7-29-99

Supporting Information for:

Synthesis of Four Diastereomeric 3,5-Dialkoxy-2,4-dimethylalkanals by a Simple Extension of the Non-aldol Aldol Process to Bis(propionates)

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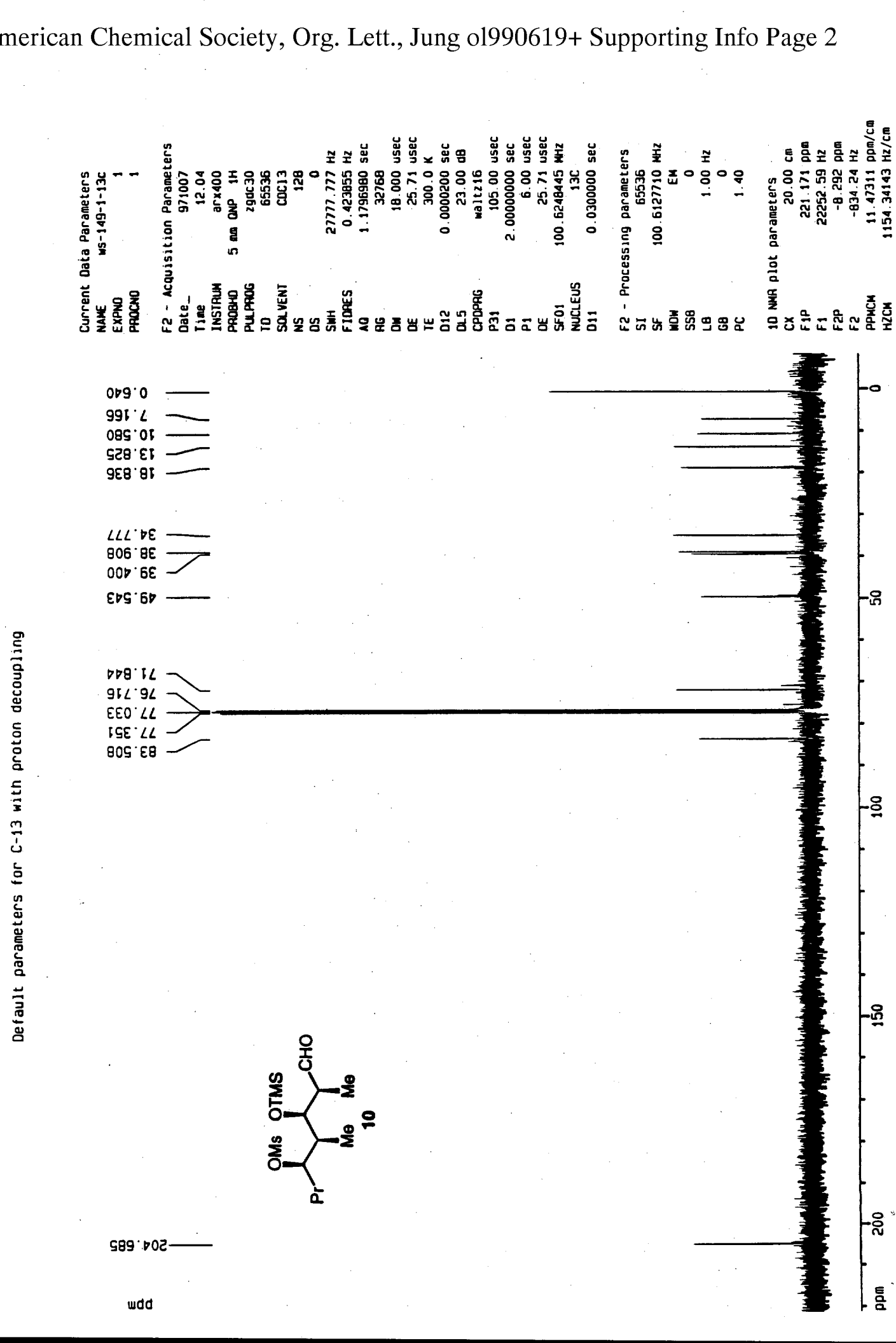
General Procedure For Epoxide Rearrangement

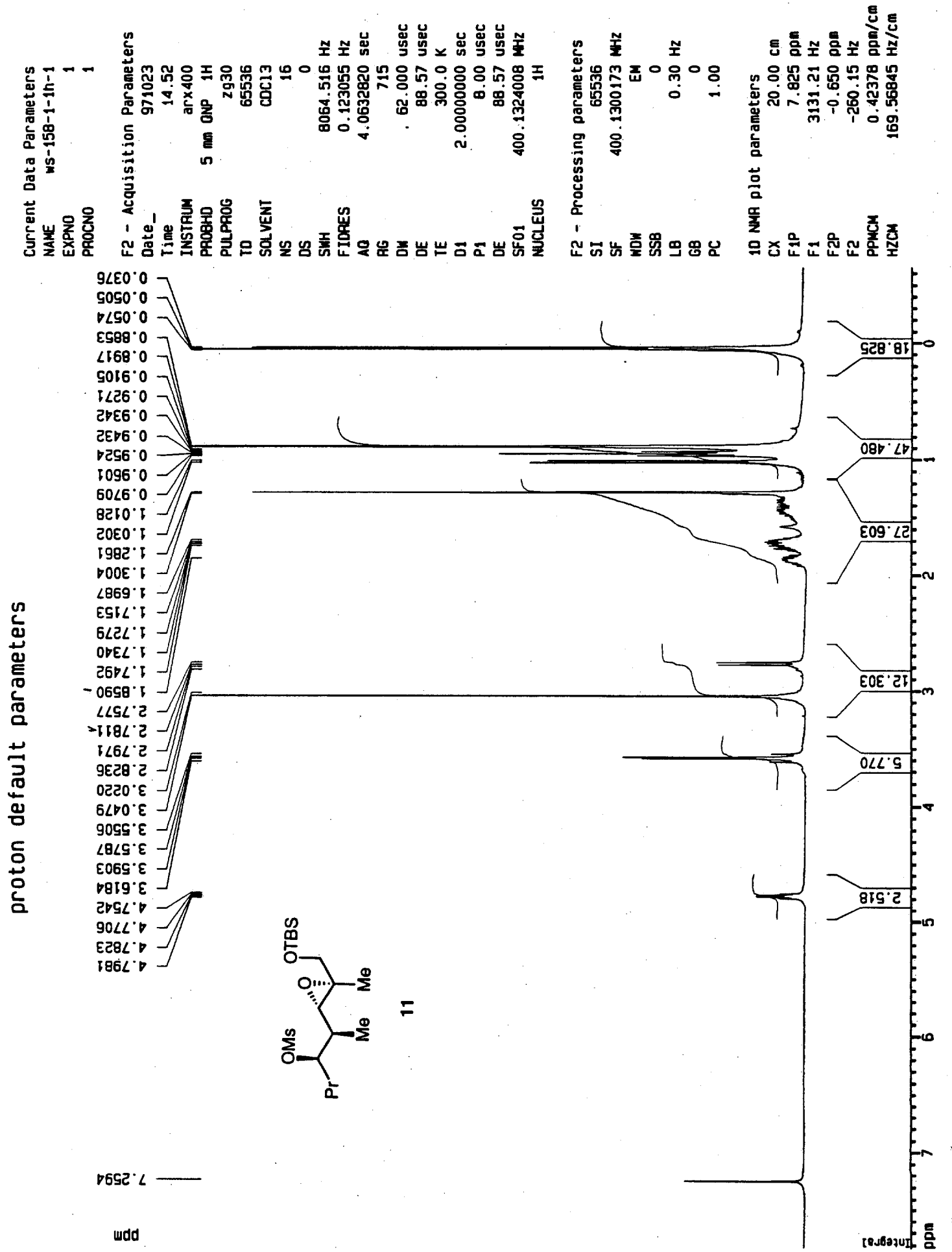
Rearrangement of Epoxides From *E*-allylic Alcohols

The epoxide silyl ether **9** or **11** (0.17 mmol, 1 eq) was dissolved in 3 ml of dichloro-methane and treated with diisopropylethylamine (DIPEA, 6 eq). The solution was cooled to -78^{0}C and treated with trimethylsilyl triflate (TMSOTf, 6 eq). After the solution stirred for 3.5 h, the reaction mixture was quenched with water and extracted with ether. The organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting oil was chromatographed (50% ether/ 50% hexane) to give the aldehyde **10** or **12** in 82% or 70% yield respectively.

