

## Supplementary Materials

# Disulfated Ophiuroid Type Steroids from the Far Eastern Starfish *Pteraster marsippus* and their Cytotoxic Activity on the Models of 2D and 3D Cultures

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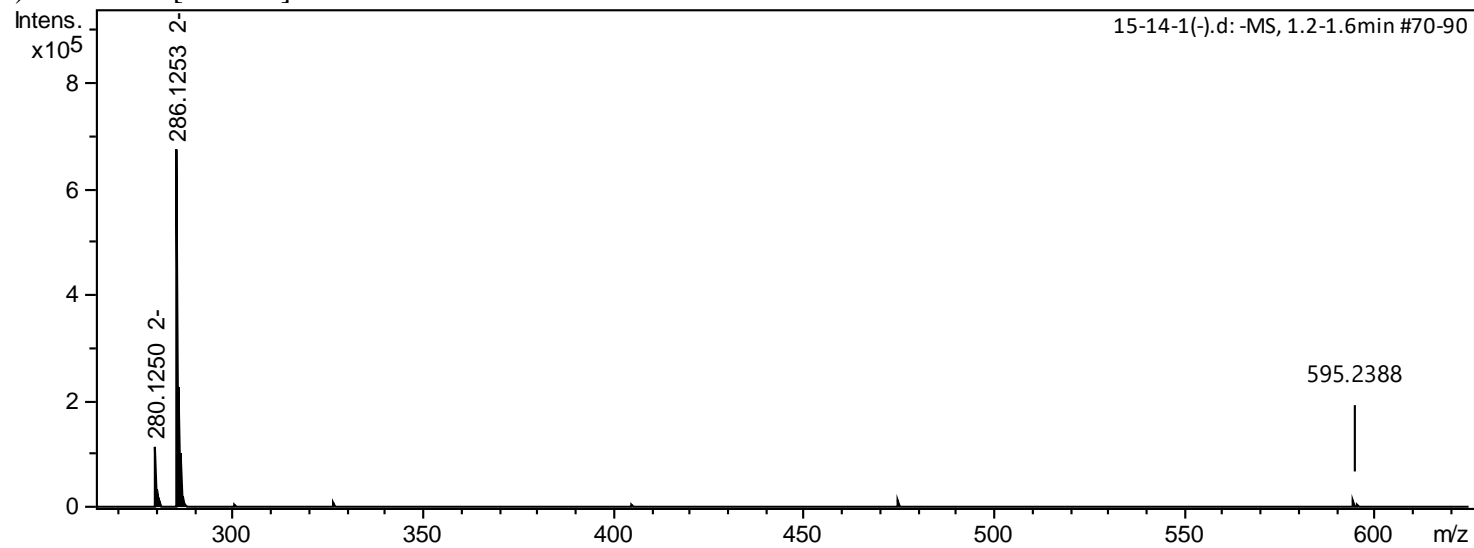
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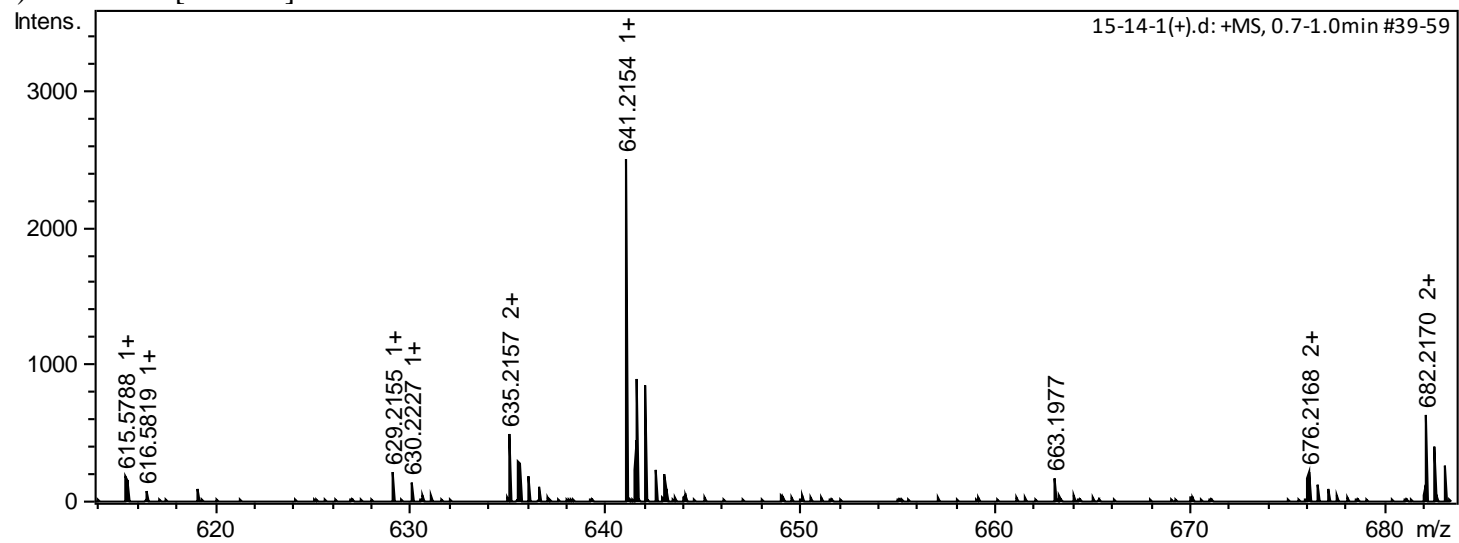
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**Figure S1.** HRESIMS spectra of compound **1**.

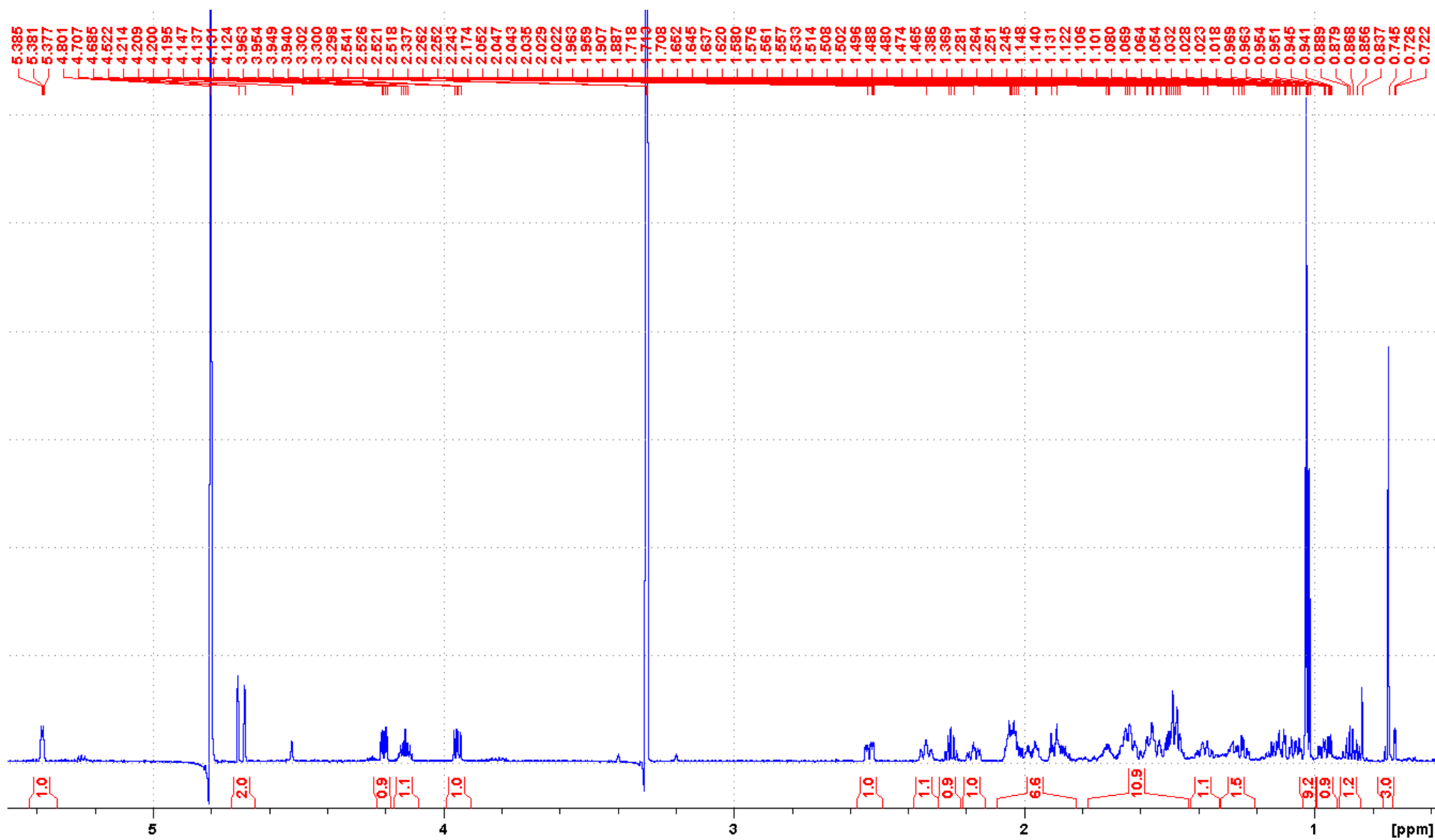
(-)HRESIMS  $[M - Na]^-$  ion



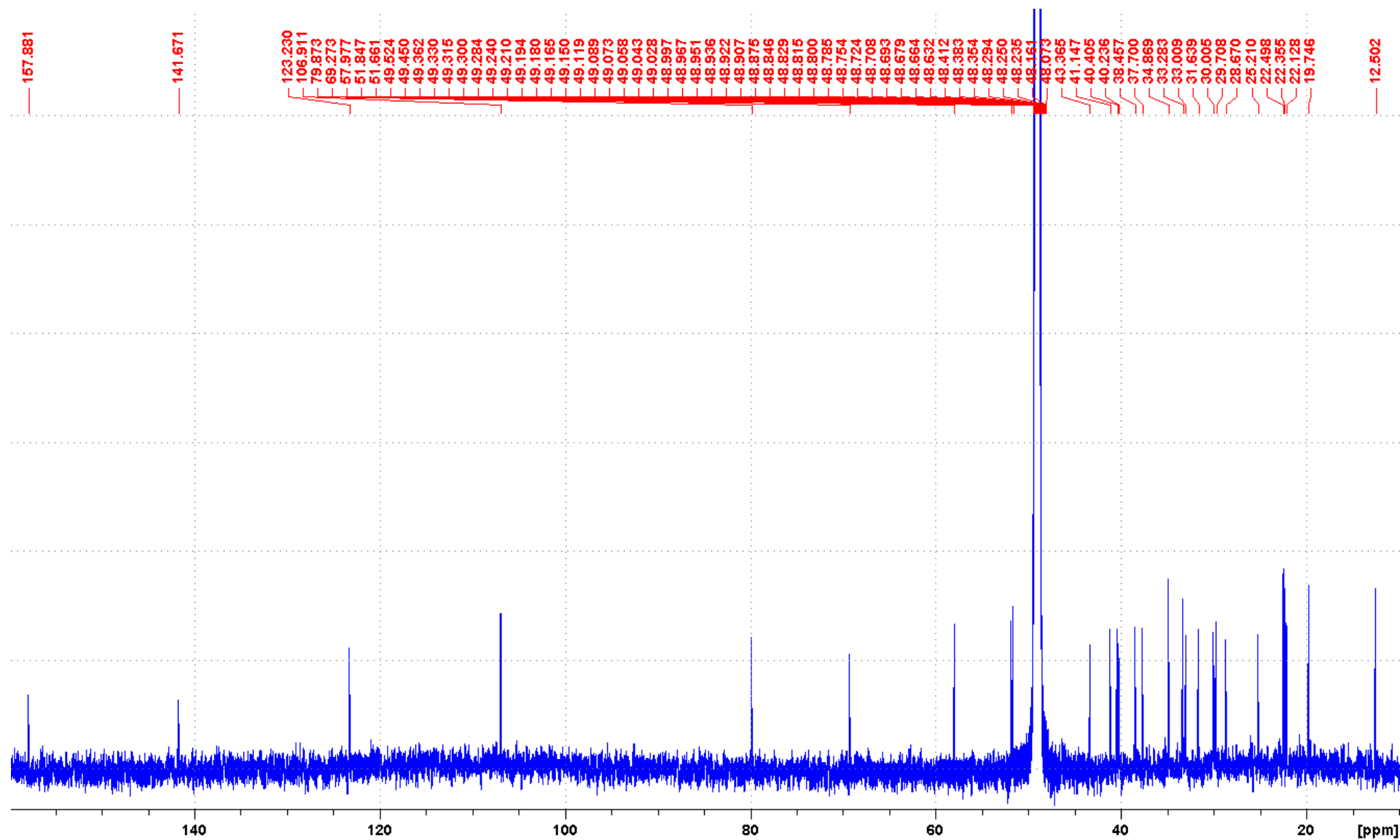
(+)HRESIMS  $[M + Na]^+$  ion



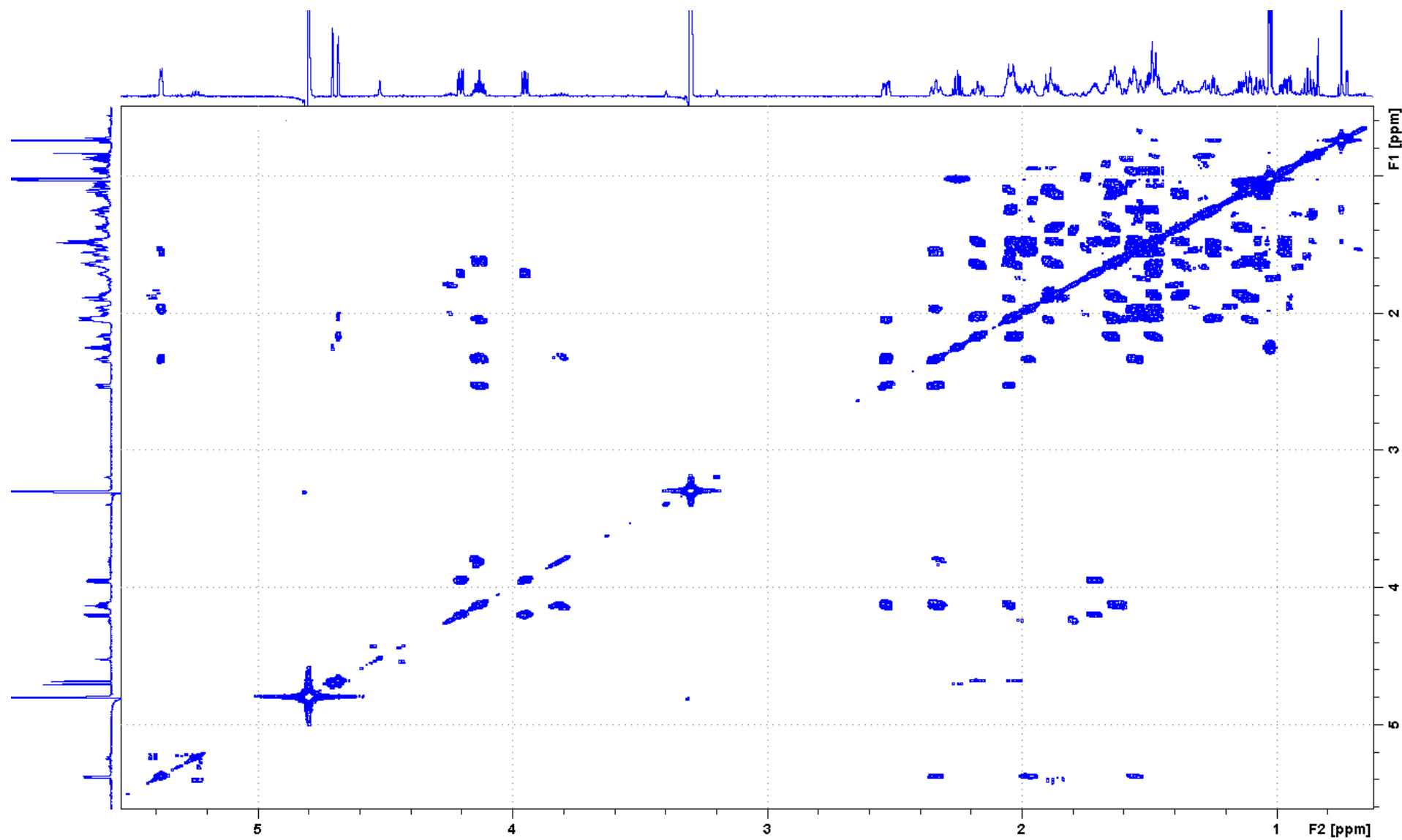
**Figure S2.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **1**.



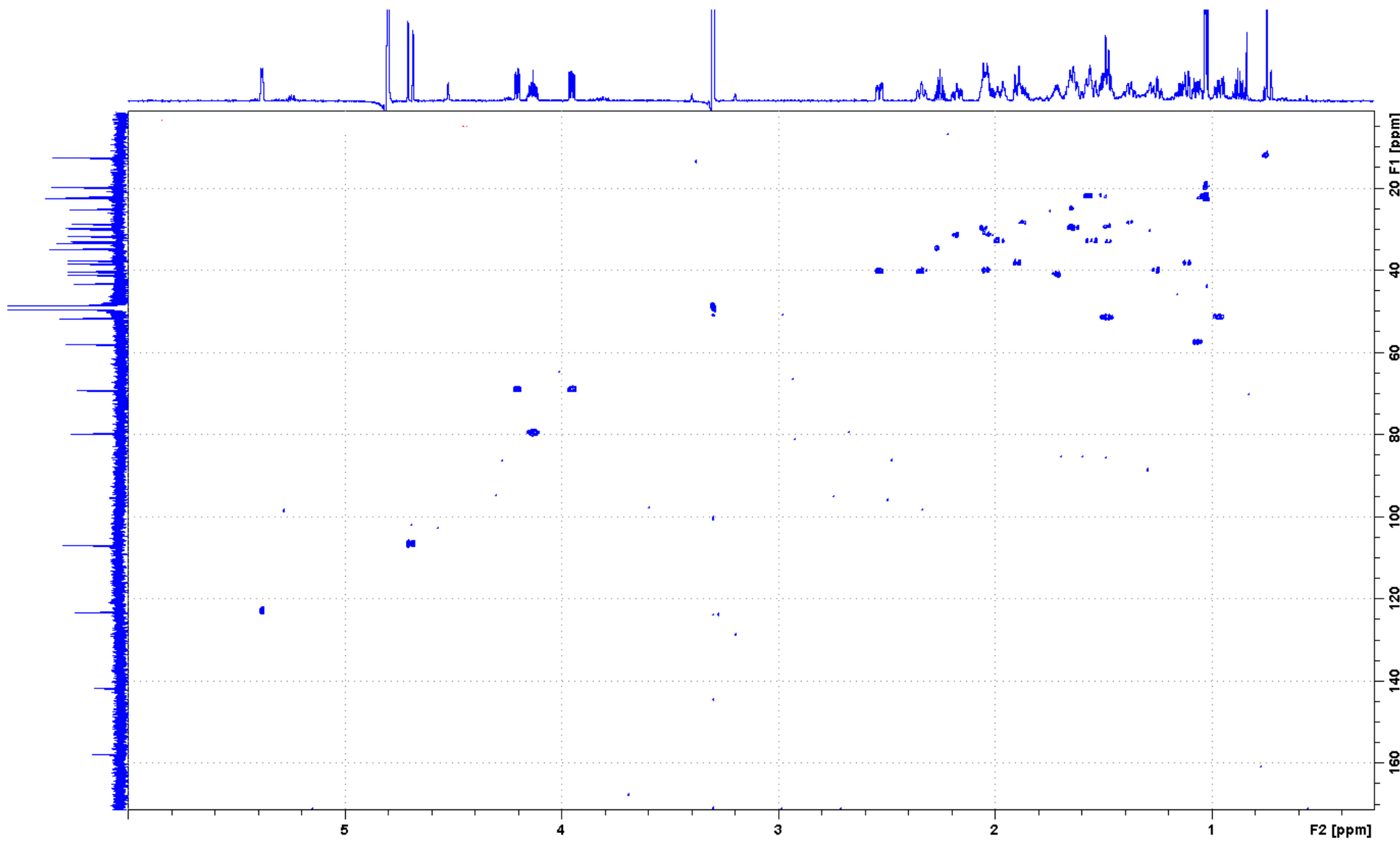
**Figure S3.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **1**.



