

Supplementary Materials: The Missing Piece in Biosynthesis of Amphidinols: First Evidence of Glycolate as a Starter Unit in New Polyketides from *Amphidinium carterae*

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Figure S1. ^1H NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S2. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S3. ^{13}C Jmod spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S4. ^1H - ^1H COSY spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S5. TOCSY spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S6. edHSQC spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S7. HMBC ($J = 7$ Hz) spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S8. NOESY (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

Figure S9. ^1H NMR spectrum (600 MHz, CD_3OD) of **2**.

Figure S10. ^{13}C Jmod spectrum (600 MHz, CD_3OD) of **2**.

Figure S11. ^1H - ^1H COSY spectrum (600 MHz, CD_3OD) of **2**.

Figure S12. TOCSY spectrum (600 MHz, CD_3OD) of **2**.

Figure S13. edHSQC spectrum (600 MHz, CD_3OD) of **2**.

Figure S14. HMBC ($J = 7$ Hz) spectrum in CD_3OD (600 MHz) of **2**.

Figure S15. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1-^{13}\text{C}]$ -acetate.

Figure S16. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[2-^{13}\text{C}]$ -acetate.

Figure S17. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1,2-^{13}\text{C}_2]$ -acetate.

Figure S18. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1-^{13}\text{C}]$ -glycolate.

Figure S19. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1-^{13}\text{C}]$ -glycolate/SHAM.

Figure S20. ^{13}C NMR spectrum (600 MHz, CD_3OD) of **2** from the experiment with $[1-^{13}\text{C}]$ -glycolate/SHAM.

Figure S21. ESI⁺ MS/MS of **1** on molecular ion sodium adduct $[\text{M}+\text{Na}]^+$ at m/z 1361.8.

Figure S22. ESI⁻ MS/MS of **2** on molecular ion $[\text{M}-\text{H}]^-$ at m/z 1417.8.

Figure S23. ESI⁺ MS/MS of **2** on molecular ion sodium adduct $[\text{M}-\text{H}+2\text{Na}]^+$ at m/z 1463.8.

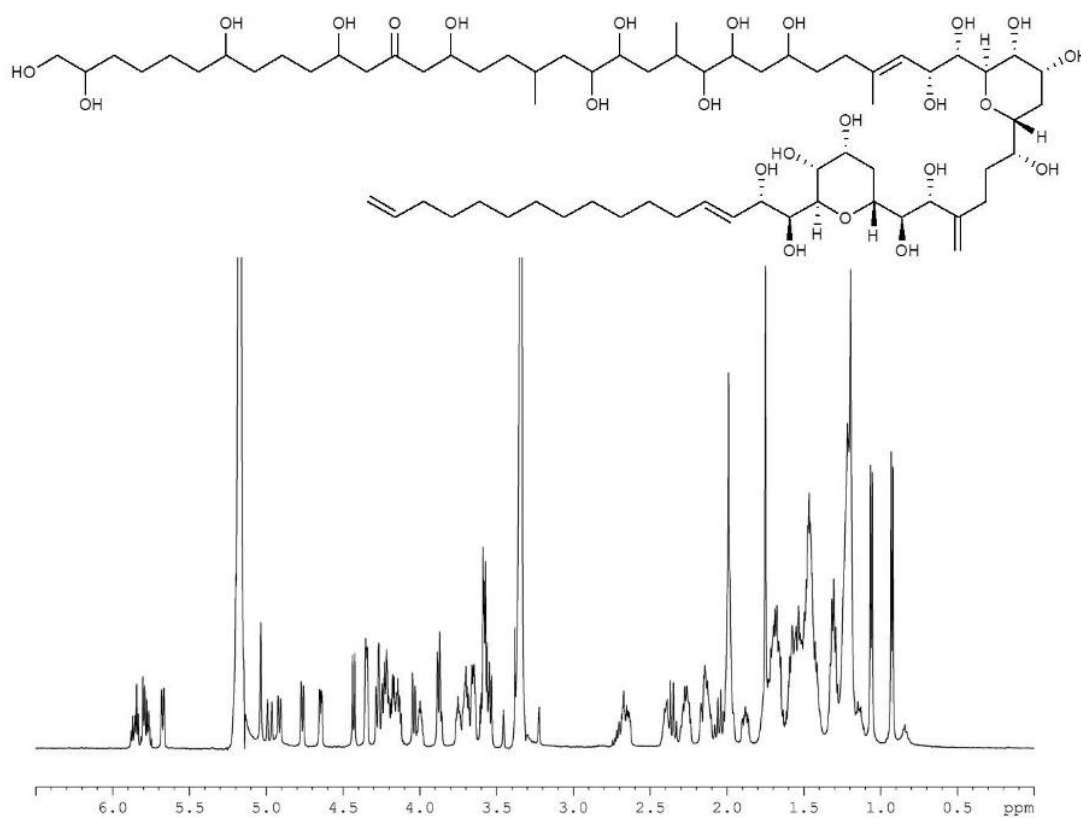


Figure S1. ^1H NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of 1.

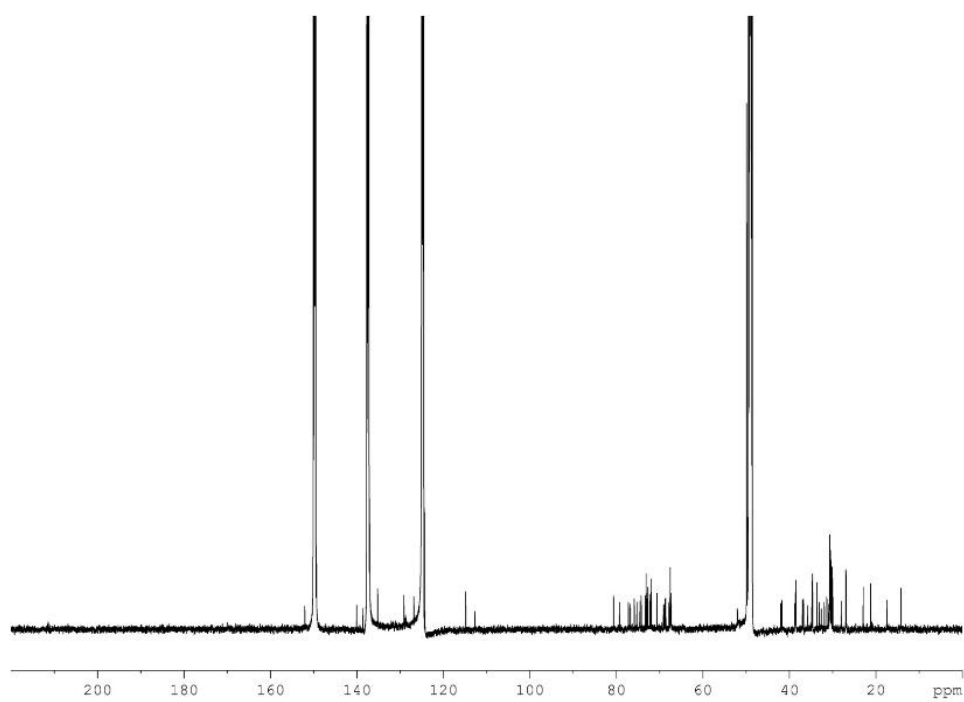


Figure S2. ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of 1.

