Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Synthesis of LNA 5′-phosphoramidites for 5′→3′-oligonucleotide synthesis

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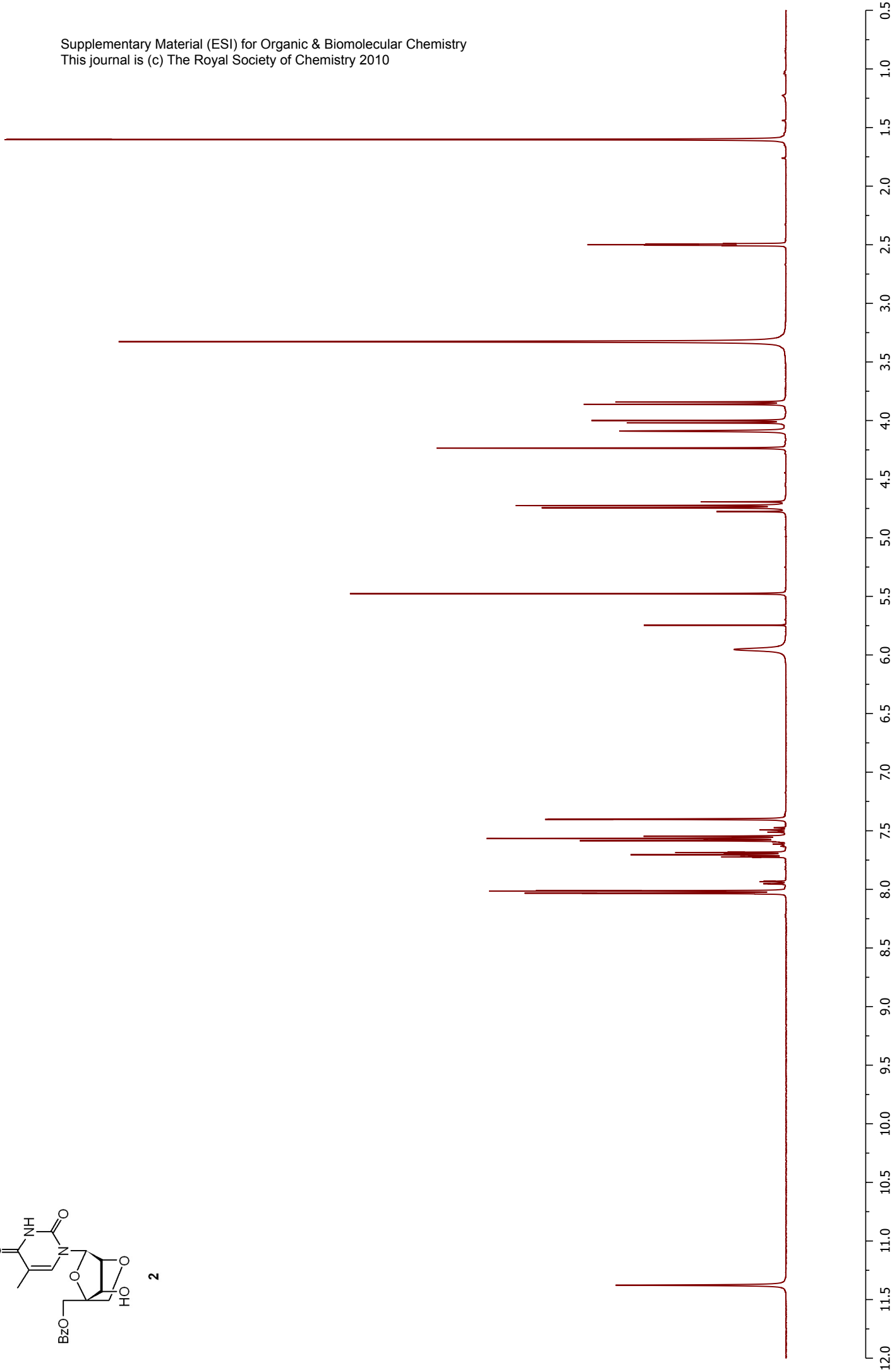
Supporting Information