**Figure S4.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **1**.

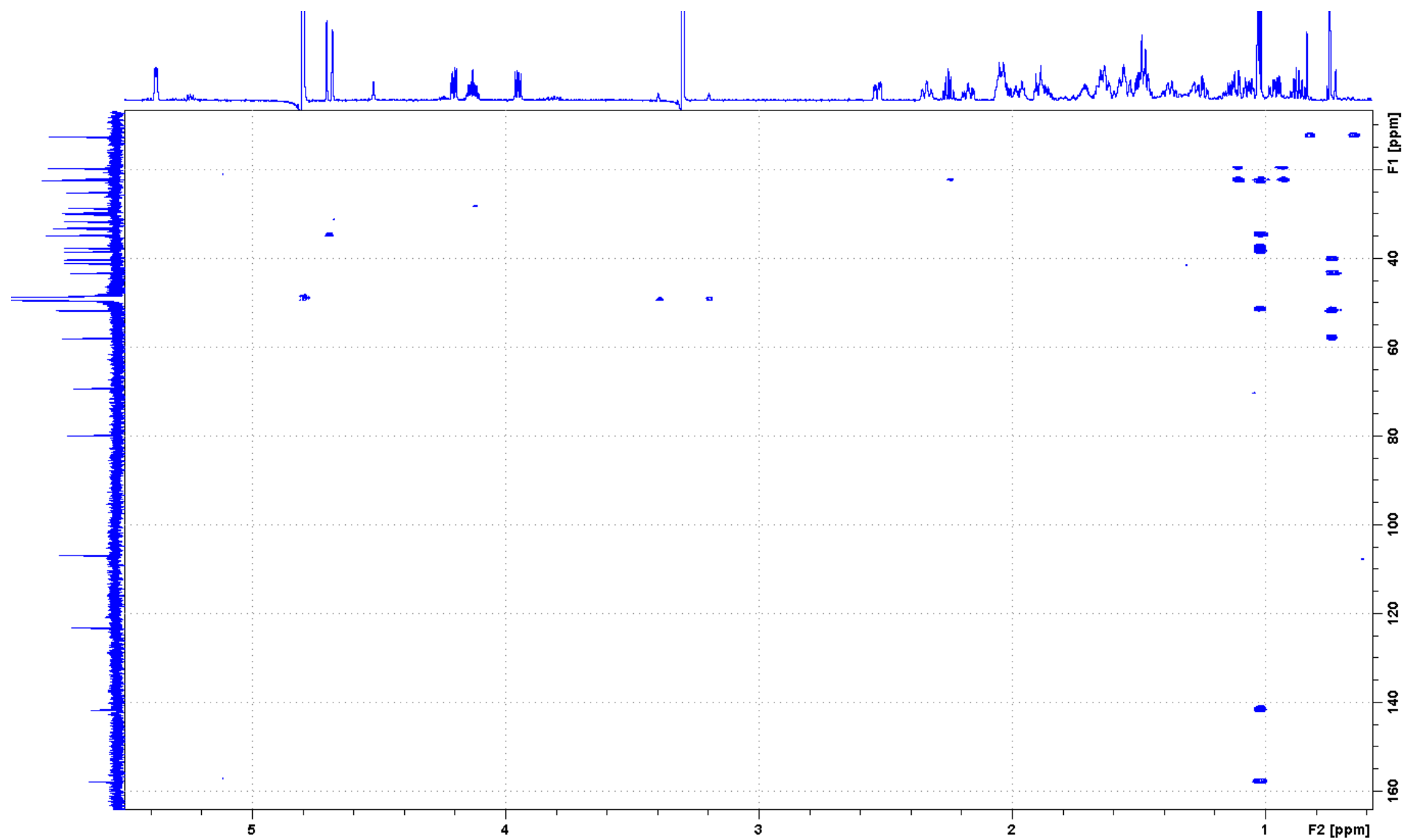


**Figure S5.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **1**.

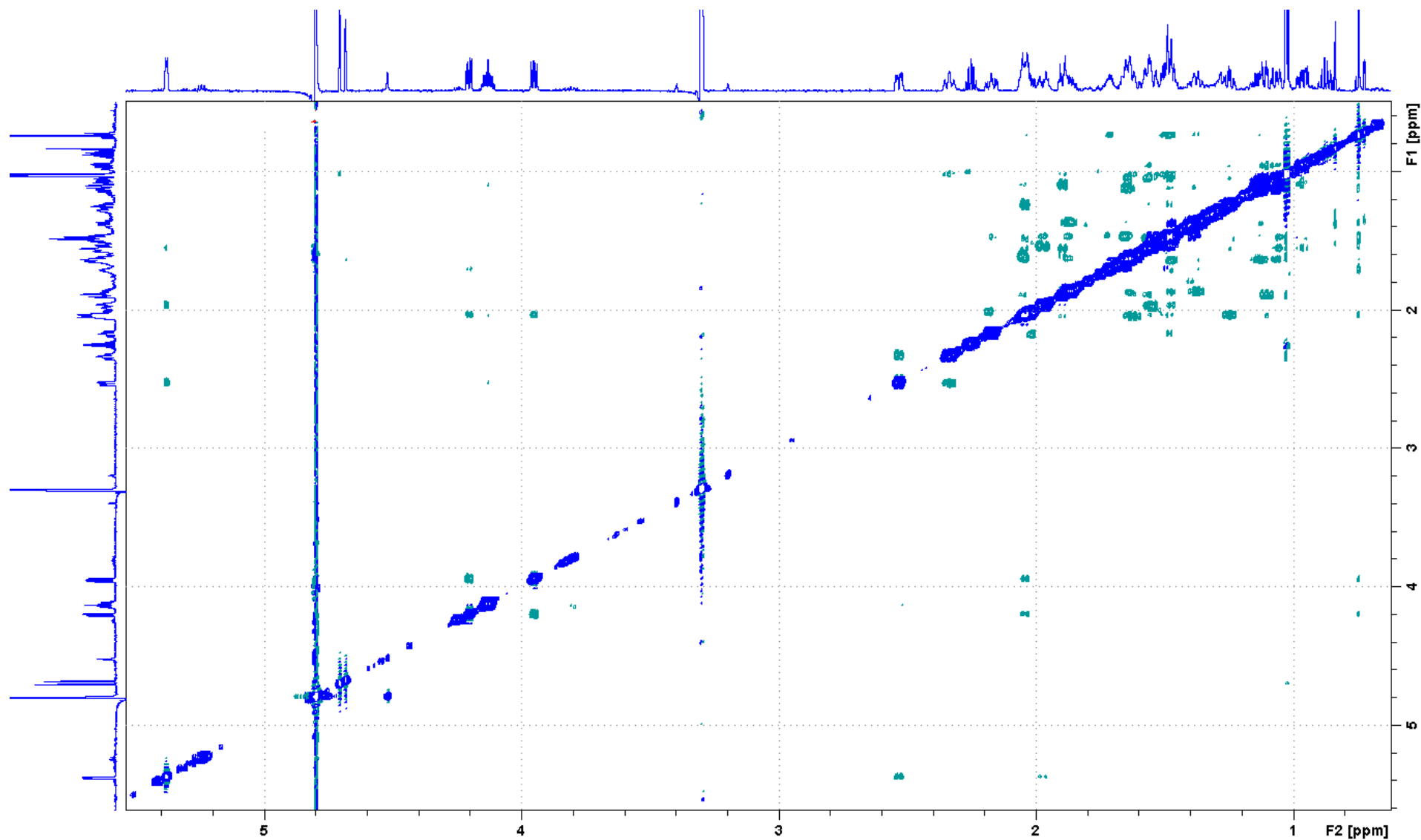




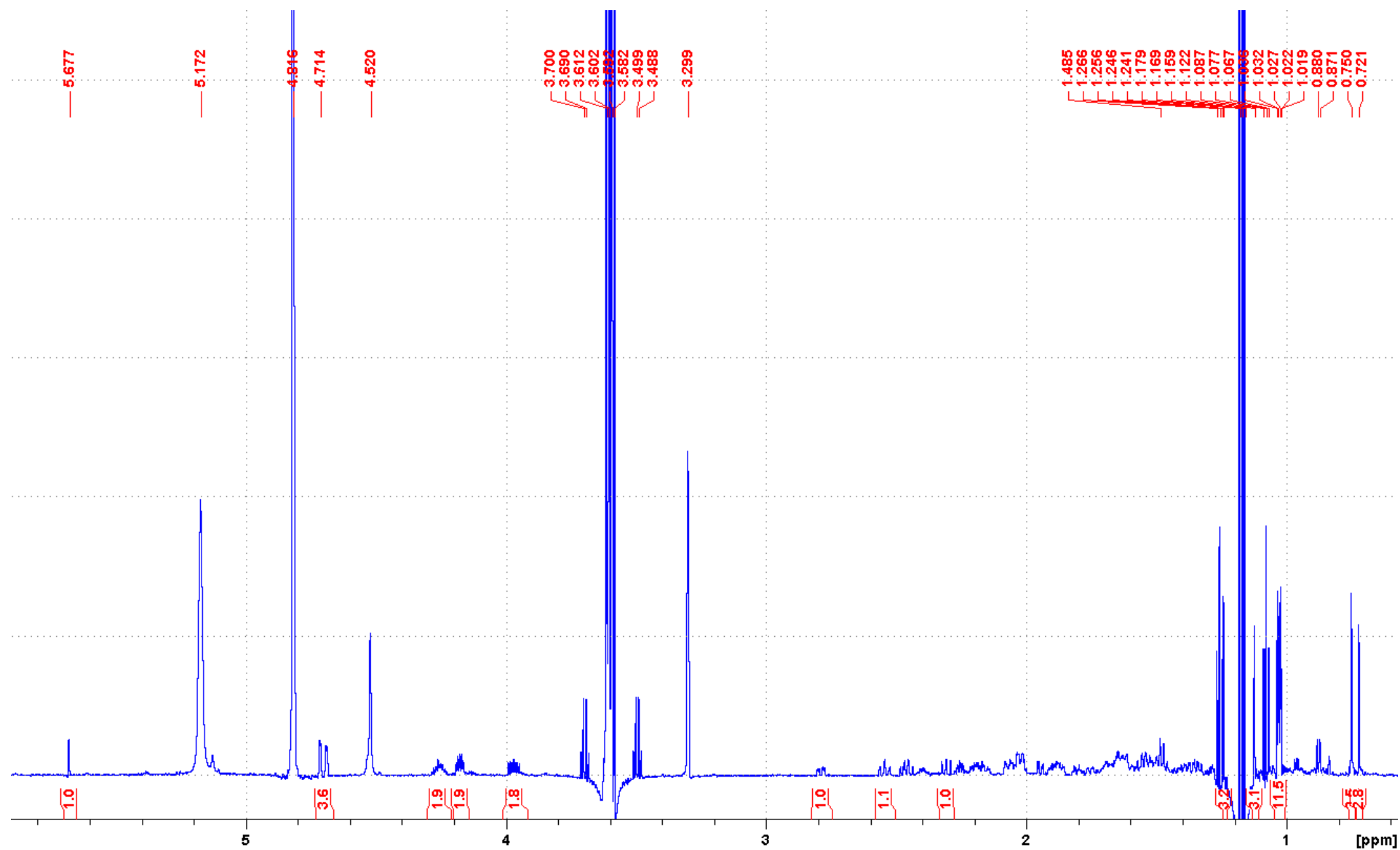
**Figure S6.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **1**.



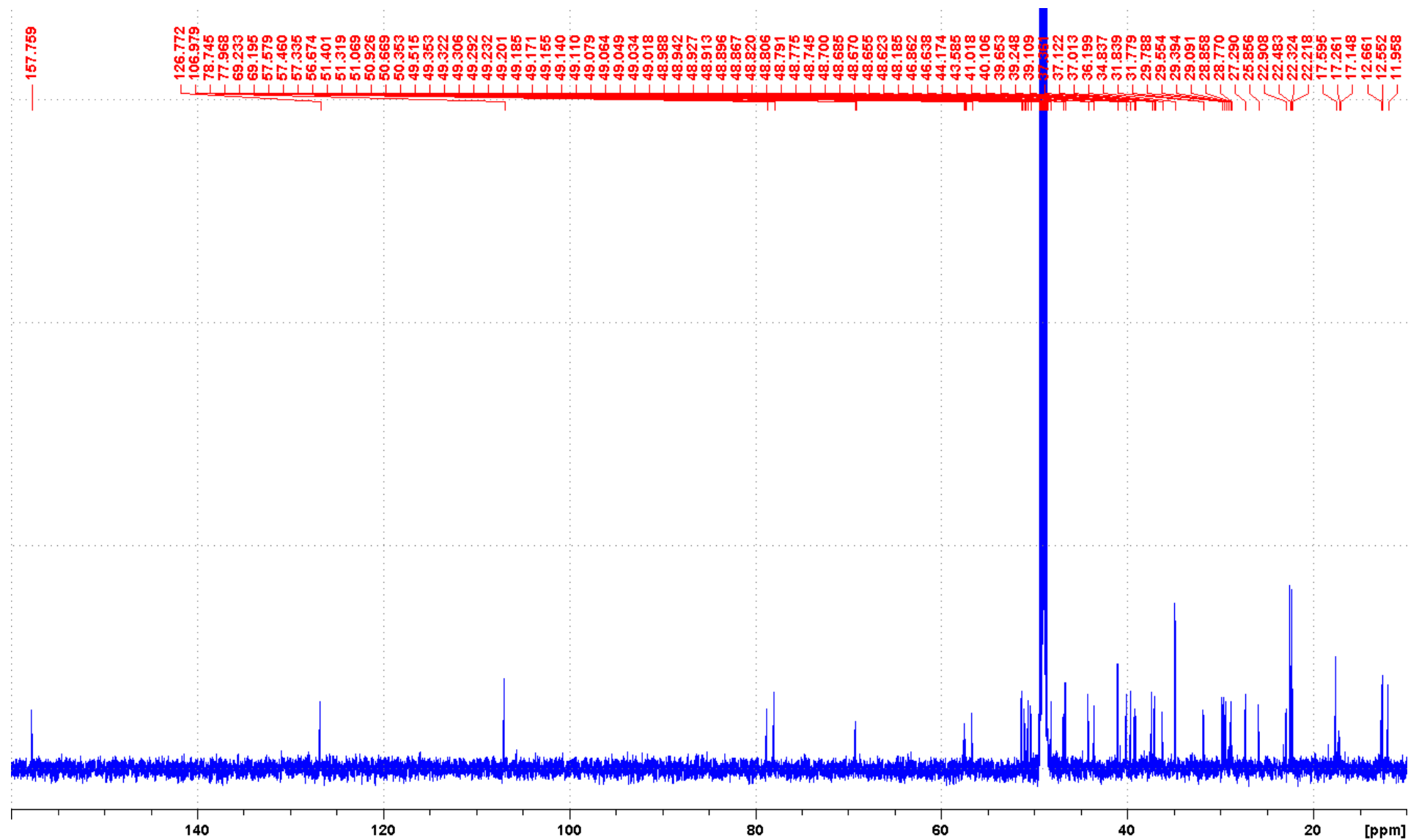
**Figure S7.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **1**.



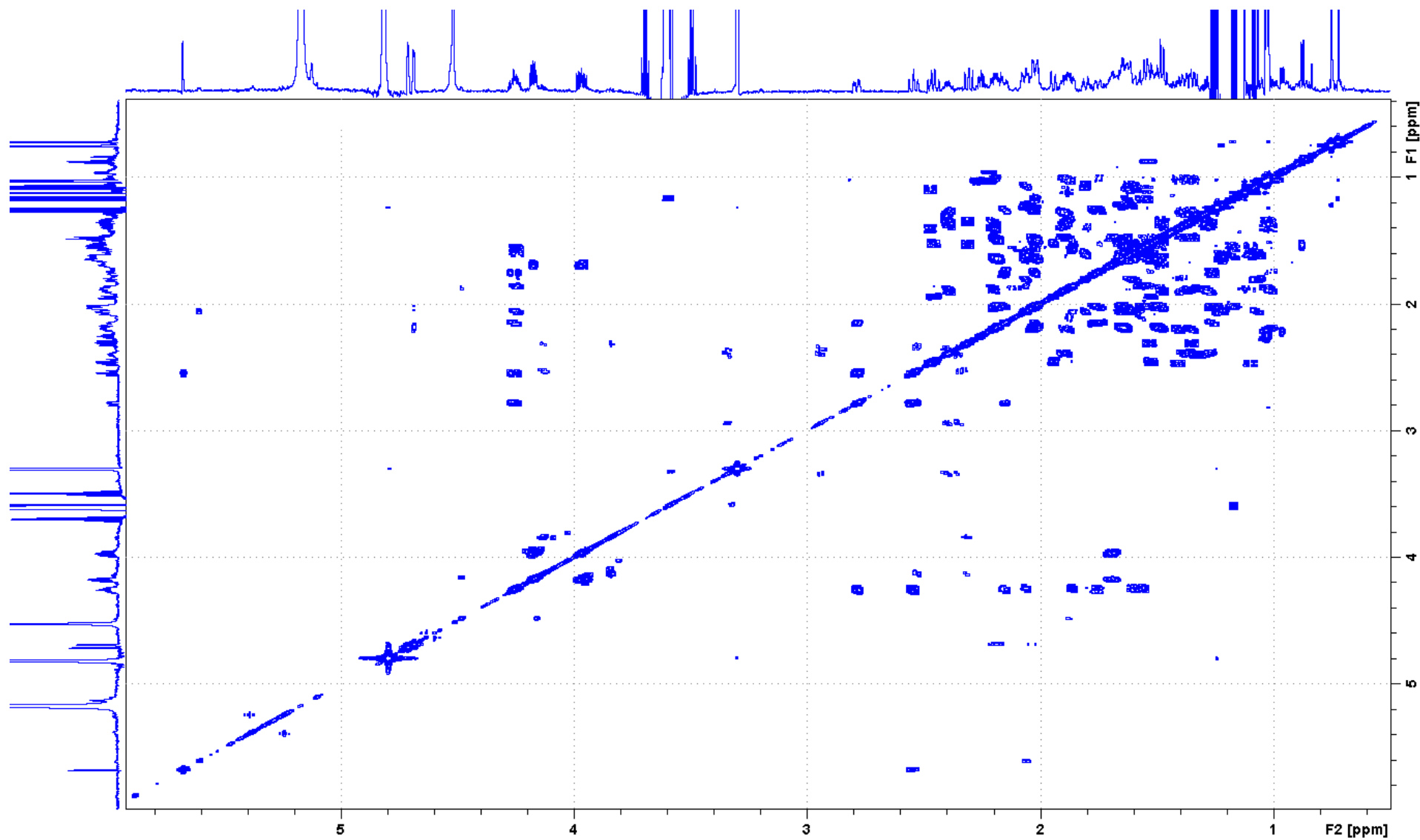
**Figure S8.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of the mixture of **2** and **3**.



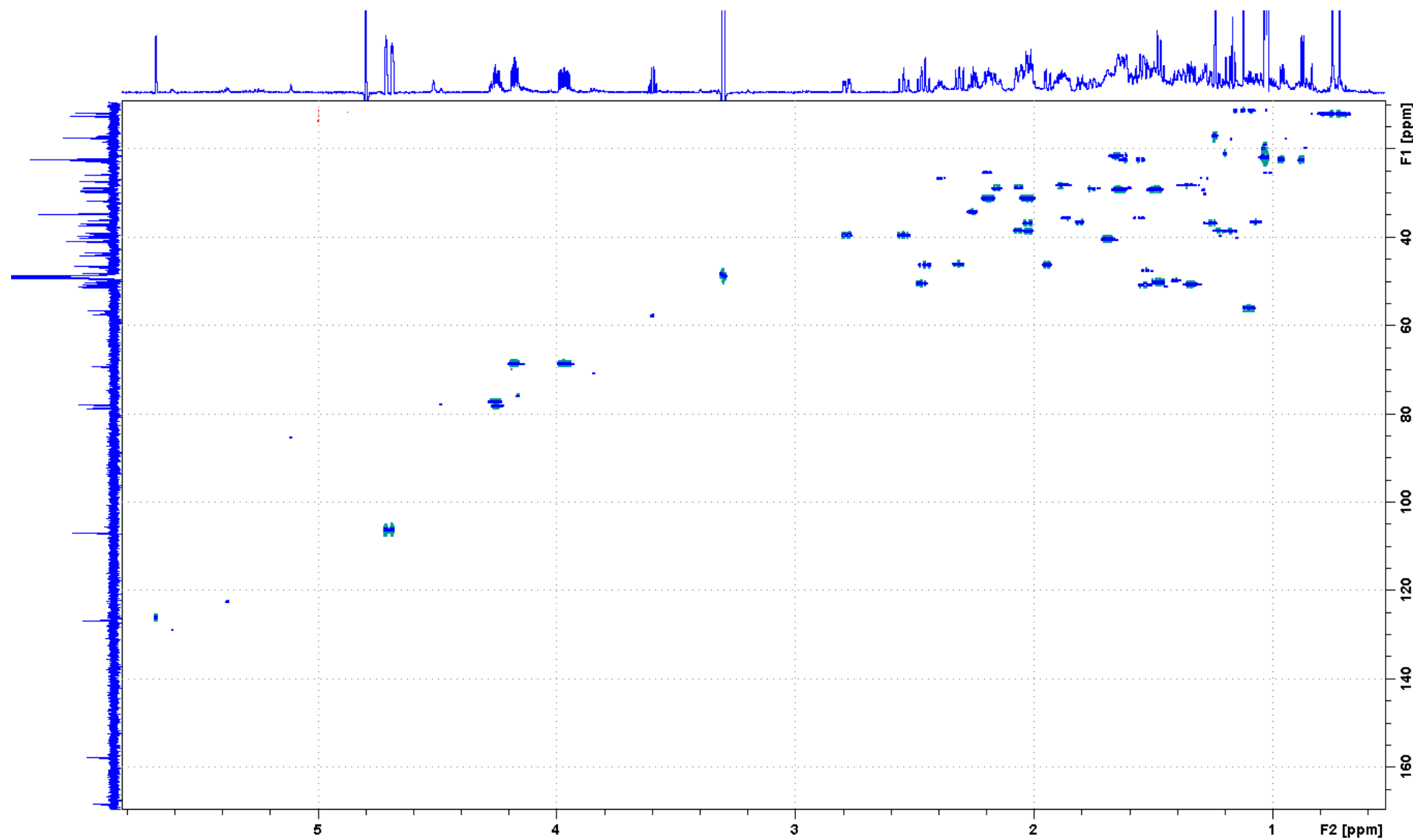
**Figure S9.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of the mixture of **2** and **3**.



