Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of Cassane-Type Diterpenes from Abietane Compounds: First Synthesis of Taepeenin F

Pilar Gutierrez,[§] Joaquín Altarejos,[†] Pablo J. Linares-Palomino,[†] Rachid Chahboun,[§]* and Enrique Alvarez-Manzaneda[§]*

[§]*Departamento de Química Orgánica, Facultad de Ciencias, Instituto de Biotecnología, Universidad de Granada, 18071 Granada, Spain.*

[†]*Departamento de Química Inorgánica y Orgánica, Facultad de Ciencias Experimentales, Universidad de Jaén, 23071 Jaén, Spain.*

*E-mail: rachid@ugr.es; eamr@ugr.es

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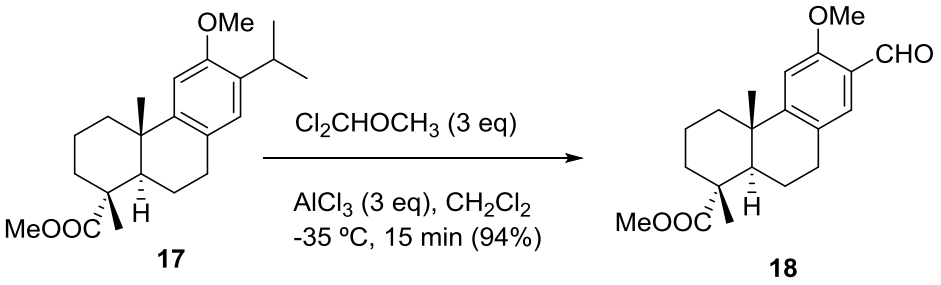
General Experimental Procedures

Unless stated otherwise, reactions were performed in oven-dried glassware under an argon atmosphere using dry solvents. Solvents were dried as follows: Tetrahydrofuran (THF), and diethyl ether (Et_2O) over Na-benzophenone. Dichloromethane (DCM) and methanol (MeOH) over CaH_2. Ethyl acetate (AcOEt) was dried over 4Å molecular sieves. Thin-layer chromatography (TLC) was performed using F254 precoated plates (0.25 mm) and visualized by UV fluorescence quenching and phosphomolybdic acid solution in ethanol staining. Flash chromatography was performed on silica gel (230-400 mesh). Chromatography separations were carried out by conventional column on silica gel 60 (230-400 Mesh), using hexanes-AcOEt (AcOEt-hexane) mixtures of increasing polarity. ^{1}H and ^{13}C NMR spectra were recorded at 600, 500 and 400 MHz, and at 150, 125 and 100 MHz, respectively. $CDCl_3$ was treated with K_2CO_3. Chemical shifts (δ H) are quoted in parts per million (ppm) referenced to the appropriate residual solvent peak and tetramethylsilane. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm) (multiplicity, coupling constant (Hz), integration), with the abbreviations s, br s, d, br d, t, q, sext and m denoting singlet, broad singlet, doublet, broad doublet, triplet, quartet, sextet and multiplet, respectively. *J* = coupling constant in Hertz (Hz). Data for ^{13}C NMR spectra are reported in terms of chemical shift relative to Me_4Si (δ 0.0) and the signals were assigned utilizing DEPT experiments and on the basis of heteronuclear correlations. Infrared spectra (IR) were recorded as thin films or as solids on a FTIR spectrophotometer with samples between sodium chloride plates or as potassium bromide pellets and are reported in frequency of absorption (cm^{-1}). Only selected absorbances (ν_{max}) are reported. ($[\alpha]_D$) measurements were carried out in a polarimeter; utilizing a 1dm length cell and $CHCl_3$ as a solvent. Concentration is expressed in mg/mL. HRMS were recorded on a spectrometer, utilizing a Q-TOF analyzer, and ESI^+ ionization.

Experimental details and characterization data for compounds

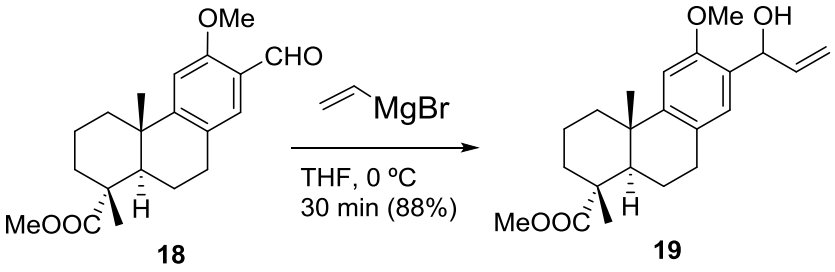
Treatment of methyl 12-methoxy-8,11,13-abietatrien-18-oate (17) with dichloromethyl methyl ether and aluminium chloride. Obtention of compound 18.



To a solution of methyl 12-methoxy-8,11,13-abietatrien-18-oate (**17**) (9.9 g, 28.8 mmol) in anhydrous dichloromethane (80 mL) cooled to -35 °C and under argon atmosphere, dichloromethyl methyl ether (7.7 ml, 86.3 mmol) was added. To this vigorously stirred mixture, aluminum chloride (11.5 g, 86.6 mmol) was added in small portions over a 15 min period. The reaction mixture was stirred at -35 °C for 1 h, at which time TLC showed no starting material. The mixture was slowly poured into ice-cold 10% aqueous HCl and extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with water (3 x 40 mL) and brine (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5% AcOEt/hexane) to yield aldehyde **18** (8.9 g, 94%) as a light yellow solid.

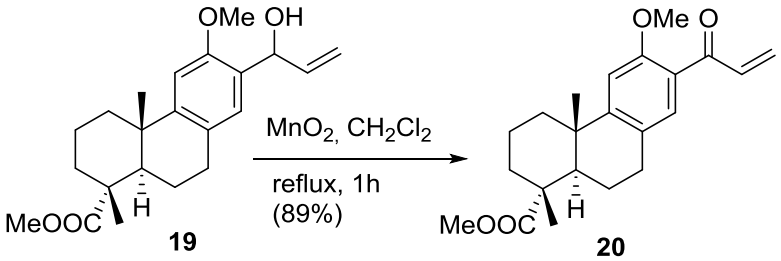
*(1R,4aS,10aR)-methyl 7-formyl-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**18**).* mp 78−80 °C. $[\alpha]_D^{25}$ = + 53.4 (c 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.21 (s, 3H), 1.26 (s, 3H), 1.38 – 1.45 (m, 2H), 1.51 – 1.82 (m, 5H), 2.18 (dd, *J* = 12.5, 2.1 Hz, 1H), 2.28 (m, 1H), 2.84 (dd, J = 9.0, 4.6 Hz, 2H), 3.66 (s, 3H), 3.87 (s, 3H), 6.82 (s, 1H), 7.47 (s, 1H), 10.35 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.5 (CH_2), 21.5 (CH_2), 24.8 (CH_3), 28.9 (CH_2), 36.6 (CH_2), 37.9 (CH_2), 38.3 (C), 44.4 (CH), 47.7 (C), 52.1 (CH_3), 55.7 (CH_3), 107.3 (CH), 122.9 (C), 127.7 (C), 129.2 (CH), 158.2 (C), 160.1 (C), 178.8 (C), 189.6 (C). IR (film): 2935, 2864, 1722, 1678, 1607, 1490, 1409, 1244, 1220, 1175, 1132, 1037, 986, 754 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{27}O_4$ ($M+H^+$) 331.1909, found: 331.1914.

(1R,4aS,10aR)-methyl 7-(1-hydroxyallyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (19).



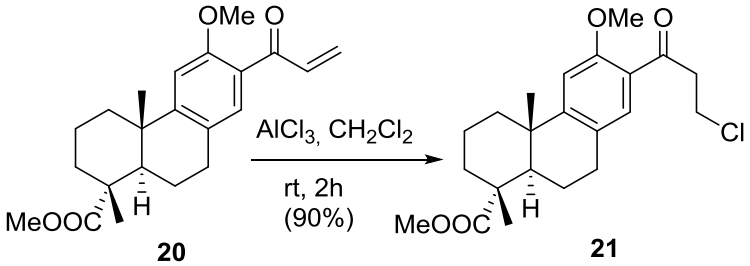
To a solution of aldehyde **18** (1.6 g, 4.73 mmol) in dry THF (50 mL) was slowly added 1M vinylmagnesium bromide solution in THF (5.68 ml, 5.68 mmol) at 0°C and under argon atmosphere. The reaction mixture was stirred at 0 °C for 30 min., at which time TLC showed no starting material. The reaction was quenched with water (5 mL); the solvent was removed under vacuum, and the mixture was extracted with ether (2 × 20 mL). The combined organic extracts were washed with water (20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, and the solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel (20% AcOEt/hexane), affording a 1:1 mixture of diastereomers of alcohol **19** (1.5 g, 88%) as a colorless syrup. ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) of both isomers: 1.21 (s, 6H), 1.27 (s, 6H), 1.48 – 1.55 (m, 2H), 1.63 – 1.65 (m, 2H), 1.70 – 1.84 (m, 10H), 2.21 (br d, *J* = 12.5 Hz, 2H), 2.24 – 2.29 (m, 2H), 2.77 – 2.84 (m, 4H), 3.67 (s, 6H), 3.83 (s, 6H), 5.14 – 5.18 (m, 2H), 5.32 – 5.35 (m, 4H), 6.06 – 6.18 (m, 2H), 6.75 (s, 2H), 6.91 (s, 1H), 6.93 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm): Common signals: 16.67 (2 CH_3), 18.72 ($2CH_2$), 21.85 ($2CH_2$), 29.27 ($2CH_2$), 36.72 ($2CH_2$), 37.60 (2C), 44.95 (2CH), 47.81 (2C), 52.10 ($2CH_3$), 55.61 ($2CH_3$), 114.55 (CH_2), 149.96 (C), 155.09 (C), 179.14 (C); signals assignable to diastereomer A: 25.09 (CH_3), 38.21 (CH_2), 71.48 (CH), 106.77 (CH), 127.42 (C), 128.02 (CH), 128.39 (C), 139.69 (CH); signals assignable to diastereomer B: 25.11 (CH_3), 38.19 (CH_2), 72.08 (CH), 106.86 (CH), 127.45 (C), 128.18 (CH), 128.36 (C), 139.75 (CH). IR (film): 3519, 2930, 1724, 1499, 1248, 1219, 1133, 1040, 773 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{30}O_4Na$ ($M+Na^+$) 381.2042, found: 381.2030.

(1R,4aS,10aR)-methyl 7-acryloyl-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (20).



To a solution of alcohol **19** (1.28 g, 3.57 mmol) in dichloromethane (30 mL) was added MnO_2 (6.2 g, 71.5 mmol) and was vigorously stirred and refluxed for 1 h. The mixture was directly filtered by flash chromatography on silica gel (30% AcOEt/hexane) to yield enone **20** (1.13 g, 89%) as a white solid; mp 130−132 °C. $[\alpha]_D^{25}$ = + 57.0 (c 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.27 (s, 3H), 1.38 (m, 1H), 1.54 (m, 1H), 1.62 – 1.87 (m, 5H), 2.20 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.28 (m, 1H), 2.80 – 2.87 (m, 2H), 3.66 (s, 3H), 3.83 (s, 3H), 5.73 (dd, *J* = 10.4, 1.7 Hz, 1H), 6.28 (dd, *J* = 17.2, 1.7 Hz, 1H), 6.81 (s, 1H), 7.04 (dd, *J* = 17.2, 10.4 Hz, 1H), 7.29 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.6 (CH_2), 21.7 (CH_2), 24.9 (CH_3), 29.0 (CH_2), 36.6 (CH_2), 38.0 (CH_2), 38.0 (C), 44.6 (CH), 47.7 (C), 52.1 (CH_3), 55.8 (CH_3), 107.6 (CH), 126.2 (C), 127.6 (C), 127.8 (CH_2), 131.3 (CH), 136.8 (CH), 155.2 (C), 156.8 (C), 178. 9 (C), 192.6 (C). IR (KBr): 2935, 1722, 1661, 1610, 1494, 1409, 1245, 1225, 1177, 1155, 1134, 1110, 1037, 985 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{29}O_4$ ($M+H^+$) 357.2066, found: 357.2060.

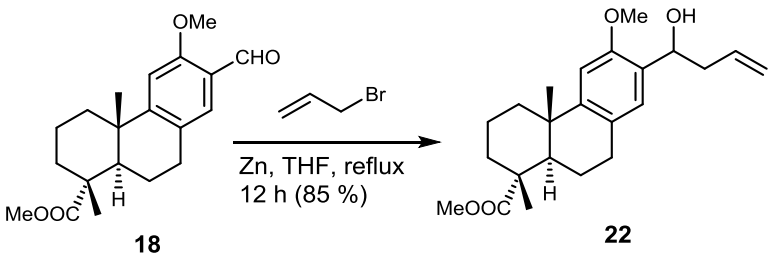
Treatment of enone 20 with aluminium chloride. Obtention of compound 21.



To a solution of enone **20** (32 mg, 0.09 mmol) in anhydrous dichloromethane (3 mL) was added aluminum chloride (15 mg, 0.113 mmol) cooled to 0 °C and under argon atmosphere. The reaction mixture was stirred at room temperature for 2 h. Then, the reaction was poured into ice and extracted with ethyl acetate (15 mL), washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel (5% AcOEt/hexane), affording compound **21** (32 mg, 90%) as a white solid.

*(1R,4aS,10aR)-methyl 7-(3-chloropropanoyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**21**).* mp 110–115 °C. $[\alpha]_D^{25}$ = + 50.1 (c 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, chloroform-d) δ (ppm) 1.23 (s, 3H), 1.28 (s, 3H), 1.42 (m, 1H), 1.62 (m, 1H), 1.70 – 1.87 (m, 5H), 2.19 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.28 (m, 1H), 2.81 – 2.88 (m, 2H), 3.45 (t, *J* = 6.9 Hz, 2H), 3.67 (s, 3H), 3.84 – 3.88 (m, 2H), 3.89 (s, 3H), 6.82 (s, 1H), 7.47 (s, 1H). ^{13}C NMR (100 MHz, chloroform-d) δ (ppm) 16.7 (CH_3), 18.6 (CH_2), 21.7 (CH_2), 24.9 (CH_3), 28.9 (CH_2), 36.6 (CH_2), 38.0 (CH_2), 38.1 (C), 39.5 (CH_2), 44.6 (CH), 46.7 (CH_2), 47.8 (C), 52.2 (CH_3), 55.6 (CH_3), 107.4 (CH), 124.9 (C), 127.8 (C), 131.4 (CH), 156.3 (C), 157.4 (C), 178.9 (C), 198.0 (C). IR (KBr): 2926, 2854, 1724, 1670, 1606, 1494, 1463, 1405, 1245, 1219, 1177, 1134, 1109, 1036, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{30}O_4Cl$ ($M+H^+$) 393.1833, found: 393.1829.

(1R,4aS,10aR)-methyl 7-(1-hydroxybut-3-en-1-yl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (22).

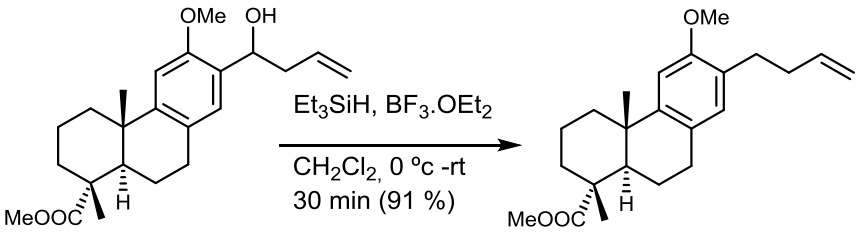


18 **22**

To a suspension of zinc dust (4.4 g, 67 mmol) in anhydrous THF (35 mL) cooled in a cold-water bath, was slowly added allyl bromide (5.7 ml, 67 mmol) and a solution of aldehyde **18** (8.9 g, 27 mmol) in anhydrous

THF (25 mL) was added. The reaction mixture was heated to reflux for 12 h. The reaction was quenched with sat. aqueous ammonium chloride solution (10 mL) at 0°C, and the solvent was evaporated under vacuum. The residue was extracted with ethyl acetate (3 x 30 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered and concentrated to give a 1:1 mixture of diastereomers of alcohol **22** (8.5 g, 85%) as a colorless syrup. ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm): Common signals: 1.22 (s, 6H), 1.27 (s, 6H), 1.34 – 1.45 (m, 2H), 1.47 – 1.57 (m, 2H), 1.60 – 1.90 (m, 10H), 2.16 – 2.31 (m, 4H), 2.43 – 2.63 (m, 6H), 2.82 (m, 4H), 5.07 – 5.18 (m, 4H), 5.81 – 5.93 (m, 2H), 6.74 (s, 2H); signals assignable to diastereomer A: 3.67 (s, 3H), 3.82 (s, 3H), 4.83 (dd, *J* = 8.1, 5.0 Hz, 1H), 6.95 (s, 1H); signals assignable to diastereomer B: 3.66 (s, 3H), 3.81 (s, 3H), 4.90 (dd, *J* = 8.3, 4.5 Hz, 1H), 6.99 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm): Common signals: 16.65 (CH_3), 18.71 (CH_2), 21.87 (CH_2), 25.10 (CH_3), 29.33 (CH_2), 36.71 (CH_2), 37.54 (C), 38.19 (CH_2), 42.03 (CH_2), 47.8 (C), 52.07 (CH_3), 55.46 (CH_3), 127.13 (C), 179.14 (C); signals assignable to diastereomer A: 45.01 (CH), 70.27 (CH), 106.51 (CH), 117.39 (CH_2), 127.55 (CH), 129.33 (C), 135.68 (CH), 149.43 (C), 154.86 (C); signals assignable to diastereomer B: 44.98 (CH), 69.34 (CH), 106.40 (CH), 117.54 (CH_2), 127.26 (CH), 129.43 (C), 135.63 (CH), 149.39 (C), 154.74 (C). IR (film): 3524, 2931, 1722, 1498, 1463, 1434, 1245, 1208, 1132, 1109, 1040, 991, 910, 753 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{31}O_3$ ($M+H^+-H_2O$) 355.2273, found: 355.2274.

(1R,4aS,10aR)-methyl 7-(but-3-en-1-yl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (23).

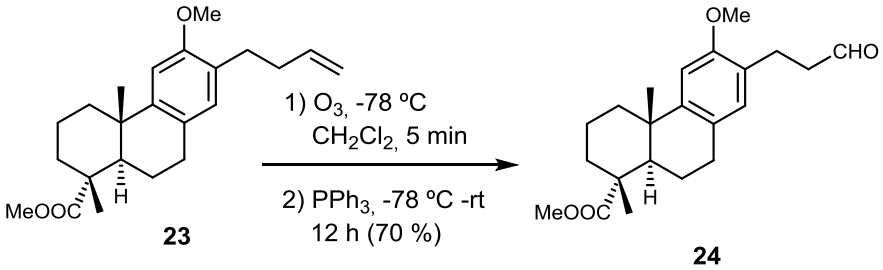


22 **23**

To a solution of alcohol **22** (8.5 g, 22.8 mmol) in dry dichloromethane (60 mL) at 0°C and under argon atmosphere Et_3SiH (9.6 mL, 59.5 mmol) and $BF_3{\cdot}OEt_2$ (2.3 mL, 19 mmol) were added and the mixture was stirred at this temperature for 30 min, at which time TLC showed no starting material. Then, sat $NaHCO_3$

solution (3 mL) was slowly added to quench the reaction, and the solvent was removed under vacuum. Et_2O (50 mL) was added to the crude product and the organic phase was washed with water (3 x 20 mL) and brine (20 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrate under vacuum to give a crude product which was directly purified by flash chromatography (5% AcOEt/hexane) to yield compound **23** (7.38 g, 91%) as a colorless syrup. $[\alpha]_D^{25}$ = + 55.1 (c 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 1.23 (s, 3H), 1.28 (s, 3H), 1.55 (dd, *J* = 12.5, 4.4 Hz, 2H), 1.67 – 1.61 (m, 2H), 1.85 – 1.74 (m, 2H), 2.24 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.36 – 2.25 (m, 4H), 2.71 – 2.53 (m, 2H), 2.85 – 2.76 (m, 2H), 3.67 (s, 3H), 3.79 (s, 3H), 4.96 (m, 1H), 5.05 (m, 1H), 5.89 (m, 1H), 6.71 (s, 1H), 6.79 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.7 (CH_3), 18.8 (CH_2), 22.0 (CH_2), 25.2 (CH_3), 29.3 (CH_2), 29.5 (CH_2), 34.1 (CH_2), 36.8 (CH_2), 37.5 (C), 38.2 (CH_2), 45.1 (CH), 47.9 (C), 52.0 (CH_3), 55.6 (CH_3), 106.3 (CH), 114.4 (CH_2), 126.7 (C), 128.0 (C), 130.3 (C), 139.1 (CH), 148.1 (C), 155.8 (C), 179.2 (C). IR (film): 2927, 2855, 1726, 1501, 1463, 1245, 1132, 1108, 1042, 908, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{33}O_3$ ($M+H^+$) 357.2430, found: 357.2425.

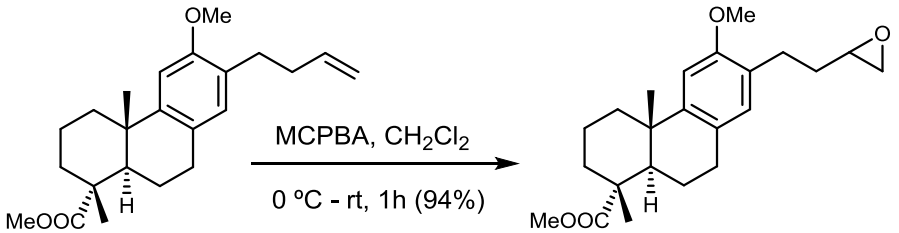
(1R,4aS,10aR)-methyl 6-methoxy-1,4a-dimethyl-7-(3-oxopropyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (24).



A stirred solution of **23** (115 mg, 0.32 mmol) in dry CH_2Cl_2 - MeOH (60 : 2 mL) was slowly bubbled with an O_3/O_2 mixture at -78°C and the course of the reaction was monitored by TLC. When the starting material was consumed (5 min), the solution was flushed with argon for 15 min, and PPh_3 was added (170 mg, 0.64 mmol). The mixture was further stirred for 12 h at room temperature and the solvent was removed. Flash chromatography on silica gel (20% AcOEt/hexane) gave aldehyde **24** (80 mg, 70%), as a colorless syrup. $[\alpha]_D^{25}$ = + 41.9 (c 0.9, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.27 (s, 3H), 1.40

(m, 1H), 1.52 (m, 1H), 1.61 – 1.86 (m, 5H), 2.21 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.28 (m, 1H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.76 – 2.82 (m, 2H), 2.82 – 2.93 (m, 2H), 3.66 (s, 3H), 3.78 (s, 3H), 6.71 (s, 1H), 6.78 (s, 1H), 9.79 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ (ppm) 16.6 (CH_3), 18.7 (CH_2), 21.8 (CH_2), 23.2 (CH_2), 25.1 (CH_3), 29.2 (CH_2), 36.7 (CH_2), 37.4 (C), 38.2 (CH_2), 44.0 (CH_2), 45.0 (CH), 47.8 (C), 52.0 (CH_3), 55.3 (CH_3), 106.2 (CH), 126.1 (C), 126.8 (C), 130.4 (CH), 148.7 (C), 155.7 (C), 179.1 (C), 202.8 (CH). IR (film): 2928, 1721, 1501, 1463, 1437, 1246, 1208, 1176, 1132, 1041 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_4$ ($M+H^+$) 359.2222, found: 359.2230.

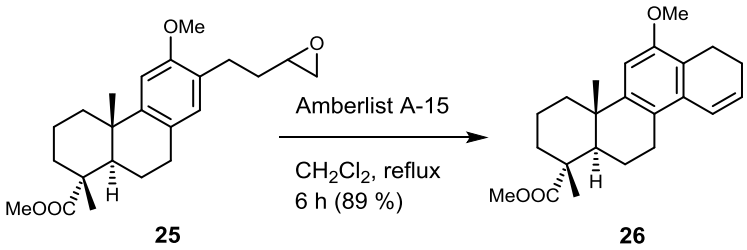
(1R,4aS,10aR)-methyl 6-methoxy-1,4a-dimethyl-7-(2-(oxiran-2-yl)ethyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (25).



To a solution of compound **23** (7.3 g, 20.5 mmol) in dichloromethane (60 ml) at 0°C was added *m*-chloroperoxybenzoic acid (70%; 5.78 g, 23.5 mmol) and the reaction was stirred at room temperature until TLC checks the complete conversion of the alkene. The reaction was quenched with Na_2SO_3 at 5% (10 mL) and stirred for an additional 10 min. Then, the solvent was removed in vacuum and ethyl acetate (70 mL) was added to the crude product. The organic phase was washed with sat. aq. $NaHCO_3$ (5 x 30 mL) and brine (2 x 30 mL), dried over anhydrous Na_2SO_4 and concentrate under vacuum to give a crude product which was directly purified by flash chromatography (10% AcOEt/hexane) to yield a inseparable mixture of isomers of **25** (7.17 g, 94%) as a yellow syrup. $[\alpha]_D^{25}$ = + 57.3 (c 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm): 1.22 (s, 3H), 1.27 (s, 3H), 1.39 (m, 1H), 1.52 (m, 1H), 1.64 (m, 1H), 1.69 – 1.85 (m, 6H), 2.22 (dd, *J* = 12.5, 2.1 Hz, 1H), 2.28 (m, 1H), 2.48 (dd, *J* = 5.0, 2.8 Hz, 1H), 2.64 – 2.83 (m, 5H), 2.96 (m, 1H), 3.66 (s, 3H), 3.79 (s, 3H), 6.71 (s, 1H), 6.80 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm): 16.6 (CH_3), 18.7 (CH_2), 21.9 (CH_2), 25.2 (CH_3), 26.5 (CH_2), 29.3 (CH_2), 32.8 (CH_2), 36.7 (CH_2), 37.5 (C), 38.2 (CH), 45.1 (CH), 47.3 (CH_2), 47.8 (C), 52.1 (CH_3), 52.3 (CH), 55.5 (CH_3), 106.2 (CH), 126.8 (C),

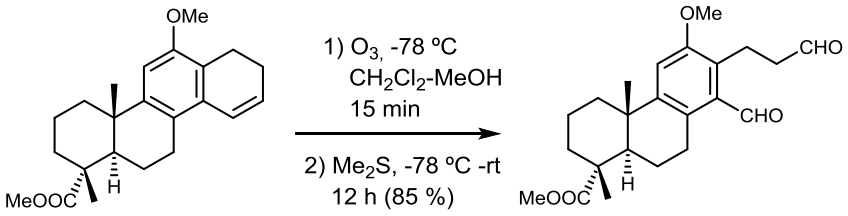
127.3 (C), 130.4 (CH), 148.3 (C), 155.8 (C), 179.2 (C). IR (film): 2929, 1724, 1501, 1454, 1246, 1209, 1176, 1132, 1108, 1041 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{33}O_4$ ($M+H^+$) 373.2379, found: 373.2367.

(1R,4aS,12aR)-methyl 6-methoxy-1,4a-dimethyl-1,2,3,4,4a,7,8,11,12,12a-decahydrochrysene-1-carboxylate (26).



To a solution of epoxide **25** (5.3 g, 14.24 mmol) in dry dichloromethane (40 mL), was added Amberlyst A-15 ion-exchange (2.5 g) and the reaction mixture was heated to reflux for 6 h, at which time TLC showed no compound **25**. Then the mixture was filtered by cotton, washed with ethyl acetate (40 mL), concentrated in vacuo and purified by flash chromatography (5% AcOEt/hexane) to obtain compound **26** (4.48 g, 89%) as a light yellow syrup. $[\alpha]_D^{25}$ = + 51.3 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 1.26 (s, 3H), 1.28 (s, 3H), 1.50 (m, 1H), 1.64 (m, 1H), 1.70 – 1.86 (m, 5H), 2.18 – 2.25 (m, 2H), 2.30 (m, 1H), 2.65 – 2.82 (m, 3H), 2.81 – 2.92 (m, 2H), 3.67 (s, 3H), 3.81 (s, 3H), 6.10 (dt, *J* = 9.9, 4.5 Hz, 1H), 6.61 (dt, *J* = 9.9, 1.9 Hz, 1H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.6 (CH_3), 18.8 (CH_2), 20.0 (CH_2), 21.8 (CH_2), 22.3 (CH_2), 25.2 (CH_3), 26.9 (CH_2), 36.7 (CH_2), 37.7 (C), 38.6 (CH_2), 44.5 (CH), 47.8 (C), 52.0 (CH_3), 55.8 (CH_3), 106.2 (CH), 121.6 (C), 122.8 (C), 124.4 (CH), 129.3 (CH), 132.7 (C), 148.3 (C), 154.5 (C), 179.2 (C). IR (film): 2931, 2835, 1725, 1463, 1269, 1247, 1219, 1133, 1101, 774 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{31}O_3$ ($M+H^+$) 355.2273, found: 355.2271.

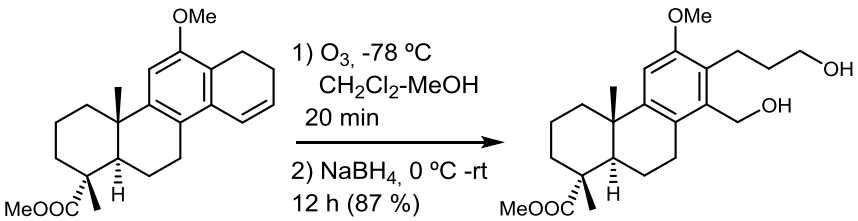
(1R,4aS,10aR)-methyl 8-formyl-6-methoxy-1,4a-dimethyl-7-(3-oxopropyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (27).



26 **27**

A stirred solution of **26** (3 g, 8.5 mmol) in dry CH_2Cl_2 - MeOH (60 : 2 mL) was slowly bubbled with an O_3/O_2 mixture at -78°C and the course of the reaction was monitored by TLC. When the starting material was consumed (15 min), the solution was flushed with argon for 20 min, and Me_2S was added (6 mL). The mixture was further stirred for 12 h at room temperature and the solvent was removed. Flash chromatography on silica gel (20% AcOEt/hexane) gave the dialdehyde **27** (2.8 g, 85%), as a colorless syrup. $[\alpha]_D^{25}$ = + 57.2 (c 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 1.25 (s, 3H), 1.27 (s, 3H), 1.38 (m, 1H), 1.63 – 1.70 (m, 2H), 1.69 – 1.91 (m, 4H), 2.21 (dd, *J* = 12.6, 2.1 Hz, 1H), 2.28 (m, 1H), 2.67 (br t, *J* = 7.6, 2H), 3.03 – 3.17 (m, 4H), 3.67 (s, 3H), 3.81 (s, 3H), 6.96 (s, 1H), 9.79 (s, 1H), 10.53 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.6 (CH_3), 18.7 (CH_2), 18.9 (CH_2), 21.6 (CH_2), 25.1 (CH_3), 27.2 (CH_2), 36.5 (CH_2), 37.9 (C), 38.5 (CH_2), 44.2 (CH), 44.5 (CH_2), 47.6 (C), 52.2 (CH_3), 55.7 (CH_3), 111.1 (CH), 128.4 (C), 128.8 (C), 134.2 (C), 149.7 (C), 156.0 (C), 178.9(C), 195.1 (CH), 202.5 (CH). IR (film): 2935, 1722, 1688, 1463, 1249, 1221, 1187, 1135, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{31}O_5$ ($M+H^+$) 387.2171, found: 387.2163.

(1R,4aS,10aR)-methyl 8-(hydroxymethyl)-7-(3-hydroxypropyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (28).

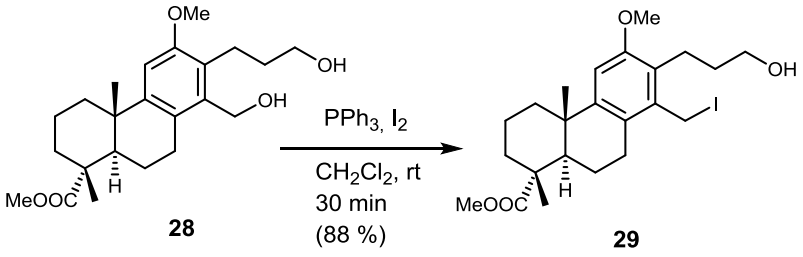


26 **28**

An ozone stream was bubbled into a solution of **26** (2.62 g, 7.42 mmol) into a 10 : 1 mixture of CH_2Cl_2 and MeOH (60 : 6 mL) cooled at -78 ºC and the course of the reaction was monitored by TLC. When the starting material was consumed (20 min), the solution was flushed out with an argon stream for eliminating the

ozone excess. Then, $NaBH_4$ (1.68 g, 44.52 mmol) was added to the cooled solution and stirred for 12 h letting the temperature increase to room temperature, at which time TLC showed no ozonide remaining. The reaction was quenched with water (80 mL) at 0 ºC, the phases were shaken and separated and the organic phase was washed with water (2 x 70 mL), brine (2 x 70 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated to give dialcohol **28** (2.52 g, 87%) as a white solid; mp 91−93 °C. $[\alpha]_D^{25}$ = + 44.0 (c 1.2, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 1.24 (s, 3H), 1.27 (s, 3H), 1.47 (m, 1H), 1.60 – 1.67 (m, 2H), 1.68 – 1.90 (m, 6H), 2.21 (dd, *J* = 12.6, 2.1 Hz, 1H), 2.28 (m, 1H), 2.79 – 2.96 (m, 4H), 3.02 (d, *J* = 6.2 Hz, 1H), 3.06 (d, *J* = 6.3 Hz, 1H), 3.48 – 3.58 (m, 2H), 3.67 (s, 3H), 3.80 (s, 3H), 4.67 (d, *J* = 11.8 Hz, 1H), 4.71 (d, *J* = 11.8 Hz, 1H), 6.78 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.6 (CH_3), 18.8 (CH_2), 21.8 (CH_2), 21.9 (CH_2), 25.2 (CH_3), 26.9 (CH_2), 32.9 (CH_2), 36.6 (CH_2), 37.8 (C), 38.6 (CH_2), 44.6 (CH), 47.7 (C), 52.1 (CH_3), 55.7 (CH_3), 58.7 (CH_2), 61.5 (CH_2), 106.8 (CH), 126.9 (C), 127.2 (C), 137.5 (C), 148.8 (C), 156.1 (C), 179.2 (C). IR (KBr): 3328, 2927, 1724, 1462, 1250, 1220, 1192, 1134, 1040, 772 cm^{-1}. . HRMS (ESI) m/z: calcd for $C_{23}H_{34}O_5Na$ ($M+Na^+$) 413.2304, found: 413.2291.

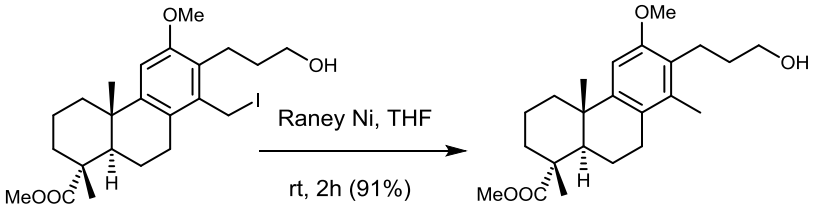
(1R,4aS,10aR)-methyl 7-(3-hydroxypropyl)-8-(iodomethyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (29).



To a solution of PPh_3 (1.45 g, 5.25 mmol) in dichloromethane (25 mL) was added I_2 (1.33 g, 5.25 mmol), and the mixture was stirred at room temperature for 5 min. After that time, the mixture was added over a solution of dialcohol **28** (2.1 g, 5.38 mmol) in dichloromethane (5 mL). The resulting mixture was stirred at room temperature for 30 min, at which time TLC showed no remaining starting material. Then, the reaction was quenched with 10% aqueous $NaHSO_3$ (5 mL). The solvent was removed under vacuum, ether:water (30:10 mL) was added, the phases were shaken and separated, and the organic phase was washed with water (15 mL) and brine (15 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated to give a

crude product which was purified by flash chromatography (30% AcOEt/hexane) to give compound **29** (2.37 g, 88%) as a colorless syrup. $[\alpha]_D^{25}$ = + 0.9 (c 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.23 (s, 3H), 1.28 (s, 3H), 1.50 (m, 1H), 1.62 – 1.92 (m, 6H), 2.20 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.26 (m, 1H), 2.61 – 2.93 (m, 6H), 3.60 (td, *J* = 6.0, 2.1 Hz, 2H), 3.68 (s, 3H), 3.80 (s, 3H), 4.38 (br d, 1H), 4.48 (d, *J* = 9.5 Hz, 1H), 6.78 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ (ppm) 3.2 (CH_2), 16.6 (CH_3), 18.7 (CH_2), 21.7 (CH_2), 21.9 (CH_2), 25.3 (CH_3), 26.6 (CH_2), 32.4 (CH_2), 36.6 (CH_2), 37.8 (C), 38.4 (CH_2), 44.5 (CH), 47.7 (C), 52.1 (CH_3), 55.8 (CH_3), 62.1 (CH_2), 107.1 (CH), 126.7 (C), 126.9 (C), 135.2 (C), 149.2 (C), 156.0 (C), 179.1 (C). IR (film): 3431, 2929, 1723, 1594, 1462, 1249, 1135, 1041, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{34}O_4I$ ($M+H^+$) 501.1502, found: 501.1497.

(1R,4aS,10aR)-methyl 7-(3-hydroxypropyl)-6-methoxy-1,4a,8-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (30).

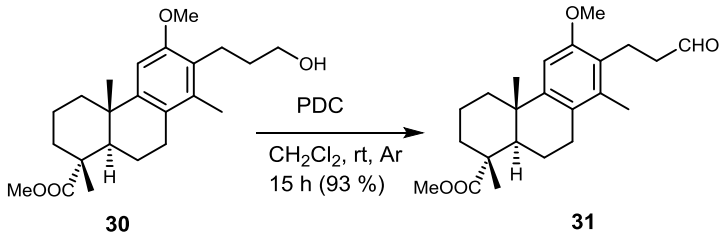


29 **30**

A 70% Raney-Nickel dispersion in water (3 mL) was added to a stirred solution of **29** (1.9 g, 3.8 mmol) in THF (30 mL), and the mixture was stirred at room temperature for 2 h, at which time TLC showed no starting material. Then, the resulting mixture was filtered through silica gel and washed with ethyl acetate (100 mL). The solvent was dried over anhydrous Na_2SO_4 and evaporated to yield alcohol **30**(1.3 g, 91%), as a colorless syrup. $[\alpha]_D^{25}$ = + 45.6 (c 1.1, $CHCl_3$). ^{1}H NMR (600 MHz, chloroform-*d*) δ (ppm) 1.24 (s, 3H), 1.28 (s, 3H), 1.49 (m, 1H), 1.64 (m, 1H), 1.69 – 1.86 (m, 5H), 2.13 (s, 3H), 2.21 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.28 (m, 1H), 2.57 – 2.66 (m, 2H), 2.68 – 2.83 (m, 5H), 3.54 (br t, *J* = 5.8 Hz, 2H), 3.67 (s, 3H), 3.81 (s, 3H), 6.69 (s, 1H). ^{13}C NMR (150 MHz, Chloroform-d) δ (ppm) 15.2 (CH_3), 16.6 (CH_3), 18.8 (CH_2), 21.7 (CH_2), 22.0 (CH_2), 25.2 (CH_3), 28.3 (CH_2), 32.2 (CH_2), 36.7 (CH_2), 37.7 (C), 38.6 (CH_2), 44.5 (CH), 47.8 (C), 52.1 (CH_3), 55.9 (CH_3), 61.9 (CH_2), 104.3 (CH), 125.8 (C), 126.6 (C), 135.9 (C), 148.1 (C), 155.8 (C),

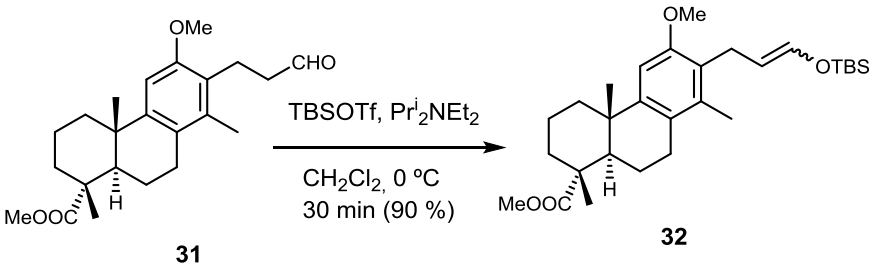
179.2 (C). IR (film): 3425, 2928, 1725, 1462, 1248, 1134, 1041, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{35}O_4$ ($M+H^+$) 375.2535, found: 375.2532.

(1R,4aS,10aR)-methyl 6-methoxy-1,4a,8-trimethyl-7-(3-oxopropyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (31).



Pyridinium dichromate (PDC) (2.4 g, 6.38 mmol) was added to a solution of **30** (1.2 g, 3.21 mmol) in dry CH_2Cl_2 (30 mL) and the mixture was stirred at room temperature under argon for 15 h, at which time TLC showed no remaining starting material. Then the mixture was directly filtered through a silica gel column (20 g) and washed with CH_2Cl_2 (2 x 20 mL). The filtrates was washed with 2N HCl solution (2 x 20 mL) , brine (2 x 20 mL), dried over anhydrous Na_2SO_4 and filtered. Removal the solvent at vacuum afforded a crude product (1.4 g) which was purified by column chromatography (10% AcOEt/hexane) to give **31** (1.11 g, 93%) (colourless oil).

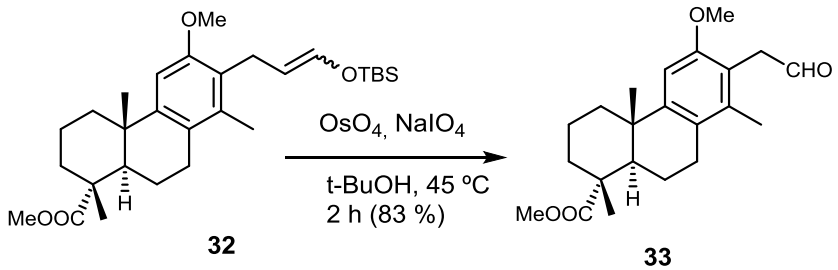
(1R,4aS,10aR)-methyl 7-(3-((tert-butyldimethylsilyl)oxy)allyl)-6-methoxy-1,4a,8-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (32).



To a solution of aldehyde **31** (0.98 g, 2.63 mmol) in anhydrous dichloromethane (20 mL) cooled to 0°C and under argon atmosphere, ^{i}PrNEt (1.3 ml, 7.89 mmol) and TfOTBS (0.6 ml, 2.63 mmol) were added. The mixture was stirred at 0°C for 30 min, at which time TLC showed no starting material. Then, the reaction was quenched with saturated aqueous $NaHCO_3$ (1 mL) and Et_2O (25 mL) was added, the phases were

shaken and separated, and the organic phase was washed with water (20 mL), brine (20 mL) and dried over anhydrous Na_2SO_4. Removal of the solvent at vacuum gave a crude product which was purified by flash chromatography (5% AcOEt/hexane) to give a mixture of cis/trans isomers of compound **32** (1.15 g, 90%) as a colorless syrup. ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm): Common signals: 1.24 (s, 6H), 1.28 (s, 6H), 1.43 – 1.54 (m, 4H), 1.65 – 1.87 (m, 10H), 2.19 – 2.24 (m, 2H), 2.29 (d, *J* = 11.5 Hz, 2H), 2.57 – 2.67 (m, 2H), 2.68 – 2.75 (m, 2H), 3.20 – 3.31 (m, 2H), 3.48 (d, J = 1.8 Hz, 1H), 3.49 (d, *J* = 1.8 Hz, 1H); signals assignable to the major isomer: 0.10 (s, 6H), 0.89 (s, 9H), 2.12 (s, 3H), 3.67 (s, 3H), 3.78 (s, 3H), 5.04 (dt, *J* = 12.0, 7.0 Hz, 1H), 6.26 (dt, *J* = 11.9, 1.4 Hz, 1H), 6.67 (s, 1H); signals assignable to the minor isomer: 0.16 (s, 6H), 0.97 (s, 9H), 2.15 (s, 3H), 3.67 (s, 3H), 3.79 (s, 3H), 4.45 (td, *J* = 7.0, 5.8 Hz, 1H), 6.18 (dt, *J* = 5.8, 1.7 Hz, 1H), 6.68 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ (ppm): Common signals: 16.64 (CH_3), 18.42 (C), 18.85 (CH_2), 21.15 (CH_2), 24.23 (CH_2), 25.21 (CH_3), 36.68 (CH_2), 47.81 (C), 179.29 (C); signals assignable to the major isomer: -5.05 (CH_3), 15.06 (CH_3), 22.07 (CH_2), 25.84 (CH_3), 28.25 (CH_2), 37.63 (C), 38.60 (CH_2), 44.52 (CH), 52.04 (CH_3), 55.81 (CH_3), 104.51 (CH), 109.80 (CH), 125.69 (C), 125.96 (C), 135.64 (C), 140.75 (CH), 144.96 (C), 155.65 (C); signals assignable to the minor isomer: -5.13 (CH_3), 15.28 (CH_3), 22.09 (CH_2), 25.82 (CH_3), 28.27 (CH_2), 37.61 (C), 38.61 (CH_2), 44.49 (CH), 52.02 (CH_3), 55.94 (CH_3), 104.61 (CH), 109.21 (CH), 126.09 (C), 126.50 (C), 136.13 (C), 137.88 (CH), 147.79 (C), 155.74 (C). IR (film): 2929, 2857, 1726, 1658, 1463, 1249, 1189, 1155, 1133, 1090, 836, 779 cm^{-1}.

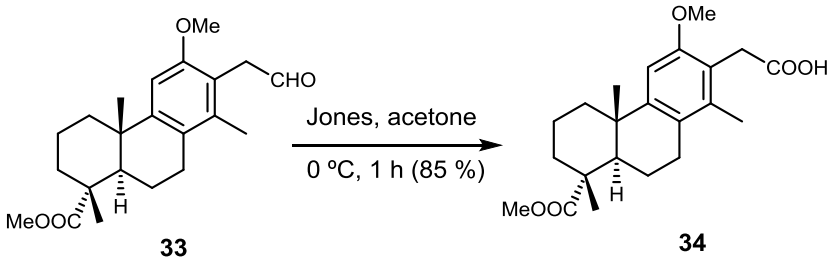
(1R,4aS,10aR)-methyl 6-methoxy-1,4a,8-trimethyl-7-(2-oxoethyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (33).



Sodium periodate (0.53 g, 2.46 mmol) and osmium tetroxide 0.2% aq. sol. (1 mL, 7.7 x 10^{-3} mmol) were added to a stirred solution of **32** (0.41 g, 0.84 mmol) in *tert*-butanol (10 mL). The mixture was further stirred at 45°C for 2h, at which time TLC showed no starting material. Then Et_2O-water (10:5 mL) was added, the

phases were shaken and separated, and the aqueous phase was extracted again with Et_2O (10 mL). The combined organic phases were washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and evaporate to afford a crude, which was purified by flash chromatography on silica gel (5% AcOEt/hexane) to give (249 mg, 83%) of **33** as a colorless syrup. $[\alpha]_D^{25}$ = + 47.1 (c 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.25 (s, 3H), 1.28 (s, 3H), 1.50 (m, 1H), 1.65 (m, 1H), 1.70 – 1.87 (m, 5H), 2.07 (s, 3H), 2.22 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.30 (m, 1H), 2.59 – 2.76 (m, 2H), 3.67 (s, 3H), 3.74 (d, *J* = 2.2 Hz, 1H), 3.76 (d, *J* = 2.2 Hz, 1H), 3.79 (s, 3H), 6.73 (s, 1H), 9.59 (t, *J* = 2.2 Hz, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ (ppm) 15.7 (CH_3), 16.6 (CH_3), 18.8 (CH_2), 21.9 (CH_2), 25.1 (CH_3), 28.2 (CH_2), 36.6 (CH_2), 37.8 (C), 38.6 (CH_2), 41.9 (CH_2), 44.4 (CH), 47.7 (C), 52.1 (CH_3), 55.6 (CH_3), 104.3 (CH), 117.5 (C), 126.4 (C), 136.9 (C), 149.8 (C), 155.8 (C), 179.1 (C), 200.6 (CH). IR (film): 2932, 1722, 1463, 1248, 1190, 1134, 1097 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_4$ ($M+H^+$) 359.2222, found: 359.2227.

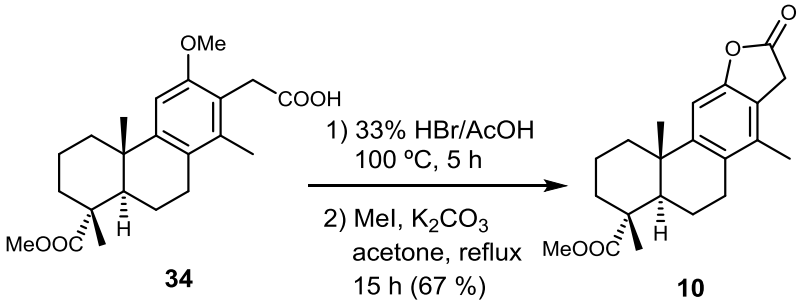
2-((4bS,8R,8aR)-3-methoxy-8-(methoxycarbonyl)-1,4b,8-trimethyl-4b,5,6,7,8,8a,9,10-octahydrophenanthren-2-yl)acetic acid (34).



