Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Synthesis of polycyclic naphthols and naphthalenes via tandem Ti(O*i*-Pr)$_4$-promoted photoenolization Diels–Alder reaction and aromatization

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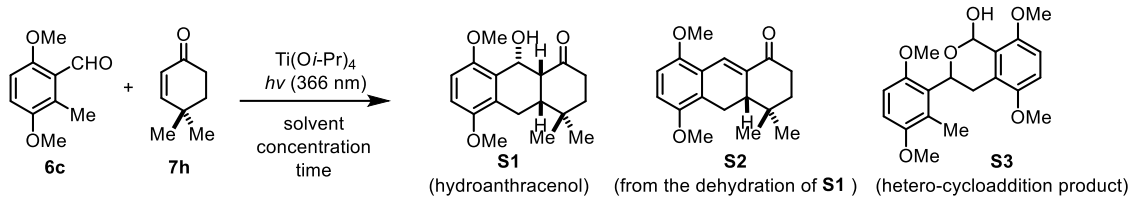
General experimental procedures

All reactions were carried out under an inert nitrogen atmosphere with dry solvents under anhydrous conditions unless otherwise noted. Anhydrous dichloromethane and toluene were purified by the PS-MD-5 (Innovative Technology) solvent purification system. Dimethyl sulfoxide used for IBX oxidation was purchased from commercially available anhydrous solvent. Anhydrous 1,4-dioxane was distilled from sodium. TLC analyses were performed on EMD 250 μm Silica Gel HSGF$_{254}$ plates and visualized by quenching of UV fluorescence (λmax= 254 nm), or by staining phosphomolybdic acid, or potassium permanganate. Flash column chromatography was performed as described by Still [1], employing SiliCycle UltraPure Silica Gels: SilicaFlash® P60 40 – 63 μm (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500, 400 spectrometers. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent ($CDCl_3$: δ 7.26, 77.0 ppm;) and the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were acquired on Waters Micromass GCT Premier or Bruker Daltonics, Inc. APEXIII 7.0 TESLA FTMS. Mass spectra were acquired on Agilent 5975C. Infrared (IR) spectra was obtained using a Shimatzu IRTracer-100 fourier transform infrared spectroscopy (FTIR).

Screening conditions of PEDA reaction

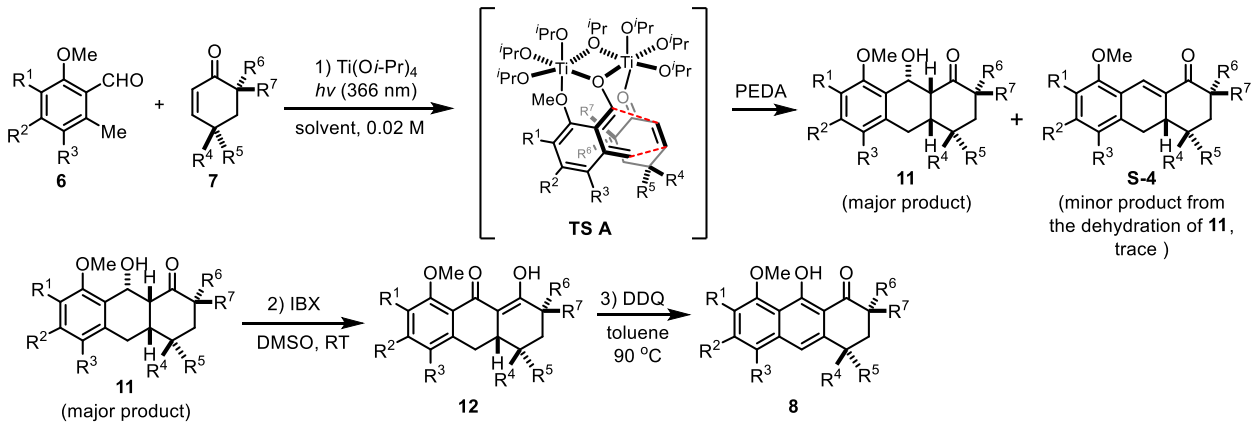
Table S1. Screening conditions using **6c** and **7h** as reactants



entry	6c	7h	solvent	concentration	$Ti(O\textit{i}\text{-}Pr)_4$	time	result[a]
1	1.5 equiv.	1.0 equiv.	toluene	0.03 M	0	1 h	**7h**+**S3**
2	1.5 equiv.	1.0 equiv.	toluene	0.03 M	2.0 equiv.	1 h	trace **S1; 6c**:**7h**:**S2** = 3.2:1.7:1.0
3	1.0 equiv.	2.0 equiv.	toluene	0.03 M	2.0 equiv.	3 h	trace **S1; 6c**:**7h**:**S2** = 0.8:3.0:1.0
4	1.0 equiv.	2.0 equiv.	toluene	0.03 M	3.0 equiv.	3 h	trace **S1; 6c**:**7h**:**S2** = 0.9:2.5:1.0
5	1.0 equiv.	2.0 equiv.	toluene	0.02 M	2.0 equiv.	3 h	trace **S1; 6c**:**7h**:**S2** = 0.1:3.4:1 25% isolated yield for **S2**
6	1.0 equiv.	2.0 equiv.	1,4-dioxane	0.02 M	2.0 equiv.	3 h	**6c**:**7h**:**S1**:**S2** = 0.05:6.2:0.6:1

[a] The ration of SM and produts were determined by ^{1}H NMR spectroscopic crude analysis.

Experimental procedures and spectroscopic data of PEDA/oxidation/aromatization sequence



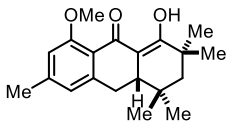
General procedure A for PEDA reaction and oxidation: Step 1: To a solution of dienophile **7** (1.0 equiv.) and aromatic aldehyde **6** (1.5 equiv.) in anhydrous and degassed solvent as indicated below (concentration for dienophile is 0.02 M) in quartz tube sealed with rubber plug was added titanium(IV) isopropoxide (2.0 equiv.) under nitrogen, after homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at 366 nm until the dienophile **7** was completely consumed by TLC analysis. Then saturated $NaHCO_3$ was added to the solution and stirred for 5 minutes. The mixture was filtered through silica gel and washed with ethyl acetate for six times, separated the organic layer and washed with brine. The organic layer was dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography to obtain the corresponding hydroanthracenol product **11**.

Step 2: To a 0.02 M stirred solution of compound **11** in anhydrous DMSO was added IBX (2.0 equiv.) at room temperature and stirred at room temperature until the starting material was consumed completely by TLC

analysis. Then the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (v/v = 1:1) at 0 °C and extracted with ethyl acetate for three times. The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel column chromatography to give the corresponding product **12**.

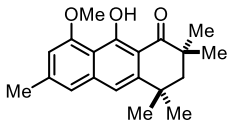
General procedure B for aromatization: To a 0.01 M stirred solution of the compound **12** in anhydrous toluene was added DDQ (3.0 equiv.) at room temperature and stirred at 90 °C until the starting material was consumed completely by TLC analysis. Then the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (v/v = 1:1) solution at 0 °C and extracted with ethyl acetate for three times. The combined organic layers were washed with saturated Na_2SO_3/$NaHCO_3$ (v/v = 1:1), brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography to obtain the corresponding naphthol product **8**.

All starting materials **6** and **7** are known compounds except **7b** and **7c**.



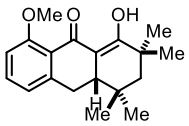
12aa

Compound **12aa** (107 mg, 51% yield for two steps) was prepared according to general procedure A from **7a** (102 mg, 0.67 mmol, 1.0 equiv.) and aldehyde **6a** (164 mg, 1.0 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.38 (10% ethyl acetate – petroleum ether); White solid, m.p. 161 – 164 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.06 (s, 1H), 6.65 (s, 1H), 6.61 (s, 1H), 3.90 (s, 3H), 2.62 – 2.40 (m, 3H), 2.34 (s, 3H), 1.51 (s, 2H), 1.31 (s, 3H), 1.17 (s, 3H), 1.00 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.8, 187.4, 159.7, 144.4, 144.3, 120.9, 118.2, 111.1, 106.1, 56.0, 52.5, 43.6, 36.7, 31.7, 31.4, 31.0, 29.7, 27.4, 22.0, 21.9 ppm; IR ν_{max} 2957, 2912, 2845, 1705, 1608, 1481, 1215, 1097, 858, 835 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{26}O_3$, 314.1882, found, 314.1885.



8aa

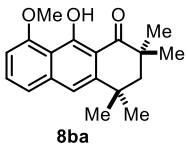
Compound **8aa** (102 mg, 96% yield) was prepared according to general procedure B from the above obtained compound **12aa**. R_f = 0.50 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 192 – 195 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.59 (s, 1H), 7.05 (s, 1H), 7.00 (s, 1H), 6.62 (s, 1H), 4.01 (s, 3H), 2.45 (s, 3H), 1.90 (s, 2H), 1.41 (s, 6H), 1.33 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.7, 166.2, 159.5, 147.6, 141.4, 140.8, 119.7, 113.4, 113.1, 108.9, 107.6, 56.1, 50.0, 41.4, 33.5, 32.5 (2C), 28.9 (2C), 22.1 ppm; IR ν_{max} 2963, 2932, 1628, 1578, 1389, 1369, 1267, 1163, 1119, 1053 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_3$, 312.1725, found, 312.1727.



12ba

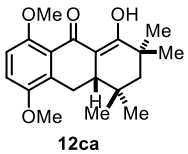
Compound **12ba** (41 mg, 34% yield for two steps) was prepared according to general procedure A from **7a** (61 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6b** (90 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.44 (10% ethyl acetate – petroleum ether); Light yellow solid, m.p.

122 – 124 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.03 (s, 1H), 7.34 (t, *J* = 7.8 Hz, 1H), 6.86 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.92 (s, 3H), 2.66 (dd, *J* = 13.1, 3.0 Hz, 1H), 2.54 (t, *J* = 13.6 Hz, 1H), 2.47 (dd, *J* = 14.1, 3.0 Hz, 1H), 1.53 (s, 2H), 1.33 (s, 3H), 1.19 (s, 3H), 1.02 (s, 3H), 0.98 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.7, 187.2, 159.6, 144.5, 133.2, 120.7, 120.1, 110.4, 106.4, 56.1, 52.5, 43.6, 36.8, 31.8, 31.5, 31.1, 29.7, 27.5, 22.0 ppm; IR ν_{max} 2978, 2906, 1718, 1682, 1593, 1560, 1267, 1194, 1097, 1082 cm^{-1}; HRMS–EI (*m/z*): [M]$^{+}$ calculated for $C_{19}H_{24}O_3$, 300.1725, found, 300.1728.



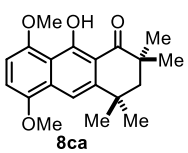
8ba

Compound **8ba** (35 mg, 85% yield) was prepared according to general procedure B from the above obtained compound **12ba**. R_f = 0.60 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 130 – 132 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.55 (s, 1H), 7.47 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 9.6 Hz, 1H), 7.09 (s, 1H), 6.80 (d, *J* = 7.9 Hz, 1H), 4.02 (s, 3H), 1.92 (s, 2H), 1.42 (s, 6H), 1.34 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.1, 166.1, 159.7, 147.5, 140.6, 130.7, 120.1, 114.9, 114.0, 109.4, 105.5, 56.2, 49.8, 41.5, 33.6, 32.5 (2C), 28.9 (2C) ppm; IR ν_{max} 2982, 2907, 1749, 1680, 1579, 1570, 1265, 1193, 1167, 1101 cm^{-1}; HRMS–EI (*m/z*): [M]$^{+}$ calculated for $C_{19}H_{22}O_3$, 298.1569, found, 298.1566.



12ca

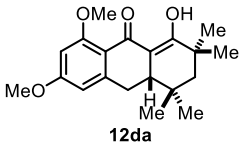
Compound **12ca** (75 mg, 34% yield for two steps) was prepared according to general procedure A from **7a** (102 mg, 0.67 mmol, 1.0 equiv.) and aldehyde **6c** (180 mg, 1.0 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.36 (10% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.99 (s, 1H), 6.96 (d, *J* = 9.1 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.18 (dd, *J* = 15.2, 4.2 Hz, 1H), 2.40 (dd, *J* = 14.4, 4.2 Hz, 1H), 2.08 (t, *J* = 14.6 Hz, 1H), 1.54 (s, 2H), 1.33 (s, 3H), 1.19 (s, 3H), 1.05 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 190.2, 186.9, 153.6, 149.5, 132.7, 121.7, 115.3, 110.2, 106.5, 56.5, 56.2, 52.6, 43.0, 36.9, 31.9, 31.5, 29.8, 27.5, 22.5, 22.1 ppm; IR ν_{max} 2976, 2904, 1749, 1682, 1583, 1560, 1286, 1265, 1193, 1080 cm^{-1}; HRMS–EI (*m/z*): [M]$^{+}$ calculated for $C_{20}H_{26}O_4$, 330.1831, found, 330.1829.



8ca

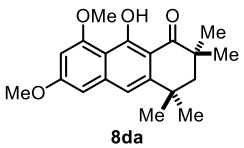
Compound **8ca** (72 mg, 97% yield) was prepared according to general procedure B from the above obtained compound **12ca**. R_f = 0.42 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 144 – 146 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.32 (s, 1H), 7.59 (s, 1H), 6.87 (d, *J* = 8.6 Hz, 1H), 6.72 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 1.92 (s, 2H), 1.45 (s, 6H), 1.33 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.4, 165.3, 153.3, 148.7, 147.2, 131.5, 115.7, 110.0, 108.7, 107.9, 105.5, 56.8, 55.9, 50.0, 41.7, 33.8, 32.7 (2C), 28.9 (2C) ppm; IR ν_{max} 2912, 1749, 1622, 1583,

1491, 1389, 1265, 1194, 1115, 1080 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_4$, 328.1675, found, 328.1678.



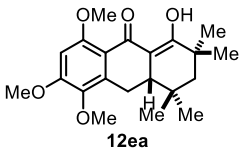
12da

Compound **12da** (46 mg, 35% yield for two steps) was prepared according to general procedure A from **7a** (61 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6d** (108 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.2 (10% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.06 (s, 1H), 6.36 (d, *J* = 2.2 Hz, 1H), 6.32 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 2.61 (dd, *J* = 13.6, 3.8 Hz, 1H), 2.53 (t, *J* = 13.6 Hz, 1H), 2.45 (dd, *J* = 13.7, 3.9 Hz, 1H), 1.51 (s, 2H), 1.31 (s, 3H), 1.17 (s, 3H), 1.01 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 187.7, 187.3, 163.6, 161.6, 146.6, 114.5, 105.6, 104.5, 97.4, 56.0, 55.4, 52.4, 43.5, 36.5, 31.8, 31.7, 31.4, 29.8, 27.4, 22.1 ppm; IR ν_{max} 2910, 1738, 1695, 1599, 1375, 1306, 1246, 1159, 1095, 1047 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{26}O_4$, 330.1831, found, 330.1833.



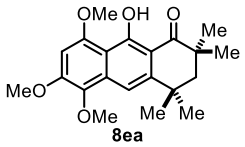
8da

Compound **8da** (46 mg, quantitative yield) was prepared according to general procedure B from the above obtained compound **12da**. R_f = 0.38 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 144 – 147 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.67 (s, 1H), 6.97 (s, 1H), 6.60 (d, *J* = 2.2 Hz, 1H), 6.42 (d, *J* = 2.2 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 1.89 (s, 2H), 1.41 (s, 6H), 1.32 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.3, 166.3, 161.8, 161.1, 148.3, 142.2, 113.3, 110.3, 108.2, 99.1, 97.9, 56.1, 55.4, 49.9, 41.3, 33.5, 32.5 (2C), 28.9 (2C) ppm; IR ν_{max} 2977, 1737, 1620, 1583, 1321, 1223, 1203, 1166, 1066, 937 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_4$, 328.1675, found, 328.1679.



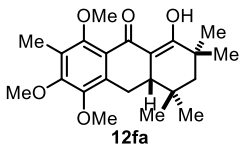
12ea

Compound **12ea** (55 mg, 38% yield for two steps) was prepared according to general procedure A from **7e** (61 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6a** (126 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.30 (10% ethyl acetate – petroleum ether); Light yellow solid, m.p. 167 – 169 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.05 (s, 1H), 6.40 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.72 (s, 3H), 3.16 (dd, *J* = 14.7, 3.8 Hz, 1H), 2.35 (dd, *J* = 14.3, 3.8 Hz, 1H), 2.11 (t, *J* = 14.5 Hz, 1H), 1.52 (s, 2H), 1.31 (s, 3H), 1.17 (s, 3H), 1.04 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.0, 187.3, 157.6, 156.7, 138.7, 137.5, 113.8, 105.7, 95.1, 60.8, 56.4, 55.7, 52.5, 43.2, 36.6, 31.8, 31.4, 29.8, 27.4, 23.2, 22.0 ppm; IR ν_{max} 2976, 1734, 1593, 1560, 1337, 1282, 1238, 1207, 1092, 1049 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{28}O_5$, 360.1937, found, 360.1940.



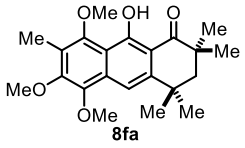
8ea

Compound **8ea** (44 mg, 81% yield) was prepared according to general procedure B from the above obtained compound **12ea**. R_f = 0.58 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 107 – 109 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 15.8 (s, 1H), 7.4 (s, 1H), 6.6 (s, 1H), 4.0 (s, 6H), 3.9 (s, 3H), 1.9 (s, 2H), 1.4 (s, 6H), 1.3 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.5, 166.9, 157.4, 152.7, 148.0, 136.1, 135.0, 110.1, 108.0, 106.8, 95.0, 60.9, 56.7, 56.4, 50.0, 41.3, 33.8, 32.6 (2C), 29.0 (2C) ppm; IR ν_{max} 2958, 1733, 1618, 1585, 1346, 1238, 1146, 1113, 1033, 872 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{26}O_5$, 358.1780, found, 358.1782.



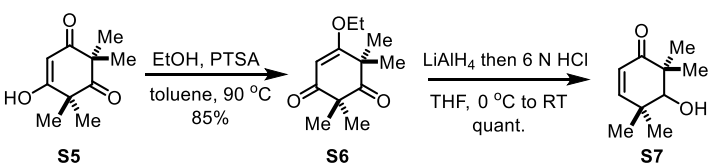
12fa

Compound **12fa** (95 mg, 70% yield for two steps) was prepared according to general procedure A from **7a** (61 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6f** (134 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.24 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 17.19 (s, 1H), 3.89 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.10 (dd, *J* = 14.8, 4.1 Hz, 1H), 2.39 (dd, *J* = 14.3, 4.0 Hz, 1H), 2.17 (s, 3H), 2.11 (t, *J* = 14.6 Hz, 1H), 1.54 (s, 2H), 1.32 (s, 3H), 1.18 (s, 3H), 1.05 (s, 3H), 1.00 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 191.2, 185.5, 155.50, 155.45, 145.4, 134.3, 124.9, 120.9, 106.0, 61.5, 60.6, 60.2, 52.5, 43.1, 37.0, 31.9, 31.5, 29.7, 27.6, 22.8, 22.1, 9.0 ppm; IR ν_{max} 1761, 1616, 1580, 1375, 1321, 1286, 1242, 1207, 1128, 1047 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{30}O_5$, 340.2093, found, 340.2097.

