Supplementary Information (SI) for Analytical Methods.

Supplementary Information

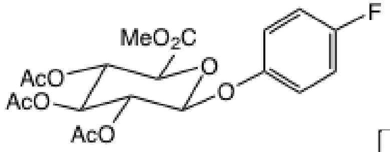
Characterisation

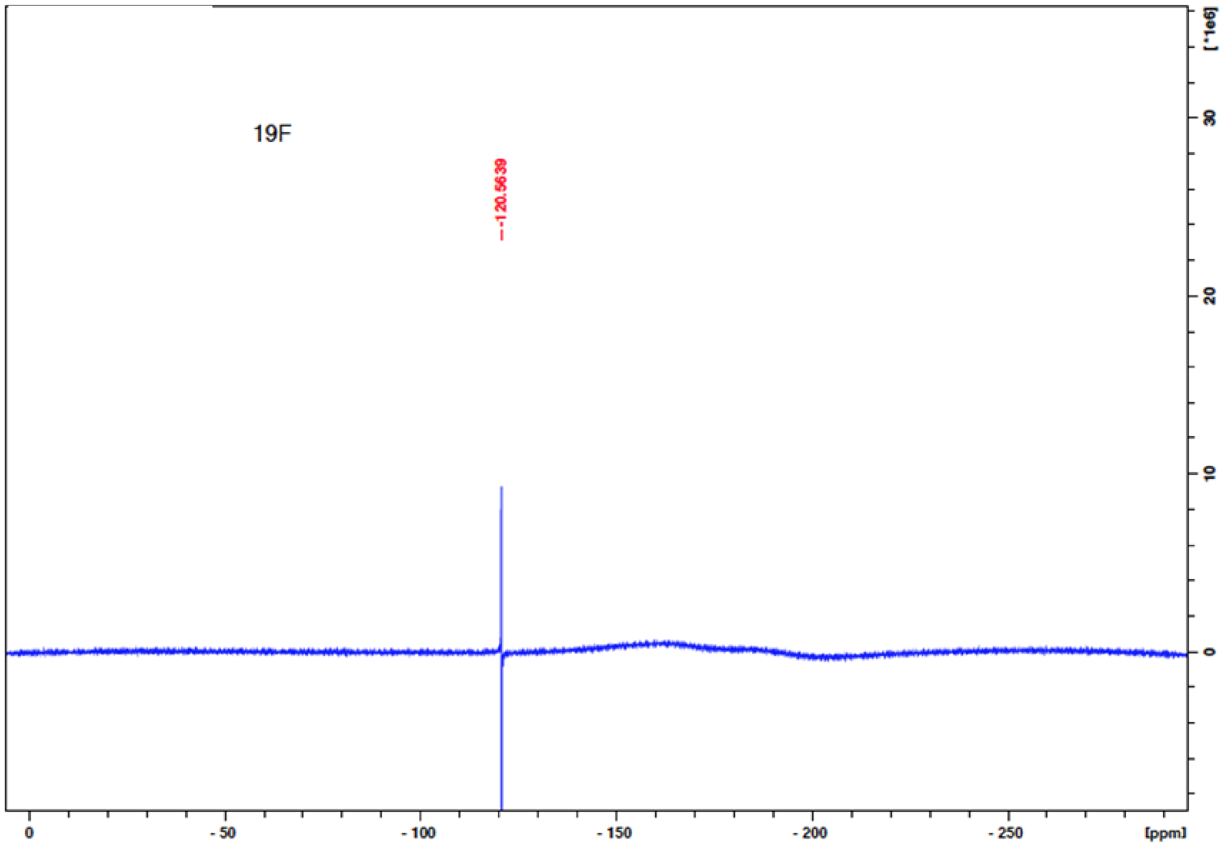
Reproducibility

Full scale spectra

Expanded spectra

Compound (**1**). Methyl-1-(4-fluorophenyl)-2,3,4-tri-O-acetyl- β-D-glucopyranosyluronate





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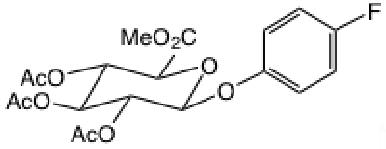

