Electronic Supplementary Material (ESI) for RSC Advances.


Supporting Information

# Towards understanding of laccase-catalysed oxidative oligomerisation of dimeric lignin model compounds

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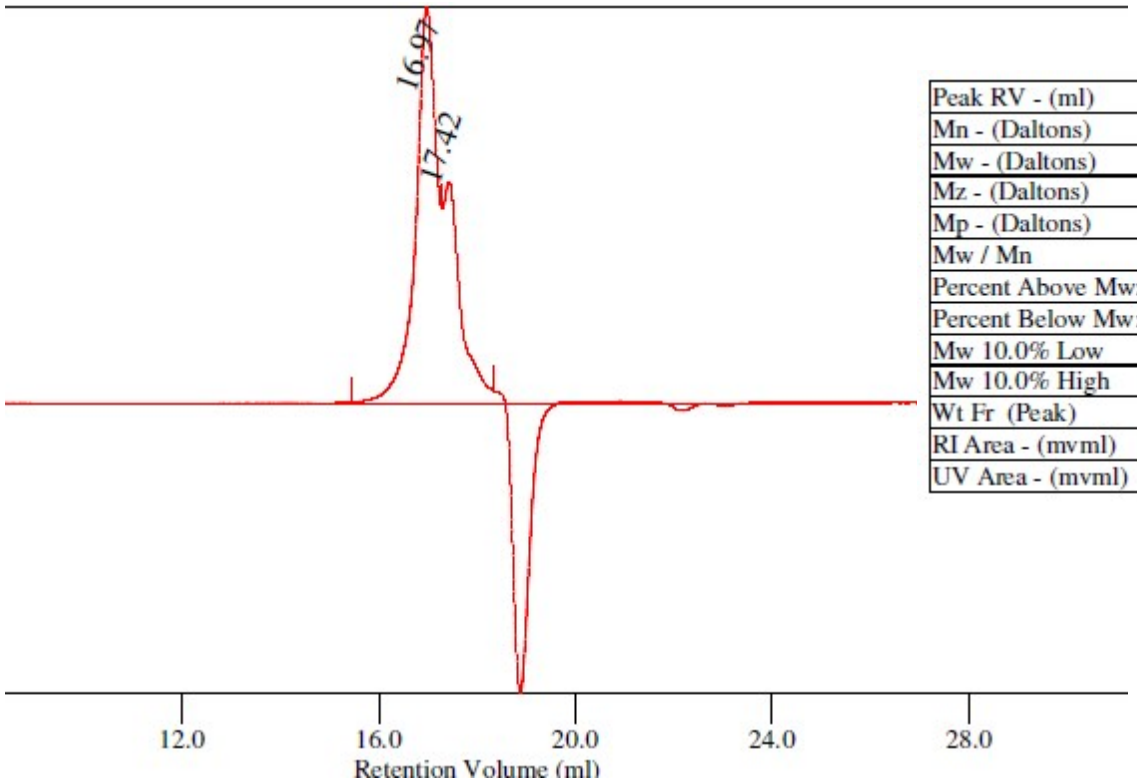
## 1. General information

**Methods**: Analytical thin layer chromatography (TLC) separations were performed on Merck's silica gel 60 $F_{254}$-precoated aluminum sheets. Visualization was accomplished with UV light and/or aqueous potassium permanganate solution (0.1 N) stain.

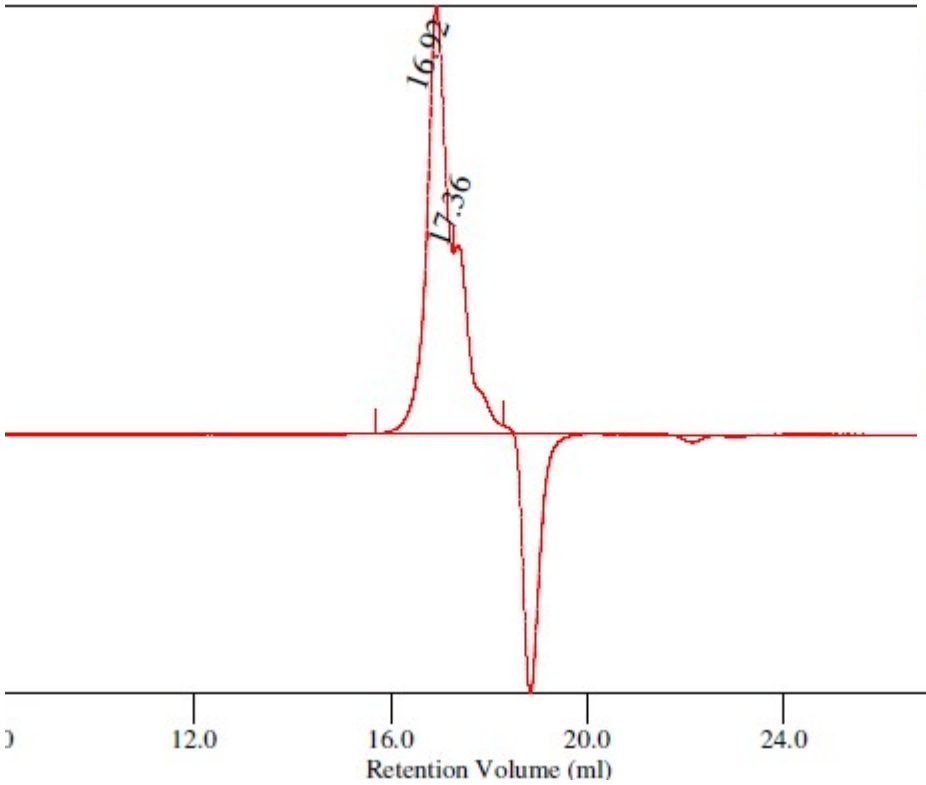
$^{1}H$ and $^{13}C$ nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 400 UltraShield Spectrometer operating at 400 MHz and 100 MHz respectively. Chemical shifts for $^{1}H$ NMR were recorded in parts per million (ppm) downfield from proton signal of residual non-deuterated solvent (δ 7.26 ppm for $CDCl_3$ and 2.05 ppm for Acetone-$D_6$) as the internal signal. Coupling constants are indicated in Hertz (Hz). For $^{13}C$ NMR spectra, chemical shifts are reported relative to the central line of the triplet at δ 77.2 ppm and 206.3 ppm resonance respectively for non-deuterated residuals originated from $CDCl_3$ and acetone-$D_6$. The following abbreviations are used for spin multiplicity: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet and br=broad.

HPLC analysis on the reaction progress and quantification of unreacted HPLC analysis was performed on Agilent 1200 series. HPLC-MS was performed on Agilent 1260 infinity equipped with Agilent 6120 quadrupole LC/MS system. Phenomenex C12 column (Jupiter 4μm Proteo 90 Å, LC Column 150 x 4.60 mm) was used for the HPLC analysis. Trifluoroacetic acid (1%) in water and Trifluoroacetic acid (1%) in acetonitrile were used as mobile phase under the gradient flow (30 min) starting from 90% $H_2O$ to 30% $H_2O$. 0.5 mL/min flow, 25 °C, 280 nm. Mass spectrometry was run by the electrospray ionization time-of-flight (ESI-TOF) mode on an Agilent 6210 mass spectrometer.




| | | |
|---|---|---|
| Peak RV - (ml) | 16.968 | 17.416 |
| Mn - (Daltons) | 2,095 | 1,286 |
| Mw - (Daltons) | 2,165 | 1,333 |
| Mz - (Daltons) | 2,263 | 1,371 |
| Mp - (Daltons) | 2,044 | 1,486 |
| Mw / Mn | 1.033 | 1.037 |
| Percent Above Mw: 0 | 100.000 | 100.000 |
| Percent Below Mw: 0 | 0.000 | 0.000 |
| Mw 10.0% Low | 1,691 | 848 |
| Mw 10.0% High | 3,207 | 1,604 |
| Wt Fr (Peak) | 0.682 | 0.318 |
| RI Area - (mvml) | 171.79 | 80.05 |
| UV Area - (mvml) | 0.00 | 0.00 |