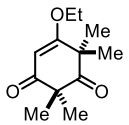


8fa

Compound **8fa** (57mg, 60% yield) was prepared according to general procedure B from the above obtained compound **12fa**. R_f = 0.26 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 15.42 (s, 1H), 7.42 (s, 1H), 3.98 (s, 3H), 3.92 (s, 3H), 3.85 (s, 3H), 2.32 (s, 3H), 1.93 (s, 2H), 1.45 (s, 6H), 1.35 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.3, 165.0, 153.6, 152.7, 146.6, 142.7, 133.3, 123.8, 115.3, 108.9, 107.1, 61.6, 60.9, 60.4, 50.0, 41.5, 33.8, 32.7 (2C), 28.9 (2C), 9.3 ppm; IR ν_{max} 2995, 1762, 1616, 1448, 1392, 1243, 1201, 1053 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{28}O_5$, 338.1937, found, 338.1932.



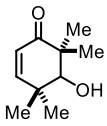
S5 **S6** **S7**



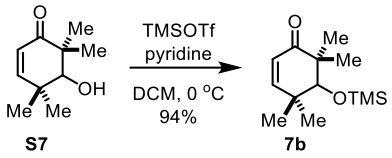
S6

To a stirred solution of **S5** [2] (800 mg, 4.40 mmol, 1.0 equiv.) in 30 mL anhydrous toluene was added anhydrous ethanol (12.8 mL, 220 mmol, 50.0 equiv.) and PTSA (152 mg, 0.88 mmol, 0.2 equiv.) under nitrogen atmosphere at room temperature. Then the solution was stirred at 90 ^oC for 4 hours and cooled to room temperature. The cooled solution was concentrated and purified by silica gel flash

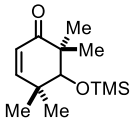
chromatography (20% to 50% ethyl acetate – petroleum ether) to obtain **S6** as yellow viscous oil (767 mg, 85%). R_f = 0.60 (30% ethyl acetate – petroleum ether).


S7

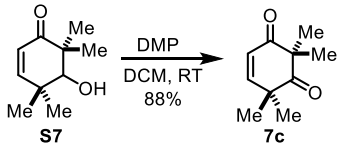
To a stirred solution of above obtained **S6** (767 mg, 3.60 mmol, 1.0 equiv.) in 30 mL anhydrous THF was slowly added $LiAlH_4$ (5.4 mL, 10.8 mmol, 3.0 equiv., 2 N in THF) under nitrogen atmosphere at 0 °C. After stirring at 0 °C for 30 minutes, the solution was quenched with saturated NH_4Cl (60 mL) and then added 6 N HCl (60 mL). The mixture was slowly warm to room temperature and stirred for another 1 hour. The mixture was extracted with ethyl acetate (3×50 mL) and the combined organic layer was washed with water, saturated $NaHCO_3$, brine. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 15% ethyl acetate – petroleum ether) to obtain **S7** as colorless viscous oil (608 mg, quantitative yield). R_f = 0.42 (20% ethyl acetate – petroleum ether). Colorless viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.58 (d, *J* = 10.2 Hz, 1H), 5.84 (d, *J* = 10.2 Hz, 1H), 3.56 (d, *J* = 6.1 Hz, 1H), 2.02 (br, 1H), 1.21 (s, 3H), 1.20 (s, 3H), 1.18 (s, 3H), 1.10 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.4, 156.3, 124.8, 79.7, 47.7, 38.3, 29.8, 23.2, 21.1, 20.2 ppm; IR ν_{max} 3475, 2972, 2873, 1656, 1381, 1362, 1276, 1122, 1060, 831 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{10}H_{16}O_2$, 168.1150, found, 168.1149.



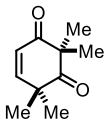
S7 **7b**


7b

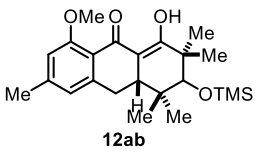
To a stirred solution of **S7** (336 mg, 2.00 mmol, 1.0 equiv.) in 20 mL anhydrous DCM was added pyridine (950 mg, 12.0 mmol, 6.0 equiv.) and TMSOTf (1.34 g, 6.00 mmol, 3.0 equiv.) at 0 °C under nitrogen atmosphere. Then the solution was stirred at room temperature for 30 minutes and quenched with saturated $NaHCO_3$.The solution was extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (5% ethyl acetate – petroleum ether) to obtain **7b** as a colorless viscous oil (452 mg, 94%). R_f = 0.65 (20% ethyl acetate – petroleum ether); Colorless viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.54 (d, *J* = 10.2 Hz, 1H), 5.82 (d, *J* = 10.2 Hz, 1H), 3.57 (s, 1H), 1.13 (s, 3H), 1.12 (s, 3H), 1.11 (s, 3H), 1.05 (s, 3H), 0.16 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.9, 156.5, 124.6, 81.4, 48.3, 38.8, 30.4, 23.7, 21.6, 20.7, 0.7 (3C) ppm; IR ν_{max} 2925, 2857, 1626, 1579, 1419, 1375, 1309, 1265, 1203, 1120 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{13}H_{24}O_2Si$, 240.1546, found, 240.1549.



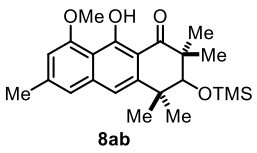
S7 **7c**


7c

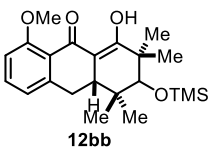
To a stirred solution of **S7** (110 mg, 0.60 mmol, 1.0 equiv.) in 10 mL anhydrous DCM was added DMP (382 mg, 0.90 mmol, 1.5 equiv.) at room temperature. After stirring at room temperature for 30 minutes, the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (5 mL, v/v = 1:1) and extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (5% ethyl acetate – petroleum ether) to obtain **7c** as a colorless viscous oil (88 mg, 88%). R_f = 0.40 (10% ethyl acetate – petroleum ether); Colorless viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.77 (d, *J* = 10.4 Hz, 1H), 6.11 (d, *J* = 10.4 Hz, 1H), 1.32 (s, 6H), 1.31 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 213.3, 201.4, 153.7, 125.0, 57.7, 44.8, 27.0 (2C), 23.6 (2C) ppm; IR ν_{max} 2925, 2857, 1626, 1579, 1419, 1375, 1309, 1265, 1203, 1120 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{10}H_{14}O_2$, 166.0994, found, 166.0996.


12ab

Compound **12ab** (274 mg, 68% yield for two steps) was prepared according to general procedure A from **7b** (240 mg, 1.0 mmol, 1.0 equiv.) and aldehyde **6a** (246 mg, 1.5 mmol, 1.5 equiv.). The PEDA reaction time was 30 minutes under λ_{max} = 366 nm UV light using anhydrous toluene as solvent. R_f = 0.28 (10% ethyl acetate – petroleum ether); White solid, m.p. 156 – 158 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 17.00 (s, 1H), 6.66 (s, 1H), 6.64 (s, 1H), 3.91 (s, 3H), 3.33 (s, 1H), 2.84 (dd, *J* = 13.0, 5.8 Hz, 1H), 2.60 – 2.46 (m, 2H), 2.35 (s, 3H), 1.33 (s, 3H), 1.18 (s, 3H), 1.06 (s, 3H), 0.96 (s, 3H), 0.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.9, 186.6, 159.7, 144.7, 144.1, 121.1, 118.3, 111.1, 106.3, 85.1, 56.0, 42.7, 37.4, 37.1, 30.3, 27.3, 27.1, 27.0, 22.5, 22.0, 0.9 (3C) ppm; IR ν_{max} 2956, 2916, 1703, 1606, 1483, 1319, 1068, 1012 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{34}O_4Si$, 402.2226, found, 402.2232.

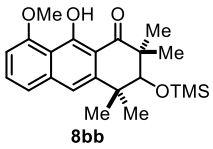

8ab

Compound **8ab** (212 mg, 78% yield) was prepared according to general procedure B from the above obtained compound **12ab**. R_f = 0.42 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 146 – 148 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 15.63 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.63 (s, 1H), 4.00 (s, 3H), 3.74 (s, 1H), 2.45 (s, 3H), 1.44 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 0.21 (s, 9H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 209.8, 167.1, 160.5, 146.9, 142.6, 141.5, 120.7, 115.2, 113.9, 109.5, 108.7, 81.7, 57.1, 48.9, 41.0, 29.6, 28.2, 27.4, 23.2, 22.7, 1.8 (3C) ppm; IR ν_{max} 2957, 1706, 1624, 1578, 1385, 1367, 1315, 1120, 1097. 1051 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{32}O_4Si$, 400.2070, found, 400.2073.


12bb

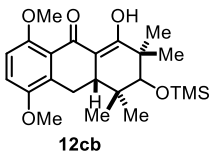
Compound **12bb** (85 mg, 73% yield for two steps) was prepared according to general procedure A from **7b** (72 mg, 0.3 mmol, 1.0 equiv.) and aldehyde **6b** (68 mg, 0.45 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using

anhydrous 1, 4-dioxane as solvent. R_f = 0.28 (5% ethyl acetate – petroleum ether); White solid, m.p. 191 – 193 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.97 (s, 1H), 7.33 (t, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 7.5 Hz, 1H), 3.91 (s, 3H), 3.34 (s, 1H), 2.86 (t, *J* = 9.4 Hz, 1H), 2.57 (d, *J* = 8.6 Hz, 2H), 1.33 (s, 3H), 1.18 (s, 3H), 1.06 (s, 3H), 0.96 (s, 3H), 0.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 188.9, 186.2, 159.6, 144.7, 133.1, 120.7, 120.2, 110.4, 106.5, 85.0, 56.0, 42.8, 37.2, 37.1, 30.2, 27.2, 27.1, 27.0, 22.4, 0.8 (3C) ppm; IR ν_{max} 2953, 1702, 1595,1388, 1348, 1151, 1082, 875 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{32}O_4Si$, 388.2070, found, 388.2075.



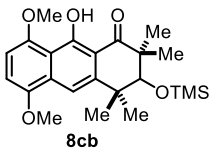
8bb

Compound **8bb** (66 mg, 78% yield) was prepared according to general procedure B from the above obtained compound **12bb**. R_f = 0.34 (5% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.58 (s, 1H), 7.48 (t, *J* = 8.0 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.17 (s, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 4.02 (s, 3H), 3.75 (s, 1H), 1.46 (s, 3H), 1.32 (s, 3H), 1.29 (s, 3H), 1.27 (s, 3H), 0.22 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 209.1, 166.1, 159.7, 145.8, 140.3, 130.8, 120.2, 114.9, 114.7, 109.0, 105.7, 80.7, 56.2, 48.0, 40.0, 28.6, 27.3, 26.4, 21.7, 0.8 (3C) ppm; IR ν_{max} 2956, 1700, 1622, 1575, 1493, 1352, 1266, 1105, 1010, 895 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{30}O_4Si$, 386.1913, found, 386.1917.



12cb

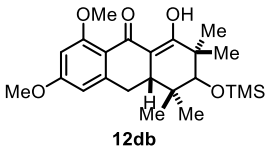
Compound **12cb** (28 mg, 38% yield for two steps) was prepared according to general procedure A from **7b** (42 mg, 0.175 mmol, 1.0 equiv.) and aldehyde **6c** (47 mg, 0.26 mmol, 1.5 equiv.). The PEDA reaction time was 30 minutes under λ_{max} = 366 nm UV light using anhydrous toluene as solvent. R_f = 0.2 (10% ethyl acetate – petroleum ether); White solid, m.p. 190 – 192 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.91 (s, 1H), 6.96 (d, *J* = 9.1 Hz, 1H), 6.80 (d, *J* = 9.1 Hz, 1H), 3.88 (s, 3H), 3.82 (s, 3H), 3.35 (s, 1H), 3.09 (dd, *J* = 15.2, 4.3 Hz, 1H), 2.77 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.12 (t, *J* = 15.0 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 3H), 1.09 (s, 3H), 0.98 (s, 3H), 0.11 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.5, 186.8, 154.7, 150.7, 133.9, 122.9, 116.2, 111.3, 107.5, 86.2, 57.5, 57.2, 43.9, 38.3, 37.8, 28.2, 28.14, 28.10, 23.6, 22.9, 1.9 (3C) ppm; IR ν_{max} 2918, 2849, 1703, 1568, 1483, 1266, 1013, 897, 871, 841 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{34}O_5Si$, 418.2176, found, 418.2184.



8cb

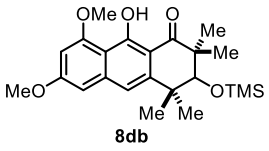
Compound **8cb** (26 mg, 94% yield) was prepared according to general procedure B from the above obtained compound **12cb**. R_f = 0.38 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 127 – 129 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.34 (s, 1H), 7.68 (s, 1H), 6.88 (d, *J* = 8.6 Hz, 1H), 6.73 (d, *J* = 8.6 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 3.75 (s, 1H), 1.48 (s, 3H), 1.31 (s, 3H), 1.29 (s, 3H), 1.28 (s, 3H), 0.21 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.6, 166.2, 154.3, 149.8, 146.5, 132.2, 116.7, 110.7, 109.8, 109.6, 106.7, 81.9, 57.8, 56.9, 49.2, 41.4, 29.9, 28.2, 27.5,

22.7, 1.8 (3C) ppm; IR ν_{max} 3003, 2954, 2833, 1701, 1622, 1585, 1493, 1383, 1107, 893 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{32}O_5Si$, 416.2019, found, 416.2022.



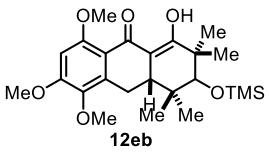
12db

Compound **12db** (77 mg, 61% yield for two steps) was prepared according to general procedure A from **7b** (72 mg, 0.3 mmol, 1.0 equiv.) and aldehyde **6d** (81 mg, 0.45 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.19 (5% ethyl acetate – petroleum ether); White solid, m.p. 190 – 192 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.00 (s, 1H), 6.36 (d, *J* = 2.2 Hz, 1H), 6.34 (d, *J* = 2.0 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H), 3.32 (s, 1H), 2.83 (dd, *J* = 13.4, 5.3 Hz, 1H), 2.64 – 2.48 (m, 2H), 1.32 (s, 3H), 1.17 (s, 3H), 1.06 (s, 3H), 0.96 (s, 3H), 0.10 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 186.9, 186.3, 163.5, 161.6, 146.9, 114.6, 105.7, 104.7, 97.4, 85.1, 56.0, 55.4, 42.4, 37.3, 37.1, 31.0, 27.3, 27.1, 27.0, 22.5, 0.9 (3C) ppm; IR ν_{max} 2957, 2873, 1690, 1599, 1458, 1325, 1282, 1264, 1251, 1205, 1159, 1089 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{34}O_5Si$, 418.2176, found, 418.2180.



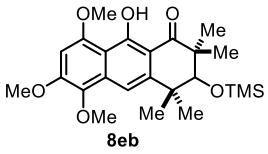
8db

Compound **8db** (73 mg, 96% yield) was prepared according to general procedure B from the above obtained compound **12db**. R_f = 0.36 (5% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.70 (s, 1H), 7.05 (s, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 6.43 (d, *J* = 2.2 Hz, 1H), 3.98 (s, 3H), 3.91 (s, 3H), 3.73 (s, 1H), 1.44 (s, 3H), 1.31 (s, 3H), 1.27 (s, 3H), 1.26 (s, 3H), 0.21 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.3, 166.3, 162.0, 161.1, 146.7, 141.9, 114.0, 110.2, 107.8, 99.2, 98.0, 80.8, 56.2, 55.4, 47.8, 40.0, 28.6, 27.2, 26.3, 21.7, 0.8 (3C) ppm; IR ν_{max} 3005, 2988, 1691, 1620, 1585, 1383, 1315, 1159, 1119, 1087, 1066, 895 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{32}O_5Si$, 416.2019, found, 416.2024.



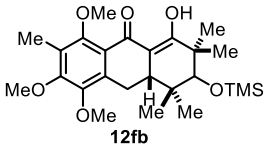
12eb

Compound **12eb** (86 mg, 64% yield for two steps) was prepared according to general procedure A from **7b** (72 mg, 0.3 mmol, 1.0 equiv.) and aldehyde **6e** (95 mg, 0.45mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.26 (20% ethyl acetate – petroleum ether); White solid, m.p. 206 – 208 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.97 (s, 1H), 6.40 (s, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.72 (s, 3H), 3.33 (s, 1H), 3.07 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.71 (dd, *J* = 14.6, 4.0 Hz, 1H), 2.15 (t, *J* = 14.7 Hz, 1H), 1.32 (s, 3H), 1.17 (s, 3H), 1.08 (s, 3H), 0.98 (s, 3H), 0.09 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 186.1, 185.7, 156.7, 155.8, 138.0, 137.0, 113.1, 104.9, 94.3, 84.3, 60.0, 55.6, 54.9, 41.7, 36.4, 36.2, 26.4, 26.2, 26.1, 21.69, 21.66, 0.0 (3C) ppm; IR ν_{max} 2916, 2849, 1738, 1691, 1645, 1591, 1556, 1329, 1286, 1236, 1089, 1070 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{24}H_{36}O_6Si$, 448.2281, found, 448.2279.



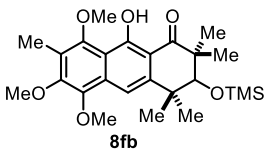
8eb

Compound **8eb** (77 mg, 90% yield) was prepared according to general procedure B from the above obtained compound **12eb**. R_f = 0.48 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.83 (s, 1H), 7.45 (s, 1H), 6.56 (s, 1H), 4.01 (s, 3H), 4.00 (s, 3H), 3.87 (s, 3H), 3.74 (s, 1H), 1.47 (s, 3H), 1.31 (s, 3H), 1.28 (s, 3H), 1.26 (s, 3H), 0.21 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.4, 166.8, 157.4, 152.8, 146.2, 136.1, 134.7, 109.9, 107.6, 107.4, 95.1, 80.8, 60.9, 56.6, 56.4, 47.7, 40.3, 28.6, 27.3, 26.4, 21.7, 0.8 (3C) ppm; IR ν_{max} 2988, 2847, 1691, 1618, 1593, 1425, 1387, 1315, 1213, 1115, 1066, 1032 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{24}H_{34}O_6Si$, 446.2125, found, 446.2129.