To a solution of aldehyde **33** (94 mg, 0.26 mmol) in acetone (5 mL) cooled to 0°C, Jones reagent was added drop by drop until the color of the mixture turned red. The mixture was stirred at 0°C for 45 min, at which time TLC showed no starting material. Then, the mixture was evaporated under reduced pressure, ethyl acetate-water (15:5 mL) was added and the phases were shaken and separated. The organic phase was washed with water (5 mL) and brine (5 mL), dried over anhydrous Na_2SO_4 and evaporate to afford a crude, which was purified by flash chromatography on silica gel (40% AcOEt/hexane) to give compound **34** (83 mg, 85%) as a white solid; mp 151−153 °C. $[\alpha]_D^{25}$ = +41.9 (c 1.0, $CHCl_3$). ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm) 1.20 (s, 3H), 1.34 (s, 3H), 1.64 – 1.85 (m, 7H), 2.27 (d, *J* = 11.3 Hz, 1H), 2.36 (m, 1H), 2.50 (s,

3H), 2.56 – 2.73 (m, 2H), 3.65 (s, 3H), 3.75 (d, *J* = 17.3 Hz, 1H), 3.82 (d, *J* = 17.3 Hz, 1H), 3.88 (s, 3H), 6.72 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.8 (CH_3), 18.0 (CH_3), 18.4 (CH_2), 23.5 (CH_3), 29.9 (CH_2), 31.3 (CH_2), 36.8 (CH_2), 37.8 (CH_2), 38.3 (C), 39.1 (CH_2), 42.5 (CH), 46.4 (C), 52.3 (CH_3), 55.8 (CH_3), 102.6 (CH), 121.2 (C), 125.3 (C), 141.7 (C), 157.8 (C), 160.6 (C), 176.9 (C), 178.0 (C,). IR (KBr): 2928, 1722, 1666, 1582, 1460, 1283, 1240, 1188, 1137, 1109, 1091, 755 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_5$ ($M+H^+$) 375.2171, found: 375.2177.

Taepeenin F (10).



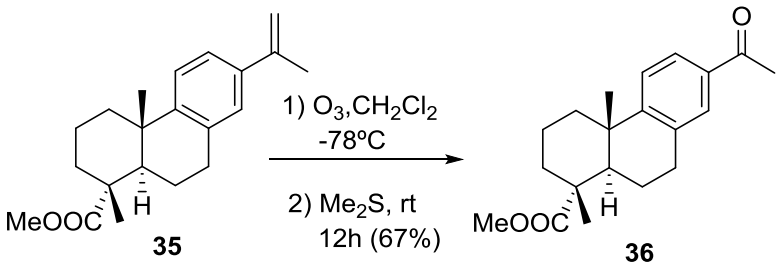
A solution of compound **34** (73 mg, 0.195 mmol) in HBr (33% in glacial acetic acid, 2 mL) was stirred at 100°C for 5 h. After the mixture was cooled, and the reaction was quenched by adding water (2 mL) in a cold-water bath. Ethyl acetate (15 mL) was added, the phases were shaken and separated, and the aqueous phase was extracted again with ethyl acetate (10 mL). The combined organic phases were washed with water (10 x 7 mL) and brine (2 x 7 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo. This crude (69 mg) was directly esterified. It was diluted in acetone (5 mL), and K_2CO_3 (45 mg, 0.326 mmol), methyl iodide (57 mg, 0.4 mmol) were added and the mixture was refluxed for 15 h. then, the solvent was evaporated under reduced pressure, and the mixture was diluted with AcOEt - water (15 : 5 mL) and the phases were shaken and separated. The organic phase was washed with water (10 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and evaporated in vacuo to afford a crude, which was purified by flash chromatography on silica gel (5% AcOEt/hexane) to give compound **10** (45 mg, 67%) as a white solid; mp 193−195 °C (lit.[9a] mp 194-195 °C). $[\alpha]_D^{25}$ = +25.0 (c 0.6, $CHCl_3$) (lit.[9a] +23.3 (c 0.003, $CHCl_3$)). ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.28 (s,

3H), 1.47 (m, 1H), 1.52 (m, 1H), 1.66 (m, 1H), 1.70 – 1.75 (m, 2H), 1.78 (m, 1H), 1.83 (m, 1H), 2.11 (s, 3H), 2.18 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.25 (m, 1H), 2.59 – 2.78 (m, 2H), 3.61 (s, 2H), 3.68 (s, 3H), 6.91 (s, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 16.5 (CH_3), 16.6 (CH_3), 18.7 (CH_2), 21.6 (CH_2), 25.2 (CH_3), 27.6 (CH_2), 32.7 (CH_2), 36.7 (CH_2), 37.9 (C), 38.6 (CH_2), 44.4 (CH), 47.7 (C), 52.1 (CH_3), 104.2 (CH), 119.9 (C), 129.3 (C), 133.0 (C), 150.8 (C), 152.9 (C), 174.8 (C), 179.1 (C). IR (KBr): 2926, 2853, 1816, 1731, 1249, 1168, 1136, 1012 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{21}H_{27}O_4$ ($M+H^+$) 343.1909, found: 343.1909.

Table 1. ^{1}H and ^{13}C NMR data for the synthetic and natural taepeenin F (10)

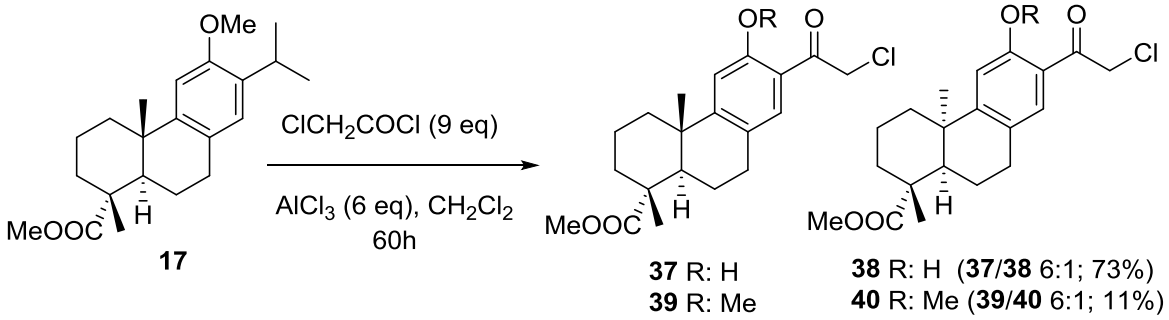
	^{1}H NMR		^{13}C NMR	
Position	Synthetic Taepeenin F (**10**)	Natural Taepeenin F (**10**) (ref. 9a)	Synthetic Taepeenin F (**10**)	Natural Taepeenin F (**10**) (ref. 9a)
1	2.25 m, 1.47 m	2.27 m, 1.47 m	38.6	38.4
2	1.73 m	1.79 m	18.7	18.5
3	1.78 m, 1.66 m	1.78 m, 1.65 m	36.7	36.5
4	-	-	47.7	47.6
5	2.18 dd (*J*=12.7, 2.1 Hz)	2.19 dd (*J*=12.6, 2.1 Hz)	44.4	44.2
6	1.83 m, 1.52 m	1.54 m	21.6	21.4
7	2.69 m	2.74 m, 2.64 m	27.6	27.4
8	-	-	129.3	129.2
9	-	-	150.8	150.7
10	-	-	37.9	37.8
11	6.91 s	6.90 s	104.2	104.1
12	-	-	152.9	152.7
13	-	-	119.9	119.8
14	-	-	133.0	132.9
15	3.61 s	3.61 s	32.7	32.5
16	-	-	174.8	174.7
17	2.11 s	2.10 s	16.5	16.4
18	-	-	179.1	179.0
19	1.22 s	1.25 s	16.6	16.5
20	1.28 s	1.28 s	25.2	25.1
-OCO*Me*	3.68 s	3.68 s	52.1	52.0

(1R,4aS,10aR)-methyl 7-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (36).



A stirred solution of (1R,4aS,10aR)- methyl 1,4a-dimethyl-7-(prop-1-en-2-yl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**35**)[24] (1.08 g, 3.4 mmol) in dry CH_2Cl_2: MeOH (60:15 mL) was slowly bubbled with an O_3/O_2 mixture at -78°C and the course of the reaction was monitored by TLC. When the starting material was consumed (35 min), the solution was flushed with argon for 20 min, and Me_2S was added (10 mL). The mixture was further stirred for 12 h at room temperature and the solvent was removed. Flash chromatography on silica gel (5% AcOEt/hexane) gave the 10β-13-acetyl ester **36** (0.73 g, 67%), as a colorless syrup. $[\alpha]_D^{25}$ = + 60.4 (c 1.1, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.20 (s, 3H), 1.28 (s, 3H), 1.43 – 1.52 (m, 2H), 1.63 – 1.69 (m, 1H), 1.71 – 1.86 (m, 4H), 2.21 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.32 (d, *J* = 12.5 Hz, 1H), 2.54 (s, 3H), 2.92 – 2.97 (m, 2H), 3.66 (s, 3H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.63 (s, 1H), 7.70 (dd, *J* = 8.3, 2.0 Hz, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.6 (CH_3), 18.5 (CH_2), 21.5 (CH_2), 24.9 (CH_3), 26.6 (CH_3), 30.0 (CH_2), 36.6 (CH_2), 37.8 (C), 37.8 (CH_2), 44.6 (CH), 47.7 (C), 52.1 (CH_3), 124.6 (CH), 125.9 (CH), 129.4 (CH), 134.6 (C), 135.5 (C), 155.0 (C), 178.9 (C), 198.1 (C). IR (film): 2937, 1724, 1681, 1603, 1432, 1357, 1248, 1177, 1126, 1110, 1038, 754 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{27}O_3$ ($M+H^+$) 315.1960, found: 315.1974.

Treatment of methyl 12-methoxy-8,11,13-abietatrien-18-oate (17) with chloroacetyl chloride and aluminium chloride. Obtention of compounds 37, 38, 39 and 40.



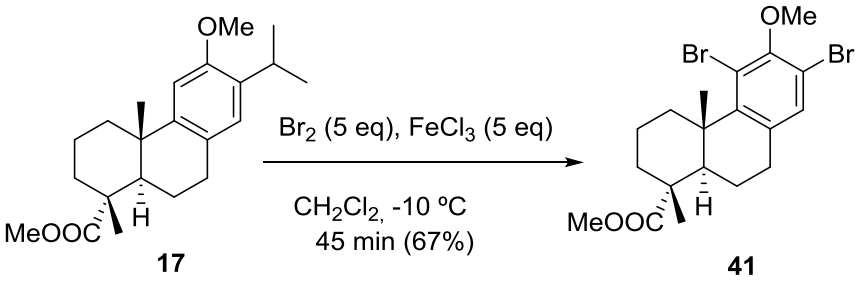
These compounds were prepared using the procedure described in ref 18. To a solution of methyl 12-acetyl-8,11,13-abietatrien-18-oate (**17**) (842 mg, 2.45 mmol) in dry dichloromethane (10 mL), at 0 °C and under argon atmosphere, chloroacetyl chloride (1.75 mL, 21.7 mmol) was added. To this vigorously stirred mixture, aluminium chloride (1.99 g, 14.7 mmol) was added in small portions over a 10 min period. The reaction mixture was stirred at 0 °C for 30 min and then was allowed to gradually warm to ambient temperature. The reaction was stirred at room temperature for 60 h and then was slowly poured into ice-cold 10% aqueous HCl. The mixture was extracted with Et_2O (3 x 10 mL), and the combined organic phases were washed with saturated aqueous $NaHCO_3$ (2 x 10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The oily residue thus obtained was partially purified by flash column chromatography on silica gel (5% AcOEt/hexane) to give a mixture of compounds **37**, **38** (651 mg, 73%) (ratio 6:1) as a yellow syrup and **39**, **40** (102 mg, 11%) (ratio (6:1), as a yellow syrup.

*(1R,4aS,10aR)-methyl 7-(2-chloroacetyl)-6-hydroxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**37**) and (1R,4aR,10aR)-methyl 7-(2-chloroacetyl)-6-hydroxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**38**).* ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm): Signals assignable to **37:** 1.20 (s, 3H), 1.27 (s, 3H), 1.41 – 1.54 (m, 2H), 1.63 – 1.87 (m, 6H), 2.17 (dd, *J* = 12.5, 2.4 Hz, 1H), 2.22 – 2.27 (m, 1H), 2.82 – 2.87 (m, 2H), 3.67 (s, 3H), 4.66 (s, 2H), 6.89 (s, 1H), 7.33 (s, 1H), 11.33 (s, 1H).); signals assignable to **38:** 1.03 (s, 3H), 1.19 (s, 3H), 3.68 (s, 3H), 4.67 (s, 2H), 6.92 (s, 1H), 7.26 (s, 1H), 11.32 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm): Signals assignable to **37:** 16.7 (CH_3), 18.5 (CH_2), 21.6 (CH_2), 24.6 (CH_3), 29.0 (CH_2), 36.6 (CH_2), 37.7 (CH_2), 38.2 (C), 44.2 (CH), 45.3 (CH_2), 47.7 (C), 52.2 (CH_3), 114.1 (CH), 115.5 (C), 126.6 (C), 129.9 (CH), 160.6 (C),

160.8 (C), 178.8 (C), 195.8 (C); signals assignable to **38** 11.5 (CH_3), 14.2 (CH_3), 19.5 (CH_2), 20.2 (CH_2), 22.2 (CH_3), 22.8 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 36.5 (CH_2), 39.5 (C), 41.4 (C), 45.3 (CH_2), 45.4 (CH), 51.9 (CH_3), 115.4 (C), 115.9 (CH), 127.7 (C), 129.3 (CH), 160.6 (C), 160.8 (C), 179.2 (C), 195.8 (C).

*(1R,4aS,10aR)-methyl 7-(2-chloroacetyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**39**) and (1R,4aR,10aR)-methyl 7-(2-chloroacetyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**40**).* ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm): Common signals to **37** and **38**-**40**: 1.37 – 1.88 (m, 20H), 2.15 – 2.33 (m, 7H), 2.89 – 2.77 (m, 6H); signals assignable to **39:** 1.22 (s, 3H), 1.27 (s, 3H), 3.66 (s, 3H), 3.90 (s, 3H), 4.75 (s, 2H), 6.82 (s, 1H), 7.55 (s, 1H); signals assignable to **40:** 1.06 (s, 3H), 1.24 (s, 3H), 3.68 (s, 3H), 3.89 (s, 3H), 4.75 (s, 2H), 6.84 (s, 1H), 7.56 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm): Signals assignable to **39**: 16.69 (CH_3), 18.58 (CH_2), 21.58 (CH_2), 24.85 (CH_3), 28.86 (CH_2), 36.60 (CH_2), 37.96 (CH_2), 38.14 (C), 44.49 (CH), 45.28 (CH_2), 47.72 (C), 52.16 (CH_3), 55.70 (CH_3), 107.31 (CH), 115.54 (C), 126.59 (C), 131.99 (CH), 157.03 (C), 157.31 (C), 178.85 (C), 191.76 (C).

Treatment of methyl 12-methoxy-8,11,13-abietatrien-18-oate (17) with bromine and aluminium chloride. Obtention of compound 41.

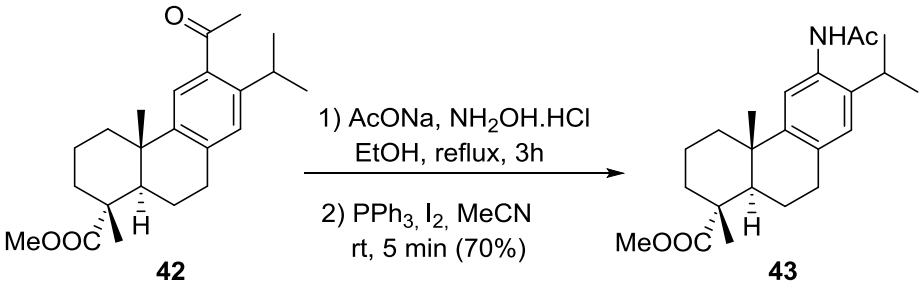


To a solution of methyl 12-acetyl-8,11,13-abietatrien-18-oate (**17**) (64 mg, 0.18 mmol) in anhydrous dichloromethane (5 mL) cooled to -10 °C and under argon atmosphere, bromine (0.05 ml, 0.93 mmol) was added. To this vigorously stirred mixture, aluminium chloride (0.126 g, 0.93 mmol) was slowly added. The reaction mixture was stirred at -10 °C for 45 min. The mixture was slowly poured into ice-cold 10% aqueous HCl and extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with water (15

mL), 10% aqueous $NaHSO_3$ (15 mL), again with water (15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5% AcOEt/hexane) to yield compound **41** (57 mg, 67 %) as a light yellow syrup.

*(1R,4aS,10aR)-methyl 5,7-dibromo-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**41**).* $[\alpha]_D^{25}$ = + 46.2 (c 0.8, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.27 (s, 3H), 1.42 – 1.53 (m, 2H), 1.61 – 1.89 (m, 5H), 2.15 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.27 (m, 1H), 2.73 (m, 1H), 2.92 (m, 1H), 3.68 (s, 3H), 3.87 (s, 3H), 6.82 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.6 (CH_3), 18.7 (CH_2), 22.0 (CH_2), 25.1 (CH_3), 32.7 (CH_2), 36.5 (CH_2), 38.0 (C), 38.4 (CH_2), 44.1 (CH), 47.7 (C), 52.2 (CH_3), 56.8 (CH_3), 107.4 (CH), 113.2 (C), 128.9 (C), 129.4 (C), 151.1 (C), 155.1 (C), 178.9 (C). IR (film): 2928, 2853, 1724, 1582, 1456, 1437, 1242, 1187, 1135, 1040 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{19}H_{25}O_3Br_2$ ($M+H^+$) 459.0170, found: 459.0151.

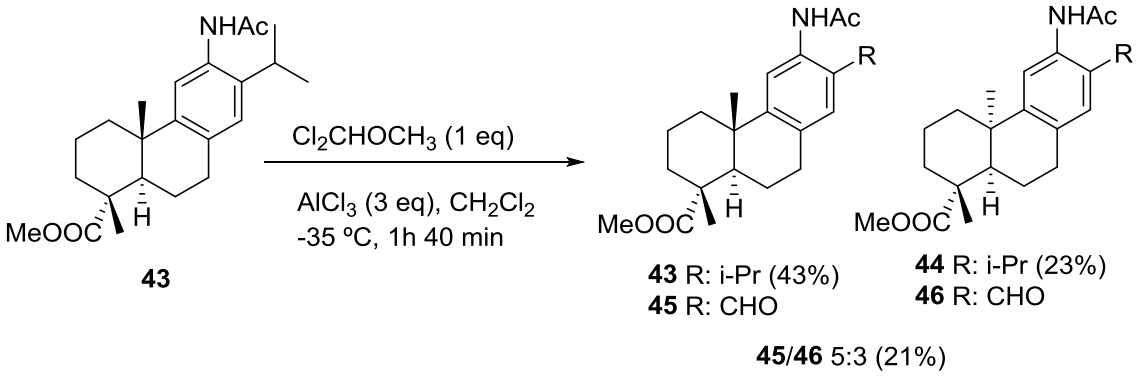
(1R,4aS,10aR)-methyl 6-acetamido-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (43).



A mixture of methyl 12-acetyl-8,11,13-abietatrien-18-oate (**42**) (0.524 g, 1.47 mmol), AcONa (0.145 g, 1.76 mmol) and $NH_2OH{\cdot}HCl$ (0.102 g, 1.47 mmol) in EtOH (15 mL) was stirred under reflux for 3 h. Then the mixture was cooled, followed by evaporating the solvent in vacuum. The residue was dissolved in ethyl acetate (25 mL) and washed with water (3 x 10 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated to give the crude oxime (0.371 g, 68%), which was directly used to obtain the acetamide **43**.

To a solution of PPh_3 (0.044 g, 0.17 mmol) in MeCN (10 mL) was added I_2 (0.042 g, 0.17 mmol), and the mixture was stirred at room temperature for 5 min. After that time, the mixture was added over a solution of the crude oxime (309 mg, 0.83 mmol) in MeCN (5 mL). The resulting mixture was refluxed overnight. Then, the reaction was cooled to room temperature and concentrated in vacuo. The residue was dissolved in ethyl acetate (20 mL) and washed with saturated sodium thiosulfate solution (10 mL) and brine (10 mL). The organic phase was dried over anhydrous Na_2SO_4 and concentrated to give a crude product which was purified by flash chromatography (30% AcOEt/hexane) to give amide **43** (216 mg, 70%) as a white solid; mp 118−120 °C. $[\alpha]_D^{25}$ = + 67.7 (c 1.1, $CHCl_3$). ^{1}H NMR (600 MHz, chloroform-*d*) δ (ppm) 1.19 (d, *J* = 6.9 Hz, 6H), 1.20 (s, 3H), 1.26 (s, 3H), 1.36 – 1.53 (m, 2H), 1.60 – 1.84 (m, 5H), 2.17 (s, 3H), 2.20 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.26 (m, 1H), 2.83 – 2.87 (m, 2H), 2.95 (hept, *J* = 6.9 Hz, 1H), 3.65 (s, 3H), 6.91 (s, 1H), 7.03 (s, 1H), 7.41 (s, 1H). ^{13}C NMR (150 MHz, chloroform-*d*) δ (ppm) 16.6 (CH_3), 18.6 (CH_2), 21.8 (CH_2), 23.2 (CH_3), 23.5 (CH_3), 24.2 (CH_3), 25.1 (CH_3), 27.8 (CH), 29.7 (CH_2), 36.8 (CH_2), 37.1 (C), 38.0 (CH_2), 44.8 (CH), 47.7 (C), 52.0 (CH_3,), 121.7 (CH), 126.2 (CH), 131.8 (C), 133.3 (C), 138.8 (C), 147.6 (C), 169.0 (C), 179.2 (C). IR (KBr): 3267, 2931, 2868, 1724, 1658, 1521, 1433, 1244, 1134, 752 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{34}O_3N$ ($M+H^+$) 372.2539, found: 372.2538.

Treatment of (1R,4aS,10aR)-methyl 6-acetamido-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (43) with dichloromethyl methyl ether and aluminium chloride. Obtention of compounds 44, 45 and 46.



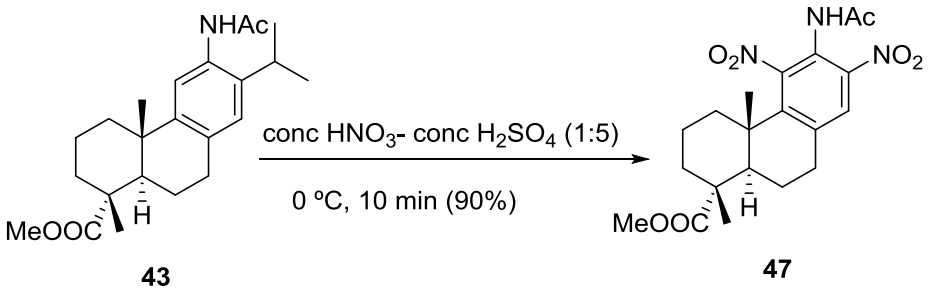
To a solution of acetamide **43** (148 mg, 0.4 mmol) in anhydrous dichloromethane (10 mL) cooled to -35 °C and under argon atmosphere, dichloromethyl methyl ether (0.106 ml, 1.2 mmol) was added. To this vigorously stirred mixture, aluminum chloride (0.162 g, 1.2 mmol) was slowly added. The reaction mixture was stirred at -35 °C for 20 min. Then, the mixture was slowly poured into ice-cold 10% aqueous HCl and extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with water (3 x 15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5% AcOEt/hexane) to yield a 5:3 mixture of epimers *trans/cis* 10β-methyl-12-acetamido ester **45** and 10α-methyl-12-acetamido ester **46** (30 mg, 21%) as a colorless syrup, compound **44** (34 mg, 23%) as a white solid, the starting material **43** (63 mg, 43%) and a mixture of unidentified deisopropylation compounds (0.016 g).

*(1R,4aS,10aR)-methyl 6-acetamido-7-formyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**45**) and (1R,4aR,10aR)-methyl 6-acetamido-7-formyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**46**).* ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm): Common signals: 1.36 – 1.95 (m, 7H), 2.37 (d, *J* = 3.6 Hz, 1H), 2.42 (m, 1H), 2.85 – 2.94 (m, 2H); signals asignable to *trans*-epimer **45** (major epimer): 1.24 (s, 3H), 1.29 (s, 3H), 2.22 (s, 3H), 3.68 (s, 3H), 7.30 (s, 1H), 8.70 (s, 1H), 9.81 (s, 1H), 10.94 (s, 1H); signals assignable to *cis*-epimer **46** (minor epimer): 1.24 (s, 3H), 1.25 (s, 3H), 2.22 (s, 3H), 3.69 (s, 3H), 7.30 (s, 1H), 8.73 (s, 1H), 9.82 (s, 1H), 10.94 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ (ppm): Common signals: 16.7 (CH_3), 24.6 (CH_3), 37.8 (CH_2), 47.8 (C), 138.9 (C), 158.8 (C), 169.6 (C); signals assignable to *trans*-epimer **45** (major epimer): 18.5 (CH_2), 21.5 (CH_2), 25.6 (CH_3), 29.2 (CH_2), 36.8 (CH_2), 38.5 (C), 44.5 (CH), 52.2 (CH_3), 116.1 (CH), 120.0 (C), 130.2 (C), 137.0 (CH), 179.0 (C), 195.2 (CH); signals assignable to *cis*-epimer **46** (minor epimer) 19.6 (CH_2), 20.1 (CH_2), 25.5 (CH_3), 29.8 (CH_2), 36.5 (CH_2), 39.8 (C), 45.7 (CH), 51.9 (CH_3), 117.8 (CH), 119.9 (C), 131.4 (C), 136.4 (CH), 179.4 (C), 195.1 (CH). IR (film): 3303, 2927, 2854, 1727, 1699, 1667, 1583, 1517, 1244, 772 cm^{-1}.

*(1R,4aR,10aR)-methyl 6-acetamido-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**44**).* mp 66−68 °C. $[\alpha]_D^{25}$= + 52.0 (c 1.3, $CHCl_3$). ^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm) 1.18 (dd, *J* = 9.3, 6.8 Hz, 6H), 1.23 (s, 3H), 1.27 (s, 3H), 1.39 – 1.52 (m, 2H), 1.52 – 1.91 (m, 5H), 2.15 (s, 3H), 2.20 (d, *J* = 2.1 Hz, 1H), 2.29 (m, 1H), 2.68 – 2.92 (m, 2H), 3.09 (hept, *J* = 6.9 Hz, 1H), 3.67

(s, 3H), 7.09 (s, 1H), 7.13 (s, 1H), 7.37 (s, 1H). ^{13}C NMR (100 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.8 (CH_2), 21.8 (CH_2), 23.3 (CH_3), 23.7 (CH_3), 24.8 (CH_3), 25.3 (CH_3), 26.6 (CH_2), 28.5 (CH), 36.7 (CH_2), 37.9 (C), 38.6 (CH_2), 44.4 (CH), 47.8 (C), 52.1 (CH_3), 114.1 (CH), 114.5 (CH), 128.2 (C), 136.0 (C), 147.7 (C), 150.6 (C), 168.2 (C), 179.3 (C). IR (KBr): 3300, 2927, 2869, 1726, 1662, 1600, 1542, 1465, 1413, 1246, 1134, 1112, 756 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{34}O_3N$ ($M+H^+$) 372.2539, found: 372.2536.

Treatment of (1R,4aS,10aR)-methyl 6-acetamido-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (43) with conc. HNO_3 and conc. H_2SO_4. Obtention of compound 47.



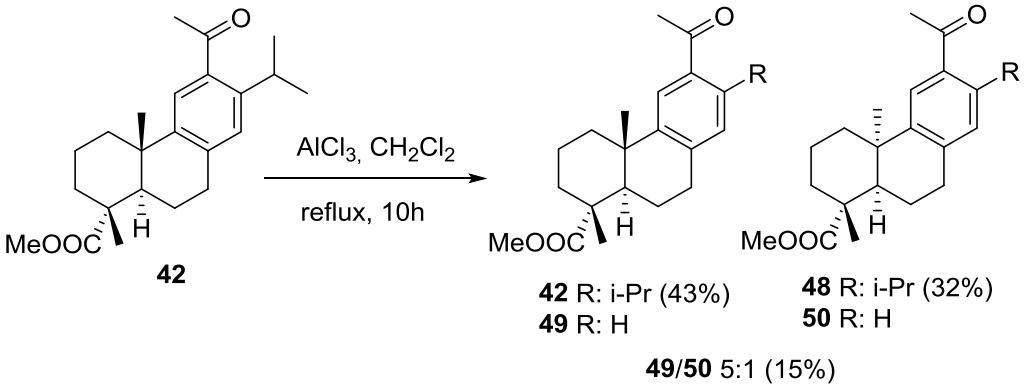
43 **47**

To a solution of acetamide **43** (104 mg, 0.32 mmol) in conc. H_2SO_4 (2 mL) cooled to 0 °C and under argon atmosphere, a mixture of conc. H_2SO_4/conc. HNO_3 (1:1, 1 mL) was added drop by drop. The reaction mixture was stirred at 0 °C for 10 min., at which time TLC showed no starting material. Then, the mixture was poured into ice and extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with water (3 x 15 mL) and brine (15 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (20% AcOEt/hexane) to yield compound **47** (120 mg, 90 %) as a light yellow solid.

*(1R,4aS,10aR)-methyl 6-acetamido-1,4a-dimethyl-5,7-dinitro-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**47**).* mp 241−243 °C. $[\alpha]_D^{25}$ = + 196.9 (c 1.0, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.24 (s, 3H), 1.27 (s, 3H), 1.49 – 1.56 (m, 2H), 1.65 – 1.85 (m, 5H), 2.17 (dd, *J* = 12.6, 2.3 Hz, 1H), 2.26 (s, 3H), 2.34 (m, 1H), 2.73 – 2.88 (m, 2H), 3.68 (s, 3H), 8.66 (s, 1H), 9.28 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.4 (CH_2), 20.2 (CH_2), 24.5 (CH_2), 24.7 (CH_3), 25.4 (CH_3), 36.4

(CH_2), 37.9 (CH_2), 38.9 (C), 43.4 (CH), 47.5 (C), 52.4 (CH_3), 121.0 (CH), 124.5 (C), 129.3 (C), 131.8 (C), 145.2 (C), 158.8 (C), 169.1 (C), 178.4 (C). IR (KBr): 3294, 2948, 1720, 1545, 1473, 1366, 1349, 1250, 1135, 753 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{26}O_7N_3$ ($M+H^+$) 420.1771, found: 420.1767.

Treatment of methyl 12-acetyl-8,11,13-abietatrien-18-oate (42) with aluminium chloride. Obtention of compounds 48, 49 and 50.



To a solution of methyl 12-acetyl-8,11,13-abietatrien-18-oate (**42**) (0.315 g, 0.88 mmol) in anhydrous dichloromethane (15 mL) cooled to 0 °C and under argon atmosphere, aluminium chloride (0.359 g, 2.65 mmol) was slowly added. The reaction was heated under reflux for 10 h. Then, the mixture was slowly poured into ice-cold 10% aqueous HCl and extracted with ethyl acetate (2 x 50 mL). The combined organic layers were washed with water (3 x 40 mL) and brine (40 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (5% AcOEt/hexane) to yield the starting material **42** (135 mg, 43%), its epimer **48** (100 mg, 32%), and a mixture of epimers 10β-methyl-12-acetyl ester **49** and 10α-methyl-12-acetyl ester **50** (41 mg, 15%) (ratio 5:1), all of them as a yellow syrup.

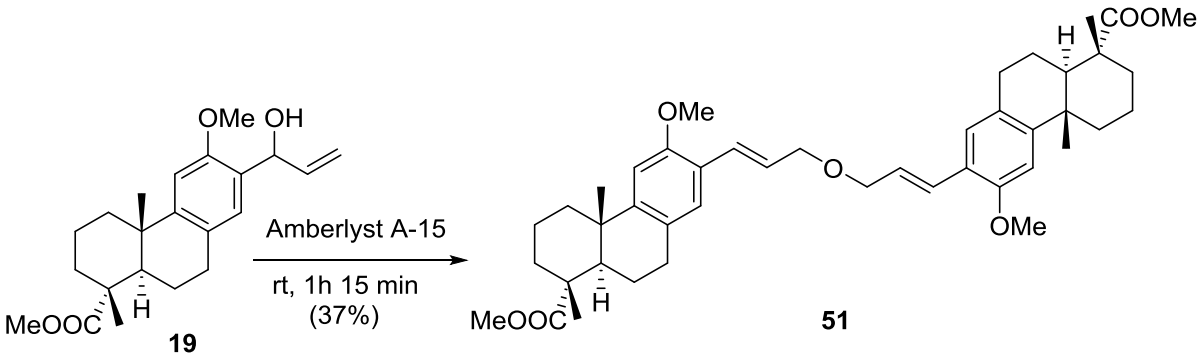
*(1R,4aR,10aR)-methyl 6-acetyl-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**48**).* $[\alpha]_D^{25}$ = + 4.4 (c 1.2, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.11 (s, 3H), 1.20 (d, *J* = 6.8 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H), 1.22 (s, 3H), 1.47 – 1.65 (m, 3H), 1.70 – 1.89 (m, 2H), 2.00 – 2.07 (m, 3H), 2.34 (dd, *J* = 11.3, 3.2 Hz, 1H), 2.54 (s, 3H), 2.82 – 2.88 (m, 2H), 3.46 (hept, *J* = 6.8 Hz, 1H), 3.68 (s, 3H), 7.04 (s, 1H), 7.41 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 19.8 (CH_2), 20.0 (CH_2), 24.2 (CH_3), 24.3 (CH_3), 24.3 (CH_3), 27.7 (CH), 28.8 (CH_3), 30.6 (CH_3), 30.8 (CH_2), 31.8 (CH_2),

37.0 (CH_2), 38.5 (C), 45.0 (C), 46.0 (CH), 51.8 (CH_3), 126.6 (CH), 126.8 (CH), 136.7 (C), 139.7 (C), 143.7 (C), 144.9 (C), 179.6 (C), 203.4 (C). IR (film): 2935, 2872, 1725, 1682, 1462, 1258, 1192, 1136, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{33}O_3$ ($M+H^+$) 357.2430, found: 357.2441.

*(1R,4aS,10aR)-methyl 6-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**49**).* $[\alpha]_D^{25}$ = + 53.5 (c 1.3, $CHCl_3$). ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.29 (s, 3H), 1.42 – 1.56 (m, 2H), 1.62 – 1.70 (m, 2H), 1.72 – 1.90 (m, 3H), 2.21 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.42 (m, 1H), 2.56 (s, 3H), 2.89 – 2.98 (m, 2H), 3.67 (s, 3H), 7.11 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.65 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.89 (d, *J* = 1.8 Hz, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.6 (CH_2), 21.4 (CH_2), 25.2 (CH_3), 26.7 (CH_3), 30.2 (CH_2), 36.8 (CH_2), 37.5 (C), 38.0 (CH_2), 44.8 (CH), 47.7 (C), 52.1 (CH_3), 124.5 (CH), 125.7 (CH), 129.5 (CH), 135.2 (C), 141.4 (C), 150.0 (C), 179.1 (C), 198.3 (C). IR (film): 2931, 1723, 1680, 1431, 1356, 1246, 1222, 1176, 1128, 1109 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{20}H_{27}O_3$ ($M+H^+$) 315.1960, found: 315.1969.

*(1R,4aS,10aR)-methyl 6-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**49**) and (1R,4aR,10aR)-methyl 6-acetyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**50**).* ^{1}H NMR (500 MHz, chloroform-*d*) δ (ppm): Common signals to epimers **49** and **50**: 1.43 – 1.70 (m, 8H), 1.71 – 1.91 (m, 6H), 2.21 (dd, *J* = 12.6, 2.3 Hz, 2H), 2.88 – 2.98 (m, 4H), 7.09 – 7.13 (m, 2H), 7.65 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.89 (d, *J* = 1.8 Hz, 2H); signals assignable to epimer **50**: 1.06 (s, 3H), 1.24 (s, 3H), 2.36 (m, 1H), 2.57 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm): Common signals to epimers **49** and **50**: 16.7 (CH_3), 18.6 (CH_2), 21.4 (CH_2), 25.2 (CH_3), 26.7 (CH_3), 30.2 (CH_2), 36.8 (CH_2), 37.5 (C), 38.0 (CH_2), 44.8 (CH), 47.7 (C), 52.1 (CH_3), 124.5 (CH), 125.7 (CH), 129.5 (CH), 135.2 (C), 141.4 (C), 150.0 (C), 179.1 (C), 198.3 (C) ; signals assignable to epimer **50**: 19.7 (CH_2), 19.9 (CH_2), 36.9 (CH_2), 45.8 (CH), 51.9 (CH_3), 125.6 (CH), 129.1 (CH), 135.4 (C), 142.3 (C), 179.5 (C), 198.2 (C).

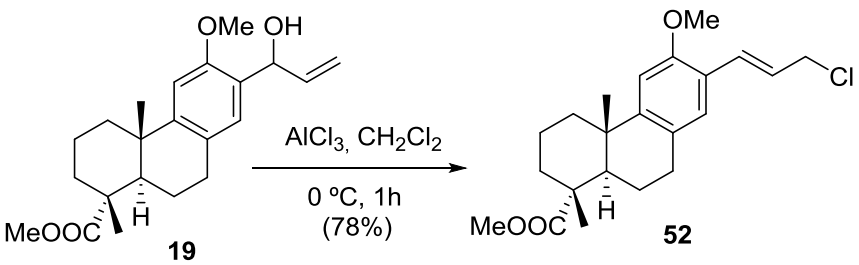
Treatment of alcohol 19 with Amberlyst A-15. Obtention of compound 51.



To a solution of **19** (43 mg, 0.12 mmol) in anhydrous dichloromethane (3 mL) was added Amberlyst A-15 ion-exchange (50 mg) and the reaction mixture was stirred at room temperature for 1h 15 min. Filtration and concentration gave 31 mg of **51** (37%) as a colorless syrup.

*(1R,1'R,4aS,4a'S,10aR,10a'R)-dimethyl 7,7'-((1E,1'E)-oxybis(prop-1-ene-3,1-diyl))bis(6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate) (**51**).* $[\alpha]_D^{25}$ = + 56.9 (c 0.8, $CHCl_3$). ^1H NMR (400 MHz, chloroform-d) δ (ppm) 1.26 (s, 3H), 1.28 (s, 3H), 1.52 (m, 1H), 1.64 (m, 1H), 1.68 – 1.89 (m, 5H), 2.22 (dd, *J* = 12.4, 2.2 Hz, 1H), 2.27 (m, 1H), 2.78 – 2.85 (m, 2H), 3.67 (s, 3H), 3.81 (s, 3H), 4.13 (d, 2H), 6.26 (dt, *J* = 16.0, 6.3 Hz, 1H), 6.73 (s, 1H), 6.83 (d, *J* = 16.0 Hz, 1H), 7.11 (s, 1H). ^{13}C NMR (100 MHz, chloroform-d) δ (ppm) 16.7 (CH_3), 18.7 (CH_2), 21.9 (CH_2), 25.1 (CH_3), 29.3 (CH_2), 36.7 (CH_2), 37.7 (C), 38.2 (CH_2), 45.0 (CH), 47.8 (C), 52.1 (CH_3), 55.8 (CH_3), 72.0 (CH_2), 106.9 (CH), 123.7 (C), 126.5 (CH), 127.2 (C), 127.3 (CH), 127.6 (CH), 150.2 (C), 155.2 (C), 179.2 (C). IR (film): 2926, 2854, 1726, 1497, 1463, 1247, 1133, 1105, 1041, 972, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{44}H_{59}O_7$ ($M+H^+$) 699.4261, found: 699.4233.

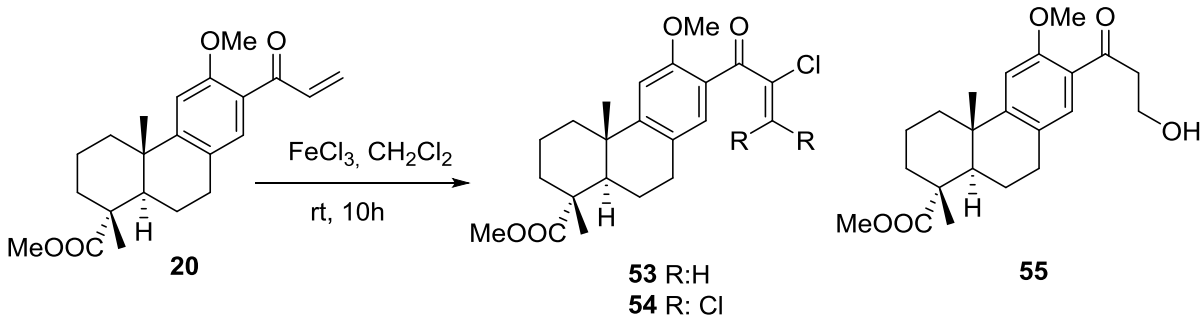
Treatment of alcohol 19 with aluminum chloride. Obtention of compound 52.



To a solution of compound **19** (118 mg, 0.33 mmol) in anhydrous dichloromethane (6 mL), cooled to 0 °C and under argon atmosphere, aluminum chloride (44 mg, 0.33 mmol) was added. The reaction mixture was stirred at 0 °C for 1 h. Then, the reaction was poured into ice and extracted with ethyl acetate (15 mL), washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel (5% AcOEt/hexane), affording compound **52** (97 mg, 78%) as a colorless syrup.

*(1R,4aS,10aR)-methyl 7-((Z)-3-chloroprop-1-en-1-yl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**52**).* $[\alpha]_D^{25}$ = + 54.4 (c 1.3, $CHCl_3$). ^{1}H NMR (400 MHz, chloroform-d) δ (ppm) 1.22 (s, 3H), 1.28 (s, 3H), 1.38 – 1.46 (m, 1H), 1.48 – 1.57 (m, 1H), 1.63 – 1.85 (m, 5H), 2.21 (dd, *J* = 12.5, 2.2 Hz, 1H), 2.24 – 2.30 (m, 1H), 2.78 – 2.86 (m, 2H), 3.67 (s, 3H), 3.82 (s, 3H), 4.24 (dd, *J* = 7.3, 1.1 Hz, 2H), 6.30 (dt, *J* = 15.7, 7. Hz, 1H), 6.74 (s, 1H), 6.89 (d, *J* = 16.1 Hz, 1H), 7.09 (s, 1H). ^{13}C NMR (100 MHz, chloroform-d) δ (ppm) 16.7 (CH_3), 18.7 (CH_2), 21.8 (CH_2), 25.0 (CH_3), 29.2 (CH_2), 36.7 (CH_2), 37.7 (C), 38.1 (CH_2), 44.9 (CH), 46.5 (CH_2), 47.8 (C), 52.1 (CH_3), 55.7 (CH_3), 106.9 (CH), 122.7 (C), 125.0 (CH), 127.3 (C), 127.9 (CH), 129.2 (CH), 150.9 (C), 155.4 (C), 179.1 (C). IR (film): 2930, 1722, 1496, 1462, 1244, 1133, 1040, 851, 755 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{30}O_3Cl$ ($M+H^+$) 377.1883, found: 377.1866.

Treatment of enone 20 with ferric chloride. Obtention of compounds 53, 54 and 55.



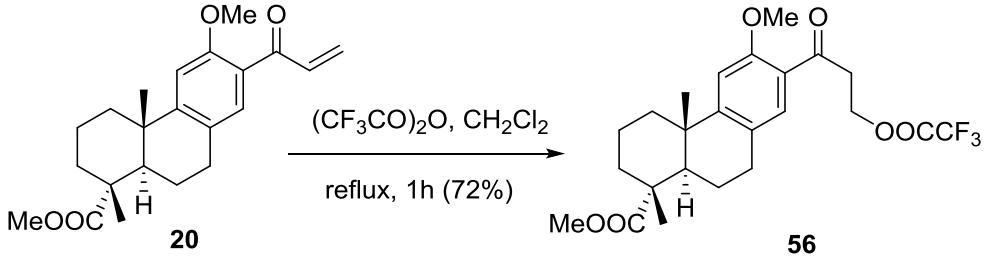
To a solution of enone **20** (31 mg, 0.087 mmol) in anhydrous dichloromethane (3 mL) was added ferric chloride (16 mg, 0.1 mmol) at room temperature and under argon atmosphere. The reaction mixture was stirred for 10 h. Then, the reaction was quenched with water (1 mL) in a cold-water bath and the mixture was extracted with ethyl acetate (15 mL), washed with water (5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel (5% AcOEt/hexane), affording hydroxyketone **55** (16 mg, 49%) as a white solid, and an unresolvable mixture 1:1 of compounds **53** and **54** (10 mg) as a colorless syrup.

*(1R,4aS,10aR)-methyl 7-(3-hydroxypropanoyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**55**).* mp 80−82 °C. $[\alpha]_D^{25}$ = + 24.8 (c 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-*d*) δ (ppm) 1.22 (s, 3H), 1.28 (s, 3H), 1.38 – 1.87 (m, 7H), 2.19 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.28 (m, 1H), 2.87 – 2.79 (m, 2H), 3.27 (t, *J* = 7.0 Hz, 2H), 3.67 (s, 3H), 3.79 (t, *J* = 6.9 Hz, 2H), 3.86 (s, 3H), 6.80 (s, 1H), 7.41 (s, 1H). ^{13}C NMR (125 MHz, chloroform-*d*) δ (ppm) 16.7 (CH_3), 18.7 (CH_2), 21.7 (CH_2), 24.9 (CH_3), 29.0 (CH_2), 29.9 (CH_2), 36.7 (CH_2), 38.0 (CH_2), 38.0 (C), 44.2 (CH_2), 44.7 (CH), 47.8 (C), 52.2 (CH_3), 55.6 (CH_3), 107.4 (CH), 125.8 (C), 127.5 (C), 131.2 (C), 155.6 (C), 157.2 (C), 179.0 (C), 200.0 (C). IR (KBr): 2925, 2854, 1727, 1671, 1607, 1494, 1464, 1405, 1247, 1133, 1110, 1037, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{22}H_{31}O_5$ ($M+H^+$) 375.2171, found: 375.2169.

*(1R,4aS,10aR)-methyl 7-(2-chloroacryloyl)-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**53**) and (1R,4aS,10aR)-methyl 6-methoxy-1,4a-dimethyl-7-(2,3,3-trichloroacryloyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**54**).* ^{1}H NMR (500 MHz, Chloroform-d) δ (ppm) δ 1.21 (s, 3H), 1.22 (s, 3H), 1.28 (s, 6H), 1.38 – 1.45 (m, 2H), 1.47 – 1.58 (m, 2H), 1.63 – 1.87 (m, 10H), 2.20 (dt, *J* = 12.5, 2.4 Hz, 2H), 2.24 – 2.32 (m, 2H), 2.77 – 2.87 (m, 2H), 3.18 (td, *J* = 7.1, 1.4 Hz, 2H), 3.67 (s, 6H), 3.70 (s, 3H), 3.85 (s, 3H), 5.63 (d, *J* = 0.9 Hz, 1H), 5.86 (d, *J* = 1.3 Hz, 1H), 6.76 (s, 1H), 6.80 (s, 1H), 6.90 (s, 1H), 7.39 (s, 1H). ^{13}C NMR (125 MHz, chloroform-d) δ (ppm) 16.70 (CH_3), 16.73 (CH_3), 18.66 (CH_2), 18.67 (CH_2), 21.73 (CH_2), 21.75 (CH_2), 24.94 (CH_3), 25.02 (CH_3), 26.10 (CH_2), 28.96 (CH_2), 29.11 (CH_2), 36.67 (CH_2), 36.71 (CH_2), 37.88 (C), 38.02 (C), 38.04 (CH_2), 38.08 (CH_2), 42.36 (CH_2), 44.69 (CH), 44.80 (CH), 47.80 (C), 47.80 (C), 52.15 (CH_3), 52.17 (CH_3), 55.63 (CH_3), 55.96 (CH_3), 107.43 (CH), 107.58 (CH), 126.06 (C), 127.02 (C), 127.20 (C), 127.45 (C), 127.86 (CH_2),

129.94 (CH), 131.12 (CH), 149.10 (C), 153.01 (C), 155.28 (C), 155.64 (C), 157.05 (C), 179.01 (C), 179.01 (C), 198.55 (C), 201.4 (C).

Treatment of enone 20 with trifluoroacetic anhydride. Obtention of compound 56.

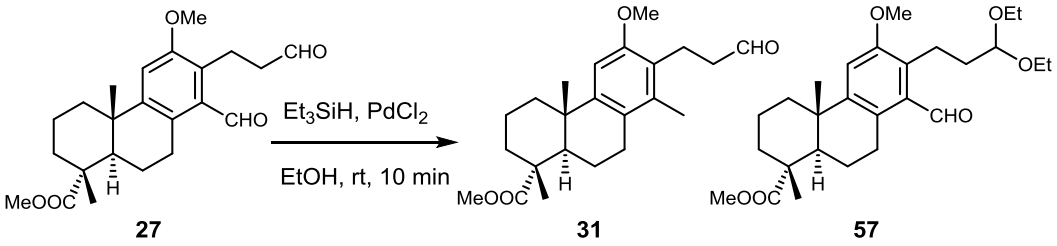


To a solution of enone **20** (40 mg, 0.11 mmol) in anhydrous dichloromethane (3 mL) and under argon atmosphere, trifluoroacetic anhydride was added. The reaction mixture was stirred at reflux for 1 h. Then, the reaction was poured into ice and extracted with ethyl acetate (15 mL), washed with water (5 x 5 mL) and brine (5 mL) and dried over anhydrous Na_2SO_4. The solvent was evaporated to give a crude product which was purified by flash chromatography on silica gel (5% AcOEt/hexane), affording compound **56** (37 mg, 72%) as a colorless syrup.

*(1R,4aS,10aR)-methyl 6-methoxy-1,4a-dimethyl-7-(3-(2,2,2-trifluoroacetoxy)propanoyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**56**).* $[\alpha]_D^{25}$ = + 45.0 (c = 1.1, $CHCl_3$).^{1}H NMR (400 MHz, chloroform-*d*) δ (ppm) 1.23 (s, 3H), 1.28 (s, 3H), 1.36 – 1.49 (m, 1H), 1.49 – 1.59 (m, 1H), 1.62 – 1.87 (m, 5H), 2.19 (dd, *J* = 12.5, 2.3 Hz, 1H), 2.23 – 2.34 (m, 1H), 2.77 – 2.91 (m, 2H), 3.42 (td, *J* = 6.4, 2.4 Hz, 2H), 3.67 (s, 3H), 3.89 (s, 3H), 4.74 (t, *J* = 6.4 Hz, 2H), 6.83 (s, 1H), 7.48 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.7 (CH_3), 18.6 (CH_2), 21.6 (CH_2), 24.9 (CH_3), 28.9 (CH_2), 36.6 (CH_2), 38.0 (CH_2), 38.1 (C), 42.0 (CH_2), 44.6 (CH), 47.8 (C), 52.2 (CH_3), 55.6 (CH_3), 63.8 (CH_2), 107.4 (CH), 124.5 (C), 127.9 (C), 127.9 (C), 131.4 (CH), 156.6 (C), 157.5 (C), 178.9 (C), 196.8 (C). IR (film): 2934, 1786, 1725, 1672, 1607, 1494, 1407, 1247, 1219, 1151, 1037, 774 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{24}H_{30}O_6F_3$ ($M+H^+$) 471.1994, found: 471.1998.

