Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Asymmetric Total Syntheses of Sarbracholide and Shizukaol B

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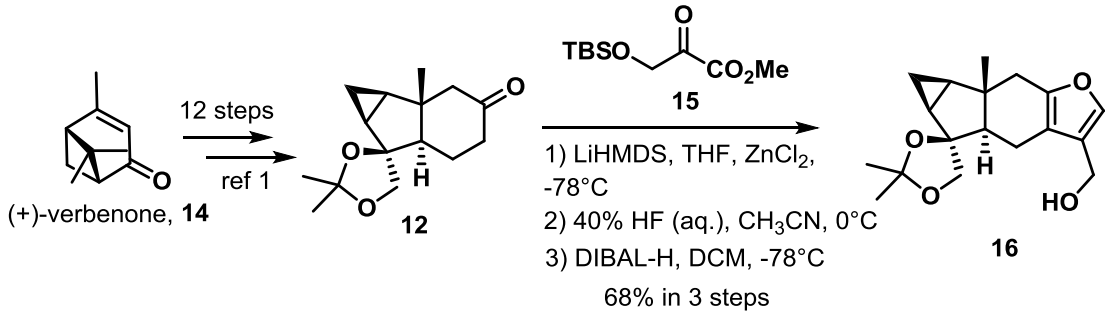
1. **General Information**

All reactions were performed under an argon atmosphere with dry solvents under anhydrous conditions unless otherwise stated. DCM, DCE, PhMe, MeCN and DMSO were distilled from calcium hydride under argon; MeOH was distilled from magnesium and iodine under argon; THF was distilled firstly from sodium and then from $LiAlH_4$ under argon. Unless otherwise noted, all the other chemicals were purchased commercially and used without further purification. Reactions requiring anhydrous conditions were run under a dry atmosphere of argon; glassware was either flame dried immediately prior to use after placing in an oven (120 °C) for at least 2 hours and allowed to cool under an atmosphere of argon; liquid reagents, solutions or solvents were added via syringe through rubber septum. Column chromatography was performed using silica gel (200-300 mesh). Thin layer chromatography (TLC) was used for monitoring reactions and visualized by a UV lamp (254 nm and 365 nm), I2 and developing the plates with *p*-anisaldehyde. ^{1}H and ^{13}C NMR were recorded on Bruker DRX-400 or 600 MHz NMR spectrometer with TMS as the internal standard and were calibrated using residual undeuterated solvent as an internal reference ($CDCl_3$: ^{1}H NMR = 7.26 ppm, ^{13}C NMR = 77.16 ppm; CD_3COCD_3: ^{1}H NMR = 2.05 ppm, ^{13}C NMR = 29.84 ppm). Abbreviations in ^{1}H NMR data are illustrated as follows: s =singlet, d = doublet, t = triplet, dd = doublet of doublet, ddd = doublet of doublet of doublet, dt = doublet of triplet, td = triplet of doublet, tdd = triplet of doublet of doublet, m = multiplet, br = broad. Coupling constants (J) are reported in Hertz (Hz). Optical rotations were recorded on digital automatic polarimeter with a 100 mm path length cell. High resolution mass spectra (HRMS) were recorded by using Bruker-FT-MS spectrometers (ESI-TOF). Infrared (IR) spectra were recorded on a NEXUS 670 FT-IR device and are reported in wavenumbers (cm^{-1}).

2. Experimental procedure

2.1 Initial Synthetic route

Procedure for preparation of compound 16



1) Aldol reaction

A solution of LiHMDS (50.2 mg, 0.300 mmol, 1.5 eq) in THF (0.5 mL) was added **12** (50.0 mg, 0.200 mmol, 1.0 eq) in 0.47 mL THF at -78 ℃. After stirring for 20 min, the solution was added $ZnCl_2$ (49.1 mg, 0.300 mmol, 1.5 eq) at -78 ℃. After stirring for 5 min, compound **15** (48.8 mg, 0.210 mmol, 1.05 eq) was added to above solution. Then the mixture of ethyl acetate (10 mL) and NH_4Cl (aq.) (10 mL) were cooled to -78℃ and poured into the reaction solution during 15 min. The resulting solution was diluted with water (30 mL) and extracted by ethyl acetate (3 x 30 mL). The organic layers were dried over Na_2SO_4, filtered, and evaporated under vacuum. The residue was directly used in the next step without further purification.

2) Desilylation reaction

The above residue was dissolved in MeCN (20 mL) and cooled to 0 ℃. 40% HF (aq.) (1.5 mL, 0.600 mmol, 3.0 eq) was added into the above solution and stirred at 0 ℃ for 1 h. Then the mixture was diluted with ethyl acetate (30 mL) and dried over Na_2SO_4, filtered by celite pad, evaporated under vacuum. The residue was used in the next step without further purification.

3) Reduction

The above crude product was dissolved in DCM (4 mL) and cooled to -78 ℃. 1.5 M DIBAL-H in toluene (0.4 mL, 0.600 mmol, 3.0 eq) was added to the solution. After stirring at -78 ℃ for 90 min, the mixture was quenched slowly with potassium sodium

tartrate (aq.) (30 mL). The mixture was gradually warmed to room temperature and stirred for another 6 h. The aqueous layer was extracted by ethyl acetate (3 x 30 mL). The combined organic layers were dried by Na_2SO_4, filtrated by celite pad, concentrated under vacuum. The residue was purified by flash chromatography (EA:PE = 1:4) to provide compound **16** (41.4 mg, 68% in 3 steps) as colorless oil.

$[\alpha]_D^{20} = +291.7$ (c = 0.160 mg/mL, MeOH);

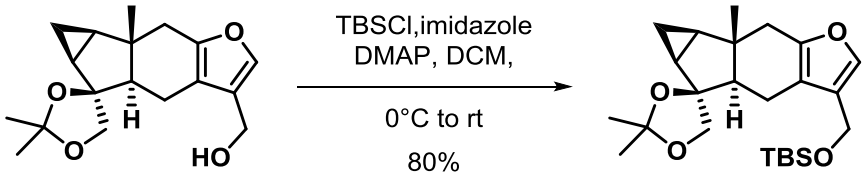
IR (neat, cm^{-1}): 2959, 2927, 2858, 1462, 1379, 1170, 1117, 1103, 1057, 1019, 875, 794, 731.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (s, 1H), 4.52 – 4.46 (m, 2H), 4.03 (d, J = 8.0 Hz, 1H), 3.89 (d, J = 8.0 Hz, 1H), 2.64 (s, 2H), 2.29 – 2.15 (m, 2H), 1.97 (dd, J = 10.5, 5.7 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.46 (s, 4H), 1.36 (s, 3H), 1.23 – 1.18 (m, 2H), 0.86 (s, 3H), 0.73 (td, J = 8.7, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.66, 138.82, 124.66, 116.50, 109.95, 86.27, 72.62, 59.83, 55.97, 40.34, 39.80, 30.41, 30.09, 26.77, 26.59, 18.56, 16.81, 12.53.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{18}H_{25}O_4$ 305.1748, found 305.1749.

Procedure for preparation of compound 17



16 **17**

Imidazole (21.2 mg, 0.312 mmol, 1.8 eq) and TBSCl (31.3 mg, 0.208 mmol, 1.2 eq) were added to a solution of compound **16** (52.8 mg, 0.173 mmol, 1.0 eq) in DCM (1.73 mL). After stirring for at rt for 4 h, the resulting solution was directly purified by flash chromatography (EA:PE = 1:20 to 1:10) to provide compound **17** (61.6 mg, 85%) as colorless oil.

$[\alpha]_D^{20} = +68.2$ (c = 0.220 mg/mL, MeOH);

IR (neat, cm^{-1}): 3756, 3699, 2959, 2928, 2857, 1970, 1463, 1408, 1380, 1103, 1019, 839, 776, 731.

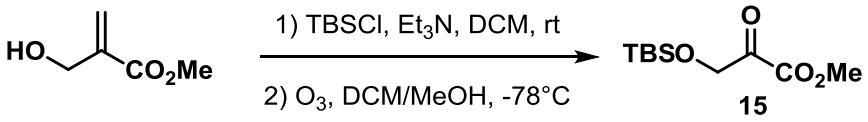
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 4.52 (s, 2H), 4.03 (d, *J* = 8.0 Hz, 1H), 3.87 (d, *J* = 8.0 Hz, 1H), 2.71 – 2.55 (m, 2H), 2.22 (dt, *J* = 15.7, 7.3 Hz, 2H), 1.95 (dd, *J* = 10.8, 5.3 Hz, 1H), 1.66 – 1.60 (m, 1H), 1.48 – 1.41 (m, 4H), 1.34 (s, 3H), 1.23 – 1.17 (m, 1H), 0.90 (s, 9H), 0.85 (s, 3H), 0.72 (td, *J* = 8.7, 5.4 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.34, 138.04, 125.05, 116.66, 110.02, 86.44, 72.73, 59.96, 57.02, 40.44, 39.95, 30.51, 30.22, 26.78, 26.04, 18.64, 18.49, 17.32, 12.59, -5.12.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{24}H_{39}O_4Si$ 419.2613, found 419.2613.

2.2 Optimized Synthetic Route

Procedure for preparation of compound 15



A solution of methyl 2-(hydroxymethyl)acrylate (600 mg, 7.16 mmol, 1.0 eq) and triethylamine (3.84 mL, 38.0 mmol, 5.3 eq) in DCM (19.0 mL) was added TBSCl (2.32 g, 15.4 mmol, 2.15 eq). After stirring for 4 h, the solution was transferred into a three neck flask. The solution was added MeOH (19.0 mL), and cooled to -78℃, then bubbled with O_3 for 1h until the solution turned blue. Then the reaction was bubbled with O_2 for 20 min to remove excess O_3 and further quenched by Me_2S (1.48 mL, 20.2 mmol, 2.82 eq). The solution was slowly warmed up to room temperature and stirred for another 10 h. The resulting mixture then was concentrated under vacuum and the residue was purified flash column chromatography (EA: PE = 1:10 to 1:6) to provide compound **15** (803.1 mg, 45%) as colorless oil.

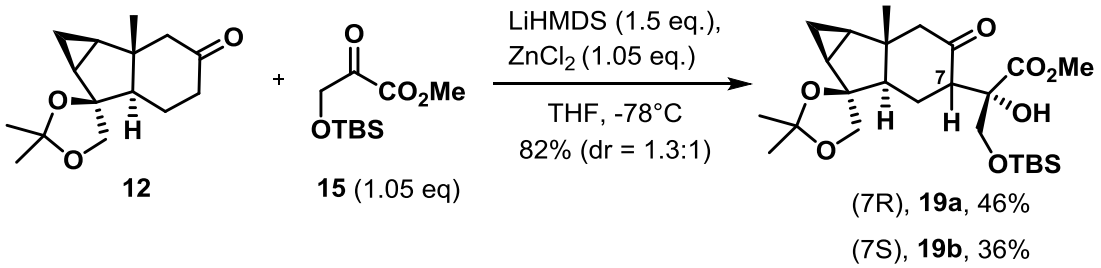
IR (thin film): 3359.45, 2923.71, 2853.63, 2361.44, 1742.46, 1654.79, 1463.49, 1256.11, 839.42.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.74 (s, 2H), 3.86 (s, 3H), 0.91 (s, 9H), 0.09 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.14, 161.21, 67.82, 52.97, 25.82, 18.52, -5.34.

HRMS (ESI/$[M+Na]^+$) calcd for $C_{10}H_{20}O_4Si$, found 255.1020 .

Procedure for preparation of compound 19a, 19b



A solution of LiHMDS (50.2 mg, 0.300 mmol, 1.5 eq) in 0.5 mL THF was added **12** (50.0 mg, 0.200 mmol, 1.0 eq) in 0.47 mL THF at -78 ℃. After stirring for 20 min, the solution was added $ZnCl_2$ (49.1 mg, 0.300 mmol, 1.5 eq) and cooled to -78 ℃. After stirring for 5 min, compound **15** (48.8 mg, 0.210 mmol, 1.05 eq) was added to the solution. The mixture was stirred for 15 min and quenched by pouring into a mixture of ethyl acetate (10 mL) and NH_4Cl (aq.) (10 mL) at -78 ℃. The resulting solution was diluted with water (30 mL) and extracted by ethyl acetate (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum, the crude was purified by flash column chromatography (EA: PE = 1:12 to 1:6) to provide both **19a** (44.8 mg, 46%) and **19b** (34.4 mg, 36%) as white solids.

19a:

$[\alpha]_D^{20} = +66.7$ (c = 0.225 mg/mL, MeOH);

IR (neat, cm^{-1}): 3846, 2958, 2919, 2851, 2358, 2084, 1725, 1692, 1662, 1597, 1465, 1267, 1103, 1020, 800, 736.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.10 (d, J = 8.2 Hz, 1H), 3.90 (d, J = 10.1 Hz, 1H), 3.83 (d, J = 8.2 Hz, 1H), 3.77 (s, 3H), 3.63 (s, 1H), 3.54 (d, J = 10.1 Hz, 1H), 2.72 (dd, J = 13.6, 3.5 Hz, 1H), 2.69 – 2.62 (m, 2H), 2.53 (d, J = 14.1 Hz, 1H), 1.82 – 1.71 (m, 1H), 1.64 (ddd, J = 9.0, 7.2, 3.6 Hz, 1H), 1.40 (d, J = 5.7 Hz, 4H), 1.28 (s, 3H), 1.17 – 1.13 (m, 1H), 0.83 (s, 9H), 0.79 (s, 3H), 0.72 (td, J = 8.7, 5.6 Hz, 1H), 0.01 (s, 3H), -0.00 (s, 3H).

^{13}C NMR (400 MHz, $CDCl_3$) δ 212.40, 174.12, 109.89, 86.66, 82.30, 72.60, 67.97, 58.15, 57.37, 52.91, 49.25, 41.23, 30.93, 30.22, 26.82, 26.45, 25.77, 21.80, 20.92, 18.16, 13.15, -5.34, -5.52.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{25}H_{43}O_7Si$ 483.2773, found 483.2774.

19b:

$[\alpha]_D^{20} = +47.7$ (c = 0.440 mg/mL, MeOH);

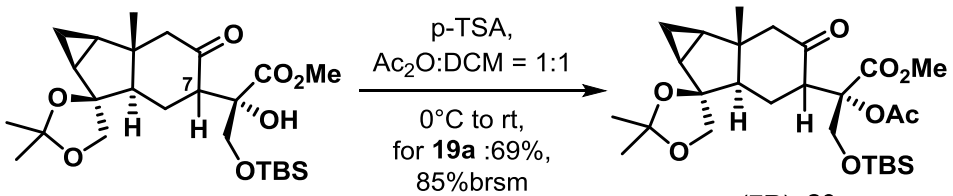
IR (neat, cm^{-1}): 3735.53, 2954.07, 2925.22, 2854.51, 2361.09, 1734.07, 1460.26, 1378.31, 1254.81, 1175.73, 1122.61, 1060.00, 976.38, 839.35, 778.87, 740.30.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.07 (d, J = 8.1 Hz, 1H), 3.87 (d, J = 8.2 Hz, 1H), 3.76 (s, 3H), 3.74 (d, J = 10.8 Hz, 1H), 3.65 (d, J = 9.8 Hz, 1H), 3.52 (s, 1H), 3.03 (dd, J = 9.8, 3.3 Hz, 1H), 2.56 – 2.42 (m, 2H), 2.12 (dd, J = 13.4, 4.7 Hz, 1H), 1.84 (td, J = 13.5, 9.9 Hz, 1H), 1.72 (dt, J = 13.6, 4.1 Hz, 1H), 1.68 – 1.59 (m, 2H), 1.43 (s, 3H), 1.36 (dd, J = 8.4, 4.2 Hz, 1H), 1.32 (s, 4H), 1.18 – 1.13 (m, 1H), 0.95 (s, 3H), 0.85 (d, J = 3.1 Hz, 10H), 0.72 (td, J = 8.7, 5.5 Hz, 1H), 0.02 (d, J = 6.4 Hz, 7H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 212.52, 175.19, 110.04, 86.73, 79.66, 72.60, 67.10, 58.60, 57.06, 52.76, 49.58, 40.08, 31.03, 26.74, 26.50, 25.75, 21.42, 18.21, 18.00, 13.03, -5.37, -5.56.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{25}H_{43}O_7Si$ 483.2773, found 483.2772.

Procedure for preparation of compound 20a, 20b



(7R), **19a**, 46%

(7S), **19b**, 36%

(7R), **20a**

(7S), **20b**

20a: A solution of **19a** (414.7 mg, 0.859 mmol, 1.0 eq) in DCM (10.7 mL) was added Ac_2O (10.7 mL) and *p*-TSA·H_2O (81.7 mg, 0.430 mmol, 0.5 eq) at 0 ℃. The reaction was warmed to room temperature slowly. After stirring for 12 h, the solution was poured into aqueous $NaHCO_3$ solution (50 mL) at 0 ℃ (containing 36 g $NaHCO_3$). After stirring for 6 h, the aqueous solution was extracted by ethyl acetate (3 x 30 mL). The combined organic solution was dried over Na_2SO_4, filtered, and concentrated under vacuum, the residue was purified by flash column chromatography (EA:PE = 1:12 to

1:10) to provide **20a** (312.2 mg, 69%) as colorless oil and **19a** (78.2 mg, 19%) as white solid.

20b: A solution of **19b** (204.0 mg, 0.423 mmol, 1.0 eq) in 5.3 mL DCM (5.3 mL) was added Ac_2O (5.3 mL) and *p*-TSA·H_2O (44.4 mg, 0.211 mmol, 0.5 eq) at 0 ℃. The reaction was warmed to room temperature slowly. After stirring for 6 h, the solution was poured into 50 mL $NaHCO_3$ aqueous solution (containing 36g $NaHCO_3$) at 0 ℃. After stirring for 6 h, the organic layer was isolated and the aqueous solution was extracted by ethyl acetate (3 x 30 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum, the residue was purified by flash column chromatography (EA:PE = 1:10 to 1:6) to provide **20b** (152.1 mg, 69%) as colorless oil.

20a:

$[\alpha]_D^{20} = +57.1$ (*c* = 0.175 mg/mL, MeOH);

IR (neat, cm^{-1}): 2958, 2928, 2858, 2361, 1463, 1379, 1116, 1019, 840, 731.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.21 (d, *J* = 10.7 Hz, 1H), 4.14 (d, *J* = 10.7 Hz, 1H), 4.06 (d, *J* = 7.9 Hz, 1H), 3.91 (d, *J* = 7.9 Hz, 1H), 3.75 (s, 3H), 2.89 (d, *J* = 9.5 Hz, 1H), 2.61 (d, *J* = 14.2 Hz, 1H), 2.51 (d, *J* = 14.3 Hz, 1H), 2.39 (dd, *J* = 13.4, 4.0 Hz, 1H), 2.09 (s, 3H), 1.80 (ddd, *J* = 14.3, 4.1, 1.8 Hz, 1H), 1.72 (dd, *J* = 13.6, 8.7 Hz, 1H), 1.68 – 1.60 (m, 1H), 1.43 (s, 3H), 1.39 (ddd, *J* = 8.4, 7.2, 4.2 Hz, 1H), 1.30 (s, 3H), 1.18 (dt, *J* = 5.5, 4.0 Hz, 1H), 0.86 (s, 9H), 0.82 (s, 3H), 0.73 (td, *J* = 8.8, 5.7 Hz, 1H), 0.05 (s, 3H), 0.02 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 208.85, 169.84, 169.15, 110.01, 86.54, 84.37, 72.43, 61.41, 57.67, 57.46, 52.45, 50.32, 40.92, 30.77, 30.40, 26.66, 26.43, 25.78, 21.12, 20.35, 19.06, 18.41, 13.00, -5.63, -5.89.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{27}H_{45}O_8Si$ 525.2878, found 525.2878.

20b:

$[\alpha]_D^{20} = +91.7$ (*c* = 0.600 mg/mL, MeOH);

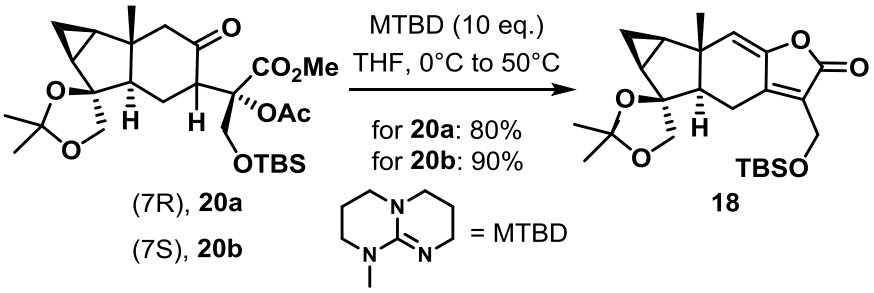
IR (neat, cm^{-1}): 3735.72, 3614.91, 2954.05, 2360.74, 2338.37, 1747.15, 1650.46, 1521.09, 1508.28, 1492.19, 1471.48, 1339.15, 1251.01, 1114.90, 840.32, 779.36, 670.85, 456.97, 420.06.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (d, *J* = 11.1 Hz, 1H), 4.10 (d, *J* = 11.1 Hz, 1H), 4.06 (d, *J* = 7.9 Hz, 1H), 3.91 (d, *J* = 7.9 Hz, 1H), 3.71 (s, 3H), 3.14 (d, *J* = 9.3 Hz, 1H), 2.58 – 2.47 (m, 2H), 2.26 – 2.19 (m, 1H), 2.10 (s, 4H), 1.81 (td, *J* = 14.1, 9.3 Hz, 1H), 1.64 (ddd, *J* = 9.0, 7.2, 3.6 Hz, 1H), 1.44 (s, 3H), 1.38 (td, *J* = 7.9, 7.4, 4.2 Hz, 1H), 1.32 (d, *J* = 4.1 Hz, 3H), 1.20 – 1.16 (m, 1H), 0.88 (d, *J* = 3.4 Hz, 9H), 0.85 (s, 3H), 0.73 (td, *J* = 8.8, 5.6 Hz, 1H), 0.07 (s, 3H), 0.04 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 210.43, 110.21, 86.84, 84.45, 72.62, 63.74, 58.29, 57.60, 52.49, 49.64, 40.56, 30.92, 30.55, 26.77, 26.59, 25.92, 21.35, 20.88, 18.83, 18.42, 13.06, -5.38, -5.54.

HRMS (ESI/$[M+H]^+$) calcd. for 525.2878, found 525.2884.

Procedure for preparation of compound 18



For **20a**: A solution of **20a** (7.8 mg, 0.0149 mmol, 1.0 eq) in THF (1.5 mL) was added MTBD (22.8 mg, 0.149 mmol, 10.0 eq) at 0 ℃. The reaction was warmed to 50 ℃ slowly and stirred for 6 h. The resulting solution was directly purified by flash column chromatography (EA:PE = 1:10) to provide compound **18** (5.2 mg, 80%) as white solid.

For **20b**: The synthetic procedure is identical to **20a**. yield = 90%

$[\alpha]_D^{20} = +25.9$ (*c* = 0.580 mg/mL, MeOH);

IR (neat, cm^{-1}): 3790, 3700, 3661, 2924, 2855, 2361, 1585, 1550, 1531, 1410, 1382, 1269, 1166, 1118, 1020, 966, 732.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.26 (s, 1H), 4.55 (s, 2H), 4.06 (d, *J* = 8.2 Hz, 1H), 3.88 (d, *J* = 8.2 Hz, 1H), 2.95 (dd, *J* = 17.5, 3.4 Hz, 1H), 2.54 (ddt, *J* = 17.6, 16.2, 2.2 Hz, 1H), 2.27 – 2.19 (m, 1H), 1.64 (ddd, *J* = 9.1, 3.9, 1.4 Hz, 2H), 1.44 (s, 3H), 1.33 (s, 3H), 1.30 – 1.26 (m, 1H), 1.07 (s, 3H), 0.92 (s, 9H), 0.84 – 0.78 (m, 1H), 0.10 (d, *J* = 1.8 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.14, 153.46, 150.37, 149.30, 124.87, 122.67, 110.21, 85.99, 72.01, 61.23, 57.74, 41.84, 30.04, 28.76, 26.61, 26.38, 25.86, 23.03, 20.90, 13.54, -5.56.;

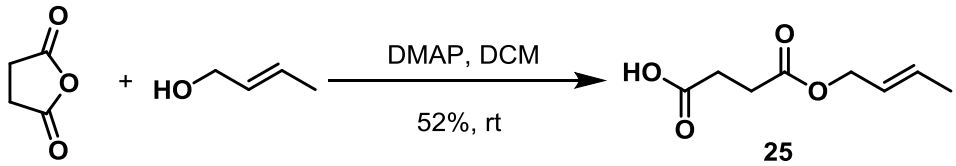
HRMS (ESI/$[M+Na]^+$) calcd. for $C_{25}H_{39}O_5SiNa$ 470.2459, found 470.2451.

Optimization conditions to synthesize compound 18 [a]

Entry	Condition	Yield [b]
1	**10 eq. MTBD, THF, 0 to 50 °C**	**80%**
2	10 eq. DBU, THF, 0 to 40 °C	70%
3	10 eq. DBN, THF, 0 to 40 °C	12%
4	*t*-BuOK, THF, -78 to 0 °C	42%
5	KHMDS, THF, -78 to 0 °C	ND

[a] The reaction was conducted on 0.0149 mmol. [b] Isolated yield.

Procedure for preparation of compound 25



A solution of succinic anhydride (1.73 g, 24.0 mmol, 1.2 eq) and DMAP (1.22 g, 10.0 mmol, 0.5 eq) in DCM (200 mL) was added crotonyl alcohol (2.08 g, 20.0 mmol, 1.0 eq) at 0 ℃. The reaction was warmed up to room temperature slowly. After stirring for overnight, the solution was poured into $NaHCO_3$ (aq.) (100 mL) at 0 ℃. The solution was washed by methyl tert-butyl ether (3 x 50 mL), then the water layer was added 3 N HCl (aq.) until the pH = 2. The aqueous layer was extracted by ethyl ether (3 x 50 mL).

The combined organic layers were dried by Na_2SO_4, filtered by celite pad, and concentrated under vacuum to provide compound **25** (1.77g, 52%) as yellow oil.

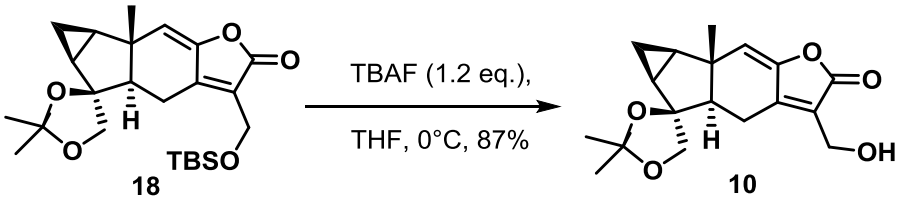
IR (neat, cm^{-1}): 3673.60, 2923.82, 2853.96, 2361.18, 2337.43, 1736.65, 1715.68, 1651.59, 1540.36, 1513.42, 1456.61, 1260.91, 1167.14, 966.36, 801.97, 672.16, 465.23, 422.17.

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 – 5.72 (m, 1H), 5.58 (dtd, *J* = 15.1, 6.6, 1.6 Hz, 1H), 4.53 (d, *J* = 6.6 Hz, 2H), 2.73 – 2.57 (m, 4H), 1.72 (d, *J* = 7.8 Hz, 3H).;

^{13}C NMR (400 MHz, $CDCl_3$) δ 178.10, 172.15, 131.89, 124.93, 65.77, 29.01, 17.93.;

HRMS (ESI/$[M+H]^+$) calcd. for $C_8H_{12}O_4$ 173.0808, found 173.0809.

Procedure for preparation of compound 10



18 10

A solution of compound **18** (9.2 mg, 0.0213 mmol, 1.0 eq) in THF (2.13 mL) was added 1.0 M TBAF in THF (0.03 mL, 0.03 mmol, 1.4 eq) at 0 ℃. After stirring for 30 min, the solution was treated with brine (10 mL) and the aqueous layer was extracted by ethyl acetate (3 x 15 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum, the residue was purified by flash column chromatography (EA: PE = 1: 1.5) on silica gel to provide compound **10** (5.9 mg, 87%) as colorless oil.

$[\alpha]_D^{20} = +70.0$ (*c* = 0.200 mg/mL, MeOH);

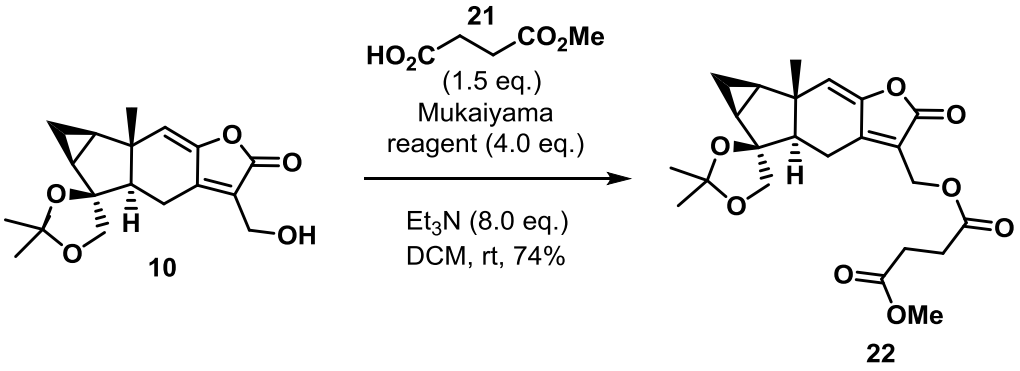
IR (neat, cm^{-1}): 3846, 3701, 3577, 2958, 2920, 2852, 2360, 2073, 1764, 1725, 1692, 1662, 1641, 1586, 1550, 1531, 1465, 1409, 1380, 1268, 1118, 1019, 751.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.34 (s, 1H), 4.47 (s, 2H), 4.08 (d, *J* = 8.3 Hz, 1H), 3.91 (d, *J* = 8.3 Hz, 1H), 2.71 (dd, *J* = 17.2, 3.6 Hz, 1H), 2.59 – 2.47 (m, 1H), 2.25 (dd, *J* = 13.5, 3.6 Hz, 1H), 1.65 (dt, *J* = 8.8, 4.0 Hz, 2H), 1.44 (s, 3H), 1.36 (s, 3H), 1.32 – 1.28 (m, 1H), 1.08 (s, 3H), 0.85 – 0.81 (m, 1H).;

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.18, 150.52, 149.04, 124.31, 123.95, 110.24, 85.83, 72.01, 61.33, 55.19, 42.16, 29.95, 28.67, 26.69, 26.11, 22.98, 20.21, 13.61.;

HRMS (ESI/$[M+H]^+$) calcd. for $C_{19}H_{26}O_5$ 334.1775, found 334.1777.

