Supplementary Materials

First Identification of 12β-Deoxygonyautoxin 5 (12α-Gonyautoxinol) in the Cyanobacterium *Dolichospermum Circinale* (TA04), and 12β-Deoxysaxitoxin (12α- Saxitoxinol) in *D. Circinale* (TA04) and the Dinoflagellate *Alexandrium pacificum* (Group IV) (120518kureac)

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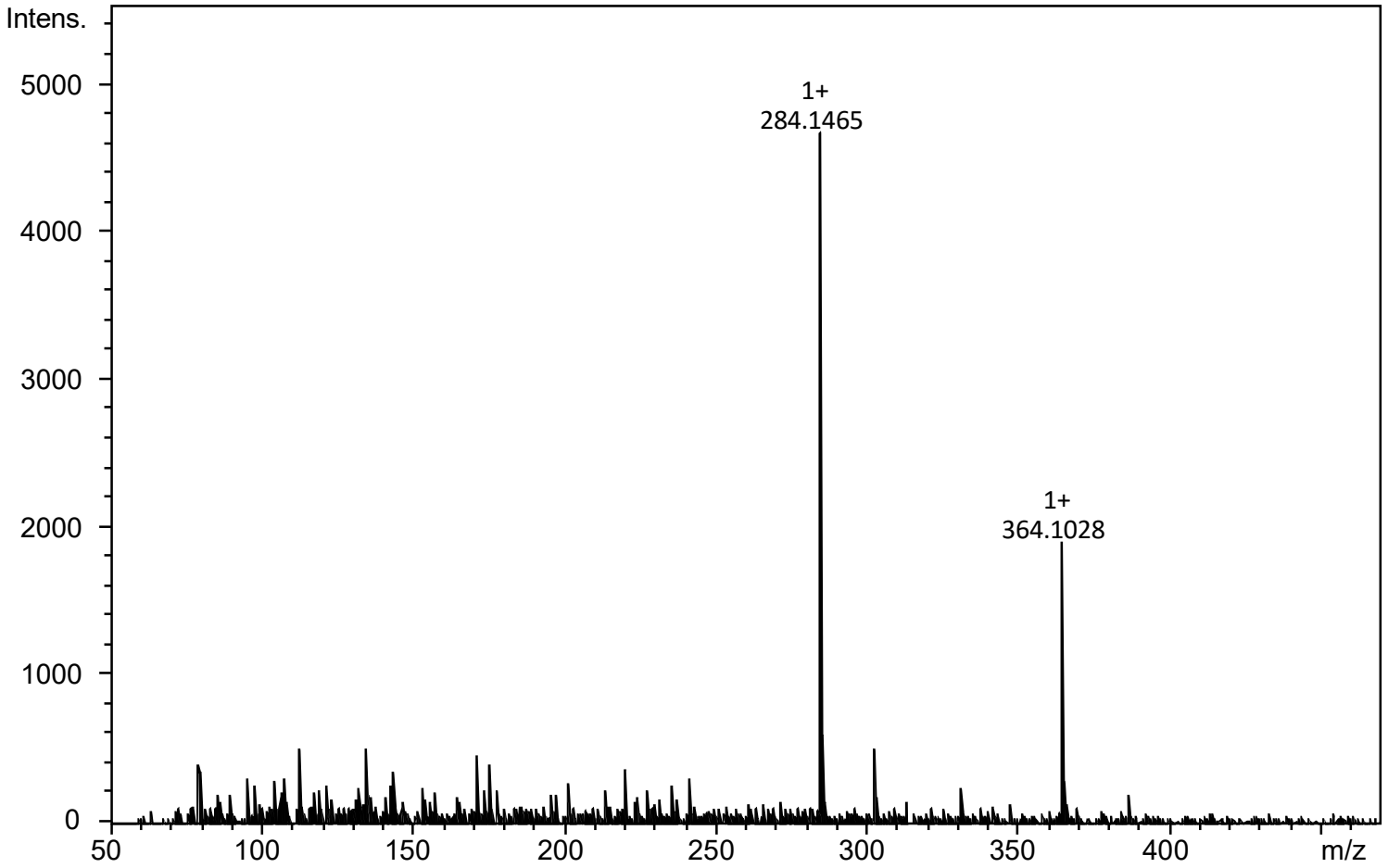

Figure S1. The ESI-HRMS spectrum of synthetic 12β-deoxyGTX5 (**2**).

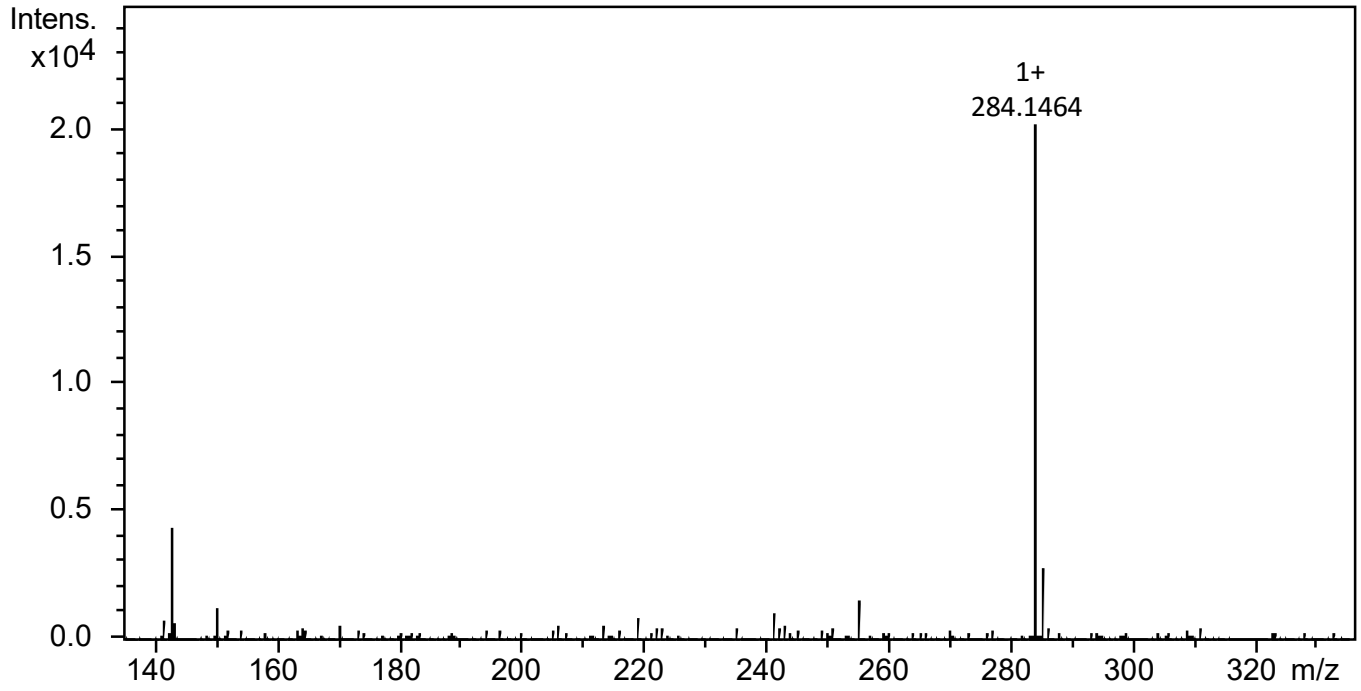

Figure S2. The ESI-HRMS spectrum of synthetic 12β-deoxySTX (**3**).