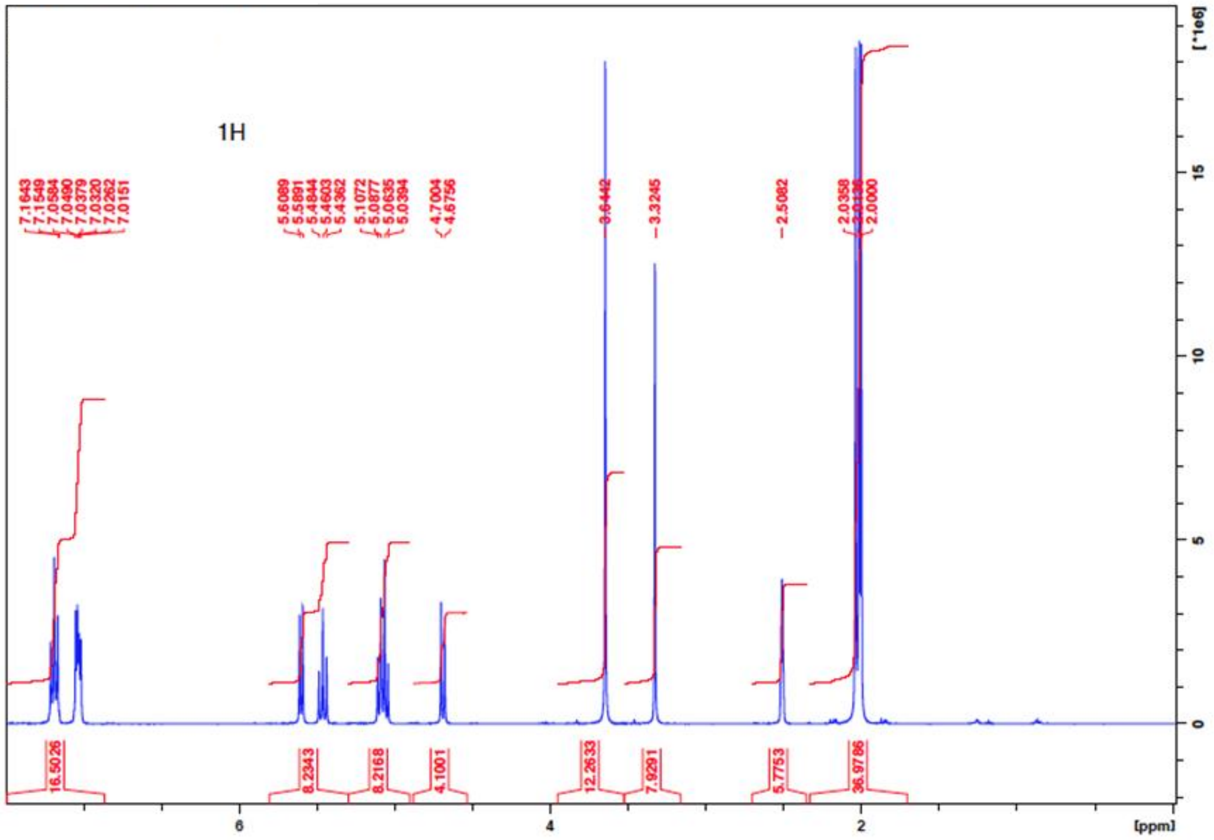

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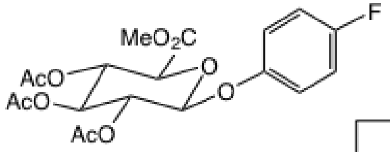
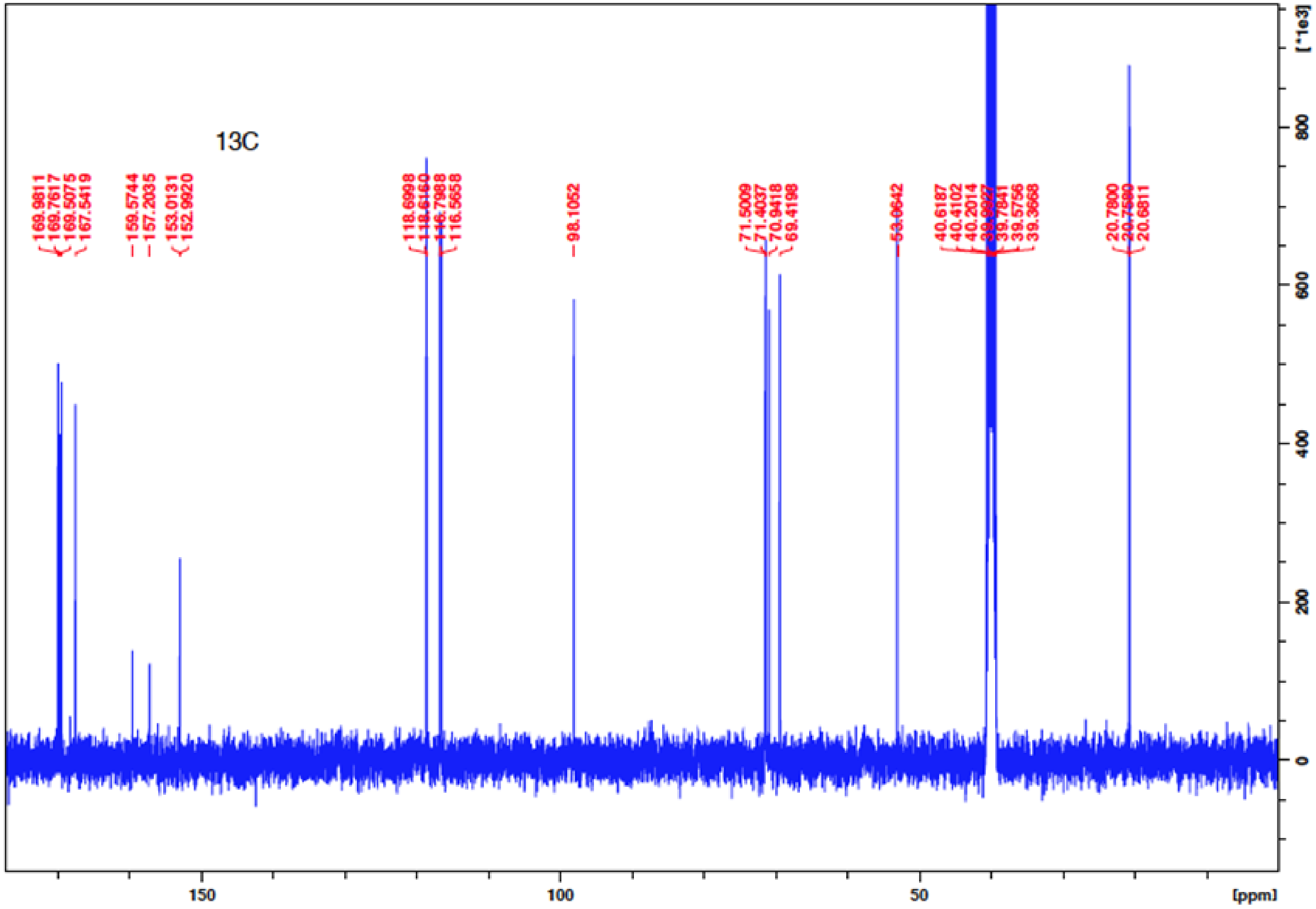
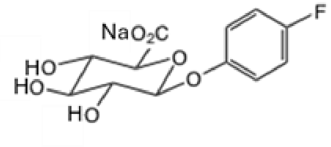
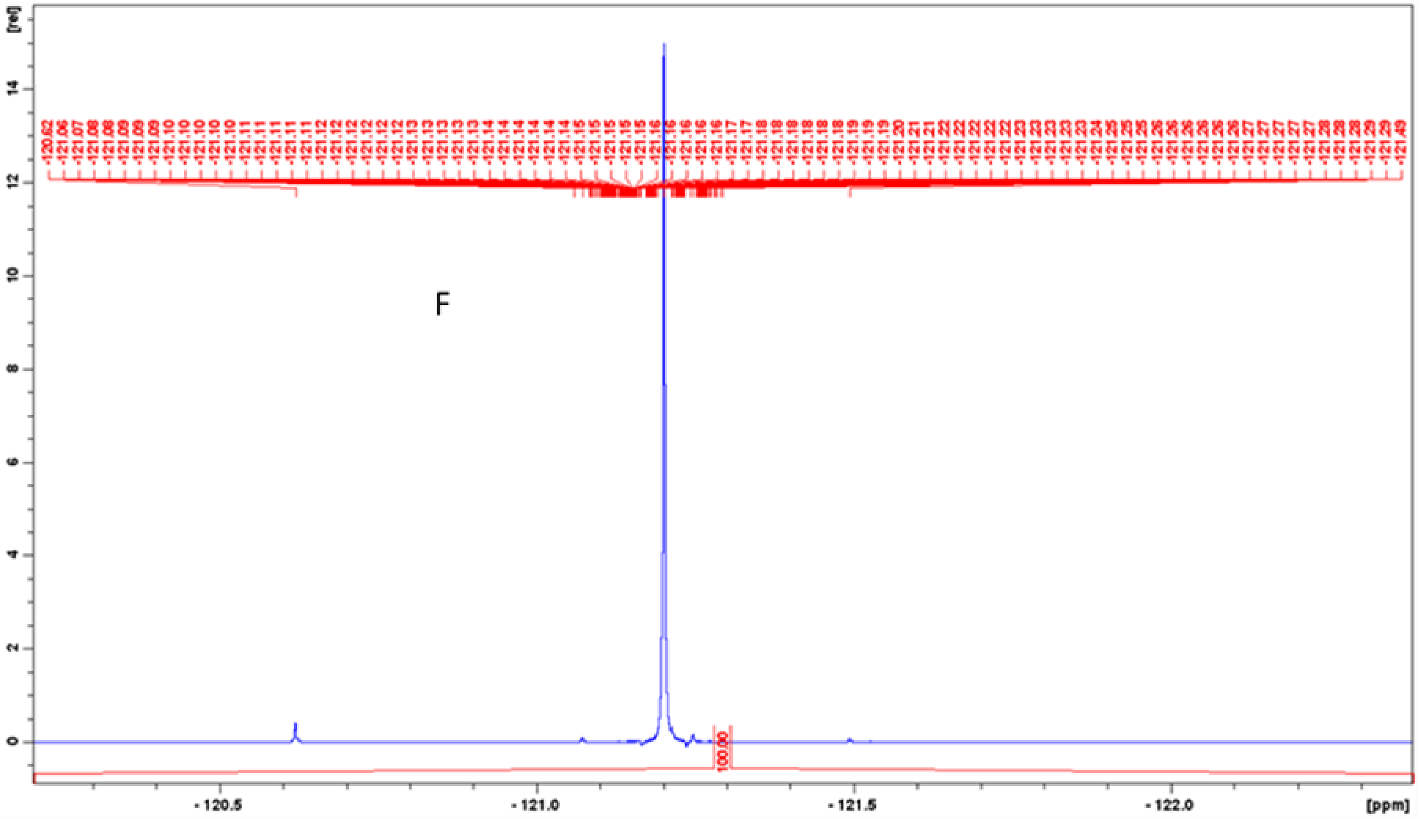




Compound (**2**). 4-fluorophenyl-β-D-glucopyranosyluronate, sodium salt





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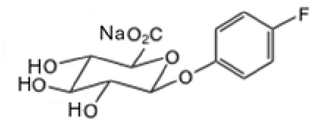