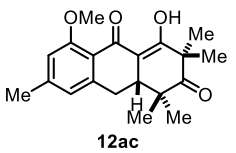
12fb

Compound **12fb** (99 mg, 71% yield for two steps) was prepared according to general procedure A from **7b** (72mg, 0.3 mmol, 1.0 equiv.) and aldehyde **6f** (100 mg, 0.45 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.56 (5% ethyl acetate – petroleum ether); White solid, m.p. 136 – 138 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 17.10 (s, 1H), 3.89 (s, 3H), 3.79 (s, 3H), 3.77 (s, 3H), 3.36 (s, 1H), 3.02 (dd, *J* = 14.8, 4.3 Hz, 1H), 2.77 (dd, *J* = 14.7, 4.3 Hz, 1H), 2.17 (s, 3H), 2.16 (t, *J* = 14.6 Hz, 1H), 1.33 (s, 3H), 1.18 (s, 3H), 1.09 (s, 3H), 0.97 (s, 3H), 0.11 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 189.8, 183.5, 154.7, 154.5, 144.6, 133.7, 124.1, 120.1, 105.2, 84.2, 60.7, 59.7, 59.4, 42.2, 36.4, 36.0, 26.4, 26.3, 26.2, 21.6, 21.3, 8.1, 0.0 (3C) ppm; IR ν_{max} 1691, 1645, 1587, 1556, 1388, 1329, 1207, 1116, 1084, 902 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{38}O_6Si$, 462.2438, found, 462.2443.



8fb

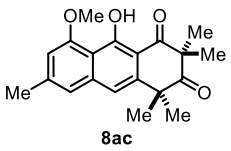
Compound **8fb** (35.5 mg, 36% yield) was prepared according to general procedure B from the above obtained compound **12fb**. R_f = 0.62 (5% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.44 (s, 1H), 7.51 (s, 1H), 3.99 (s, 3H), 3.93 (s, 3H), 3.85 (s, 3H), 3.76 (s, 1H), 2.32 (s, 3H), 1.49 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 0.22 (s, 9H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 208.5, 164.0, 152.8, 151.9, 144.1, 141.9, 132.2, 123.2, 114.4, 107.7, 107.0, 80.0, 60.8, 60.1, 59.6, 47.2, 39.4, 28.0, 26.4, 25.7, 20.9, 8.5, 0.0 (3C) ppm; IR ν_{max} 2988, 1733, 1692, 1614, 1568, 1390, 1118, 1089, 1055, 1003 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{25}H_{36}O_6Si$, 460.2281, found, 460.2285.



12ac

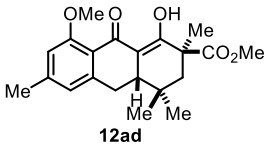
Compound **12ac** (12 mg, 20% yield for two steps) was prepared according to general procedure A from **7c** (30 mg, 0.18 mmol, 1.0 equiv.) and aldehyde **6a** (45 mg, 0.27 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous toluene as solvent. R_f = 0.3 (10% ethyl acetate – petroleum ether); Light yellow solid, m.p. 185 – 187 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.83 (s, 1H), 6.70 (s, 1H), 6.67 (s, 1H), 3.93 (s, 3H), 2.85 –

2.64 (m, 3H), 2.37 (s, 3H), 1.42 (s, 3H), 1.28 (s, 3H), 1.23 (s, 3H), 1.09 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 216.1, 189.9, 184.8, 160.9, 146.0, 143.4, 122.5, 118.1, 112.6, 105.7, 57.1, 50.9, 47.4, 39.2, 30.7, 26.7, 24.3, 23.0, 22.3, 20.9 ppm; IR ν_{max} 3014, 1707, 1608, 1421, 1313, 1267, 1205, 1097 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_4$, 328.1675, found, 328.1679.



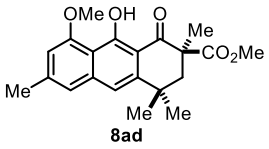
8ac

Compound **8ac** (9 mg, 75% yield) was prepared according to general procedure B from the above obtained compound **12ac**. R_f = 0.4 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 146 – 148 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 14.56 (s, 1H), 7.10 (s, 2H), 6.69 (s, 1H), 4.03 (s, 3H), 2.48 (s, 3H), 1.55 (s, 6H), 1.44 (s, 6H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 213.3, 205.9, 165.9, 160.5, 143.2, 142.9, 141.3, 121.0, 115.4, 114.0, 109.34, 109.28, 57.2, 56.0, 49.1, 29.3 (2C), 25.5 (2C), 23.2 ppm; IR ν_{max} 3053, 2943, 1709, 1624, 1578, 1385, 1367, 1333, 1161, 1118 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{22}O_4$, 326.1518, found, 326.1516.



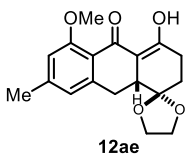
12ad

Compound **12ad** (57 mg, 80% yield for two steps) was prepared according to general procedure A from **7d** (40 mg, 0.2 mmol, 1.0 equiv.) and aldehyde **6a** (49 mg, 0.3 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.40 (20% ethyl acetate – petroleum ether); White solid, m.p. 160 – 162 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.76 (s, 1H), 6.68 (s, 1H), 6.64 (s, 1H), 3.92 (s, 3H), 3.66 (s, 3H), 2.70 – 2.46 (m, 3H), 2.36 (s, 3H), 2.03 (d, *J* = 13.8 Hz, 1H), 1.64 (d, *J* = 13.8 Hz, 1H), 1.60 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.8, 181.0, 175.2, 160.1, 144.9, 144.4, 121.1, 117.9, 111.3, 107.4, 56.1, 52.6, 49.0, 48.1, 42.9, 31.9, 30.8, 29.5, 22.9, 22.7, 22.0 ppm; IR ν_{max} 3057, 2957, 1738, 1607, 1479, 1460, 1265, 1230, 1155, 1097, 876, 835 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{26}O_5$, 358.1780, found, 358.1784.



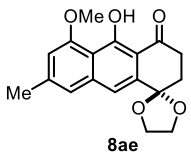
8ad

Compound **8ad** (48.4 mg, 85% yield) was prepared according to general procedure B from the above obtained compound **12ad**. R_f = 0.6 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 181 – 183 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.69 (s, 1H), 7.04 (s, 1H), 6.98 (s, 1H), 6.64 (s, 1H), 4.02 (s, 3H), 3.65 (s, 3H), 2.49 (d, *J* = 14.2 Hz, 1H), 2.46 (s, 3H), 2.04 (d, *J* = 14.1 Hz, 1H), 1.59 (s, 3H), 1.44 (s, 3H), 1.24 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 201.6, 174.7, 167.1, 159.7, 146.6, 142.0, 140.8, 119.7, 113.8, 113.0, 109.7, 107.8, 56.2, 52.7, 52.0, 47.9, 33.5, 31.6, 30.5, 24.7, 22.2 ppm; IR ν_{max} 2988, 1734, 1626, 1578, 1267, 1227, 1151, 897 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{24}O_5$, 356.1624, found, 356.1622.



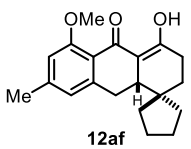
12ae

Compound **12ae** (20 mg, 32% yield for two steps) was prepared according to general procedure A from **7e** (31 mg, 0.2 mmol, 1.0 equiv.) and aldehyde **6a** (49 mg, 0.3 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.26 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 177 – 180 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.55 (s, 1H), 6.66 (s, 1H), 6.65 (s, 1H), 4.14 – 3.98 (m, 4H), 3.91 (s, 3H), 3.00 (ddd, *J* = 11.0, 7.0, 1.6 Hz, 1H), 2.80 – 2.64 (m, 3H), 2.48 (ddd, *J* = 18.6, 6.0, 1.5 Hz, 1H), 2.35 (s, 3H), 1.94 (ddd, *J* = 13.2, 6.5, 1.6 Hz, 1H), 1.81 (td, *J* = 13.0, 6.1 Hz, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.0, 180.9, 160.2, 144.8, 144.3, 121.5, 117.9, 111.2, 107.9, 106.3, 65.6, 64.9, 56.0, 40.6, 29.9, 29.8, 29.0, 22.0 ppm; IR ν_{max} 3055, 2883, 1718, 1606, 1414, 1337, 1277, 1267, 1147, 1089, 1049, 926 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{20}O_5$, 316.1311, found, 316.1308.



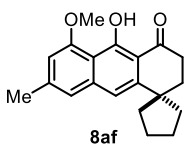
8ae

Compound **8ae** (20 mg, quantitative yield) was prepared according to general procedure B from the above obtained compound **12ae**. R_f = 0.32 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 185 – 189 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.26 (s, 1H), 7.20 (s, 1H), 7.12 (s, 1H), 6.70 (s, 1H), 4.24 – 4.10 (m, 4H), 4.01 (s, 3H), 2.96 (t, *J* = 6.6 Hz, 2H), 2.47 (s, 3H), 2.30 (t, *J* = 6.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.9, 166.0, 159.6, 142.0, 140.1, 137.4, 120.6, 114.3, 113.5, 110.0, 108.7, 105.7, 65.2 (2C), 56.2, 35.5, 32.8, 22.2 ppm; IR ν_{max} 2914, 2849, 1722, 1610, 1579, 1275, 1267, 1116, 1090, 1026 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{18}O_5$, 314.1154, found, 314.1150.



12af

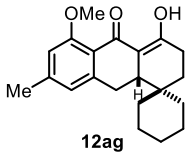
Compound **12af** (24.4 mg, 30% yield for two steps) was prepared according to general procedure A from **7f** (40 mg, 0.26 mmol, 1.0 equiv.) and aldehyde **6a** (64 mg, 0.39 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.38 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 167 – 169 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.63 (s, 1H), 6.66 (s, 1H), 6.64 (s, 1H), 3.91 (s, 3H), 2.67 (d, *J* = 11.2 Hz, 1H), 2.62 – 2.50 (m, 2H), 2.47 (dd, *J* = 12.4, 6.3 Hz, 1H), 2.38 – 2.29 (m, CH_3 + 1/2 CH_2, 4H), 1.79 – 1.63 (m, 5H), 1.62 – 1.49 (m, 3H), 1.43 – 1.35 (m, 1H), 1.34 – 1.23 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.9, 181.9, 160.0, 144.9, 144.5, 121.2, 118.1, 111.2, 108.8, 56.0, 43.3, 41.6, 38.0, 34.1, 31.4, 30.3, 28.7, 26.8, 25.0, 22.0 ppm; IR ν_{max} 2916, 2848, 1720, 1608, 1541, 1421, 1339, 1265 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_3$, 312.1725, found, 312.1722.



8af

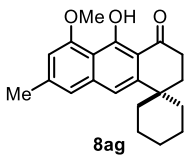
Compound **8af** (24.2 mg, quantitative yield) was prepared according to general procedure B from the above obtained compound **12af**. R_f = 0.54 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 136 – 138 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.67 (s, 1H), 7.04

(s, 1H), 6.91 (s, 1H), 6.62 (s, 1H), 4.00 (s, 3H), 2.79 (t, *J* = 6.6 Hz, 2H), 2.45 (s, 3H), 2.02 (t, *J* = 6.6 Hz, 4H), 1.93 – 1.71 (m, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) ^{13}C NMR (100 MHz, Chloroform-d) δ 204.3, 166.4, 159.6, 147.3, 141.7, 140.6, 119.8, 113.7, 113.0, 110.6, 107.6, 56.1, 46.0, 39.8 (2C), 35.9, 34.9, 25.0 (2C), 22.2 ppm; IR ν_{max} 2951, 2854, 1718, 1625, 1577, 1419, 1267, 1199, 1120, 1003 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{22}O_3$, 310.1569, found, 310.1566.



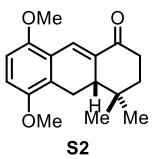
12ag

Compound **12ag** (25.4 mg, 26% yield for two steps) was prepared according to general procedure A from **7g** (31 mg, 0.3 mmol, 1.0 equiv.) and aldehyde **6a** (49 mg, 0.45 mmol, 1.5 equiv.). The PEDA reaction time was 60 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.28 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 206 – 209 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 16.62 (s, 1H), 6.66 (s, 1H), 6.64 (s, 1H), 3.91 (s, 3H), 2.68 (dd, *J* = 14.1, 3.4 Hz, 1H), 2.51 (t, *J* = 14.2 Hz, 1H), 2.35 (s, 3H), 2.35 – 2.28 (m, 2H), 2.27 – 2.20 (m, 1H), 1.76 – 1.65 (m, 2H), 1.64 – 1.53 (m, 5H), 1.45 – 1.28 (m, 1H), 1.27 – 1.09 (m, 4H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 187.9, 181.6, 160.0, 145.1, 144.5, 121.1, 118.1, 111.2, 107.8, 56.0, 43.6, 35.7, 34.1, 30.7, 27.3, 27.2, 27.1, 26.6, 22.1, 21.6, 21.3 ppm; IR ν_{max} 2924, 1708, 1608, 1417, 1309, 1267, 1107, 1092, 897, 816 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{26}O_3$, 326.1882, found, 326.1886.



8ag

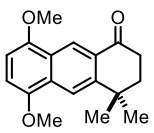
Compound **8ag** (25.2 mg, quantitative yield) was prepared according to general procedure B from the above obtained compound **12ag**. R_f = 0.42 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 158 – 160 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 15.69 (s, 1H), 7.08 (s, 1H), 7.05 (s, 1H), 6.62 (s, 1H), 4.00 (s, 3H), 2.72 (t, *J* = 6.7 Hz, 2H), 2.45 (s, 3H), 2.10 (t, *J* = 6.7 Hz, 2H), 1.84 – 1.73 (m, 5H), 1.72 – 1.64 (m, 2H), 1.64 – 1.51 (m, 2H), 1.39 – 1.27 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.1, 166.5, 159.6, 148.3, 141.6, 140.8, 119.9, 112.89, 112.86, 110.5, 107.7, 56.1, 36.7, 36.4 (2C), 33.6, 27.7, 26.0, 22.2, 22.0 (2C) ppm; IR ν_{max} 2925, 2857, 1626, 1579, 1419, 1375, 1309, 1265, 1203, 1120 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{24}O_3$, 324.1725, found, 324.1729.



S2

Compound **S2** (71.5 mg, 25% yield for one step) was prepared according to the step 1 of general procedure A from **7h** (248 mg, 2.0 mmol, 2.0 equiv.) and aldehyde **6c** (180 mg, 1.0 mmol, 1.0 equiv.). The PEDA reaction time was 3 hours under λ_{max} = 366 nm UV light using anhydrous toluene as solvent. R_f = 0.30 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 153 - 155 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (d, *J* = 3.0 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 3.19 (dd, *J* = 15.8, 5.9 Hz, 1H), 2.61 – 2.43 (m, 3H), 2.23 (t, *J* = 16.4 Hz, 1H), 1.78 – 1.68 (m, 2H), 1.15 (s, 3H), 0.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.1, 152.0, 150.2, 133.8, 130.1, 126.9, 122.6, 113.1, 108.7, 56.0, 55.9, 44.0, 36.7, 35.1, 31.6, 29.2, 22.2, 20.8 ppm; IR ν_{max} 2935, 1747,

1670, 1593, 1566, 1483, 1281, 1261, 1101, 1078 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{22}O_3$, 286.1569, found, 286.1566.



S8

Compound **S8** (51 mg, 72% yield) was prepared according to general procedure B from the above obtained compound **S2**. R_f = 0.46 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 120 – 122 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.96 (s, 1H), 8.19 (s, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.95 (s, 3H), 2.82 (t, *J* = 3.2 Hz, 2H), 2.08 (t, *J* = 6.8 Hz, 2H), 1.49 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.7, 151.2, 148.9, 147.7, 129.3, 129.0, 124.5, 123.5, 118.2, 106.0, 102.9, 55.8, 55.7, 37.1, 35.5, 34.2, 30.1 (2C) ppm; IR ν_{max} 2970, 1749, 1683, 1626, 1585, 1462, 1286, 1269, 1120, 1092 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{20}O_3$, 284.1412, found, 284.1413.

Experimental procedures and spectroscopic data of synthesis of the isomer of garveatin C

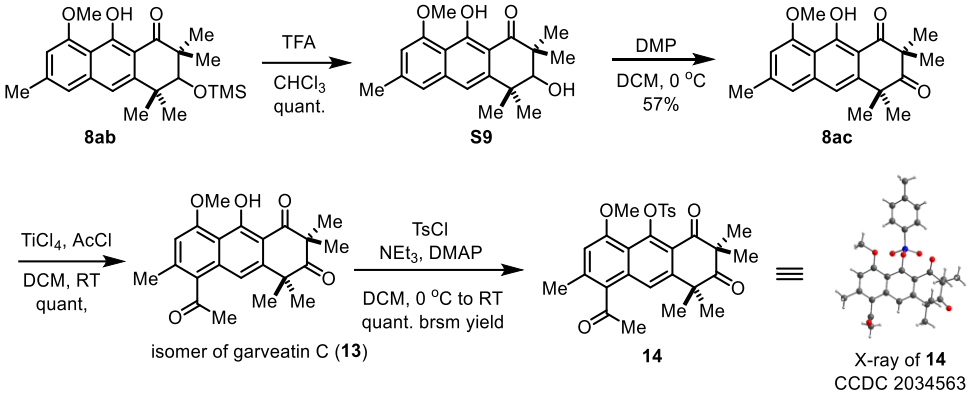
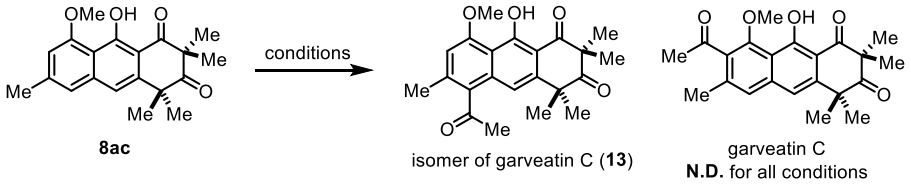
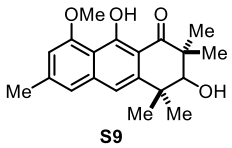


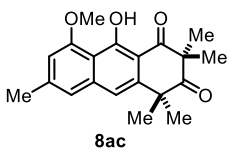
Table S2. Screening acetylation conditions of **8ac**



entry	condition	result
1	$AlCl_3$, AcCl, DCM, 0 °C to RT to 50 °C	trace **13**
2	$AlCl_3$, Ac_2O, DCM, 0 °C to RT to 50 °C	trace **13**
3	$BF_3{\cdot}Et_2O$, AcCl, DCM, RT to 50 °C	trace **13**
4	$BF_3{\cdot}Et_2O$, Ac_2O, DCM, RT to 50 °C	trace **13**
5	$TiCl_4$, AcCl, DCM, 0 °C to RT	quant. **13**
6	*n*-BuLi then AcCl, THF, 0 °C to RT	N.R.

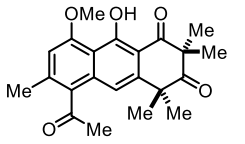


To a stirred solution of compound **8ab** (72 mg, 0.18 mmol, 1.0 equiv.) in 5 mL AR grade chloroform was added TFA (0.50 mL) at room temperature. After stirring at room temperature for 1 hour, the mixture was quenched with saturated $NaHCO_3$ at 0 °C and extracted with ethyl acetate (3×20 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (15% ethyl acetate – petroleum ether) to obtain the corresponding product **S9** as yellow solid (60 mg, quantitative yield). R_f = 0.18 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 176 – 178 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 15.67 (s, 1H), 7.08 (s, 1H), 7.06 (s, 1H), 6.64 (s, 1H), 4.01 (s, 3H), 3.69 (d, *J* = 6.2 Hz, 1H), 2.46 (s, 3H), 1.88 (d, *J* = 6.3 Hz, 1H), 1.52 (s, 3H), 1.39 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 208.1, 166.5, 159.6, 145.4, 141.8, 140.6, 119.7, 114.4, 113.1, 108.4, 107.9, 79.3, 56.2, 47.3, 39.5, 28.9, 26.6, 26.0, 22.2, 21.6 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_4$, 328.1675, found, 328.1678.



