Supporting information

Lathyrane Diterpenoids as Novel hPXR Agonists: Isolation, Structural Modification, and Structure-Activity Relationships

Dong Huang[†], Rui-Min Wang[†], Wei Li, Ying-Yuan Zhao, Fang-Yu Yuan, Xue-Long Yan, Ye Chen, Gui-Hua Tang, Hui-Chang Bi*, and Sheng Yin*

School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China

*Corresponding author: yinsh2@mail.sysu.edu.cn (S. Yin); bihchang@mail.sysu.edu.cn (H.-C. Bi)

[†]These authors contribute equally.

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1. Experimental section

1.1. General experimental procedures

X-ray data were collected using an Angilent Xcalibur Nova X-ray diffractometer. Melting point was measured on an X-4 melting instrument and uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. UV spectra were recorded on a Shimadzu UV-2450 spectrophotometer. IR spectra were determined on a Bruker Tensor 37 infrared spectrophotometer with KBr disks. NMR spectra were measured on a Bruker AM-400/500 spectrometer at 25 °C. HRESIMS were carried out on a Finnigan LCQ Deca instrument. A Shimadzu LC-20AT equipped with an SPD-M20A PDA detector was used for HPLC, and a YMC-pack ODS-A column (250 × 10 mm, S-5 μm, 12 nm) was used for semipreparative HPLC separation. Silica gel (300–400 mesh, Qingdao Haiyang Chemical Co. Ltd.), reversed-phase C_{18} (Rp-C_{18}) silica gel (12 nm, S-50 μm, YMC Co. Ltd.), Sephadex LH-20 gel (Amersham Biosciences), and MCI gel (CHP20P, 75–150 μm, Mitsubishi Chemical Industries Ltd.) were used for column chromatography (CC). All solvents were of analytical grade (Guangzhou Chemical Reagents Company, Ltd.). The purity of the samples was determined by HPLC, conducted on a Shimadzu LC-20AT series system with Inertsil ODS-SP columns (4.6 mm × 150 mm, 5 μm or 4.6 mm × 100 mm, 5 μm). The samples were eluted with a 90:10 acetonitrile/H_2O mixture at a flow rate of 3 mL/min. The purity of all biologically evaluated compounds is greater than 95%.

1.2. Plant material

Seeds of *E. lathyris* were collected in January 2018 in Anhui Province, P. R. China, and were authenticated by one of the authors (G. H. Tang). A voucher specimen (accession number: QJZ201801) has been deposited at the School of Pharmaceutical Sciences, Sun Yat-sen University.

1.3. Extraction and bioassay-guided isolation

The seeds of *E. lathyris* (8 kg) were extracted with 95% EtOH (75 L × 3) at room temperature to give 817.2 g of crude extract. The extract was suspended in H_2O (3 L) and successively partitioned with petroleum ether, EtOAc, and *n*-BuOH. EtOAc fraction that showed potent agonistic activity on hPXR was selected for further chemical investigation. The EtOAc extract (352.8 g) was subjected to a D101 macroporous adsorptive resins eluted with a MeOH/H_2O gradient (6:4 → 10:0) to afford three fractions (Fr. I–III). Fr. II (215.6 g) was applied to silica gel CC (PE/EtOAc, 50:1 → 1:1) to give four fractions (Fr. IIA–IID). Fr. IIA was recrystallized with MeOH to afford **14** (13.2 g). Fr. IIB (15.7 g) was subjected to silica gel CC (PE/EtOAc, 40:1 → 0:1) to give three fractions (Fr. IIB_1–IIB_3). Fr. IIB_1 (246.2 mg) was separated by silica gel CC (PE/EtOAc, 50:1), followed by semi-preparative HPLC (MeCN/H_2O, 80/20, 3 mL/min) to give **9** (12.6 mg, t_R 10.6 min) and **10** (22.7 mg, t_R 11.3 min). Fr. IIB_2 and Fr. IIB_3 were recrystallized with MeOH to afford **16** (3.2 g) and **15** (7.6 g), respectively. Fr. IIC (2.9 g) was separated by Rp-C_{18} silica gel CC (MeOH/H_2O, 6:4 → 10:0) to give five fractions (Fr. IIC_1–IIC_5). Fr. IIC_1 (132.2

mg) was subjected to silica gel CC (CH_2Cl_2/MeOH, 100:1 → 0:1), followed by semi-preparative chiral HPLC (MeCN/H_2O, 75/25, 3 mL/min) to yield **3** (34 mg, t_R 13.0 min). Fr. IIC_2 (1.435 g) was separated by Sephadex LH-20 (MeOH), followed by silica gel CC (PE/EtOAc, 10:1 → 0:1) to give three fractions (Fr. IIC_{2a}–IIC_{2c}). Fr. IIC_{2a} (207.2 mg) was separated by silica gel CC (PE/EtOAc, 15:1 → 0:1), followed by semi-preparative chiral HPLC (MeCN/H_2O, 70/30, 3 mL/min) to give **8** (67.3 mg, t_R 8.9 min), **6** (29.1 mg, t_R 11.4 min), and **7** (16.8 mg, t_R 14.6 min). Fr. IIC_{2b} (367.8 mg) was subjected to Rp-C_{18} silica gel CC (MeOH/H_2O, 7:3 → 10:0), followed by semi-preparative chiral HPLC (MeCN/H_2O, 70/30, 3 mL/min) to give **4** (31.2 mg, t_R 15.6 min) and **5** (18.0 mg, t_R 14.6 min). Fr. IIC_{2b1} was subjected to silica gel CC (PE/EtOAc, 15:1 → 0:1) and then further purified by Sephadex LH-20 (EtOH) to give **2** (90.8 mg) and **1** (24.6 mg). Fr. IIC_{2c} (179.3 mg) was applied to silica gel CC (PE/EtOAc, 20:1 → 0:1) to give three fractions (Fr. IIC_{2c1}–IIC_{2c3}). Fr. IIC_{2c2} (69.2 mg) was separated on Sephadex LH-20 (MeOH) and followed by semi-preparative chiral HPLC (MeCN/H_2O, 70/30, 3 mL/min) to yield **12** (10.5 mg, t_R 13.8 min) and **11** (16.2 mg, t_R 14.4 min). Fr. IIC_{2c3} (44.6 mg) was subjected to Sephadex LH-20 (MeOH) yield **13** (24.1 mg). ^1H and ^{13}C NMR data of **1**–**5** were summarized in Table S1.1.

*Compound **1***. Colorless oil; $[\alpha]^{25}_D$ +109.1 (*c* 3.0, MeCN); UV (MeCN) λ_{max} (log ε) 273 (3.97), 232 (4.18) nm; IR ν_{max} 3460, 2928, 1722, 1659, 1453, 1370, 1272, 1113, 1004, 714 cm^{-1}; HRESIMS *m/z* 517.2193 $[M + Na]^+$ (calcd for $C_{29}H_{34}O_7Na^+$,

517.2197).

Compound ***2***. Colorless oil; $[\alpha]^{25}_{D}$ –25.0 (*c* 3.0, MeCN); UV (MeCN) λ_{max} (log ε) 274 (4.15), 232 (4.17) nm; IR ν_{max} 3446, 2926, 1717, 1606, 1452, 1268, 1108, 1057, 714 cm^{-1}; HRESIMS *m/z* 439.2487 $[M + H]^+$ (calcd for $C_{27}H_{35}O_5^+$, 439.2479).

Compound ***3***. Colorless oil; $[\alpha]^{25}_{D}$ +55.3 (*c* 3.0, MeCN); UV (MeCN) λ_{max} (log ε) 233 (4.53), 272 (4.31) nm; IR ν_{max} 2931, 1722, 1629, 1453, 1369, 1275, 1236, 1112, 1024, 943, 712 cm^{-1}; HRESIMS *m/z* 559.2306 $[M + Na]^+$ (calcd for $C_{31}H_{36}O_8Na^+$, 559.2302).

Compound ***4***. Colorless oil; $[\alpha]^{25}_{D}$ +202.7 (*c* 3.0, MeCN); UV (MeCN) λ_{max} (log ε) 275 (4.38) nm; IR ν_{max} 2926, 1738, 1630, 1450, 1369, 1273, 1228, 1114, 906, 769 cm^{-1}; HRESIMS *m/z* 571.2659 $[M + Na]^+$ (calcd for $C_{33}H_{40}O_7Na^+$, 571.2666).

Compound ***5***. Colorless oil; $[\alpha]^{25}_{D}$ –46.7 (*c* 3.0, MeCN); UV (MeCN) λ_{max} (log ε) 275 (4.26) nm; IR ν_{max} 3478, 2929, 1739, 1623, 1455, 1375, 1245, 1154, 1021 cm^{-1}; HRESIMS *m/z* 499.2295 $[M + Na]^+$ (calcd for $C_{26}H_{36}O_8Na^+$, 499.2302).

1.4. Preparation of **17** and **27** by alkaline hydrolysis of **15** and **14**, respectively

To a solution of **15** (30 mg, 0.047 mmol) or **14** (30 mg, 0.057 mmol) in 2 mL of MeOH was added 1% NaOH at rt for 1 h. The mixture was then diluted with 5 mL of H_2O, followed by the extraction of EtOAc (5 mL × 3). The organic layer was dried, evaporated and purified by silica gel CC (PE/EtOAc, 10:1) to afford **17** (15.3 mg) and **27** (17.2 mg).

3,5,7,15-Tetrahydroxy-14-oxolathyra-6(17),12*E*-diene (**17**). The spectroscopic

data was identical to that reported.[1]

3,5,15-Trihydroxy-14-oxolathyra-6(17),12*E*-diene (**27**). The spectroscopic data was identical to that reported.[1]

1.5. Preparation of **18**–**22** by acylation of **17**

To a solution of **17** (20 mg, 0.057 mmol) in freshly distilled pyridine (2 mL) was added excess acyl chlorides. The reaction mixture was stirred at rt or 0 °C for 2 h and then quenched by adding 2 mL of H_2O. After removal of the solvent under vacuum, the residue was purified by semi-preparative HPLC (MeCN/H_2O = 75:25, 3 mL/min). The acyl chlorides used in this experiment were acetic anhydride, 2-furoyl chloride, thiophene-2-carbonyl chloride and benzoyl chloride to give the acylation products compounds **19** (11.3 mg, t_R 14.5 min), **18** (10.6 mg, t_R 9.4 min), **20** (11.8 mg, t_R 10.2 min), **21** (9.6 mg, t_R 12.7 min), and **22** (12.41 mg, t_R 13.2 min), respectively.

7-Acetoxy-3,5,15-trihydroxy-14-oxolathyra-6(17),12*E*-diene (**18**). The spectroscopic data was identical to that reported.[2]

3,5,7-Triacetoxy-15-hydroxy-14-oxolathyra-6(17),12*E*-diene (**19**). The spectroscopic data was identical to that reported.[3]

7-(2-Furoyl)-3,5,15-trihydroxy-14-oxolathyra-6(17),12*E*-diene (**20**). Colorless oil; $[\alpha]^{25}_D$ −53.3 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 253 (3.94) nm; IR (KBr) ν_{max} 3419, 2925, 1718, 1672, 1614, 1471, 1393, 1298, 1178, 1115, 1073, 1010, 925, 763 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.81 (1H, d, *J* = 9.3 Hz, H-12), 5.32 (1H, s, H-17a), 5.18 (1H, s, H-17b), 5.00 (1H, d, *J* = 8.2 Hz, H-7), 4.39 (1H, brs, H-3), 4.23

(1H, brs, H-5), 2.74 (1H, dd, J = 14.7, 10.2 Hz, H-1a), 2.51 (1H, brs, H-4), 2.30 (1H, m, H-2), 2.05 (3H, s, H-20), 2.04 (1H, m, H-8a), 1.76 (1H, dd, J = 14.7, 9.8 Hz, H-1b), 1.39 (1H, d, J = 9.3 Hz, H-11), 1.27 (1H, m, H-8b), 1.25 (1H, m, H-9), 1.16 (3H, d, J = 6.3 Hz, H-16), 1.15 (3H, s, H-19), 1.12 (3H, s, H-18), for 7-*O*-2-furoyl: 7.62 (1H, m), 7.28 (1H, m), 6.56 (1H, m); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 207.9 (C-14), 148.1 (C-6), 139.4 (C-13), 137.0 (C-12), 108.5 (C-17), 87.9 (C-15), 76.3 (C-3), 75.3 (C-7), 69.5 (C-5), 52.3 (C-4), 45.9 (C-1), 38.1 (C-2), 31.0 (C-9), 30.6 (C-8), 28.3 (C-18), 25.5 (C-11), 23.5 (C-10), 15.3 (C-19), 14.0 (C-16 and C-20), for 7-*O*-2-furoyl: 158.4, 146.7, 144.3, 118.3, 112.0; HRESIMS m/z 467.2048 $[M + Na]^+$ (calcd for $C_{25}H_{32}O_7Na^+$, 467.2040).

3,5,15-Trihydroxy-7-(thiophene-2-carbonyl)-14-oxolathyra-6(17),12*E*-diene (**21**). Colorless oil; $[\alpha]^{25}_D$ –49.3 (c 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 265 (4.20), 253 (4.30) nm; IR (KBr) ν_{max} 3422, 2925, 1707, 1679, 1613, 1525, 1417, 1362, 1260, 1149, 1090, 1073, 1005, 918, 751, 722, 578 cm^{-1}; ^{1}H NMR (CD_3OD, 400 MHz) δ_H 6.53 (1H, d, J = 10.6 Hz, H-12), 5.22 (1H, s, H-17a; 1H, m, H-7), 5.17 (1H, s, H-17b), 4.62 (1H, d, J = 3.0 Hz, H-5), 4.29 (1H, dd, J = 3.7, 3.7 Hz, H-3), 2.77 (1H, dd, J = 13.5, 8.3 Hz, H-1a), 2.44 (1H, dd, J = 3.0, 3.7 Hz, H-4), 2.10 (1H, ddd, J = 15.4, 6.9, 4.1 Hz, H-8a), 1.99 (1H, m, H-2), 1.92 (3H, d, J = 1.0 Hz, H-20), 1.71 (1H, dd, J = 13.5, 11.0 Hz, H-1b), 1.68 (1H, m, H-8b), 1.55 (1H, dd, J = 10.6, 8.8 Hz, H-11), 1.35 (1H, m, H-9), 1.20 (3H, s, H-19), 1.18 (3H, s, H-18), 1.09 (3H, d, J = 6.8 Hz, H-16), for 7-*O*-2-thiophene-2-carbonyl: 7.88 (1H, dd, J = 3.8, 1.2 Hz), 7.79 (1H, dd, J = 5.0, 1.2 Hz), 7.19 (1H, dd, J = 5.0, 3.8 Hz); ^{13}C NMR (CD_3OD, 100 MHz) δ_C 207.0

(C-14), 151.0 (C-6), 141.6 (C-12), 138.9 (C-13), 110.0 (C-17), 88.5 (C-15), 78.3 (C-3), 78.0 (C-7), 69.1 (C-5), 53.6 (C-4), 47.2 (C-1), 39.2 (C-2), 32.4 (C-9), 31.2 (C-8), 28.8 (C-18), 27.8 (C-11), 25.3 (C-10), 15.9 (C-19), 14.0 (C-16), 13.7 (C-20), for 7-*O*-thiophene-2-carbonyl: 163.3, 134.8 × 2, 134.3, 129.1; HRESIMS *m*/*z* 483.1817 $[M + Na]^+$ (calcd for $C_{25}H_{32}O_6SNa^+$, 483.1812).

5,7-Dibenzoyloxy-3,15-dihydroxy-14-oxolathyra-6(17),12*E*-diene (**22**). Colorless oil; $[\alpha]^{25}_D$ +63.00 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 272 (4.08), 232 (4.41) nm; IR (KBr) ν_{max} 3443, 2926, 1719, 1619, 1452, 1271, 1109, 1069, 1026, 995, 709 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 6.94 (1H, d, *J* = 8.5 Hz, H-12), 5.96 (1H, d, *J* = 7.1 Hz, H-5), 5.41 (1H, t, *J* = 5.4 Hz, H-7), 5.37 (1H, s, H-17a), 5.26 (1H, s, H-17b), 4.13 (1H, dd, *J* = 2.9, 2.9 Hz, H-3), 2.99 (1H, dd, *J* = 14.5, 10.1 Hz, H-1a), 2.69 (1H, dd, *J* = 7.1, 2.9 Hz, H-4), 2.23 (1H, m, H-2), 2.15 (1H, m, H-8a), 2.03 (1H, m, H-8b), 1.93 (3H, s, H-20), 1.72 (1H, dd, *J* = 14.5, 10.0 Hz, H-1b), 1.52 (1H, dd, *J* = 10.9, 8.5 Hz, H-11), 1.37 (1H, m, H-9), 1.26 (3H, s, H-19), 1.17 (3H, s, H-18), 1.14 (3H, d, *J* = 6.8 Hz, H-16), for 5-*O*Bz: 7.82 (2H, m), 7.22 (2H, t, *J* = 7.5 Hz), 7.40 (1H, t, *J* = 7.5 Hz), 7-*O*Bz: 7.78 (2H, m), 7.18 (2H, t, *J* = 7.5 Hz), 7.37 (1H, t, *J* = 7.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 203.7 (C-14), 145.4 (C-12), 143.0 (C-6), 137.3 (C-13), 116.0 (C-17), 88.6 (C-15), 77.3 (C-3), 77.0 (C-7), 69.3 (C-5), 54.6 (C-4), 48.7 (C-1), 37.8 (C-2), 31.9 (C-9), 30.0 (C-8), 28.4 (C-18), 27.1 (C-11), 24.5 (C-10), 15.9 (C-19), 14.4 (C-16), 13.3 (C-20), for 5-*O*Bz: 166.6, 133.1, 129.7 × 2, 129.5, 128.2 × 2; for 7-*O*Bz: 165.7, 132.8, 129.4 × 2, 129.2, 128.0 × 2; HRESIMS *m*/*z* 581.2517 $[M + Na]^+$ (calcd for $C_{34}H_{38}O_7Na^+$, 581.2510).

1.6. Preparation of **23** and **31** by reduction of **15** and **14**, respectively

To a solution of **15** (30.0 mg, 0.047 mmol) or **14** (30.0 mg, 0.057 mmol) in MeOH (2 mL) was added $NaBH_4$ (3.5 mg, 0.093 mmol). The reaction mixture was stirred at rt for 15 min and then quenched by adding excess glacial acetic acid. After removal of the solvent under vacuum, the residue was purified by semi-preparative HPLC (MeCN/H_2O = 85:15, 3 mL/min) to afford compounds **23** (13.0 mg, t_R 15.5 min) and **31** (9.0 mg, t_R 13.8 min).

5,14-Diacetoxy-3,7-dibenzoyloxy-15-hydroxylathyra-6(17),12*E*-diene (**23**). Colorless oil; $[\alpha]^{25}_D$ +60.00 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.32) nm; IR (KBr) ν_{max} 3489, 2925, 1718, 1452, 1373, 1276, 1241, 1110, 1026, 916, 713 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.84 (1H, dd, *J* = 3.2, 3.2 Hz, H-3), 5.80 (1H, brs, H-5), 5.65 (1H, d, *J* = 10.0 Hz, H-12), 5.47 (1H, s, H-14), 5.14 (1H, d, *J* = 8.2 Hz, H-7), 5.10 (1H, s, H-17a), 4.92 (1H, s, H-17b), 2.54 (1H, dd, *J* = 14.3, 9.8 Hz, H-1a), 2.46 (1H, d, *J* = 3.2 Hz, H-4), 2.41 (1H, m, H-2), 2.05 (1H, m, H-8α), 1.98 (1H, dd, *J* = 14.3, 9.2 Hz, H-1b), 1.93 (3H, s, H-20), 1.62 (1H, m, H-8β), 1.37 (1H, t, *J* = 10.0 Hz, H-11), 1.18 (1H, m, H-9; 3H, s, H-19), 1.09 (3H, s, H-18), 1.05 (3H, d, *J* = 6.7 Hz, H-16), for 3-*O*Bz: δ_H 8.10 (2H, m), 7.47 (2H, m), 7.59 (1H, m); 5-*O*Ac: δ_H 1.46 (3H, s); 7-*O*Bz: δ_H 8.10 (2H, m), 7.44 (2H, m), 7.55 (1H, m); 14-*O*Ac: δ_H 2.14 (3H, s); 15-*O*H: δ_H 3.16 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 146.1 (C-6), 132.1 (C-13), 123.8 (C-12), 107.3 (C-17), 82.1 (C-15), 78.8 (C-14), 76.8 (C-3), 75.1 (C-7), 69.8 (C-5), 49.8 (C-4), 48.0 (C-1), 36.1 (C-2), 30.2 (C-8), 29.9 (C-9), 28.6 (C-18), 24.9

(C-11), 22.3 (C-10), 16.6 (C-20), 15.1 (C-19), 14.7 (C-16), for 3-OBz: 165.3, 133.1, 130.0, 129.7 × 2, 128.5 × 2; 5-*O*Ac: δ_C 170.1, 20.5; 7-*O*Bz: δ_C 166.1, 132.9, 130.8, 129.6 × 2, 128.4 × 2; 14-*O*Ac: δ_C 169.8, 20.9; HRESIMS *m*/*z* 667.2888 $[M + Na]^+$ (calcd for $C_{38}H_{44}O_9Na^+$, 667.2878).

5-Acetoxy-3-benzoyloxy-12,15-epoxylathyra-6(17),13*Z*-diene (**31**). Colorless crystals; mp 131.4–132.8 °C; $[\alpha]^{25}_D$ +81.33 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.29) nm; IR (KBr) ν_{max} 2925, 1724, 1452, 1371, 1272, 1236, 1112, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.58 (1H, dd, *J* = 4.2, 4.2 Hz, H-3), 5.53 (1H, d, *J* = 11.5 Hz, H-5), 5.41 (1H, brs, H-14), 4.93 (1H, brs, H-12), 4.93 (1H, s, H-17a), 4.89 (1H, s, H-17b), 2.84 (1H, dd, *J* = 11.5, 4.2 Hz, H-4), 2.54 (1H, dd, *J* = 11.5, 5.9 Hz, H-7β), 2.10 (1H, m, H-1α), 2.03 (1H, m, H-2), 1.93 (1H, m, H-7α), 1.92 (1H, m, H-8β), 1.90 (1H, m, H-1β), 1.84 (1H, m, H-8α),1.69 (3H, s, H-20), 1.14 (3H, s, H-19), 1.05 (3H, s, H-18), 0.91 (3H, d, *J* = 6.3 Hz, H-16), 0.56 (1H, d, *J* = 10.0 Hz, H-11), 0.44 (1H, m, H-9), for 3-*O*Bz: δ_H 8.05 (2H, m), 7.54 (1H, t, *J* = 7.5 Hz), 7.43 (2H, t, *J* = 7.5 Hz); 5-*O*Ac: δ_H 1.87 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 144.5 (C-6), 135.6 (C-13), 129.2 (C-14), 114.1 (C-17), 94.4 (C-15), 84.5 (C-12), 78.4 (C-3), 68.7 (C-5), 52.9 (C-4), 47.9 (C-1), 38.3 (C-7), 36.4 (C-2), 29.2 (C-9), 28.8 (C-18), 27.1 (C-11), 22.7 (C-8), 15.4 (C-19), 14.8 (C-10), 13.7 (C-16), 12.5 (C-20), for 3-*O*Bz: 166.1, 132.7, 130.4, 129.6 × 2, 128.3 × 2; 5-*O*Ac: δ_C 170.0, 21.2; HRESIMS *m*/*z* 487.2454 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_5Na^+$, 487.2455).

1.7. Preparation of **24** and **25** by epoxidation of **15**

To a stirred solution of **15** (80.0 mg, 0.125 mmol) in CH_2Cl_2 (2 mL) was added

m-CPBA (24.1 mg, 0.150 mmol) at 60 °C for 1 h. After that, excess saturated $NaHCO_3$ solution was added to the reaction mixture for another 10 min. The reaction mixture was washed with H_2O and extracted with EtOAc. After removal of the solvent under vacuum, the residue was purified with silica gel flash column chromatography (PE:EtOAc = 15:1) and followed by semi-preparative HPLC (MeCN/H_2O = 80:20, 3 mL/min) to afford **24** (22.4 mg, t_R 11.7 min) and **25** (27.6 mg, t_R 14.1 min).

5,15-Diacetoxy-3,7-dibenzoyloxy-6,17)-12,13-diepoxy-14-oxolathyra (**24**). White powder; $[\alpha]^{25}_D$ +76.33 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 233 (4.46) nm; IR (KBr) ν_{max} 2922, 1718, 1458, 1375, 1276, 1239, 1113, 714 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.98 (1H, m, H-3), 5.40 (1H, s, H-5), 5.30 (1H, d, J = 8.2 Hz, H-7), 3.50 (1H, brs, H-4), 3.12 (1H, d, J = 9.8 Hz, H-12), 3.02 (1H, d, J = 4.5 Hz, H-17a), 2.96 (1H, dd, J = 15.4, 8.6 Hz, H-1α), 2.66 (1H, m, H-2), 2.64 (1H, d, J = 4.5 Hz, H-17b), 2.48 (1H, dd, J = 15.4, 11.3 Hz, H-1β), 2.19 (1H, m, H-8α), 1.85 (3H, s, H-20), 1.82 (1H, m, H-8β), 1.30 (3H, s, H-19), 1.13 (3H,s, H-18), 1.12 (1H, m, H-9), 1.10 (3H, d, J = 6.6 Hz, H-16), 0.46 (1H, t, J = 9.8 Hz, H-11), for 3-*O*Bz: δ_H 8.04 (2H, d, J = 7.5 Hz), 7.58 (1H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz); 5-*O*Ac: δ_H 1.33 (3H, s); 7-*O*Bz: δ_H 8.08 (2H, d, J = 7.5 Hz), 7.63 (1H, t, J = 7.5 Hz), 7.49 (2H, t, J = 7.5 Hz); 15-*O*Ac: δ_H 2.08 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 201.3 (C-14), 92.3 (C-15), 76.2 (C-3), 72.9 (C-7), 65.5 (C-5), 62.7 (C-13), 62.5 (C-12), 60.4 (C-6), 50.4 (C-4), 46.8 (C-17), 44.4 (C-1), 37.9 (C-2), 28.4 (C-18), 26.8 (C-9), 25.3 (C-8), 22.8 (C-11), 21.5 (C-10), 15.0 (C-19 and 20), 13.9 (C-16), for 3-*O*Bz: 165.5, 133.4, 130.1, 129.5 × 2, 128.4 × 2; 5-*O*Ac: δ_C 168.7, 19.7; 7-*O*Bz: δ_C 166.7, 133.8, 129.9 × 2, 128.8, 128.6 × 2;

15-*O*Ac: δ_C 169.7, 21.1; HRESIMS *m*/*z* 697.2608 $[M + Na]^+$ (calcd for $C_{38}H_{42}O_{11}Na^+$, 697.2619).

5,15-Diacetoxy-3,7-dibenzoyloxy-12,13-epoxy-14-oxolathyra-6(17)-ene (**25**). White powder; $[\alpha]^{25}_D$ +61.33 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.30) nm; IR (KBr) ν_{max} 2926, 1718, 1453, 1371, 1275, 1111, 1068, 1026, 714 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ_H 5.84 (1H, brs, H-3), 5.79 (1H, brs, H-5), 5.44 (1H, t, *J* = 5.2 Hz, H-7), 5.34 (1H, s, H-17a), 5.10 (1H, s, H-17b), 3.25 (1H, brs, H-4), 3.15 (1H, d, *J* = 9.5 Hz, H-12), 2.90 (1H, dd, *J* = 15.2, 9.0 Hz, H-1α), 2.49 (1H, m, H-2), 2.29 (1H, dd, *J* = 15.2, 11.9 Hz, H-1β), 2.22 (1H, m, H-8α), 2.01 (1H, m, H-8β), 1.69 (3H, s, H-20), 1.27 (3H, s, H-19), 1.14 (3H, s, H-18), 1.13 (1H, m, H-9), 1.02 (3H, d, *J* = 6.5 Hz, H-16), 0.49 (1H, d, *J* = 9.5 Hz, H-11), for 3-*O*Bz and 7-*O*Bz: δ_H 8.09 (2H, d, *J* = 7.3 Hz), 8.06 (2H, d, *J* = 7.3 Hz), 7.58 (2H, t, *J* = 7.3 Hz), 7.45 (4H, m); 5-*O*Ac: δ_H 1.31 (3H, s); 15-*O*Ac: δ_H 2.13 (3H, s); ^{13}C NMR ($CDCl_3$, 125 MHz) δ_C 204.0 (C-14), 142.8 (C-6), 113.2 (C-17), 91.2 (C-15), 77.0 (C-3 and C-7), 67.8 (C-5), 63.8 (C-13), 61.8 (C-12), 52.4 (C-4), 46.4 (C-1), 37.1 (C-2), 28.6 (C-8), 28.4 (C-18), 27.3 (C-9), 22.6 (C-11), 20.5 (C-10), 15.5 (C-19), 14.9 (C-20), 14.1 (C-16), for 3-*O*Bz and 7-*O*Bz: 166.1, 165.5, 133.4, 133.1, 130.3 × 2, 129.7 × 2, 129.6 × 2, 128.5 × 2, 128.3 × 2; 5-*O*Ac: δ_C 168.9, 20.3; 15-*O*Ac: δ_C 169.8, 21.2; HRESIMS *m*/*z* 681.2668 $[M + Na]^+$ (calcd for $C_{38}H_{42}O_{10}Na^+$, 681.2670).

1.8. Preparation of **26** by hydrogenation of **15**

To a stirred solution of **15** (80.0 mg, 0.125 mmol) in EtOAc (2 mL) was added 10% Pd/C under an atmosphere of hydrogen at 50 °C for 24 h. After that, the reaction

mixture was filtered and evaporated to dryness. The obtained residue was purified with silica gel flash column chromatography (PE:EtOAc = 30:1) and followed by semi-preparative HPLC (MeCN/H_2O = 80:20, 3 mL/min) to afford **26** (18.6 mg, t_R 15.3 min).

5,15-Diacetoxy-3,7-dibenzoyloxy-14-oxolathyra-6(17)-ene (**26**). Colorless crystals; mp 146.7–147.9 °C; $[\alpha]^{25}_D$ +49.67 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.29) nm; IR (KBr) ν_{max} 2924, 1720, 1455, 1370, 1275, 1231, 1111, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.64 (1H, dd, *J* = 3.2, 3.2 Hz, H-3), 5.39 (1H, d, *J* = 11.0 Hz, H-5), 5.14 (1H, d, *J* = 6.1 Hz, H-7), 3.41 (1H, dd, *J* = 11.0, 3.2 Hz, H-4), 3.25 (1H, m, H-13), 2.61 (1H, dd, *J* = 14.1, 6.8 Hz, H-1α), 2.40 (1H, m, H-2), 2.13 (1H, dd, *J* = 14.1, 14.1 Hz, H-1β), 1.81 (1H, brd, *J* = 15.0 Hz, H-8α), 1.69 (1H, m, H-6), 1.62 (1H, m H-12α), 1.43 (1H, m, H-12β), 1.36 (1H, m, H-8β), 1.27 (6H, d, *J* = 7.0 Hz, H-17 and 20), 1.04 (3H, s, H-18), 0.99 (1H, m, H-11), 0.92 (1H, m, H-9), 0.90 (3H, d, *J* = 6.6 Hz, H-16), 0.78 (3H, s, H-19), for 3-*O*Bz and 7-*O*Bz: δ_H 7.99 (2H, d, *J* = 7.5 Hz), 7.91 (2H, d, *J* = 7.5 Hz), 7.53 (2H, m), 7.41 (4H, m); 5-*O*Ac: δ_H 1.40 (3H, s); 15-*O*Ac: δ_H 2.30 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 217.2 (C-14), 93.6 (C-15), 78.2 (C-3), 72.8 (C-7), 71.7 (C-5), 56.3 (C-4), 48.7 (C-1), 39.3 (C-6), 38.4 (C-2), 38.0 (C-13), 30.1 (C-8), 29.0 (C-12), 28.7 (C-18), 25.6 (C-10), 20.0 (C-20), 19.4 (C-11), 16.4 (C-10), 15.2 (C-19), 13.3 (C-11), 12.6 (C-17), for 3-*O*Bz and 7-*O*Bz: 165.9, 165.5, 133.0, 132.9, 130.7, 130.3, 129.4 × 2, 129.3 × 2, 128.4 × 2, 128.3 × 2; 5-*O*Ac: δ_C 170.3, 20.5; 15-OAc: δ_C 170.0, 22.1; HRESIMS *m*/*z* 669.3028 $[M + Na]^+$ (calcd for $C_{38}H_{46}O_9Na^+$, 669.3034).

1.9. Preparation of **28** by oxidation of **27**

To a stirred solution of **27** (25.0 mg, 0.075 mmol) in CH_2Cl_2 (2 mL) was added Dess-Martin periodinane reagent (31.7 mg, 0.075 mmol) at rt for 3 h. After that, the reaction mixture was filtered and evaporated to dryness. The obtained residue was purified with silica gel flash column chromatography (PE:EtOAc = 15:1) to afford **28** (17.3 mg).

3,15-Dihydroxy-5,14-dioxolathyra-6(17),12*E*-diene (**28**). White powder; $[\alpha]^{25}_{D}$ +146.00 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 248 (4.21) nm; IR (KBr) ν_{max} 3452, 2926, 1642, 1453, 1379, 1260, 1230, 1150, 1113, 1057, 1000, 904, 861 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 7.02 (1H, dd, *J* = 11.6, 1.0 Hz, H-12), 5.80 (1H, s, H-17a), 5.61 (1H, s, H-17b), 4.24 (1H, dd, *J* = 2.9, 2.9 Hz, H-3), 3.35 (1H, dd, *J* = 13.5, 8.5 Hz, H-1a; 1H, d, *J* = 2.9 Hz, H-4), 2.97 (1H, dd, *J* = 13.7, 5.7 Hz, H-7a), 1.99 (2H, m, H-7b and 8a), 1.90 (1H, m, H-2), 1.74 (3H, d, *J* = 1.0 Hz, H-20), 1.63 (1H, dd, *J* = 13.5, 11.7 Hz, H-1b), 1.55 (1H, m, H-8b), 1.39 (1H, dd, *J* = 11.6, 8.2 Hz, H-11), 1.14 (3H, s, H-18), 1.11 (3H, d, *J* = 6.7 Hz, H-16), 1.09 (1H, m, H-9), 1.01 (3H, s, H-19), for 3-*O*H: δ_H 4.63 (1H, brs), 15-*O*H: δ_H 3.43 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 203.9 (C-5), 197.2 (C-14), 151.1 (C-12), 149.9 (C-6), 133.3 (C-13), 127.3 (C-17), 90.7 (C-15), 79.4 (C-3), 56.1 (C-4), 47.1 (C-1), 38.8 (C-2), 35.3 (C-9), 32.7 (C-7), 29.0 (C-11 and 18), 25.4 (C-10), 22.0 (C-8), 16.1 (C-19), 13.3 (C-16), 12.6 (C-20); HRESIMS *m*/*z* 355.1873 $[M + Na]^+$ (calcd for $C_{20}H_{28}O_4Na^+$, 355.1880).

1.10. Preparation of **29** and **30** by hydrogenation of **14**

A total of **14** (80.0 mg, 0.153 mmol) was prepared following the same procedure used in *section 4.8*. The obtained residue was purified with silica gel flash column chromatography (PE:EtOAc = 35:1) and followed by semi-preparative HPLC (MeCN/H_2O = 80:20, 3 mL/min) to afford **29** (19.2 mg, t_R 15.3 min) and **30** (16.8 mg, t_R 15.9 min).

5,15-Diacetoxy-3-benzoyloxy-14-oxolathyra-6(17)-ene (**29**). White powder; $[\alpha]^{25}_D$ –21.67 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.32) nm; IR (KBr) ν_{max} 2924, 1742, 1719, 1453, 1370, 1272, 1231, 1111, 1025, 735, 710 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 5.82 (1H, d, *J* = 9.5 Hz, H-5), 5.76 (1H, dd, *J* = 4.4, 4.4 Hz, H-3), 5.41 (1H, s, H-17a), 5.15 (1H, s, H-17b), 3.31 (1H, dd, *J* = 11.7, 7.2 Hz, H-13), 3.17 (1H, dd, *J* = 9.5, 4.4 Hz, H-4), 2.84 (1H, dd, *J* = 11.8, 4.8 Hz, H-1α), 2.35 (1H, m, H-7β), 2.10 (1H, m, H-2), 2.07 (1H, m, H-1β), 1.88 (2H, m, H-7α and 8α), 1.76 (1H, m, H-12α), 1.27 (1H, m H-12β), 1.02 (3H, d, *J* = 6.7 Hz, H-20; 1H, m, H-8β), 0.99 (3H, s, H-18), 0.93 (3H, d, *J* = 6.2 Hz, H-16), 0.83 (3H, s, H-19), 0.50 (1H, m, H-11), 0.34 (1H, m, H-9); for 3-*O*Bz: δ_H 8.03 (2H, m), 7.56 (1H, t, *J* = 7.5 Hz), 7.44 (2H, t, *J* = 7.5 Hz); 5-*O*Ac: δ_H 1.81 (3H, s); 15-*O*Ac: δ_H 2.18 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 211.8 (C-14), 147.2 (C-6), 117.7 (C-17), 92.1 (C-15), 78.3 (C-3), 73.6 (C-5), 50.6 (C-4), 43.9 (C-1), 38.4 (C-13), 37.3 (C-2), 30.4 (C-7), 28.8 (C-18), 28.5 (C-12), 28.4 (C-9), 22.6 (C-8), 21.8 (C-11), 18.8 (C-20), 17.3 (C-10), 15.2 (C-19), 13.2 (C-16), for 3-*O*Bz: 165.9, 133.0, 130.0, 129.5 × 2, 128.4 × 2; 5-*O*Ac: δ_C 169.2, 20.9; 15-*O*Ac: δ_C 169.7, 21.7; HRESIMS *m*/*z* 547.2653 $[M + Na]^+$ (calcd for $C_{31}H_{40}O_7Na^+$, 547.2666).

5,15-Diacetoxy-3-benzoyloxy-14-oxolathyra-12*E*-ene (**30**). Colorless oil; $[\alpha]^{25}_{D}$ +51.33 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 273 (4.54), 232 (4.47) nm; IR (KBr) ν_{max} 2926, 1738, 1652, 1621, 1453, 1368, 1271, 1233, 1114, 1028, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 6.76 (1H, d, *J* = 11.5 Hz, H-12), 6.02 (1H, d, *J* = 7.7 Hz, H-5), 5.69 (1H, dd, *J* = 3.4, 3.4 Hz, H-3), 3.47 (1H, dd, *J* = 13.9, 7.7 Hz, H-1α), 2.28 (1H, dd, *J* = 7.7, 3.4 Hz, H-4), 2.26 (1H, m, H-2), 1.87 (3H, br. s, H-20), 1.82 (1H, m, H-8α), 1.75 (1H, m, H-8β), 1.62 (1H, m, H-6), 1.61 (1H, m, H-1β), 1.49 (1H, dd, *J* = 11.5, 8.3 Hz, H-11), 1.21 (3H, s, H-19), 1.19 (3H, s, H-18; 2H, m, H-7α and β), 1.11 (1H, ddd, *J* = 11.5, 8.3, 4.1 Hz, H-9), 0.92 (3H, d, *J* = 6.7 Hz, H-16), 0.81 (3H, d, *J* = 6.7 Hz, H-17), for 3-*O*Bz: δ_H 7.99 (2H, m), 7.57 (1H, t, *J* = 7.5 Hz), 7.43 (2H, t, *J* = 7.5 Hz); 5-*O*Ac: δ_H 1.65 (3H, s); 15-*O*Ac: δ_H 2.22 (3H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 196.8 (C-14), 146.1 (C-12), 133.9 (C-13), 92.0 (C-15), 80.8 (C-3), 66.4 (C-5), 54.7 (C-4), 48.0 (C-1), 38.5 (C-2), 36.6 (C-9), 35.8 (C-6), 32.8 (C-7), 29.2 (C-18), 29.1 (C-11), 25.4 (C-10), 20.1 (C-8), 16.8 (C-19), 14.8 (C-17), 14.0 (C-16), 12.6 (C-20), for 3-*O*Bz: 166.0, 133.1, 130.1, 129.5 × 2, 128.5 × 2; 5-*O*Ac: δ_C 170.2, 20.5; 15-*O*Ac: δ_C 169.8, 21.7; HRESIMS *m*/*z* 547.2662 $[M + Na]^+$ (calcd for $C_{31}H_{40}O_7Na^+$, 547.2666).

1.11. Preparation of **32**–**34** by cyclopropane ring-opening of **14**

To a stirred solution of **14** (150.0 mg, 0.287 mmol) in MeOH (2 mL) was added $NaBH_4$ (13.0 mg, 0.344 mmol) at rt for 15 min, and followed treated with 10% hydrochloric acid at 60 °C for 30 min. After that, the reaction mixture was evaporated to dryness. The obtained residue was purified with silica gel flash column

chromatography (PE:EtOAc = 40:1) and followed by semi-preparative HPLC (MeCN/H_2O = 75:25, 3 mL/min) to afford **32** (21.2 mg, t_R 15.9 min), **33** (13.8 mg, t_R 15.4 min) and **34** (15.8 mg, t_R 13.6 min).

5-Acetoxy-3-benzoyloxy-15-hydroxy-10,11-*seco*lathyra-6(17),10(18),11*E*,13*Z*-te traene (**32**). White powder; $[\alpha]^{25}_D$ +43.67 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.26) nm; IR (KBr) ν_{max} 3476, 2926, 1718, 1452, 1371, 1275, 1114, 1026, 900, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 6.24 (1H, d, *J* = 16.2 Hz, H-12), 5.85 (1H, d, *J* = 7.0 Hz, H-5), 5.71 (1H, dd, *J* = 4.5, 4.5 Hz, H-3), 5.59 (1H, dd, *J* = 16.2, 7.8 Hz, H-11), 5.48 (1H, s, H-14), 5.04 (1H, s, H-17a), 4.96 (1H, s, H-17b), 4.76 (1H, s, H-18a), 4.75 (1H, s, H-18b), 3.20 (1H, dd, *J* = 7.0, 4.5 Hz, H-4), 2.66 (1H, ddd, *J* = 12.0, 7.8, 3.0 Hz, H-9), 2.34 (1H, m, H-7α), 2.08 (2H, m, H-1α and β), 2.07 (1H, m, H-2), 1.97 (1H, m, H-8α), 1.95 (1H, m, H-7β), 1.83 (3H, s, H-20), 1.75 (1H, m, H-8β), 1.72 (3H, s, H-19), 0.94 (3H, d, *J* = 5.5 Hz, H-16), for 3-*O*Bz: δ_H 8.06 (2H, m), 7.57 (1H, t, *J* = 7.5 Hz), 7.45 (2H, t, *J* = 7.5 Hz); 5-*O*Ac: δ_H 1.77 (3H, s); 15-OH: 2.40 (1H, brs); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 147.6 (C-10), 147.2 (C-6), 134.6 (C-13), 134.4 (C-11), 133.9 (C-14), 129.7 (C-12), 113.5 (C-17), 110.2 (C-18), 80.0 (C-15), 78.9 (C-3), 73.6 (C-5), 52.5 (C-9), 51.8 (C-1), 49.4 (C-4), 35.6 (C-2), 30.2 (C-7), 29.5 (C-8), 23.8 (C-20), 20.9 (C-19), 13.7 (C-16), for 3-*O*Bz: 165.8, 133.0, 130.1, 129.6 × 2, 128.4 × 2; 5-*O*Ac: δ_C 169.7, 21.0; HRESIMS *m*/*z* 487.2445 $[M + Na]^+$ (calcd for $C_{29}H_{36}O_5Na^+$, 487.2455).

5-Acetoxy-3-benzoyloxy-15-hydroxy-10-methoxy-10,11-*seco*lathyra-6(17),11*E*, 13*Z*-triene (**33**). White powder; $[\alpha]^{25}_D$ +58.67 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε)

232 (4.30) nm; IR (KBr) ν_{max} 3450, 2926, 1717, 1453, 1368, 1275, 1179, 1114, 1071, 907, 712 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 6.19 (1H, d, J = 16.1 Hz, H-12), 5.84 (1H, d, J = 6.2 Hz, H-5), 5.70 (1H, dd, J = 4.0, 4.0 Hz, H-3), 5.58 (1H, dd, J = 16.1, 8.6 Hz, H-11), 5.47 (1H, s, H-14), 4.93 (1H, s, H-17a), 4.89 (1H, s, H-17b), 3.19 (1H, m, H-4), 2.34 (1H, m, H-7β), 2.17 (1H, m, H-9), 2.12 (1H, m, H-1α), 2.07 (1H, m, H-2), 2.05 (1H, m, H-1β), 2.01 (1H, m, H-8α), 1.84 (1H, m, H-7α), 1.82 (3H, s, H-20), 1.50 (1H, m, H-8β), 1.12 (3H, s H-19), 1.11 (3H, s H-18), 0.94 (3H, d, J = 5.7 Hz, H-16), for 3-*O*Bz: δ_H 8.06 (2H, m), 7.56 (1H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz); 5-*O*Ac: δ_H 1.76 (3H, s); 10-*O*Me: δ_H 3.19 (3H, s); 15-OH: δ_H 2.53 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 147.1 (C-6), 134.2 (C-13), 133.3 (C-11), 133.0 (C-14), 130.7 (C-12), 112.7 (C-17), 80.3 (C-15), 78.9 (C-3), 76.3 (C-10), 73.2 (C-5), 54.0 (C-9), 51.8 (C-1), 49.0 (C-4), 35.6 (C-2), 30.6 (C-7), 24.8 (C-8), 24.5 (C-20), 23.5 (C-18), 21.9 (C-19), 13.9 (C-16), for 3-*O*Bz: 165.8, 133.0, 130.1, 129.6 × 2, 128.4 × 2; 5-*O*Ac: δ_C 169.7, 21.0; 10-*O*Me: δ_C 48.9; HRESIMS *m*/*z* 519.2710 $[M + Na]^+$ (calcd for $C_{30}H_{40}O_6Na^+$, 519.2717).

5-Acetoxy-3-benzoyloxy-10,15-dihydroxy-10,11-*seco*lathyra-6(17),11*E*,13*Z*-triene (**34**). White powder; $[\alpha]^{25}_D$ +57.00 (*c* 0.3, MeCN); UV (MeCN) λ_{max} (log ε) 232 (4.27) nm; IR (KBr) ν_{max} 3447, 2965, 1716, 1452, 1371, 1277, 1118, 1026, 908, 713 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ_H 6.23 (1H, d, J = 16.1 Hz, H-12), 5.84 (1H, d, J = 6.1 Hz, H-5), 5.71 (1H, dd, J = 4.0, 4.0 Hz, H-3), 5.61 (1H, dd, J = 16.1, 8.7 Hz, H-11), 5.47 (1H, s, H-14), 4.91 (1H, s, H-17a), 4.86 (1H, s, H-17b), 3.19 (1H, m, H-4), 2.34 (1H, dd, J = 13.3, 10.0 Hz, H-7β), 2.13 (1H, m, H-1α), 2.07 (1H, m, H-2), 2.03

(1H, m, H-9; 1H, m, H-1β; 1H, m, H-8α), 1.85 (1H, m, H-7α), 1.82 (3H, s, H-20), 1.55 (1H, m, H-8β), 1.19 (6H, s, H-18 and H-19), 0.93 (3H, d, J = 5.8 Hz, H-16), for 3-*O*Bz: δ_H 8.05 (2H, m), 7.56 (1H, t, J = 7.5 Hz), 7.44 (2H, t, J = 7.5 Hz); 5-*O*Ac: δ_H 1.76 (3H, s); 15-OH: δ_H 2.55 (1H, brs); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 146.8 (C-6), 134.2 (C-13), 133.0 (C-11 and 14), 131.8 (C-12), 112.6 (C-17), 80.3 (C-15), 78.9 (C-3), 72.9 (C-5), 72.2 (C-10), 56.9 (C-9), 51.9 (C-1), 48.9 (C-4), 35.5 (C-2), 30.8 (C-7), 28.1 (C-18), 26.9 (C-19), 25.2 (C-8), 24.7 (C-20), 13.9 (C-16), for 3-*O*Bz: 165.8, 133.0, 130.0, 129.6 × 2, 128.4 × 2; 5-*O*Ac: δ_C 169.8, 21.0; HRESIMS *m*/*z* 505.2568 $[M + Na]^+$ (calcd for $C_{29}H_{38}O_6Na^+$, 505.2561).

1.12. X-ray crystallographic analysis

Compound **26** was recrystallized from MeCN/H_2O (20:1) to afford colorless needles. $C_{38}H_{46}O_9 \cdot 2MeCN$ (M = 728.85 g/mol): orthorhombic, space group $P2_12_12_1$, a = 8.76640(10) Å, b = 9.56870(10) Å, c = 47.6317(6) Å, V = 3995.49(8) Å3, Z = 4, T = 100 K, μ (Cu Kα) = 0.690 mm^{-1}, *Dcalc* = 1.212 g/cm^3, 39757 reflections measured (7.424° ≤ 2Θ ≤ 153.90°), 8304 unique (R_{int} = 0.0464, R_{sigma} = 0.0327) which were used in all calculations. The final R_1 was 0.0416 (I > 2σ (I)) and wR_2 was 0.0916 (all data). Flack parameter = 0.02 (6). Crystallographic data for the structure of **26** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 2080912).

Compound **30** was recrystallized from petroleum ether/ethanol (20:1) to afford colorless needles. $C_{31}H_{40}O_7$ (M = 524.63 g/mol): orthorhombic, space group $P2_1$, a =

9.9964(2) Å, b = 8.27010(10) Å, c = 17.4475(3) Å, V = 1408.61(4) Å3, Z = 2, T = 100 K, μμ (Cu Kα) = 0.702 mm^{-1}, *Dcalc* = 1.237 g/cm^3, 27407 reflections measured (5.186° ≤ 2Θ ≤ 153.572°), 5740 unique (R_{int} = 0.0533, R_{sigma} = 0.0353) which were used in all calculations. The final R_1 was 0.0384 (I > 2σ (I)) and wR_2 was 0.1059 (all data). Flack parameter = –0.13 (8). Crystallographic data for the structure of **30** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 2080915).

Compound **31** was recrystallized from MeCN/H_2O (20:1) to afford colorless needles. $C_{29}H_{36}O_5$ (M = 464.58 g/mol): orthorhombic, space group $P2_12_12_1$, a = 10.50870(10) Å, b = 13.93090(10) Å, c = 17.2371(3) Å, V = 2523.44 (4) Å3, Z = 4, T = 100 K, μ (Cu Kα) = 0.658 mm^{-1}, Dcalc = 1.223 g/cm^3, 25420 reflections measured (8.16° ≤ 2Θ ≤ 154.202°), 5247 unique (R_{int} = 0.0546, R_{sigma} = 0.0353) which were used in all calculations. The final R_1 was 0.0415 (I > 2σ (I)) and wR_2 was 0.1068 (all data). Flack parameter = 0.00 (10). Crystallographic data for the structure of **31** have been deposited in the Cambridge Crystallographic Data Centre (deposition number: CCDC 2080917).

These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033

1.13. Cell Culture

HEK293T cells, purchased from ATCC, were cultivated in DMEM (Corning, USA) medium supplemented with 10% fetal bovine serum (FBS, Coring, USA) and 1% penicillin/streptomycin (PS, Gibco, USA). Human hepatoma cell line HepaRG (Thermo Fisher Scientific, USA) was cultured to confluence in Williams' E medium (Thermo Fisher Scientific, USA) supplemented with 10% FBS, 1% ITS (Thermo Fisher Scientific, USA), 1% GlutaMAX (Thermo Fisher Scientific, USA), 100U PS and 0.1 μM dexamethasone (Sigma-Aldrich, USA) for two weeks. Then HepaRG cells differentiate in medium containing 2% dimethylsulfoxide (DMSO, MP Biomedicals, USA). Cells were all incubated at 37 °C with 5% CO_2.

1.14. Dual luciferase reporter Assays

Dual-luciferase reporter gene assay was performed as described in our previous reports.[4-6] HEK293T cells were seeded in 96-well plates at a density of 1.2×10^4 cells per well without antibiotics. 100 ng pGL3-CYP3A4-XREM-Luc, 50 ng pSG5-hPXR, and 3 ng pGL4.74 [hRluc/TK] control vector were co-transfected into each well using MegaTran 1.0 (Origene, USA) according to the manufacturer's instructions. 6 hours later, the transfection mixtures were replaced by culture medium containing 10 μM hPXR positive agonist RIF or the tested compounds. After incubation for 24 h, dual-luciferase activity was measured using a Dual Reporter Assay System (Promega, Madison, WI) in an Amersham Pharmacia Biotech luminometer. *Renilla* activity was measured as normalization to firefly luciferase activity for each well.

1.15. Quantitative reverse-transcription polymerase chain reaction

Trizol reagent was used to purify total RNA from HepaRG according to the manufacturer's instruction (Invitrogen, Grand Island, NY). Approximately 1000 ng RNA was isolated and randomly reverse-transcribed to cDNA with PrimeScript RT reagent kit (Accurate biology, China). RT-qPCR analysis for specific genes was performed using SYBR Premix Ex Taq II kit (Accurate biology, China) in Applied Biosystems 7500 Real-Time PCR System. ACTB of HepaRG was used as normalized control. The gene-specific primer sequences used in the experiment are listed in Table. S1.2.

1.16. Molecular modeling

All the molecular docking studies, including protein preparation, ligand preparation and docking simulation, were performed using MOE2014.0901. Crystal structure of hPXR and RIF complex (PDB ID: 1SKX) was downloaded from RCSB Protein Data Bank (http://www.rcsb.org/), with a resolution of 2.8 Å. The forcefield environment was set as default Amber10: EHT, and the LigX module was applied to preprocess the ligand-protein complex. Small molecules (draw by Chemdraw 17.0) were imported into the MOE software and built as a candidate compound library while the force-field parameters set as MMFF94 × default environment. After energy minimizing and optimization, a stochastic conformational search was performed. Each compound can generate up to 1000 conformations. The candidate molecules were docked into the suggested active site using the default induced fit docking protocol and rescoring via London dG and GBVI/WSA dG algorithm.

1.17. Statistical Analysis

All the presented data and results were confirmed by at least three independent experiments. The data were presented as means ± the standard deviation (S.D.) and analyzed with GraphPad Prism 7.0 software (GraphPad Software, U.S.). Statistical differences between two groups were determined using student-T-test. A value of $P < 0.05$ was accepted as statistically significant.

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2. Table S1. ^{1}H and ^{13}C NMR spectral data of compounds **1**–**3** in $CDCl_3$ (J in Hz, δ in ppm)

no.	**1**[a]		**2**[b]		**3**[a]	
	δ_H, mult	δ_C	δ_H, mult	δ_C	δ_H, mult	δ_C
1α	3.76, dd (14.8, 9.3)	44.0	3.48, dd (13.6, 9.3)	45.8	3.33, dd (14.5, 8.3)	47.0
1β	1.71, dd (14.8, 10.7)		1.46, dd (13.6, 10.0)		1.88, dd (14.5, 11.4)	
2	2.46, m	38.6	2.06, m	38.9	2.41, m	37.2
3	5.65, dd (3.8, 3.8)	81,1	4.06, dd (3.0, 3.0)	80.9	5.94, dd (3.8, 3.8)	79.4
4	3.02, dd (10.8, 3.8)	51.8	2.54, dd (10.9, 3.0)	52.5	2.81, m	55.8
5	6.59, d (10.8)	137.1	6.03, d (10.9)	127.1	6.08, d (10.2)	67.1
6		143.3		138.9		147.7
7α		203.7	2.15, m	31.9		199.9
7β			2.49, m			
8α	2.61, dd (12.1, 4.3)	36.3	2.26, m	28.4	2.79, dd (13.8, 7.5)	33.7
8β	2.95, dd (12.1, 12.1)		1.59, m		3.01, dd (13.8, 8.0)	
9	1.22, m	31.8	1.16, m	34.5	1.60, m	31.5
10		24.8		25.1		25.4
11	1.51, dd (11.7, 8.4)	27.7	1.50, dd (11.5, 7.0)	29.7	1.56, m	28.1
12	6.70, dd (11.7, 1.0)	145.4	7.38, d (11.5)	152.1	6.43, d (10.7)	143.3
13		133.8		132.6		136.0
14		193.1		197.2		196.2
15		95.6		92.8		92.2
16	1.05, d (6.8)	14.4	1.12, d (6.8)	14.2	0.98, d (6.8)	14.0
17	4.13, brs	58.0	a 4.61, d (12.1)	64.9	a 6.13, s	128.0
			b 4.32, d (12.1)		b 5.77, s	
18	1.19, s	28.5	1.19, s	29.2	1.19, s	28.4
19	1.15, s	16.2	1.09, s	16.2	1.23, s	15.9
20	1.82, d (1.0)	12.5	1.86, s	12.5	1.77, s	12.8
5-OAc					1.78, s	20.6
						169.7
15-OAc	2.16, s	21.6			2.22, s	21.8
		169.2				169.8
OBz	3-		17-		3-	
C=O		165.5		166.5		165.8
1′		129.9		130.3		129.9
2′,6′	8.09, m	129.6	7.98, m	129.5	8.01, m	129.4
3′,5′	7.49, t (7.7)	128.6	7.41, t (7.8)	128.4	7.45, t (7.5)	128.5
4′	7.62, m	133.4	7.54, t (7.8)	133.0	7.58, t (7.5)	133.2
15-OH			3.05, brs			

[a]Recorded at ^{1}H (400 MHz), ^{13}C NMR (100 MHz); [b]Recorded at ^{1}H (500 MHz), ^{13}C NMR (125 MHz)

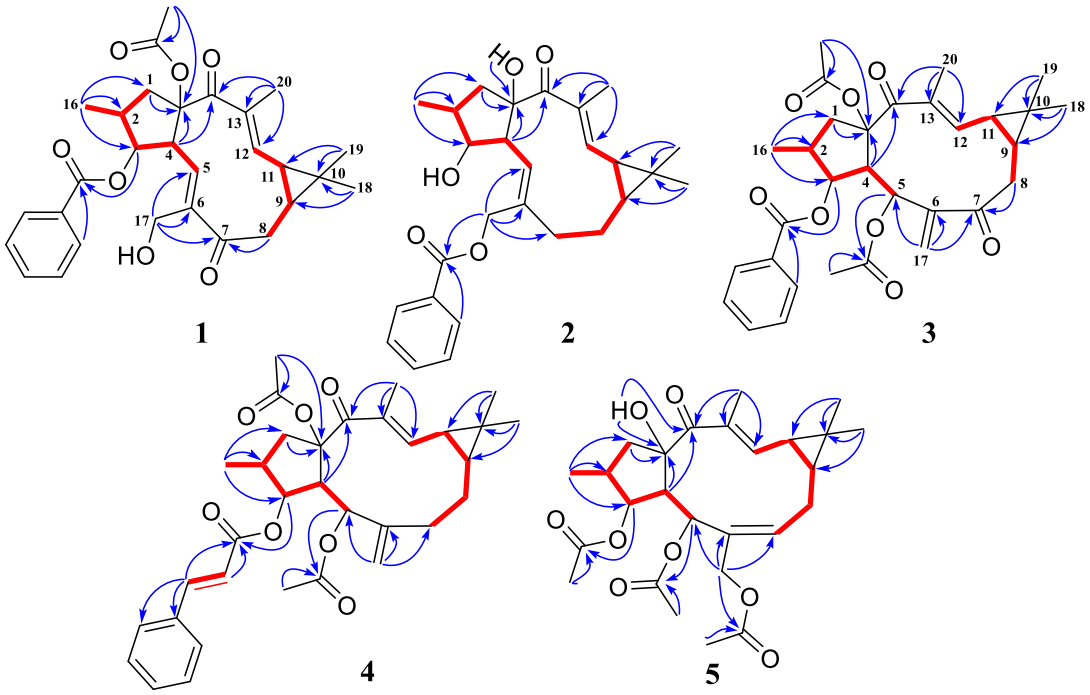
3. Table S2. ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) spectral data of compounds **4** and **5** in $CDCl_3$ (J in Hz, δ in ppm)

no.	**4**		**5**	
	δ_H, mult	δ_C	δ_H, mult	δ_C
1α	3.48, dd (14.3, 8.4)	48.4	3.31, dd (14.4, 10.2)	51.0
1β	1.63, dd (14.3, 11.9)		1.50, dd (10.2, 5.3)	
2	2.32, m	37.7	2.27, m	36.6
3	5.69, dd (3.5, 3.5)	80.4	5.66, dd (3.5, 3.5)	82.2
4	2.83, dd (10.0, 3.5)	52.0	2.59, m	54.2
5	6.17, d (10.0)	65.5	6.24, d (10.2)	65.8
6		144.6		130.1
7	α 2.07, m	34.9	5.58, dd (12.5, 3.6)	136.2
	β 2.23, m			
8α	1.97, m	21.6	2.35, m	24.5
8β	1.77, m		2.62, m	
9	1.15, m	35.3	1.23, m	30.7
10		25.2		25.5
11	1.39, dd (11.4, 8.3)	28.5	1.48, d (11.3)	28.2
12	6.52, dd (11.4, 0.8)	146.5	7.69, d (11.3)	150.1
13		134.1		134.5
14		196.7		198.2
15		92.3		90.1
16	0.94, d (6.7)	14.1	0.94, d (6.8)	14.6
17a	5.00, s	115.4	4.42, d (12.3)	65.2
17b	4.75, s		4.36, d (12.3)	
18	1.17, s	29.0	1.18, s	28.5
19	1.17, s	16.8	1.32, s	16.4
20	1.71, d (0.8)	12.4	1.71, br s	12.0
3-OAc			2.07, s	20.9
				169.4
5-OAc	1.92, s	21.1	1.89, s	21.2
		170.3		169.6
15-OAc	2.18, s	22.1		
		169.8		
17-OAc			2.03, s	21.1
				171.0
cinnamyl	3			
C=O		166.5		
1′		134.3		
2′,6′	7.52, m	128.1		
3′,5′	7.38, m	128.8		
4′	7.37, m	130.4		
7′	7.67, d (16.0)	145.1		
8′	6.39, d (16.0)	117.9		
15-OH			2.98, s	

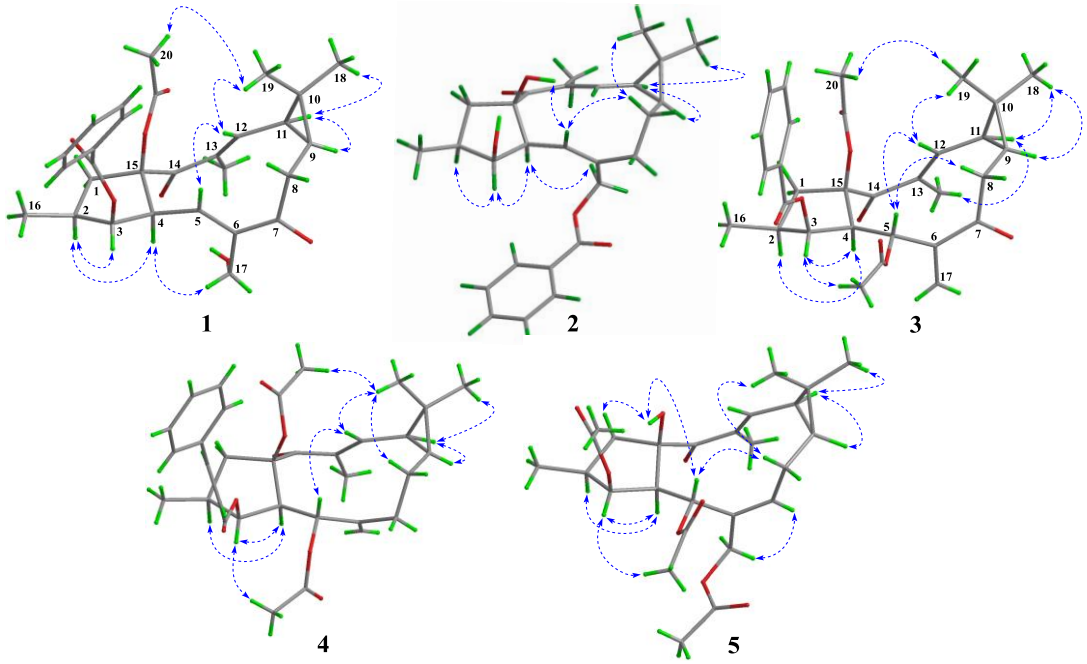
4. Table S3. The gene-specific primer sequences for RT-qPCR.

Gene	Species	Forward primer (5'→3')	Reverse primer (5'→3')
ACTB	Human	CCTTGCACATGCCGGAG	GCACAGAGCCTCGCCTT
CYP3A4	Human	GTGGGGCTTTTATGATGGTCA	GCCTCAGATTTCTCACCAACACA
CYP2B6	Human	CCGGGGATATGGTGTGATCTT	CCGAAGTCCCTCATAGTGGTC
MDR1	Human	CCATAGCTCGTGCCCTTGTTAGA	CGGTGAGCAATCACAATGCAG

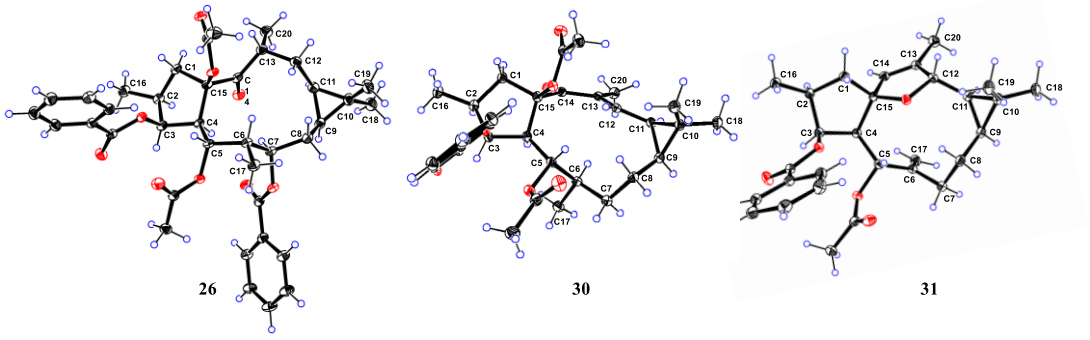
5. Figure S1. The key ^{1}H–^{1}H COSY (—) and HMBC (→) correlations of compounds **1**–**5**.



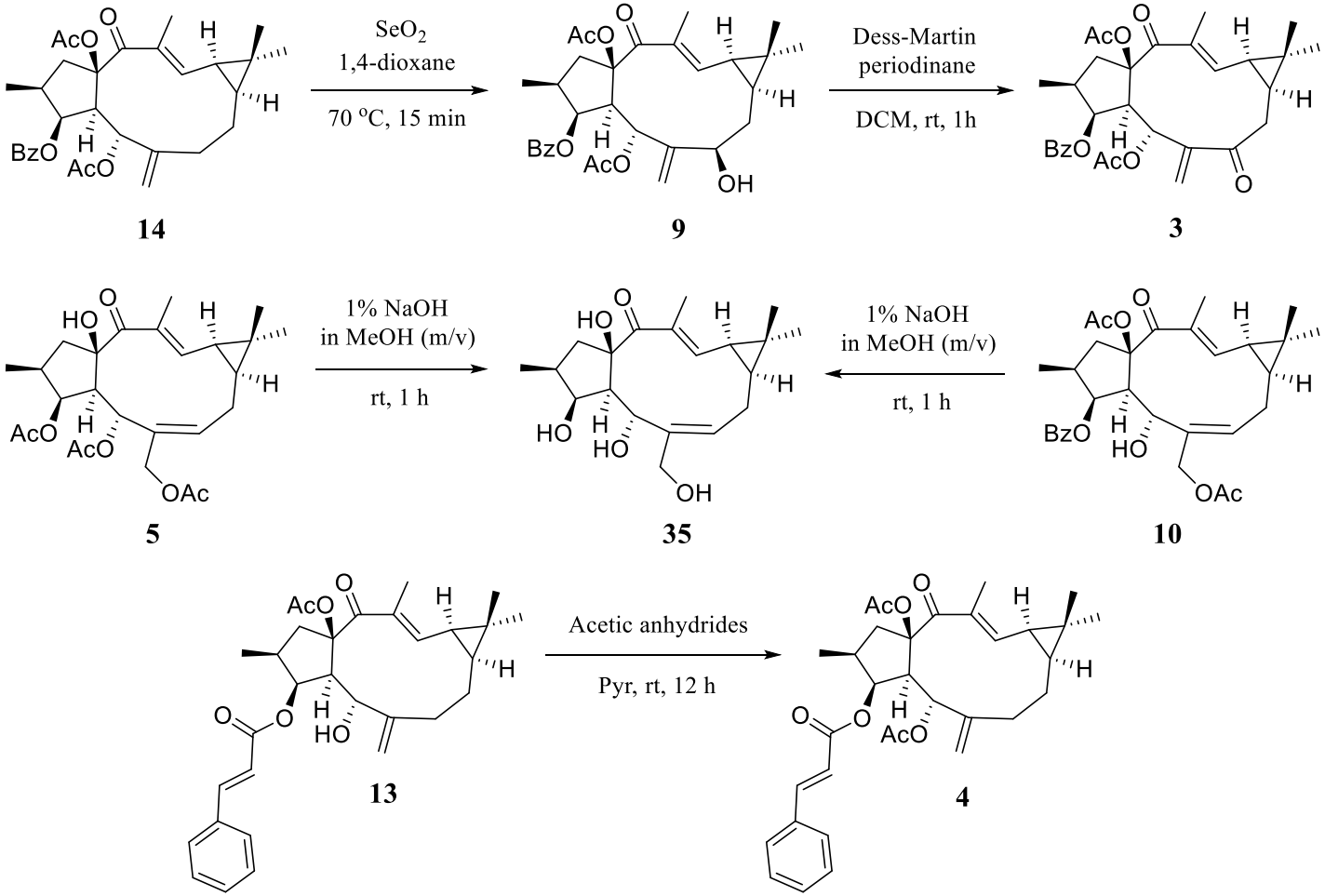
6. S2. The key NOE (◄- - -►) correlations of compounds **1**–**5**.



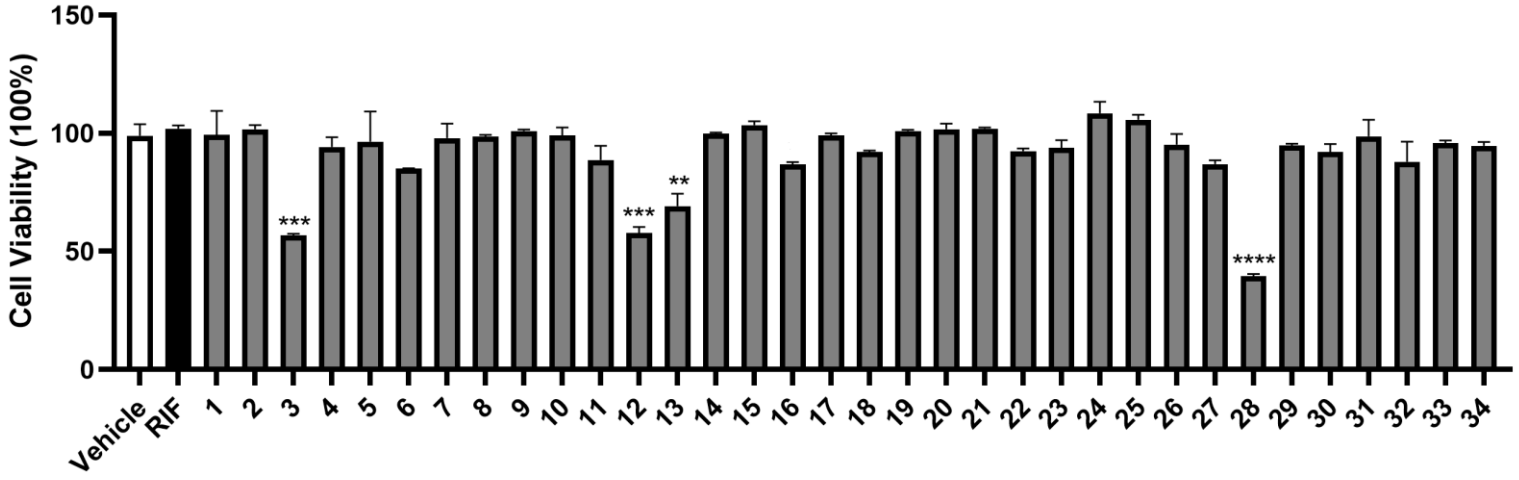
7. Figure S3. ORTEP diagram of compounds **26**, **30**, and **31**.



8. Figure S4. Chemical correlations of compounds **3**, **4**, **5**, **9**, **10**, **13**, **14**, and **35**.



9. Figure S5. The cytotoxicity of compounds **1–34**.



Cell Counting Kit-8 (CCK8) assay was applied to test cytotoxicity of compounds. HEK-293T cells were seeded in a 96-well plate (1×10^4/well) and treated with RIF or compounds at 10 μM for 24 h. After that, 10 μL CCK8 was applied to each well and incubated for an hour at 37 ℃. Cell viability was quantified by measuring optical density at 450 nm with a microplate reader.

10. Figure S6–S115.

Figure S6. ^{1}H NMR spectrum of **1** in $CDCl_3$.

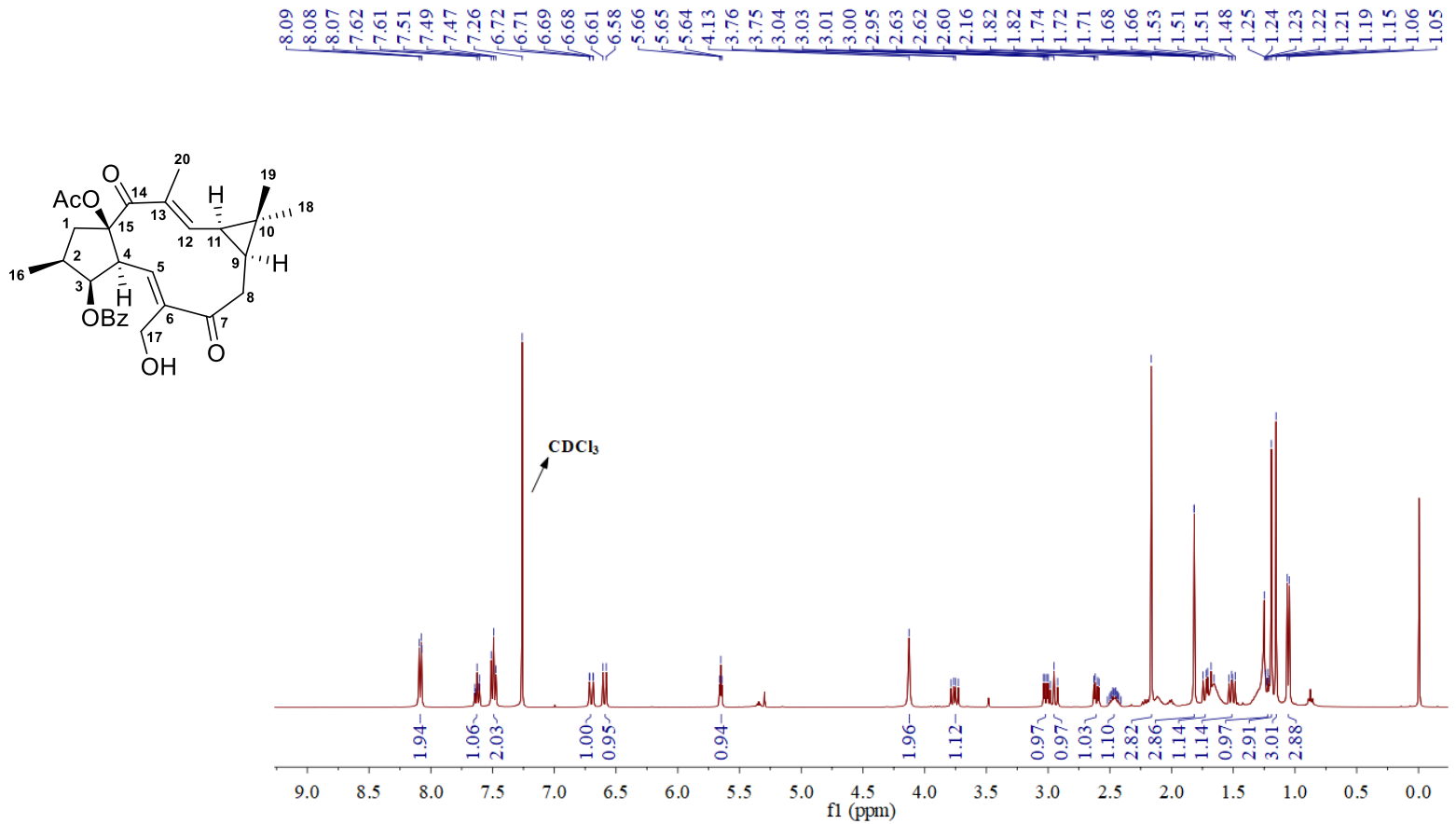


Figure S7. ^{13}C NMR and DEPT 135 spectra of **1** in $CDCl_3$.

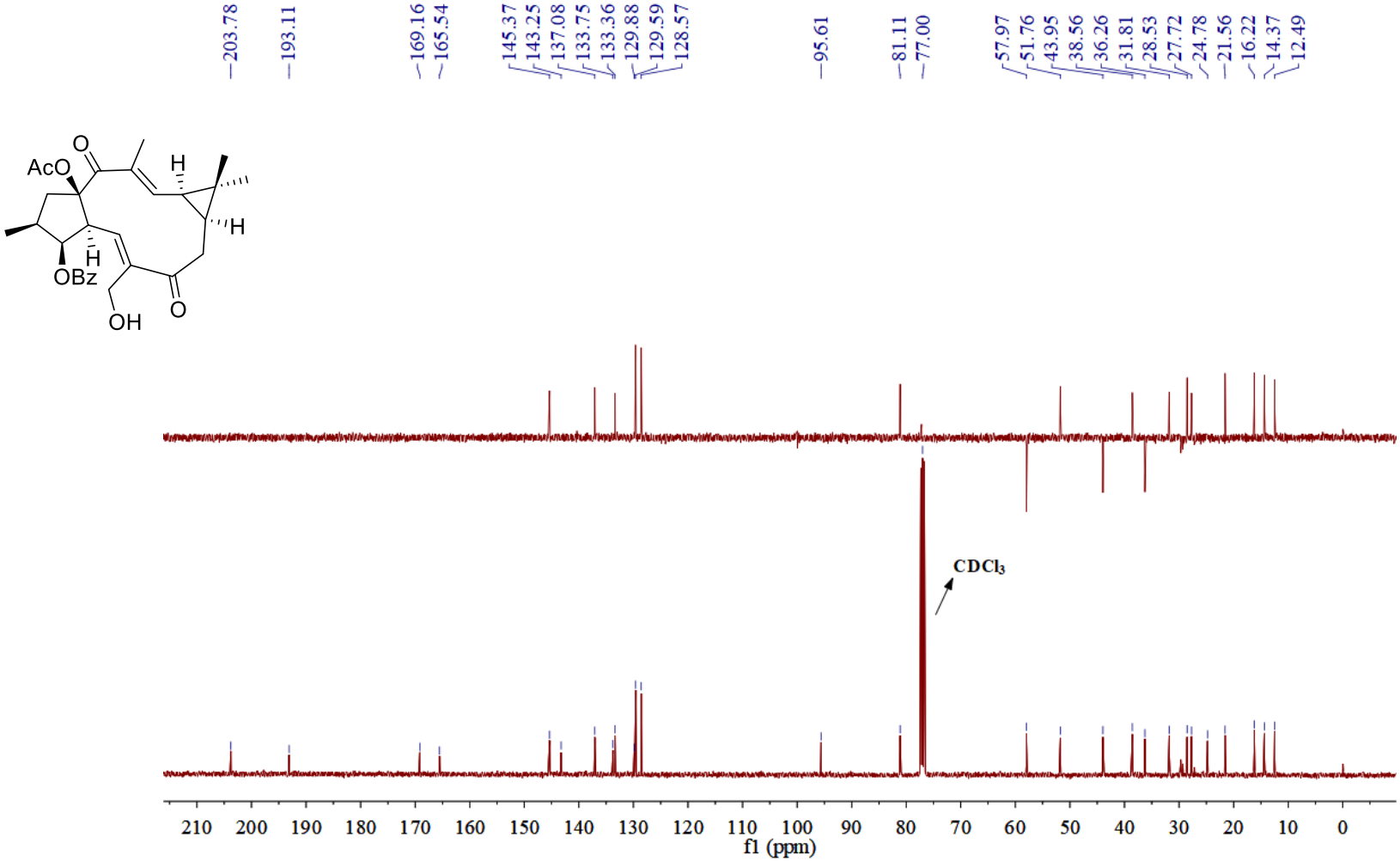


Figure S8. HSQC spectrum of **1** in $CDCl_3$.

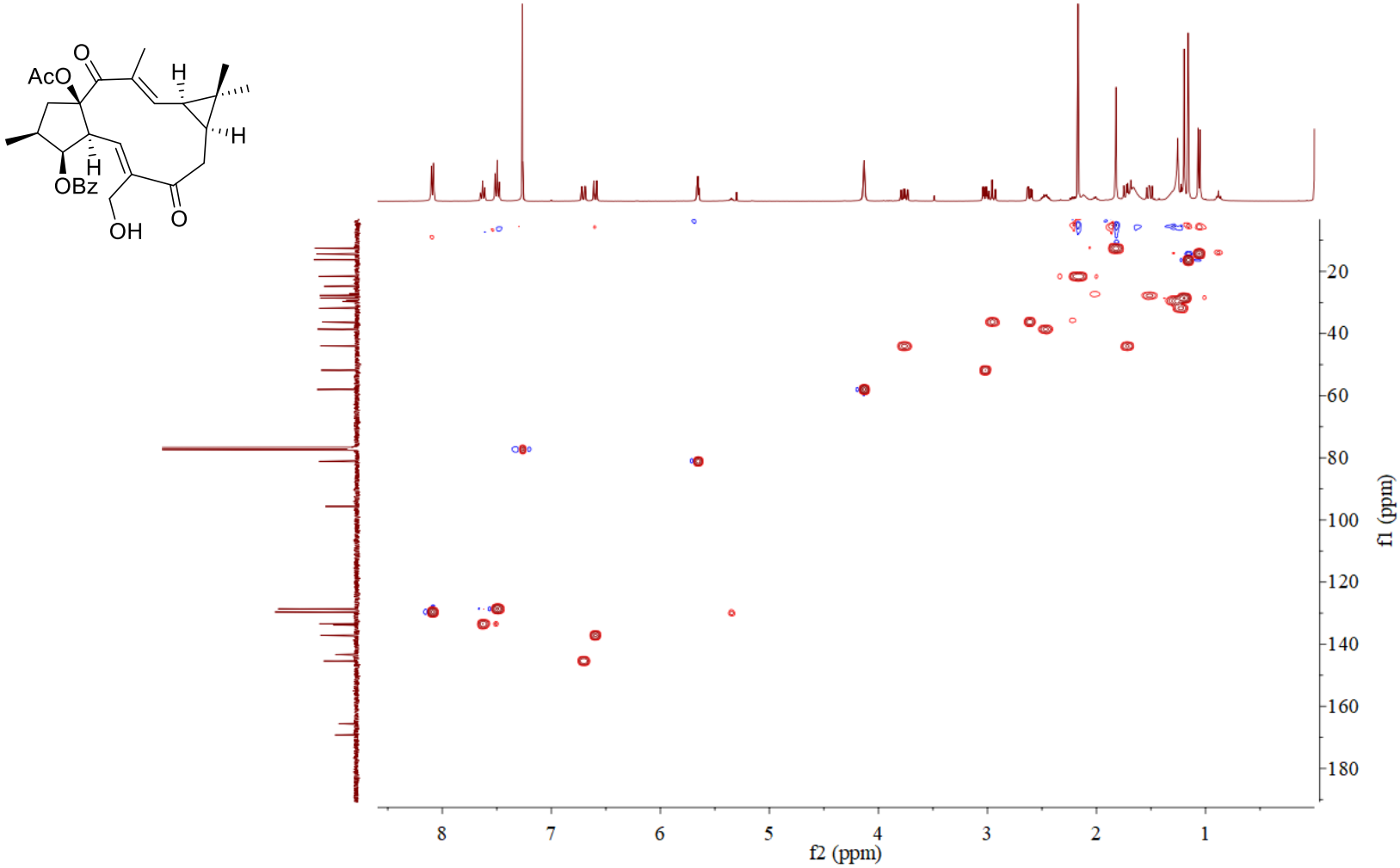


Figure S9. HMBC spectrum of **1** in $CDCl_3$.

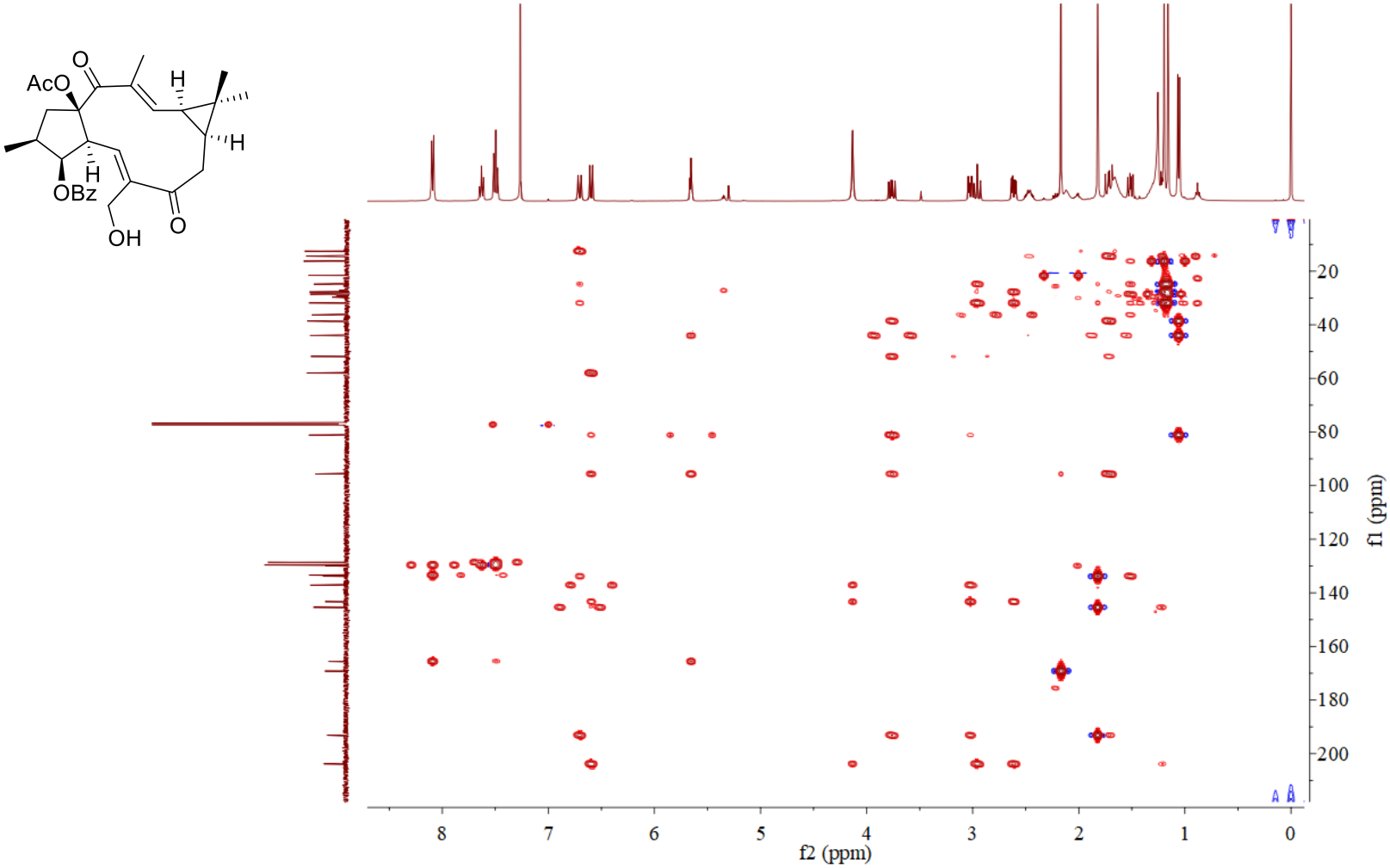


Figure S10. ^{1}H–^{1}H COSY spectrum of **1** in $CDCl_3$.

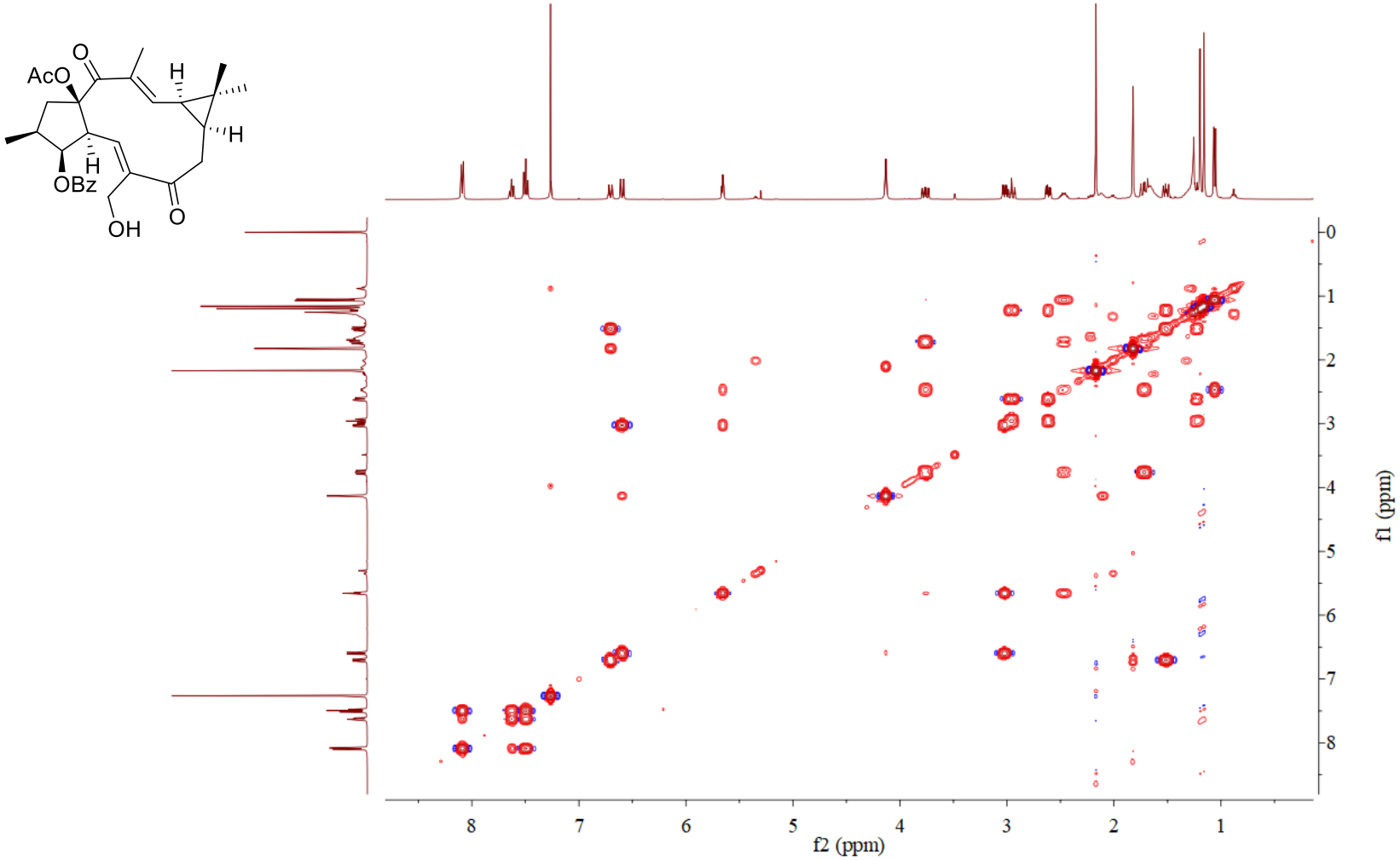


Figure S11. NOESY spectrum of **1** in $CDCl_3$.

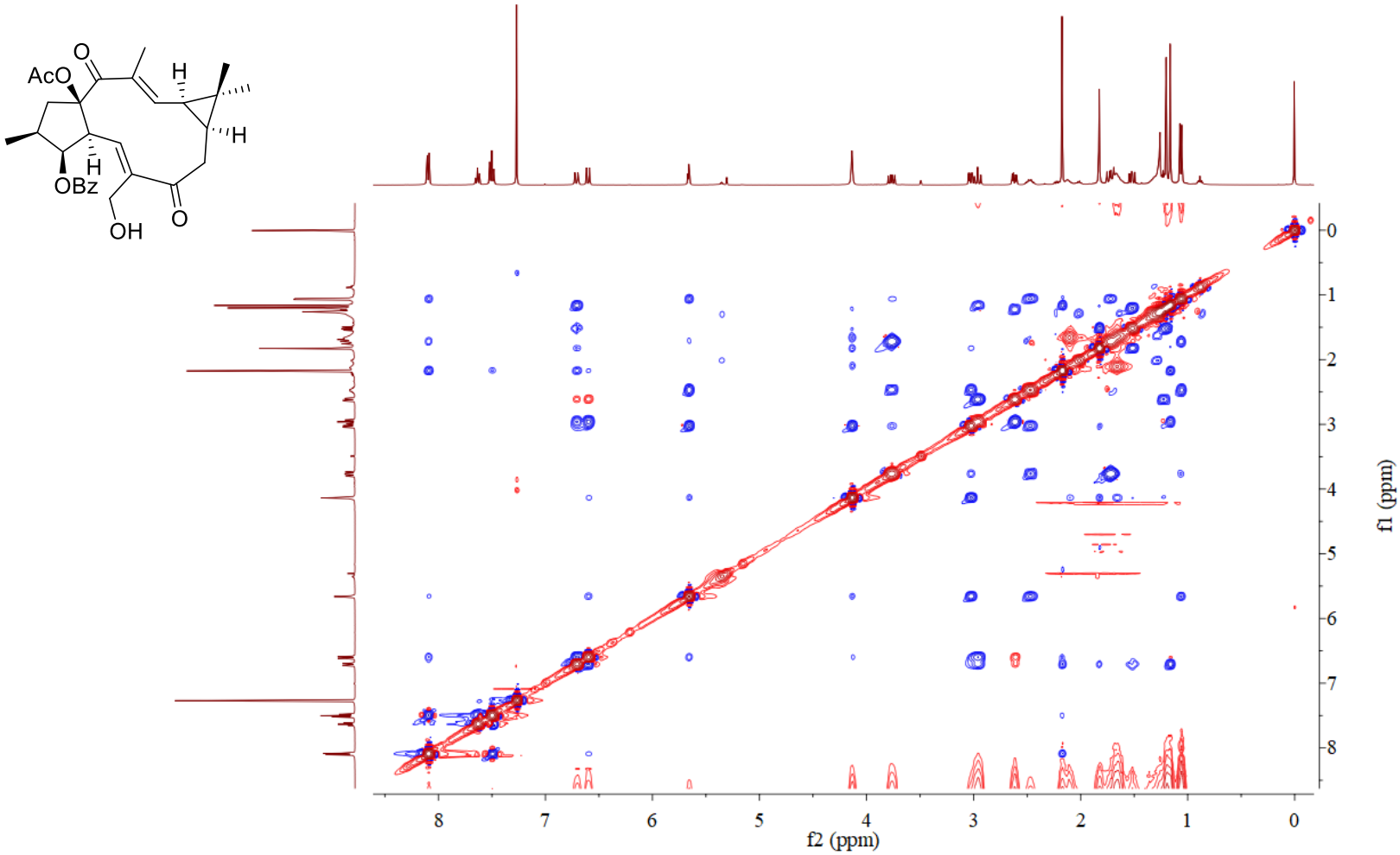


Figure S12. ^{1}H NMR spectrum of **2** in $CDCl_3$.

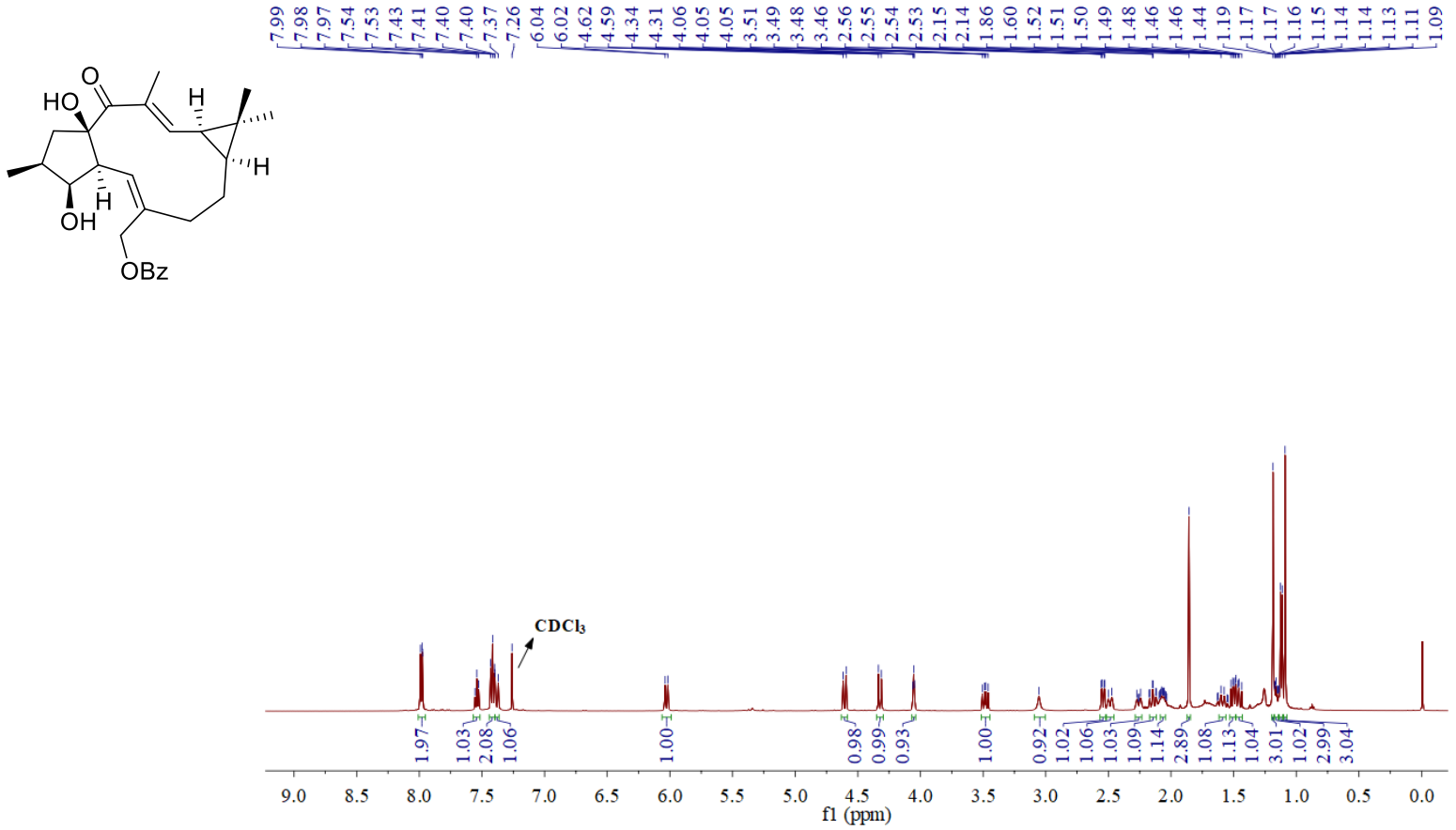


Figure S13. ^{13}C NMR and DEPT 135 spectra of **2** in $CDCl_3$.