General experimental section. All reagents and solvents were of analytical grade and used without further purification as obtained from commercial suppliers, except for dichloromethane and $POCl_3$, which was distilled before use. Petroleum ether (PE) of the distillation range 60–80 °C was used. Anhydrous acetonitrile was dried through storage over activated 3Å molecular sieves. Dichloromethane, 1,2-dichloroethane, triethylamine, 2,6-lutidine and pyridine for use in anhydrous reactions was dried through storage over activated 4Å molecular sieves. Anhydrous THF was dried over sodium and distilled before use. Reactions were conducted under an atmosphere of argon whenever anhydrous solvents were used. All reactions were monitored by thin-layer chromatography (TLC) using silica gel coated plates (analytical SiO_2-60, F-254). TLC plates were visualized under UV light and by dipping in either (a) 5% conc. sulfuric acid in abs. ethanol (v/v) or (b) a solution of molybdato-phosphoric acid (12.5 g/L) and cerium(IV)sulfate (5 g/L) in 3% conc. sulfuric acid in water (v/v) followed by heating with a heat gun. Silica gel column chromatography was performed using an automated purification system. After column chromatography, appropriate fractions were pooled and dried at high vacuum for at least 12 h to give obtained products. Evaporation of solvents was carried out under reduced pressure at a temperature below 40 °C. ^{1}H NMR, ^{13}C NMR and ^{31}P NMR were recorded at 400 MHz, 101 MHz and 162 MHz, respectively. Chemical shifts are reported in ppm relative to deuterated solvent as internal standard (δ_H: DMSO-d_6 2.50 ppm; δ_C: DMSO-d_6 39.51 ppm) or external standard (δ_P: 85% H_3PO_4 0.00 ppm). Exchangeable (ex) protons were detected by disappearance of peaks upon addition of D_2O. Assignments of NMR spectra are based on correlation spectroscopy (COSY, HSQC, and HMBC spectra) and follow standard nucleoside nomenclature. Systematic compound names are given according to von Baeyer nomenclature.[S1] ESI-HRMS were recorded in positive ion mode.

References

(S1) *Eur. J. Biochem.* **1983**, *131*, 5-7.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f1 (ppm)