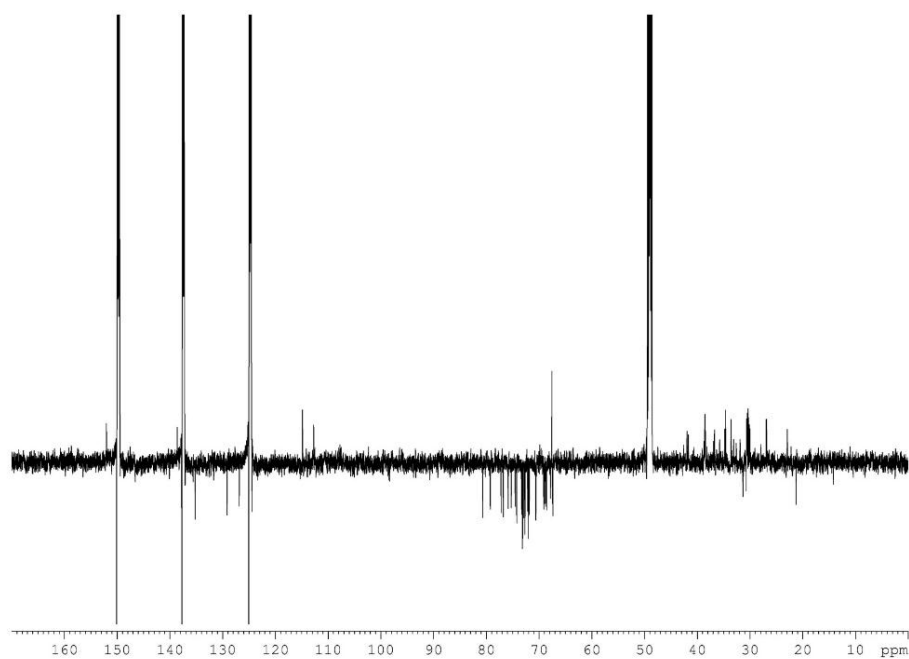


Figure S3. ^{13}C Jmod spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

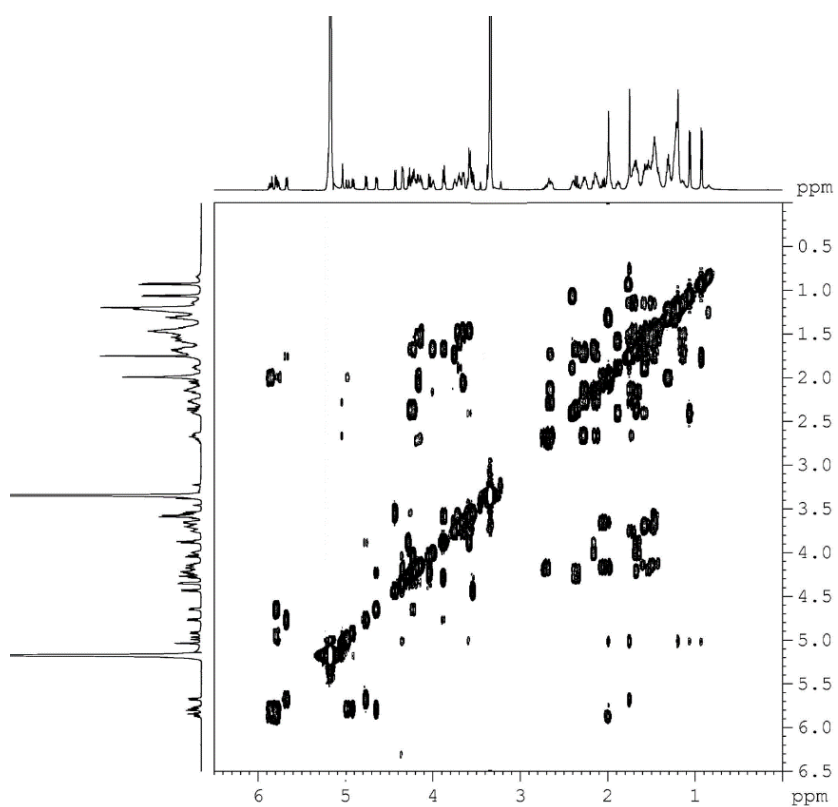


Figure S4. ^1H - ^1H COSY spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

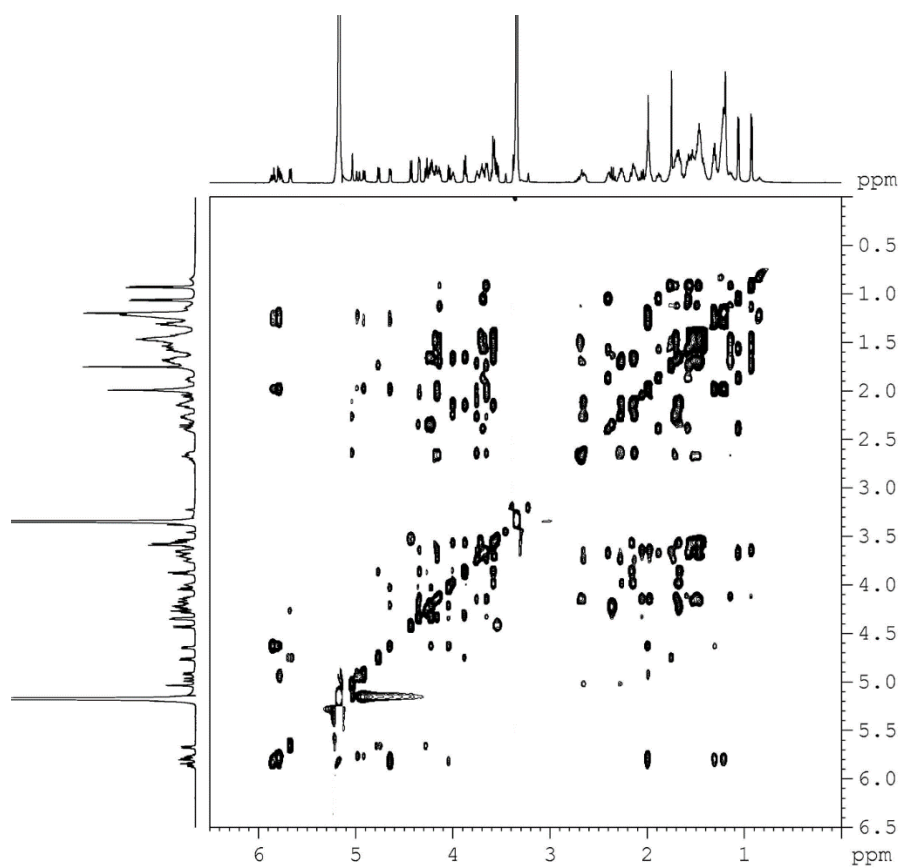


Figure S5. TOCSY spectrum (600 MHz, CD₃OD/C₅D₅N 2:1) of **1**.

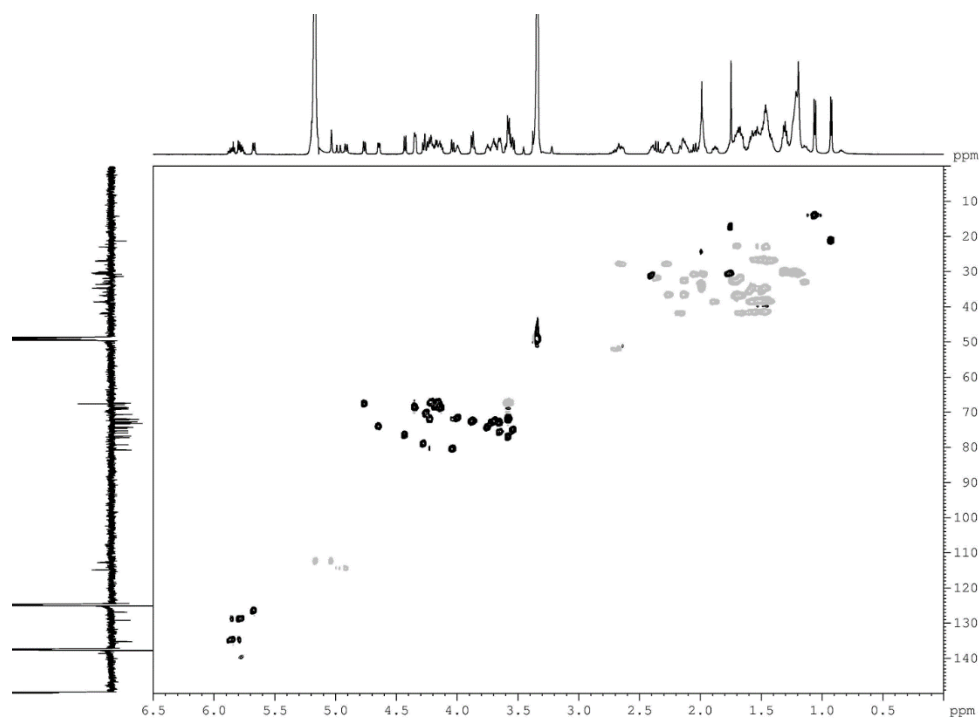


Figure S6. edHSQC spectrum (600 MHz, CD₃OD/C₅D₅N 2:1) of **1**.

