SUPPORTING INFORMATION

Discovery of Four Modified Classes of Triterpenoids Delineated a Metabolic Cascade: Compound Characterization and Biomimetic Synthesis

Bin Zhou,[a,‡] Xin-Hua Gao,[a,‡] Min-Min Zhang,[b] Cheng-Yu Zheng,[a] Hong-Chun Liu,[b] and Jian-Min Yue*[a]

[a]State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203, People's Republic of China

[b]Division of Anti-tumor Pharmacology, State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, 555 Zuchongzhi Road, Shanghai 201203, People's Republic of China

‡The authors contribute equally to this work.

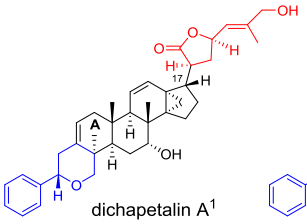
*Correspondence and requests for materials should be addressed to J. M. Yue (email: jmyue@simm.ac.cn)

Table of Contents

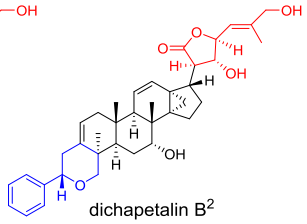
1. Summary of the Structural Types of Dichapetalins

1. Ordinary dichapetalin-type triterpenoids with a 2-phenylpyran moiety fused to the A ring

1.1 With a **lactone** side chain at C-17

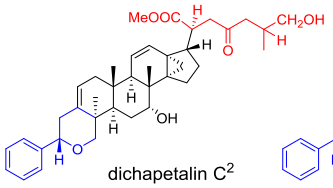


dichapetalin A[1]

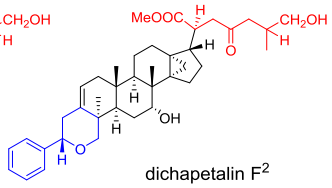


dichapetalin B[2]

1.2 With a **methyl ester** side chain at C-17

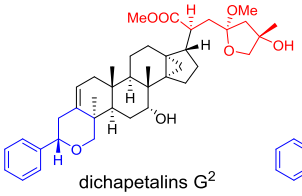


dichapetalin C[2]

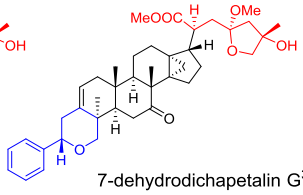


dichapetalin F[2]

1.3 With a **lactol** side chain at C-17

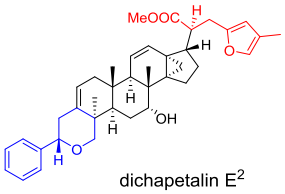


dichapetalins G[2]

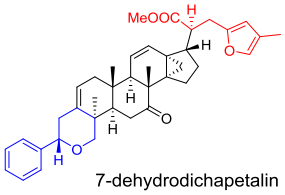


7-dehydrodichapetalin G[3]

1.4 With a **furan** side chain at C-17

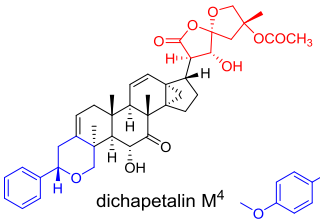


dichapetalin E[2]

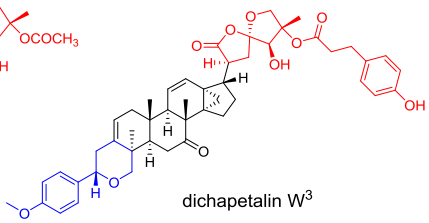


7-dehydrodichapetalin E[3]

1.5 With a **spiroketal** side chain at C-17



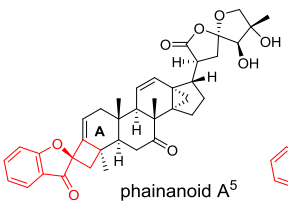
dichapetalin M[4]



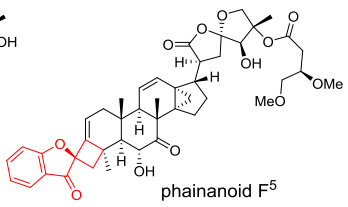
dichapetalin W[3]

2. Skeletal new dichapetalin-type triterpenoids

2.1 With a 4,5-spirocyclic system fused to the A ring

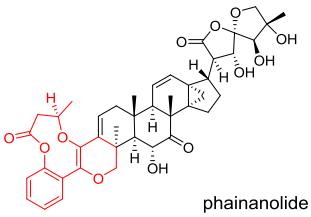


phainanoid A[5]



phainanoid F[5]

2.1 With a 6/9/6 heterotricyclic system fused to the A ring



phainanolide A[6]

Chart S1. Representative structures of previously reported dichapetalin-type triterpenoids.

References

(1) Achenbach, H.; Asunka, S. A.; Waibel, R.; Addae-Mensah, I.; Oppong, I. V. *Nat. Prod. Lett.*, 1995, **7**, 93–100.

(2) Addae-Mensah, I.; Waibel, R.; Asunka, S. A.; Oppong, I. V.; Achenbach, H. *Phytochemistry*, 1996, **43**, 649–656.

(3) Jing, S. X.; Luo, S. H.; Li, C. H.; Hua, J.; Wang, Y. L.; Niu, X. M.; Li, X. N.; Liu, Y.; Huang, C. S.; Wang, Y.; Li, S. H. *J. Nat. Prod.*, 2014, **77**, 882–893.

(4) Osei-Safo, D.; Chama, M. A.; Addae-Mensah, I.; Waibel, R.; Asomaning, W. A.; Oppong, I. V. *Phytochemisty Lett.*, 2008, **1**, 147–150.

(5) Fan, Y. Y.; Zhang, H.; Zhou, Y.; Liu, H. B.; Tang, W.; Zhou, B.; Zuo, J. P.; Yue, J. M. *J. Am. Chem. Soc.*, 2015, **137**, 138–141.

(6) Fan, Y. Y.; Gan, L. S.; Liu, H. C.; Li, H.; Xu, C. H.; Zuo, J. P.; Ding, J.; Yue, J. M. *Org. Lett.*, 2017, **19**, 4580–4583.

2. Experimental Section

2.1 General Experimental Procedures

The melting points were measured on an SGM X-4 analyzer (Shanghai Precision & Scientific Instrument Co. Ltd.) and were uncorrected. The X-ray crystallography was performed on a Bruker APEX-II CCD diffractometer equipped with graphite-monochromated Cu Kα radiation (λ = 1.54178 Å). Optical rotations were determined on an Autopol VI polarimeter at room temperature; concentrations were reported in g/100 mL. UV data were obtained using a Shimadzu UV-2550 spectrophotometer. IR spectra were acquired on a Thermo IS5 spectrometer with KBr disks. NMR spectra were obtained on a Bruker AM-500 NMR spectrometer. ESIMS data were recorded via a Shimadzu LC-MS-2020 or Thermo Fisher Finnigan LCQ-DECA mass spectrometer, and HRMS (ESI) data were carried out on a Waters-Micromass Q-TQF Ultima Global or an Agilent 1290-6545 UHPLC-QTOF mass spectrometer, respectively. Semipreparative HPLC was performed on a Waters 1525 binary pump system with a Waters 2487 detector (210 nm) using a YMC-Pack ODS-A (250 × 10 mm, *S*-5 μm). Silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd., China), C18 reversed-phase (RP-C18) silica gel (20–45 μM, Fuji Silysia Chemical Ltd., Japan), CHP20P MCI gel (75–150 μM, Mitsubishi Chemical Corporation), and Sephadex LH-20 gel (Amersham Biosciences) were used for column chromatography (CC). Pre-coated silica gel GF254 plates (Qingdao Haiyang Chemical Co., Ltd.) were used for TLC detection. All solvents used for CC and synthesis were of analytical grade (Shanghai Chemical Reagents Co., Ltd.), and solvents used for HPLC were of HPLC grade. (J & K Scientific Ltd.)

2.2 Plant Material

The twigs and leaves of *Dichapetalum gelonioides* were collected from Ganning in Hainan Province, People's Republic of China, and were authenticated by Prof. S. M. Huang of Hainan University. A voucher specimen (accession no.: DG-2018HN-1Y) has been deposited in the Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

2.3 Extraction and Isolation

The dried powders of *D. gelonioides* (8 kg) was percolated with 95% EtOH (3 × 25 L, RT) and the crude extract (200 g) was partitioned with EtOAc/H_2O. The EtOAc soluble fraction (90 g) was fractionated using an MCI gel column eluted with MeOH/H_2O (from 3:7 to 10:0) to afford five major fractions (A–E). Fraction C (7.2 g) was separated by passage over a silica gel CC (petroleum ether/acetone, 8:1 to 1:2) to give five fractions (C1–C5). Fraction C4 (2.1 g) was subjected to a silica gel CC (petroleum ether/EtOAc, 5:1 to 1:5) and yielded six major fractions (C4a–C4f). C4c (130 mg) was purified by semipreparative HPLC (75% CH_3CN in H_2O, 3 mL/min) to afford **2** (13 mg) and **3** (24 mg). C4d (100

mg) was purified by semipreparative HPLC (75% CH_3CN in H_2O, 3 mL/min) to afford compound **13** (3.1 mg). Fraction C4e (700 mg) was fractionated on a column of silica gel (dichloromethane/methanol, 100:1 to 10:1), then purified by semipreparative HPLC (70–80% CH_3CN in H_2O, 3 mL/min) to afford compounds **7** (7.5 mg) and **9** (6.2 mg). Fraction D (7.9 g) was fractionated by a series of CC columns, including a reversed C-18 silica gel column (MeOH/H_2O, 5:5 to 10:0), and two steps of silica gel columns (fist eluted by petroleum ether-acetone, from 20:1 to 1:5, then dichloromethane-isopropanol, from 40:1 to 25:1), before being purified by semipreparative HPLC (70–80% CH_3CN in H_2O, 3 mL/min) to afford compounds **14** (1.5 mg), **18** (10 mg) and **20** (8.2 mg). Fraction E (8.2 g) was chromatographed over a silica gel CC (petrol ether-acetone, 20:1 to 1:1) to afford six subfractions E1−E6. Fraction E3 (720 mg) was orthogonally chromatographed on a reversed column (MeOH/H_2O, 5:5 to 10:0) and a normal (dichloromethane-isopropanol, 80:1 to 25:1) silica gel columns before being purified by semipreparative HPLC to afford compounds **4** (15 mg). Fraction E4 (1.1 g) was fractionated by silica gel CC (dichloromethane-isopropanol, 80:1 to 25:1) to afford E4a−E4f. Application of semipreparative HPLC (80% MeOH in H_2O, 3 mL/min) led to the purification of **8** (2.7 mg), **11** (9.0 mg) and **12** (9.6 mg) from fraction E4a; **10** (9.1 mg, 80% MeOH in H_2O, 3 mL/min) from E4b; **15** (5.5 mg, 65% CH_3CN in H_2O, 3 mL/min) from E4c; **6** (8.5 mg, 65% CH_3CN in H_2O, 3 mL/min) from E4d; and **1** (15 mg, 75% CH_3CN in H_2O, 3 mL/min) from E4e, respectively. Fraction E5 (570 mg) was chromatographed on a reversed C-18 silica gel column, and then purified by semipreparative HPLC to afford **5** (4.1 mg) and **17** (12 mg).

2.4 Physical constants and spectral data of 1–20

*Compound **1** (5R, 7R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: colorless crystals (MeOH); mp: 236–238 °C; $[\alpha]^{22}_D$ +4 (*c* 0.6, MeOH); UV (MeOH) λ_{max} (log ε) 283 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 285 (+1), 226 (–4) nm; IR (KBr) ν_{max} 3467, 2962, 1748, 1599, 1391, 1299, 1197, 1168, 1028, 968, 754, 695 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 1; (–)-ESIMS *m/z* 629 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 629.3492 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_7$, 629.3484).

*Compound **2** (5R, 7R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: white, amorphous powder; $[\alpha]^{22}_D$ +22 (*c* 0.5, MeOH); UV (MeOH) λ_{max} (log ε) 283 (4.3) nm; ECD (MeOH) λ_{max} (log ε) 287 (+3), 227 (–5) nm; IR (KBr) ν_{max} 3432, 2962, 2875, 1760, 1593, 1447, 1385, 1308, 1191, 1093, 1043, 986, 751, 695 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 1; (–)-ESIMS *m/z* 629 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 629.3452 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_7$, 629.3484).

*Compound **3** (5R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: colorless crystals (MeOH); mp: 232–234 °C; $[\alpha]^{22}_D$ –32 (*c* 0.5, MeOH); UV(MeOH) λ_{max} (log ε) 280 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 301 (–2),

266 (+2), 227 (–10) nm; IR (KBr) ν_{max} 3506, 2962, 2914, 1787, 1700, 1448, 1422, 1294, 1271, 1159, 985, 751, 694 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 1; (–)-ESIMS *m/z* 627 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 627.3329 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_7$, 627.3327).

*Compound **4** (5R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: white, amorphous powder; $[\alpha]^{22}_D$ –17 (*c* 0.4, MeOH); UV(MeOH) λ_{max} (log ε) 281 (4.0) nm; ECD (MeOH) λ_{max} (log ε) 299 (–2), 265 (+2), 227 (–6) nm; IR (KBr) ν_{max} 3397, 2964, 1765, 1704, 1448, 1389, 1373, 1268, 1194, 1092, 994, 737, 694, 658 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 1; (–)-ESIMS *m/z* 627 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 627.3327 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_7$, 627.3327).

*Compound **5** (2S, 5R, 7R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S, 2′S)*: white, amorphous powder; $[\alpha]^{22}_D$ –40 (*c* 0.4, MeOH); ECD (MeOH) λ_{max} (log ε) 286 (–1), 256 (–1), 220 (–7) nm; IR (KBr) ν_{max} 3411, 2954, 2872, 1759, 1453, 1386, 1267, 1194, 1161, 1055, 995, 735, 698 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 2; (+)-ESIMS *m/z* 617 $[M + H]^+$; (–)-ESIMS *m/z* 615 $[M - H]^-$, 661 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 661.3381 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_9$, 661.3382).

*Compound **6** (2R, 5R, 7R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S, 2′R)*: white, amorphous powder; $[\alpha]^{22}_D$ –55 (*c* 0.5, MeOH); ECD (MeOH) λ_{max} (log ε) 285 (–1), 255 (–1), 225 (–16) nm; IR (KBr) ν_{max} 3416, 2937, 1762, 1452,1385, 1265, 1161, 1029, 1002, 986, 914, 734, 699 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 2; (–)-ESIMS *m/z* 661 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 661.3378 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_9$, 661.3382).

*Compound **7** (2S, 5R, 7R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R, 2′S)*: white, amorphous powder; $[\alpha]^{22}_D$ –42 (*c* 0.8, MeOH); ECD (MeOH) λ_{max} (log ε) 276 (–1), 251 (–1), 219 (–7) nm; IR (KBr) ν_{max} 3426, 2956, 2872, 1772, 1620, 1447, 1385, 1325, 1200, 1090, 1049, 995, 763, 698, 662 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 2; (–)-ESIMS *m/z* 661 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 661.3376 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_9$, 661.3382).

*Compound **8** (2R, 5R, 7R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R, 2′R)*: white, amorphous powder; $[\alpha]^{22}_D$ –28 (*c* 0.4, MeOH); ECD (MeOH) λ_{max} (log ε) 287 (–1), 251 (0), 223 (–9) nm; IR (KBr) ν_{max} 3438, 2926, 1759, 1452, 1389, 1326, 1260, 1193, 1090, 1041, 995, 941, 734, 698, 661 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 2; (–)-ESIMS *m/z* 661 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 661.3381 $[M + HCO_2]^-$ (calcd for $C_{39}H_{49}O_9$, 661.3382).

*Compound **9** (2S, 5R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S, 2′S)*: white, amorphous powder; $[\alpha]^{22}_D$ –83 (*c* 0.3, MeOH); ECD (MeOH) λ_{max} (log ε) 292 (–6), 254 (–2), 222 (–9) nm; IR (KBr) ν_{max} 3434, 2958, 1767, 1705, 1453, 1389, 1272, 1167, 1070, 999, 759, 735, 699 cm^{-1}; ^{1}H and ^{13}C NMR ($CDCl_3$, 500

MHz), see Table 3; (+)-ESIMS *m/z* 615 $[M + H]^+$; (–)-ESIMS *m/z* 659 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 659.3201 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_9$, 659.3226).

*Compound **10** (2R, 5R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S, 2′R)*: white powder; $[\alpha]^{22}_D$ –113 (*c* 0.3, MeOH); ECD (MeOH) λ_{max} (log ε) 294 (–3), 255 (–1), 222 (–14) nm; IR (KBr) ν_{max} 3407, 2938, 2877, 1768, 1704, 1452, 1391, 1166, 1074, 699 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 3; (+)-ESIMS *m/z* 615.5 $[M + H]^+$; (–)-ESIMS *m/z* 659.5 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 659.3216 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_9$, 659.3226).

*Compound **11** (2S, 5R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R, 2′S)*: white, amorphous powder; $[\alpha]^{22}_D$ –91 (*c* 0.3, MeOH); ECD (MeOH) λ_{max} (log ε) 296 (–4), 245 (0), 219 (–8) nm; IR (KBr): ν_{max} 3418, 2958, 2876, 1766, 1705, 1602, 1453, 1389, 1195, 1056, 758, 735, 699, 660 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 3; (+)-ESIMS *m/z* 615.5 $[M + H]^+$; (–)-ESIMS *m/z* 659.5 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 659.3224 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_9$, 659.3226).

*Compound **12** (2R, 5R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R, 2′R)*: white, amorphous powder; $[\alpha]^{22}_D$ –50 (*c* 0.3, MeOH); ECD (MeOH) λ_{max} (log ε) 292 (–4), 255 (–2), 225 (–6) nm; IR (KBr) ν_{max} 3435, 2923, 2854, 1766, 1704, 1454, 1375, 1326, 1264, 1193, 1092, 966, 940, 878, 736, 699 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 3; (–)-ESIMS *m/z* 613 $[M - H]^-$, *m/z* 659 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 613.3184 $[M - H]^-$ (calcd for $C_{38}H_{45}O_7$, 613.3171).

*Compound **13** (5R, 7R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: white, amorphous powder; $[\alpha]^{22}_D$ –69 (*c* 0.2, MeOH); UV(MeOH) λ_{max} (log ε) 223 (4.0), 293 (4.2) nm; ECD (MeOH) λ_{max} (log ε) 279 (–4), 257 (–3), 234 (–7), 210 (–1) nm; IR (KBr) ν_{max} 3414, 2927, 1762, 1603, 1449, 1384, 1265, 1161, 1068, 1002, 760, 736, 693 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 4; (–)-ESIMS *m/z* 643 $[M + HCO_2]^-$, 579 $[M - H_2O - H]^-$; (+)-HRMS (ESI) *m/z* 599.3376 $[M + H]^+$(calcd for $C_{38}H_{47}O_6$, 599.3367).

*Compound **14** (5R, 7R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: colorless crystals (MeOH); mp: 190–192 °C; $[\alpha]^{22}_D$ –54 (*c* 0.3, MeOH); UV(MeOH) λ_{max} (log ε) 223 (4.0), 295 (4.2) nm; ECD (MeOH) λ_{max} (log ε) 286 (–3), 245 (–1), 232 (–5), 216 (+2) nm; IR (KBr) ν_{max} 3397, 2958, 1761, 1602, 1384, 1196, 760, 693 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 4; (+)-ESIMS *m/z* 599.5 $[M + H]^+$, (–)-ESIMS *m/z* 643.6 $[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 643.3262 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_8$, 643.3276).

*Compound **15** (5R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: white, amorphous powder; $[\alpha]^{22}_D$ –131 (*c* 0.2, MeOH); UV(MeOH) λ_{max} (log ε) 222 (4.0), 293 (4.2) nm; IR (KBr): ν_{max} 3417, 2961, 2878, 1770, 1705, 1602, 761, 736, 694 cm^{-1}; ECD (MeOH) λ_{max} (log ε) 294 (–7), 251 (–1), 232 (–9), 214 (+3) nm; ^1H and ^{13}C NMR ($CDCl_3$, 500 MHz), see Table 4; (+)-ESIMS *m/z* 597.6 $[M + H]^+$, (–)-ESIMS *m/z* 641.4

$[M + HCO_2]^-$; (–)-HRMS (ESI) *m/z* 641.3101 $[M + HCO_2]^-$ (calcd for $C_{39}H_{45}O_8$, 641.3120).

Compound ***16*** *(5R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: white, amorphous powder; $[\alpha]^{22}_D$ −100 (*c* 0.1, MeOH); UV(MeOH) λ_{max} (log ε) 222 (3.9), 292 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 294 (−7), 251 (−1), 232 (−5), 214 (+3) nm; IR (KBr): ν_{max} 3443, 2961, 2878, 1770, 17065, 1603, 1165, 1069, 760, 736, 693 cm^{-1}; ^1H and ^{13}C NMR data ($CDCl_3$, 500 MHz), see Table 4; (+)-ESIMS *m/z* 597.4 $[M + H]^+$, (–)-ESIMS *m/z* 595.0 $[M - H]^-$; (+)-HRMS (ESI) *m/z* 597.3219 $[M + H]^+$ (calcd for $C_{38}H_{45}O_6$, 597.3211).

Compound ***17*** *(5R, 7R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: white, amorphous powder; $[\alpha]^{22}_D$ −24 (*c* 0.3, MeOH); UV(MeOH) λ_{max} (log ε) 224 (4.1), 255 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 288 (+1), 220 (–8) nm; IR (KBr): ν_{max} 3425, 2959, 2927, 2876, 1767, 1683, 1661, 1597, 1448, 1384, 1264, 735, 694 cm^{-1}; ^1H and ^{13}C NMR data (acetone-d_6, 500 MHz), see Table 5; (+)-ESIMS *m/z* 615.6 $[M + H]^+$; (–)-ESIMS *m/z* 659.5 $[M + HCO_2]^-$; (–)-HRESIMS *m/z* 659.3220 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_9$, 659.3226).

Compound ***18*** *(5R, 7R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: white, amorphous powder; $[\alpha]^{22}_D$ –11 (*c* 0.4, MeOH); UV(MeOH) λ_{max} (log ε) 219 (4.0), 255 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 278 (+1), 219 (–5) nm; IR (KBr): ν_{max} 3444, 2960, 2877, 1765, 1687, 1661, 1597, 1448, 1391, 1327, 1195, 734, 693 cm^{-1}; ^1H and ^{13}C NMR data (acetone-d_6, 500 MHz), see Table 5; (+)-ESIMS *m/z* 615.8 $[M + H]^+$; (–)-ESIMS *m/z* 659.5 $[M + HCO_2]^-$; (–)-HRESIMS *m/z* 659.3215 $[M + HCO_2]^-$ (calcd for $C_{39}H_{47}O_9$, 659.3226).

Compound ***19*** *(5R, 8R, 9R, 10S, 13S, 14S, 17S, 20R, 22R, 23S)*: white, amorphous powder; $[\alpha]^{22}_D$ –40 (*c* 0.1, MeOH); UV(MeOH) λ_{max} (log ε) 215 (4.1), 253 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 295 (–4), 263 (–1), 220 (–10) nm; IR (KBr): ν_{max} 3397, 2970, 2926, 1770, 1705, 1663, 1597, 1449, 1393, 1271, 1196, 1172, 735, 701 cm^{-1}; ^1H and ^{13}C NMR data (acetone-d_6, 500 MHz), see Table 5; (+)-ESIMS *m/z* 613.3 $[M + H]^+$, (–)-ESIMS 611.3 $[M - H]^-$; (−)-HRMS (ESI) *m/z* 613.3160 $[M + H]^-$ (calcd for $C_{38}H_{45}O_7$, 613.3160).

Compound ***20*** *(5R, 8R, 9R, 10S, 13S, 14S, 17R, 20R, 23R)*: white, amorphous powder; $[\alpha]^{22}_D$ –85 (*c* 0.3, MeOH); UV(MeOH) λ_{max} (log ε) 215 (4.1), 251 (4.1) nm; ECD (MeOH) λ_{max} (log ε) 293 (–4), 266 (–1), 219 (–7) nm; IR (KBr): ν_{max} 3444, 2963, 2879, 1766, 1704, 1662, 1597, 1448, 1195, 735, 702 cm^{-1}; ^1H and ^{13}C NMR data (acetone-d_6, 500 MHz), see Table 5; (+)-ESIMS *m/z* 613.3 $[M + H]^+$, (–)-ESIMS 657.6 $[M + HCO_2]^-$; (−)-HRMS (ESI) *m/z* 657.3057 $[M + HCO_2]^-$ (calcd for $C_{39}H_{45}O_9$, 657.3069).

2.5 X-ray Crystallographic Analysis for Compounds 1, 3 and 14

2.5.1 X-ray Crystallographic Data of 1

Colorless single crystals of compound **1** were obtained in MeOH at room temperature. A suitable crystal with approximate dimensions 0.12 × 0.1 × 0.08 mm^3, was selected for the X-ray crystallographic analysis on the Bruker APEX-II CCD diffractometer using Cu Kα radiation (λ = 1.34139 Å). Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using least-squares minimisation.[1] Crystallographic data of **1** were deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2010767). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Crystallographic data of **1***. $C_{38}H_{48}O_5$, M = 584.76, Monoclinic, space group was $P121$, a = 46.6254(9) Å, b = 6.72390(10) Å, c = 10.3609(2) Å, $\alpha = \gamma = 90$ °, β = 96.1270(10) °, V = 3229.63(10) $Å^3$, Z = 4, T = 169.98 K, D_{calcd} = 1.203 g/cm^3, μ(Cu Kα) = 0.396 mm^{-1}, and F(000) = 1264. A total of 21379 reflections were collected in the range 6.636 °< 2θ< 109.770 °, including 6014 independent reflections (R_{int} = 4.67%, R_{sigma} = 3.96%). The final R_1 was 0.0554 ($I > 2\sigma(I)$), and wR_2 was 0.1514 (all data). The goodness of fit on F^2 was 1.021. The absolute configuration was determined by the Flack parameter = 0.04 (13).

2.5.2 X-ray Crystallographic Data of 3

Colorless single crystals of compound **3** were obtained in MeOH at room temperature. A suitable crystal with approximate dimensions 0.09 × 0.06 × 0.04 mm^3, was selected for the X-ray crystallographic analysis on the Bruker D8 VENTURE diffractometer using Cu Kα radiation (λ = 1.54178 Å). Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using least-squares minimisation.[1] Crystallographic data of **3** were deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2082769). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Crystallographic data of **3***. $C_{38}H_{46}O_5$, M = 582.75, Monoclinic, space group was $C2$, a = 18.0938(10) Å, b = 7.0743(4) Å, c = 24.2239(14) Å, $\alpha = \gamma = 90$ °, β = 92.505(3) °, V = 3097.7(3) $Å^3$, Z = 4, T = 170.0 K, D_{calcd} = 1.250 g/cm^3, μ(Cu Kα) = 0.641 mm^{-1}, and F(000) = 1256.0. A total of 19994 reflections were collected in the range 3.65 °< 2θ< 144.206 °, including 5765 independent reflections (R_{int} = 5.67%, R_{sigma} = 5.50%). The final R_1 was 0.0516 ($I > 2\sigma(I)$), and wR_2 was 0.1279 (all data). The goodness of fit on F^2 was 1.087. The absolute configuration was determined by the Flack parameter = 0.13 (12).

2.5.3 X-ray Crystallographic Data of 14

Colorless single crystals of compound **14** were obtained in MeOH at room temperature. A suitable crystal with approximate dimensions 0.12 × 0.08 × 0.06 mm^3, was selected for the X-ray crystallographic analysis on the Bruker APEX-II CCD diffractometer using Cu Kα radiation (λ = 1.34139 Å). Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using least-squares minimisation.[1] Crystallographic data of **14** were deposited at the Cambridge Crystallographic Data Centre (deposition number: CCDC 2010766). Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: + 44(0)-1233-336033 or e-mail: deposit@ccdc.cam.ac.uk].

*Crystallographic data of **14***. $C_{39}H_{50}O_7$, M = 630.79, orthorhombic, space group was $P2_12_12_1$, a = 10.4979(3) Å, b = 43.8716(9) Å, c = 7.7286(2) Å, $\alpha = \beta = \gamma = 90$ °, V = 3508.99(13) $Å^3$, Z = 4, T = 170.02 K, D_{calcd} = 1.194 g/cm^3, μ (Cu Kα) = 0.415 mm^{-1}, and F(000) = 1360. A total of 36336 reflections were collected in the range 7.012 °< 2θ< 109.848 °, including 6629 independent reflections (R_{int} = 3.97%, R_{sigma} = 2.55%). The final R_1 was 0.0384 ($I > 2\sigma(I)$), and wR_2 was 0.0998 (all data). The goodness of fit on F^2 was 1.013. The absolute configuration was determined by the Flack parameter = 0.03 (5).

3. Structural Elucidation Section

3.1 structure elucidation of 1–20

The structure of dichapegenin A (**1**) was assigned by the COSY, HMBC, and NOESY data, as drawn (Figure S1).

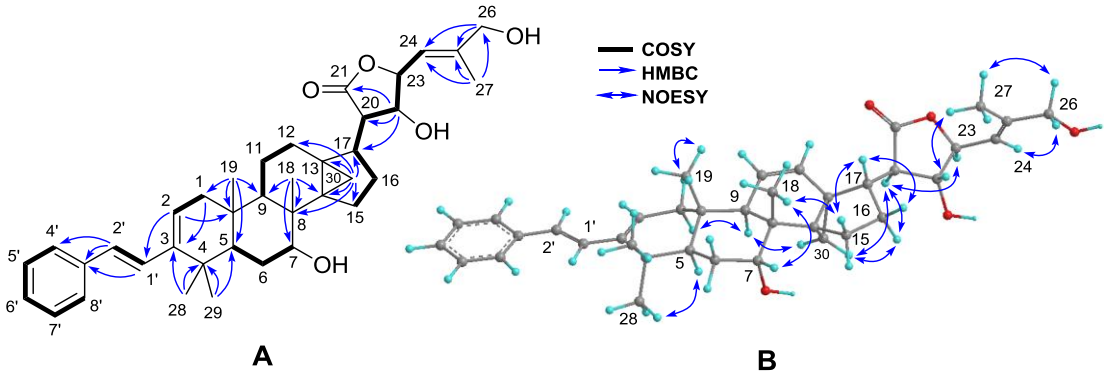


Figure S1. (A) Key HMBC, COSY (bold bonds), and (B) NOESY correlations for **1**.

Dichapegenin B (**2**) shared the molecular formula, $C_{38}H_{48}O_5$, with **1** based on the HRMS (ESI) and ^{13}C NMR data. Analysis of the NMR data (Table 1) of **2** revealed its structure to be closely related with that of compound **1**, with the only difference being the location of the hydroxy group within the γ-lactone moiety. Instead of having a HO-22 group in **1**, compound **2** contained a HO-20 group, as deduced by the HMBC correlations (Figure S29) from H_2-22 to C-20 (δ_C 79.8) and C-21 (δ_C 177.1). Observed negative Cotton effect at ~230 nm in the ECD spectrum caused by a γ-lactone n→π* transition, suggested a 23*S* absolute configuration for **2**.[2] The downfield shifted H-23 ($\Delta\delta_H$ 0.29) of **2** to that in dichapetalin A,[3] caused by a 1,3-diaxial steric hindrance effect between HO-20 and H-23, indicated that the HO-20 group is α-oriented. The stereochemistry for other chiral carbons in compound **2** was assigned the same as these in compound **1**, as supported by their similar NMR and NOESY data (Figure S30).

The molecular formula, $C_{38}H_{46}O_5$, of **3**, established by the HR ESIMS and ^{13}C NMR data combined with initial interpretation of the NMR data (Table S1), suggested compound **3** to be a structural analogue of **1**. Comparison of the NMR data revealed compound **3** contains a C-7 keto-carbonyl group instead of the HO-7 group in **1**, based on the HMBC correlations from H_3-18 (δ_H 1.20, s) and H-5 (δ_H 1.67, dd, J = 14.3, 3.0 Hz) to C-7 (δ_C 214.7). The structure of dichapegenin C (**3**), established by the HMBC and NOESY data (Figures S38 and S39), was thus assigned as shown.

Analysis of the NMR data indicated that compound **4** is structurally related with that of compound **2**, with the major difference being the presence of an extra keto-carbonyl group. The carbonyl group was attached to C-7, as verified by the HMBC cross-peaks from H_3-18 (δ_H 1.21, s) and H-5 (δ_H 1.68, dd, J = 14.3, 3.0 Hz) to C-7 (δ_C 214.7). The structure of dichapelonin D (**4**) was thus established by the HMBC and NOESY data (Figures S47 and S48), as shown.

Four pairs of isolates **5**/**6**, **7**/**8**, **9**/**10**, and **11**/**12**, each sharing a common 2D structure with a novel phenyl-endoperoxide functionality, were established by their HMBC and COSY correlations (Figure S2A). Compounds **13**–**15** were verified to possess a new phenyl-furan moiety that fused with the A ring through C-2 and C-3 (Figure S2B). Compounds **17**, **18**, and **20** were assigned to possess a novel phenyl-enedione functionality that furnished between the A ring and C-3 appendage (Figure S2C).

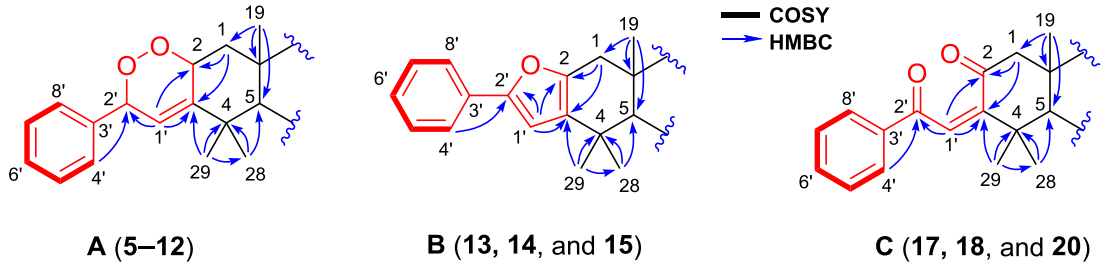


Figure S2. Key HMBC and COSY (bold bonds) correlations for the shared partial structures of (A) compounds **5**–**12**, (B) compounds **13**–**15**, and (C) compounds **17**, **18**, and **20**.

Table S1. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **1–4** in $CDCl_3$.

No.	**1**			**2**			**3**			**4**		
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type
1α	1.76, brd (17.3)	42.0	CH_2	1.77, brd (17.4)	42.0	CH_2	1.73, brd (17.4)	41.8	CH_2	1.72, brd (17.5)	41.8	CH_2
1β	2.23, dd (17.3, 6.6)			2.23, dd (17.4, 6.6)			2.31, dd (17.4, 6.6)			2.30, dd (17.5, 6.6)		
2	5.85, dd (6.6, 1.9)	119.8	CH	5.85, dd (6.6, 2.1)	119.9	CH	5.85, dd (6.6, 2.1)	119.3	CH	5.86, dd (6.6 2.1)	119.4	CH
3		144.4	C		144.4	C		143.9	C		143.9	C
4		36.4	C		36.4	C		37.4	C		37.4	C
5	1.84*	44.2	CH	1.84*	44.2	CH	1.67, dd (14.3, 3.0)	54.1	CH	1.68, dd (14.3, 3.0)	54.1	CH
6α	1.84*	25.9	CH_2	1.82*	25.9	CH_2	2.32, dd (13.0, 3.0)	37.4	CH_2	2.32, dd (13.0, 3.0)	37.4	CH_2
6β							2.82, dd (13.0, 14.3)			2.81, dd (13.0, 14.3)		
7	3.98, brs	72.8	CH	3.97, brt (2.7)	72.9	CH		214.7	C		214.7	C
8		36.3	C		36.2	C		48.1	C		48.0	C
9	2.01, dd (2.9, 2.4)	46.1	CH	2.00, dd (3.0, 2.5)	45.7	CH	1.94, dd (3.0, 2.6)	53.0	CH	1.96, dd (3.1, 2.4)	52.6	CH
10		35.7	C		35.7	C		35.7	C		35.7	C
11	5.52, dd (10.0, 2.4)	125.2	CH	5.43, dd (10.0, 2.5)	124.1	CH	5.44, dd (9.9, 2.6)	121.5	CH	5.37, dd (10.1, 2.4)	120.4	CH
12	6.13, dd (10.0, 2.9)	128.4	CH	6.49, dd (10.0, 3.0)	131.3	CH	6.24, dd (9.9, 3.0)	130.5	CH	6.60, dd (10.1, 3.1)	133.5	CH
13		29.5	C		29.1	C		30.8	C		30.3	C
14		35.7	C		35.7	C		35.9	C		36.0	C
15α	1.71, dd (12.7, 8.3)	25.0	CH_2	1.68, dd (12.6, 8.3)	24.9	CH_2	2.14, dd (13.0, 8.3)	27.1	CH_2	2.16, dd (13.1, 8.5)	26.9	CH_2
15β	2.08, m			2.05*			1.99, m			1.98, m		
16α	1.16*	23.1	CH_2	1.10*	24.7	CH_2	1.20*	23.3	CH_2	1.13*	24.9	CH_2
16β	1.82*			1.81*			1.76*			1.77*		
17	2.67, ddd (11.8, 7.4, 4.8)	40.1	CH	2.54, dd (11.1, 7.4)	47.8	CH	2.57, ddd (12.1, 7.5, 5.0)	40.2	CH	2.46, dd (11.1, 7.6)	47.8	CH
18	0.93, s	17.6	CH_3	0.94, s	17.6	CH_3	1.20, s	17.1	CH_3	1.21, s	17.1	CH_3
19	0.99, s	17.8	CH_3	0.99, s	17.8	CH_3	1.19, s	17.4	CH_3	1.18, s	17.4	CH_3
20	3.12, dd (9.6, 4.8)	48.9	CH		79.8	C	3.06, dd (9.3, 5.0)	48.9	CH		79.9	C
21		175.3	C		177.1	C		175.3	C		177.2	C
22α		74.3	CH	2.40, dd (13.8, 5.6)	38.3	CH_2		74.3	CH	2.38, dd (13.6, 5.7)	38.5	CH_2
22β	4.22, dd (9.6, 7.8)			2.04*			4.22, dd (9.3, 7.5)			2.04, dd (13.6, 9.4)		
23	4.90, dd (8.7, 7.8)	79.3	CH	5.43, m	74.9	CH	4.89, dd (8.9, 7.5)	79.2	CH	5.43, ddd (9.4, 8.7, 5.7)	74.9	CH
24	5.53, dq (8.7, 1.4)	119.6	CH	5.51, dq (8.7, 1.3)	121.5	CH	5.49, dq (8.9, 1.5)	119.7	CH	5.52, dq (8.7, 1.5)	121.6	CH
25		144.3	C		142.5	C		144.2	C		142.5	C
26a	4.08, d (15.2)	67.3	CH_2	4.06, d (15.2)	67.2	CH_2	4.07, d (15.0)	67.3	CH_2	4.09, brs	67.3	CH_2
26b	4.11, d (15.2)			4.09, d (15.2)			4.09, d (15.0)					
27	1.81, d (1.4)	14.6	CH_3	1.77, d (1.3)	14.3	CH_3	1.79, d (1.5)	14.6	CH_3	1.77, d (1.5)	14.3	CH_3
28	1.14, s	29.5	CH_3	1.14, s	29.5	CH_3	1.11, s	29.3	CH_3	1.11, s	29.3	CH_3
29	1.02, s	21.3	CH_3	1.02, s	21.3	CH_3	1.06, s	21.0	CH_3	1.05, s	21.0	CH_3
30a	0.90, d (5.0)	15.1	CH_2	0.96, d (5.2)	16.1	CH_2	0.95, d (5.9)	13.9	CH_2	1.00, d (6.1)	14.9	CH_2
30b	1.23, brd (5.0)			1.31, brd (5.2)			1.17, brd (5.9)			1.28, brd (6.1)		
1′	6.81, d (15.8)	129.0	CH	6.81, d (15.8)	129.1	CH	6.78, d (15.7)	128.2	CH	6.78, d (15.8)	128.3	CH
2′	6.70, d (15.8)	128.5	CH	6.70, d (15.8)	128.5	CH	6.71, d (15.7)	129.2	CH	6.71, d (15.8)	129.2	CH
3′		138.1	C		138.2	C		137.9	C		137.9	C
4′(8′)	7.40, brd (7.6)	126.4	CH	7.40, brd (7.6)	126.4	CH	7.40, brd (7.2)	126.5	CH	7.40, brd (7.2)	126.5	CH
5′(7′)	7.30, brt (7.6)	128.7	CH	7.31, brt (7.6)	128.7	CH	7.31, brt (7.6)	128.7	CH	7.31, brt (7.6)	128.7	CH
6′	7.20, brt (7.2)	127.2	CH	7.21, brt (7.3)	127.1	CH	7.22, brt (7.3)	127.4	CH	7.21, brt (7.3)	127.4	CH

*Signals are overlapped.

Table S2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **5–8** in $CDCl_3$.

No.	**5**			**6**			**7**			**8**		
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type
1α	1.85, dd (13.3, 9.9)	45.6	CH_2	0.97, dd (11.9, 11.9)	43.8	CH_2	1.87, dd (13.2, 9.9)	45.6	CH_2	0.97, dd (11.9, 12.1)	43.5	CH_2
1β	1.96, dd (13.3, 7.9)			2.20, dd (11.9, 4.9)			1.96, dd (13.2, 8.3)			2.20, dd (11.9, 4.8)		
2	4.85, ddt (9.9, 7.9, 2.1)	75.3	CH	5.00, ddt (11.9, 4.9, 1.9)	75.0	CH	4.85, ddt (9.9, 8.3, 2.1)	75.3	CH	5.01, ddt (12.1, 4.8, 1.9)	75.0	CH
3		146.6	C		147.3	C		146.6	C		147.3	C
4		37.5	C		38.8	C		37.6	C		38.7	C
5	1.99, dd (11.9, 3.8)	42.5	CH	1.72, dd (12.7, 2.1)	47.4	CH	1.99, m	42.5	CH	1.72, dd (12.6, 2.3)	47.3	CH
6α	1.75–1.80*	26.4	CH_2	1.91, ddd (14.2, 3.5, 2.1)	25.4	CH_2	1.75–1.80*	26.4	CH_2	1.92, ddd (14.2, 3.7, 2.5)	25.5	CH_2
6β				1.83, ddd (14.2, 12.7, 2.2)						1.84*		
7	3.95, brt (2.6)	72.4	CH	3.96, dd (3.5, 2.2)	72.6	CH	3.93, brt (2.4)	72.4	C	3.95, dd (3.6, 2.2)	72.6	C
8		36.4	C		36.9	C		36.3	C		36.8	C
9	2.14, dd (3.1, 2.4)	47.1	CH	1.94, dd (3.0, 2.4)	47.8	CH	2.13, dd (3.1, 2.4)	46.8	CH	1.95, dd (3.0, 2.5)	47.4	CH
10		37.9	C		37.7	C		37.9	C		37.6	C
11	5.46, dd (10.0, 2.4)	125.2	CH	5.47, dd (10.0, 2.4)	124.5	CH	5.36, dd (10.0, 2.4)	124.2	CH	5.38, dd (10.2, 2.5)	123.5	CH
12	6.13, dd (10.0, 3.1)	128.7	CH	6.09, dd (10.0, 3.0)	128.7	CH	6.48, dd (10.0, 3.1)	131.7	CH	6.45, dd (10.2, 3.0)	131.7	CH
13		29.4	C		29.6	C		29.2	C		29.3	C
14		35.4	C		35.1	C		35.4	C		35.2	C
15α	1.70, dd (12.8, 8.3)	25.0	CH_2	1.68, dd (12.9, 8.3)	25.0	CH_2	1.66, dd (12.9, 8.5)	24.9	CH_2	1.66, dd (12.9, 8.5)	24.9	CH_2
15β	2.06, m			2.06, m			2.03, m			2.07, m		
16α	1.15*	23.0	CH_2	1.13*	23.0	CH_2	1.08*	24.6	CH_2	1.09, m	24.7	CH_2
16β	1.83*			1.81*			1.83*			1.82*		
17	2.67, ddd (11.9, 7.3, 4.7)	39.9	CH	2.65, ddd (11.9, 7.3, 4.7)	39.9	CH	2.51, dd (11.1, 7.4)	47.7	CH	2.52, dd (11.1, 7.5)	47.7	CH
18	0.89, s	17.2	CH_3	0.91, s	17.6	CH_3	0.89, s	17.2	CH_3	0.93, s	17.6	CH_3
19	1.12, s	20.7	CH_3	1.14, s	18.6	CH_3	1.11, s	20.7	CH_3	1.13, s	18.5	CH_3
20	3.12, dd (9.6, 4.7)	48.7	CH	3.09, dd (9.6, 4.7)	48.7	CH		79.8	C		79.8	C
21		175.2	C		175.3	C		177.0	C		177.0	C
22α		74.2	CH		74.1	CH	2.42, dd (13.8, 5.6)	38.2	CH_2	2.39, dd (13.8, 5.6)	38.1	CH_2
22β	4.21, ddd (9.6, 7.7, 3.8)			4.18, dd (9.6, 7.7)			2.05, dd (13.8, 9.2)			2.02, dd (13.8, 9.4)		
23	4.89, dd (8.8, 7.7)	79.2	CH	4.87, dd (8.9, 7.7)	79.2	CH	5.44, ddd (9.2, 8.8, 5.6)	74.9	CH	5.44, ddd (9.4, 8.8, 5.6)	75.0	CH
24	5.52, dq (8.8, 1.5)	119.5	CH	5.52, dq (8.9, 1.5)	119.5	CH	5.50, dq (8.8, 1.5)	121.4	CH	5.49, dq (8.8, 1.5)	121.3	CH
25		144.4	C		144.5	C		142.6	C		142.6	C
26	4.10, brs	67.2	CH_2	4.09, brs	67.2	CH_2	4.08, brs	67.2	CH_2	4.07, brs	67.2	CH_2
27	1.80, d (1.5)	14.6	CH_3	1.79, d (1.5)	14.6	CH_3	1.76, d (1.5)	14.3	CH_3	1.76, d (1.5)	14.3	CH_3
28	1.16, s	32.0	CH_3	1.21, s	27.5	CH_3	1.15, s	32.0	CH_3	1.20, s	27.5	CH_3
29	1.16, s	22.2	CH_3	1.06, s	24.0	CH_3	1.16, s	22.2	CH_3	1.06, s	24.1	CH_3
30a	0.92, d (5.0)	15.2	CH_2	0.85, d (5.0)	14.9	CH_2	0.95, d (5.4)	16.2	CH_2	0.93, d (5.0)	16.0	CH_2
30b	1.20, brd (5.0)			1.16, brd (5.0)			1.29, brd (5.4)			1.28, brd (5.0)		
1′	5.86, brt (2.1)	117.1	CH	5.90, dd (3.8, 1.6)	116.1	CH	5.85, brt (2.1)	117.1	CH	5.90, dd (3.8, 1.6)	116.1	CH
2′	5.57, brt (2.2)	80.6	CH	5.43, dd (3.8, 1.8)	81.0	CH	5.57, brt (2.2)	80.6	CH	5.43, dd (3.8, 1.8)	81.0	CH
3′		138.2	C		139.2	C		138.2	C		139.3	C
4′(8′)	7.36*	128.7	CH	7.38*	128.7	CH	7.37*	128.7	CH	7.39*	128.7	CH
5′(7′)	7.36*	128.8	CH	7.35*	128.5	CH	7.37*	128.8	CH	7.36*	128.5	CH
6′	7.36*	129.0	CH	7.31*	128.5	CH	7.37*	129.0	CH	7.33*	128.5	CH

*Signals are overlapped.

Table S3. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **9–12** in $CDCl_3$.

No.	**9**			**10**			**11**			**12**		
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type
1α	1.84, dd (13.6, 9.7)	45.0	CH_2	0.98, dd (12.0, 12.0)	43.8	CH_2	1.84, dd (13.6, 9.9)	44.9	CH_2	0.98, dd (12.1, 12.4)	43.7	CH_2
1β	2.03, dd (13.6, 7.9)			2.30, dd (12.0, 4.9)			2.02, dd (13.6, 7.9)			2.30, dd (12.1, 4.8)		
2	4.79, ddt (9.7, 7.9, 2.1)	74.7	CH	5.01, ddt (12.0, 4.8, 1.9)	74.5	CH	4.79, ddt (10.0, 8.0, 2.0)	74.8	CH	5.02, ddt (12.4, 4.8, 1.9)	74.6	CH
3		145.3	C		146.1	C		145.4	C		146.2	C
4		38.2	C		39.6	C		38.2	C		39.6	C
5	1.84, dd (14.2, 3.5)	52.1	CH	1.45, dd (14.4, 2.4)	56.6	CH	1.84, dd (14.2, 3.5)	52.1	CH	1.46, dd (14.4, 2.4)	56.6	CH
6α	2.23, dd (13.2, 3.5)	37.4	CH_2	2.42, dd (13.2, 2.4)	37.0	CH_2	2.22, dd (13.2, 3.5)	37.4	CH_2	2.41, dd (13.3, 2.4)	37.0	CH_2
6β	2.81, dd (13.2, 14.2)			2.85, dd (13.2, 14.4)			2.80, dd (13.2, 14.2)			2.84, dd (13.3, 14.4)		
7		213.8	C		213.2	C		214.0	C		213.3	C
8		47.9	C		48.4	C		47.6	C		48.2	C
9	2.08, dd (3.1, 2.6)	53.8	CH	1.92, dd (3.1, 2.6)	53.8	CH	2.07, dd (3.1, 2.6)	53.5	CH	1.92, dd (3.0, 2.5)	53.4	CH
10		37.9	C		37.7	C		37.8	C		37.7	C
11	5.40, dd (10.0, 2.6)	121.6	CH	5.43, dd (10.0, 2.6)	121.0	CH	5.29, dd (10.0, 2.6)	120.3	CH	5.33, dd (10.0, 2.5)	120.0	CH
12	6.22, dd (10.0, 3.1)	131.0	CH	6.19, dd (10.0, 3.1)	130.9	CH	6.58, dd (10.0, 3.1)	134.1	CH	6.56, dd (10.0, 3.1)	133.8	CH
13		30.7	C		31.1	C		30.4	C		30.6	C
14		35.8	C		35.7	C		35.8	C		35.8	C
15α	2.16, dd (13.3, 8.3)	27.1	CH_2	2.18, dd (13.3, 8.3)	27.2	CH_2	2.12, dd (13.2, 8.5)	26.9	CH_2	2.16, dd (13.4, 8.5)	27.1	CH_2
15β	1.97, m			2.00, m			1.92, m			1.98, m		
16α	1.15*	23.1	CH_2	1.10*	23.3	CH_2	1.07, m	24.8	CH_2	1.10*	24.9	CH_2
16β	1.78*			1.76*			1.74*			1.77*		
17	2.58, ddd (11.7, 7.4, 4.8)	40.1	CH	2.57, ddd (11.7, 7.4, 4.9)	40.1	CH	2.41, dd (11.1, 7.5)	47.8	CH	2.43, dd (11.1, 7.5)	47.8	CH
18	1.18, s	16.8	CH_3	1.18, s	17.2	CH_3	1.17, s	16.7	CH_3	1.18, s	17.1	CH_3
19	1.32, s	20.2	CH_3	1.34, s	18.1	CH_3	1.31, s	20.1	CH_3	1.34, s	18.1	CH_3
20	3.08, dd (9.5, 4.8)	48.9	CH	3.06, dd (9.5, 4.9)	48.9	CH		79.9	C		79.9	C
21		175.2	C		175.3	C		177.1	C		177.0	C
22α		74.3	CH		74.3	CH	2.38, dd (13.8, 5.6)	38.2	CH_2	2.37, dd (13.8, 5.6)	38.3	CH_2
22β	4.22, dd (9.4, 7.7)			4.20, dd (9.5, 7.6)			2.03, dd (13.8, 9.4)			2.02, dd (13.8, 9.4)		
23	4.89, dd (8.9, 7.7)	79.1	CH	4.87, dd (8.8, 7.6)	79.2	CH	5.43, ddd (9.4, 8.7, 5.7)	75.0	CH	5.42, ddd (9.4, 8.8, 5.6)	74.9	CH
24	5.52, dq (8.9, 1.5)	119.6	CH	5.52, dq (8.8, 1.5)	119.7	CH	5.50, dq (8.7, 1.5)	121.6	CH	5.51, dq (8.8, 1.5)	121.5	CH
25		144.3	C		144.3	C		142.5	C		142.6	C
26	4.11, brs	67.3	CH_2	4.10, brs	67.3	CH_2	4.07, brs	67.3	CH_2	4.08, brs	67.3	CH_2
27	1.80, d (1.5)	14.6	CH_3	1.79, d (1.5)	14.6	CH_3	1.75, d (1.5)	14.3	CH_3	1.76, d (1.5)	14.3	CH_3
28	1.15, s	31.8	CH_3	1.18, s	27.2	CH_3	1.15, s	31.8	CH_3	1.18, s	27.2	CH_3
29	1.18, s	22.0	CH_3	1.10, s	23.3	CH_3	1.18, s	22.0	CH_3	1.10, s	23.4	CH_3
30a	0.94, d (5.6)	14.1	CH_2	0.91, d (5.9)	13.8	CH_2	0.94, d (6.2)	15.1	CH_2	0.96, d (5.0)	14.9	CH_2
30b	1.16, brd (5.6)			1.18, brd (5.9)			1.23, d (6.2)			1.27, d (5.0)		
1′	5.92, brt (2.1)	118.1	CH	5.92, dd (3.7, 1.7)	117.4	CH	5.92, brt (2.1)	118.0	CH	5.92, dd (3.7, 1.7)	117.3	CH
2′	5.58, brt (2.1)	80.5	CH	5.45, dd (3.7, 1.8)	80.8	CH	5.58, brt (2.1)	80.5	CH	5.46, dd (3.7, 1.8)	80.9	CH
3′		137.9	C		138.8	C		137.9	C		138.8	C
4′(8′)	7.37*	129.1	CH	7.31–7.36*	128.5	CH	7.37*	128.7	CH	7.31–7.36*	128.5	CH
5′(7′)	7.37*	128.8	CH	7.31–7.36*	128.6	CH	7.37*	128.8	CH	7.31–7.36*	128.6	CH
6′	7.37*	128.6	CH	7.31–7.36*	128.7	CH	7.37*	129.1	CH	7.31–7.36*	128.7	CH

*Signals are overlapped.

Table S4. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **13–16** in $CDCl_3$.

No.	**13**			**14**			**15**			**16**		
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type
1α	2.25, d (15.7)	39.5	CH_2	2.25, d (15.7)	39.5	CH_2	2.24, d (15.8)	39.4	CH_2	2.24, d (15.6)	39.4	CH_2
1β	2.79, d (15.7)			2.79, d (15.7)			2.87, d (15.8)			2.88, d (15.6)		
2		147.7	C		147.8	C		147.0	C		147.1	C
3		128.1	C		128.1	C		127.6	C		127.6	C
4		33.5	C		33.5	C		34.4	C		34.4	C
5	1.95, dd (12.9, 2.9)	44.3	CH	1.95, dd (13.1, 2.9)	44.3	CH	1.78, dd (14.4, 3.1)	54.0	CH	1.80, dd (14.4, 3.1)	54.1	CH
6α	1.85–1.92*	25.7	CH_2	1.86, m	25.7	CH_2	2.38, dd (13.2, 3.1)	36.9	CH_2	2.37, dd (13.1, 3.1)	36.9	CH_2
6β				1.89, ddd (14.1, 13.1, 2.9)						2.84, dd (13.1, 14.4)		
7	4.00, brt (2.8)	72.6	CH	3.98, brt (2.9)	72.6	CH	2.85, dd (13.2, 14.4)	214.1	C		214.2	C
8		36.6	C		36.5	C		48.0	C		47.8	C
9	2.19, dd (3.0, 2.4)	46.0	CH	2.19, dd (3.2, 2.9)	45.6	CH	2.14, dd (3.1, 2.6)	52.5	CH	2.14, dd (3.1, 2.6)	52.1	CH
10		38.9	C		38.8	C		38.8	C		38.8	C
11	5.56, dd (10.0, 2.4)	124.8	CH	5.46, dd (10.0, 2.9)	123.6	CH	5.51, dd (10.0, 2.6)	121.0	CH	5.42, dd (10.1, 2.6)	121.6	CH
12	6.19, dd (10.0, 3.0)	128.8	CH	6.55, dd (10.1, 3.2)	131.9	CH	6.28, dd (10.0, 3.1)	131.1	CH	6.66, dd (10.1, 3.1)	134.0	CH
13		29.5	C		29.3	C		30.9	C		30.4	C
14		35.7	C		35.7	C		36.1	C		36.1	C
15α	1.73, dd (12.6, 8.3)	25.1	CH_2	1.69, dd (12.6, 8.3)	24.9	CH_2	2.20, dd (12.9, 8.3)	27.2	CH_2	2.18, dd (13.0, 8.5)	27.0	CH_2
15β	2.10, m			2.05*			2.00, m			1.99, m		
16α	1.18*	23.1	CH_2	1.11*	24.7	CH_2	1.19*	23.3	CH_2	1.15*	24.9	CH_2
16β	1.84*			1.83*			1.80*			1.78*		
17	2.71, ddd (11.8, 7.4, 4.8)	40.0	CH	2.56, dd (11.2, 7.5)	47.8	CH	2.61, ddd (11.8, 7.4, 4.9)	40.3	CH	2.47, dd (11.3, 7.6)	47.8	CH
18	0.95, s	17.6	CH_3	0.96, s	17.5	CH_3	1.23, s	17.2	CH_3	1.24, s	17.1	CH_3
19	1.01, s	18.3	CH_3	1.01, s	18.2	CH_3	1.23, s	17.9	CH_3	1.22, s	17.8	CH_3
20	3.14, dd (9.6, 4.8)	48.9	CH		79.8	C	3.10, dd (9.5, 5.0)	49.0	CH		79.9	C
21		175.2	C		177.2	C		175.3	C		177.1	C
22α		74.3	CH	2.42, dd (13.8, 5.6)	38.3	CH_2		74.4	CH	2.42, dd (13.8, 5.6)	38.6	CH_2
22β	4.24, dd (9.6, 7.7)			2.05, dd (13.8, 9.4)			4.24, ddd (9.5, 7.7, 3.3)			2.05, dd (13.8, 9.4)		
23	4.92, dd (8.9, 7.7)	79.2	CH	5.44, ddd (9.4, 8.7, 5.6)	75.0	CH	4.91, dd (8.9, 7.7)	79.3	CH	5.44, ddd (9.4, 8.7, 5.6)	74.9	CH
24	5.54, dq (8.9, 1.5)	119.6	CH	5.49, dq (8.7, 1.4)	121.5	CH	5.55, dd (8.9, 1.5)	119.7	CH	5.52, dq (8.7, 1.5)	119.9	CH
25		144.4	C		142.6	C		144.3	C		142.6	C
26	4.11, brs	67.3	CH_2	4.09, brs	67.2	CH_2	4.11, brs	67.3	CH_2	4.09, brs	67.3	CH_2
27	1.81, d (1.5)	14.6	CH_3	1.77, d (1.4)	14.3	CH_3	1.81, d (1.5)	14.6	CH_3	1.77, d (1.5)	14.3	CH_3
28	1.22, s	31.5	CH_3	1.22, s	31.5	CH_3	1.20, s	31.3	CH_3	1.20, s	31.3	CH_3
29	1.12, s	23.5	CH_3	1.12, s	23.5	CH_3	1.15, s	23.2	CH_3	1.15, s	23.2	CH_3
30a	0.93, d (5.0)	15.2	CH_2	0.99, d (5.0)	16.2	CH_2	0.96, d (5.8)	14.0	CH_2	1.03, d (5.8)	15.1	CH_2
30b	1.25, brd (5.0)			1.34, brd (5.0)			1.21, brd (5.8)			1.31, brd (5.8)		
1′	6.57, s	104.0	CH	6.57, s	104.0	CH	6.56, s	103.8	CH	6.56, s	103.8	CH
2′		152.4	C		152.4	C		153.1	CH		153.0	CH
3′		131.5	C		131.5	C		131.2	C		131.3	C
4′(8′)	7.61, brd (8.4)	123.3	CH	7.61, brd (8.4)	123.3	CH	7.61, brd (8.4)	123.4	CH	7.61, brd (8.3)	123.4	CH
5′(7′)	7.34, brt (7.8)	128.7	CH	7.34, brt (7.8)	128.7	CH	7.35, brt (7.8)	128.8	CH	7.35, brt (7.8)	128.8	CH
6′	7.19, brt (7.4)	126.8	CH	7.19, brt (7.4)	126.8	CH	7.21, brt (7.4)	127.1	CH	7.21, brt (7.4)	127.0	CH

*Signals are overlapped.

Table S5. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compounds **17–20** in acetone-d_6.

No.	**17**			**18**			**19**			**20**		
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	δ_C	type
1α	2.16, d (15.7)	57.1	CH_2	2.15, d (15.7)	57.0	CH_2	2.26, d (15.7)	55.9	CH_2	2.26, d (15.7)	55.9	CH_2
1β	2.67, d (15.7)			2.66, d (15.7)			2.70, d (15.7)			2.70, d (15.7)		
2		203.7	C		203.8	C		202.5	C		202.5	C
3		159.7	C		159.8	C		157.4	C		157.5	C
4		41.7	C		41.7	C		41.9	C		41.9	C
5	2.22, dd (12.6, 3.1)	46.0	CH	2.21, dd (12.8, 2.9)	45.9	CH	2.06*	54.3	CH	2.07, dd (14.0, 3.1)	54.4	CH
6α	1.84, dt (13.9, 3.4)	28.0	CH_2	1.83, ddd (13.9, 3.6, 2.9)	28.0	CH_2	2.31, dd (13.3, 3.1)	37.9	CH_2	2.33, dd (13.5, 3.1)	37.9	CH_2
6β	1.95, m			1.95, dd (13.9, 12.8)			3.03*			3.04, dd (14.0, 13.5)		
7	3.97, brt (2.8)	72.3	CH	3.96, dd (3.6, 3.1)	72.0	CH		212.7	C		212.5	C
8		37.3	C		37.0	C		48.9	C		48.5	C
9	2.26, dd (3.1, 2.4)	46.7	CH	2.26, dd (3.1, 2.4)	46.4	CH		52.5	CH	2.27, dd (3.1, 2.5)	52.2	CH
10		39.9	C		39.9	C		39.7	C		39.7	C
11	5.36, dd (10.1, 2.4)	122.6	CH	5.51, dd (10.1, 2.4)	122.3	CH	5.39, dd (10.0, 2.6)	119.8	CH	5.36, dd (10.1, 2.5)	119.6	CH
12	6.35, dd (10.1, 3.1)	132.3	CH	6.59, dd (10.1, 3.1)	134.4	CH	6.41, dd (10.0, 2.9)	133.7	CH	6.67, dd (10.1, 3.1)	135.7	CH
13		31.0	C		30.2	C		32.5	C		31.8	C
14		37.1	C		36.7	C		36.8	C		36.5	C
15α	1.76, m	25.2	CH_2	1.74*	25.0	CH_2	2.08, m	27.7	CH_2	2.10*	27.8	CH_2
15β	2.01, m			2.02*			1.97, m			1.99, m		
16α	1.38, m	24.7	CH_2	1.12*	25.3	CH_2	1.41, m	24.7	CH_2	1.16, m	25.1	CH_2
16β	1.70, dt (13.1, 8.0)			1.69, dt (13.1, 8.0)			1.68, dt (12.9, 8.0)			1.66, dt (13.1, 8.1)		
17	2.52, ddd (11.1, 7.5, 5.6)	42.0	CH	2.60, dd (11.3, 7.5)	47.8	CH	2.46, ddd (11.1, 7.7, 6.0)	42.0	CH	2.54, dd (11.3, 7.6)	47.7	CH
18	0.93, s	17.9	CH_3	0.95, s	17.8	CH_3	1.22, s	17.0	CH_3	1.23, s	17.0	CH_3
19	1.14, s	18.8	CH_3	1.14, s	18.7	CH_3	1.34, s	18.1	CH_3	1.34, s	18.1	CH_3
20	3.00, dd (8.9, 5.6)	50.0	CH		80.2	C	2.99*	49.9	CH		80.3	C
21		176.4	CH		177.2	C		176.5	C		177.1	C
22α		75.5	CH	2.30, dd (13.6, 5.3)	38.7	CH_2		75.5	CH	2.27, dd (13.6, 5.4)	38.7	CH_2
22β	4.18, dd (8.9, 7.1)			2.15, dd (13.6, 9.4)			4.17, brt (7.9)			2.20, dd (13.6, 9.4)		
23	4.88, dd (9.0, 7.1)	81.0	CH	5.44, ddd (9.4, 8.8, 5.3)	75.0	CH	4.87, dd (9.0, 7.0)	81.0	CH	5.43, ddd (9.4, 9.0, 5.4)	75.1	CH
24	5.51, dq (9.0, 1.4)	120.6	CH	5.51, dq (8.8, 1.4)	122.0	CH	5.50, dq (9.0, 1.4)	120.6	CH	5.52, dq (9.0, 1.4)	122.1	CH
25		144.4	C		143.2	C		144.4	C		143.3	C
26	3.99, brs	67.0	CH_2	3.97, brs	66.9	CH_2	3.98, brs	67.0	CH_2	4.00, brs	67.0	CH_2
27	1.74, d (1.4)	14.4	CH_3	1.74, d (1.4)	14.0	CH_3	1.74, d (1.4)	14.4	CH_3	1.73, d (1.4)	14.0	CH_3
28	1.30, s	31.5	CH_3	1.30, s	31.4	CH_3	1.34, s	31.1	CH_3	1.34, s	31.1	CH_3
29	1.29, s	24.7	CH_3	1.28, s	24.6	CH_3	1.33, s	24.5	CH_3	1.33, s	24.5	CH_3
30a	1.05, d (5.8)	17.2	CH_2	1.04, d (5.8)	17.4	CH_2	1.00, d (6.3)	15.0	CH_2	1.02, d (6.1)	15.2	CH_2
30b	1.24, brd (5.8)			1.26, brd (5.8)			1.26, brd (6.3)			1.30, brd (6.1)		
1′	6.85, s	129.8	CH	6.85, s	129.8	CH	6.90, s	131.6	CH	6.91, s	131.4	CH
2′		194.5	C		194.4	C		194.7	C		194.6	C
3′		138.1	C		138.0	C		137.9	C		137.9	C
4′(8′)	7.92, brd (8.2)	129.1	CH	7.92, brd (8.0)	129.1	CH	7.91, brd (7.7)	129.1	CH	7.91, brd (8.2)	129.1	CH
5′(7′)	7.49, brt (7.8)	129.4	CH	7.49, brt (7.8)	129.4	CH	7.49, brt (7.9)	129.4	CH	7.50, brt (7.7)	129.4	CH
6′	7.59, brt (7.5)	133.7	CH	7.59, brt (7.4)	133.7	CH	7.60, brt (7.4)	133.7	CH	7.59, brt (7.4)	133.7	CH

*Signals are overlapped.

Table S6. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR data of compound **21a** in acetone-d_6.

No.	**21a**			**21b**	
	δ_H, mult (*J* in Hz)	δ_C	type	δ_H, mult (*J* in Hz)	type
1α	2.10, d (14.9)	49.3	CH_2	1.27, d (13.9)	CH_2
1β	2.37, d (14.9)			3.10, d (13.9)	
2		115.7	C		C
3		148.2	C		C
4		35.7	C		C
5	2.02, dd (14.6, 3.6)	51.4	CH	1.38*	CH
6α	2.14*	37.2	CH_2	2.20, dd (13.5, 2.2)	CH_2
6β	2.81*			2.97*	
7		213.2	C		C
8		48.3	C		C
9	2.01, dd (2.9, 2.4)	54.0	CH	1.99*	CH
10		38.6	C		C
11	5.44, dd (10.0, 2.4)	120.7	CH	5.49, dd (10.2, 2.4)	CH
12	6.42, dd (10.0, 2.9)	133.6	CH	6.39, dd (10.2, 3.1)	CH
13		32.3	C		C
14		36.8	C		C
15α	1.93*	27.6	CH_2		CH_2
15β	2.04*				
16α	1.37*	24.6	CH_2		CH_2
16β	1.65, ddd (13.5, 8.0, 8.0)				
17	2.67, m	42.0	CH		CH
18	1.14, s	16.9	CH_3		CH_3
19	1.03, s	19.3	CH_3	1.54, s	CH_3
20	3.01, dd (9.6, 4.8)	49.9	CH	2.99*	CH
21		176.5	C		C
22α		75.4	CH		CH
22β	4.20, dd (8.8, 7.0)			4.20*	
23	4.88, dd (8.9, 7.1)	81.0	CH	4.88*	CH
24	5.51, dq (8.9, 1.5)	120.5	CH	5.51*	CH
25		144.4	C		C
26	3.98*	67.0	CH_2	3.98*	CH_2
27	1.75, brs	14.4	CH_3		CH_3
28	1.24, s	31.1	CH_3	1.26, s	CH_3
29	1.14, s	24.0	CH_3	1.20, s	CH_3
30a	1.01, d (6.1)	15.2	CH_2		CH_2
30b	1.24, brd (6.1)				
1′	6.01, s	128.5	CH	5.89, s	CH
2′		112.3	C		C
3′		141.8	C		C
4′(8′)	7.57, brd (7.4)	127.3	CH	7.49, brd (7.4)	CH
5′(7′)	7.40, brt (7.6)	129.2	CH	7.33, brt (7.6)	CH
6′	7.20, brt (7.3)	128.9	CH	7.27, brt (7.3)	CH
HOO-2	10.36, s		HOO	10.58, s	HOO
CH_3O-2′	3.22, s		CH_3	3.23, s	CH_3

*Signals are overlapped.

Due to small amount of **21b**, only part of its ^{1}H NMR data were assigned.

3.2 NMR Calculations

The ChemDraw_15.0 software with the MM2 force field was used to establish the initial conformers for the target molecules. A molecular mechanics conformational analysis was carried out using mixed torsional/low-mode sampling method with the MMFF force field (gas phase) on Maestro 10.2 software (Maestro Technologies, Inc., Trenton, NJ, USA). The lowest energy conformers within 21.0 kcal/mol were subjected to further DFT calculations. The geometries of the conformers were optimized at the B3LYP/6-31+G (d,p) level in gas using the Gaussian 09 program (Gaussian, Inc., Wallingford, CT, USA),[4] and the following NMR calculations were performed at the B3LYP/6-311+G (2d,p) level in chloroform (SMD model). The calculated chemical shifts of each conformer were empirically scaled according to the formula $\delta_{cal} = (b - \sigma)/-m$, where δ_{cal} is the calculated chemical shift relative to TMS, σ is the computed isotropic shielding constant, m is the slope, and b is the intercept. The ^{13}C shifts used the generic scaling factors $m = -1.0537$, and $b = 181.7815$, as obtained from the CHESHIRE Web page.[5] The final chemical shifts were generated by averaging the data of all the conformers according to their Boltzmann distribution at 298.15 K.

Table S7. Differential carbon chemical shifts ($\Delta\delta_C$) for selected carbons of isomeric pairs.

$\Delta\delta$	**5** vs. **6**	**7** vs.**8**	**9** vs.**10**	**11** vs.**12**	Mα-Ph vs. Mβ-Ph	Mα-Me vs. Mβ-Me	Mα-H vs. Mβ-H
C-1	1.8	2.1	1.2	1.2	–0.2	–0.5	–0.2
C-2	0.3	0.3	0.2	0.2	0.4	0.1	0.4
C-3	–0.7	–0.7	–0.8	–0.8	–1.2	–1.0	–1.2
C-4	–1.3	–1.1	–1.4	–1.4	–1.3	–1.5	–1.3
C-5	–4.9	–4.8	–4.5	–4.5	–4.9	–4.8	–4.9
C-6	1	0.9	0.4	0.4	1.4	1.5	1.4
C-19	2.1	2.2	2.1	2	1.9	2.1	1.9
C-28	4.5	4.5	4.6	4.6	3.9	3.6	3.9
C-29	–1.8	–1.9	–1.3	–1.4	–2.5	–2.4	–2.5

Table S8. Re-optimized conformers, energies, and proportions for Mα/Mβ-Ph.

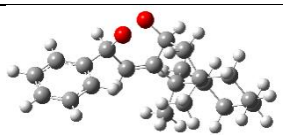
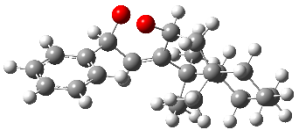
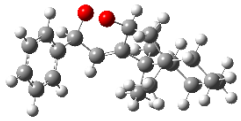
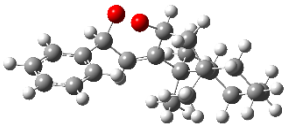
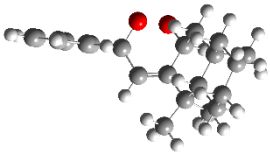
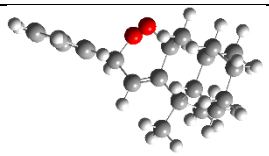
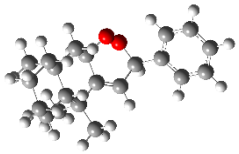
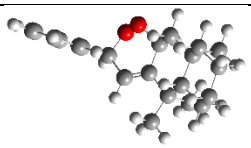
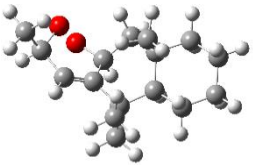
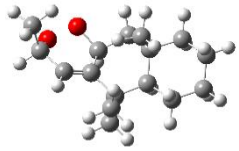
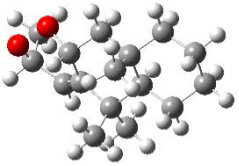
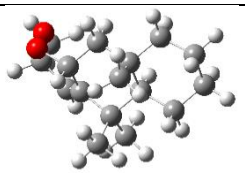
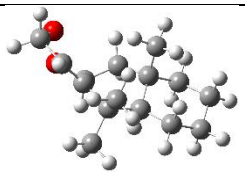
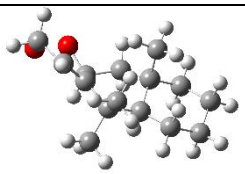
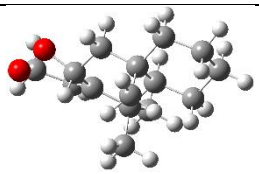
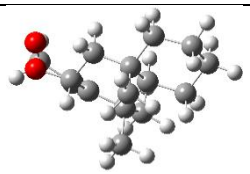
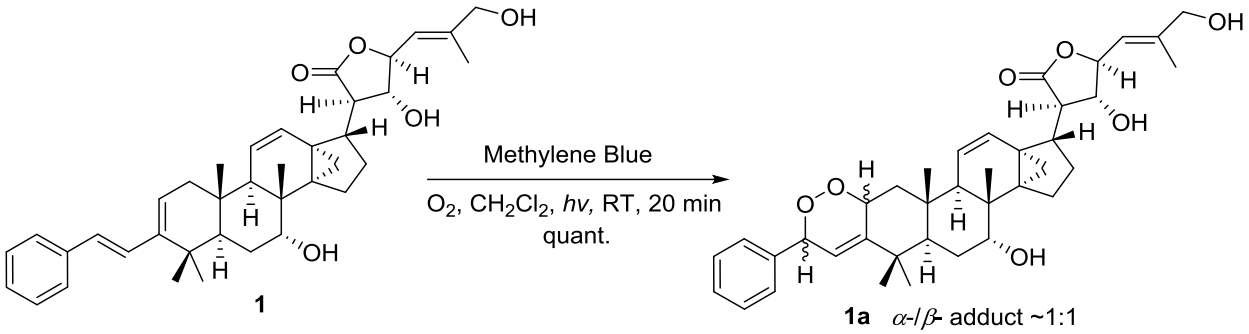
Number	Conformer	Energy (hartree)	Energy (Kcal/mol)	Proportion (%)
	Mα-Ph			
1		-967.4830459	-607105.2861	75.49
2		-967.4810624	-607104.0415	9.22
3		-967.4806521	-607103.784	5.97
4		-967.4810719	-607104.0474	9.32
	Mβ-Ph			
1		-967.4854005	-607106.764	29.05
2		-967.4854213	-607106.777	29.70
3		-967.4845715	-607106.243	12.07
4		-967.4854047	-607106.766	29.18

Table S9. Re-optimized conformers, energies, and proportions for Mα/Mβ-Me and –H.

Number	Conformer	Energy (hartree)	Energy (Kcal/mol)	Proportion (%)
	Mα-Me			
1		-775.7462211	-486788.511	81.76
2		-775.7448054	-486787.623	18.24
	Mβ-Me			
1		-775.7488	-486790.1429	62.52
2		-775.7483	-486789.84	37.48
	Mα-H			
1		-736.4239	-462113.382	74.60
2		-736.4229	-462112.744	25.40
	Mβ-H			
3		-736.4269	-462115.2558	73.02
4		-736.426	-462114.6662	26.98

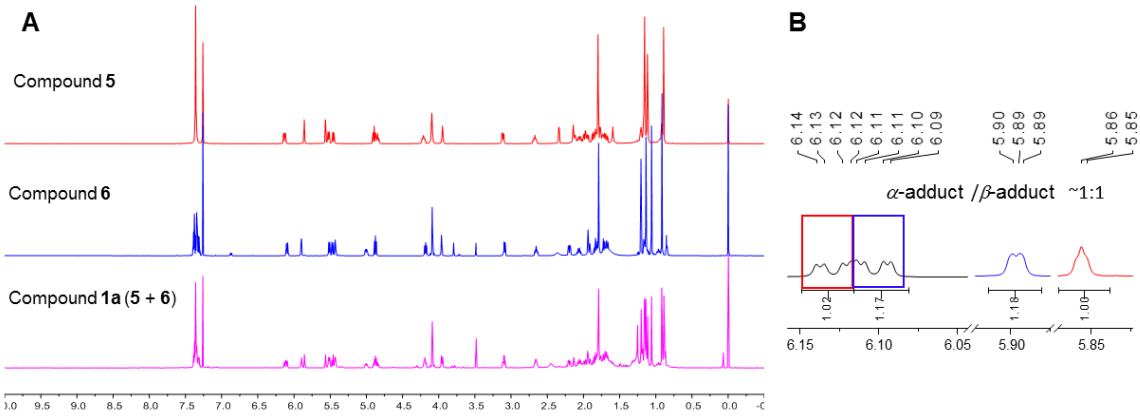
4. Synthesis Section

4.1 Biomimetic synthesis of 1a from 1

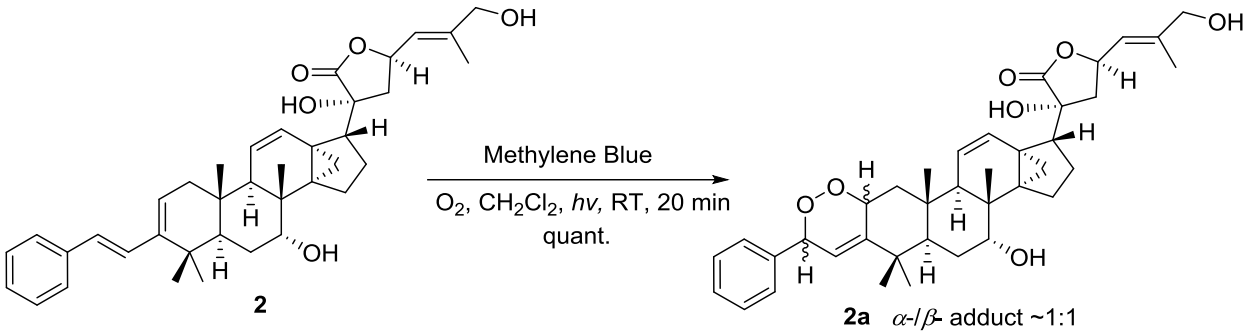


To an oxygen bubbled solution of **1** (4.5 mg, 7.7 μmol) in CH_2Cl_2 (1.5 mL) at room temperature was added methylene blue (0.2 mg, 0.6 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was then subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to give **1a** (4.8 mg, ~99%) as white powder. ESI-MS: *m/z* 617.2 $[M + H]^+$, 615.4 $[M - H]^-$. The ^{1}H NMR spectra (Figure S3) showed **1a** contain a mixture of an equal proportion of α- and β-adducts, similar to these of phyenyl-endoperoxides **5** and **6**.

Figure S3. (A) Comparison of the ^{1}H NMR spectra of **1a** with **5** and **6**, and (B) expanded ^{1}H NMR spectra of **1a**

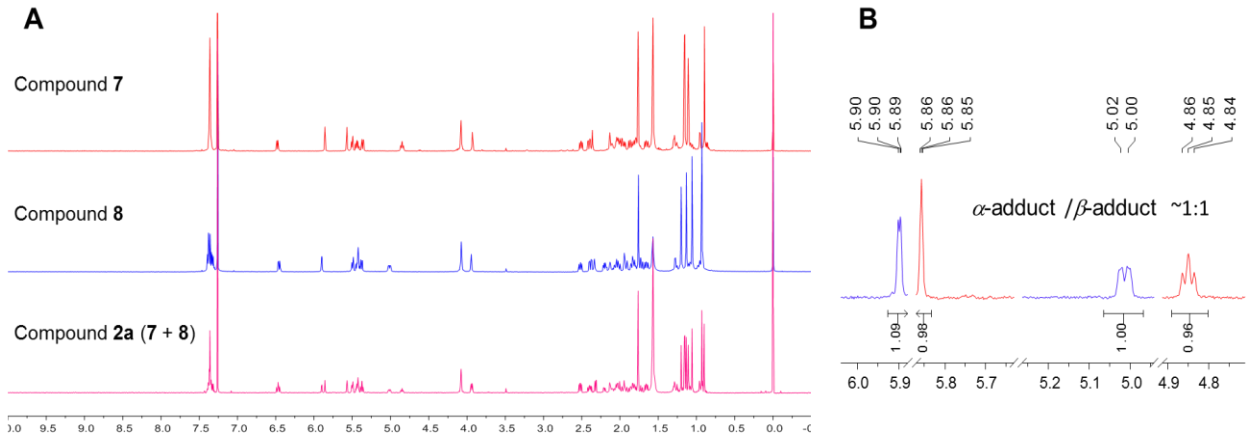


4.2 Biomimetic synthesis of 2a from 2

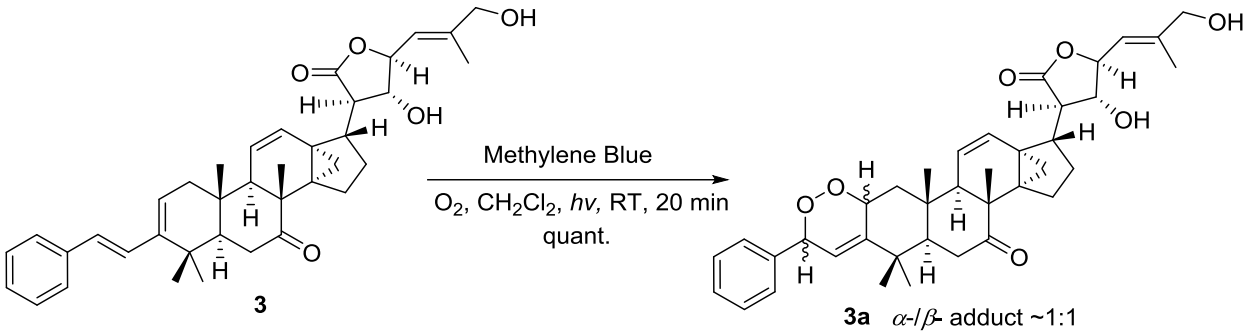


To an oxygen bubbled solution of **2** (3.8 mg, 6.5 μmol) in CH_2Cl_2 (1.5 mL) at room temperature was added methylene blue (0.2 mg, 0.6 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was then subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to give **2a** (4.1 mg, ~99%) as white powder. ESI-MS: *m/z* 615.4 $[M - H]^-$. The ^{1}H NMR data (Figure S4) showed **2a** contain a mixture of an equal proportion of α- and β-adducts, similar to these of phyenyl-endoperoxides **7** and **8**.

Figure S4. (A) Comparison of the ^{1}H NMR spectra of **2a** with **7** and **8**, and (B) expanded ^{1}H NMR spectra of **2a**

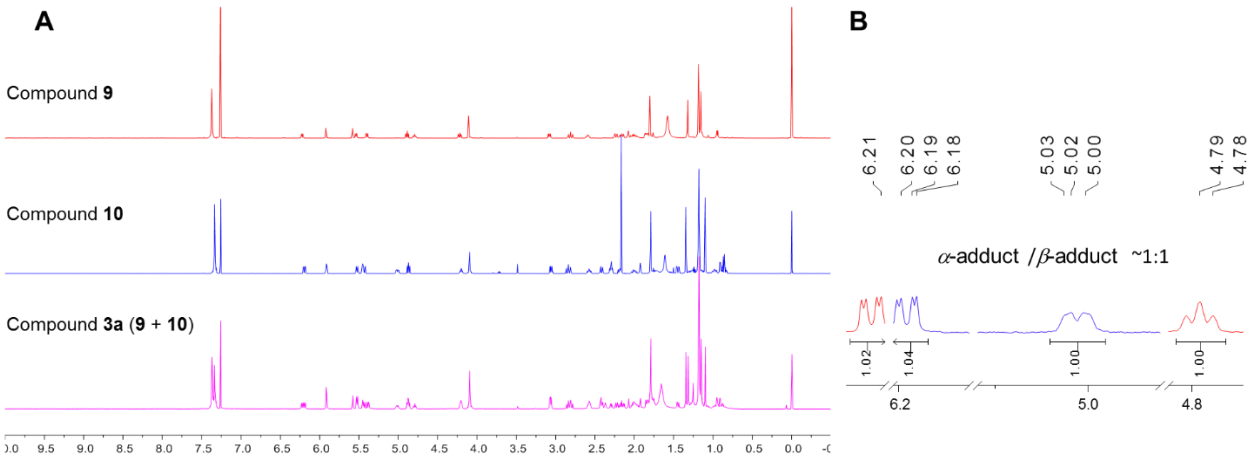


4.3 Biomimetic synthesis of 3a from 3

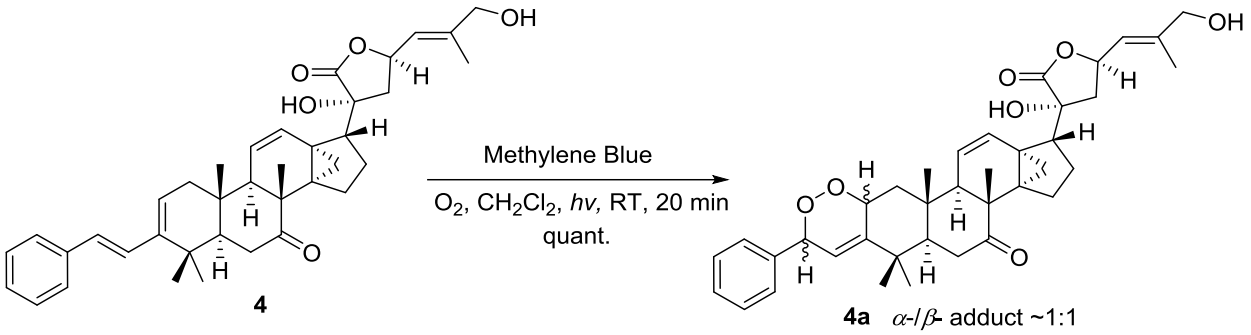


To an oxygen bubbled solution of **3** (6.5 mg, 11 μmol) in CH_2Cl_2 (1.5 mL) at room temperature was added methylene blue (0.2 mg, 0.6 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was then subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to give **3a** (6.8 mg, ~99%) as white powder. ESI-MS: *m/z* 615.4 $[M + H]^+$, 613.5 $[M - H]^-$. ^{1}H NMR analysis (Figure S5) showed **3a** contain a mixture of an equal proportion of α- and β-adducts, similar to these of phyenyl-endoperoxides **9** and **10**.

Figure S5. (A) Comparison of the ^{1}H NMR spectra of **3a** with **9** and **10**, and (B) expanded ^{1}H NMR spectra of **3a**

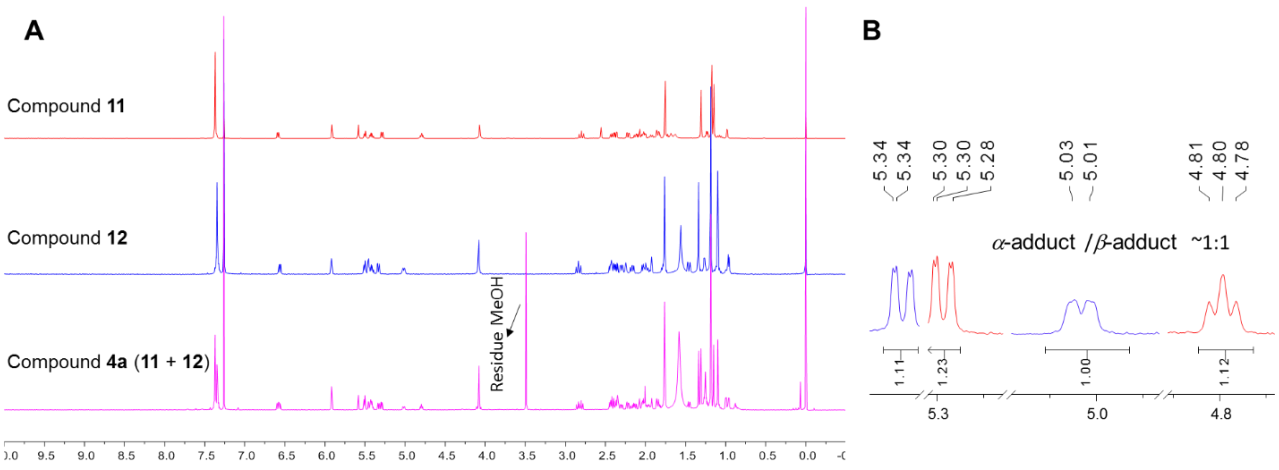


4.4 Biomimetic synthesis of 4a from 4

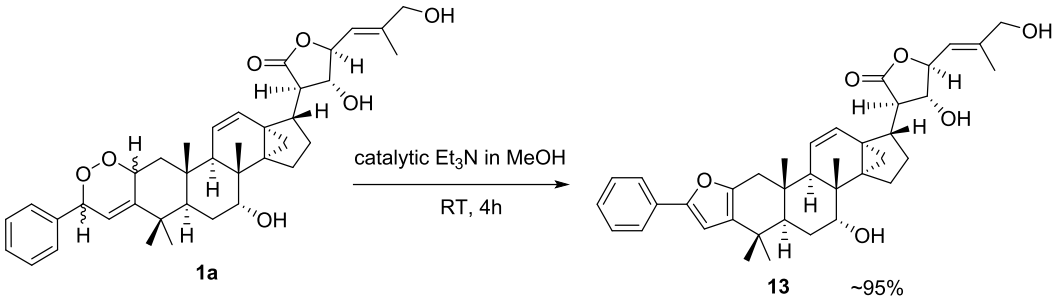


To an oxygen bubbled solution of **4** (2.2 mg, 3.8 μmol) in CH_2Cl_2 (1.5 mL) at room temperature was added methylene blue (0.2 mg, 0.6 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was then subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to give **4a** (2.3 mg, ~99%) as white powder. ESI-MS: *m/z* 613.3 $[M - H]^-$, 1227.3 $[2M - H]^-$. ^{1}H NMR analysis (Figure S6) showed **4a** containe a mixture of an equal proportion of α- and β-adducts, similar to these of phyenyl-endoperoxides **11** and **12**.

Figure S6. (A) Comparison of the ^{1}H NMR spectra of **4a** with **11** and **12**, and (B) expanded ^{1}H NMR spectra of **4a**

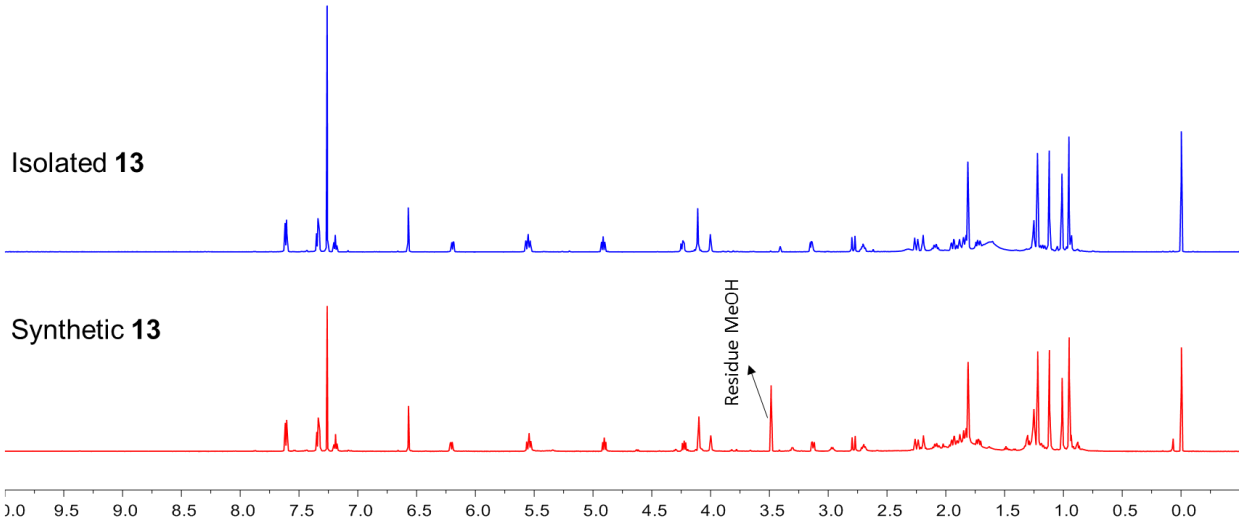


4.5 Biomimetic synthesis of 13 from 1a

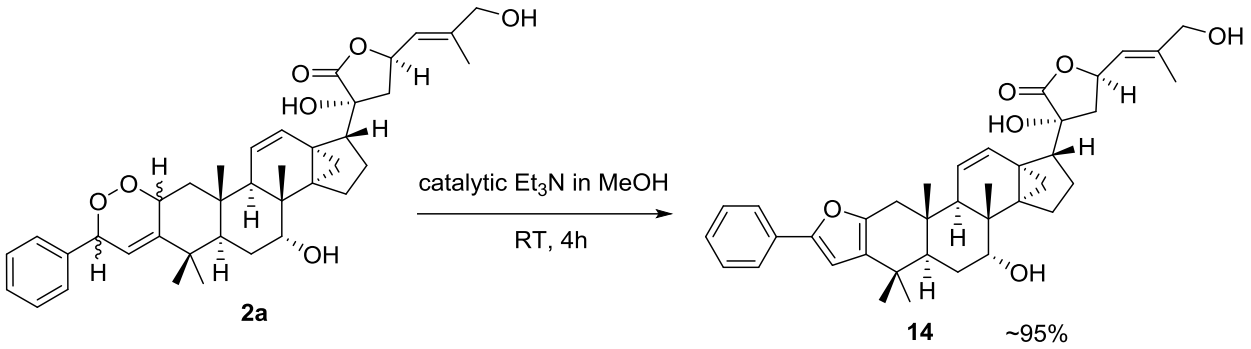


To 1.0 mL methanol solution of **1a** (3.8 g, 6.2 μmol), catalytic Et_3N (20 μL) was added and the solution was kept at room temperature until a complete conversion of the starting material was detected by TLC (~4 h). Methanol and residue Et_3N were removed in vacuo to afford **13** (3.5 mg, ~95%) as white powder. ESI-MS: *m/z* 597.3 $[M - H]^-$, 579.4 $[M - H_2O - H]^-$.

Figure S7. (A) Comparison of the ^1H NMR spectra of synthetic **13** and isolated **13**

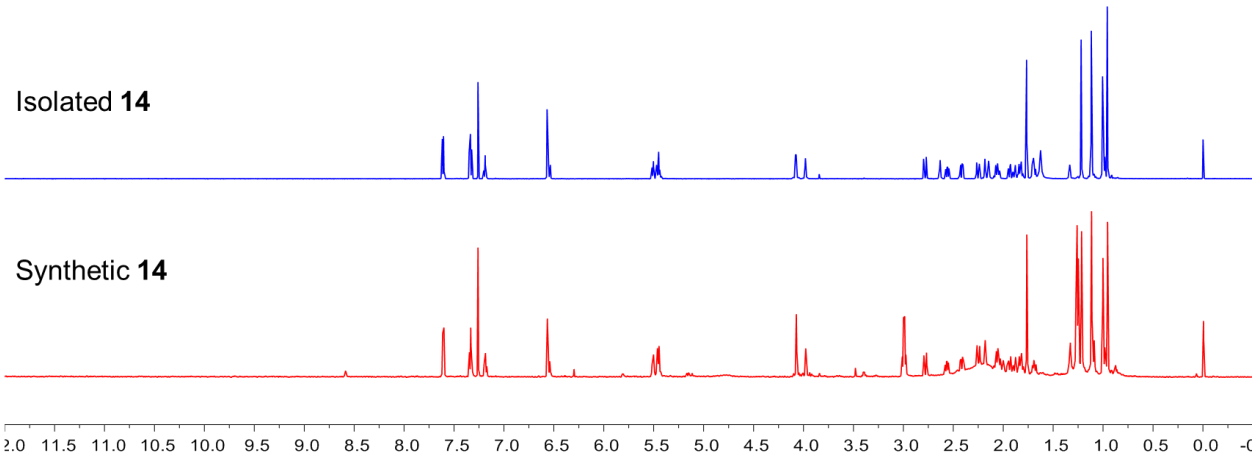


4.6 Biomimetic synthesis of 14 from 2a

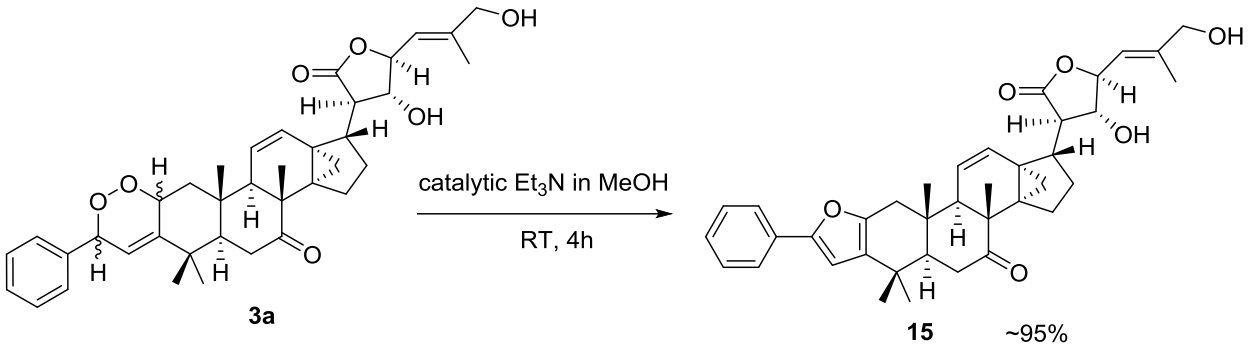


To 1.0 mL methanol solution of **2a** (2.8 g, 4.5 μmol), catalytic Et_3N (15 μL) was added and the solution was kept at room temperature until a complete conversion of the starting material was detected by TLC (~4 h). Methanol and residue Et_3N were removed in vacuo to afford **14** (2.7 mg, ~95%) as white powder. ESI-MS: *m/z* 599.4 $[M + H]^+$, 597.1 $[M - H]^-$.

Figure S8. (A) Comparison of the ^1H NMR spectra of synthetic **14** and isolated **14**

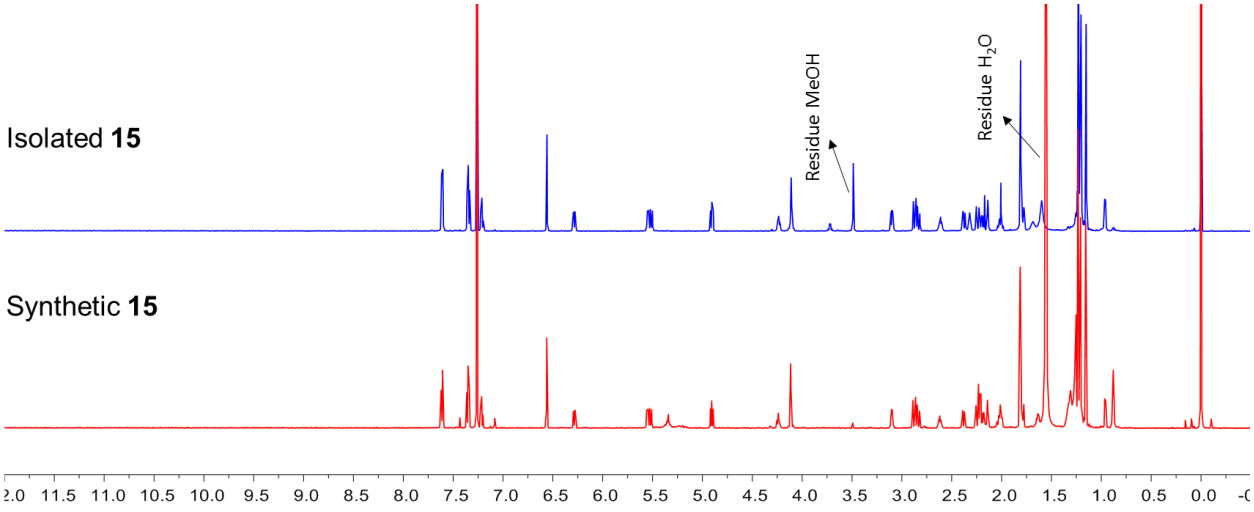


4.7 Biomimetic synthesis of 15 from 3a

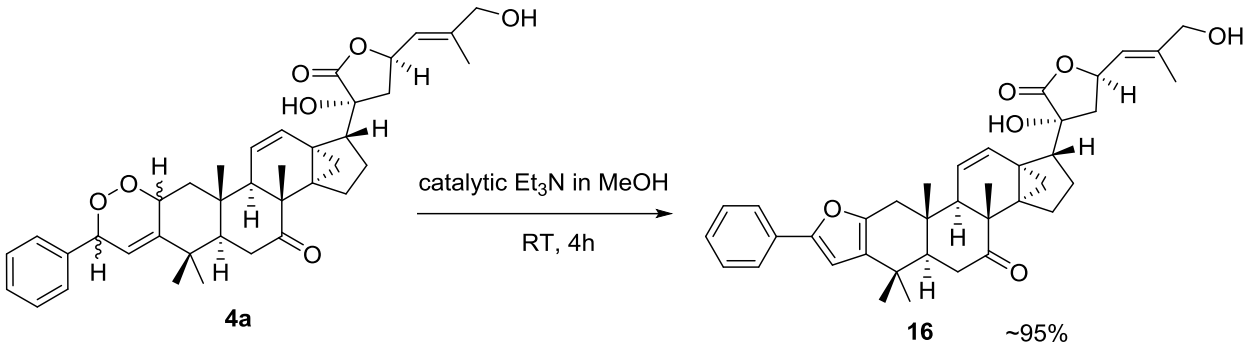


To 1.0 mL methanol solution of **3a** (3.8 g, 6.2 μmol), catalytic Et_3N (20 μL) was added and the solution was kept at room temperature until a complete conversion of the starting material was detected by TLC (~4 h). Methanol and residue Et_3N were removed in vacuo to afford **15** (3.7 mg, ~95%) as white powder. ESI-MS: *m/z* 595.2 $[M - H]^-$, 1190.9 $[2M - H]^-$.

Figure S9. (A) Comparison of the ^1H NMR spectra of synthetic **15** and isolated **15**



4.8 Biomimetic synthesis of 16 from 4a



To 1.0 mL methanol solution of **4a** (1.8 g, 2.9 μmol), catalytic Et_3N (10 μL) was added and the solution was kept at room temperature until a complete conversion of the starting material was detected by TLC (~4 h). Methanol and residue Et_3N were removed in vacuo to afford **16** (1.7 mg, ~95%) as white powder. ESI-MS: *m/z* 595.0 $[M - H]^-$, 597.4 $[M + H]^+$. HRMS (ESI): *m/z* 597.3219 $[M + H]^+$ (calcd for $C_{38}H_{45}O_6$, 597.3211). The structure of compound **16** was established as shown by analysis of its 1D and 2D NMR data (Figures S10, and S151–156), which was not obtained in our isolation.

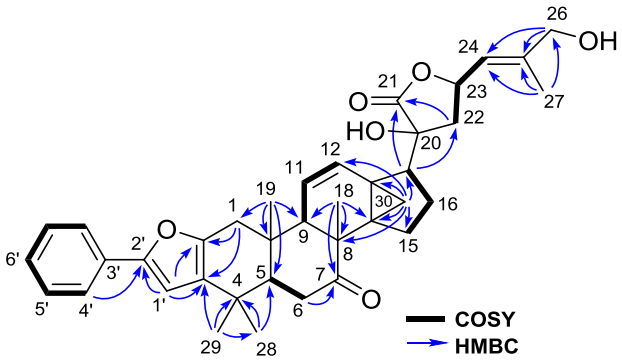
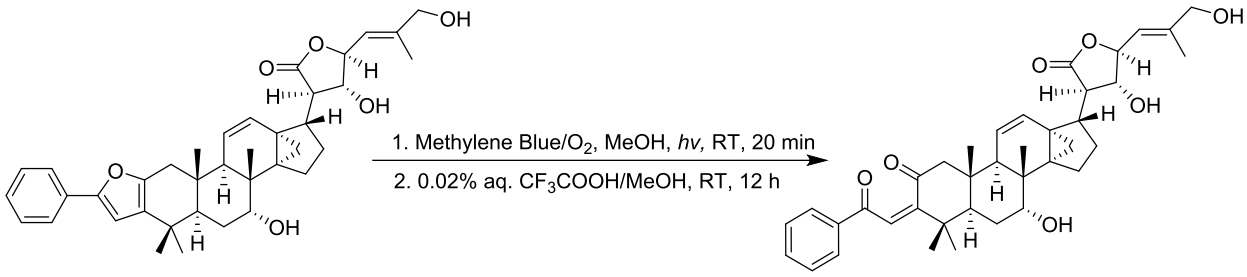


Figure S10. Key HMBC and COSY (bold bonds) correlations for **16**.

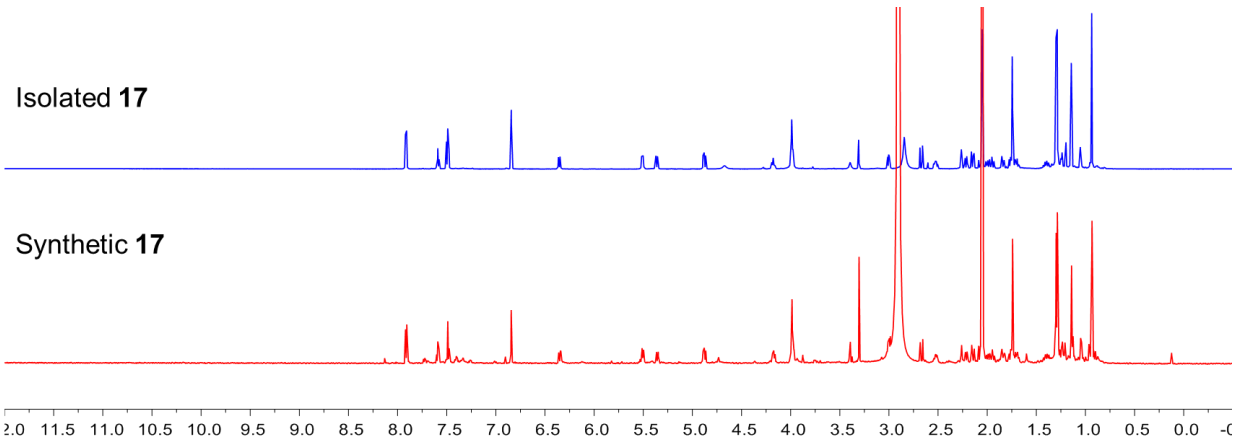
4.9 Biomimetic synthesis of 17 from 13



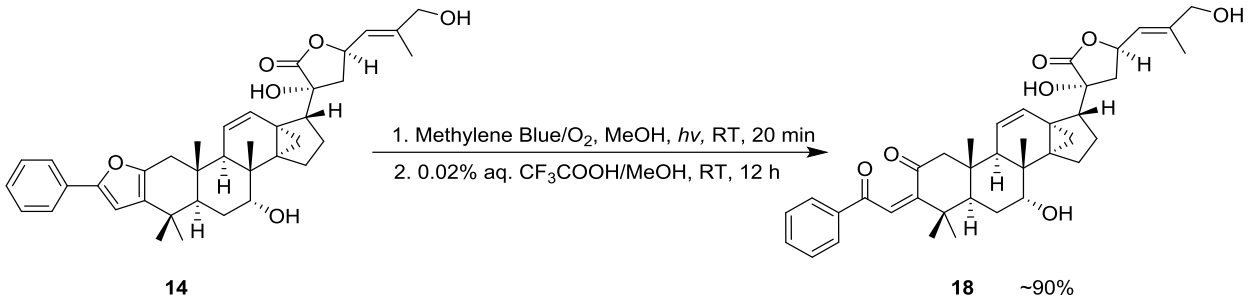
13 **17** ~90%

To an oxygen bubbled solution of synthetic **13** (1.0 mg, 1.7 μmol) in MeOH (1.0 mL) at room temperature was added methylene blue (0.1 mg, 0.3 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to remove methylene blue. The concentrated product was dissolved in 500 μL MeOH, followed by adding 100 μL aqueous CF_3COOH solution (0.02%), the reaction mixture was kept in room temperature for overnight (~12 h). Methanol and residue CF_3COOH were removed in vacuo to afford **17** (1.0 mg, ~90%) as white powder. ESI-MS: *m/z* 613.2 $[M - H]^-$, 615.4 $[M + H]^+$, 637.5 $[M + Na]^+$.