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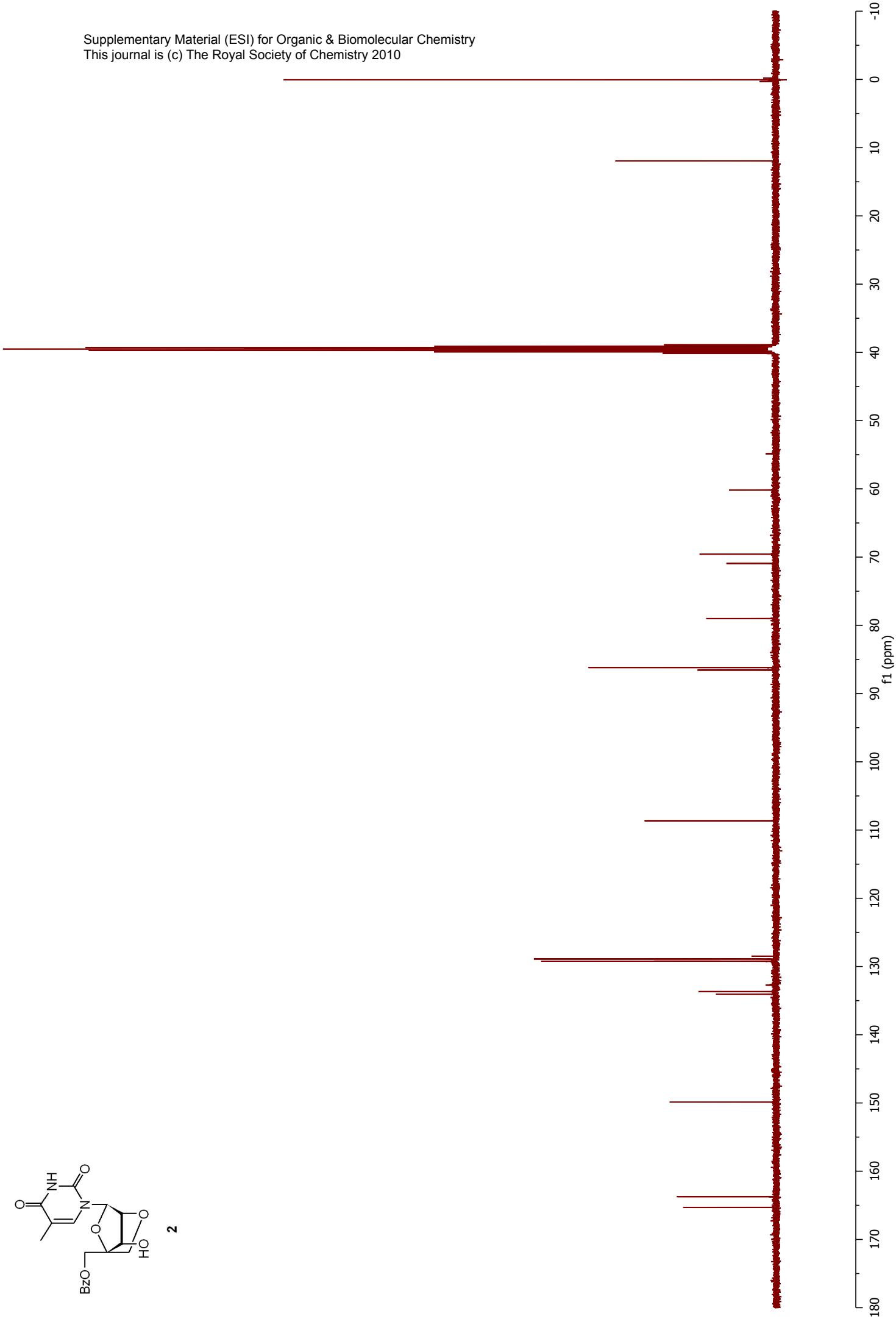
BzO