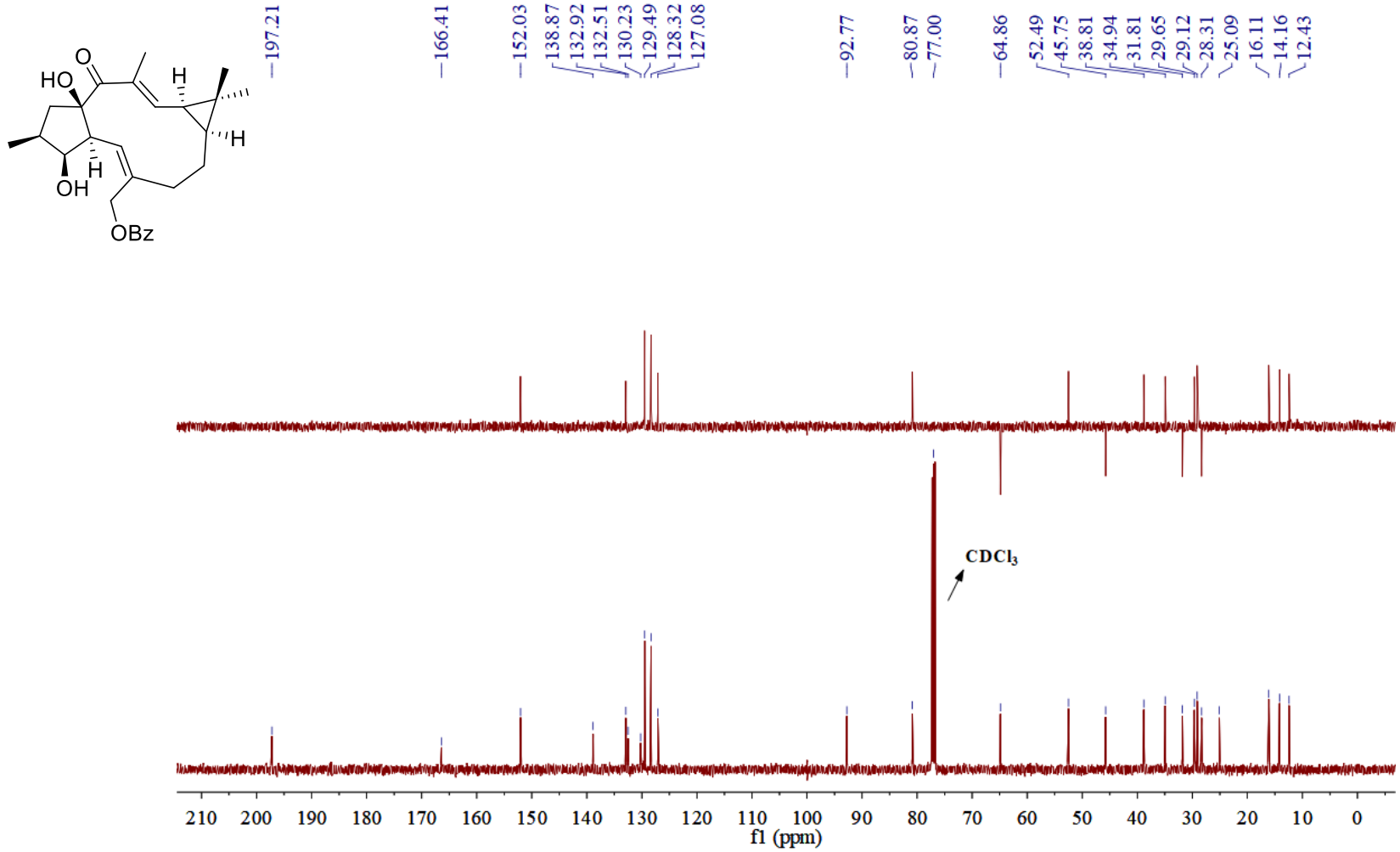


Figure S14. HSQC spectrum of **2** in $CDCl_3$.

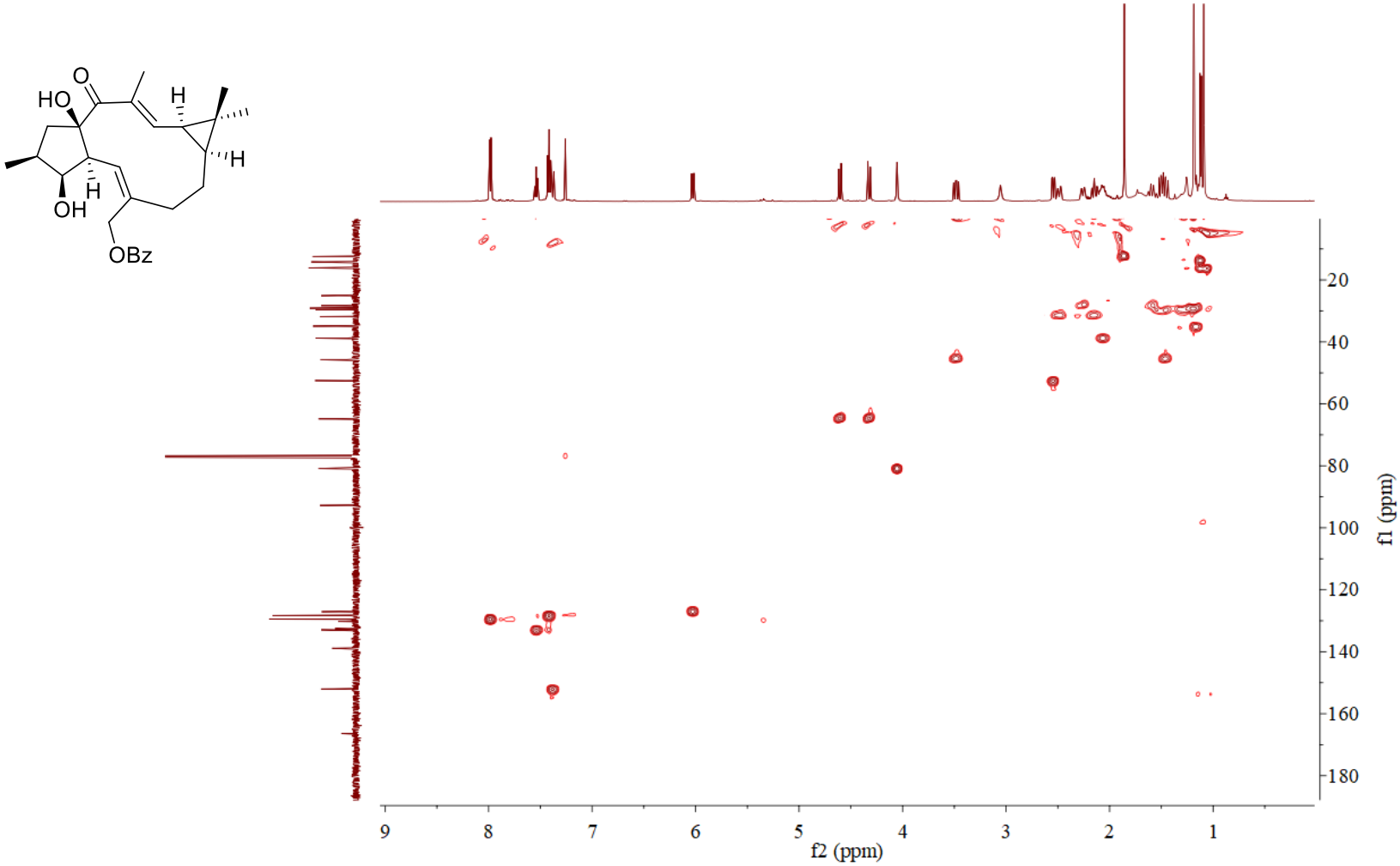


Figure S15. HMBC spectrum of **2** in $CDCl_3$.

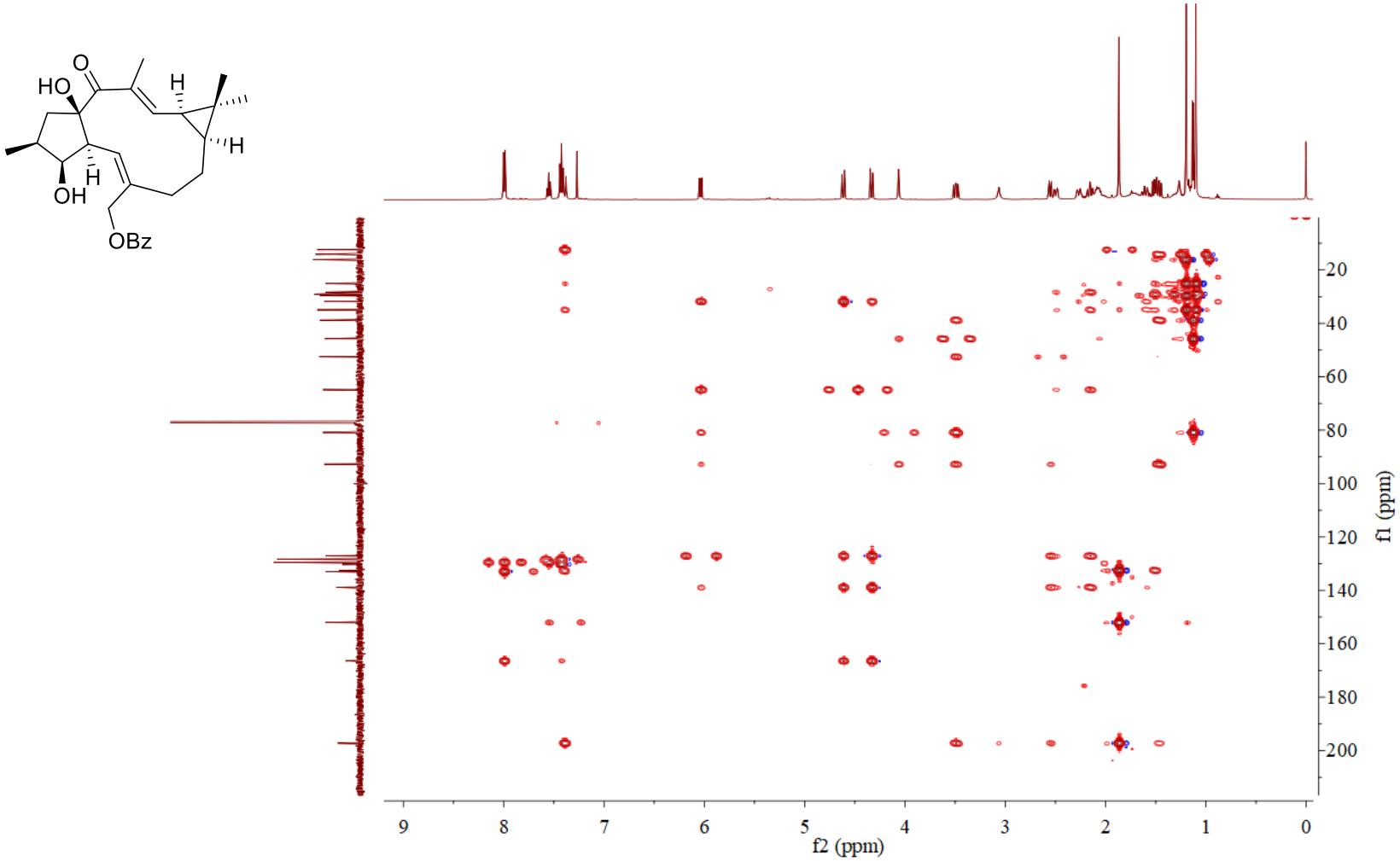


Figure S16. $^{1}H–^{1}H$ COSY spectrum of **2** in $CDCl_3$.

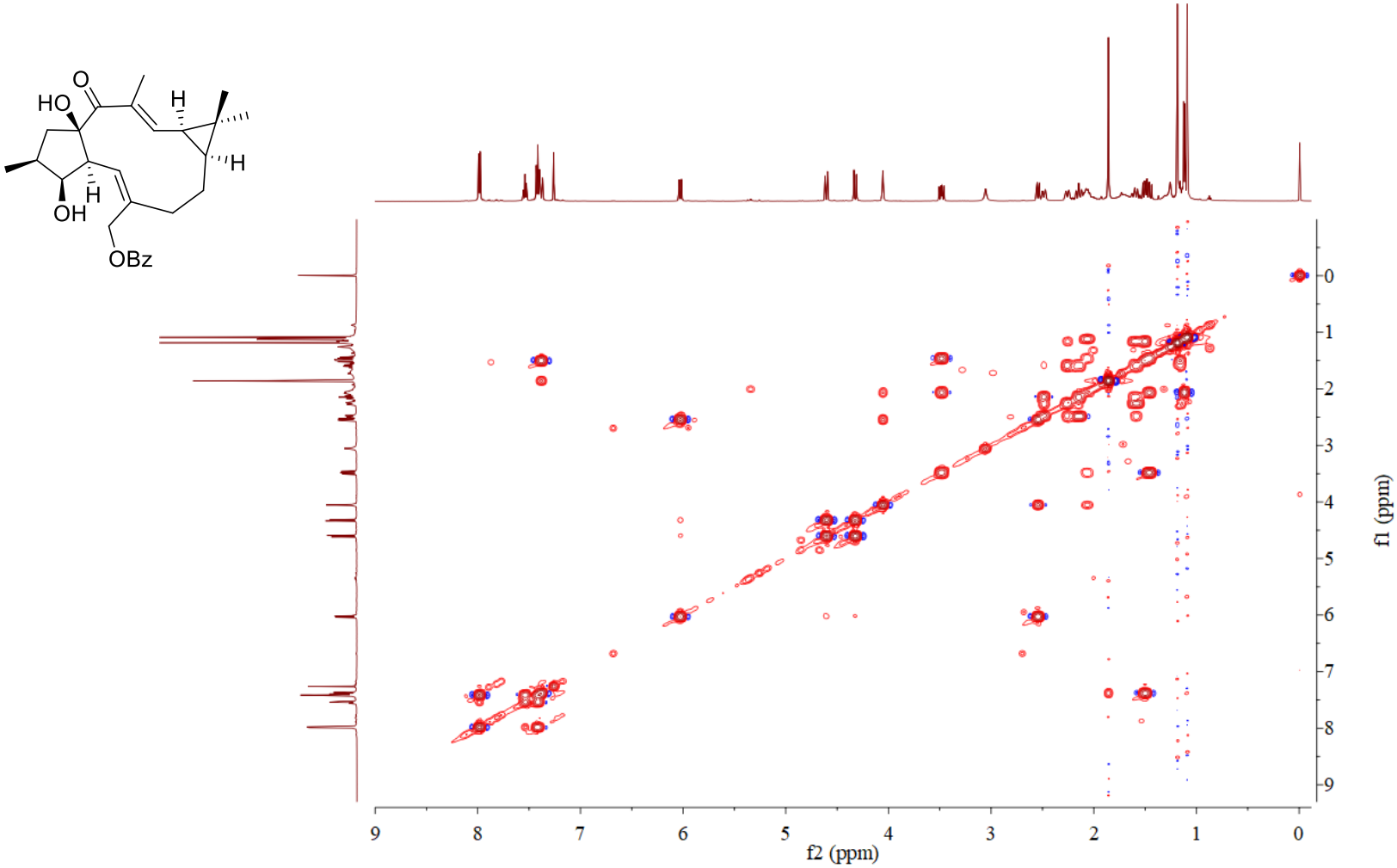


Figure S17. NOESY spectrum of **2** in $CDCl_3$.

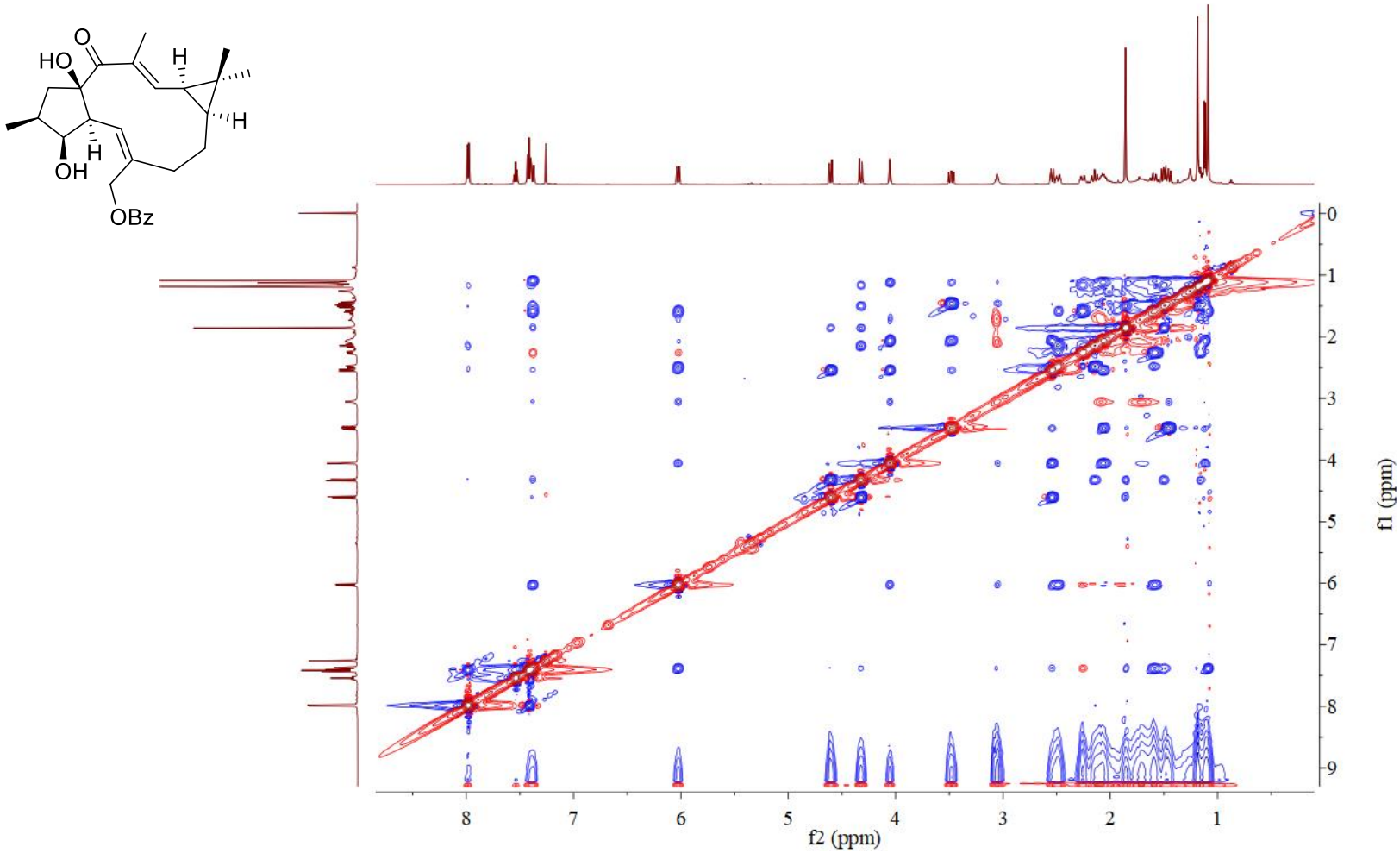


Figure S18. ^{1}H NMR spectrum of **3** in $CDCl_3$.

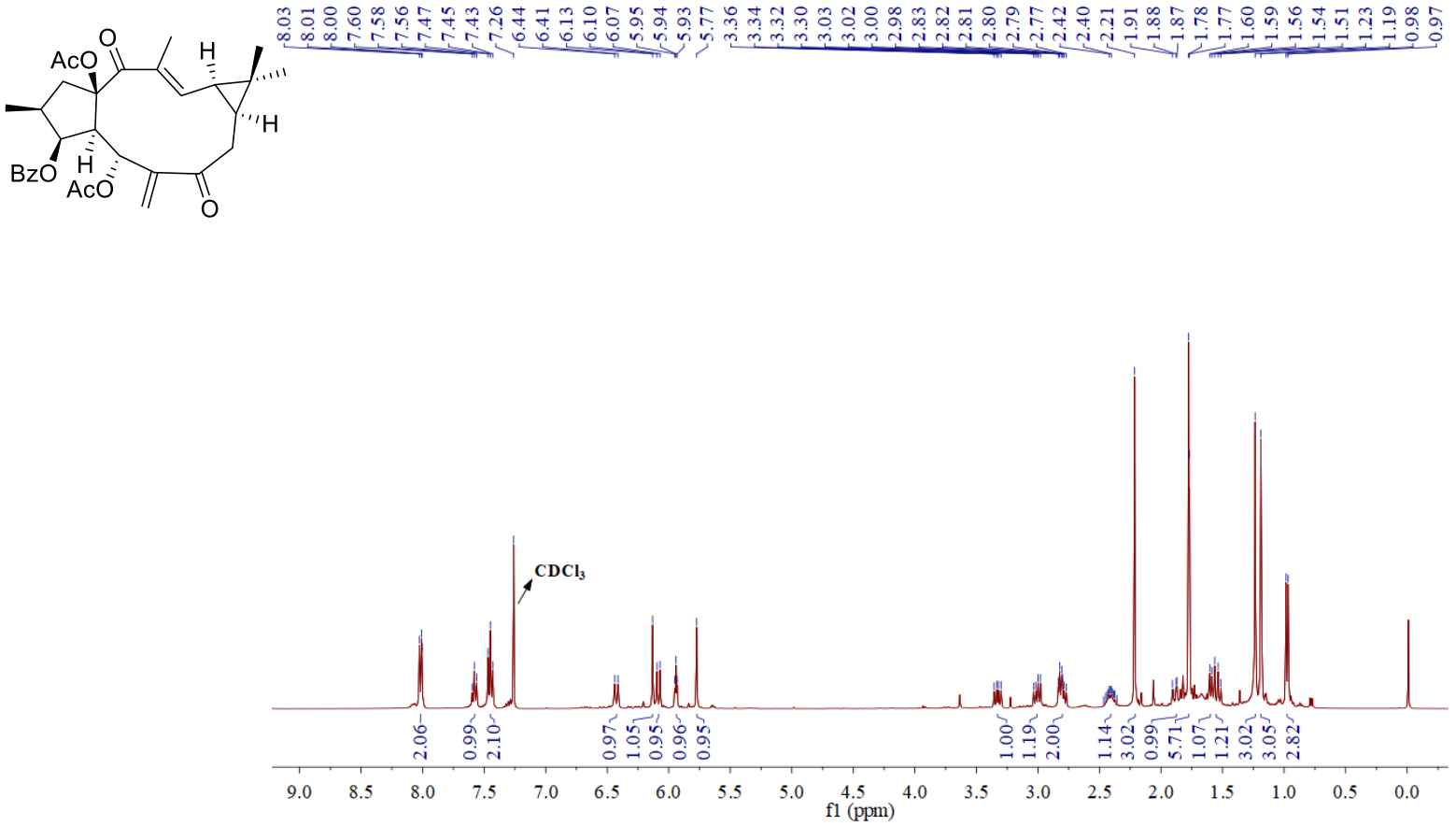


Figure S19. ^{13}C NMR and DEPT 135 spectra of **3** in $CDCl_3$.

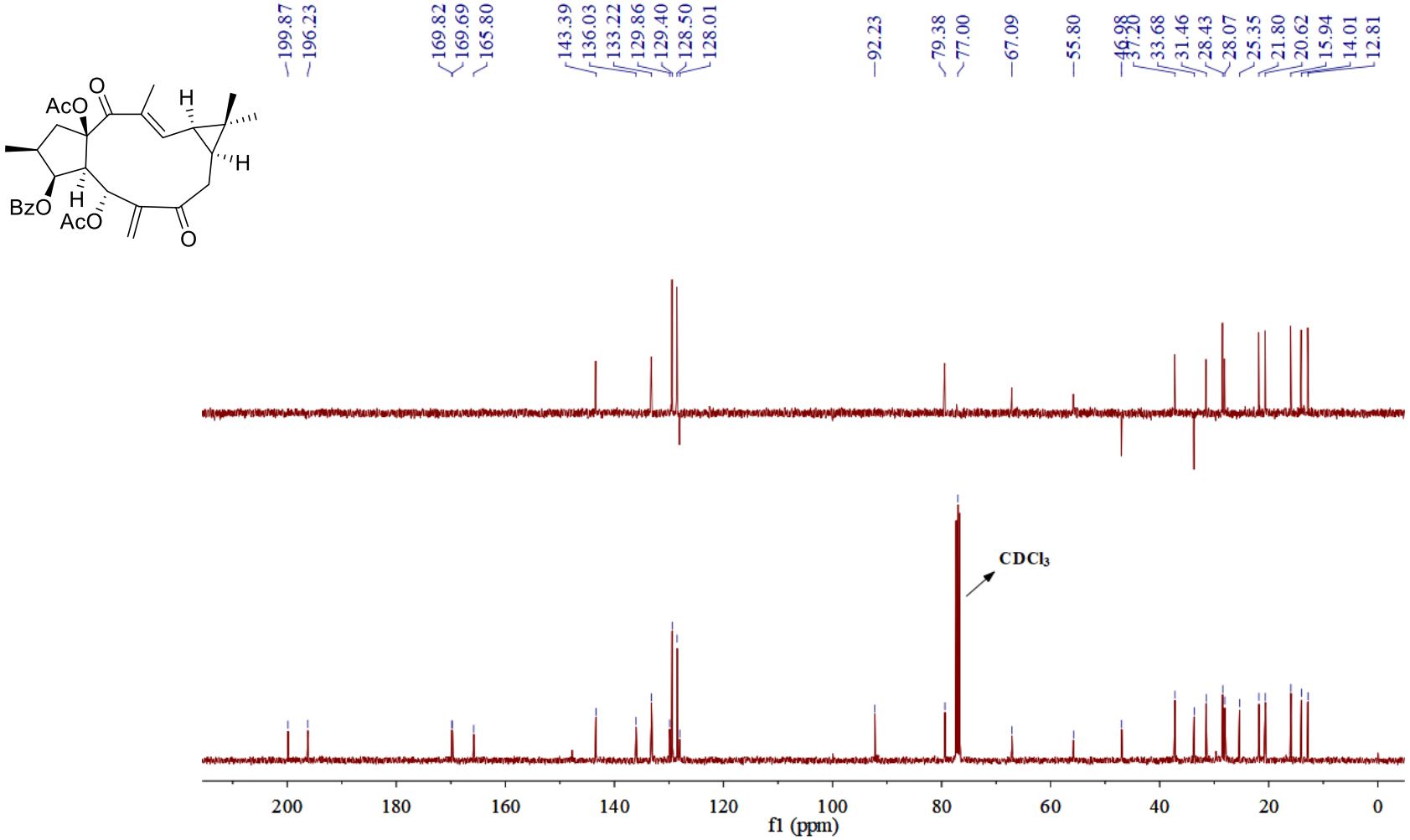
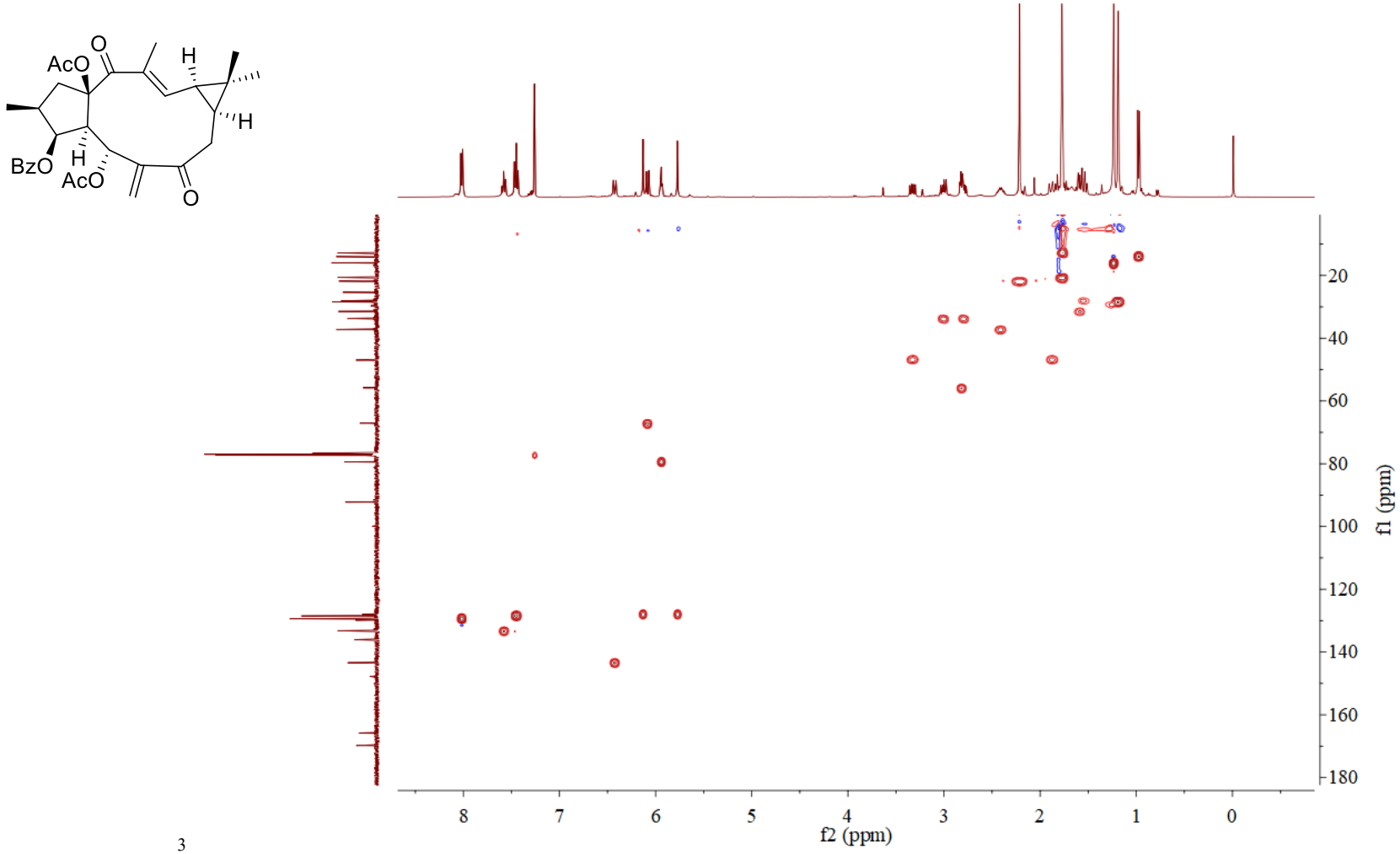


Figure S20. HSQC spectrum of **3** in $CDCl_3$.



3

Figure S21. HMBC spectrum of **3** in $CDCl_3$.

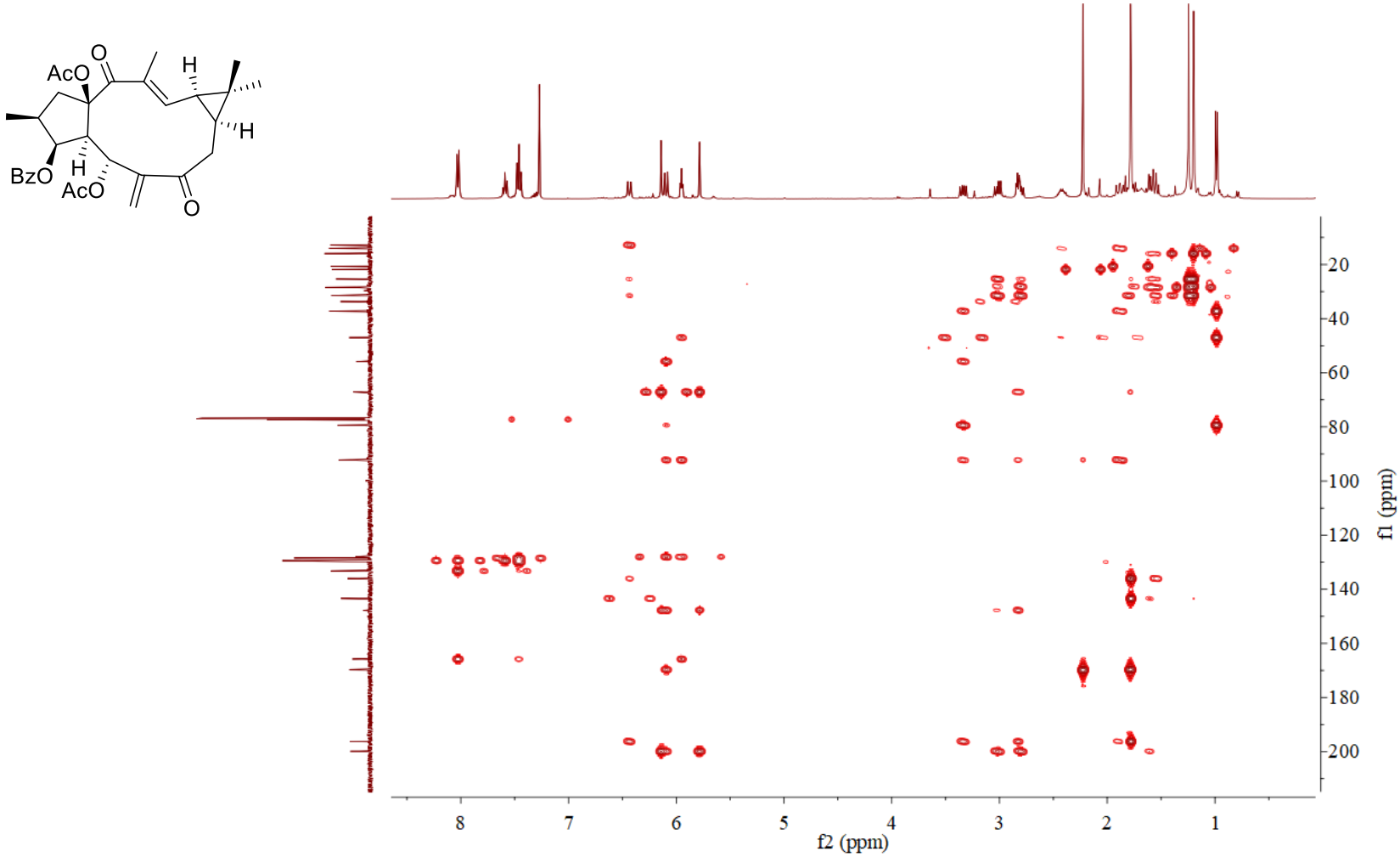


Figure S22. $^{1}H–^{1}H$ COSY spectrum of **3** in $CDCl_3$.

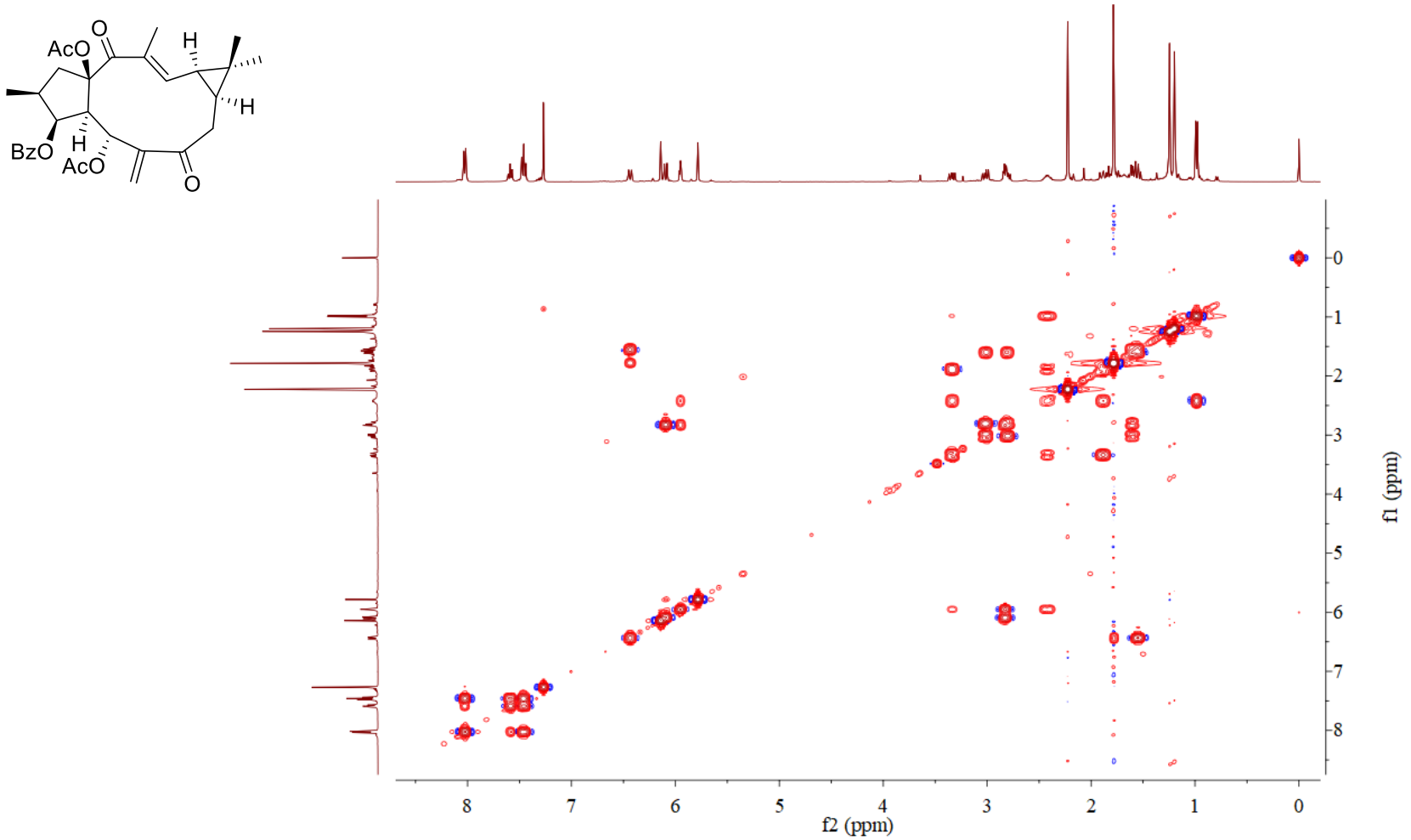


Figure S23. NOESY spectrum of **3** in $CDCl_3$.

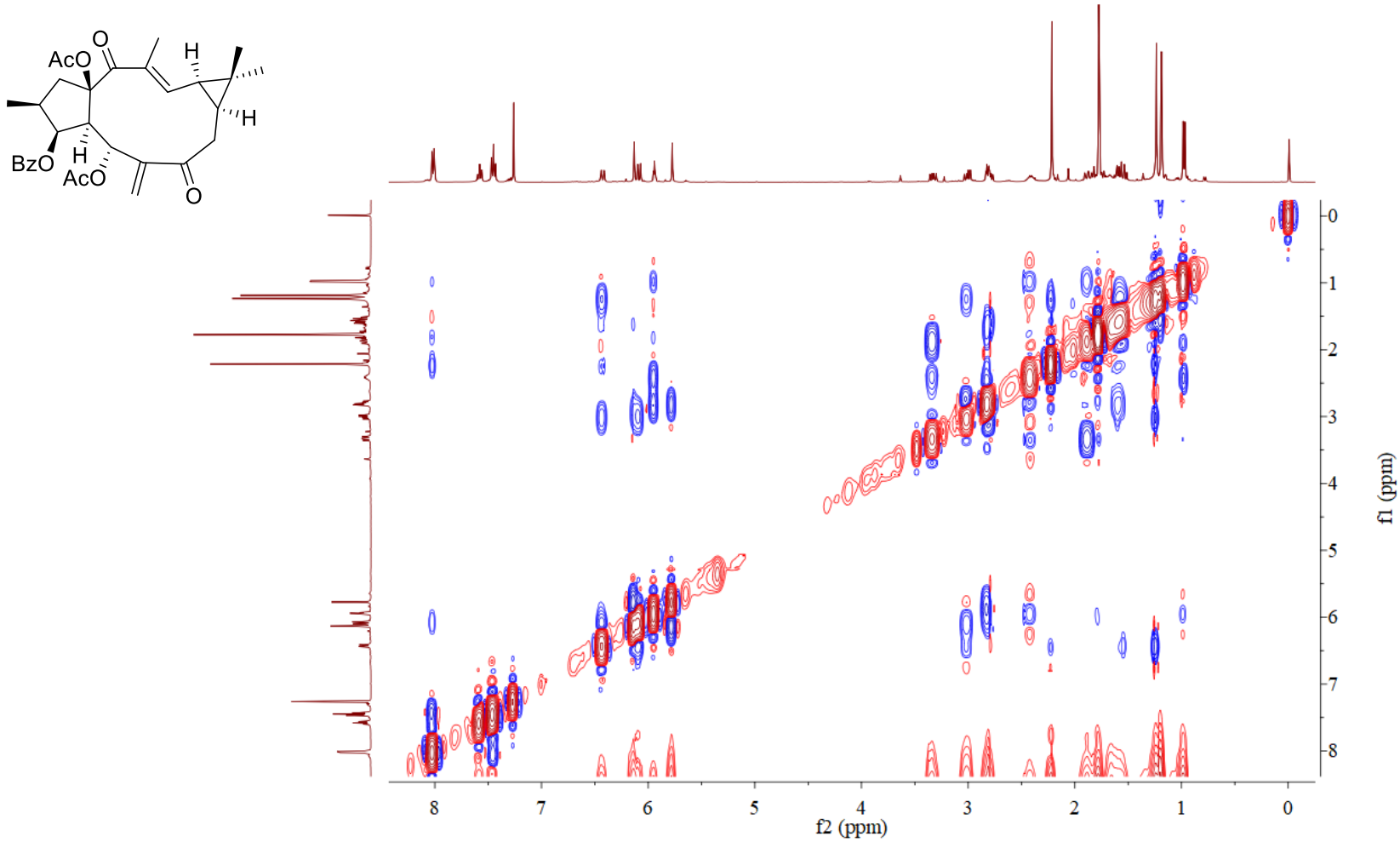


Figure S24. ^{1}H NMR spectrum of **4** in $CDCl_3$.

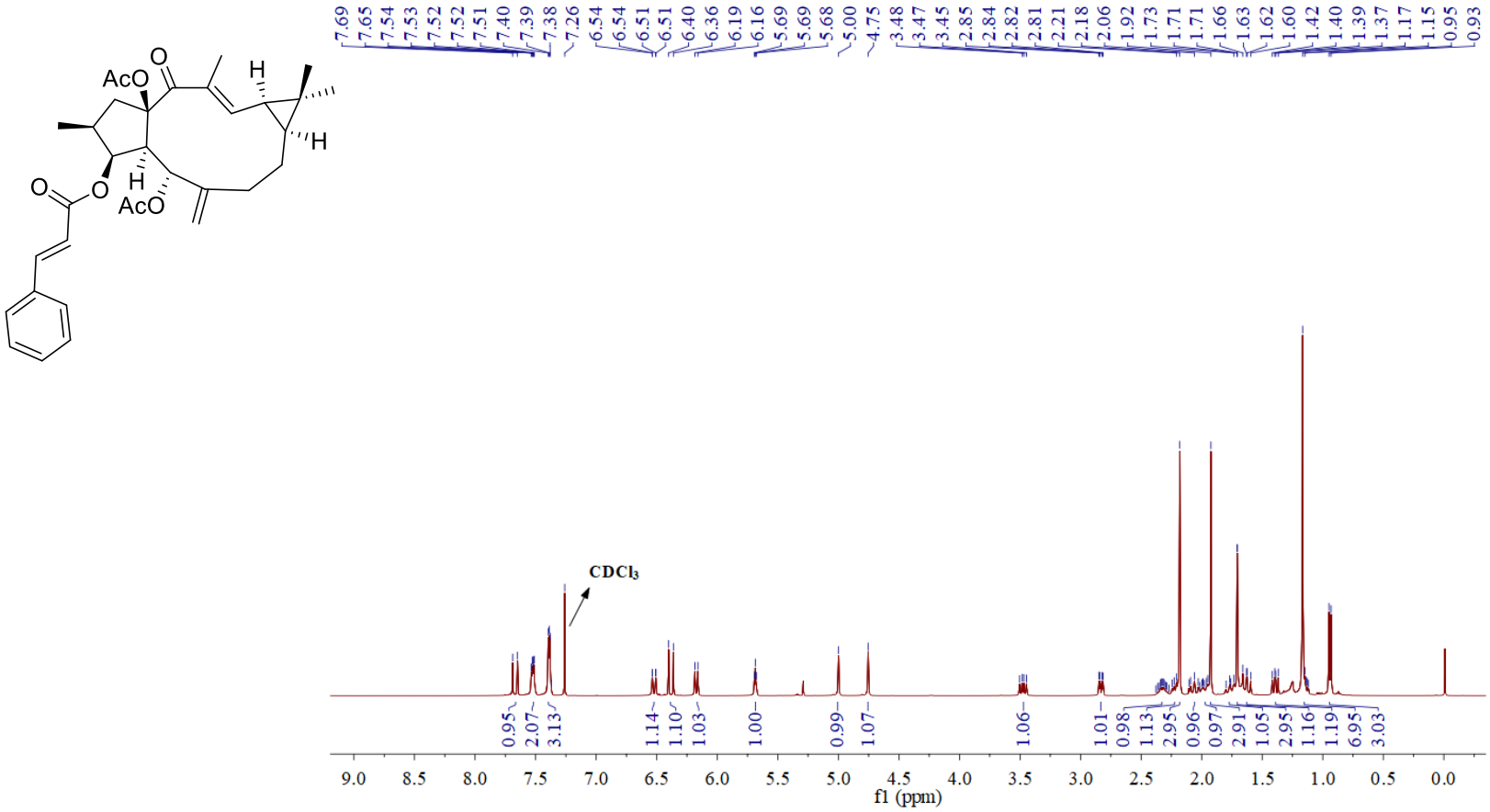


Figure S25. ^{13}C NMR and DEPT 135 spectra of **4** in $CDCl_3$.

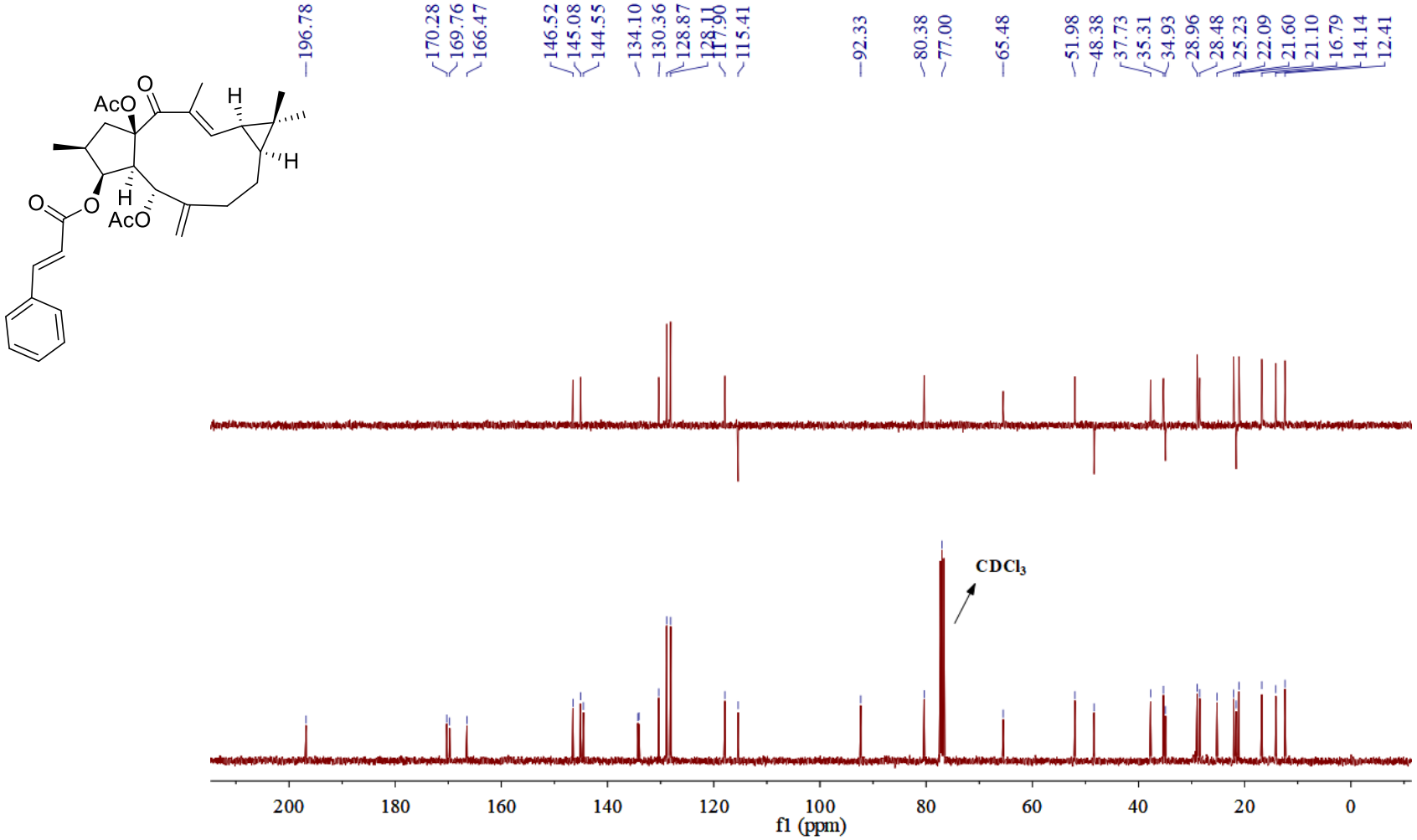


Figure S26. HSQC spectrum of **4** in $CDCl_3$.

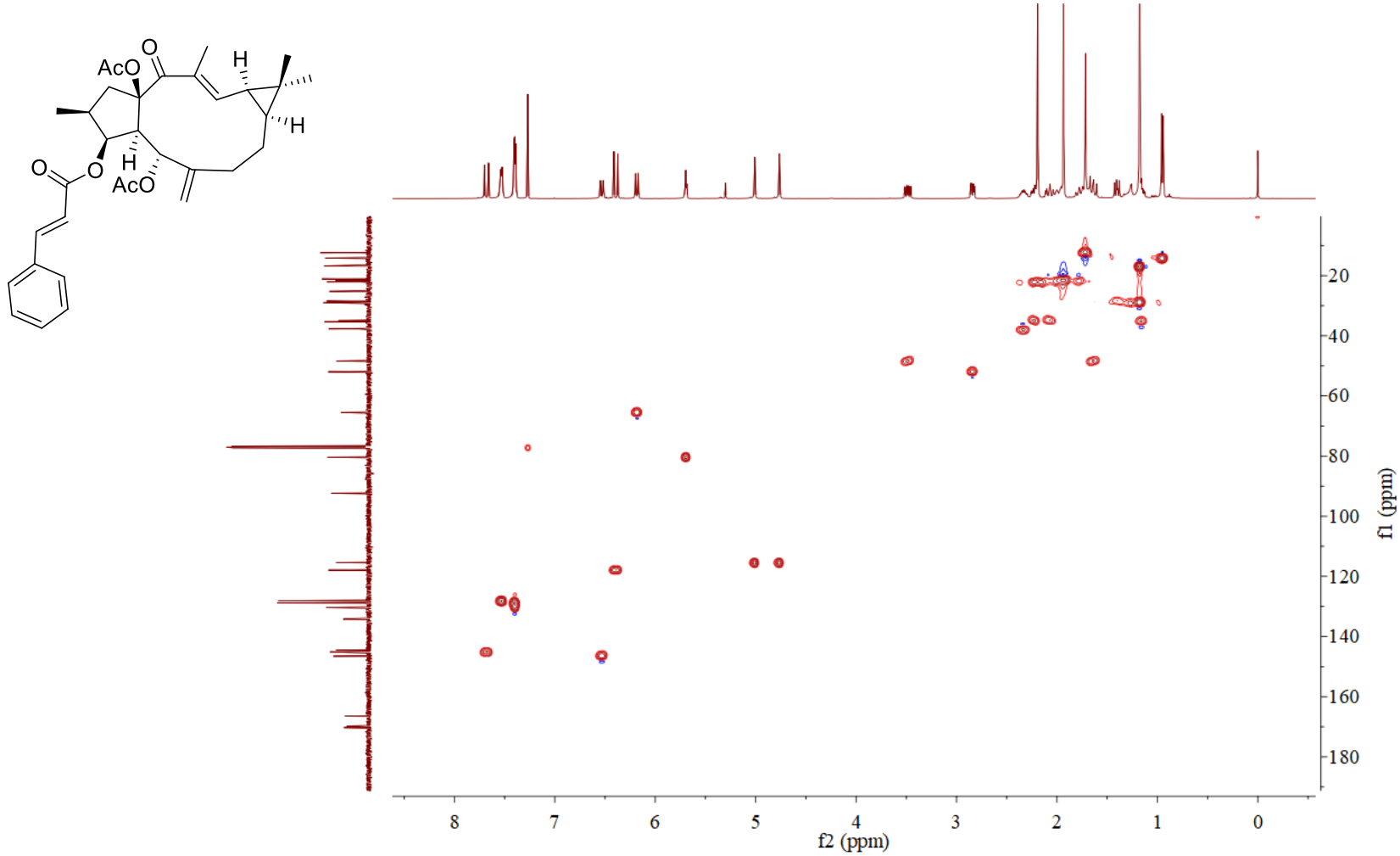


Figure S27. HMBC spectrum of **4** in $CDCl_3$.

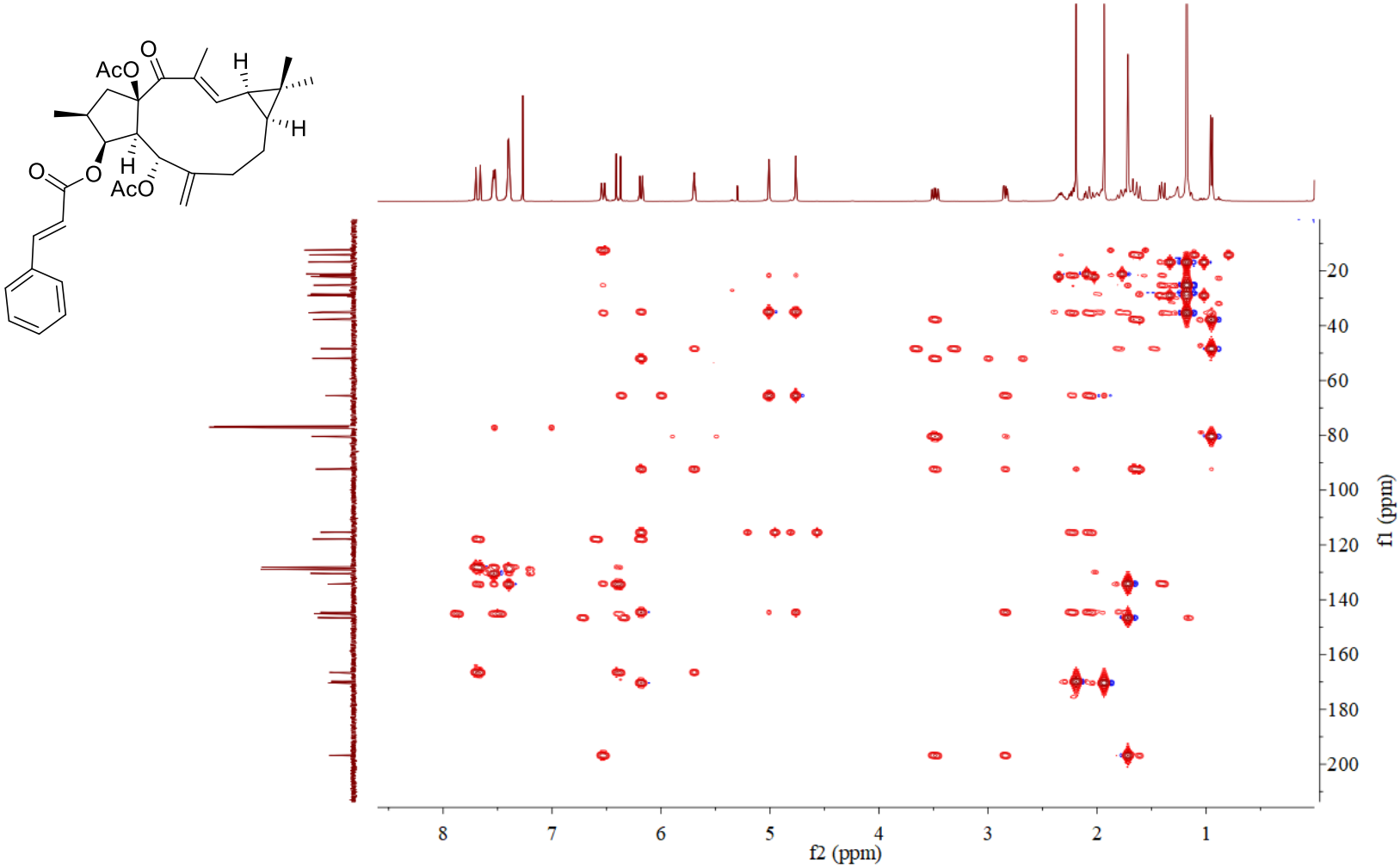


Figure S28. $^{1}H–^{1}H$ COSY spectrum of **4** in $CDCl_3$.

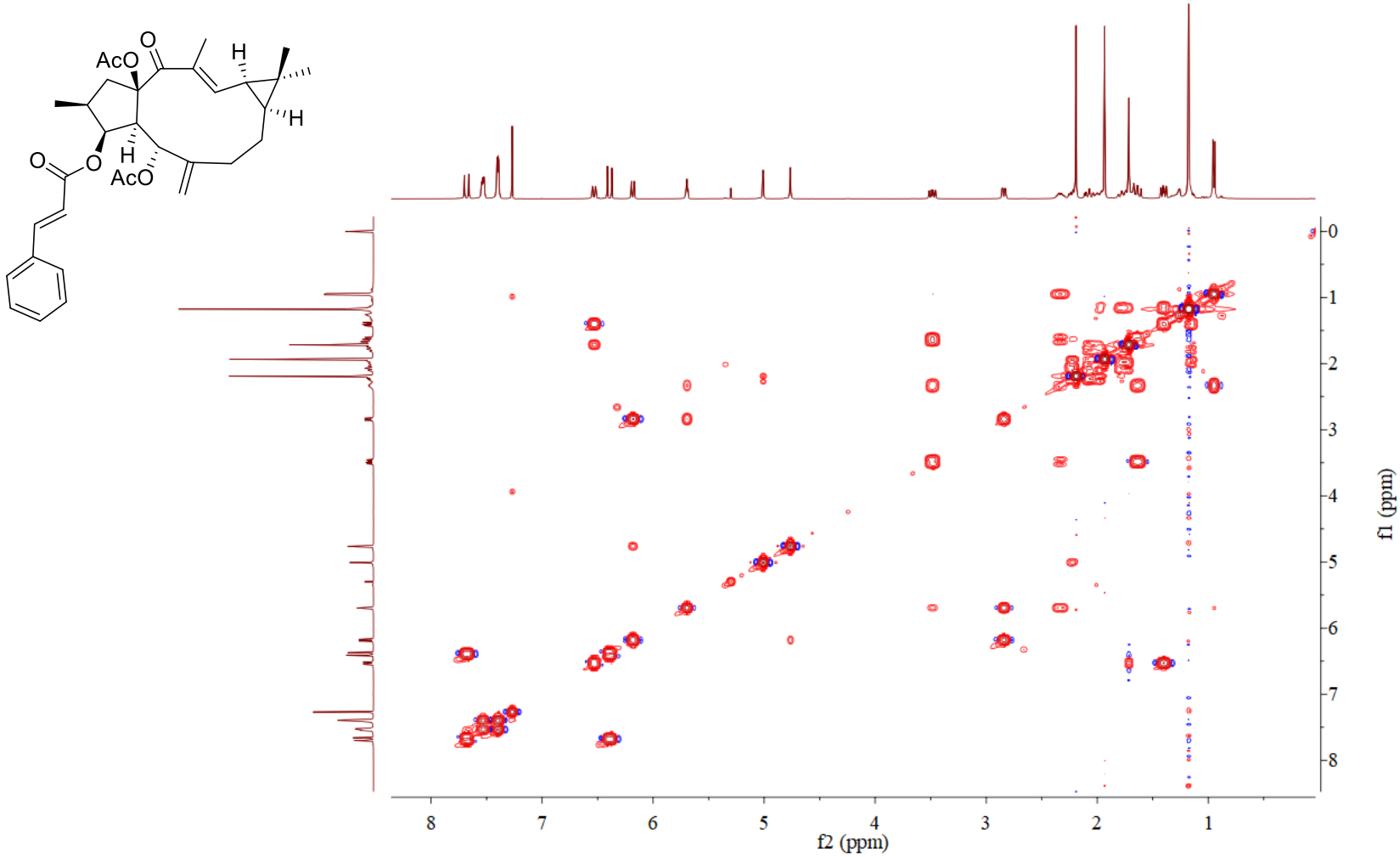


Figure S29. NOESY spectrum of **4** in $CDCl_3$.

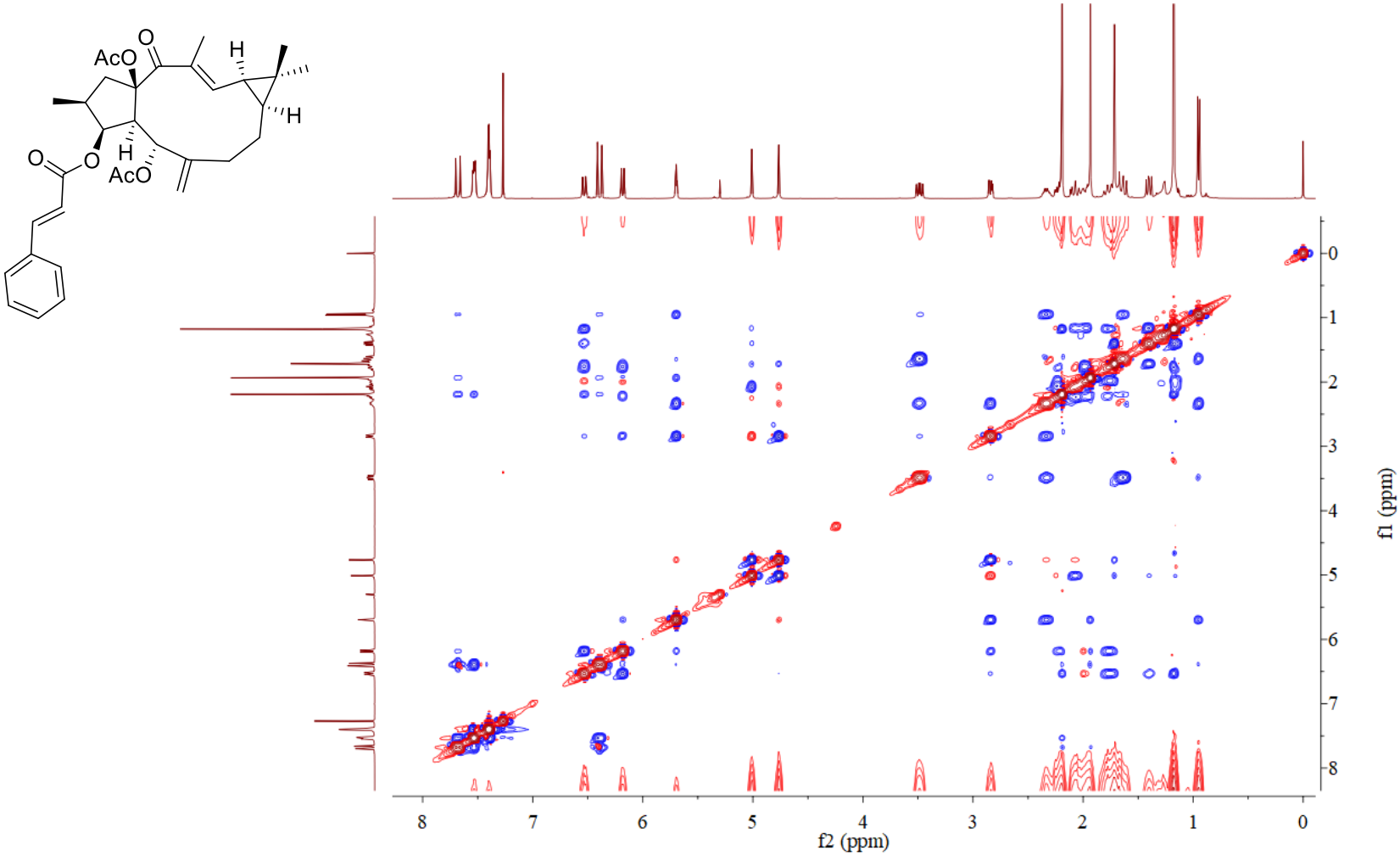


Figure S30. ^{1}H NMR spectrum of **5** in $CDCl_3$.

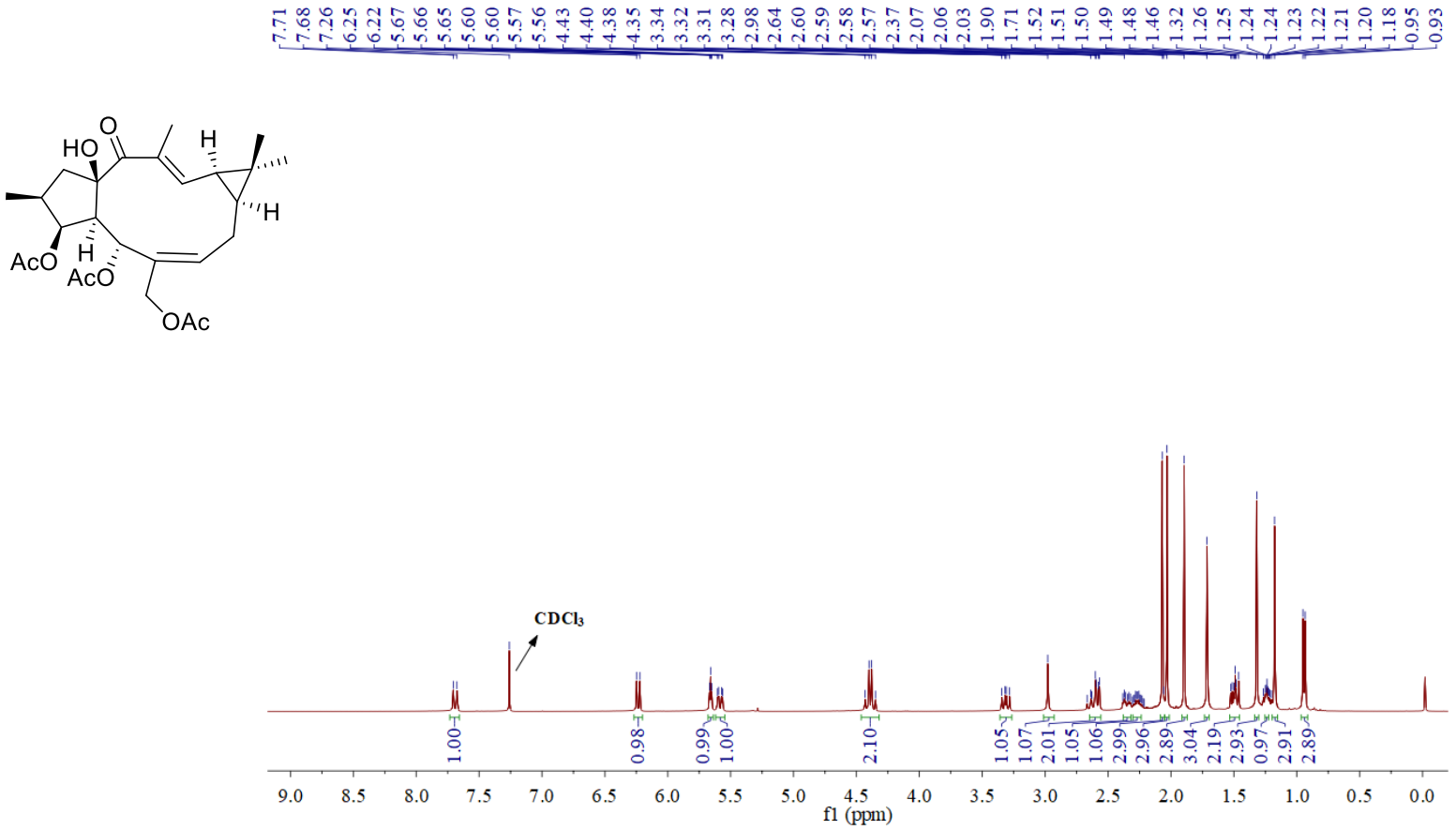


Figure S31. ^{13}C NMR and DEPT 135 spectra of **5** in $CDCl_3$.

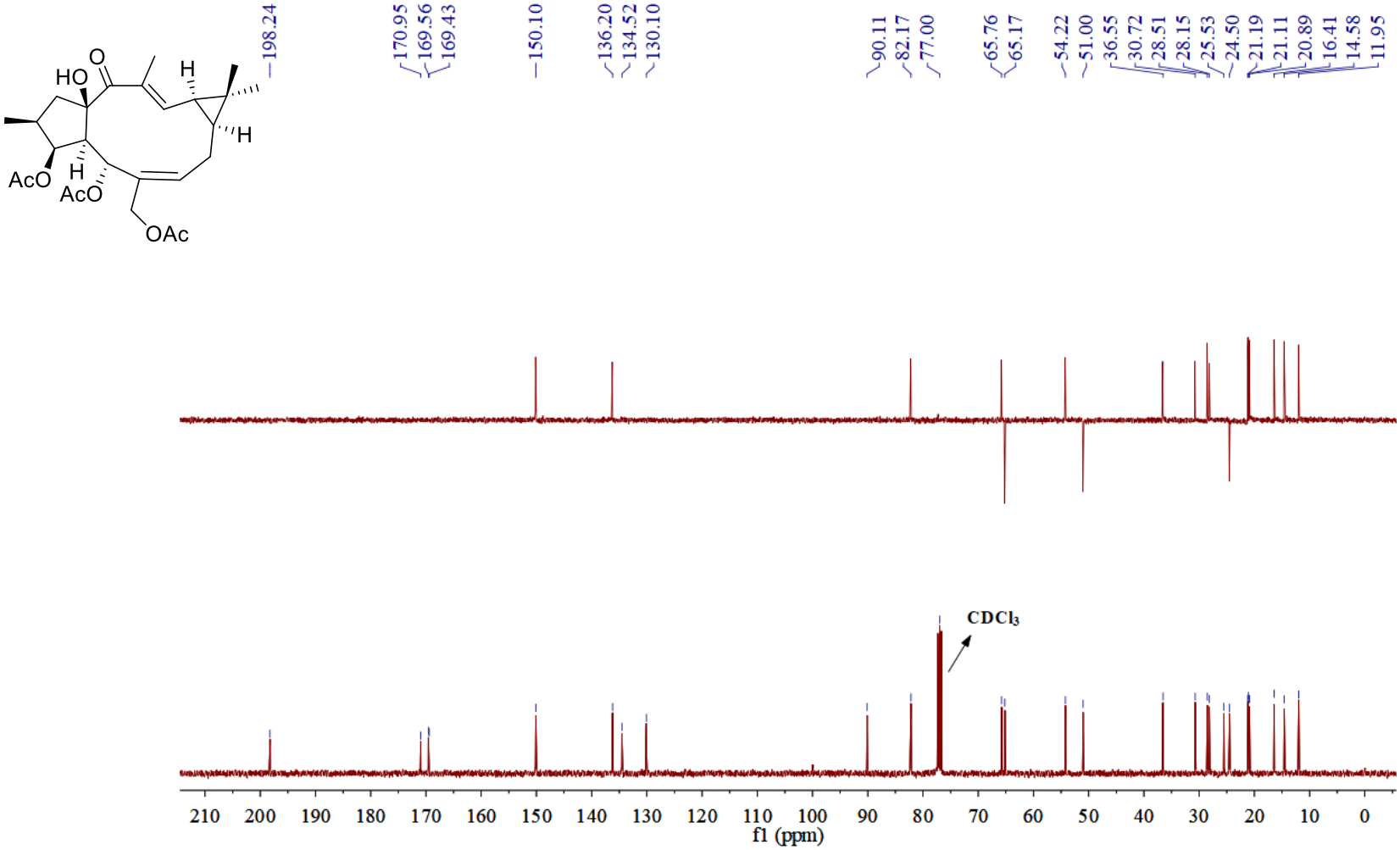


Figure S32. HSQC spectrum of **5** in $CDCl_3$.

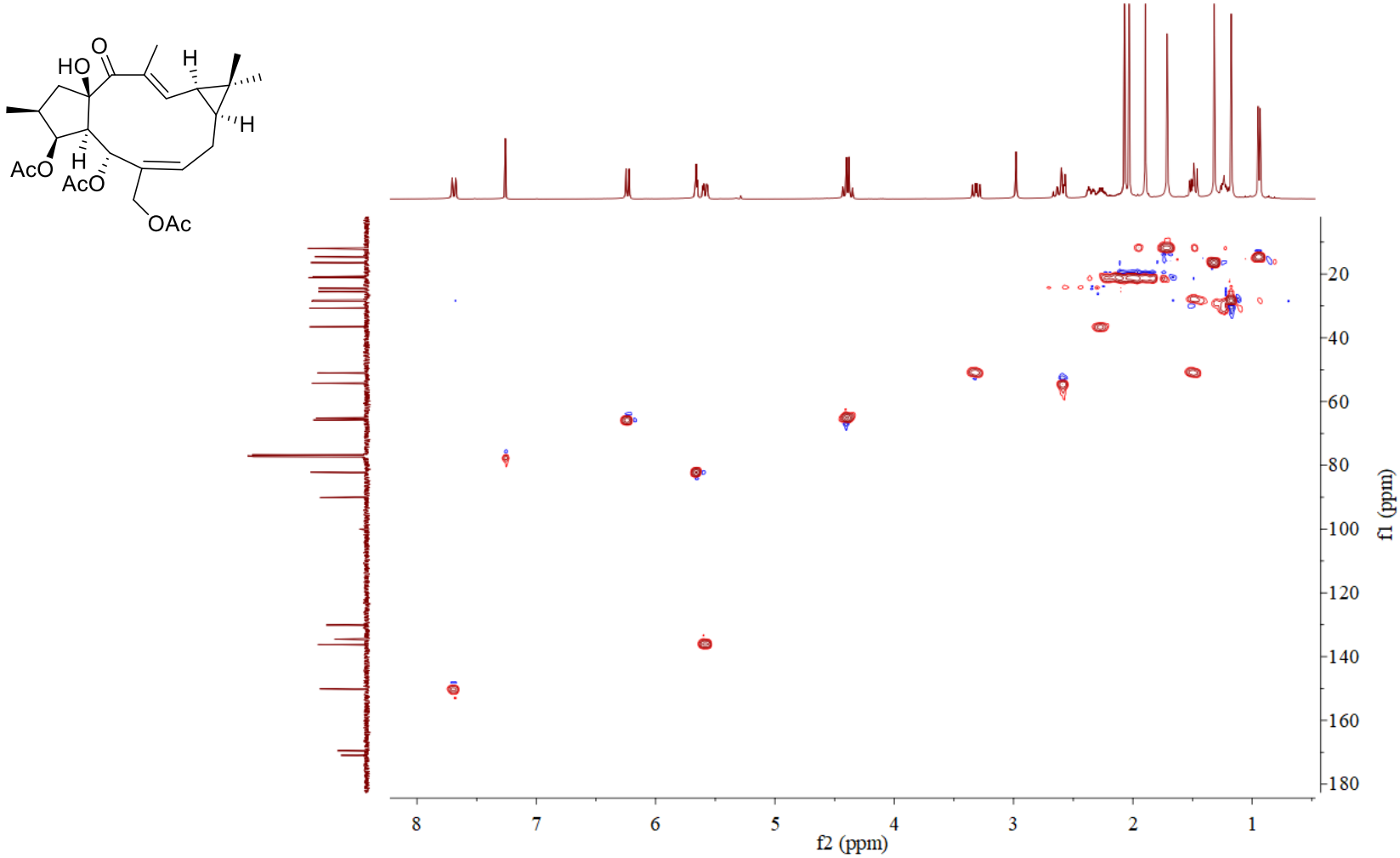


Figure S33. HMBC spectrum of **5** in $CDCl_3$.

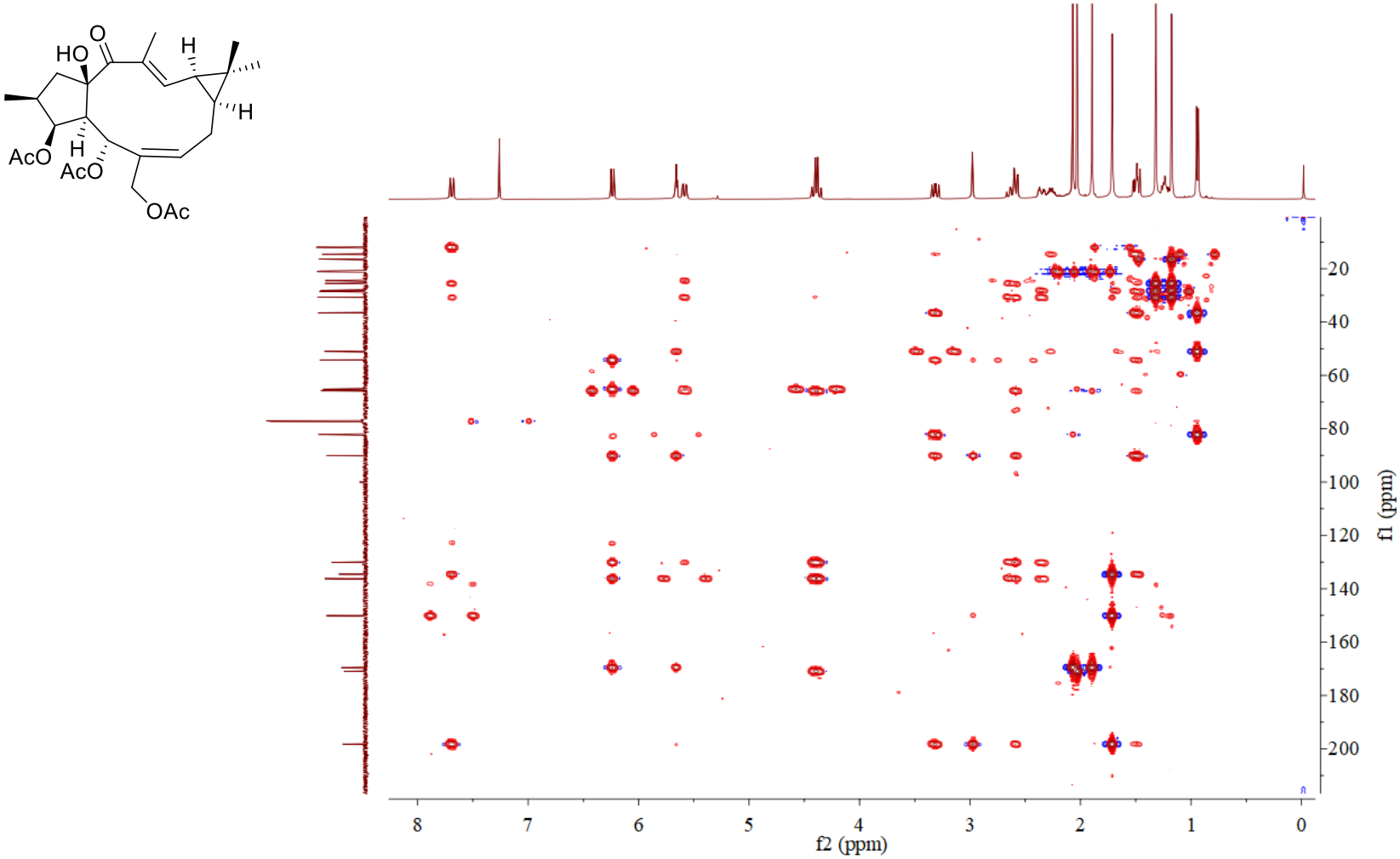


Figure S34. $^{1}H–^{1}H$ COSY spectrum of **5** in $CDCl_3$.

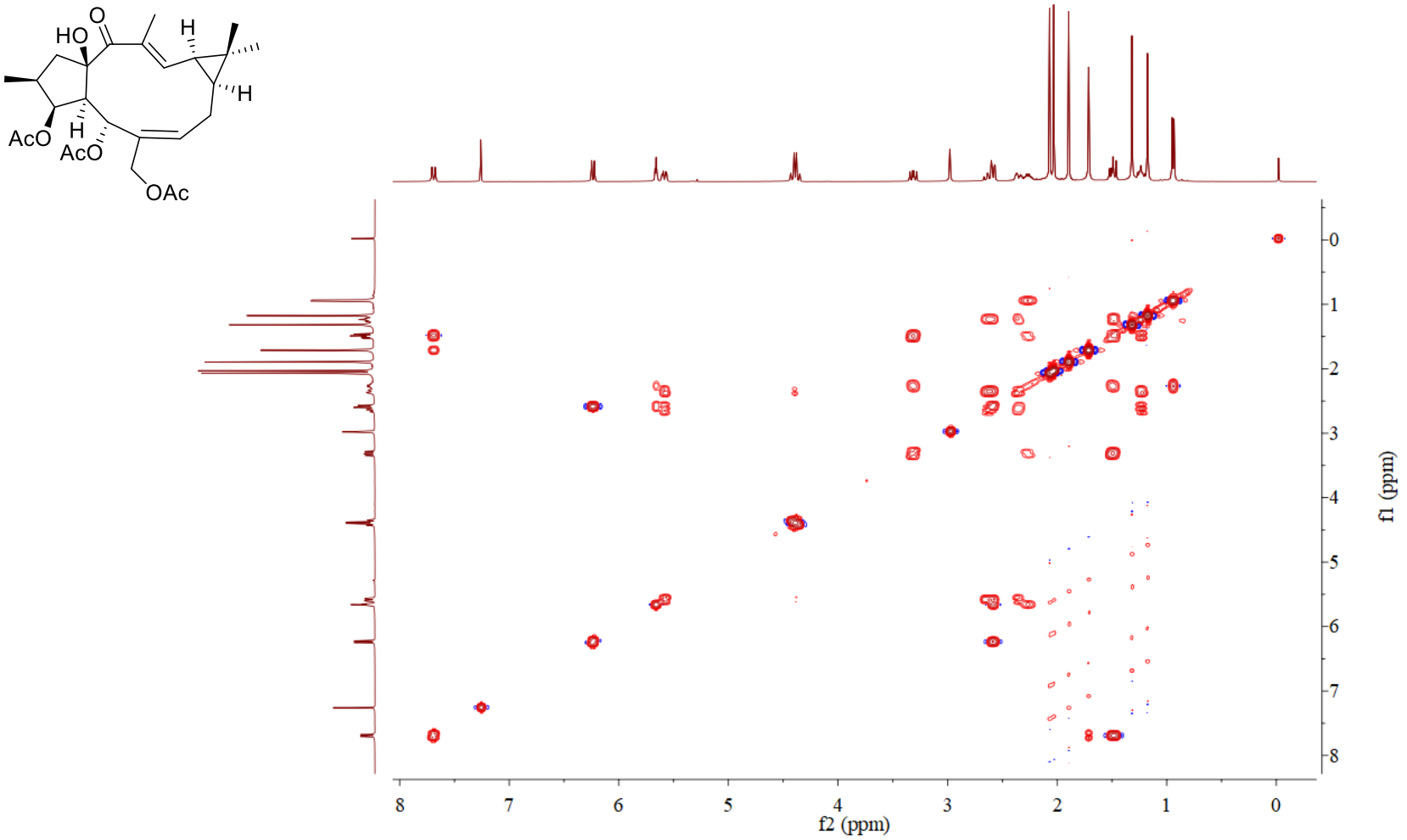


Figure S35. NOESY spectrum of **5** in $CDCl_3$.

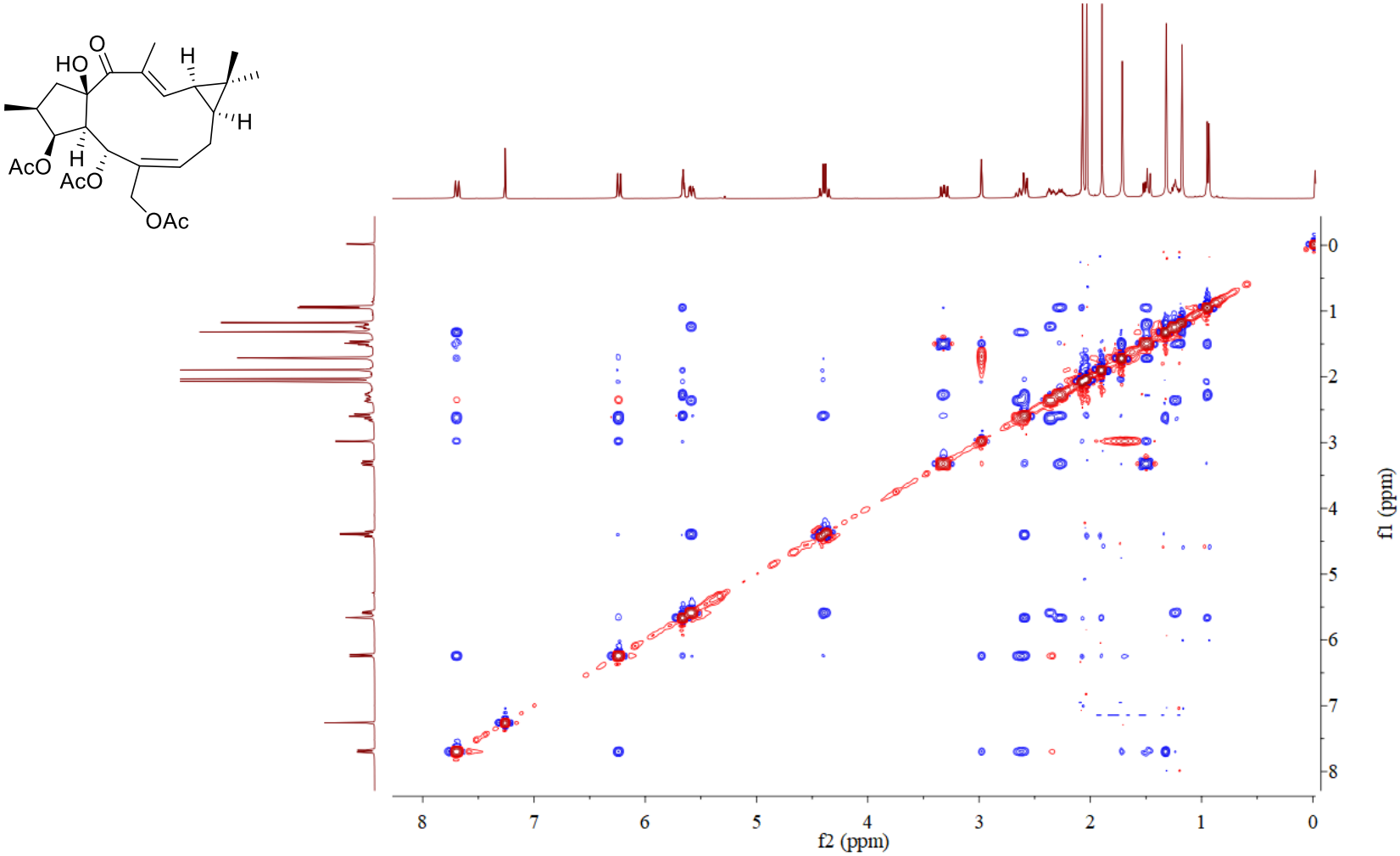


Figure S36. ^{1}H NMR spectrum of **20** in $CDCl_3$.

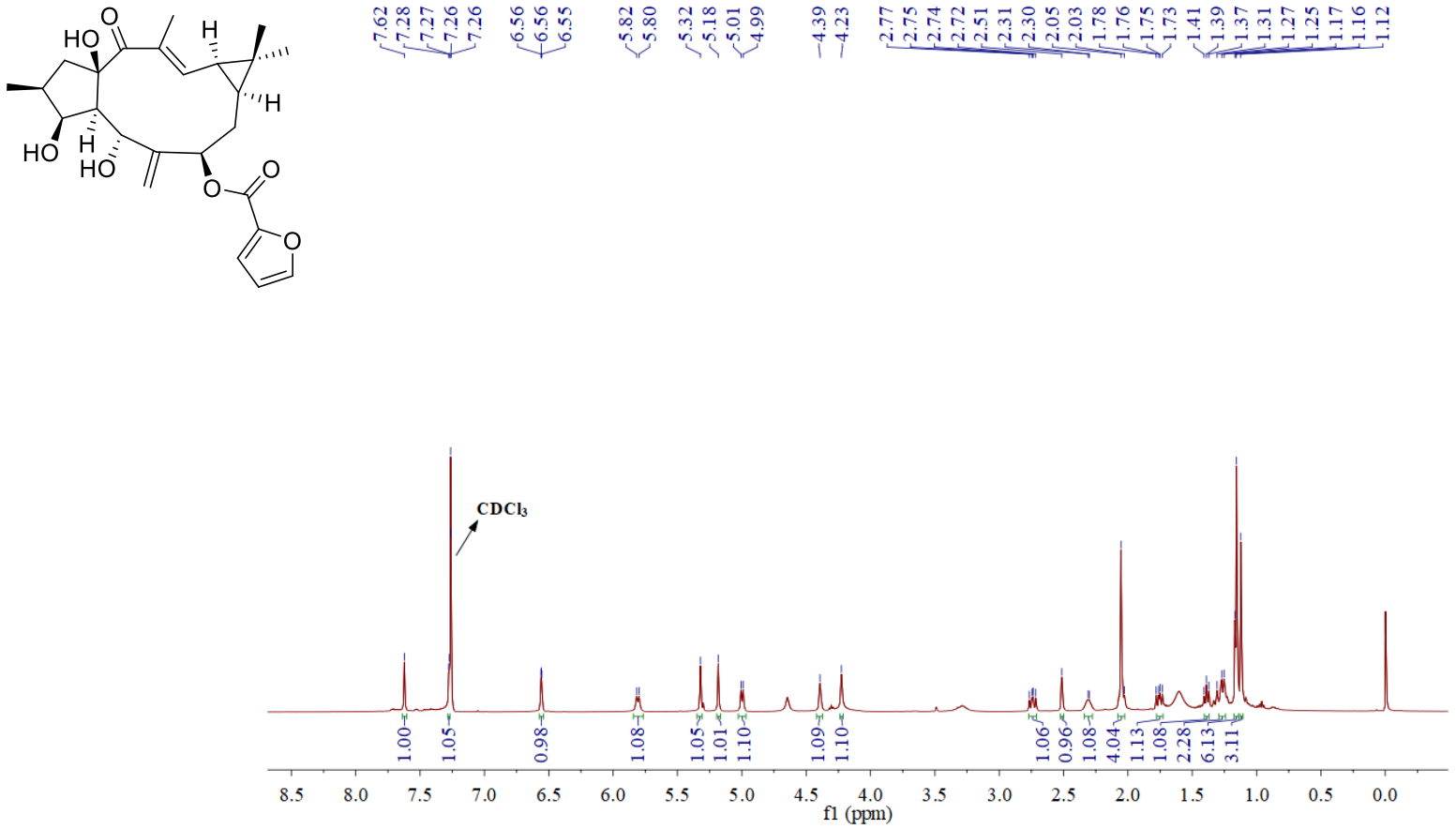


Figure S37. ^{13}C NMR and DEPT 135 spectra of **20** in $CDCl_3$.

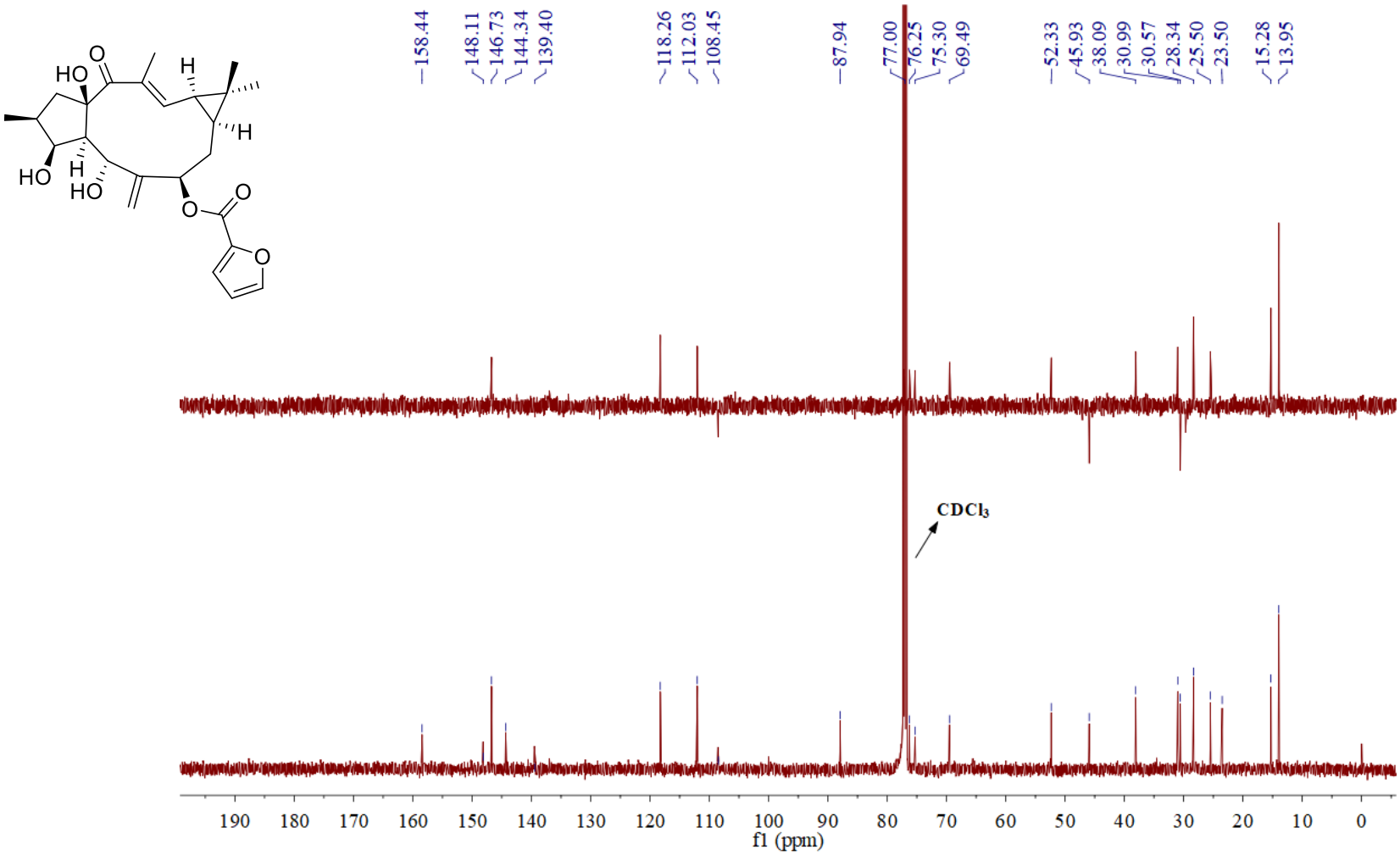


Figure S38. HSQC spectrum of **20** in $CDCl_3$.

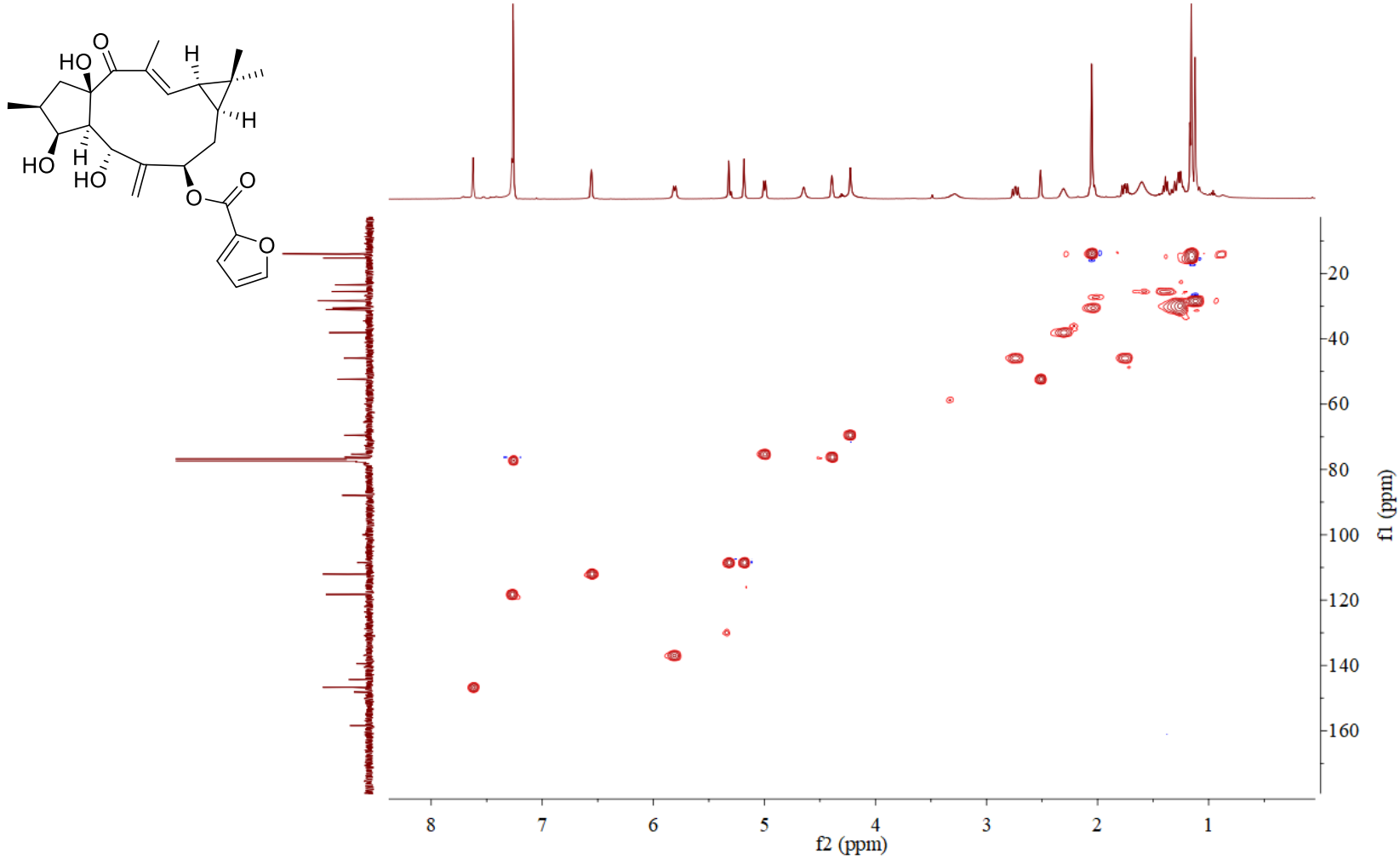


Figure S39. HMBC spectrum of **20** in $CDCl_3$.

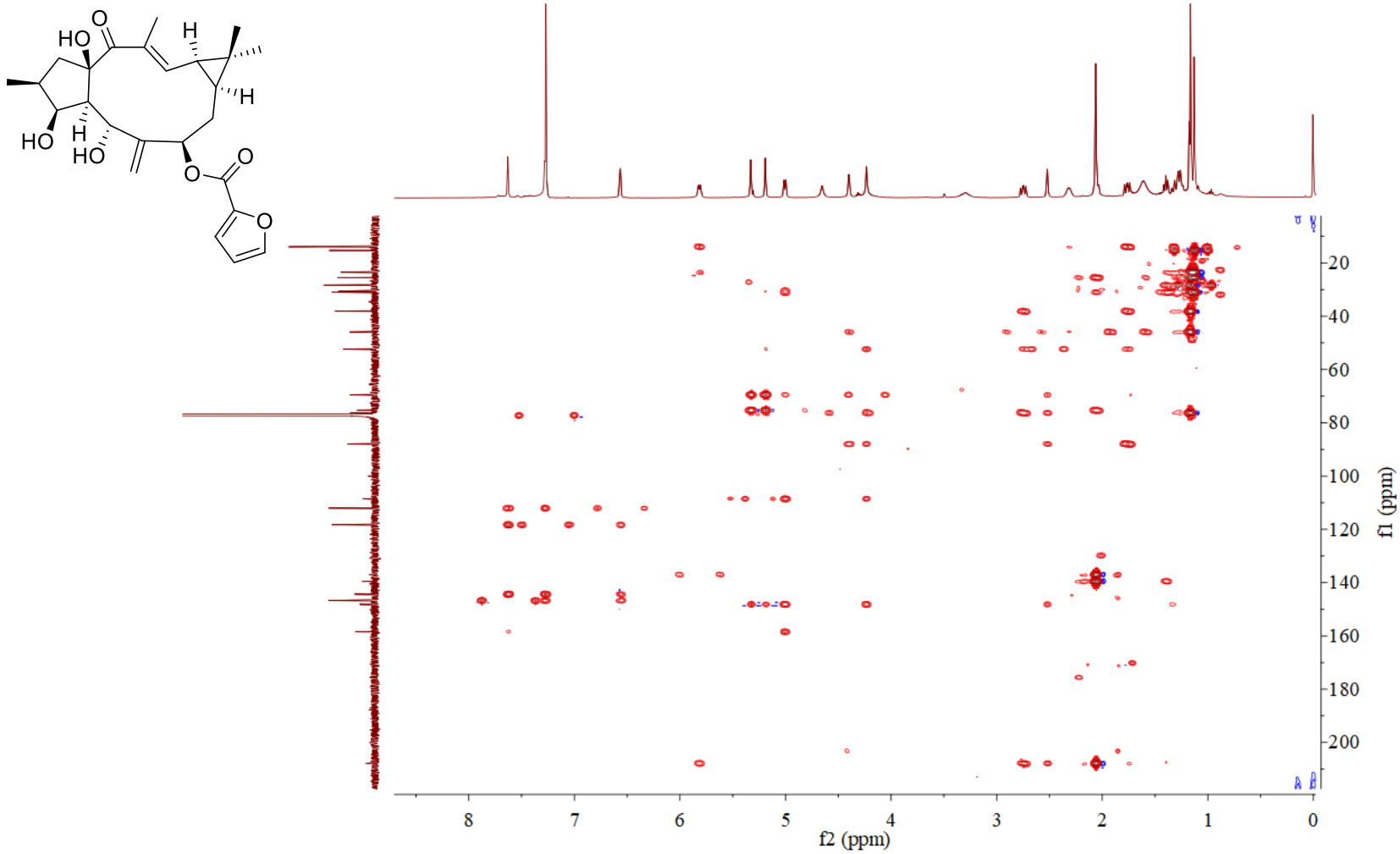


Figure S40. $^{1}H–^{1}H$ COSY spectrum of **20** in $CDCl_3$.