Figure S11. (A) Comparison of the ^1H NMR spectra of synthetic **17** and isolated **17**



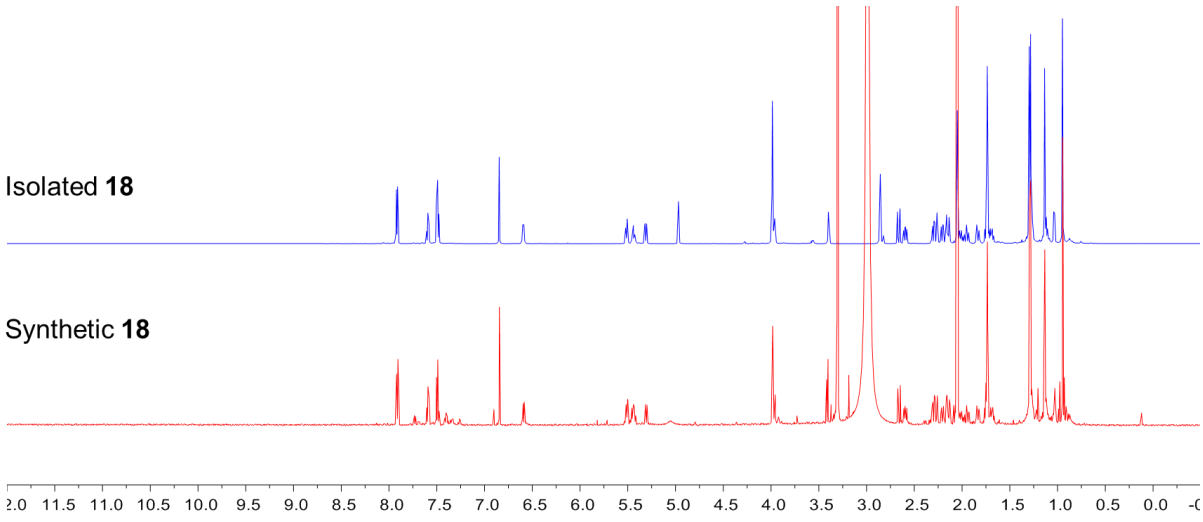
4.10 Biomimetic synthesis of 18 from 14



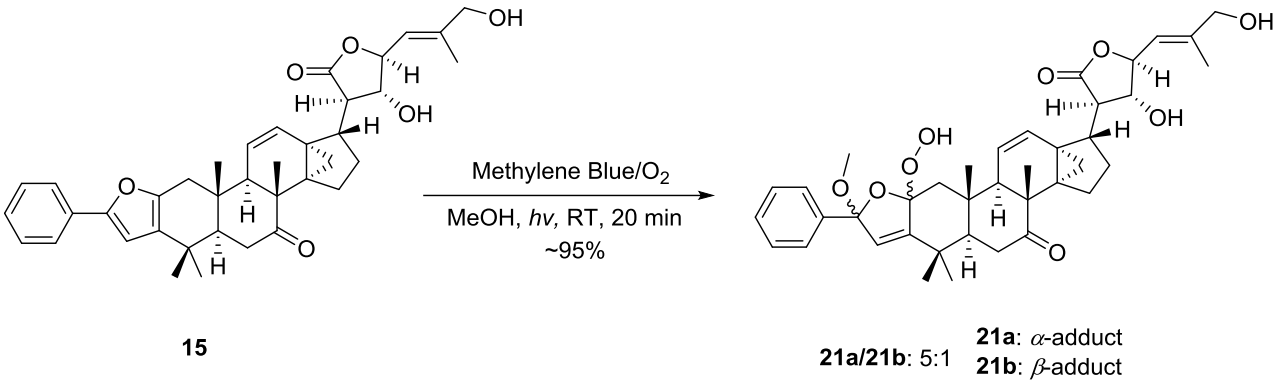
14 **18** ~90%

To an oxygen bubbled solution of synthetic **14** (1.0 mg, 1.7 μmol) in MeOH (1.0 mL) at room temperature was added methylene blue (0.1 mg, 0.3 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to remove methylene blue. The concentrated product was dissolved in 500 μL MeOH, followed by adding 100 μL aqueous CF_3COOH solution (0.02%), the reaction mixture was kept in room temperature for overnight (~12 h). Methanol and residue CF_3COOH were removed in vacuo to afford **18** (1.0 mg, ~90%) as white powder. ESI-MS: *m/z* 613.2 $[M - H]^-$, 615.4 $[M + H]^+$, 637.4 $[M + Na]^+$.

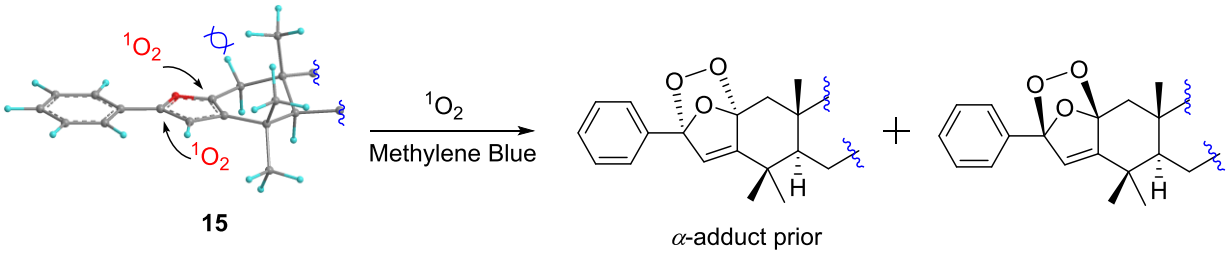
Figure S12. (A) Comparison of the ^1H NMR spectra of synthetic **18** and isolated **18**



4.11 Biomimetic synthesis of 21 from 15



To an oxygen bubbled solution of **15** (2.0 mg, 3.4 μmol) in MeOH (1.0 mL) at room temperature was added methylene blue (0.1 mg, 0.3 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to afford **21** (2.0 mg, ~95%) as white powder. ESI-MS: *m/z* 659.3 $[M - H]^-$, 683.2 $[M + Na]^+$. HRMS (ESI): *m/z* 683.3192 $[M + Na]^+$ (calcd for $C_{39}H_{48}O_9Na$, 683.3191). **21** were elucidated as a pair of diastereoisomers (**21a**/**21b** = 5:1) by analysis of 1D and 2D NMR data. The predominant α-adduct **21a** was actually resulted from the formation of intermediate **i** via a [4 + 2] Diels-Alder cycloaddition, and was probably caused by the relatively less steric hindrance of the α-face in the furan ring.



The 2D and 3D structures of **21** was established by analysis of the COSY, HMBC, and NOESY data (Figures S13, and S198–S200). The major component **21a** was verified with α-oriented HOO-2 and CH_3O-2 groups, based on the NOESY correlations of HOO-2/H_3-28, CH_3O-2′, and H-1α. In contrast, both the HOO-2 and CH_3O-2 groups in **21b** were elucidated in a β-configuration by the NOESY correlations from HOO-2 to CH_3O-2′, H_3-19, and H_3-29.

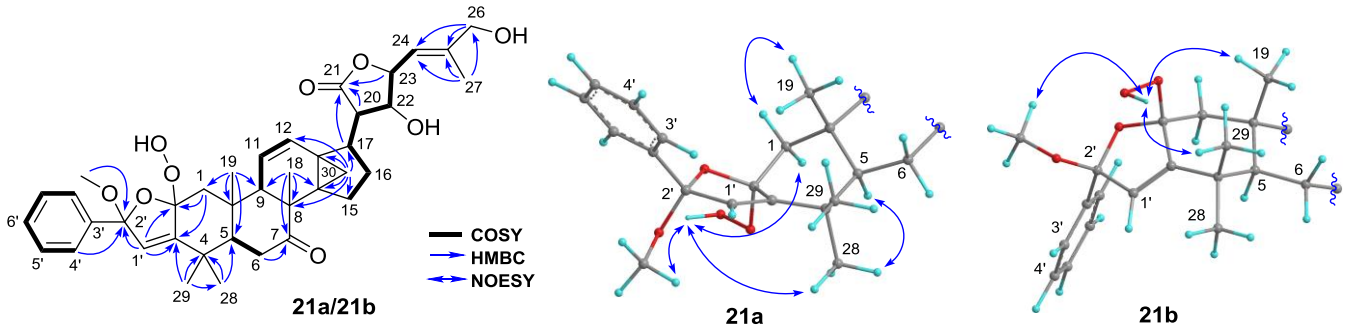
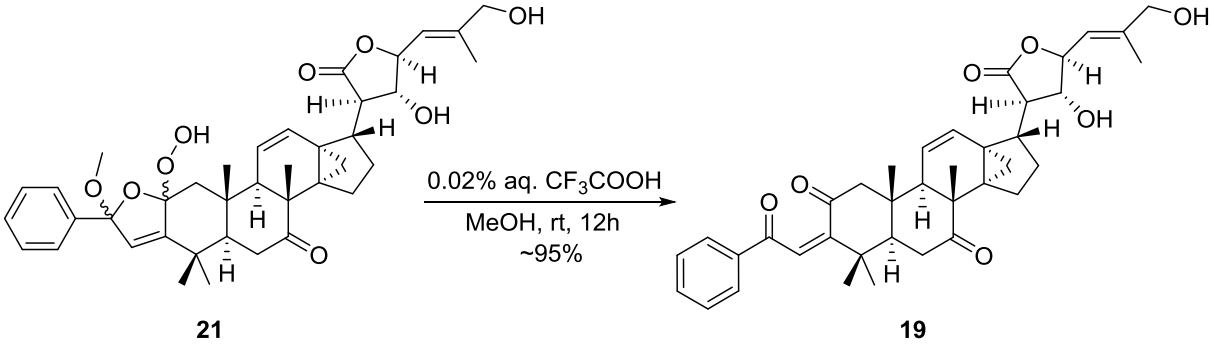


Figure S13. Key HMBC, COSY (bold bonds), and NOESY correlations for **21a/21b**.

4.12 Biomimetic synthesis of 19 from 21



Compound **21** (2.0 mg, 3.0 μmol) dissolved in 500 μL MeOH, followed by adding 100 μL aqueous CF_3COOH solution (0.02%), the reaction mixture was kept in room temperature for overnight (~12 h). Methanol and residue CF_3COOH were removed in vacuo to afford **19** (1.9 mg, 90% pure) as white powder. ESI-MS: *m/z* 611.3 $[M - H]^-$, 613.4 $[M + H]^+$. HRMS (ESI): *m/z* 613.3160 $[M + H]^+$ (calcd for $C_{38}H_{45}O_7$, 613.3160). The structure of **19** was unambiguously assigned by NMR and MS data (Figures S14), which was not obtained in the isolation.

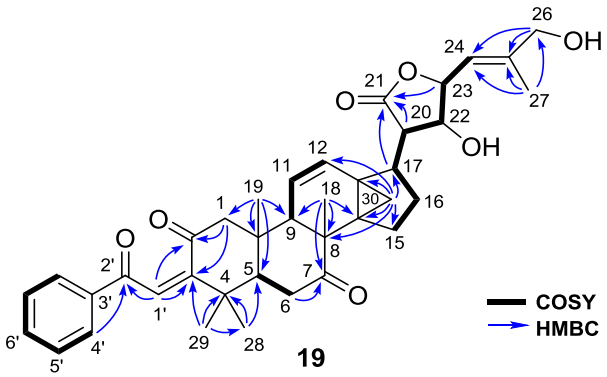
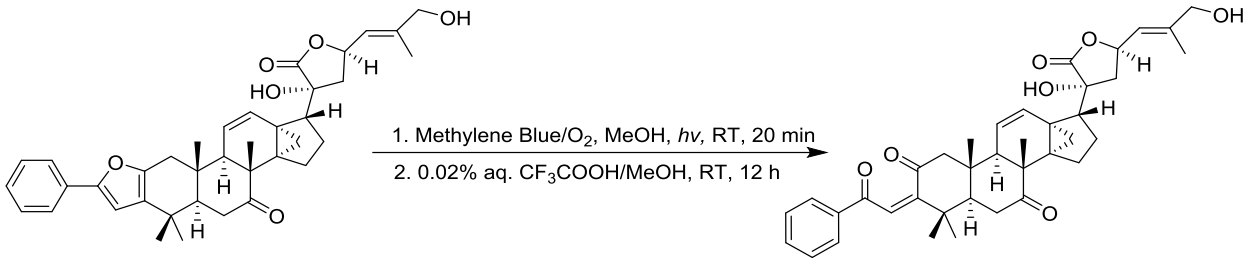


Figure S14. Key HMBC and COSY (bold bonds) correlations for **19**.

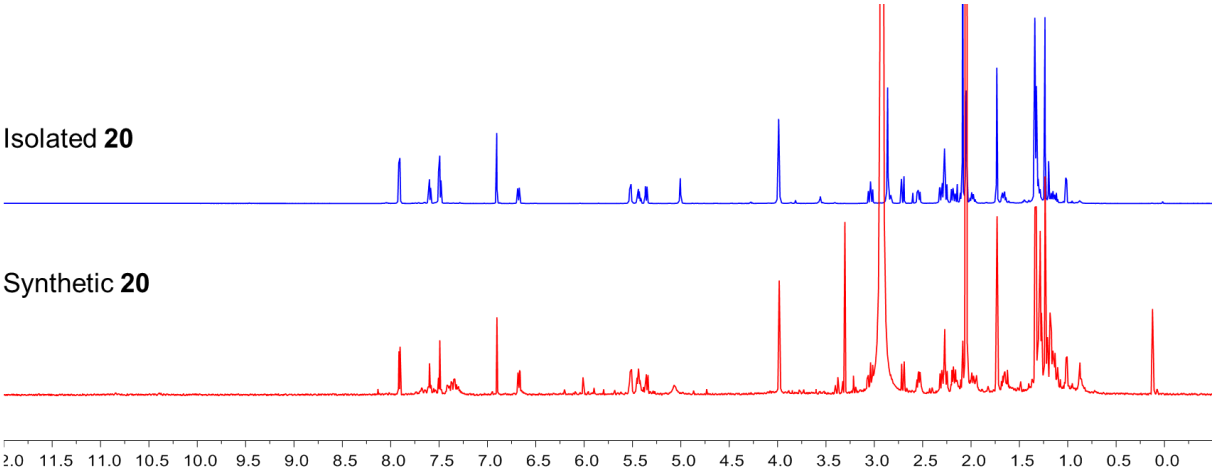
4.13 Biomimetic synthesis of 20 from 16



16 **20** ~90%

To an oxygen bubbled solution of **16** (1.0 mg, 1.7 μmol) in MeOH (1.0 mL) at room temperature was added methylene blue (0.1 mg, 0.3 μmol). The reaction mixture was irradiated with a U-shaped fluorescent lamp (Essential 23 W, PHILIPS, distance ~2 cm) at room temperature until complete consumption of the starting material was detected by TLC (~20 min). The reaction solvent was removed in vacuo to give a residue that contained methylene blue. The residue was subjected to column chromatography (using a dropper that loaded with 200~300 mesh silica gel), and quickly eluted with acetone to remove methylene blue. The concentrated product was dissolved in 500 μL MeOH, followed by adding 100 μL aqueous CF_3COOH solution (0.02%), the reaction mixture was kept in room temperature for overnight (~12 h). Methanol and residue CF_3COOH were removed in vacuo to afford **20** (1.0 mg, ~90%) as white powder. ESI-MS: *m/z* 611.4 $[M - H]^-$, 613.4 $[M + H]^+$.

Figure S15. Comparison of the ^{1}H NMR spectra of synthetic **20** and isolated **20**



5. Cytotoxicity Assays

5.1 Methods

The cytotoxic activities of compounds **1**–**20** against three human tumor cell lines, including human burkitt lymphoma cell line (NAMALWA), human alveolar basal epithelial cell line (A549), and human liver hepatocellular carcinoma cell line (Hep G2), were evaluated (Tables S9–S11).

The antiproliferative activities of the compounds were evaluated against NAMALWA using the CCK-8 (cell counting kit 8, Life ilab Bio, Shanghai) assay performed according to the manufacturer's instructions, with adriamycin as the positive control.[6] Briefly, 90 μL of the cells in logarithmic phase were seeded into 96-well plates (1.2×10^4 cell/well) and incubated overnight. Then, the cells were incubated with compounds in triplicate at various concentrations for 72 h followed by the addition of 10 μL CCK-8 reagent, and kept in the incubator for further 4 h. The OD value of each well was measured at 450 nm using multiwell spectrophotometer (SpectraMax, Molecular Devices, U.S.A).

The growth inhibition of human tumor cell lines (A549 and Hep G2) was determined by sulforhodamine B (SRB) assay.[7] Briefly, A549 and Hep G2 (2×10^3 cell/well) were seeded into 96-well plates in triplicates. After incubation overnight, Cells were then treated with increasing concentrations of compounds and cultured at 37 °C for another 72 h. At the end of exposure time, the cells were fixed with 10% pre-cooled trichloroacetic acid overnight and stained with 4 mg/mL sulforhodamine B (SRB, Sigma, St. Louis, MO) in 1% acetic acid. The SRB in the cells was dissolved in 10 mM Tris-HCl and measured at 560 nm using multiwell spectrophotometer (SpectraMax, Molecular Devices, U.S.A).

Table S10. Cytotoxic Activities of Compounds 1–20 against the NAMALWA Cells.

Cmpd	Concentration (μM)						IC_{50} (μM)	IC_{50} ± SD (μM)
	10	3.333	1.111	0.370	0.123	0.041		
	77.8	79.3	79.1	76.6	45.7	27.2	0.135	
1	74.5	75.2	75.3	70.1	36.0	17.1	0.175	0.182 ±0.051
	83.6	63.1	65.8	62.7	28.8	9.1	0.236	
	78.6	76.8	77.4	77.5	71.5	29.2	0.064	
2	75.3	74.3	73.6	72.8	69.0	31.5	0.063	0.078 ±0.025
	77.9	60.2	62.9	64.3	53.3	29.0	0.106	
	79.7	76.7	75.3	73.9	57.0	19.8	0.103	
3	74.1	74.4	73.4	70.2	57.0	24.1	0.097	0.151 ±0.089
	78.8	59.6	60.9	60.5	37.5	12.2	0.254	
	87.3	79.4	75.2	75.5	72.2	33.9	0.061	
4	86.7	74.9	73.8	72.4	68.1	41.4	0.056	0.067 ±0.015
	76.3	61.1	64.1	64.8	56.1	34.3	0.084	
	77.7	34.0	12.6	12.5	10.1	13.1	4.352	
1a (**5** + **6**)	70.8	39.9	18.9	14.2	14.4	12.3	4.575	4.593 ±0.250
	74.2	31.5	9.1	6.1	7.4	8.2	4.852	
	72.2	19.1	8.3	10.2	8.9	8.8	3.647	
2a (**7** + **8**)	71.5	23.5	11.2	5.0	8.2	5.7	7.113	5.611 ±1.779
	67.0	21.7	3.1	0.8	1.2	2.8	6.074	
	86.8	41.8	7.3	8.0	9.0	4.6	3.746	
3a (**9** + **10**)	88.5	52.0	13.2	5.1	4.7	4.2	3.199	3.682 ±0.454
	64.5	36.4	1.1	0.7	0.2	1.0	4.101	
	55.9	18.2	7.9	12.0	10.4	15.8	3.841	
4a (**11** + **12**)	50.1	20.0	16.1	9.8	10.2	9.9	10.031	7.843 ±3.471
	52.9	11.3	6.7	3.4	3.5	5.1	9.656	
	37.9	8.9	13.2	8.9	10.6	12.2	>10	
13	34.9	8.2	8.6	7.2	9.2	8.3	>10	>10
	20.7	5.0	7.0	6.3	6.8	9.2	>10	
	89.2	30.9	10.2	4.0	3.8	5.1	5.144	
14	87.4	31.2	9.2	4.5	5.4	6.0	4.975	5.030 ±0.098
	66.9	33.2	7.1	5.0	3.9	4.3	4.972	
	88.1	51.4	0.0	0.0	0.0	0.0	3.325	
15	86.8	44.3	1.3	0.0	0.0	0.0	3.613	3.874 ±0.716
	63.6	49.0	3.9	2.8	4.2	3.5	4.684	
	55.7	22.0	11.6	10.3	7.0	9.2	8.701	
16	41.2	17.6	12.8	5.2	3.6	5.7	>10	>10
	28.3	14.2	10.0	8.3	8.5	8.2	>10	
	50.7	17.7	14.3	11.4	11.8	11.3	9.900	
17	51.6	23.3	18.6	15.2	16.0	15.4	9.679	9.790 ±0.156
	44.6	17.0	10.2	8.3	8.0	9.7	>10	
	55.6	26.6	17.4	13.6	10.5	11.4	8.620	
18	54.0	22.7	14.9	10.3	6.3	8.5	9.143	8.882 ±0.370
	33.3	10.0	8.0	6.0	4.7	0.0	>10	
	43.4	11.9	8.5	8.6	8.4	10.8	>10	
19	42.9	10.3	6.9	4.7	5.3	4.3	>10	>10
	38.3	9.6	4.8	2.4	2.8	1.9	>10	
	37.0	21.4	12.9	14.5	12.9	12.5	>10	
20	37.0	21.4	12.9	14.5	12.9	12.5	>10	>10
	36.0	9.1	8.0	6.2	4.8	4.3	>10	
	79.3	76.6	57.0	20.5	33.5	18.5	0.315	
Doxorubicin	76.6	75.5	55.2	24.3	25.0	21.8	0.365	0.352 ±0.033
	65.0	61.8	50.8	27.4	18.9	8.4	0.376	

Table S11. Cytotoxic Activities of Compounds 1–20 against the A549 Cells.

Cmpd	Concentration (μM)						IC_{50} (μM)	IC_{50} ± SD (μM)
	10	3.333	1.111	0.370	0.123	0.041		
	63.7	50.2	39.6	19.9	6.7	4.2	2.530	
1	65.3	47.9	38.6	15.4	5.5	2.1	2.831	3.021 ± 0.609
	64.5	45.6	32.0	9.2	5.0	2.1	3.703	
	58.1	52.4	46.3	34.6	21.4	5.7	1.683	
2	58.6	51.3	41.8	31.1	14.9	0.0	2.103	2.430 ± 0.297
	64.3	45.7	38.1	26.2	5.8	0.9	3.505	
	68.0	48.5	42.2	25.0	13.1	2.4	2.624	
3	67.5	49.2	43.1	22.4	19.4	1.3	2.752	2.832 ± 0.257
	64.5	47.5	37.5	13.1	5.8	0.7	3.119	
	81.9	54.6	45.2	33.0	13.6	3.6	1.864	
4	84.6	50.4	44.1	32.4	12.9	0.0	1.968	2.007 ± 0.167
	72.1	47.7	42.1	35.2	12.0	1.8	2.190	
	40.7	6.9	5.2	5.2	4.8	5.0	>10	
1a (**5** + **6**)	43.7	3.8	0.0	0.9	4.7	5.6	>10	>10
	44.3	9.4	3.7	5.4	3.7	5.3	>10	
	50.8	10.5	4.2	3.0	6.3	5.1	4.272	
2a (**7** + **8**)	42.6	1.5	0.0	0.0	2.2	1.8	>10	4.026 ± 0.349
	78.3	9.5	3.8	4.2	5.9	3.7	3.779	
	70.9	16.8	5.9	2.8	4.7	3.4	7.367	
3a (**9** + **10**)	66.0	7.7	0.0	0.0	0.0	1.2	3.762	5.899 ± 1.893
	59.2	8.4	4.2	3.8	6.0	7.2	6.568	
	37.9	4.3	3.2	5.8	7.0	5.6	>10	
4a (**11** + **12**)	3.8	18.8	0.0	0.0	0.0	2.1	>10	>10
	41.3	12.6	9.2	8.4	10.7	8.5	>10	
	39.0	12.4	0.0	1.4	8.4	5.3	>10	
13	24.4	5.2	3.3	2.0	7.4	3.1	>10	>10
	43.9	19.0	7.7	6.9	7.0	3.4	>10	
	81.7	23.7	8.2	0.0	4.0	7.5	5.743	
14	88.7	17.7	7.1	2.0	5.7	5.1	6.870	6.911 ± 1.190
	90.5	6.4	4.2	4.5	4.1	0.1	8.121	
	83.2	46.8	13.2	6.6	7.8	5.3	3.570	
15	80.2	42.4	8.7	3.0	8.2	6.6	3.827	5.123 ± 2.471
	58.3	20.7	7.8	7.3	7.3	4.3	7.972	
	40.7	11.8	11.3	6.2	9.2	5.7	>10	
16	44.0	14.4	5.5	7.4	4.4	5.5	>10	>10
	42.7	10.5	10.1	10.7	14.3	6.0	>10	
	24.4	3.9	4.7	3.7	0.0	0.0	>10	
17	28.7	6.8	7.3	8.8	8.9	6.9	>10	>10
	38.3	10.6	4.2	5.0	4.7	4.5	>10	
	49.9	18.1	14.9	8.7	7.6	4.7	>10	
18	16.5	17.4	9.8	11.1	5.4	6.2	>10	>10
	34.3	16.6	9.5	7.0	2.5	1.0	>10	
	14.2	6.5	8.6	6.2	6.9	0.7	>10	
19	12.4	7.2	6.9	6.3	8.1	7.3	>10	>10
	14.6	4.8	2.5	0.8	0.0	0.0	>10	
	9.8	11.1	6.5	10.6	10.9	7.8	>10	
20	18.0	16.3	8.8	6.8	7.5	7.7	>10	>10
	34.1	14.0	9.1	5.1	2.9	1.9	>10	
	92.9	79.3	57.0	46.0	20.0	7.8	0.204	
Doxorubicin	92.8	79.7	57.7	46.9	30.1	4.7	0.182	0.22 ±0.039
	92.9	70.3	56.9	42.3	18.5	10.1	0.258	

Table S12. Cytotoxic Activities of Compounds 1–20 against the Hep G2 Cells.

Cmpd	Concentration (μM)						IC_{50} (μM)	IC_{50} ± SD (μM)
	10	3.333	1.111	0.370	0.123	0.041		
	62.1	42.5	19.8	0.0	0.0	2.8	4.253	
1	73.8	49.7	36.4	12.4	9.2	8.4	2.911	3.662 ±0.685
	66.3	45.1	31.9	10.9	6.4	5.0	3.821	
	53.1	42.9	36.6	20.1	1.9	3.2	8.929	
2	59.3	51.0	42.4	28.8	3.1	4.3	8.791	6.989 ±3.242
	68.5	43.5	37.9	27.5	10.2	0.0	3.246	
	63.5	45.5	34.8	6.2	0.0	0.0	3.031	
3	75.6	52.5	42.3	16.0	5.3	6.2	2.214	2.637 ±0.409
	67.7	49.9	39.8	15.5	9.5	5.9	2.666	
	66.0	43.3	40.7	25.6	0.0	0.0	2.703	
4	73.4	50.6	42.9	28.6	0.0	0.0	1.926	2.134 ±0.498
	87.6	53.4	45.2	35.4	19.8	11.2	1.774	
	35.1	0.0	0.0	0.0	2.0	0.2	>10	
1a (**5** + **6**)	53.6	9.9	4.3	4.3	9.5	0.0	>10	>10
	49.1	21.3	11.7	11.1	13.1	11.7	>10	
	81.5	4.3	2.1	1.6	0.0	0.5	8.380	
2a (**7** + **8**)	91.6	9.9	10.9	0.0	7.9	4.2	7.706	6.620 ±2.487
	88.1	11.8	4.5	9.6	7.0	9.4	3.775	
	67.7	0.7	0.0	0.0	1.0	0.4	4.325	
3a (**9** + **10**)	56.8	15.8	6.9	1.4	3.8	4.3	8.859	6.592 ±3.206
	45.9	10.9	3.4	5.7	7.5	5.7	>10	
	27.5	2.5	1.2	0.5	0.0	-0.7	>10	
4a (**11** + **12**)	45.1	12.0	13.3	11.2	5.0	3.2	>10	>10
	58.3	17.8	12.9	8.5	9.4	12.3	8.923	
	45.4	11.7	5.5	1.6	5.9	-0.3	>10	
13	33.1	8.9	5.3	7.1	4.5	4.1	>10	6.592 ±3.206
	75.6	28.0	18.6	16.0	18.3	11.4	6.708	
	95.1	39.5	15.4	3.3	6.5	5.3	4.260	
14	95.9	19.3	6.9	4.7	3.0	3.5	6.512	5.960 ±1.502
	93.6	17.1	13.8	13.9	9.4	4.3	7.107	
	95.1	82.2	15.8	8.4	13.2	3.5	2.038	
15	95.9	63.2	10.5	4.5	6.5	4.7	2.763	4.156 ±3.062
	74.0	19.7	13.1	12.2	11.3	10.5	7.666	
	53.9	12.2	15.4	10.1	6.1	3.8	9.525	
16	41.6	10.2	4.0	3.8	4.2	5.5	>10	8.802 ±1.022
	66.5	22.2	17.6	13.5	16.7	15.8	8.079	
	30.5	4.4	0.0	0.8	0.0	0.6	>10	
17	30.1	0.0	0.0	0.0	0.0	0.0	>10	>10
	57.8	23.5	12.0	14.8	13.3	7.9	>10	
	43.1	10.8	7.8	0.0	1.8	2.4	>10	
18	51.5	19.1	15.1	8.6	4.4	2.9	>10	>10
	54.4	26.0	16.5	10.0	8.7	7.6	>10	
	14.9	2.4	5.9	3.7	1.0	0.8	>10	
19	22.6	7.7	9.1	5.0	3.8	2.1	>10	>10
	40.4	15.1	12.4	9.7	8.0	8.2	>10	
	23.4	9.8	4.0	3.4	3.0	1.1	>10	
20	28.6	11.5	7.1	5.2	7.2	7.5	>10	>10
	49.2	24.5	17.6	13.0	16.8	13.2	>10	
	93.7	89.2	75.1	62.0	44.5	17.4	0.064	
Doxorubicin	92.9	87.8	76.5	61.1	43.8	22.0	0.064	0.069 ±0.009
	92.5	82.5	66.6	53.8	44.1	28.9	0.079	

6. NMR, MS, and IR spectra of compounds 1–21

6.1 NMR, MS, and IR spectra of compound 1

Figure S16. ^{1}H NMR spectrum (500 MHz) of **1** in $CDCl_3$

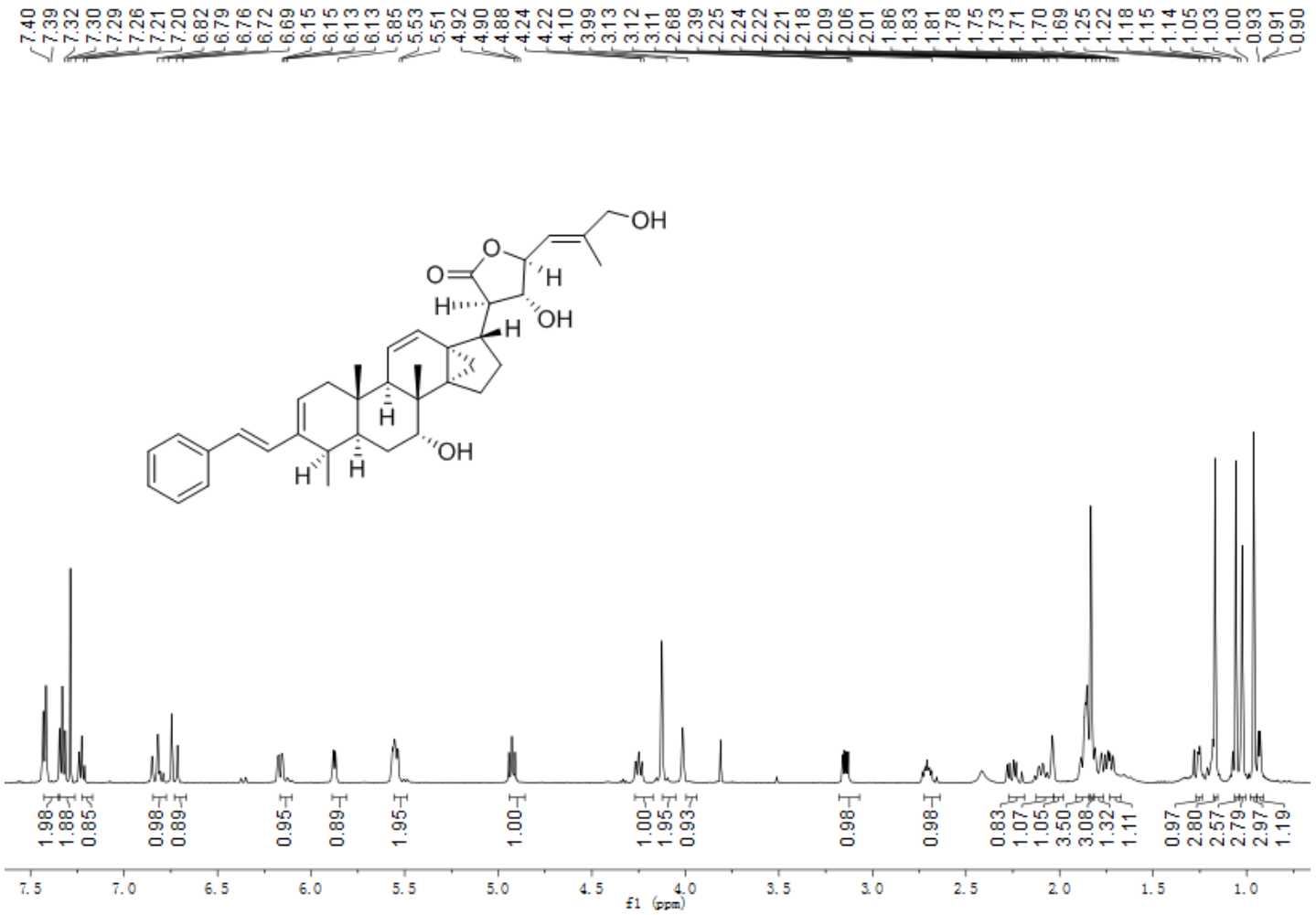


Figure S17. ^{13}C NMR spectrum (125 MHz) of **1** in $CDCl_3$

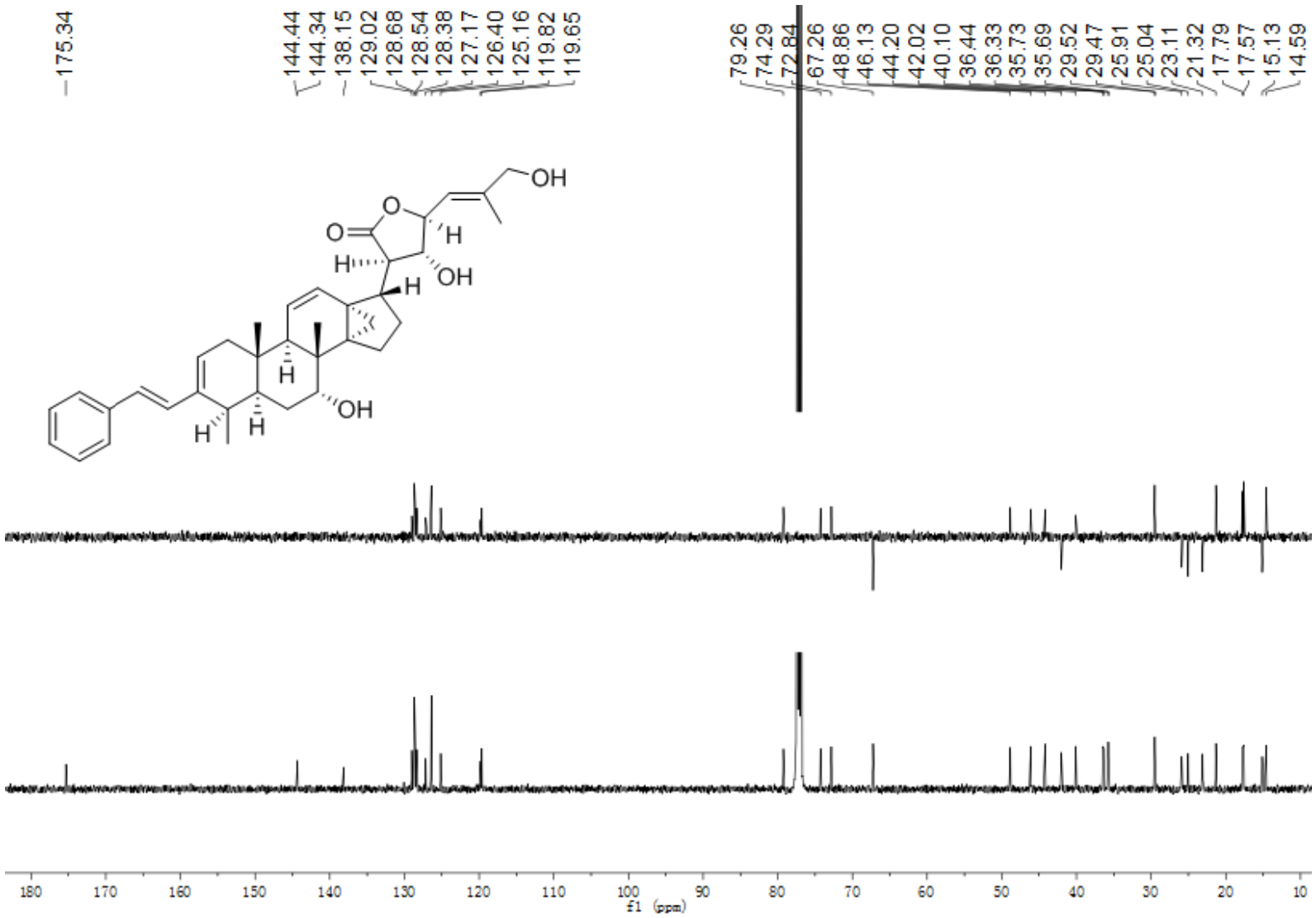


Figure S18. ^{1}H–^{1}H COSY spectrum of **1** in $CDCl_3$

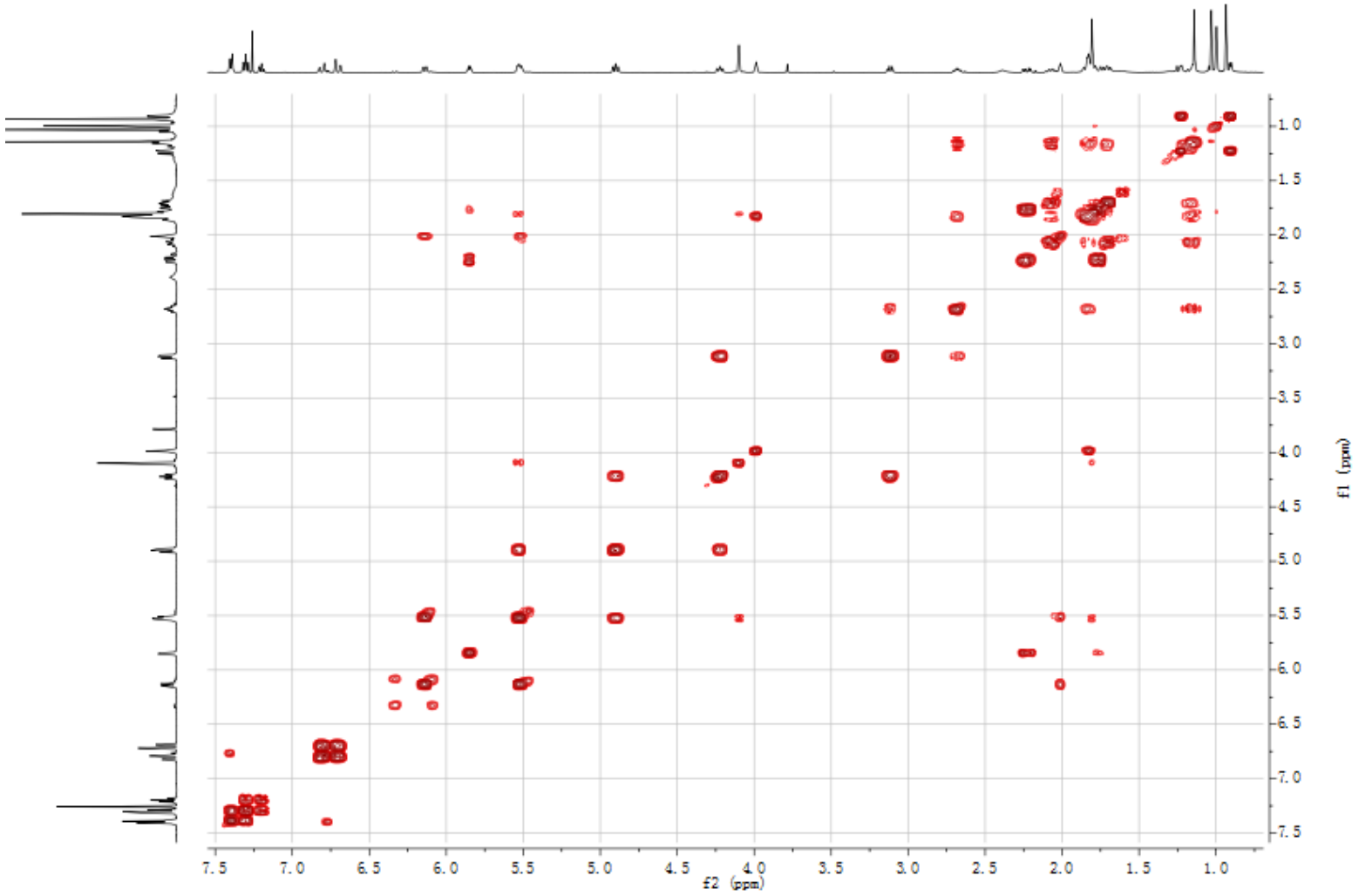


Figure S19. HSQC spectrum of **1** in $CDCl_3$

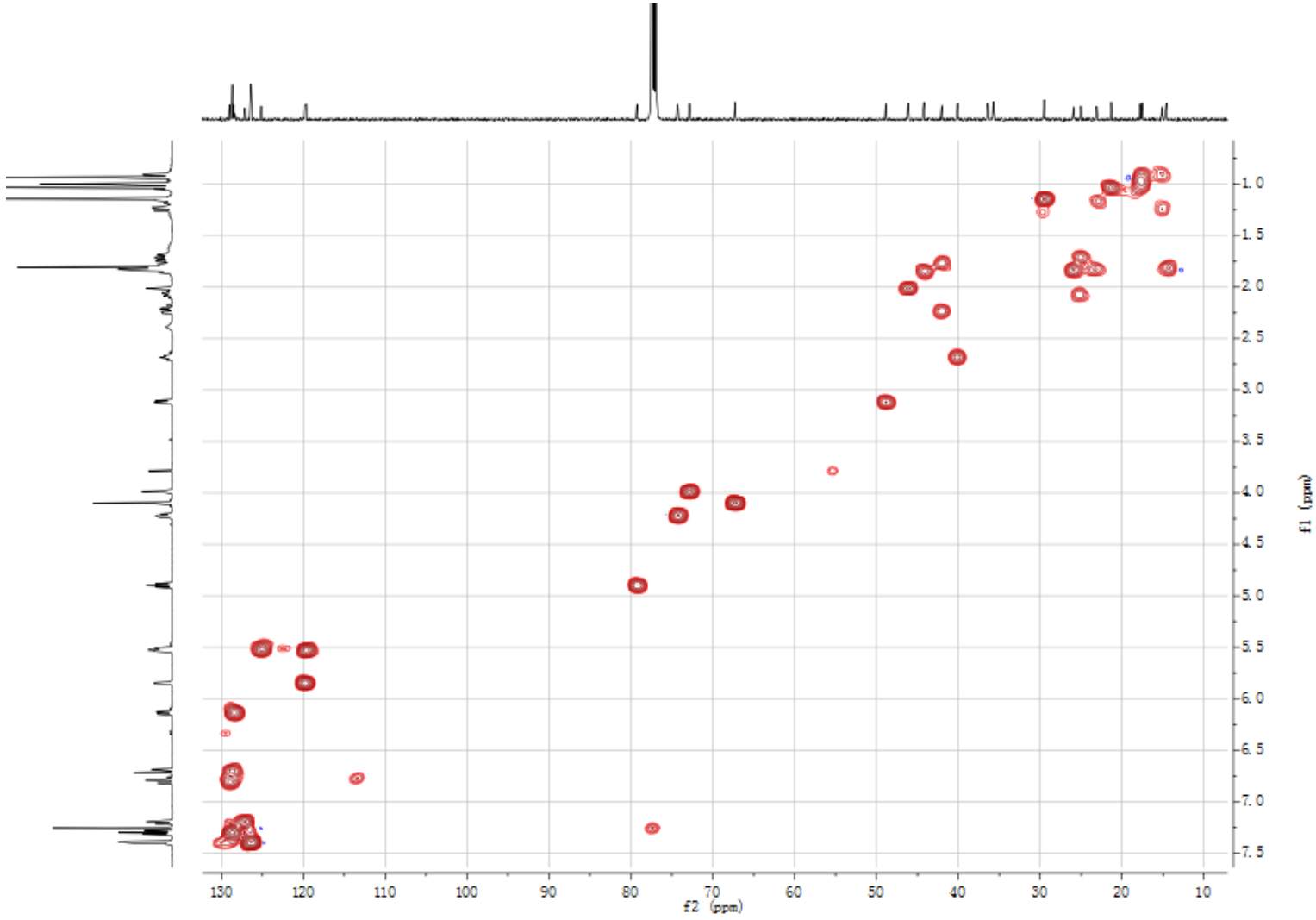


Figure S20. HMBC spectrum of **1** in $CDCl_3$

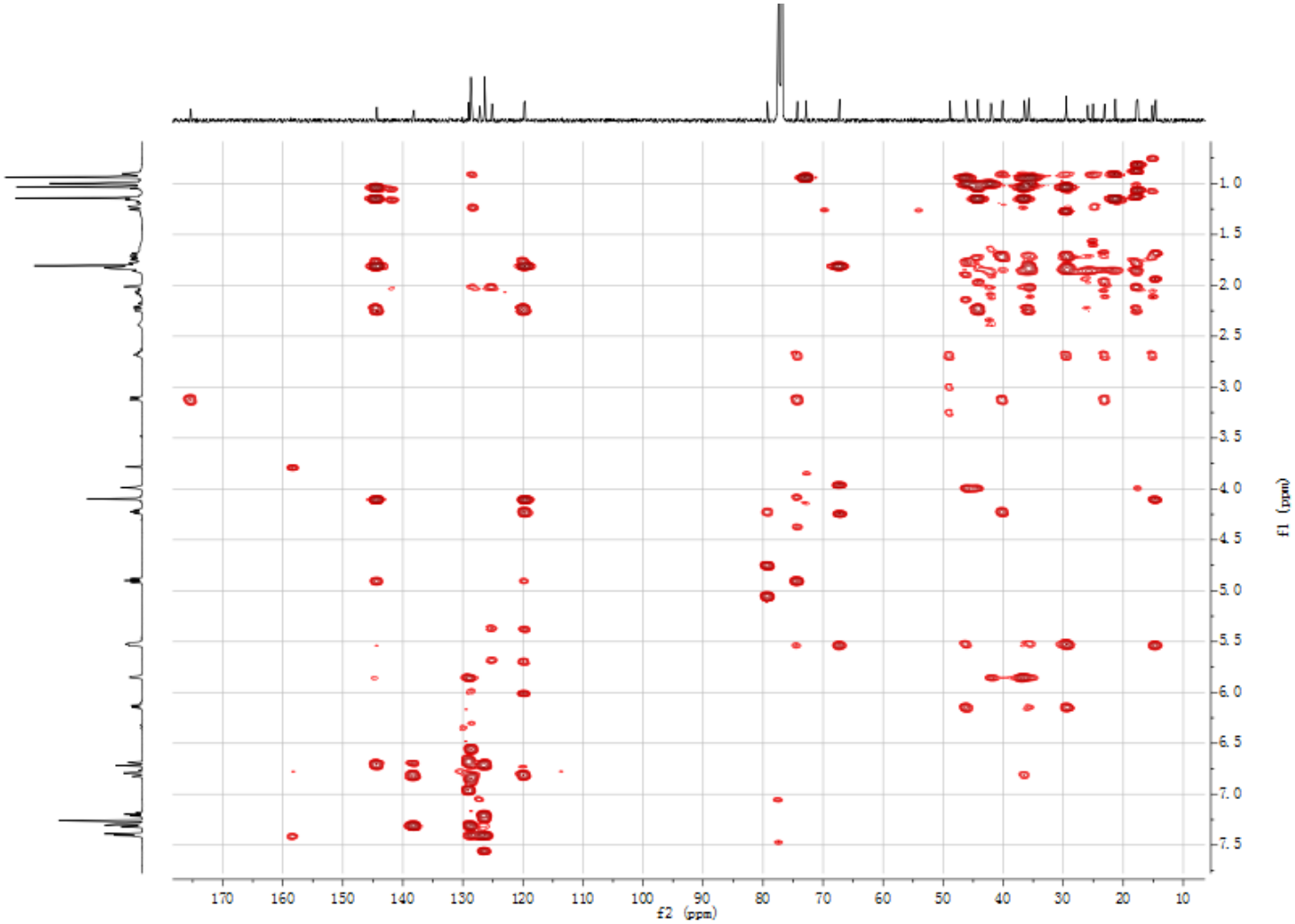


Figure S21. NOESY spectrum of **1** in $CDCl_3$

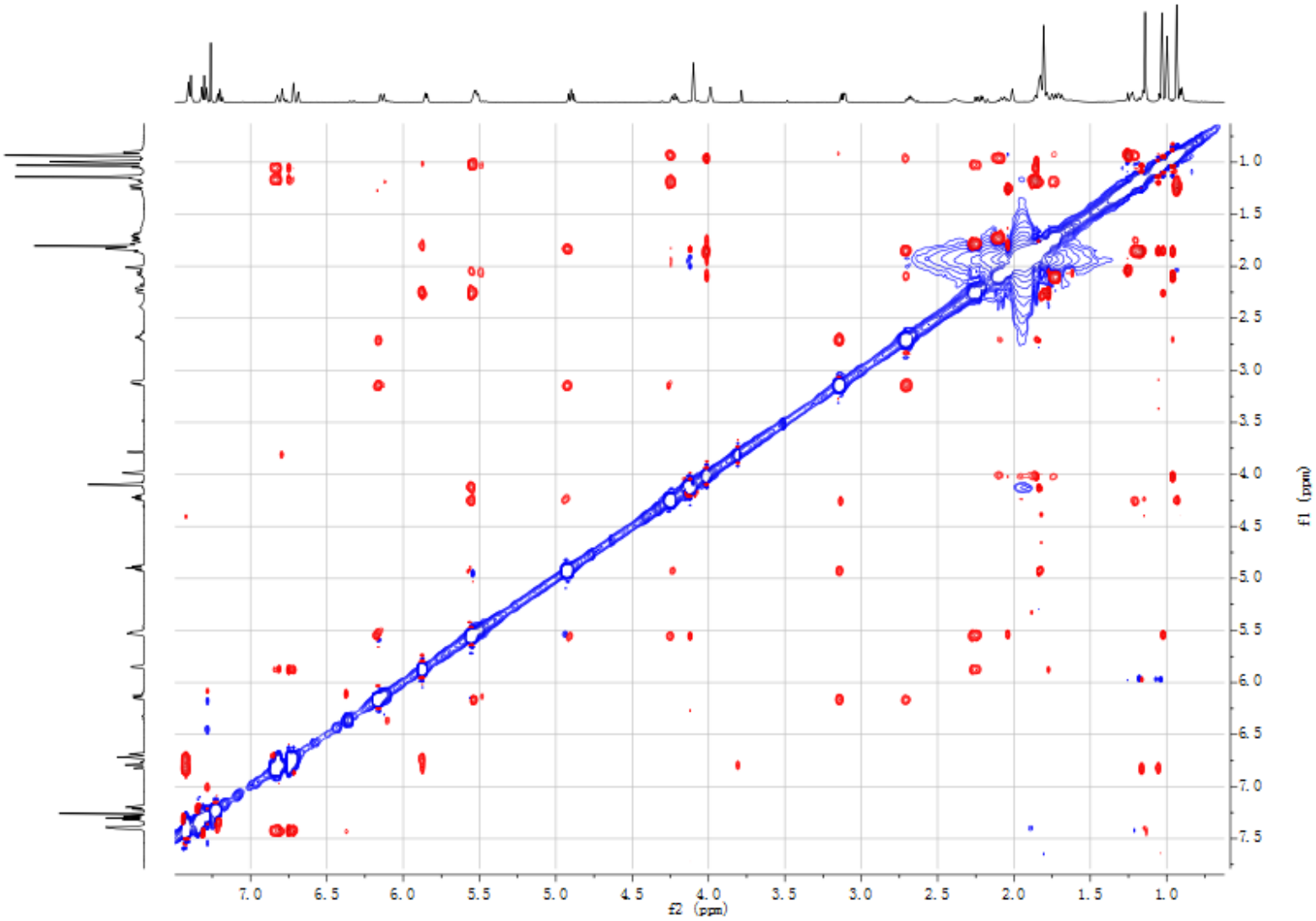


Figure S22. (±)-ESIMS spectra of **1**

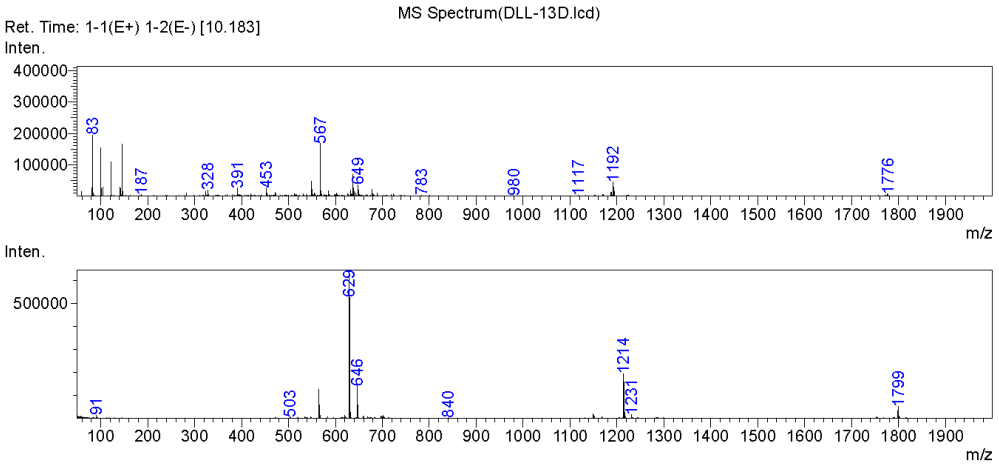


Figure S23. (–)-HRESIMS spectrum of **1**

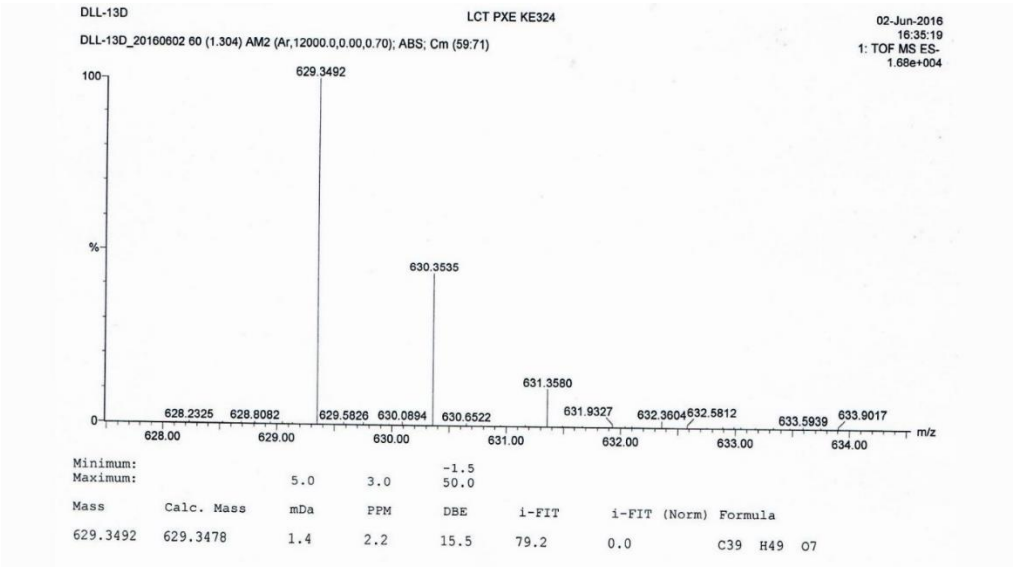
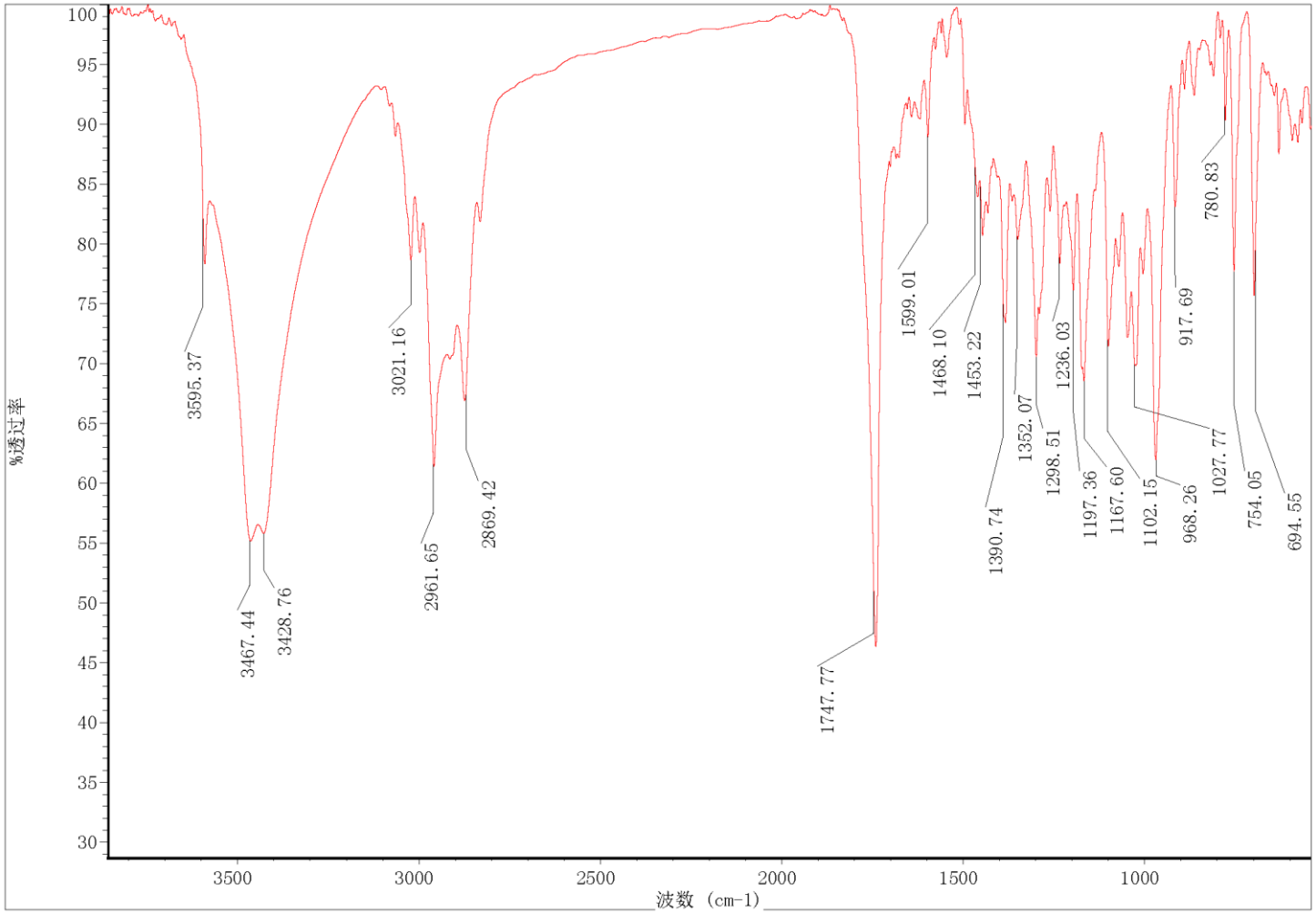


Figure S24. IR spectrum of **1**



6.2 NMR, MS, and IR spectra of compound 2

Figure S25. ^{1}H NMR spectrum (500 MHz) of **2** in $CDCl_3$

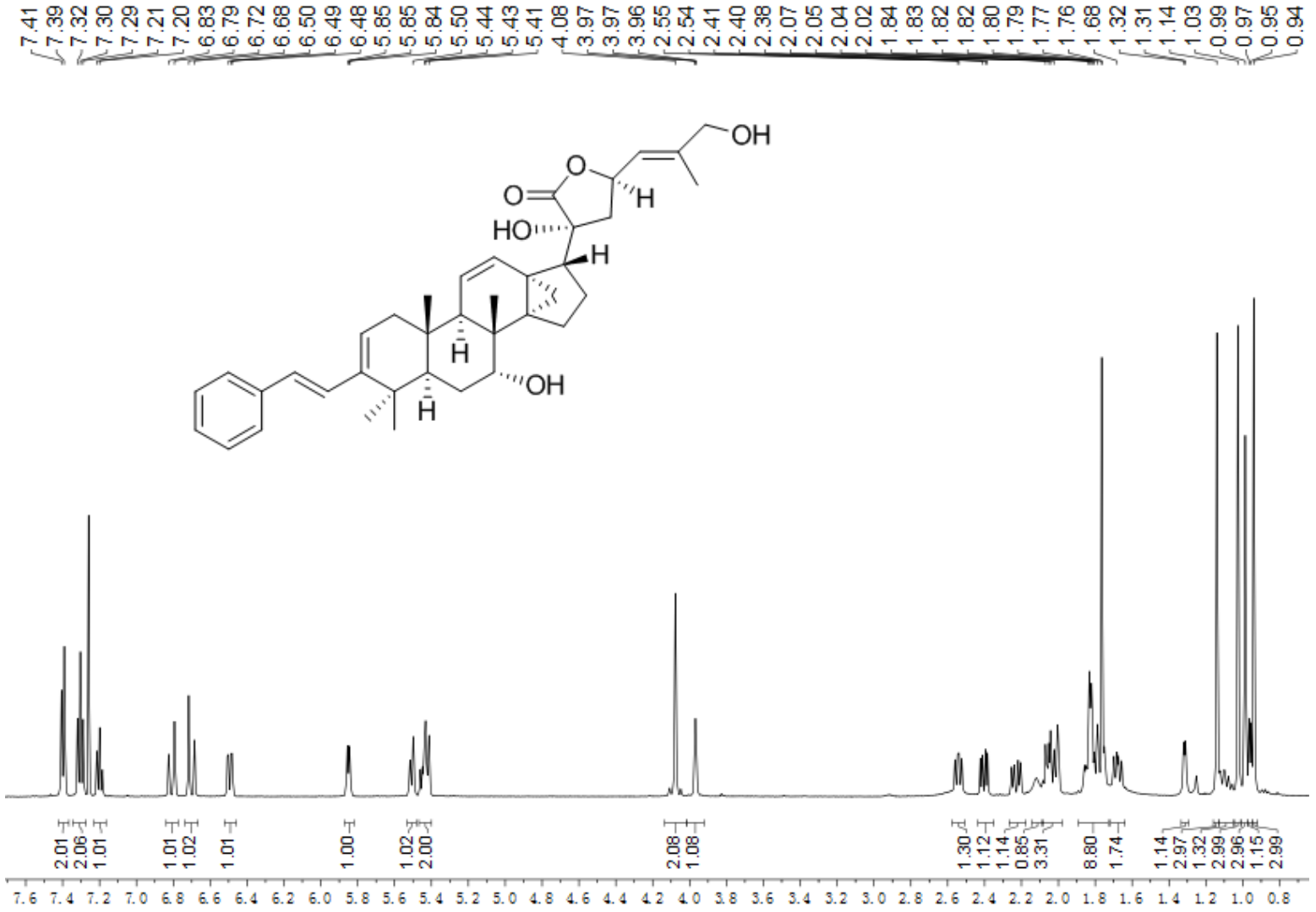


Figure S26. ^{13}C NMR spectrum (125 MHz) of **2** in $CDCl_3$

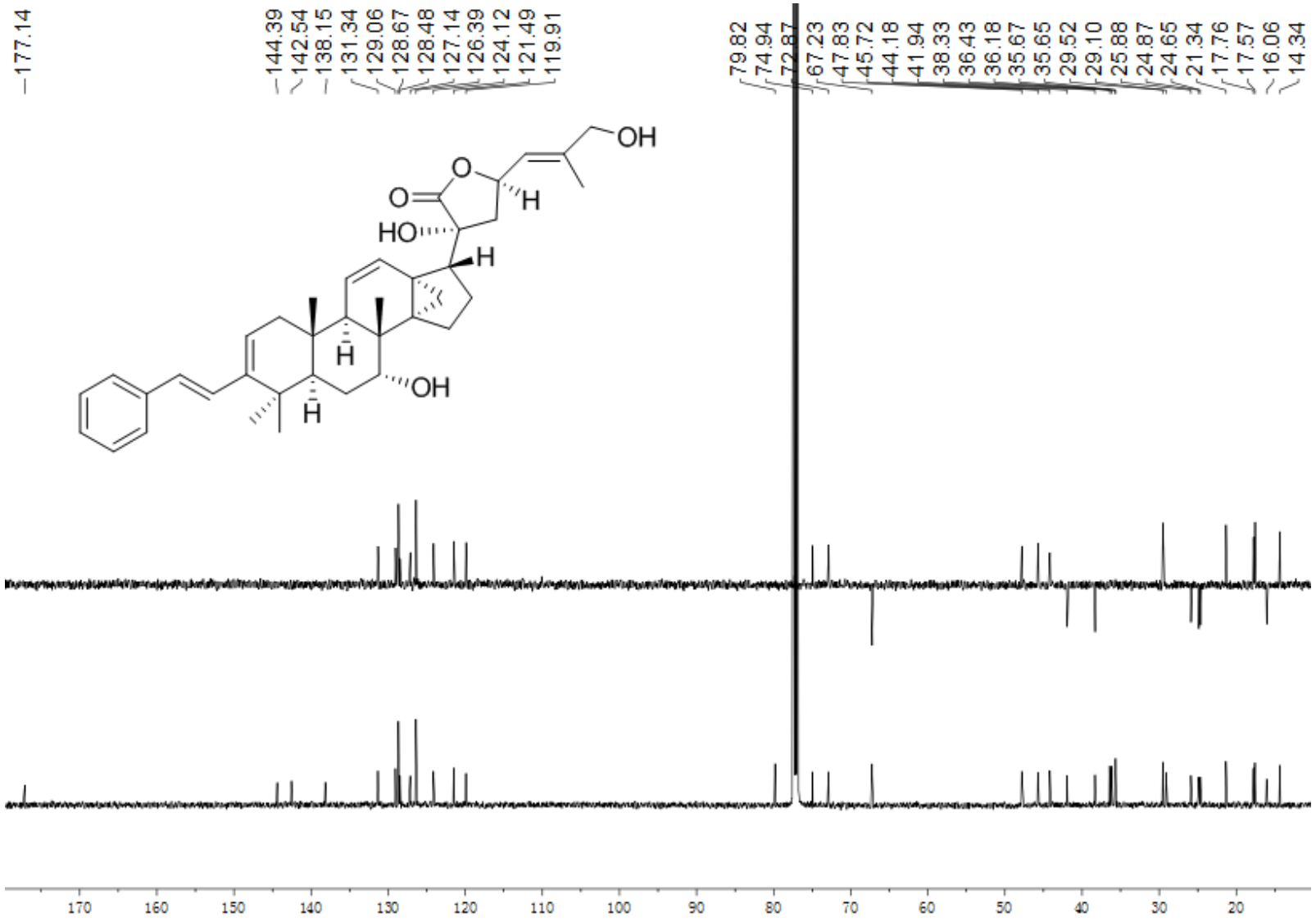


Figure S27. $^{1}H–^{1}H$ COSY spectrum of **2** in $CDCl_3$

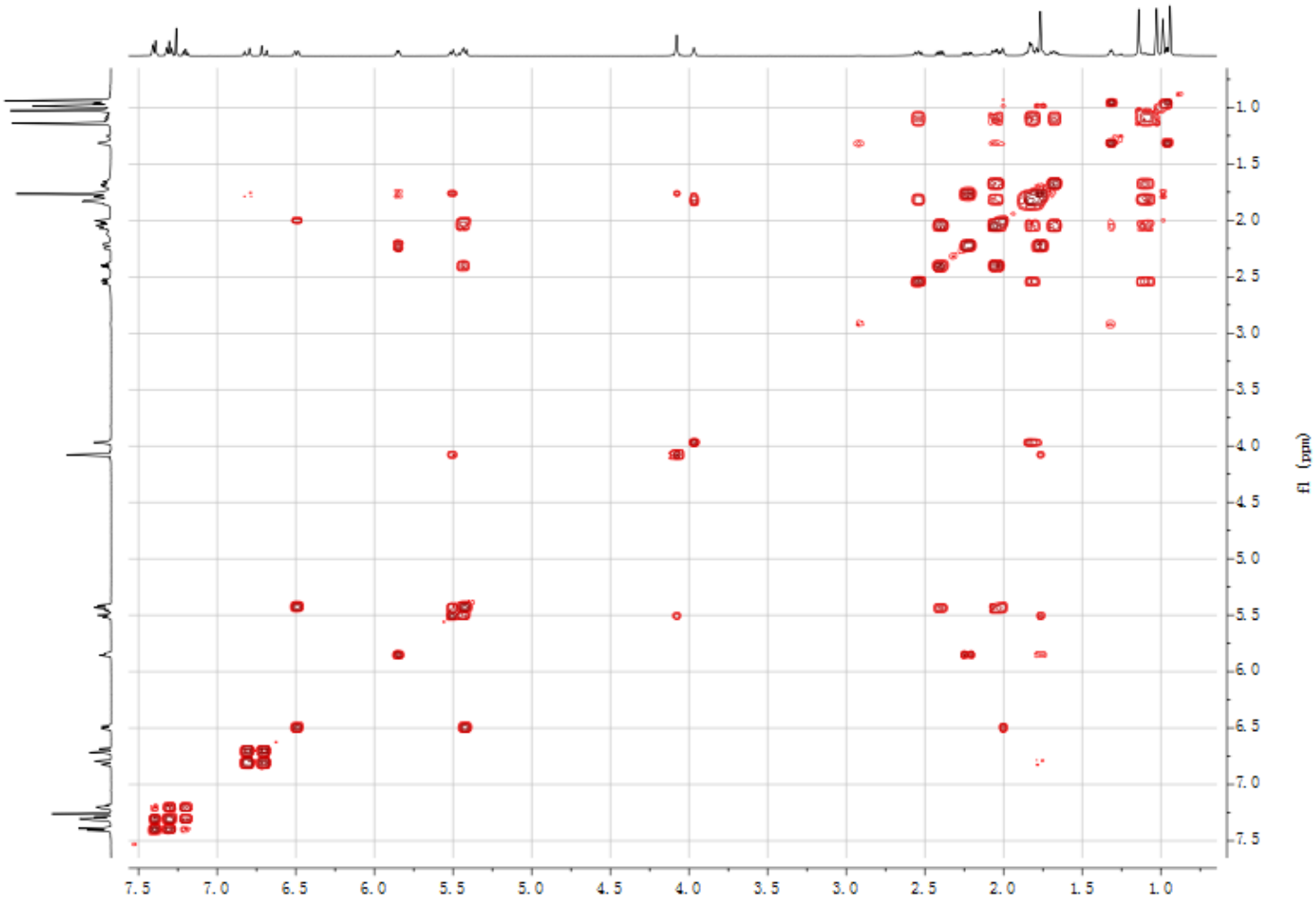


Figure S28. HSQC spectrum of **2** in $CDCl_3$

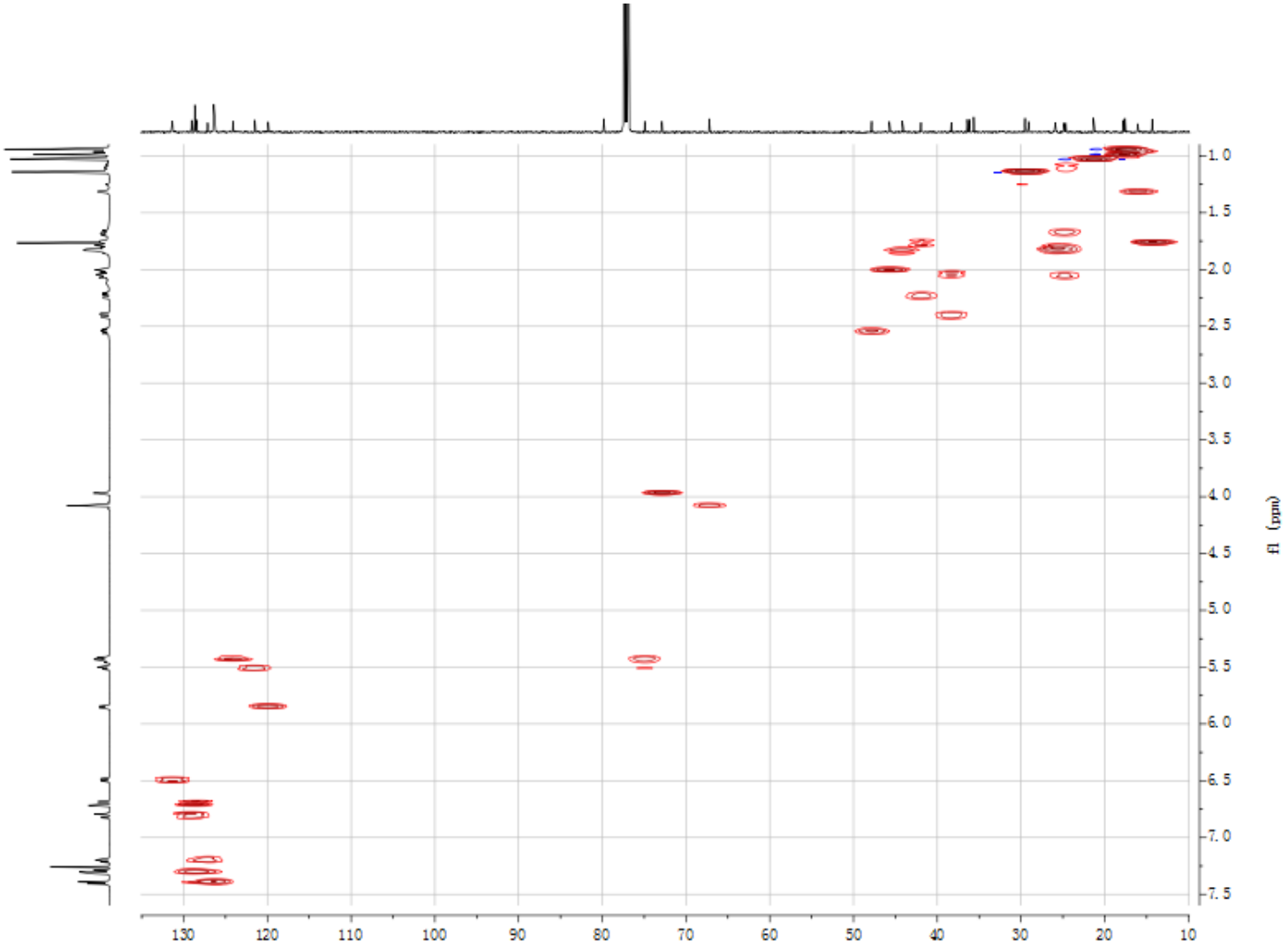


Figure S29. HMBC spectrum of **2** in $CDCl_3$

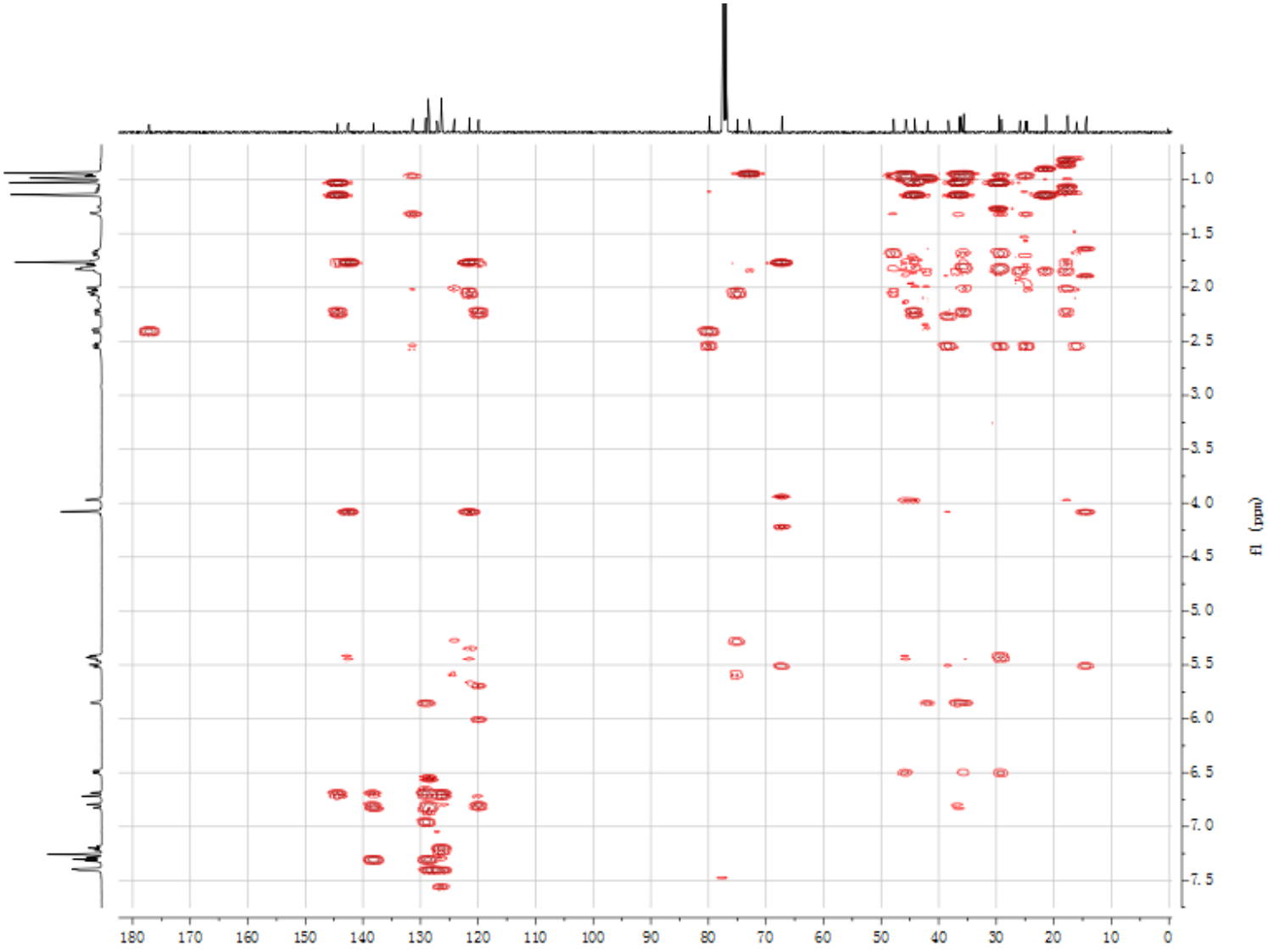


Figure S30. NOESY spectrum of **2** in $CDCl_3$

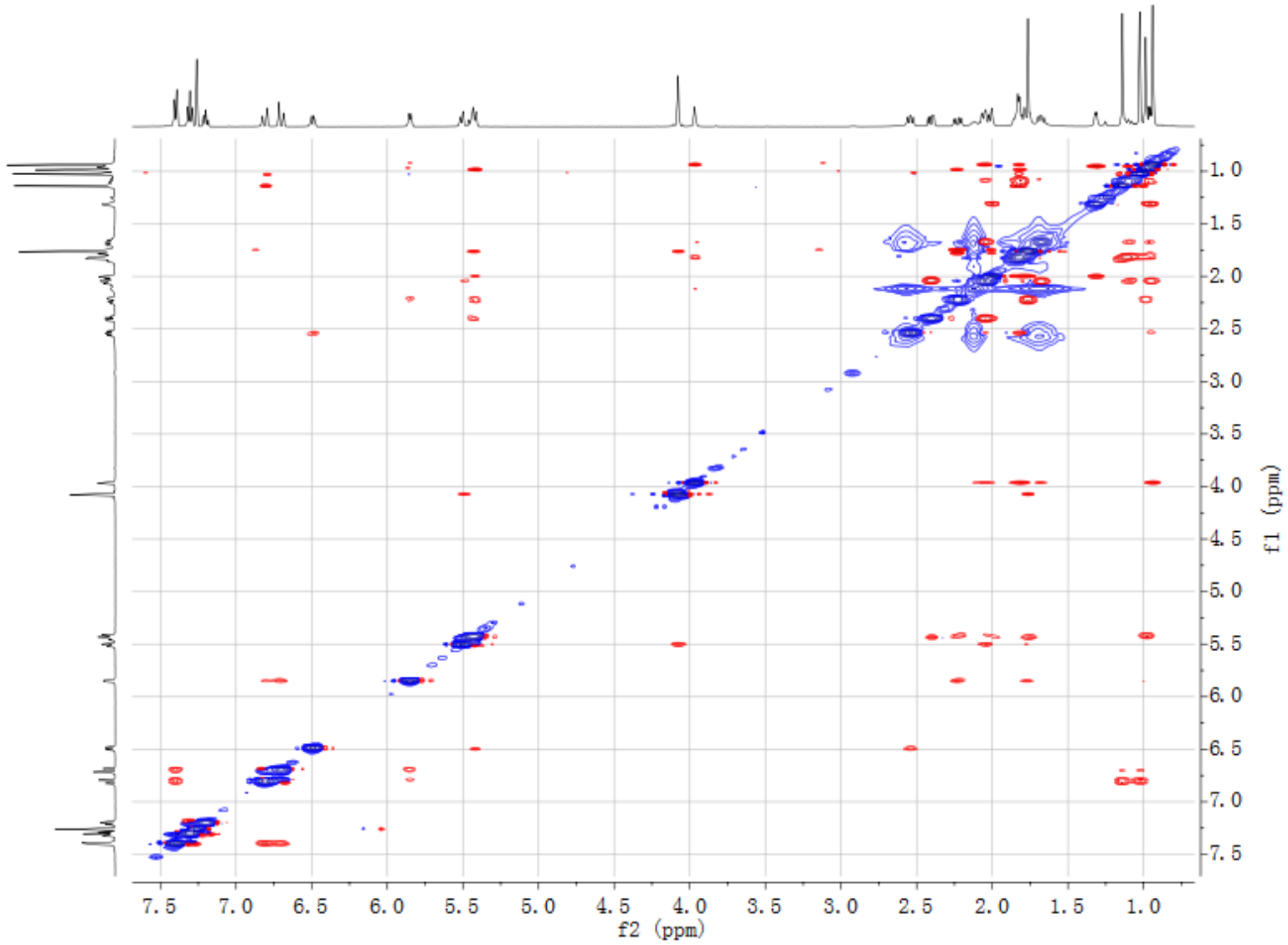


Figure S31. (±)-ESIMS spectra of **2**

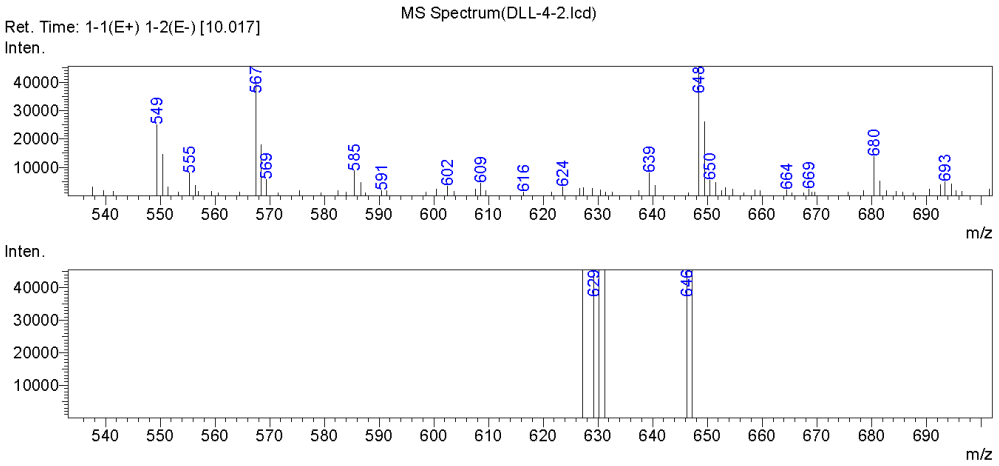


Figure S32. (–)-HRESIMS spectrum of **2**

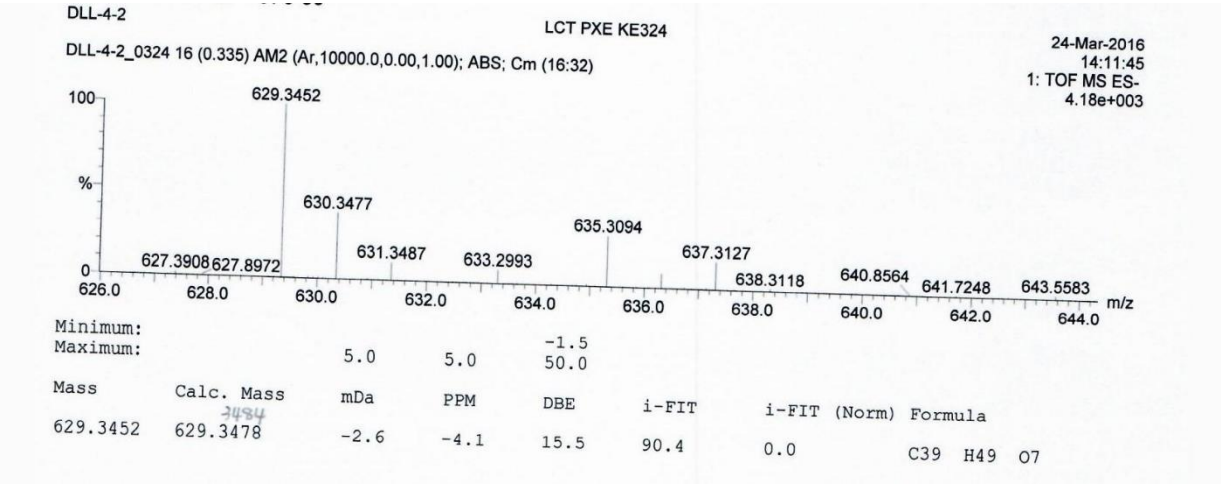
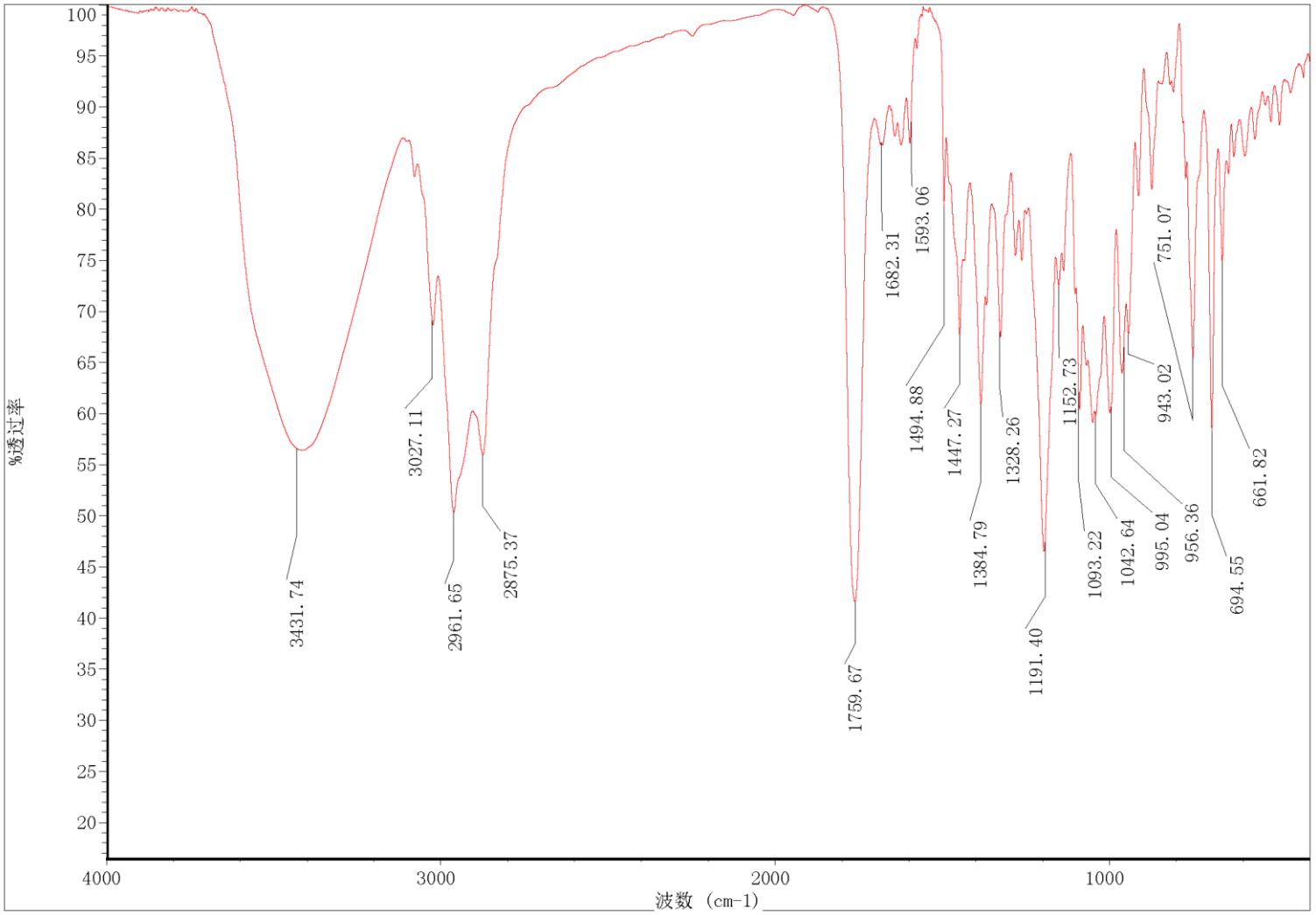


Figure S33. IR spectrum of **2**



6.3 NMR, MS, and IR spectra of compound 3

Figure S34. ^{1}H NMR spectrum (500 MHz) of **3** in $CDCl_3$

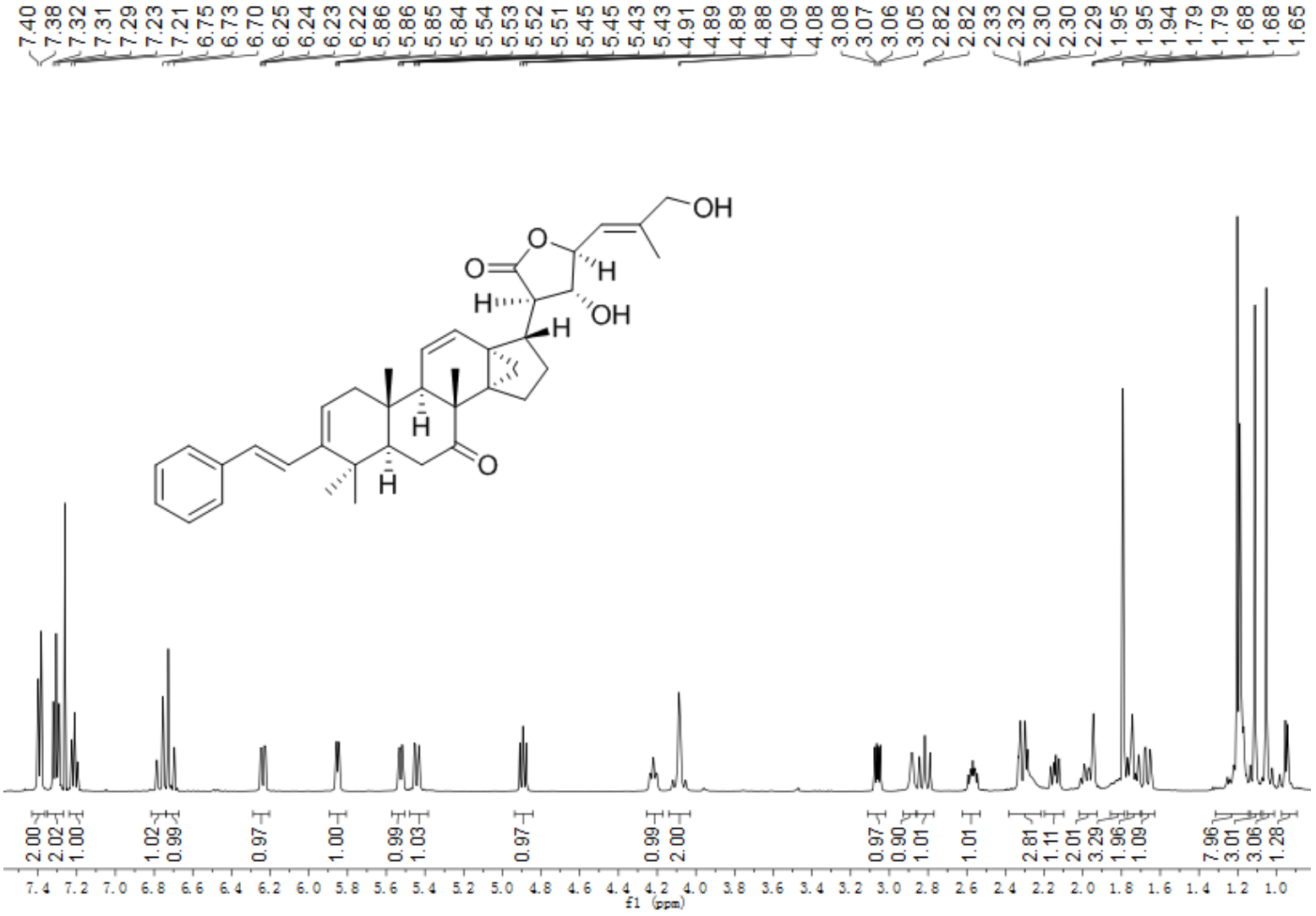


Figure S35. ^{13}C NMR spectrum (125 MHz) of **3** in $CDCl_3$

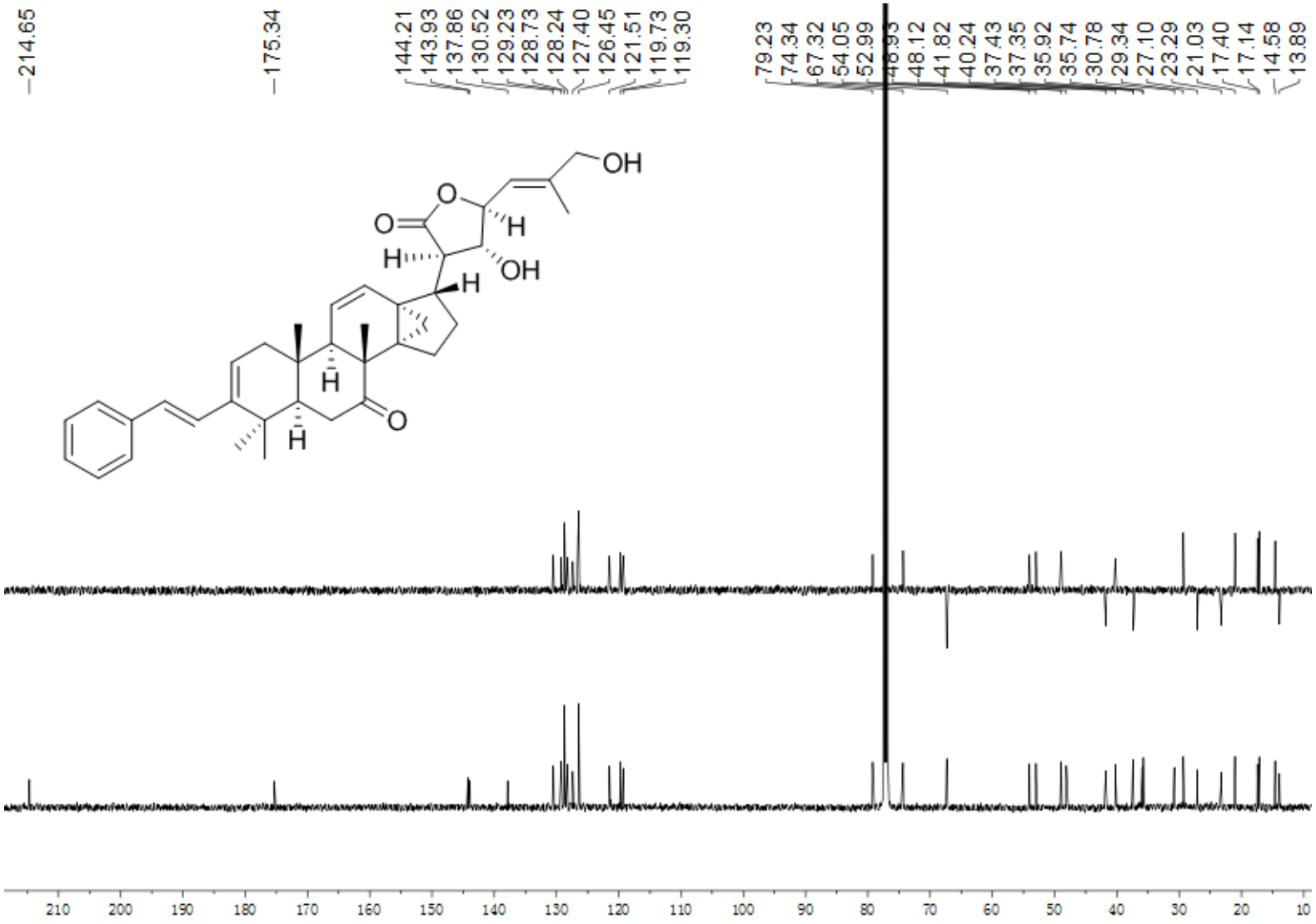


Figure S36. $^{1}H–^{1}H$ COSY spectrum of **3** in $CDCl_3$

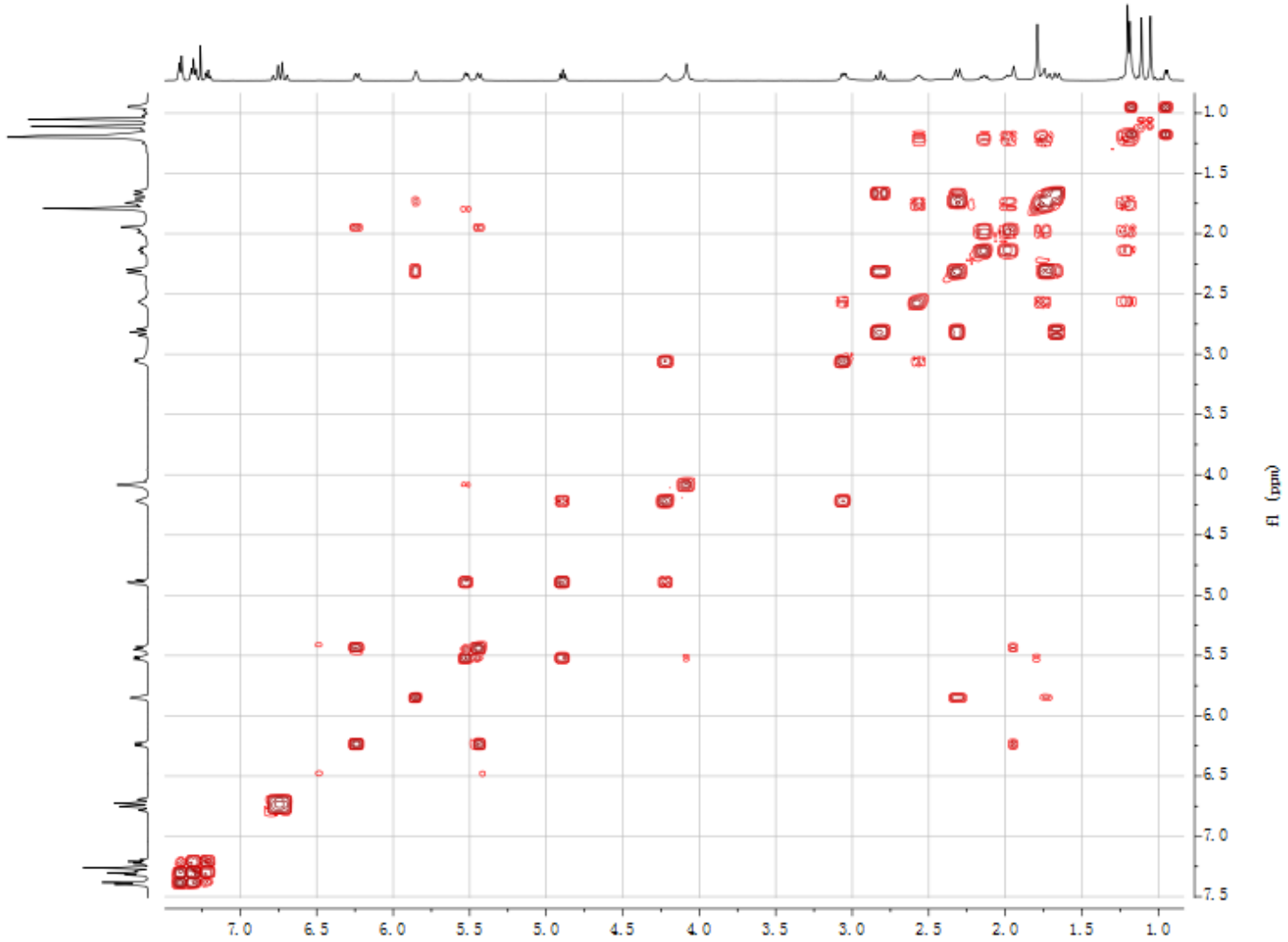


Figure S37. HSQC spectrum of **3** in $CDCl_3$

Figure S38. HMBC spectrum of **3** in $CDCl_3$

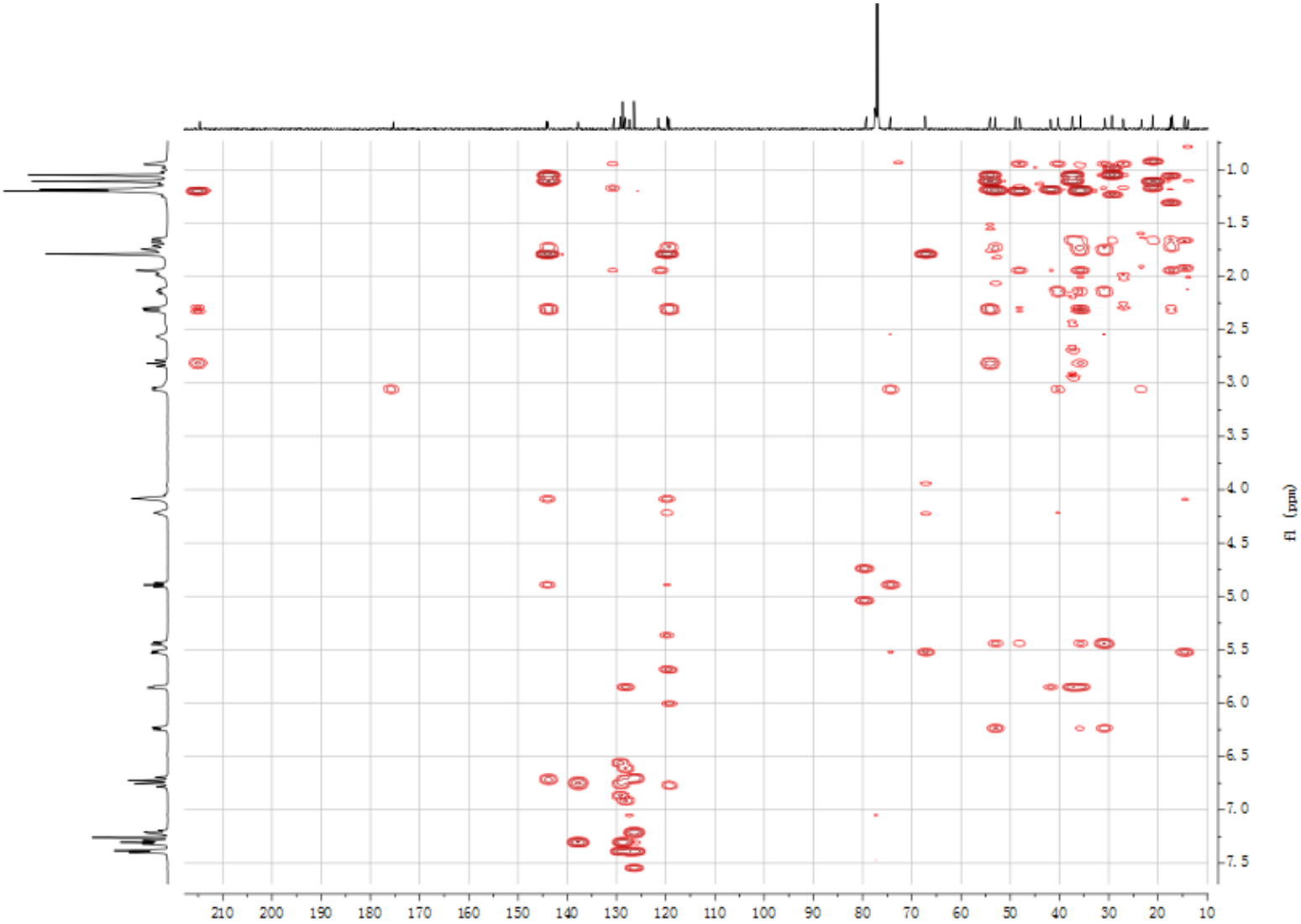


Figure S39. NOESY spectrum of **3** in $CDCl_3$

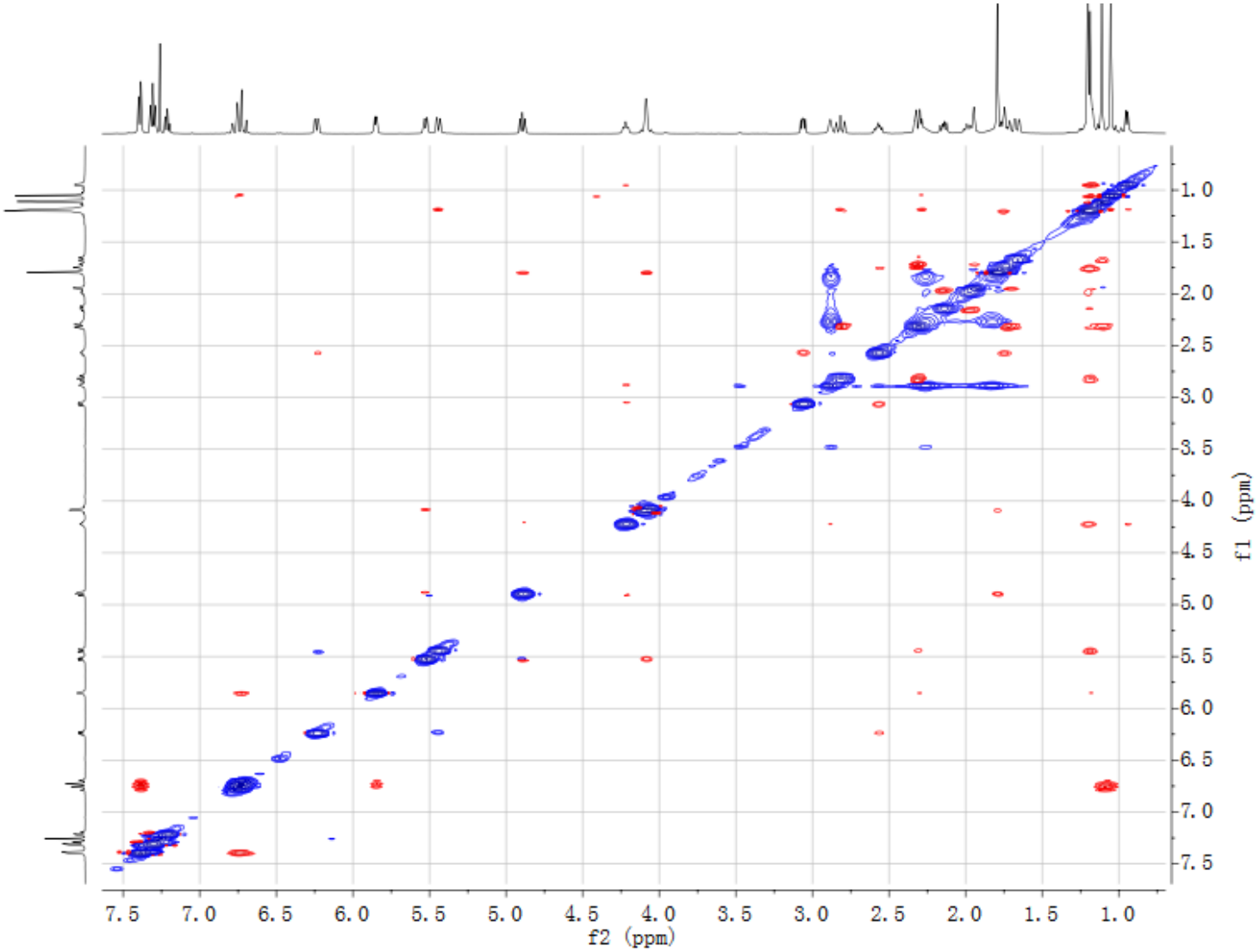


Figure S40. (±)-ESIMS spectra of **3**

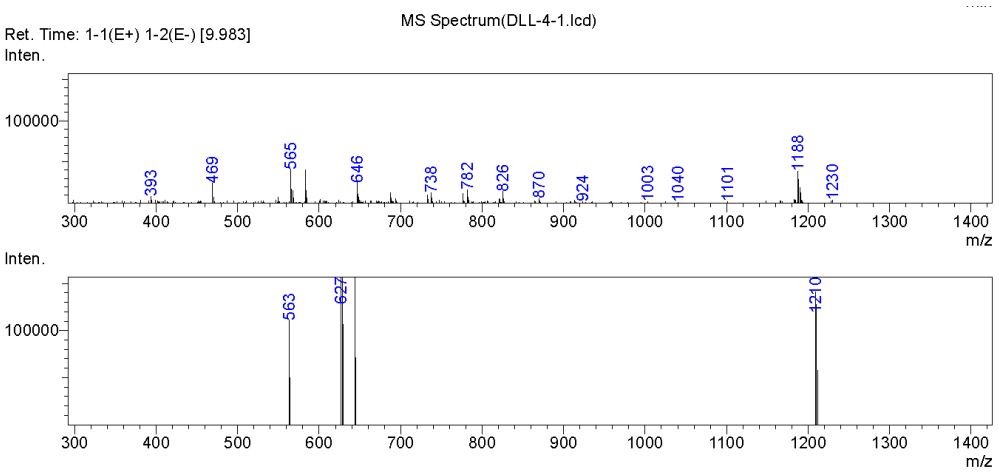


Figure S41. (–)-HRESIMS spectrum of **3**

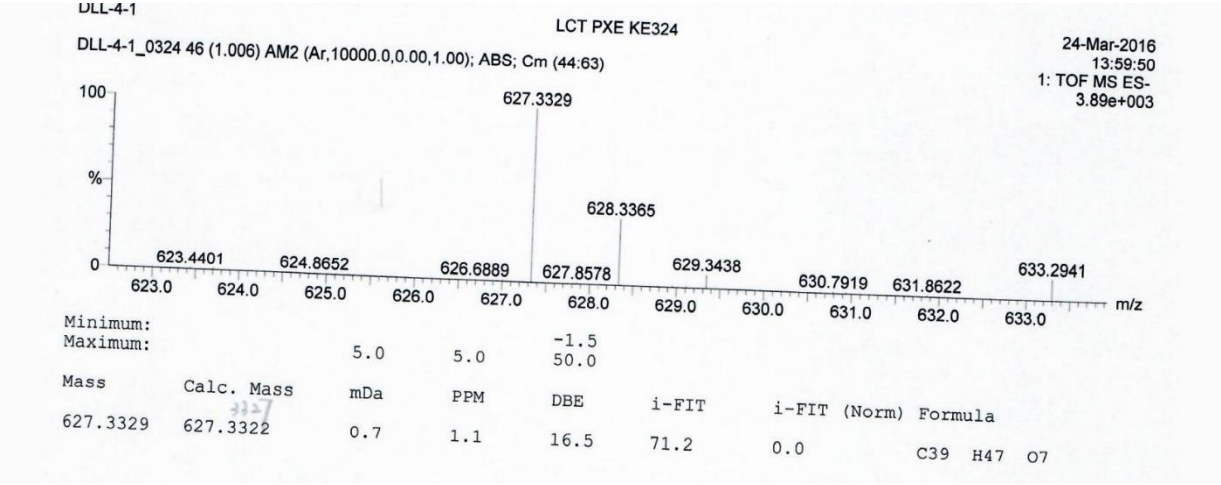
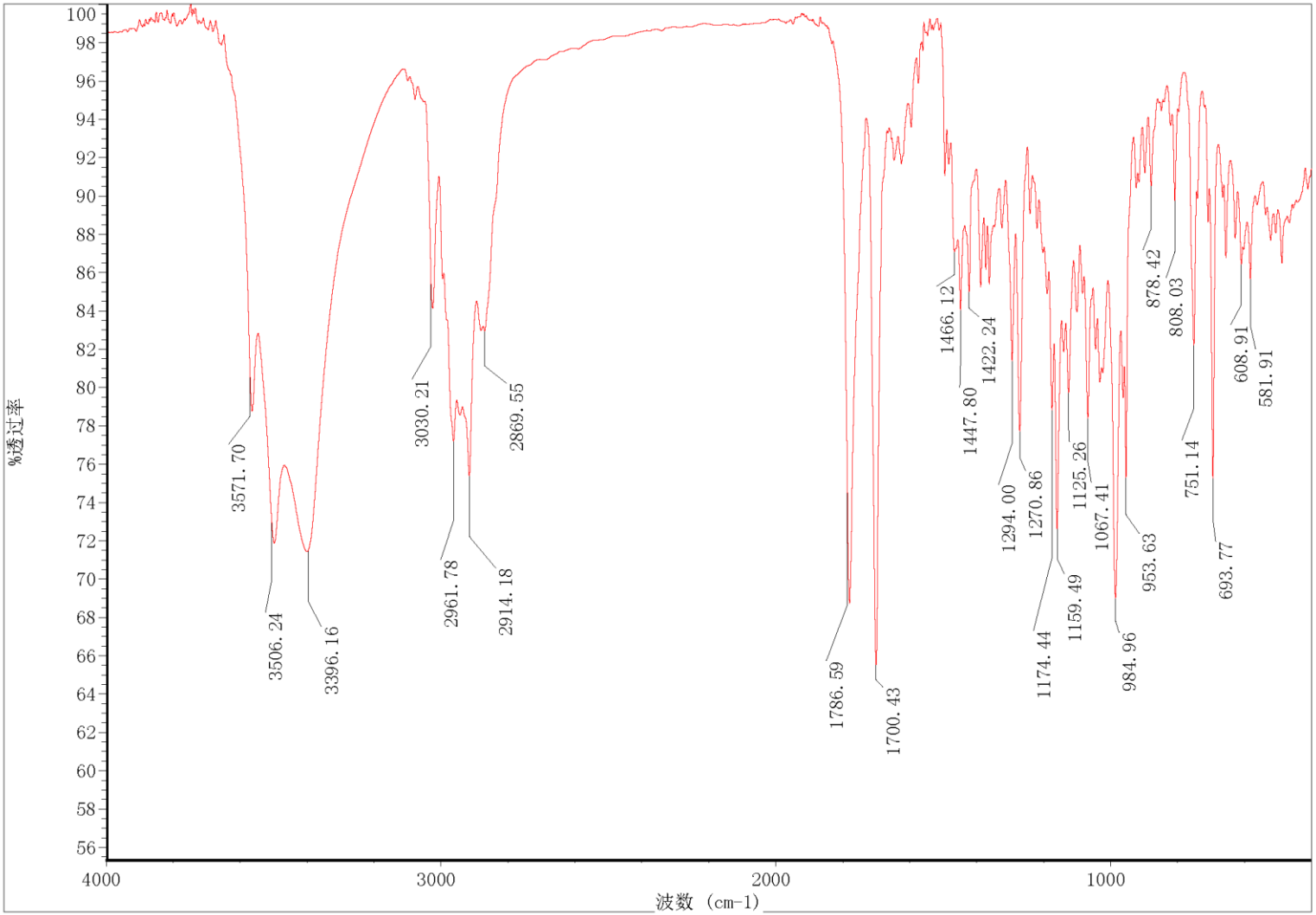