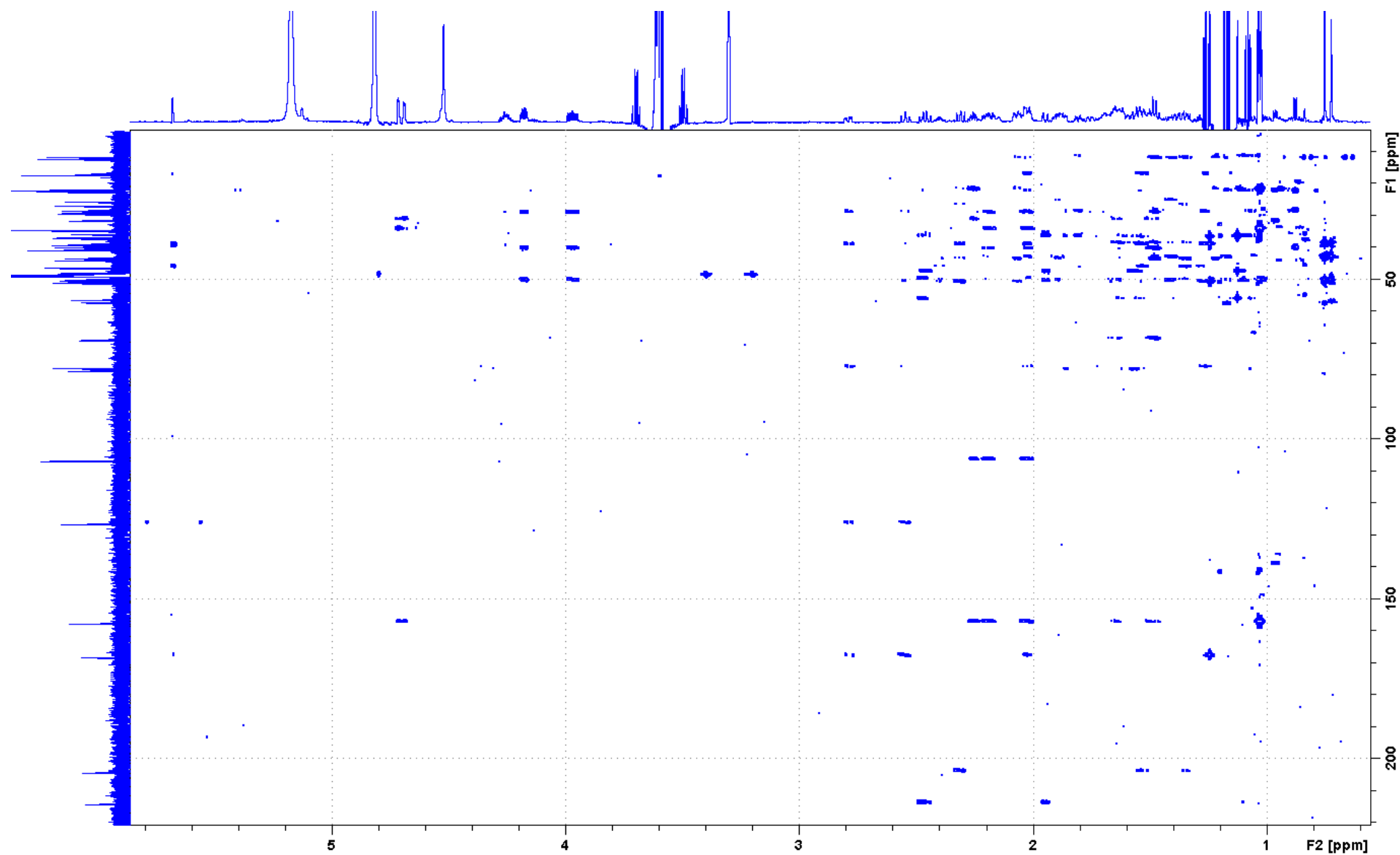
**Figure S10.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of the mixture of **2** and **3**.



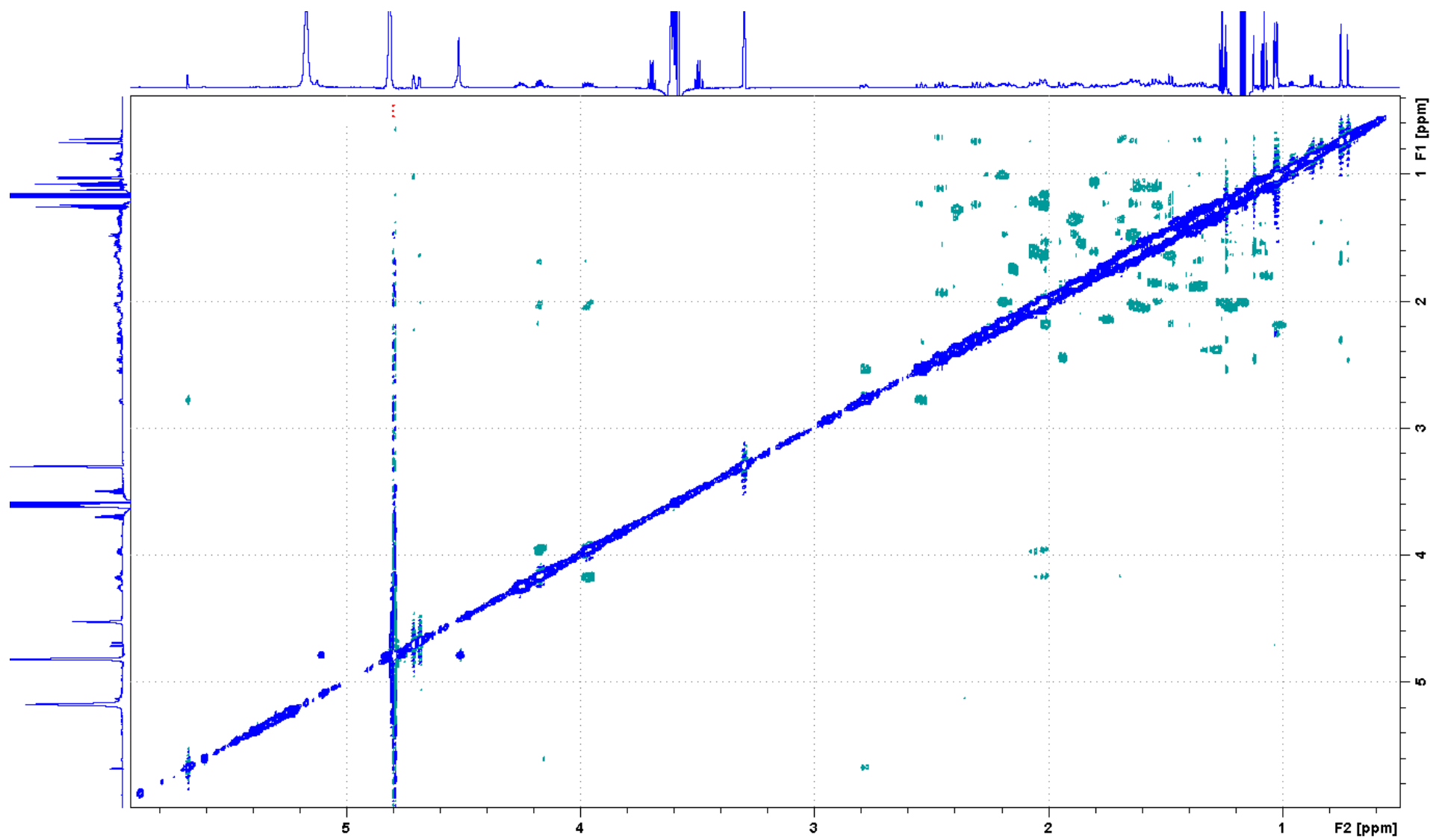
**Figure S11.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of the mixture of **2** and **3**.



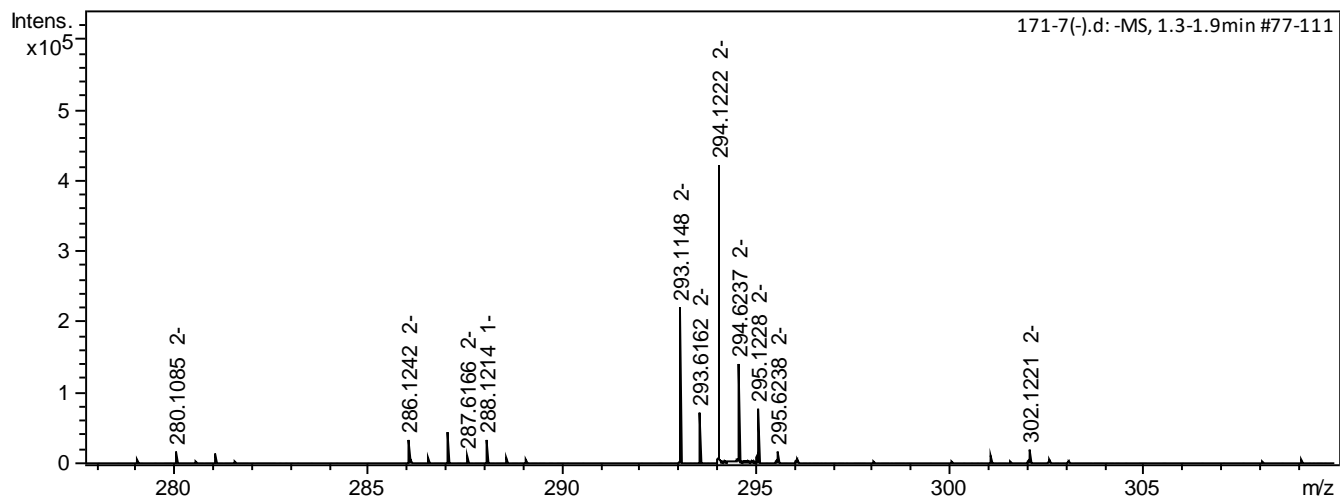
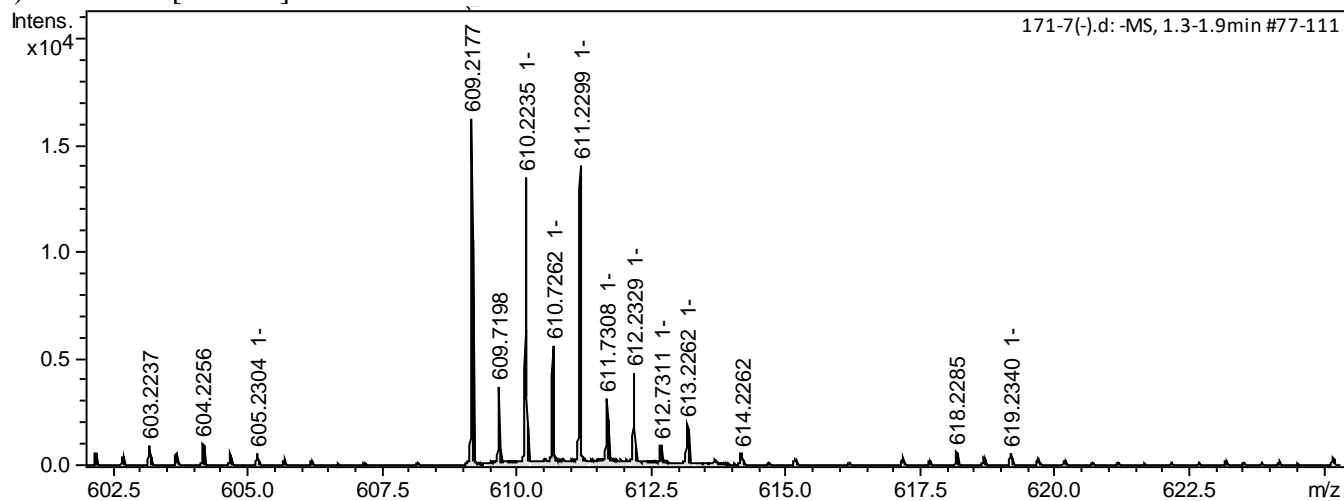
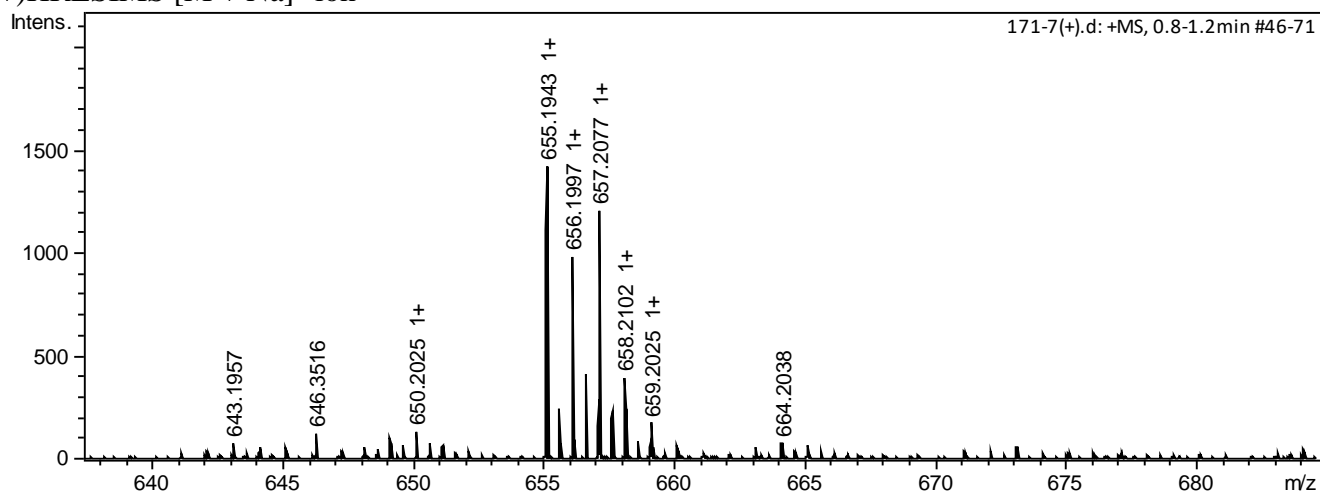
**Figure S12.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of the mixture of **2** and **3**.

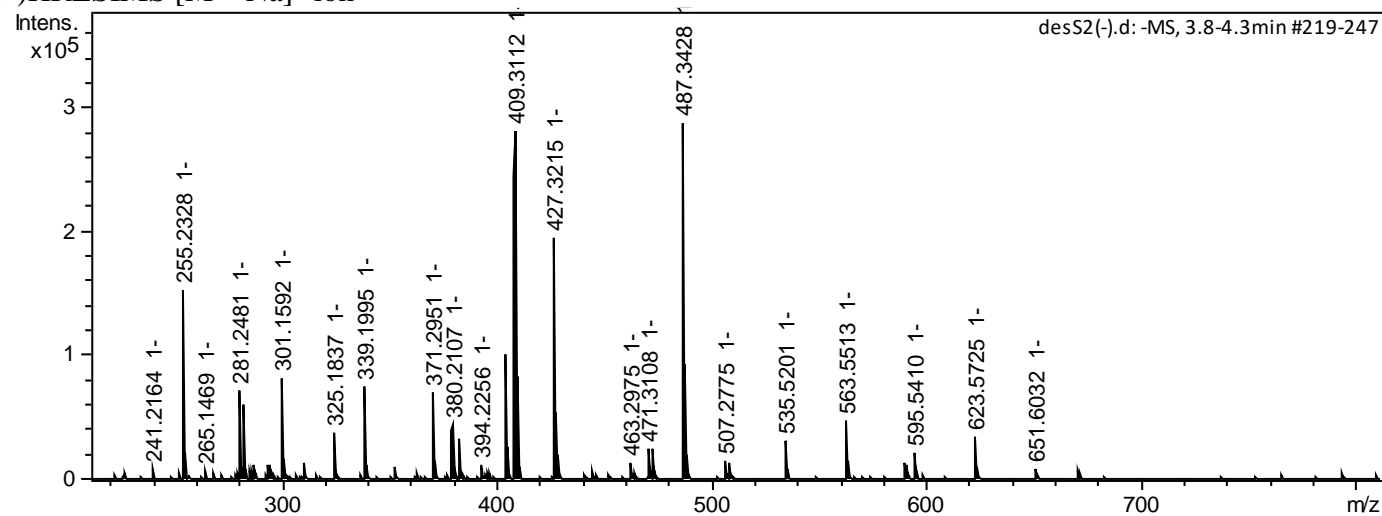
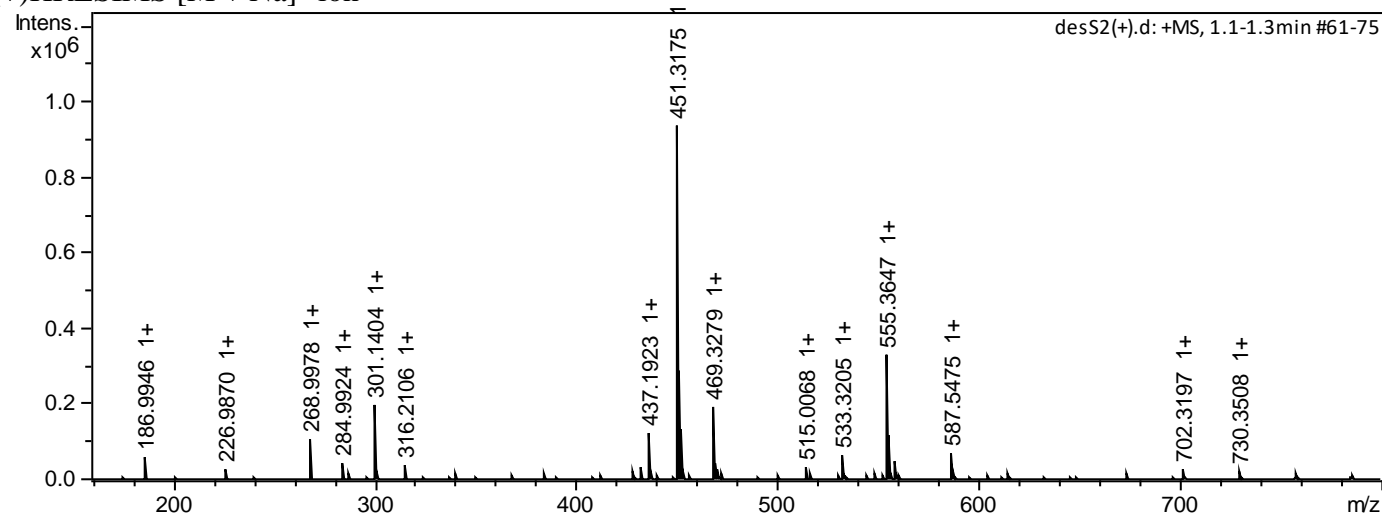


