SUPPORTING INFORMATION

Cytotoxic Clerodane Diterpenoids from the Leaves and Twigs of *Casearia balansae*

Bo Wang,[†] Xiao-Ling Wang,[‡] Shu-Qi Wang,[†] Tao Shen,[†] Yong-Qing Liu,[§] Hui-Qing Yuan,[§] Hong-Xiang Lou,[†] and Xiao-Ning Wang[*,†]

[†]Department of Natural Product Chemistry, Key Laboratory of Chemical Biology (Ministry of Education), School of Pharmaceutical Sciences, Shandong University, 44 West Wenhua Road, Jinan 250012, P. R. China

[‡]The Second Hospital of Shandong University, 247 Bei-Yuan Street, Jinan 250033, P. R. China

[§]Department of Biochemistry and Molecular Biology, School of Medicine, Shandong University, 44 West Wenhua Road, Jinan 250012, P. R. China

[*]Corresponding Author. Tel: 86-531-88382012. Fax: 86-531-88382548. E-mail: wangxn@sdu.edu.cn.

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Part 1. Experimental section

Extraction and isolation. The air-dried and powdered plant material (7.5 kg) was extracted with 90% aq. EtOH (4×20 L, 5 days each) at room temperature. The combined extracts were concentrated under reduced pressure to afford a dark gum (430 g, 5.7%), which was suspended in 80% aq. MeOH, and partitioned with petroleum ether (5×1 L). The combined petroleum ether fraction was evaporated under reduced pressure to afford a brown gum (84 g, 1.1%). The 80% aq. MeOH fraction was diluted to 50% MeOH by addition of H_2O and then extracted with CH_2Cl_2. Evaporation of CH_2Cl_2 under reduced pressure yielded a brown semisolid (105 g, 1.4%). The petroleum ether soluble fraction showed similar TLC than the CH_2Cl_2 soluble fraction, hence they were combined and subjected to silica gel CC with a gradient of petroleum ether–EtOAc (100:1→1:1) to yield eight fractions (Fr. 1–Fr. 8). Fr. 5 (10.7 g, 0.14%) was first separated by CC on silica gel and then purified by CC of reversed-phase C_{18} to give **18** (10.0 mg, 0.00013%). Fr. 6 (25.5 g, 0.34%) was first separated by silica gel CC eluted with petroleum ether–EtOAc (40:1) to give four fractions (Fr. 6.1– Fr.6.4). Fr. 6.3 (18.6 g, 0.25%) was further purified by MCI-gel (0→80% aq. EtOH) to afford five fractions (Fr. 6.3.1– Fr. 6.3.5), and then Fr. 6.3.1 (2.3 g, 0.031%) was separated by a column of C_{18} reversed-phase silica gel (50→90% aq. MeOH) to give six parts (Fr. 6.3.1.1– Fr. 6.3.1.6). Fr. 6.3.1.1 (1.09 g, 0.015%) was further separated by silica gel CC (petroleum ether-EtOAc 30:1→3:1) to afford two major parts. The less polar part (287.3 mg, 0.0038%) was purified by HPLC (80% aq. MeOH, 1.7 mL/min) to give **6** (44.6 mg, 0.00059%, t_R= 22.5 min), and the more polar part (219.3 mg, 0.0029%) was also purified by HPLC (76% aq. MeOH, 1.8 mL/min) to give **9** (13.3 mg, 0.00018%, t_R= 18.3 min) and **17** (26.8 mg, 0.00036%, t_R= 21.6 min). Fr. 6.3.1.3 (1.02 g, 0.014%) was first separated by silica gel CC (petroleum ether-EtOAc 30:1→5:1) to afford three major parts. The least polar part (269.1 mg, 0.0036%) was purified by Sephadex LH-20 (MeOH) and HPLC (83% aq. MeOH, 1.5 mL/min) to give **14** (16.2 mg, 0.00022%, t_R= 27.1 min). The moderately polar part (126.5 mg, 0.0017%) was purified by

silica gel CC and HPLC (77% aq. MeOH, 0.8 mL/min) to give **13** (6.0 mg, 0.00008%, t_R= 16.1 min) and **8** (1.6 mg, 0.000021%, t_R= 21.5 min), and the most polar part (94.2 mg, 0.0013%) was purified by HPLC (86% aq. MeOH, 1.4 mL/min) to give **7** (18.9 mg, 0.00025%, t_R= 25.0 min) and **16** (13.7 mg, 0.00018%, t_R= 27.1 min). Fr. 6.3.1.4 (230 mg, 0.0031%) was first separated by silica gel CC (petroleum ether-EtOAc 30:1→8:1) to afford two major parts, which were further purified by HPLC to give **5** (15.0 mg, 0.0002%, 76% aq. MeOH, 2.2 mL/min, t_R= 35.1 min) and **10** (7.0 mg, 0.000093%, 73% aq. MeOH, 2.3 mL/min, t_R= 37.4 min), respectively. Fr. 6.4 (9.1 g, 0.12%) was separated by CC of MCI-gel (30→85% aq. EtOH) and reversed-phase silica gel to give two fractions (Fr. 6.4.1 and Fr. 6.4.2). Fr. 6.4.1 (67.5 mg, 0.0009%) was further purified by reversed-phase silica gel to give **3** (57.0 mg, 0.00076%) and **4** (4.8 mg, 0.000064%). Fr. 6.4.2 (78.5 mg, 0.001%) was purified by HPLC (78% aq. MeOH, 2.2 mL/min) to give **11** (75.0 mg, 0.001%, t_R= 30.9 min). Fr. 7 (15.7 g, 0.21%) was first separated by MCI-gel (0→90% aq. EtOH) to give seven fractions (Fr. 7.1– Fr. 7.7). Fr. 7.2 (7.0 g, 0.93%) was purified by Sephadex LH-20 (MeOH) and silica gel CC (petroleum ether/CH_2Cl_2/EtOAc 20:20:1→1:1:4) to give **12** (50.7 mg, 0.00068%). Fr. 7.3 (3.1 g, 0.041%) was separated by silica gel CC (petroleum ether-CH_2Cl_2 5:1) to give two major fractions (Fr. 7.3.1 and Fr. 7.3.2). Fr. 7.3.1 (42 mg, 0.00056%) was further purified by HPLC (86 % aq. MeOH, 1.5 mL/min) to give **1** and **2** as a mixture (19.5 mg, 0.00026%, t_R= 22.5 min), and Fr. 7.3.2 (27.2 mg, 0.00036%) was also purified by HPLC (85% aq. MeOH, 1.8 mL/min) to give **15** (1.9 mg, 0.000025%, t_R= 14.4 min).

Caseabalansin A (1) and 18-epicaseabalansin A (2): White amorphous solid; $[\alpha]^{25}_D$ −1.6 (*c* 0.19, MeOH); UV (MeOH) λ_{max} (log ε) 223 (2.41) nm; IR (KBr) ν_{max} 3469, 3255, 2954, 2867, 1593, 1451, 1375, 1141, 993, 884 cm^{-1}; For ^1H and ^{13}C NMR data, see Tables 1 and 3; HRESIMS *m/z* 341.2084 $[M+Na]^+$ (calcd for $C_{20}H_{30}O_3Na$, 341.2093).

Caseabalansin B (3): Colorless oil; $[\alpha]^{25}_D$ +32.5 (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε) 223 (4.12) nm; IR (KBr) ν_{max} 3546, 2966, 2936, 2877, 1735, 1596, 1461, 1370, 1226, 1042, 962,

894 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 1 and 3; HRESIMS *m/z* 466.3145 $[M+NH_4]^+$ (calcd for $C_{26}H_{44}O_6N$, 466.3169), 301.2154 $[M+H-AcOH-CH_3(CH_2)_2COOH]^+$.

2-Epicaseabalansin B (4): Colorless oil; $[\alpha]^{25}_D$ –27.5 (*c* 0.17, MeOH); UV (MeOH) λ_{max} (log ε) 222 (2.07) nm; IR (KBr) ν_{max} 3430, 2965, 2935, 2877, 1749, 1456, 1373, 1225, 1052, 959, 904 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 1 and 3; HRESIMS *m/z* 466.3171 $[M+NH_4]^+$ (calcd for $C_{26}H_{44}O_6N$, 466.3169), 301.2170 $[M+H-AcOH-CH_3(CH_2)_2COOH]^+$.

Caseabalansin C (5): Colorless oil; $[\alpha]^{25}_D$ –36.2 (*c* 0.07, MeOH); UV (MeOH) λ_{max} (log ε) 222 (2.13) nm; IR (KBr) ν_{max} 3363, 2970, 2930, 2882, 1735, 1596, 1372, 1223, 1106, 1055, 947, 892 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 1 and 3; ESIMS *m/z* 499.5 $[M+Na]^+$; HRESIMS *m/z* 357.2436 $[M+H-2(AcOH)]^+$.

2-Epicaseabalansin C (6): White amorphous powder; $[\alpha]^{25}_D$ +34.3 (*c* 0.13, MeOH); UV (MeOH) λ_{max} (log ε) 222 (2.30) nm; IR (KBr) ν_{max} 2971, 2932, 1738, 1373, 1228, 1109, 1057, 947, 893 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 2 and 3; HRESIMS *m/z* 494.3126 $[M+NH_4]^+$ (calcd for $C_{27}H_{44}O_7N$, 494.3118), 417.2649 $[M+H-AcOH]^+$.

Caseabalansin D (7): White amorphous powder; $[\alpha]^{25}_D$ +33.3 (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ε) 223 (2.04) nm; IR (KBr) ν_{max} 3489, 2971, 2933, 2876, 1749, 1727, 1451, 1378, 1222, 1113, 1039, 945, 895 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 2 and 3; HRESIMS *m/z* 527.2980 $[M+Na]^+$ (calcd for $C_{29}H_{44}O_7Na$, 527.2985).

Caseabalansin E (8): White amorphous solid; $[\alpha]^{25}_D$ +53.3 (*c* 0.045, MeOH); UV (MeOH) λ_{max} (log ε) 222 (2.65) nm; IR (KBr) ν_{max} 3453, 2962, 2934, 2874, 1727, 1285, 1113, 1073, 899 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 2 and 3; HRESIMS *m/z* 485.2865 $[M+Na]^+$ (calcd for $C_{27}H_{42}O_6Na$, 485.2879).

Caseabalansin F (9): Colorless oil; $[\alpha]^{25}_D$ –24.3 (*c* 0.11, MeOH); UV (MeOH) λ_{max} (log ε) 222 (2.09) nm; IR (KBr) ν_{max} 2966, 2931, 1756, 1676, 1373, 1223, 1100, 944 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 2 and 3; HRESIMS *m/z* 464.2647 $[M+NH_4]^+$ (calcd for $C_{25}H_{38}O_7N$,

464.2648).

Caseabalansin G (10): Colorless oil; $[\alpha]^{25}_{D}$ –22.8 (*c* 0.23, MeOH); UV (MeOH) λ_{max} (log ε) 222 (1.93) nm; IR (KBr) ν_{max} 2965, 2933, 2878, 1755, 1677, 1373, 1289, 1218, 1101, 1065, 945 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Tables 2 and 3; HRESIMS *m/z* 492.2969 $[M+NH_4]^+$ (calcd for $C_{27}H_{42}O_7N$, 492.2961), 327.1967 $[M+H-AcOH-CH_3(CH_2)_2COOH]^+$.

Balansinone (11): White needle crystal; m.p. 157 °C; $[\alpha]^{25}_{D}$ –79.5 (*c* 0.022, MeOH); UV (MeOH) λ_{max} (log ε) 237 (3.85), 268 (3.61) nm; IR (KBr) ν_{max} 3364, 2963, 2939, 2874, 1734, 1657, 1626, 1468, 1379, 1139, 1083, 888 cm^{-1}; For ^{1}H and ^{13}C NMR data, see Table 4; HRESIMS *m/z* 467.3517 $[M+H]^+$ (calcd for $C_{31}H_{47}O_3$, 467.3525).

Preparation of 1a and 2a. A solution of the mixture of **1** and **2** (10.0 mg) in pyridine (0.5 mL) was added with acetic anhydride (0.5 mL), and the mixture was stirred at room temperature for 21 h. After evaporation of excess reagent under vacuum, the residue was separated by column chromatography of silica gel eluted with petroleum ether/acetone (40:1) to give the major product, which was separated by HPLC (Phenomenex Luna C_{18} column, 4.6 mm × 250 mm, 5 μm; 78% aq. MeOH, 0.8 mL/min) to give **1a** (2.2 mg, t_R= 17.3 min) and **2a** (6.7 mg, t_R= 18.5 min). **1a:** HRESIMS *m/z* 399.1925 $[M+K]^+$ (calcd for $C_{22}H_{32}O_4K$, 399.1938). **2a:** HRESIMS *m/z* 399.1931 $[M+K]^+$ (calcd for $C_{22}H_{32}O_4K$, 399.1938). For ^{1}H and ^{13}C NMR data of **1a** and **2a**, see Supporting Information.

X-ray Crystallographic Study of Balansinone (11). Single crystals suitable for X-ray analysis were obtained by recrystallization from methanol. A colorless platelet crystal having approximate dimensions of 0.45×0.18×0.11 mm^3 was used for analysis. All measurements were made on a Bruker APEX2 CCD area-detector diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 293 K and operating in the ϕ-ω scan mode. Crystal data of

11: $C_{31}H_{46}O_3 \cdot CH_3OH$, M = 498.72, monoclinic, space group $P2_1$, a = 11.856 (15) Å, b = 7.685 (10) Å, c =17.460 (2) Å, α = 90.00 °, β = 108.815(15) °, γ = 90.00 °, V = 1506 (3) Å^3, Z = 2, D_{calcd} = 1.100 Mg/cm^3, $F(000)$ = 548, and μ (Mo-Kα) = 0.070 mm^{-1}. Cell refinement and data reduction: APEX2 Software Suite.[1] Program used to refine structure: SHELXL-97;[2] refinement on F^2, full-matrix least-squares calculations. All non-hydrogen atoms were refined anisotropically, and all hydrogen atoms were placed in geometrically calculated positions and refined as riding atoms with the relative isotropic parameters. A total of 9355 reflections (6382 unique, R_{int} = 0.0527) were collected from 1.23° to 27.95° in θ and index ranges: 15≥ h ≥ -12, 9≥ k ≥ -9, 22 ≥ l ≥ -22. The final stage converged to R_1 = 0.0548 (wR_2 = 0.1435) for 2410 observed reflections [with $I > 2\sigma(I)$] and 336 variable parameters, and R_1 = 0.1510 (wR_2 = 0.1837) for all unique reflections and GOF = 0.777. The refined fractional atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). CCDC-899324 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/deposit, or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: C44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

Cytotoxicity Assay. The cells for assay were cultured in 96-well plate at 37 °C. Samples and control standard drugs were prepared at a concentration of 0, 5, 10, 20, and 40 μM. After seeding 3~4×10^4 cells/mL in a 96-well plate for 24 h, 10 μL of sample or standard agent was placed in each well and incubated at 37 °C for 72 h. Then 10 μL of MTT solution was added into the assay plates (final concentration, 0.5 mg/mL) and the plates were returned to incubator and kept for 4 h. The supernatants were removed carefully, followed by the addition of 100 μL of DMSO to each well and shaking to dissolve the precipitate. Then, the absorbance was measured at 570 nm with a Model 680 microplate reader (Bio-Rad, USA). The percent viability was expressed as absorbance in the presence of test compound as a percentage of that in the vehicle control. Paclitaxel and

DMSO were used as positive and negative controls.

Analysis of the Acetone Extract of the Plant and 5–8 by HPLC. The air-dried and powdered plant material (6.0 g) was refluxed with 90% aq. acetone for four times. The combined extracts were concentrated under reduced pressure to afford a dark gum (521.2 mg). The extract was dissolved in a mixture of CH_2Cl_2 and acetone and filtered with microporous membrane (0.45 μm) for analysis. Compounds **5** and **6** were dissolved in methanol for analysis, while **7** and **8** were dissolved in a mixture of methanol and acetone for analysis. HPLC was performed on an Agilent 1100 G1310A isopump equipped with an Agilent 1100 G1322A degasser, an Agilent 1100 G1314A VWD detector, and a Phenomenon Luna C_{18} column (4.6 mm × 150 mm, 5 μm). The mobile phases were composed of methanol and water with a gradient program as follows: 0–10 min, 60–70% methanol; 10–25 min, 70–80% methanol; after 25 min, 80% methanol. A pre-equilibration period of 8 min was used between individual runs. The flow rate was kept constant at 0.8 mL/min. The effluent was monitored by DAD detection at 240 nm. It was observed that there was a peak with exactly the same retention time with **8** in the chromatogram of the extract (See Figure S4), while no peaks were observed corresponding to compounds **5**, **6**, or **7**. Therefore, it is obvious that compound **8** was a natural product in the plant, whereas compounds **5**–**7** were absent in the plant, which may be formed in the extraction and isolation processes due to workup with ethanol.

References

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Part 2. Tables

Table S1. ^{1}H and ^{13}C NMR Spectroscopic Data for **5** and **6** in methanol-d_4[a]

position	**5**		**6**	
	δ_H	δ_C	δ_H	δ_C
1α	1.77, td (13.5, 9.8)	27.6	1.94, dd (14.0, 2.0)	27.9
1β	2.20, ddd (13.1, 7.0, 2.5)		2.12, m	
2	5.48, dd (7.6, 7.6)	72.8	5.43, d (4.2)	68.3
3	5.90, br s	124.6	5.98, d (3.7)	122.1
4		147.1		148.1
5		54.3		54.2
6	3.56, m	84.7	3.41, dd (12.1, 3.7)	83.5
7α	1.91, d (13.4)	32.6	1.89, dt (13.3, 3.7)	32.3
7β	1.48, m		1.50, q (13.0)	
8	1.85, m	38.1	1.82, m	37.9
9		39.2		38.5
10	2.36, d (13.1)	42.5	2.28, dd (14.0, 3.3)	37.7
11	1.25, td (11.7, 3.0)	28.9	1.32, m	29.3
	1.47, m		1.53, m	
12	2.14, m	24.9	2.15, m	25.0
13		147.1		147.2
14	6.45, dd (17.6, 10.9)	141.6	6.46, dd (17.6, 10.9)	141.6
15	5.28, d (17.6)	113.2	5.27, d (17.6)	113.1
	5.03, d (10.9)		5.05, d (10.9)	
16	5.00, s	115.5	5.02, s	115.6
	4.91, s		4.94, s	
17	0.96, d (8.7)	16.2	0.97, d (6.9)	16.2
18	5.41, s	104.5	5.46, s	105.1
19	6.26, s	99.0	6.33, s	99.5
20	0.98, s	26.0	0.96, s	25.8
1′	3.70, dq (9.7, 7.1)	65.3	3.71, dq (9.5, 7.1)	65.3
	3.56, dq (9.7, 7.1)		3.57, dq (9.7, 7.1)	
2′	1.16, t (7.1)	15.8	1.18, t (7.1)	15.8
1″		171.9		172.0
2″	1.82, s	22.0	1.84, s	22.0
1‴		172.5		172.4
2‴	2.07, s	21.2	2.09, s	21.2
6-OMe	3.31, s	57.8	3.28, s	57.8

[a]Recorded at 600 and 150 MHz for ^{1}H and ^{13}C, respectively, δ_H in ppm, and J in Hz. Assignments were made on the basis of HSQC, HMBC, and ^{1}H-^{1}H COSY spectral data.

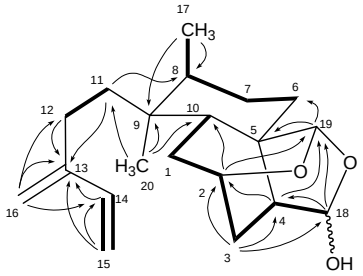
Table S2. ^{1}H and ^{13}C NMR Spectroscopic Data for **1a** and **2a** in $CDCl_3$[a]

position	**1a**[a]		**2a**[a]	
	δ_H	δ_C	δ_H	δ_C
1	1.22 dd (11.1, 4.3) 1.89 m	29.6	1.14 dd (12.9, 6.2) 1.88 m	29.5
2	4.03 dd (4.9, 4.9)	64.0	4.03 dd (4.7, 4.7)	65.0
3	1.48 m 2.52 dd (13.8, 5.1)	26.8	1.80 m 2.02 m	32.6
4	2.80 dd (9.7, 3.9)	37.5	2.65 d (9.9)	40.2
5		43.5		41.0
6	1.40 m 2.15 m	24.7	1.38 m 2.06 m	24.8
7	1.49 m 1.89 m	25.3	1.40 m 1.83 m	25.2
8	1.86 m	34.5	1.86 m	35.0
9		38.1		38.3
10	1.92 m	35.6	1.95 dd (11.5, 6.1)	34.6
11	1.30 m 1.44 m	36.7	1.28 m 1.41 m	36.6
12	2.18 m (2H)	23.9	2.16 m (2H)	23.9
13		147.0		147.0
14	6.41 (17.6, 10.8)	139.1	6.39, dd (17.6, 10.8)	139.1
15	5.09 d (10.8) 5.26 d (17.6)	113.1	5.07 d (10.8) 5.24 d (17.6)	113.1
16	5.01 s 5.04 s	115.6	4.99 s 5.01 s	115.5
17	1.01 d (7.0)	14.1	1.01 d (6.9)	14.3
18	6.33 d (3.9)	98.8	5.97 s	106.6
19	4.85 s	107.4	5.00 s	108.4
20	1.09 s	19.7	1.05 s	19.6
CH_3CO		170.0		170.0
CH_3CO	2.17 s	21.3	2.07 s	21.4

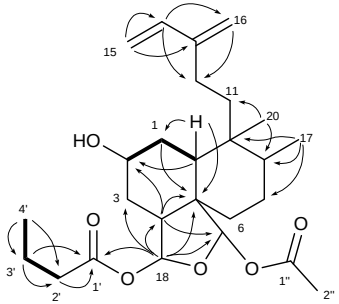
[a]Recorded at 600 and 150 MHz for ^{1}H and ^{13}C, respectively, δ_H in ppm, and J in Hz. Assignments were made on the basis of HSQC, HMBC, and ^{1}H-^{1}H COSY spectral data.

Part 3. Figures

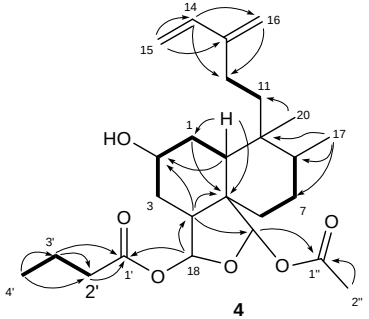
Figure S1. Selected HMBC (H→C) and ^{1}H-^{1}H COSY (▬) correlations of **1**–**10**.



1/2



3



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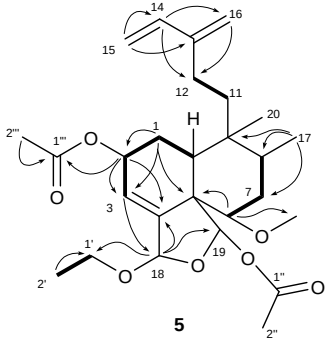

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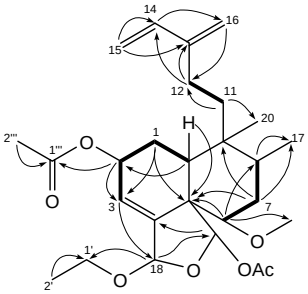

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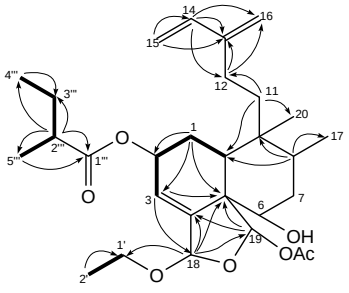

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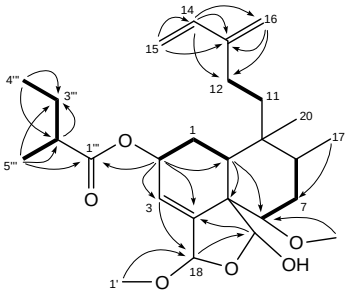

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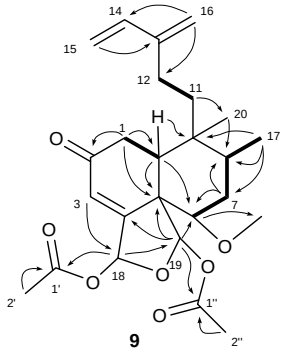

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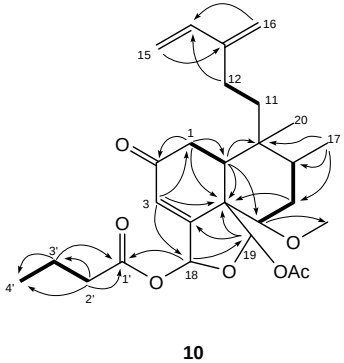
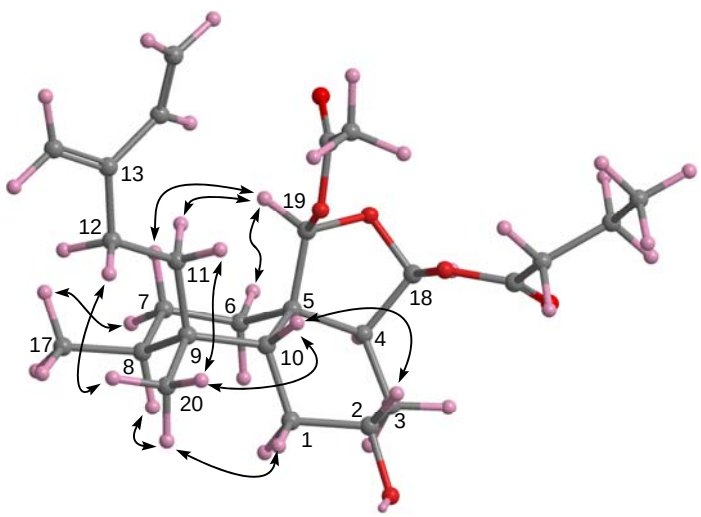
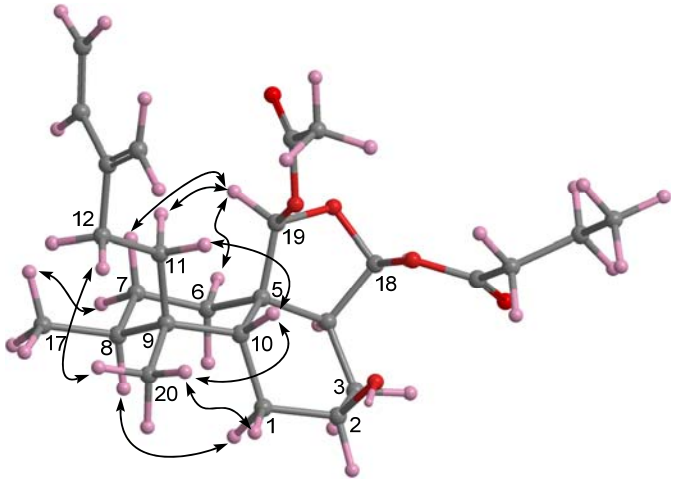


10

Figure S2. Selected NOESY (H↔H) correlations of **3**–**10**.



3



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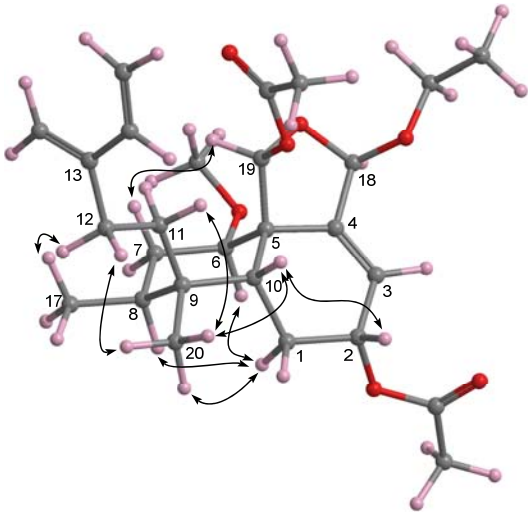

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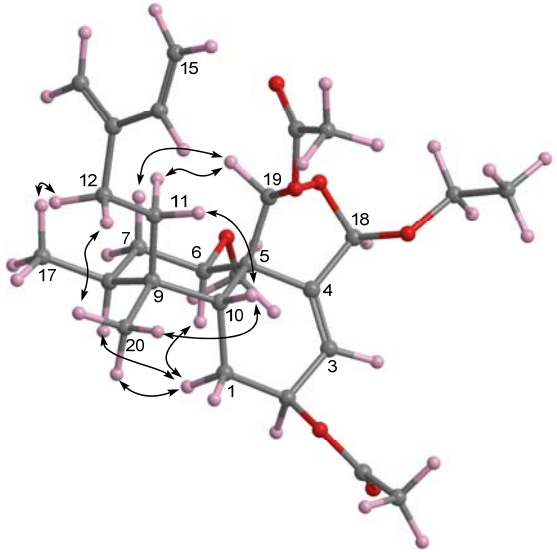

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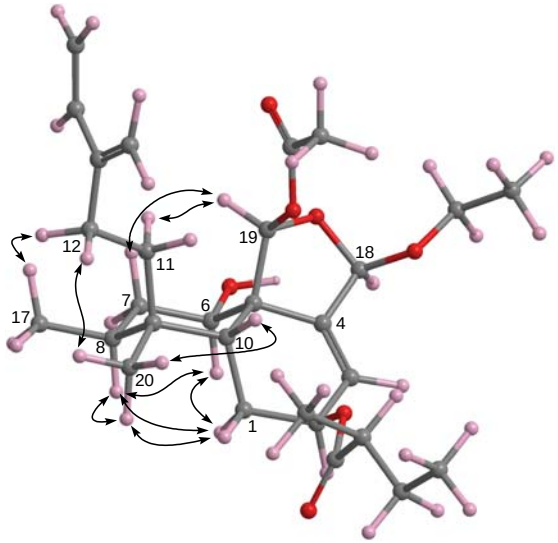

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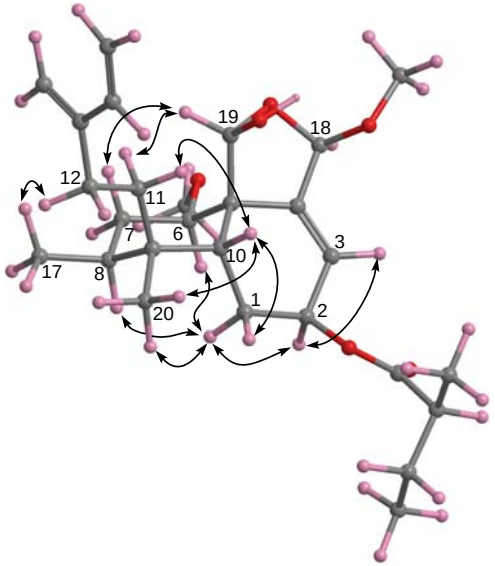

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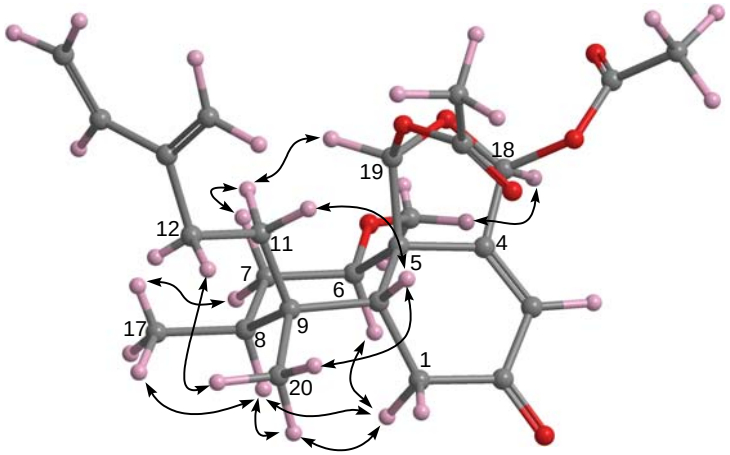
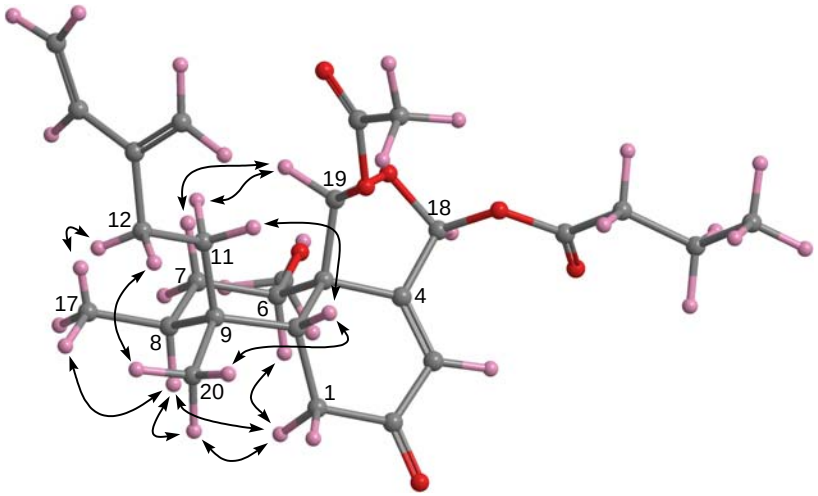


9



10

Figure S3. Structures of the known compounds **12–18**.

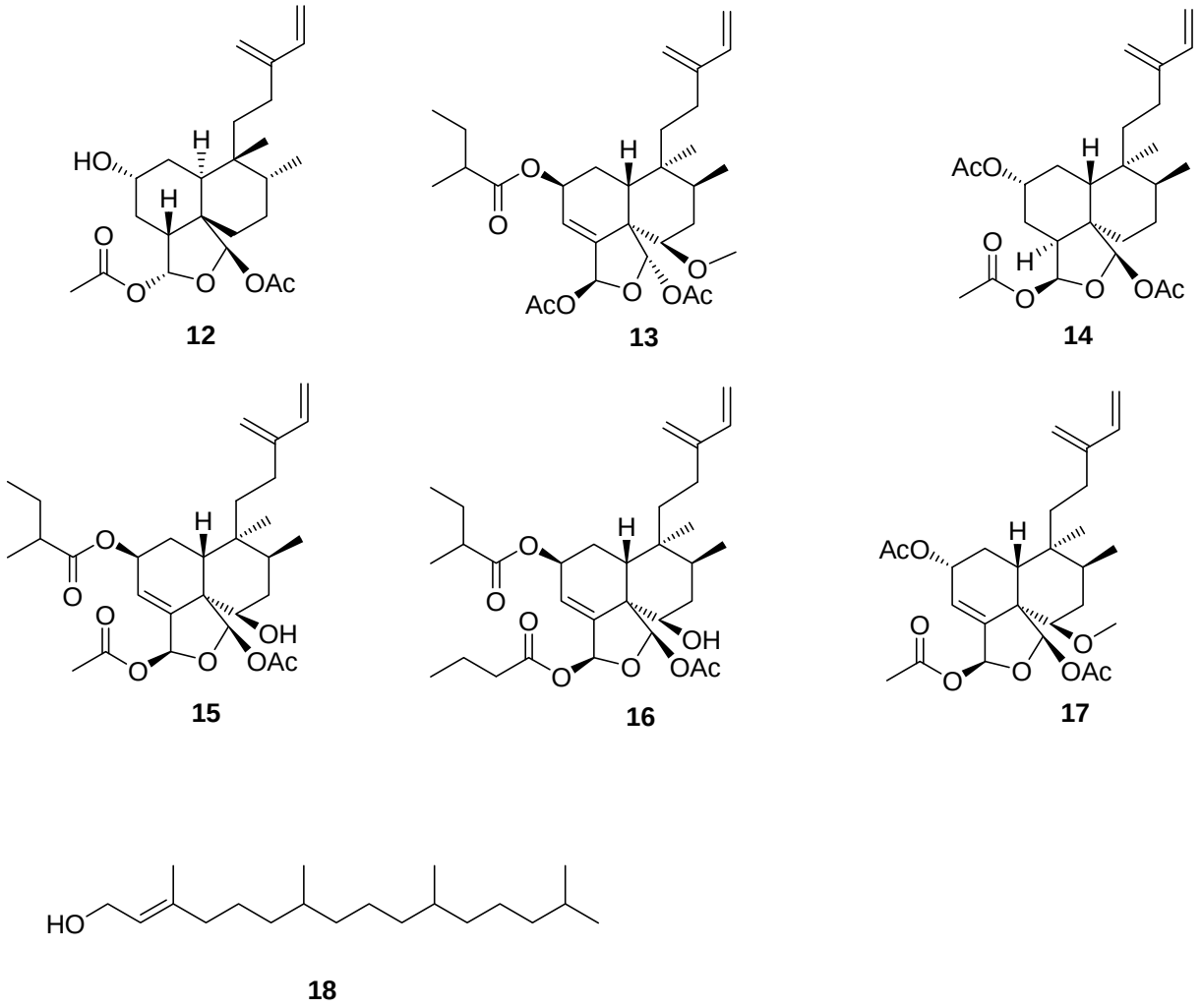


Figure S4. HPLC Chromatogram of the acetone extract of the plant together with **5**–**8**.

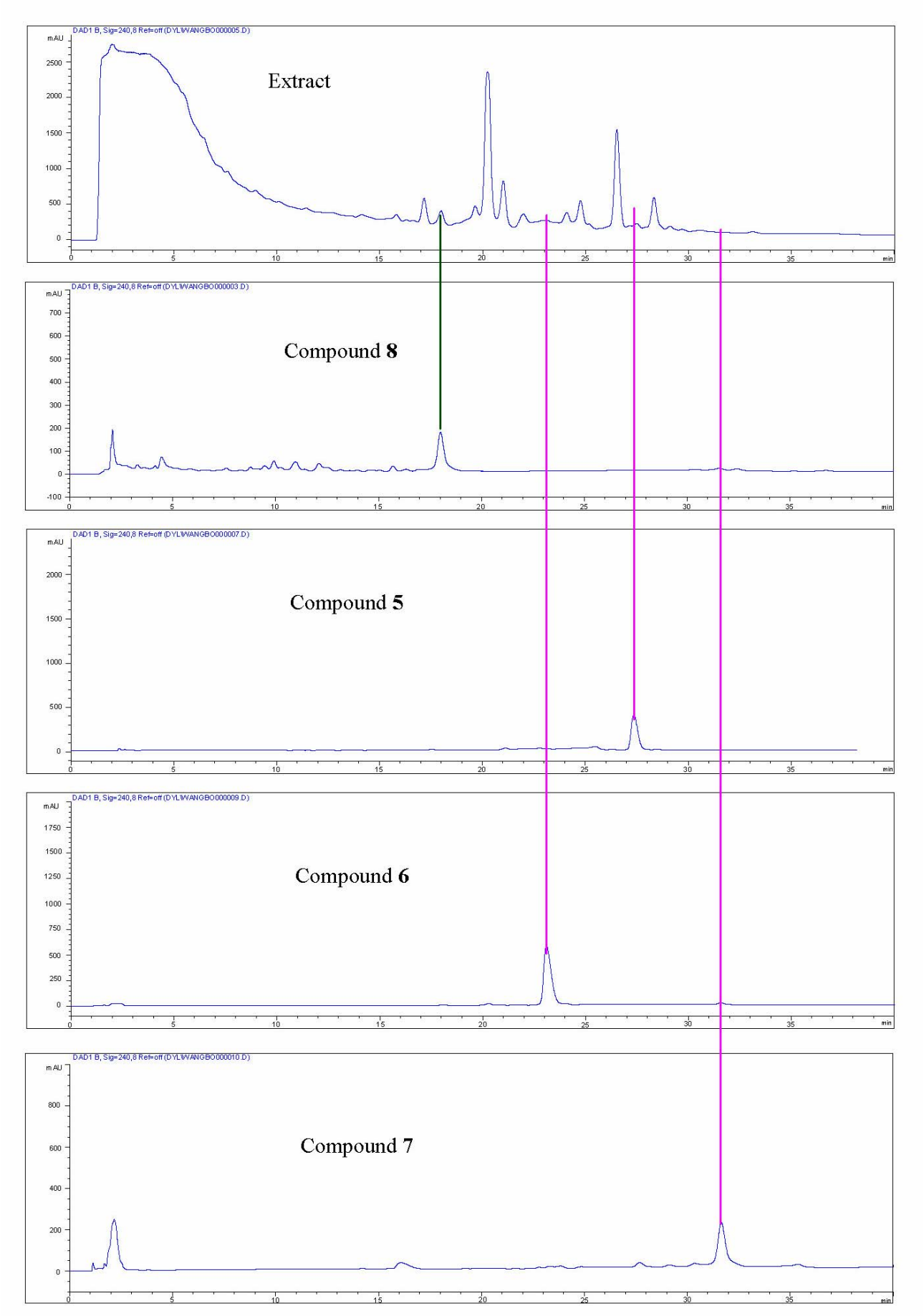


Figure S5. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **1** and **2**

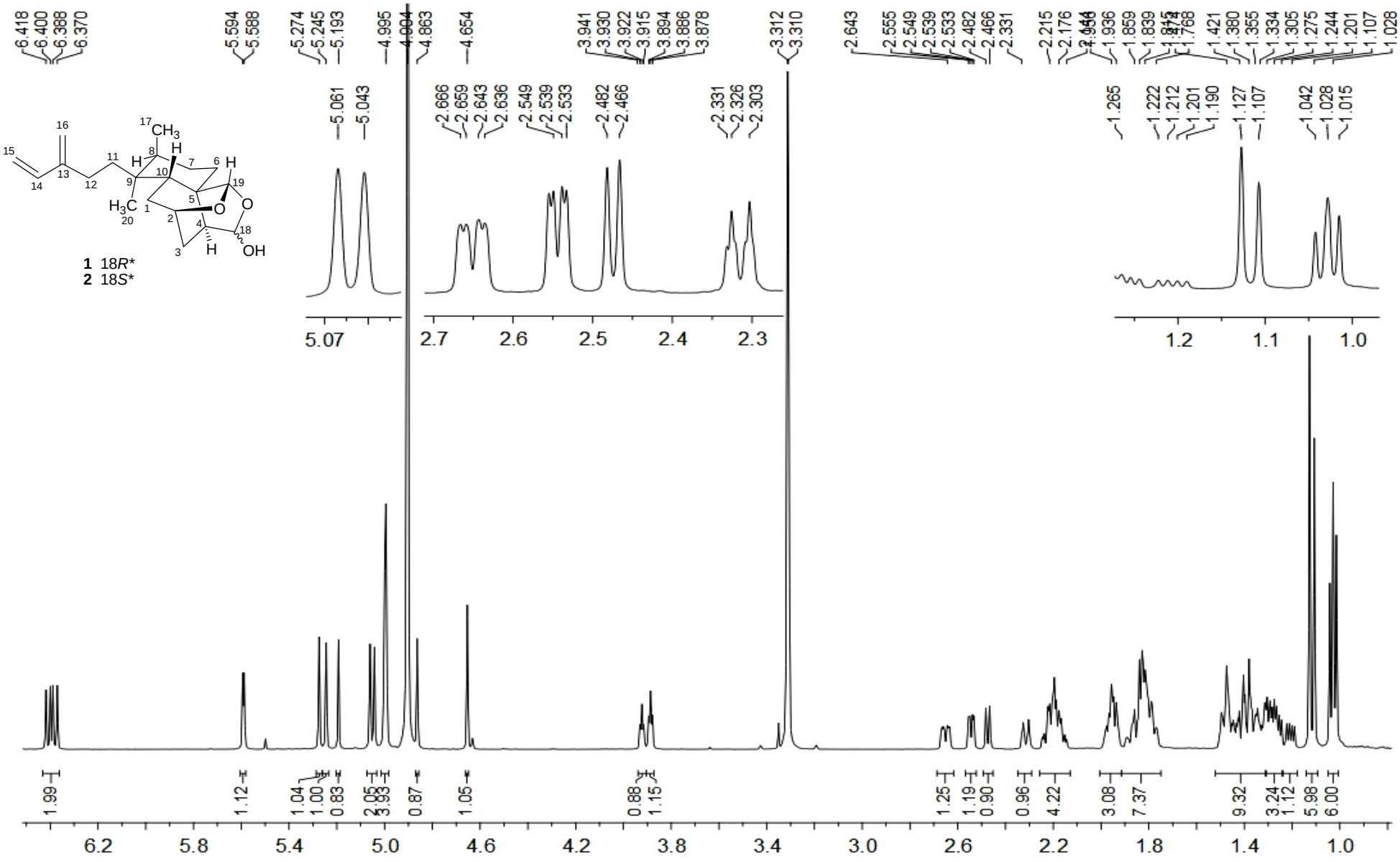


Figure S6. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **1** and **2**

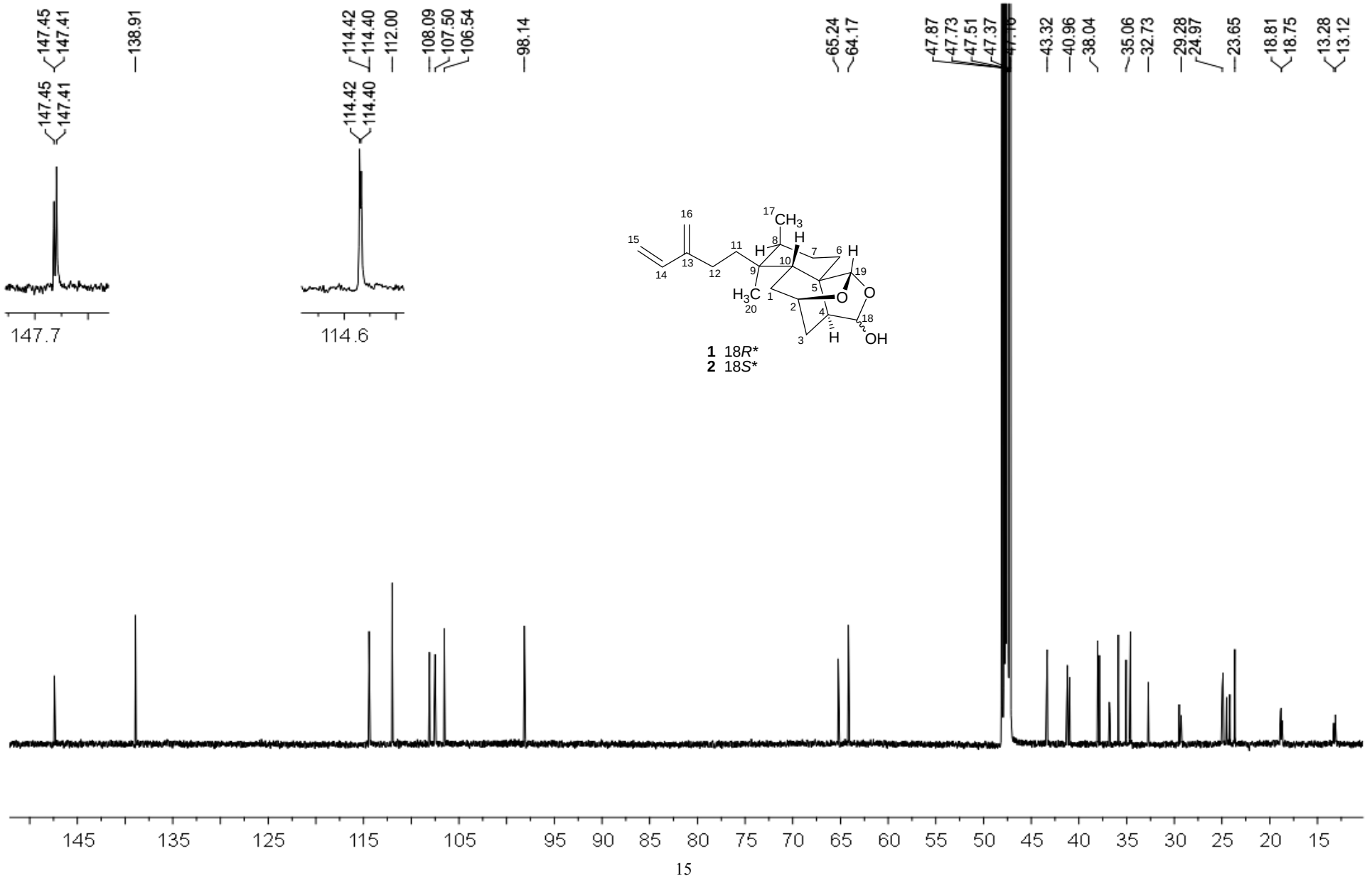


Figure S7. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **1** and **2** (expansion δ 14.0-42.0)