2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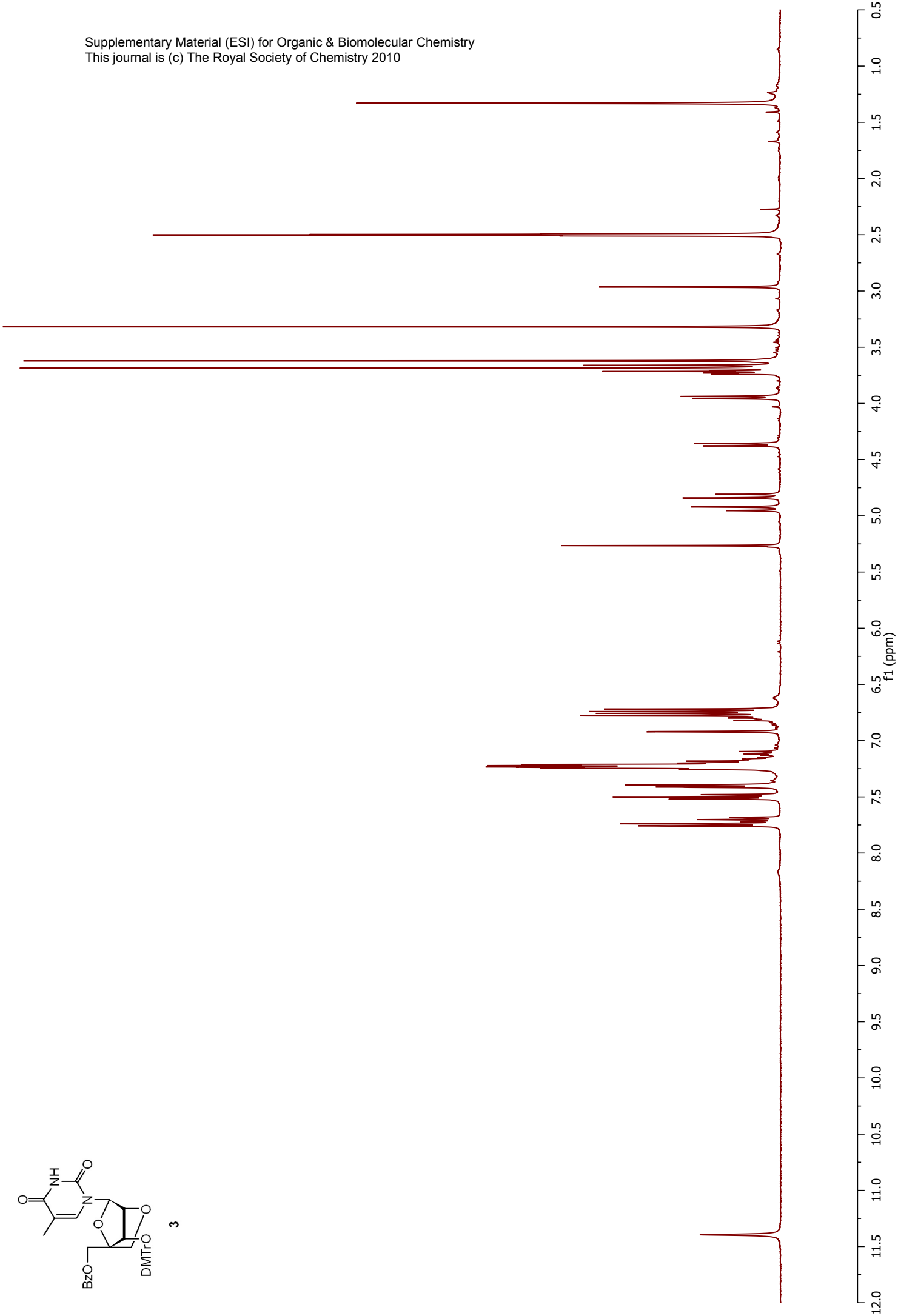