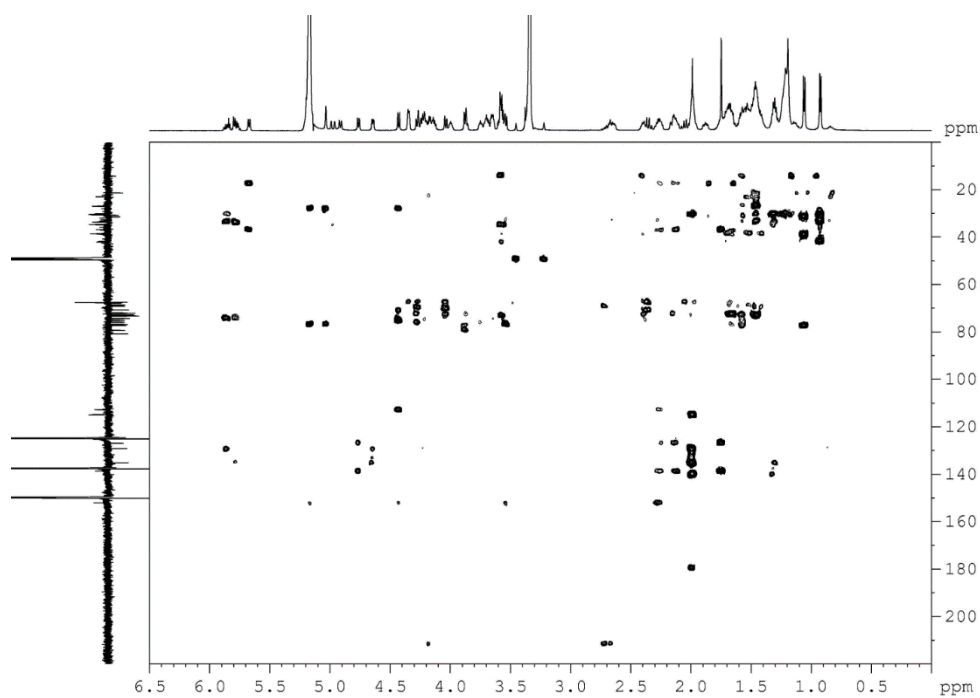


Figure S7. HMBC ($J = 7$ Hz) spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

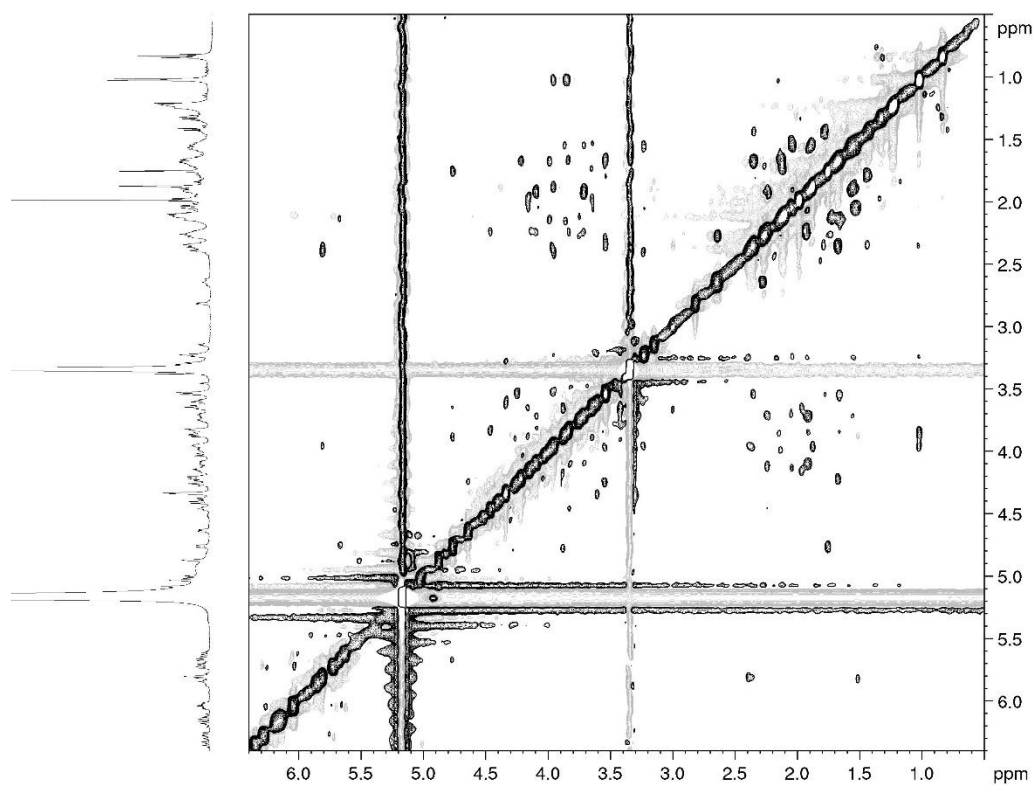


Figure S8. NOESY (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1**.

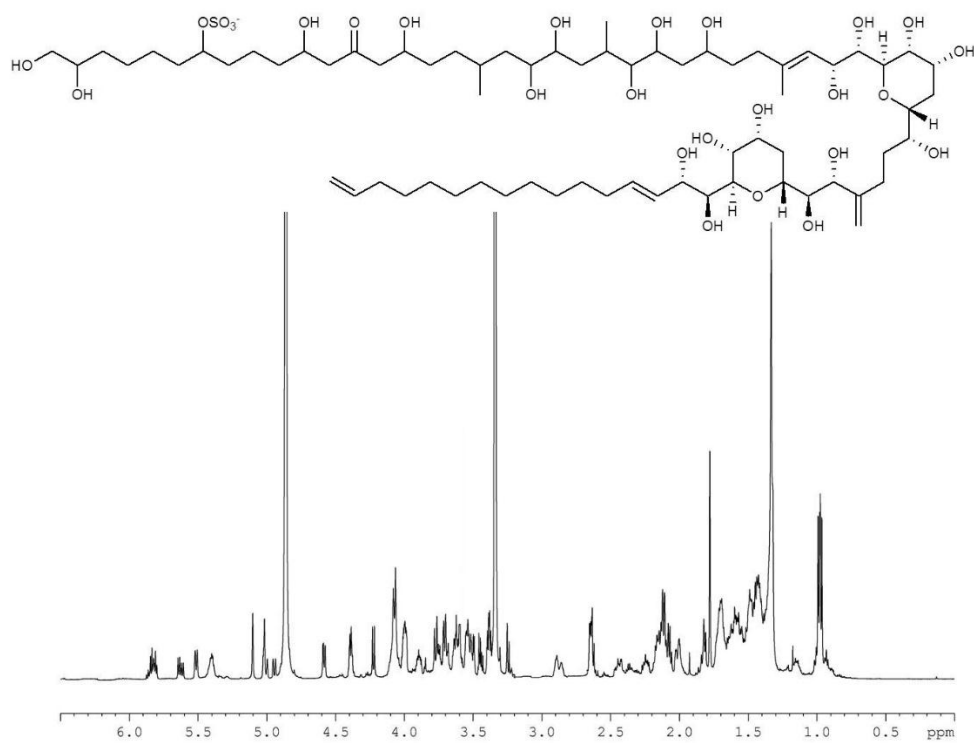


Figure S9. ¹H NMR spectrum (600 MHz, CD₃OD) of 2.