Procedure for preparation of compound 22



To a solution of mono-methyl succinate (43.9 mg, 0.332 mmol, 1.5 eq) and Mukaiyama reagent (135.9 mg, 0.532 mmol, 4.0 eq) in DCM (1.2 mL) was added Et_3N (0.15 mL, 1.06 mmol, 8.0 eq) and compound **10** (44.3 mg, 0.133 mmol, 1.0 eq) in DCM (1.5 mL) at 0 ℃ in sequence. After stirring for 4h at room temperature, the solution was purified by flash column chromatography (EA:PE = 1:5) on silica gel to provide compound **22** (44.2 mg, 74%) as colorless oil.

$[\alpha]_D^{20} = -22.5$ (c = 0.400 mg/mL, MeOH);

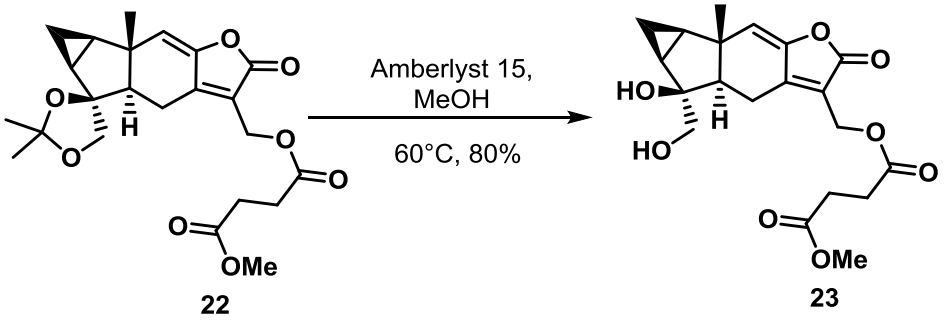
IR (neat, cm^{-1}): 3790, 2958, 2922, 2853, 2349, 2095, 1724, 1464, 1379, 1268, 1117, 1020, 800, 731.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 4.88 (d, J = 2.8 Hz, 2H), 4.08 (d, J = 8.3 Hz, 1H), 3.94 (d, J = 8.3 Hz, 1H), 3.68 (s, 3H), 2.77 (dd, J = 17.4, 3.5 Hz, 1H), 2.64 (s, 4H), 2.62 – 2.48 (m, 1H), 2.30 – 2.22 (m, 1H), 1.65 (dt, J = 8.6, 3.8 Hz, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.25 (s, 1H), 1.08 (s, 3H), 0.83 (td, J = 8.6, 5.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.70, 172.00, 153.68, 149.05, 124.67, 120.49, 110.41, 86.00, 72.14, 61.30, 55.88, 52.05, 42.37, 30.12, 29.05, 28.95, 26.83, 26.36, 23.08, 20.63, 13.75, 1.17.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{23}H_{29}O_8$ 433.1857, found 433.1855.

Procedure for preparation of compound 23



22 23

To a solution of compound **22** (39.2 mg, 0.0988 mmol, 1.0 eq) in MeOH (1.98 mL) was added 44.2 mg Amberlyst 15. Then the reaction was warmed to 60 ℃. and stirred for 10 h. The resulting solution was filtered by celite and concentrated under vacuum. The residue was purified by flash column chromatography (EA to EA: MeOH = 20: 1) on silica gel to provide compound **23** (27.7 mg, 80%) as white solid.

$[\alpha]_D^{20} = -185$ (c = 0.200 mg/mL, MeOH)

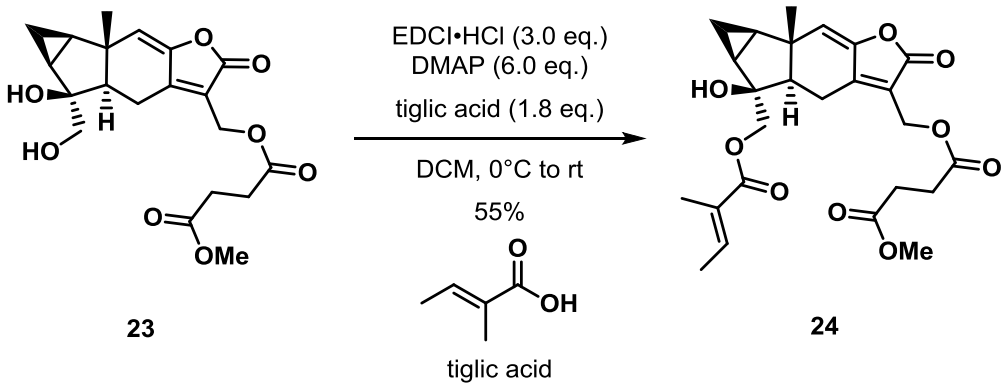
IR (neat, cm^{-1}): 2360.71, 2339.25, 1771.46, 1650.29, 1557.75, 1521.10, 750.36, 671.15;

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 4.91 (s, 2H), 3.83 – 3.71 (m, 2H), 3.69 (s, 3H), 2.93 (dd, J = 17.4, 3.4 Hz, 1H), 2.65 (s, 4H), 2.59 (dd, J = 17.4, 13.9 Hz, 1H), 2.30 – 2.21 (m, 2H), 2.08 (s, 1H), 1.67 (td, J = 8.0, 4.0 Hz, 1H), 1.59 – 1.55 (m, 1H), 1.41 – 1.34 (m, 1H), 1.18 (s, 3H), 0.81 (td, J = 8.6, 6.0 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.24, 172.01, 153.68, 148.94, 133.80, 124.72, 120.44, 79.47, 69.72, 62.36, 56.15, 52.19, 42.89, 29.85, 28.95, 28.88, 28.14, 27.92, 23.03, 21.45, 21.20, 14.34, 12.54.

HRMS (ESI/$[M+Na]^+$) calcd. for $C_{20}H_{24}O_8Na$ 415.1364, found 415.1365.

Procedure for preparation of compound 24



23 tiglic acid 24

To a solution of compound **23** (3.0 mg, 7.65 mmol, 1.0 eq) in DCM (1.99 mL) was added tiglic acid (1.2 mg, 0.0119 mmol, 1.8 eq), EDCI·HCl (2.9 mg, 0.015 mmol, 3.0 eq), DMAP (3.6 mg, 0.0298 mmol, 6.0 eq) at 0 ℃ in sequence. After stirring for 1 h at this temperature, the mixture was purified by flash column chromatography (EA:PE = 1:2) on silica gel to provide compound **24** (2.0 mg, 55%) as colorless oil.

$[\alpha]_D^{20} = -75$ (c = 0.200 mg/mL, MeOH);

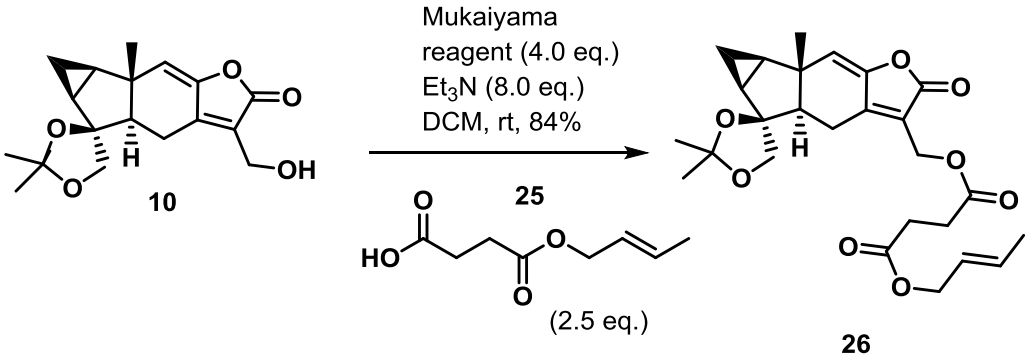
IR (neat, cm^{-1}): 2921.64, 2360.60, 2339.38, 1771.18, 1746.20, 1650.17, 1521.06, 1458.03, 1272.98, 1158.20, 750.17, 671.37, 419.83;

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.54 (s, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.43 (s, 1H), 5.62 (s, 1H), 4.91 (d, J = 14.2 Hz, 1H), 4.81 (d, J = 13.0 Hz, 1H), 4.32 (d, J = 11.2 Hz, 1H), 4.29 – 4.19 (m, 1H), 3.90 (s, 1H), 3.61 (s, 3H), 3.11 – 2.98 (m, 1H), 2.65 – 2.59 (m, 5H), 2.21 (p, J = 2.2 Hz, 3H), 1.89 (p, J = 2.2 Hz, 3H), 1.86 – 1.76 (m, 6H), 1.72 (dd, J = 8.6, 3.9 Hz, 2H), 1.42 – 1.38 (m, 1H), 1.19 (s, 3H), 0.77 (td, J = 8.7, 5.6 Hz, 1H).;

HRMS (ESI/$[M+H]^+$) calcd. for $C_{25}H_{31}O_9$ 475.1963, found 475.1963.

Note: compound **24** is unstable and would decompose at room temperature. So, we are not able to provide its ^{13}C NMR spectrum.

Procedure for preparation of compound 26



To a solution of compound **25** (114.3 mg, 0.664 mmol, 2.5 eq) and Mukaiyama reagent (271.8 mg, 1.06 mmol, 4.0 eq) in DCM (2.4 mL) was added Et_3N (0.30 mL, 2.13 mmol, 8.0 eq) and compound **10** (88.6 mg, 0.266 mmol, 1.0 eq) in DCM (3.0 mL) at 0 ℃ in sequence. After stirring for 4h at room temperature, the resulting solution was purified by column chromatography (EA:PE = 1:5) on silica gel to provide compound **26** (108.8

mg, 84%) as colorless oil.

$[\alpha]_D^{20} = +14.0$ (c = 2.86 mg/mL, MeOH);

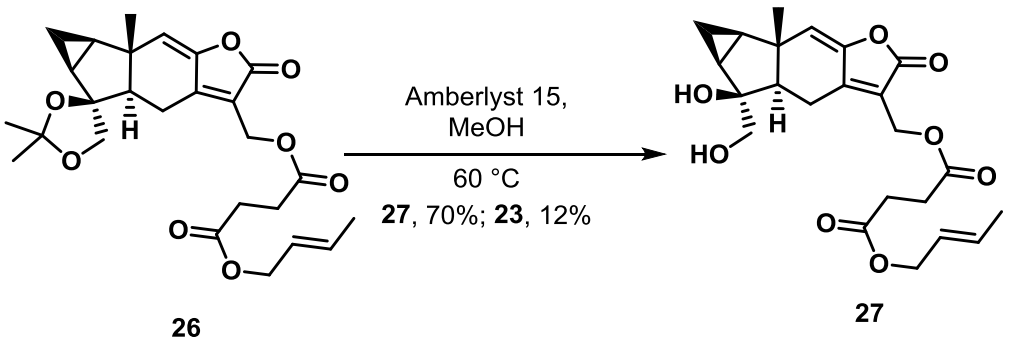
IR (neat, cm^{-1}): 2925, 1771, 1737, 1643, 1442, 1375, 1156, 1058, 1020, 969, 863.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.36 (s, 1H), 5.79 (dd, *J* = 15.2, 6.5 Hz, 1H), 5.64 – 5.52 (m, 1H), 4.88 (s, 2H), 4.51 (d, *J* = 6.5 Hz, 2H), 4.08 (d, *J* = 8.3 Hz, 1H), 3.94 (d, *J* = 8.3 Hz, 1H), 2.77 (dd, *J* = 17.3, 3.5 Hz, 1H), 2.64 (s, 4H), 2.55 (dd, *J* = 17.3, 13.8 Hz, 1H), 2.25 (dd, *J* = 13.6, 3.5 Hz, 1H), 1.72 (d, *J* = 6.4 Hz, 3H), 1.65 (dt, *J* = 8.7, 3.8 Hz, 2H), 1.44 (s, 3H), 1.37 (s, 3H), 1.30 (dd, *J* = 9.7, 4.0 Hz, 2H), 1.25 (s, 3H), 1.08 (s, 3H), 0.88 – 0.80 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.04, 168.52, 153.63, 149.06, 131.79, 125.03, 124.63, 120.51, 110.40, 86.00, 72.13, 65.70, 61.28, 55.89, 42.37, 30.12, 29.85, 29.18, 29.05, 28.82, 26.84, 26.37, 23.08, 20.63, 17.93, 13.75, 1.17.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{26}H_{33}O_8$ 473.2170, found 473.2169.

Procedure for preparation of compound 27



26 **27**

To a solution of compound **26** (108.8 mg, 0.223 mmol, 1.0 eq) in MeOH (4.46 mL) was added 108.8 mg Amberlyst 15. Then the mixture was warmed to 60 ℃ and stirred for 10 h. The resulting solution was filtered by celite pad and concentrated under vacuum. The residue was purified by flash column chromatography (EA to EA: MeOH = 20: 1) on silica gel to provide compound **27** (67.9 mg, 70%) as white solid and compound **23** (10.6 mg, 12%) as colorless oil.

$[\alpha]_D^{20} = -46.5$ (c = 0.380 mg/mL, MeOH);

IR (neat, cm^{-1}): 3789, 3700, 3661, 3493, 2920, 2851, 2359, 1769, 1725, 1641, 1550,

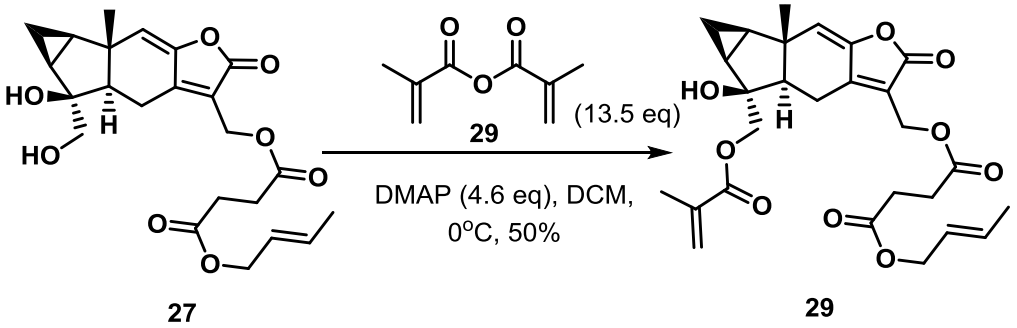
1531, 1448, 1379, 1269, 1157, 1018, 969, 750.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 6.17 (s, 1H), 5.86 – 5.73 (m, 1H), 5.68 – 5.63 (m, 1H), 5.62 – 5.51 (m, 1H), 4.91 (dd, *J* = 12.9, 6.9 Hz, 2H), 4.50 (d, *J* = 6.6 Hz, 2H), 4.38 (d, *J* = 11.2 Hz, 1H), 4.27 (d, *J* = 11.2 Hz, 1H), 2.88 (dd, *J* = 17.4, 3.5 Hz, 1H), 2.64 (s, 5H), 2.29 (dd, *J* = 13.8, 3.5 Hz, 1H), 1.99 (d, *J* = 7.0 Hz, 4H), 1.72 (dd, *J* = 6.5, 1.4 Hz, 4H), 1.69 – 1.65 (m, 2H), 1.40 (dt, *J* = 5.8, 3.9 Hz, 1H), 1.17 (s, 3H), 0.84 – 0.78 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.25, 172.02, 169.06, 167.48, 153.32, 148.90, 135.98, 131.90, 126.65, 124.93, 124.51, 120.68, 78.36, 70.71, 65.79, 62.19, 55.99, 42.87, 29.03, 28.88, 28.09, 23.07, 21.21, 18.56, 17.94, 12.58.

HRMS (ESI/$[M+Na]^+$) calcd. for $C_{23}H_{28}O_8Na$ 455.1677, found 455.1678.

Procedure for preparation of compound 29



27 29

To a solution of compound **27** (2.7 mg, 6.24 μmol, 1.0 eq) in DCM (1.0 mL) was added DMAP (3.4 mg, 0.0278 mmol, 4.6 eq) and compound **28** (13 mg, 0.0843 mmol, 13.5 eq) at 0 ℃. The solution was stirred for 2 h at this temperature. Then the resulting solution was directly purified by flash column chromatography on silica gel (EA: PE = 1: 2) to provide compound **29** (1.6 mg, 3.12 mmol) as colorless oil.

$[\alpha]_D^{20} = -21.2$ (*c* = 0.440 mg/mL, MeOH);

IR (neat, cm^{-1}): 3501, 2920, 2852, 1766, 1734, 1642, 1459, 1377, 1268, 1157, 1101, 1020, 968, 837, 796, 734.

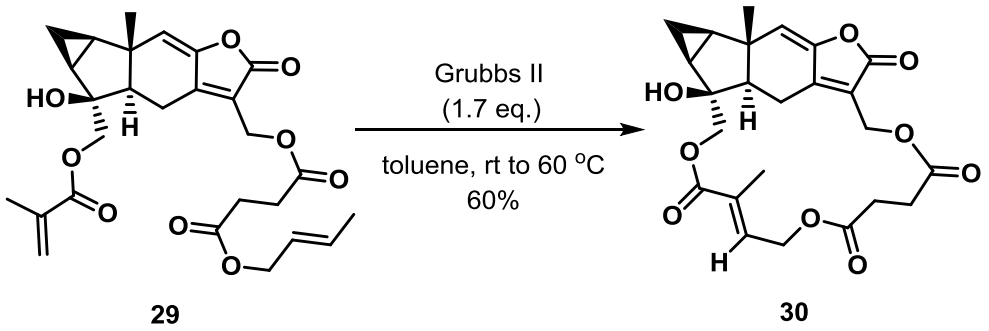
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 5.87 – 5.73 (m, 1H), 5.56 (dtd, *J* = 15.0, 6.6, 1.6 Hz, 1H), 4.91 (s, 2H), 4.50 (d, *J* = 6.6 Hz, 2H), 3.76 (qd, *J* = 10.7, 5.3 Hz, 2H),

2.93 (dd, *J* = 17.4, 3.4 Hz, 1H), 2.65 (s, 4H), 2.63 – 2.53 (m, 1H), 2.33 (t, *J* = 5.4 Hz, 1H), 2.26 (dd, *J* = 13.9, 3.4 Hz, 1H), 2.13 (s, 1H), 1.72 (d, *J* = 7.5 Hz, 3H), 1.67 (td, *J* = 7.9, 3.9 Hz, 1H), 1.58 – 1.53 (m, 1H), 1.41 – 1.35 (m, 1H), 1.17 (s, 3H), 0.80 (td, *J* = 8.6, 5.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.62, 172.04, 169.14, 153.64, 148.90, 132.08, 124.78, 120.41, 79.46, 69.71, 65.91, 62.35, 56.18, 42.86, 29.09, 28.92, 28.11, 27.88, 23.04, 21.45, 17.95, 12.53.

HRMS (ESI/$[M+Na]^+$) calcd. for $C_{27}H_{32}O_9Na$ 523.1939, found 523.1940.

Procedure for preparation of compound 30



29 **30**

To a solution of compound **29** (7.2 mg, 0.0144 mmol, 1.0 eq) in toluene (2.4 mL) was added Grubbs II catalyst (20.6 mg, 0.0242 mmol, 1.7 eq). After stirring for 24 h, the solution was purified by column chromatography (EA:PE = 1:2 to 1:1) on silica gel to provide compound **30** (3.3 mg, 60%) as colorless oil.

$[\alpha]_D^{20} = -80.0$ (*c* = 0.229 mg/mL, MeOH);

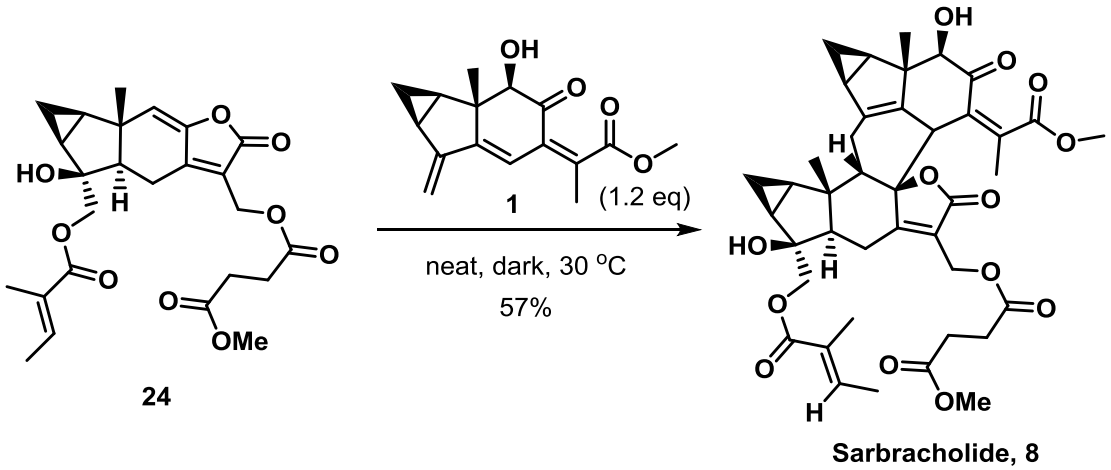
IR (neat, cm^{-1}): 2959, 2919, 2851, 1721, 1462, 1378, 1267, 1119, 1020, 736, 705.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.77 – 6.69 (m, 1H), 6.38 (s, 1H), 4.88 – 4.83 (m, 1H), 4.83 – 4.78 (m, 3H), 4.77 (s, 1H), 4.15 – 4.10 (m, 1H), 3.00 (dd, *J* = 17.3, 3.5 Hz, 1H), 2.82 – 2.57 (m, 7H), 2.44 (dd, *J* = 13.8, 3.5 Hz, 1H), 1.89 (dd, *J* = 4.9, 1.2 Hz, 4H), 1.79 – 1.70 (m, 3H), 1.52 – 1.48 (m, 1H), 1.48 – 1.44 (m, 1H), 1.19 (s, 3H), 0.90 – 0.79 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.50, 170.83, 167.03, 154.98, 148.78, 135.84, 129.68, 124.76, 119.94, 78.69, 72.64, 64.10, 62.09, 56.35, 43.34, 29.62, 28.99, 28.30, 27.82, 22.94, 22.16, 13.21, 12.35.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{24}H_{27}O_9$ 459.1650, found 459.1648.

Procedure for preparation of compound sarbracholide (8)



Compound **24** (2.0 mg, 4.21 mmol, 1.0 eq) and compound **1** (0.5 mg, 1.83 mmol, 0.4 eq) in DCM (0.5 mL) were added to a 10 mL test tube. Then the solution was removed under vacuum. The residue was placed in darkness at 30 ℃. Then another portion of compound **1** (0.5 mg, 1.83 mmol, 0.4 eq) in DCM (0.5 mL) was added to the reaction tube after 8 h and 16 h respectively while DCM was removed sequentially under vacuum. The mixture was dissolved in DCM and purified by flash column chromatography (EA:PE = 1:1) to provide sarbracholide (1.8 mg, 57%) as light yellow oil.

$[\alpha]_D^{20} = -120$ (c = 0.400 mg/mL, MeOH);

IR (neat, cm^{-1}): 3735.36, 2360.73, 2339.31, 1699.53, 1540.24, 1271.52, 1157.37, 992.37, 736.46.

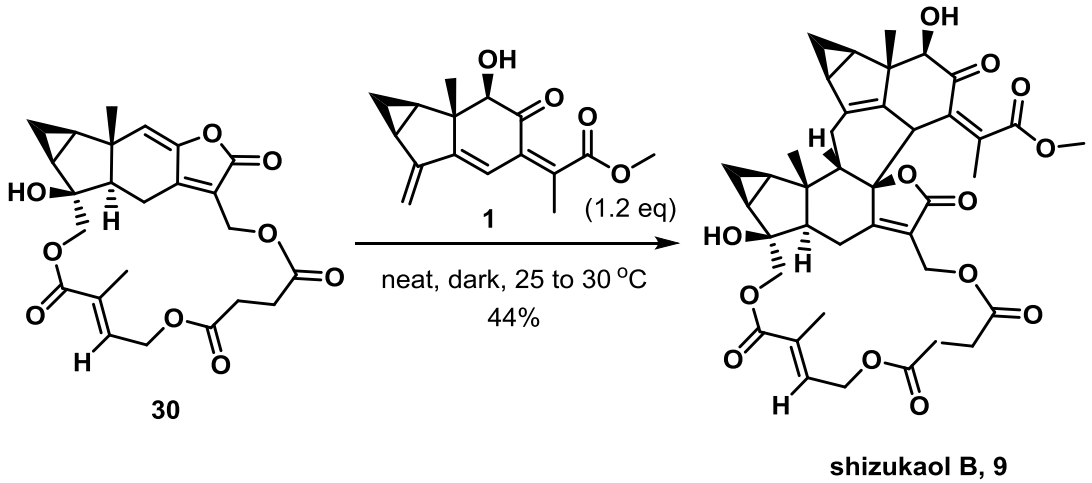
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (dd, J = 6.7, 1.1 Hz, 1H), 4.86 (s, 2H), 4.19 (d, J = 11.6 Hz, 1H), 3.95 (d, J = 1.4 Hz, 1H), 3.93 – 3.90 (m, 1H), 3.83 (d, J = 11.6 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H), 3.46 – 3.35 (m, 1H), 2.82 – 2.68 (m, 2H), 2.65 (s, 4H), 2.63

– 2.59 (m, 1H), 2.38 (d, *J* = 5.4 Hz, 2H), 2.10 – 2.02 (m, 1H), 1.89 – 1.82 (m, 12H), 1.81 – 1.75 (m, 1H), 1.29 (d, *J* = 6.0 Hz, 1H), 1.06 – 0.95 (m, 4H), 0.87 (s, 3H), 0.76 – 0.67 (m, 1H), 0.29 (q, *J* = 4.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.41, 172.89, 172.15, 172.06, 171.41, 170.53, 168.31, 147.49, 142.50, 138.87, 131.87, 131.42, 128.23, 123.52, 93.44, 80.31, 77.51, 71.03, 60.61, 55.75, 55.63, 52.69, 52.16, 51.21, 44.80, 40.95, 29.85, 28.78, 28.69, 28.23, 26.47, 25.87, 25.46, 25.40, 24.88, 22.74, 20.56, 16.05, 15.38, 14.68, 12.27, 12.03.

HRMS (ESI/$[M+Na]^+$) calcd. for $C_{27}H_{45}O_8Si$ 771.2987, found 771.2995.

Procedure for preparation of compound *Shizukaol B* (9)



Compound **30** (2.0 mg, 4.36 mmol, 1.0 eq) and compound **1** (0.5 mg, 1.83 mmol, 0.4 eq) in DCM (0.5 mL) were added to a 10 mL test tube, the solution was removed under vacuum. This mixture is placed in the darkness and reacted at 30 ℃. Another portion of compound **1** (0.5 mg, 1.83 mmol, 0.4 eq) in DCM (0.5 mL) was added to the reaction tube after 8 and 16 h respectively while DCM was removed sequentially under vacuum. The mixture was dissolved in DCM and purified by flash column chromatography (EA: PE = 1:1) to provide shizukaol B (1.4 mg, 44%) as light yellow oil.

$[\alpha]_D^{20} = -116.2$ (*c* = 0.400 mg/mL, MeOH);

IR (neat, cm^{-1}): 2918.30, 2849.70, 2360.67, 2339.33, 1734.34, 1434.80, 1265.03, 1174.58, 994.55, 736.10, 703.35.

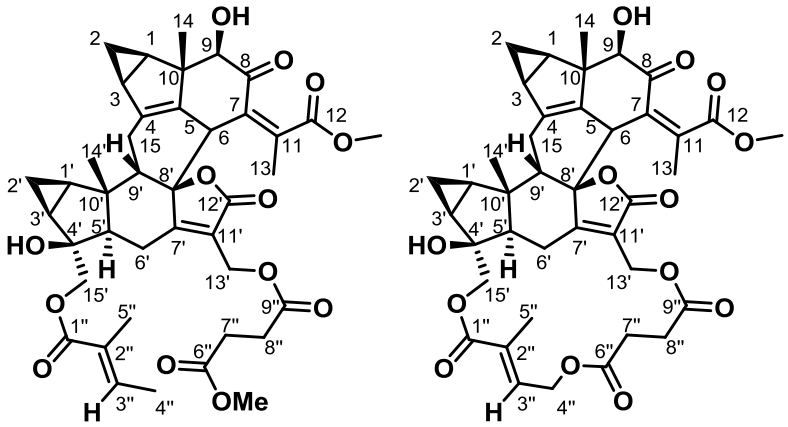
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.67 – 6.59 (m, 1H), 5.07 (d, *J* = 12.0 Hz, 2H), 4.67 – 4.62 (m, 1H), 4.57 (dd, *J* = 23.9, 11.9 Hz, 2H), 3.99 – 3.86 (m, 2H), 3.71 (s, 3H), 3.62

(d, *J* = 11.8 Hz, 1H), 3.29 (s, 1H), 2.95 – 2.84 (m, 1H), 2.84 – 2.74 (m, 2H), 2.74 – 2.65 (m, 1H), 2.65 – 2.55 (m, 1H), 2.54 – 2.44 (m, 2H), 2.06 (dt, *J* = 10.0, 4.4 Hz, 1H), 1.96 (s, 3H), 1.92 – 1.91 (m, 3H), 1.89 (d, *J* = 6.6 Hz, 1H), 1.86 (d, *J* = 6.1 Hz, 2H), 1.60 (s, 2H), 1.45 – 1.36 (m, 1H), 1.34 (dd, *J* = 5.5, 4.2 Hz, 1H), 1.03 (s, 4H), 0.82 (s, 3H), 0.74 (td, *J* = 8.8, 5.8 Hz, 1H), 0.33 (q, *J* = 4.1 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 200.86, 174.68, 172.10, 171.83, 171.69, 170.33, 167.16, 147.81, 135.69, 132.22, 131.40, 129.34, 123.50, 93.37, 80.11, 77.11, 71.98, 61.84, 61.39, 55.63, 54.46, 52.56, 51.12, 45.05, 41.19, 29.28, 28.76, 27.87, 26.18, 26.09, 25.72, 25.52, 24.93, 23.50, 20.30, 16.13, 15.42, 13.17, 11.82.

HRMS (ESI/$[M+H]^+$) calcd. for $C_{27}H_{45}O_8Si$ 771.2987, found 771.2997.