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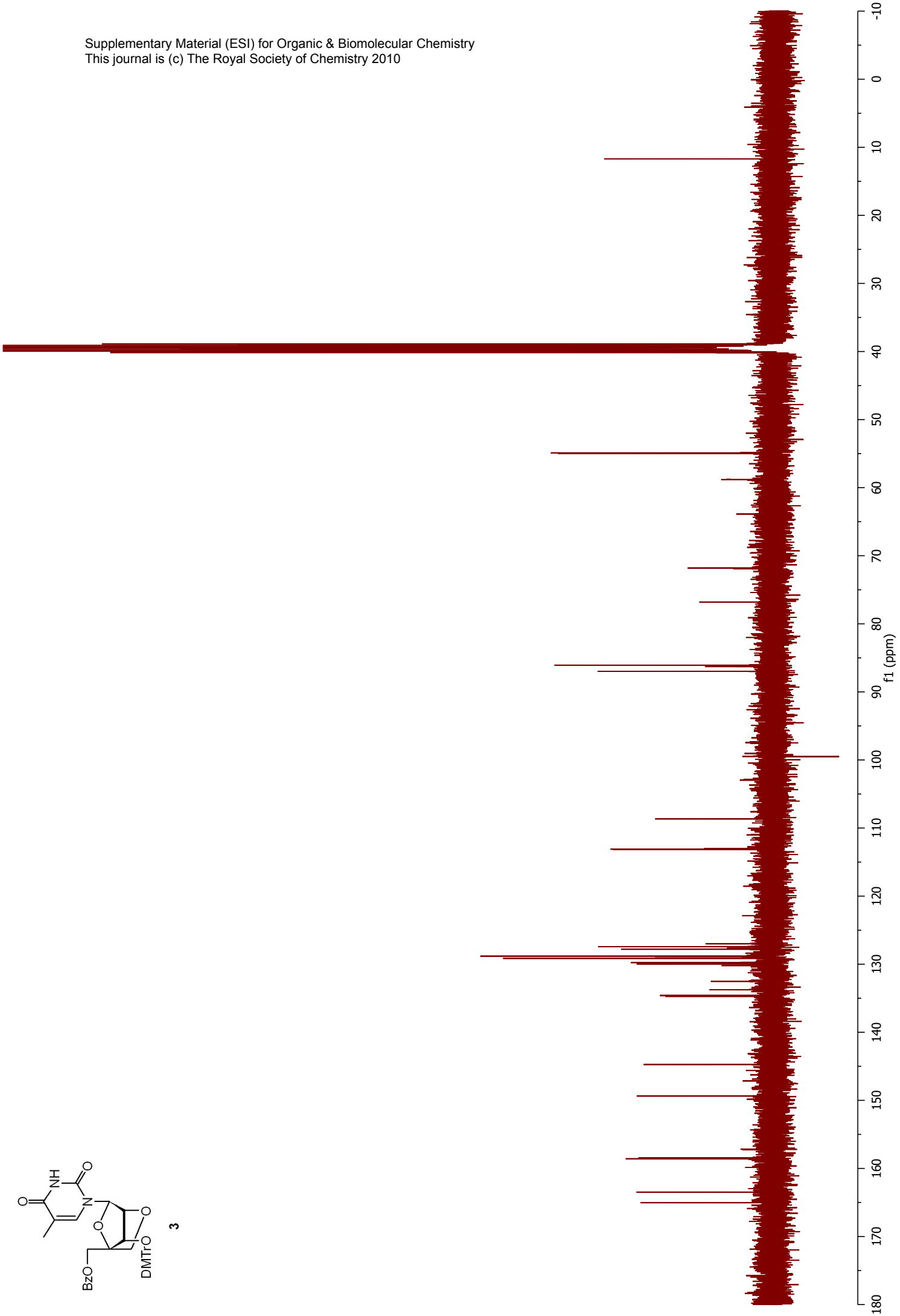