Treatment of dialdehyde 27 with Et_3SiH and $Pd(Cl)_2$.

Assay 1. Obtention of compounds 31 and 57.



27 **31** **57**

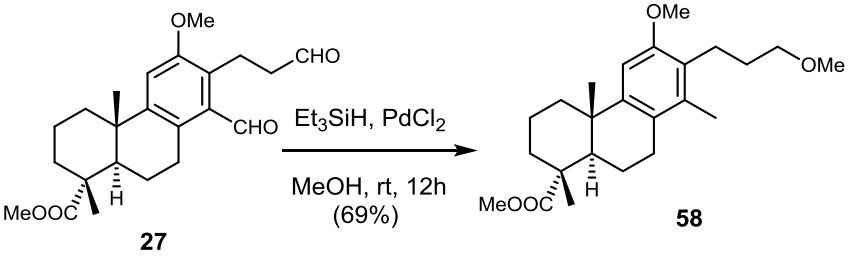
To a solution of dialdehyde **27** (28 mg, 0.072 mmol) in dry absolute ethanol (2 mL) and under argon atmosphere, was added Et_3SiH (0.025 mL, 0.145 mmol) and $PdCl_2$ (1.3 mg, 0.0073 mmol). The reaction mixture was stirred at room temperature for 10 min. Then the crude was filtered by cotton, washed with ethyl acetate (10 mL) and concentrated in vacuo to give a crude product which was purified by flash chromatography (5% AcOEt/hexane) to obtain compound **57** (22 mg, 66%) and aldehyde **31** (6 mg, 22%) both of them as a colorless syrup.

*(1R,4aS,10aR)-methyl 7-(3,3-diethoxypropyl)-8-formyl-6-methoxy-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**57**).* $[\alpha]_D^{25}$ = + 50.1 (c 0.9, $CHCl_3$). ^{1}H NMR (500 MHz, Chloroform-d) δ (ppm) 1.20 (t, *J* = 7.0 Hz, 6H), 1.24 (s, 3H), 1.27 (s, 3H), 1.43 – 1.53 (m, 2H), 1.64 (m, 1H), 1.71 – 1.88 (m, 6H), 2.19 (dd, *J* = 12.6, 2.0 Hz, 1H), 2.28 (m, 1H), 2.85 – 2.92 (m, 2H), 2.97 – 3.13 (m, 2H), 3.46 – 3.53 (m, 4H), 3.67 (s, 3H), 3.81 (s, 3H), 4.55 (t, *J* = 5.7 Hz, 1H), 6.95 (s, 1H), 10.55 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ (ppm) 15.5 (CH_3), 16.6 (CH_3), 18.7 (CH_2), 20.6 (CH_2), 21.6 (CH_2), 25.1 (CH_3), 27.7 (CH_2), 34.2 (CH_2), 36.5 (CH_2), 37.9 (C), 38.6 (CH_2), 44.3 (CH), 47.6 (C), 52.2 (CH_3), 55.9 (CH_3), 60.7 (CH_2), 60.8 (CH_2), 102.6 (CH), 111.2 (CH), 128.4 (C), 131.2 (C), 134.0 (C), 149.1 (C), 156.0 (C), 179.0 (C), 195.4 (CH). IR (film): 2931, 1725, 1690, 1462, 1248, 1134, 1061, 1042, 772 cm^{-1}.

*(1R,4aS,10aR)-methyl 6-methoxy-1,4a,8-trimethyl-7-(3-oxopropyl)-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**31**).* $[\alpha]_D^{25}$ = + 51.0 (c 1.1, $CHCl_3$). ^{1}H NMR (400 MHz, Chloroform-d) δ (ppm) 1.24 (s, 3H), 1.28 (s, 3H), 1.48 (m, 1H), 1.64 (m, 1H), 1.70 – 1.86 (m, 5H), 2.12 (s, 3H), 2.21 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.29 (m, 1H), 2.52 – 2.75 (m, 5H), 2.90 – 3.06 (m, 2H), 3.67 (s, 3H), 3.78 (s, 3H), 6.67 (s, 1H), 9.80 (t, *J* = 1.9 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-d) δ (ppm) 15.2 (CH_3),

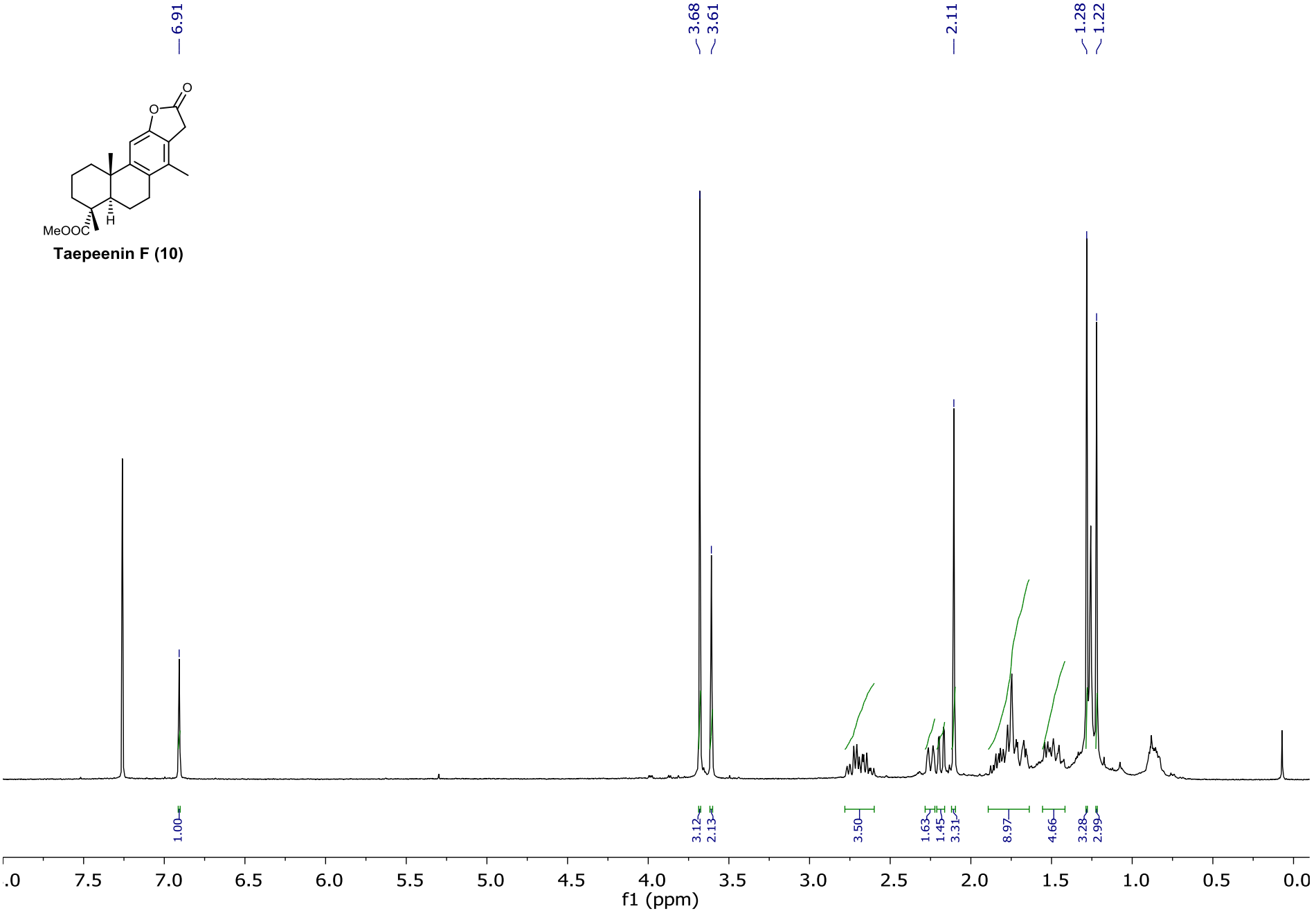
16.6 (CH_3), 18.8 (CH_2), 19.3 (CH_2), 22.0 (CH_2), 25.2 (CH_3), 28.3 (CH_2), 36.6 (CH_2), 37.7 (C), 38.6 (CH_2), 43.8 (CH_2), 44.5 (CH), 47.8 (C), 52.1 (CH_3), 55.4 (CH_3), 104.1 (CH), 124.8 (C), 126.1 (C), 135.5 (C), 148.5 (C), 155.6 (C), 179.2 (C), 203.0 (CH). IR (film): 2931, 1723, 1463, 1248, 1220, 1177, 1134, 1101, 1041, 772 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{23}H_{33}O_4$ ($M+H^+$) 373.2379, found: 373.2386.

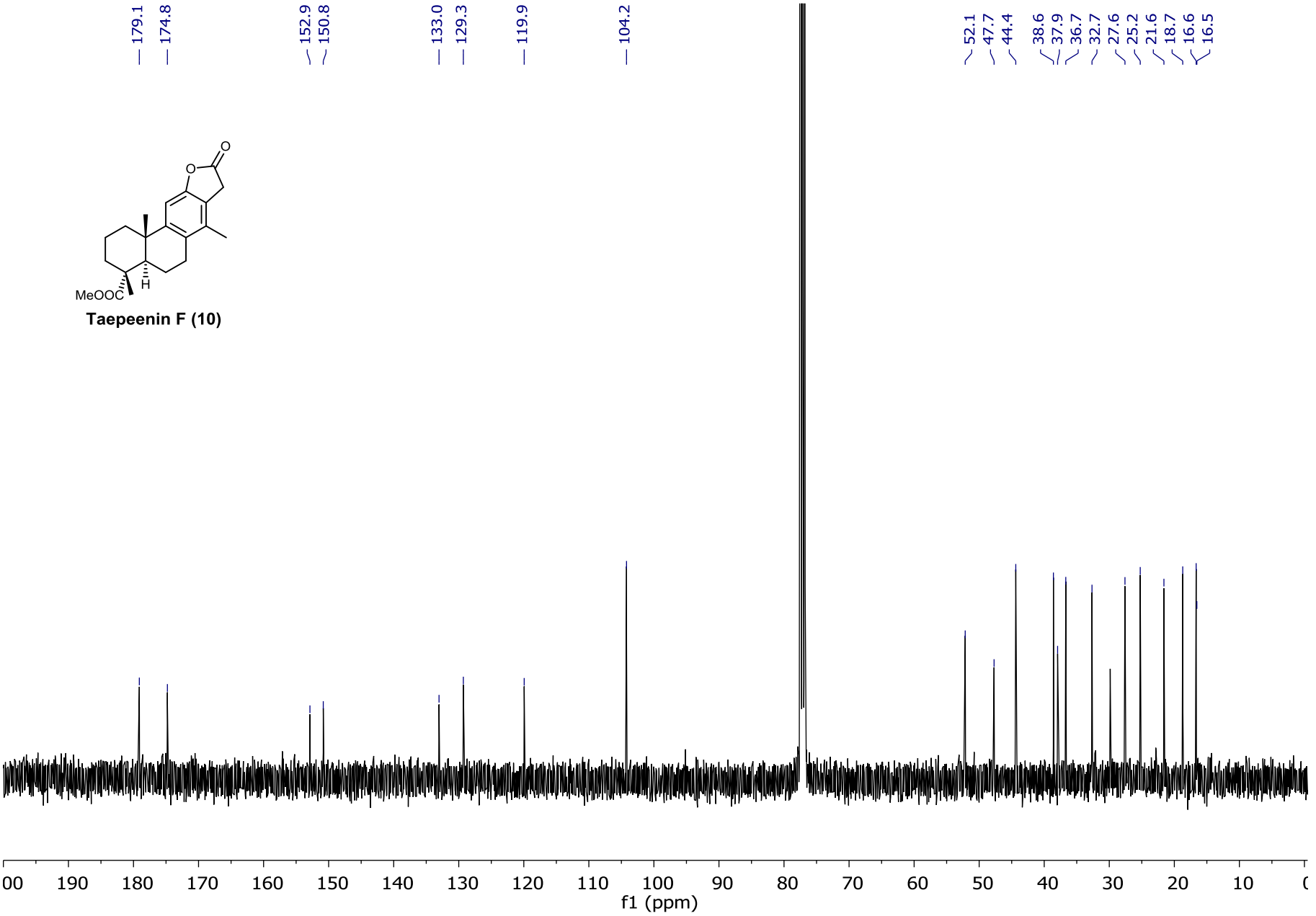
Assay 2. Obtention of compound 58.

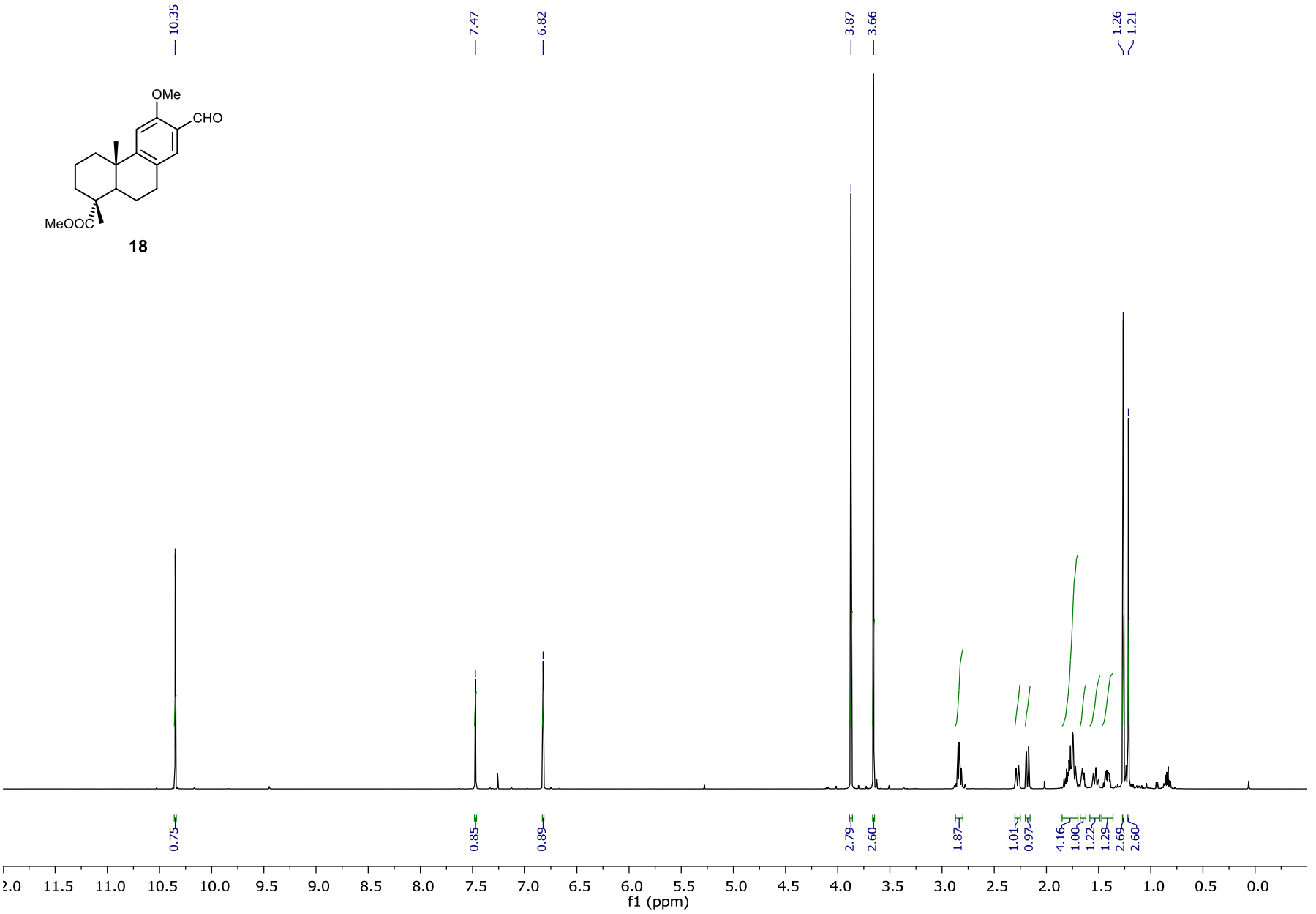


To a solution of dialdehyde **27** (36 mg, 0.093 mmol) in dry methanol (2 mL) and under argon atmosphere, was added Et_3SiH (0.03 mL, 0.186 mmol) and $PdCl_2$ (1.6 mg, 0.0093 mmol). The reaction mixture was stirred at room temperature for 12 h. Then the crude was filtered by cotton, washed with ethyl acetate (10 mL), concentrated in vacuo and purified by flash chromatography (5% AcOEt/hexane) to obtain compound **58** (25 mg, 69%) and aldehyde **27** (9 mg, 26%) both of them as a colorless syrup.

*(1R,4aS,10aR)-methyl 6-methoxy-7-(3-methoxypropyl)-1,4a,8-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (**58**).* $[\alpha]_D^{25}$ = + 36.9 (c 0.8, $CHCl_3$). ^1H NMR (500 MHz, Chloroform-d) δ (ppm) 1.24 (s, 3H), 1.27 (s, 3H), 1.44 – 1.58 (m, 4H), 1.70 – 1.86 (m, 5H), 2.13 (s, 3H), 2.22 (dd, *J* = 12.7, 2.1 Hz, 1H), 2.28 (m, 1H), 2.80 – 2.56 (m, 4H), 3.35 (s, 3H), 3.42 (t, *J* = 6.5 Hz, 2H), 3.67 (s, 3H), 3.78 (s, 3H), 6.67 (s, 1H). ^{13}C NMR (125 MHz, Chloroform-d) δ (ppm) 15.2 (CH_3), 16.6 (CH_3), 18.9 (CH_2), 22.1 (CH_2), 23.0 (CH_2), 25.2 (CH_3), 28.3 (CH_2), 29.7 (CH_2), 36.7 (CH_2), 37.6 (C), 38.6 (CH_2), 44.5 (CH), 47.8 (C), 52.1 (CH_3), 55.7 (CH_3), 58.6 (CH_3), 73.0 (CH_2), 104.2 (CH), 125.9 (C), 126.8 (C), 135.7 (C), 147.8 (C), 155.9 (C), 179.3 (C). IR (film): 2926, 2855, 1727, 1462, 1247, 1190, 1134, 1119 cm^{-1}. HRMS (ESI) m/z: calcd for $C_{24}H_{37}O_4$ ($M+H^+$) 389.2692, found: 389.2692.


6.91
3.68
3.61
2.11
1.28
1.22
MeOOC
H
O
O
Taepeenin F (10)
1.00
3.12
2.13
3.50
1.63
1.45
3.31
8.97
4.66
3.28
2.99
f1 (ppm)


179.1
174.8
152.9
150.8
133.0
129.3
119.9
104.2
52.1
47.7
44.4
38.6
37.9
36.7
32.7
27.6
25.2
21.6
18.7
16.6
16.5
O
O
H
MeOOC
Taepeenin F (10)
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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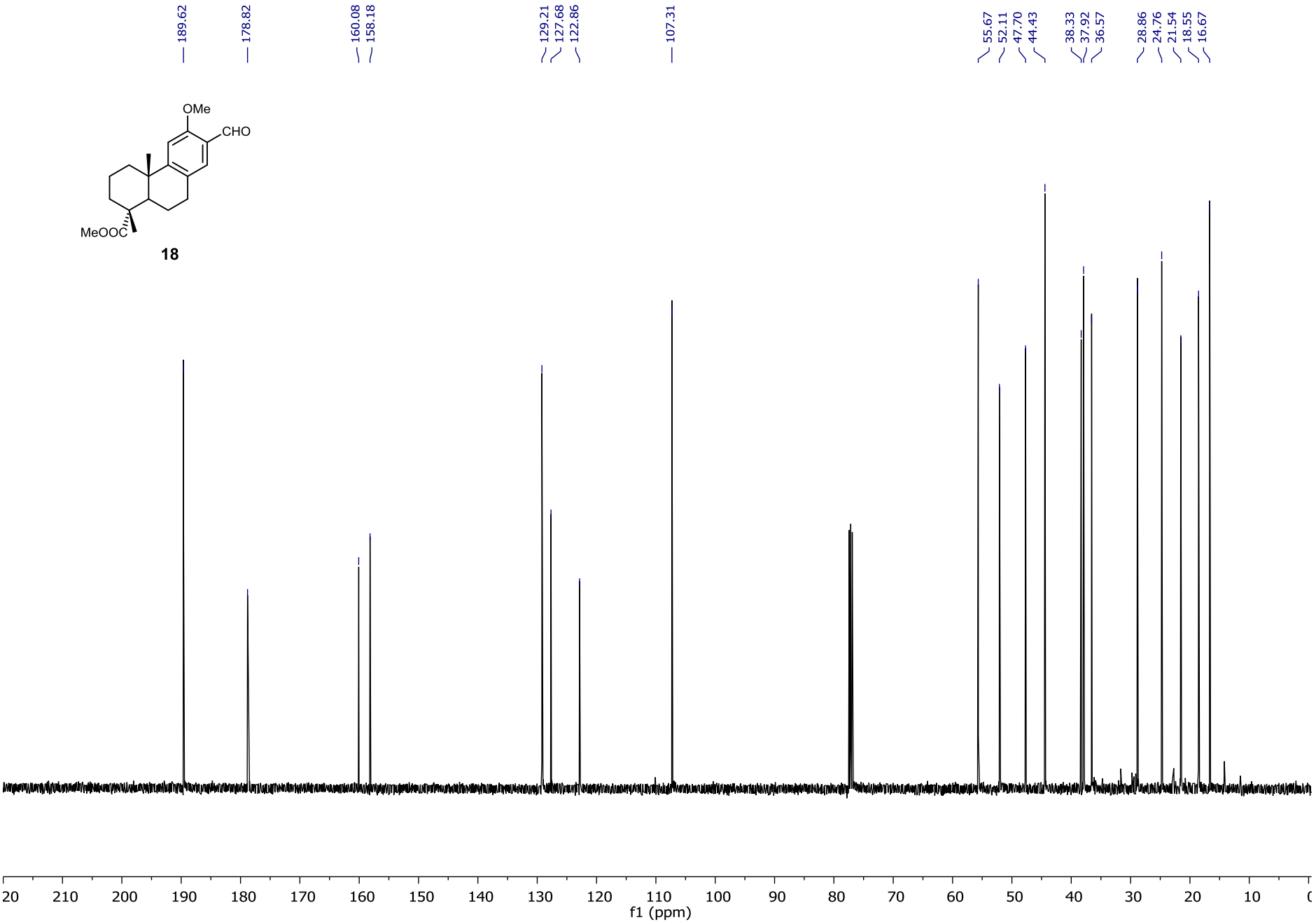
7.47
6.82
3.87
3.66
1.26
1.21
OMe
CHO
MeOOC
18
0.75
0.85
0.89
2.79
2.60
1.87
1.01
0.97
4.16
1.00
1.22
1.29
2.69
2.60
f1 (ppm)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178.82
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158.18
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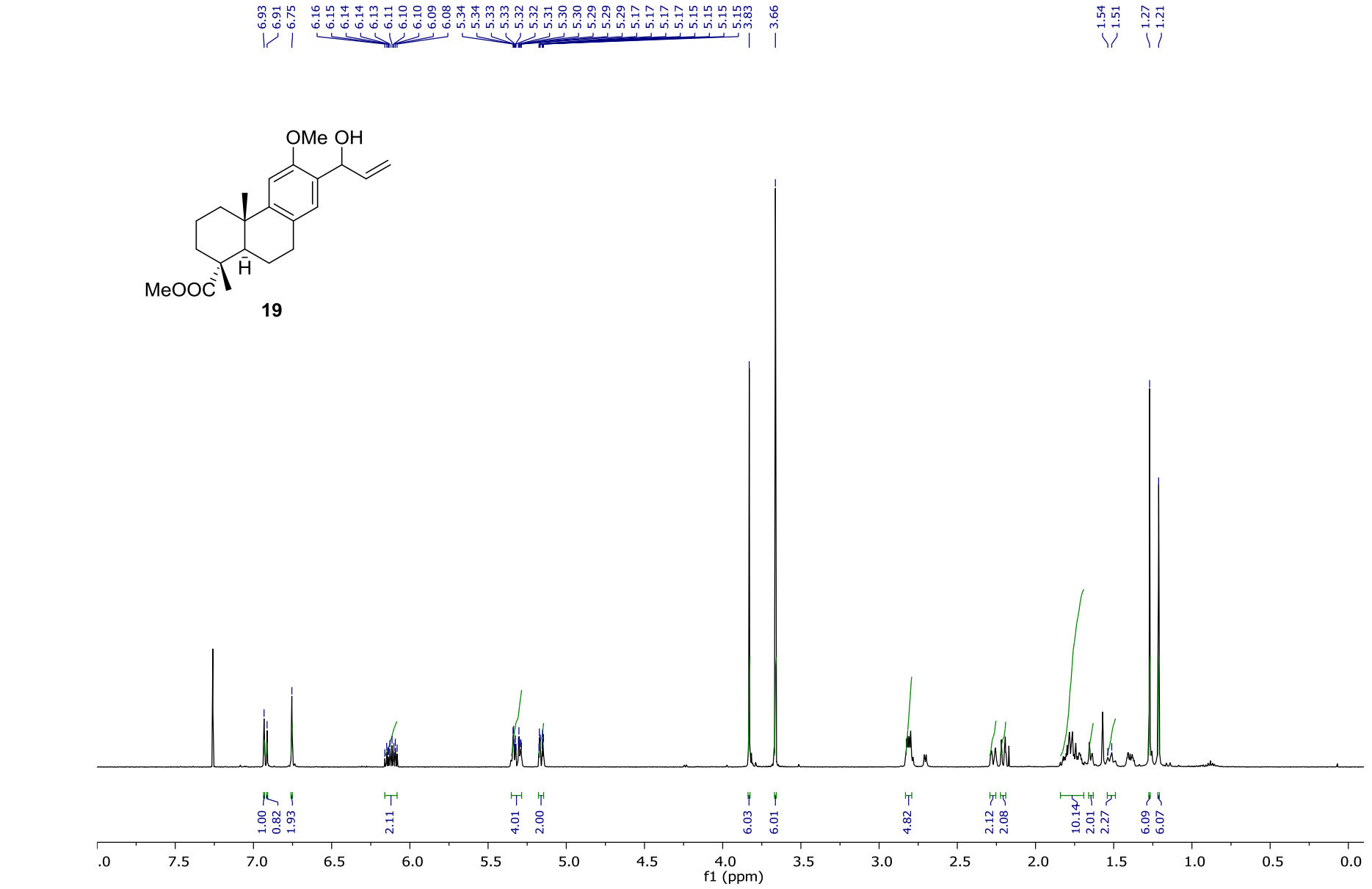
127.68
122.86
107.31
55.67
52.11
47.70
44.43
38.33
37.92
36.57
28.86
24.76
21.54
18.55
16.67
OMe
CHO
MeOOC
18
f1 (ppm)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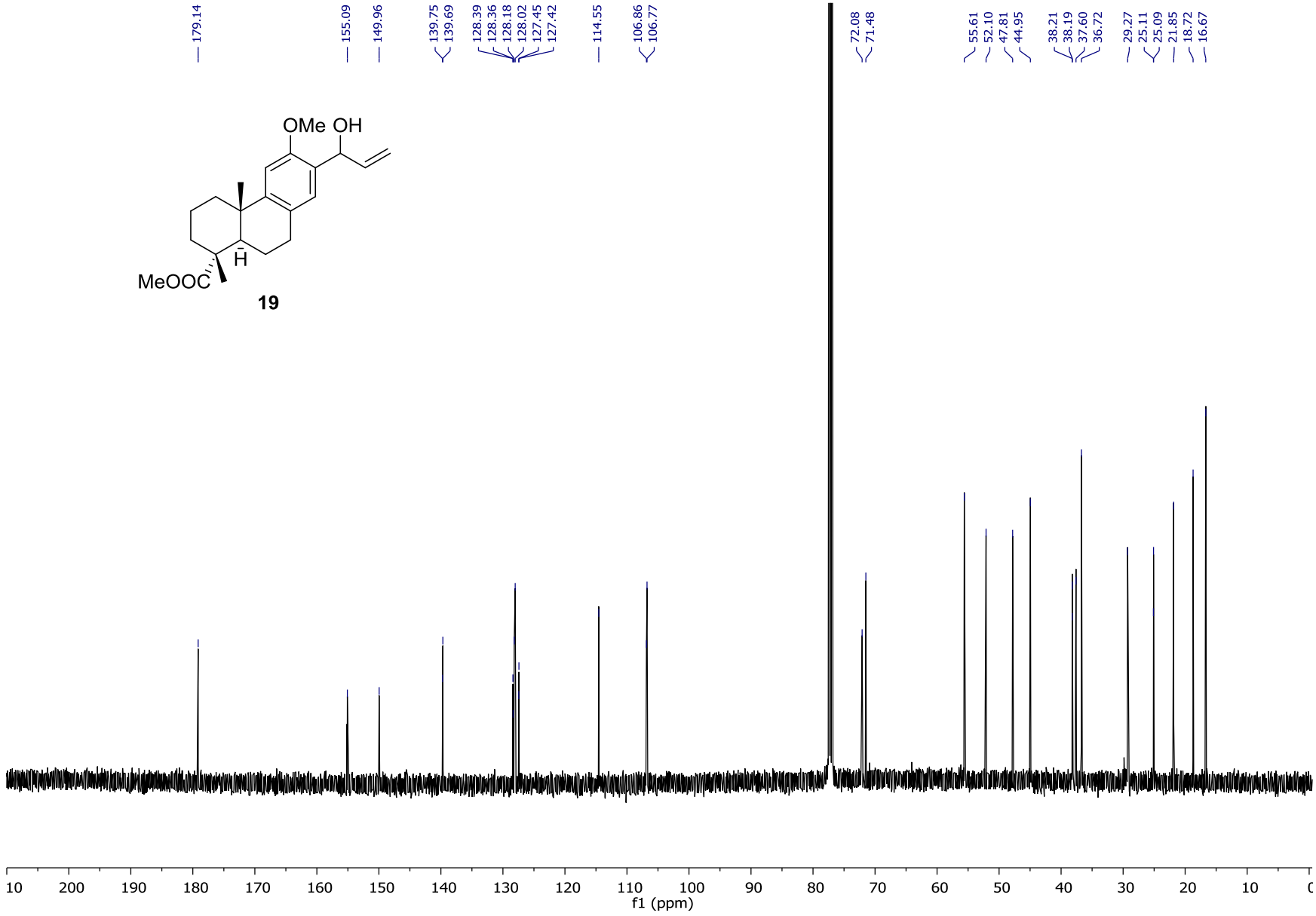
6.14
6.14
6.13
6.11
6.10
6.10
6.09
6.08
5.34
5.34
5.33
5.33
5.32
5.32
5.31
5.30
5.30
5.29
5.29
5.29
5.17
5.17
5.17
5.17
5.15
5.15
5.15
5.15
3.83
3.66
1.54
1.51
1.27
1.21
OMe OH
H
MeOOC
19
1.00
0.82
1.93
2.11
4.01
2.00
6.03
6.01
4.82
2.12
2.08
10.14
2.01
2.27
6.09
6.07
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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155.09
149.96
139.75
139.69
128.39
128.36
128.18
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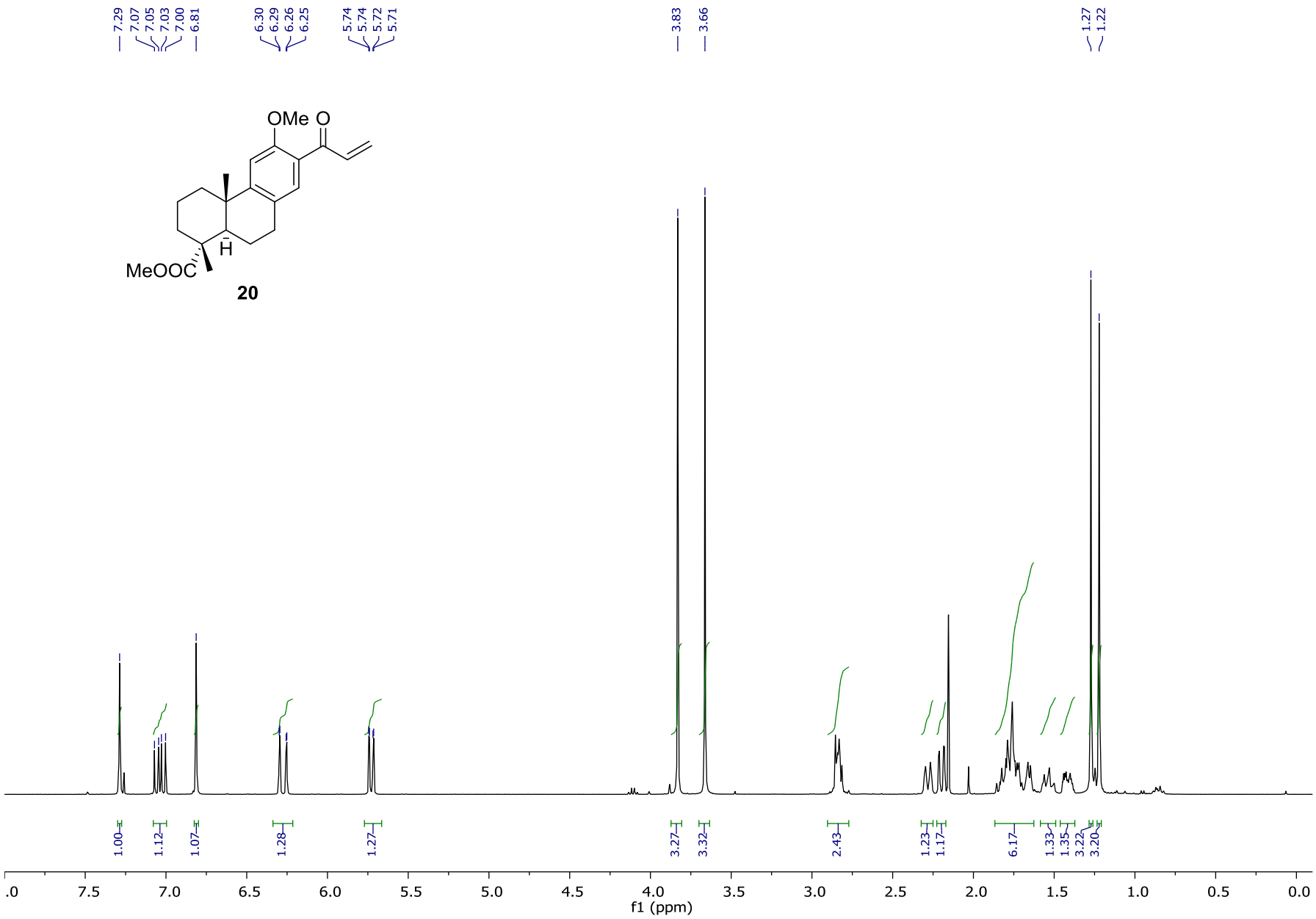
127.45
127.42
114.55
106.86
106.77
72.08
71.48
55.61
52.10
47.81
44.95
38.21
38.19
37.60
36.72
29.27
25.11
25.09
21.85
18.72
16.67
OMe OH
H
MeOOC
19
f1 (ppm)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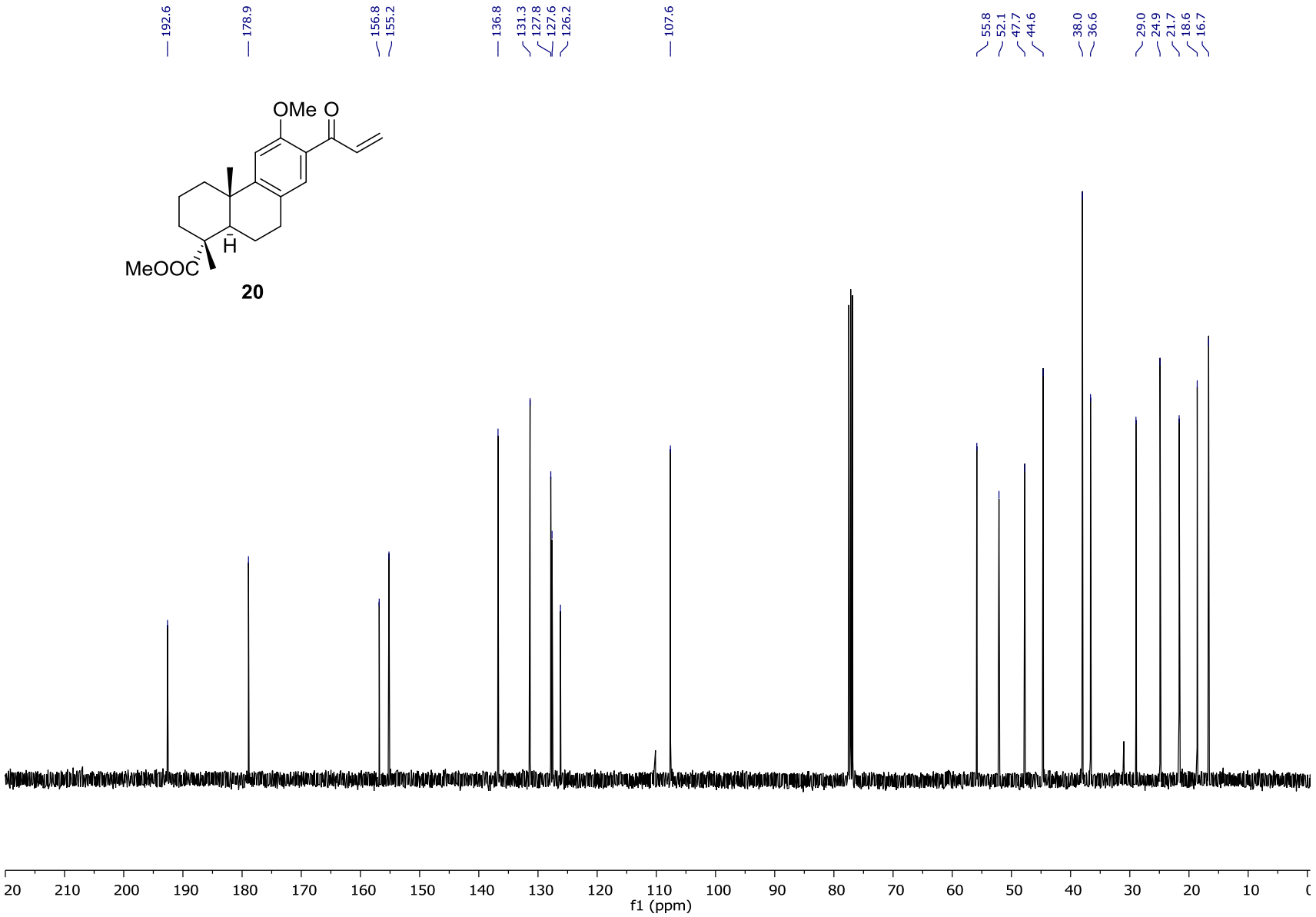
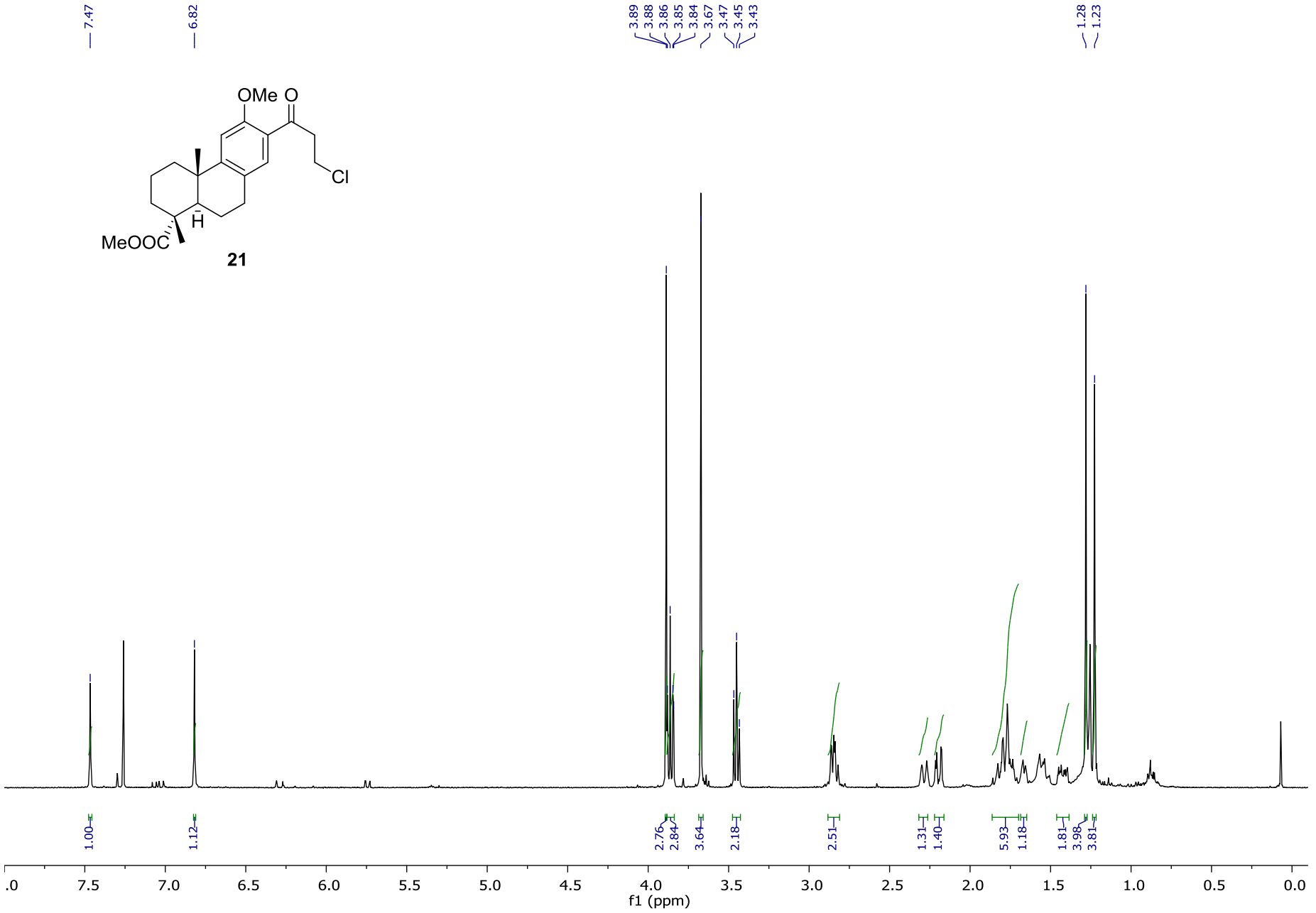
7.03
7.00
6.81
6.30
6.29
6.26
6.25
5.74
5.74
5.72
5.71
3.83
3.66
1.27
1.22
OMe O
H
MeOOC
20
1.00
1.12
1.07
1.28
1.27
3.27
3.32
2.43
1.23
1.17
6.17
1.33
1.35
3.22
3.20
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