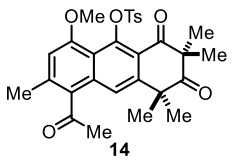
To a stirred solution of compound **S9** (60 mg, 0.18 mmol, 1.0 equiv.) in 10 mL anhydrous DCM was added DMP (60 mg, 0.18 mmol, 1.0 equiv.) at room temperature. After stirring at room temperature for 30 minutes, the mixture was quenched with saturated

Na_2SO_3/$NaHCO_3$ (5 mL, v/v = 1:1) and extracted with ethyl acetate (3×20 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% ethyl acetate – petroleum ether) to obtain **8ac** as yellow solid (33 mg, 57%).



isomer of garveatin C **(13)**

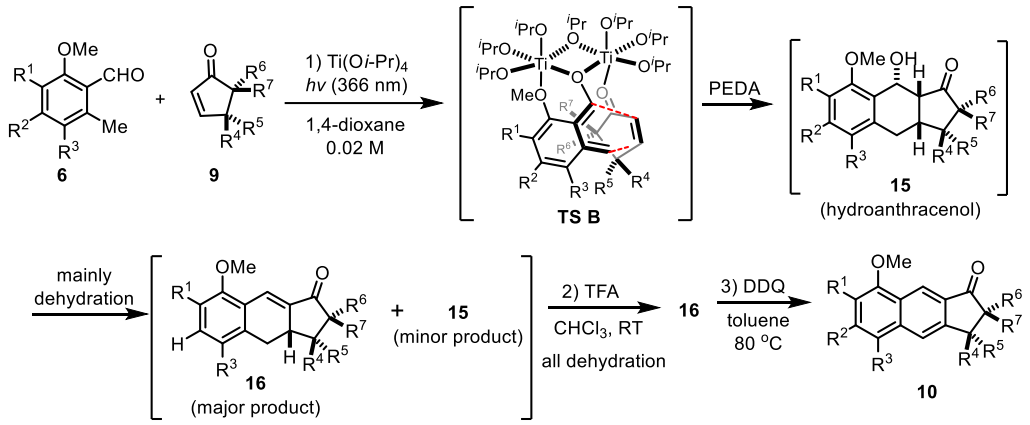
To a stirred solution of compound **8ac** (20 mg, 0.06 mmol, 1.0 equiv.) in 3 mL anhydrous DCM was added acetyl chloride (190 mg, 2.40 mmol, 40.0 equiv.) and titanium tetrachloride (228 mg, 1.20 mmol, 20.0 equiv.) at 0 °C. After stirring at room temperature for 5 hours, the mixture was quenched with saturated $NaHCO_3$ (5 mL) and extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (10% to 20% ethyl acetate – petroleum ether) to obtain compound **13** as yellow viscous oil (23 mg, quantitative yield). R_f = 0.38 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 14.52 (s, 1H), 6.92 (s, 1H), 6.68 (s, 1H), 4.04 (s, 3H), 2.59 (s, 3H), 2.41 (s, 3H), 1.52 (s, 6H), 1.44 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 211.7, 207.3, 205.2, 164.8, 159.7, 143.2, 137.3, 135.8, 131.8, 113.3, 110.9, 108.6, 108.5, 56.3, 55.2, 48.3, 33.0, 28.3 (2C), 24.5 (2C), 20.2 ppm; IR ν_{max} 3009, 2949, 1791, 1699, 1618, 1423, 1352, 1153, 1055, 1006 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{24}O_5$, 368.1624, found, 368.1629.



14

To a stirred solution of compound **13** (23 mg, 0.06 mmol, 1.0 equiv.) in 3 mL anhydrous DCM was added triethylamine (30 mg, 0.30 mmol, 5.0 equiv.), DMAP (3.7 mg, 0.03 mmol, 0.5 equiv.) and TsCl (11.5 mg, 0.12 mmol, 2.0 equiv.) at 0 °C. After stirring at room temperature for 3 hours, the mixture was concentrated and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain compound **14** as yellow solid (15 mg, 54%) and starting material **13** (10 mg, 46%). R_f = 0.2 (20% ethyl acetate – petroleum ether); Compound **14** was recrystallized from 1,2-dichloroethane/hexane (v/v = 1/4) at room temperature to obtain yellow crystals, CCDC (2034563). m.p. 175–177 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.53 (s, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 6.61 (s, 1H), 3.69 (s, 3H), 2.63 (s, 3H), 2.46 (s, 3H), 2.41 (s, 3H), 1.47 (s, 6H), 1.33 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.9, 207.0, 198.0, 157.0, 145.0, 142.6, 142.1, 135.5, 134.1, 134.0, 131.1, 129.4 (2C), 128.4 (2C), 124.8, 119.0 117.8, 109.3, 58.2, 55.5, 49.0, 33.2, 27.4 (2C), 22.9 (2C), 21.7 , 20.2 ppm; IR ν_{max} 2954, 2916, 1697, 1614, 1421, 1352, 1172, 1151, 1008, 866 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{29}H_{30}O_7S$, 522.1712, found, 522.1722.

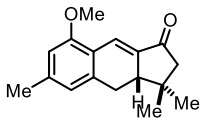
Experimental procedures and spectroscopic data of PEDA/dehydration/aromatization sequence



General procedure C for PEDA reaction and dehydration: To a solution of dienophile **9** (1.0 equiv.) and aromatic aldehyde **6** (1.5 equiv.) in anhydrous and degassed 1,4-dioxane (concentration for dienophile is 0.02 M) in quartz tube sealed with rubber plug was added titanium(IV) isopropoxide (2.0 equiv.) under N_2, after homogeneous mixing, the solution was photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at 366 nm until the dienophile **9** was completely consumed by TLC analysis. Then saturated $NaHCO_3$ was added and stirred for 5 minutes. The mixture was filtered through silica gel and washed with ethyl acetate for six times, separated the organic layer and washed with brine. The organic layer was dried over anhydrous sodium sulfate, concentrated to obtain the crude dehydration product **16** with a part of hydroanthracenol product **15**. These crude products were dissolved in AR grade chloroform and then added TFA (2.0 equiv.) at room temperature. The solution was stirred at room temperature until the hydroanthracenol product **15** was consumed completely by TLC analysis. Then the mixture was quenched with saturated $NaHCO_3$ at 0 °C and extracted with ethyl acetate for three times. The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography to obtain the corresponding product **16**.

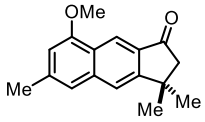
General procedure D for aromatization: To a 0.01 M stirred solution of the above obtained product **16** in anhydrous toluene was added DDQ (3.0 equiv.) at room temperature and stirred at 80 °C until the starting material was consumed completely by TLC analysis. Then the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (v/v = 1:1) at 0 °C and extracted with ethyl acetate for three times. The combined organic layers were washed with saturated Na_2SO_3/$NaHCO_3$ (v/v = 1:1) solution, brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography to obtain the corresponding naphthalene product **10**.

All starting materials of **6** and **9** are known compounds except **9h** and **9i**.



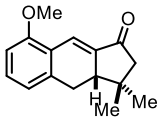
16aa

Compound **16aa** (58 mg, 36% yield for two steps) was prepared according to general procedure C from **9a** (70 mg, 0.63 mmol, 1.0 equiv.) and aldehyde **6a** (154 mg, 0.945 mmol, 1.5 equiv.). The PEDA reaction time was 45 min under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.75 (20% ethyl acetate – petroleum ether); Light yellow solid, m.p. 69 - 71 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.7 Hz, 1H), 6.61 (s, 1H), 6.54 (s, 1H), 3.81 (s, 3H), 2.87 – 2.66 (m, 3H), 2.33 (s, 3H), 2.29 (d, *J* = 7.7 Hz, 2H), 1.25 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.0, 157.9, 141.4, 137.9, 136.7, 124.5, 121.7, 119.3, 110.1, 55.51, 55.46, 46.2, 36.3, 28.6, 27.4, 24.1, 22.0 ppm; IR ν_{max} 3053, 2962, 2848, 1735, 1682, 1265, 1099, 802, 705 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{20}O_2$, 256.1463, found, 256.1467.



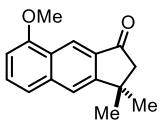
10aa

Compound **10aa** (58 mg, quantitative yield) was prepared according to general procedure D from the above obtained compound **16aa**. R_f = 0.45 (10% ethyl acetate – petroleum ether); Light yellow solid, m.p. 125 - 127 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.70 (s, 1H), 7.21 (s, 1H), 6.61 (s, 1H), 3.98 (s, 3H), 2.67 (s, 2H), 2.50 (s, 3H), 1.49 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.0, 158.2, 157.4, 139.5, 138.7, 132.0, 123.5, 120.4, 119.2, 119.1, 106.0, 55.5, 53.8, 38.2, 30.5 (2C), 22.5 ppm; IR ν_{max} 3054, 2960, 2916, 1708, 1627, 1267, 744 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{18}O_2$, 254.1307, found, 254.1311.



16ba

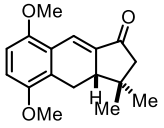
Compound **16ba** (91 mg, 47% yield for two steps) was prepared according to general procedure C from **9a** (88 mg, 0.8 mmol, 1.0 equiv.) and aldehyde **6b** (180 mg, 1.2 mmol, 1.5 equiv.). The PEDA reaction time was 1.75 hours under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.32 (5% ethyl acetate – petroleum ether); Light yellow solid, m.p. 63 - 65 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 2.4 Hz, 1H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.5 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 3.81 (s, 3H), 2.89 – 2.72 (m, 3H), 2.32 (d, *J* = 17.3 Hz, 1H), 2.26 (d, *J* = 17.3 Hz, 1H), 1.25 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.0, 157.7, 137.9, 137.6, 130.6, 124.2, 121.8, 120.7, 109.1, 55.5, 55.3, 46.0, 36.2, 28.5, 27.3, 24.1 ppm; IR ν_{max} 3055, 2958, 2837, 1707, 1629, 1573, 1309, 1267, 705 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{16}H_{18}O_2$, 242.1307, found, 242.1311.



10ba

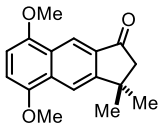
Compound **10ba** (83 mg, 92% yield) was prepared according to general procedure D from the above obtained compound **16ba**. R_f = 0.34 (5% ethyl acetate – petroleum ether); Light yellow solid, m.p. 68 - 70 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.81 (s, 1H), 7.45 (dt, *J* = 15.5, 8.3 Hz, 2H), 6.77 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 3H), 2.68 (s, 2H), 1.49 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.1, 157.9, 157.5, 138.4, 132.7, 128.9, 125.0, 121.2, 120.0, 119.2, 103.6, 55.5, 53.7,

38.3, 30.5 (2C) ppm; IR ν_{max} 3056, 2959, 1708, 1627, 1311, 1267, 794, 746, 706 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{16}H_{16}O_2$, 240.1150, found, 240.1148.



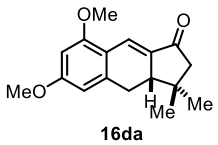
16ca

Compound **16ca** (120 mg, 55% yield for two steps) was prepared according to general procedure C from **9a** (88 mg, 0.8 mmol, 1.0 equiv.) and aldehyde **6c** (216 mg, 1.2 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.62 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 128 - 130 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 3.3 Hz, 1H), 6.82 (d, *J* = 9.0 Hz, 1H), 6.66 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.23 (dd, *J* = 16.0, 7.6 Hz, 1H), 2.75 (ddd, *J* = 16.6, 7.6, 3.3 Hz, 1H), 2.42 – 2.24 (m, 3H), 1.27 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.5, 152.3, 150.7, 137.7, 125.4, 124.3, 122.8, 113.3, 109.0, 56.0, 55.9, 55.4, 45.4, 36.5, 27.3, 24.1, 20.8 ppm; IR ν_{max} 3053, 2956, 2835, 1707, 1633, 1485, 1259, 1093, 796, 746 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{20}O_3$, 272.1412, found, 272.1415.



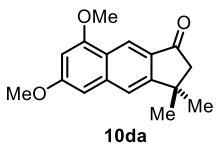
10ca

Compound **10ca** (114 mg, 96% yield) was prepared according to general procedure D from the above obtained compound **16ca**. R_f = 0.42 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 122 - 124 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 8.26 (s, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.64 (d, *J* = 8.3 Hz, 1H), 3.97 (s, 3H), 3.94 (s, 3H), 2.68 (s, 2H), 1.50 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.3, 157.6, 151.3, 149.0, 133.0, 130.3, 125.7, 118.8, 115.9, 105.9, 102.9, 55.7 (2C), 53.8, 38.5, 30.6 (2C) ppm; IR ν_{max} 3055, 2958, 1708, 1627, 1604, 1338, 1265, 1114, 804, 744 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{18}O_3$, 270.1256, found, 270.1260.



16da

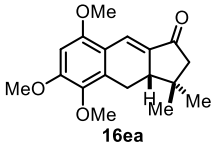
Compound **16da** (109 mg, 50% yield for two steps) was prepared according to general procedure C from **9a** (88 mg, 0.8 mmol, 1.0 equiv.) and aldehyde **6d** (216 mg, 1.2 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.28 (10% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 2.4 Hz, 1H), 6.34 (d, *J* = 1.6 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.88 – 2.64 (m, 3H), 2.31 (d, *J* = 17.2 Hz, 1H), 2.24 (d, *J* = 17.6 Hz, 1H), 1.24 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.9, 162.1, 159.2, 139.7, 134.9, 124.7, 115.3, 106.0, 96.2, 55.5, 55.4, 55.3, 46.1, 36.3, 29.2, 27.4, 24.1 ppm; IR ν_{max} 2959, 2837, 1701, 1629, 1599, 1573, 1462, 1323, 1138, 744 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{20}O_3$, 272.1412, found, 272.1410.



10da

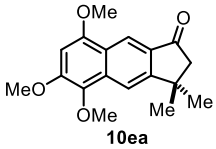
Compound **10da** (100 mg, 93% yield) was prepared according to general procedure D from the above obtained compound **16da**. R_f = 0.30 (10% ethyl acetate – petroleum ether); Light yellow solid, m.p. 134 - 136 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.66

(s, 1H), 6.72 (s, 1H), 6.42 (s, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 2.64 (s, 2H), 1.47 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.6, 160.7, 159.1, 158.5, 139.7, 130.8, 121.3, 119.8, 119.2, 97.8, 97.6, 55.6, 55.4, 53.6, 38.2, 30.4 (2C) ppm; IR ν_{max} 2958, 1703, 1627, 1585, 1325, 1271, 1161, 887, 827, 738 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{17}H_{18}O_3$, 270.1256, found, 270.1259.



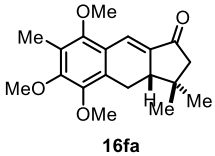
16ea

Compound **16ea** (99 mg, 41% yield for two steps) was prepared according to general procedure C from **9a** (88 mg, 0.8 mmol, 1.0 equiv.) and aldehyde **6e** (252 mg, 1.2 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.40 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 115 - 117 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 3.2 Hz, 1H), 6.31 (s, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.74 (s, 3H), 3.20 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.71 (ddd, *J* = 16.3, 7.0, 3.2 Hz, 1H), 2.39 (t, *J* = 16.0 Hz, 1H), 2.31 (d, *J* = 17.2 Hz, 1H), 2.23 (d, *J* = 17.2 Hz, 1H), 1.26 (s, 3H), 0.96 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.9, 155.3, 155.2, 140.4, 135.2, 131.0, 124.4, 114.8, 94.5, 60.6, 56.0, 55.8, 55.5, 45.6, 36.4, 27.3, 24.0, 21.6 ppm; IR ν_{max} 2960, 2839, 1703, 1575, 1487, 1273, 1267, 1140, 763, 747 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{22}O_4$, 302.1518, found, 302.1521.



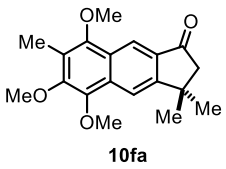
10ea

Compound **10ea** (99 mg, quantitative yield) was prepared according to general procedure D from the above obtained compound **16ea**. R_f = 0.44 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 150 - 152 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (s, 1H), 8.03 (s, 1H), 6.60 (s, 1H), 4.02 (s, 3H), 3.98 (s, 3H), 3.93 (s, 3H), 2.66 (s, 2H), 1.50 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.9, 158.5, 155.0, 151.0, 136.2, 133.5, 131.1, 120.7, 119.6, 114.4, 94.5, 61.1, 56.9, 55.8, 53.8, 38.4, 30.5 (2C) ppm; IR ν_{max} 2961, 2841, 1705, 1624, 1339, 1265, 1105, 764 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{20}O_4$, 300.1362, found, 300.1359.



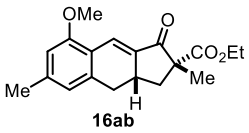
16fa

Compound **16fa** (175 mg, 69% yield for two steps) was prepared according to general procedure C from **9a** (88 mg, 0.8 mmol, 1.0 equiv.) and aldehyde **6f** (268 mg, 1.2 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.60 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 87 - 89 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 3.3 Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 3.68 (s, 3H), 3.18 (dd, *J* = 15.6, 7.2 Hz, 1H), 2.75 (ddd, *J* = 16.4, 7.2, 3.3 Hz, 1H), 2.40 (t, *J* = 16.3 Hz, 1H), 2.33 (d, *J* = 17.6 Hz, 1H), 2.27 (d, *J* = 17.2 Hz, 1H), 2.15 (s, 3H), 1.27 (s, 3H), 0.97 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.3, 154.5, 154.0, 147.1, 137.8, 128.1, 124.5, 123.5, 122.2, 62.1, 60.4, 60.3, 55.5, 45.9, 36.5, 27.4, 24.1, 21.2, 9.2 ppm; IR ν_{max} 2953, 1711, 1632, 1462, 1406, 1358, 1213, 1120, 1076, 735 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{24}O_4$, 316.1675, found, 316.1679.



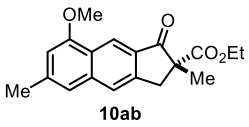
10fa

Compound **10fa** (137 mg, 79% yield) was prepared according to general procedure D from the above obtained compound **16fa**. R_f = 0.32 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 117 - 119 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.45 (s, 1H), 8.12 (s, 1H), 3.98 (s, 6H), 3.88 (s, 3H), 2.68 (s, 2H), 2.35 (s, 3H), 1.51 (s, 6H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.3, 157.2, 152.4, 151.0, 143.1, 132.6, 132.2, 124.9, 123.5, 118.8, 115.4, 61.8, 60.9, 60.4, 53.8, 38.4, 30.6 (2C), 9.8 ppm; IR ν_{max} 2957, 1713, 1618, 1454, 1390, 1323, 1238, 1221, 1078, 1010 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{22}O_4$, 314.1518, found, 314.1521.