**Fig. S1.** GPC of oligomers that was obtained upon treatment of POL with **1**. PMMA (Poly(methyl methacrylate)) was used for calibration.




| | | |
|---|---|---|
| Peak RV - (ml) | 16.920 | 17.363 |
| Mn - (Daltons) | 2,119 | 1,322 |
| Mw - (Daltons) | 2,167 | 1,368 |
| Mz - (Daltons) | 2,226 | 1,405 |
| Mp - (Daltons) | 2,112 | 1,548 |
| Mw / Mn | 1.023 | 1.035 |
| Percent Above Mw: 0 | 100.000 | 100.000 |
| Percent Below Mw: 0 | 0.000 | 0.000 |
| Mw 10.0% Low | 1,730 | 886 |
| Mw 10.0% High | 2,940 | 1,635 |
| Wt Fr (Peak) | 0.726 | 0.274 |
| RI Area - (mvml) | 174.07 | 65.83 |
| UV Area - (mvml) | 0.00 | 0.00 |

**Fig. S2.** GPC of oligomers that was obtained upon treatment of TVL (2 units/mL) with **1**. PMMA (Poly(methyl methacrylate)) was used for calibration.

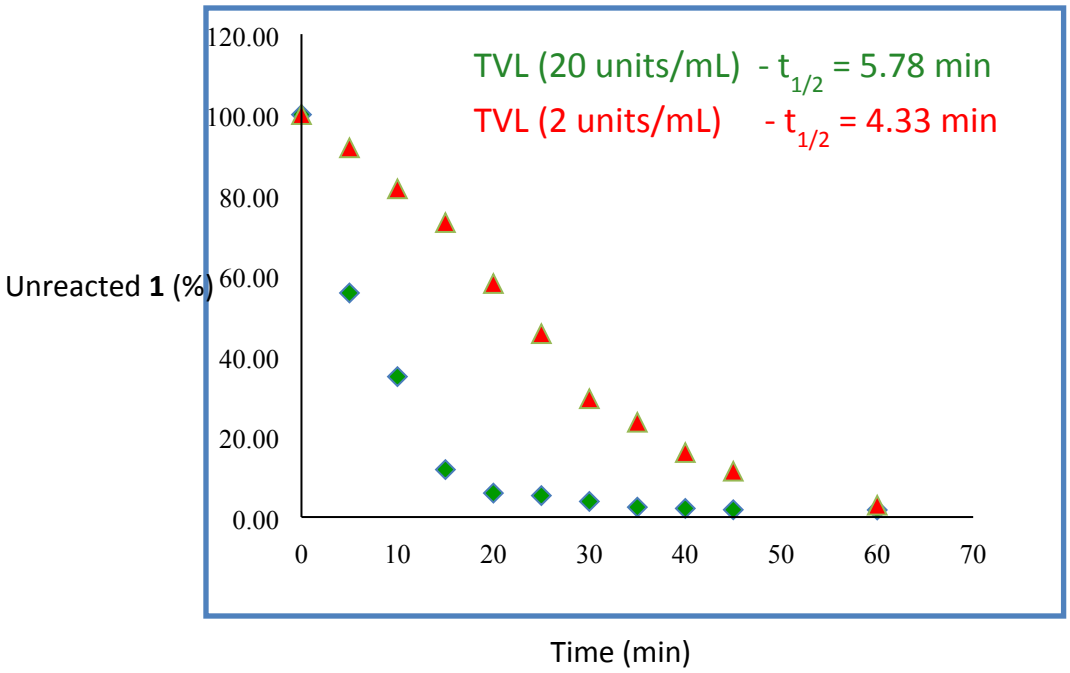



**Fig. S3.** Comparison of initial reactivity of TVL with **1** at two different concentrations.

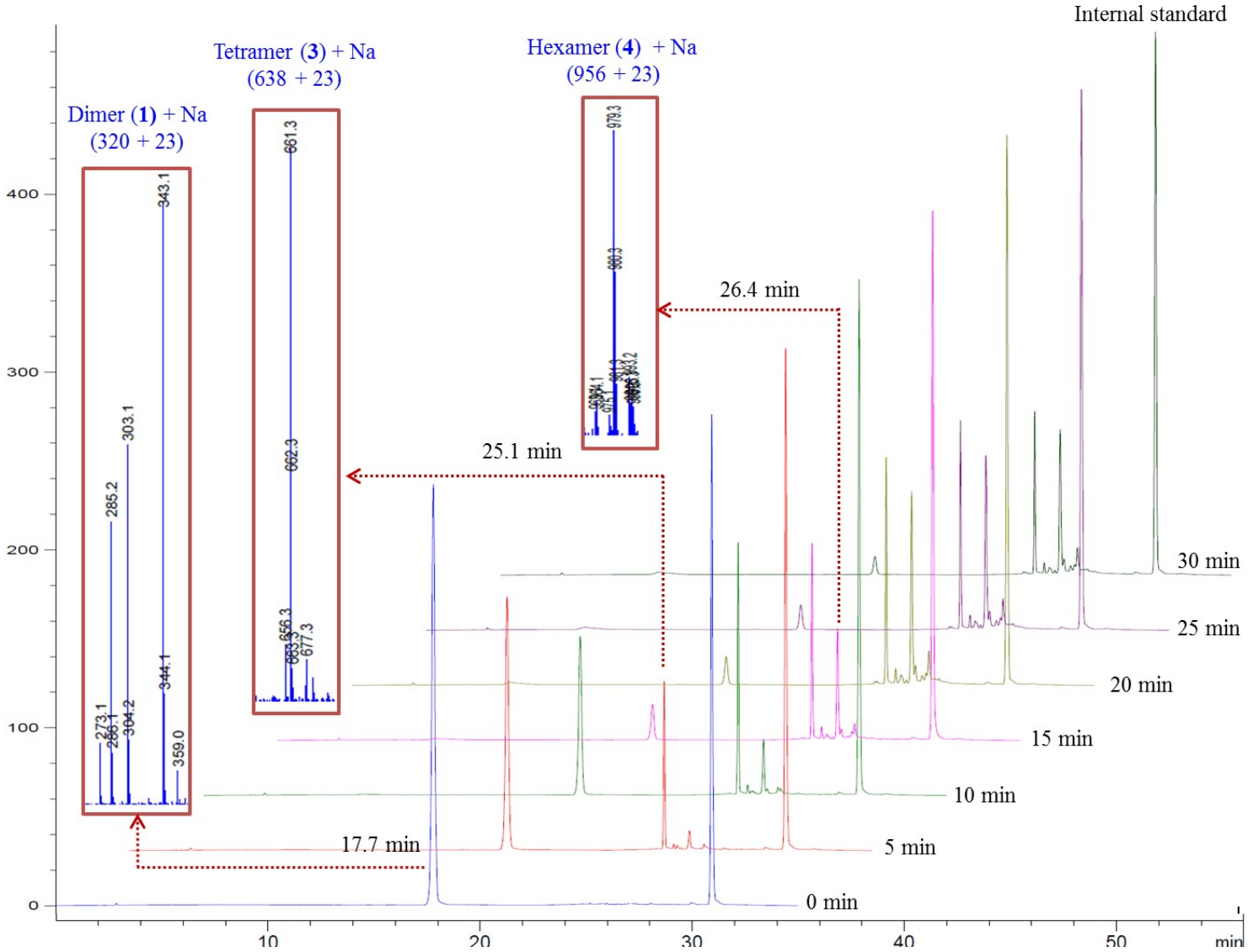



**Fig. S4**. LC-MS traces of laccase-catalysed oxidation of **1** at regular time intervals. 9-Acetylphenanthrene was used as an internal standard for quantification.

