Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Enantioselective Synthesis of (–)-Phaseic Acid

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Supporting Information

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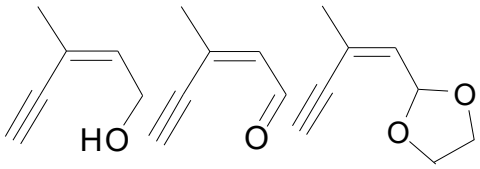
General Procedures. Unless indicated, all commercial available reagents and anhydrous solvents were purchased at the highest commercial quality and were used as received without further purification. All non-aqueous reactions were carried out under argon atmosphere using dry glassware that had been flame-dried under a stream of argon unless otherwise noted. Flash column chromatography was performed on silica gel (Qingdao Haiyang Chemical Co., Ltd., 300-400, 200-300, and 100-200 mesh) using hexane-EtOAc mixtures of increasing polarity. The progress of all the reactions was monitored by thin-layer chromatography (TLC) using glass plates precoated with silica gel-HSGF$_{254}$ to a thickness of 0.2 ± 0.03mm. ^{13}C NMR and ^{1}H NMR spectra were recorded on either 400 MHz/500 MHz Bruker instrument. $CDCl_3$ was treated with flame dried K_2CO_3, chemical shifts (δ) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak ($CDCl_3$ or CD_3OD), with the abbreviations s, br s, d, t, q, and m denoting singlet, broad singlet, doublet, triplet, quartet and multiplet respectively. *J* = coupling constants given in Hertz (Hz). High resolution Mass spectra (HRMS) were recorded on a Thermo Scientific^{TM} Q-exactive hybrid quadrupole-orbitrap mass spectrometer. Optical rotation data were collected on an Autopol automatic polarimeter (Rudolph Research Analytical) using HPLC grade anhydrous MeOH.

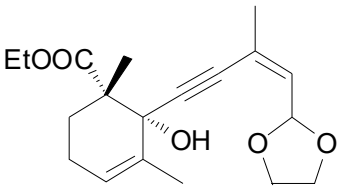


3 **4** **5**

5: To a solution of **3** (6 mL, 58.7 mmol) in dry DCM was added MnO_2 (102 g, 20 eq., 1174.0 mmol) slowly. The resulting mixture was stirred at RT overnight. After the starting material was consumed completely, the reaction mixture was filtered through a pad of celite, and concentrated via high-vaccum pump to afford compound **4**, which was used directly in the next step.

Compound **4** (58.7 mmol), ethylene glycol (10.8 mL, 3eq., 176.1 mmol), pyridinium p-toluenesulphonate (1.506 g, 0.1 eq., 5.87 mmol) were subsequently added into toluene (60 mL). The resulting mixture was stirred and heated under reflux for 2.0 h with provision for azeotropic removal of water. Upon completion, the reaction was quenched with brine and extracted with EtOAc twice. The combined organic solutions were washed with brine, dried over Na_2SO_4 and concentrated. The residue was then purified by column chromatography (Hexane) to give the compound **5** as light yellow oil (5.92 g, 73% over 2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (d, *J* = 8.1 Hz, 1H), 5.72 (d, *J* = 7.7 Hz, 1H), 4.03 (dd, *J* = 8.8, 5.0 Hz, 2H), 3.94 (dd, *J* = 8.8, 5.1 Hz, 2H), 3.21 (s, 1H), 1.96 (s, 3H); HRMS (ESI) m/e 139.0751 $[M+H]^+$ calcd for $C_8H_{11}O_2^+$: 139.0754.

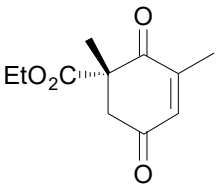


7

7: To a solution of **5** (63 mg, 3.0 eq., 0.46 mmol) in THF (1 mL) was added n-BuLi (1.54 mol/L, 3.5 eq., 0.35 mL) dropwise at -78 °C. The mixture was stirred at -78 °C for 1 h. Compound **6** (30 mg, 0.153 mmol) in THF (1 mL) was then added dropwise to the mixture mentioned above. After stirring at -78 °C for another 3 h, saturated aqueous NH_4Cl were added to quench the reaction. The organic phase was separated and the aqueous phase was extracted with EtOAc (2 × 5 mL). The combined organic phases were washed with brine (10 mL), dried over anhydrous Na_2SO_4, filtered,

and concentrated under reduced pressure. The resulting residue was purified by column chromatography to give the product **7** (24 mg, 46%) as light yellow oil.

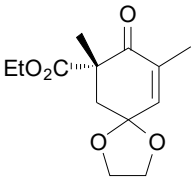
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.62 (dd, *J* = 7.7, 1.2 Hz, 1H), 5.57 (d, *J* = 7.8 Hz, 1H), 5.43 (s, 1H), 4.31 – 4.21 (m, 2H), 4.17 (s, 1H), 4.00 (m, 2H), 3.91 (m, 2H), 2.17 – 2.07 (m, 3H), 1.98 (m, 1H), 1.88 (d, *J* = 1.1 Hz, 3H), 1.87 (d, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 134.0, 132.3, 125.2, 122.9, 101.5, 97.0, 81.4, 71.8, 65.0, 65.0, 61.2, 50.0, 27.8, 23.4, 21.7, 17.9, 16.9, 14.2; HRMS (ESI) m/e 335.1841 $[M+H]^+$ calcd for $C_{19}H_{27}O_5^+$: 335.1853



11

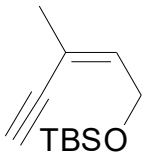
11: To a solution of **6** (1.0 g, 5.1 mmol, $[\alpha]_D^{20}$ 22.2° (c = 0.10, MeOH)) in anhydrous EtOAc (20 mL) was added tert-butyl hydroperoxide (10mL, ~ 10 eq., 5.5 M in decane) and 3Å molecular sieves (1.5 g). The mixture was stirred at 0 °C for 30 min. Manganese(III) acetate dihydrate (670 mg, 0.5eq., 2.5 mmol) was then added to the reaction mixture in one portion, and the resulting mixture was stirred at RT for 48 h. Upon completion of the reaction, the solution was filtered through a pad of celite. Concentration of the filtrate followed by column chromatography afforded the compound **11** as a clear oil (0.8 g, 75%).

$[\alpha]_D^{20}$ 9.1° (c = 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.56 (s, 1H), 4.17 (dt, *J* = 7.0, 2.1 Hz, 2H), 3.32 (d, *J* = 16.6 Hz, 1H), 2.66 (d, *J* = 16.7 Hz, 1H), 2.04 (s, 3H), 1.49 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.0, 194.9, 171.0, 150.4, 137.5, 62.3, 56.3, 47.2, 20.4, 16.9, 13.9; HRMS (ESI) m/e 211.0961 $[M+H]^+$ calcd for $C_{11}H_{15}O_4^+$: 211.0965.



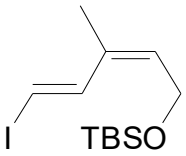
12 **12:** To a solution of **11** (350 mg, 1.67 mmol) in dry DCM (6 mL) was added ethylene glycol(93 µL, 1.0 eq., 1.67 mmol). The reaction mixture was cooled to -78 °C under nitrogen atmosphere, 1,2-Bis(trimethylsilyloxy)ethane (0.819 mL, 2.0 eq., 3.34 mmol) and TMSOTf (30.5 µL, 0.1 eq., 0.167 mmol) was then added. After stirring for 30 min at -78 °C, the reaction was allowed to warm up to RT slowly. After stirring at room temperature for another 3 h, saturated aqueous $NaHCO_3$ were added. The organic phase was separated and the aqueous phase was extracted with EtOAc (2 × 15 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, concentrated under reduced pressure and purified by column chromatography to give the product **12** (390 mg, 92%).

$[\alpha]_D^{20}$ 9.2° (c = 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.33 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.07 – 3.90 (m, 4H), 2.68 (d, *J* = 13.8 Hz, 1H), 2.11 (d, *J* = 13.9 Hz, 1H), 1.86 (s, 3H), 1.43 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.2, 173.1, 140.1, 137.4, 103.2, 65.1, 64.7, 61.4, 52.9, 43.5, 21.6, 16.2, 13.9; HRMS (ESI) m/e 255.1221 $[M+H]^+$ calcd for $C_{13}H_{19}O_5^+$: 255.1227.



9 **9:** To a stirred solution of **3** (5 mL, 49 mmol) in DCM (50 mL) were added TBSCl (11.5 g, 77 mmol) at 0 °C, then Et_3N (14 mL, 101.2 mmol) was added dropwise. The reaction mixture was stirred at °C for 30 min and warmed to RT. After stirring at RT overnight, saturated aqueous $NaHCO_3$ (50 mL) was added to quench and extracted with DCM (3 × 50 mL). The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography to give the compound **9** as light yellow oil (10.1 g, 98% yield).

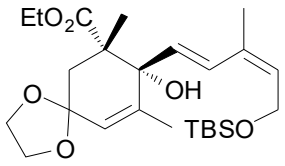
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 – 5.84 (m, 1H), 4.40 (dd, *J* = 6.4, 1.2 Hz, 2H), 3.16 (s, 1H), 1.90 (d, *J* = 1.4 Hz, 3H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 117.7, 82.1, 81.8, 62.2, 26.0, 22.9, 18.4, -5.1; HRMS (ESI) m/e 211.1505 $[M+H]^+$ calcd for $C_{12}H_{23}OSi^+$: 211.1513.



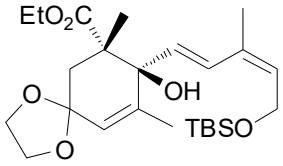
10

10: To a solution of **9** (2.1 g, 10.0 mmol) in THF (40 mL) was charged with HCp_2ZrCl (3.1 g, 1.2 eq., 12 mmol) at 23 °C while shielding the reaction from daylight. After stirring for 2 h, a solution of I_2 (3.8 g, 1.5 eq., 15 mmol) in THF (10 mL) was added via cannula at -78 °C. The reaction mixture was stirred at -78 °C for 0.5 h, and then quenched with a mixture of $Na_2S_2O_3$ (sat.) and $NaHCO_3$ (sat.) solution (1:1), extracted with Et_2O, washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified via silica gel flash column chromatography (EtOAc: Hexane = 2: 98) to afford the title compound **10** (3.04 g, 90%) as oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 14.5 Hz, 0.8Hz, 1H), 6.39 (d, *J* = 14.5 Hz, 1H), 5.46 (t, *J* = 6.4 Hz, 1H), 4.31 (dd, *J* = 6.4 Hz, 1.0 Hz, 2H), 1.83 (d, *J* = 1.2 Hz, 3H), 0.93 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 133.5, 130.4, 78.4, 59.4, 26.0, 19.6, 18.4, -5.10; HRMS (ESI) m/e 339.0627 $[M+H]^+$ calcd for $C_{12}H_{24}OISi^+$: 339.0636.



13

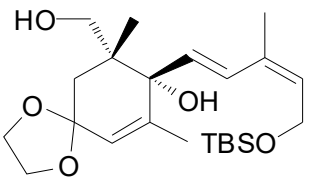


13a

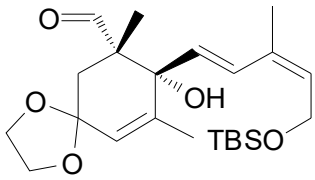
13: To a solution of **10** (624 mg, 2.53 mmol) in Et_2O (15 mL) was added a solution of *t*-BuLi (6.8 mL, 3.5 eq., 1.3 M, 8.84 mmol) in Et_2O (15 mL) dropwise through cannula at -78 °C. After stirring at -78 °C for 1 h, the solution of **12** (2.56 g, 3.0 eq., 7.57 mmol) in Et_2O (15 mL) was added and stirred for 2h. The reaction was quenched with sat. aq. NH_4Cl at -78 °C and slowly warmed up

to RT. The aqueous portion was extracted with EtOAc (3 × 25 mL) and organic phases were combined, washed with sat. aq. NaCl, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc: Hexane = 1: 10) to provide a mixture of **13** and epimer **13a** (total 823 mg, 70 %). Further purification with flash column chromatography on silica gel (EtOAc: Hexane = 0.1: 10 to 1: 10) to afford pure **13** (482 mg, 41%).

$[\alpha]_D^{20}$ – 33.8° (c = 0.10, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (d, *J* = 15.5 Hz, 1H), 5.70 (d, *J* = 15.5 Hz, 1H), 5.50 (t, *J* = 6.6 Hz, 1H), 5.37 (s, 1H), 4.35 (d, *J* = 6.6 Hz, 2H), 4.13 (m, 2H), 3.93 – 4.08 (m, 4H), 2.42 (d, *J* = 14.9 Hz, 1H), 2.11 (dd, *J* = 14.9, 1.7 Hz, 1H), 1.78 (d, *J* = 0.9 Hz, 3H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.46 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H), 0.92 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 176.5, 140.2, 132.1, 130.8, 130.6, 127.3, 122.6, 104.6, 77.3, 64.8, 64.0, 61.2, 59.4, 50.6, 38.9, 26.0, 20.6, 19.7, 18.4, 17.2, 14.2, -5.1; HRMS (ESI) m/e 467.2810 $[M+H]^+$ calcd for $C_{25}H_{43}O_6Si^+$: 467.2823; HRMS (ESI) m/e 489.2634 $[M+Na]^+$ calcd for $C_{25}H_{42}O_6NaSi^+$: 489.2643.



14



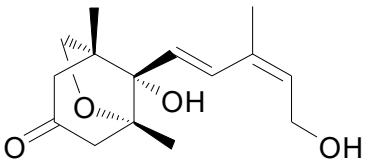
14a

14: To a solution of **13** (351 mg, 0.753 mmol) in THF (30 mL) was added a suspension of $LiAlH_4$ (1.13 mL, 1.5 eq., 1.13 mmol, 1 M) dropwise at 0 °C. After stirring for 1 h, the mixture was allowed to warm to room temperature and stirred for another 3 h. The reaction mixture was then cooled to 0 °C and quenched with seignette salt (20 mL). The aqueous portion was extracted with EtOAc (2 × 25 mL) and organic phases were combined, washed with sat. aq. NaCl, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel (EtOAc: Hexane = 1: 10 to 2: 10) to provide **14** (160 mg, 50%) and **14a** (120 mg, 38 %); **14a** (120 mg, 0.284 mmol) can be reduced using the same procedure above to give the compound **14** (96 mg, 80%, total 80.2%).