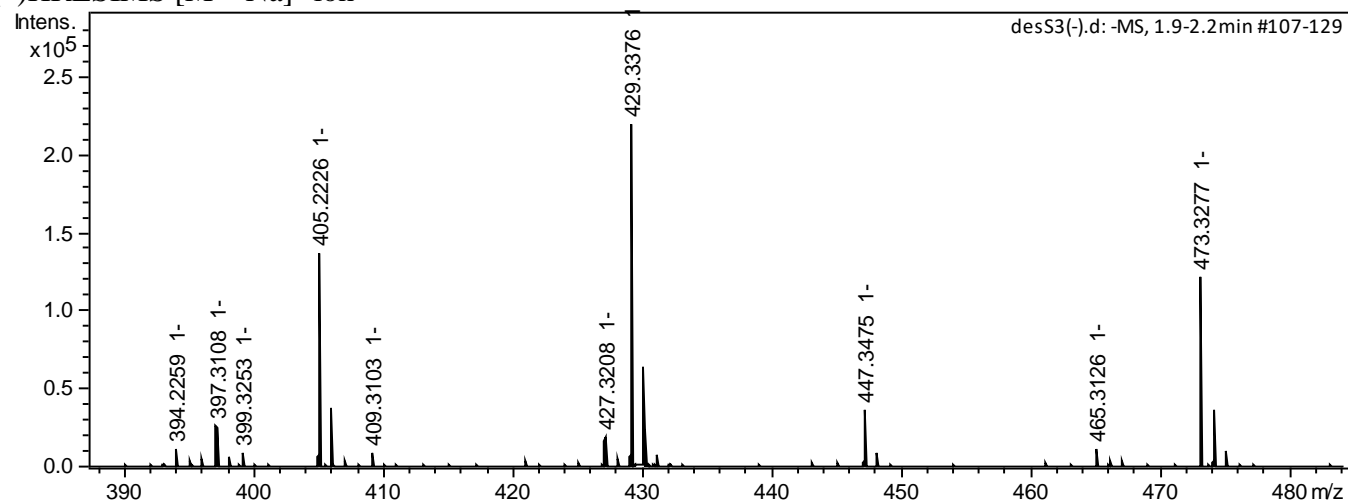
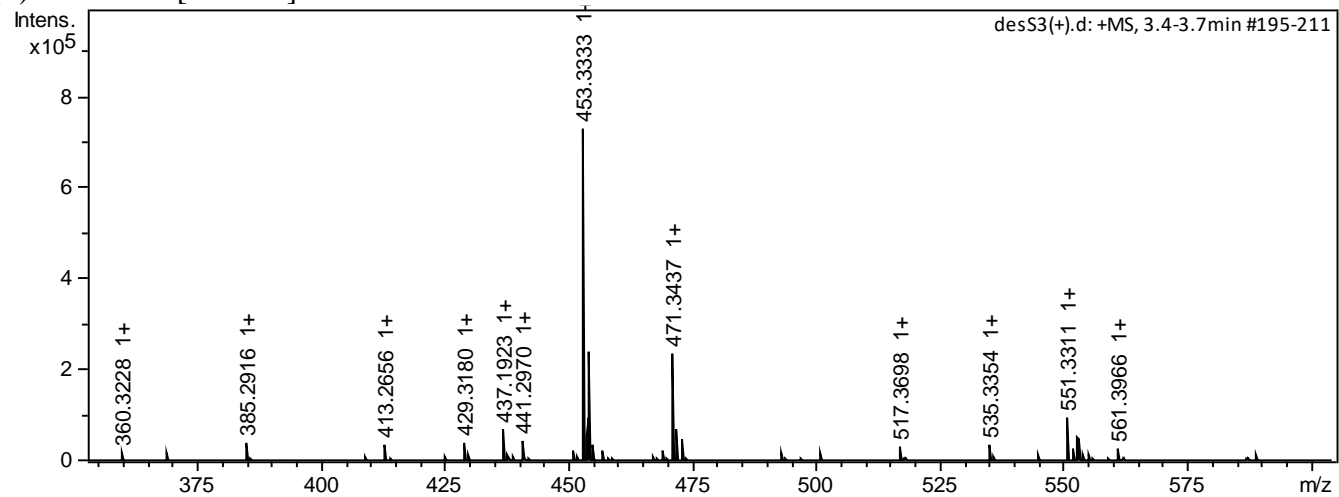
**Figure S13.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of the mixture of **2** and **3**.



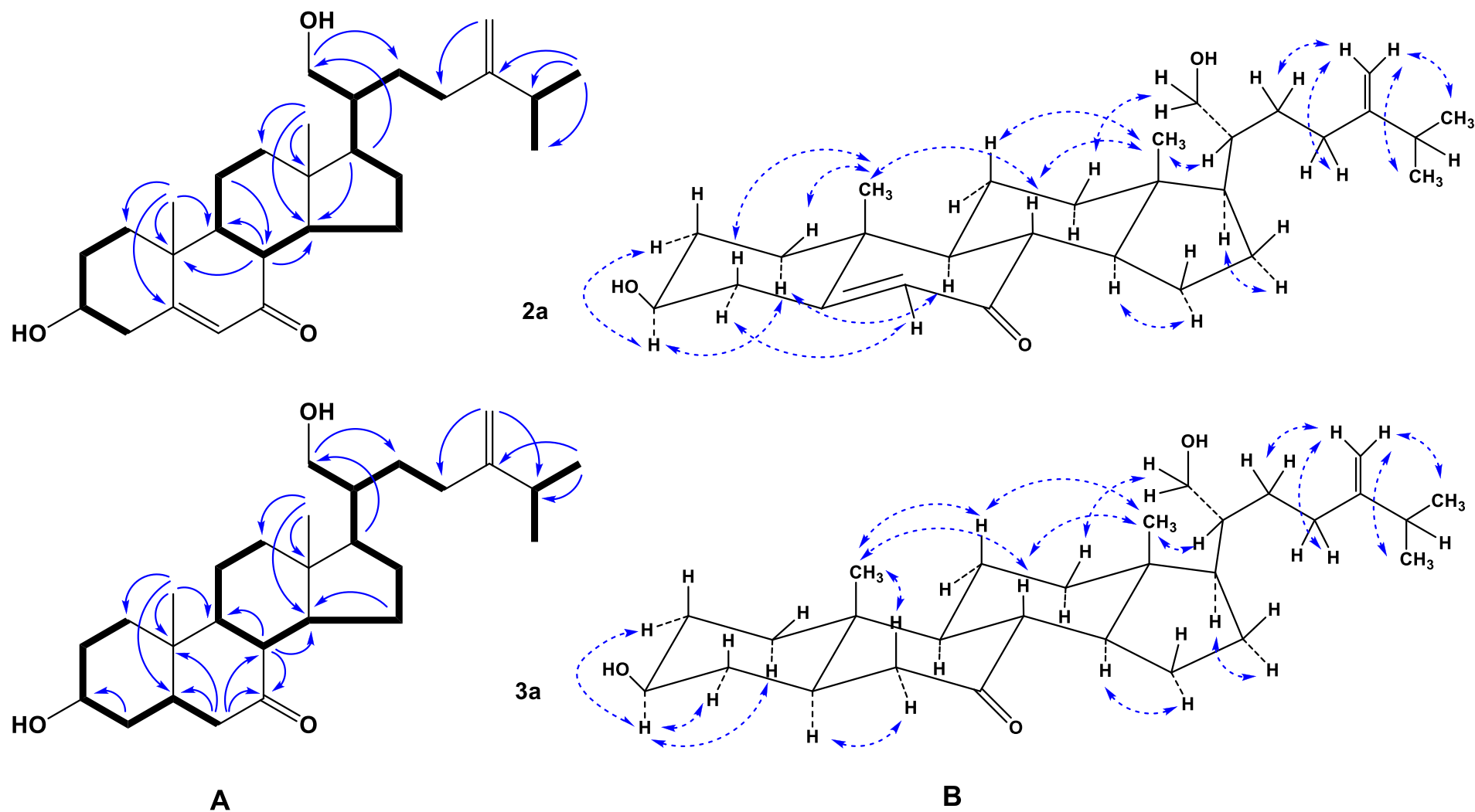


**Figure S14.** HRESIMS spectra of the mixture of **2** and **3**.**(-)HRESIMS**  $[M - Na]^-$  ion**(+)HRESIMS**  $[M + Na]^+$  ion

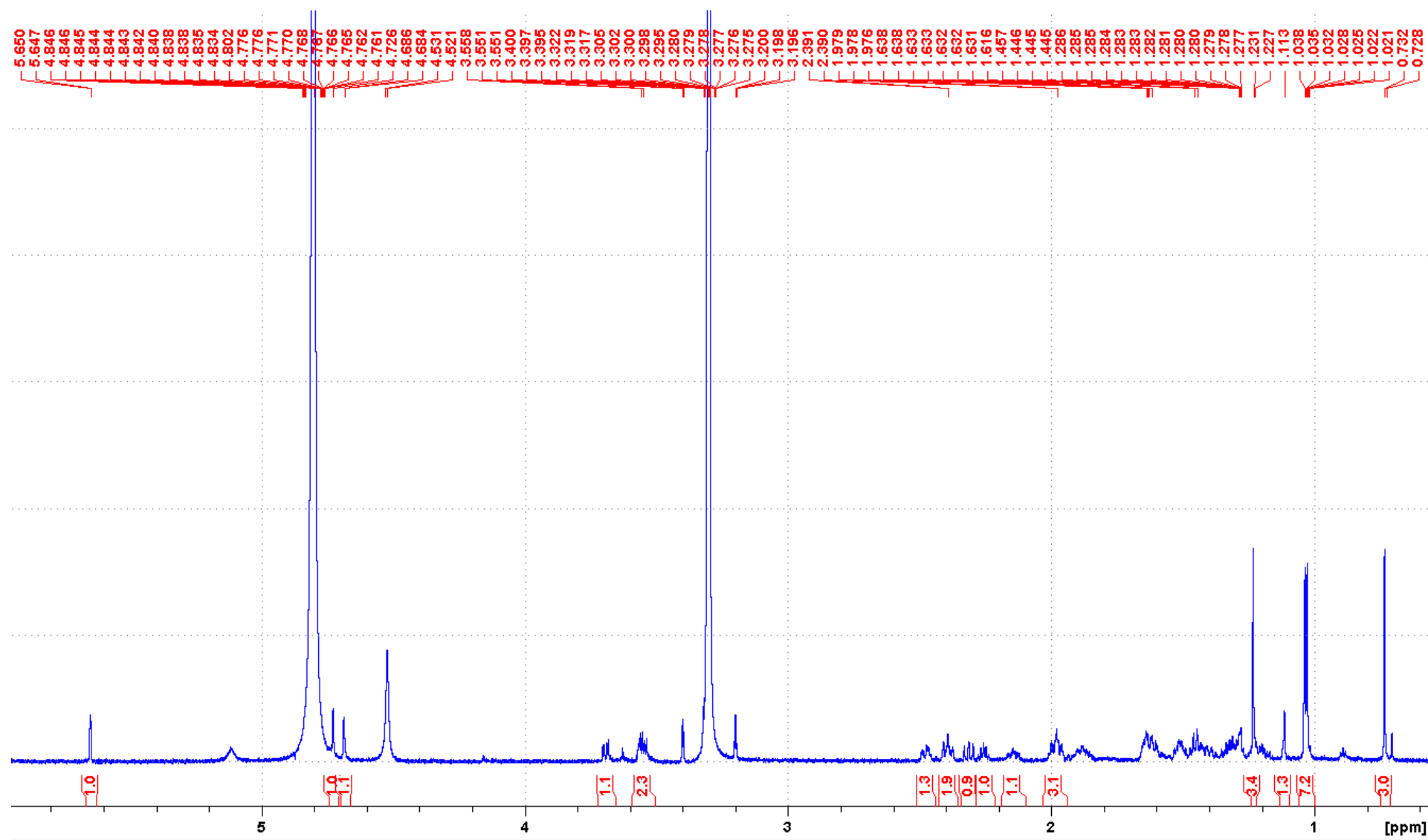
**Figure S15.** HRESIMS spectra of compound **2a**.**(-)HRESIMS [M – Na]<sup>–</sup> ion****(+)HRESIMS [M + Na]<sup>+</sup> ion**

**Figure S16.** HRESIMS spectra of compound **3a**.**(-)HRESIMS**  $[M - Na]^-$  ion**(+)HRESIMS**  $[M + Na]^+$  ion

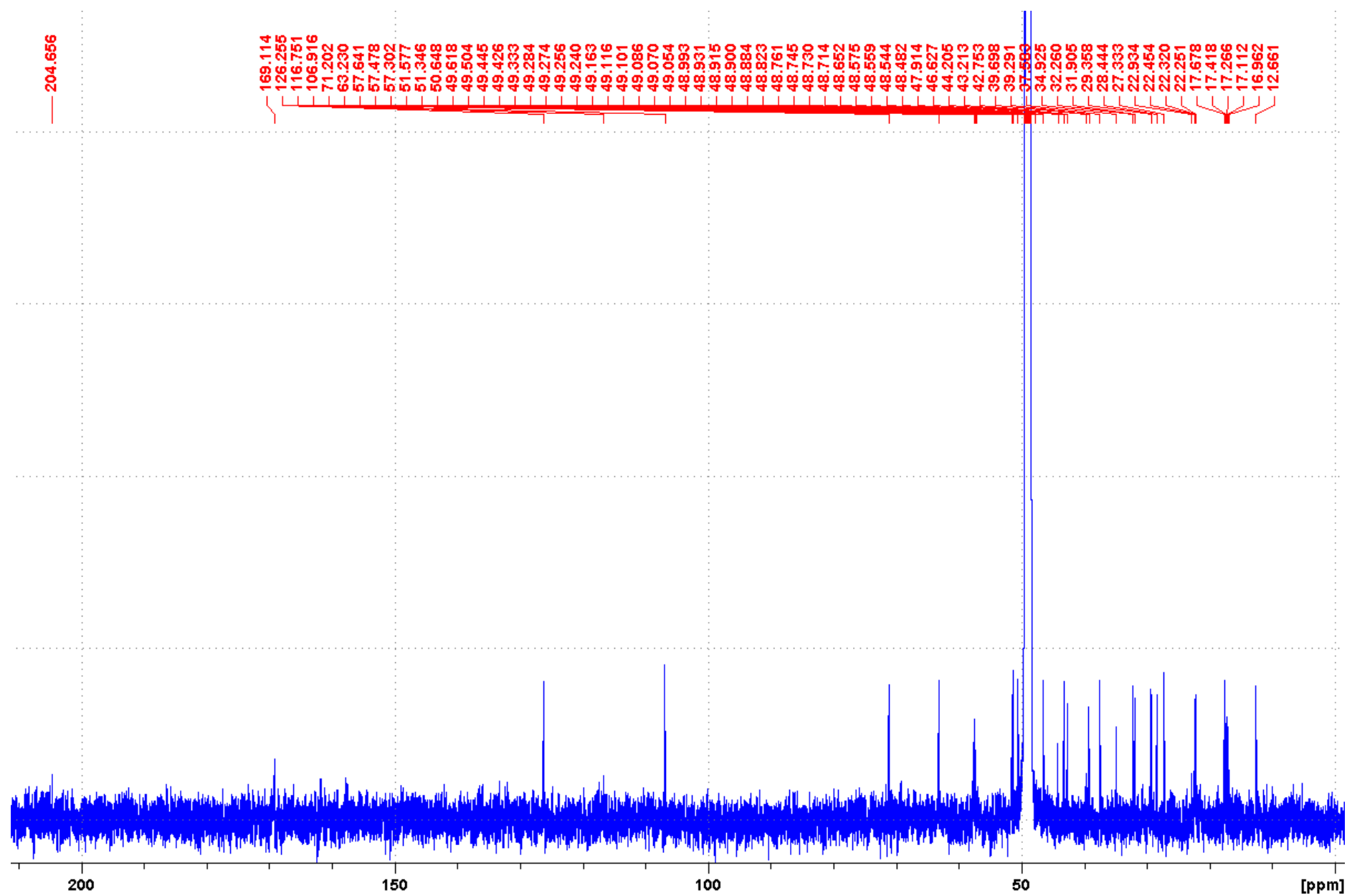
**Figure S17.** (A) COSY and key HMBC correlations of the mixture of compounds **2a** and **3a**. (B) Key ROESY correlations of the mixture of compounds **2a** and **3a**.



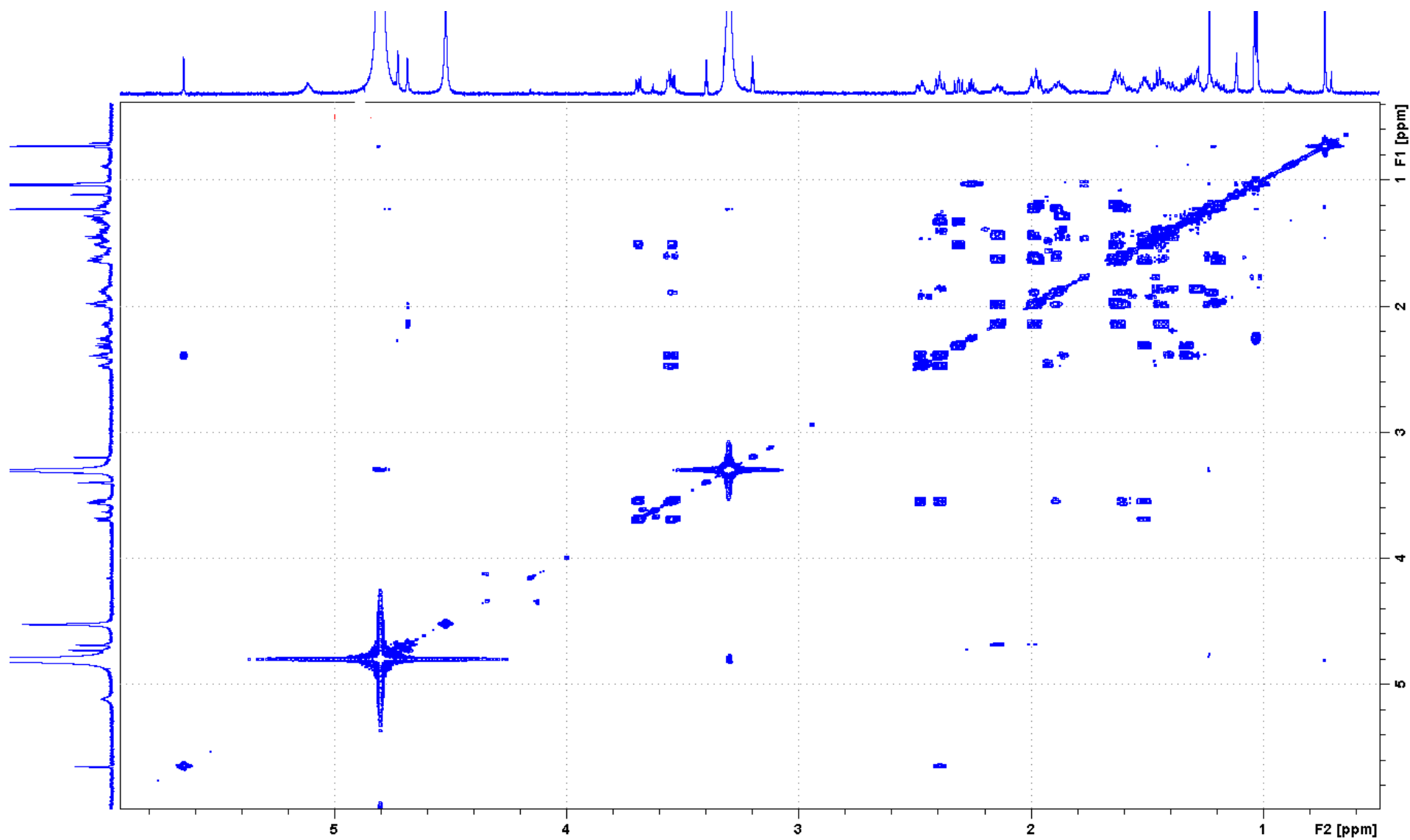
**Figure S18.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **2a**.