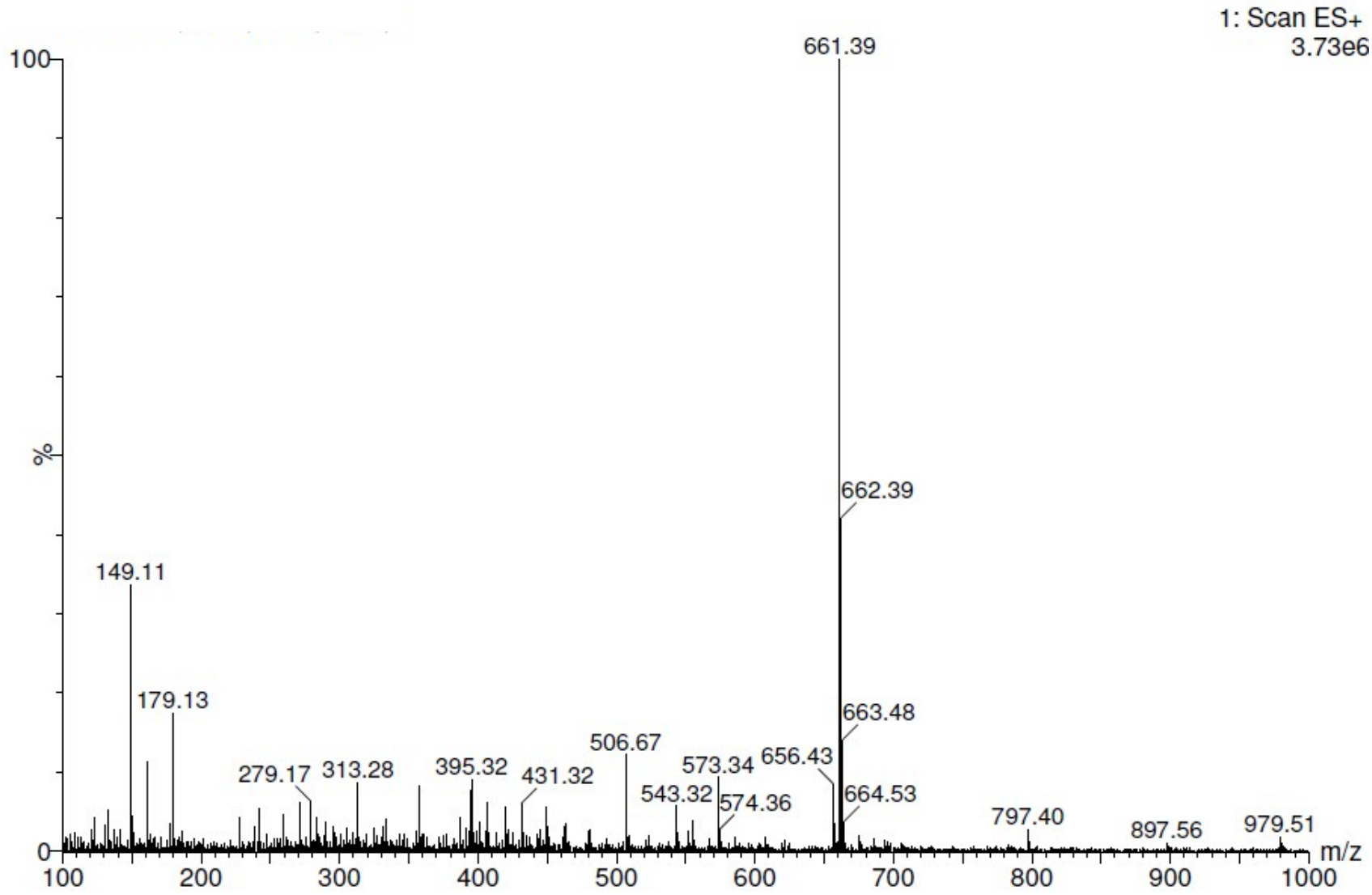



**Fig. S5.** ES-Mass spectrum of the tetramer (**3**) major product (retention time – 25.2 min).

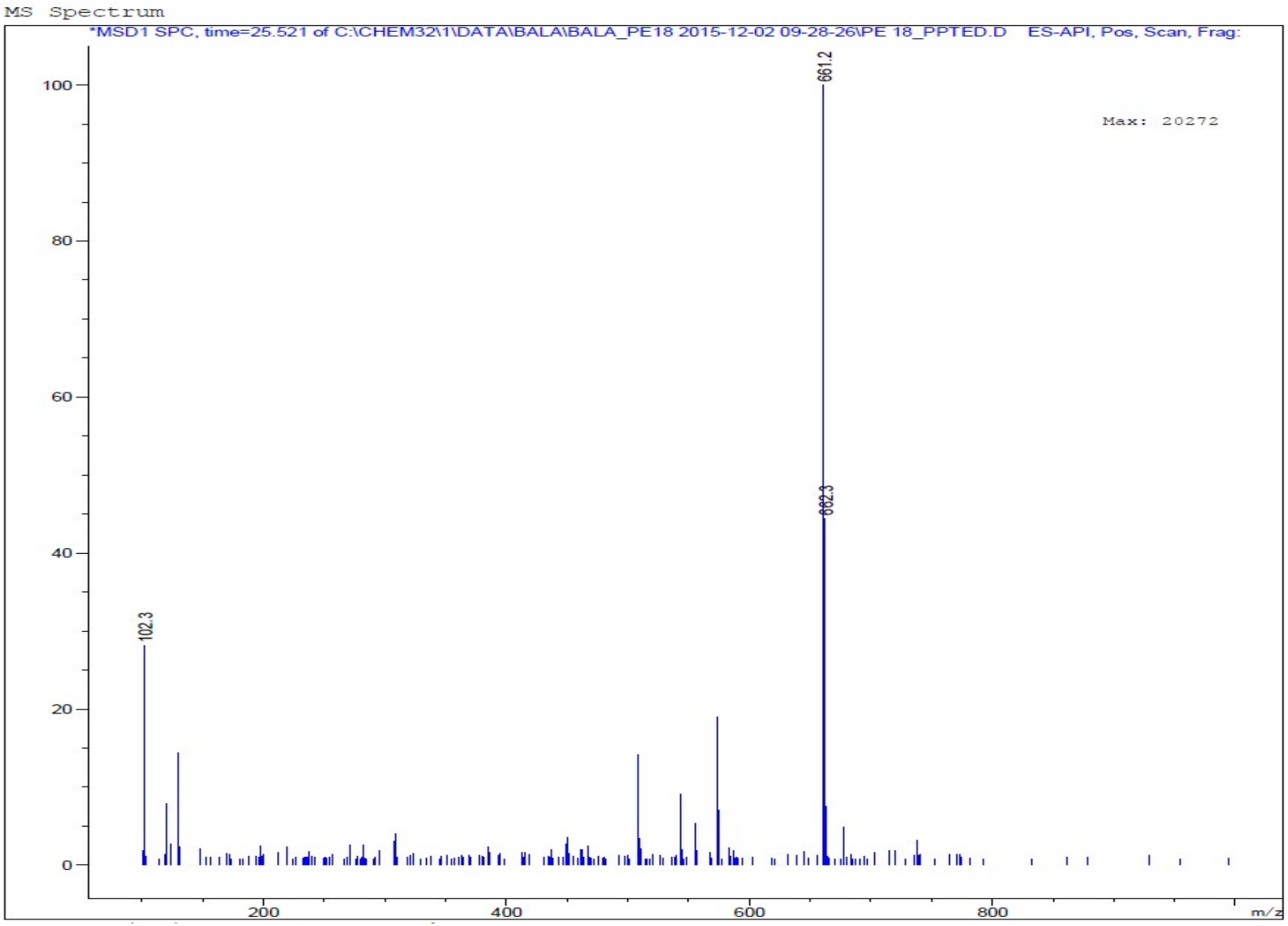



**Fig. S6.** ES-Mass spectrum of the tetramer (**3**) minor product (retention time – 25.6 min).