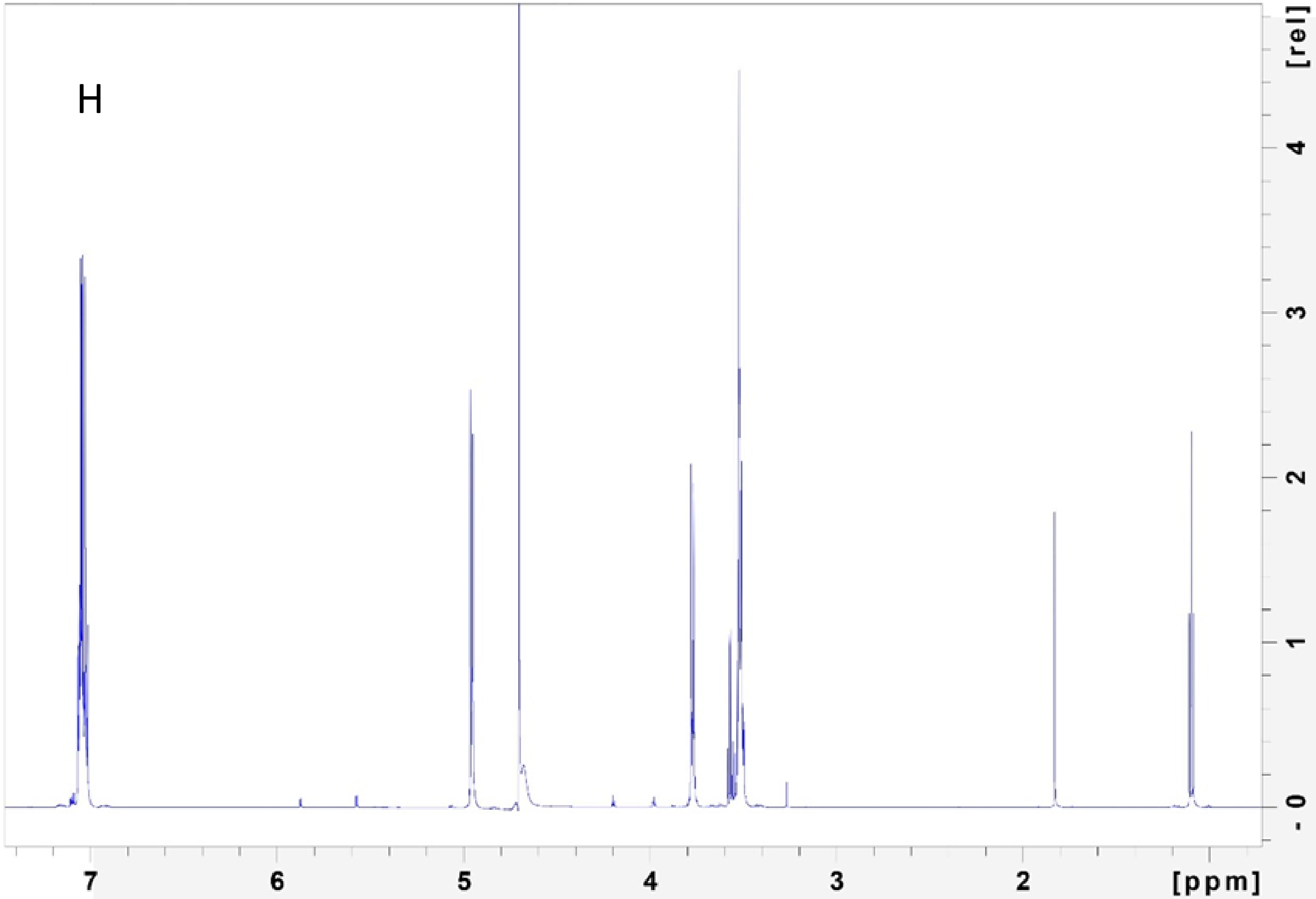

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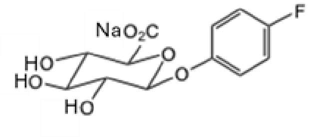

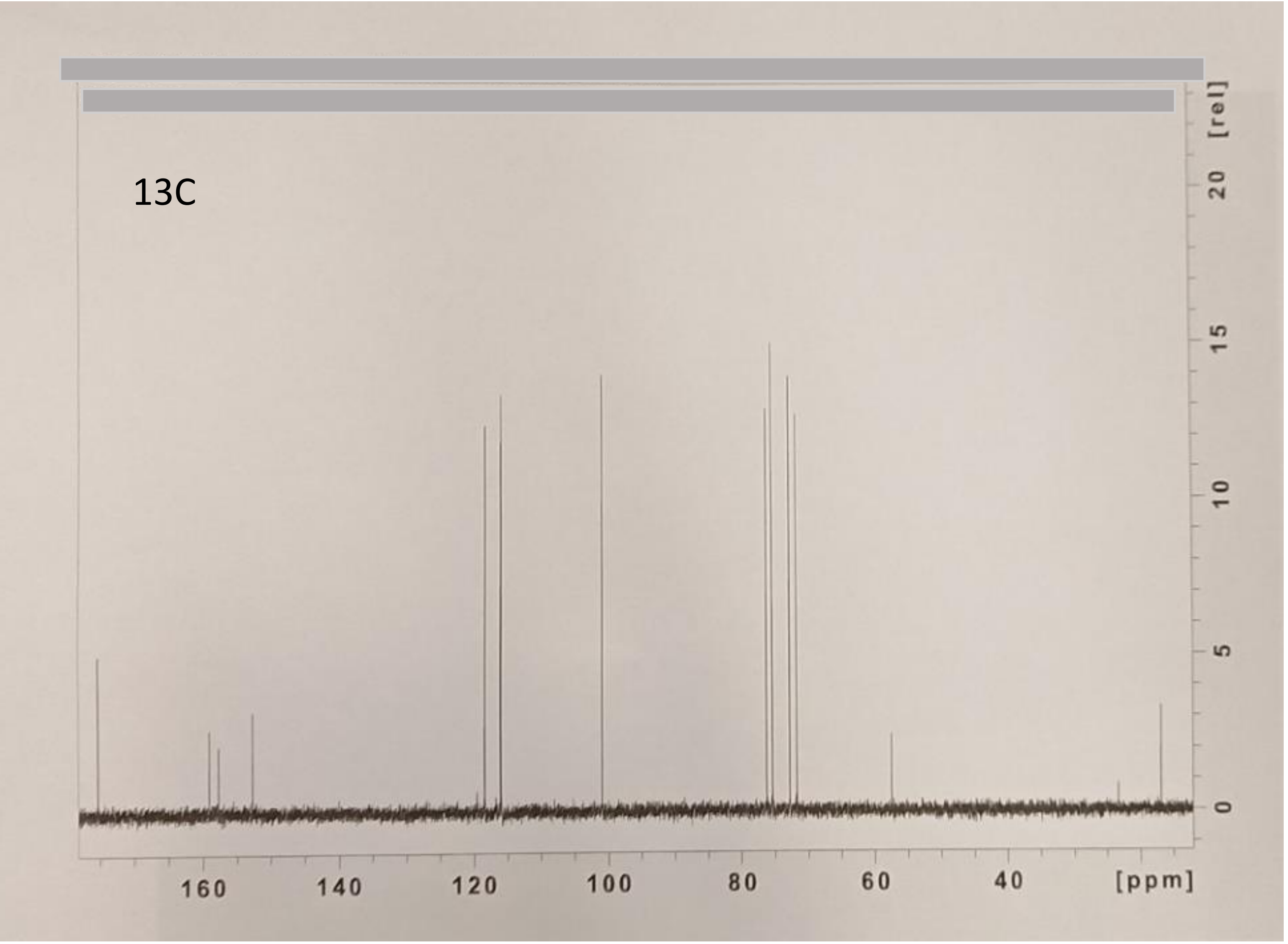
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General Experimental Procedures.