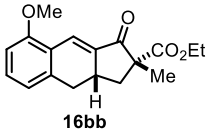
16ab

Compound **16ab** (81 mg, 64% yield for two steps) was prepared according to general procedure C from **9b** (67 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6a** (98 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.28 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 98 - 100 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 3.0 Hz, 1H), 6.61 (s, 1H), 6.57 (s, 1H), 4.10 (qd, *J* = 7.1, 1.2 Hz, 2H), 3.83 (s, 3H), 3.17 – 3.05 (m, 1H), 2.95 (dd, *J* = 15.2, 6.7 Hz, 1H), 2.83 (dd, *J* = 12.8, 7.4 Hz, 1H), 2.53 (t, *J* = 15.7 Hz, 1H), 2.34 (s, 3H), 1.46 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.4, 172.2, 158.0, 142.0, 138.4, 136.3, 126.6, 121.5, 119.7, 110.2, 61.3, 57.5, 55.5, 41.2, 35.9, 33.0, 22.0, 20.5, 14.0 ppm; IR ν_{max} 2982, 2932, 1736, 1705, 1564, 1501, 1148, 1248, 1194, 798 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{22}O_4$, 314.1518, found, 314.1521.



10ab

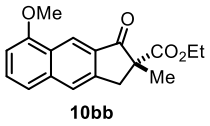
Compound **10ab** (66 mg, 83% yield) was prepared according to general procedure D from the above obtained compound **16ab**. R_f = 0.30 (10% ethyl acetate – petroleum ether); Yellow solid, m.p. 105 - 107 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (s, 1H), 7.69 (s, 1H), 7.19 (s, 1H), 6.63 (s, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 3H), 3.82 (d, *J* = 17.1 Hz, 1H), 3.11 (d, *J* = 17.2 Hz, 1H), 2.51 (s, 3H), 1.55 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.5, 172.3, 157.3, 146.1, 140.1, 138.9, 131.2, 123.8, 123.2, 121.1, 118.9, 106.2, 61.4, 56.7, 55.6, 39.6, 22.6, 21.2, 14.0 ppm; IR ν_{max} 2984, 1742, 1709, 1630, 1504, 1323, 1296, 1092, 1014, 737 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{20}O_4$, 312.1362, found, 312.1365.



16bb

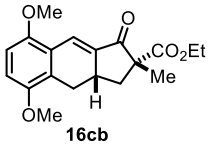
Compound **16bb** (128 mg, 85% yield for two steps) was prepared according to general procedure C from **9b** (84 mg, 0.5 mmol, 1.0 equiv.) and aldehyde **6b** (112 mg, 0.75 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.44 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 3.1 Hz, 1H), 7.22 (t, *J* = 7.9 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.10 (qd, *J* = 7.1, 0.4 Hz, 2H), 3.84 (s, 3H), 3.18 – 3.07 (m, 1H), 3.01 (dd, *J* =

15.2, 6.7 Hz, 1H), 2.84 (dd, *J* = 12.8, 7.4 Hz, 1H), 2.55 (t, *J* = 15.7 Hz, 1H), 1.48 (dd, *J* = 12.9, 10.8 Hz, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.5, 172.0, 158.0, 138.4, 137.3, 131.0, 126.3, 122.1, 120.4, 109.3, 61.3, 57.4, 55.5, 41.2, 35.7, 32.8, 20.4, 14.0 ppm; IR ν_{max} 2983, 1739, 1626, 1447, 1300, 1269, 1248, 1194, 1128, 783 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{20}O_4$, 300.1362, found, 300.1358.



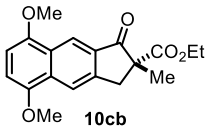
10bb

Compound **10bb** (106 mg, 83% yield) was prepared according to general procedure D from the above obtained compound **16bb**. R_f = 0.46 (20% ethyl acetate – petroleum ether); Light brown solid, m.p. 69 - 71 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (s, 1H), 7.79 (s, 1H), 7.49 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 7.5 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.84 (d, *J* = 17.1 Hz, 1H), 3.13 (d, *J* = 17.6 Hz, 1H), 1.56 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.5, 172.2, 157.5, 145.7, 138.6, 131.8, 129.4, 125.3, 124.0, 121.1, 119.8, 103.8, 61.4, 56.7, 55.6, 39.6, 21.1, 14.0 ppm; IR ν_{max} 2981, 2934, 1742, 1628, 1379, 1292, 1269, 1131, 986, 797 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{18}O_4$, 298.1205, found, 298.1202.



16cb

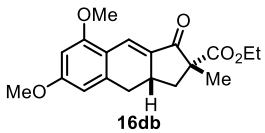
Compound **16cb** (149 mg, 90% yield for two steps) was prepared according to general procedure C from **9b** (84 mg, 0.5 mmol, 1.0 equiv.) and aldehyde **6c** (135 mg, 0.75 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.4 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 95 - 97 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 3.1 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 1H), 4.14 – 4.06 (m, 2H), 3.80 (s, 3H), 3.79 (s, 3H), 3.47 (dd, *J* = 16.0, 7.3 Hz, 1H), 3.09 - 2.99 (m, 1H), 2.85 (dd, *J* = 12.8, 7.5 Hz, 1H), 2.12 (t, *J* = 16.1 Hz, 1H), 1.49 (dd, *J* = 12.6, 11.1 Hz, 1H), 1.44 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 201.8, 172.1, 152.5, 150.4, 137.5, 126.2, 126.1, 123.2, 113.8, 109.1, 61.3, 57.4, 56.1, 55.9, 41.4, 32.2, 28.0, 20.4, 14.0 ppm; IR ν_{max} 2984, 2833, 1739, 1630, 1583, 1485, 1298, 1265, 1078, 796 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{22}O_5$, 330.1467, found, 330.1464.



10cb

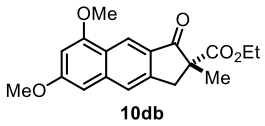
Compound **10cb** (77 mg, 52% yield) was prepared according to general procedure D from the above obtained compound **16cb**. R_f = 0.4 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.76 (s, 1H), 8.25 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.67 (d, *J* = 8.3 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 3.97 (s, 3H), 3.96 (s, 3H), 3.85 (d, *J* = 17.1 Hz, 1H), 3.15 (d, *J* = 17.1 Hz, 1H), 1.55 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.8, 172.2, 151.3, 149.0, 145.5, 132.3, 130.5, 126.0, 120.7, 118.8, 106.5, 103.1, 61.4, 56.8, 55.9, 55.8,

39.9, 21.1, 14.0 ppm; IR ν_{max} 2981, 2933, 1738, 1731, 1342, 1292, 1265, 1182, 1022, 995, 804 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{20}O_5$, 328.1311, found, 328.1313.



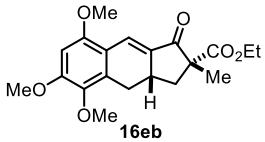
16db

Compound **16db** (112 mg, 68% yield for two steps) was prepared according to general procedure C from **9b** (84 mg, 0.5 mmol, 1.0 equiv.) and aldehyde **6d** (135 mg, 0.75 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.38 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 94 - 96 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 2.6 Hz, 1H), 6.32 (s, 1H), 6.27 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 6H), 3.18 – 3.03 (m, 1H), 2.93 (dd, *J* = 15.2, 6.6 Hz, 1H), 2.81 (dd, *J* = 12.7, 7.4 Hz, 1H), 2.52 (t, *J* = 15.7 Hz, 1H), 1.46 (d, *J* = 11.8 Hz, 1H), 1.41 (s, 3H), 1.17 (td, *J* = 7.1, 1.4 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.0, 172.1, 162.5, 159.4, 140.1, 134.5, 126.6, 115.6, 105.8, 96.3, 61.2, 57.4, 55.5, 55.3, 41.2, 36.4, 32.8, 20.5, 14.0 ppm; IR ν_{max} 2978, 2935, 1734, 1697, 1597, 1570, 1456, 1271, 1249, 1223 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{22}O_5$, 330.1467, found, 330.1464.



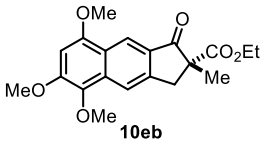
10db

Compound **10db** (89 mg, 80% yield) was prepared according to general procedure D from the above obtained compound **16db**. R_f = 0.38 (20% ethyl acetate – petroleum ether); Light yellow solid, m.p. 92 - 94 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (s, 1H), 7.63 (s, 1H), 6.68 (d, *J* = 1.9 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 4.14 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 3.92 (s, 3H), 3.80 (d, *J* = 17.1 Hz, 1H), 3.08 (d, *J* = 17.1 Hz, 1H), 1.54 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.1, 172.3, 161.2, 158.5, 147.0, 140.0, 129.9, 122.6, 121.6, 121.1, 97.8, 97.7, 61.4, 56.7, 55.6, 55.4, 39.6, 21.2, 14.0 ppm; IR ν_{max} 2982, 2935, 1739, 1705, 1624, 1585, 1323, 1296, 1159, 1086 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{20}O_5$, 328.1311, found, 328.1313.



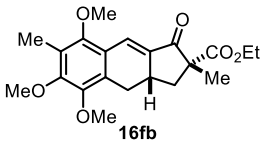
16eb

Compound **16eb** (135 mg, 75% yield for two steps) was prepared according to general procedure C from **9b** (84 mg, 0.5 mmol, 1.0 equiv.) and aldehyde **6e** (157 mg, 0.75 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.3 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 98 - 100 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (d, *J* = 2.9 Hz, 1H), 6.33 (s, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.89 (s, 3H), 3.83 (s, 3H), 3.72 (s, 3H), 3.44 (dd, *J* = 15.7, 6.8 Hz, 1H), 3.08 – 2.94 (m, 1H), 2.84 (dd, *J* = 12.7, 7.4 Hz, 1H), 2.17 (t, *J* = 15.7 Hz, 1H), 1.47 (t, *J* = 11.8 Hz 1H), 1.42 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 201.3, 172.2, 155.7, 155.5, 140.1, 134.8, 131.5, 126.5, 115.2, 94.5, 61.3, 60.6, 57.5, 56.0, 55.8, 41.4, 32.5, 28.8, 20.5, 14.0 ppm; IR ν_{max} 2980, 2933, 1705, 1626, 1591, 1489, 1325, 1269, 1203, 1124 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_6$ 360.1573, found, 360.1578.



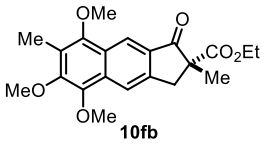
10eb

Compound **10eb** (98 mg, 73% yield) was prepared according to general procedure D from the above obtained compound **16eb**. R_f = 0.32 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 128 - 130 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.71 (s, 1H), 8.02 (s, 1H), 6.61 (s, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 4.03 (s, 3H), 3.99 (s, 3H), 3.91 (s, 3H), 3.83 (d, *J* = 17.5 Hz, 1H), 3.13 (d, *J* = 17.3 Hz, 1H), 1.54 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.4, 172.3, 155.0, 151.4, 146.4, 135.9, 133.6, 130.1, 121.5, 120.9, 117.2, 94.5, 61.4, 61.1, 56.8, 56.7, 55.8, 39.8, 21.2, 14.0 ppm; IR ν_{max} 2984, 2935, 1739, 1709, 1618, 1338, 1296, 1269, 1236, 997 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{22}O_6$, 358.1416, found, 358.1418.



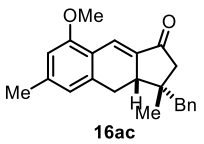
16fb

Compound **16fb** (165 mg, 88% yield for two steps) was prepared according to general procedure C from **9b** (84 mg, 0.5 mmol, 1.0 equiv.) and aldehyde **6f** (168 mg, 0.75 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.4 (20% ethyl acetate – petroleum ether); Yellow solid, m.p. 102 - 105 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 3.1 Hz, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.85 (s, 3H), 3.77 (s, 3H), 3.72 (s, 3H), 3.41 (dd, *J* = 15.7, 7.0 Hz, 1H), 3.11 – 2.96 (m, 1H), 2.87 (dd, *J* = 12.8, 7.5 Hz, 1H), 2.24 – 2.13 (m, CH_3 + 1/2 CH_2, 4H), 1.50 (dd, *J* = 12.8, 10.8 Hz, 1H), 1.44 (s, 3H), 1.19 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 172.0, 154.7, 154.3, 146.8, 137.3, 128.6, 126.5, 123.7, 122.5, 62.2, 61.4, 60.4, 60.3, 57.5, 41.3, 32.7, 28.4, 20.5, 14.0, 9.2 ppm; IR ν_{max} 2983, 2936, 1738, 1707, 1626, 1460, 1406, 1296, 1078, 1008 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{26}O_6$, 374.1729, found, 374.1726.



10fb

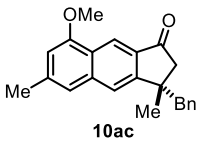
Compound **10fb** (136 mg, 83% yield) was prepared according to general procedure D from the above obtained compound **16fb**. R_f = 0.4 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.55 (s, 1H), 8.11 (s, 1H), 4.15 (q, *J* = 7.1 Hz, 2H), 4.00 (s, 3H), 3.97 (s, 3H), 3.89 (s, 3H), 3.85 (d, *J* = 17.2 Hz, 1H), 3.15 (d, *J* = 17.2 Hz, 1H), 2.36 (s, 3H), 1.56 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.8, 172.2, 152.4, 151.5, 145.0, 142.9, 132.4, 131.7, 125.1, 123.7, 120.7, 118.3, 61.9, 61.5, 61.0, 60.5, 56.8, 39.8, 21.2, 14.0, 9.9 ppm; IR ν_{max} 2984, 2935, 1741, 1620, 1456, 1390, 1325, 1294, 1190, 1012 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{21}H_{24}O_6$, 372.1573, found, 372.1577.



16ac

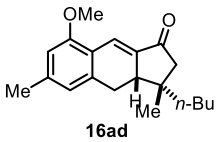
Compound **16ac** (135 mg, 58% yield for two steps, mixture of two isomers, d.r. = 1:1) was prepared according to general procedure C from **9c** (130 mg, 0.7 mmol, 1.0 equiv.) and aldehyde **6a** (172 mg, 1.05 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. One isomer: R_f = 0.20 (5% ethyl

acetate – petroleum ether), the other isomer: R_f = 0.24 (5% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*, mixture of two isomers) δ 7.64 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 3.1 Hz, 1H), 7.24 – 7.10 (m, 6H), 7.06 (d, *J* = 6.8 Hz, 2H), 7.00 (d, *J* = 7.0 Hz, 2H), 6.56 (s, 1H), 6.47 (s, 2H), 6.44 (s, 1H), 3.73 (s, 3H), 3.69 (s, 3H), 2.99 – 2.56 (m, 7H), 2.53 – 2.30 (m, 5H), 2.25 (s, 3H), 2.23 (s, 3H), 2.06 (d, *J* = 17.1 Hz, 1H), 1.82 (d, *J* = 17.5 Hz, 1H), 1.13 (s, 3H), 0.89 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*, mixture of two isomers) δ 204.7, 204.3, 157.9, 157.7, 141.6, 141.5, 138.2, 137.8, 137.6 (2C), 136.3, 136.1, 130.8 (2C), 130.1 (2C), 128.1 (2C), 128.0 (2C), 126.4, 126.1, 124.7, 124.6, 121.8, 121.6, 119.2, 119.1, 110.1, 110.0, 55.5, 55.4, 52.9, 50.3, 47.7, 46.4, 43.6, 41.6, 40.5, 39.9, 28.8, 27.9, 24.4, 22.8, 21.98, 21.95 ppm; IR ν_{max} 2962, 1707, 1634, 1607, 1566, 1458, 1408, 1300, 1010 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{24}O_2$, 332.1776, found, 332.1772.



10ac

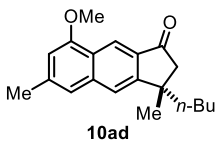
Compound **10ac** (135 mg, quantitative yield) was prepared according to general procedure D from the above obtained compound **16ac**. R_f = 0.22 (5% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.60 (s, 1H), 7.65 (s, 1H), 7.22 (s, 1H), 7.20 – 7.09 (m, 3H), 6.90 (dd, *J* = 7.3, 2.0 Hz, 2H), 6.64 (s, 1H), 3.99 (s, 3H), 3.10 (d, *J* = 13.3 Hz, 1H), 2.98 (d, *J* = 13.3 Hz, 1H), 2.90 (d, *J* = 18.6 Hz, 1H), 2.53 (s, 3H), 2.47 (d, *J* = 18.6 Hz, 1H), 1.56 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 205.3, 157.3, 156.2, 139.5, 138.3, 137.6, 132.7, 130.3 (2C), 127.9 (2C), 126.5, 123.6, 121.4, 119.2, 119.0, 106.1, 55.5, 50.7, 48.8, 42.7, 28.6, 22.5 ppm; IR ν_{max} 3030, 2916, 1709, 1582, 1499, 1452, 1298, 1265, 1194, 737 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{23}H_{22}O_2$, 330.1620, found, 330.1617.



16ad

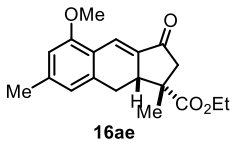
Compound **16ad** (94 mg, 45% yield for two steps, mixture of two isomers, d.r. = 1:1) was prepared according to general procedure C from **9d** (106 mg, 0.7 mmol, 1.0 equiv.) and aldehyde **6a** (172 mg, 1.05 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. R_f = 0.28 (5% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*, mixture of two isomers) δ 7.65 (d, *J* = 2.7 Hz, 1H), 7.61 (d, *J* = 2.1 Hz, 1H), 6.60 (d, *J* = 3.3 Hz, 2H), 6.53 (s, 2H), 3.80 (s, 6H), 2.91 – 2.63 (m, 6H), 2.51 (d, *J* = 17.5 Hz, 1H), 2.32 (s, 6H), 2.24 (t, *J* = 17.1 Hz, 2H), 2.14 (d, *J* = 17.5 Hz, 1H), 1.66 – 1.54 (m, 1H), 1.47 – 1.42 (m, 1H), 1.39 – 1.23 (m, 10H), 1.20 (s, 3H), 0.95 (s, 3H), 0.92 (t, *J* = 6.8 Hz, 3H), 0.86 (t, *J* = 5.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*, mixture of two isomers) δ 205.1, 205.0, 157.8, 157.7, 141.4, 141.3, 137.88, 137.87, 137.1, 136.5, 124.5, 123.7, 121.71, 121.66, 119.28, 119.26, 110.0, 109.9, 55.4 (2C), 53.5, 51.7, 47.4, 45.4, 41.2, 39.4, 38.8, 36.2, 29.3, 28.2, 27.5, 26.8, 25.6, 23.5, 23.4, 21.94 (2C), 21.89,

14.04, 13.96 ppm; IR ν_{max} 2916, 1709, 1607, 1447, 1265, 1194, 1080, 739 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{26}O_2$, 298.1933, found, 298.1929.