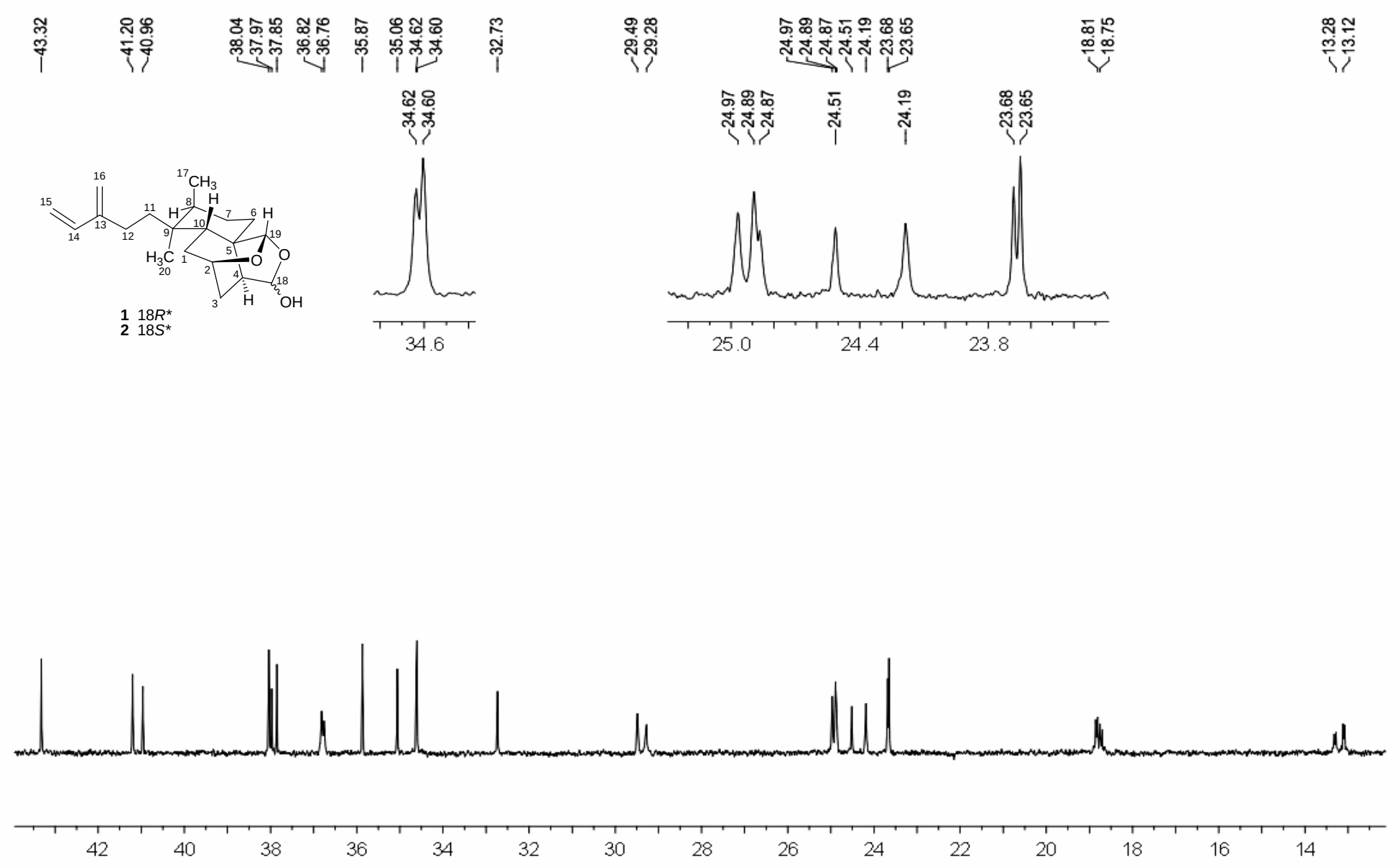


Figure S8. HSQC (600 MHz, methanol-d_4) spectrum of **1** and **2**

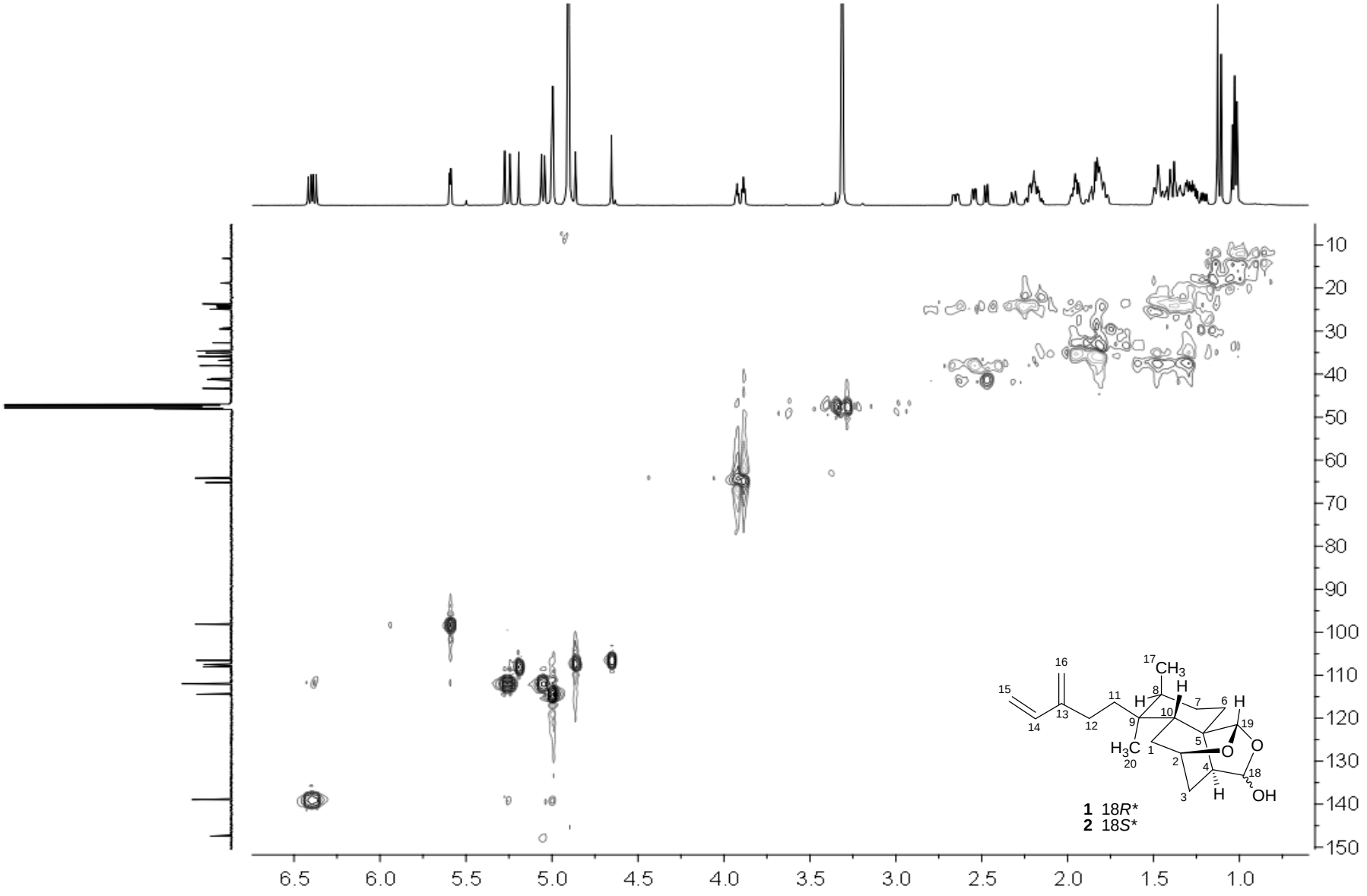


Figure S9. HMBC (600 MHz, methanol-d_4) spectrum of **1** and **2**

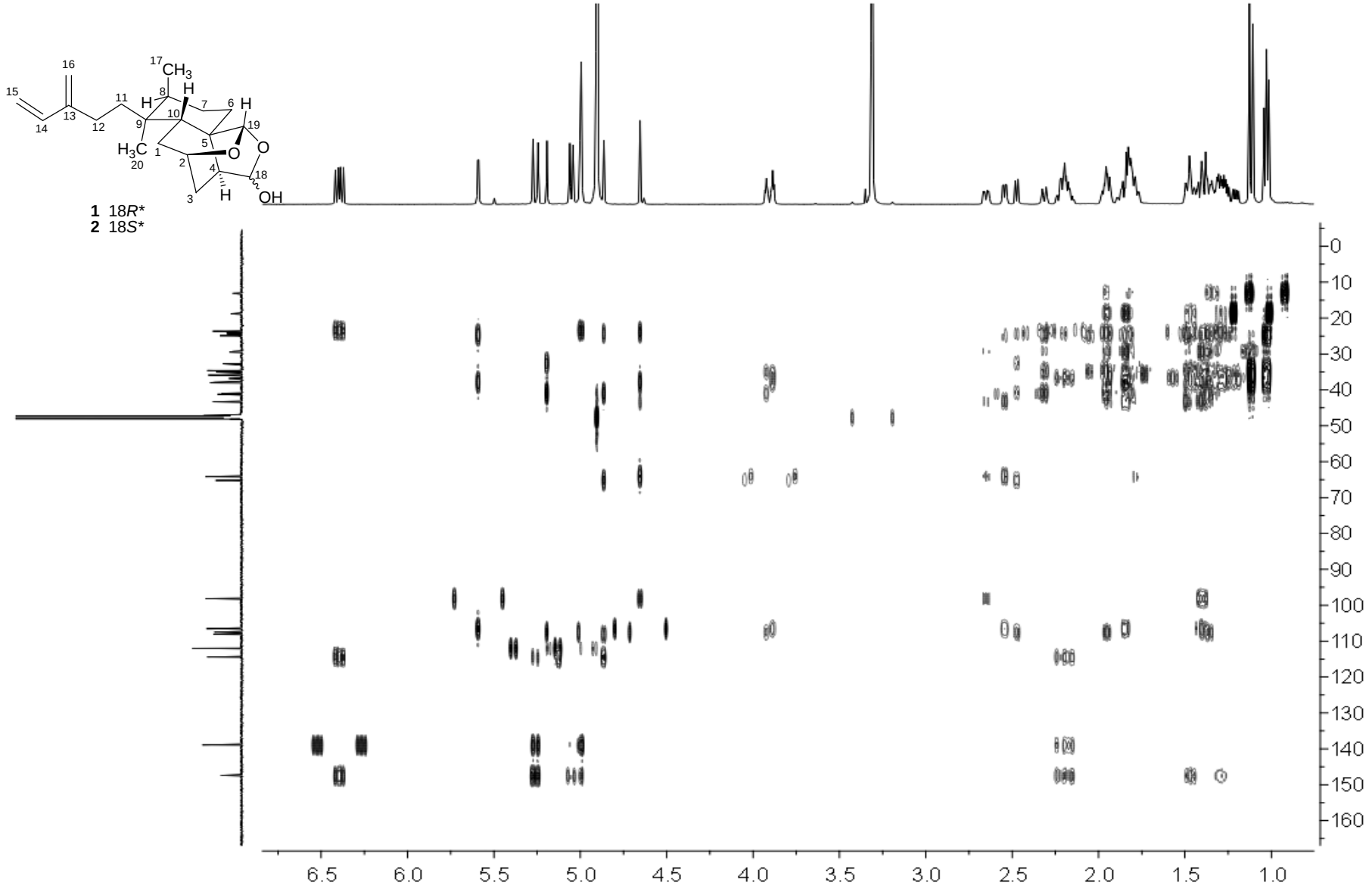


Figure S10. ^{1}H-^{1}H COSY (600 MHz, methanol-d_4) spectrum of **1** and **2**

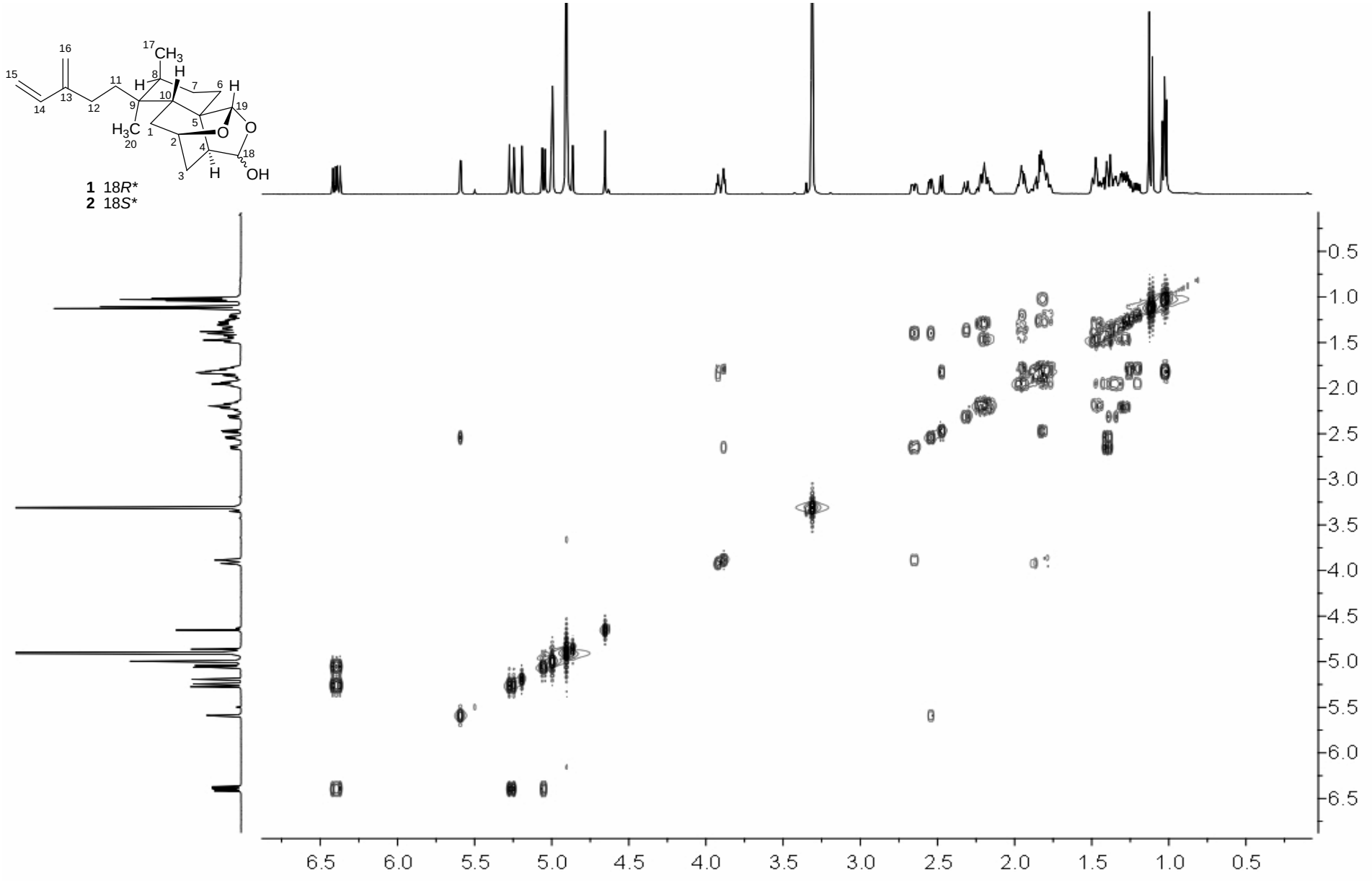


Figure S11. NOESY (600 MHz, methanol-d_4) spectrum of **1** and **2**

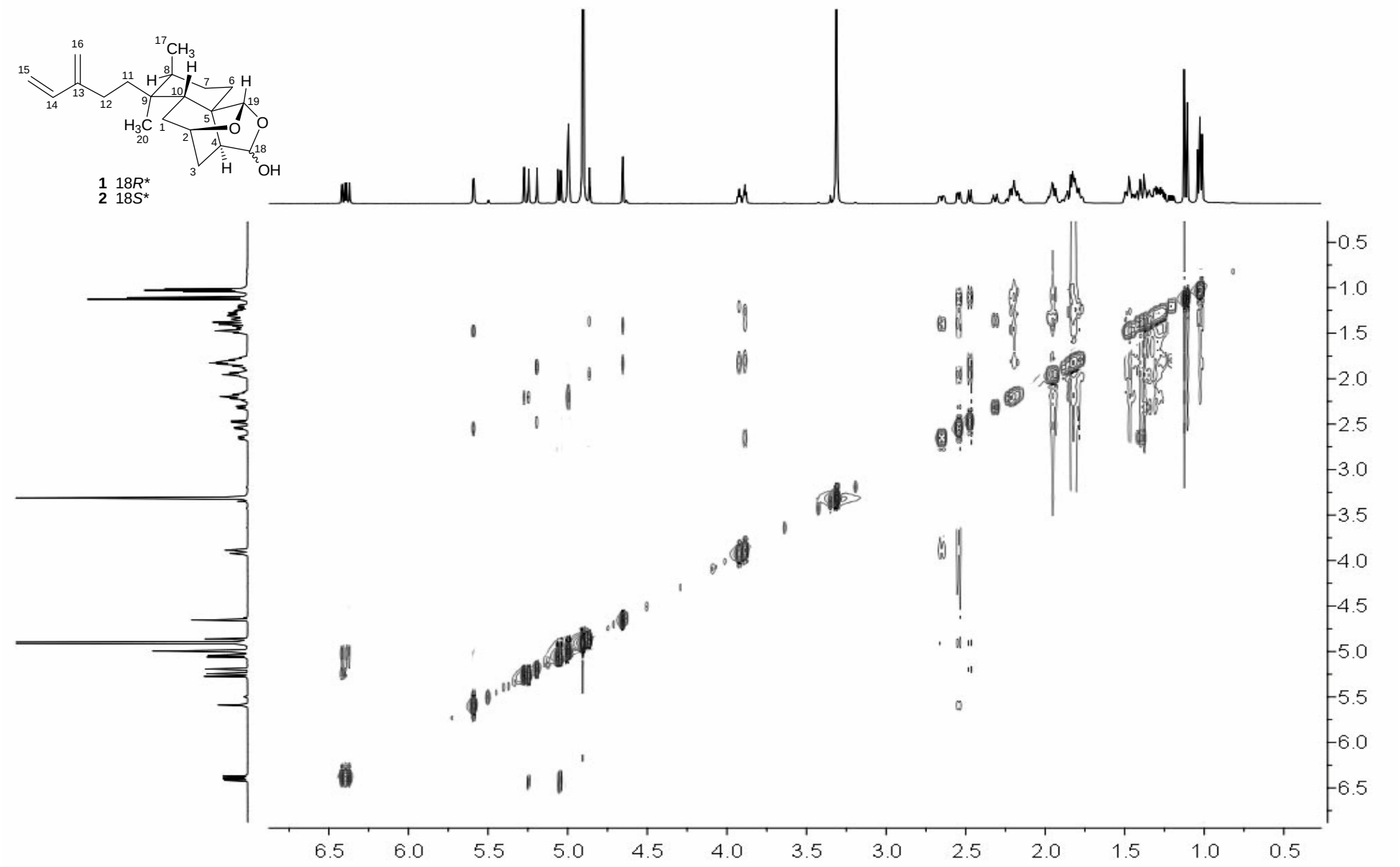


Figure S12. HRESIMS spectrum of **1** and **2**

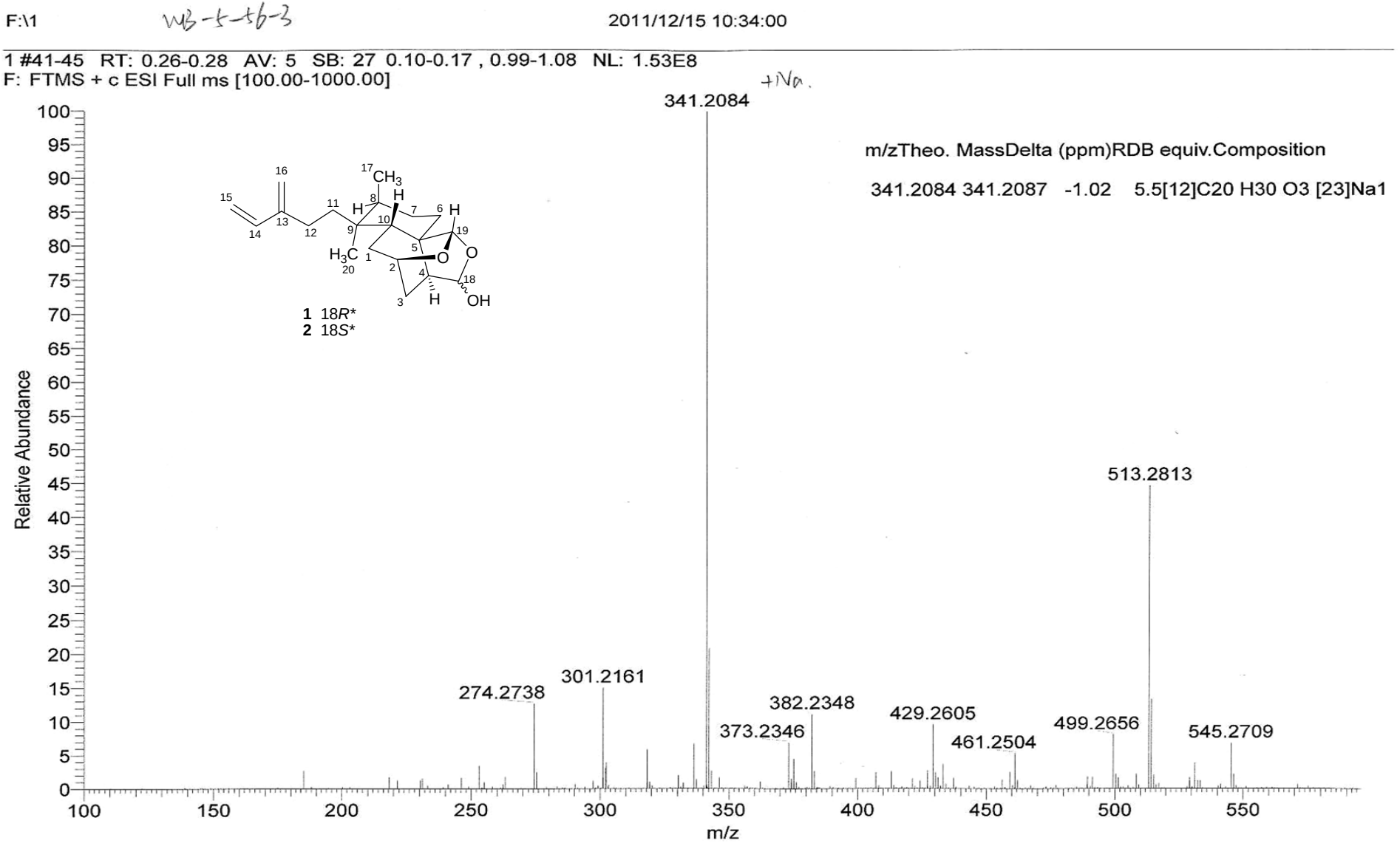


Figure S13. IR spectrum of **1** and **2**

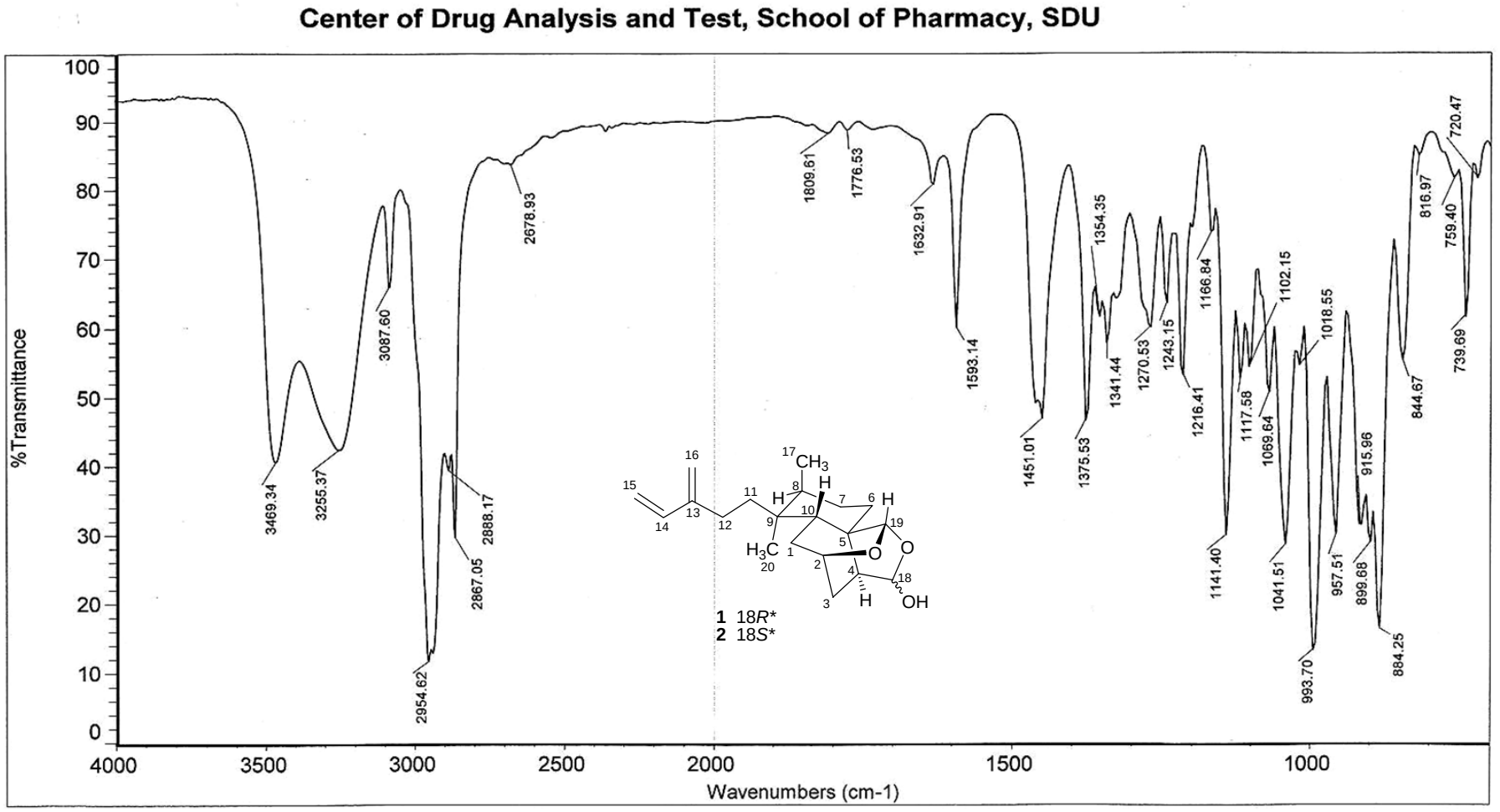
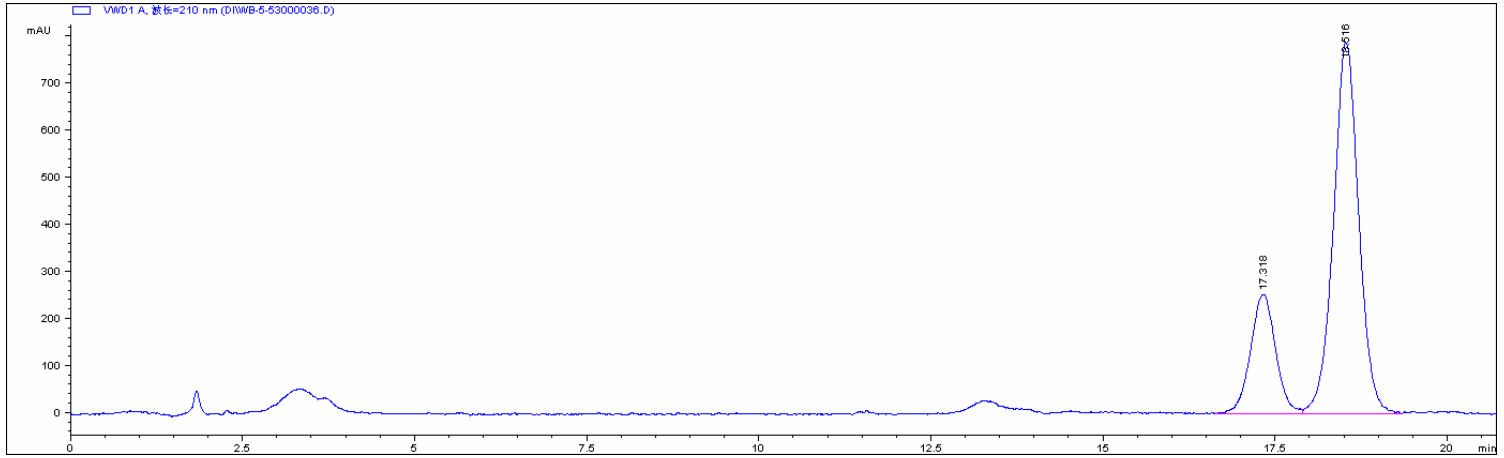
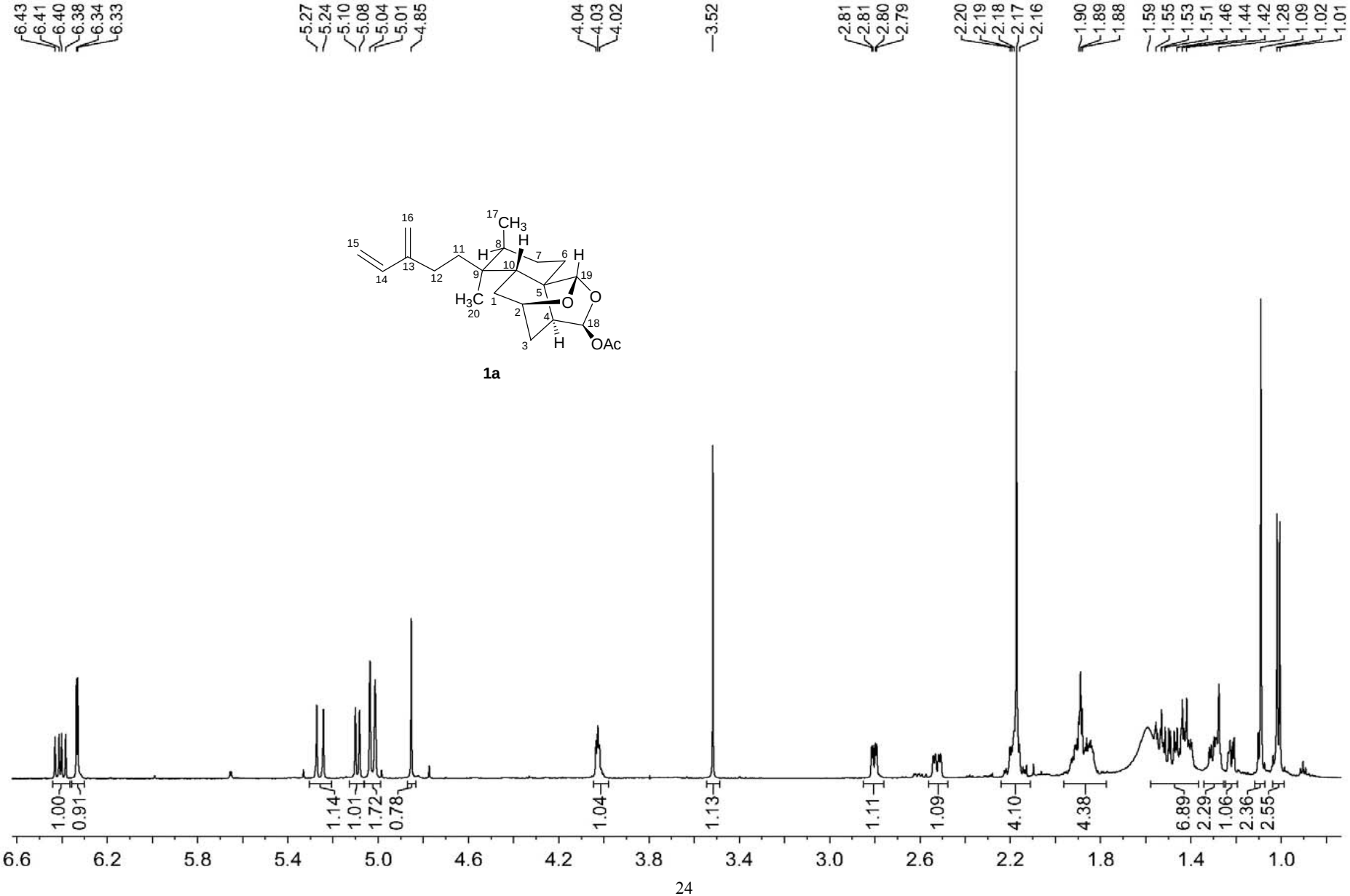


Figure S14. HPLC chromatogram for the sepatarion of **1a** and **2a**



	Retention time	Peak area	Percentage
1a	17.318 min	6508.5	24.331%
2a	18.516 min	20241.1	75.669%

Figure S15. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **1a**



1a

Figure S16. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **1a**

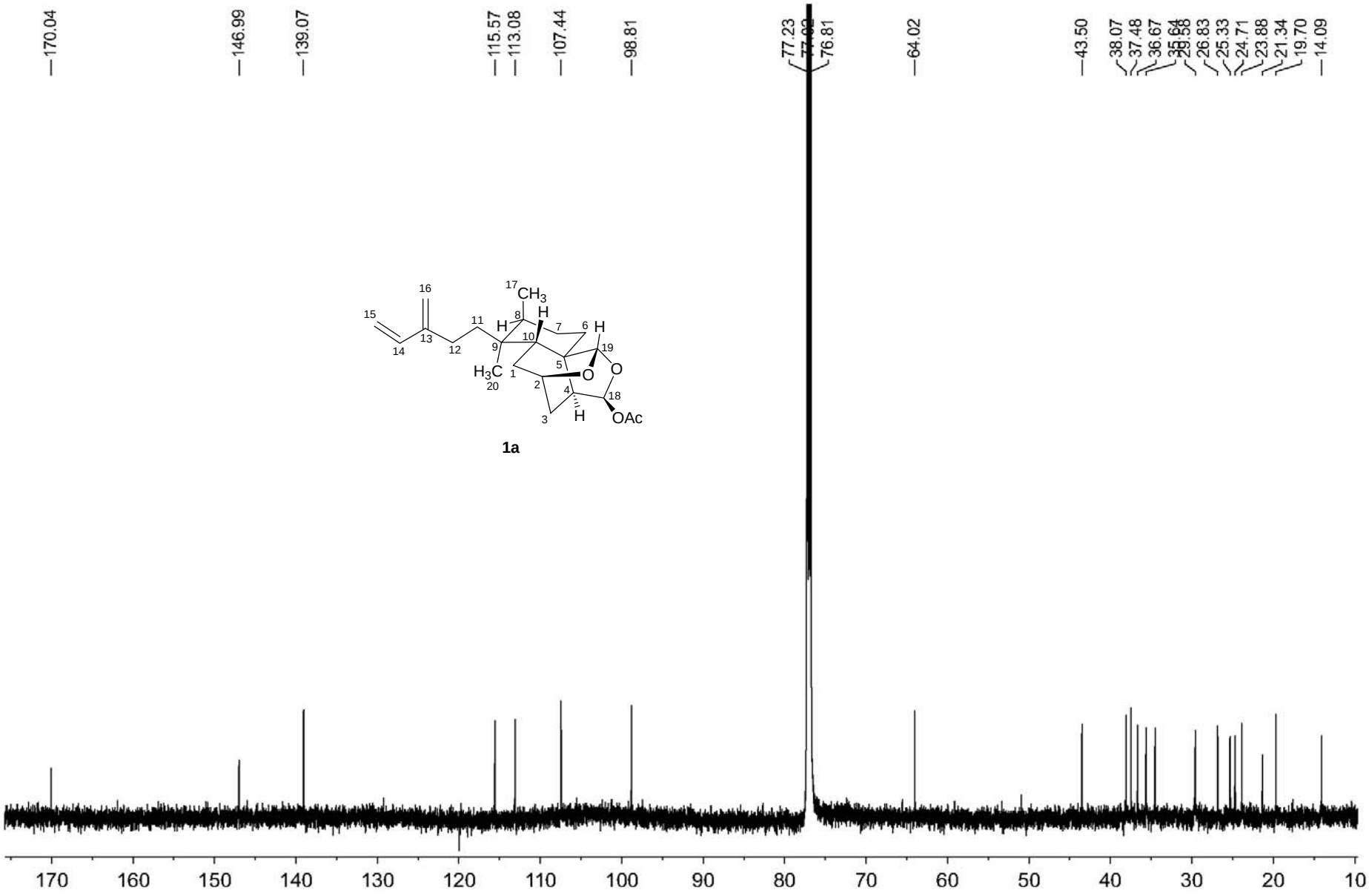
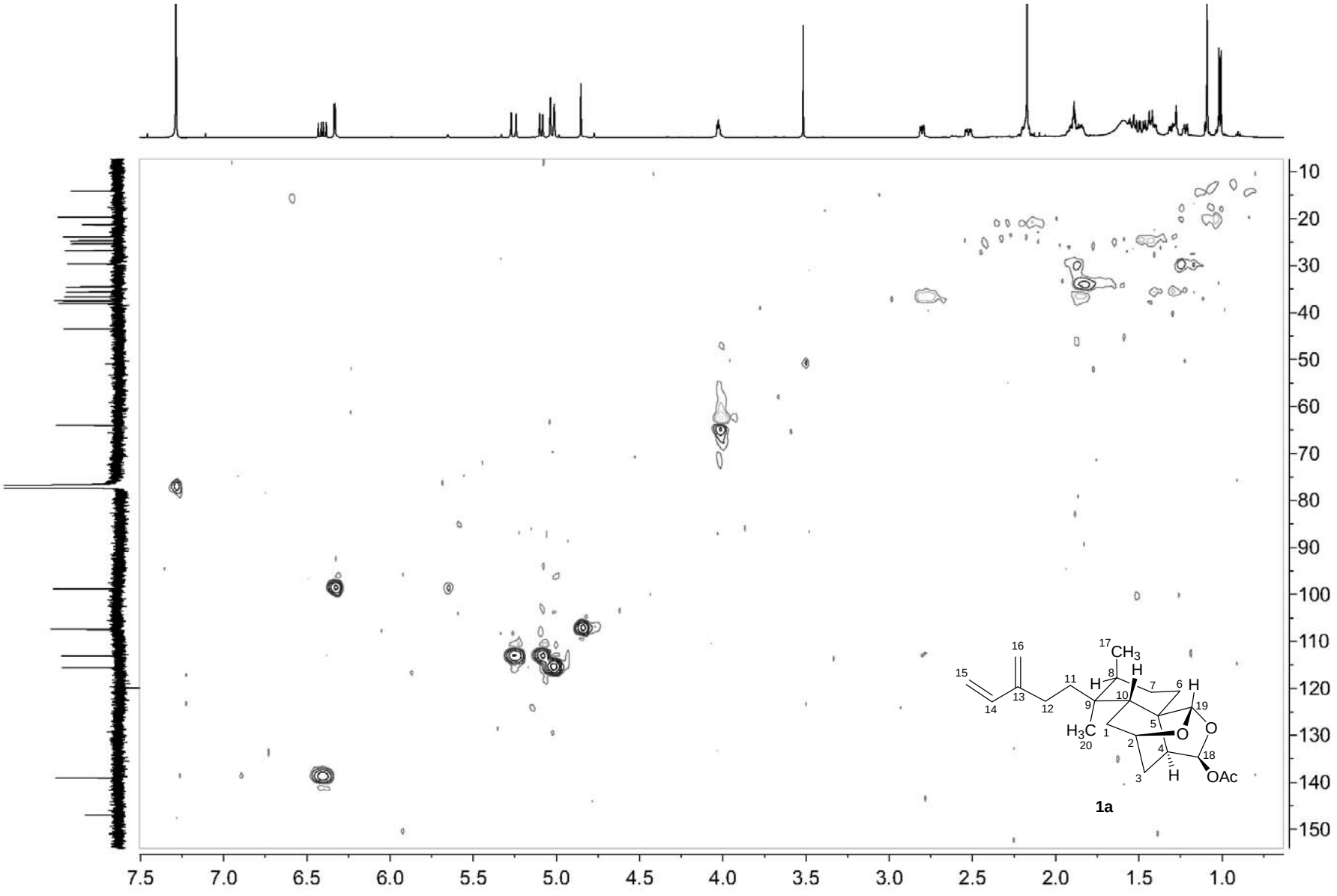
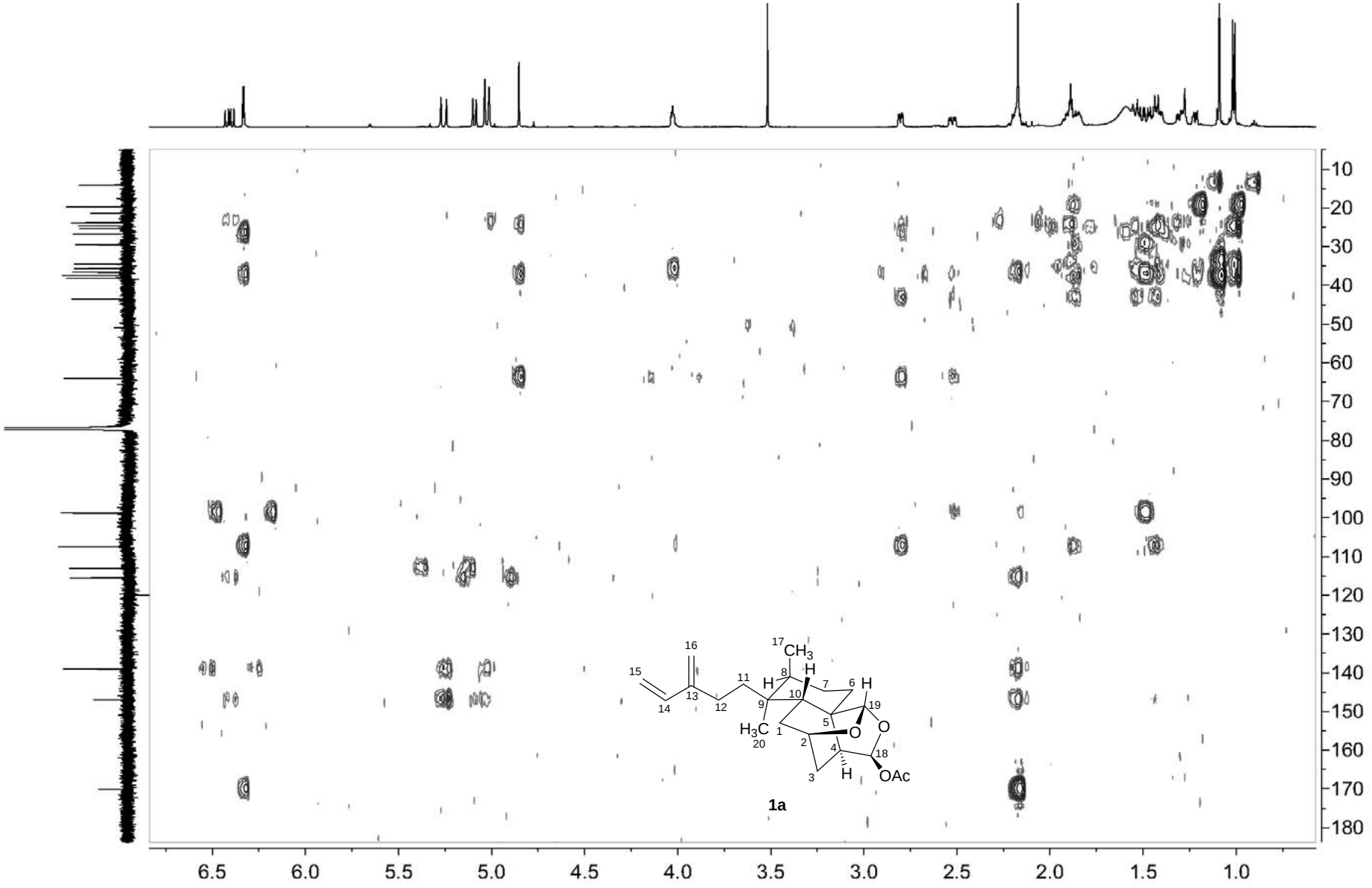


Figure S17. HSQC (600 MHz, $CDCl_3$) spectrum of **1a**



1a

Figure S18. HMBC (600 MHz, $CDCl_3$) spectrum of **1a**



1a

Figure S19. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **1a**

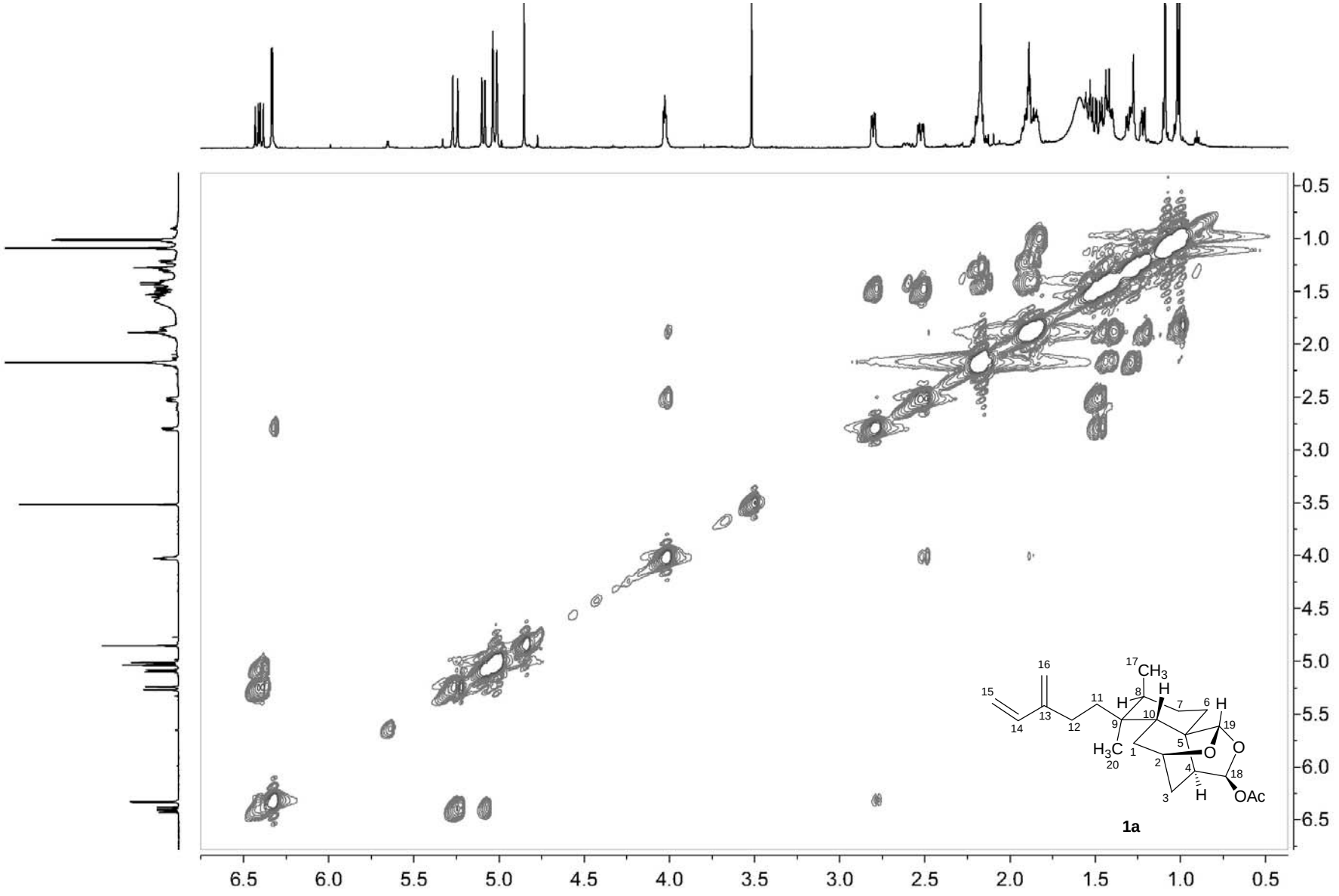


Figure S20. NOESY (600 MHz, $CDCl_3$) spectrum of **1a**

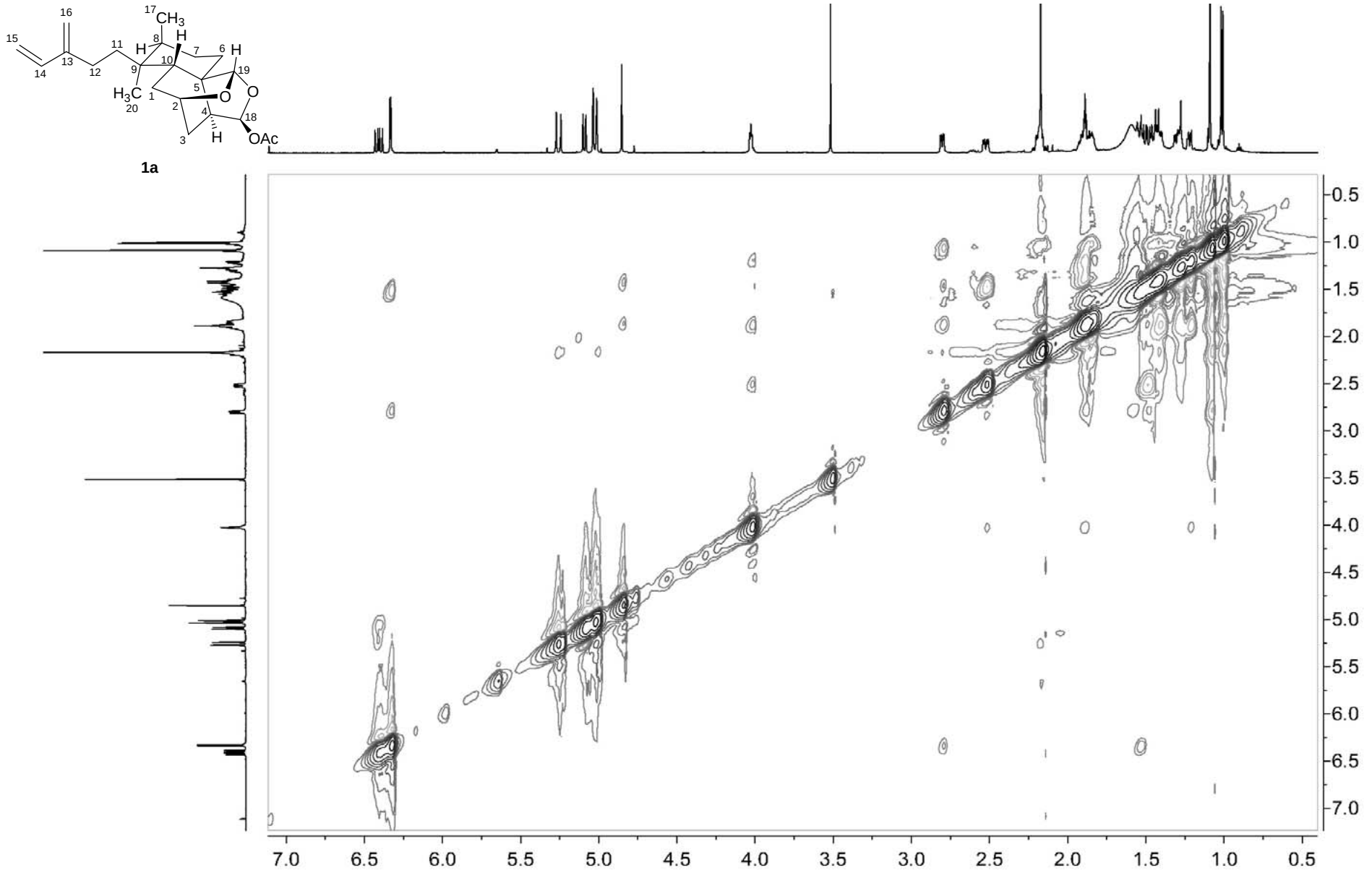


Figure S21. HRESIMS spectrum of **1a**

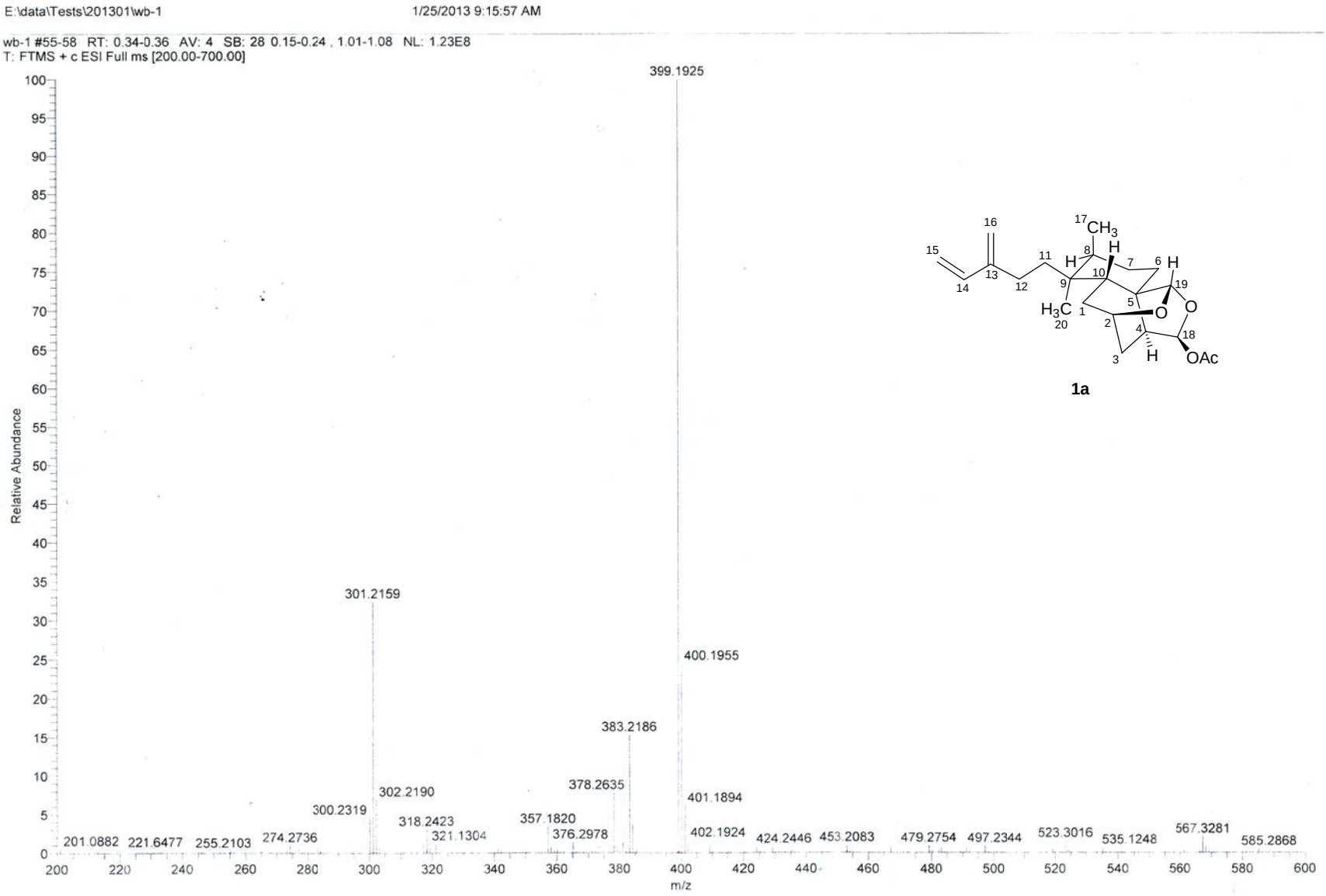
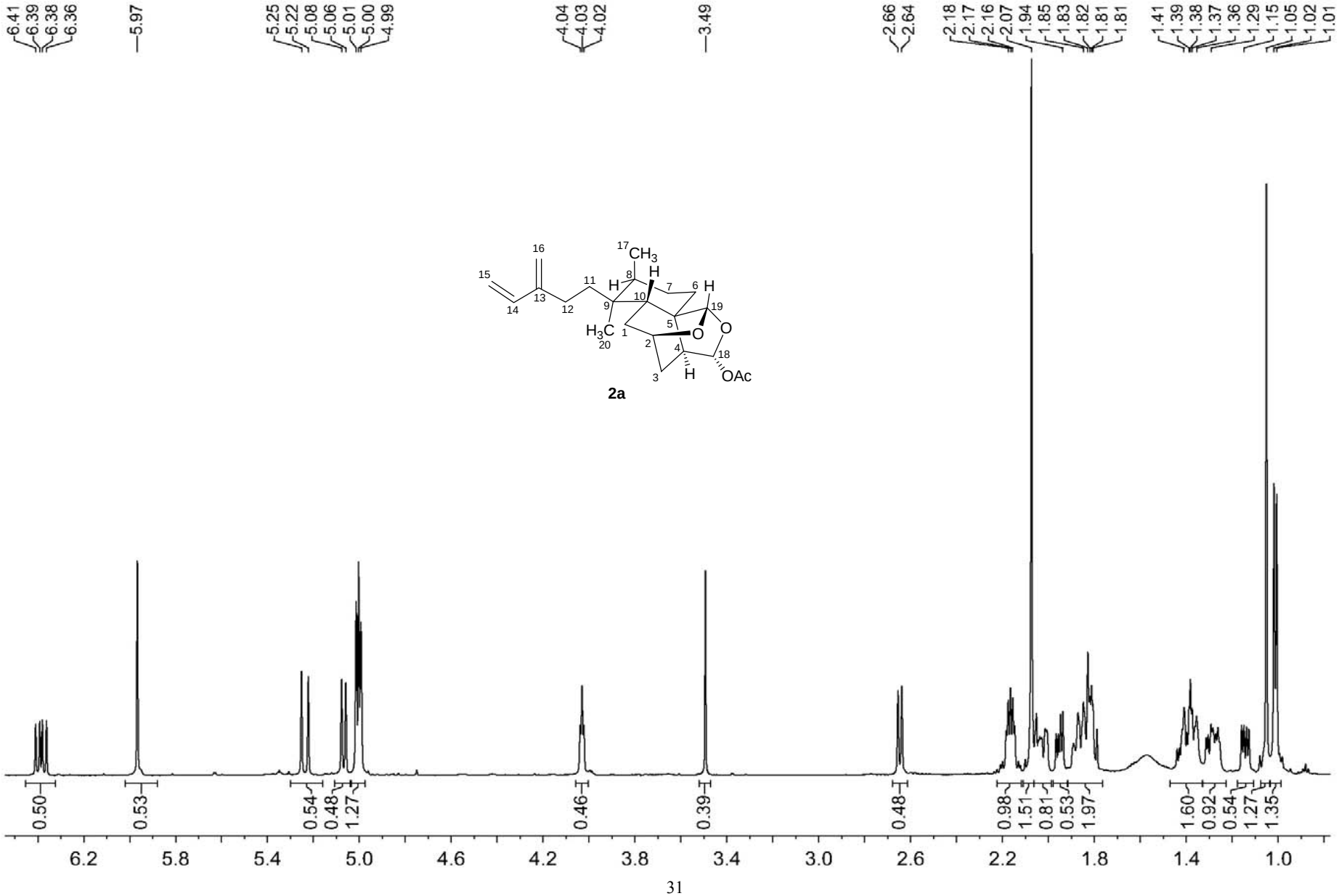