14: $[\alpha]_D^{20}$ – 11.7° (c = 0.10, MeOH); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (d, *J* = 15.6 Hz, 1H), 5.74 (d, *J* = 15.6 Hz, 1H), 5.49 (t, *J* = 6.6 Hz, 1H), 5.38 (s, 1H), 4.35 (d, *J* = 3.2 Hz, 2H), 4.05 – 3.92 (m, 4H), 3.60 (d, *J* = 10.5 Hz, 1H), 3.32 (d, *J* = 10.5 Hz, 1H), 1.84 (s,

3H), 1.81 (d, *J* = 14.2 Hz, 1H), 1.65 (d, *J* = 1.1 Hz, 3H), 1.56 (d, *J* = 14.2 Hz, 1H), 1.21 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.2, 132.6, 131.4, 129.8, 126.8, 122.8, 104.9, 79.2, 70.1, 64.7, 64.0, 59.4, 42.9, 39.7, 26.0, 20.7, 18.4, 18.3, 17.4, -5.04; HRMS (ESI) m/e 425.2703 $[M+H]^+$ calcd for $C_{23}H_{41}O_5Si^+$: 425.2718; HRMS (ESI) m/e 447.2528 $[M+Na]^+$ calcd for $C_{23}H_{40}O_5NaSi^+$: 447.2537.

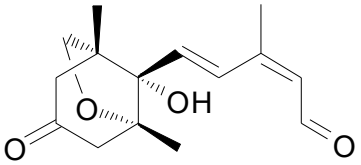
14a: $[\alpha]_D^{20}$ – 1.7° (c = 0.10, MeOH);^{1}H NMR (400 MHz, $CDCl_3$) δ 9.57 (s, 1H), 6.61 (dd, *J* = 15.6, 0.5 Hz, 1H), 5.55 (d, *J* = 15.6 Hz, 1H), 5.44 (t, *J* = 6.4 Hz, 1H), 5.38 (s, 1H), 4.26 (dd, *J* = 6.6, 1.0 Hz, 2H), 3.97 – 3.86 (m, 4H), 2.11 (d, *J* = 14.6 Hz, 1H), 1.91 (dd, *J* = 13.5, 1.4 Hz, 1H), 1.70 (d, *J* = 1.1 Hz, 3H), 1.62 (d, *J* = 1.4 Hz, 3H), 1.20 (s, 3H), 0.83 (s, 9H), 0.01 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 140.3, 132.1, 131.0, 129.7, 128.1, 124.4, 104.3, 77.2, 64.8, 64.2, 59.3, 53.4, 37.6, 26.0, 20.5, 18.4, 17.3, 16.1, -5.1; HRMS (ESI) m/e 423.2566 $[M+H]^+$ calcd for $C_{23}H_{39}O_5Si^+$: 423.2561.



15

15: A solution of **14** (42 mg, 0.1 mmol) and p-toluenesulfonic acid monohydrate (19 mg, 1.0 eq., 0.1 mmol) in acetone (80 mL) and water (2 drops) was stirred at room temperature overnight. The reaction mixture was poured into saturated aqueous $NaHCO_3$. The organic layer was removed via evaporate and the residue was dissolved in EtOAc. The aqueous layer was extracted with EtOAc. Combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified via silica gel flash column chromatography (Hexane: EtOAc = 1: 2) to afford the product **15** (18.4 mg, 69%) as a colorless oil.

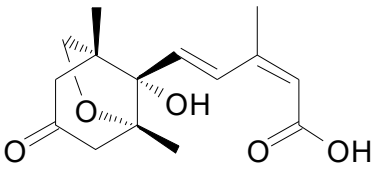
$[\alpha]_D^{20}$ – 16.8° (c = 0.10, MeOH);^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, *J* = 15.4 Hz, 1H), 5.89 (d, *J* = 15.4 Hz, 1H), 5.69 (t, *J* = 7.0 Hz, 1H), 4.38 (d, *J* = 7.1 Hz, 2H), 3.94 (dd, *J* = 8.2, 1.7 Hz, 1H), 3.78 (d, *J* = 8.2 Hz, 1H), 2.63 (s, 2H), 2.57 (dd, *J* = 18.4, 2.0 Hz, 1H), 2.45 (d, *J* = 18.3 Hz, 1H), 1.88 (s, 3H), 1.21 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 134.2, 130.8, 130.1, 125.3, 85.7, 82.4, 77.2, 58.4, 52.6, 52.5, 48.1, 20.6, 18.8, 15.7; HRMS (ESI) m/e 267.1582 $[M+H]^+$ calcd for $C_{15}H_{23}O_4^+$: 267.1591.



16

16: To a solution of **15** (9 mg, 0.0338 mmol) in DCM (5 mL) was added Dess–Martin periodinane (72.0 mg, 5.0 eq., 0.17 mmol) at 0 ºC. After stirring for 30 min, the reaction was quenched with saturated aqueous $Na_2S_2O_3$ (5 mL). The reaction mixture was extracted with EtOAc, combined organic layers were washed with saturated aqueous $NaHCO_3$, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified via silica gel flash column chromatography (EtOAc: Hexane = 0.5: 1 to 2: 1) to afford the product **16** as a colorless oil (8.93 mg, quant.).

$[\alpha]_D^{20}$ – 22.7° (c = 0.10, MeOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.26 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 15.3 Hz, 1H), 6.26 (d, *J* = 15.2 Hz, 1H), 5.97 (d, *J* = 7.8 Hz, 1H), 3.96 (dd, *J* = 8.5, 2.7 Hz, 1H), 3.82 (d, *J* = 8.5 Hz, 1H), 2.70 (dd, *J* = 18.4, 1.9 Hz, 1H), 2.63 (d, *J* = 18.5 Hz, 1H), 2.58 (dd, *J* = 18.6, 2.5 Hz, 1H), 2.52 (dd, *J* = 18.4, 1.7 Hz, 1H), 2.10 (d, *J* = 0.9 Hz, 3H), 1.24 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 207.6, 190.3, 152.3, 132.0, 130.0, 129.8, 85.9, 82.7, 77.4, 52.5, 52.5, 48.6, 21.4, 19.0, 15.9; HRMS (ESI) m/e 265.1433 $[M+H]^+$ calcd for $C_{15}H_{21}O_4^+$: 265.1434.

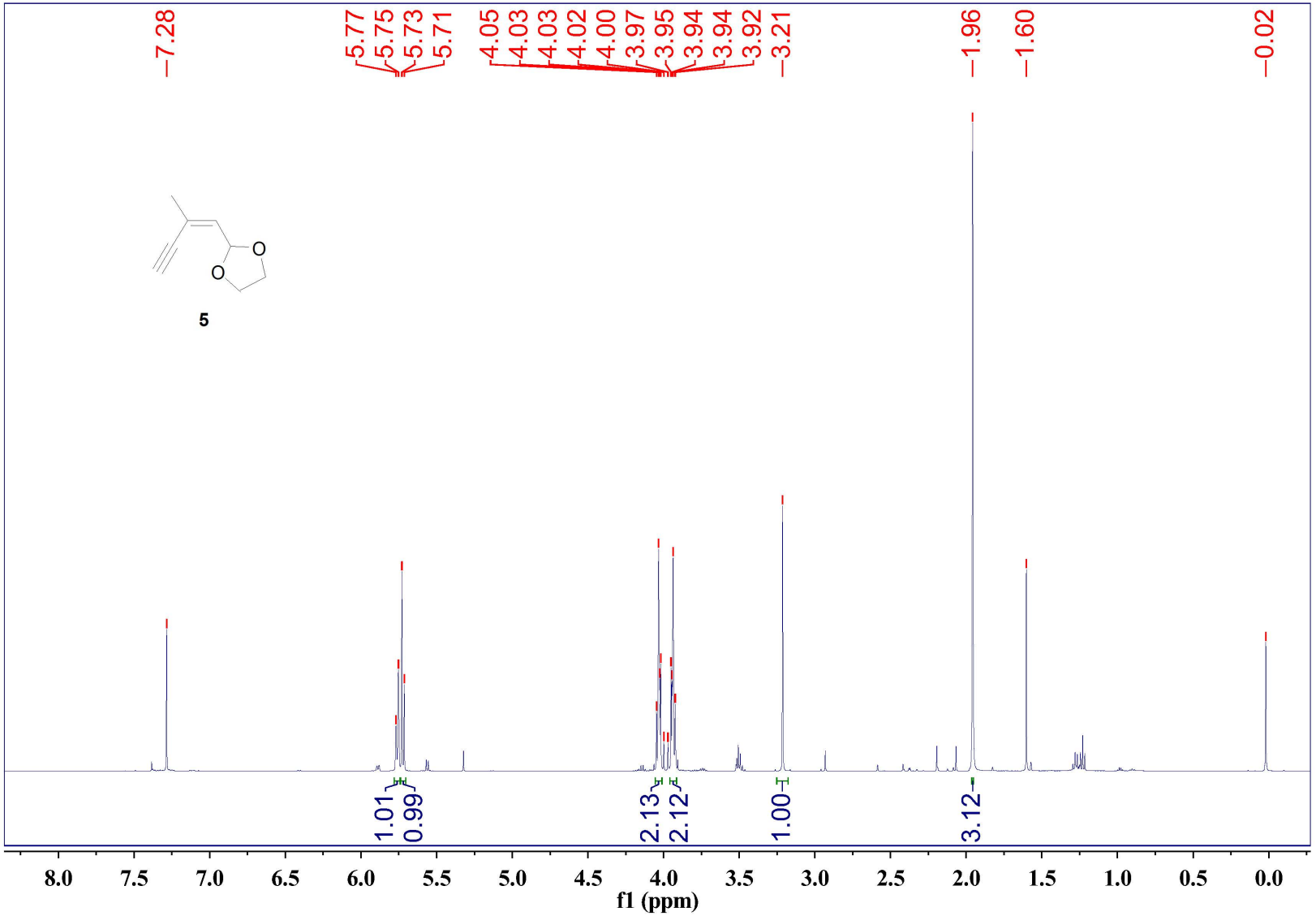


Phaseic acid (2)

2: To a solution of **16** (15.0 mg, 0.057 mmol) in *t*-BuOH/H_2O (3 mL/1 mL) was added KH_2PO_4 (28 mg, 4 eq., 0.233 mol), 2-methyl-2-butene (122 μL, 20 eq., 1.14 mmol) and $NaClO_2$ (65 mg, 10 eq., 0.57 mmol, wt. 80%) subsequently at RT. After stirring for 30 min, the reaction mixture was acidified with HCl (1 N) and extracted with EtOAc, dried over Na_2SO_4, and concentrated. The residue was purified via silica gel flash column chromatography (EtOAc: Hexane: AcOH = 2: 1: 0.1%) to afford the product **2** as a white solid (14.2 mg, 89%).

$[\alpha]_D^{16}$ – 17.1° (c = 0.10, MeOH); ^{1}H NMR (500 MHz, CD_3OD_SPE) δ 8.10 (d, *J* = 15.9 Hz, 1H), 6.46 (d, *J* = 15.9 Hz, 1H), 5.78 (s, 1H), 3.93 (dd, *J* = 7.6, 2.9 Hz, 1H), 3.66