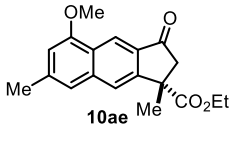
10ad

Compound **10ad** (94 mg, 90% yield) was prepared according to general procedure D from the above obtained compound **16ad**. R_f = 0.30 (5% ethyl acetate – petroleum ether); Light Yellow solid, m.p. 83 - 85 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (s, 1H), 7.66 (s, 1H), 7.22 (s, 1H), 6.61 (s, 1H), 3.98 (s, 3H), 2.75 (d, *J* = 18.8 Hz, 1H), 2.53 (d, *J* = 19.2 Hz, 1H), 2.50 (s, 3H), 1.81 – 1.68 (m, 2H), 1.47 (s, 3H), 1.31 – 1.13 (m, 3H), 1.00 – 0.87 (m, 1H), 0.81 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.2, 157.3, 157.2, 139.4, 138.6, 132.8, 123.5, 120.7, 119.1, 119.0, 105.9, 55.5, 51.1, 42.7, 41.6, 28.9, 27.2, 23.1, 22.5, 13.9 ppm; IR ν_{max} 2955, 2928, 1711, 1580, 1502, 1396, 1325, 1196, 1115, 736 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_2$, 296.1776, found, 296.1775.



16ae

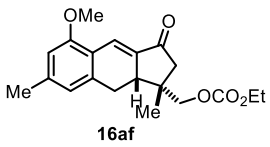
Compound **16ae** (111 mg, 88% yield for two steps, mixture of two isomers, d.r. = 2:1) was prepared according to general procedure C from **9e** (67 mg, 0.4 mmol, 1.0 equiv.) and aldehyde **6a** (98 mg, 0.6 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. One isomer, R_f = 0.6 (20% ethyl acetate – petroleum ether), the other isomer: R_f = 0.44 (20% ethyl acetate – petroleum ether); One isomer: light yellow viscous oil, the other isomer: light yellow solid, m.p. 85 - 87 °C; One isomer: ^{1}H NMR (400 MHz, Chloroform-*d*,) δ 7.74 (d, *J* = 3.2 Hz, 1H), 6.62 (s, 1H), 6.55 (s, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.82 (s, 3H), 3.38 (ddd, *J* = 13.4, 10.6, 3.2 Hz, 1H), 2.94 (t, *J* = 17.6 Hz,, 2H), 2.87 (d, *J* = 10.3 Hz, 1H), 2.42 (d, *J* = 17.6 Hz, 1H), 2.33 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.27 (s, 3H) ppm, ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.3, 176.0, 158.0, 142.1, 137.6, 134.1, 126.2, 121.8, 119.0, 110.2, 61.1, 55.5, 51.1, 46.1, 42.8, 29.5, 22.0, 20.0, 14.2 ppm; The other isomer: ^{1}H NMR (400 MHz, Chloroform-*d*,) δ 7.64 (d, *J* = 3.2 Hz, 1H), 6.59 (s, 1H), 6.56 (s, 1H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 2.96 (ddd, *J* = 16.5, 6.8, 3.2 Hz, 1H), 2.90 (dd, *J* = 17.2, 6.8 Hz, 1H), 2.85 (d, *J* = 17.6 Hz, 1H), 2.46 (t, *J* = 15.7 Hz, 1H), 2.32 (s, 3H), 2.28 (d, *J* = 17.6 Hz, 1H), 1.48 (s, 3H), 1.17 (t, *J* = 7.1 Hz, 3H) ppm, ^{13}C NMR (100 MHz, Chloroform-*d*) δ 202.4, 174.7, 157.9, 141.6, 136.9, 135.5, 123.7, 121.6, 119.2, 110.3, 60.9, 55.5, 50.7, 47.7, 46.9, 30.4, 22.6, 22.0, 14.1 ppm; IR ν_{max} 2978, 1714, 1633, 1606, 1568, 1460, 1311, 1240, 1188, 1020 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{22}O_4$, 314.1518, found, 314.1522.



10ae

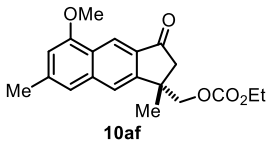
Compound **10ae** (97 mg, 88% yield) was prepared according to general procedure D from the above obtained compound **16ae**. R_f = 0.6 (20% ethyl acetate – petroleum ether); Light yellow solid, m.p. 88 - 90 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 7.86 (s, 1H), 7.23 (s, 1H), 6.65 (s, 1H), 4.22 – 4.04 (m, 2H), 3.99 (s, 3H), 3.49 (d, *J* = 18.7 Hz, 1H), 2.61 (d, *J* = 18.7

Hz, 1H), 2.51 (s, 3H), 1.75 (s, 3H), 1.18 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.1, 174.5, 157.3, 151.2, 140.0, 138.5, 131.7, 124.0, 122.2, 119.7, 119.4, 106.6, 61.5, 55.6, 49.5, 48.4, 26.3, 22.5, 14.0 ppm; IR ν_{max} 2984, 1717, 1626, 1582, 1504, 1325, 1294, 1269, 1240, 1084 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{19}H_{20}O_4$, 312.1362, found, 312.1359.



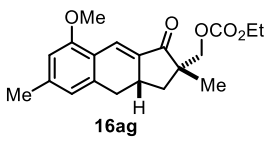
16af

Compound **16af** (40 mg, 42% yield for two steps, mixture of two isomers, d.r. = 1.2:1) was prepared according to general procedure C from **9f** (55mg, 0.278 mmol, 1.0 equiv.) and aldehyde **6a** (68 mg, 0.417 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. One isomer: R_f = 0.6 (20% ethyl acetate – petroleum ether), the other isomer: R_f = 0.56 (20% ethyl acetate – petroleum ether); Light yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*, mixture of two isomers) δ 7.63 (d, *J* = 3.2 Hz, 1H), 7.57 (d, *J* = 3.2 Hz, 1H), 6.54 (s, 2H), 6.48 (d, *J* = 3.7 Hz, 2H), 4.18 – 4.03 (m, 6H), 3.97 (q, *J* = 9.6 Hz, 2H), 3.74 (s, 6H), 2.97 (ddd, *J* = 15.2, 8.1, 3.1 Hz, 1H), 2.84 (ddd, *J* = 17.2, 6.4, 3.2 Hz, 1H), 2.78 – 2.61 (m, 4H), 2.50 (dd, *J* = 36.4, 17.7 Hz, 2H), 2.25 (s, 6H), 2.18 (t, *J* = 18.4 Hz, 2H), 1.29 – 1.15 (m, 9H), 0.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*, mixture of two isomers) δ 203.2, 203.1, 158.0 (2C), 155.2, 155.0, 141.9, 141.7, 137.6, 137.5, 136.2, 135.1, 125.6, 124.3, 121.8, 121.7, 119.3, 119.1, 110.3, 110.2, 73.6, 71.7, 64.2 (2C), 55.5 (2C), 50.5, 50.4, 45.6, 41.7, 40.0, 39.5, 29.4, 28.7, 23.1, 22.0 (2C), 19.8, 14.3 (2C) ppm; IR ν_{max} 2939, 1745, 1566, 1313, 1294, 1265, 1192, 1012, 790, 734 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_5$, 344.1624, found, 344.1625.



10af

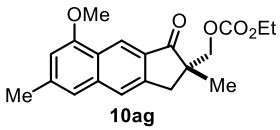
Compound **10af** (35 mg, 86% yield) was prepared according to general procedure D from the above obtained compound **16af**. R_f = 0.63 (20% ethyl acetate – petroleum ether); Light yellow solid, m.p. 81 - 83 ^{o}C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.69 (s, 1H), 7.76 (s, 1H), 7.23 (s, 1H), 6.64 (s, 1H), 4.27 (q, *J* = 11.7 Hz, 2H), 4.13 (qd, *J* = 7.1, 0.8 Hz, 2H), 3.99 (s, 3H), 2.89 (d, *J* = 18.8 Hz, 1H), 2.58 (d, *J* = 18.8 Hz, 1H), 2.51 (s, 3H), 1.54 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.4, 157.3, 155.1, 152.7, 139.9, 138.5, 132.6, 123.9, 121.6, 119.6, 119.3, 106.5, 74.2, 64.1, 55.6, 48.9, 41.9, 25.2, 22.5, 14.2 ppm; IR ν_{max} 2984, 1745, 1714, 1628, 1581, 1502, 1265, 1254, 1013, 895 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{22}O_5$, 342.1467, found, 342.1472.



16ag

Compound **16ag** (41 mg, 62% yield for two steps, mixture of two isomers, d.r = 1:1) was prepared according to general procedure C from **9g** (38 mg, 0.19 mmol, 1.0 equiv.) and aldehyde **6a** (46 mg, 0.285 mmol, 1.5 equiv.). The PEDA reaction time was 45 minutes under λ_{max} = 366 nm UV light using anhydrous 1, 4-dioxane as solvent. One isomer: R_f = 0.58, (20% ethyl acetate – petroleum ether), the other isomer: R_f = 0.56 (20% ethyl acetate – petroleum ether); Light

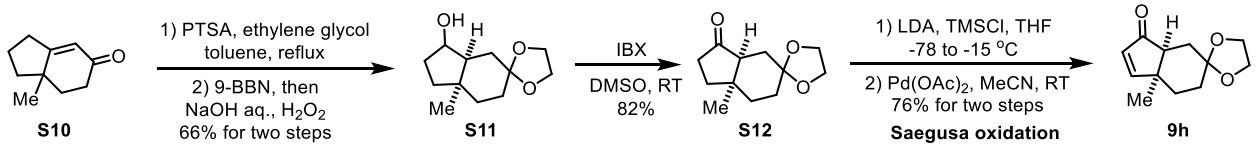
yellow solid, m.p. 62 - 64 °C; ^{1}H NMR (500 MHz, Chloroform-*d*, mixture of two isomers) δ 7.72 (d, *J* = 2.8 Hz, 2H), 6.60 (s, 2H), 6.56 (s, 2H), 4.33 (d, *J* = 10.7 Hz, 1H), 4.21 – 4.07 (m, 6H), 3.98 (d, *J* = 10.5 Hz, 1H), 3.81 (s, 6H), 3.09 – 2.86 (m, 4H), 2.66 – 2.44 (m, 3H), 2.33 (s, 6H), 2.10 (dd, *J* = 12.2, 7.1 Hz, 1H), 1.79 (t, *J* = 11.5 Hz, 1H), 1.45 (dd, *J* = 13.0, 10.6 Hz, 1H), 1.27 (dt, *J* = 11.7, 7.1 Hz, 6H), 1.21 (s, 3H), 1.08 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*, mixture of two isomers) δ 206.3, 205.5, 158.0, 157.9, 155.1, 155.0, 141.8 (2C), 138.51, 138.45, 136.5, 135.7, 126.3, 126.1, 121.39, 121.36, 119.6, 119.5, 110.08, 110.07, 71.6, 70.8, 64.1, 64.0, 55.46, 55.45, 50.4, 50.3, 39.2, 37.6, 36.1, 35.6, 32.3, 31.5, 22.0 (2C), 20.3, 19.8, 14.19, 14.15 ppm; IR ν_{max} 2936, 1747, 1716, 1608, 1566, 1296, 1265, 1254, 1192, 1012 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{24}O_5$, 344.1624, found, 344.1620.

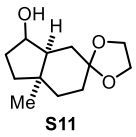


10ag

Compound **10ag** (27 mg, 67% yield) was prepared according to general procedure D from the above obtained compound **16ag**. R_f = 0.56 (20% ethyl acetate – petroleum ether); Light yellow solid, m.p. 82 - 84 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 7.67 (s, 1H), 7.17 (s, 1H), 6.61 (s, 1H), 4.37 (d, *J* = 10.5 Hz, 1H), 4.24 (d, *J* = 10.5 Hz, 1H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 3H), 3.46 (d, *J* = 17.1 Hz, 1H), 3.04 (d, *J* = 17.1 Hz, 1H), 2.50 (s, 3H), 1.28 (s, 3H), 1.22 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.5, 157.3, 155.0, 145.9, 139.8, 138.9, 131.8, 123.7, 123.4, 120.4, 118.9, 106.1, 71.5, 64.1, 55.5, 49.7, 37.4, 22.6, 21.3, 14.1 ppm; IR ν_{max} 2984, 1747, 1713, 1630, 1582, 1265, 1132, 1011, 791, 737 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{20}H_{22}O_5$, 342.1467, found, 342.1469.

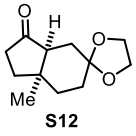
Experimental procedures and spectroscopic data of synthesis of the B-C-D-E skeleton of exiguaquinol



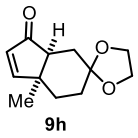

S11

To a stirred solution of compound **S10** [3] 9.90 g, 66.5 mmol, 1.0 equiv.) in 150 mL anhydrous toluene was added ethylene glycol (41.3 g, 33.8 mL, 665 mmol, 10.0 equiv.) and PTSA (1.27 g, 6.65 mmol, 0.1 equiv.) at room temperature. After stirring at 140 °C with a Dean-Stark trap for 4 hours, the mixture was quenched with saturated $NaHCO_3$ (30 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layer was washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (2% to 5% ethyl acetate – petroleum ether) to obtain ketal compound as yellow oil (10.3 g, 79% yield). R_f = 0.64 (10% ethyl acetate – petroleum ether), the NMR data are the same with the previous work [4]

To a stirred solution of above obtained compound (10.3 g, 53.0 mmol, 1.0 equiv.) in 10 mL anhydrous THF was added 9-BBN (212 mL, 106 mmol, 0.5 N in THF, 2.0 equiv.) at room temperature. The solution was stirred at room temperature for 16 hours and quenched with 10 mL methanol at 0 °C. Then 30 mL 3 N NaOH aqueous and 30 mL 30% H_2O_2 were added to the mixture at 0 °C and the mixture was further stirred at room temperature for 7 hours. After that, the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ aqueous (60 mL, v/v = 1:1) and extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain compound **S11** as light yellow viscous oil (9.45 g, 84% yield). R_f = 0.28 (20% ethyl acetate – petroleum ether), the NMR data of **S11** are the same with the previous work [4].

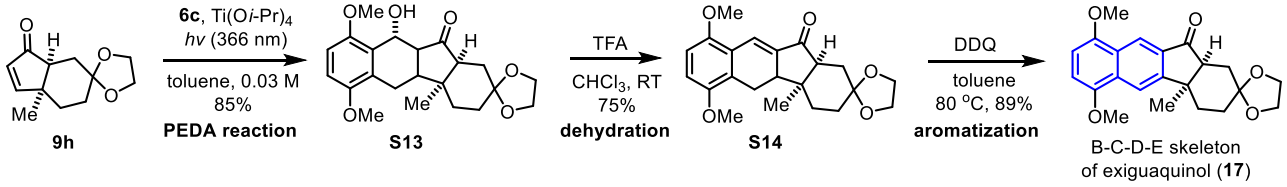

S12

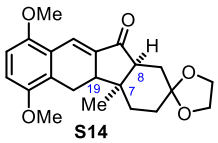
To a stirred solution of compound **S11** (9.45 g, 44.5 mmol, 1.0 equiv.) in 100 mL anhydrous DMSO was added IBX (1.87 g, 66.8 mmol, 1.5 equiv.) at room temperature. After stirring at room temperature for 9 hours, the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (60 mL, v/v = 1:1) and extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with water, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (5% to 10% ethyl acetate – petroleum ether) to obtain compound **S12** as light yellow viscous oil (7.67 g, 82% yield). R_f = 0.6 (20% ethyl acetate – petroleum ether), The NMR data of **S12** are the same with the previous work. [4]



9h

To a stirred solution of diisopropylamine (5.93 mL, 42.0 mmol, 2.1 equiv.) in 60 mL anhydrous THF at 0 °C was slowly added *n*-BuLi (16.0 mL, 40.0 mmol, 2.5 N in hexane, 2.0 equiv.). The solution was stirred at 0 °C for 30 minutes and then slowly added to the prepared cooled solution of compound **S12** (4.20 g, 20.0 mmol, 1.0 equiv.) in 20 mL anhydrous THF at -78 °C. After the mixture was stirred at -78 °C for 1.5 hours, triethylamine (11.1 mL, 80.0 mmol, 4.0 equiv.) and TMSCl (5.18 mL, 60.0 mmol, 3.0 equiv.) was added and stirred at -78 °C for 0.5 hour then further stirred at -15 °C for 3.0 hours. The mixture was quenched with saturated $NaHCO_3$ (100 mL) and extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with water, brine, then dried over anhydrous sodium sulfate, concentrated to obtain silyl enol ether crude product. The crude product (5.60 g, 19.85 mmol, 1.0 equiv.) was dissolved with 80 mL anhydrous MeCN and then added Palladium (II) Acetate (900 mg, 3.97 mmol, 0.2 equiv.). The mixture was stirred at room temperature under oxygen balloon for 8 hours. The mixture was filtered through silica gel and washed with ethyl acetate (6×50 mL). The combined organic layer was concentrated, and purified by silica gel flash chromatography (10% to 30% ethyl acetate – petroleum ether) to obtain compound **9h** as light yellow solid (3.16 g,76% yield). R_f = 0.24 (30% ethyl acetate – petroleum ether); light yellow solid, m.p. 73 - 75 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 (d, *J* = 5.7 Hz, 1H), 6.06 (d, *J* = 5.7 Hz, 1H), 4.00 – 3.80 (m, 4H), 2.22 – 2.09 (m, 2H), 1.86 – 1.74 (m, 2H), 1.73 – 1.65 (m, 1H), 1.64 – 1.51 (m, 2H), 1.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 210.1, 171.1, 130.5, 108.3, 64.2, 64.0, 52.0, 43.3, 32.6, 31.1, 30.8, 25.4 ppm; IR ν_{max} 2957, 2887, 1708, 1660, 1587, 1427, 1230, 1282, 1138, 1028 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{12}H_{16}O_3$, 208.1099 found, 208.1096.

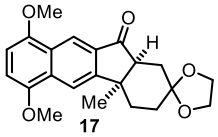




S14

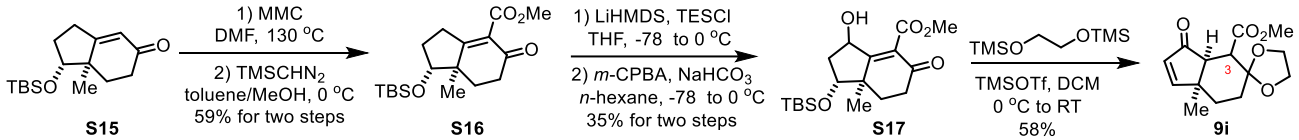
To a solution of compound **9h** (986 mg, 4.74 mmol, 1.0 equiv.) and aromatic aldehyde **6c** (1.28 g, 7.11 mmol, 1.5 equiv.) in anhydrous and degassed toluene (158 mL, 0.03 M) was added titanium(IV) isopropoxide (2.0 equiv.) under N_2. After homogeneous mixing, the solution was divided into 4 quartz tubes (4×40 mL) and photolyzed at room temperature in a Rayonet chamber reactor (16 lamps) at 366 nm for 45 minutes. Then saturated $NaHCO_3$ was added and stirred for 5 minutes. The mixture was filtered through silica gel and washed with ethyl acetate (6×50 mL). The organic layer was separated and washed with brine (50 mL). The combined organic layer was dried over anhydrous sodium sulfate, concentrated and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain compound **S13** (1.56 g, 85% yield). Then this obtained compound **S13** was dissolved in AR

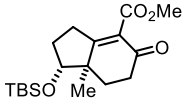
grade chloroform (100 mL) and added TFA (0.45 mL, 6.0 mmol, 1.5 equiv.) at room temperature. After stirring at room temperature for 3.5 hours, the mixture was quenched with saturated $NaHCO_3$ (20 mL) at 0 °C and extracted with ethyl acetate (3 ×50 mL). The combined organic layers were dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography to obtain the corresponding product **S14** (1.11 g, 75% yield) as yellow viscous oil. R_f = 0.38 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (d, *J* = 2.7 Hz, 1H), 6.85 (d, *J* = 8.9 Hz, 1H), 6.69 (d, *J* = 8.9 Hz, 1H), 3.95 (t, *J* = 16.0 Hz, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 3.21 – 3.07 (m, 2H), 2.47 – 2.27 (m, 2H), 1.96 – 1.69 (m, 4H), 1.68 – 1.60 (m, 1H), 1.38 (t, *J* = 13.5 Hz, 1H), 0.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 206.6, 152.3, 150.7, 136.7, 126.2, 125.6, 123.1, 113.4, 109.2, 108.0, 64.4, 64.3, 56.9 (C8), 56.0 (2C), 36.7 (C7+C19, 2C), 32.4, 30.8, 30.7, 25.9, 20.5 ppm; IR ν_{max} 2936, 1747, 1716, 1608, 1566, 1296, 1265, 1254, 1192, 1012 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{26}O_5$, 370.1780, found, 370.1786.