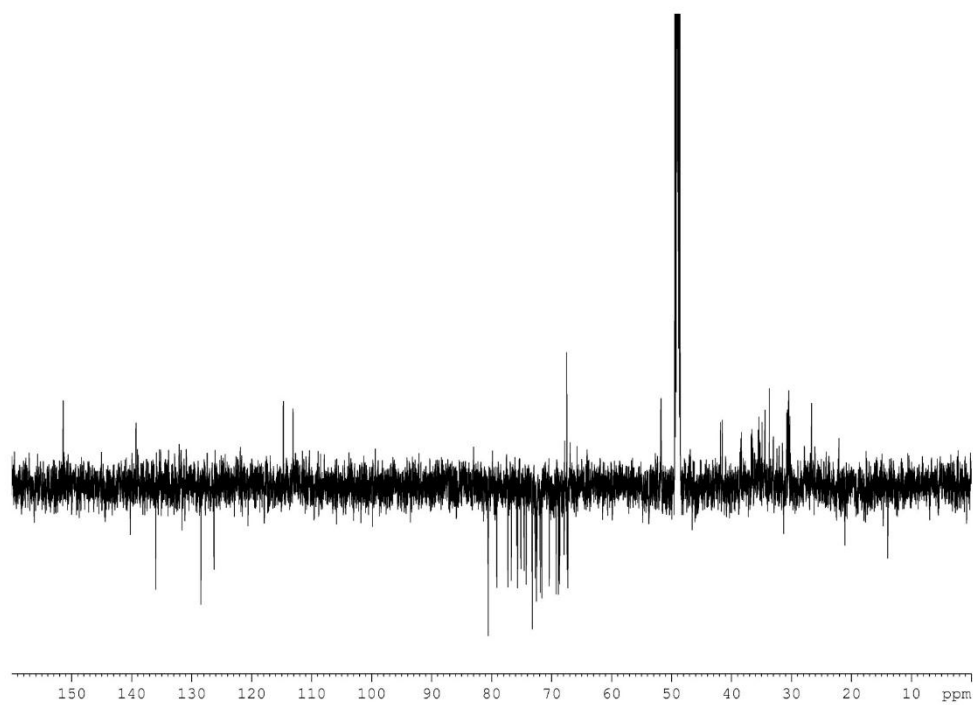


Figure S10. ¹³C Jmod spectrum (600 MHz, CD₃OD) of 2.

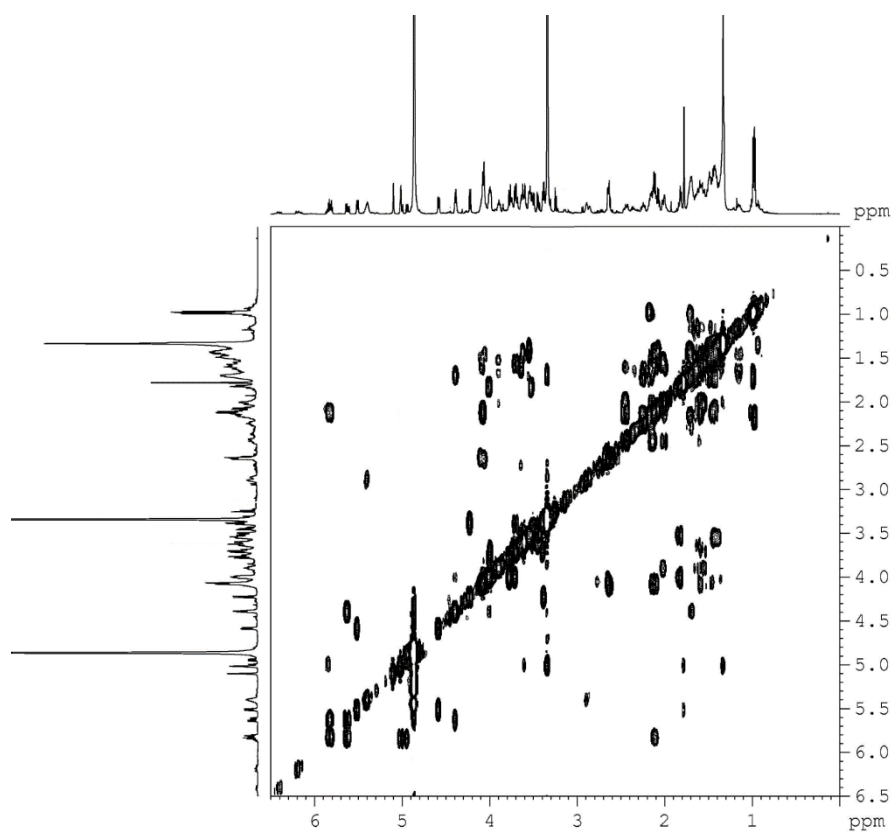


Figure S11. ^1H - ^1H COSY spectrum (600 MHz, CD_3OD) of **2**.

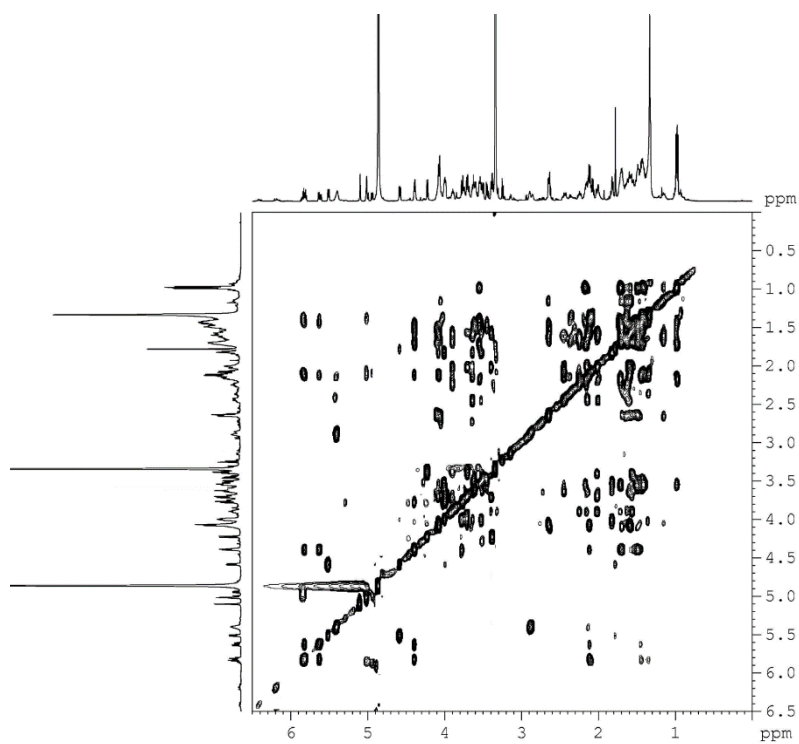


Figure S12. TOCSY spectrum (600 MHz, CD_3OD) of **2**.