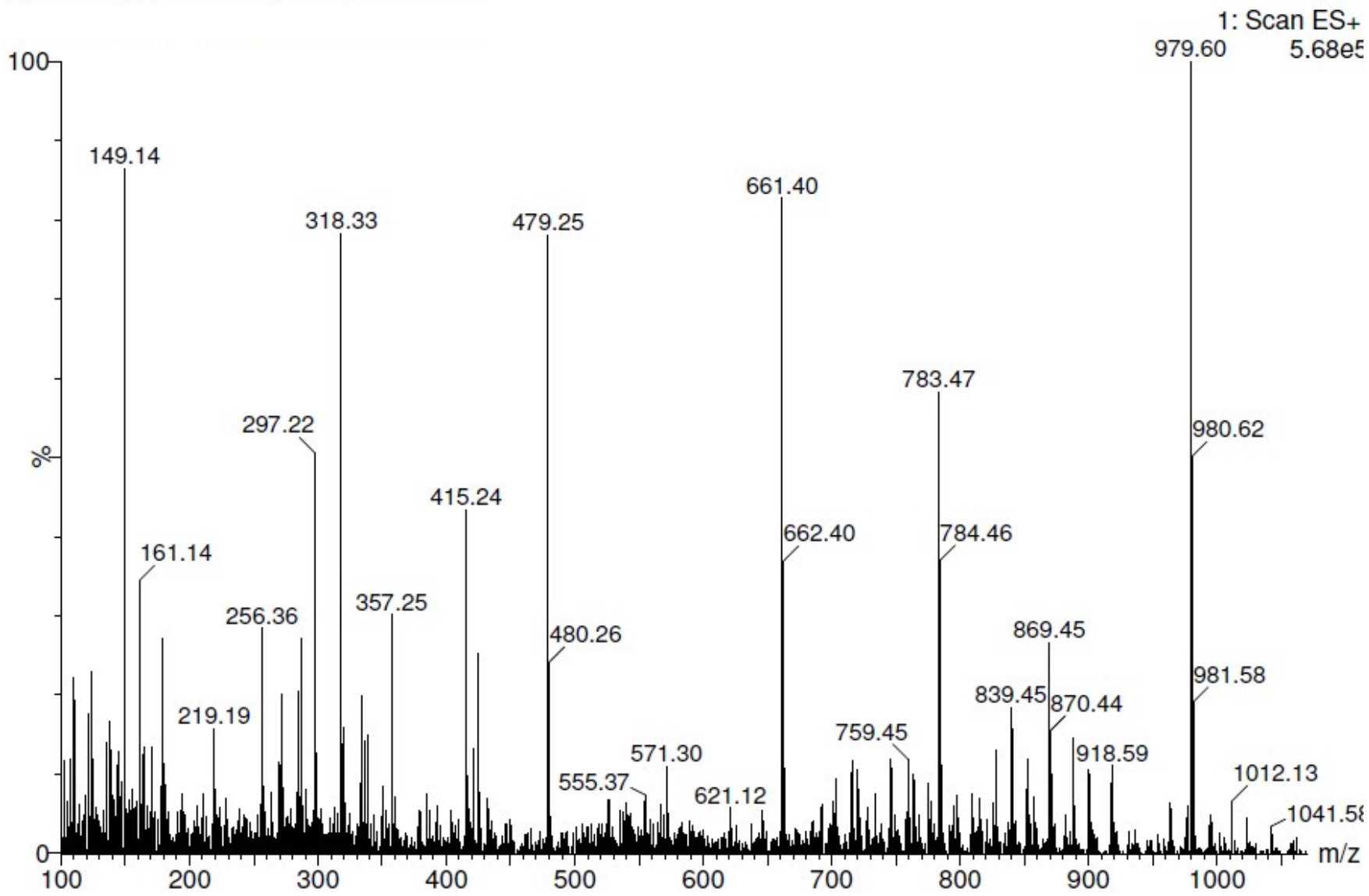



**Fig. S7.** ES-Mass spectrum of the hexamer (**4**) major product (retention time – 26.4 min).

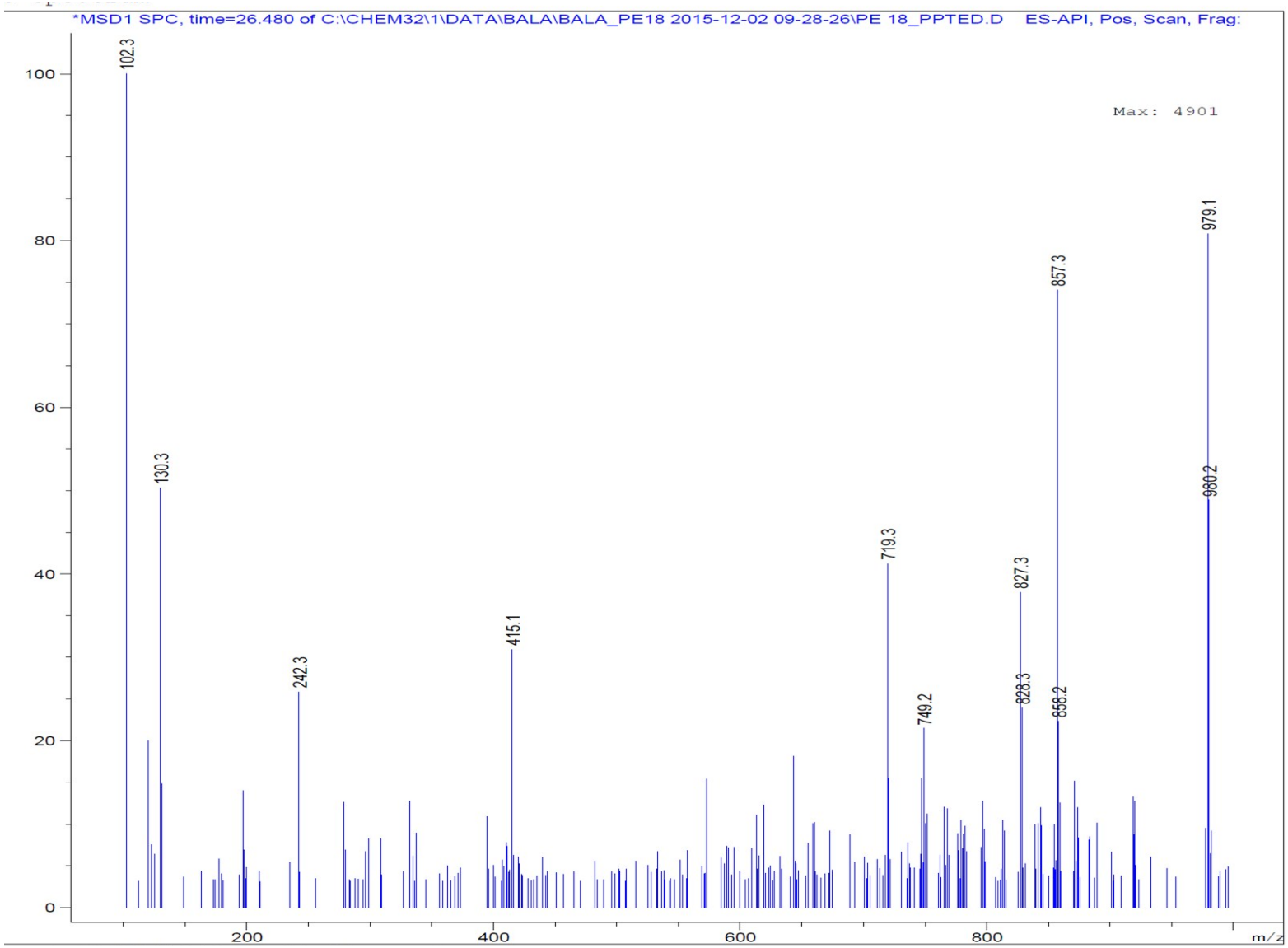



**Fig. S8.** ES-Mass spectrum of the hexamer (**4**) minor product (retention time – 27.2 min).