192.6
178.9
156.8
155.2
136.8
131.3
127.8
127.6
126.2
107.6
55.8
52.1
47.7
44.6
38.0
36.6
29.0
24.9
21.7
18.6
16.7
OMe O
H
MeOOC
20
f1 (ppm)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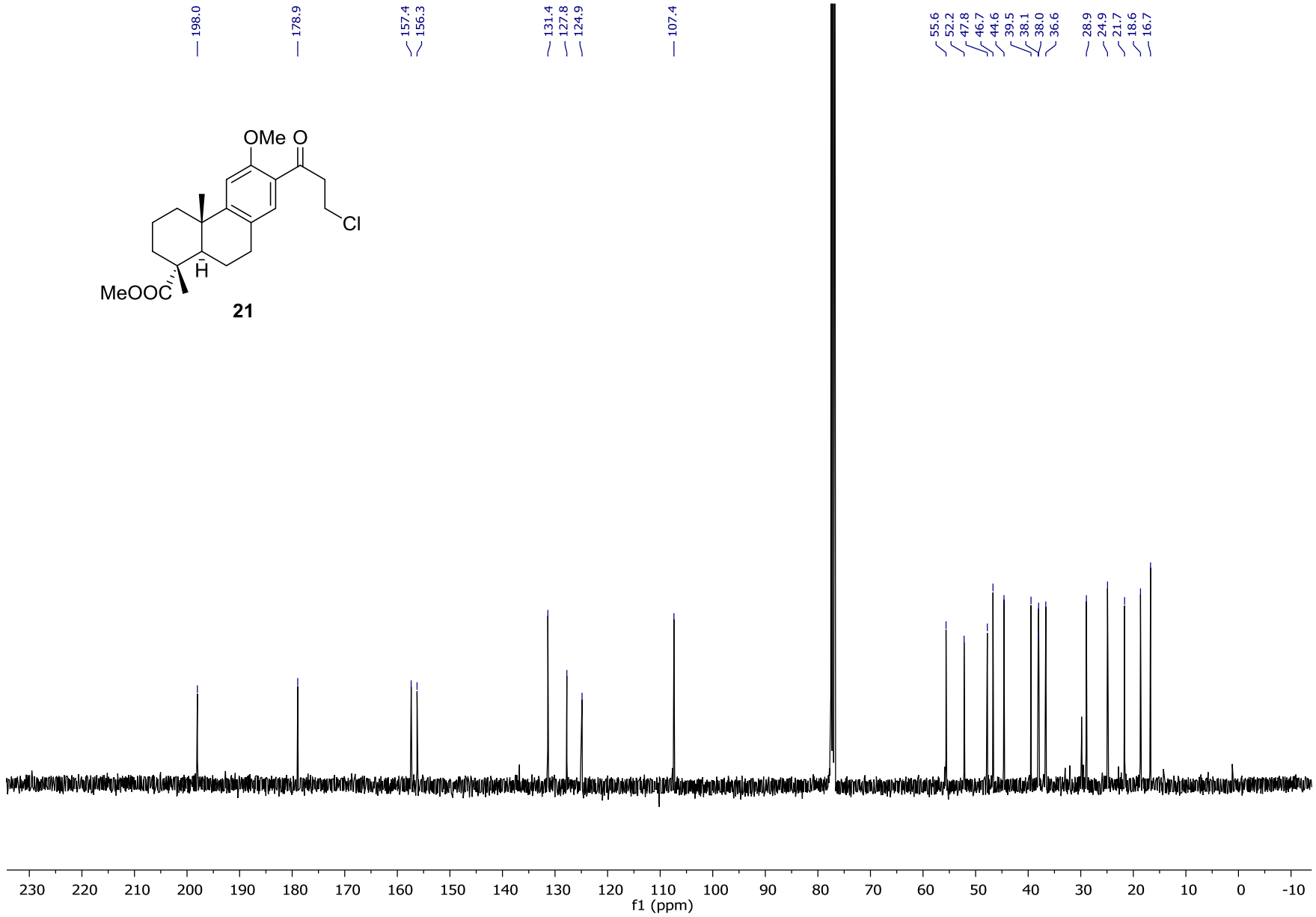
6.82
3.89
3.88
3.86
3.85
3.84
3.67
3.47
3.45
3.43
1.28
1.23
OMe O
Cl
H
MeOOC
21
1.00
1.12
2.76
2.84
3.64
2.18
2.51
1.31
1.40
5.93
1.18
1.81
3.98
3.81
f1 (ppm)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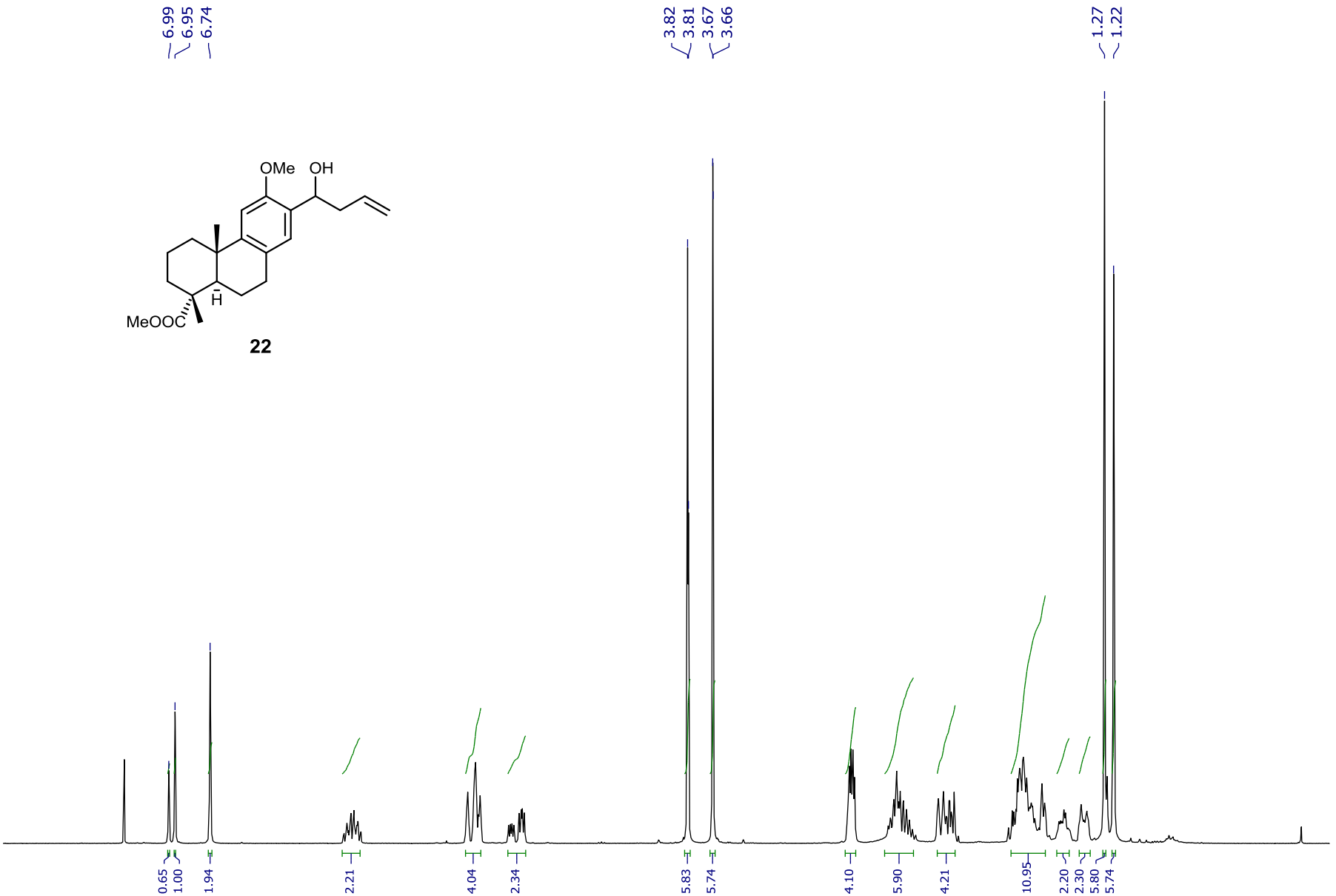
178.9
157.4
156.3
131.4
127.8
124.9
107.4
55.6
52.2
47.8
46.7
44.6
39.5
38.1
38.0
36.6
28.9
24.9
21.7
18.6
16.7
OMe
O
Cl
H
MeOOC
21
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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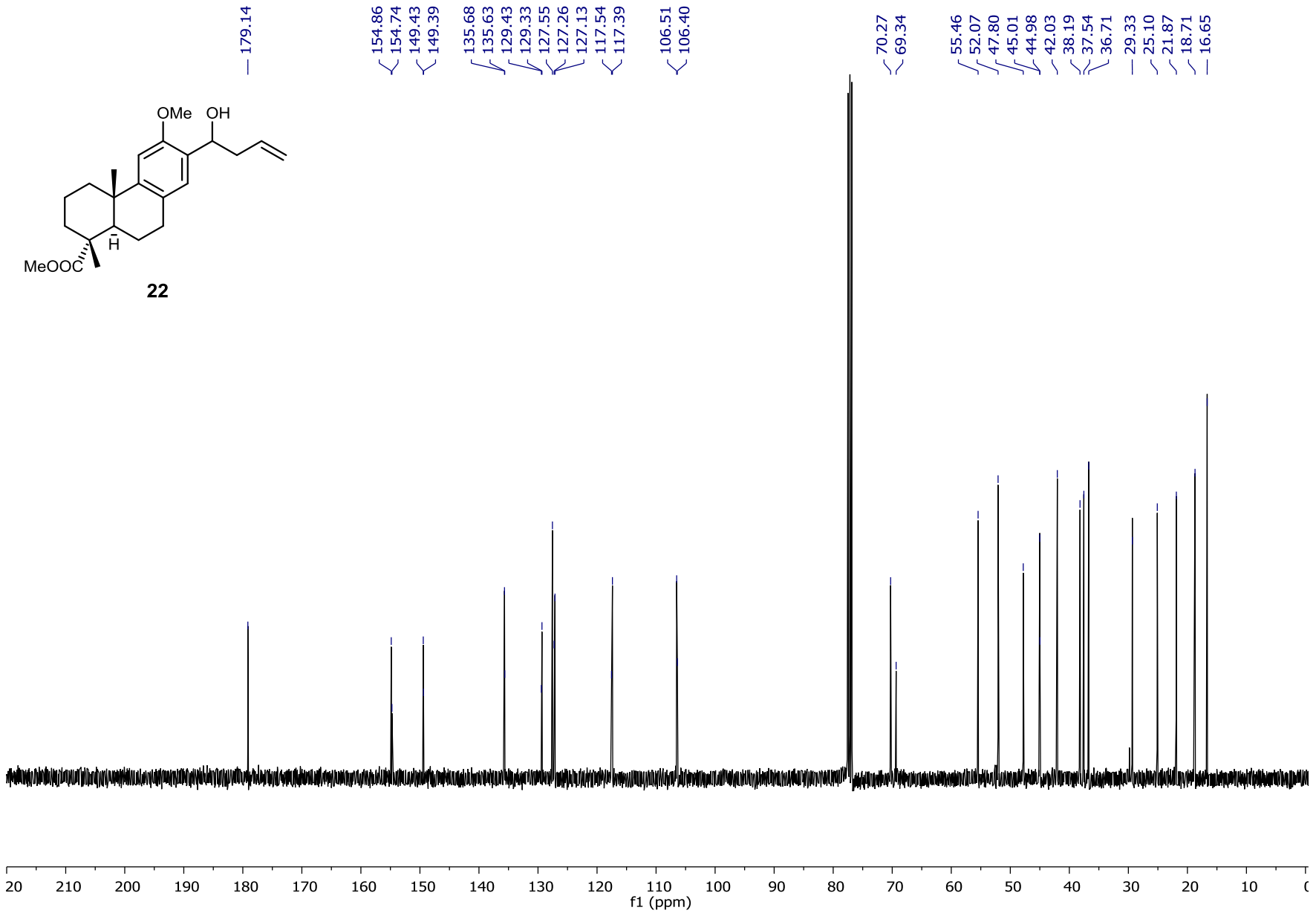
6.95
6.74
3.82
3.81
3.67
3.66
1.27
1.22
OMe
OH
H
MeOOC
22
0.65
1.00
1.94
2.21
4.04
2.34
5.83
5.74
4.10
5.90
4.21
10.95
2.20
2.30
5.80
5.74
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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154.86
154.74
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135.68
135.63
129.43
129.33
127.55
127.26
127.13
117.54
117.39
106.51
106.40
70.27
69.34
55.46
52.07
47.80
45.01
44.98
42.03
38.19
37.54
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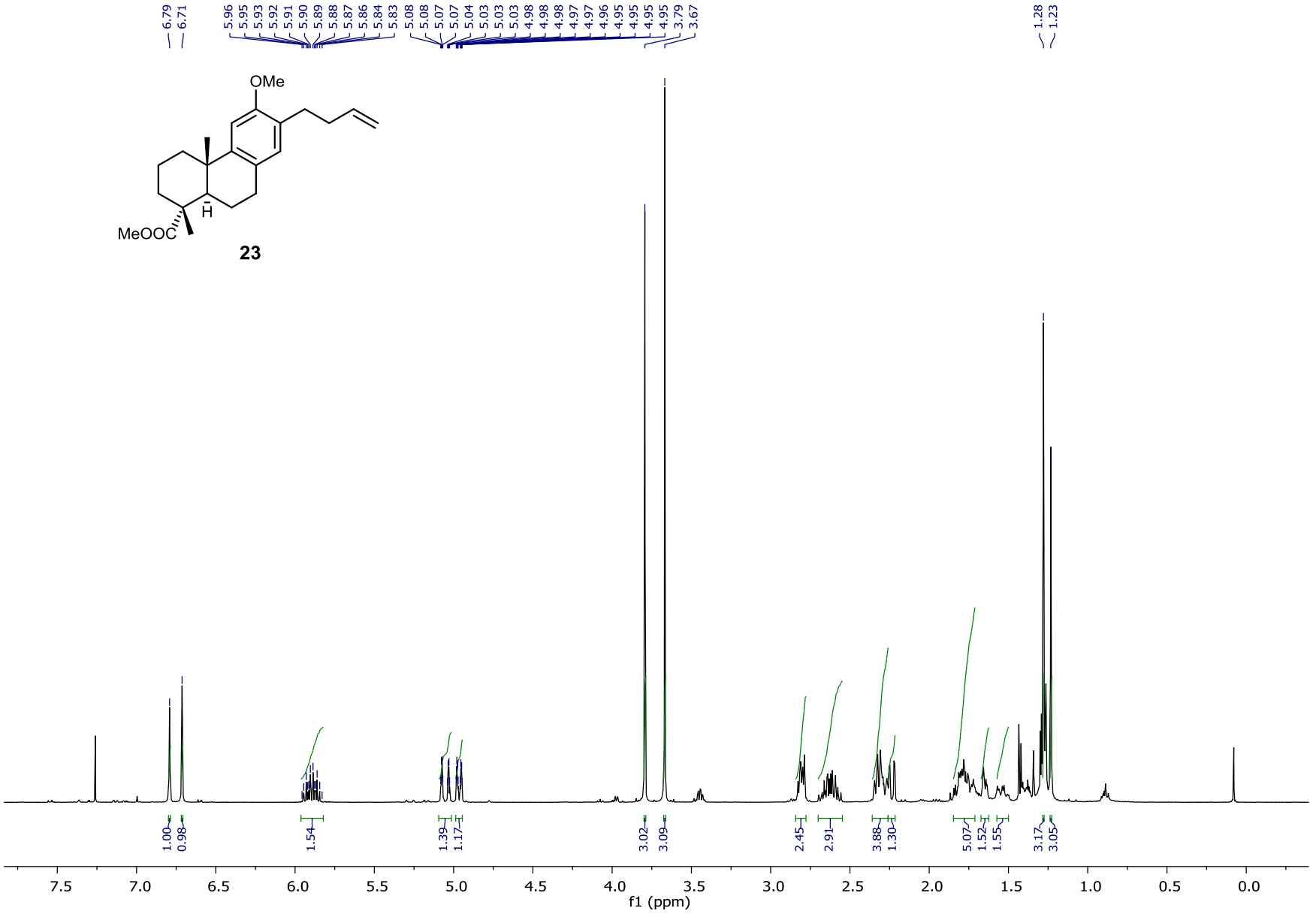
29.33
25.10
21.87
18.71
16.65
OMe
OH
H
MeOOC
22
f1 (ppm)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5.95
5.93
5.92
5.91
5.90
5.89
5.88
5.87
5.86
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5.83
5.08
5.08
5.07
5.07
5.04
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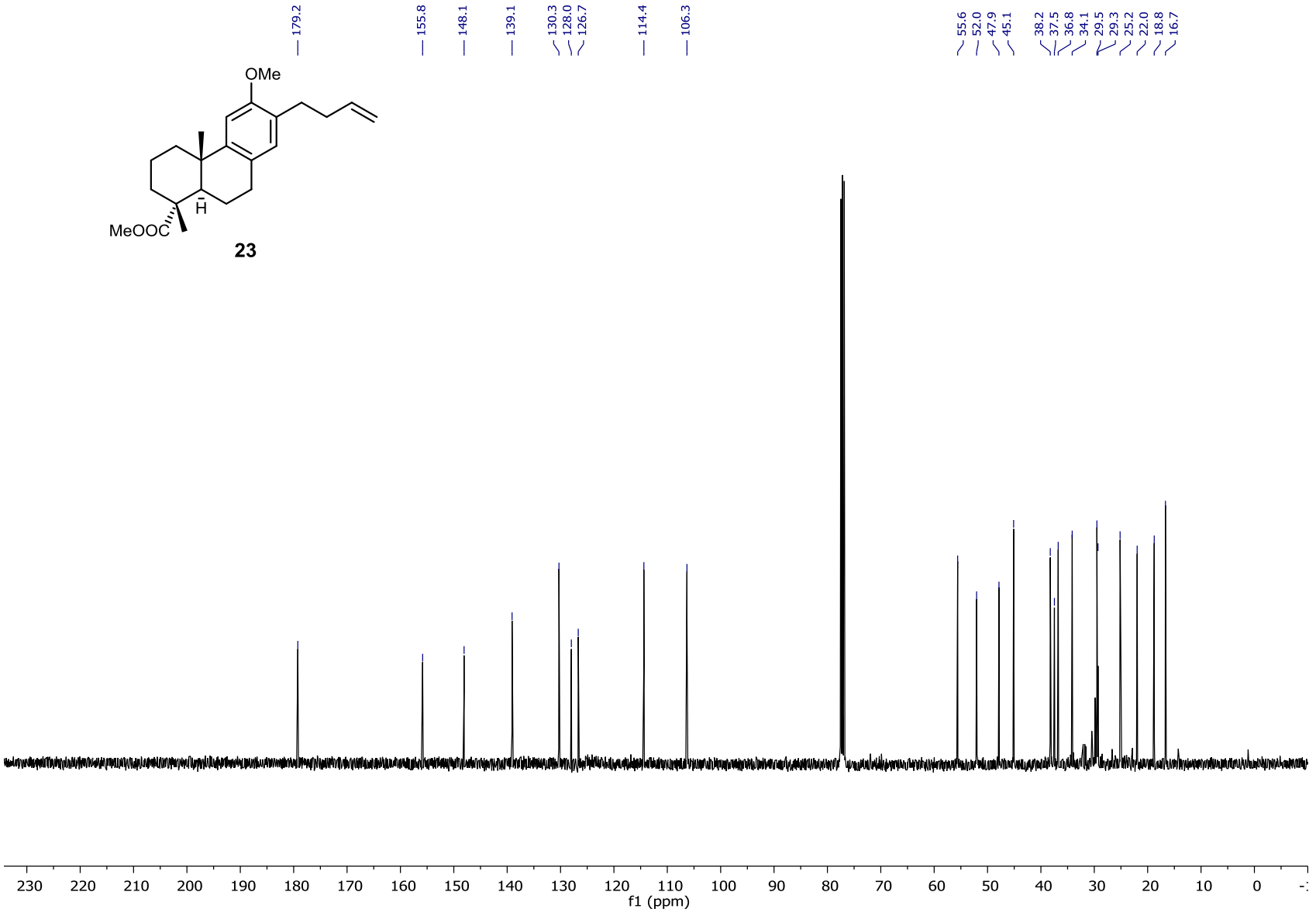
4.95
4.95
4.95
4.95
3.79
3.67
1.28
1.23
OMe
H
MeOOC
23
1.00
0.98
1.54
1.39
1.17
3.02
3.09
2.45
2.91
3.88
1.30
5.07
1.52
1.55
3.17
3.05
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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130.3
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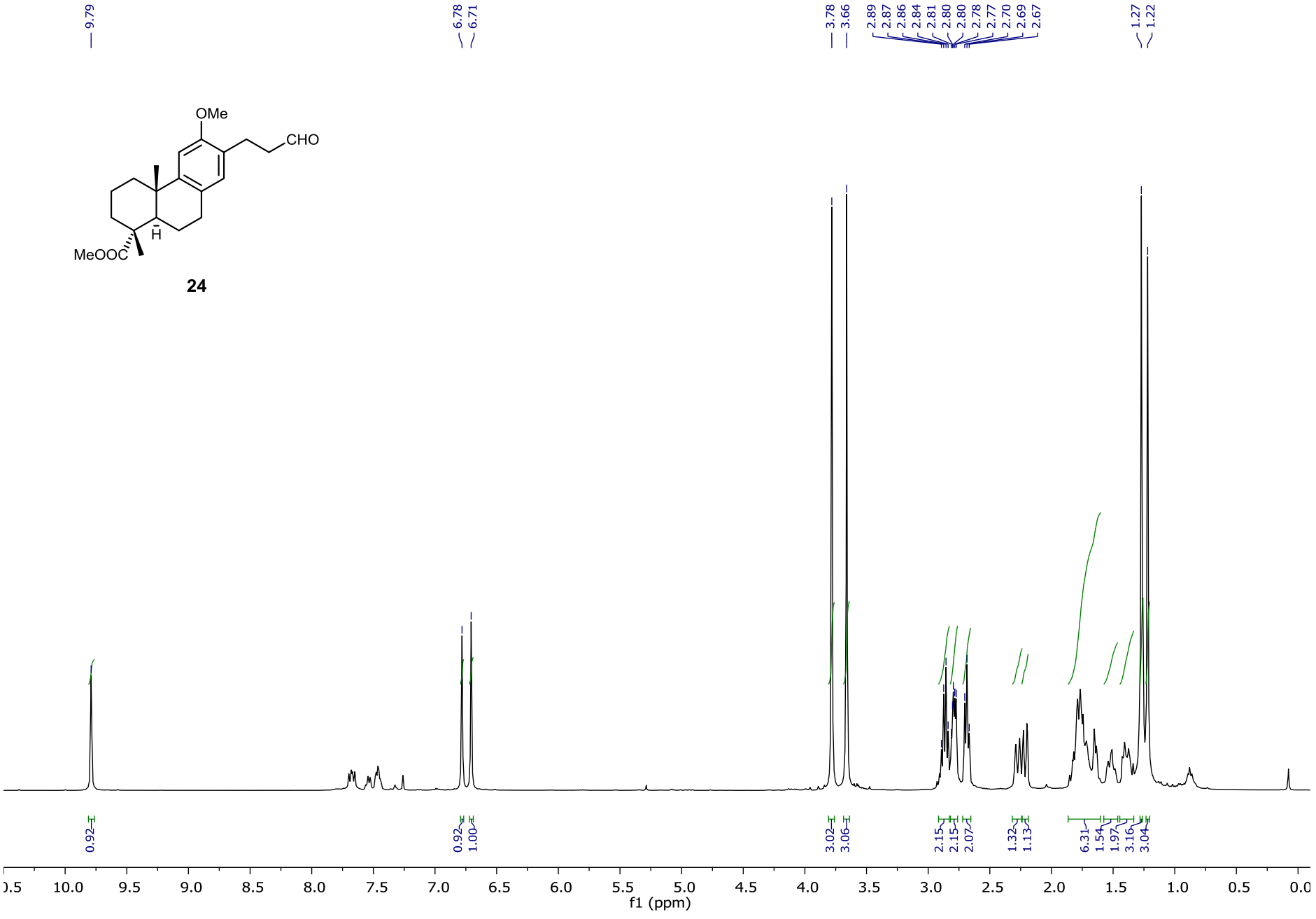
126.7
114.4
106.3
55.6
52.0
47.9
45.1
38.2
37.5
36.8
34.1
29.5
29.3
25.2
22.0
18.8
16.7
OMe
H
MeOOC
23
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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2.86
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2.81
2.80
2.80
2.78
2.77
2.70
2.69
2.67
1.27
1.22
OMe
CHO
H
MeOOC
24
0.92
0.92
1.00
3.02
3.06
2.15
2.15
2.07
1.32
1.13
6.31
1.54
1.97
3.16
3.04
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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3.5
3.0
2.5
2.0
1.5
1.0
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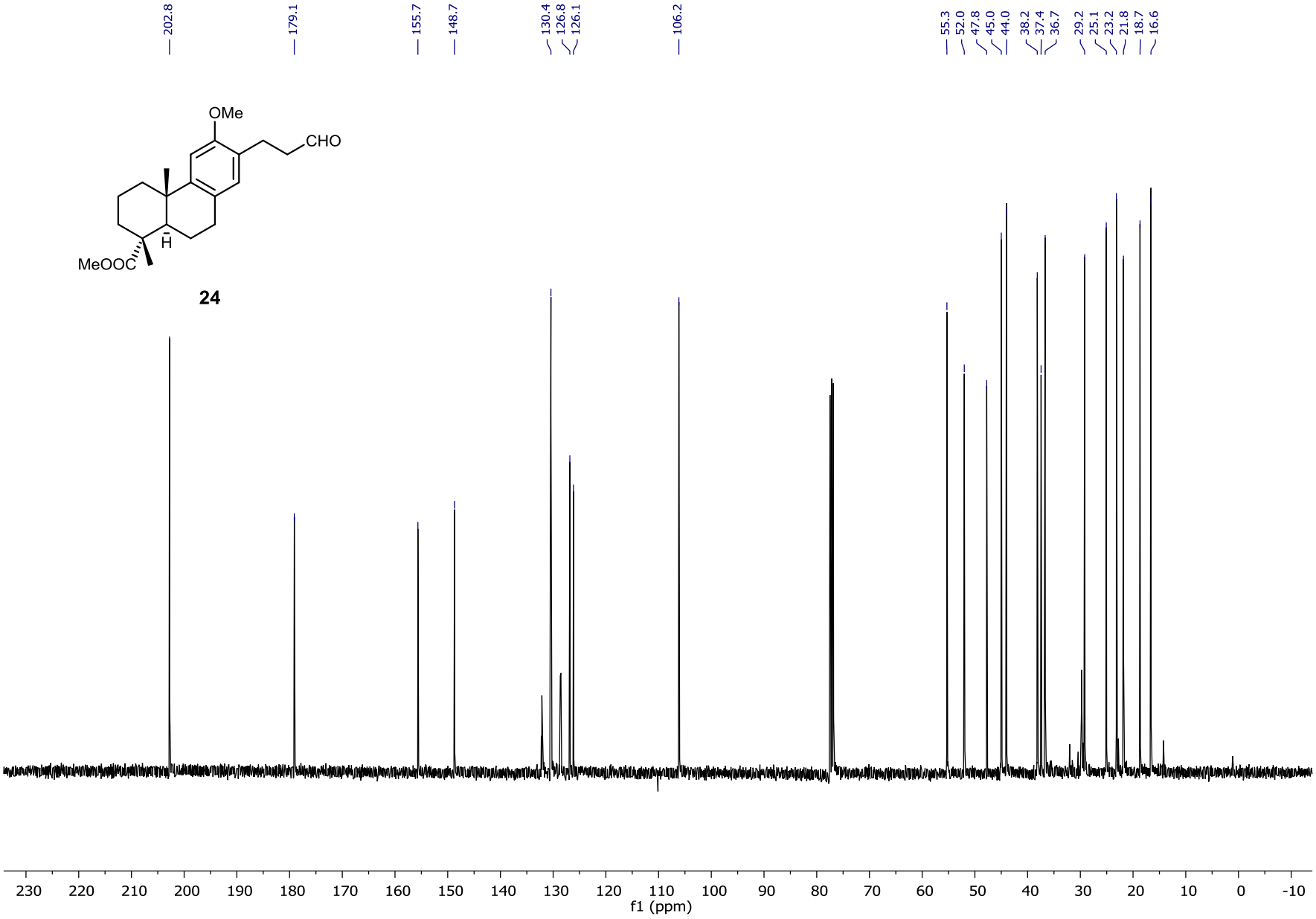
0.0
f1 (ppm)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126.1
106.2
55.3
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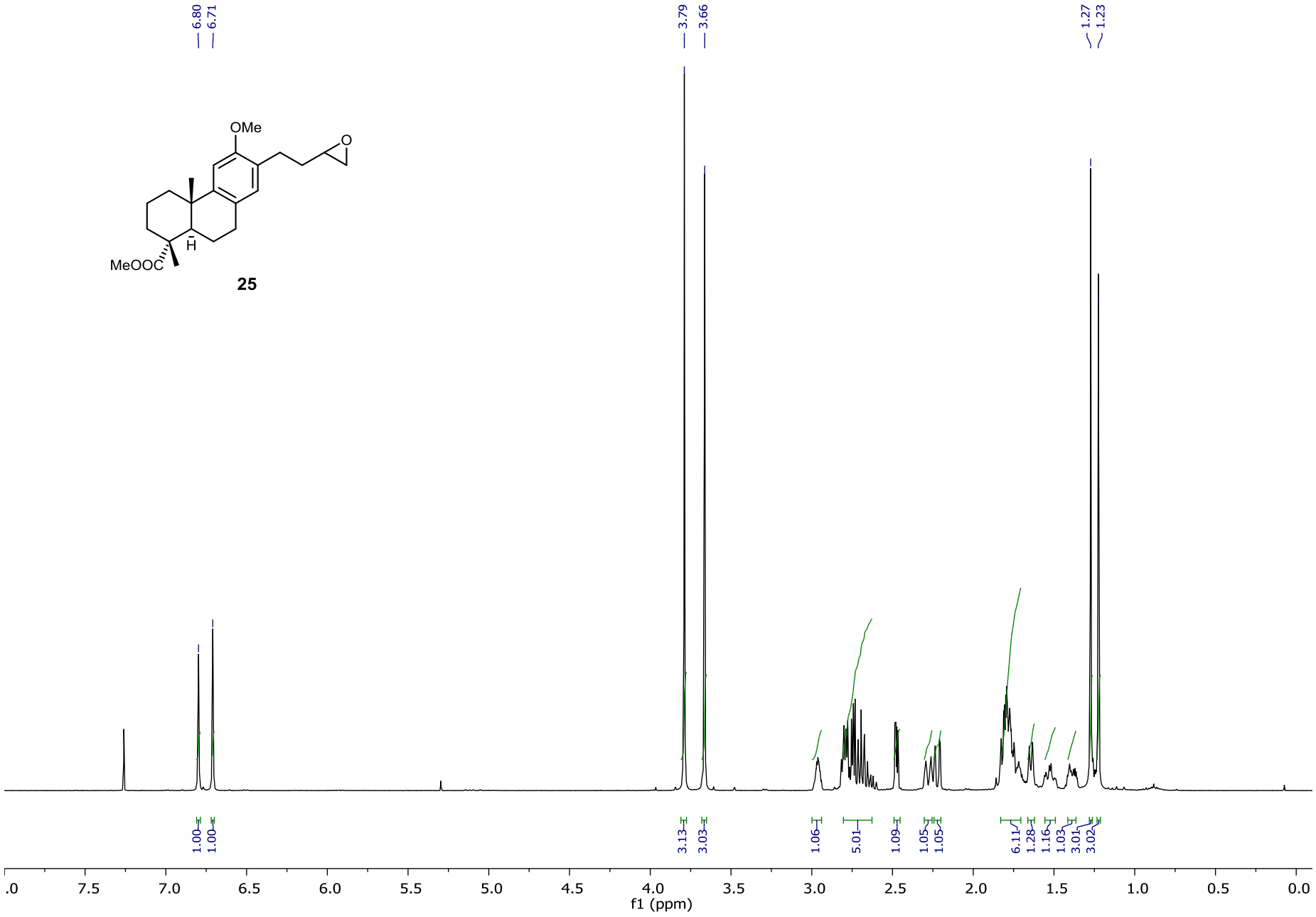
47.8
45.0
44.0
38.2
37.4
36.7
29.2
25.1
23.2
21.8
18.7
16.6
OMe
CHO
H
MeOOC
24
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.66
1.27
1.23
OMe
O
H
MeOOC
25
1.00
1.00
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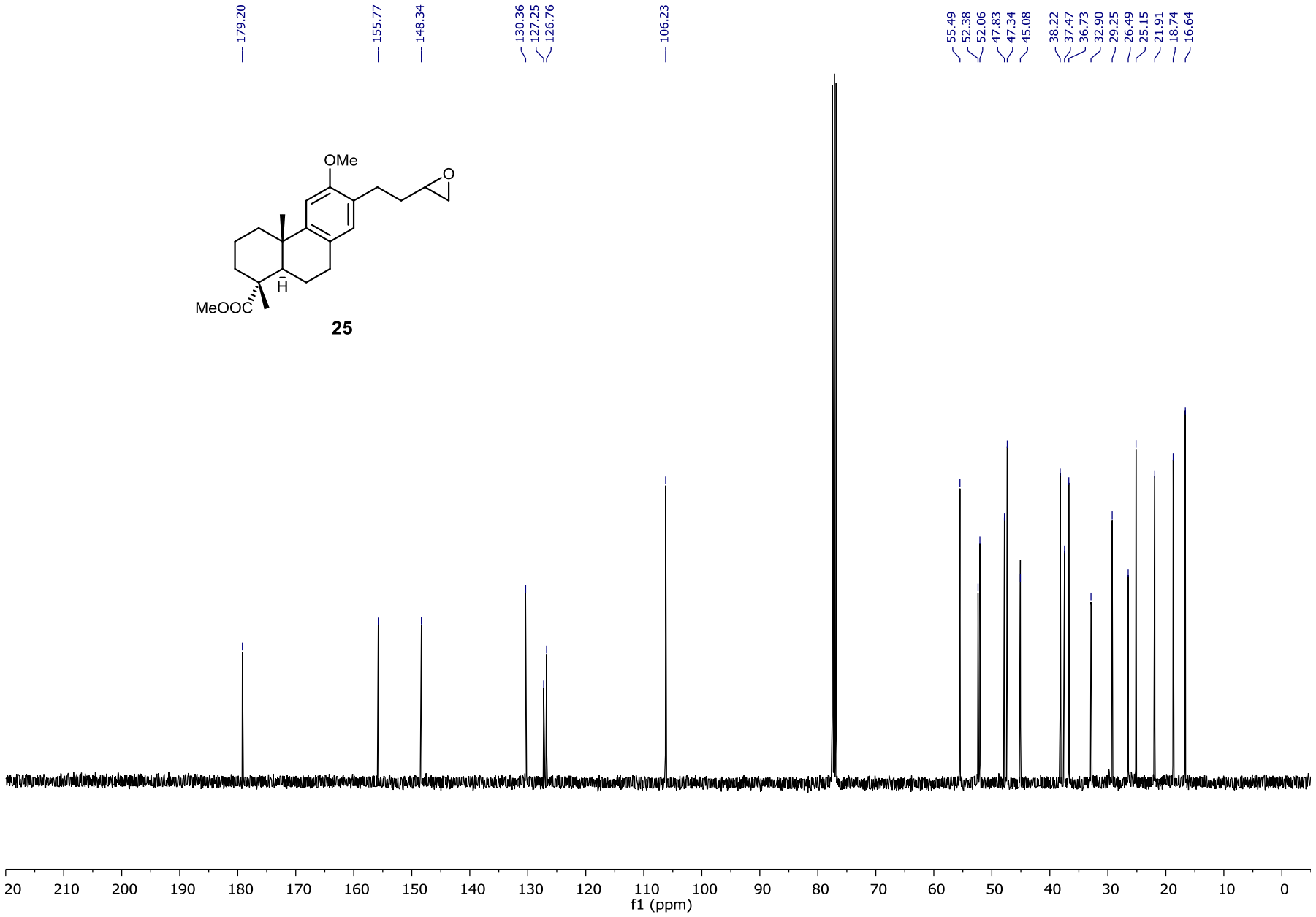
3.03
1.06
5.01
1.09
1.05
1.05
6.11
1.28
1.16
1.03
3.01
3.02
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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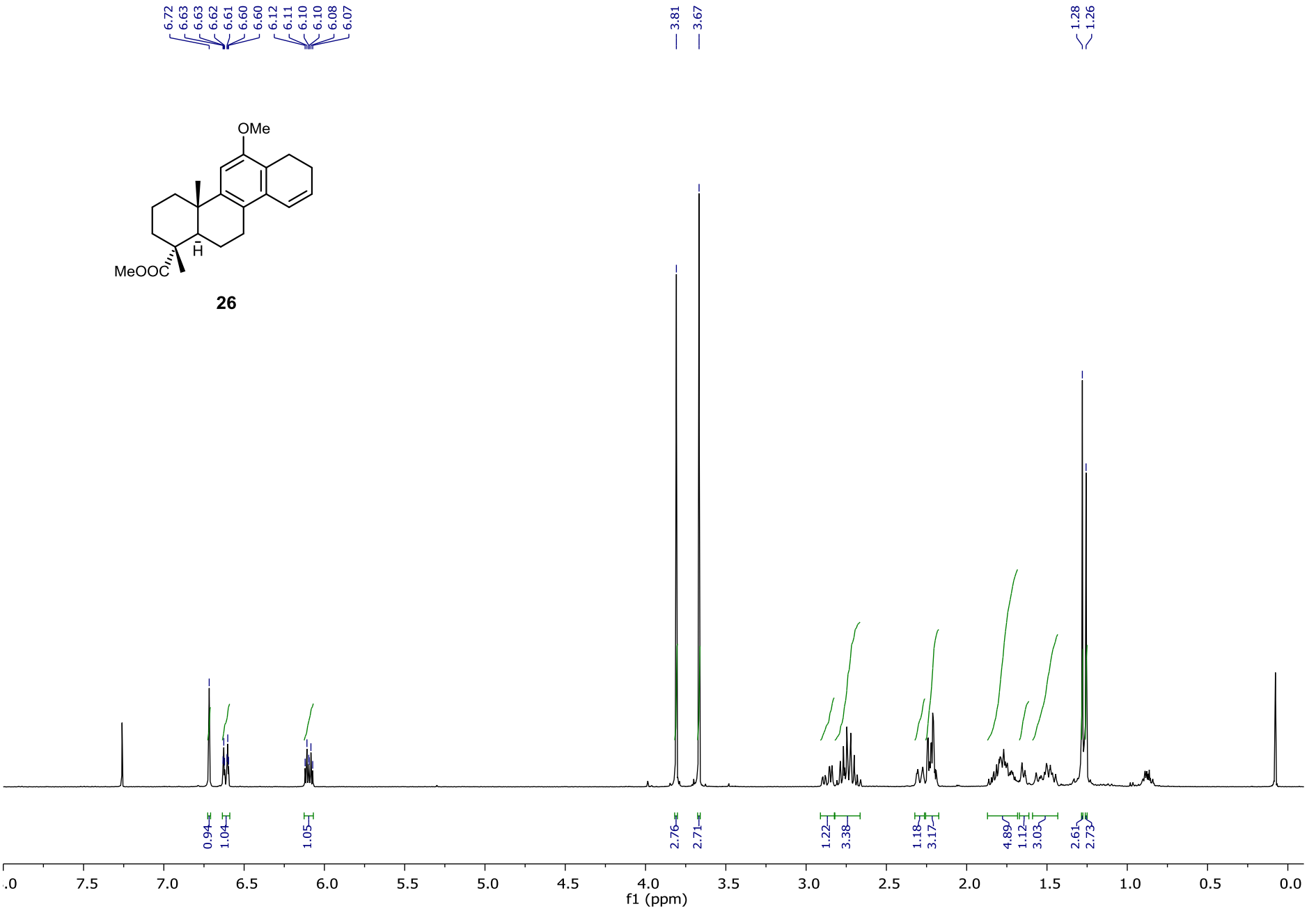
106.23
55.49
52.38
52.06
47.83
47.34
45.08
38.22
37.47
36.73
32.90
29.25
26.49
25.15
21.91
18.74
16.64
OMe
O
H
MeOOC
25
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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6.63
6.63
6.62
6.61
6.60
6.60
6.12
6.11
6.10
6.10
6.08
6.07
3.81
3.67
1.28
1.26
OMe
H
MeOOC
26
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1.04
1.05
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3.03
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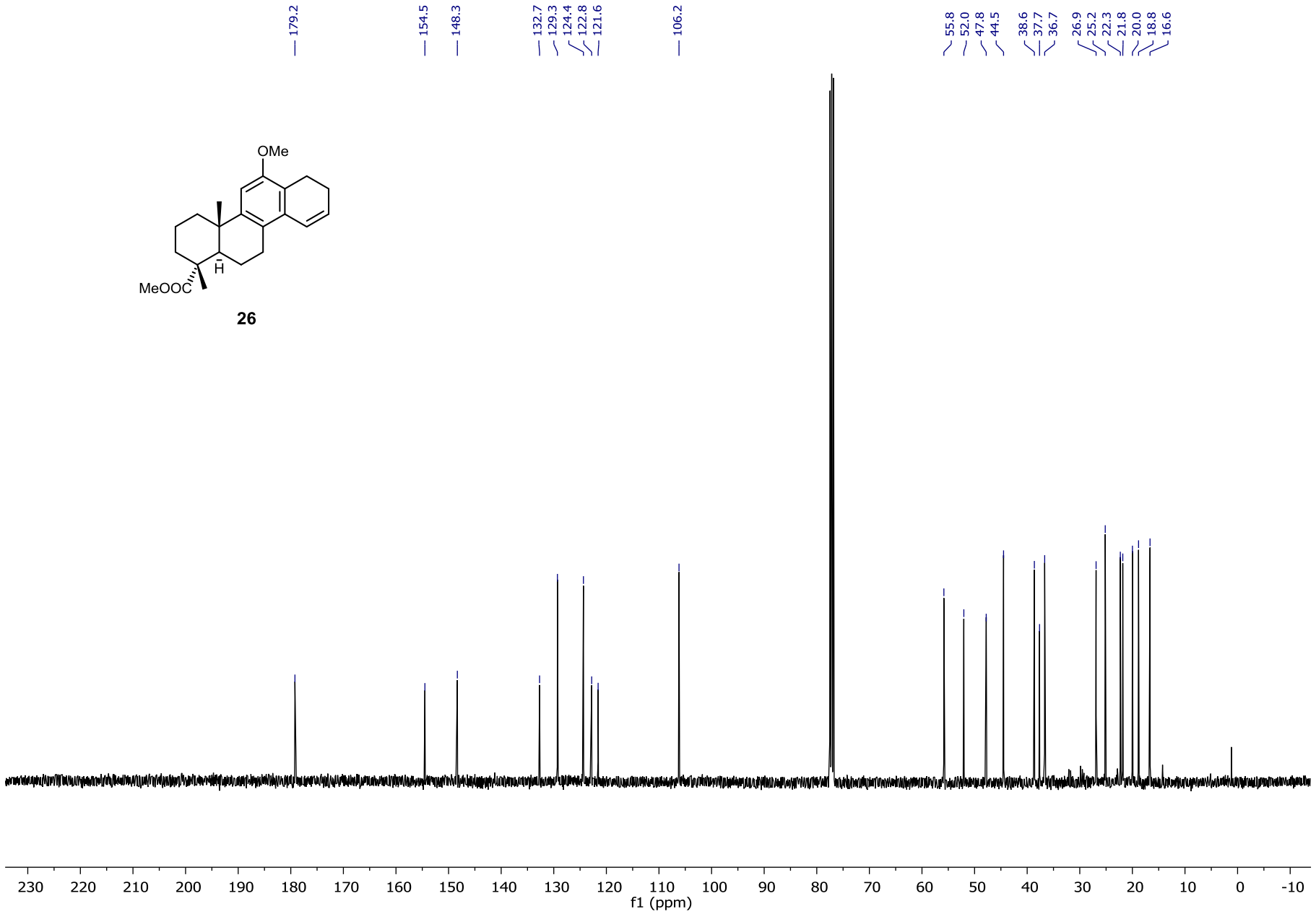
2.73
f1 (ppm)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38.6
37.7
36.7
26.9
25.2
22.3
21.8
20.0
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OMe
H
MeOOC
26
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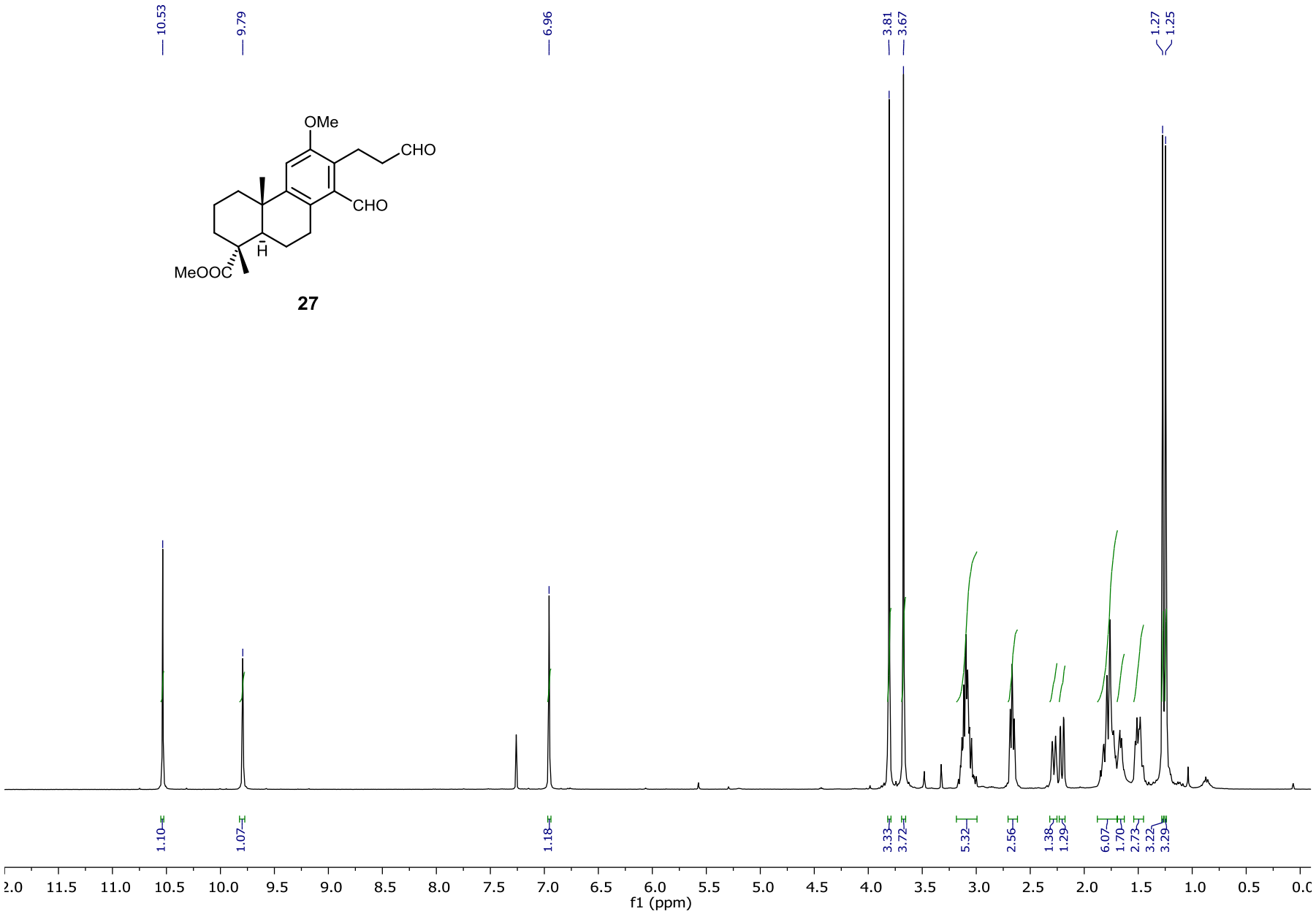
f1 (ppm)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CHO
CHO
H
MeOOC
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1.07
1.18
3.33
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1.38
1.29
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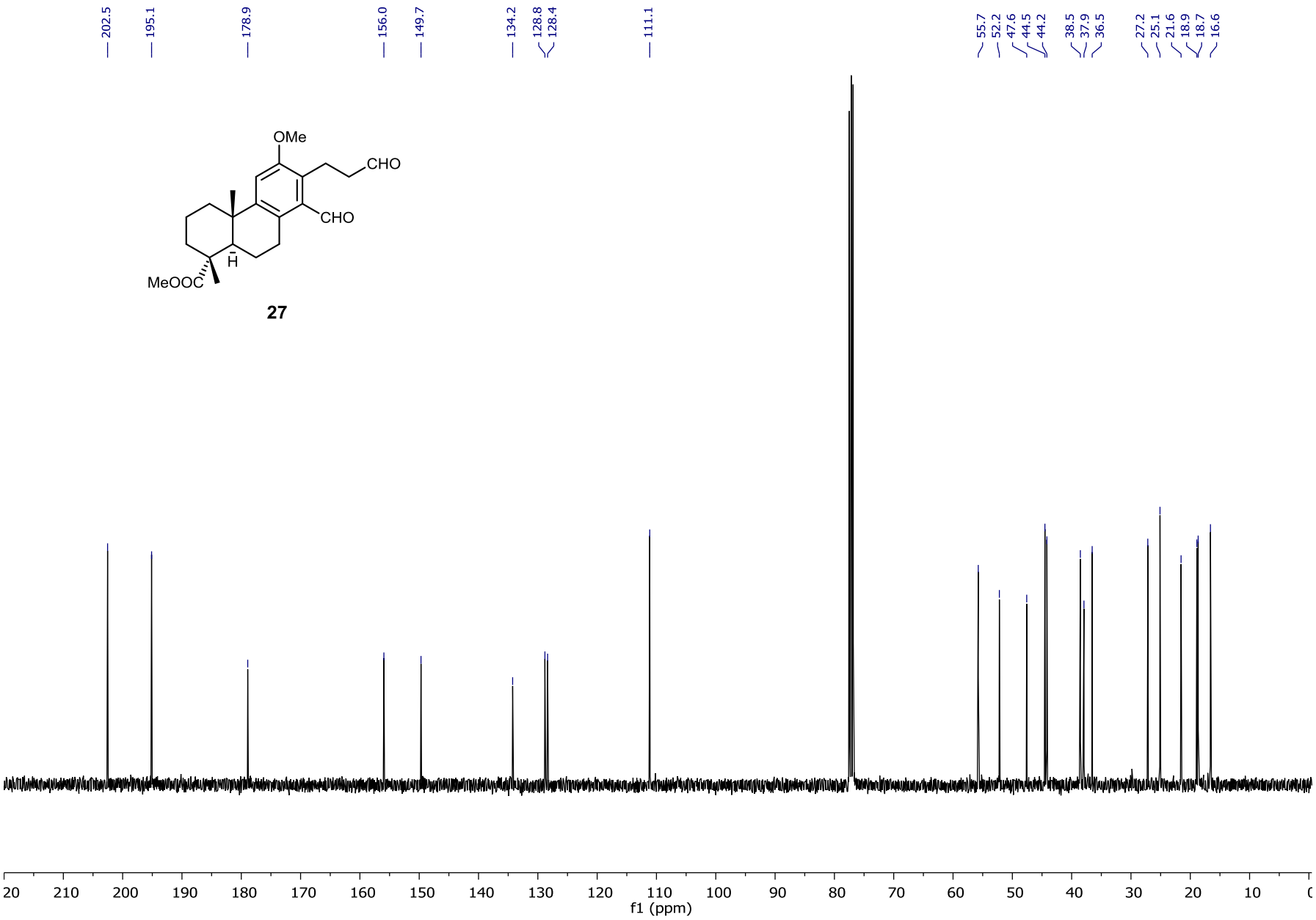
2.73
3.22
3.29
f1 (ppm)

