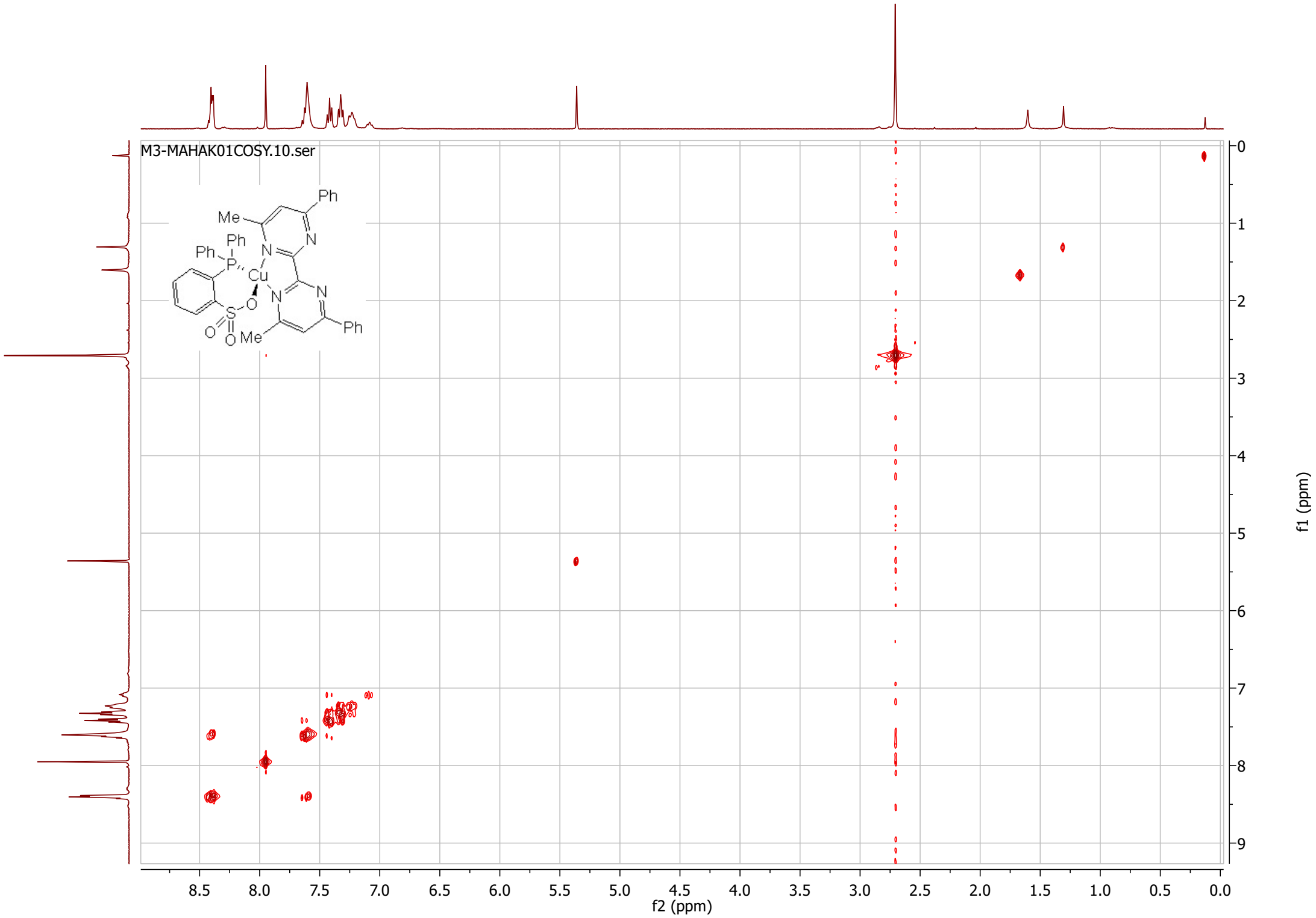
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