Figure S22. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a**



2a

Figure S23. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **2a**

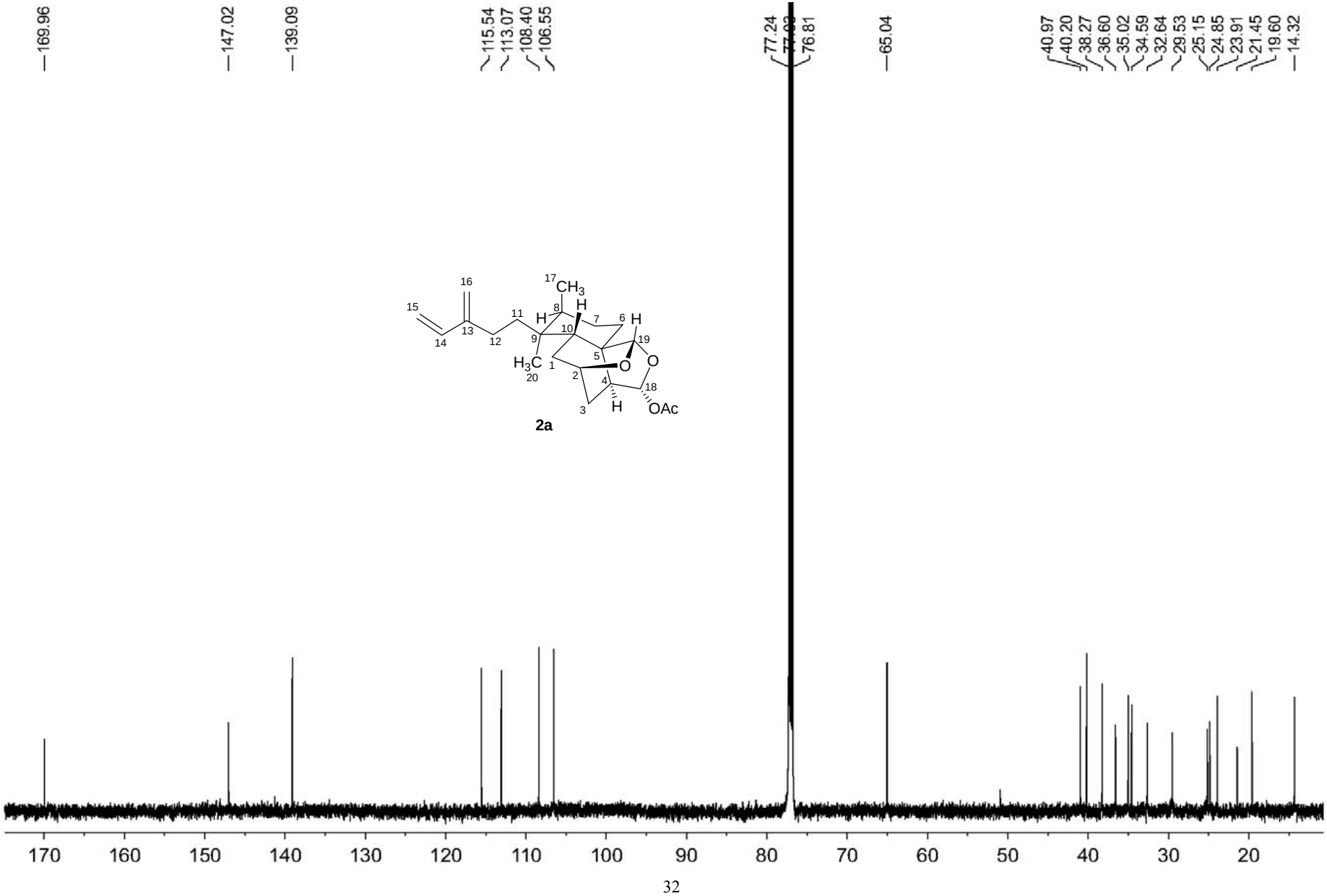


Figure S24. HSQC (600 MHz, $CDCl_3$) spectrum of **2a**

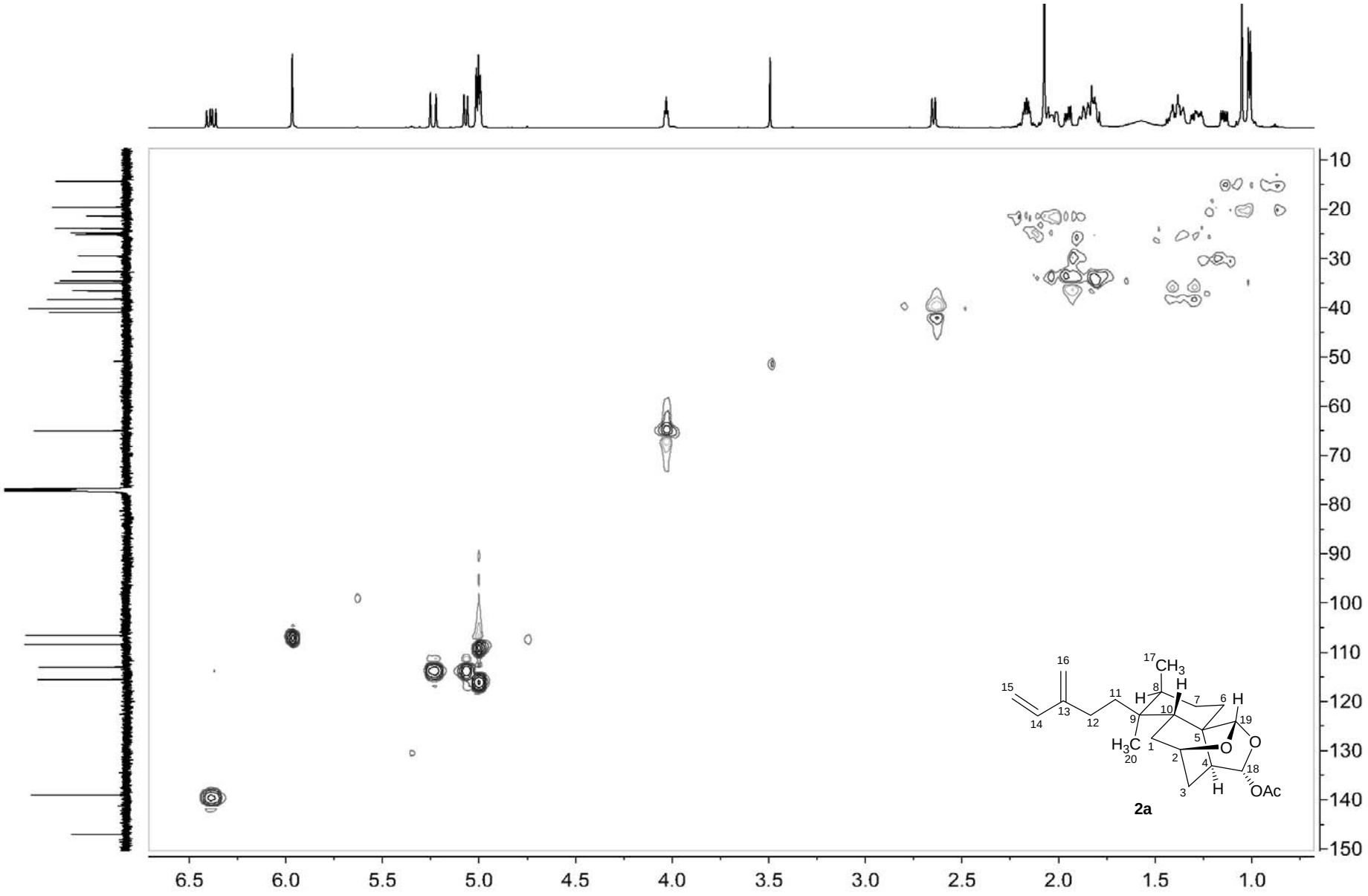


Figure S25. HMBC (600 MHz, $CDCl_3$) spectrum of **2a**

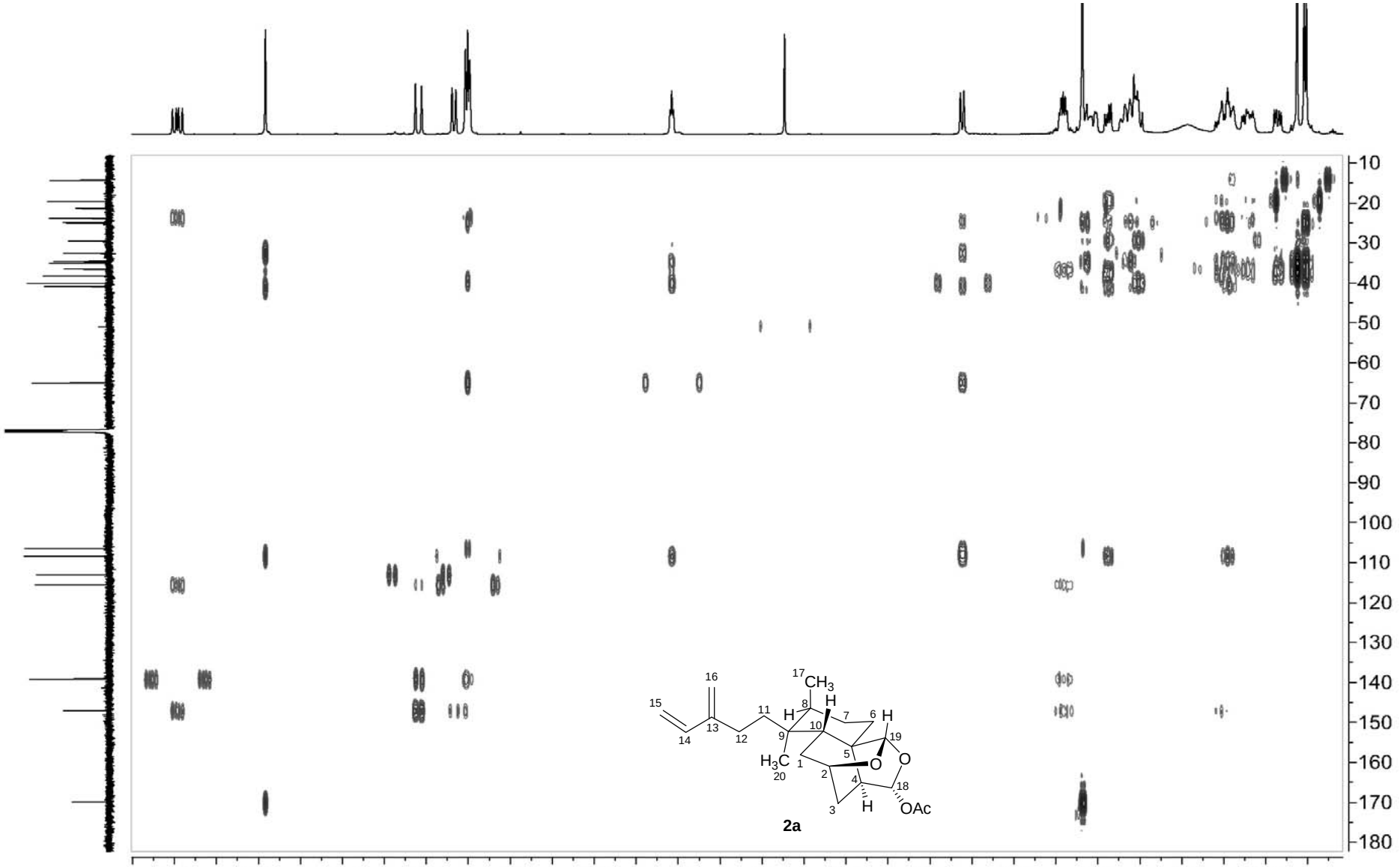


Figure S26. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **2a**

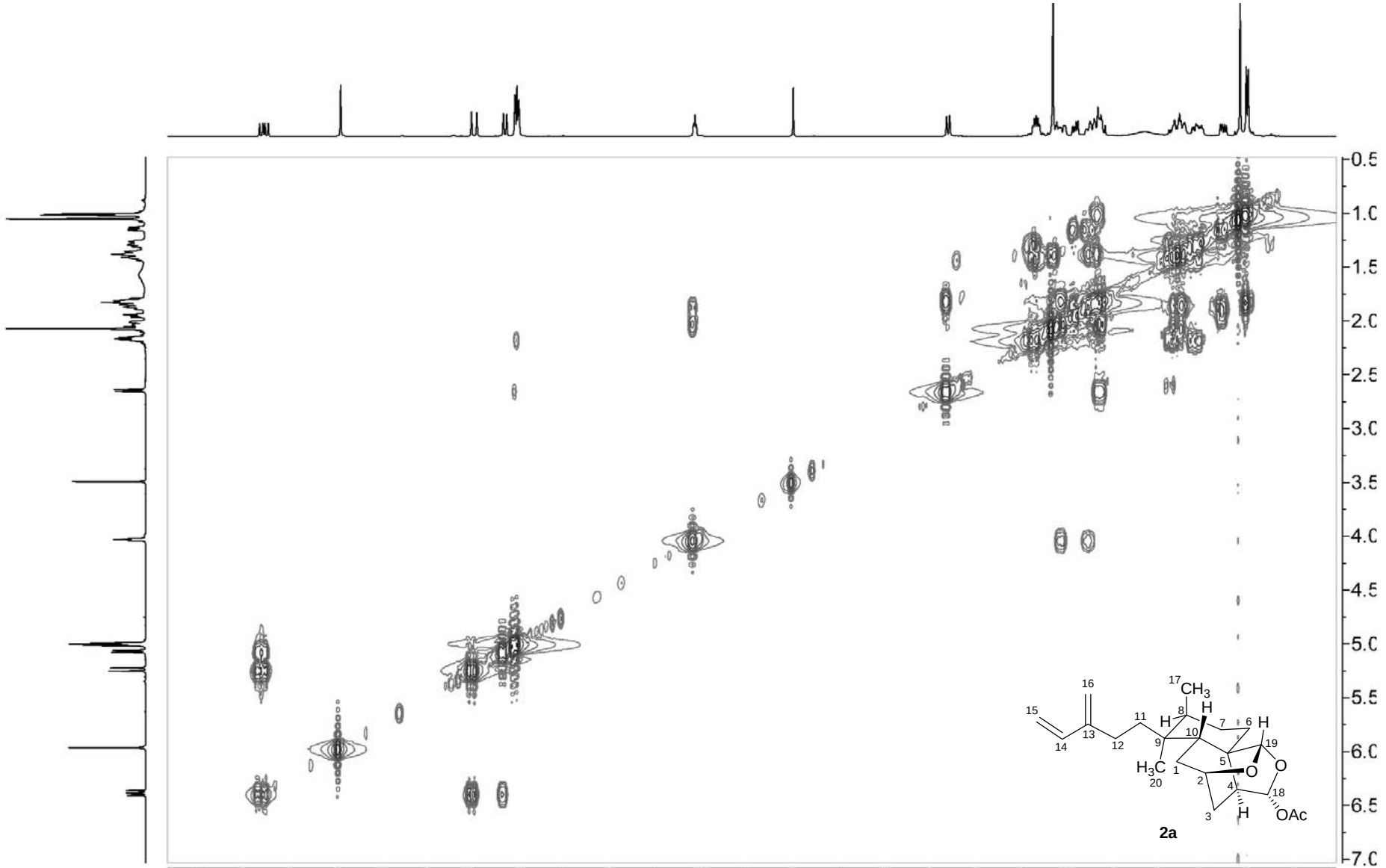


Figure S27. NOESY (600 MHz, $CDCl_3$) spectrum of **2a**

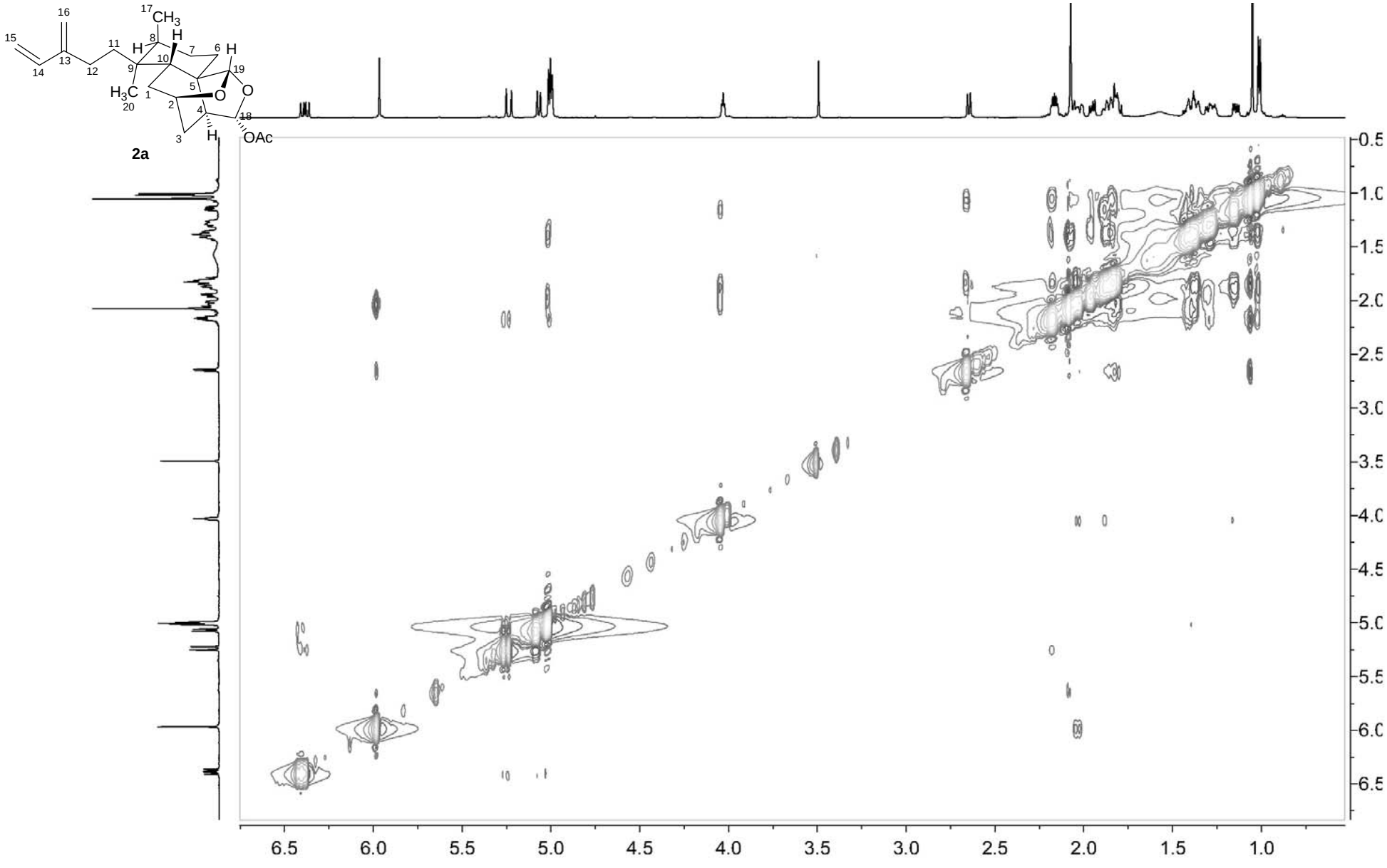


Figure S28. HRESIMS spectrum of **2a**

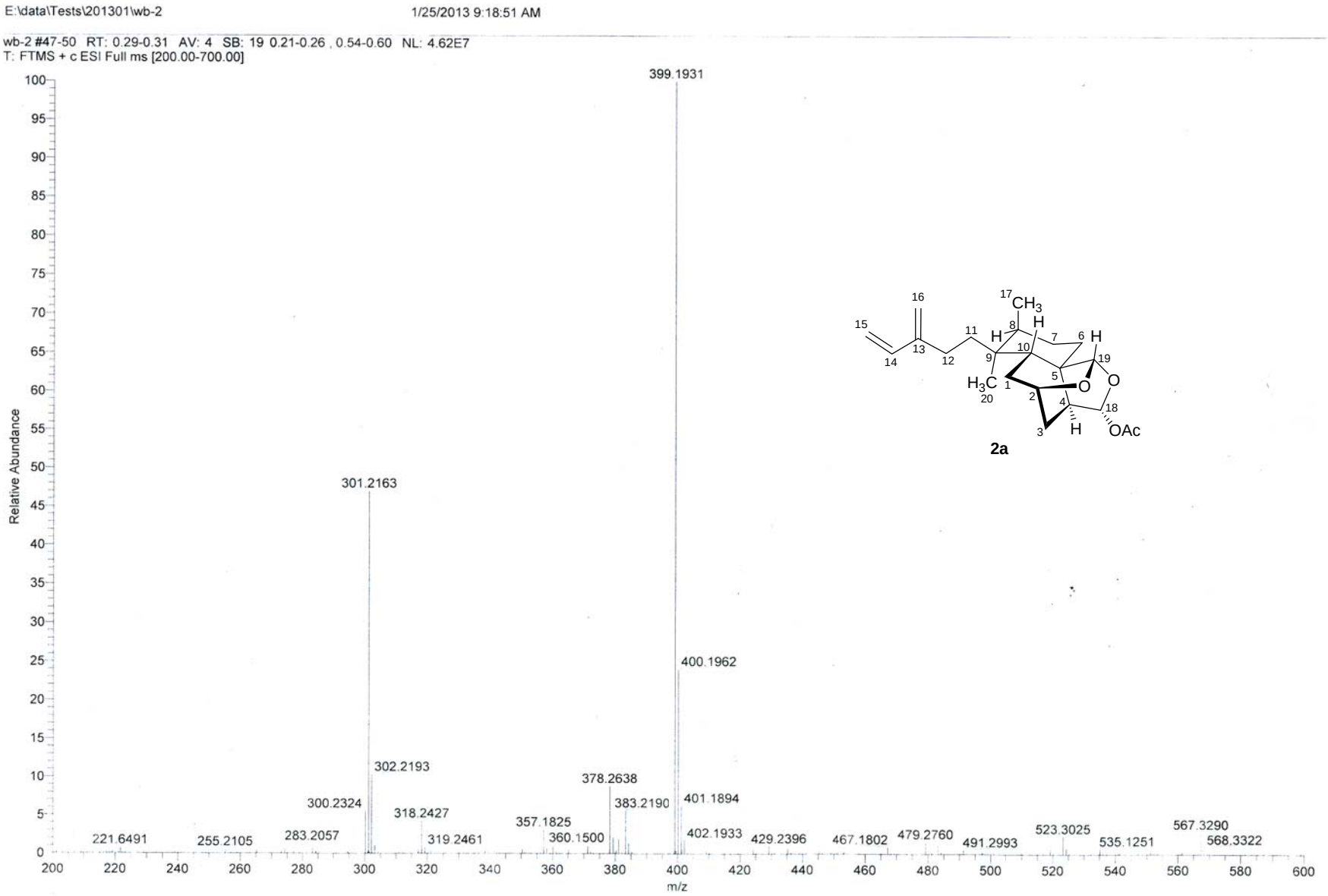


Figure S29. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **3**

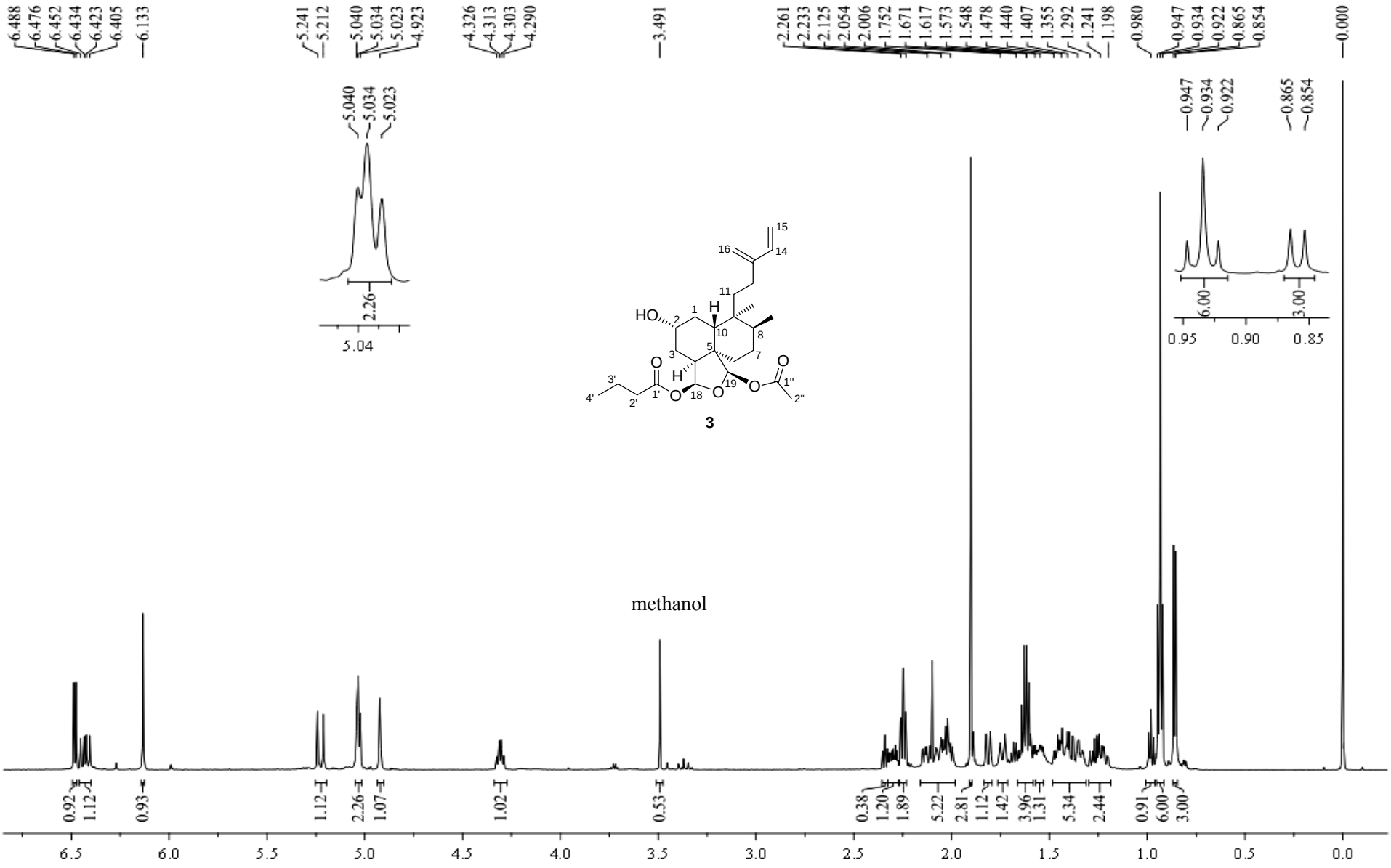
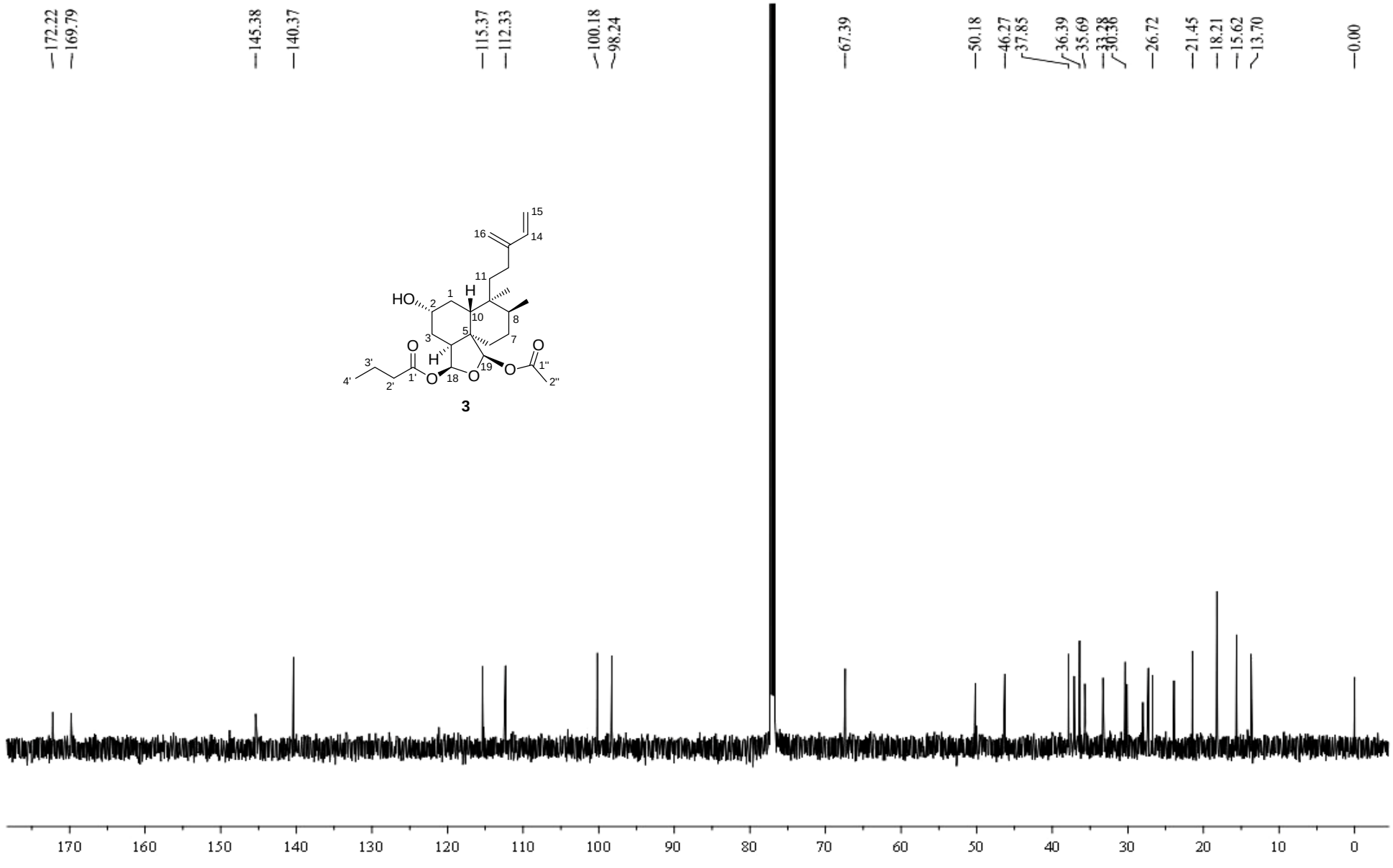


Figure S30. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **3**



3

Figure S31. HSQC (600 MHz, $CDCl_3$) spectrum of **3**

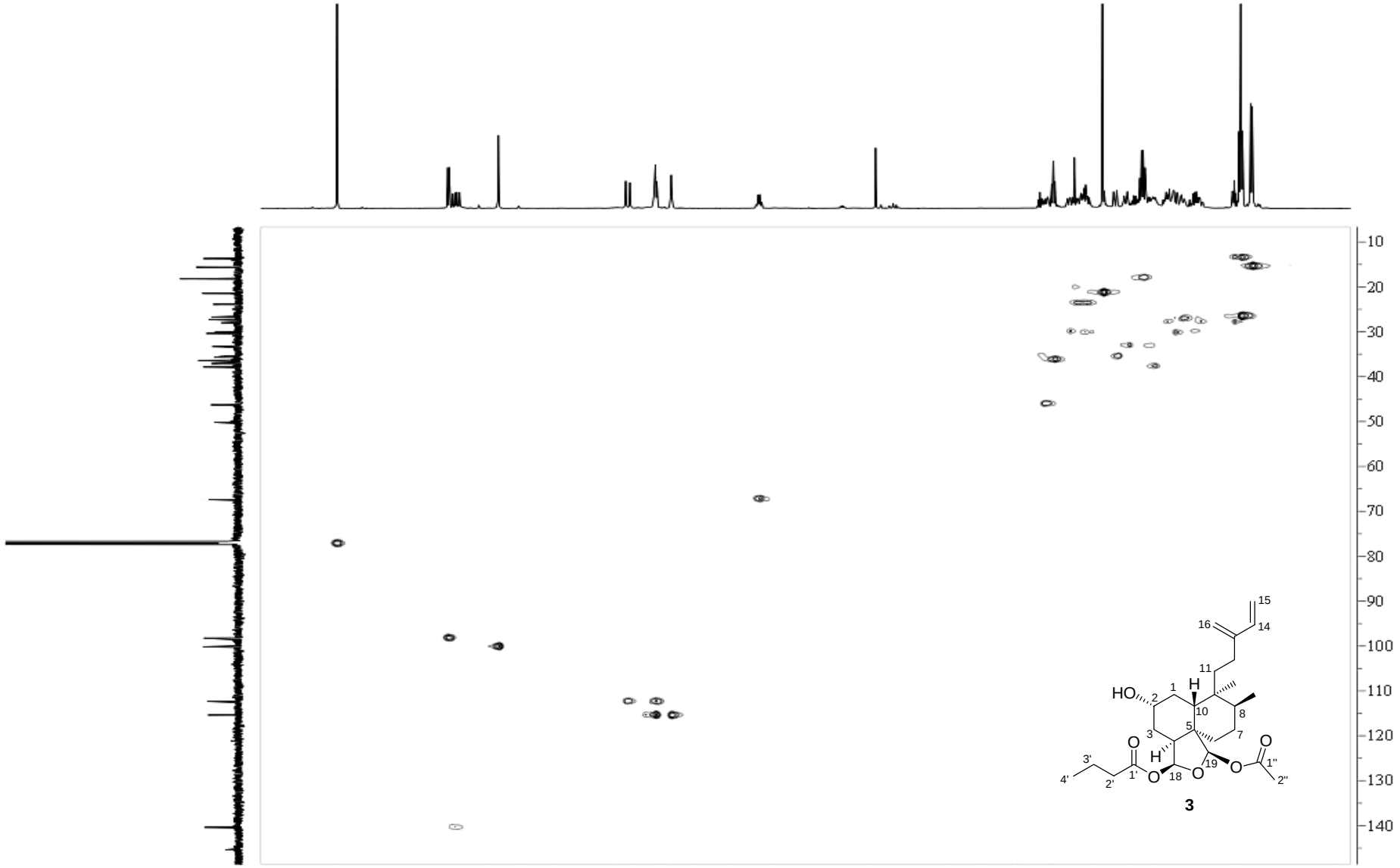


Figure S32. HMBC (600 MHz, $CDCl_3$) spectrum of **3**

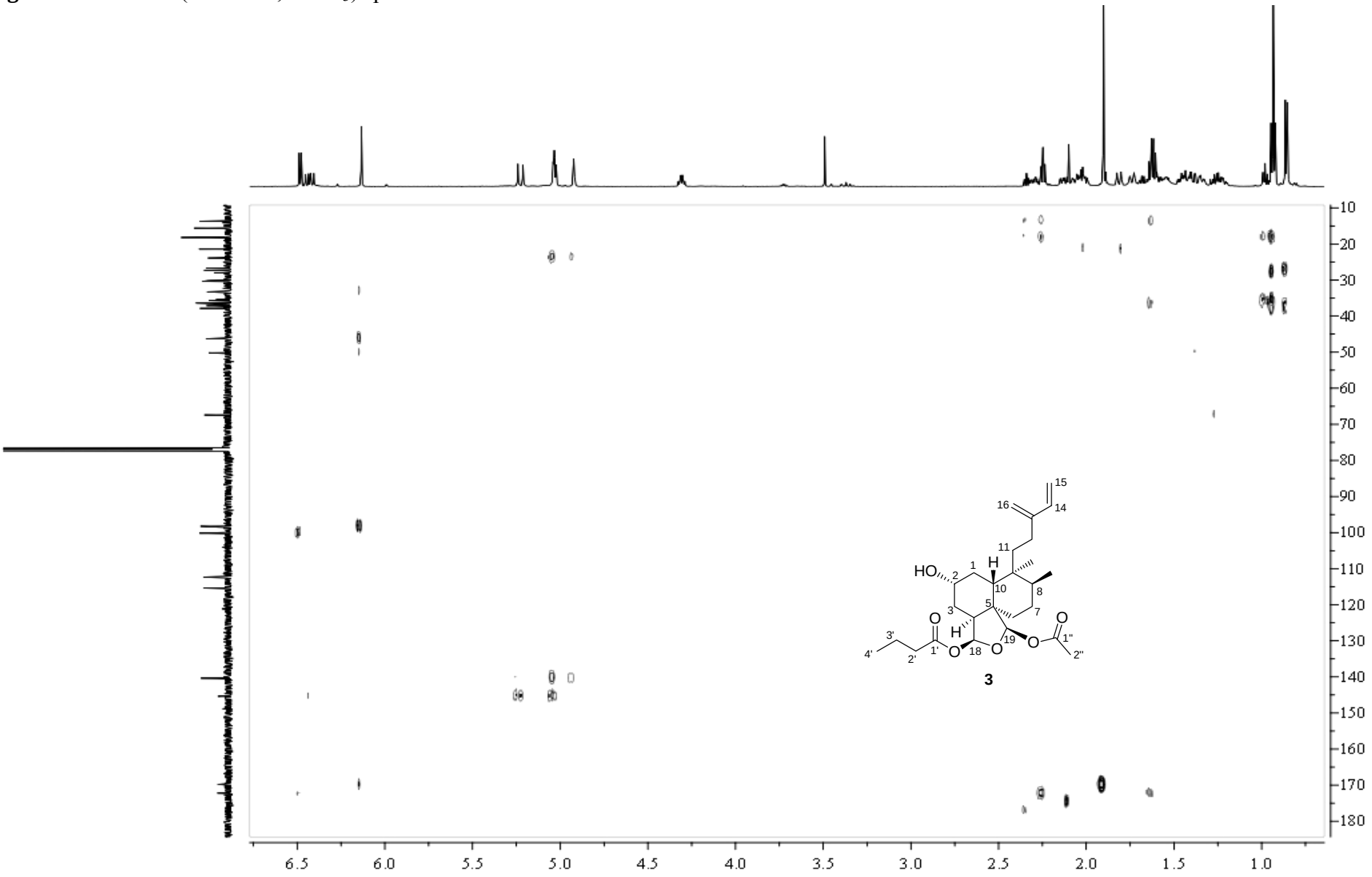


Figure S33. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **3**

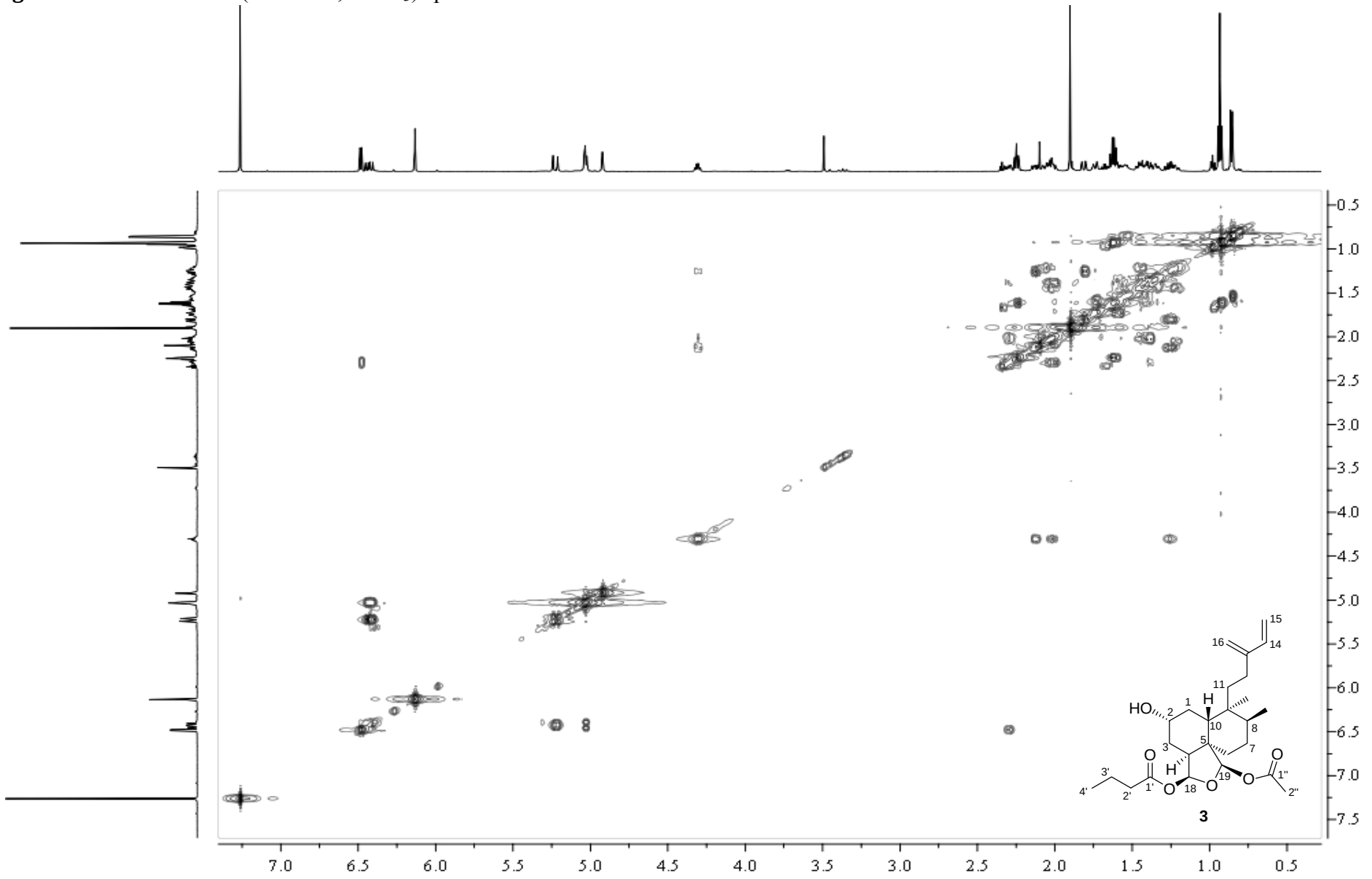
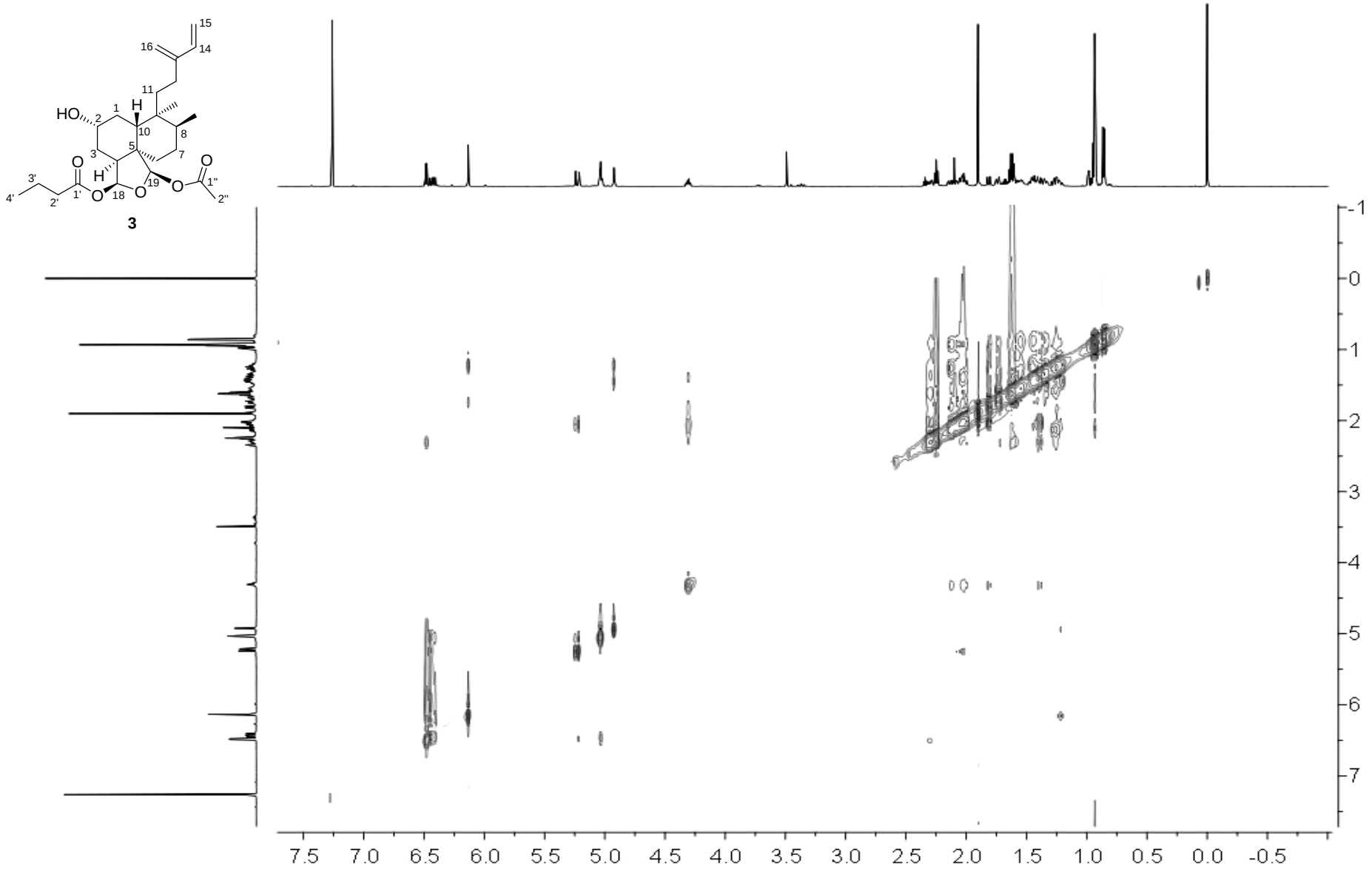