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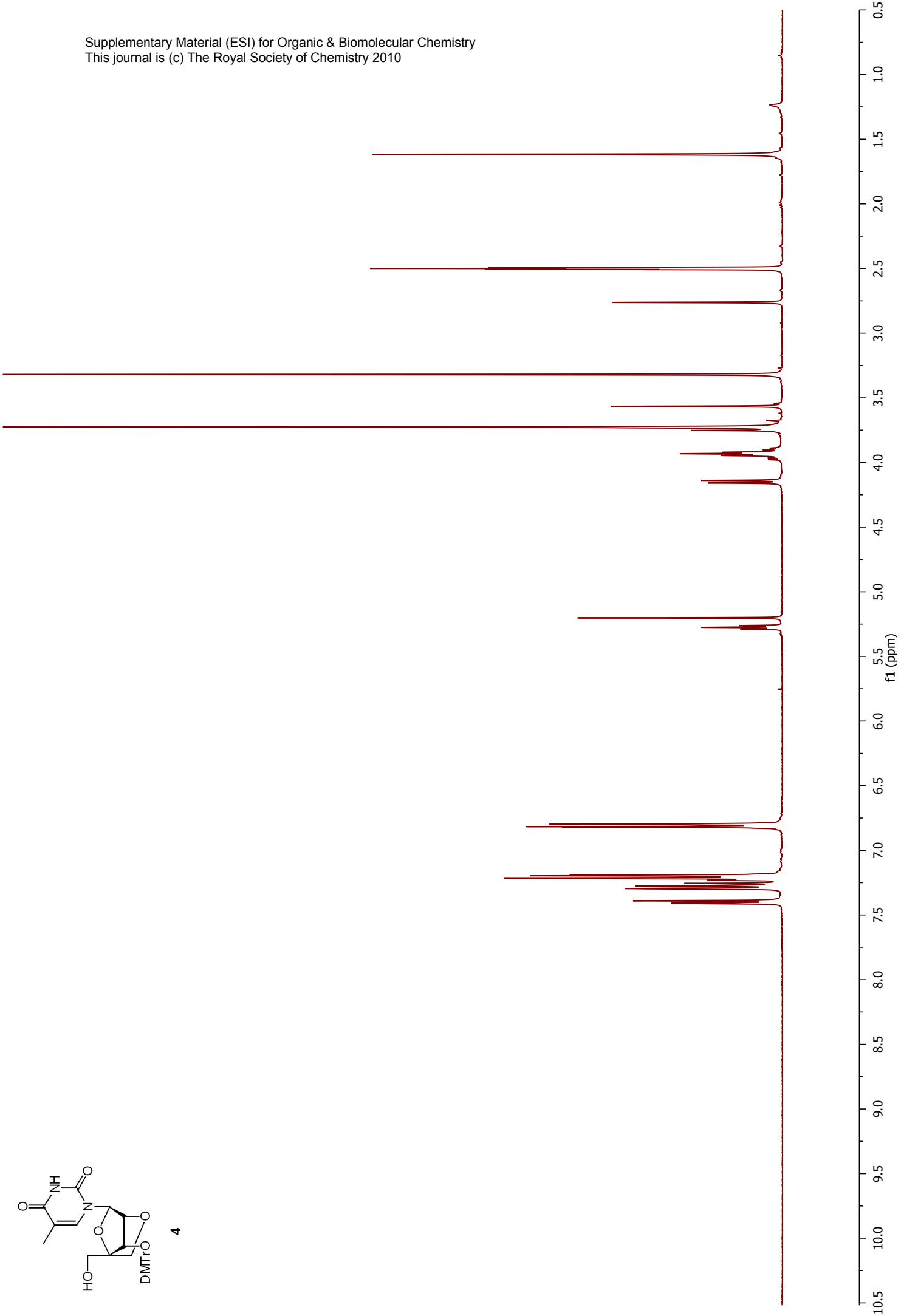