Figure S42. IR spectrum of **3**



6.4 NMR, MS, and IR spectra of compound 4

Figure S43. ^{1}H NMR spectrum (500 MHz) of **4** in $CDCl_3$

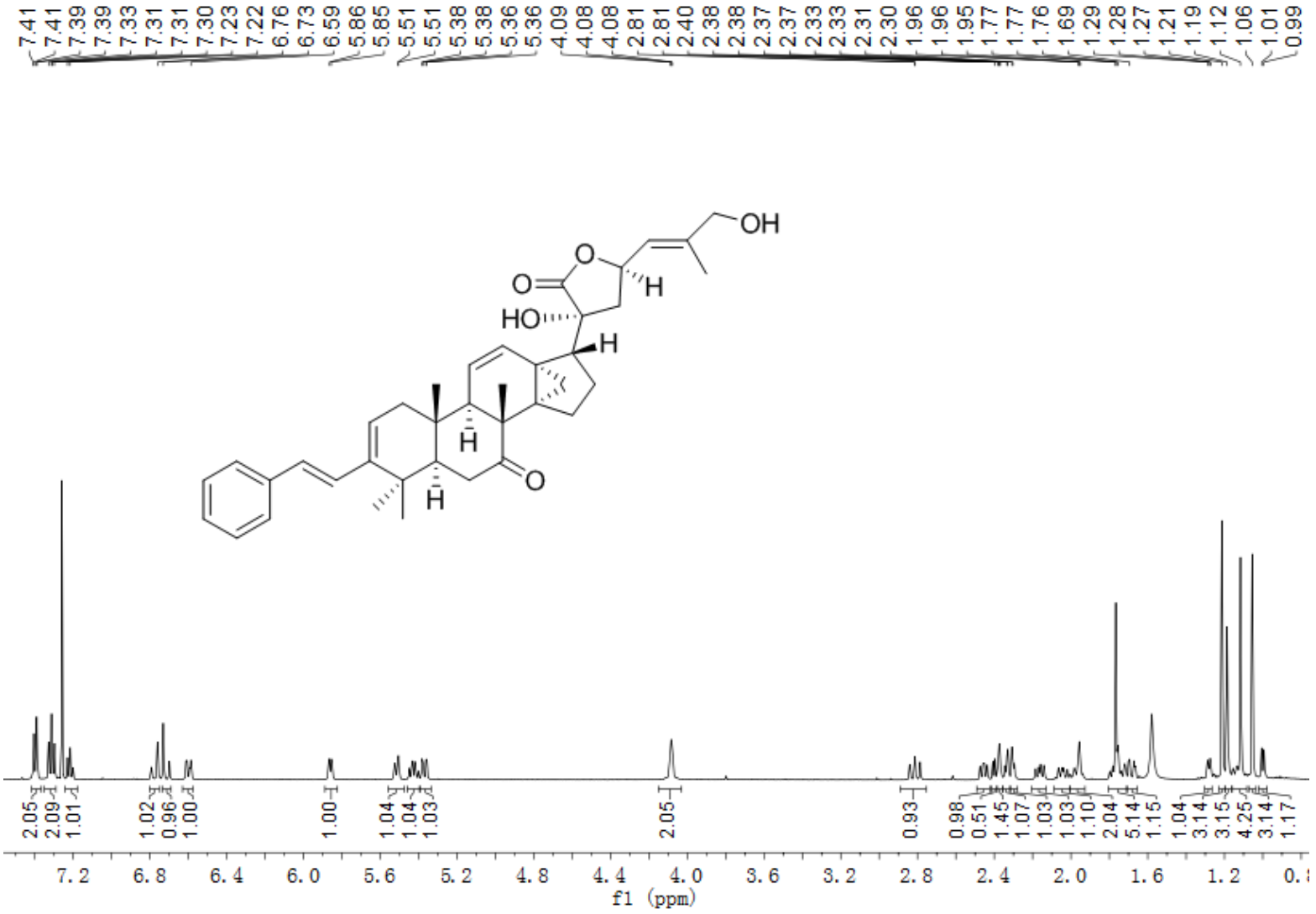


Figure S44. ^{13}C NMR spectrum (125 MHz) of **4** in $CDCl_3$

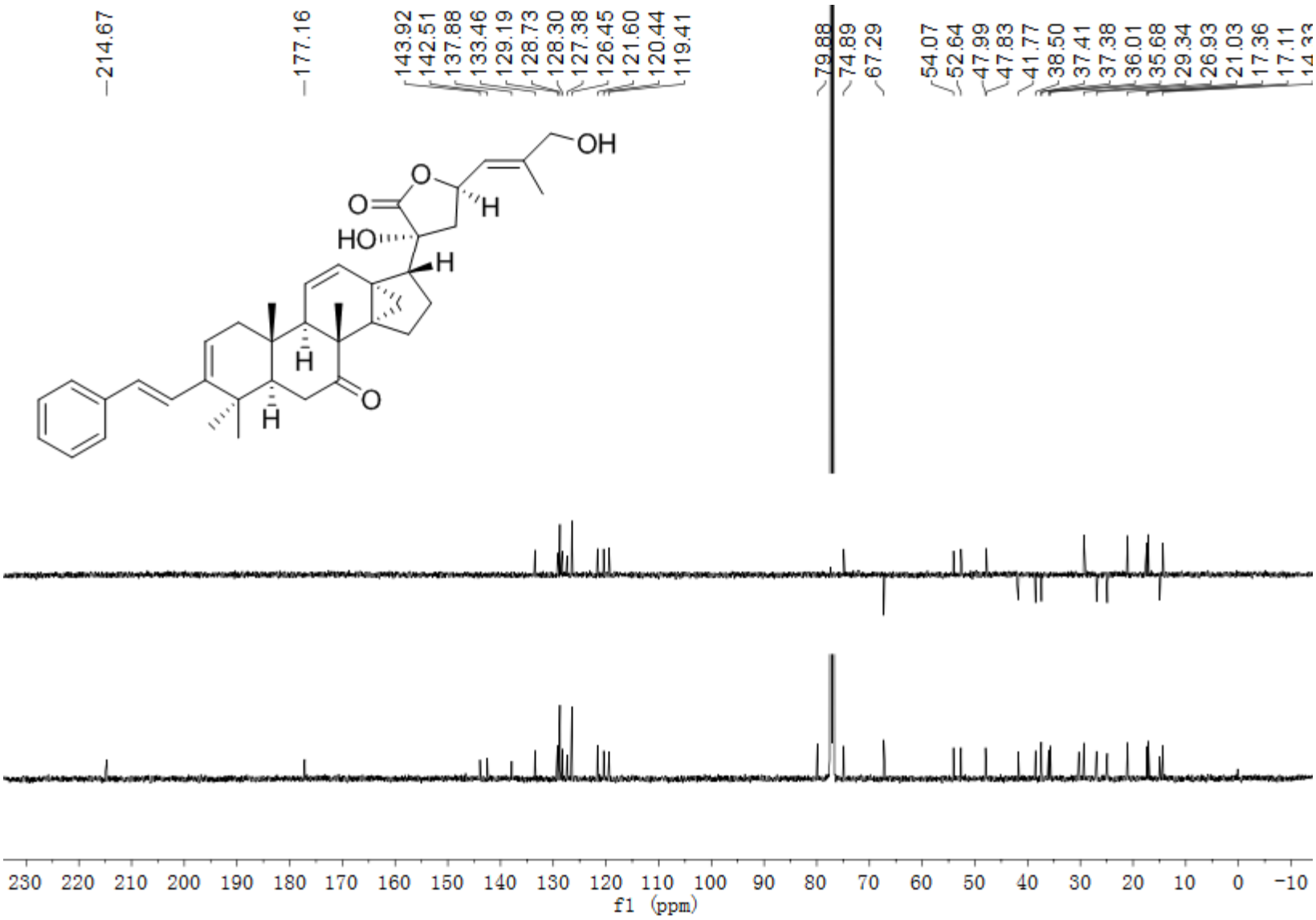


Figure S45. $^{1}H–^{1}H$ COSY spectrum of **4** in $CDCl_3$

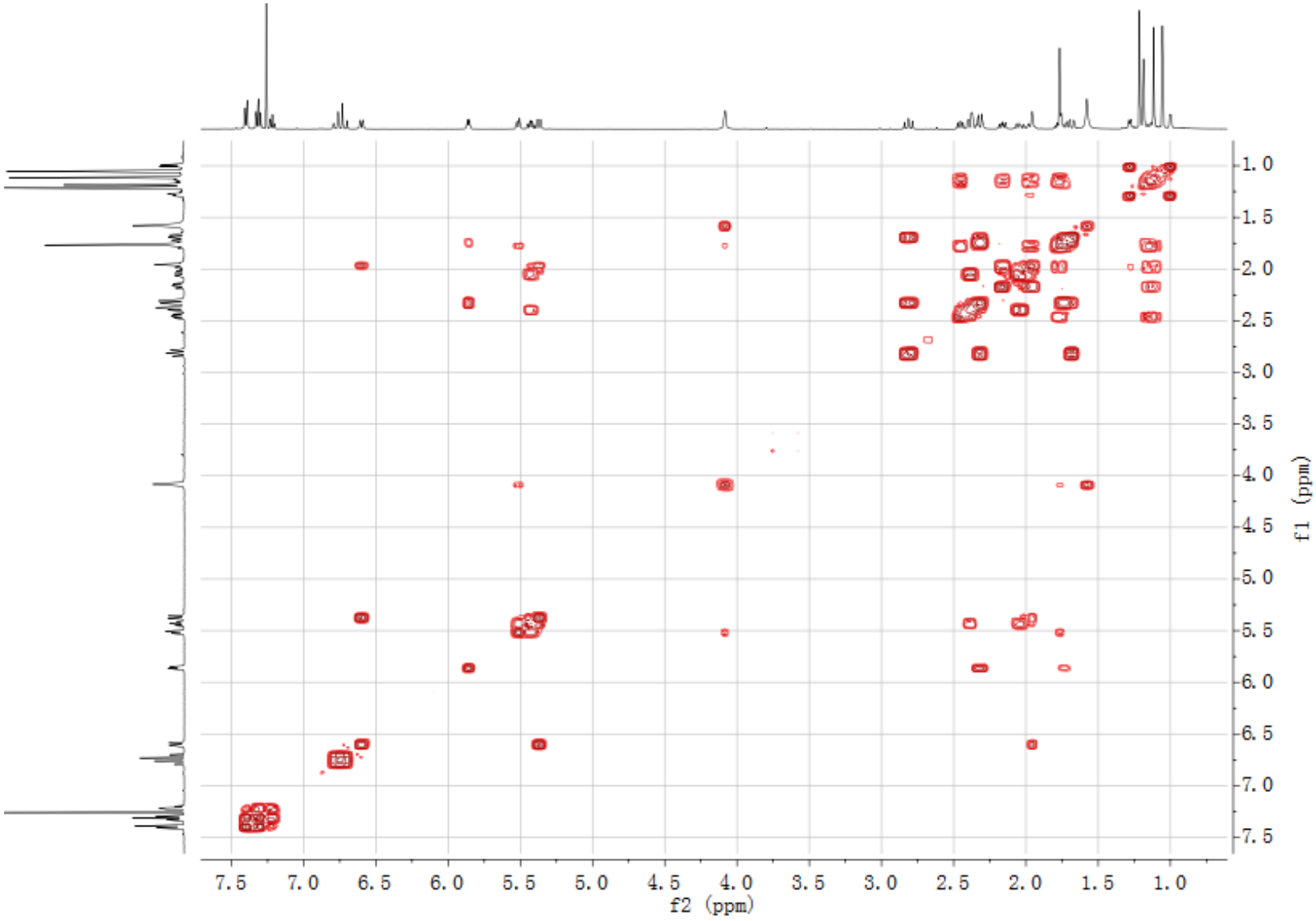


Figure S46. HSQC spectrum of **4** in $CDCl_3$

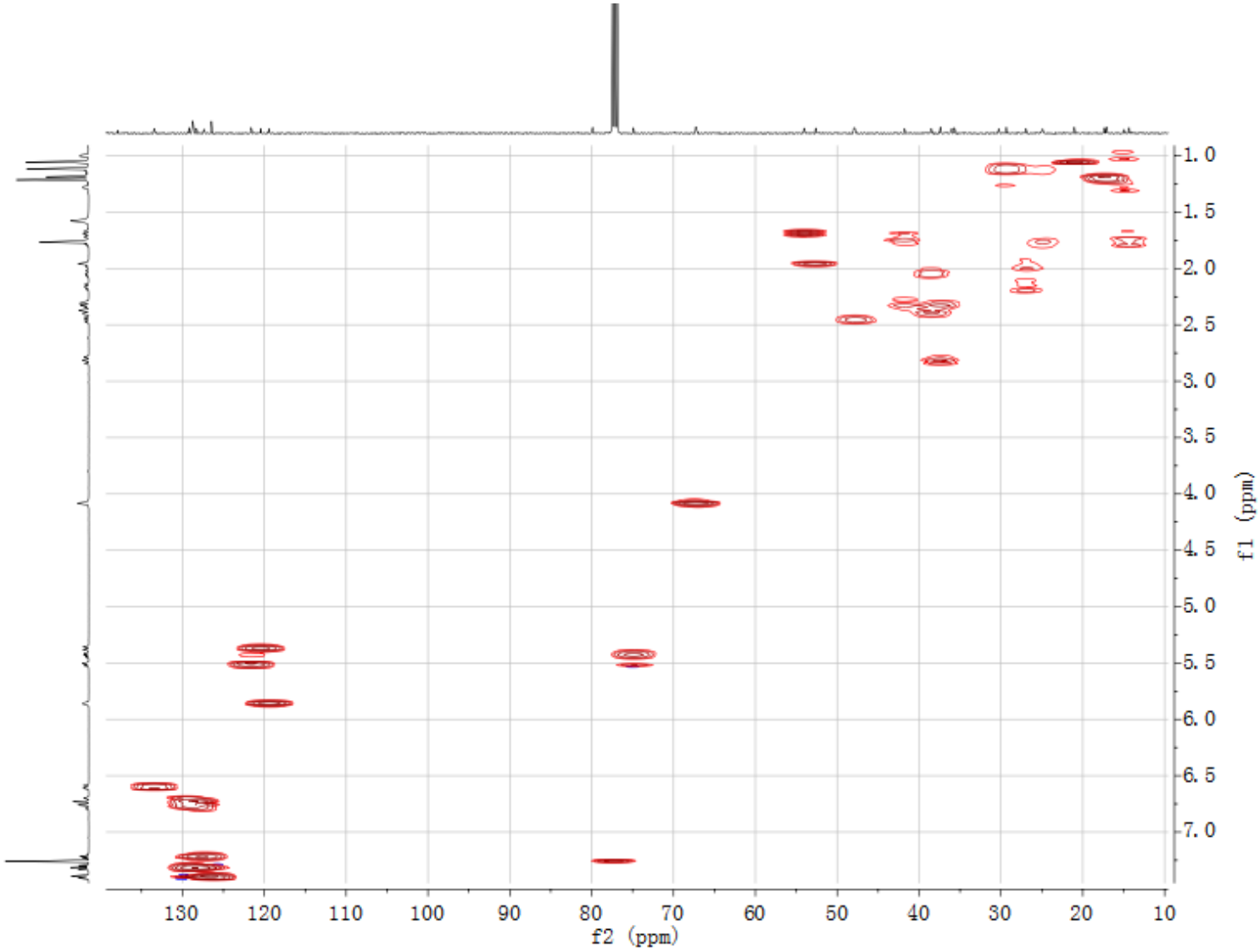
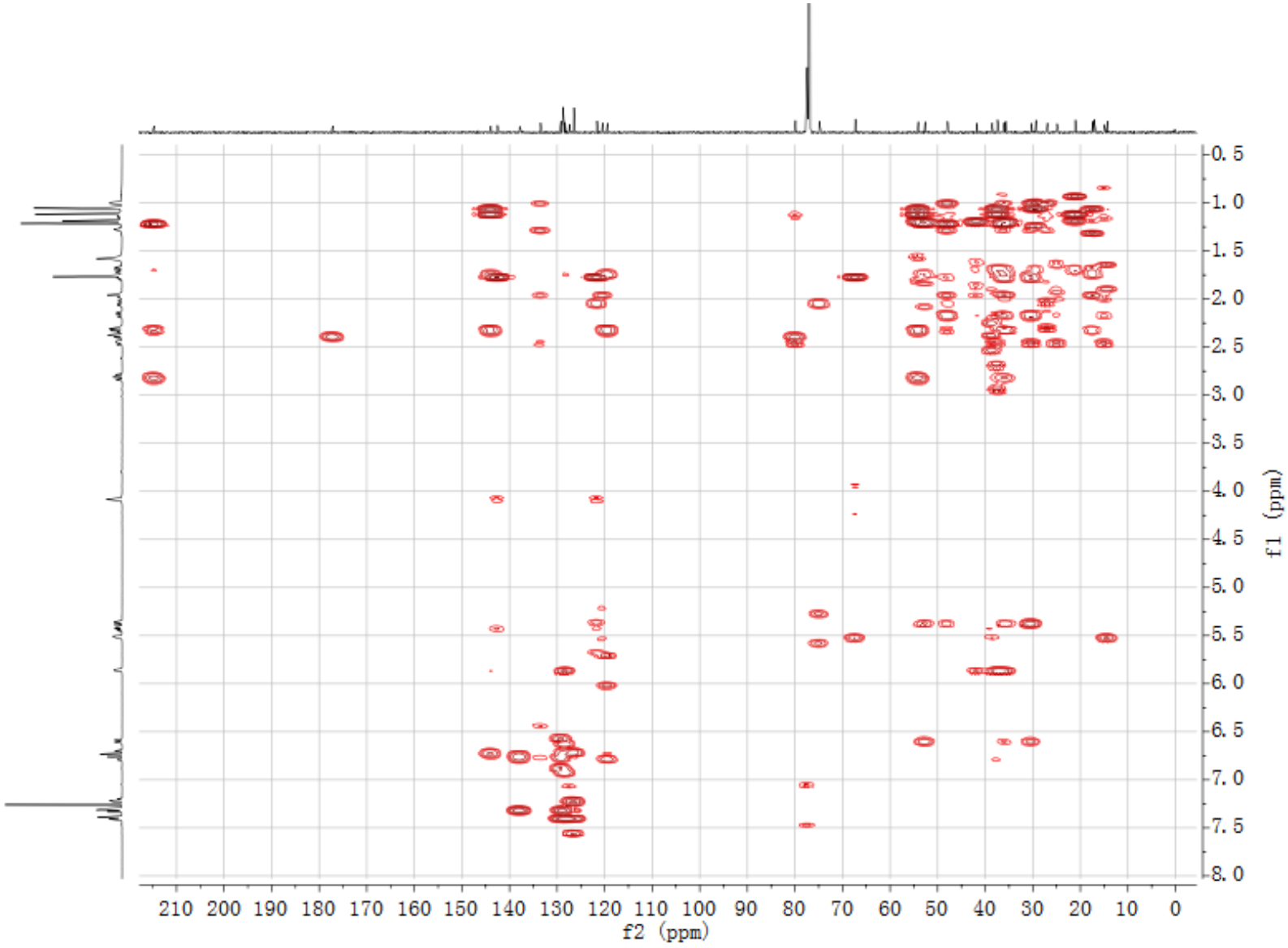


Figure S47. HMBC spectrum of **4** in $CDCl_3$



FigureS48. NOESY spectrum of **4** in $CDCl_3$

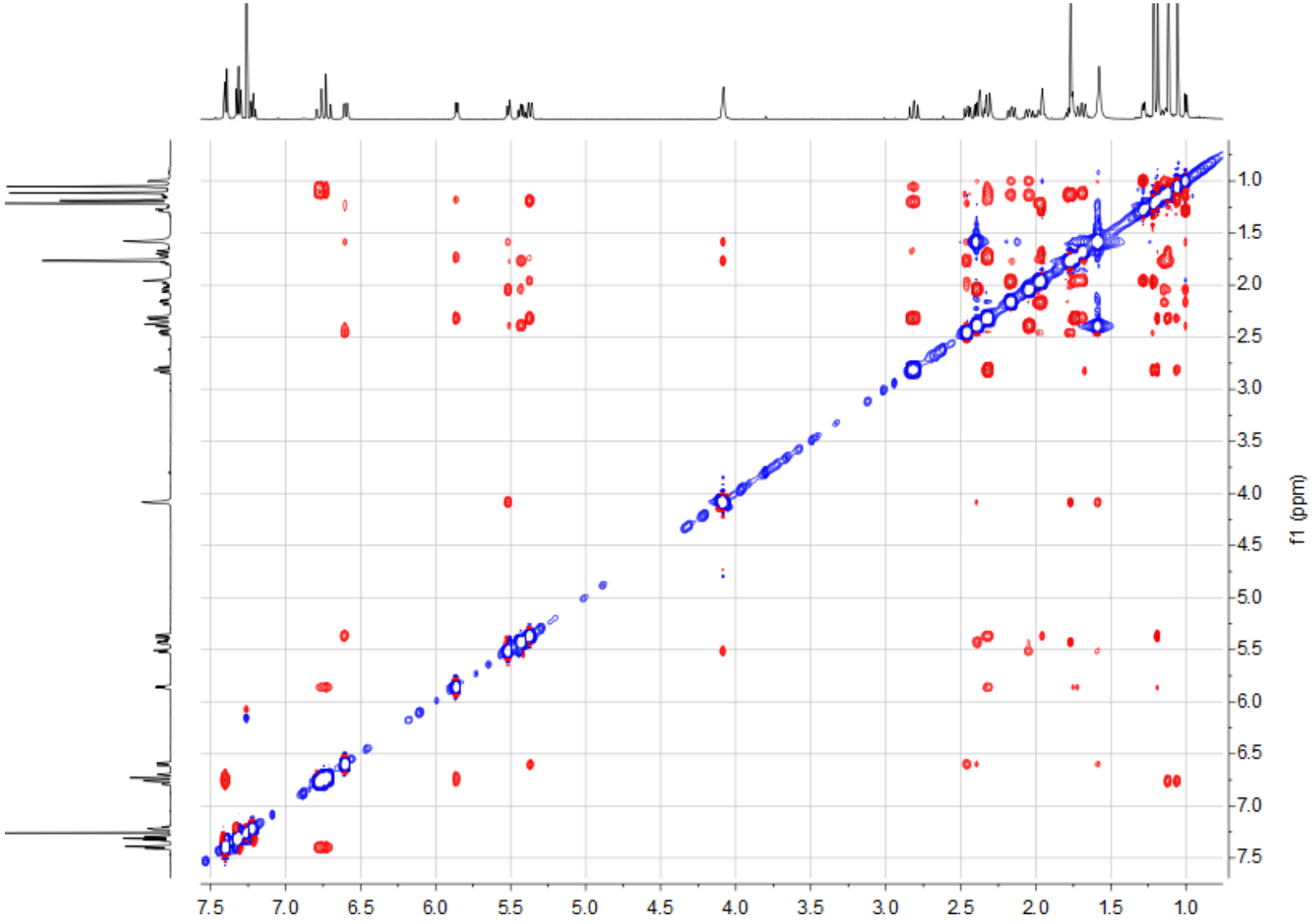


Figure S49. (±)-ESIMS spectra of **4**

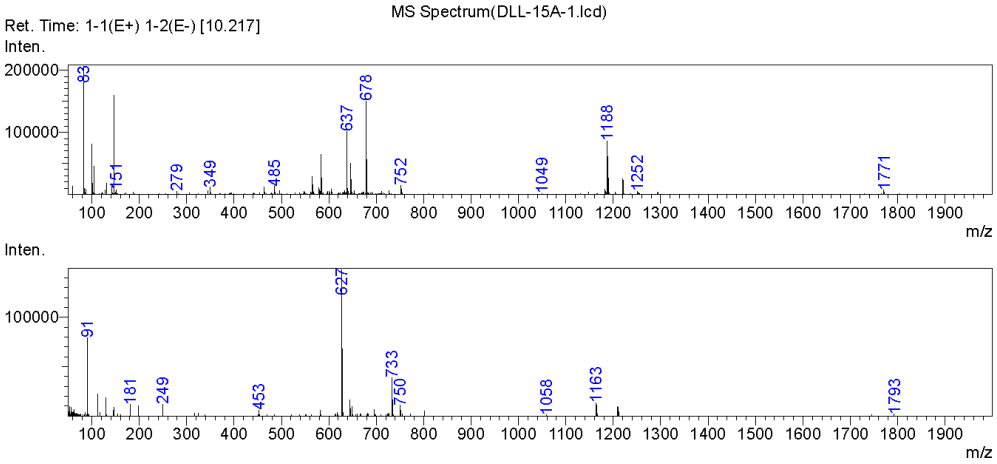


Figure S50. (–)-HRESIMS spectrum of **4**

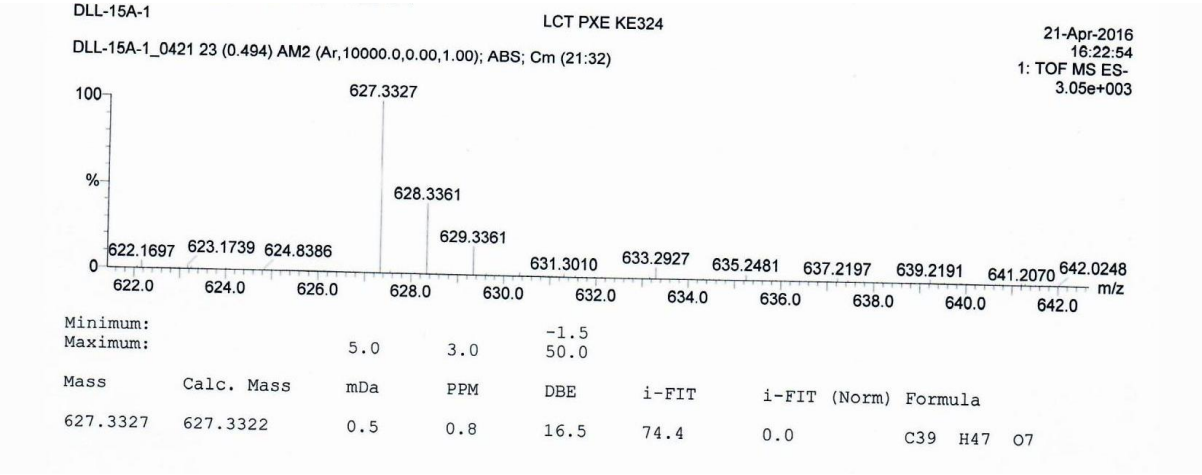
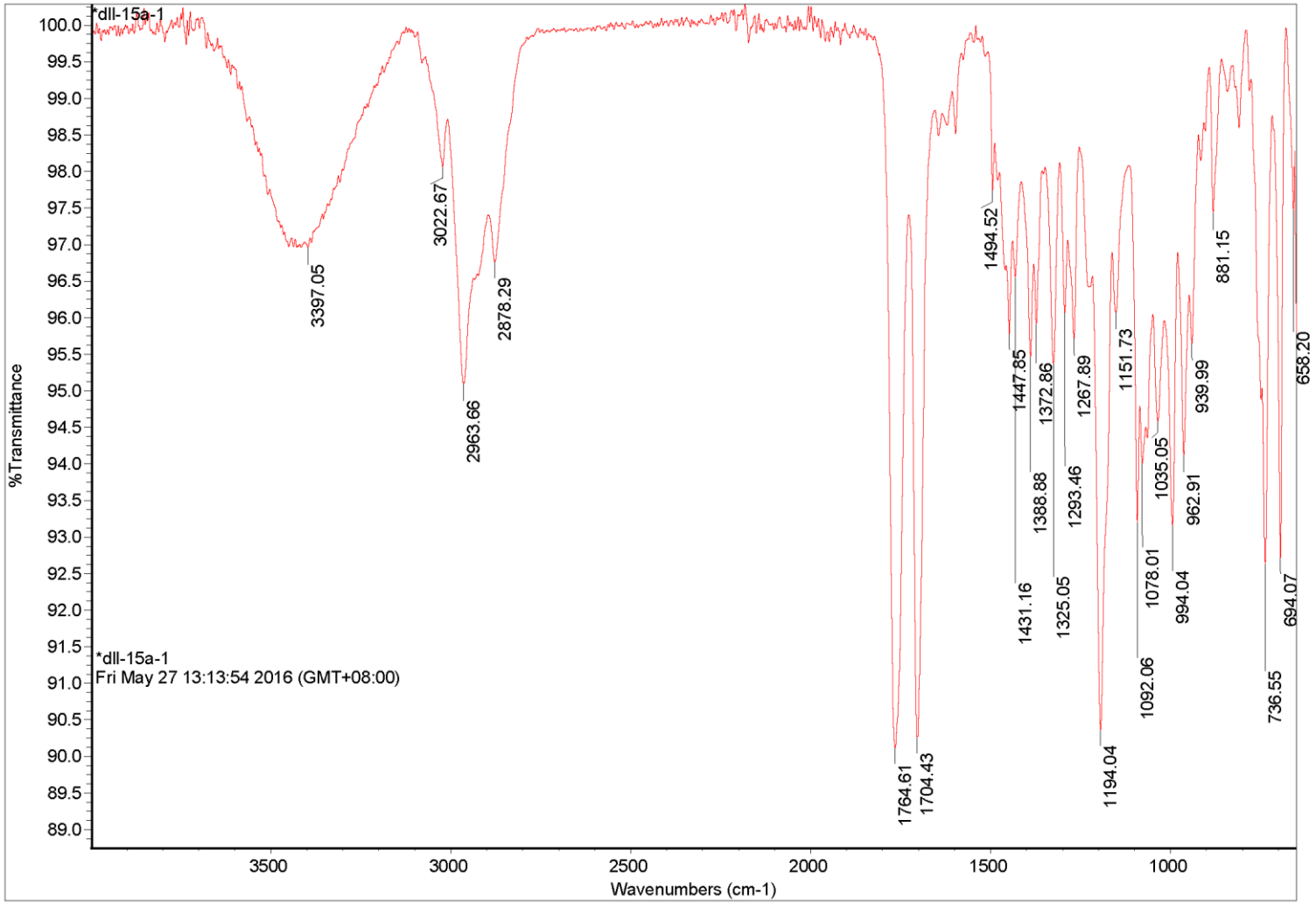


Figure S51. IR spectrum of **4**



6.5 NMR, MS, and IR spectra of compound 5

Figure S52. ^{1}H NMR spectrum (500 MHz) of **5** in $CDCl_3$

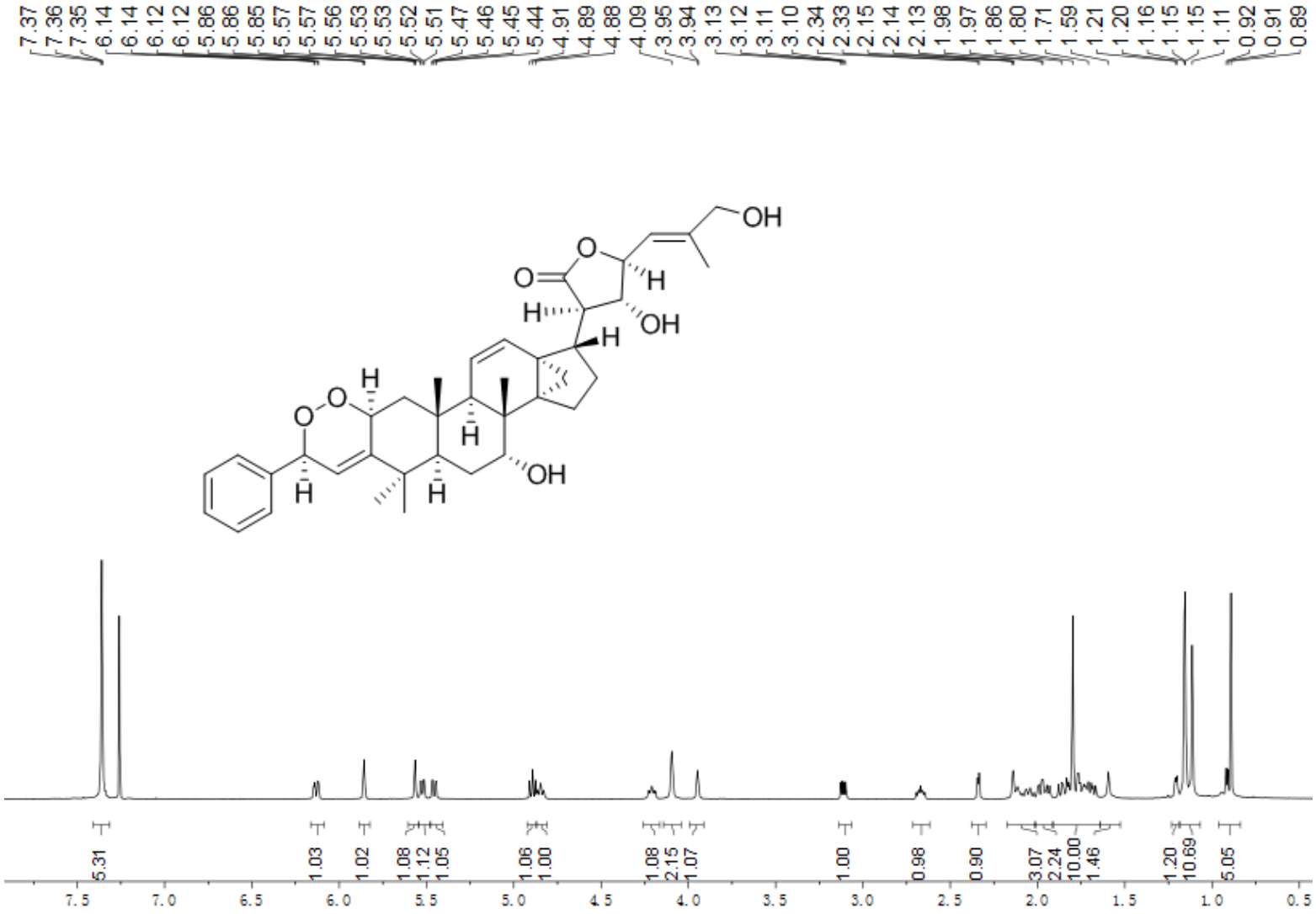


Figure S53. ^{13}C NMR spectrum (125 MHz) of **5** in $CDCl_3$

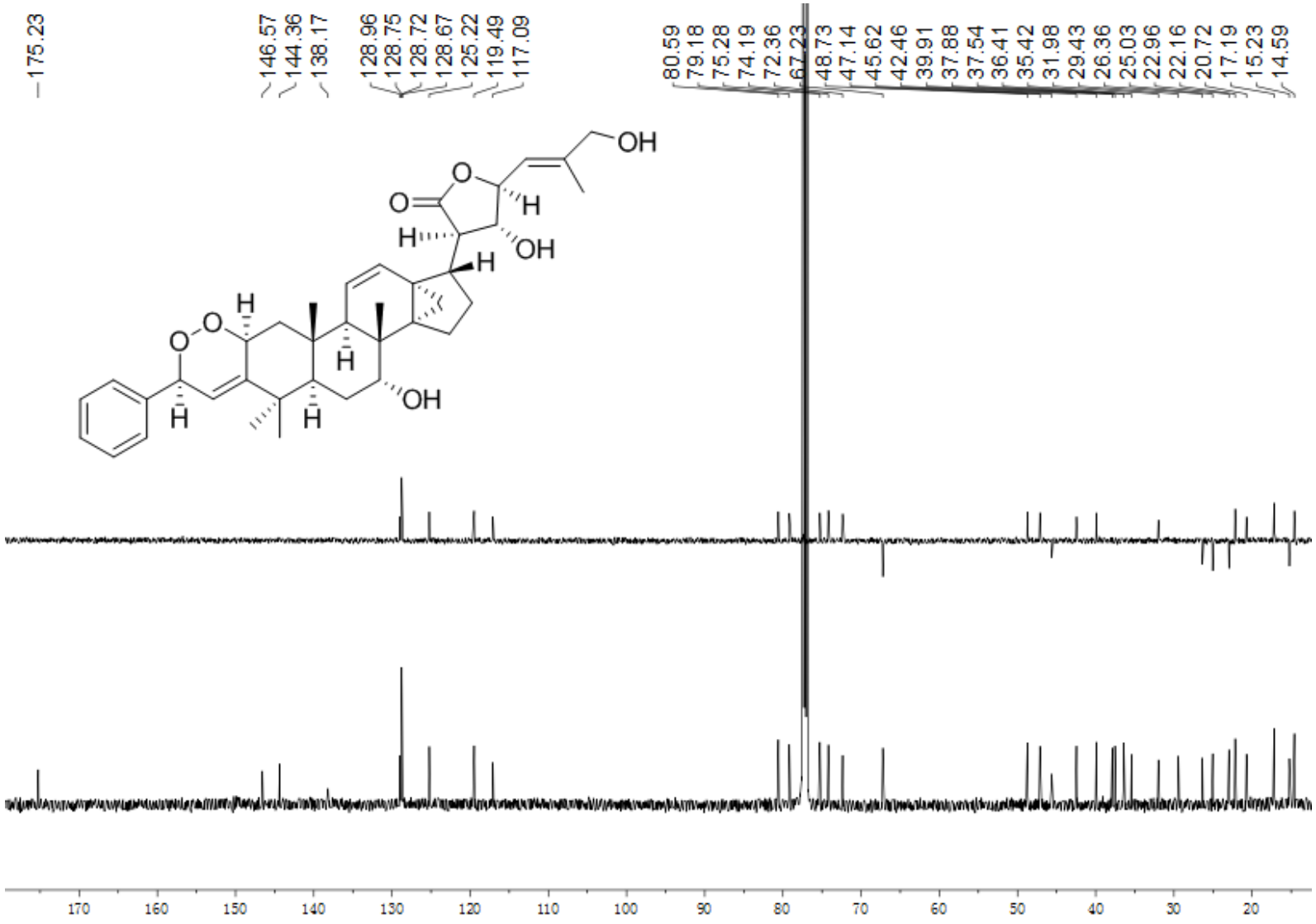


Figure S54. $^{1}H–^{1}H$ COSY spectrum of **5** in $CDCl_3$

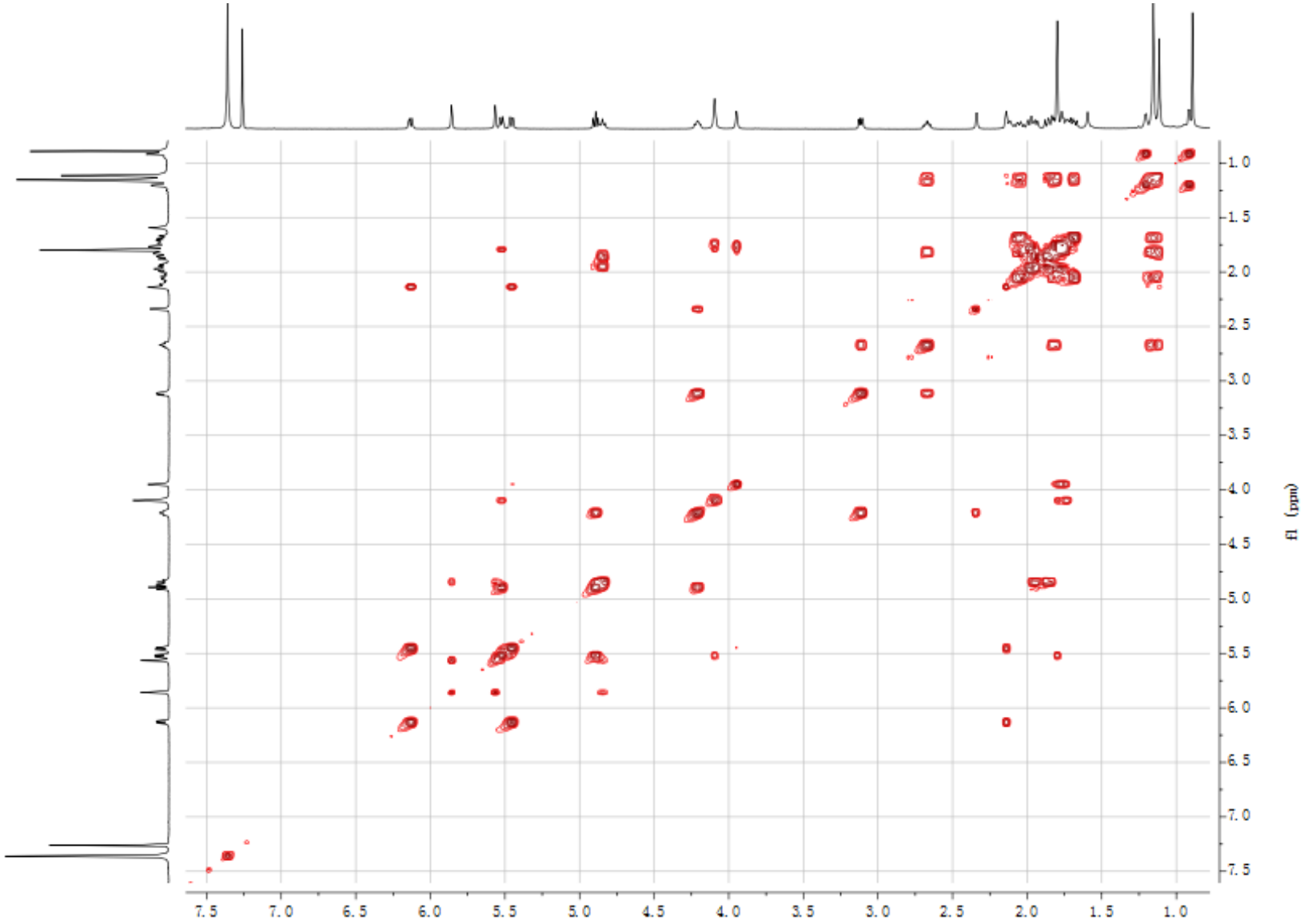


Figure S55. HSQC spectrum of **5** in $CDCl_3$

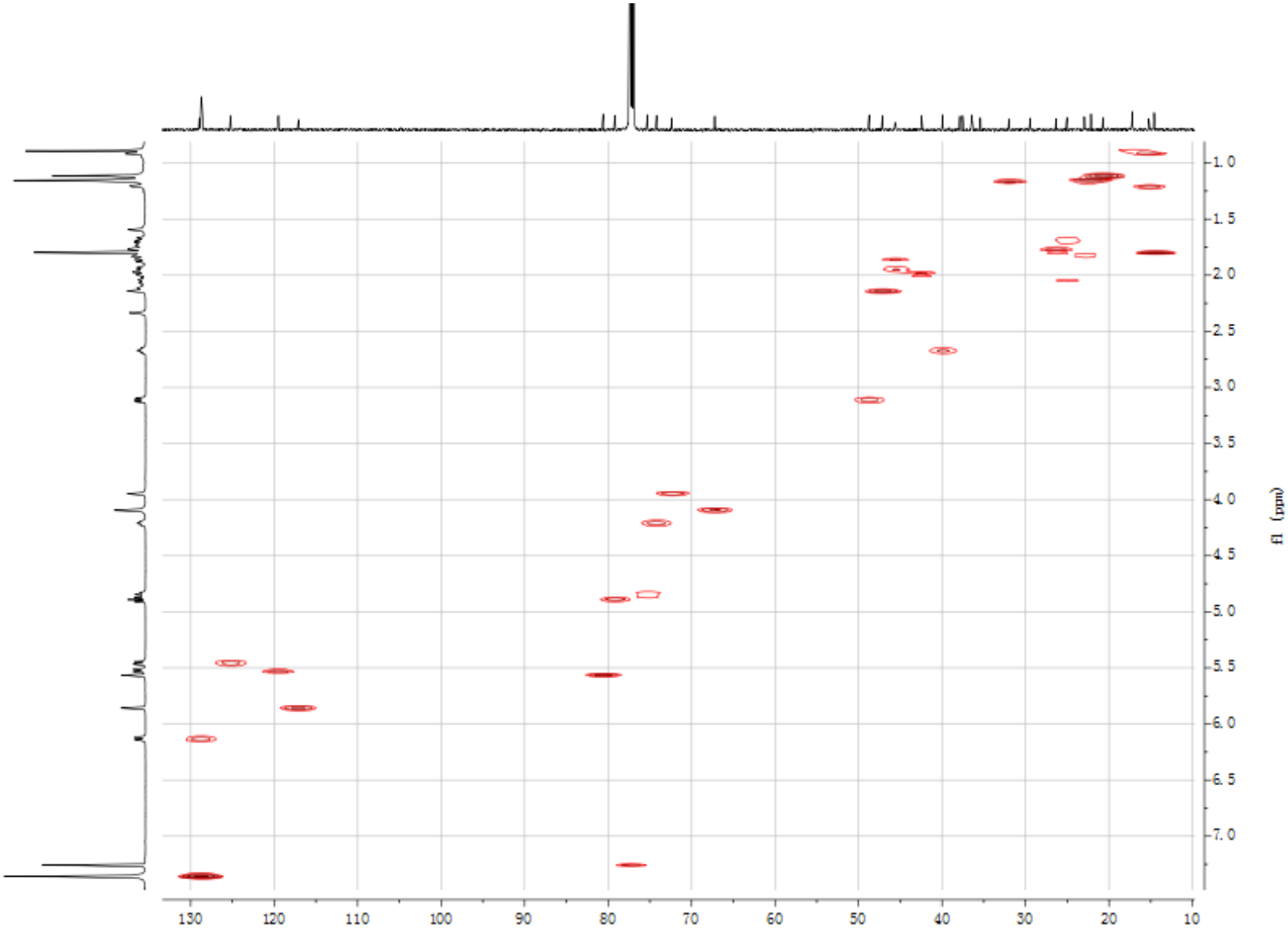


Figure S56. HMBC spectrum of **5** in $CDCl_3$

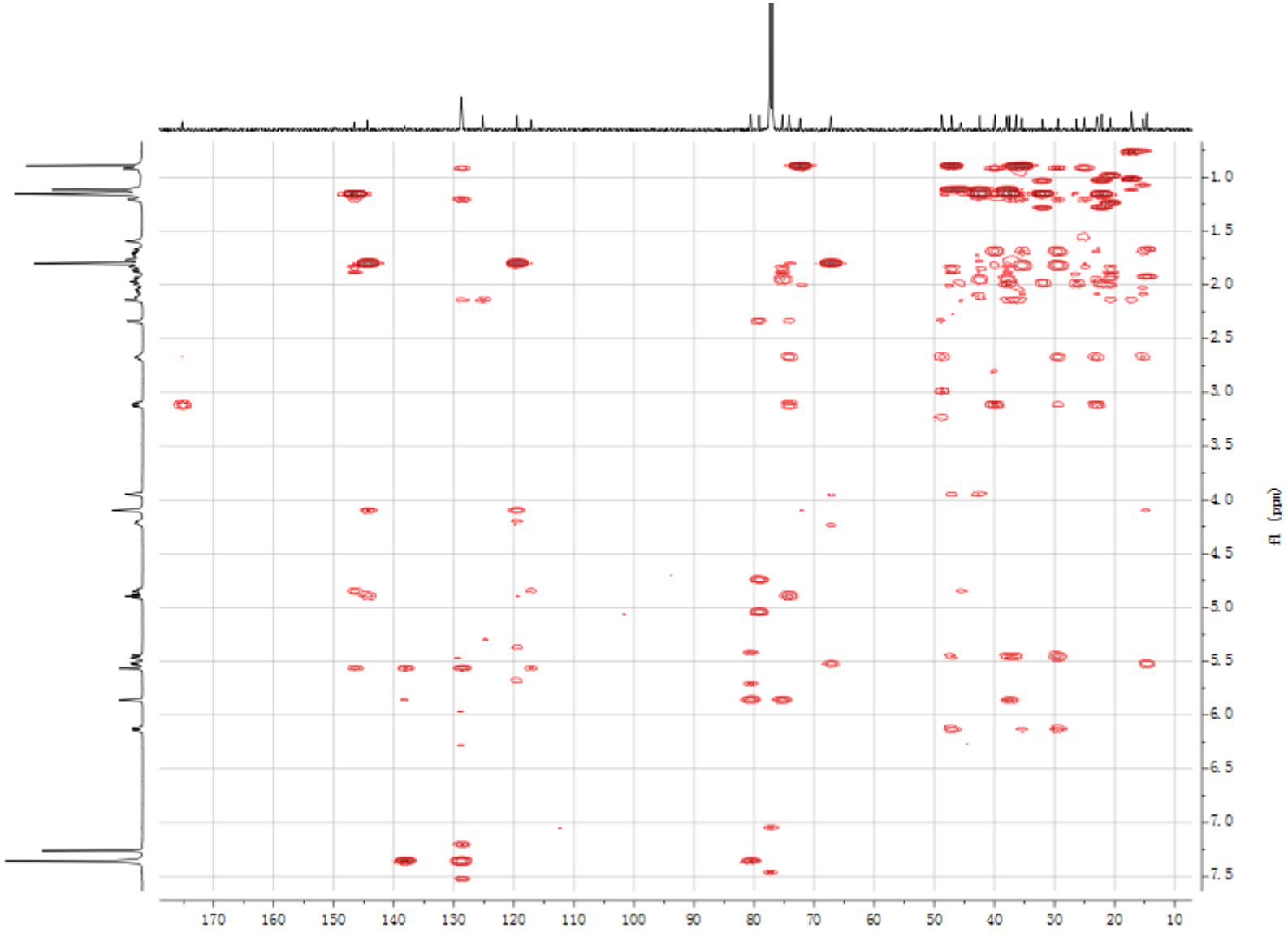


Figure S57. NOESY spectrum of **5** in $CDCl_3$

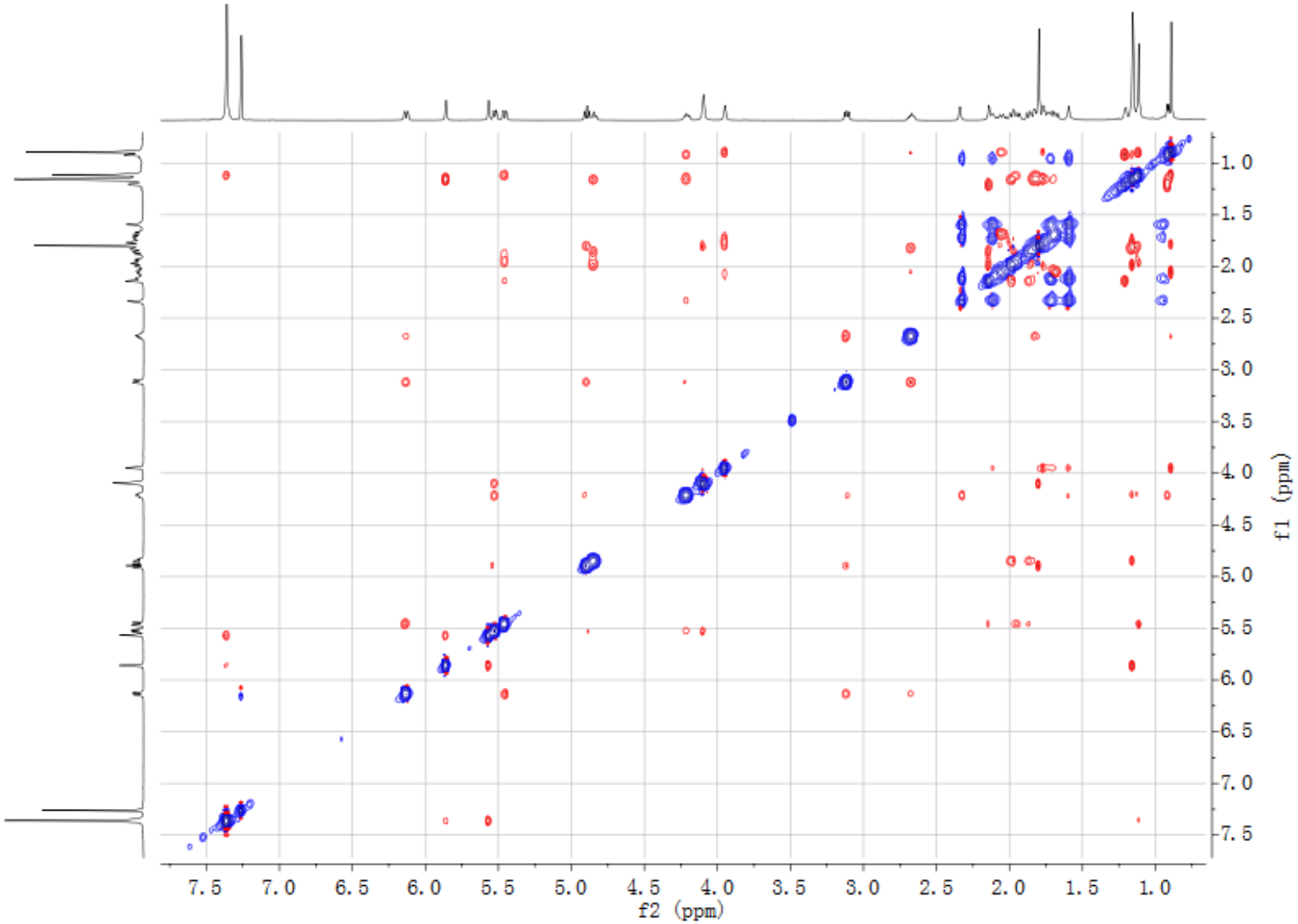


Figure S58. (±)-ESIMS spectra of **5**

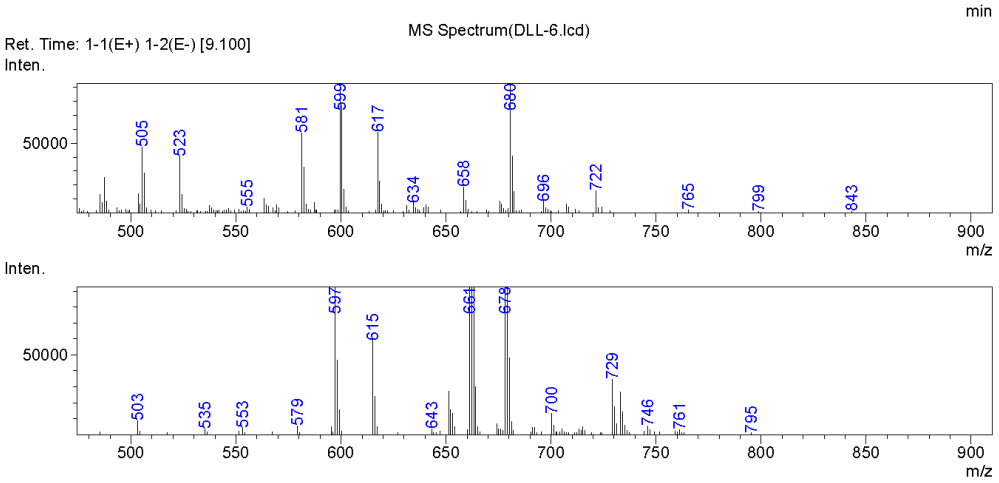


Figure S59. (–)-HRESIMS spectrum of **5**

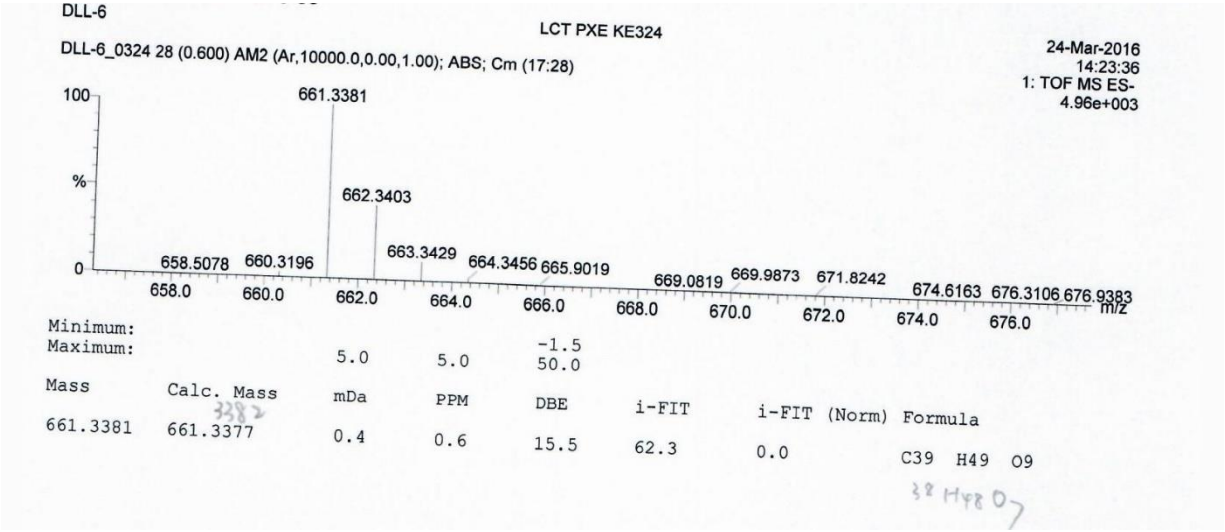
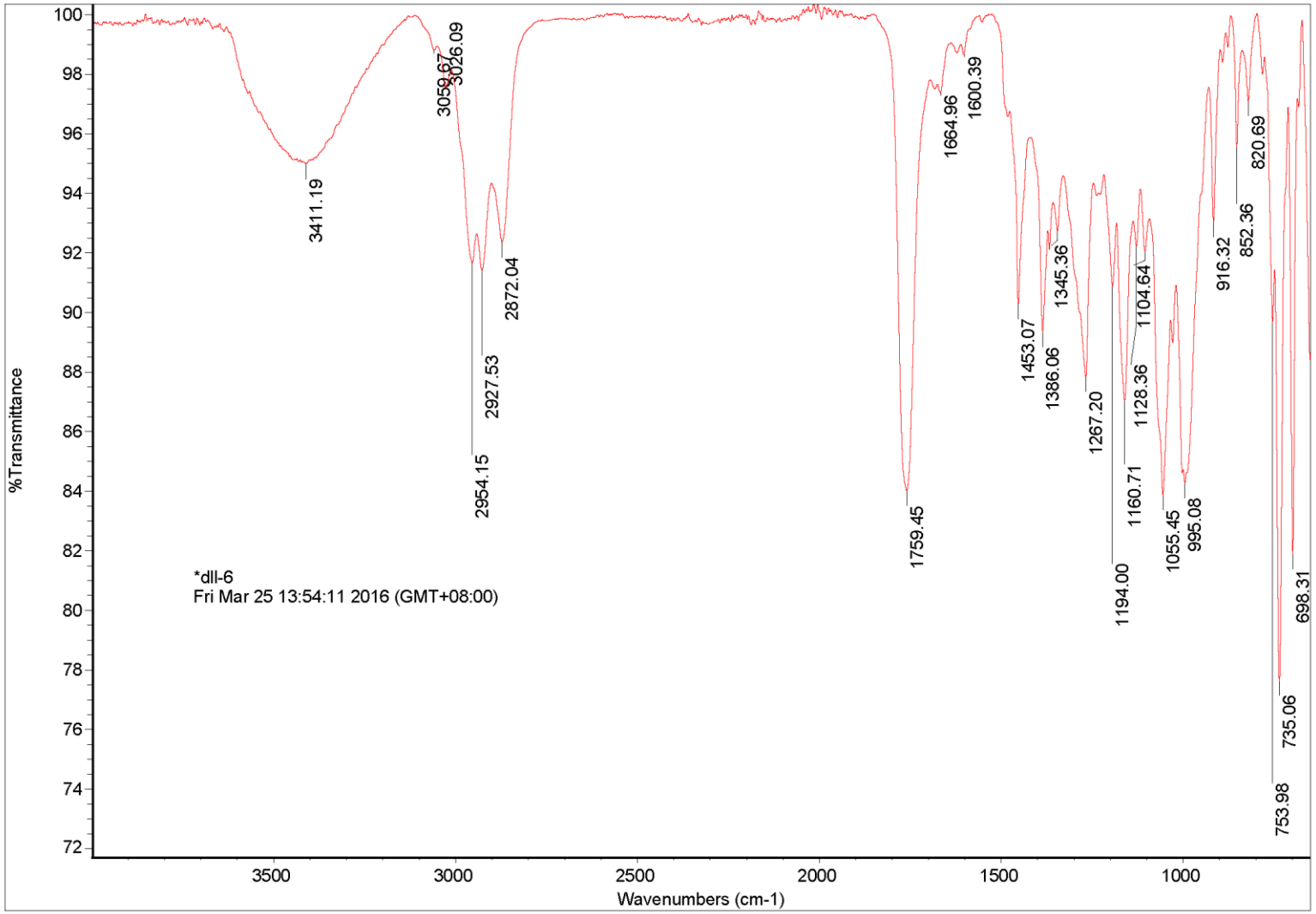


Figure S60. IR spectrum of **5**



6.6 NMR, MS, and IR spectra of compound 6

Figure S61. ^{1}H NMR spectrum (500 MHz) of **6** in $CDCl_3$

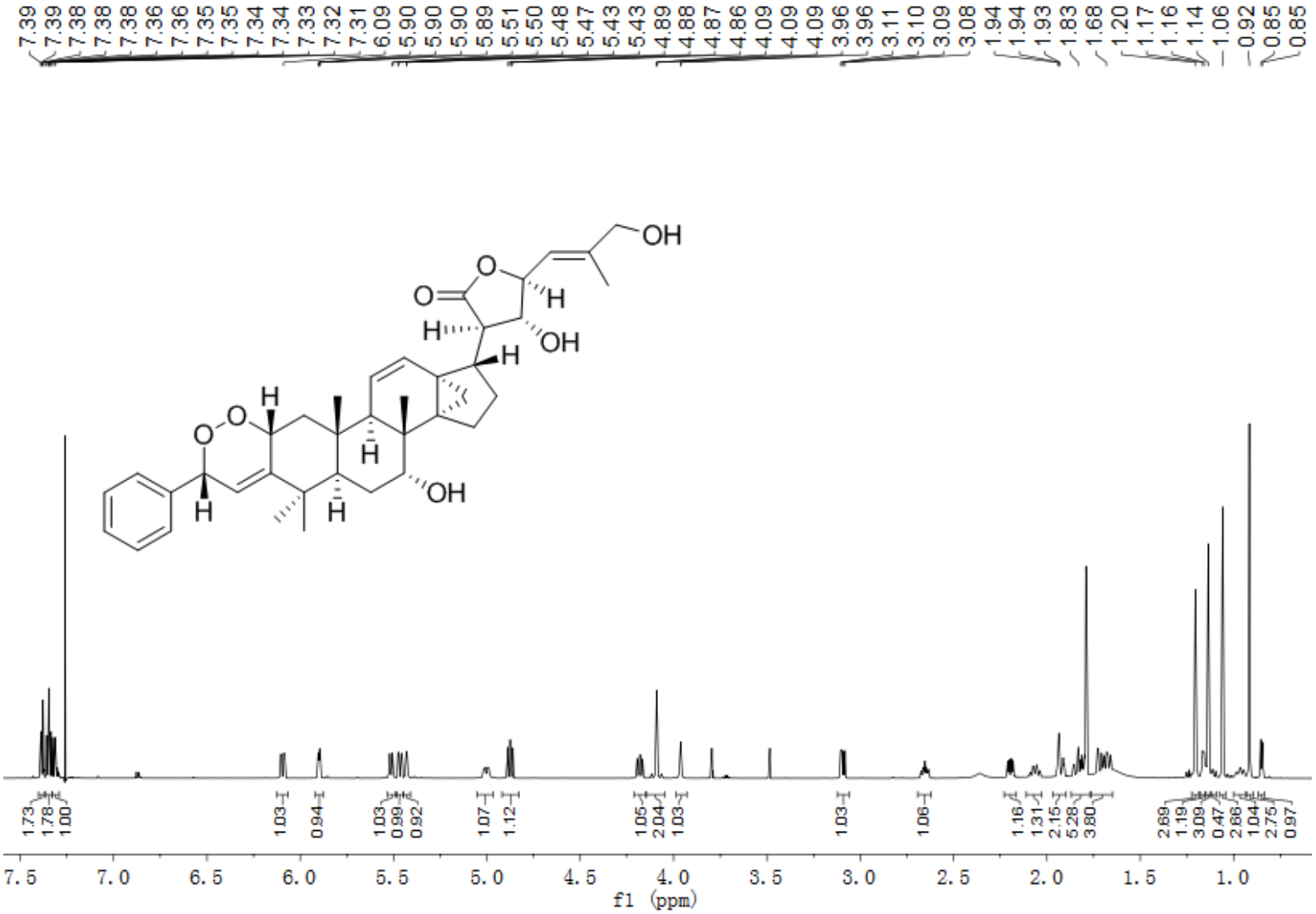


Figure S62. ^{13}C NMR spectrum (125 MHz) of **6** in $CDCl_3$

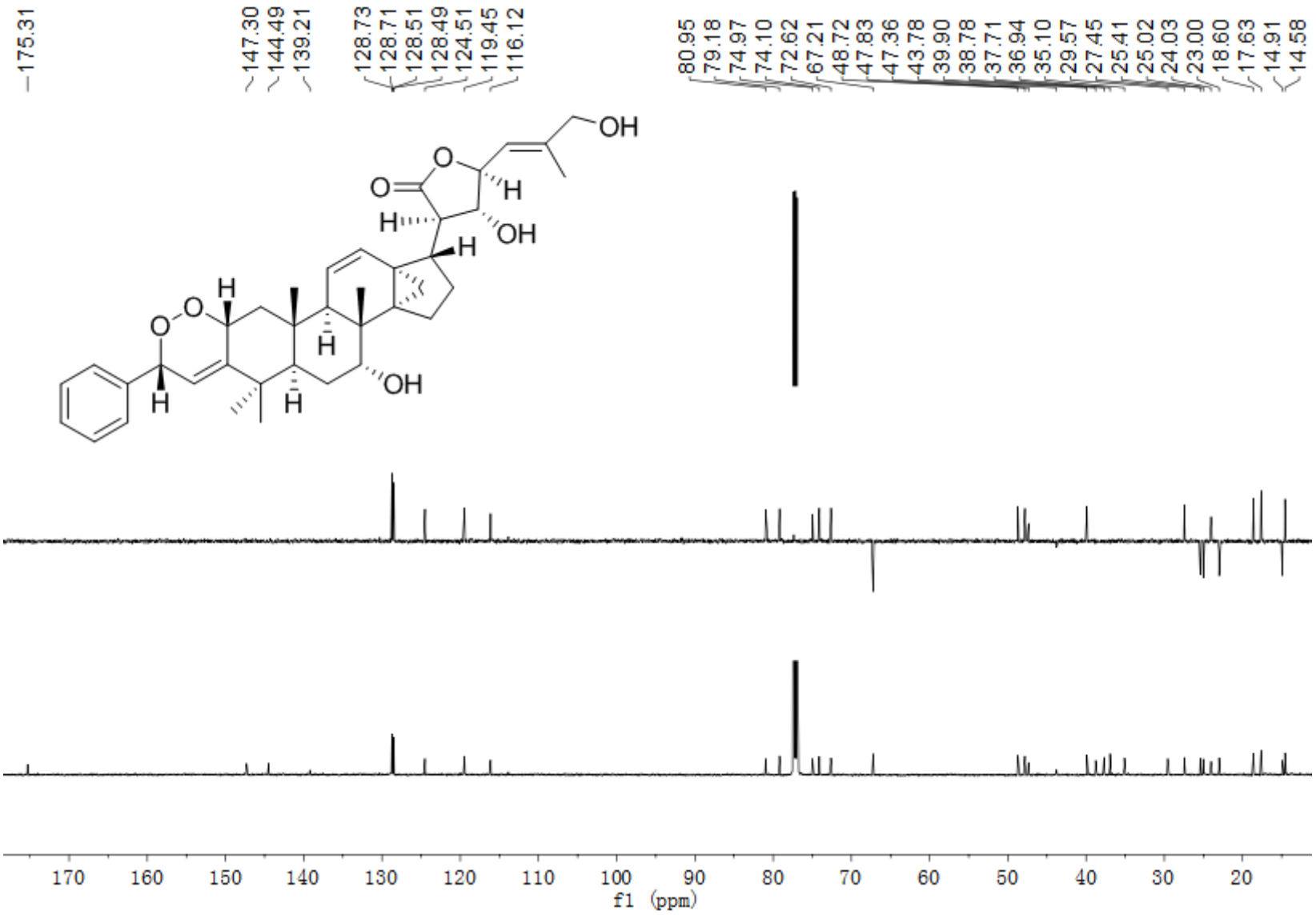


Figure S63. ^{1}H–^{1}H COSY spectrum of **6** in $CDCl_3$

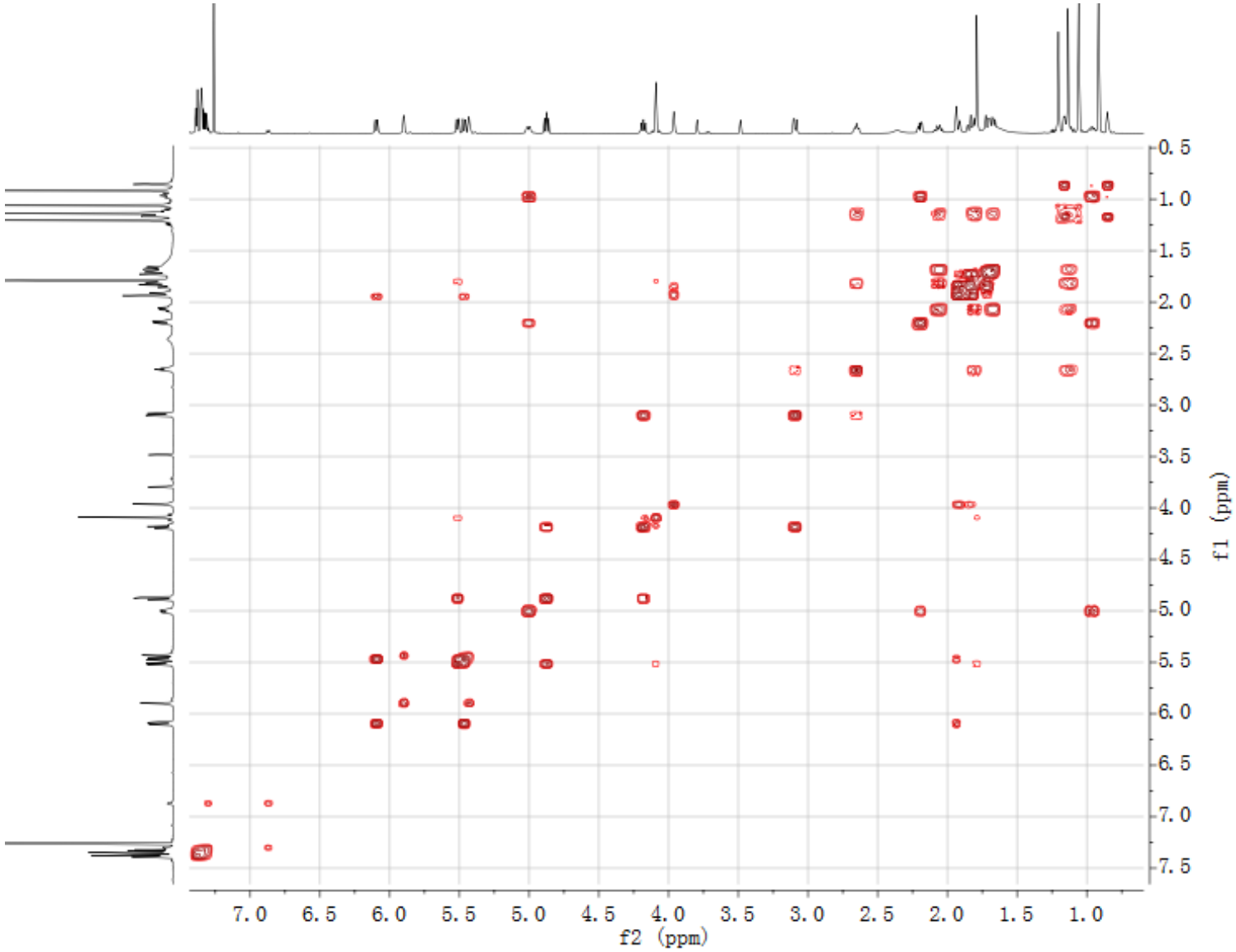


Figure S64. HSQC spectrum of **6** in $CDCl_3$

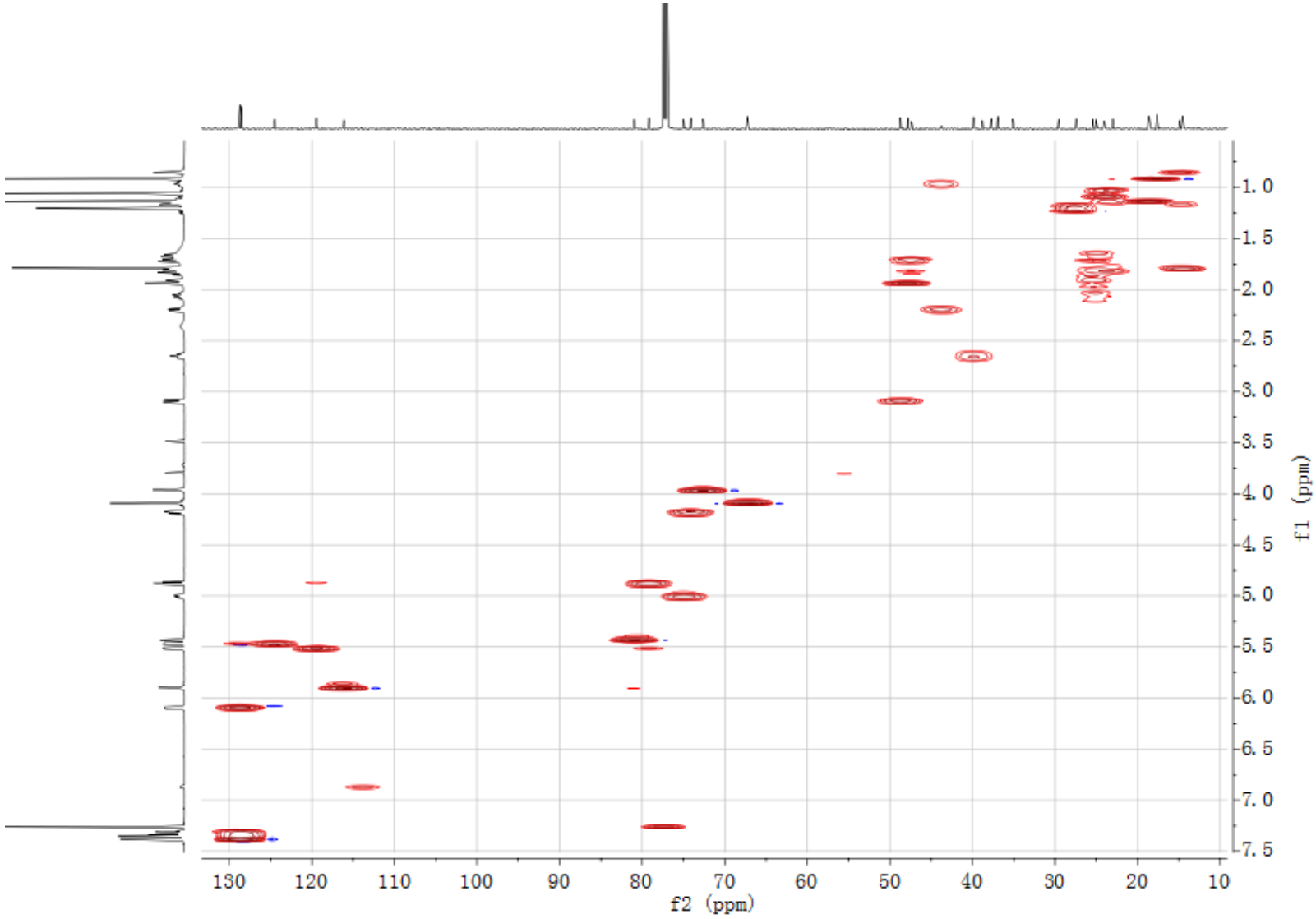


Figure S65. HMBC spectrum of **6** in $CDCl_3$

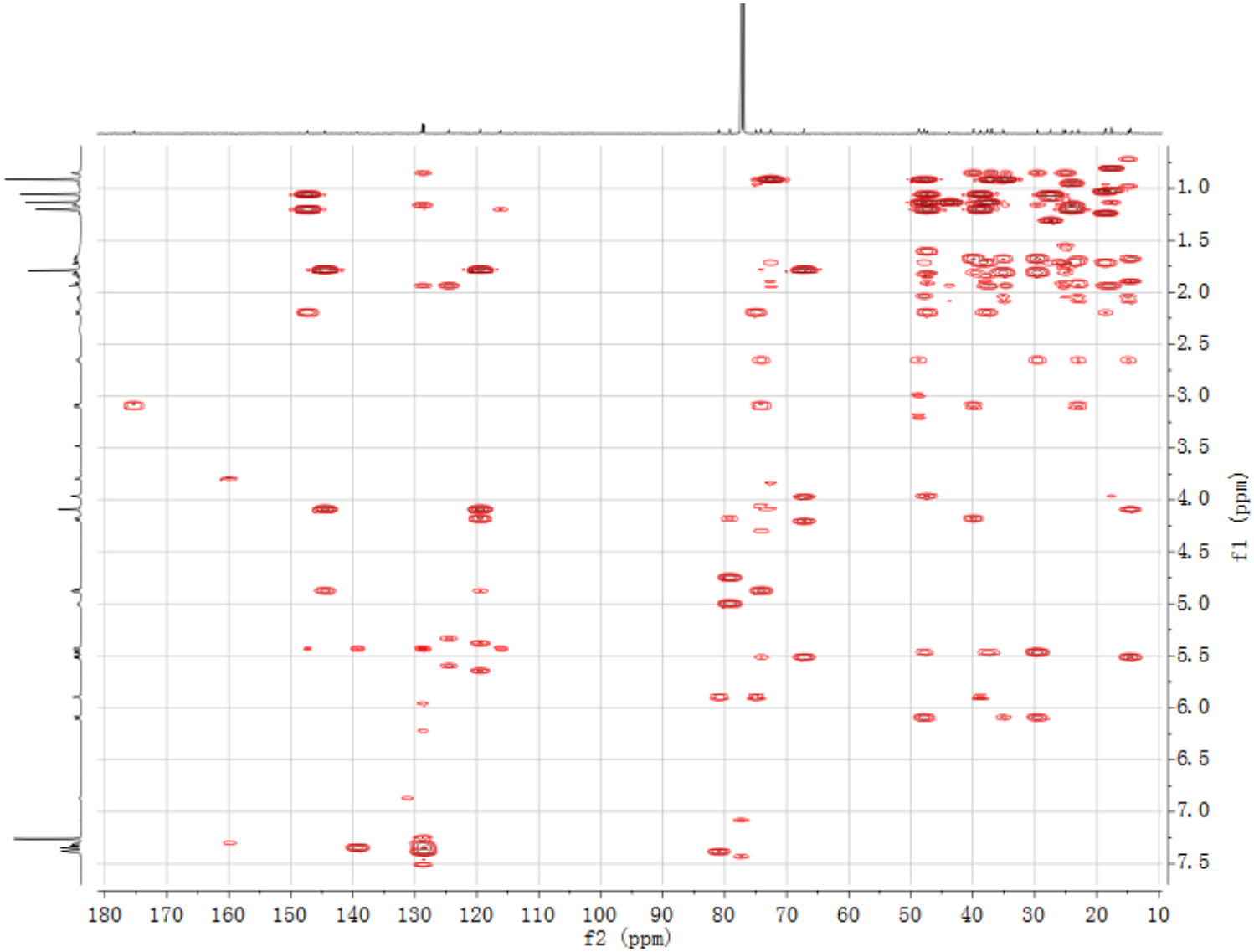


Figure S66. NOESY spectrum of **6** in $CDCl_3$

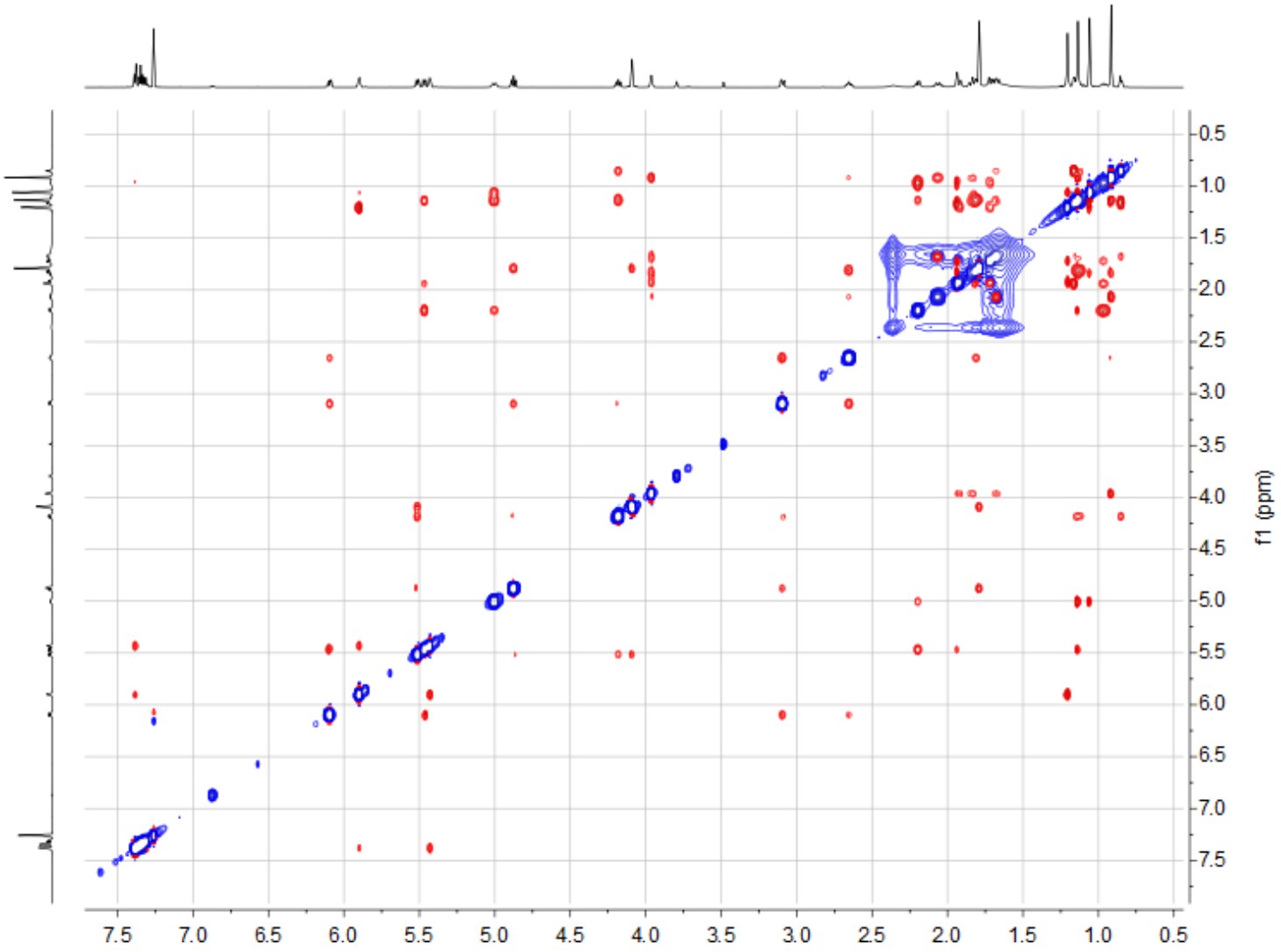


Figure S67. (±)-ESIMS spectra of **6**

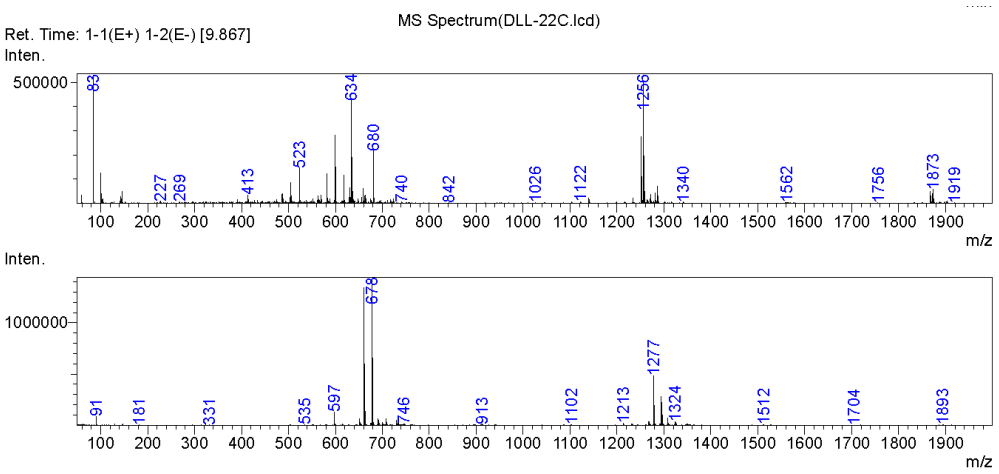


Figure S68. (–)-HRESIMS spectrum of **6**

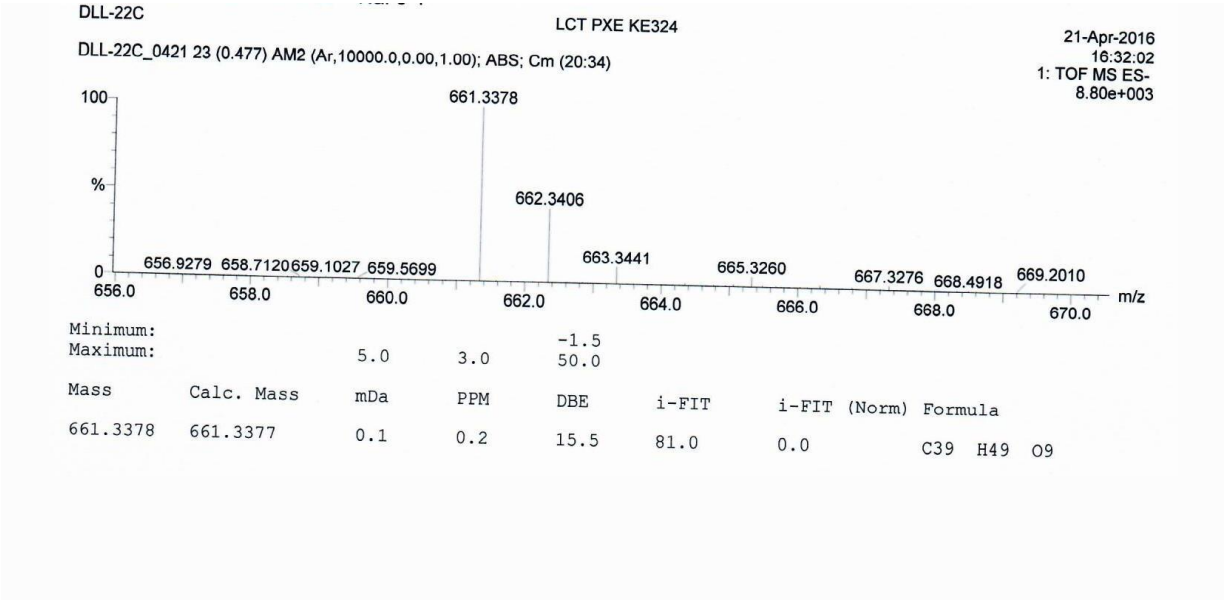
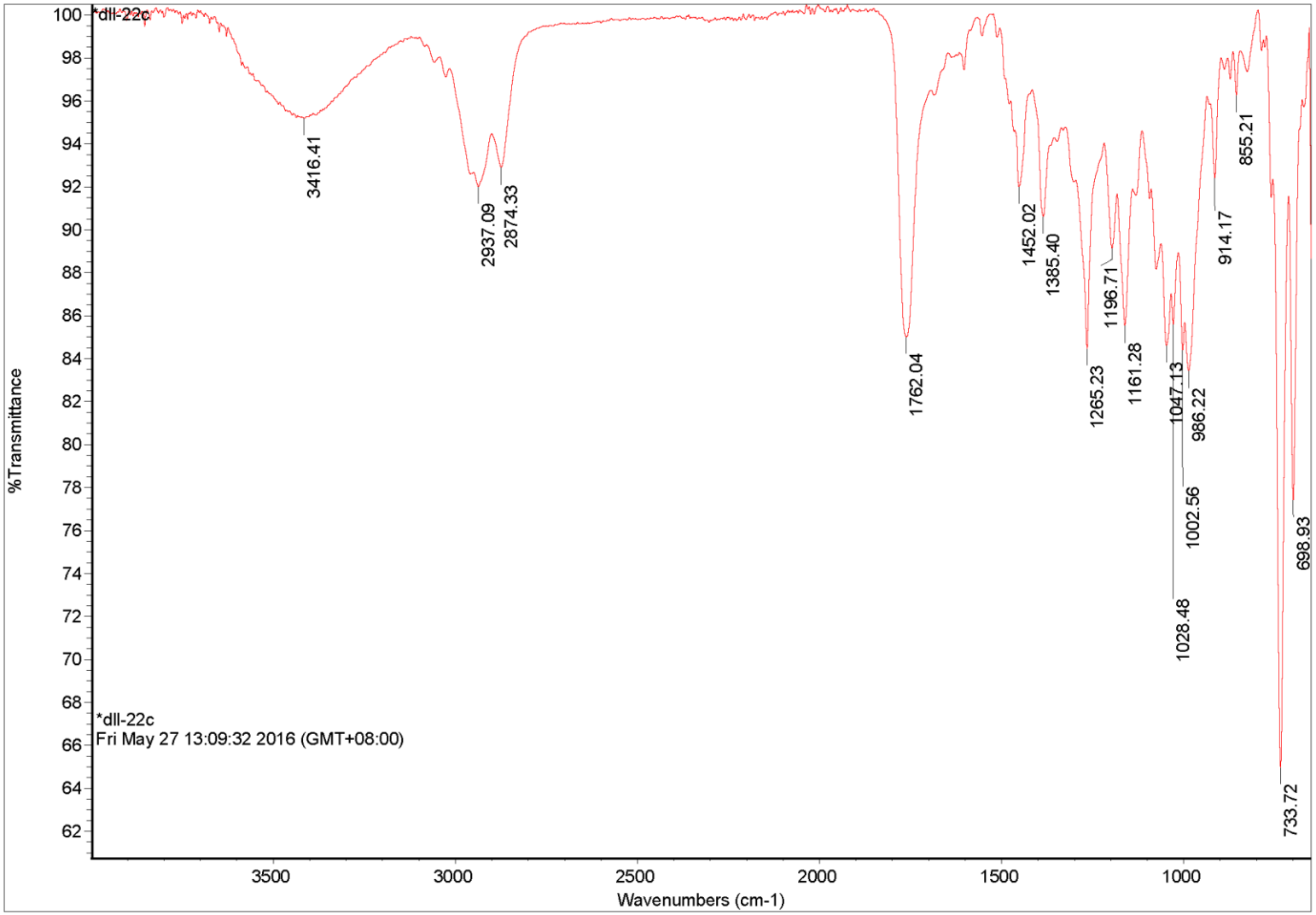