(d, J = 7.6 Hz, 1H), 2.80 (d, J = 17.9 Hz, 1H), 2.70 (dd, J = 18.0, 2.6 Hz, 1H), 2.46 (dd, J = 17.9, 2.5 Hz, 1H), 2.38 (dd, J = 18.0, 2.5 Hz, 1H), 2.06 (d, J = 1.0 Hz, 3H), 1.20 (s, 3H), 1.00 (s, 3H); ^{13}C NMR (125 MHz, CD_3OD_SPE) δ 209.5, 168.1, 149.9, 132.3, 131.5, 118.3, 86.4, 81.6, 77.2, 52.6, 51.8, 48.2, 19.8, 18.0, 14.4; HRMS (ESI) m/e 281.1381 $[M+H]^+$ calcd for $C_{15}H_{21}O_5^+$: 281.1384; HRMS (ESI) m/e 303.1195 $[M+Na]^+$ calcd for $C_{15}H_{20}O_5Na^+$: 303.1203.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1.60
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O
O
5
1.01
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2.13
2.12
1.00
3.12
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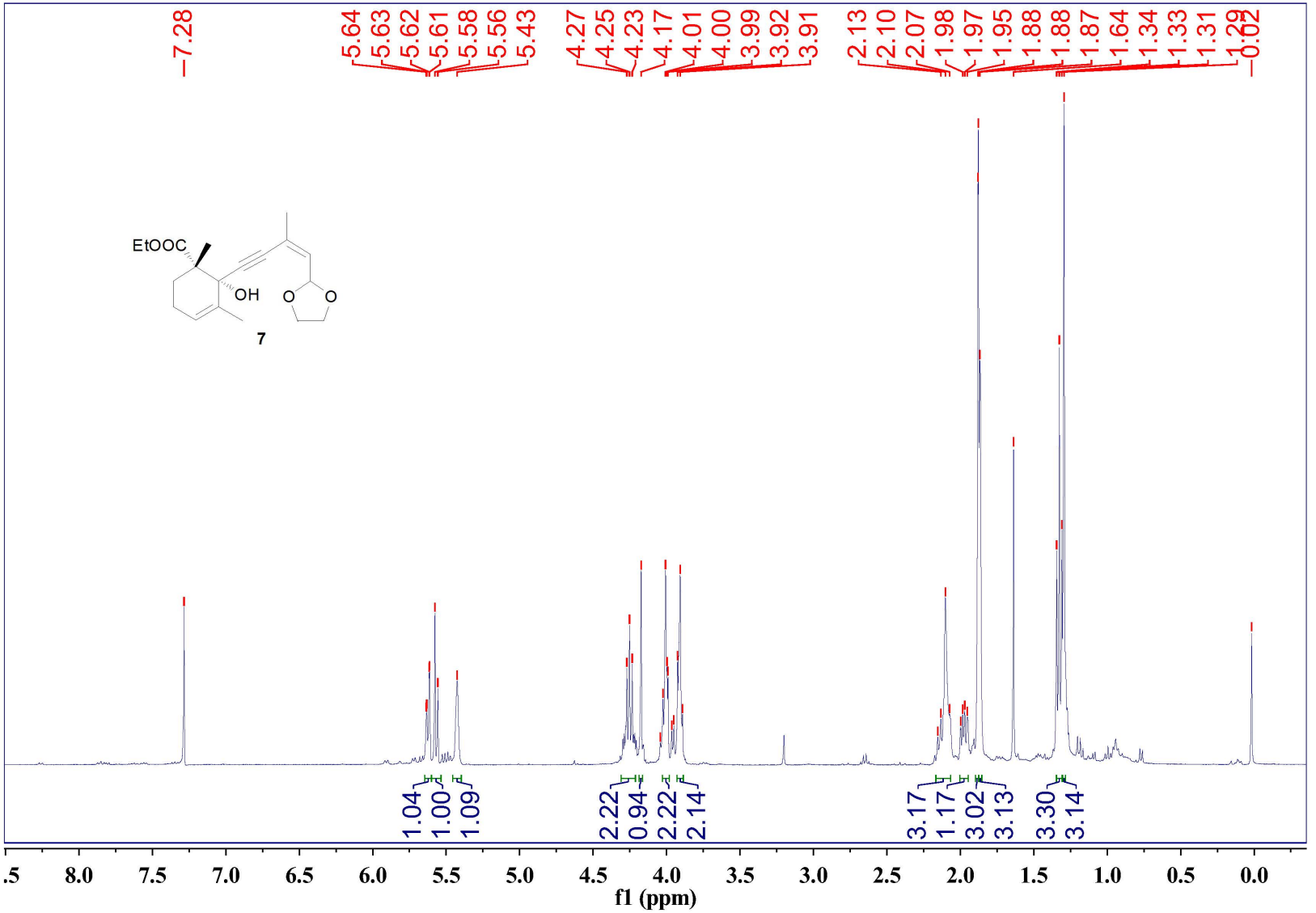
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4.00
3.99
3.92
3.91
2.13
2.10
2.07
1.98
1.97
1.95
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1.88
1.87
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1.33
1.31
1.29
0.02
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OH
O
O
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1.00
1.09
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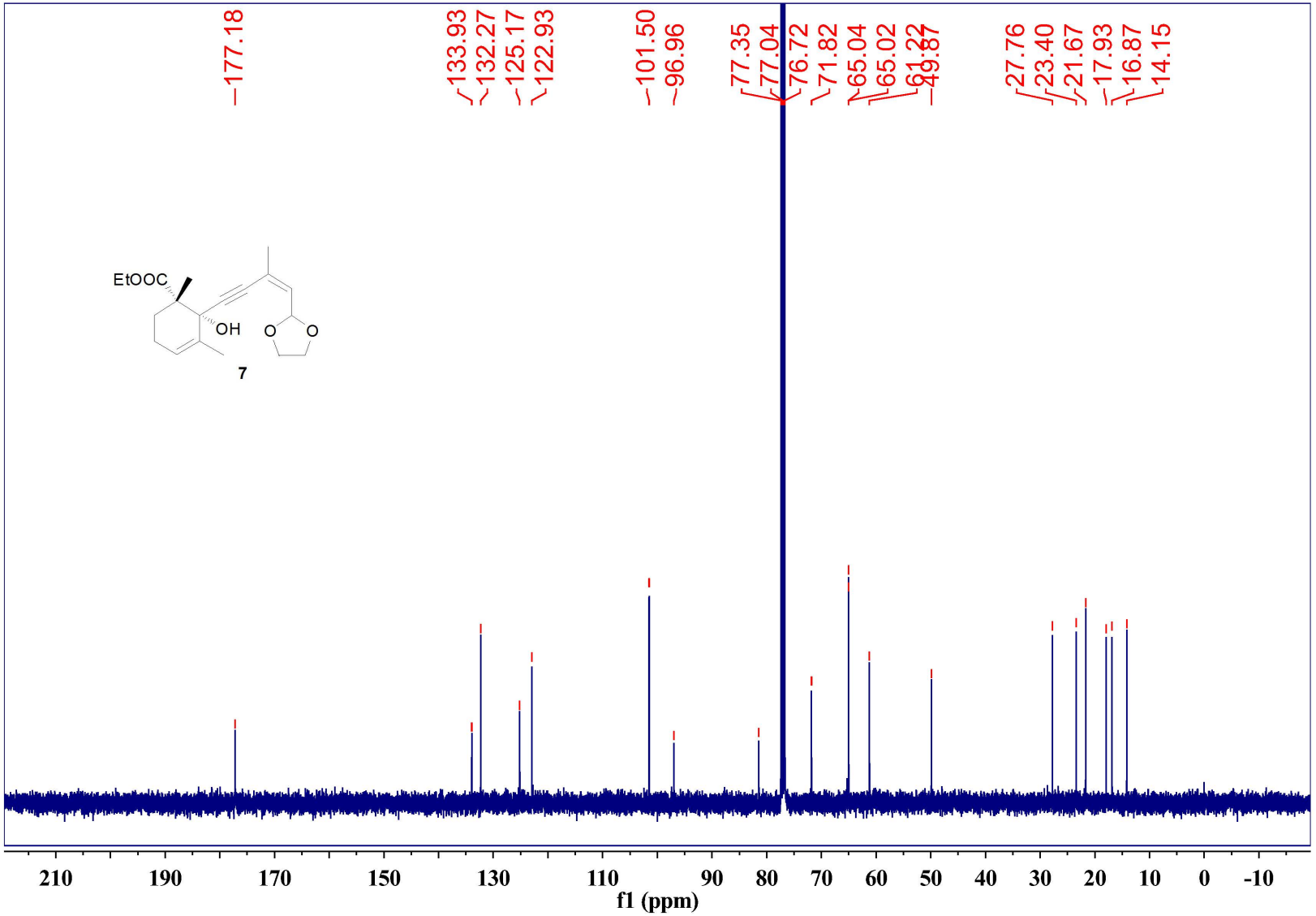