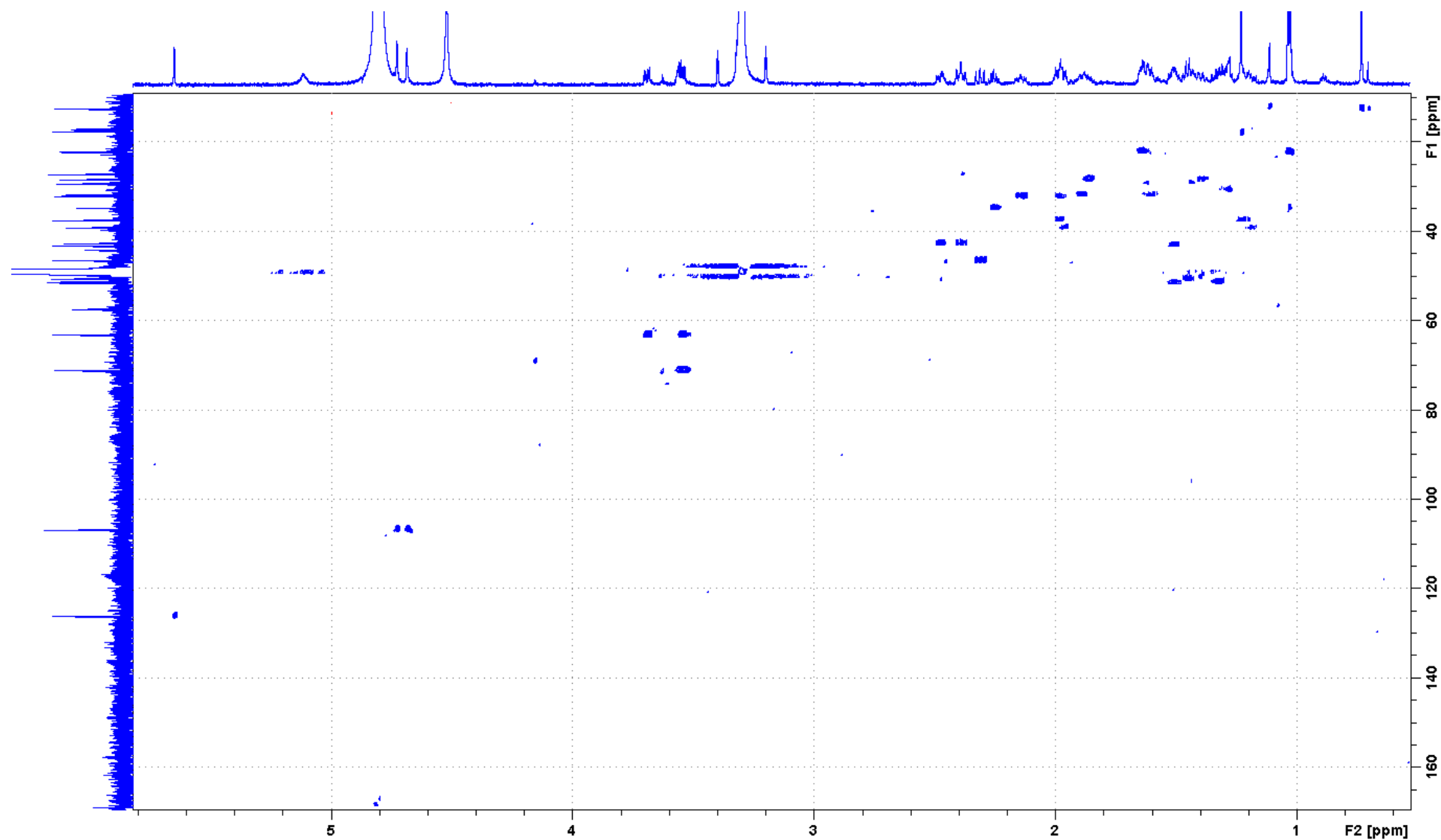
**Figure S19.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **2a**.



**Figure S20.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **2a**.

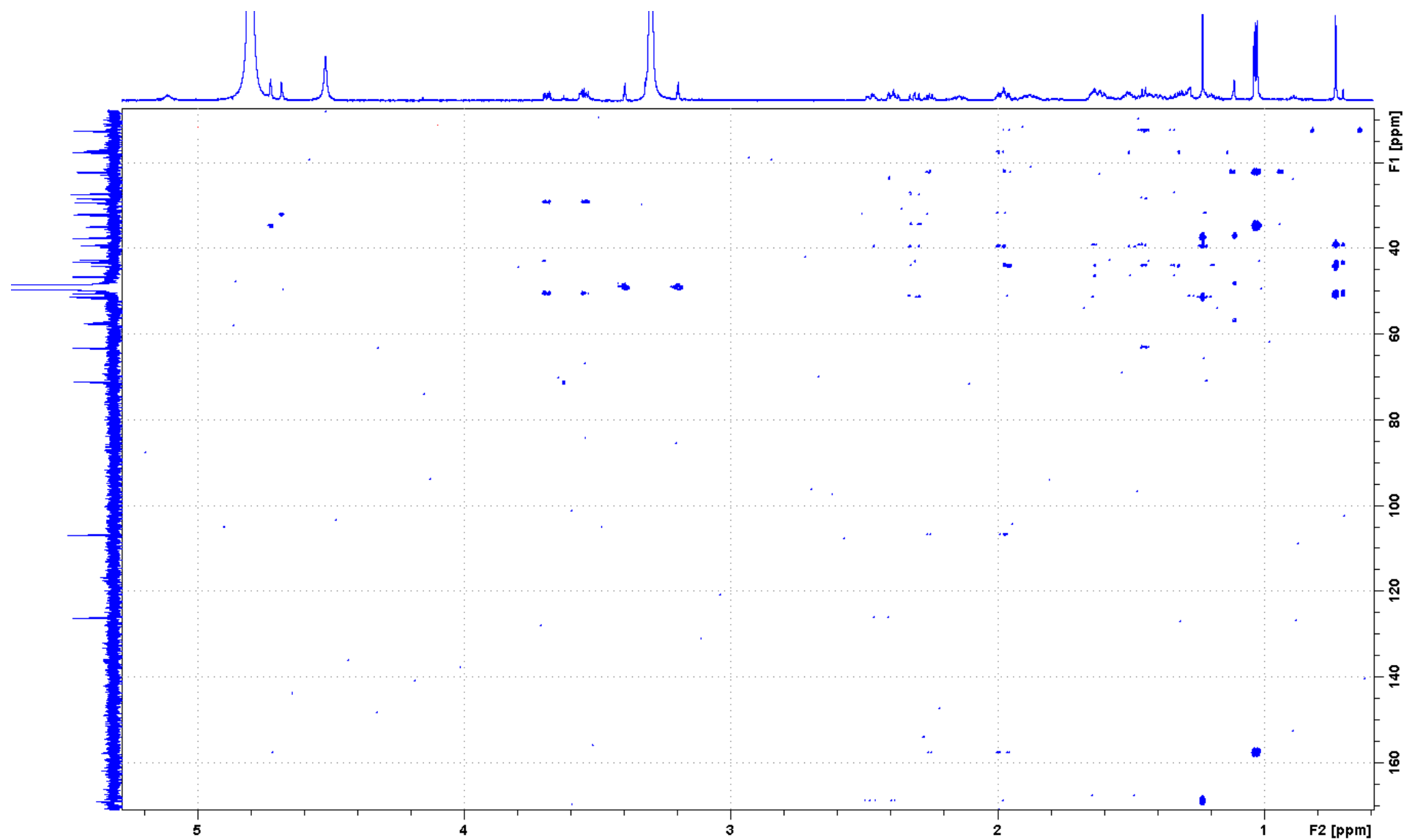


**Figure S21.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **2a**.

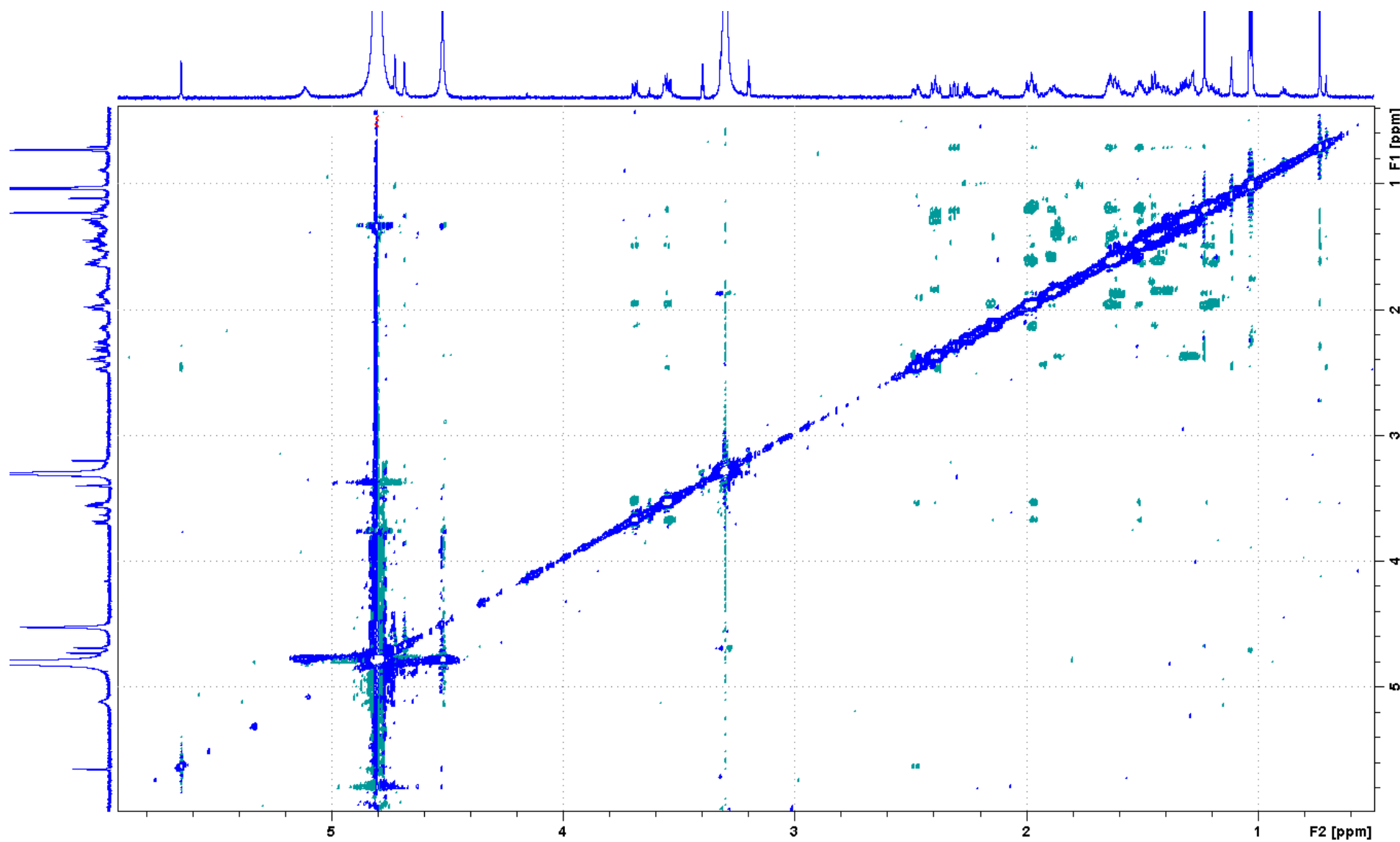




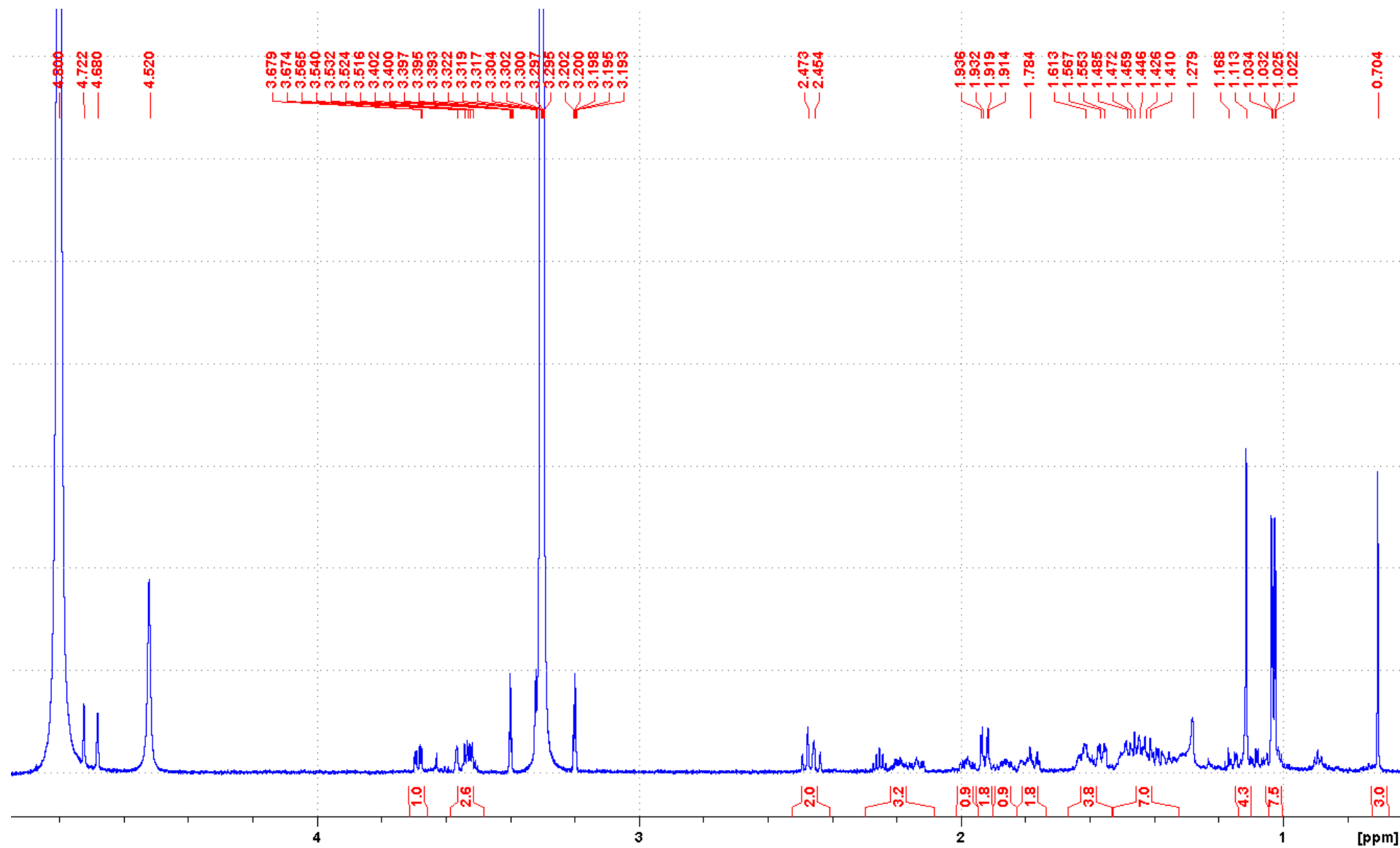
**Figure S22.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **2a**.



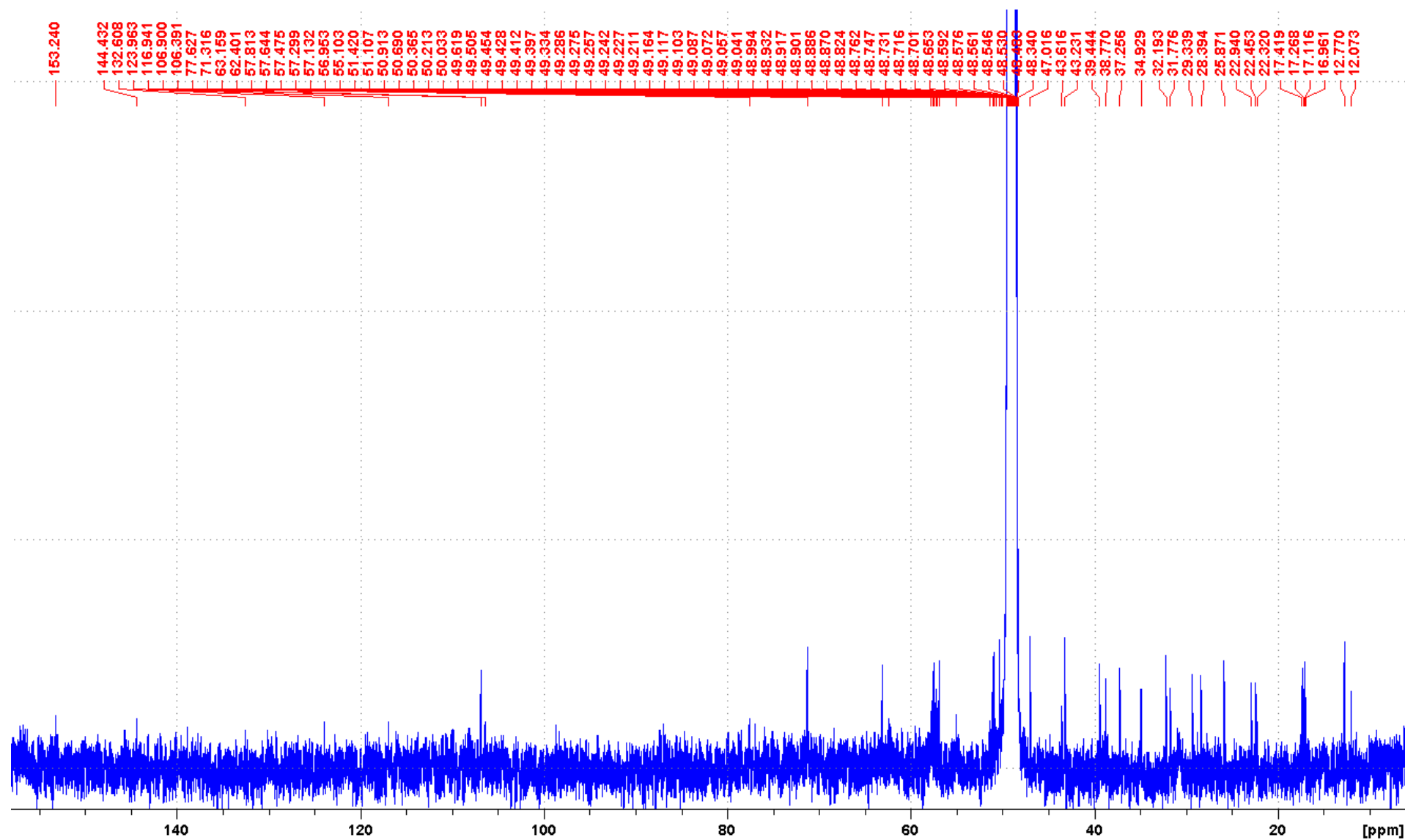
**Figure S23.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **2a**.



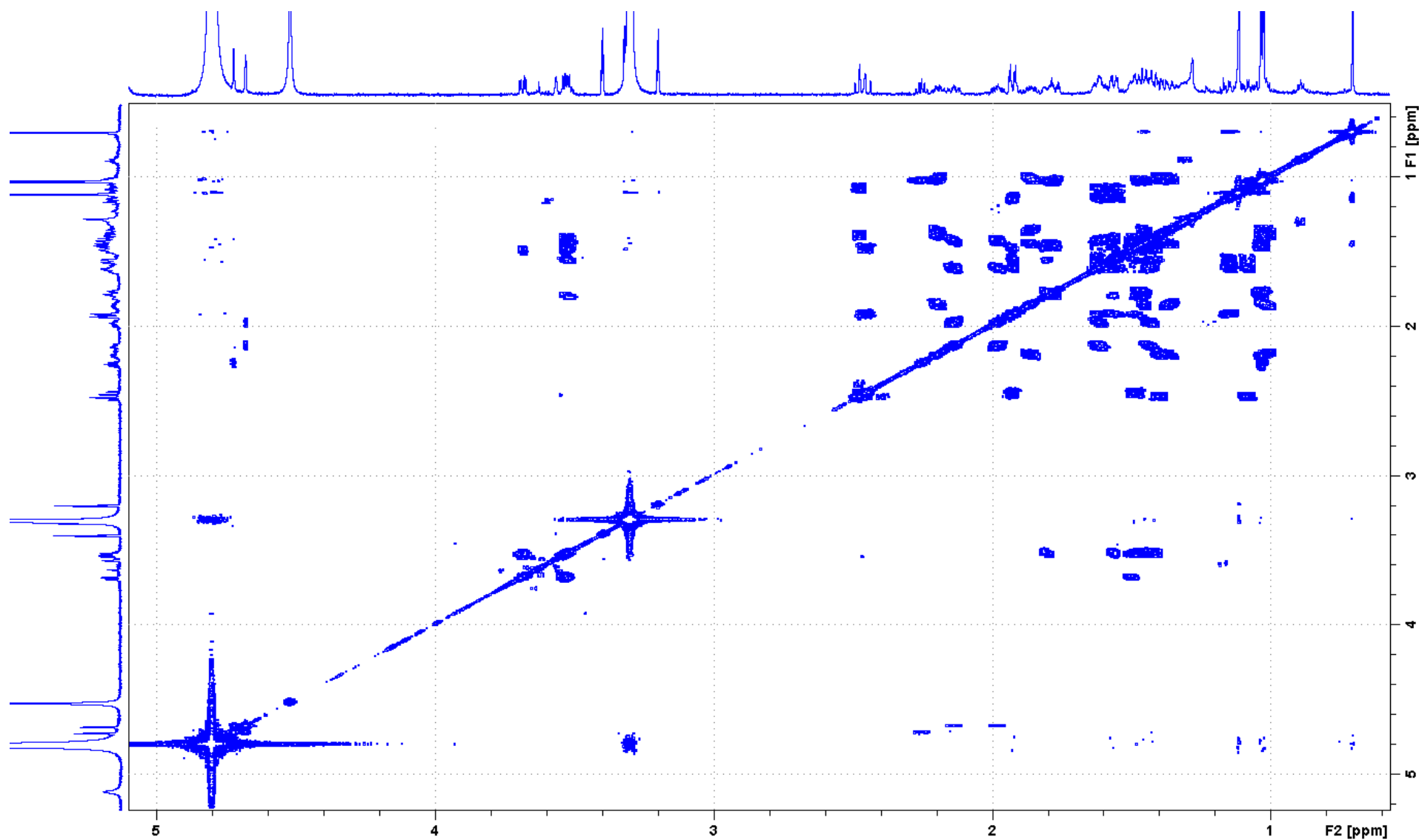
**Figure S24.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **3a**.