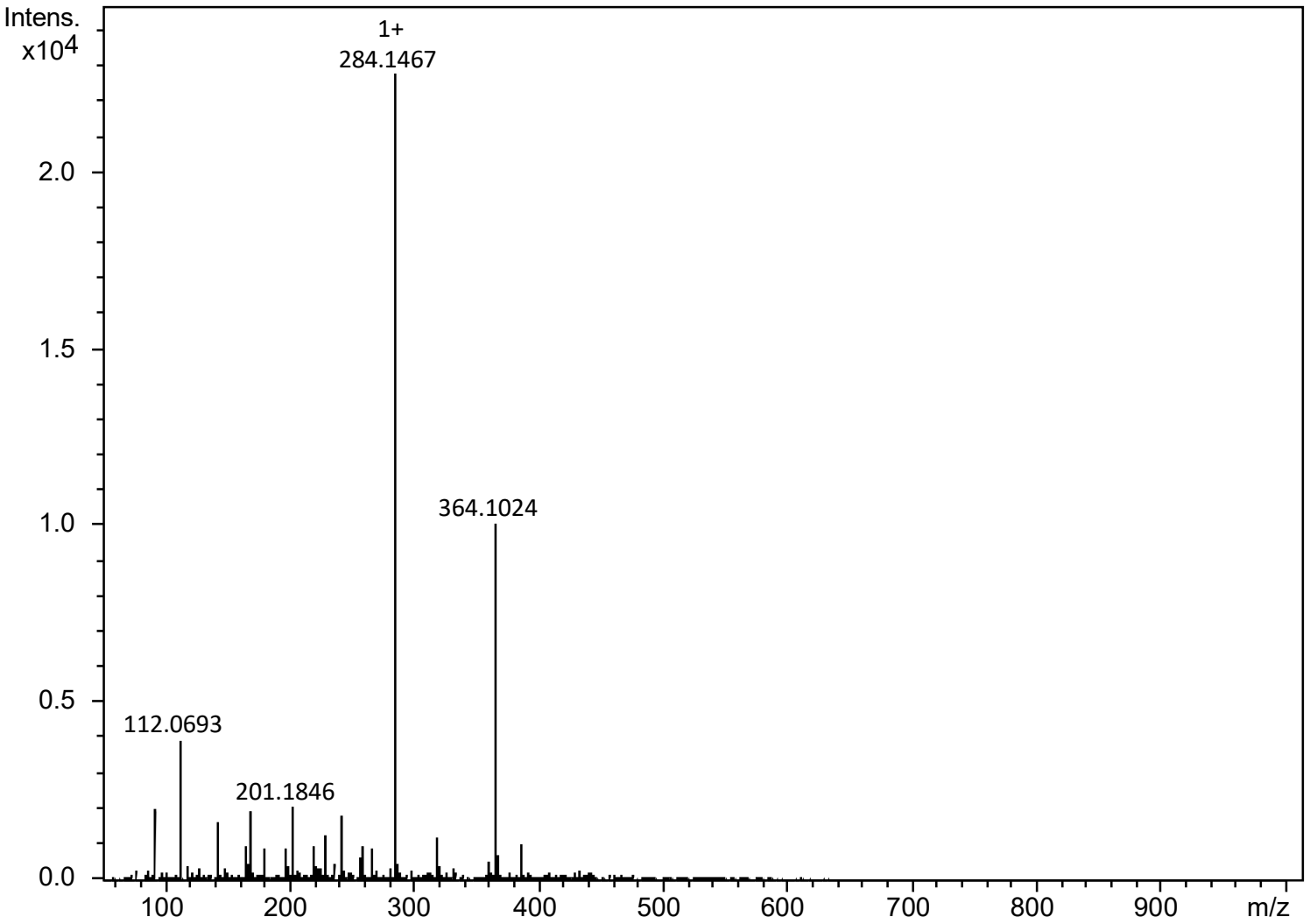

Figure S3. The ESI-HRMS spectrum of synthetic 12α-deoxyGTX5 (**5**).