3.14
f1 (ppm)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21.67
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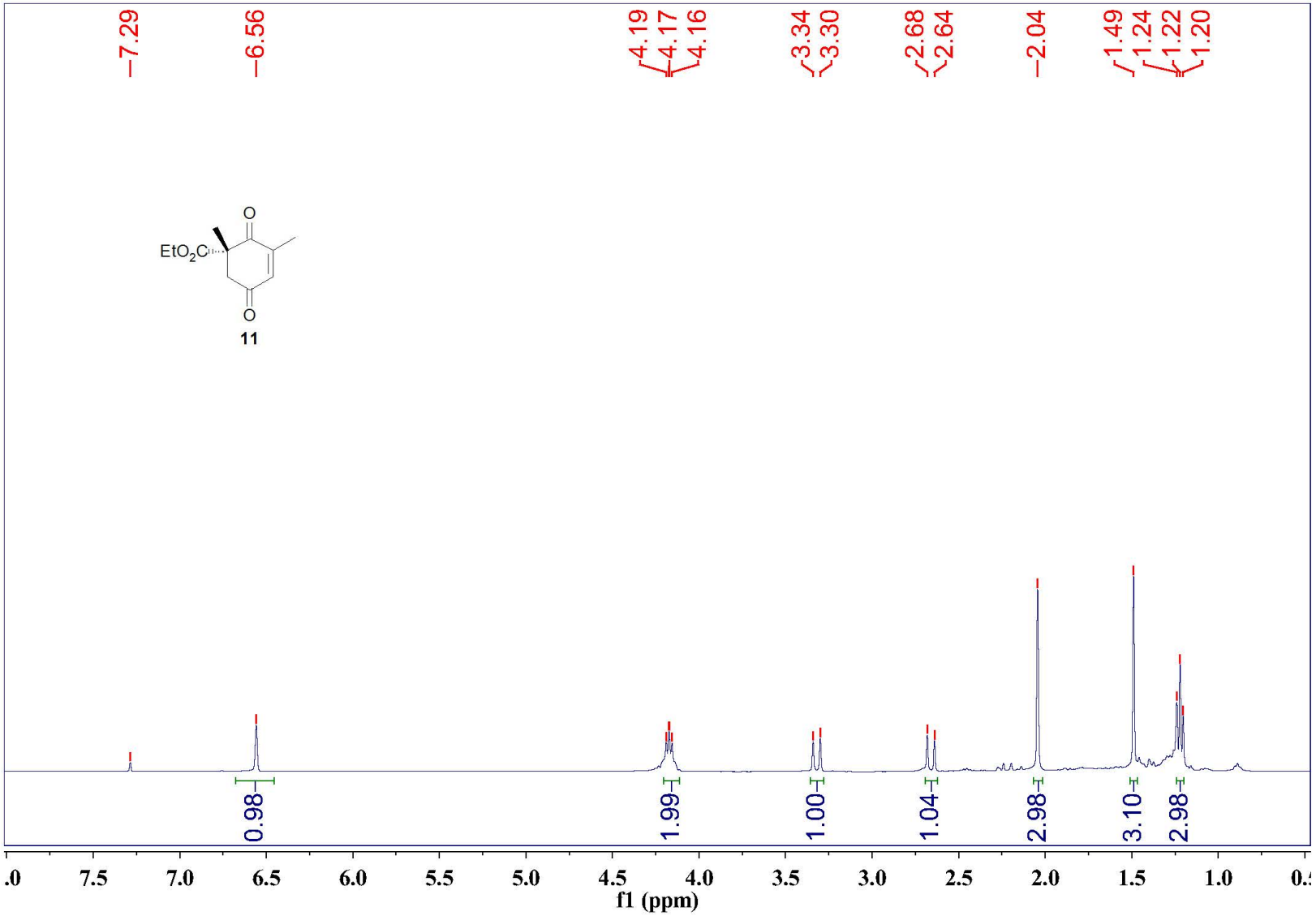
f1 (ppm)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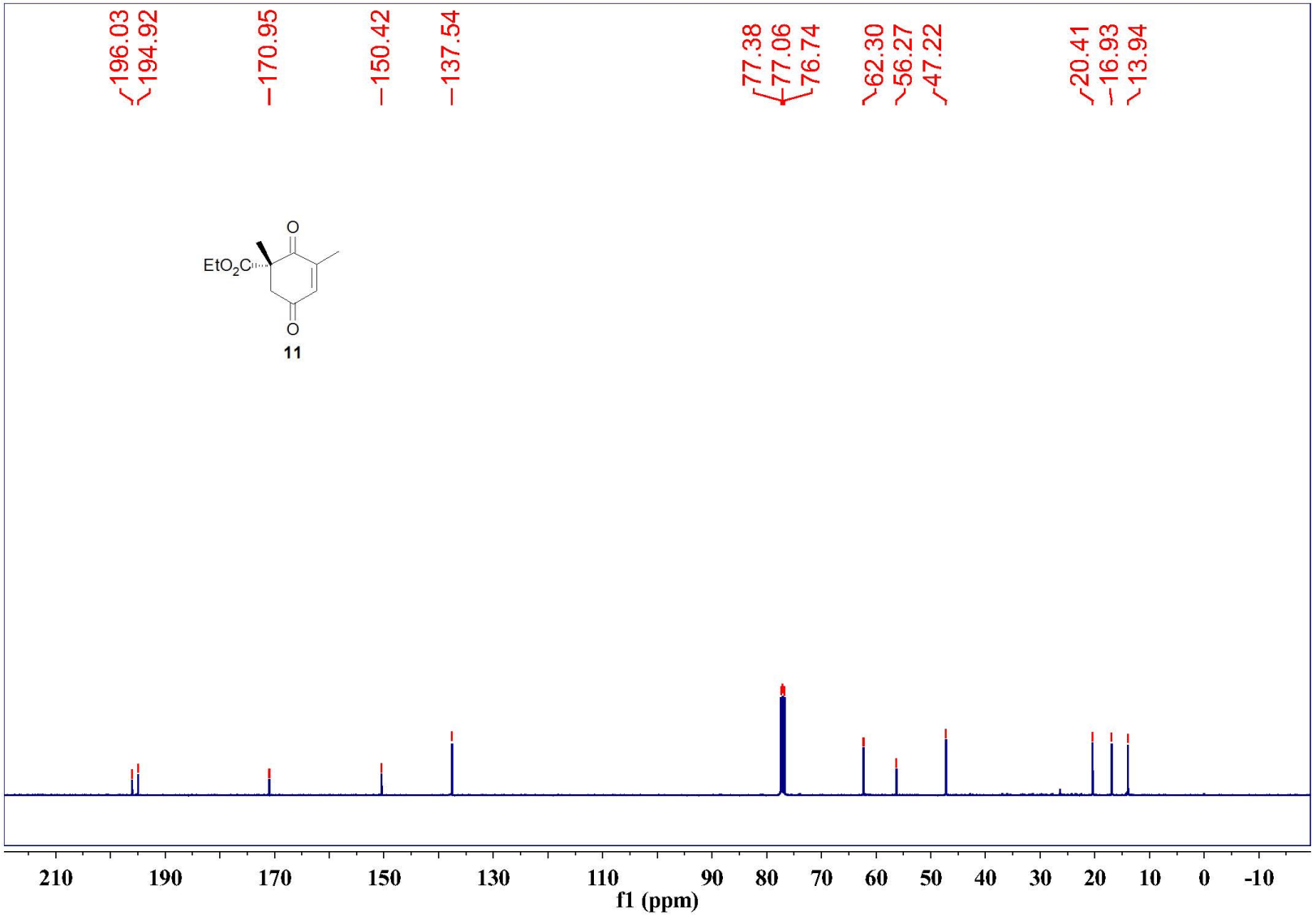
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16.93
13.94
EtO2C
O
O
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80
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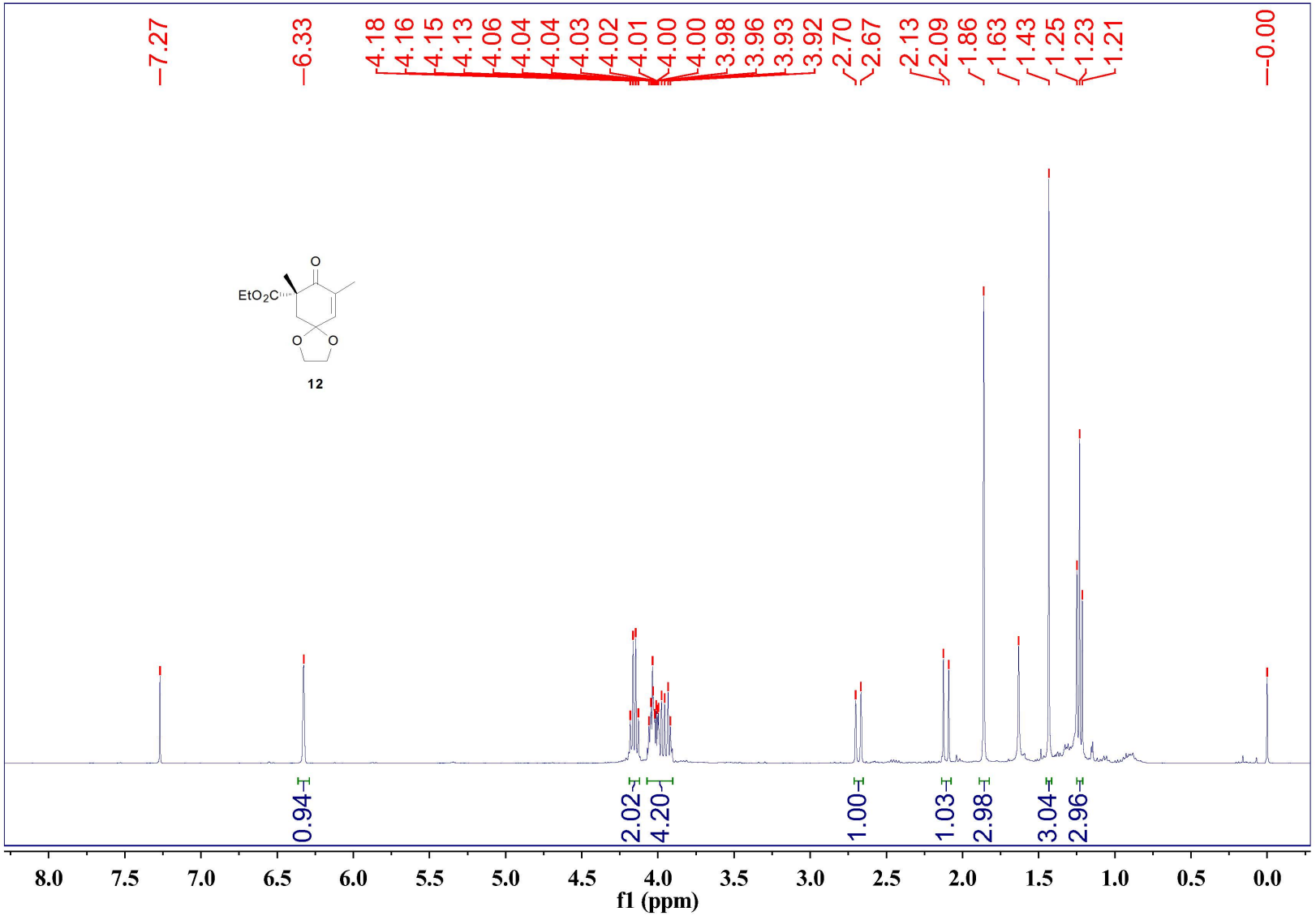
f1 (ppm)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4.00
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1.23
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O
O
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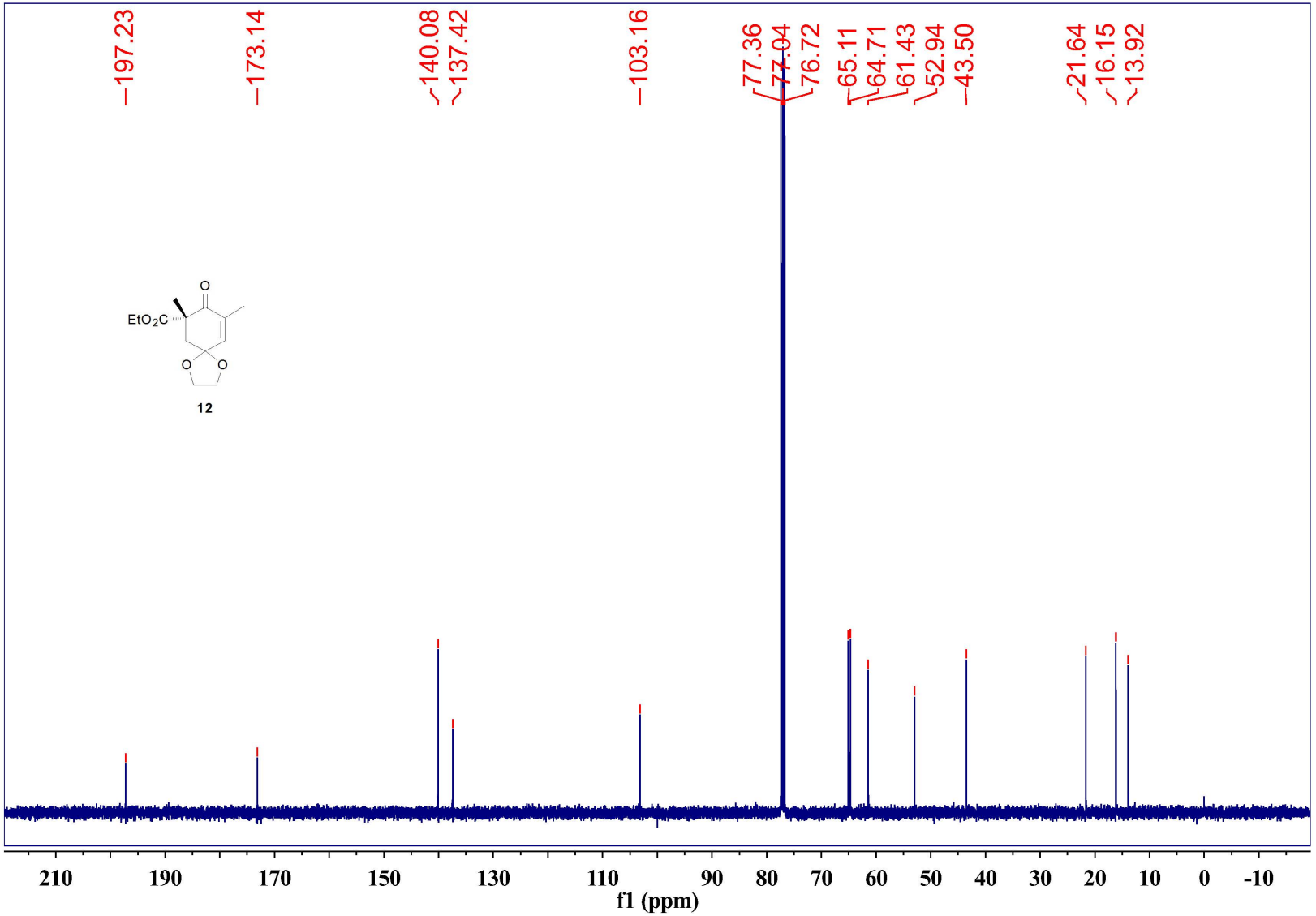
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16.15
13.92
EtO2C
O
O
O
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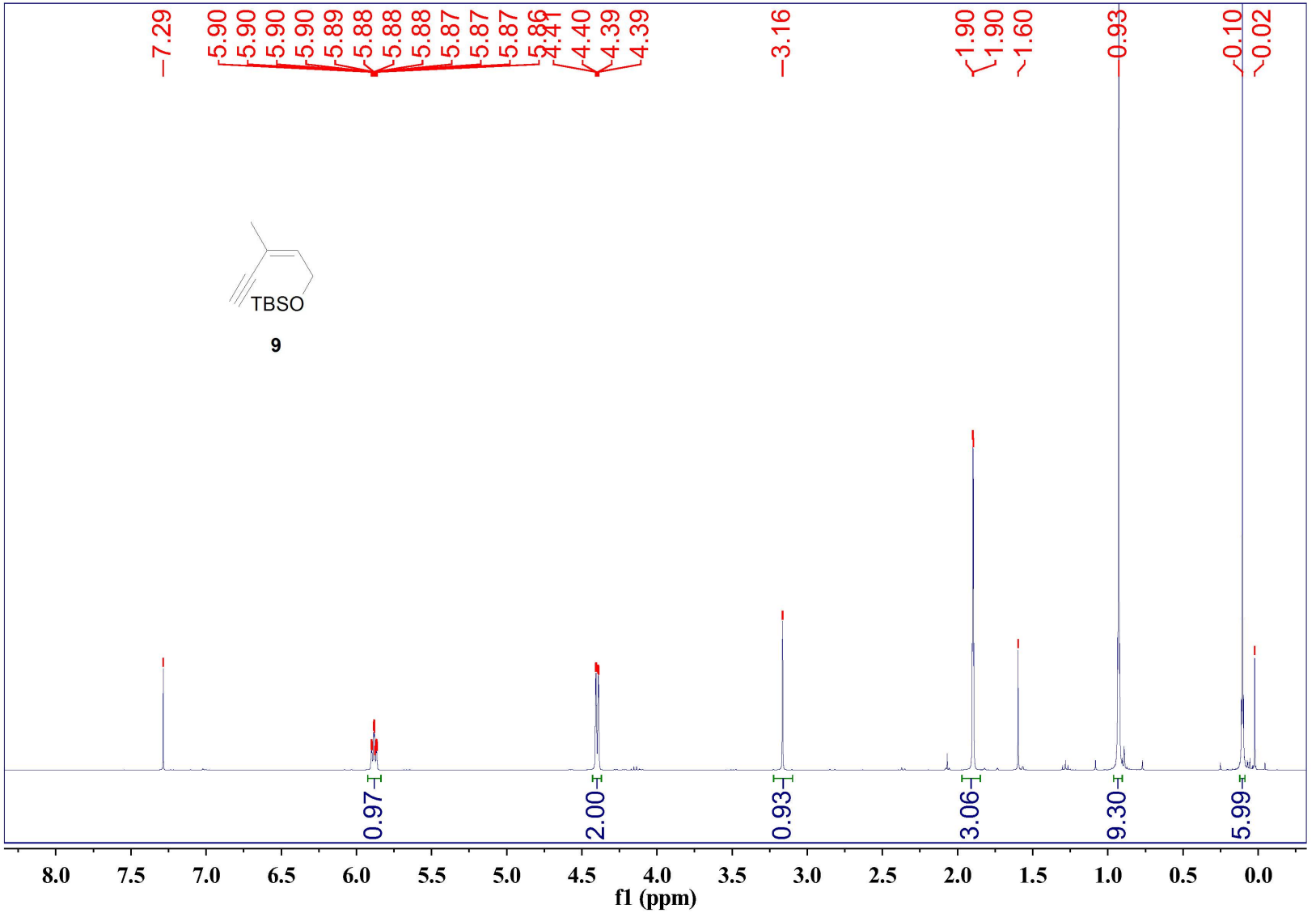
f1 (ppm)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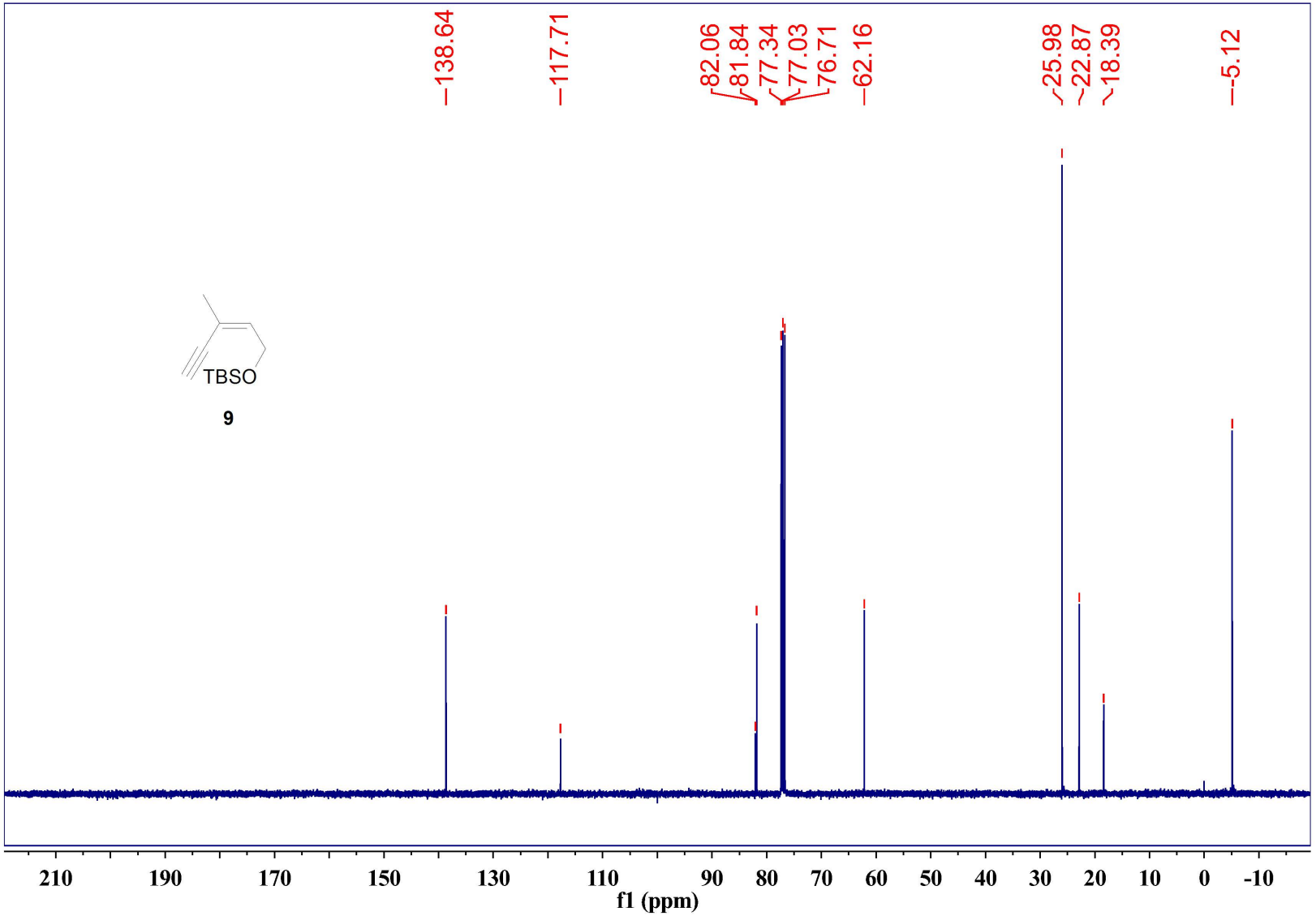
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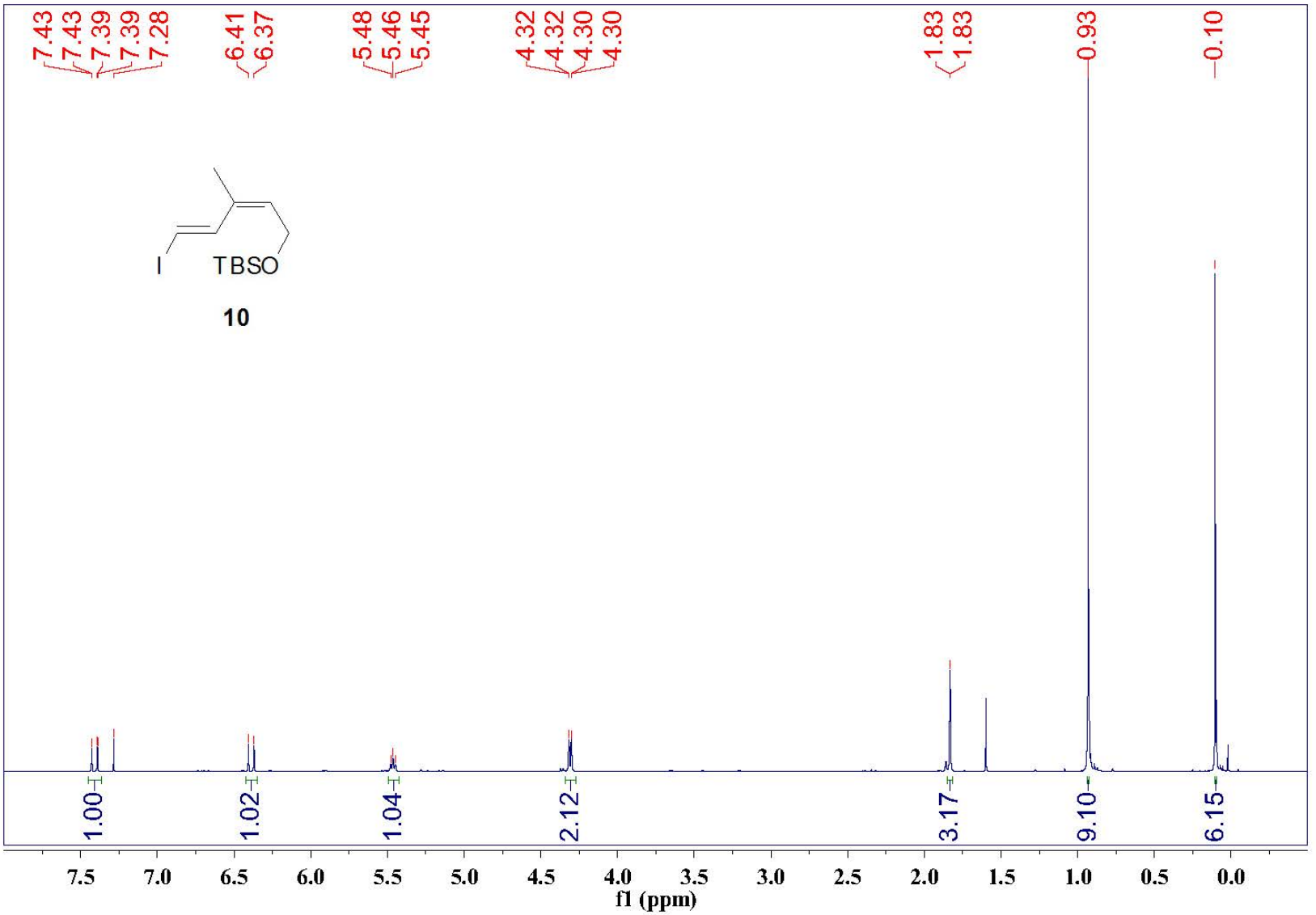
f1 (ppm)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4.30
4.30