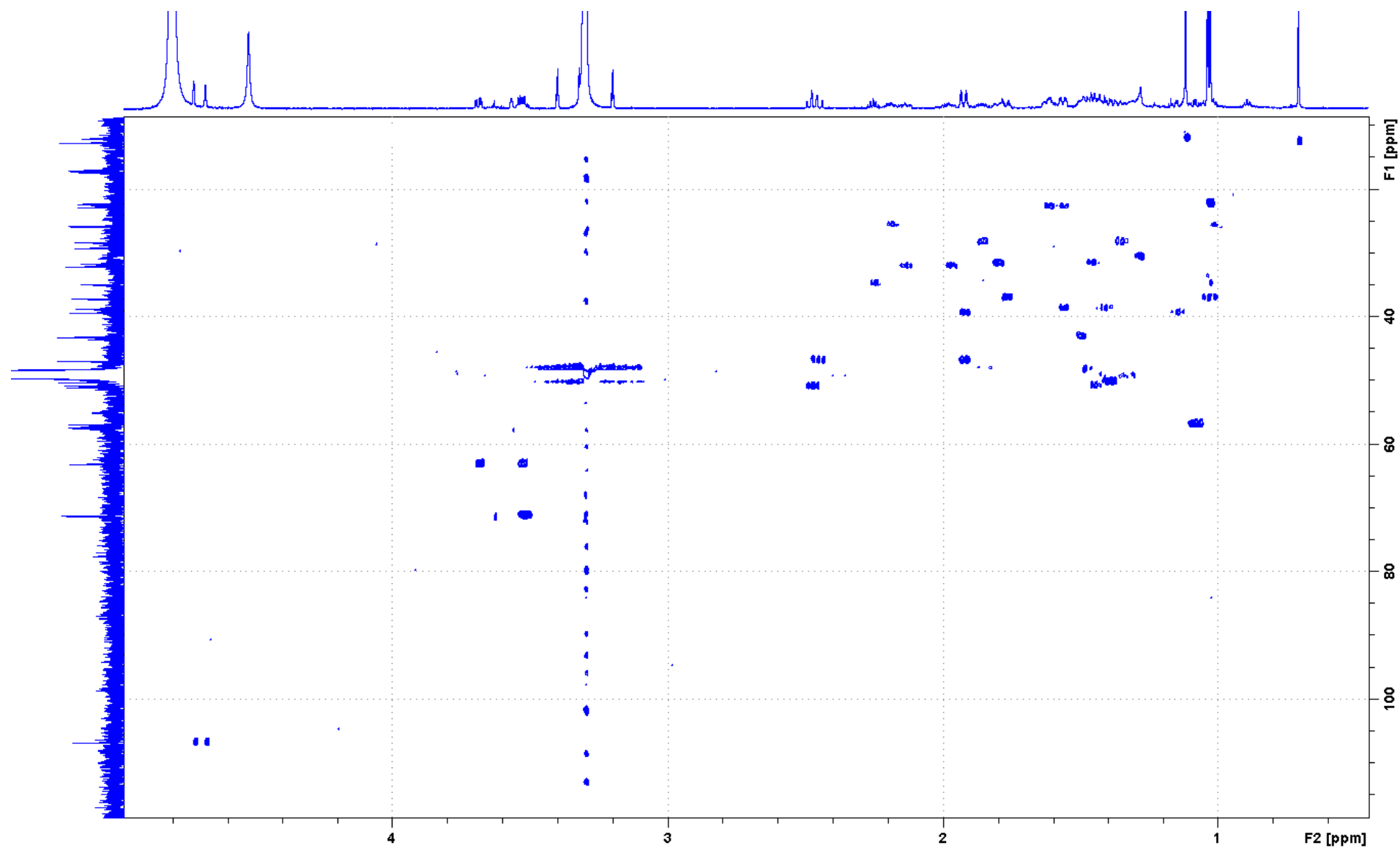
**Figure S25.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **3a**.



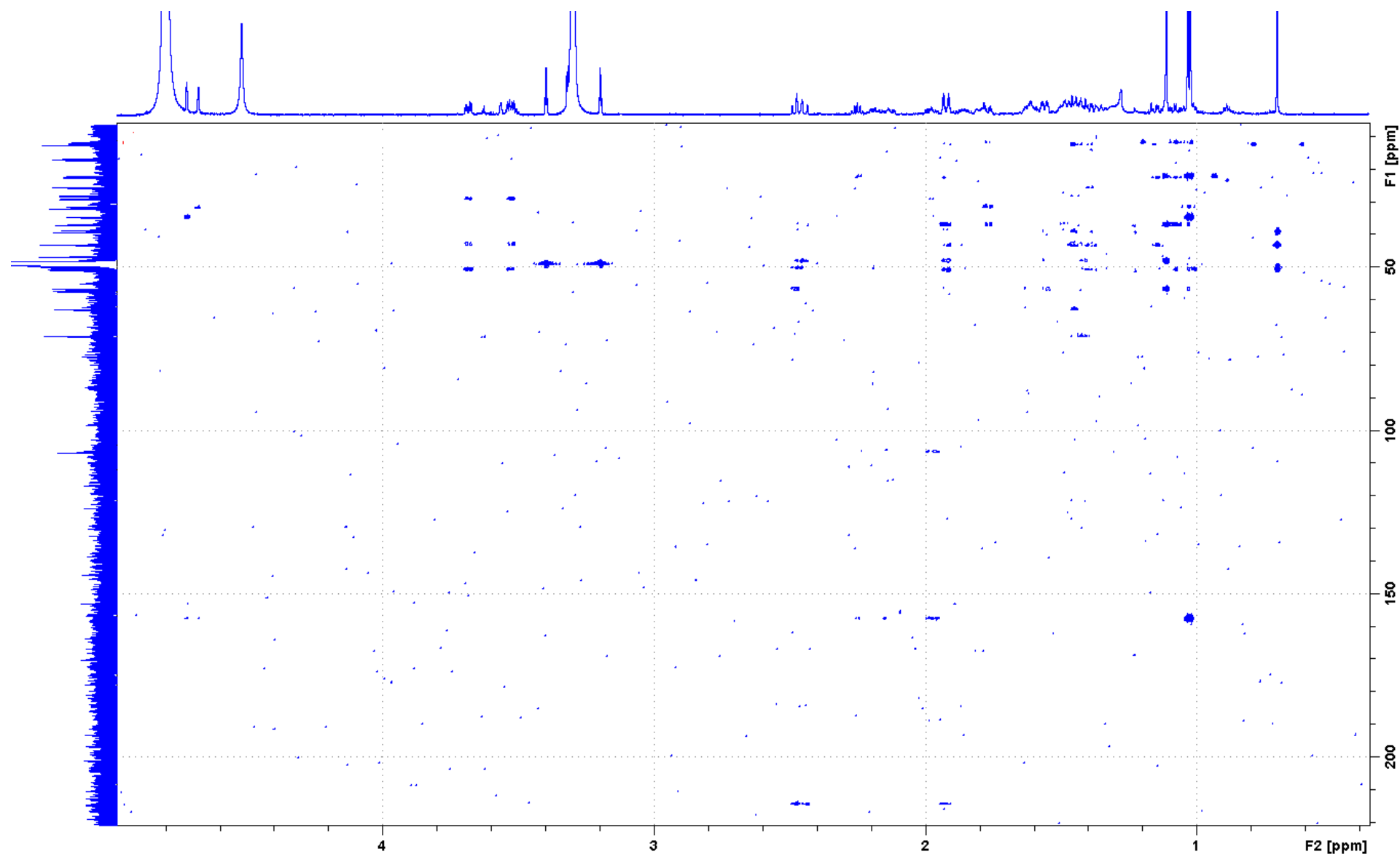
**Figure S26.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **3a**.



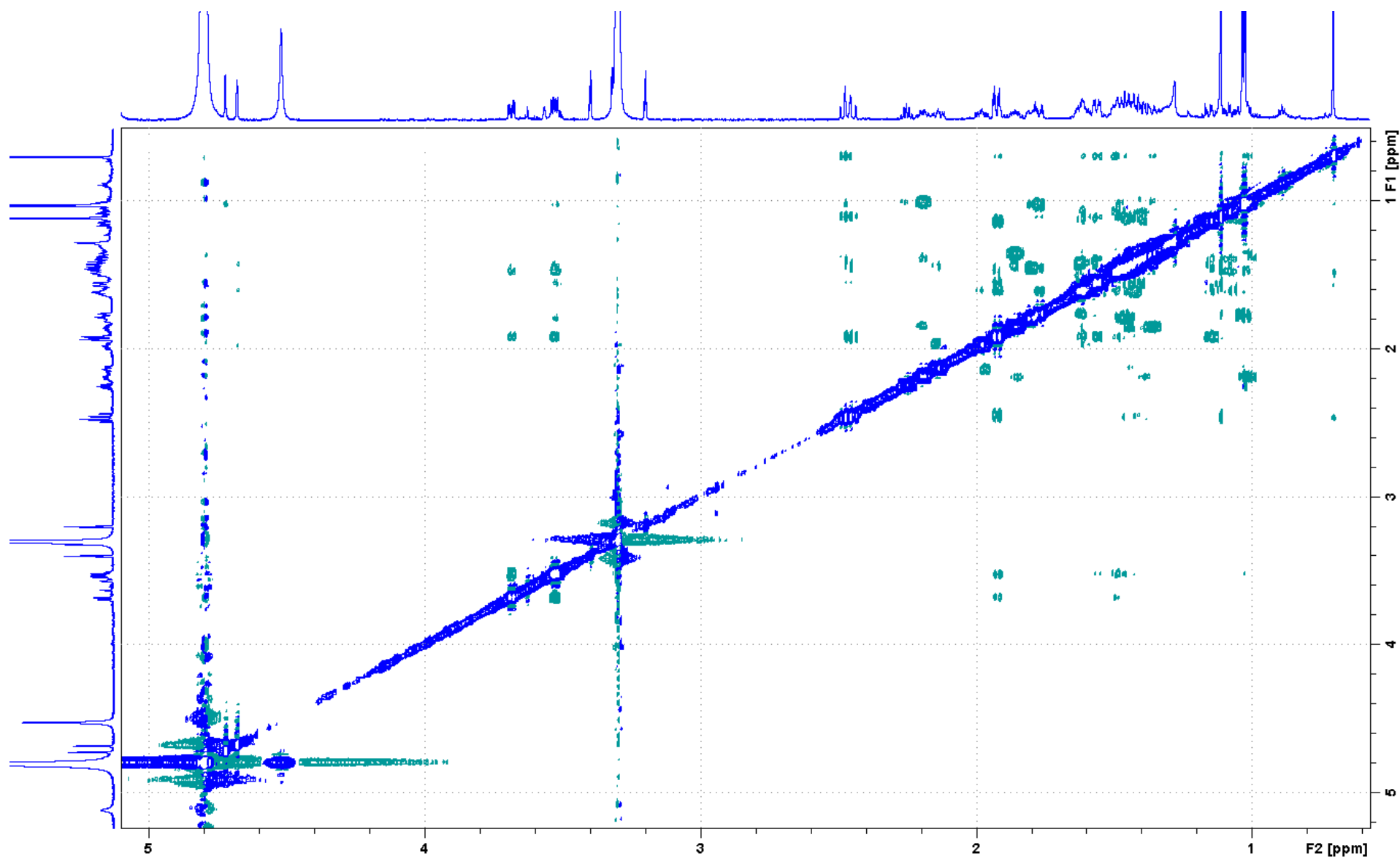
**Figure S27.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **3a**.



**Figure S28.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **3a**.



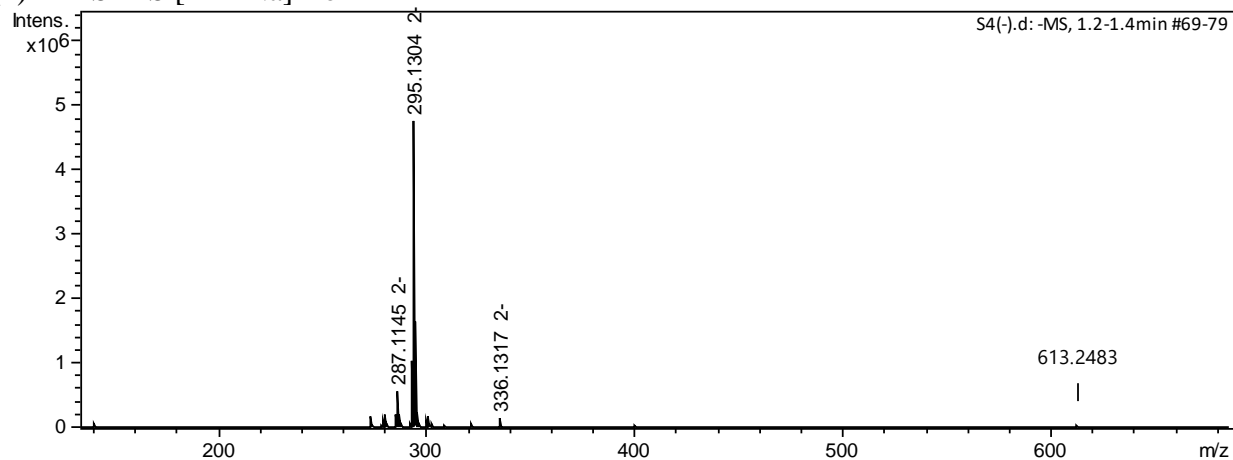
**Figure S29.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **3a**.



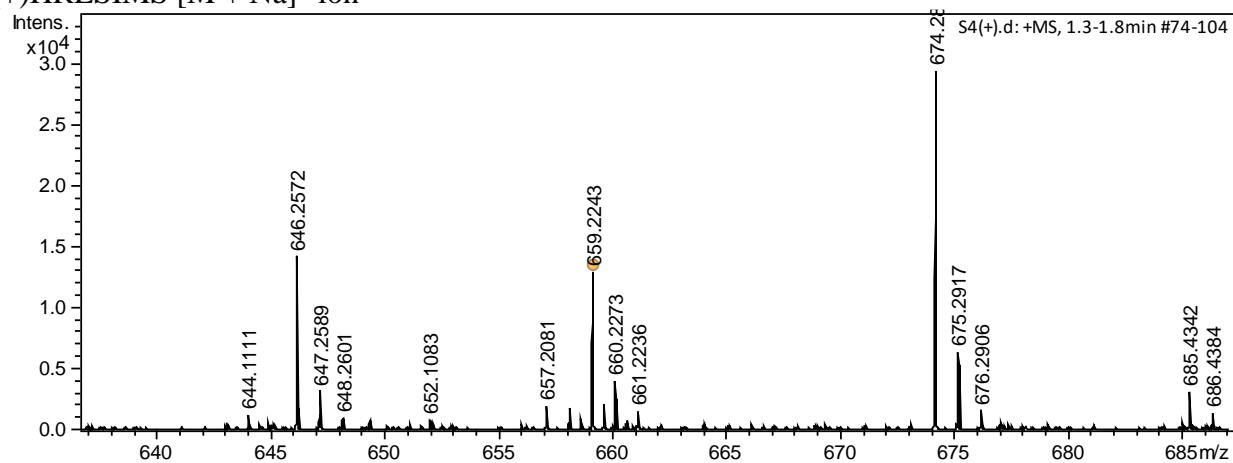


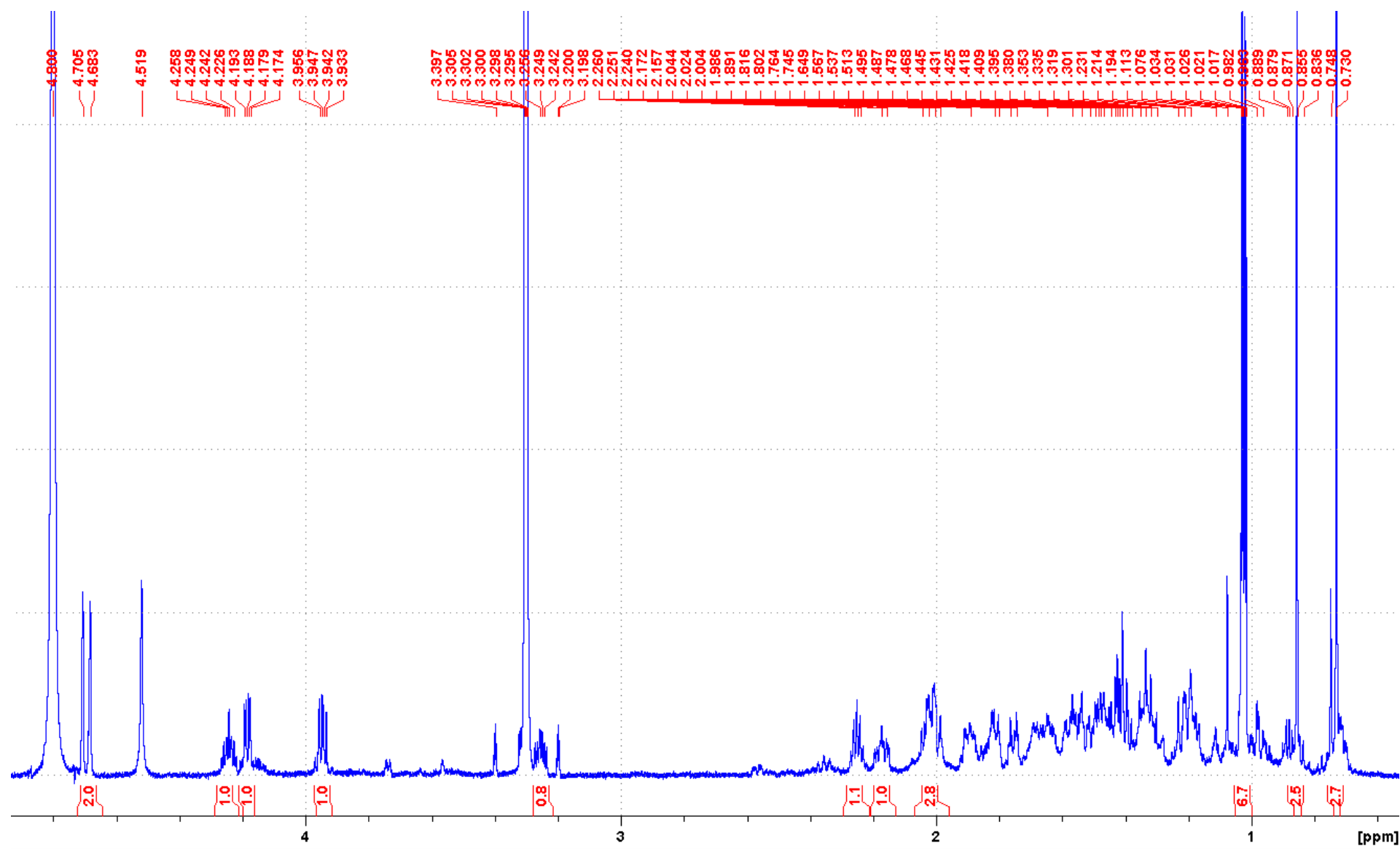
**Figure S30.** HRESIMS spectra of compound **4**