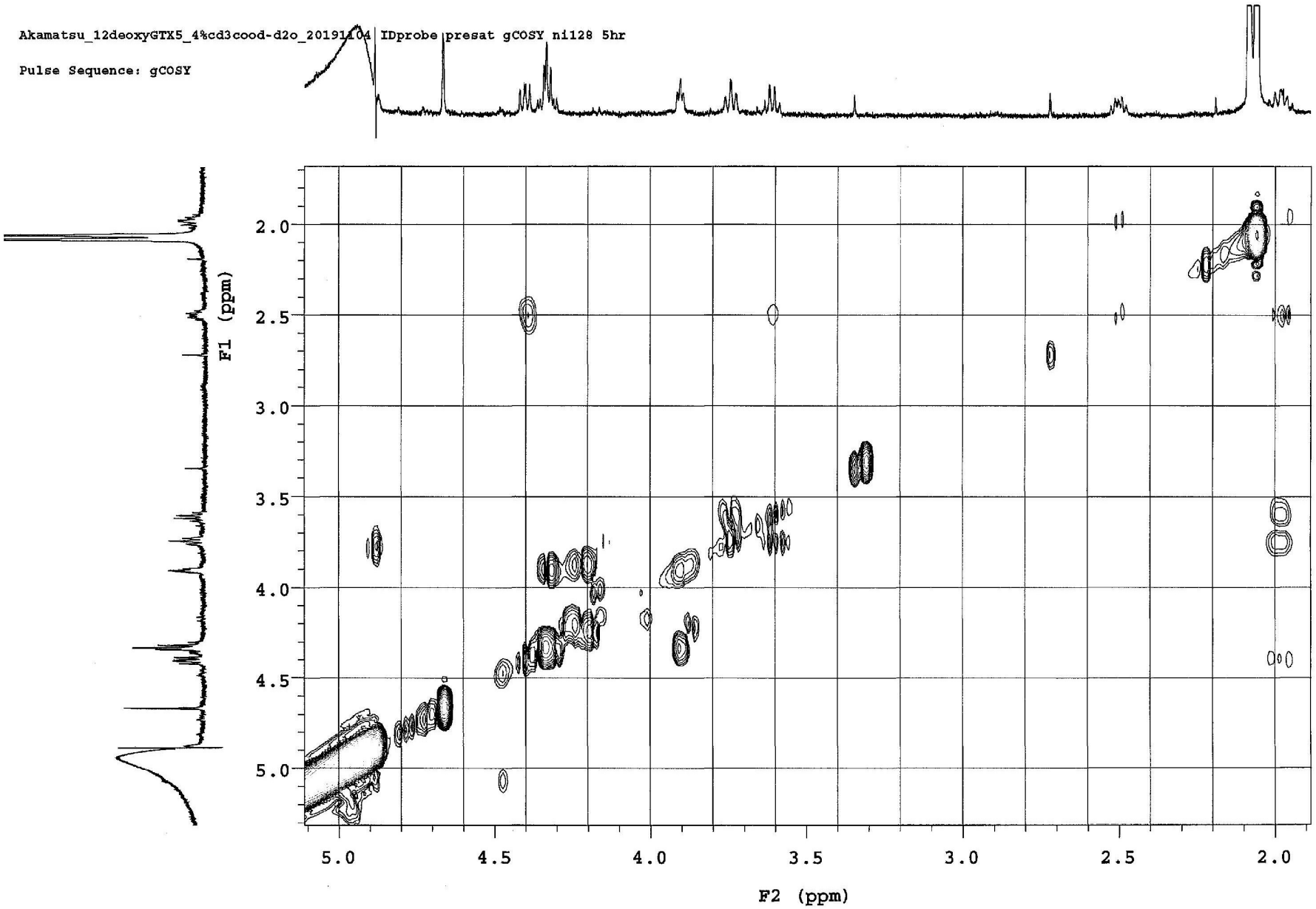

Figure S4. The COSY spectrum of synthetic 12β-deoxyGTX5 (**2**). (600 MHz, CD_3COOD-D_2O (4 : 96, v/v)).

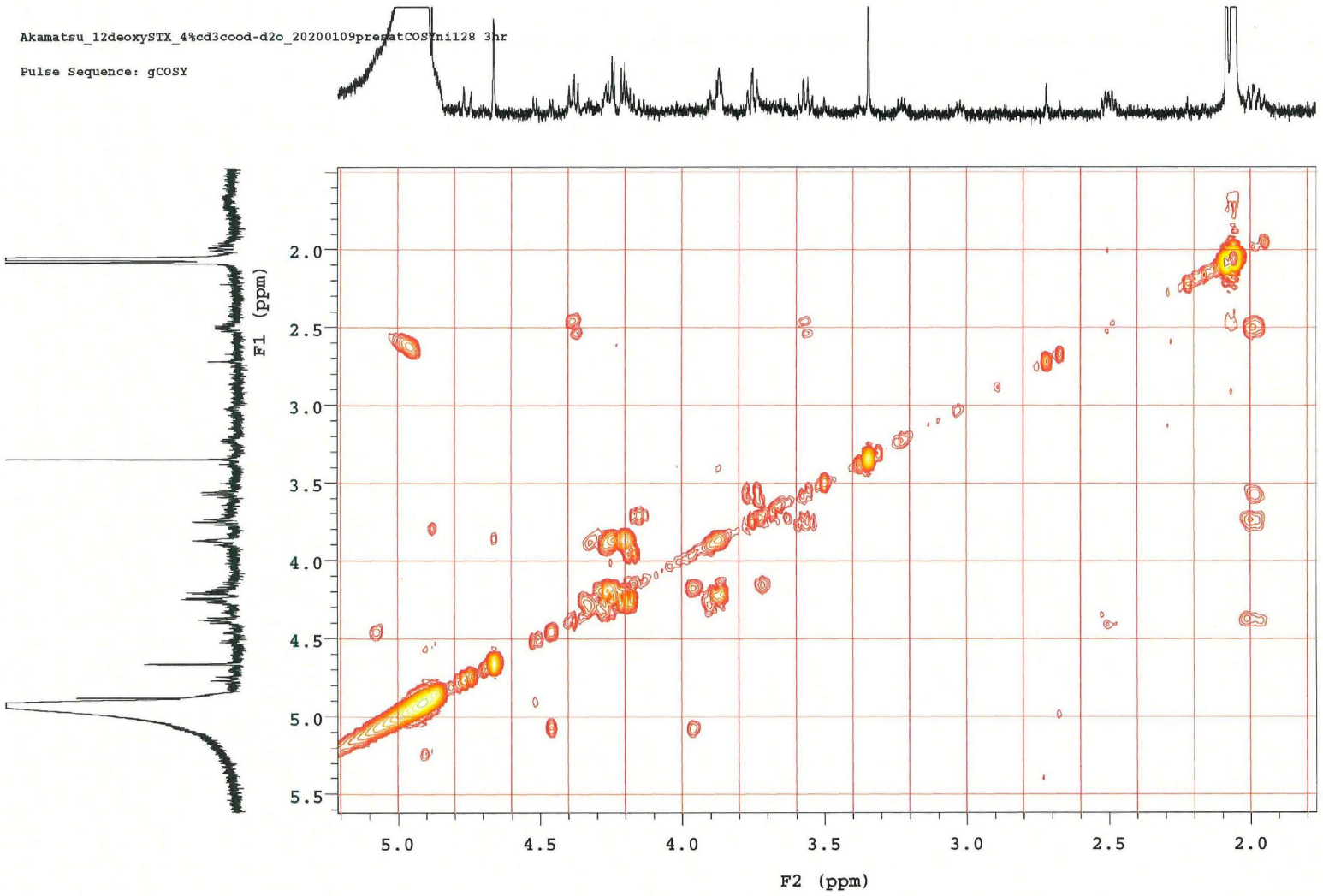

Figure S5. The COSY spectrum of synthetic 12β-deoxySTX (**3**). (600 MHz, CD_3COOD-D_2O (4 : 96, v/v)).