3 Tabular Comparison of NMR data between Synthetic Sample and Natural One



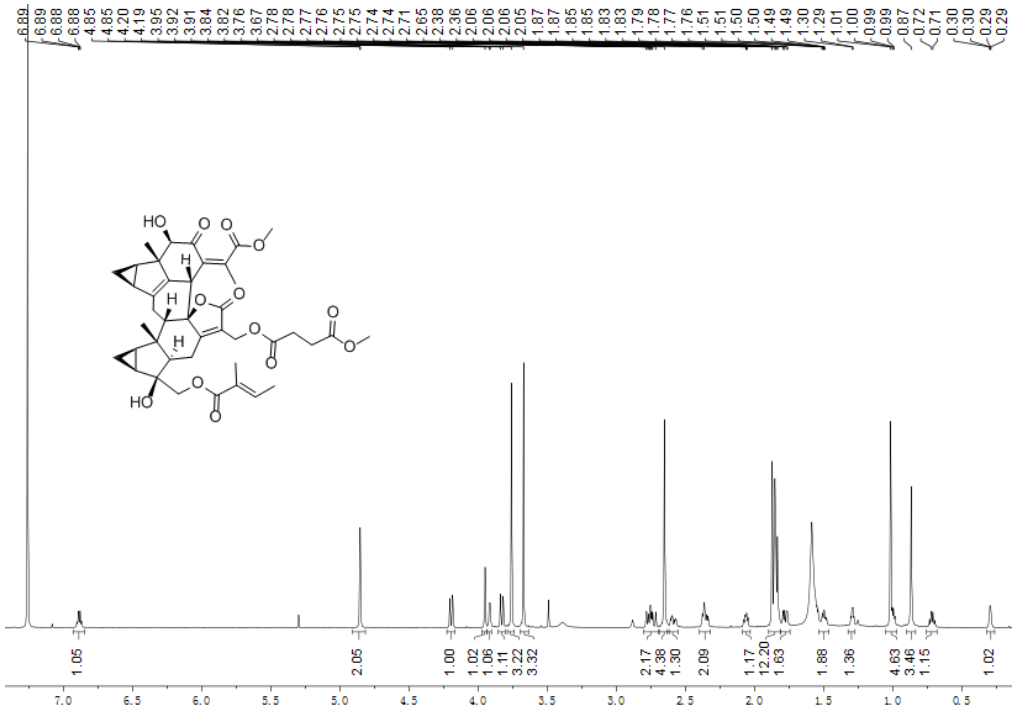
Sarbracholide, 8 Shizukaol B, 9

Table 1. Comparison of ^{1}H NMR data of natural sarbracholide and synthetic sarbracholide

No.	**Sarbracholide (Natural)[a]**	**Sarbracholide (Synthetic)[c]**	Δ/Hz
	δ_H (mult, *J* in Hz)	δ_H (mult, *J* in Hz)	
1	2.06, ddd (8.2, 5.8, 4.2)	2.10-2.02, m	0
2	α 1.01, m β 0.29, ddd (4.4,	α 1.06-0.95, m β 0.29, q(4.0)	α 0.005 β 0

	4.4, 3.0)		
3	1.83, m	1.89-1.82, m	0.025
6	3.91, brd (3.8)	3.93-3.90, m	0.005
9	3.95, s	3.95, d(1.4)	0
13	1.87, brs	1.89-1.82, m	0.015
14	1.01, s	1.06-0.95, m	0.005
15	α 2.76, dd (16.5, 1.2) β 2.58, ddd (16.5, 6.1, 4.0)	α 2.82-2.68, m β 2.63-2.59, m	α 0.01 β 0.03
1′	1.56, ddd (8.6, 7.5, 3.9)	1.56, m	0
2′	α 0.71, ddd (9.0, 8.6, 5.8) β 1.29, ddd (5.8, 3.9, 3.8)	α 0.76-0.67, m β 1.29, d(6.0)	α 0.005 β 0
3′	1.50, ddd (9.0, 7.5, 3.8)	1.53 – 1.45, m	0.01
5′	1.78, dd (13.8, 6.0)	1.81-1.75, m	0
6′	α 2.36, dd (18.5, 6.0) β 2.76, dd (18.5, 13.8)	α 2.38, d(5.4) β 2.82-2.68, m	α 0.02 β 0.01
9′	1.86, m	1.89-1.82, m	0.005
13′	4.84, s	4.86, s	0.02
14′	0.87, s	0.87, s	0
15′	4.19, d (11.6) 3.83, d (11.6)	4.19, d(11.6) 3.83, d(11.6)	0 0
3″	6.89, qq (7.0, 1.3)	6.89, dd (6.7, 1.1)	0
4″	1.84, dq (7.0, 1.2)	1.89-1.82, m	0.015
5″	1.86, dq (1.3, 1.2)	1.89-1.82, m	0.005
7″	2.65, m	2.65, s	0
8″	2.65, m	2.65, s	0
12-OMe	3.76, s	3.76, s	0
6″-OMe	3.68, s	3.67, s	

Natural sarbracholide



Synthetic sarbracholide

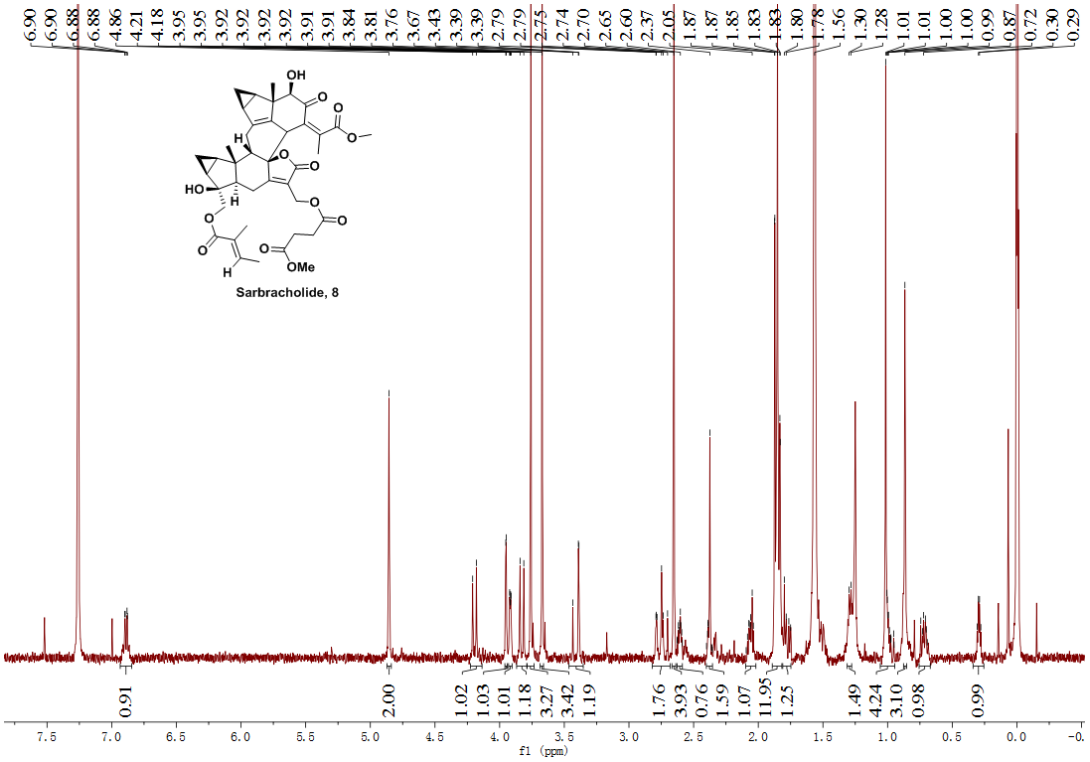
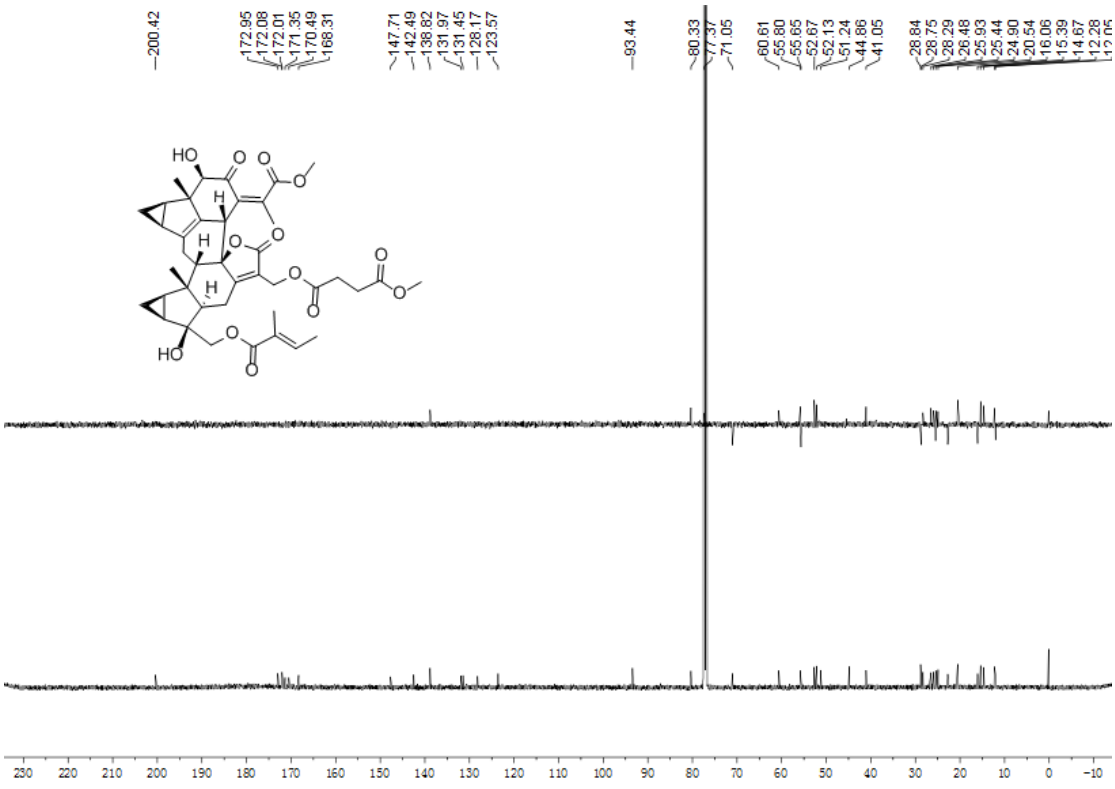


Table 2. Comparison of ^{13}C NMR data of natural sarbracholide and synthetic sarbracholide

No.	**Sarbracholide (Natural)** [a]	**Sarbracholide (Synthetic)** [b]	Δ/Hz
	δ_C	δ_C	
1	25.8	25.9	0.1
2	16.1	16.0	0.1
3	24.9	24.9	0
4	142.5	142.5	0
5	132.0	131.9	0.1
6	41.1	41.0	0.1
7	131.5	131.4	0.1
8	200.4	200.4	0
9	80.3	80.3	0
10	51.2	51.2	0
11	147.7	147.5	0.2
12	170.5	170.5	0
13	20.5	20.6	0.1
14	15.4	15.4	0
15	25.5	25.5	0
1’	25.4	25.4	0
2’	12.0	12.0	0
3’	28.3	28.2	0.1
4’	77.5	77.5	0
5’	60.6	60.6	0
6’	22.8	22.7	0.1
7’	172.0	172.1	0.1
8’	93.4	93.4	0
9’	55.8	55.8	0
10’	44.9	44.8	0.1
11’	123.6	123.5	0.1
12’	171.4	171.4	0
13’	55.7	55.6	0.1
14’	26.5	26.5	0
15’	71.1	71.0	0.1
1’’	168.3	168.3	0
2’’	128.2	128.2	0
3’’	138.8	138.9	0.1
4’’	14.7	14.7	0
5’’	12.3	12.3	0
6’’	173.0	172.9	0.1
7’’	28.9	28.8	0.1
8’’	28.8	28.7	0.1
9’’	172.1	172.2	0.1
12-OMe	52.7	52.7	0
6’’-OMe	52.1	52.2	0.1

Natural sarbracholide



Synthetic sarbracholide

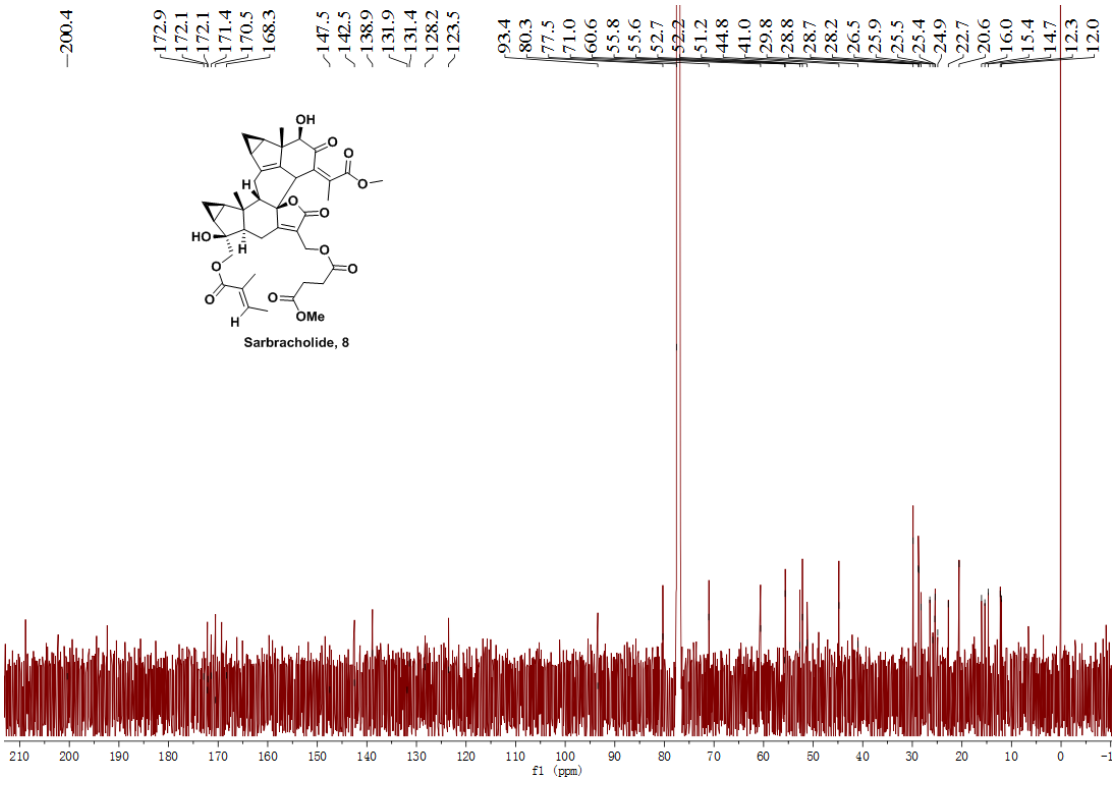


Table 3. Comparison of ^{1}H NMR data of natural shizukaol B and synthetic shizukaol B

No.	**Shizukaol B (Natural)**[b]	**Shizukaol B (Synthetic)**[c]	Δ/Hz
	δ_H (mult, *J* in Hz)	δ_H (mult, *J* in Hz)	
1	2.06, ddd(7.6, 7.6, 3.9)	2.06, dt(10.0, 4.4)	0
2	α 1.02, ddd(7.6, 7.3, 3.8) β 0.33, ddd(3.9, 3.8, 3.2)	α 1.03, s β 0.33, q(4.1)	α 0.01 β 0
3	1.88, m	1.89, d(6.6)	0.01
6	3.9, d(3.1)	3.96, d(3.7)	0.06
9	3.88, s	3.89, s	0.01
13	1.96, s	1.96, s	0
14	1.03, s	1.03, s	0
15	α 2.81, br d(16.2) β 2.59, ddd(16.2, 4.6, 3.1)	α 2.84-2.74, m β 2.65-2.55, m	α 0.02 β 0.01
1′	1.61, ddd(8.6, 7.6, 4.0)	1.60, s	0.01
2′	α 0.74, ddd(8.6, 8.6, 5.3) β 1.34, ddd(5.3, 4.0, 3.4)	α 0.74, td(8.8, 5.8) β 1.34, dd(5.2, 4.2)	α 0 β 0
3′	1.40, ddd(8.6, 7.6, 3.4)	1.45-1.36, m	0.045
5′	1.86, dd(13.3, 6.2)	1.86, d(6.1)	0
6′	α 2.5, dd(13.3, 6.2) β 2.7, dd(18.5, 13.3)	α 2.51, d(6.0) β 2.84-2.74, m	α 0 β 0.09
9′	1.85, dd(4.6, 0.9)	1.86, d(6.1)	0.01
13′	4.54, d(11.9) 5.07, d(11.9)	4.57, dd(23.9, 11.9) 5.07, d(12.0)	0.03 0
14′	0.82, s	0.82, s	0
15′	3.63, d(11.4)	3.62, d(11.8)	0.01
3″	6.62, br dd(6.9, 4.7)	6.67-6.59, m	0.01
4″	4.64, dd(14.9, 6.9)	4.67-4.62, m	0.005
5″	1.92, s	1.91, s	0.01
7″	2.48, ddd(17.3, 7.3, 2.7) 2.89, ddd(17.3, 10.2, 2.9)	2.49-2.45, m 2.95-2.84, m	0.01 0.005
8″	2.67, ddd(17.2,	2.74-2.65, m	0.025

	7.3, 2.9) 2.79, ddd(17.2, 10.2, 2.7)	2.84-2.74, m	0
12-OMe	3.71, s	3.71, s	0

[a] The data is acquired from a Bruker DRX 600 MHz NMR spectrometer. [b] The data is acquired from a Bruker DRX 500 MHz NMR spectrometer. [c] The data is acquired from a Bruker DRX 400 MHz.

Table 4. Comparison of ^{13}C NMR data of natural shizukaol B and synthetic shizukaol B

No.	**Shizukaol B (Natural)**[a]	**Shizukaol B (synthetic)**[b]	Δ/Hz
	δ_C	δ_C	
1	26.0	26.2	0.2
2	16.0	16.1	0.1
3	24.8	24.9	0.1
4	142.5	142.6	0.1
5	132.2	132.2	0
6	41.1	41.0	0.1
7	131.3	131.4	0.1
8	200.7	200.9	0.2
9	79.9	80.1	0.2
10	51.0	51.1	0.1
11	147.5	147.8	0.3
12	171.0	170.3	0.3
13	20.1	20.3	0.2
14	15.3	15.4	0.1
15	25.4	25.5	0.1
1’	25.6	25.7	0.1
2’	11.7	11.8	0.1
3’	27.8	27.9	0.1
4’	77.1	77.1	0
5’	61.2	61.4	0.2
6’	23.4	23.5	0.1
7’	174.5	174.7	0.2
8’	93.2	93.4	0.2
9’	55.5	55.6	0.1
10’	44.9	45.0	0.1
11’	123.4	123.5	0.1
12’	171.7	171.8	0.1
13’	54.3	54.5	0.2
14’	26.0	26.1	0.1
15’	72.0	72.0	0
1’’	167.0	167.2	0.2
2’’	129.0	129.3	0.3
3’’	135.5	135.7	0.2

4”	61.6	61.8	0.2
5”	13.0	13.2	0.2
6”	171.5	171.7	0.2
7”	28.6	28.8	0.2
8”	29.2	29.3	0.1
9”	172.0	172.1	0.1
12-OMe	52.4	52.6	0.2

[a] The data is acquired from a Bruker DRX 125 MHz NMR spectrometer. [b] The data is acquired from a Bruker DRX 150 MHz NMR spectrometer.

Note: There was no reported spectrum of natural shizukaol B.

4. Computational Details and Optimized Structures

4.1. Computational Methodologies

All density functional theory (DFT) calculations were performed through the Gaussian 09 software[2]. Optimized geometry and harmonic frequencies of all the structures were obtained at the B3LYP[3]/def2-SVP[4,5] level of theory. Single point energy calculations were performed at the M06-2X[6]/def2-TZVPP[7] level of theory. During the geometry optimizations and harmonic frequency calculations, Grimme’s D3 dispersion correction [8] and the IEFPCM[9,10] implicit solvation (THF) model were invoked. And during the single point energy calculations, Grimme’s D3 dispersion correction [8] and the SMD[11] implicit solvation (THF) model were invoked. Normal mode analyses were performed to all optimized structures, to confirm that these structures are corresponding to local minima (zero imaginary frequencies) or local maxima (one imaginary frequencies) on the potential energy surface. Structures of transition states were further verified by the intrinsic reaction coordinate (IRC) calculations.