(-)HRESIMS  $[M - Na]^-$  ion

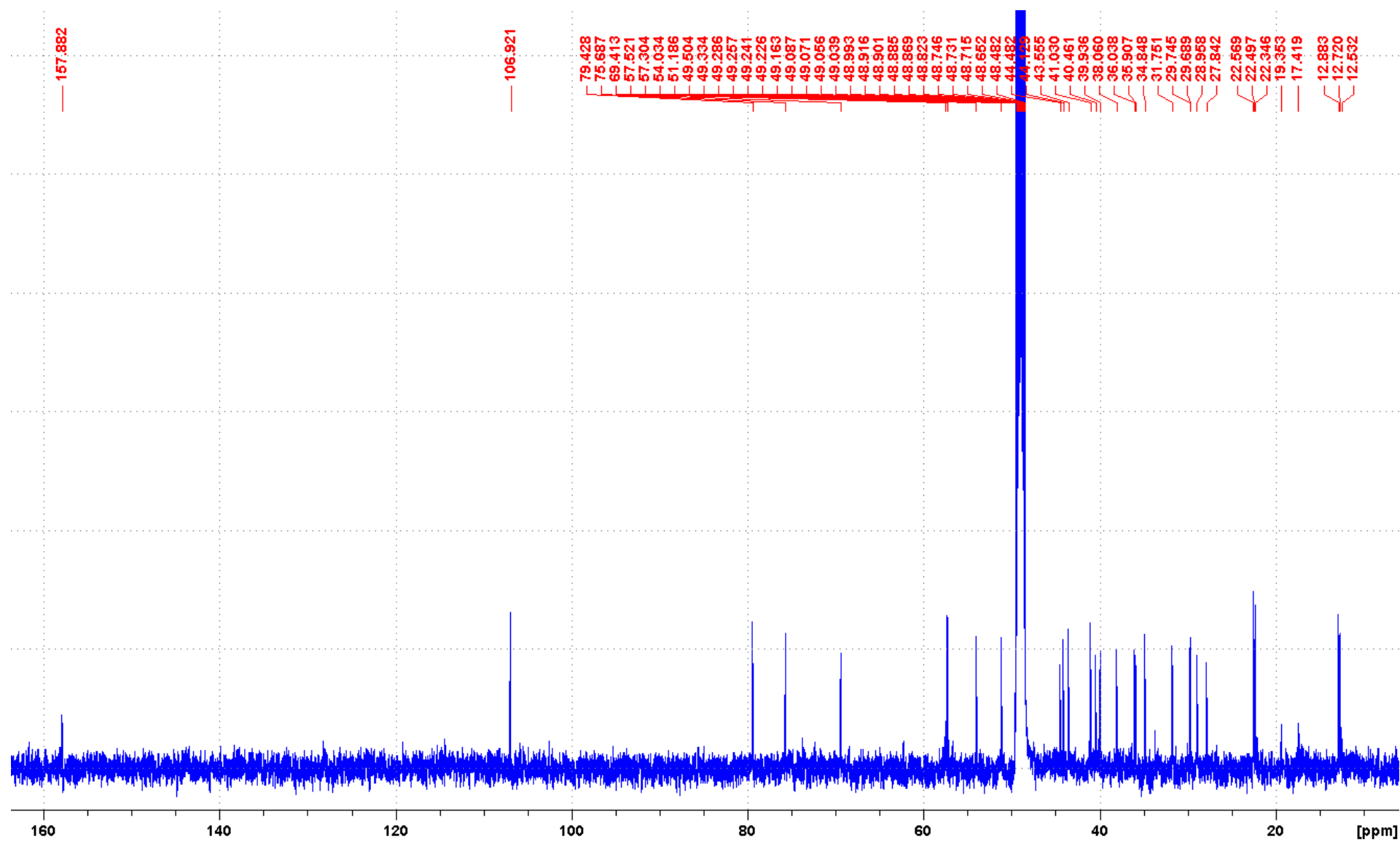


(+)HRESIMS  $[M + Na]^+$  ion

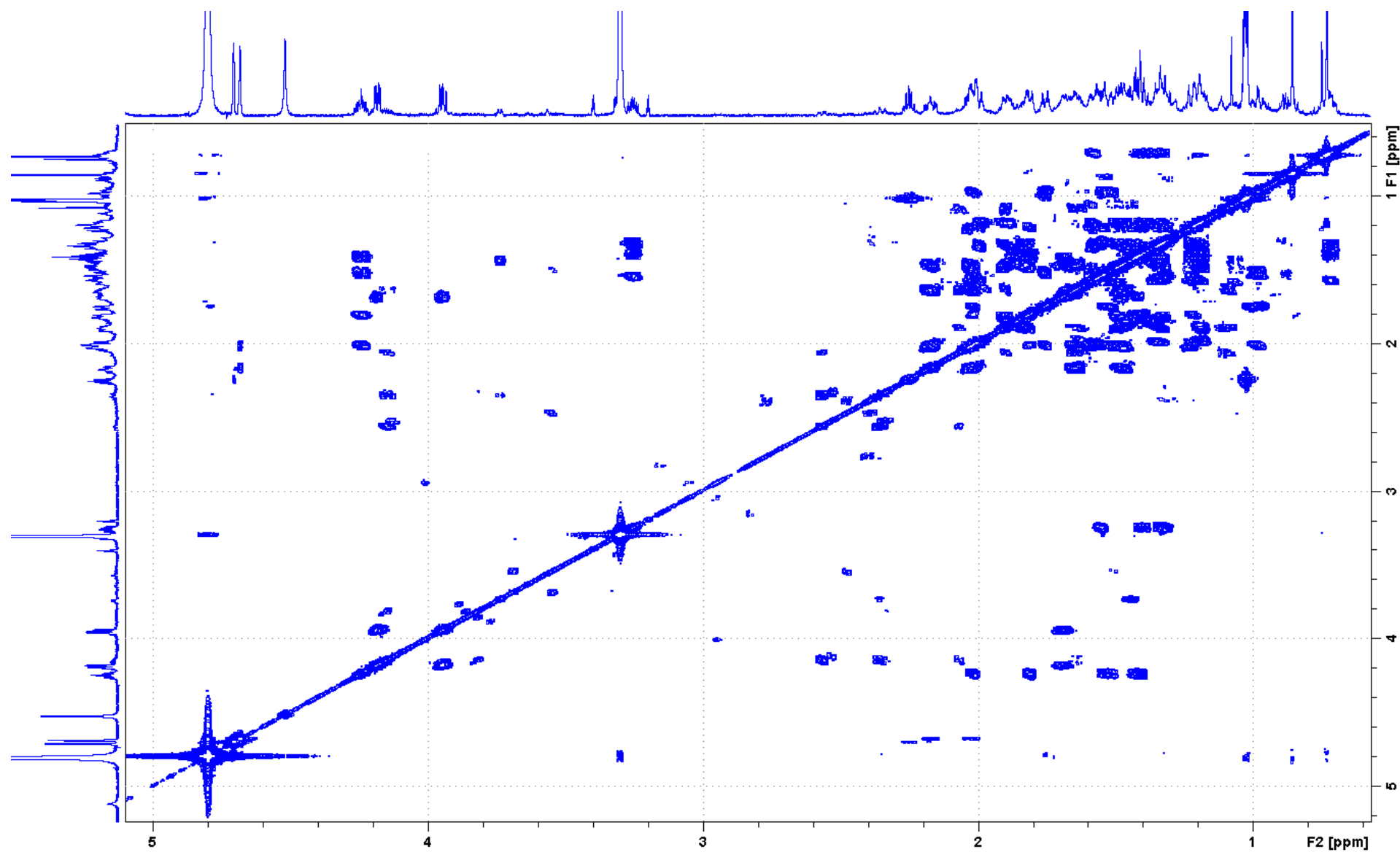


**Figure S31.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **4**

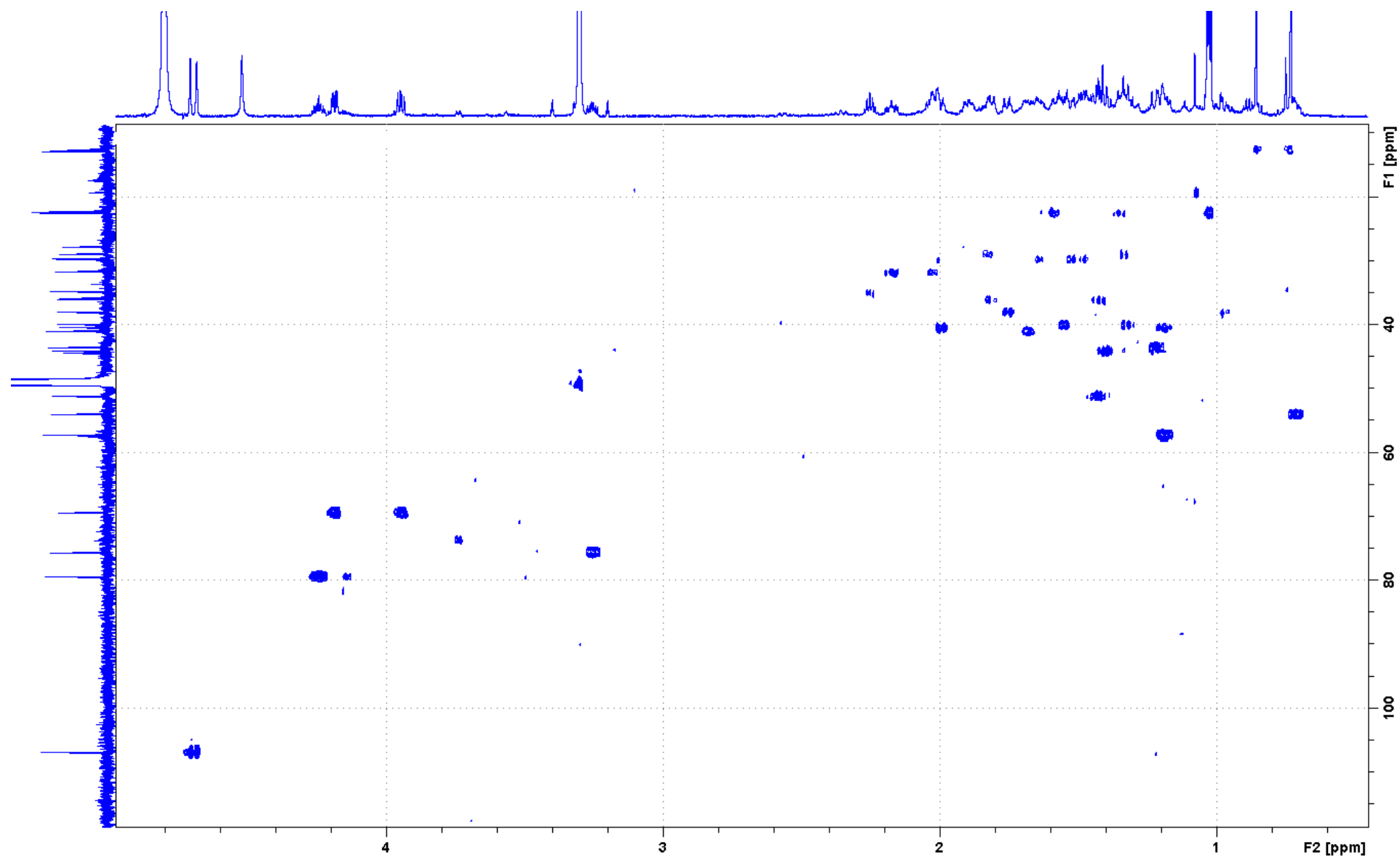
**Figure S32.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **4**



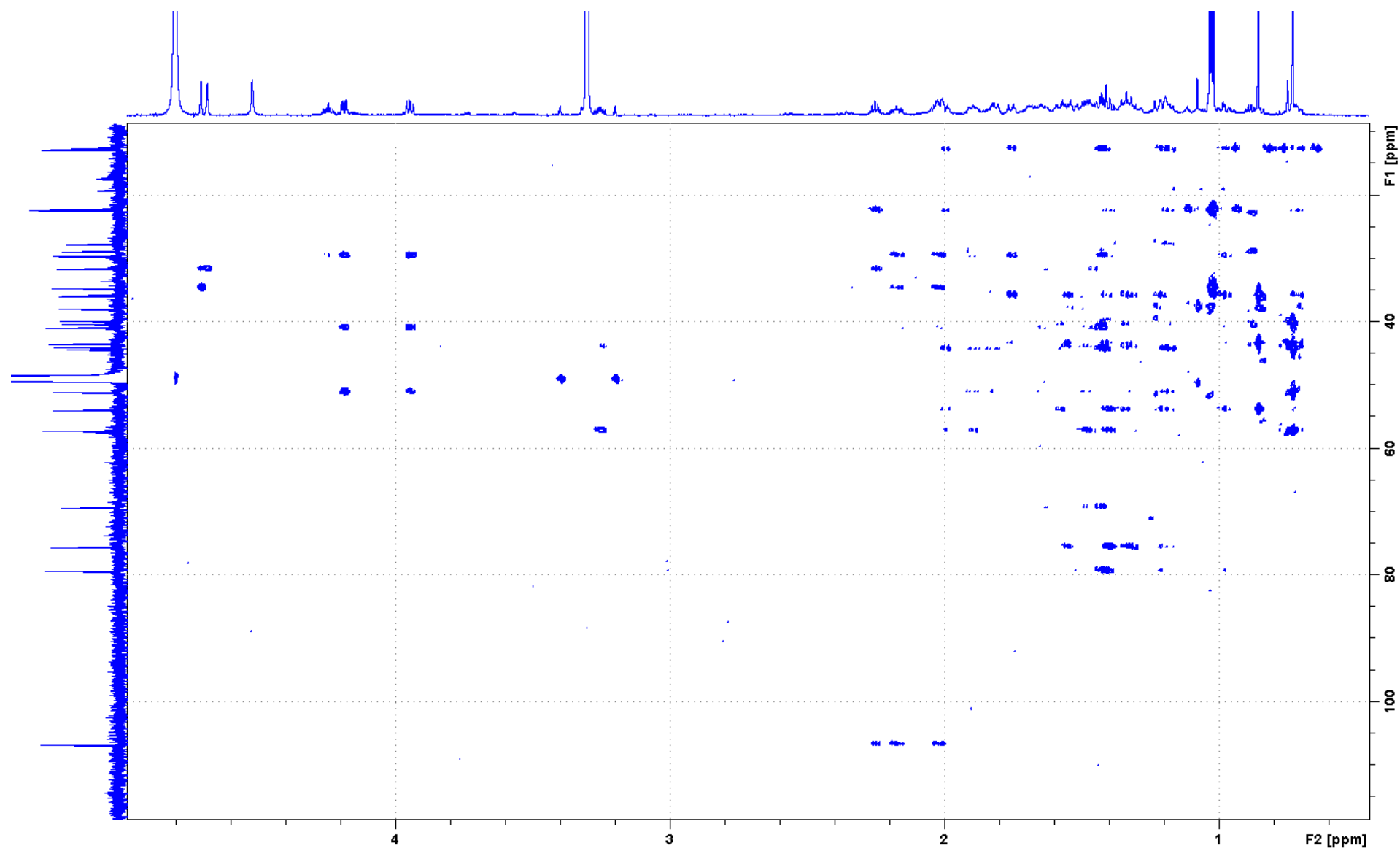
**Figure S33.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **4**



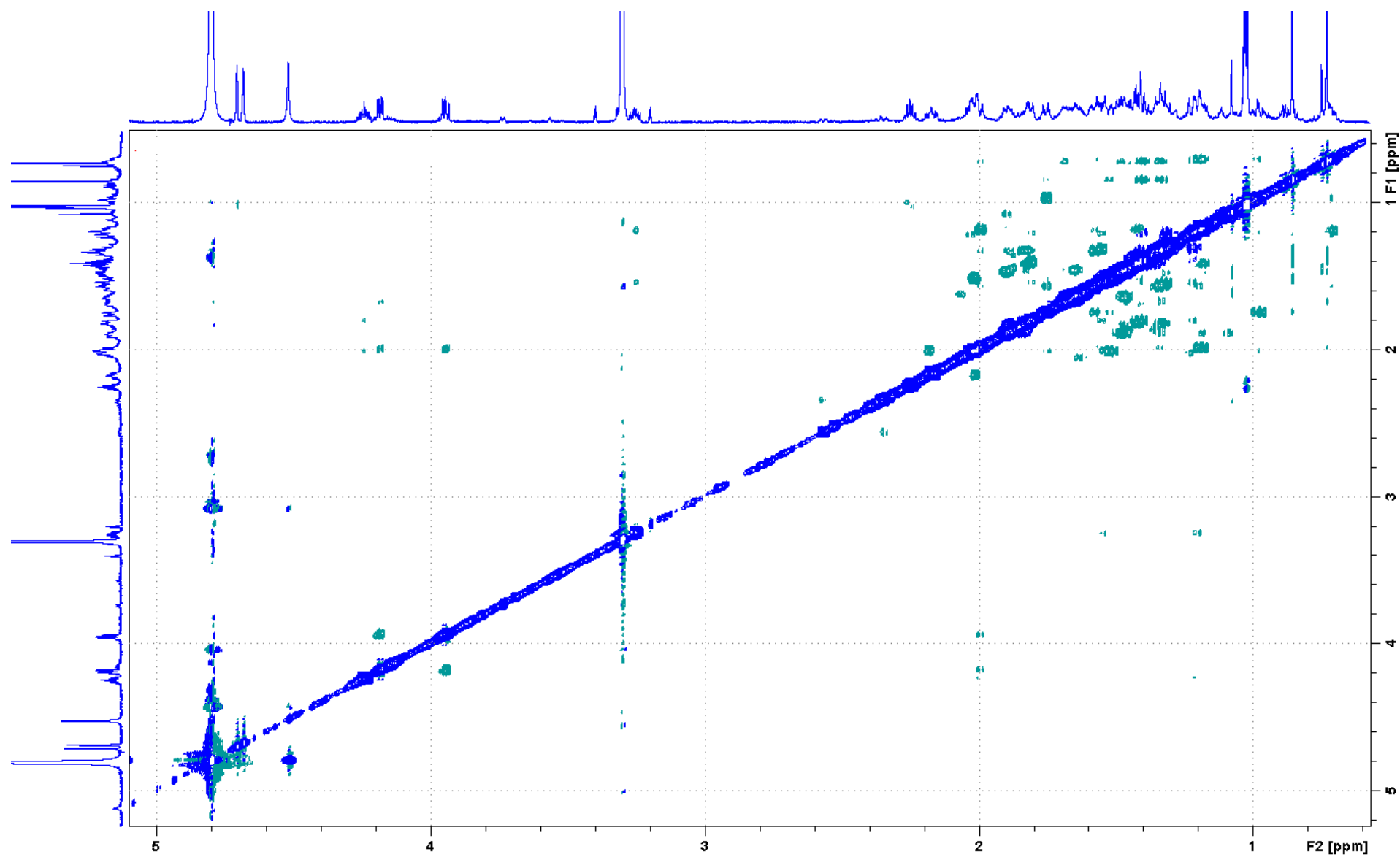
**Figure S34.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **4**

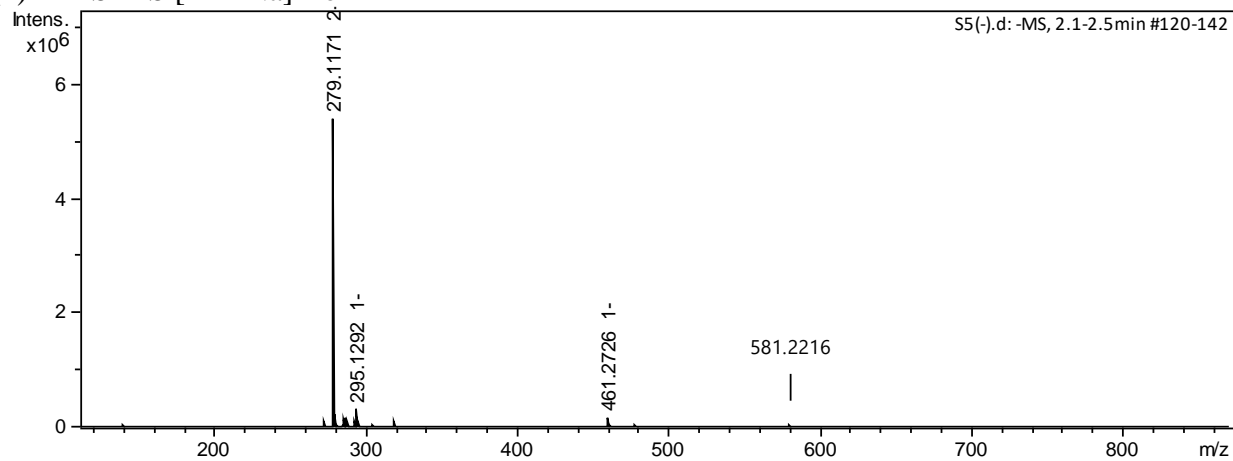
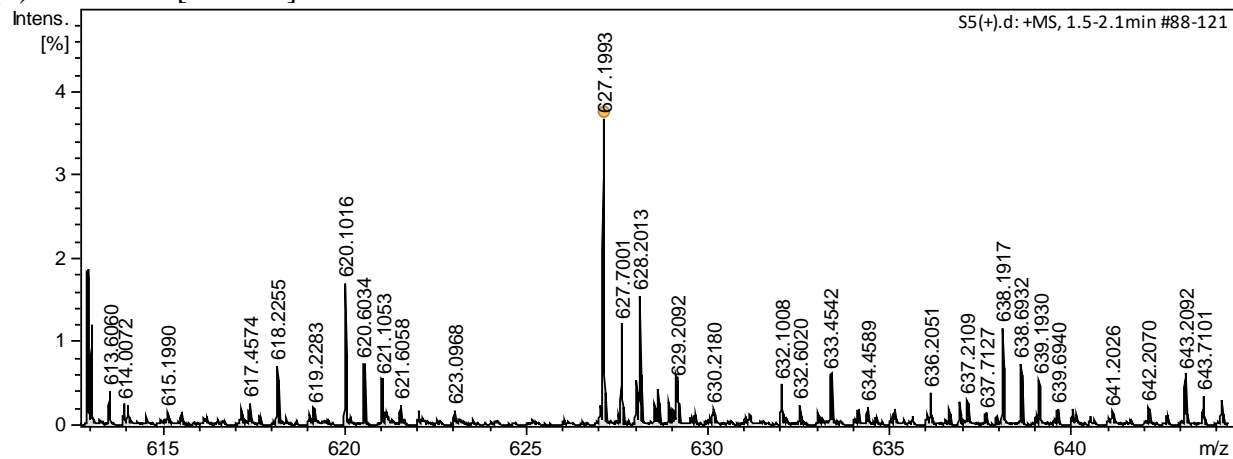