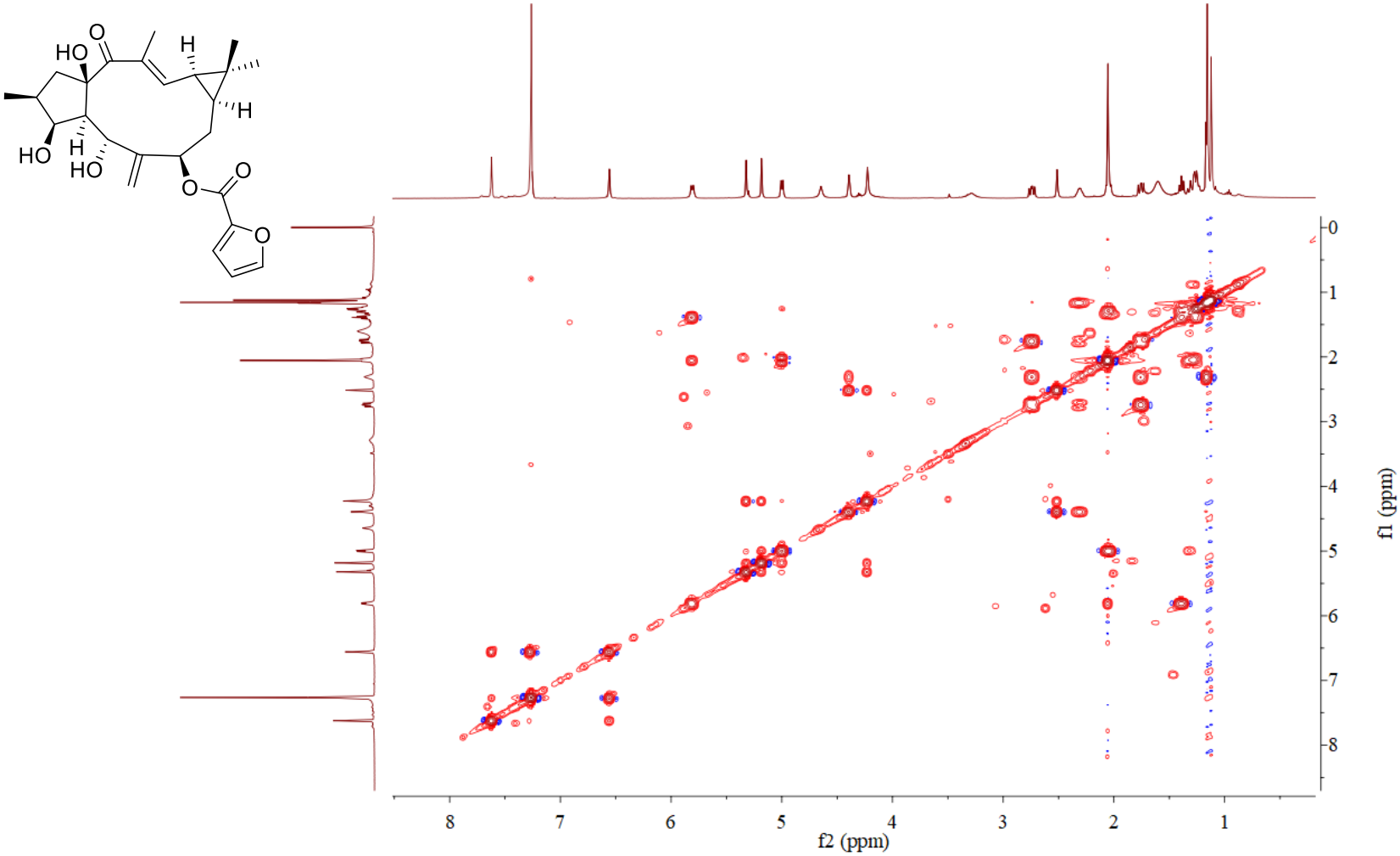


Figure S41. ^{1}H NMR spectra of **21** in $CDCl_3$.

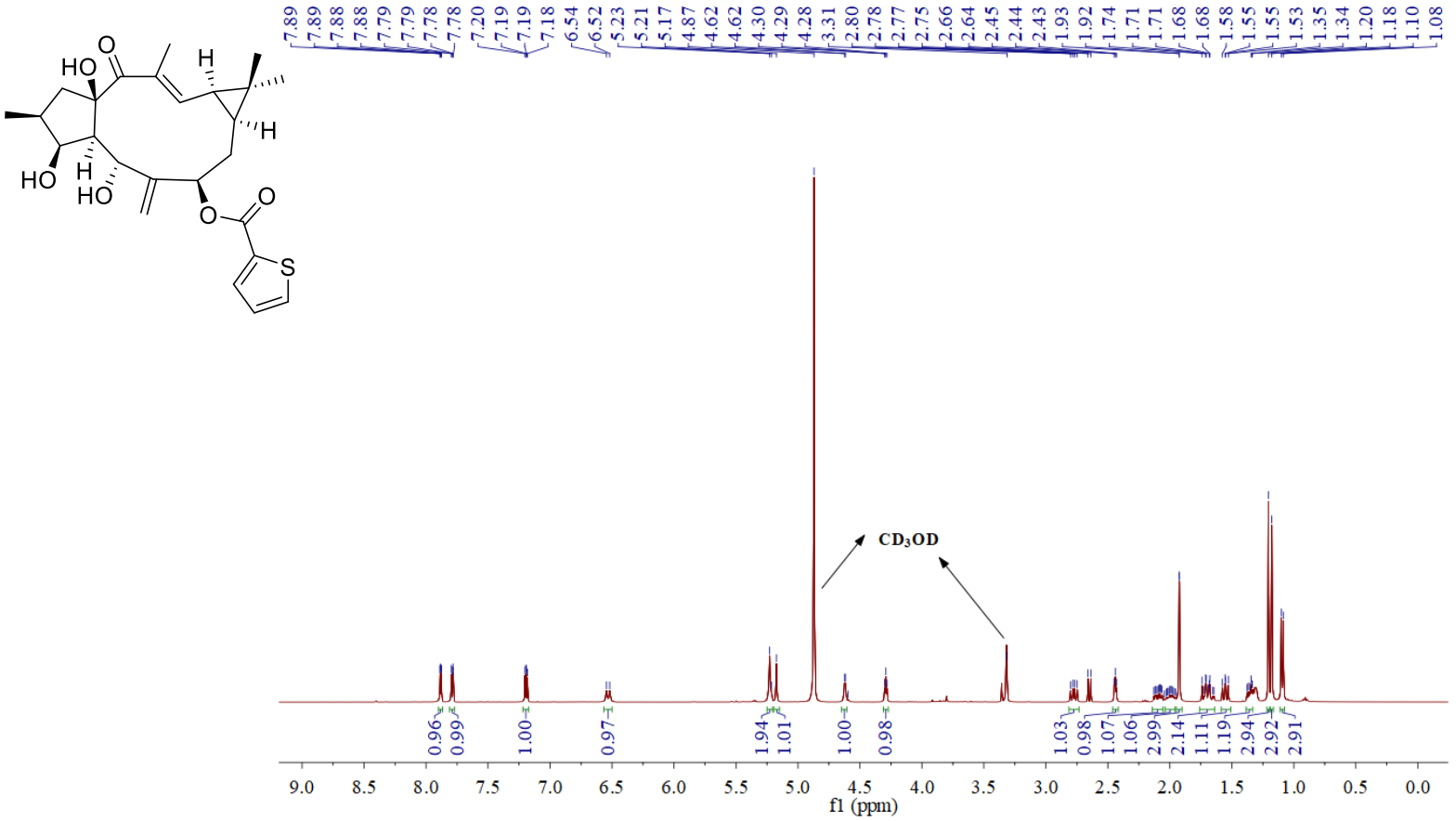


Figure S42. ^{13}C NMR and DEPT 135 spectra of **21** in $CDCl_3$.

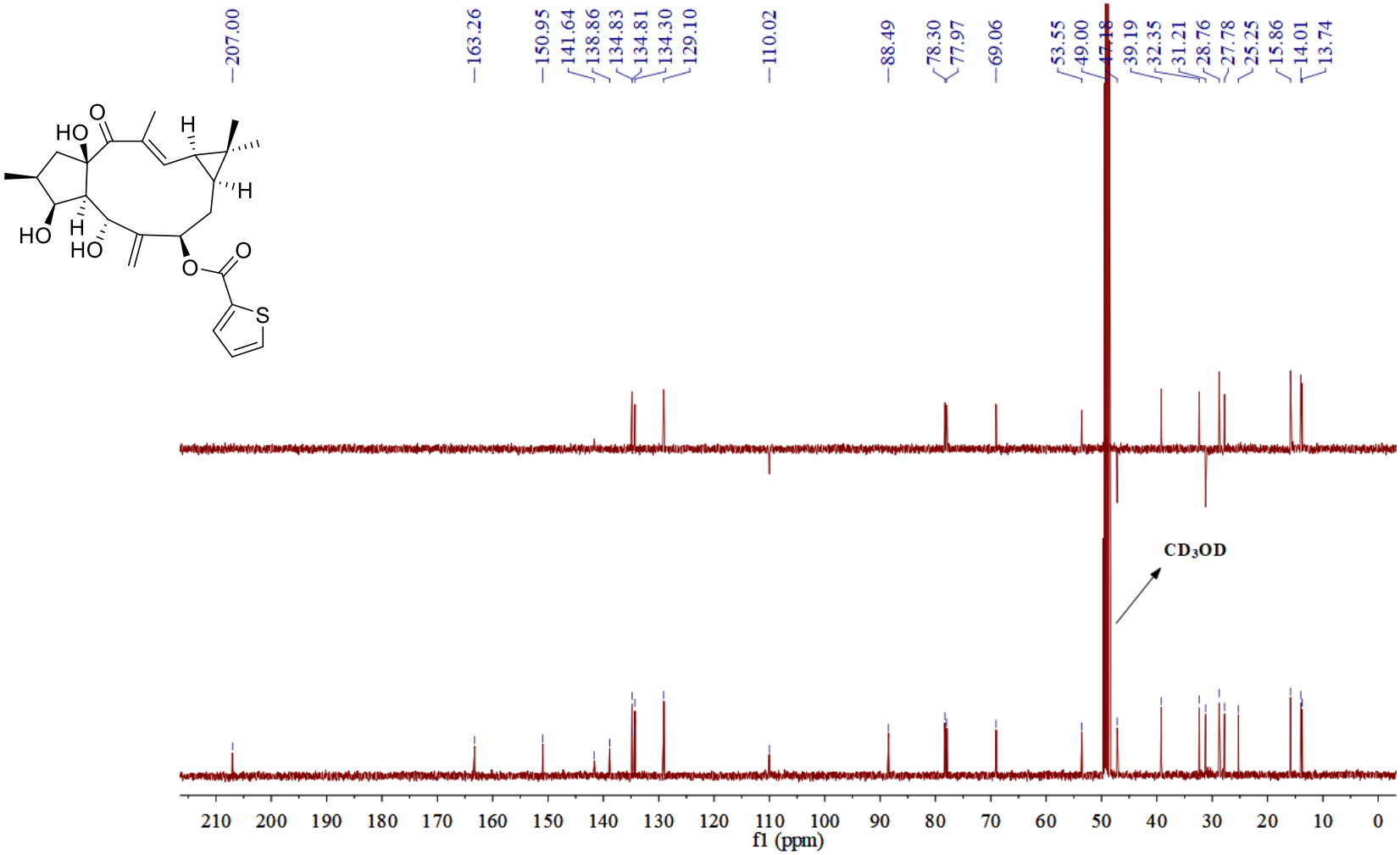


Figure S43. HSQC spectrum of **21** in $CDCl_3$.

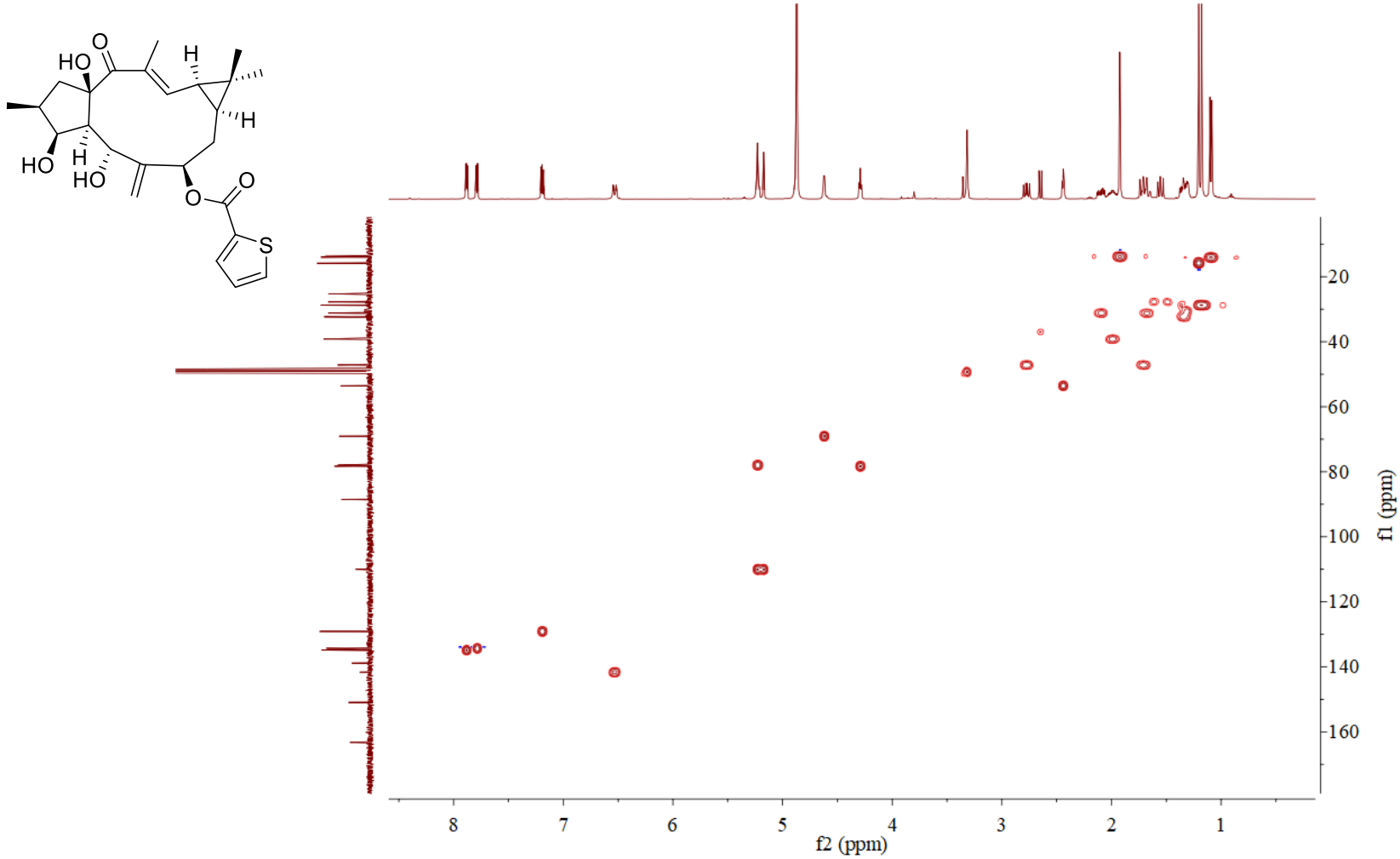


Figure S44. HMBC spectrum of **21** in $CDCl_3$.

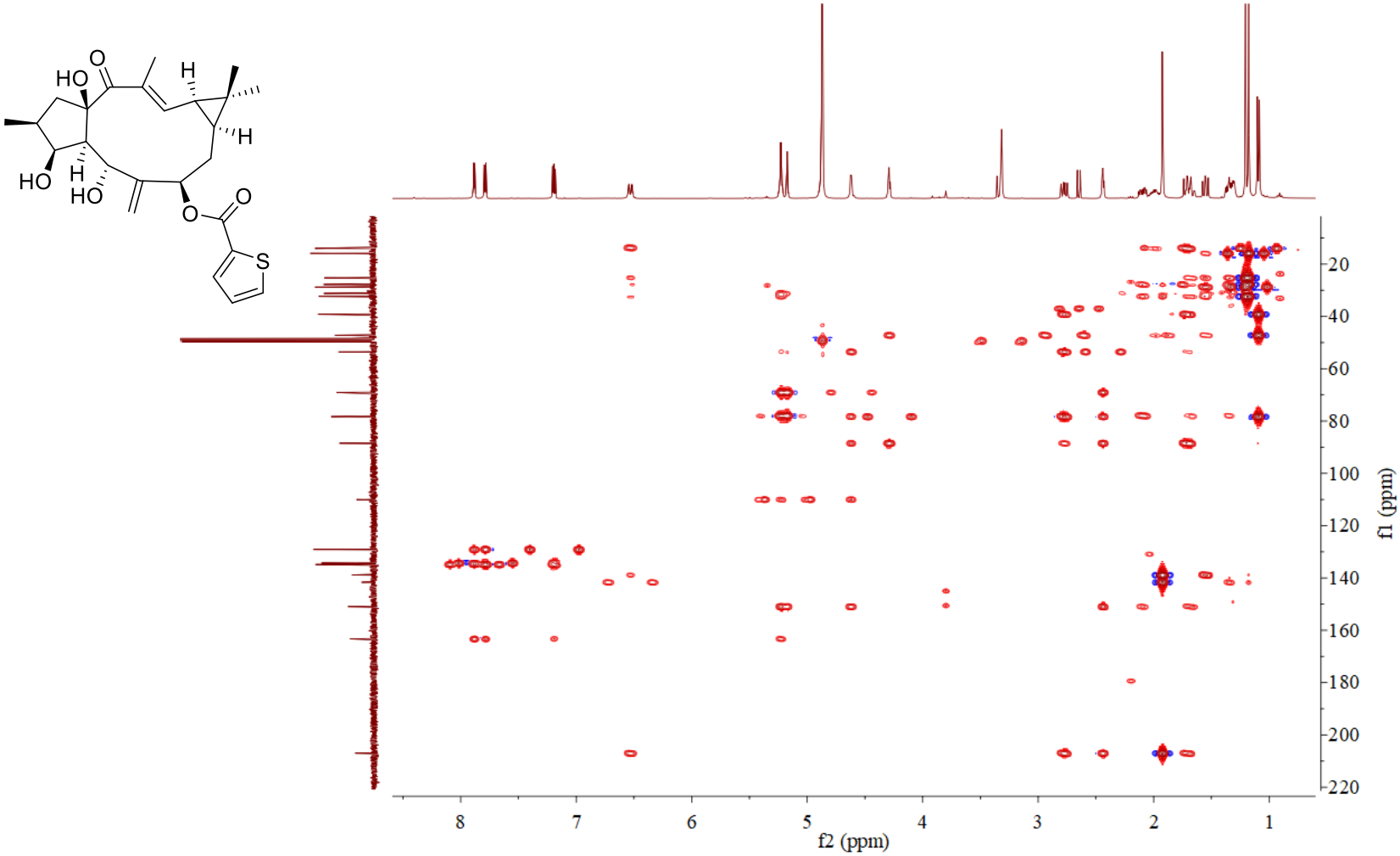


Figure S45. ^{1}H–^{1}H COSY spectra of **21** in $CDCl_3$.

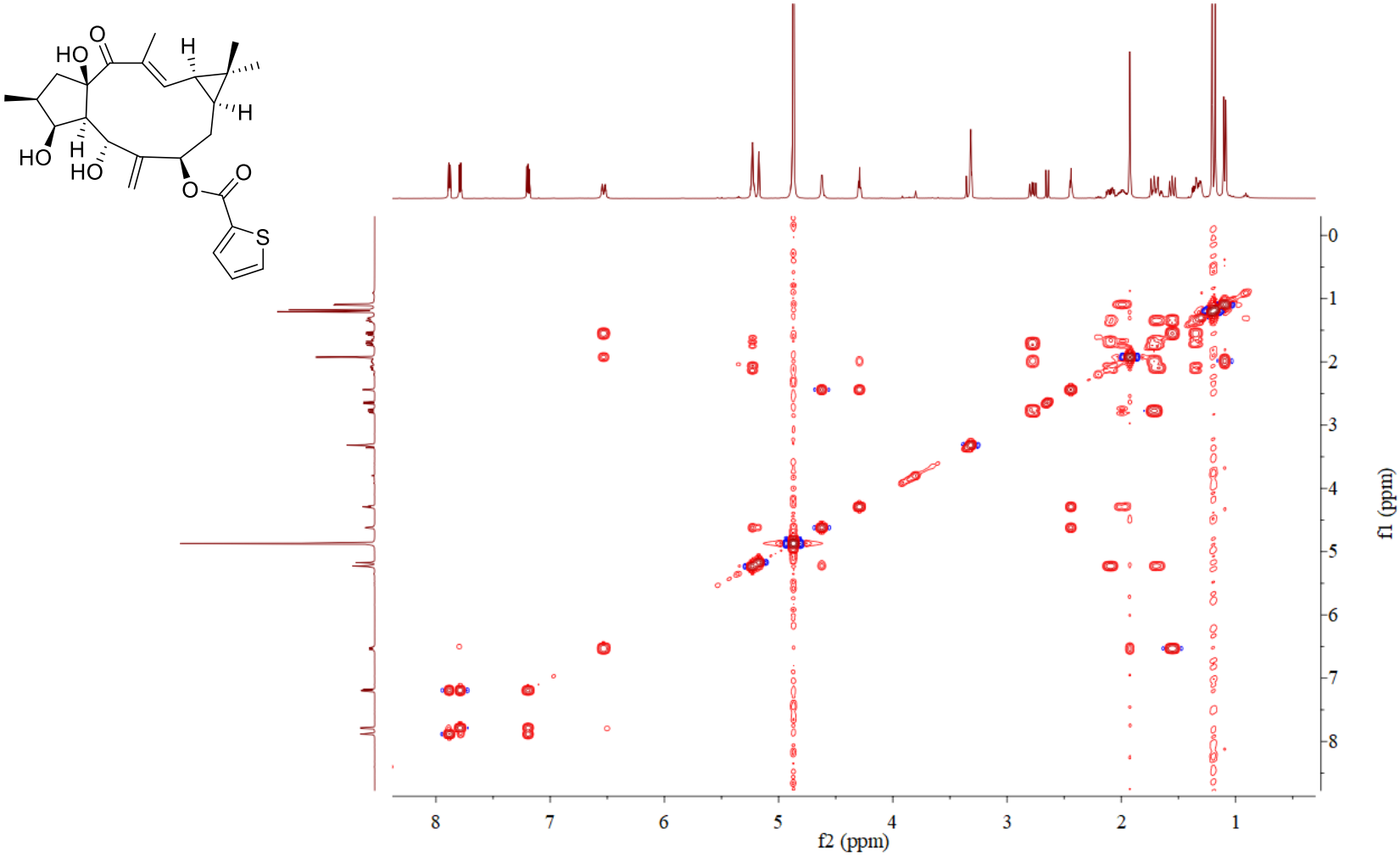


Figure S46. ^{1}H NMR spectrum of **22** in $CDCl_3$.

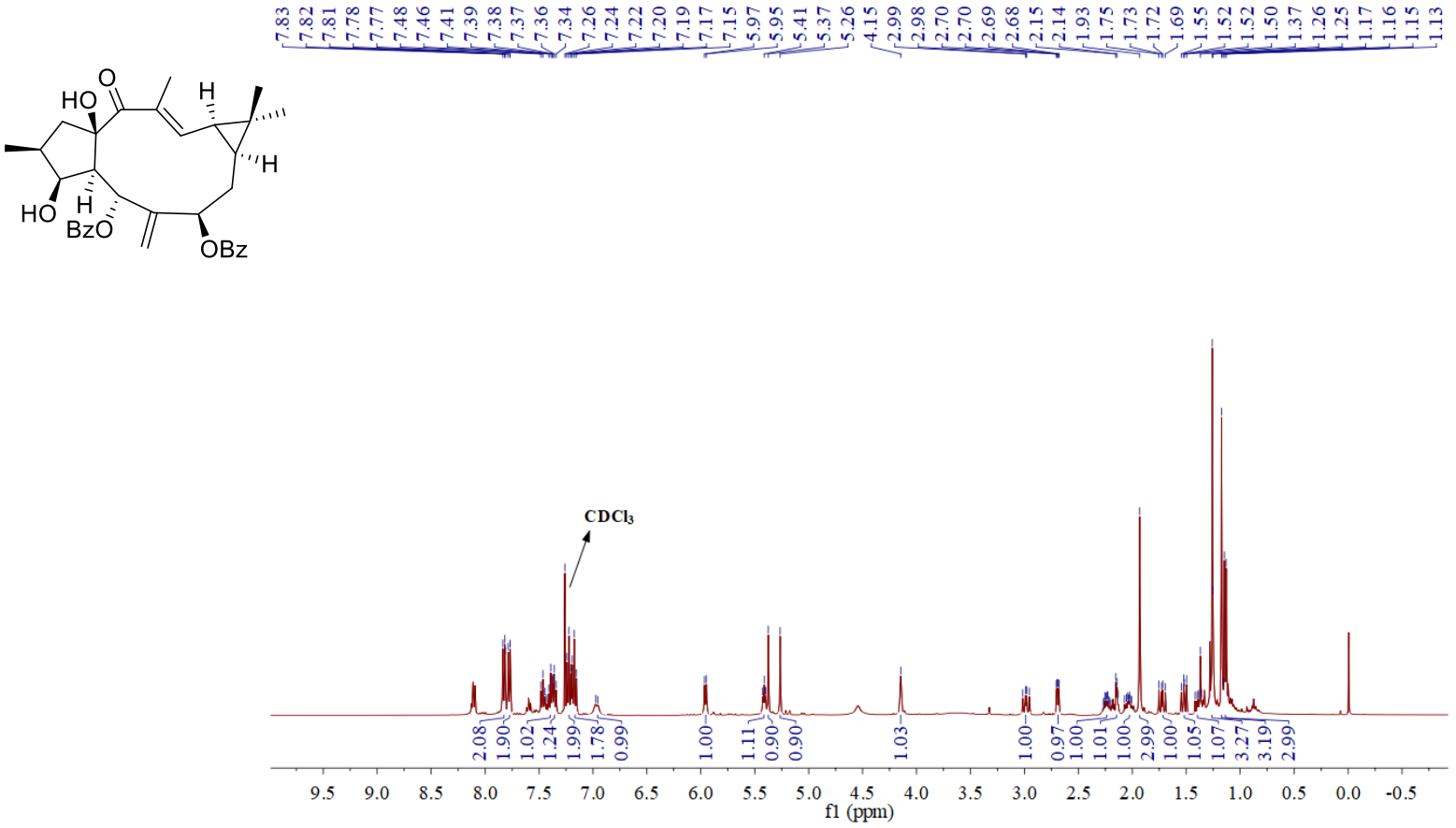


Figure S47. ^{13}C NMR and DEPT 135 spectra of **22** in $CDCl_3$.

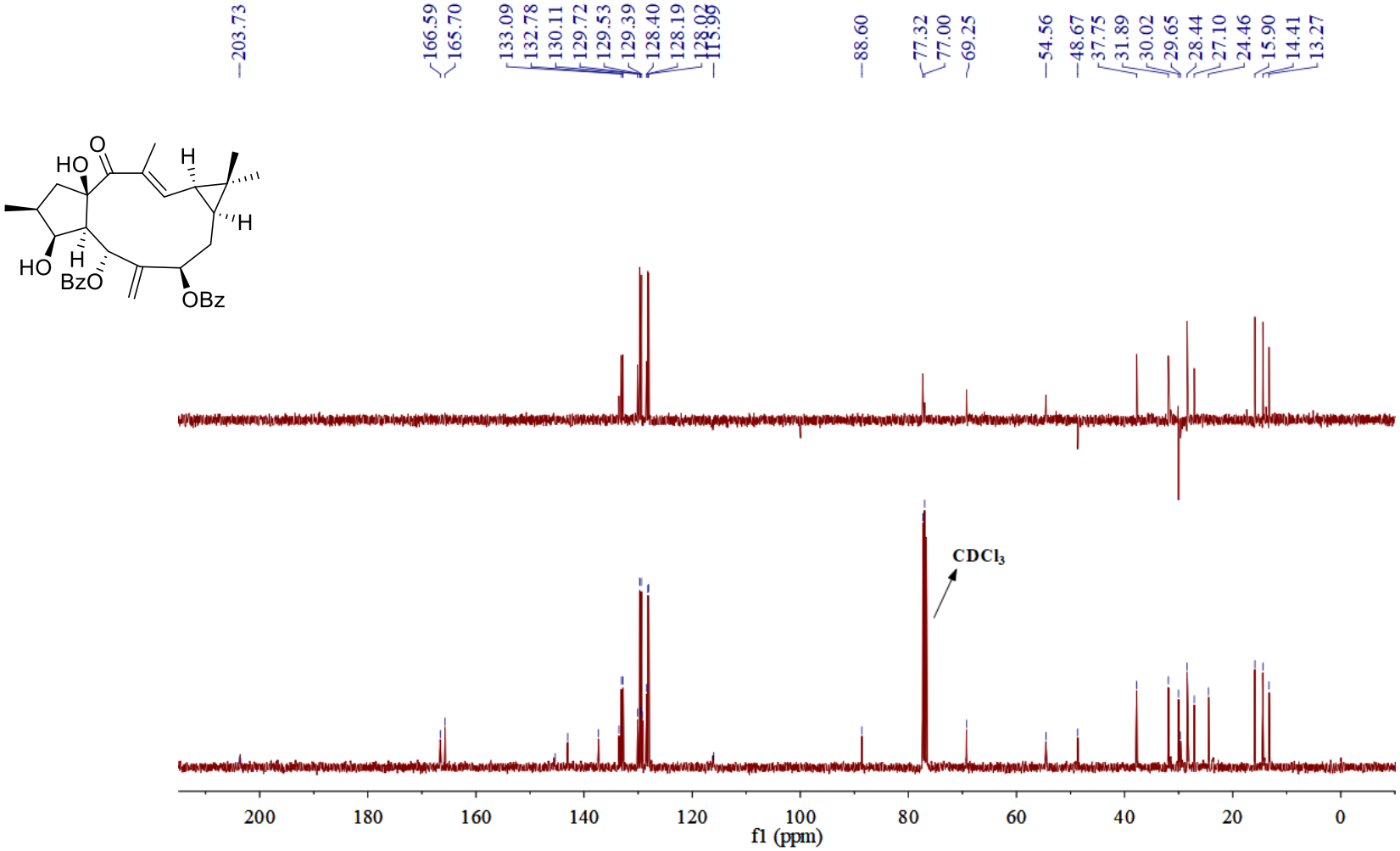


Figure S48. HSQC spectrum of **22** in $CDCl_3$.

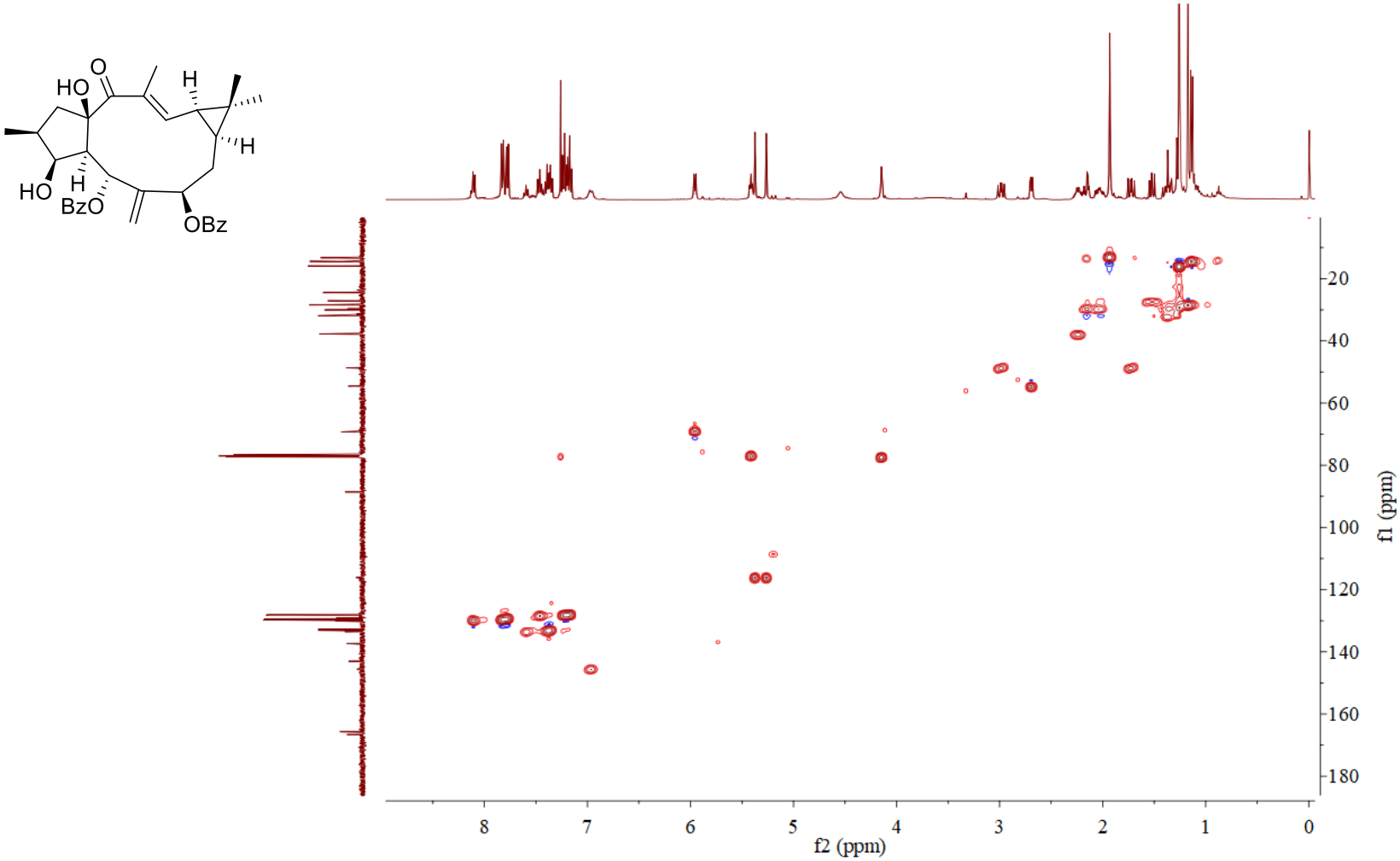


Figure S49. HMBC spectrum of **22** in $CDCl_3$.

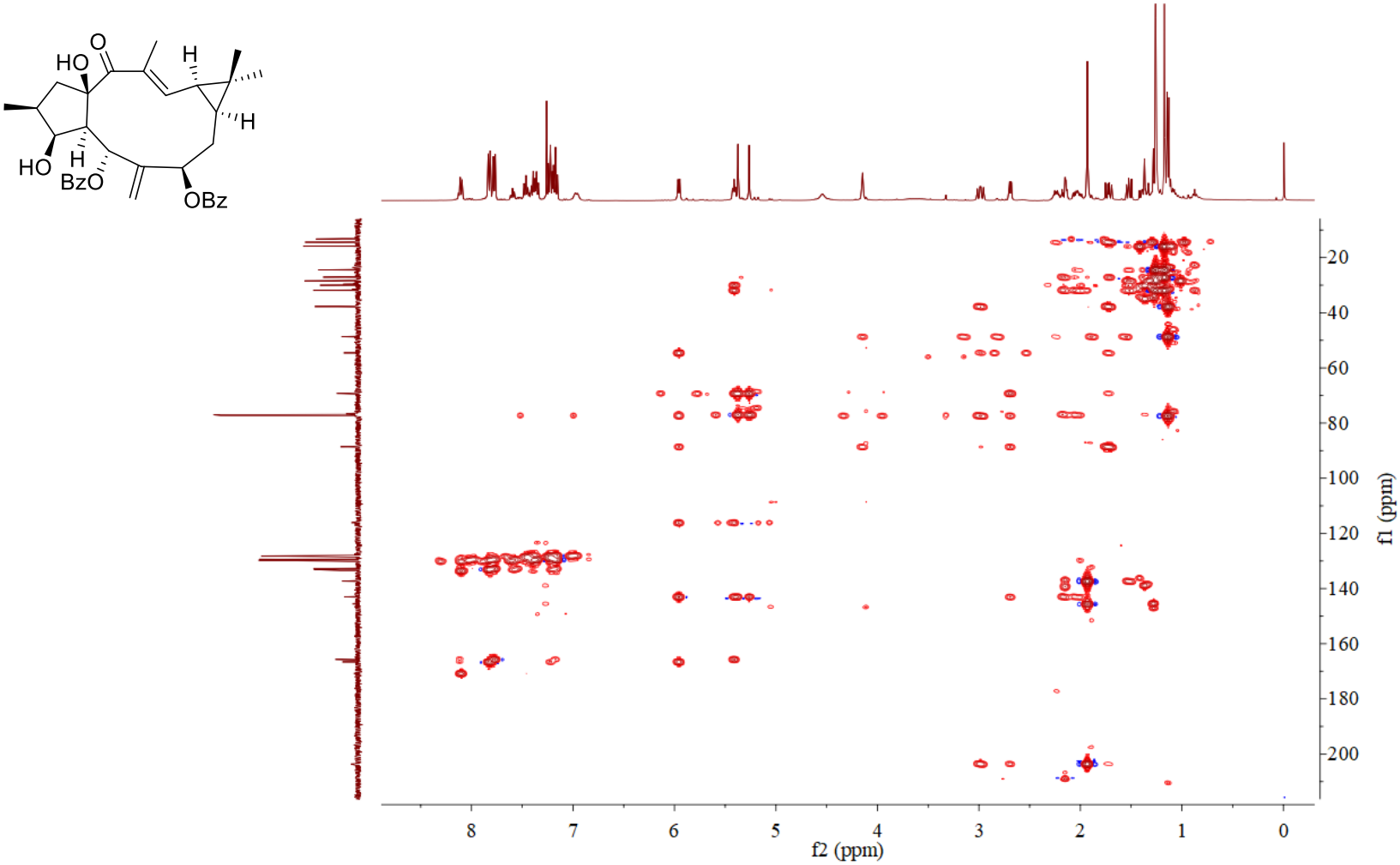


Figure S50. $^{1}H–^{1}H$ COSY spectrum of **22** in $CDCl_3$.

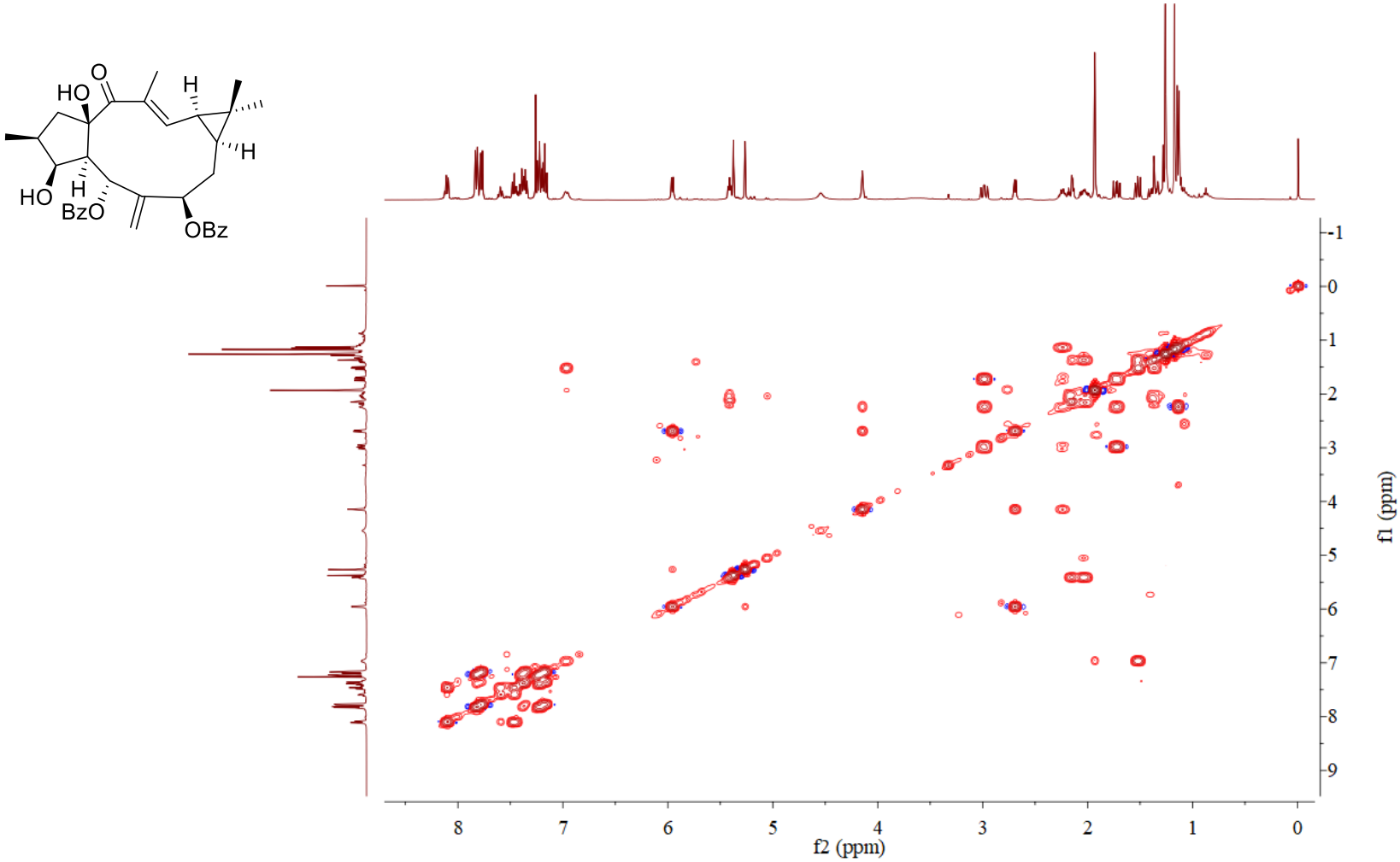


Figure S51. ^{1}H NMR spectrum of **23** in $CDCl_3$.

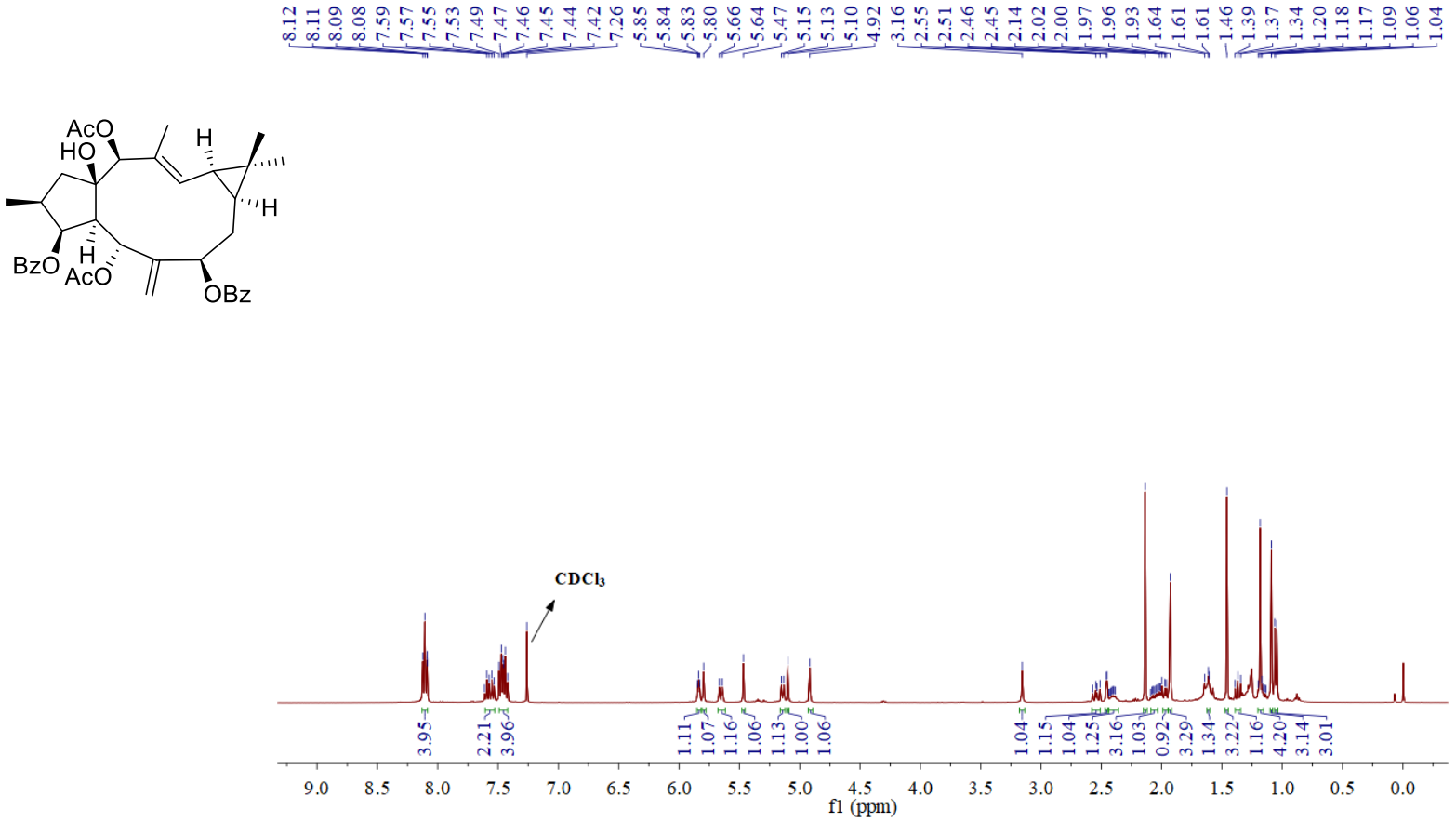


Figure S52. ^{13}C NMR and DEPT 135 spectra of **23** in $CDCl_3$.

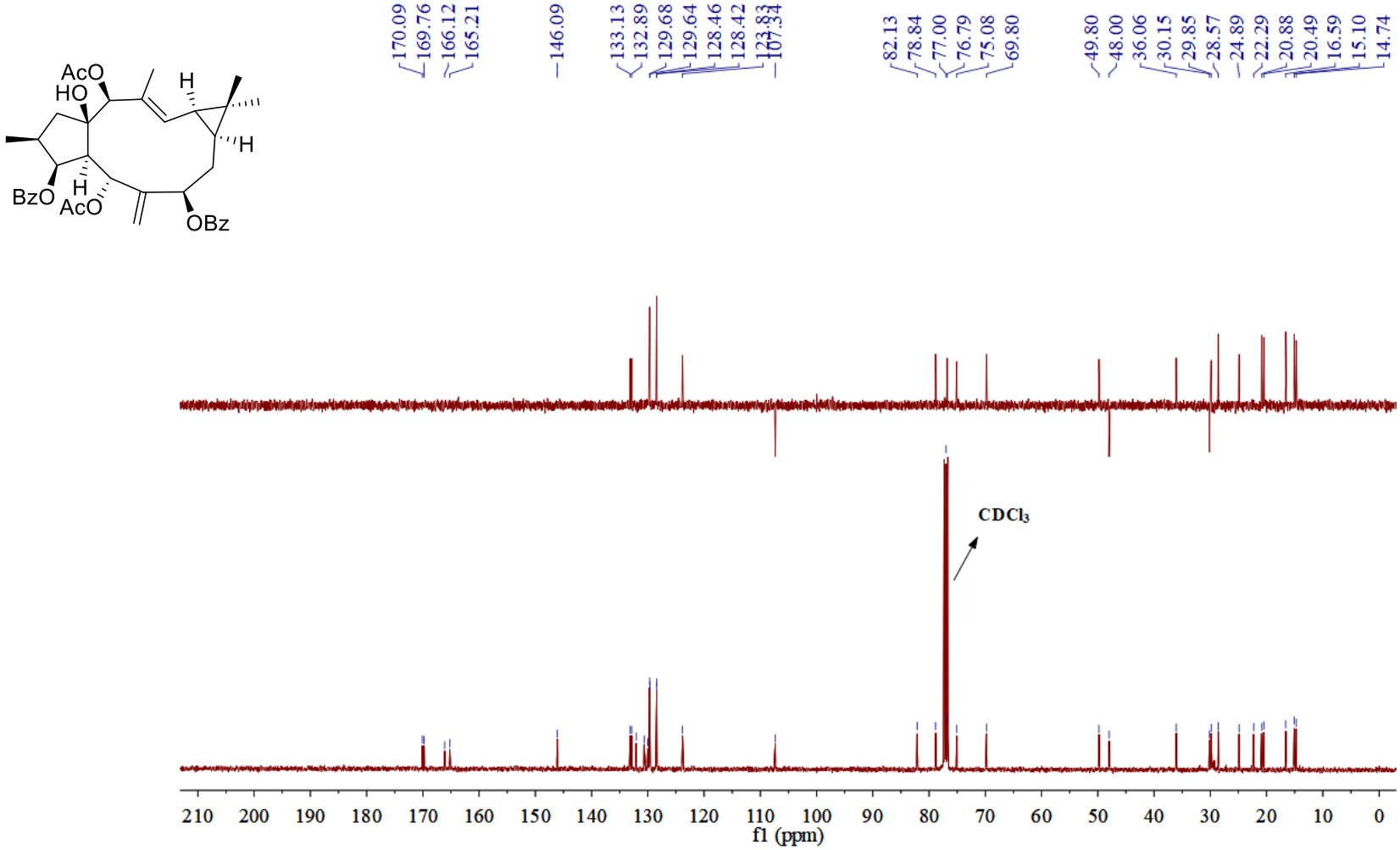


Figure S53. HSQC spectrum of **23** in $CDCl_3$.

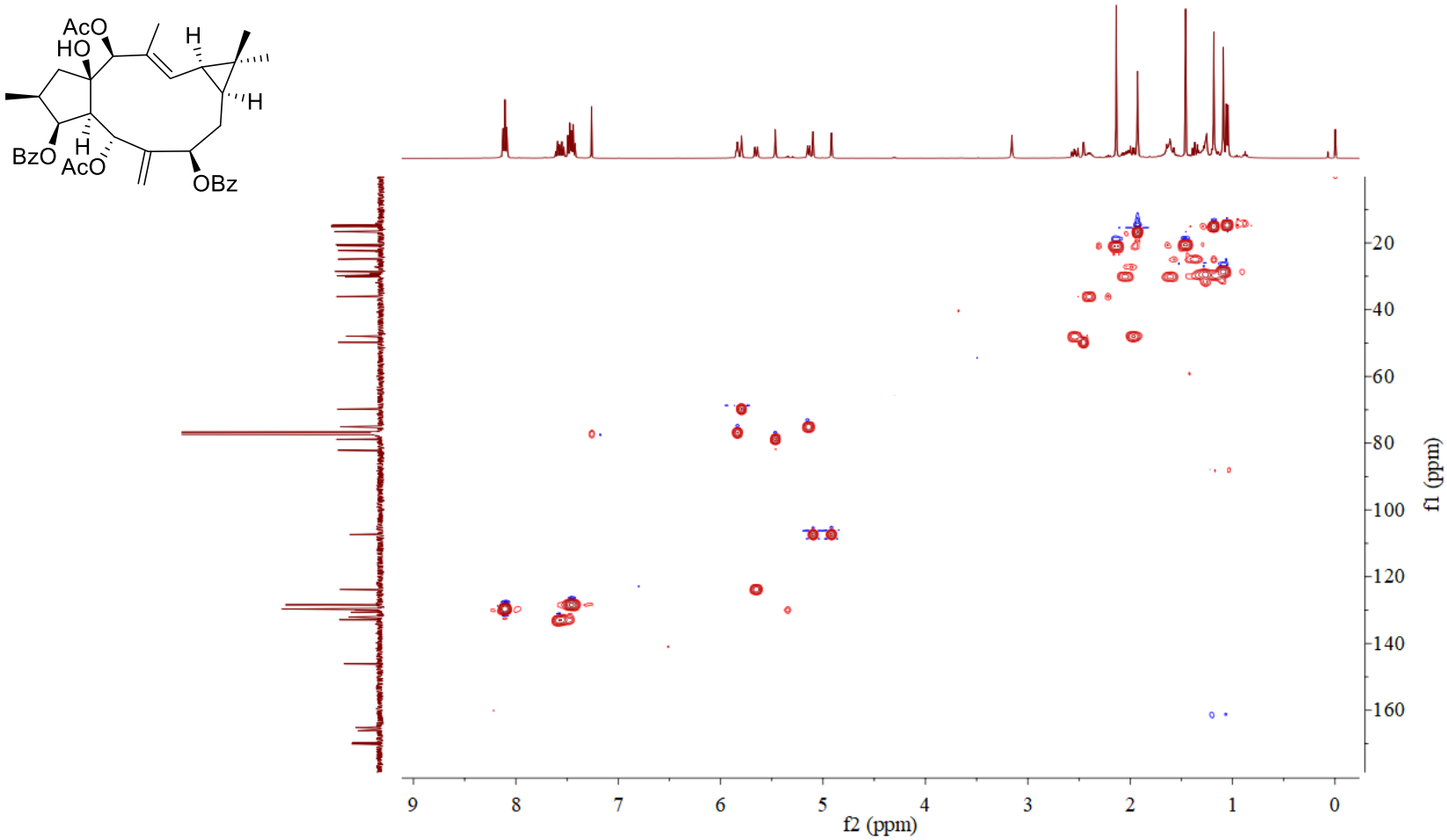


Figure S54. HMBC spectrum of **23** in $CDCl_3$.

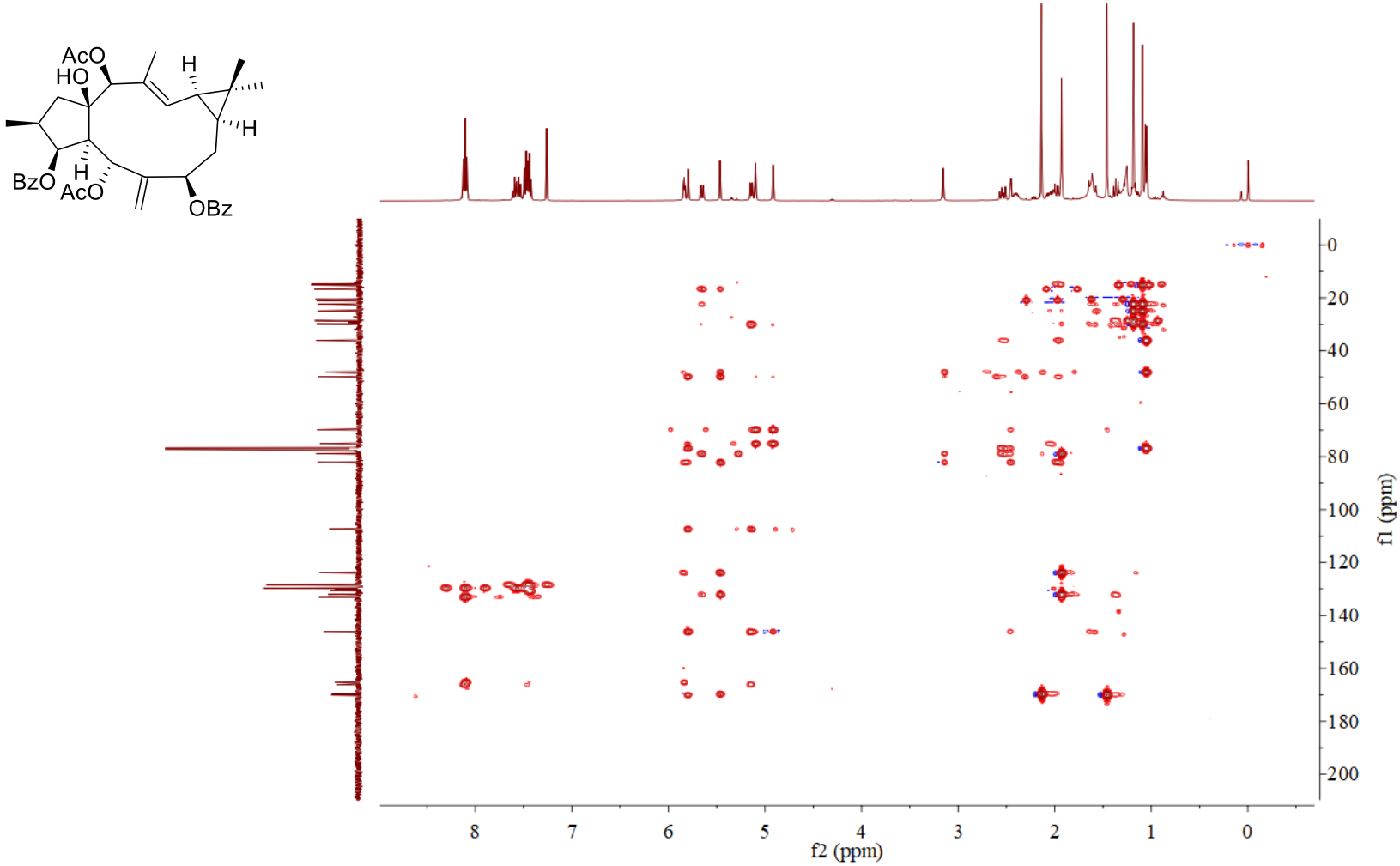


Figure S55. ^{1}H–1H COSY spectrum of **23** in $CDCl_3$.

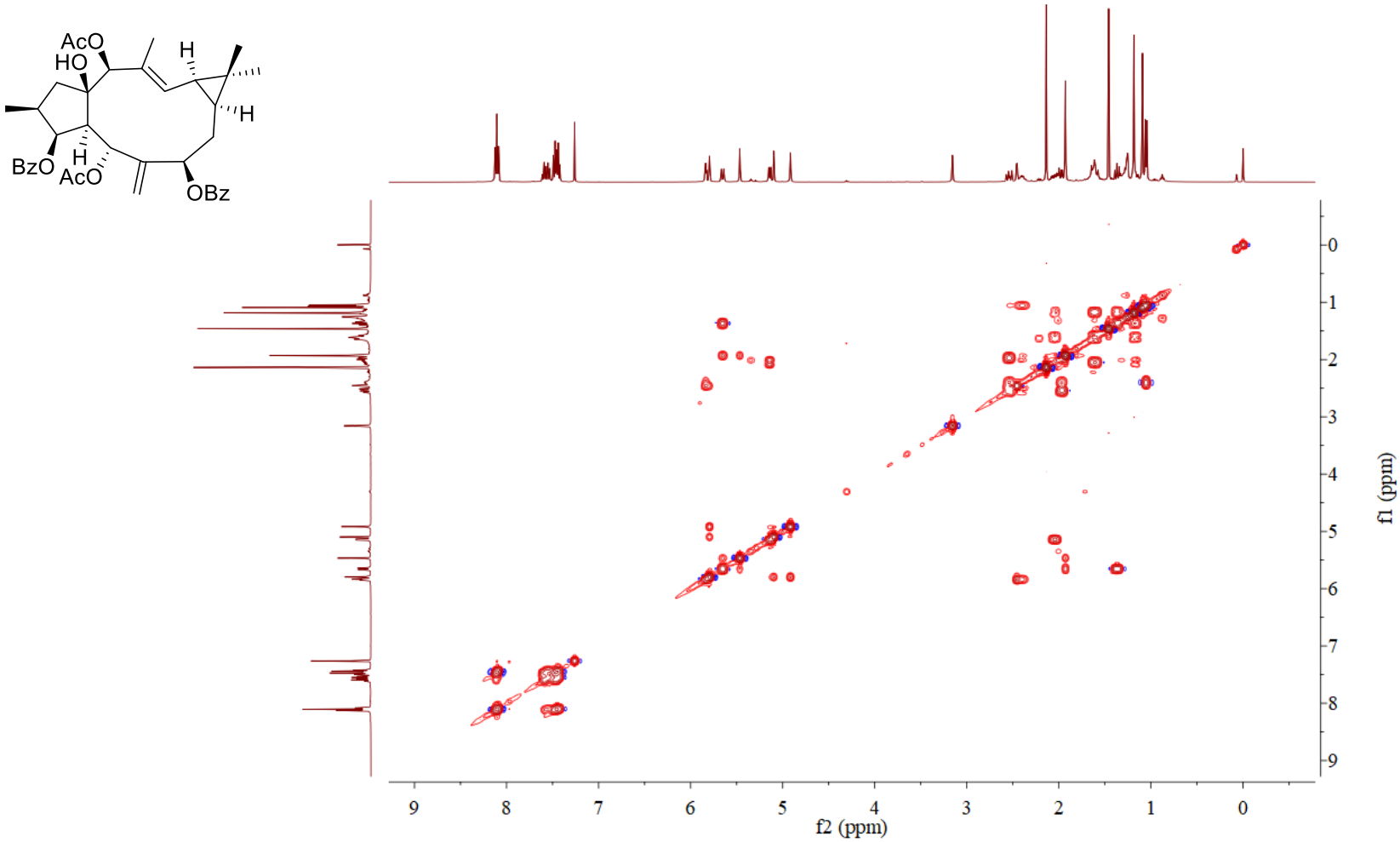


Figure S56. NOESY spectrum of **23** in $CDCl_3$.

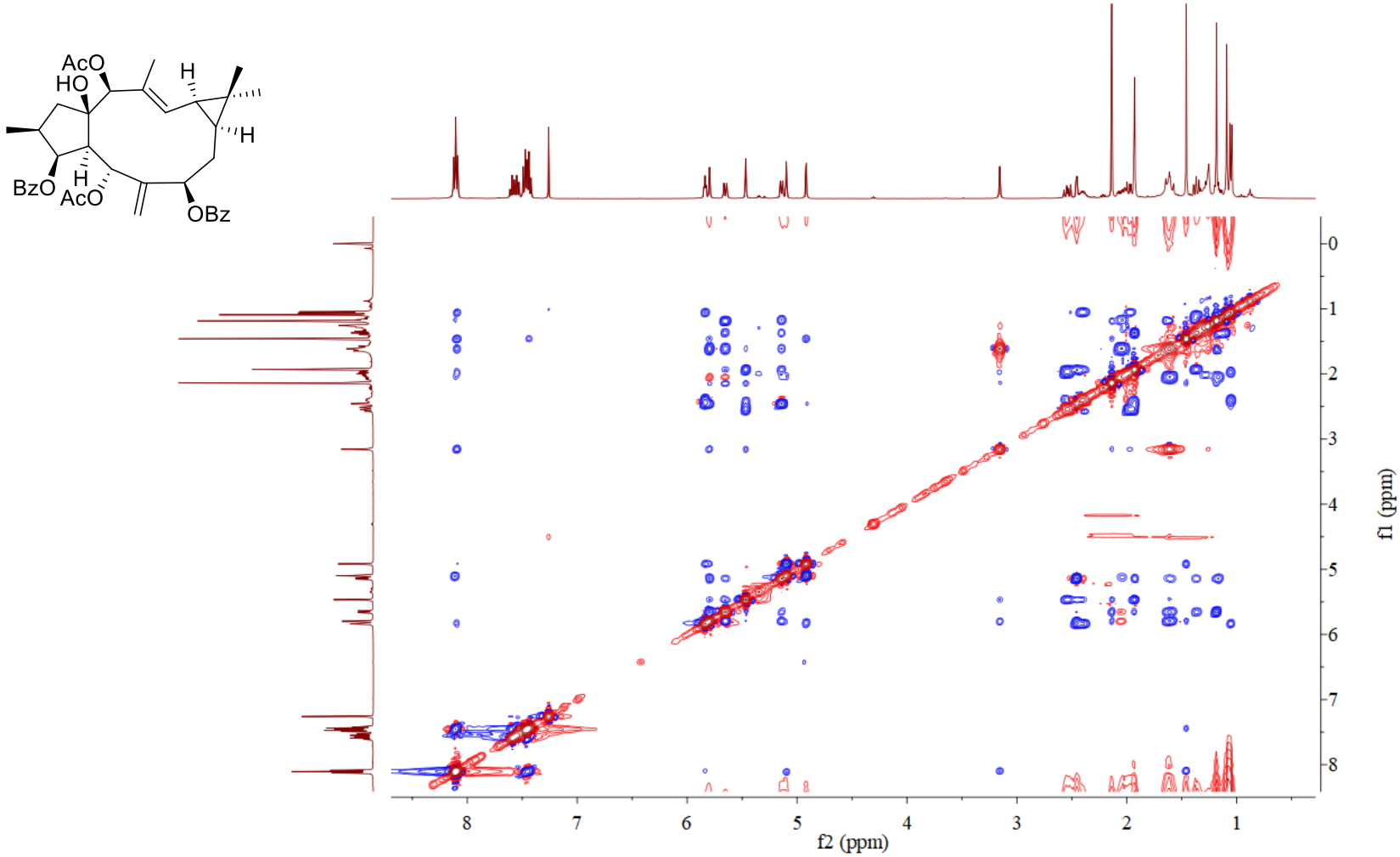


Figure S57. ^{1}H NMR spectrum of **24** in $CDCl_3$.

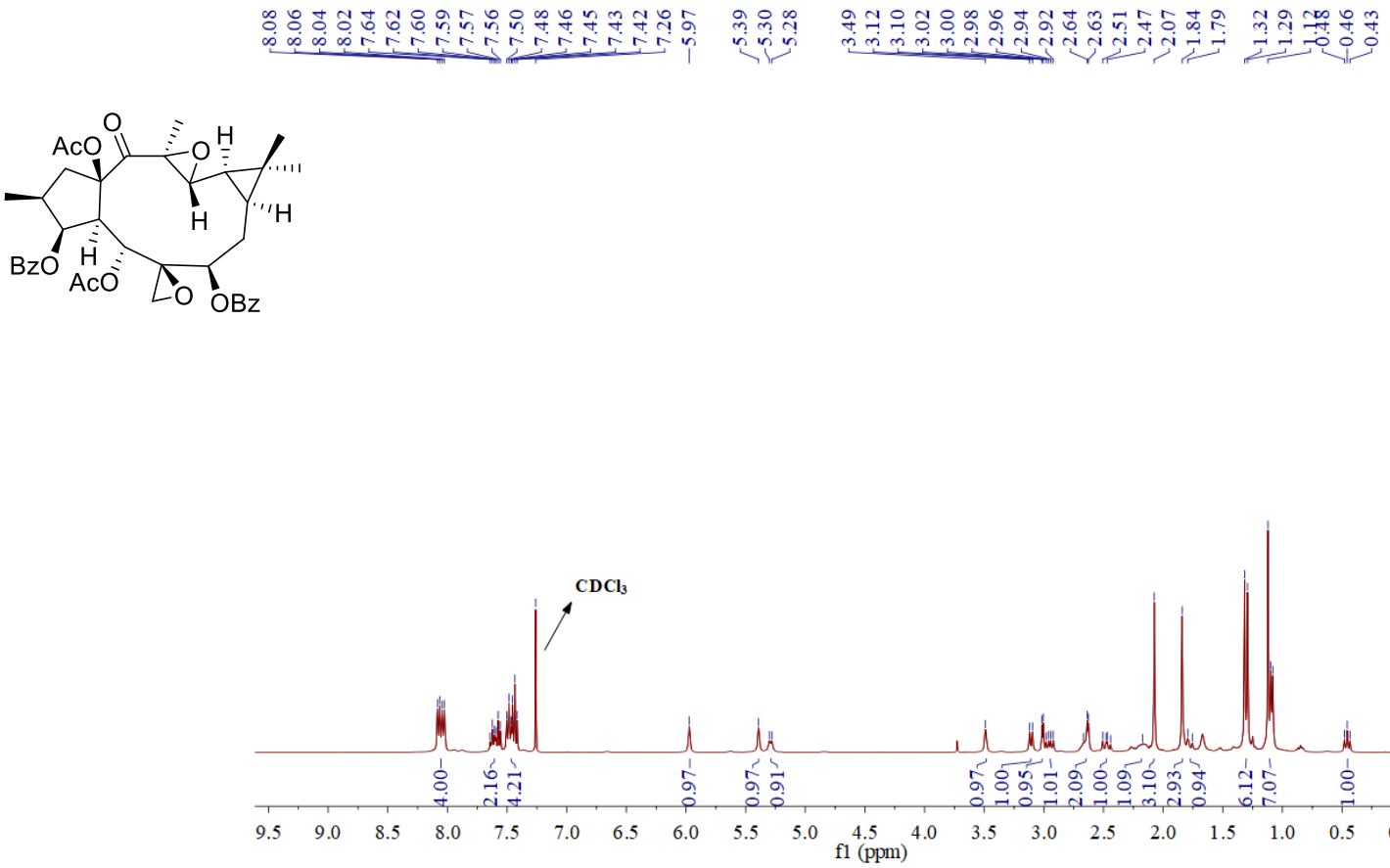


Figure S58. ^{13}C NMR and DEPT 135 spectra of **24** in $CDCl_3$.

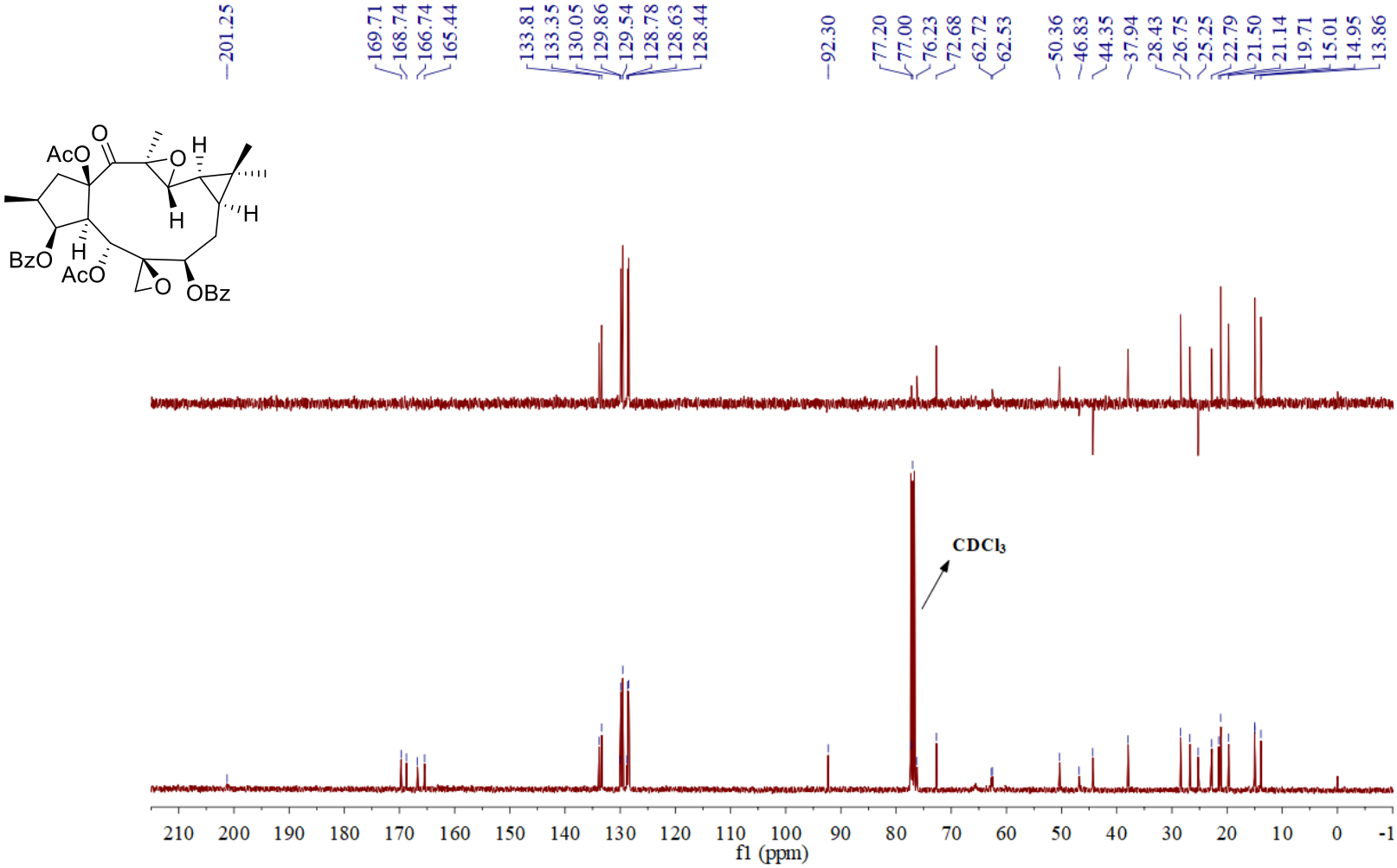


Figure S59. HSQC spectrum of **24** in $CDCl_3$.

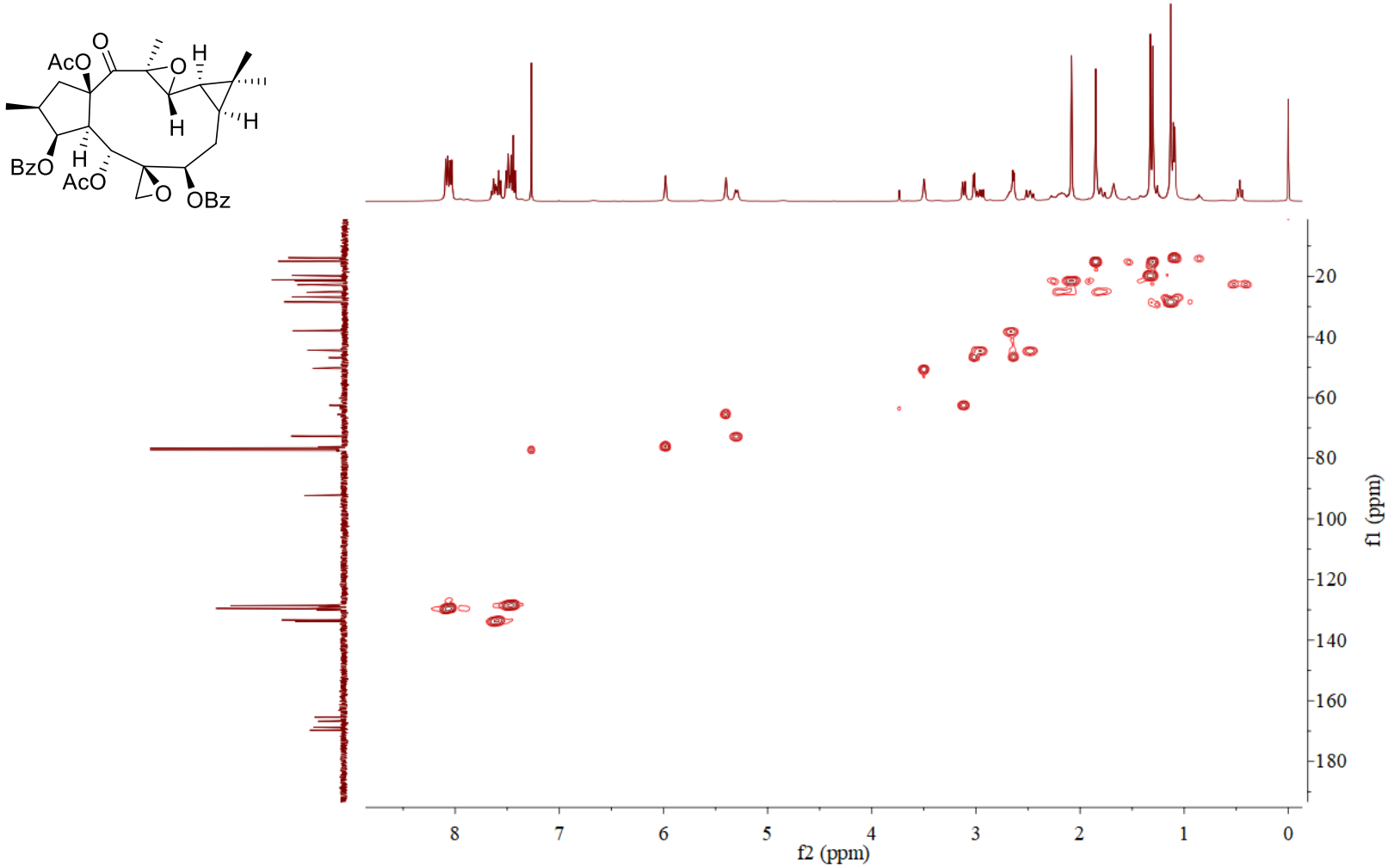


Figure S60. HMBC spectrum of **24** in $CDCl_3$.

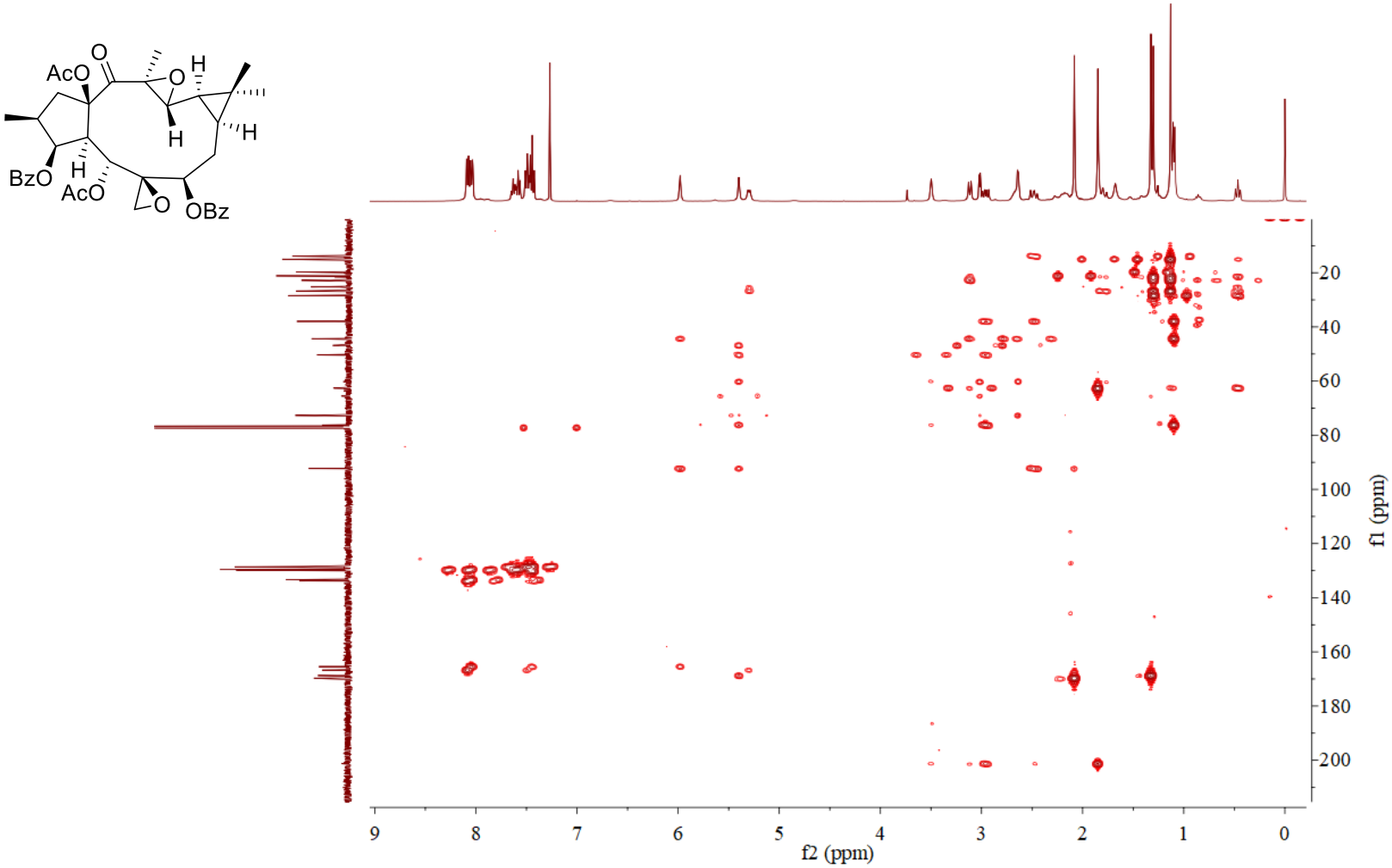


Figure S61. ^{1}H–^{1}H COSY spectrum of **24** in $CDCl_3$.

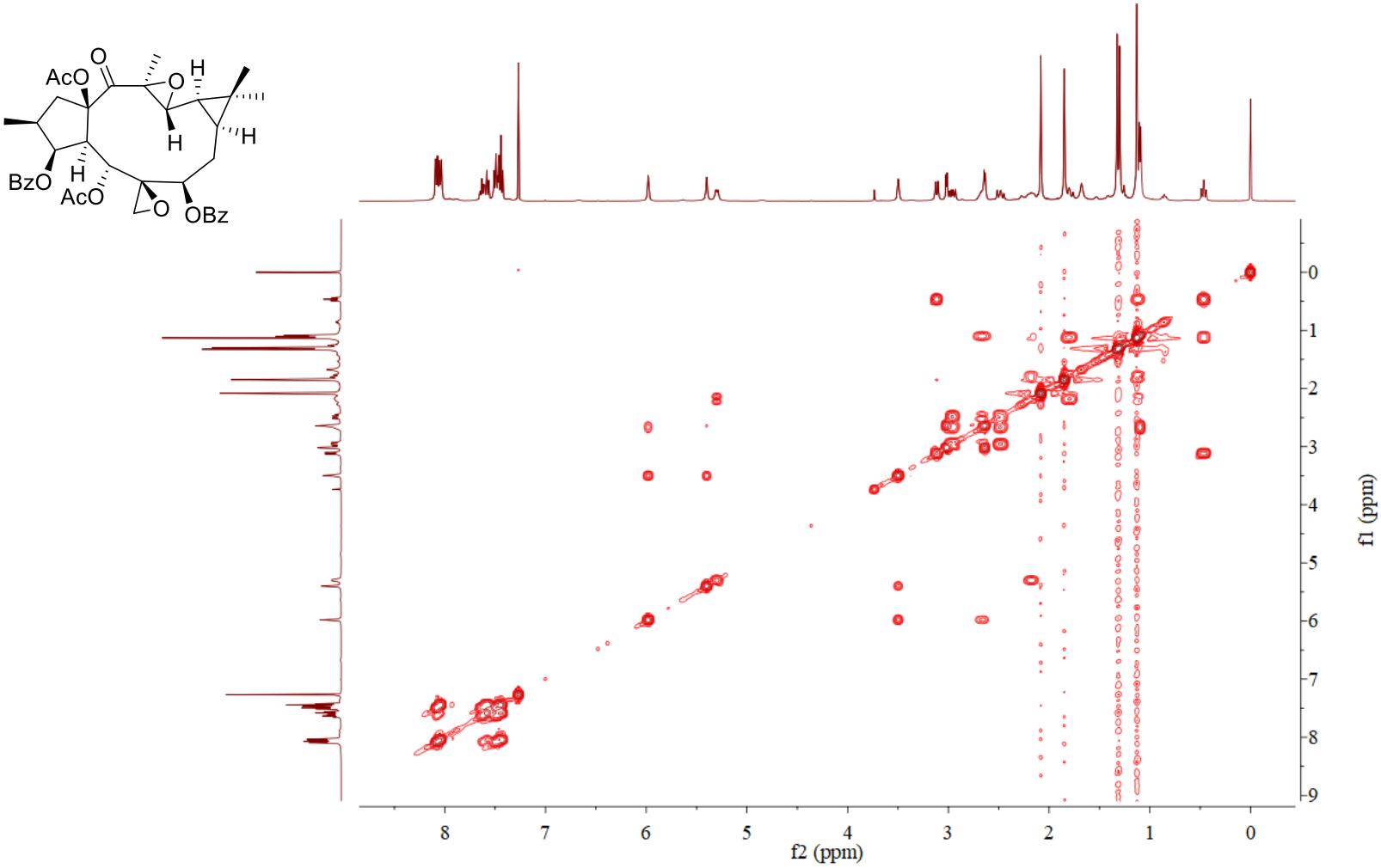


Figure S62. NOESY spectrum of **24** in $CDCl_3$.

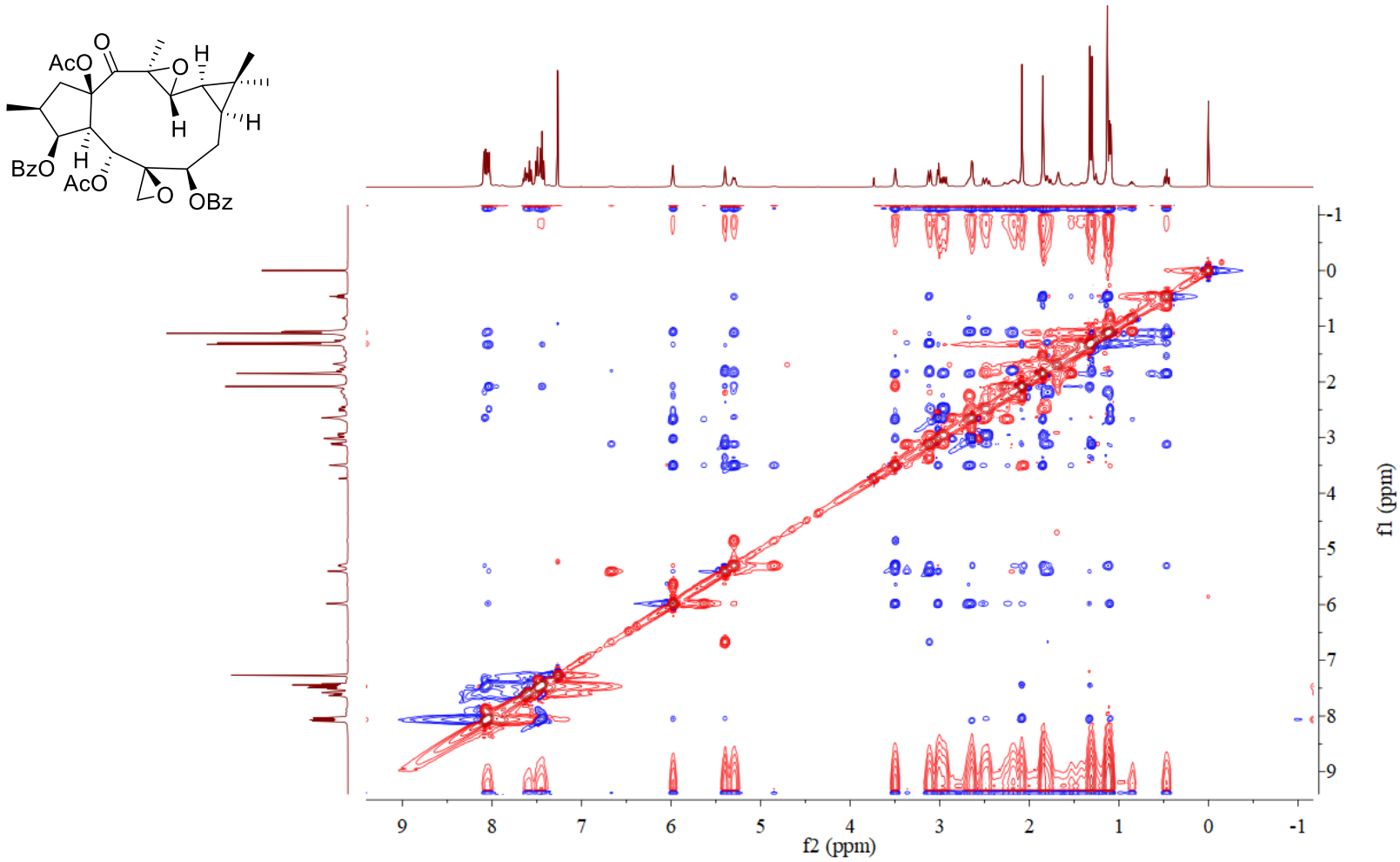


Figure S63. ^{1}H NMR spectrum of **25** in $CDCl_3$.

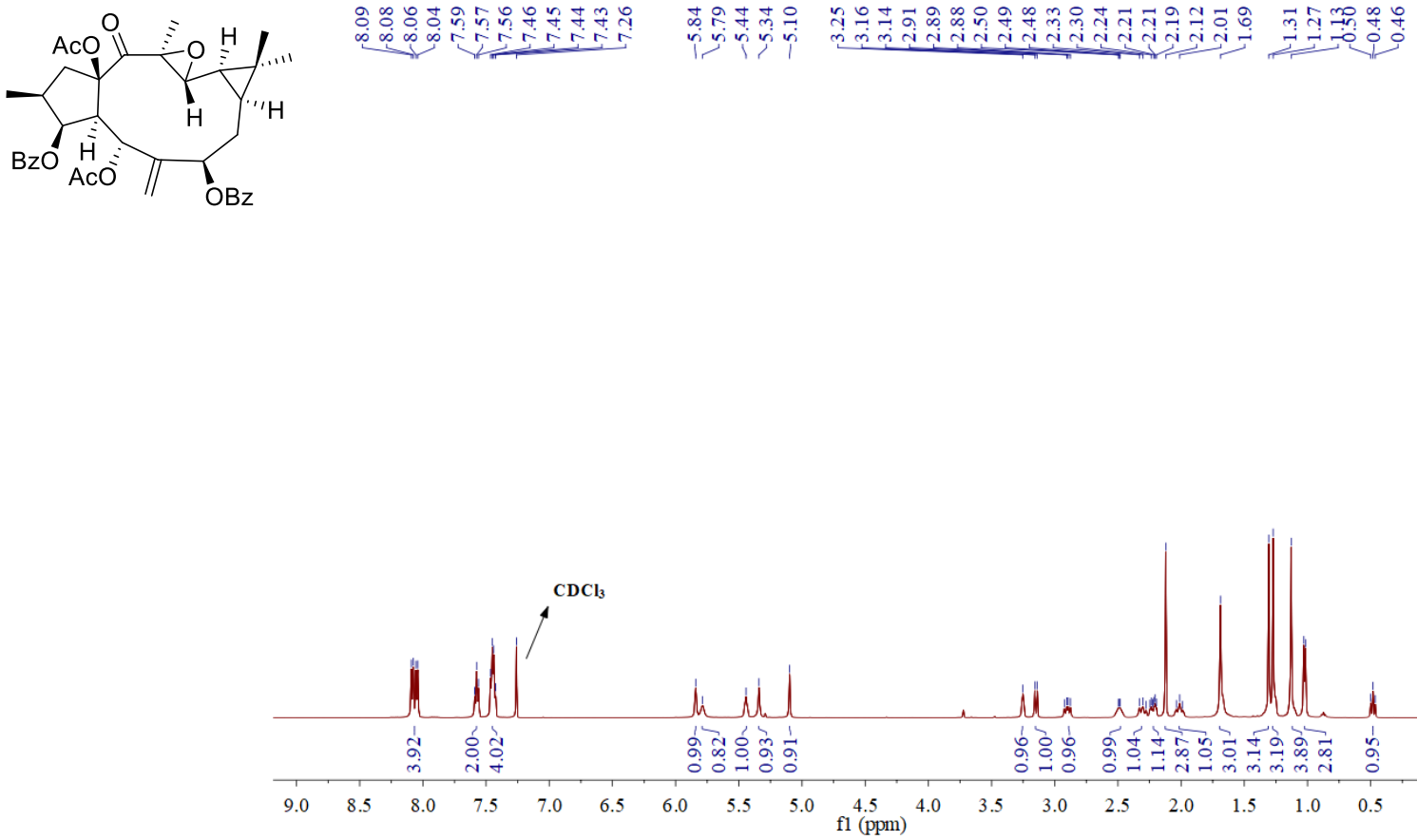


Figure S64. ^{13}C NMR and DEPT 135 spectra of **25** in $CDCl_3$.

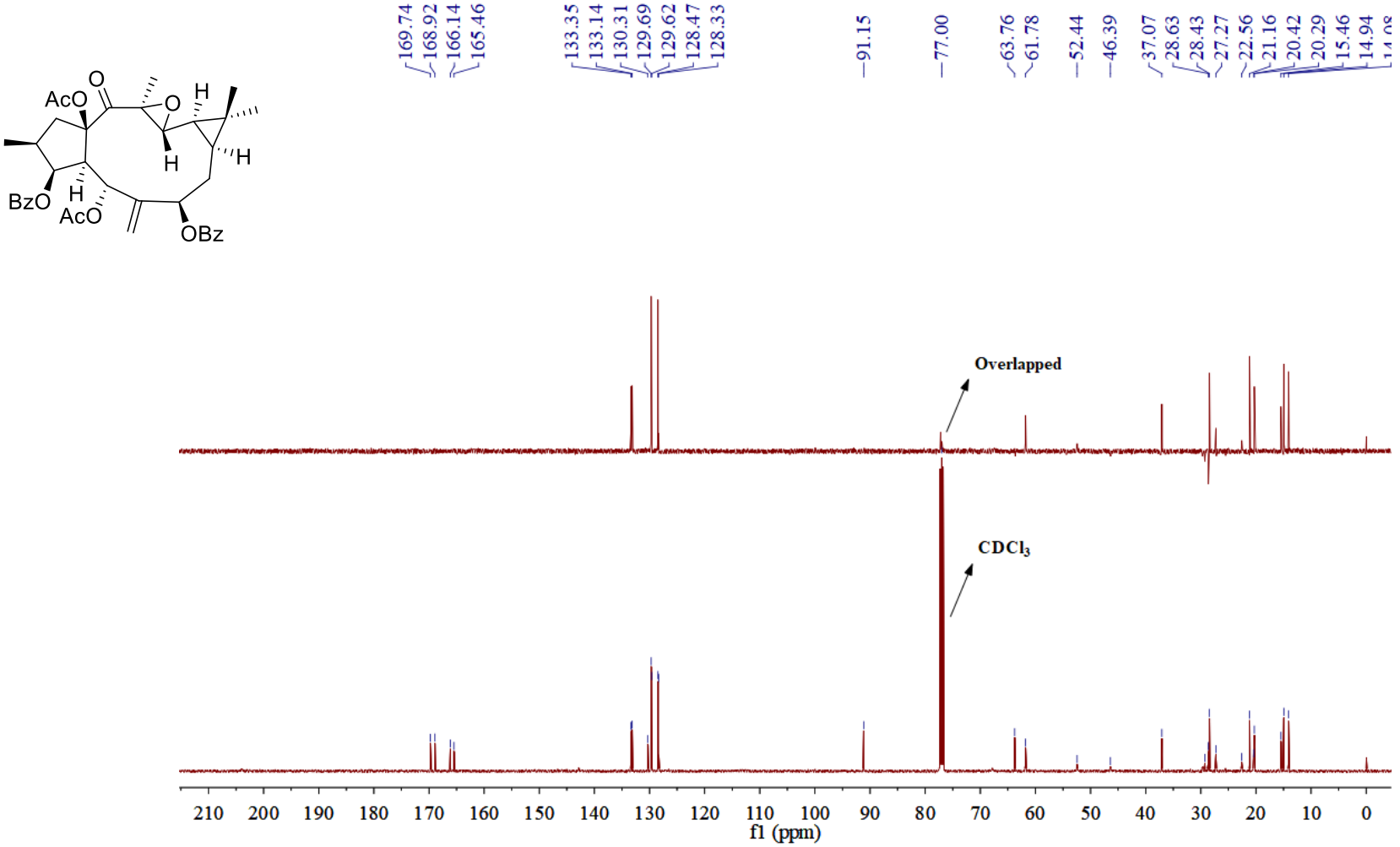


Figure S65. HSQC spectrum of **25** in $CDCl_3$.

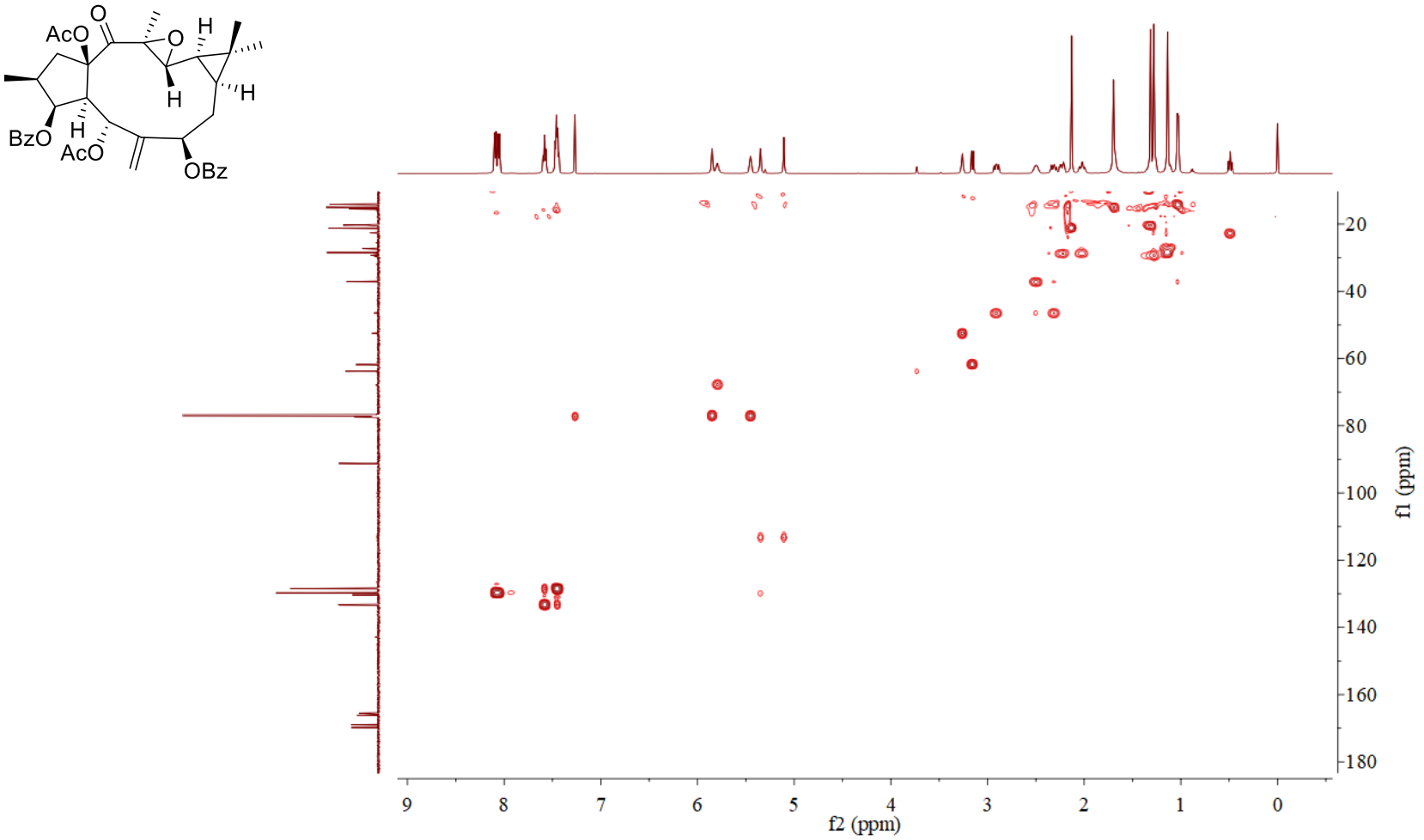


Figure S66. HMBC spectrum of **25** in $CDCl_3$.

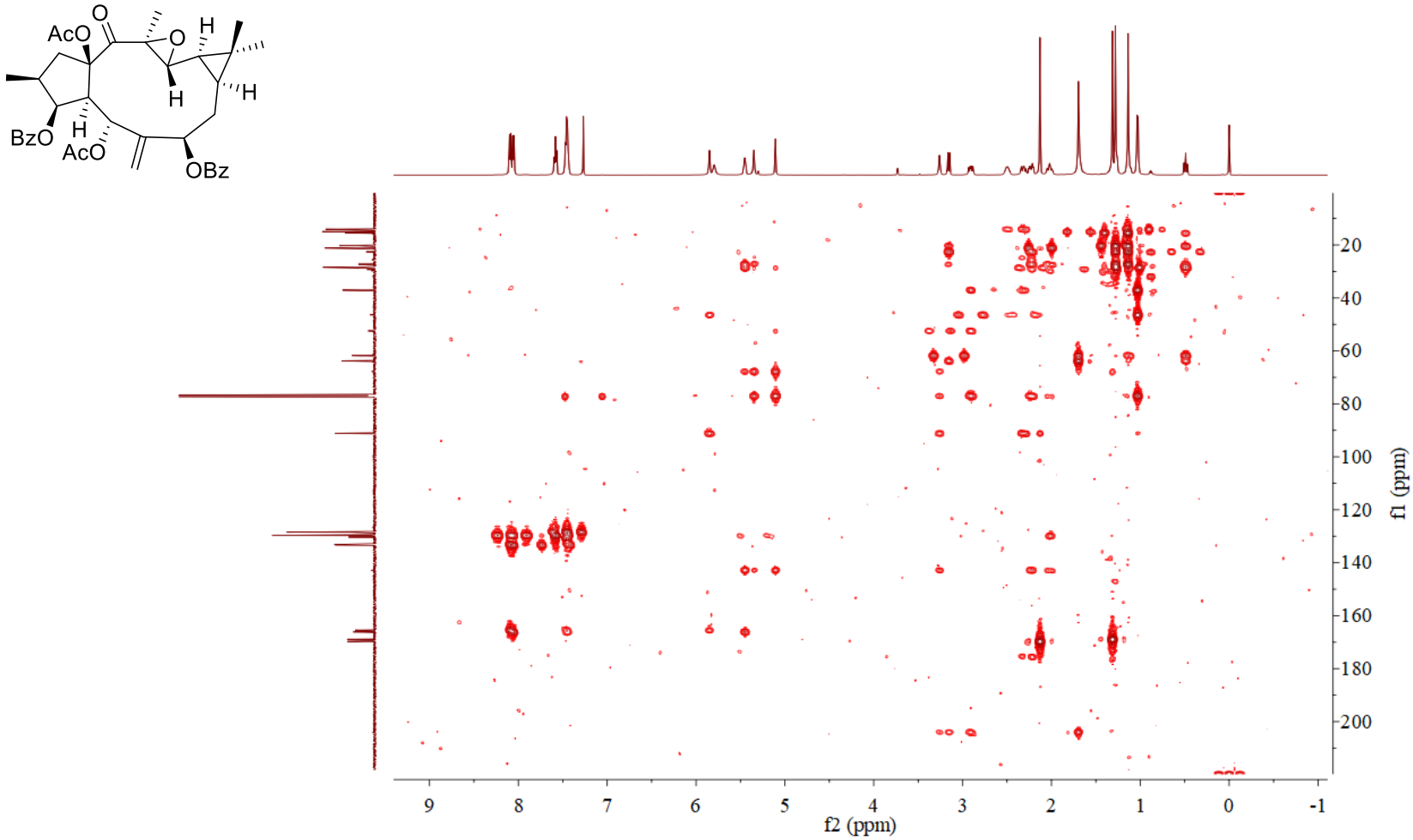


Figure S67. $^{1}H–^{1}H$ COSY spectrum of **25** in $CDCl_3$.