17

To a stirred solution of above obtained **S14** (1.11 g, 3.0 mmol, 1.0 equiv.) in anhydrous toluene (50 mL) was added DDQ (1.36 g, 6.0 mmol, 2.0 equiv.) at room temperature. After stirring at 80 °C for 1.5 hours, the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (20 mL v/v = 1:1) and extracted with ethyl acetate (3 ×30 mL). The combined organic layers were washed with saturated Na_2SO_3/$NaHCO_3$ (20 mL, v/v = 1:1), brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% ethyl acetate – petroleum ether) to obtain compound **17** as a yellow viscous oil (982 mg, 89% yield). R_f = 0.38 (20% ethyl acetate – petroleum ether); Yellow viscous oil; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.23 (s, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.99 (s, 3H), 3.96 (s, 3H), 3.94 – 3.83 (m, 2H), 2.64 (dd, *J* = 7.2, 3.8 Hz, 1H), 2.38 (ddd, *J* = 14.2, 3.9, 1.9 Hz, 1H), 1.95 – 1.89 (m, 2H), 1.88 – 1.80 (m, 2H), 1.61 (s, 3H), 1.57 – 1.51 (m, 1H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 205.8, 155.6, 151.4, 149.1, 132.0, 130.0, 125.8, 119.8, 115.3, 108.0, 106.0, 103.0, 64.4, 63.9, 56.5, 55.81, 55.77, 40.6, 36.2, 31.6, 30.1, 25.8 ppm; IR ν_{max} 2984, 1747, 1713, 1630, 1582, 1265, 1132, 1011, 791, 737 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{22}H_{24}O_5$, 368.1624, found, 368.1626.

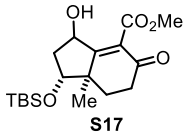




S16

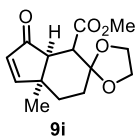
To a stirred solution of compound **S15** [5] (8.40 g, 30.0 mmol, 1.0 equiv.) in 90 mL anhydrous DMF was added magnesium methyl carbonate (45.0 mL, 90.0 mmol, 2 N in DMF, 3.0 equiv.) at room temperature. After stirring at 130 °C for 4 hours, DMF was evacuated and then diluted with 100 mL diethyl ether. The mixture was cooled to 0 °C and its pH value was adjusted to 2~3 with 2 N

HCl. Separated the organic layer and extracted aqueous layer with diethyl ether (3×50 mL). The combined organic layer was washed with brine, dried over anhydrous sodium sulfate, concentrated to obtain the corresponding crude carboxylic acid product. Then the crude product was dissolved in anhydrous toluene/MeOH (150 mL, v:v = 4:1) and added (trimethylsilyl)diazomethane (30.0 mL, 60.0 mmol, 2 N in hexane, 2.0 equiv.) at 0 °C. After stirring at 0 °C for 30 minutes, the mixture was evacuated and purified by silica gel flash chromatography (5% to 20% ethyl acetate – petroleum ether) to obtain compound **S16** as light yellow solid (5.98 g, 59% yield for two steps). R_f = 0.2 (10% ethyl acetate – petroleum ether), the NMR data of the compound **S16** are the same with the previous work [6].



S17

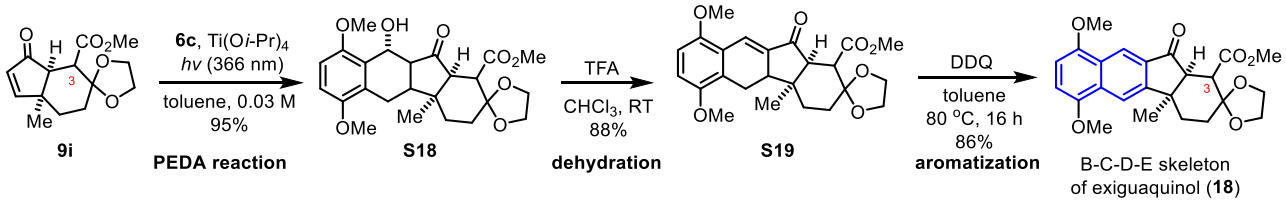
To a stirred solution of compound **S16** (3.38 g, 10.0 mmol, 1.0 equiv.) in 60 mL anhydrous THF was added LiHMDS (20.0 mL, 20.0 mmol, 1 N in THF, 2.0 equiv.) at -78 °C. TESCl (3.02 g, 3.36 mL, 20.0 mmol, 2.0 equiv.) was added and further stirred at 0 °C for 3 hours. The mixture was quenched with saturated $NaHCO_3$ (20 mL) and extracted with ethyl acetate (3×50 mL). The combined organic layer was washed with water, brine, dried over anhydrous sodium sulfate, concentrated to obtain crude silyl enol ether crude product as yellow viscous oil. Then the crude product was dissolved in anhydrous *n*-hexane (100 mL) and added solid $NaHCO_3$ (8.40 g, 100 mmol, 10.0 equiv.) then *m*-CPBA (4.06 g, 20 mmol, 85%, 2.0 equiv.) at -78 °C. After stirring at -78 °C for 30 minutes, the mixture was further stirred at 0 °C for 60 minutes. After that, the mixture was quenched with saturated Na_2SO_3/$NaHCO_3$ (60 mL, v/v = 1:1) and extracted with ethyl acetate (3×100 mL). The combined organic layer was washed with saturated $NaHCO_3$, brine, then dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain compound **S17** as light yellow solid (1.24 g, 35% yield). R_f = 0.36 (30% ethyl acetate – petroleum ether); Light yellow solid, m.p. 135 - 137 °C; ^{1}H NMR (500 MHz, Chloroform-*d*) δ 4.86 (dd, *J* = 6.7, 2.4 Hz, 1H), 4.14 (t, *J* = 9.0 Hz, 1H), 3.83 (s, 3H), 2.68 – 2.57 (m, 1H), 2.51 (dd, *J* = 18.1, 5.4 Hz, 1H), 2.15 – 1.99 (m, 3H), 1.89 (td, *J* = 13.5, 5.5 Hz, 1H), 1.12 (s, 3H), 0.89 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H) ppm; ^{13}C NMR (125 MHz, Chloroform-*d*) δ 194.9, 178.8, 167.4, 128.5, 78.3, 68.5, 52.6, 46.6, 39.7, 33.8, 33.5, 25.7 (3C), 17.9, 17.0, -4.6, -5.0 ppm; IR ν_{max} 3726, 1705, 1649, 1485, 1390, 1142, 1076, 1005 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{18}H_{30}O_5Si$, 354.1863 found, 354.1873.

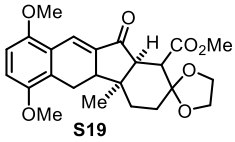


9i

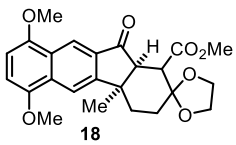
To a stirred solution of compound **S17** (1.24 g, 3.50 mmol, 1.0 equiv.) in 50 mL anhydrous DCM was added 1,2-bis(trimethylsilyloxy)ethane (2.58 mL, 10.5 mmol, 3.0 equiv.) and TMSOTf (0.63 mL, 3.50 mmol, 1.0 equiv.) at 0 °C. After stirring at room temperature for 6 hours, the mixture was quenched with saturated $NaHCO_3$ (20 mL) and extracted with ethyl acetate (3×50 mL). The combined

organic layer was washed with brine, dried over anhydrous sodium sulfate, concentrated, and purified by silica gel flash chromatography (20% to 30% ethyl acetate – petroleum ether) to obtain compound **9i** as light yellow solid (540 mg, 58% yield). R_f = 0.42 (30% ethyl acetate – petroleum ether); Light yellow solid, m.p. 85 - 87 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.45 (d, *J* = 5.7 Hz, 1H), 6.04 (d, *J* = 5.7 Hz, 1H), 4.12 – 3.99 (m, 1H), 3.96 – 3.85 (m, 3H), 3.71 (s, 3H), 3.44 (d, *J* = 1.2 Hz, 1H), 2.39 (d, *J* = 2.6 Hz, 1H), 2.25 (ddd, *J* = 13.5, 12.3, 4.1 Hz, 1H), 1.84 (dt, *J* = 13.8, 4.7 Hz, 1H), 1.65 (td, *J* = 13.7, 13.0, 4.2 Hz, 1H), 1.48 (t, *J* = 5.4 Hz, 1H), 1.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 207.4, 172.7, 172.3, 128.7, 107.8, 65.0, 63.9, 55.0, 51.9, 46.8, 42.8, 33.0, 28.9, 25.9 ppm; IR ν_{max} 2889, 1735, 1709, 1649, 1589, 1390, 1344, 1143, 1026, 949 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{14}H_{18}O_5$, 266.1154 found, 266.1157





Compound **S19** (923 mg, 84% yield for two steps) was prepared according to above similar procedure from **9i** (689 mg, 2.59 mmol, 1.0 equiv.) and aldehyde **6c** (994 mg, 3.88 mmol, 1.5 equiv.). The PEDA reaction time was 2 hours under λ_{max} = 366 nm UV light using anhydrous toluene as solvent. R_f = 0.48 (40% ethyl acetate – petroleum ether); Yellow solid, m.p. 236 – 238 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.76 (d, J = 3.2 Hz, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.69 (d, *J* = 9.0 Hz, 1H), 4.05 – 3.83 (m, 4H), 3.81 (s, 3H), 3.79 (s, 3H), 3.71 (s, 3H), 3.16 (dd, *J* = 15.5, 7.3 Hz, 1H), 3.06 (ddd, *J* = 16.0, 7.3, 3.1 Hz, 1H), 2.81 (d, *J* = 13.0 Hz, 1H), 2.61 (d, *J* = 13.0 Hz, 1H), 2.38 (t, *J* = 15.8 Hz, 1H), 1.96 – 1.81 (m, 2H), 1.66 (dt, *J* = 7.7, 3.7 Hz, 2H), 1.04 (s, 3H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 204.0, 170.7, 152.4, 150.7, 135.9, 126.9, 125.5, 123.1, 113.6, 109.2, 108.6, 65.3, 64.9, 58.9, 56.03, 56.02, 52.01, 48.5, 37.3, 37.1, 31.7, 30.5, 25.8, 20.5 ppm; IR ν_{max} 2954, 2922, 1743, 1707, 1635, 1595, 1301, 1222, 1165, 1057 cm^{-1}; HRMS–ESI (*m/z*): $[M+H]^+$ calculated for $C_{24}H_{28}O_7$, 428.1835, found, 428.1831.



Compound **18** (798 mg, 86% yield) was prepared according to above similar procedure from the above obtained compound **S19**. R_f = 0.78 (40% ethyl acetate – petroleum ether); Yellow solid, m.p. 173 – 175 ^oC; ^1H NMR (400 MHz, Chloroform-*d*) δ 8.72 (s, 1H), 8.24 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.98 (s, 3H), 3.96 (d, *J* = 2.2 Hz, 1H), 3.95 (s, 3H), 3.92 (d, *J* = 6.4 Hz, 1H), 3.91 – 3.83 (m, 1H), 3.75 (s, 3H), 3.60 (dd, *J* = 2.9, 1.4 Hz, 1H), 2.87 (dd, *J* = 2.8, 0.8 Hz, 1H), 2.42 (td, *J* = 13.2, 4.0 Hz, 1H), 2.01 (dt, *J* = 14.0, 4.5 Hz, 1H), 1.84 (td, *J* = 12.4, 4.0 Hz, 1H), 1.76 (s, 3H), 1.52 – 1.44 (m, 1H) ppm; ^{13}C NMR (100 MHz, Chloroform-*d*) δ 203.4, 172.7, 155.9, 151.4, 149.1, 130.8, 130.2, 125.8, 120.0, 115.3, 107.7, 106.1, 103.1, 65.1, 63.7, 58.6, 55.78,

55.75, 52.0, 46.3, 40.4, 36.4, 29.4, 26.5 ppm; IR ν_{max} 3007, 2891, 1736, 1716, 1629, 1606, 1338, 1145, 1076, 1022 cm^{-1}; HRMS–EI (*m/z*): $[M]^+$ calculated for $C_{24}H_{26}O_7$, 426.1679 found, 426.1673.

References

[1]. W. C. Still, M. Kahn and A. Mitra, Rapid chromatographic technique for preparative separations with moderate resolution, *J. Org. Chem.*, 1978, **43**, 2923-2925.

[2]. H. Liu, L. Huo, B. Yang, Y. Yuan, W. Zhang, Z. Xu, S. Qiu and H. Tan, Biomimetic-Inspired Syntheses of Myrtucommuacetalone and Myrtucommulone J, *Org. Lett.*, 2017, **19**, 4786-4789.

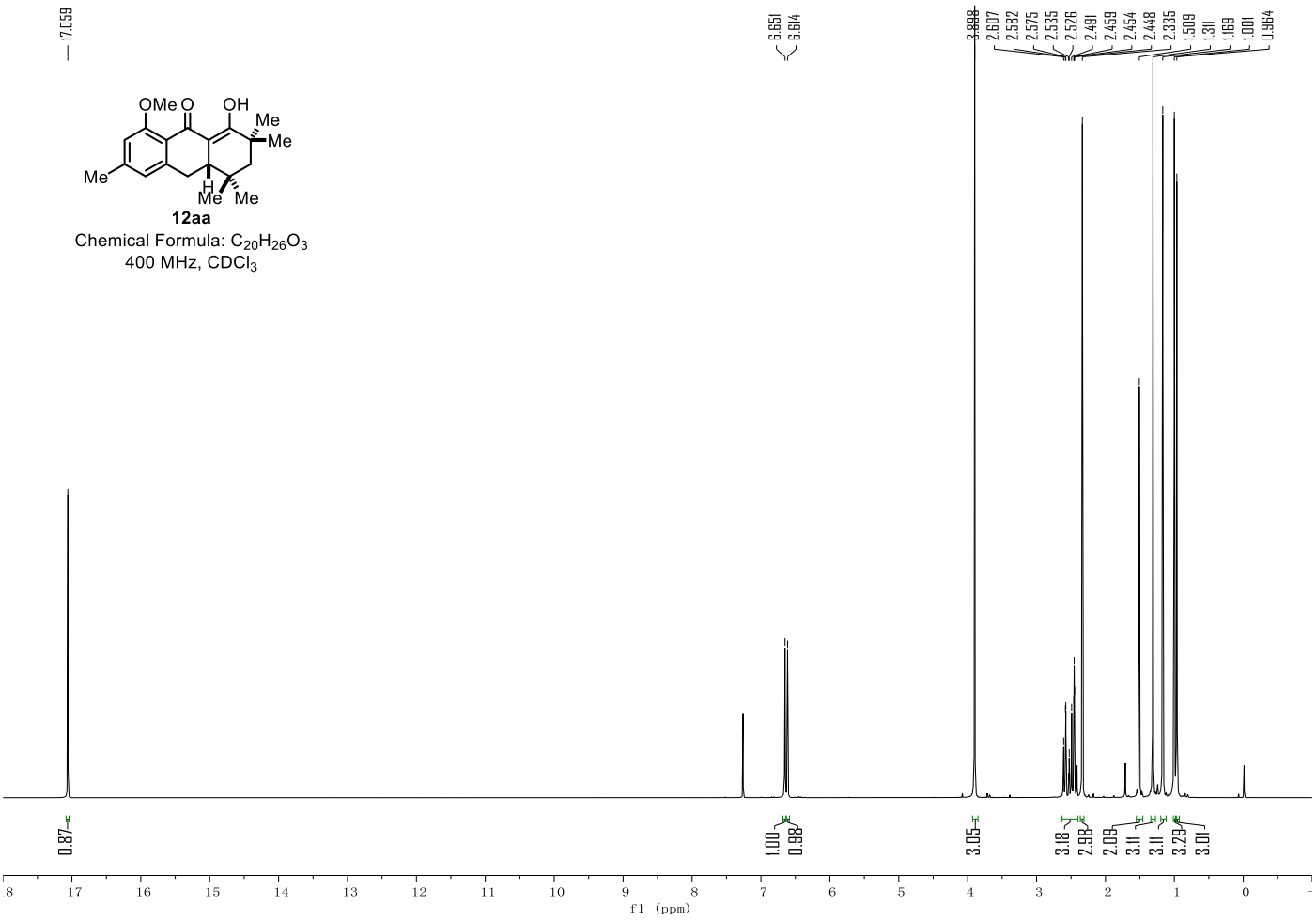
[3]. H. S. P. Rao and K. S. Reddy, A superior method for the synthesis of 7a-methyl-2,3,7,7a-tetrahydrinden-5(6H)-one, *Org. Prep. Proced. Int.*, 1994, **26**, 491-494.

[4]. B. Defaut, T. B. Parsons, N. Spencer, L. Male, B. M. Kariuki and R. S. Grainger, Synthesis of the trans-hydrindane core of dictyoxetane, *Org. Biomol. Chem.*, 2012, **10**, 4926-4932.

[5]. (a) R. C. A. Isaacs, M. J. Di Grandi and S. J. Danishefsky, Synthesis of an enantiomerically pure intermediate containing the CD substructure of taxol, *J. Org. Chem.*, 1993, **58**, 3938-3941. (b) J. L. Frie, C. S. Jeffrey and E. J. Sorensen, A Hypervalent Iodine-Induced Double Annulation Enables a Concise Synthesis of the Pentacyclic Core Structure of the Cortistatins, *Org. Lett.*, 2009, **11**, 5394-5397.

[6]. Y. Guo, T. Quan, Y. Lu and T. Luo, Enantioselective Total Synthesis of (+)-Wortmannin, *J. Am. Chem. Soc.*, 2017, **139**, 6815-6818.