**Figure S35.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **4**



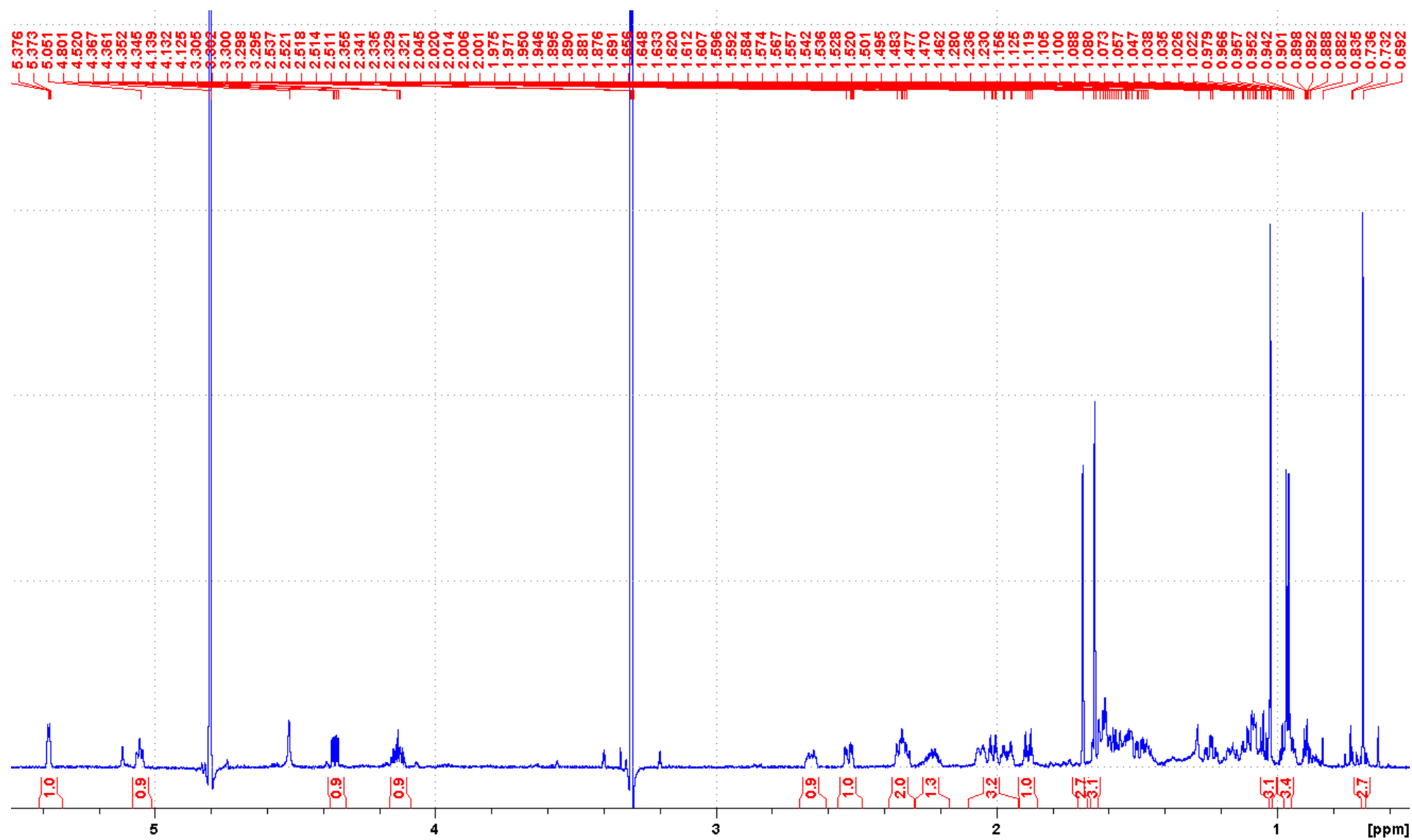
**Figure S36.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **4**



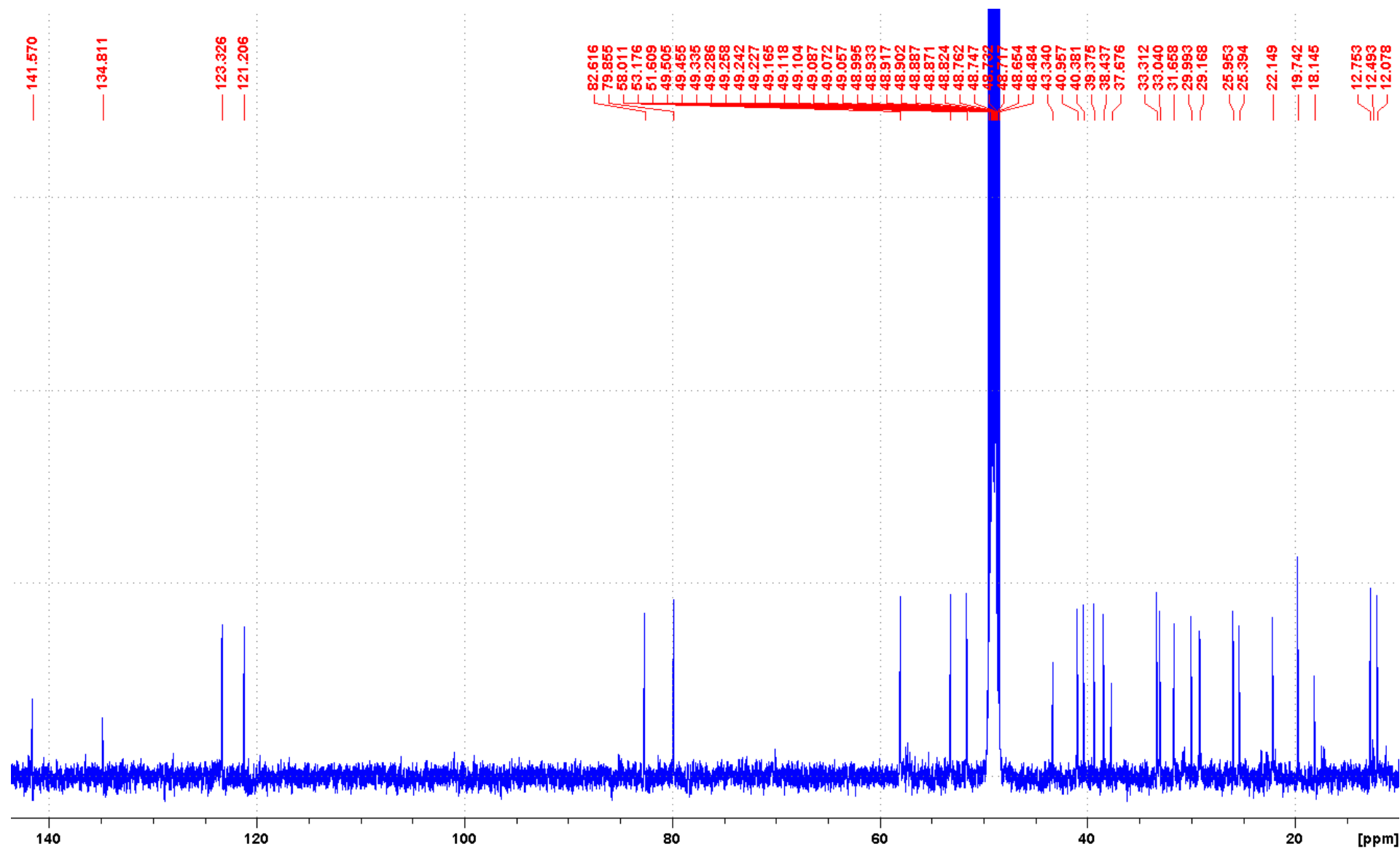
**Figure S37.** HRESIMS spectra of compound **5****(-)HRESIMS**  $[M - Na]^-$  ion**(+)HRESIMS**  $[M + Na]^+$  ion



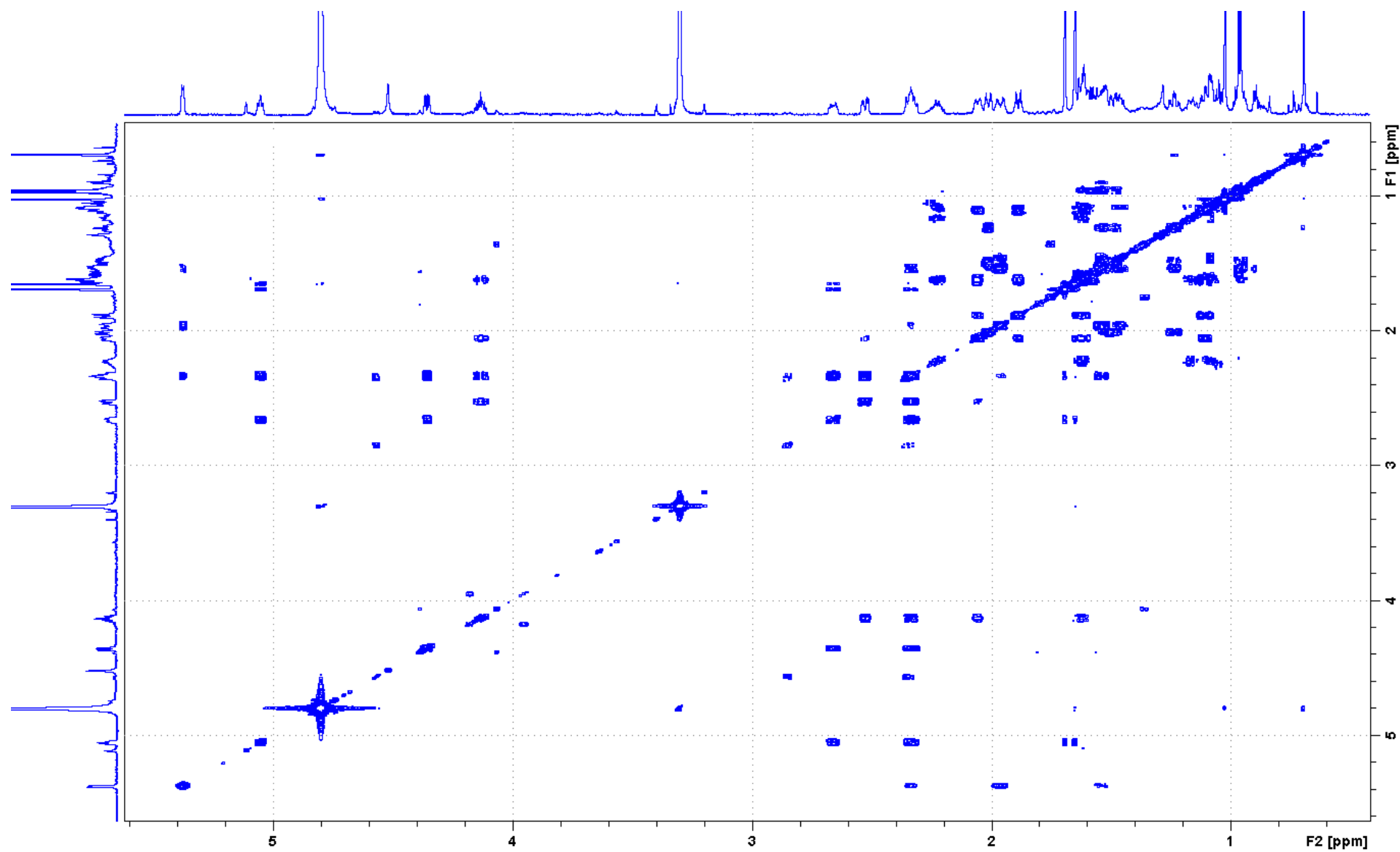
**Figure S38.**  $^1\text{H}$  NMR (700.13 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **5**



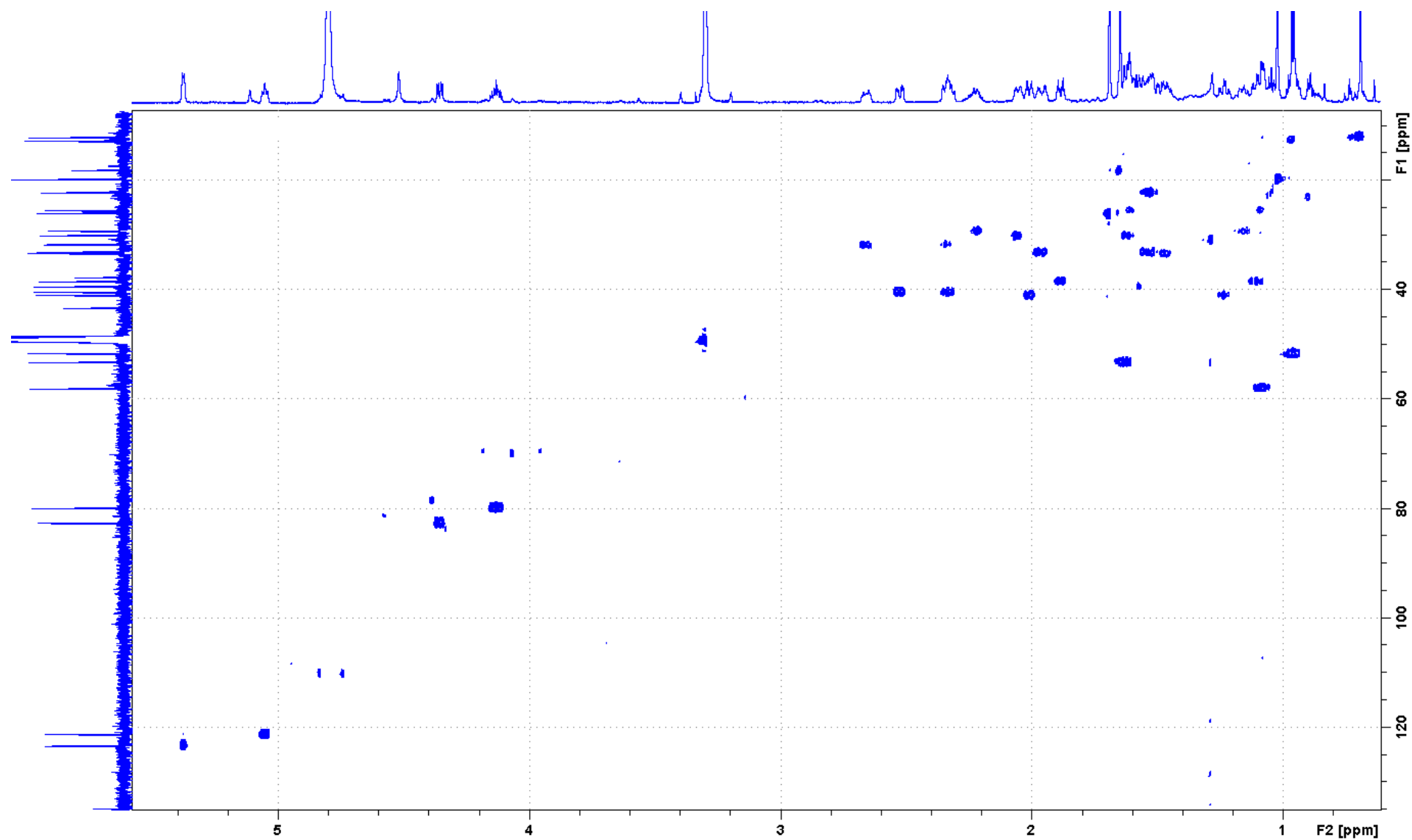
**Figure S39.**  $^{13}\text{C}$  NMR (176.04 MHz,  $\text{CD}_3\text{OD}$ ) spectrum of compound **5**



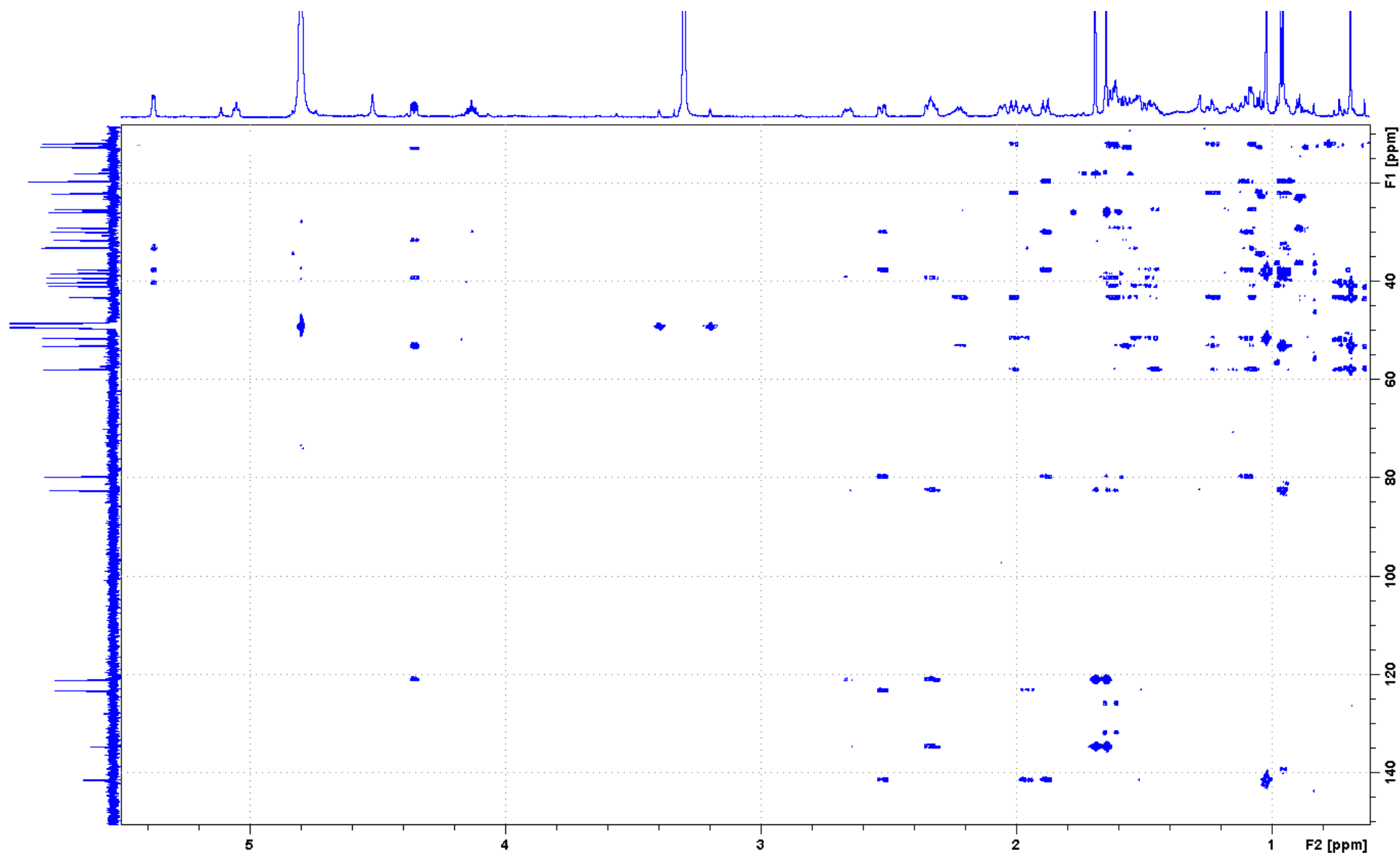
**Figure S40.** COSY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **5**



**Figure S41.** HSQC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **5**



**Figure S42.** HMBC (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **5**



**Figure S43.** ROESY (700.13 MHz, CD<sub>3</sub>OD) spectrum of compound **5**