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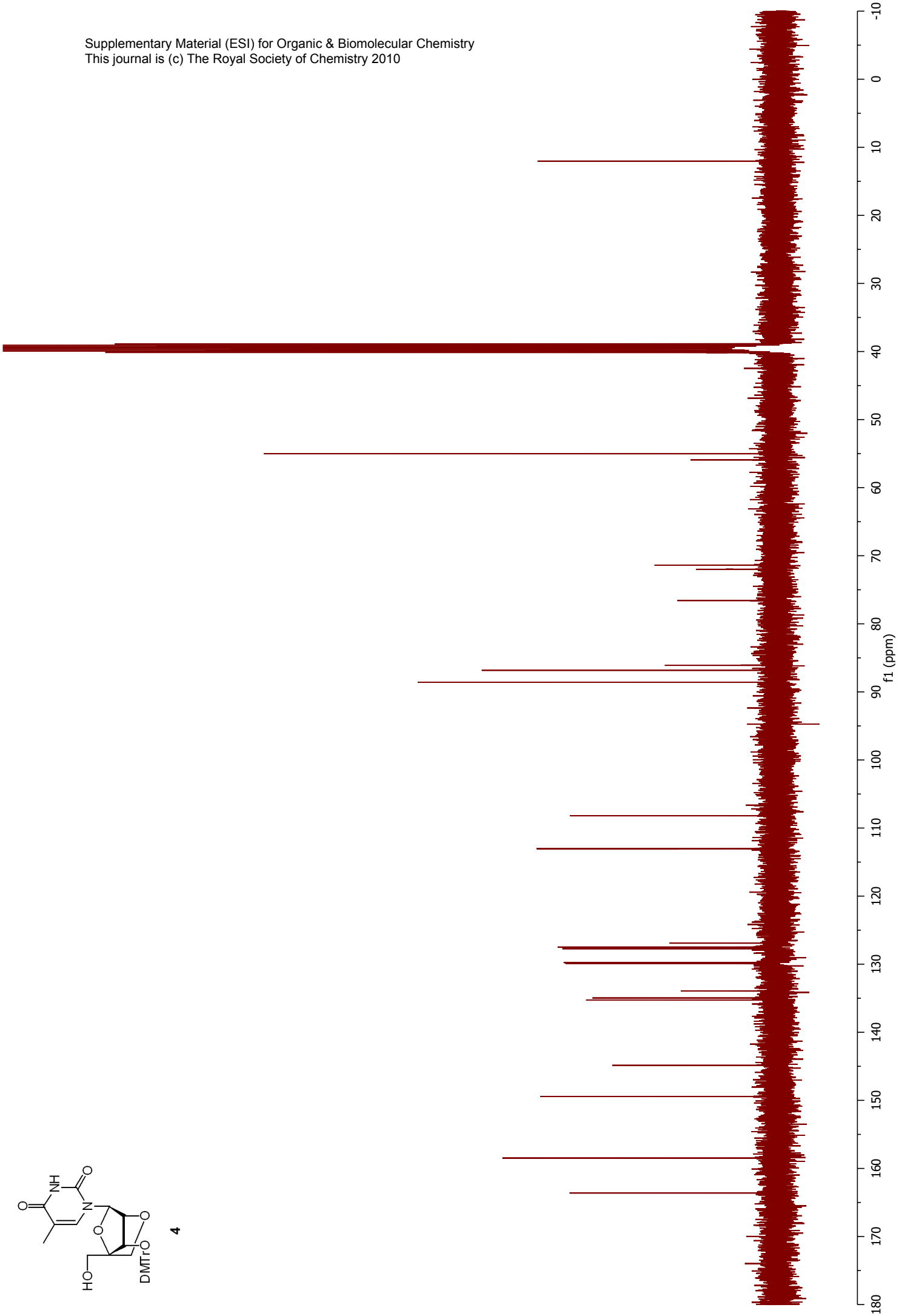
HO
DMTrO