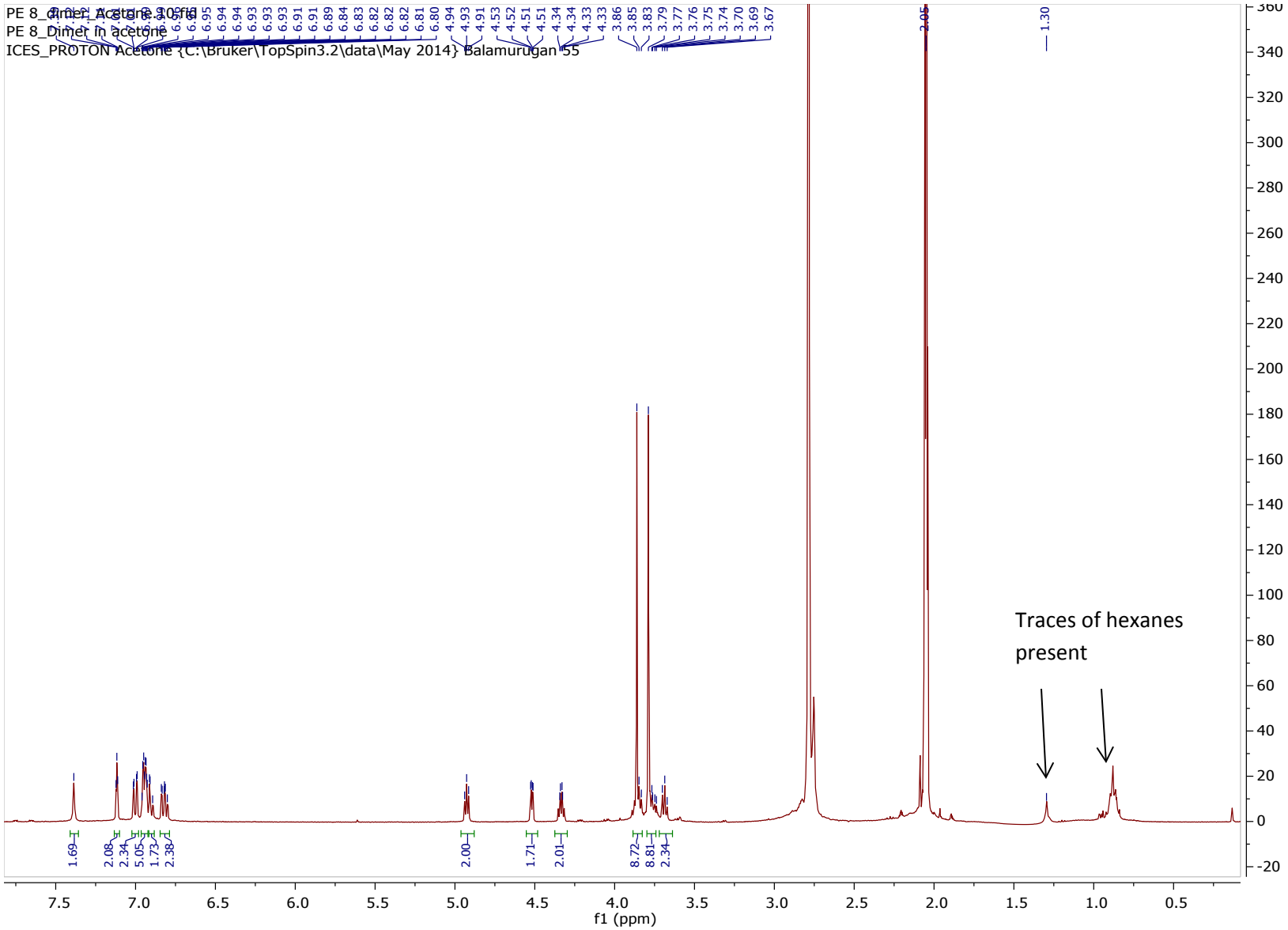



**Fig. S9**. $^{1}$H NMR spectrum of **3B**.

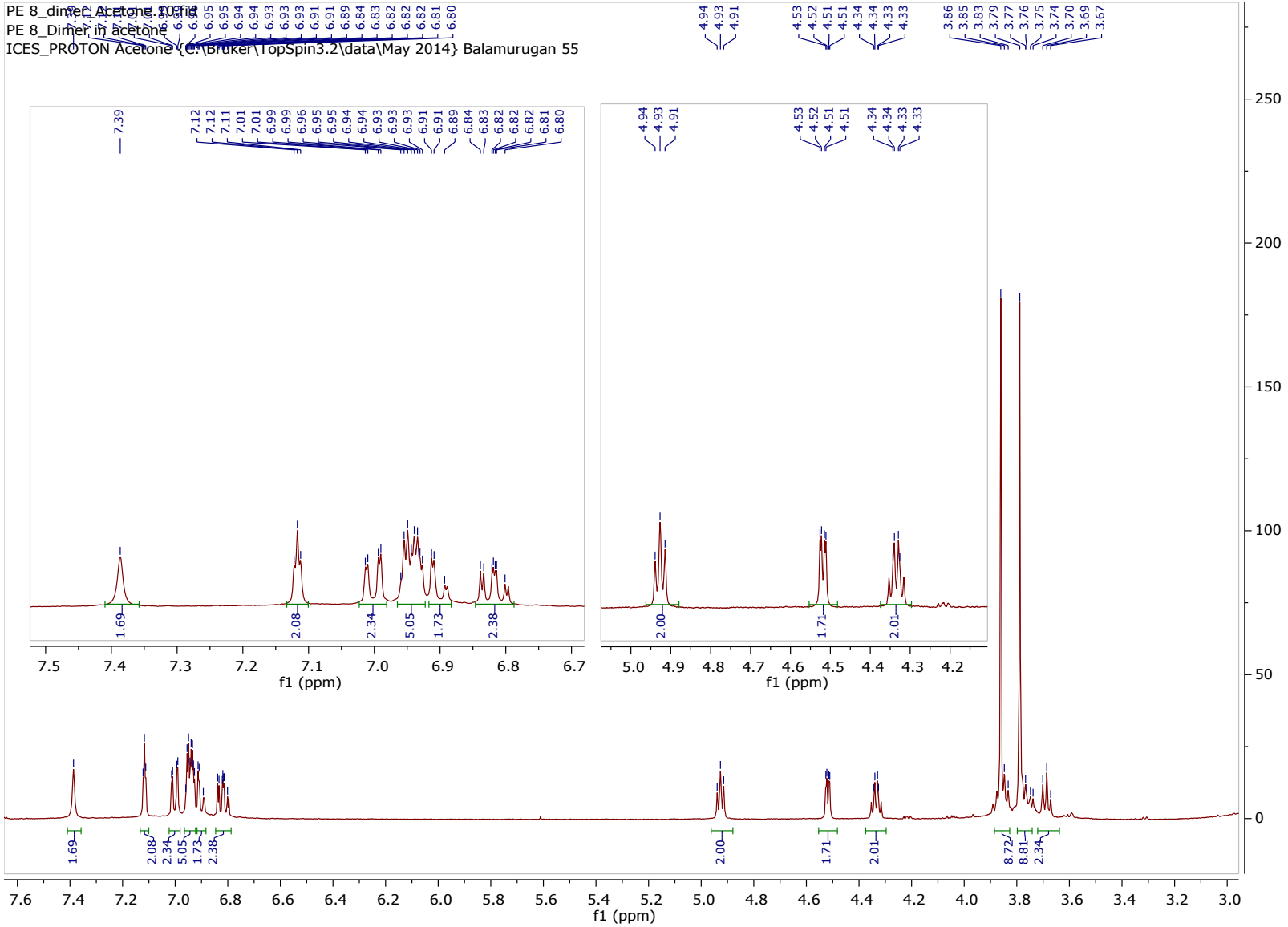



**Fig. S9a**. $^{1}$H NMR spectrum of **3B**. Expanded inserts for aliphatic and aromatic region was provided for better clarity.