Organic extracts were washed with saturated brine and dried over anhydrous Na_2SO_4 prior to rotary evaporation at <30°C. Moisture sensitive reactions were carried out in anhydrous organic solvents (purchased from Sigma-Aldrich) under a N_2 or Ar atmosphere. Reactions were monitored by analytical thin-layer chromatography using Merck Kieselgel 60 F_{254} silica plates, and were viewed under UV or by staining with $KMnO_4$ or iodine. Preparative flash column chromatography was performed on either VWR Prolabo silica gel or Sigma-Aldrich silica gel (particle size 40-63 Å). Melting points were recorded using a Bibby-Sterilin Stuart SMP3 melting point apparatus and are uncorrected. Mass spectra were obtained in either electrospray mode (ES) with a Micromass LCT or chemical ionization (CI) mode with a Micromass Trio 1000 using ammonia. Elemental analyses were performed by Mrs. Jean Ellis, University of Liverpool. ^{1}H and ^{13}C NMR spectra were obtained using Bruker Avance or Bruker DPX 400 (Dept. Chemistry, UoL), and Bruker Avance 600 MHz or Bruker Avance II+ 800 MHz instruments (LJMU and UoL) for the 400, 600 or 800 MHz respectively for 1H spectra and 100, 150 and 200 MHz for 13C spectra. Chemical shifts are reported in ppm (δ) relative to Me_4Si. Coupling constants (*J*) are reported in Hz.

Synthetic and Characterisation Details

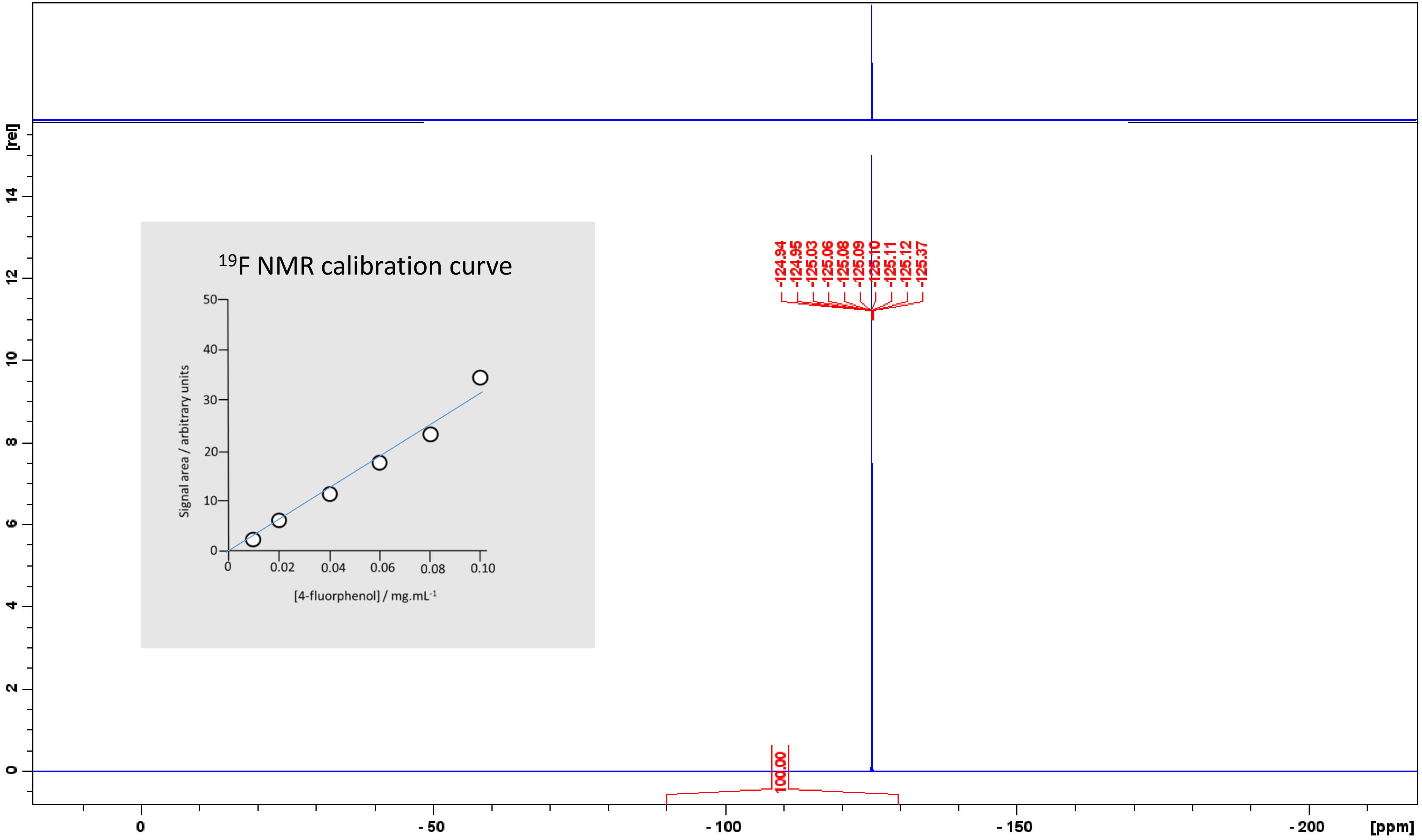
Compound (1). Methyl-1-(4-fluorophenyl)-2,3,4-tri-O-acetyl-β-D-glucopyranosyluronate:-

Compound (**1**) was prepared from 4-fluorophenol using the trichloroacetimidate methods in and 69% yields: Methyl-1,2,3,4-tetra-O-acetyl-β-D-glucopyranosyluronate (**1**) and 4-fluorophenol (1 eq. of each) were dissolved in anhydrous dichloromethane (4mL per mmol), then stirred for 2 h under N_2 [at 20°C] with 4Å molecular sieves. Trimethylsilyl trifluoromethanesulfonate (1 eq.) was added to the reaction mixture, which was stirred for a further 3.5 h. The reaction mixture was quenched with saturated aqueous sodium bicarbonate (20 mL per mmol) and diluted with ethyl acetate (20 mL per mmol). After separation, the organic layer was washed with water followed by brine, then dried with anhydrous $MgSO_4$. Following filtration and evaporation under reduced pressure, the crude product was purified by column chromatography using a gradient of 30-50% ethyl acetate in hexane to afford the glucuronide ester: 1H NMR (400 MHz, DMSO-d_6) 2.00, 2.01 and 2.04 (9 H, 3s, 3xCH_3CO), 3.64 (3H, s, CH_3O), 4.69 (1 H, d, J = 10.0 Hz, 5-H), 5.04-5.11 (2 H, m, 2-H + 4-H), 5.46 (1 H, t, J = 9.6 Hz), 5.60 (1 H, d, J = 8.0 Hz, 1-H), 7.03 (2 H, approx. dd, ArH) and 7.15 (2 H, approx. dd, ArH); 13C NMR (100 MHz, DMSO-d_6) 20.7, 20.8 (x2), 53.1, 69.4, 70.9, 71.4, 71.5, 98.1, 116.7 (d, J = 23 Hz), 118.7 (d, J = 8 Hz), 153.0 (d, J = 2 Hz), 158.4 (d, J = 237 Hz), 167.5, 169.5, 169.8 and 170.0; Found: C, 53.36; H, 4.9; m/z, 451.1016 (MNa^+, ESI +ve mode); $C_{19}H_{21}FO_{10}$ requires C, 53.3; H, 4.9%; $C_{19}H_{21}F0_{10}$.Na requires C, 54.5; H, 5.5%; $C_{19}H_{21}F0_{10}$.Na requires m/z, 451.1016.