4.2. B3LYP-D3(BJ)/def2-SVP/IEFPCM calculated Cartesian coordinates.

INT1a

```
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 C               -2.28644800   -2.83722100   -0.06617100
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 C               -5.69653700   -1.00687100   -0.86295900
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 C               -2.93234100   -1.33301700   -1.95355500
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 Si               3.65864500    1.95681200   -0.40670300
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INT1b

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H	-6.97722400	-0.49269000	-1.78754000
H	-7.12737100	0.34128800	1.37173200
H	-7.08639800	2.11223600	1.51764700
H	-7.40619100	1.36022000	-0.06142900
H	-3.83975500	2.63317900	-0.34347100
H	-5.21697000	3.45790000	0.42859900
H	-5.43488800	2.65487300	-1.14325100
H	-4.75042400	2.11064200	2.51892400
H	-4.79654100	0.33495300	2.49638800
H	-3.43485600	1.20293900	1.73285700
C	-1.02602400	1.21852200	-0.52697700
O	-1.22748500	2.11275600	0.25265500
O	-0.77149500	1.39160100	-1.82652400
C	-0.80310700	2.73720900	-2.31135200
H	-0.52660100	2.68534400	-3.37039900
H	-1.81345600	3.15750300	-2.20194900
H	-0.08977300	3.36540700	-1.75872100
O	-1.36816000	-0.30544200	1.22409600
C	-1.51978400	-1.44387500	1.89060000
C	-1.80086200	-1.19883300	3.34556400
H	-2.72153200	-0.60581800	3.44670700
H	-1.90545300	-2.15477800	3.87060500

H	-0.98285700	-0.60825600	3.78394200
O	-1.45190900	-2.55581800	1.39205800

TSa

C	-3.17938700	-1.66277400	-0.43391200
C	-2.84588800	-0.50003700	0.53537400
C	-1.49053700	0.11488300	0.24863800
C	-0.45196500	-0.98518900	0.09470000
C	-0.81195000	-2.34639100	0.11129500
C	-2.24439500	-2.80776200	-0.04019900
C	-4.66736600	-1.91984400	-0.11932900
C	-5.23358500	-0.67074000	0.53537500
C	-4.10009000	0.37619000	0.60225300
C	-5.71618100	-1.09907700	-0.82009200
C	-4.19619300	1.31135600	1.80695300
C	-2.93797600	-1.31010300	-1.91463600
O	-4.12479800	1.31699500	-0.47559300
O	-5.03537600	2.34940900	1.34112400
C	-4.79694300	2.50813200	-0.05720900
C	-3.86921400	3.68990400	-0.31441900
C	-6.14190500	2.63839100	-0.75661300
O	0.06665500	-3.28011300	0.24416700
C	0.89867000	-0.64161000	-0.14514400
C	1.21018600	0.80056400	-0.49498100
O	2.54148500	0.96904500	-0.86580500
Si	3.69931400	2.02300100	-0.21811000
C	5.33927700	1.05518200	-0.21347400
C	3.17647900	2.55329900	1.50664000
C	3.79507600	3.51785000	-1.35616900
C	6.50103100	2.02584400	0.06602700
C	5.54209000	0.38618000	-1.58499200
C	5.29444700	-0.03034900	0.87622000
H	-2.79841000	-0.96526600	1.53699500
H	-1.19562800	0.79408700	1.06715200
H	-1.54898500	0.73781800	-0.65846400
H	-2.54914100	-3.25686000	0.92177600
H	-2.24448900	-3.63021000	-0.77527000
H	-4.94694600	-2.91220300	0.24609600
H	-5.91887100	-0.73038900	1.38457700
H	-6.72366000	-1.51980400	-0.87567400
H	-5.43503100	-0.48481000	-1.67655100
H	-4.65774800	0.84355700	2.68724000
H	-3.19546700	1.69129300	2.08776300
H	-3.37909200	-0.34143900	-2.18021300
H	-1.86336800	-1.26267200	-2.14387000
H	-3.38380200	-2.08557400	-2.55648600
H	-3.61719700	3.74961600	-1.38347000
H	-4.35271200	4.63007500	-0.01112200
H	-2.93774300	3.56642700	0.25723800
H	-6.67853800	3.52413500	-0.38569000
H	-5.99824200	2.74146400	-1.84201800
H	-6.74837600	1.74415800	-0.55790100
H	0.88252100	-2.98631600	1.05752800
H	0.91249600	1.43865800	0.35256900
H	0.55066900	1.06311800	-1.34402900
H	2.31479600	3.23972900	1.47315500
H	4.00211600	3.08139600	2.01047600
H	2.89779500	1.67439100	2.10596800
H	4.12478600	3.23456400	-2.36844400
H	2.80303200	3.99104500	-1.44253500
H	4.49623000	4.27387000	-0.96734700
H	6.38439300	2.54328900	1.03302900
H	7.45842500	1.47546000	0.10381400
H	6.59489600	2.79523500	-0.71723200
H	4.73693800	-0.33254000	-1.79765700