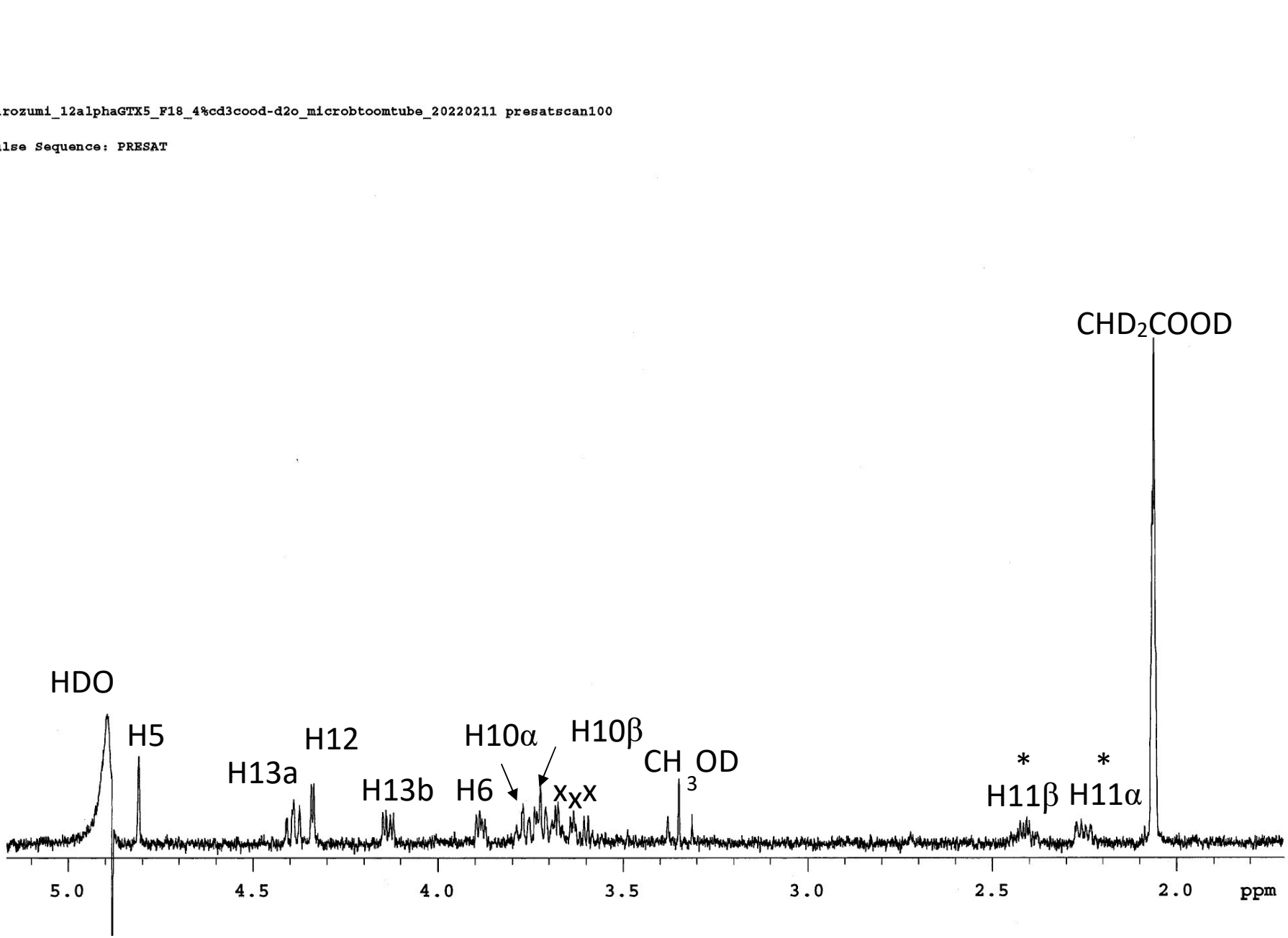

Figure S6. The ^{1}H NMR spectrum of synthetic 12α-deoxyGTX5 (**5**).
(600 MHz, microbottom tube, CD_3COOD-D_2O (4 : 96, v/v). HDO was presaturated.).
* interchangeable assignment.