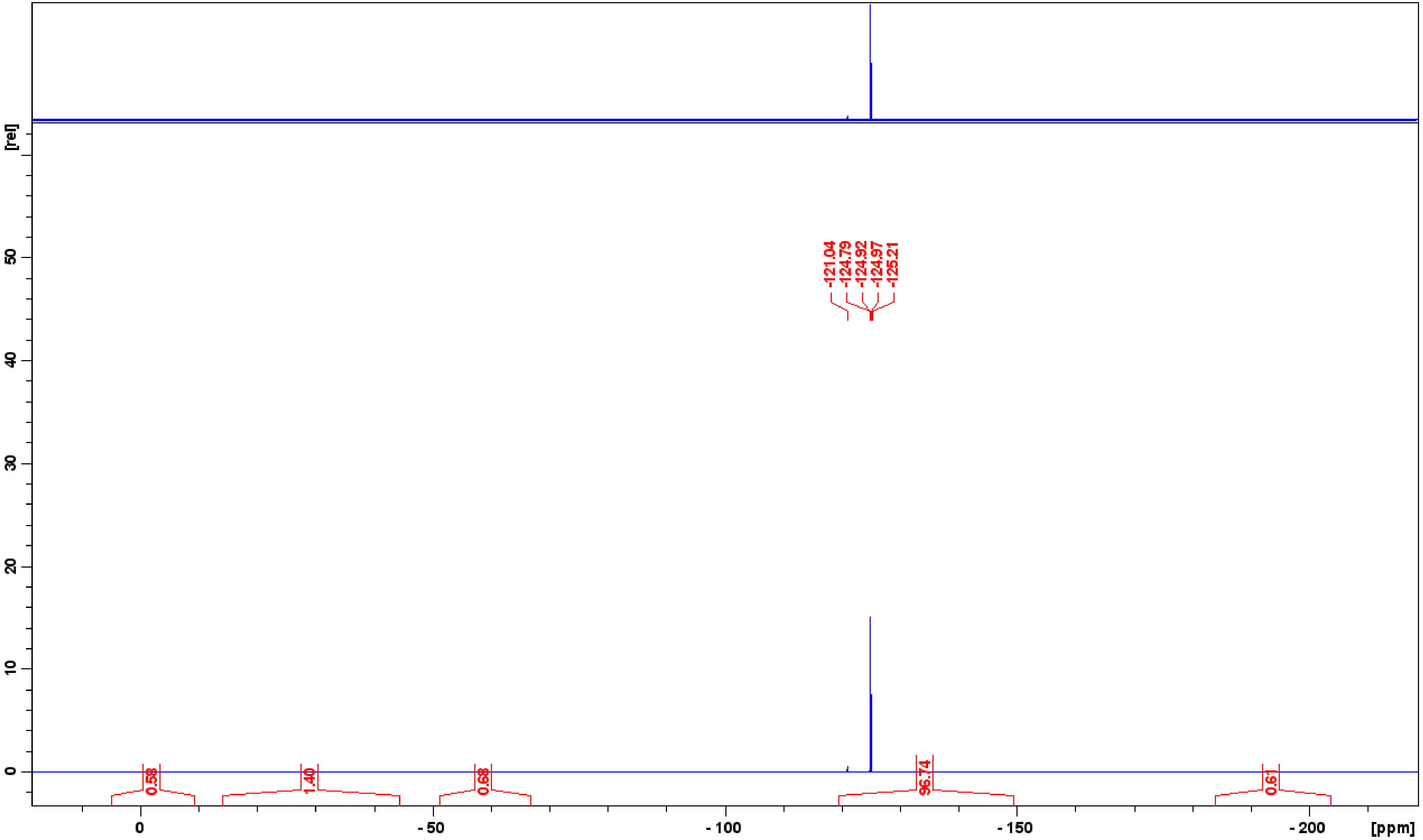
Compound (2). 4-Fluorophenyl-β-D-glucopyranosyluronate, sodium salt:-

Compound (**1**) (0.210 g, 0.49 mmol) was stirred in methanol (5 mL) at 0°C then 0.5 M NaOH (1.0 mL) was added over 12 min. The solution was allowed to regain 20°C over 1 h, then further 0.5 M NaOH (0.04 mL) was added. After stirring for another 0.25 h, the solution was evaporated to dryness then azeotroped with ethanol (3x 5 ML) to afford the product as a white solid (0.160 g), which was sufficiently pure for assays: ^{1}H NMR (700 MHz, D_2O) δ_H 3.53-3.49 (3 H, m, 2-H, 3-H, 4-H), 3.77 (1 H, d, J=8.9 Hz, 5-H), 4.95 (1 H, d, J=8.8 Hz, 1-H), 7.017-7.068 (4 H, m, ArH); (175 MHz, D_2O) δ_C 71.6, 72.8, 75.5, 76.3, 101.0, 116.1 (d, $^2J_{C\text{-}F}$ 18 Hz), 118.5, 152.8, 158.6 (d, $^1J_{C\text{-}F}$ 231 Hz) and 176.0; δ_F (564 MHz, D_2O) -125.1 (s, 1F) relative to 4-fluorphenol in D_2O (as external standard = -125.1 (s)). Found: m/z, 287.0564 (ESI -ve mode); $C_{12}H_{12}F0_7$ requires m/z, 287.0567.