4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NH
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HO
DMTrO

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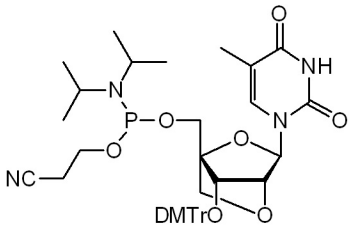

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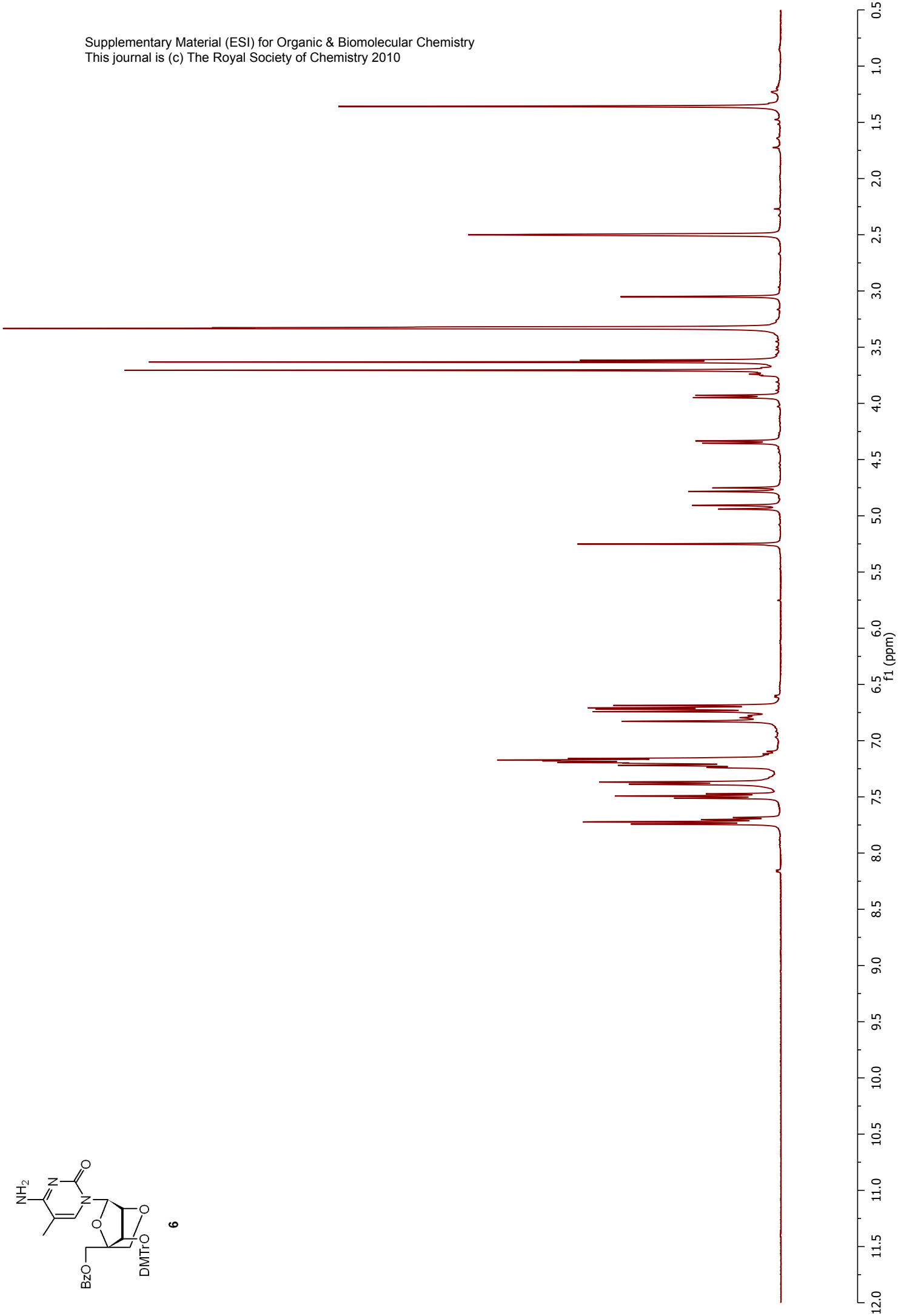
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f1 (ppm)

NH2
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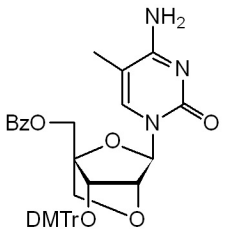
DMTrO
BzO

6



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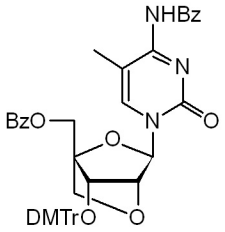

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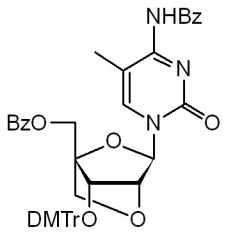

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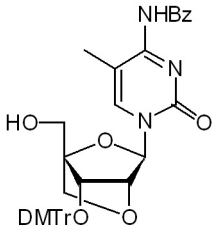

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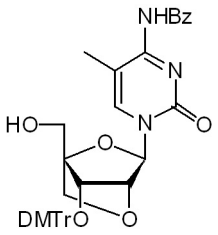

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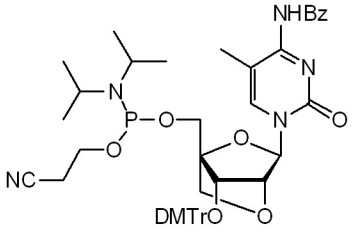

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