Figure S69. IR spectrum of **6**



6.7 NMR, MS, and IR spectra of compound 7

Figure S70. ^{1}H NMR spectrum (500 MHz) of **7** in $CDCl_3$

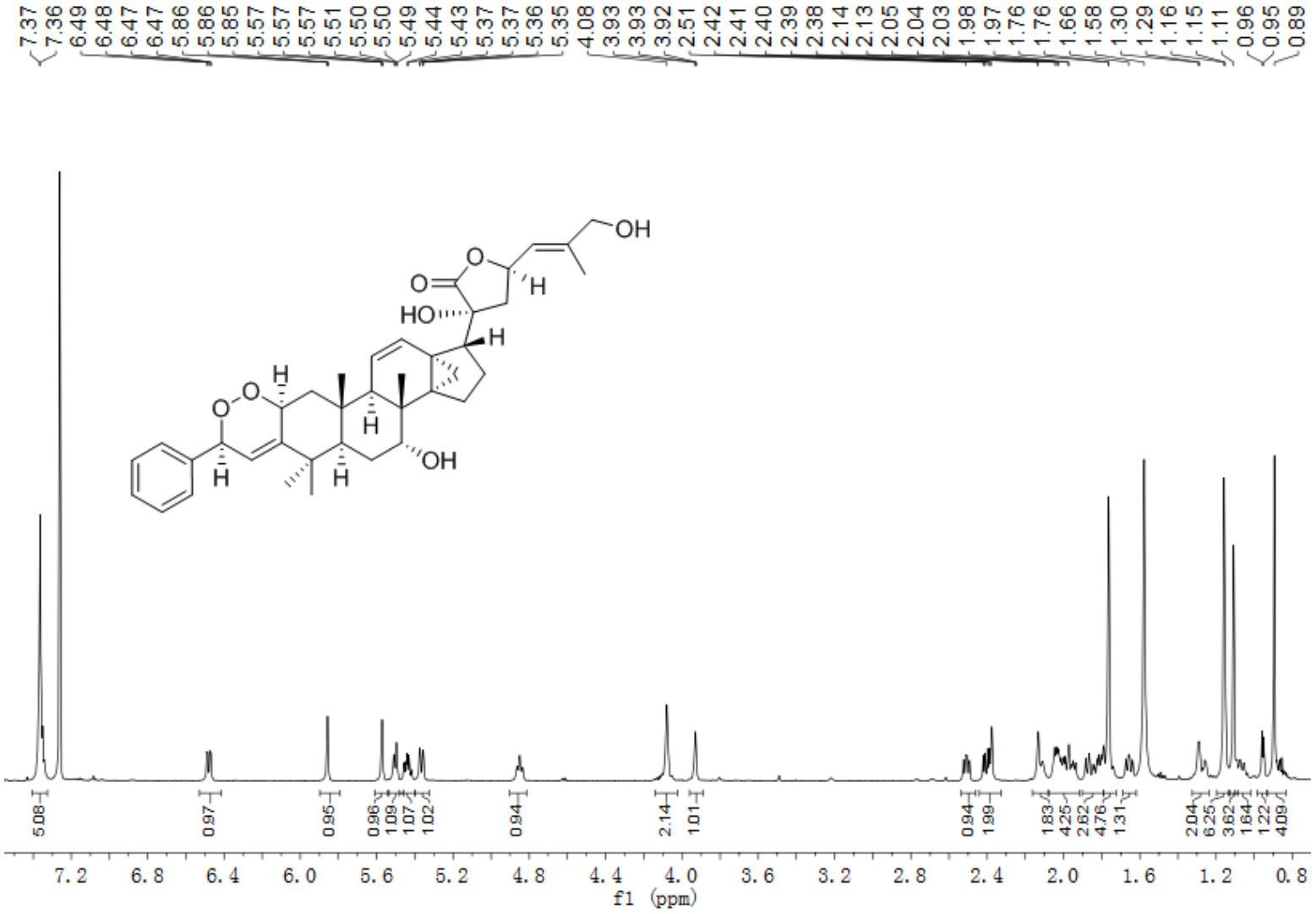


Figure S71. ^{13}C NMR spectrum (125 MHz) of **7** in $CDCl_3$

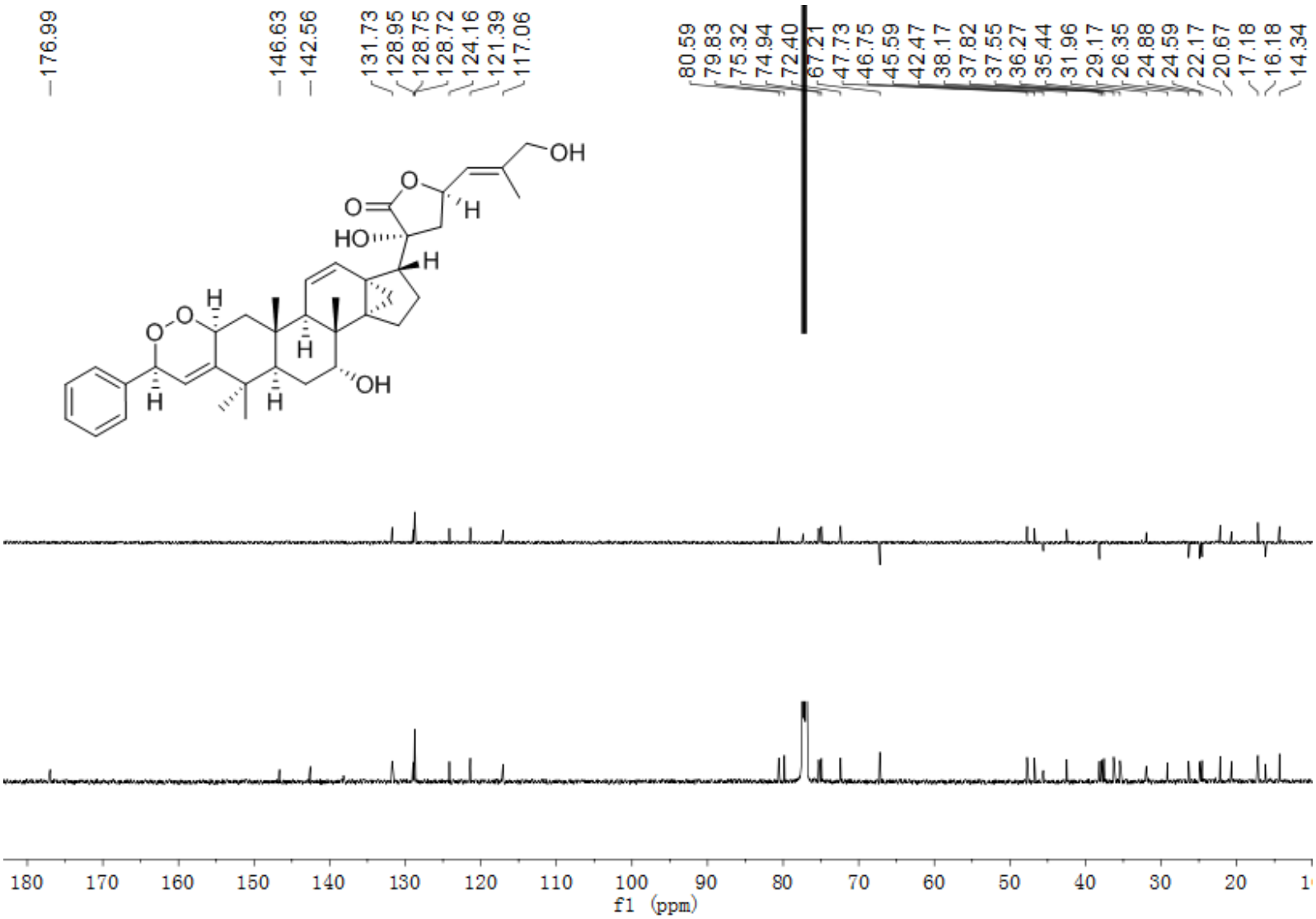


Figure S72. $^{1}H–^{1}H$ COSY spectrum of **7** in $CDCl_3$

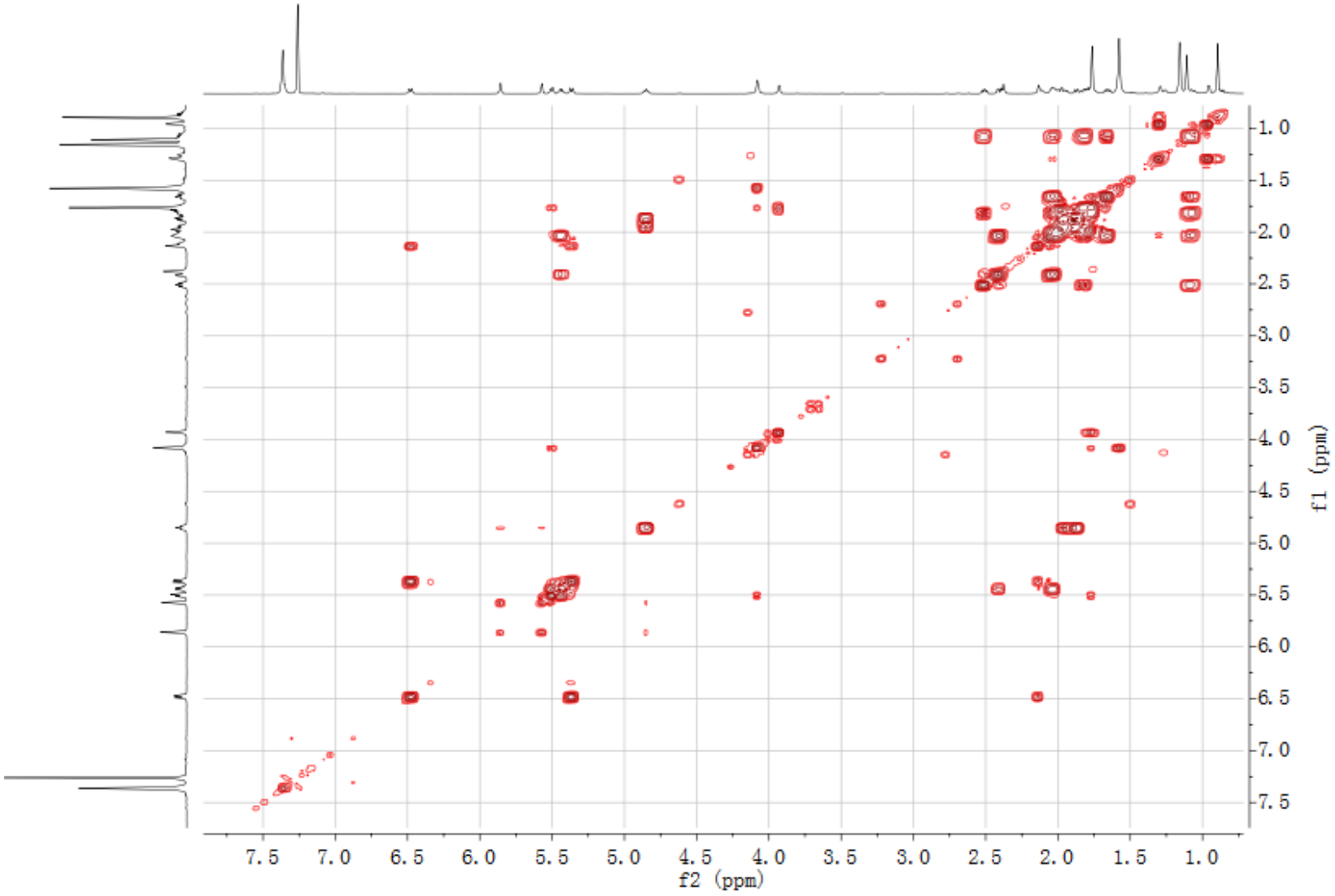


Figure S73. HSQC spectrum of **7** in $CDCl_3$

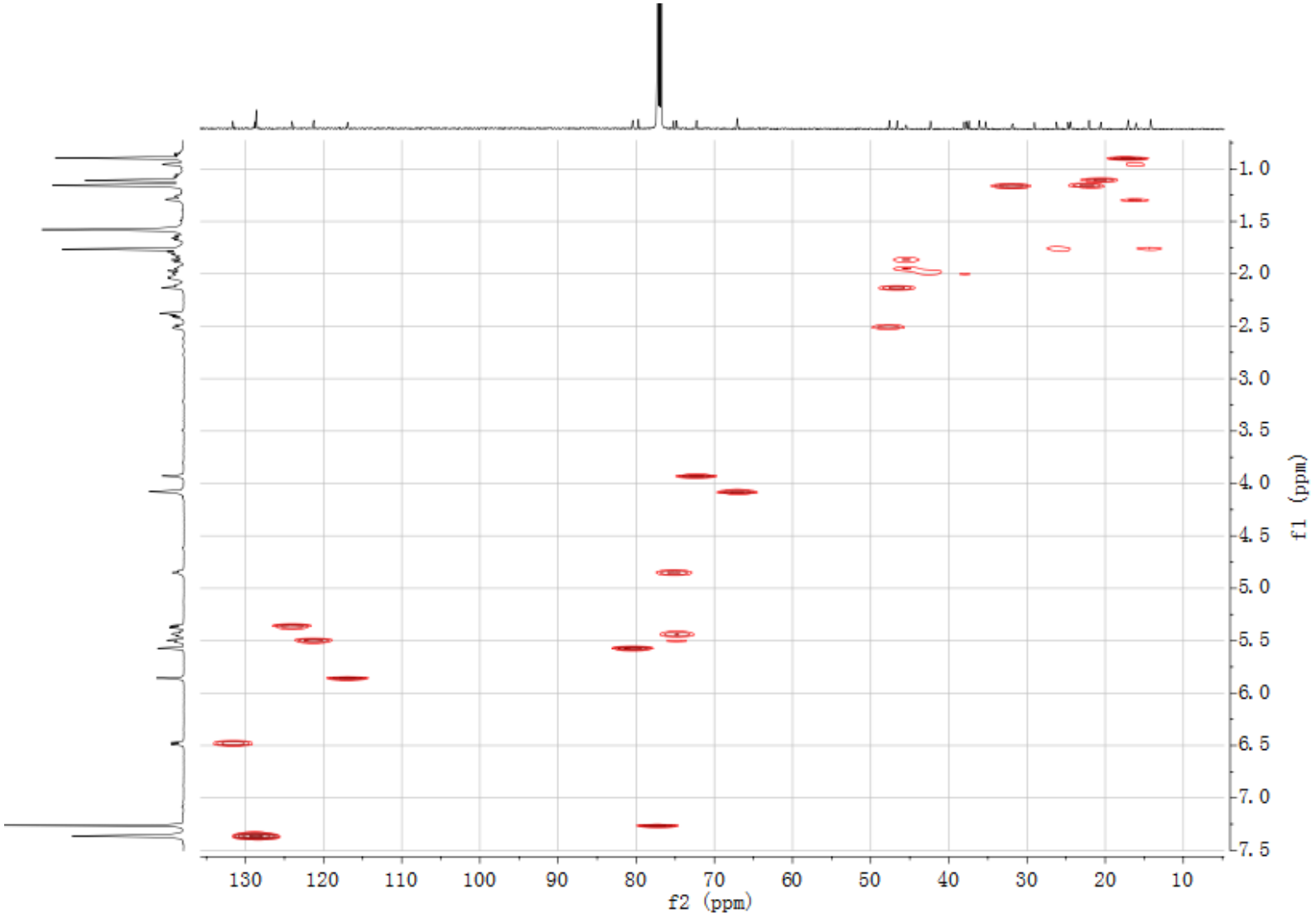


Figure S74. HMBC spectrum of **7** in $CDCl_3$

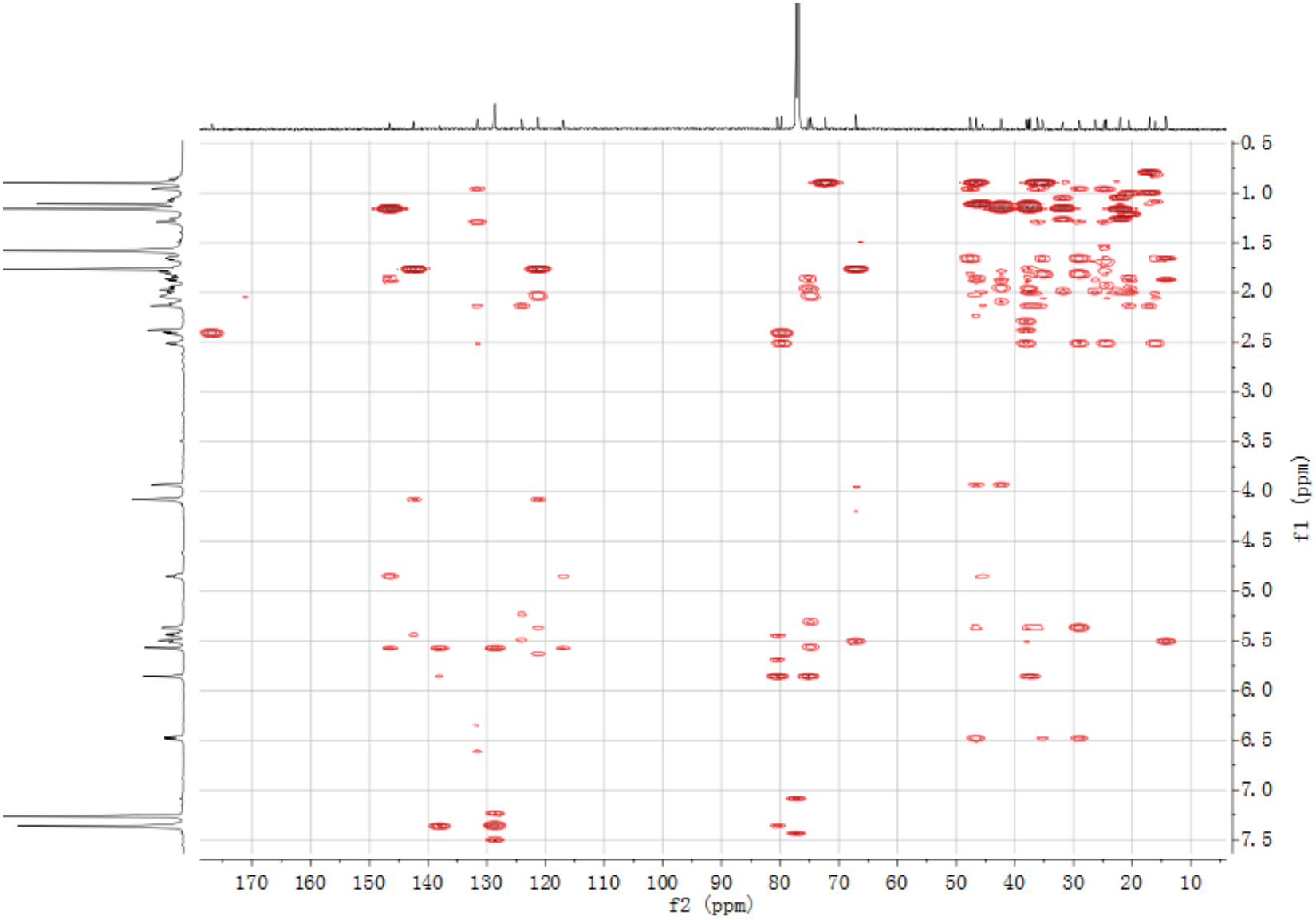


Figure S75. NOESY spectrum of **7** in $CDCl_3$

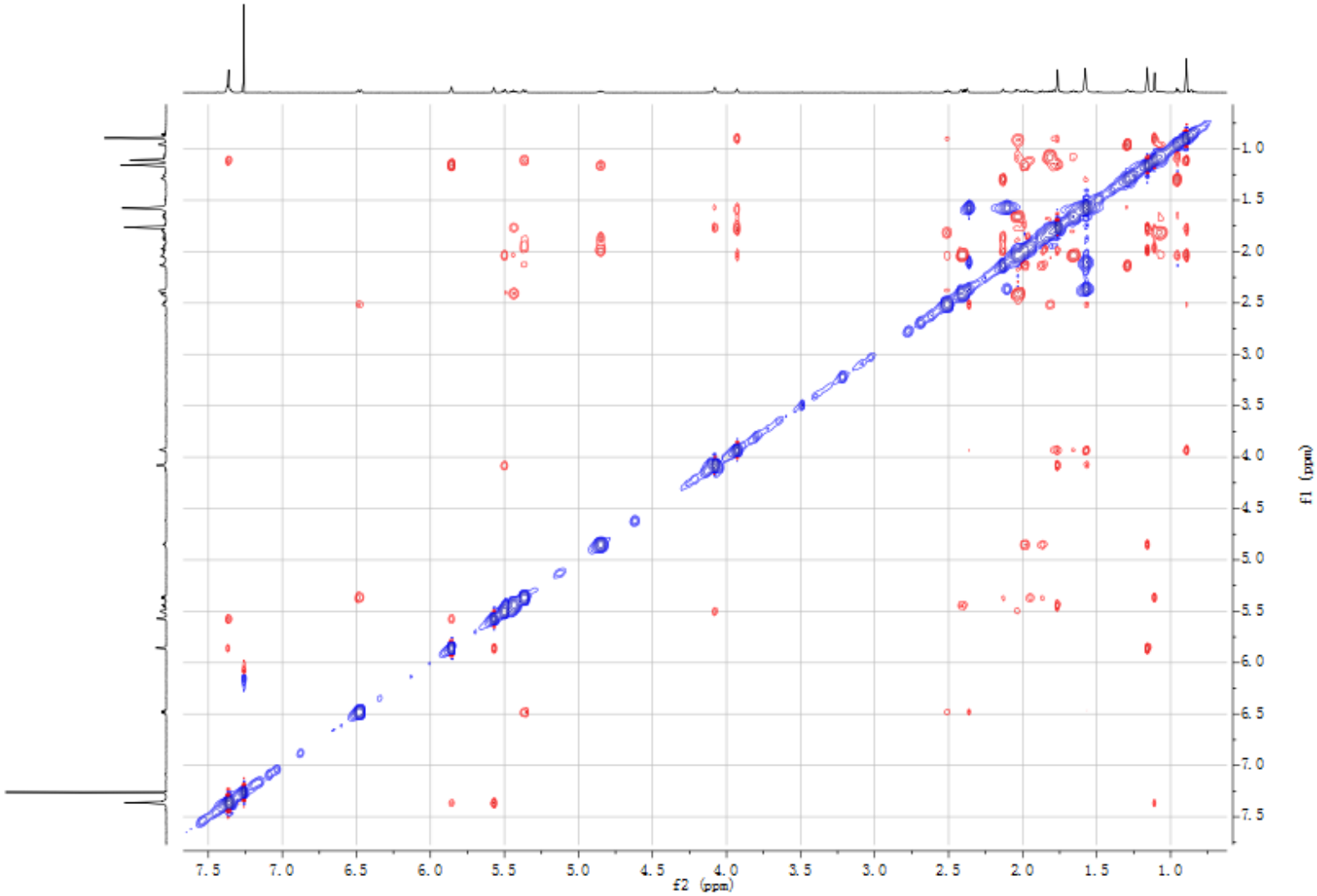


Figure S76. (±)-ESIMS spectra of **7**

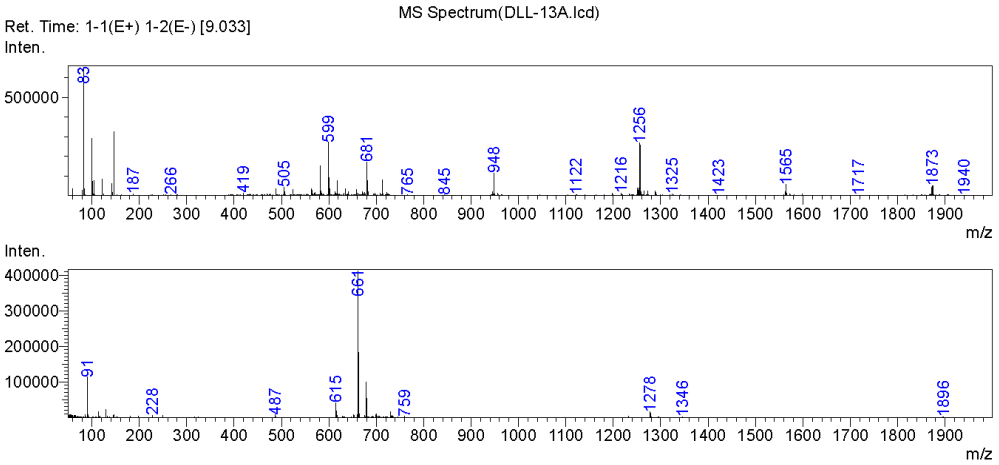


Figure S77. (–)-HRESIMS spectrum of **7**

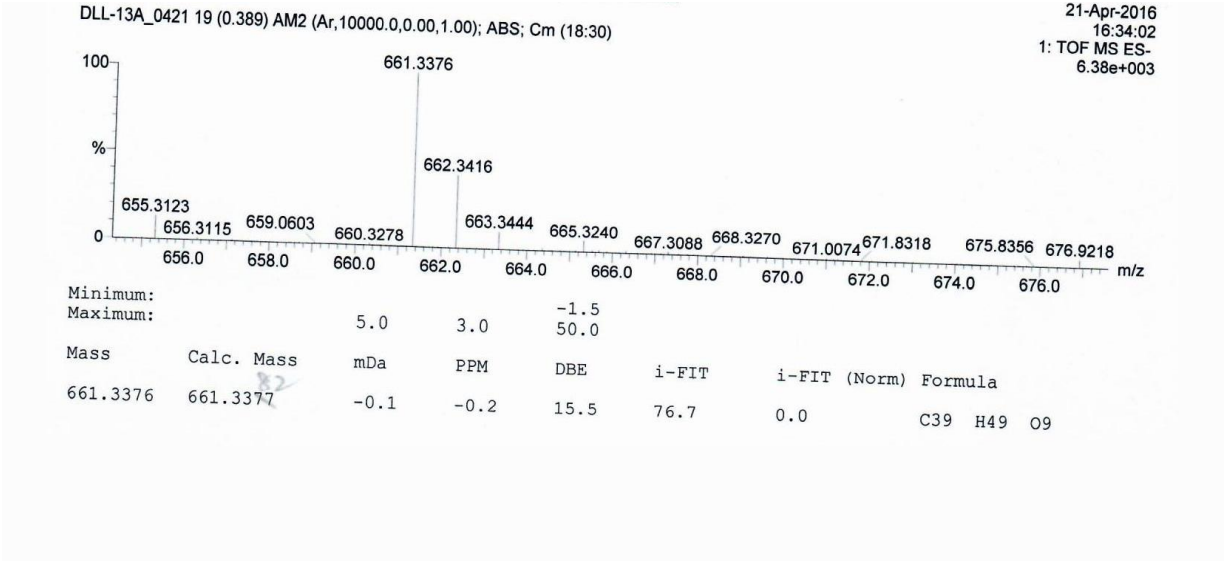
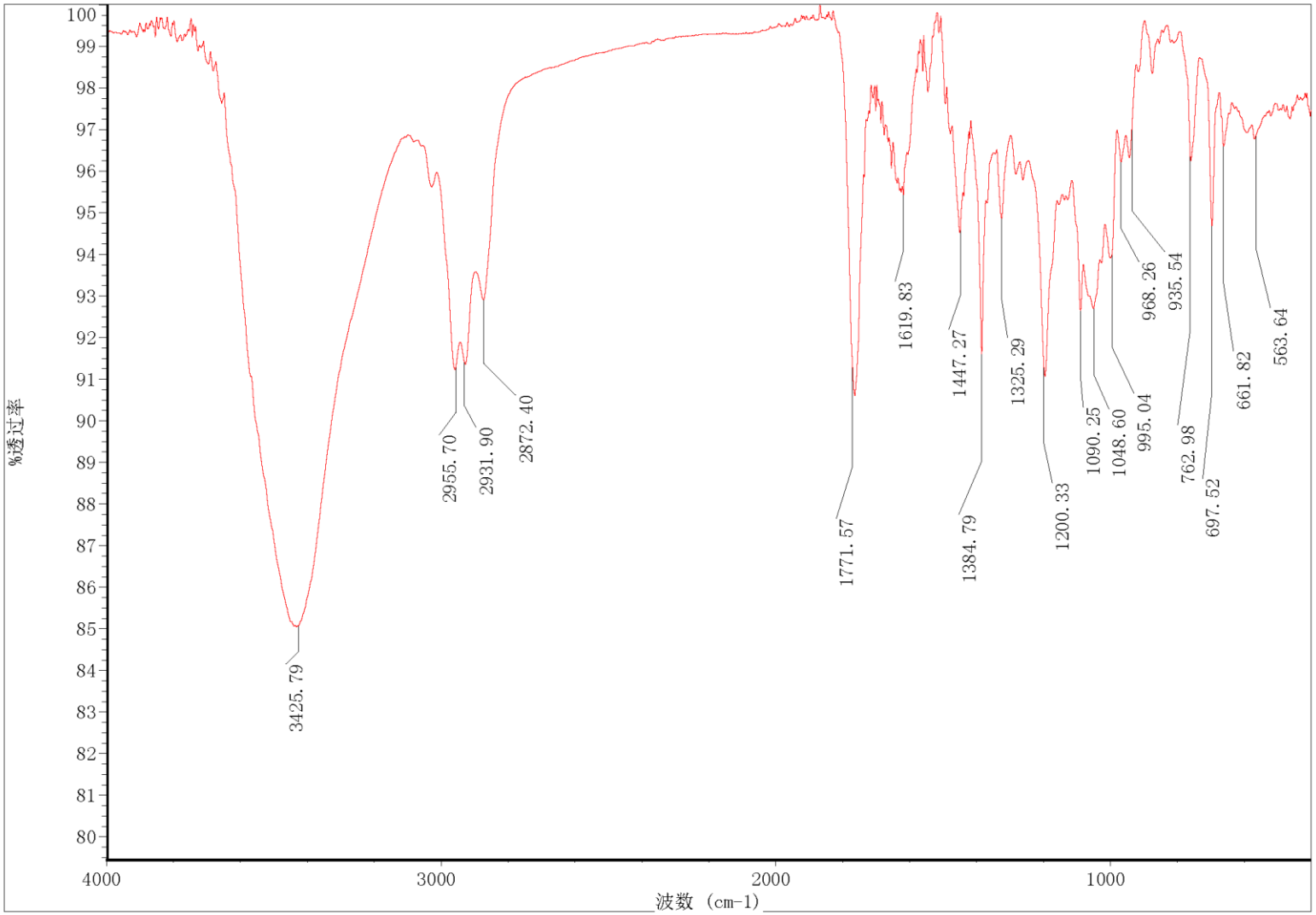


Figure S78. IR spectrum of **7**



6.8 NMR, MS, and IR spectra of compound 8

Figure S79. ^{1}H NMR spectrum (500 MHz) of **8** in $CDCl_3$

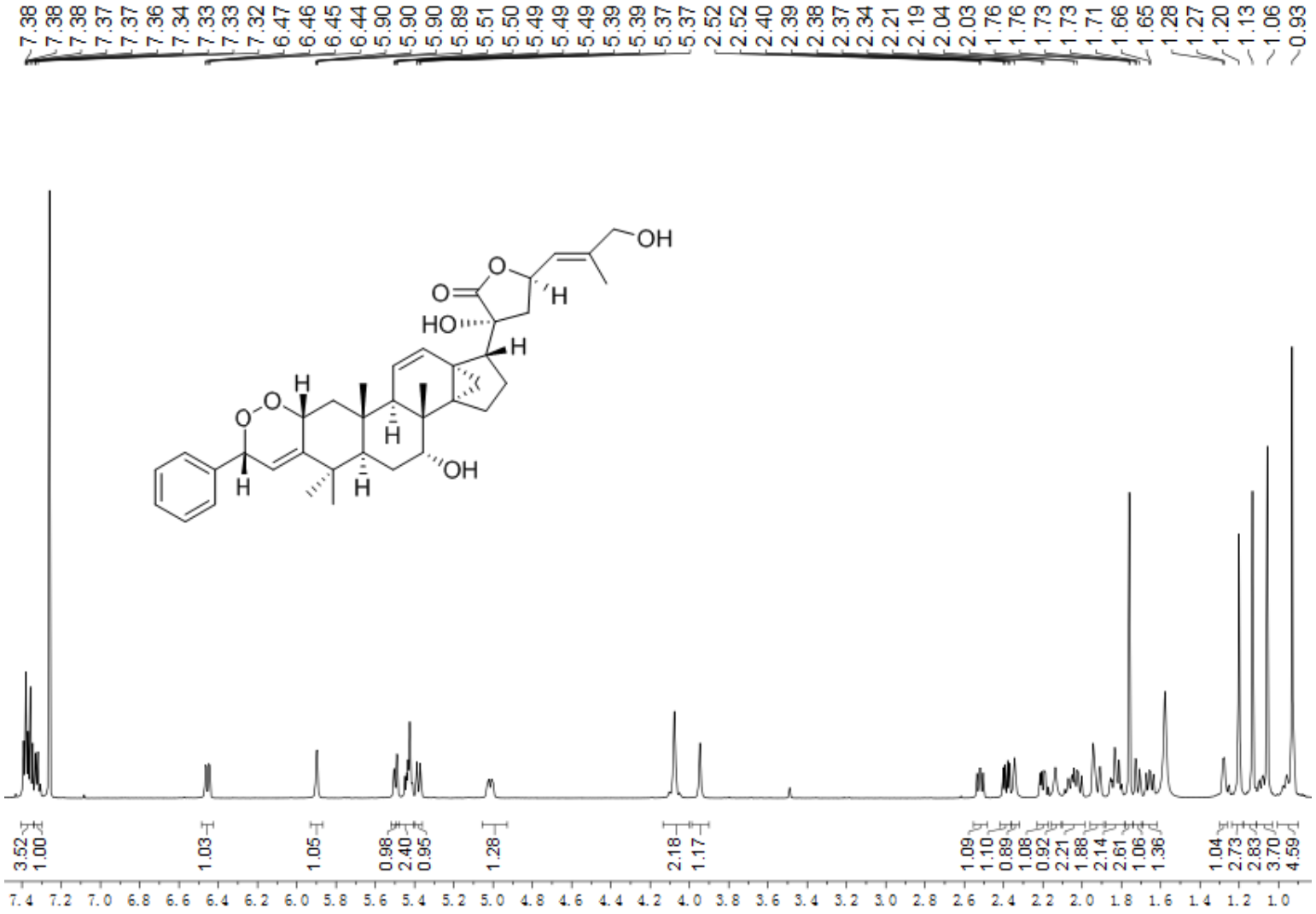


Figure S80. ^{13}C NMR spectrum (125 MHz) of **8** in $CDCl_3$

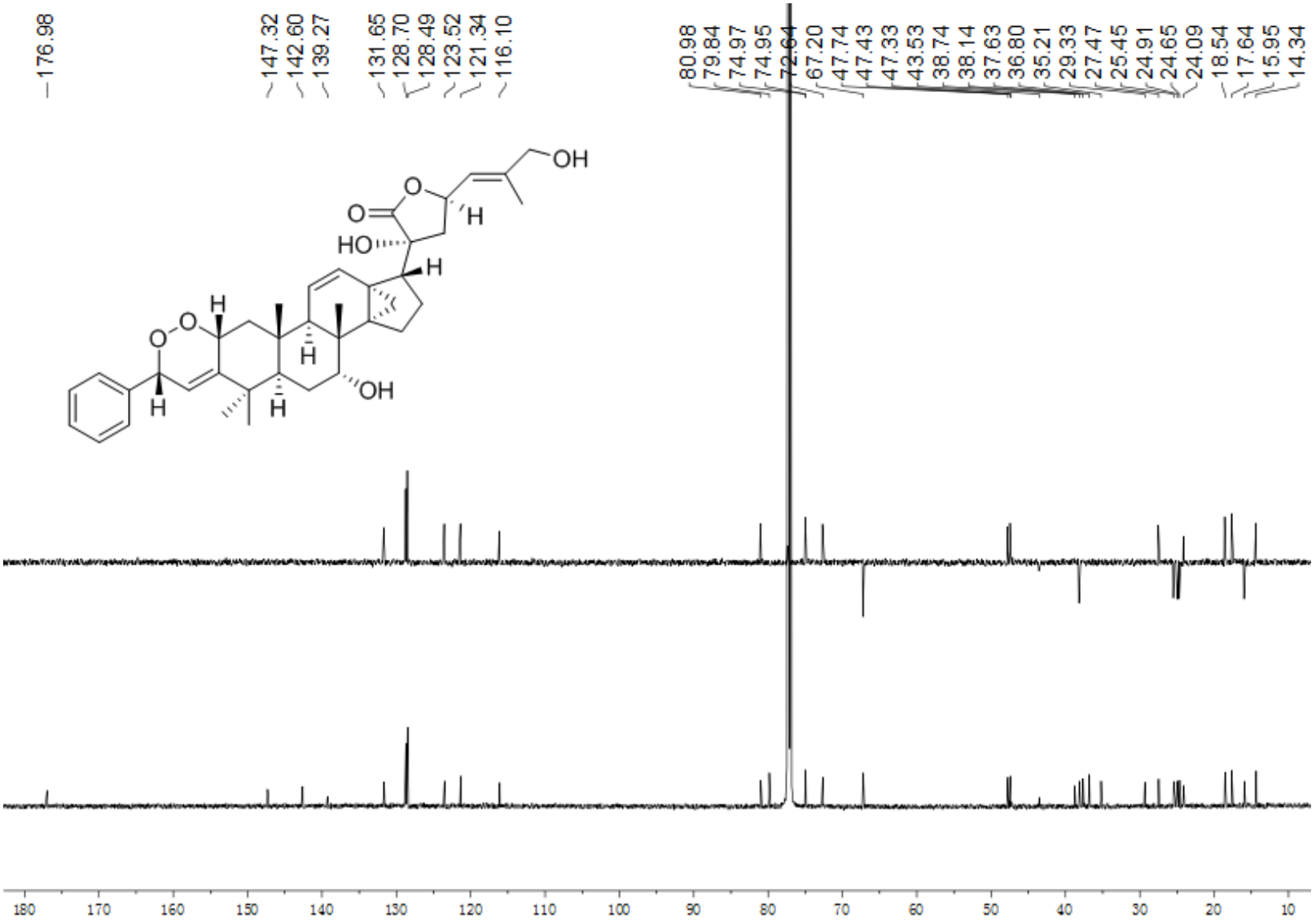


Figure S81. $^{1}H–^{1}H$ COSY spectrum of **8** in $CDCl_3$

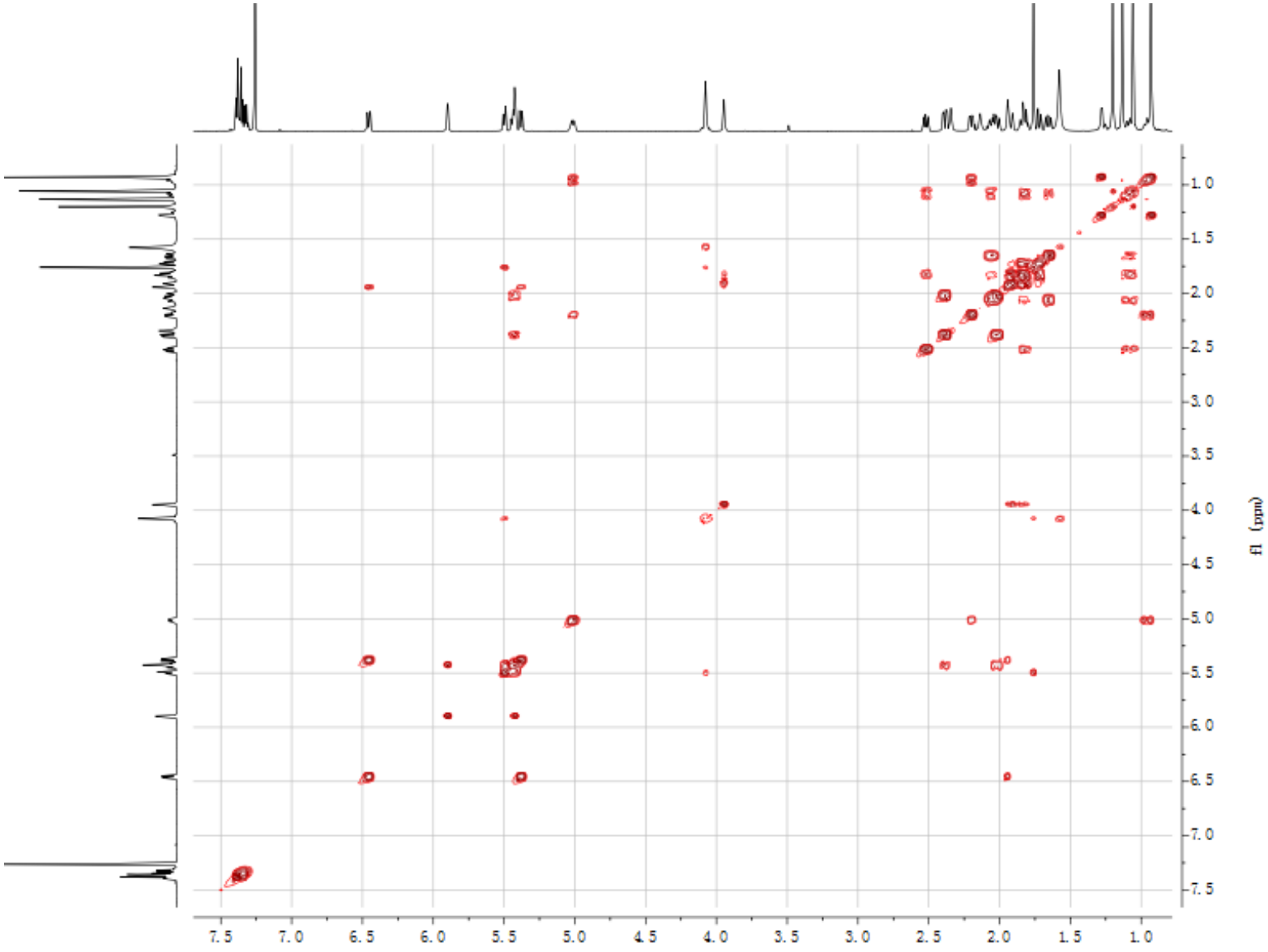


Figure S82. HSQC spectrum of **8** in $CDCl_3$

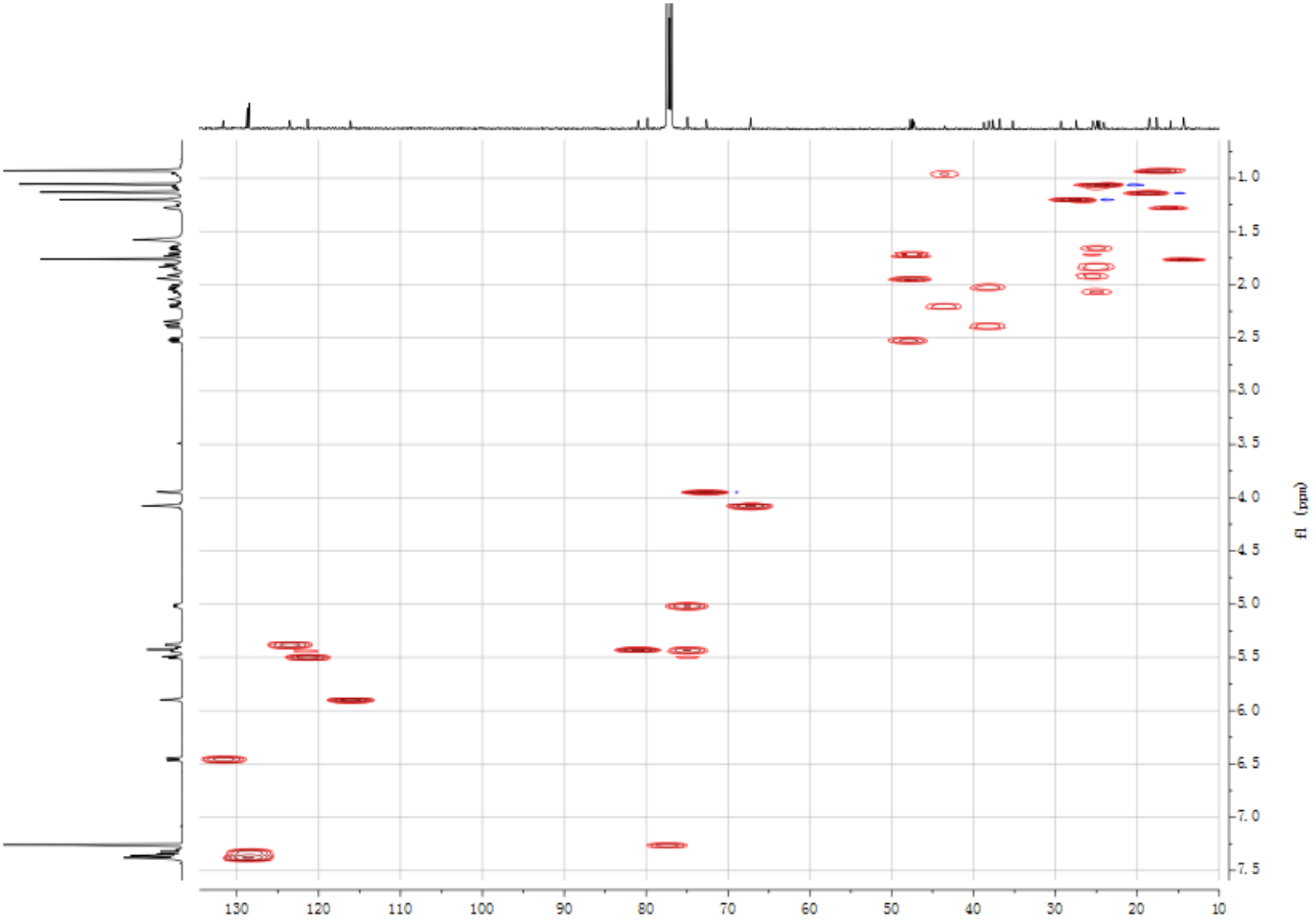


Figure S83. HMBC spectrum of **8** in $CDCl_3$

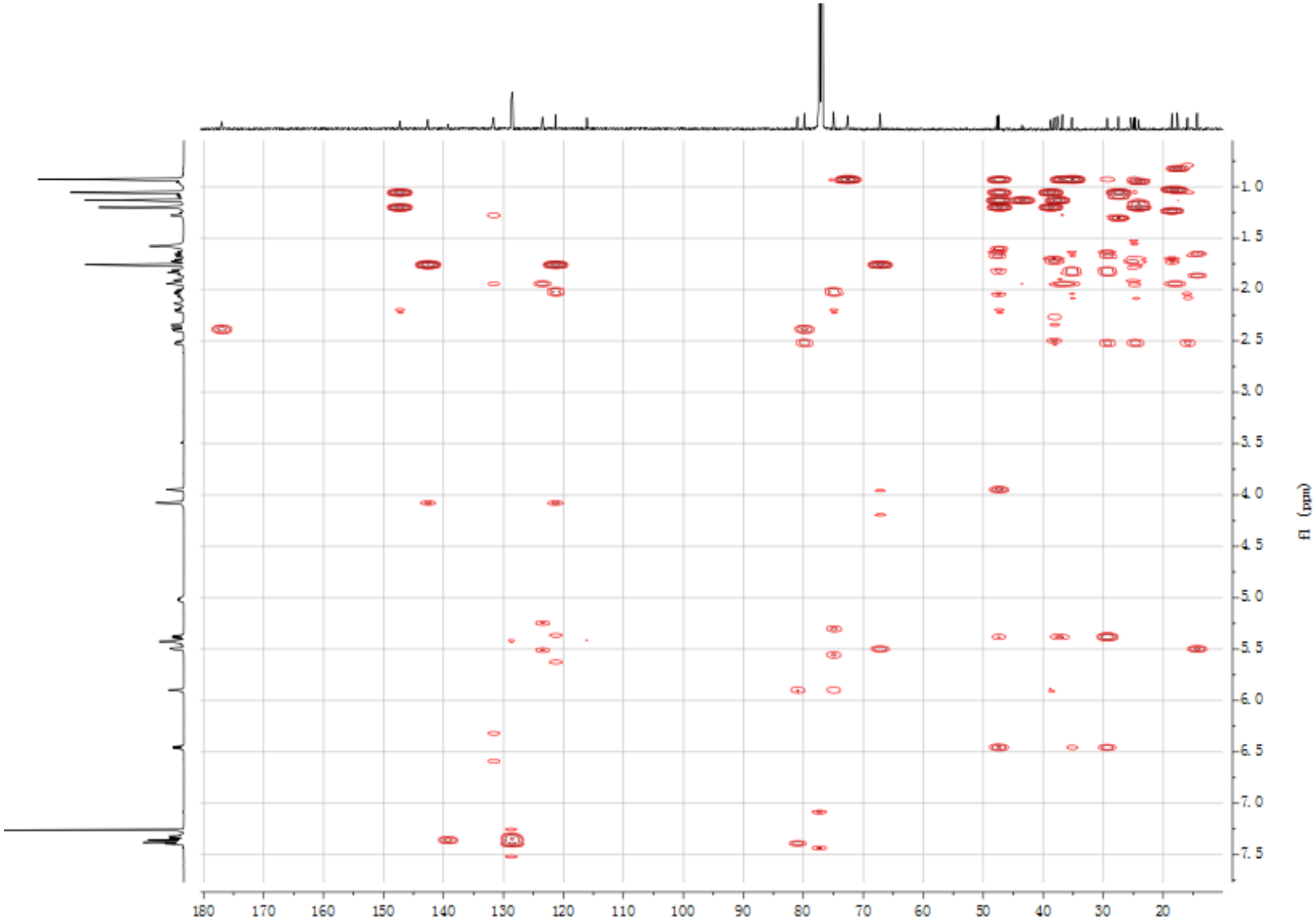


Figure S84. NOESY spectrum of **8** in $CDCl_3$

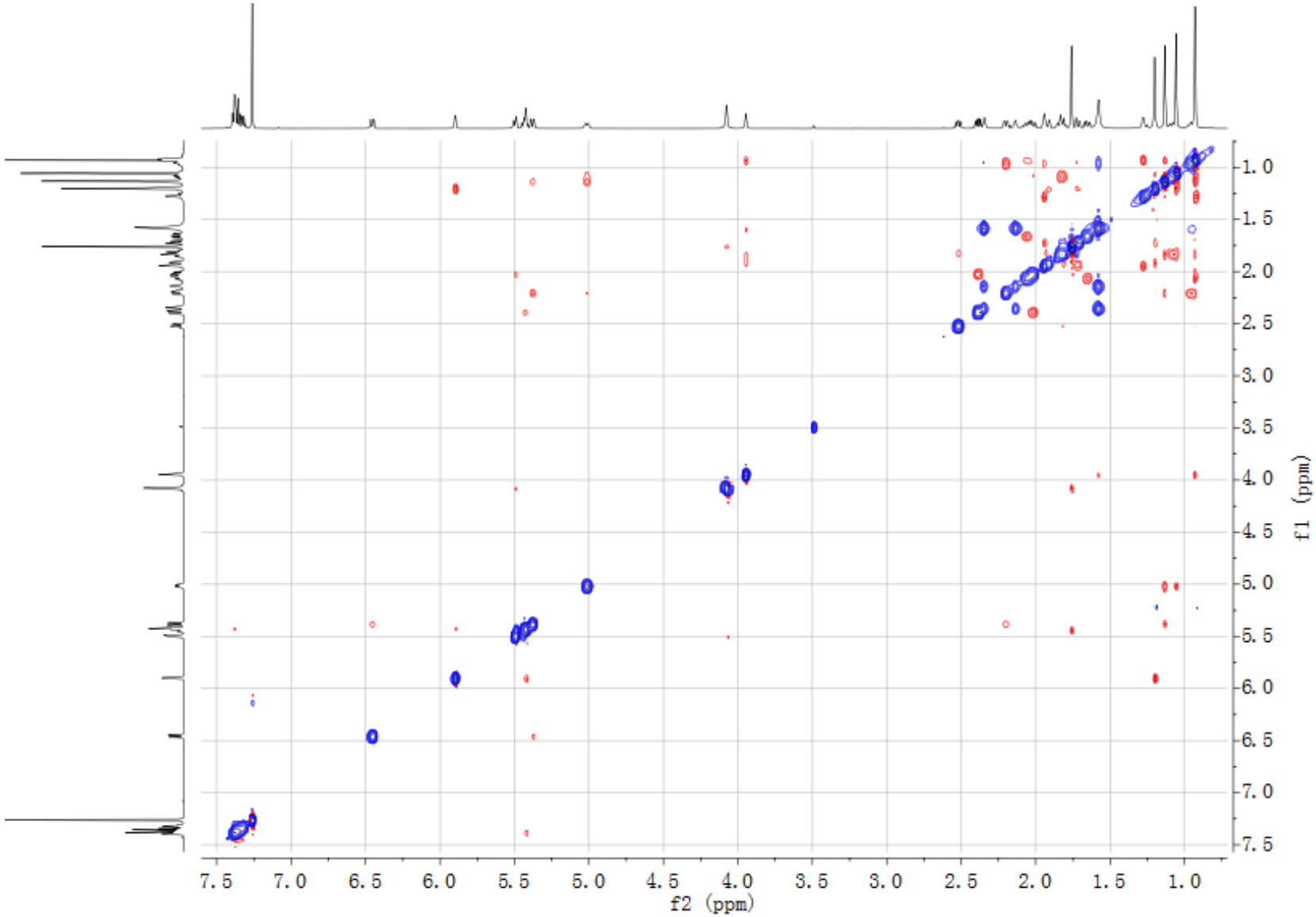


Figure S85. (±)-ESIMS spectra of **8**

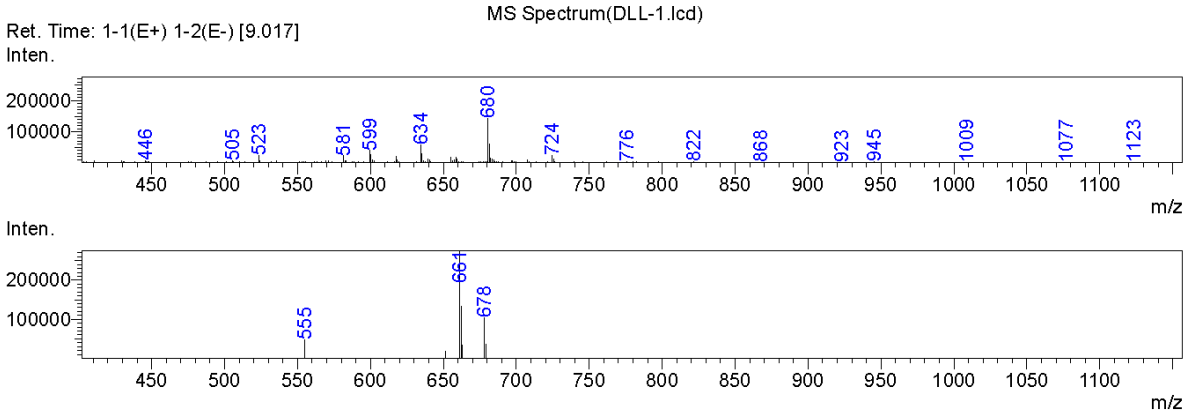


Figure S86. (–)-HRESIMS spectrum of **8**

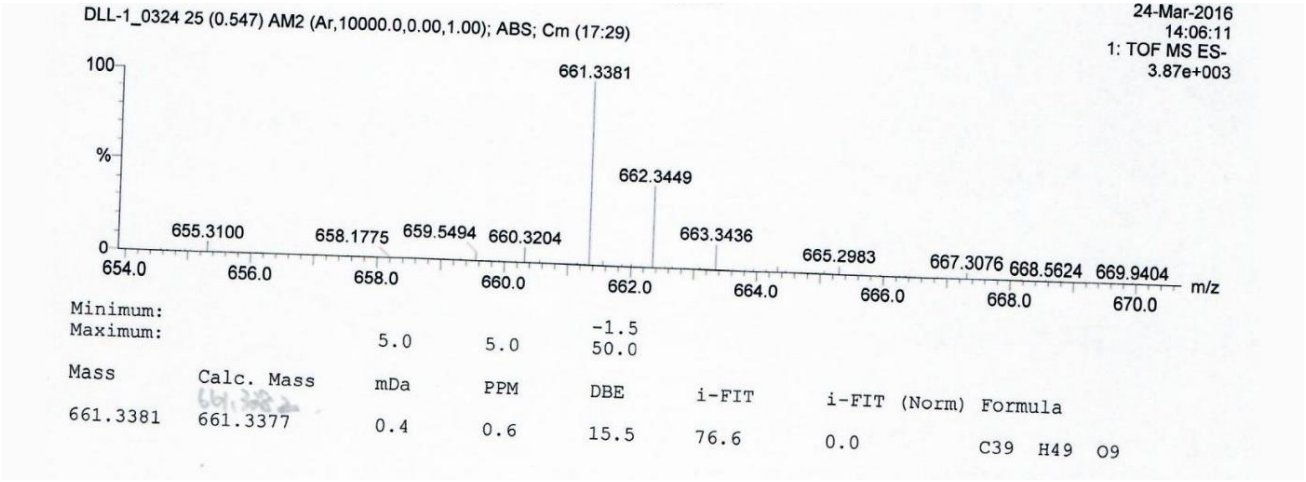
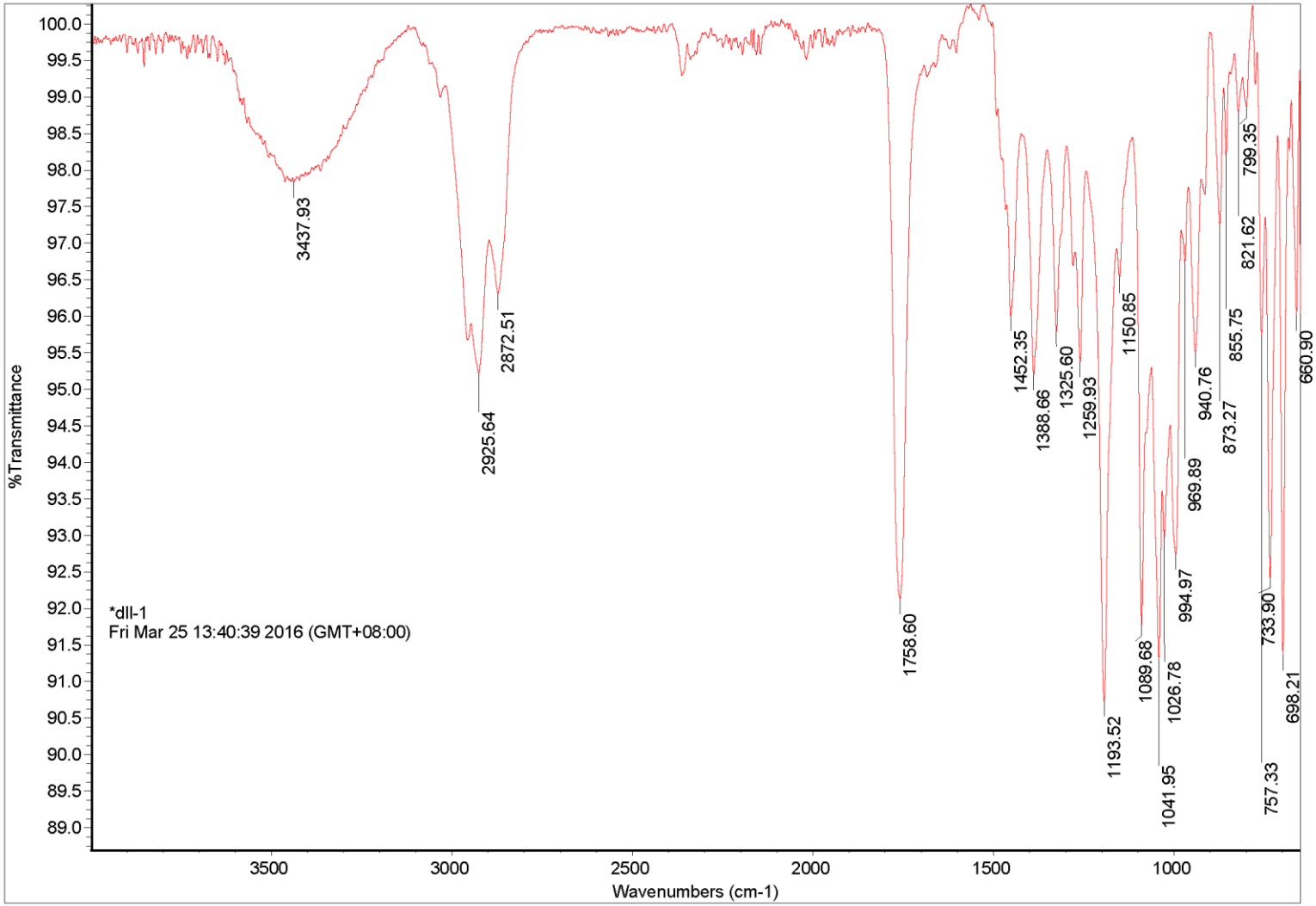


Figure S87. IR spectrum of **8**



6.9 NMR, MS, and IR spectra of compound 9

Figure S88. ^{1}H NMR spectrum (500 MHz) of **9** in $CDCl_3$

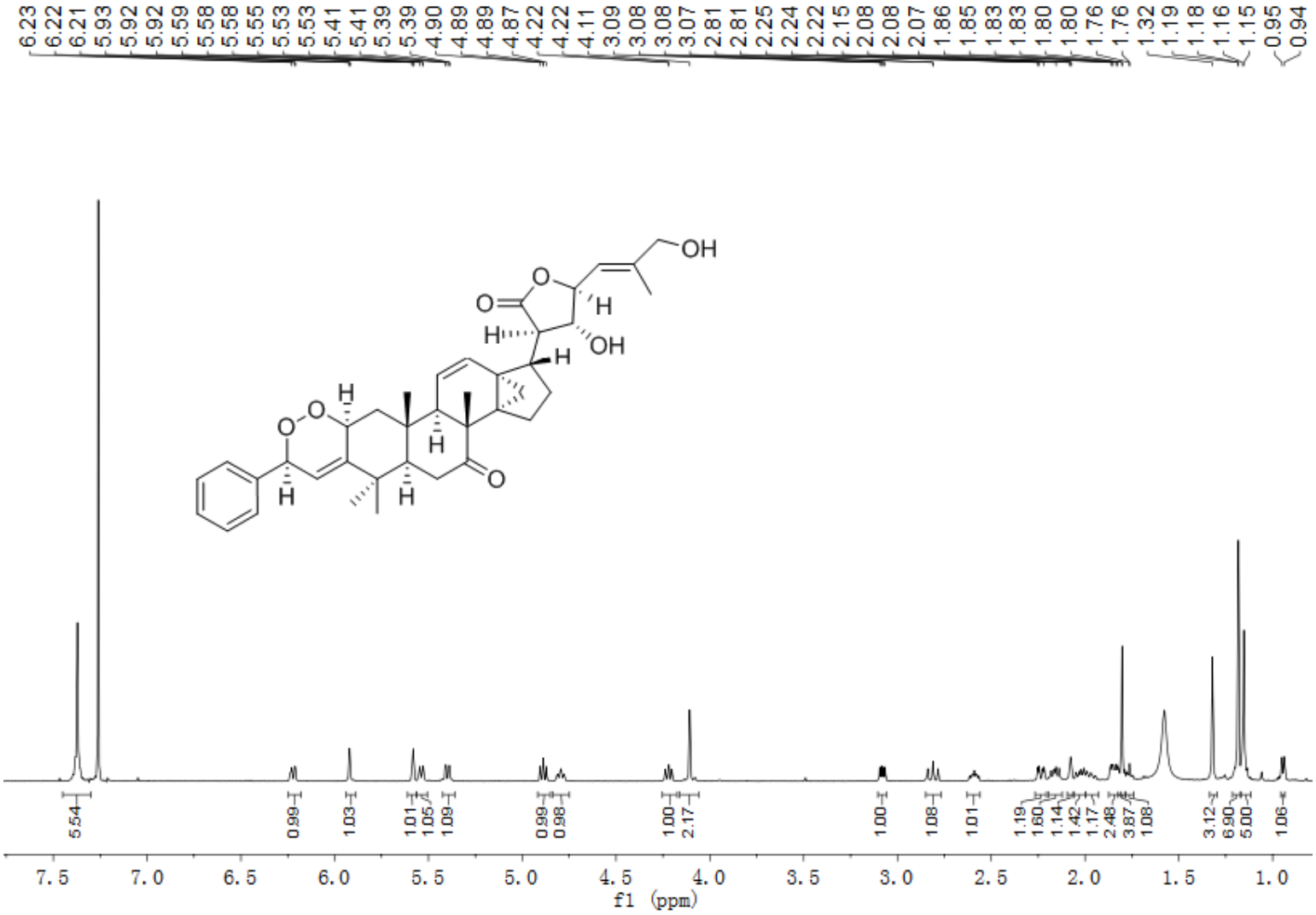


Figure S89. ^{13}C NMR spectrum (125 MHz) of **9** in $CDCl_3$

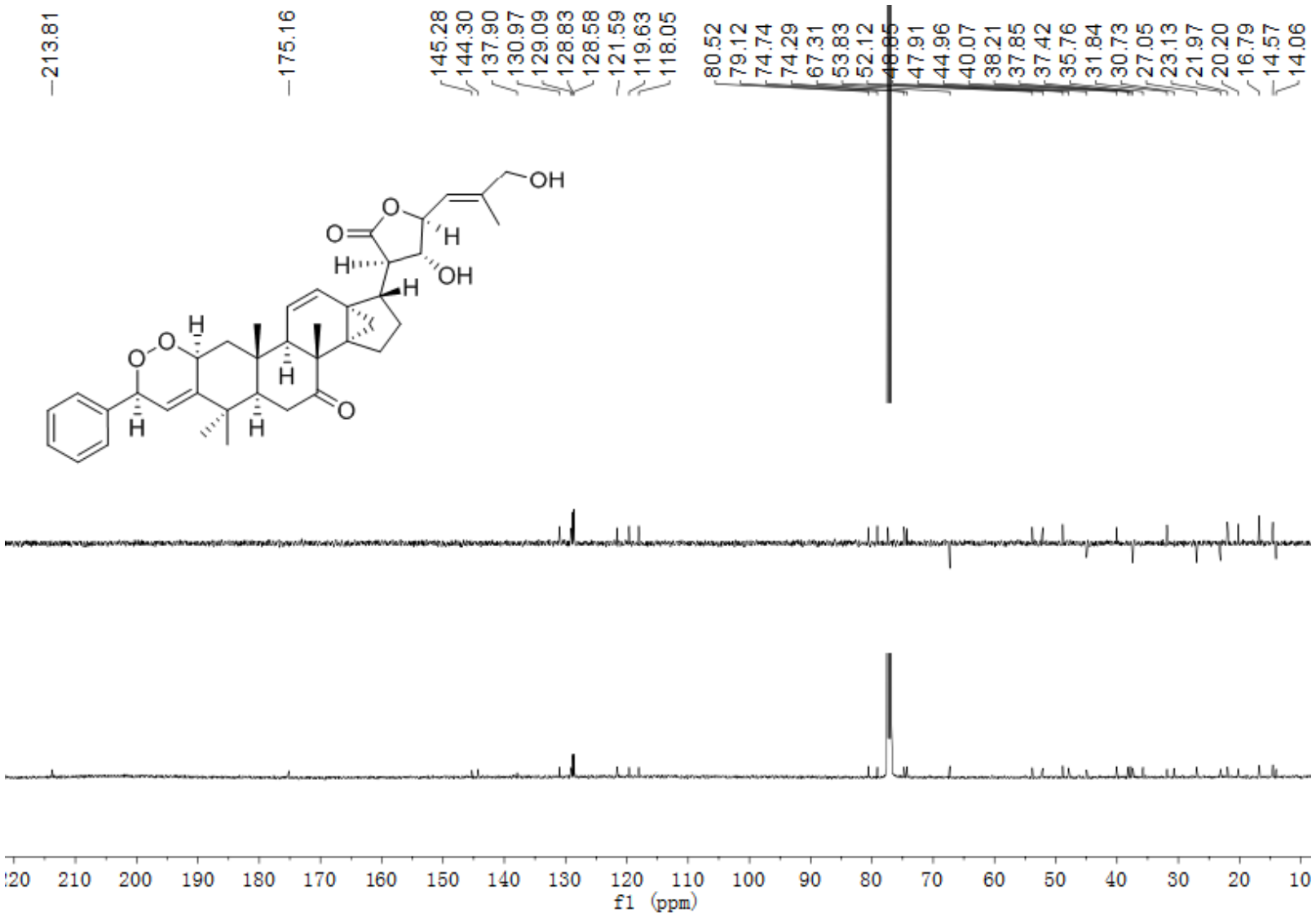


Figure S90. ^{1}H–^{1}H COSY spectrum of **9** in $CDCl_3$

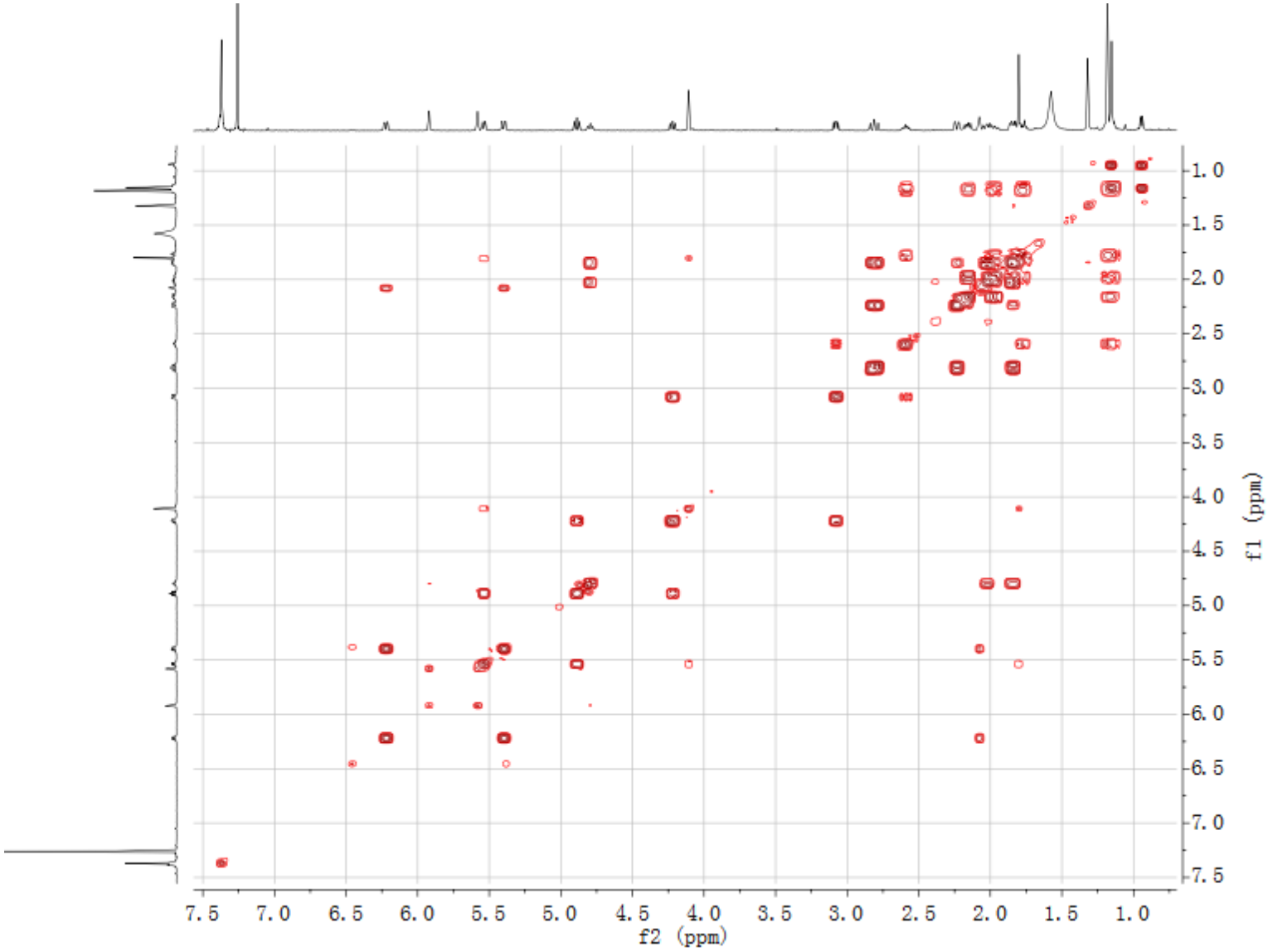


Figure S91. HSQC spectrum of **9** in $CDCl_3$

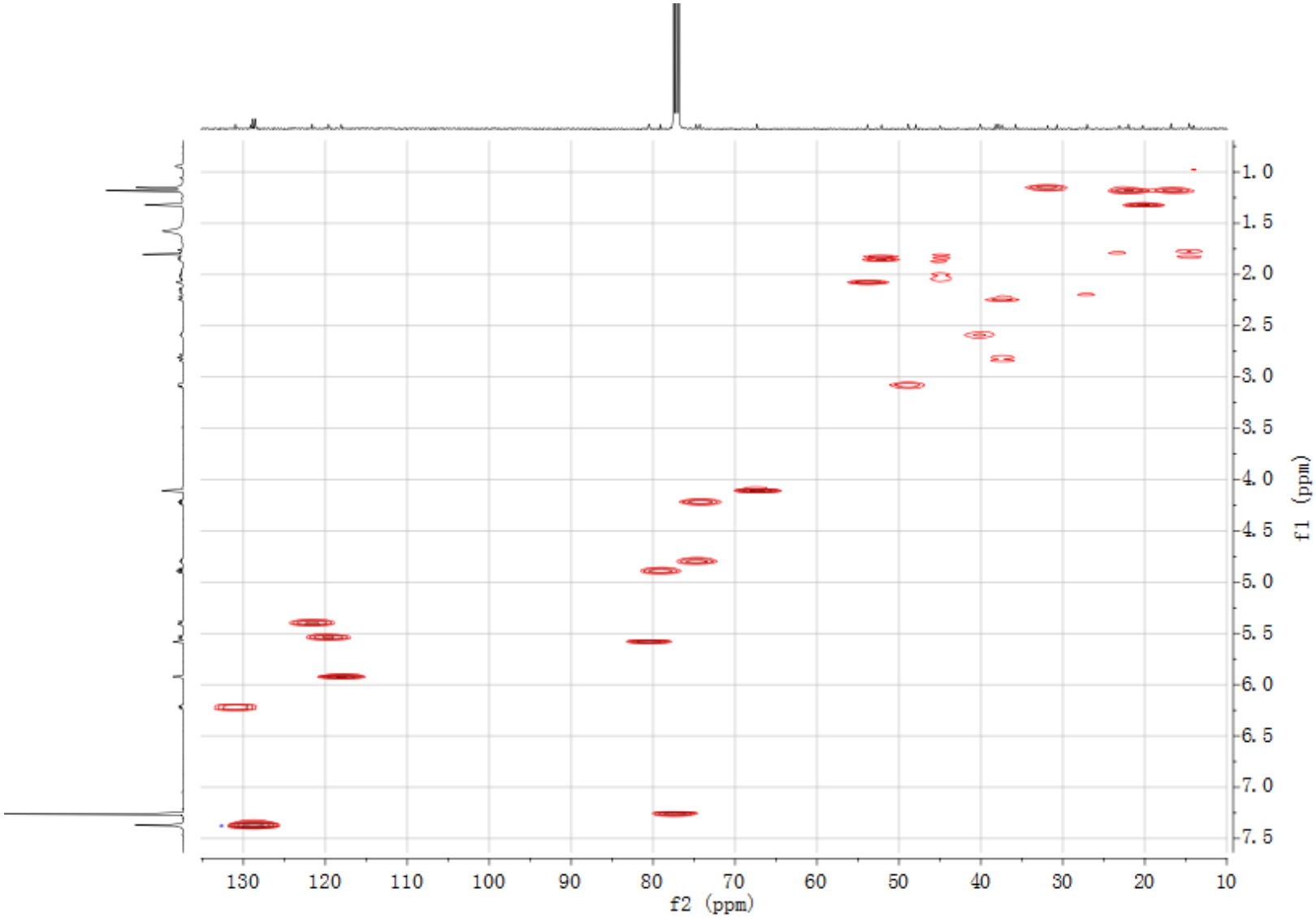


Figure S92. HMBC spectrum of **9** in $CDCl_3$

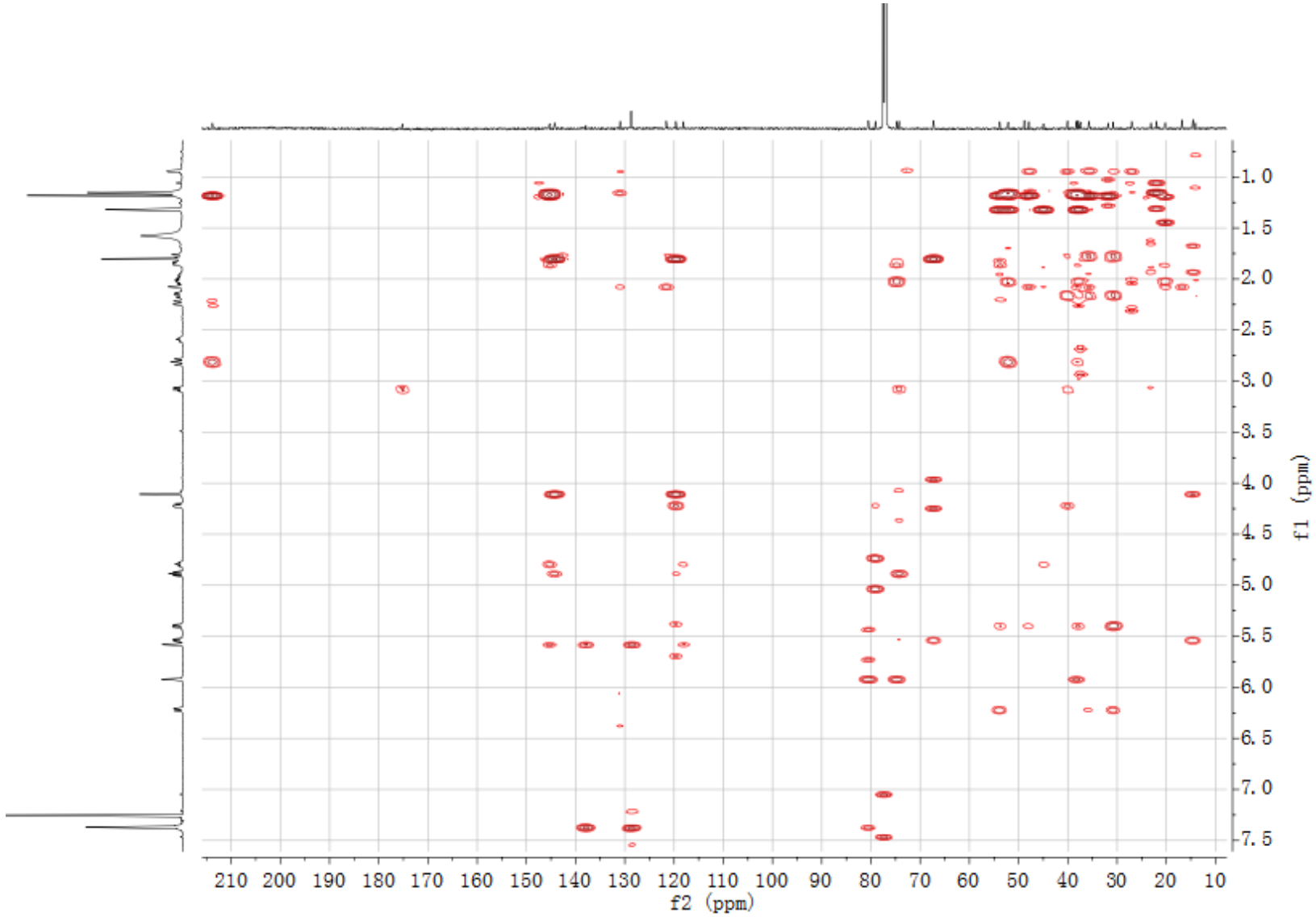


Figure S93. NOESY spectrum of **9** in $CDCl_3$

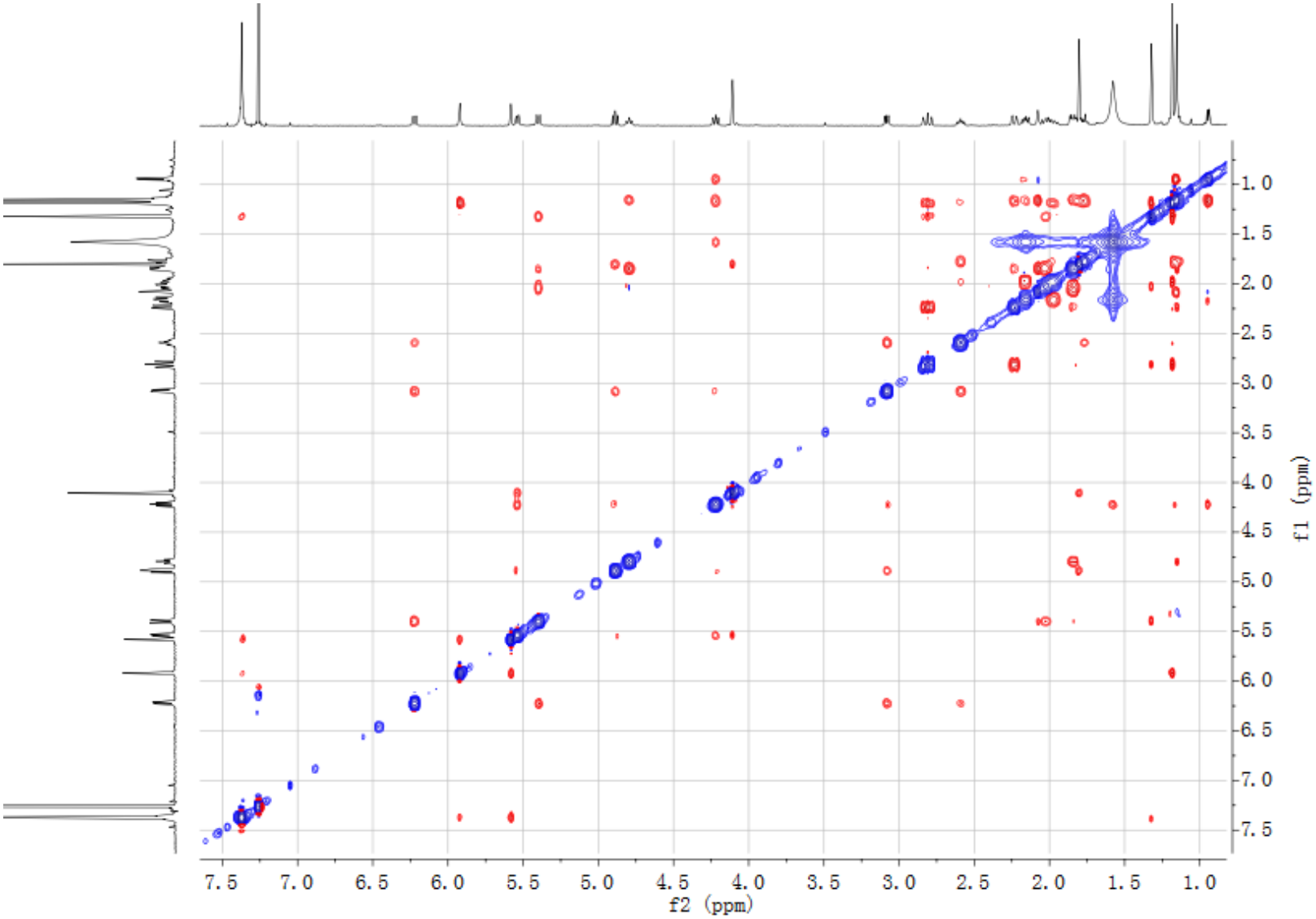


Figure S94. (±)-ESIMS spectra of **9**

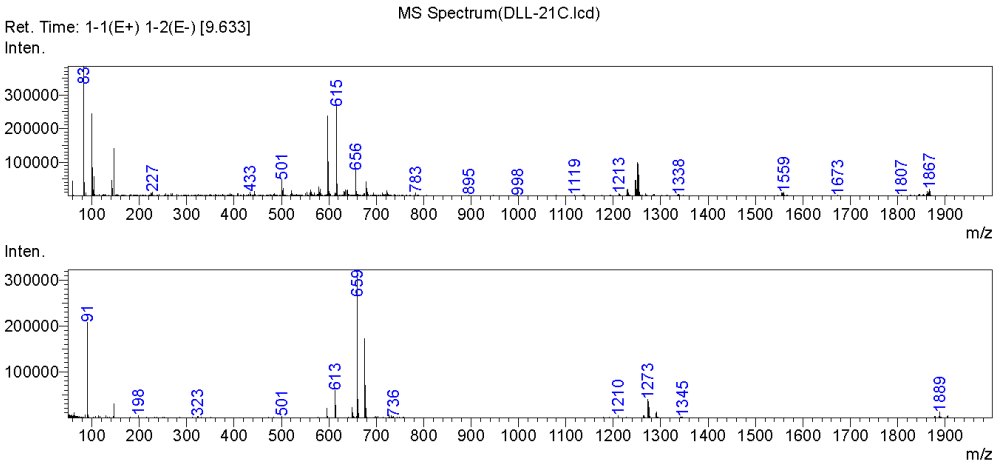


Figure S95. (–)-HRESIMS spectrum of **9**

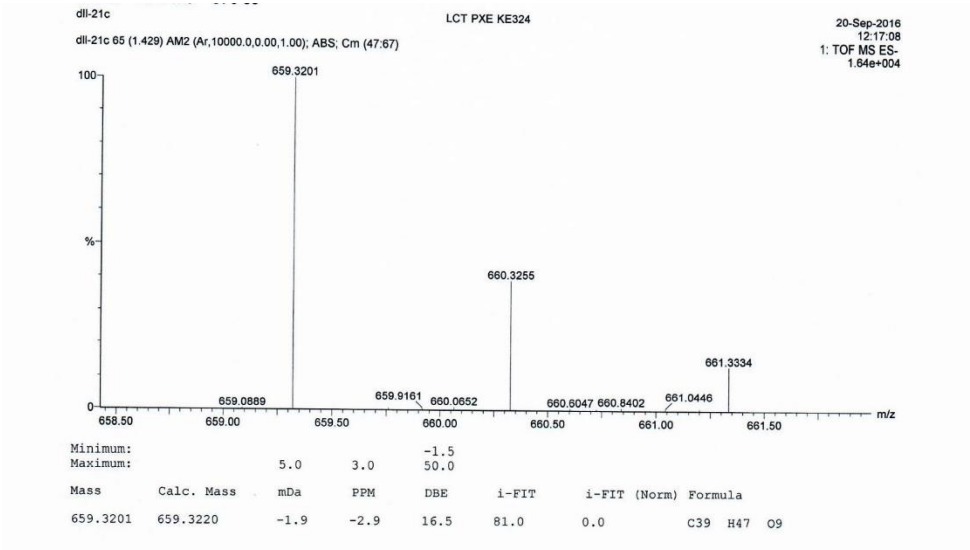
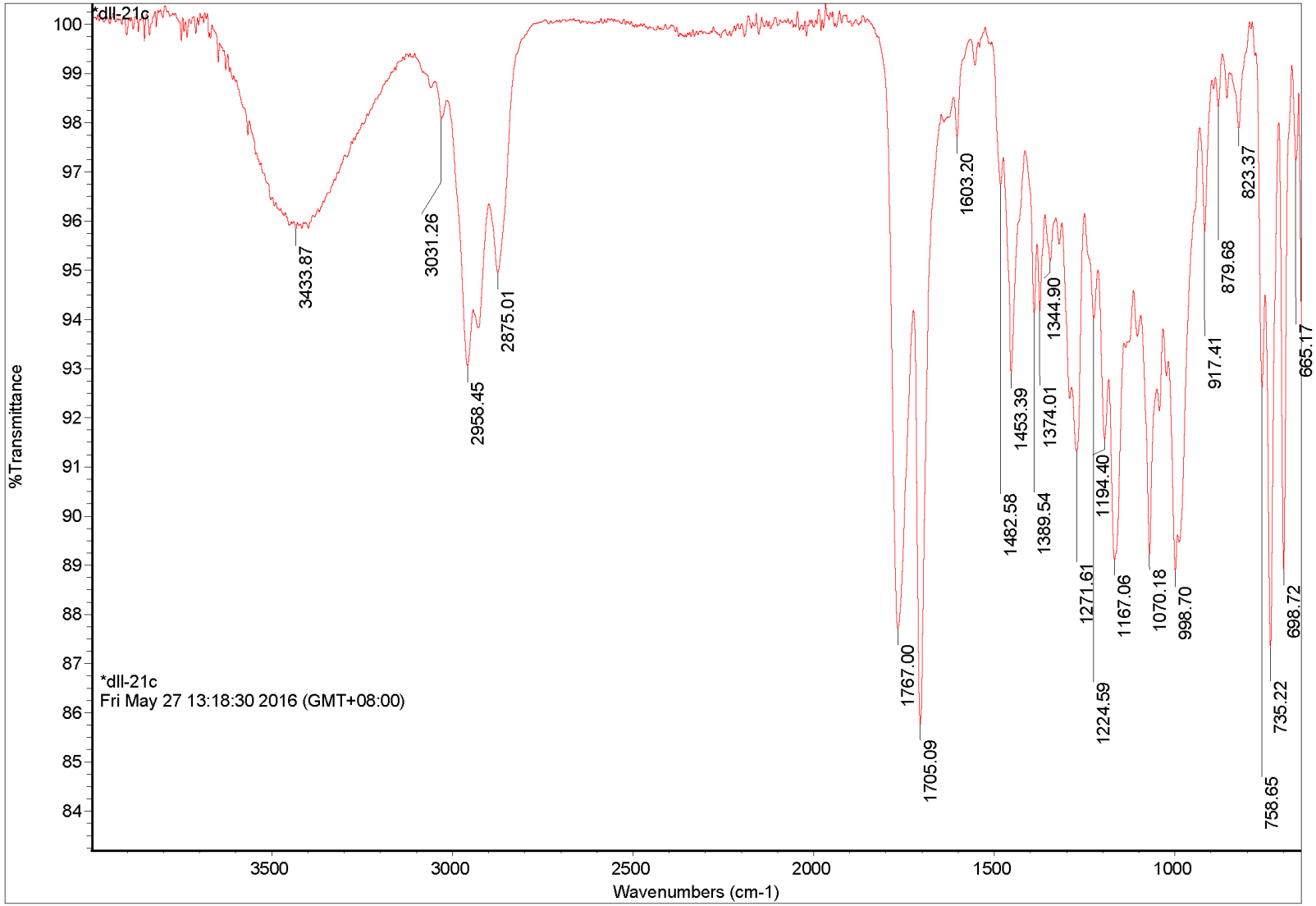


Figure S96. IR spectrum of **9**



6.10 NMR, MS, and IR spectra of compound 10

Figure S97. ^{1}H NMR spectrum (500 MHz) of **10** in $CDCl_3$

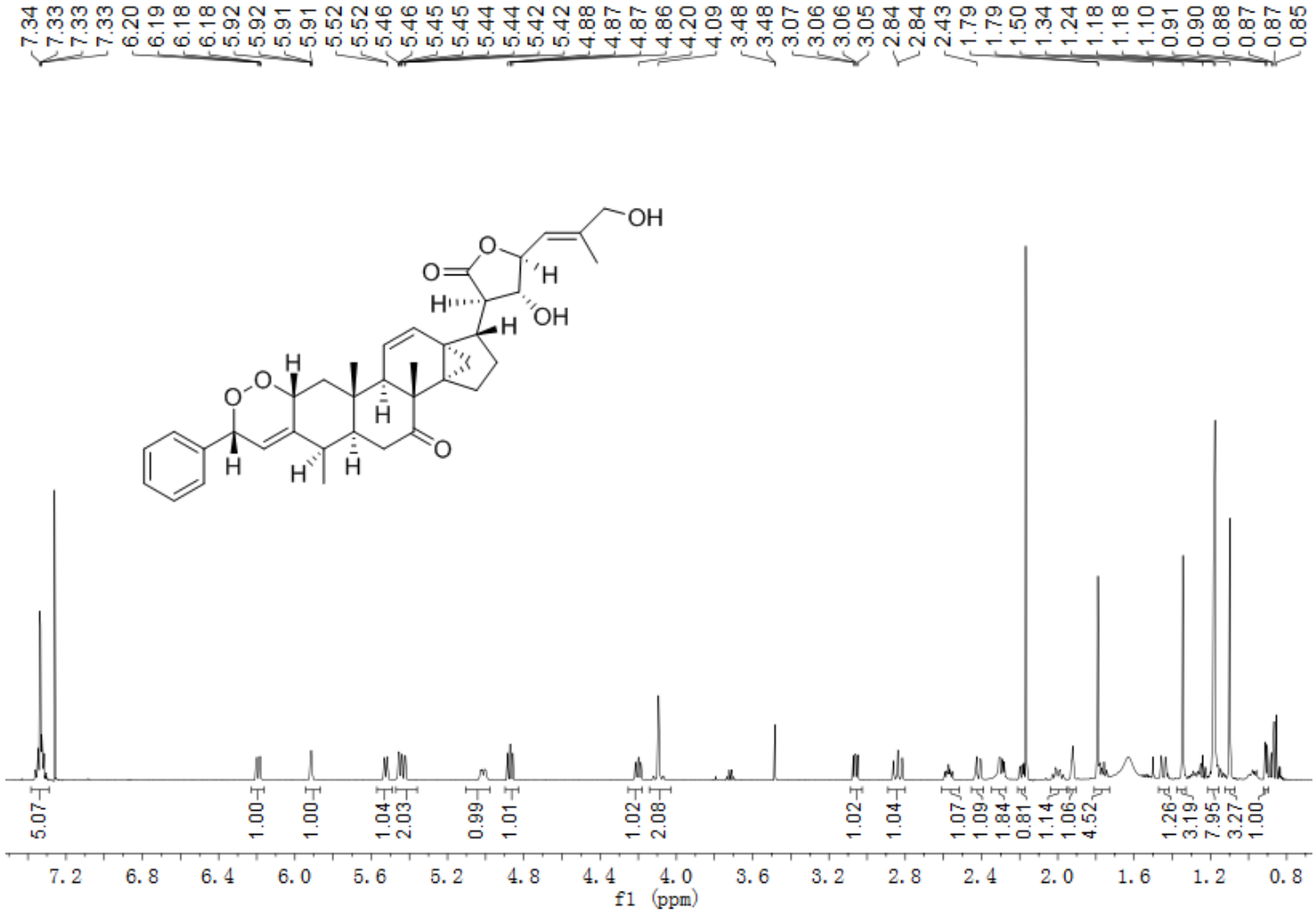


Figure S98. ^{13}C NMR spectrum (125 MHz) of **10** in $CDCl_3$

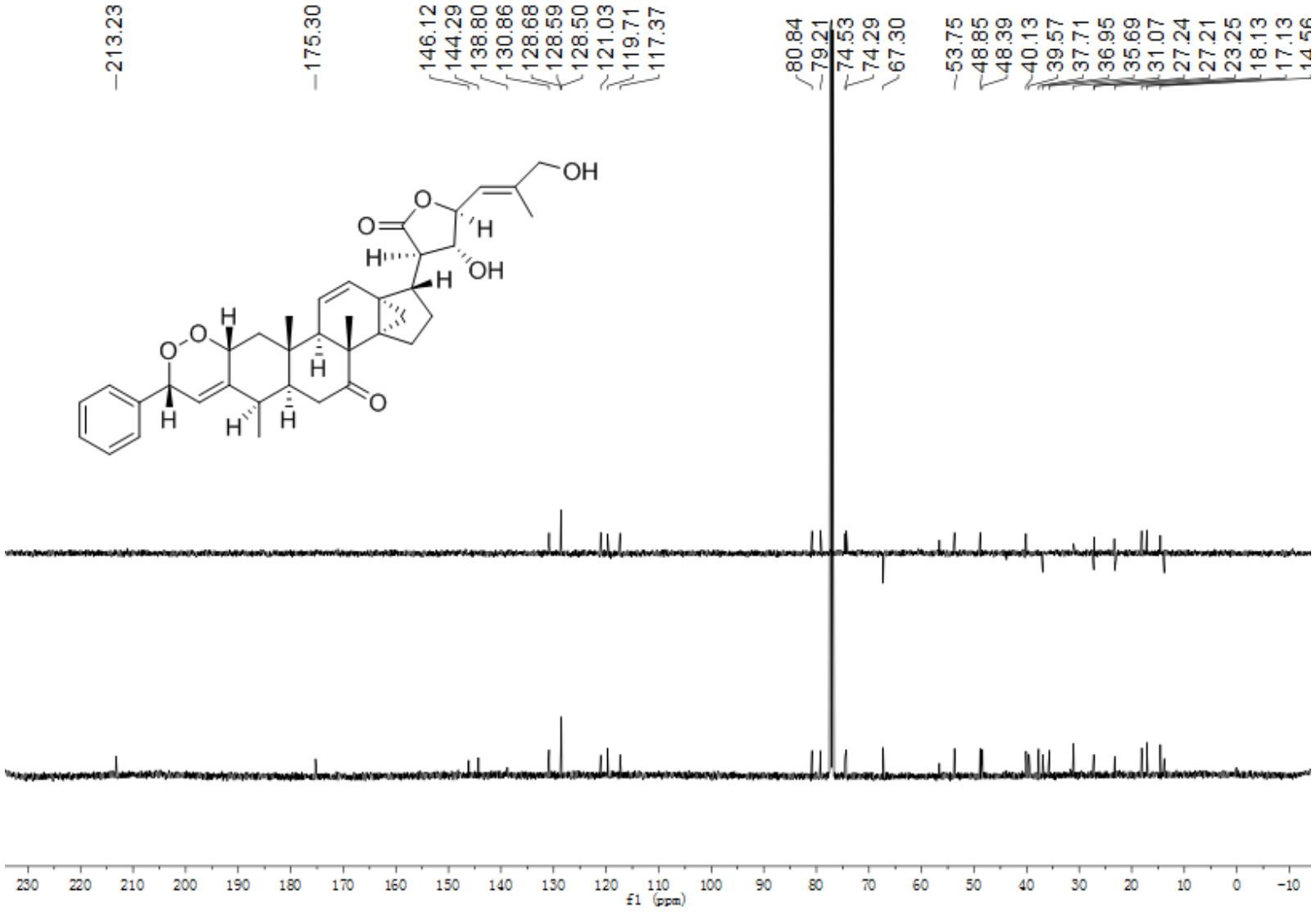


Figure S99. $^{1}H–^{1}H$ COSY spectrum of **10** in $CDCl_3$

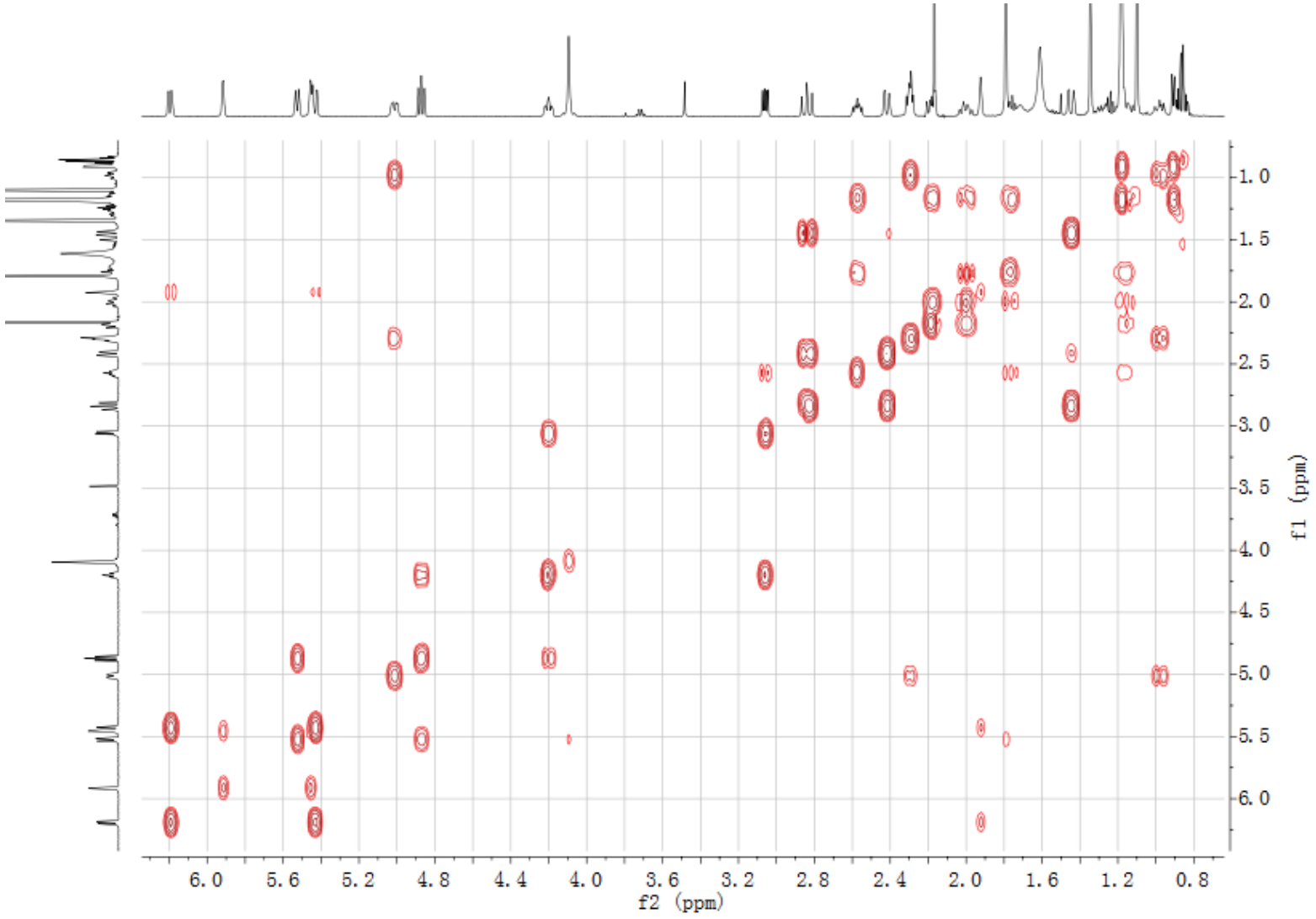


Figure S100. HSQC spectrum of **10** in $CDCl_3$

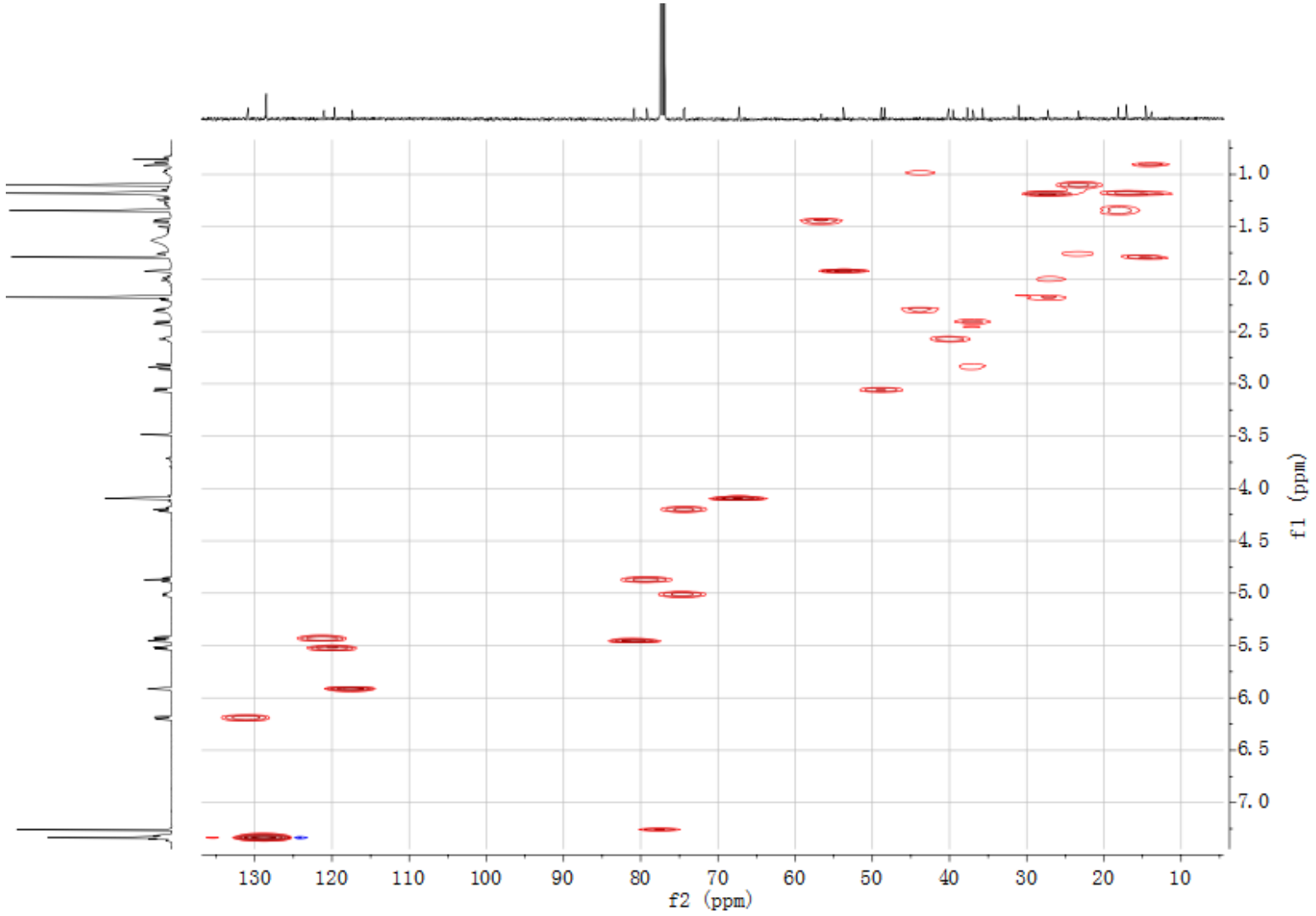


Figure S101. HMBC spectrum of **10** in $CDCl_3$

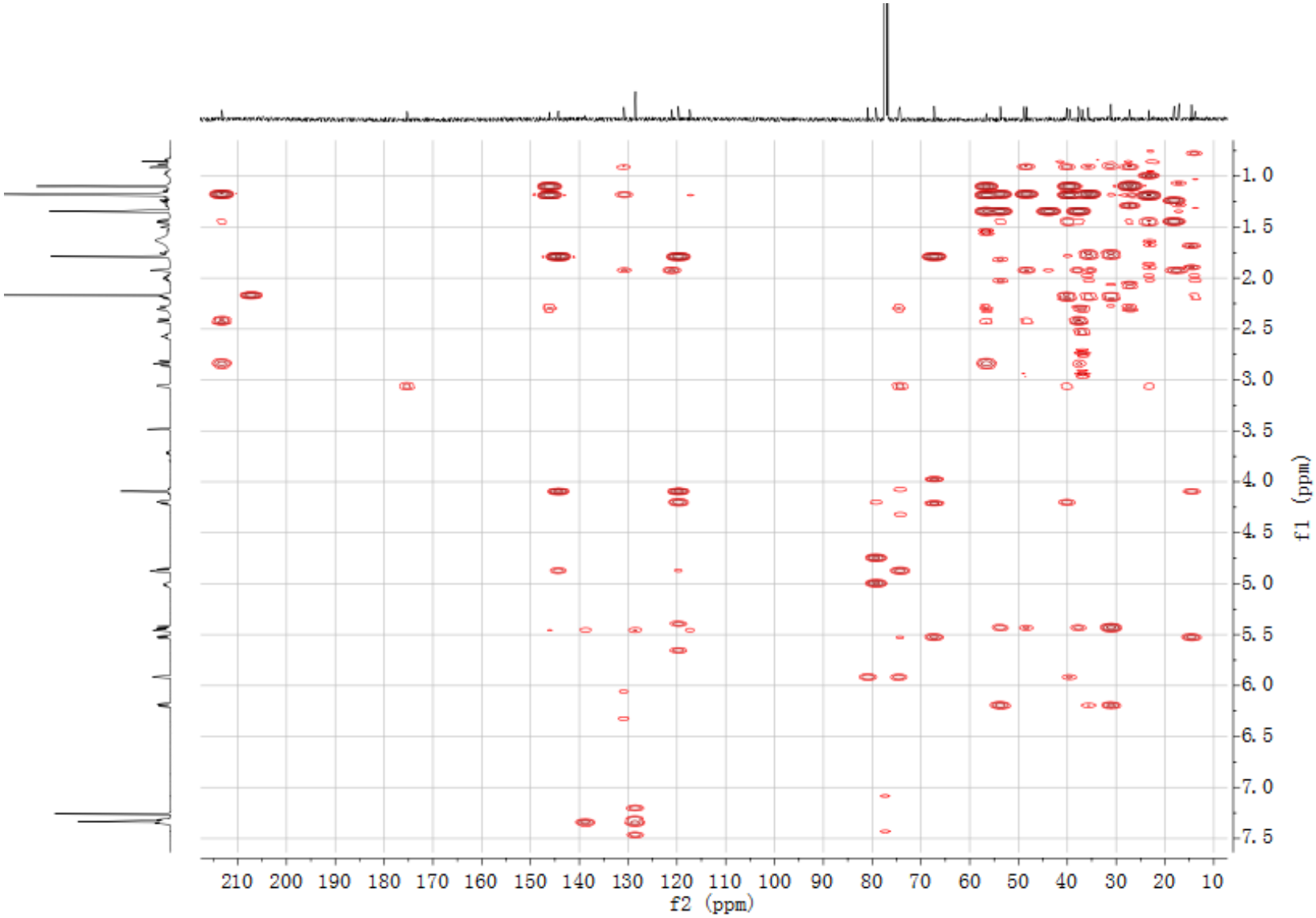


Figure S102. NOESY spectrum of **10** in $CDCl_3$

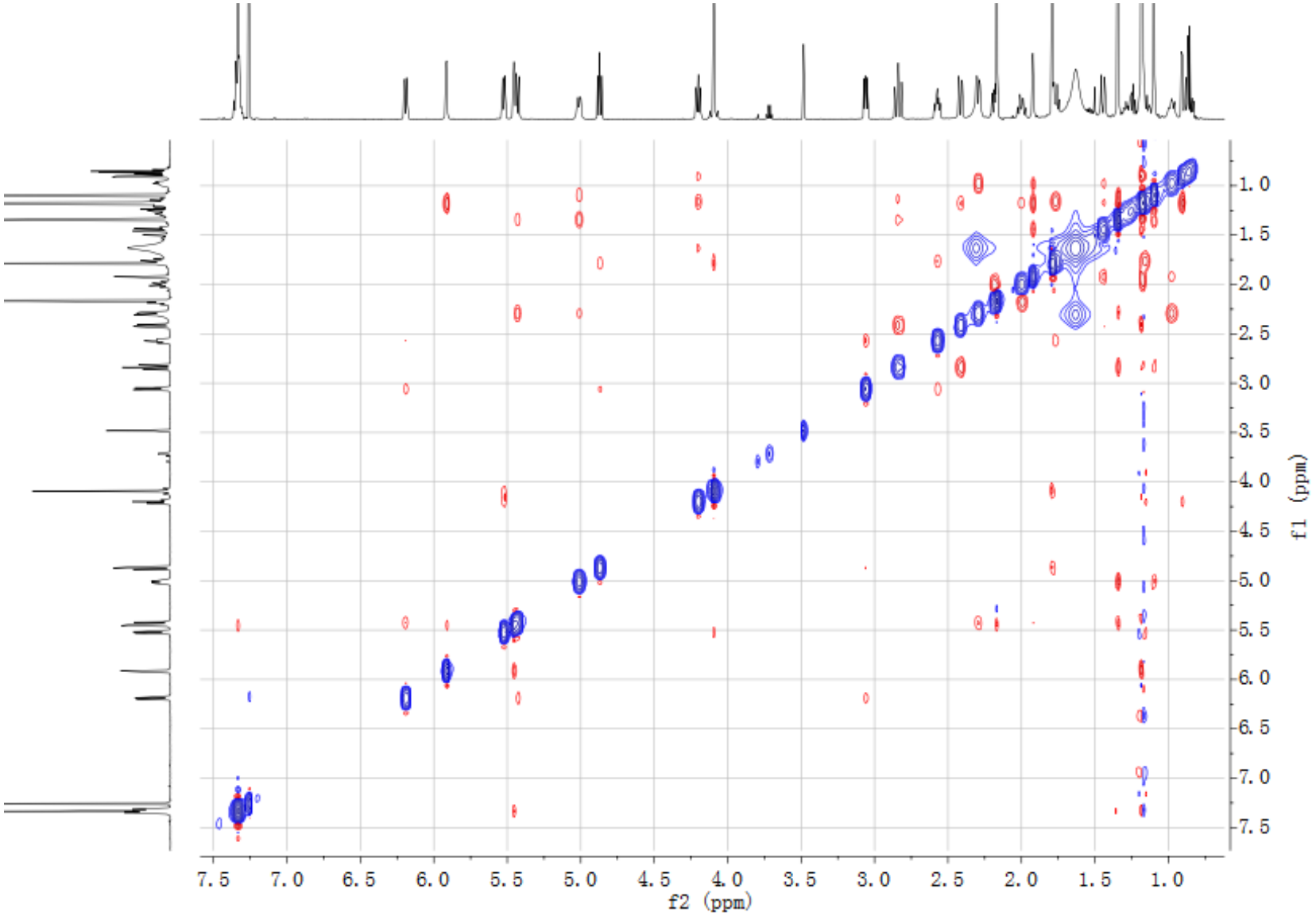


Figure S103. (±)-ESIMS spectra of **10**

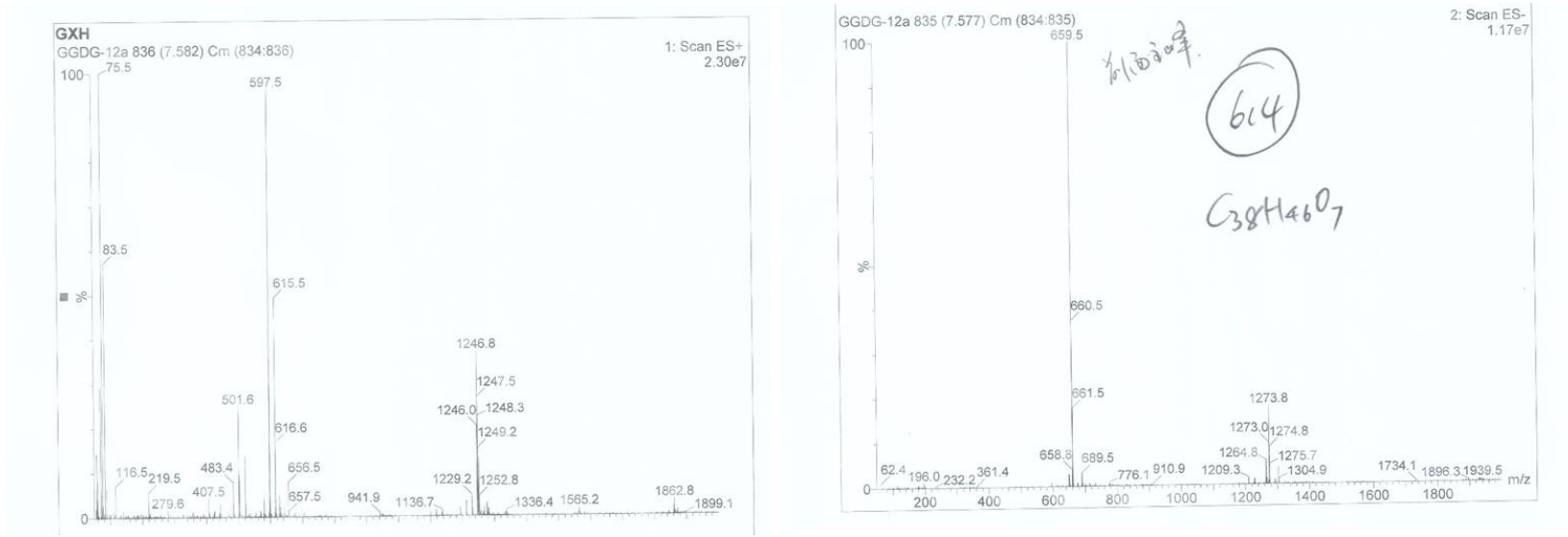
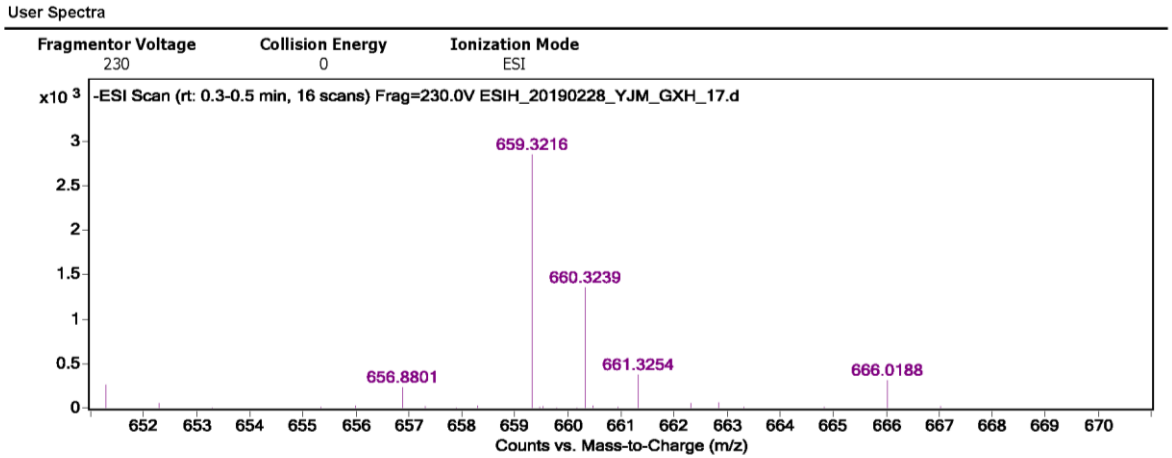


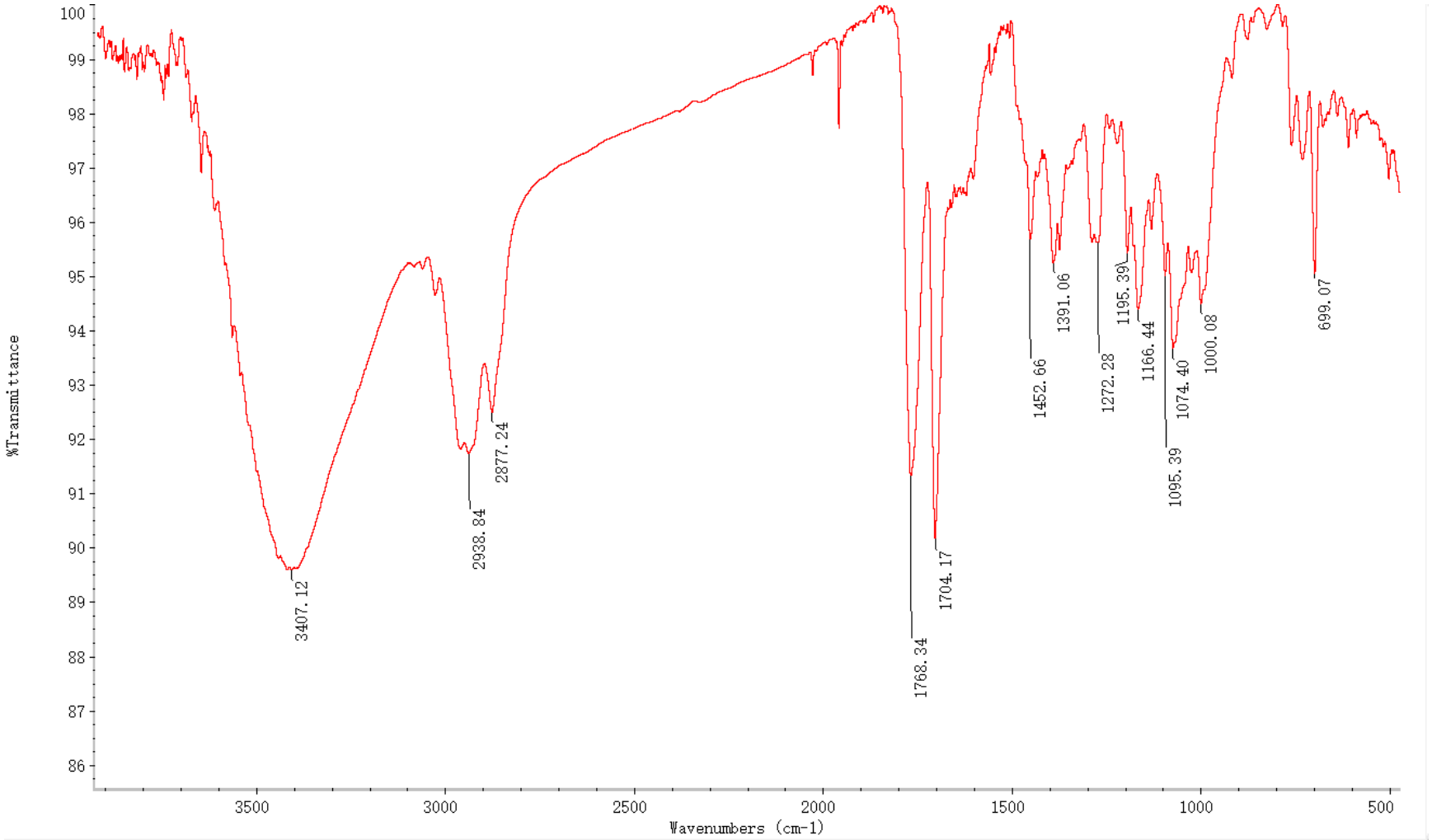
Figure S104. (–)-HRESIMS spectrum of **10**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
659.3216	659.3226	1	1.52	C39 H47 O9	(M+COOH)-