Figure S34. NOESY (600 MHz, $CDCl_3$) spectrum of **3**



3

Figure S35. HRESIMS spectrum of **3**

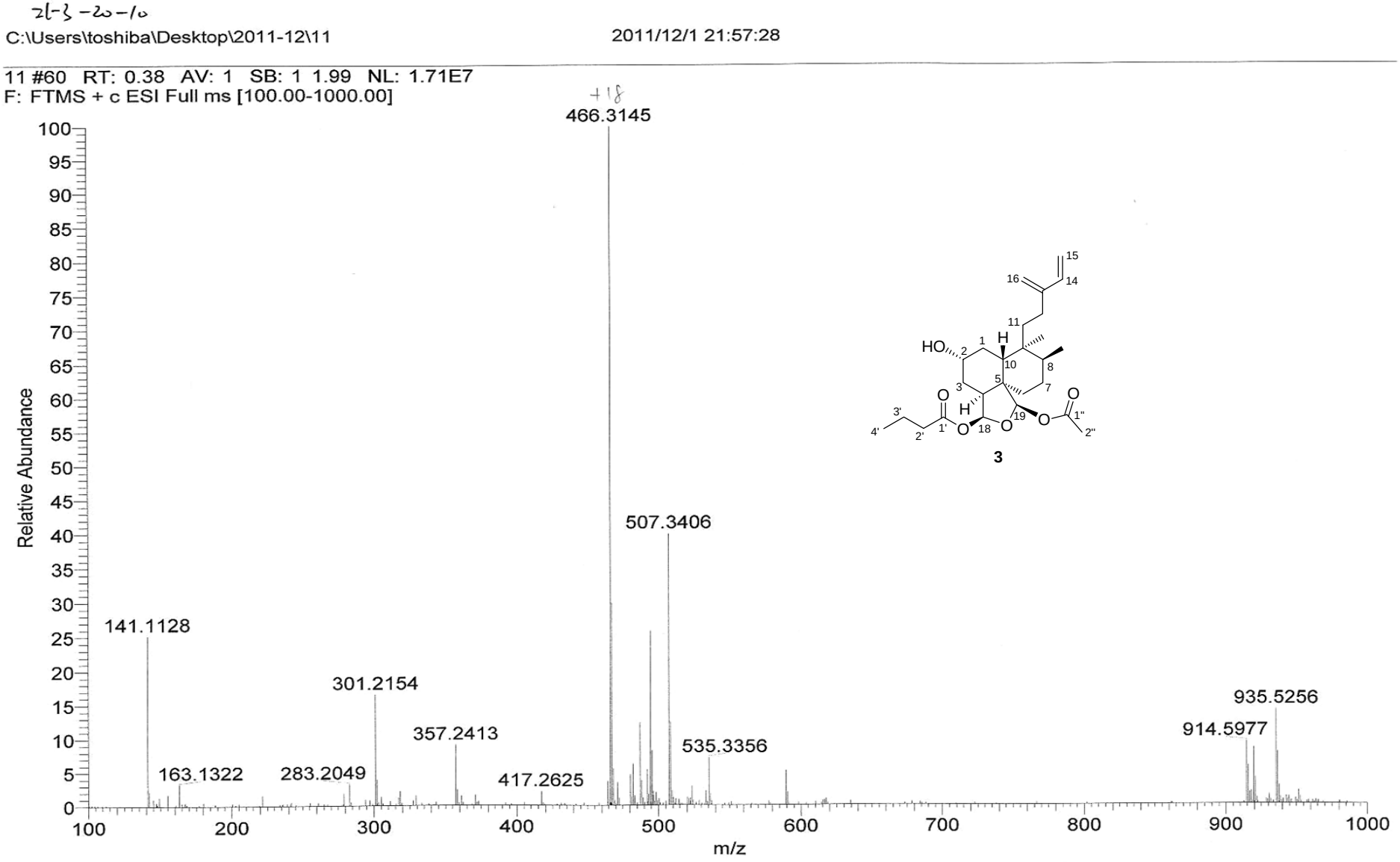


Figure S36. IR spectrum of **3**

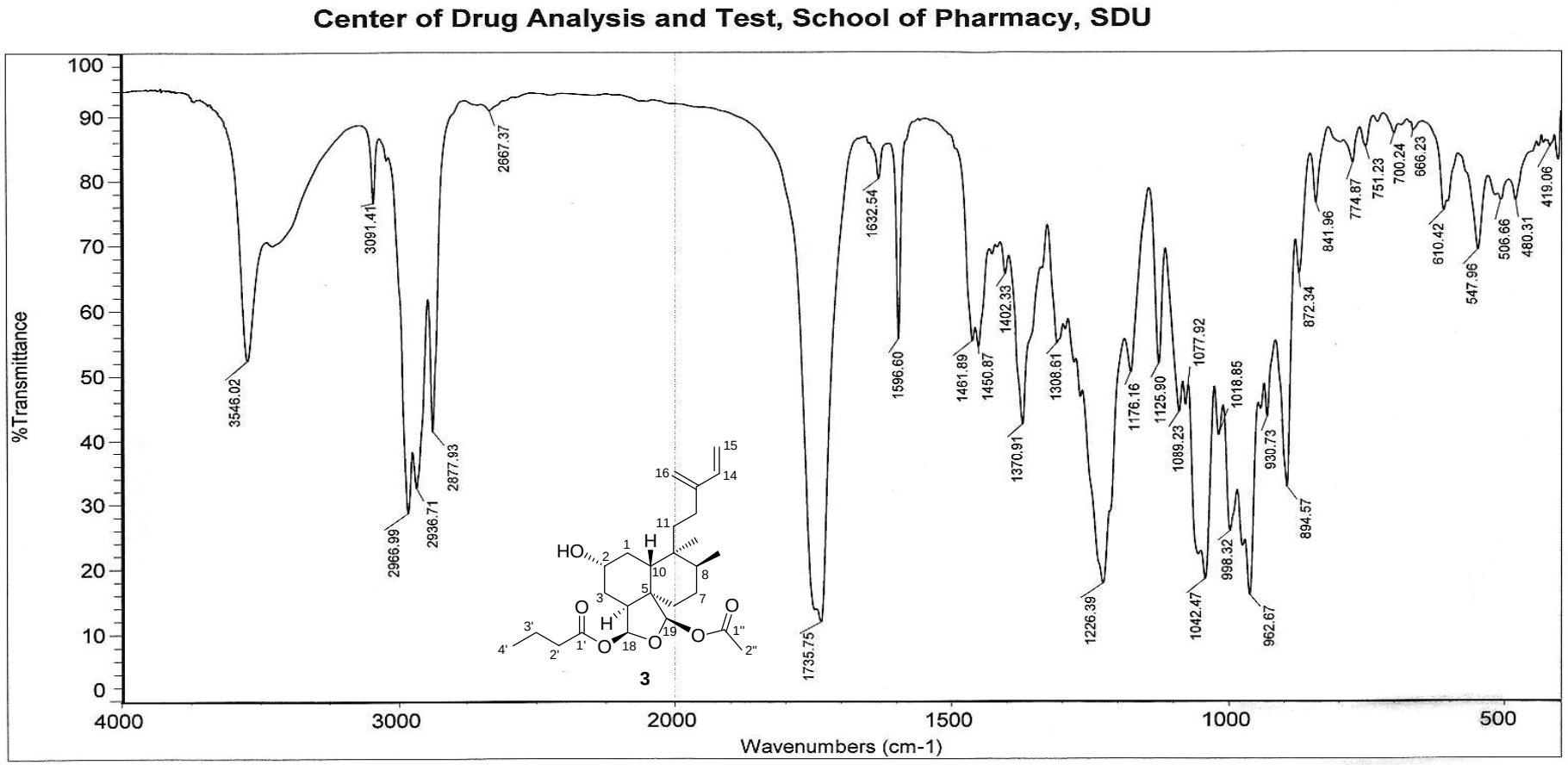


Figure S37. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4**

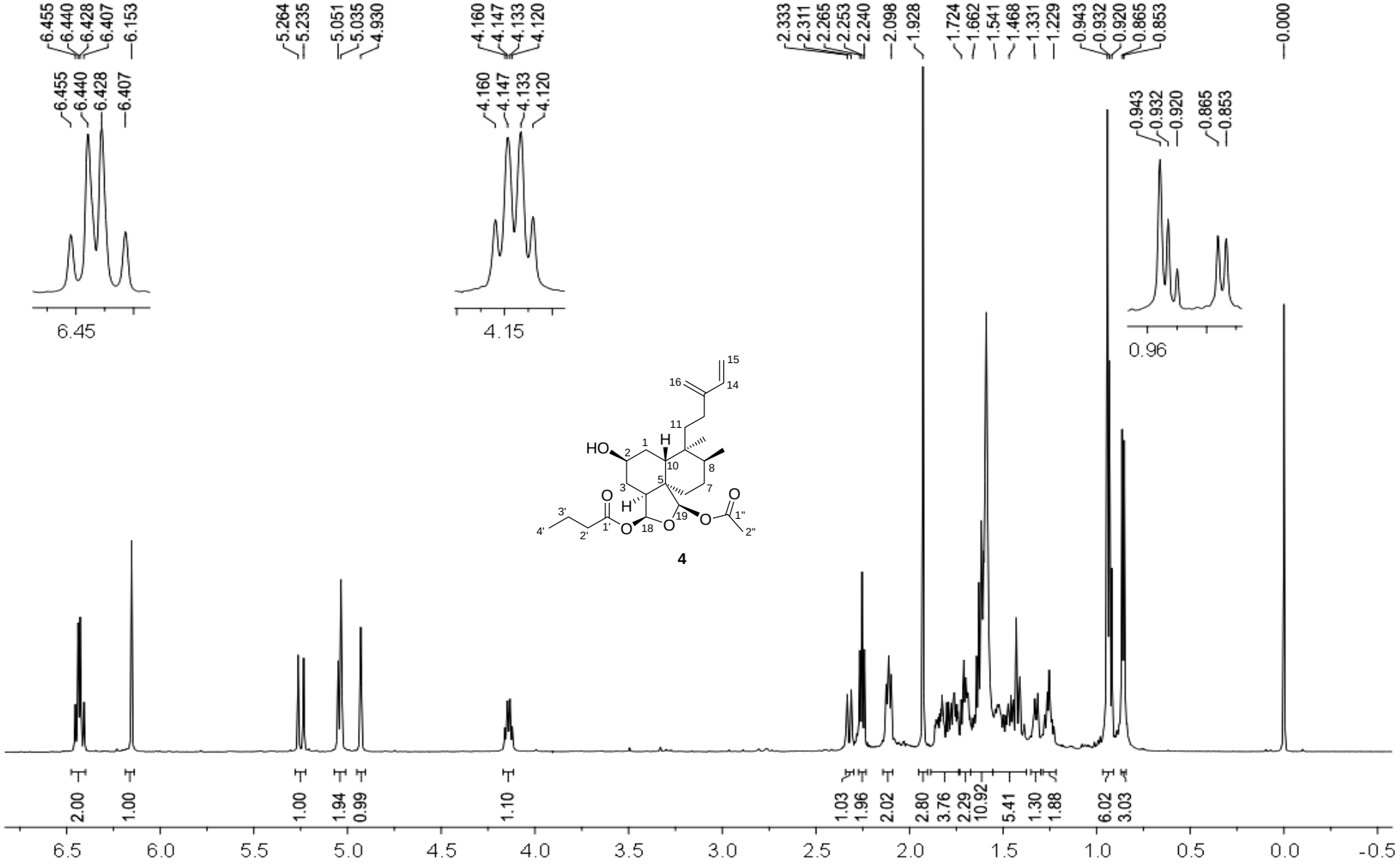


Figure S38. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **4**

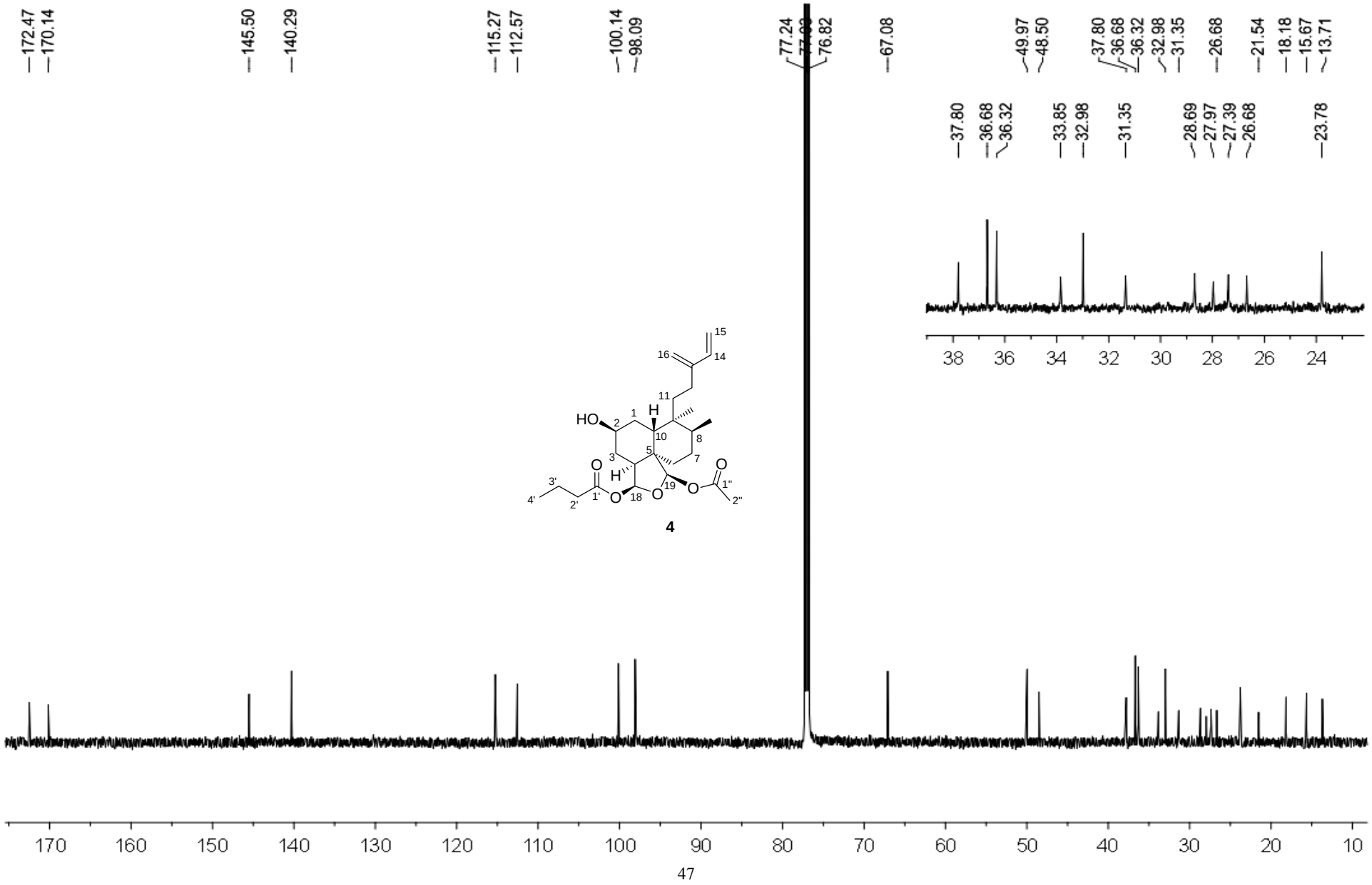


Figure S39. HSQC (600 MHz, $CDCl_3$) spectrum of **4**

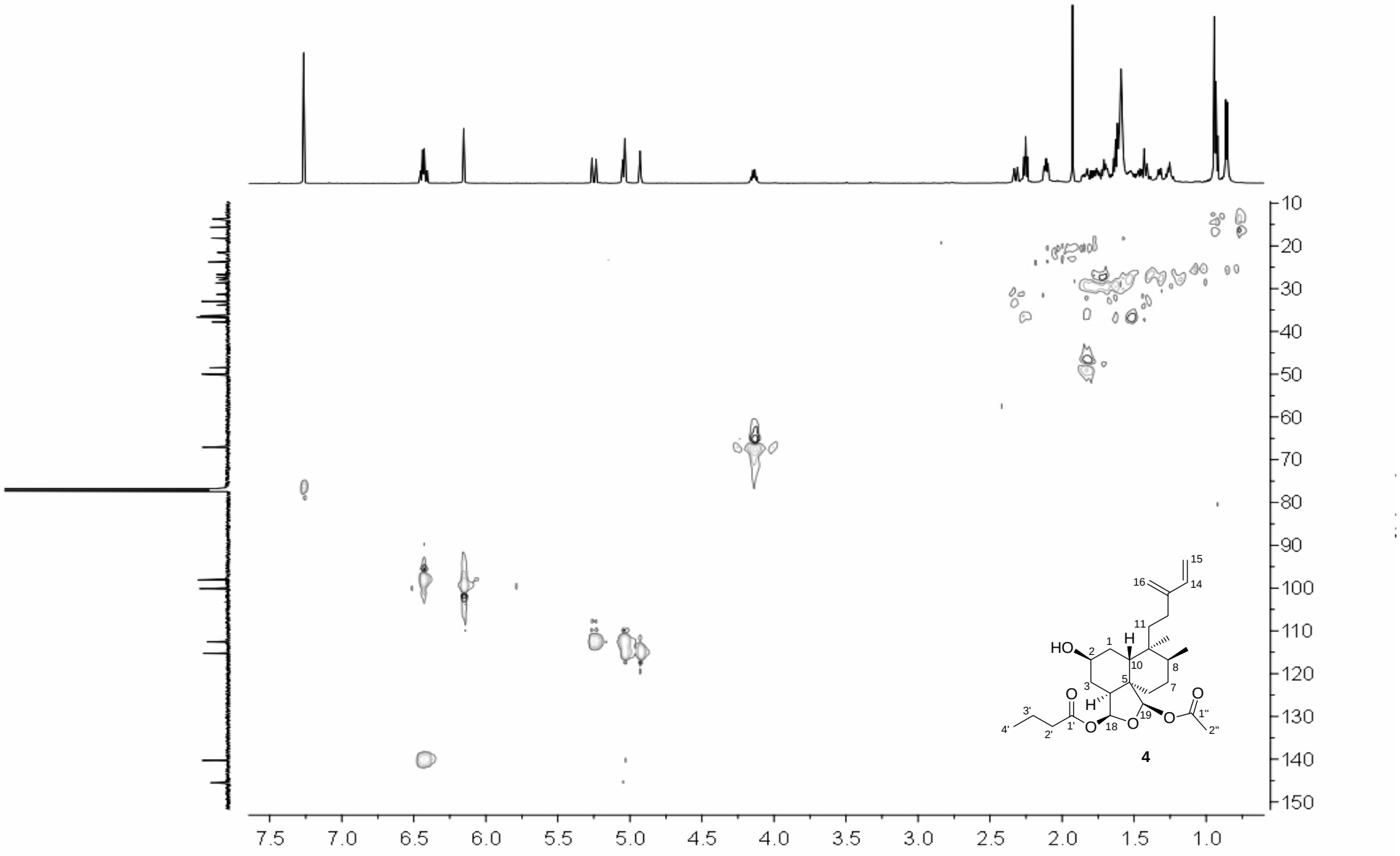


Figure S40. HMBC (600 MHz, $CDCl_3$) spectrum of **4**

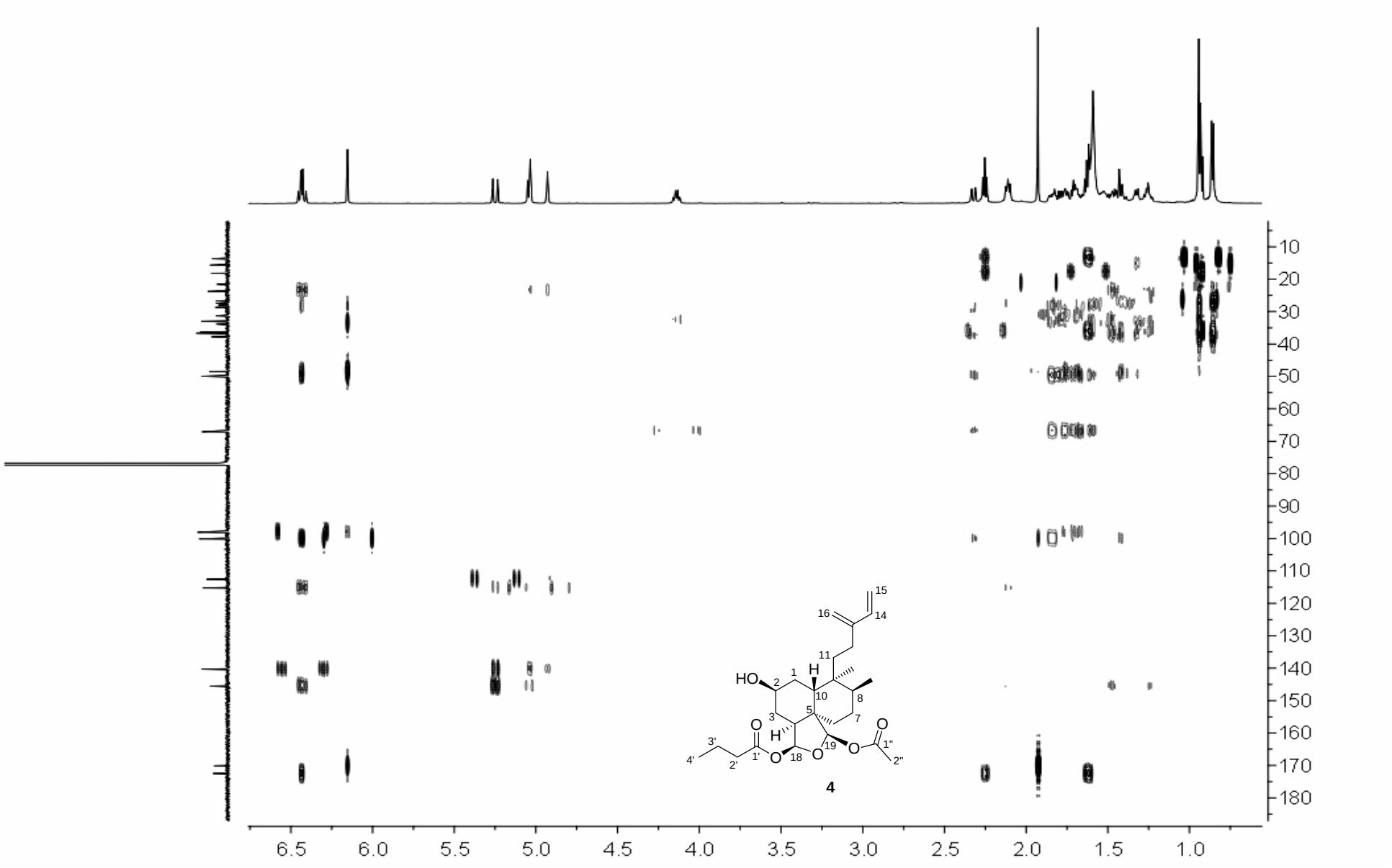


Figure S41. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **4**

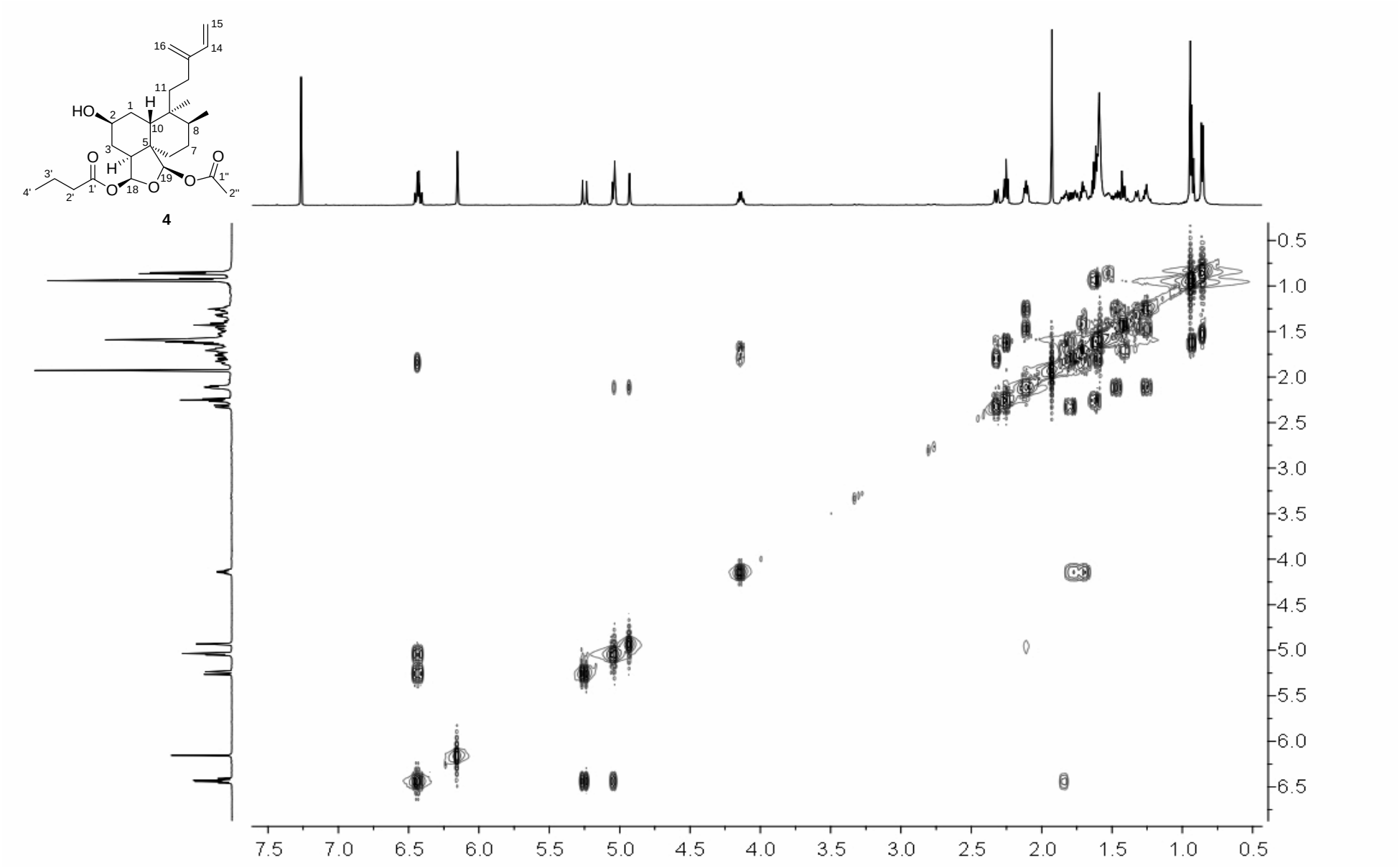


Figure S42. NOESY (600 MHz, $CDCl_3$) spectrum of **4**

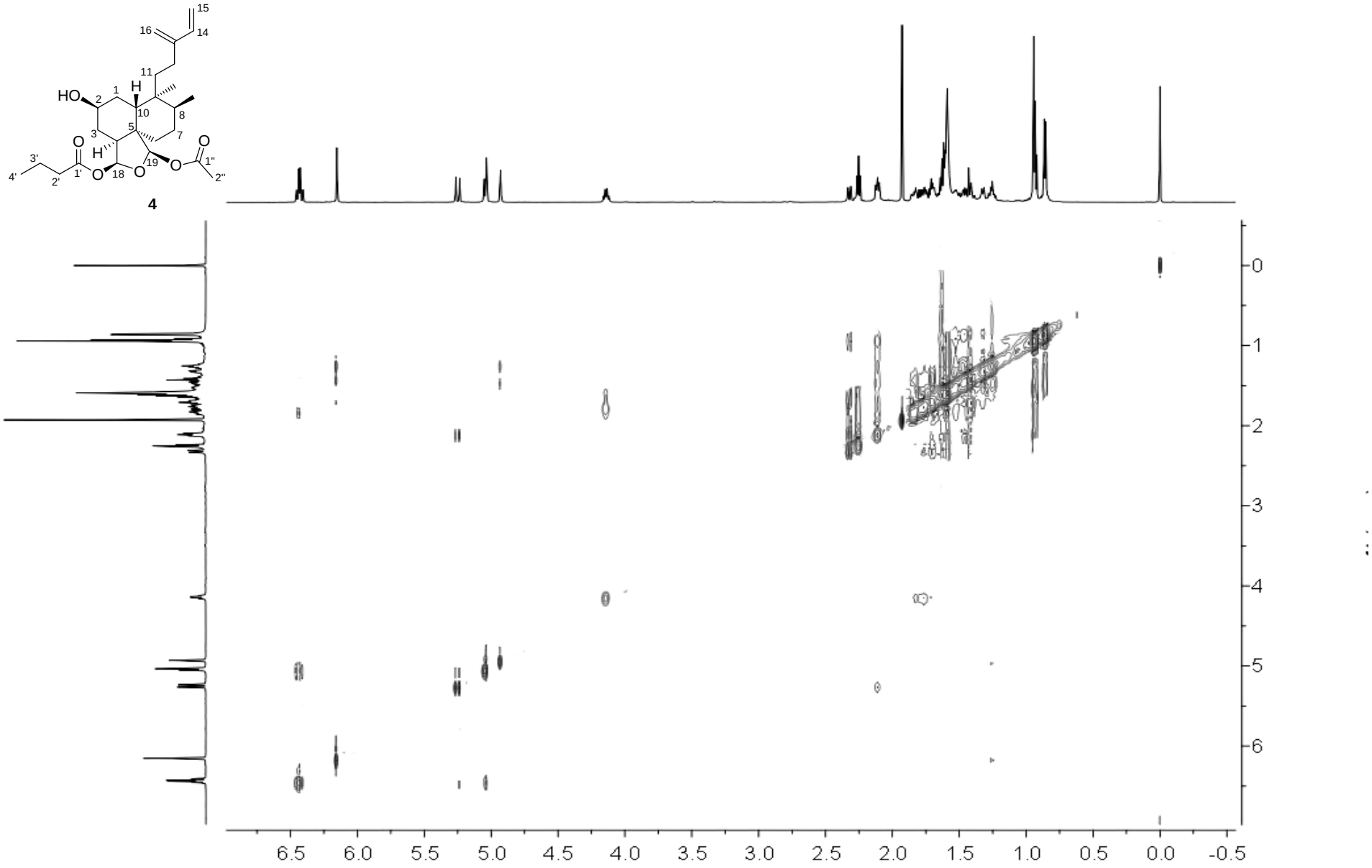


Figure S43. HRESIMS spectrum of **4**

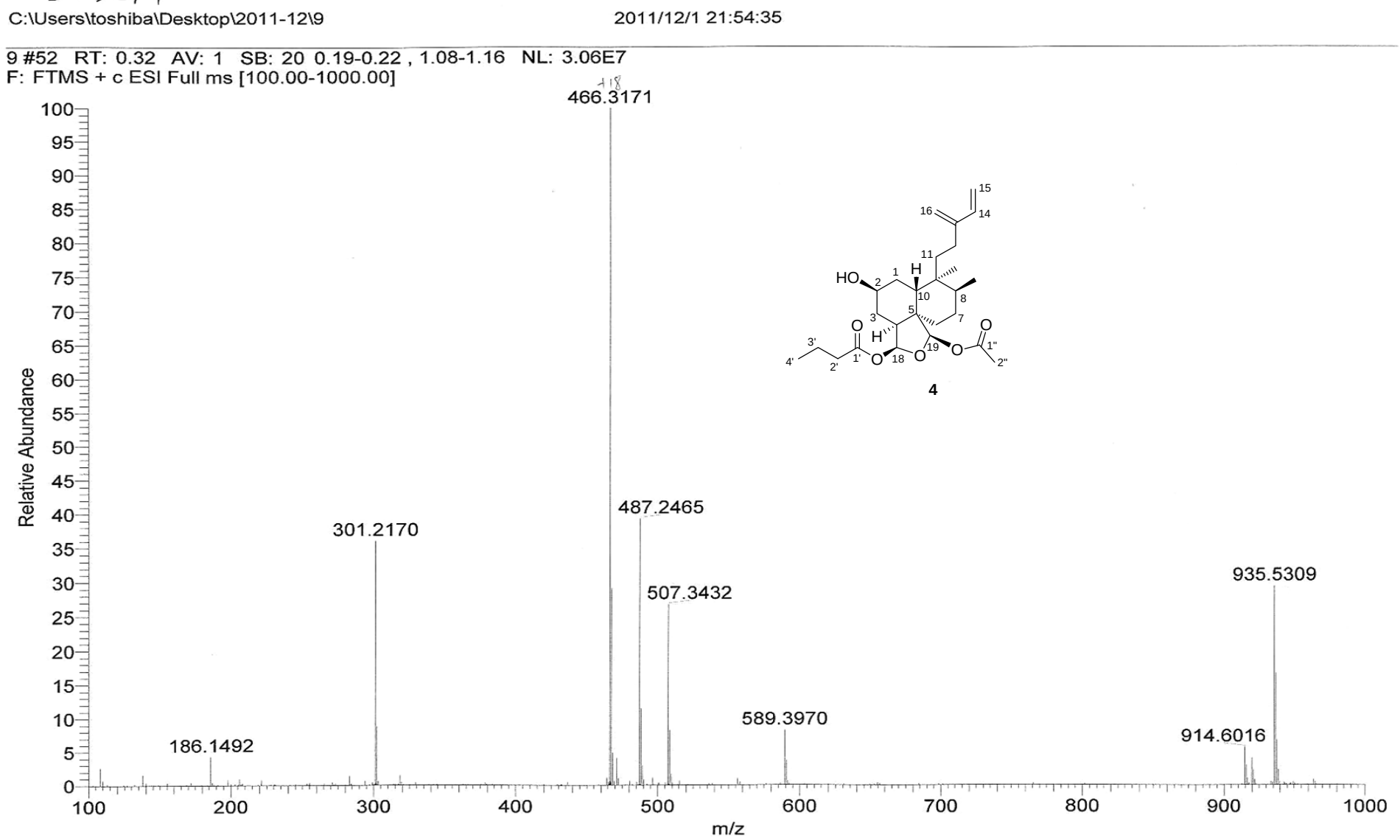


Figure S44. IR spectrum of **4**

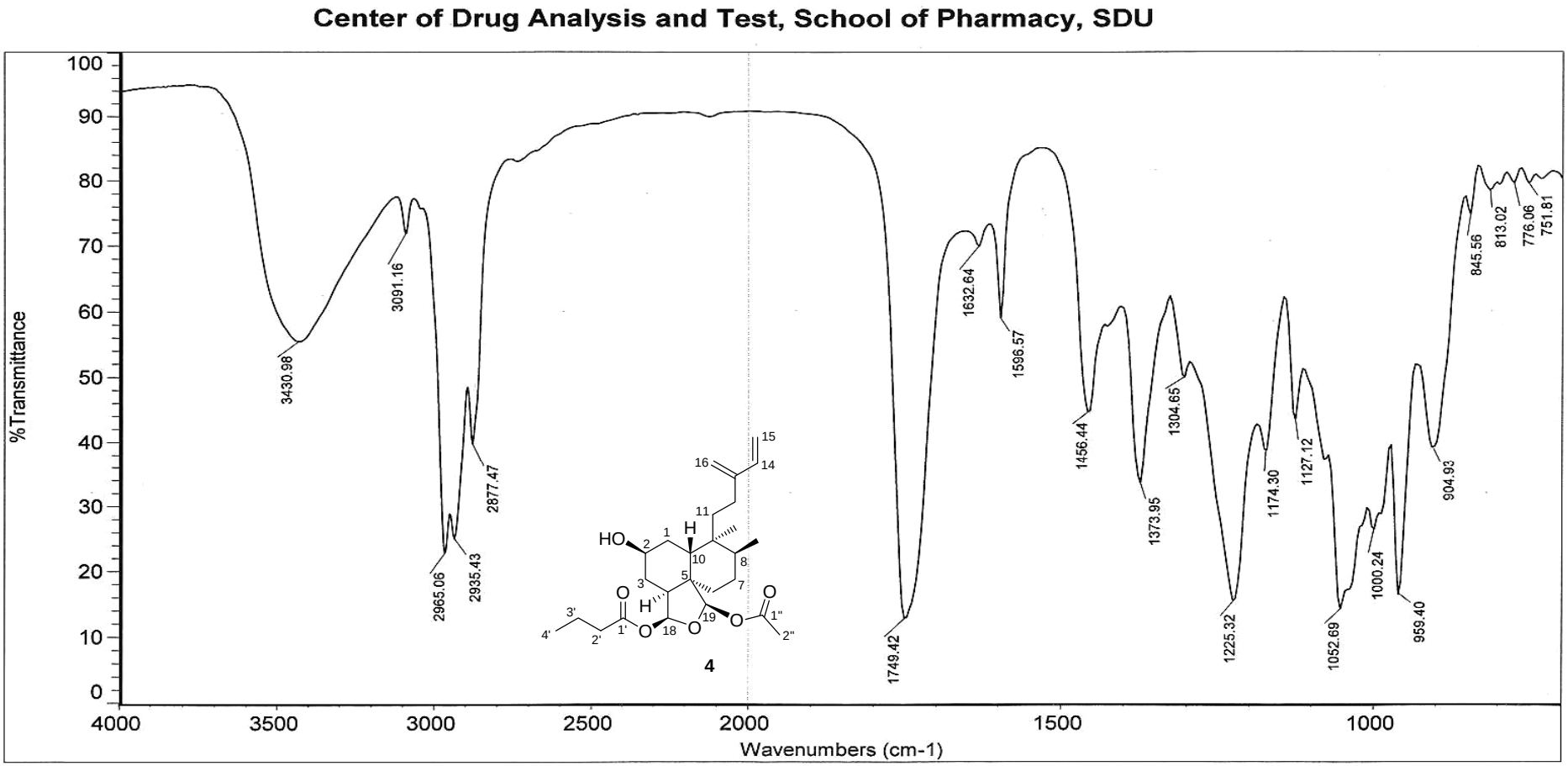


Figure S45. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **5**

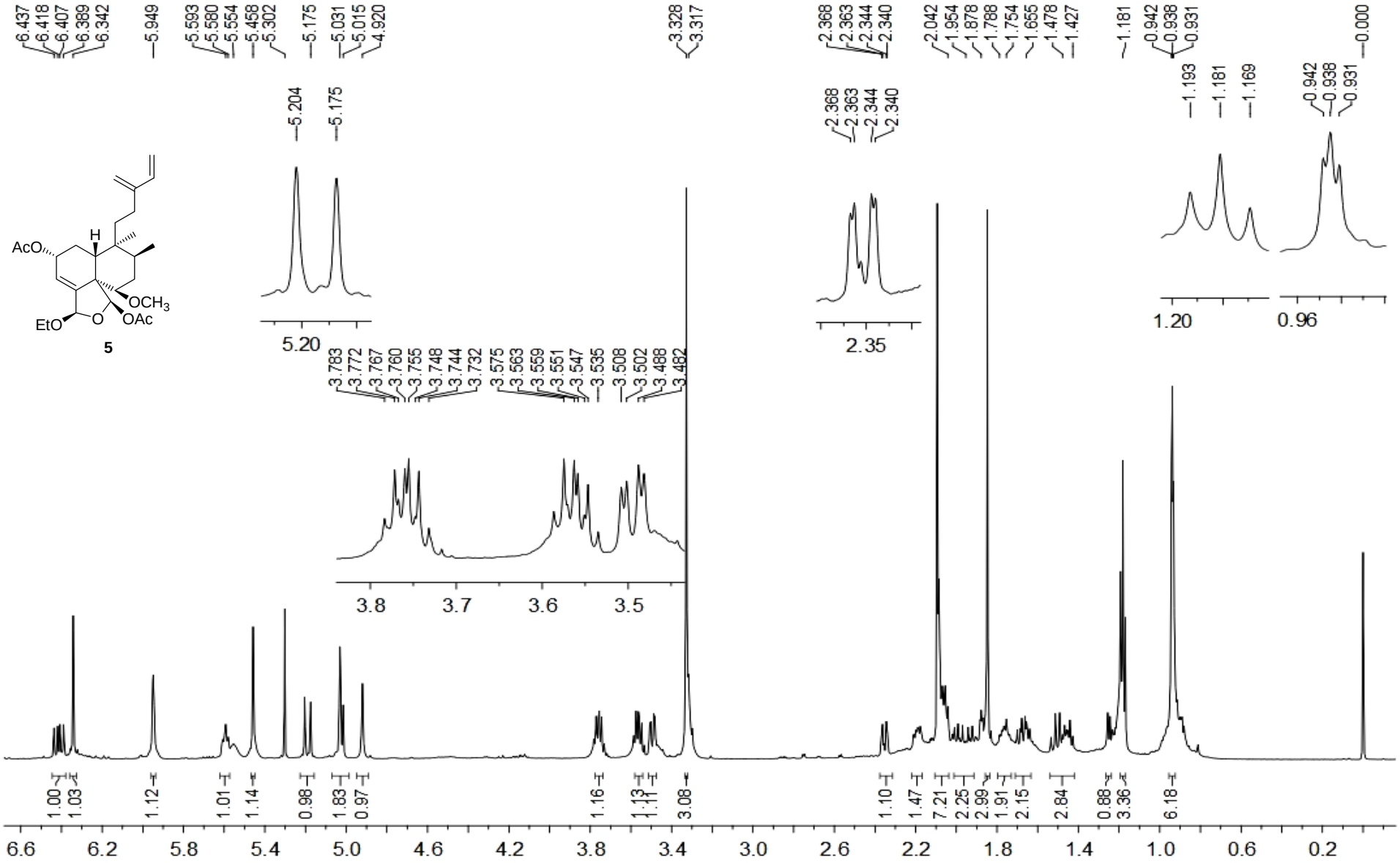


Figure S46. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **5**

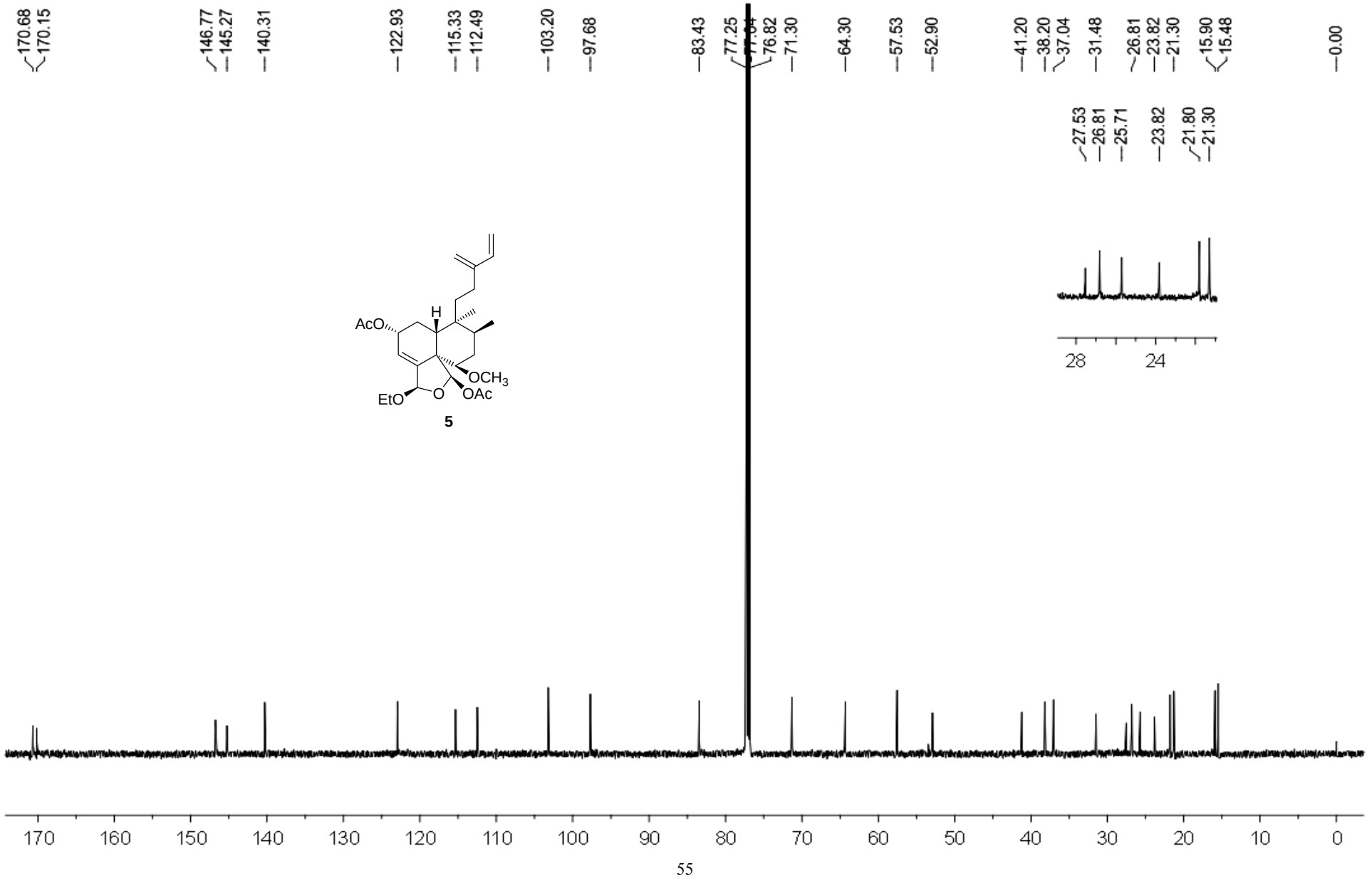


Figure S47. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **5**

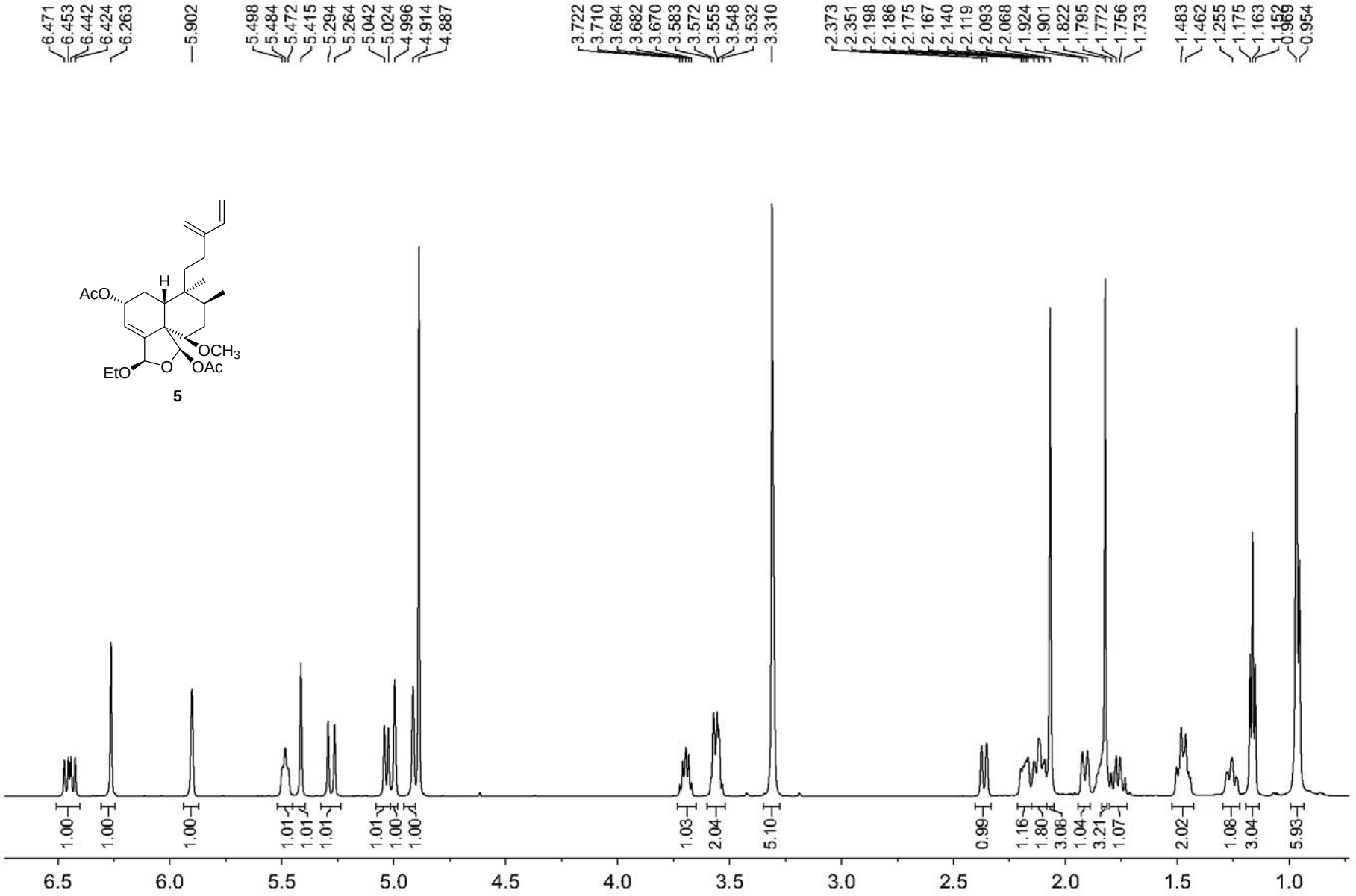


Figure S48. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **5**

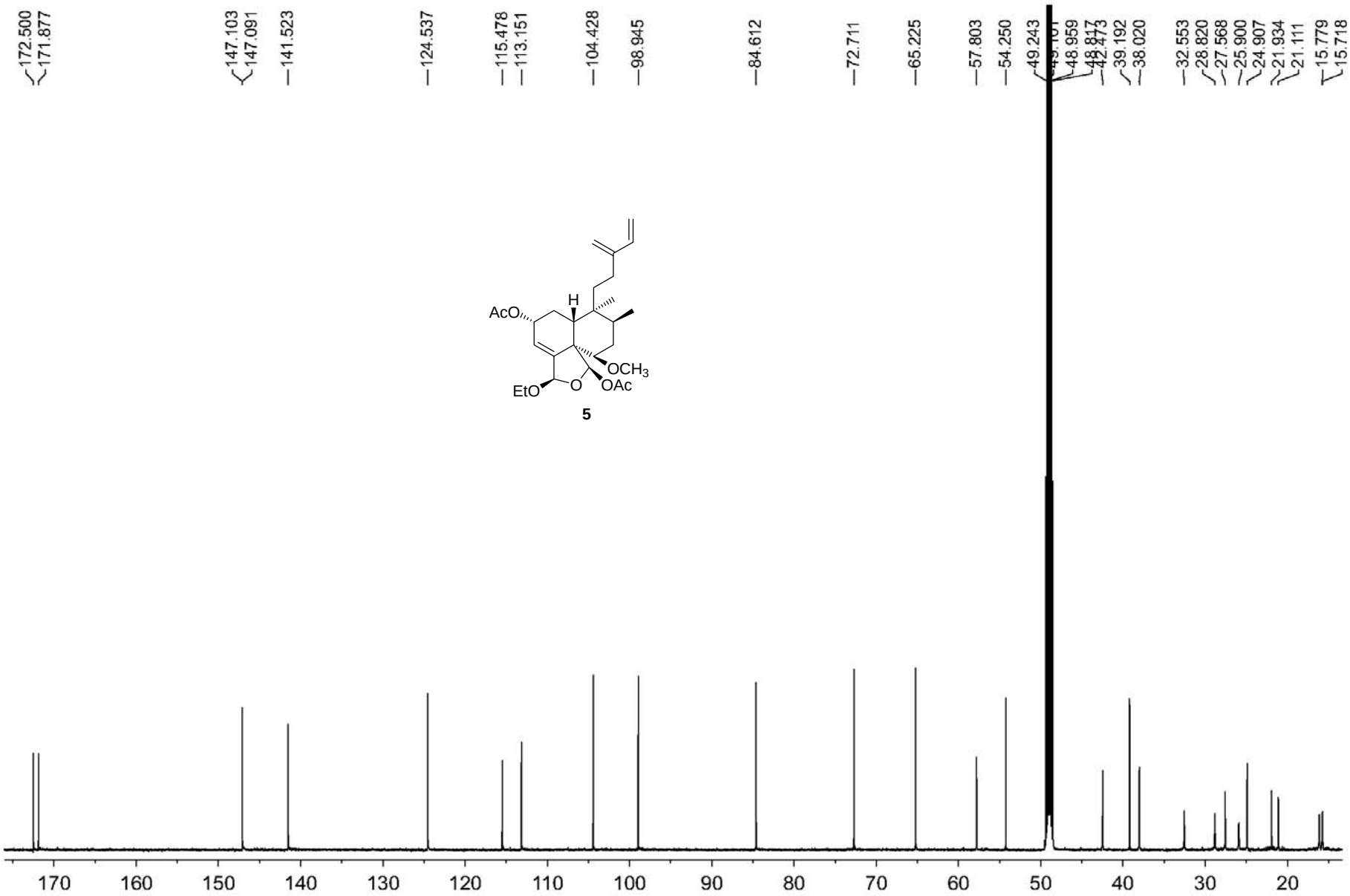