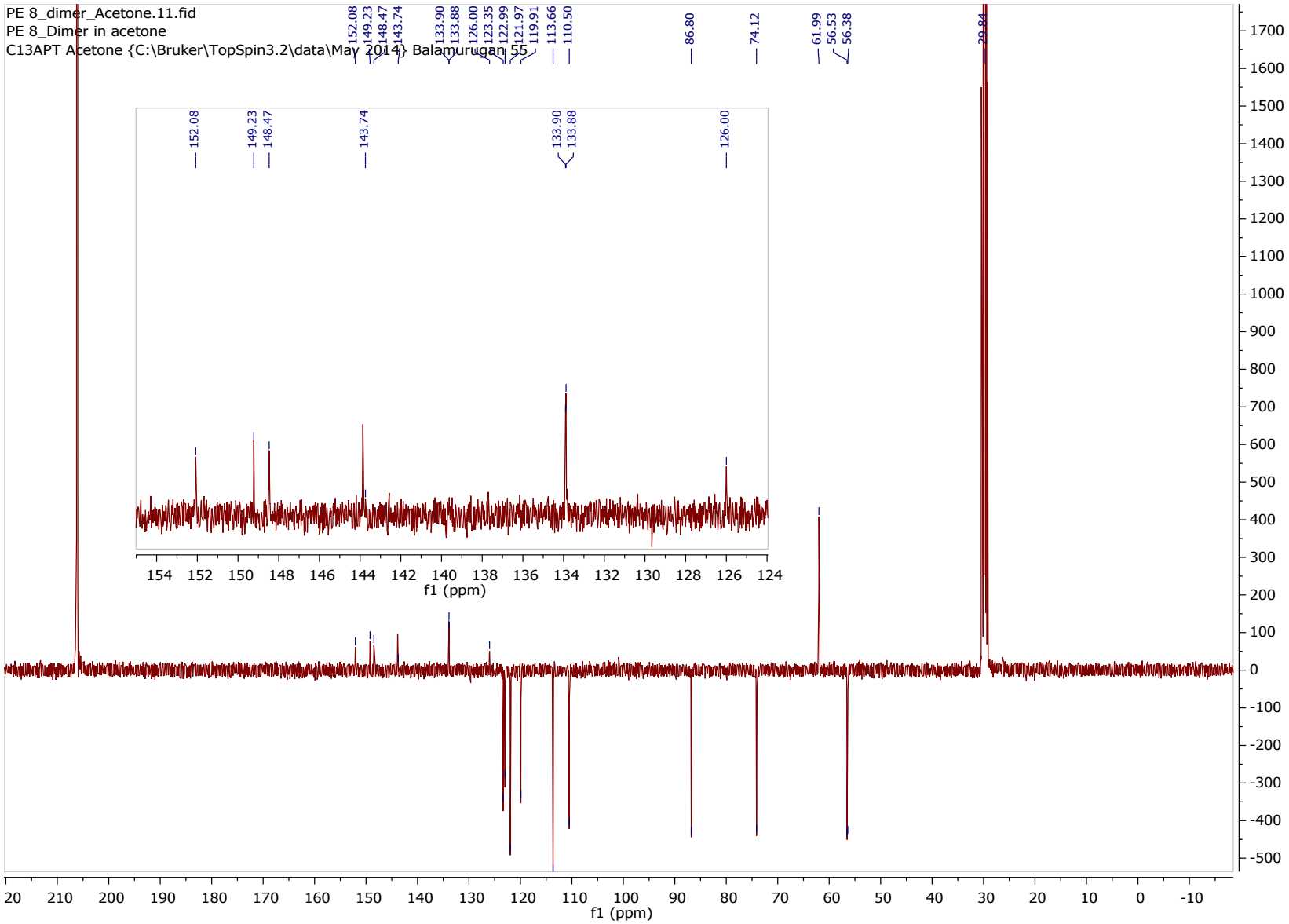



**Fig. S10**. $^{13}$C NMR (APT) spectrum of **3B**.

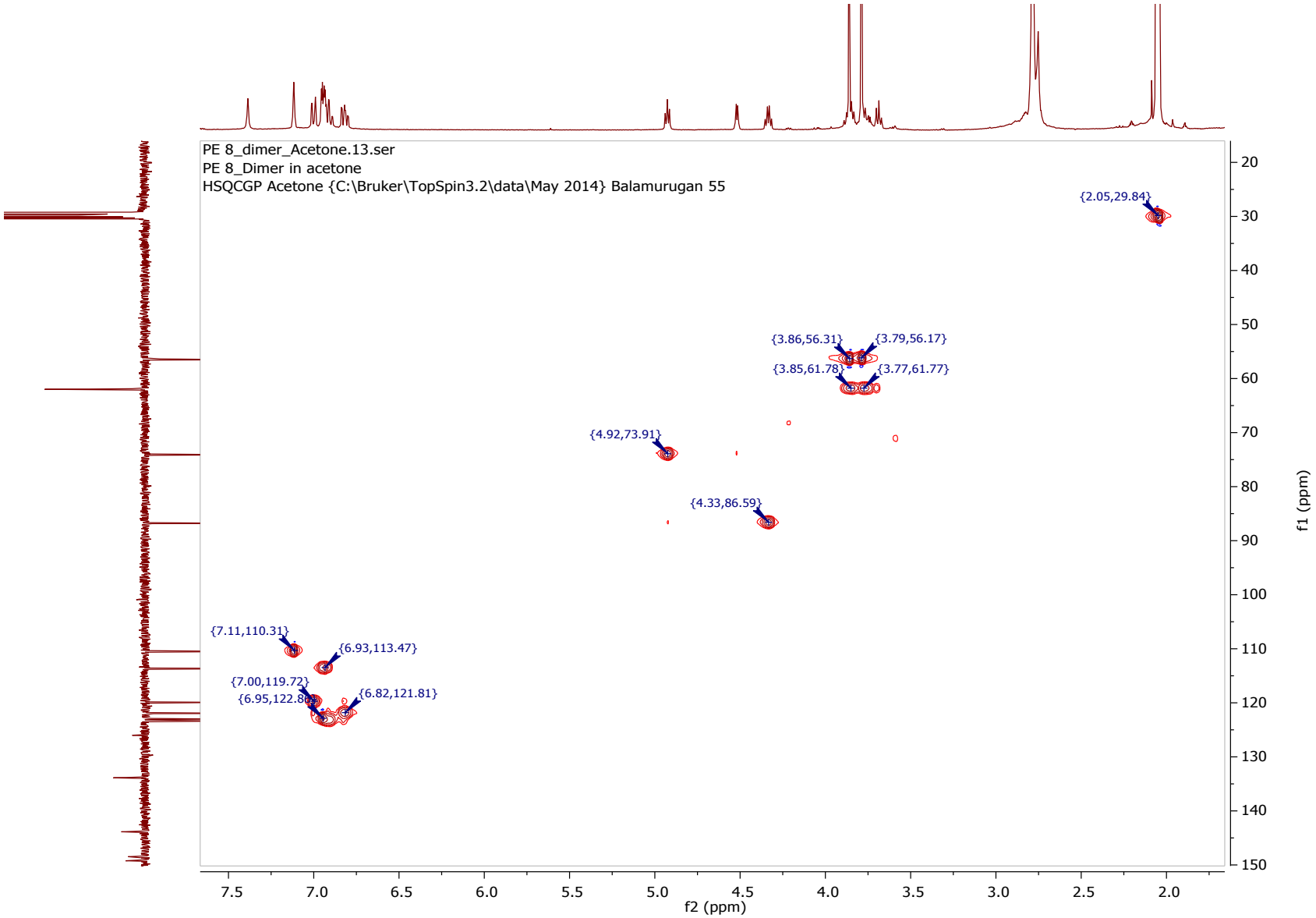



**Fig. S11**. HSQC NMR spectrum of **3B**.

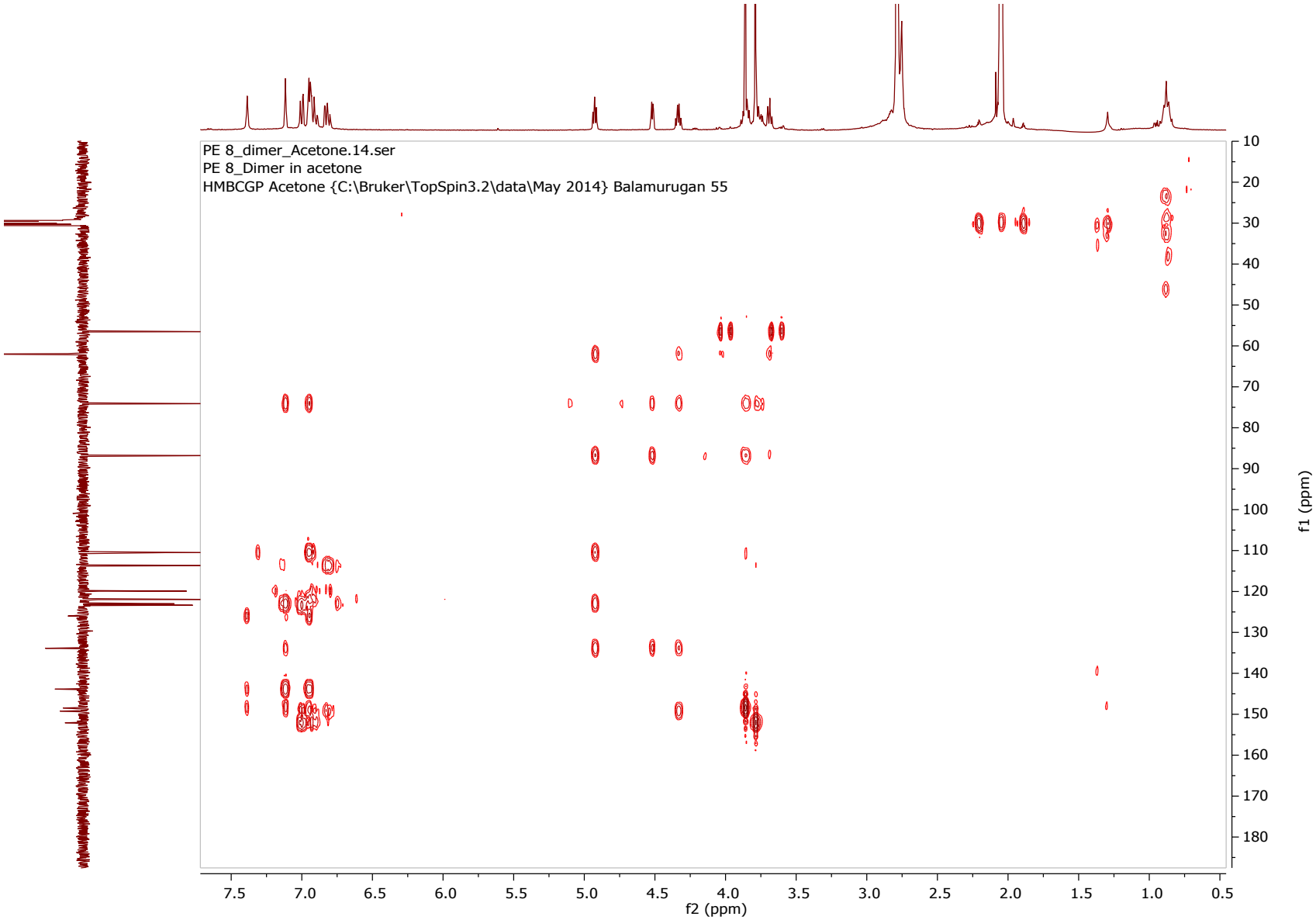