Figure S105. IR spectrum of **10**



6.11 NMR, MS, and IR spectra of compound 11

Figure S106. ^{1}H NMR spectrum (500 MHz) of **11** in $CDCl_3$

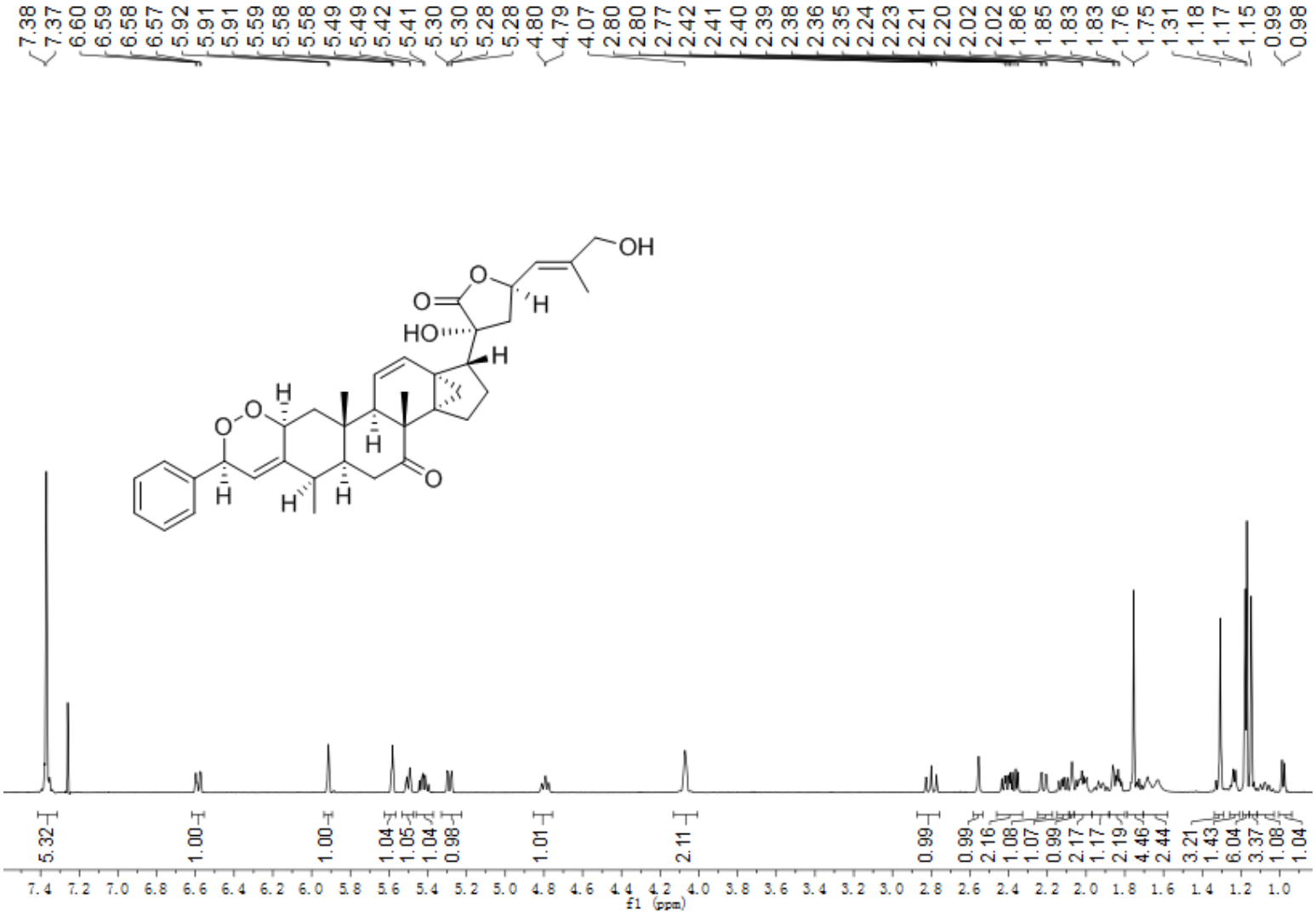


Figure S107. ^{13}C NMR spectrum (125 MHz) of **11** in $CDCl_3$

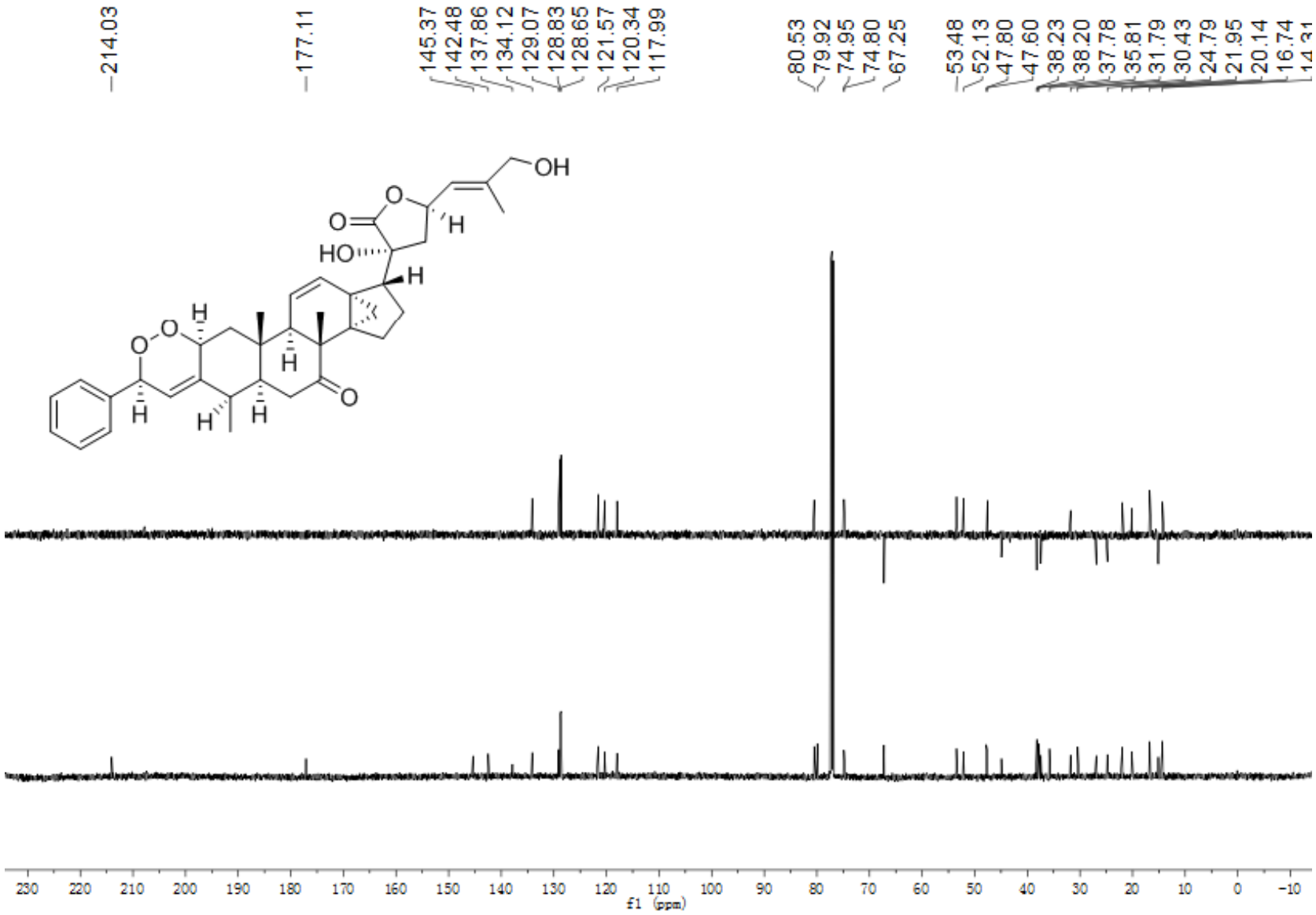


Figure S108. $^{1}H–^{1}H$ COSY spectrum of **11** in $CDCl_3$

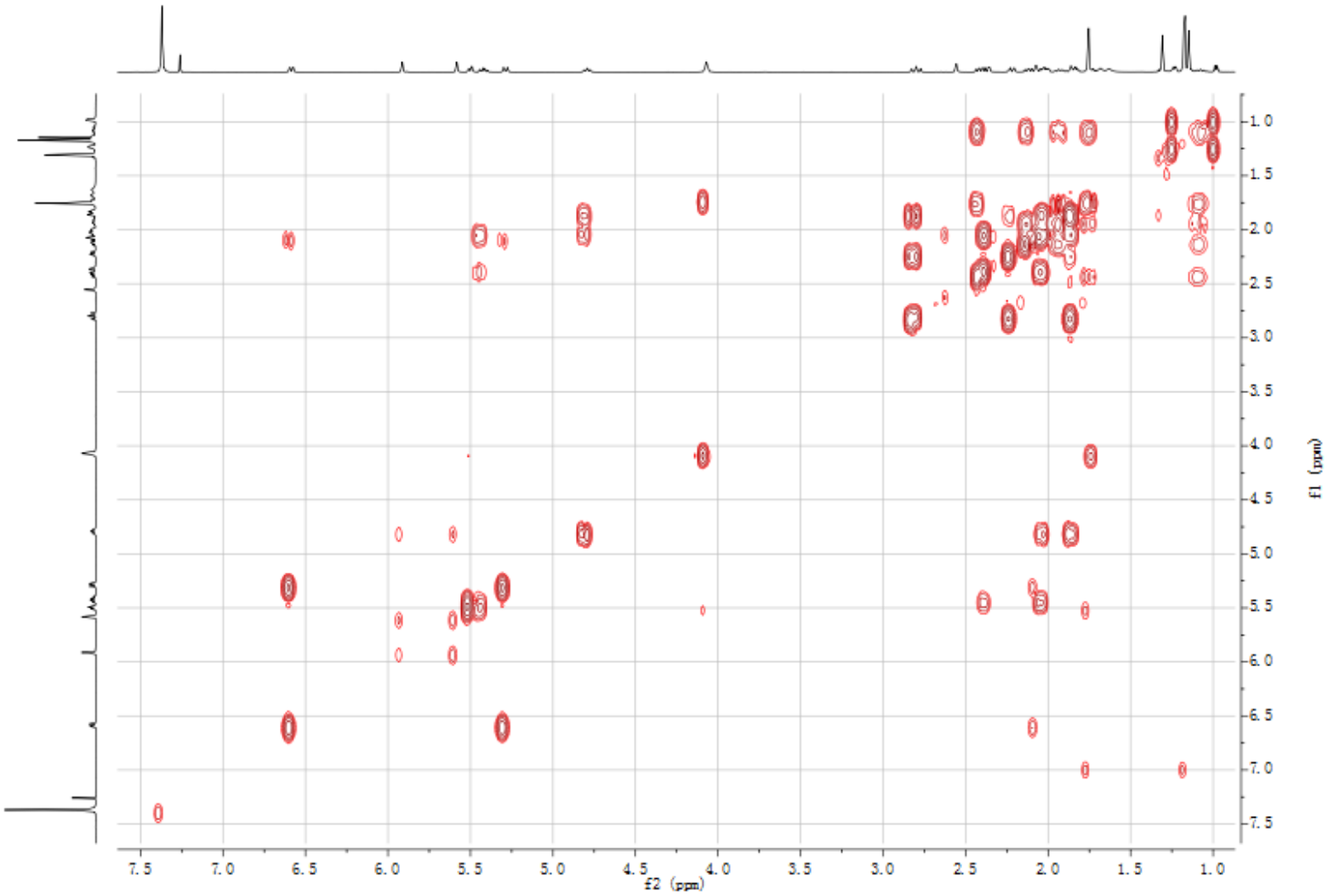


Figure S109. HSQC spectrum of **11** in $CDCl_3$

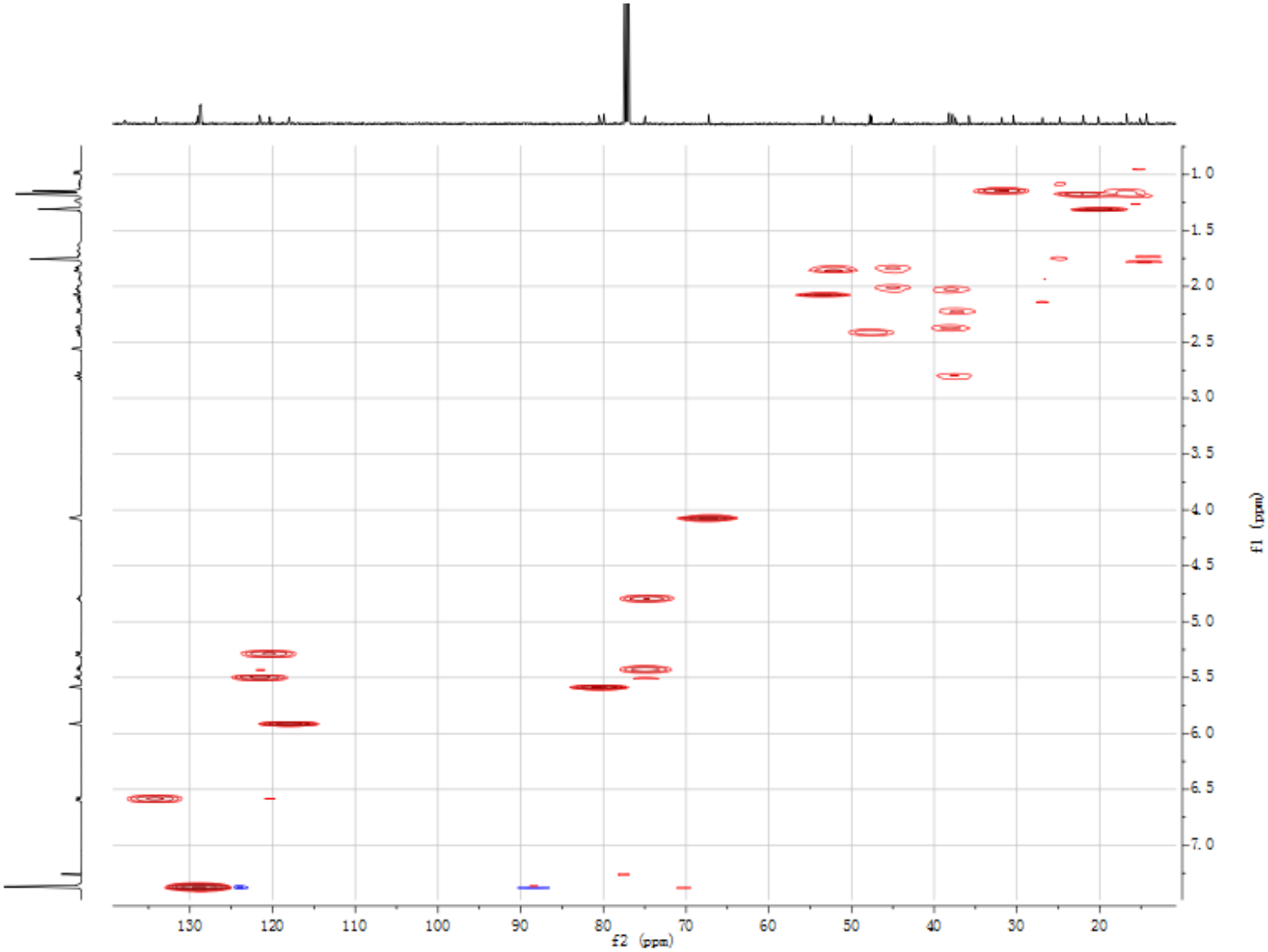


Figure S110. HMBC spectrum of **11** in $CDCl_3$

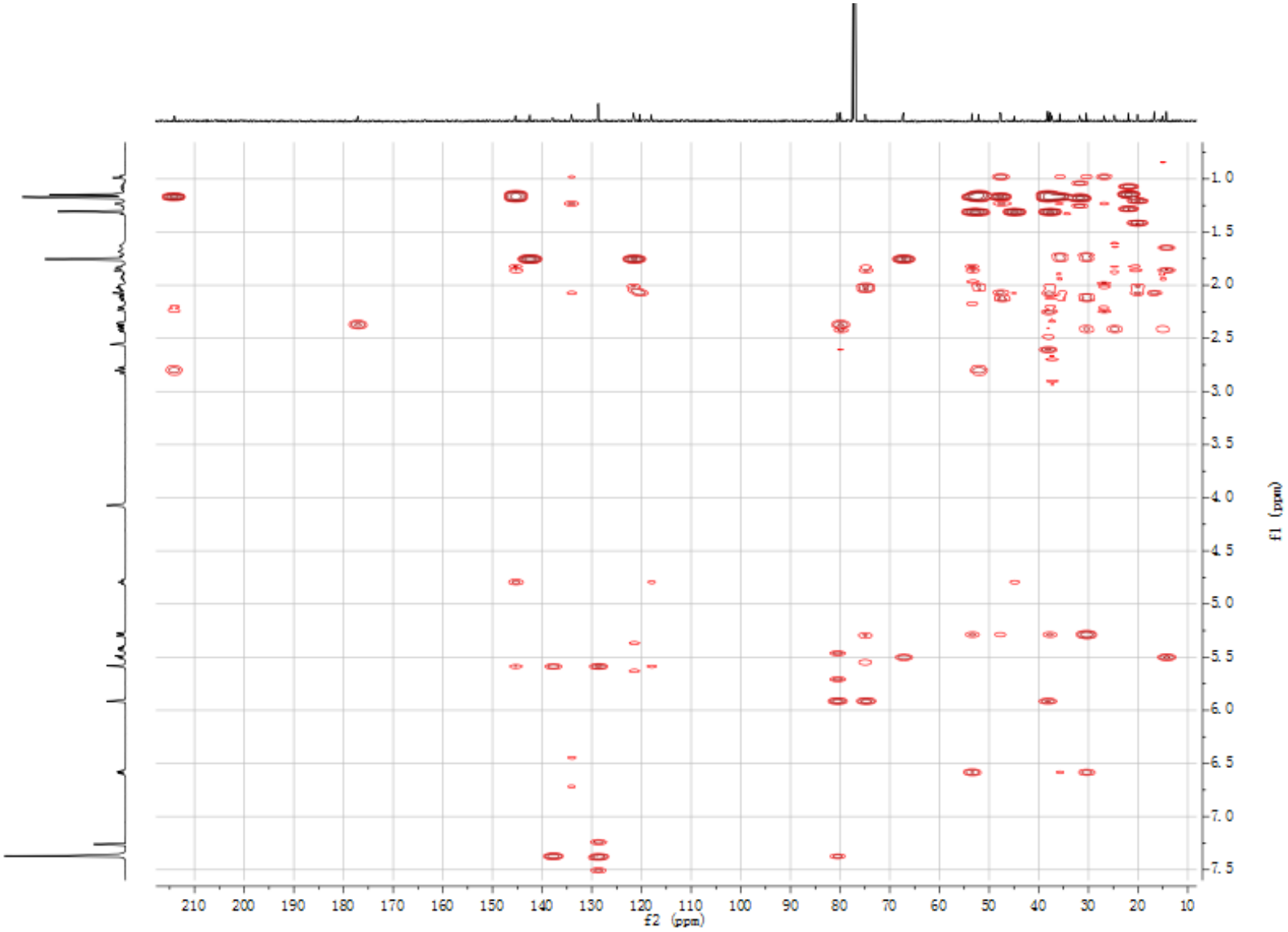


Figure S111. NOESY spectrum of **11** in $CDCl_3$

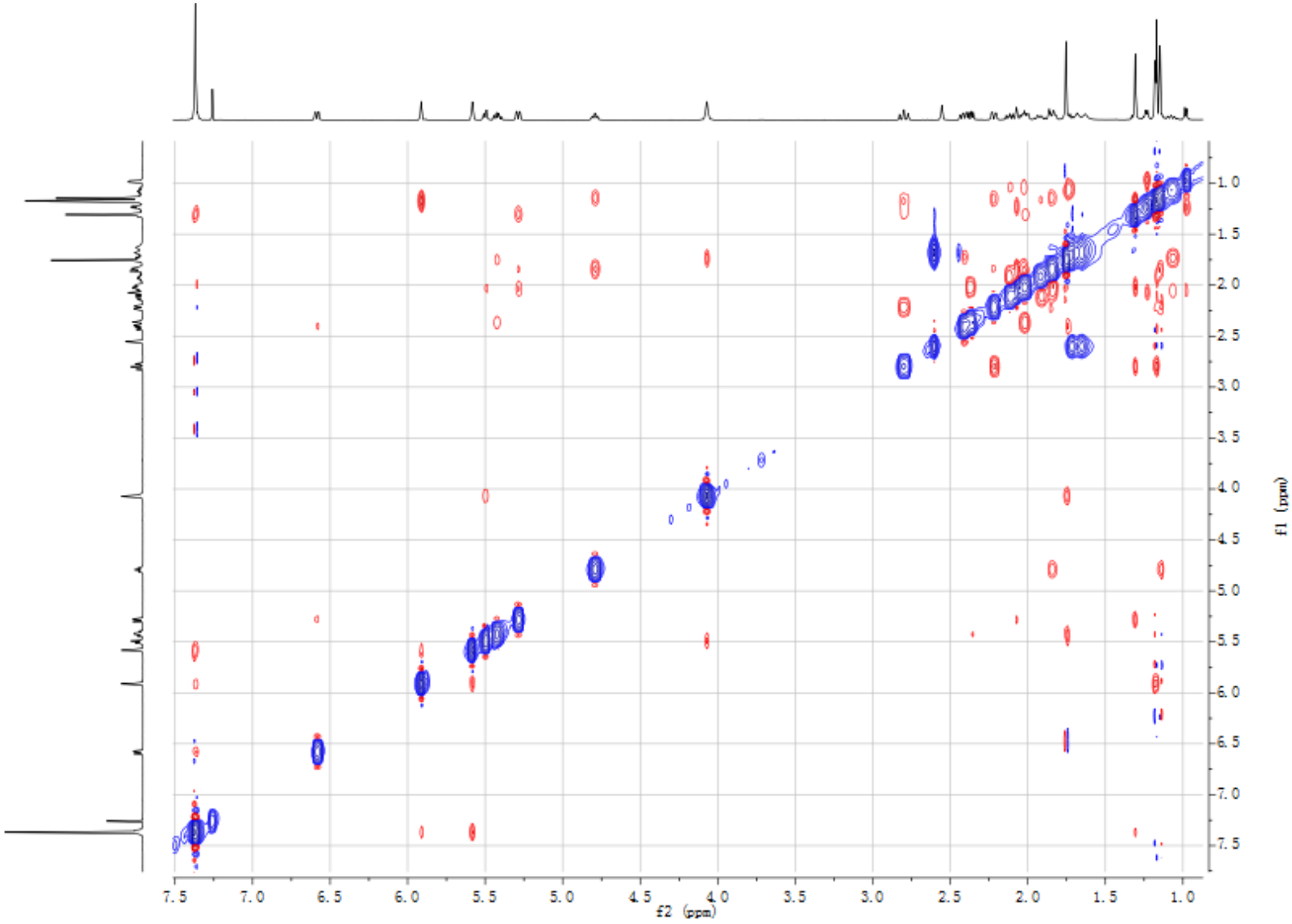


Figure S112. (±)-ESIMS spectra of **11**

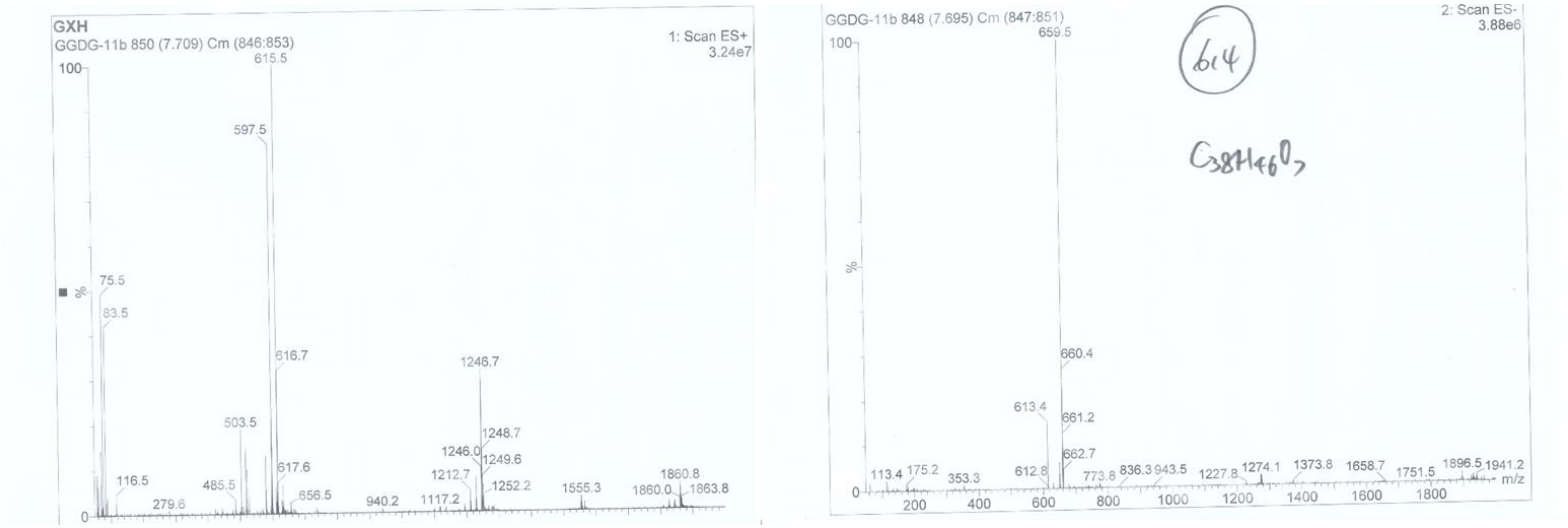
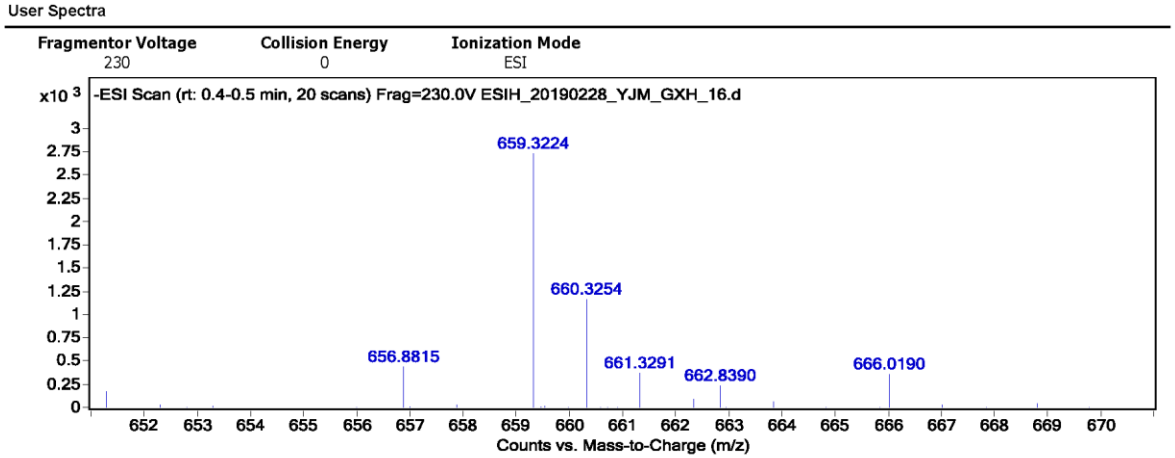


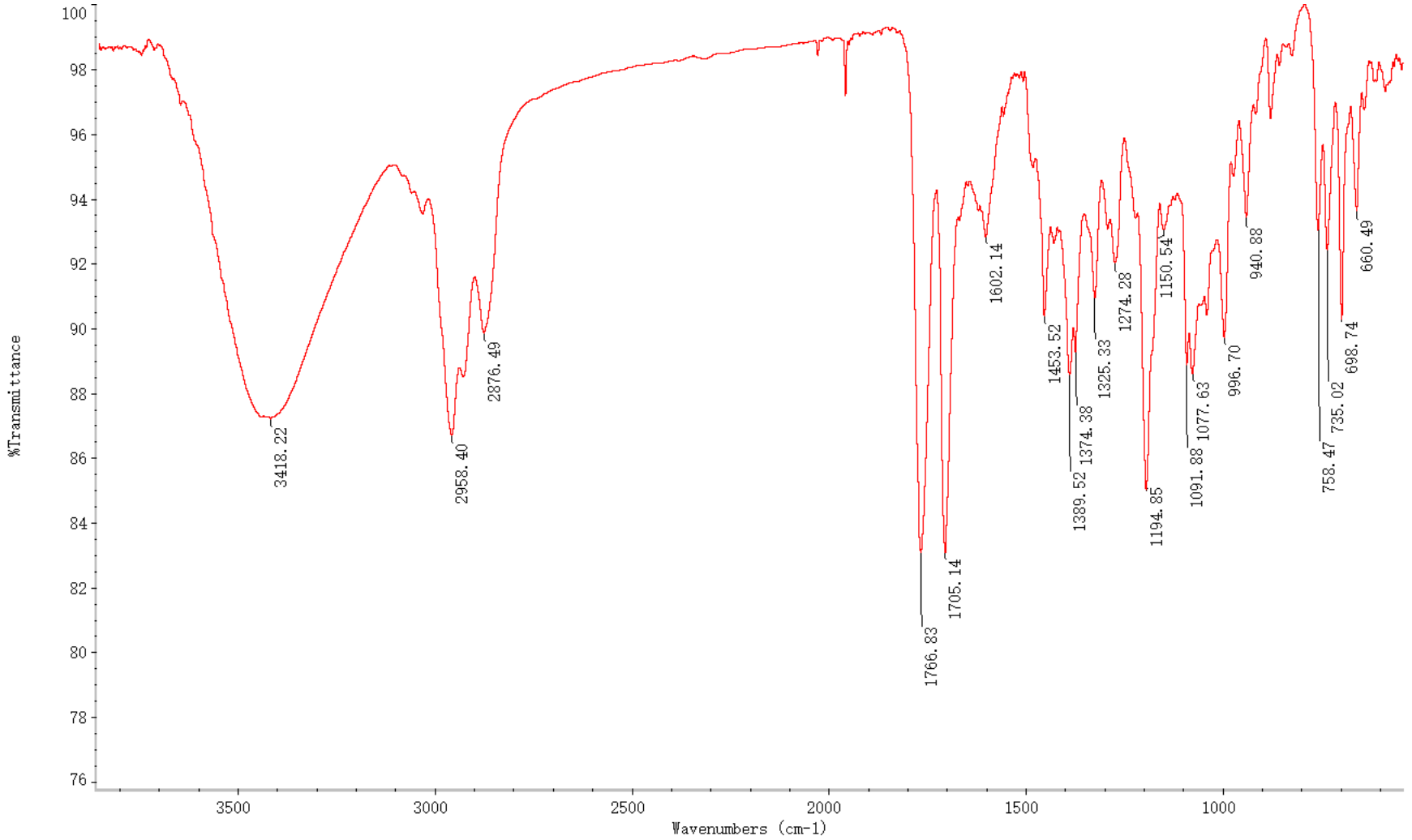
Figure S113. (−)-HRESIMS spectrum of **11**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
659.3224	659.3226	0.2	0.3	C39 H47 O9	(M+COOH)-

Figure S114. IR spectrum of **11**



6.12 NMR, MS, and IR spectra of compound 12

Figure S115. ^{1}H NMR spectrum (500 MHz) of **12** in $CDCl_3$

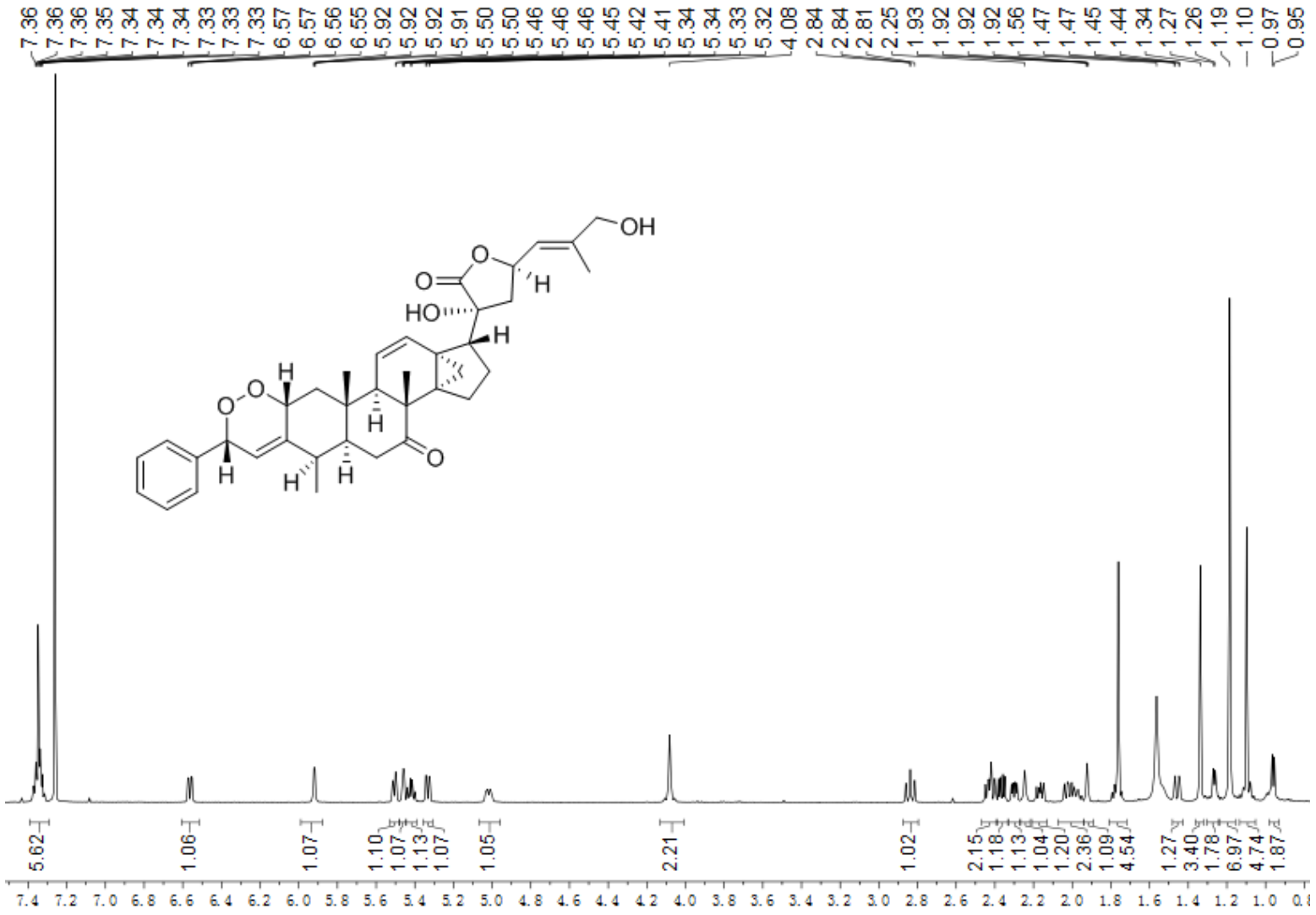


Figure S116. ^{13}C NMR spectrum (125 MHz) of **12** in $CDCl_3$

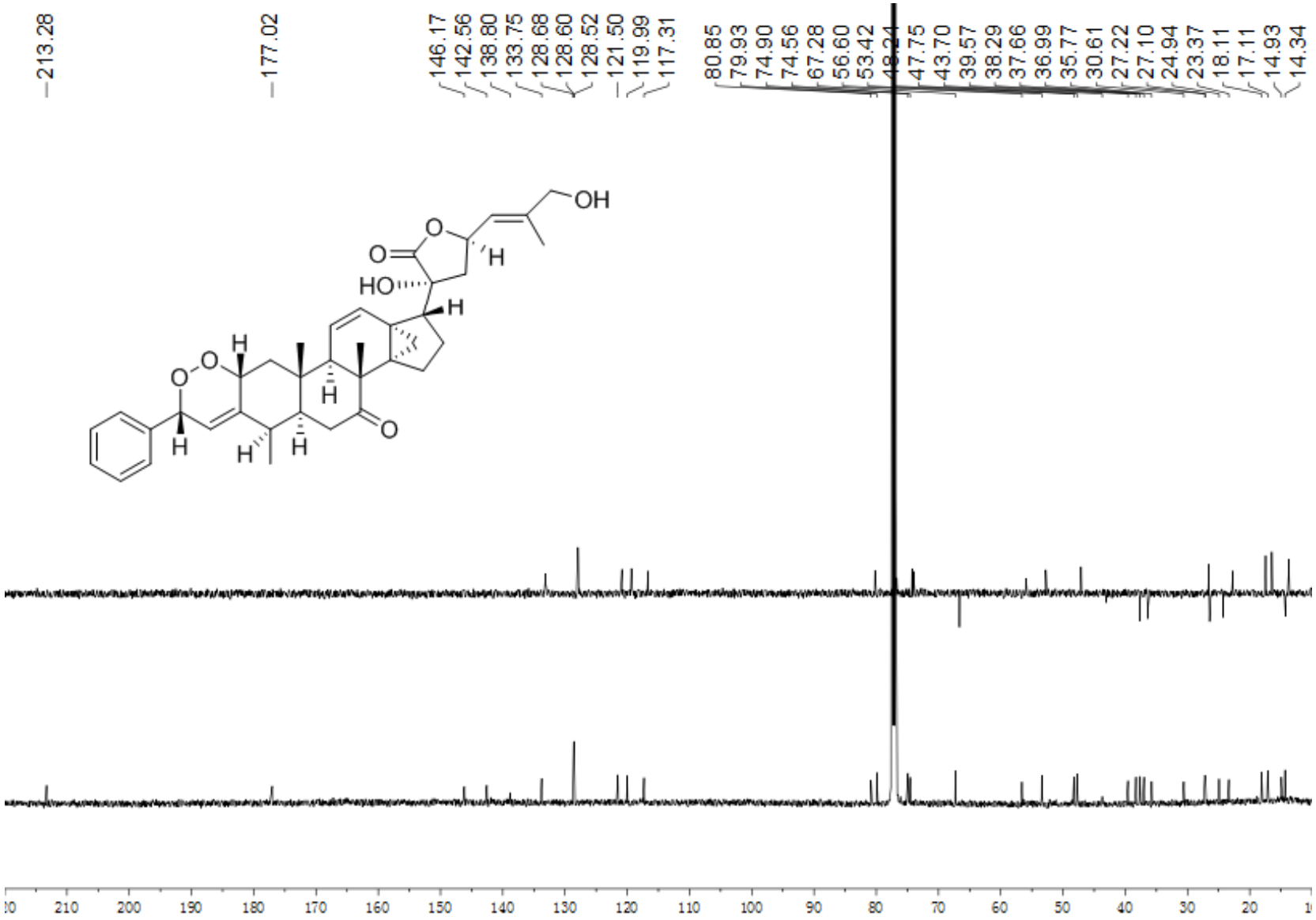


Figure S117. ^{1}H–^{1}H COSY spectrum of **12** in $CDCl_3$

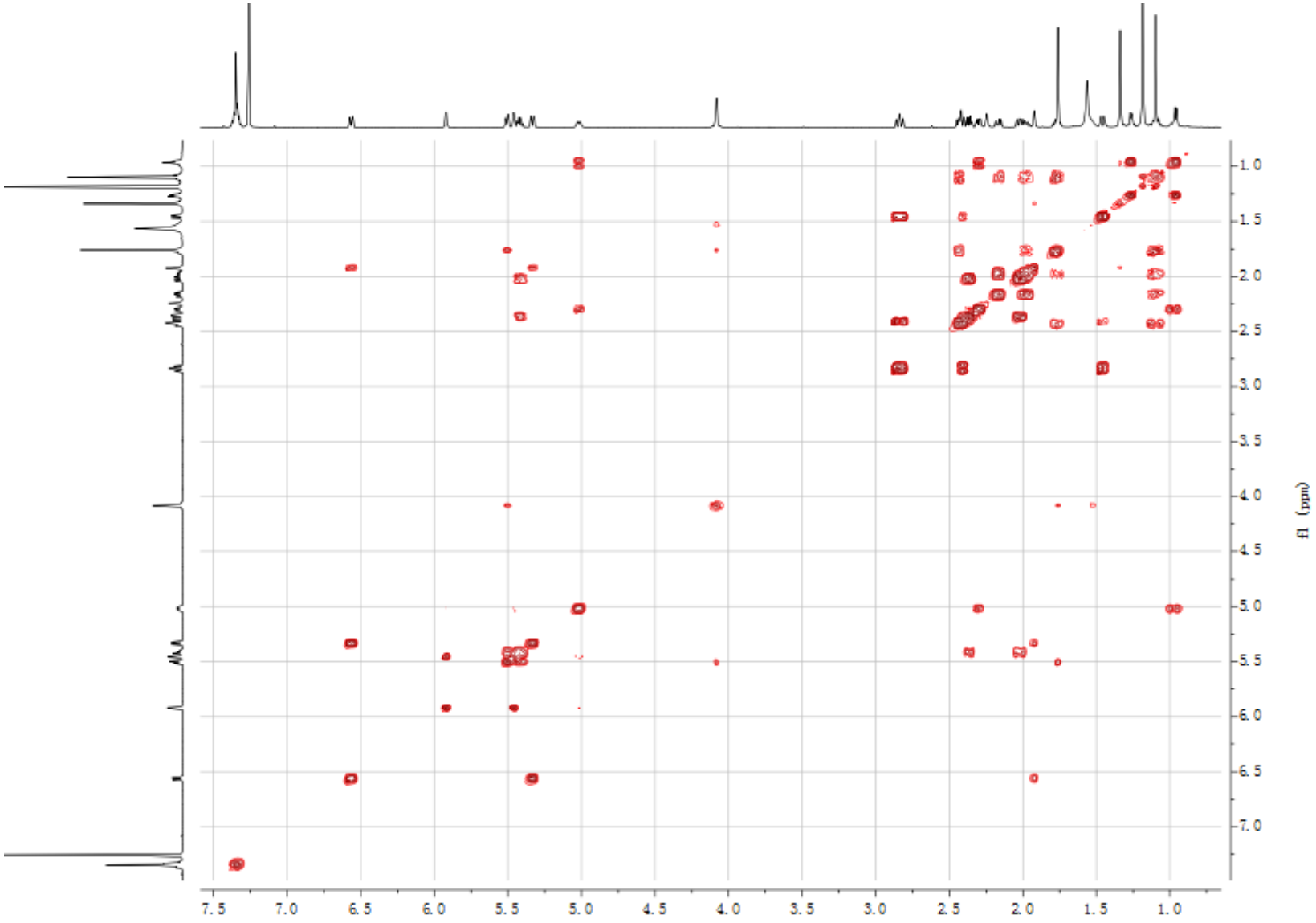


Figure S118. HSQC spectrum of **12** in $CDCl_3$

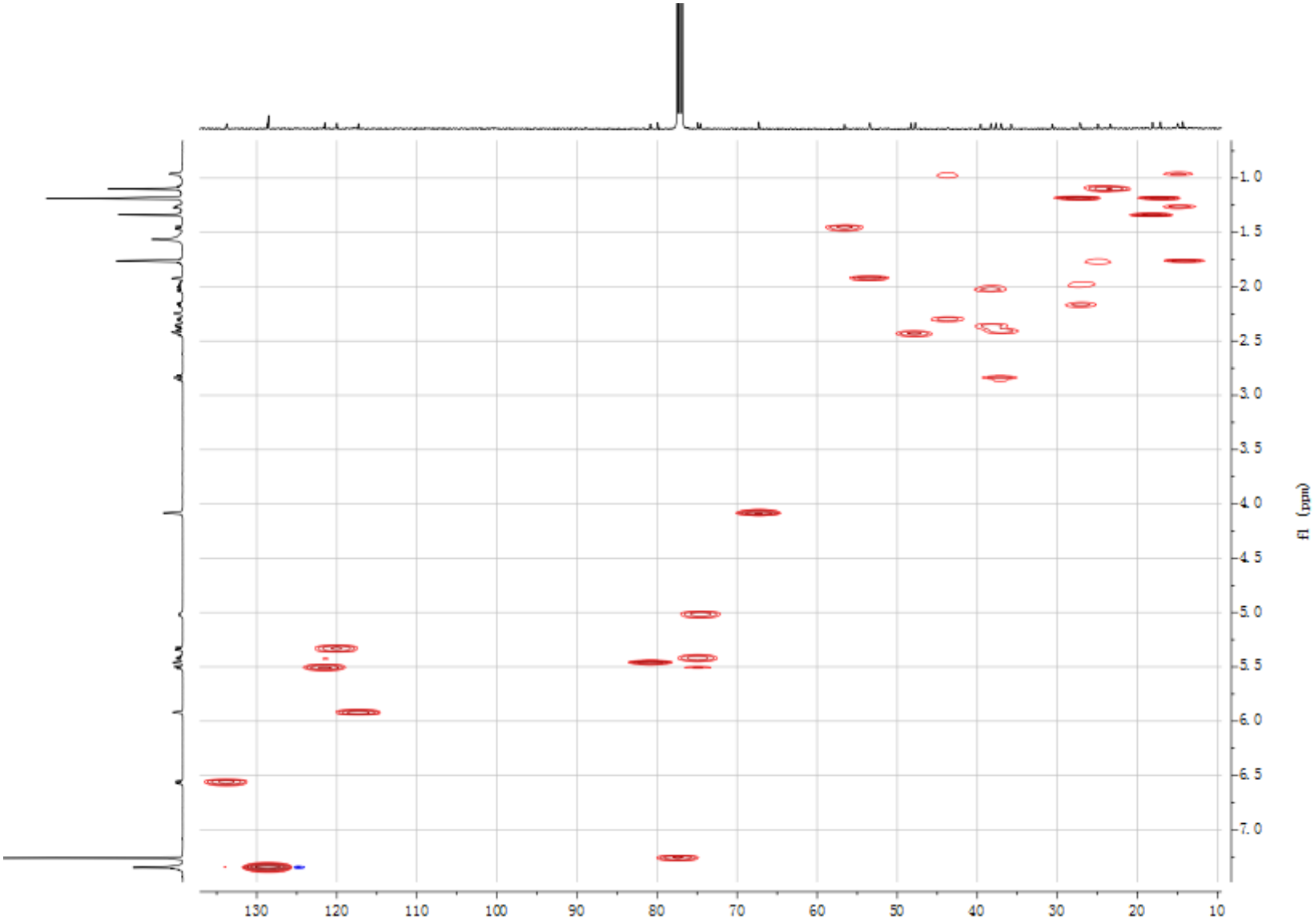


Figure S119. HMBC spectrum of **12** in $CDCl_3$

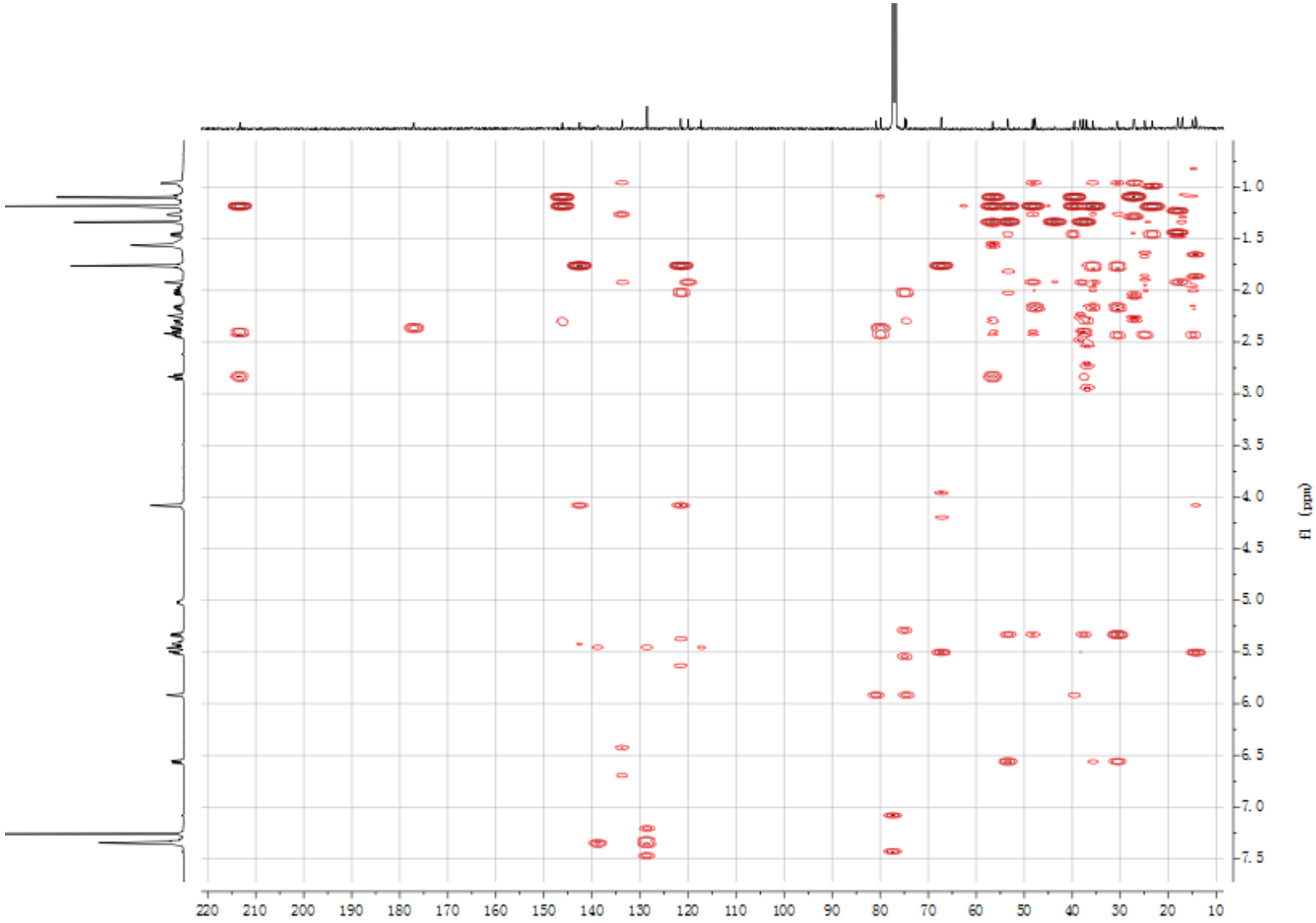


Figure S120. NOESY spectrum of **12** in $CDCl_3$

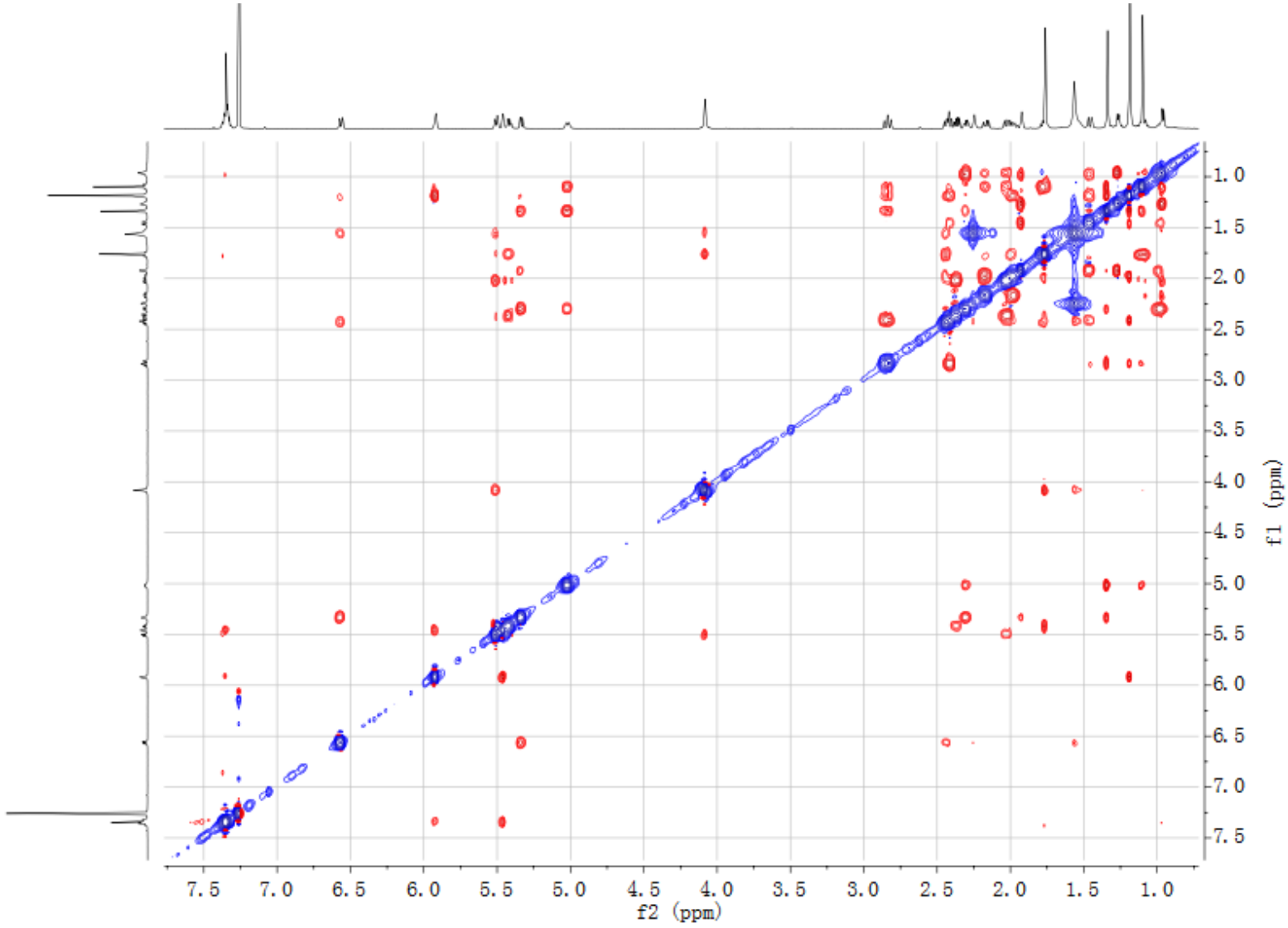


Figure S121. (±)-ESIMS spectra of **12**

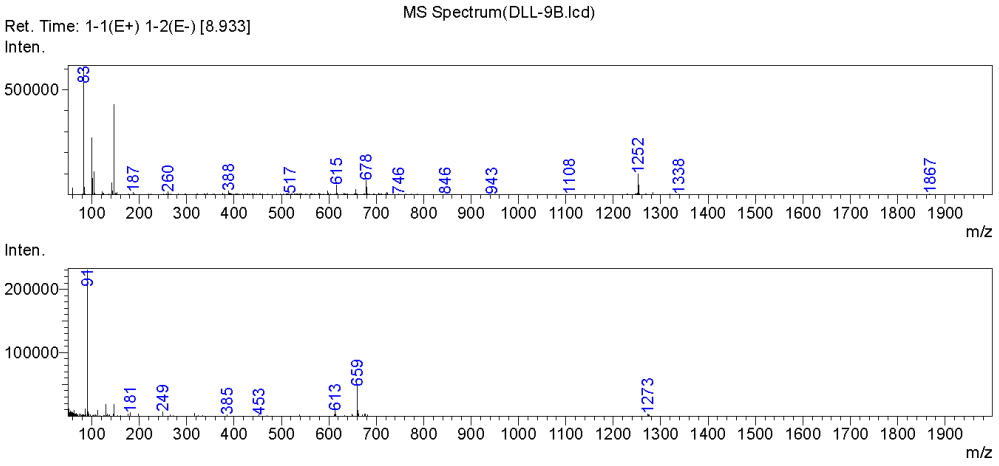


Figure S122. (–)-HRESIMS spectrum of **12**

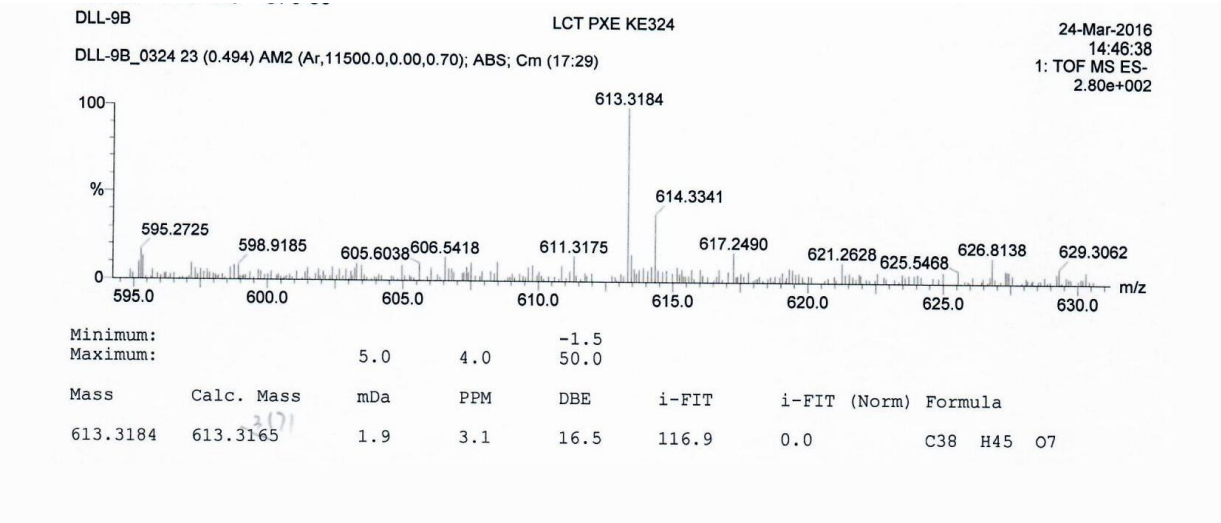
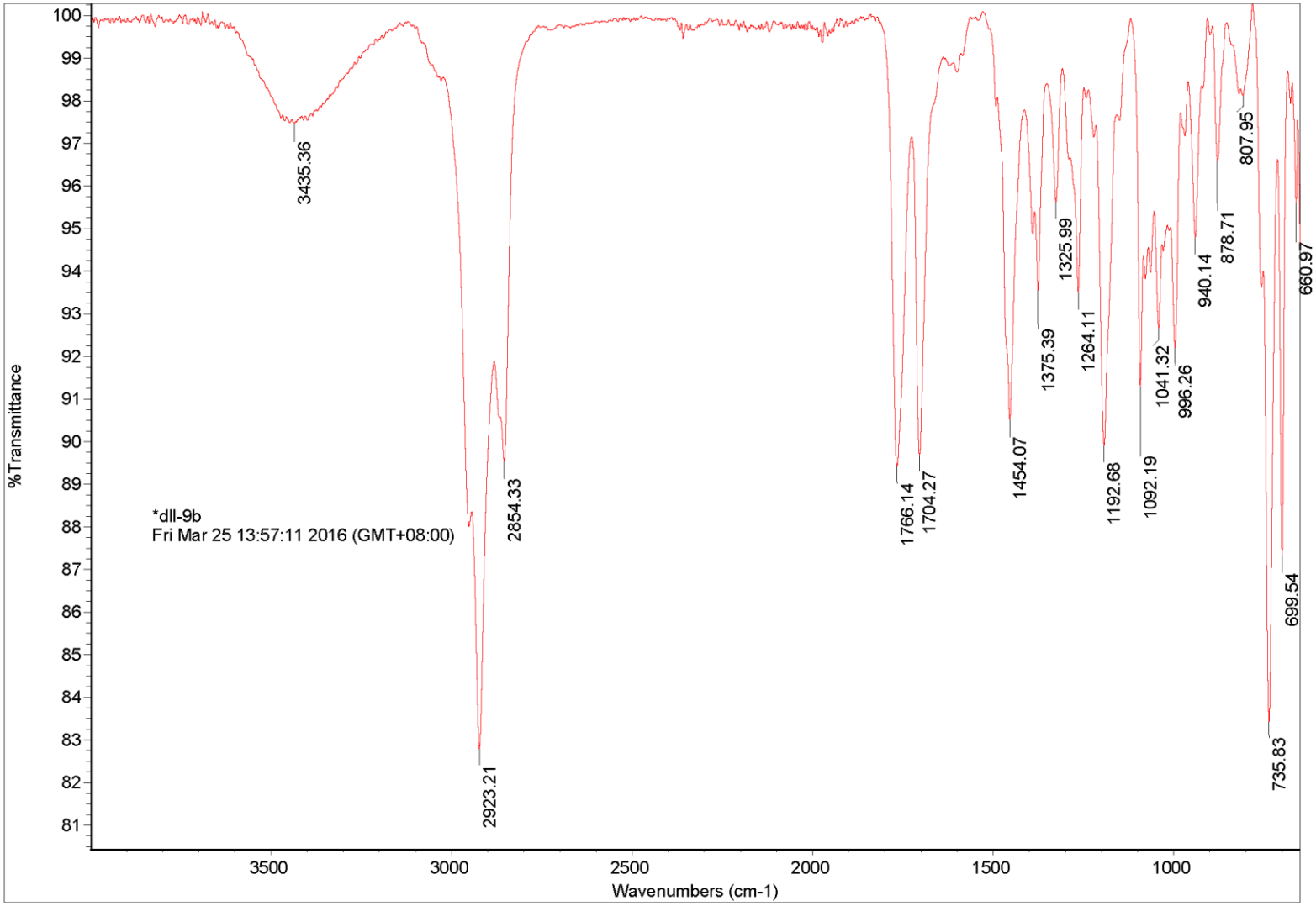


Figure S123. IR spectrum of **12**



6.13 NMR, MS, and IR spectra of compound 13

Figure S124. ^{1}H NMR spectrum (500 MHz) of **13** in $CDCl_3$

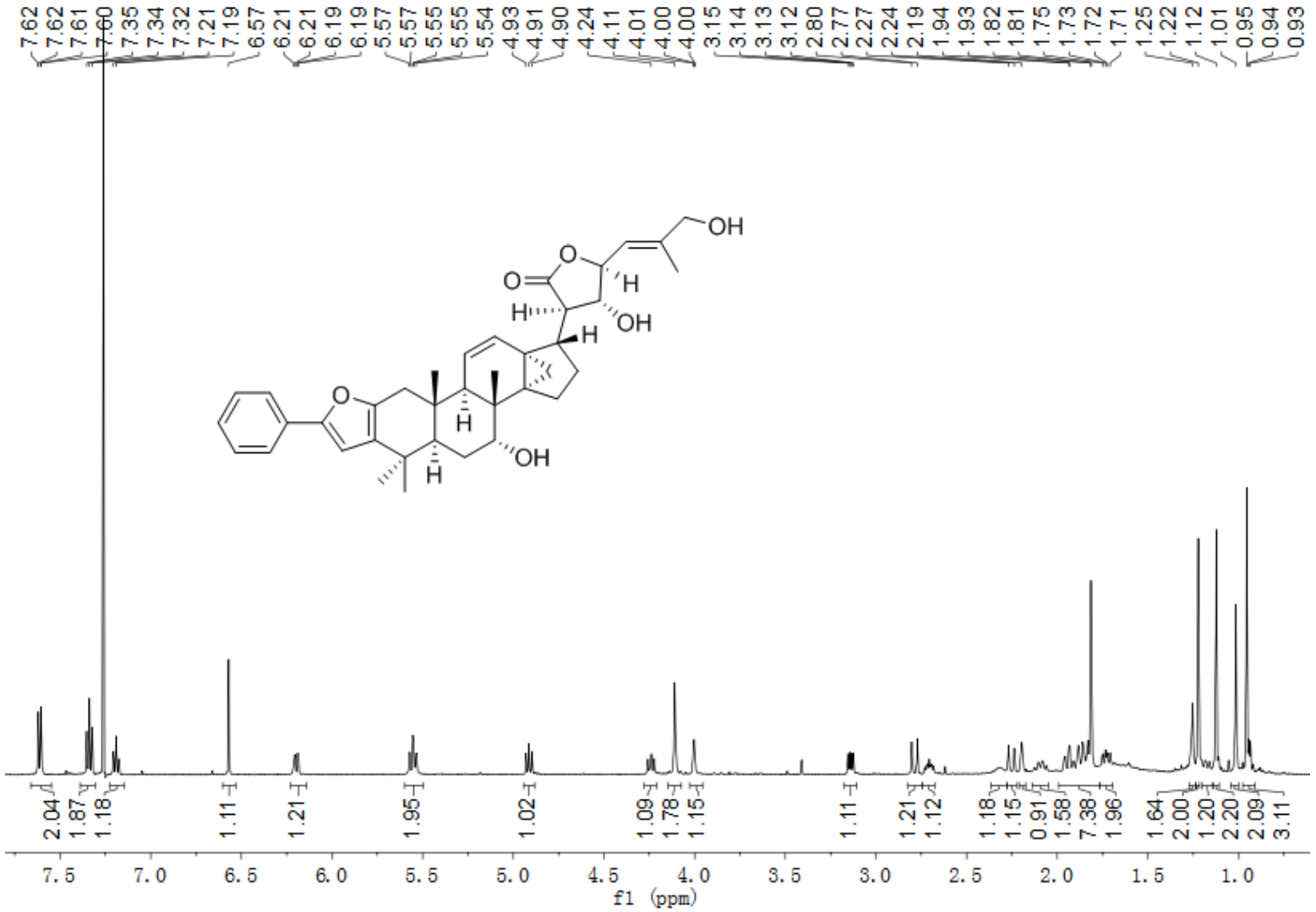


Figure S125. ^{13}C NMR spectrum (125 MHz) of **13** in $CDCl_3$

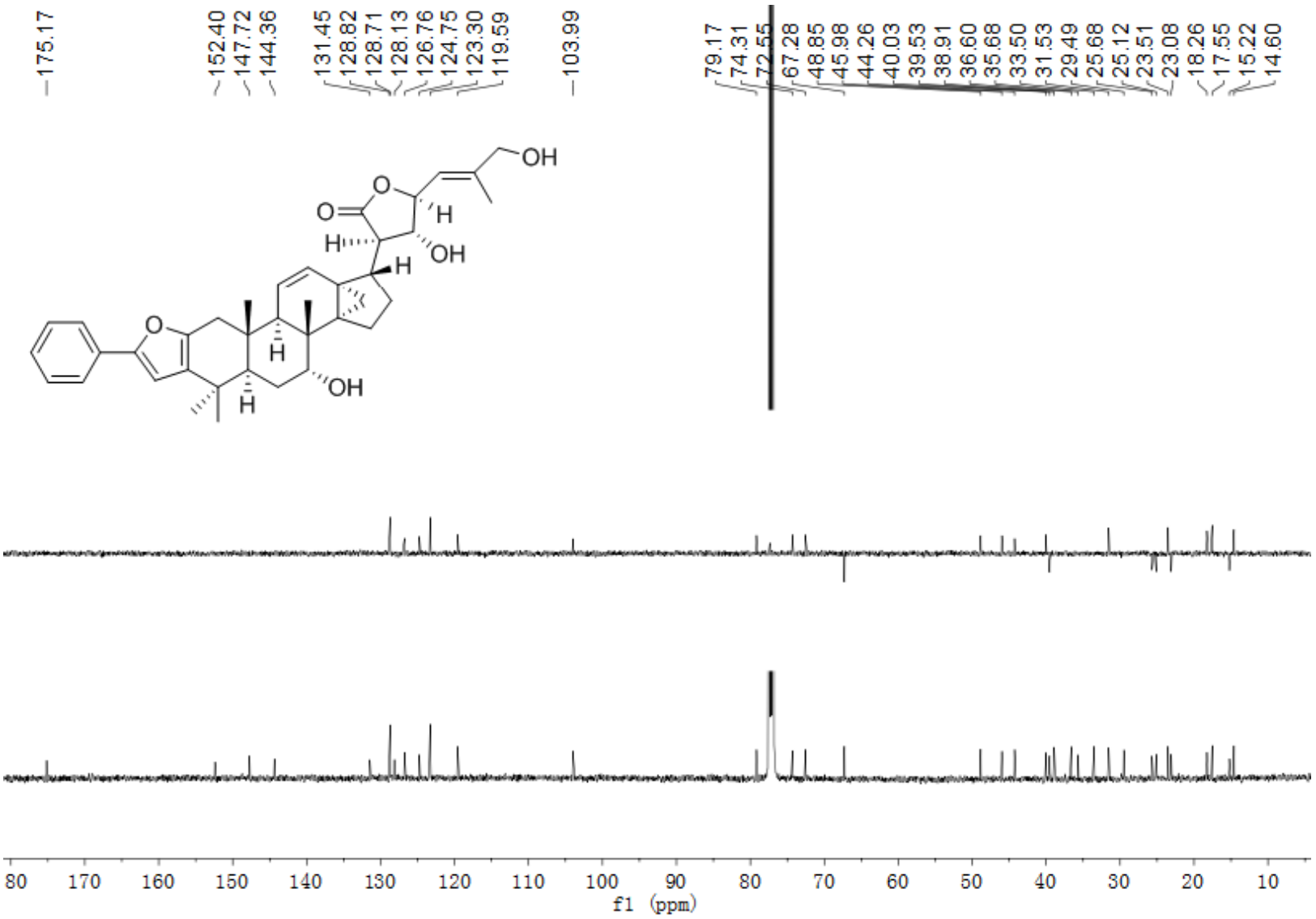


Figure S126. ^{1}H–^{1}H COSY spectrum of **13** in $CDCl_3$

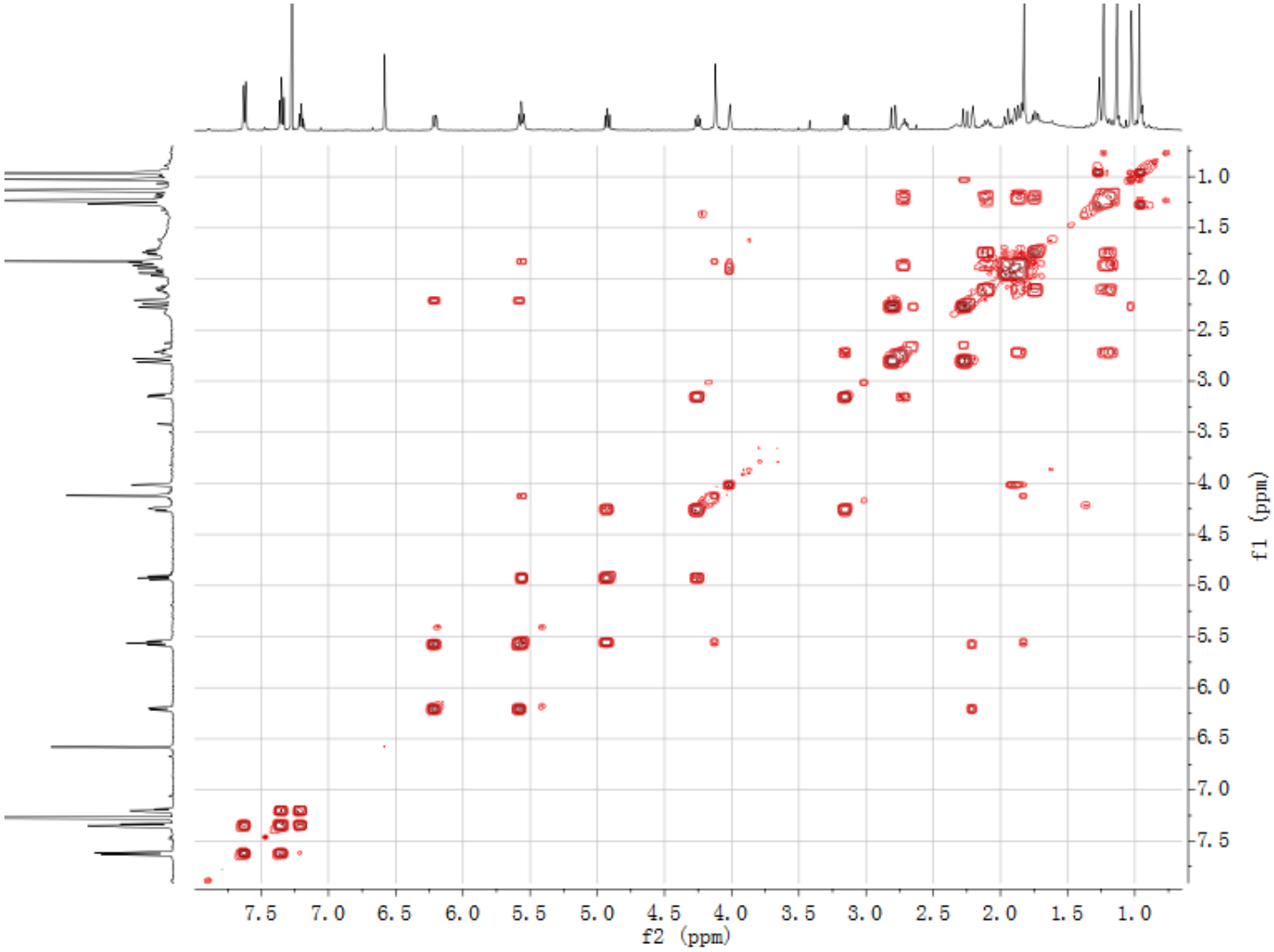


Figure S127. HSQC spectrum of **13** in $CDCl_3$

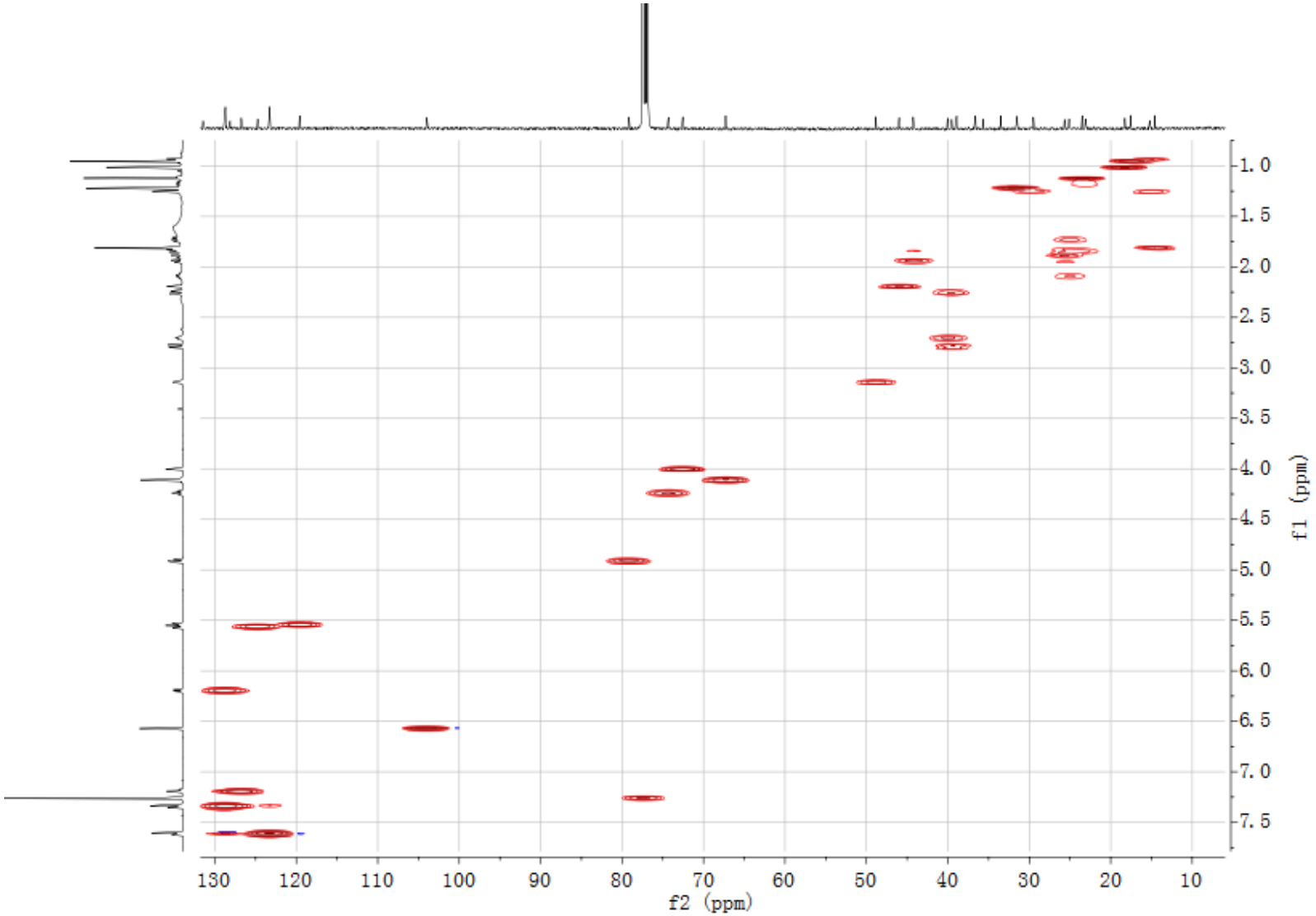


Figure S128. HMBC spectrum of **13** in $CDCl_3$

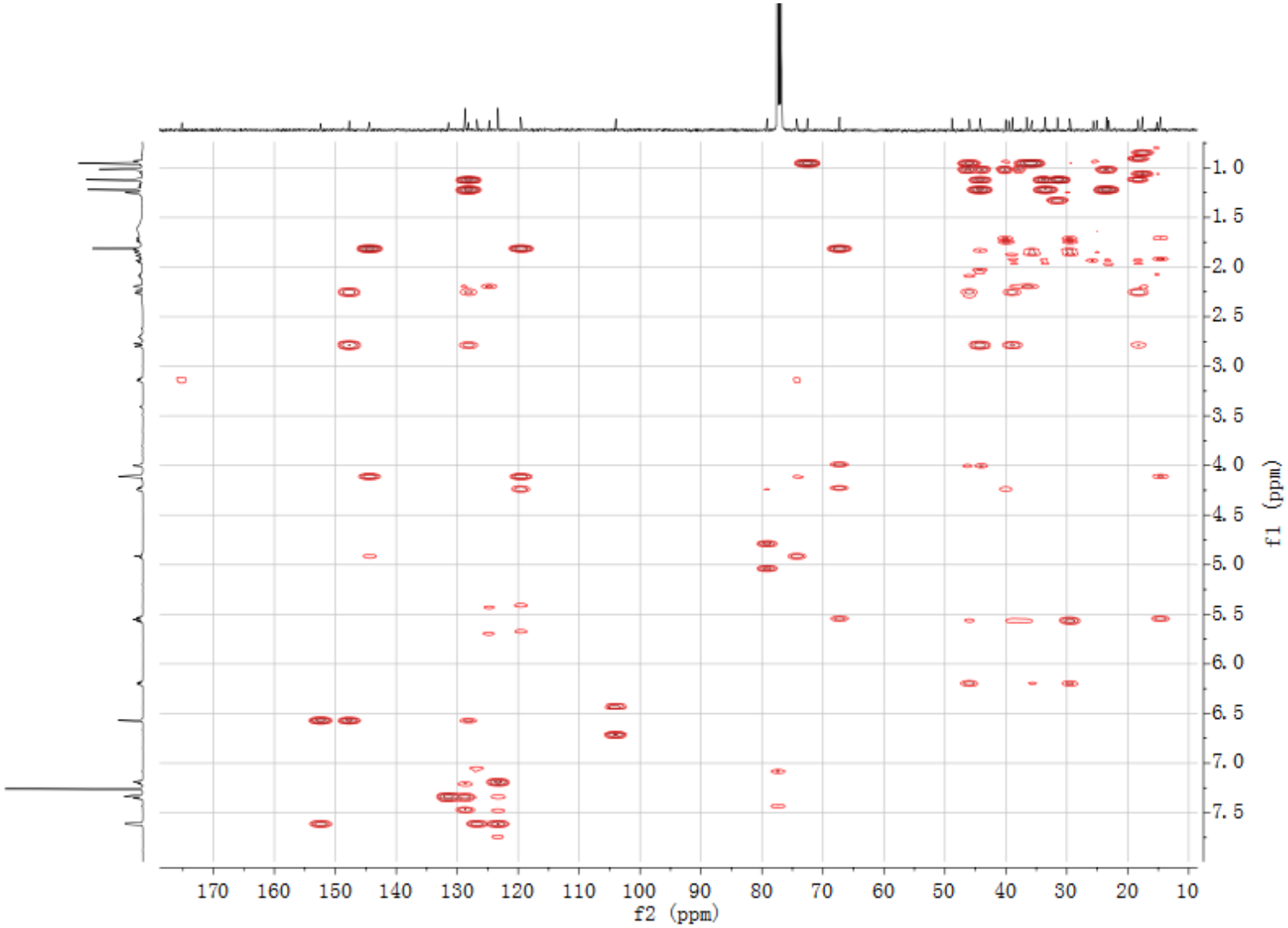


Figure S129. NOESY spectrum of **13** in $CDCl_3$

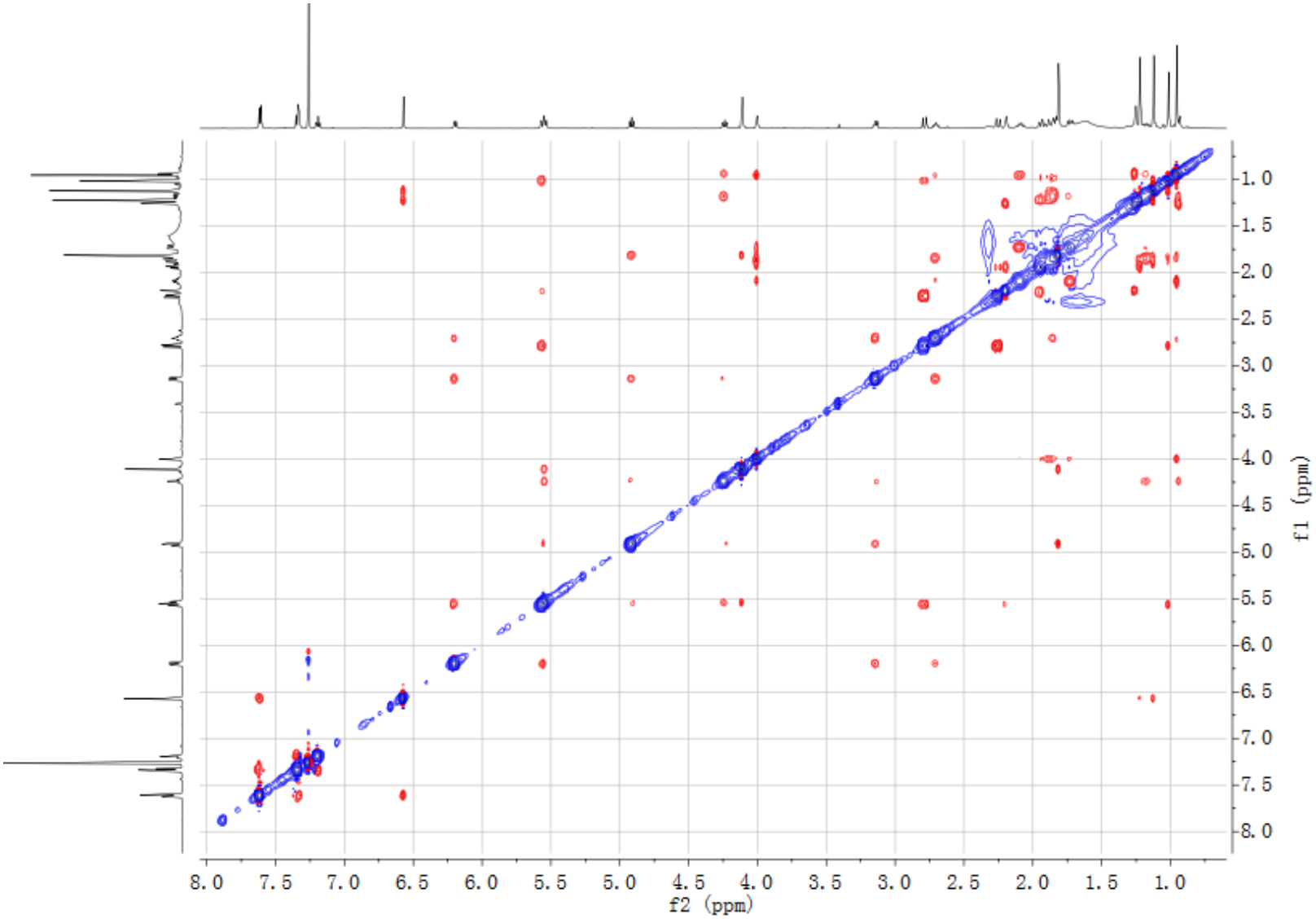


Figure S130. (±)-ESIMS spectra of **13**

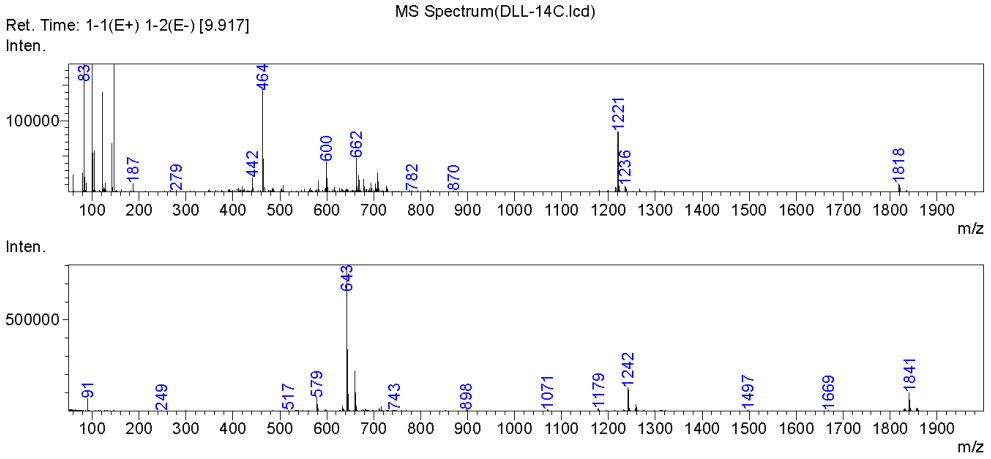
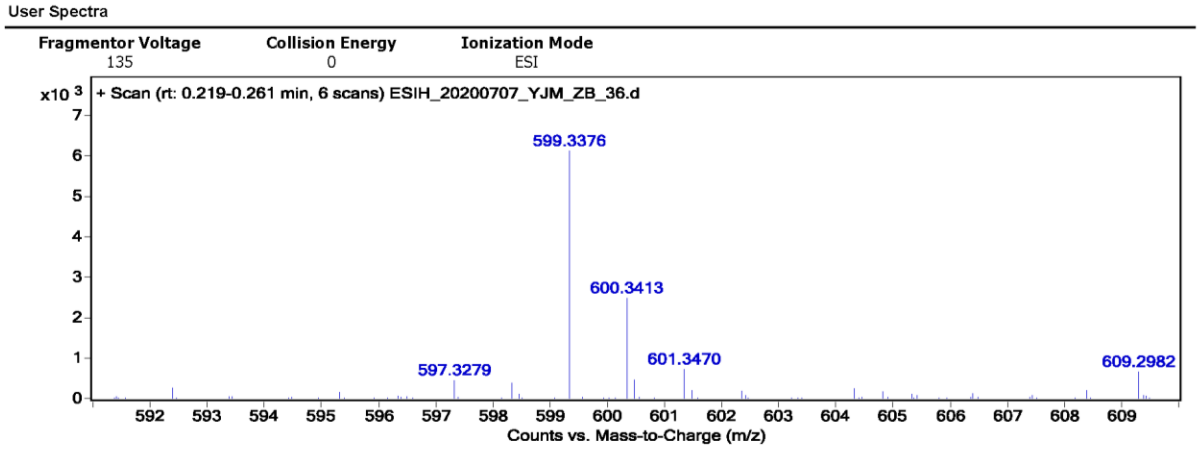


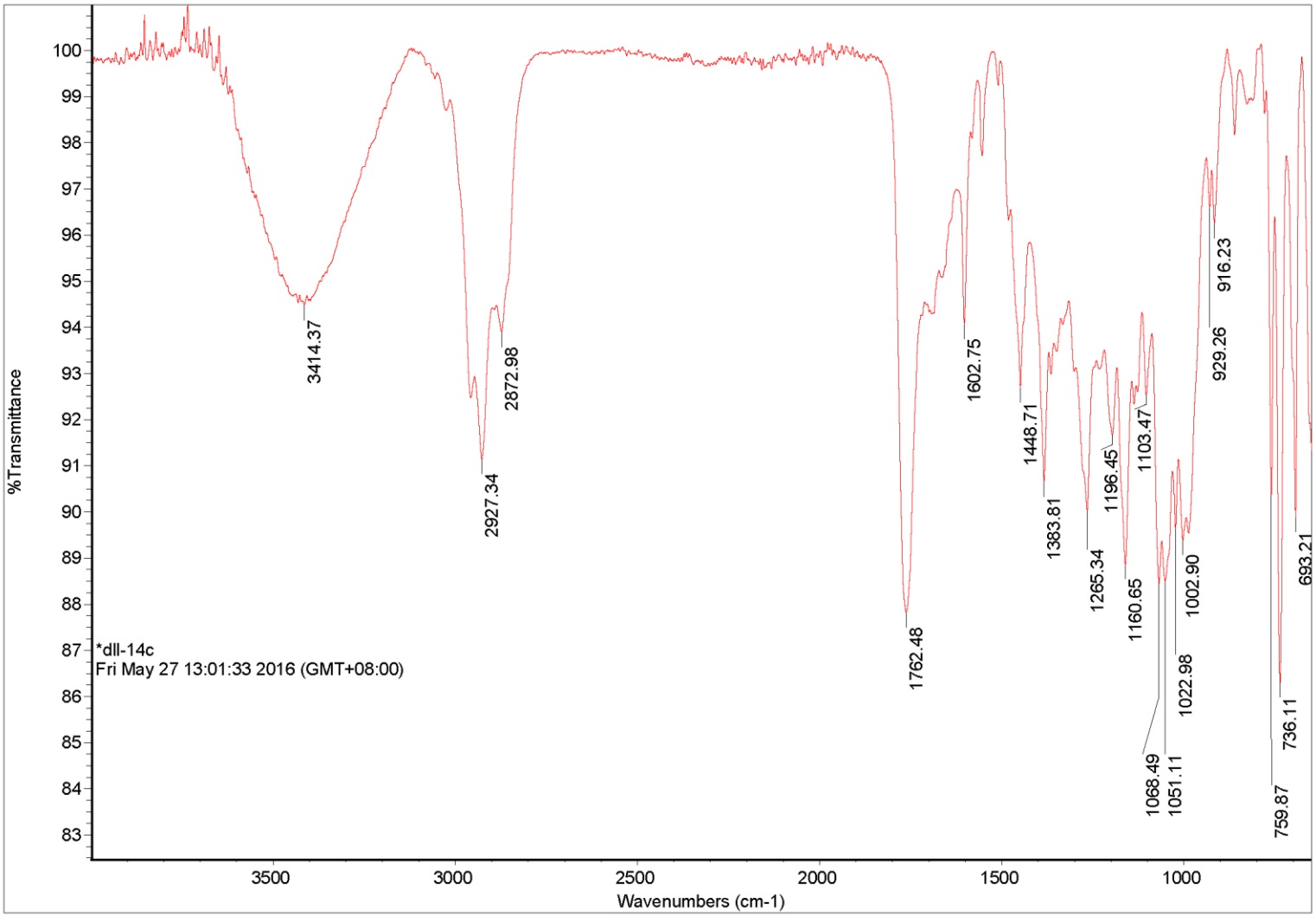
Figure S131. (–)-HRESIMS spectrum of **13**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
599.3376	599.3367	-0.91	-1.52	C38 H47 O6	(M+H)+

Figure S132. IR spectrum of **13**



6.14 NMR, MS, and IR spectra of compound 14

Figure S133. ^{1}H NMR spectrum (500 MHz) of **14** in $CDCl_3$

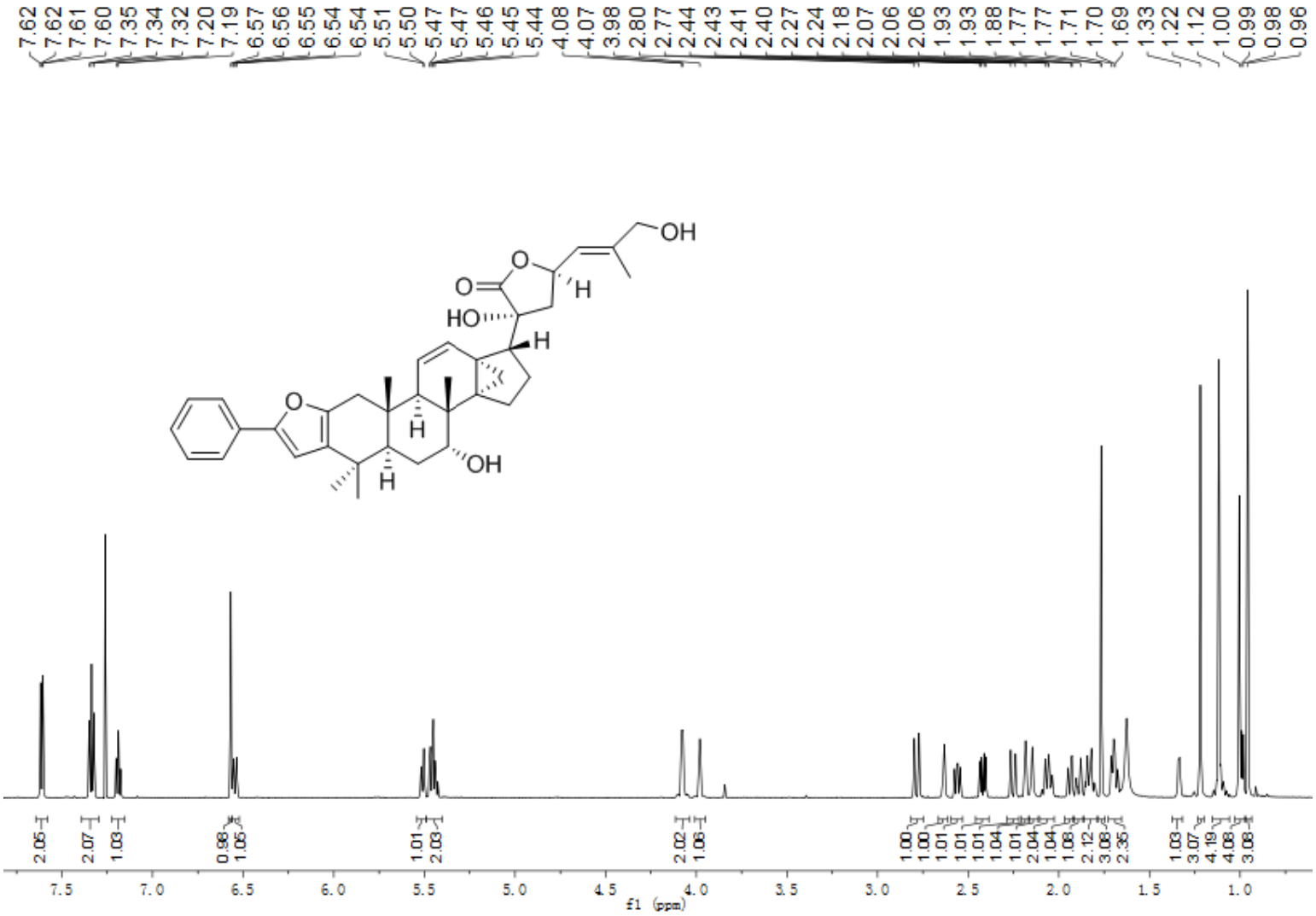


Figure S134. ^{13}C NMR spectrum (125 MHz) of **14** in $CDCl_3$

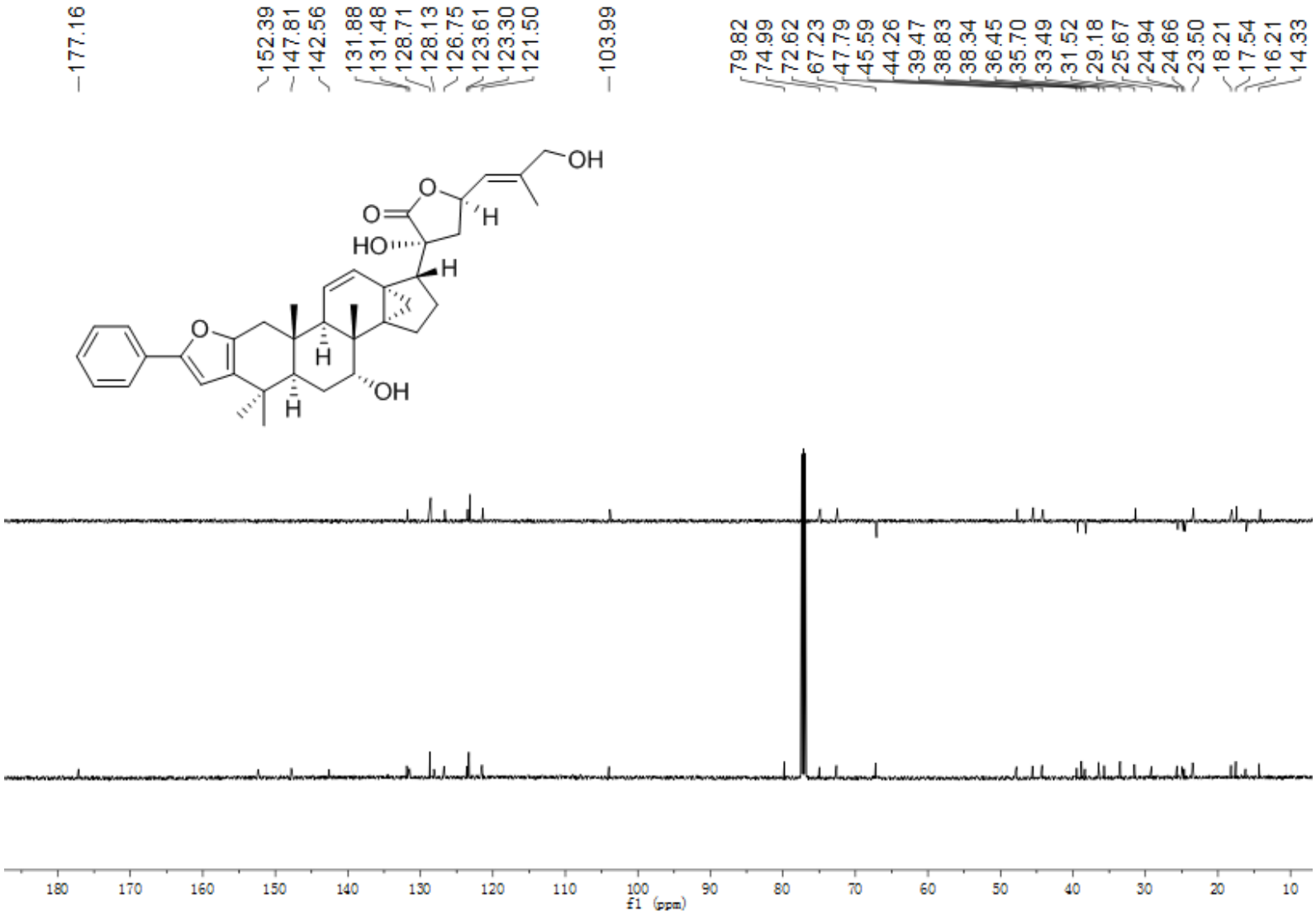


Figure S135. $^{1}H–^{1}H$ COSY spectrum of **14** in $CDCl_3$

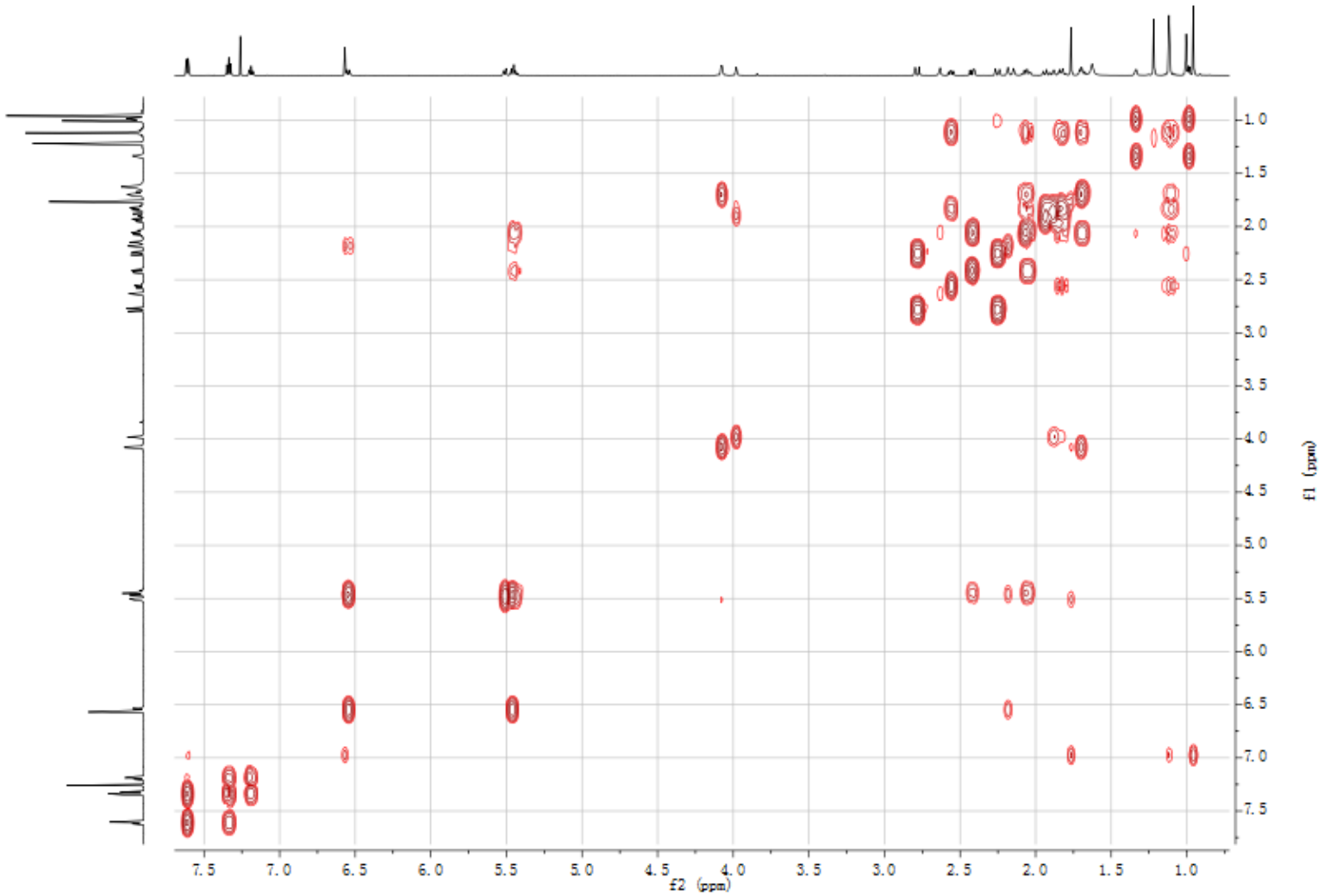


Figure S136. HSQC spectrum of **14** in $CDCl_3$

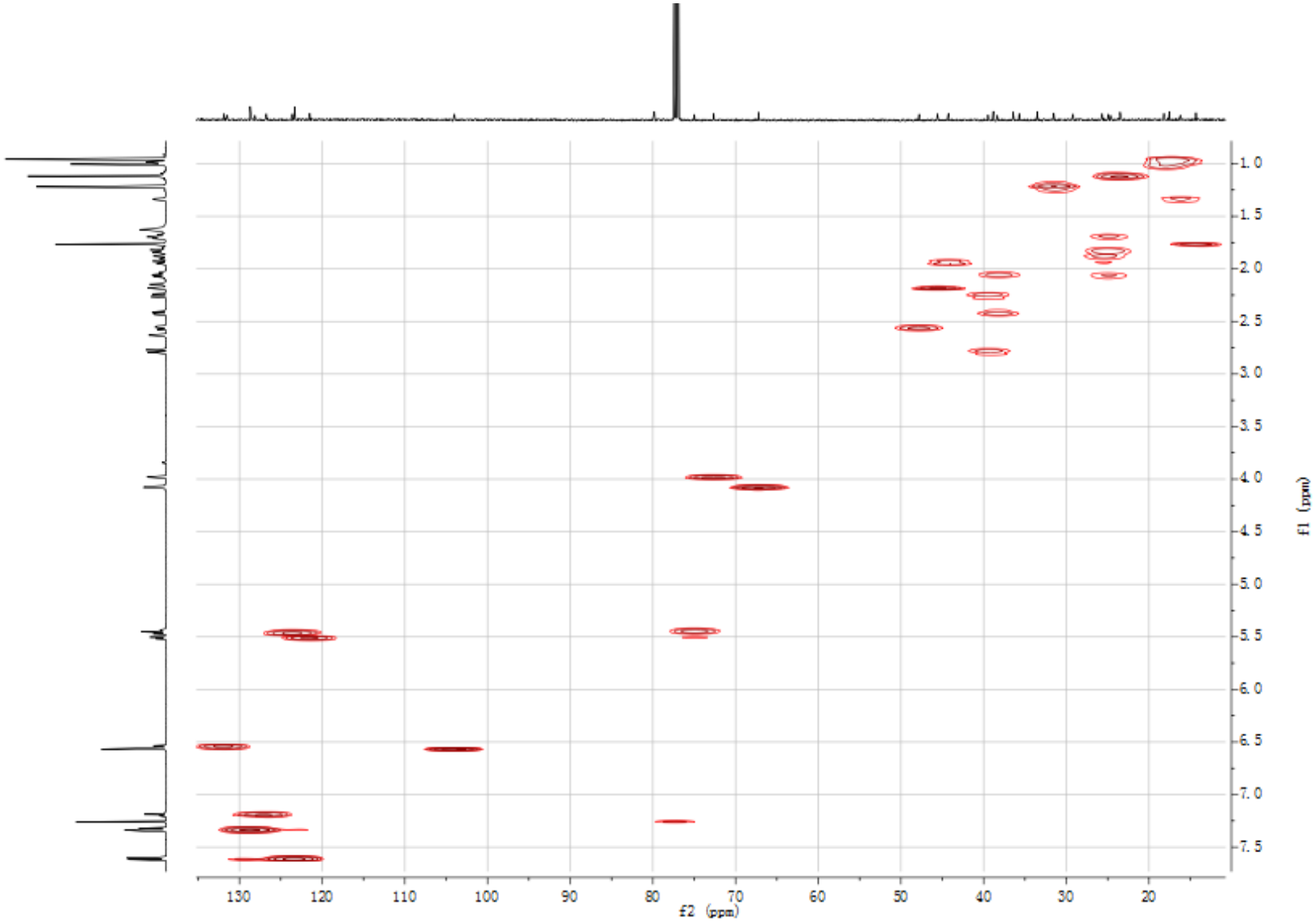


Figure 137. HMBC spectrum of **14** in $CDCl_3$

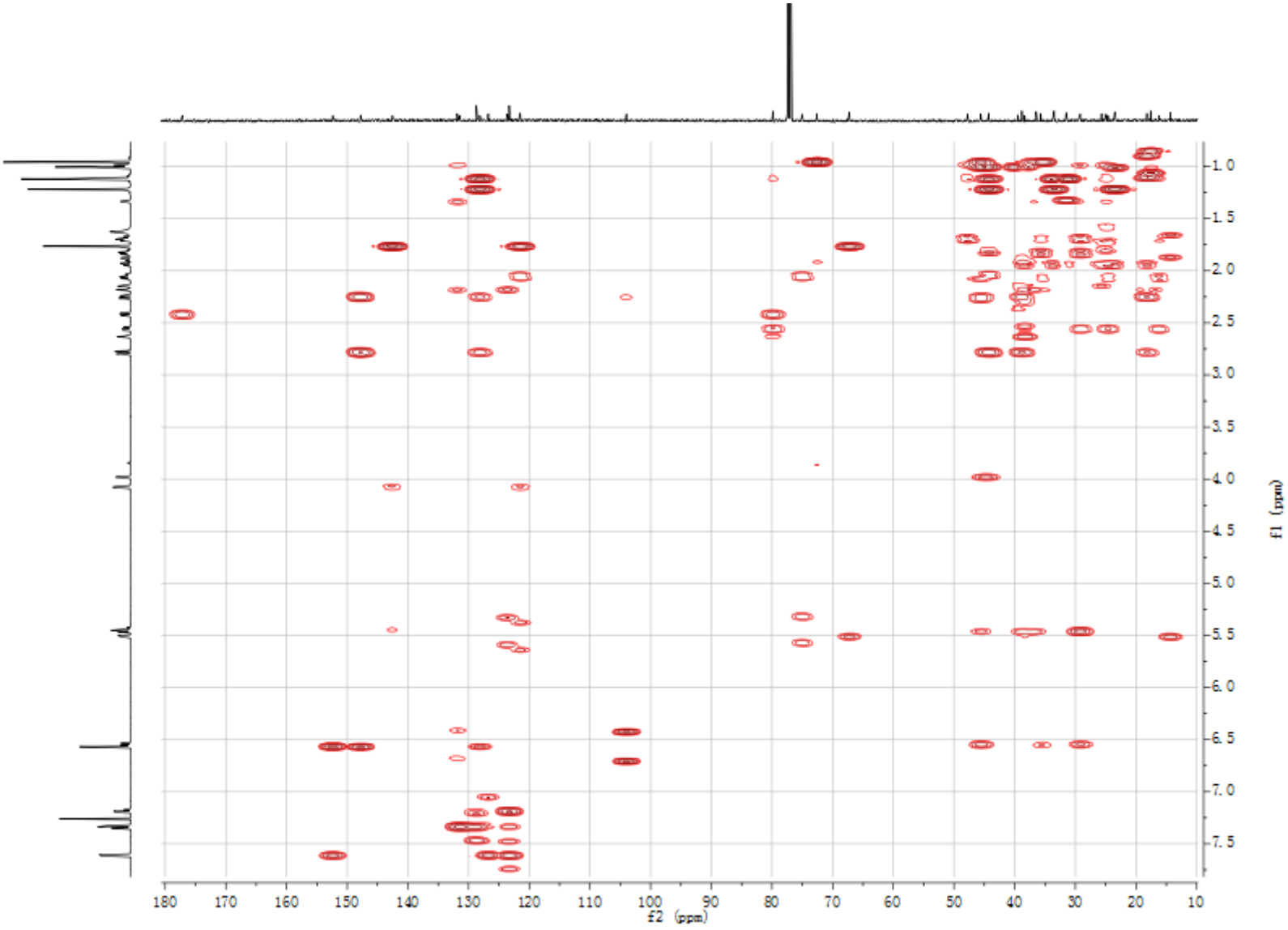


Figure S138. NOESY spectrum of **14** in $CDCl_3$

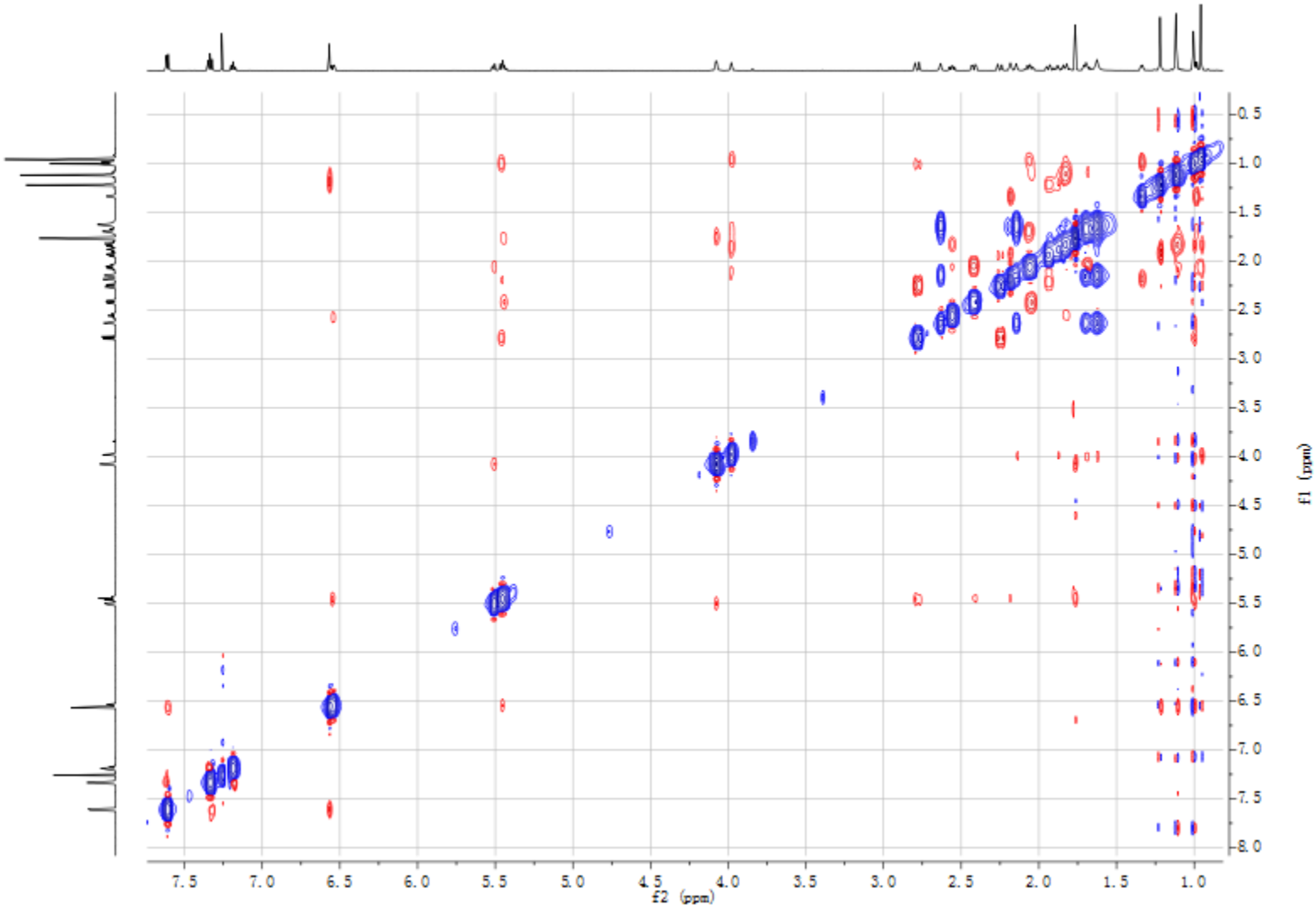


Figure S139. (±)-ESIMS spectra of **14**

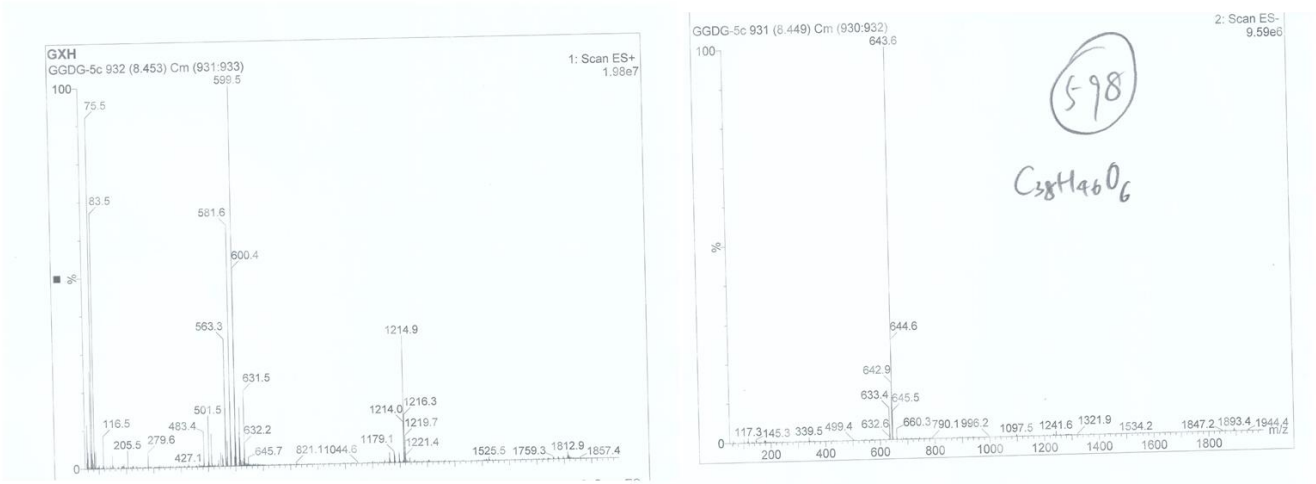
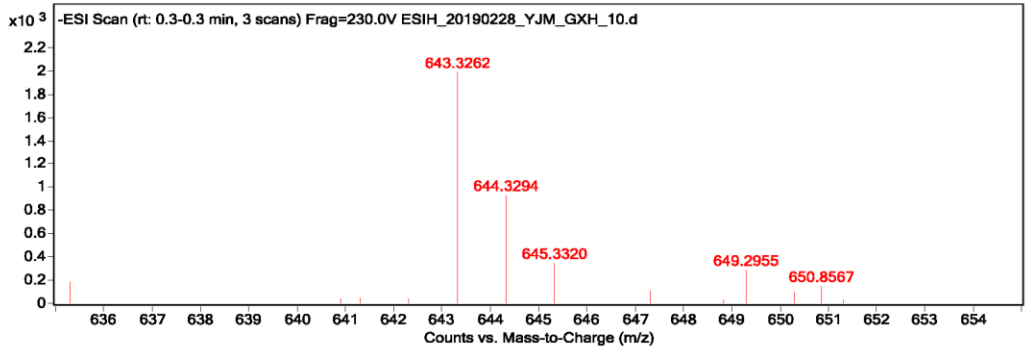