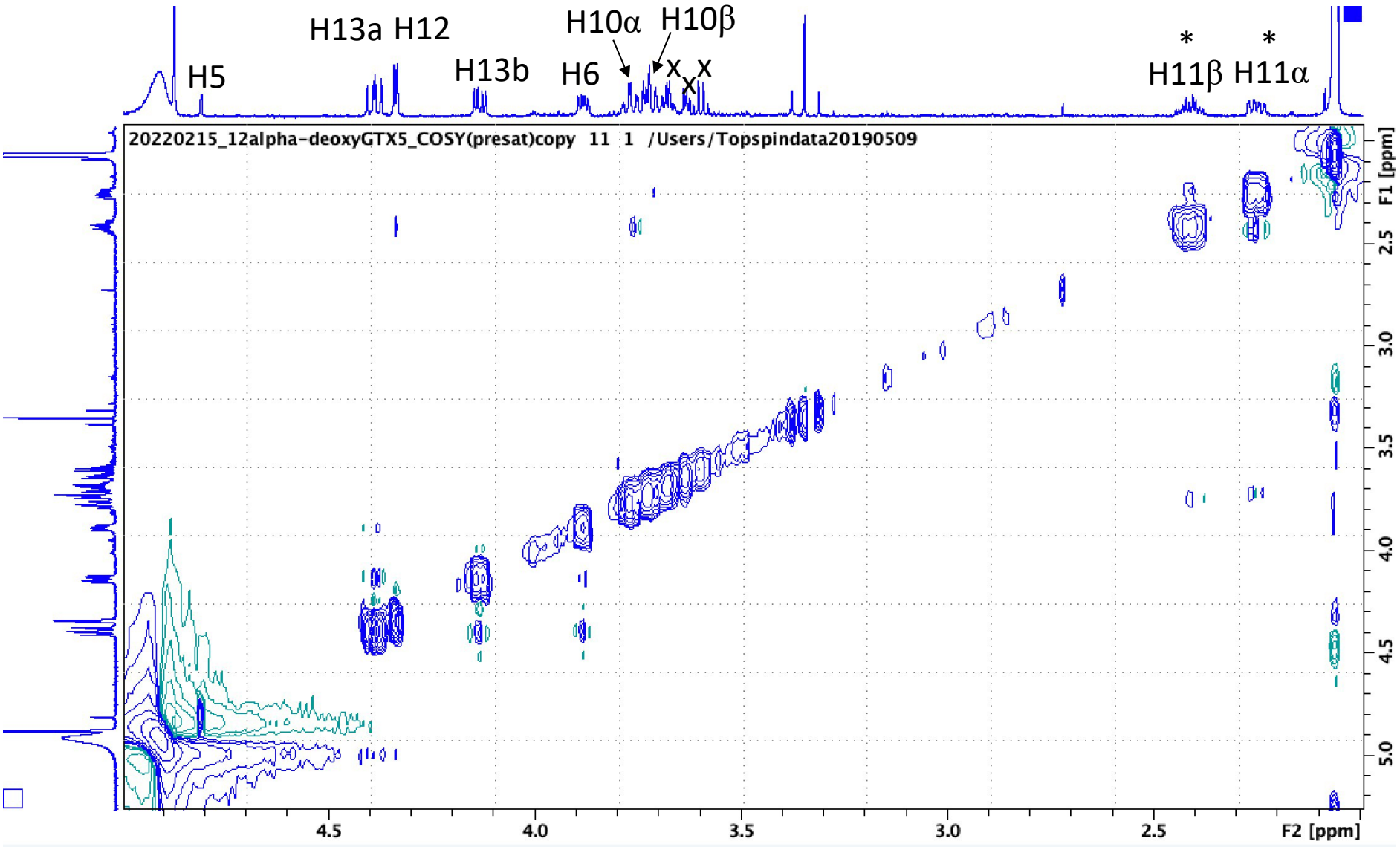

Figure S7. The COSY spectrum of synthetic 12α-deoxyGTX5 (**5**).
(600 MHz, microbottom tube, CD_3COOD-D_2O (4 : 96, v/v). HDO was presaturated. 1 h, Cryoprobe, Bruker AVANCE III), * interchangeable assignment.

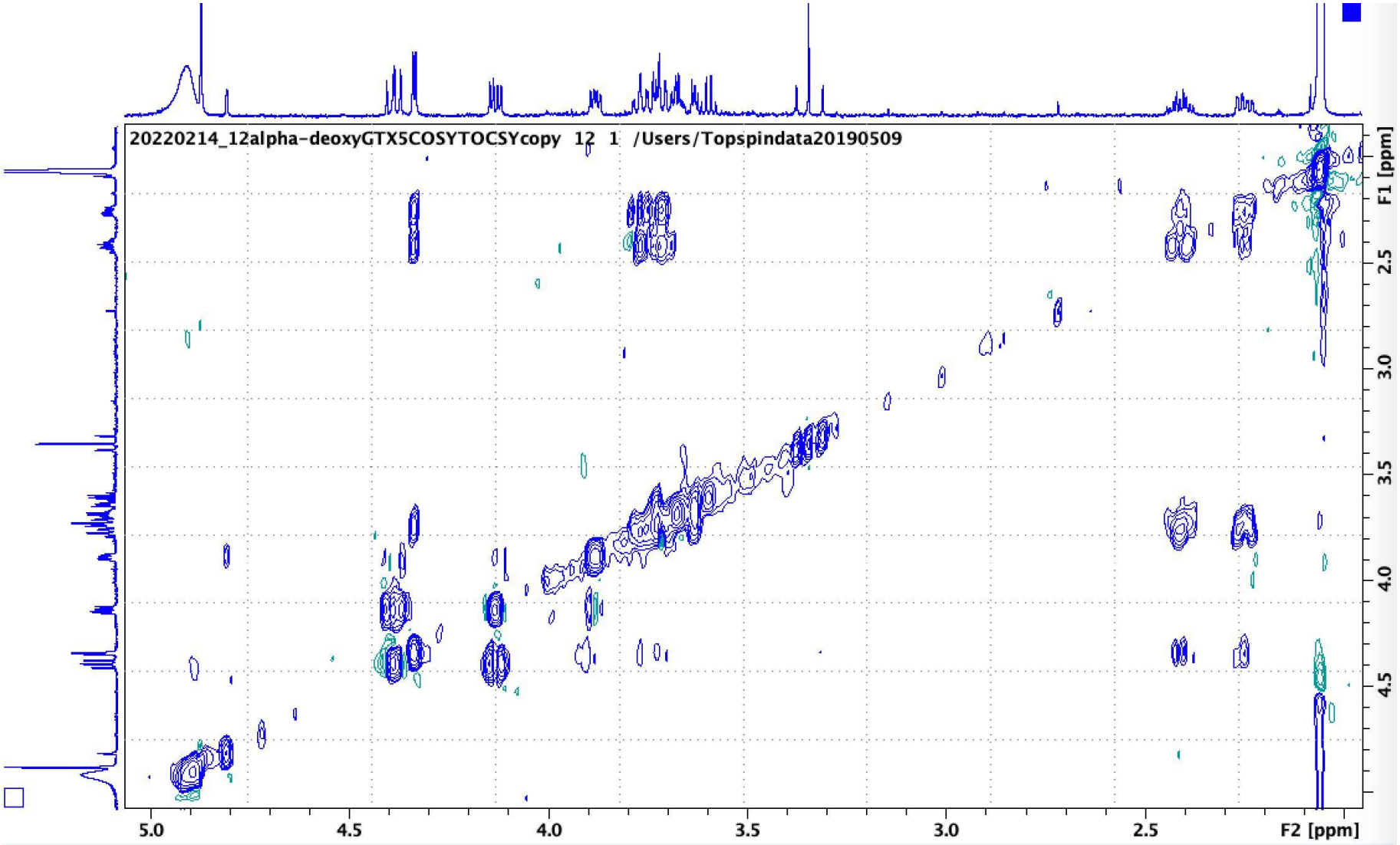

Figure S8. The TOCSY spectrum of synthetic 12α-deoxyGTX5 (**5**).
(600 MHz, microbottom tube, CD_3COOD-D_2O (4 : 96, v/v). HDO was presaturated. Cryoprobe, 10 min, Bruker AVANCE III)