27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128.4
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55.7
52.2
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44.2
38.5
37.9
36.5
27.2
25.1
21.6
18.9
18.7
16.6
OMe
CHO
CHO
H
MeOOC
27
20
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
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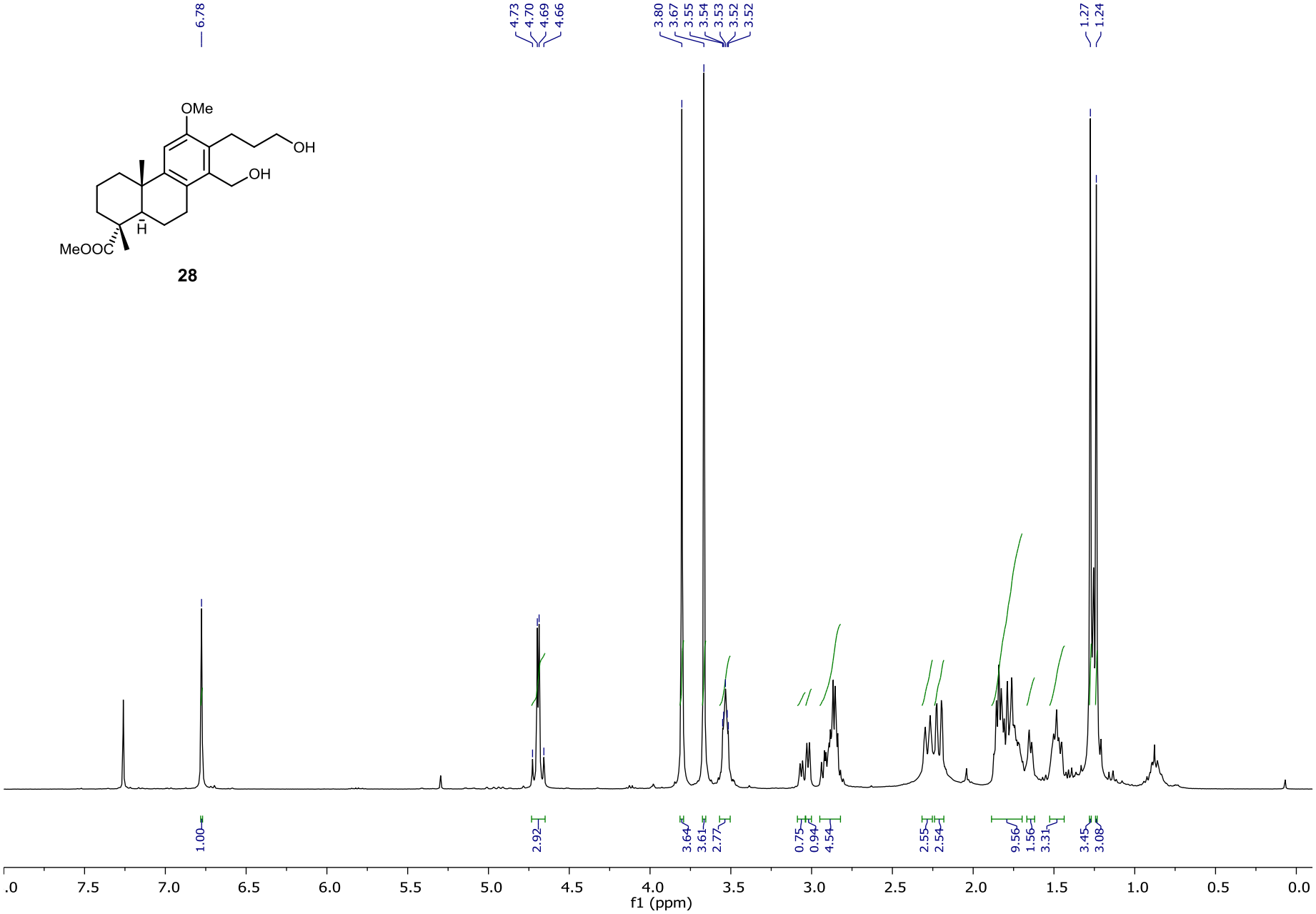
20
10
f1 (ppm)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3.67
3.55
3.54
3.53
3.52
3.52
1.27
1.24
OMe
OH
OH
H
MeOOC
28
1.00
2.92
3.64
3.61
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4.54
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2.54
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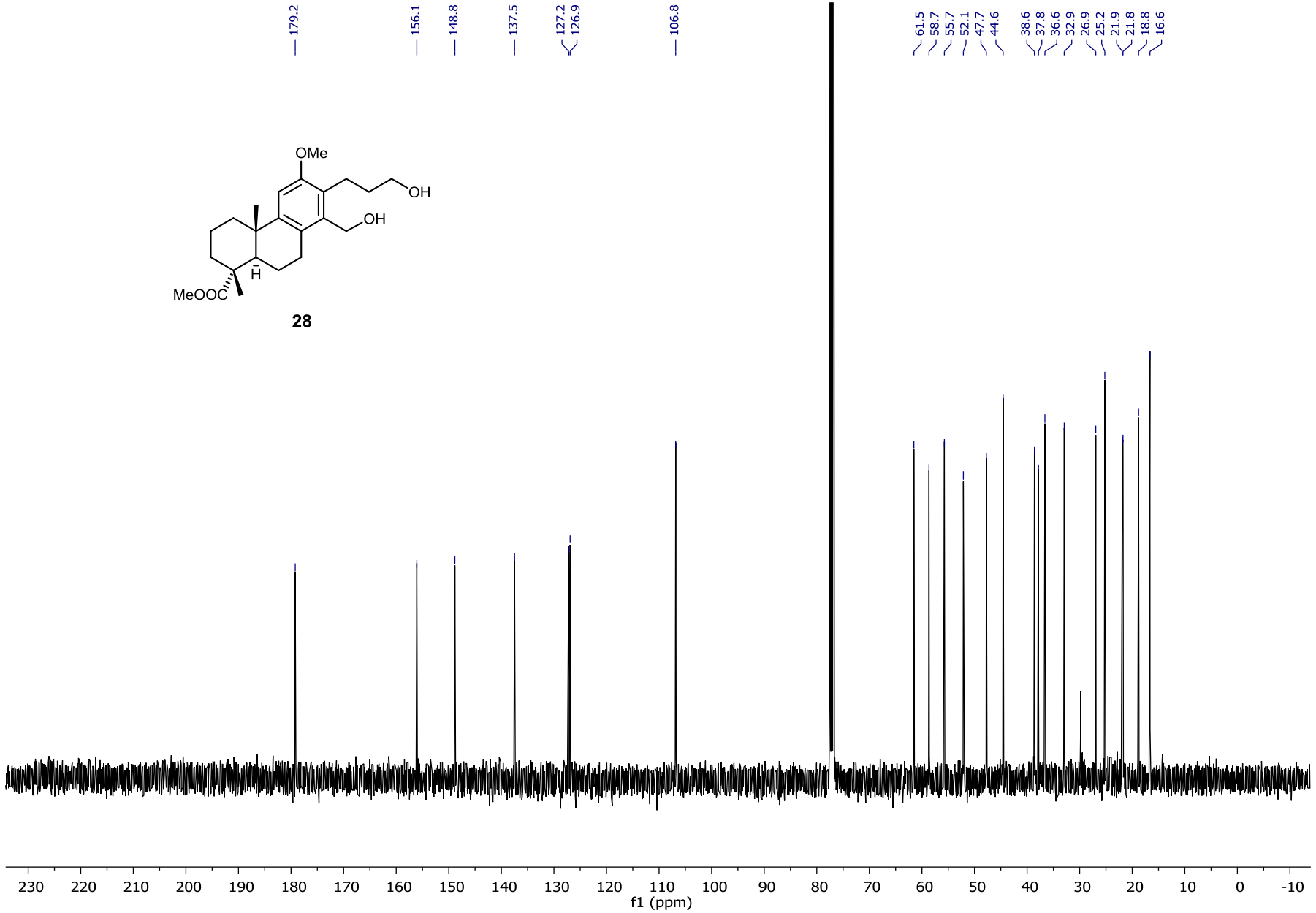
1.56
3.31
3.45
3.08
f1 (ppm)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47.7
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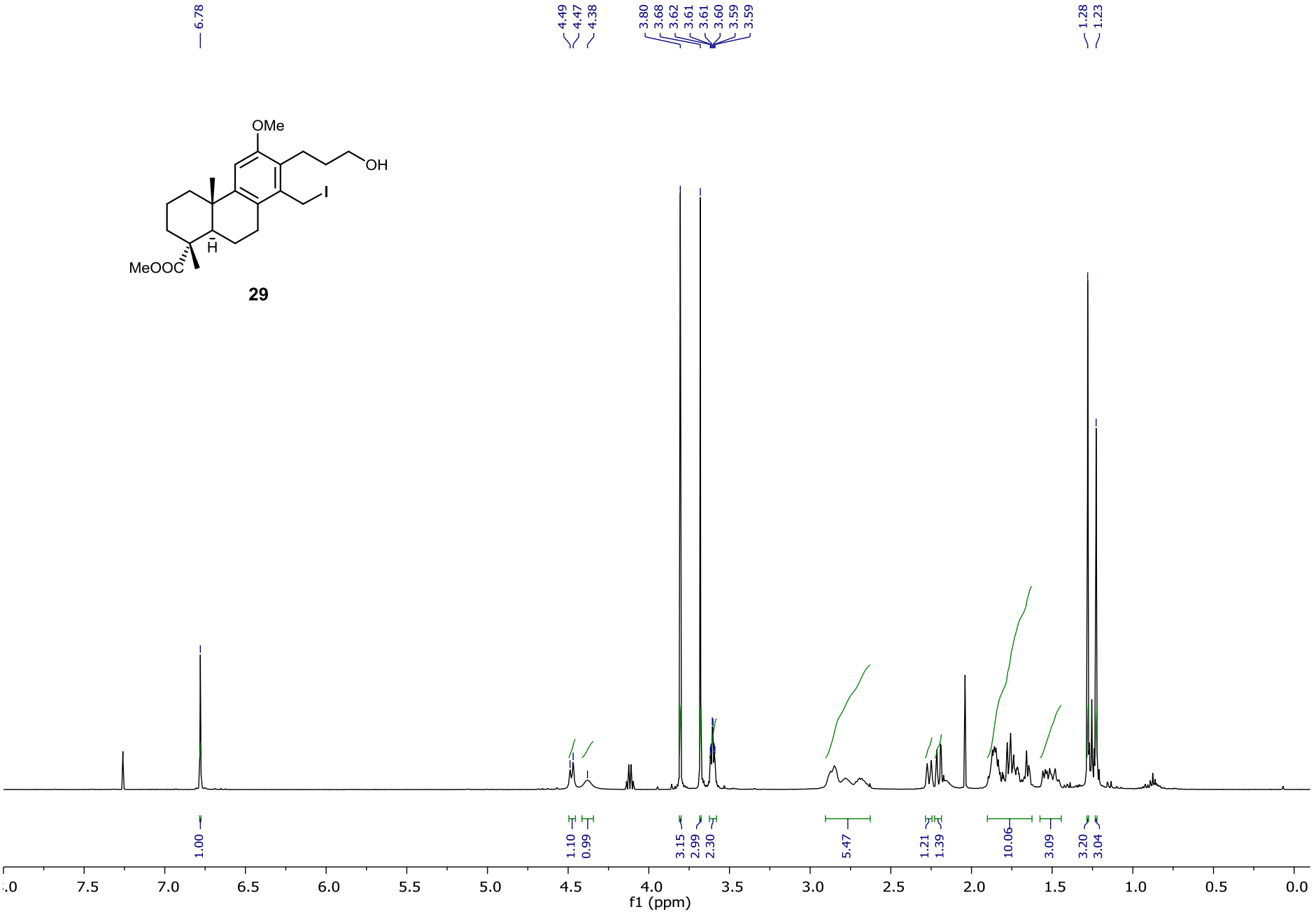
38.6
37.8
36.6
32.9
26.9
25.2
21.9
21.8
18.8
16.6
OMe
OH
OH
H
MeOOC
28
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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3.60
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3.59
1.28
1.23
OMe
OH
I
H
MeOOC
29
1.00
1.10
0.99
3.15
2.99
2.30
5.47
1.21
1.39
10.06
3.09
3.20
3.04
7.5
7.0
6.5
6.0
5.5
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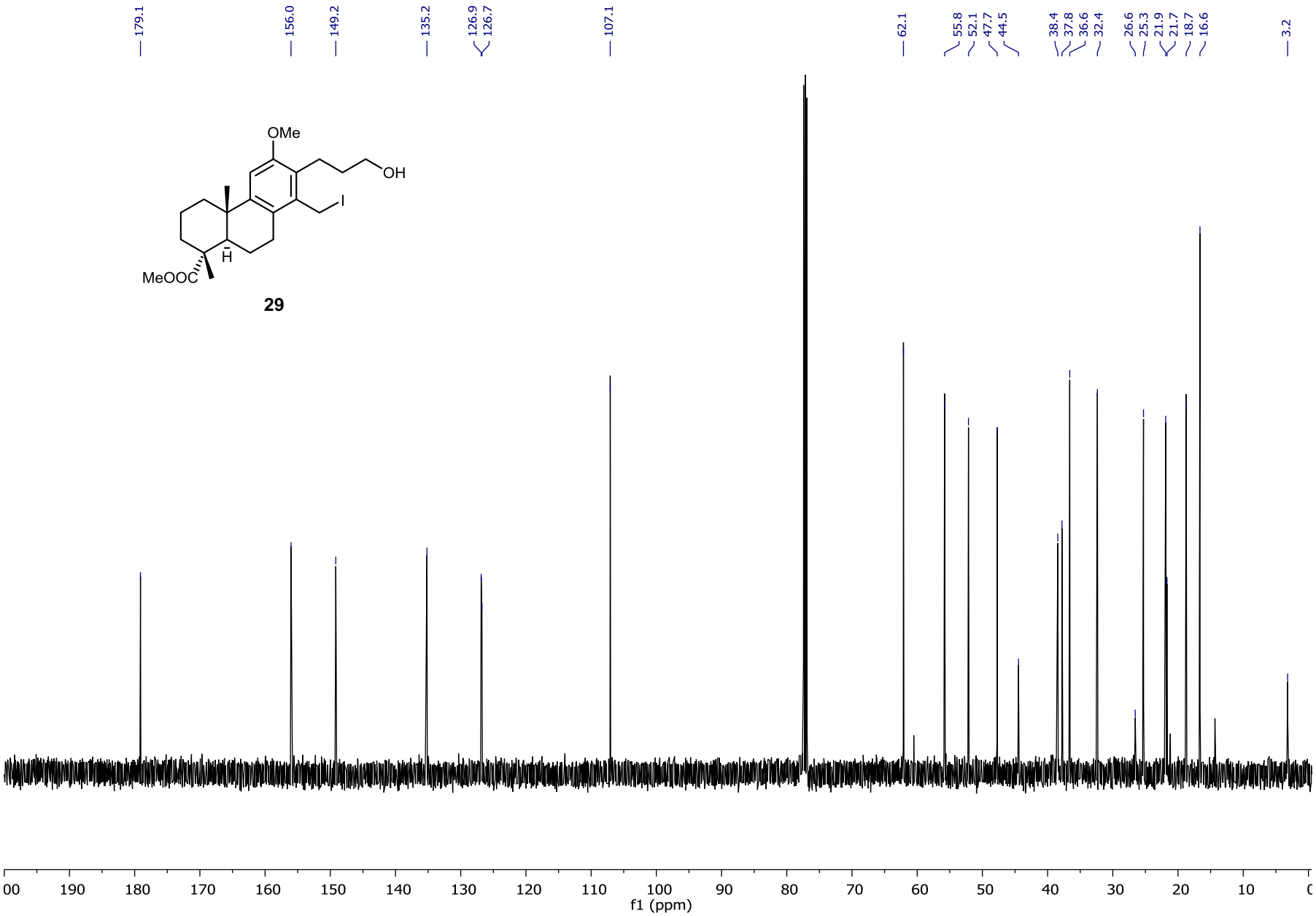
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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135.2
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126.7
107.1
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55.8
52.1
47.7
44.5
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37.8
36.6
32.4
26.6
25.3
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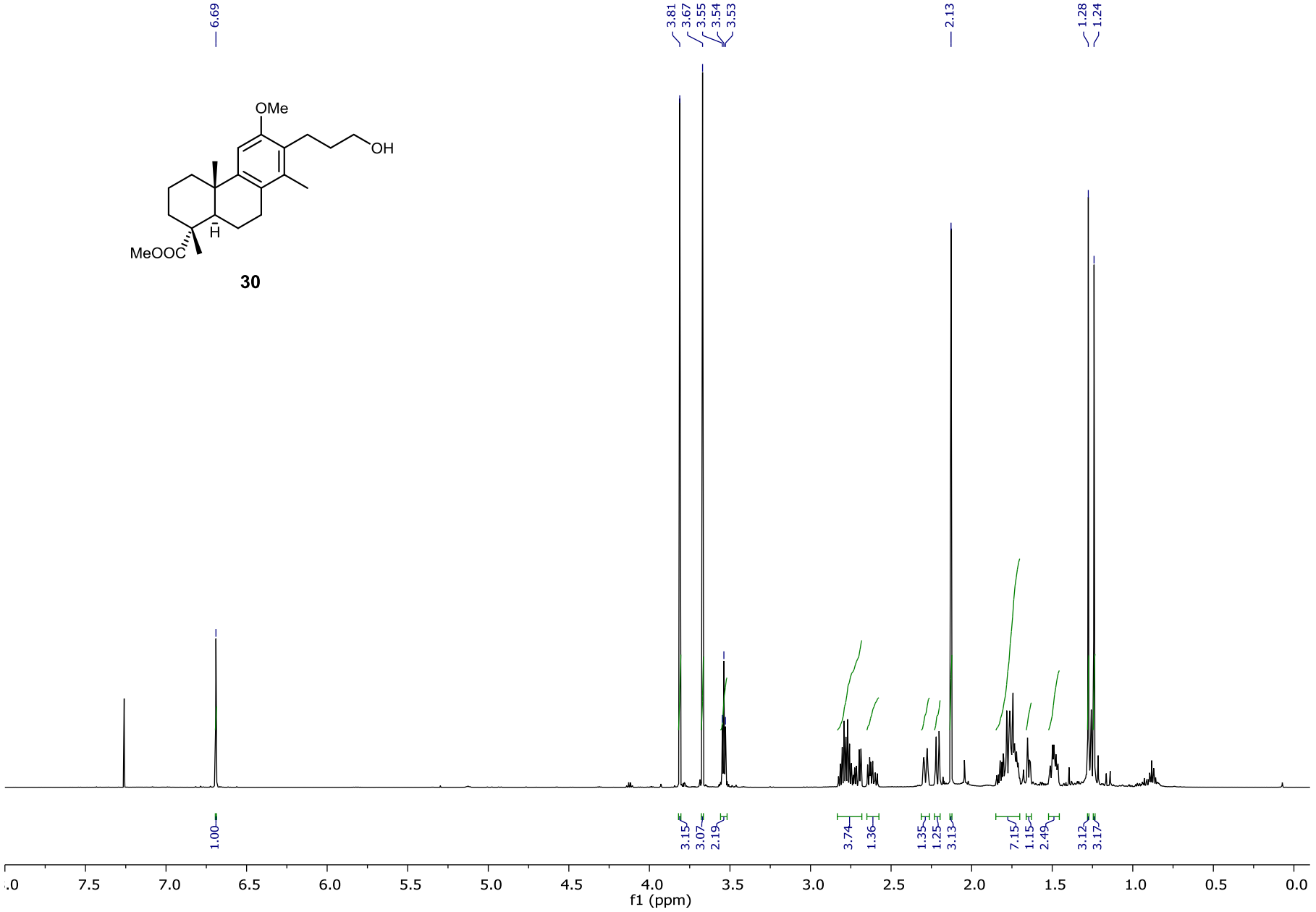
21.7
18.7
16.6
3.2
OMe
OH
I
H
MeOOC
29
f1 (ppm)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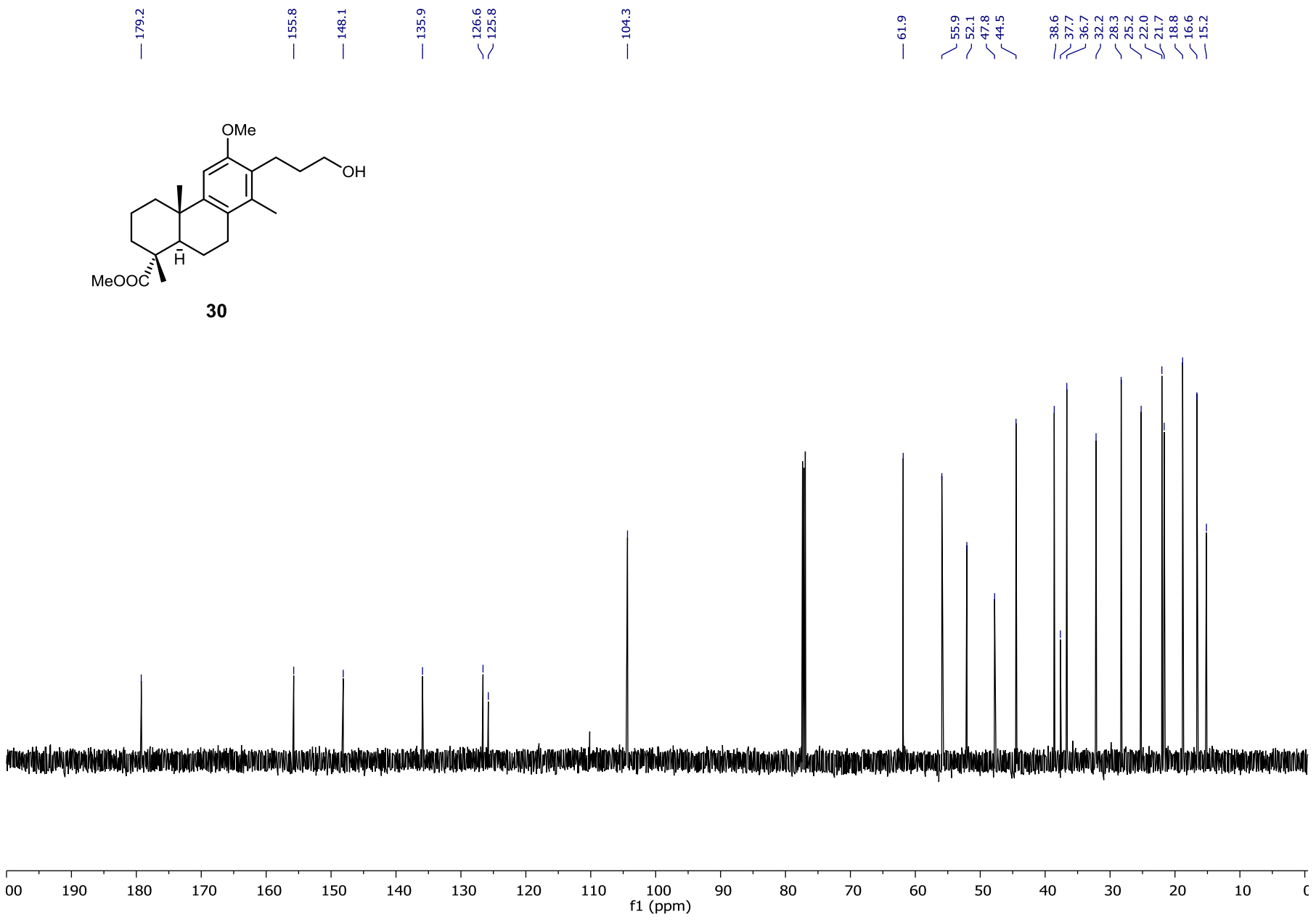
1.28
1.24
OMe
OH
H
MeOOC
30
1.00
3.15
3.07
2.19
3.74
1.36
1.35
1.25
3.13
7.15
1.15
2.49
3.12
3.17
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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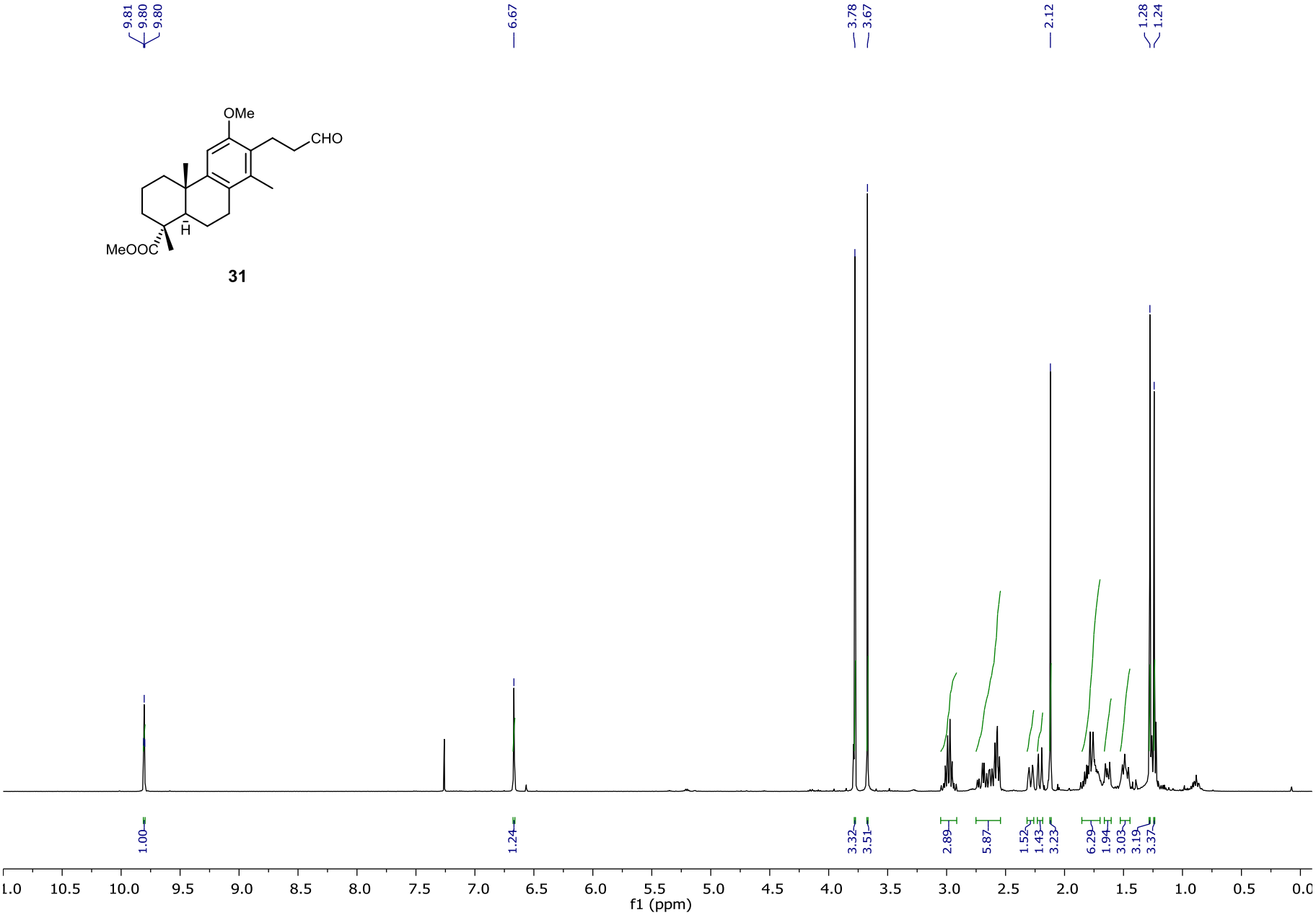
104.3
61.9
55.9
52.1
47.8
44.5
38.6
37.7
36.7
32.2
28.3
25.2
22.0
21.7
18.8
16.6
15.2
OMe
OH
H
MeOOC
30
f1 (ppm)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9.80
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3.67
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1.28
1.24
OMe
CHO
H
MeOOC
31
1.00
1.24
3.32
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2.89
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1.52
1.43
3.23
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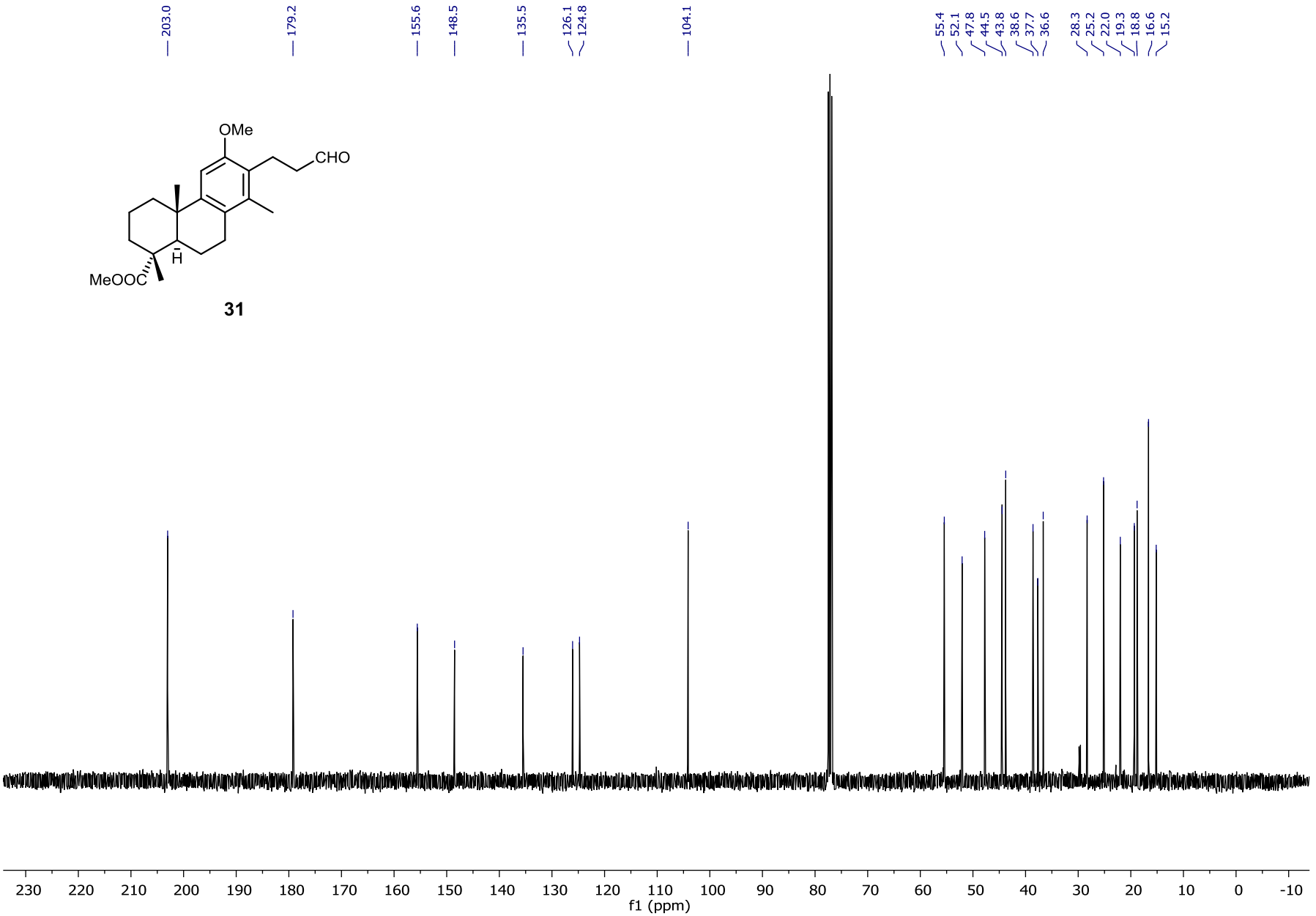
1.94
3.03
3.19
3.37
f1 (ppm)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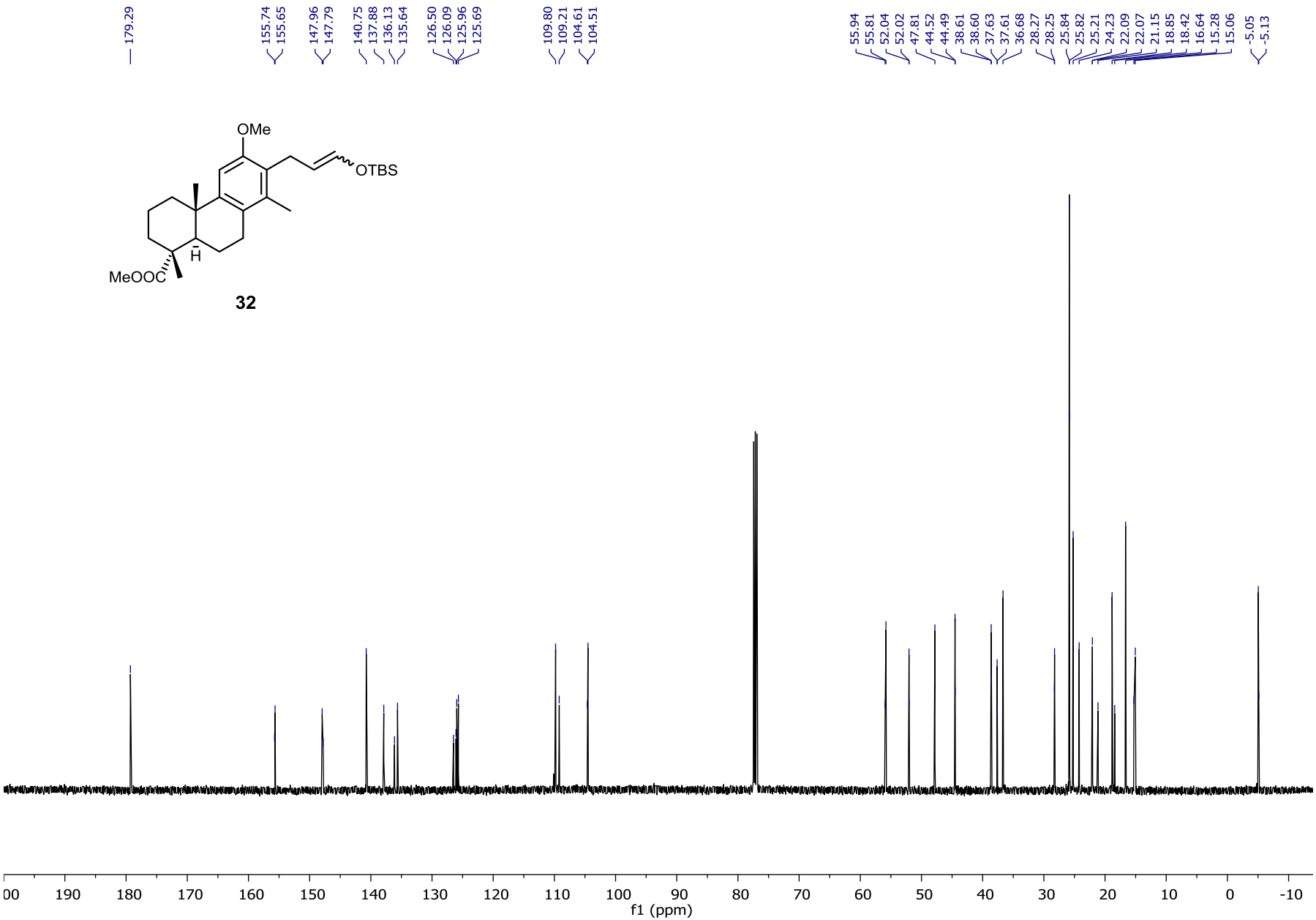
124.8
104.1
55.4
52.1
47.8
44.5
43.8
38.6
37.7
36.6
28.3
25.2
22.0
19.3
18.8
16.6
15.2
OMe
CHO
H
MeOOC
31
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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136.13
135.64
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126.09
125.96
125.69
109.80
109.21
104.61
104.51
55.94
55.81
52.04
52.02
47.81
44.52
44.49
38.61
38.60
37.63
37.61
36.68
28.27
28.25
25.84
25.82
25.21
24.23
22.09
22.07
21.15
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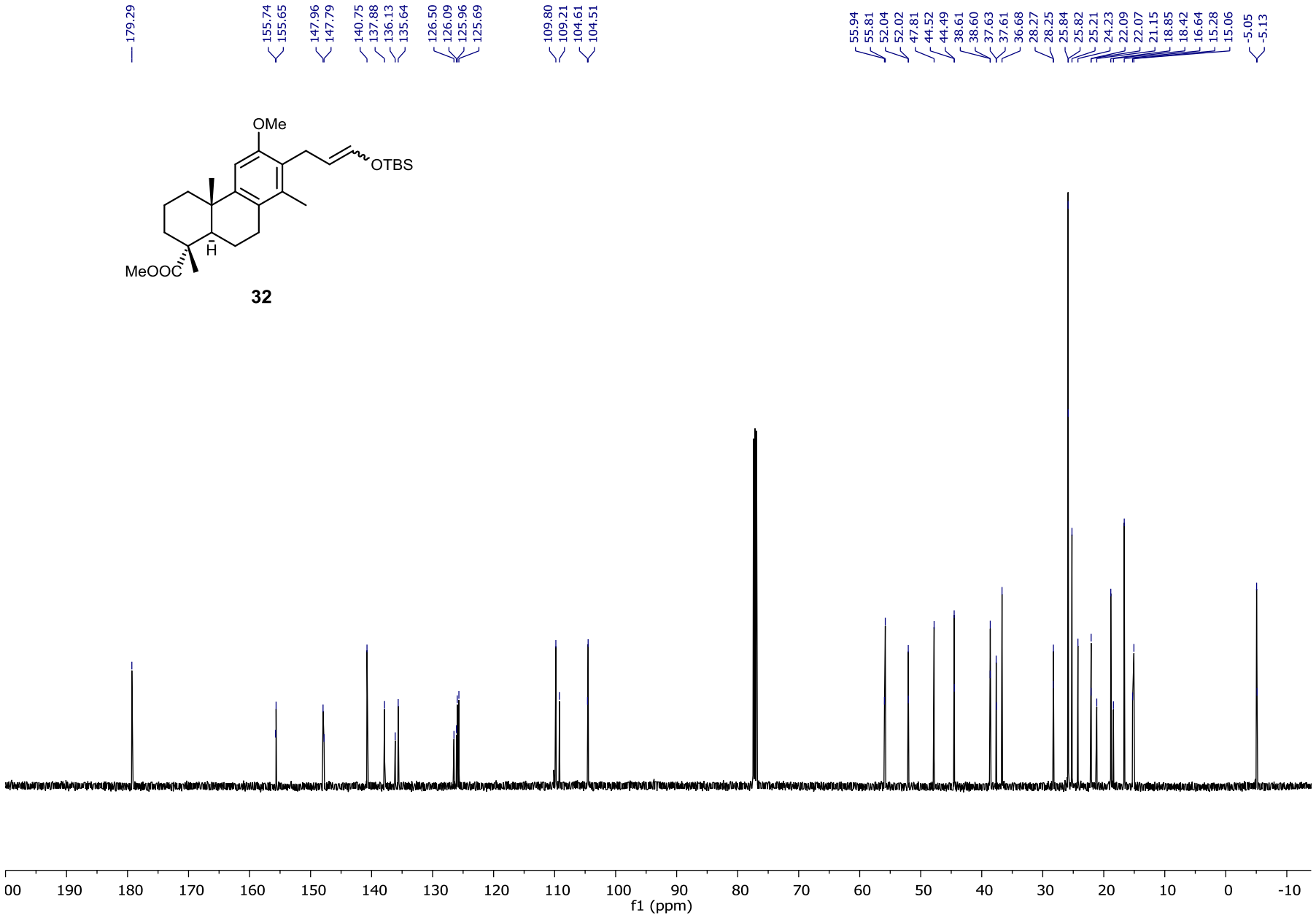
16.64
15.28
15.06
-5.05
-5.13
OMe
OTBS
H
MeOOC
32
f1 (ppm)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137.88
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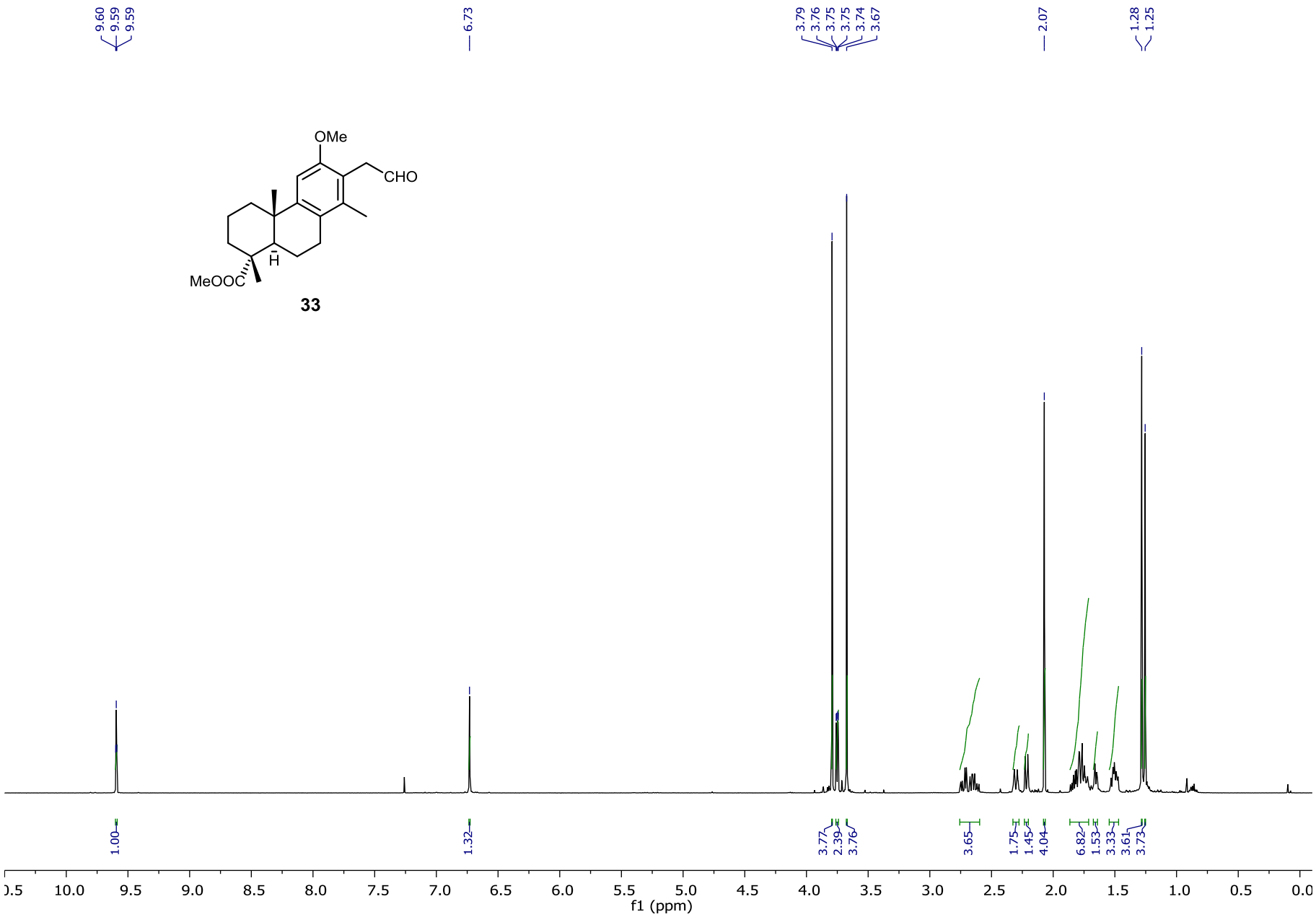
126.50
126.09
125.96
125.69
109.80
109.21
104.61
104.51
55.94
55.81
52.04
52.02
47.81
44.52
44.49
38.61
38.60
37.63
37.61
36.68
28.27
28.25
25.84
25.82
25.21
24.23
22.09
22.07
21.15
18.85
18.42
16.64
15.28
15.06
-5.05
-5.13
OMe
OTBS
H
MeOOC
32
f1 (ppm)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9.59
9.59
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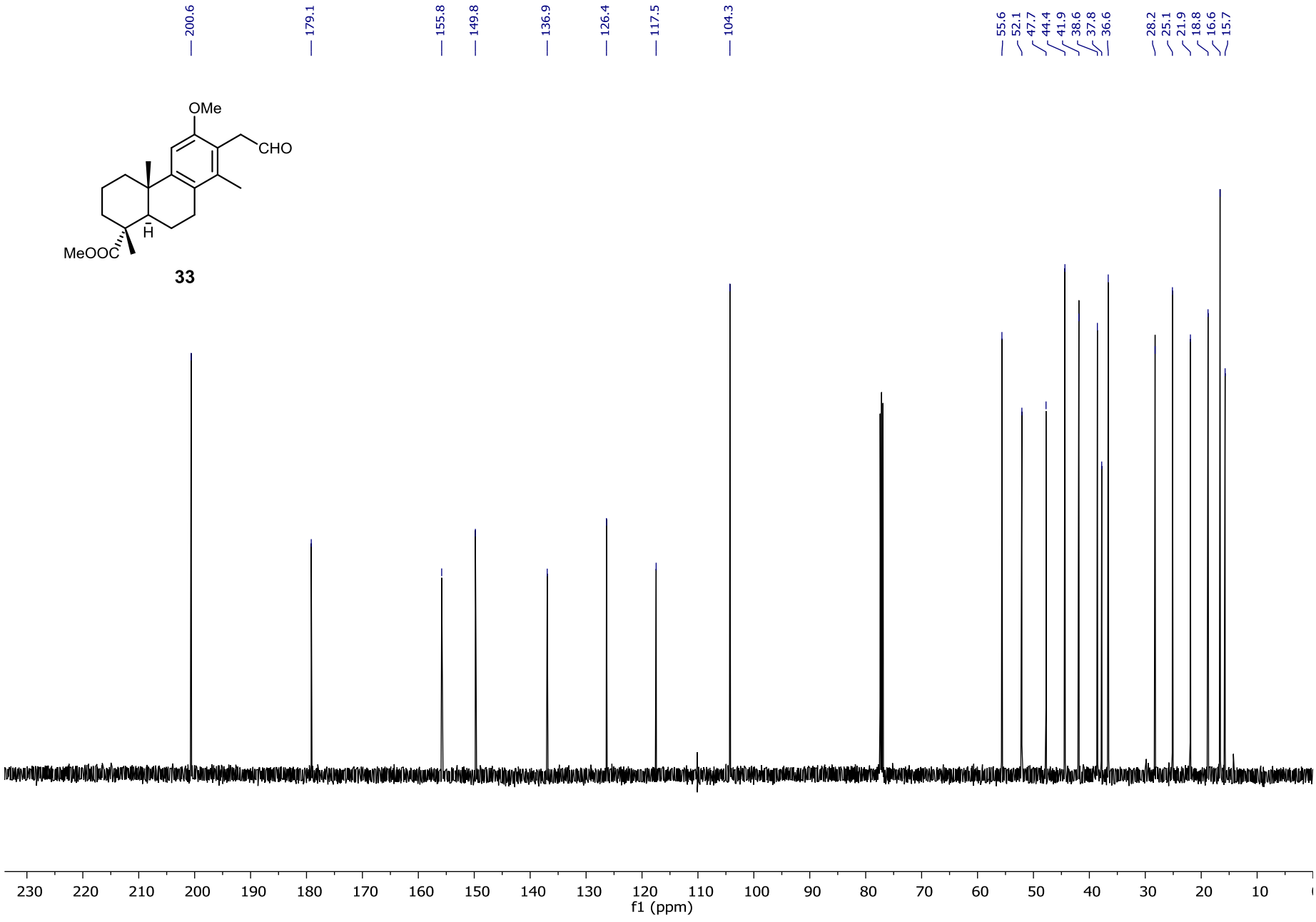
3.79
3.76
3.75
3.75
3.74
3.67
2.07
1.28
1.25
OMe
CHO
H
MeOOC
33
1.00
1.32
3.77
2.39
3.76
3.65
1.75
1.45
4.04
6.82
1.53
3.33
3.61
3.73
f1 (ppm)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136.9
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104.3
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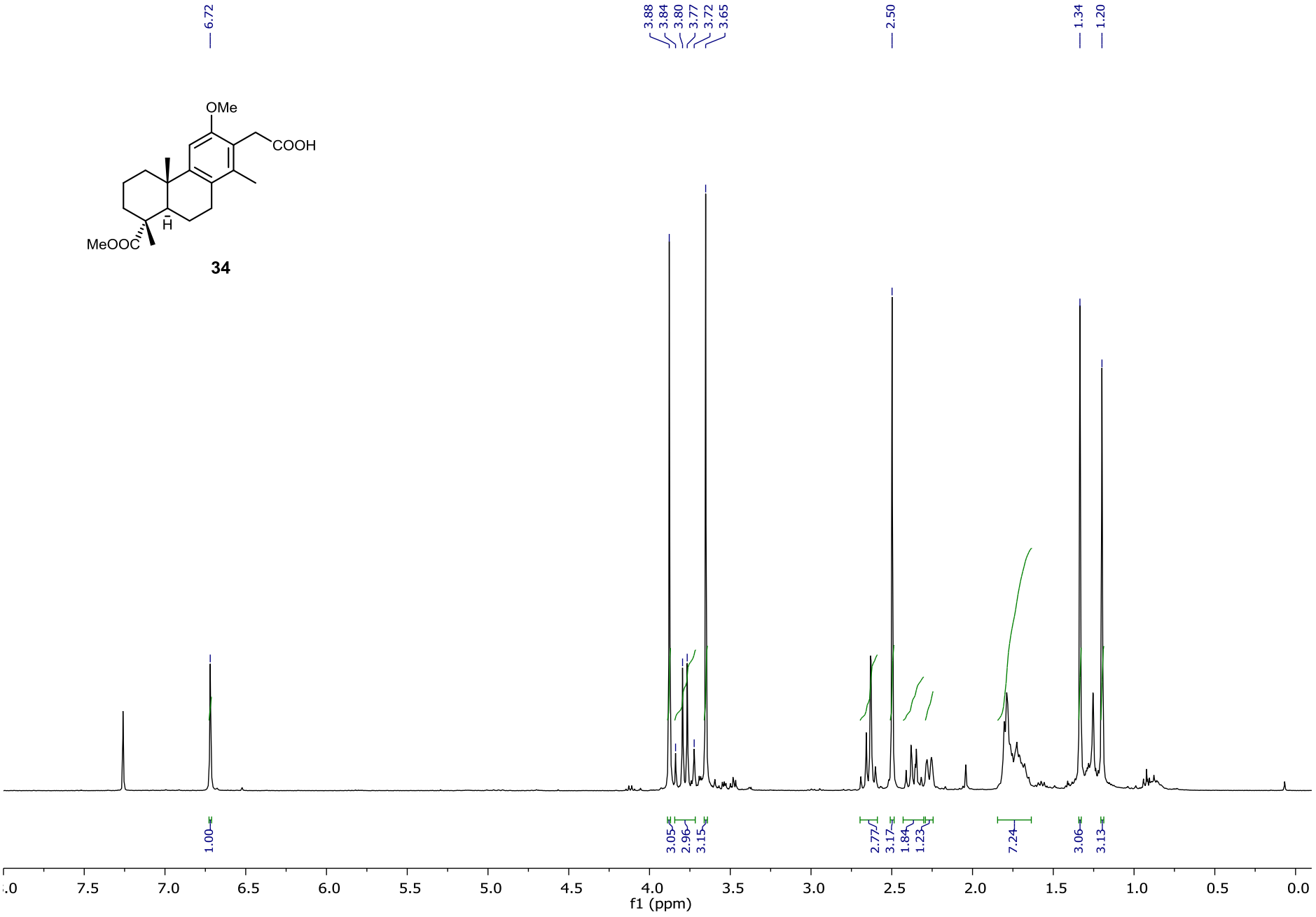
52.1
47.7
44.4
41.9
38.6
37.8
36.6
28.2
25.1
21.9
18.8
16.6
15.7
OMe
CHO
H
MeOOC
33
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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3.84
3.80
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3.72
3.65
2.50
1.34
1.20
OMe
COOH
H
MeOOC
34
1.00
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3.15
2.77
3.17
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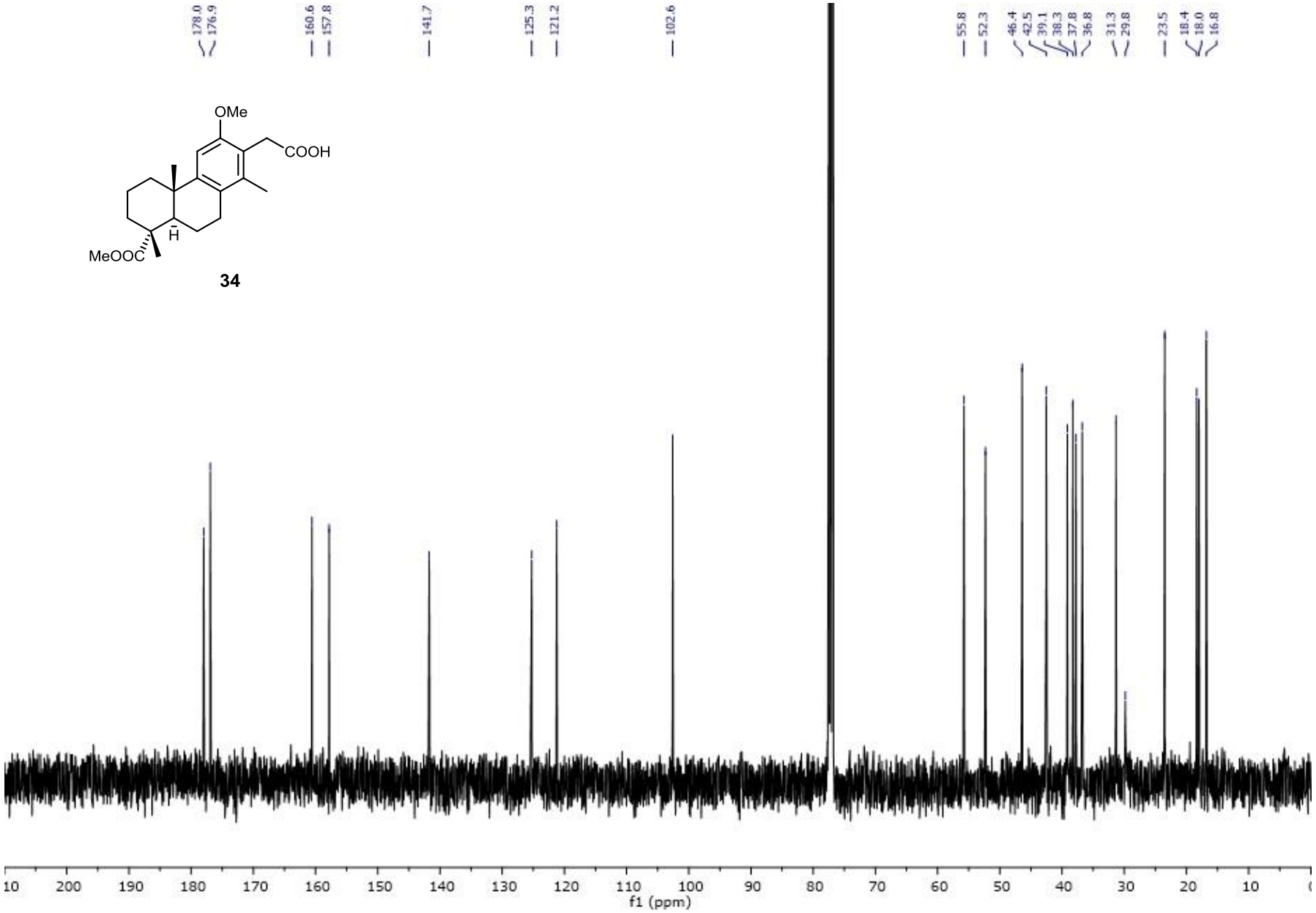
1.23
7.24
3.06
3.13
f1 (ppm)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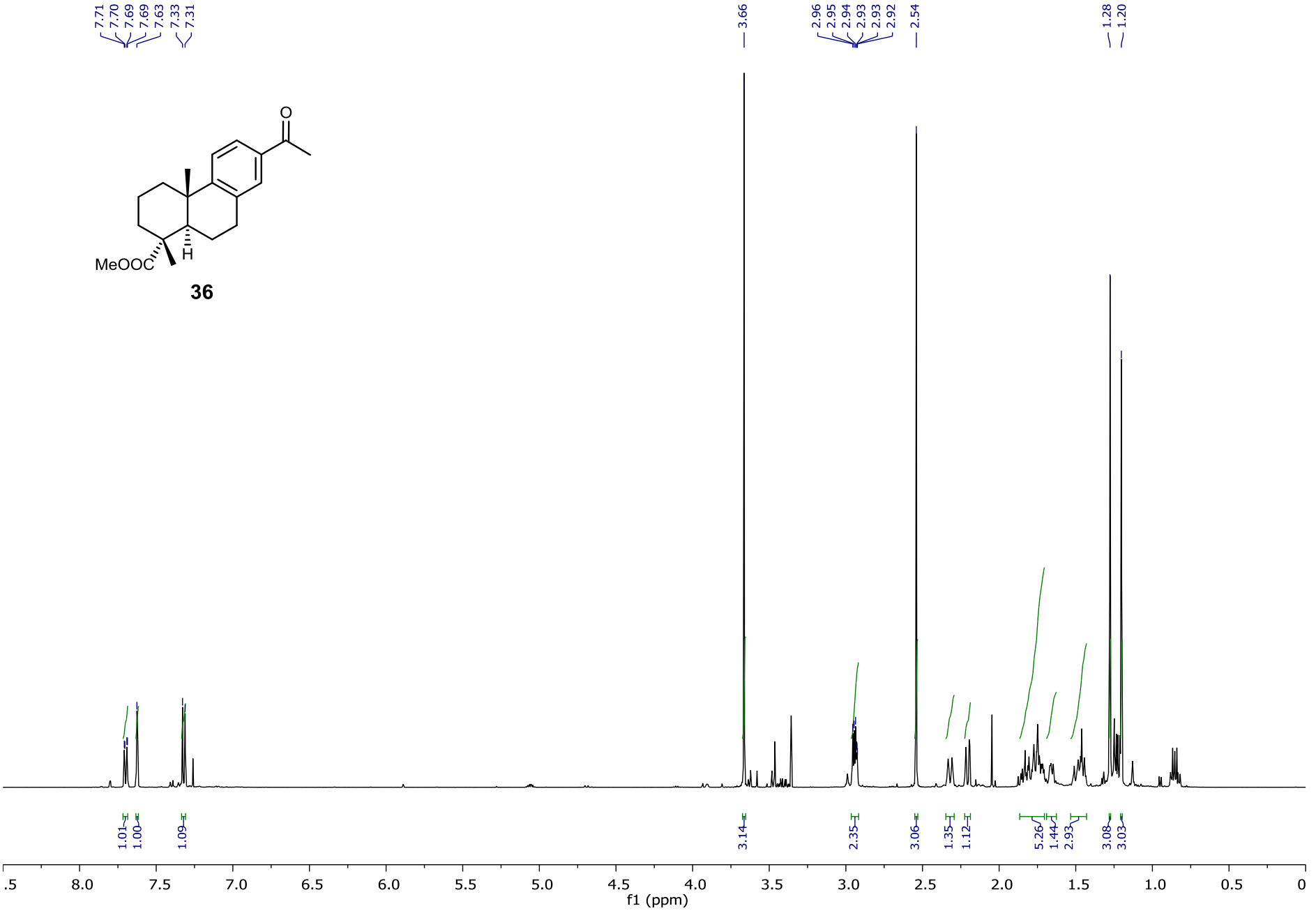
157.8
141.7
125.3
121.2
102.6
55.8
52.3
46.4
42.5
39.1
38.3
37.8
36.8
31.3
29.8
23.5
18.4
18.0
16.8
OMe
COOH
H
MeOOC
34
f1 (ppm)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2.94
2.93
2.93
2.92
2.54
1.28
1.20
O
MeOOC
H
36
1.01
1.00
1.09
3.14
2.35
3.06
1.35
1.12
5.26
1.44
2.93
3.08
3.03
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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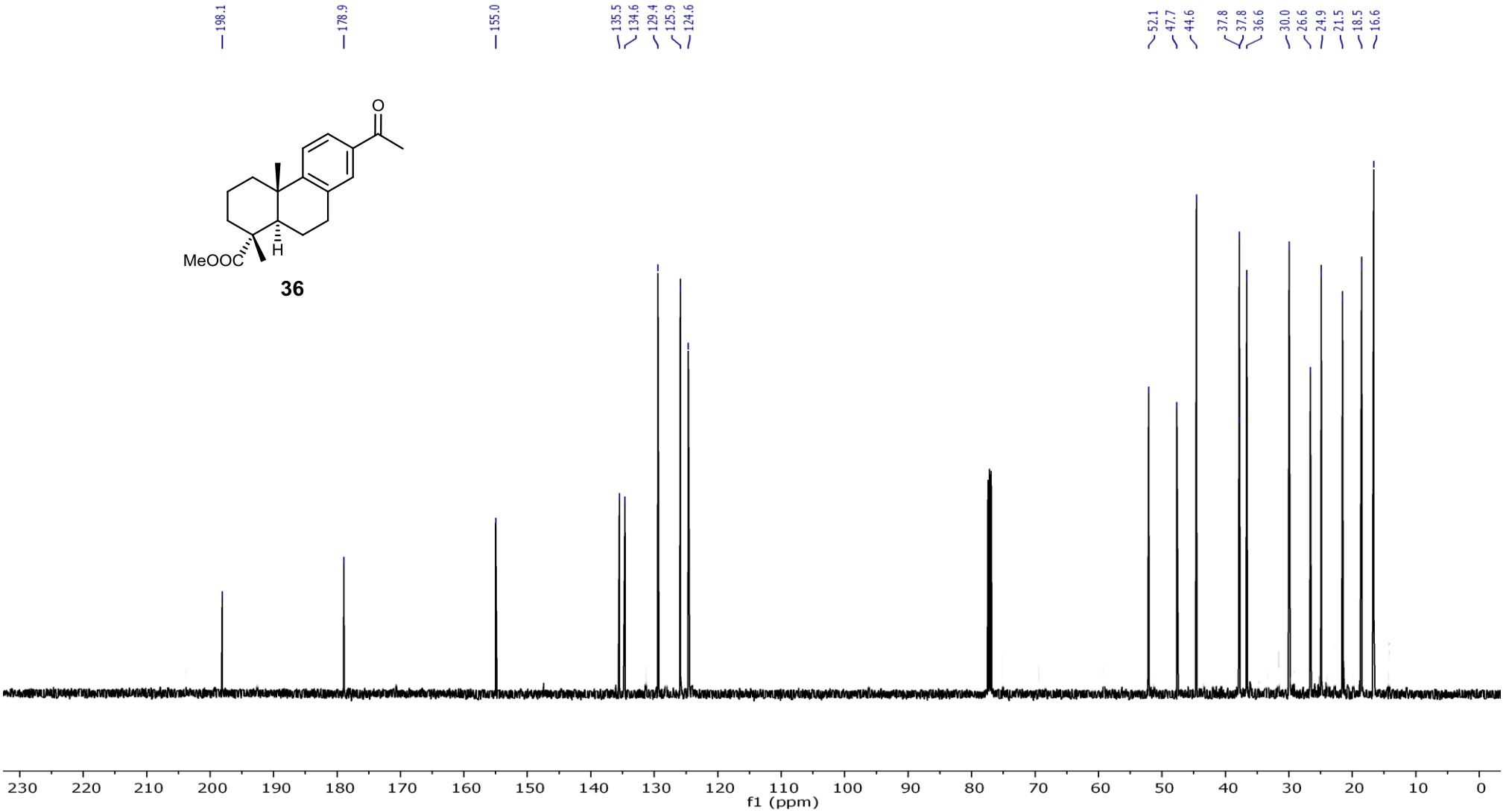
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
f1 (ppm)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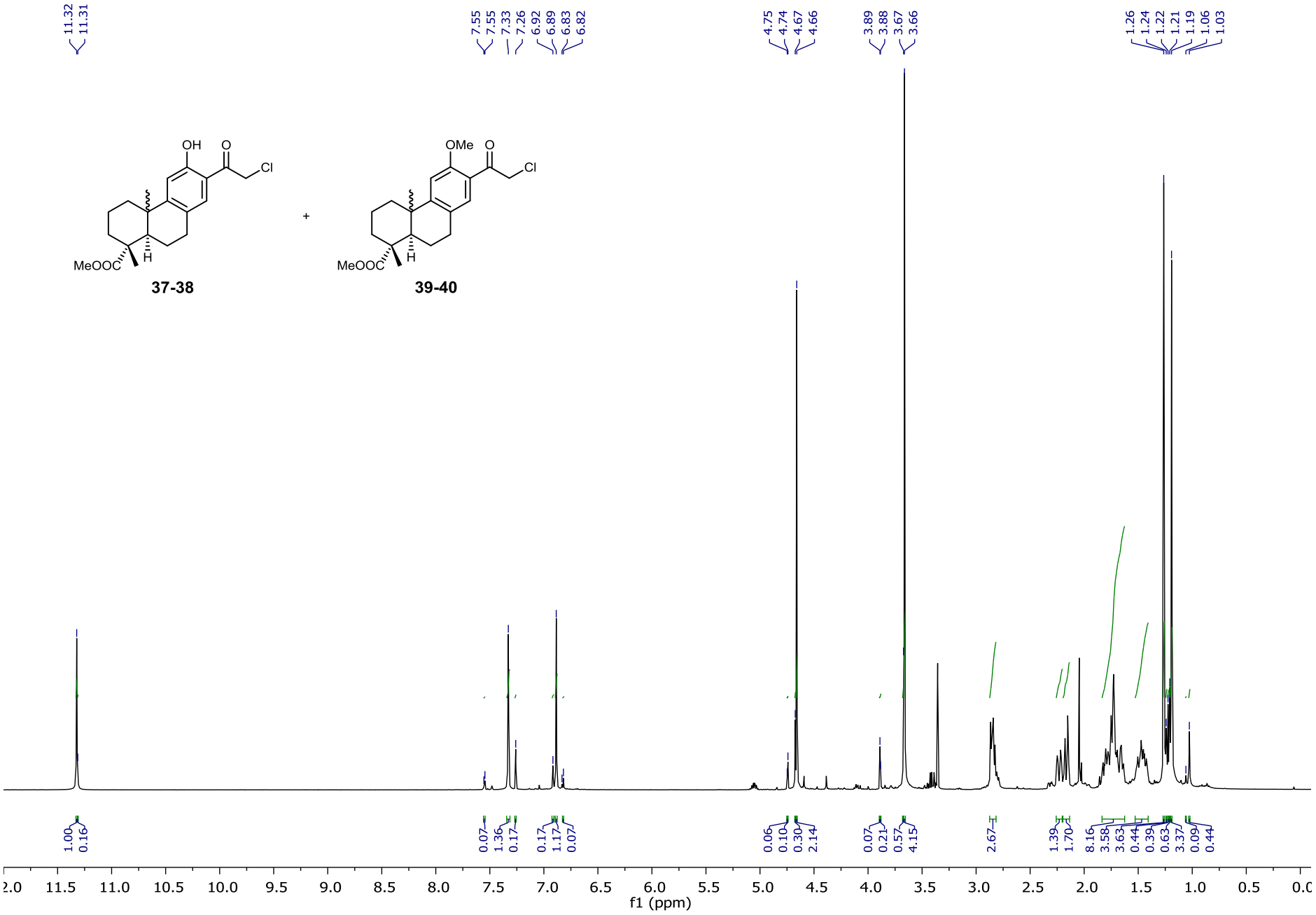
134.6
129.4
125.9
124.6
52.1
47.7
44.6
37.8
37.8
36.6
30.0
26.6
24.9
21.5
18.5
16.6
O
MeOOC
H
36
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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11.31
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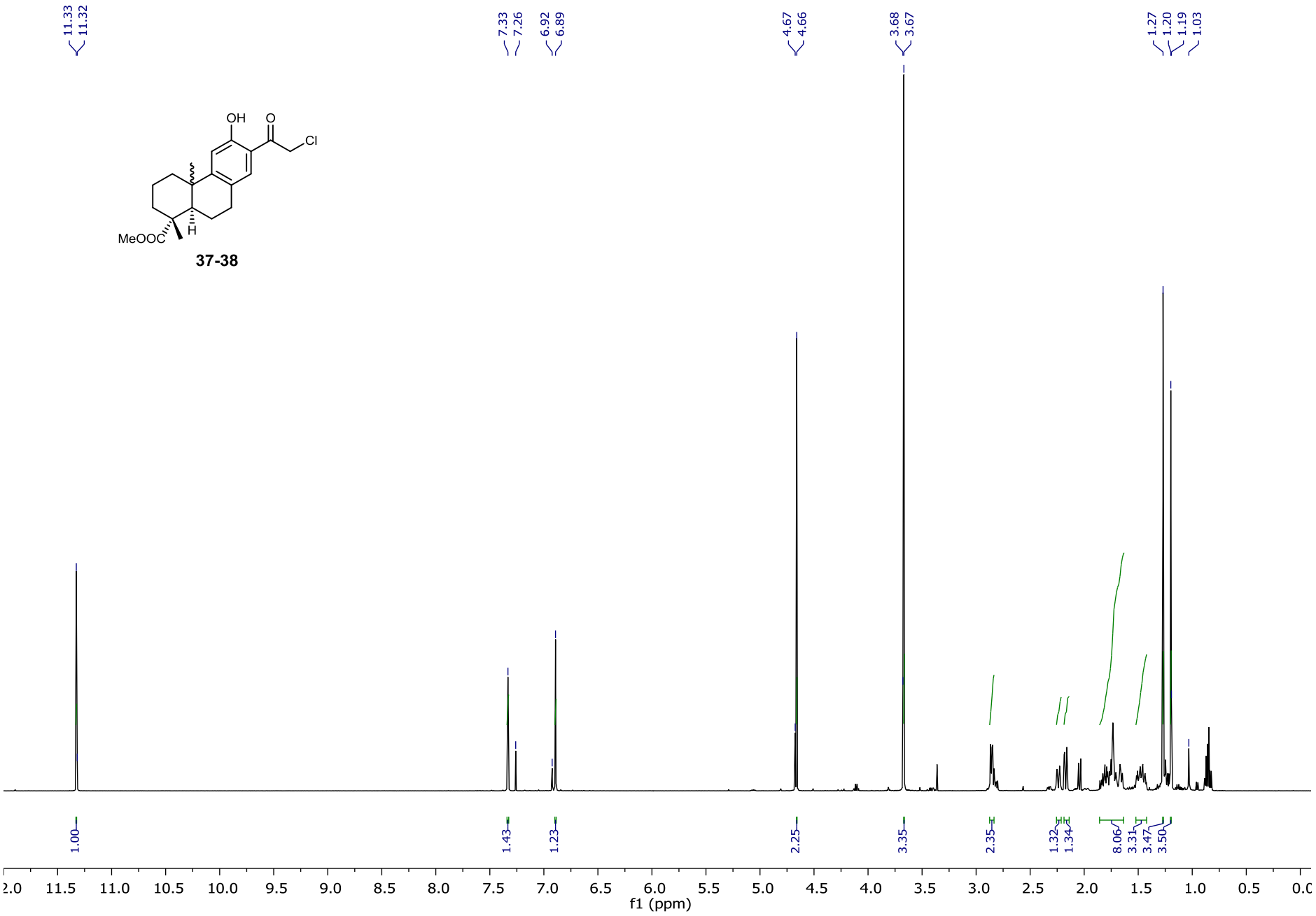
7.33
7.26
6.92
6.89
6.83
6.82
4.75
4.74
4.67
4.66
3.89
3.88
3.67
3.66
1.26
1.24
1.22
1.21
1.19
1.06
1.03
OH
O
Cl
MeOOC
H
37-38
+
OMe
O
Cl
MeOOC
H
39-40
1.00
0.16
0.07
1.36
0.17
0.17
1.17
0.07
0.06
0.10
0.30
2.14
0.07
0.21
0.57
4.15
2.67
1.39
1.70
8.16
3.58
3.63
0.44
0.39
0.63
3.37
0.09
0.44
f1 (ppm)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11.32
7.33
7.26
6.92
6.89
4.67
4.66
3.68
3.67
1.27
1.20
1.19
1.03
OH
O
Cl
MeOOC
H
37-38
1.00
1.43
1.23
2.25
3.35
2.35
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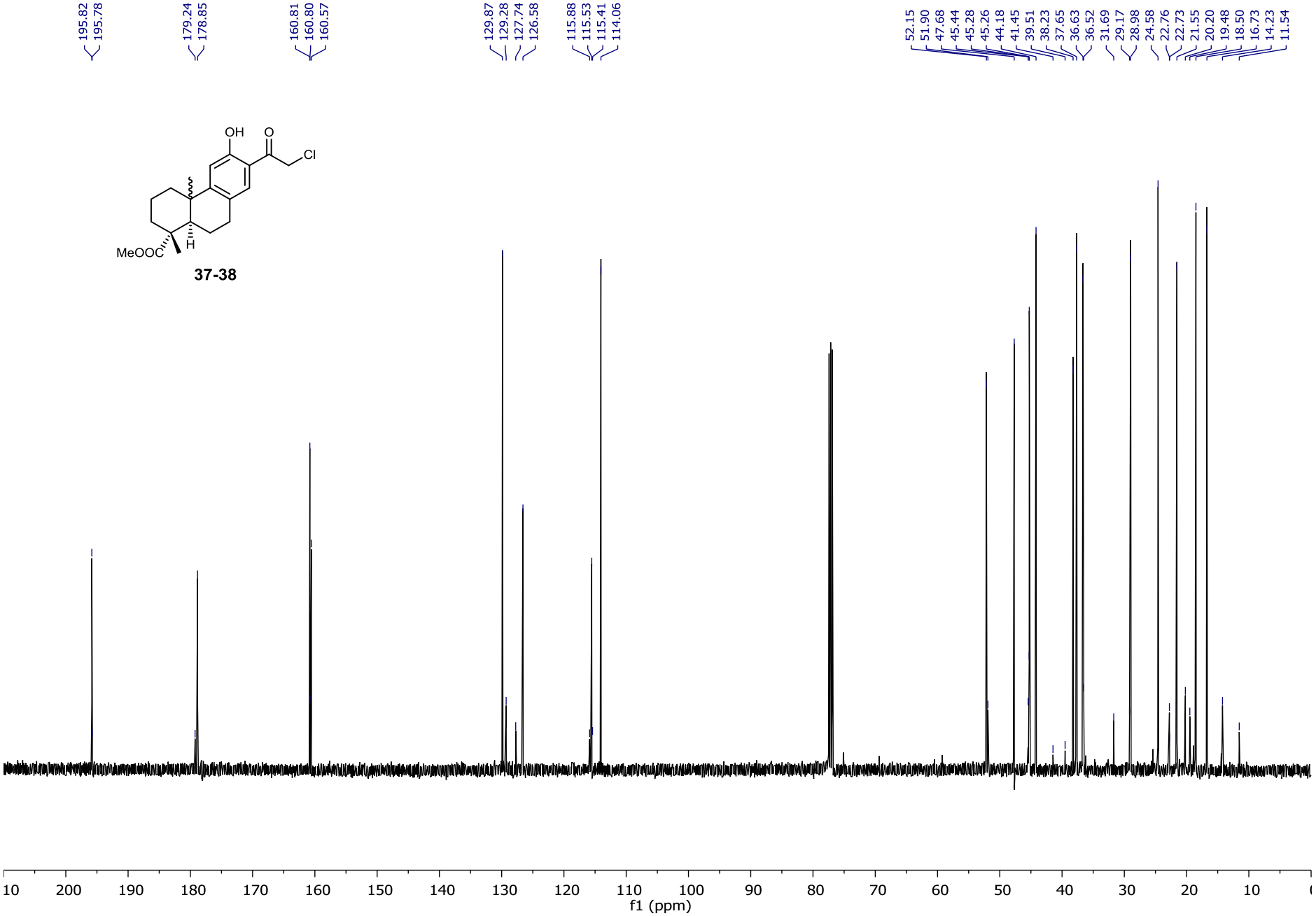
1.34
8.06
3.31
3.47
3.50
f1 (ppm)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160.80
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129.87
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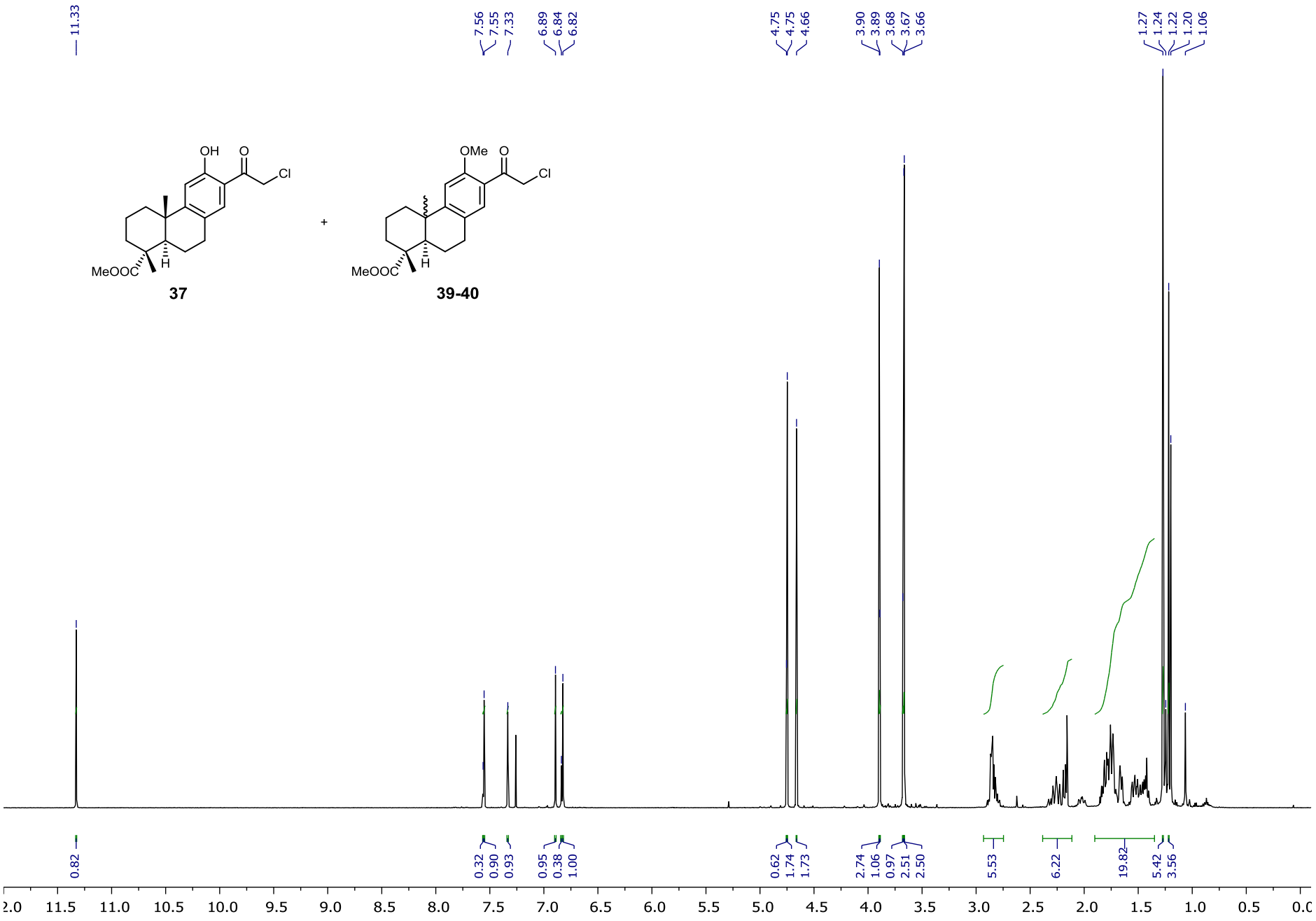
127.74
126.58
115.88
115.53
115.41
114.06
52.15
51.90
47.68
45.44
45.28
45.26
44.18
41.45
39.51
38.23
37.65
36.63
36.52
31.69
29.17
28.98
24.58
22.76
22.73
21.55
20.20
19.48
18.50
16.73
14.23
11.54
OH
O
Cl
MeOOC
H
37-38
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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4.75
4.75
4.66
3.90
3.89
3.68
3.67
3.66
1.27
1.24
1.22
1.20
1.06
OH
O
Cl
MeOOC
H
37
+
OMe
O
Cl
MeOOC
H
39-40
0.82
0.32
0.90
0.93
0.95
0.38
1.00
0.62
1.74
1.73
2.74
1.06
0.97
2.51
2.50
5.53
6.22
19.82
5.42
3.56
2.0
11.5
11.0
10.5
10.0
9.5
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6.5
6.0
5.5
5.0
4.5
4.0
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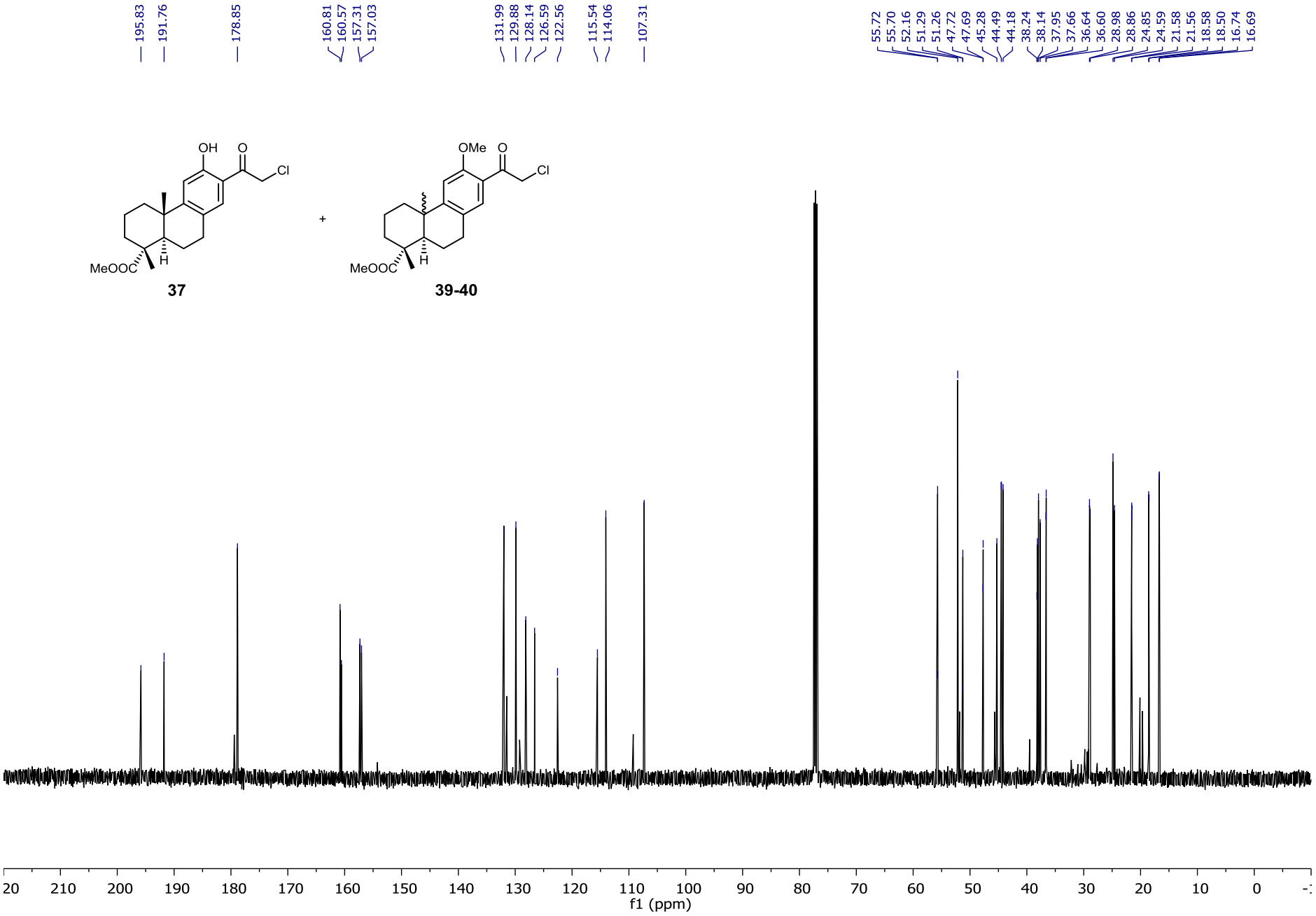
3.0
2.5
2.0
1.5
1.0
0.5
0.0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157.31
157.03
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128.14
126.59
122.56
115.54
114.06
107.31
55.72
55.70
52.16
51.29
51.26
47.72
47.69
45.28
44.49
44.18
38.24
38.14
37.95
37.66
36.64
36.60
28.98
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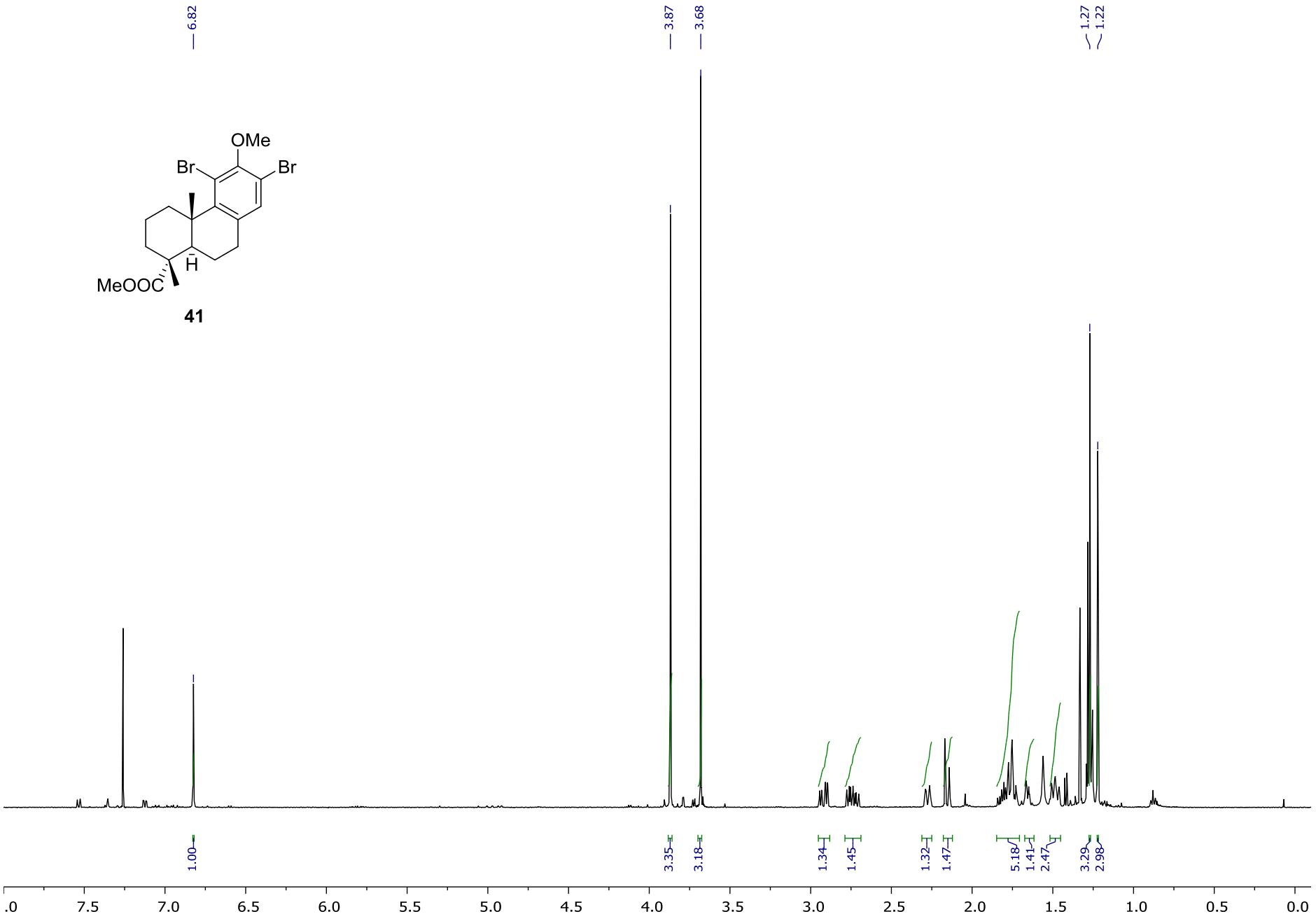
24.59
21.58
21.56
18.58
18.50
16.74
16.69
OH
O
Cl
MeOOC
H
37
+
OMe
O
Cl
MeOOC
H
39-40
f1 (ppm)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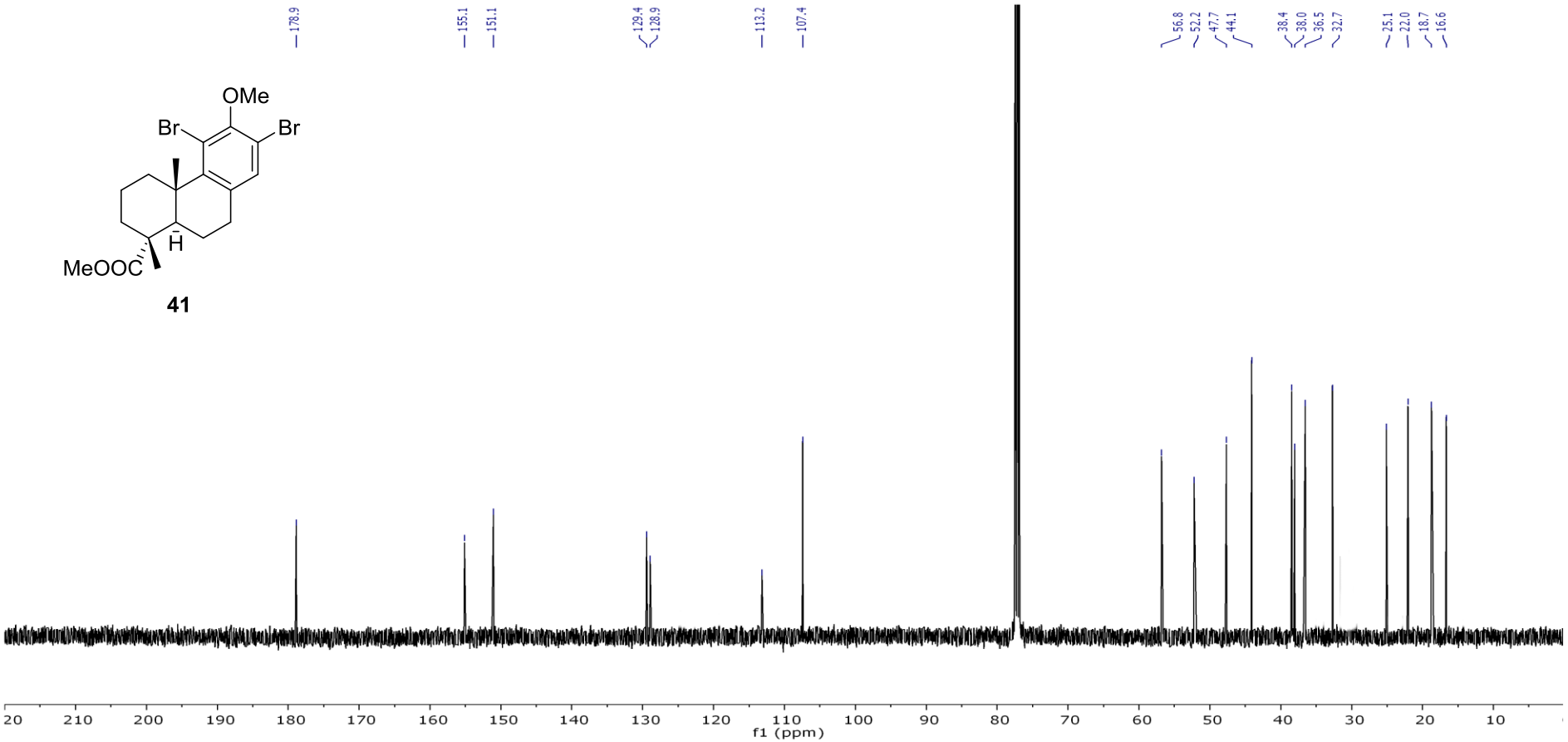
3.87
3.68
1.27
1.22
OMe
Br
Br
H
MeOOC
41
1.00
3.35
3.18
1.34
1.45
1.32
1.47
5.18
1.41
2.47
3.29
2.98
.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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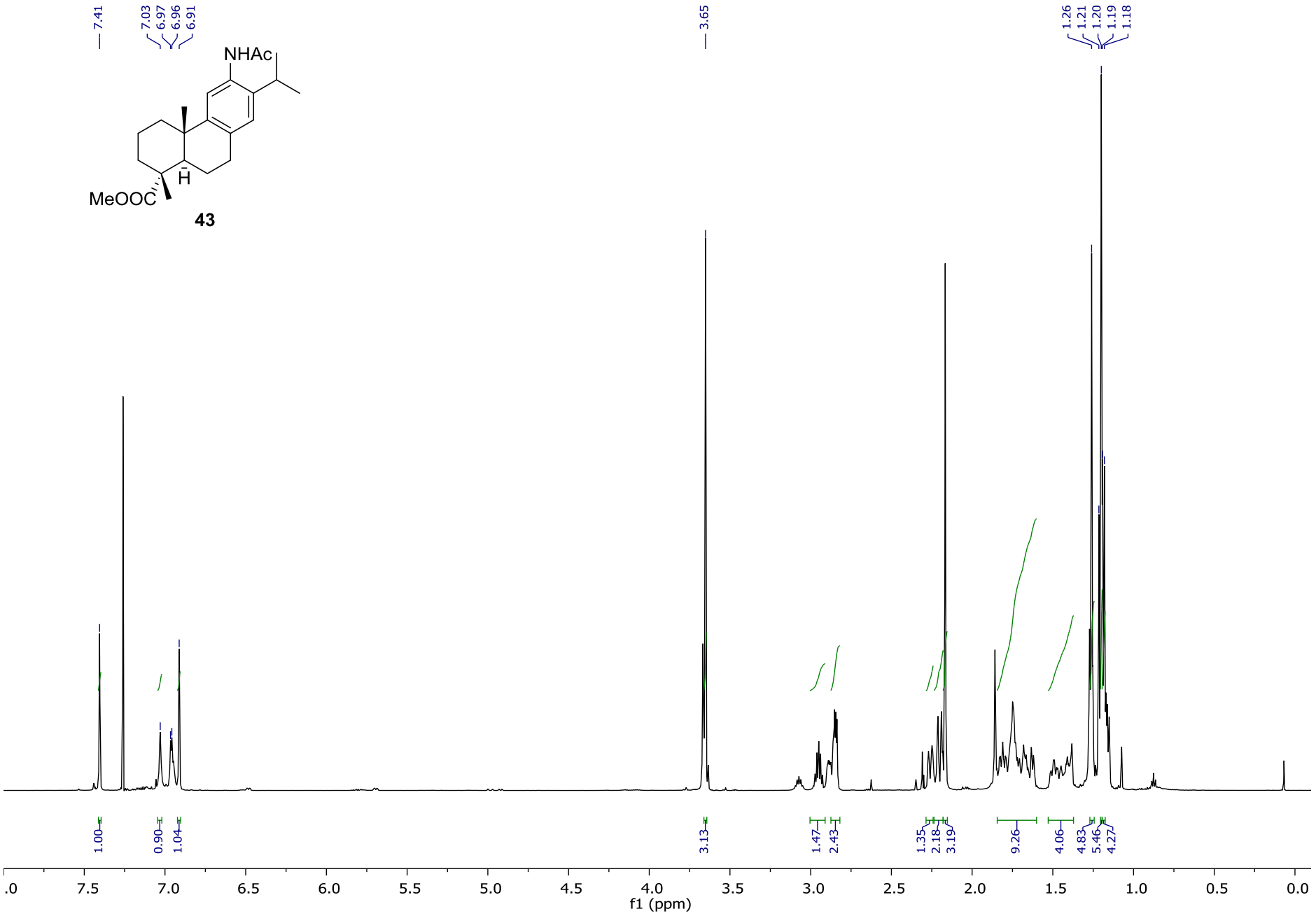
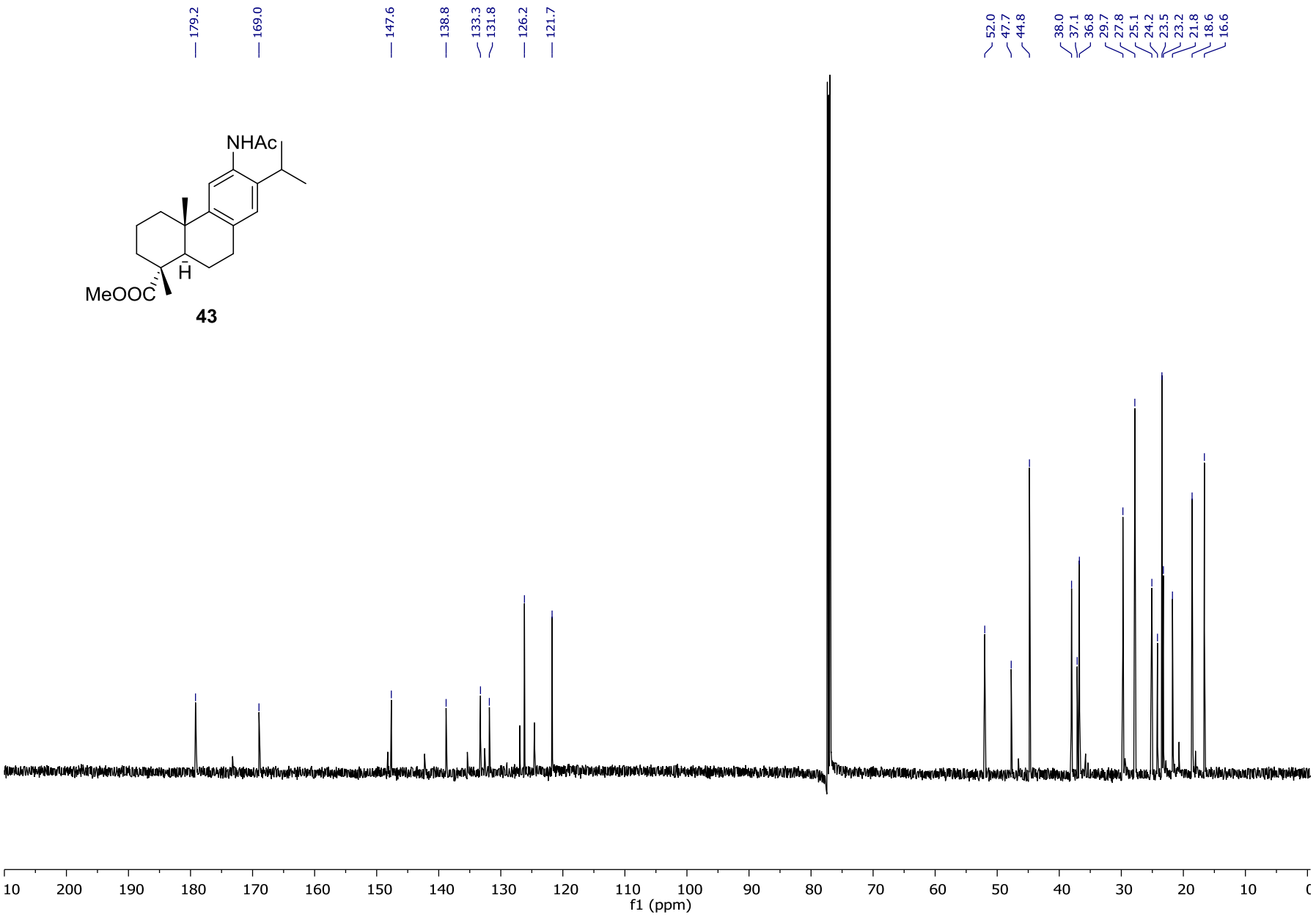
155.1
151.1
129.4
128.9
113.2
107.4
56.8
52.2
47.7
44.1
38.4
38.0
36.5
32.7
25.1
22.0
18.7
16.6
OMe
Br
Br
H
MeOOC
41
f1 (ppm)