Figure S140. (–)-HRESIMS spectrum of **14**

User Spectra

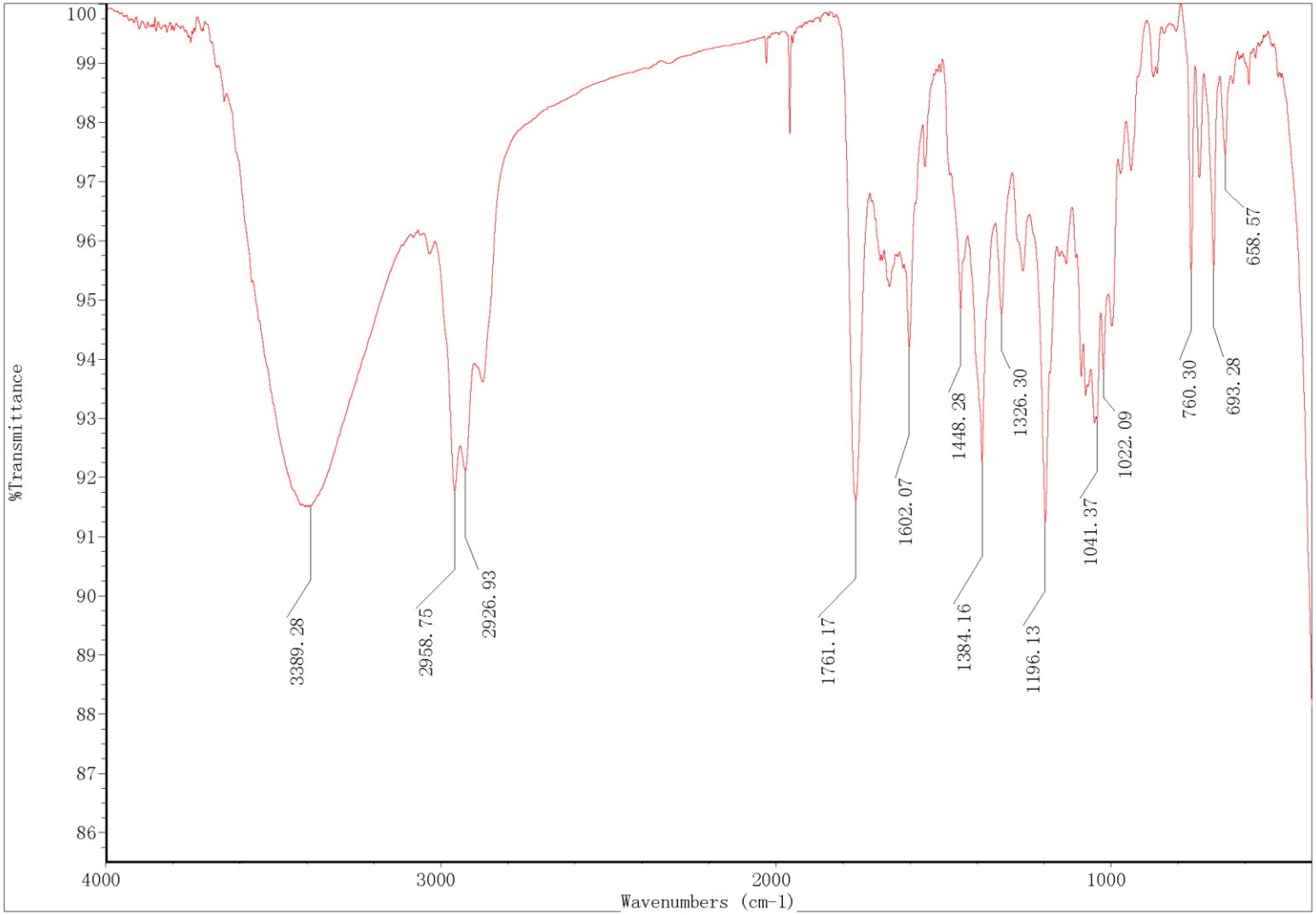
Fragmentor Voltage	Collision Energy	Ionization Mode
230	0	ESI



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
643.3262	643.3276	1.42	2.21	C39 H47 O8	(M+COOH)-

Figure S141. IR spectrum of **14**



6.15 NMR, MS, and IR spectra of compound 15

Figure S142. ^{1}H NMR spectrum (500 MHz) of **15** in $CDCl_3$

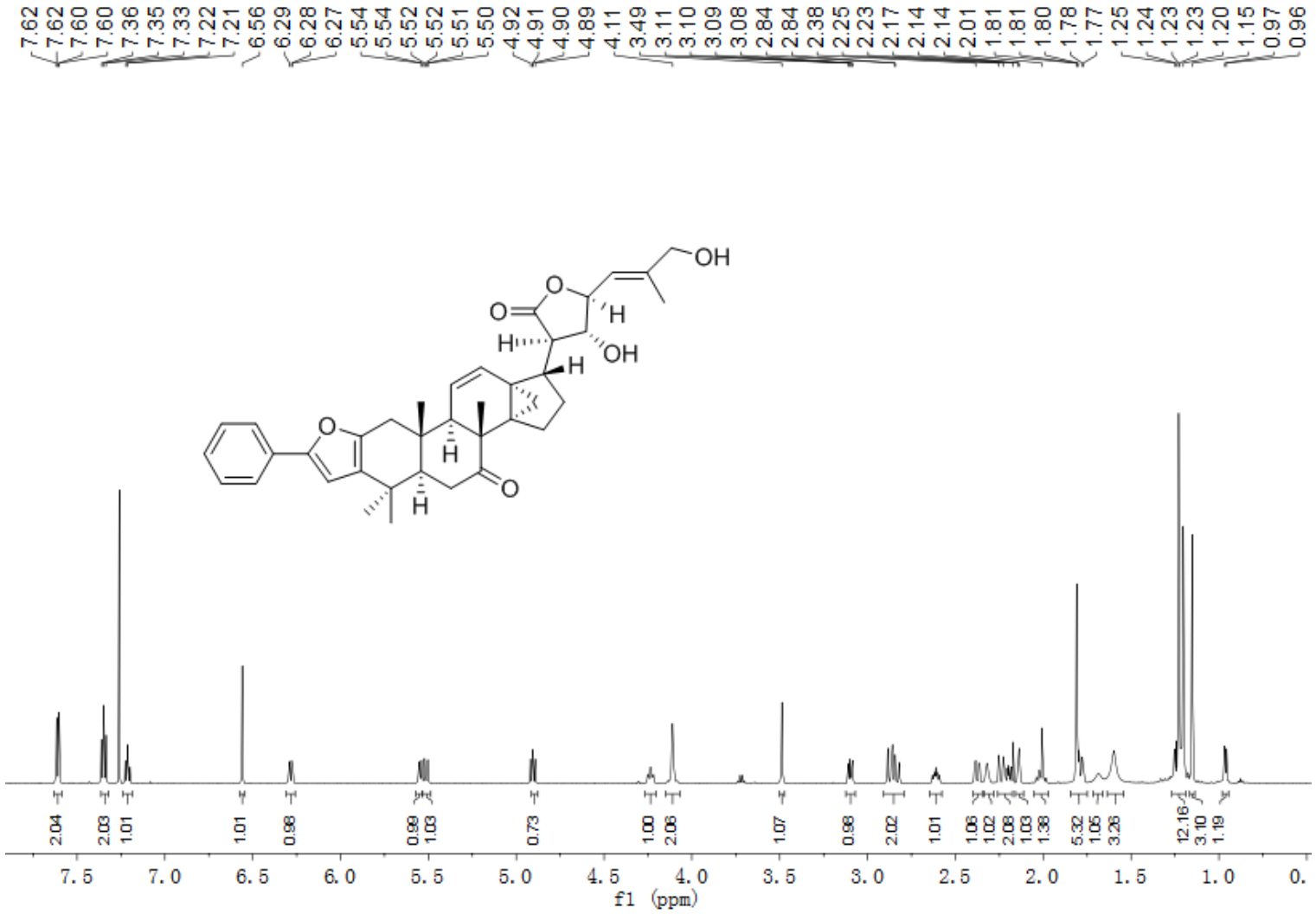


Figure S143. ^{13}C NMR spectrum (125 MHz) of **15** in $CDCl_3$

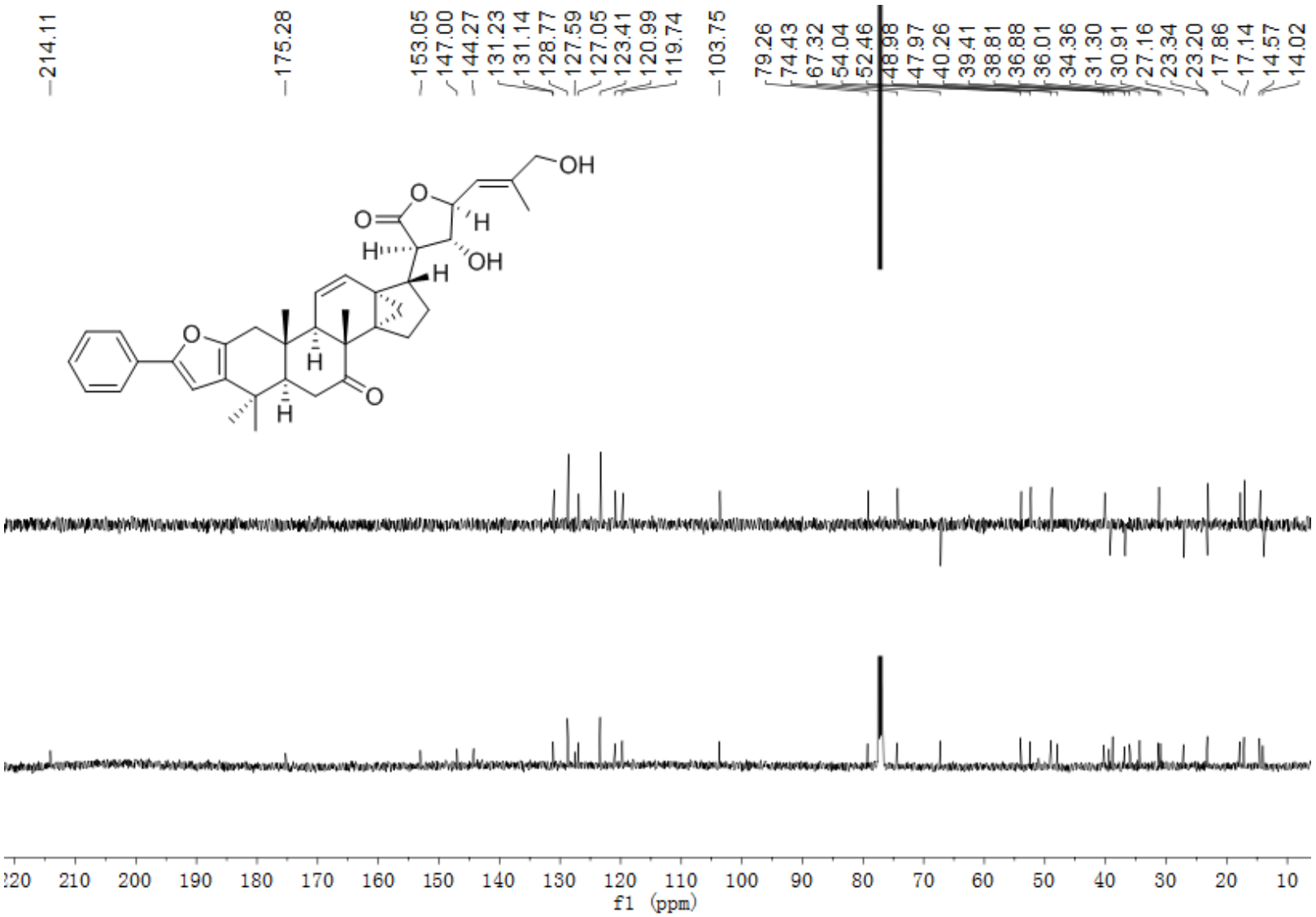


Figure S144. ^{1}H–^{1}H COSY spectrum of **15** in $CDCl_3$

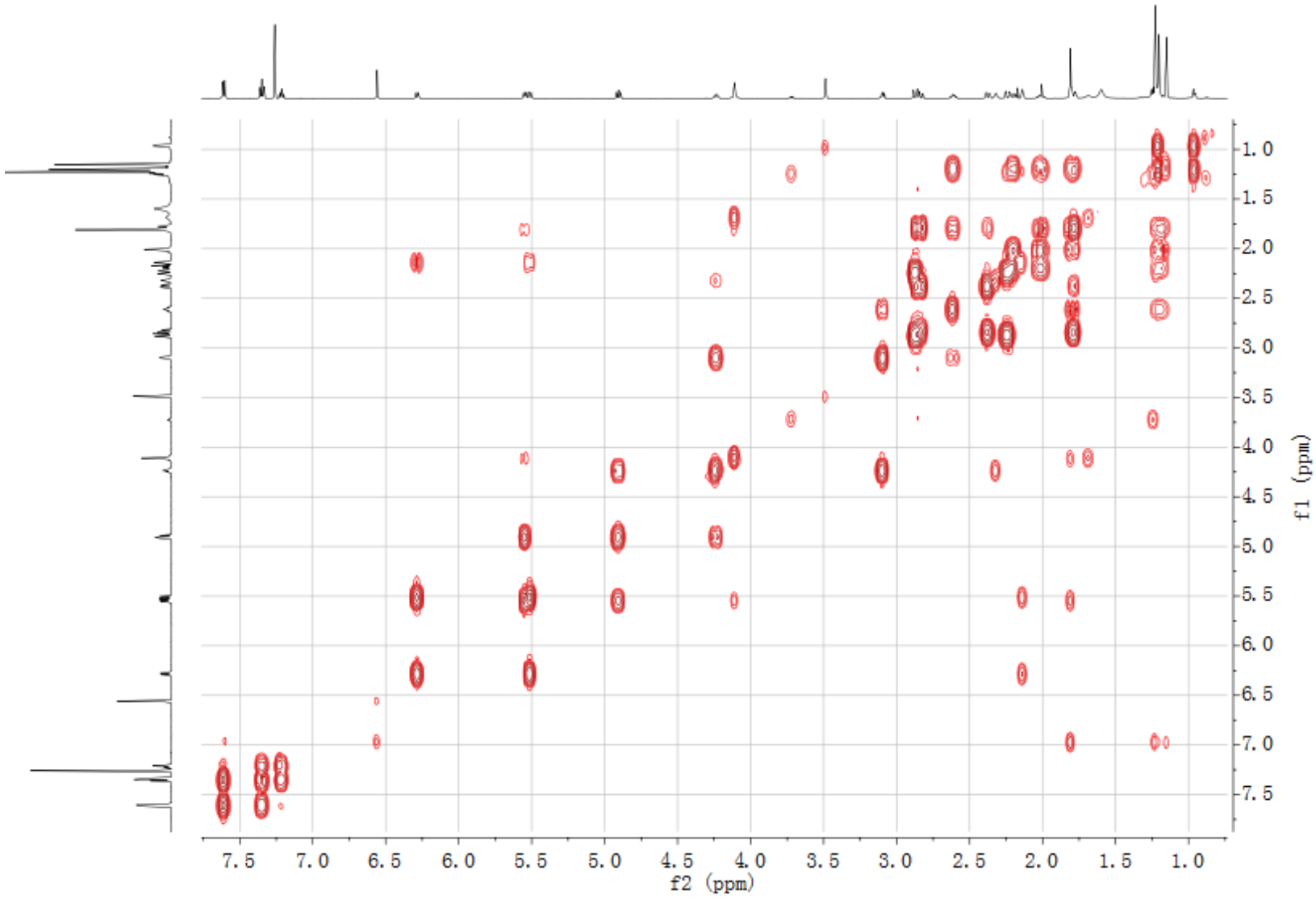


Figure S145. HSQC spectrum of **15** in $CDCl_3$

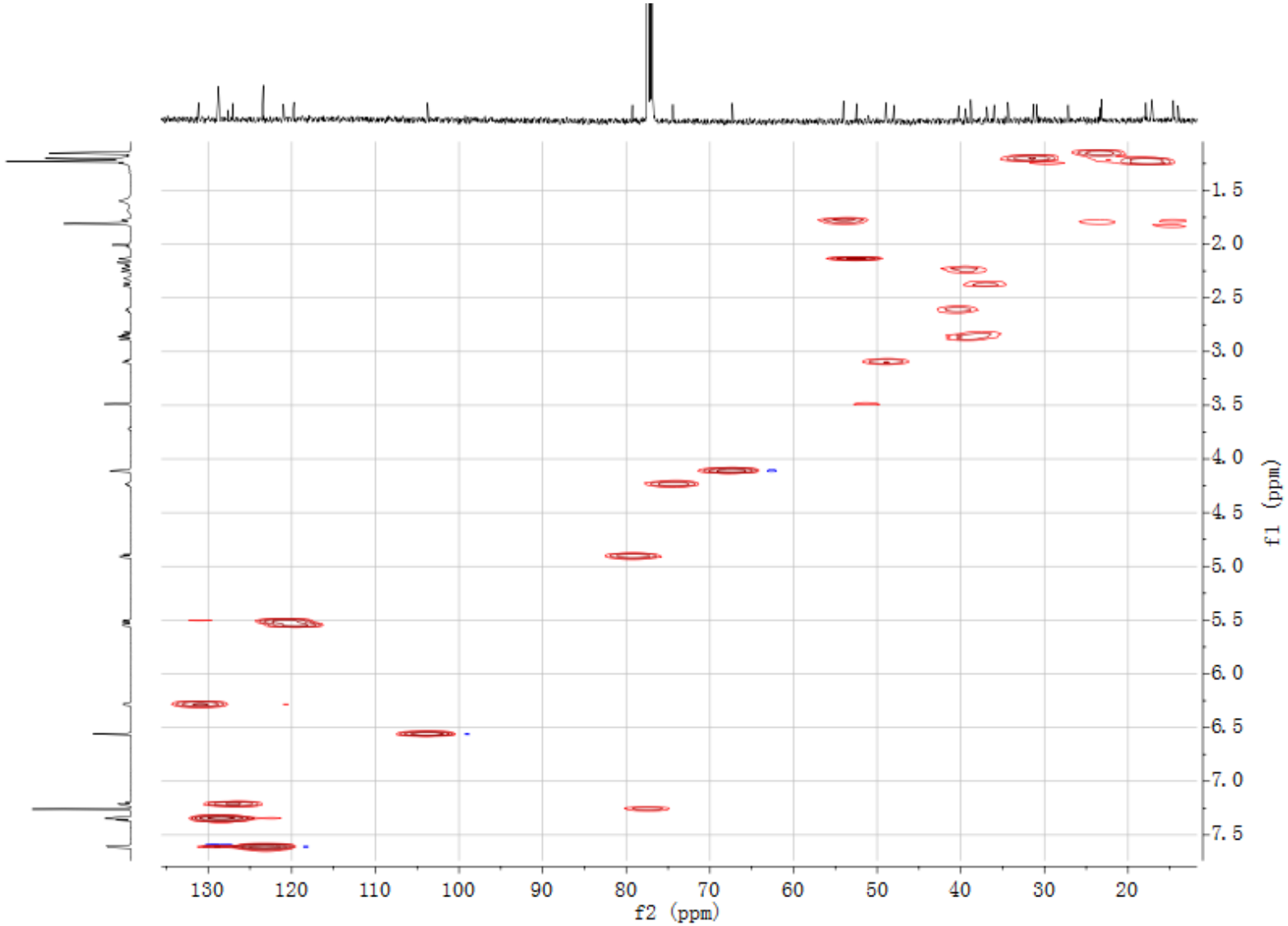


Figure S146. HMBC spectrum of **15** in $CDCl_3$

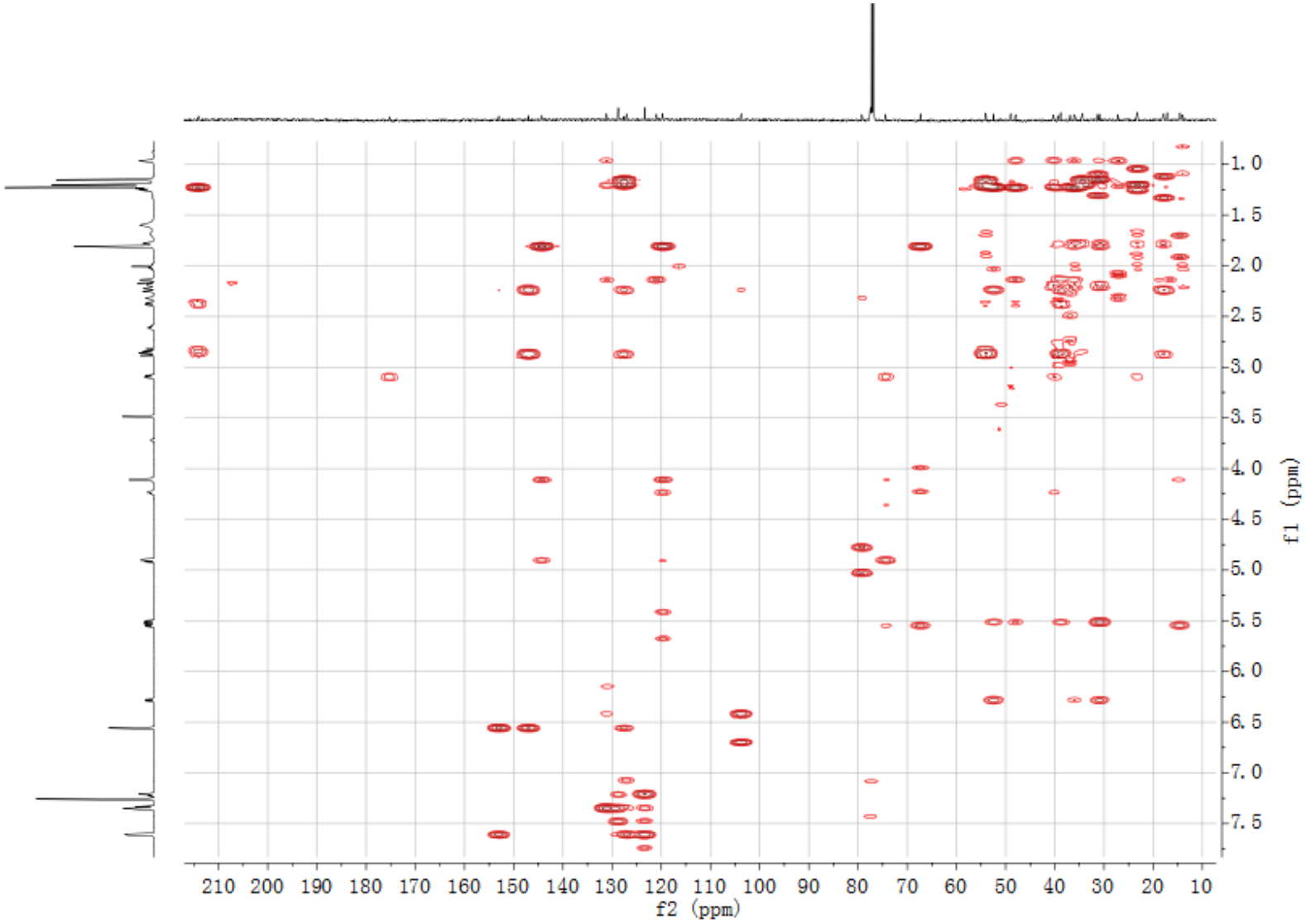


Figure S147. NOESY spectrum of **15** in $CDCl_3$

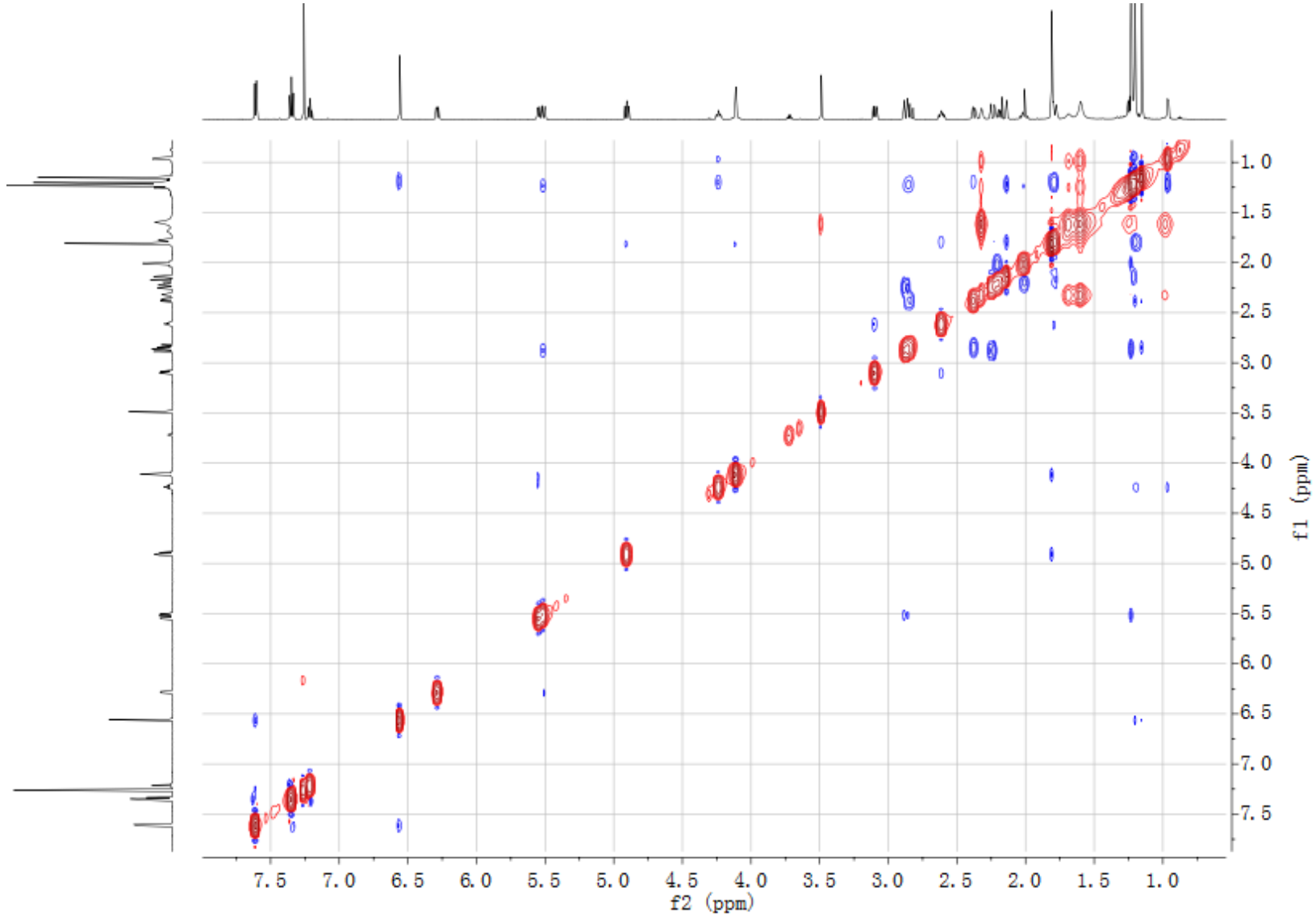


Figure S148. (±)-ESIMS spectra of **15**

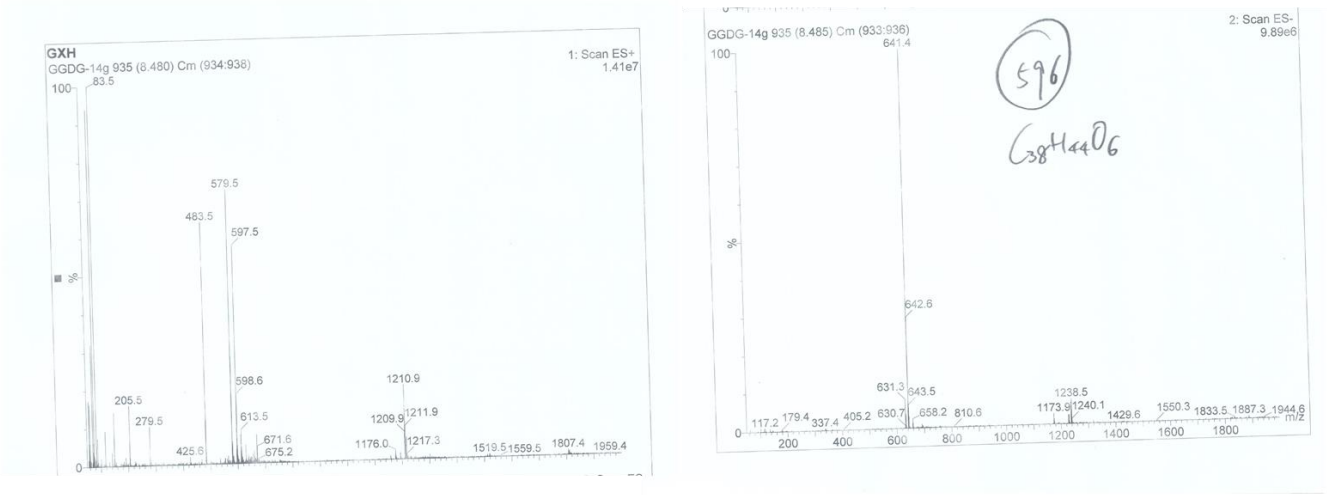
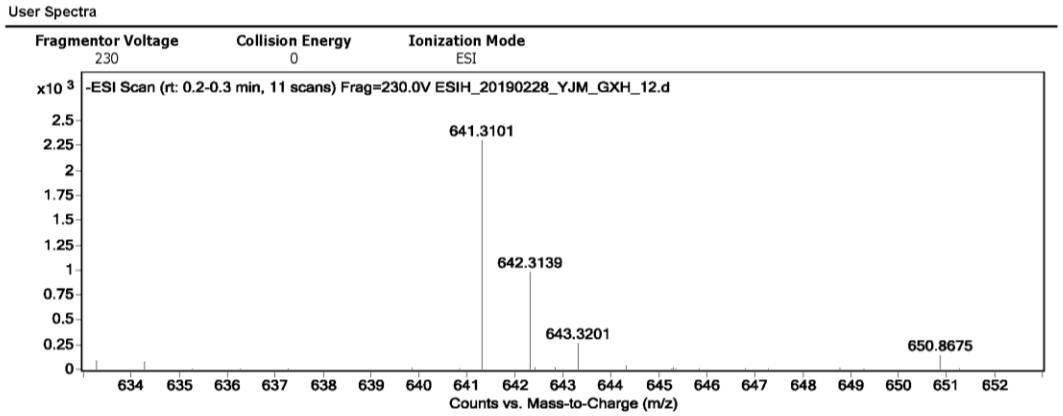


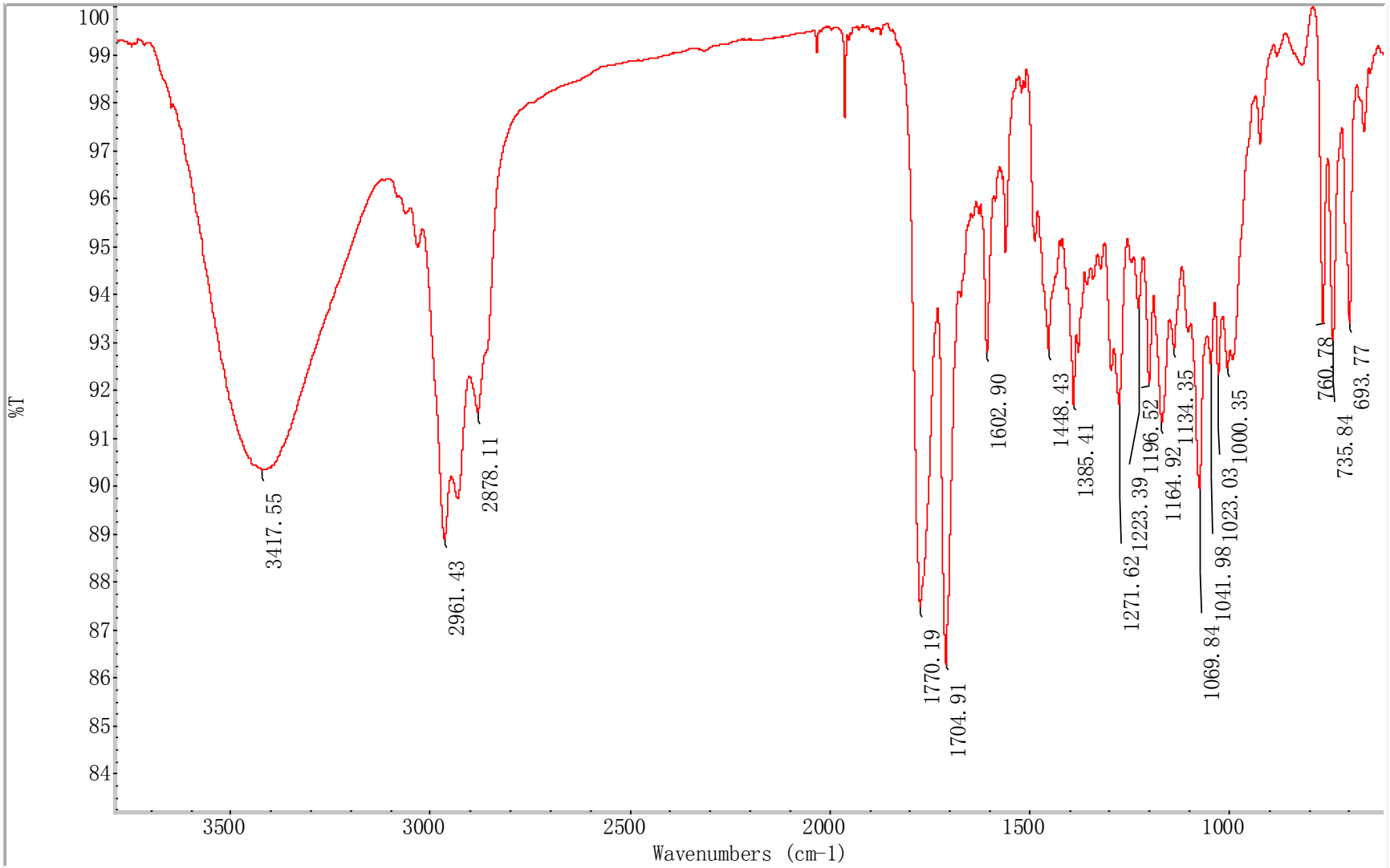
Figure S149. (–)-HRESIMS spectrum of **15**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
641.3101	641.312	1.91	2.98	C39 H45 O8	(M+COOH)-

Figure S150. IR spectrum of **15**



6.16 NMR, MS, and IR spectra of synthetic 16

Figure S151. ^{1}H NMR spectrum (500 MHz) of **16** in $CDCl_3$

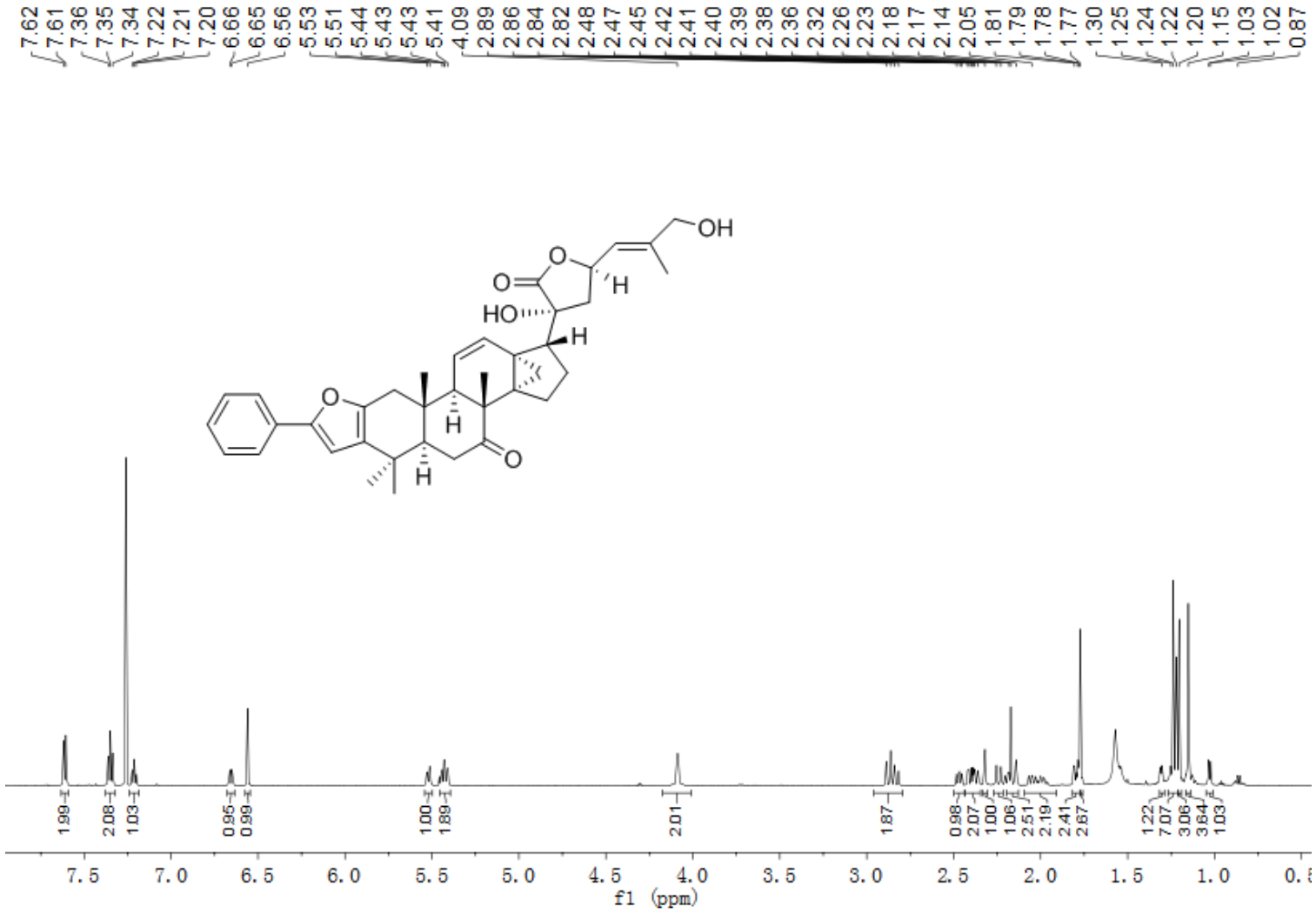


Figure S152. ^{13}C NMR spectrum (125 MHz) of **16** in $CDCl_3$

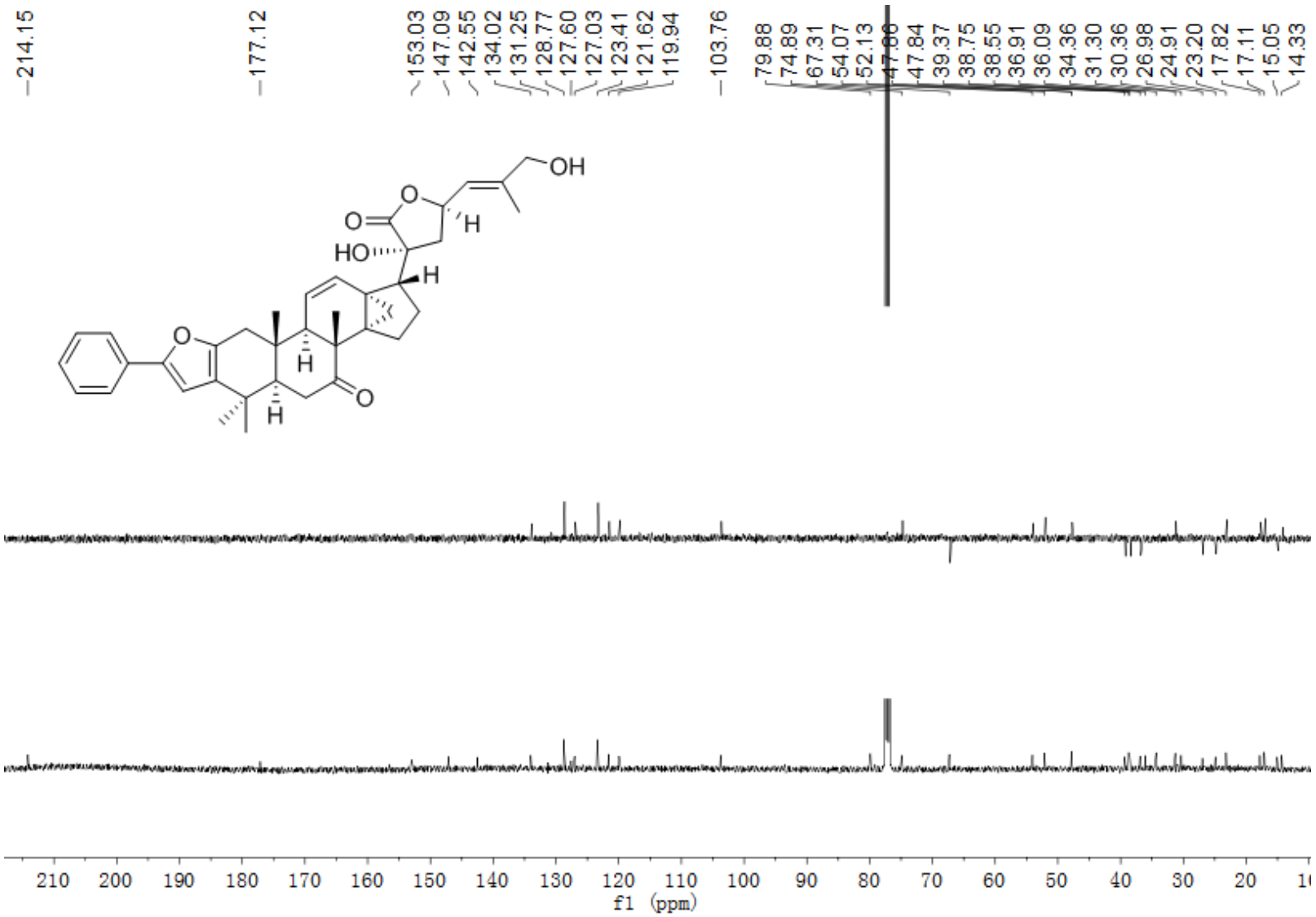


Figure S153. $^{1}H–^{1}H$ COSY spectrum of **16** in $CDCl_3$

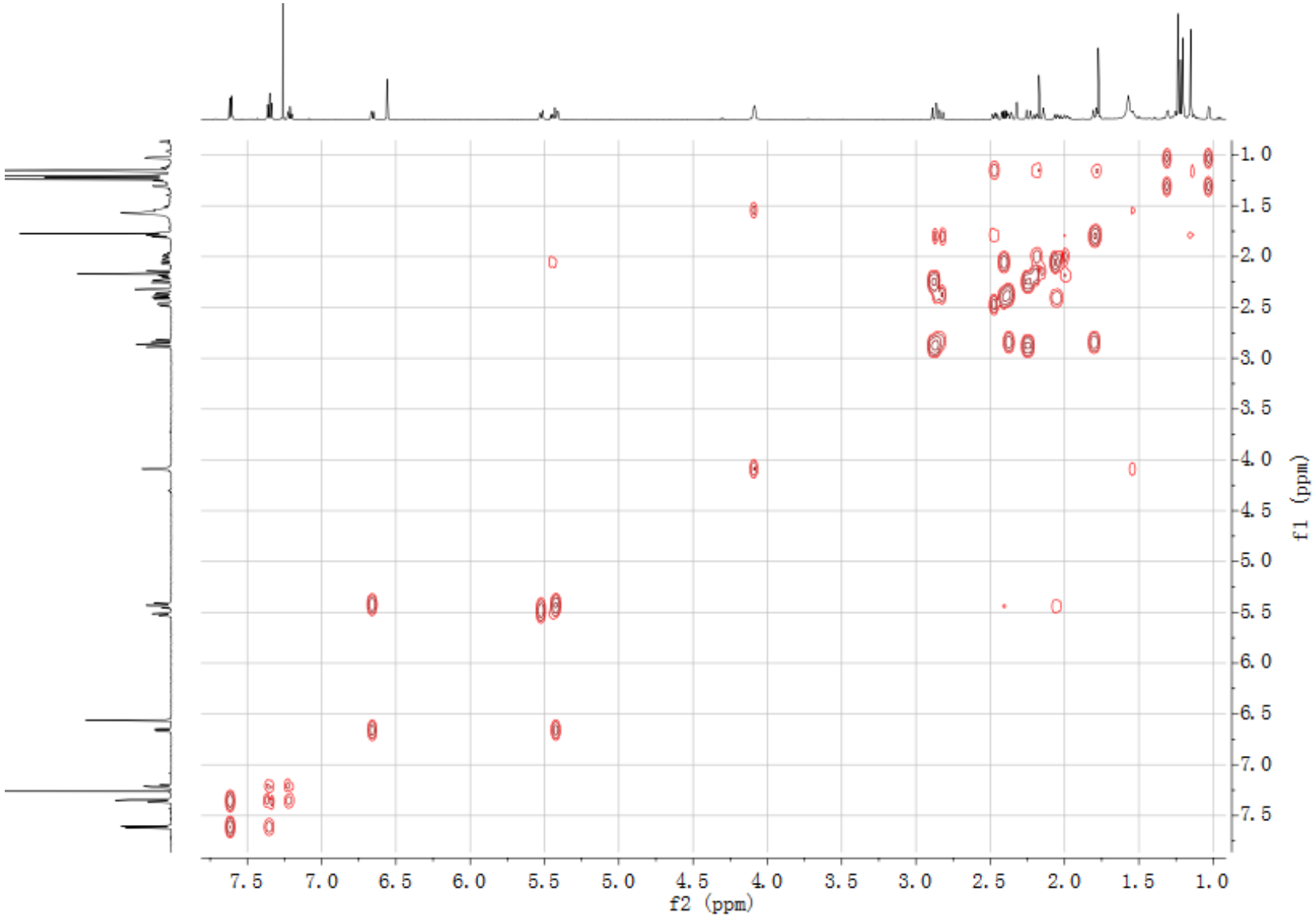


Figure S154. HSQC spectrum of **16** in $CDCl_3$

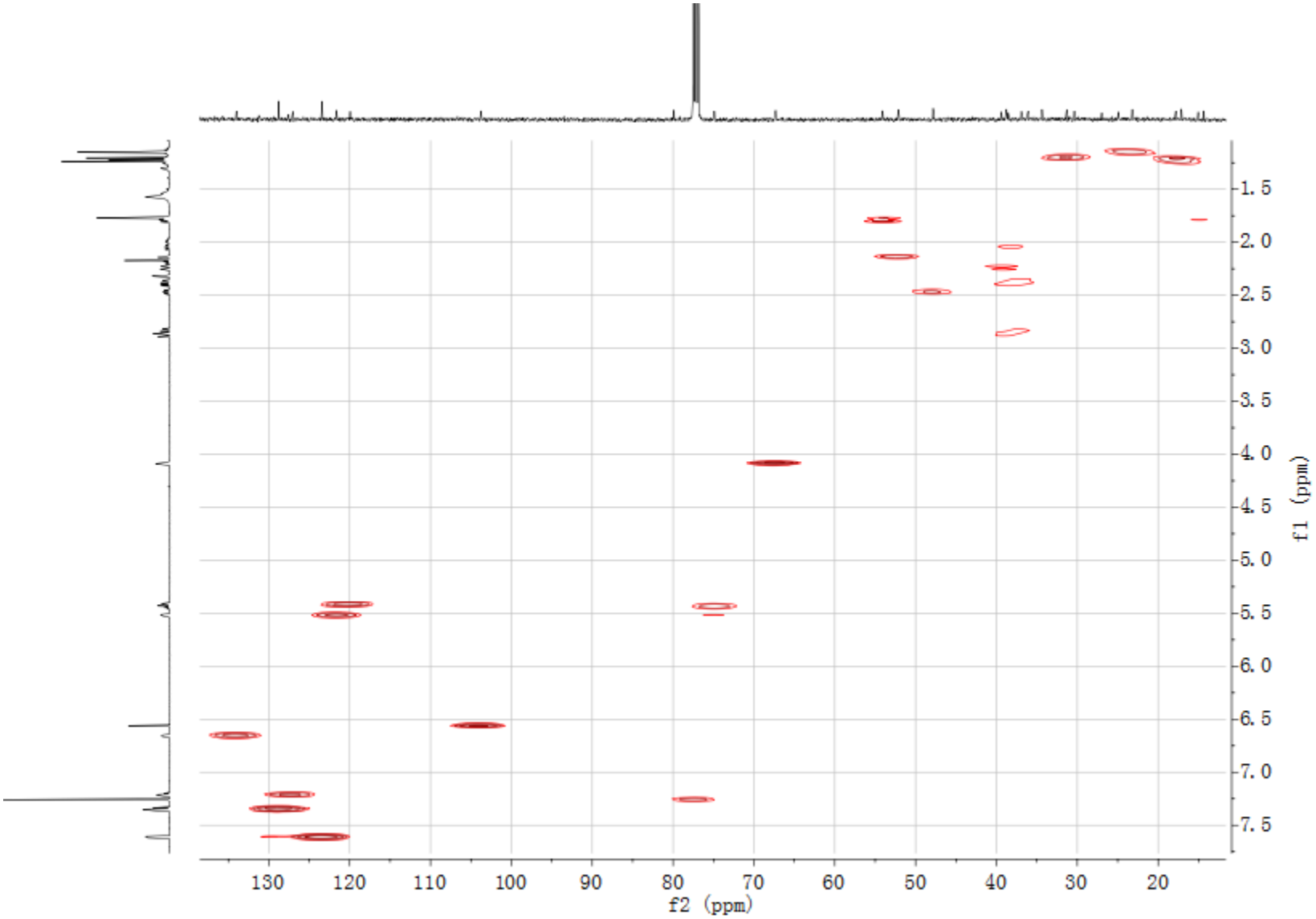


Figure S155. HMBC spectrum of **16** in $CDCl_3$

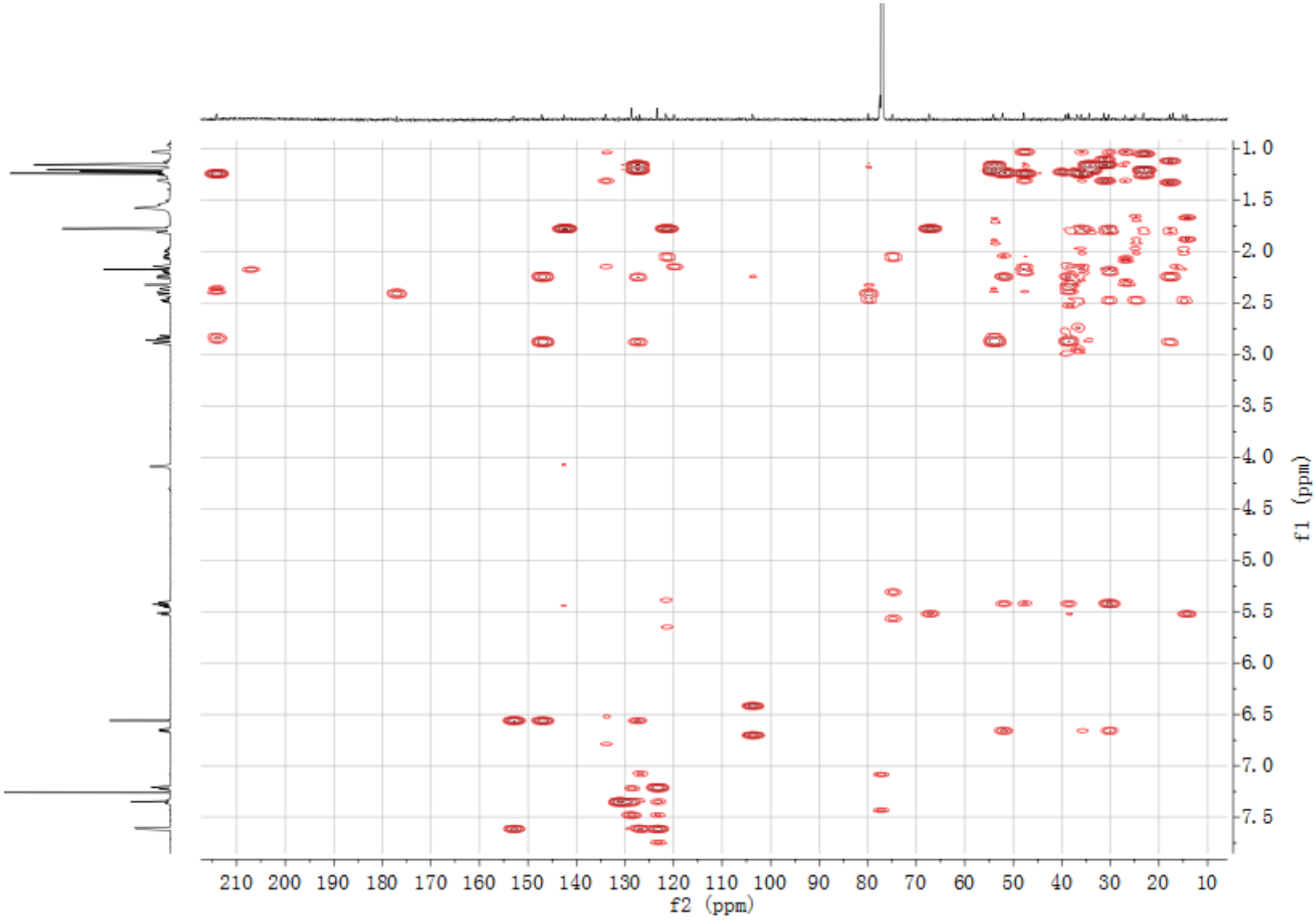


Figure S156. NOESY spectrum of **16** in $CDCl_3$

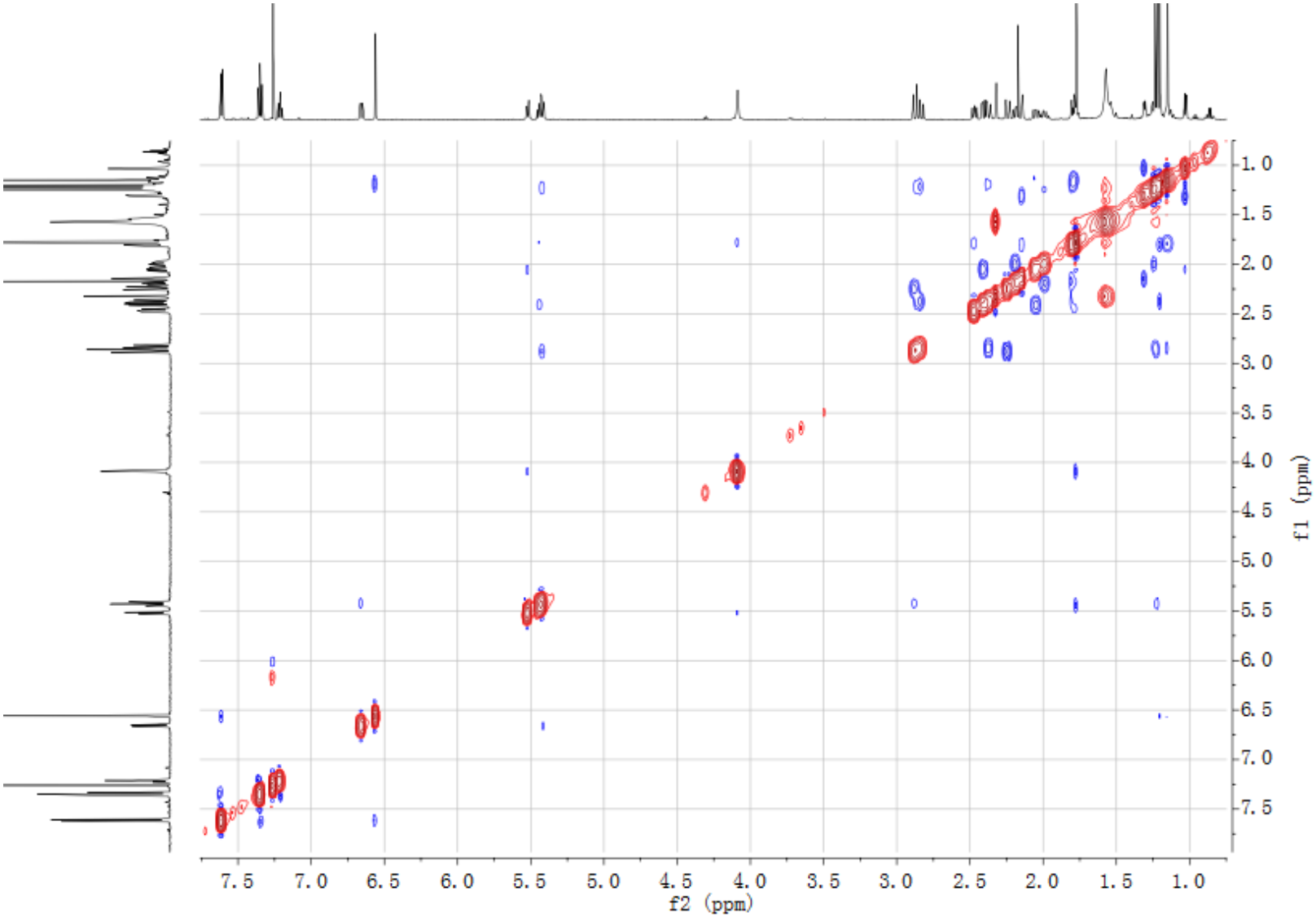


Figure S157. (±)-ESIMS spectra of **16**

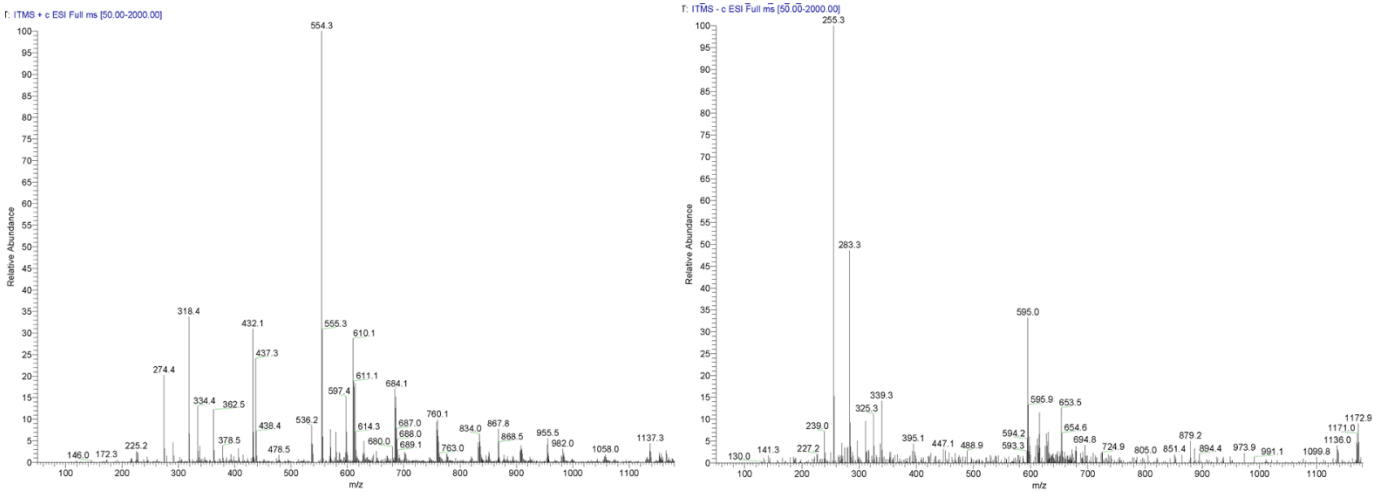
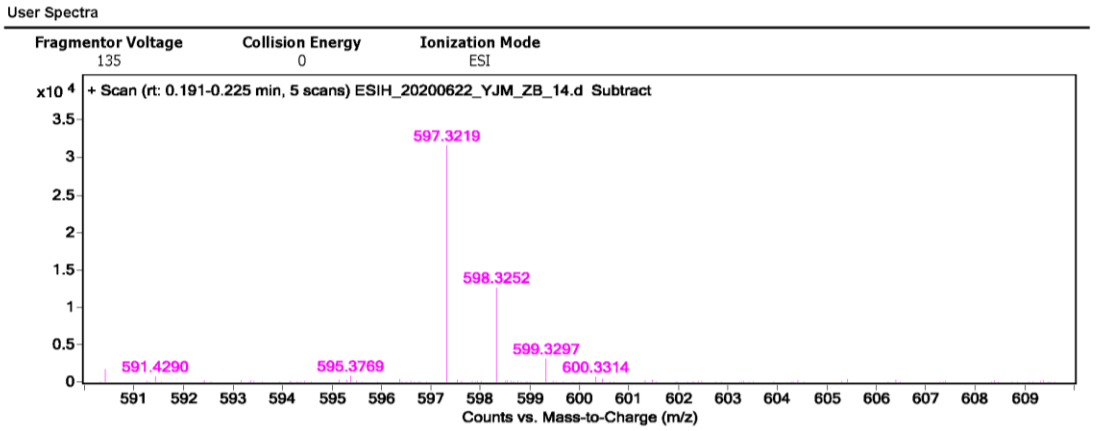


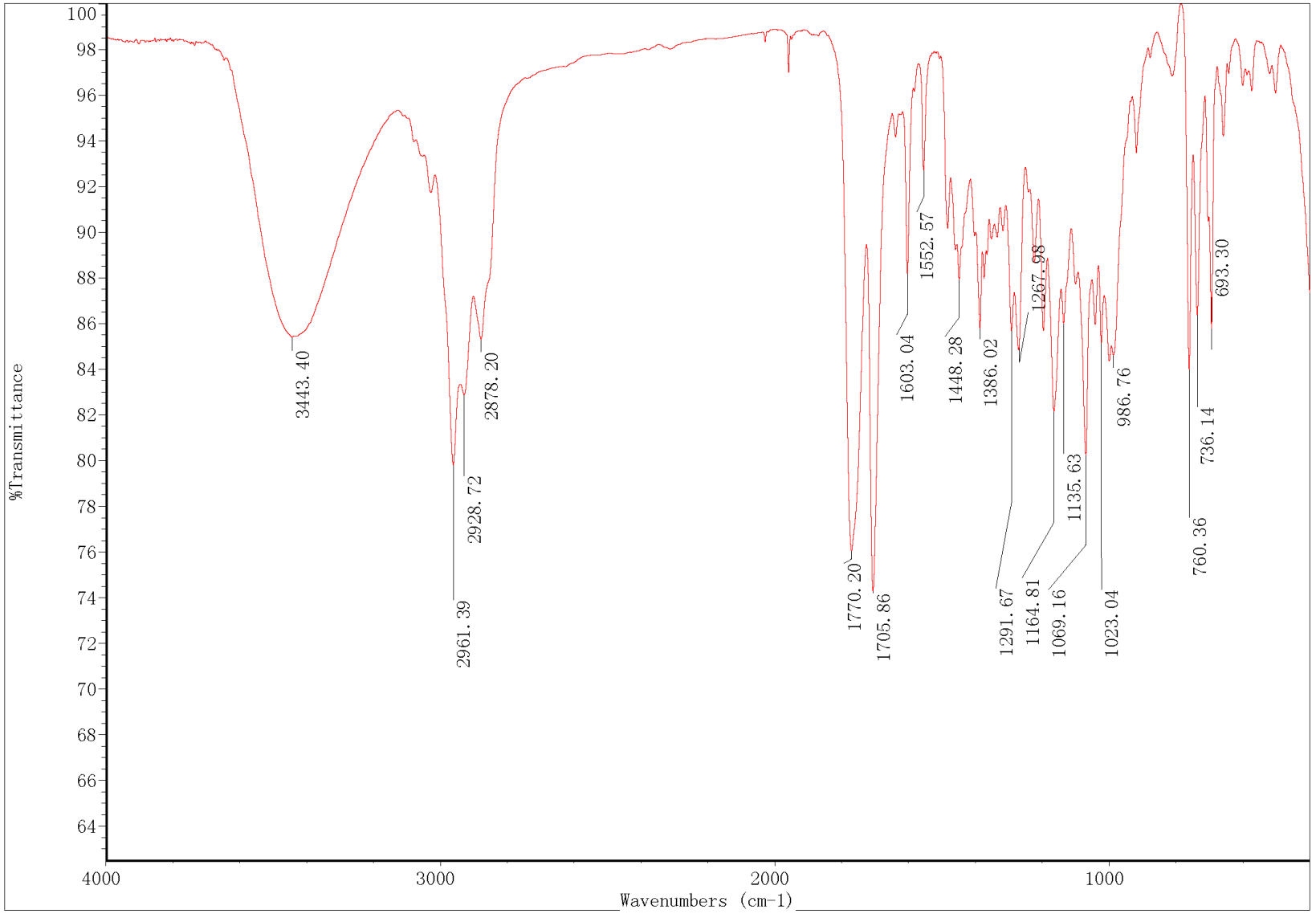
Figure S158. (–)-HRESIMS spectrum of **16**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
597.3219	597.3211	-0.8	-1.34	C38 H45 O6	(M+H)+

Figure S159. IR spectrum of **16**



6.17 NMR, MS, and IR spectra of compound 17

Figure S160. ^{1}H NMR spectrum (500 MHz) of **17** in acetone-d_6

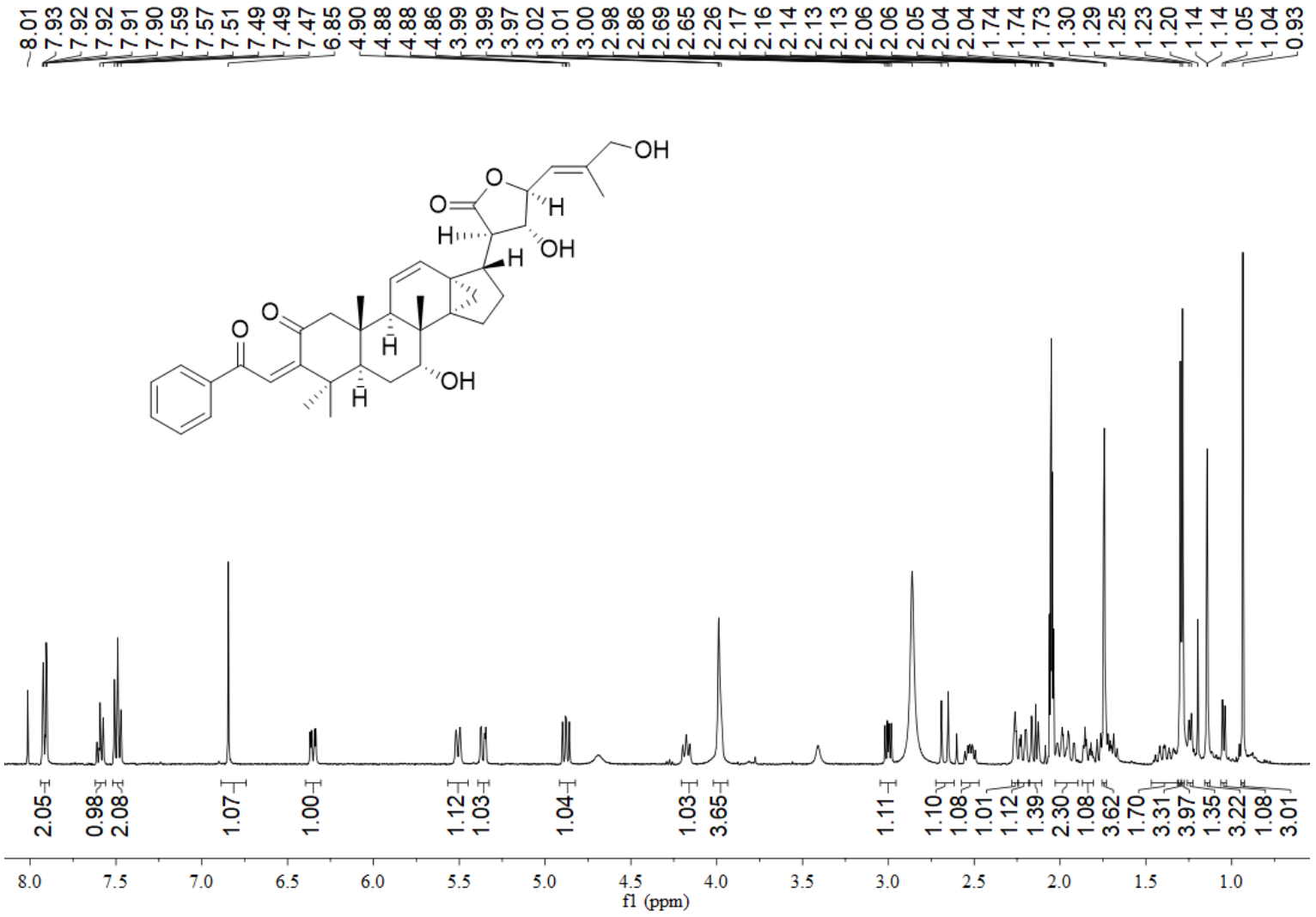


Figure S161. ^{13}C NMR spectrum (125 MHz) of **17** in acetone-d_6

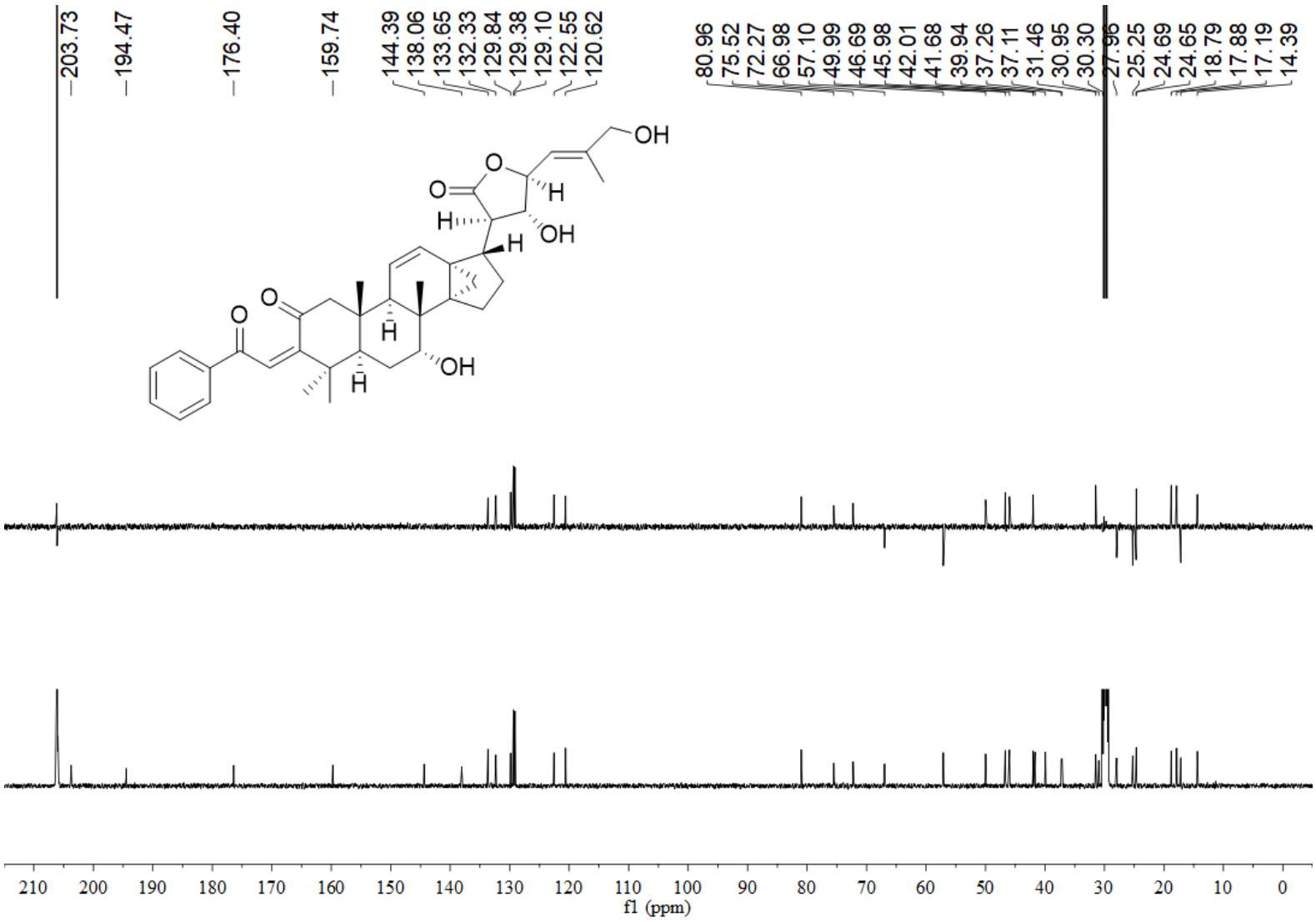


Figure S162. ^{1}H–^{1}H COSY spectrum of **17** in acetone-d_6

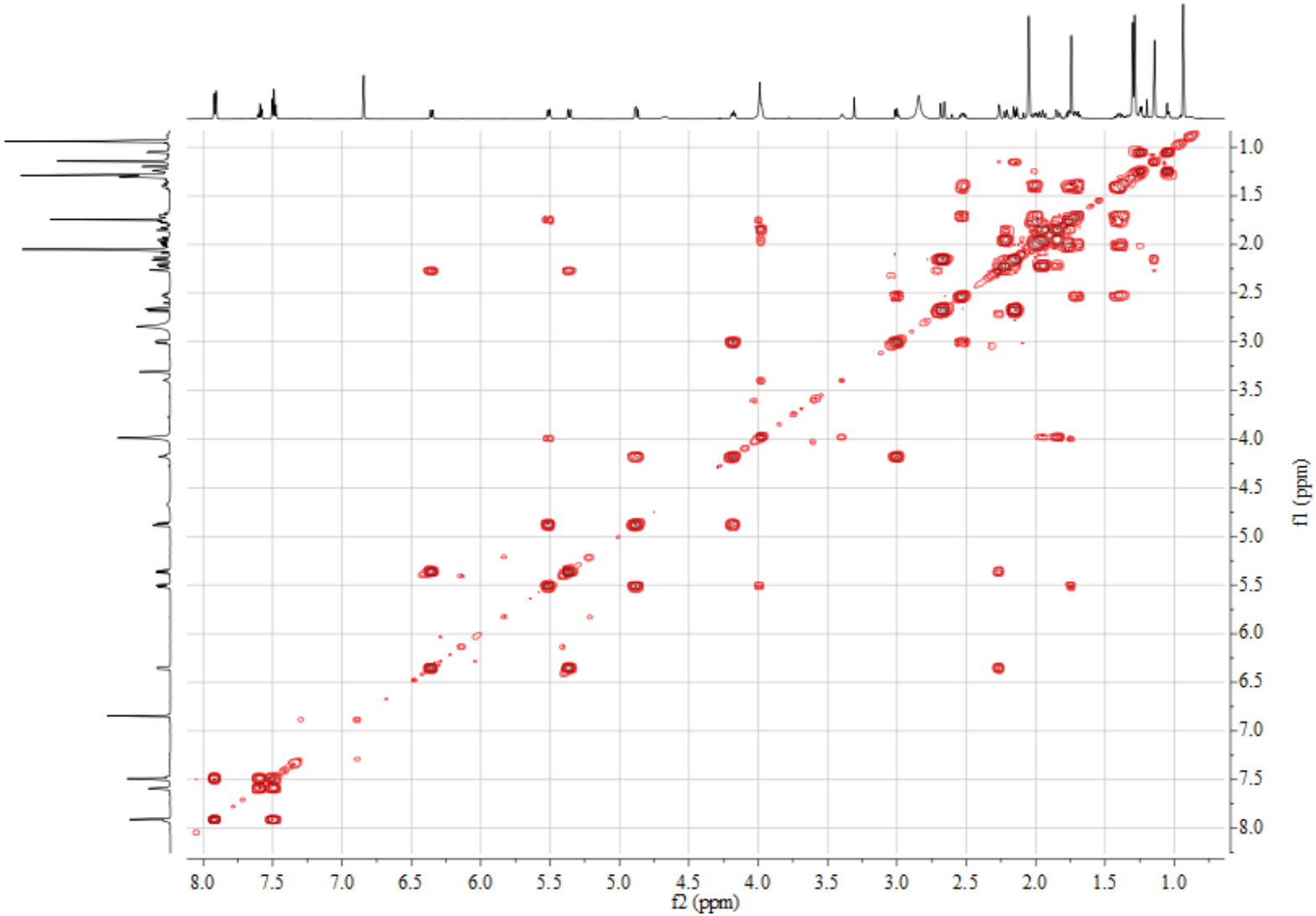


Figure S163. HSQC spectrum of **17** in acetone-d_6

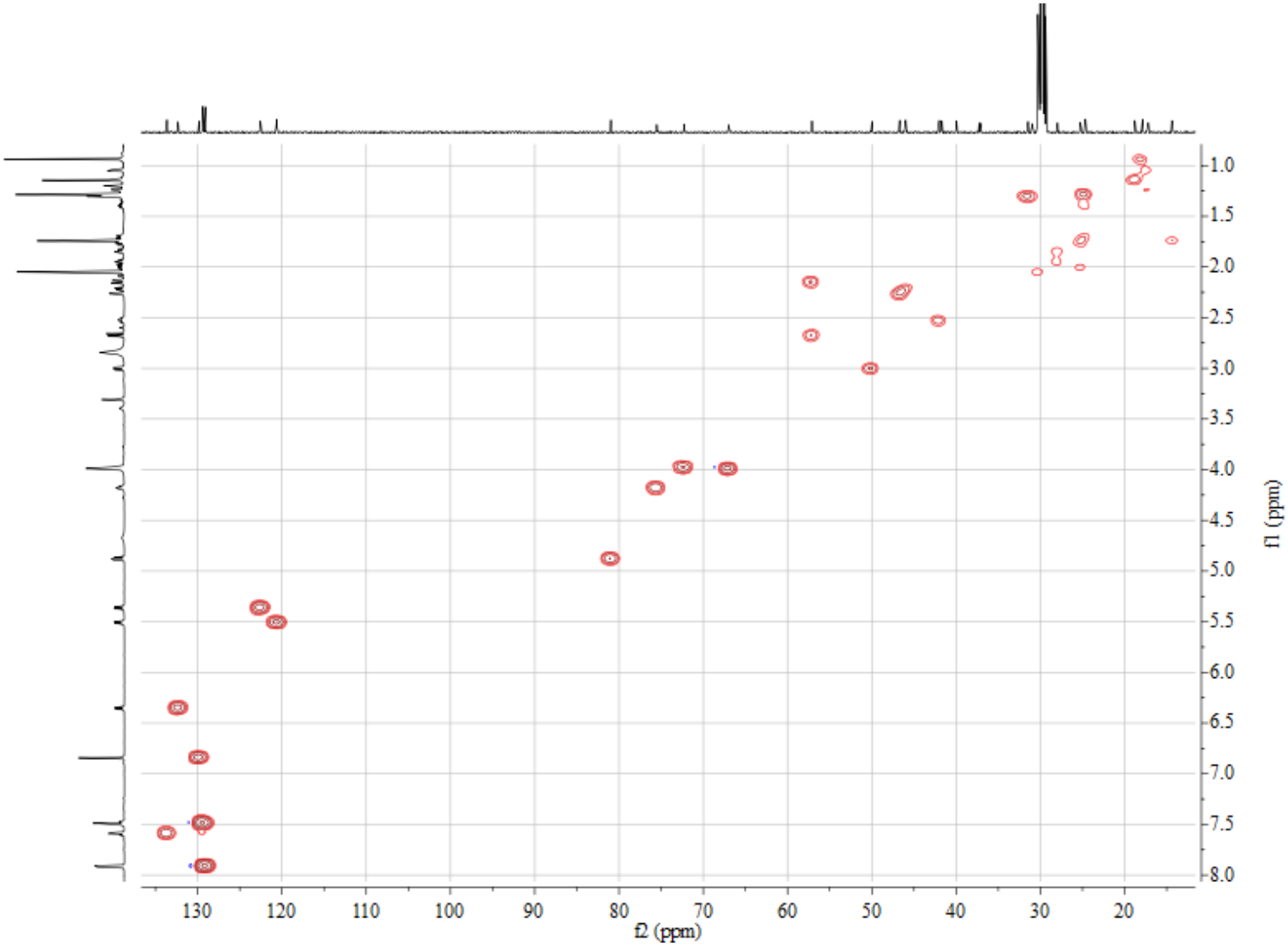


Figure S164. HMBC spectrum of **17** in acetone-d_6

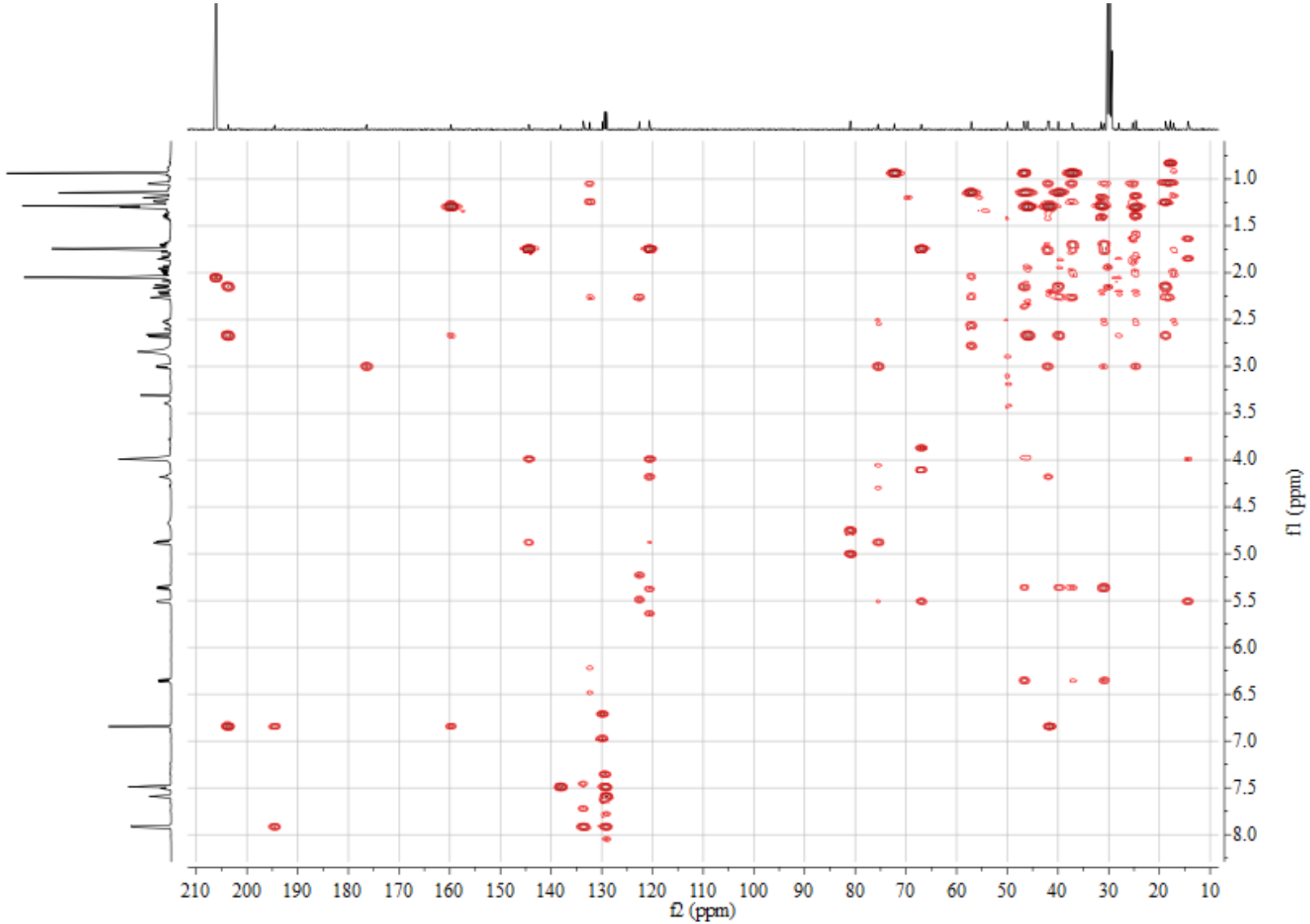


Figure S165. NOESY spectrum of **17** in acetone-d_6

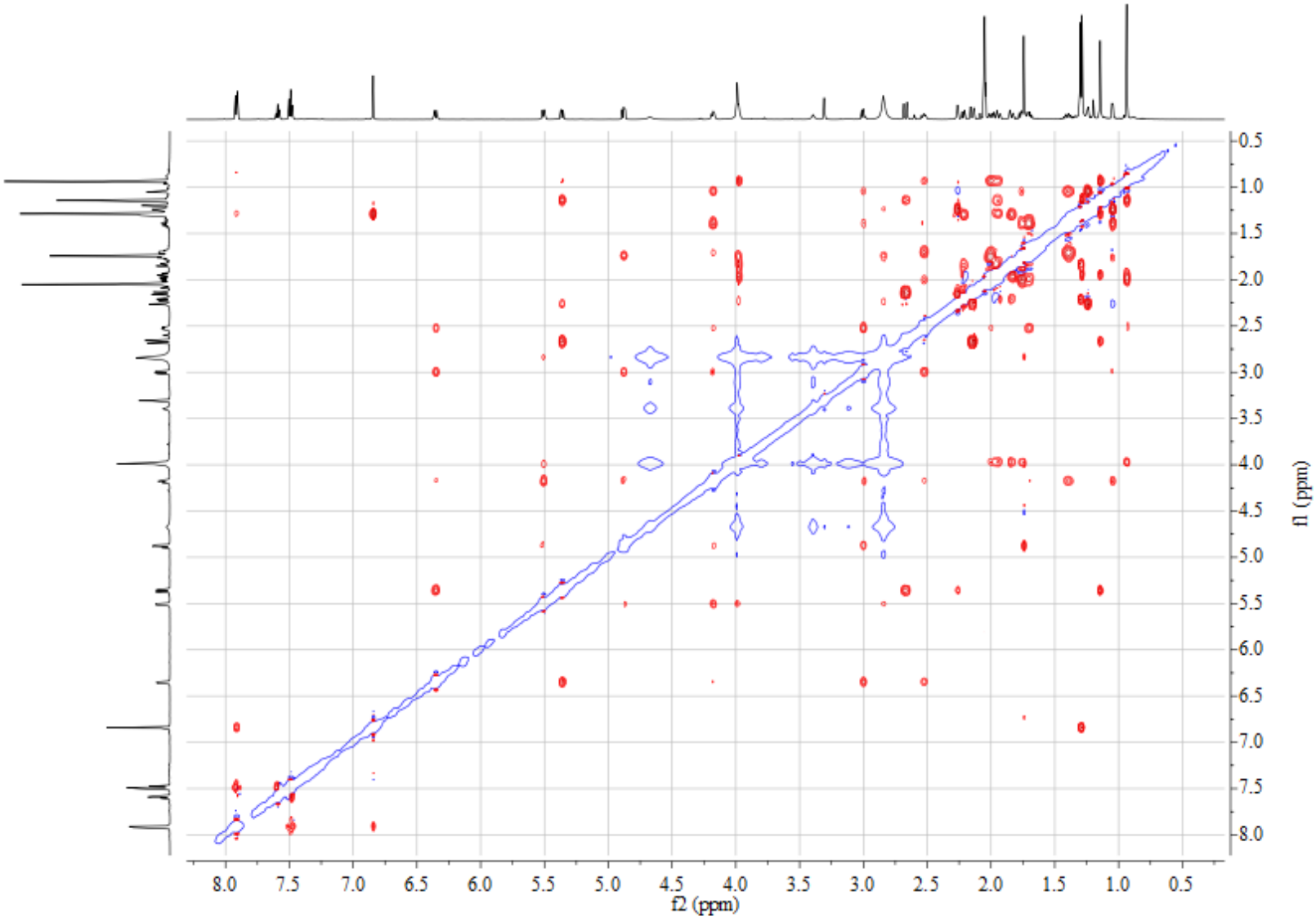


Figure S166. (±)-ESIMS spectra of **17**

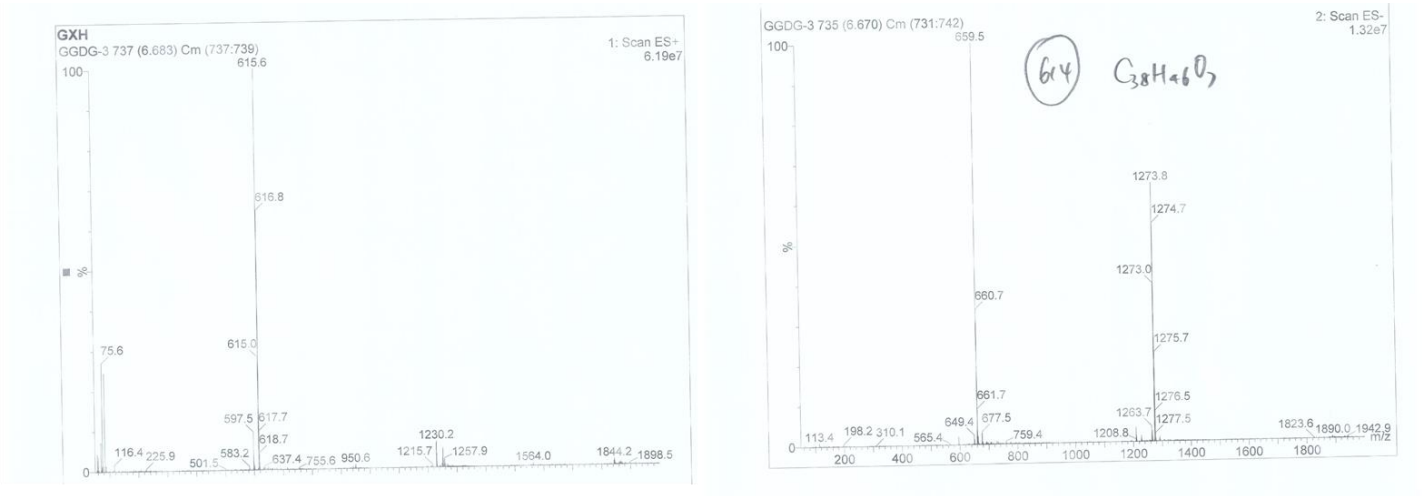
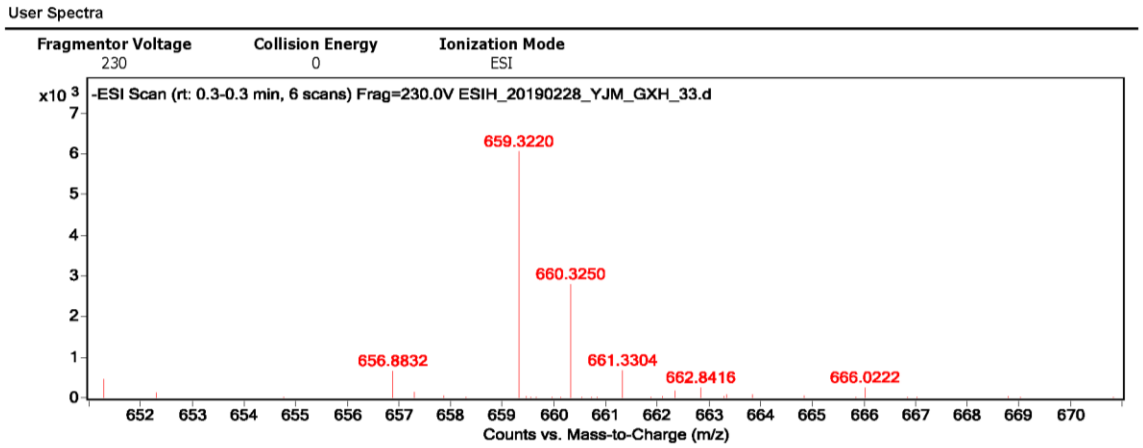


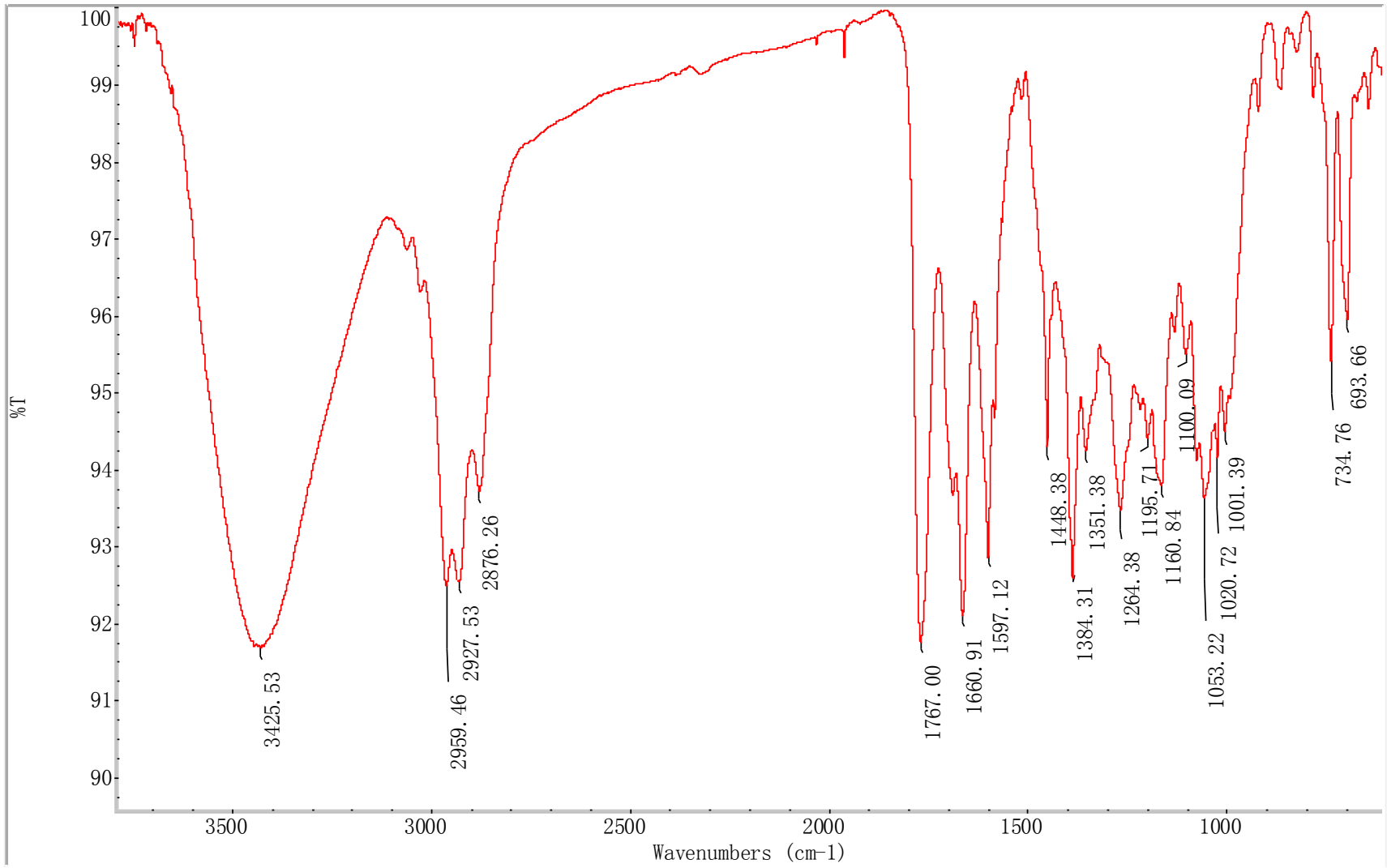
Figure S167. (–)-HRESIMS spectrum of **17**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
659.322	659.3226	0.6	0.91	C39 H47 O9	(M+COOH)-