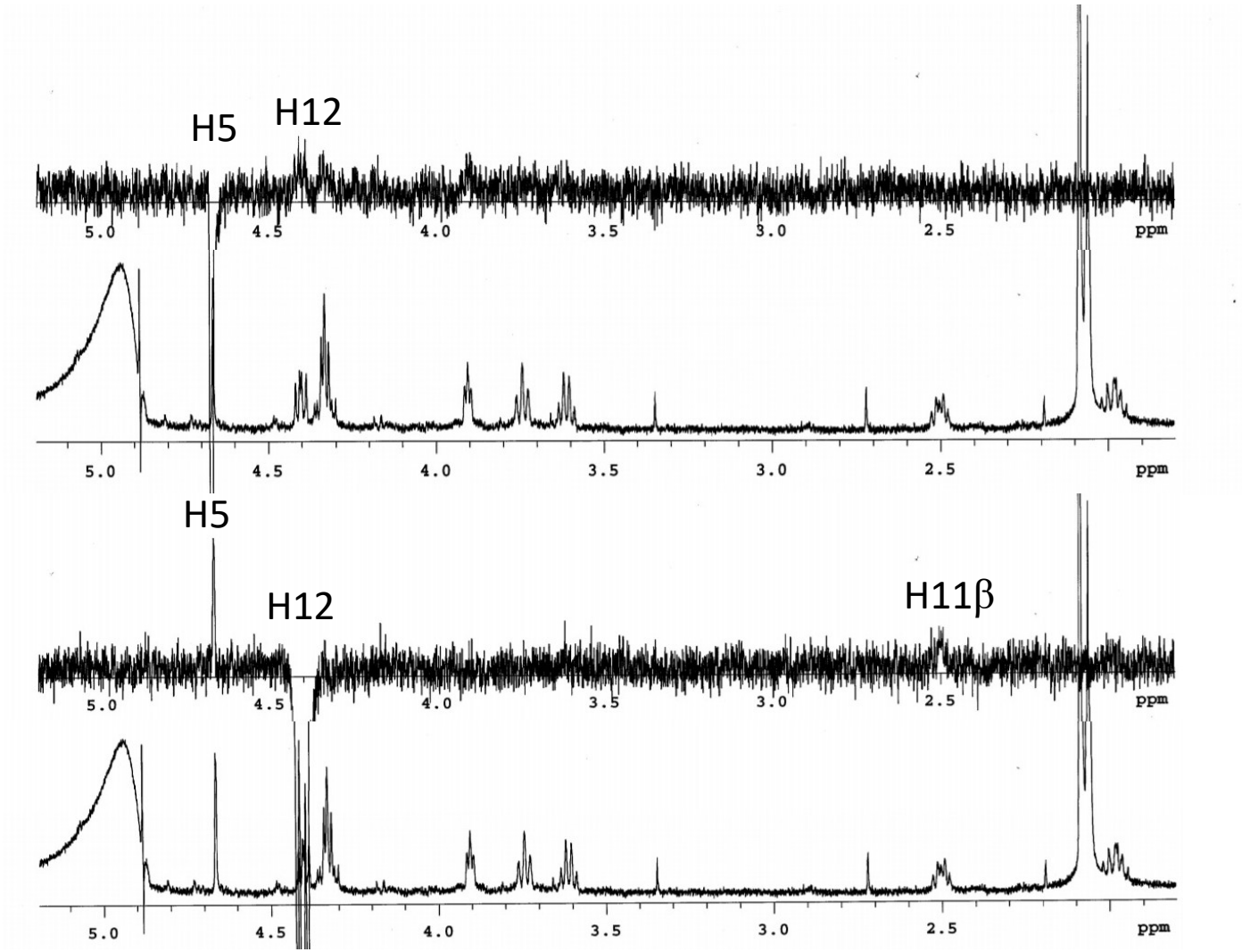

Figure S9. The NOESY 1D spectra of 12β-deoxyGTX5 (**2**) irradiate at δ_H 4.67 ppm (H5) and δ_H 4.40 ppm (H12) (600 MHz, CD_3COOD-D_2O (4 : 96, v/v)).

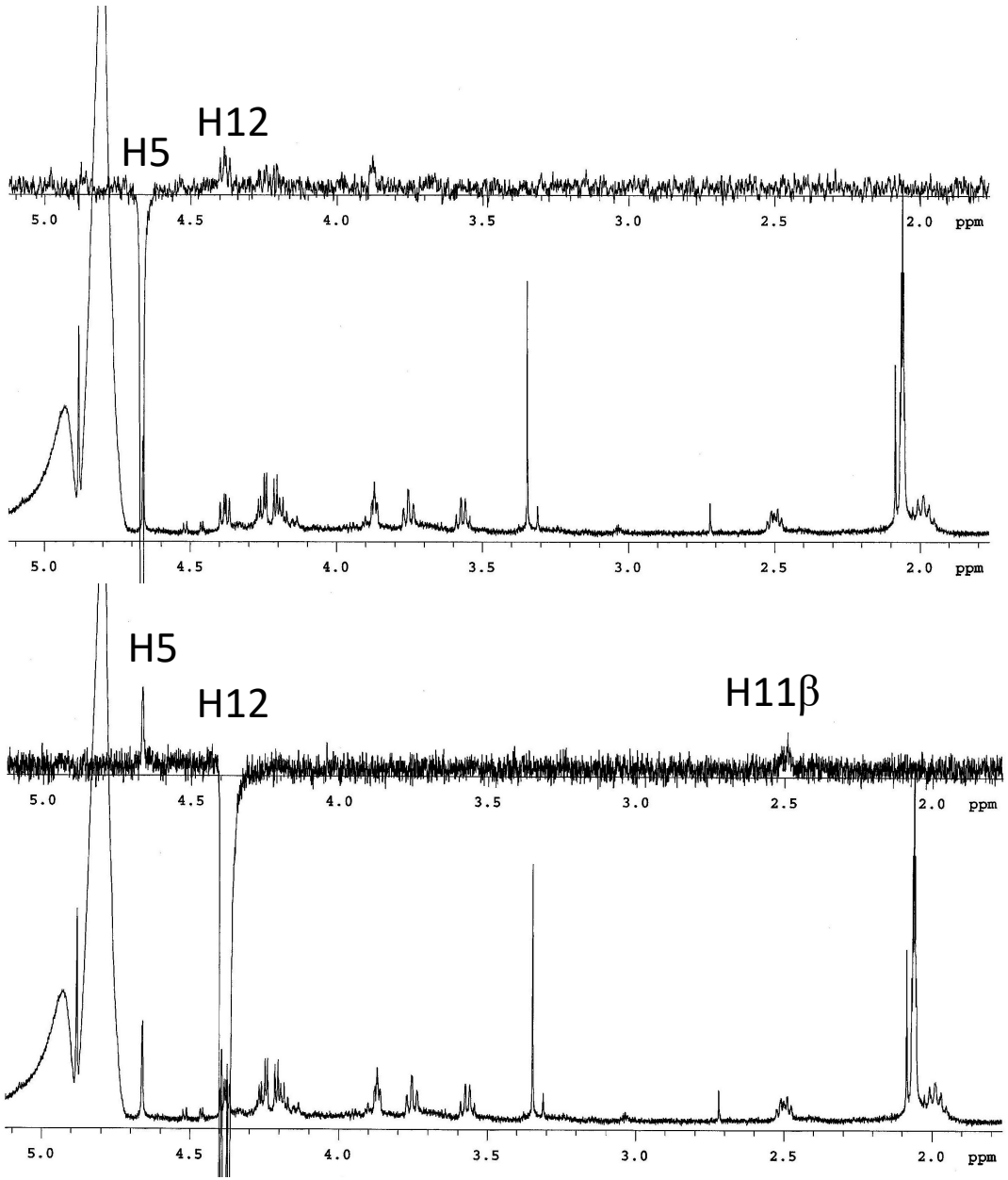

Figure S10. The NOESY 1D spectra of 12β-deoxySTX (**3**) irradiate at δ_H 4.66 ppm (H5) and δ_H 4.38 ppm (H12) (600 MHz, CD_3COOD-D_2O (4 : 96, v/v)).