7.41
7.03
6.97
6.96
6.91
3.65
1.26
1.21
1.20
1.19
1.18
NHAc
H
MeOOC
43
1.00
0.90
1.04
3.13
1.47
2.43
1.35
2.18
3.19
9.26
4.06
4.83
5.46
4.27
f1 (ppm)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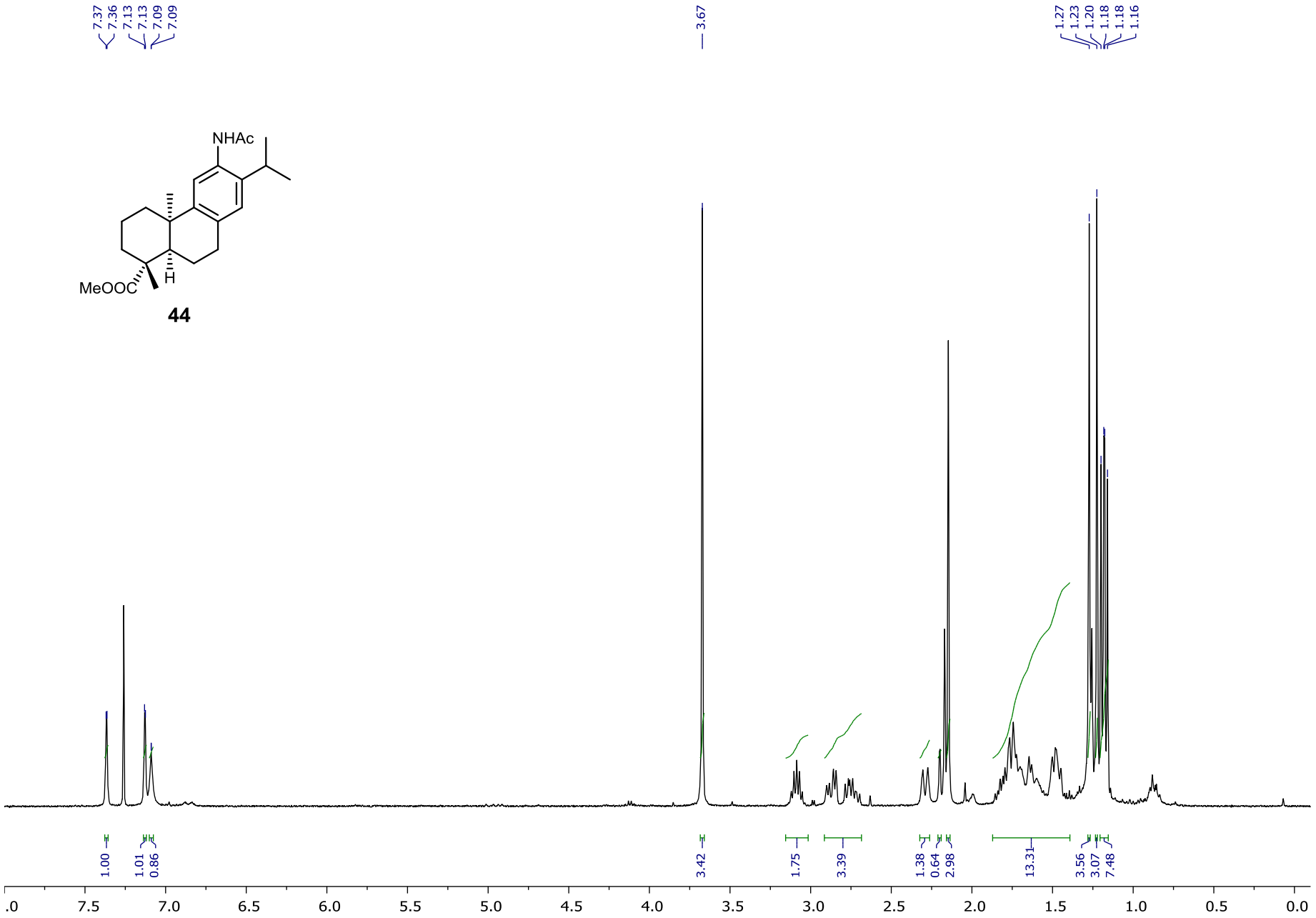
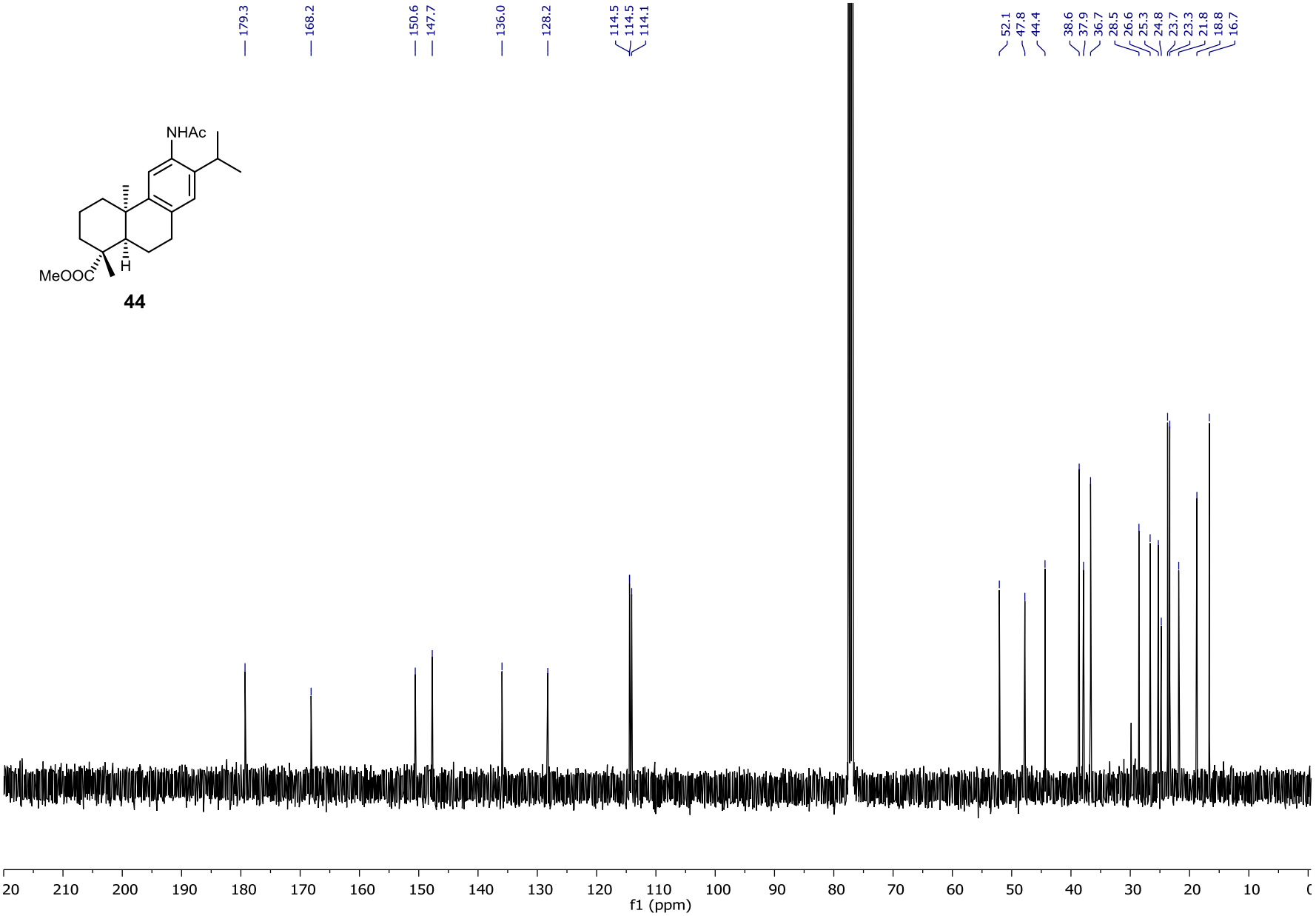
169.0
147.6
138.8
133.3
131.8
126.2
121.7
52.0
47.7
44.8
38.0
37.1
36.8
29.7
27.8
25.1
24.2
23.5
23.2
21.8
18.6
16.6
NHAc
H
MeOOC
43
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