Rearrangement of Epoxides From *Z*-allylic Alcohols

A solution of the epoxy alcohol **13** (0.1 mmol, 1 eq) in 5 ml of dichloromethane was treated successively with DIPEA (2 eq) and triethylsilyl chloride (TESCl, 1.5 eq) at 25 °C. After the solution stirred for 3 h, the mixture was poured onto 50 ml of ether and shaken with 25 ml of 0.2 M pH 7 phosphate buffer. The layers were separated, extracted with ether, washed with 0.2 M pH 7 phosphate buffer, brine, dried over $MgSO_4$, and concentrated to give the silyl epoxide. The silyl epoxide was then dissolved in 4 ml of dichloromethane and treated with DIPEA (6 eq). The solution was cooled to -42 °C and treated with TMSOTf (6 eq). After the solution stirred for 3 h, the solution was poured onto 50 ml of ether and shaken with 25 ml of 0.2 M pH 7 phosphate buffer. The layers were separated, extracted with ether, washed with 0.2 M pH 7 phosphate buffer, brine, dried ($MgSO_4$), and concentrated to give a mixture of the aldehyde **14** and the allylic silyl ether **15** in a 4:1 ratio.

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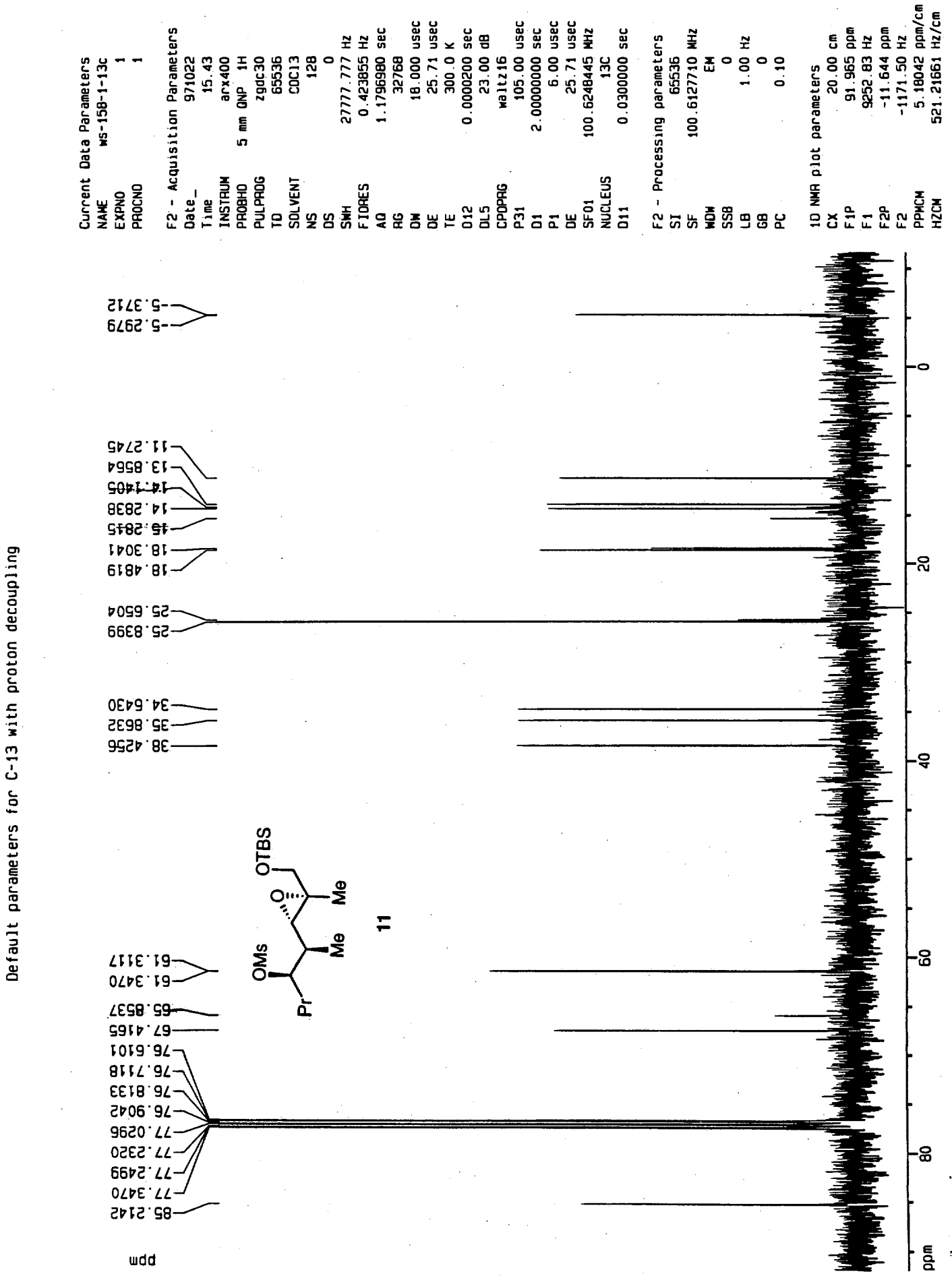