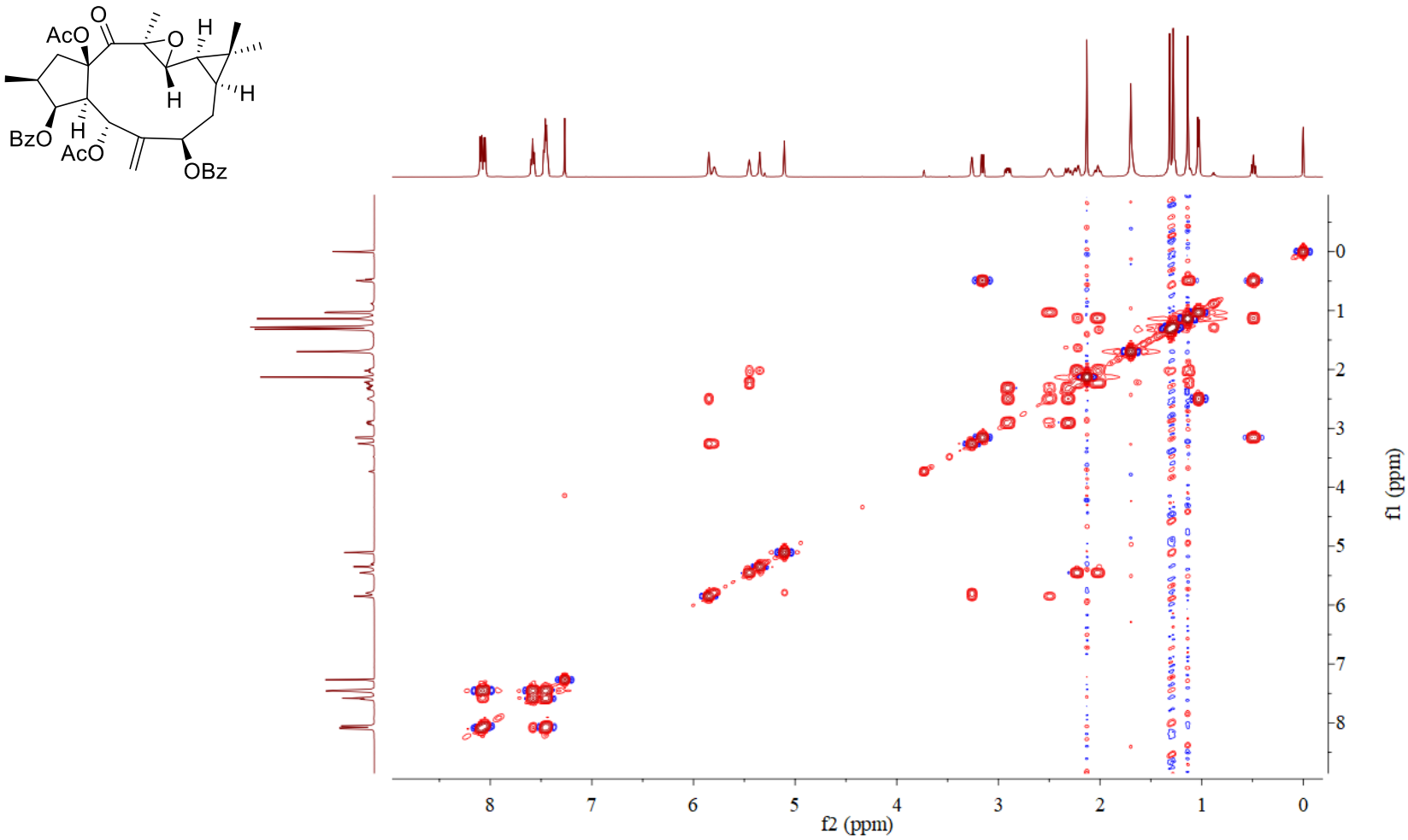


Figure S68. NOESY spectrum of **25** in $CDCl_3$.

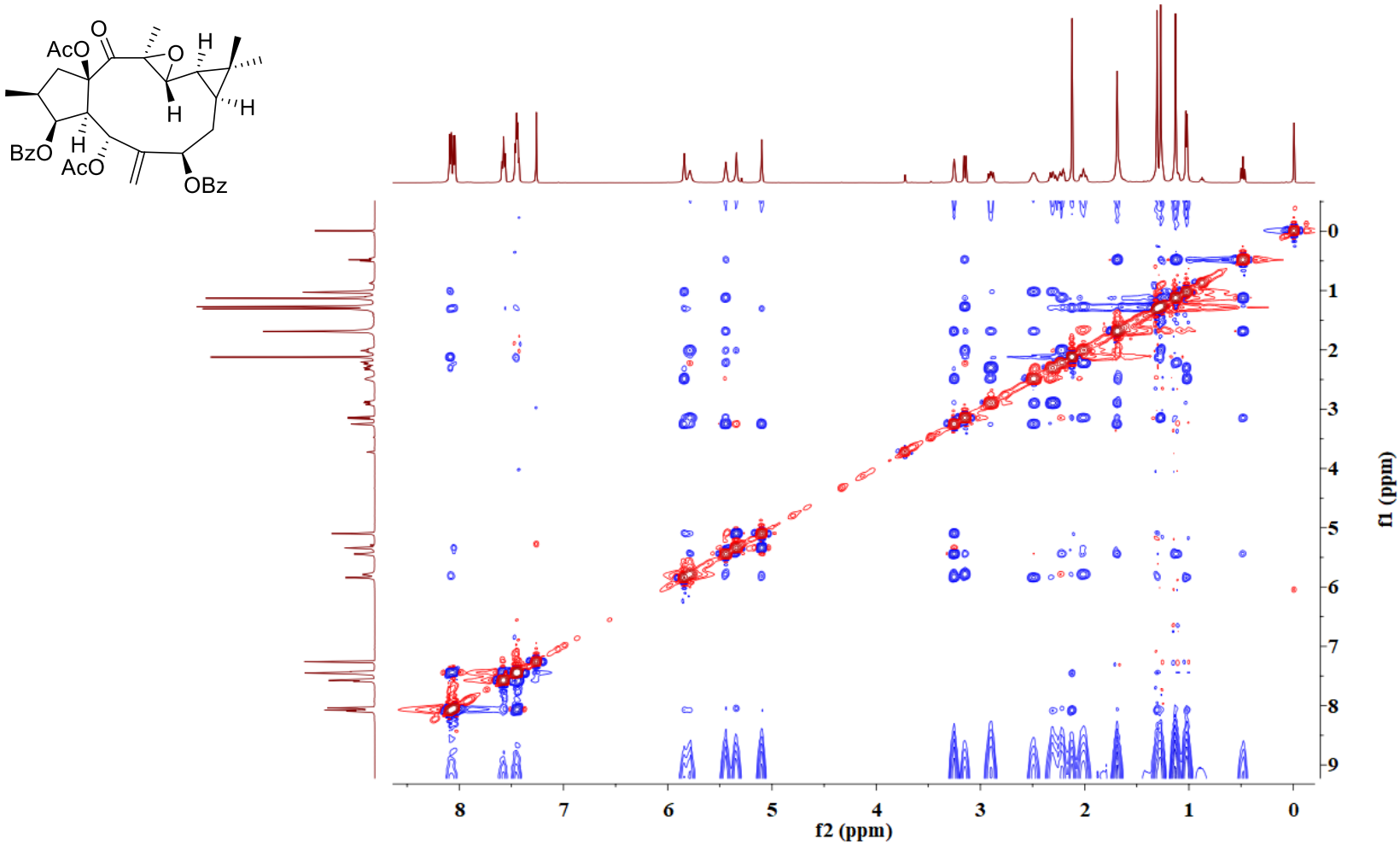


Figure S69. ^{1}H NMR spectrum of **26** in $CDCl_3$.

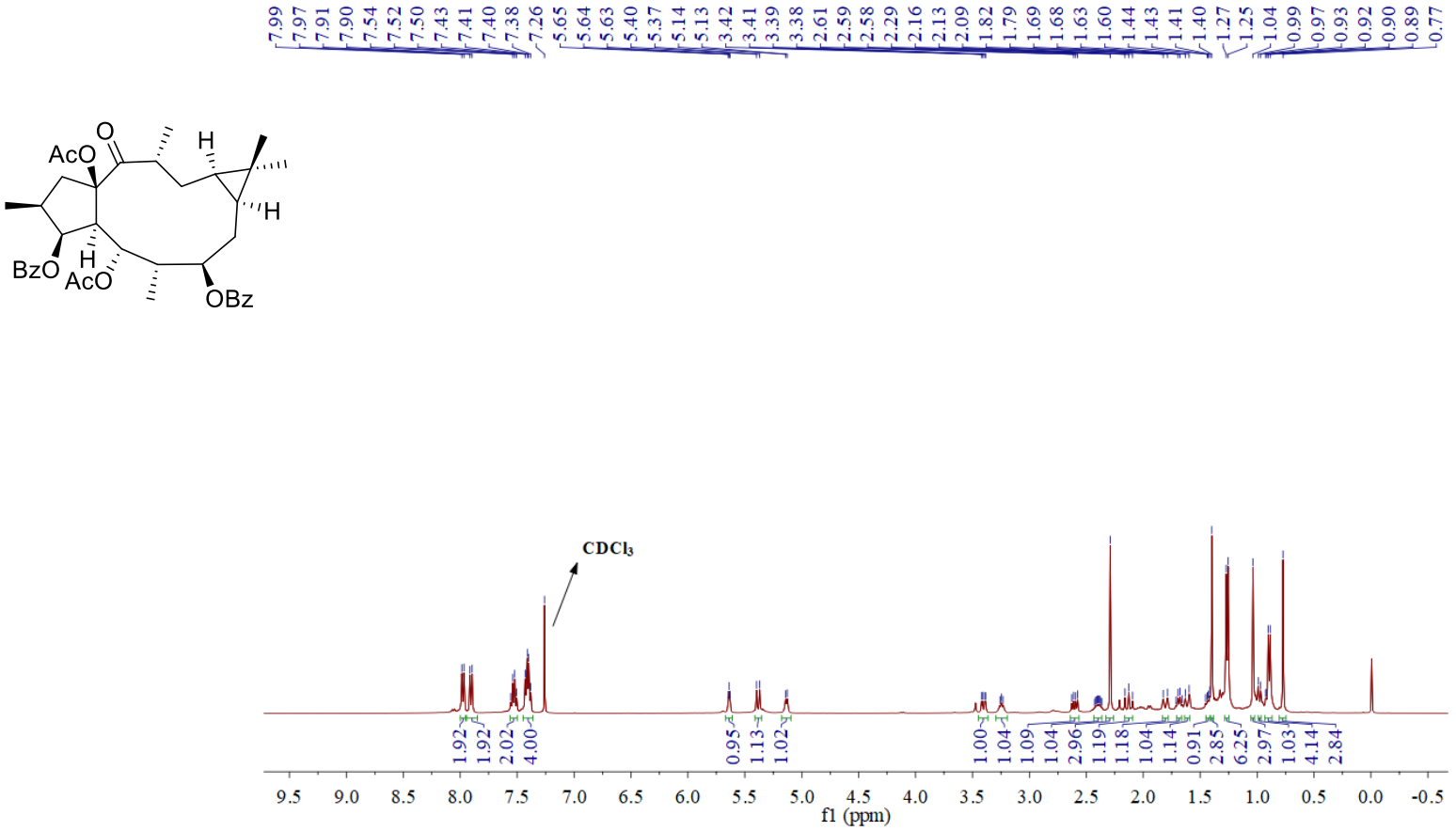


Figure S70. ^{13}C NMR and DEPT 135 spectra of **26** in $CDCl_3$.

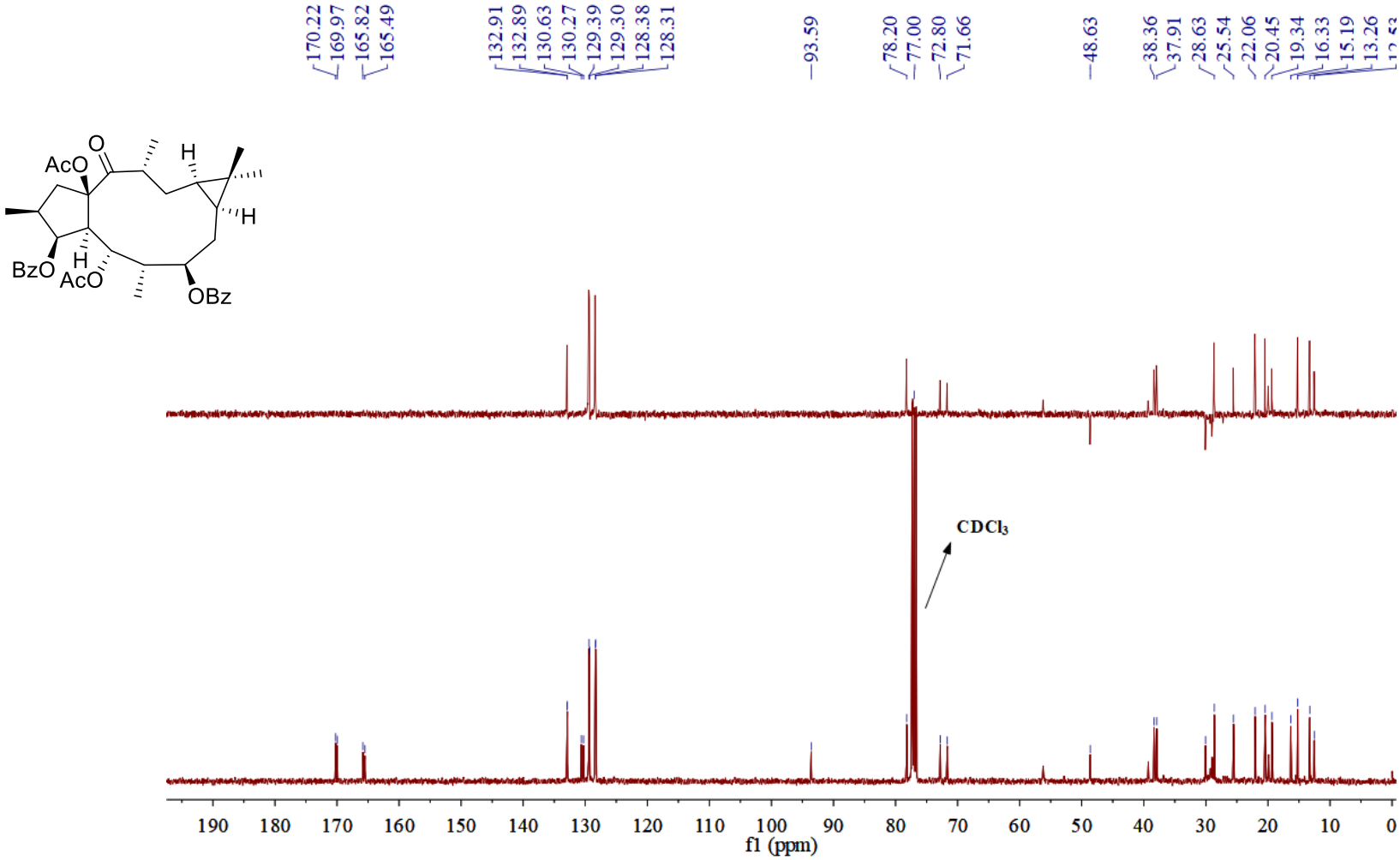


Figure S71. HSQC spectrum of **26** in $CDCl_3$.

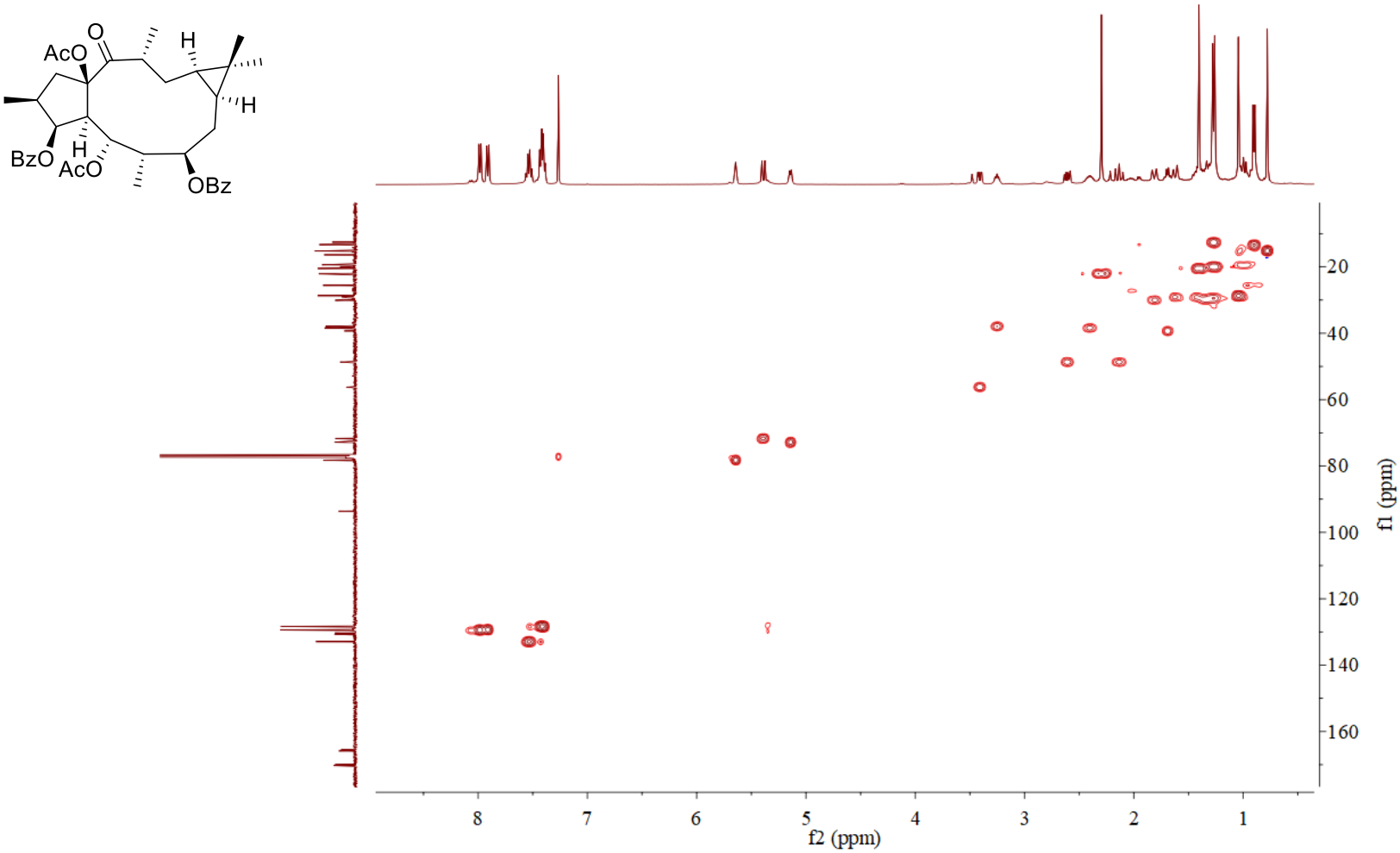


Figure S72. HMBC spectrum of **26** in $CDCl_3$.

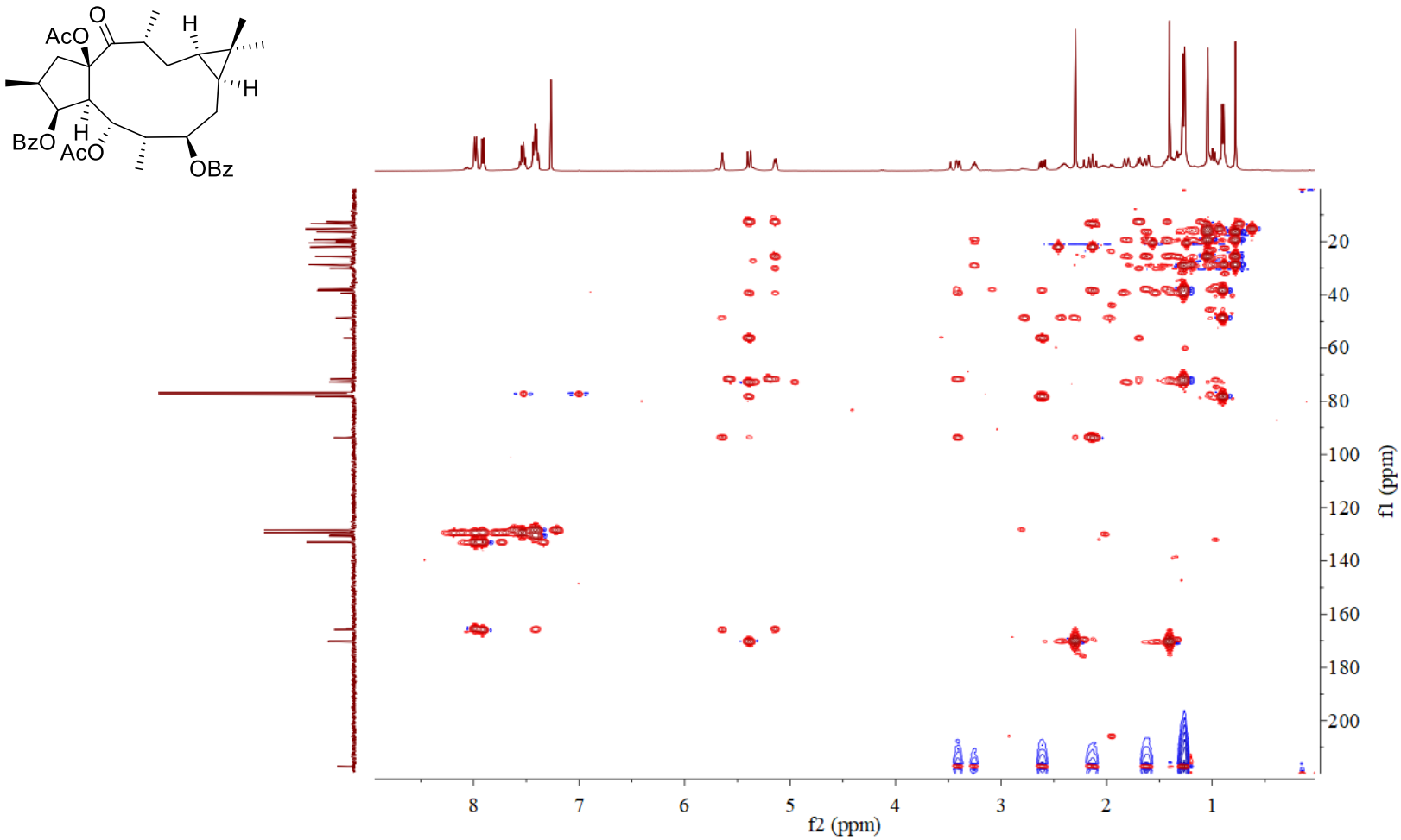


Figure S73. ^{1}H–^{1}H NMR spectrum of **26** in $CDCl_3$.

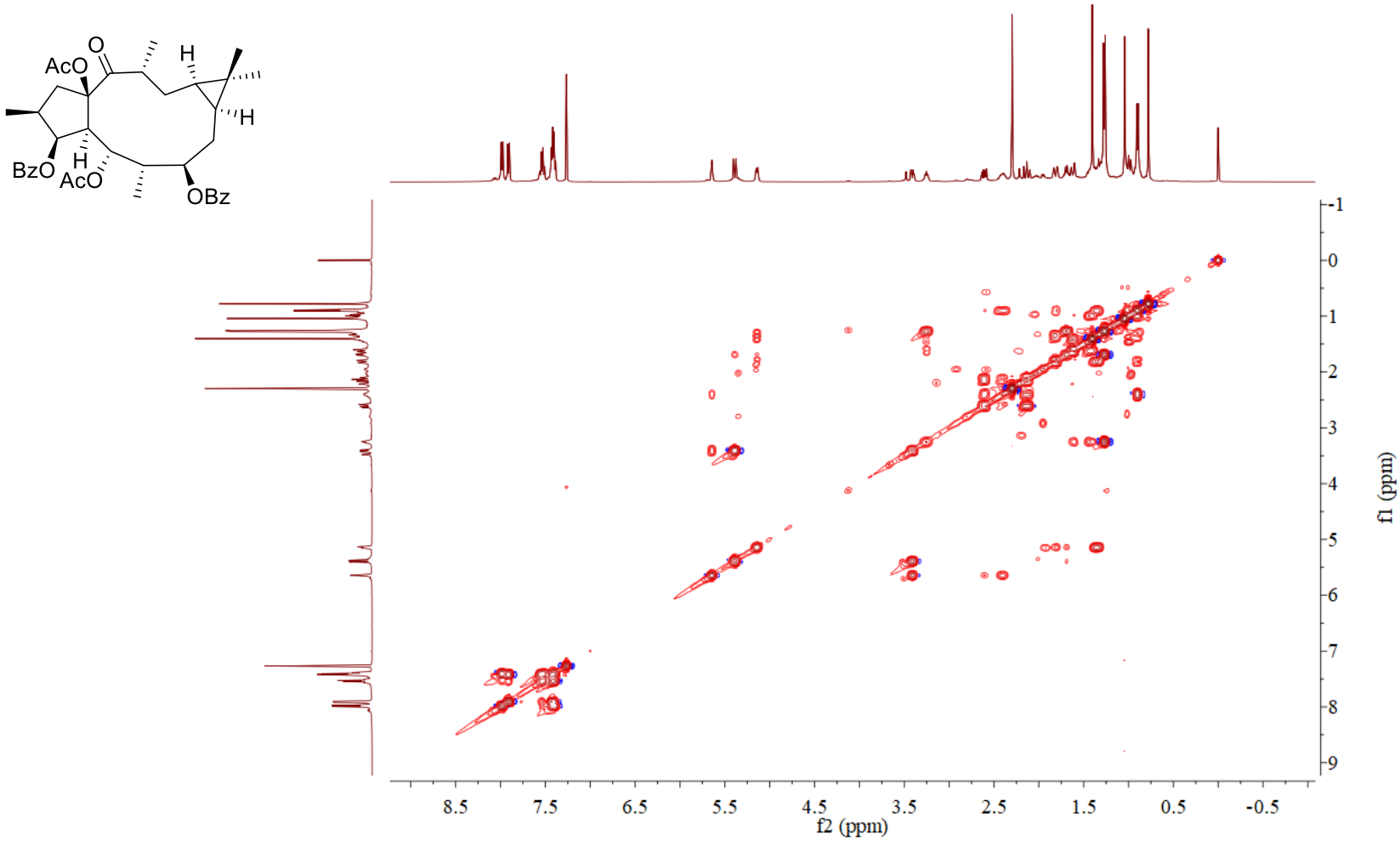


Figure S74. NOESY spectrum of **26** in $CDCl_3$.

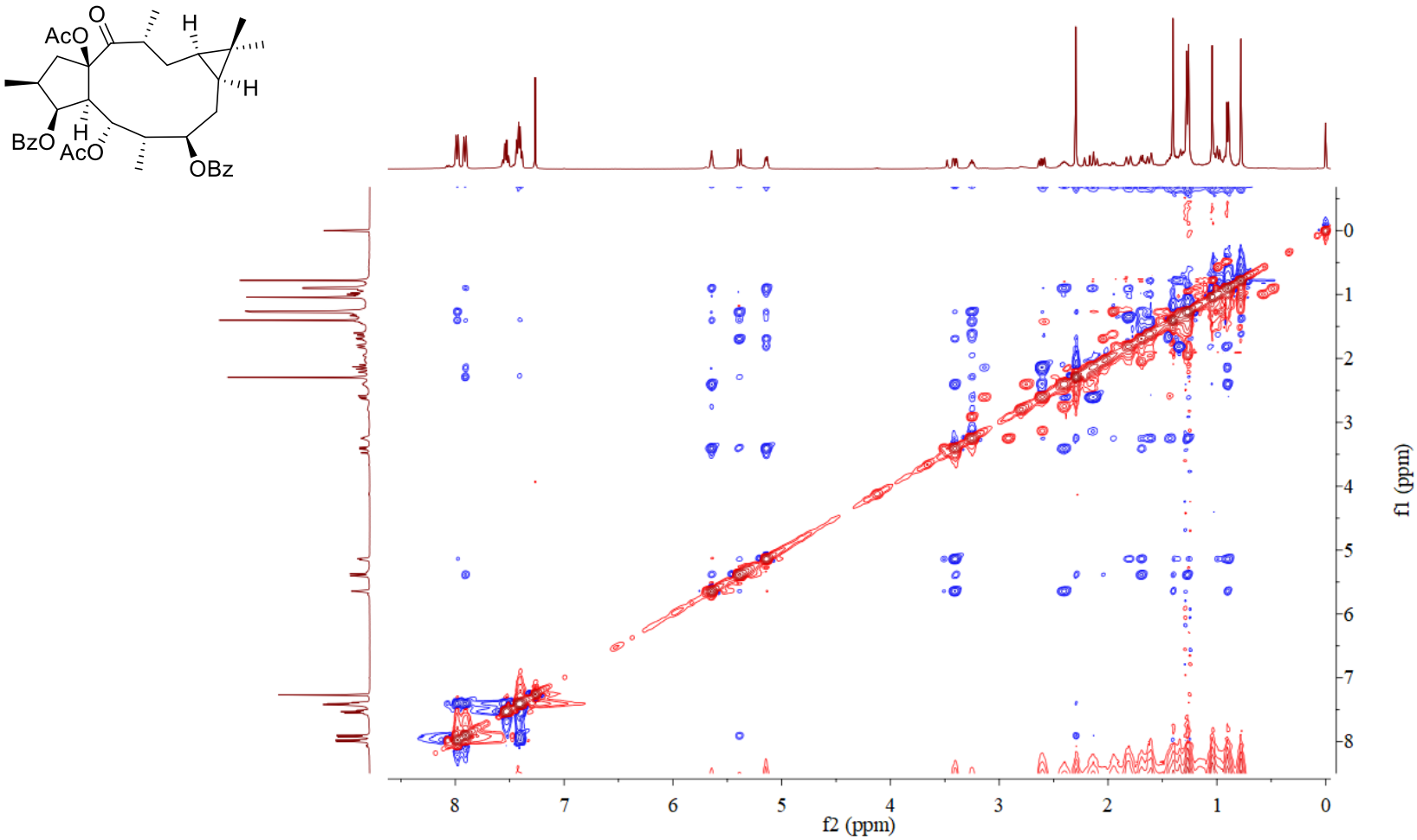


Figure S75. ^{1}H NMR spectrum of **28** in $CDCl_3$.

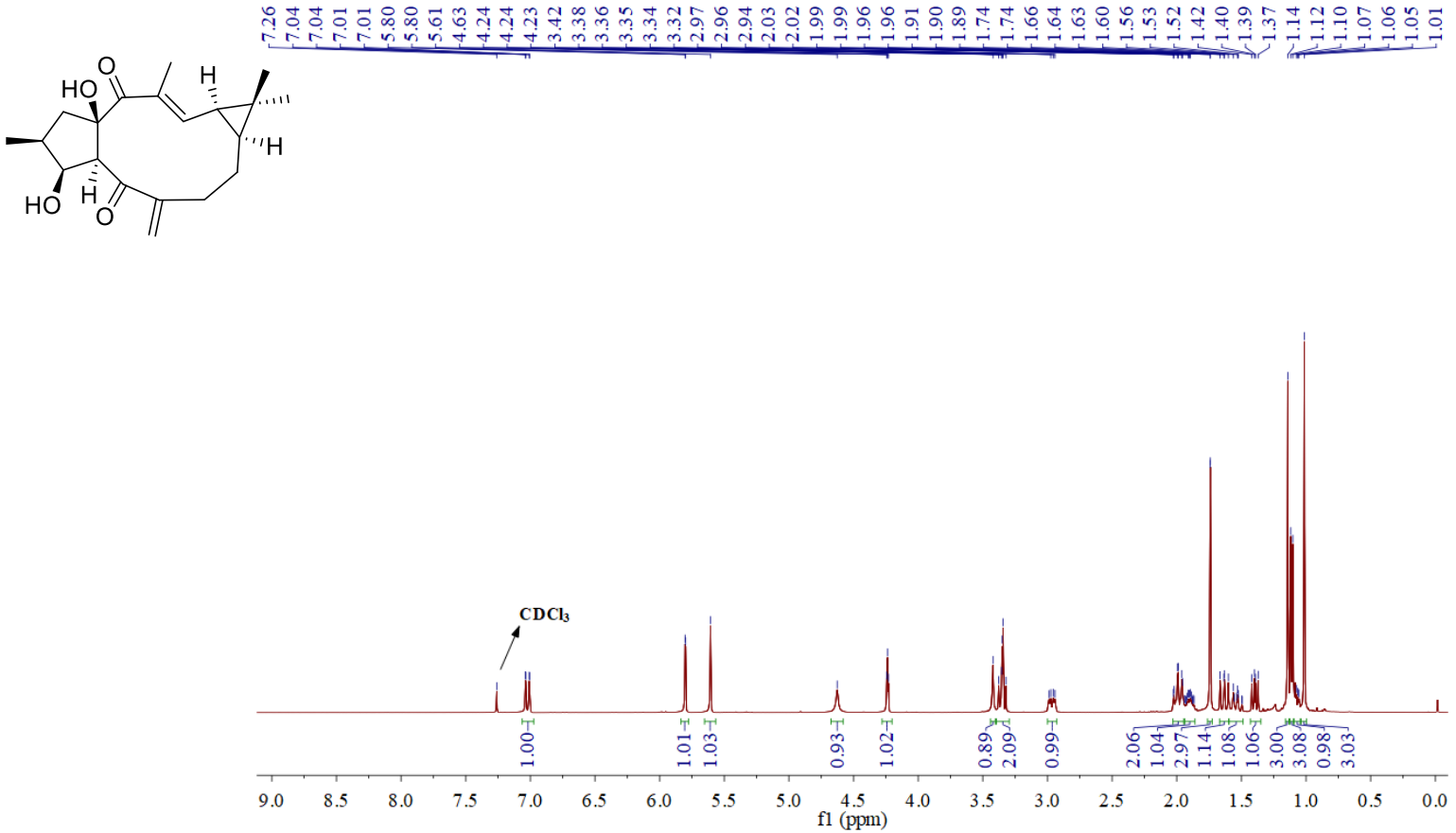


Figure S76. ^{13}C NMR and DEPT 135 spectra of **28** in $CDCl_3$.

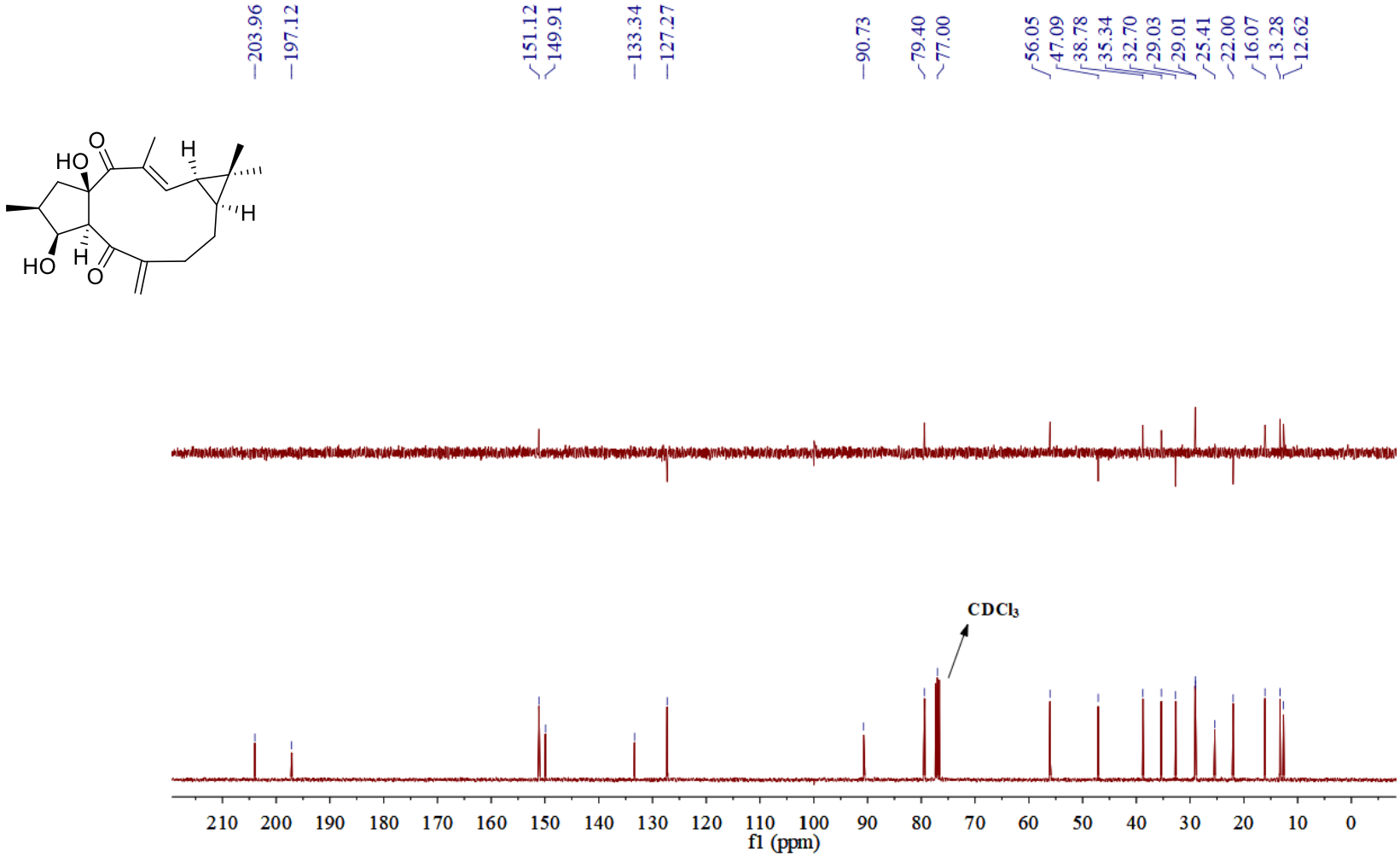


Figure S77. HSQC spectrum of **28** in $CDCl_3$.

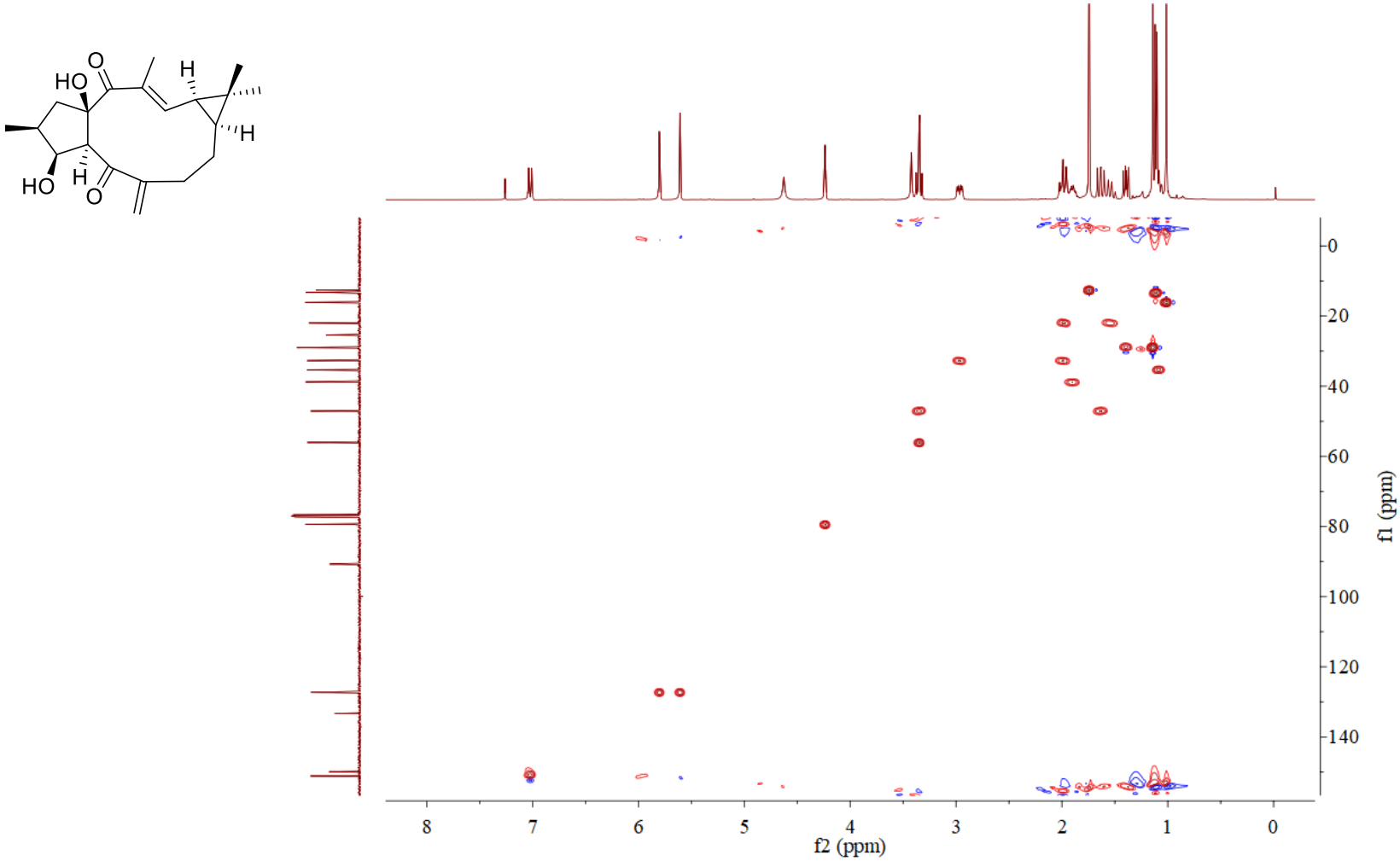


Figure S78. HMBC spectrum of **28** in $CDCl_3$.

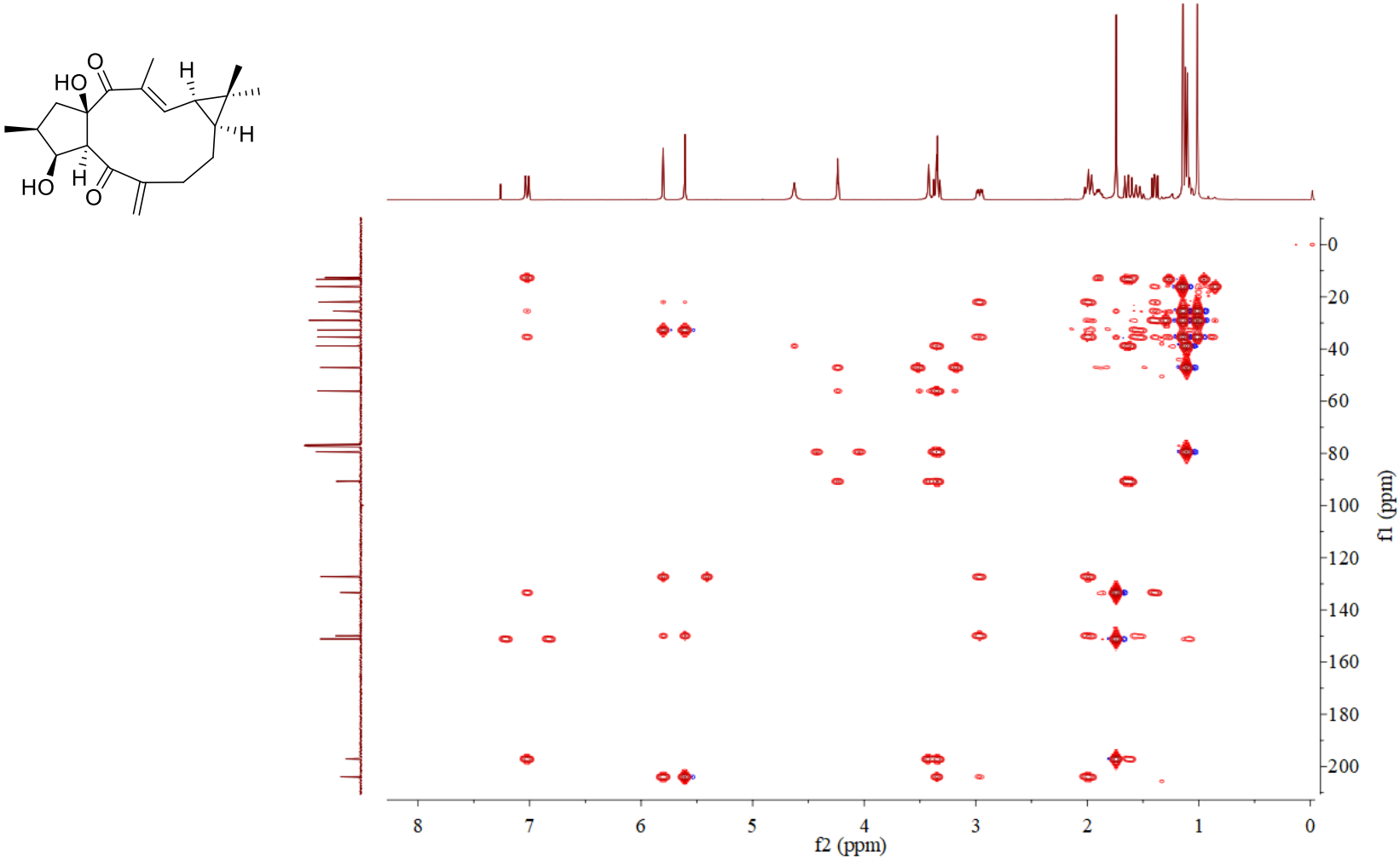


Figure S79. $^{1}H–^{1}H$ COSY spectrum of **28** in $CDCl_3$.

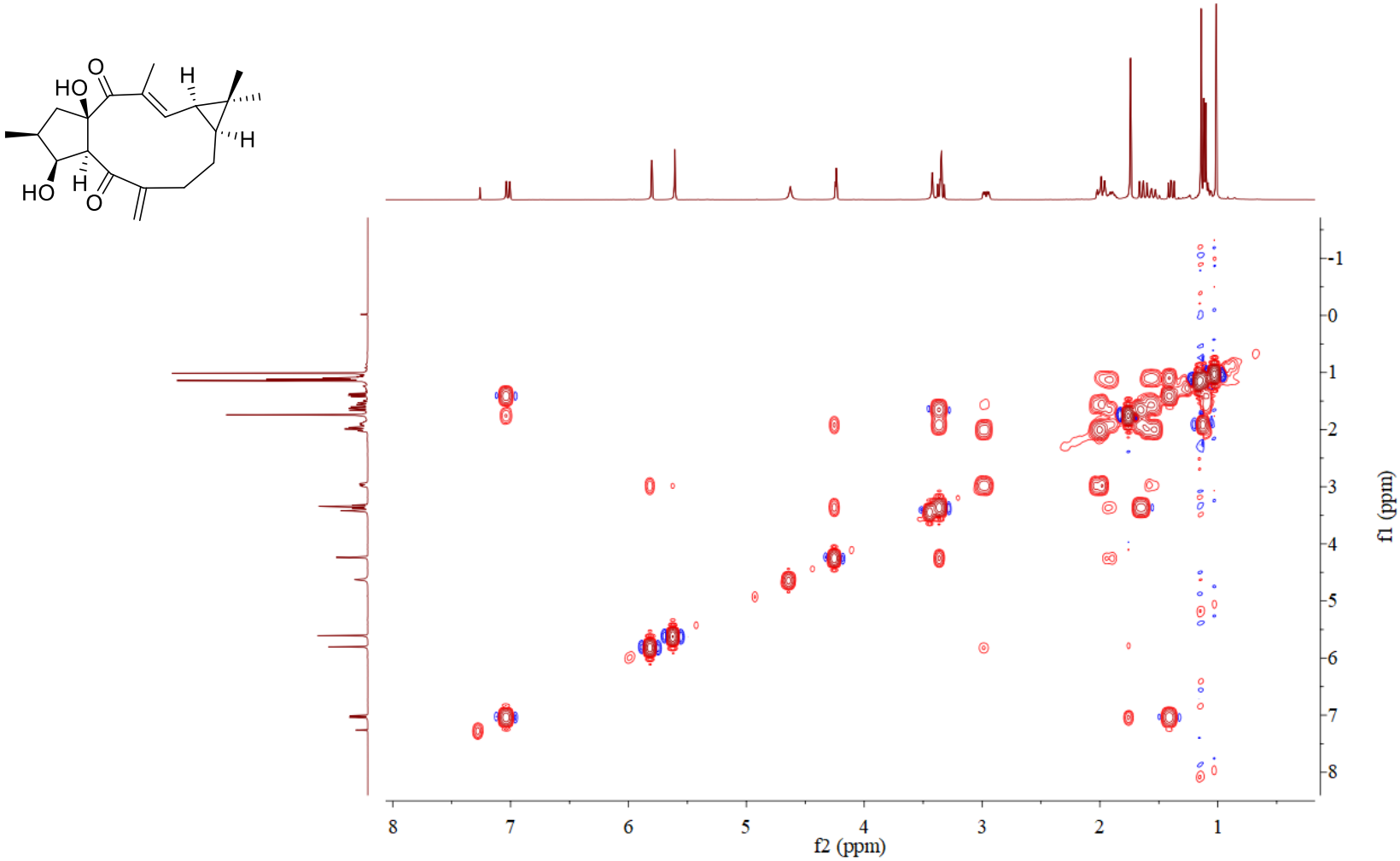


Figure S80. ^{1}H NMR spectrum of **29** in $CDCl_3$.

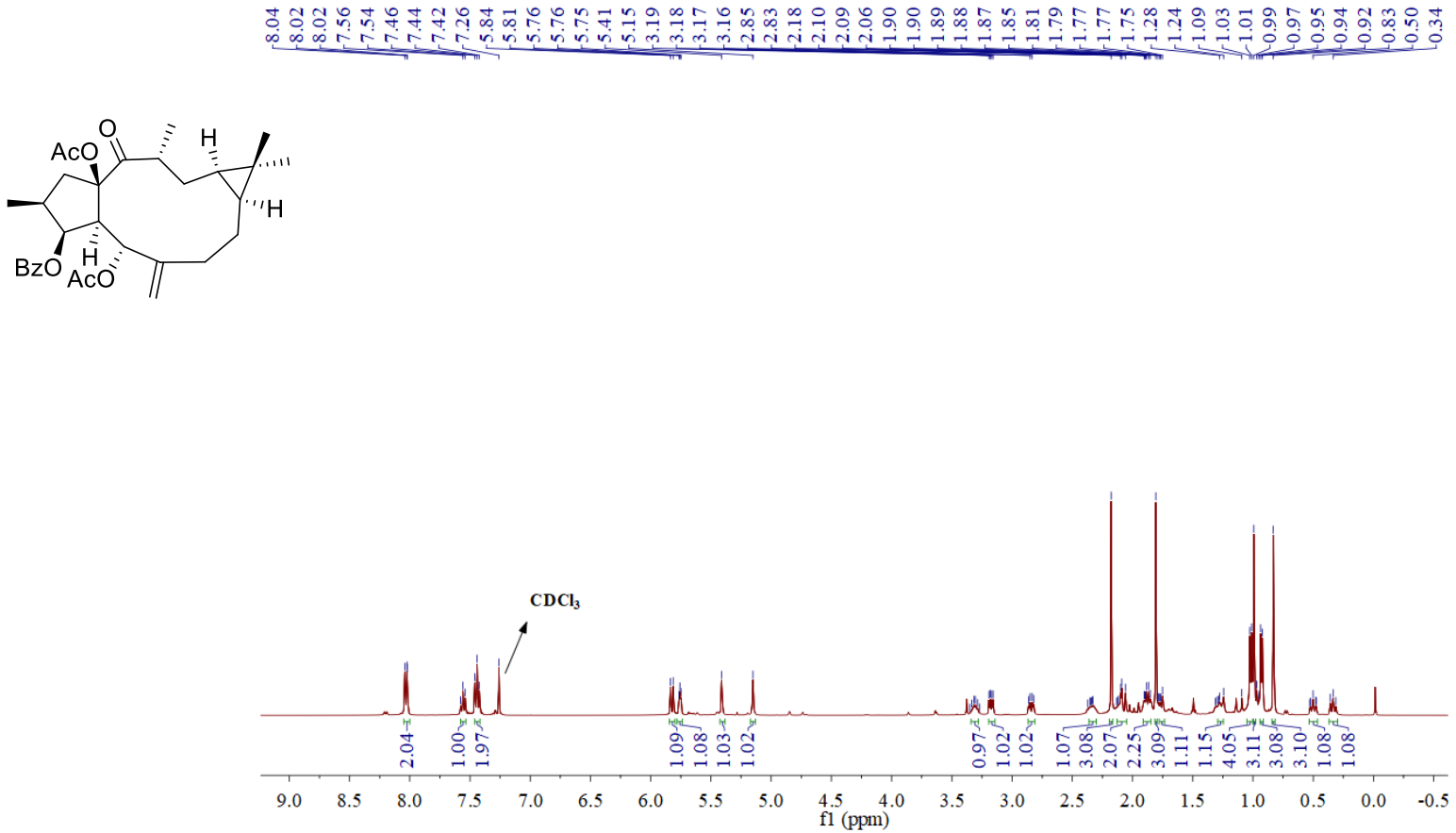


Figure S81. ^{13}C NMR and DEPT 135 spectra of **29** in $CDCl_3$.

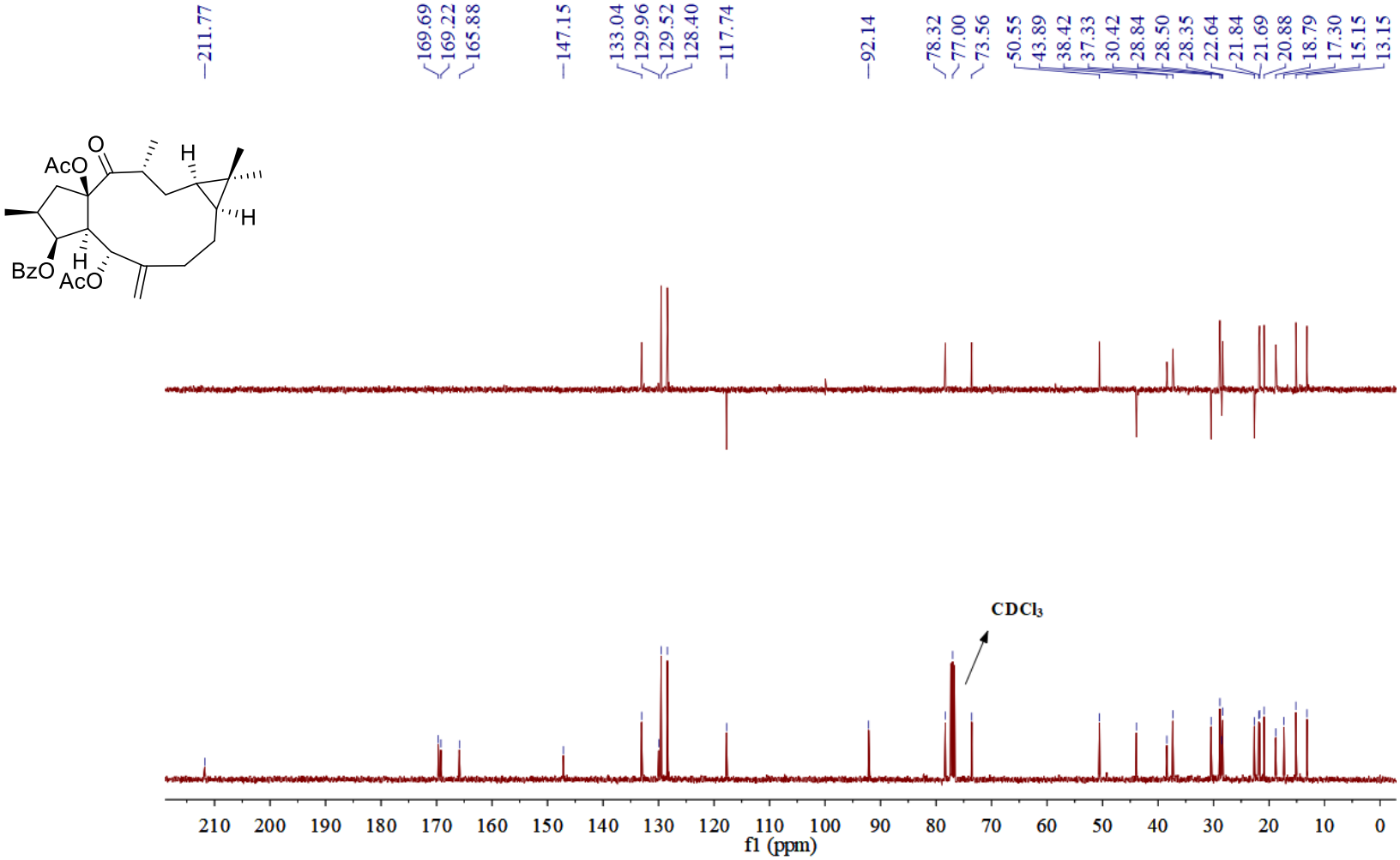


Figure S82. HSQC spectrum of **29** in $CDCl_3$.

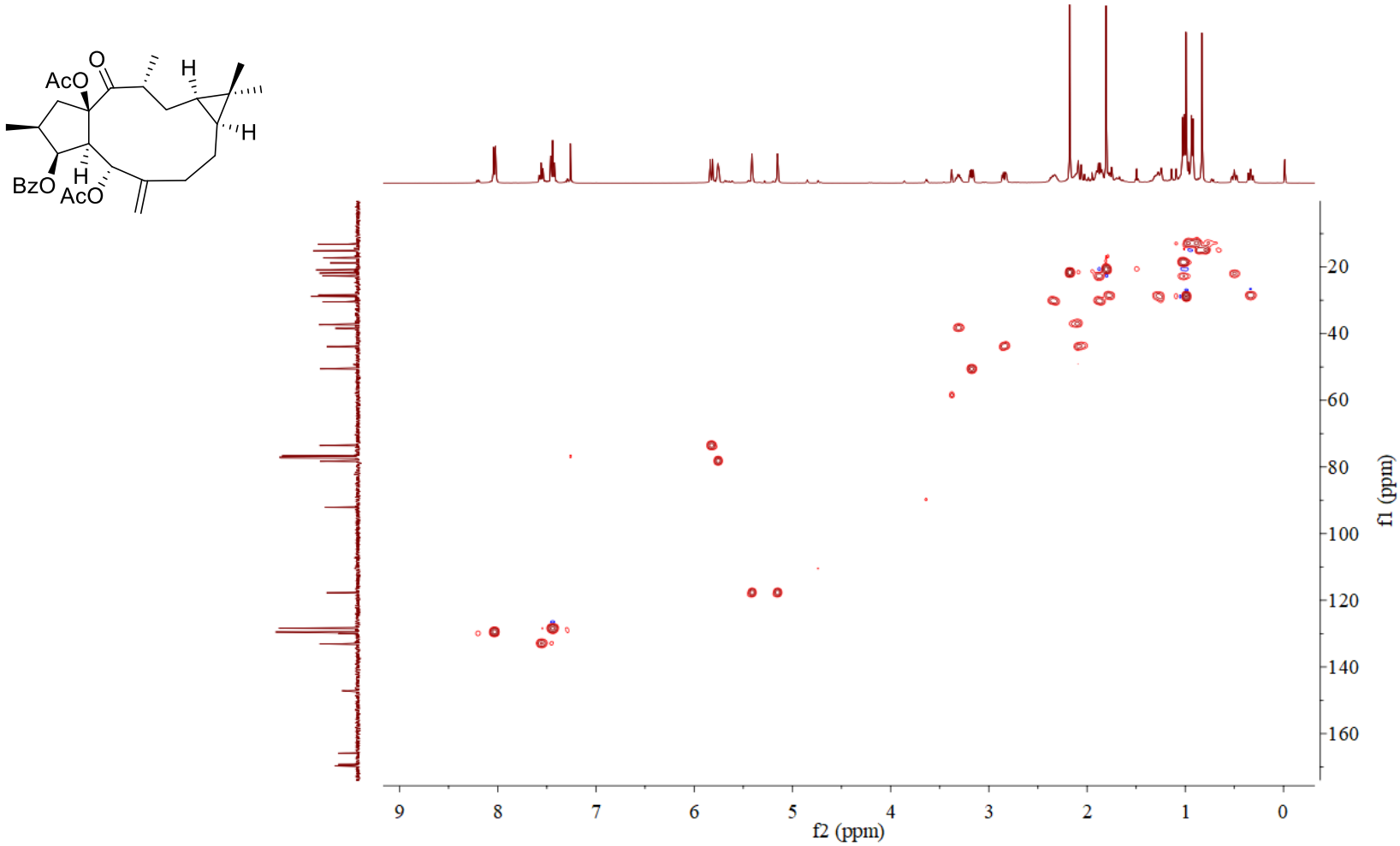


Figure S83. HMBC spectrum of **29** in $CDCl_3$.

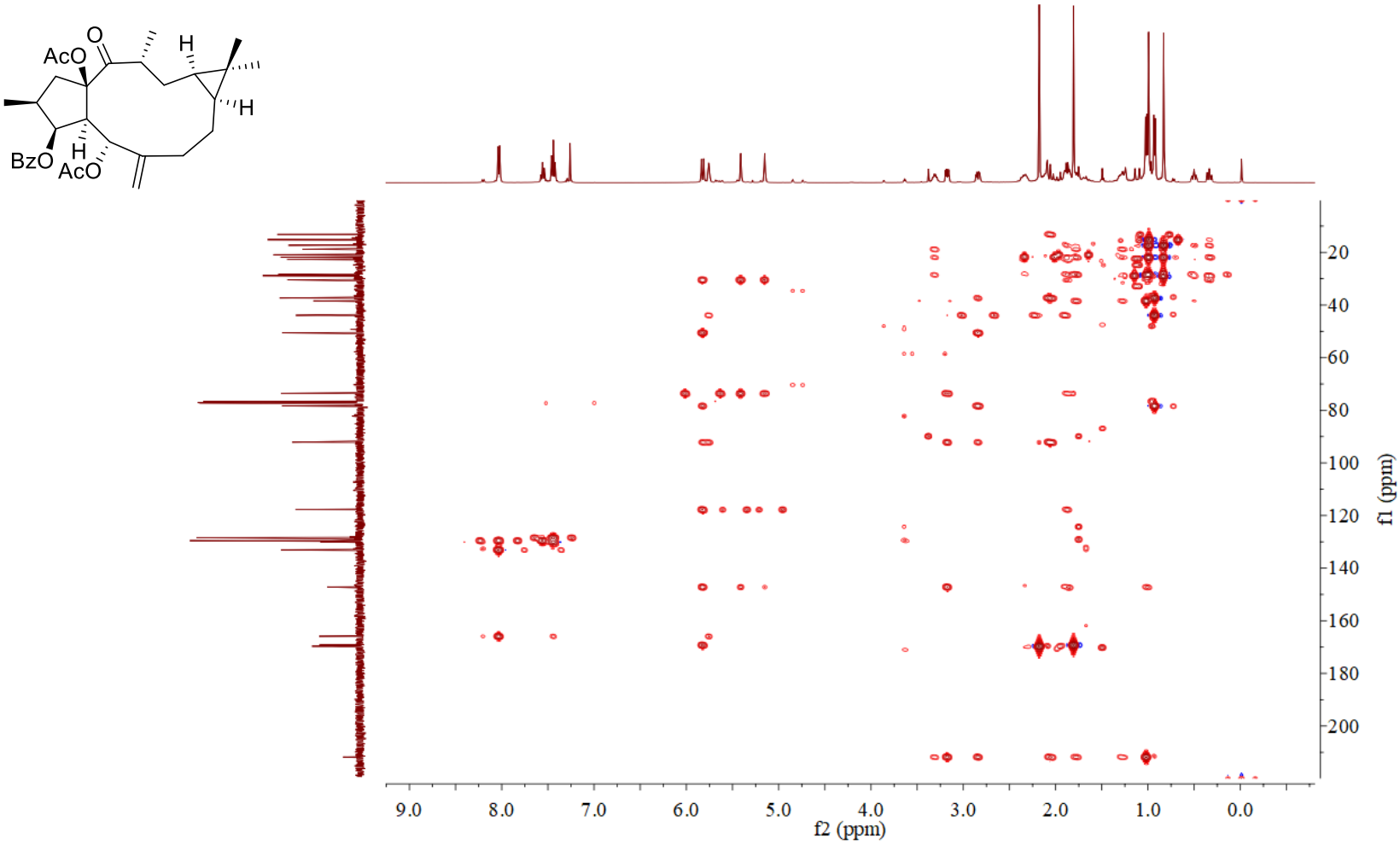


Figure S84. $^{1}H–^{1}H$ COSY spectrum of **29** in $CDCl_3$.

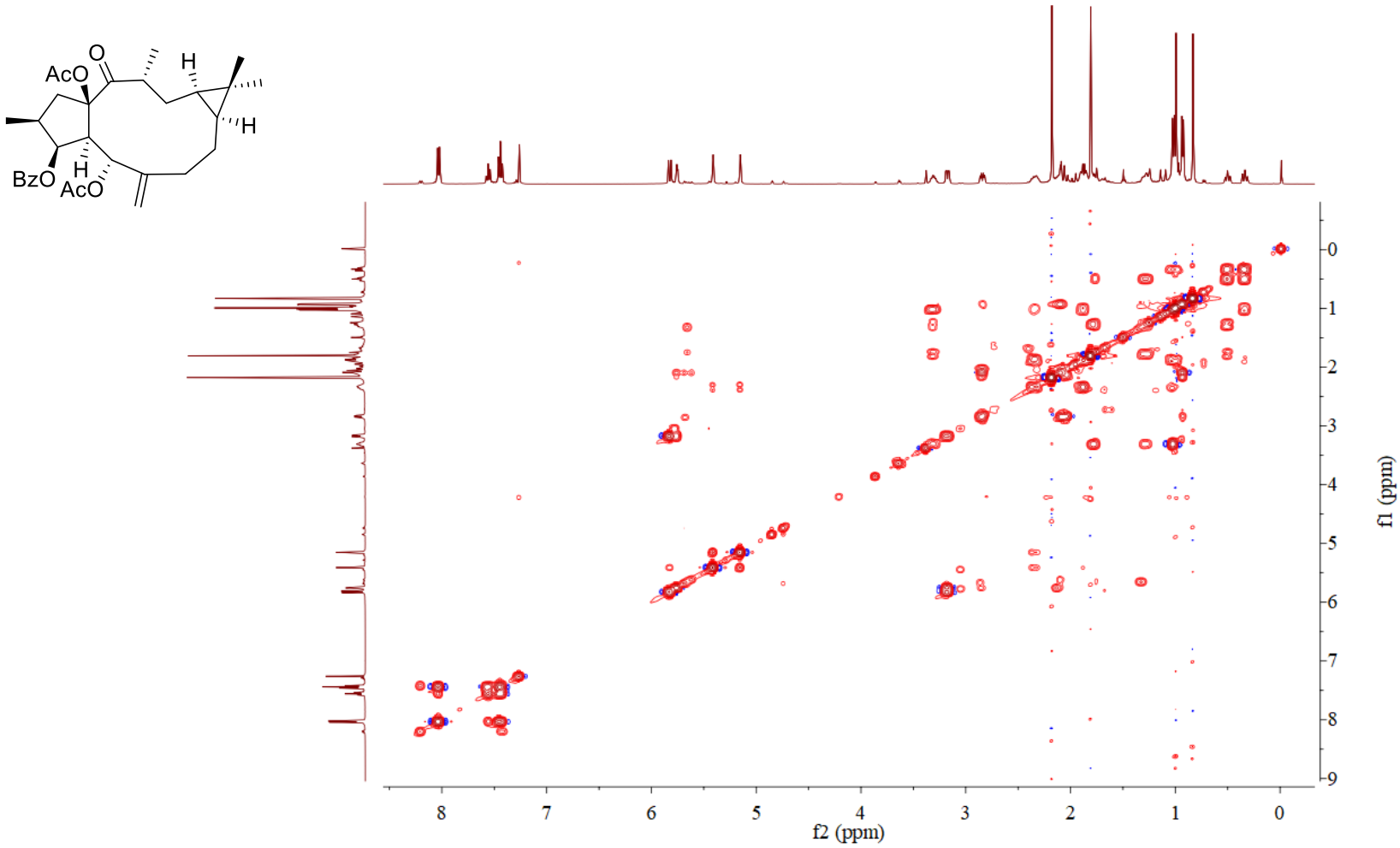


Figure S85. NOESY spectrum of **29** in $CDCl_3$.

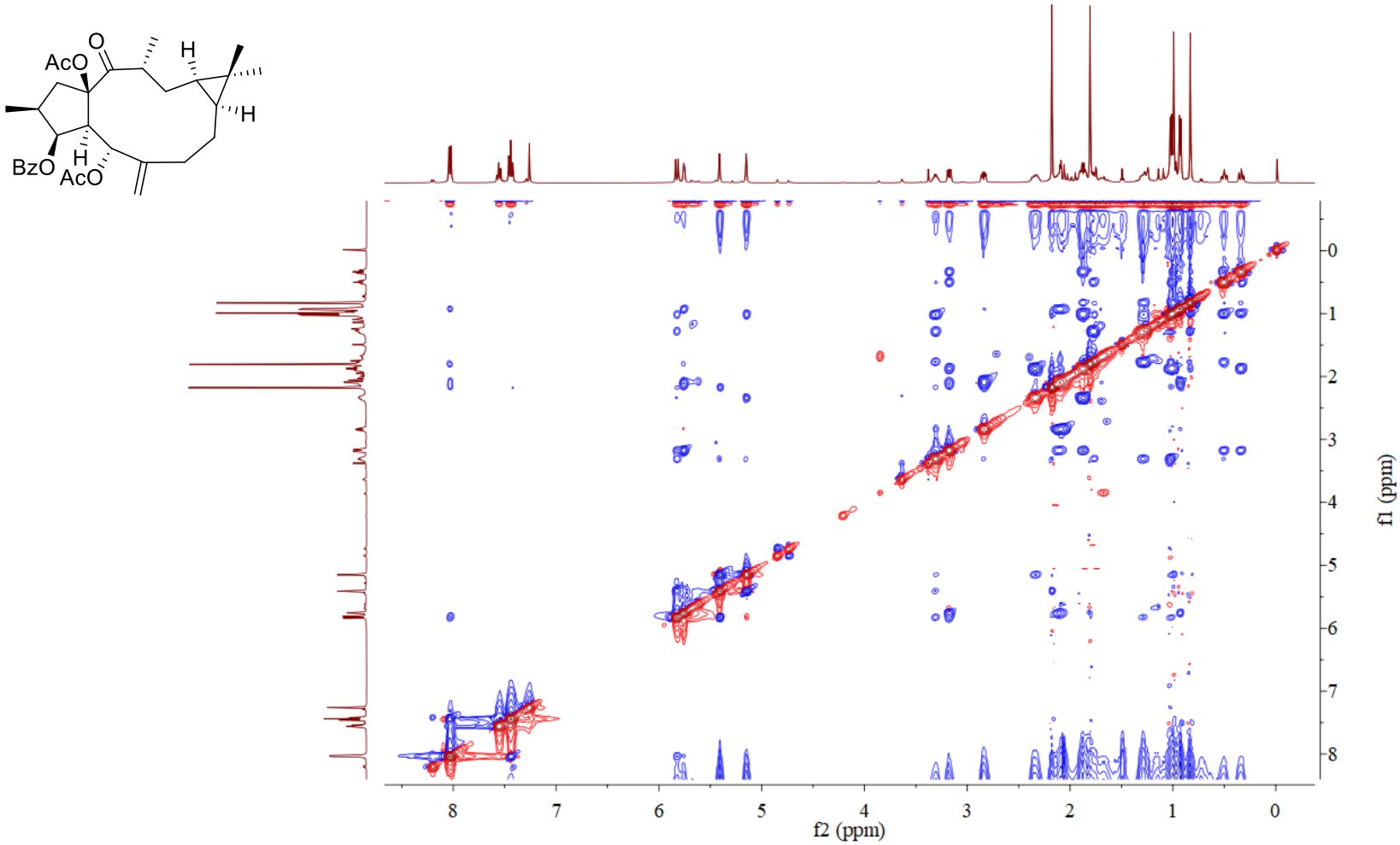


Figure S86. ^{1}H NMR spectrum of **30** in $CDCl_3$.

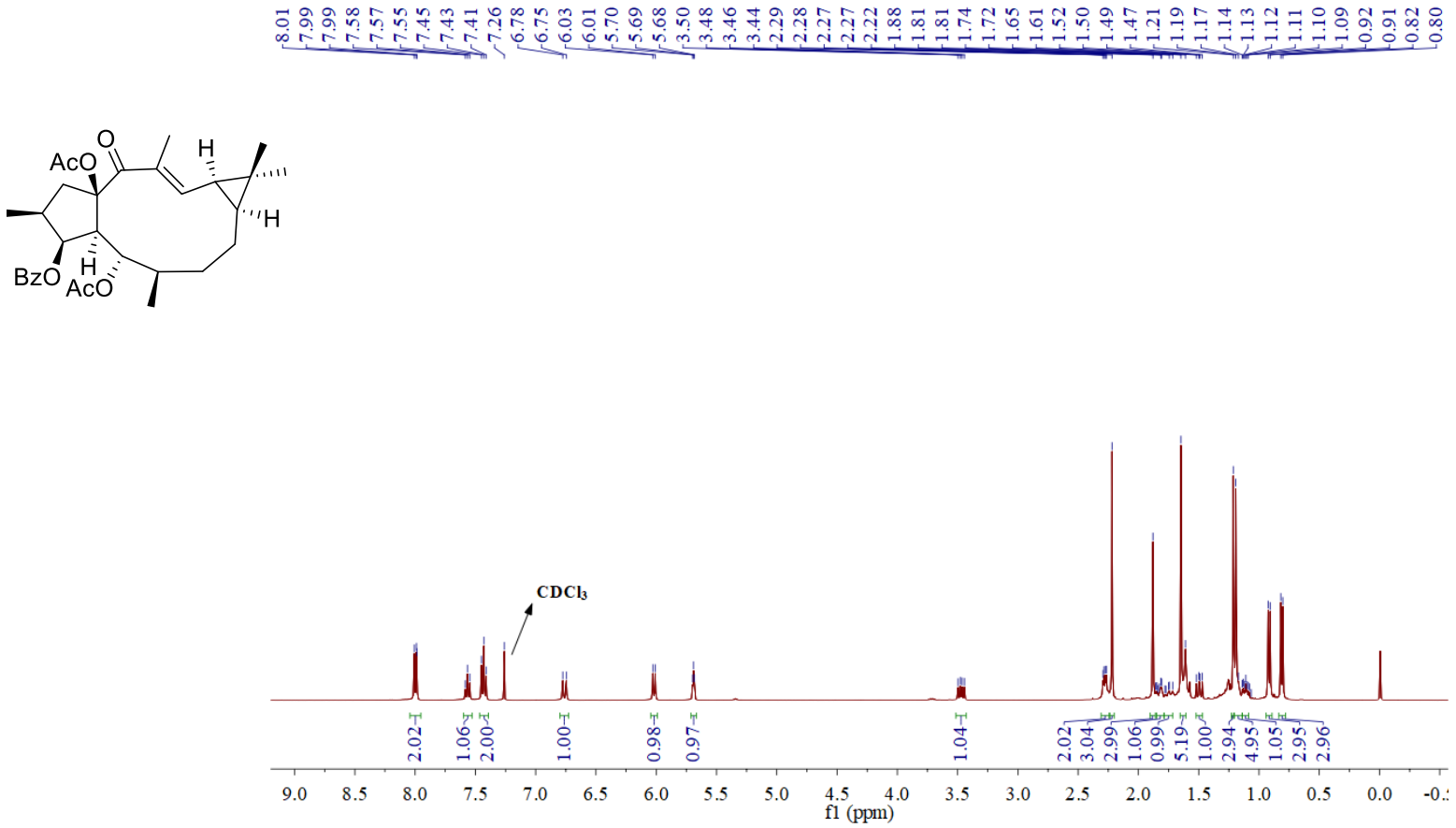


Figure S87. ^{13}C NMR and DEPT 135 spectra of **30** in $CDCl_3$.

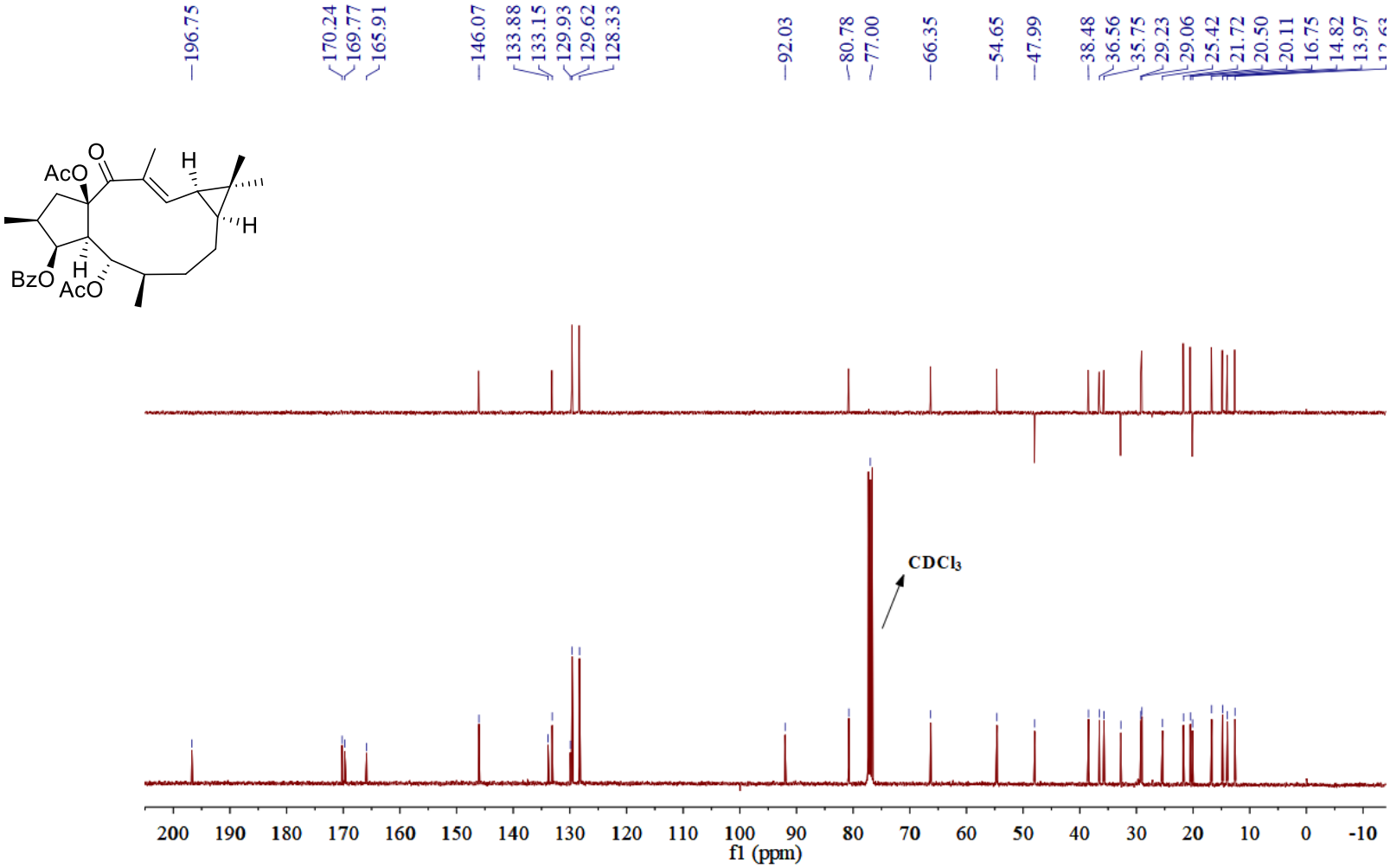


Figure S88. HSQC spectrum of **30** in $CDCl_3$.

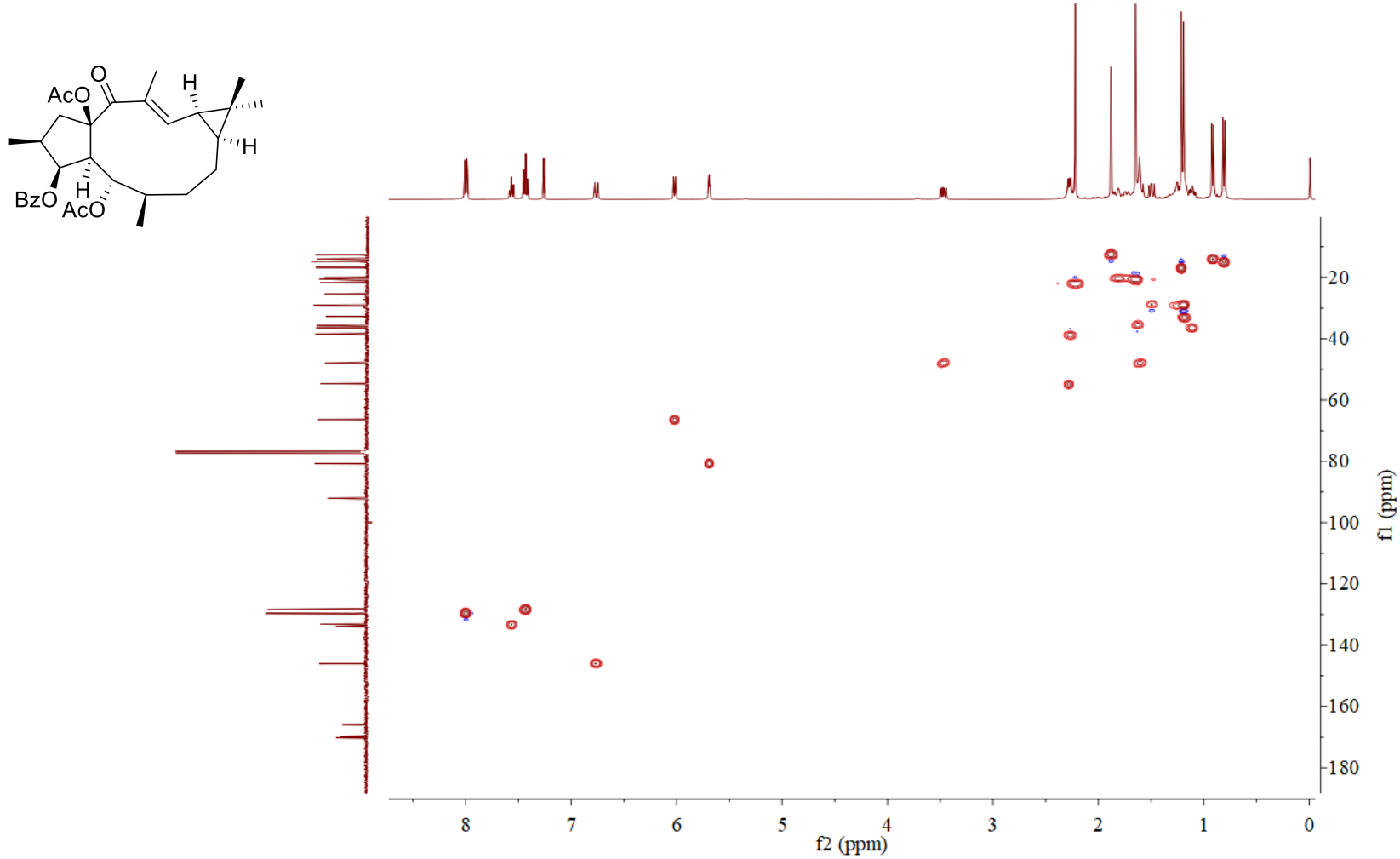


Figure S89. HMBC spectrum of **30** in $CDCl_3$.

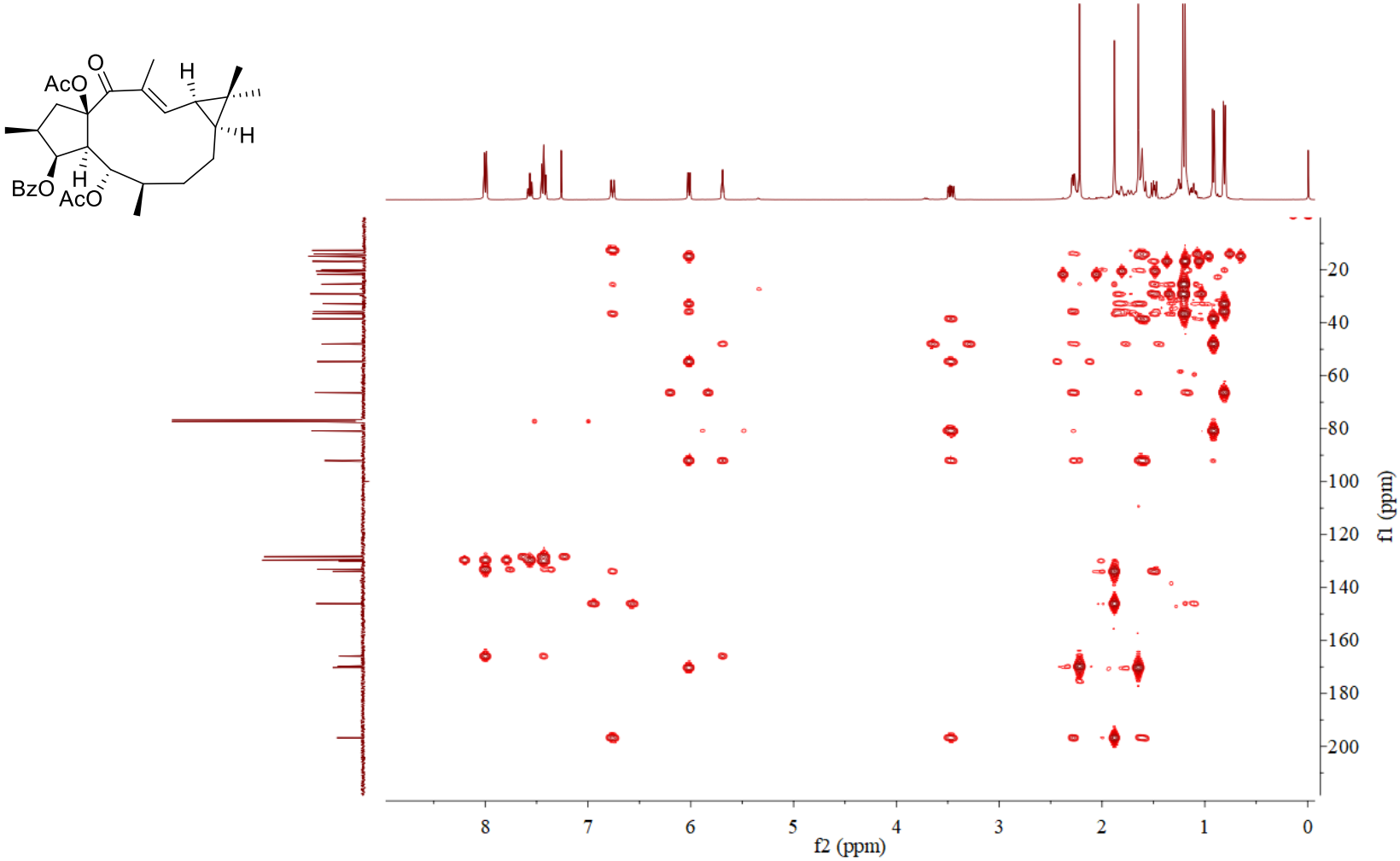


Figure S90. $^{1}H–^{1}H$ COSY spectrum of **30** in $CDCl_3$.

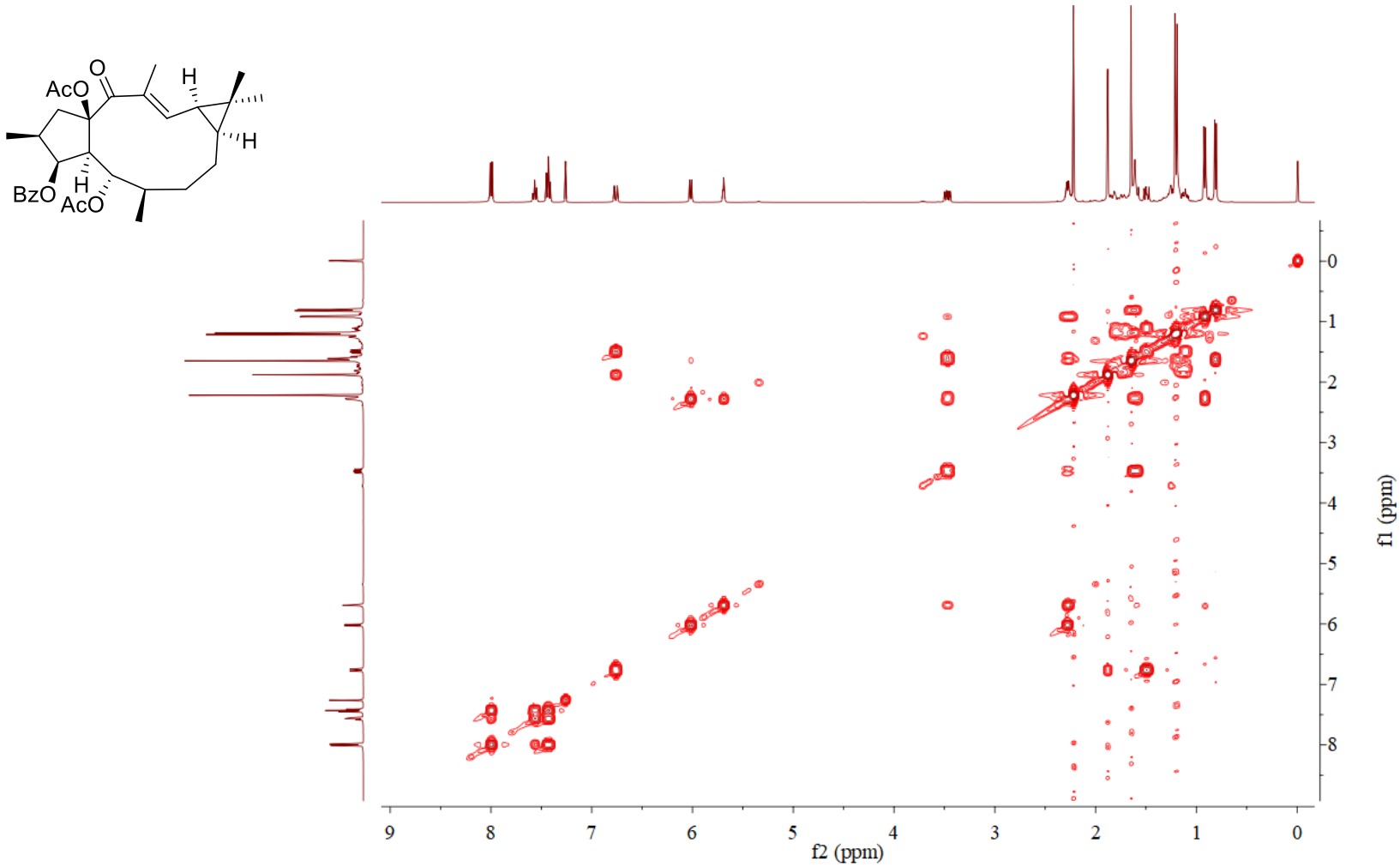


Figure S91. NOESY spectrum of **30** in $CDCl_3$.

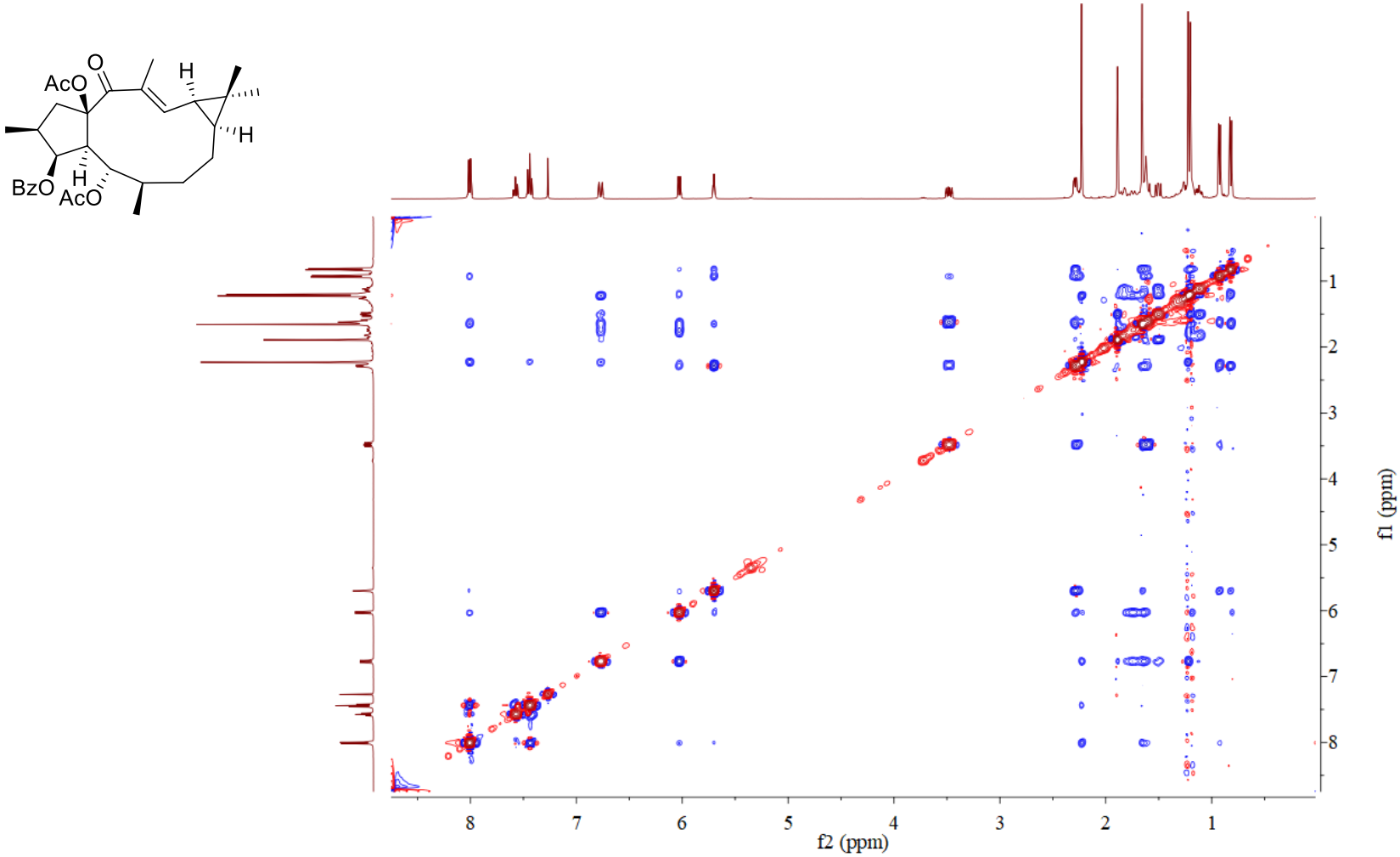


Figure S92. ^{1}H NMR spectrum of **31** in $CDCl_3$.

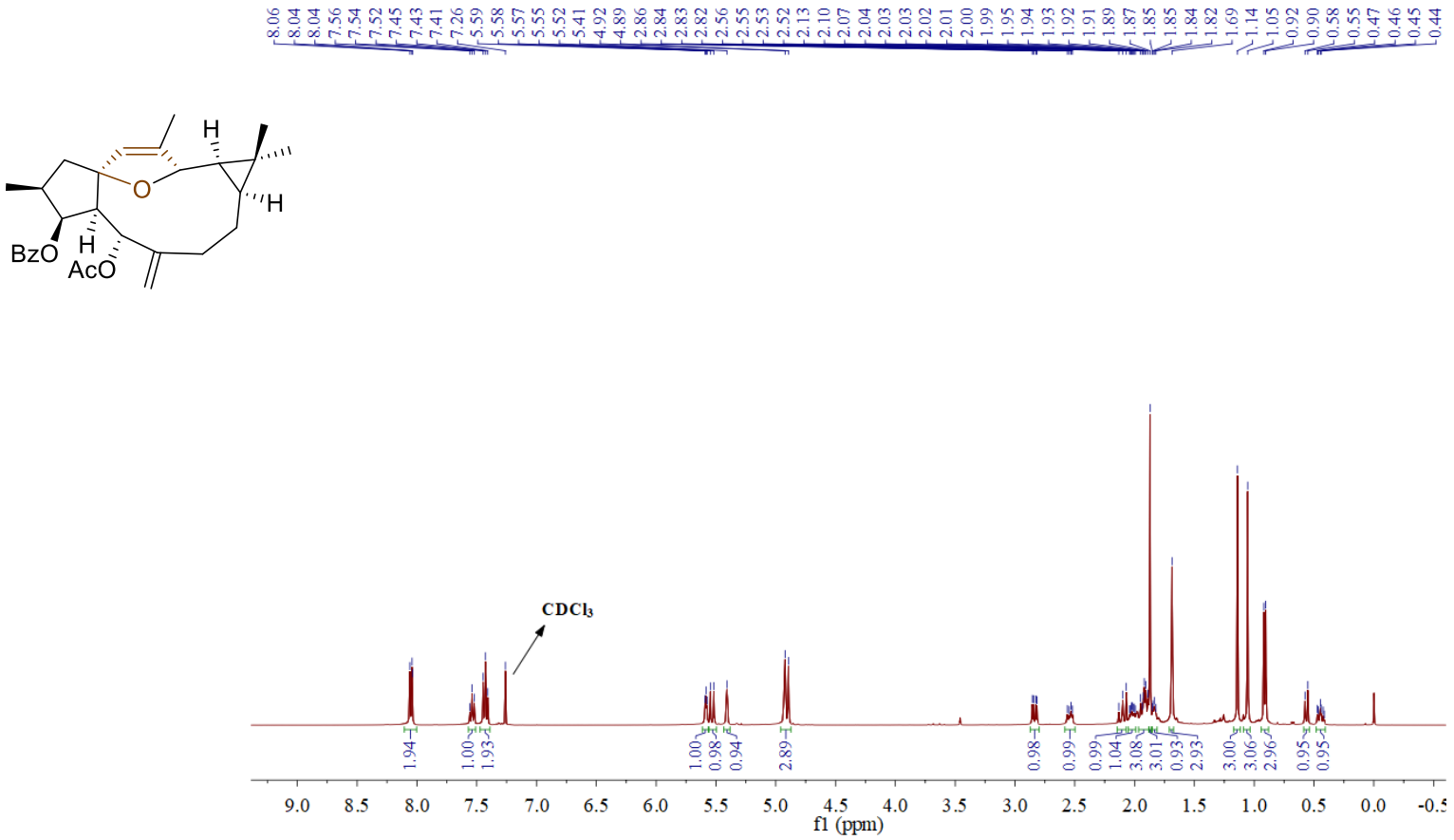


Figure S93. ^{13}C NMR and DEPT 135 spectra of **31** in $CDCl_3$.