Figure S49. HSQC (600 MHz, $CDCl_3$) spectrum of **5**

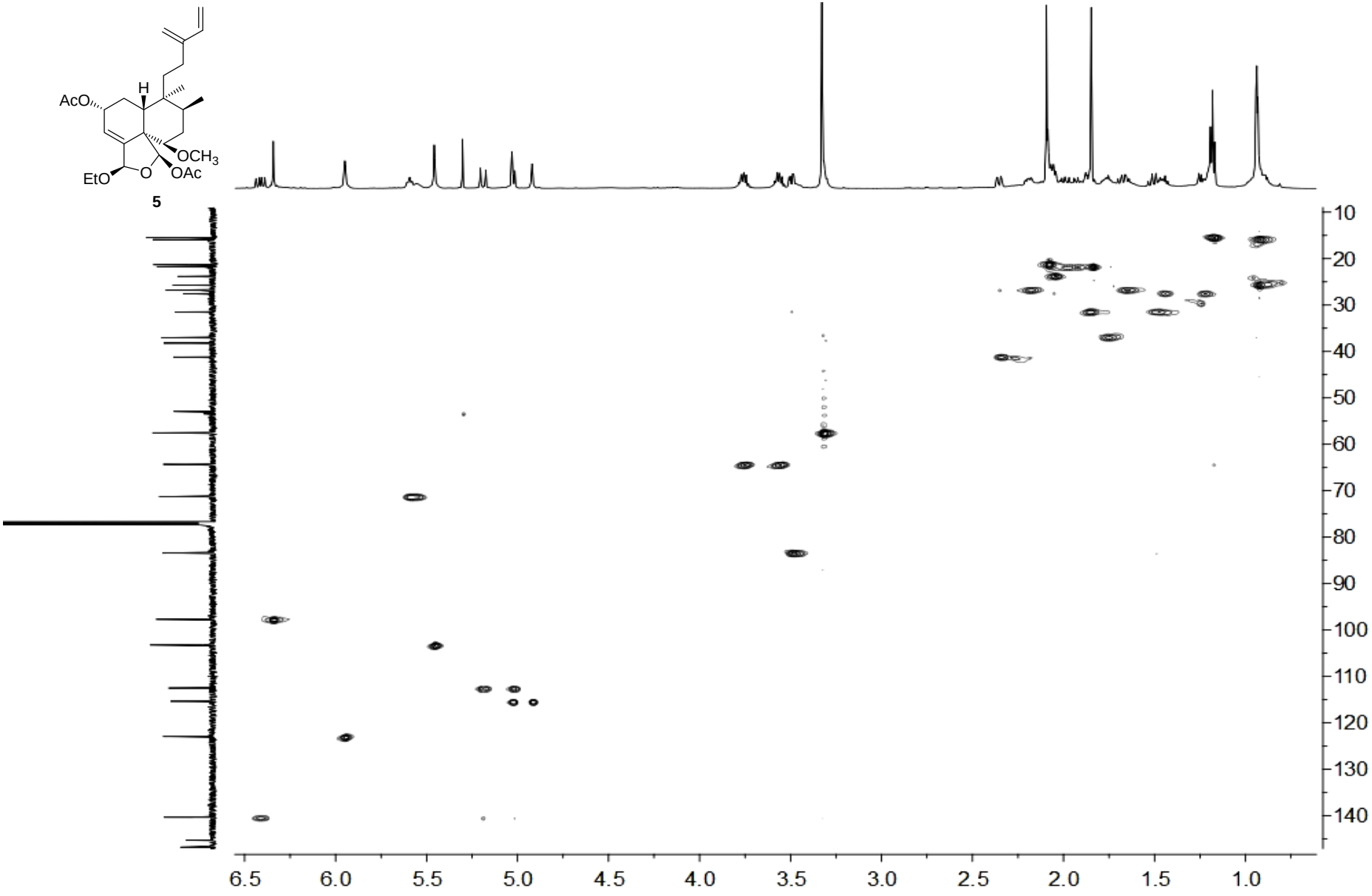


Figure S50. HMBC (600 MHz, $CDCl_3$) spectrum of **5**

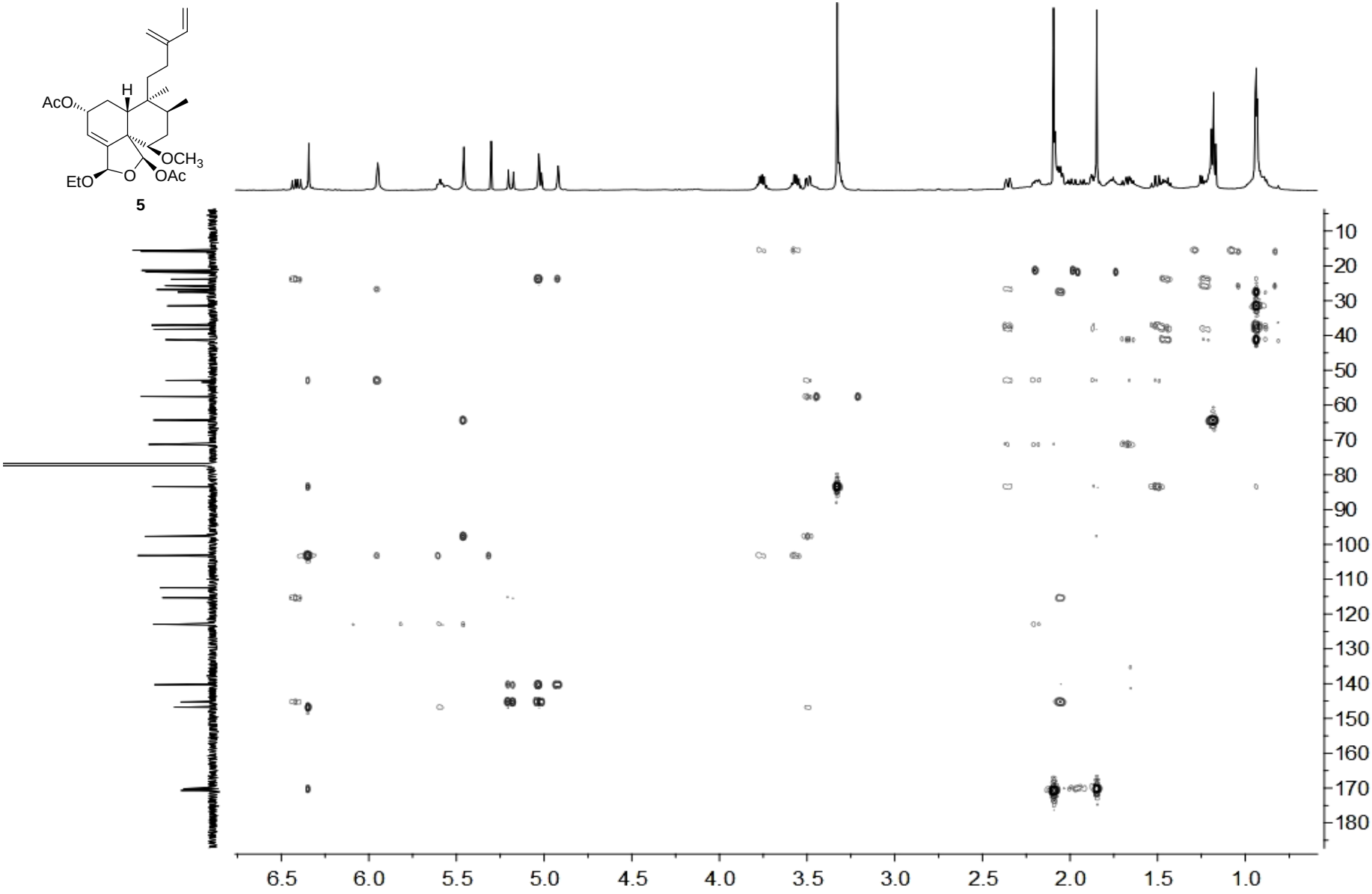


Figure S51. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **5**

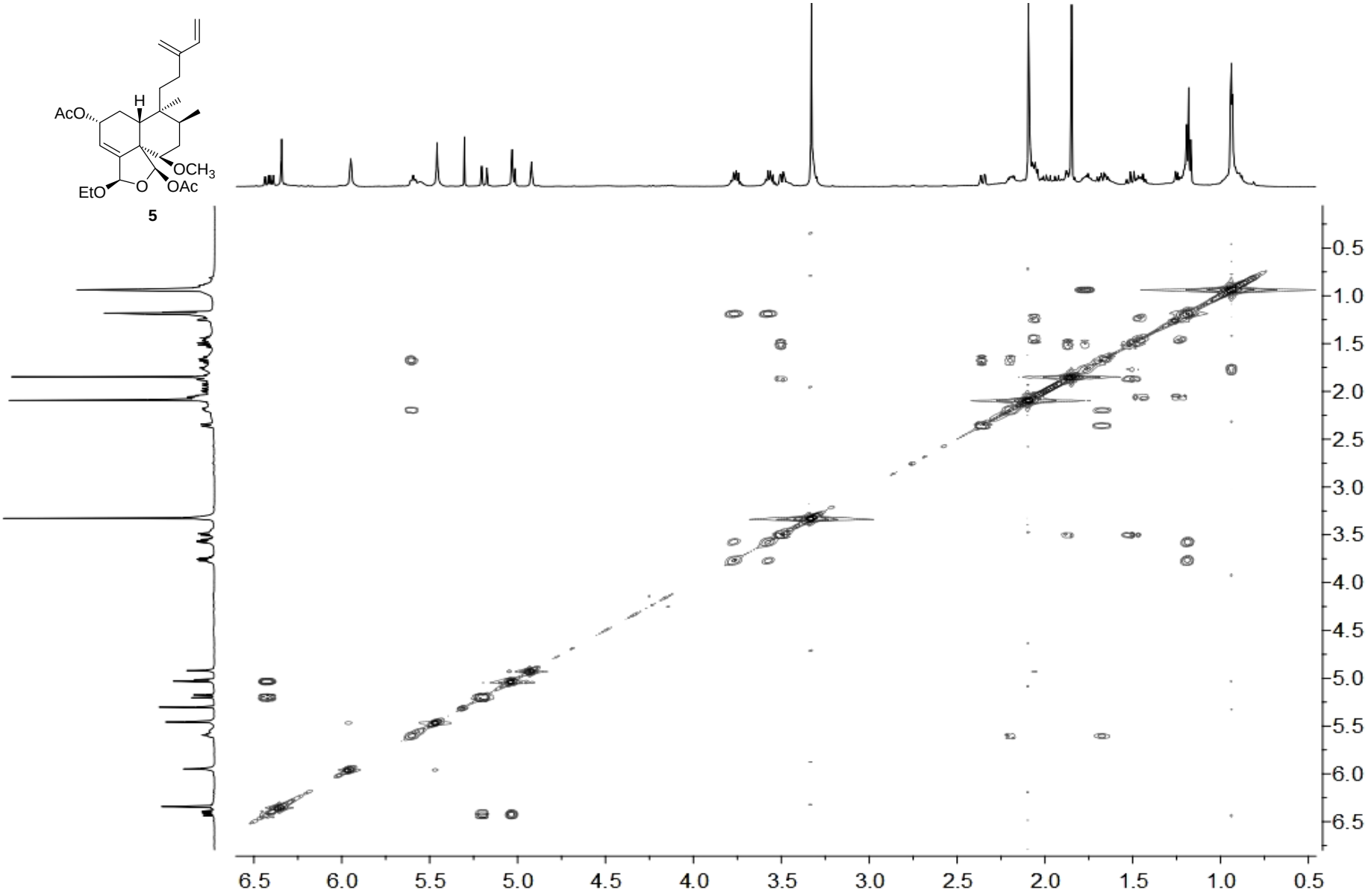


Figure S52. NOESY (600 MHz, $CDCl_3$) spectrum of **5**

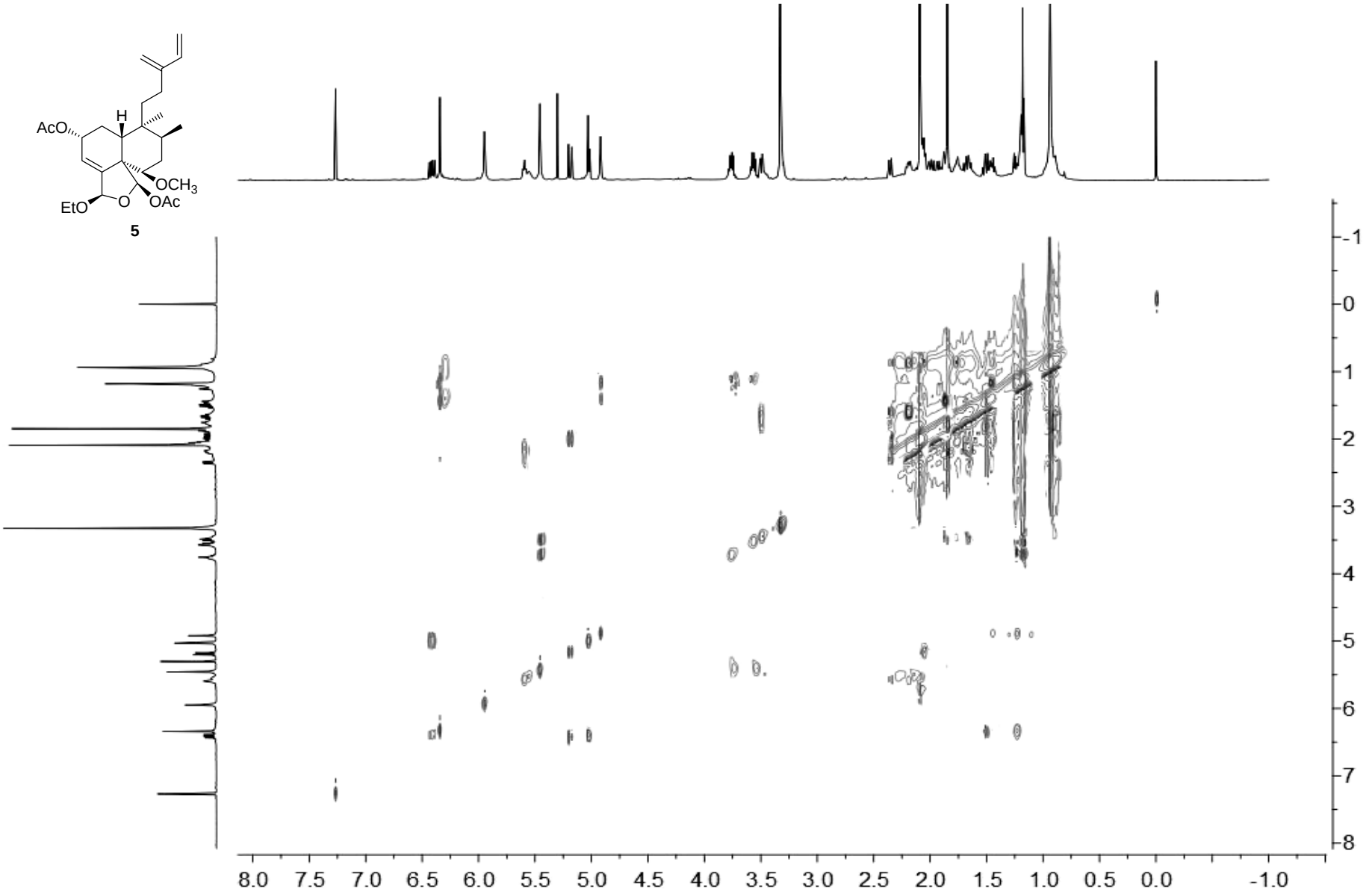


Figure S53. ESIMS spectrum of **5**

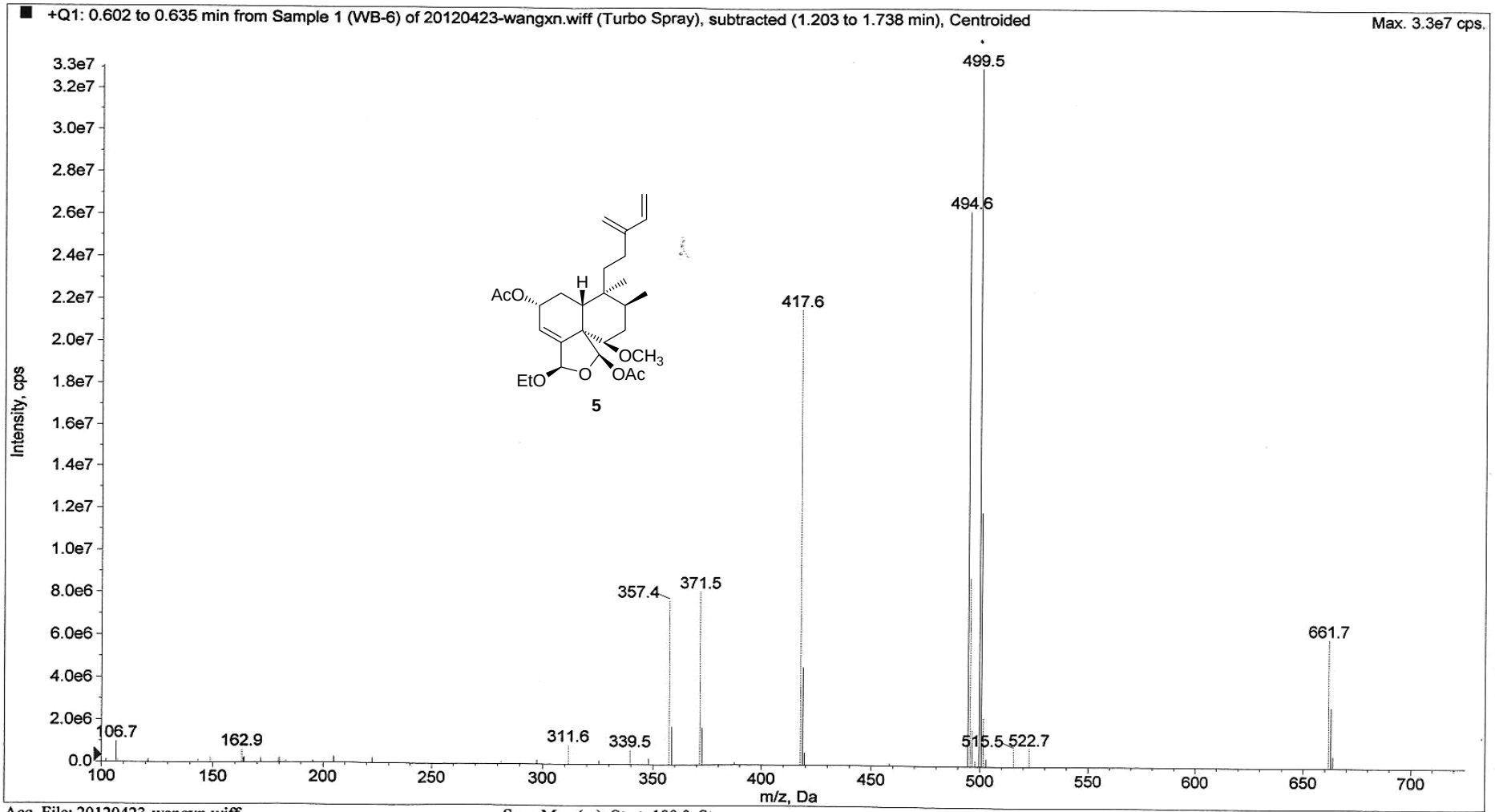


Figure S54. HRESIMS spectrum of **5**

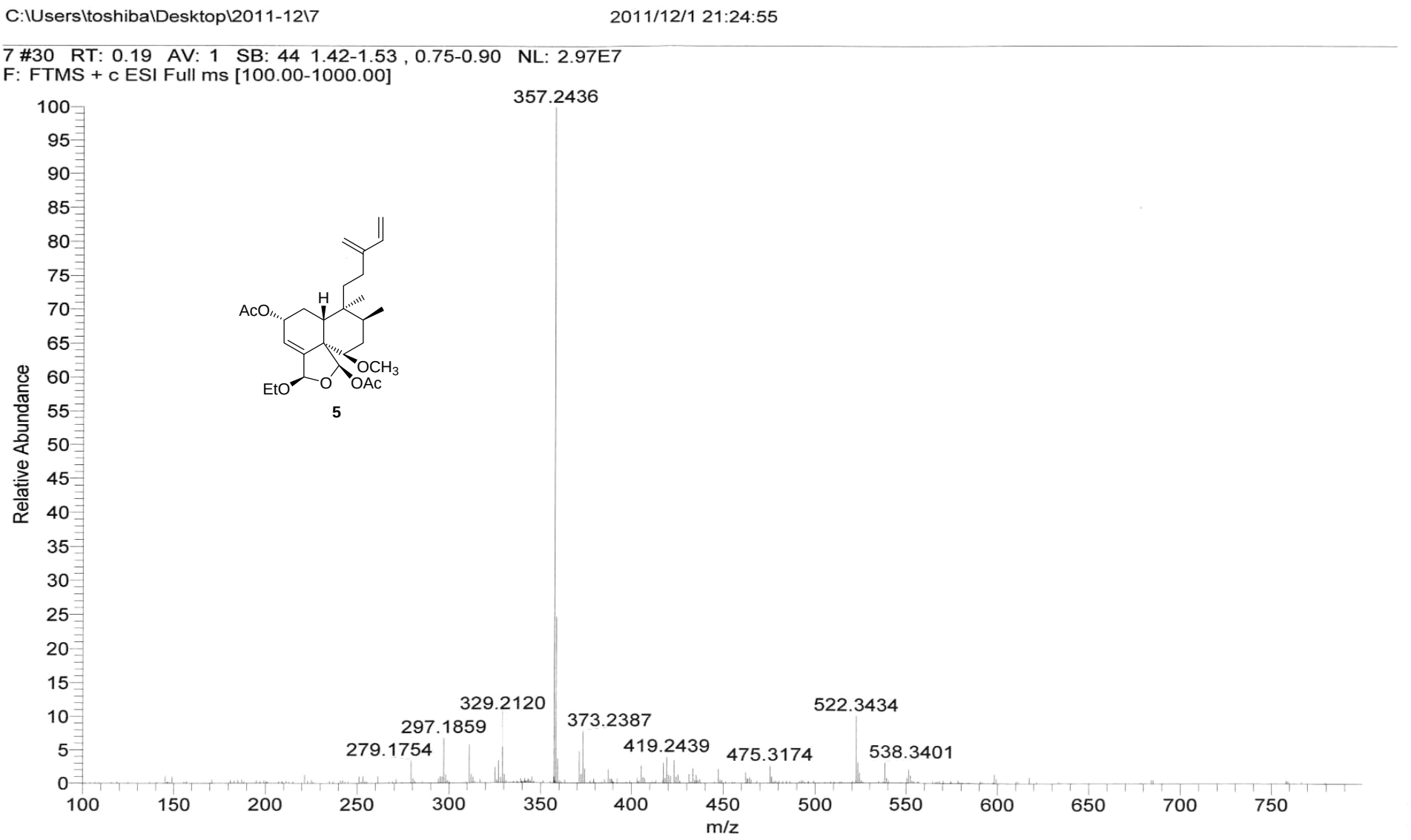


Figure S55. IR spectrum of **5**

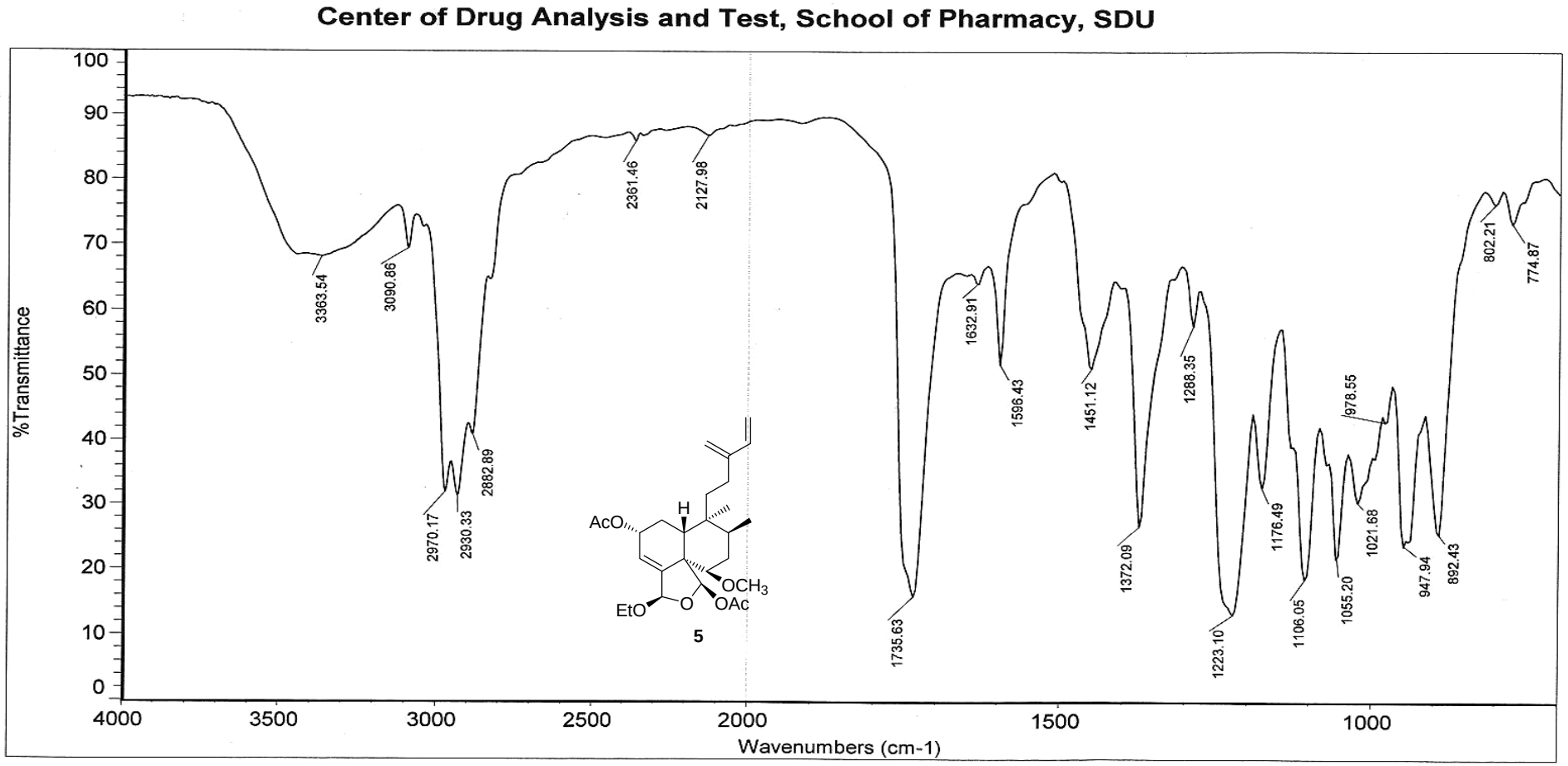


Figure S56. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6**

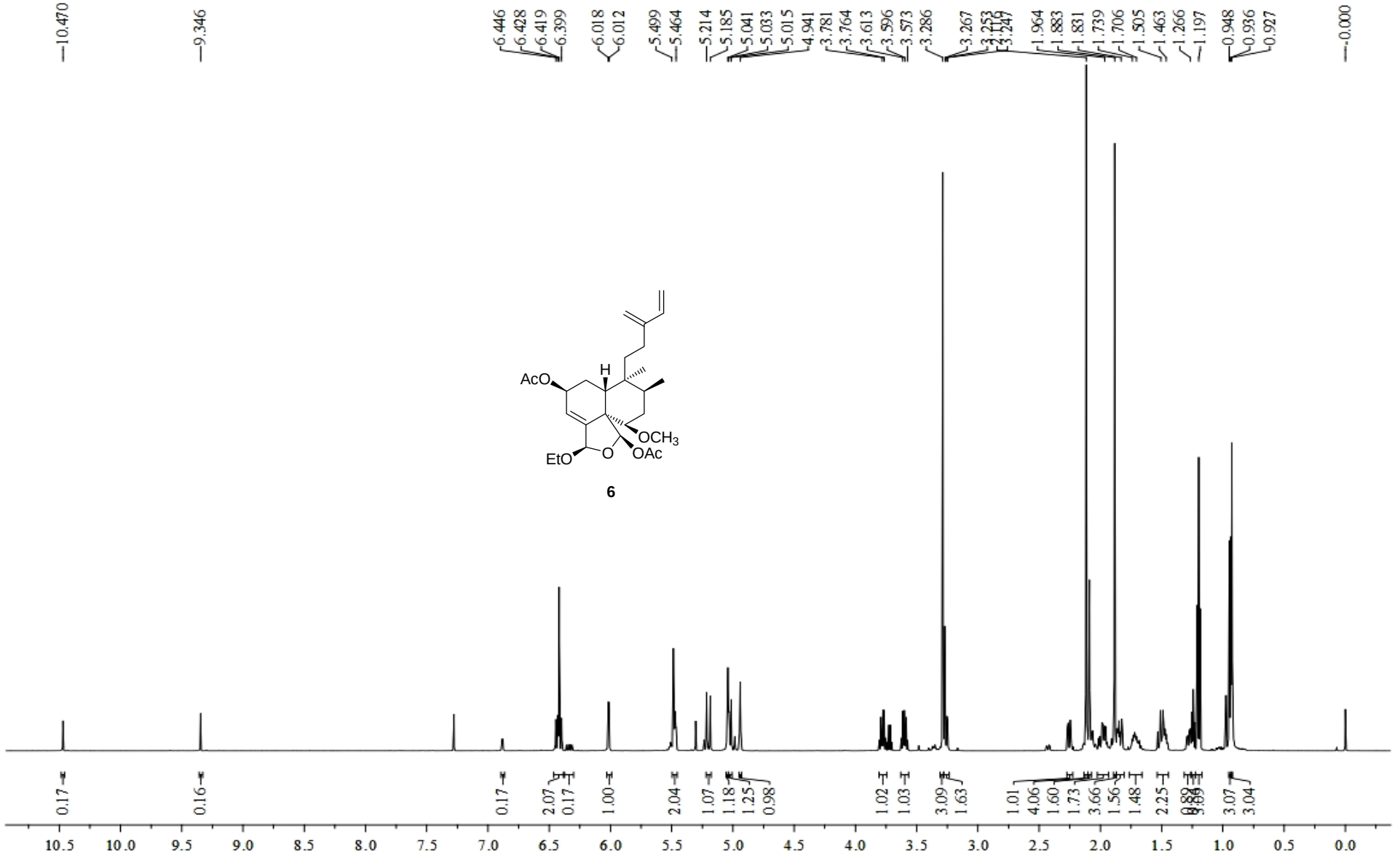


Figure S57. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6** (expansion δ 4.80-6.90)

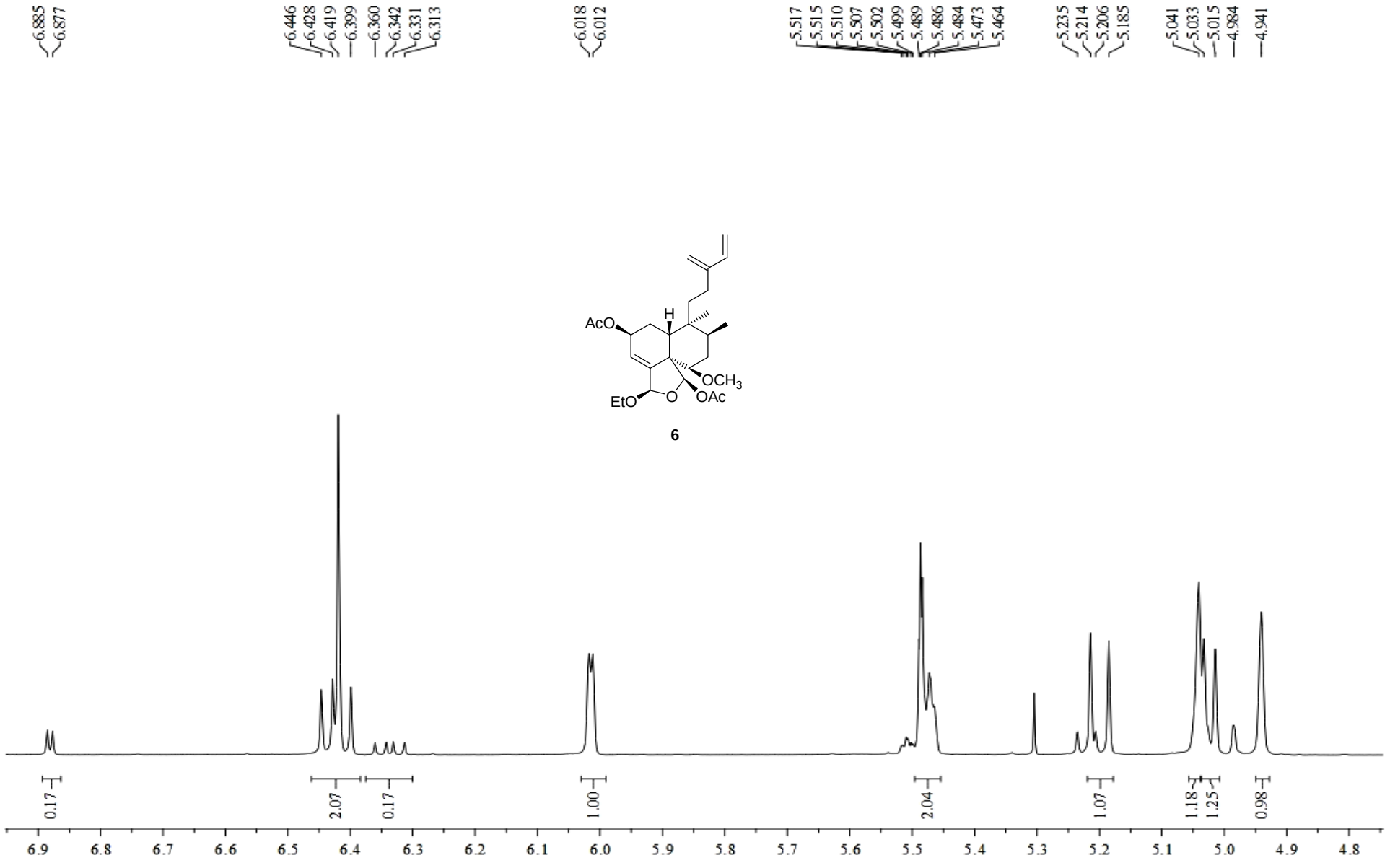


Figure S58. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6** (expansion δ 3.20-3.84)

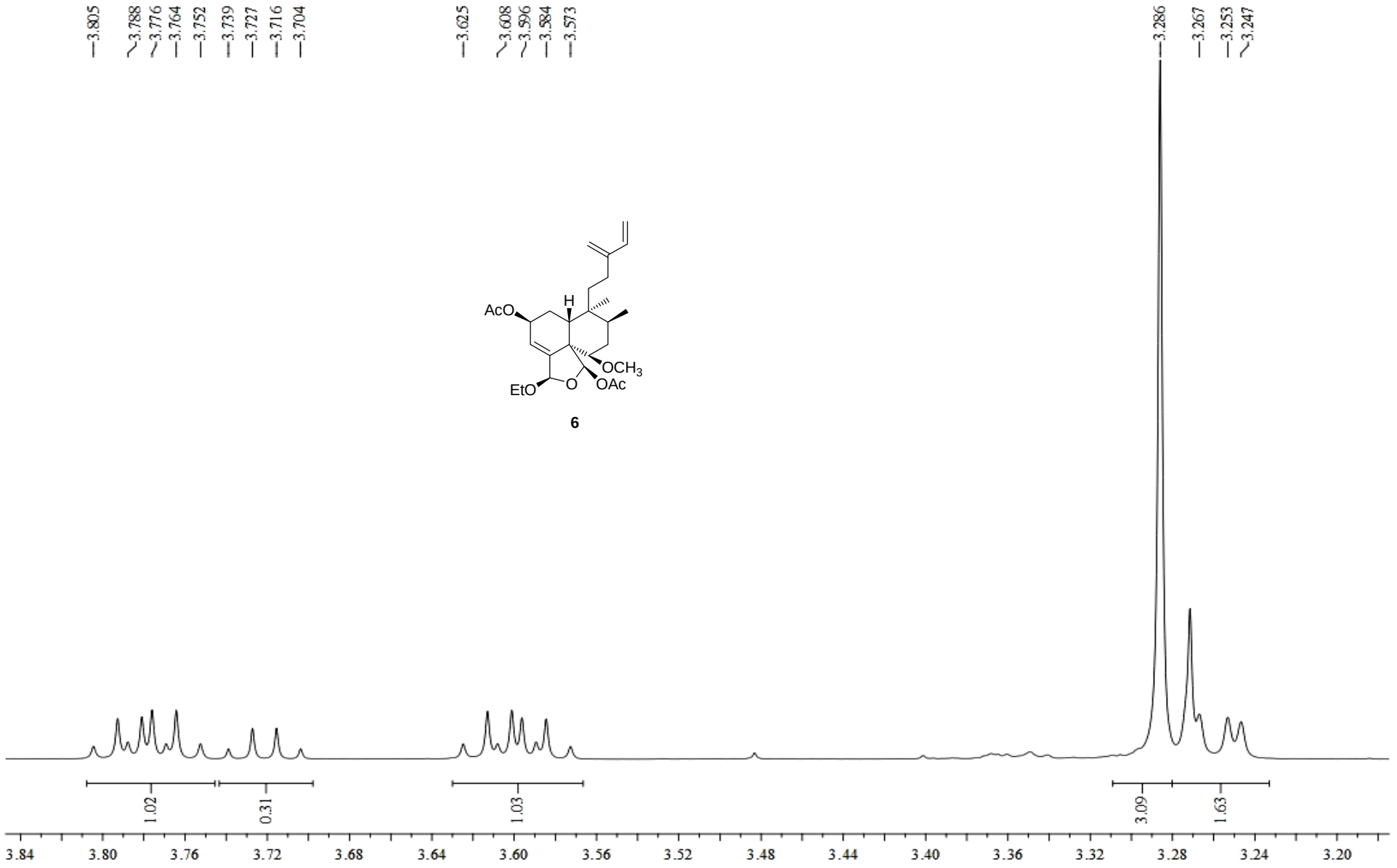


Figure S59. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **6** (expansion δ 0.60-2.50)

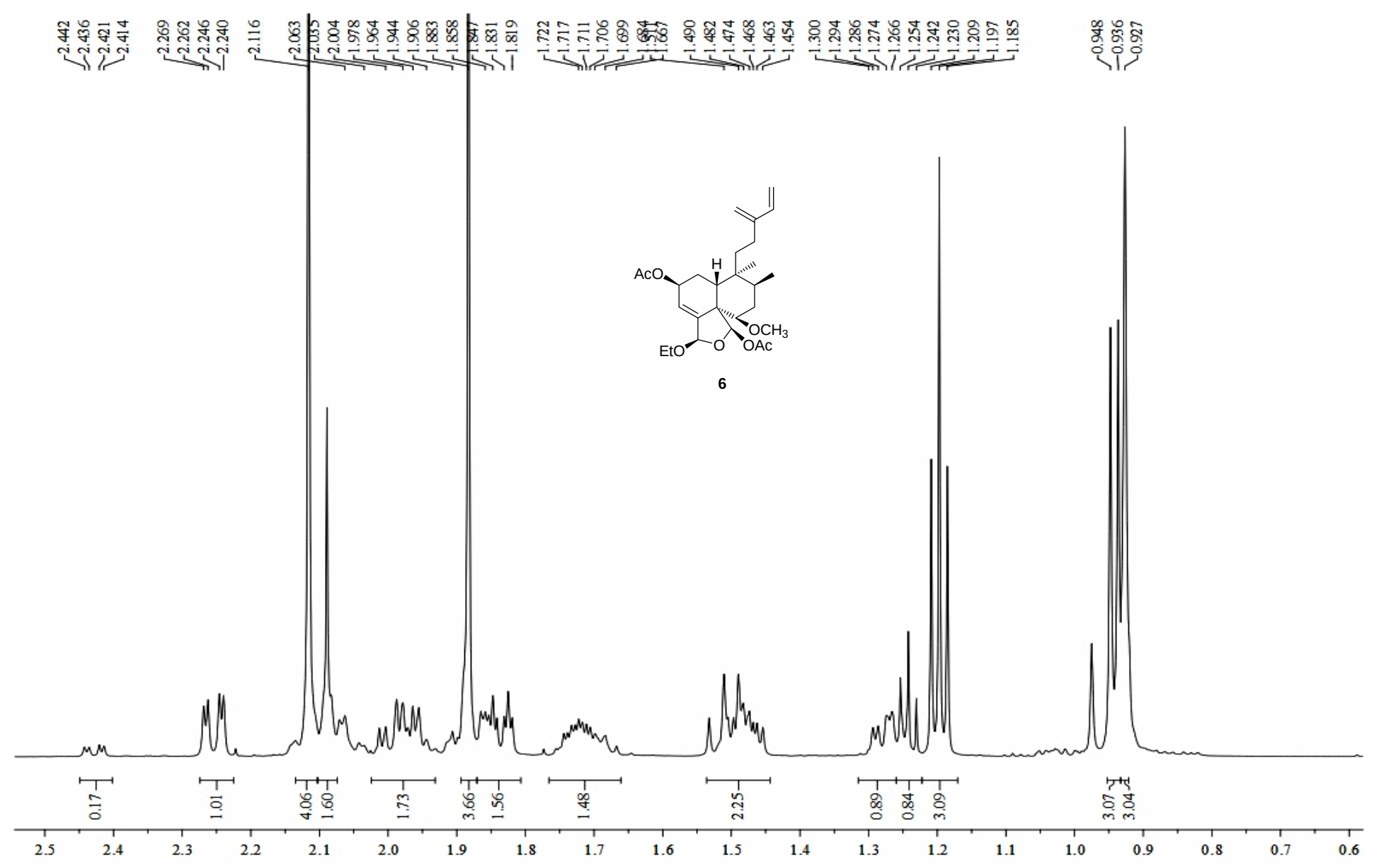


Figure S60. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6**

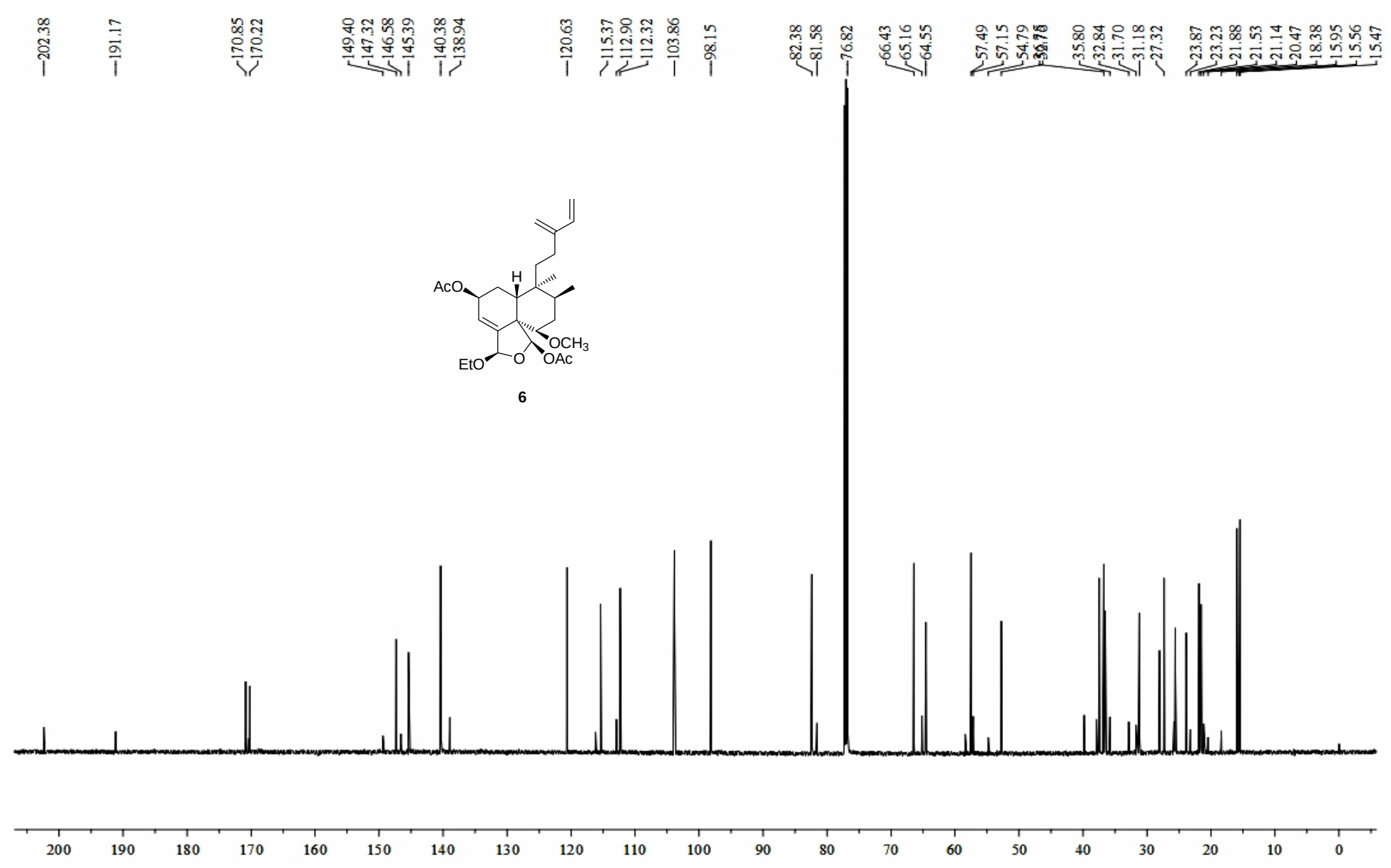


Figure S61. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6** (expansion δ 50.0-125.0)

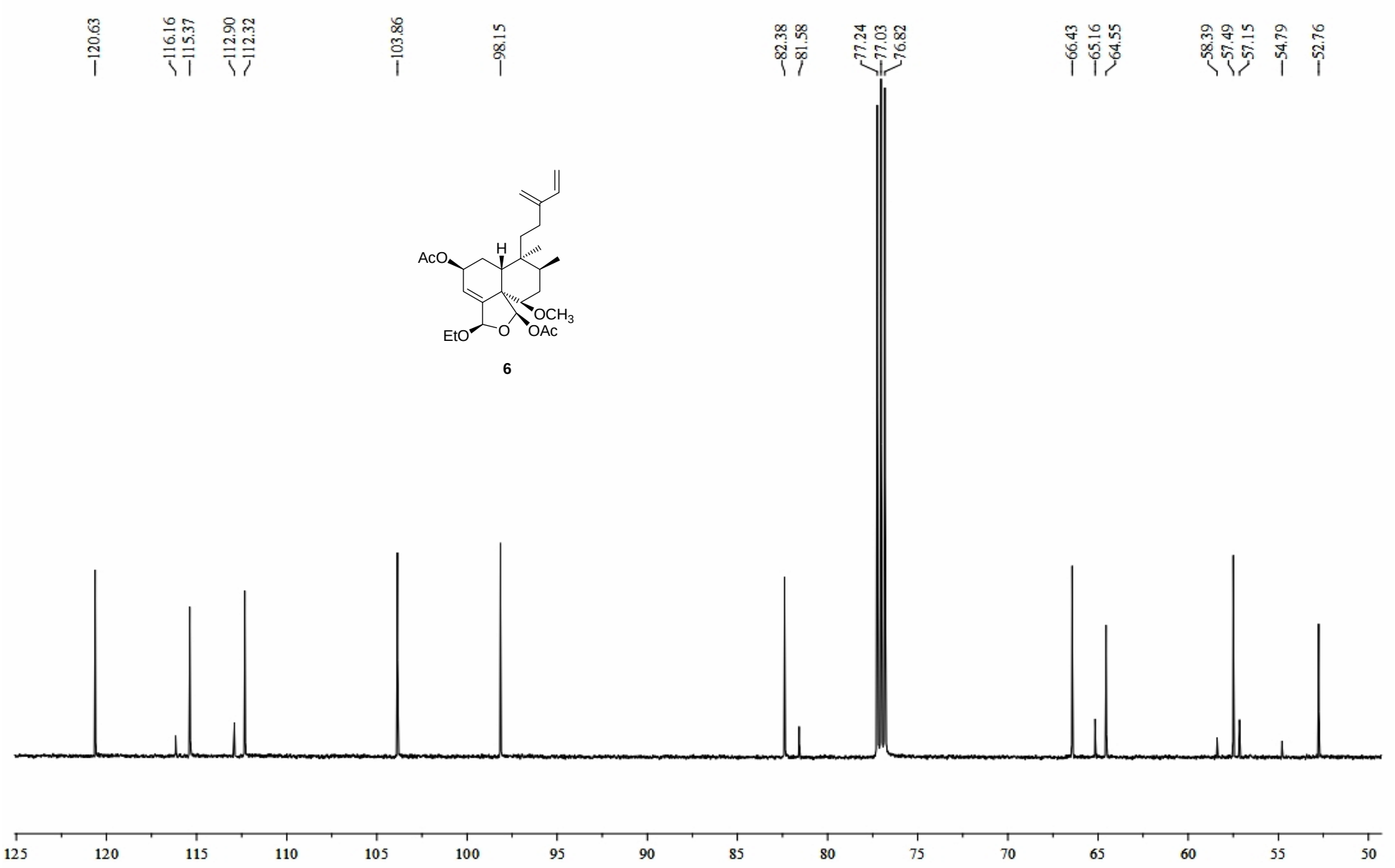


Figure S62. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **6** (expansion δ 15.0-40.0)