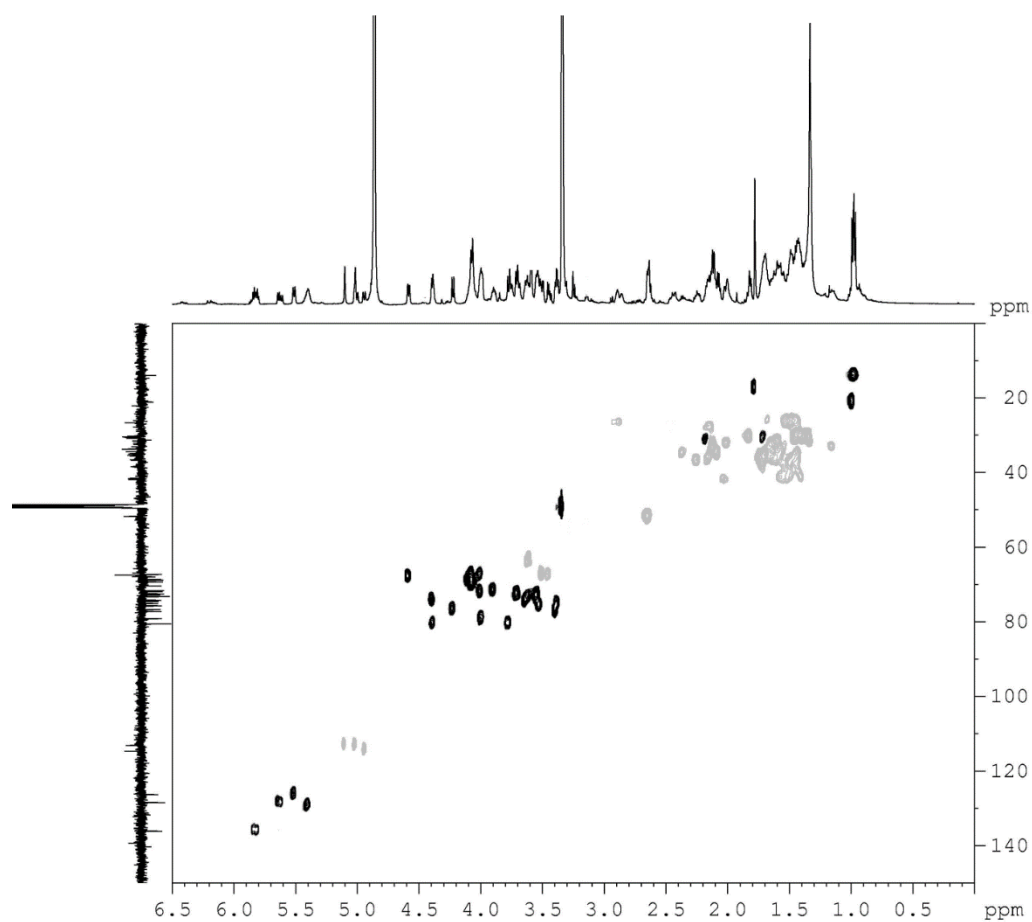


Figure S13. edHSQC spectrum (600 MHz, CD₃OD) of **2**.

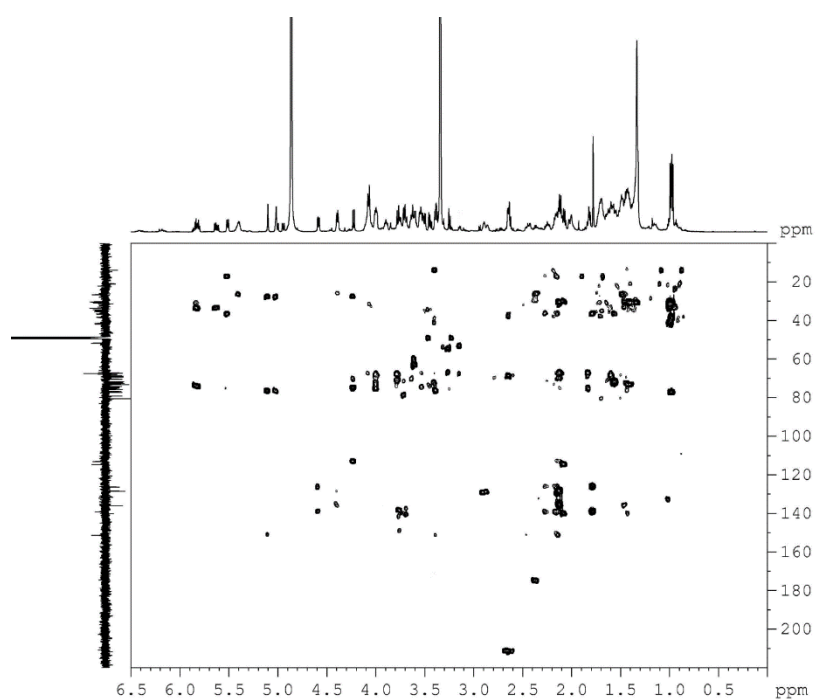


Figure S14. HMBC ($J = 7$ Hz) spectrum in CD₃OD (600 MHz) of **2**.

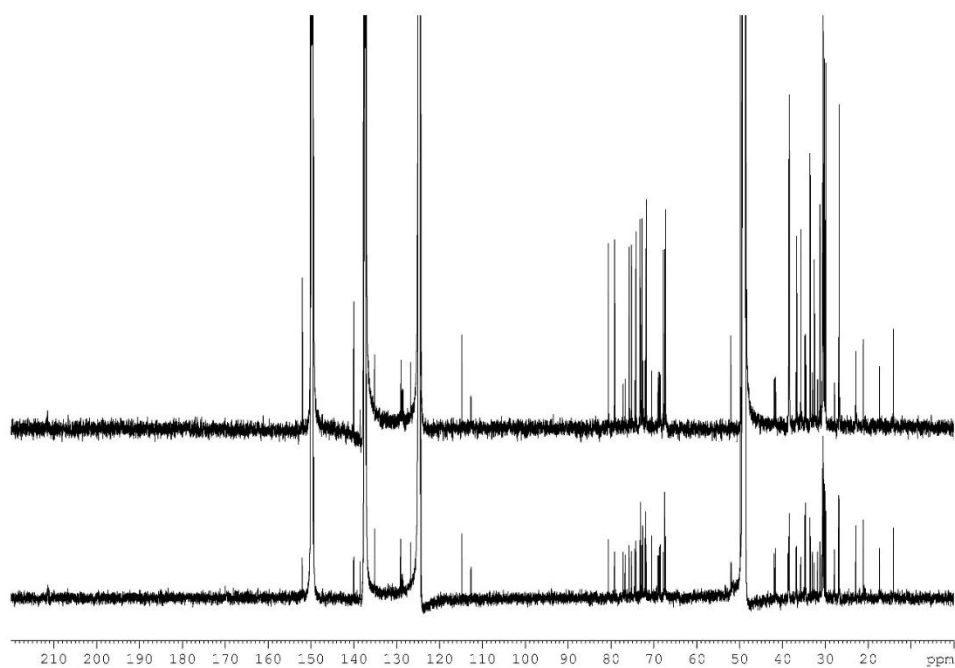


Figure S15. ¹³C NMR spectrum (600 MHz, CD₃OD/C₅D₅N 2:1) of **1** from the experiment with [1-¹³C]-acetate (upper) in comparison with the natural compound (lower).

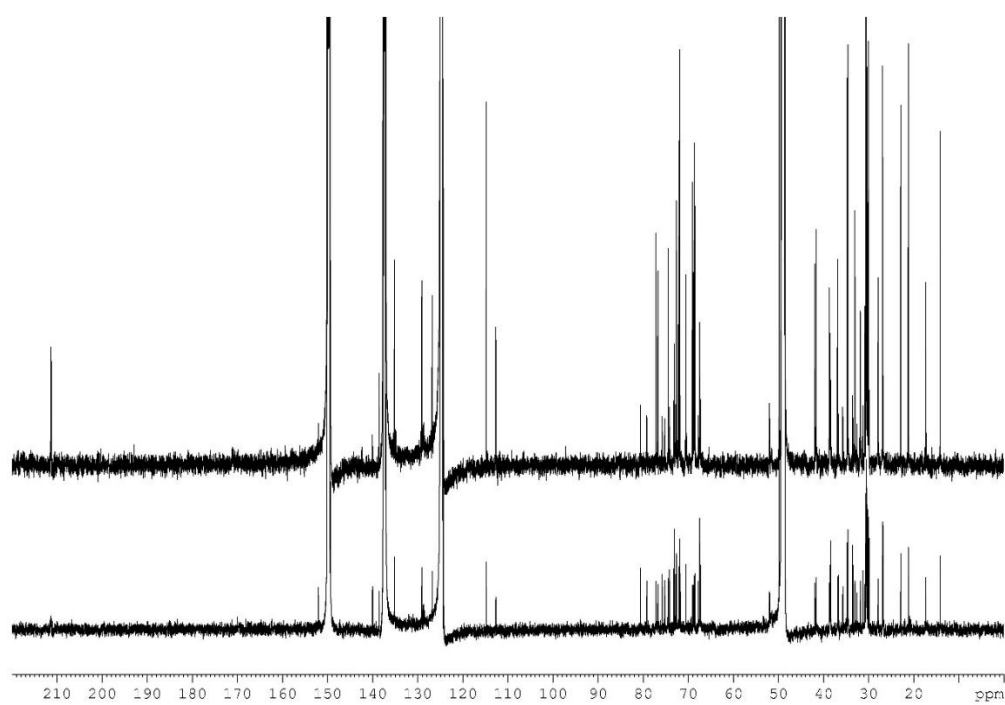


Figure S16. ¹³C NMR spectrum (600 MHz, CD₃OD/C₅D₅N 2:1) of **1** from the experiment with [2-¹³C]-acetate (upper) in comparison with the natural compound (lower).