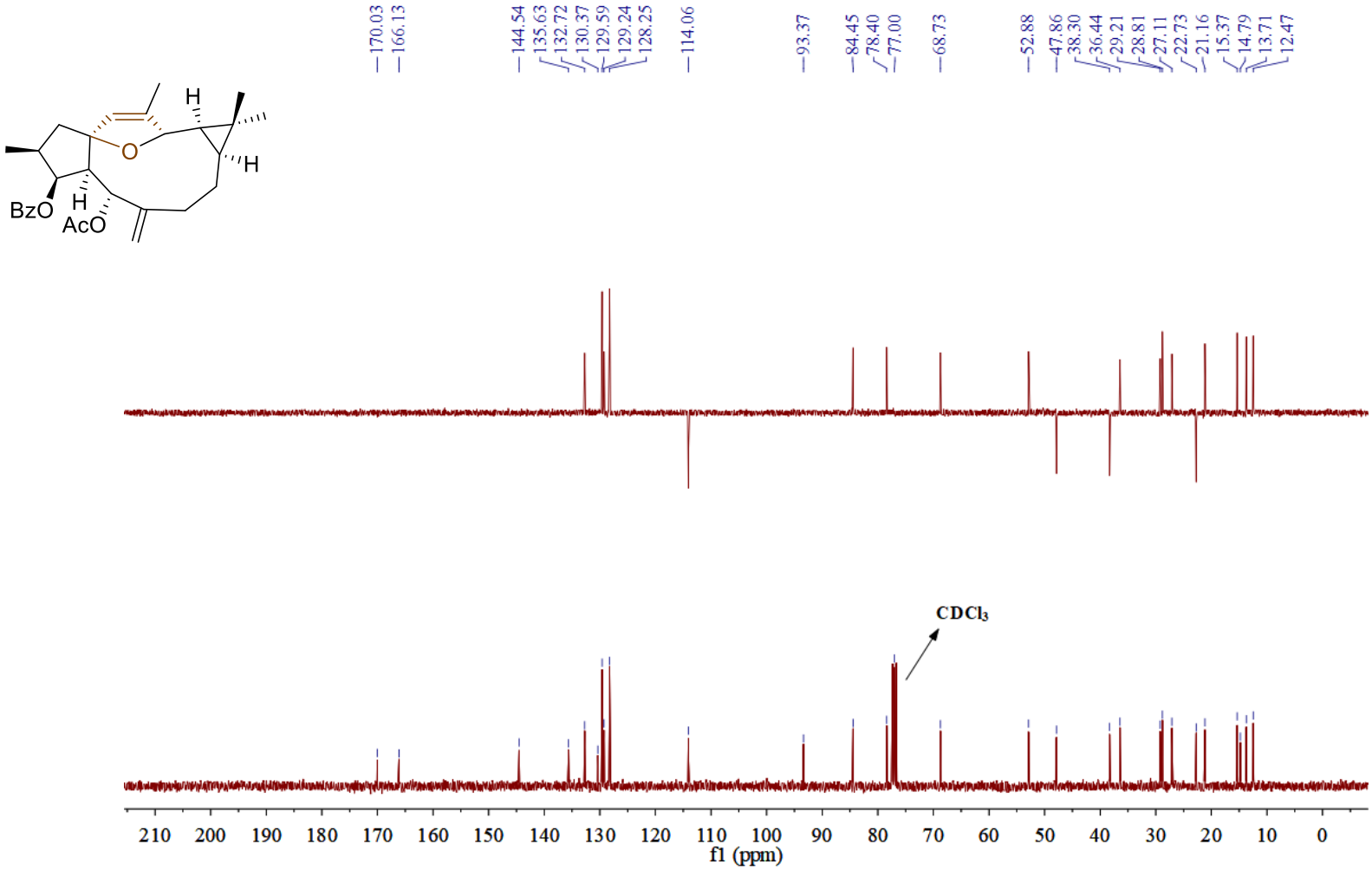


Figure S94. HSQC spectrum of **31** in $CDCl_3$.

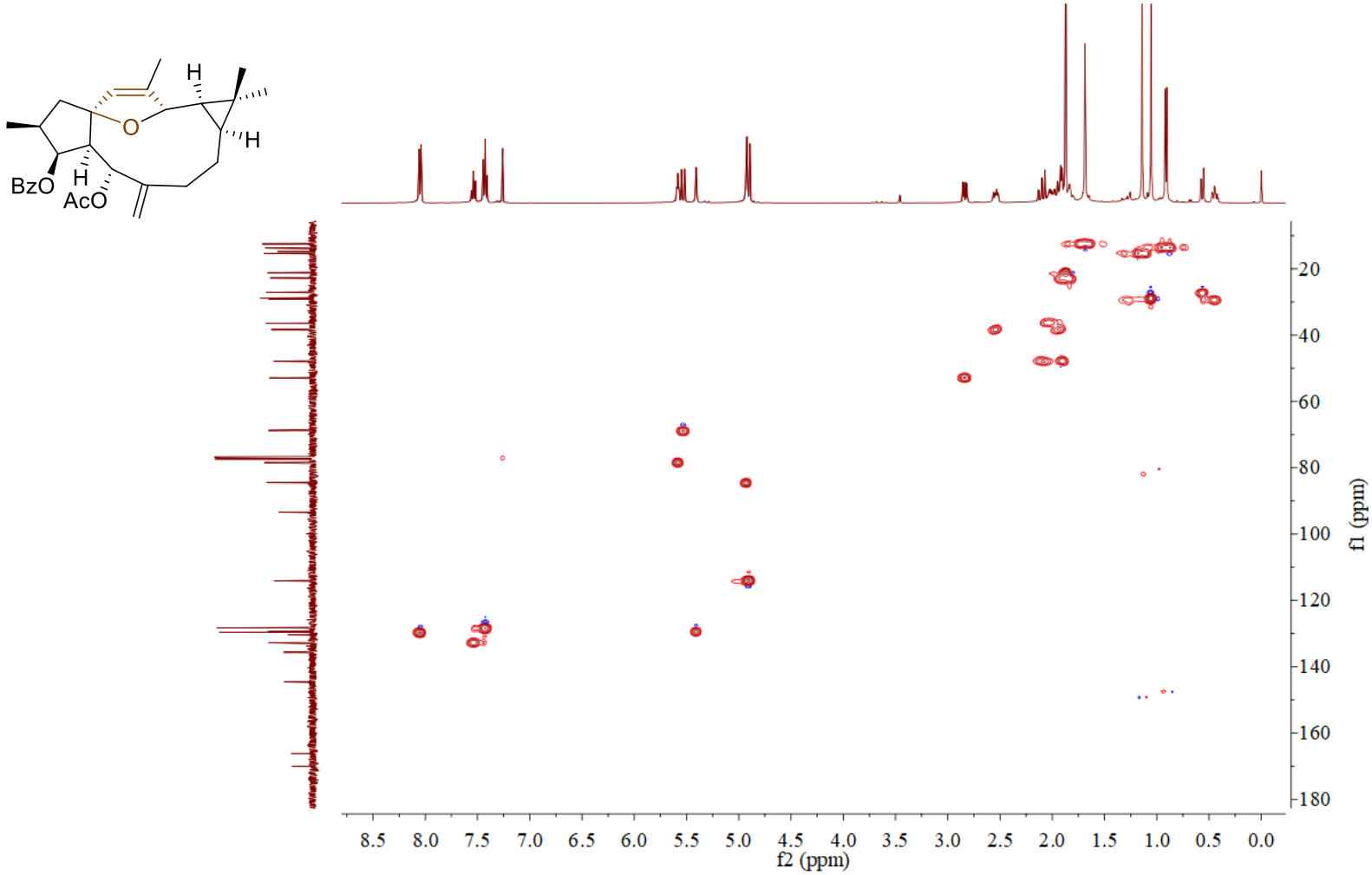


Figure S95. HMBC spectrum of **31** in $CDCl_3$.

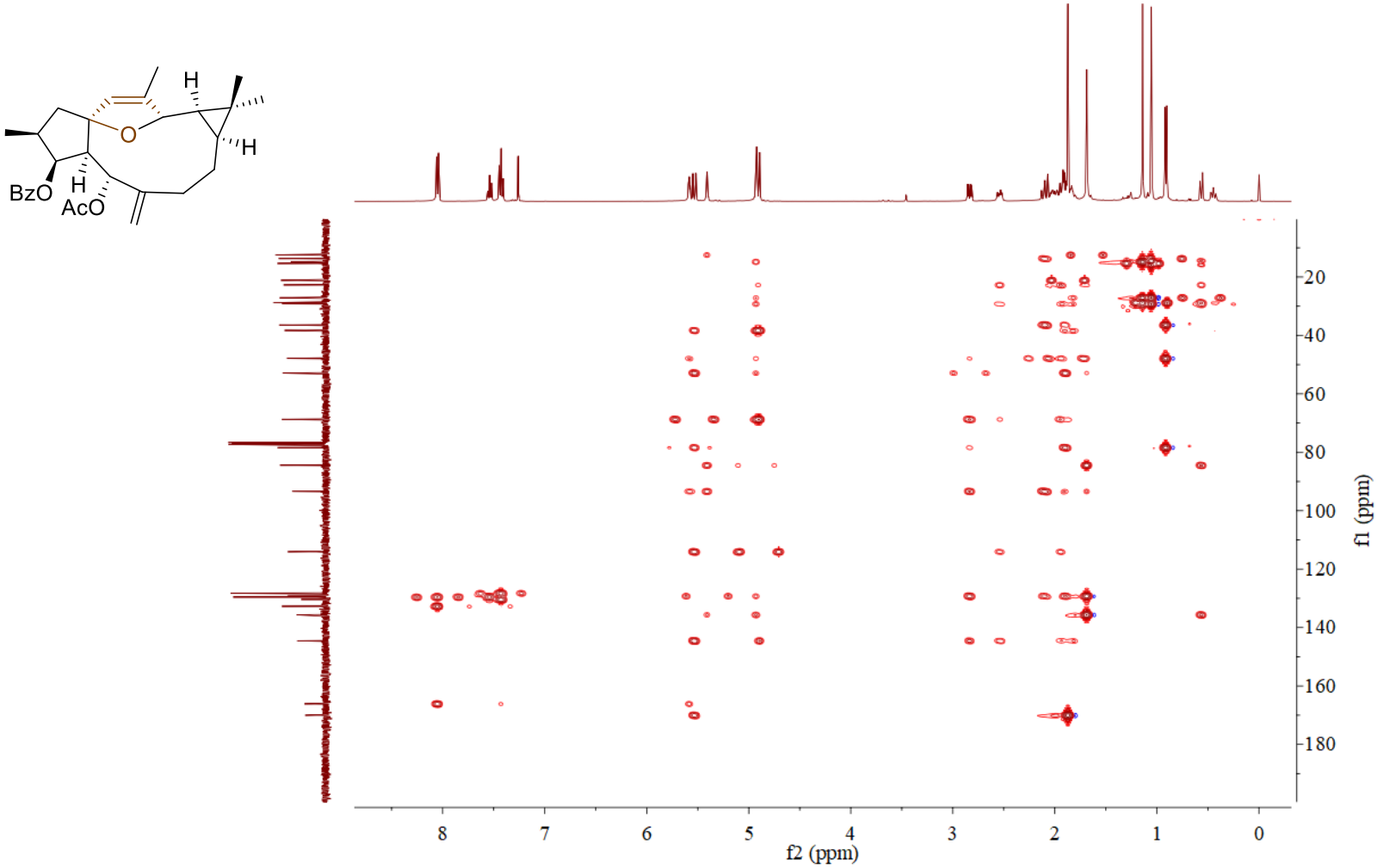


Figure S96. ^{1}H–1H COSY spectrum of **31** in $CDCl_3$.

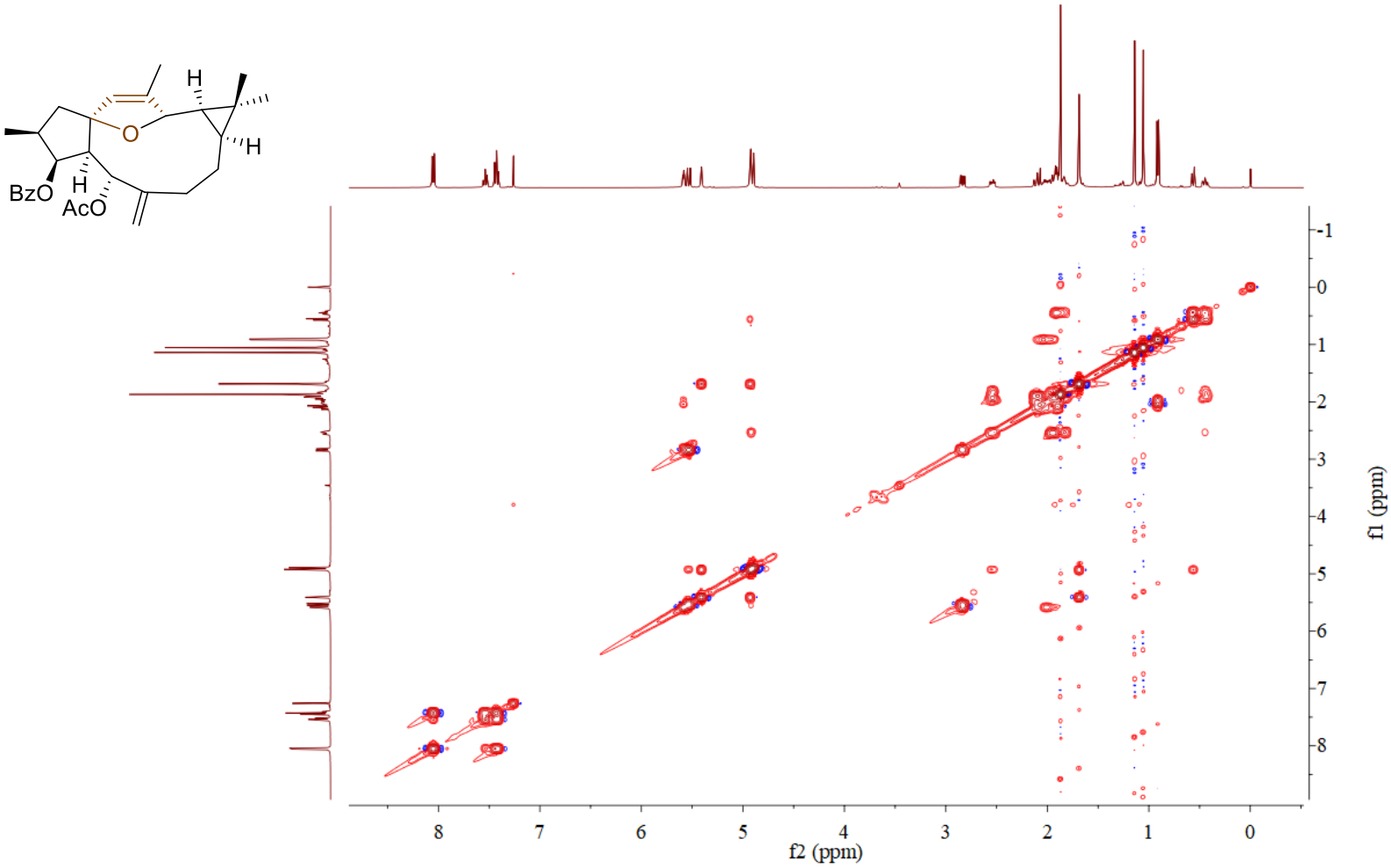


Figure S97. NOESY spectrum of **31** in $CDCl_3$.

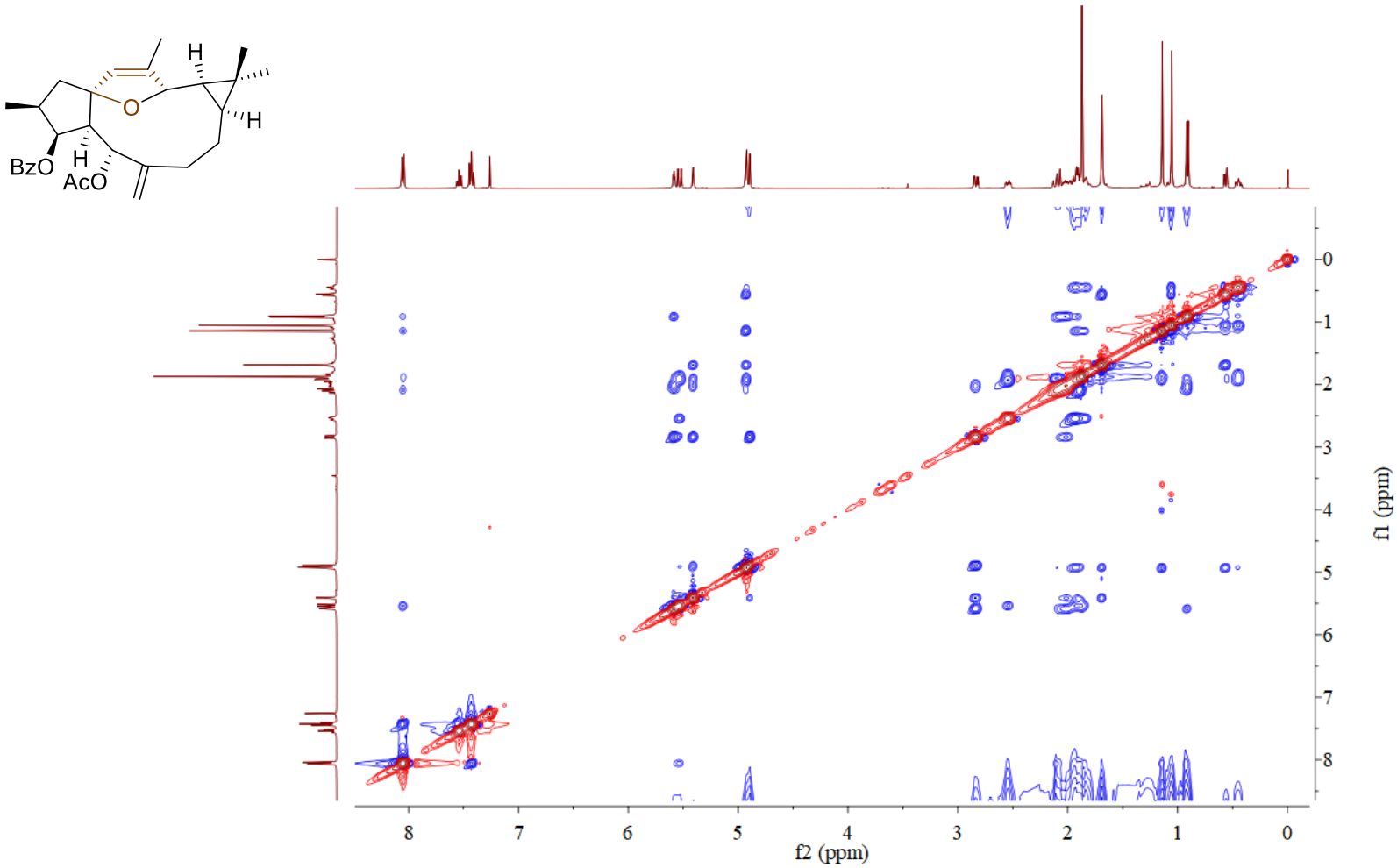


Figure S98. ^{1}H NM spectrum of **32** in $CDCl_3$.

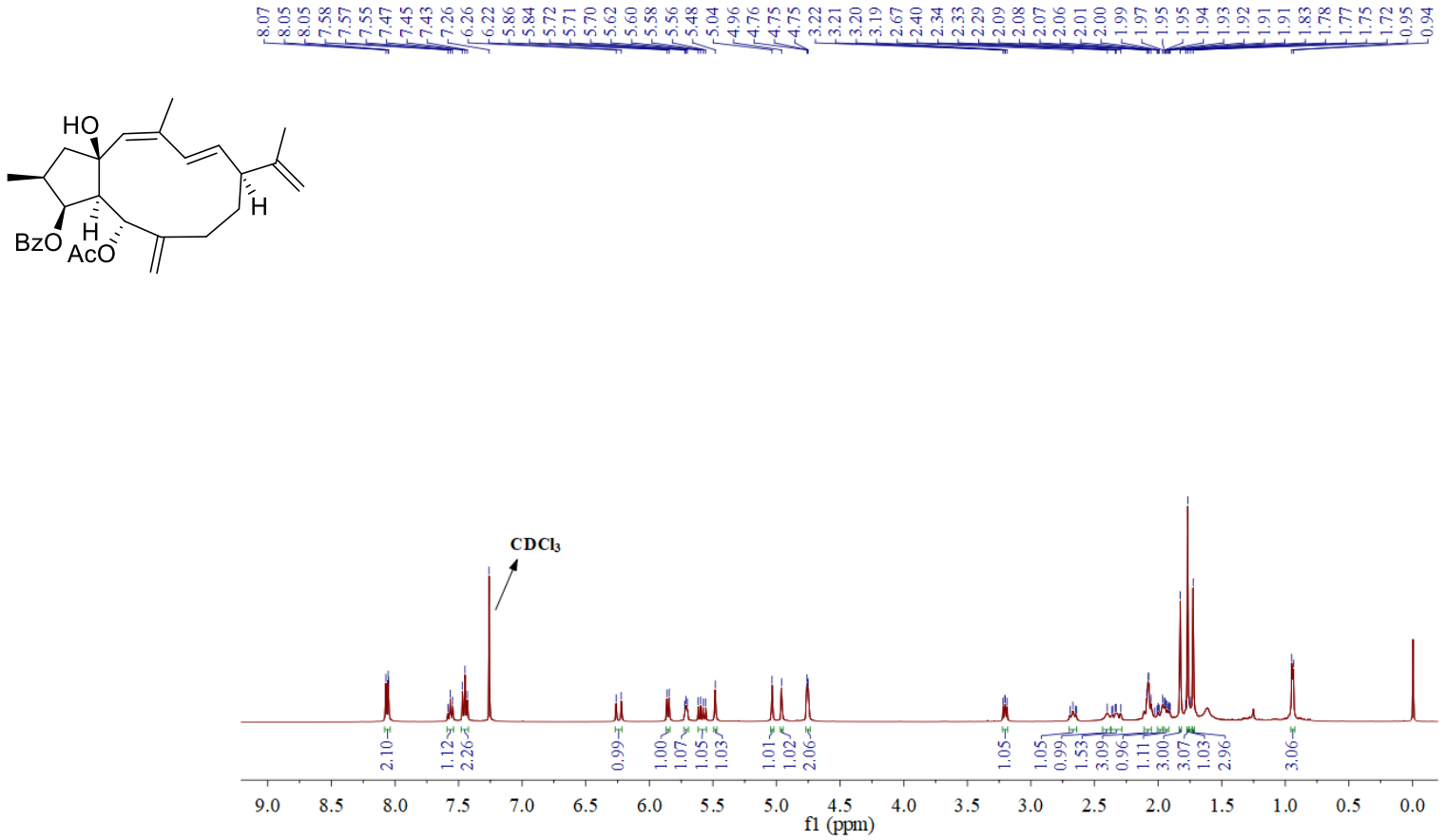


Figure S99. ^{13}C NMR and DEPT 135 spectra of **32** in $CDCl_3$.

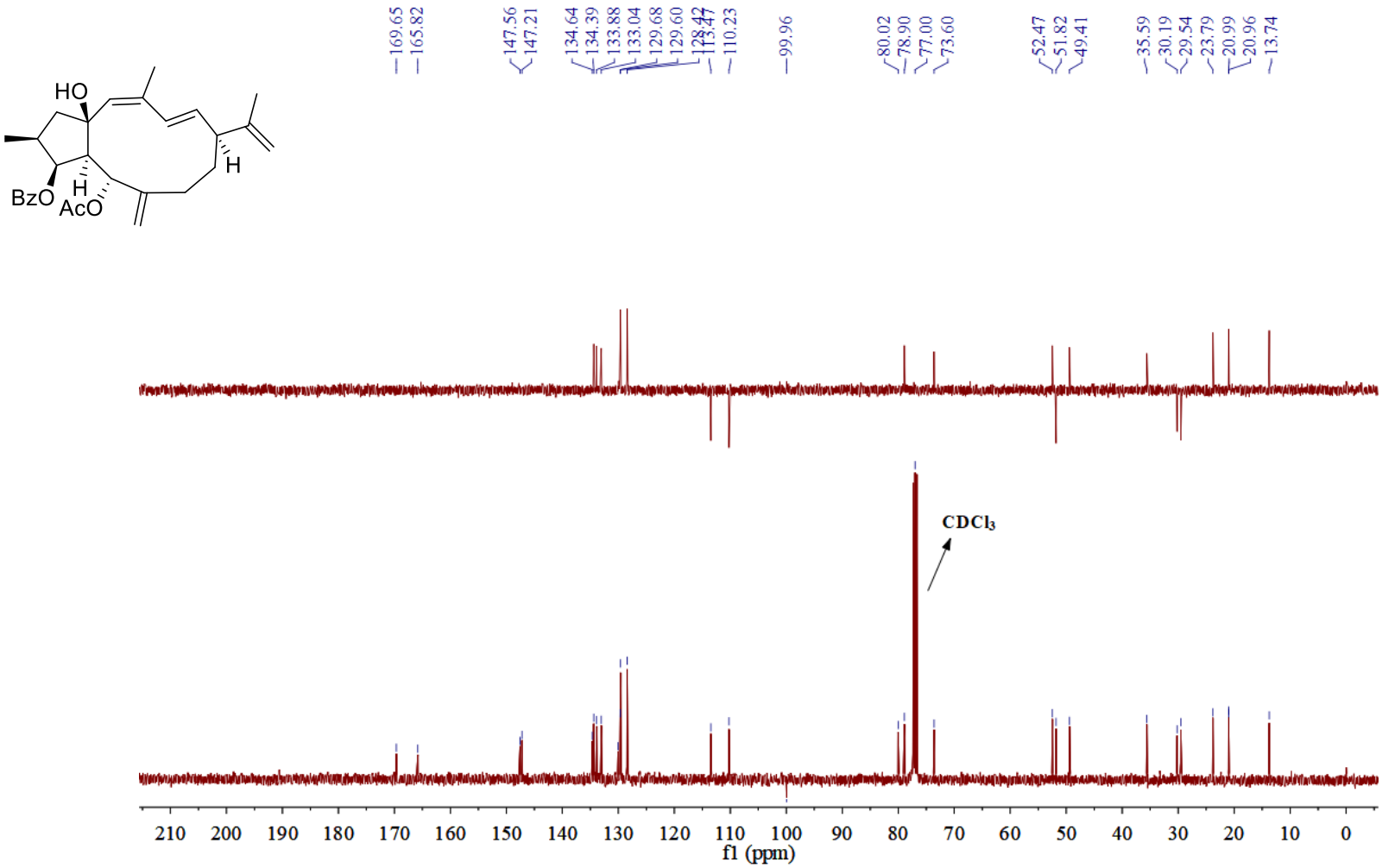


Figure S100. HSQC spectrum of **32** in $CDCl_3$.

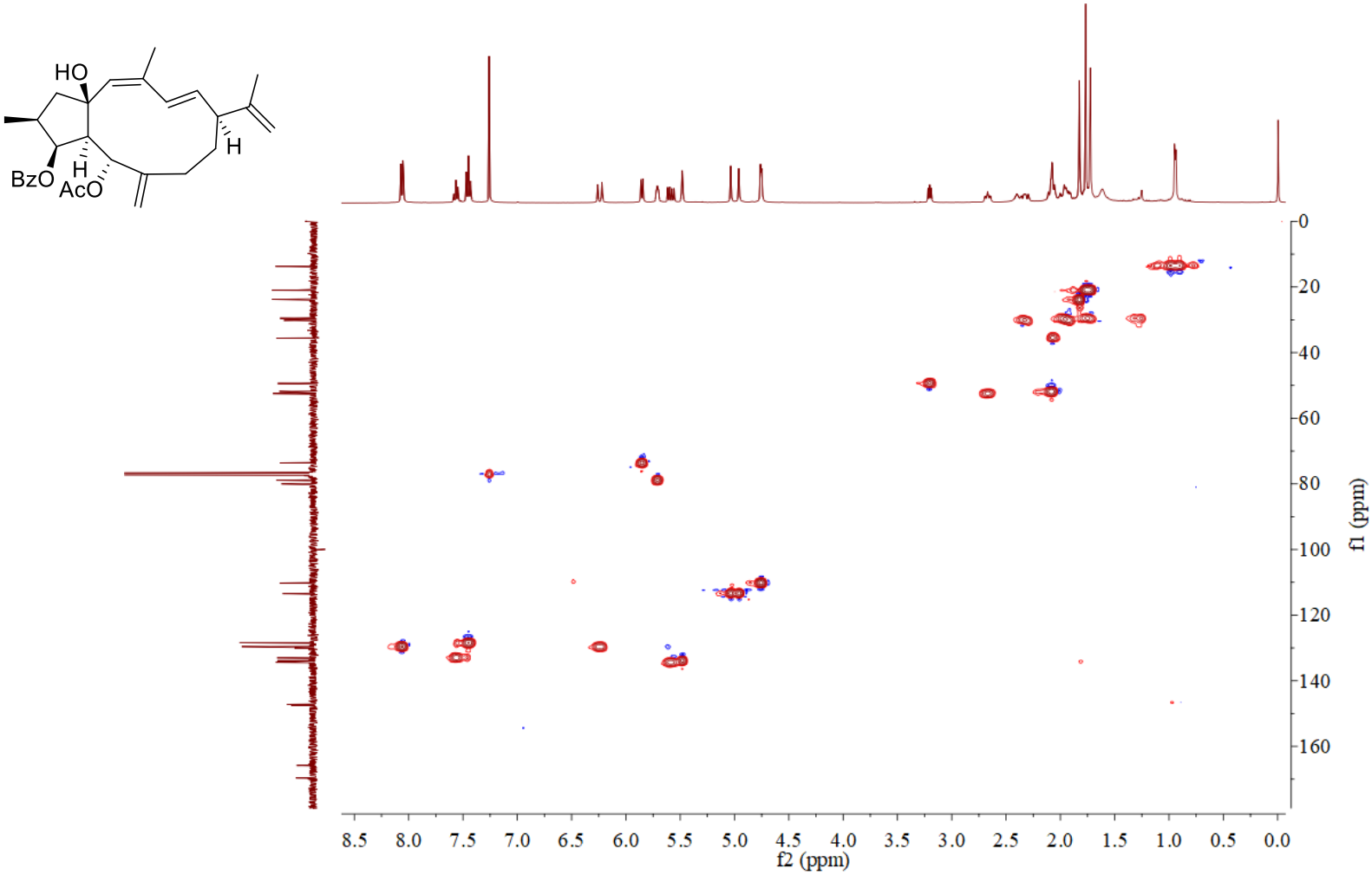


Figure S101. HMBC spectrum of **32** in $CDCl_3$.

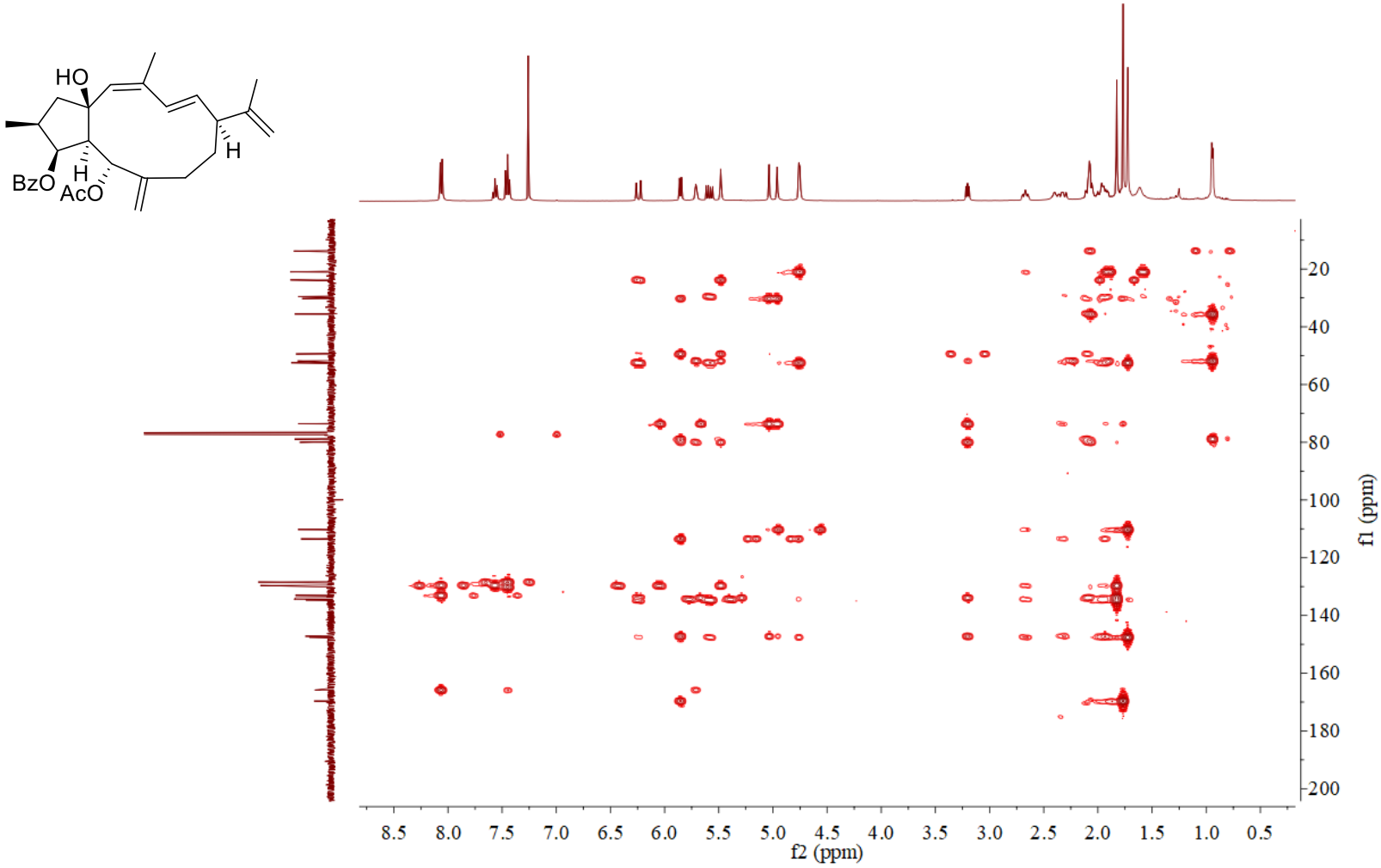


Figure S102. $^{1}H–^{1}H$ COSY spectrum of **32** in $CDCl_3$.

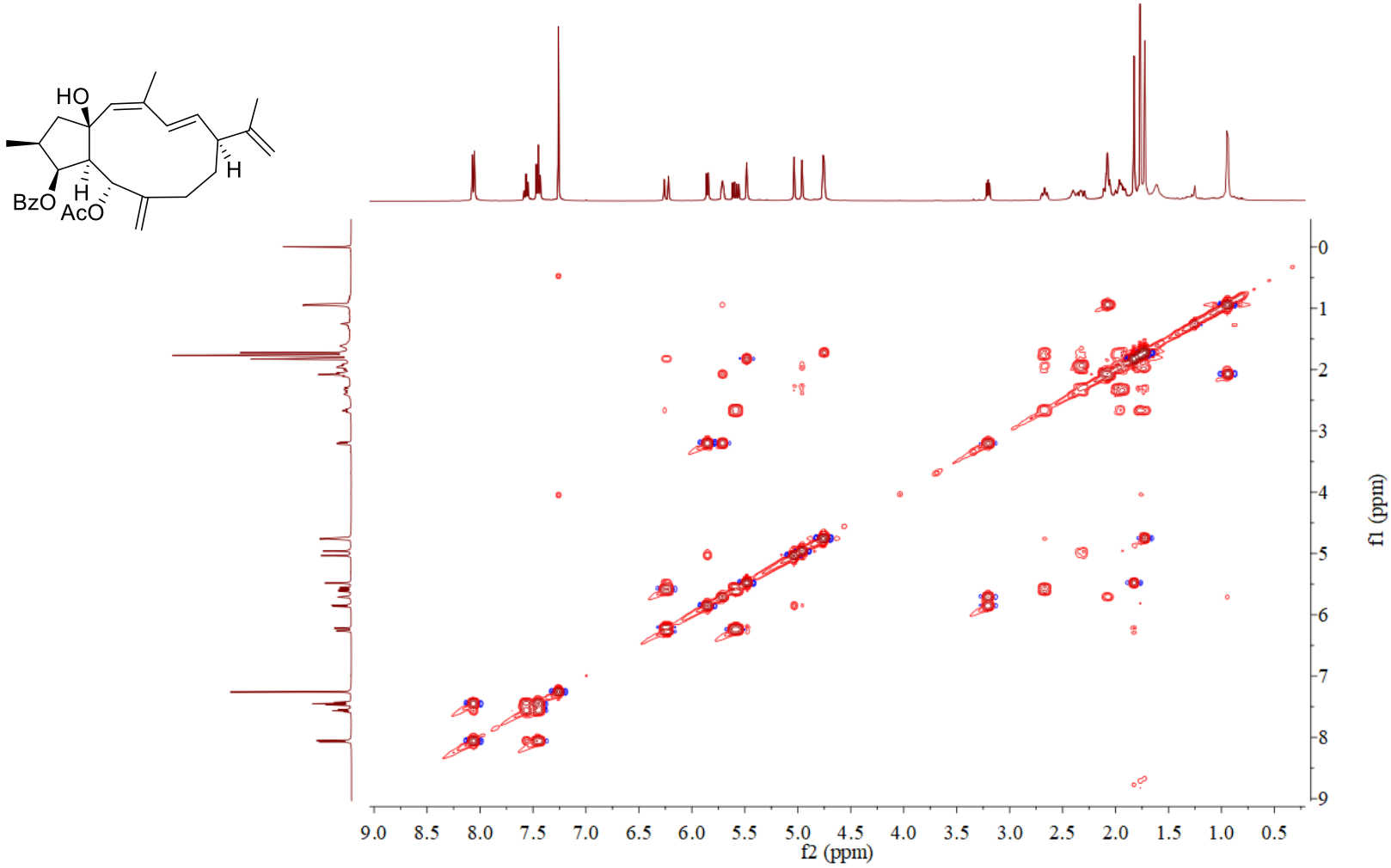


Figure S103. NOESY spectrum of **32** in $CDCl_3$.

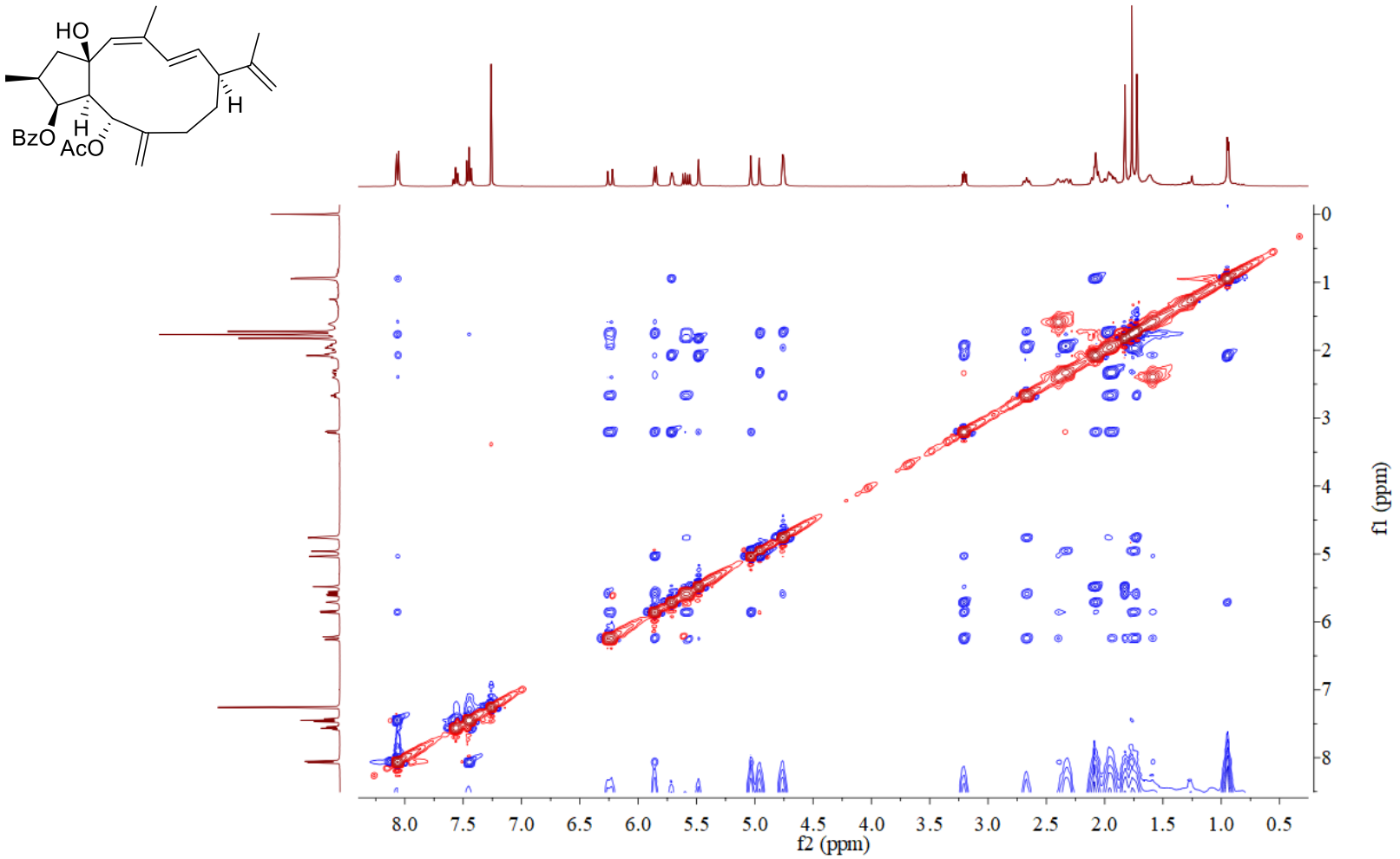


Figure S104. ^{1}H NMR spectrum of **33** in $CDCl_3$.

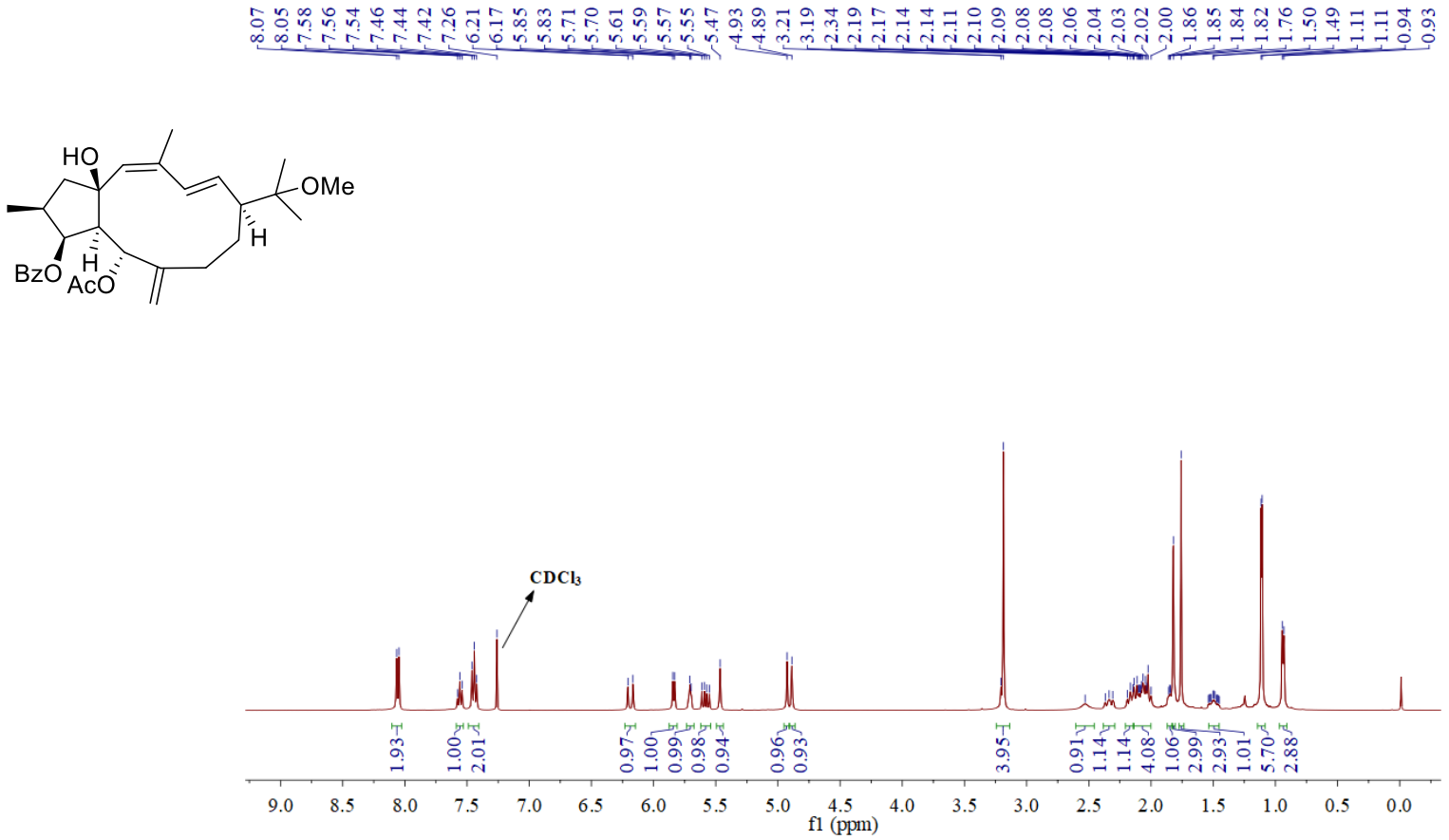


Figure S105. ^{13}C NMR and DEPT 135 spectra of **33** in $CDCl_3$.

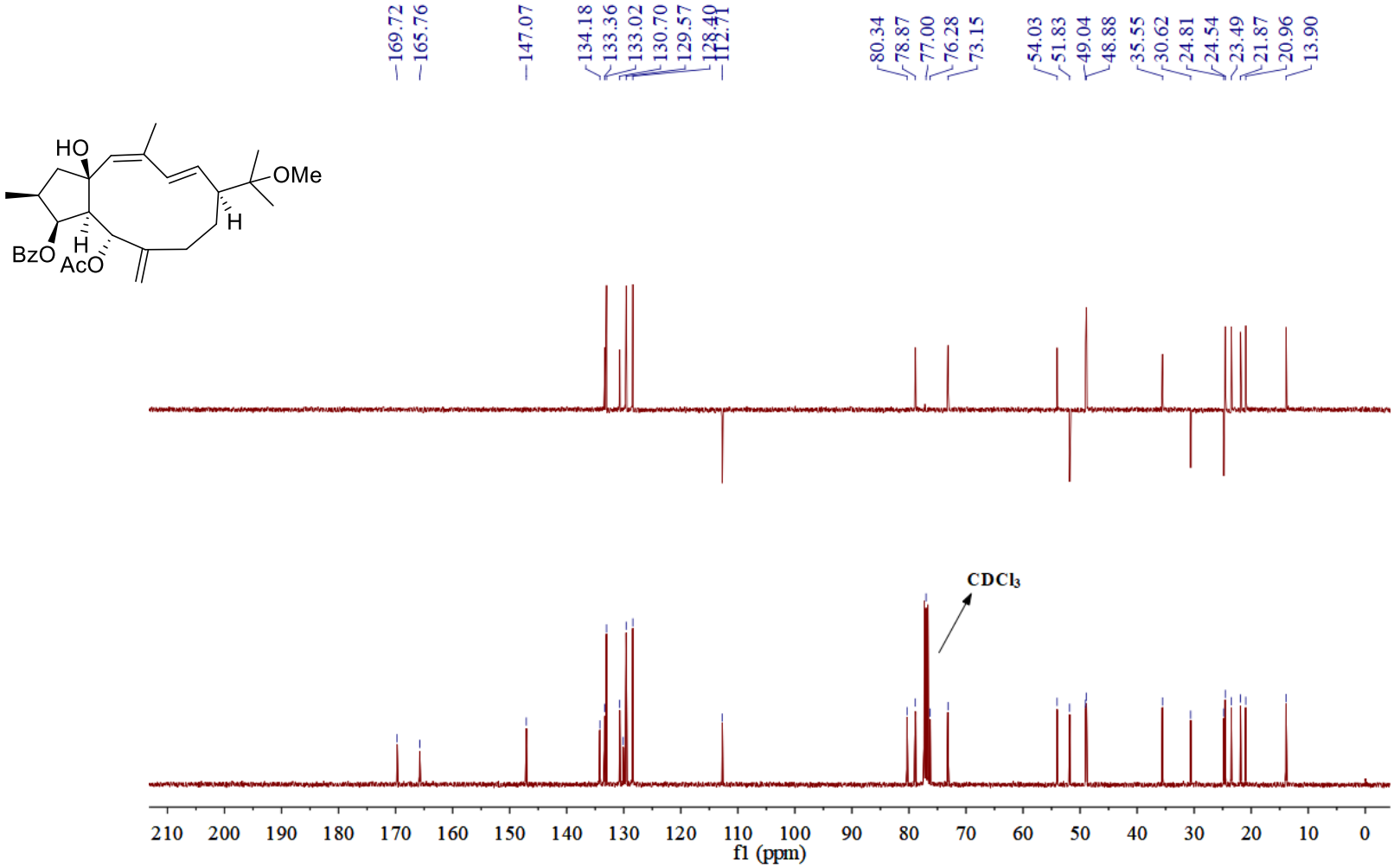


Figure S106. HSQC spectrum of **33** in $CDCl_3$.

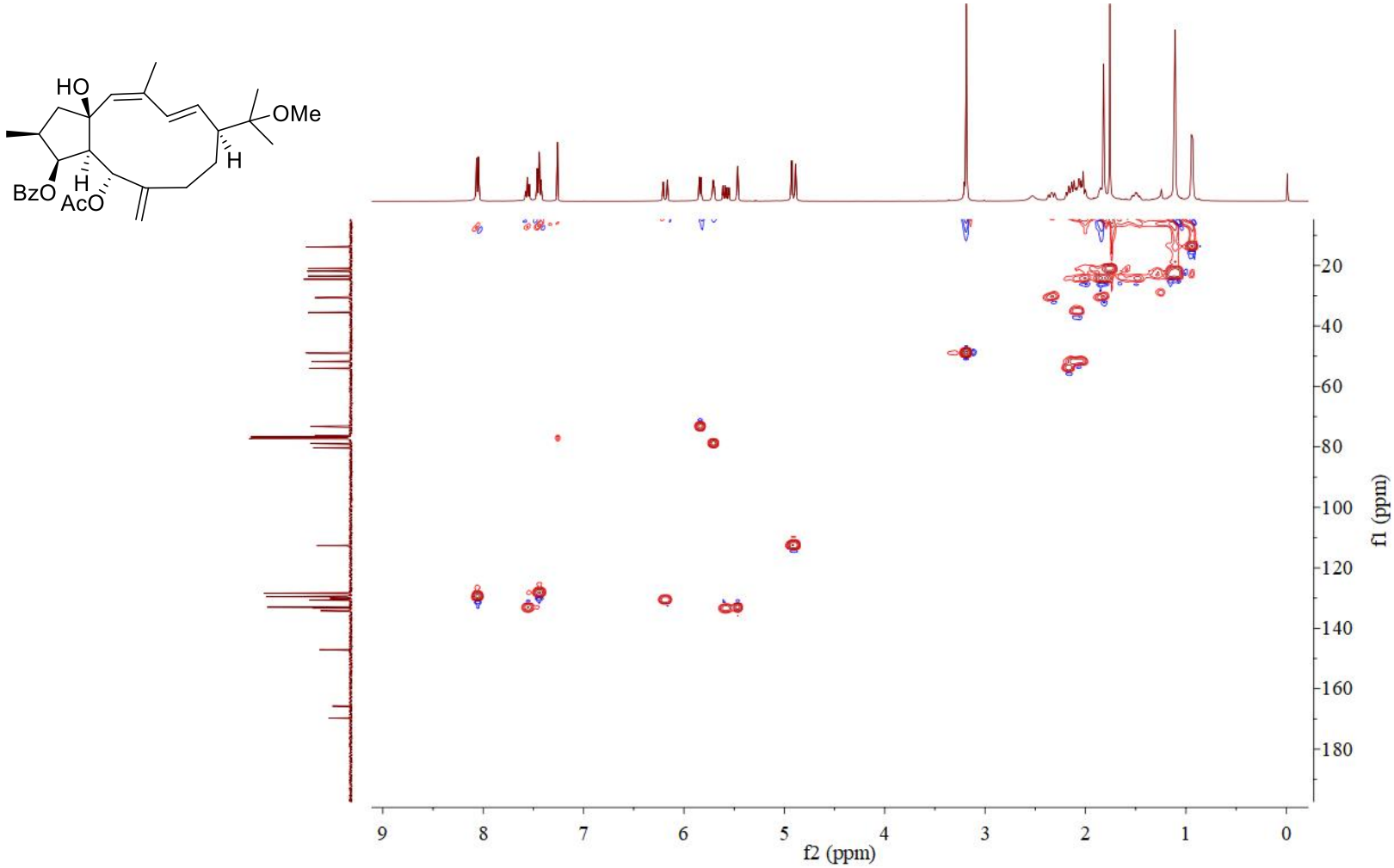


Figure S107. HMBC spectrum of **33** in $CDCl_3$.

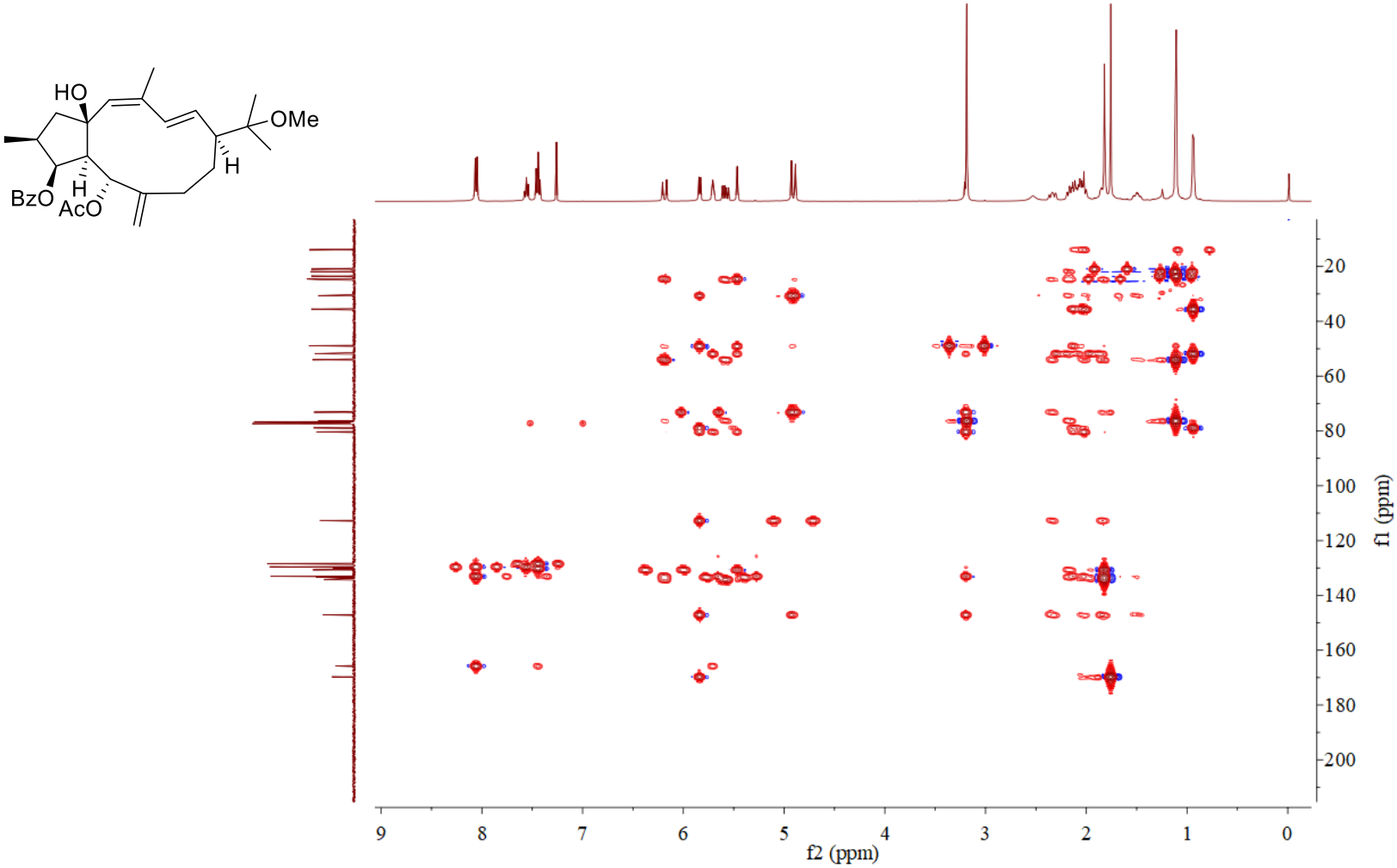


Figure S108. $^{1}H–^{1}H$ NMR spectrum of **33** in $CDCl_3$.

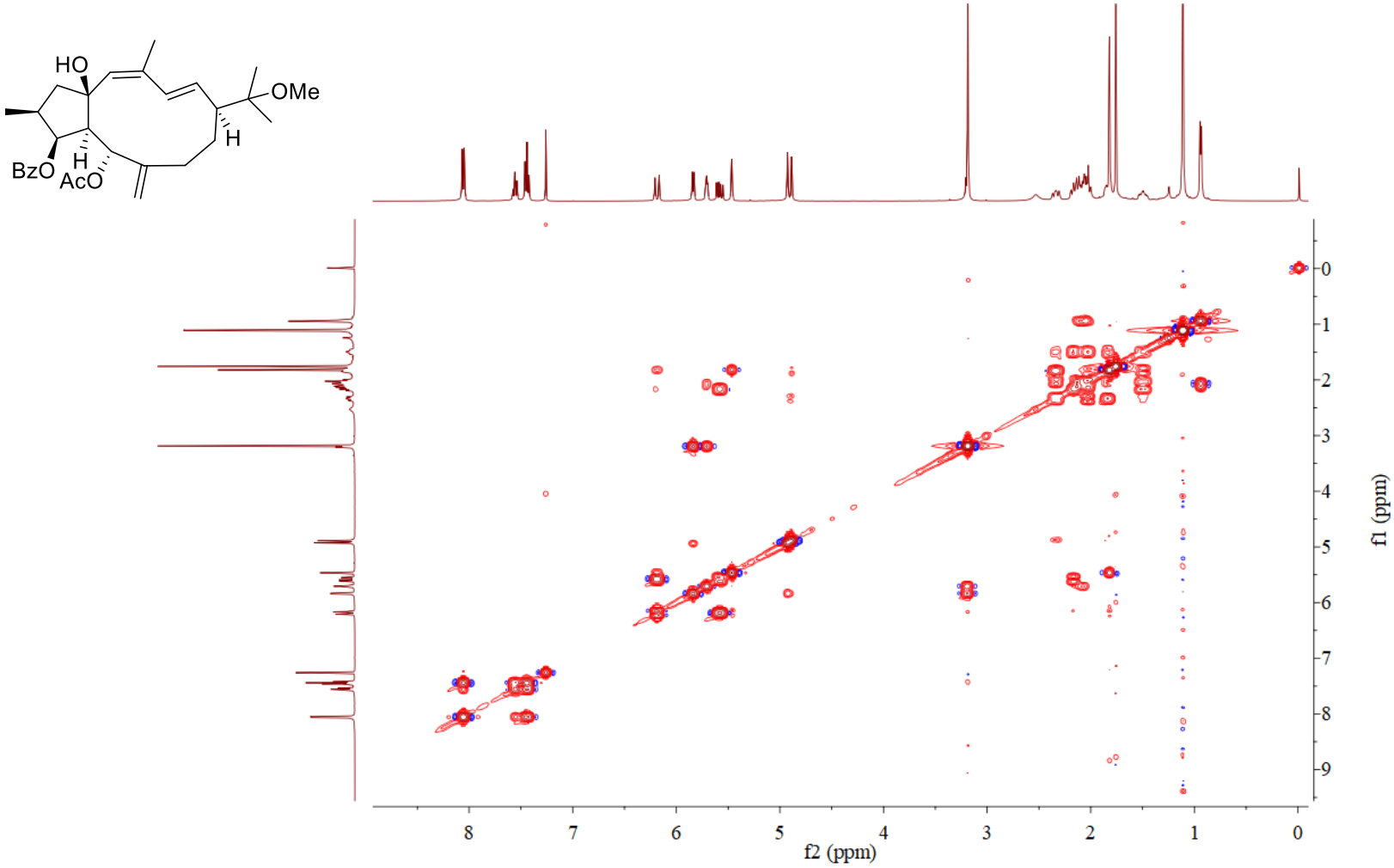


Figure S109. NOESY spectrum of **33** in $CDCl_3$.

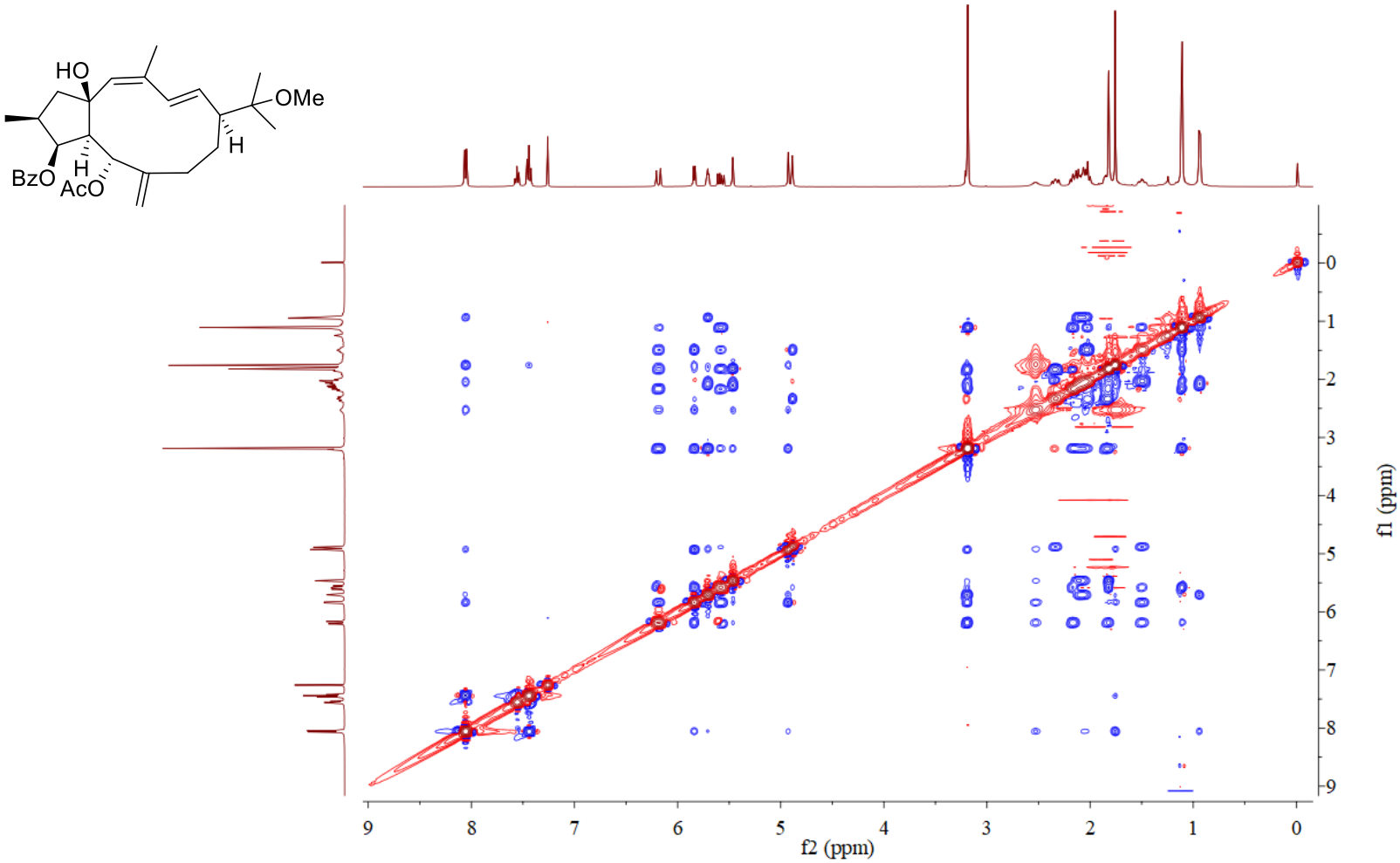


Figure S110. ^{1}H NMR spectrum of **34** in $CDCl_3$.

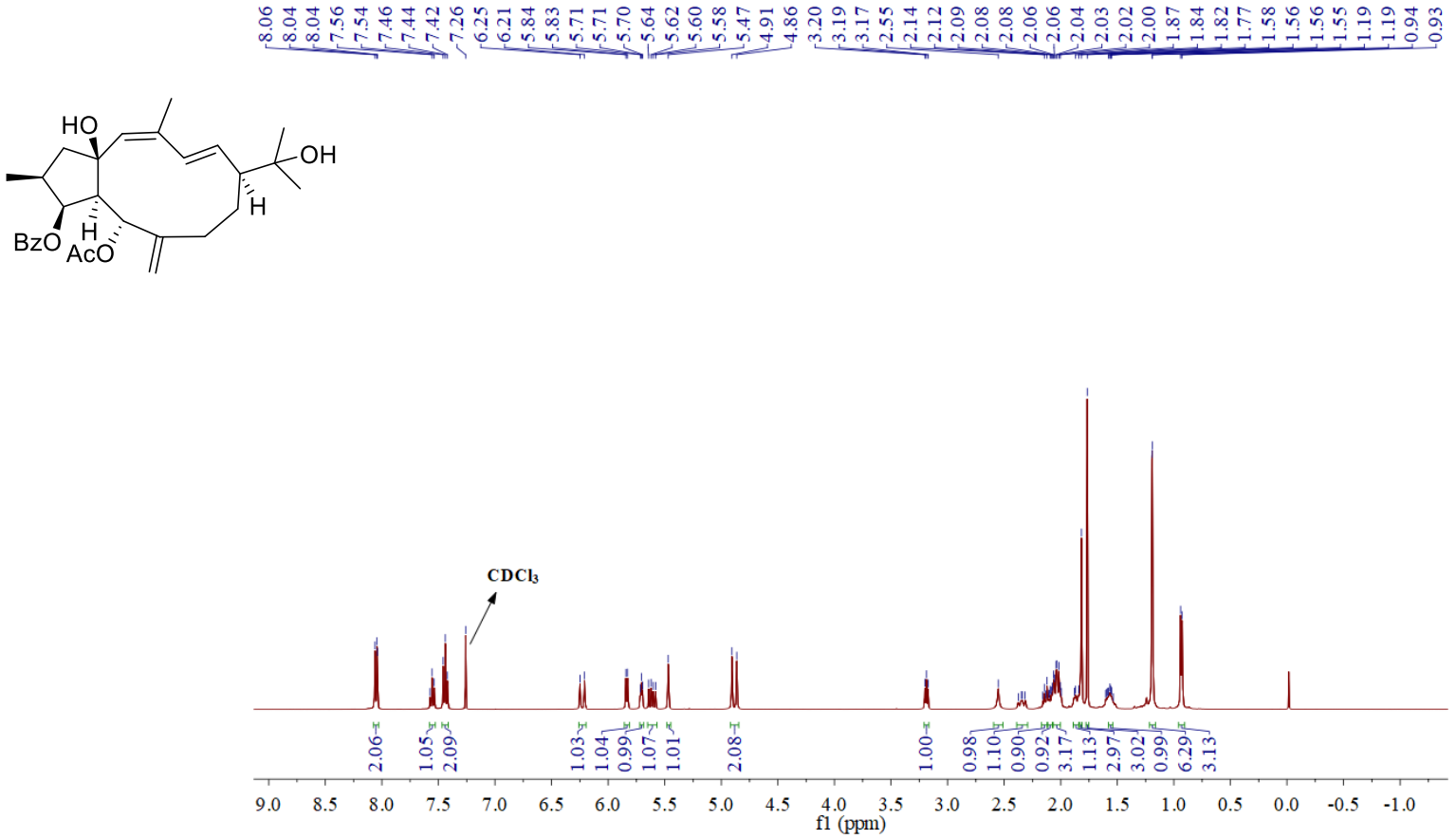


Figure S111. ^{13}C NMR and DEPT 135 spectra of **34** in $CDCl_3$.

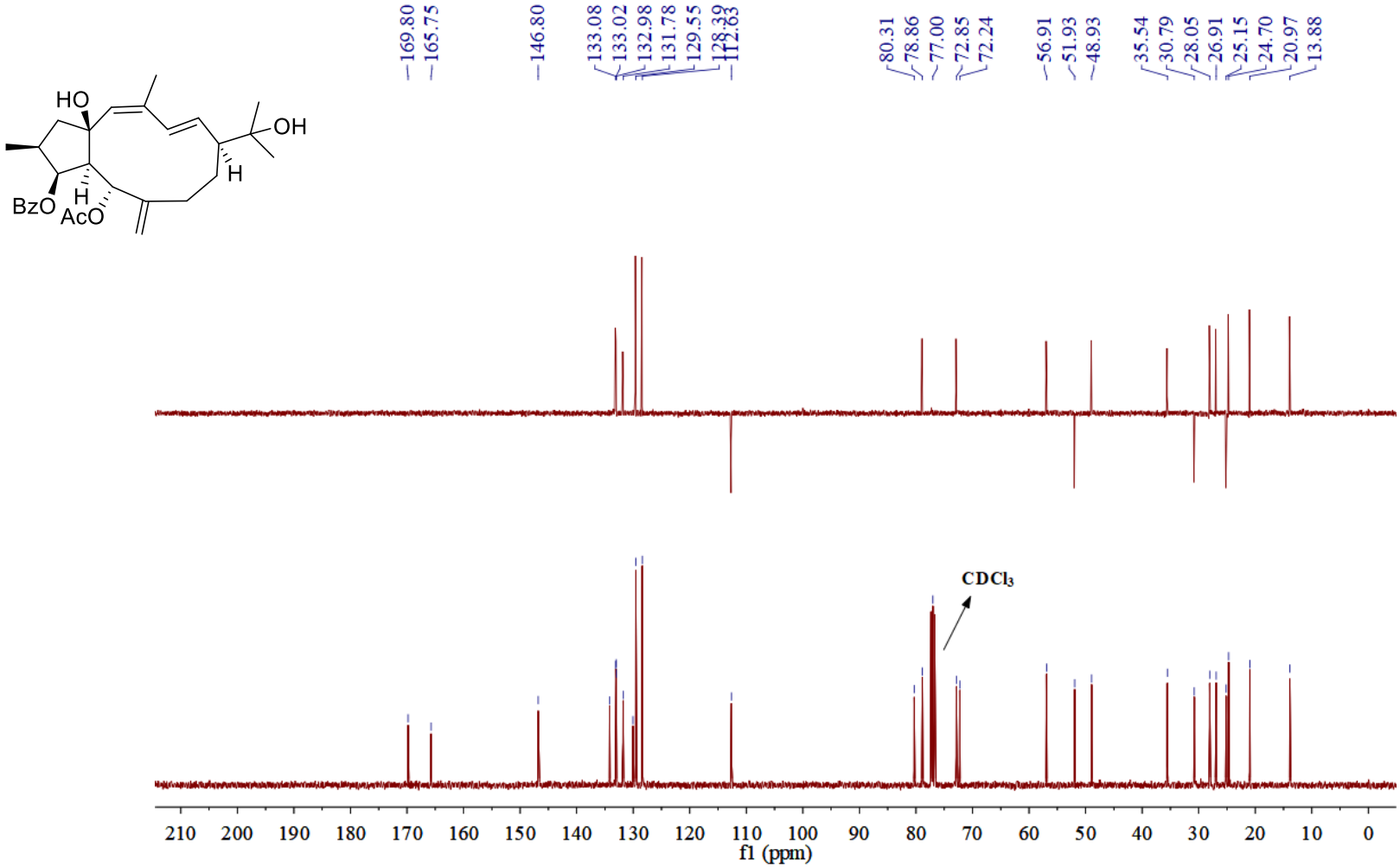


Figure S112. HSQC spectrum of **34** in $CDCl_3$.

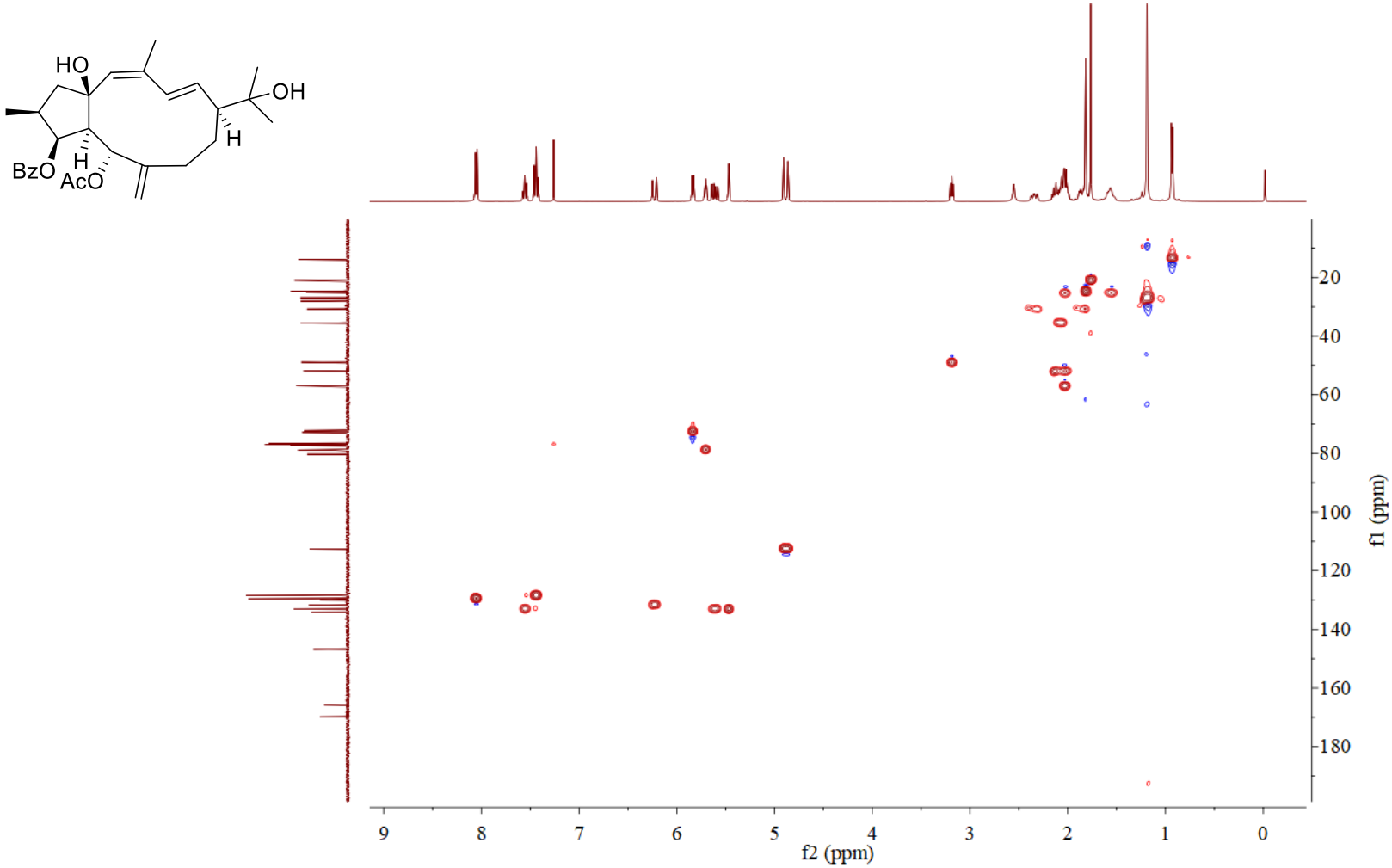


Figure S113. HMBC spectrum of **34** in $CDCl_3$.

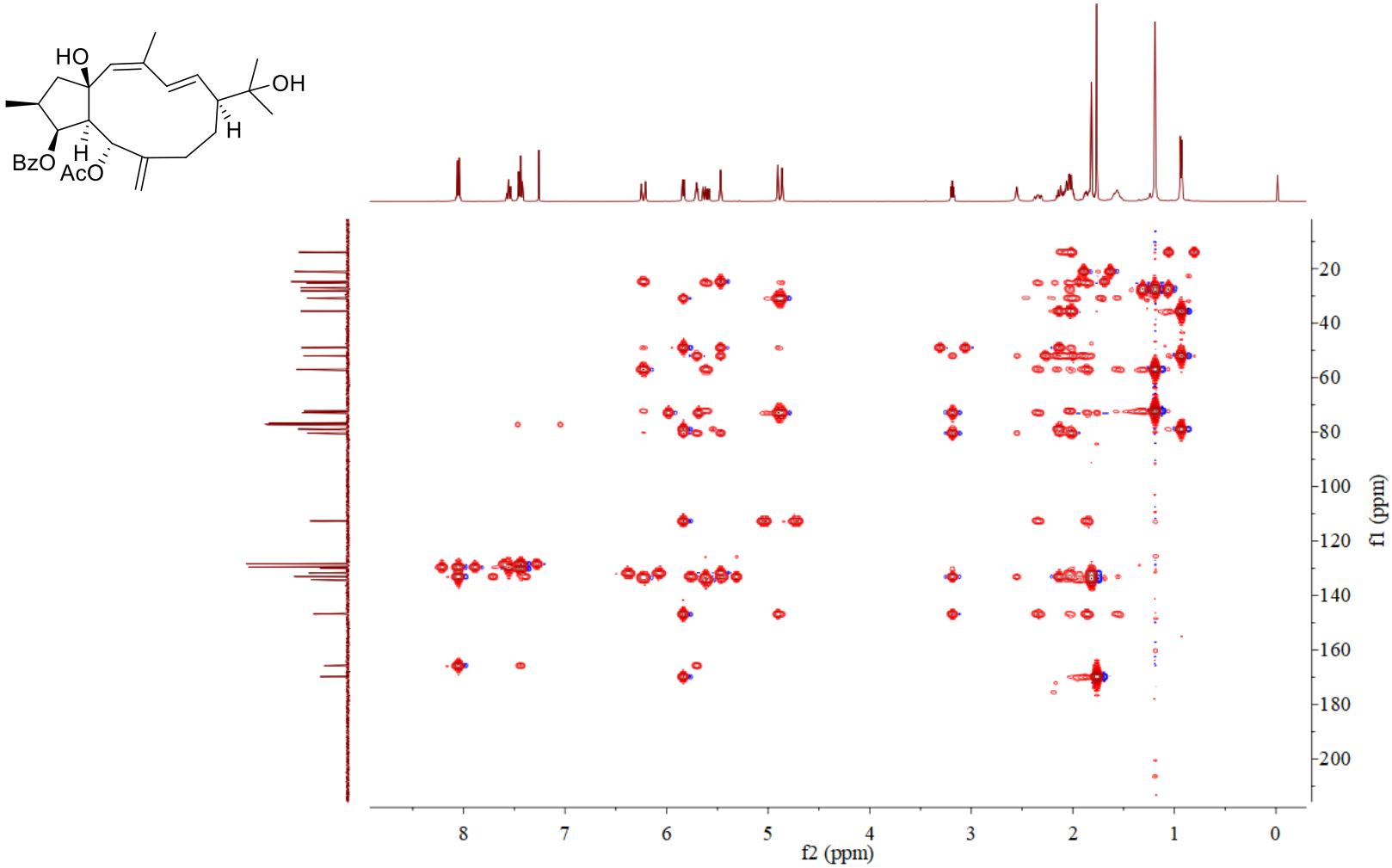


Figure S114. $^{1}H–^{1}H$ NMR spectrum of **34** in $CDCl_3$.

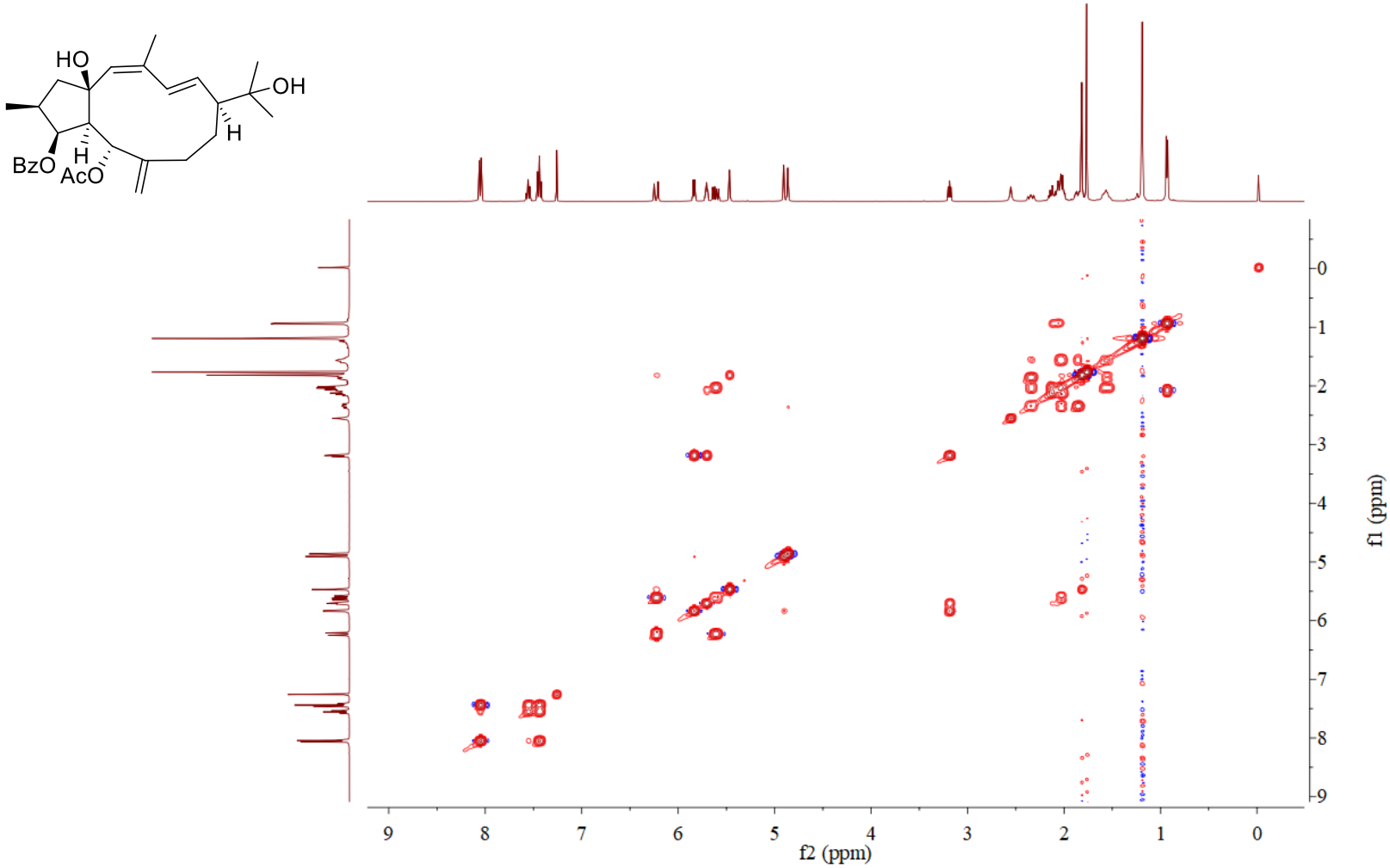
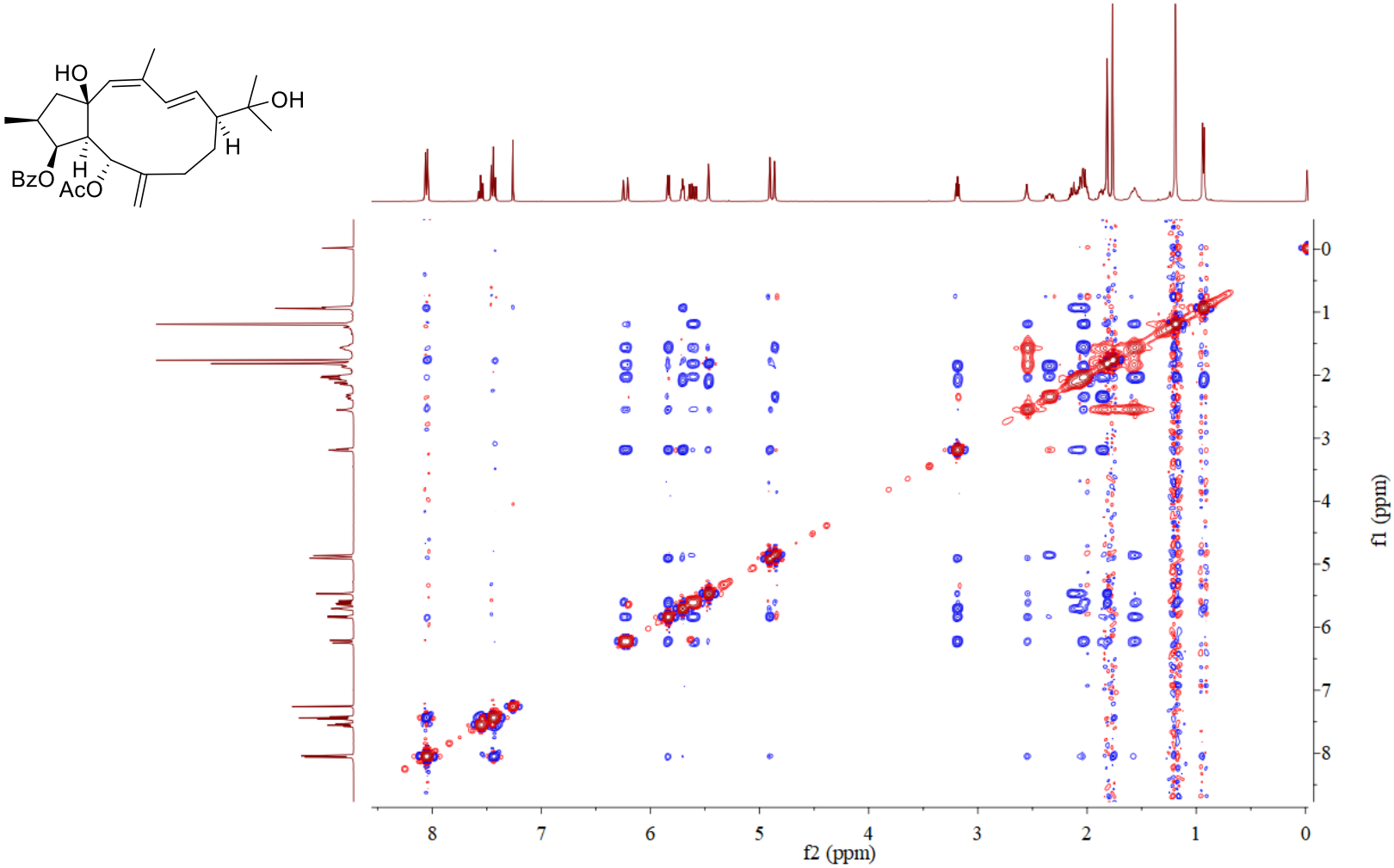


Figure S115. NOESY spectrum of **34** in $CDCl_3$.



11. Figure S116–S145.

Figure S116. ^{1}H NMR spectrum of **6** in $CDCl_3$.

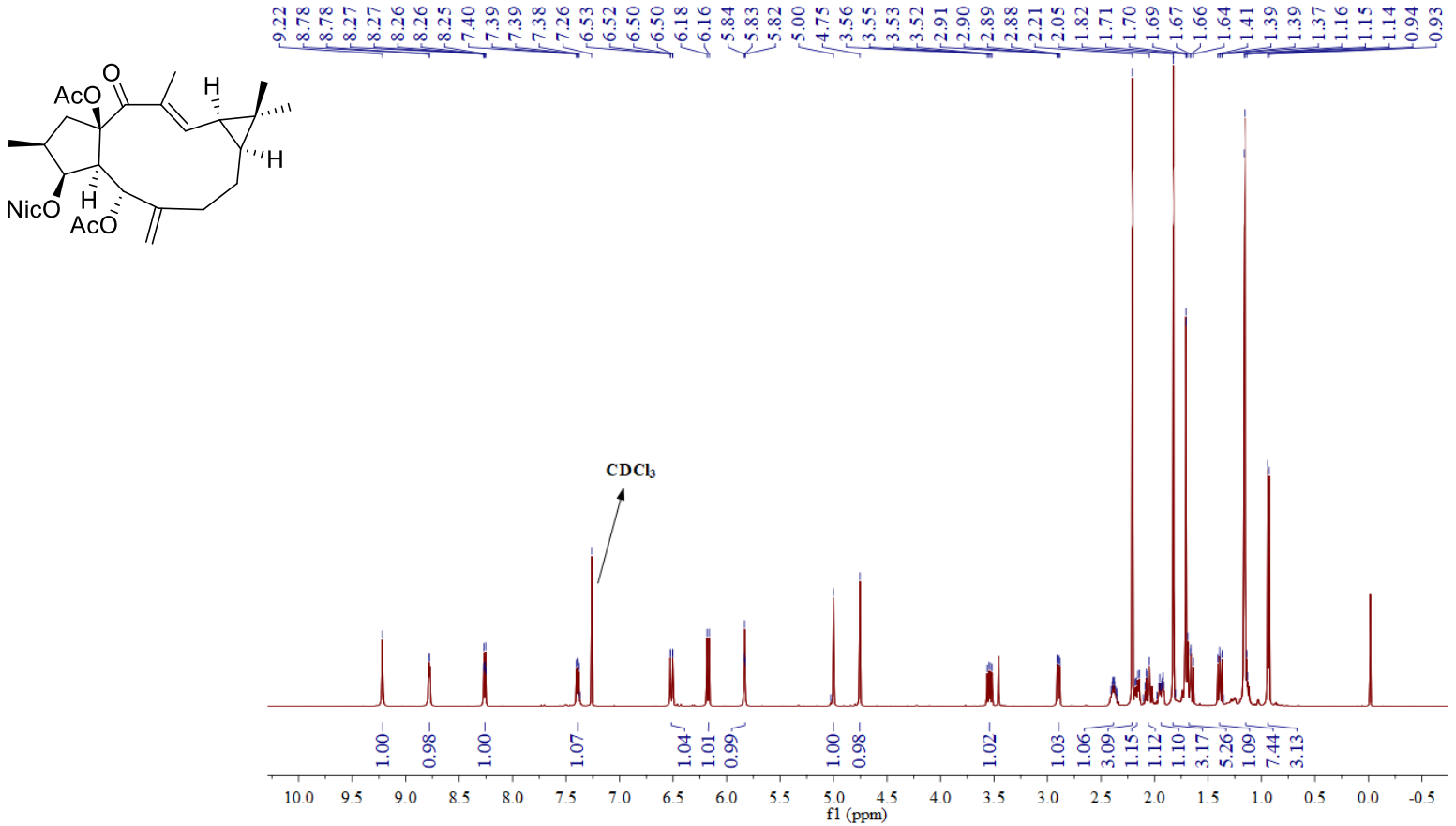


Figure S117. ^{13}C NMR and DEPT 135 spectra of **6** in $CDCl_3$.

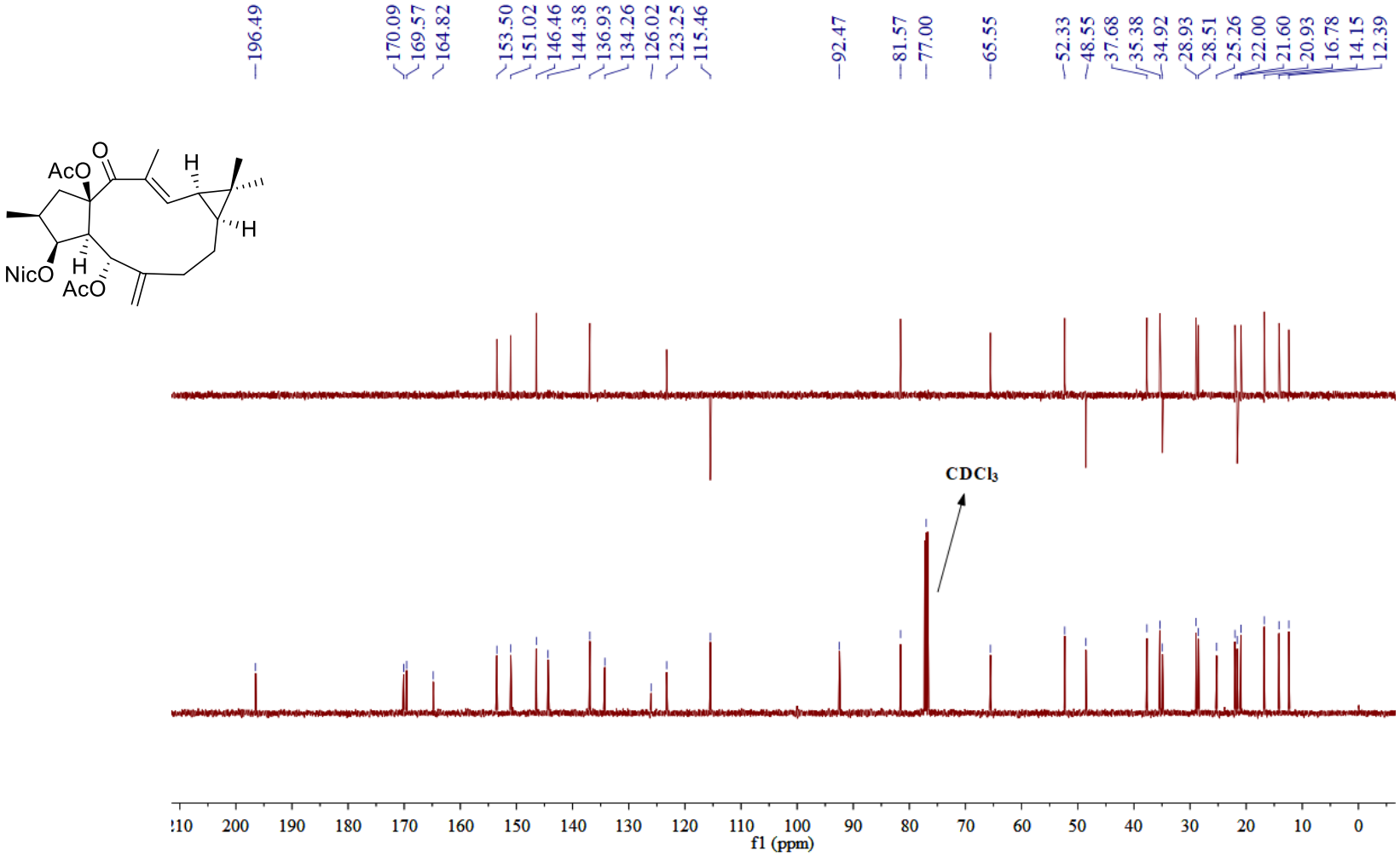


Figure S118. ^{1}H NMR spectrum of **7** in $CDCl_3$.

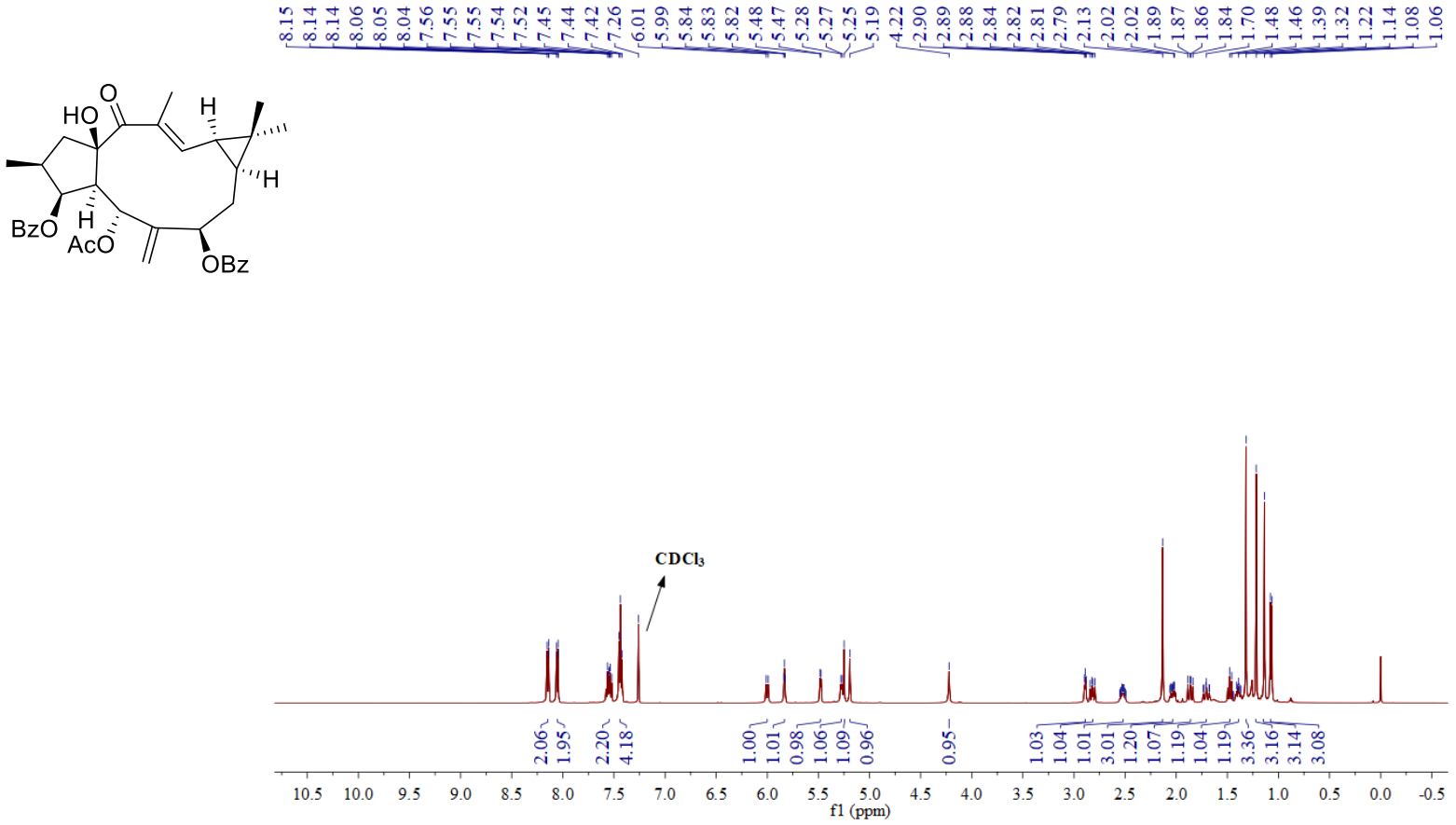


Figure S119. ^{13}C NMR and DEPT 135 spectra of **7** in $CDCl_3$.

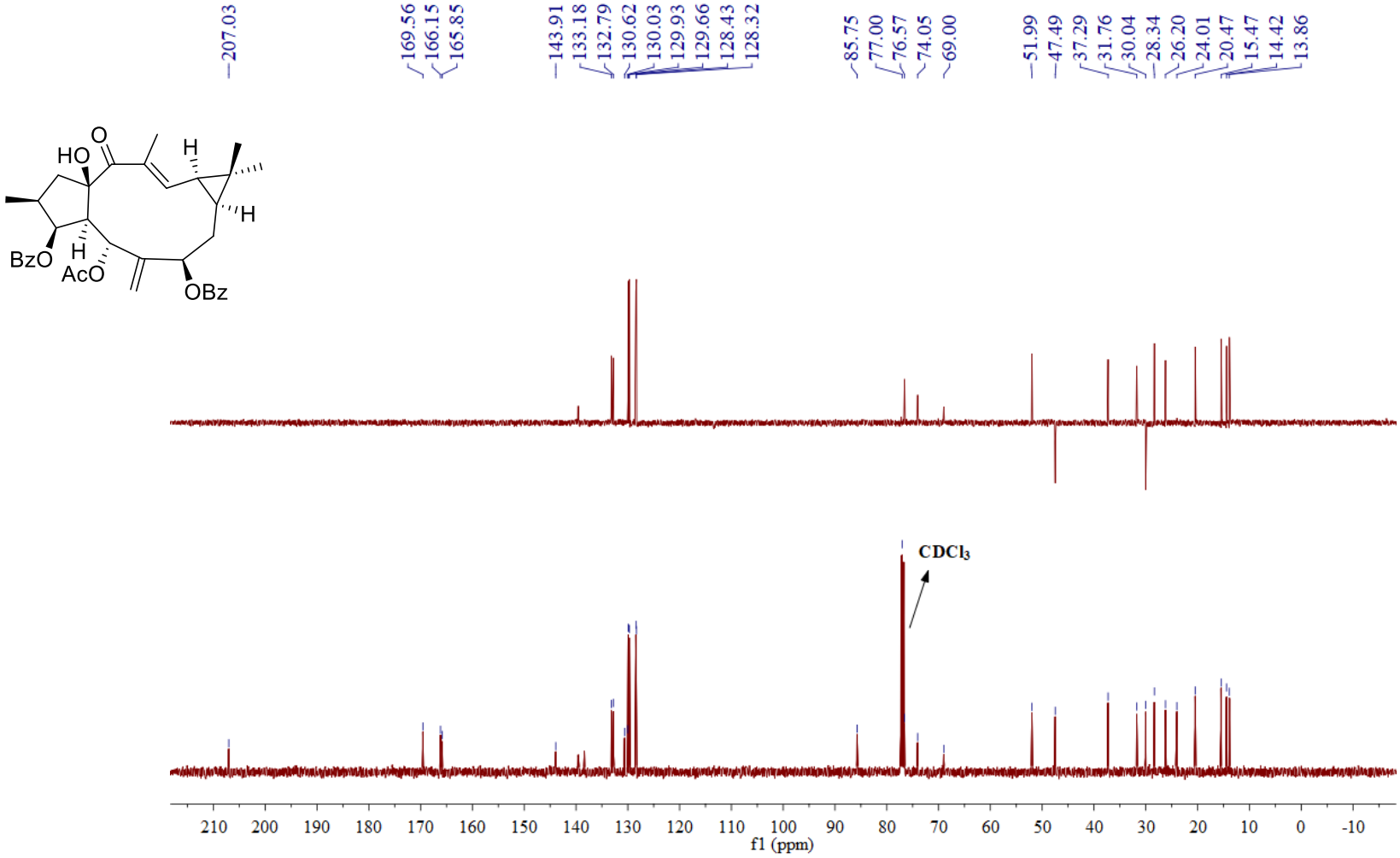


Figure S120. ^{1}H NMR spectrum of **8** in $CDCl_3$.