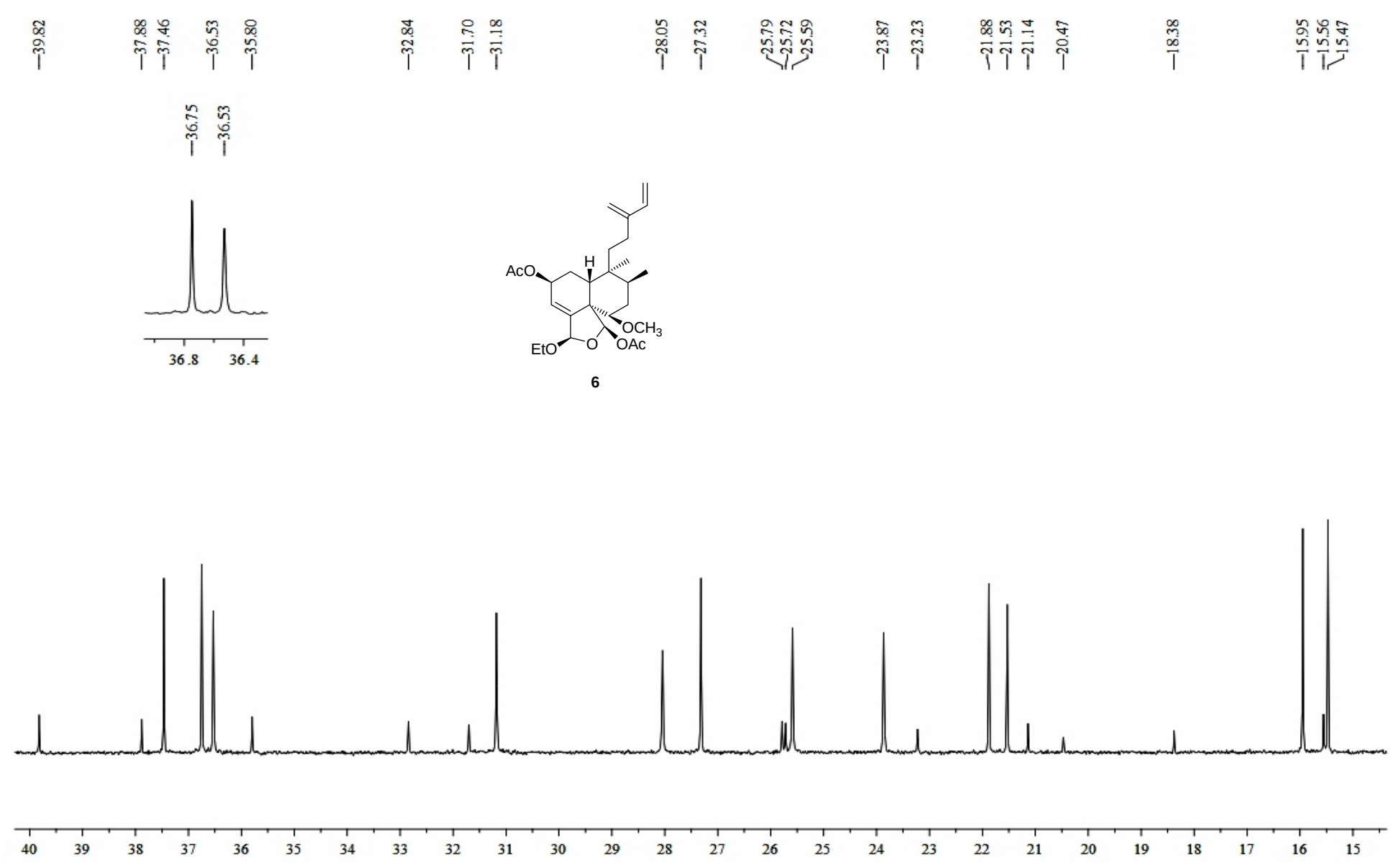


Figure S63. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **6**

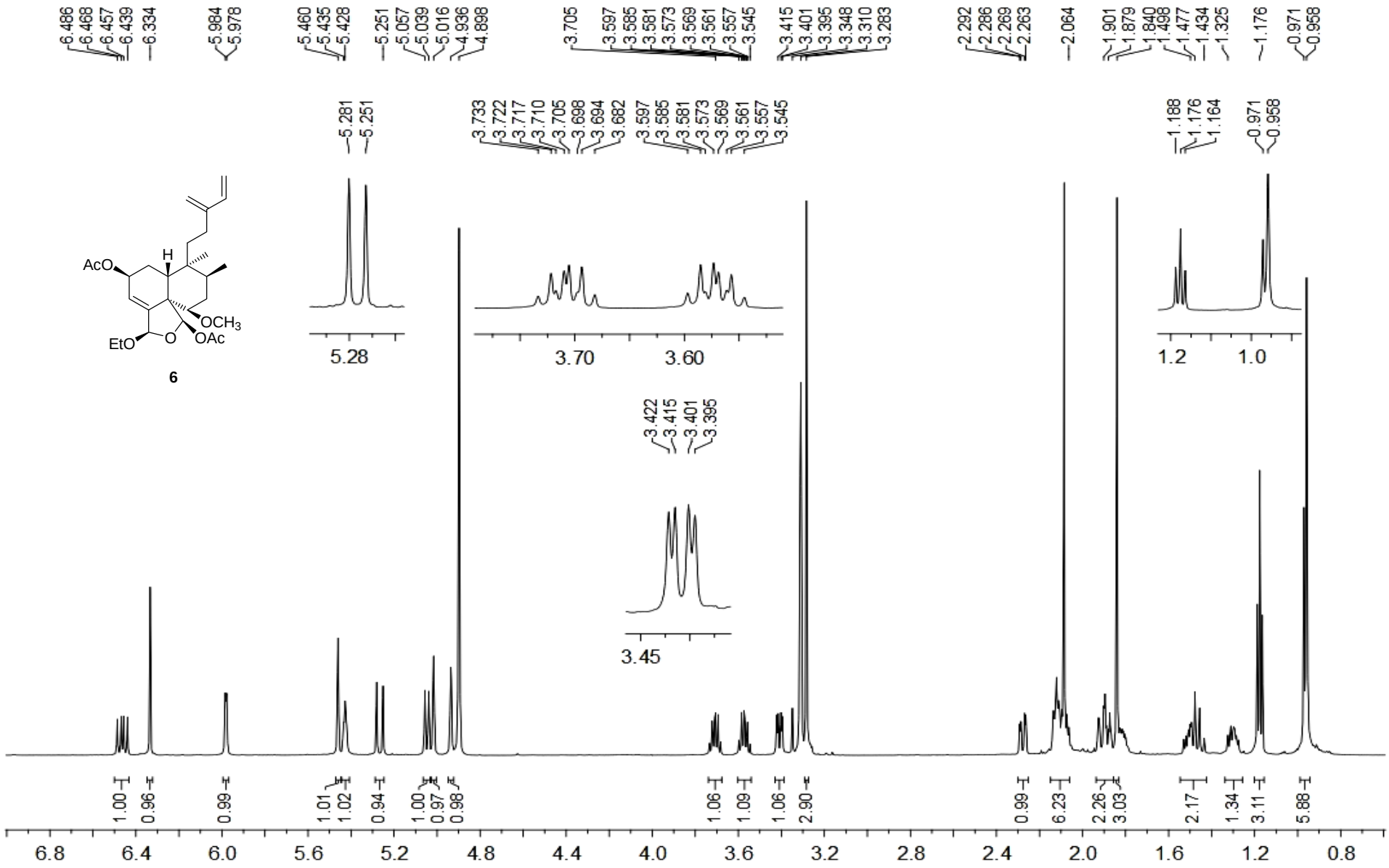


Figure S64. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **6**

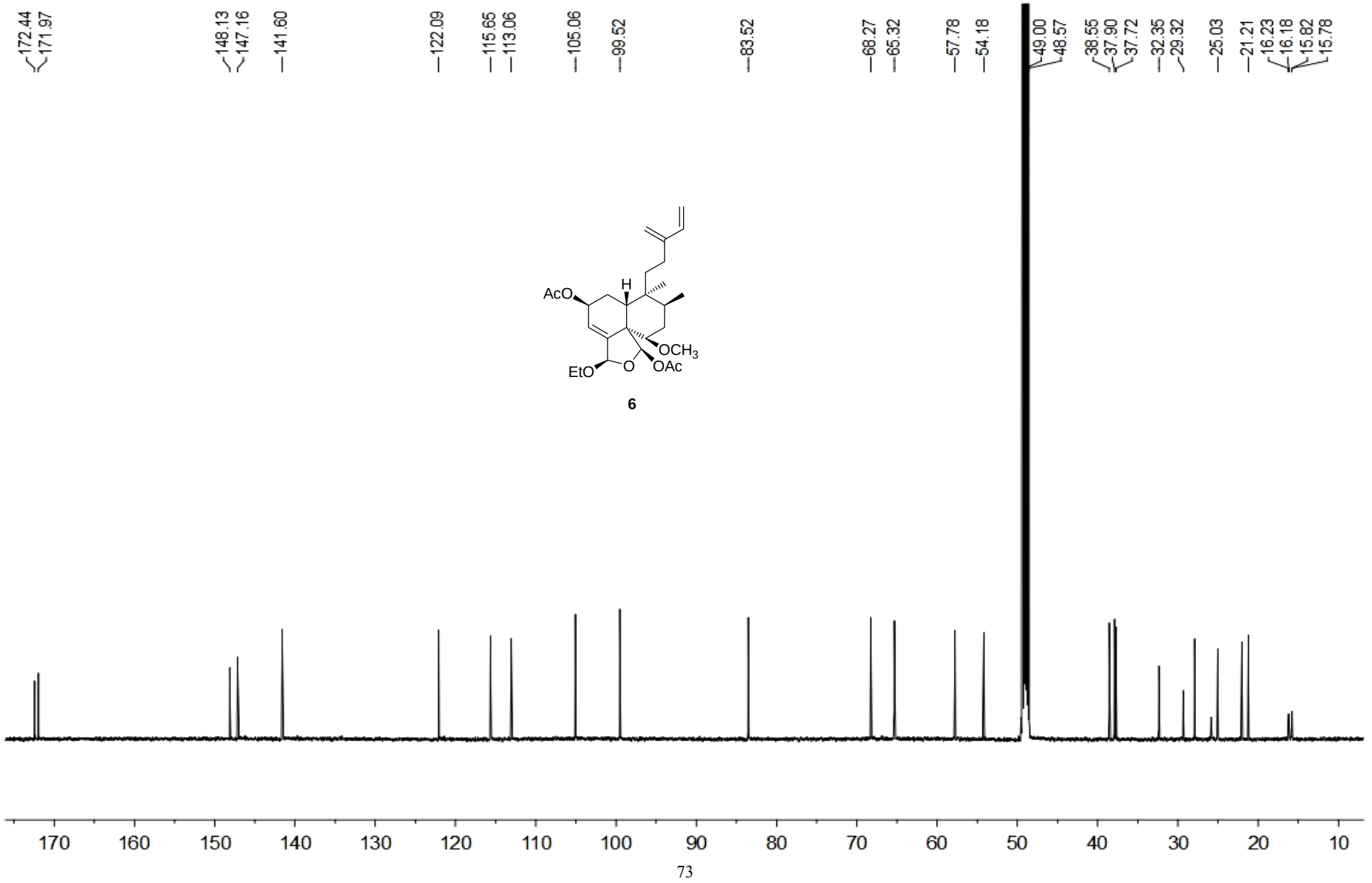


Figure S65. HSQC (600 MHz, methanol-d_4) spectrum of **6**

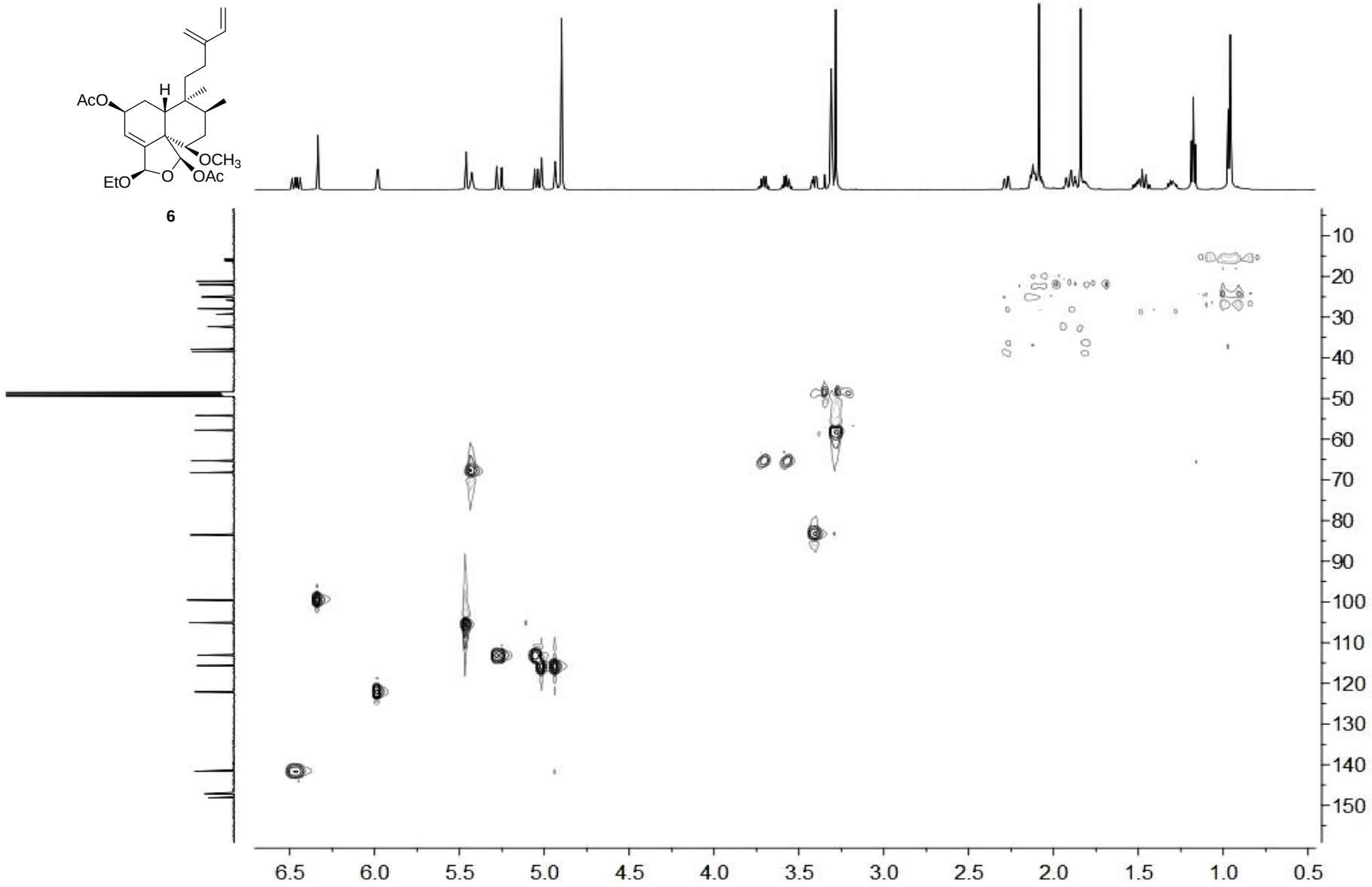


Figure S66. HMBC (600 MHz, methanol-d_4) spectrum of **6**

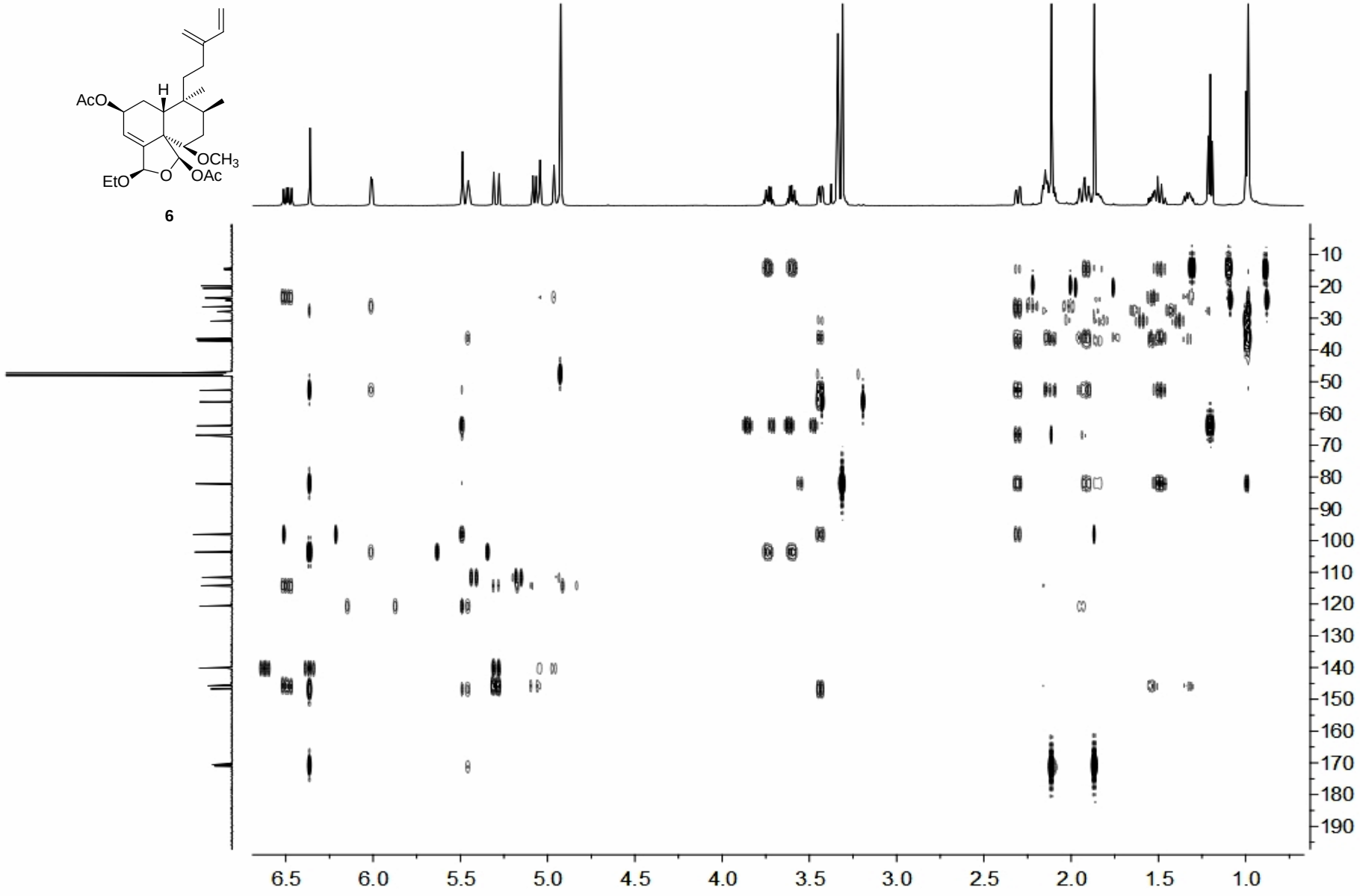


Figure S67. ^{1}H-^{1}H COSY (600 MHz, methanol-d_4) spectrum of **6**

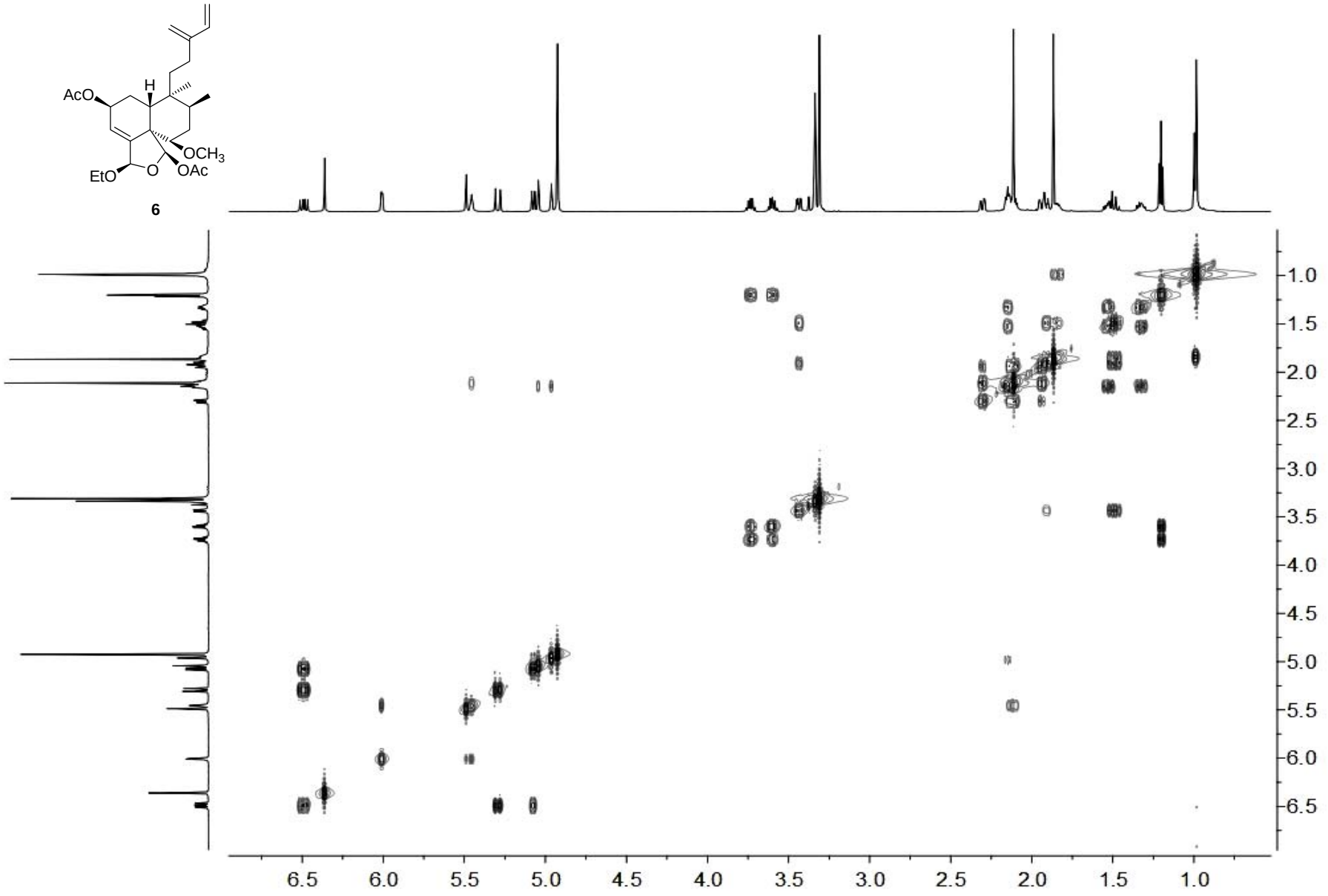


Figure S68. NOESY (600 MHz, methanol-d_4) spectrum of **6**

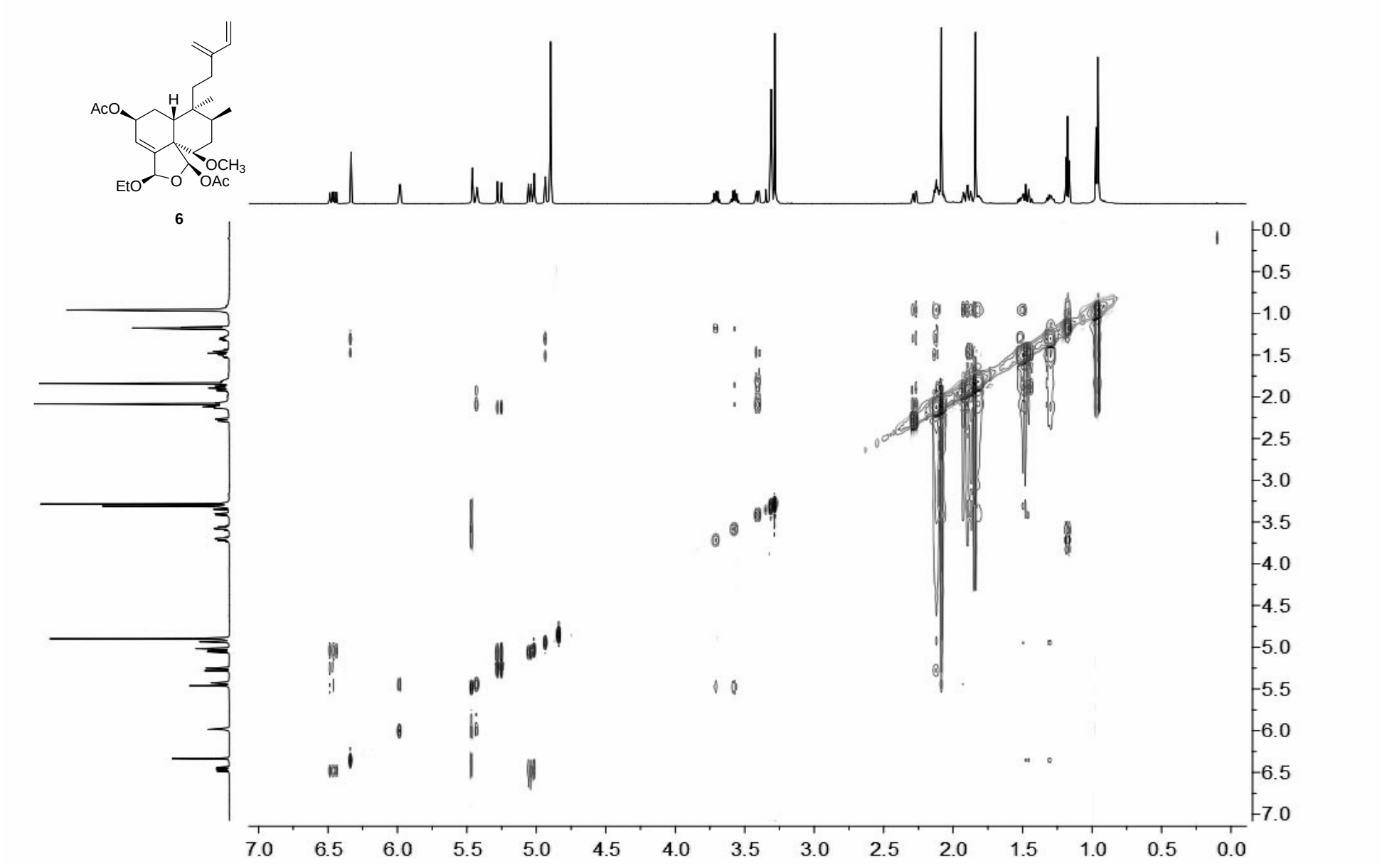


Figure S69. HRESIMS spectrum of **6**

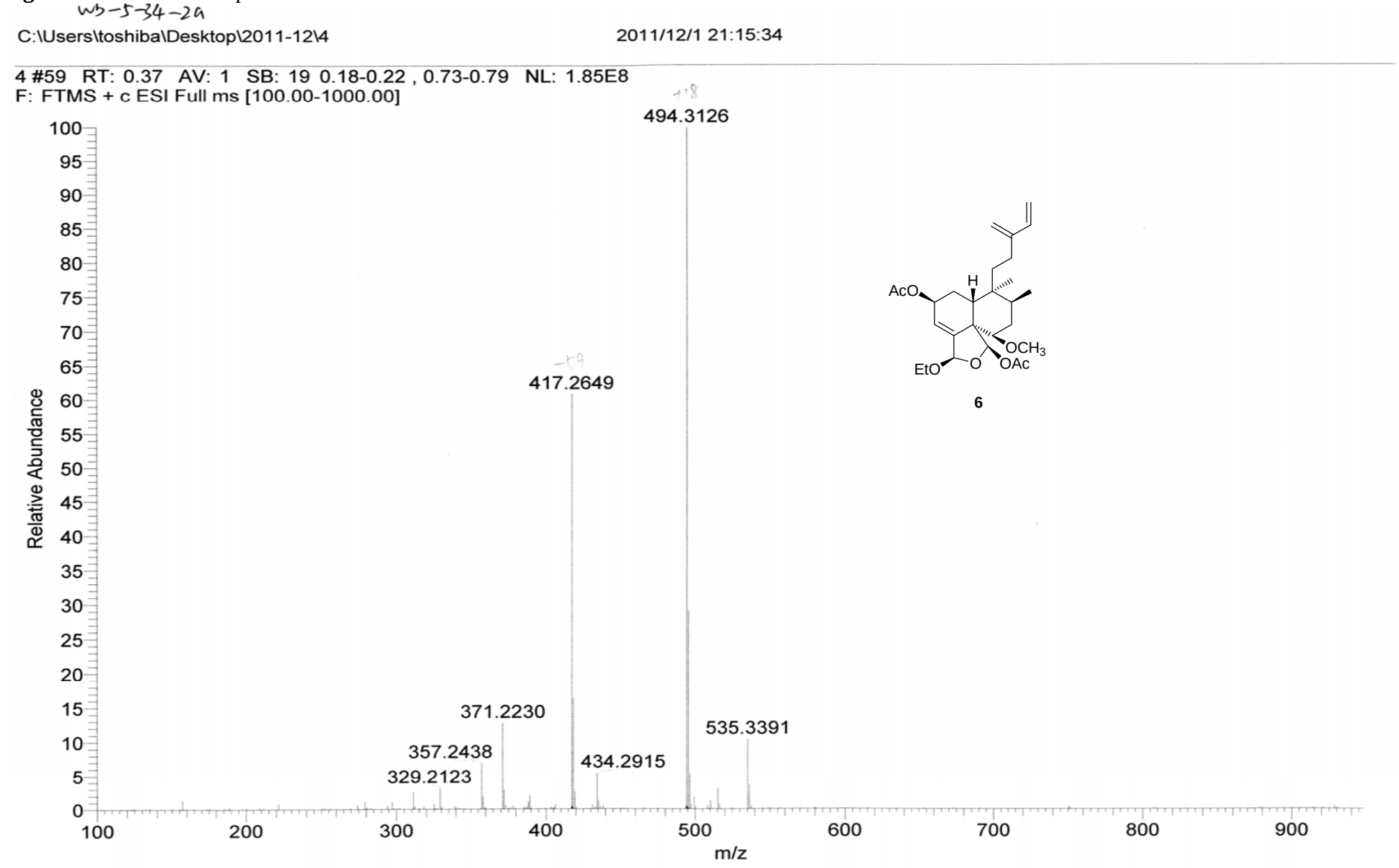


Figure S70. IR spectrum of **6**

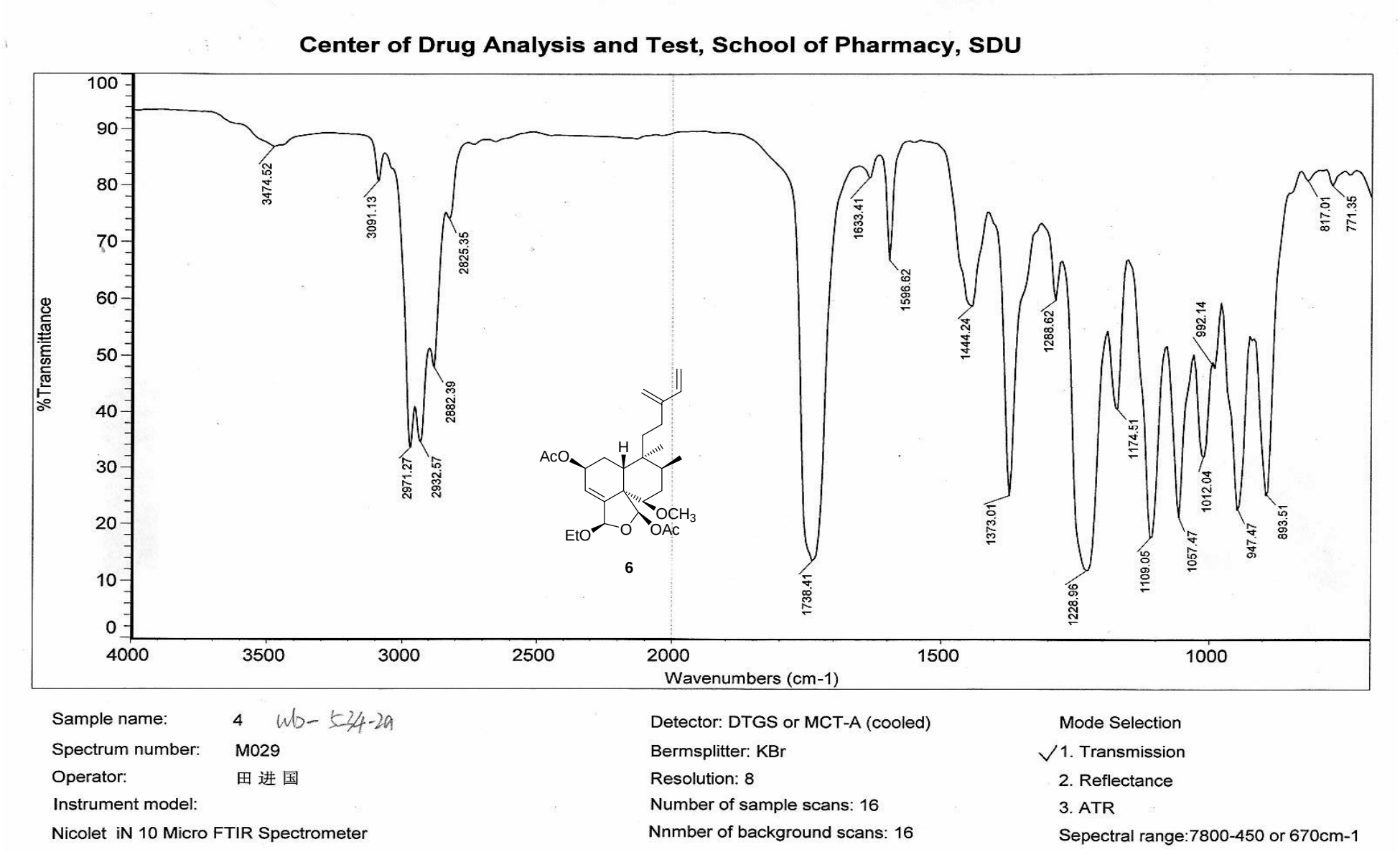


Figure S71. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **7**

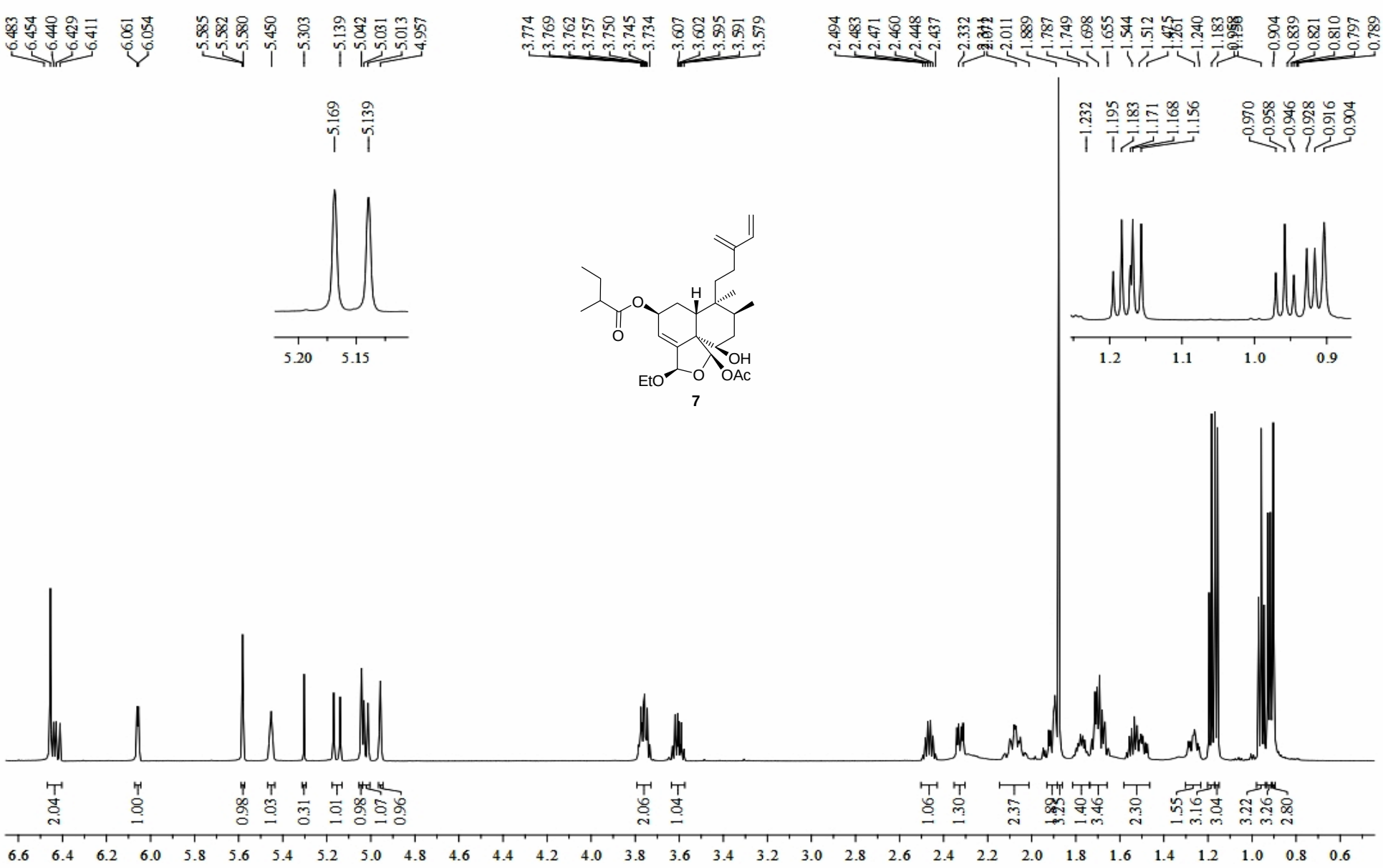


Figure S72. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **7**

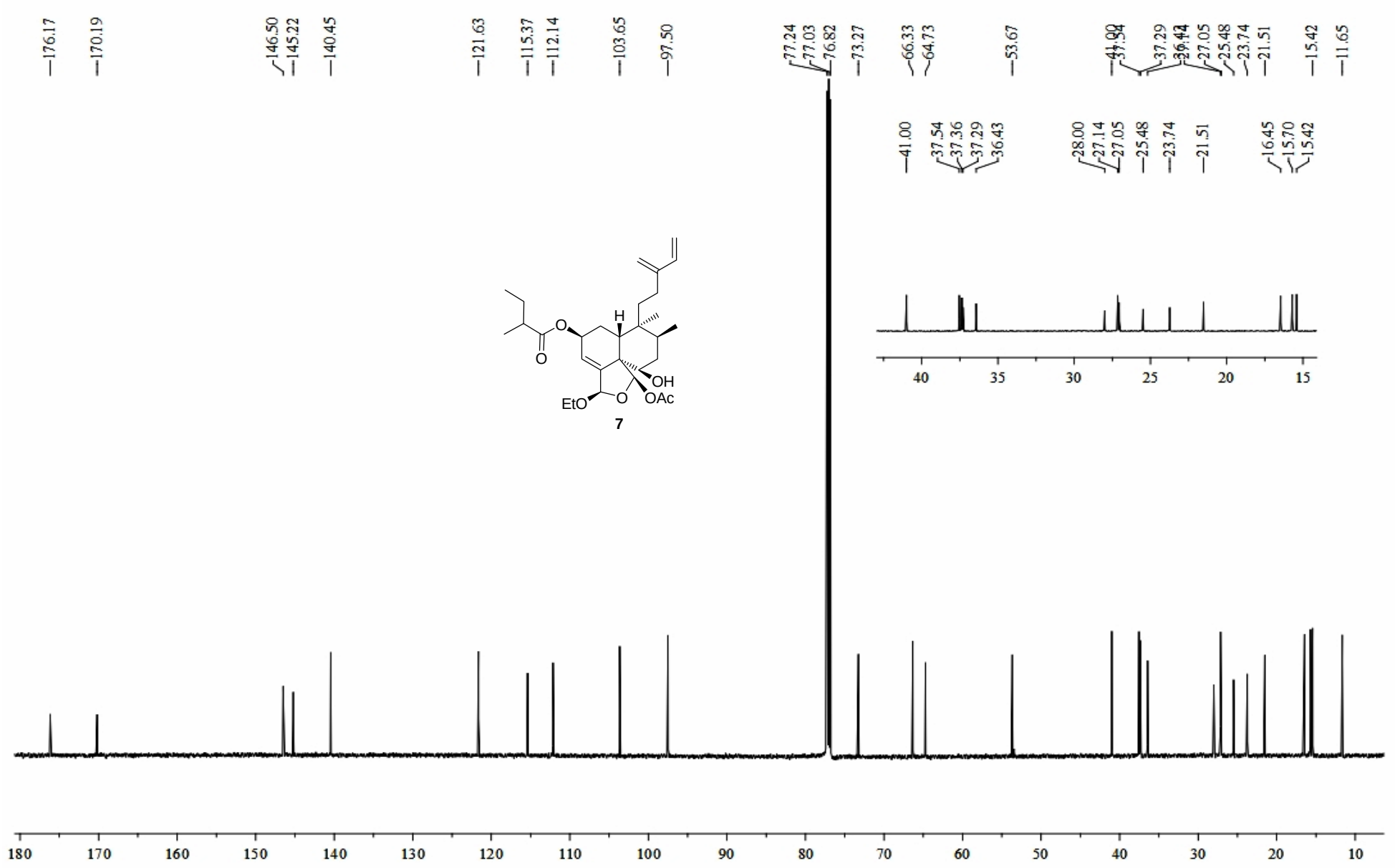


Figure S73. HSQC (600 MHz, $CDCl_3$) spectrum of **7**

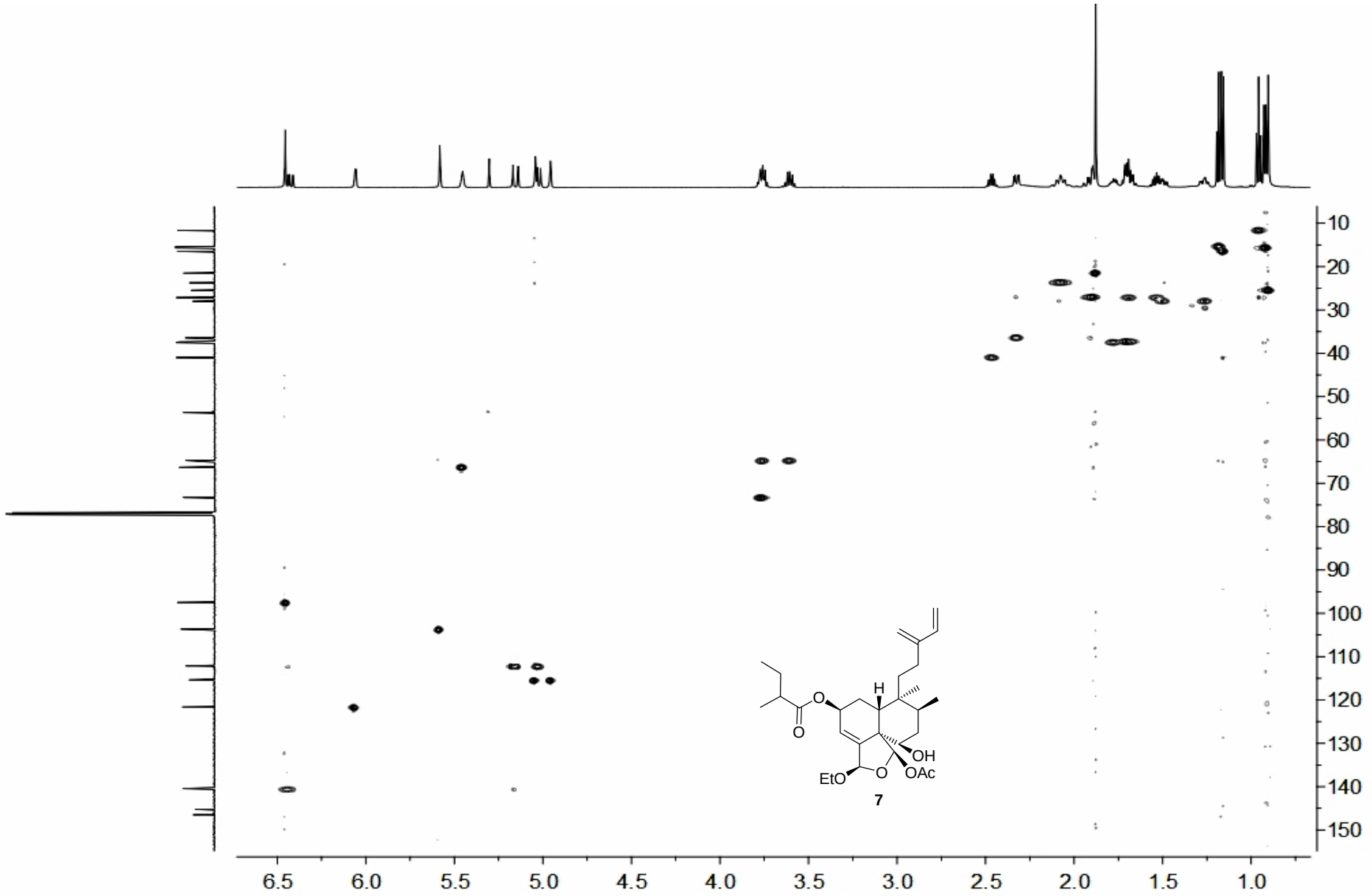


Figure S74. HMBC (600 MHz, $CDCl_3$) spectrum of **7**

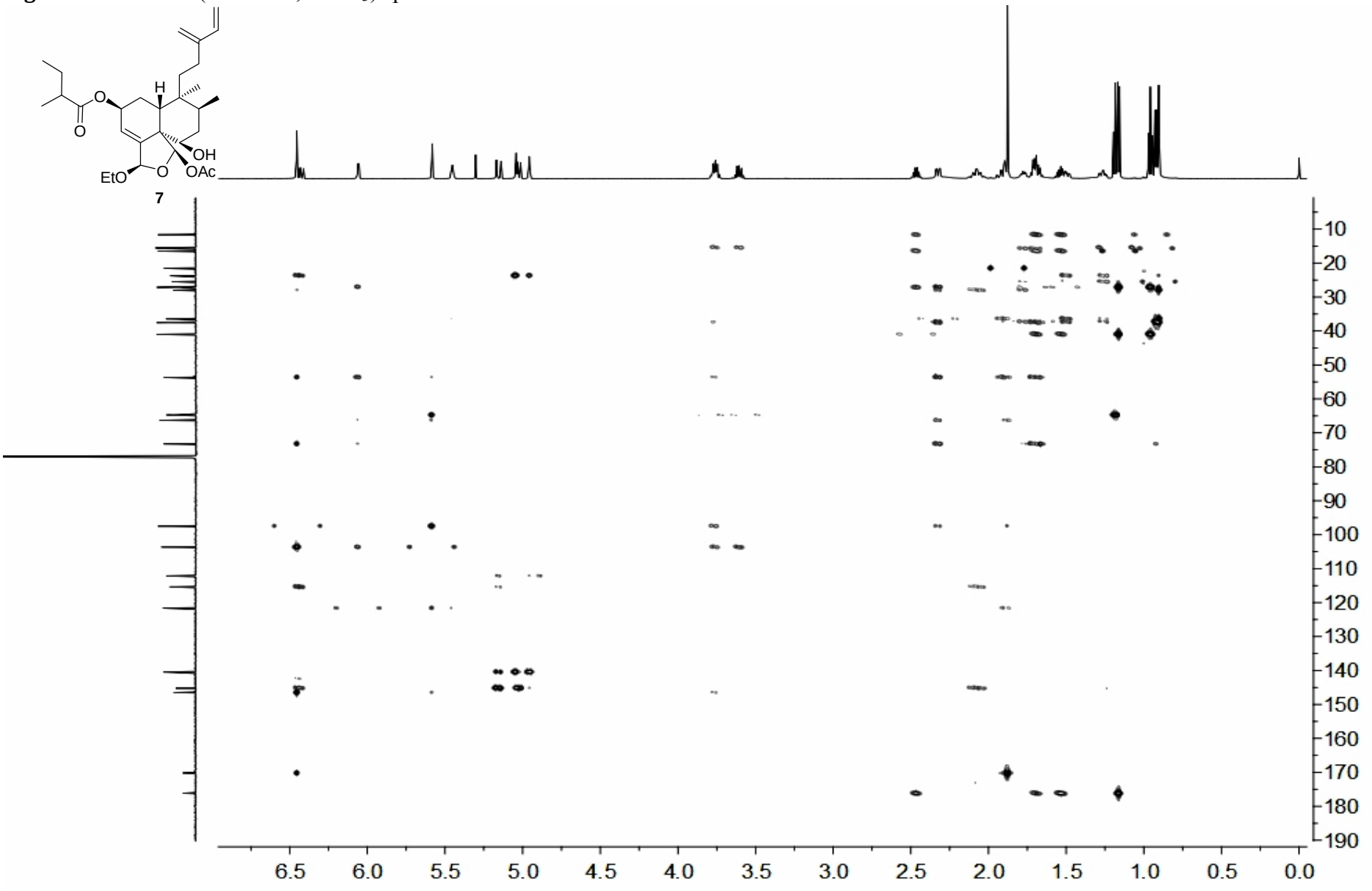


Figure S75. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **7**

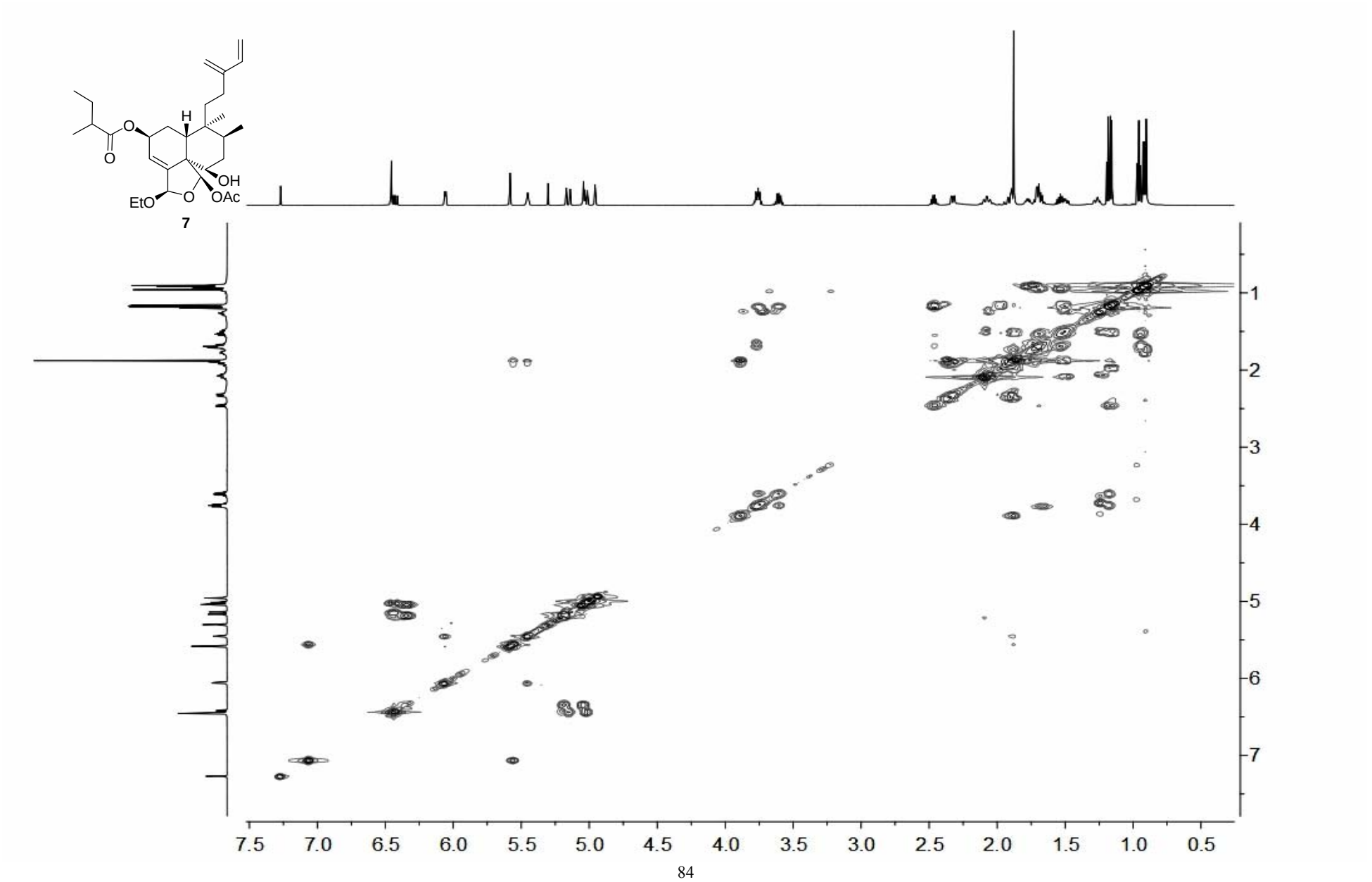


Figure S76. NOESY (600 MHz, $CDCl_3$) spectrum of **7**

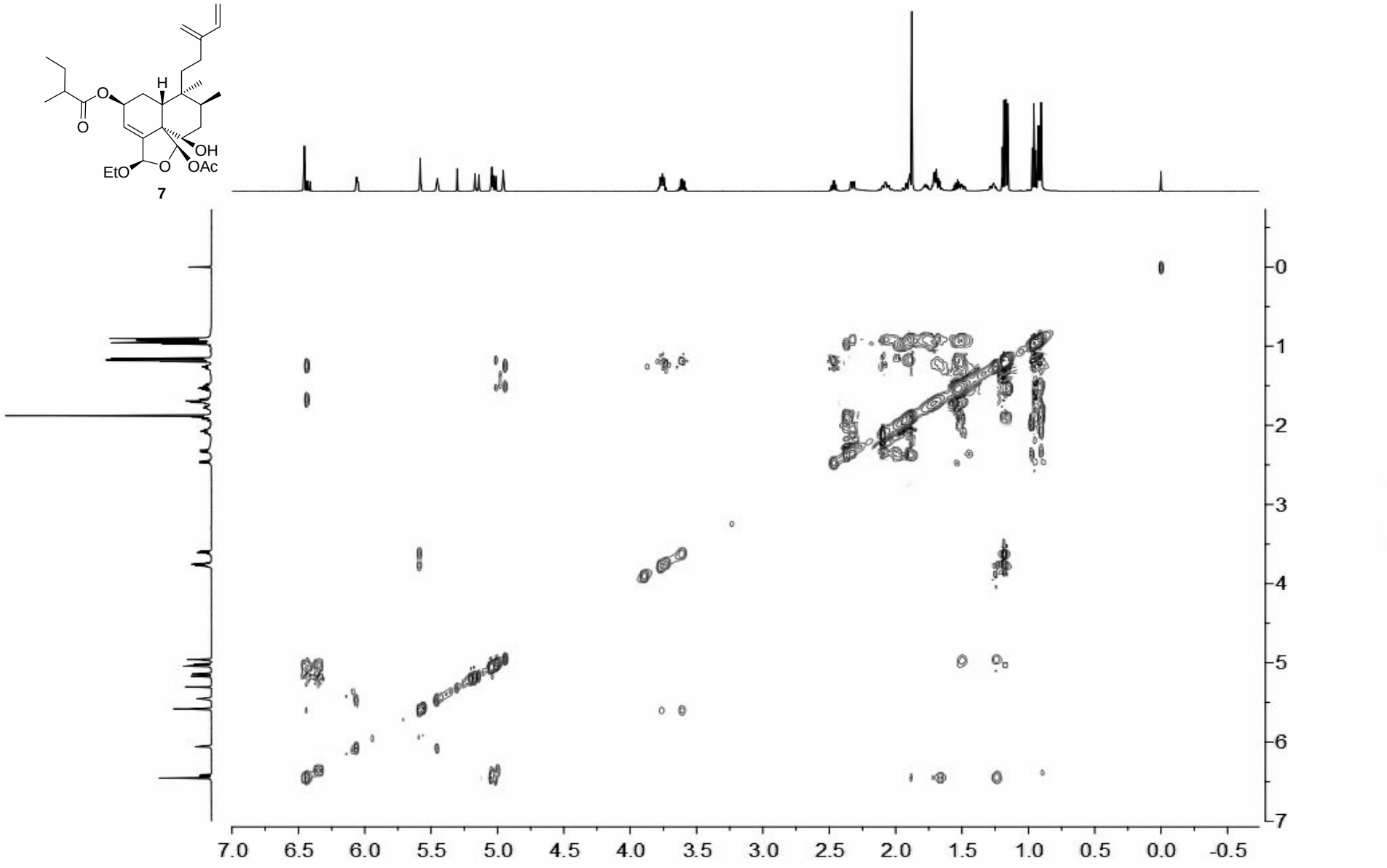


Figure S77. HRESIMS spectrum of **7**

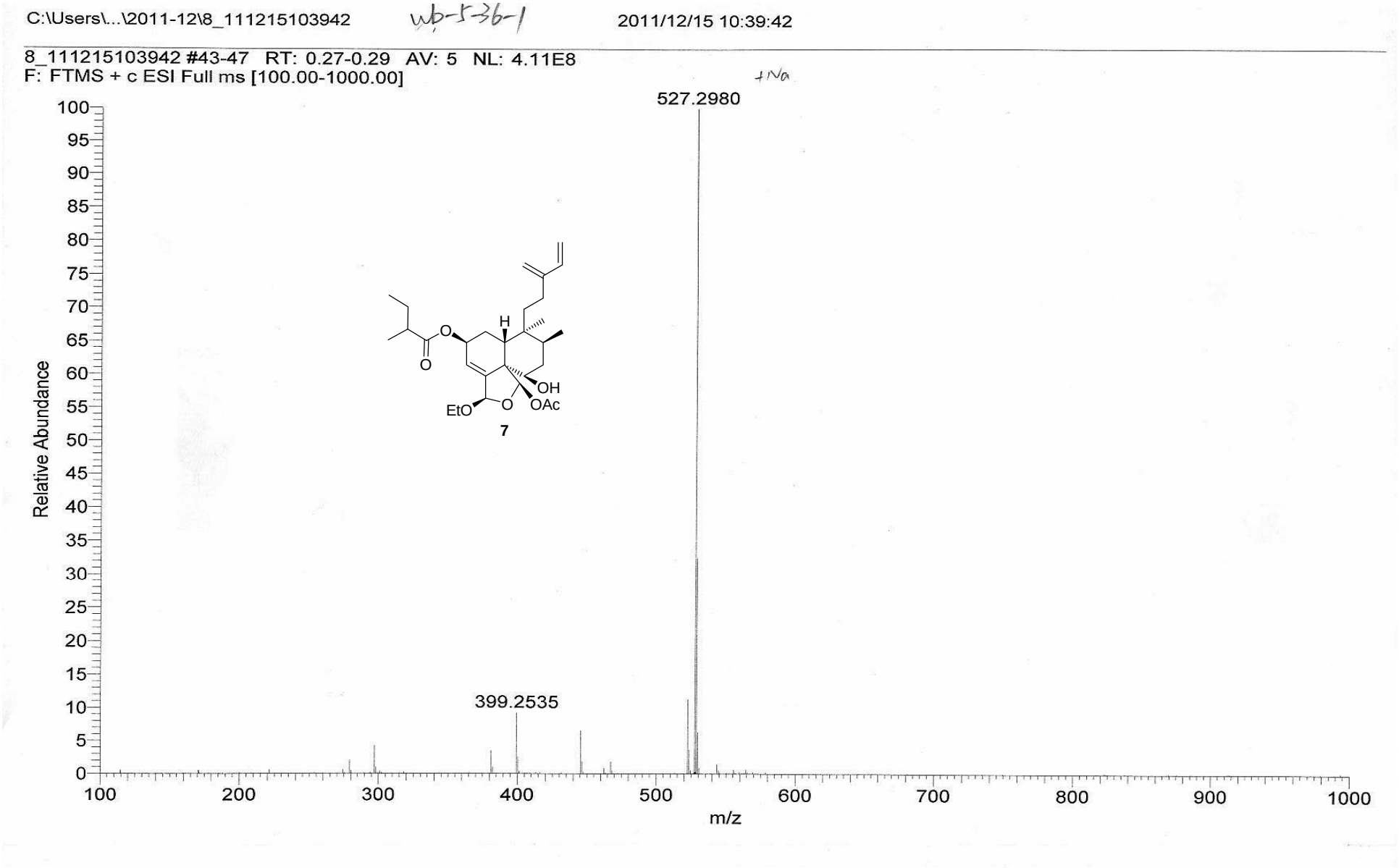


Figure S78. IR spectrum of **7**

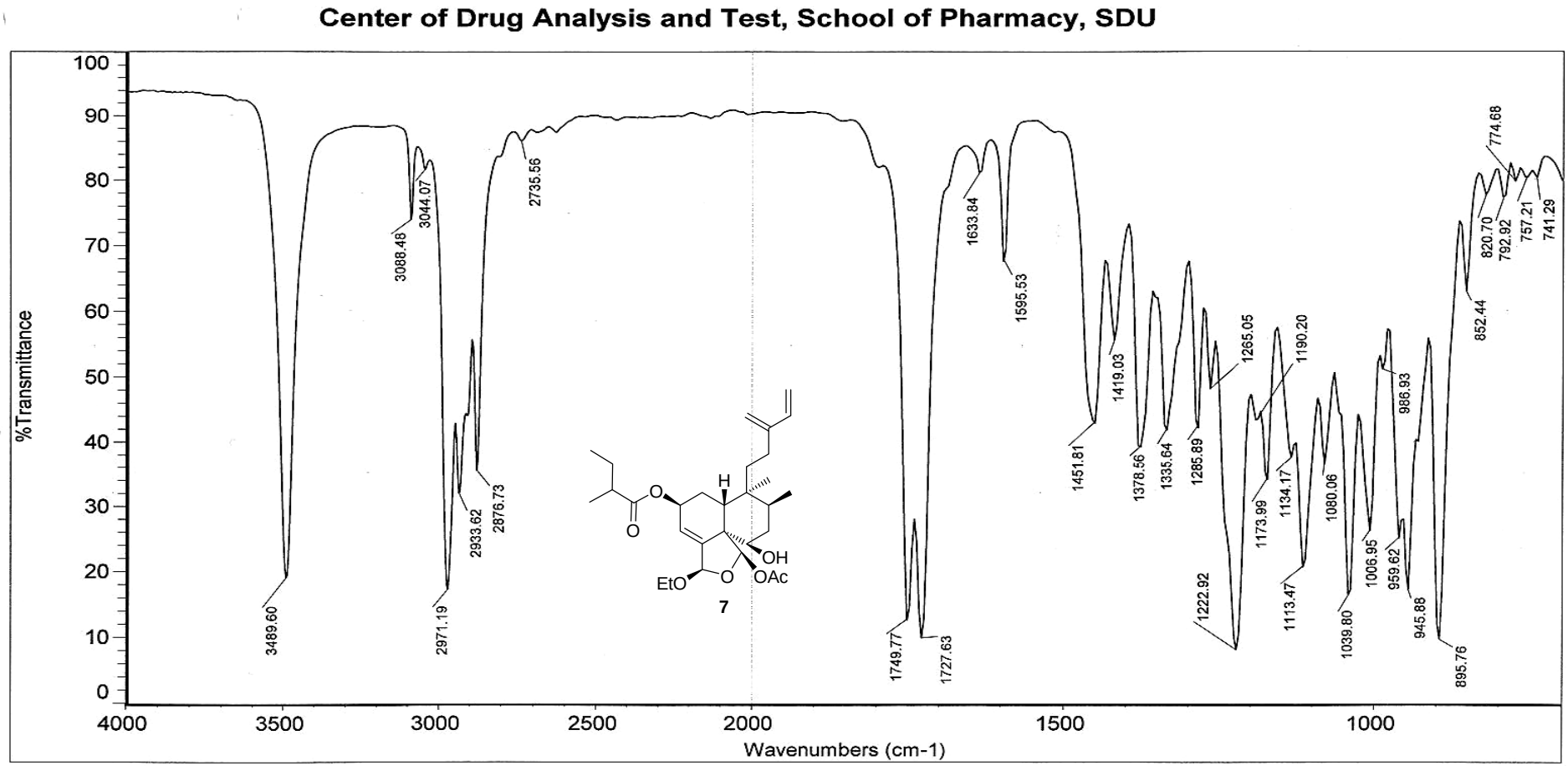


Figure S79. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **8**

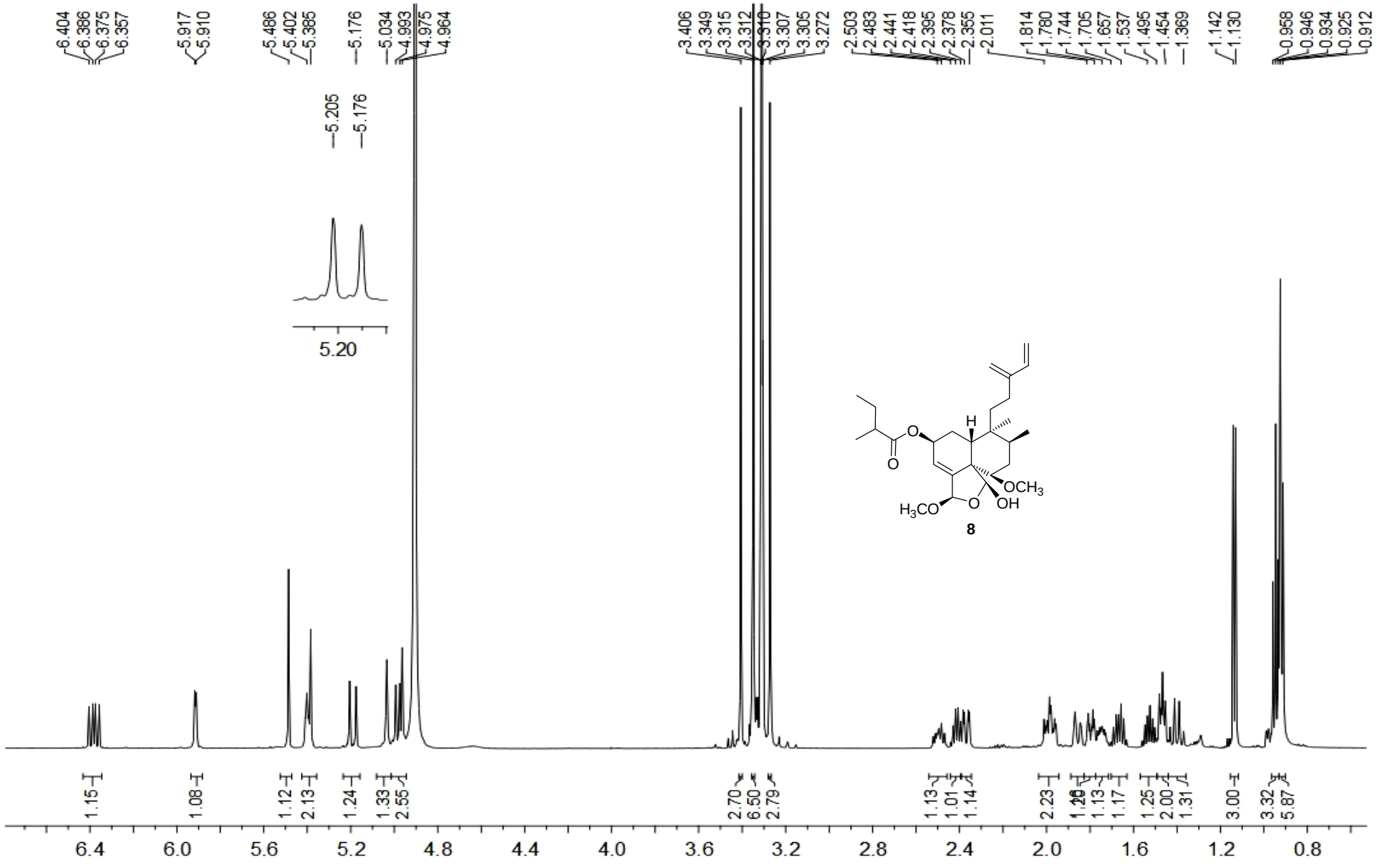


Figure S80. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **8**

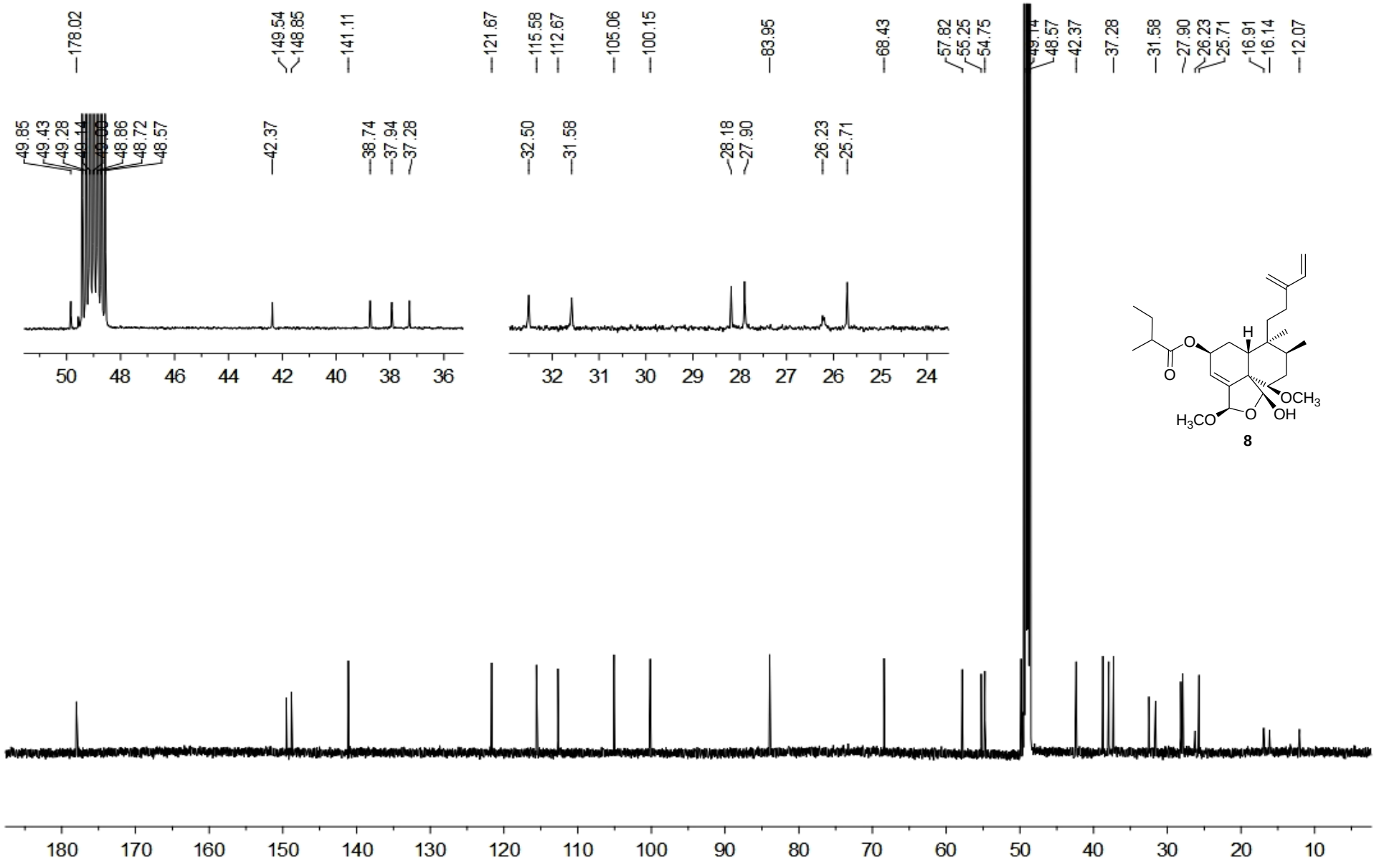


Figure S81. HSQC (600 MHz, methanol-d_4) spectrum of **8**

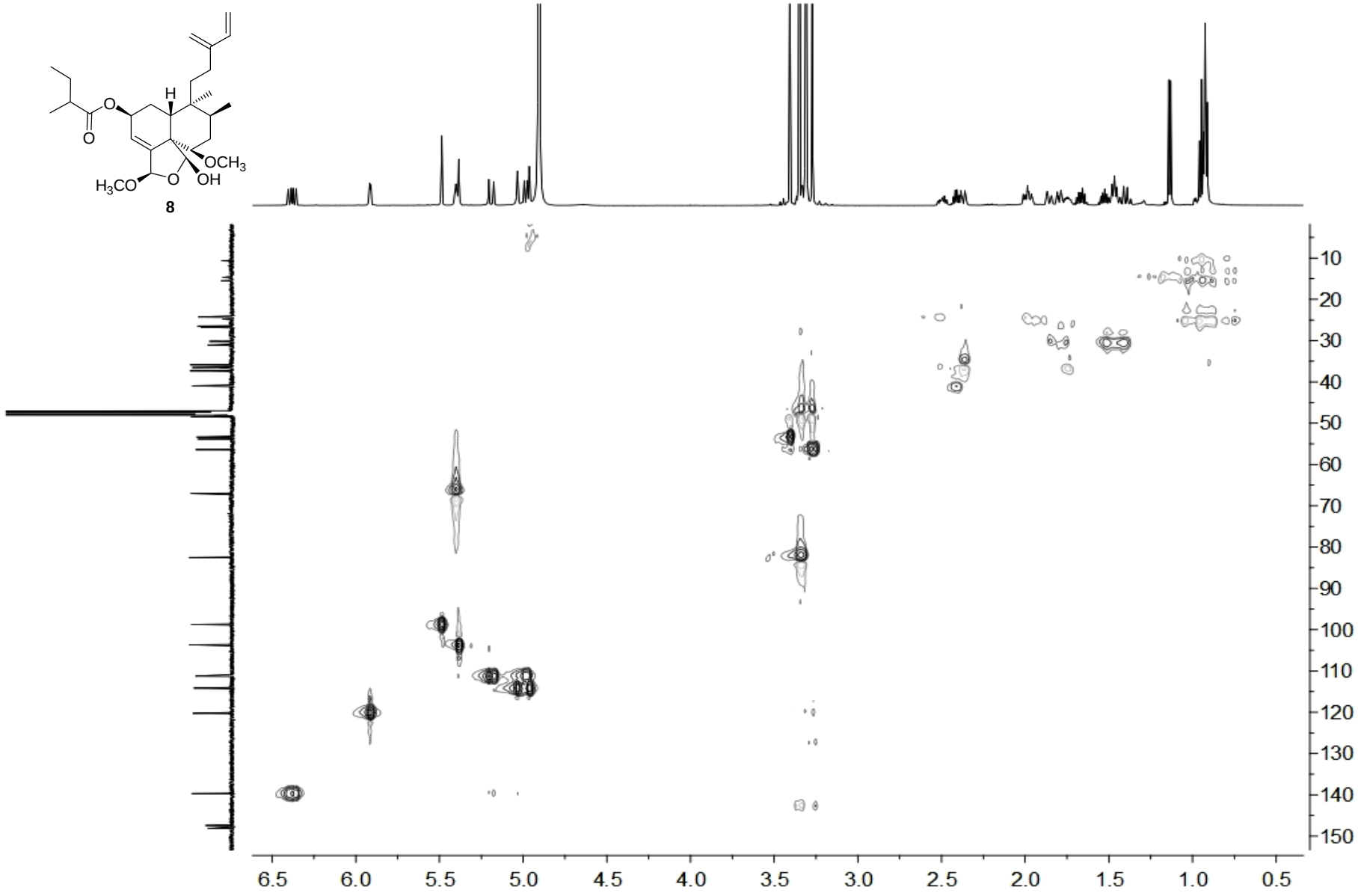


Figure S82. HMBC (600 MHz, methanol-d_4) spectrum of **8**

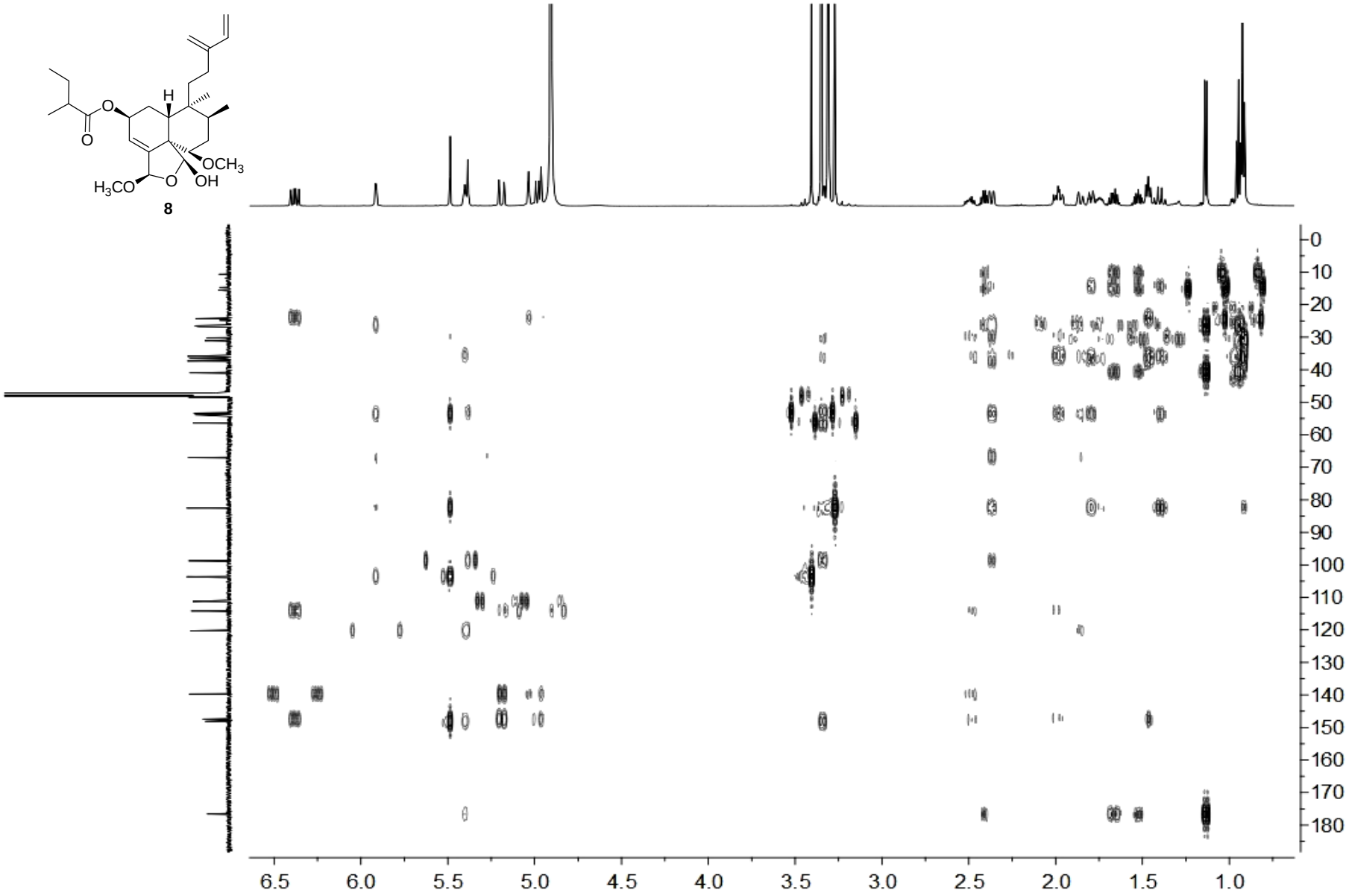


Figure S83. COSY (600 MHz, methanol-d_4) spectrum of **8**

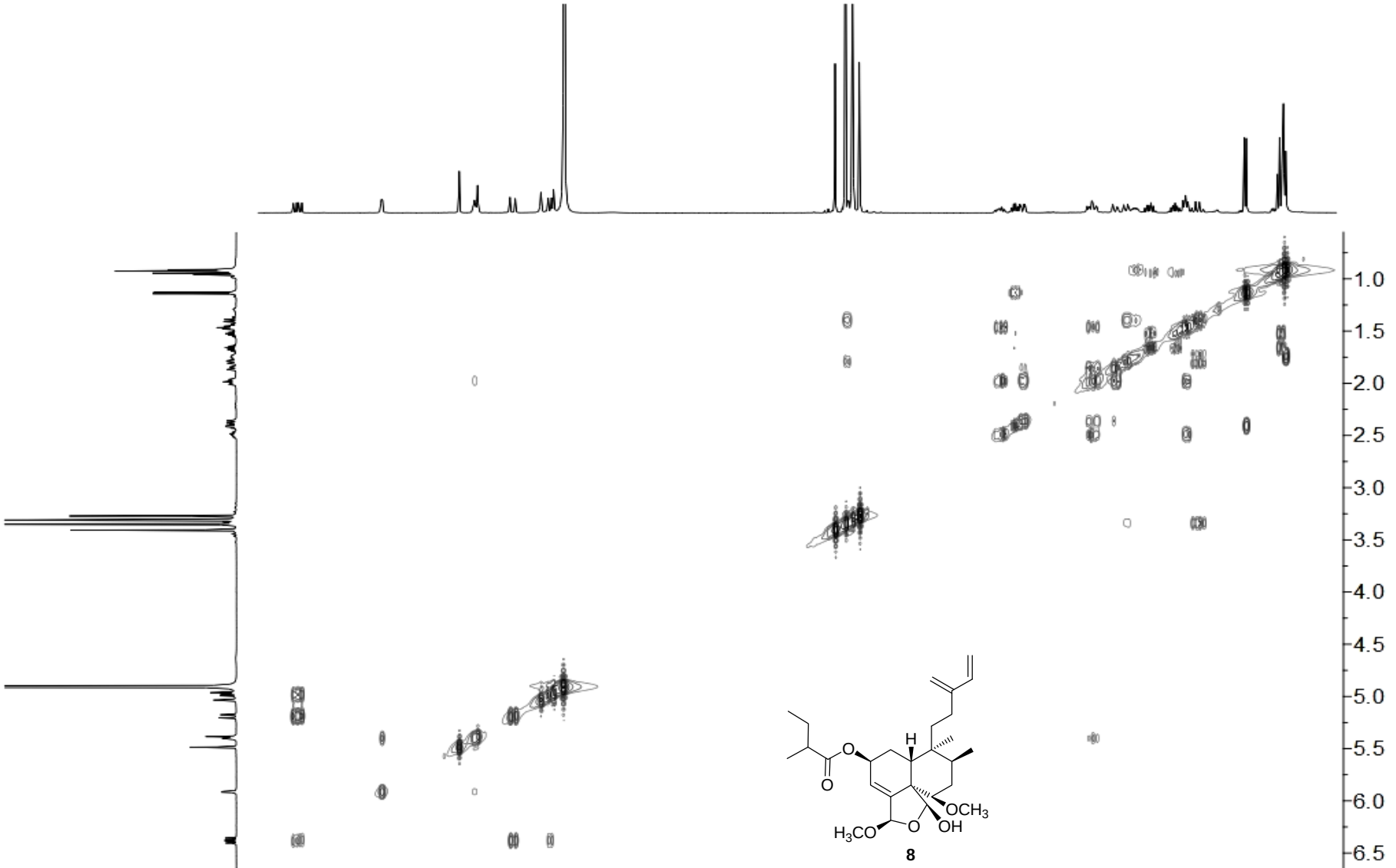
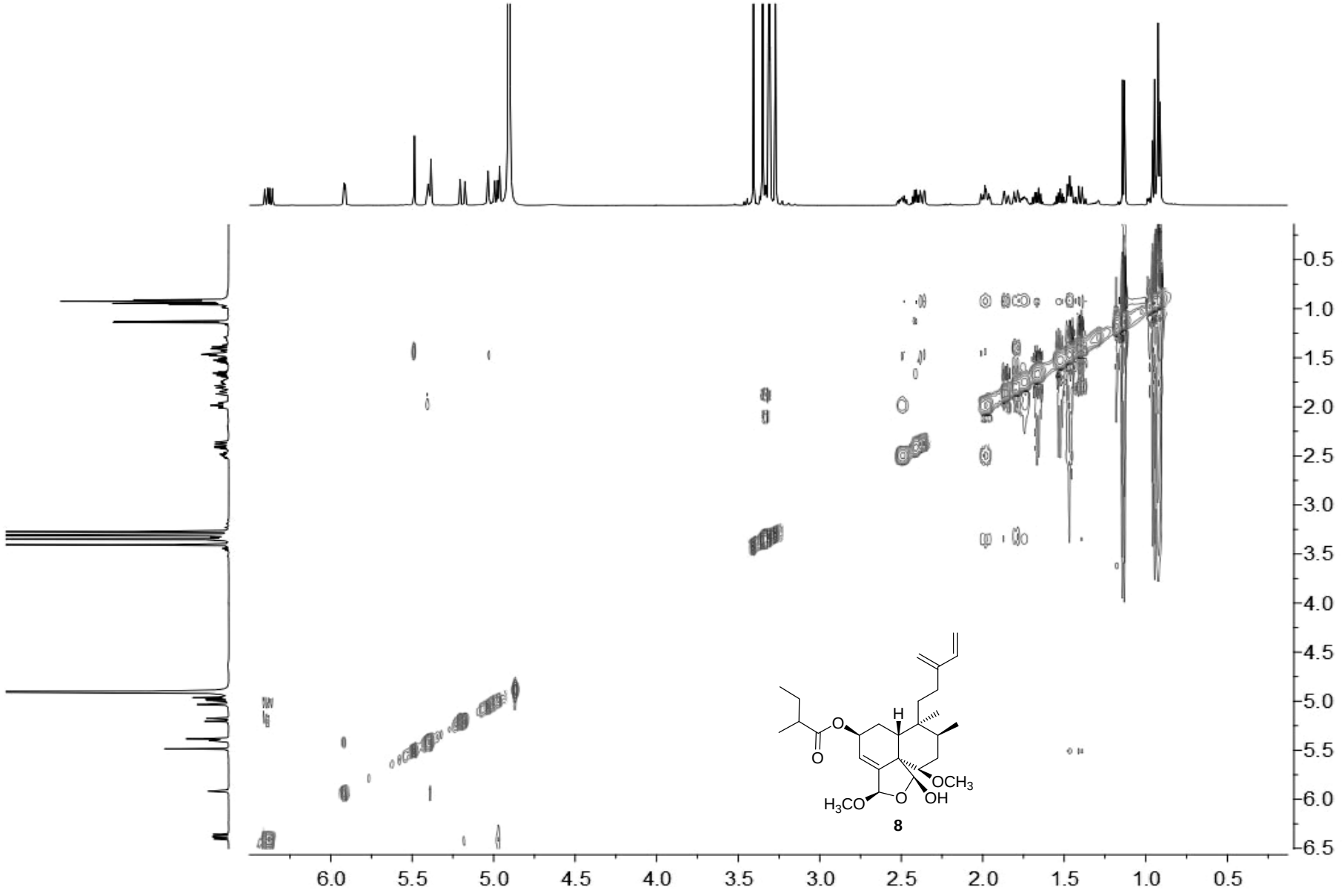