H	6.50084100	-0.16327400	-1.60391400
H	5.56976700	1.12336200	-2.40442500
H	6.23366900	-0.61333300	0.87216600
H	5.18137000	0.40431400	1.88236700

H	4.46014100	-0.72459800	0.70716700
C	1.80039200	-1.60031100	-0.92310900
O	2.83520300	-2.10358700	-0.57132700
O	1.28642500	-1.72614100	-2.15329500
C	2.02745600	-2.53963300	-3.07008900
H	1.45598200	-2.53909100	-4.00499700
H	3.03032900	-2.11941900	-3.23336200
H	2.12374600	-3.56244100	-2.67871900
O	1.90853300	-0.59036400	1.53533300
C	2.06952100	-1.61825300	2.24407100
C	2.96614500	-1.48385900	3.45217600
H	2.97190800	-0.45221300	3.82533100
H	2.65925700	-2.18523600	4.23887500
H	3.99026200	-1.74249200	3.13832600
O	1.57481300	-2.76573700	2.02804500

TSb

C	3.10163400	-1.86958100	-0.50537900
C	2.88100700	-0.36263800	-0.77332900
C	1.63840700	0.17385400	-0.09409400
C	0.43396800	-0.69814800	-0.45129900
C	0.61838300	-2.04776700	-0.83345300
C	1.97247700	-2.59607400	-1.24133700
C	4.50726200	-2.09212800	-1.09987000
C	5.20979300	-0.74438400	-1.15122600
C	4.24191400	0.30772000	-0.56480300
C	5.71501500	-1.82585300	-0.24157300
C	4.39682500	1.69958100	-1.17870200
C	3.02167200	-2.23925700	0.98819400
O	4.46809100	0.58763600	0.81880800
O	5.39051500	2.29773100	-0.37128200
C	5.24000900	1.78486900	0.95140300
C	4.45598100	2.75980000	1.82250400
C	6.62322100	1.46716000	1.49809600
O	-0.34231300	-2.90613400	-0.83855200
C	-0.86157900	-0.14387300	-0.35505500
C	-2.08009500	-0.59779100	-1.14997300
O	-3.14482800	0.26926300	-0.88725200
Si	-4.79274300	-0.08110200	-0.75218800
C	-5.43976300	1.12725000	0.56854300
C	-5.01538700	-1.88461100	-0.26350100
C	-5.59443400	0.22684600	-2.42405800
C	-6.97882000	1.11000800	0.57066600
C	-4.93645300	2.54730800	0.24970100
C	-4.91395800	0.70536200	1.95208500
H	2.71826400	-0.28312300	-1.86348400
H	1.46809800	1.21117800	-0.41465000
H	1.77754400	0.20733400	0.99859200
H	2.08006800	-2.46547500	-2.33305900
H	1.96521700	-3.67810500	-1.04376800
H	4.60494300	-2.80172600	-1.92652000
H	5.81645000	-0.44963000	-2.01113500
H	6.64807700	-2.31726100	-0.52968100
H	5.59215800	-1.68473000	0.83302300
H	4.74354800	1.68107500	-2.22087800
H	3.44246400	2.25755900	-1.13034200
H	3.63687400	-1.57585900	1.60773600
H	1.98882800	-2.17565200	1.36340200
H	3.36358700	-3.27547200	1.13351100
H	4.27377600	2.32140900	2.81466200
H	5.01523400	3.69872300	1.94649600
H	3.48386700	2.98003100	1.35750500
H	7.23226100	2.38190000	1.54853400
H	6.54358700	1.03993600	2.50821500
H	7.12109800	0.74229100	0.83924300
H	-1.04905500	-2.75518500	0.06160600
H	-2.34023600	-1.63987500	-0.94618600
H	-1.78357800	-0.53457400	-2.21462600
H	-4.79167100	-2.55312900	-1.11072100

H	-6.06045700	-2.06766900	0.03462400
H	-4.36681100	-2.17968200	0.57422500
H	-5.49703800	1.28137500	-2.72727400
H	-5.11165800	-0.39442700	-3.19622200
H	-6.66651500	-0.02754300	-2.40815800
H	-7.38020500	0.10306500	0.77410800
H	-7.36887000	1.78197700	1.35615600
H	-7.39676700	1.44990900	-0.39046300
H	-3.83768300	2.59689600	0.28108100
H	-5.32843900	3.26618200	0.99169600
H	-5.26510000	2.88993700	-0.74543100
H	-5.23885100	1.42842500	2.72193600
H	-5.30094800	-0.28295800	2.24919800
H	-3.81495800	0.66021500	1.97076500
C	-0.89755400	1.37465100	-0.18788400
O	-0.95005100	2.00946700	0.83048100
O	-0.81463100	1.91746400	-1.41128400
C	-0.87268700	3.34653000	-1.48123200
H	-0.73418400	3.60457800	-2.53720200
H	-1.85026200	3.70474900	-1.12698500
H	-0.07982900	3.79761200	-0.86768300
O	-1.60919500	-0.51669400	1.47791200
C	-1.87267800	-1.69233600	1.82947300
C	-2.52707900	-1.88407500	3.18046100
H	-3.61482200	-1.96919400	3.02987300
H	-2.17523000	-2.81703800	3.64070800
H	-2.33339600	-1.02535300	3.83429300
O	-1.67676900	-2.74771000	1.14588800

INT2a

C	-2.69505500	1.84040600	-0.55292600
C	-1.97233200	0.47954800	-0.43838600