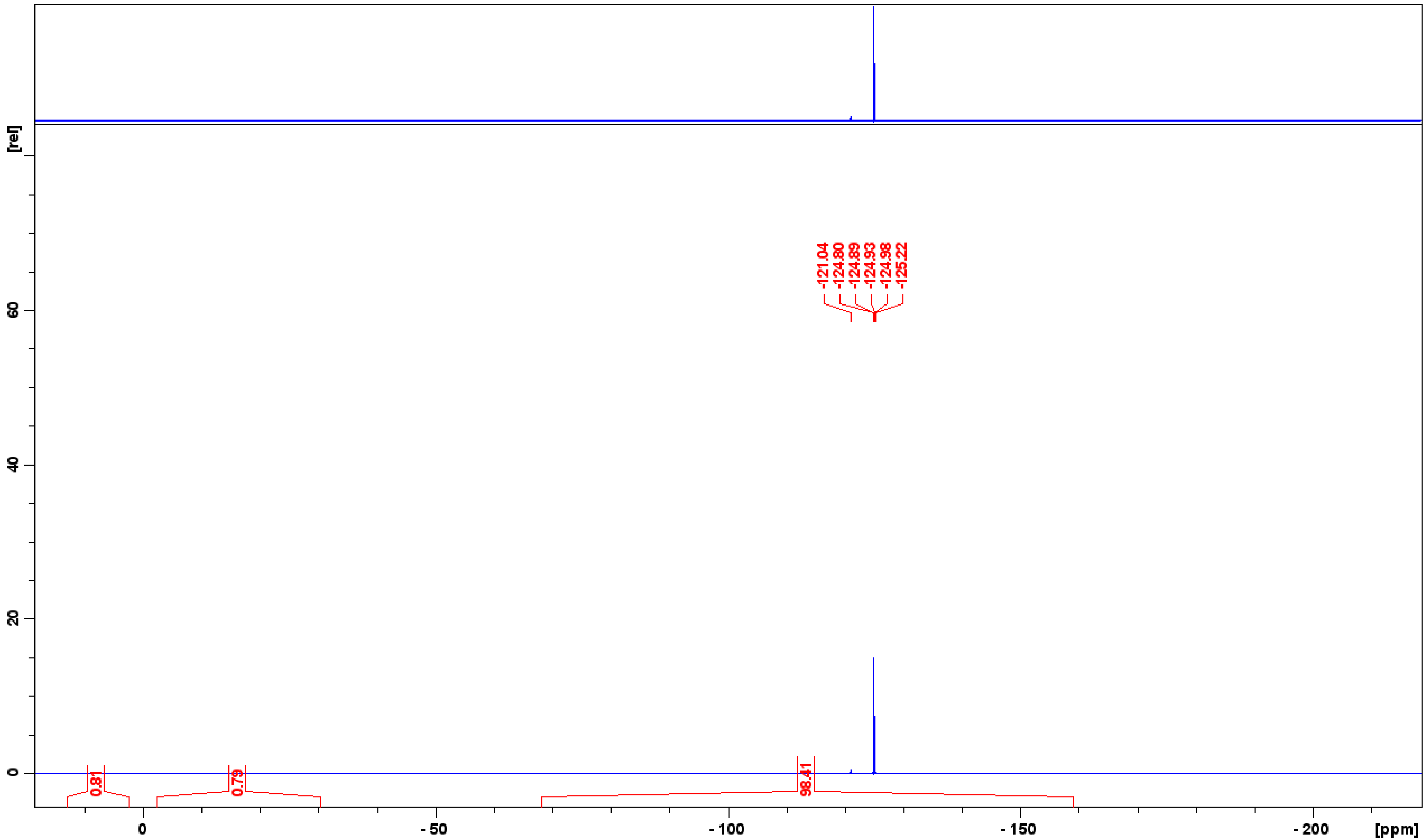
9 ^{19}F NMR of released 4F-phenol



10 ^{19}F NMR of hydrolysis control 1 – full scale



^{19}F NMR of hydrolysis control 2 – full scale



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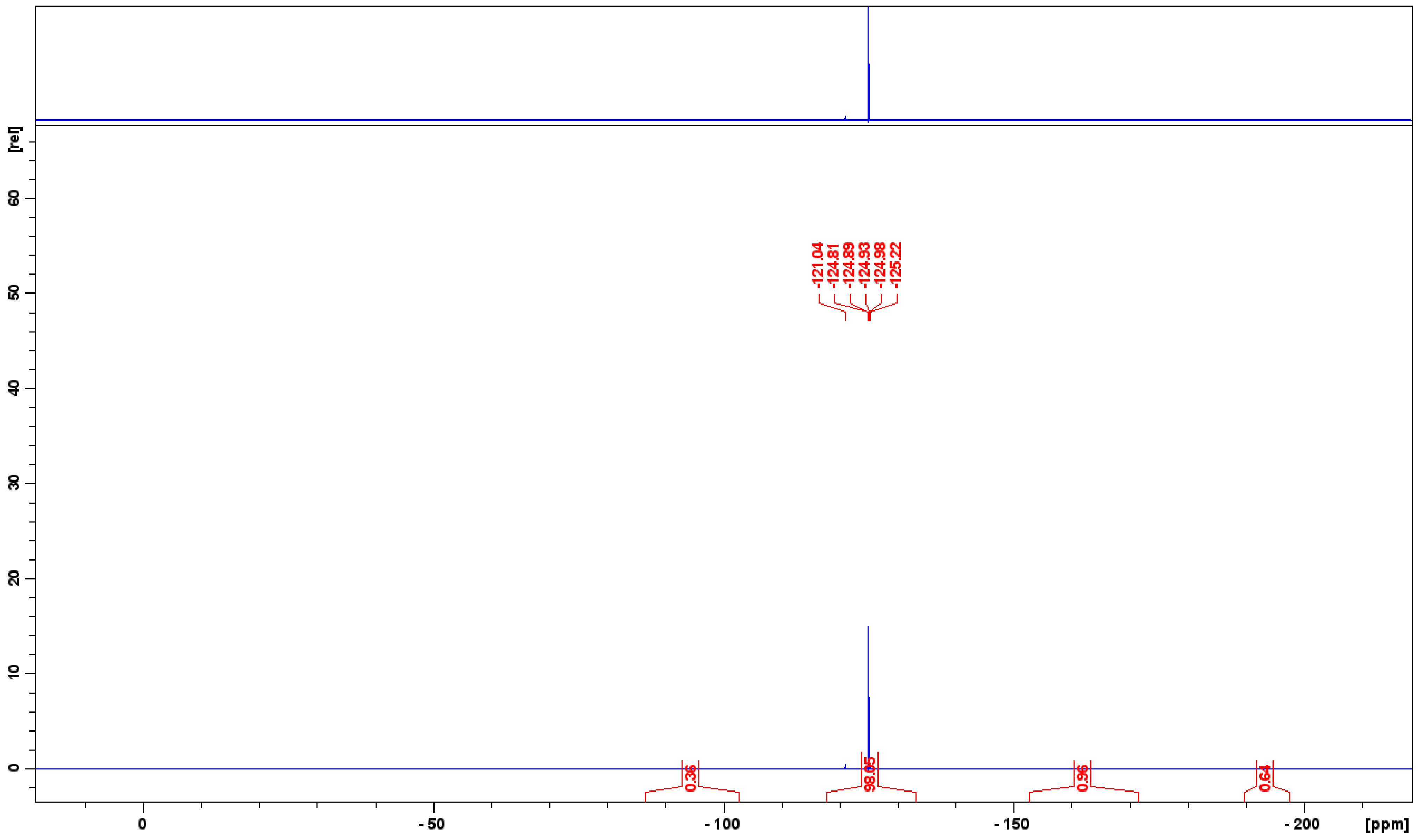