Figure S84. NOESY (600 MHz, methanol-d_4) spectrum of **8**



8

Figure S85. HRESIMS spectrum of **8**

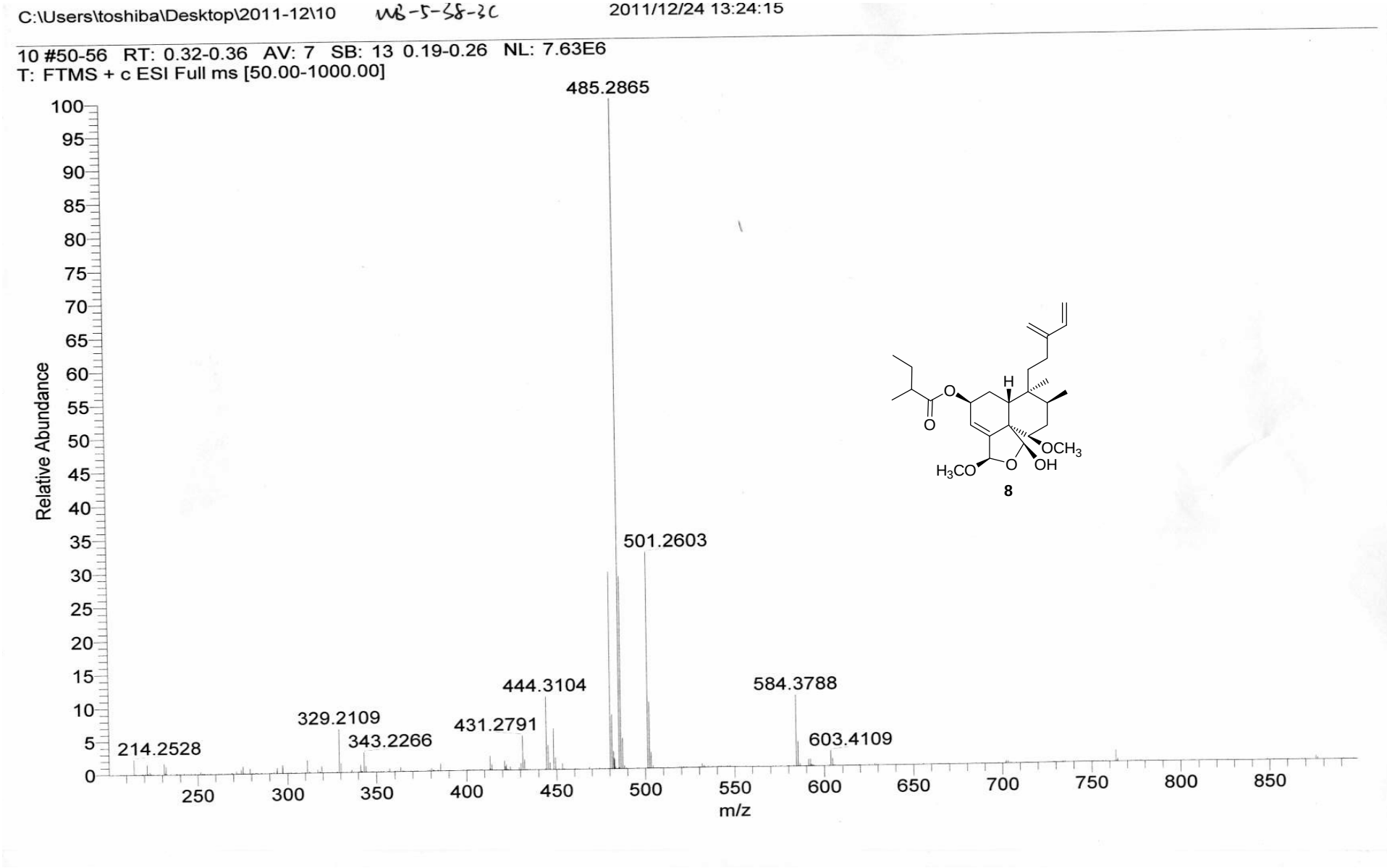


Figure S86. IR spectrum of **8**

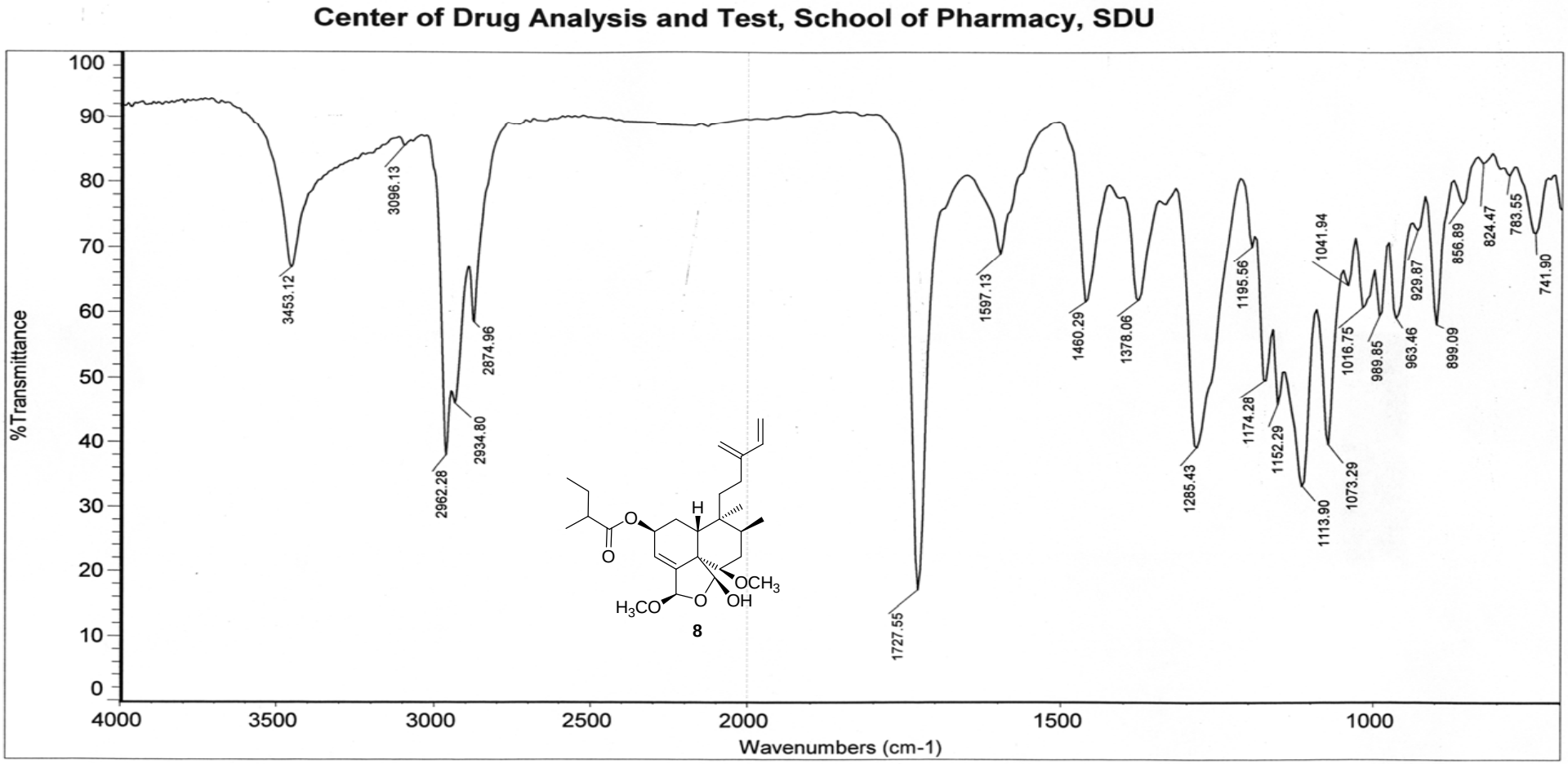


Figure S87. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9**

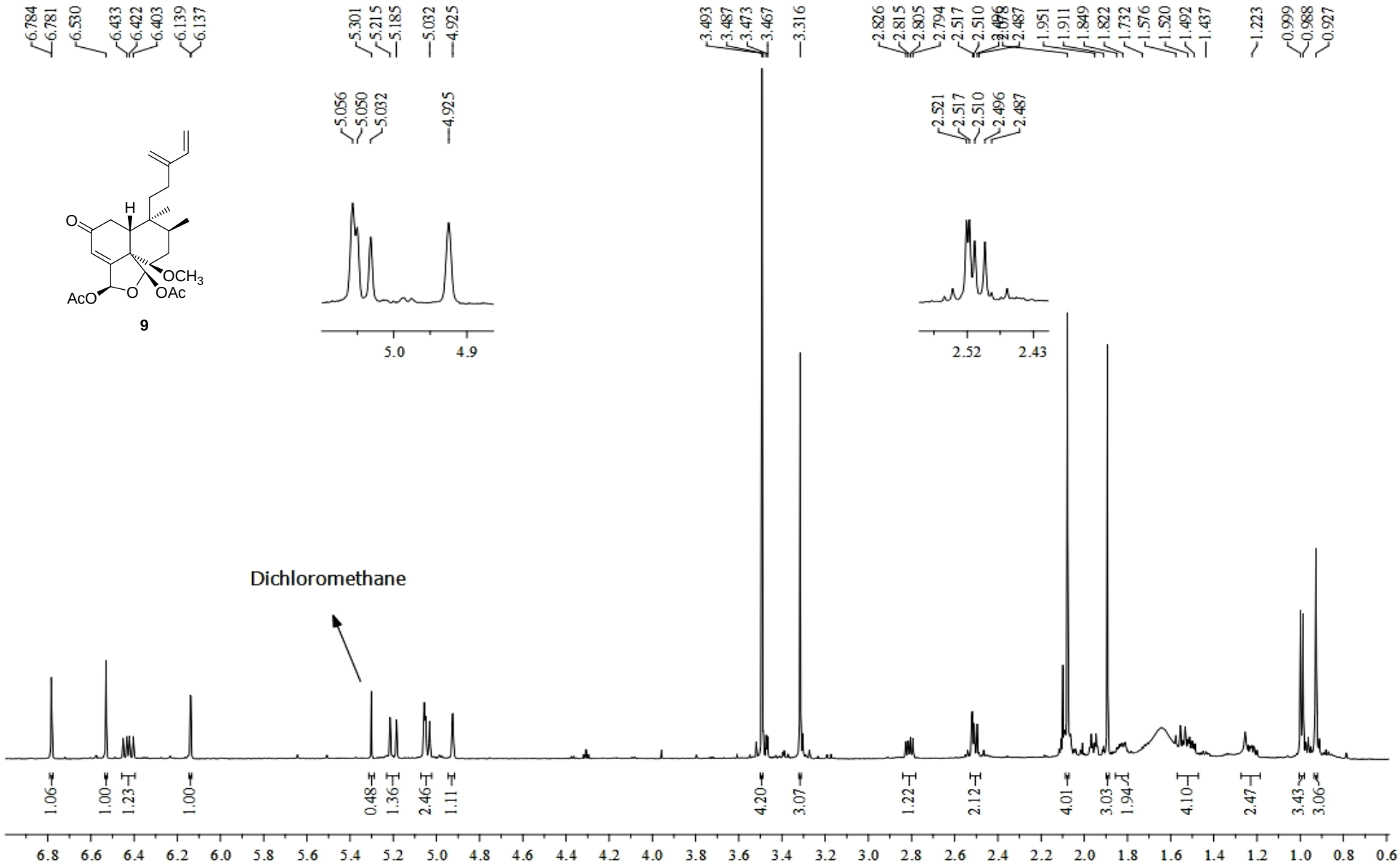


Figure S88. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **9**

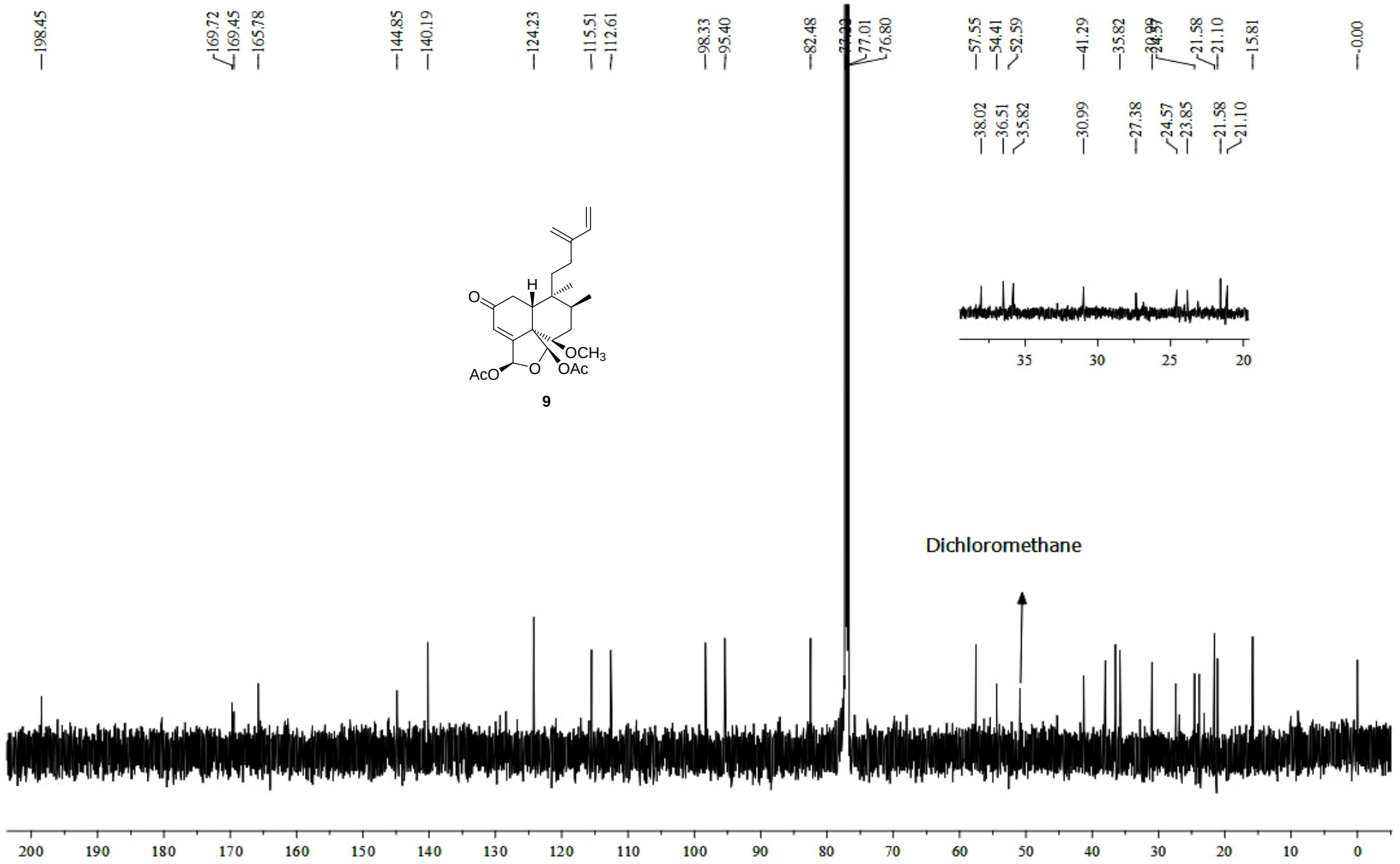


Figure S89. HSQC (600 MHz, $CDCl_3$) spectrum of **9**

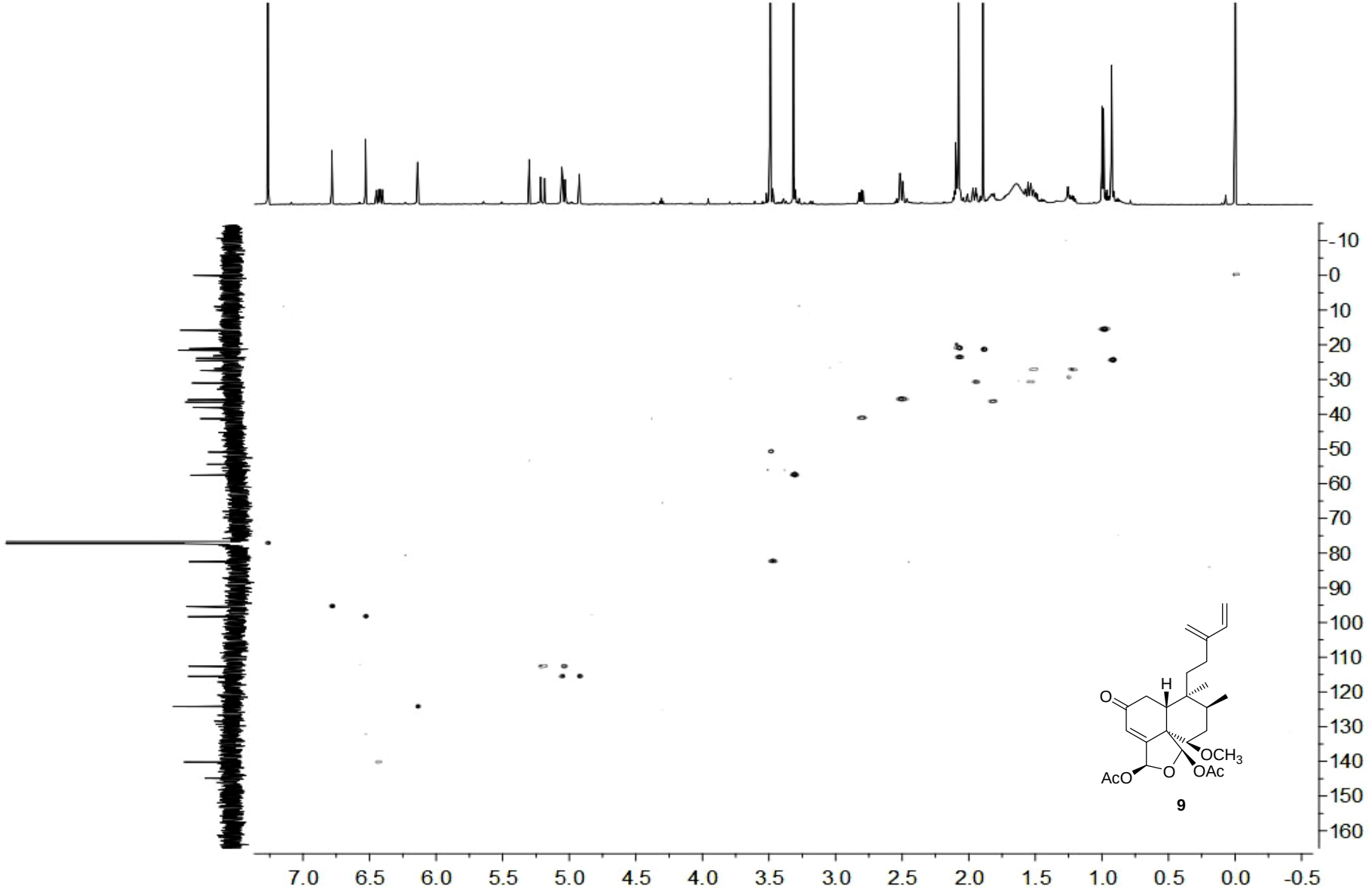


Figure S90. HMBC (600 MHz, $CDCl_3$) spectrum of **9**

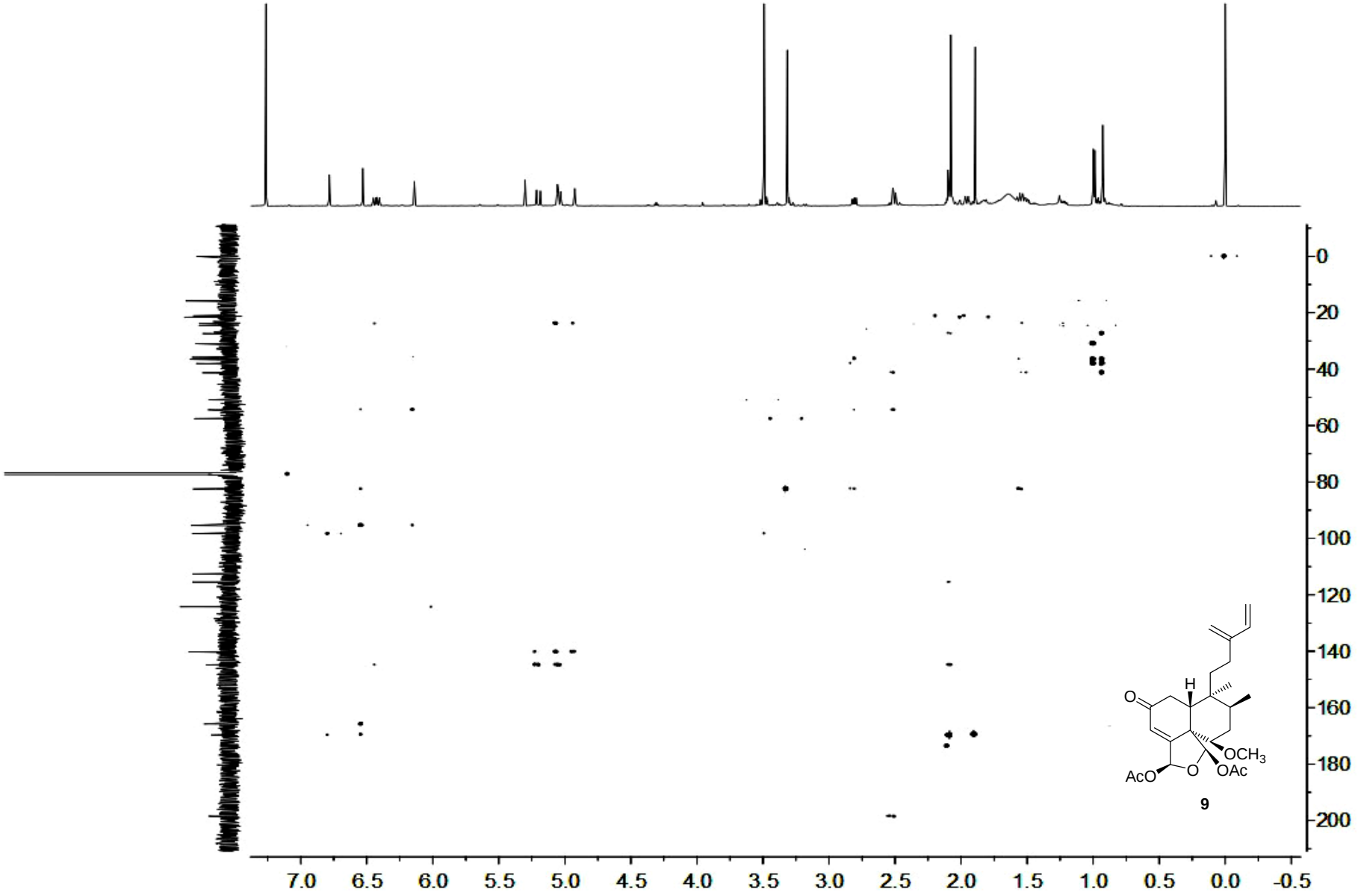


Figure S91. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **9**

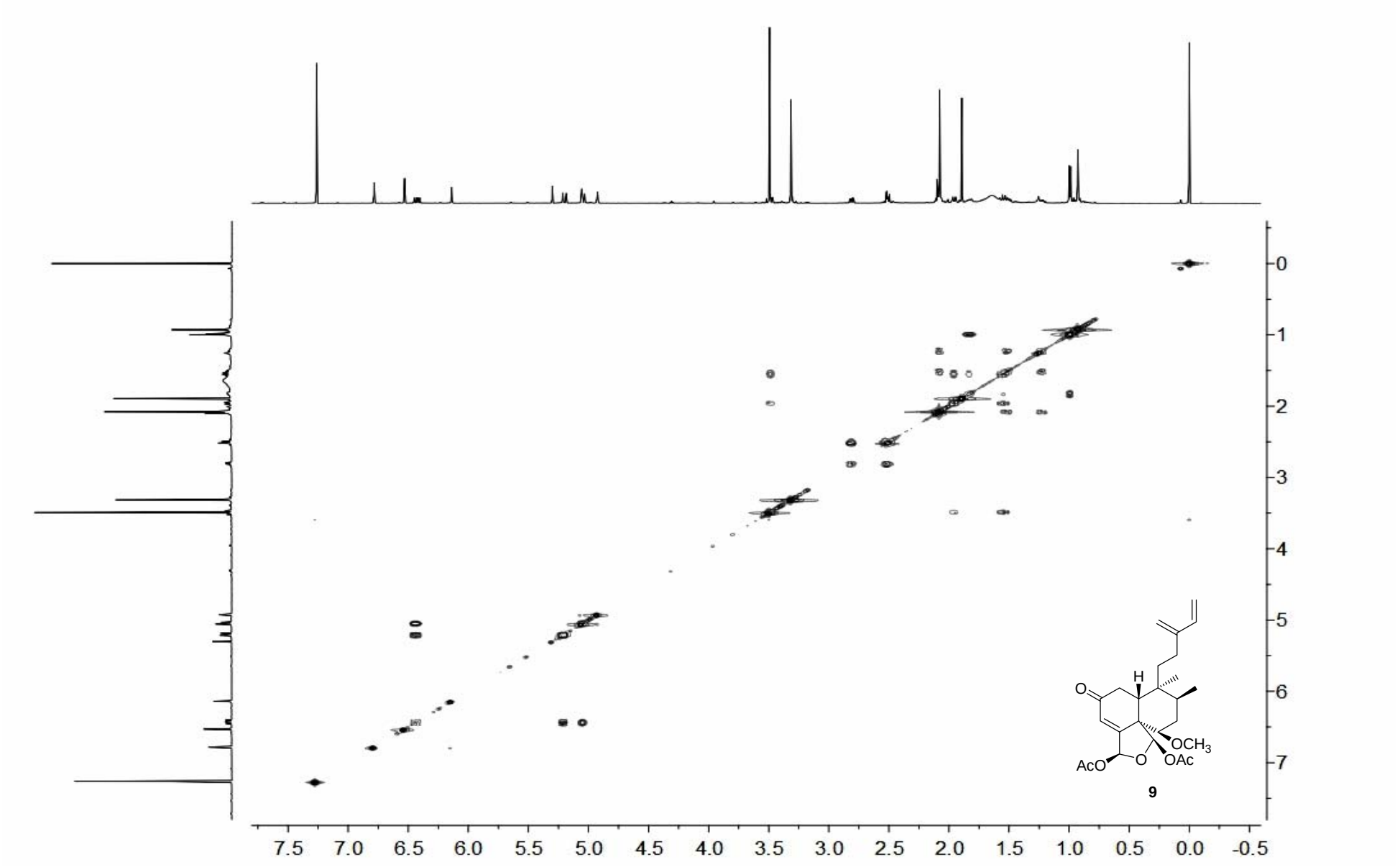


Figure S92. NOESY (600 MHz, $CDCl_3$) spectrum of **9**

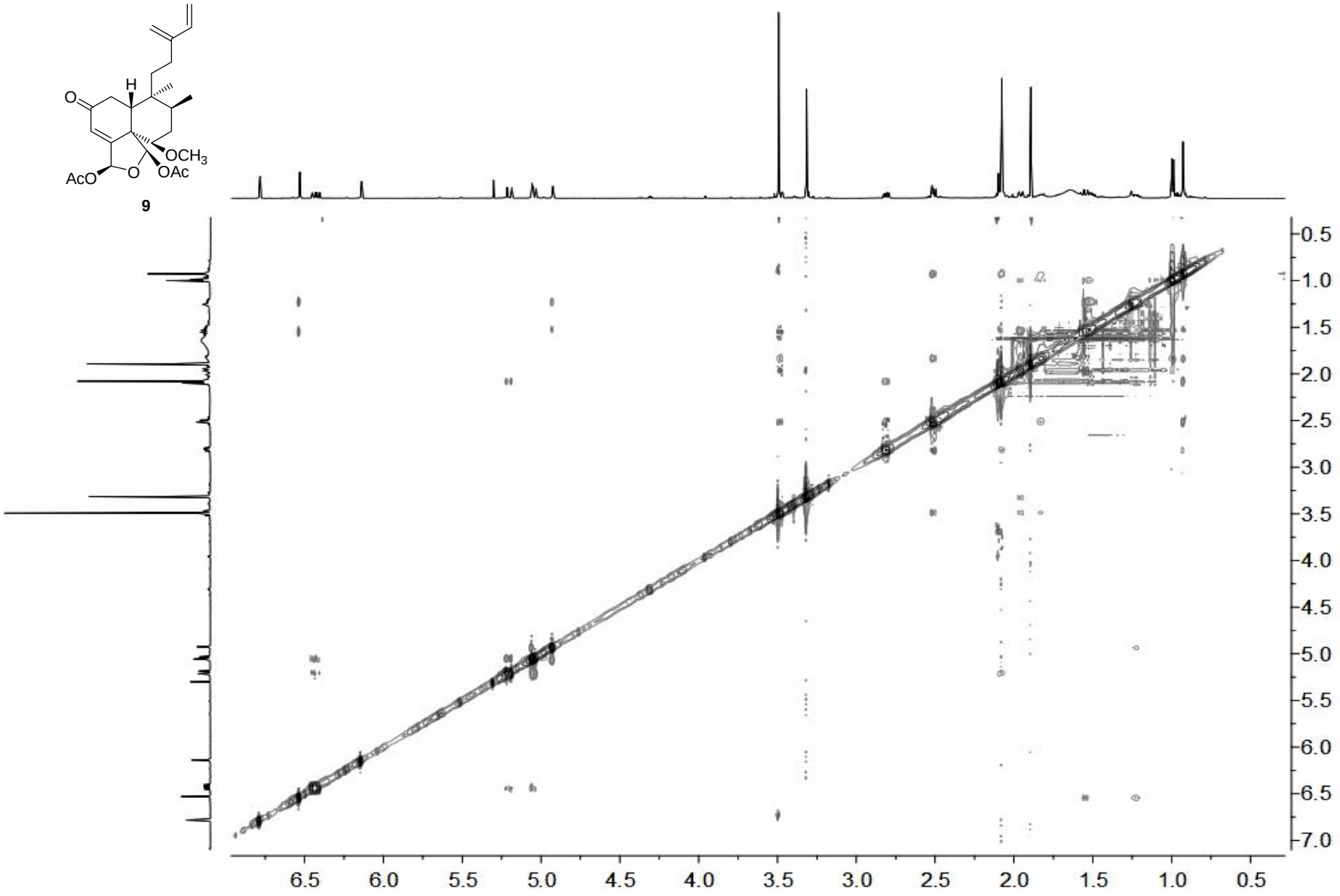


Figure S93. HRESIMS spectrum of **9**

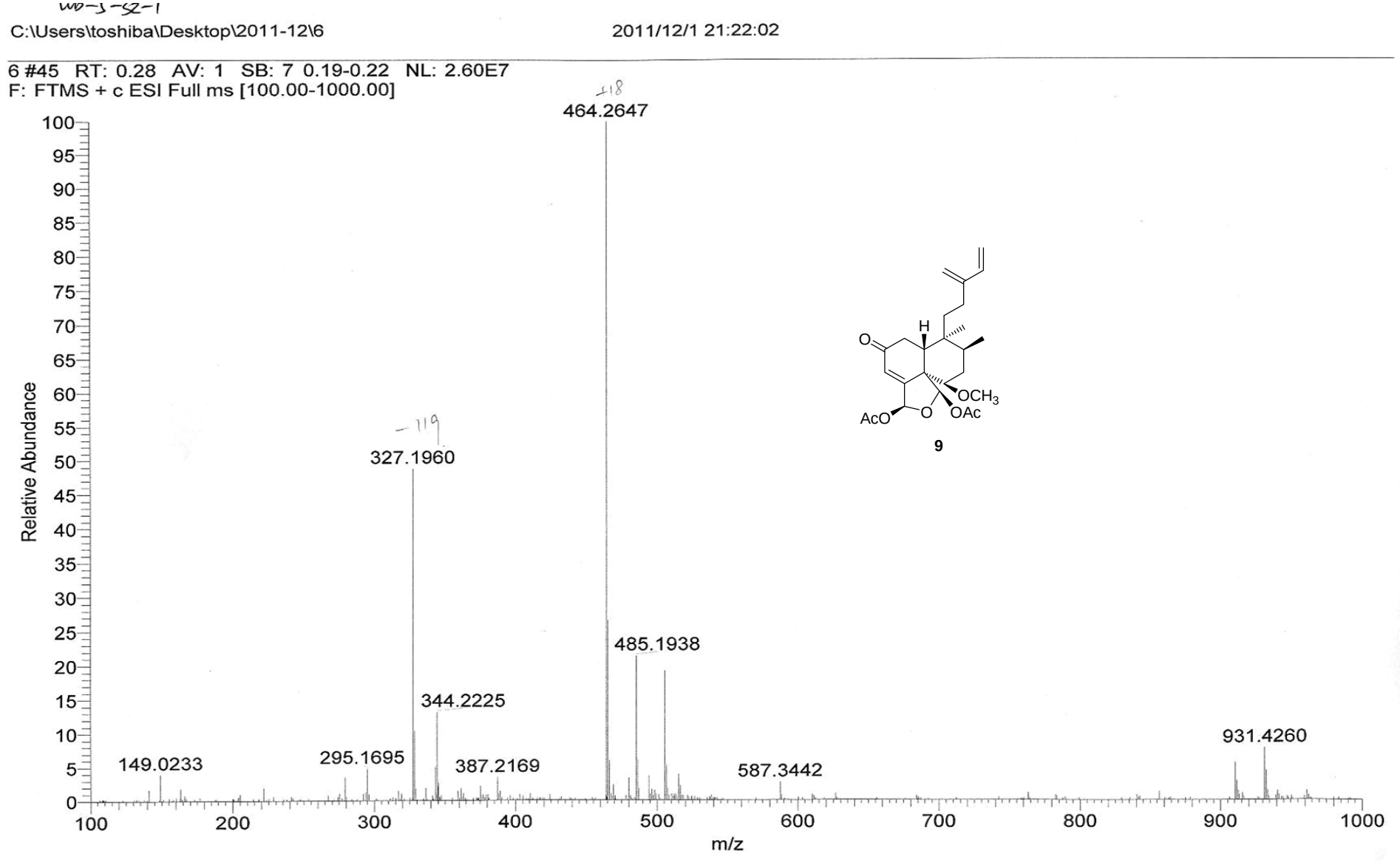


Figure S94. IR spectrum of **9**

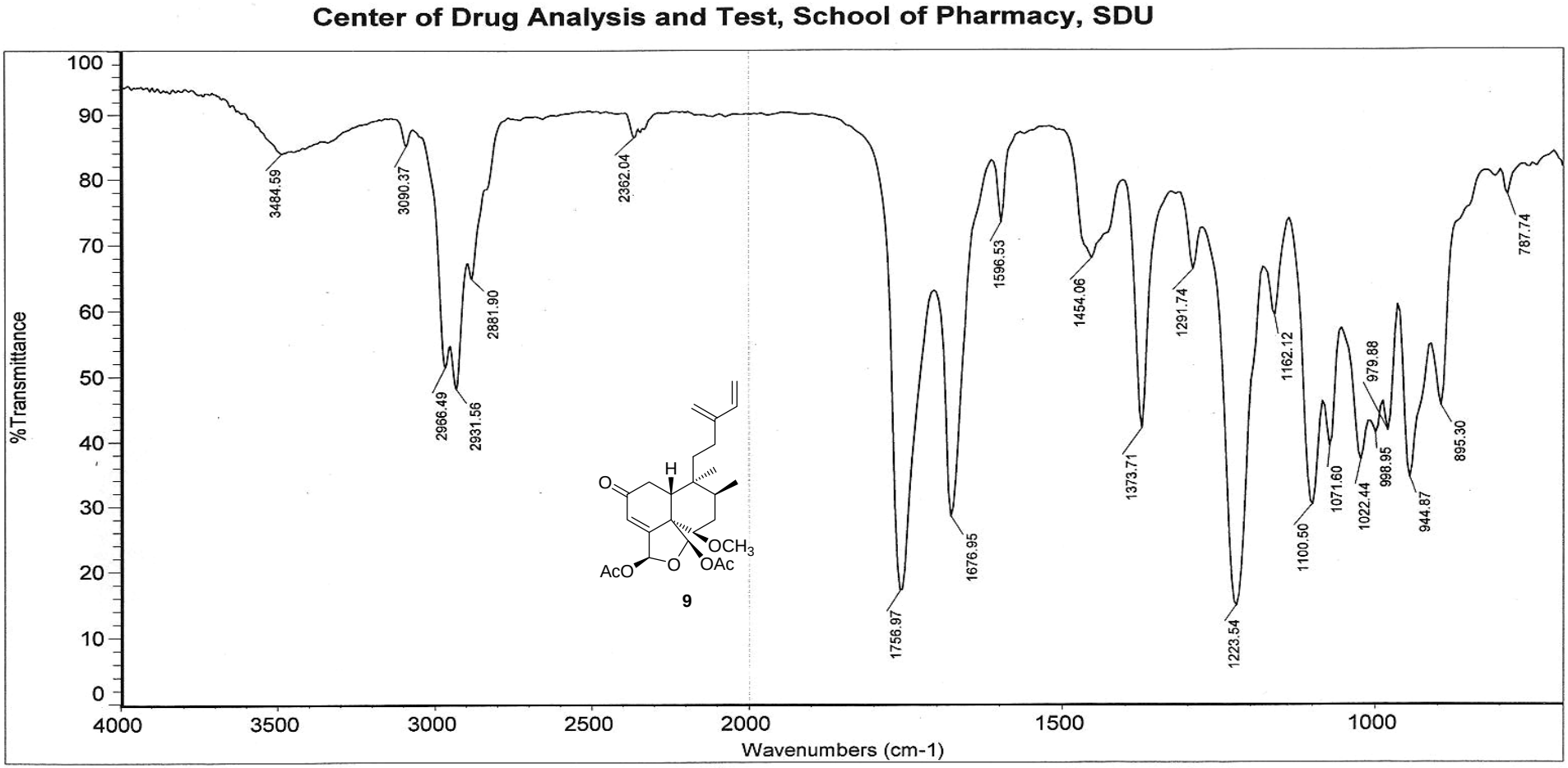


Figure S95. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **10**

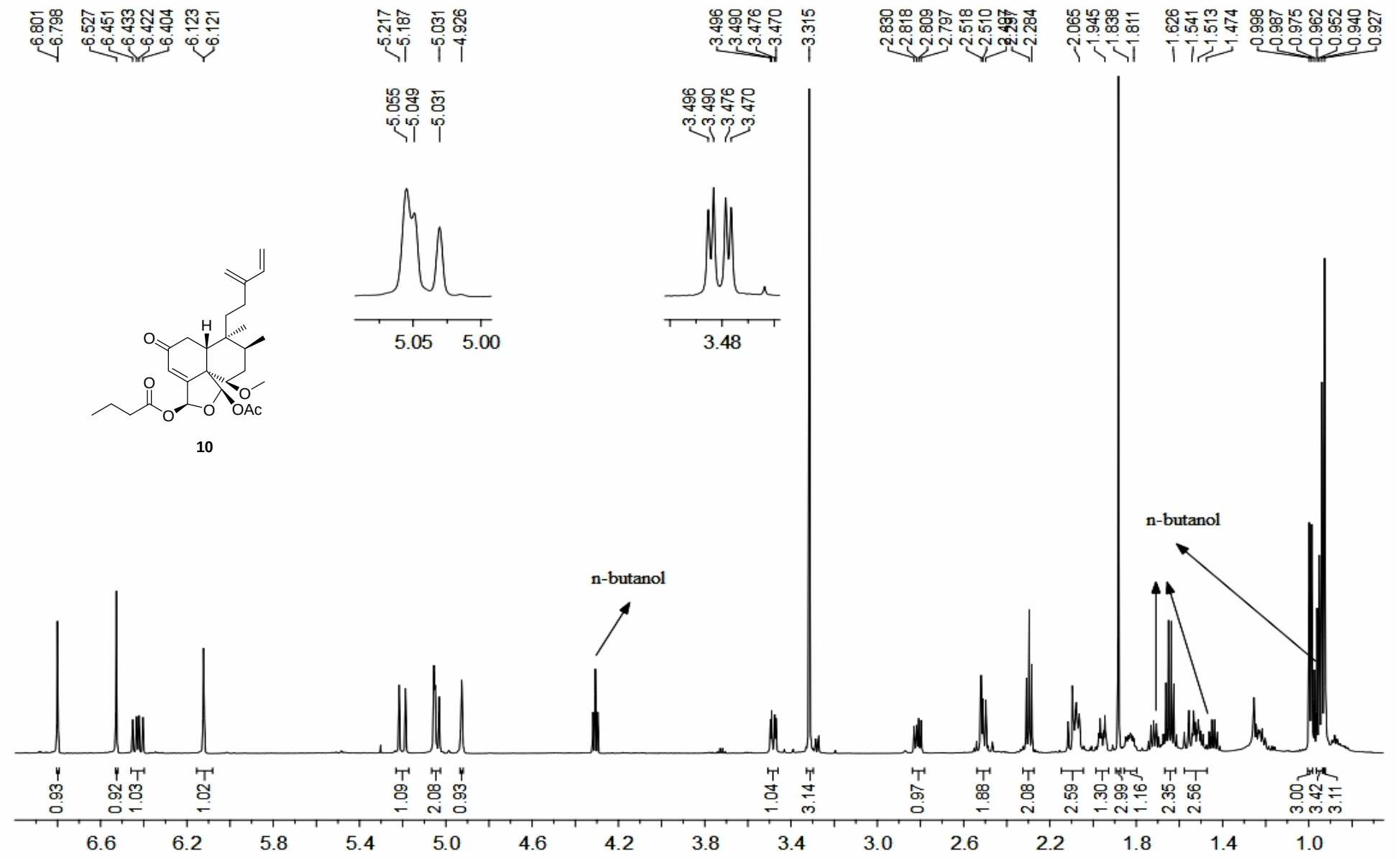


Figure S96. ^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **10** (expansion δ 0.90-2.90)

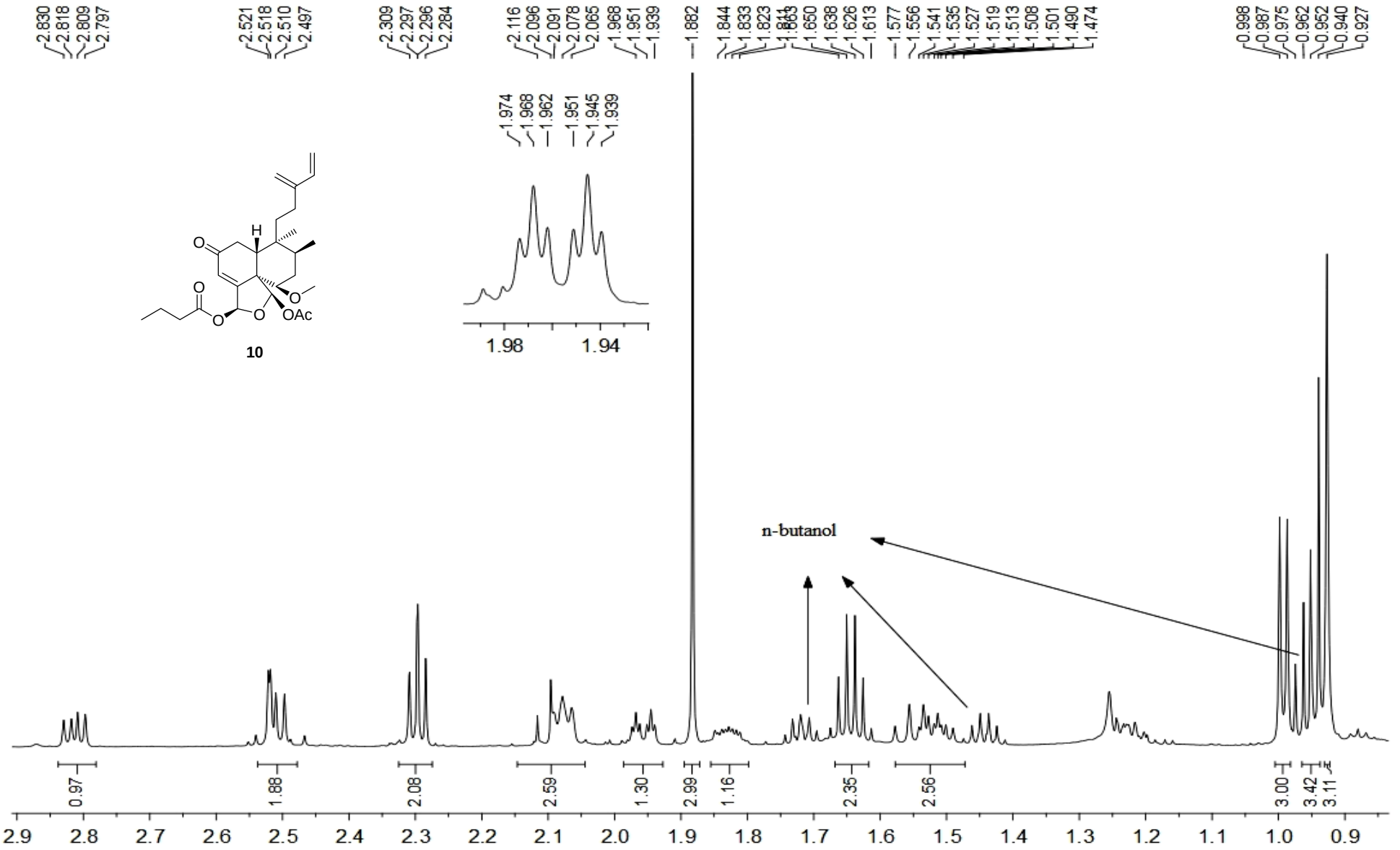


Figure S97. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **10**

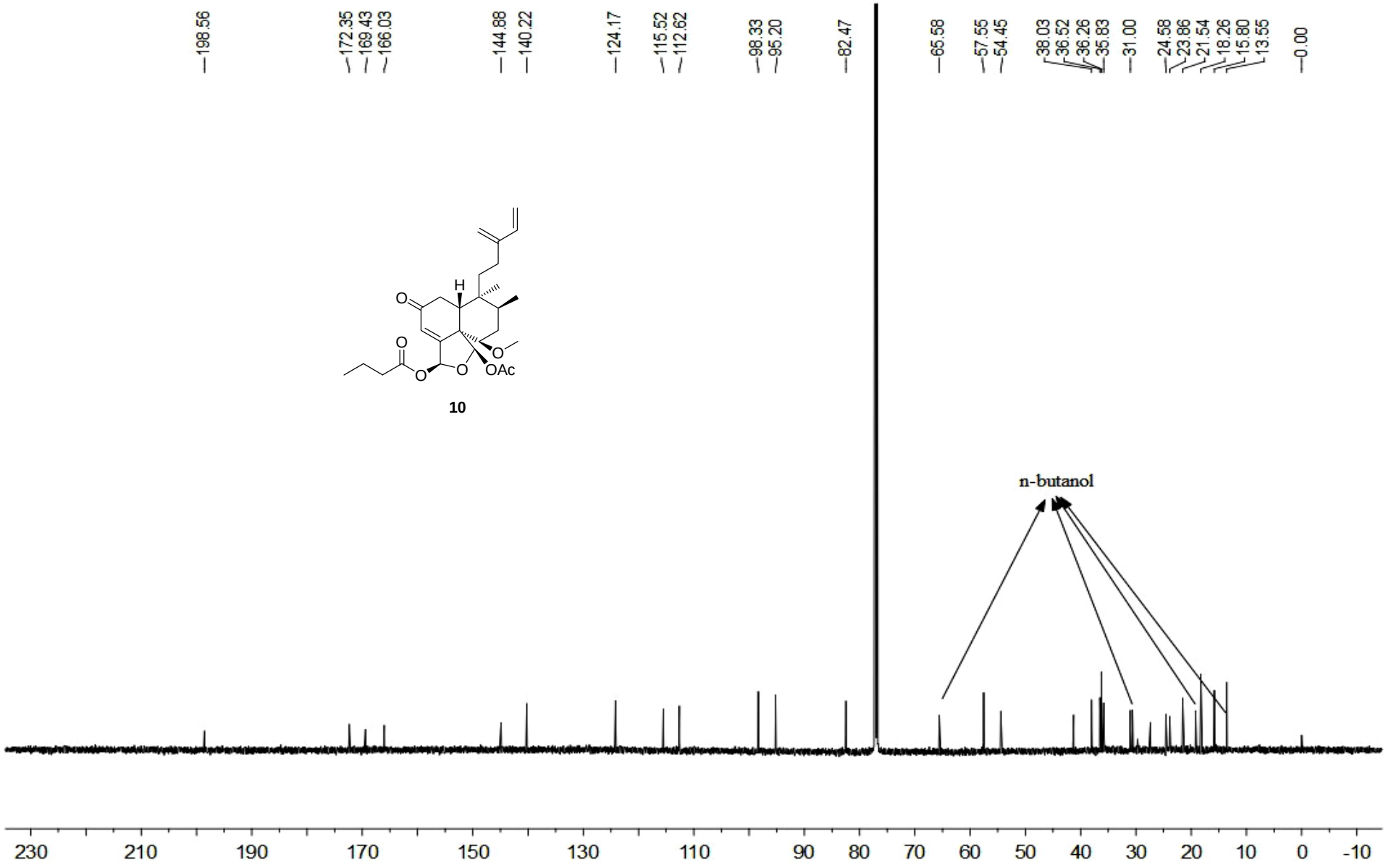


Figure S98. ^{13}C NMR (150 MHz, $CDCl_3$) spectrum of **10** (expansion δ 12.0-66.0)