C	-1.06926400	0.39362500	0.77502400
C	-0.04196700	1.50756600	0.69870700
C	-0.42937600	2.82124000	0.05567700
C	-1.61073700	2.86421700	-0.90958500
C	-3.70419000	1.55317000	-1.68560400
C	-3.89512600	0.04701100	-1.77554200
C	-3.03138500	-0.60720300	-0.68599300
C	-5.03072900	0.93067500	-1.34347600
C	-2.44608000	-1.98008200	-1.06194300
C	-3.37547100	2.28930100	0.75290800
O	-3.75600400	-0.89993400	0.51618100
O	-2.38222400	-2.66811500	0.17117900
C	-3.51267200	-2.24949900	0.92621300
C	-3.15045200	-2.28155900	2.39979900
C	-4.73762200	-3.10341400	0.60159900
O	0.21187200	3.83244100	0.28495600
C	1.22239700	1.36072800	1.15092500
C	1.74090600	0.14219100	1.87743700
O	2.77473500	-0.48100500	1.14958700
Si	2.56987500	-1.47931300	-0.20797200
C	4.35616400	-1.97400800	-0.63316600
C	1.76750400	-0.53886400	-1.62690300
C	1.49945200	-2.95510600	0.25962700
C	4.36331500	-2.95807000	-1.81632600
C	5.00954700	-2.63517300	0.59343400
C	5.14028700	-0.70311000	-1.01166000
H	-1.33088200	0.42428200	-1.33563100
H	-0.57541700	-0.58478900	0.81297100
H	-1.66889300	0.47271000	1.69483000
H	-1.19780300	2.64214200	-1.91060600
H	-1.98240100	3.89945700	-0.93372000
H	-3.63567300	2.15735300	-2.59453800
H	-3.95801100	-0.46266000	-2.74082700
H	-5.84465000	1.07156300	-2.05942500
H	-5.35109500	0.87569300	-0.30244100
H	-3.09735000	-2.50318500	-1.78538600
H	-1.43382800	-1.91875900	-1.48344100

H	-3.97729100	1.48777300	1.19849000
H	-2.63633000	2.60263600	1.50687300
H	-4.02683100	3.15415600	0.55520000
H	-3.98517000	-1.89468500	3.00132500
H	-2.93732600	-3.31301900	2.71559900
H	-2.26172100	-1.66227800	2.57938800
H	-4.56471600	-4.14941600	0.89470800
H	-5.61404700	-2.72201100	1.14511600
H	-4.96223300	-3.06871200	-0.47420800
H	0.92740300	-0.55998500	2.11480900
H	2.16499800	0.48813600	2.83553000
H	0.68330300	-0.43506300	-1.47528800
H	1.92030900	-1.07696200	-2.57652300
H	2.19167000	0.47150200	-1.71772000
H	1.45586000	-3.66883100	-0.57965300
H	1.90364500	-3.48663000	1.13556300
H	0.46027500	-2.66497200	0.48570000
H	3.90341900	-2.52365100	-2.71889900
H	5.40021000	-3.23508900	-2.07845800
H	3.82438200	-3.88993500	-1.58006500
H	4.99907900	-1.96161500	1.46385200
H	6.06098400	-2.89661800	0.37645800
H	4.49136300	-3.56465200	0.88062800
H	6.19482800	-0.95115200	-1.22928000
H	4.72344400	-0.21789100	-1.90903900
H	5.12804100	0.03601000	-0.19539000
C	2.29377600	2.39856900	0.96996400
O	2.84845500	2.94925900	1.89255200
O	2.65216600	2.53648900	-0.31308300
C	3.66044000	3.51160200	-0.58819900
H	3.86906000	3.44045800	-1.66184200
H	3.29083900	4.51695100	-0.33736000
H	4.57030600	3.30647700	-0.00630000

INT2b

C	-2.31847400	1.96143800	0.20116600
C	-2.54997000	0.74591900	-0.73157800
C	-1.29553900	-0.08499500	-0.90883300
C	-0.09169900	0.80028400	-1.21847100
C	-0.26739100	2.29329200	-1.29201700
C	-1.47129600	2.94368700	-0.60737800
C	-3.76173100	2.43920100	0.46602700
C	-4.70273100	1.28258600	0.17216000
C	-3.83789200	0.07356900	-0.24513400
C	-4.55483200	1.79929600	1.57354700
C	-4.51977400	-0.86078600	-1.24519800
C	-1.56642300	1.59656900	1.49457700
O	-3.55895900	-0.82583600	0.83103500
O	-5.21865700	-1.76592300	-0.41457800
C	-4.45305900	-1.94129200	0.77599500
C	-3.61816000	-3.21461400	0.70021900
C	-5.40548700	-1.91571700	1.96144600
O	0.53399600	3.00183100	-1.88187600
C	1.14153300	0.26366900	-1.37939700
C	2.45717100	0.96660100	-1.62585900
O	3.48866500	0.28253600	-0.94067500
Si	3.94678200	0.65954000	0.65041700
C	5.02702300	-0.80540800	1.20768100
C	2.40172400	0.85953900	1.70396700
C	4.91377900	2.27172600	0.61289700
C	5.80099700	-0.40913700	2.47879300
C	6.01950900	-1.15865200	0.08589500
C	4.13915000	-2.02530200	1.51299300
H	-2.82781500	1.17765600	-1.71067700
H	-1.42394500	-0.81807300	-1.72245100
H	-1.10242100	-0.67027700	-0.00101200
H	-2.06963600	3.40438000	-1.41243700