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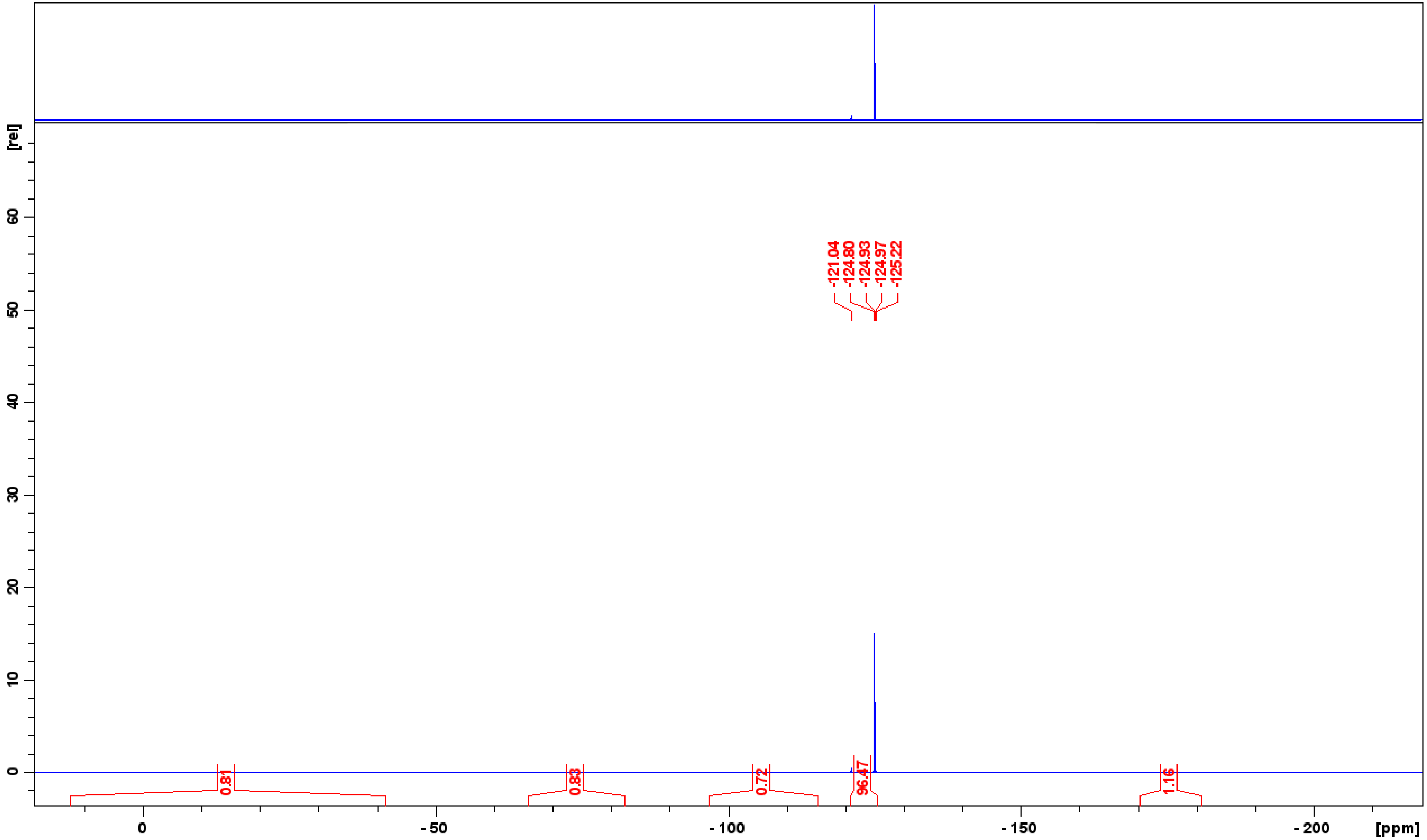
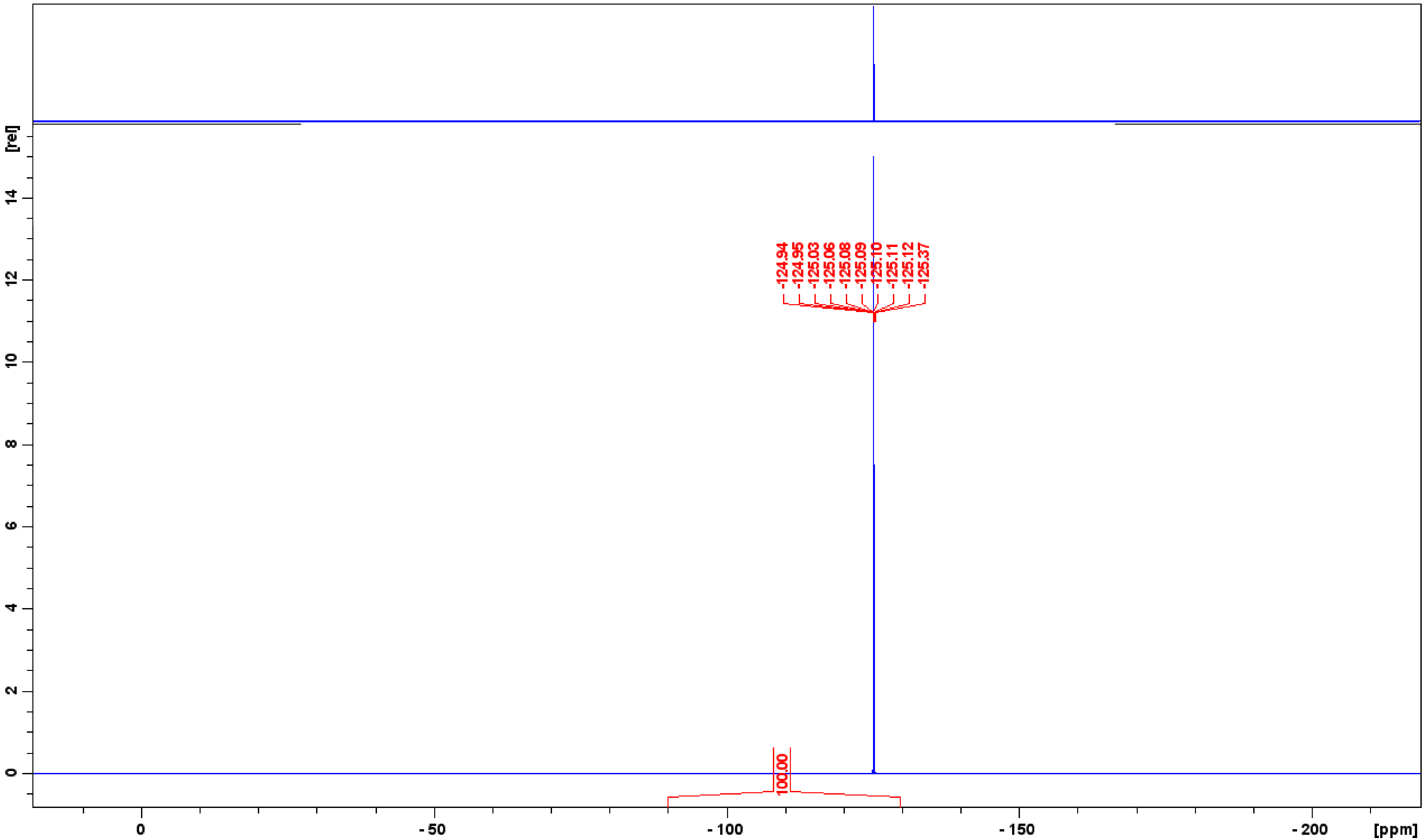


^{19}F NMR of 4F-phenol – expansion



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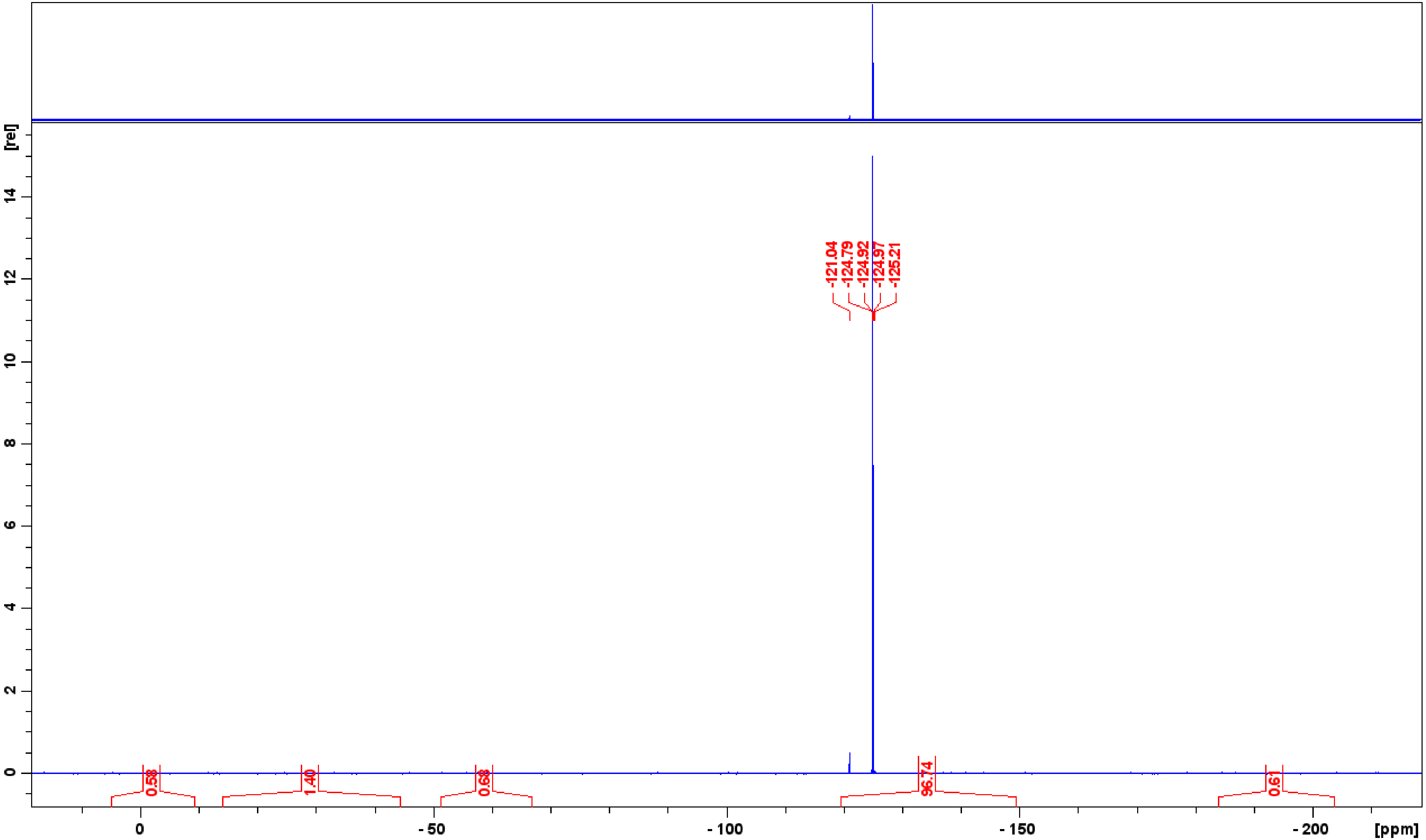