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1.83
0.93
0.10
I
TBSO
10
1.00
1.02
1.04
2.12
3.17
9.10
6.15
7.5
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6.5
6.0
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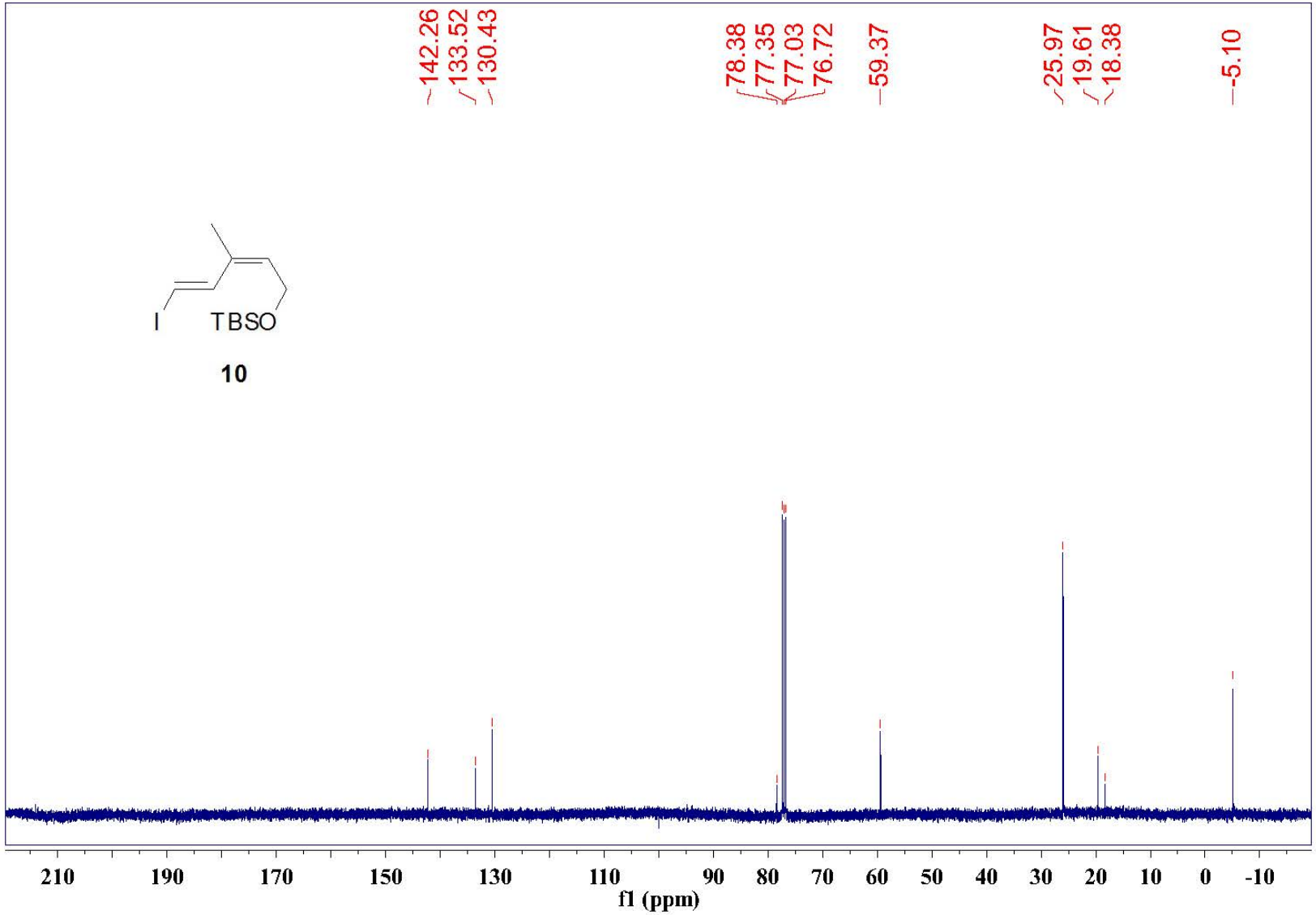
f1 (ppm)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I
TBSO
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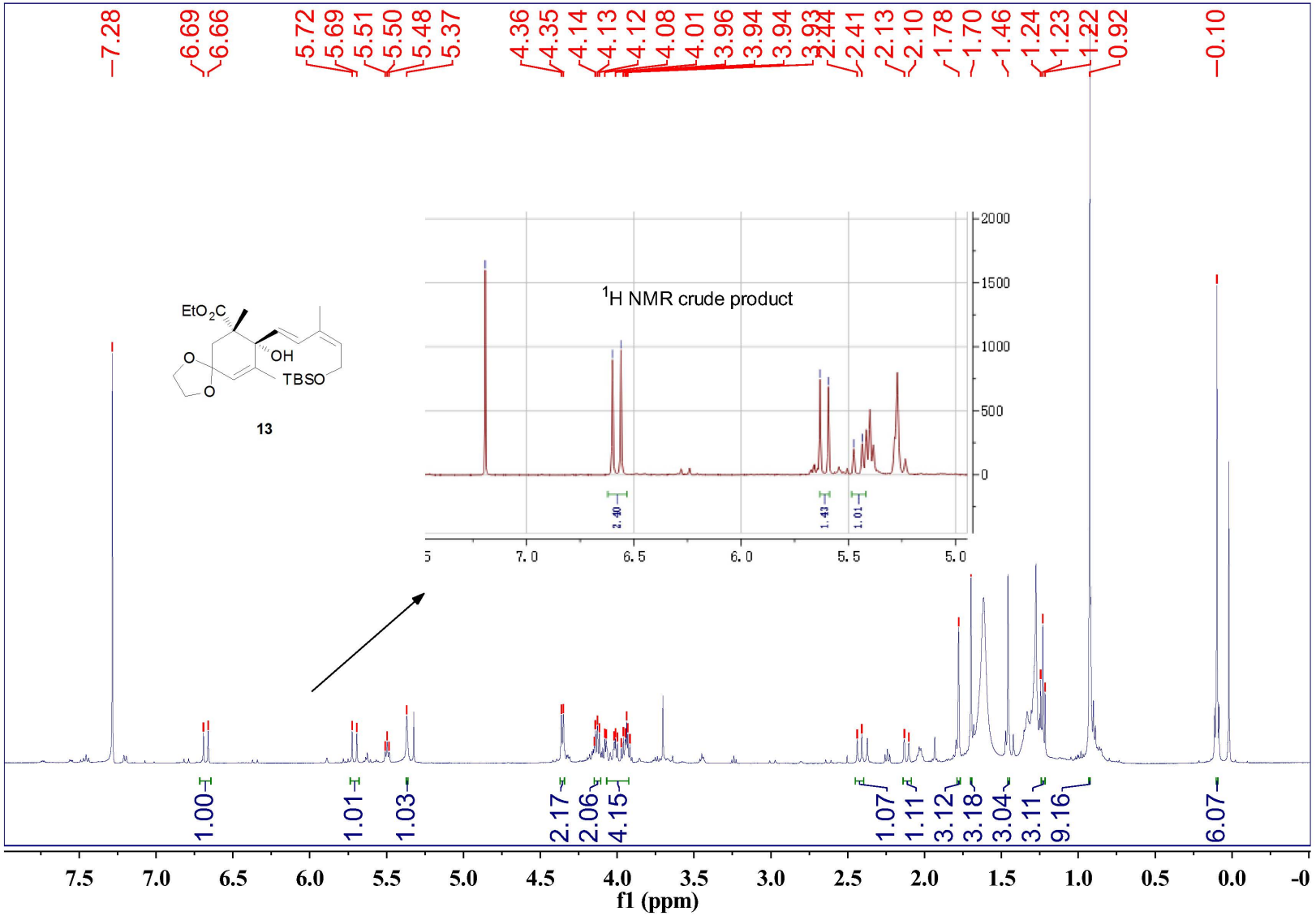
f1 (ppm)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4.08
4.01
3.96
3.94
3.94
3.93
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2.41
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2.10
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1.22
0.92
0.10
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OH
TBSO
O
O
13
1H NMR crude product
2000
1500
1000
500
0
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1.43
1.01
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5.0
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2.17
2.06
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1.07
1.11
3.12
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3.04
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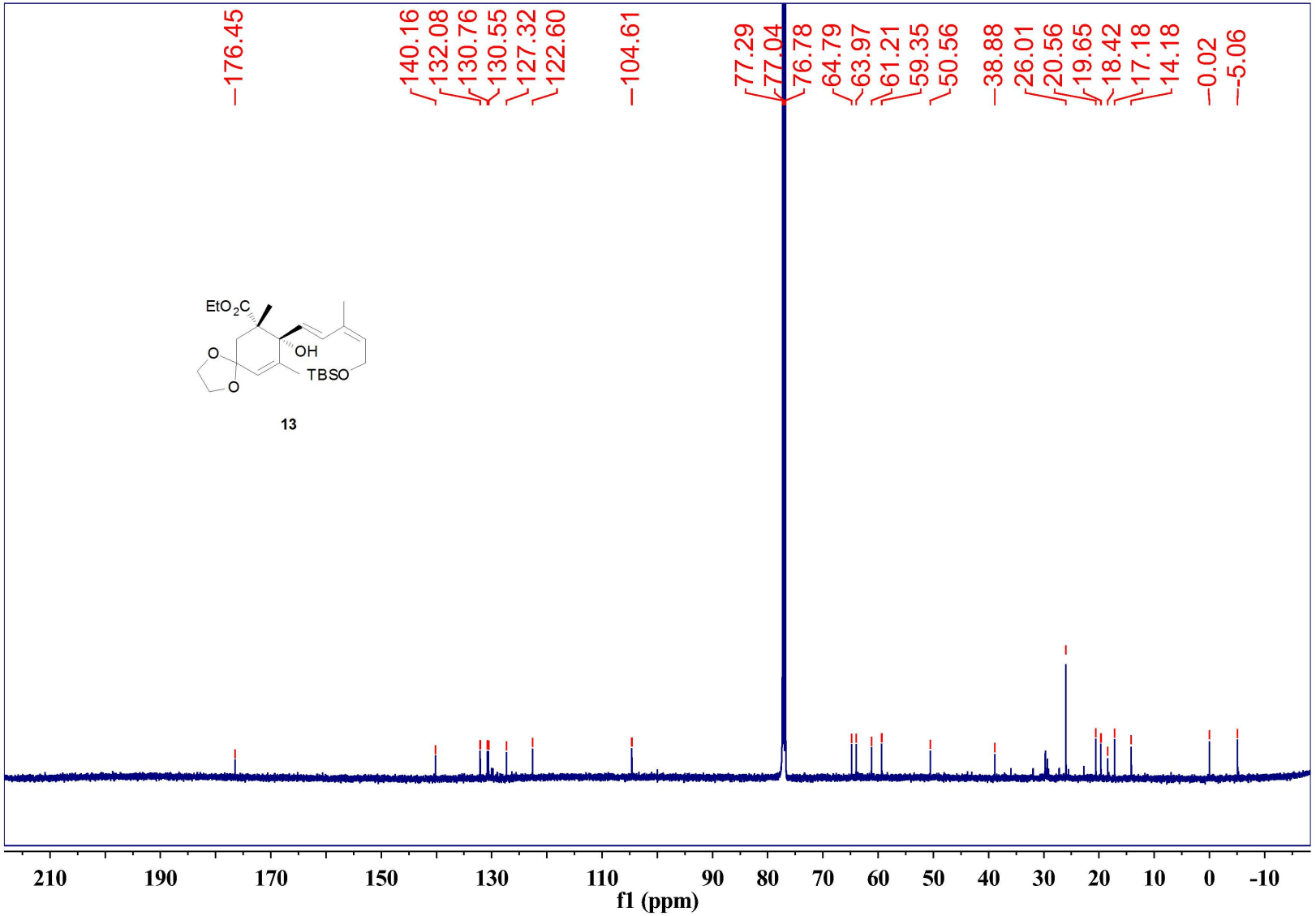