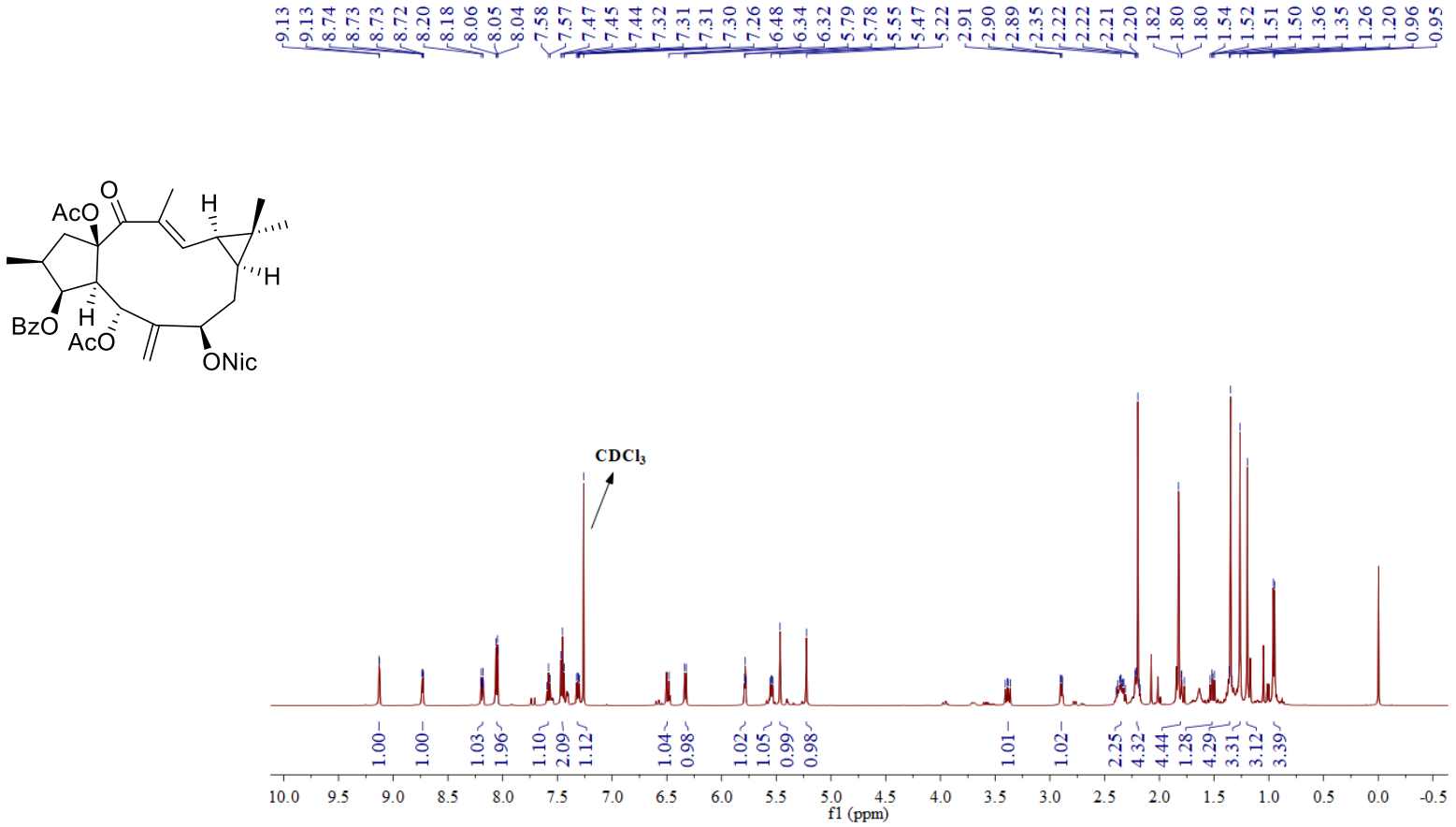


Figure S121. ^{13}C NMR and DEPT 135 spectra of **8** in $CDCl_3$.

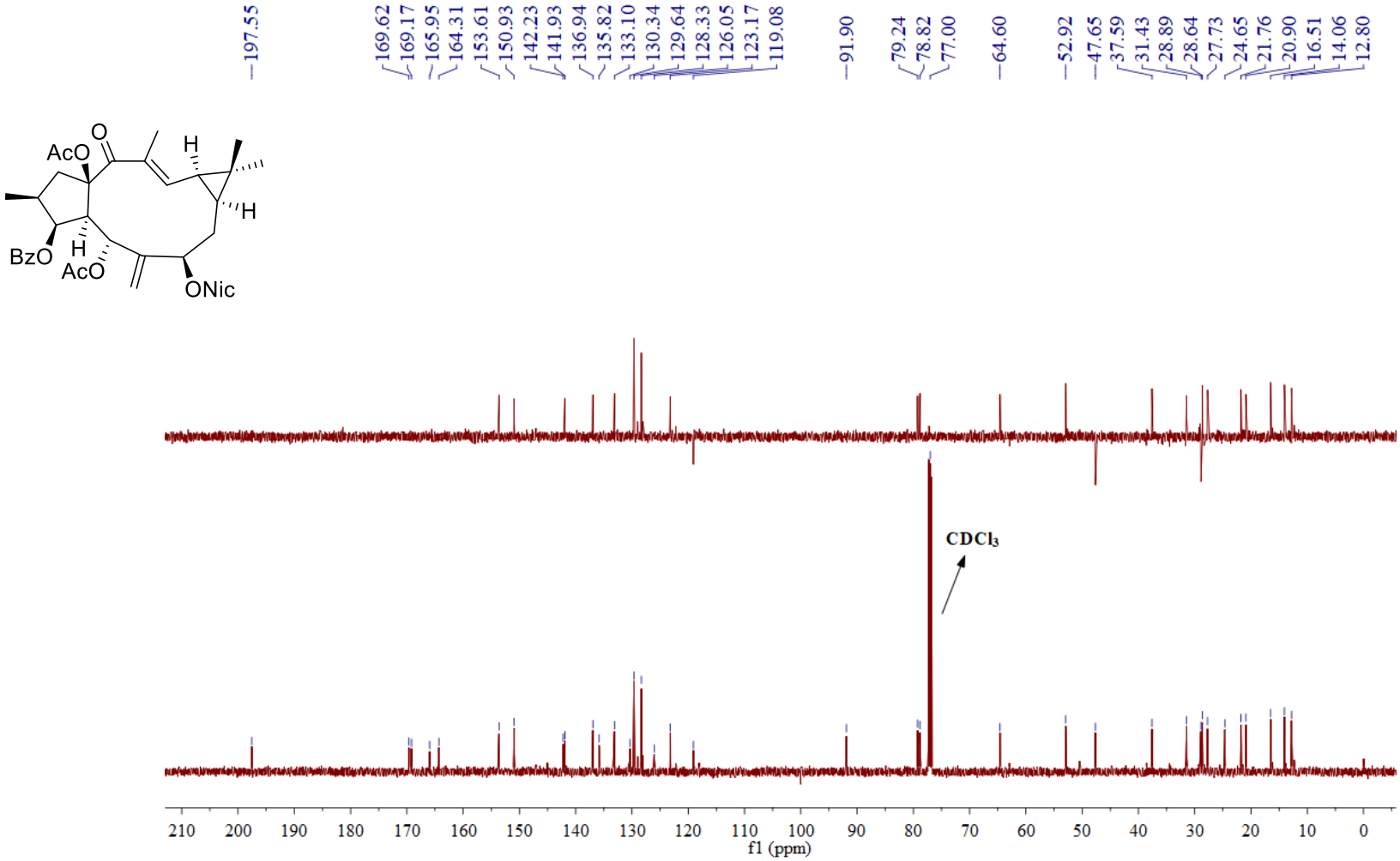


Figure S122. ^{1}H NMR spectrum of **9** in $CDCl_3$.

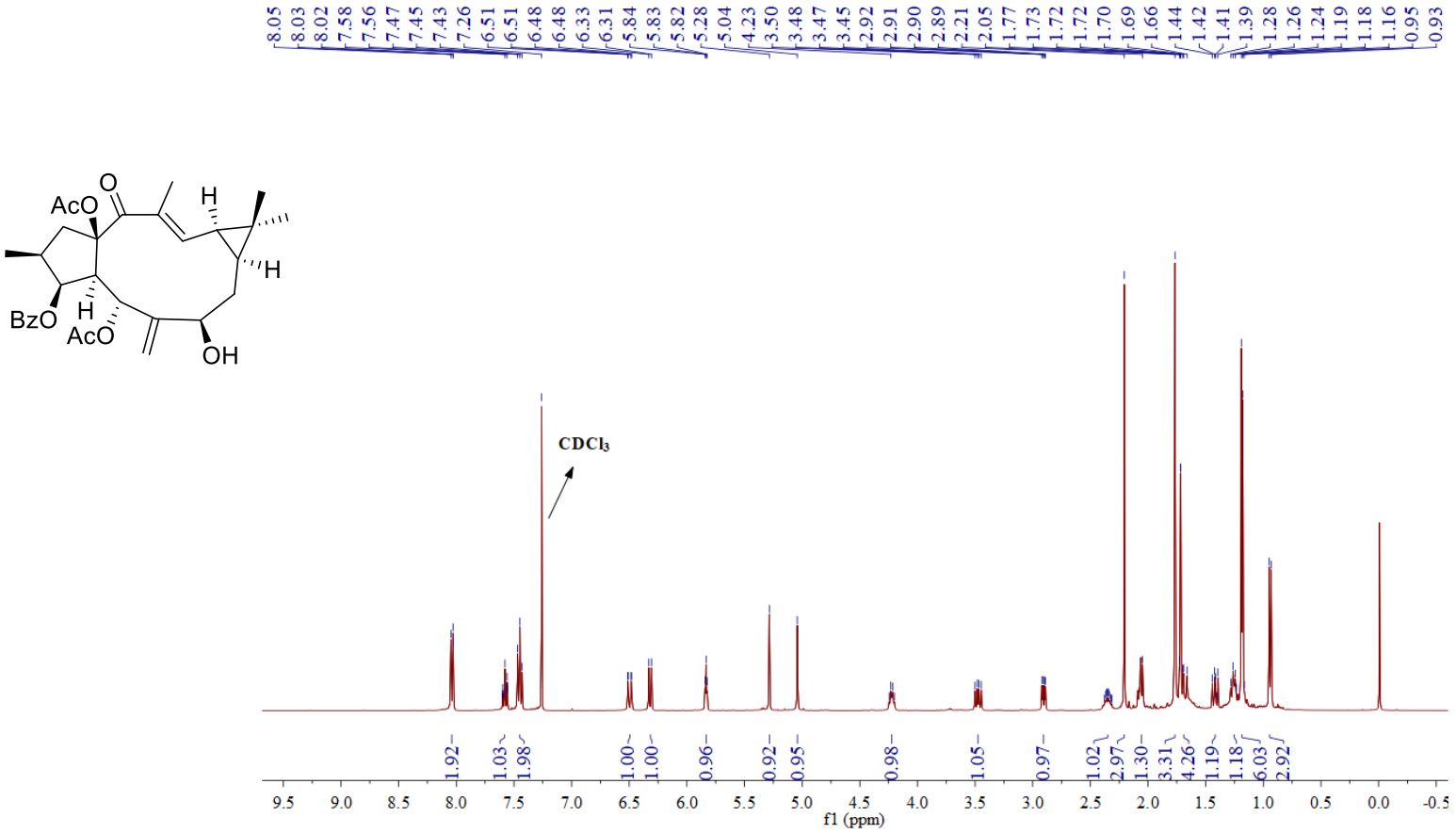


Figure S123. ^{13}C NMR and DEPT 135 spectra of **9** in $CDCl_3$.

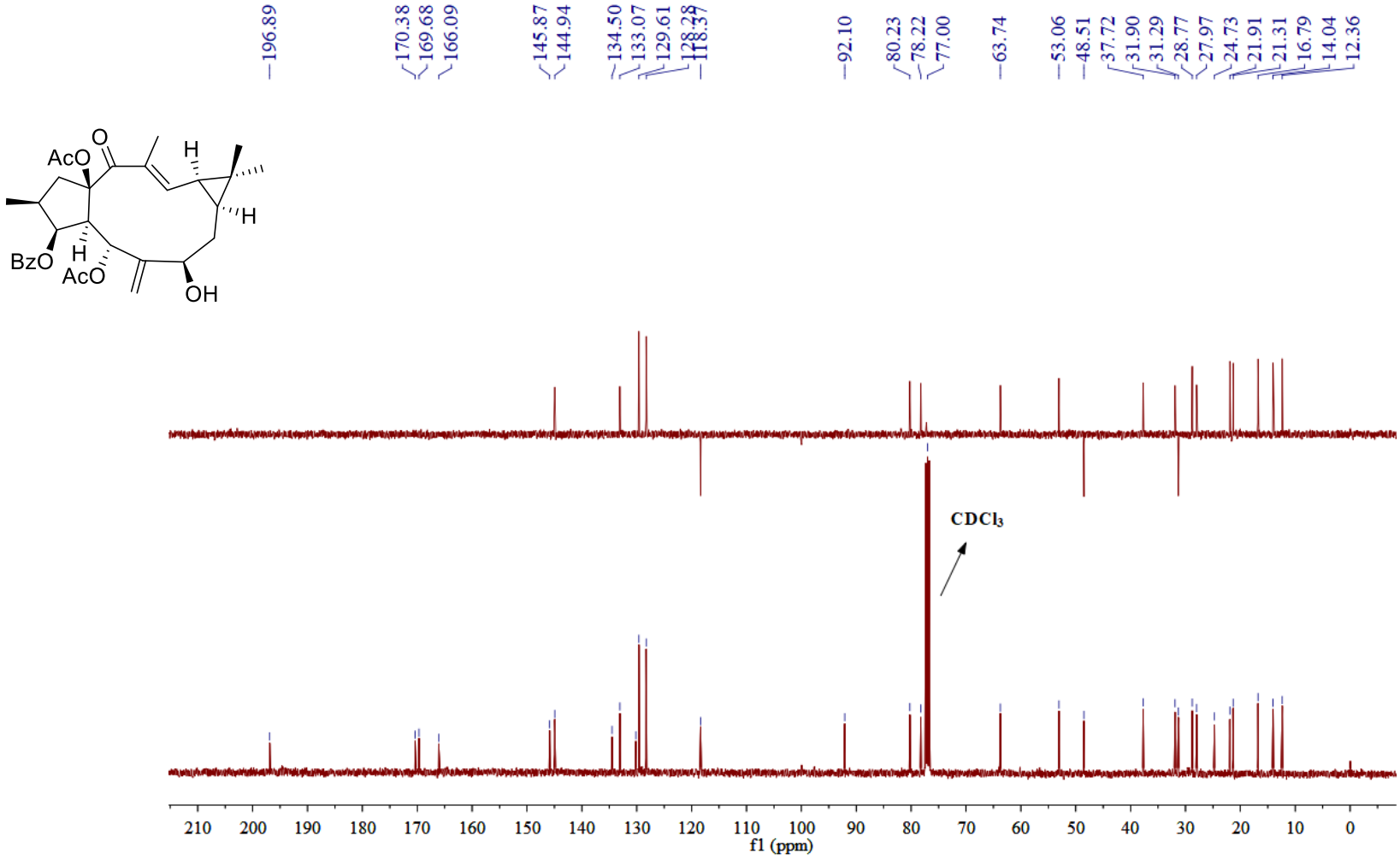


Figure S124. ^{1}H NMR spectrum of **10** in $CDCl_3$.

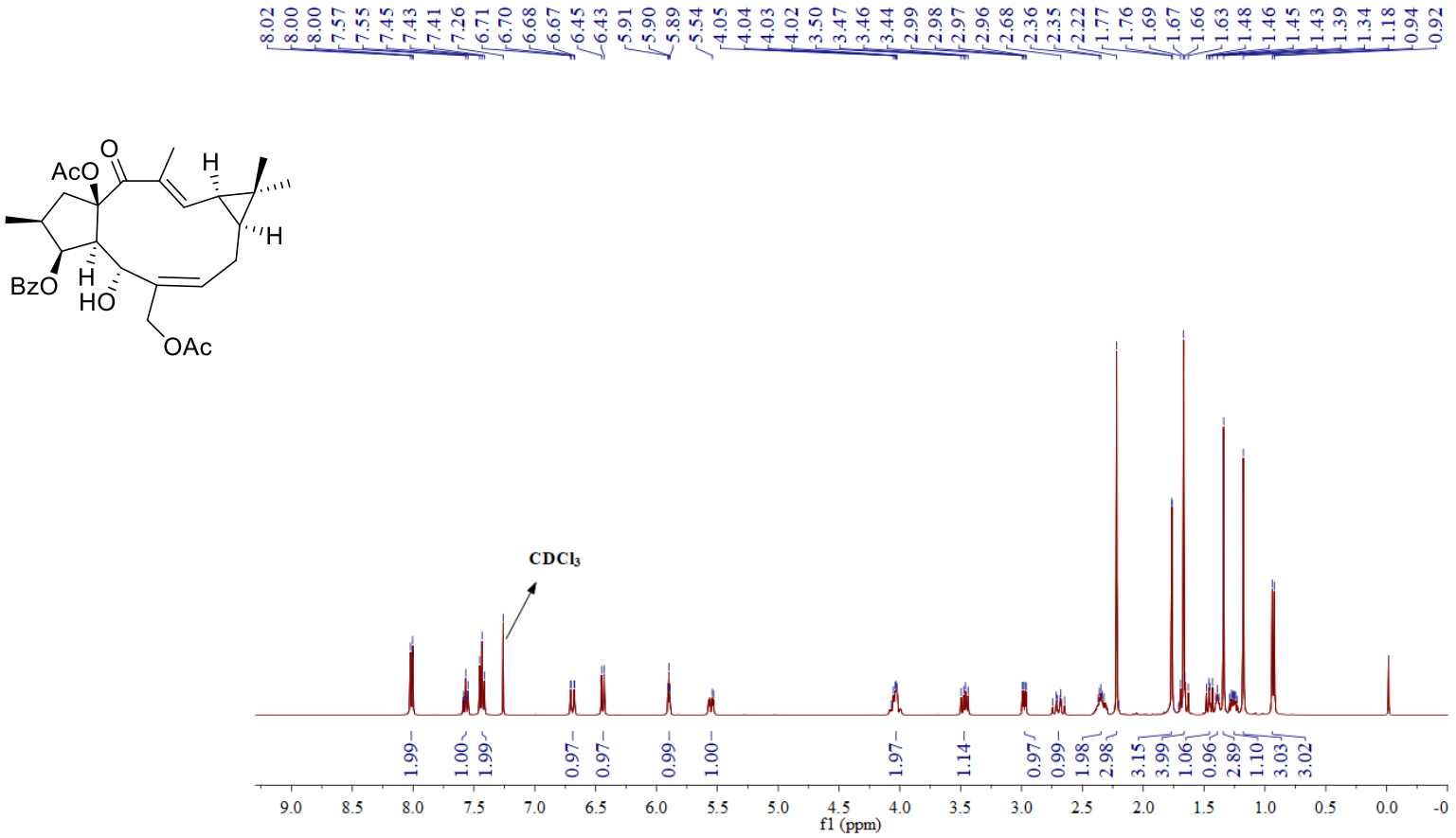


Figure S125. ^{13}C NMR and DEPT 135 spectra of **10** in $CDCl_3$.

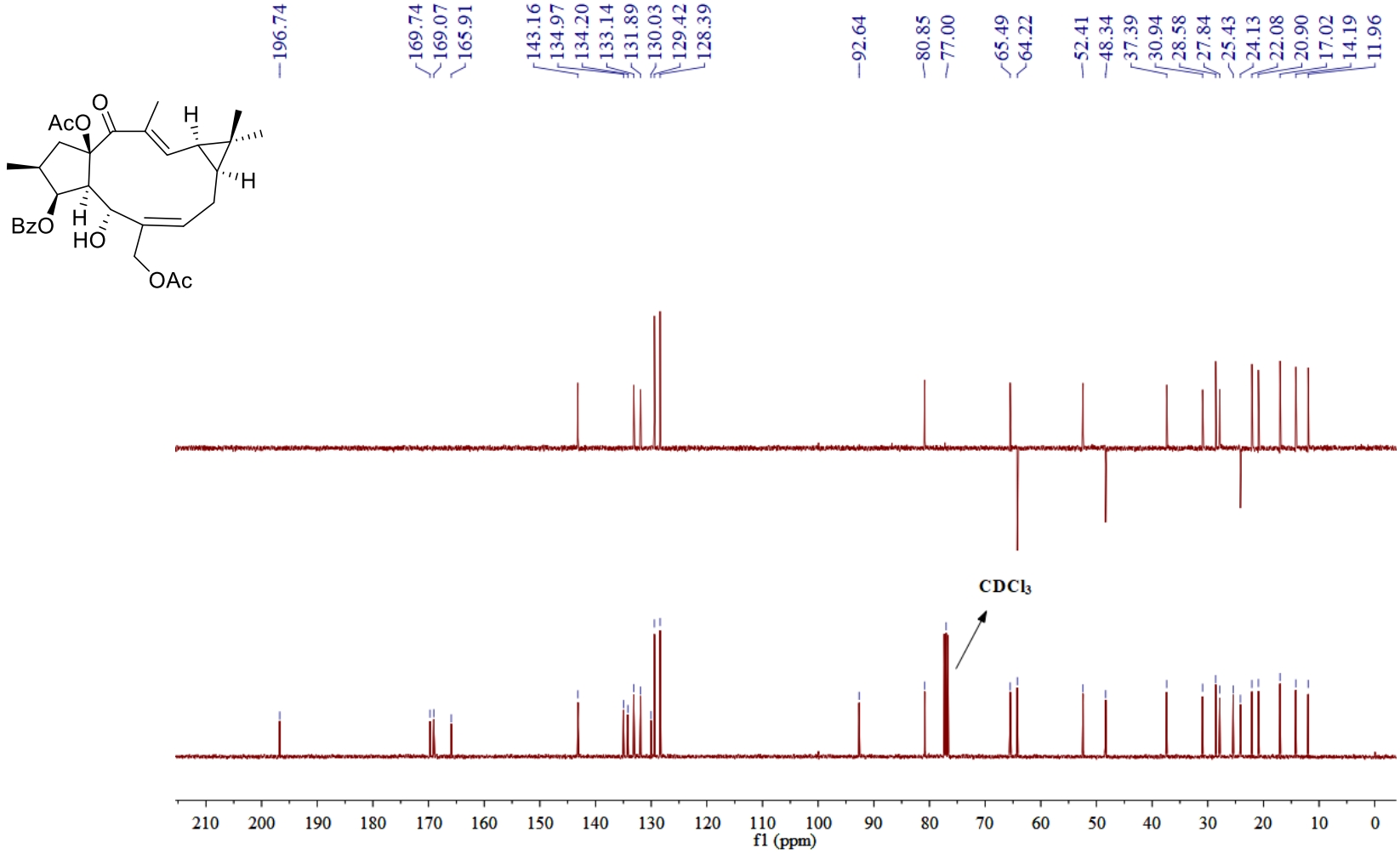


Figure S126. ^{1}H NMR spectrum of **11** in $CDCl_3$.

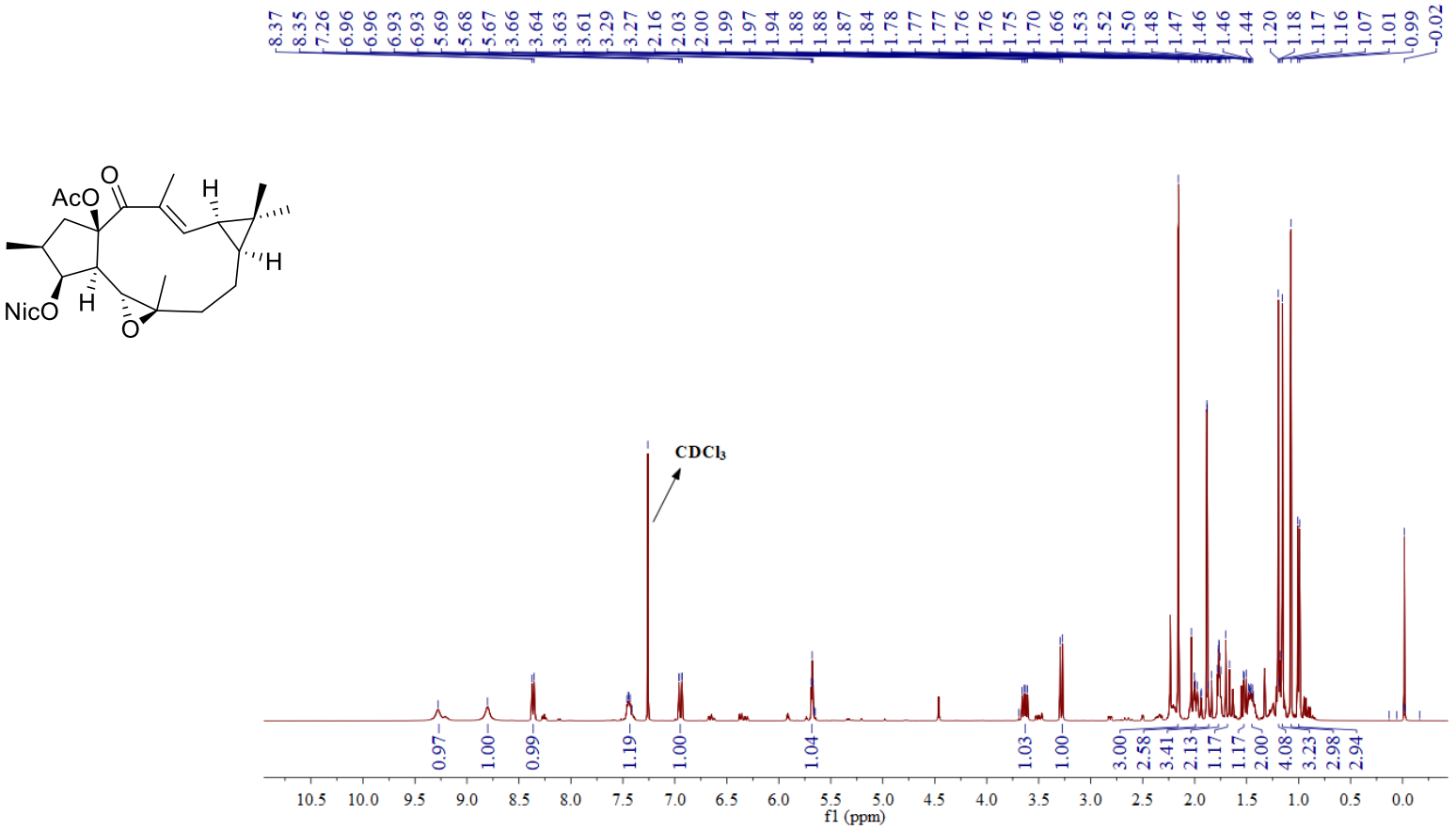


Figure S127. ^{13}C NMR and DEPT 135 spectra of **11** in $CDCl_3$.

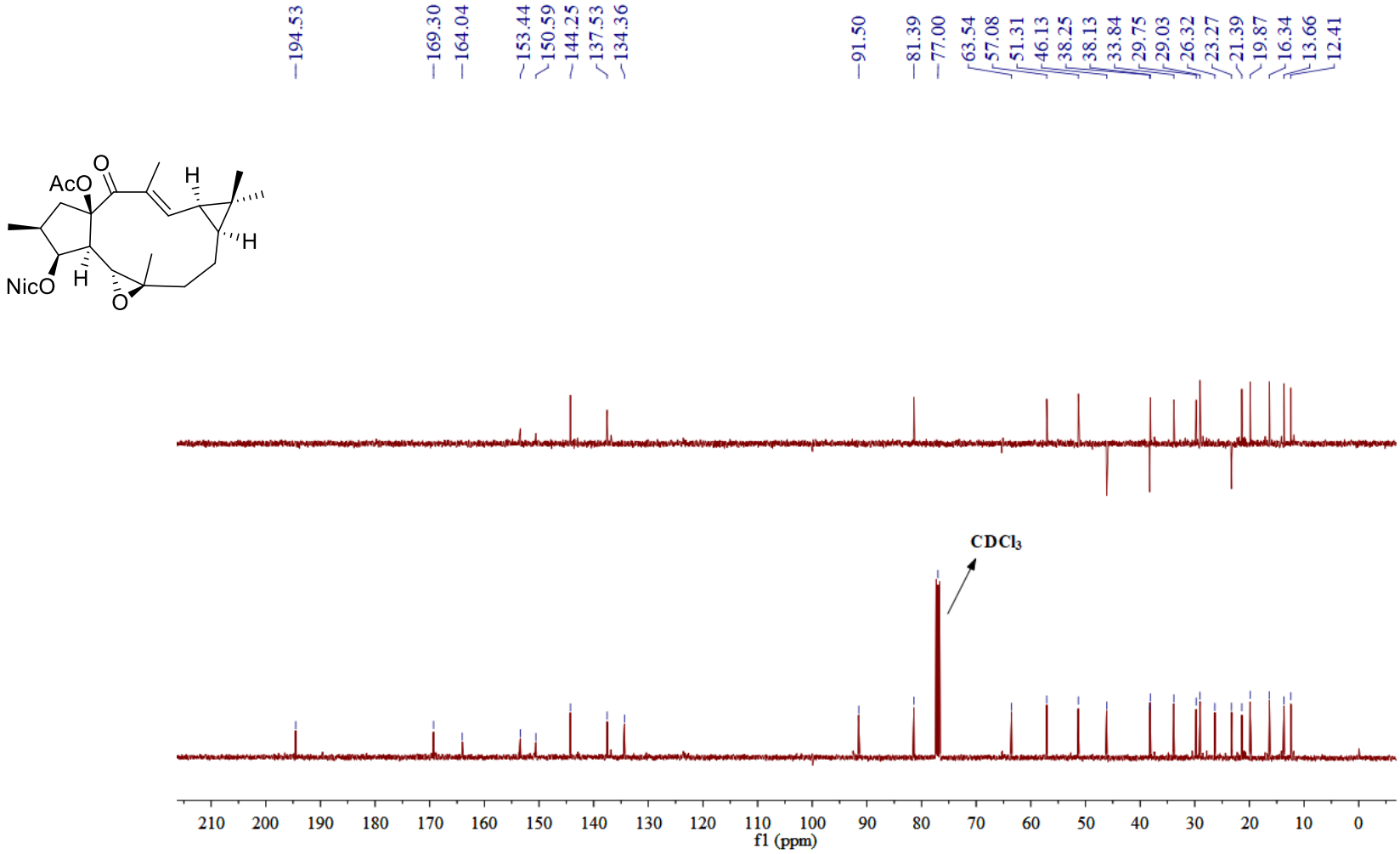


Figure S128. ^{1}H NMR spectrum of **12** in $CDCl_3$.

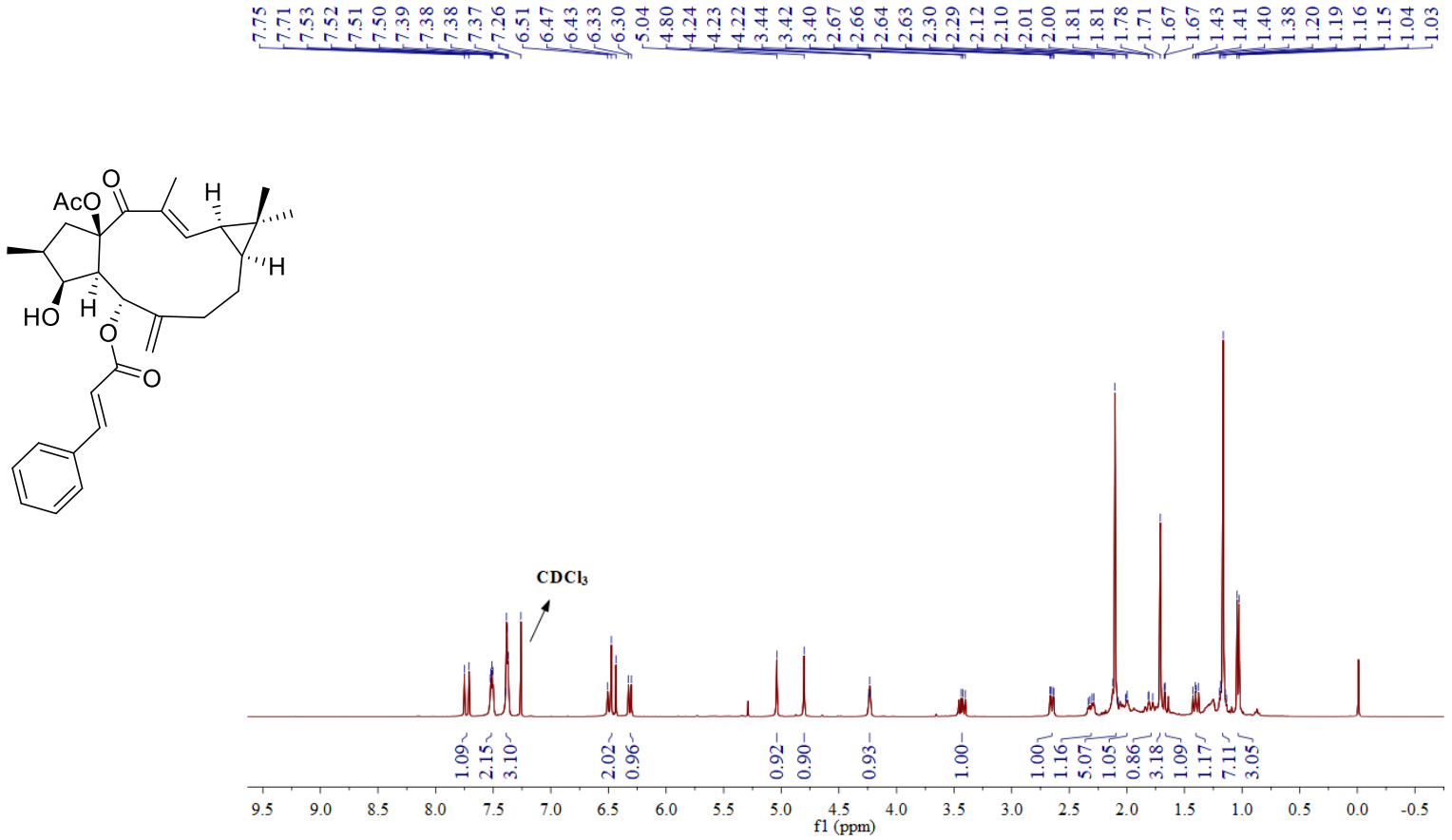


Figure S129. ^{13}C NMR and DEPT 135 spectra of 1**2** in $CDCl_3$.

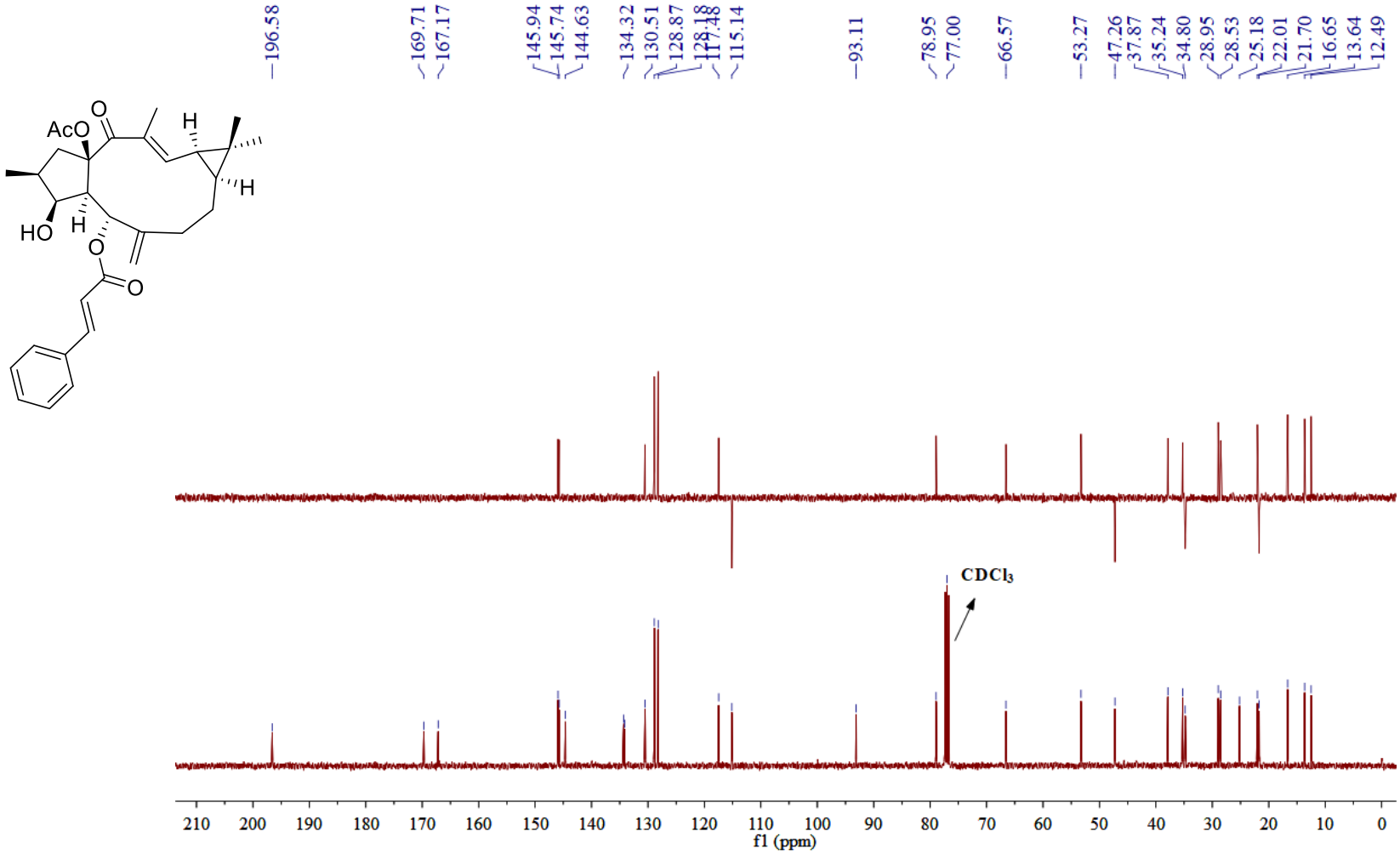


Figure S130. ^{1}H NMR spectrum of **13** in $CDCl_3$.

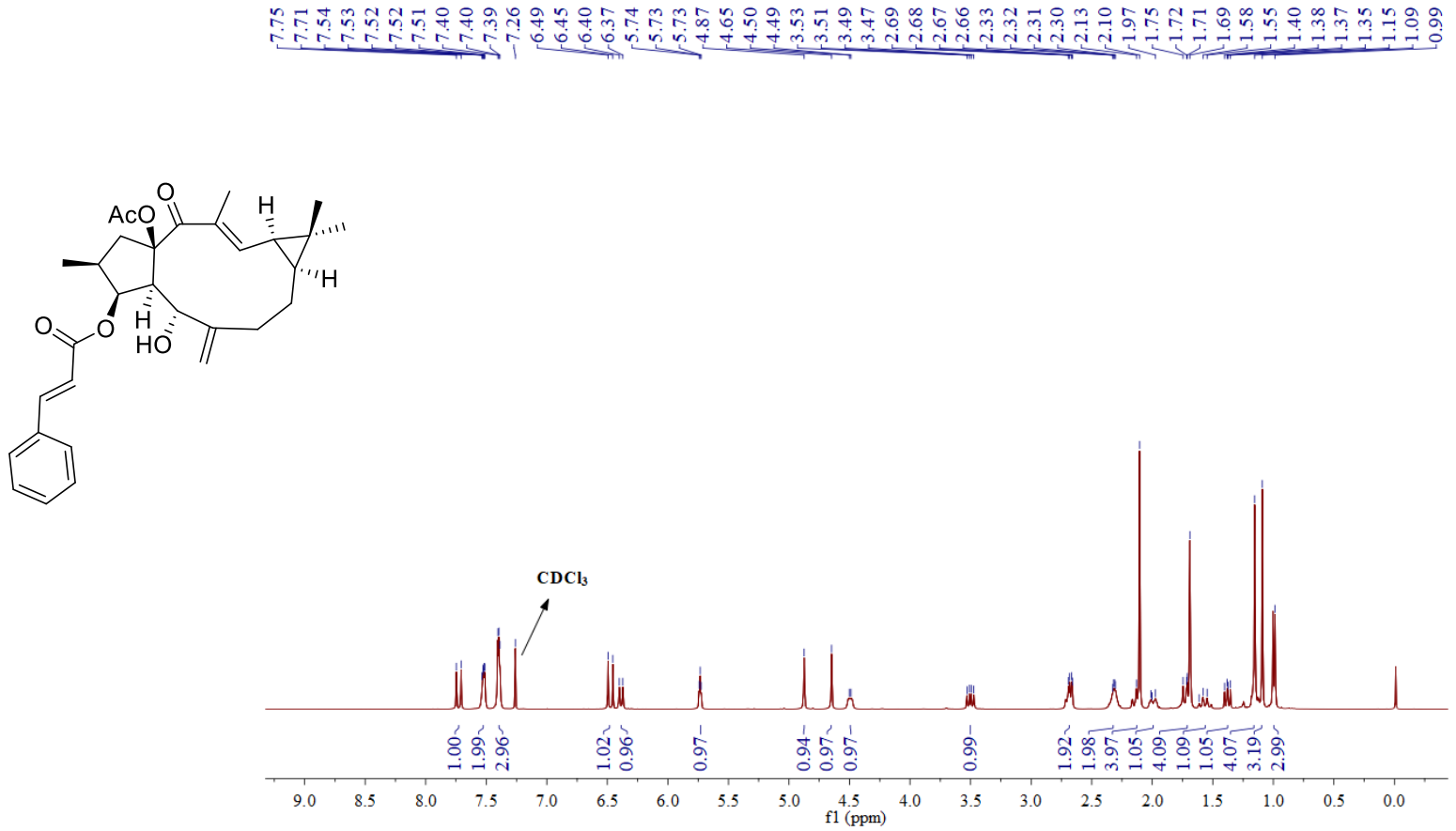


Figure S131. ^{13}C NMR and DEPT 135 spectra of **13** in $CDCl_3$.

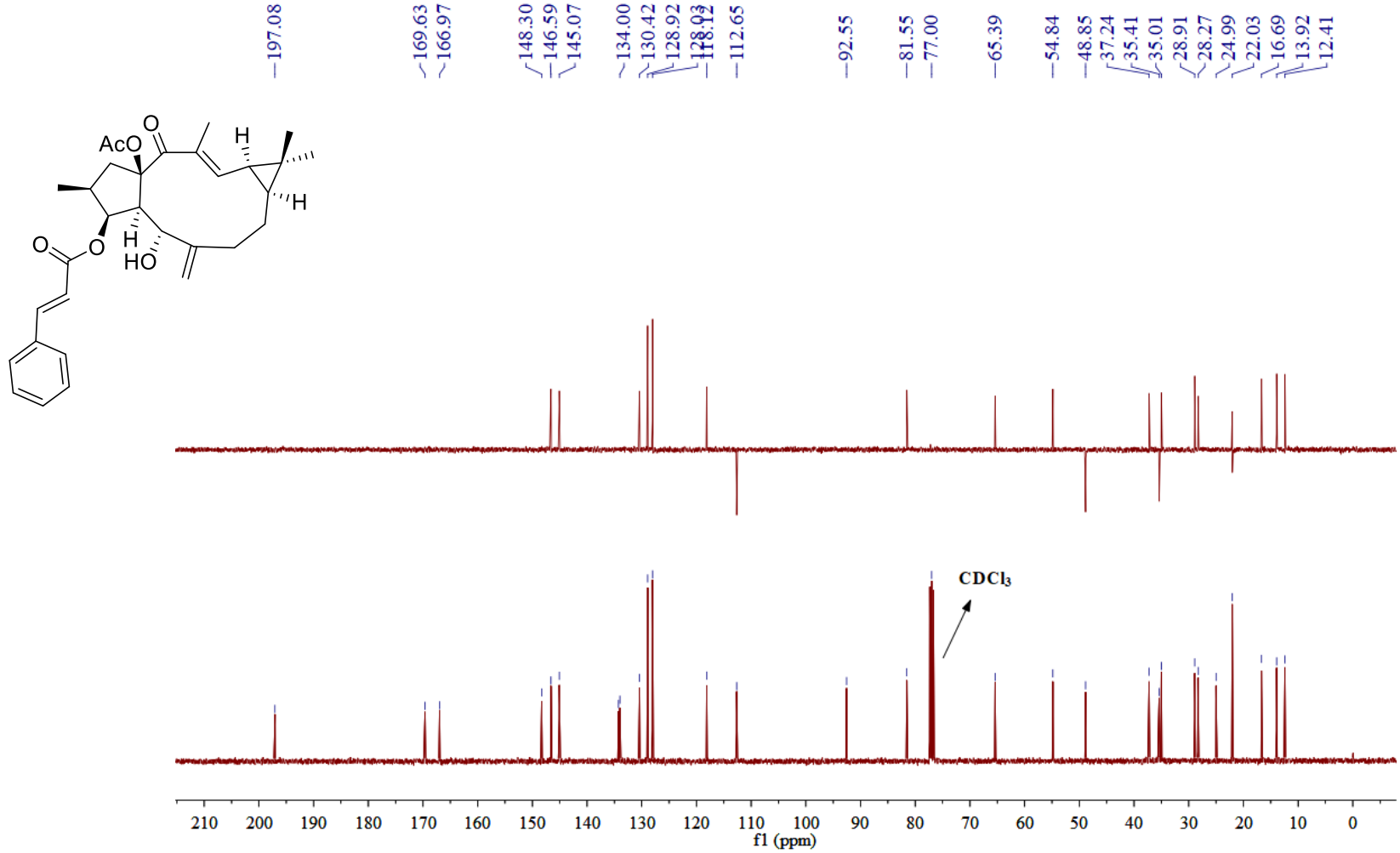


Figure S132. ^{1}H NMR spectrum of **14** in $CDCl_3$.

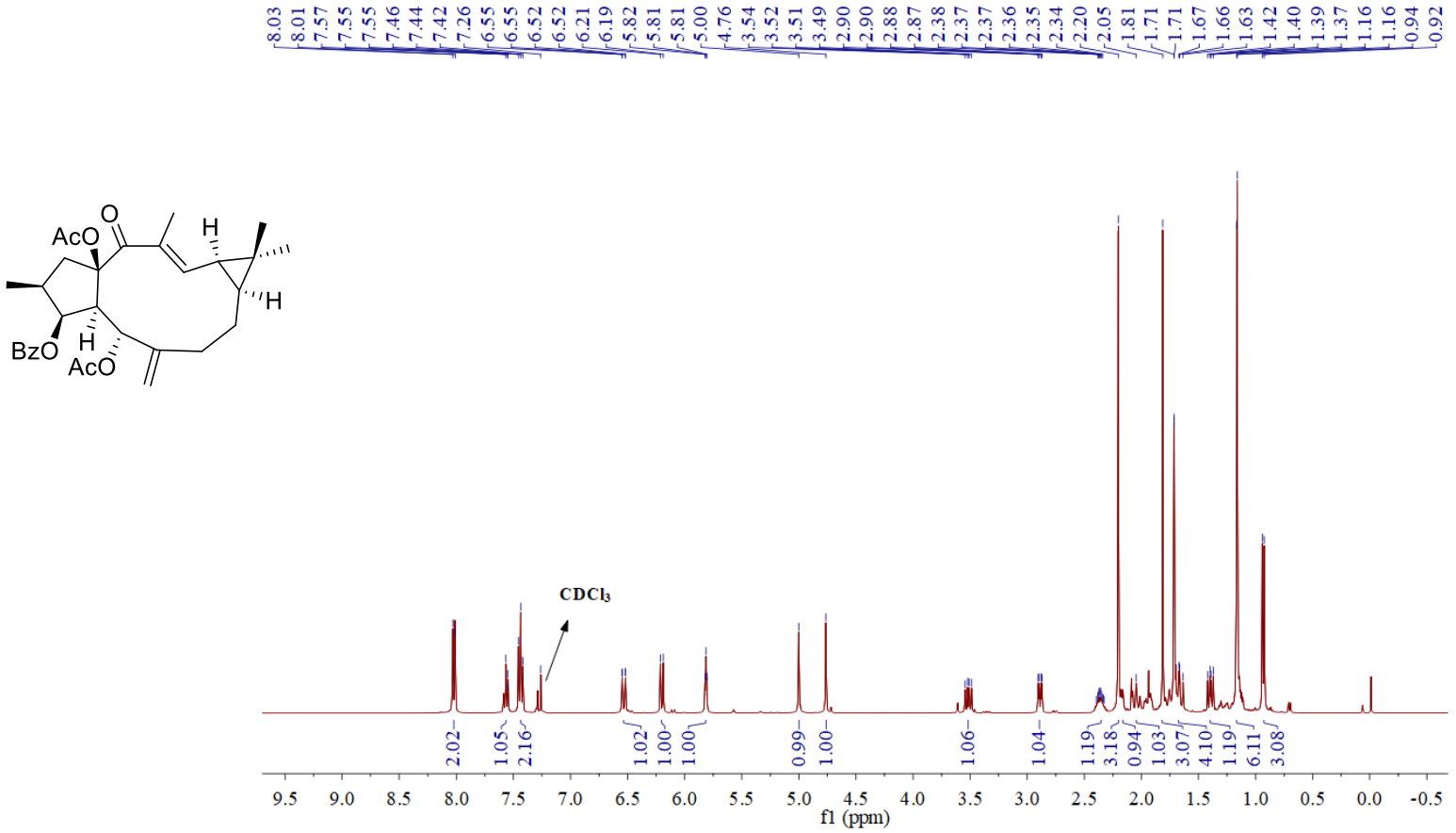


Figure S133. ^{13}C NMR and DEPT 135 spectra of **14** in $CDCl_3$.

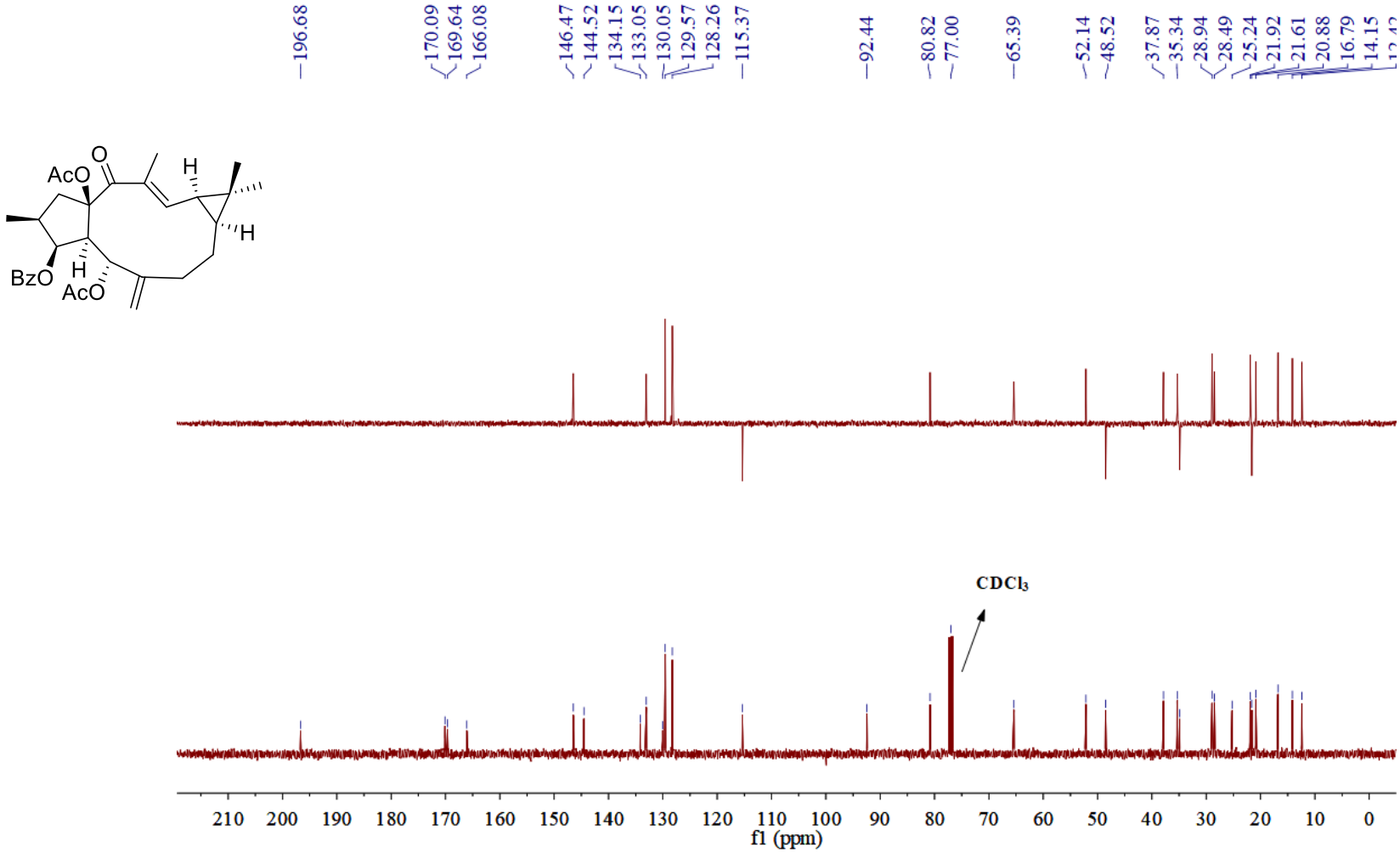


Figure S134. ^{1}H NMR spectrum of **15** in $CDCl_3$.

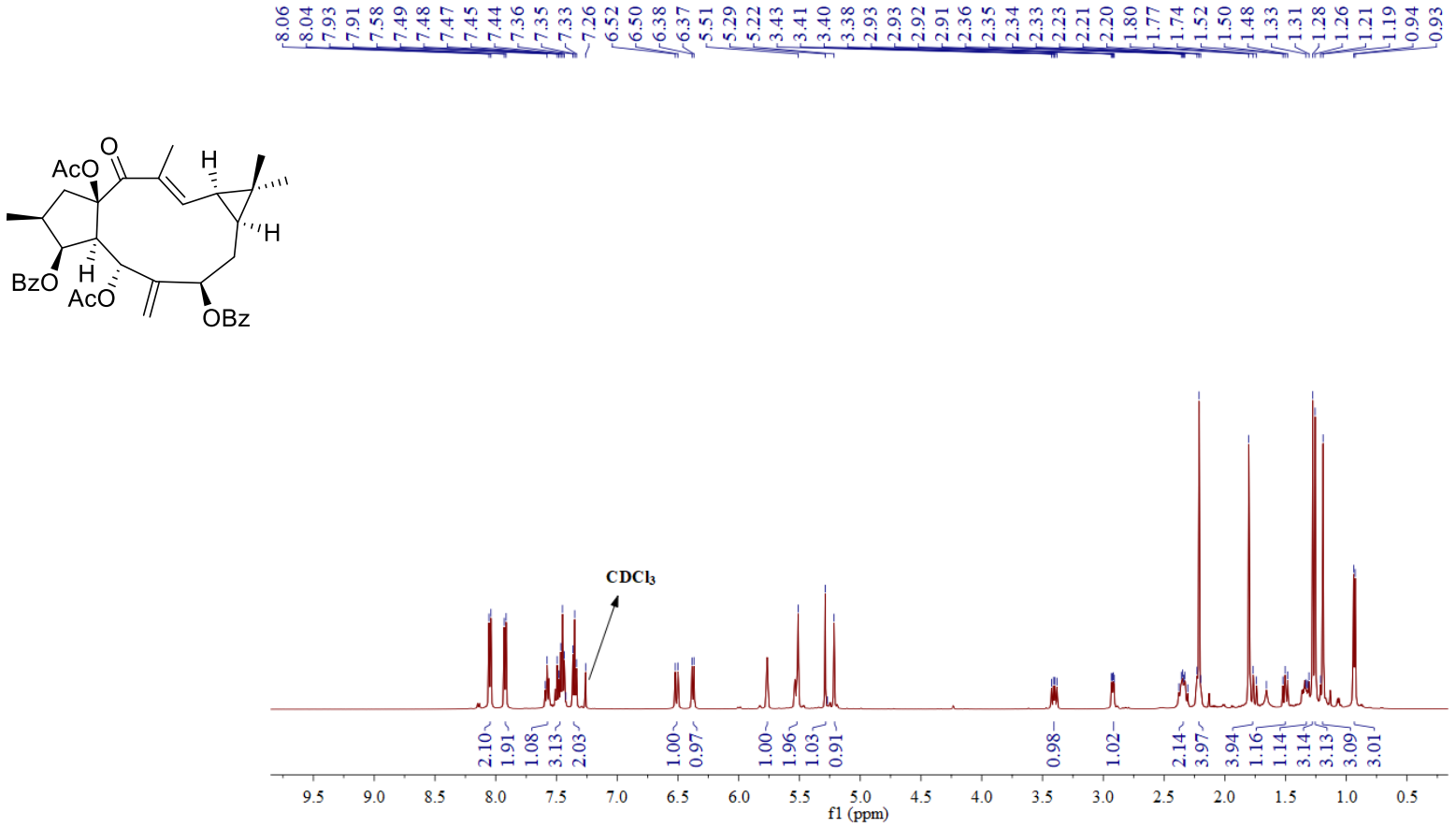


Figure S135. ^{13}C NMR and DEPT 135 spectra of **15** in $CDCl_3$.

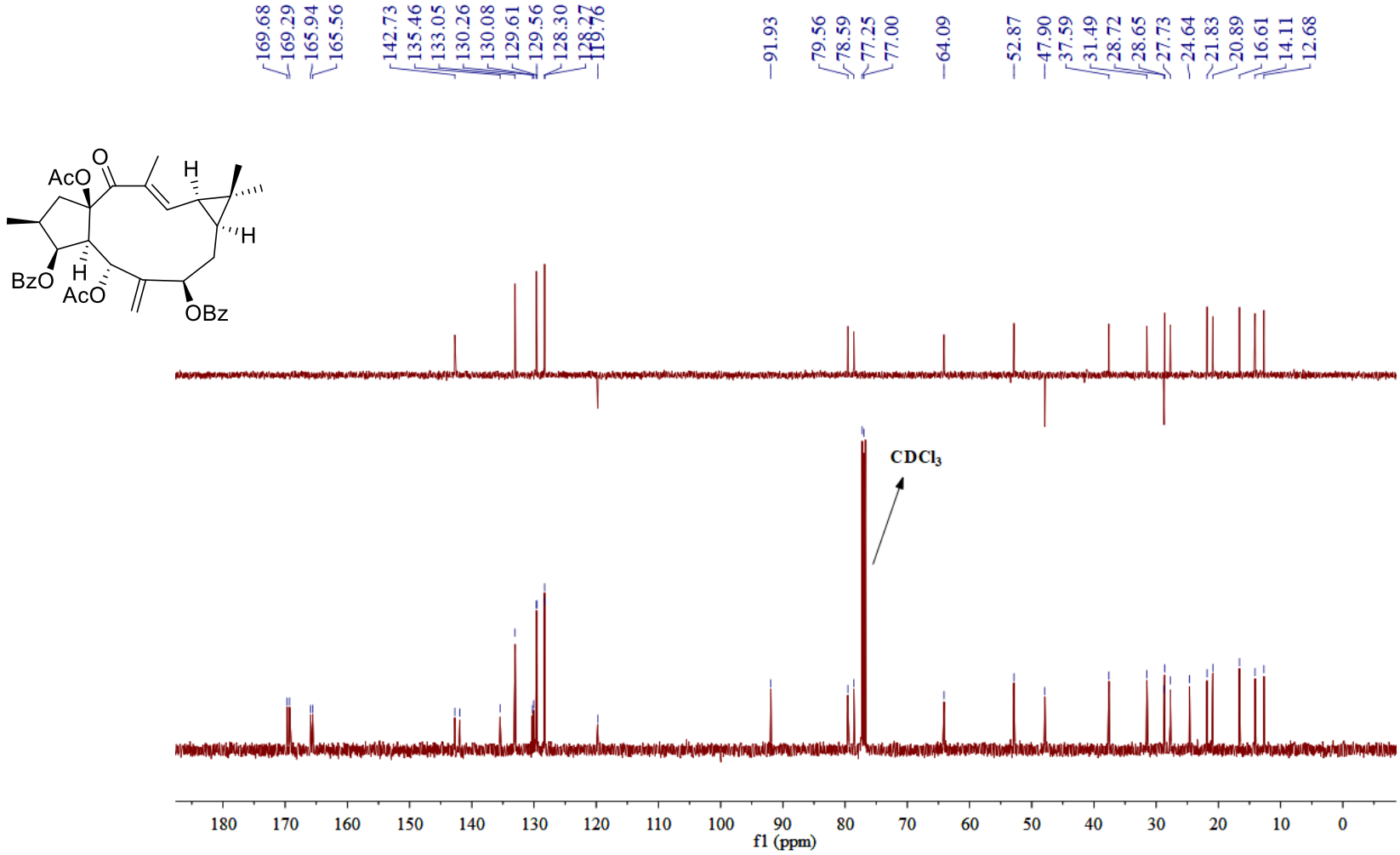


Figure S136. ^{1}H NMR spectrum of **16** in $CDCl_3$.

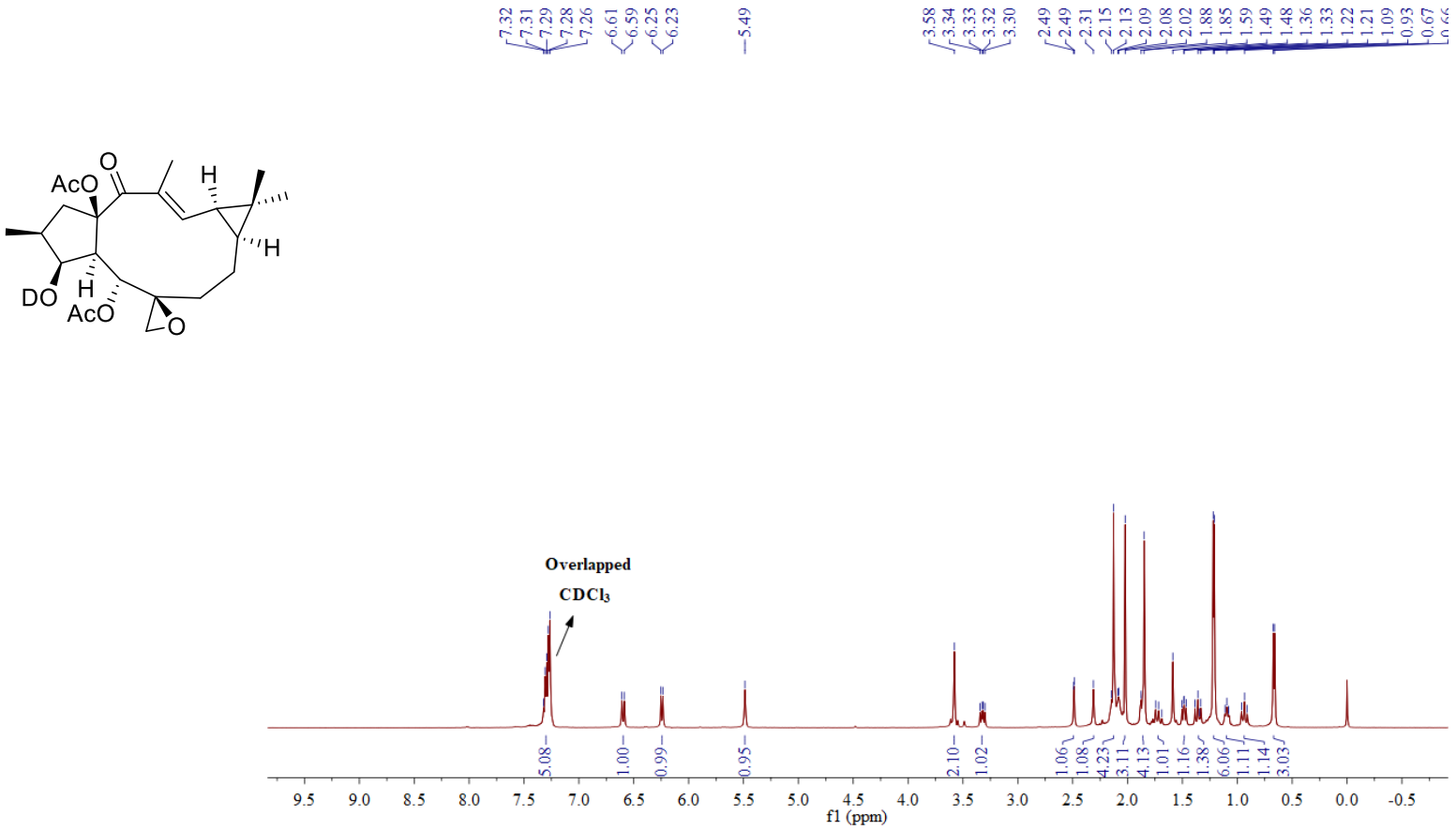


Figure S137. ^{13}C NMR and DEPT 135 spectra of **16** in $CDCl_3$.

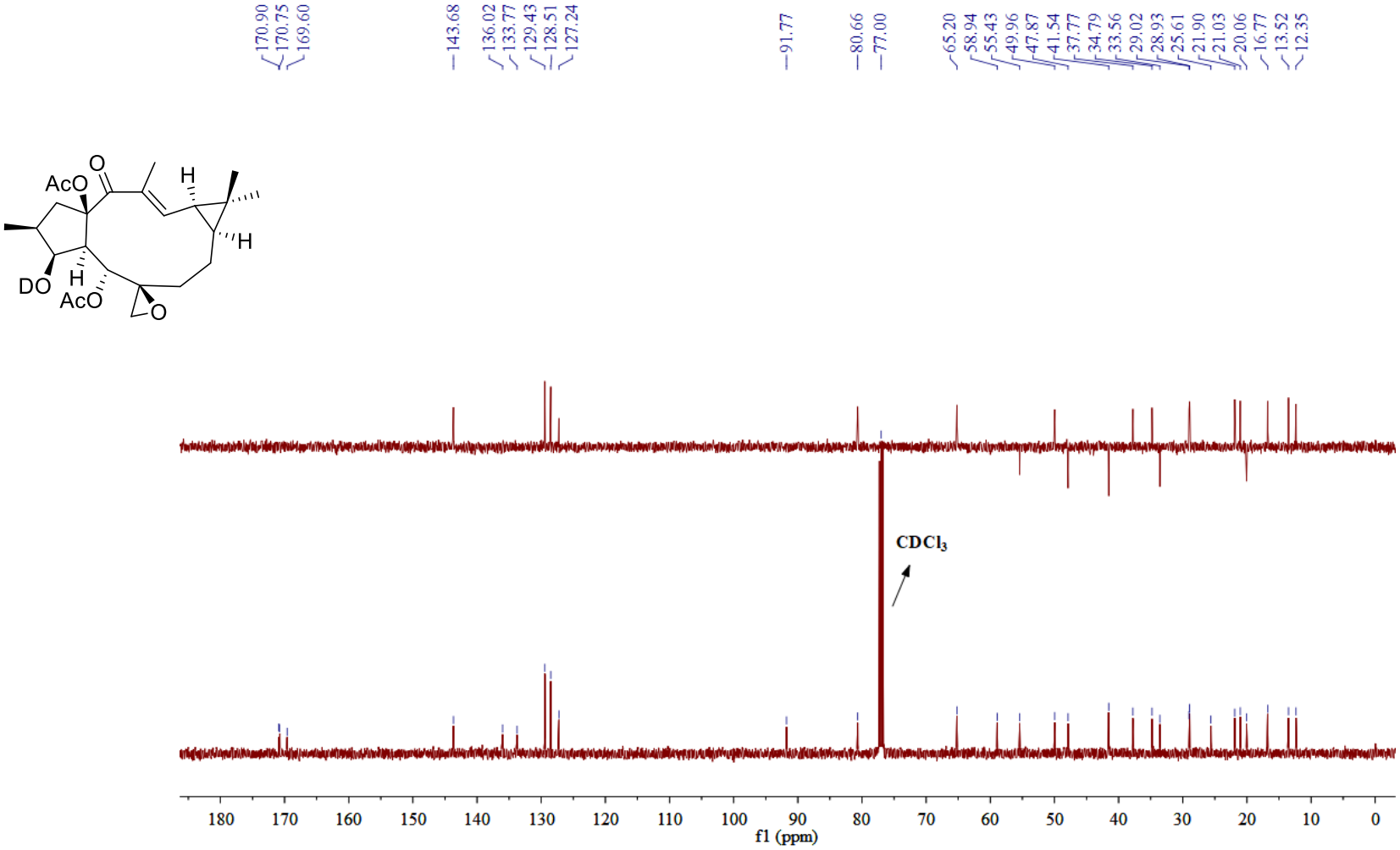


Figure S138. ^{1}H spectrum of **17** in $CDCl_3$.

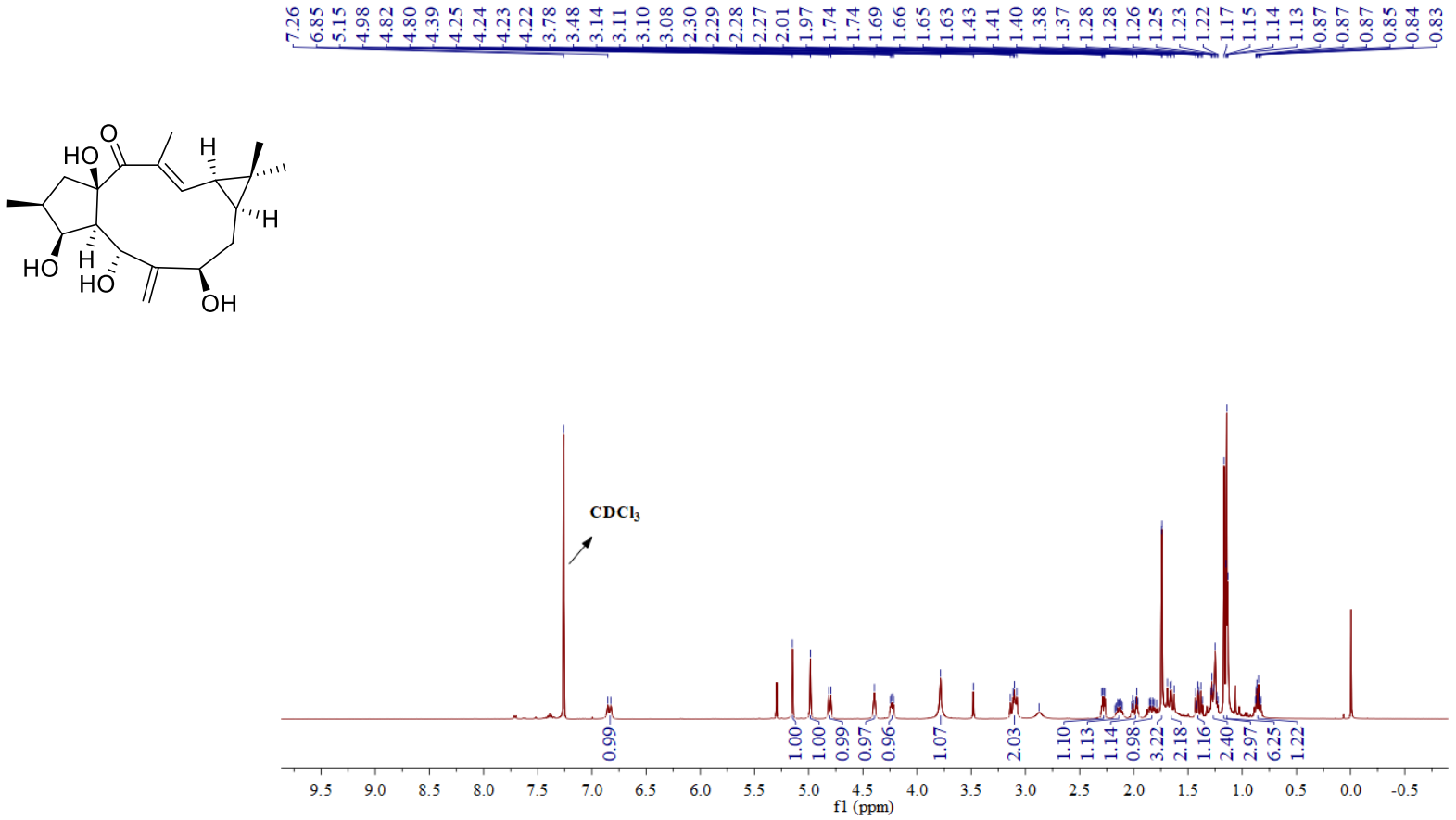


Figure S139. ^{13}C NMR and DEPT 135 spectra of **17** in $CDCl_3$.

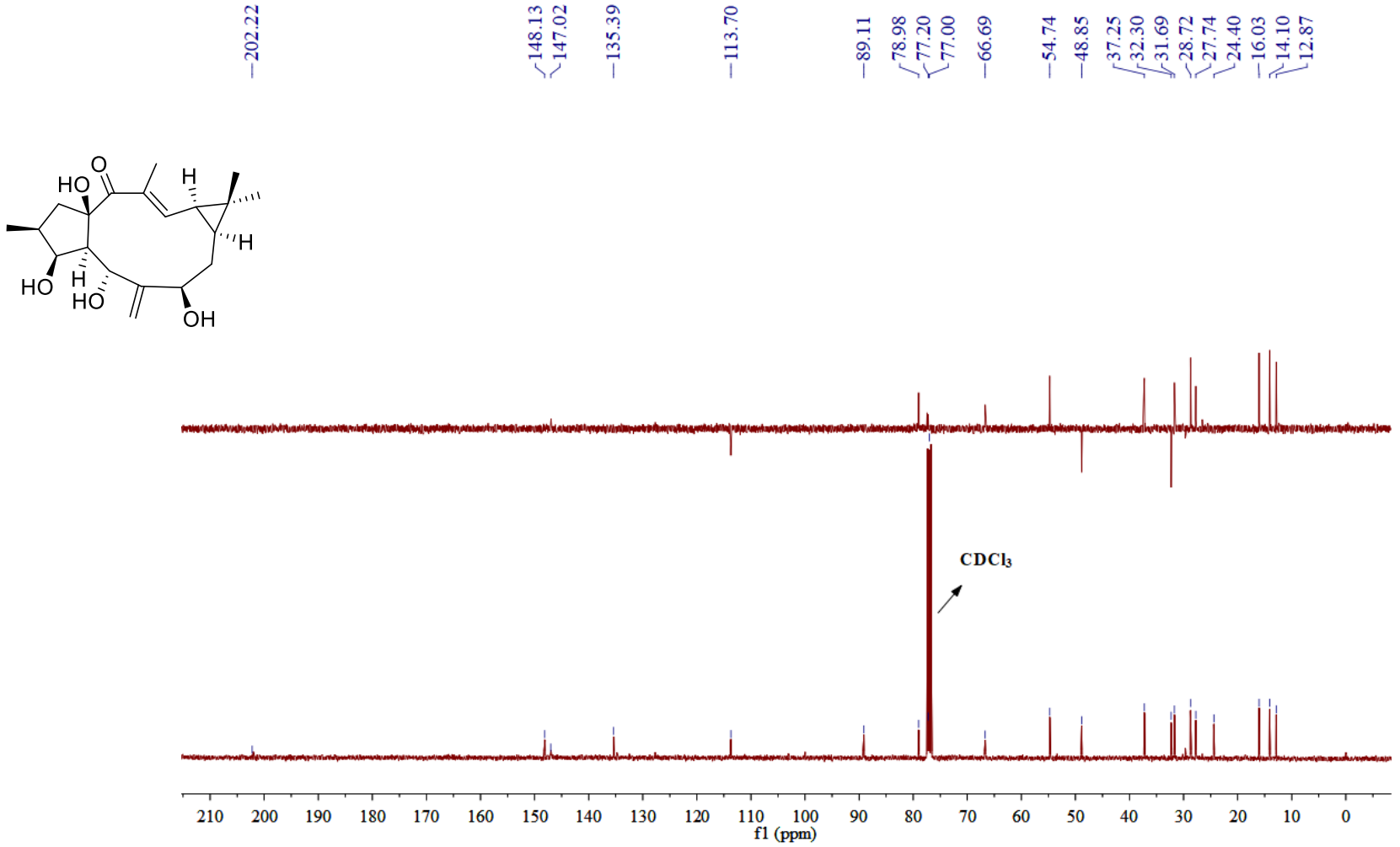


Figure S140. ^{1}H spectrum of **18** in $CDCl_3$.

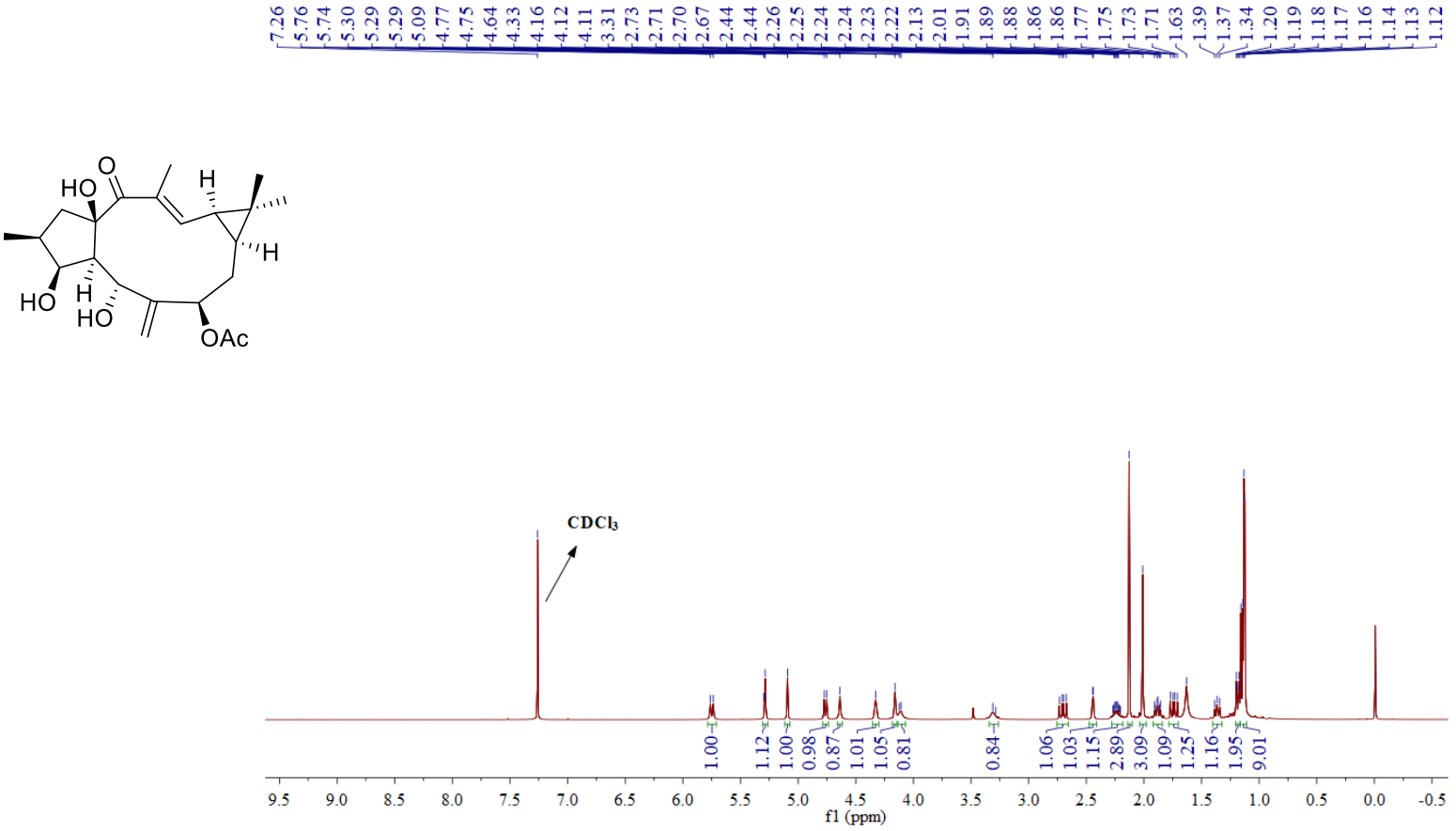


Figure S141. ^{13}C NMR and DEPT 135 spectra of **18** in $CDCl_3$.

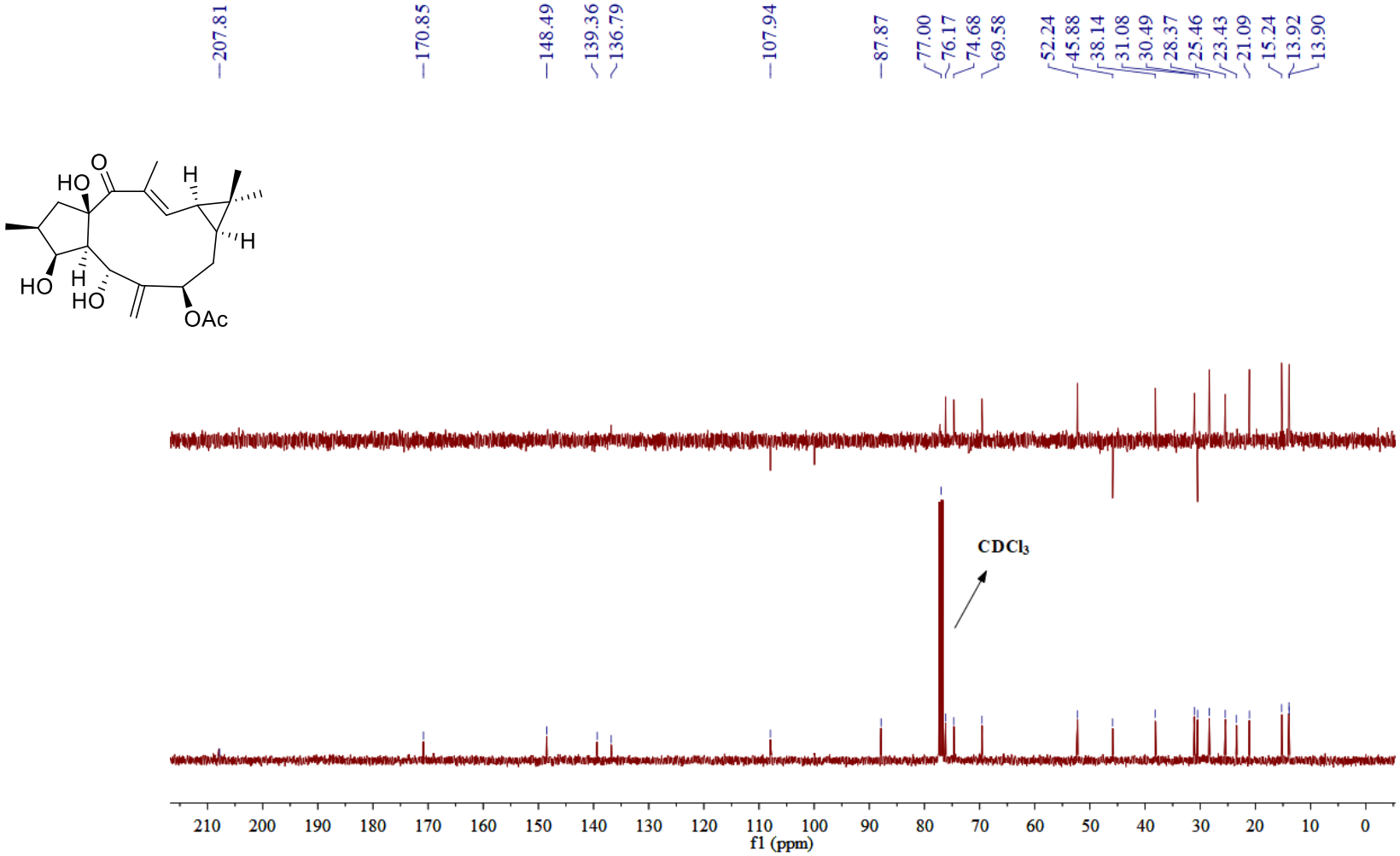


Figure S142. ^{1}H spectrum of **19** in $CDCl_3$.

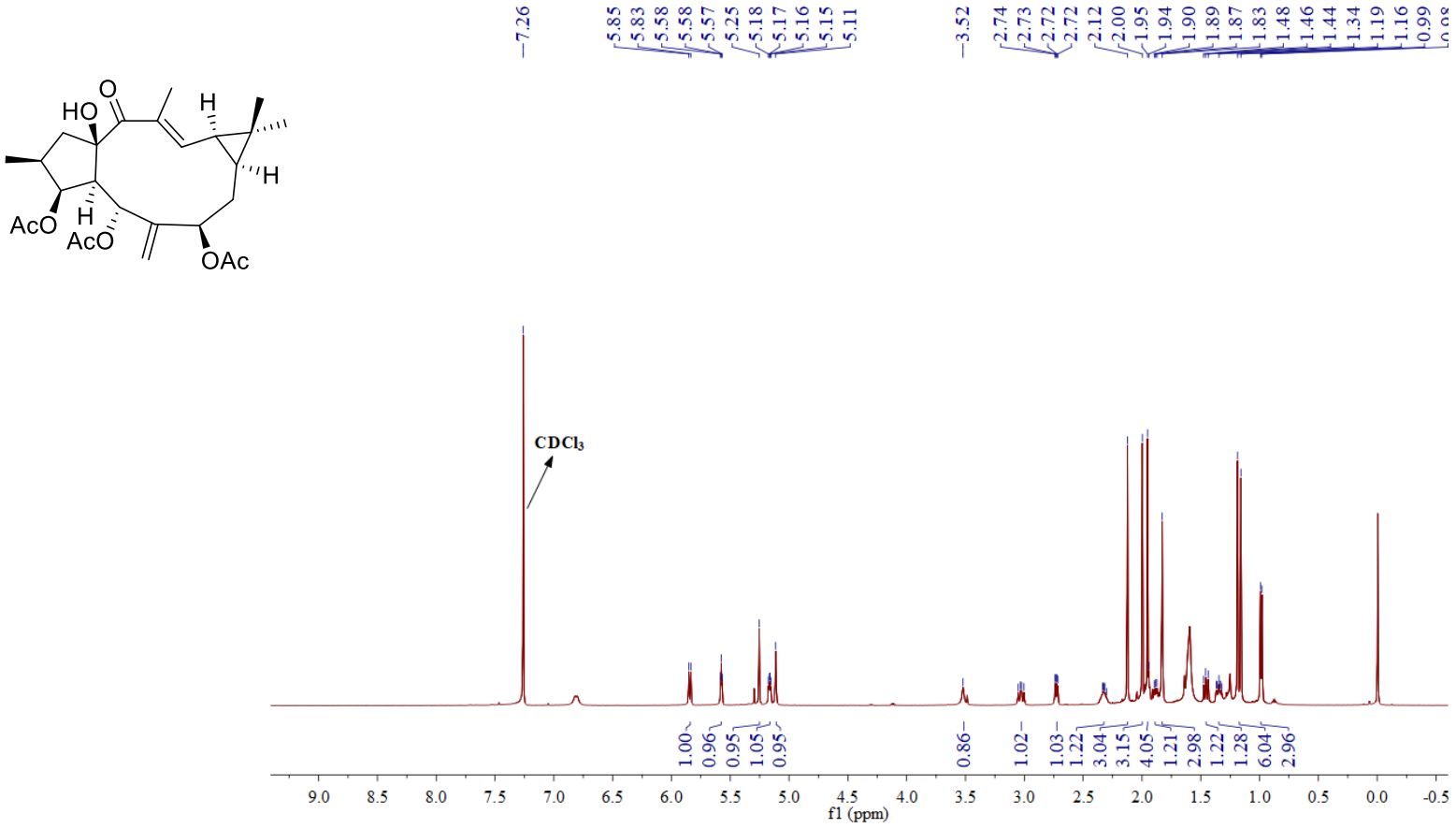


Figure S143. ^{13}C NMR spectrum of **19** in $CDCl_3$.

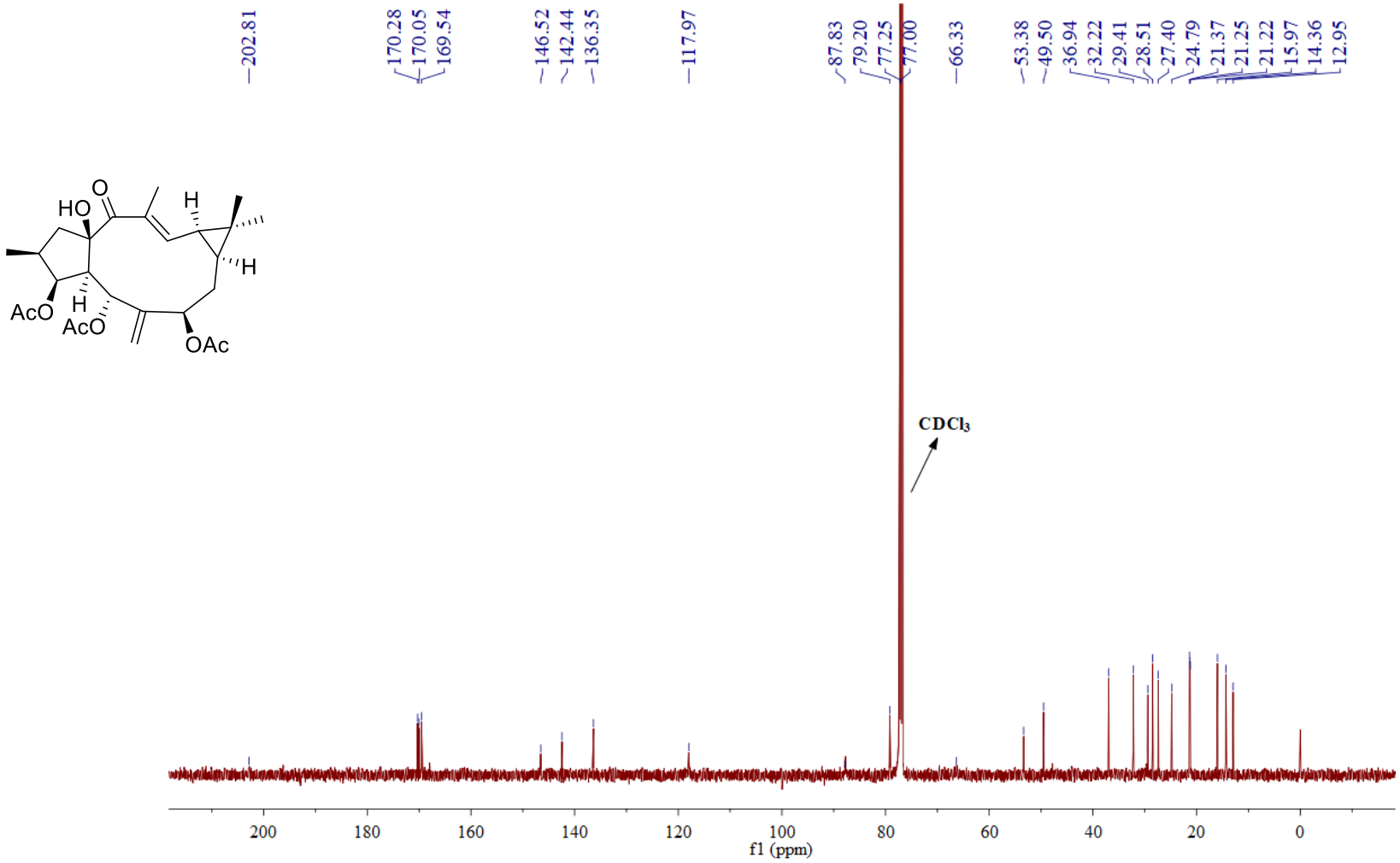


Figure S144. ^{1}H spectrum of **27** in $CDCl_3$.

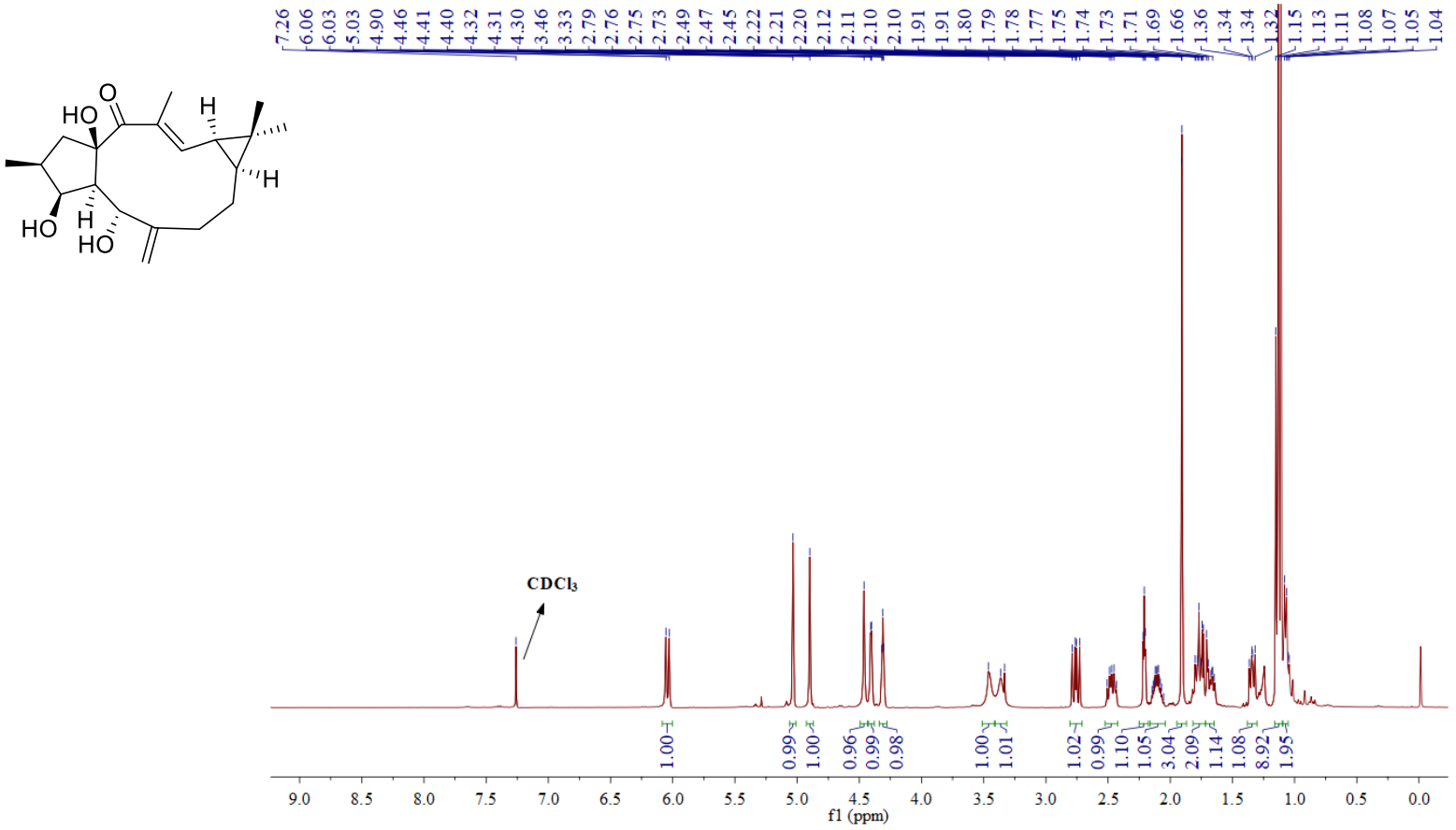
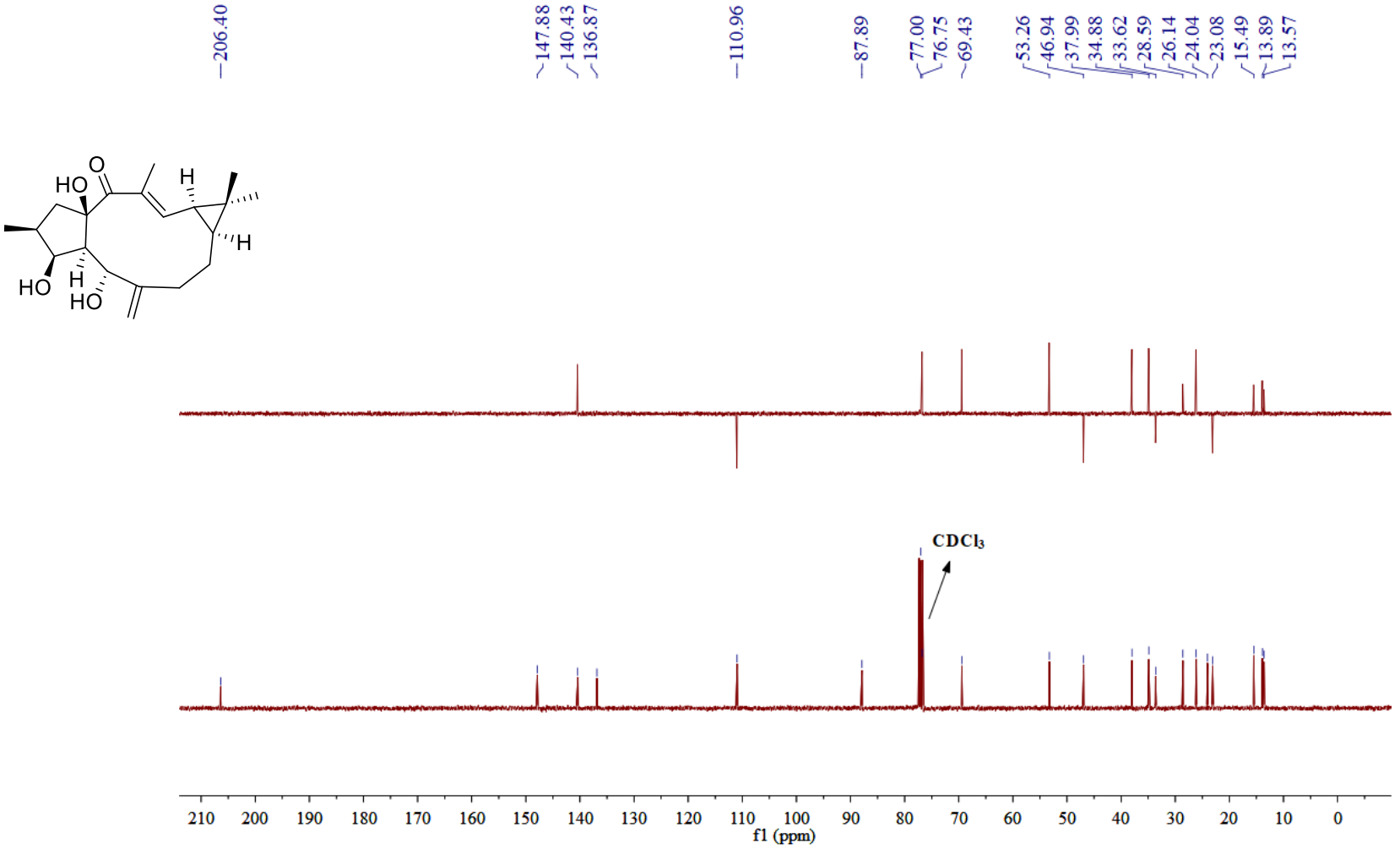
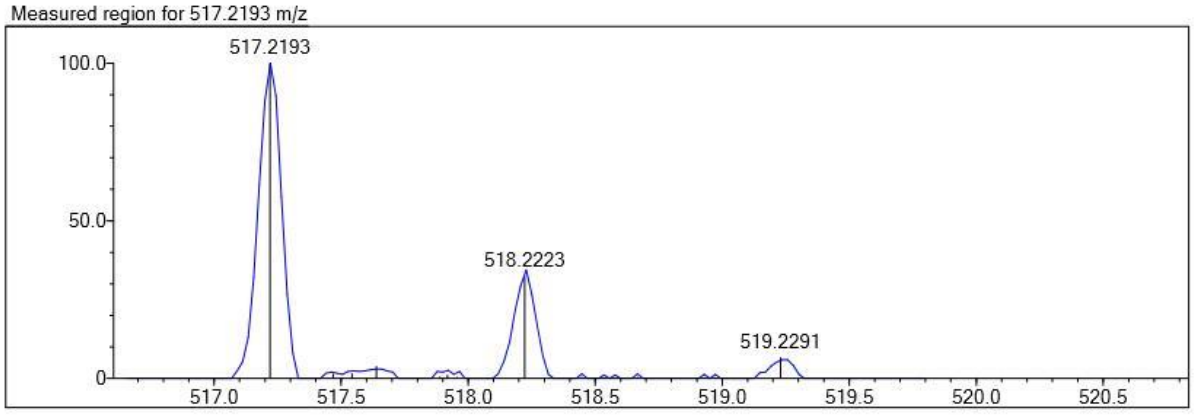


Figure S145. ^{13}C NMR and DEPT 135 spectra of **27** in $CDCl_3$.



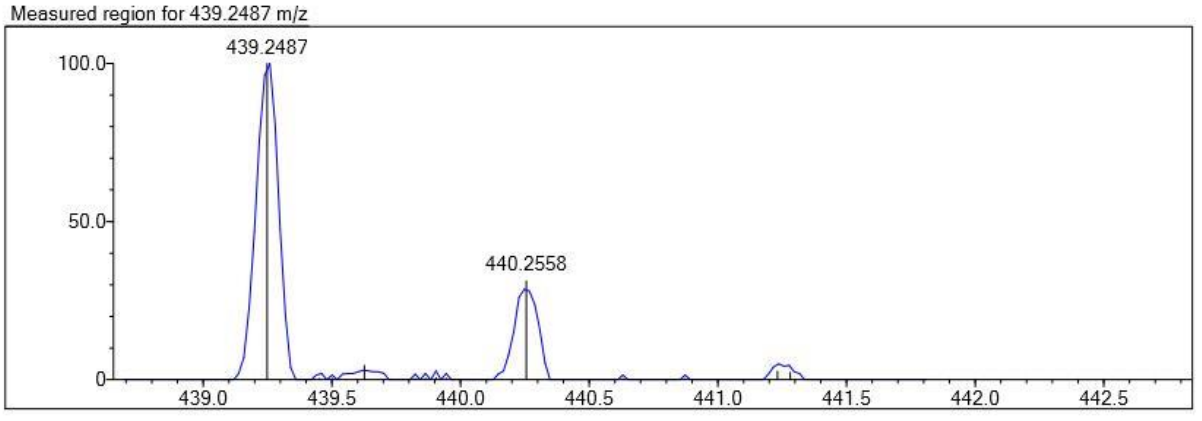
12. Figure S146–S164.