7.37
7.36
7.13
7.13
7.09
7.09
3.67
1.27
1.23
1.20
1.18
1.18
1.16
NHAc
MeOOC
H
44
1.00
1.01
0.86
3.42
1.75
3.39
1.38
0.64
2.98
13.31
3.56
3.07
7.48
.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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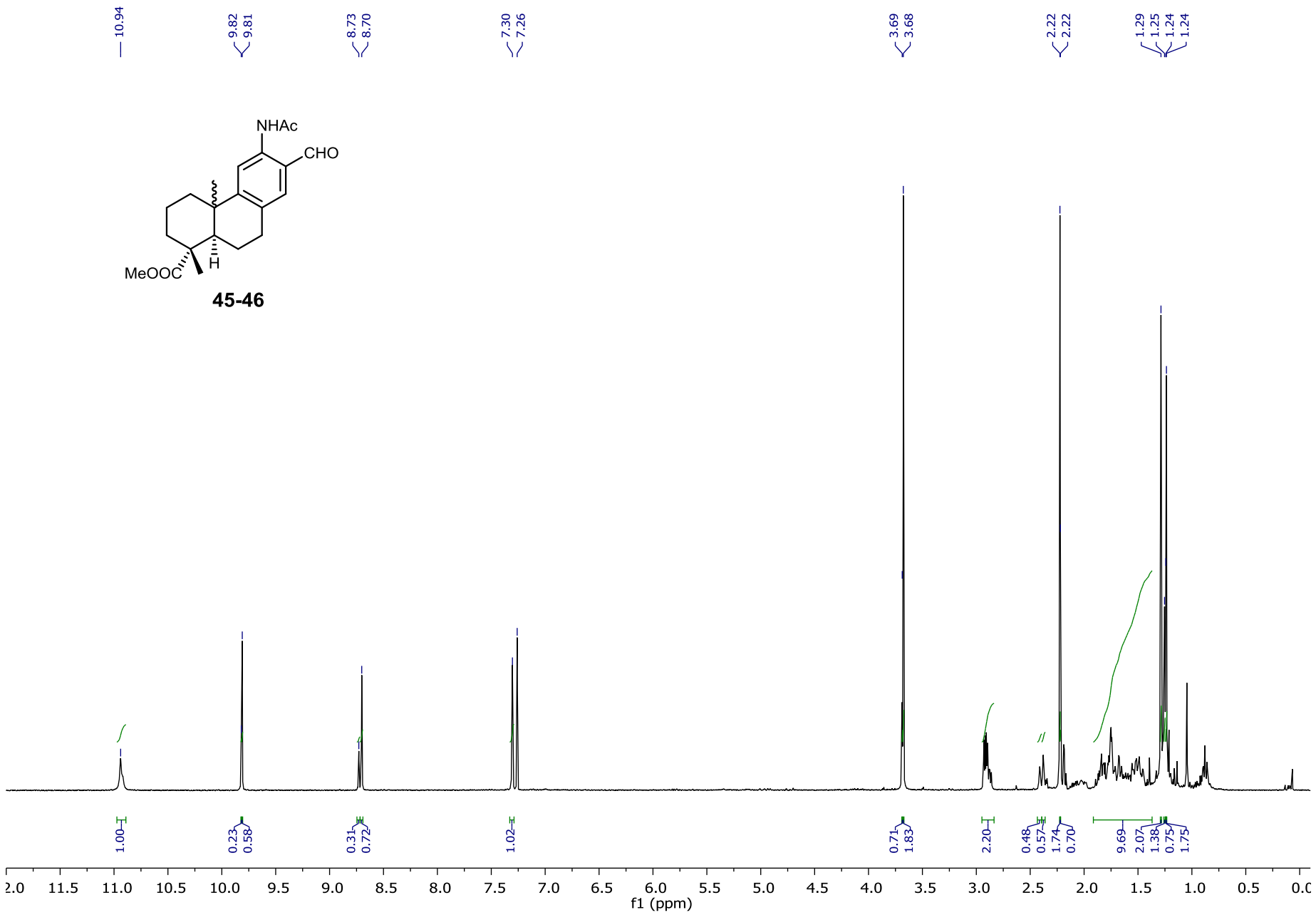
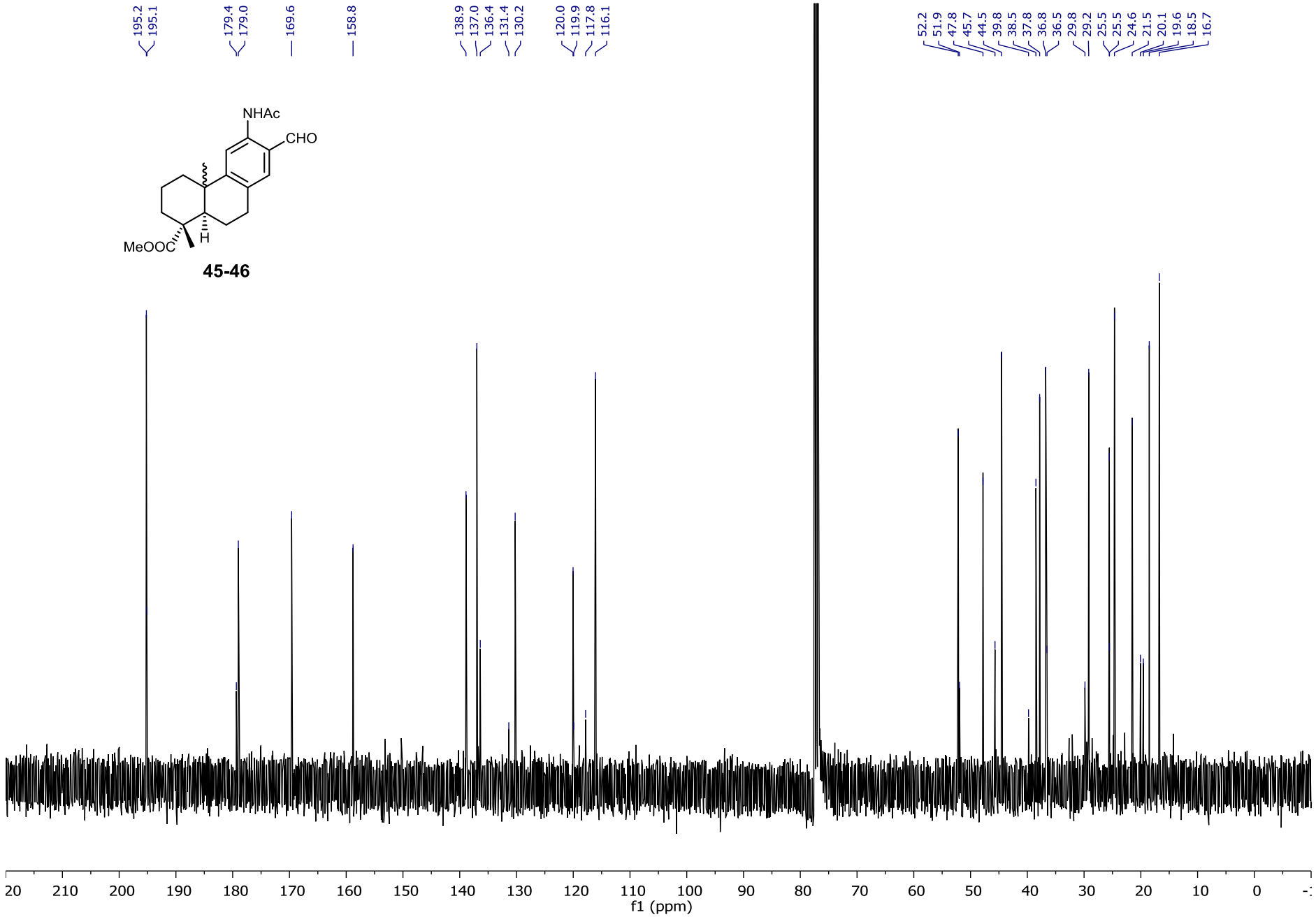
168.2
150.6
147.7
136.0
128.2
114.5
114.5
114.1
52.1
47.8
44.4
38.6
37.9
36.7
28.5
26.6
25.3
24.8
23.7
23.3
21.8
18.8
16.7
NHAc
MeOOC
H
44
f1 (ppm)


10.94
9.82
9.81
8.73
8.70
7.30
7.26
3.69
3.68
2.22
2.22
1.29
1.25
1.24
1.24
NHAc
CHO
MeOOC
H
45-46
1.00
0.23
0.58
0.31
0.72
1.02
0.71
1.83
2.20
0.48
0.57
1.74
0.70
9.69
2.07
1.38
0.75
1.75
f1 (ppm)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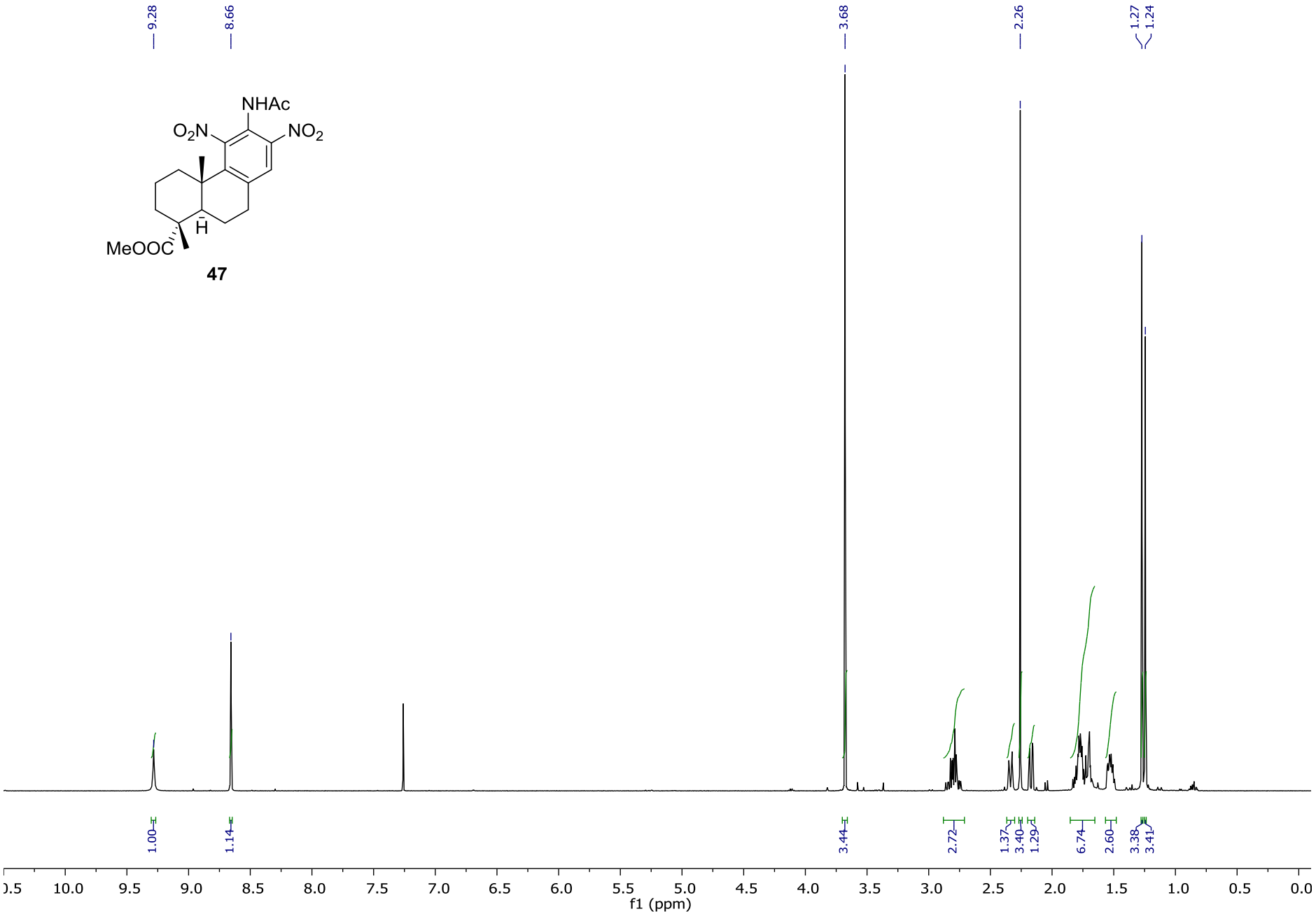
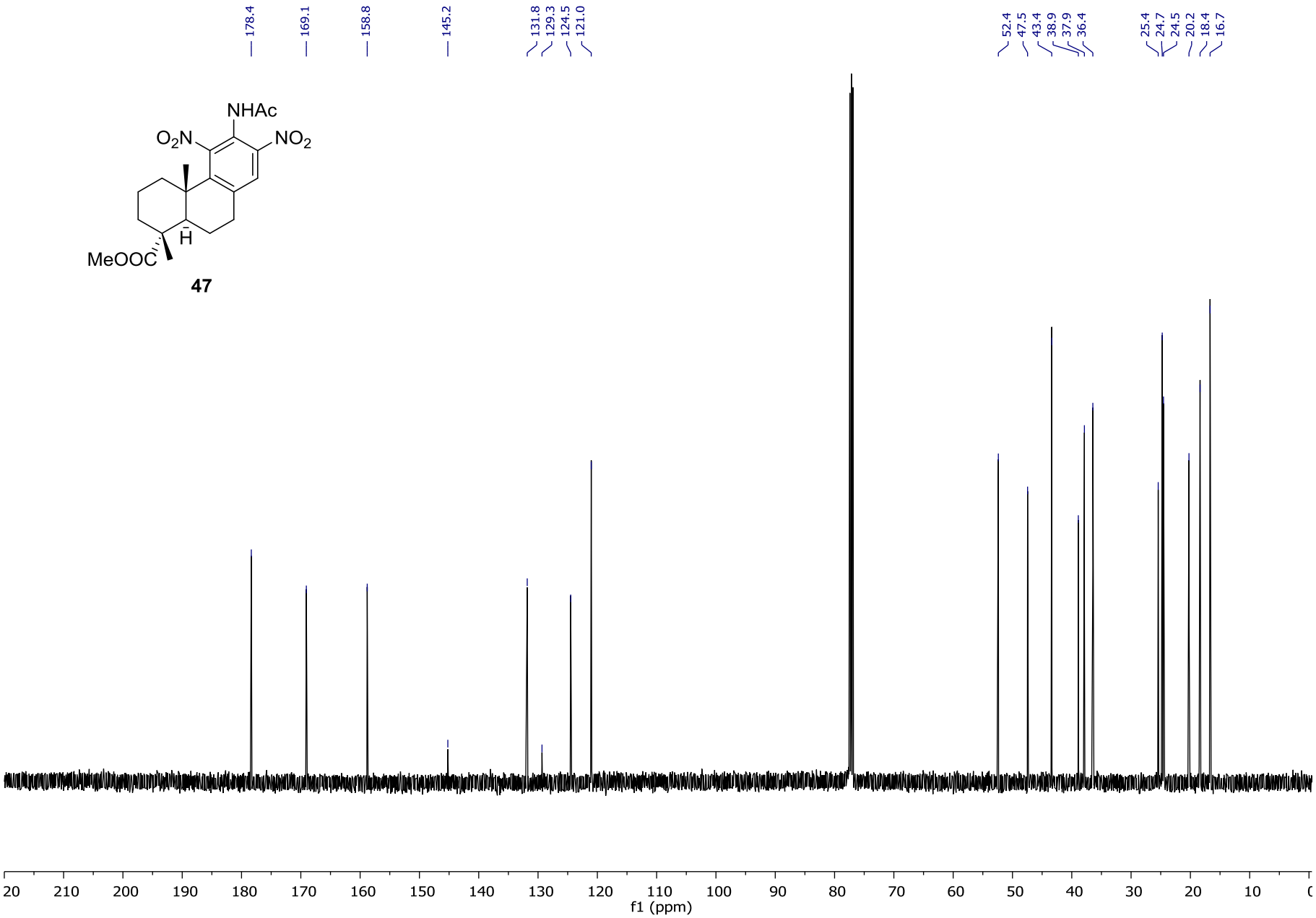
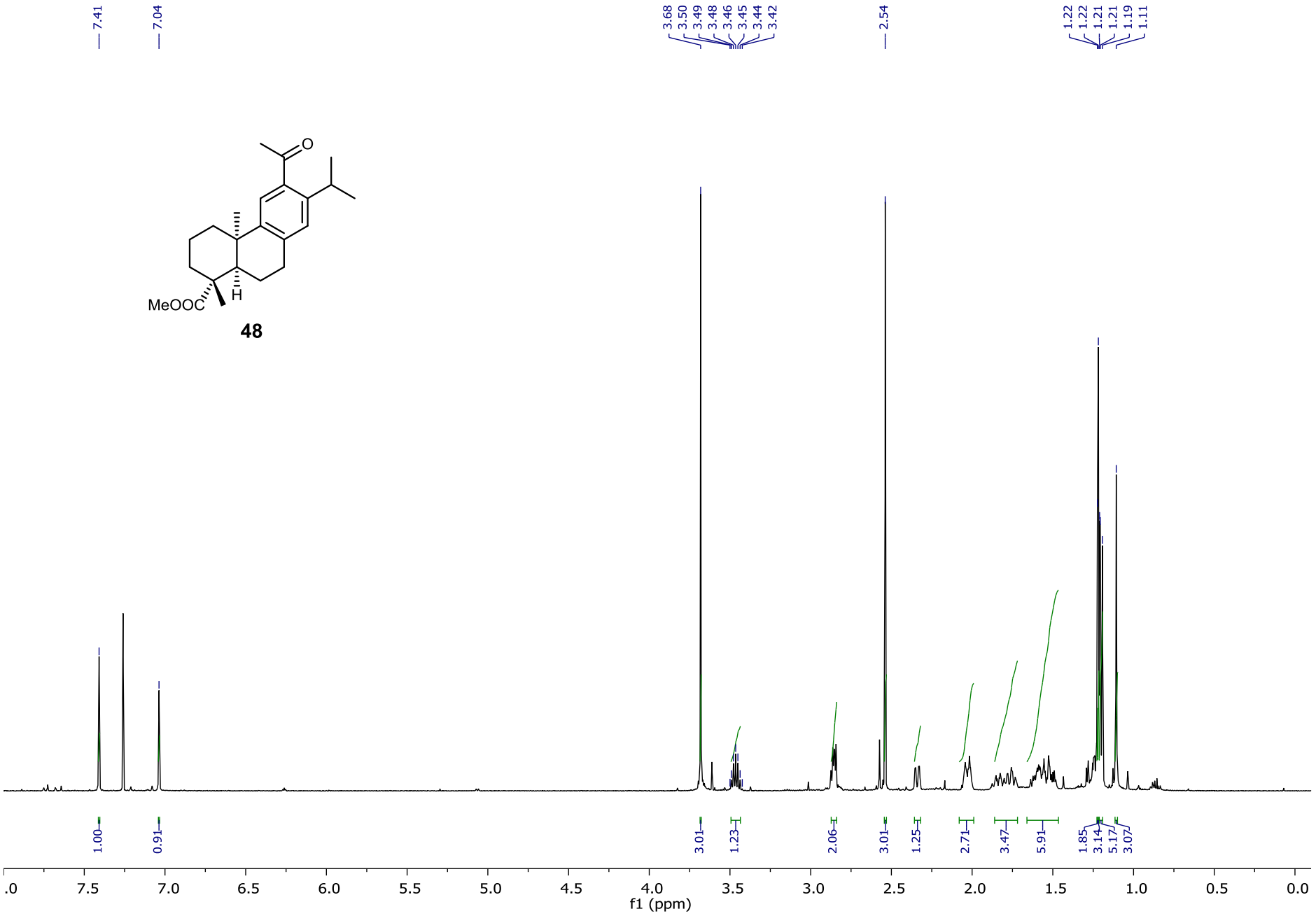
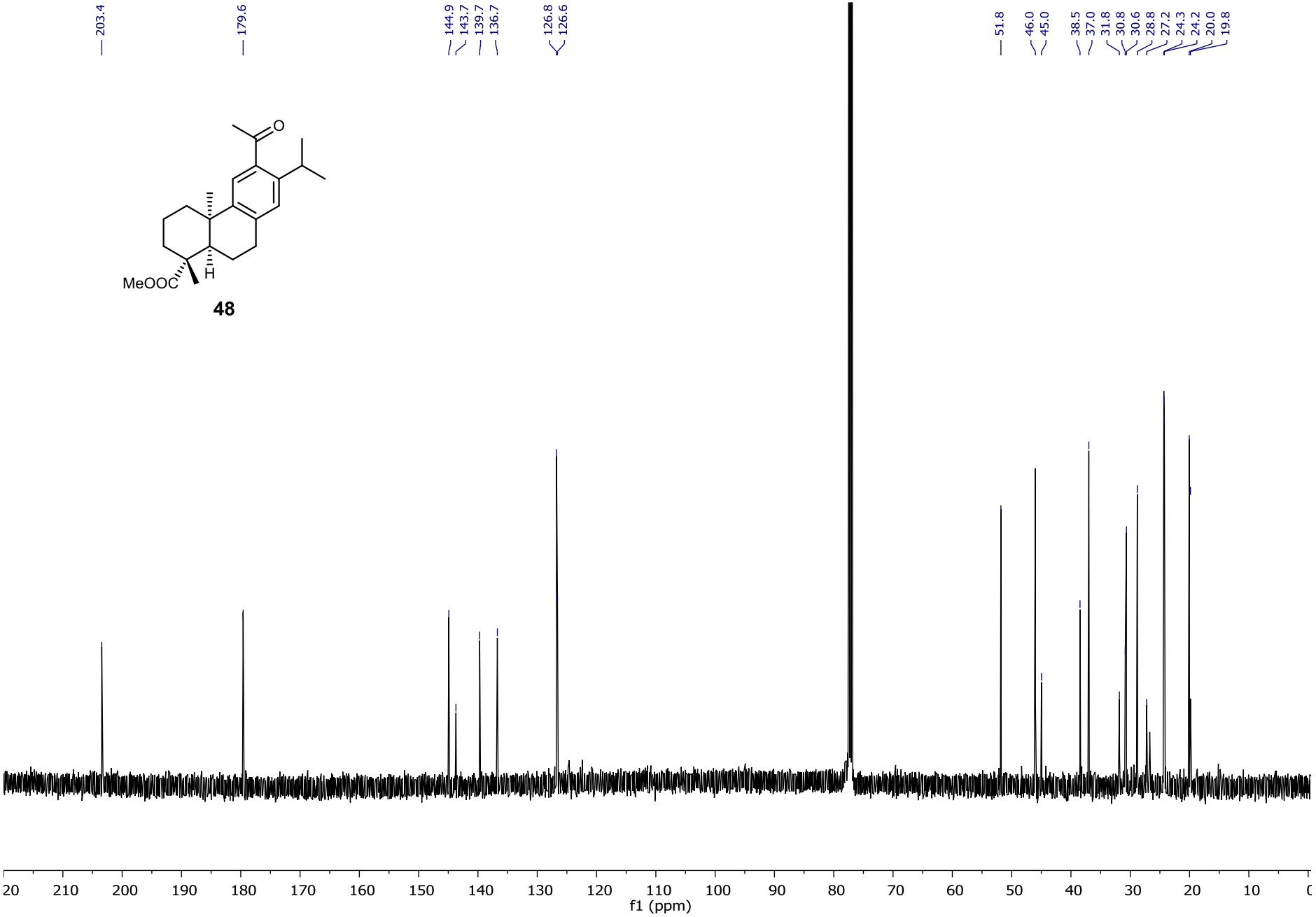
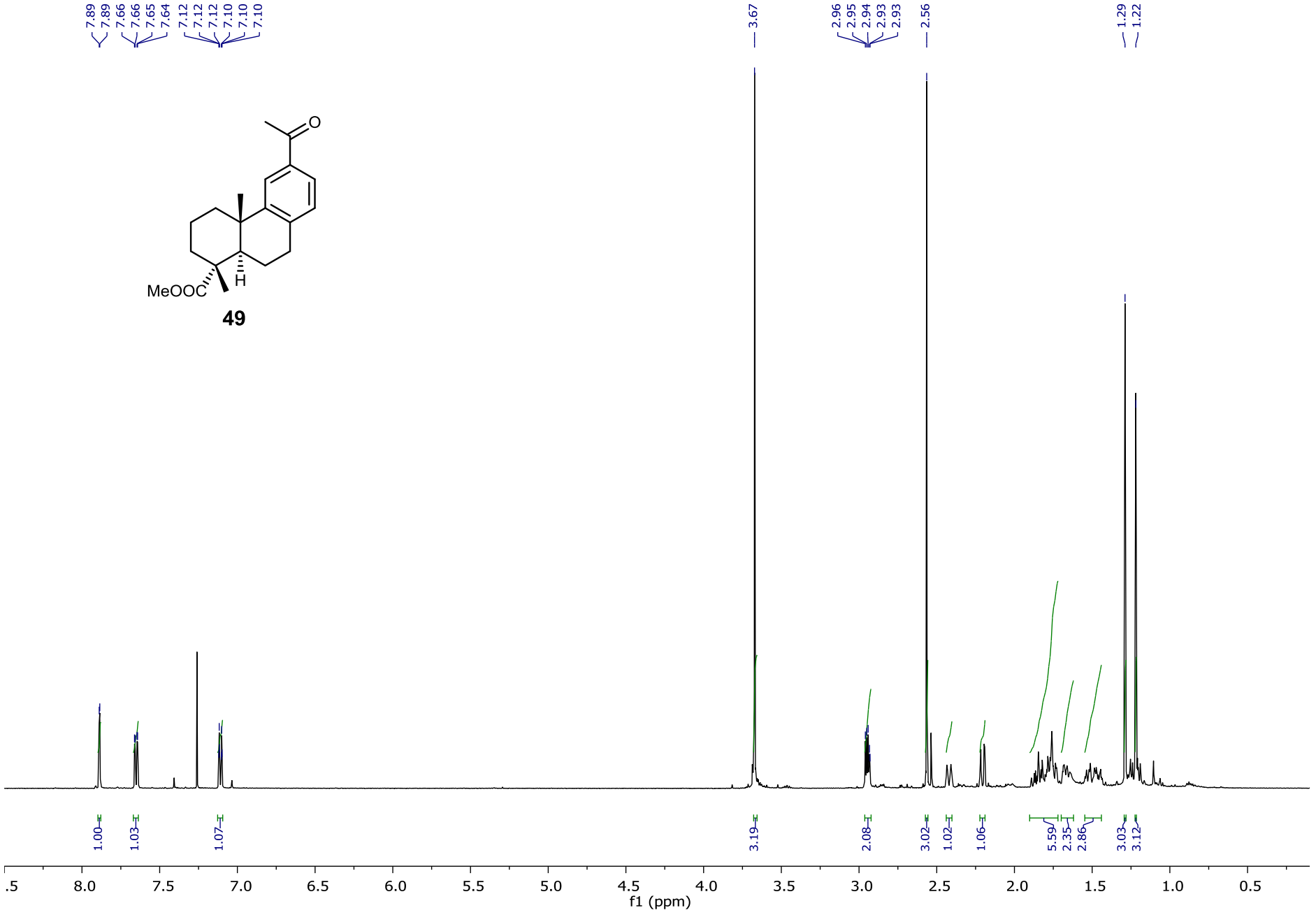
195.1
179.4
179.0
169.6
158.8
138.9
137.0
136.4
131.4
130.2
120.0
119.9
117.8
116.1
52.2
51.9
47.8
45.7
44.5
39.8
38.5
37.8
36.8
36.5
29.8
29.2
25.5
25.5
24.6
21.5
20.1
19.6
18.5
16.7
NHAc
CHO
MeOOC
H
45-46
f1 (ppm)

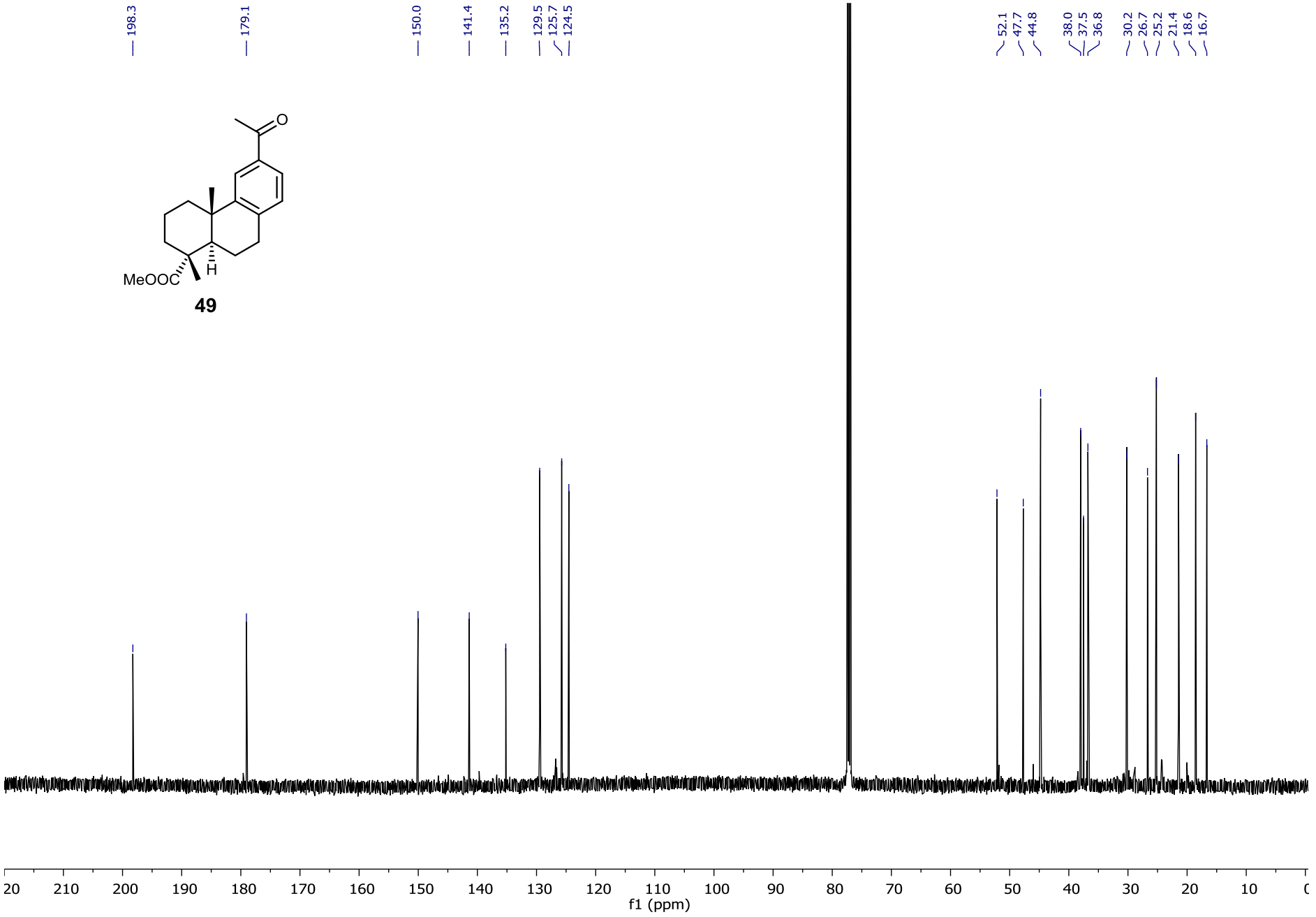

9.28
8.66
3.68
2.26
1.27
1.24
NHAc
O2N
NO2
H
MeOOC
47
1.00
1.14
3.44
2.72
1.37
3.40
1.29
6.74
2.60
3.38
3.41
f1 (ppm)


178.4
169.1
158.8
145.2
131.8
129.3
124.5
121.0
52.4
47.5
43.4
38.9
37.9
36.4
25.4
24.7
24.5
20.2
18.4
16.7
NHAc
O2N
NO2
H
MeOOC
47
f1 (ppm)


7.41
7.04
3.68
3.50
3.49
3.48
3.46
3.45
3.44
3.42
2.54
1.22
1.22
1.21
1.21
1.19
1.11
O
MeOOC
H
48
1.00
0.91
3.01
1.23
2.06
3.01
1.25
2.71
3.47
5.91
1.85
3.14
5.17
3.07
.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)


203.4
179.6
144.9
143.7
139.7
136.7
126.8
126.6
51.8
46.0
45.0
38.5
37.0
31.8
30.8
30.6
28.8
27.2
24.3
24.2
20.0
19.8
O
H
MeOOC
48
f1 (ppm)


7.89
7.89
7.66
7.66
7.65
7.64
7.12
7.12
7.12
7.10
7.10
7.10
3.67
2.96
2.95
2.94
2.93
2.93
2.56
1.29
1.22
O
MeOOC
H
49
1.00
1.03
1.07
3.19
2.08
3.02
1.02
1.06
5.59
2.35
2.86
3.03
3.12
.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
f1 (ppm)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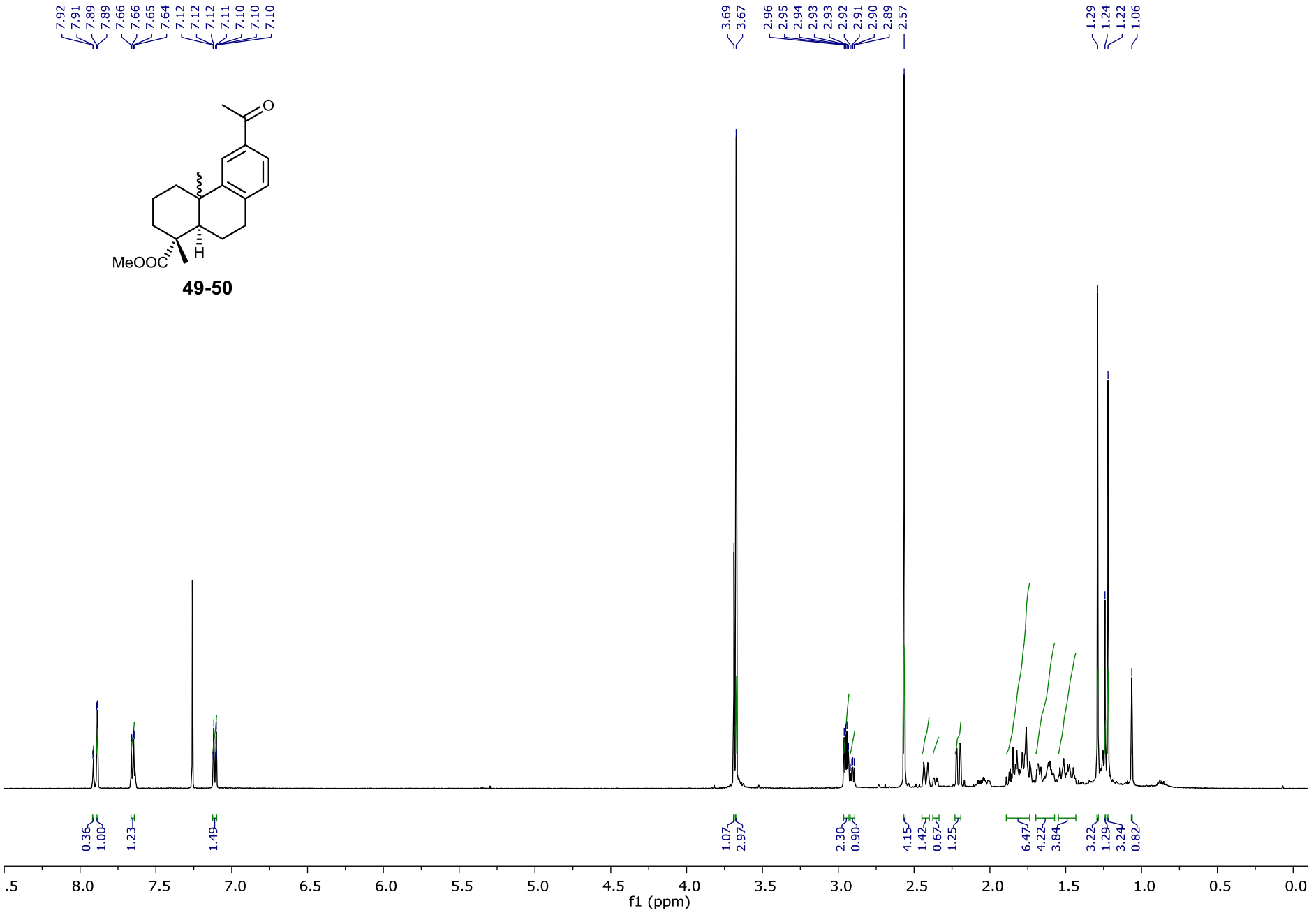
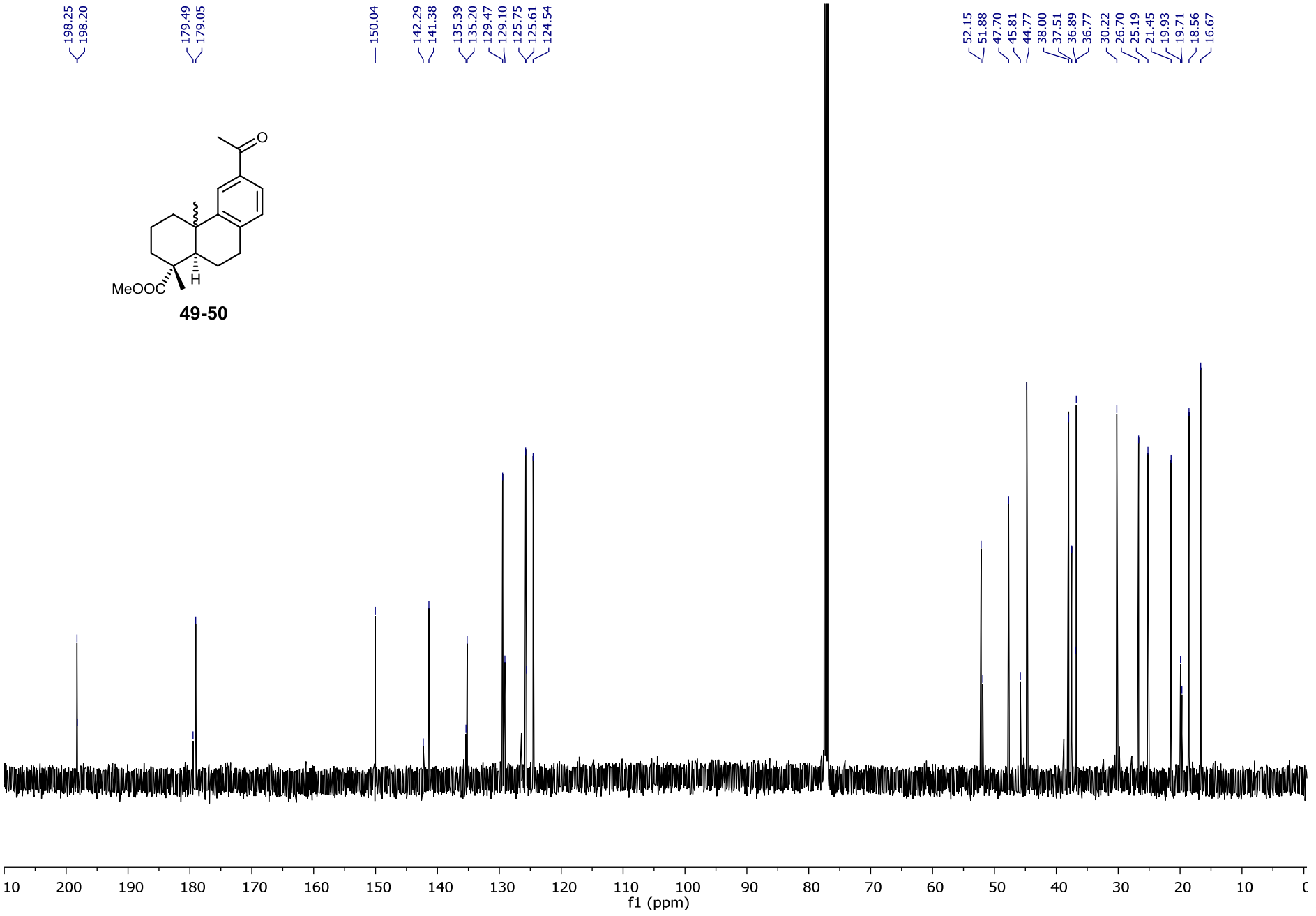
179.1
150.0
141.4
135.2
129.5
125.7
124.5
52.1
47.7
44.8
38.0
37.5
36.8
30.2
26.7
25.2
21.4
18.6
16.7
O
H
MeOOC
49
f1 (ppm)