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14.18
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EtO2C
OH
TBSO
O
O
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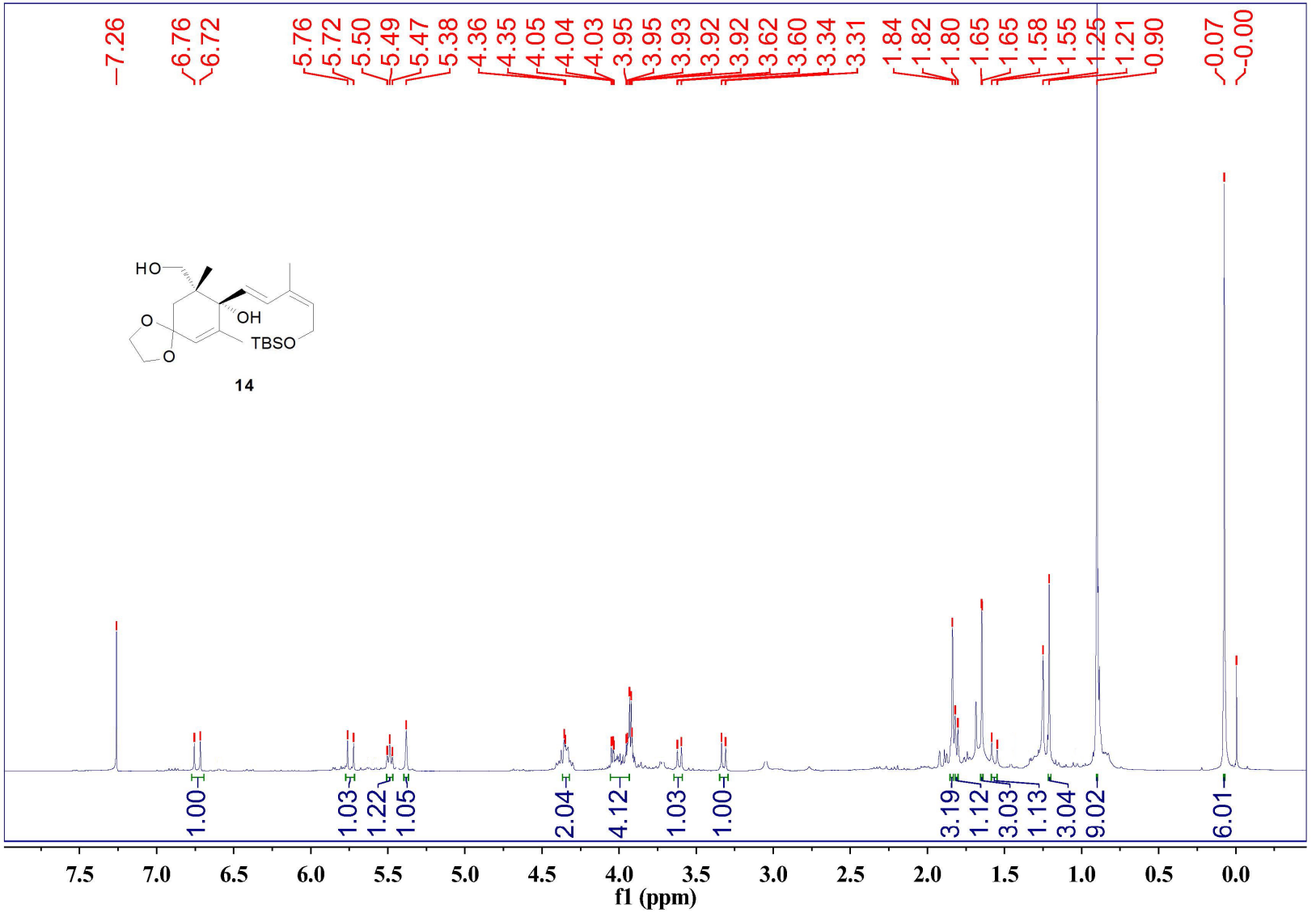
f1 (ppm)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1.80
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1.65
1.58
1.55
1.25
1.21
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0.07
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HO
OH
O
O
TBSO
14
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1.03
1.22
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2.04
4.12
1.03
1.00
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1.13
3.04
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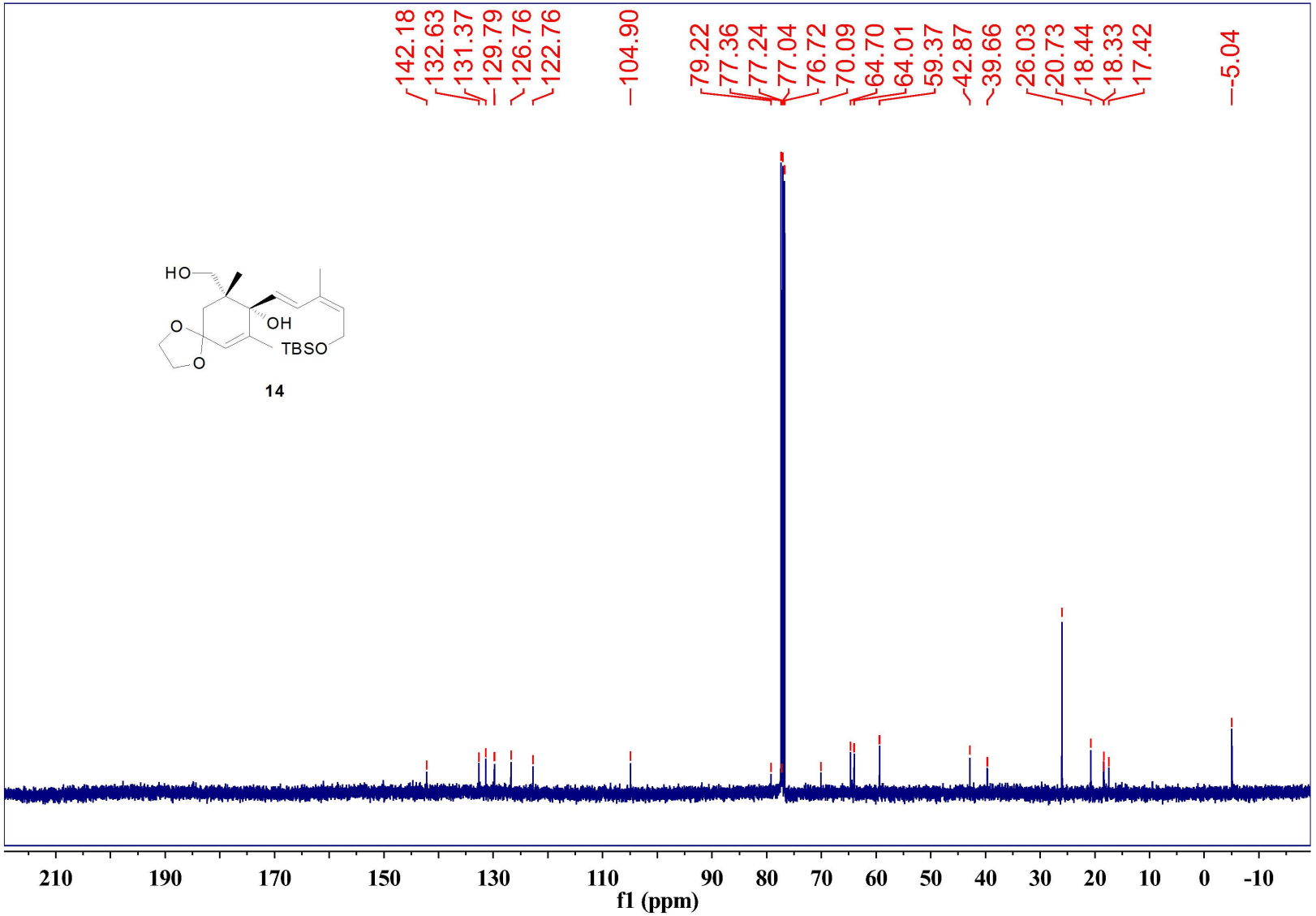
f1 (ppm)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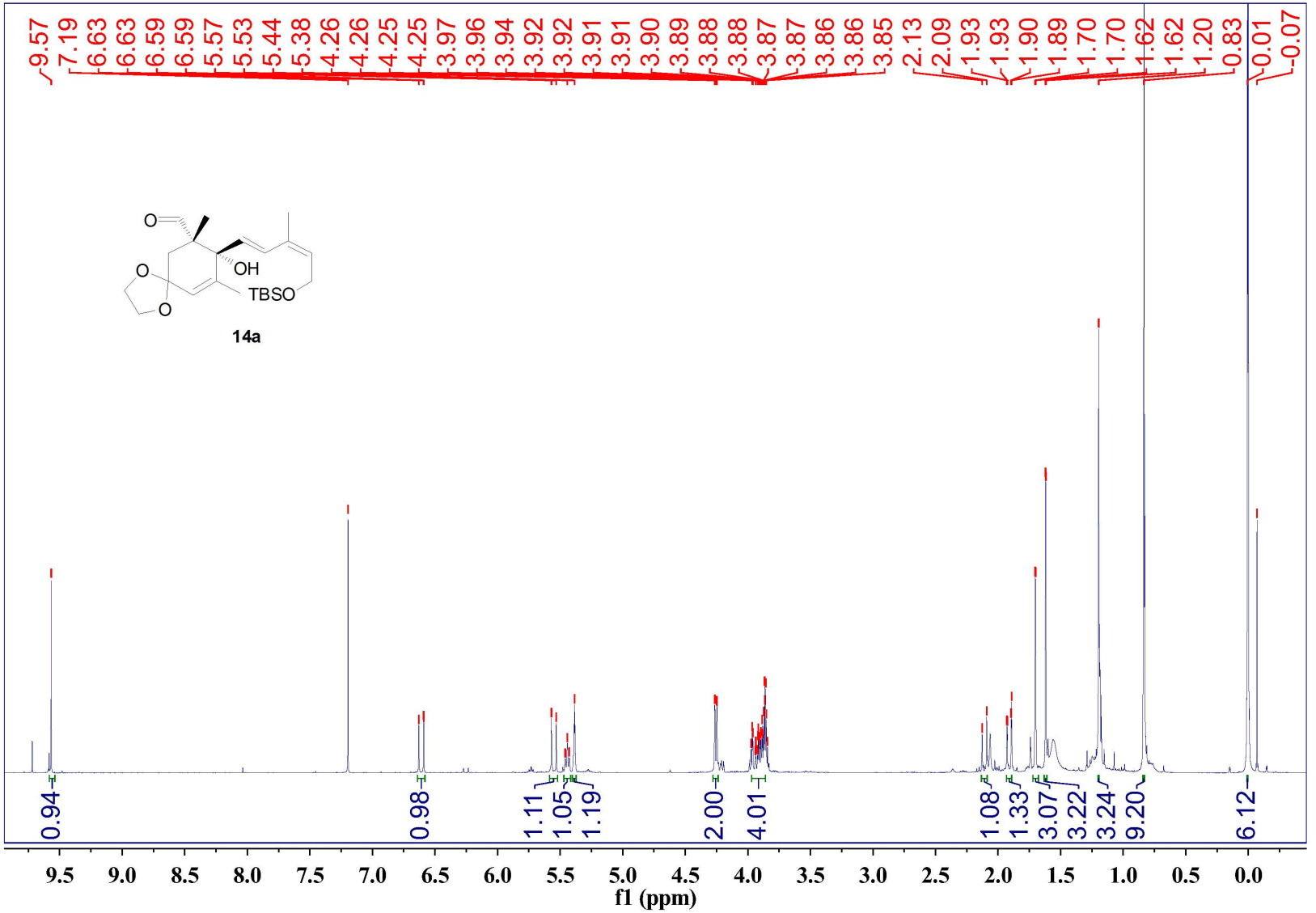
f1 (ppm)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3.96
3.94
3.92
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3.90
3.89
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3.88
3.87
3.87
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2.13
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1.90