Figure S146. HRESIMS spectrum of **1**.



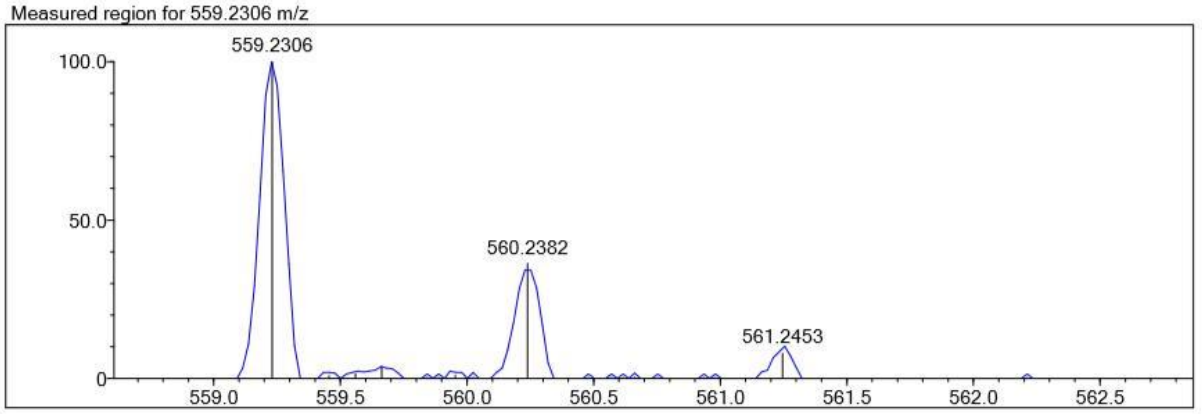
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	81.09	C29 H34 O7	[M+Na]+	517.2193	517.2197	-0.4	-0.77	81.09	13.0

Figure S147. HRESIMS spectrum of **2**.



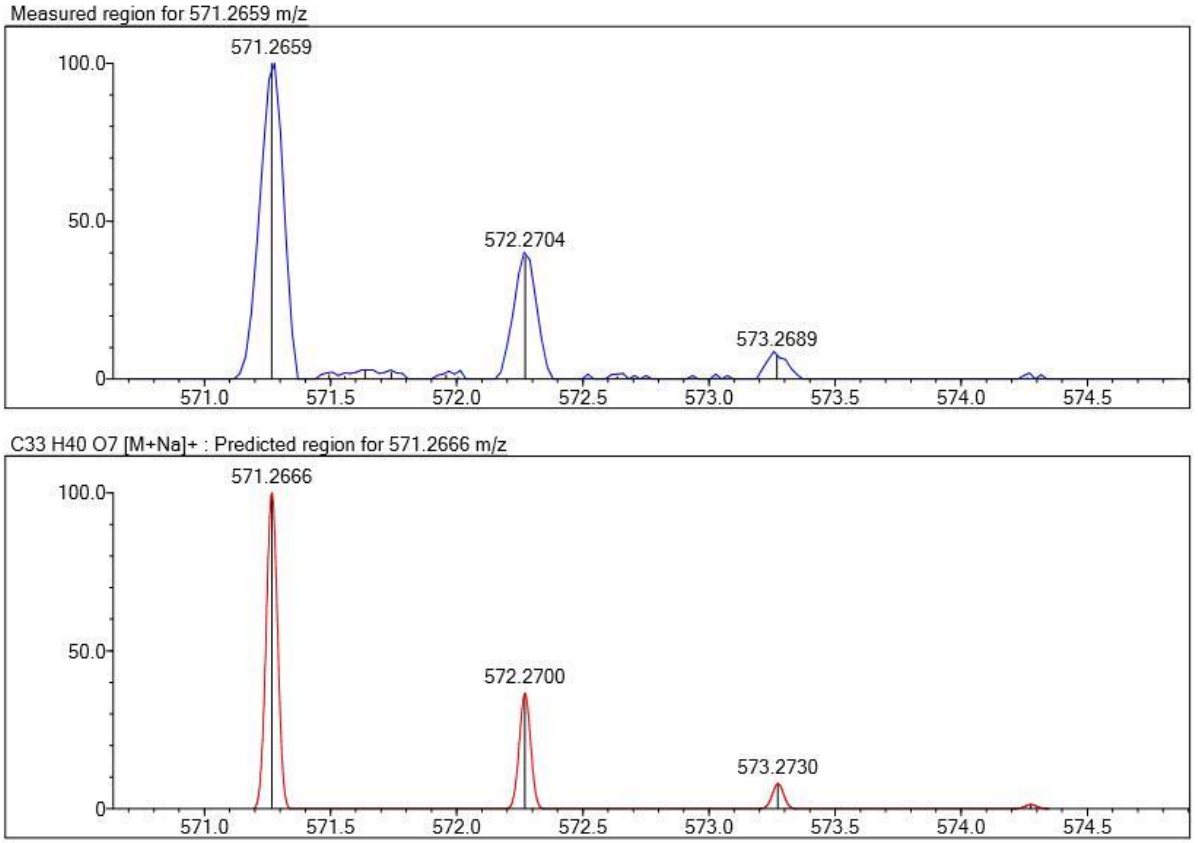
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	57.37	C27 H34 O5	[M+H]+	439.2487	439.2479	0.8	1.82	58.57	11.0

Figure S148. HRESIMS spectrum of **3**.



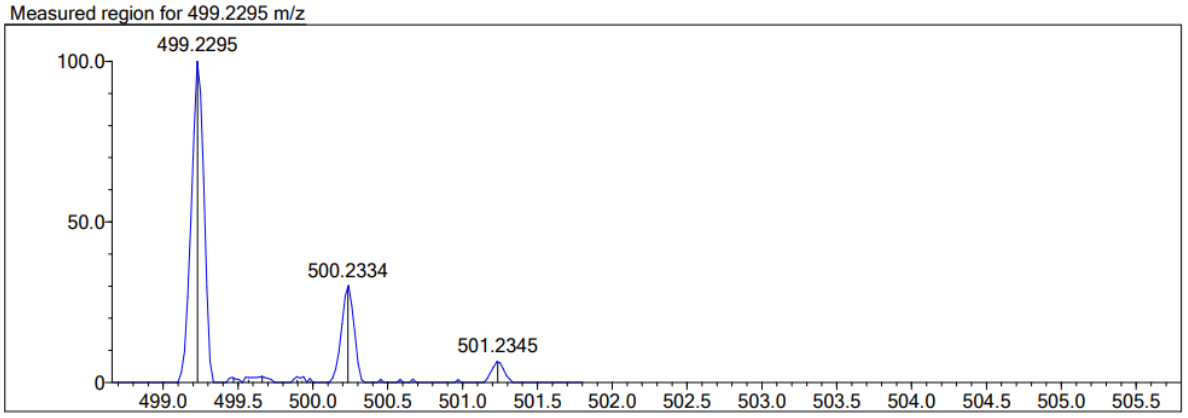
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	91.00	C31 H36 O8	[M+Na]+	559.2306	559.2302	0.4	0.72	91.00	14.0

Figure S149. HRESIMS spectrum of **4**.



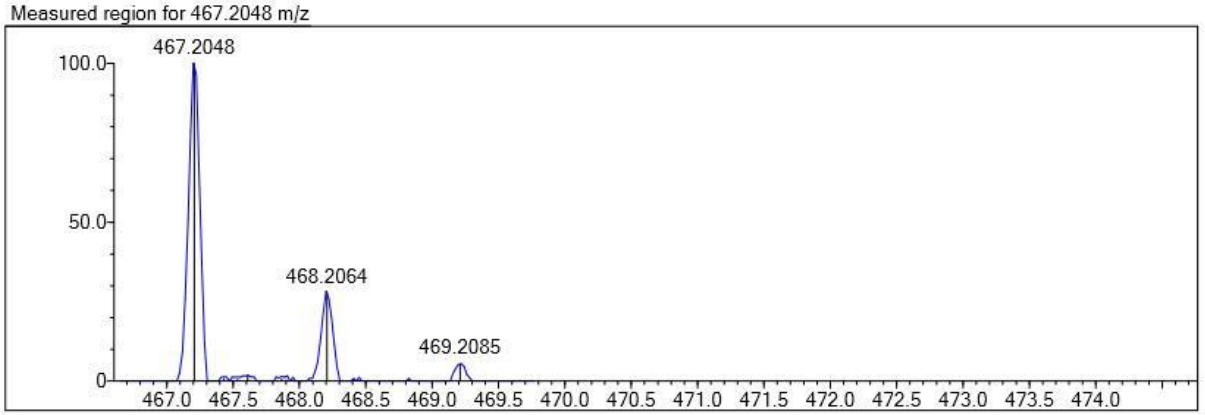
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	77.87	C33 H40 O7	[M+Na]+	571.2659	571.2666	-0.7	-1.23	78.32	14.0

Figure S150. HRESIMS spectrum of **5**.



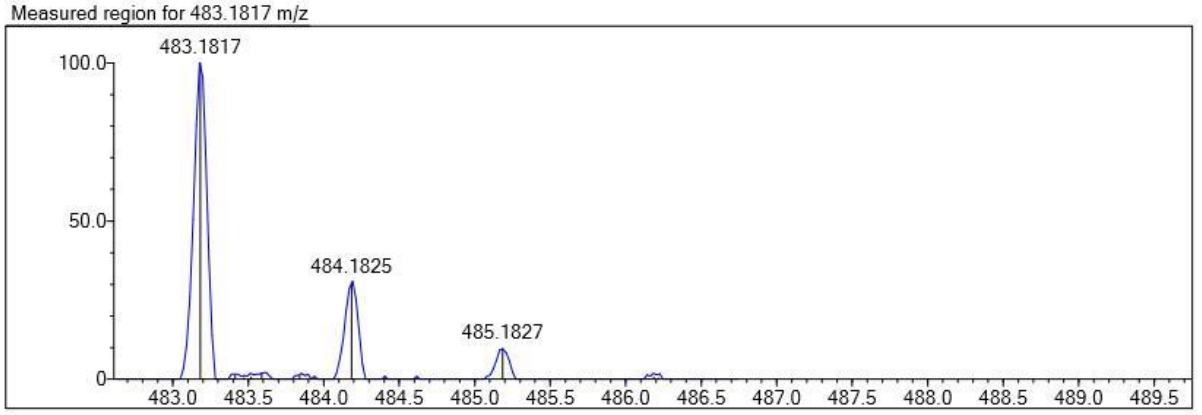
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	91.15	C26 H36 O8	[M+Na]+	499.2295	499.2302	-0.7	-1.40	92.07	9.0

Figure S151. HRESIMS spectrum of **20**.



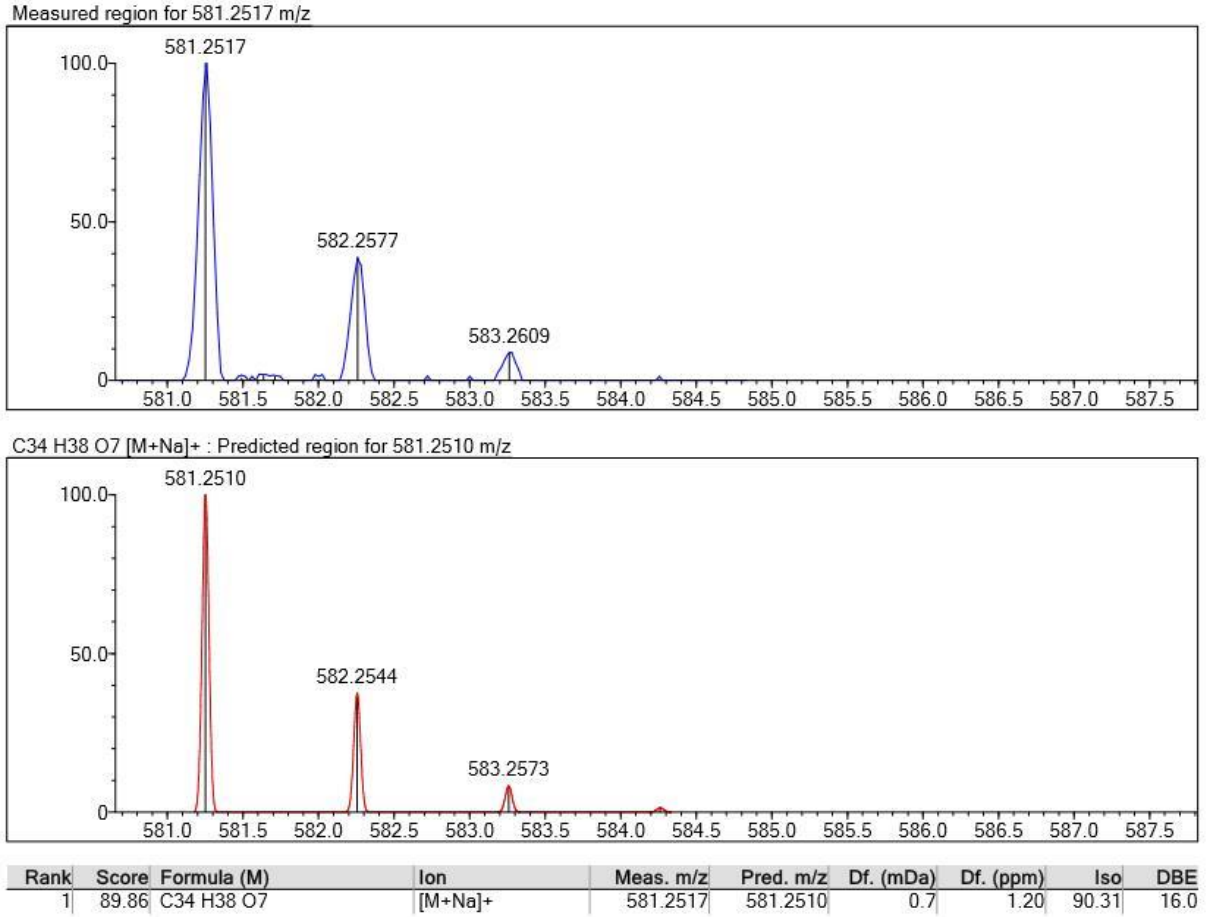
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	88.13	C25 H32 O7	[M+Na]+	467.2048	467.2040	0.8	1.71	89.72	10.0

Figure S152. HRESIMS spectrum of **21**.



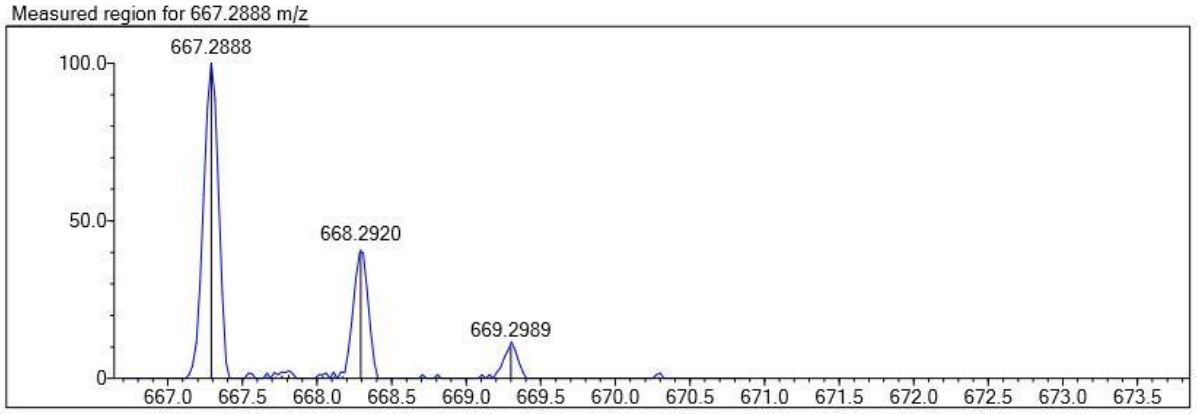
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	63.98	C25 H32 O6 S	[M+Na]+	483.1817	483.1812	0.5	1.03	64.03	10.0

Figure S153. HRESIMS spectrum of **22**.



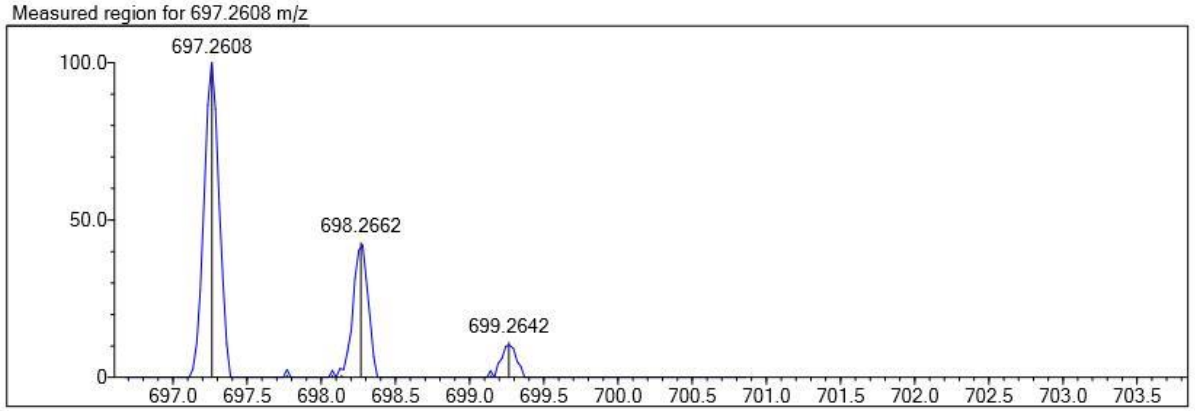
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	89.86	C34 H38 O7	[M+Na]+	581.2517	581.2510	0.7	1.20	90.31	16.0

Figure S154. HRESIMS spectrum of **23**.



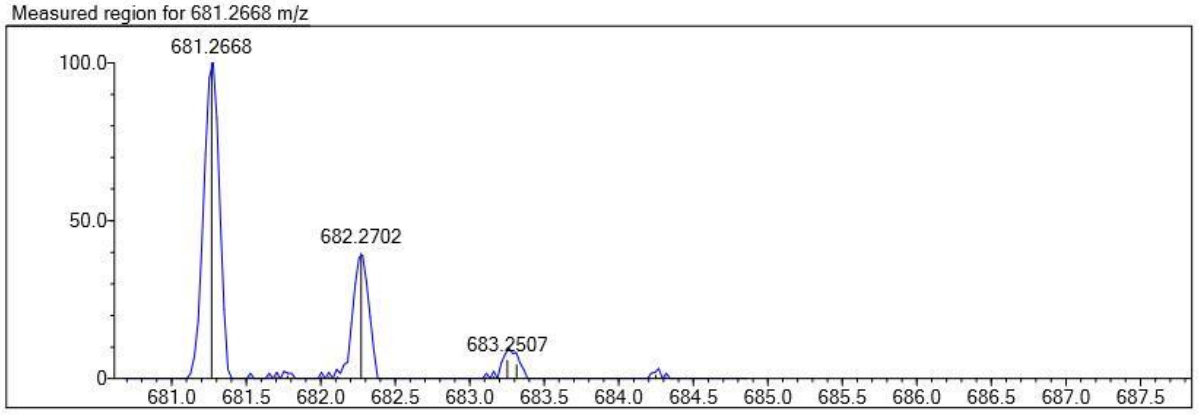
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	92.32	C38 H44 O9	[M+Na]+	667.2888	667.2878	1.0	1.50	93.49	17.0

Figure S155. HRESIMS spectrum of **24**.



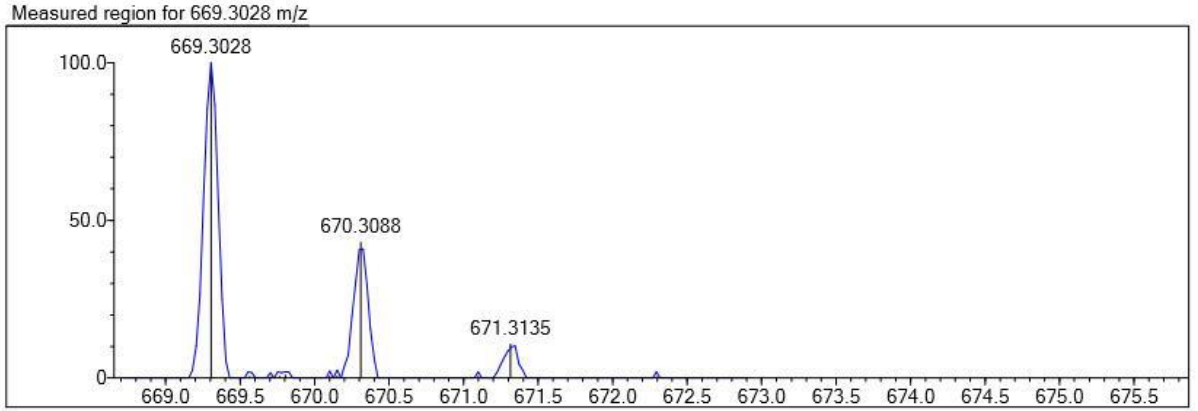
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	98.55	C38 H42 O11	[M+Na]+	697.2608	697.2619	-1.1	-1.58	100.00	18.0

Figure S156. HRESIMS spectrum of **25**.



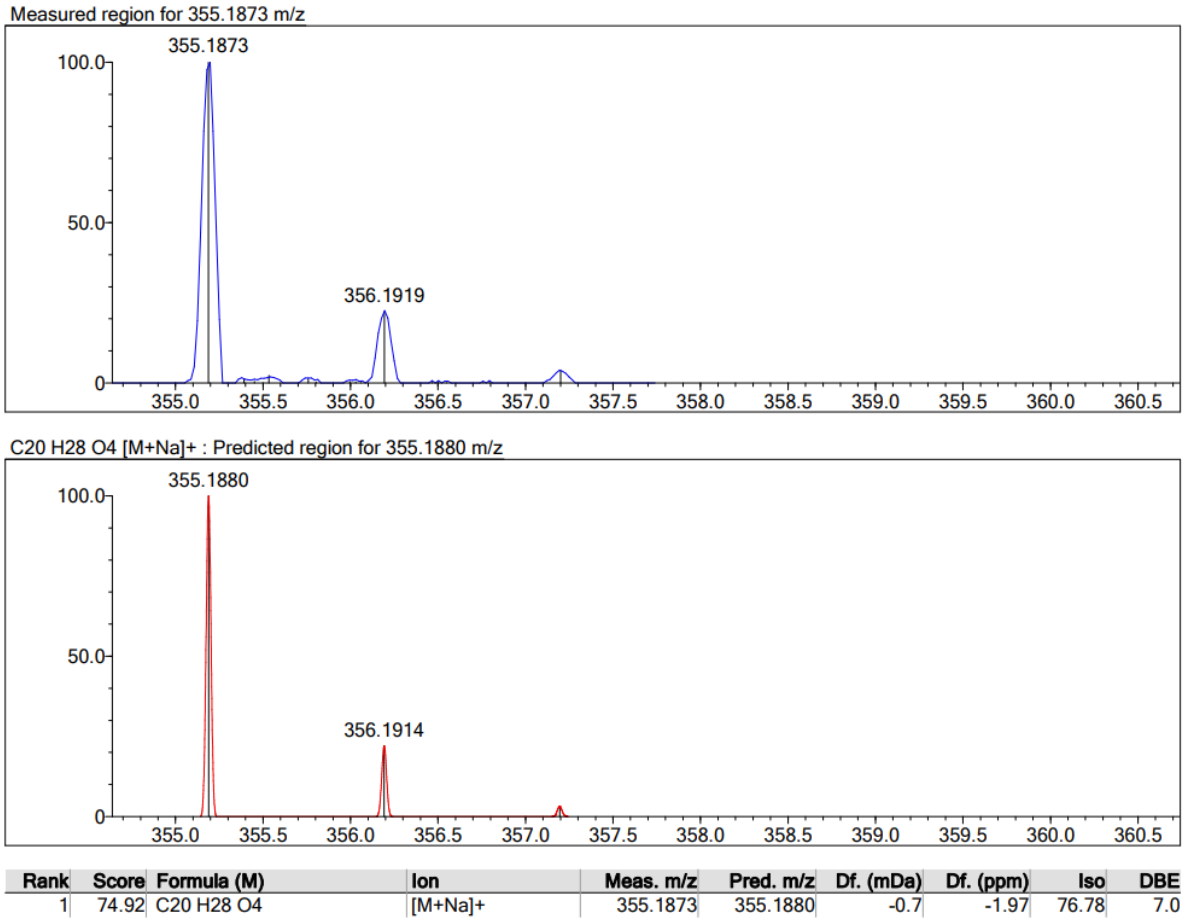
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	71.52	C38 H42 O10	[M+Na]+	681.2668	681.2670	-0.2	-0.29	71.52	18.0

Figure S157. HRESIMS spectrum of **26**.



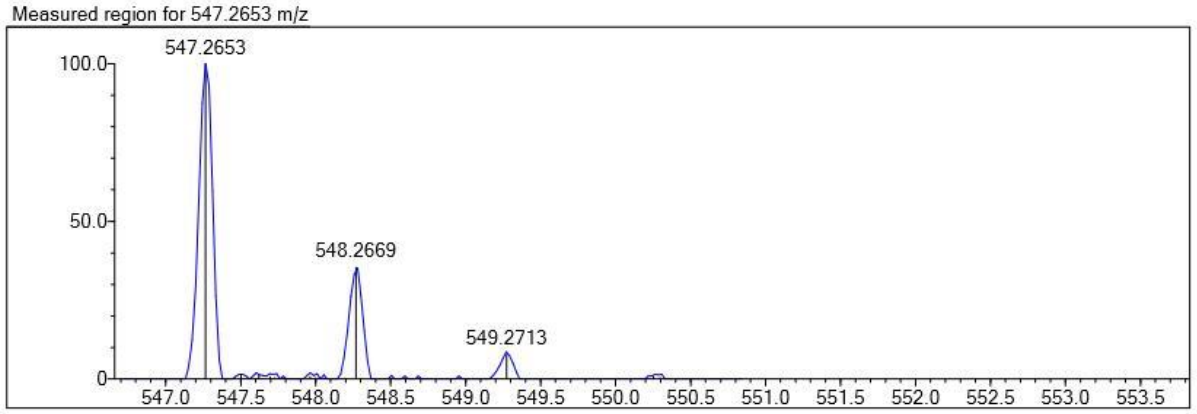
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	73.91	C38 H46 O9	[M+Na]+	669.3028	669.3034	-0.6	-0.90	73.91	16.0

Figure S158. HRESIMS spectrum of **28**.



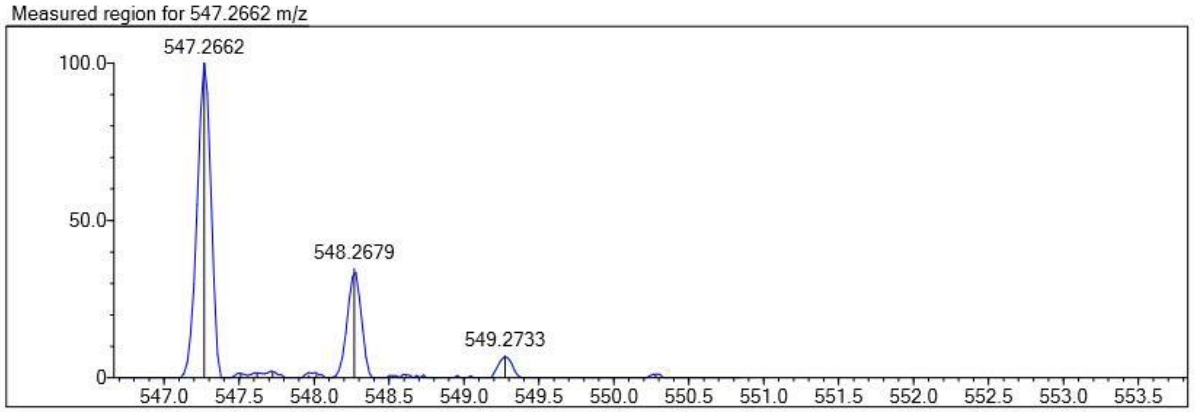
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	74.92	C20 H28 O4	[M+Na]+	355.1873	355.1880	-0.7	-1.97	76.78	7.0

Figure S159. HRESIMS spectrum of **29**.



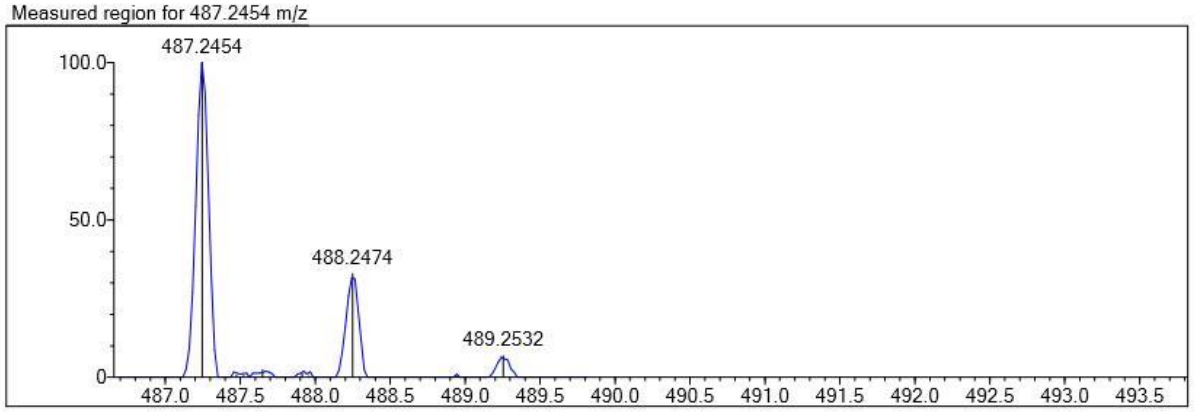
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	81.65	C31 H40 O7	[M+Na]+	547.2653	547.2666	-1.3	-2.38	84.57	12.0

Figure S160. HRESIMS spectrum of **30**.



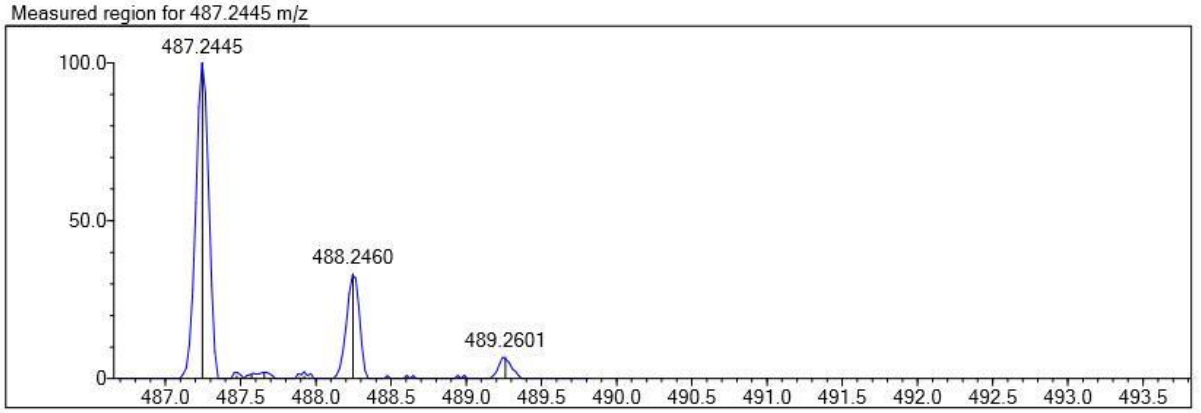
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	99.77	C31 H40 O7	[M+Na]+	547.2662	547.2666	-0.4	-0.73	99.77	12.0

Figure S161. HRESIMS spectrum of **31**.



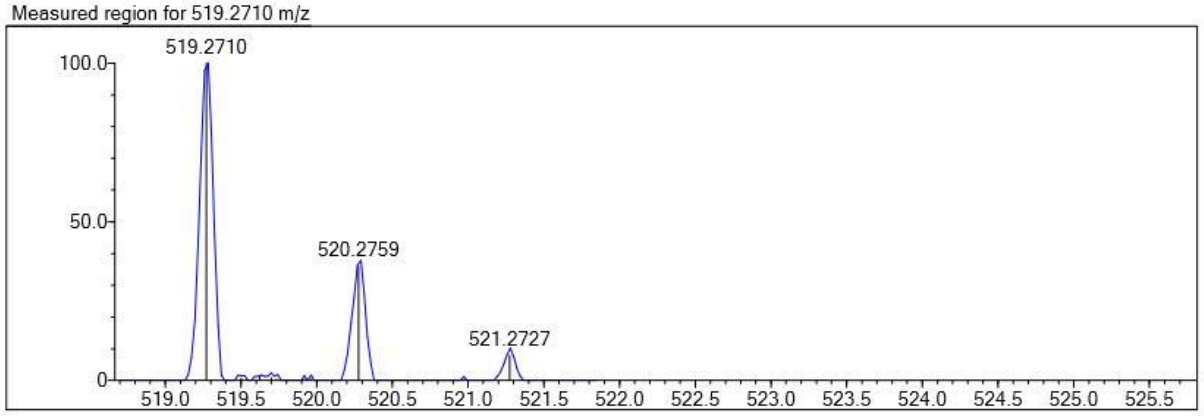
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	89.24	C29 H36 O5	[M+Na]+	487.2454	487.2455	-0.1	-0.21	89.24	12.0

Figure S162. HRESIMS spectrum of **32**.



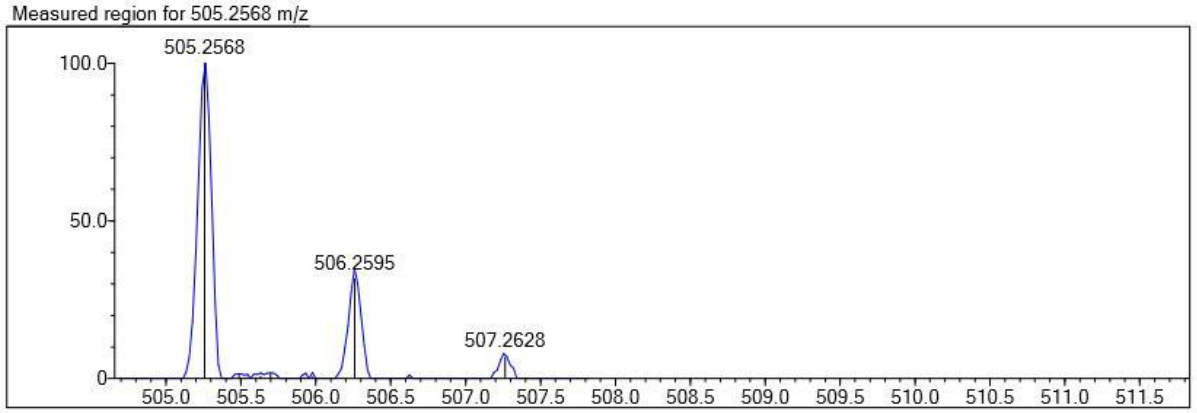
Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
1	87.61	C29 H36 O5	[M+Na]+	487.2445	487.2455	-1.0	-2.05	89.97	12.0

Figure S163. HRESIMS spectrum of **33.**



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
4	65.27	C30 H40 O6	[M+Na]+	519.2710	519.2717	-0.7	-1.35	65.85	11.0

Figure S164. HRESIMS spectrum of **34**.



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	84.69	C29 H38 O6	[M+Na]+	505.2568	505.2561	0.7	1.39	85.53	11.0

13. Figure S165–S185.

Figure S165. IR (KBr disc) spectrum of **1**.

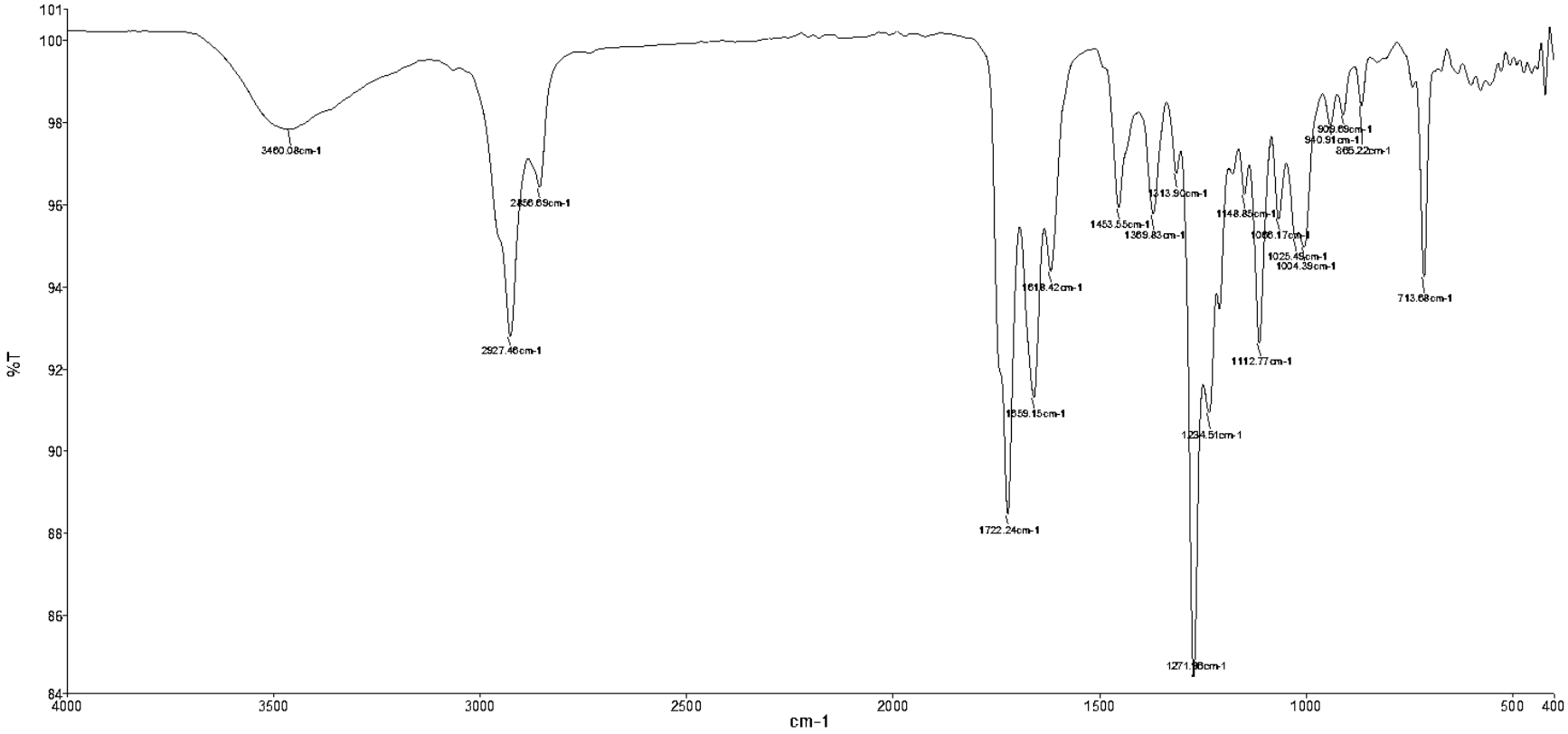


Figure S166. IR (KBr disc) spectrum of **2**.

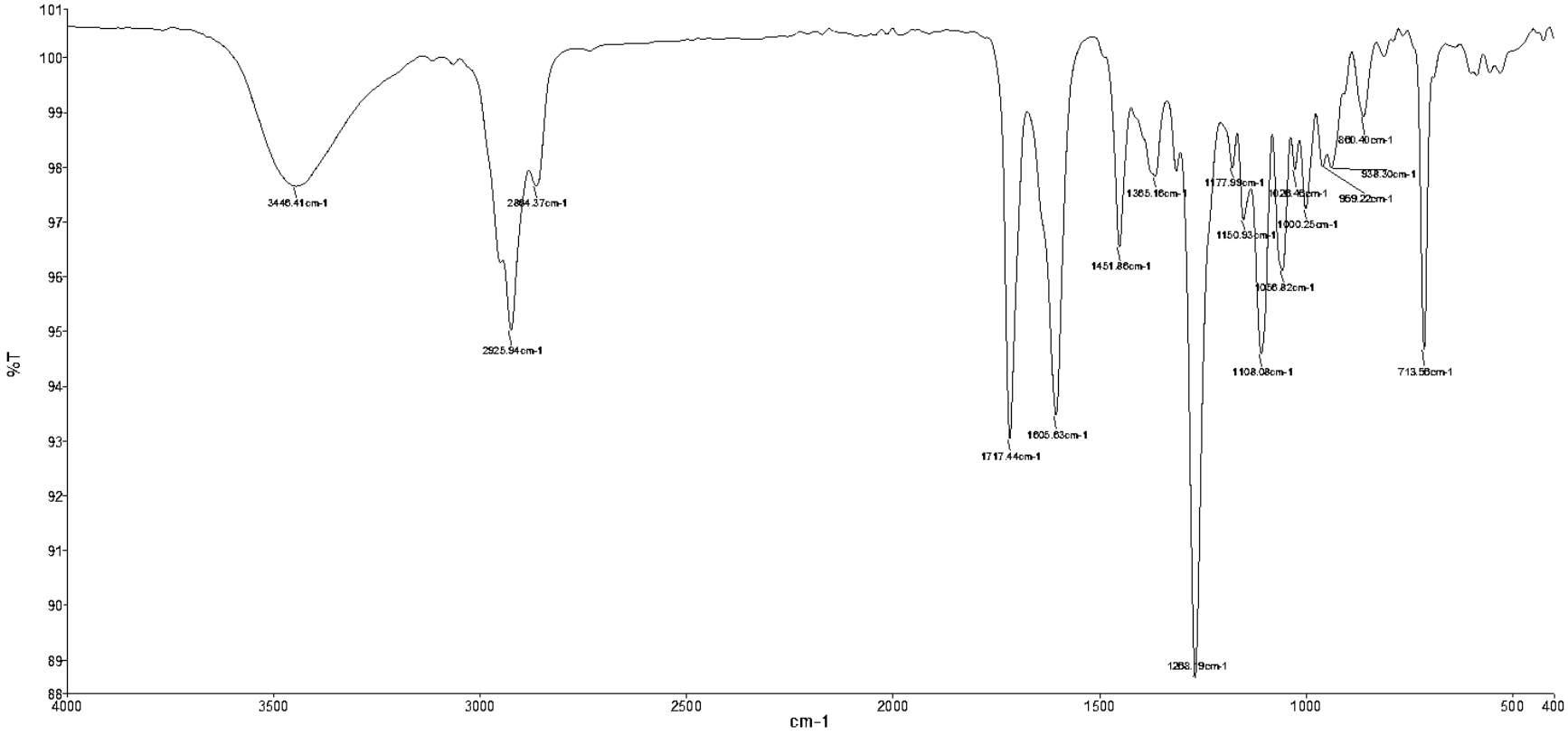


Figure S167. IR (KBr disc) spectrum of **3**.

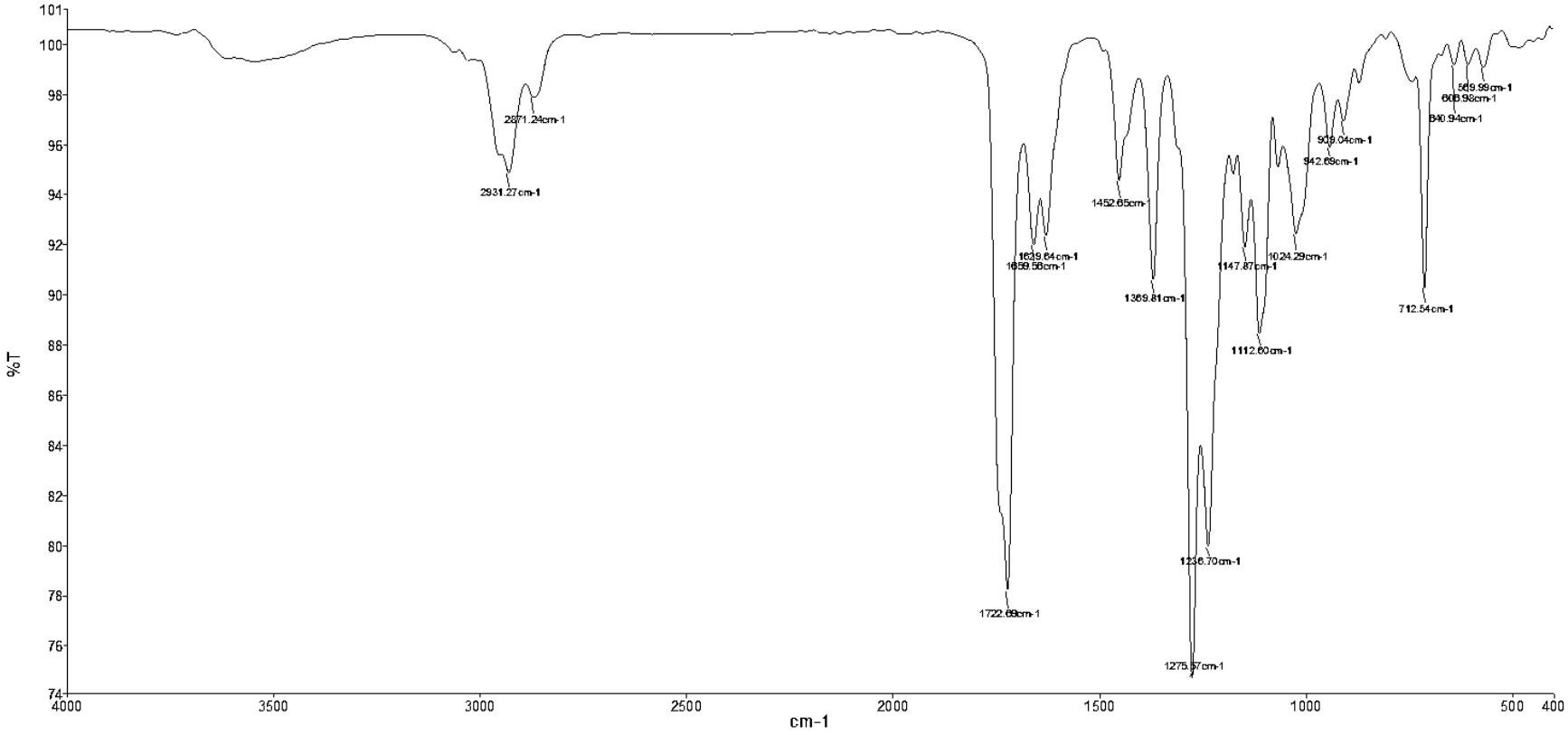


Figure S168. IR (KBr disc) spectrum of **4**.

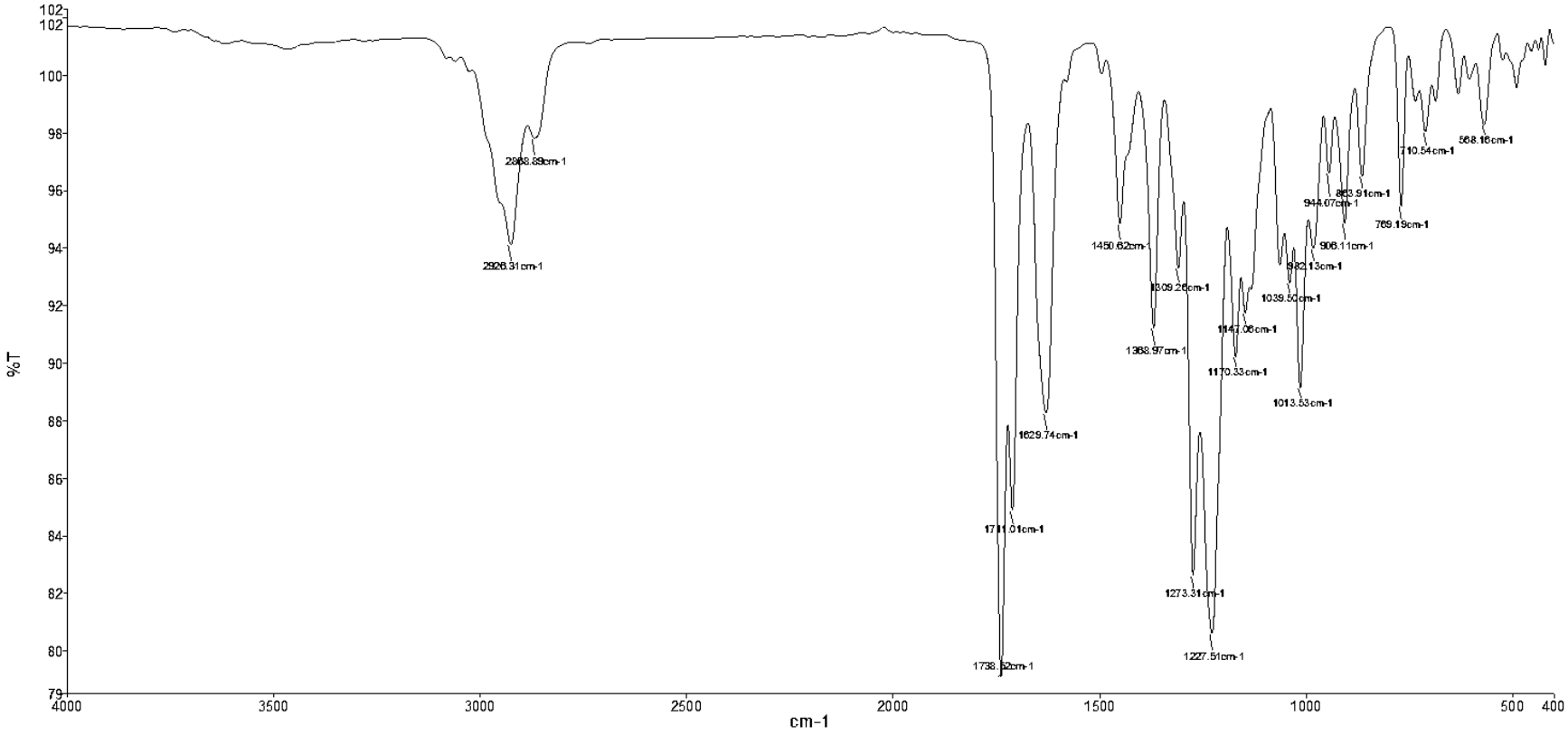


Figure S169. IR (KBr disc) spectrum of **5**.

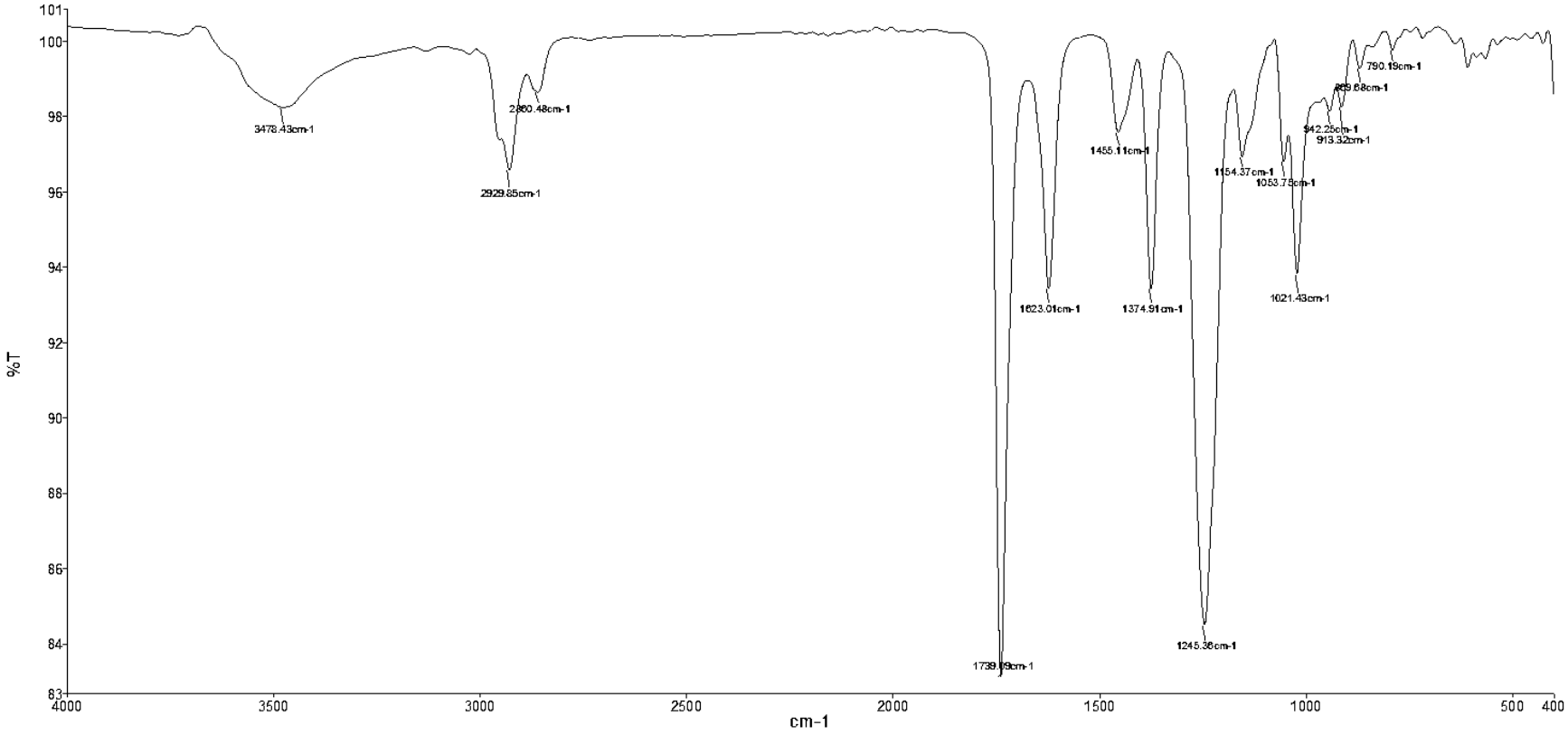


Figure S170. IR (KBr disc) spectrum of **20**.

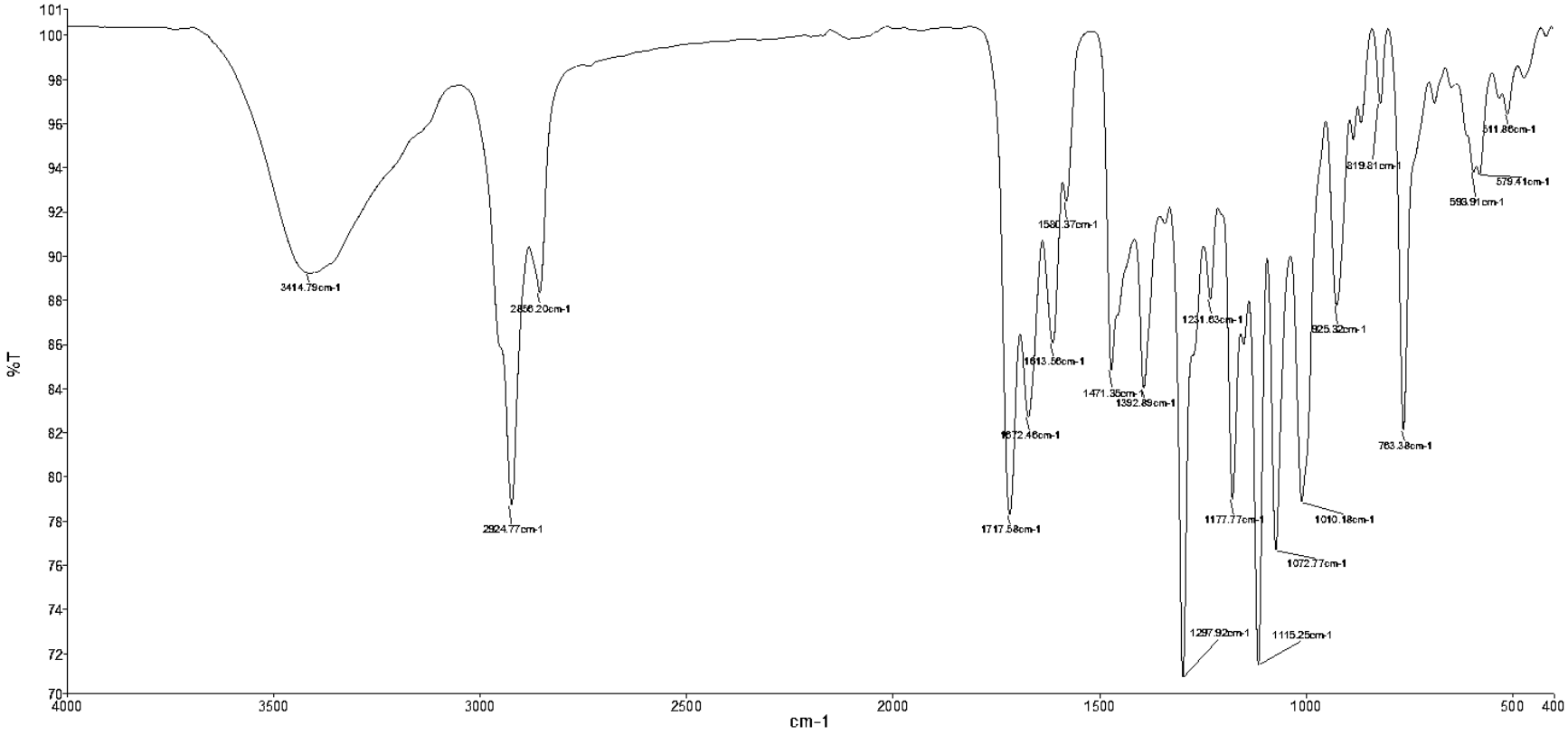


Figure S171. IR (KBr disc) spectrum of **21**.

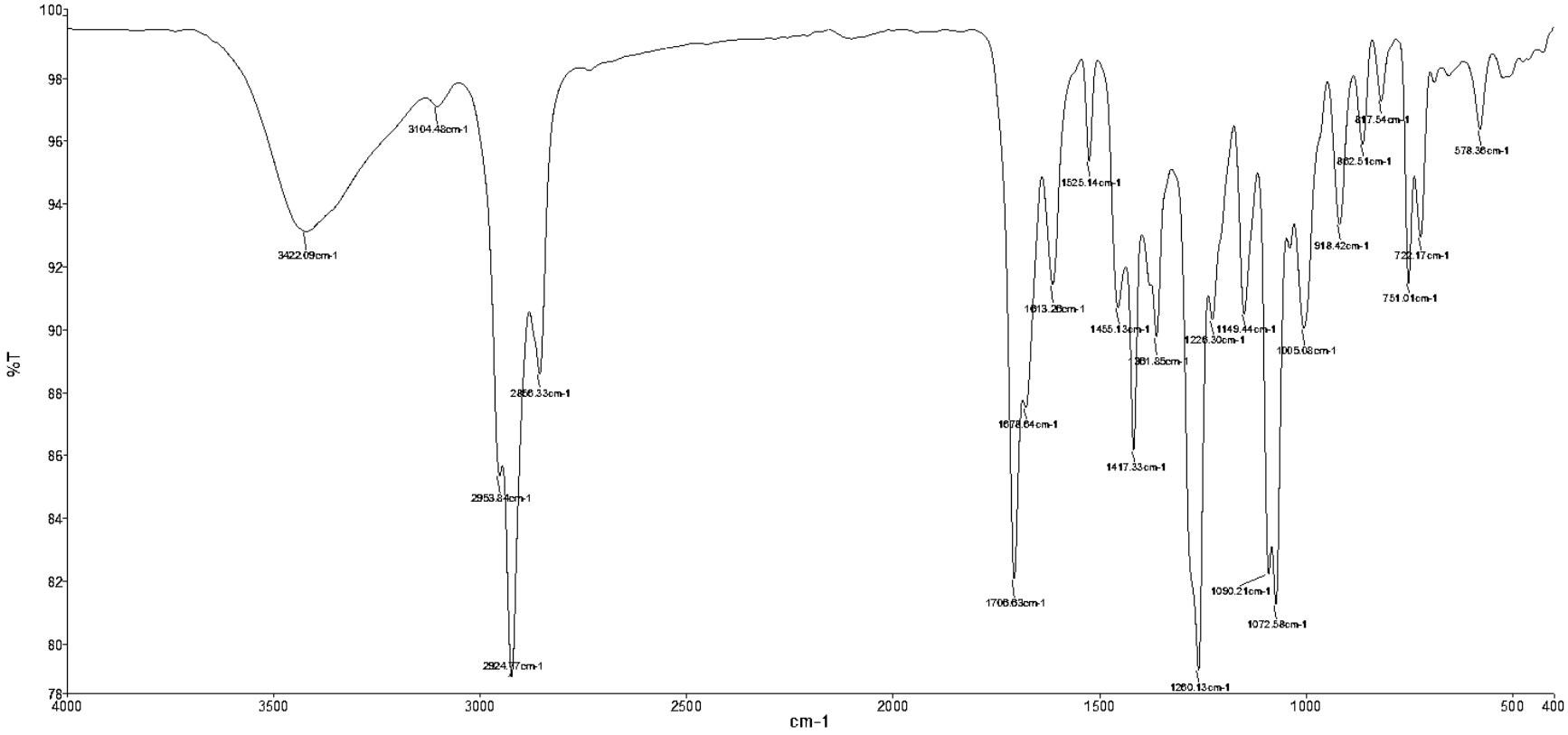


Figure S172. IR (KBr disc) spectrum of **22**.

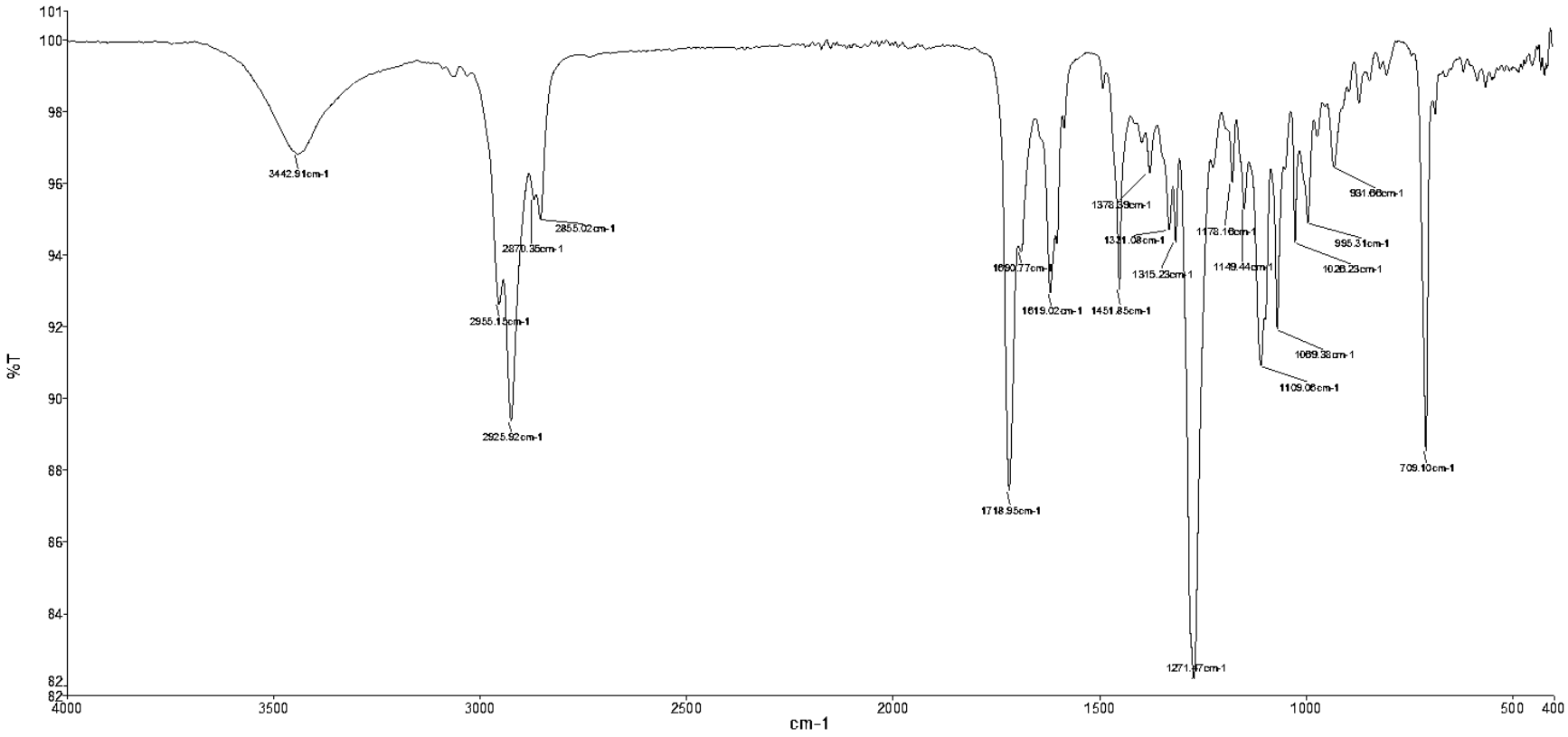


Figure S173. IR (KBr disc) spectrum of **23**.

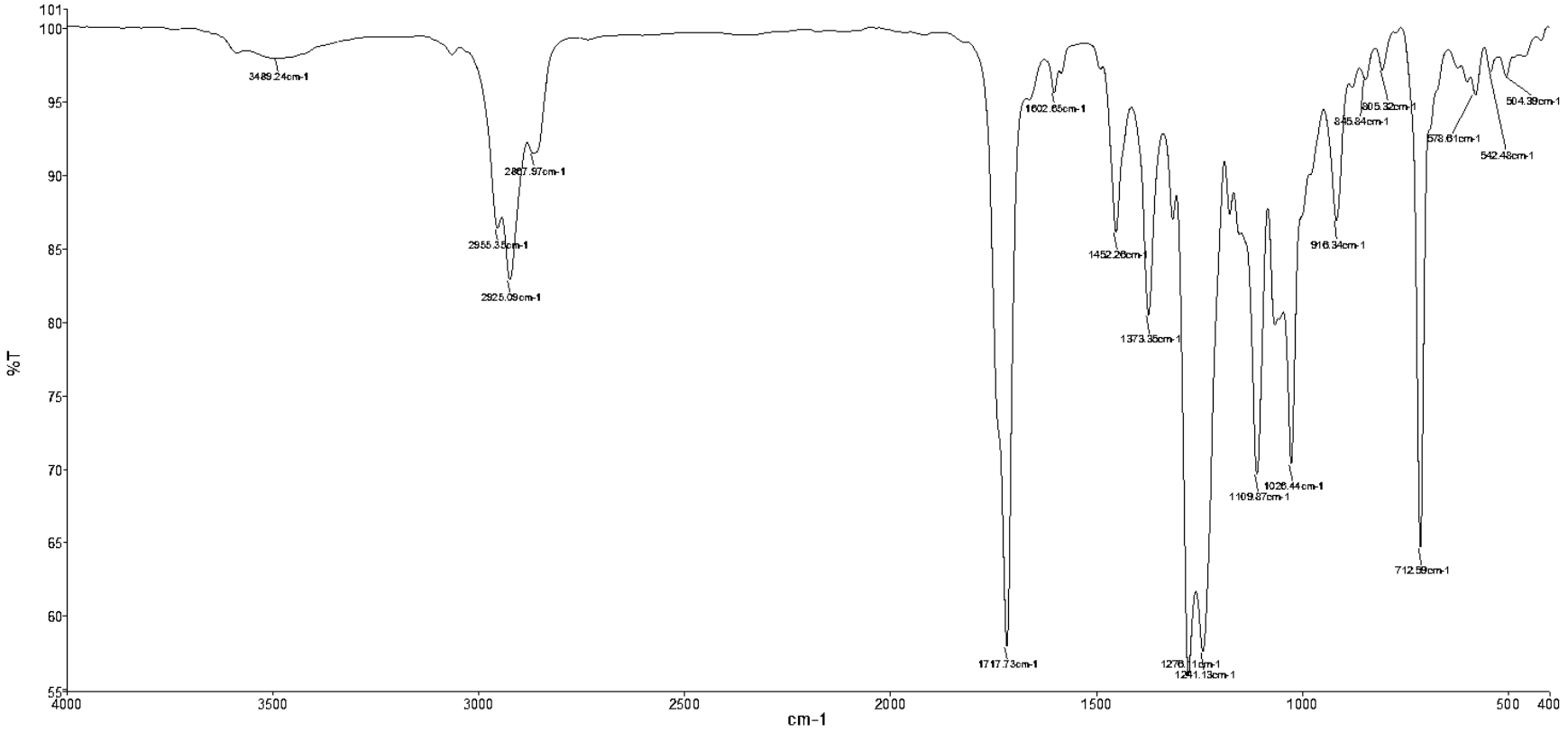


Figure S174. IR (KBr disc) spectrum of **24**.

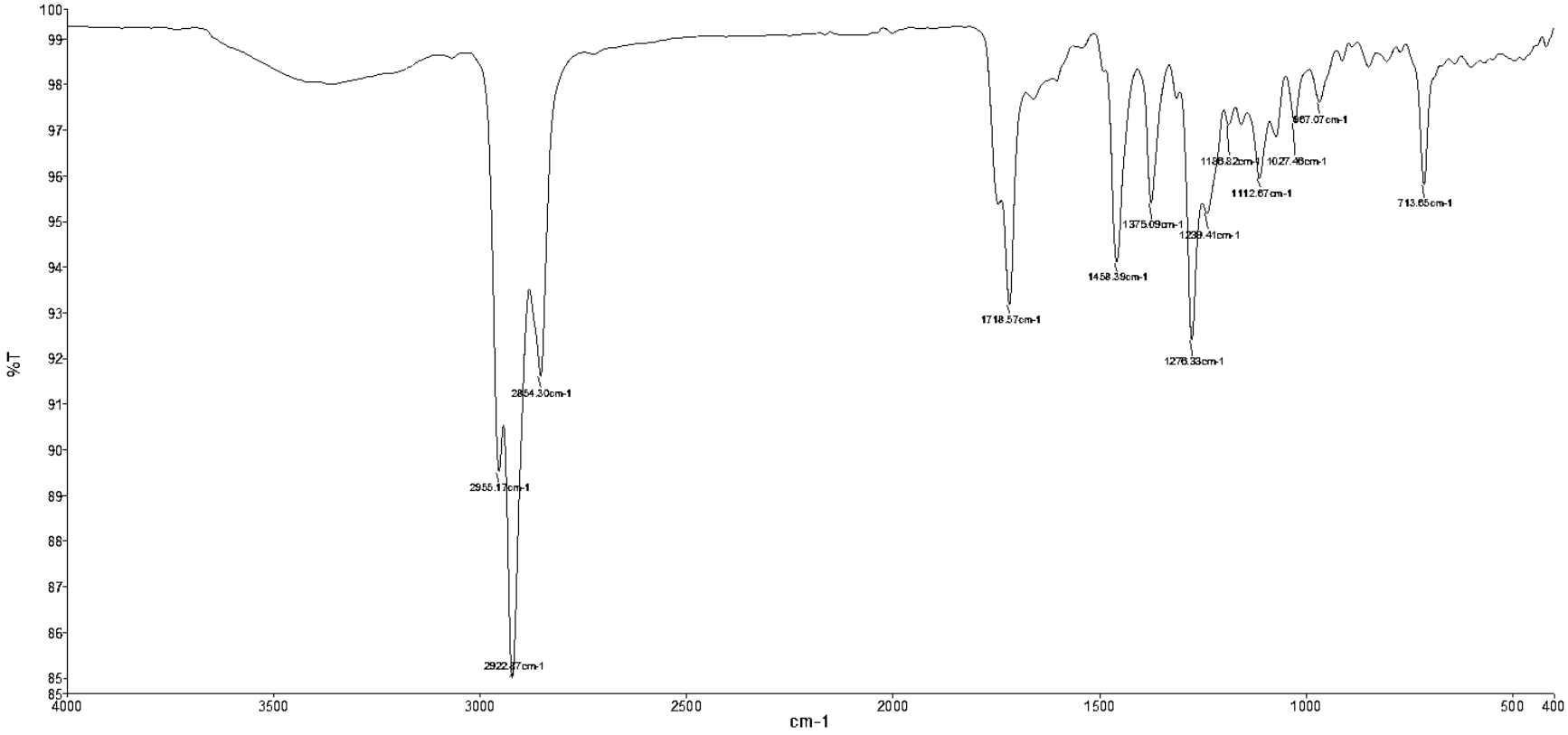


Figure S175. IR (KBr disc) spectrum of **25**.

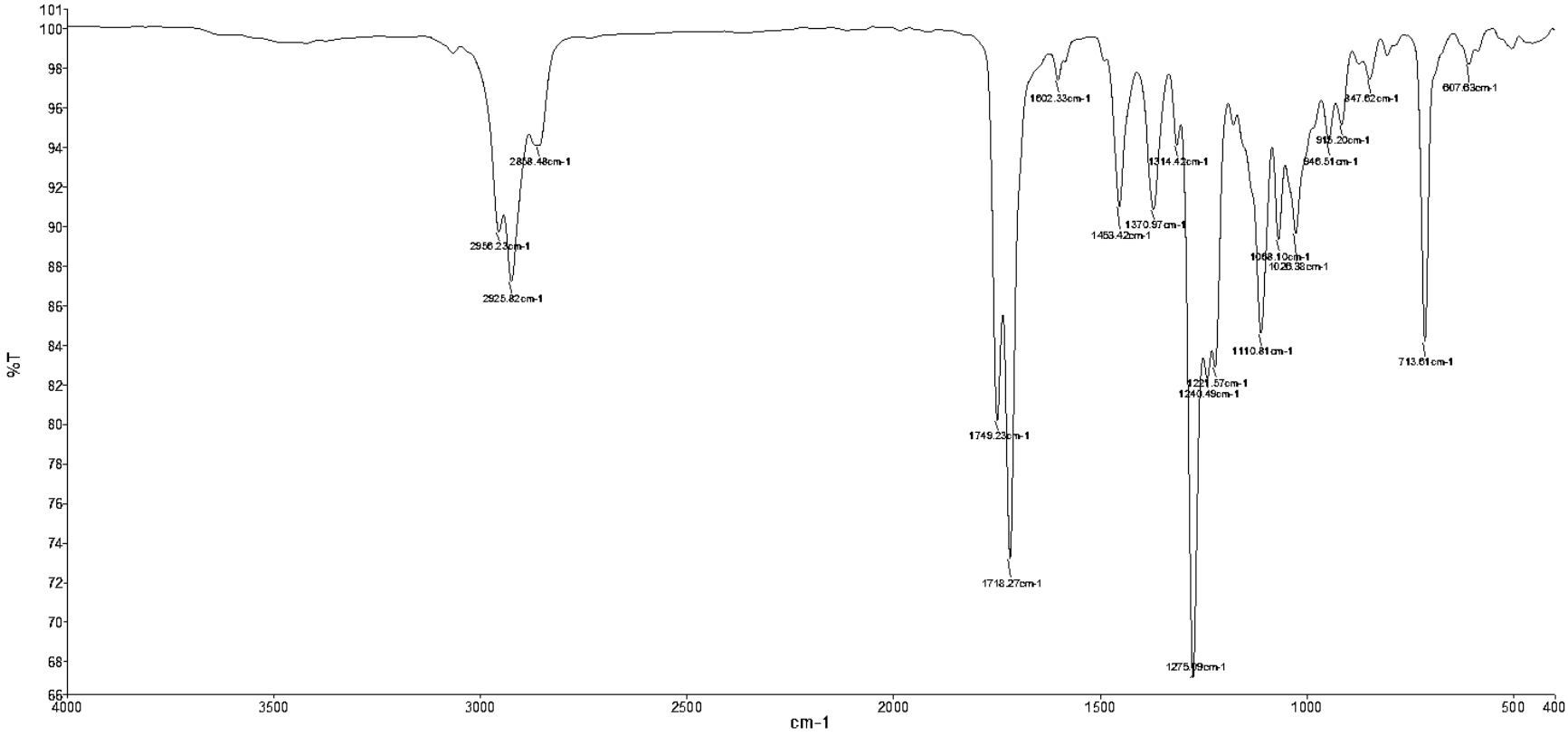


Figure S176. IR (KBr disc) spectrum of **26**.

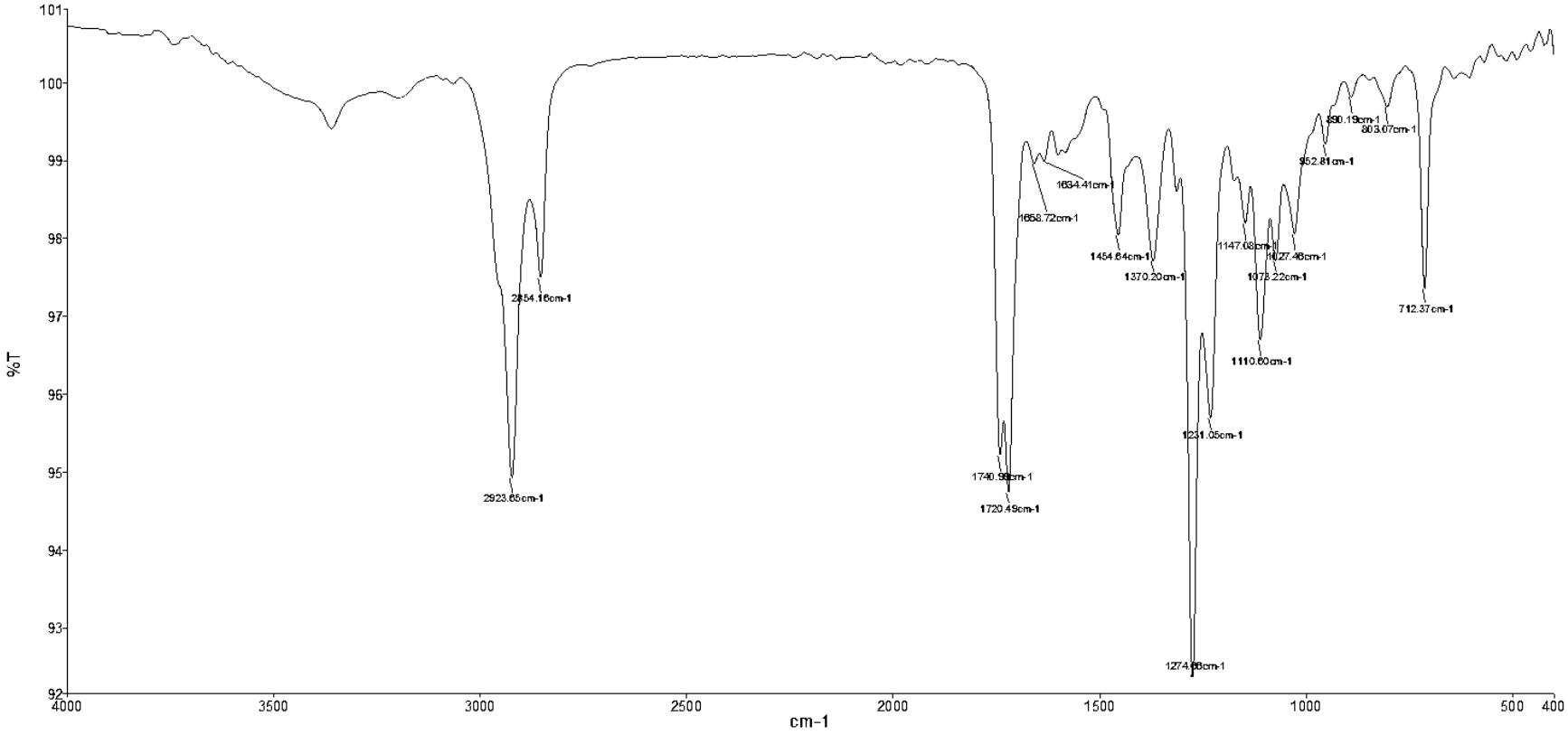


Figure S177. IR (KBr disc) spectrum of **28**.

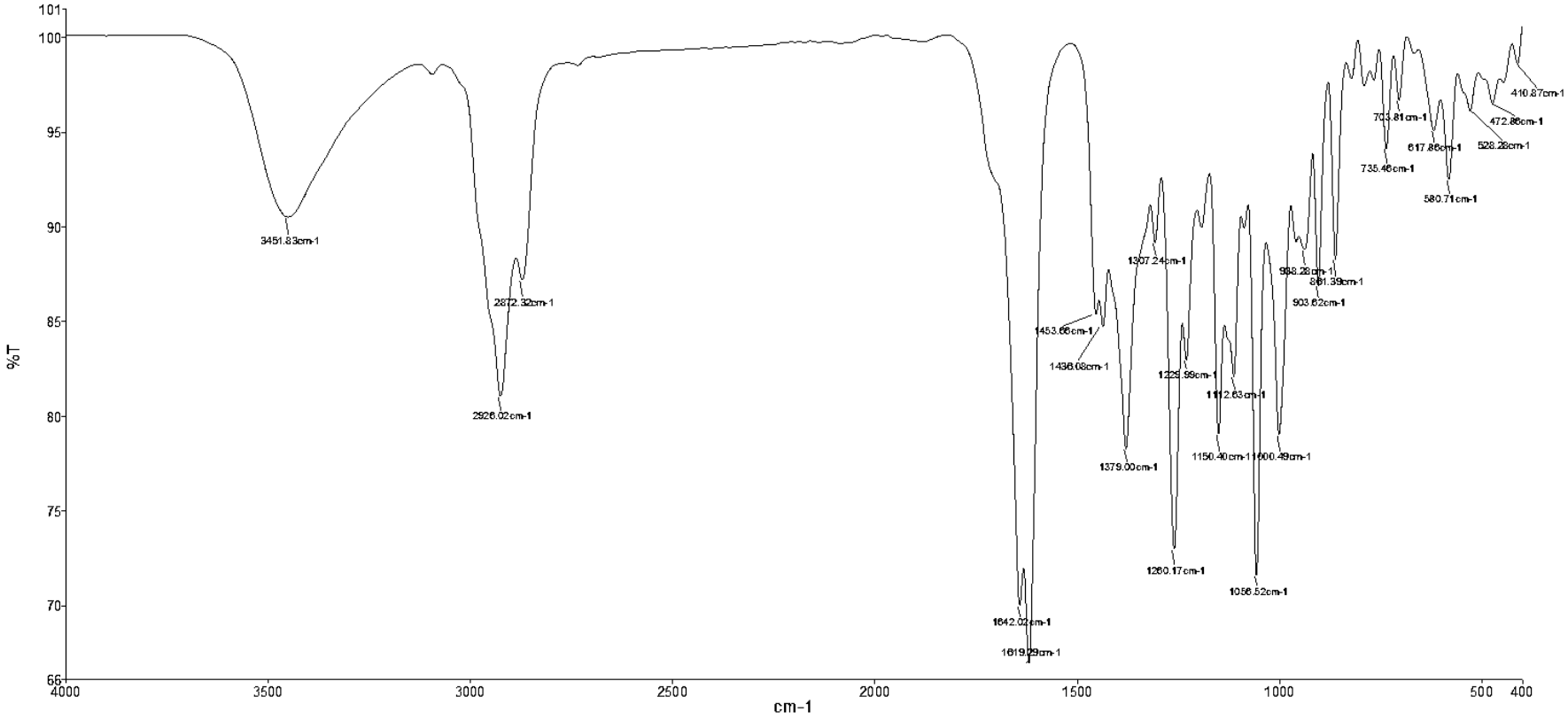


Figure S178. IR (KBr disc) spectrum of **29**.

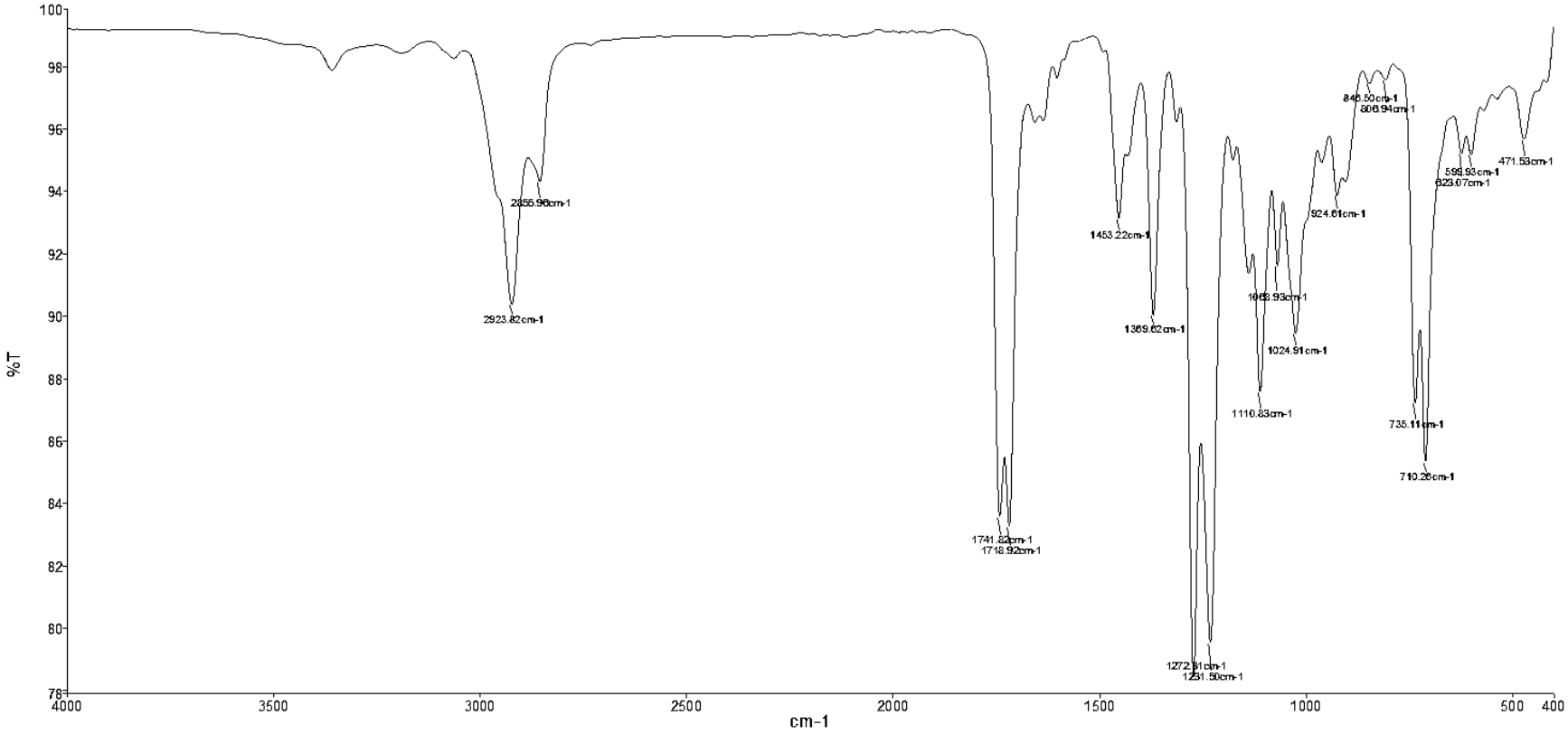


Figure S179. IR (KBr disc) spectrum of **30**.

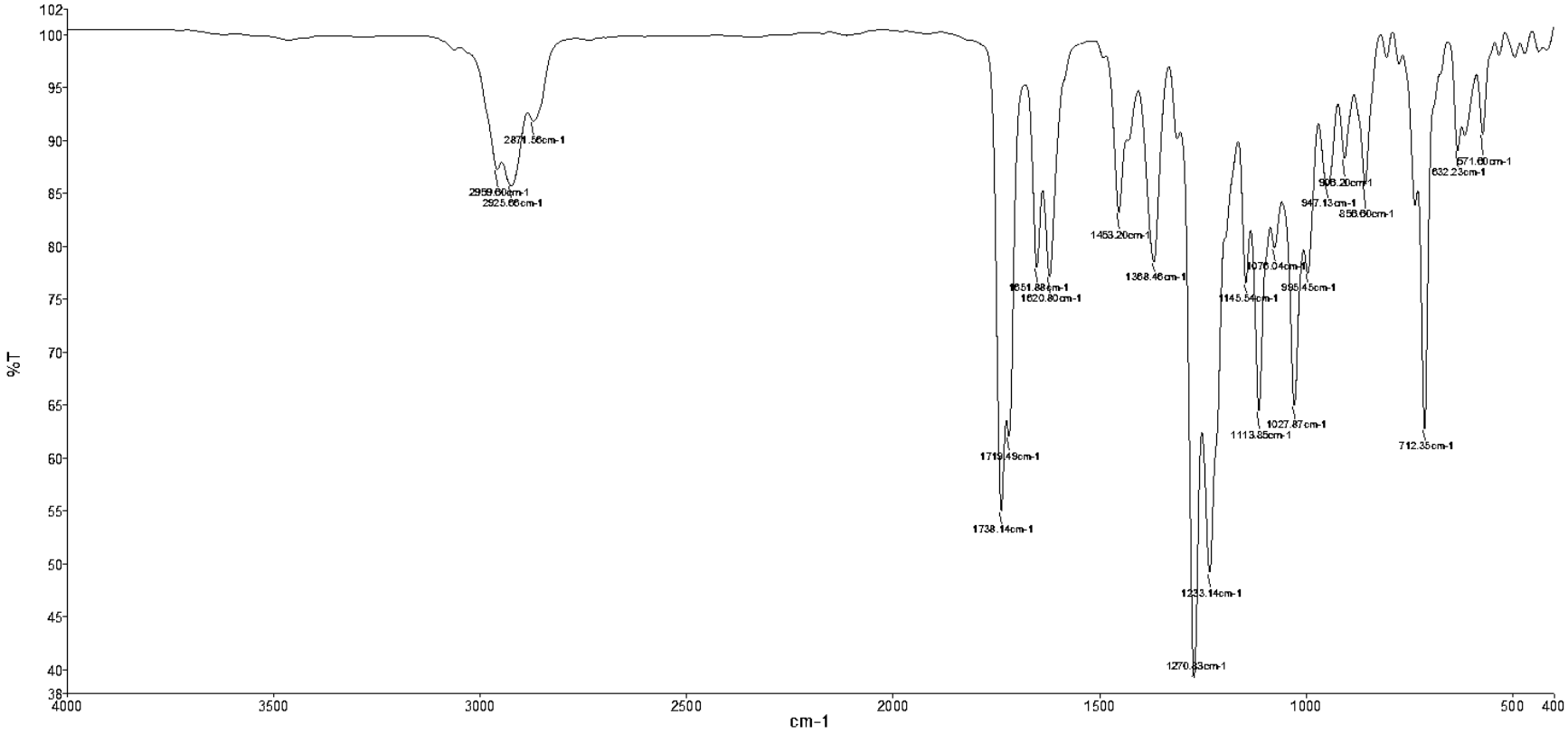


Figure S180. IR (KBr disc) spectrum of **31**.

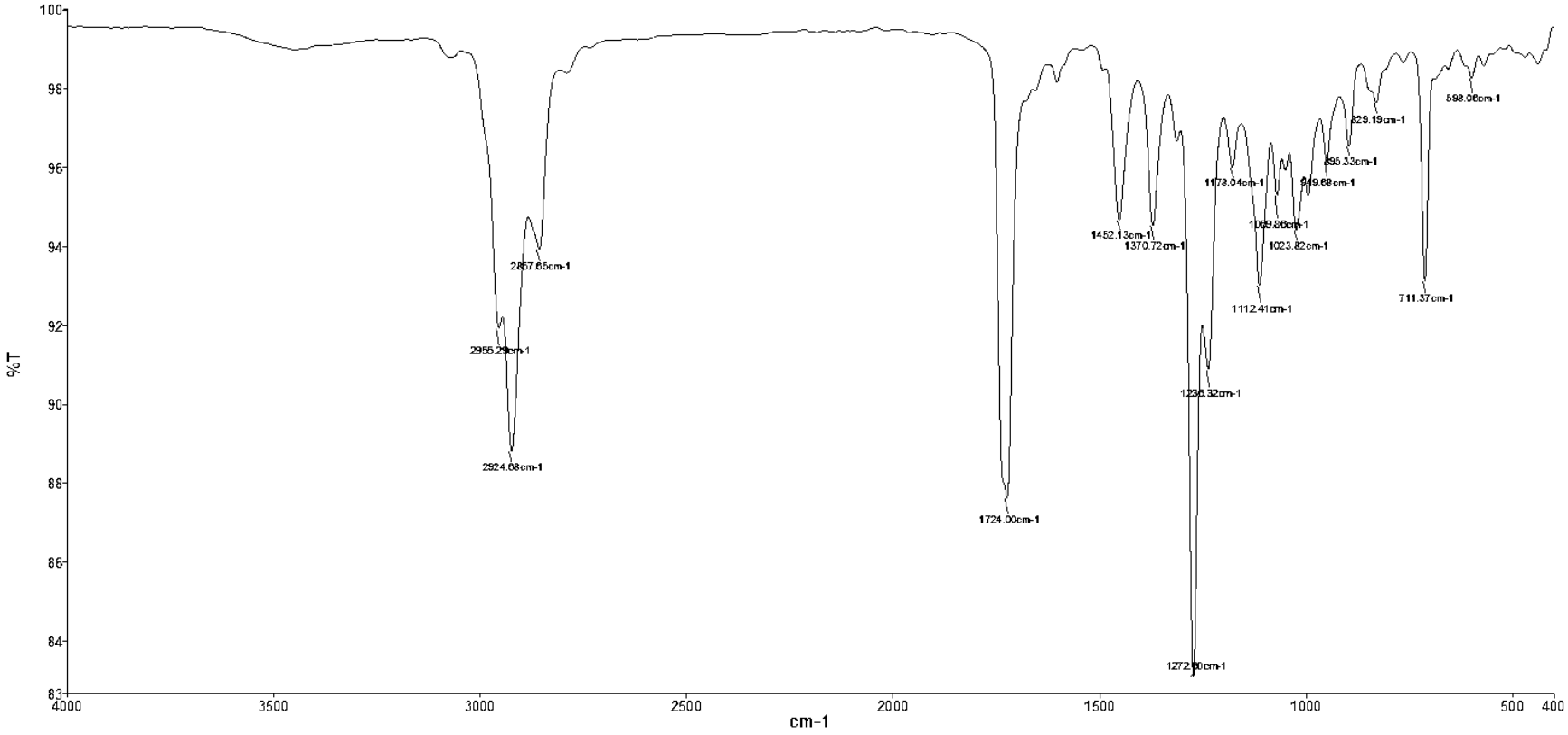


Figure S181. IR (KBr disc) spectrum of **32**.

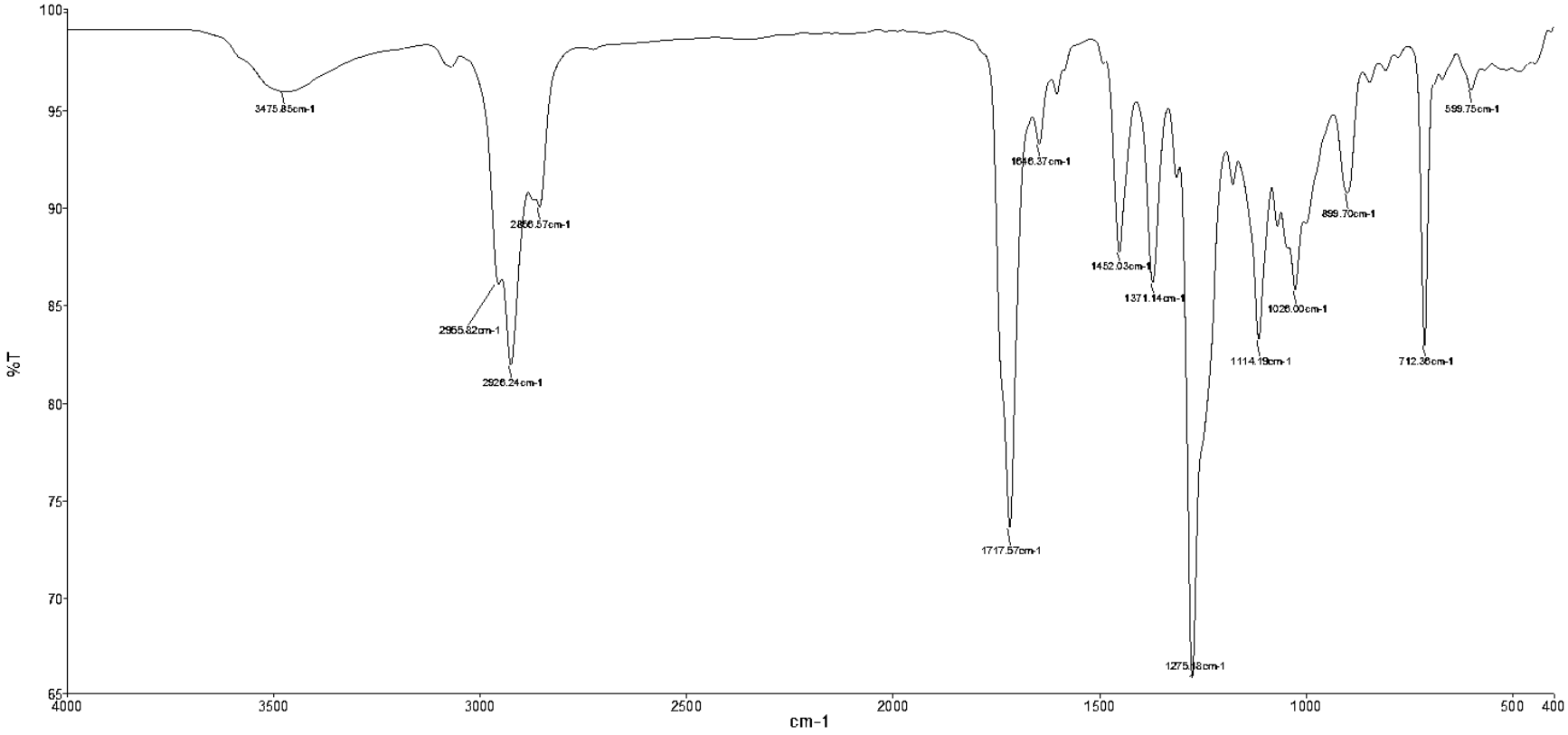


Figure S182. IR (KBr disc) spectrum of **33**.