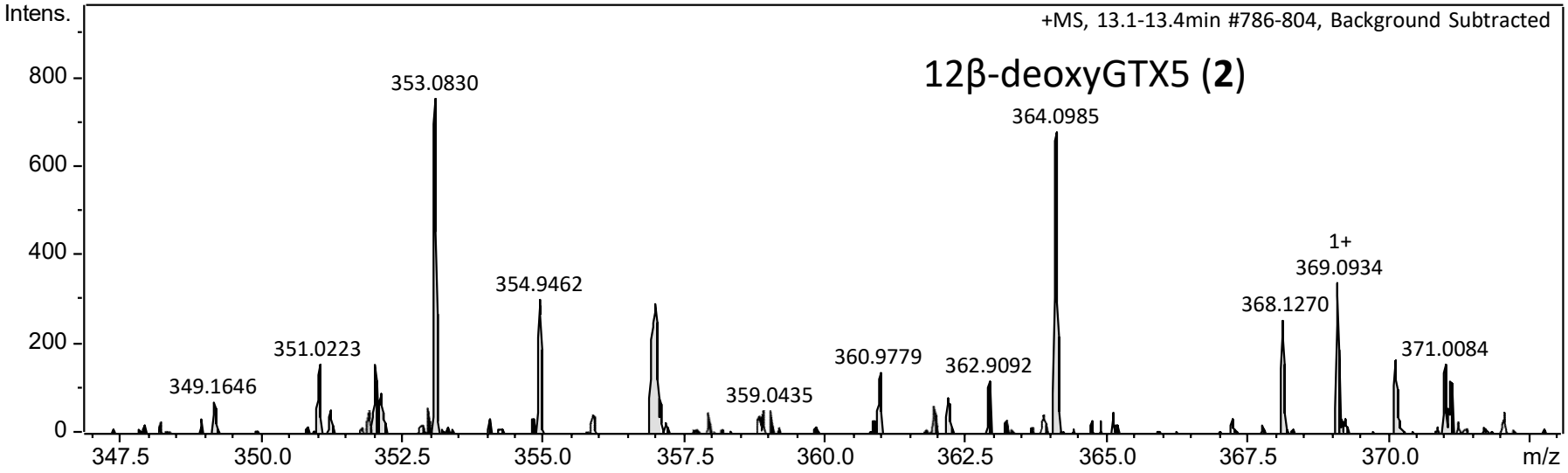

Figure S11. The ESI-HRMS spectrum of 12β-deoxyGTX5 (**2**) in *D. circinale* (TA04).

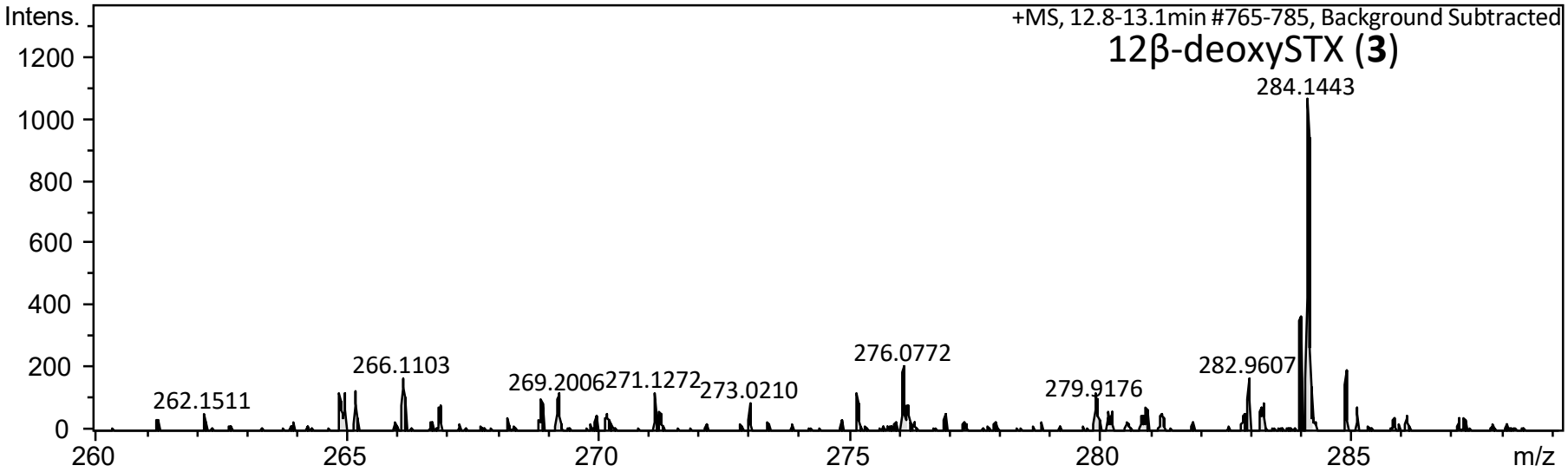

Figure S12. The ESI-HRMS spectrum of 12β-deoxySTX (**3**) (12α-saxitoxinol) in *D. circinale* (TA04).