Figure S168. IR spectrum of **17**



6.18 NMR, MS, and IR spectra of compound 18

Figure S169. ^{1}H NMR spectrum (500 MHz) of **18** in acetone-d_6

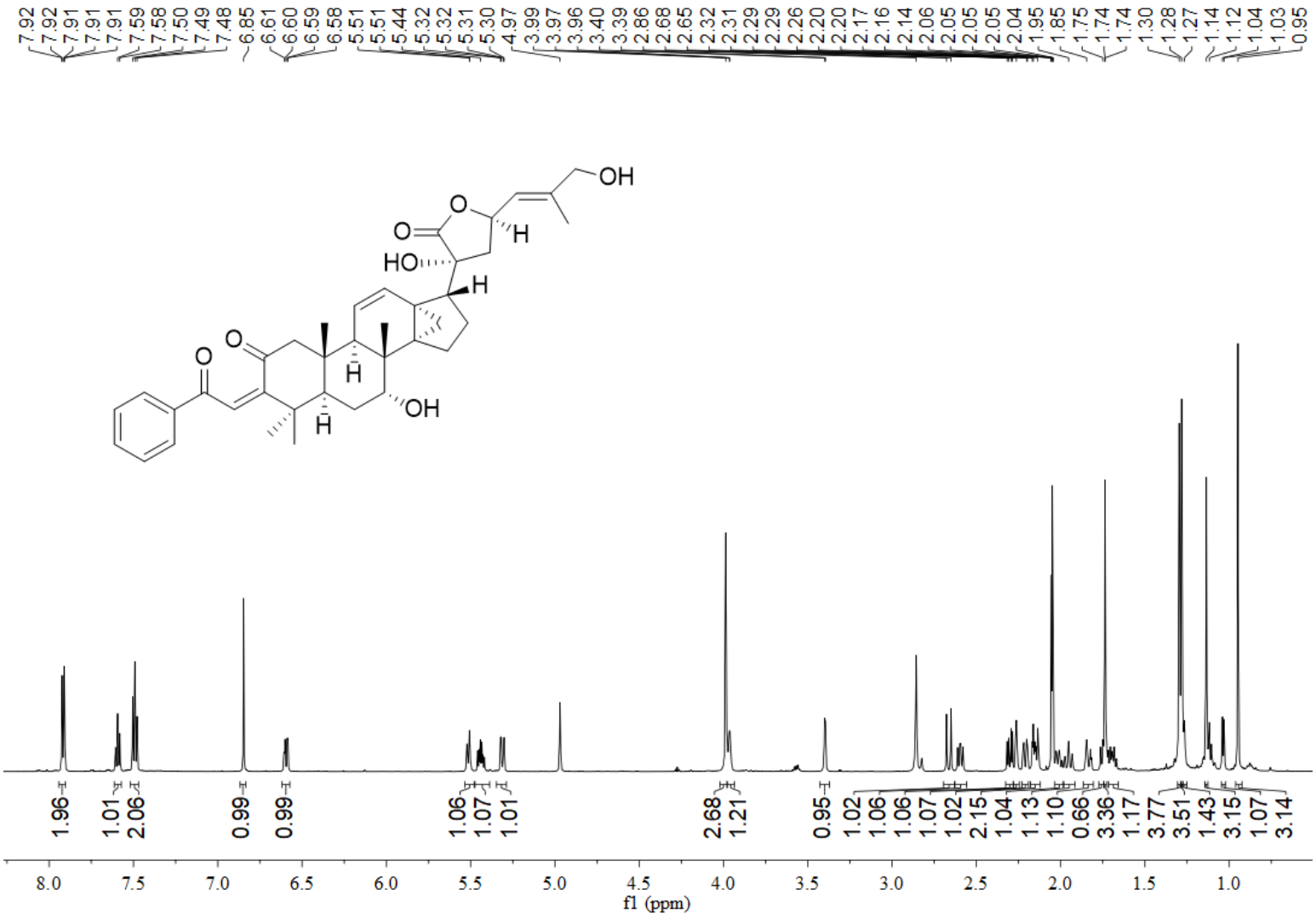


Figure S170. ^{13}C NMR spectrum (125 MHz) of **18** in acetone-d_6

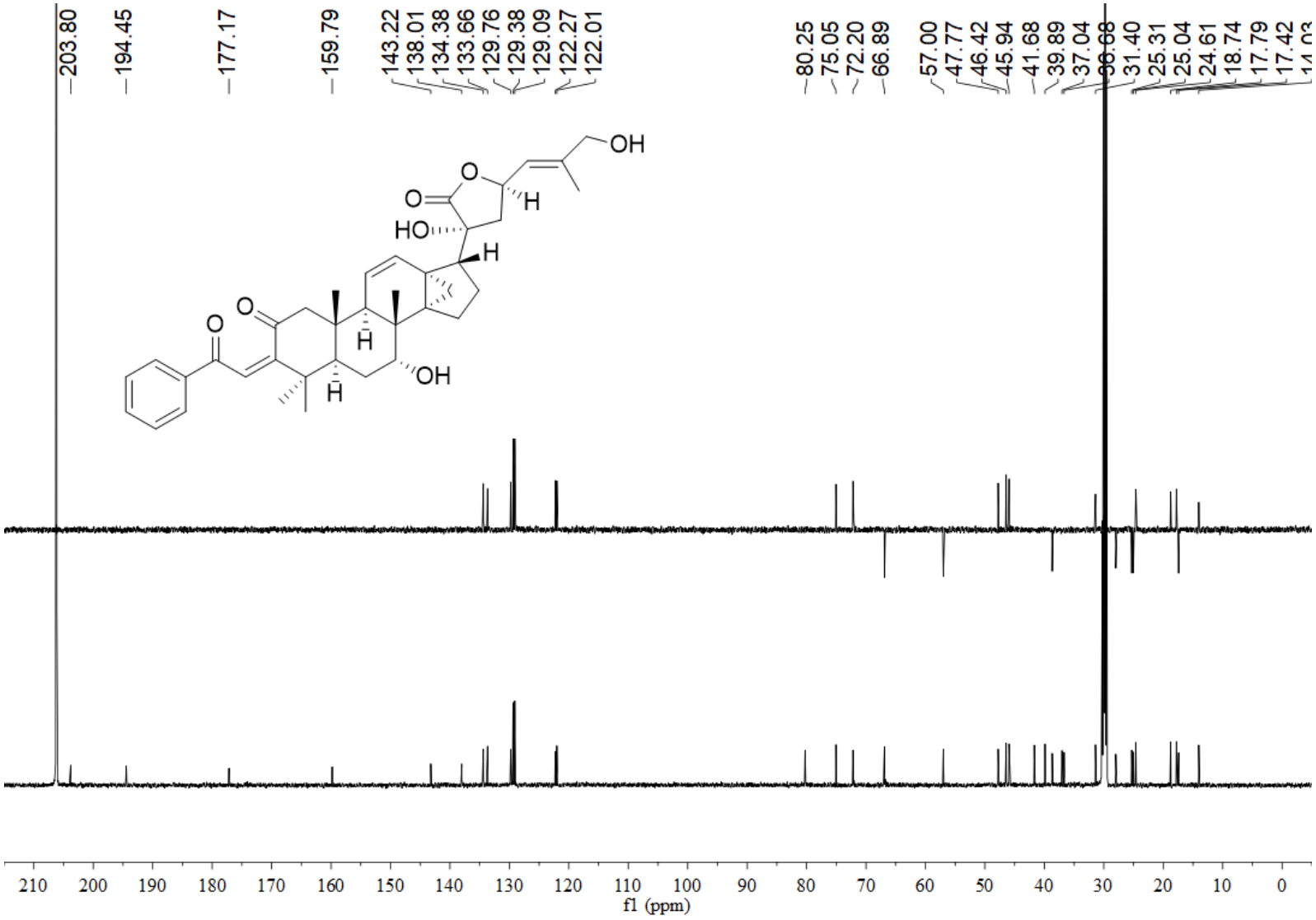


Figure S171. ^{1}H–^{1}H COSY spectrum of **18** in acetone-d_6

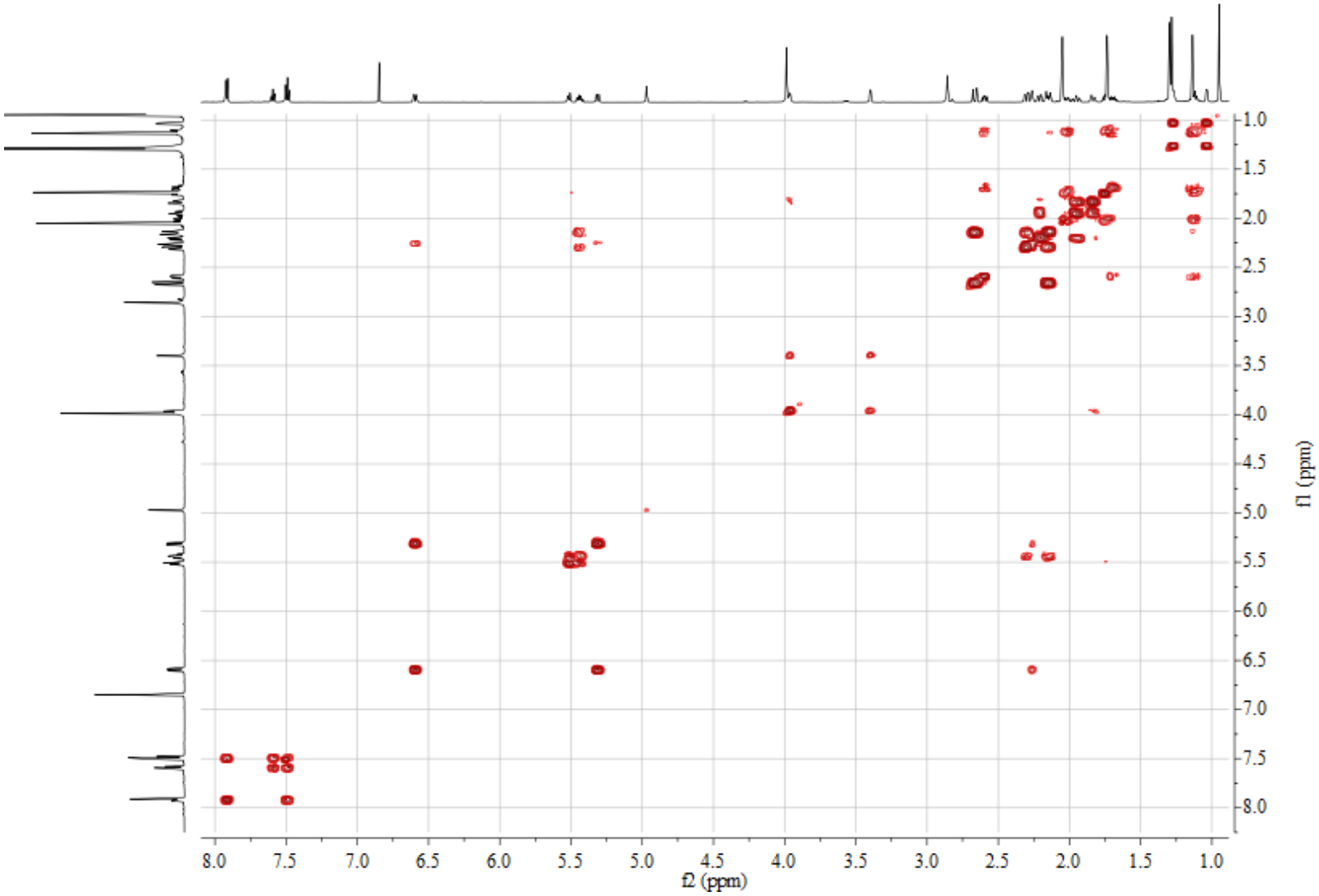


Figure S172. HSQC spectrum of **18** in acetone-d_6

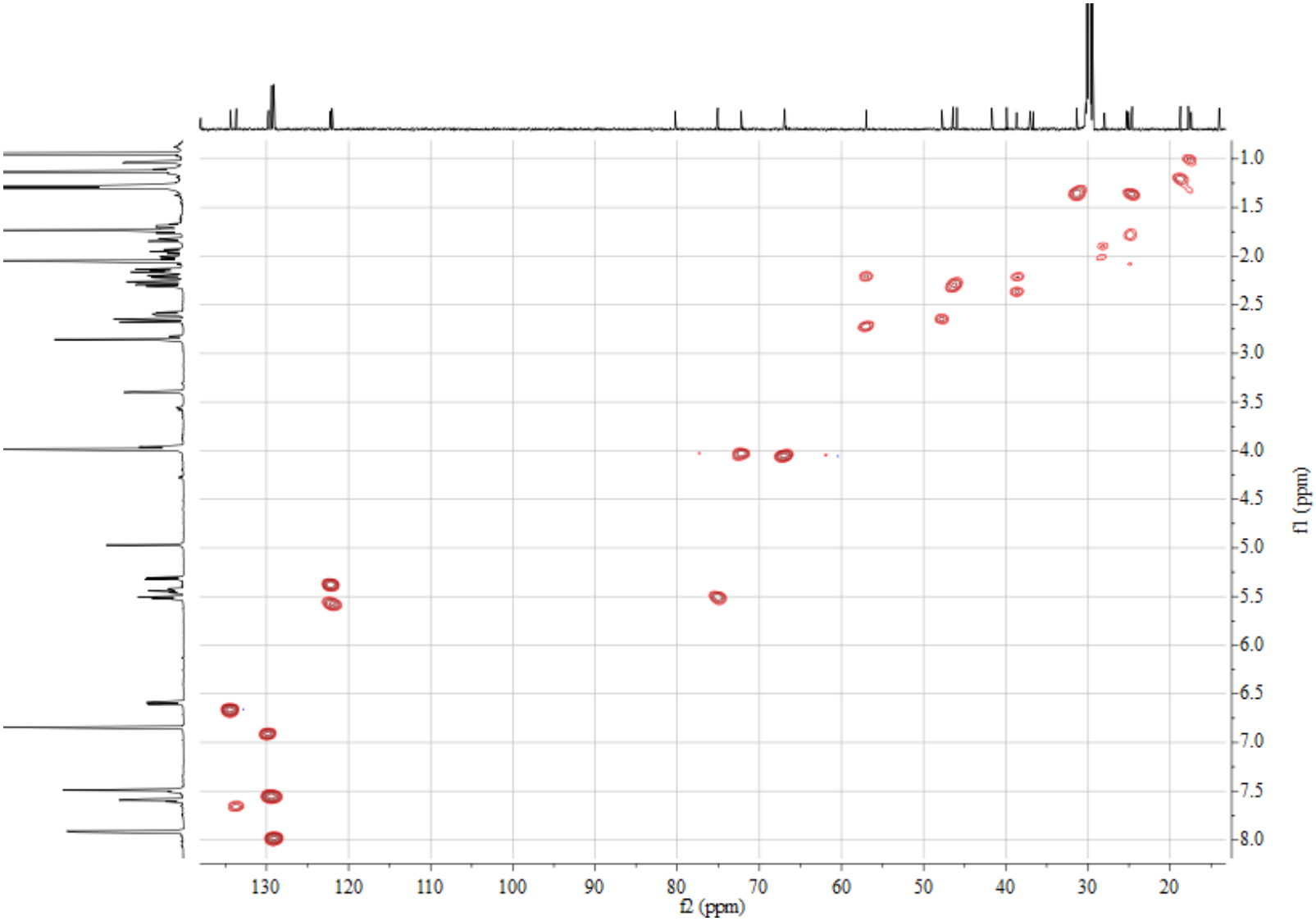


Figure S173. HMBC spectrum of **18** in acetone-d_6

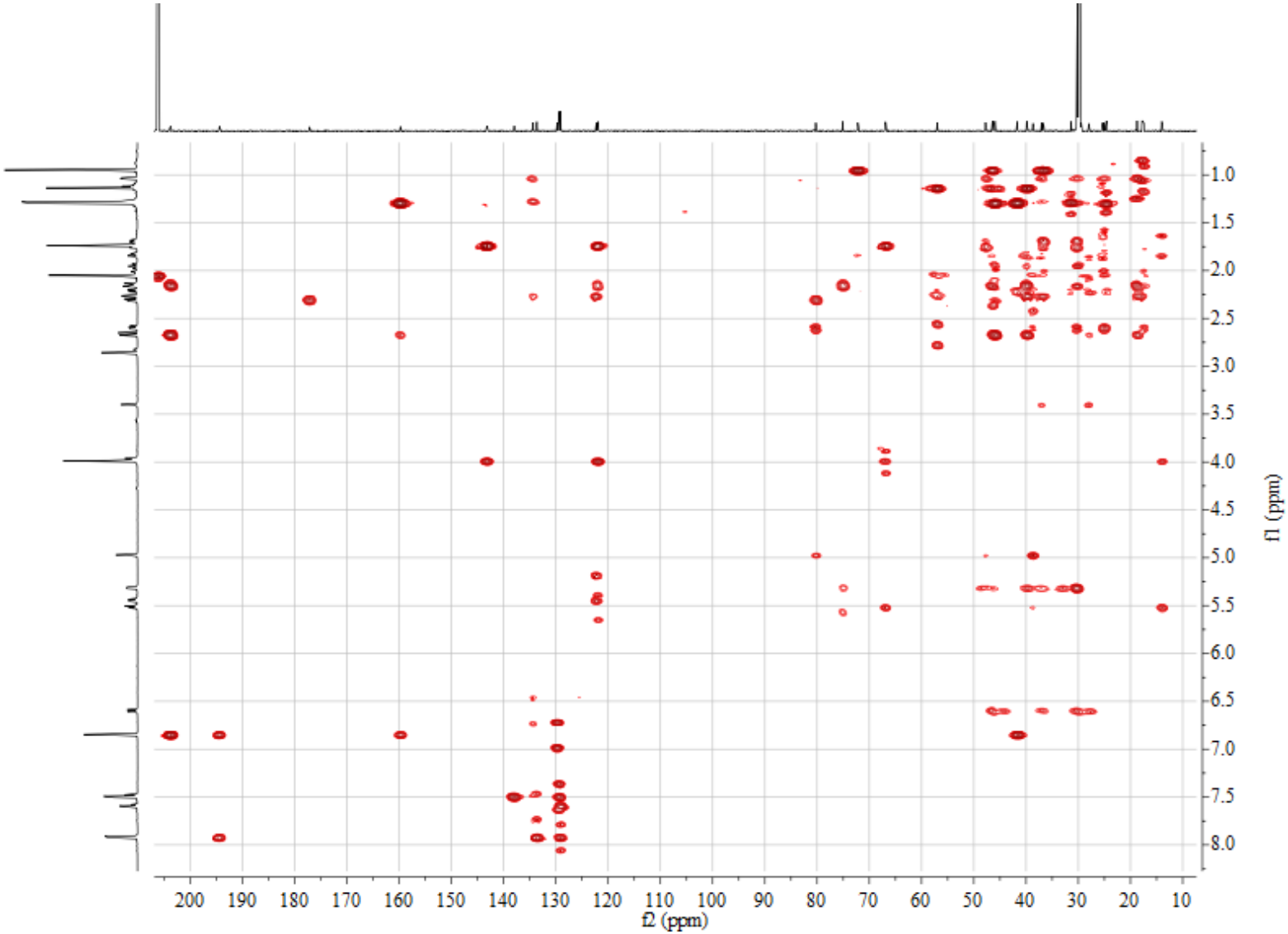


Figure S174. NOESY spectrum of **18** in acetone-d_6

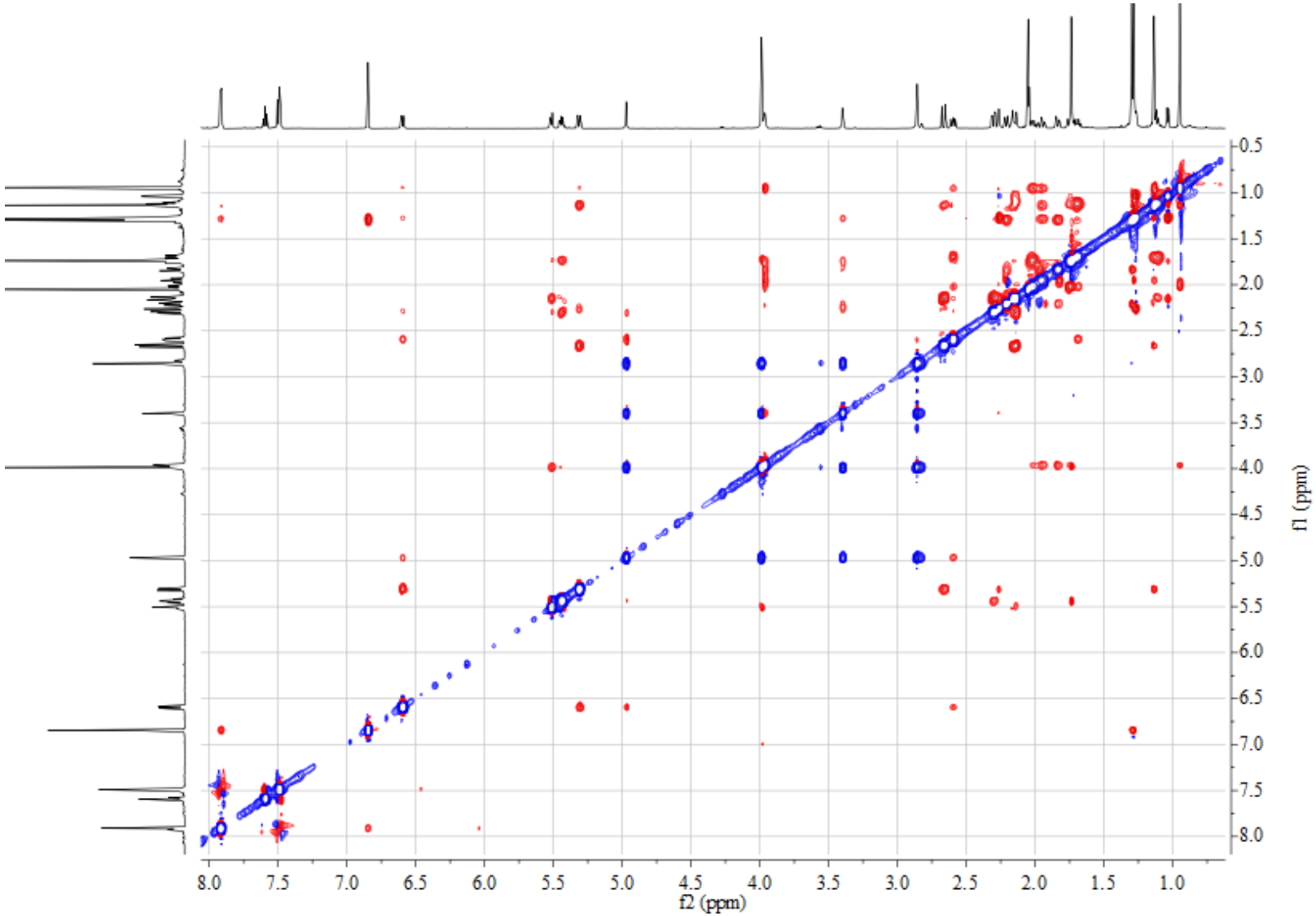


Figure S175. (±)-ESIMS spectra of **18**

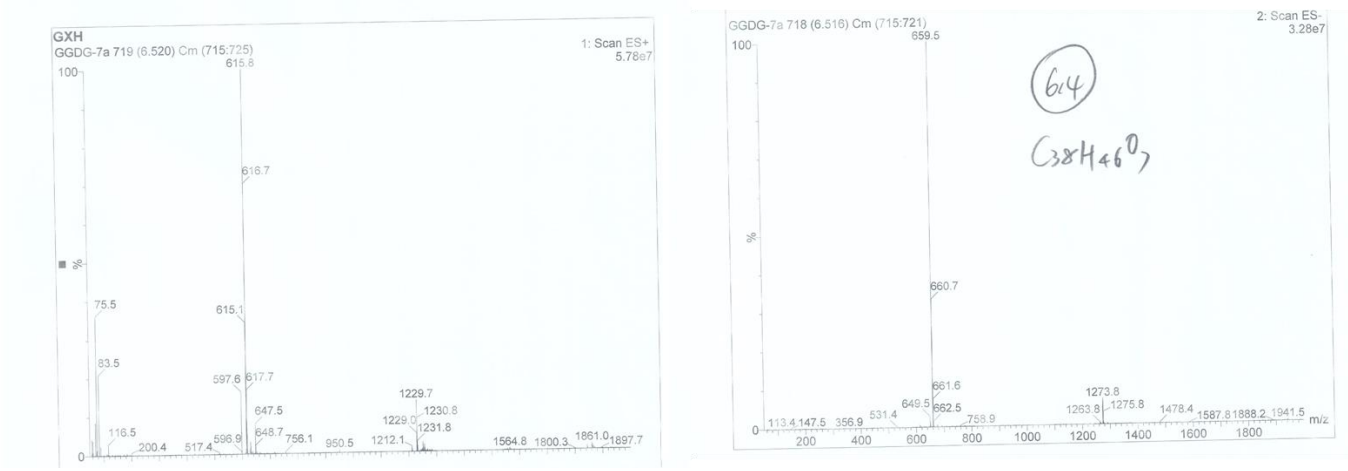
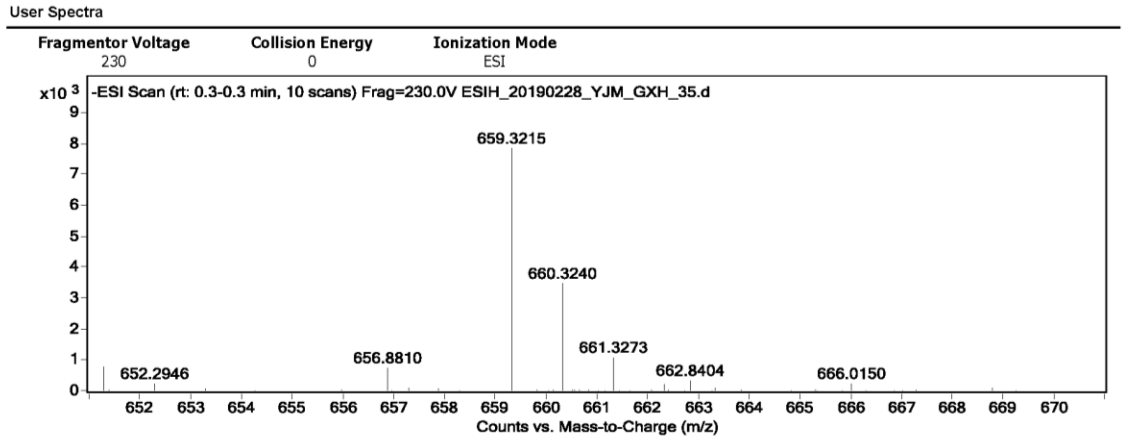


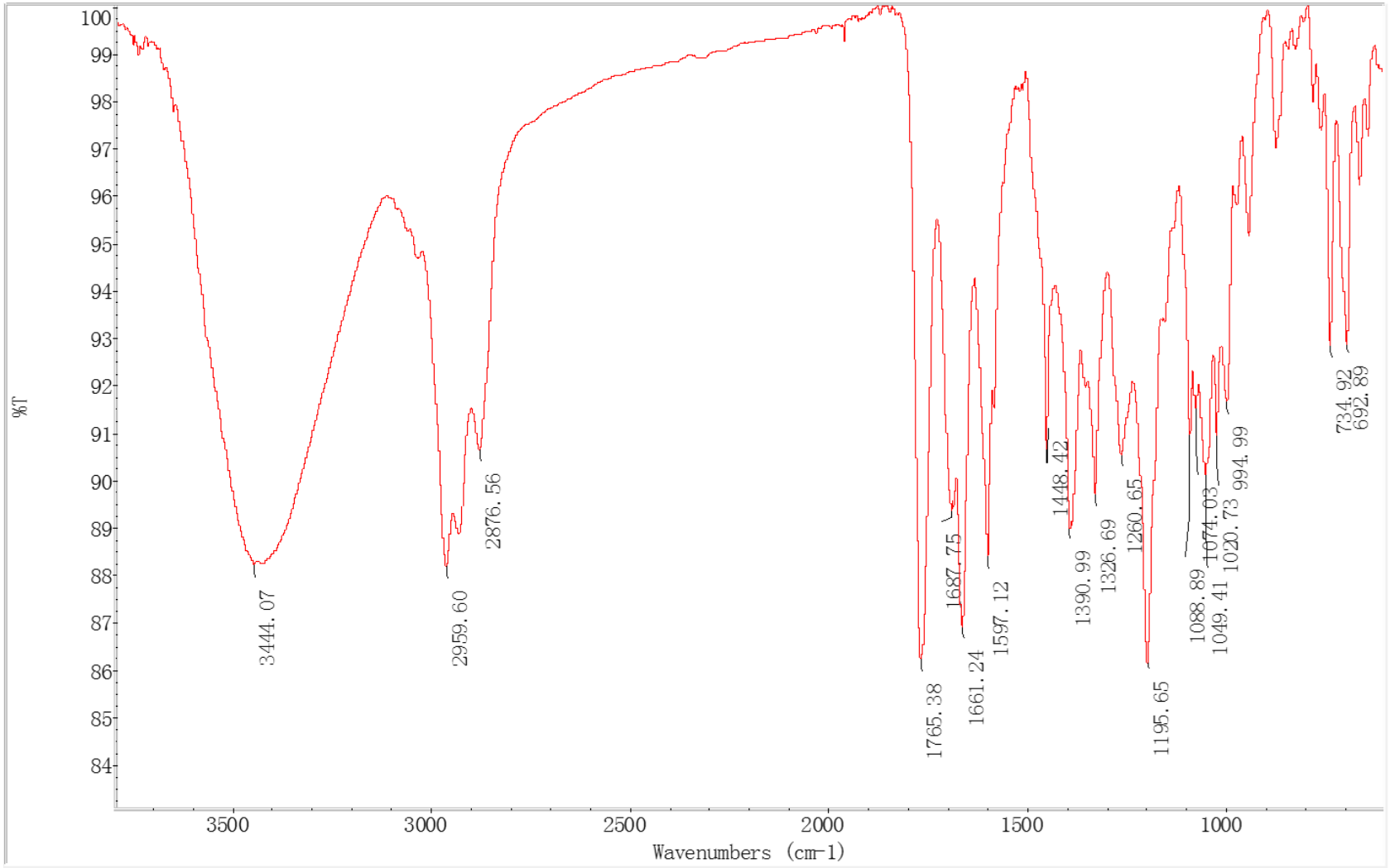
Figure S176. (–)-HRESIMS spectrum of **18**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
659.3215	659.3226	1.04	1.58	C39 H47 O9	(M+COOH)-

Figure S177. IR spectrum of **18**



6.19 NMR, MS, and IR spectra of synthetic 19

Figure S178. ^{1}H NMR spectrum (500 MHz) of **19** in acetone-d_6

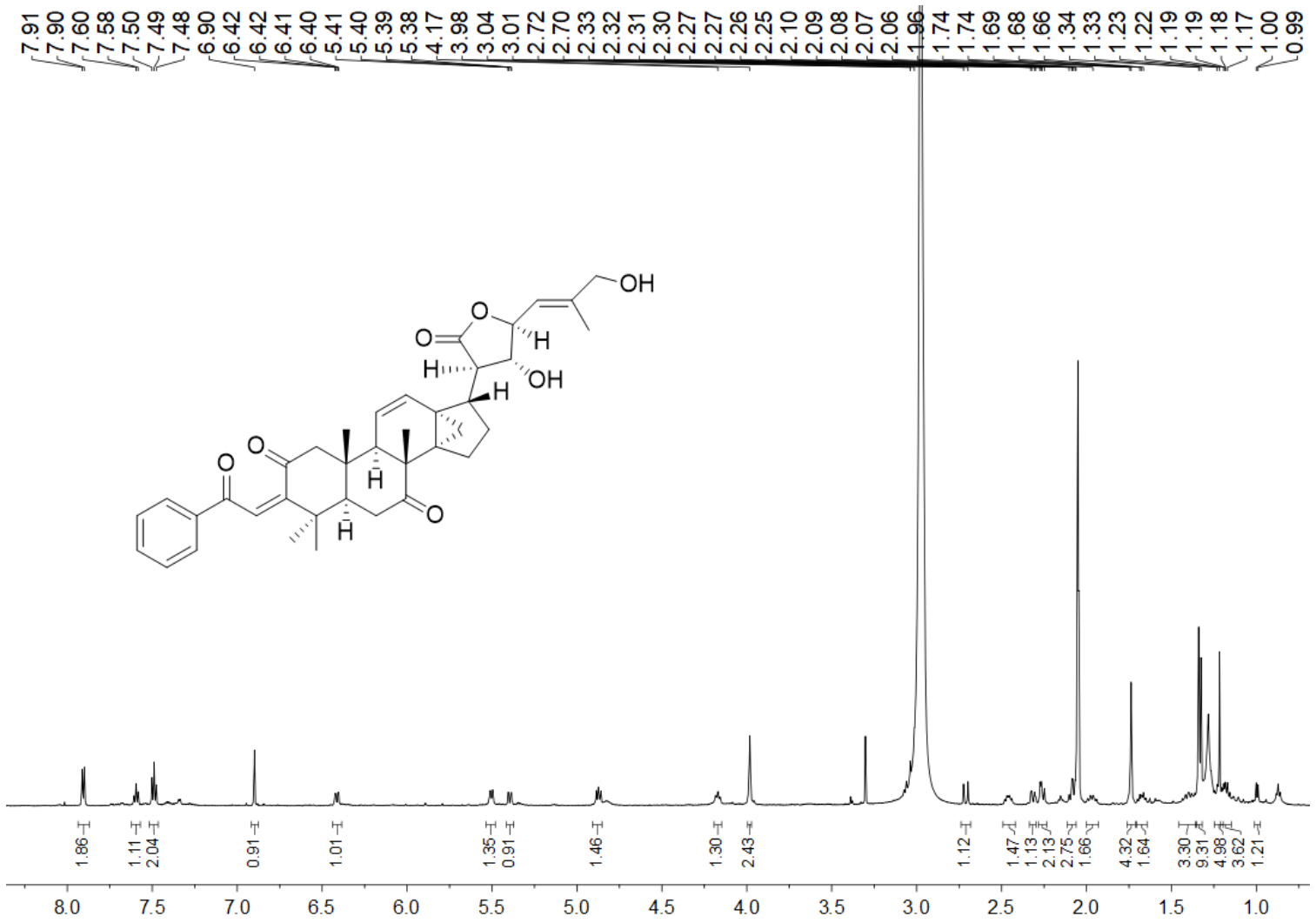


Figure S179. ^{13}C NMR spectrum (125 MHz) of **19** in acetone-d_6

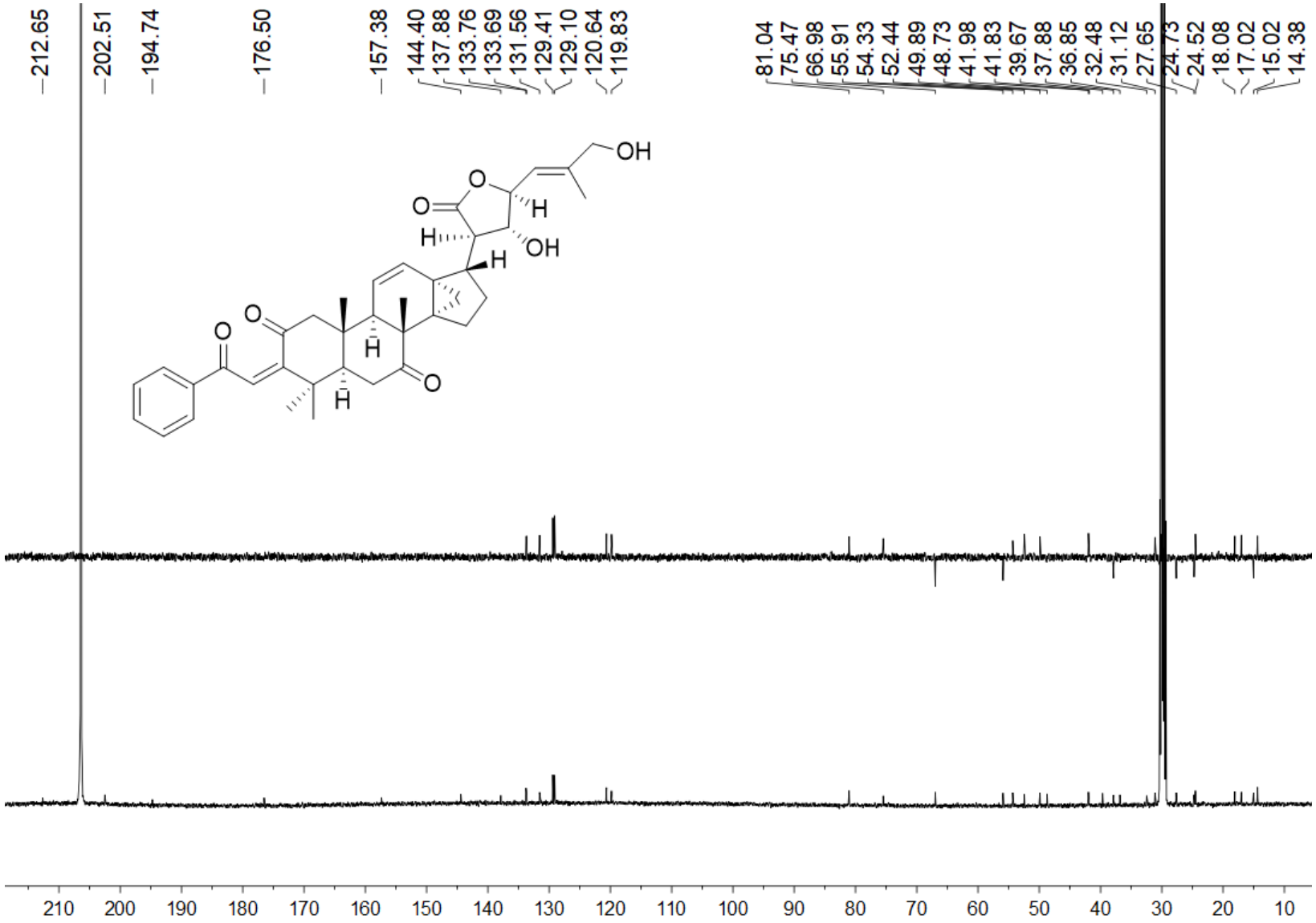


Figure S180. ^{1}H–^{1}H COSY spectrum of **19** in acetone-d_6

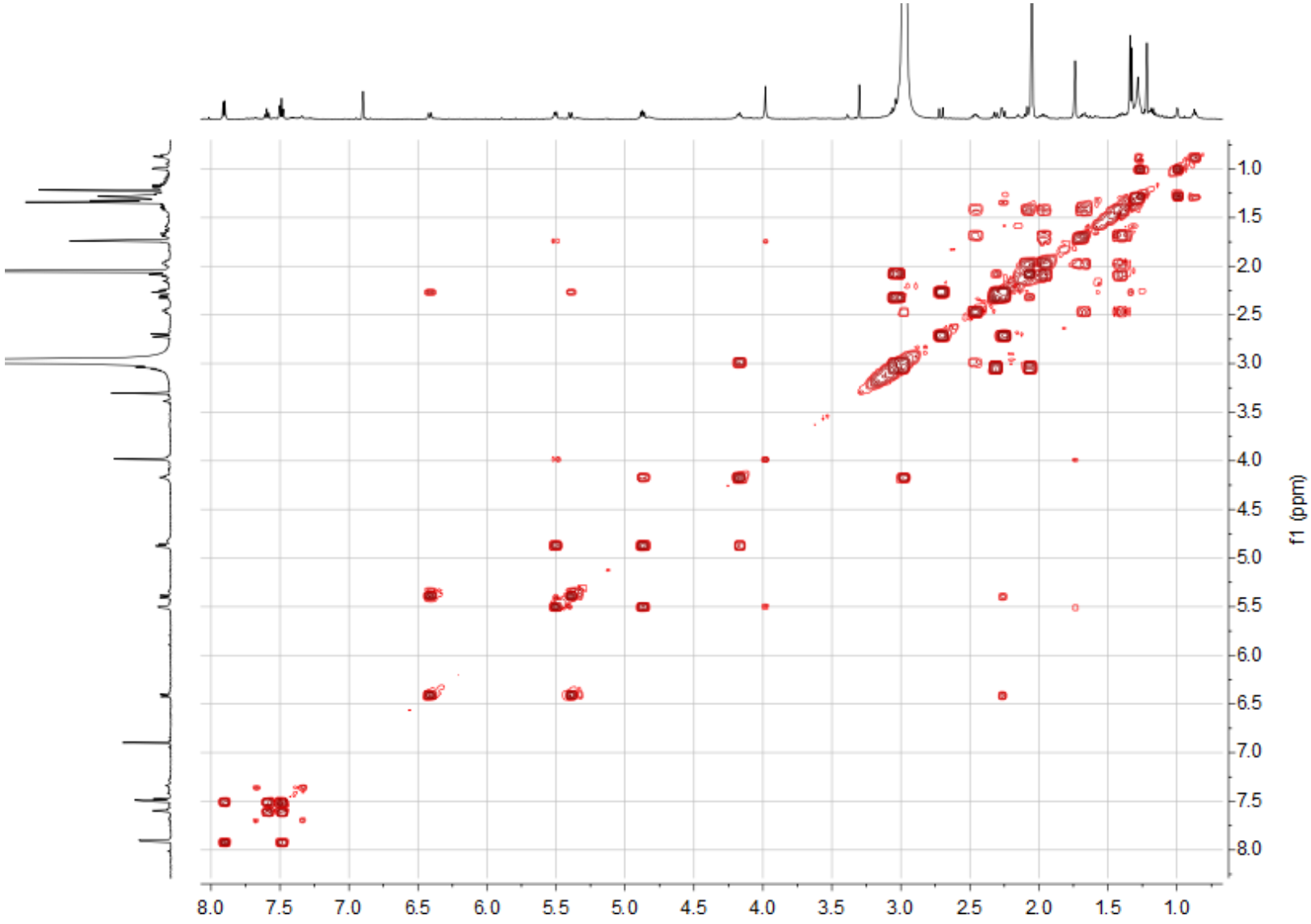


Figure S181. HSQC spectrum of **19** in acetone-d_6

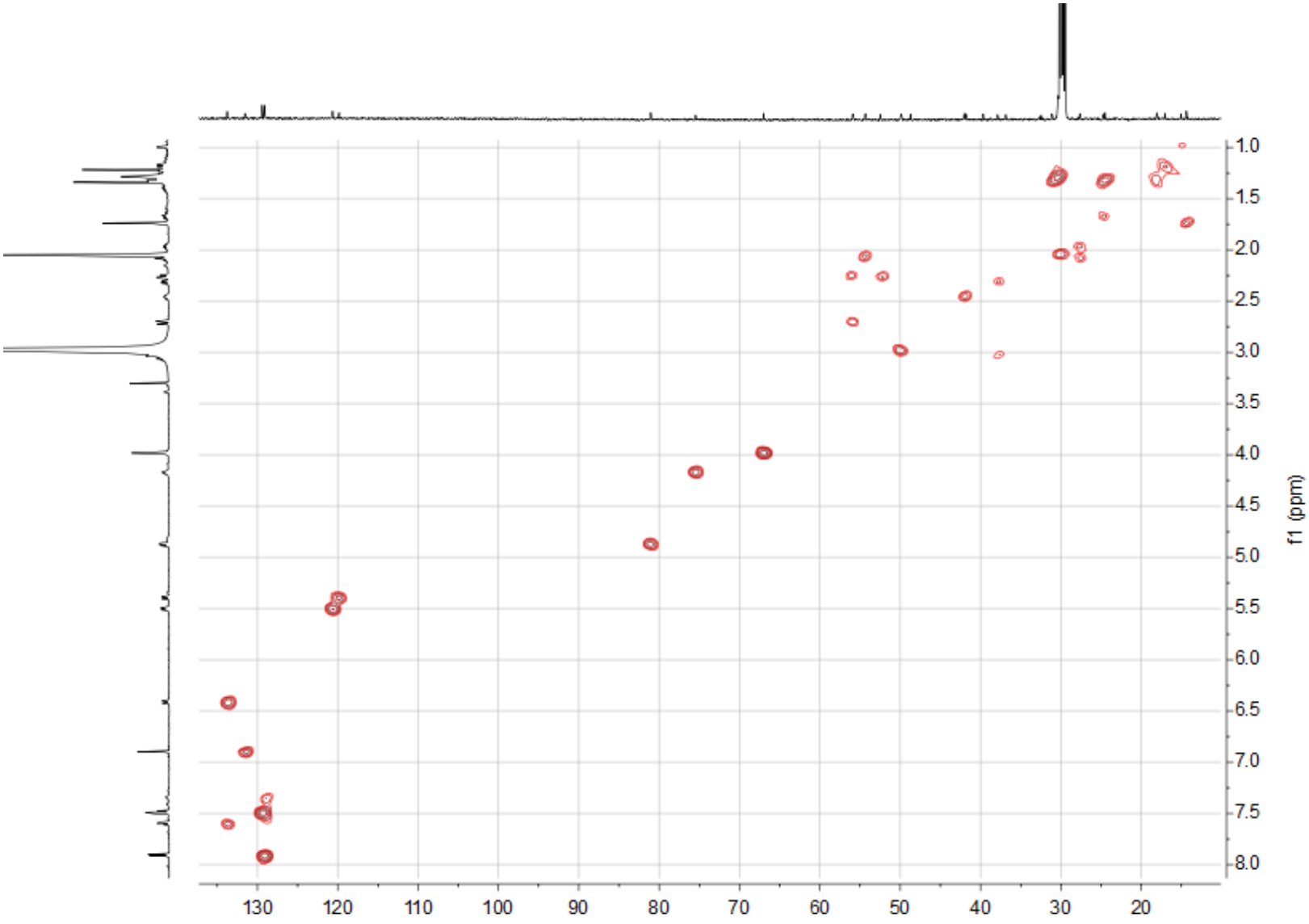


Figure S182. HMBC spectrum of **19** in acetone-d_6

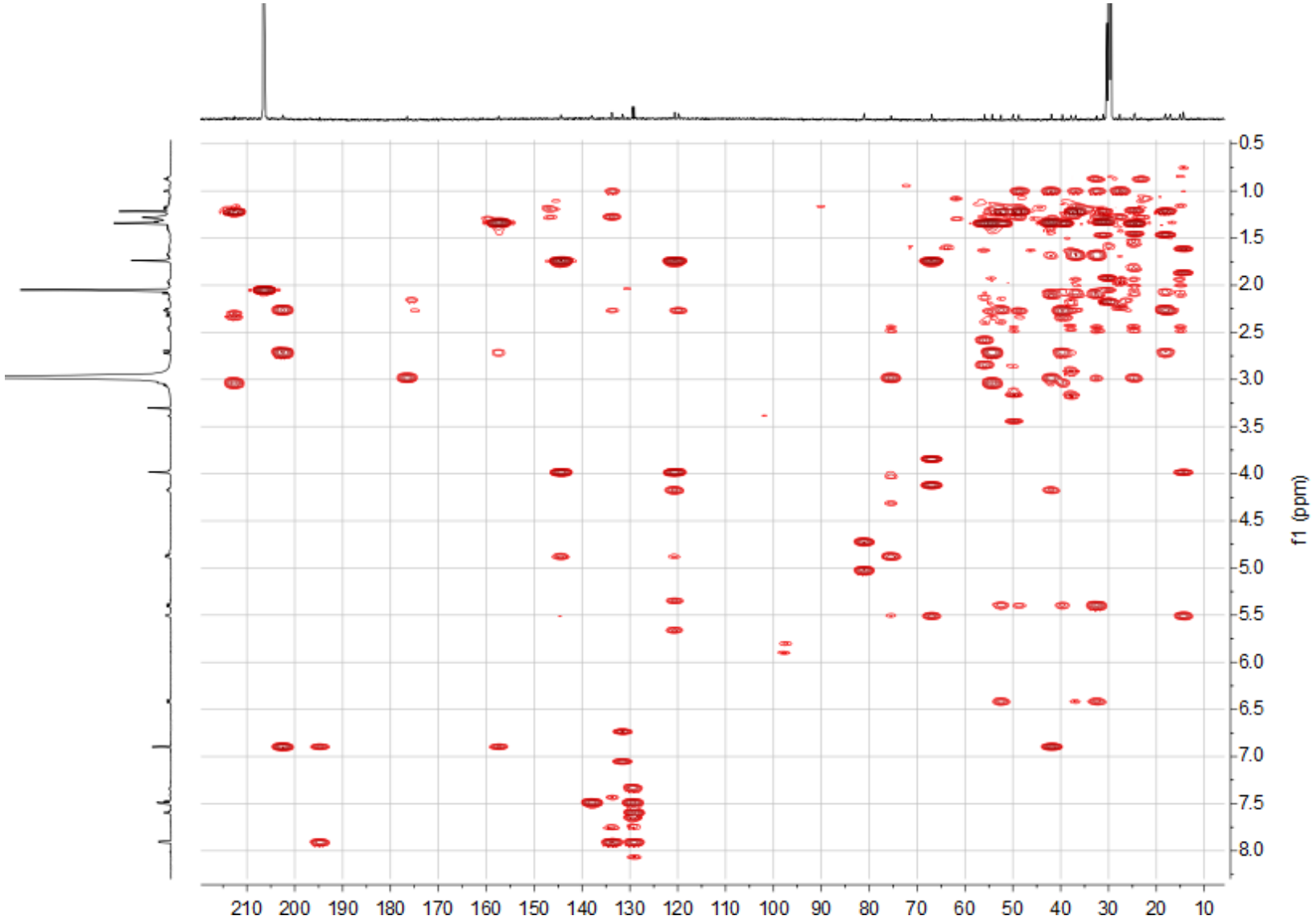


Figure S183. NOESY spectrum of **19** in acetone-d_6

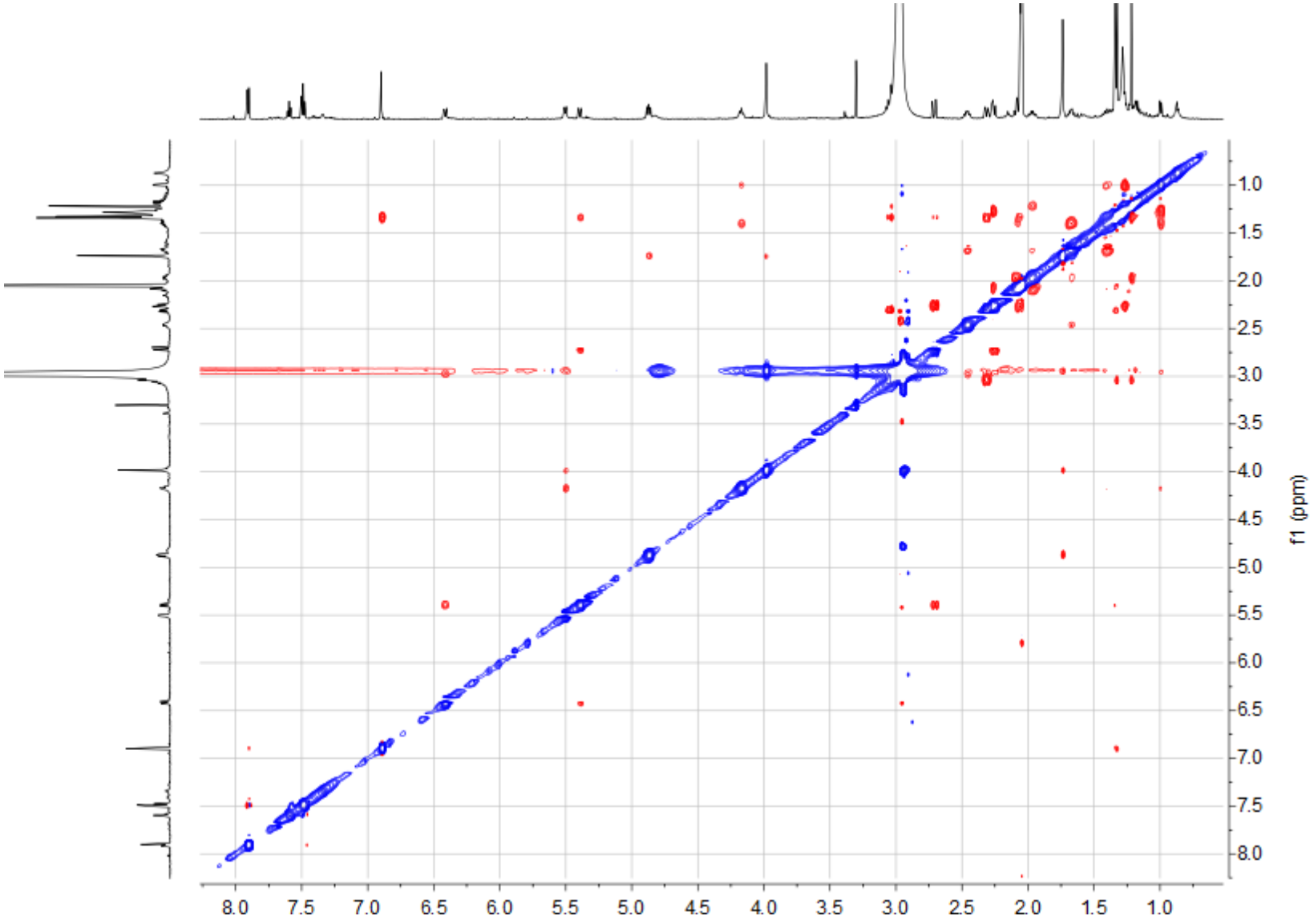


Figure S184. (±)-ESIMS spectra of **19**

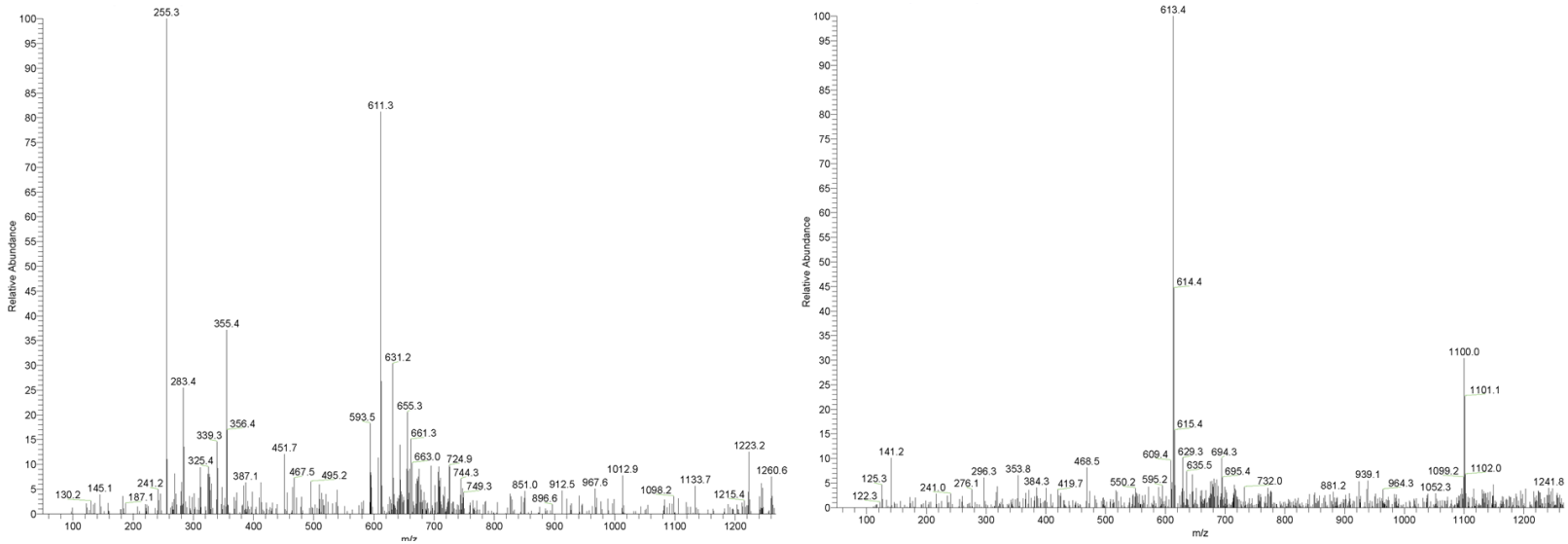
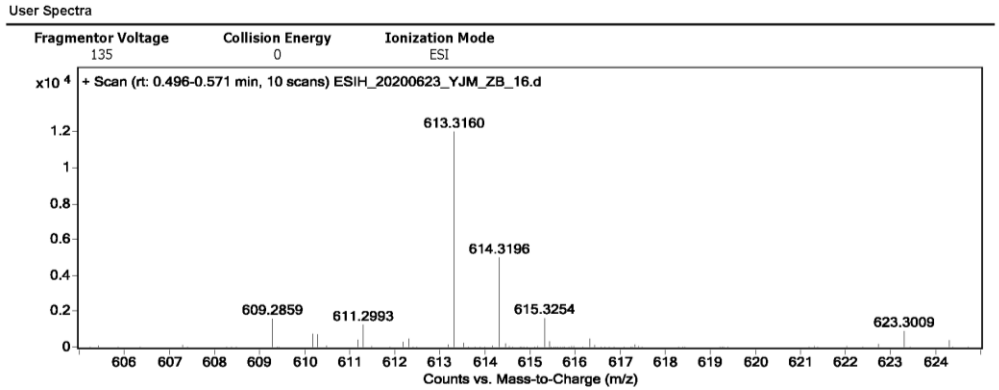


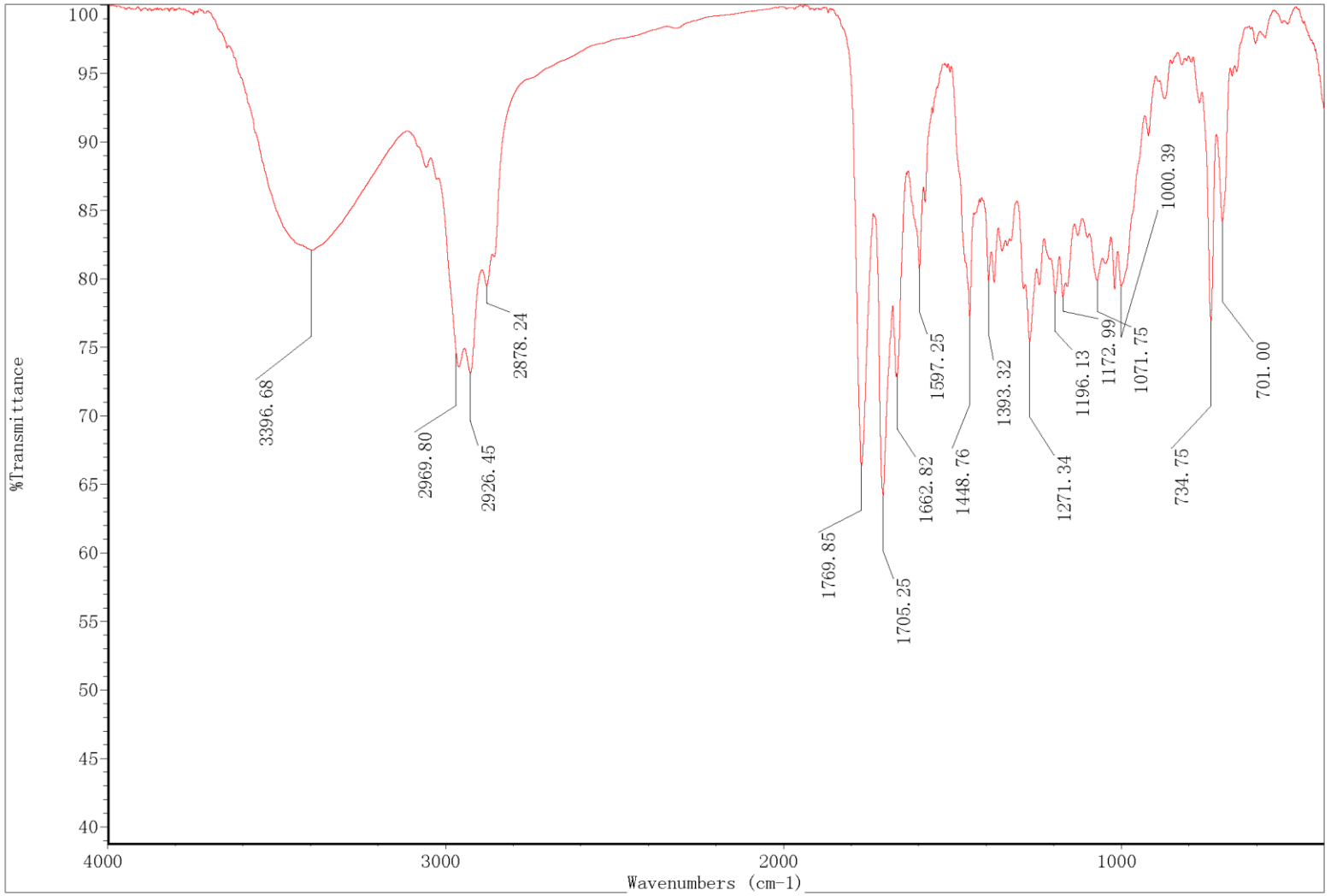
Figure S185. (–)-HRESIMS spectrum of **19**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
613.316	613.316	0.03	0.04	C38 H45 O7	(M+H)+

Figure S186. IR spectrum of **19**



6.20 NMR, MS, and IR spectra of compound 20

Figure S187. ^{1}H NMR spectrum (500 MHz) of **20** in acetone-d_6

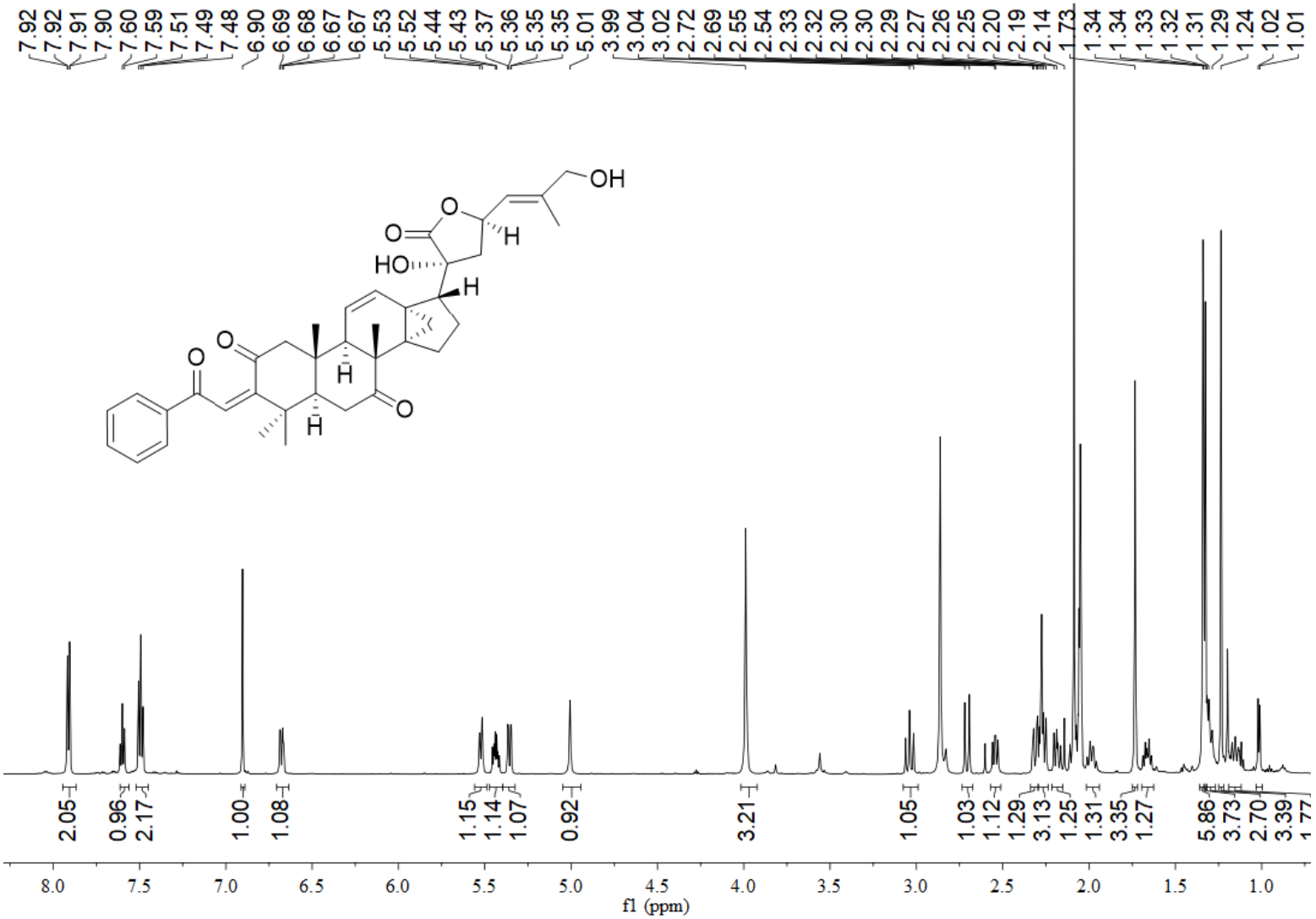


Figure S188. ^{13}C NMR spectrum (125 MHz) of **20** in acetone-d_6

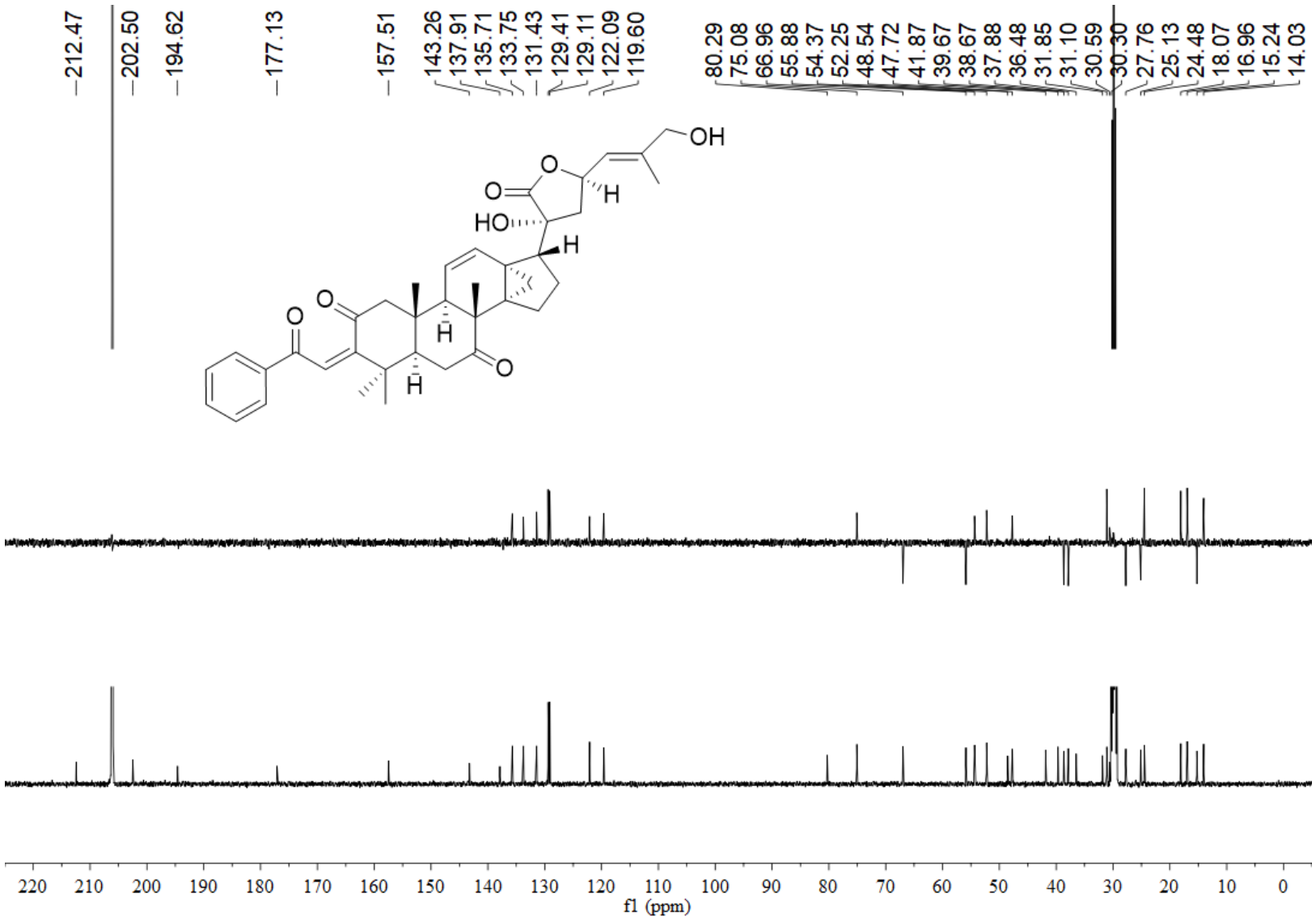


Figure S189. ^{1}H–^{1}H COSY spectrum of **20** in acetone-d_6

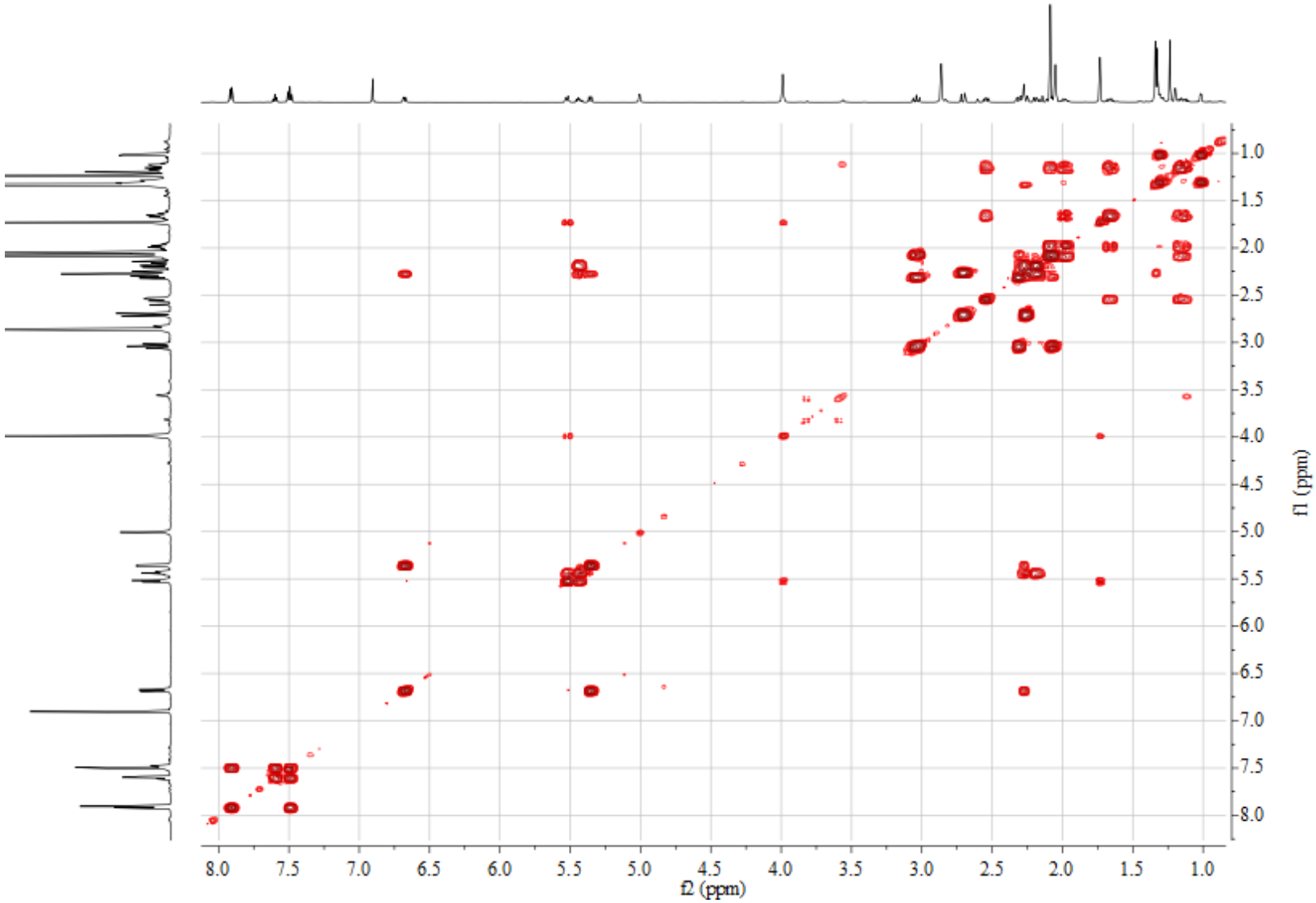


Figure S190. HSQC spectrum of **20** in acetone-d_6

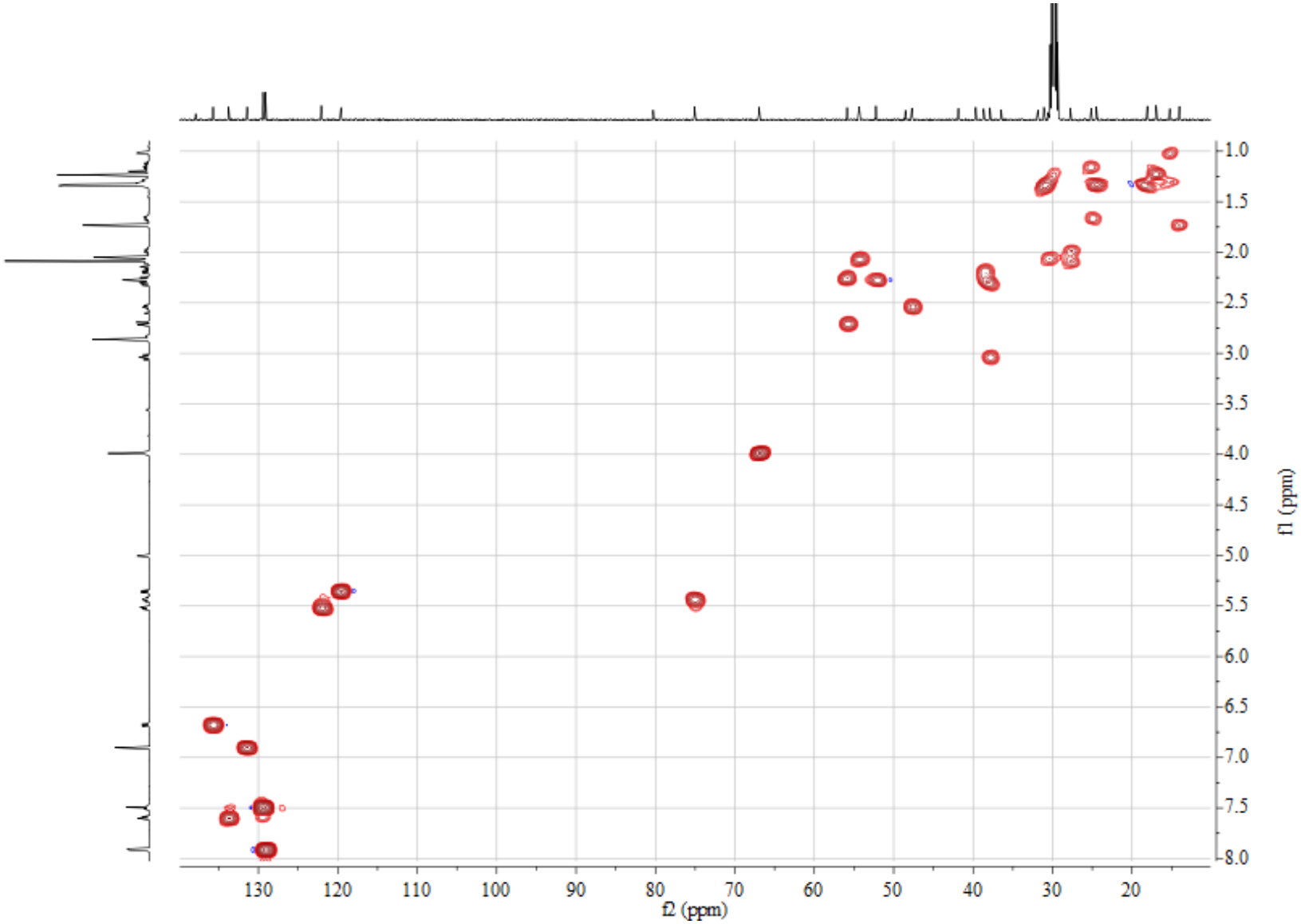


Figure S191. HMBC spectrum of **20** in acetone-d_6

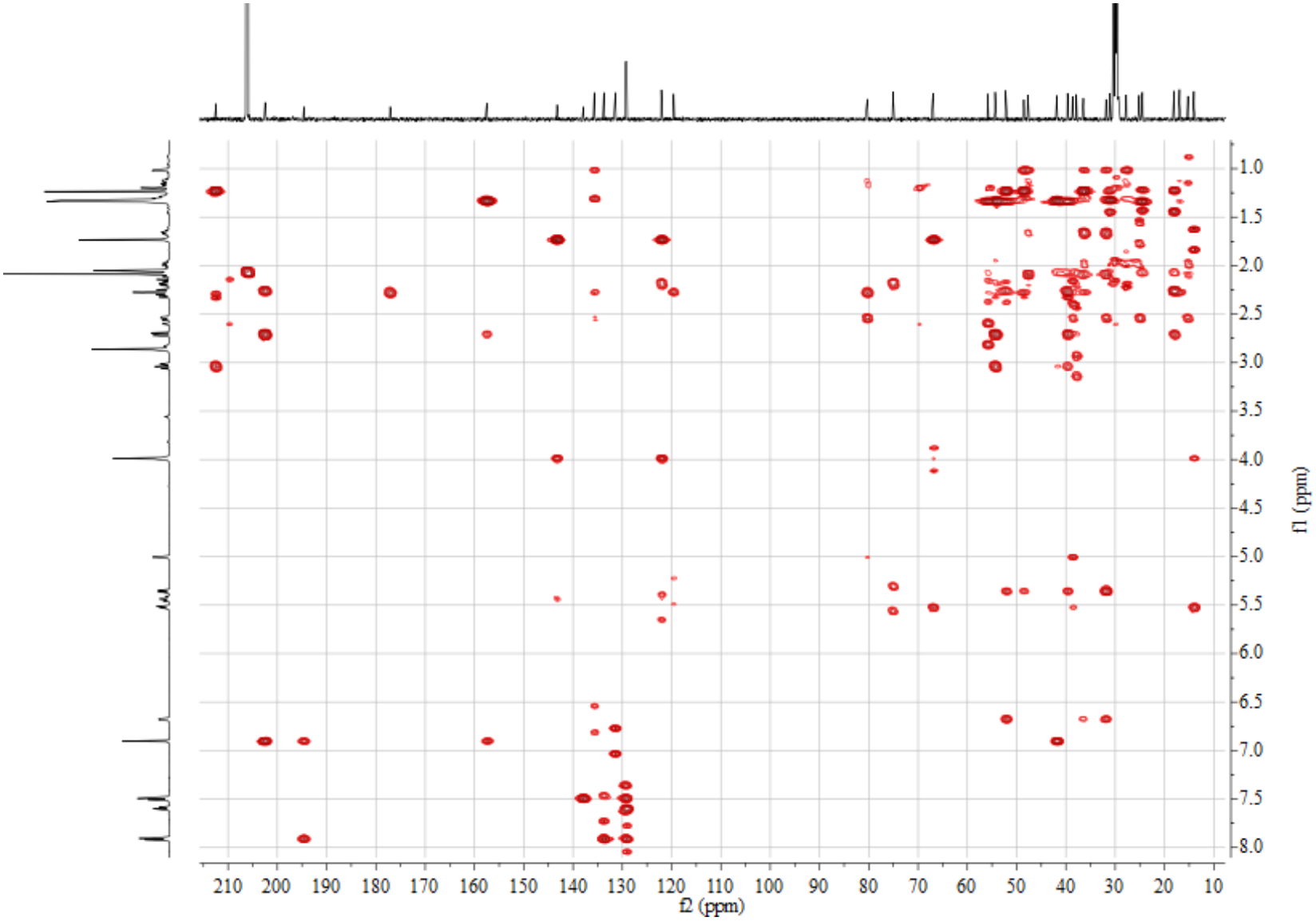


Figure S192. NOESY spectrum of **20** in acetone-d_6

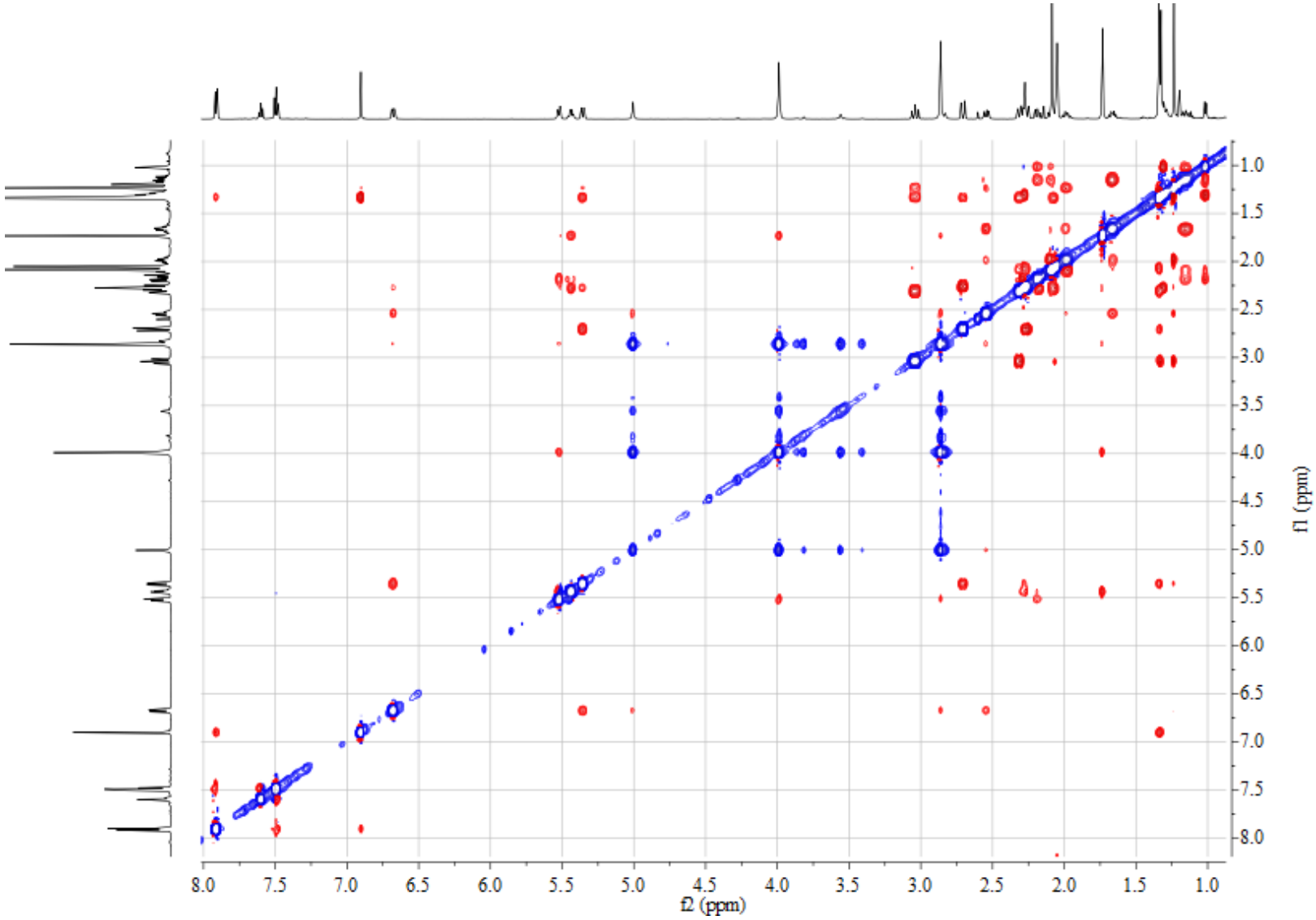


Figure S193. (±)-ESIMS spectra of **20**

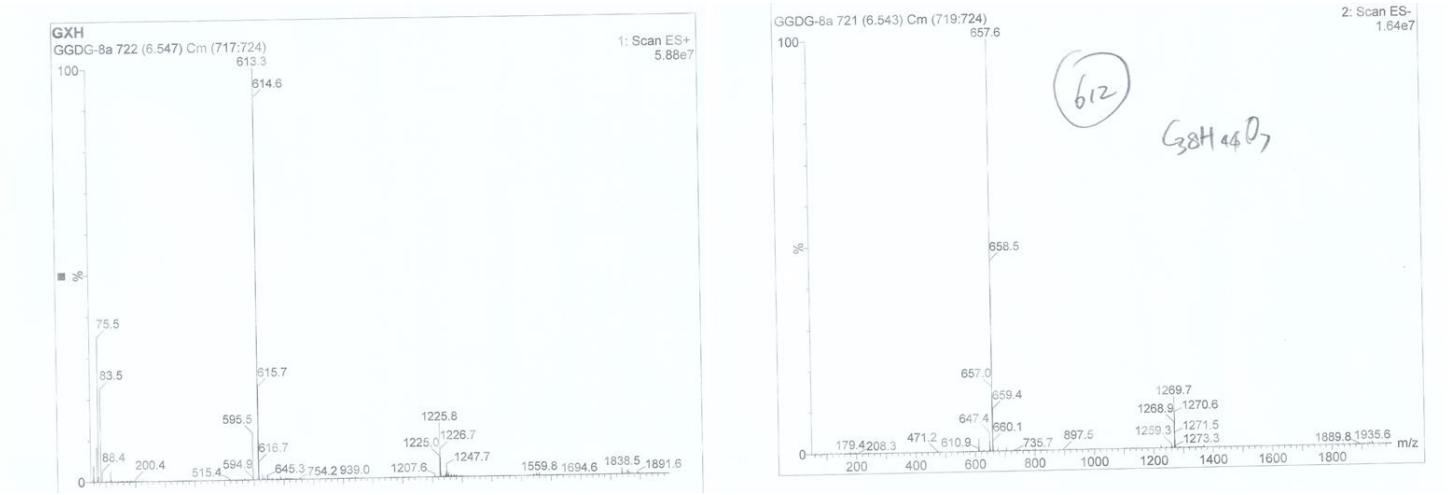
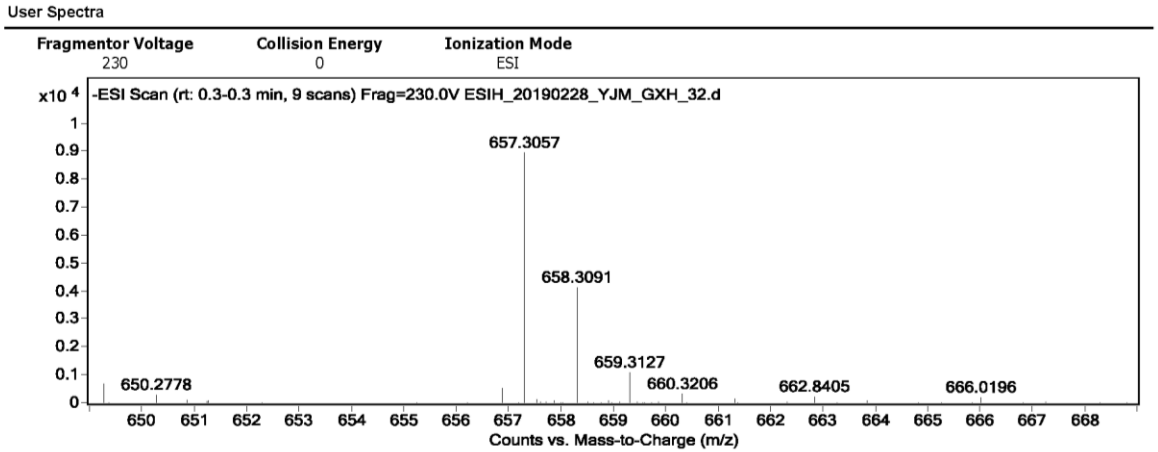


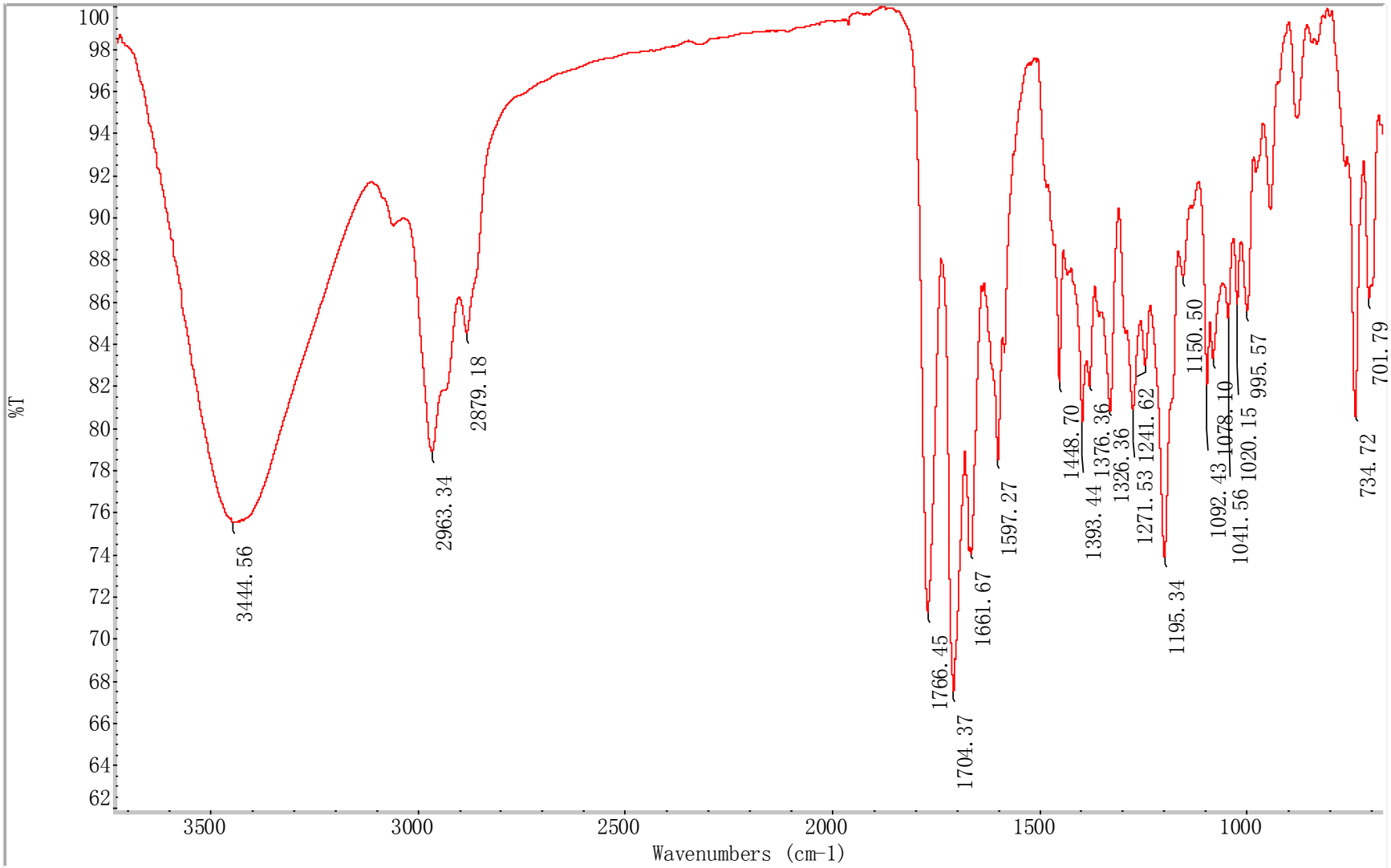
Figure S194. (–)-HRESIMS spectrum of **20**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
657.3057	657.3069	1.24	1.89	C39 H45 O9	(M+COOH)-

Figure S195. IR spectrum of **20**



6.21 NMR, MS, and IR spectra of compound 21

Figure S196. ^{1}H NMR spectrum (500 MHz) of **21** in acetone-d_6

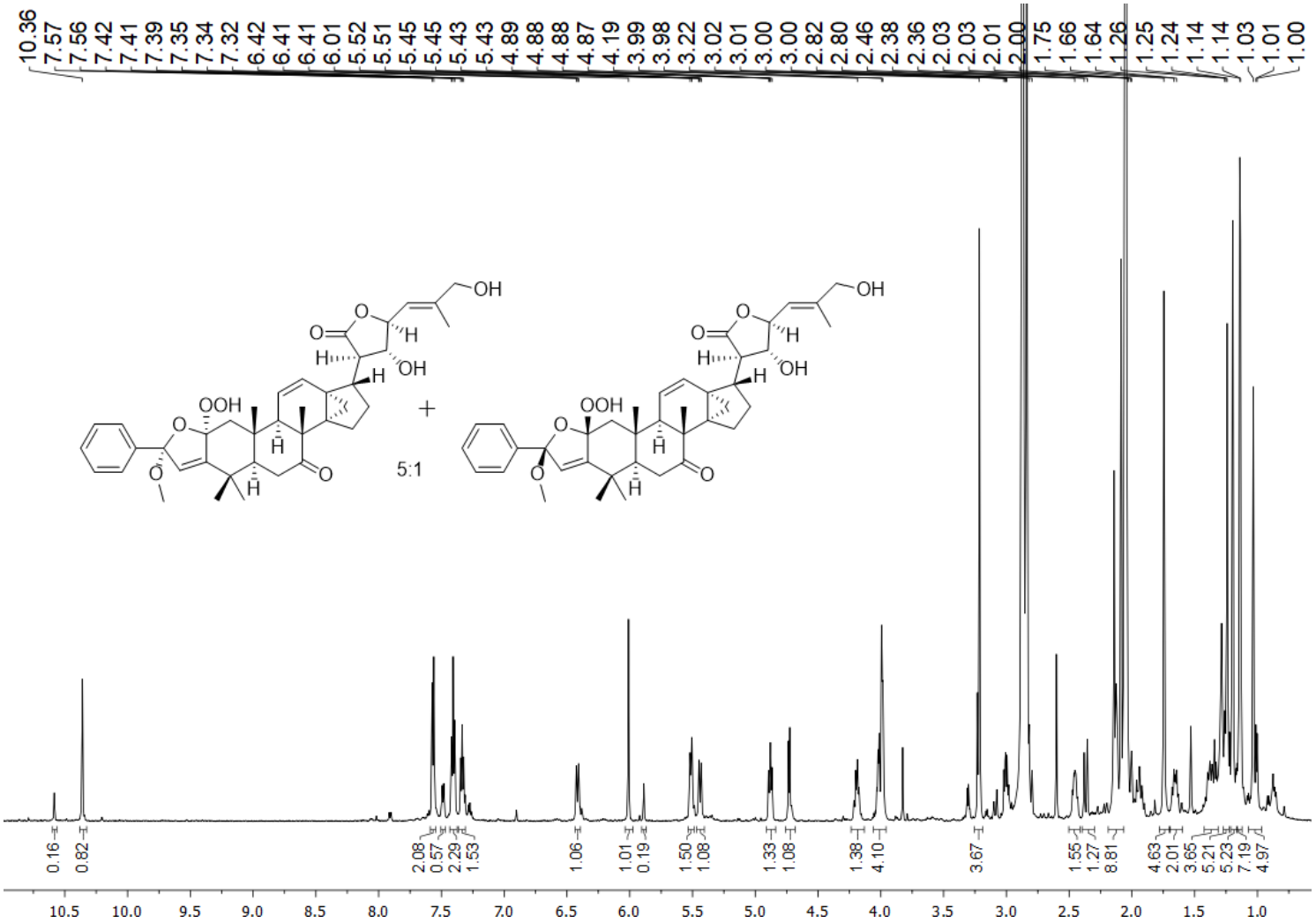


Figure S197. ^{13}C NMR spectrum (125 MHz) of **21** in acetone-d_6

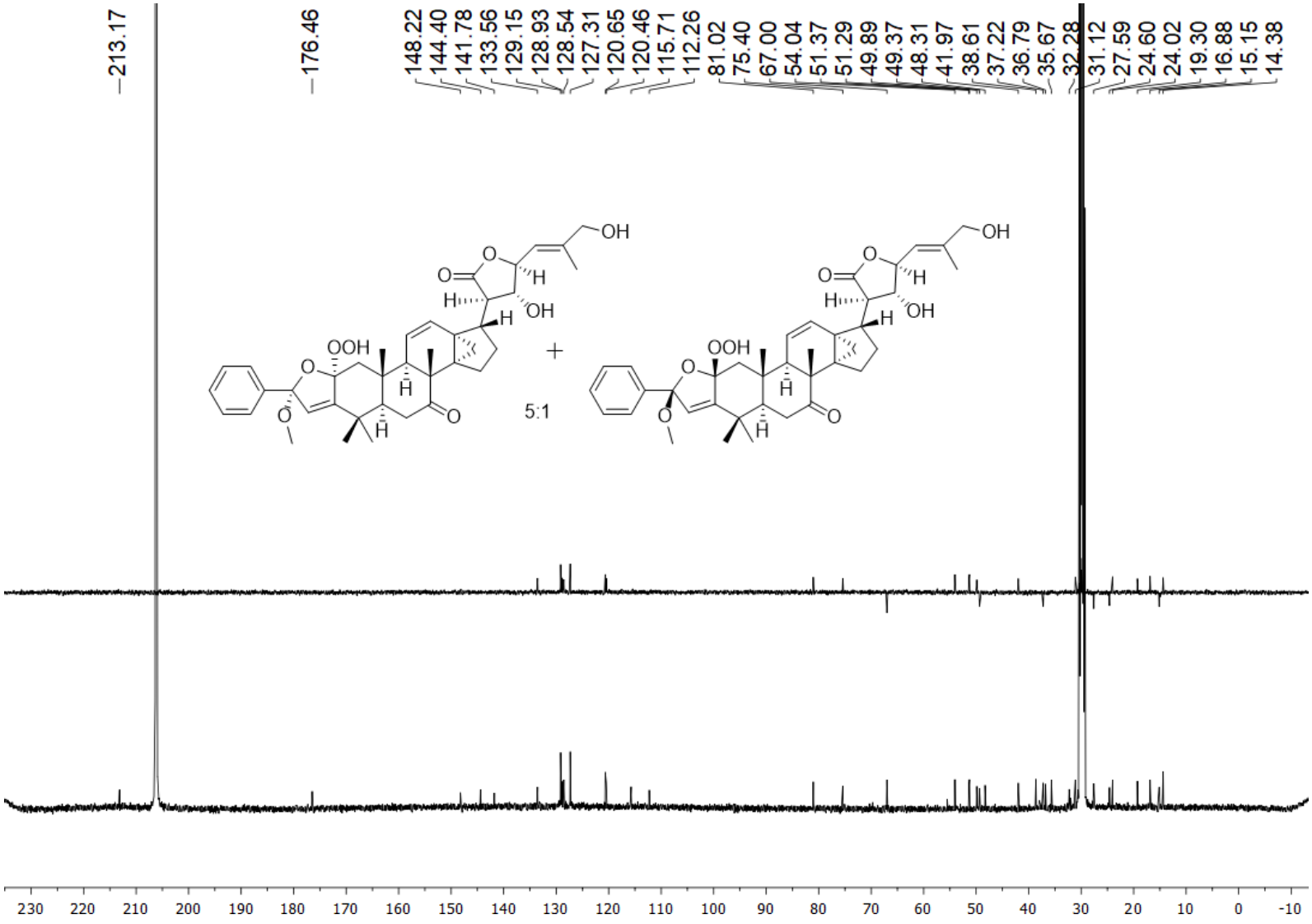


Figure S198. ^{1}H–^{1}H COSY spectrum of **21** in acetone-d_6

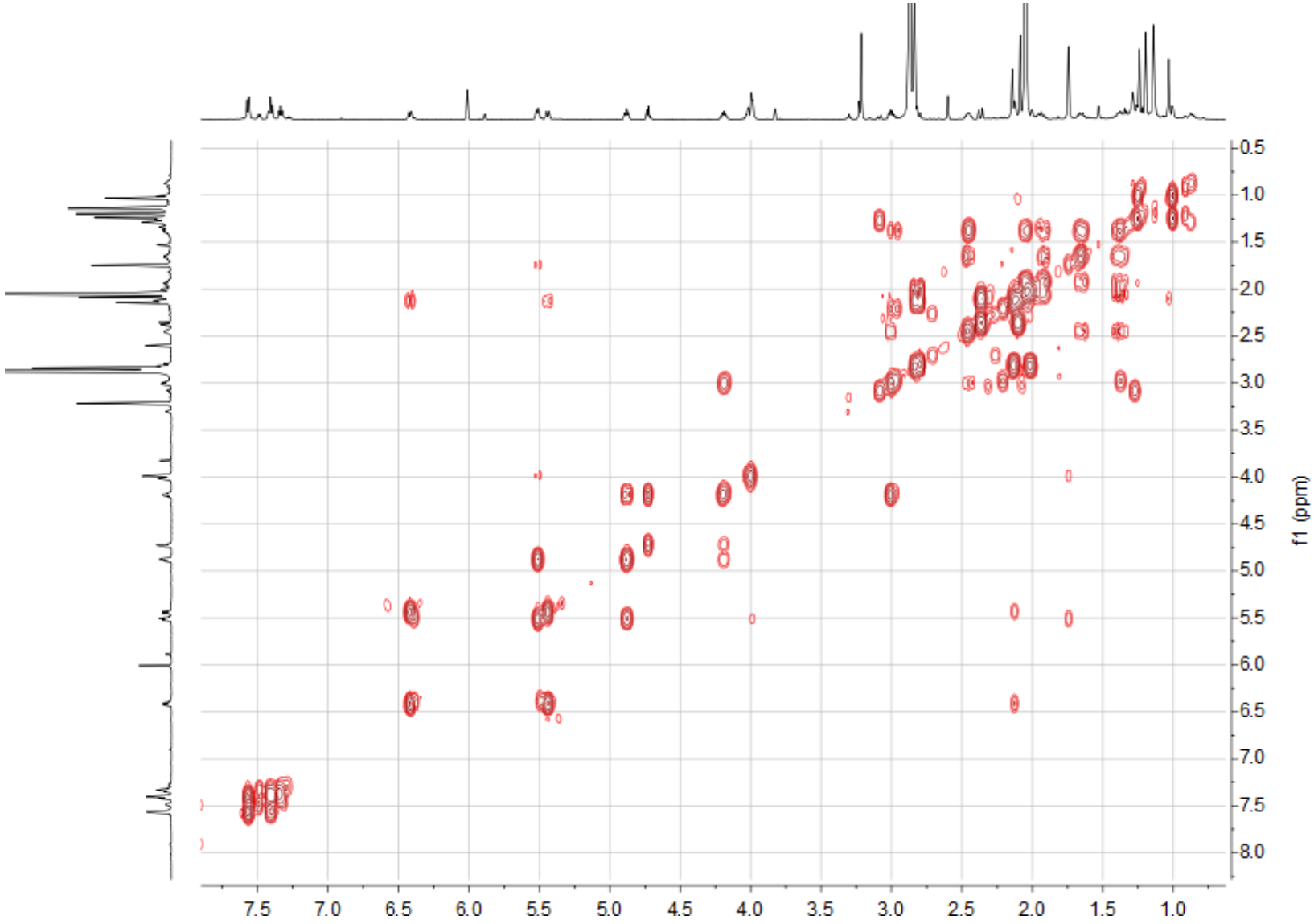


Figure S199. HSQC spectrum of **21** in acetone-d_6

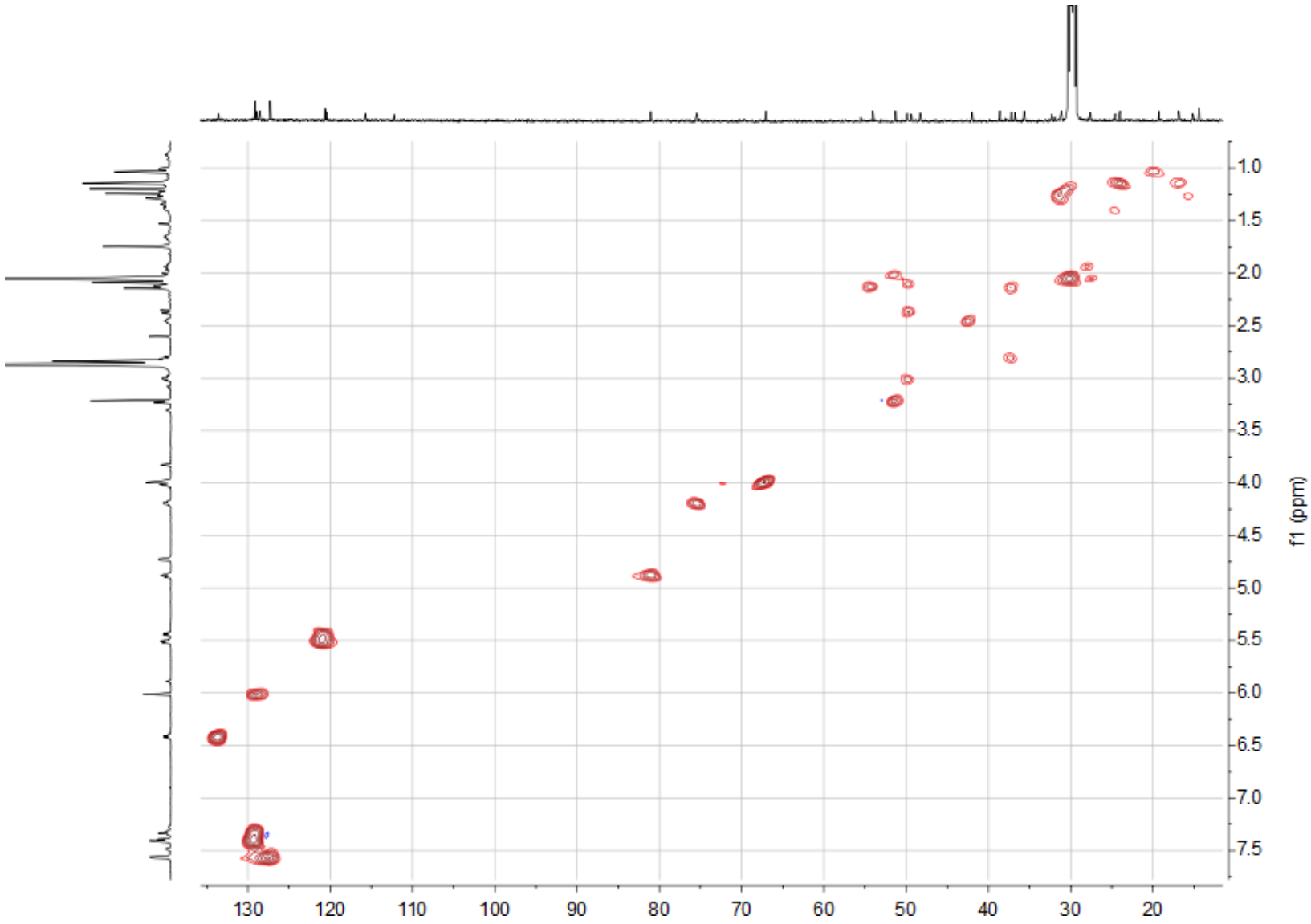


Figure S200. HMBC spectrum of **21** in acetone-d_6

Figure S201. NOESY spectrum of **21** in acetone-d_6

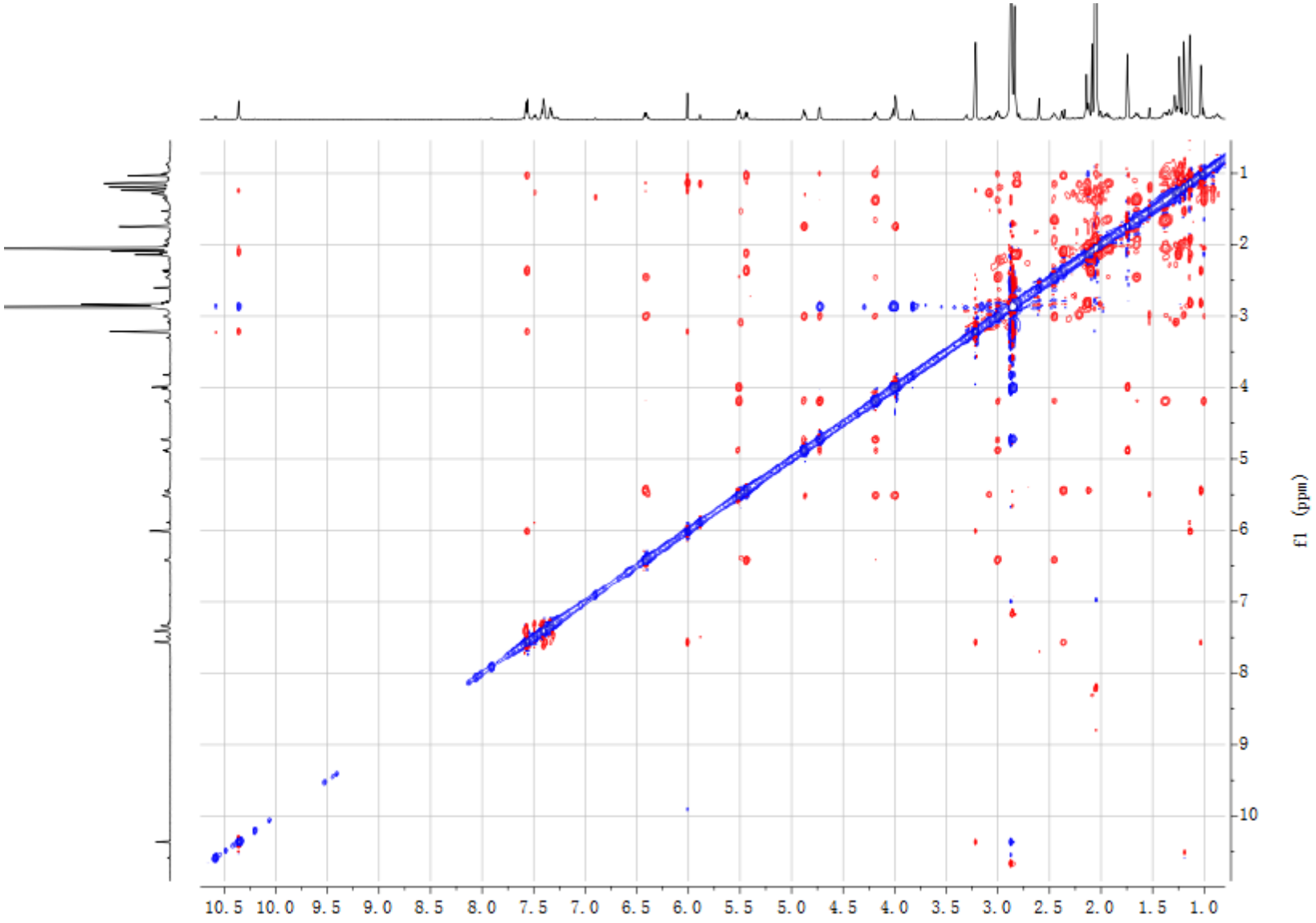


Figure S202. (±)-ESIMS spectra of **21**

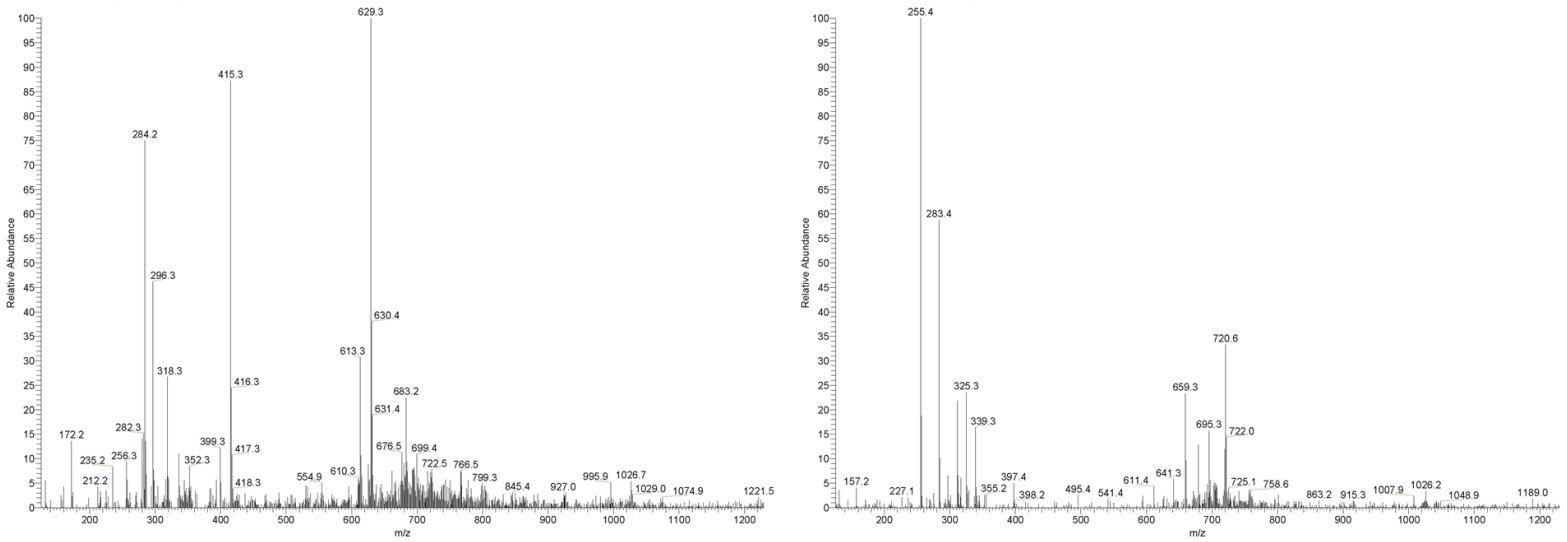
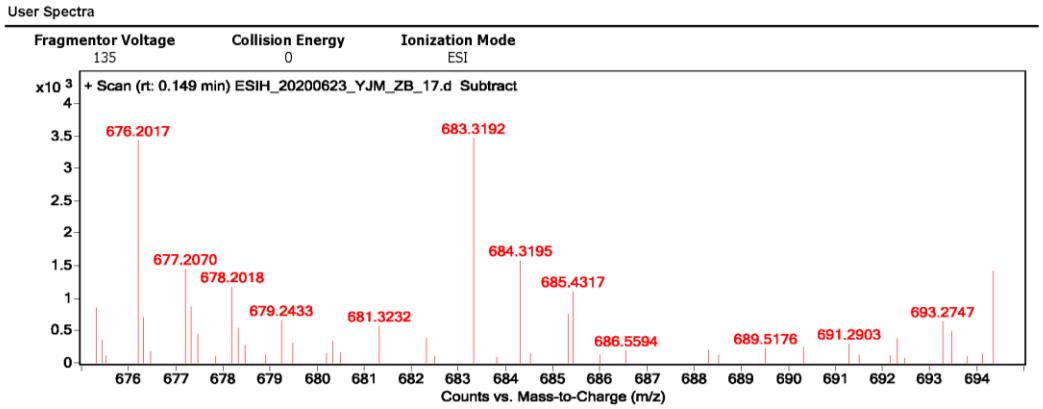


Figure S203. (–)-HRESIMS spectrum of **21**



Formula Calculator Results

m/z	Calc m/z	Diff (mDa)	Diff (ppm)	Ion Formula	Ion
683.3192	683.3191	-0.19	-0.28	C39 H48 Na O9	(M+Na)+