7.92
7.91
7.89
7.89
7.66
7.66
7.65
7.64
7.12
7.12
7.12
7.11
7.10
7.10
7.10
3.69
3.67
2.96
2.95
2.94
2.93
2.93
2.92
2.91
2.90
2.89
2.57
1.29
1.24
1.22
1.06
O
MeOOC
H
49-50
0.36
1.00
1.23
1.49
1.07
2.97
2.30
0.90
4.15
1.42
0.67
1.25
6.47
4.22
3.84
3.22
1.29
3.24
0.82
.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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198.20
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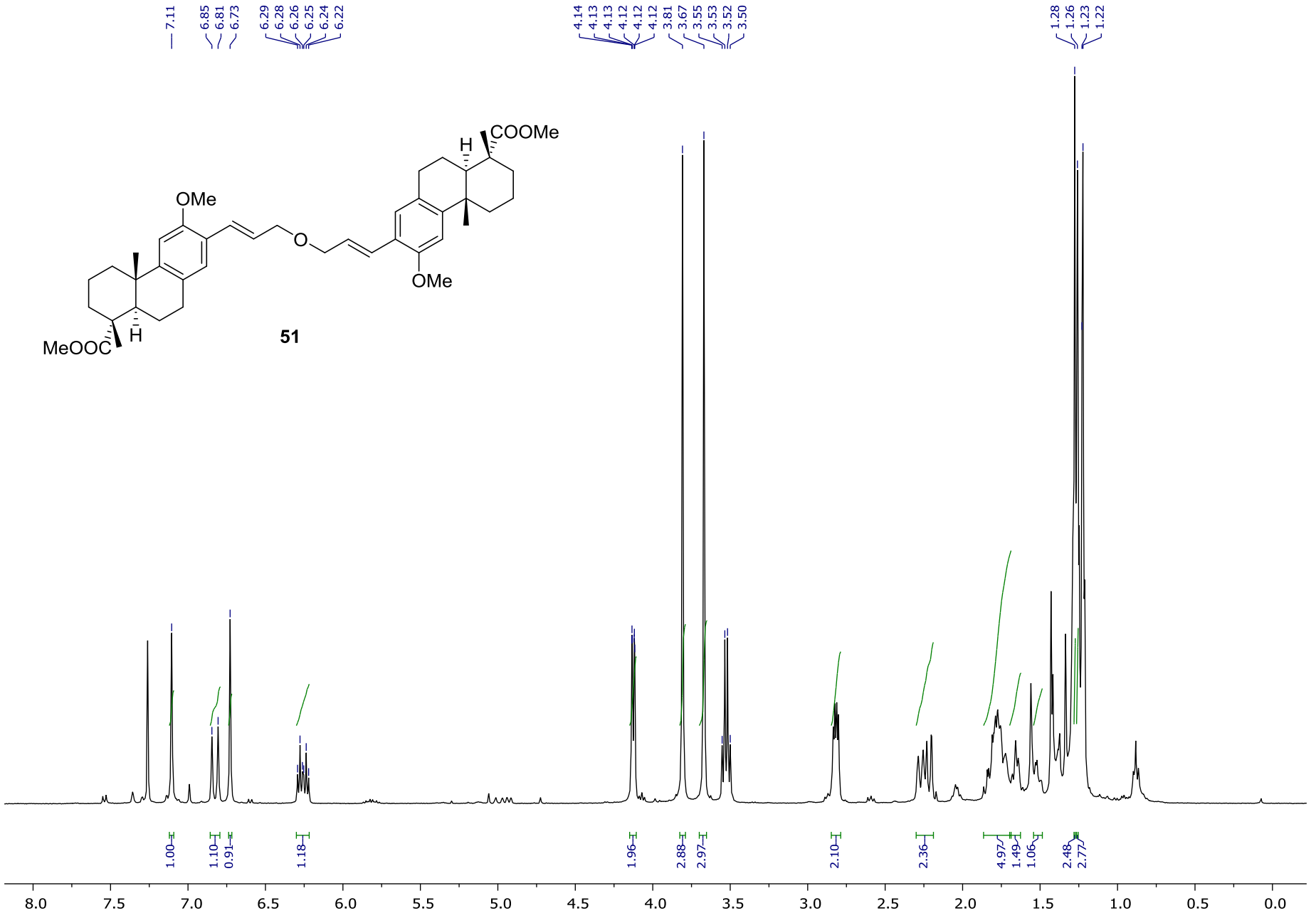
141.38
135.39
135.20
129.47
129.10
125.75
125.61
124.54
52.15
51.88
47.70
45.81
44.77
38.00
37.51
36.89
36.77
30.22
26.70
25.19
21.45
19.93
19.71
18.56
16.67
O
MeOOC
H
49-50
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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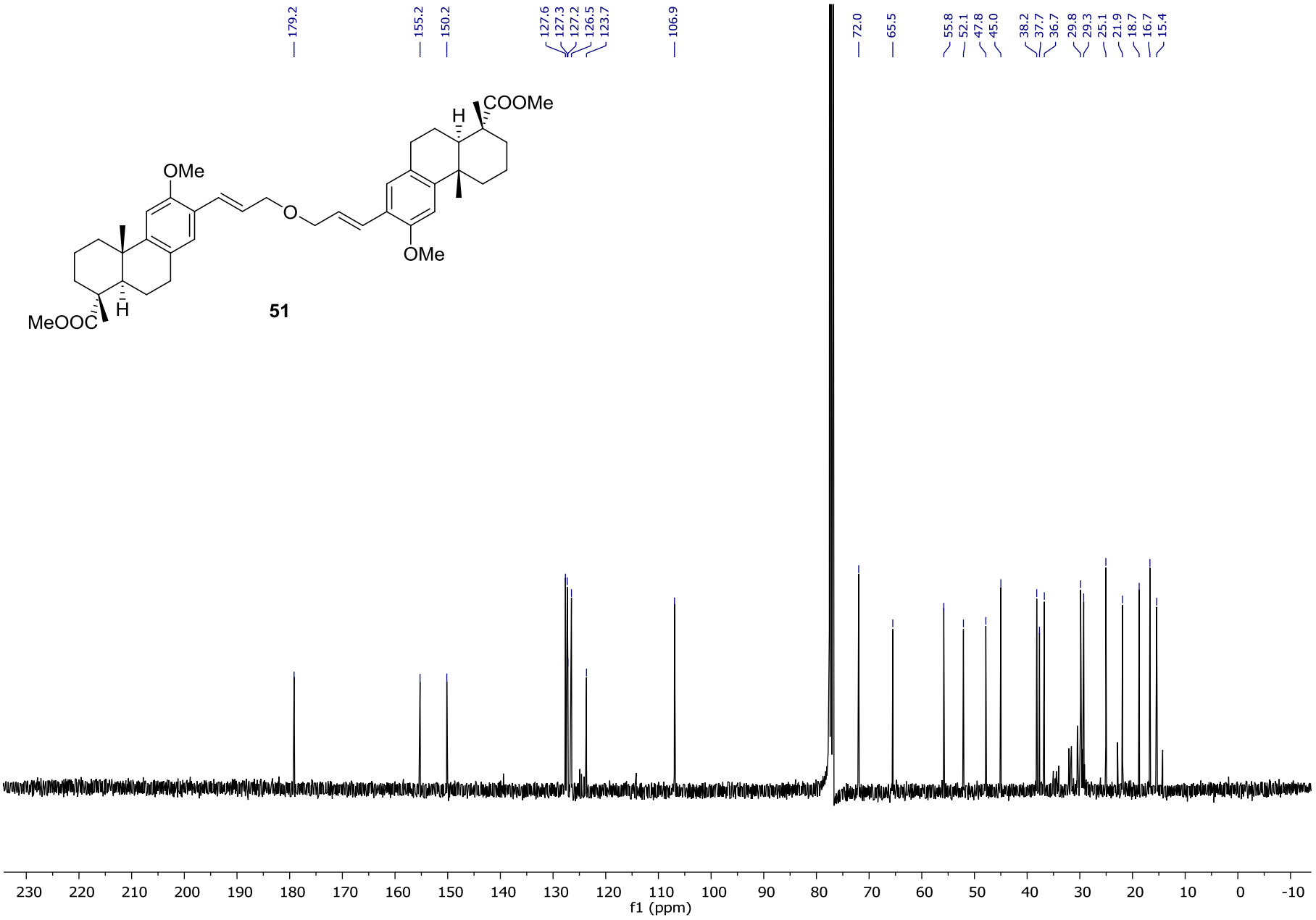
6.85
6.81
6.73
6.29
6.28
6.26
6.25
6.24
6.22
4.14
4.13
4.13
4.12
4.12
4.12
3.81
3.67
3.55
3.53
3.52
3.50
1.28
1.26
1.23
1.22
OMe
O
OMe
H
COOMe
MeOOC
H
51
1.00
1.10
0.91
1.18
1.96
2.88
2.97
2.10
2.36
4.97
1.49
1.06
2.48
2.77
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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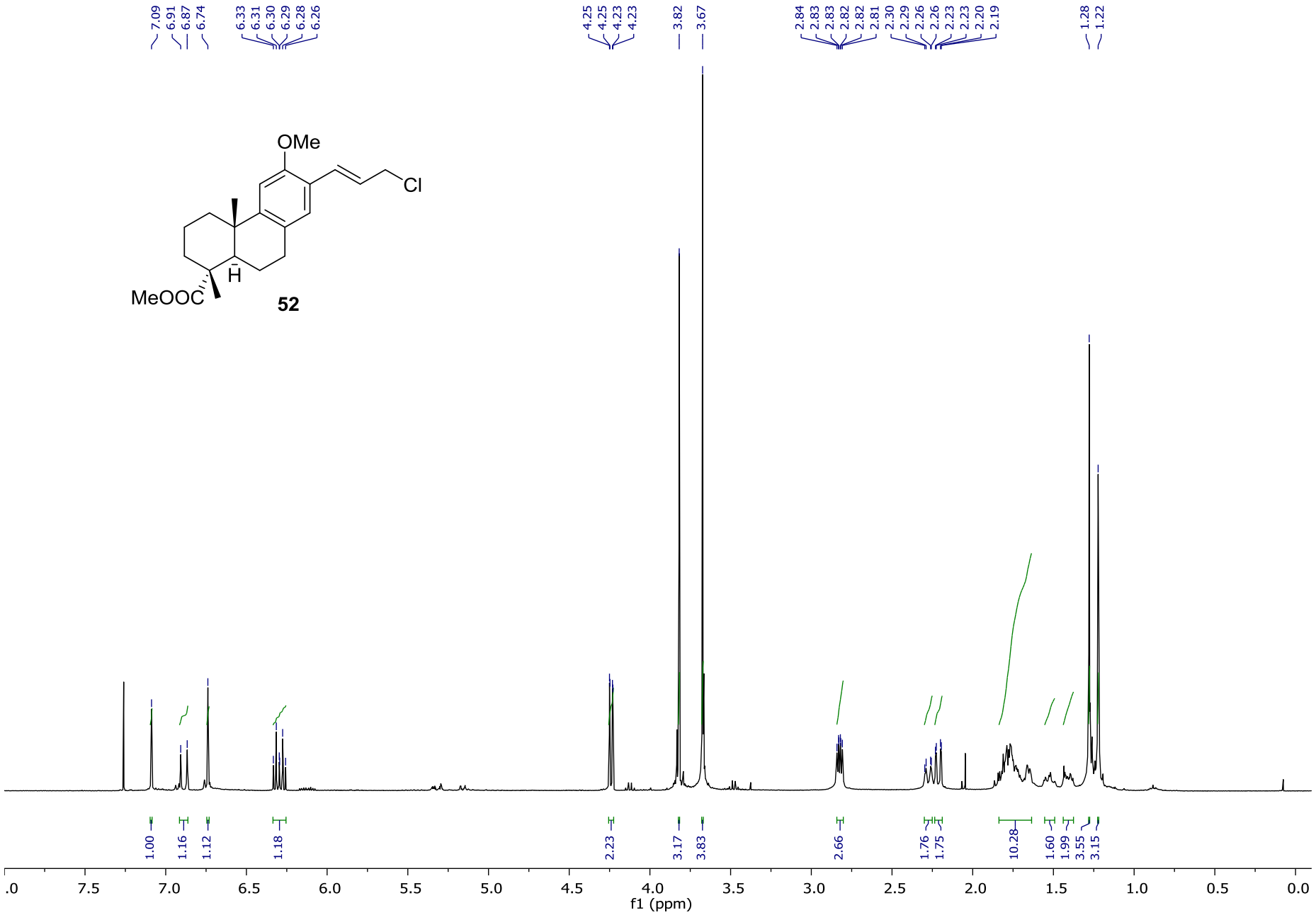
155.2
150.2
127.6
127.3
127.2
126.5
123.7
106.9
72.0
65.5
55.8
52.1
47.8
45.0
38.2
37.7
36.7
29.8
29.3
25.1
21.9
18.7
16.7
15.4
COOMe
H
OMe
O
OMe
MeOOC
H
51
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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6.91
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6.74
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6.31
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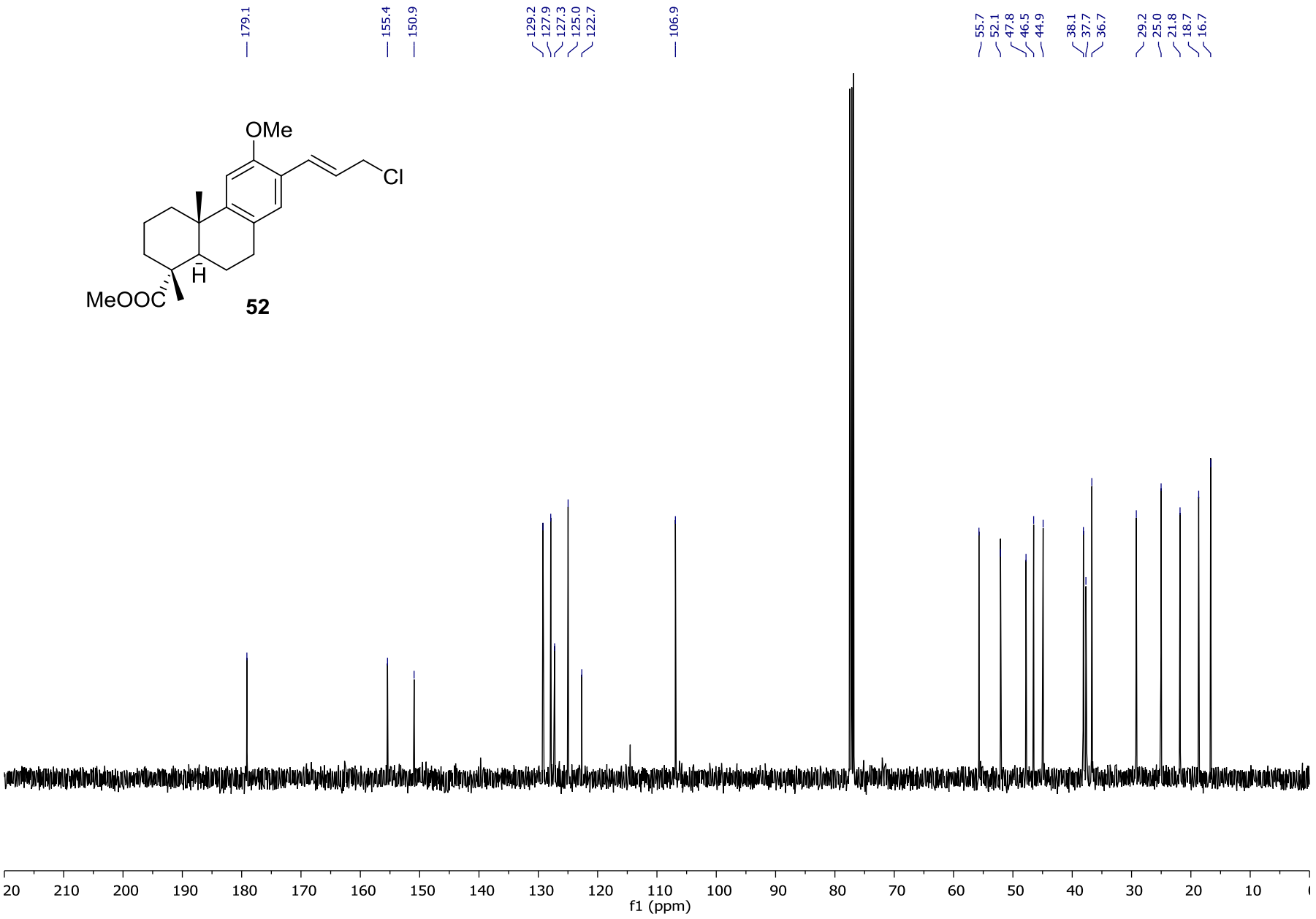
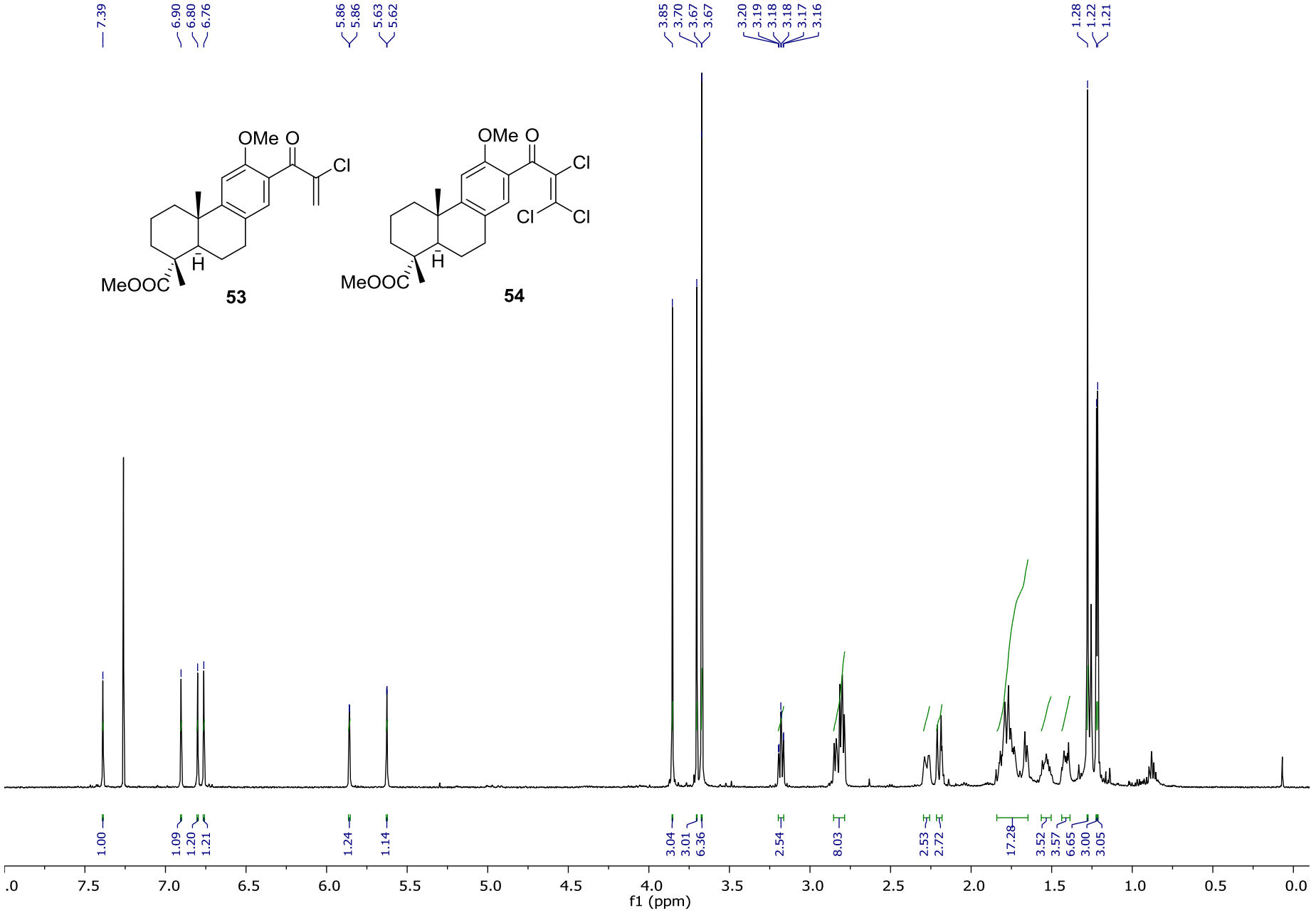
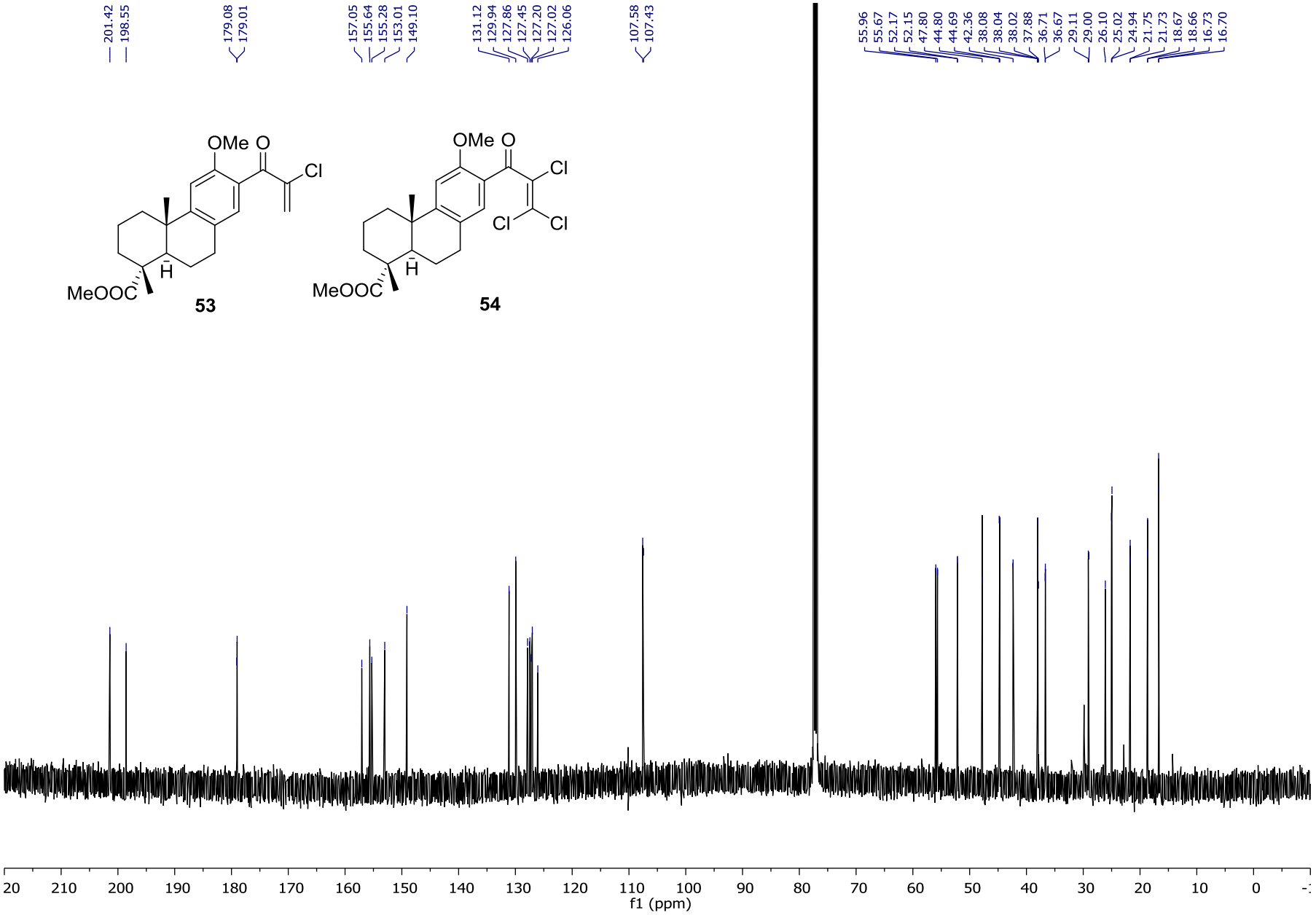
6.29
6.28
6.26
4.25
4.25
4.23
4.23
3.82
3.67
2.84
2.83
2.83
2.82
2.82
2.81
2.30
2.29
2.26
2.26
2.23
2.23
2.20
2.19
1.28
1.22
OMe
Cl
H
MeOOC
52
1.00
1.16
1.12
1.18
2.23
3.17
3.83
2.66
1.76
1.75
10.28
1.60
1.99
3.55
3.15
f1 (ppm)


179.1
155.4
150.9
129.2
127.9
127.3
125.0
122.7
106.9
55.7
52.1
47.8
46.5
44.9
38.1
37.7
36.7
29.2
25.0
21.8
18.7
16.7
OMe
Cl
H
MeOOC
52
f1 (ppm)


7.39
6.90
6.80
6.76
5.86
5.86
5.63
5.62
3.85
3.70
3.67
3.67
3.20
3.19
3.18
3.18
3.17
3.16
1.28
1.22
1.21
OMe O
Cl
MeOOC
H
53
OMe O
Cl
Cl
Cl
MeOOC
H
54
1.00
1.09
1.20
1.21
1.24
1.14
3.04
3.01
6.36
2.54
8.03
2.53
2.72
17.28
3.52
3.57
6.65
3.00
3.05
.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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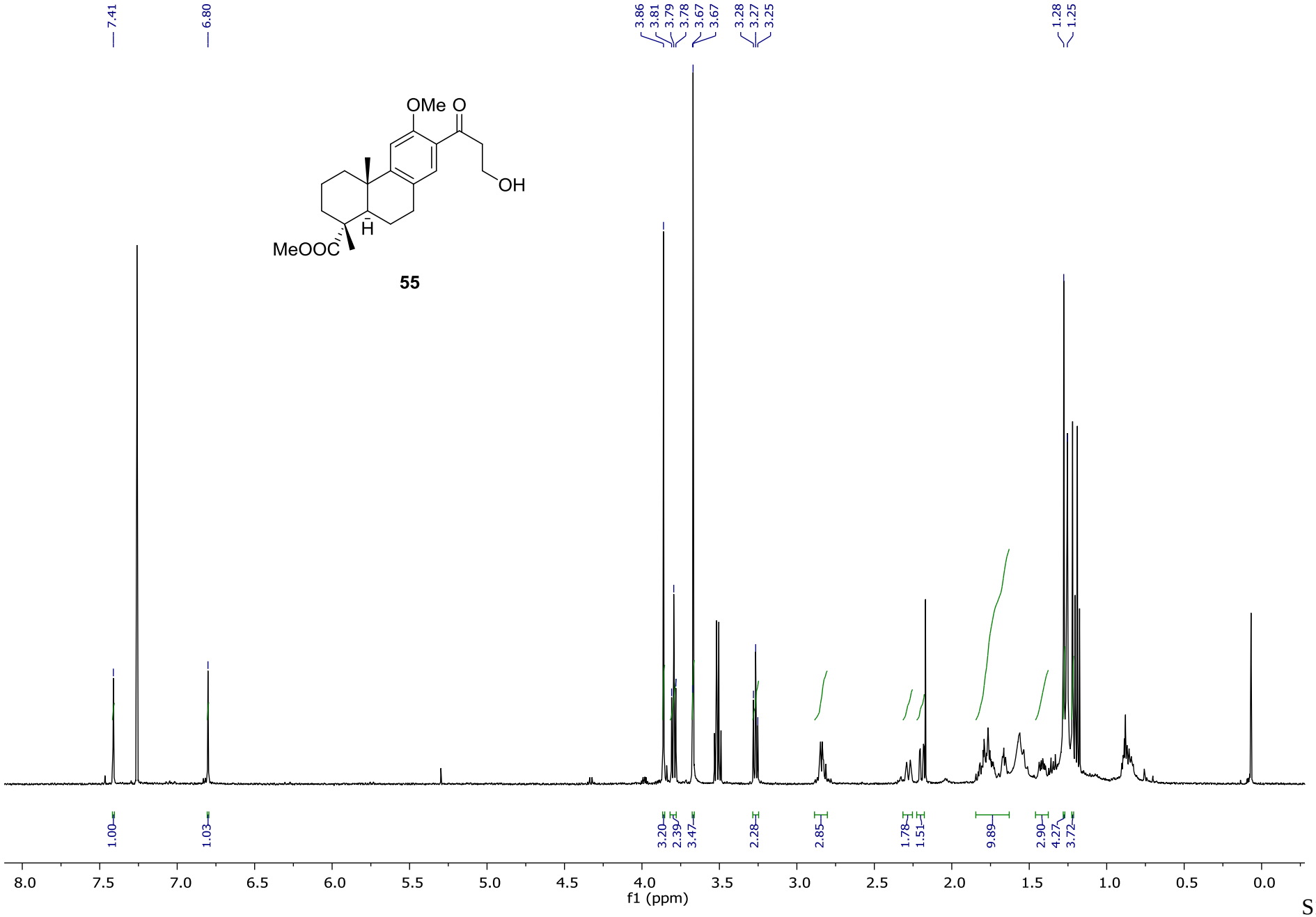
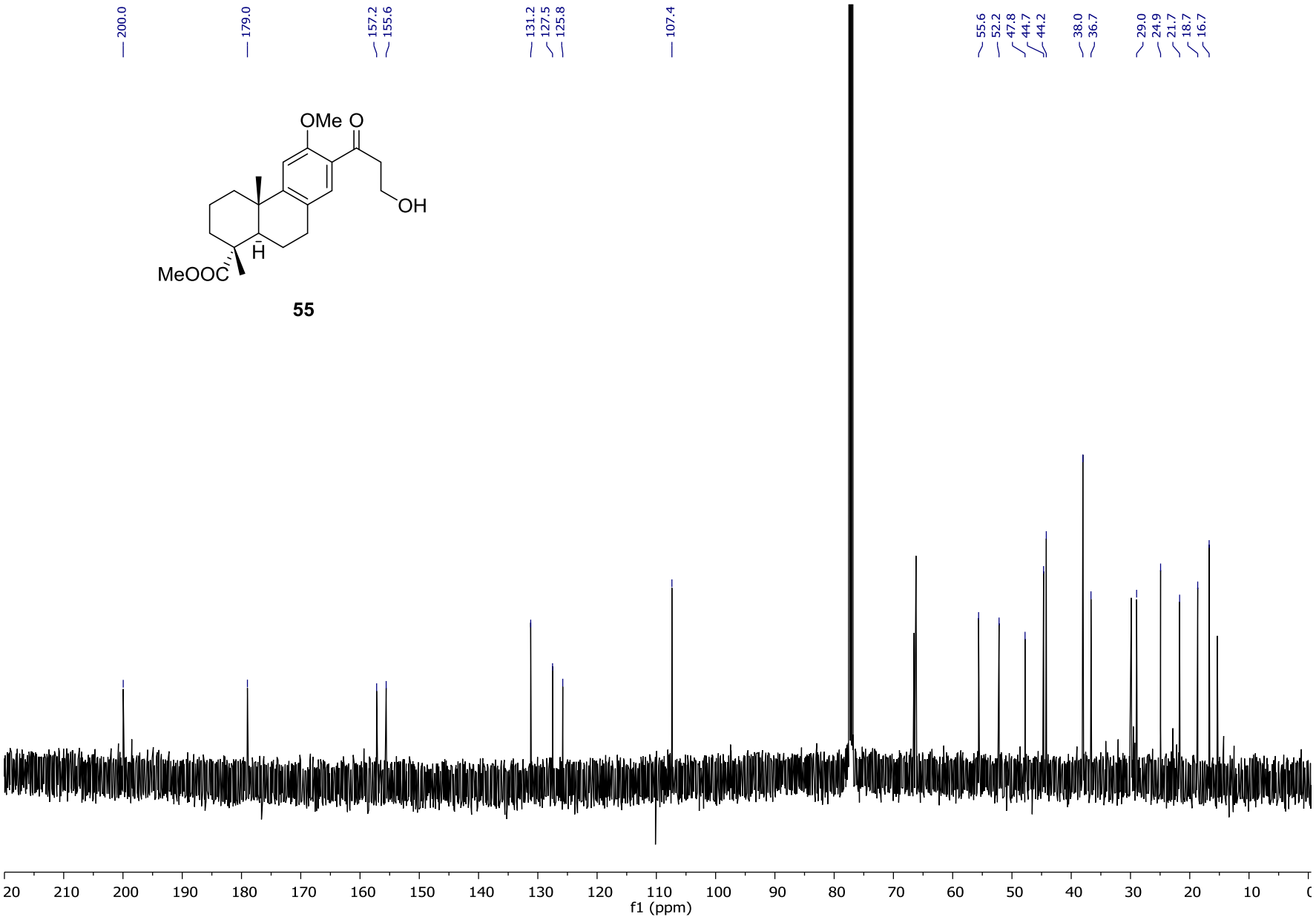
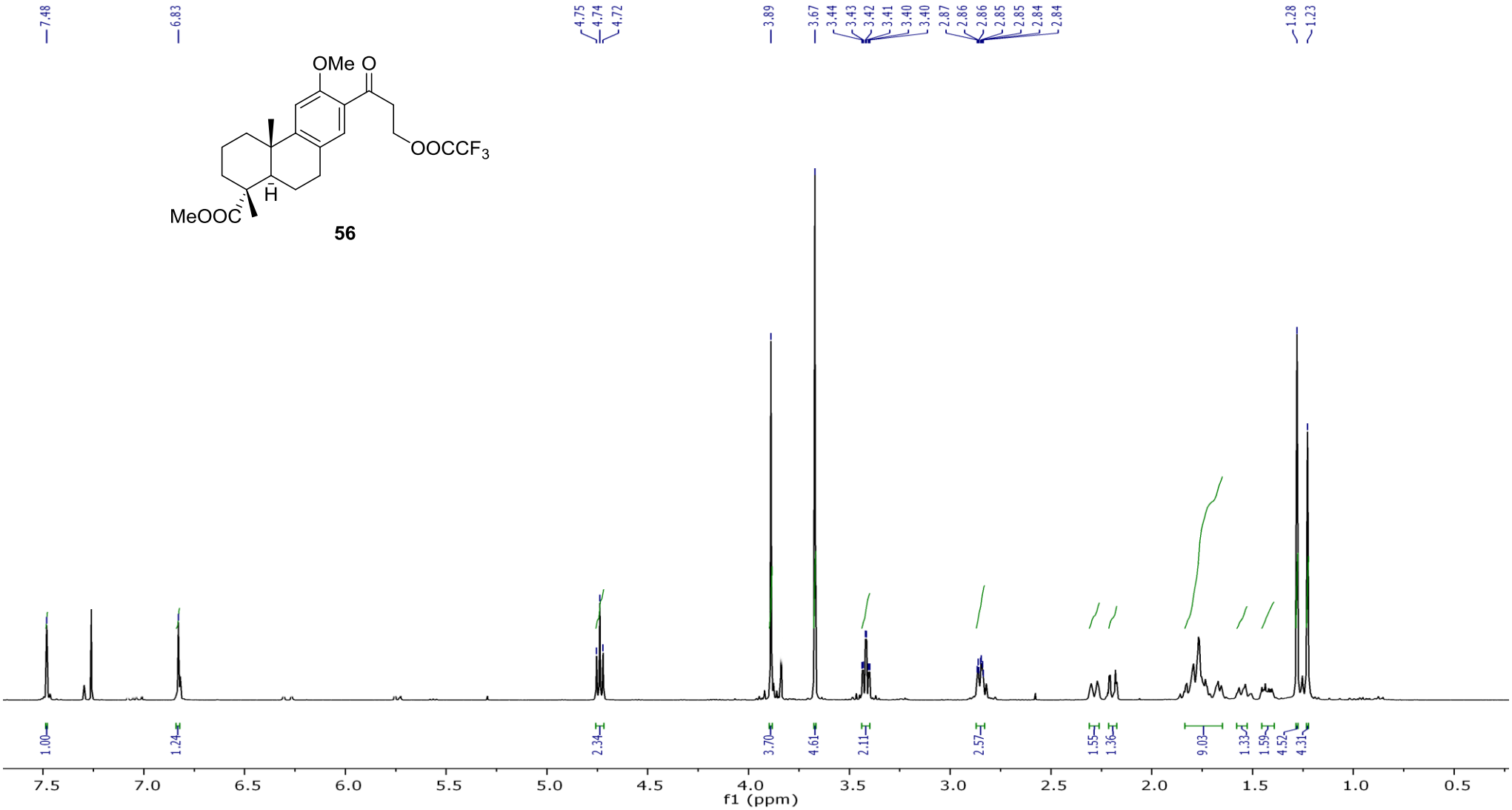
198.55
179.08
179.01
157.05
155.64
155.28
153.01
149.10
131.12
129.94
127.86
127.45
127.20
127.02
126.06
107.58
107.43
55.96
55.67
52.17
52.15
47.80
44.80
44.69
42.36
38.08
38.04
38.02
37.88
36.71
36.67
29.11
29.00
26.10
25.02
24.94
21.75
21.73
18.67
18.66
16.73
16.70
OMe O
Cl
H
MeOOC
53
OMe O
Cl
Cl
Cl
H
MeOOC
54
f1 (ppm)


7.41
6.80
3.86
3.81
3.79
3.78
3.67
3.67
3.28
3.27
3.25
1.28
1.25
OMe O
OH
H
MeOOC
55
1.00
1.03
3.20
2.39
3.47
2.28
2.85
1.78
1.51
9.89
2.90
4.27
3.72
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)


200.0
179.0
157.2
155.6
131.2
127.5
125.8
107.4
55.6
52.2
47.8
44.7
44.2
38.0
36.7
29.0
24.9
21.7
18.7
16.7
OMe O
OH
H
MeOOC
55
f1 (ppm)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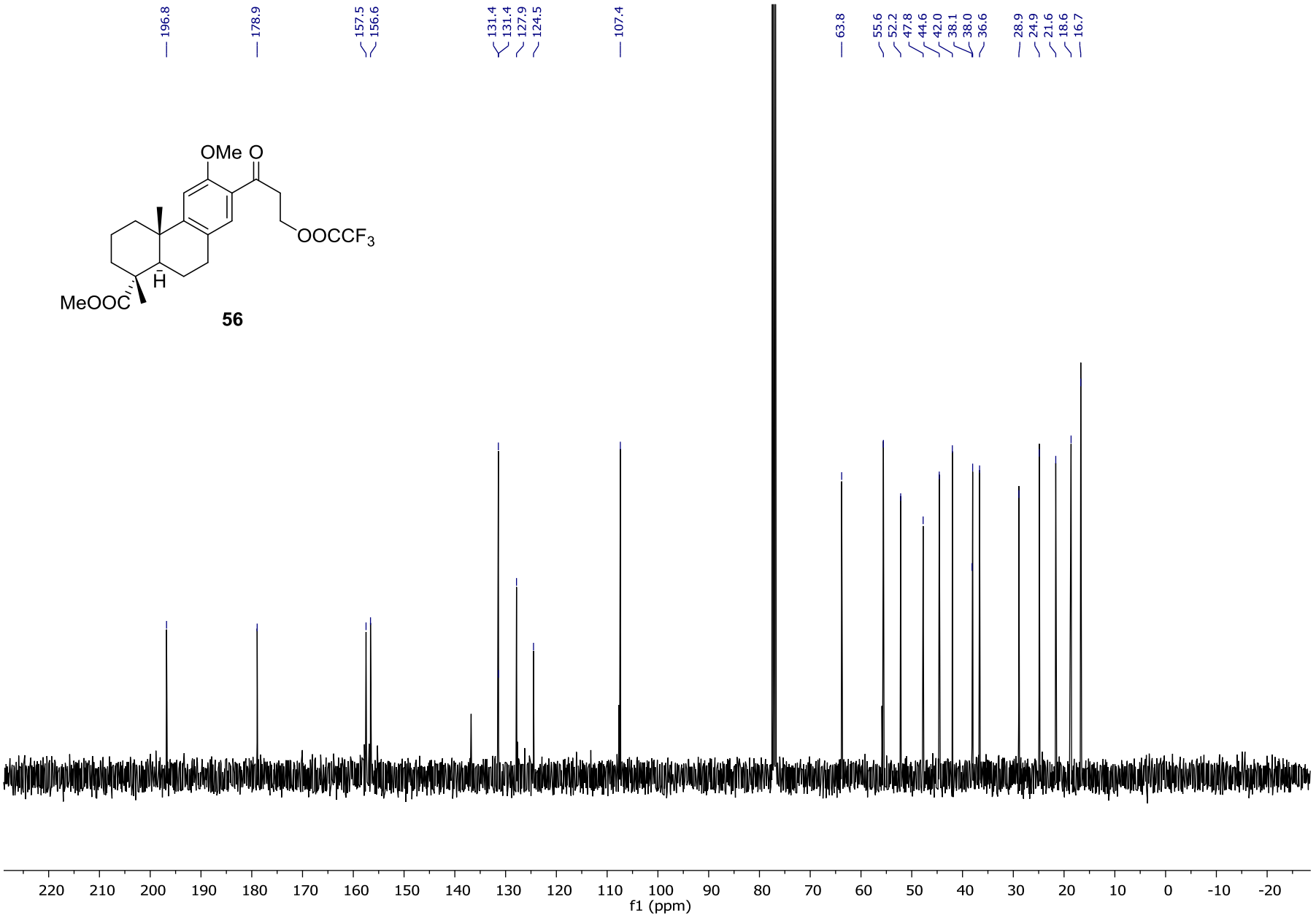
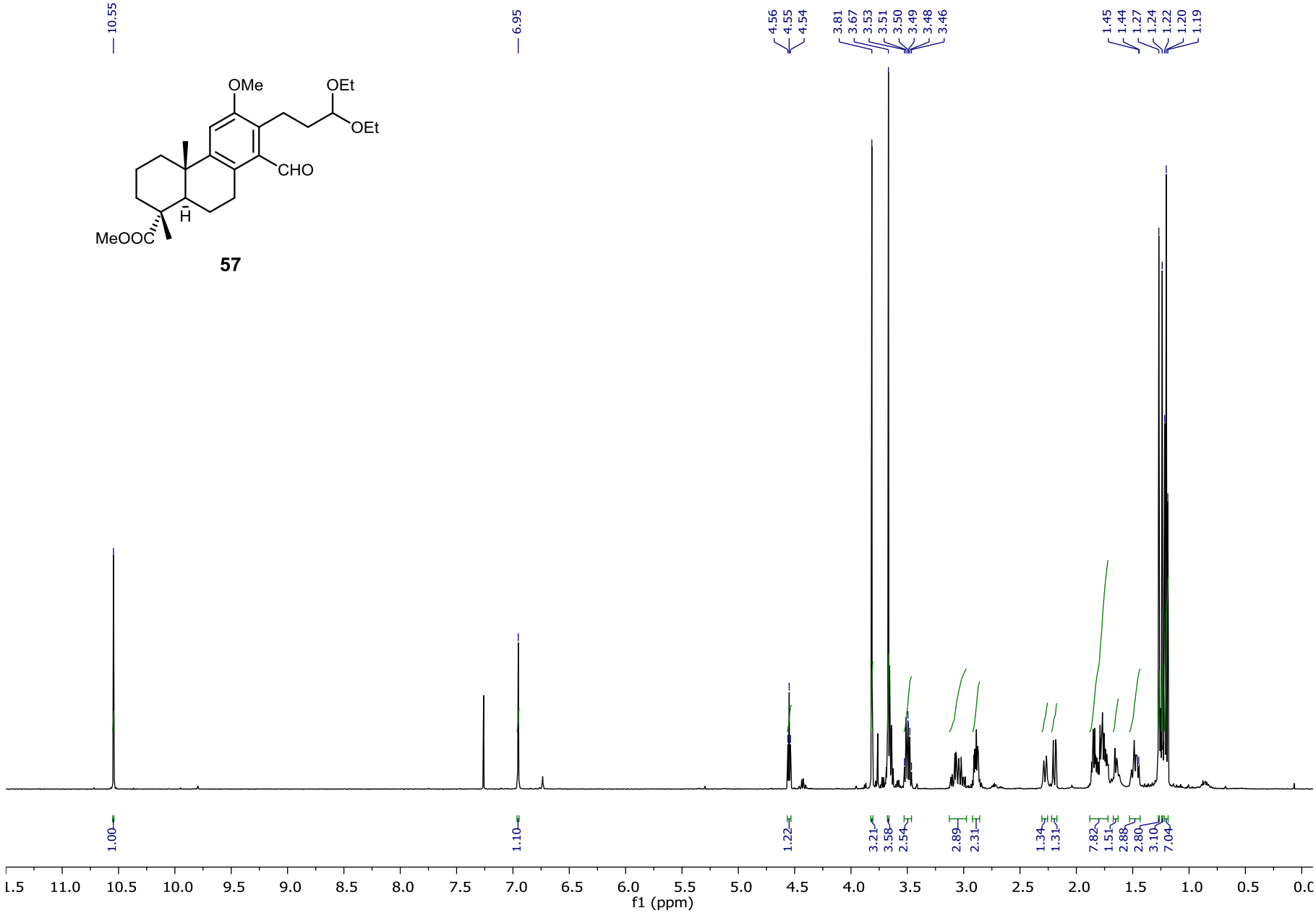
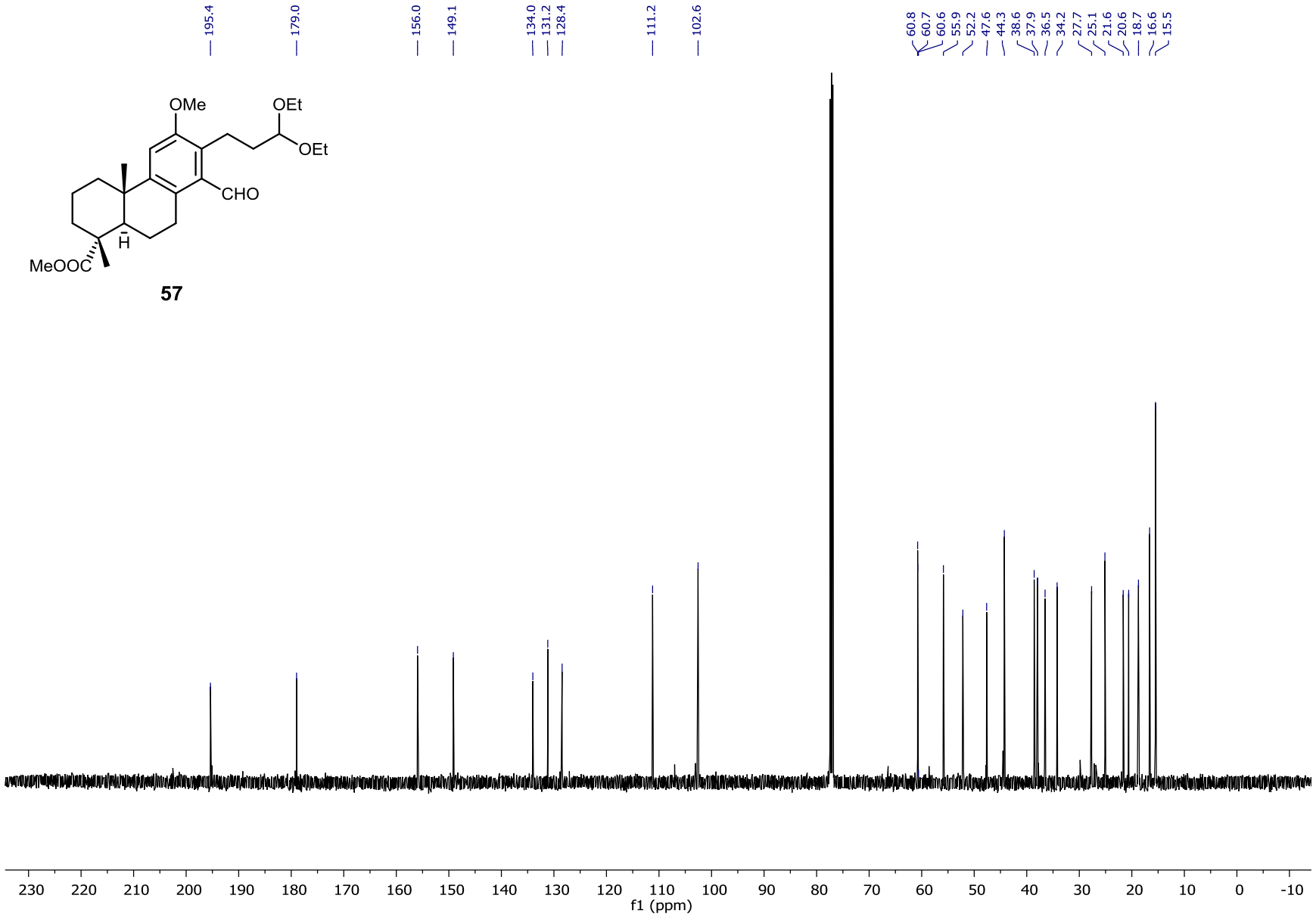
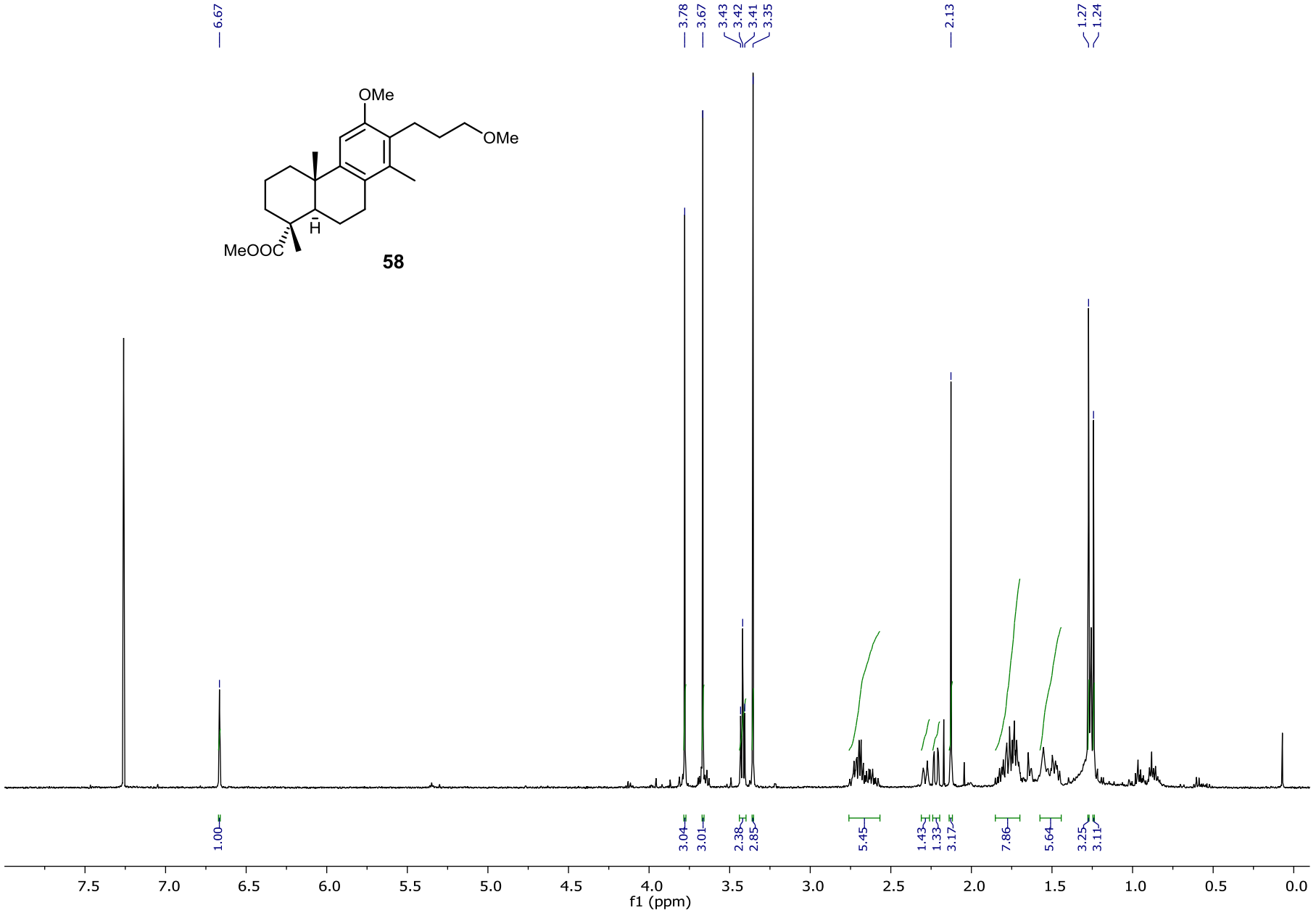
4.75
4.74
4.72
3.89
3.67
3.44
3.43
3.42
3.41
3.40
3.40
2.87
2.86
2.86
2.85
2.85
2.84
2.84
1.28
1.23
OMe O
OOCCF3
H
MeOOC
56
1.00
1.24
2.34
3.70
4.61
2.11
2.57
1.55
1.36
9.03
1.33
1.59
4.52
4.31
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

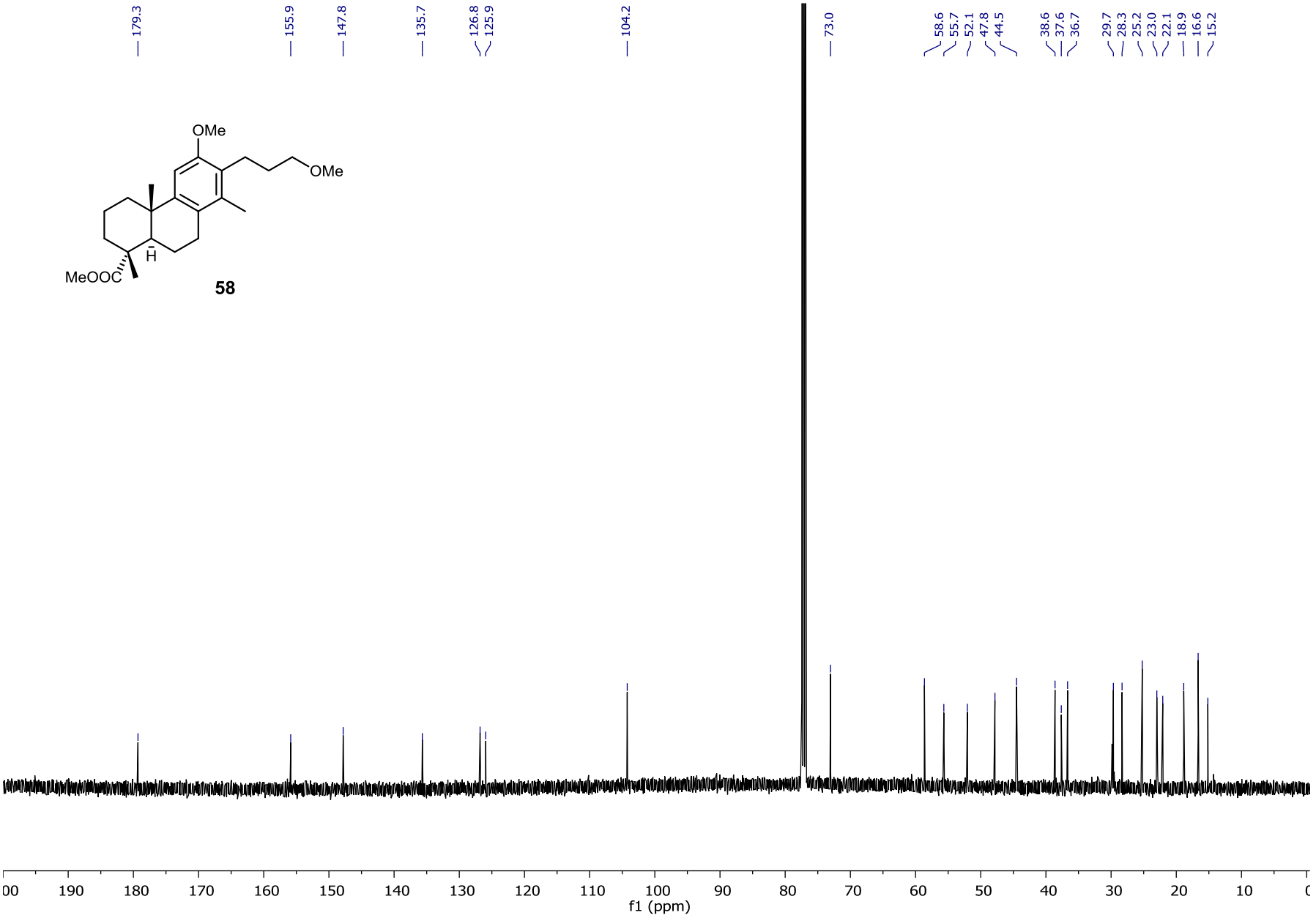

196.8
178.9
157.5
156.6
131.4
131.4
127.9
124.5
107.4
63.8
55.6
52.2
47.8
44.6
42.0
38.1
38.0
36.6
28.9
24.9
21.6
18.6
16.7
OMe O
OOCCF3
H
MeOOC
56
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


10.55
6.95
4.56
4.55
4.54
3.81
3.67
3.53
3.51
3.50
3.49
3.48
3.46
1.45
1.44
1.27
1.24
1.22
1.20
1.19
OMe
OEt
OEt
CHO
H
MeOOC
1.00
1.10
1.22
3.21
3.58
2.54
2.89
2.31
1.34
1.31
7.82
1.51
2.88
2.80
3.10
7.04
f1 (ppm)

57


195.4
179.0
156.0
149.1
134.0
131.2
128.4
111.2
102.6
60.8
60.7
60.6
55.9
52.2
47.6
44.3
38.6
37.9
36.5
34.2
27.7
25.1
21.6
20.6
18.7
16.6
15.5
OMe
OEt
OEt
CHO
H
MeOOC
57
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


6.67
3.78
3.67
3.43
3.42
3.41
3.35
2.13
1.27
1.24
OMe
OMe
H
MeOOC
58
1.00
3.04
3.01
2.38
2.85
5.45
1.43
1.33
3.17
7.86
5.64
3.25
3.11
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)


179.3
155.9
147.8
135.7
126.8
125.9
104.2
73.0
58.6
55.7
52.1
47.8
44.5
38.6
37.6
36.7
29.7
28.3
25.2
23.0
22.1
18.9
16.6
15.2
OMe
OMe
H
MeOOC
58
f1 (ppm)