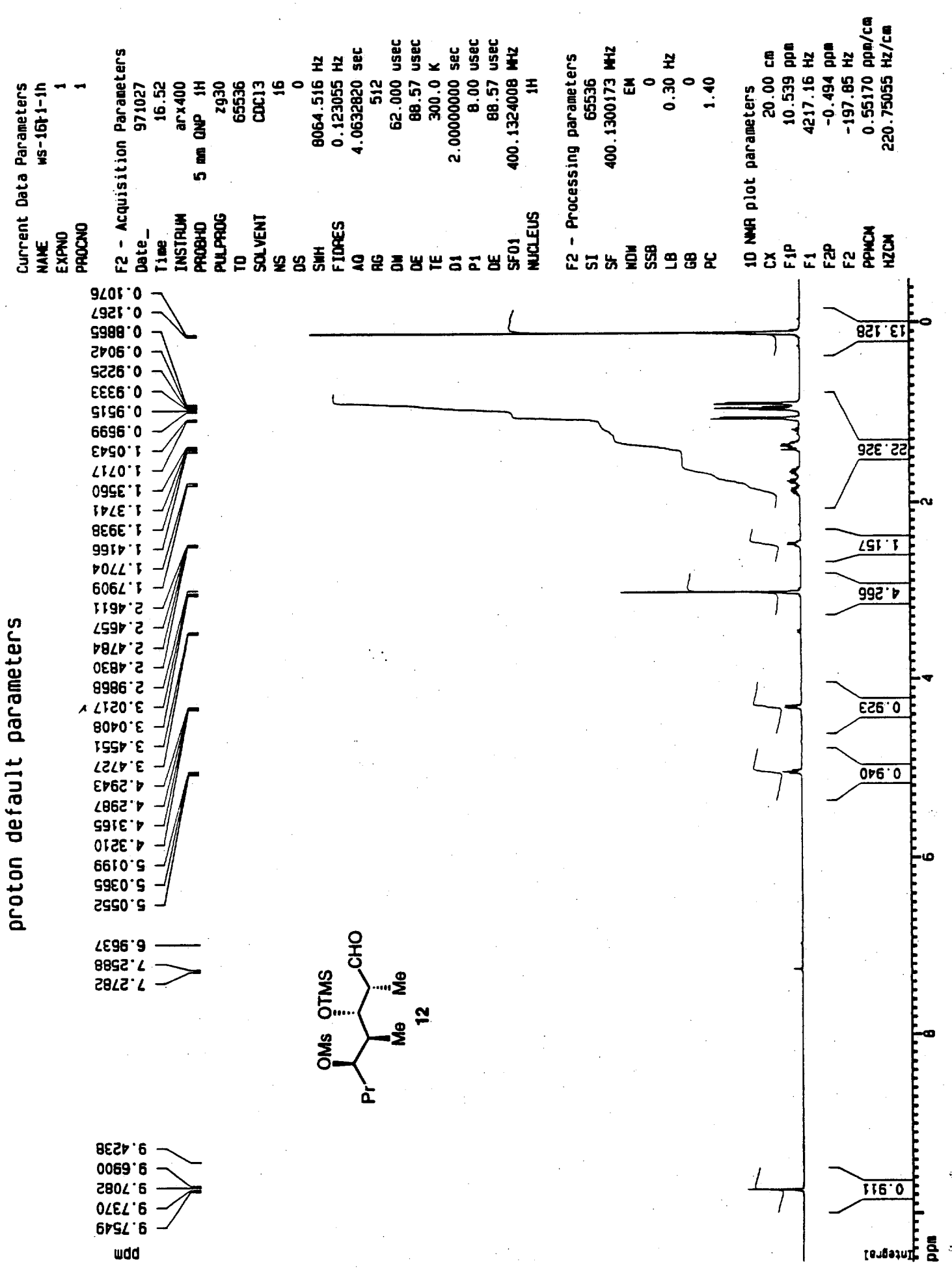

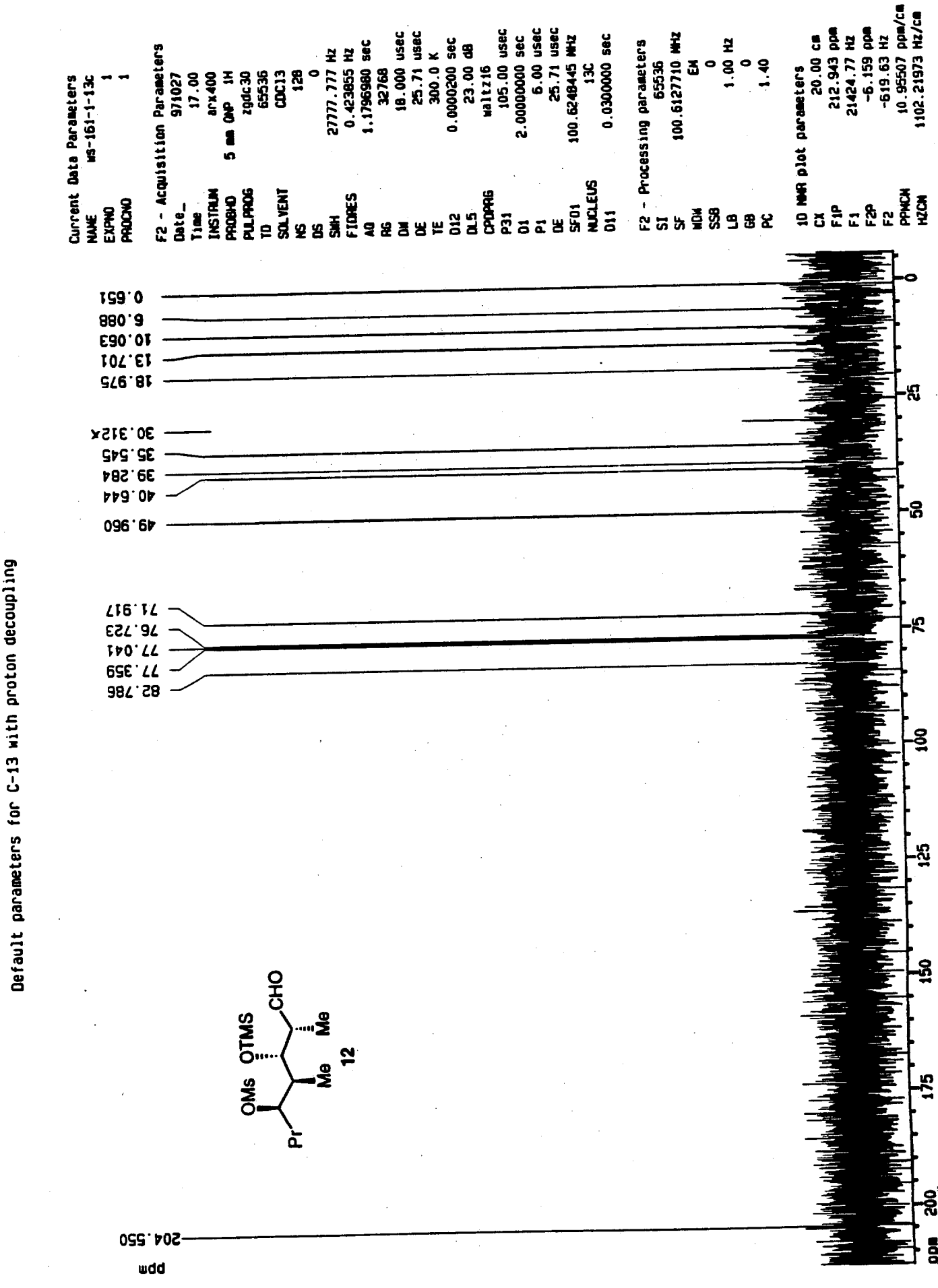

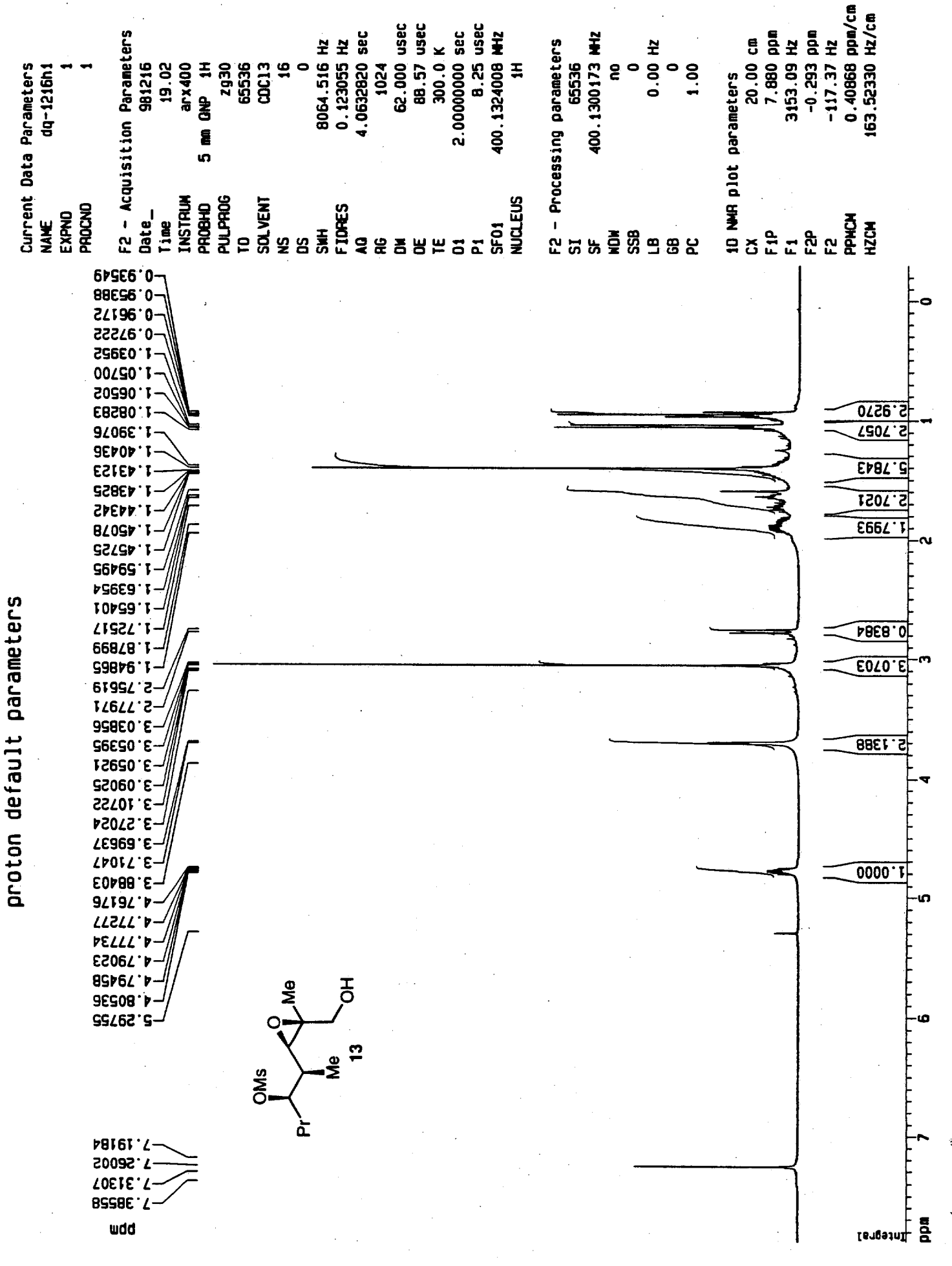
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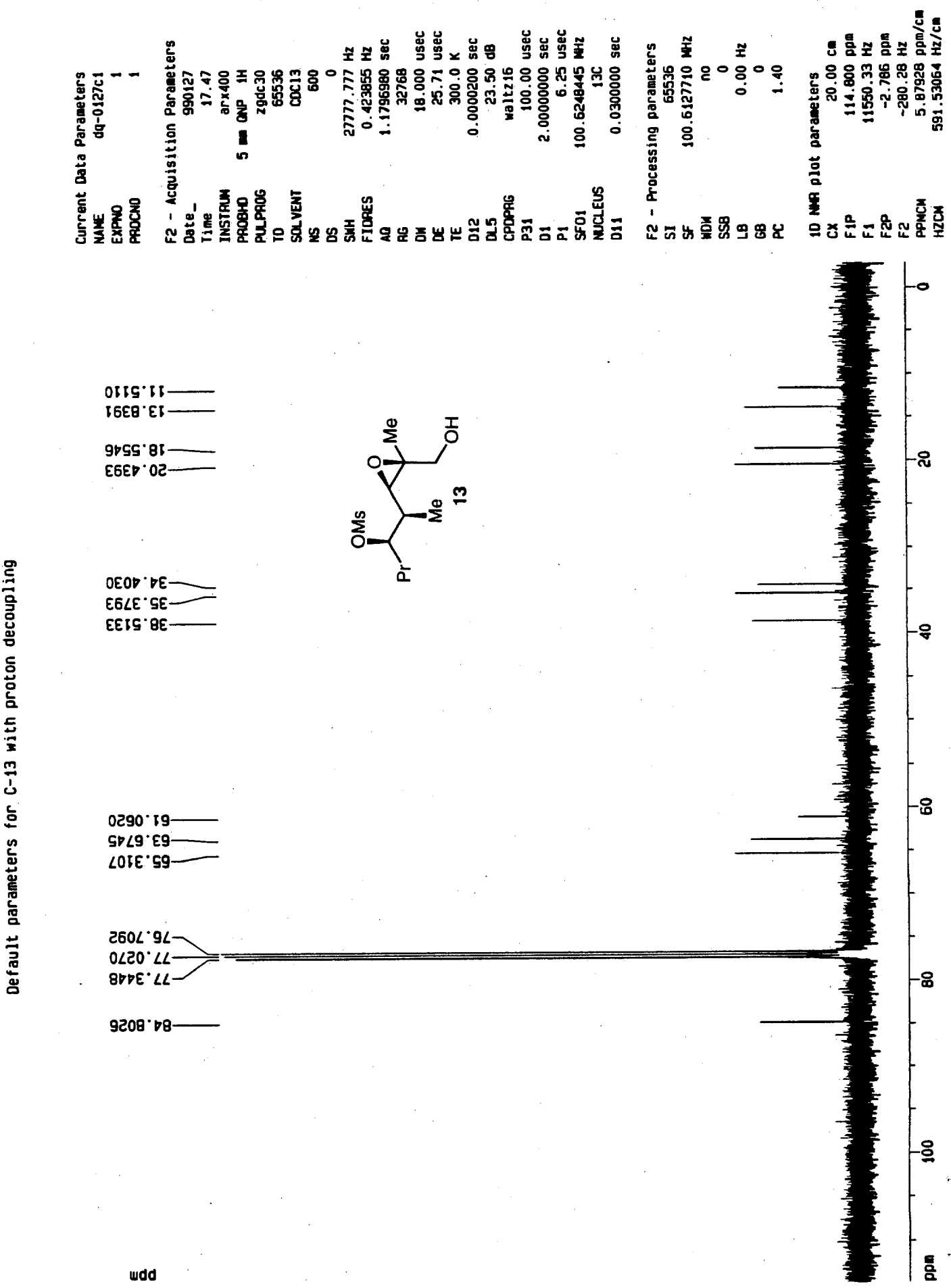
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