6.22 ^{1}H NMR and MS spectra of synthetic 1a–4a, 13–16, and 17–20

Figure S204. ^{1}H NMR spectrum (500 MHz) of **1a** in CD_3OD

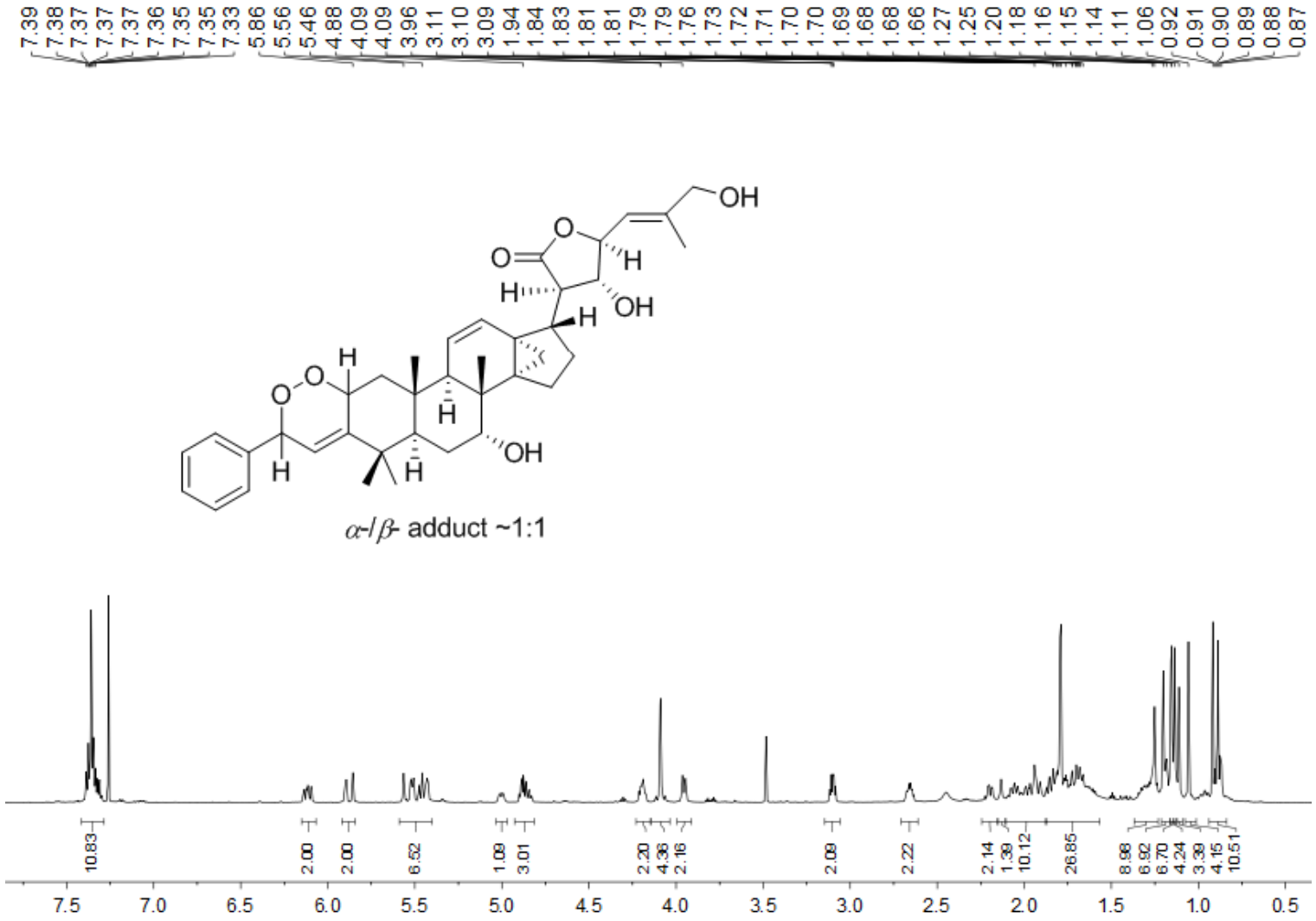


Figure S205. (±)-ESIMS spectra of **1a**

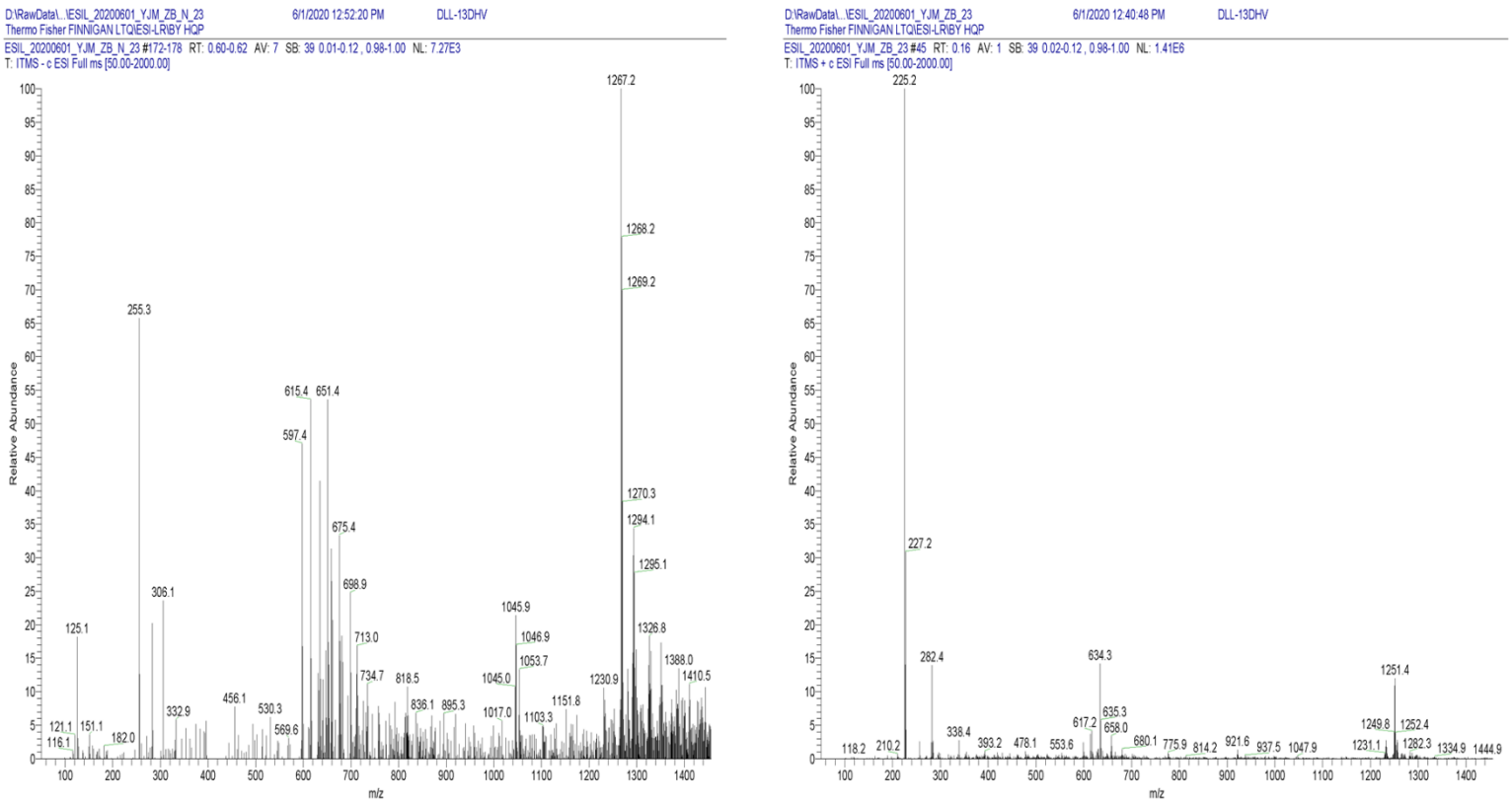


Figure S206. ^{1}H NMR spectrum (500 MHz) of **2a** in CD_3OD

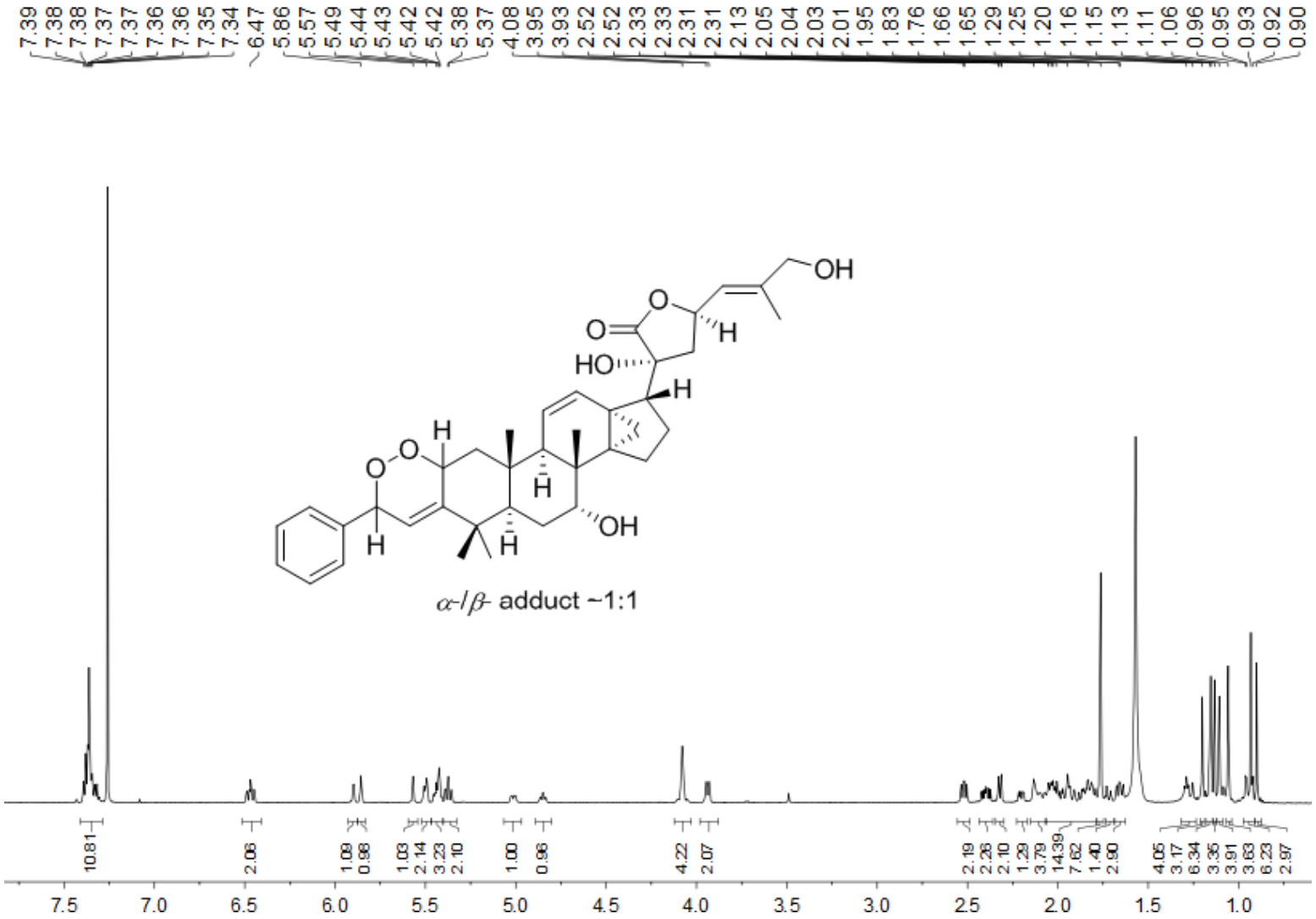


Figure S207. (±)-ESIMS spectra of **2a**

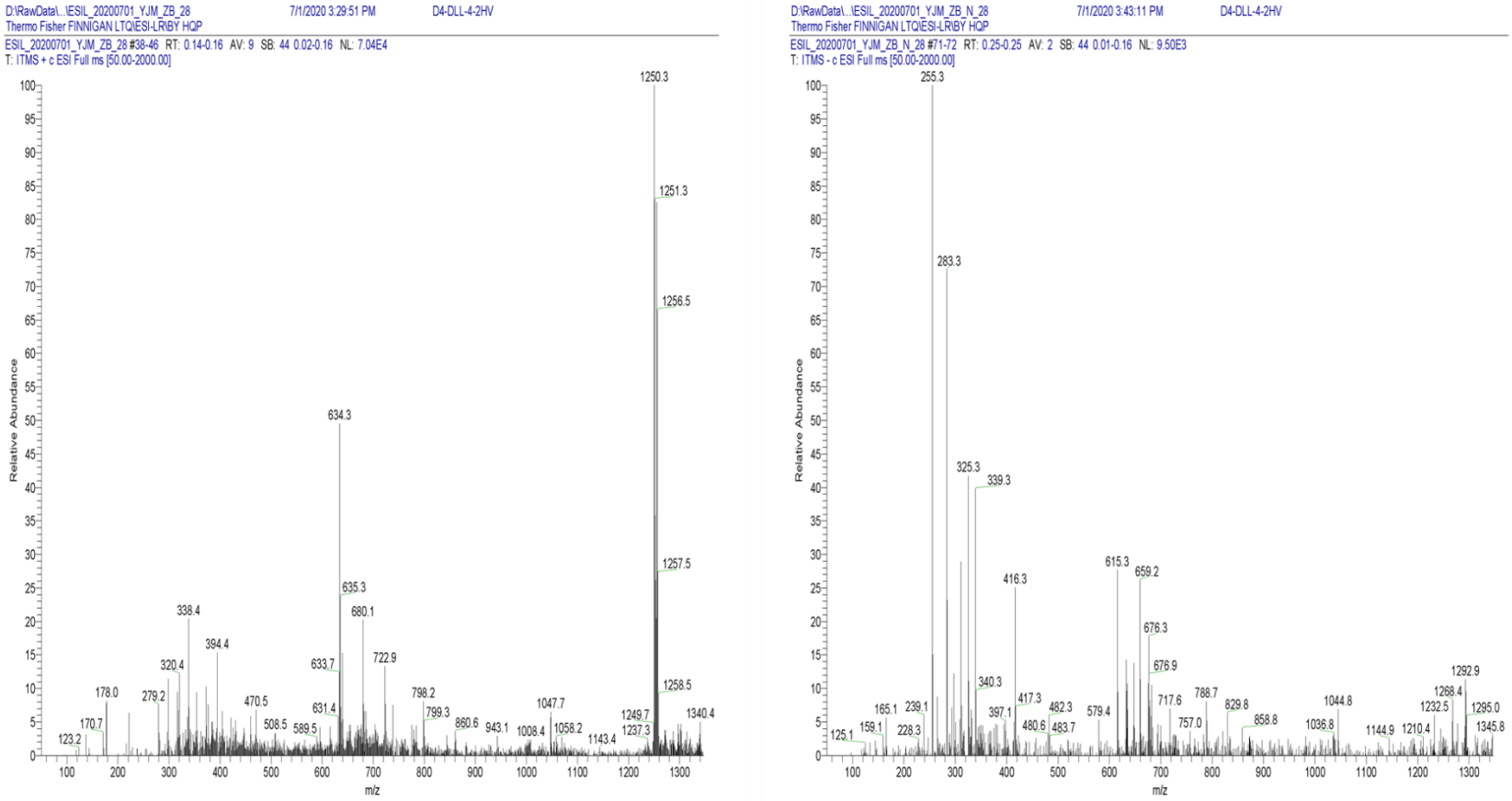


Figure S208. ^{1}H NMR spectrum (500 MHz) of **3a** in CD_3OD

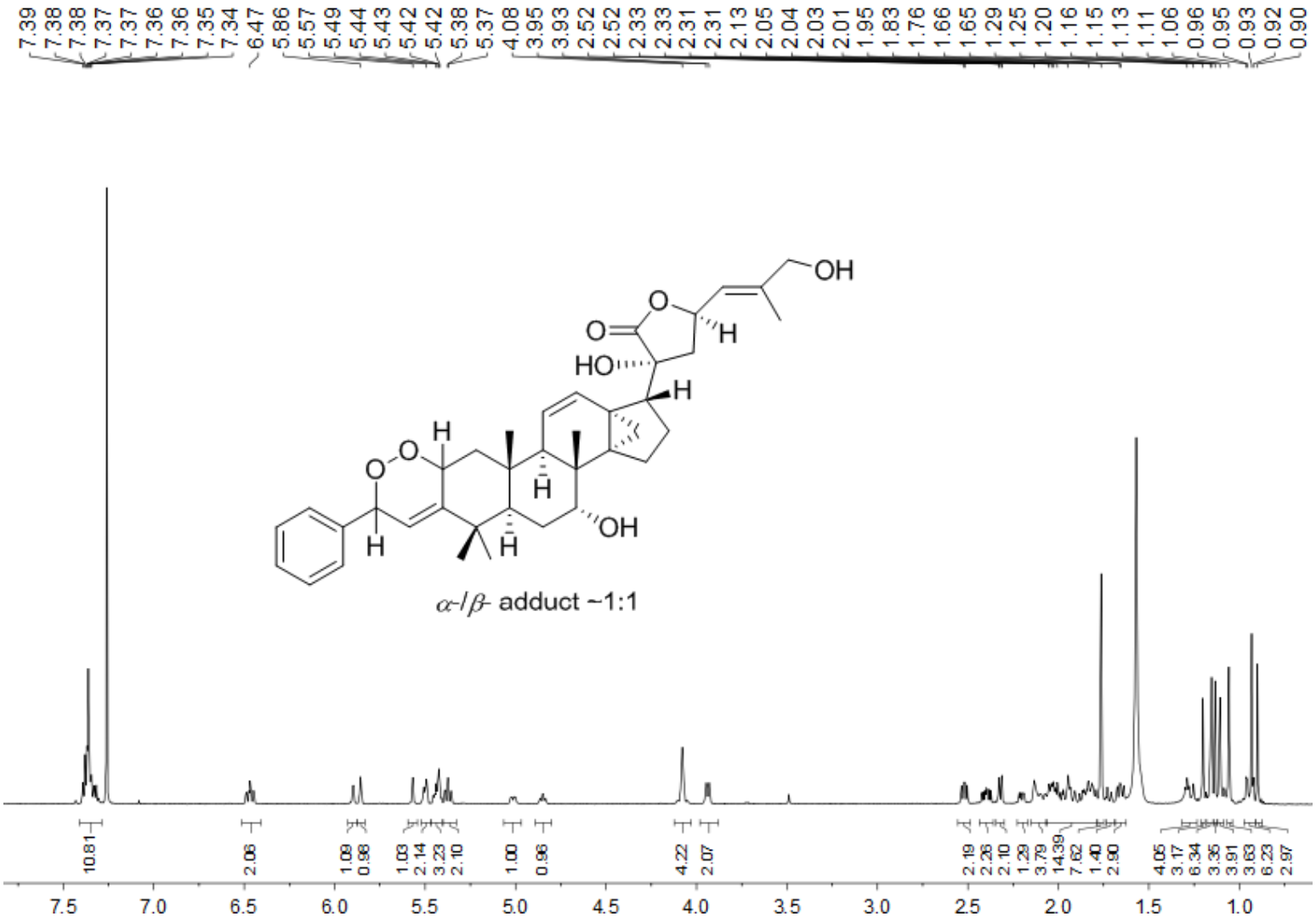


Figure S209. (±)-ESIMS spectra of **3a**

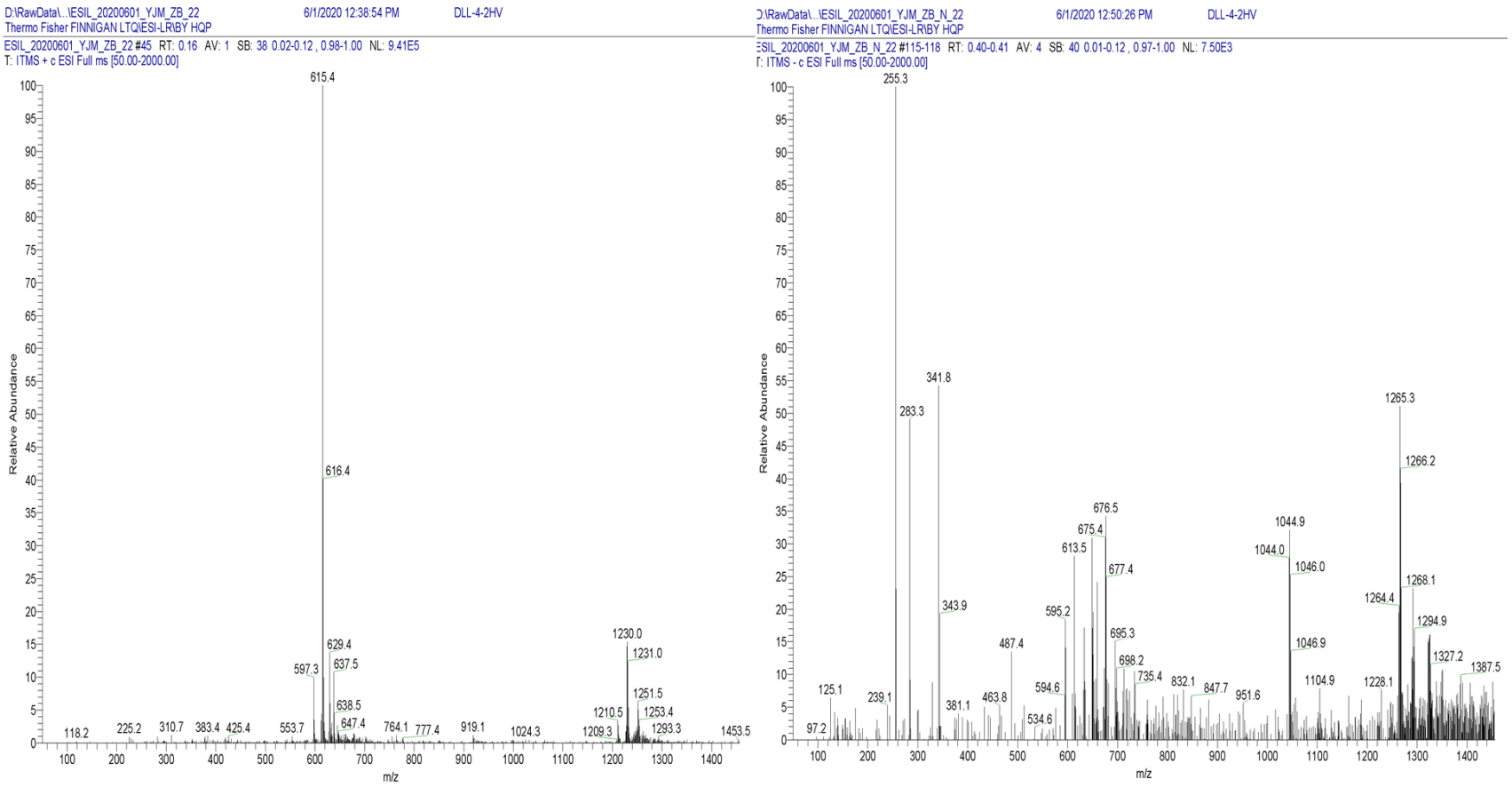


Figure S210. ^{1}H NMR spectrum (500 MHz) of **4a** in CD_3OD

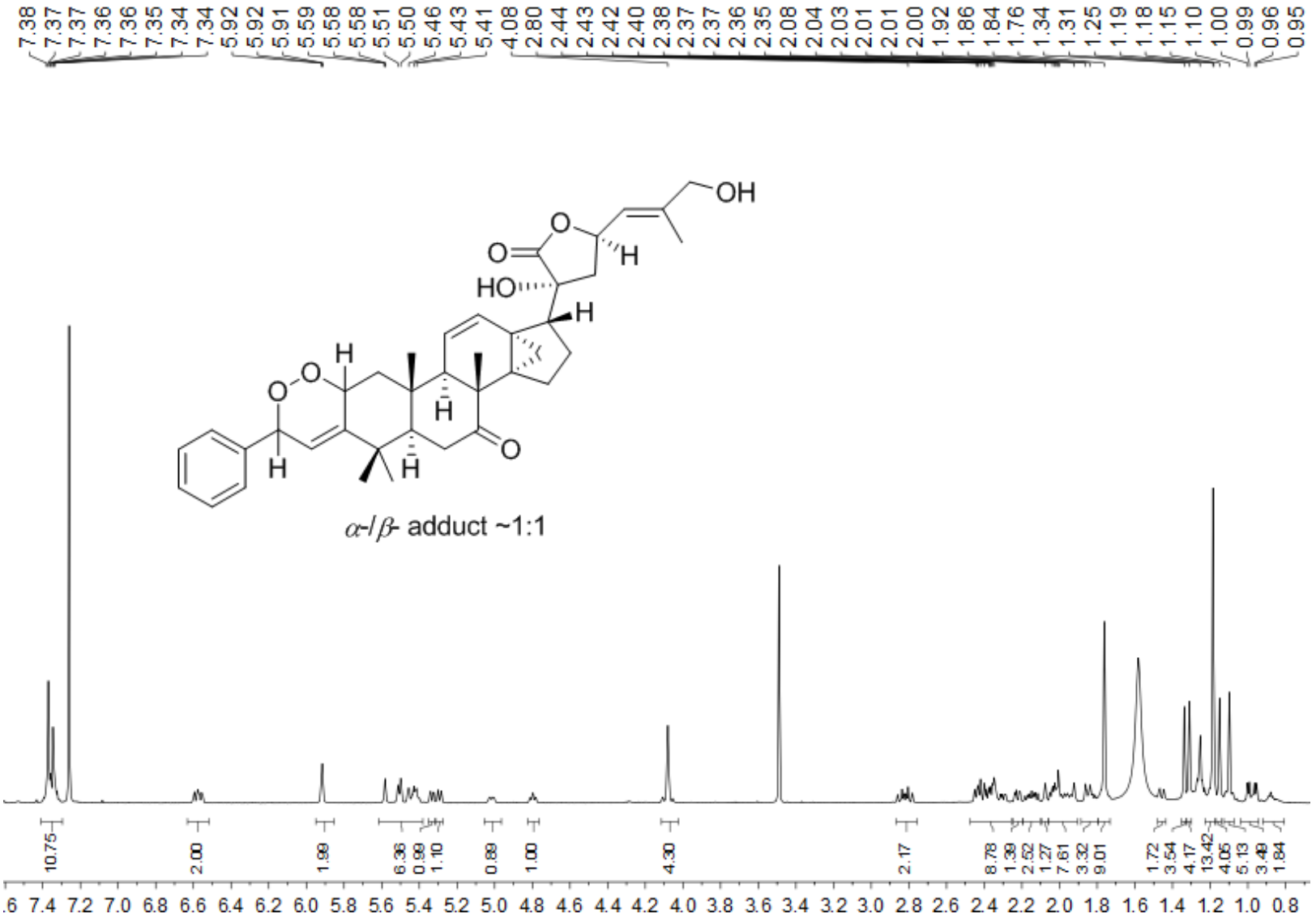


Figure S211. (±)-ESIMS spectra of **4a**

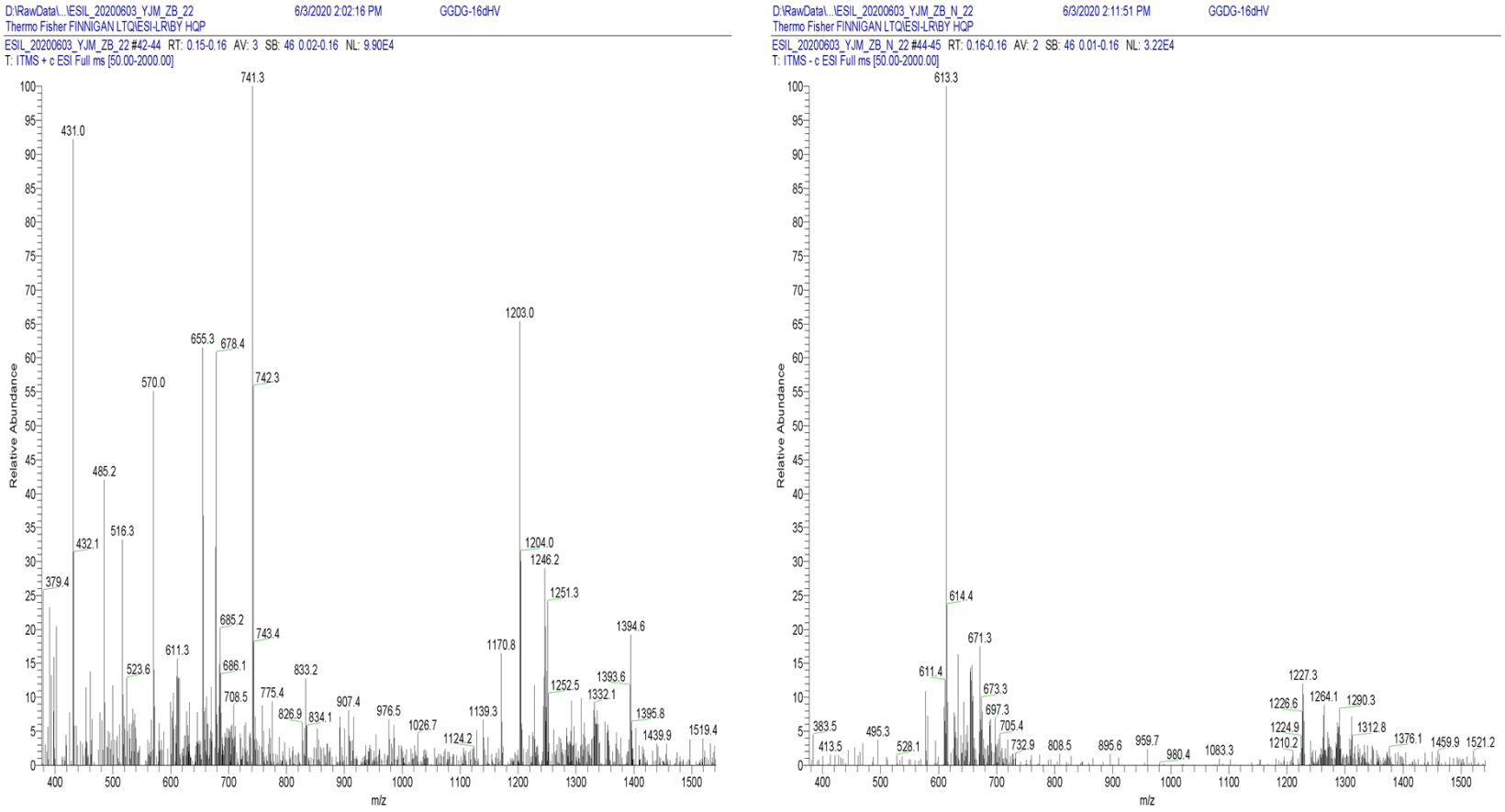


Figure S212. ^{1}H NMR spectrum (500 MHz) of **13** in CD_3OD

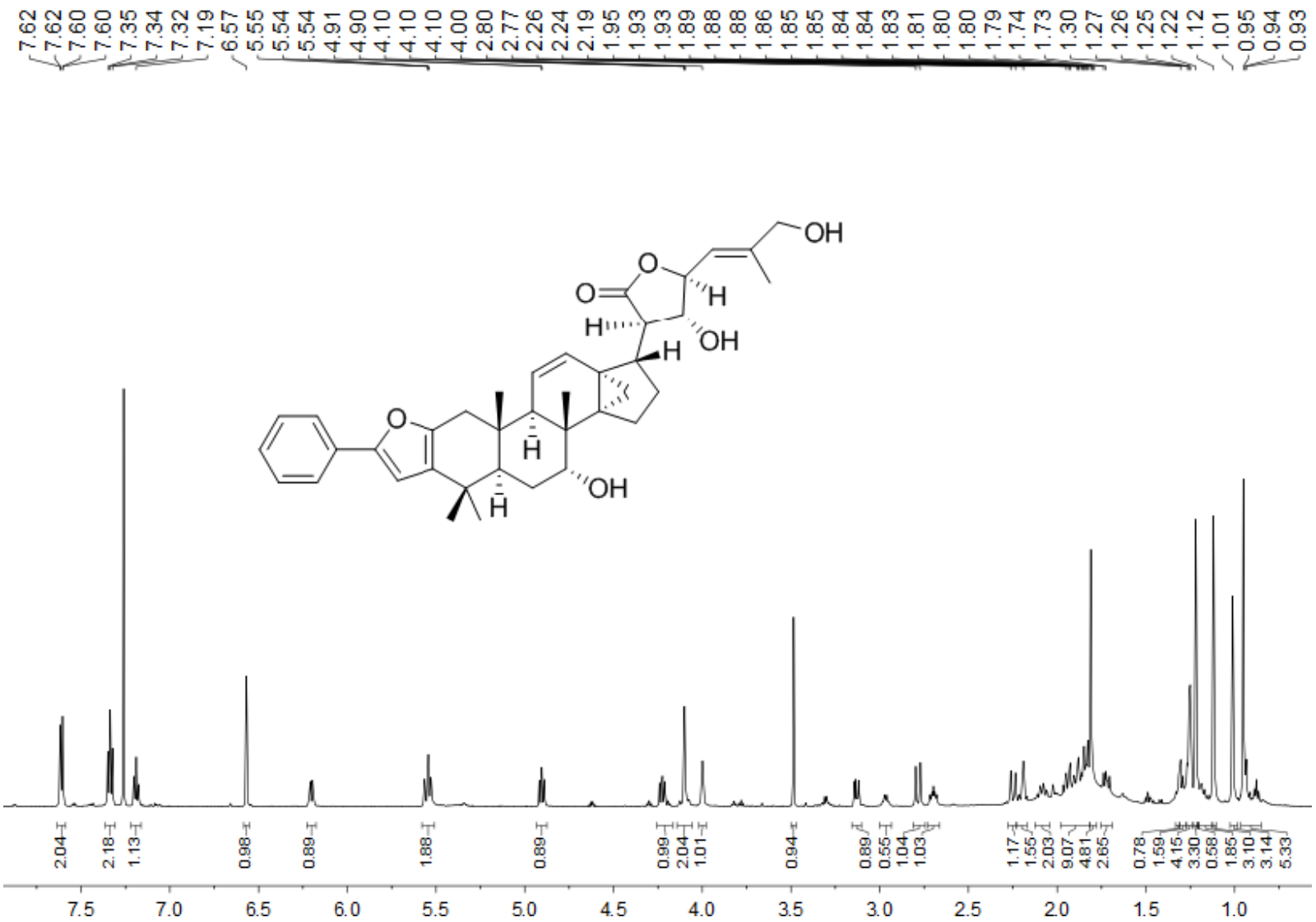


Figure S213. (±)-ESIMS spectra of **13**

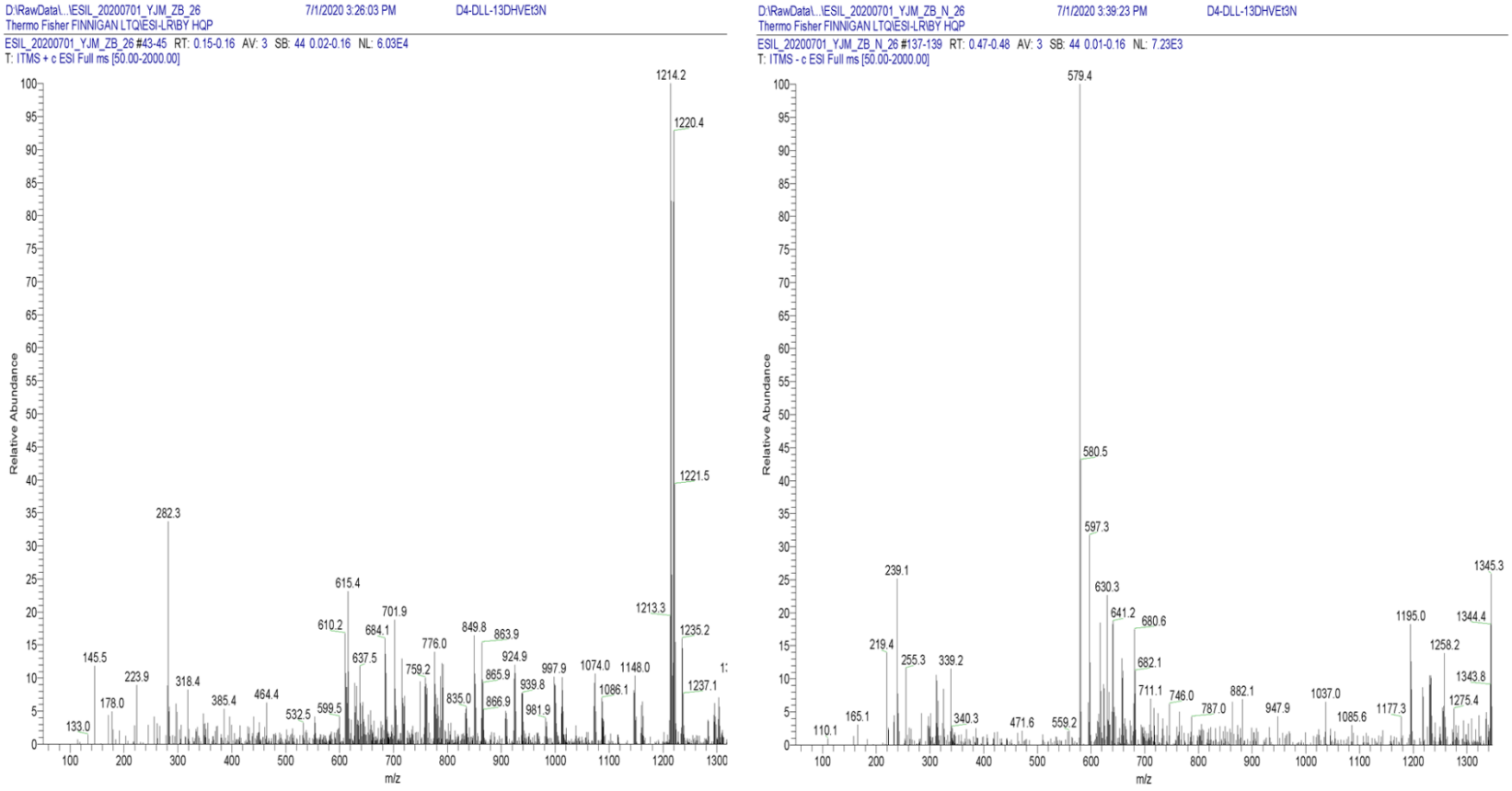


Figure S214. ^{1}H NMR spectrum (500 MHz) of **14** in CD_3OD

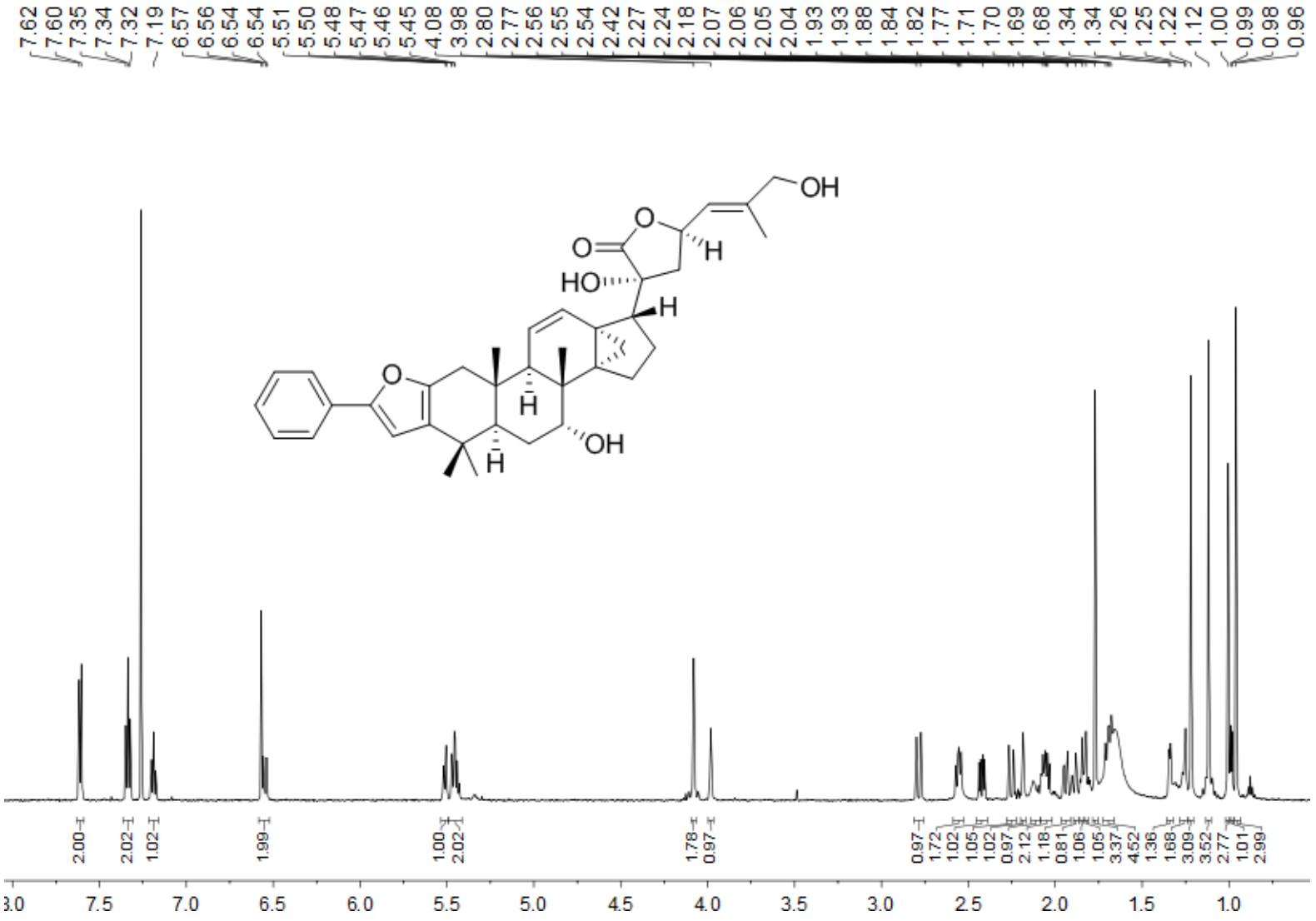


Figure S215. (±)-ESIMS spectra of **14**

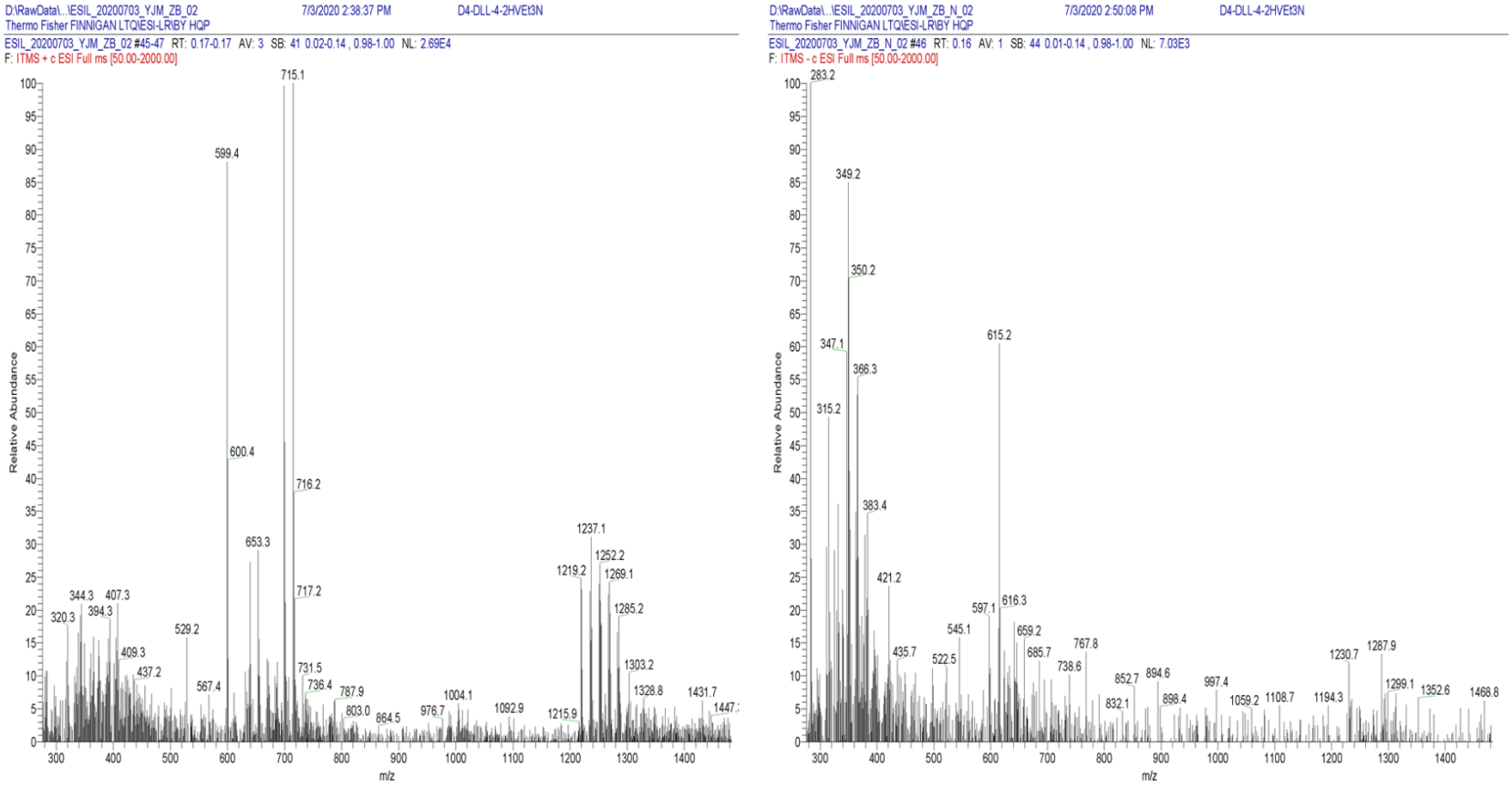


Figure S216. ^{1}H NMR spectrum (500 MHz) of **15** in CD_3OD

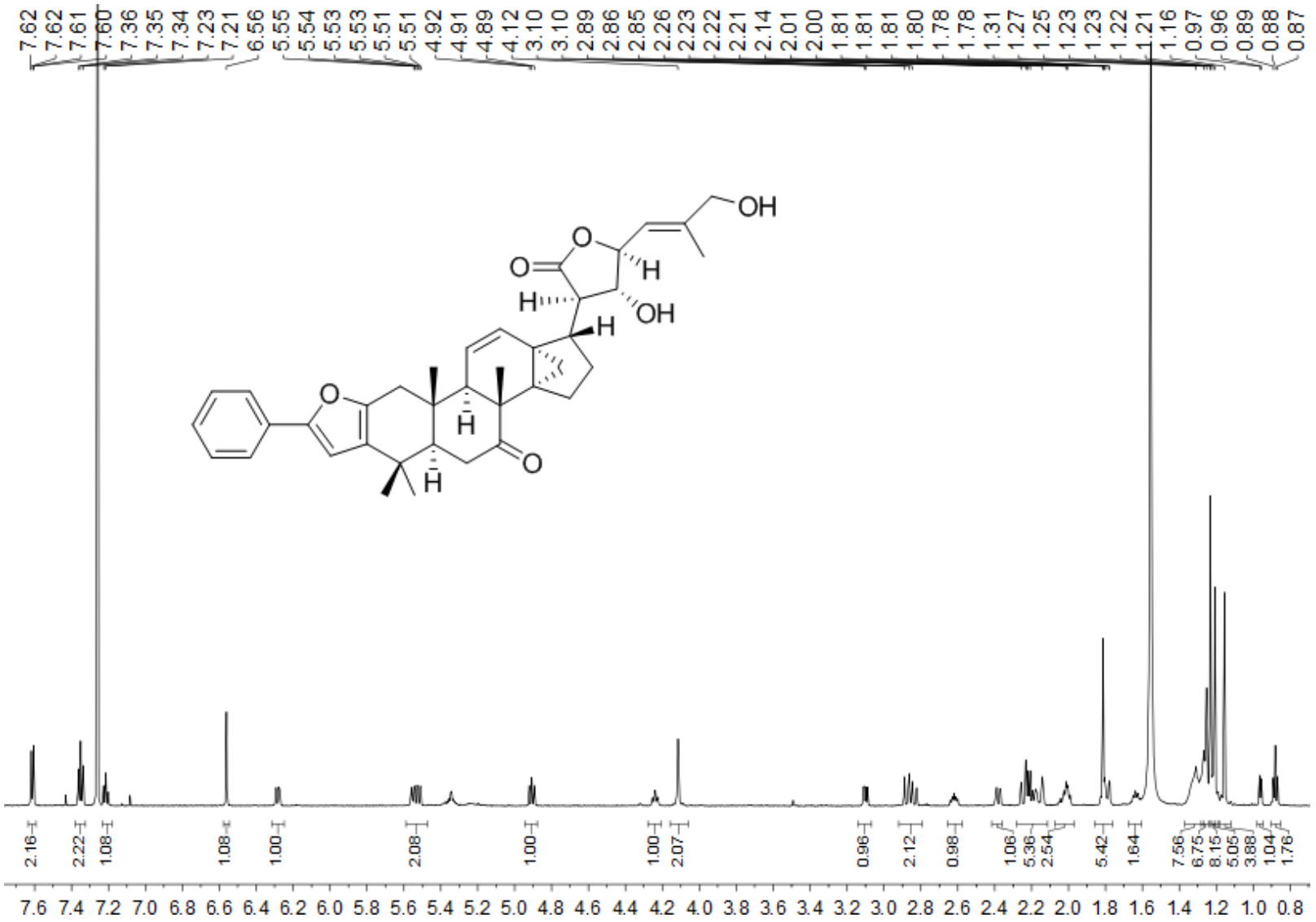


Figure S217. (±)-ESIMS spectra of **15**

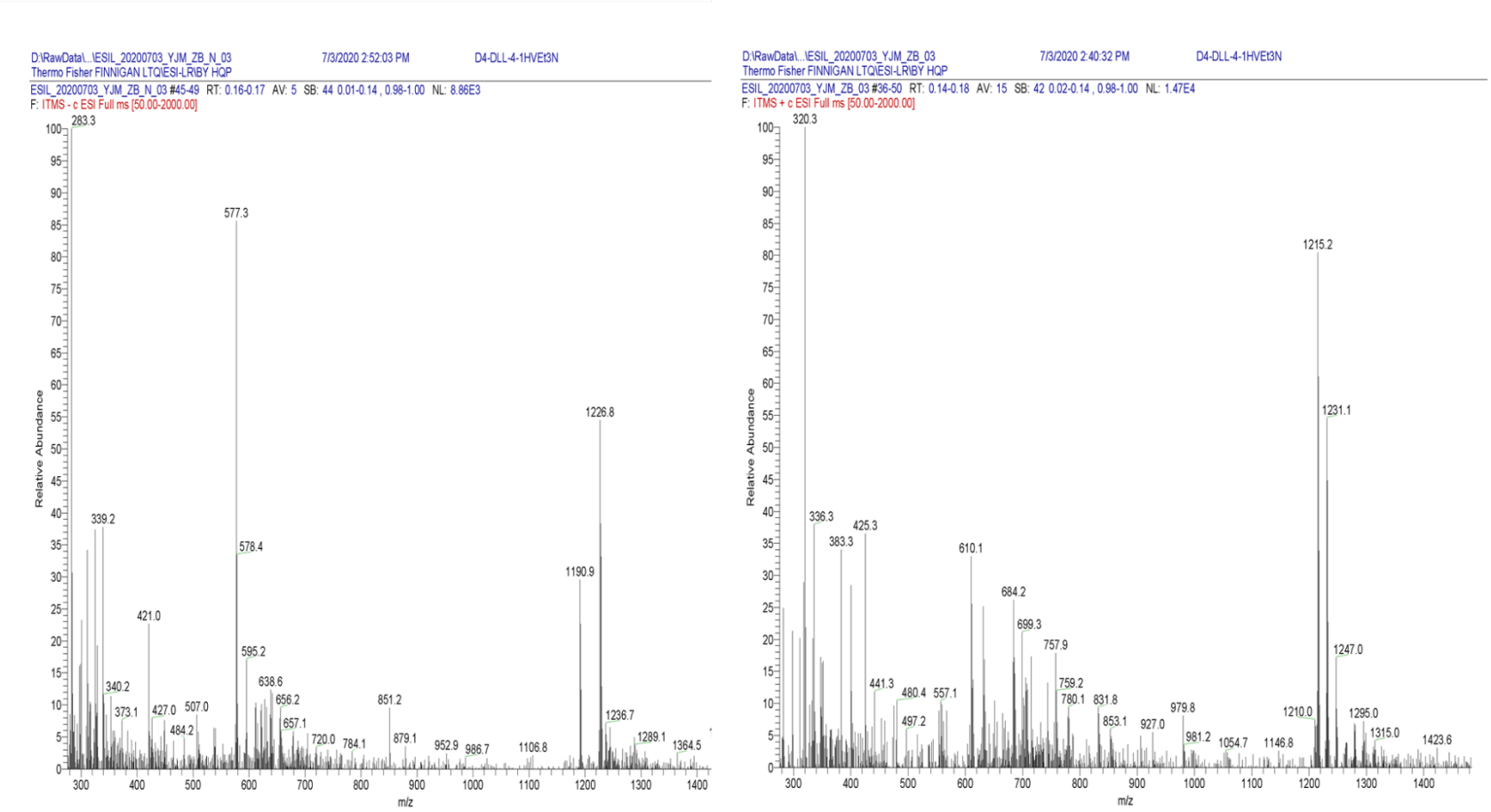


Figure S218. ^{1}H NMR spectrum (500 MHz) of **16** in CD_3OD

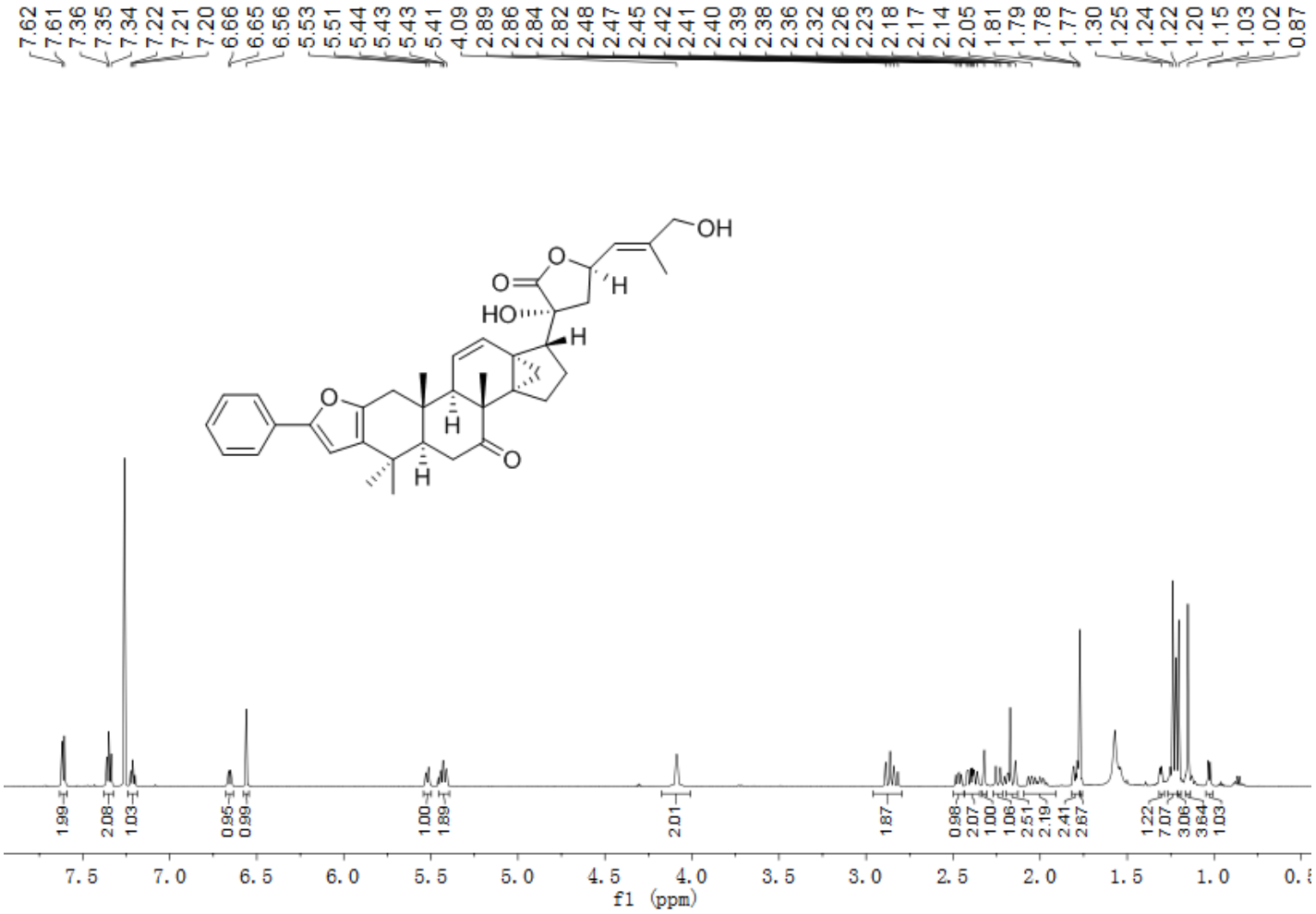


Figure S219. (±)-ESIMS spectra of **16**

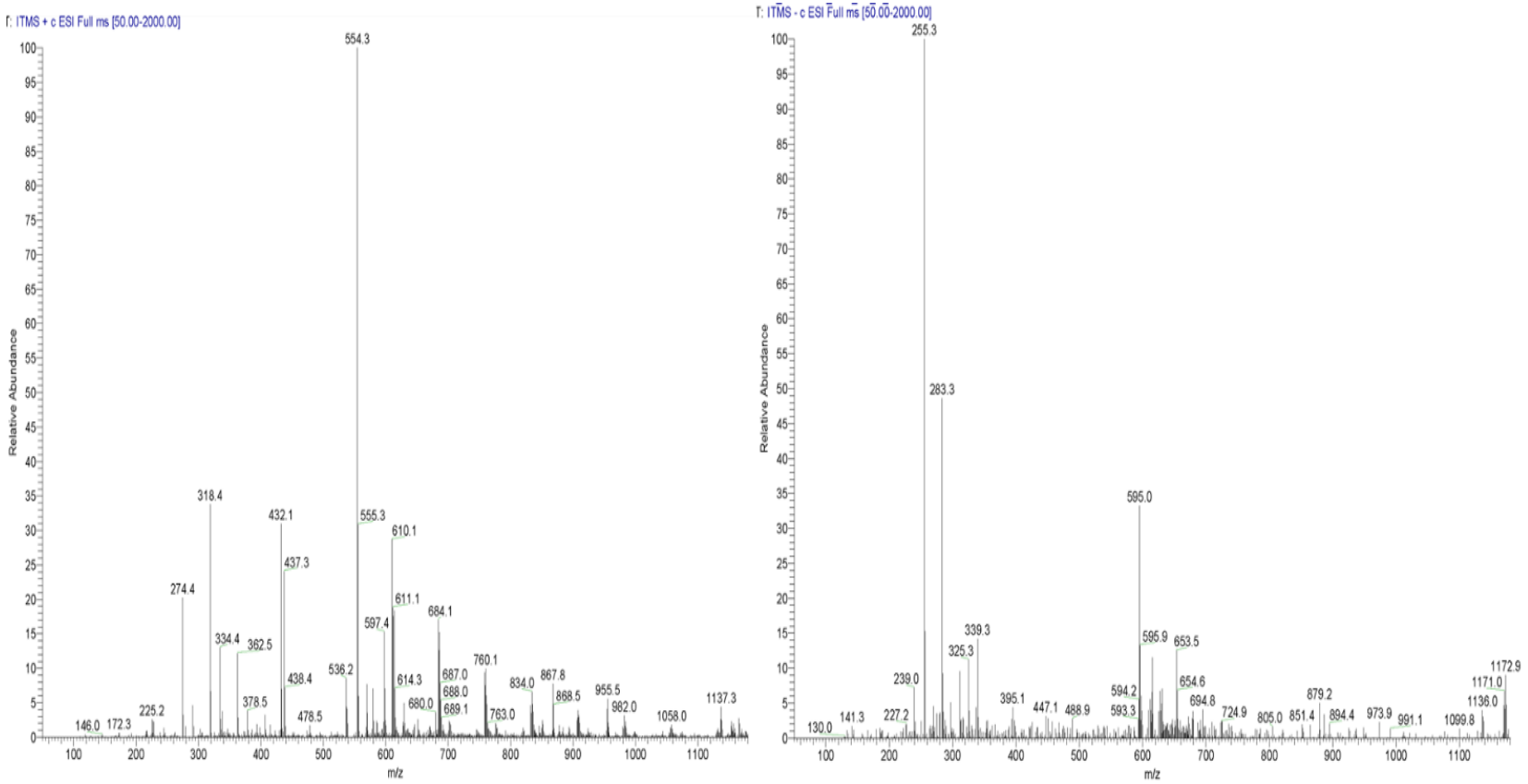


Figure S220. ^{1}H NMR spectrum (500 MHz) of **17** in CD_3OD

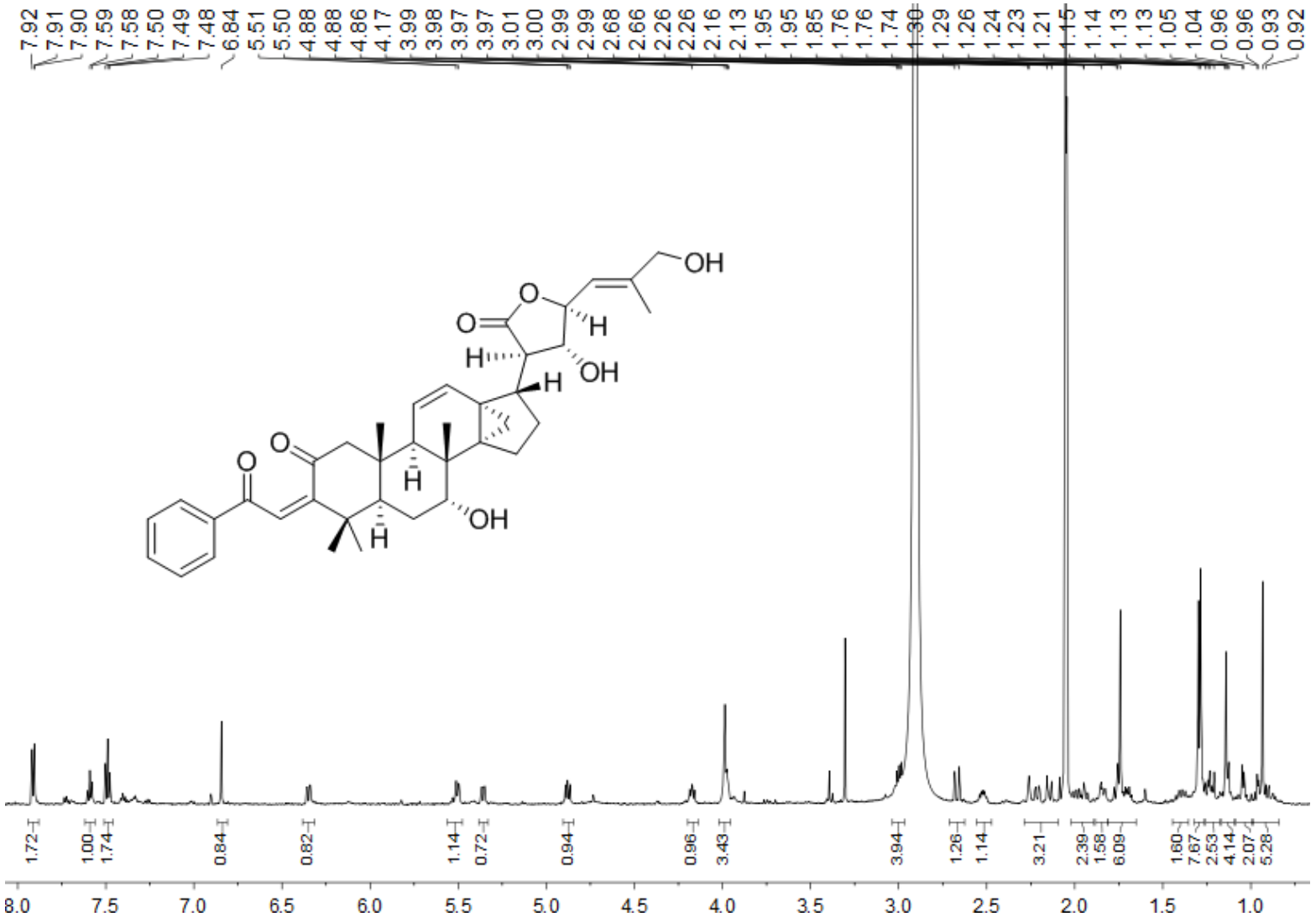


Figure S221. (±)-ESIMS spectra of **17**

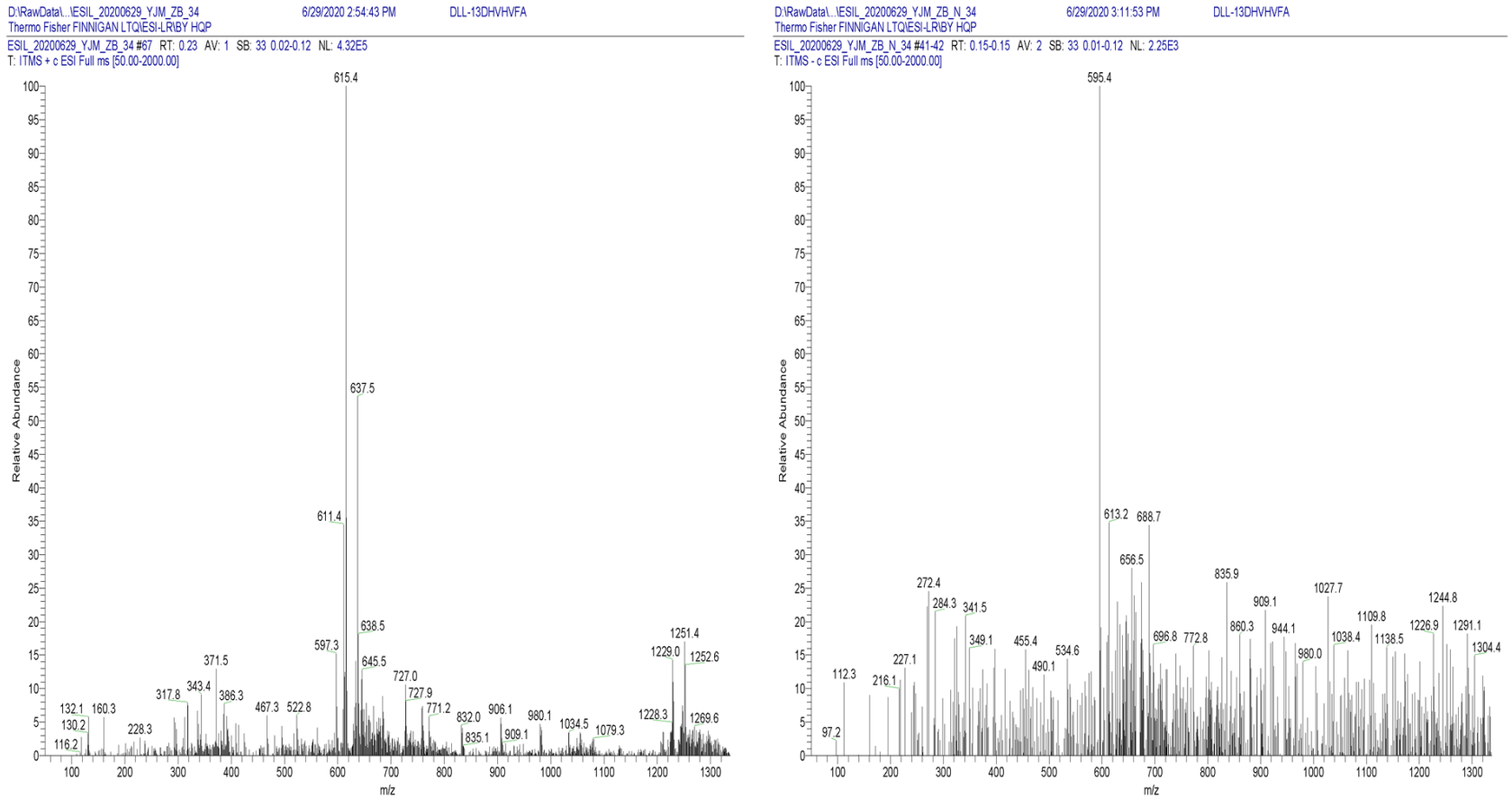


Figure S222. ^{1}H NMR spectrum (500 MHz) of **18** in CD_3OD

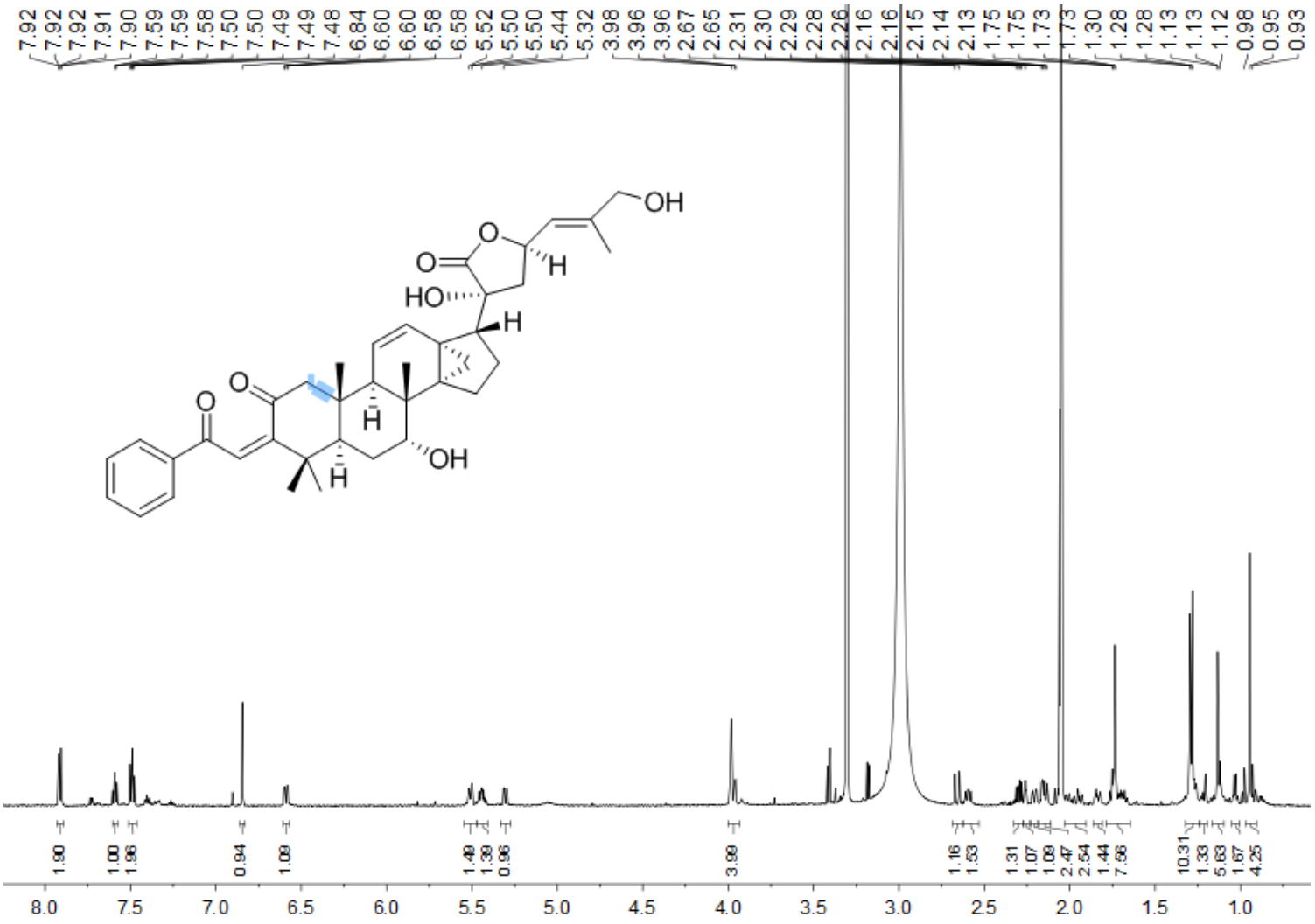


Figure S223. (±)-ESIMS spectra of **18**

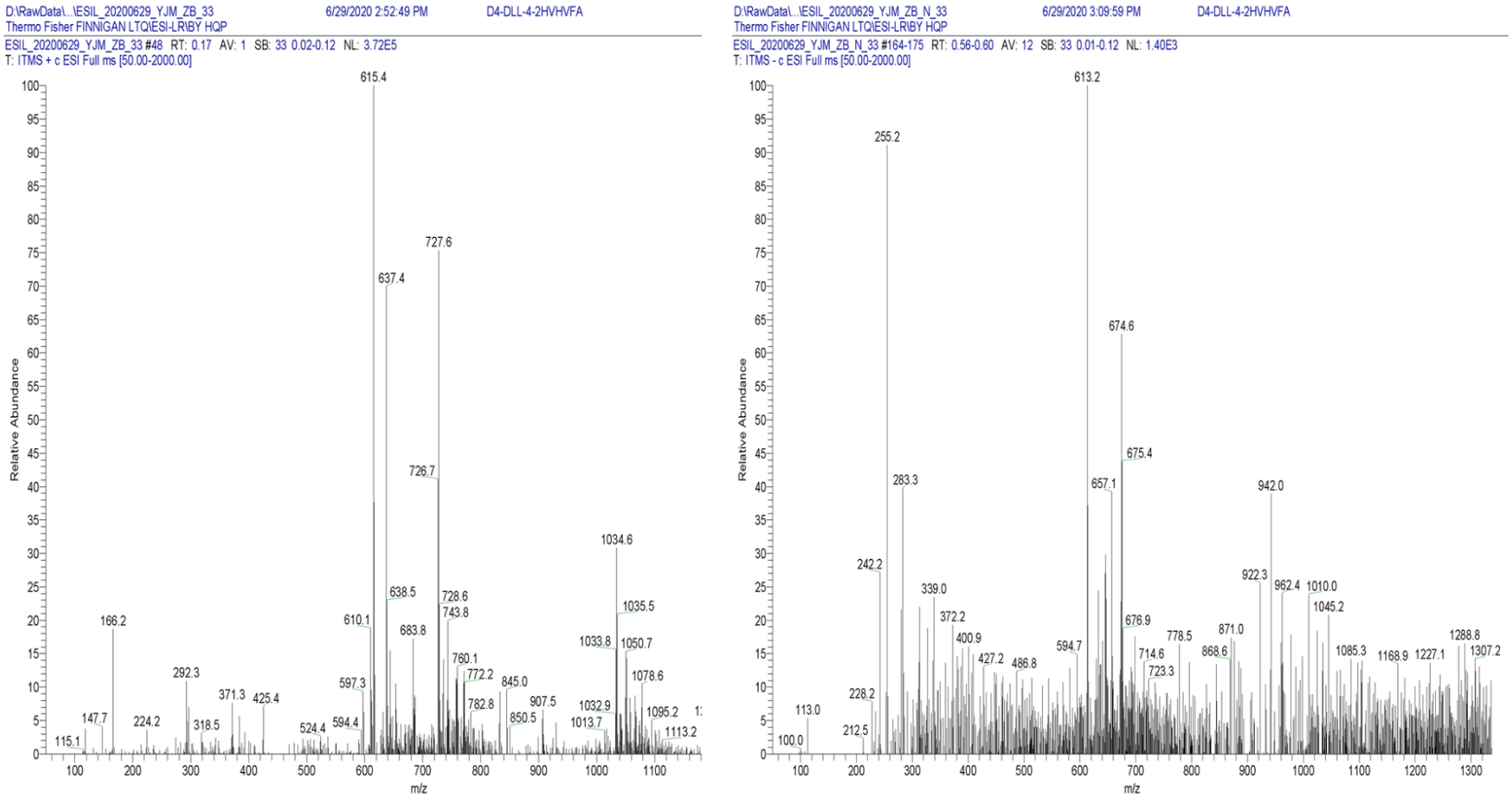


Figure S224. ^{1}H NMR spectrum (500 MHz) of **19** in CD_3OD

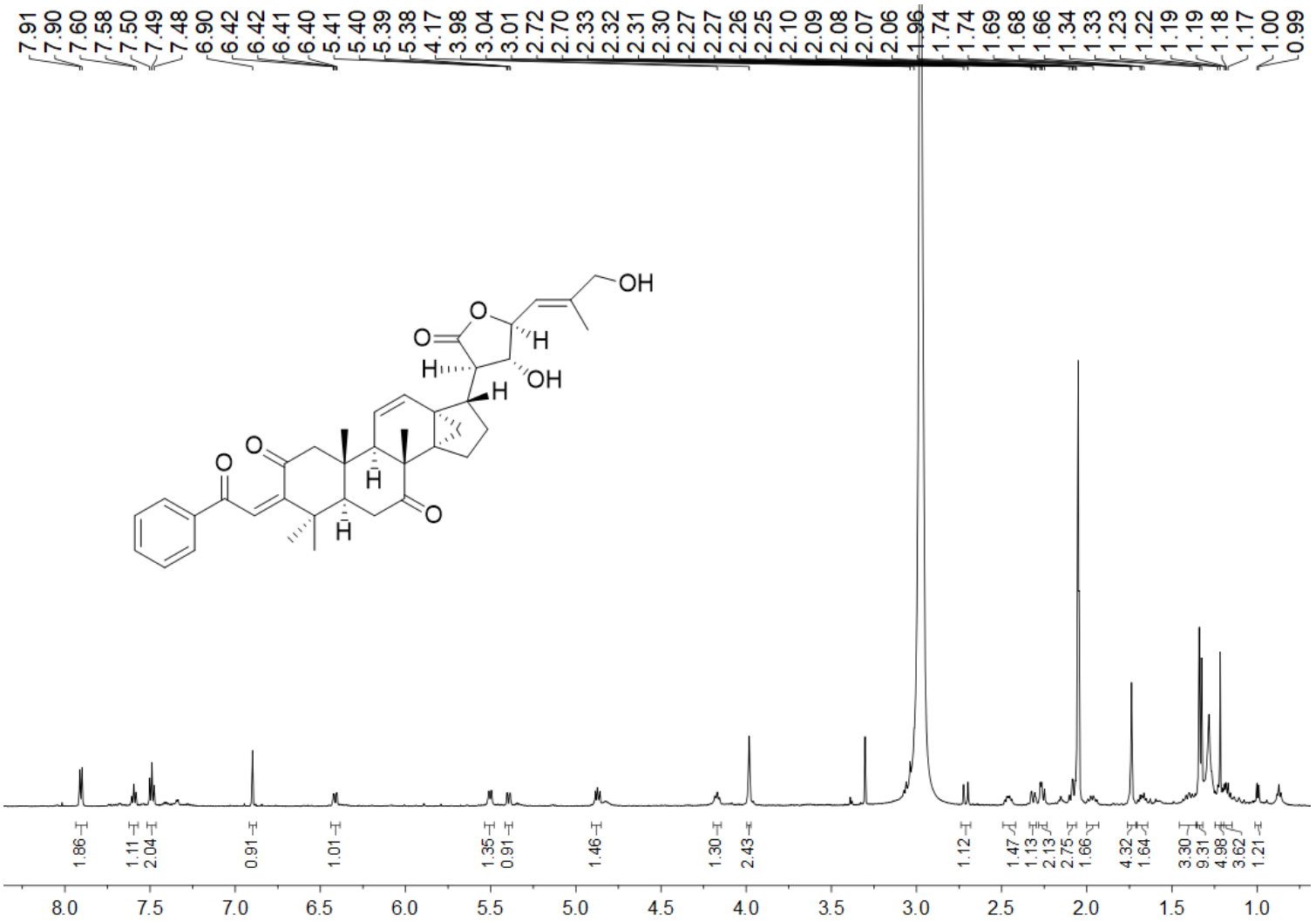


Figure S225. (±)-ESIMS spectra of **19**

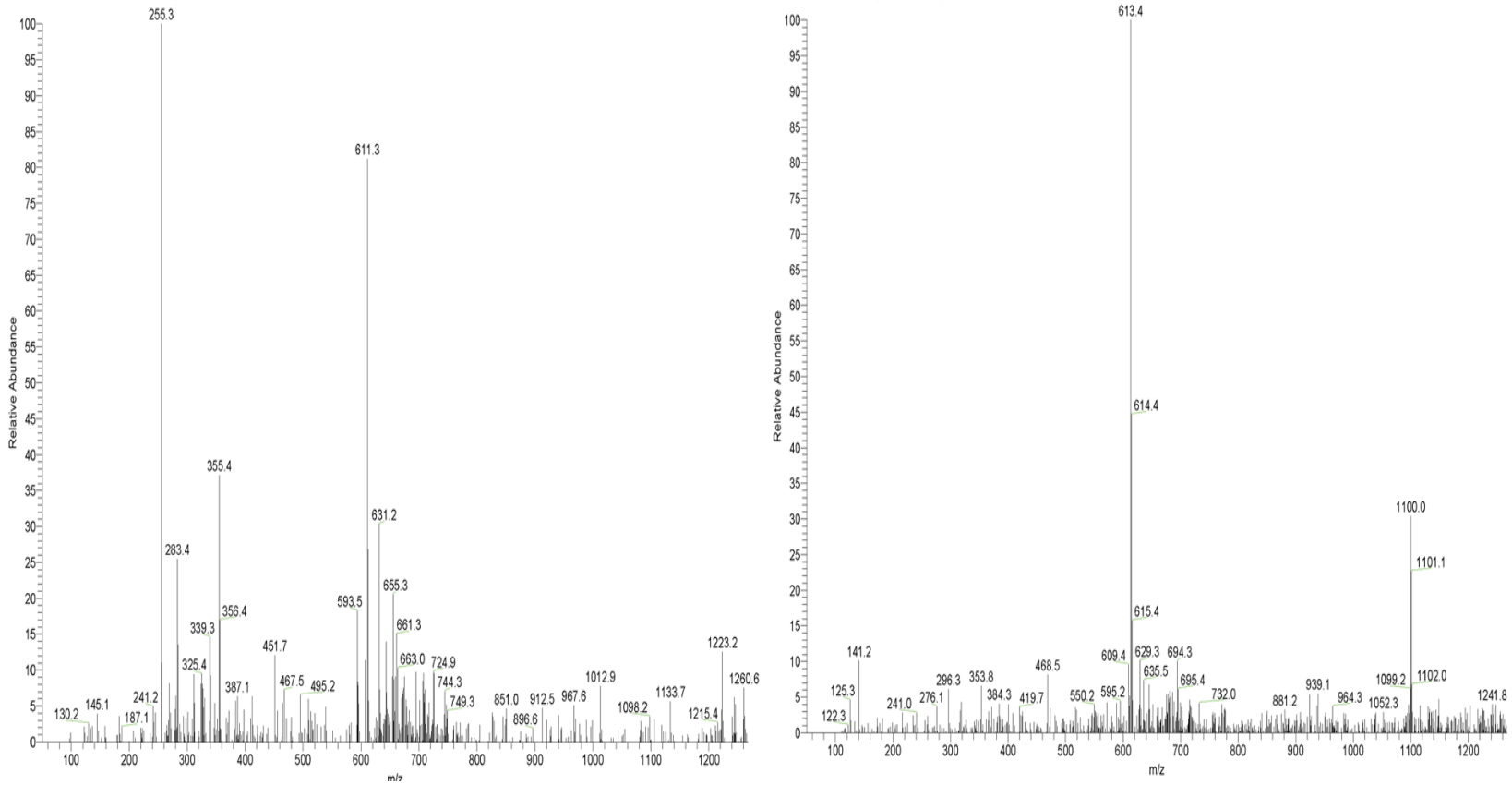


Figure S226. ^{1}H NMR spectrum (500 MHz) of **20** in CD_3OD

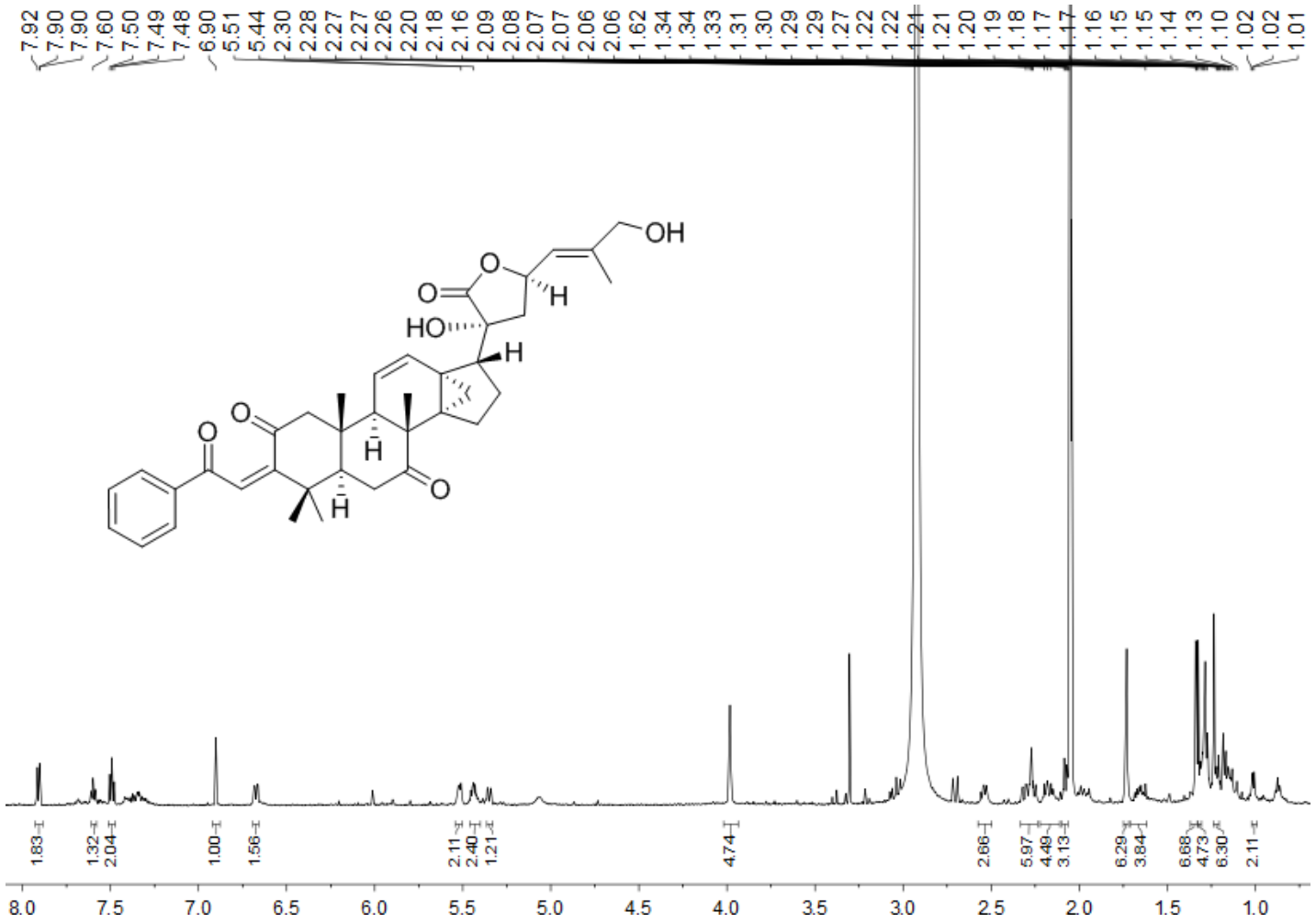
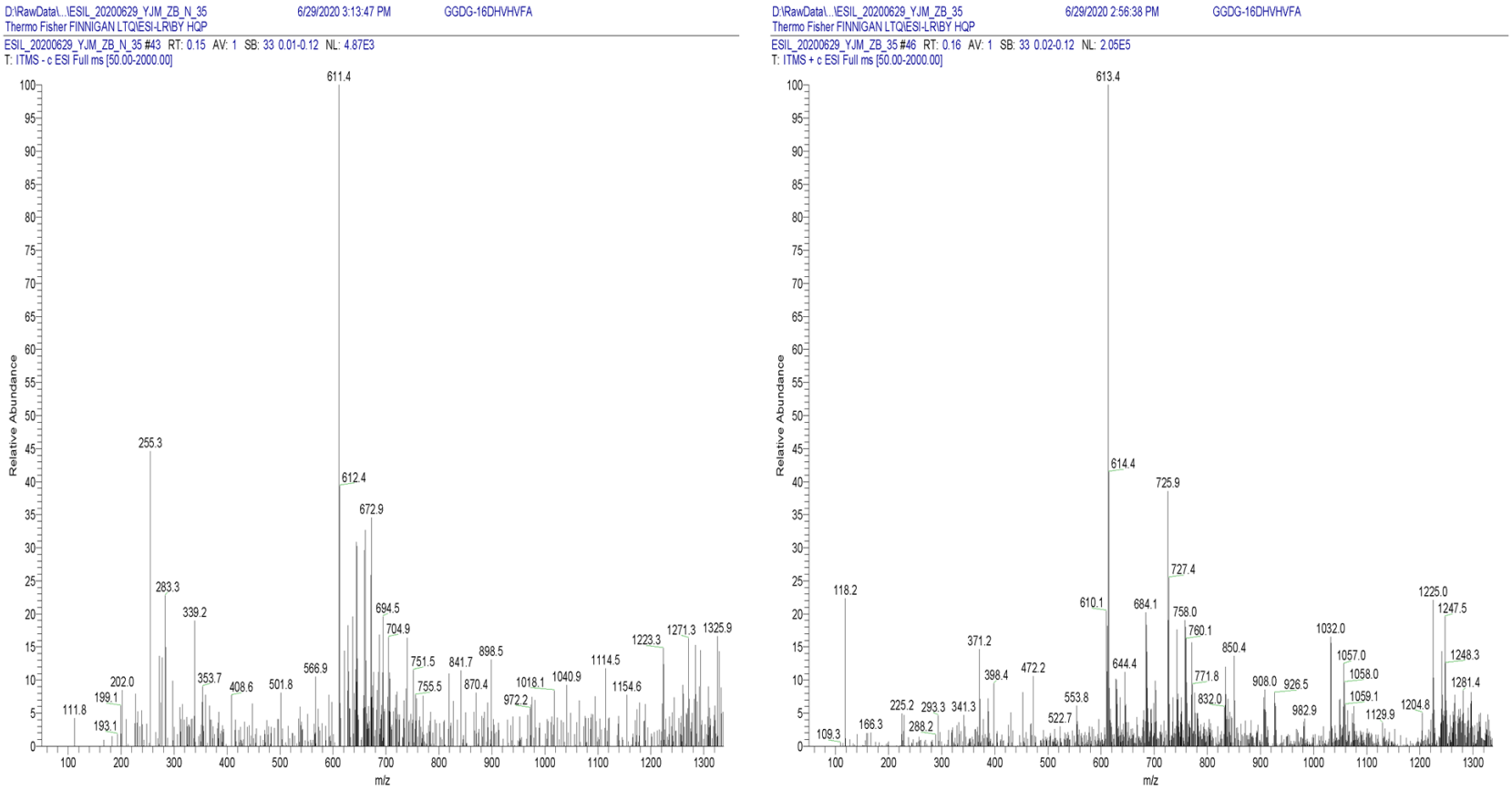


Figure S227. (±)-ESIMS spectra of **20**



7. UPLC-MS Analysis of Ethanolic Crude Extract

To verify the existence of isolated four compound classes in plant, especially **16** and **19** that were not obtained in the current study, a direct UPLC-MS(ESI) analysis of the ethanolic crude extract were carried out. Refering to the diagnostic ion peaks and retention time of isolated and synthesized reference compounds, indicating their presence in *D. gelonioides*.

Figure S228. UPLC-(+)-ESIMS (left) and UPLC-(–)-ESIMS (right) spectra of crude extract

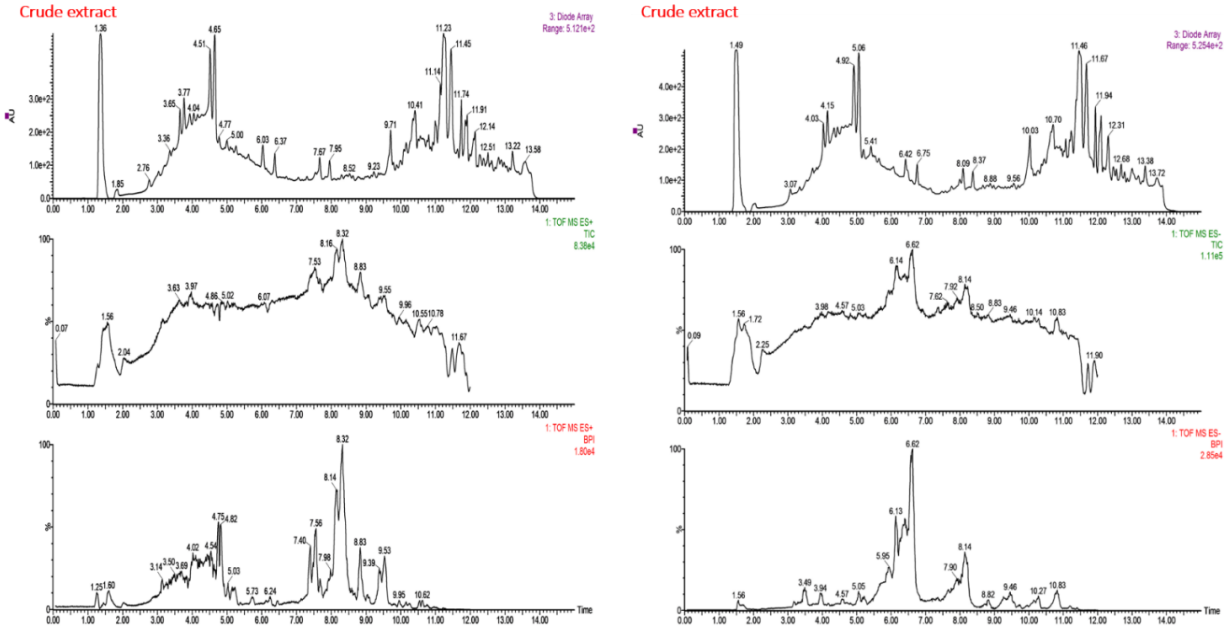


Figure S229. UPLC-(–)-ESIMS analysis of compounds **1** and **2** in crude extract

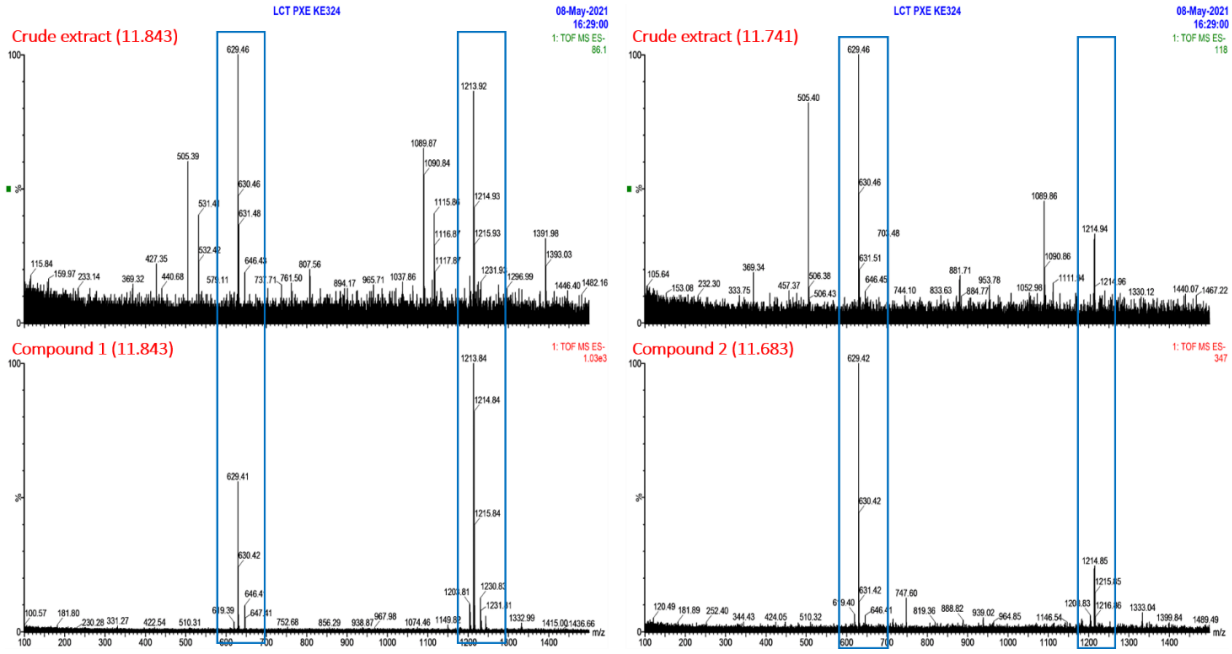


Figure S230. UPLC-(–)-ESIMS analysis of compounds **5** and **11** in crude extract

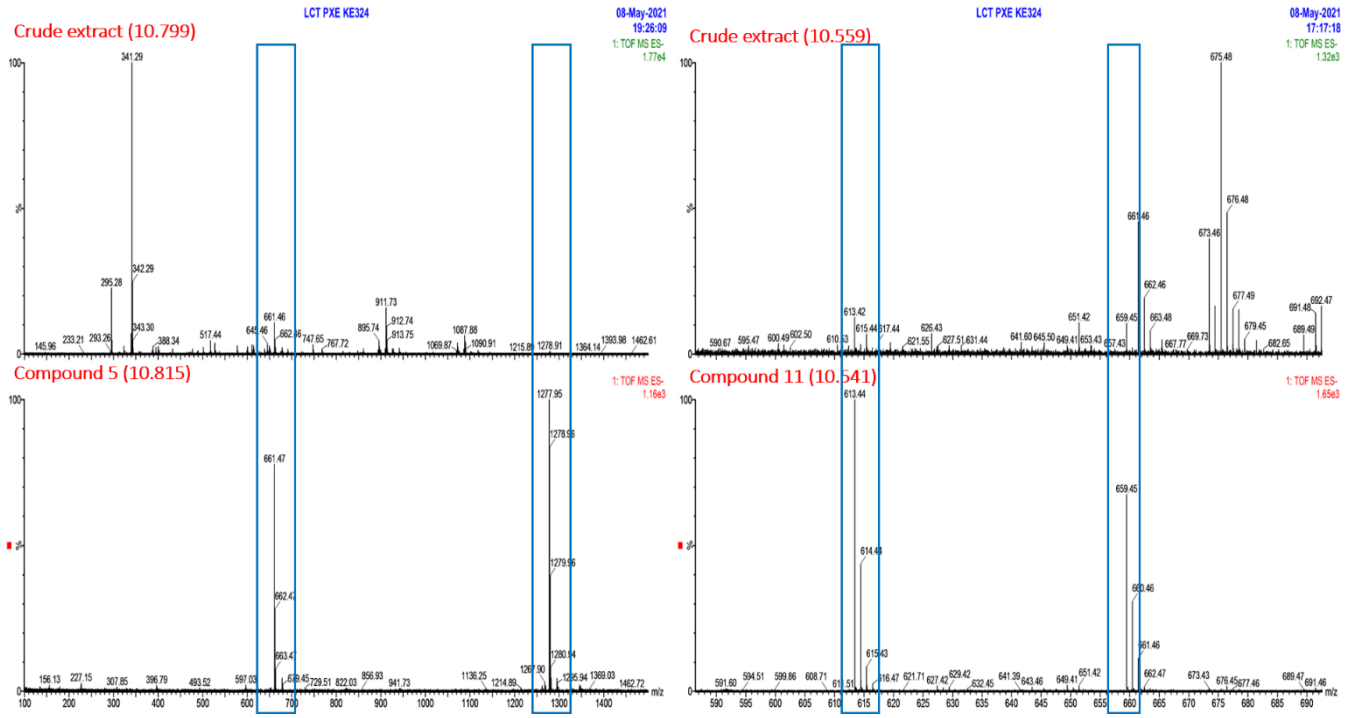


Figure S231. UPLC-(+)-ESIMS analysis of compounds **8** and **9** in crude extract

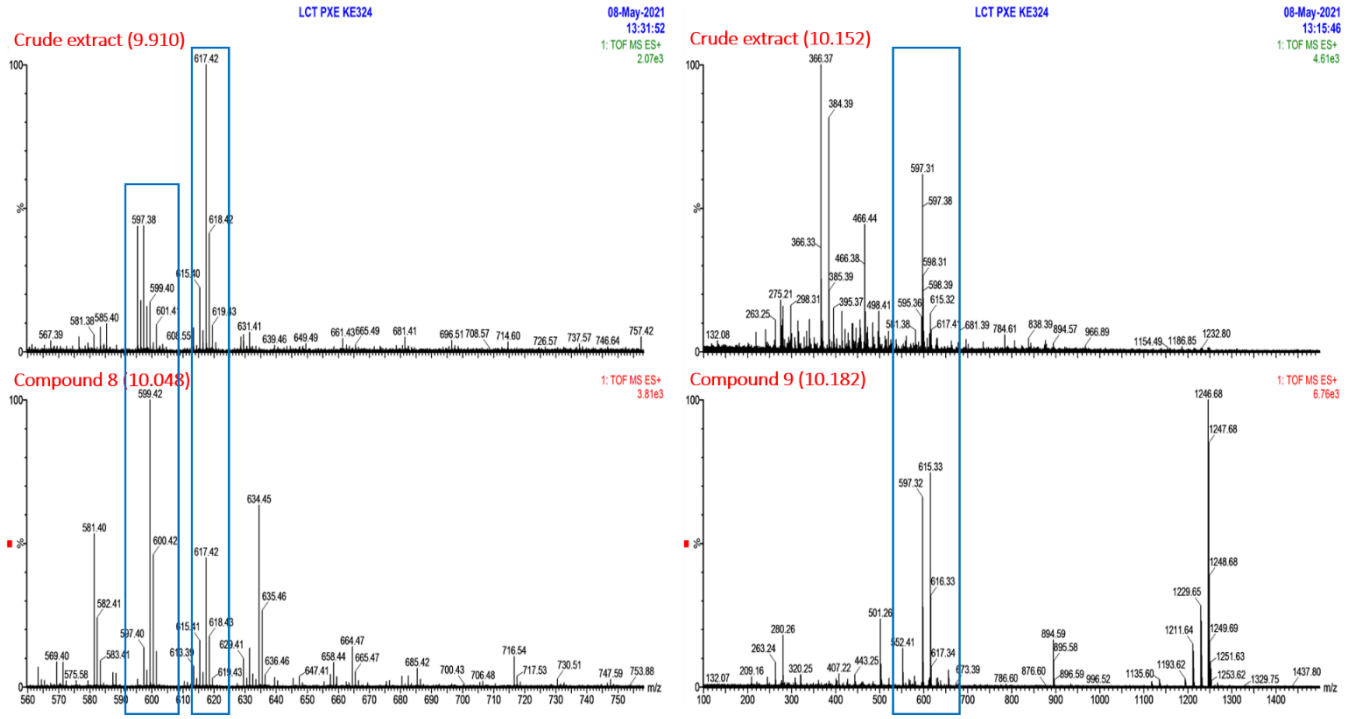


Figure S232. UPLC-(+)-ESIMS analysis of compounds **13** and **16** in crude extract

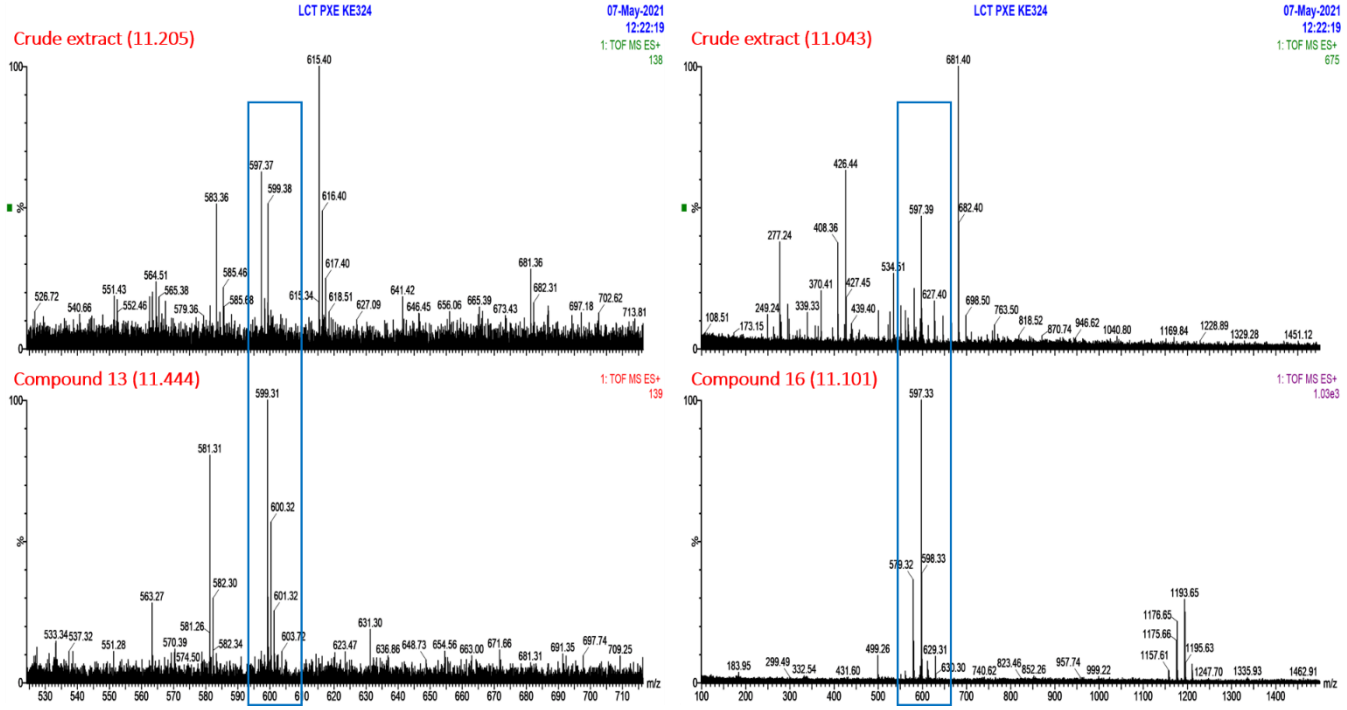
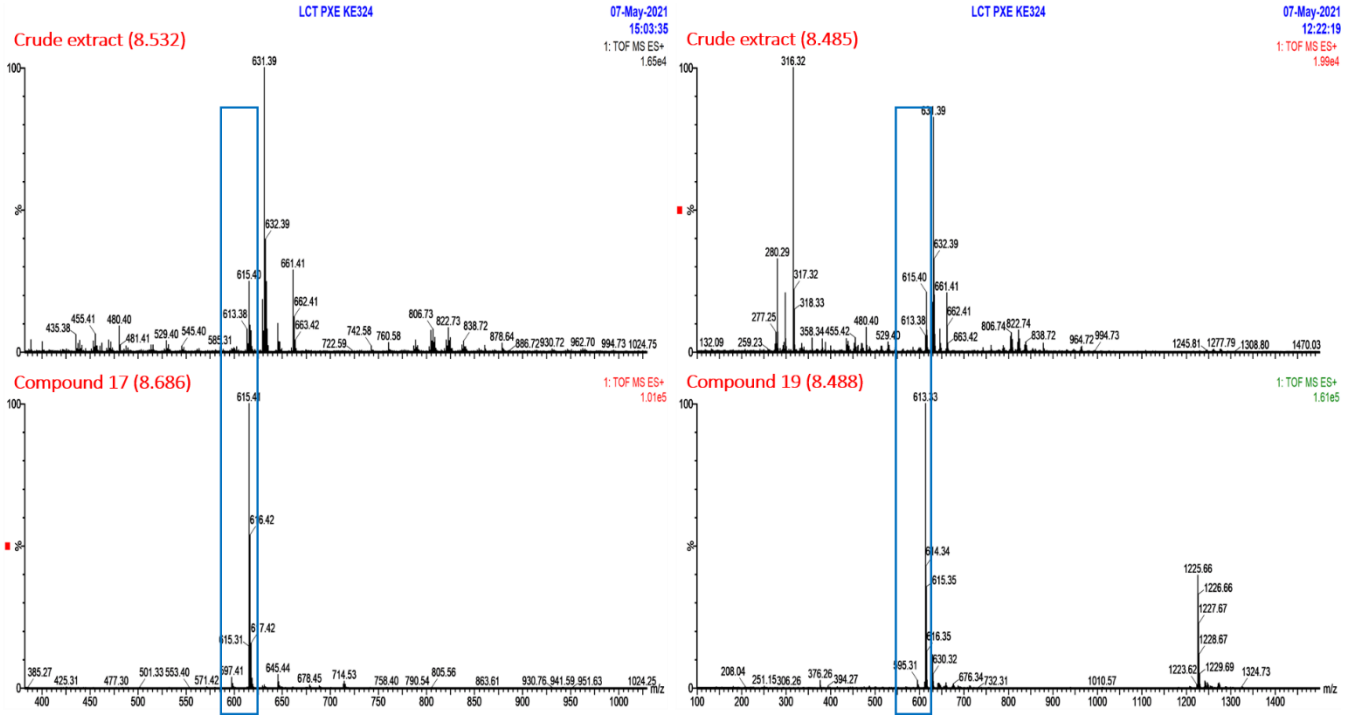


Figure S233. UPLC-(+)-ESIMS analysis of compounds **17** and **19** in crude extract



7. References

[1] a) Sheldrick, G. M. *Acta Crystallogr. Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 3–8; b) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[2] a) Gan, M. L.; Liu, M. T.; Gan, L. S.; Lin, S.; Liu, B.; Zhang, Y. L.; Zi, J. C.; Song, W. X.; Shi, J. G. *J. Nat. Prod.* **2012**, *75*, 1373–1382; b) Huang, Y. J.; Lu, H.; Yu, X. L.; Zhang, S. W.; Wang, W. Q.; Fen, L. Y.; Xuan, L. J. *J. Nat. Prod.* **2014**, *77*, 1201–1209; c) Jing, S. X.; Luo, S. H.; Li, C. H.; Hua, J.; Wang, Y. L.; Niu, X. M.; Li, X. N.; Liu, Y.; Huang, C. S.; Wang, Y.; Li, S. H. *J. Nat. Prod.* **2014**, *77*, 882–893.

[3] Addae-Mensah, I.; Waibel, R.; Asunka, S. A.; Oppong, I. V.; Achenbach, H. *Phytochemistry* **1996**, *43*, 649–656.

[4] Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; IyengarS. S.; Tomasi, J.; Cossi, M.; Rega; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R. E.; Stratmann, O.; Yazyev, A. J.; Austin, R.; Cammi, C.; Pomelli, J. W.; Ochterski, R.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision B.01; Gaussian Inc: Wallingford, CT, 2009.

[5] *http://cheshirenmr.info.*

[6] Jin, S. F.; Ma, H. L.; Liu, Z. L.; Fu, S. T.; Zhang, C. P.; He, Y. *Exp. Cell Res.* **2015**, *339*, 289–299.

[7] Skehan, P.; Storeng, R.; Scudiero, D.; Monks, A.; Mcmahon, J.; Vistica, D.; Warren, J. T.; Bokesch, H.; Kenney, S.; Boyd, M. R. *J. Natl. Cancer Inst.* **1990**, *82*, 1107–1112.