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1.70
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1.62
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O
O
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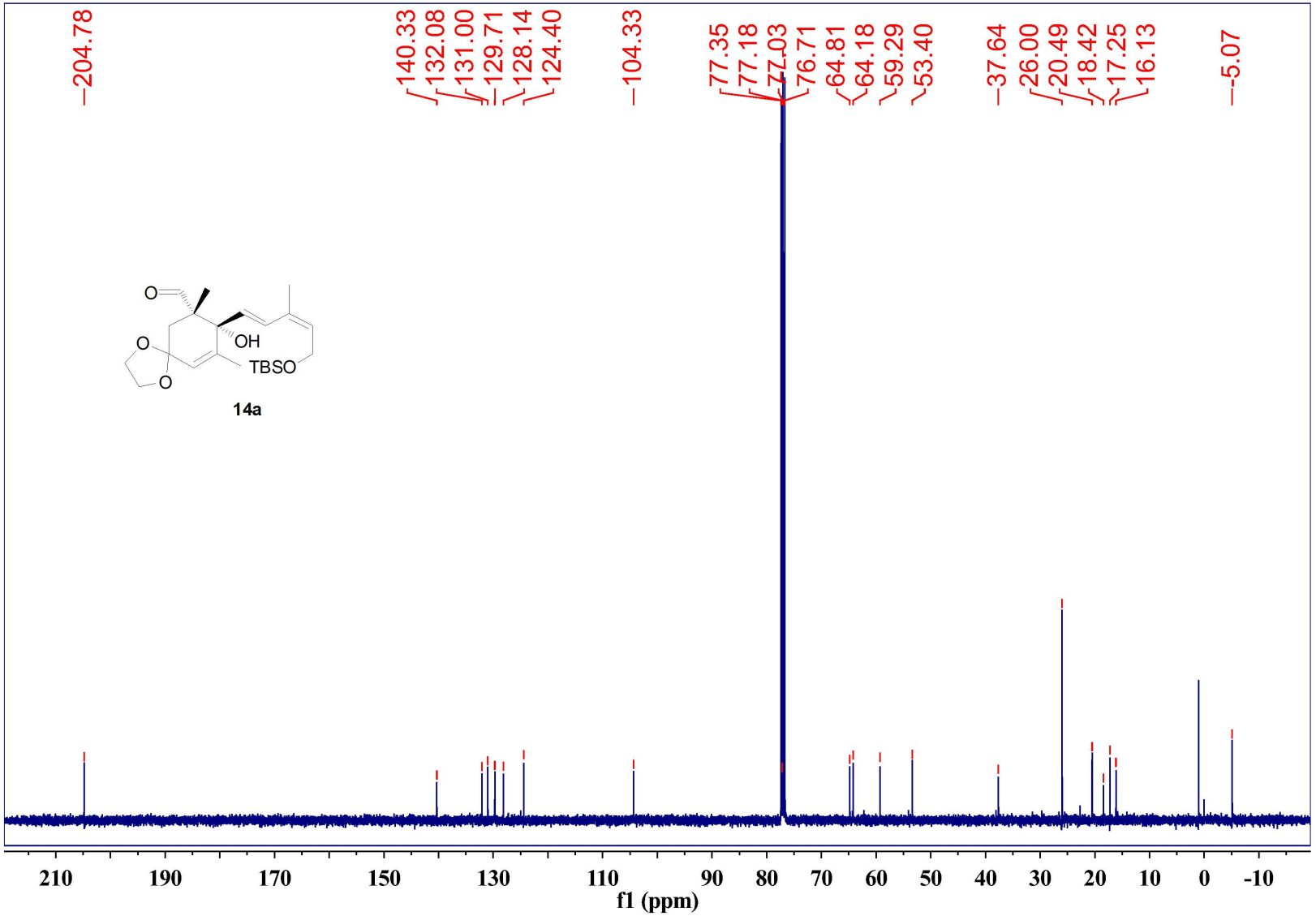
1.05
1.19
2.00
4.01
1.08
1.33
3.07
3.22
3.24
9.20
6.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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5.07
O
OH
O
TBSO
O
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30
20
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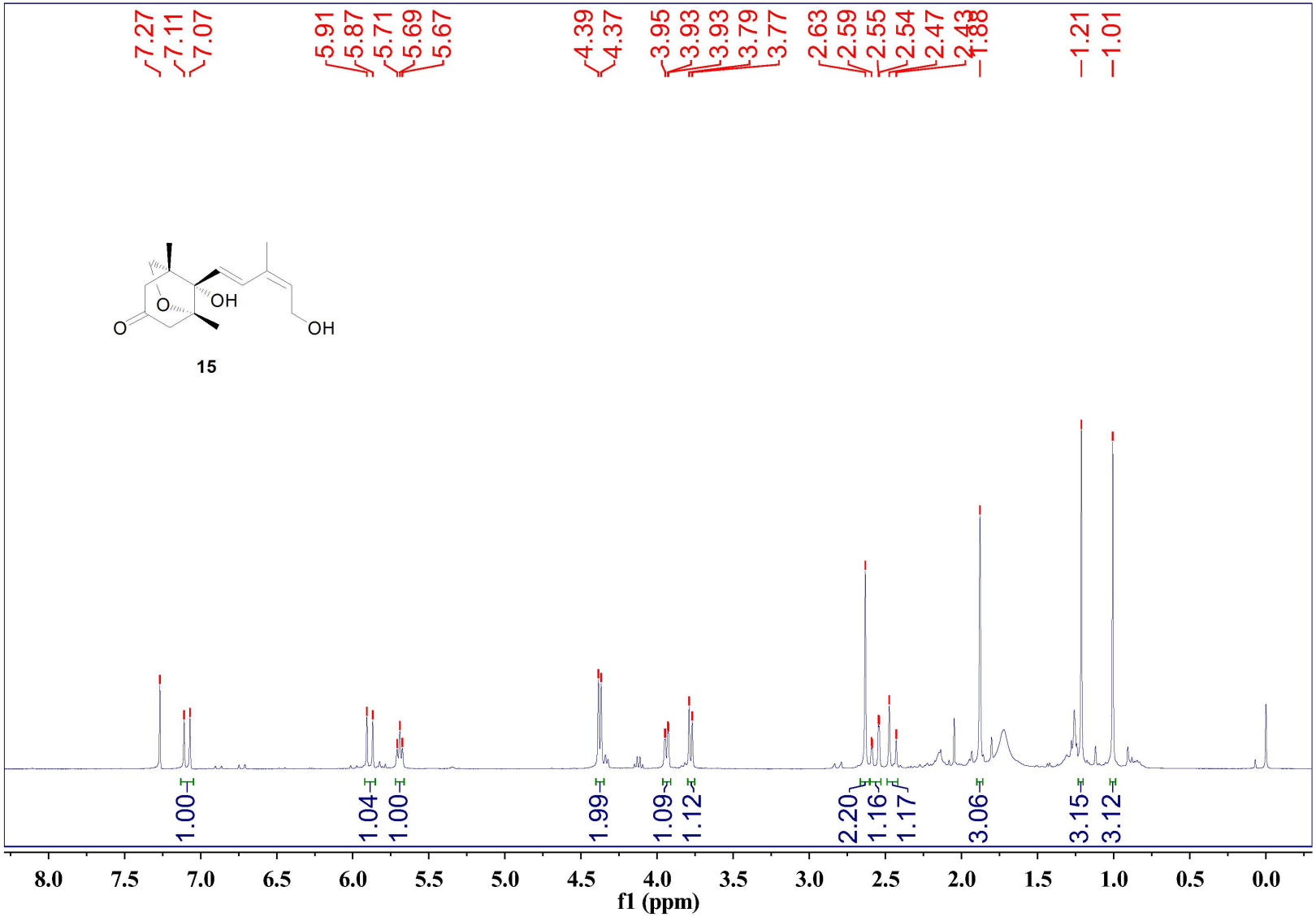
f1 (ppm)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2.54
2.47
2.43
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1.21
1.01
OH
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OH
15
1.00
1.04
1.00
1.99
1.09
1.12
2.20
1.16
1.17
3.06
3.15
3.12
8.0
7.5
7.0
6.5
6.0
5.5
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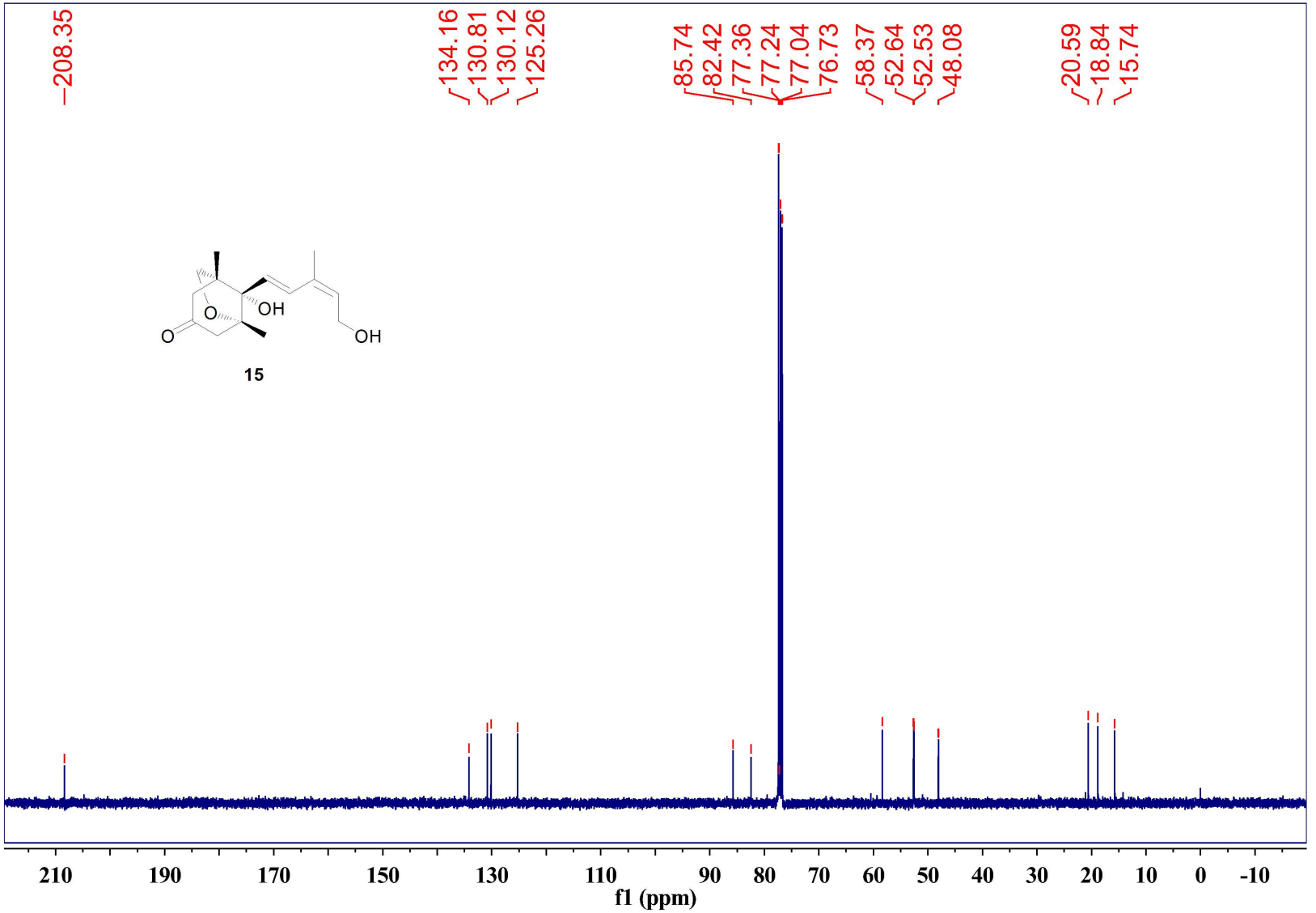
f1 (ppm)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76.73
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52.53
48.08
20.59
18.84
15.74
O
OH
O
OH
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110
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30