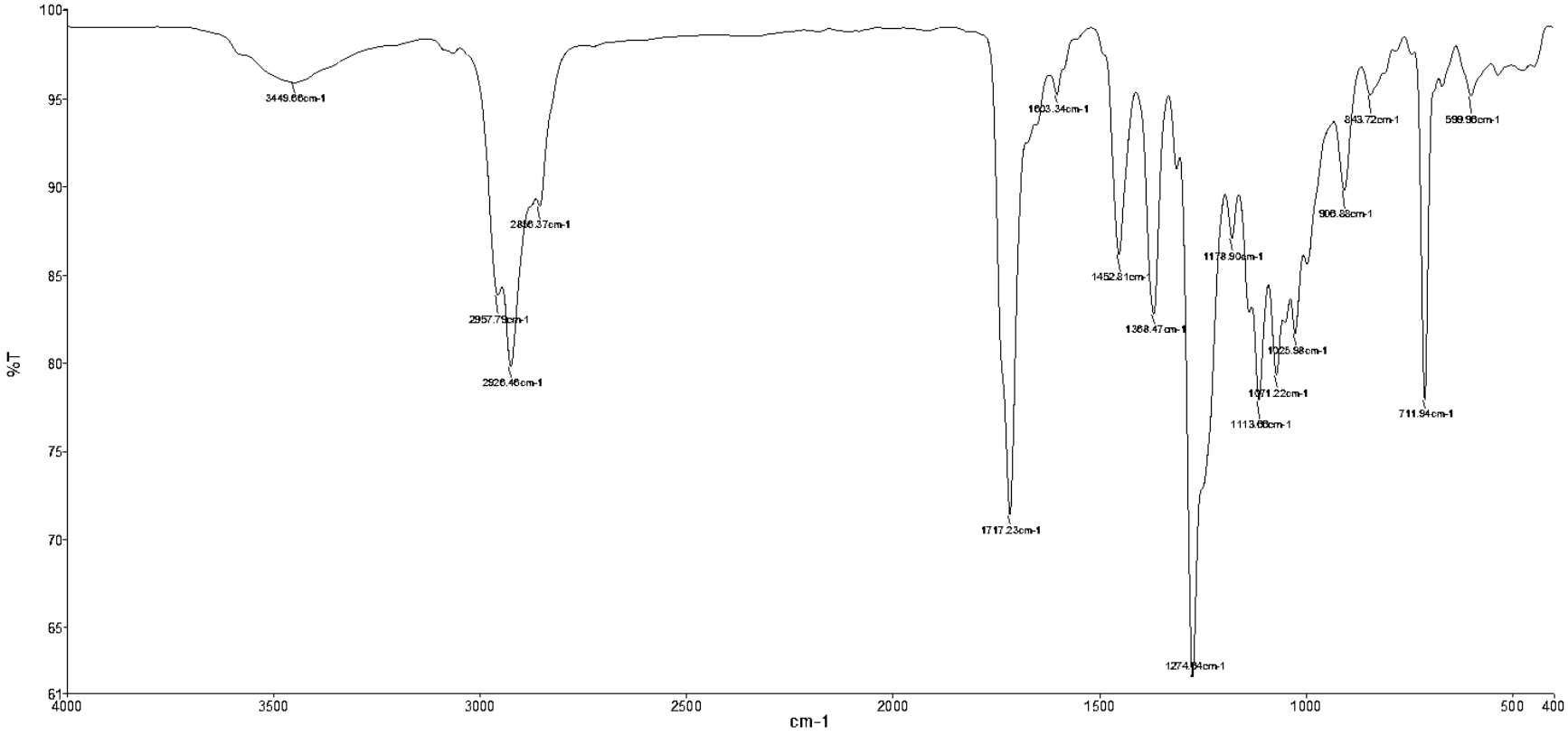
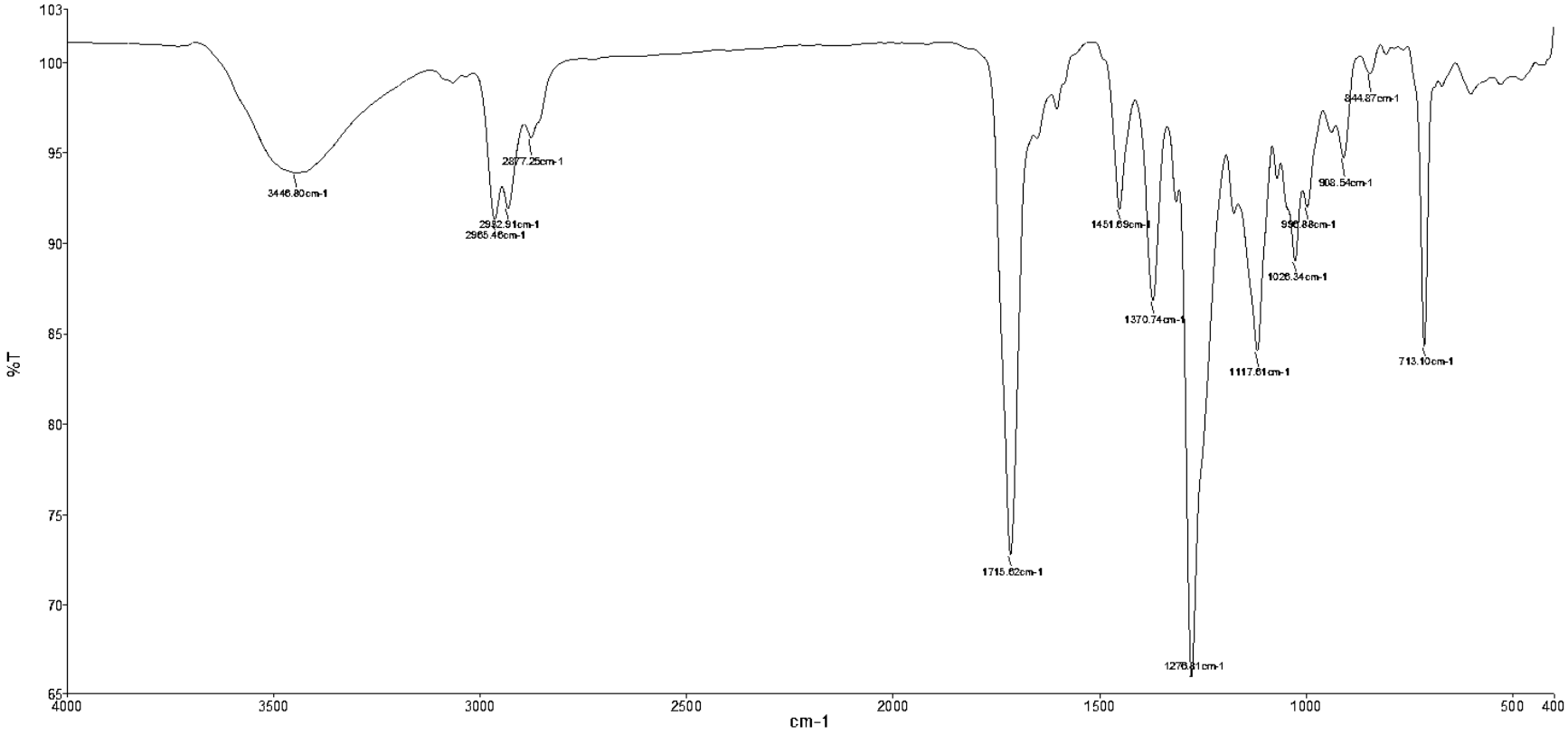
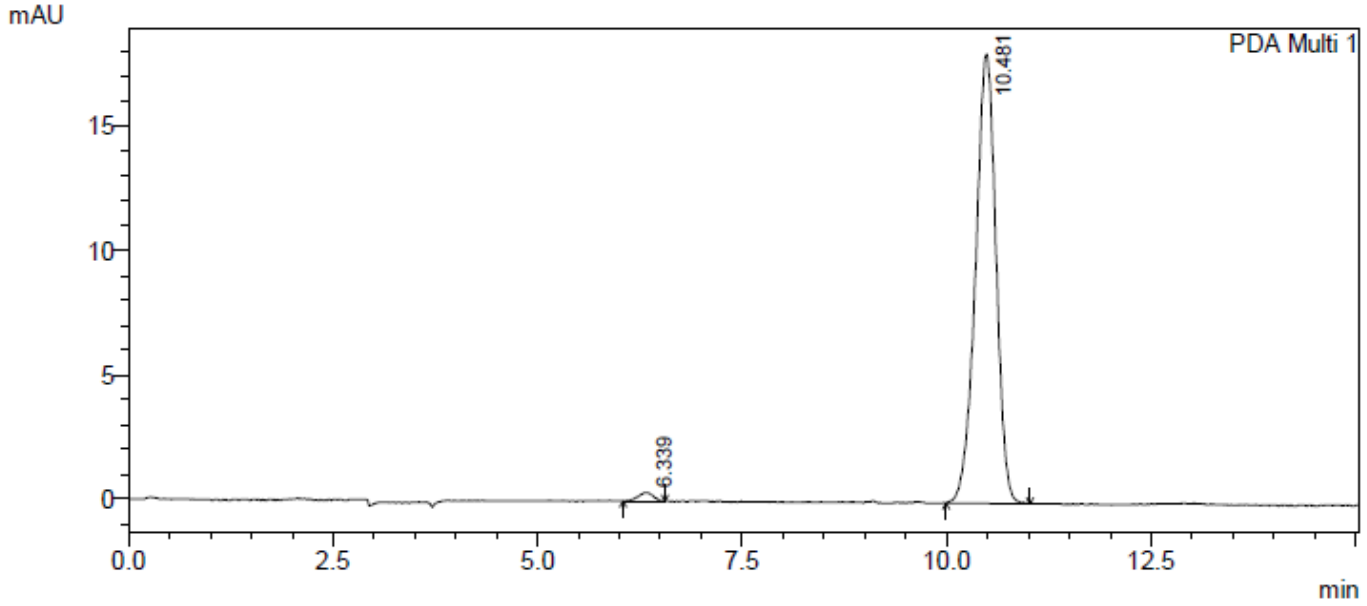


Figure S183. IR (KBr disc) spectrum of **34**.



14. Figure S184–S217.

Figure S184. HPLC chromatogram of compound **1**.



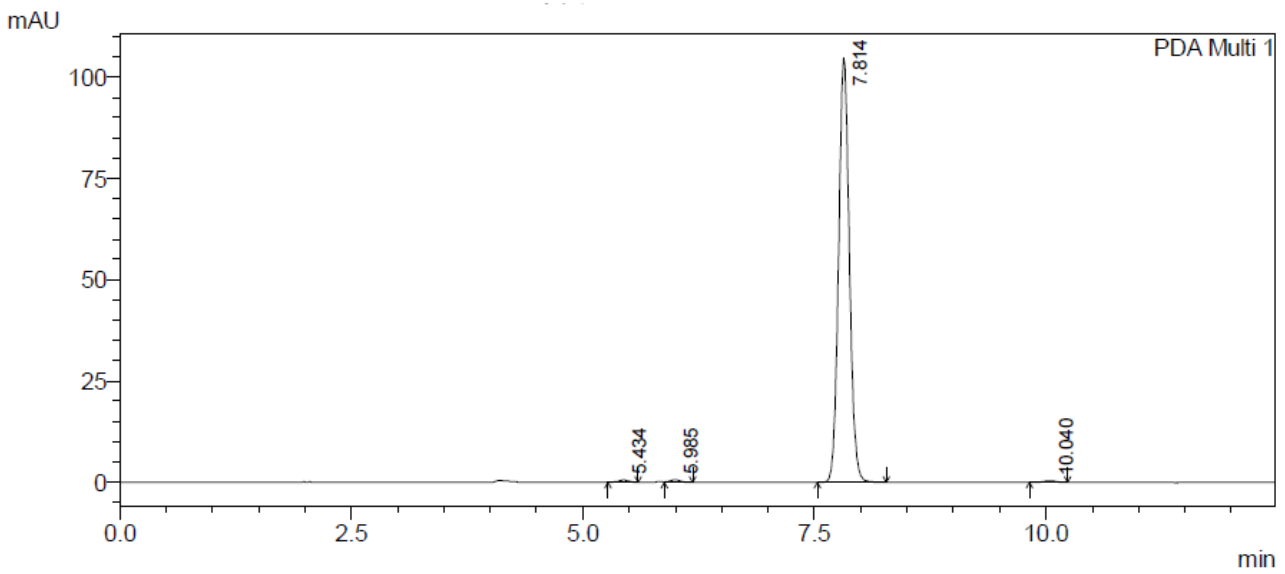
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.339	4496	354	1.407	1.924
2	10.481	314992	18061	98.593	98.076
Total		319488	18415	100.000	100.000

Figure S185. HPLC chromatogram of compound **2**.



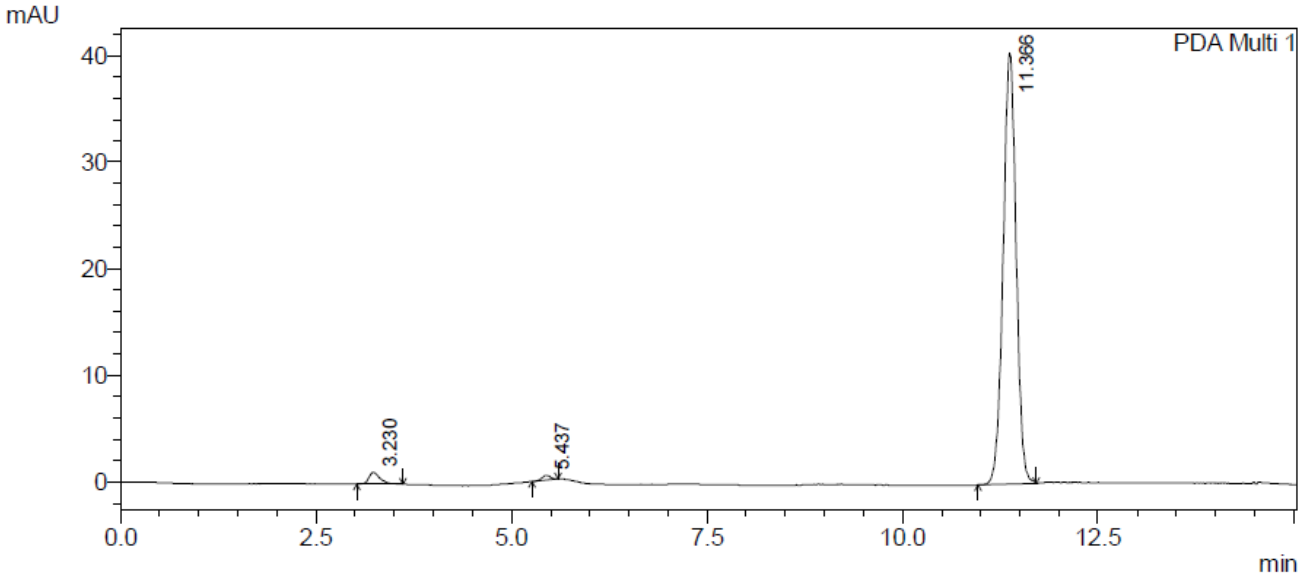
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.434	4674	622	0.543	0.584
2	5.985	4821	675	0.560	0.634
3	7.814	847251	104774	98.461	98.424
4	10.040	3751	381	0.436	0.358
Total		860497	106452	100.000	100.000

Figure S186. HPLC chromatogram of compound **3**.



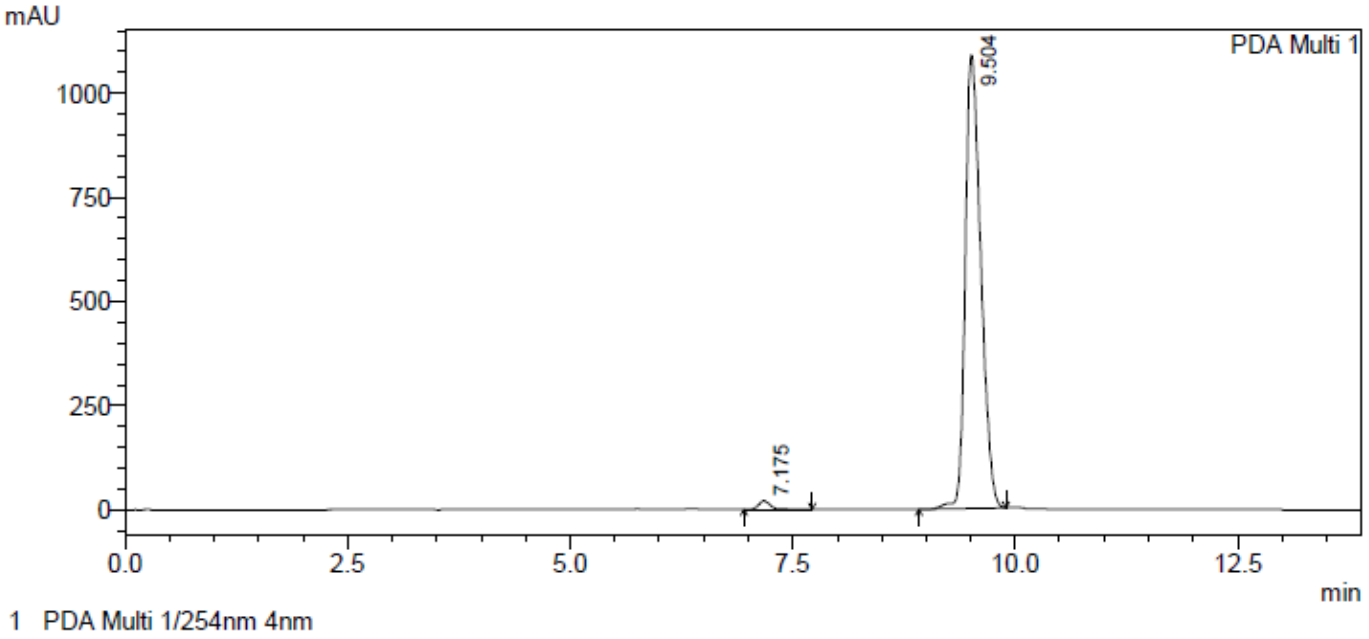
1 PDA Multi 1/270nm 4nm

PeakTable

PDA Ch1 270nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	3.230	11430	1100	2.380	2.620
2	5.437	3311	459	0.689	1.094
3	11.366	465420	40422	96.930	96.286
Total		480160	41981	100.000	100.000

Figure S187. HPLC chromatogram of compound **4**.

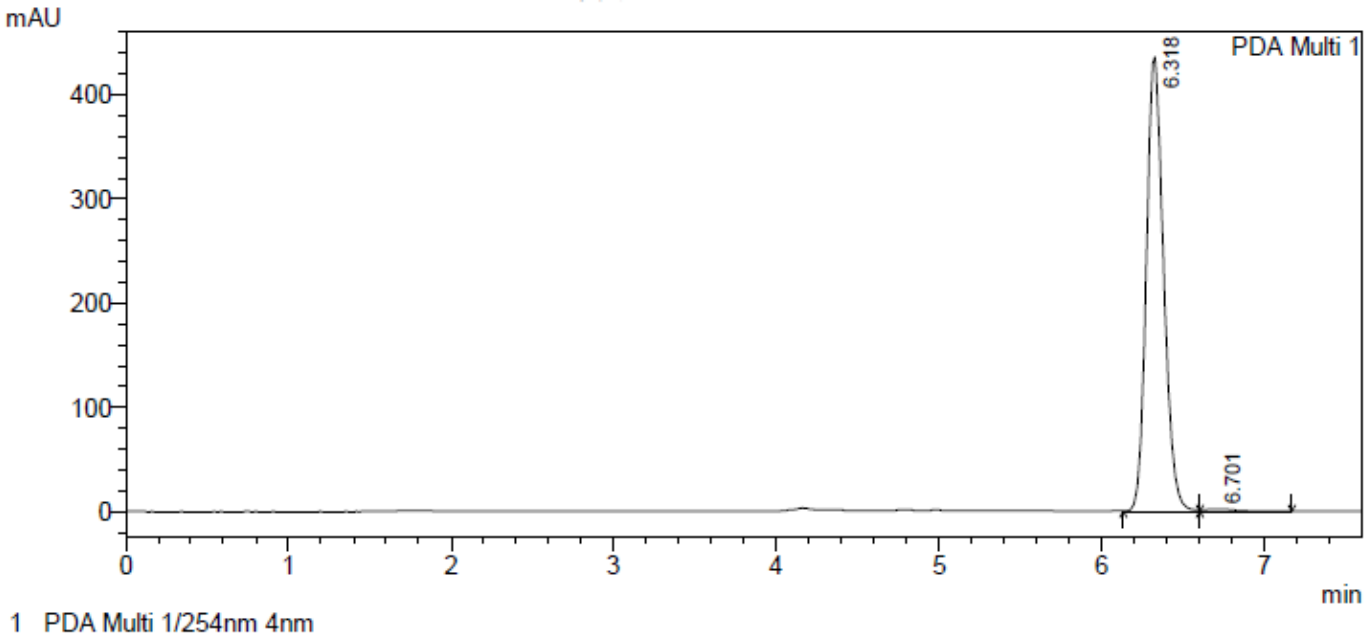


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.175	199178	20692	1.483	1.866
2	9.504	13232976	1087970	98.517	98.134
Total		13432153	1108662	100.000	100.000

Figure S188. HPLC chromatogram of compound **5**.



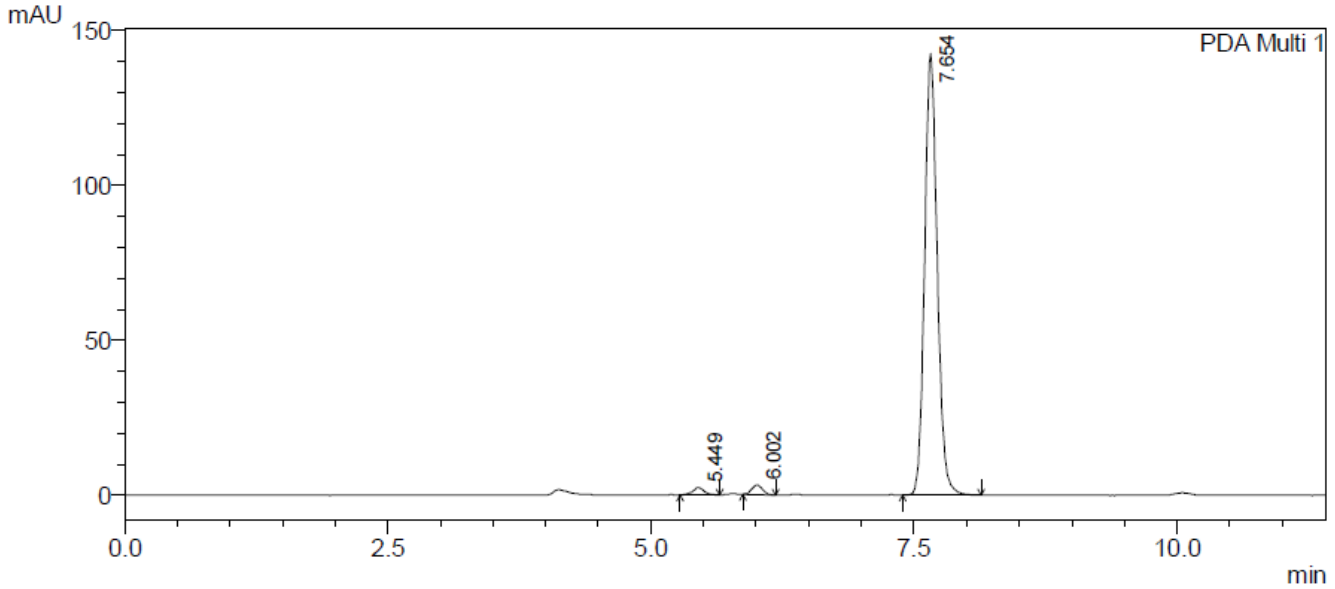
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.318	3232302	435588	99.190	99.489
2	6.701	26387	2239	0.810	0.511
Total		3258689	437827	100.000	100.000

Figure S189. HPLC chromatogram of compound **6**.



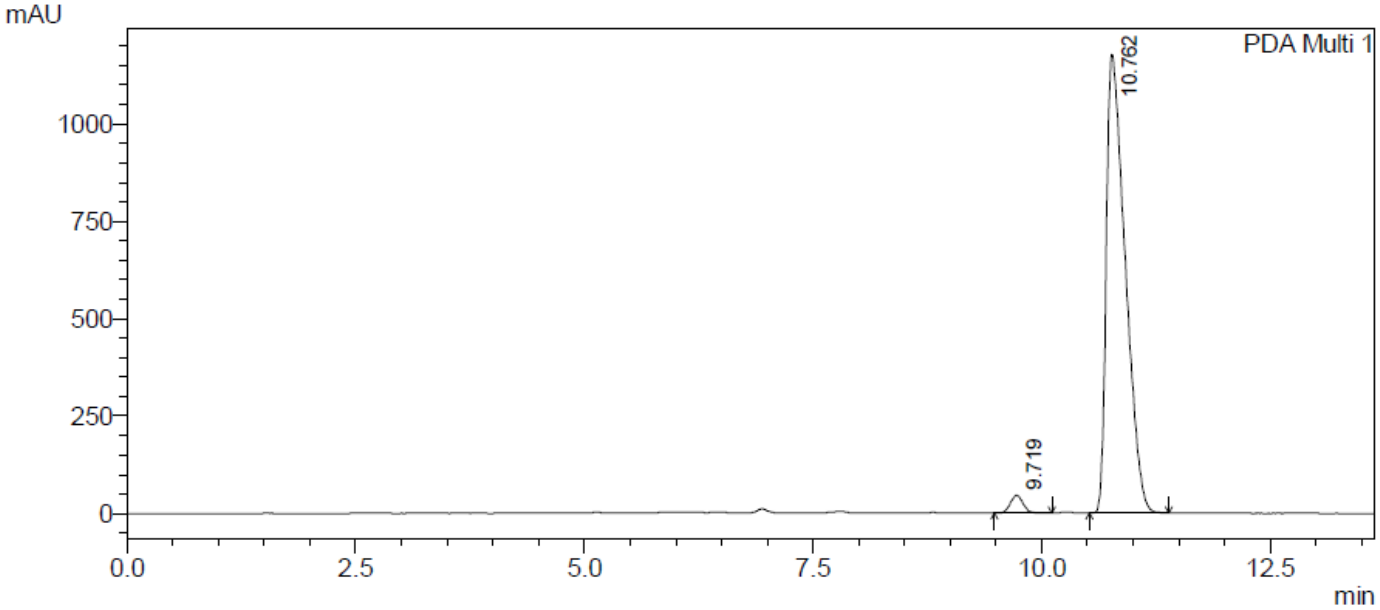
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.449	18499	2415	1.501	1.633
2	6.002	21813	3095	1.770	2.092
3	7.654	1192269	142418	96.729	96.275
Total		1232581	147928	100.000	100.000

Figure S190. HPLC chromatogram of compound **7**.



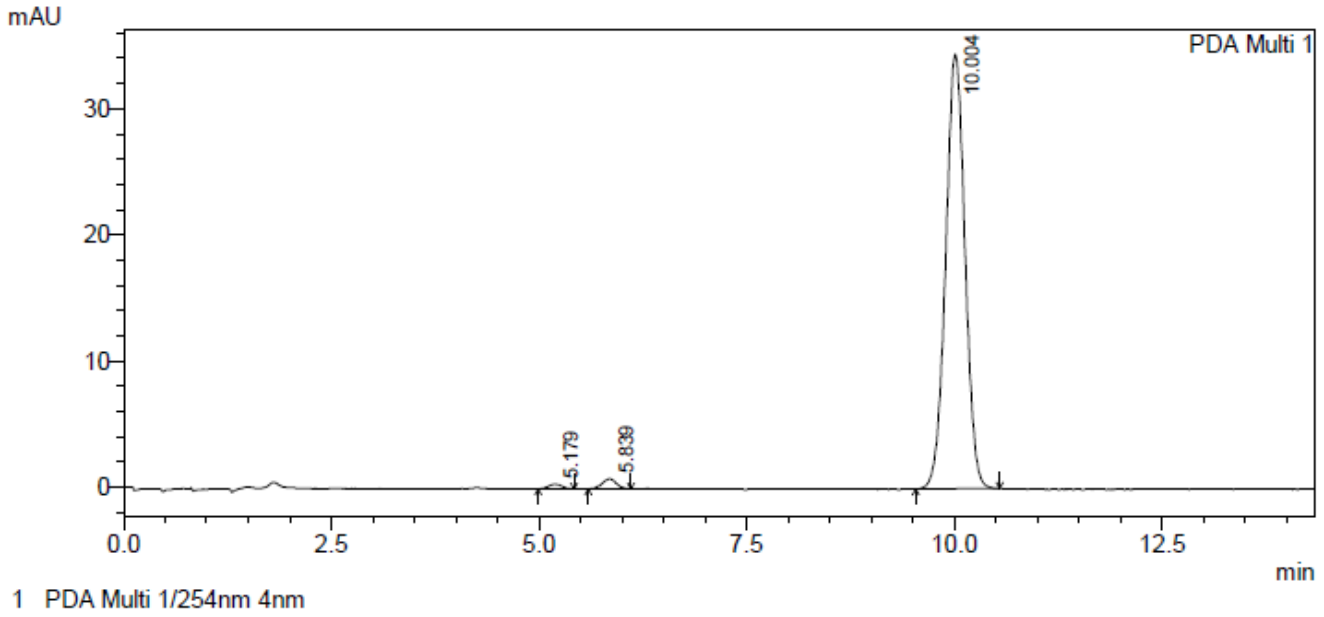
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.719	446780	45549	2.571	3.724
2	10.762	16933731	1177476	97.429	96.276
Total		17380511	1223025	100.000	100.000

Figure S191. HPLC chromatogram of compound **8**.

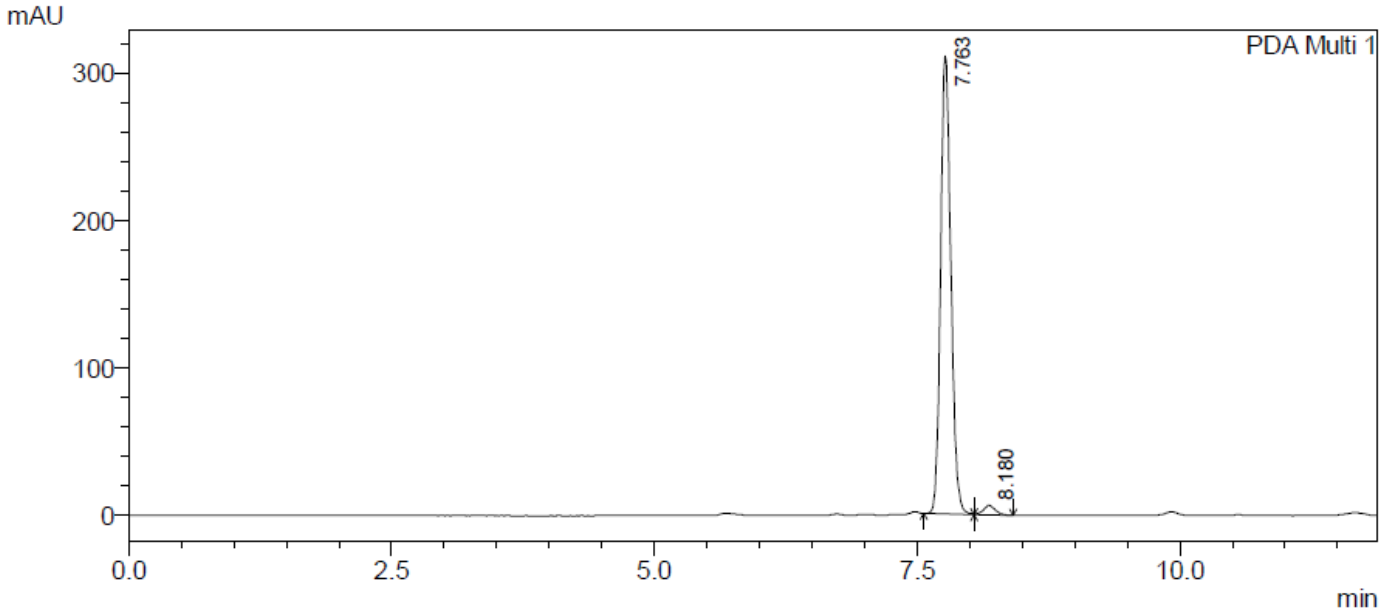


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.179	4144	387	0.726	1.086
2	5.839	9560	792	1.675	2.223
3	10.004	557220	34447	97.600	96.691
Total		570924	35625	100.000	100.000

Figure S192. HPLC chromatogram of compound **9**.



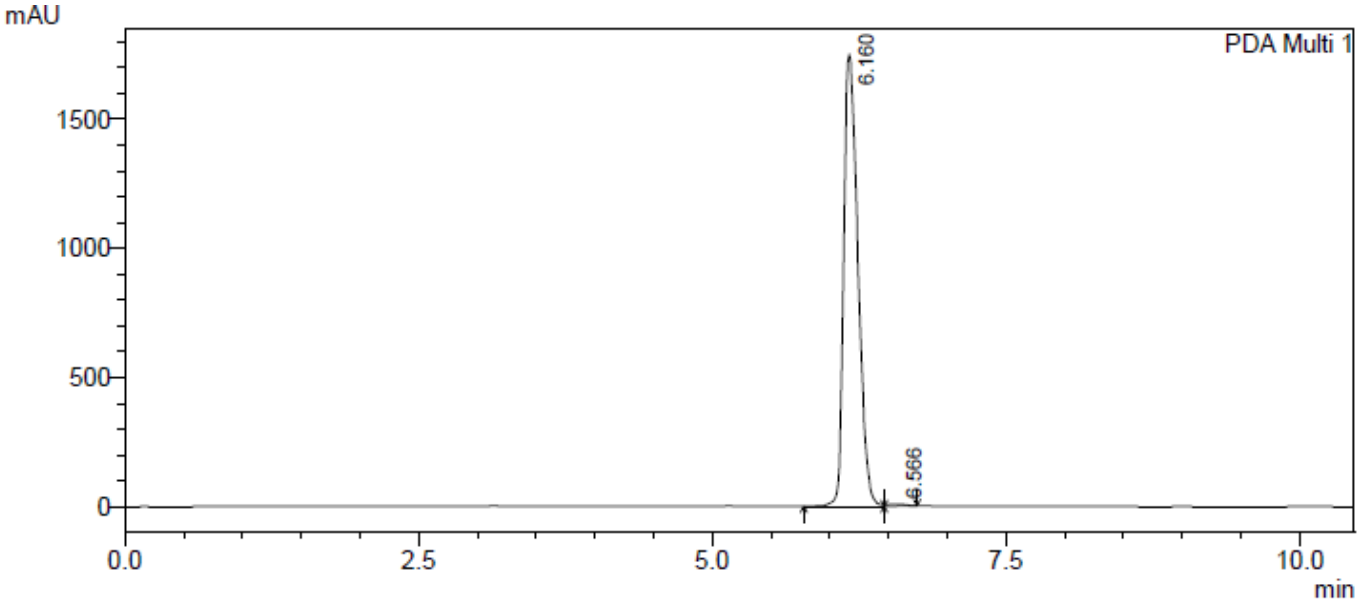
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.763	2109934	310314	97.701	97.970
2	8.180	49649	6430	2.299	2.030
Total		2159583	316743	100.000	100.000

Figure S193. HPLC chromatogram of compound **10**.



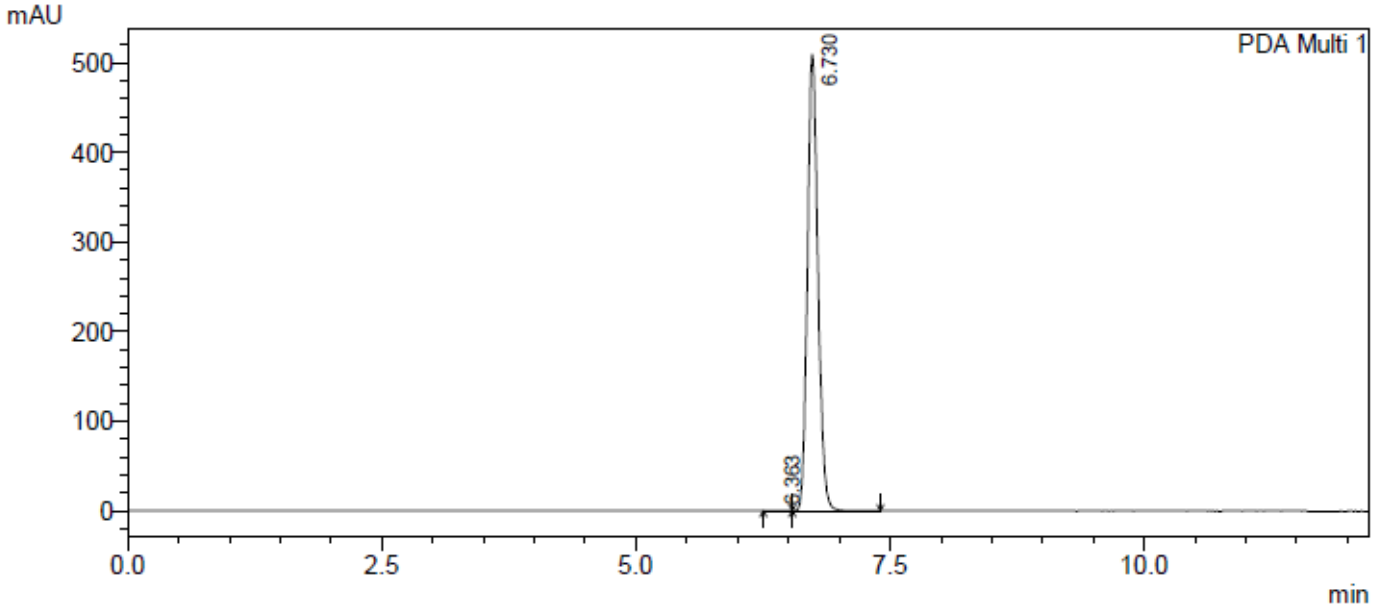
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.160	14796090	1749577	99.478	99.575
2	6.566	77613	7471	0.522	0.425
Total		14873703	1757047	100.000	100.000

Figure S194. HPLC chromatogram of compound **11**.

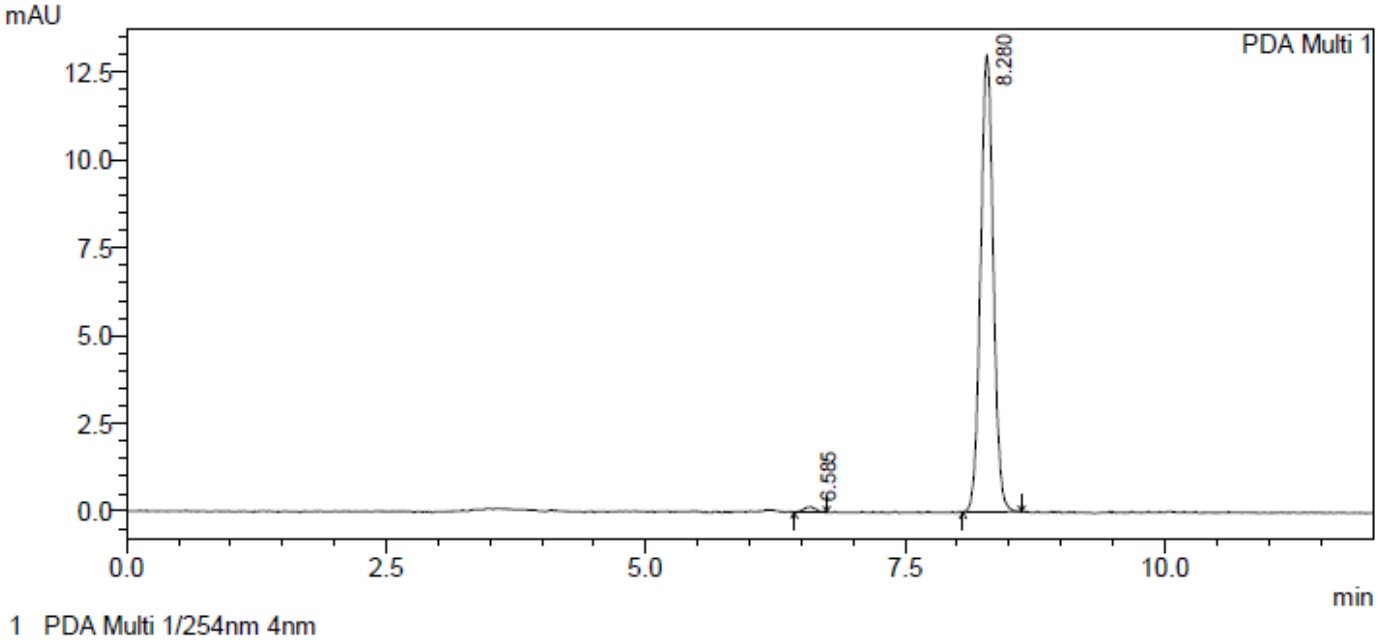


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.363	4729	664	0.128	0.130
2	6.730	3700248	508928	99.872	99.870
Total		3704977	509592	100.000	100.000

Figure S195. HPLC chromatogram of compound **12**.

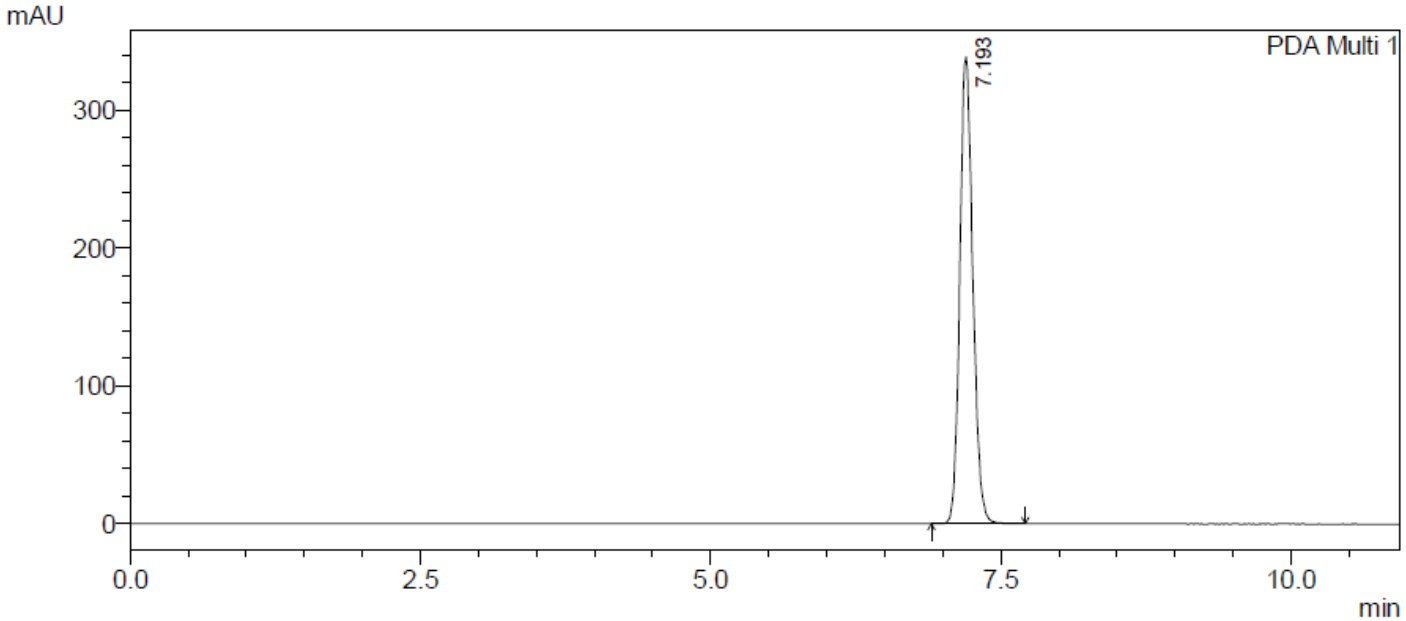


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.585	1272	156	1.126	1.182
2	8.280	111685	13008	98.874	98.818
Total		112957	13164	100.000	100.000

Figure S196. HPLC chromatogram of compound **13**.



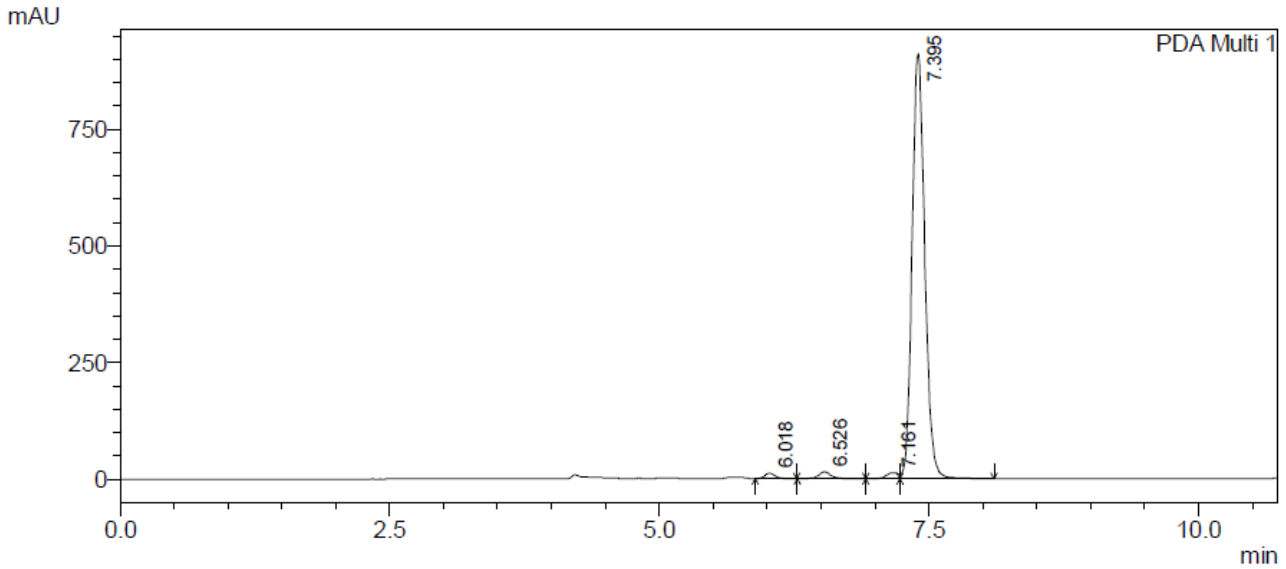
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.193	2645024	338696	100.000	100.000
Total		2645024	338696	100.000	100.000

Figure S197 HPLC chromatogram of compound **14**.



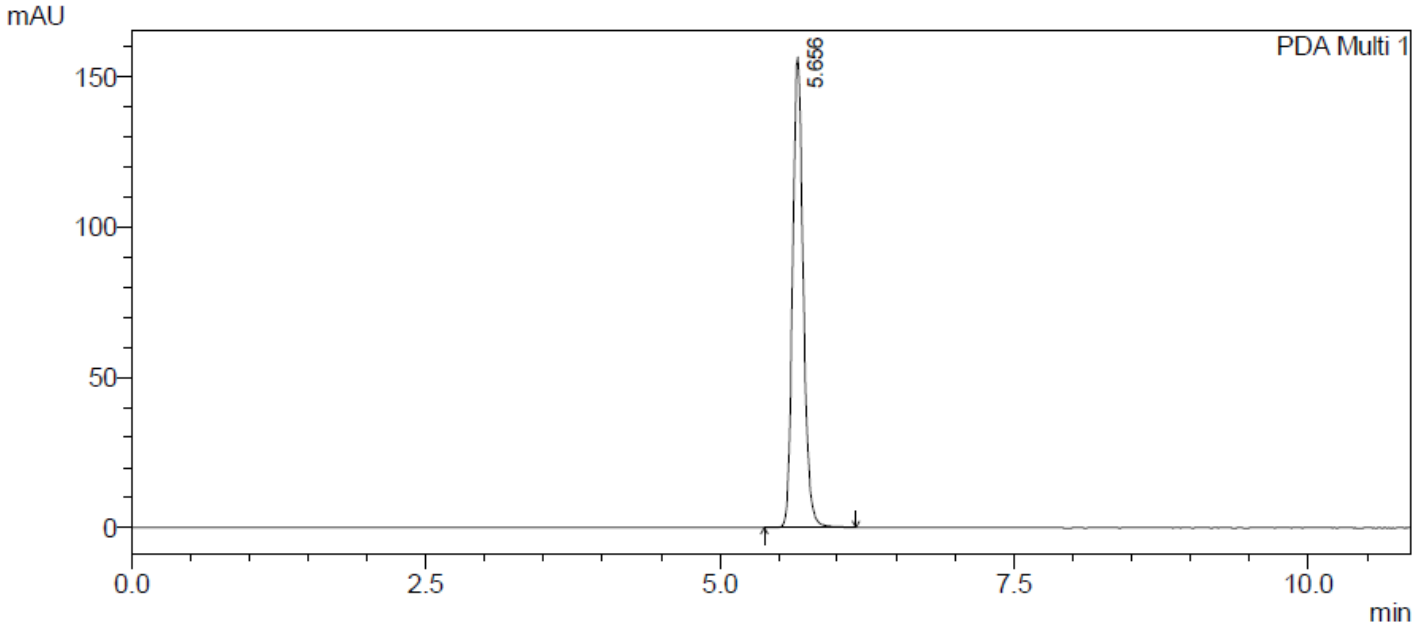
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.018	79856	11603	1.029	1.219
2	6.526	122597	14954	1.580	1.571
3	7.161	104765	13399	1.350	1.408
4	7.395	7454125	911740	96.042	95.802
Total		7761343	951696	100.000	100.000

Figure S198. HPLC chromatogram of compound **15**.



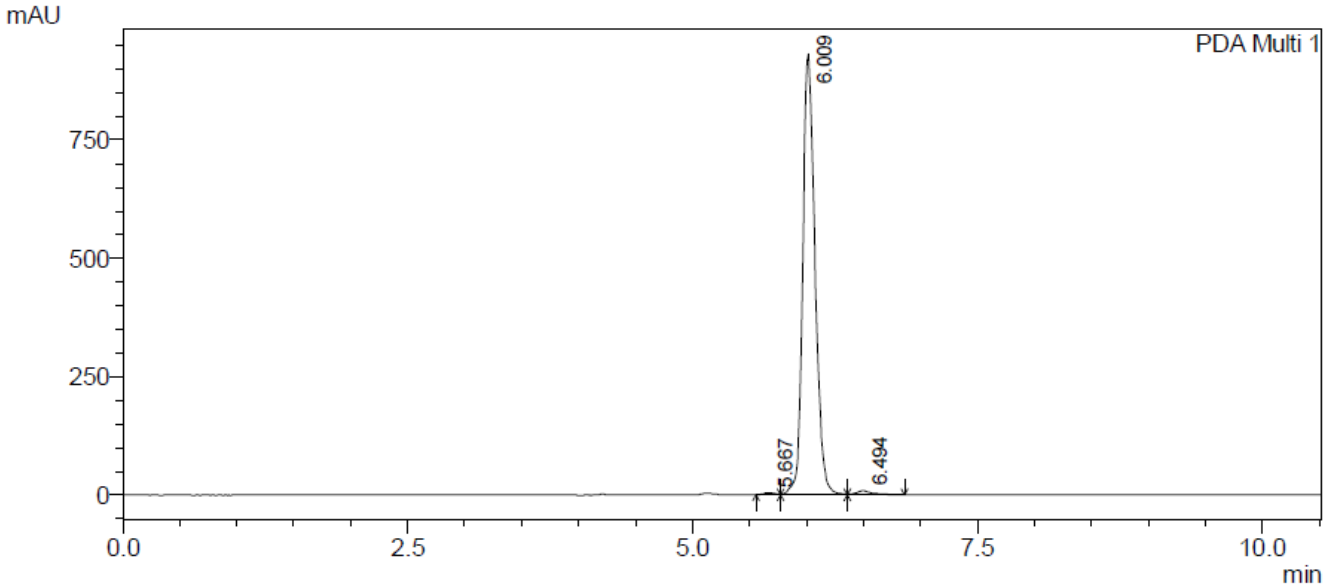
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.656	986989	156405	100.000	100.000
Total		986989	156405	100.000	100.000

Figure S199. HPLC chromatogram of compound **16**.



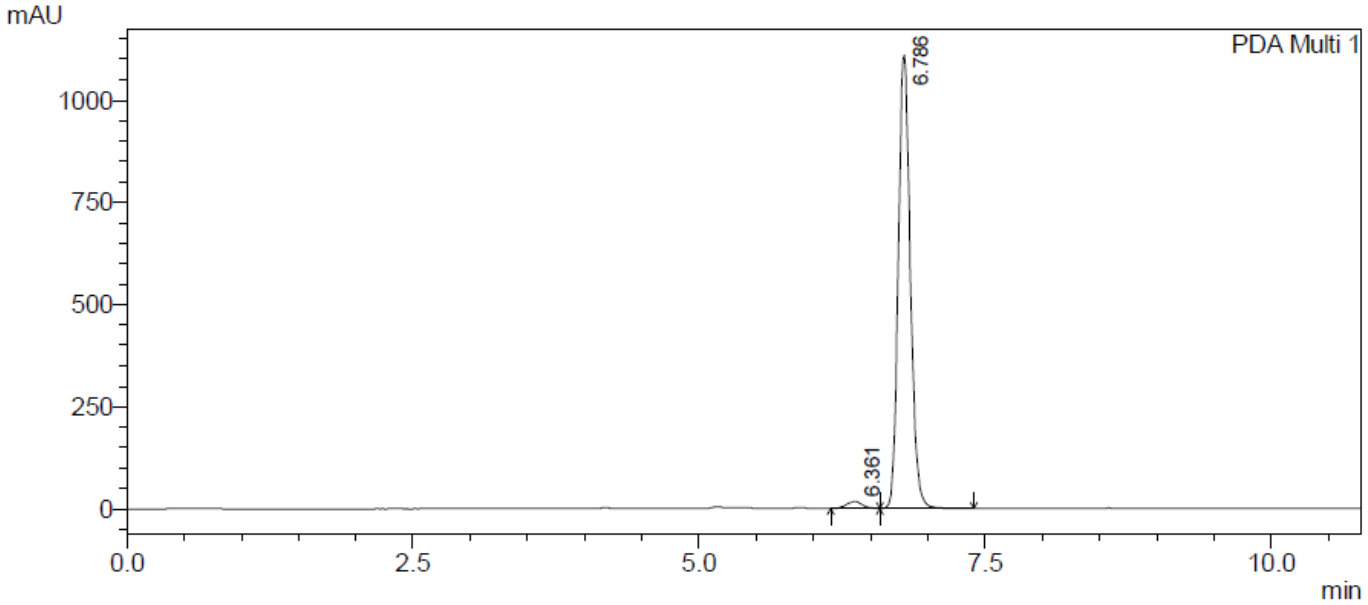
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.667	30081	4803	0.423	0.509
2	6.009	6998172	930653	98.312	98.579
3	6.494	90056	8608	1.265	0.912
Total		7118309	944063	100.000	100.000

Figure S200. HPLC chromatogram of compound **17**.



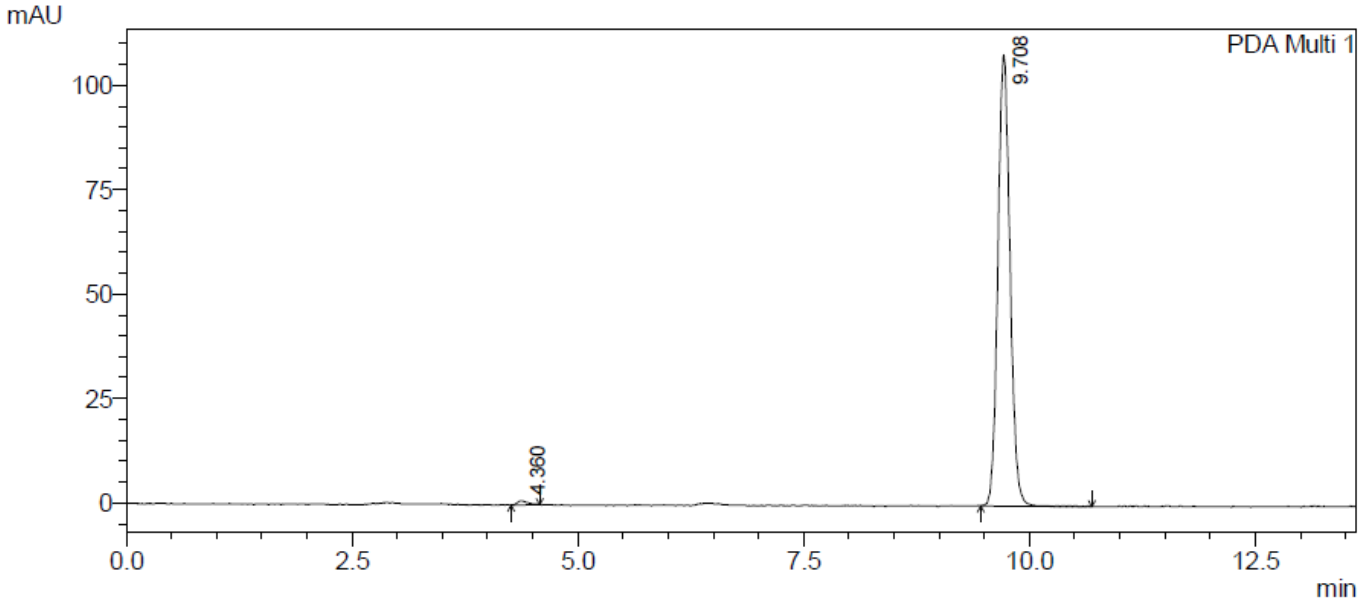
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.361	164637	17505	1.981	1.553
2	6.786	8145381	1109415	98.019	98.447
Total		8310018	1126920	100.000	100.000

Figure S201. HPLC chromatogram of compound **18**.



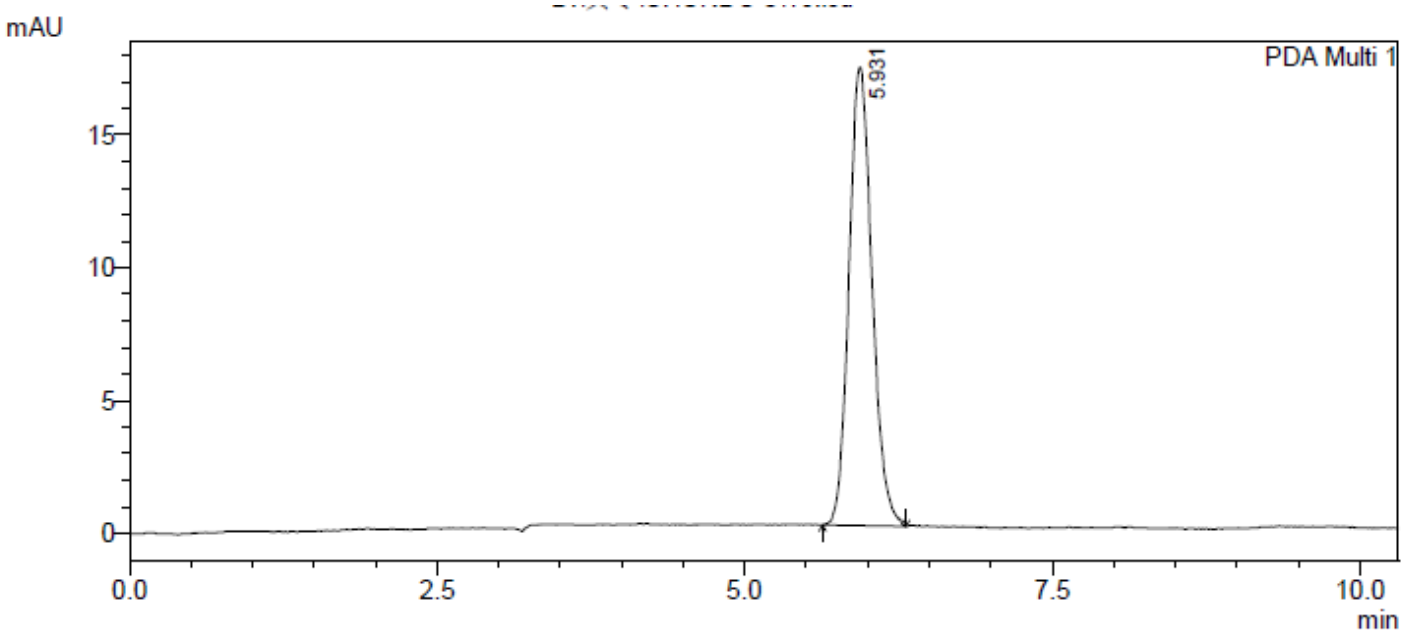
1 PDA Multi 1/200nm 4nm

PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.360	8353	1005	0.822	0.922
2	9.708	1008155	107962	99.178	99.078
Total		1016508	108967	100.000	100.000

Figure S202. HPLC chromatogram of compound **19**.



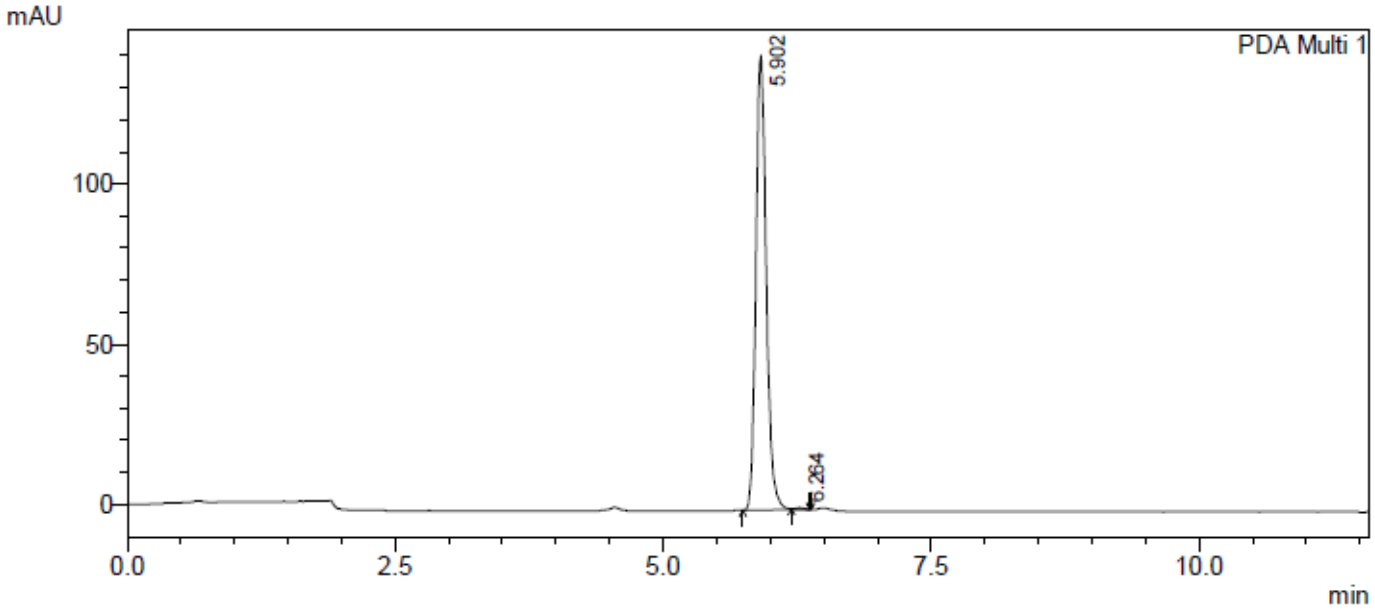
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.931	224884	17222	100.000	100.000
Total		224884	17222	100.000	100.000

Figure S203. HPLC chromatogram of compound **20**.



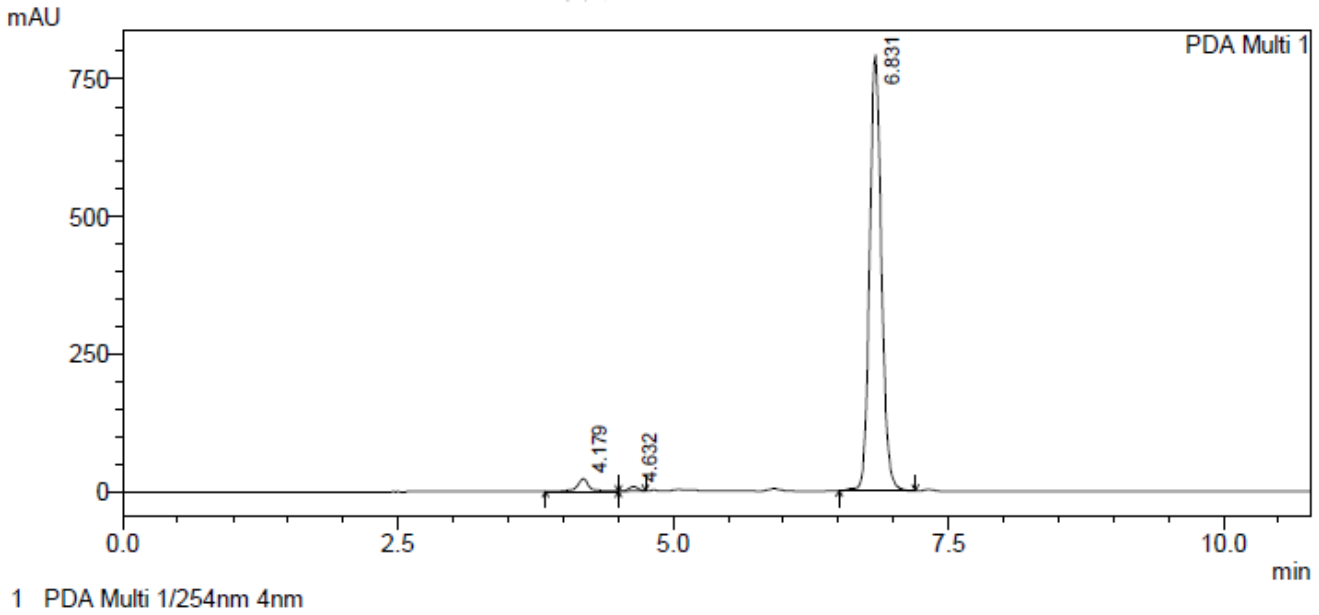
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.902	956162	141690	99.750	99.673
2	6.264	2394	465	0.250	0.327
Total		958556	142155	100.000	100.000

Figure S204. HPLC chromatogram of compound **21**.

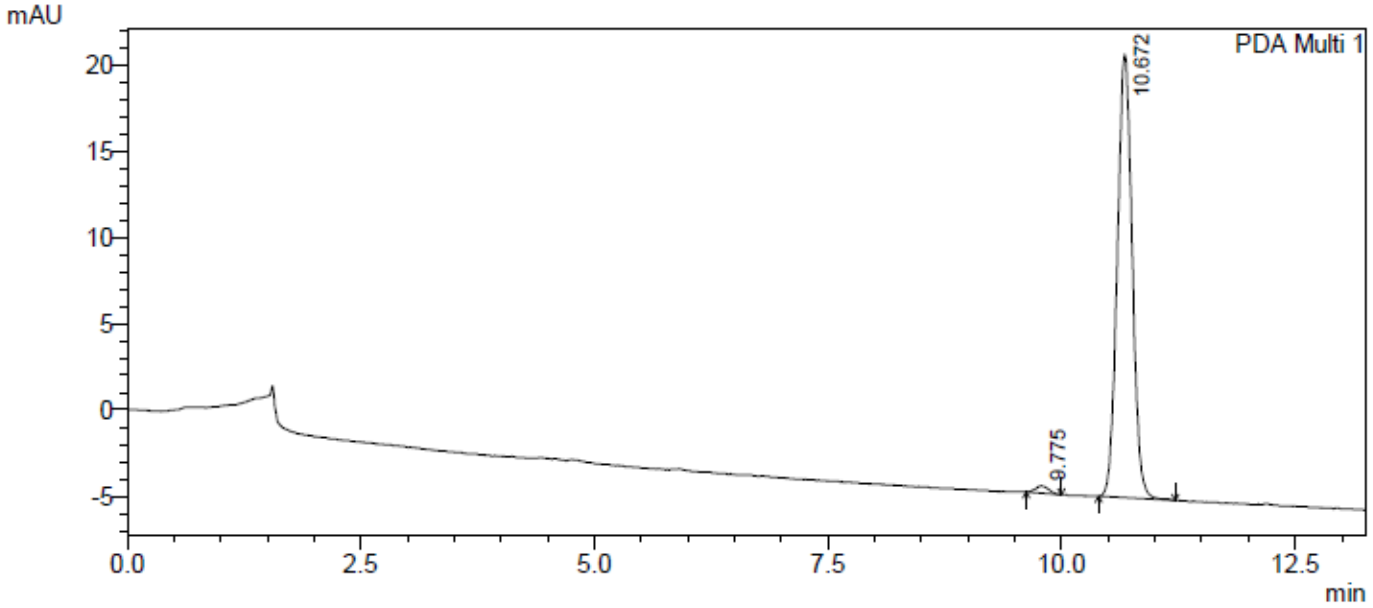


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.179	169276	22854	2.740	2.777
2	4.632	43187	7946	0.699	0.965
3	6.831	5964411	792284	96.560	96.258
Total		6176874	823084	100.000	100.000

Figure S205. HPLC chromatogram of compound **22**.



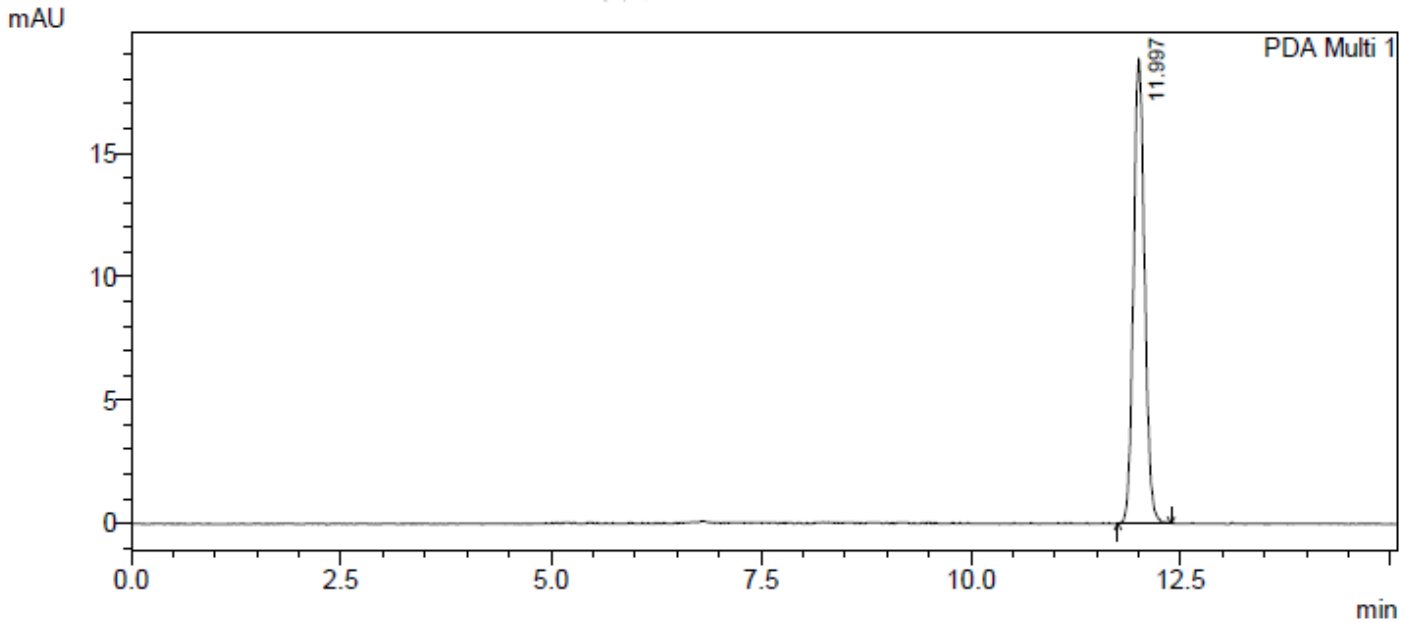
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.775	4233	428	1.460	1.639
2	10.672	285708	25678	98.540	98.361
Total		289941	26106	100.000	100.000

Figure S206. HPLC chromatogram of compound **23**.



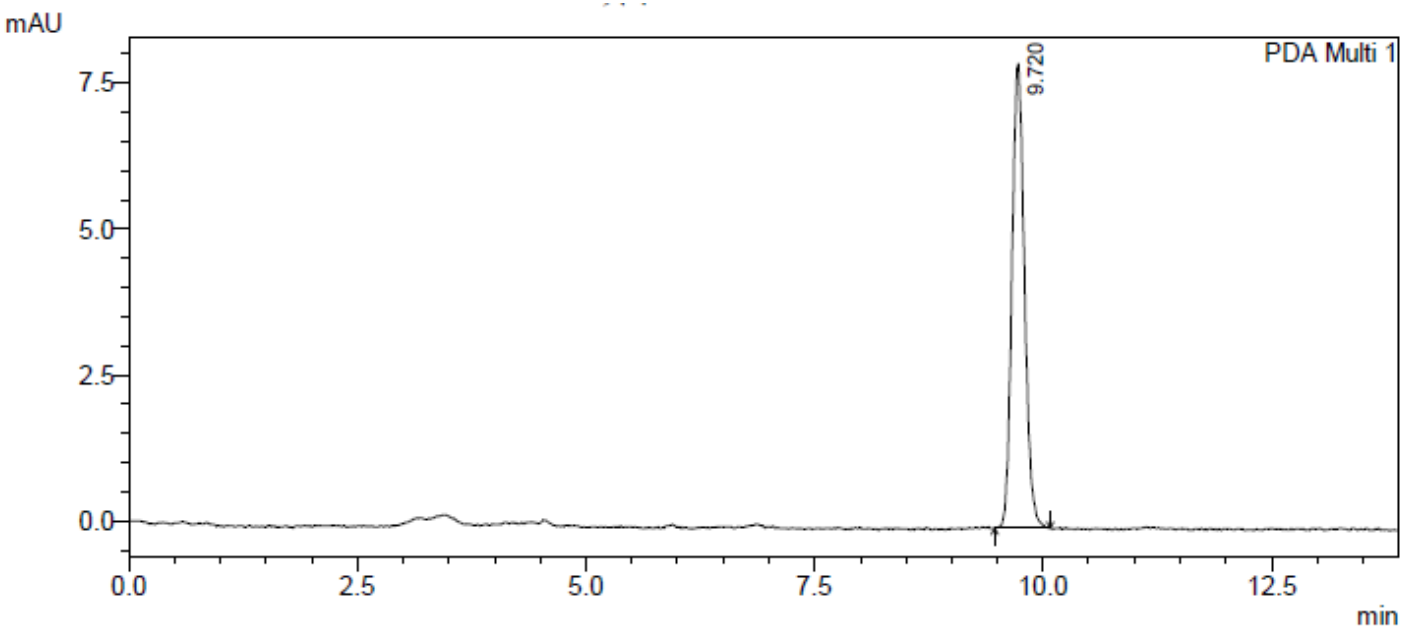
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.997	174401	18827	100.000	100.000
Total		174401	18827	100.000	100.000

Figure S207. HPLC chromatogram of compound **24**.



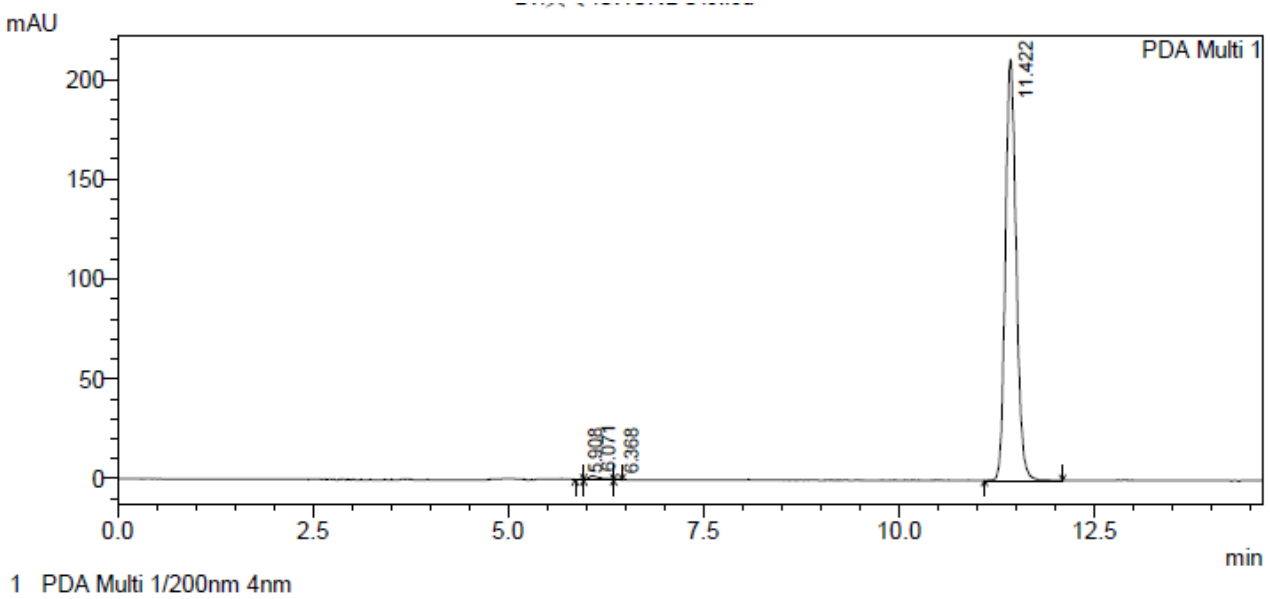
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	9.720	75775	7942	100.000
Total		75775	7942	100.000

Figure S208. HPLC chromatogram of compound **25**.

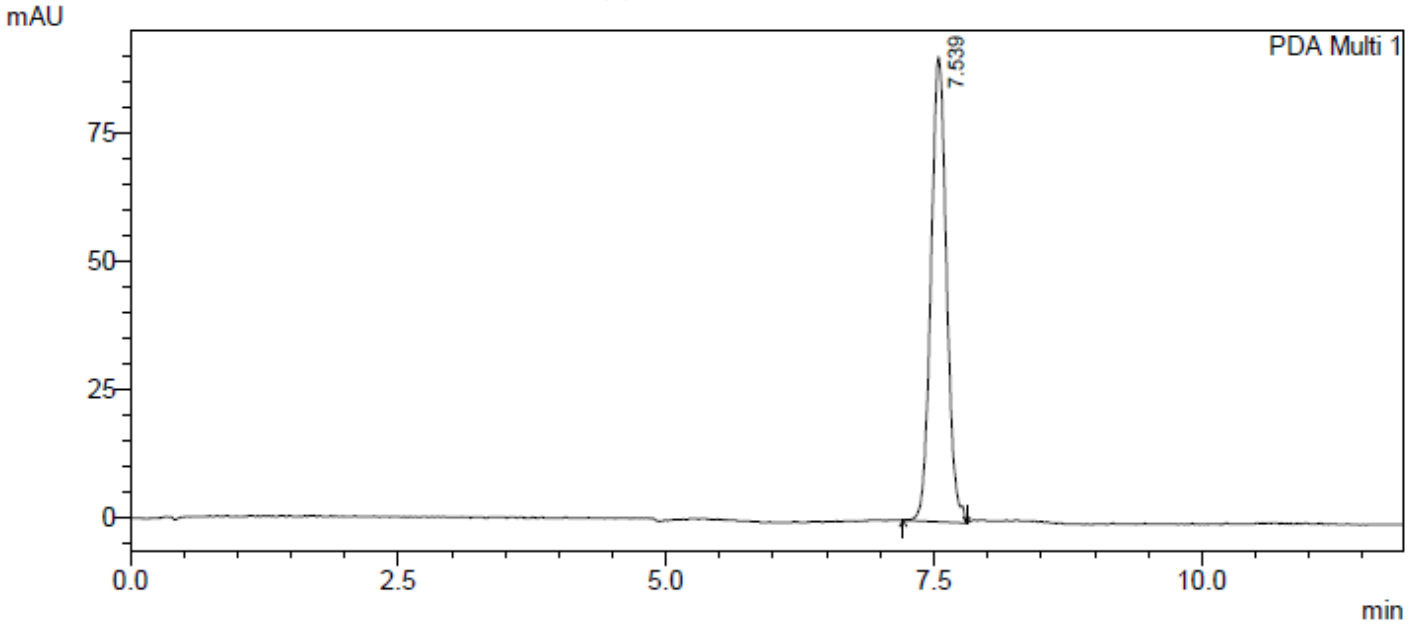


PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	5.908	205	81	0.010
2	6.071	18770	1974	0.917
3	6.368	995	286	0.049
4	11.422	2026277	210696	99.024
Total		2046248	213036	100.000

Figure S209. HPLC chromatogram of compound **26**.



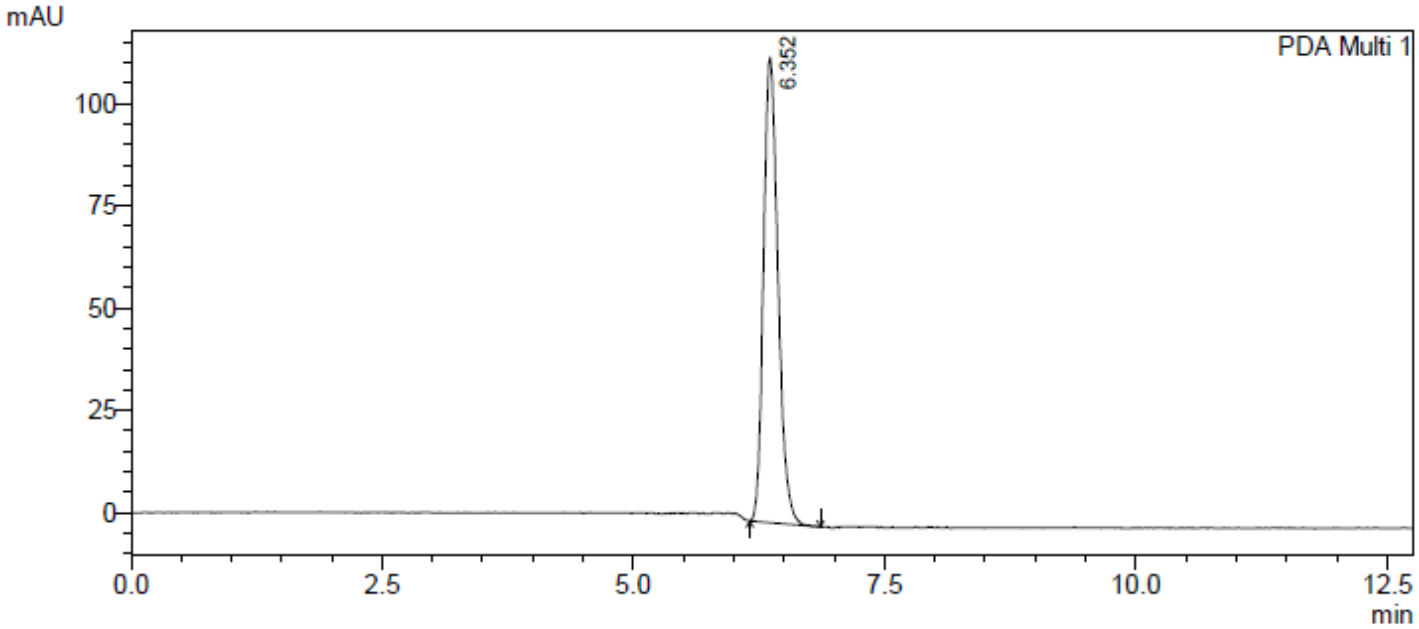
1 PDA Multi 1/200nm 4nm

PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.539	918343	90398	100.000	100.000
Total		918343	90398	100.000	100.000

Figure S210. HPLC chromatogram of compound **27**.



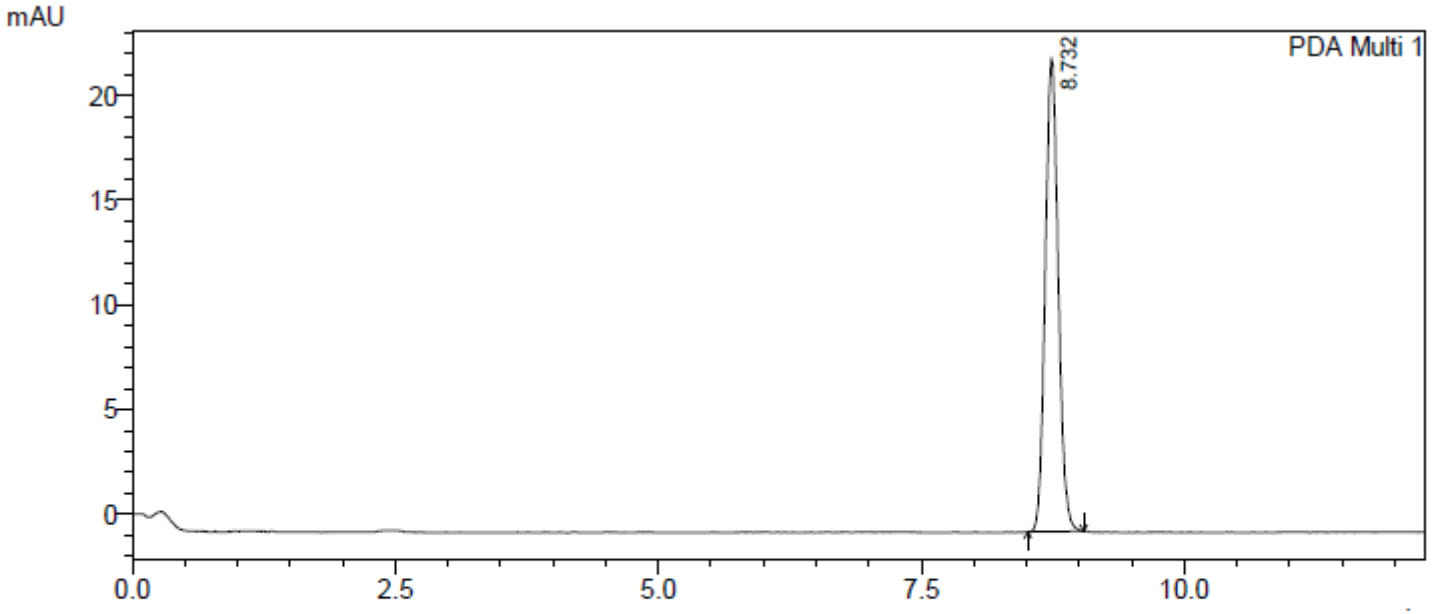
1 PDA Multi 1/200nm 4nm

PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.352	1133223	113671	100.000	100.000
Total		1133223	113671	100.000	100.000

Figure S211. HPLC chromatogram of compound **28**.



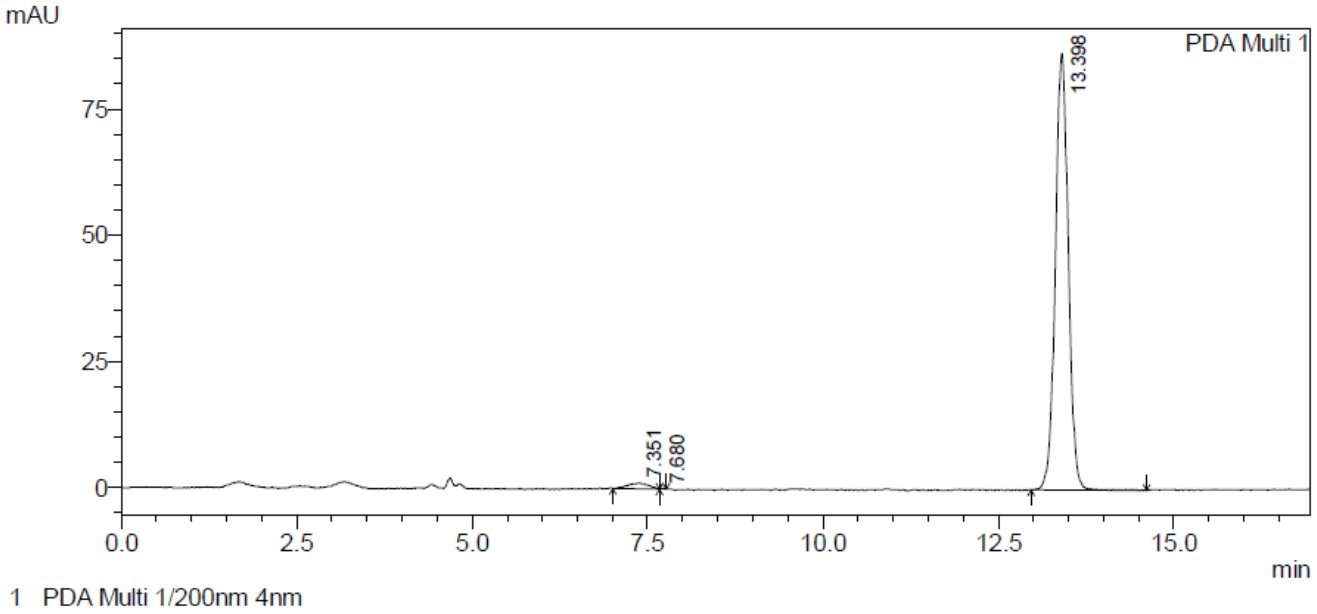
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.732	194599	22663	100.000	100.000
Total		194599	22663	100.000	100.000

Figure S212. HPLC chromatogram of compound **29**.

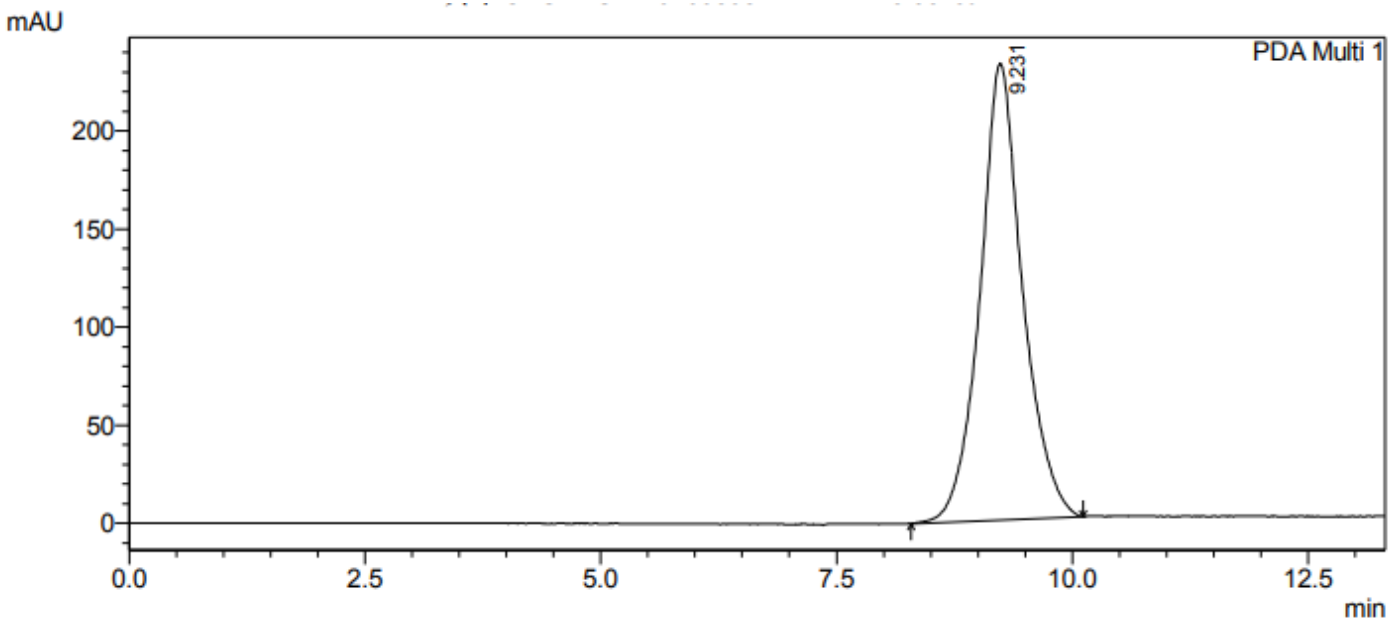


PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.351	24356	1173	2.150	1.335
2	7.680	493	171	0.044	0.194
3	13.398	1107914	86458	97.806	98.470
Total		1132763	87801	100.000	100.000

Figure S213. HPLC chromatogram of compound **30**.

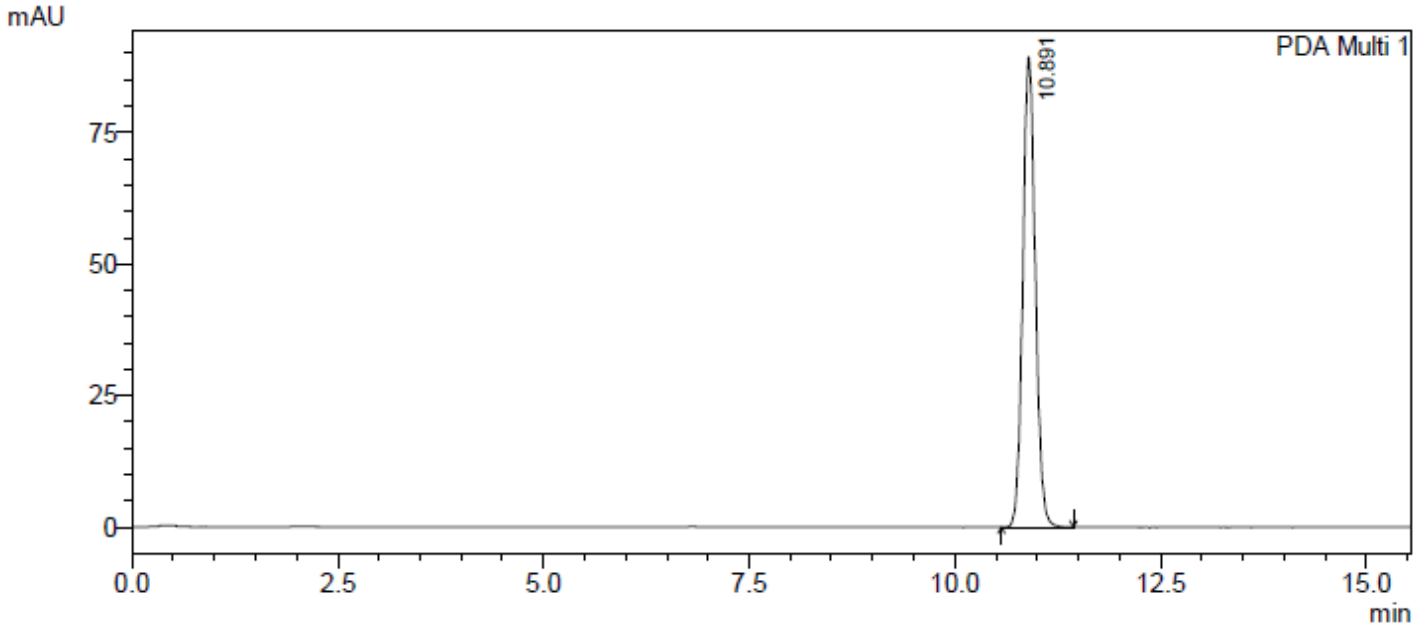


PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.231	7300284	232753	100.000	100.000
Total		7300284	232753	100.000	100.000

Figure S214. HPLC chromatogram of compound **31**.



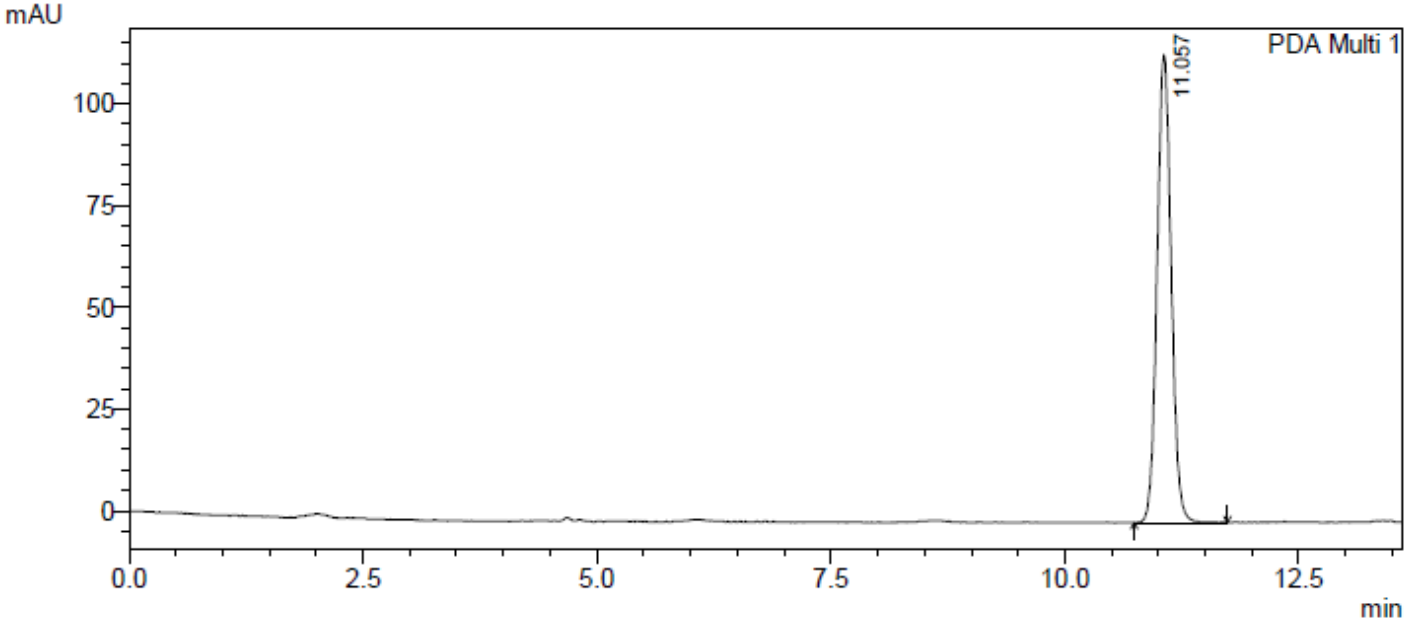
1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %
1	10.891	951694	89381	100.000
Total		951694	89381	100.000

Figure S215. HPLC chromatogram of compound **32**.



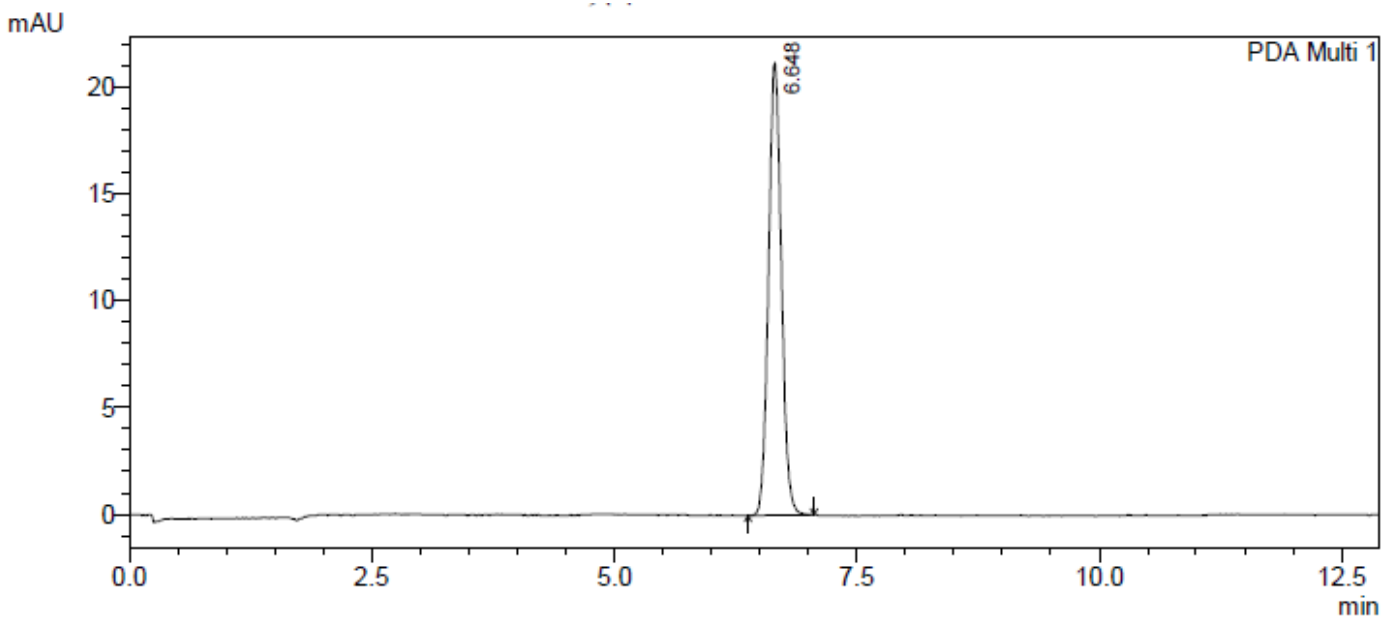
1 PDA Multi 1/200nm 4nm

PeakTable

PDA Ch1 200nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.057	1210675	114909	100.000	100.000
Total		1210675	114909	100.000	100.000

Figure S216. HPLC chromatogram of compound **33**.

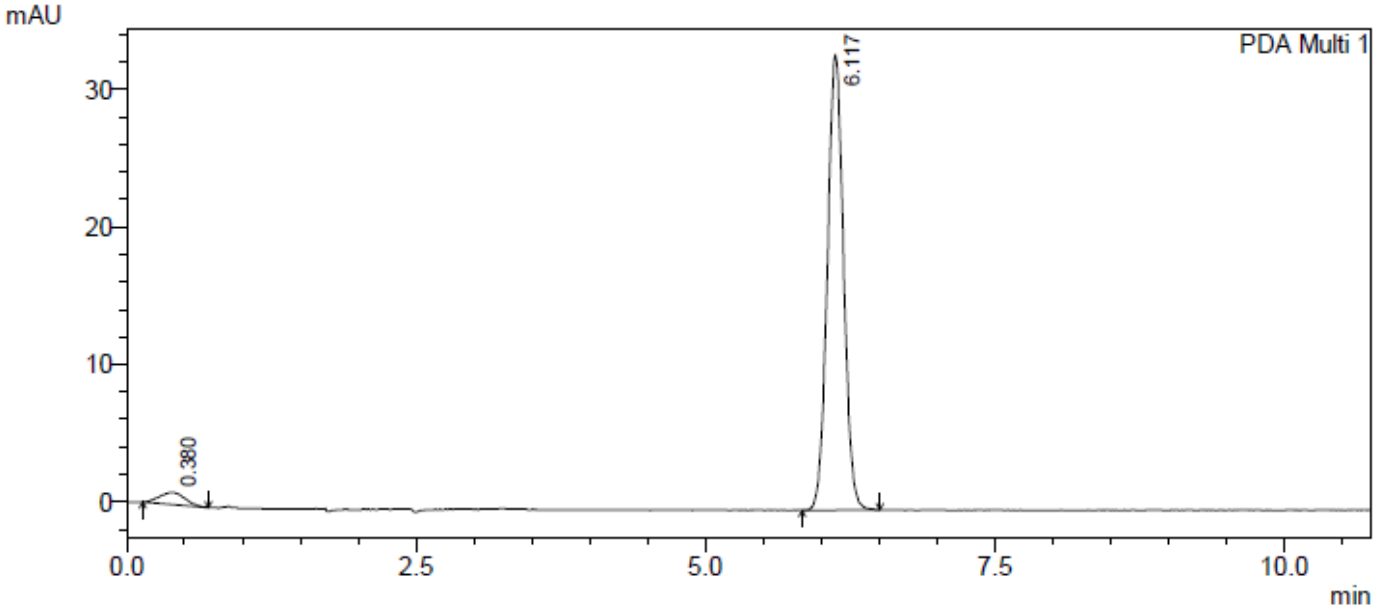


PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.648	196112	21144	100.000	100.000
Total		196112	21144	100.000	100.000

Figure S217. HPLC chromatogram of compound **34**.



1 PDA Multi 1/254nm 4nm

PeakTable

PDA Ch1 254nm 4nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	0.380	13149	868	3.931	2.555
2	6.117	321377	33083	96.069	97.445
Total		334527	33950	100.000	100.000