**Fig. S12**. HMBC NMR spectrum of **3B**. Peaks are omitted for clarity.

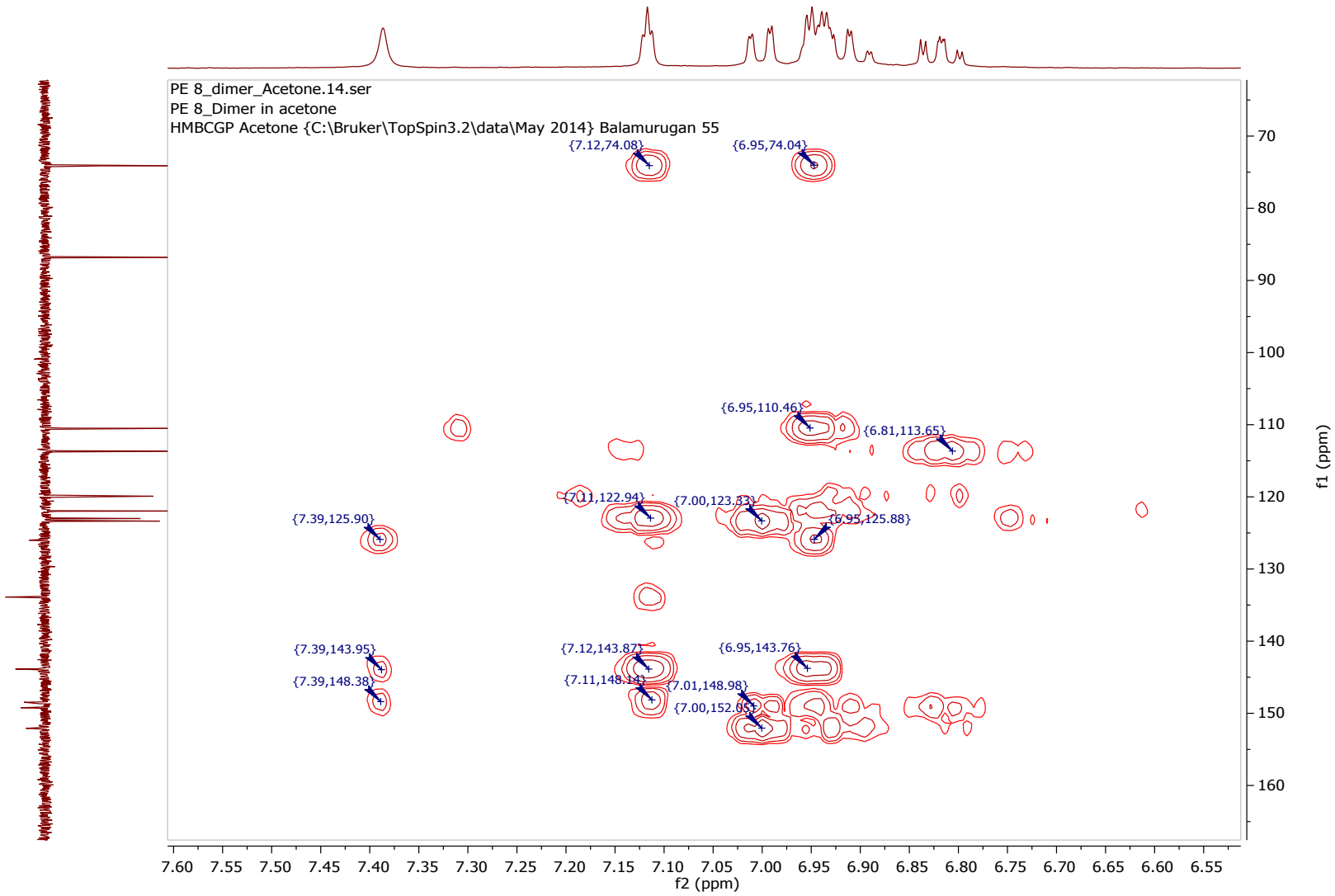



**Fig. S12a**. HMBC NMR spectrum of **3B**. Correlations in the aromatic region are shown.

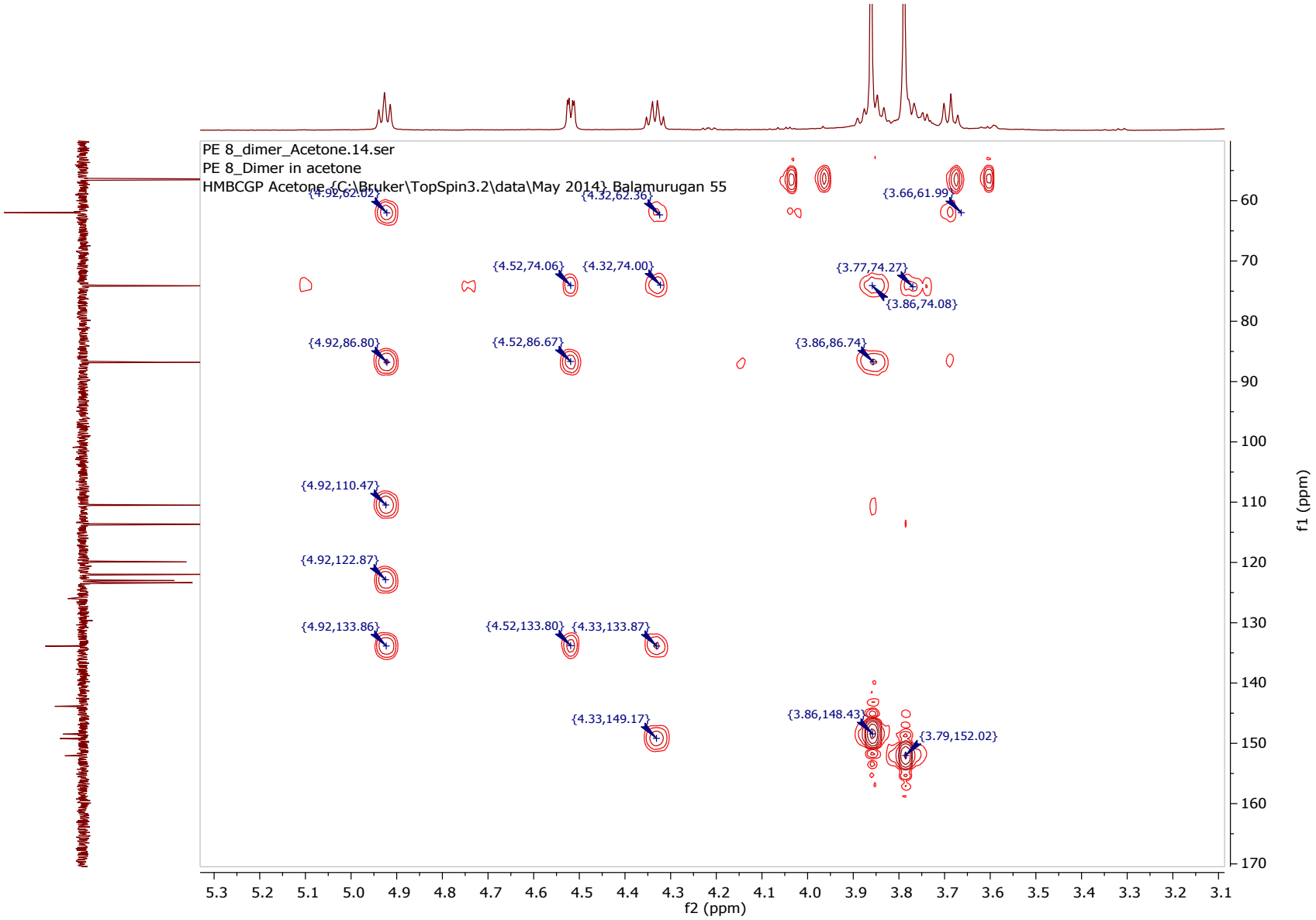