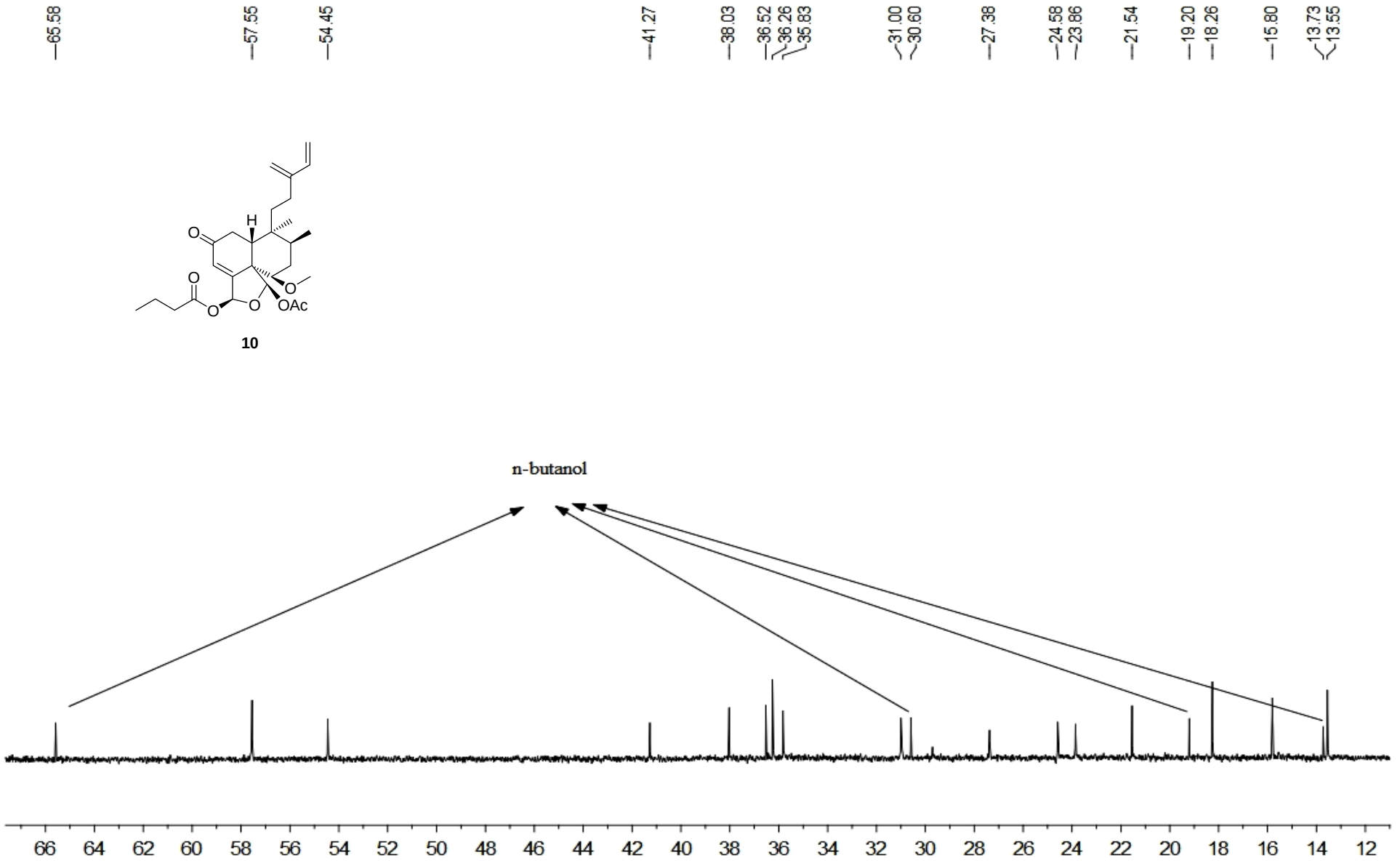
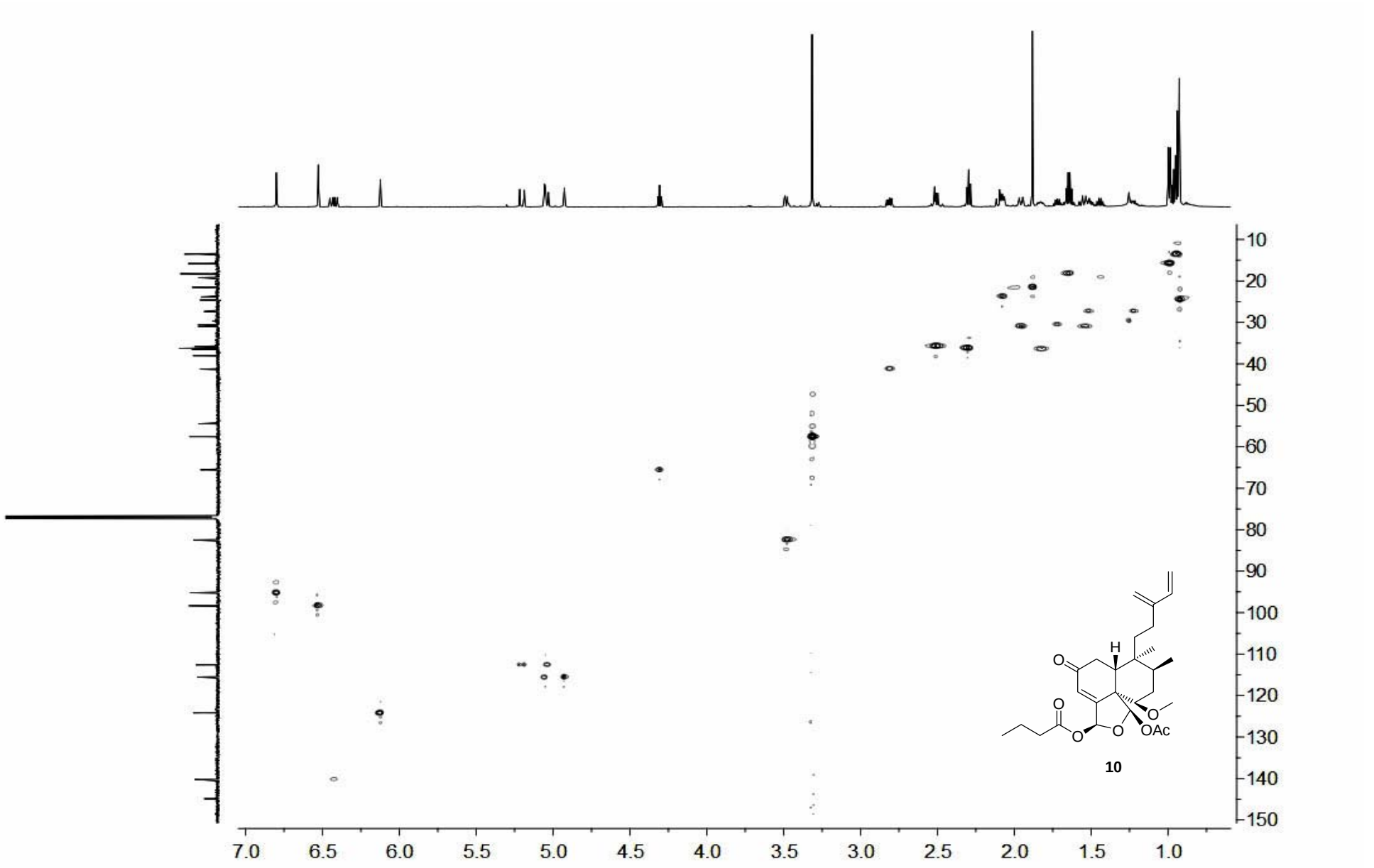


Figure S99. HSQC (600 MHz, $CDCl_3$) spectrum of **10**



10

Figure S100. HMBC (600 MHz, $CDCl_3$) spectrum of **10**

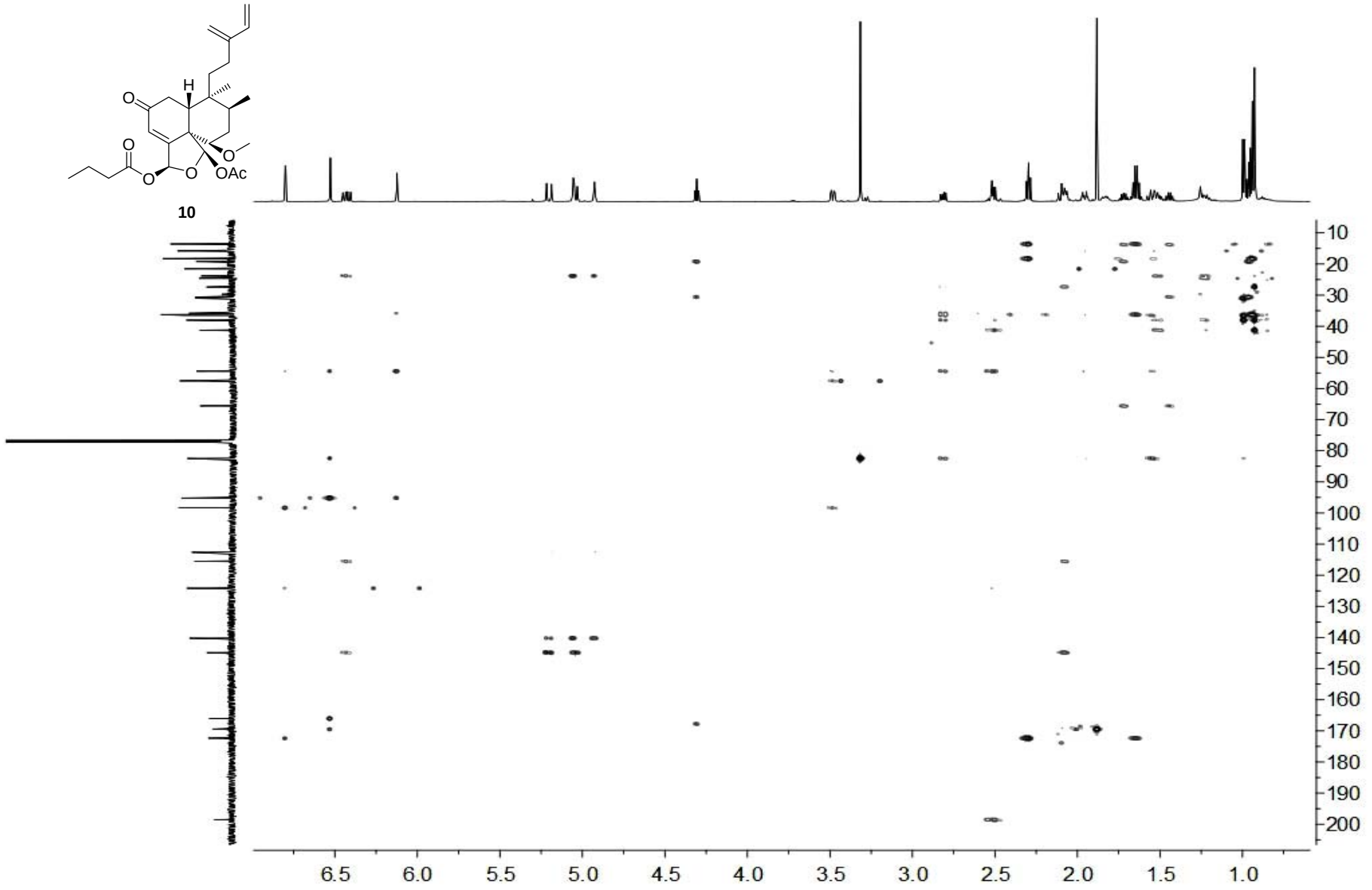


Figure S101. ^{1}H-^{1}H COSY (600 MHz, $CDCl_3$) spectrum of **10**

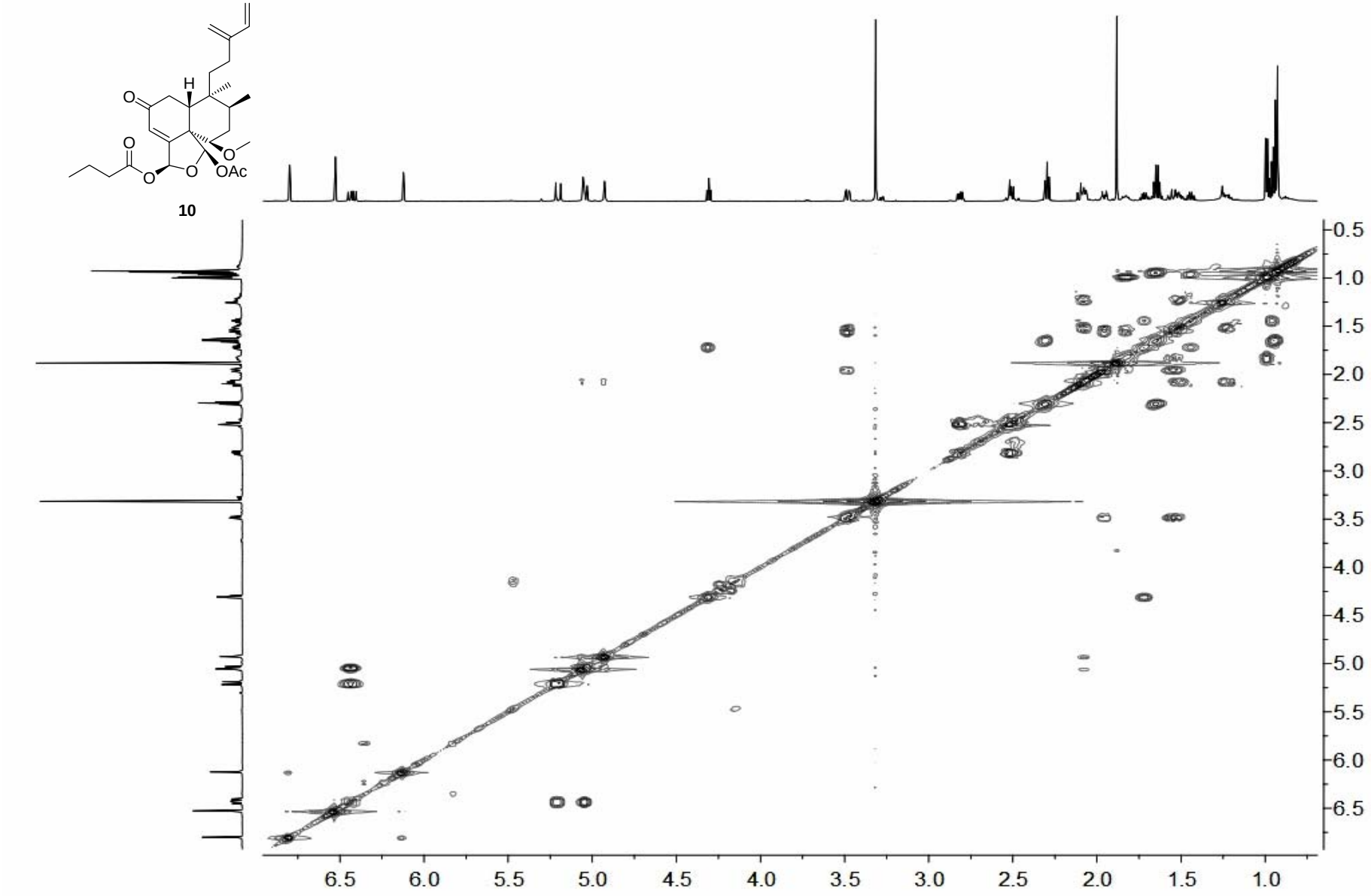


Figure S102. NOESY (600 MHz, $CDCl_3$) spectrum of **10**

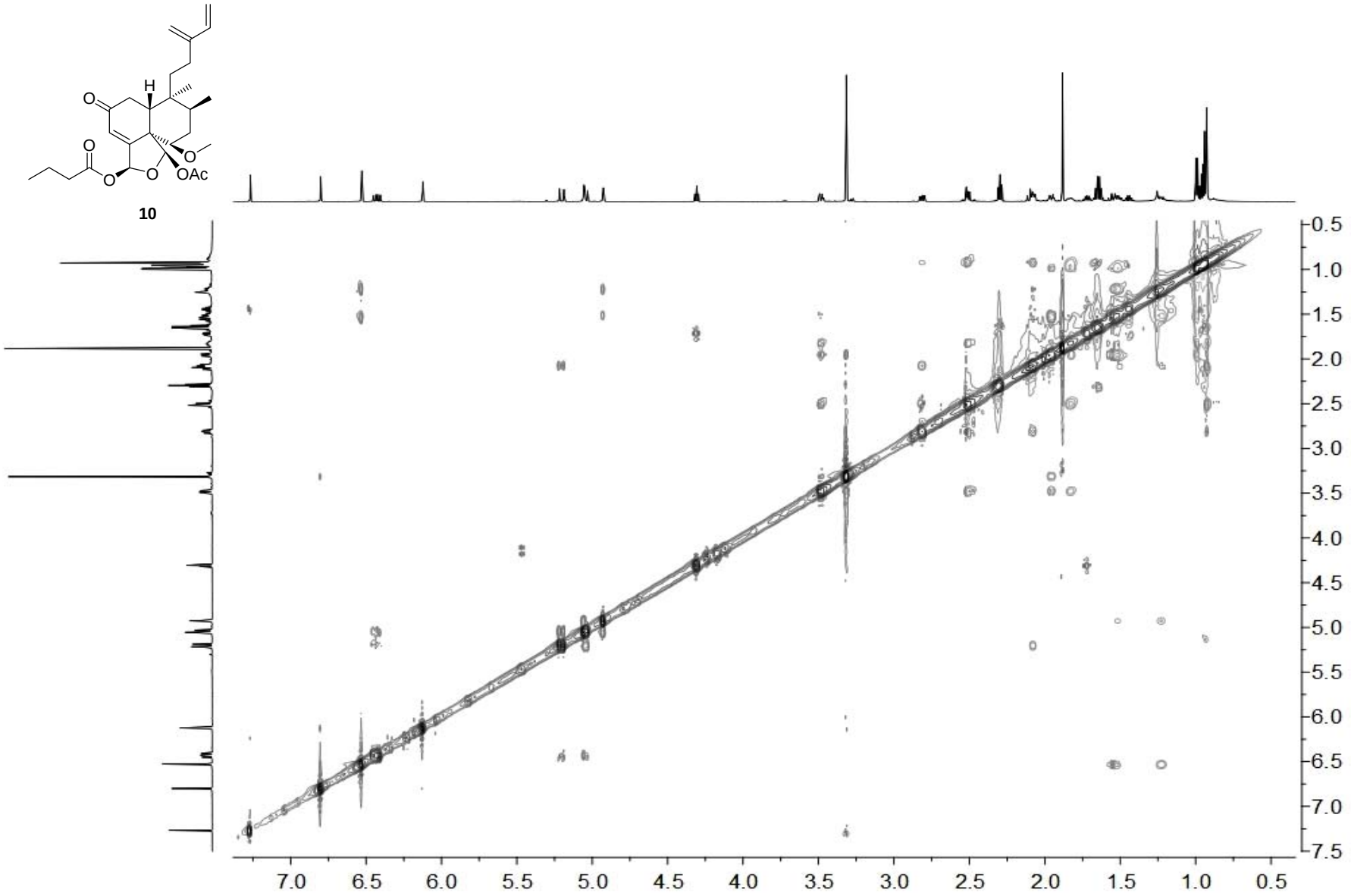


Figure S103. HRESIMS spectrum of **10**

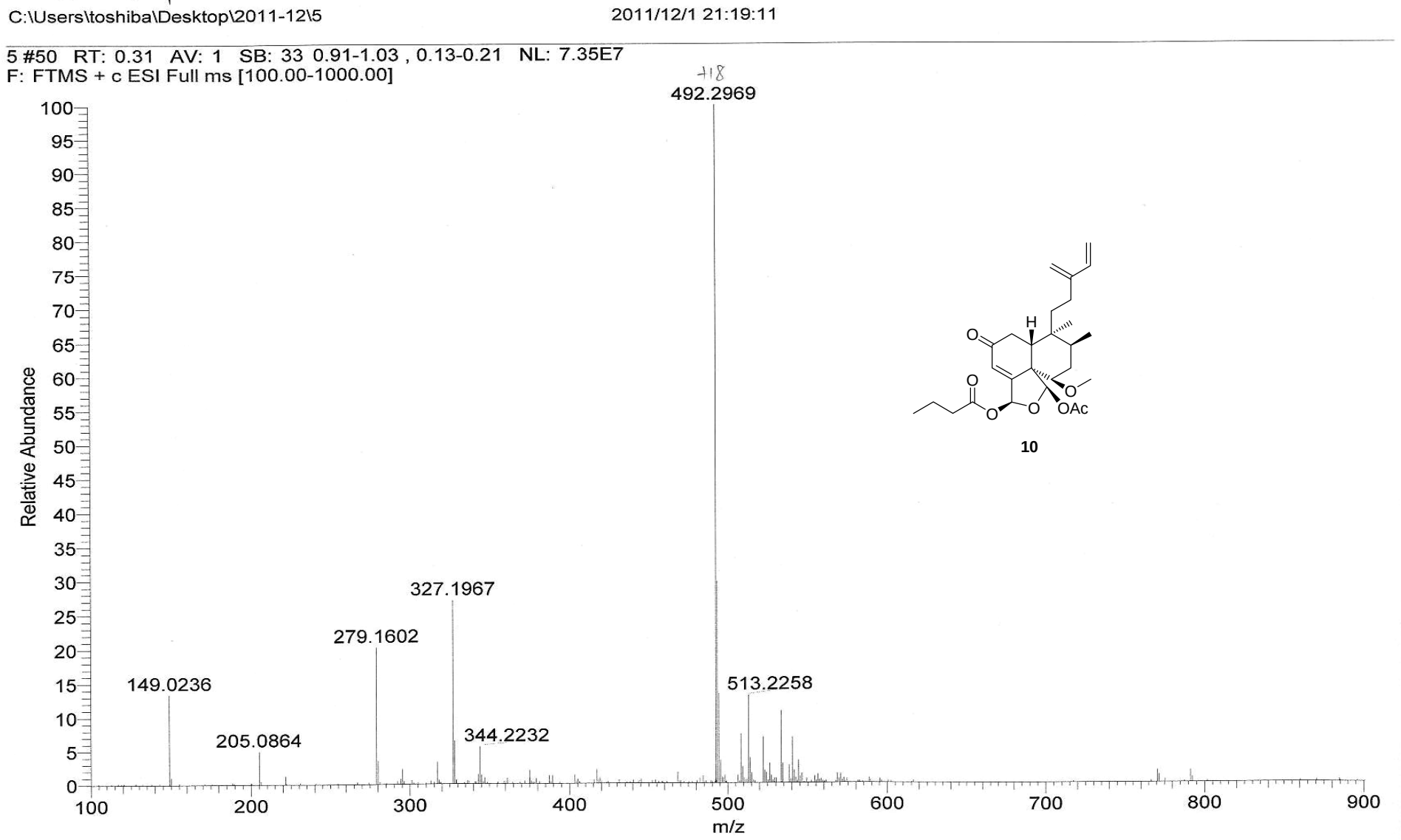


Figure S104. IR spectrum of **10**

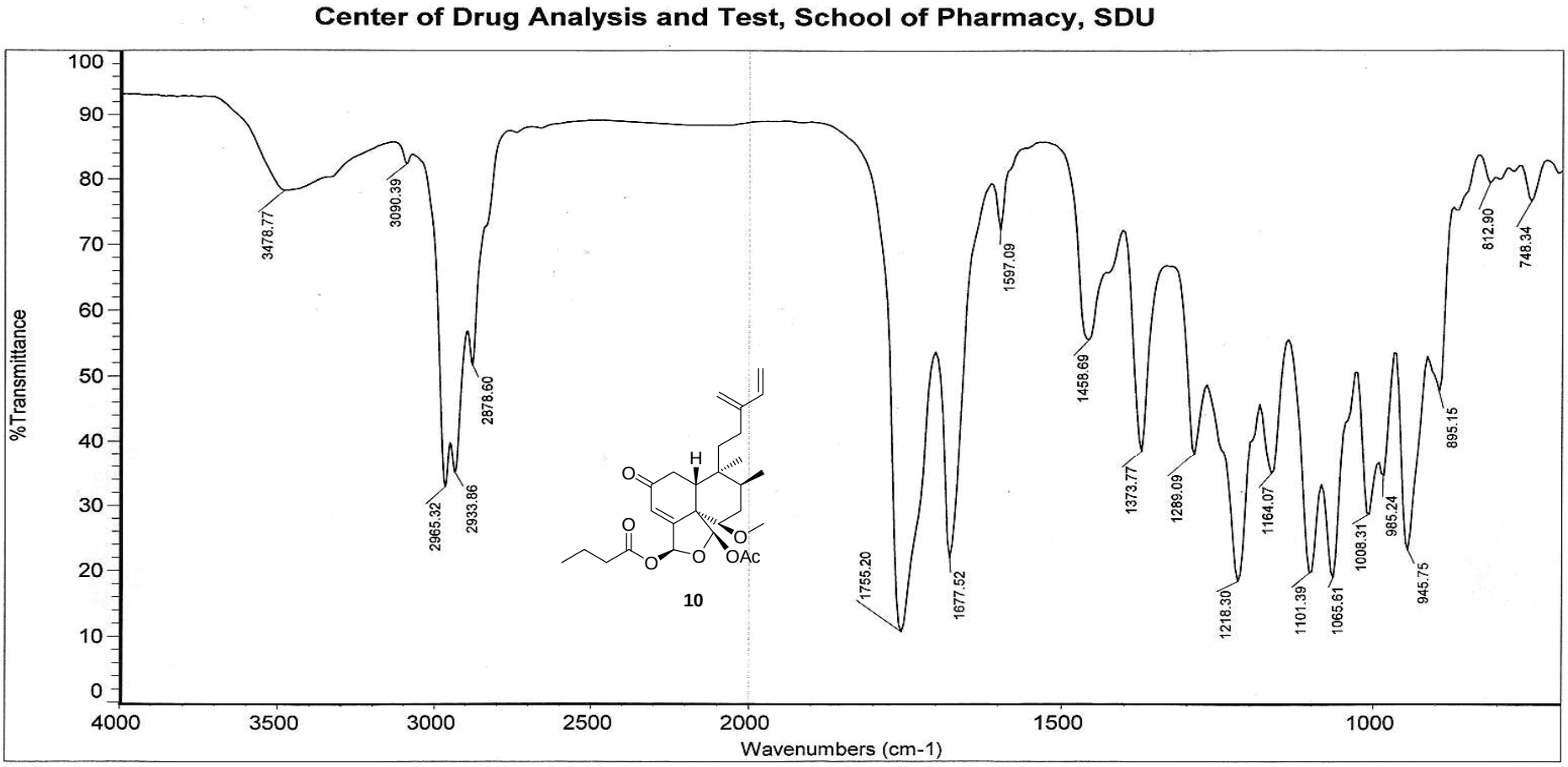


Figure S105. ^{1}H NMR (600 MHz, methanol-d_4) spectrum of **11**

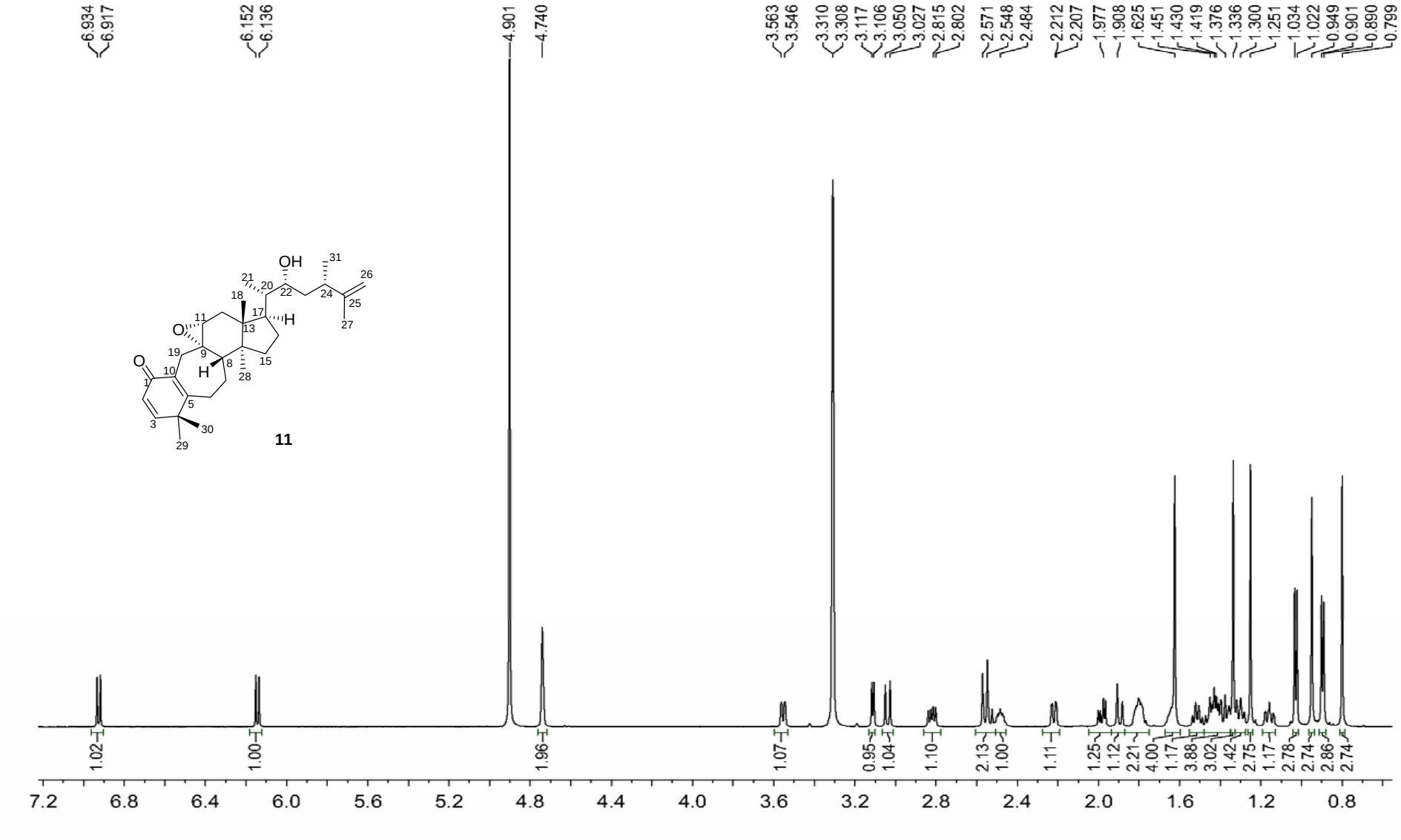
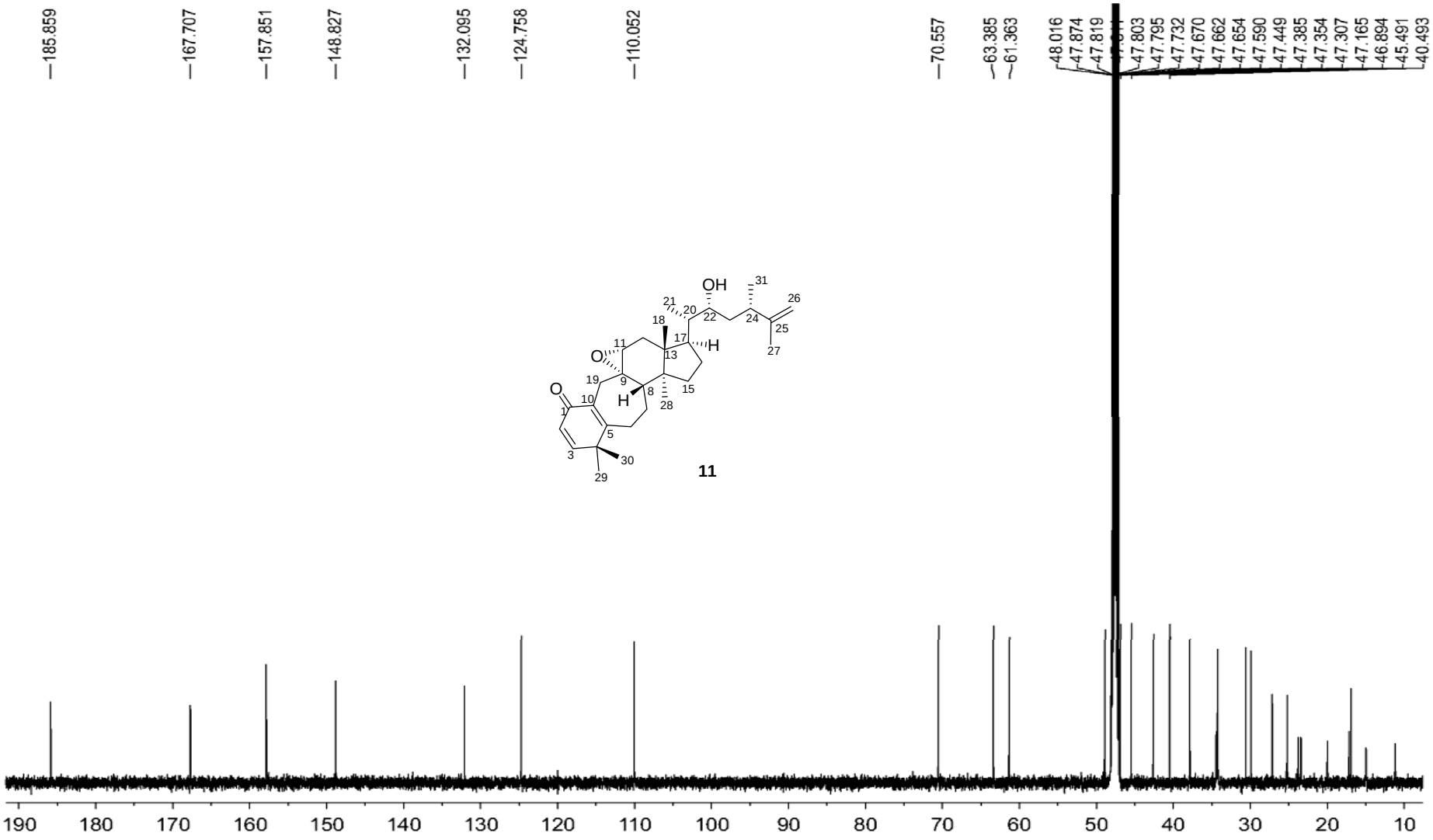


Figure S106. ^{13}C NMR (150 MHz, methanol-d_4) spectrum of **11**



11

Figure S107. HMBC (600 MHz, methanol-d_4) spectrum of **11**

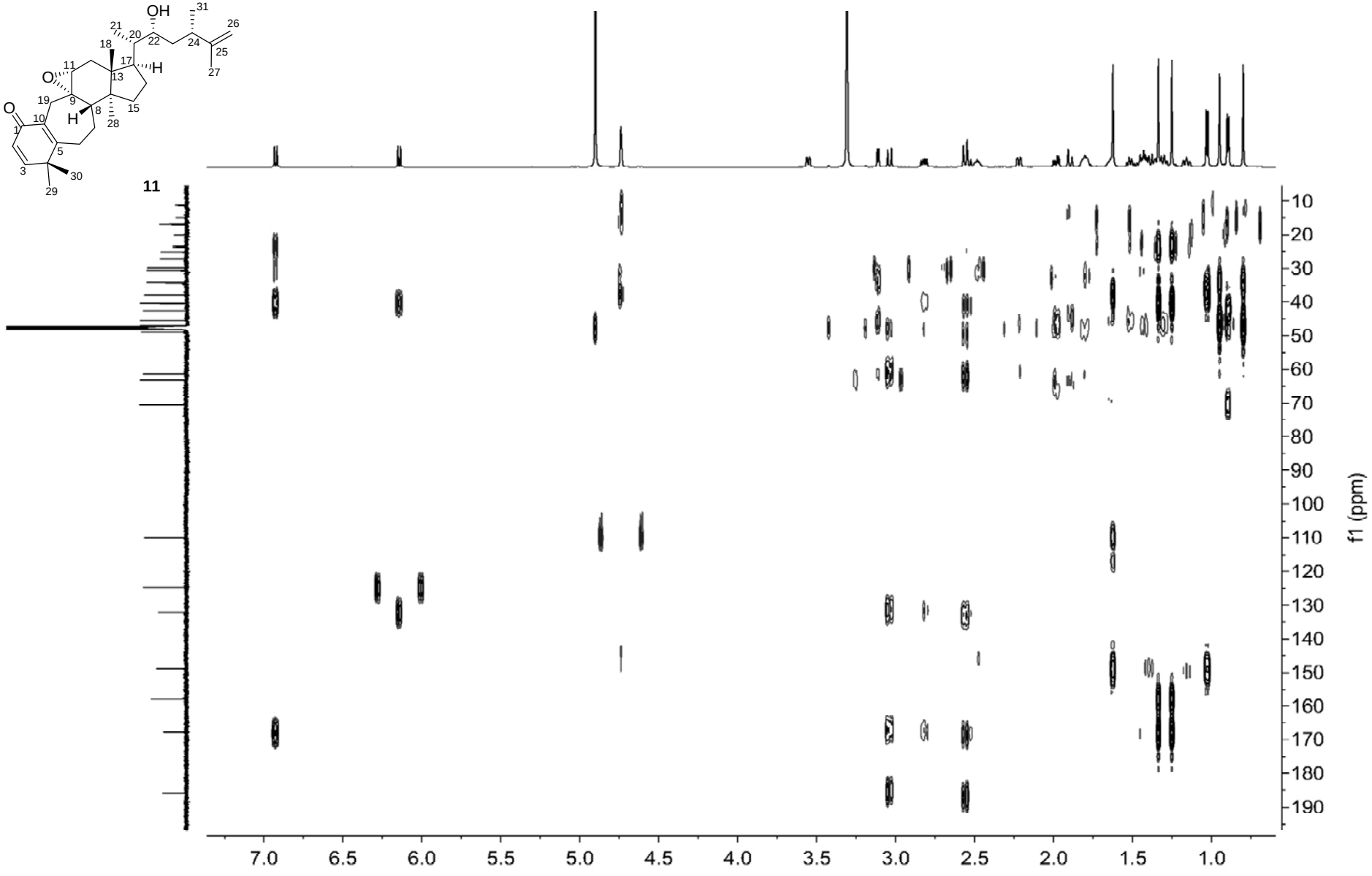


Figure S108. HSQC (600 MHz, methanol-d_4) spectrum of **11**

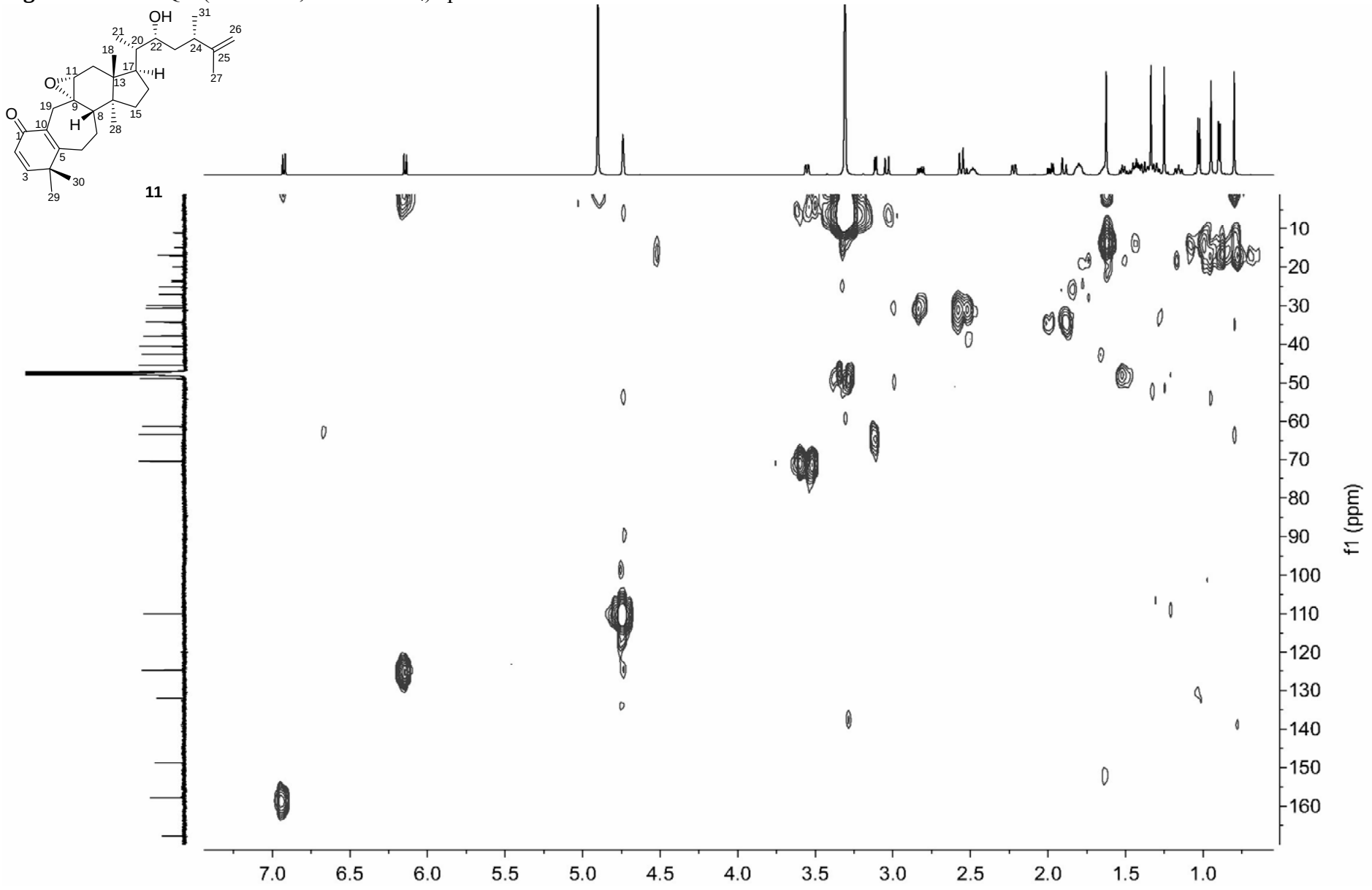


Figure S109. ^{1}H-^{1}H COSY (600 MHz, methanol-d_4) spectrum of **11**

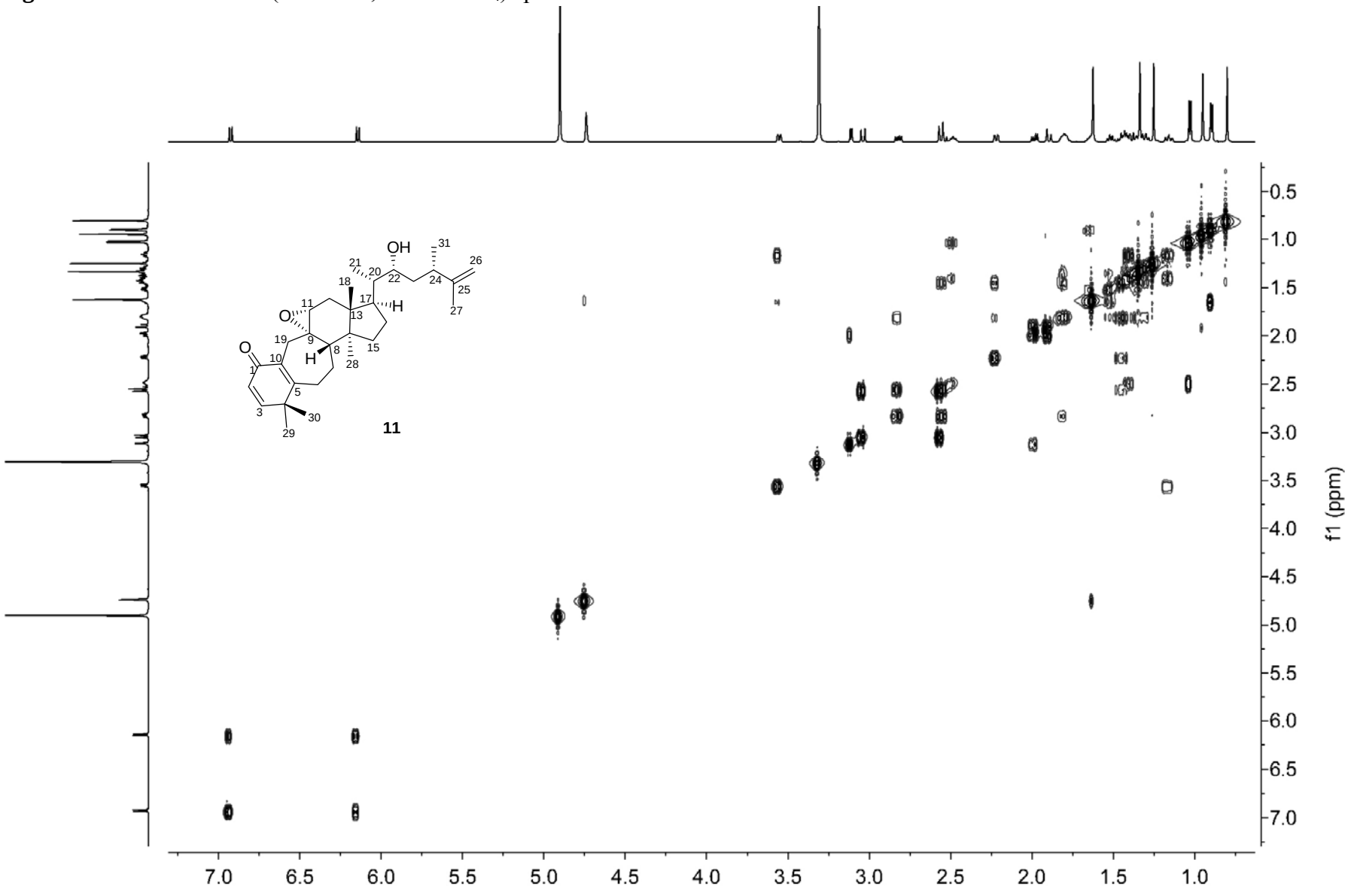


Figure S110. HRESIMS spectrum of **11**

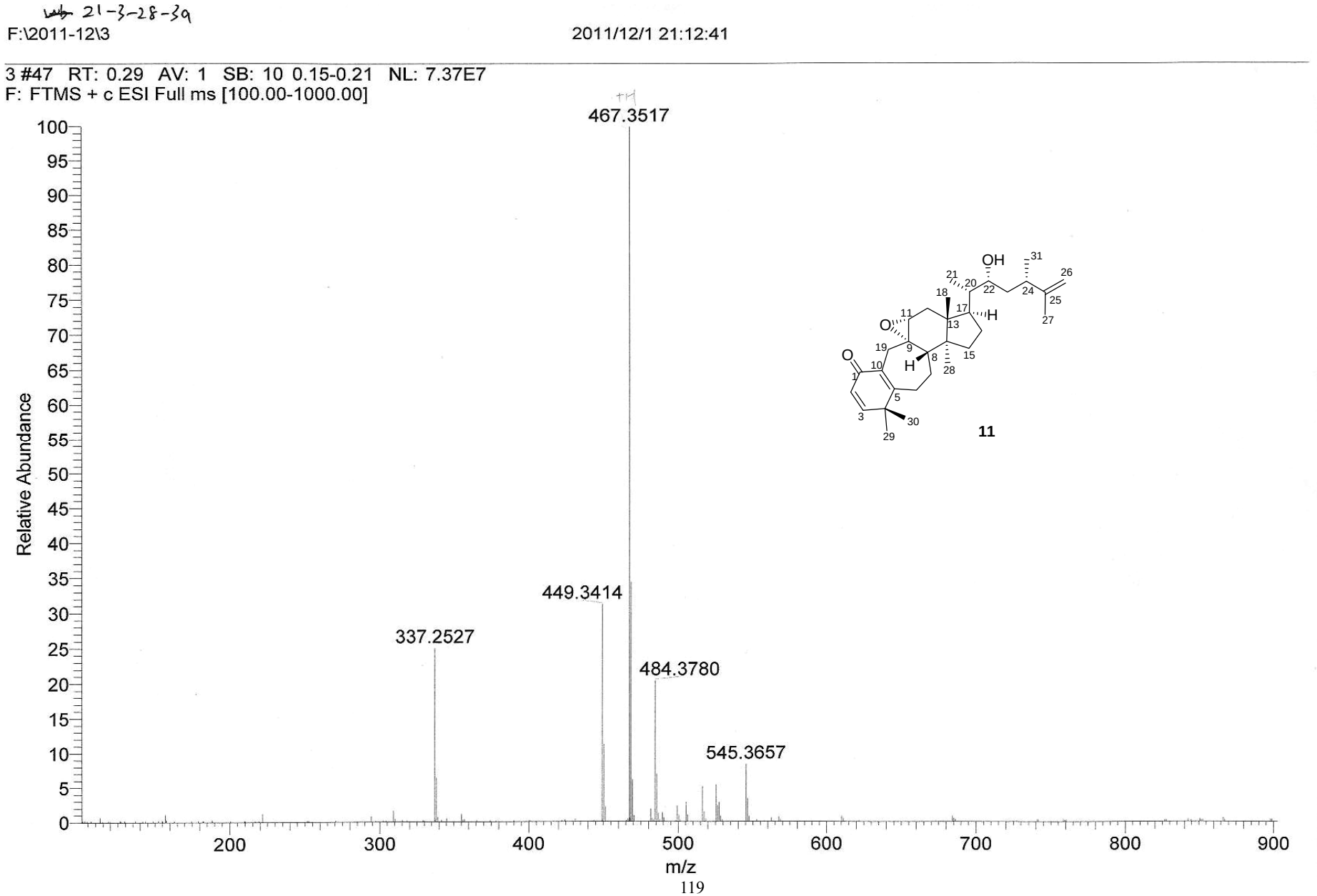
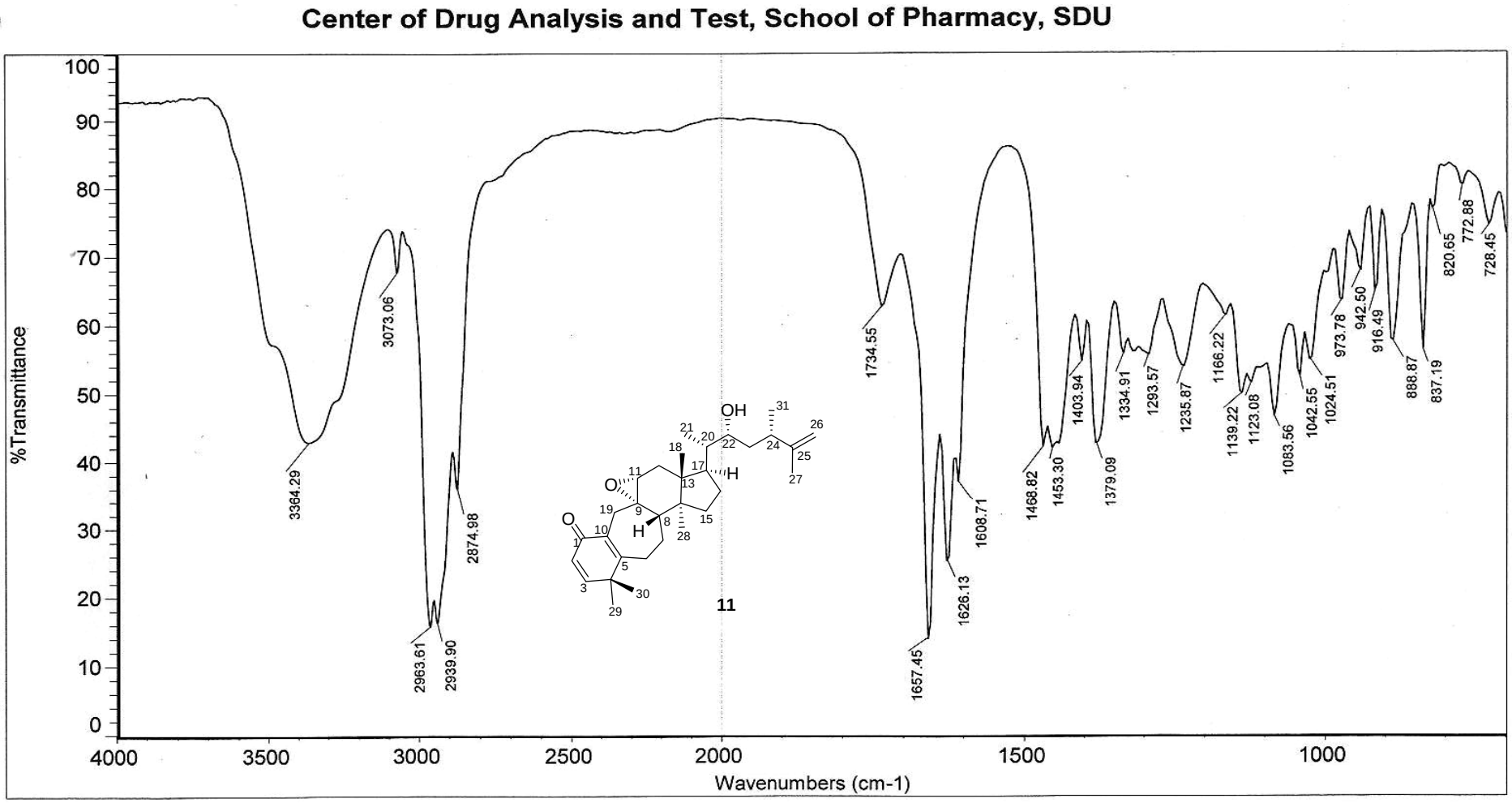


Figure S111. IR spectrum of **11**



Sample name: 2 WB-5-54-2

Spectrum number: M036

Operator: 田 进 国

Instrument model:

Nicolet iN 10 Micro FTIR Spectrometer

Detector: DTGS or MCT-A (cooled)

Bermsplitter: KBr

Resolution: 8

Number of sample scans: 16

Nnmber of background scans: 16

Mode Selection

√1. Transmission

2. Reflectance

3. ATR

Sepectral range:7800-450 or 670cm-1