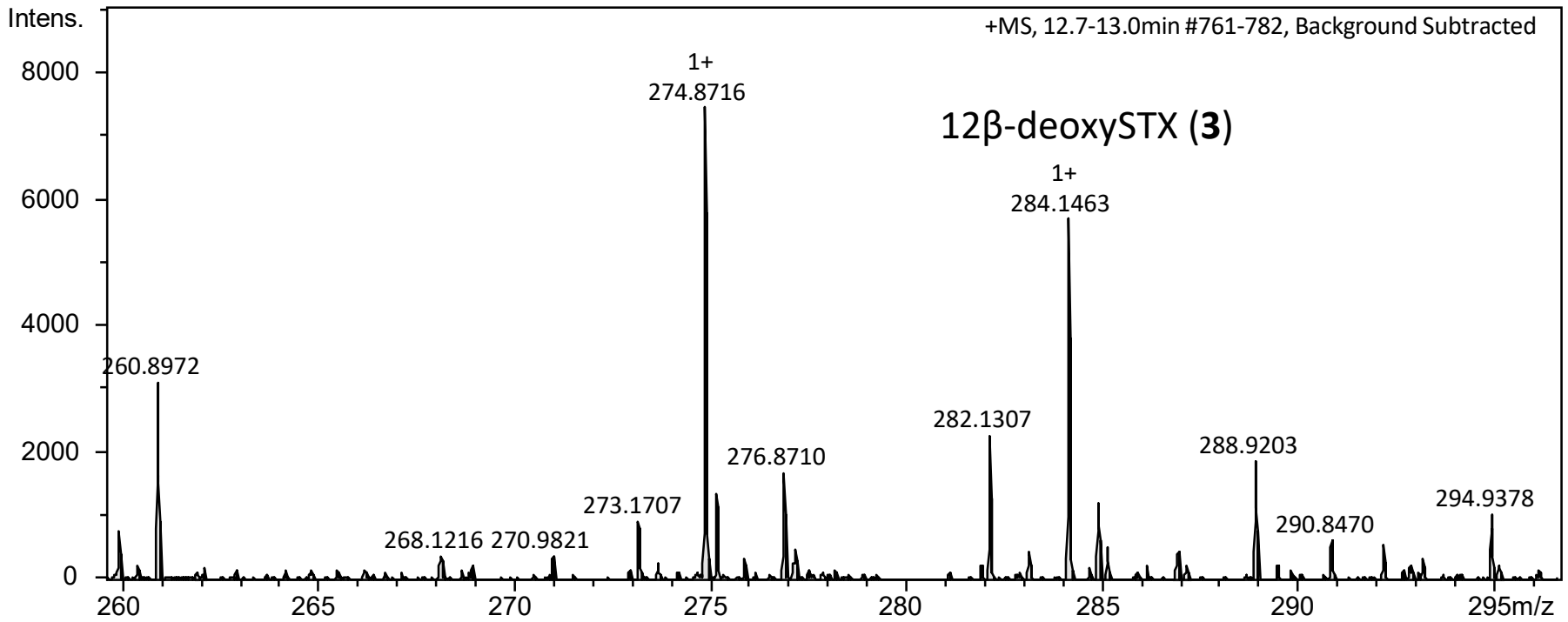

Figure S13. The ESI-HRMS spectrum of 12β-deoxySTX (**3**) (12α-saxitoxinol) in *A. pacificum* (Group IV) (Kure AC).

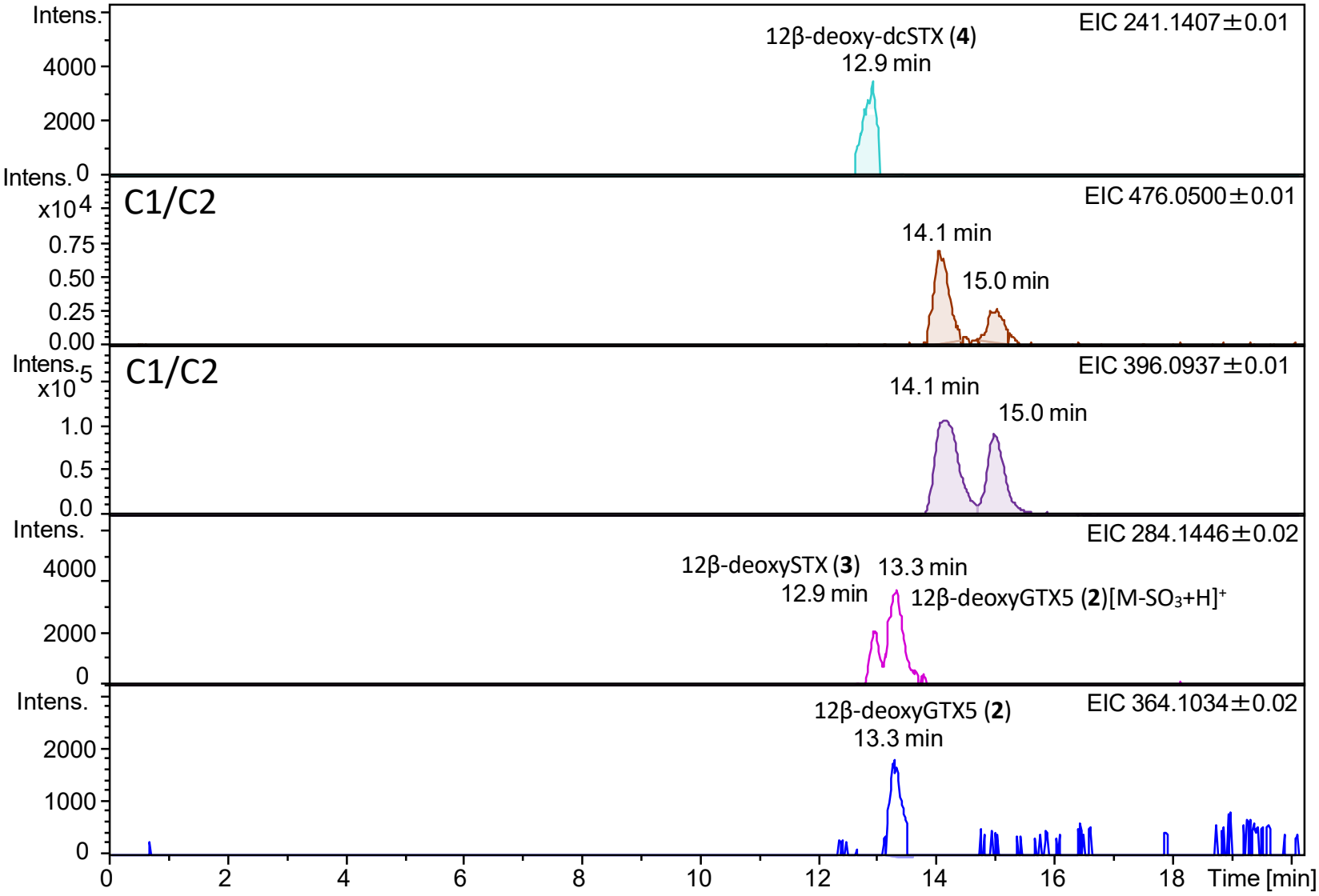

Figure S14. The HR-RP-LCMS Q1 scan of the *D. circinale* (TA04) cell extract. For LCMS condition, see text section 4.7.