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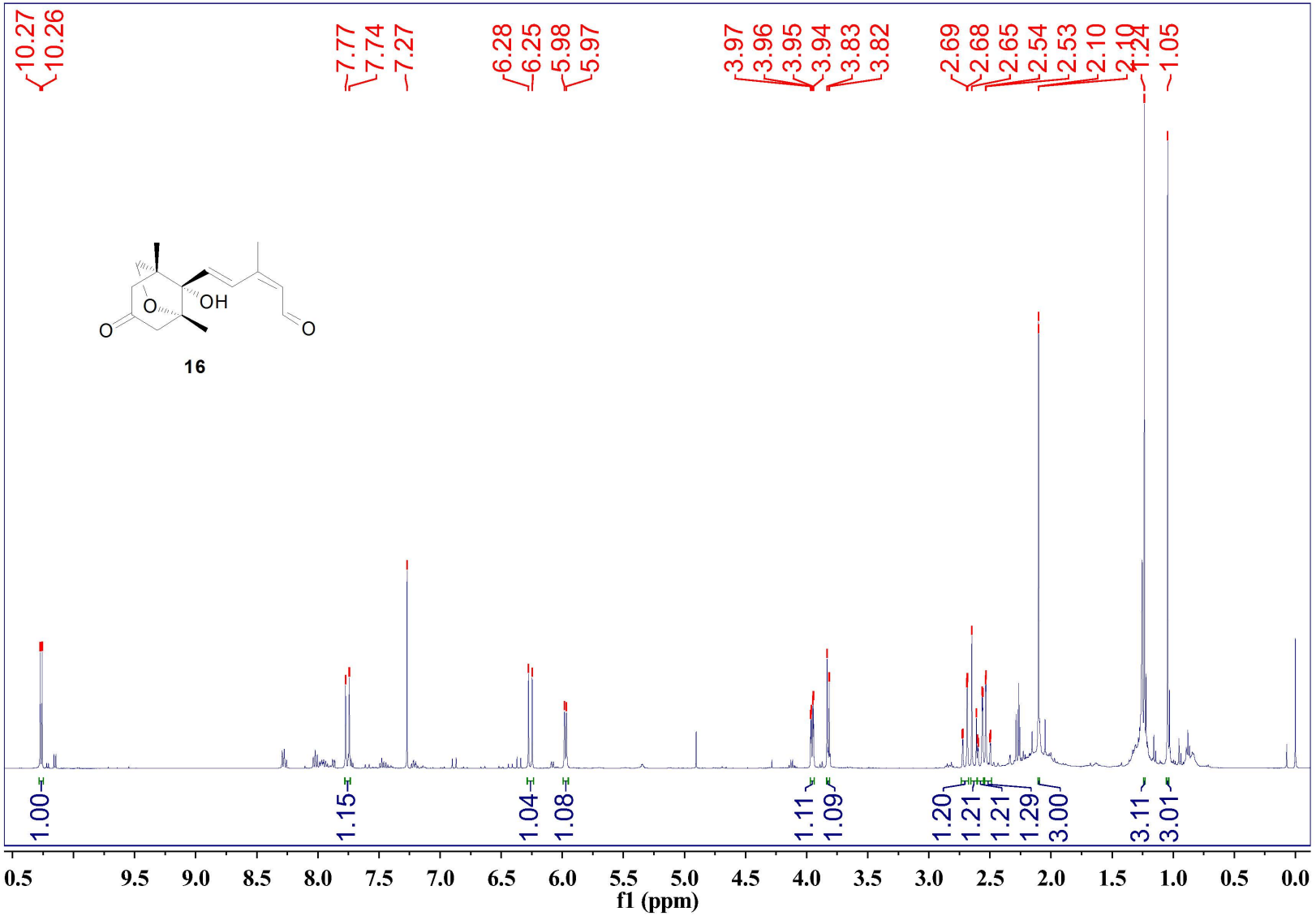
f1 (ppm)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1.15
1.04
1.08
1.11
1.09
1.20
1.21
1.21
1.29
3.00
3.11
3.01
0.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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1.0
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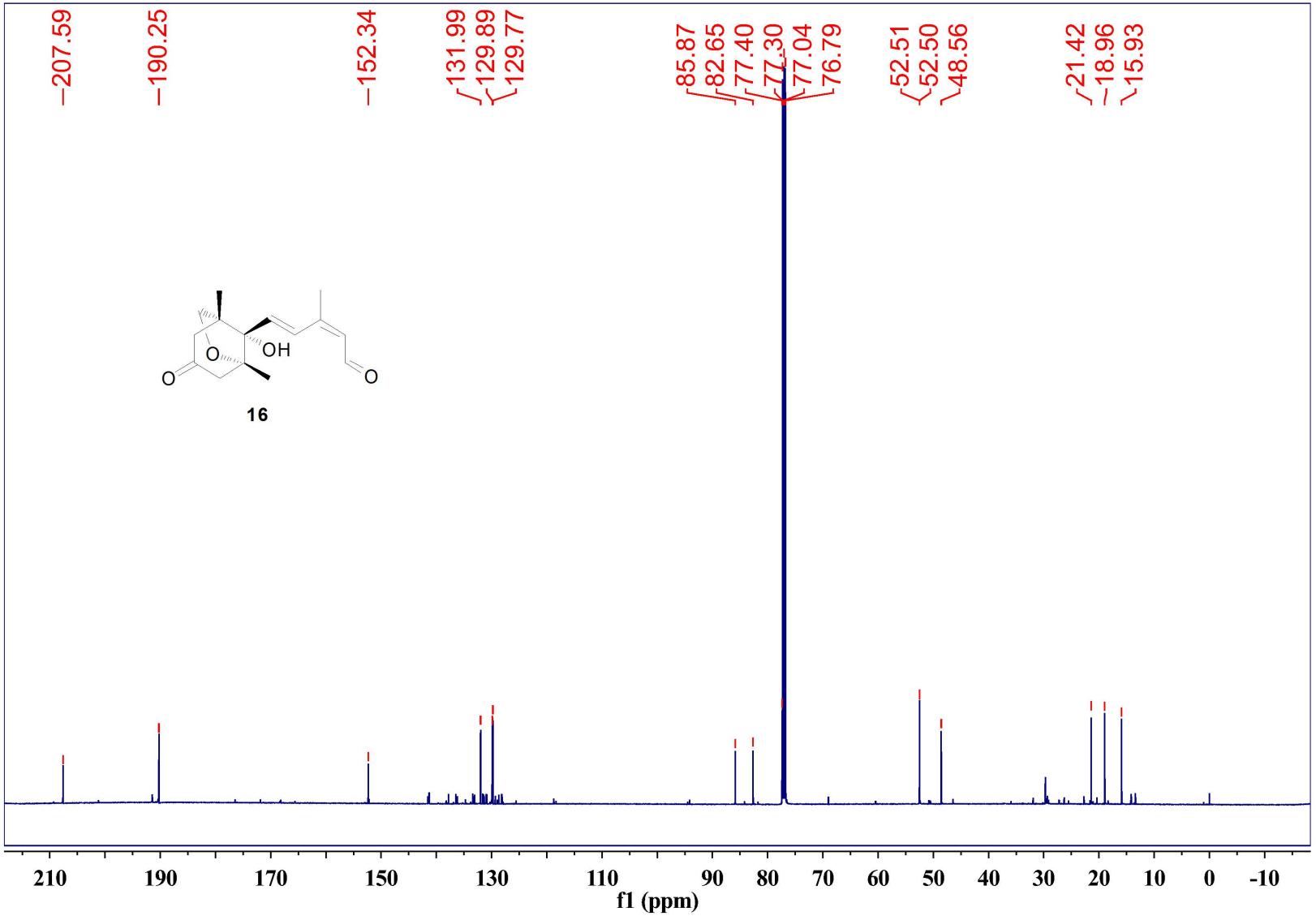
f1 (ppm)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52.50
48.56
21.42
18.96
15.93
O
OH
O
O
16
210
190
170
150
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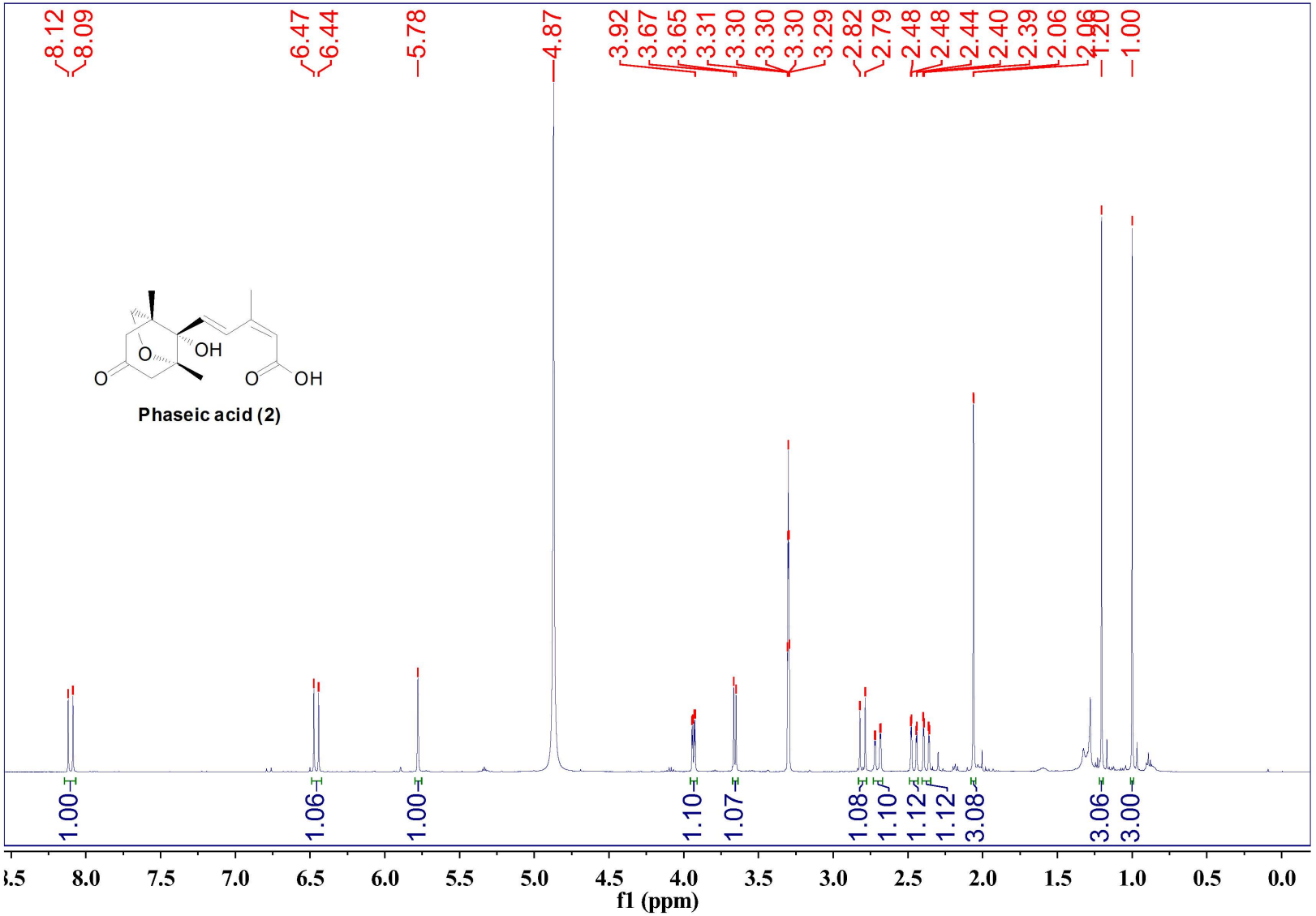
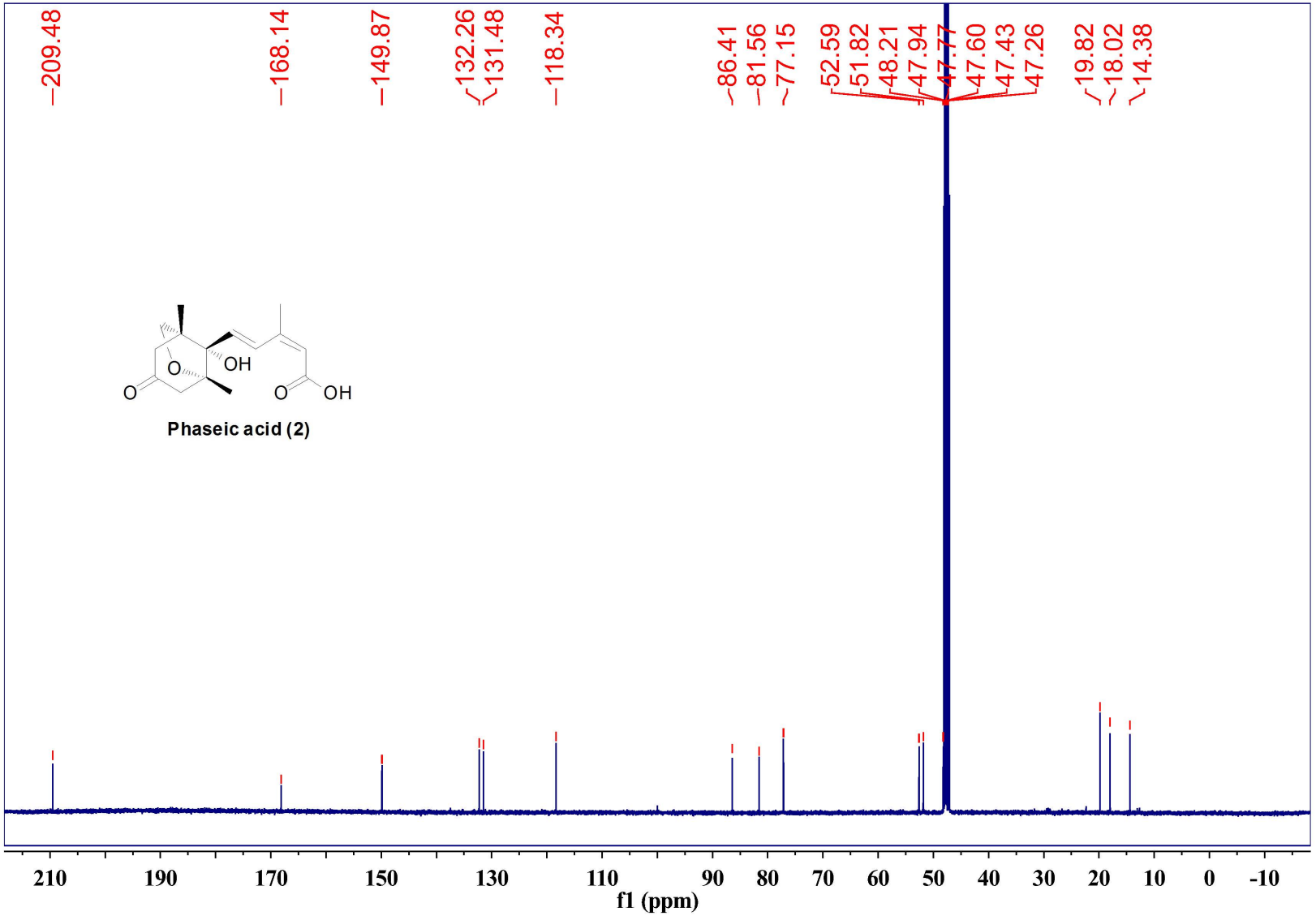
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.12
8.09
6.47
6.44
5.78
4.87
3.92
3.67
3.65
3.31
3.30
3.30
3.30
3.29
2.82
2.79
2.48
2.48
2.44
2.40
2.39
2.06
1.26
1.00
O
OH
O
O
OH
Phaseic acid (2)
1.00
1.06
1.00
1.10
1.07
1.08
1.10
1.12
1.12
3.08
3.06
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


209.48
168.14
149.87
132.26
131.48
118.34
86.41
81.56
77.15
52.59
51.82
48.21
47.94
47.77
47.60
47.43
47.26
19.82
18.02
14.38
O
OH
O
OH
Phaseic acid (2)
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)