H	-1.08125800	3.77539100	0.00233500
H	-4.02330300	3.45764700	0.16473700

H	-5.64924400	1.43327200	-0.35280000
H	-5.39269800	2.37124500	1.98077100
H	-4.04809500	1.16035600	2.29785200
H	-5.23659700	-0.34871100	-1.90145100
H	-3.76973400	-1.37883200	-1.87248800
H	-2.00286700	0.71983700	1.98839200
H	-0.50957400	1.36593200	1.29760100
H	-1.59579400	2.44678400	2.19326500
H	-2.97040200	-3.29691000	1.58531900
H	-4.27054500	-4.09893400	0.65374000
H	-2.97910200	-3.19254300	-0.19468300
H	-6.12758600	-2.74241100	1.88824300
H	-4.84474300	-2.01881500	2.90171800
H	-5.95269000	-0.96289500	1.97193300
H	2.39468200	2.02840600	-1.35044600
H	2.67830900	0.93708800	-2.70743400
H	1.85340500	1.77187400	1.42055200
H	2.65995300	0.94386700	2.77212000
H	1.72880200	-0.00076600	1.57183000
H	5.84196800	2.16844500	0.02871200
H	4.31084300	3.07212000	0.15337300
H	5.18170600	2.59908700	1.63030700
H	5.12441200	-0.11636700	3.29905200
H	6.40372500	-1.26136400	2.84077000
H	6.49155600	0.42953200	2.29674800
H	5.49293200	-1.45545500	-0.83368500
H	6.66807600	-1.99767700	0.39666000
H	6.67683000	-0.30954900	-0.16432100
H	4.76498600	-2.89466500	1.78450300
H	3.45939500	-1.83113600	2.35787400
H	3.51590400	-2.31138600	0.65278700
C	1.32662200	-1.22488600	-1.24978000
O	1.09094600	-1.87354300	-0.25507000
O	1.80601000	-1.74497200	-2.38233500
C	2.12287500	-3.14242200	-2.36752000
H	2.40935400	-3.40005800	-3.39329500
H	2.96059100	-3.33230400	-1.68052100
H	1.25411700	-3.73509400	-2.04855000

HOAc

O	-0.83962300	-1.01845300	0.00001800
C	-0.13176500	0.13214900	0.00003200
C	1.37206900	-0.02386200	-0.00000500
H	1.69812300	-0.58663900	-0.88928800
H	1.84429500	0.96516100	-0.00007500
H	1.69837100	-0.58647600	0.88928500
O	-0.71407000	1.18701300	-0.00001500
H	-0.25307100	-1.79024600	-0.00010500

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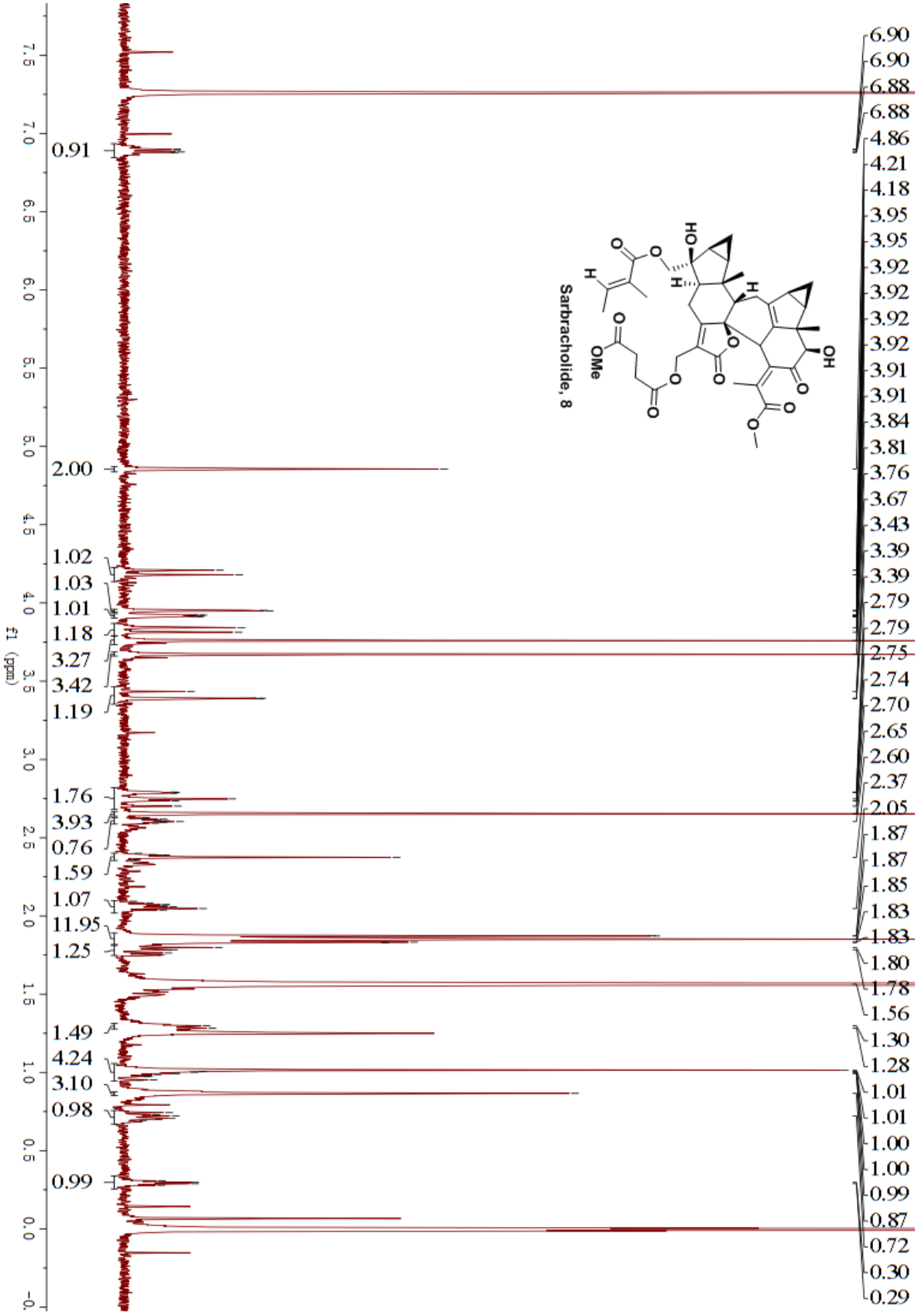
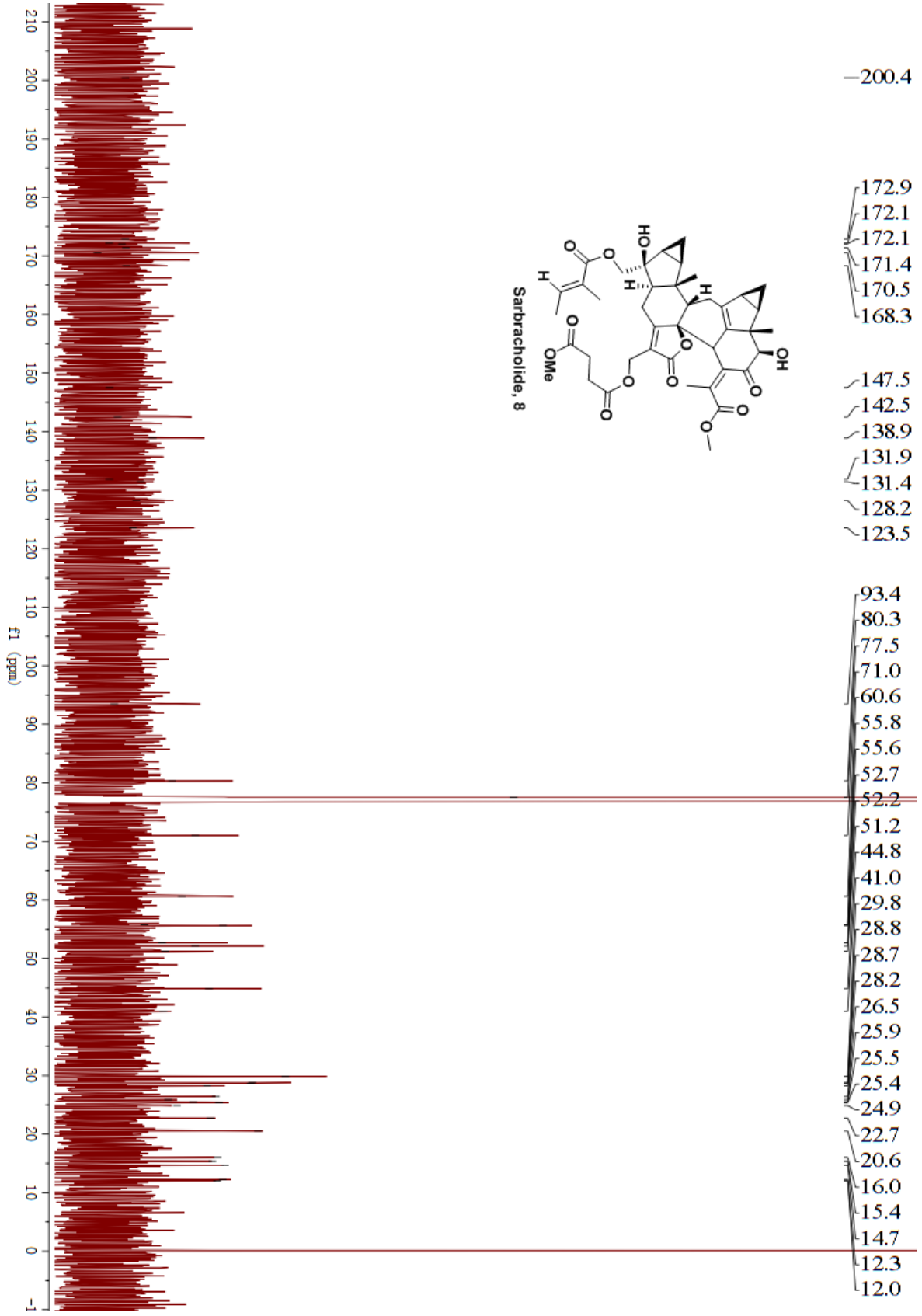
6. Spectra for New Compounds

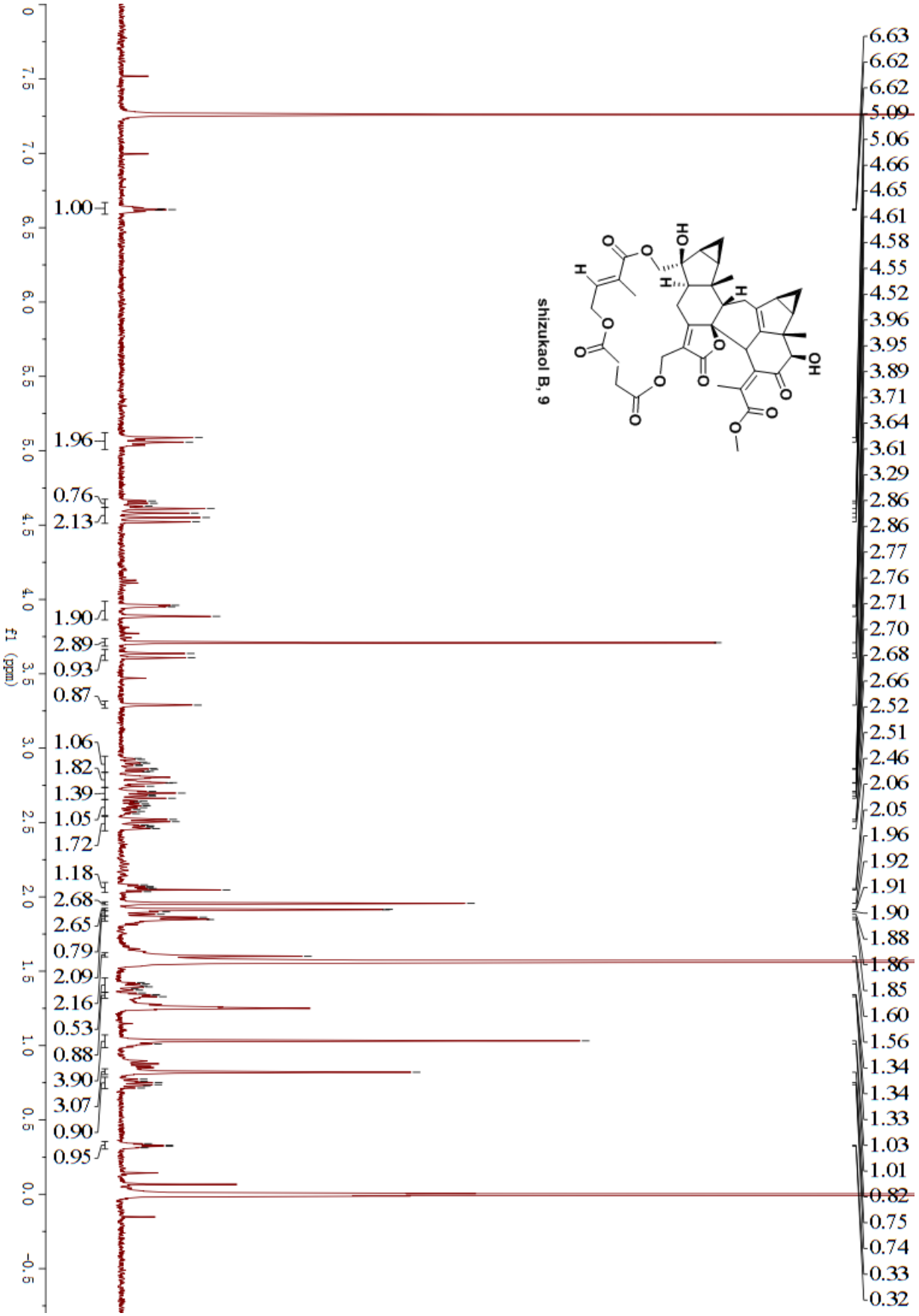
^{1}H NMR spectrum of compound **8** in $CDCl_3$ (400 MHz)



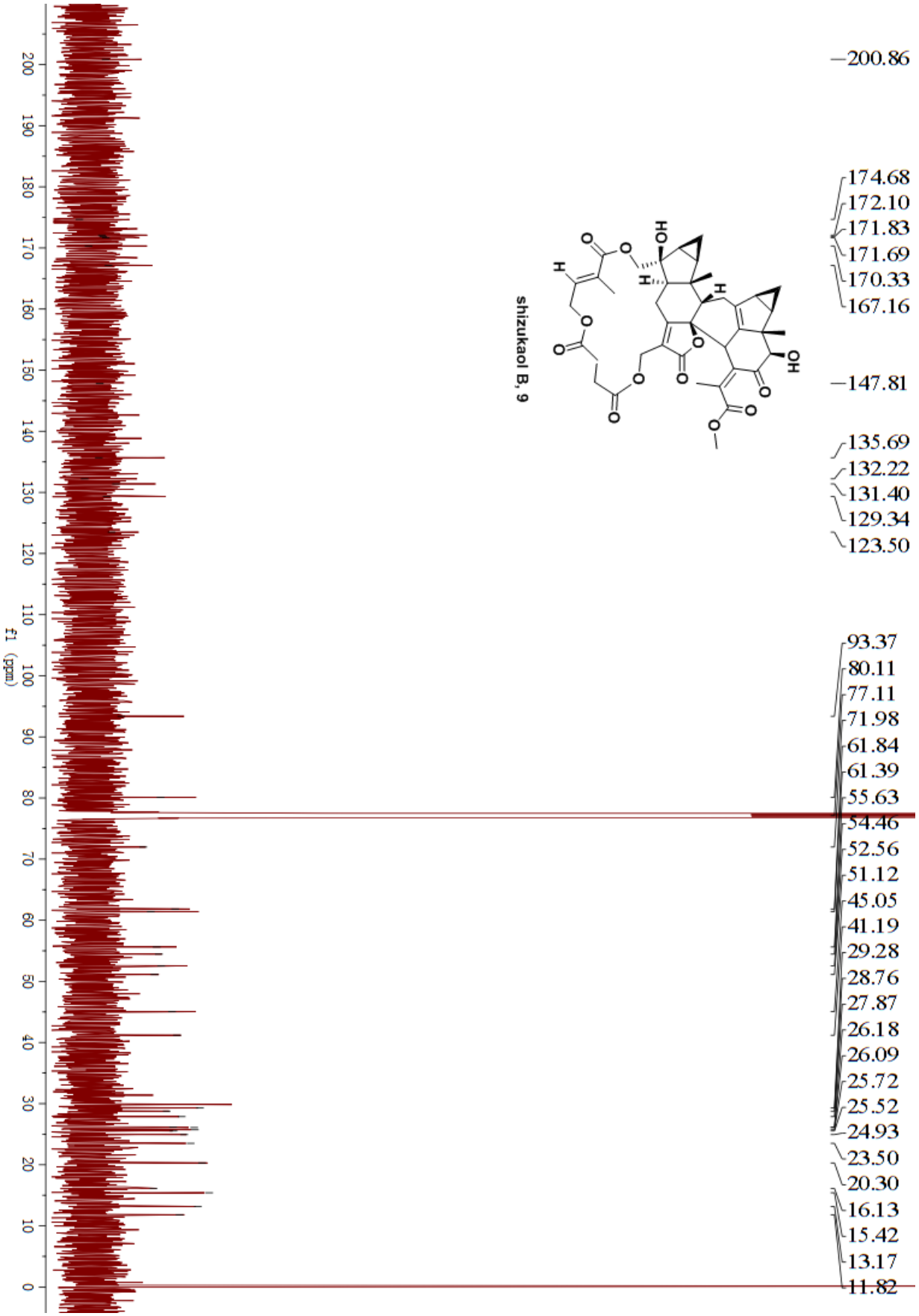
^{13}C NMR spectrum of compound **8** in $CDCl_3$ (151 MHz)



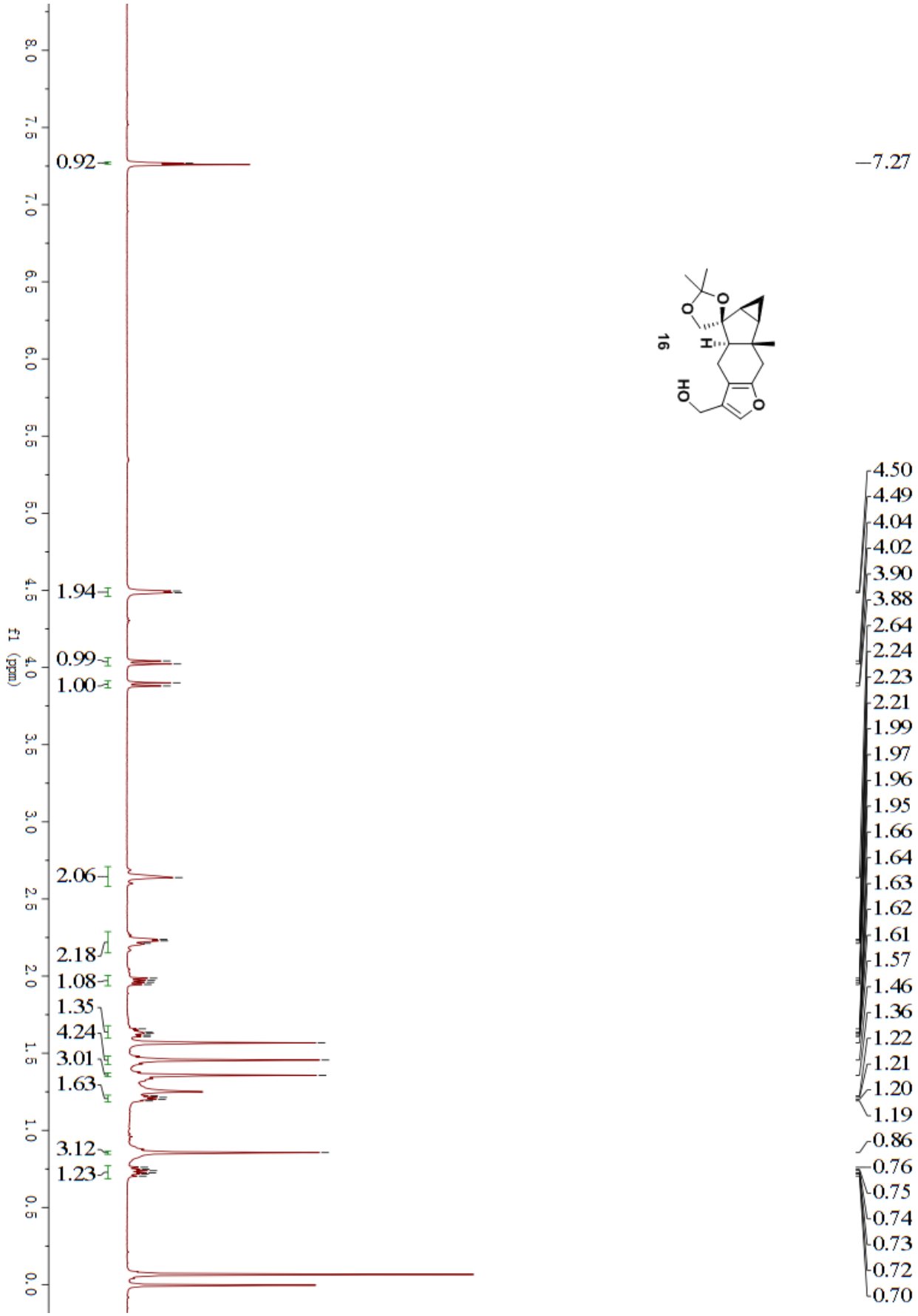
^{1}H NMR spectrum of compound **9** in $CDCl_3$ (400 MHz)



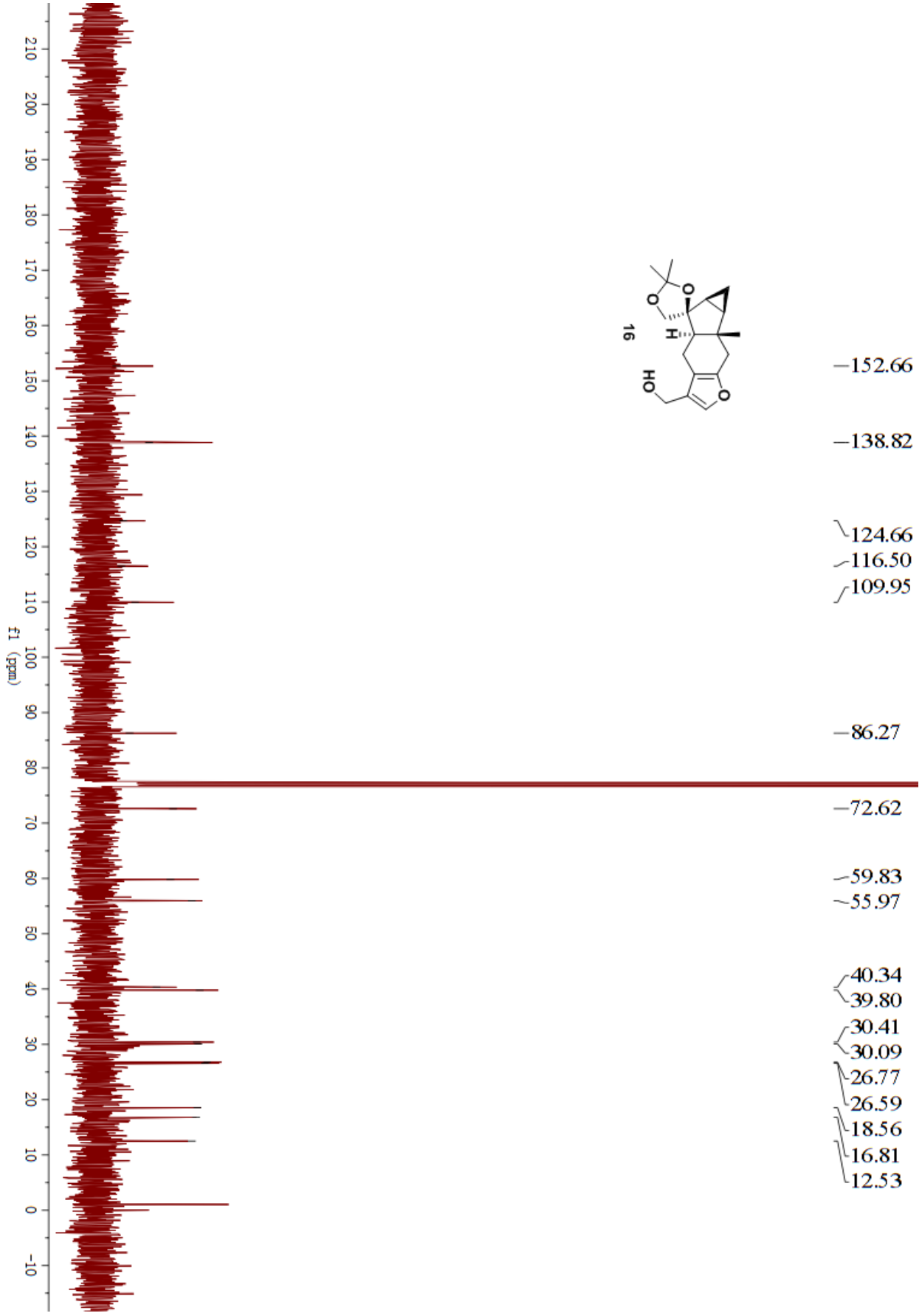
^{13}C NMR spectrum of compound **9** in $CDCl_3$ (151 MHz)



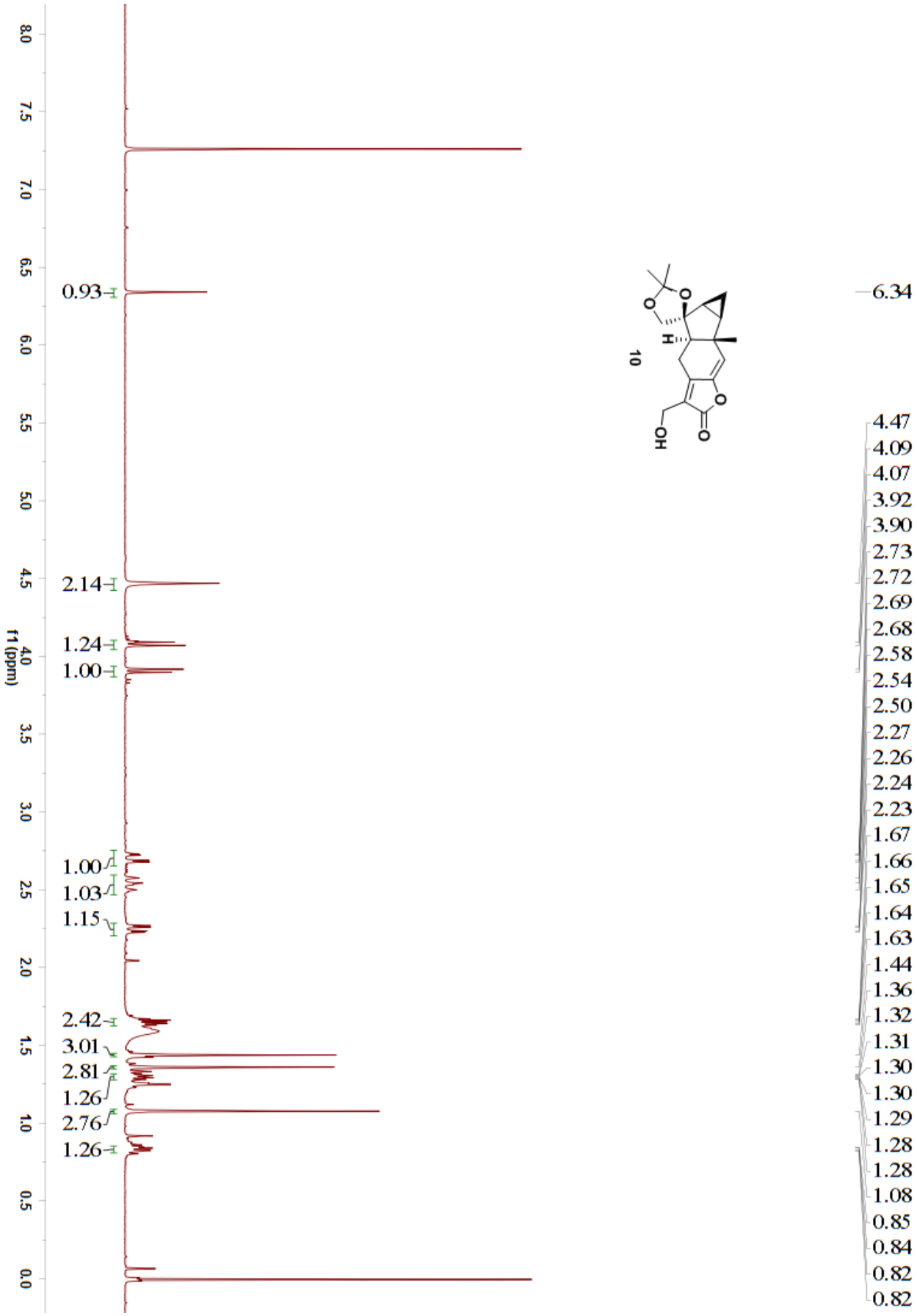
^{1}H NMR spectrum of compound **16** in $CDCl_3$ (400 MHz)



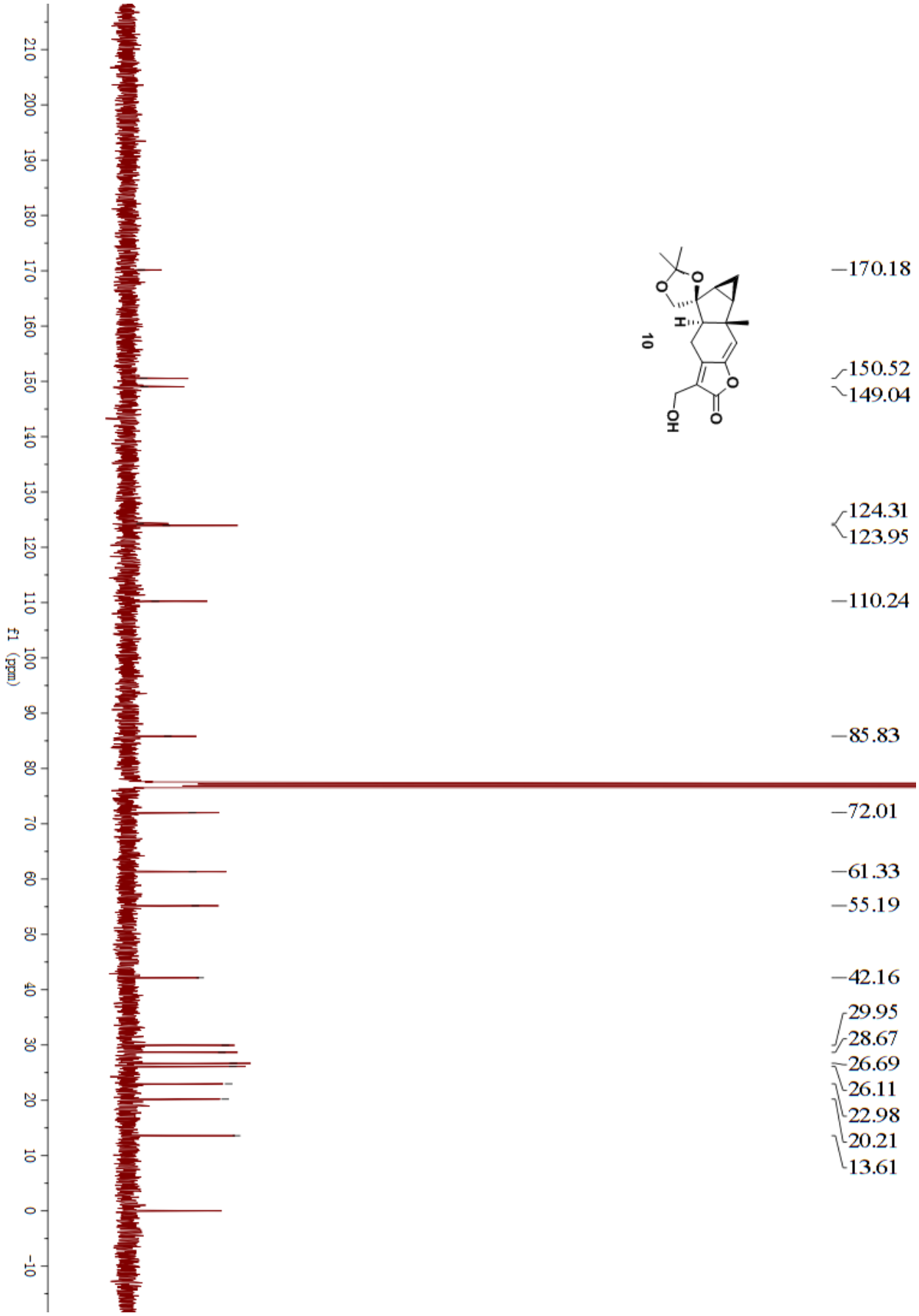
^{13}C NMR spectrum of compound **16** in $CDCl_3$ (125 MHz)



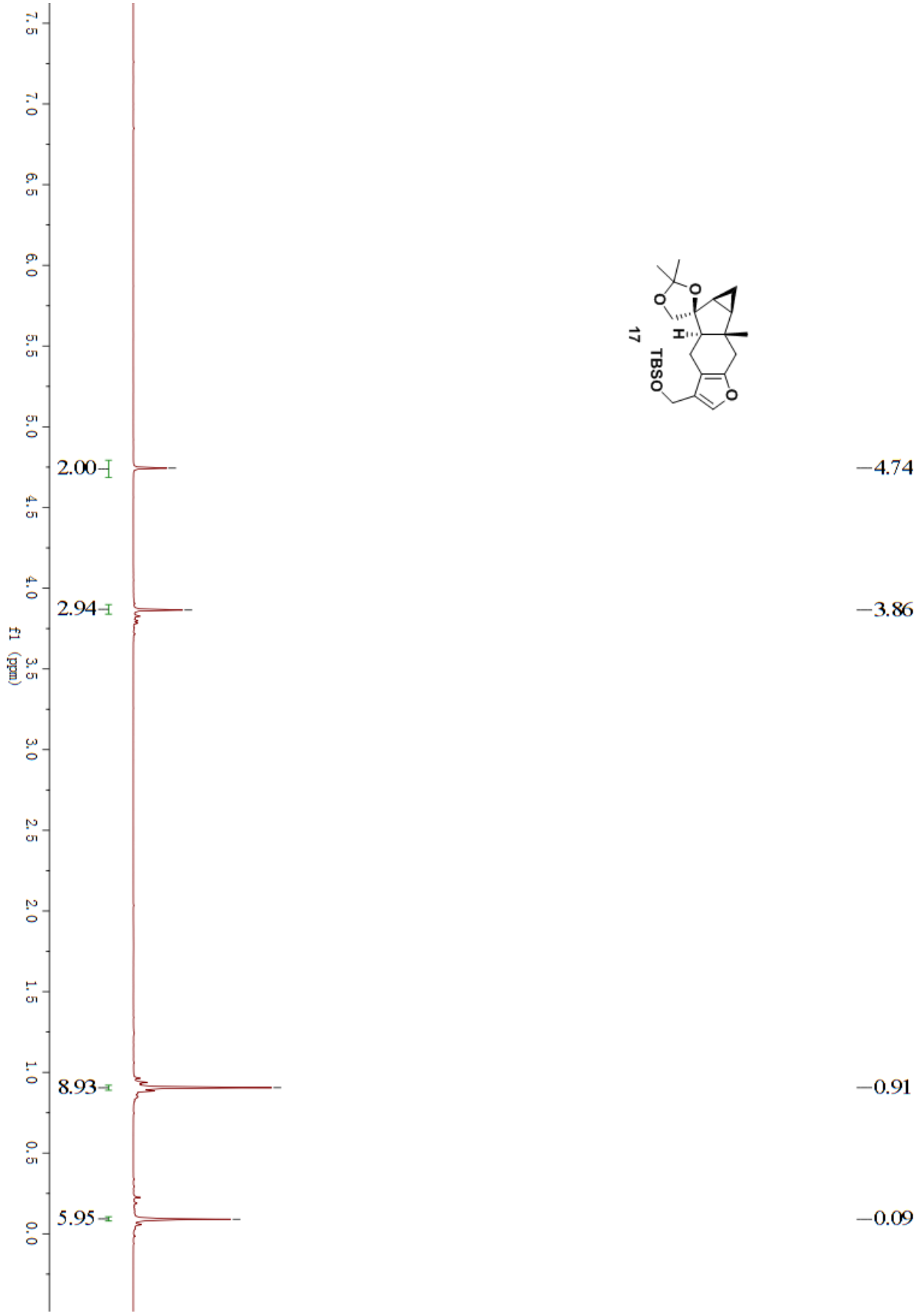
[1]H NMR spectrum of compound **10** in $CDCl_3$ (400 MHz)



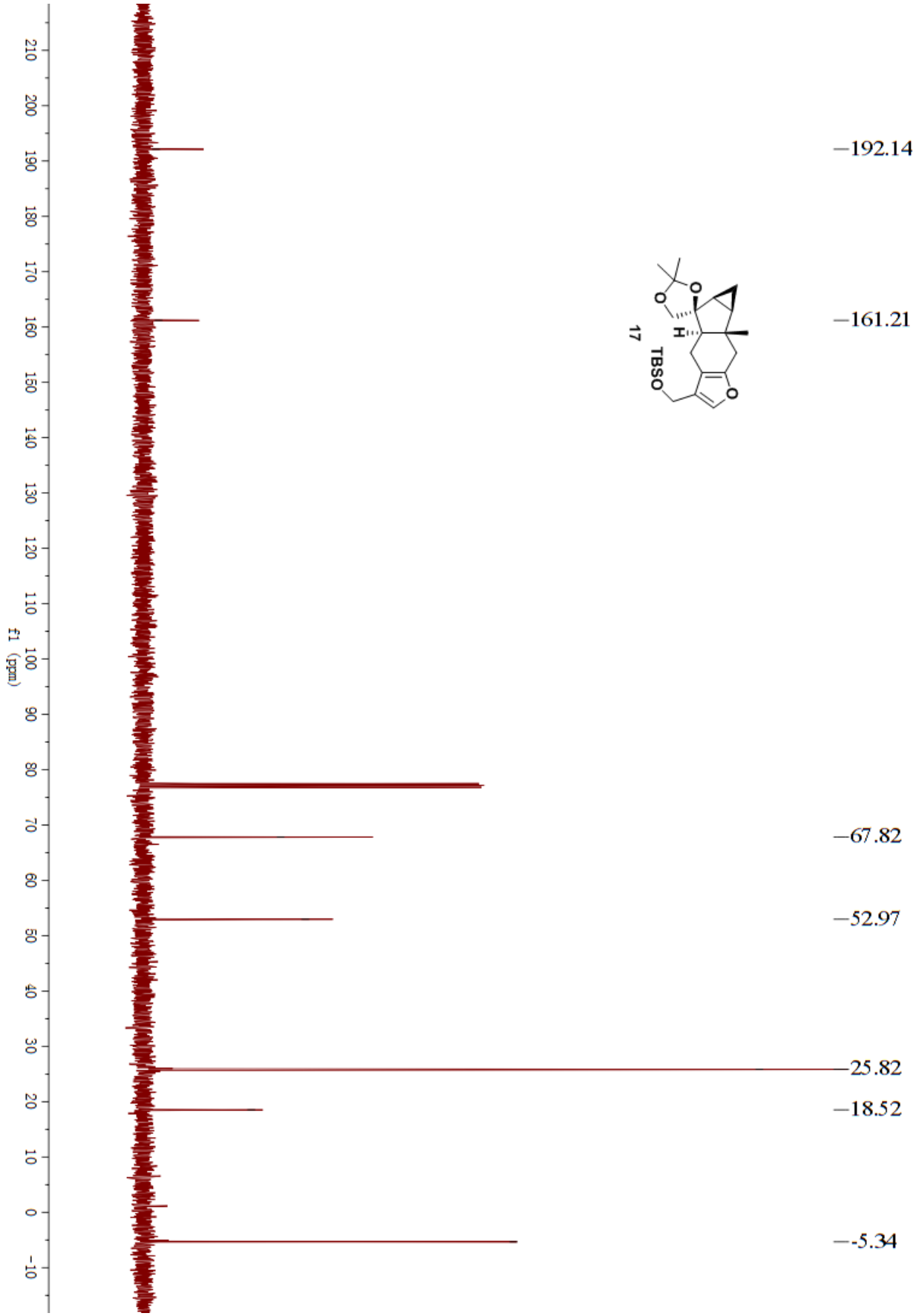
^{13}C NMR spectrum of compound **10** in $CDCl_3$ (125 MHz)



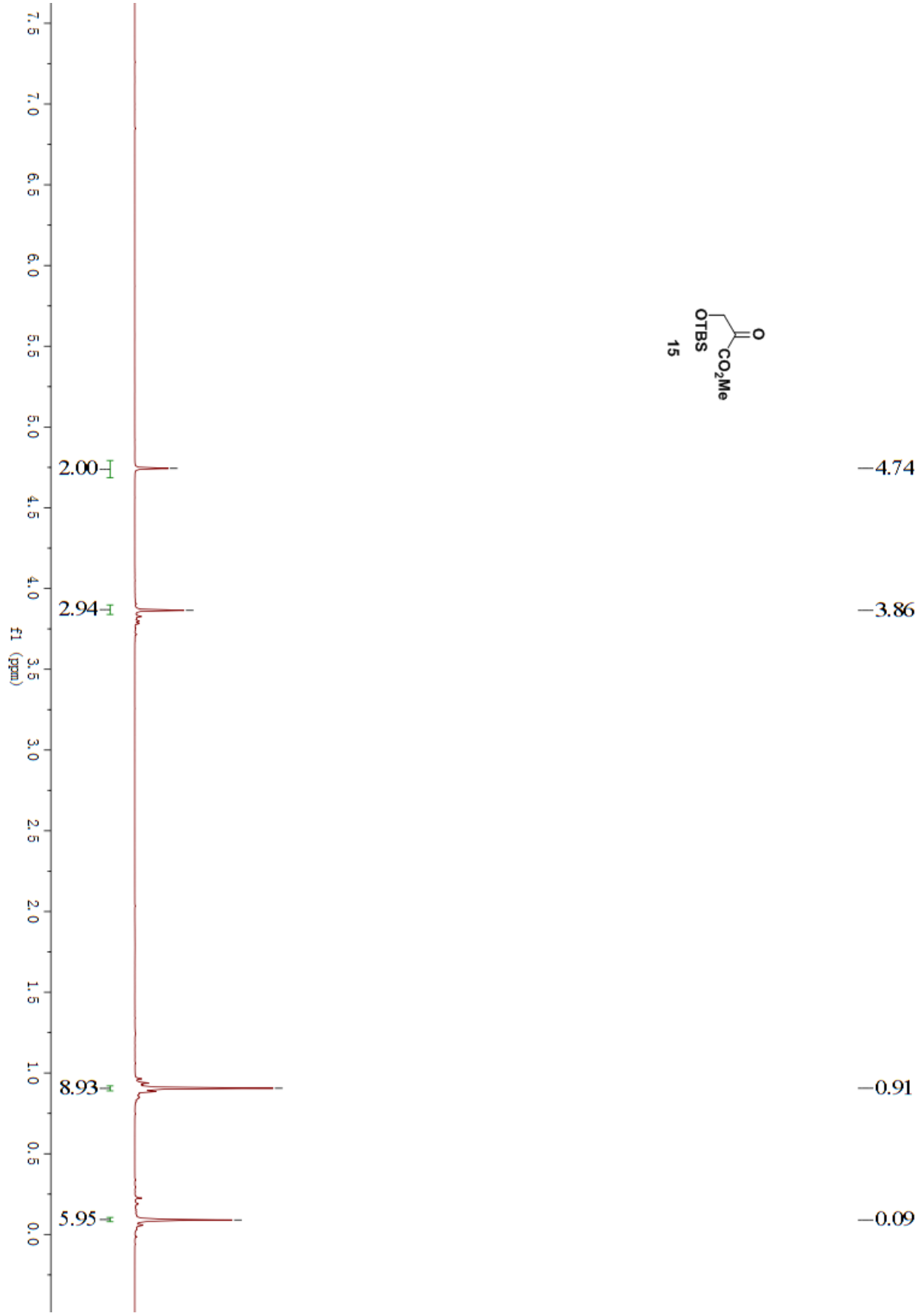
^{1}H NMR spectrum of compound **17** in $CDCl_3$ (400 MHz)



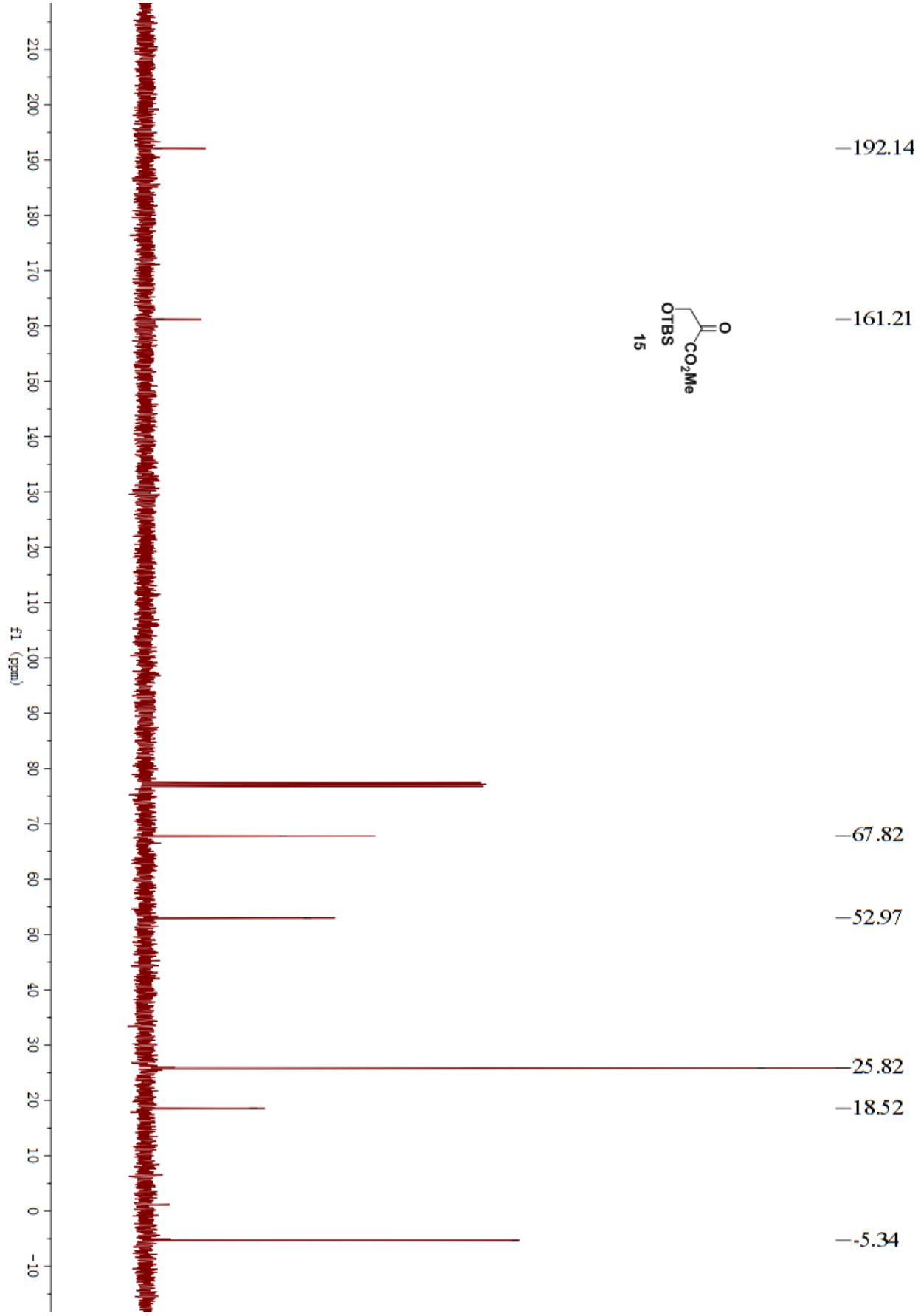
^{13}C NMR spectrum of compound **17** in $CDCl_3$ (125 MHz)



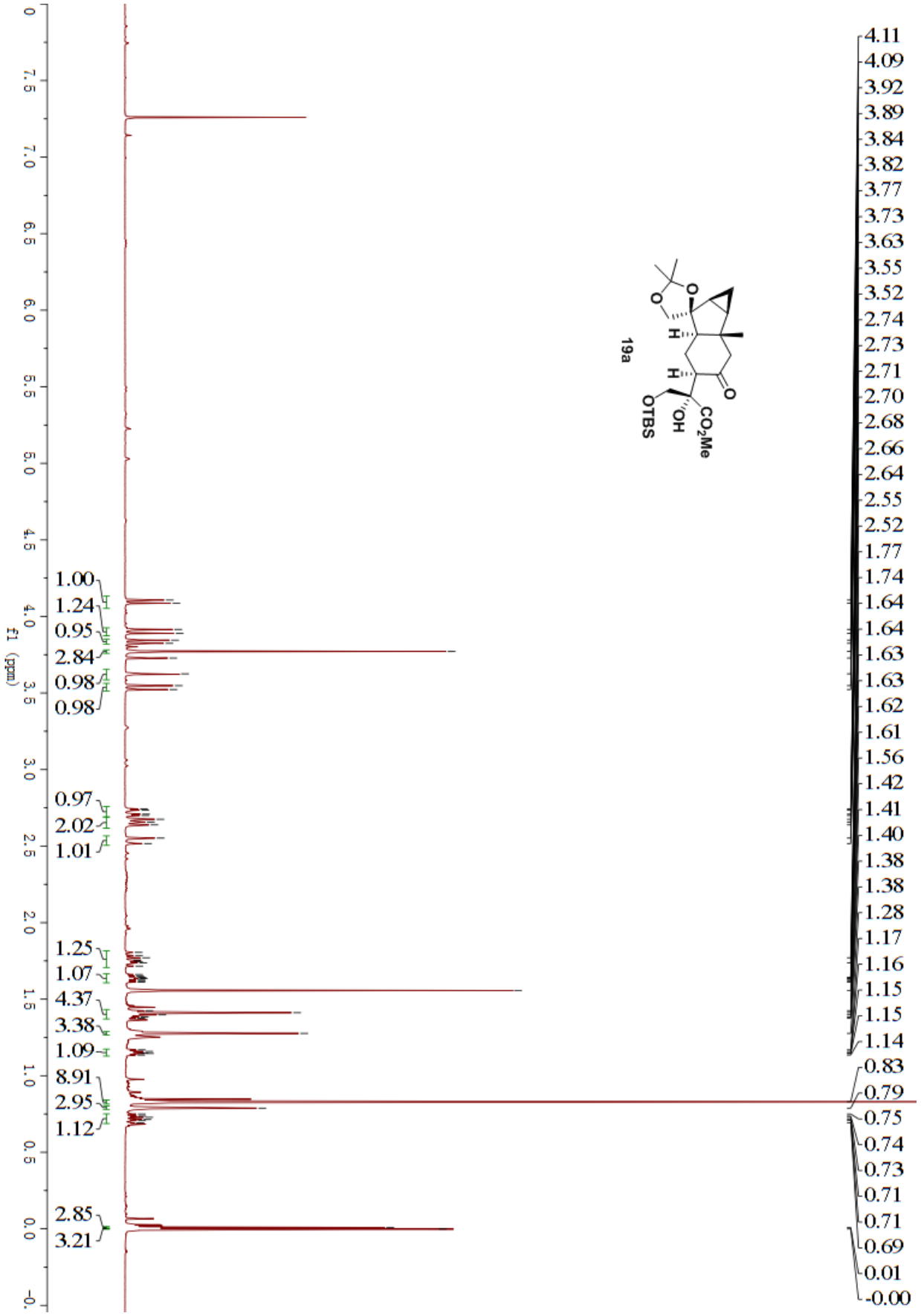
^{1}H NMR spectrum of compound **15** in $CDCl_3$ (400 MHz)



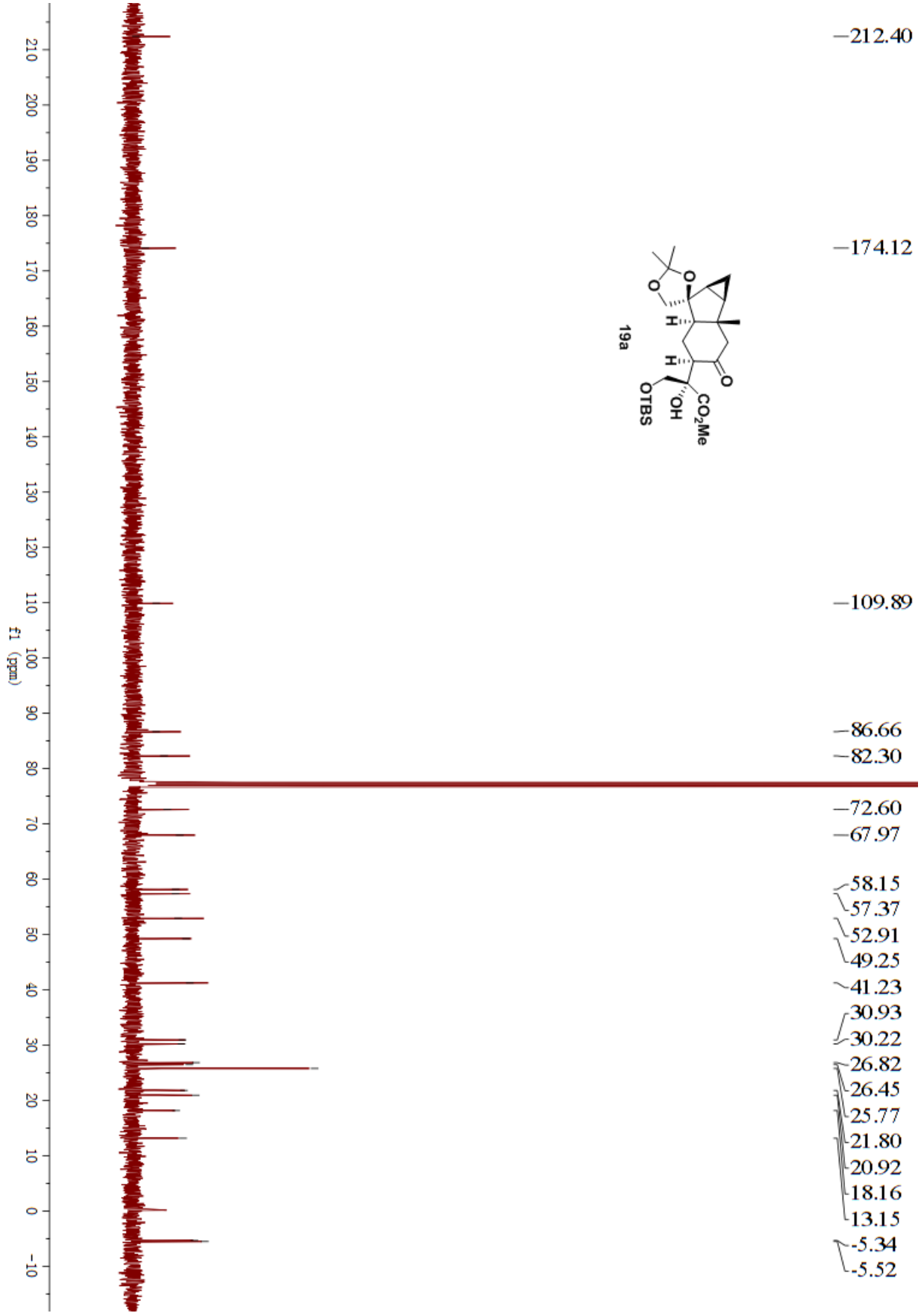
^{13}C NMR spectrum of compound **15** in $CDCl_3$ (125 MHz)



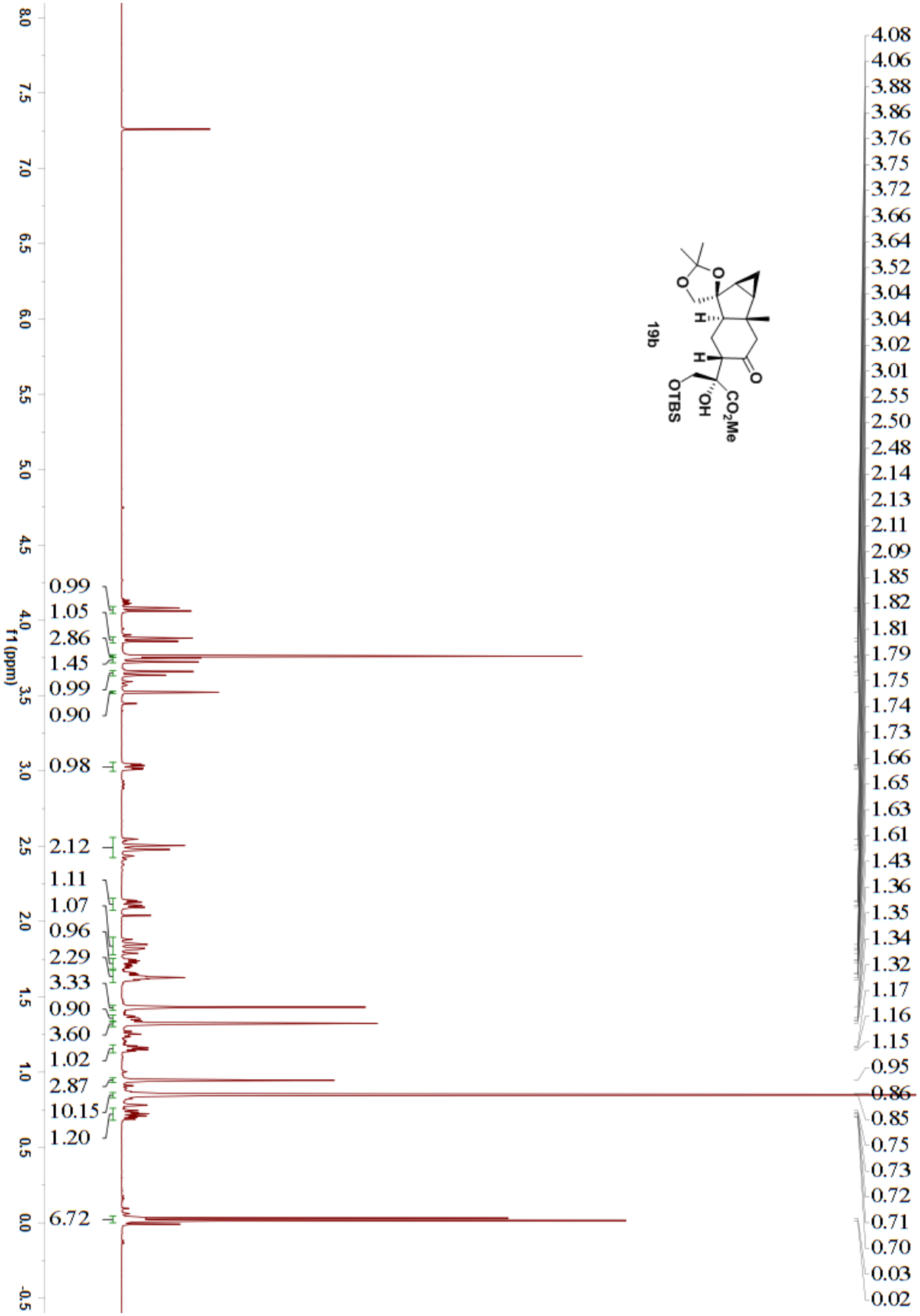
^{1}H NMR spectrum of compound **19a** in $CDCl_3$ (400 MHz)



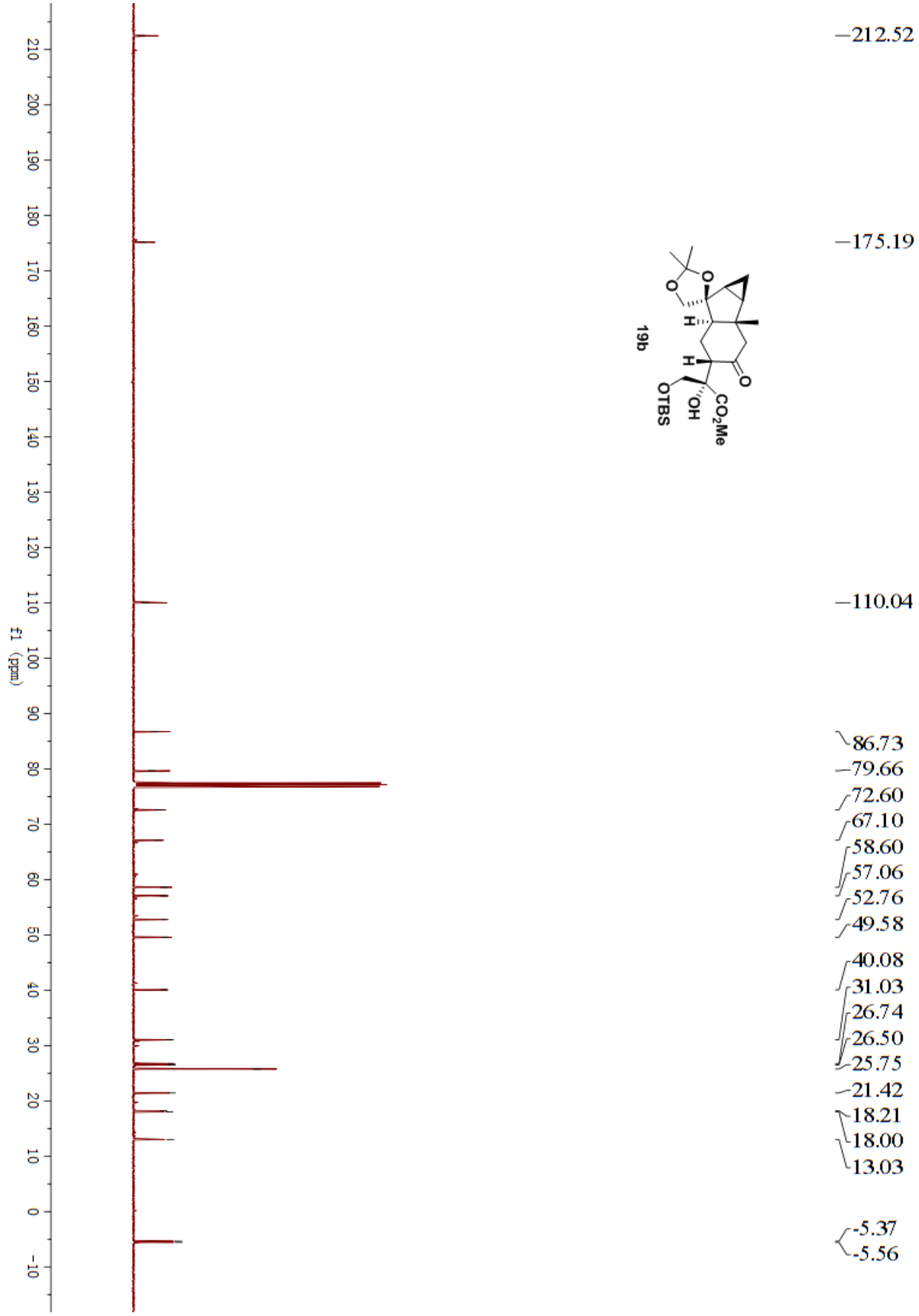
^{13}C NMR spectrum of compound **19a** in $CDCl_3$ (125 MHz)



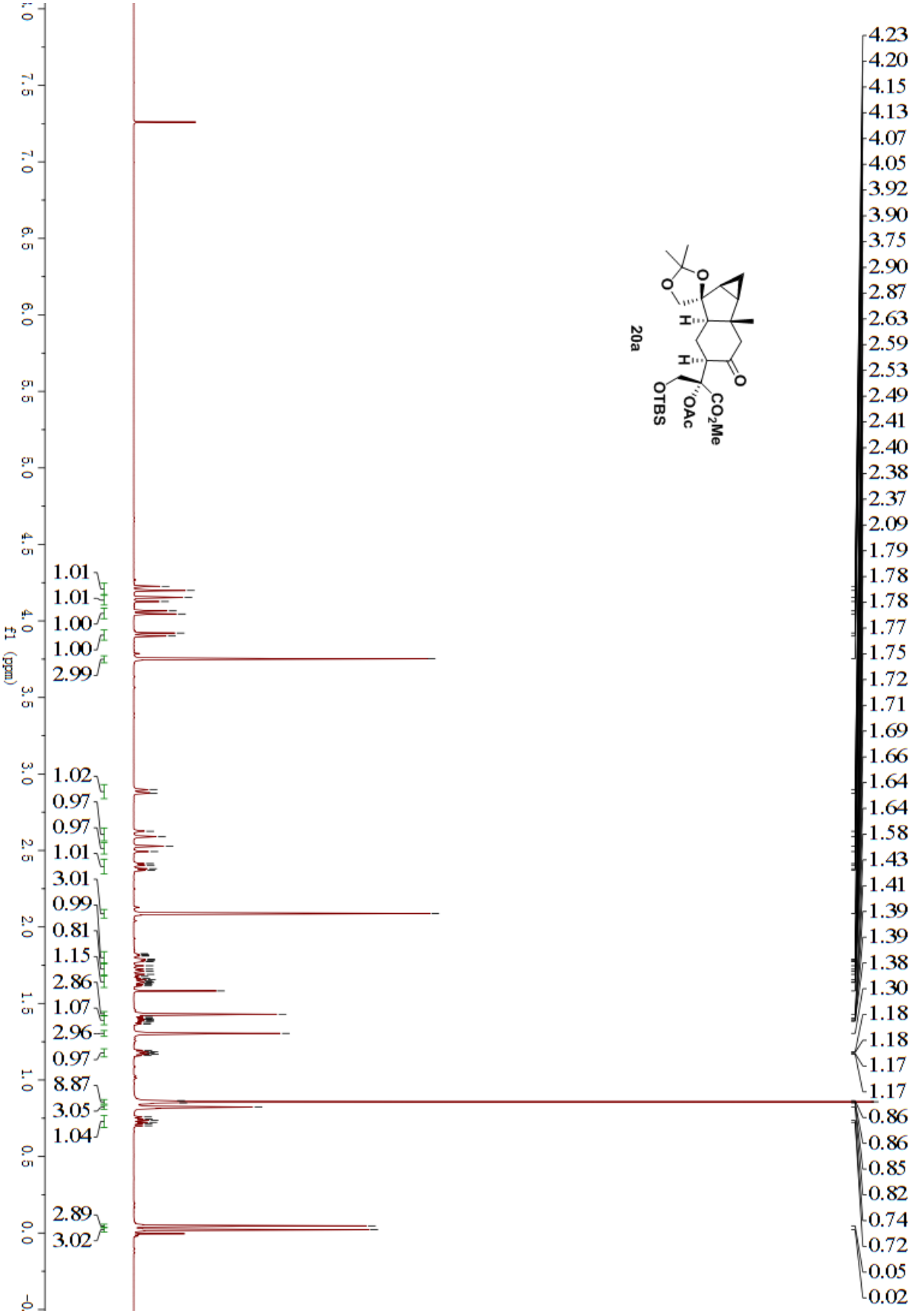
^{1}H NMR spectrum of compound **19b** in $CDCl_3$ (400 MHz)



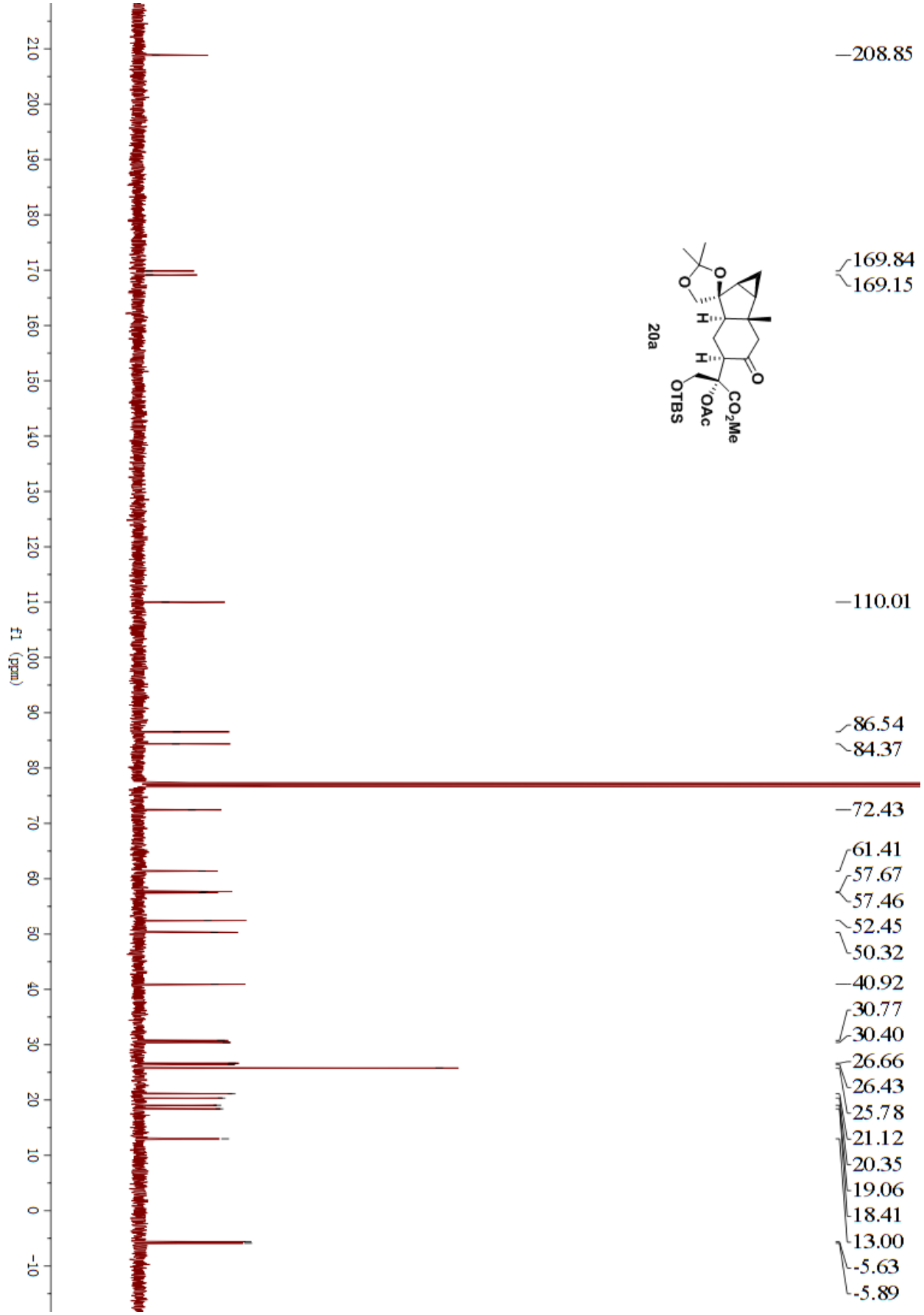
^{13}C NMR spectrum of compound **19b** in $CDCl_3$ (125 MHz)



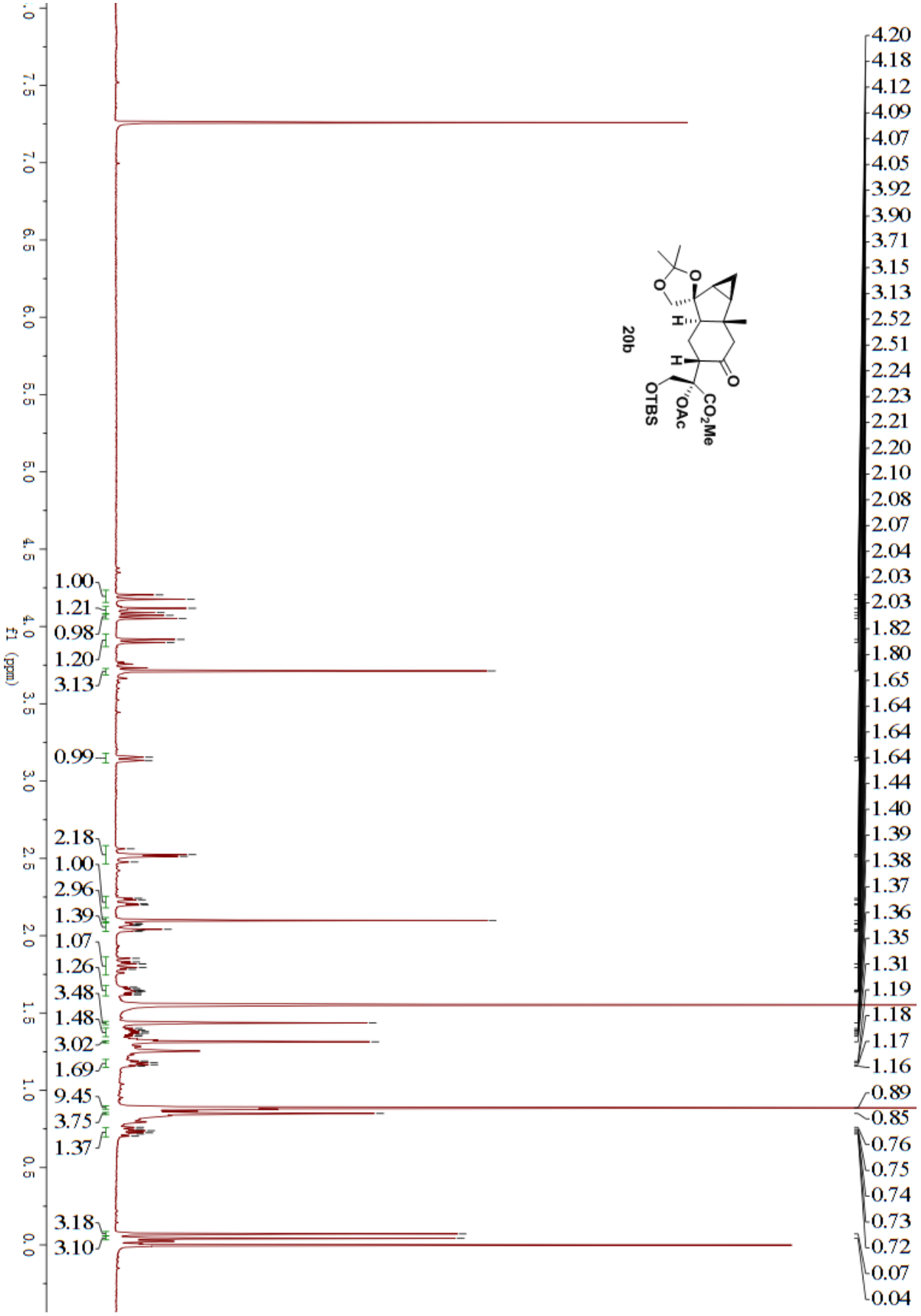
^{1}H NMR spectrum of compound **20a** in $CDCl_3$ (400 MHz)



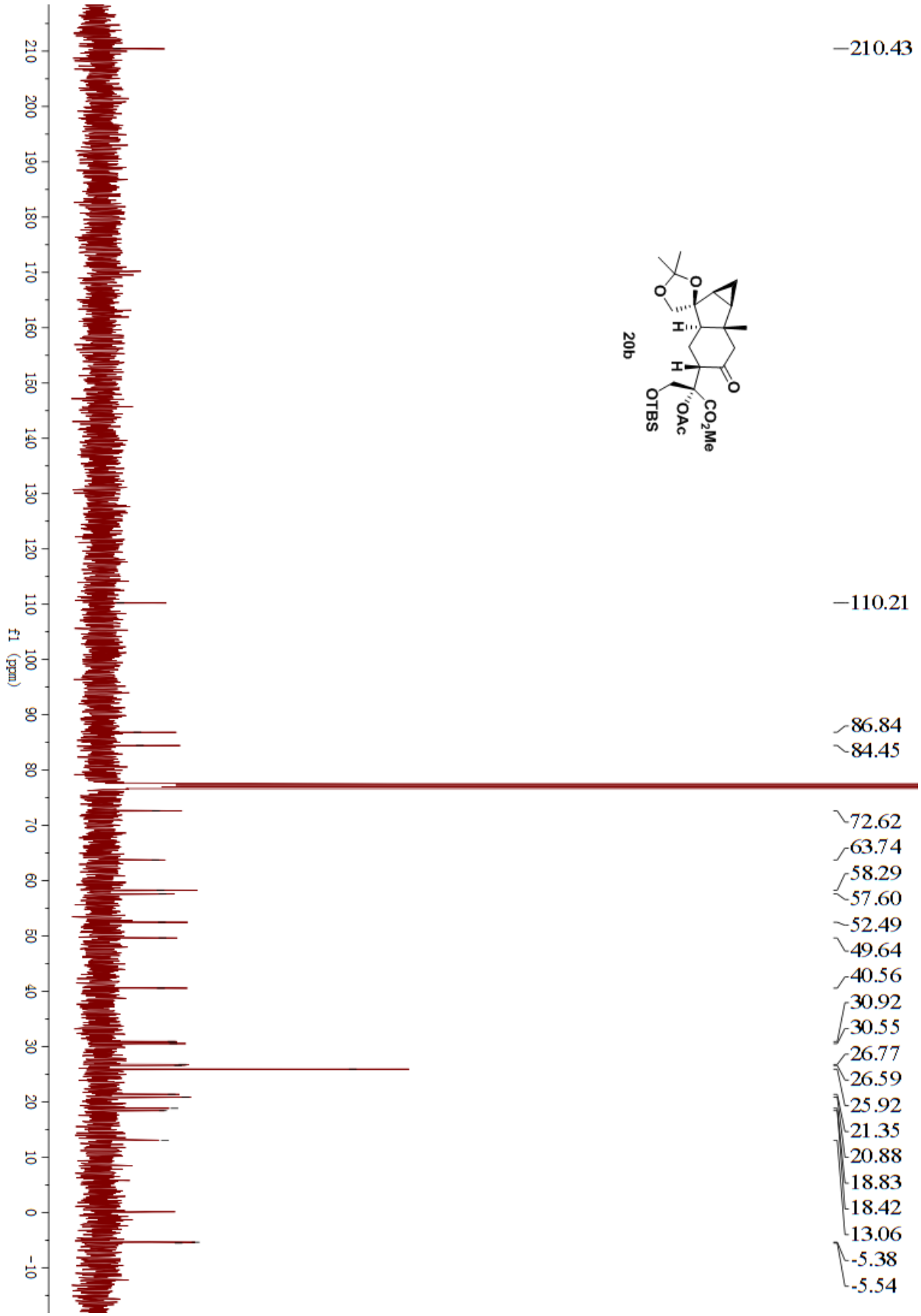