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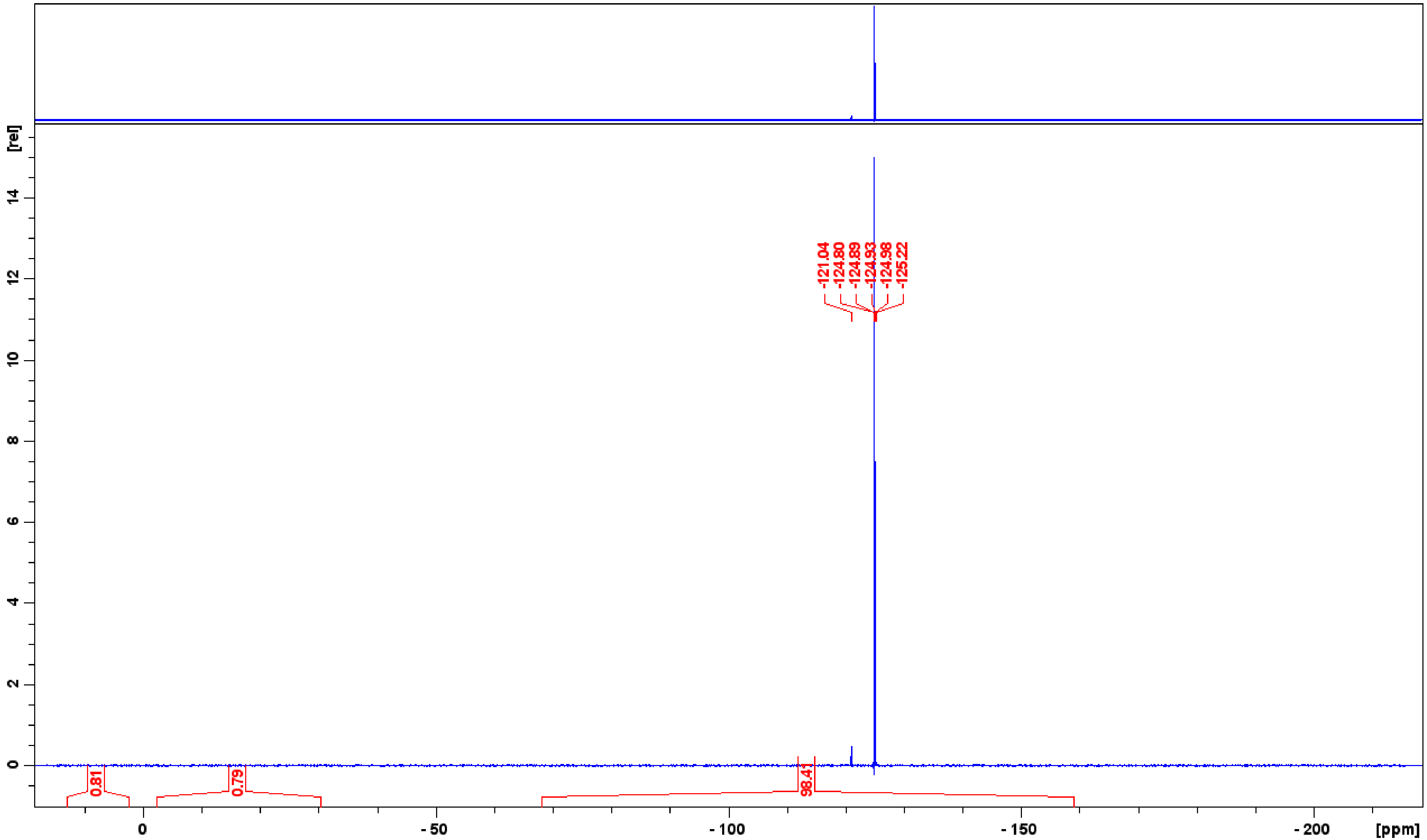

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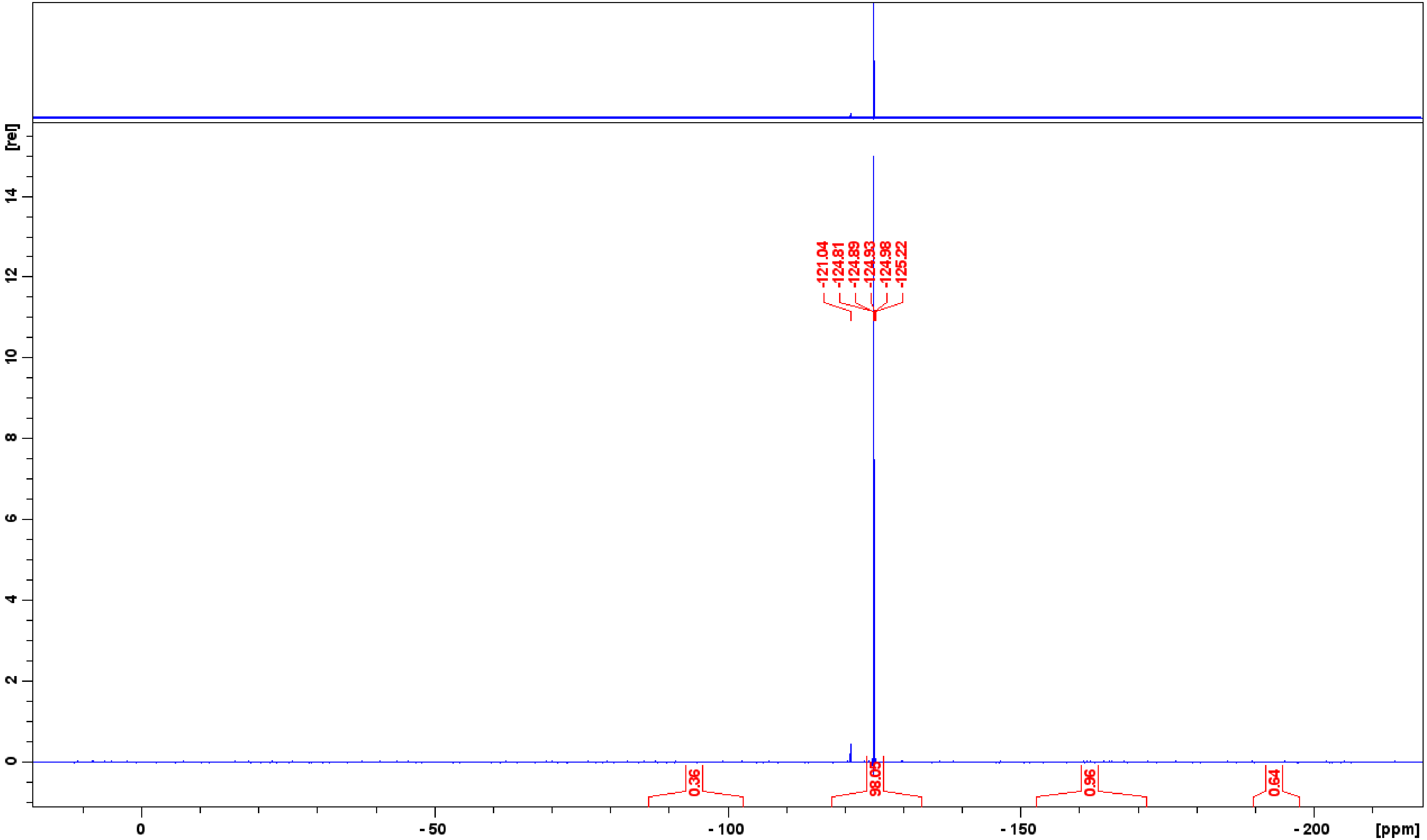

^{19}F NMR of hydrolysis control 4 – expansion