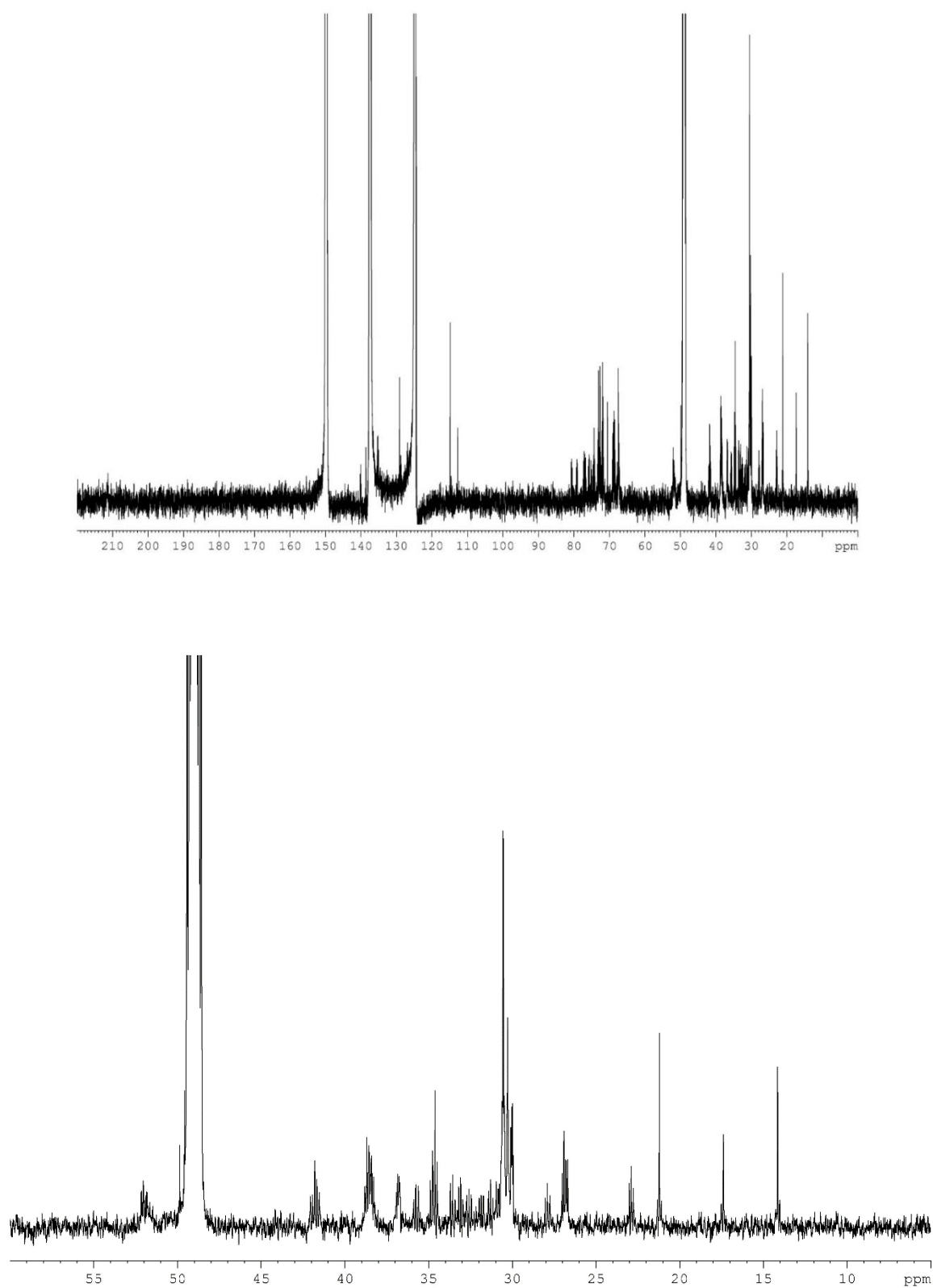


Figure S17. Two enlargements of ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1,2-^{13}\text{C}_2]$ -acetate.

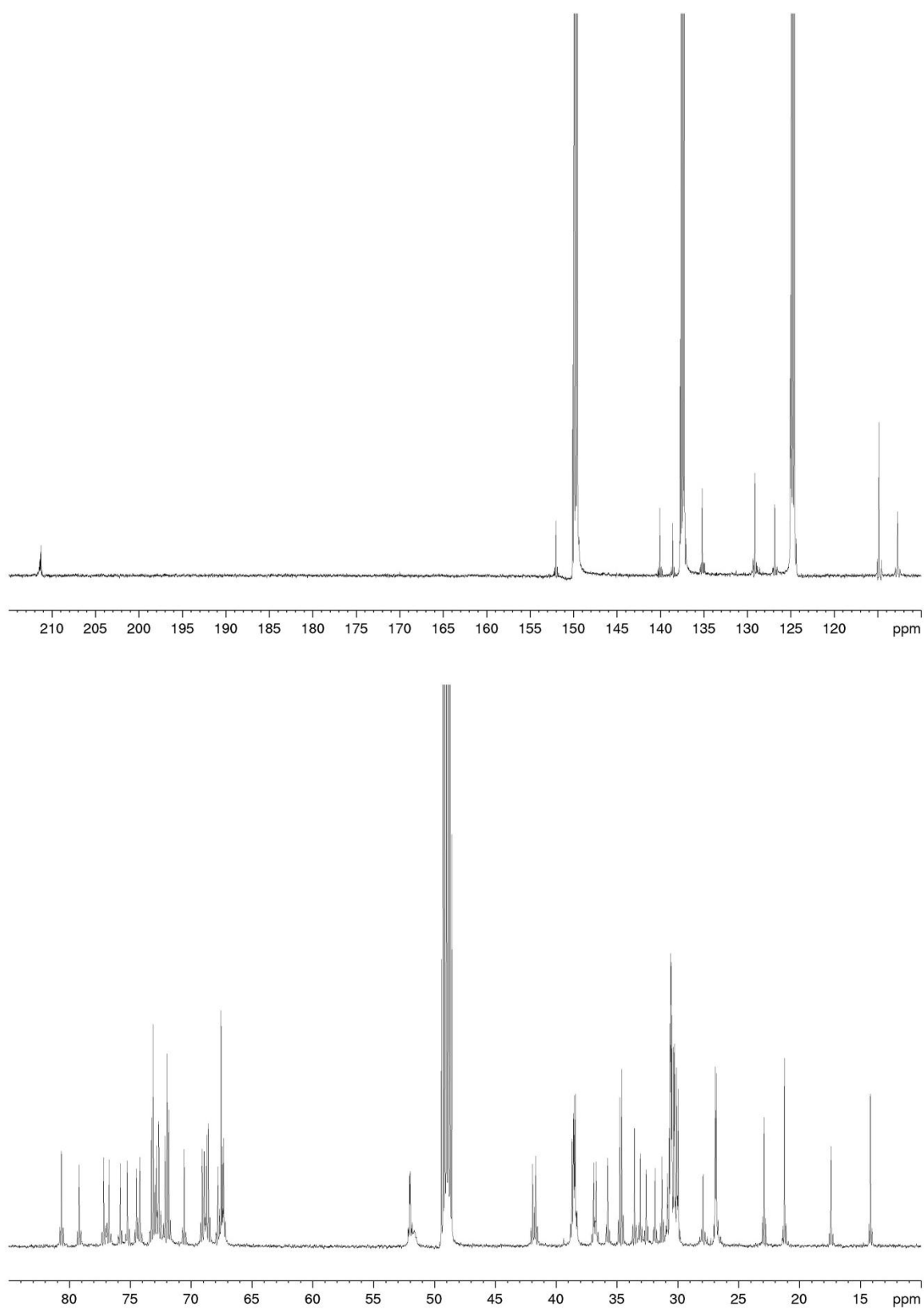


Figure S18. Two enlargements of ^{13}C NMR spectrum (600 MHz, $\text{CD}_3\text{OD}/\text{C}_5\text{D}_5\text{N}$ 2:1) of **1** from the experiment with $[1-^{13}\text{C}]$ -glycolate.