^{13}C NMR spectrum of compound **20a** in $CDCl_3$ (125 MHz)



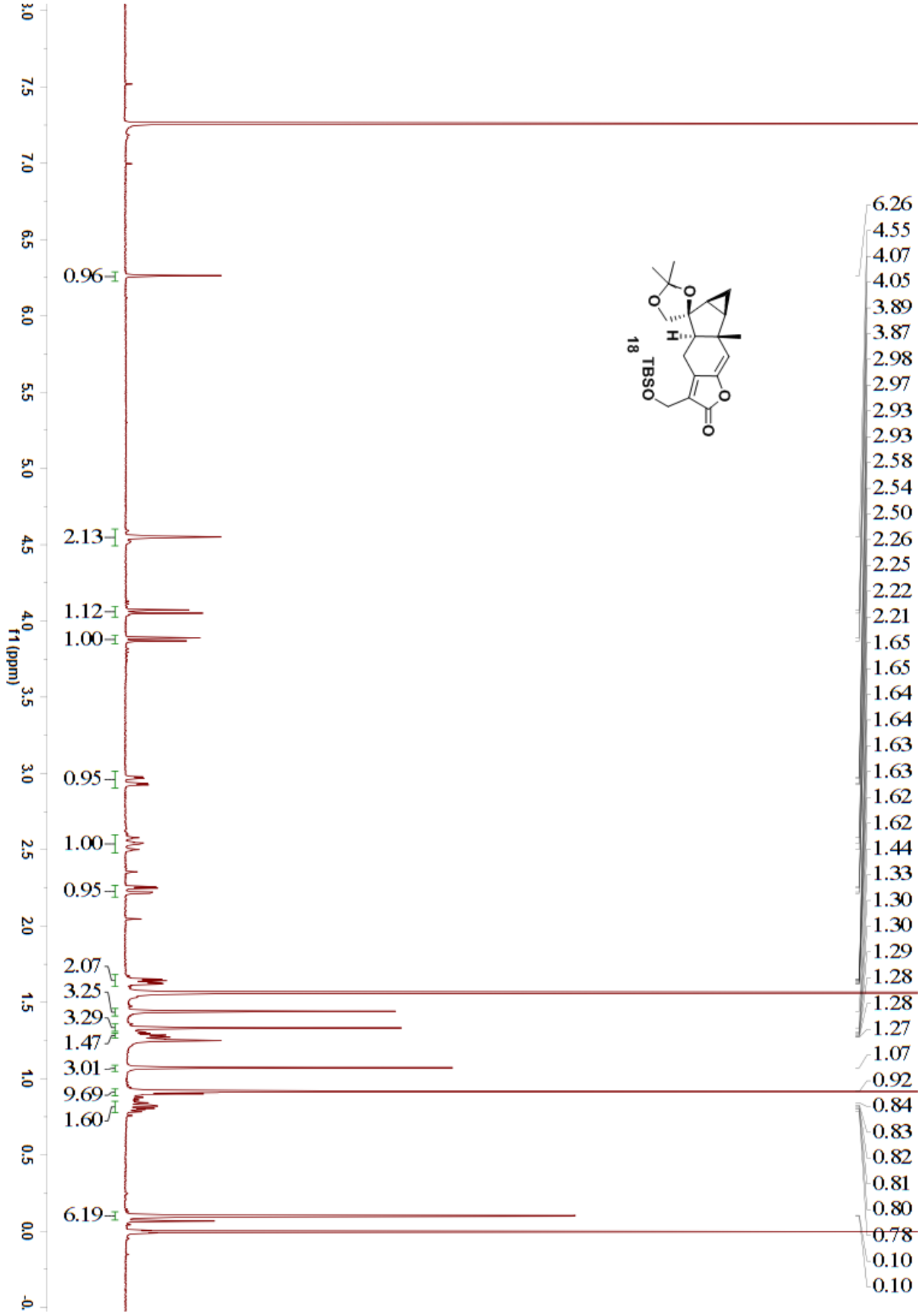
^{1}H NMR spectrum of compound **20b** in $CDCl_3$ (400 MHz)



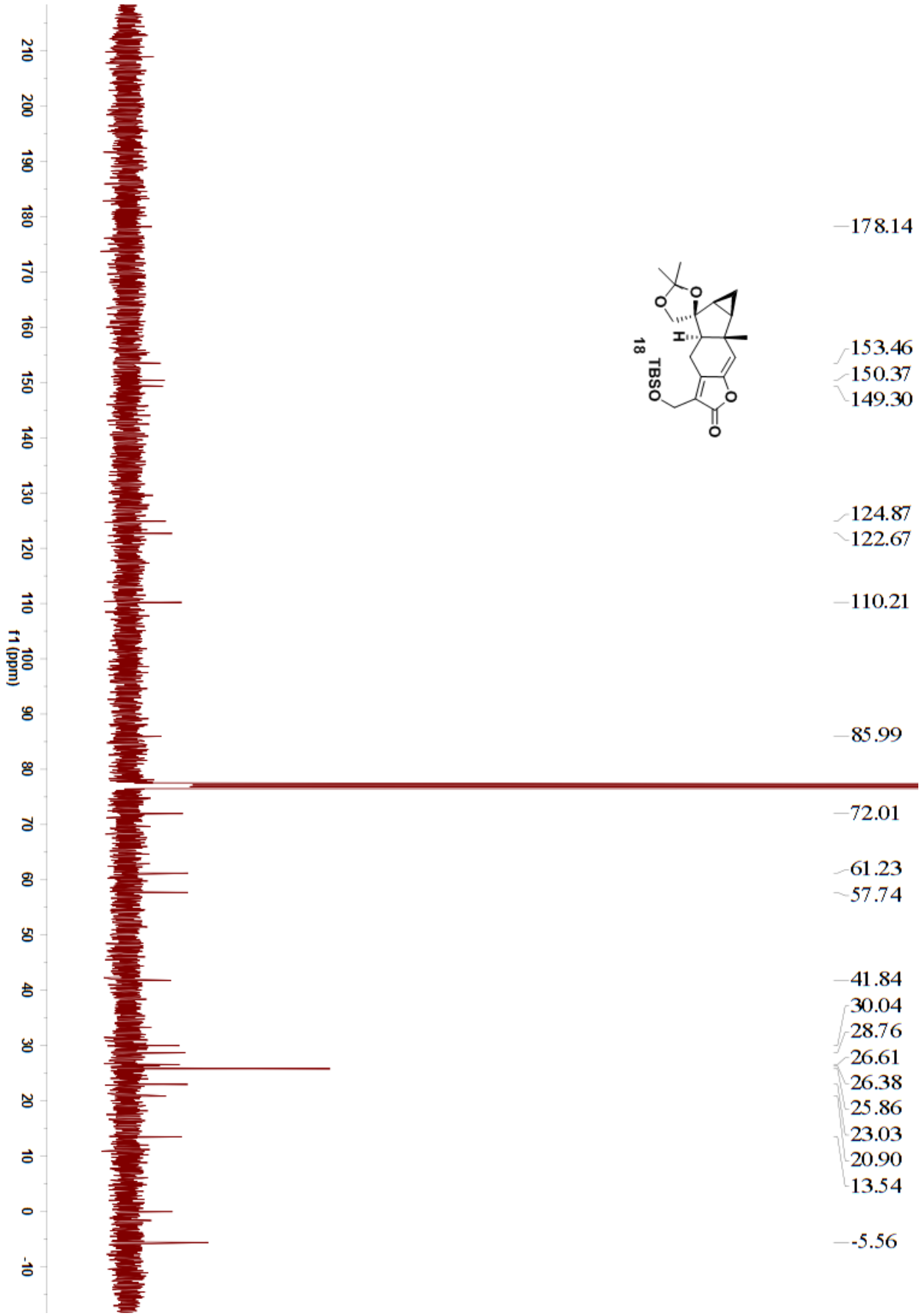
^{13}C NMR spectrum of compound **20b** in $CDCl_3$ (125 MHz)



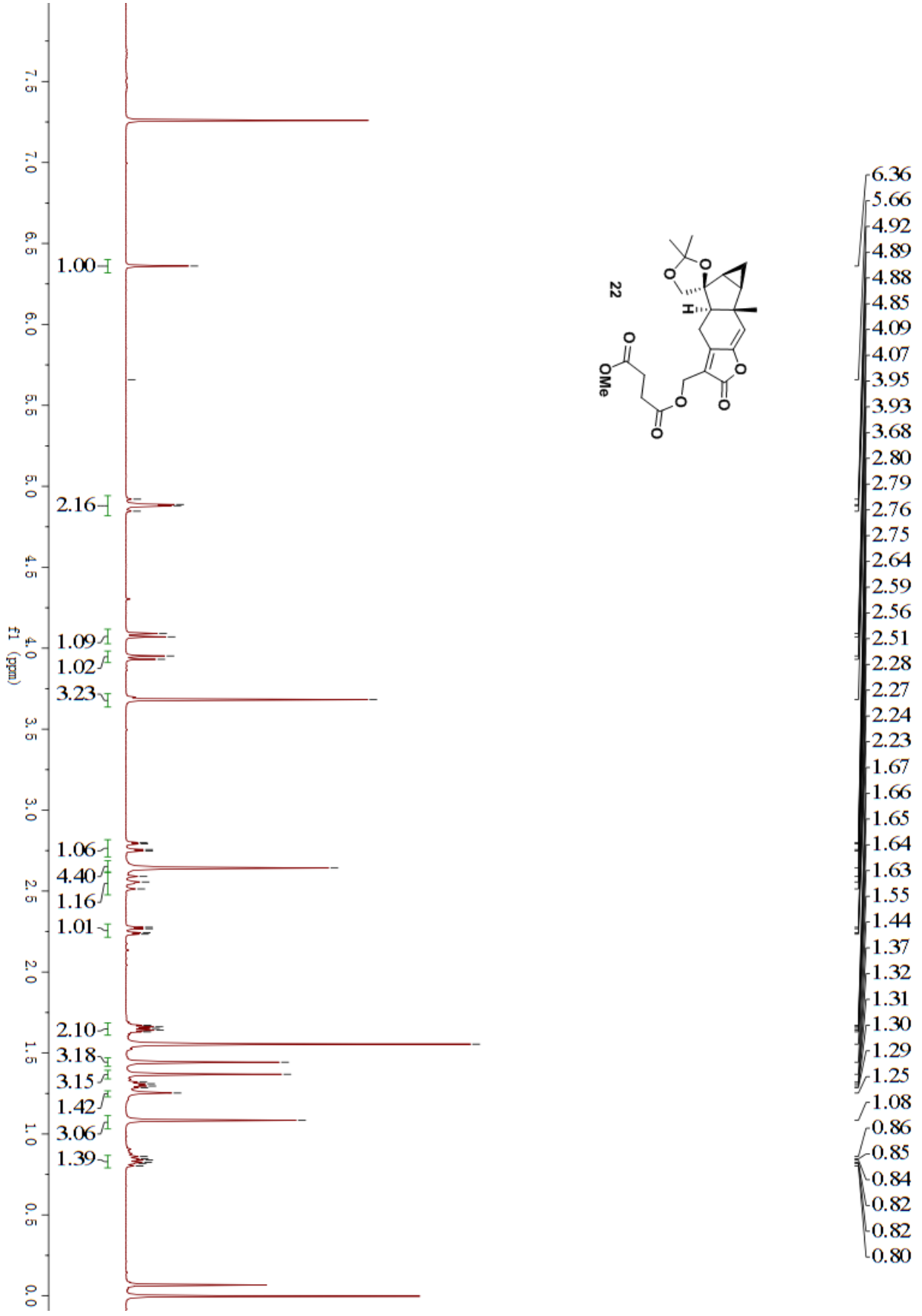
^{1}H NMR spectrum of compound **18** in $CDCl_3$ (400 MHz)



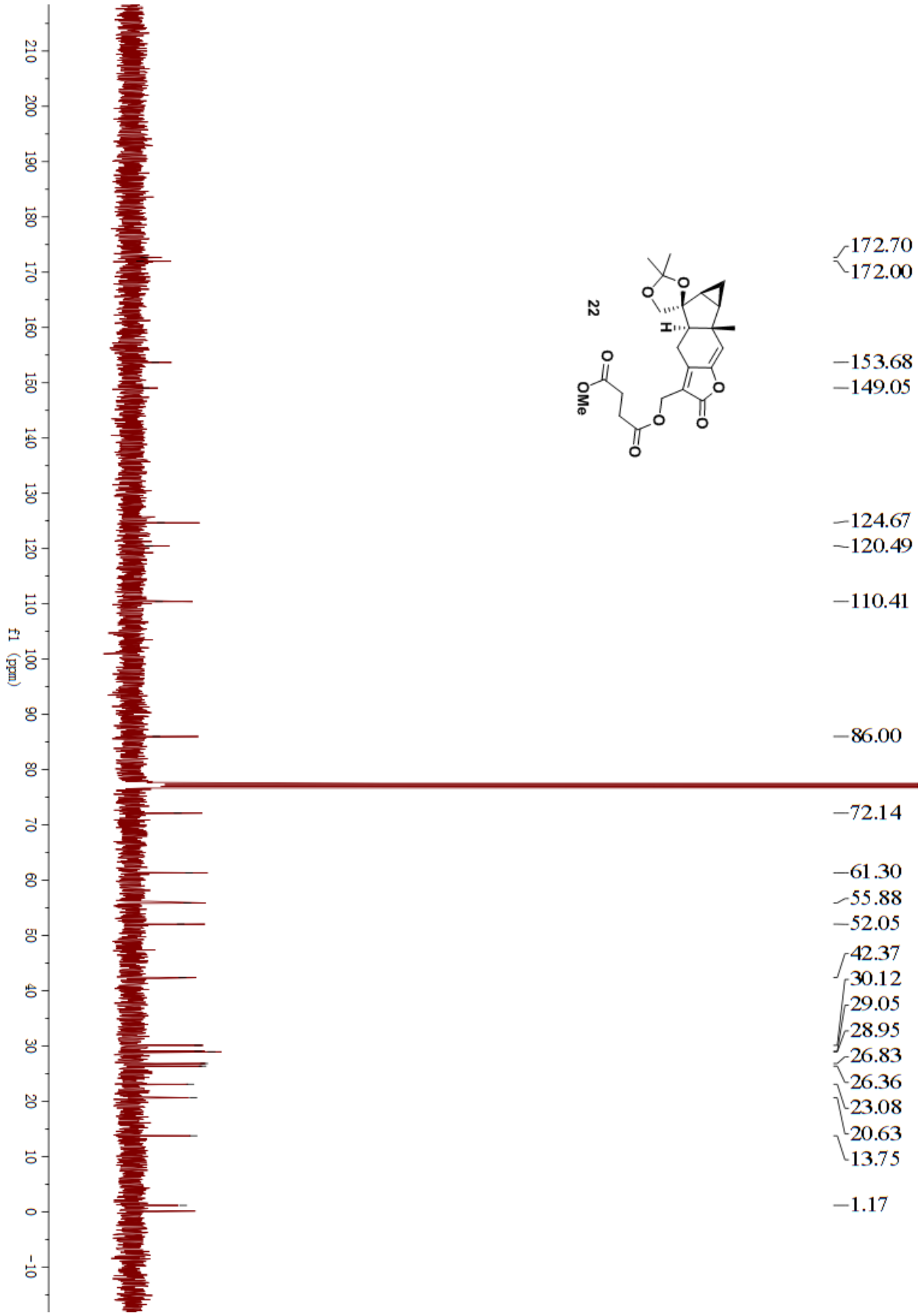
^{13}C NMR spectrum of compound **18** in $CDCl_3$ (125 MHz)



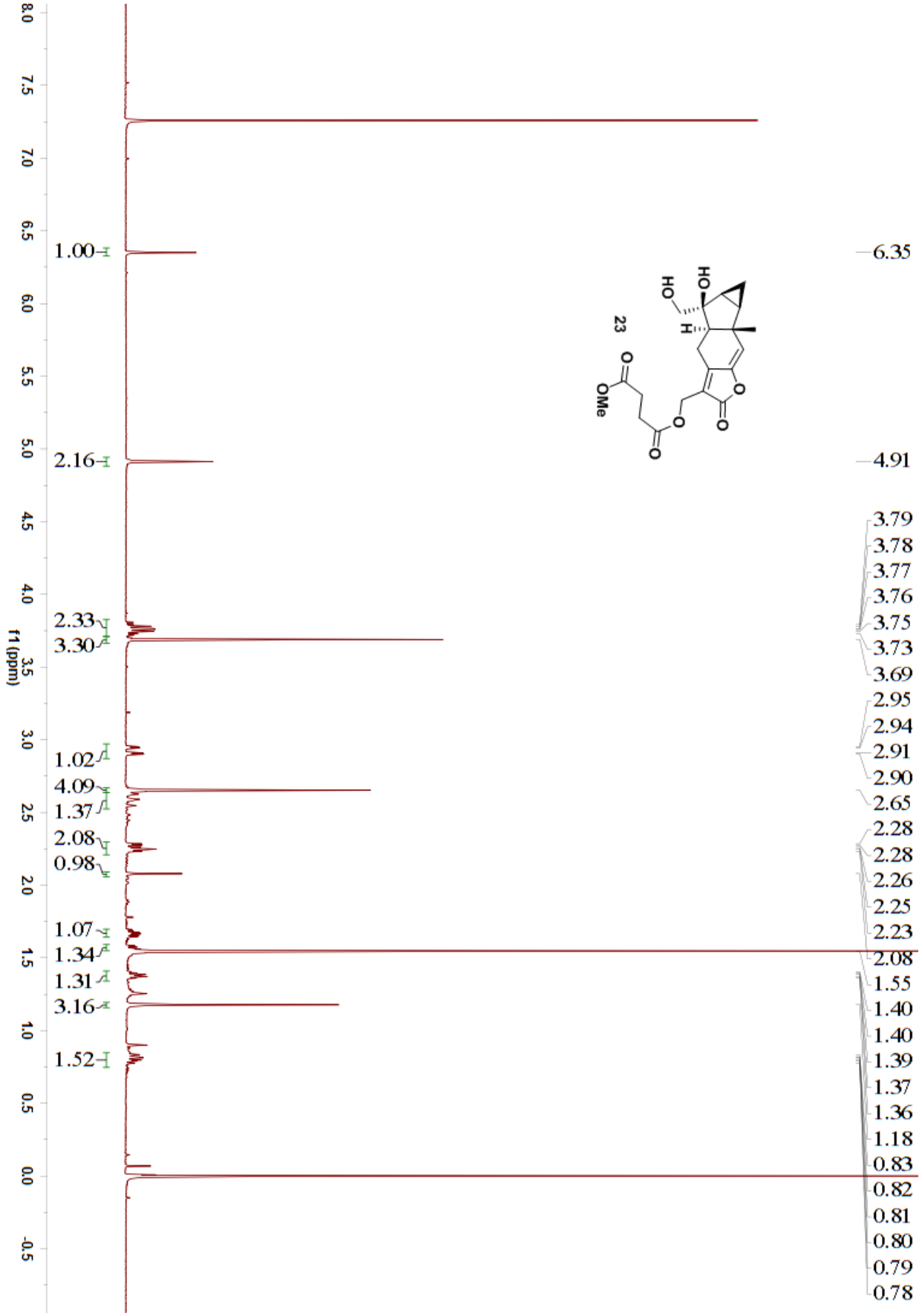
[1]H NMR spectrum of compound **22** in $CDCl_3$ (400 MHz)



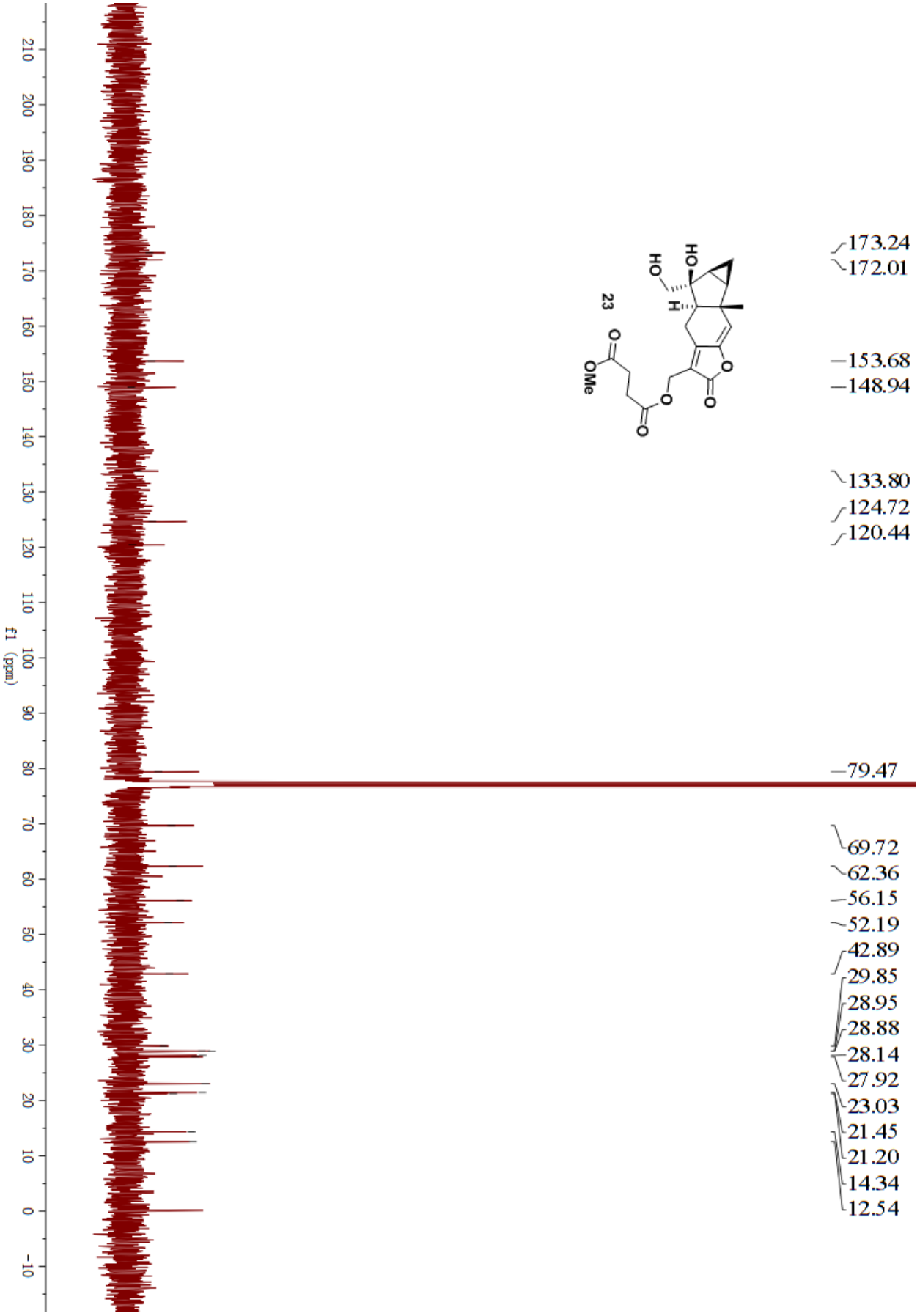
^{13}C NMR spectrum of compound **22** in $CDCl_3$ (125 MHz)



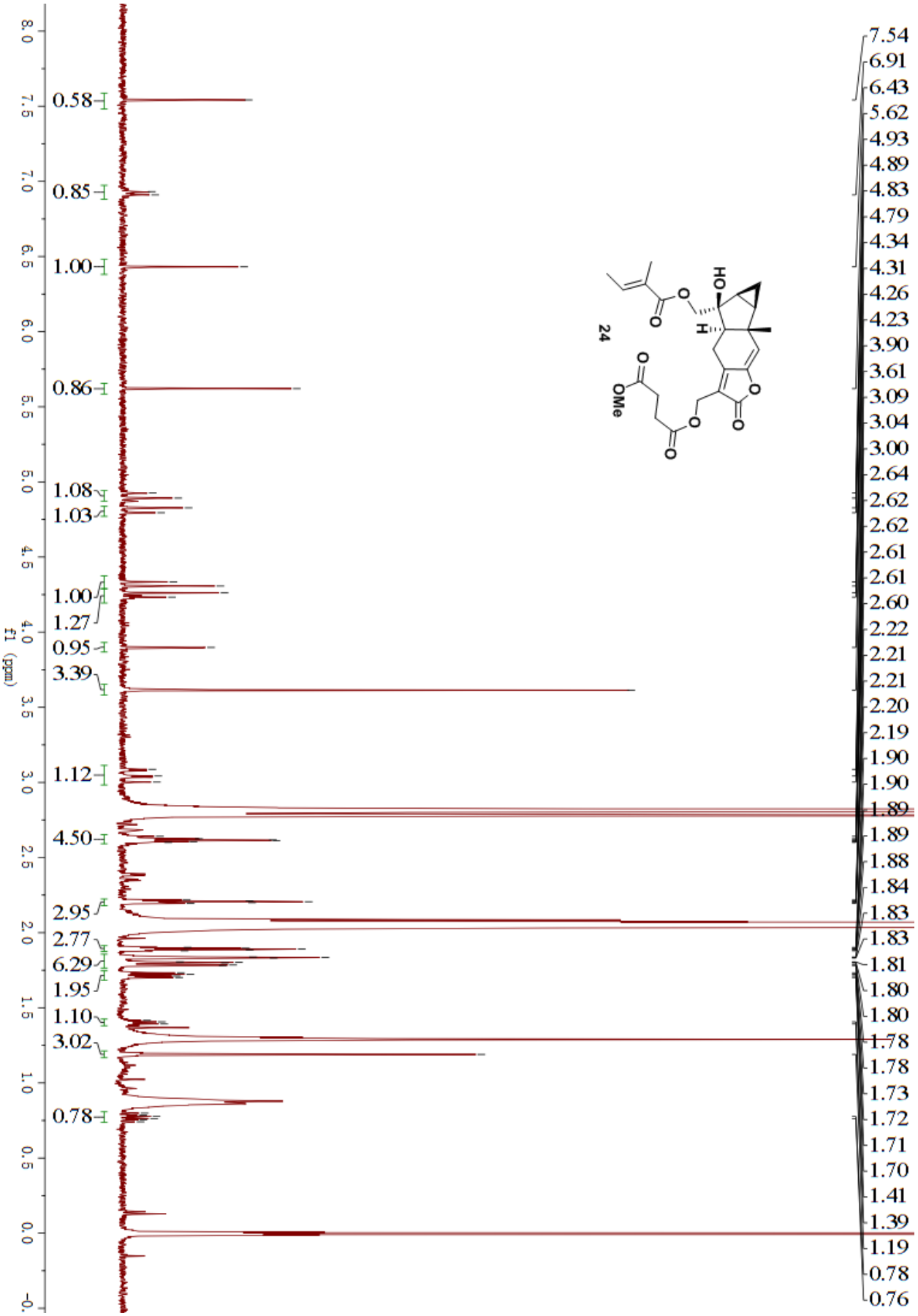
^{1}H NMR spectrum of compound **23** in $CDCl_3$ (400 MHz)



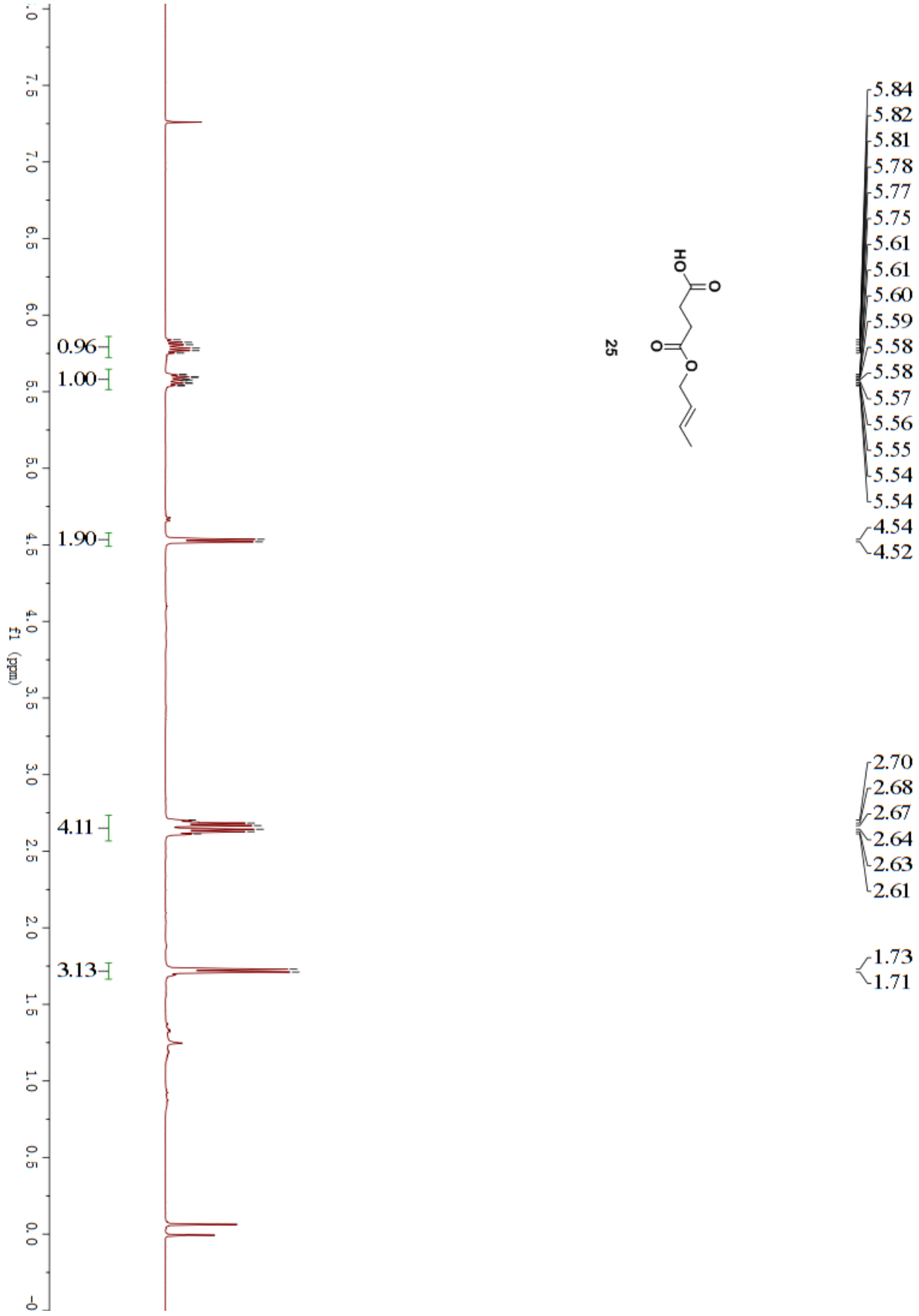
^{13}C NMR spectrum of compound **23** in $CDCl_3$ (125 MHz)



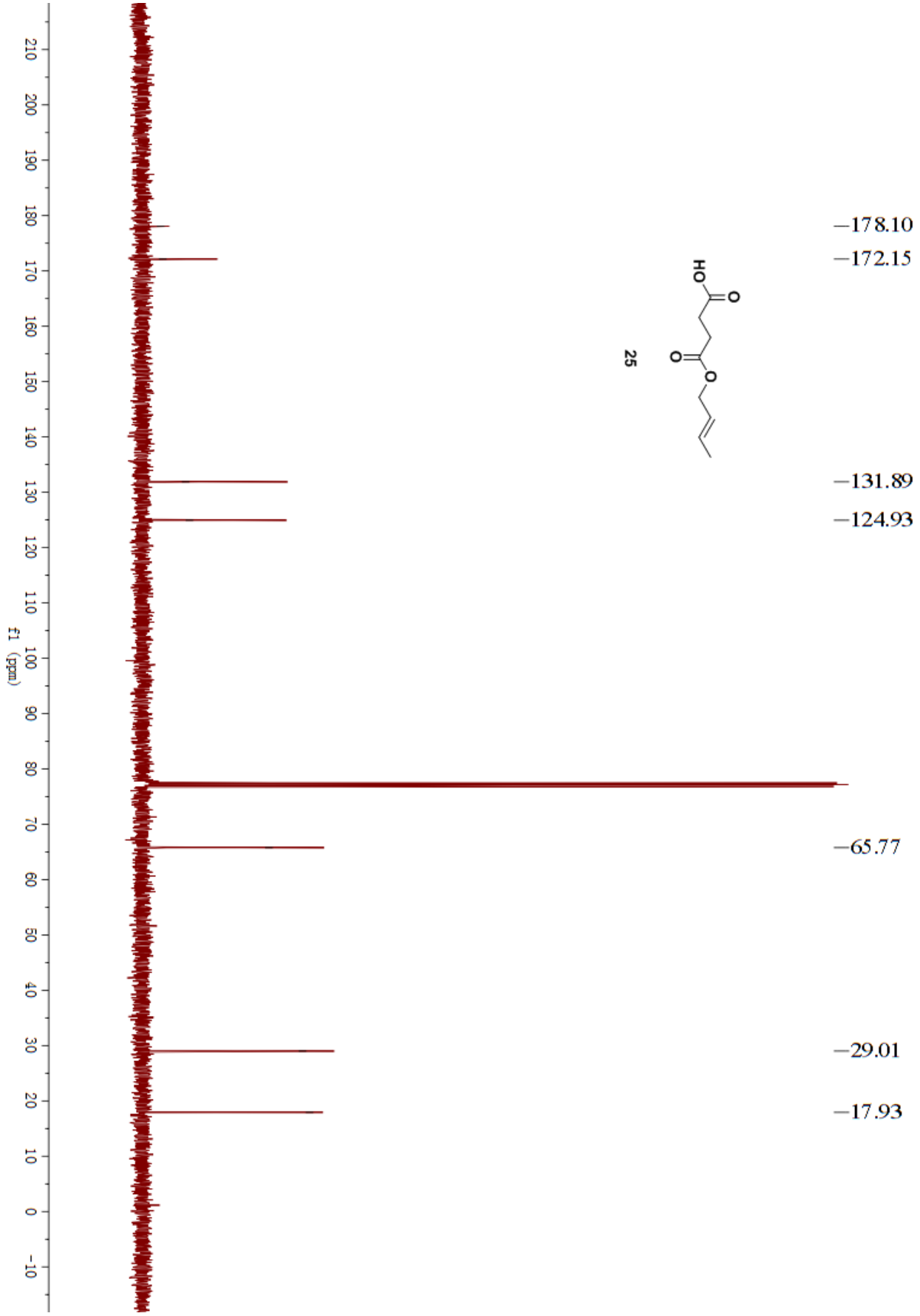
^{1}H NMR spectrum of compound **24** in $CDCl_3$ (400 MHz)



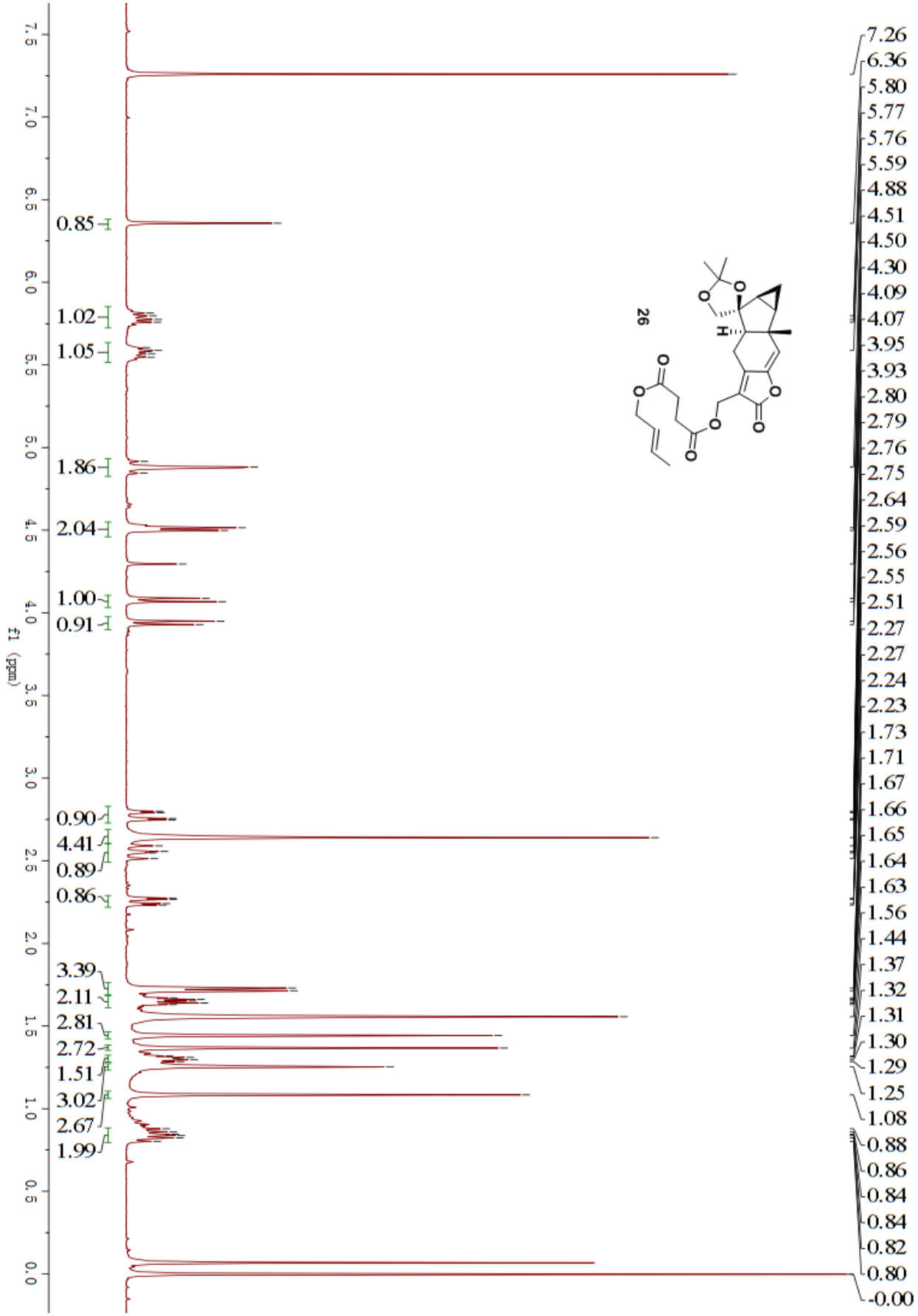
^{1}H NMR spectrum of compound **25** in $CDCl_3$ (400 MHz)



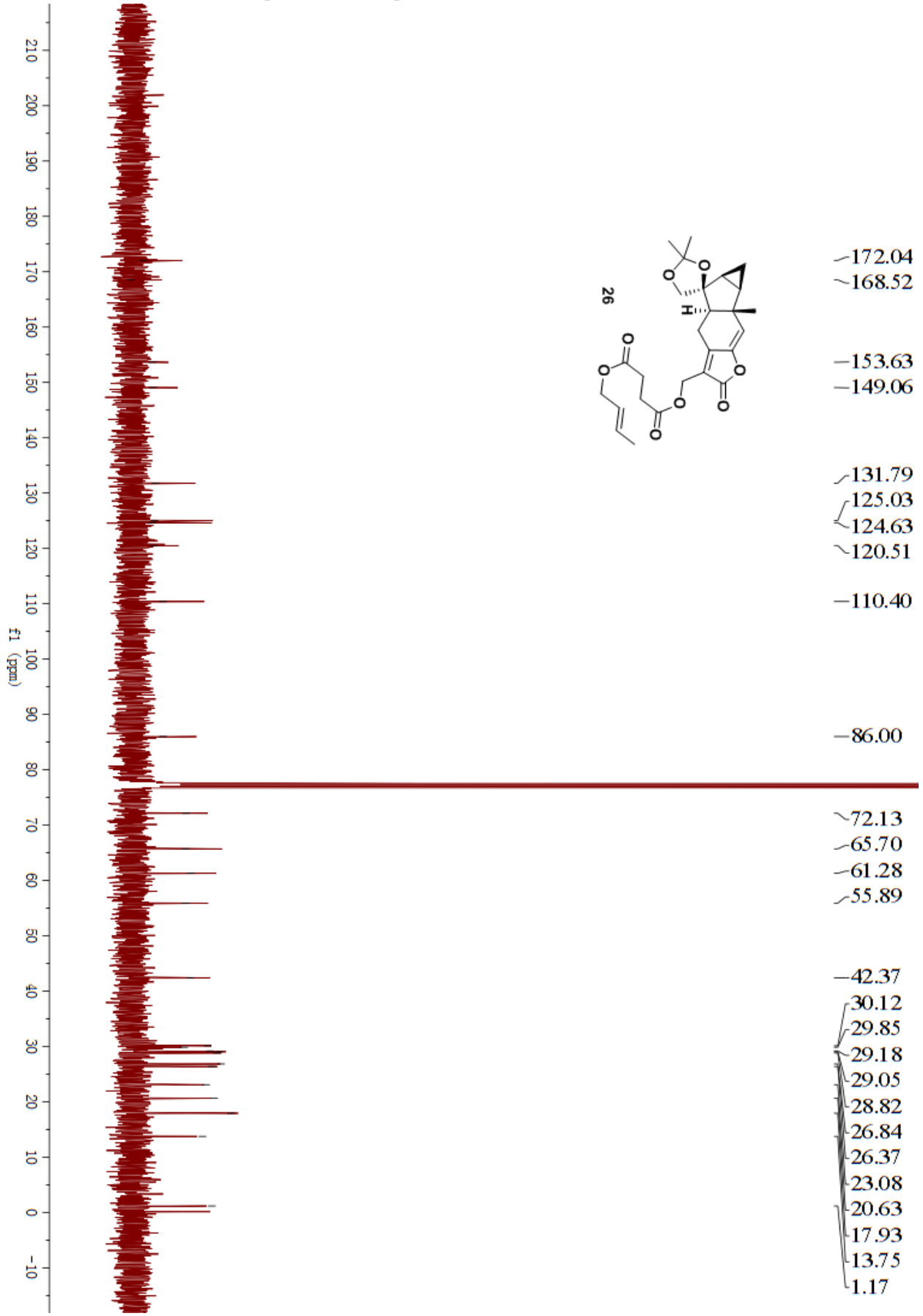
^{13}C NMR spectrum of compound **25** in $CDCl_3$ (125 MHz)



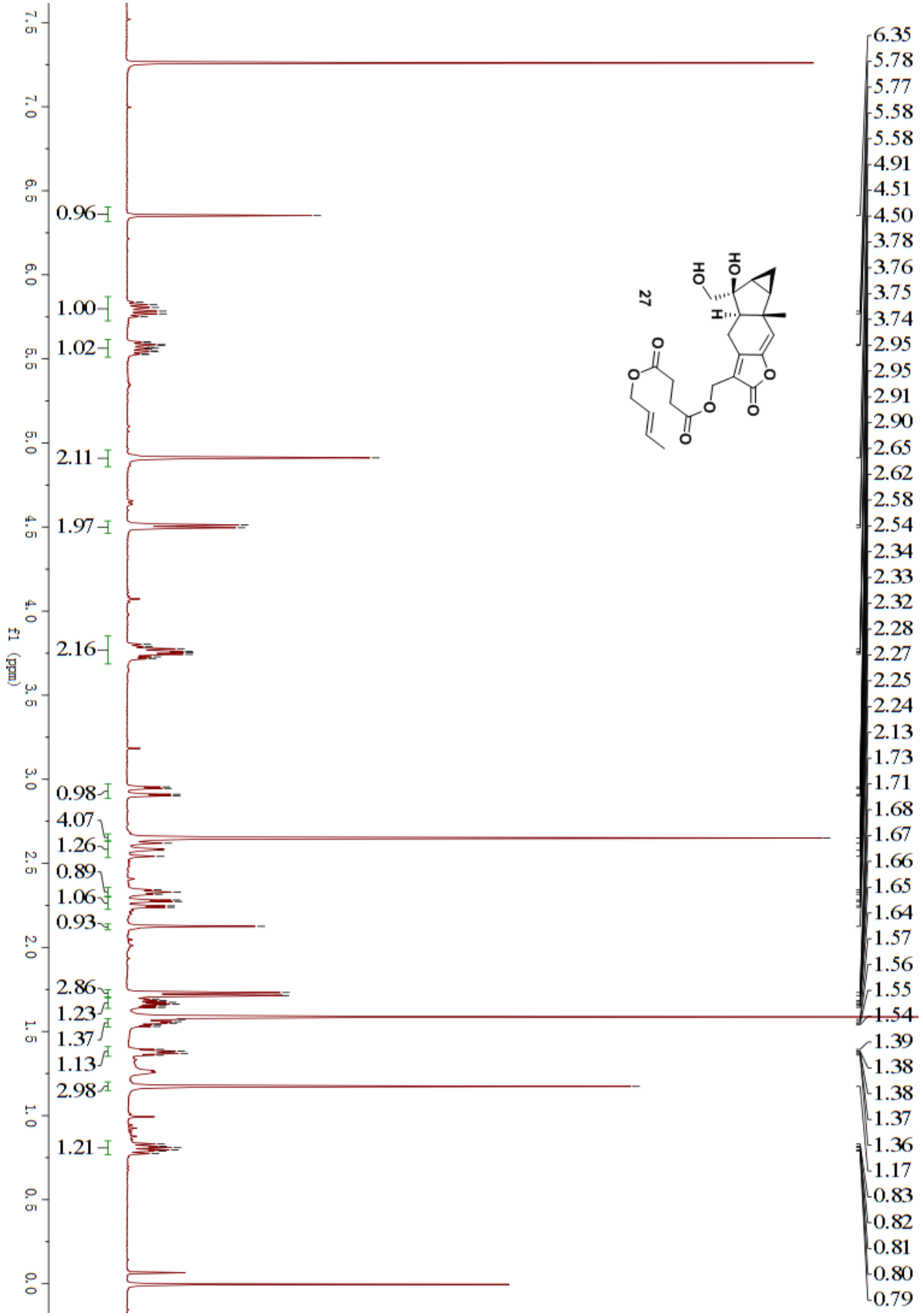
^{1}H NMR spectrum of compound **26** in $CDCl_3$ (400 MHz)



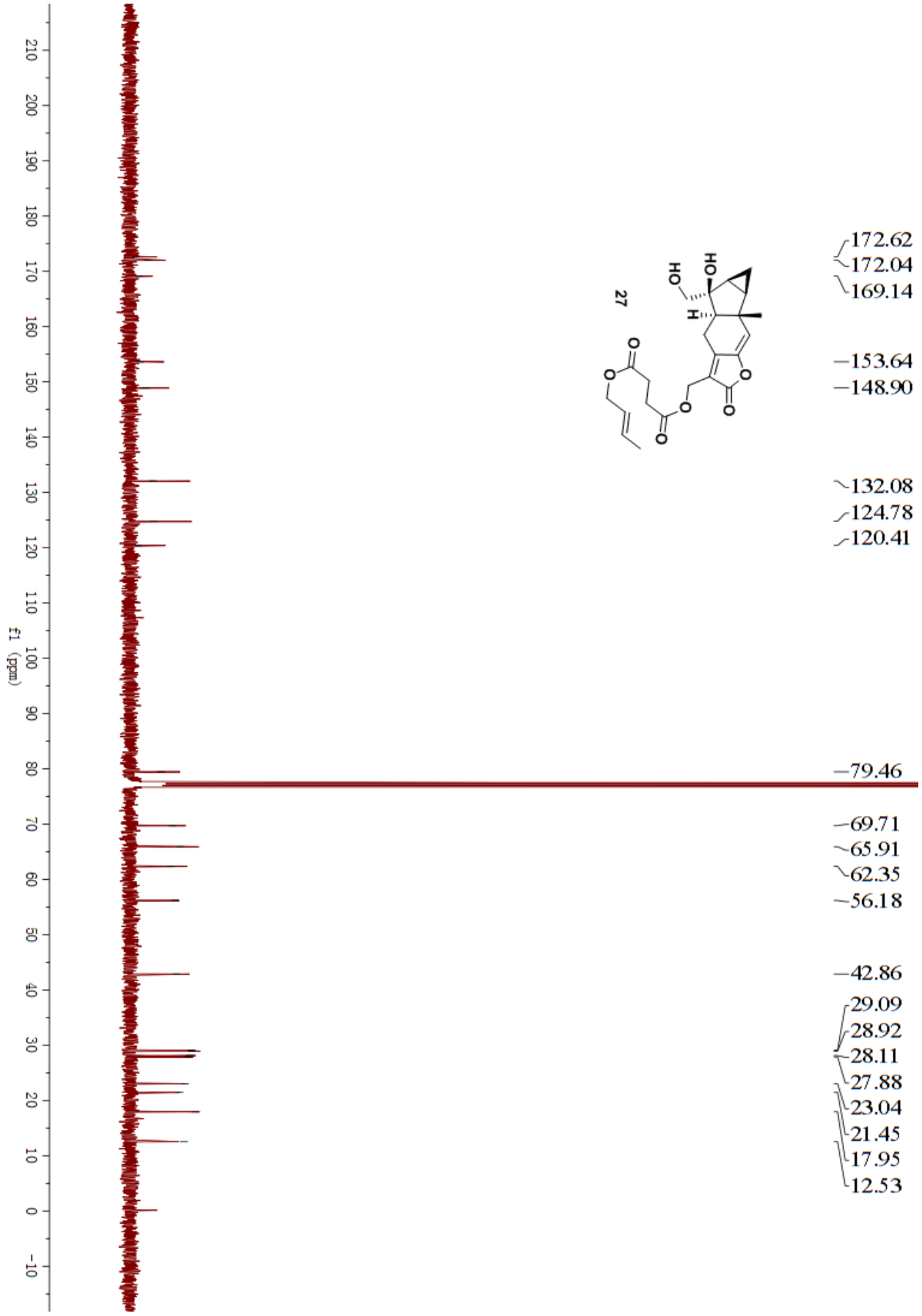
^{13}C NMR spectrum of compound **26** in $CDCl_3$ (125 MHz)



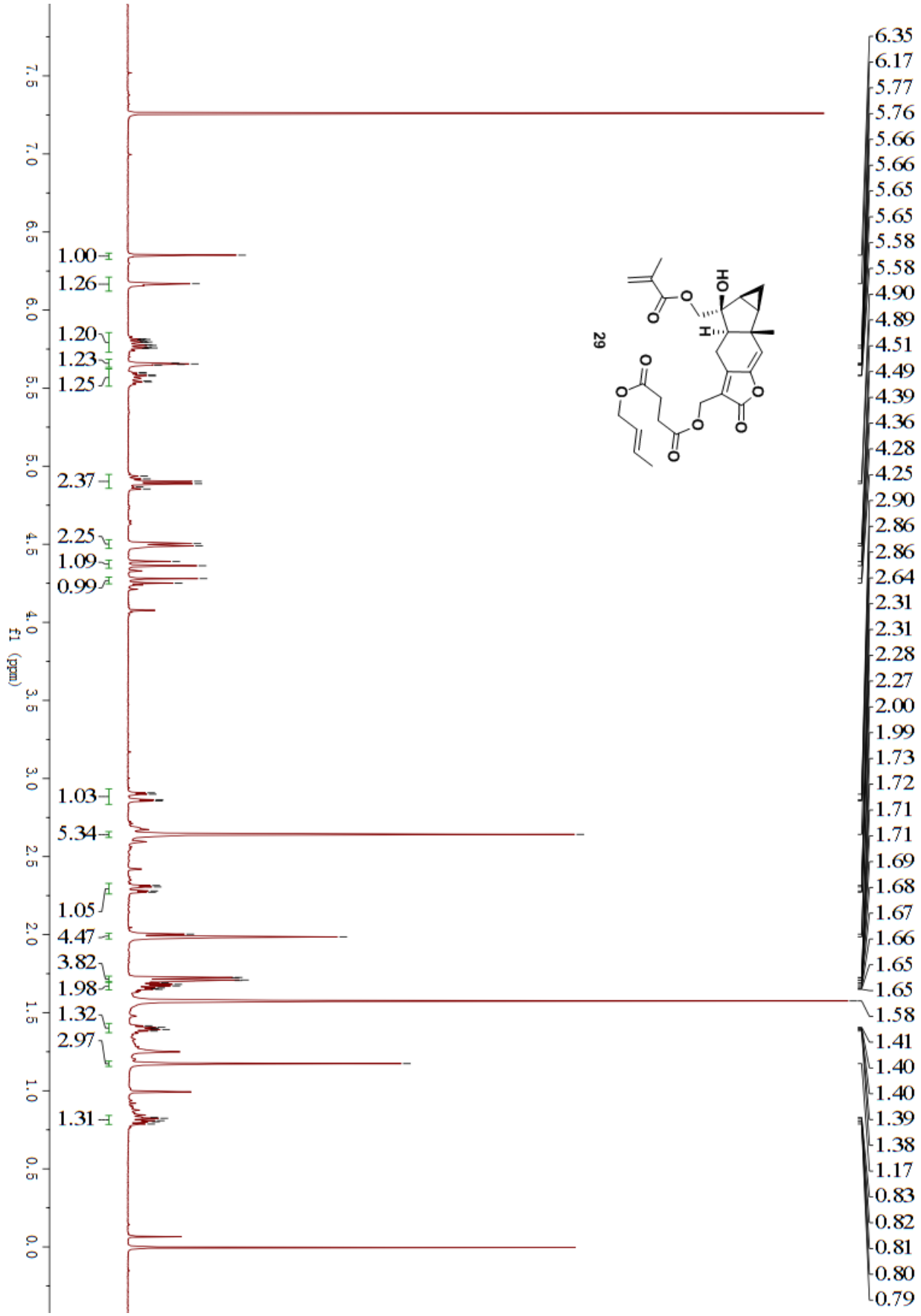
^{1}H NMR spectrum of compound **27** in $CDCl_3$ (400 MHz)



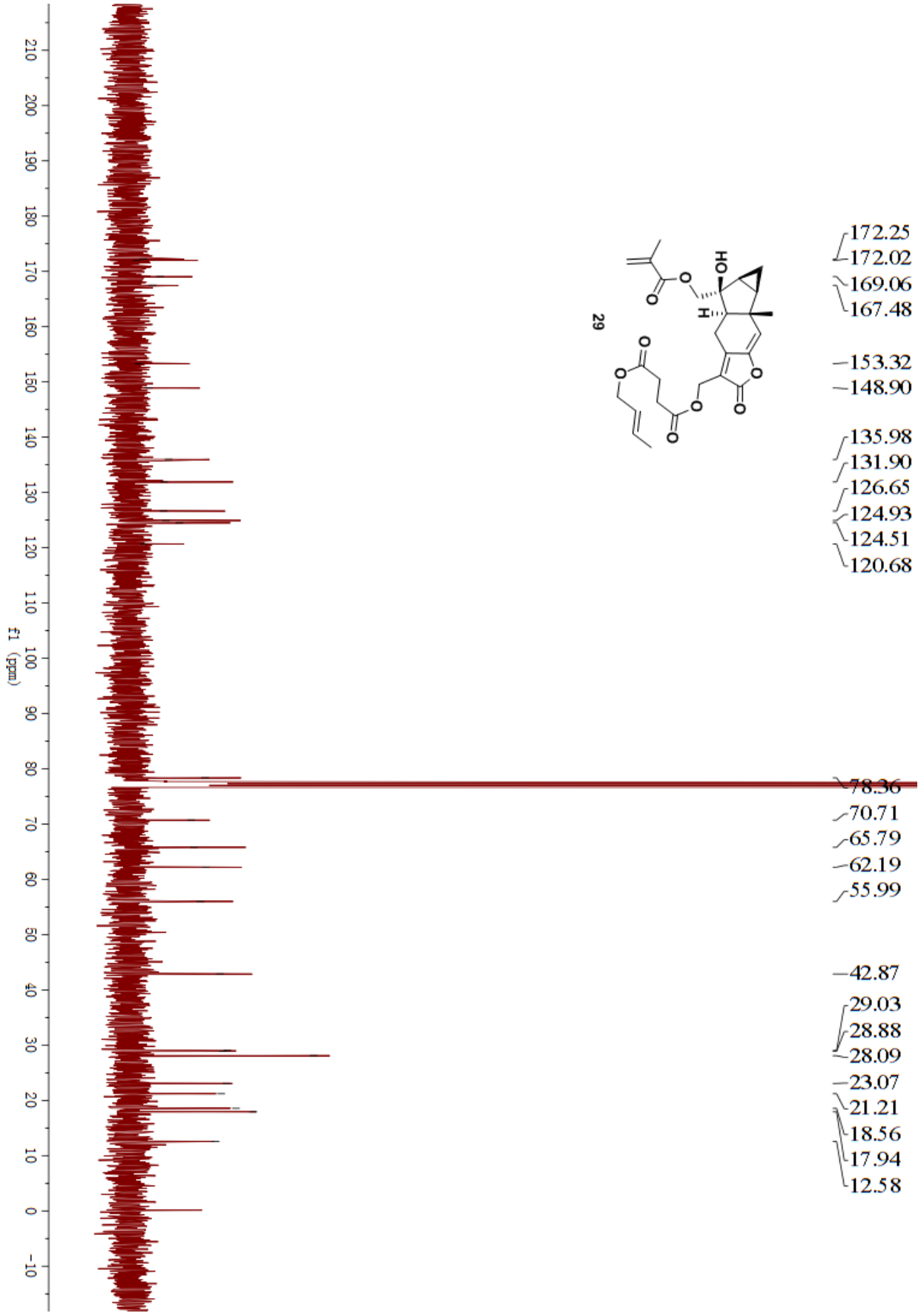
^{13}C NMR spectrum of compound **27** in $CDCl_3$ (125 MHz)



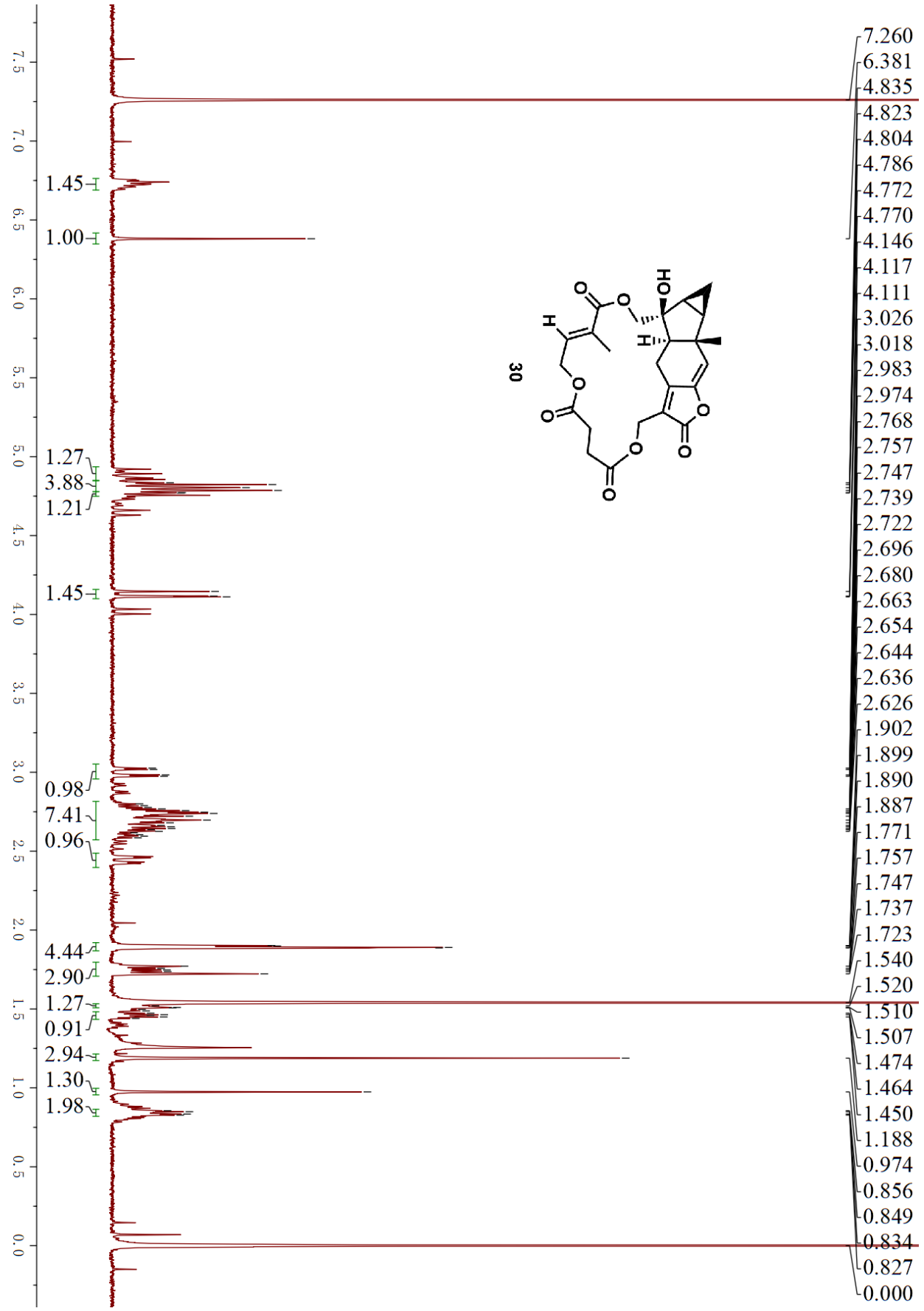
^{1}H NMR spectrum of compound **29** in $CDCl_3$ (400 MHz)



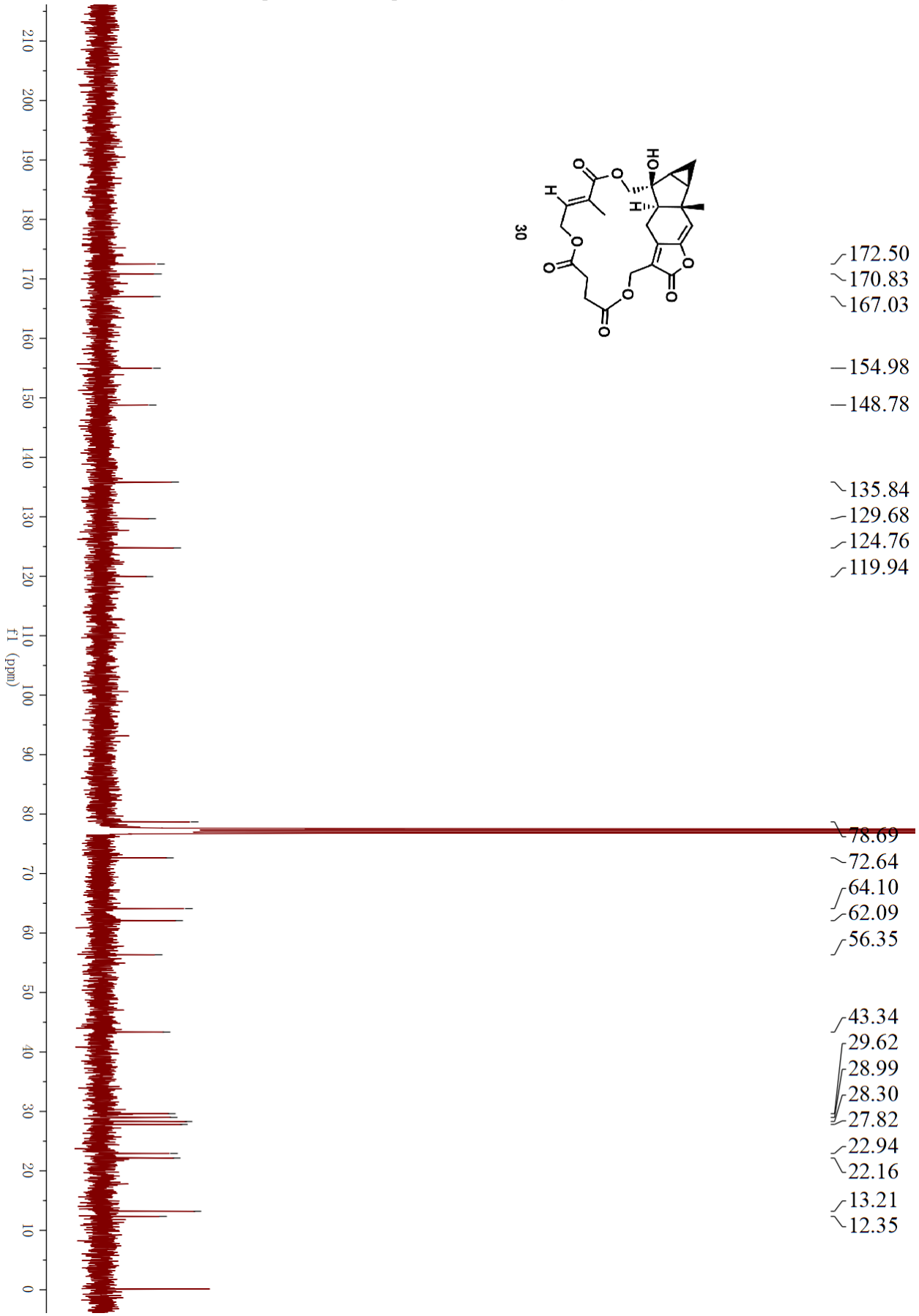
^{13}C NMR spectrum of compound **29** in $CDCl_3$ (125 MHz)



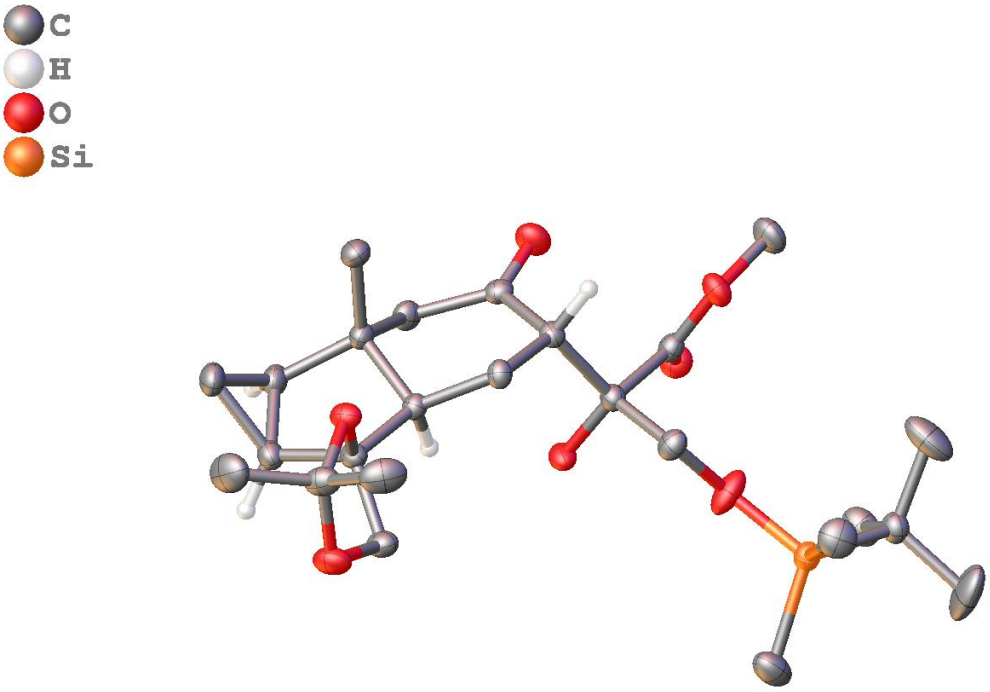
[1]H NMR spectrum of compound **30** in $CDCl_3$ (400 MHz)



^{13}C NMR spectrum of compound **30** in $CDCl_3$ (125 MHz)



7. X-ray Crystallographic Data for compound 20b.



The colourless crystal in block-shape, with approximate dimensions of 0.288 × 0.488 × 0.592 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 173(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) and OLEX 2.3 program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.

Crystal data and structure refinement for CCDC 2233894.

Identification code	lib020
Empirical formula	$C_{25}H_{42}O_7Si$
Formula weight	482.67
Temperature/K	173(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	8.3207(3)
b/Å	12.8221(5)
c/Å	24.7410(9)
α/°	90
β/°	90
γ/°	90
Volume/$Å^3$	2639.59(17)

Z	4
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	1.117
F(000)	1048.0
Crystal size/mm^3	0.592 × 0.488 × 0.288
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.146 to 136.58
Index ranges	$-10 \leq h \leq 10$, $-11 \leq k \leq 15$, $-29 \leq l \leq 27$
Reflections collected	13712
Independent reflections	4781 [R_{int} = 0.0268, R_{sigma} = 0.0276]
Data/restraints/parameters	4781/1/311
Goodness-of-fit on F^2	1.113
Final R indexes [I>=2σ (I)]	R_1 = 0.0286, wR_2 = 0.0732
Final R indexes [all data]	R_1 = 0.0292, wR_2 = 0.0744
Largest diff. peak/hole / e Å^{-3}	0.18/-0.31
Flack parameter	0.024(6)

8.Abbreviations

MTBD	1, 3, 4, 6, 7, 8-hexahydro- 1-methyl- 2H-pyrimidol-[1, 2-a]-pyrimidine
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DBN	1,5-Diazabicyclo[4.3.0]non-5-ene
p-TSA	*p*-tolylsulfonicacid
Mukaiyama Reagent	2-Chloro-1-methylpyridinium iodide
LiHMDS	Lithium bis(trimethylsilyl)amide
KHMDS	Potassium bis(trimethylsilyl)amide
EDCI·HCl	1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride
DMAP	4-Dimethylaminopyridine
DIBAL-H	Diisobutylaluminium hydride