**Fig. S12b**. HMBC NMR spectrum of **3B**. Correlations in the aliphatic region are shown.

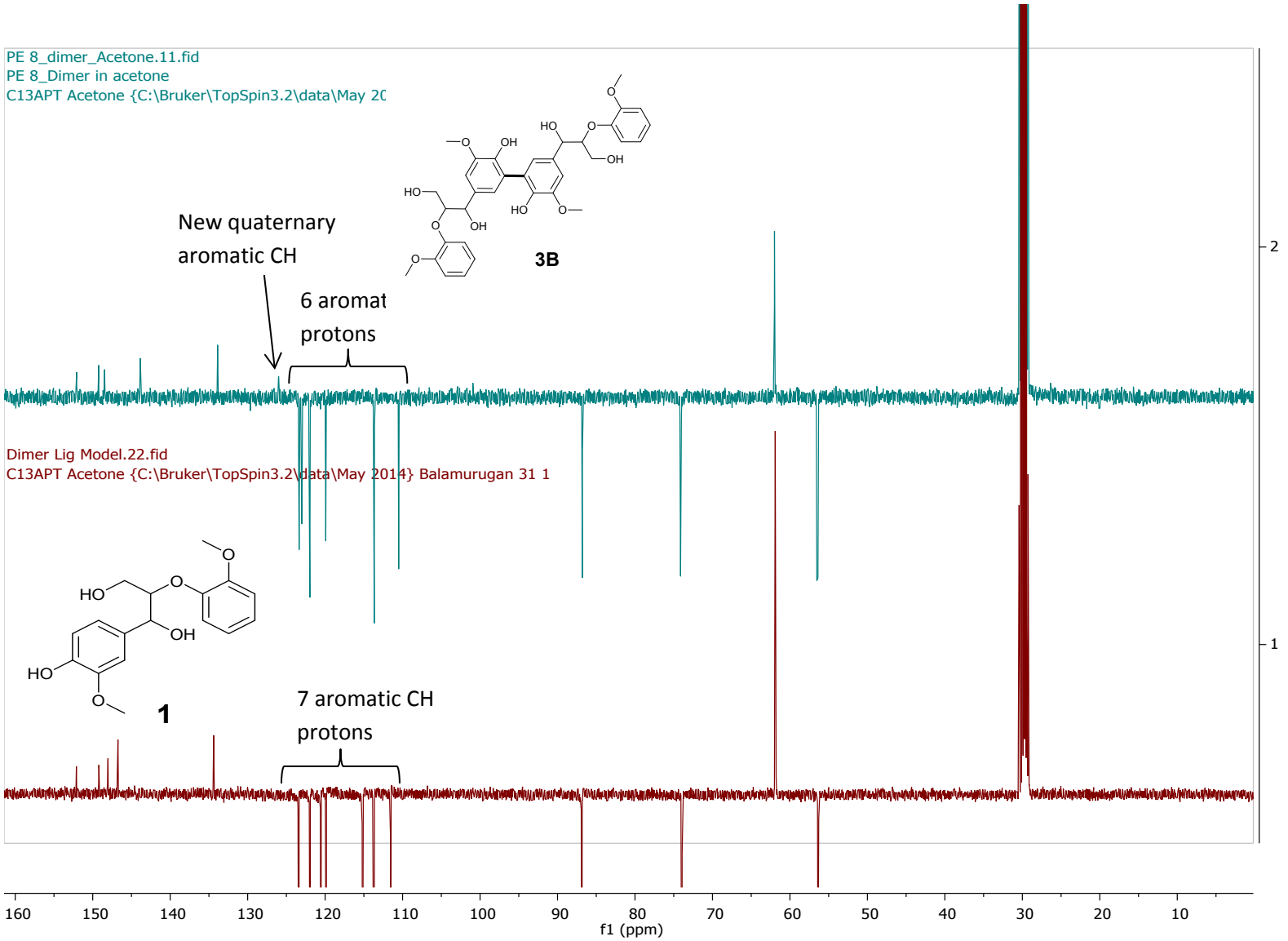



**Fig. S13**. Comparison of $^{13}$C APT spectra of **1** and **3B**.