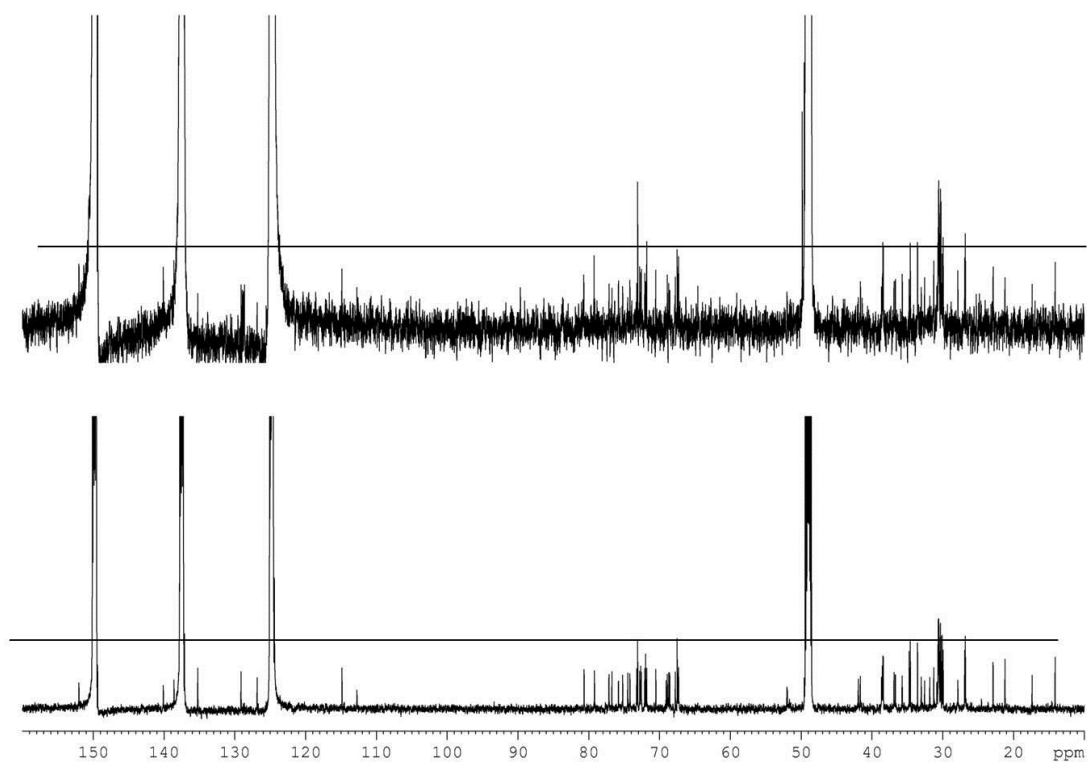


Figure S19. ¹³C NMR spectrum (600 MHz, CD₃OD/C₅D₅N 2:1) of **1** from the experiment with [1-¹³C]-glycolate/SHAM (upper) in comparison with the natural compound (lower).

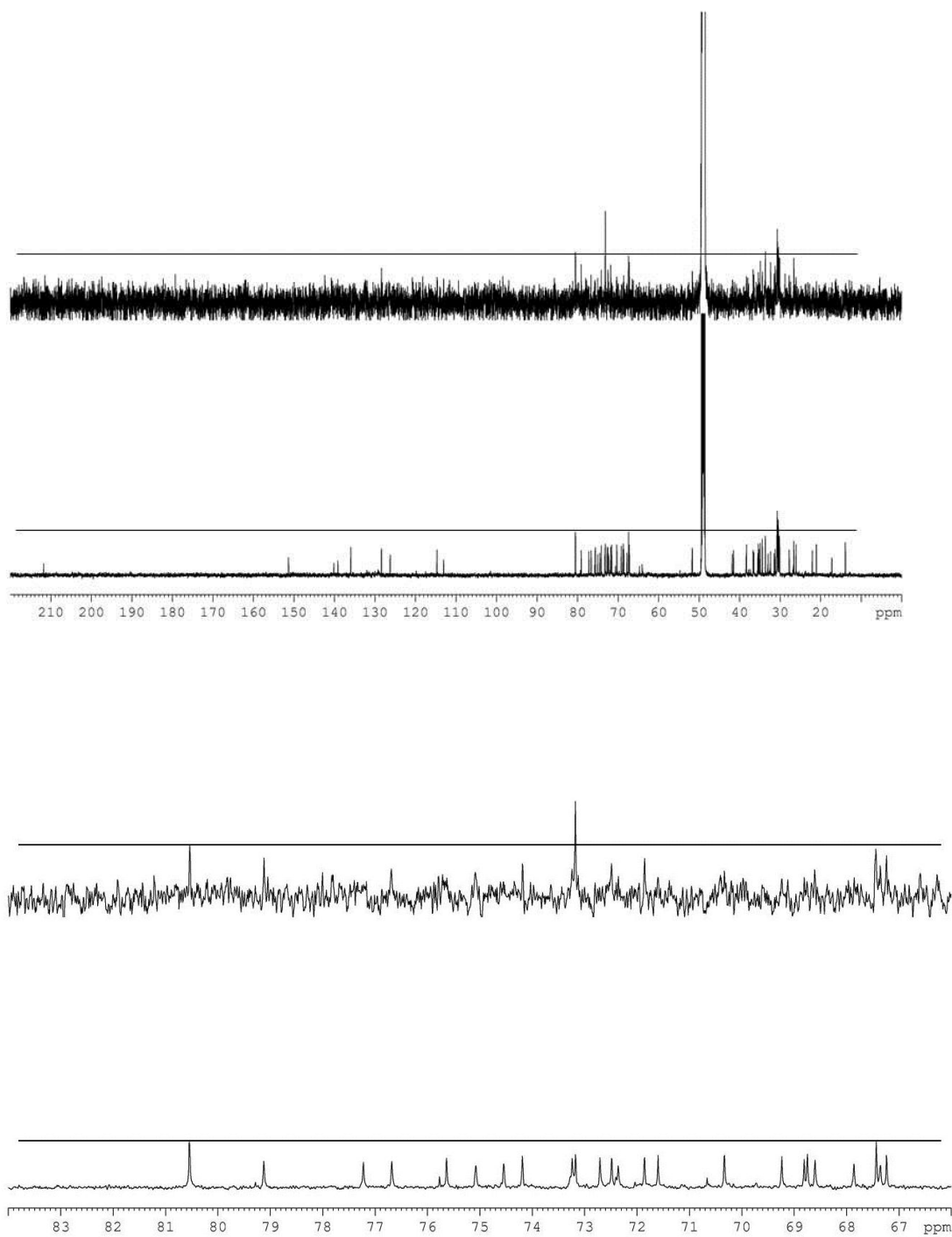


Figure S20. Two enlargements of ^{13}C NMR spectrum (600 MHz, CD_3OD) of 2 from the experiment with [1- ^{13}C]-glycolate/SHAM (upper) in comparison with the natural compound (lower).

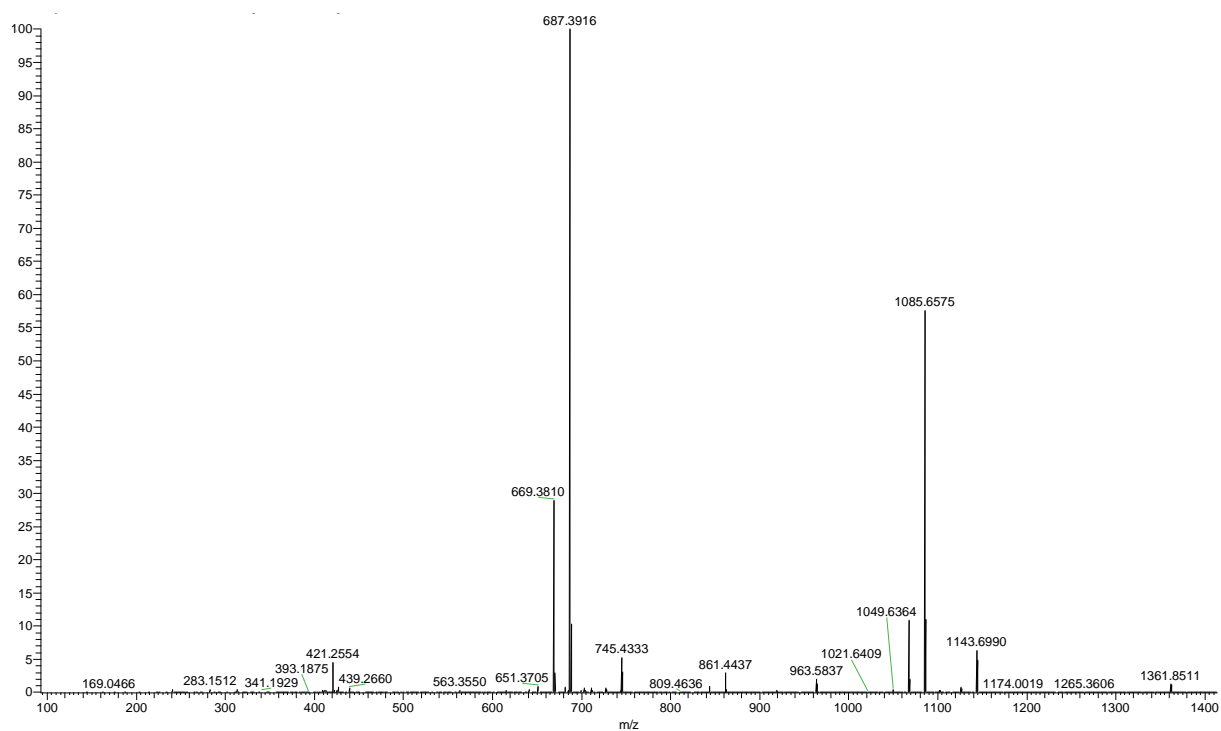


Figure S21. ESI⁺ MS/MS of 1 on molecular ion sodium adduct [M+Na]⁺ at *m/z* 1361.8.

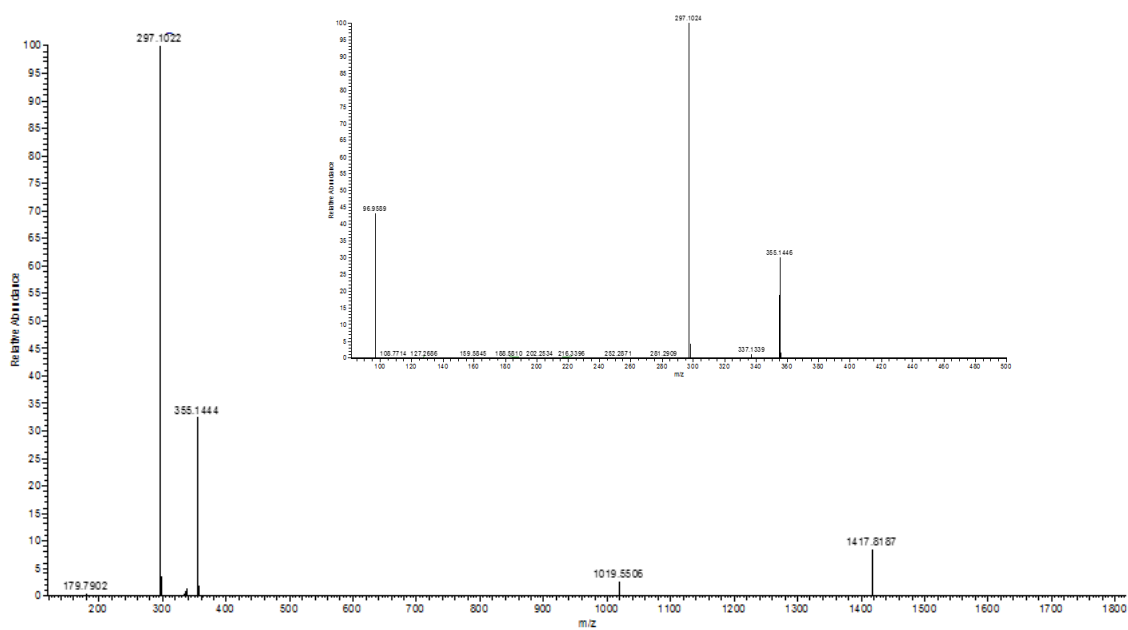


Figure S22. ESI⁻ MS/MS of 2 on molecular ion [M-H]⁻ at *m/z* 1417.8.

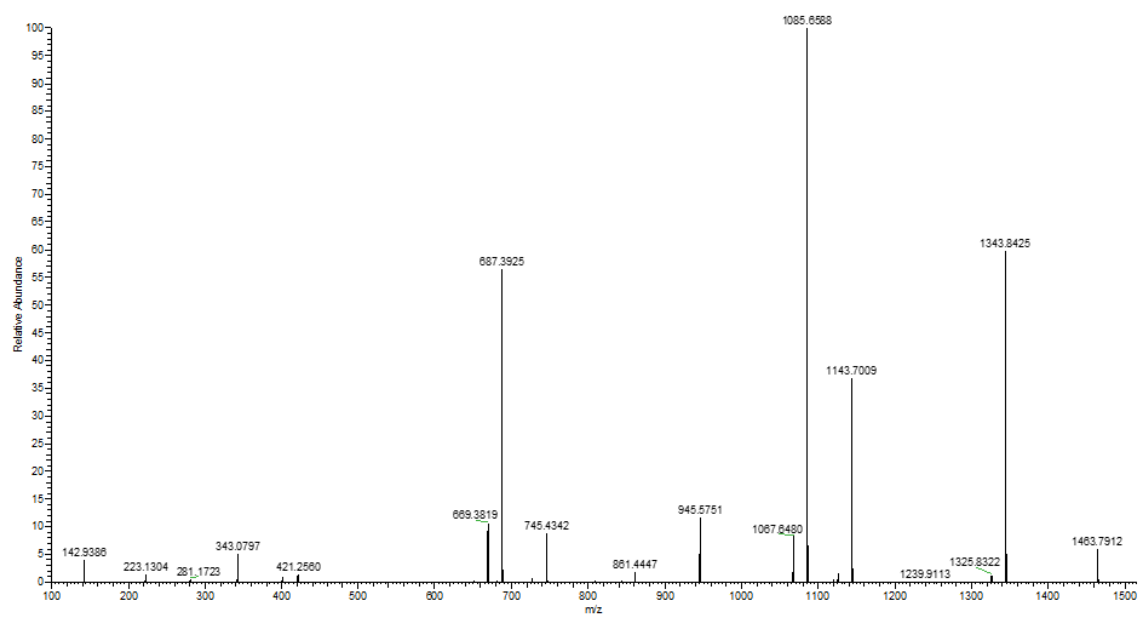


Figure S23. ESI⁺ MS/MS of 2 on molecular ion sodium adduct [M-H+2Na]⁺ at *m/z* 1463.8.