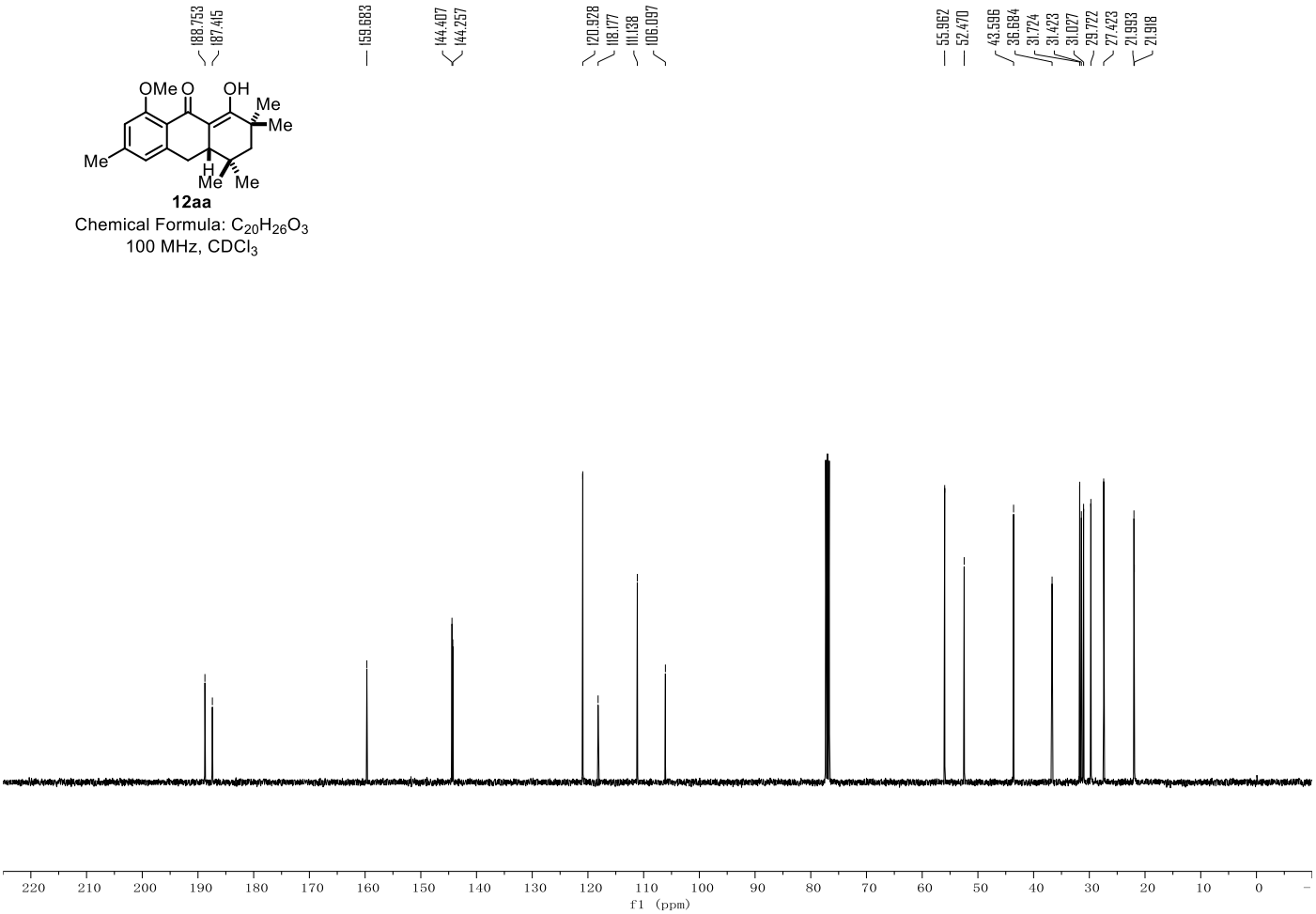
^{1}H and ^{13}C NMR spectra of the synthetic intermediates and products



12aa

Chemical Formula: $C_{20}H_{26}O_3$

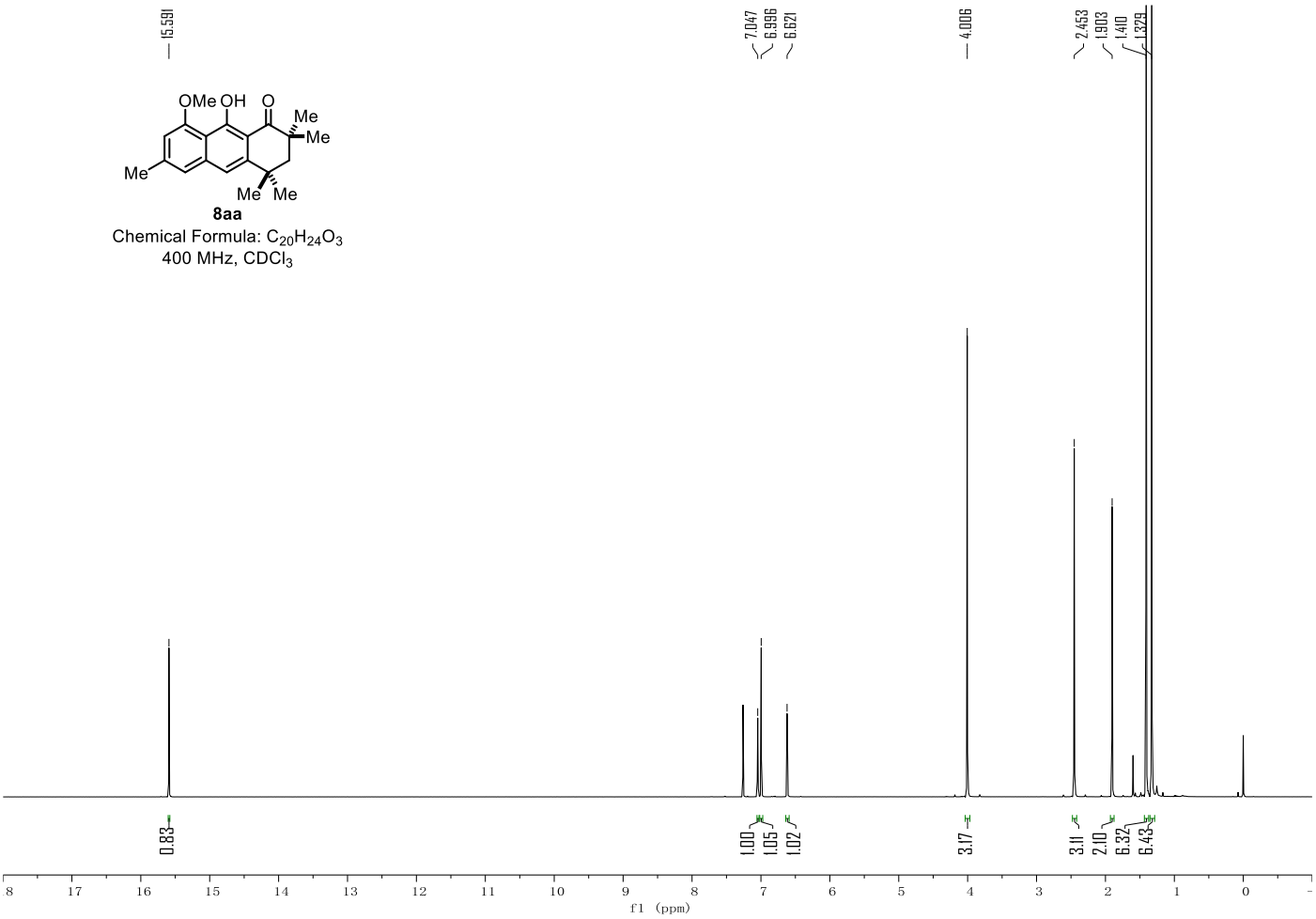
400 MHz, $CDCl_3$



12aa

Chemical Formula: $C_{20}H_{26}O_3$

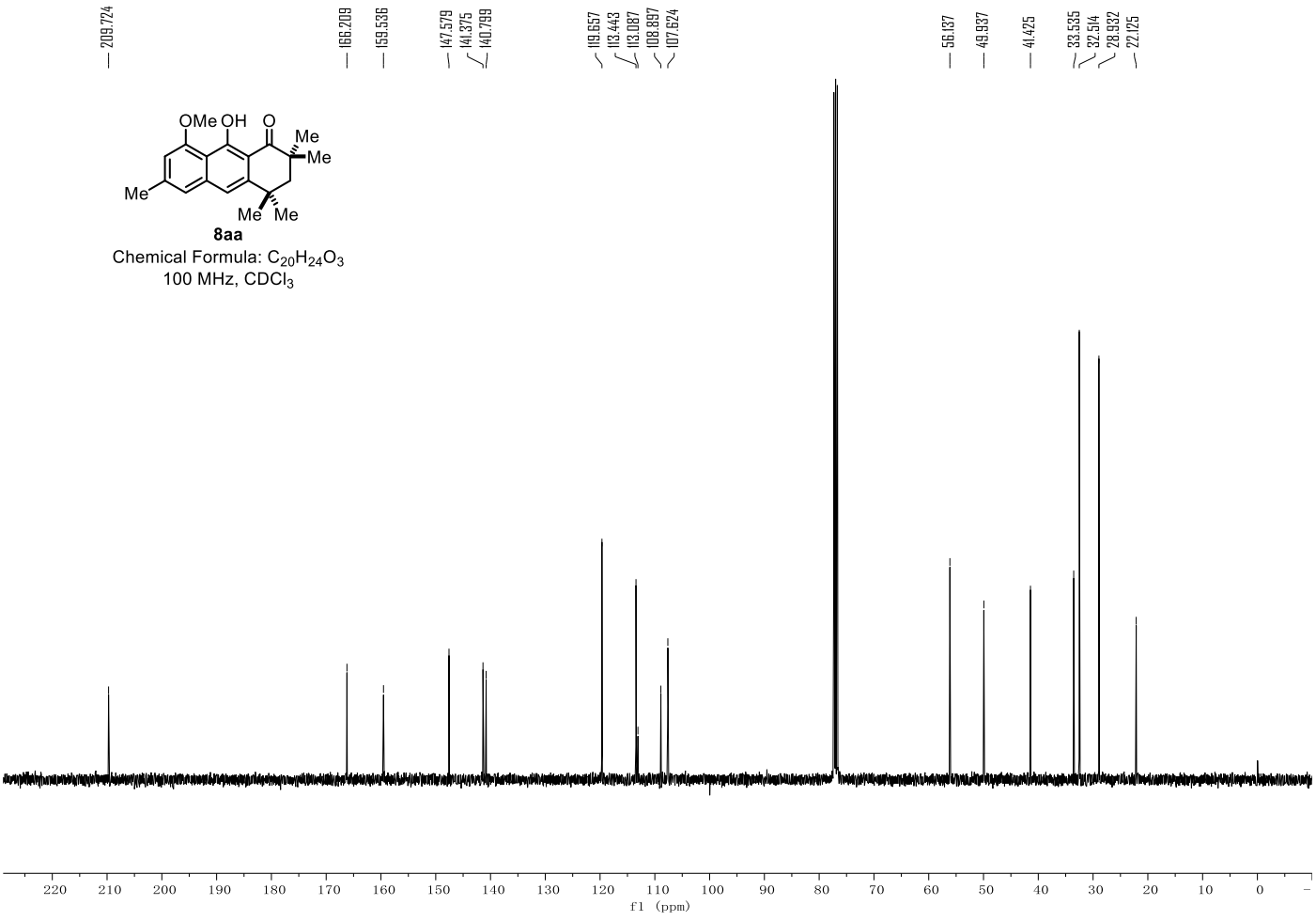
100 MHz, $CDCl_3$



8aa

Chemical Formula: $C_{20}H_{24}O_3$

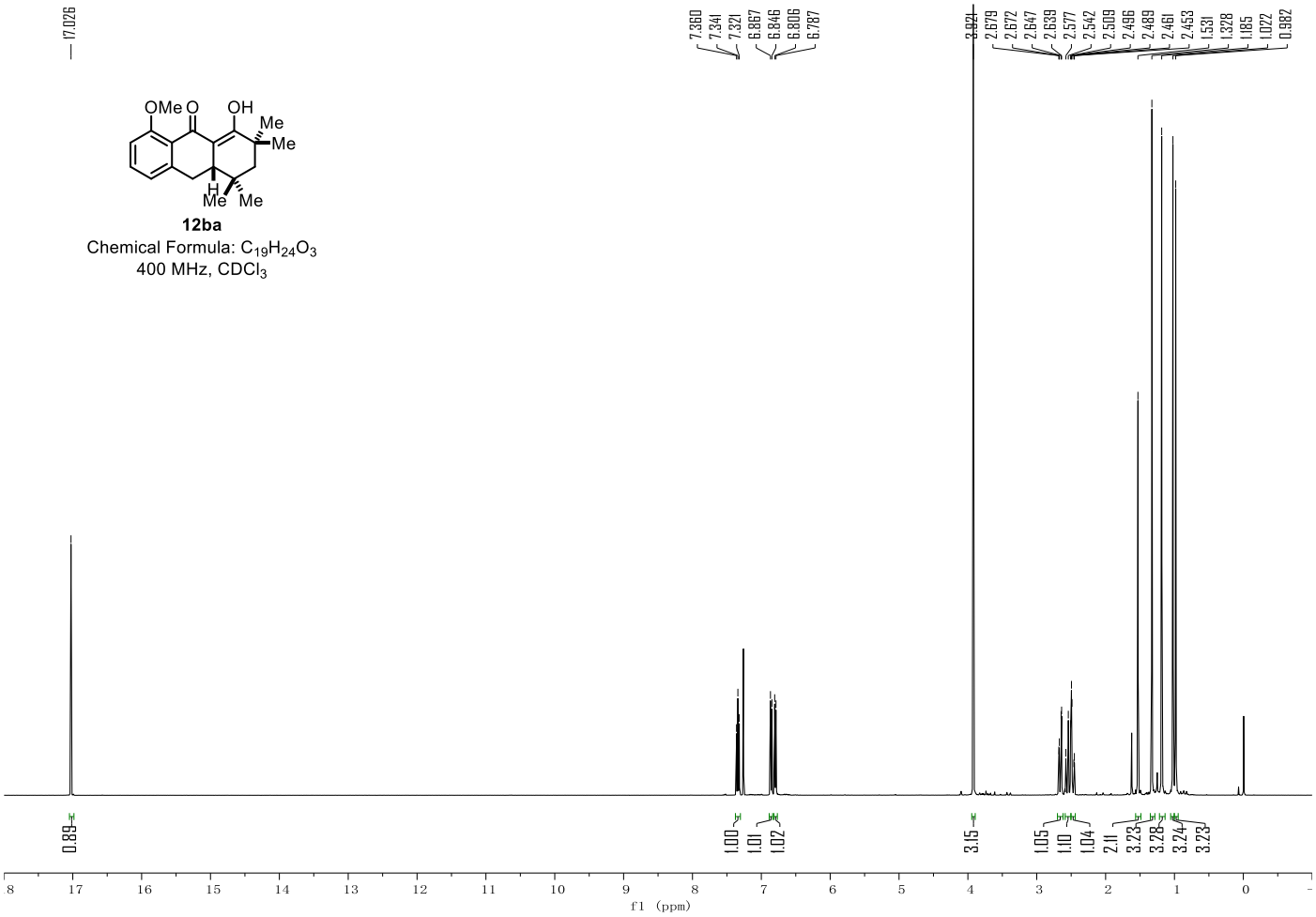
400 MHz, $CDCl_3$



8aa

Chemical Formula: $C_{20}H_{24}O_3$

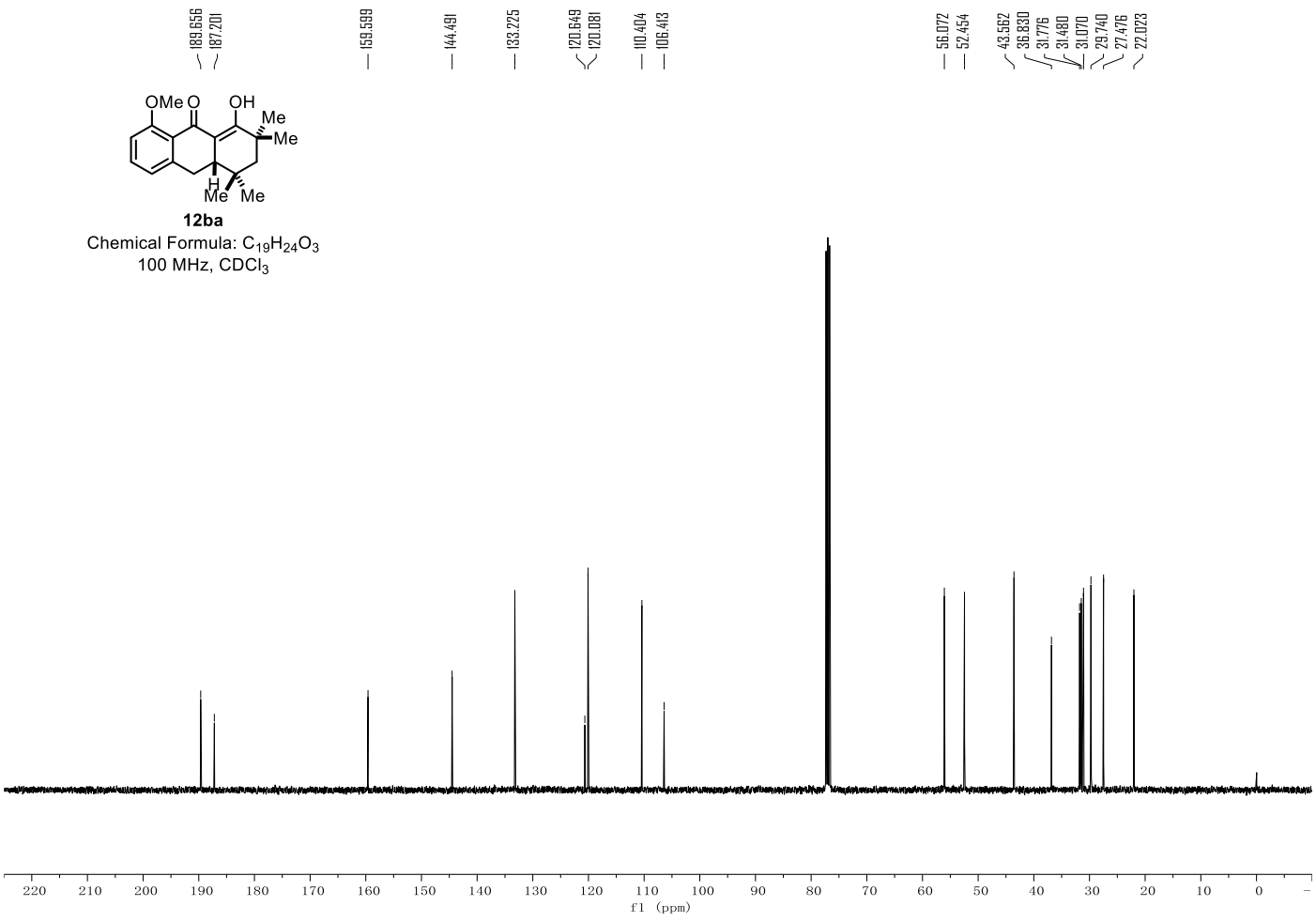
100 MHz, $CDCl_3$



12ba

Chemical Formula: $C_{19}H_{24}O_3$

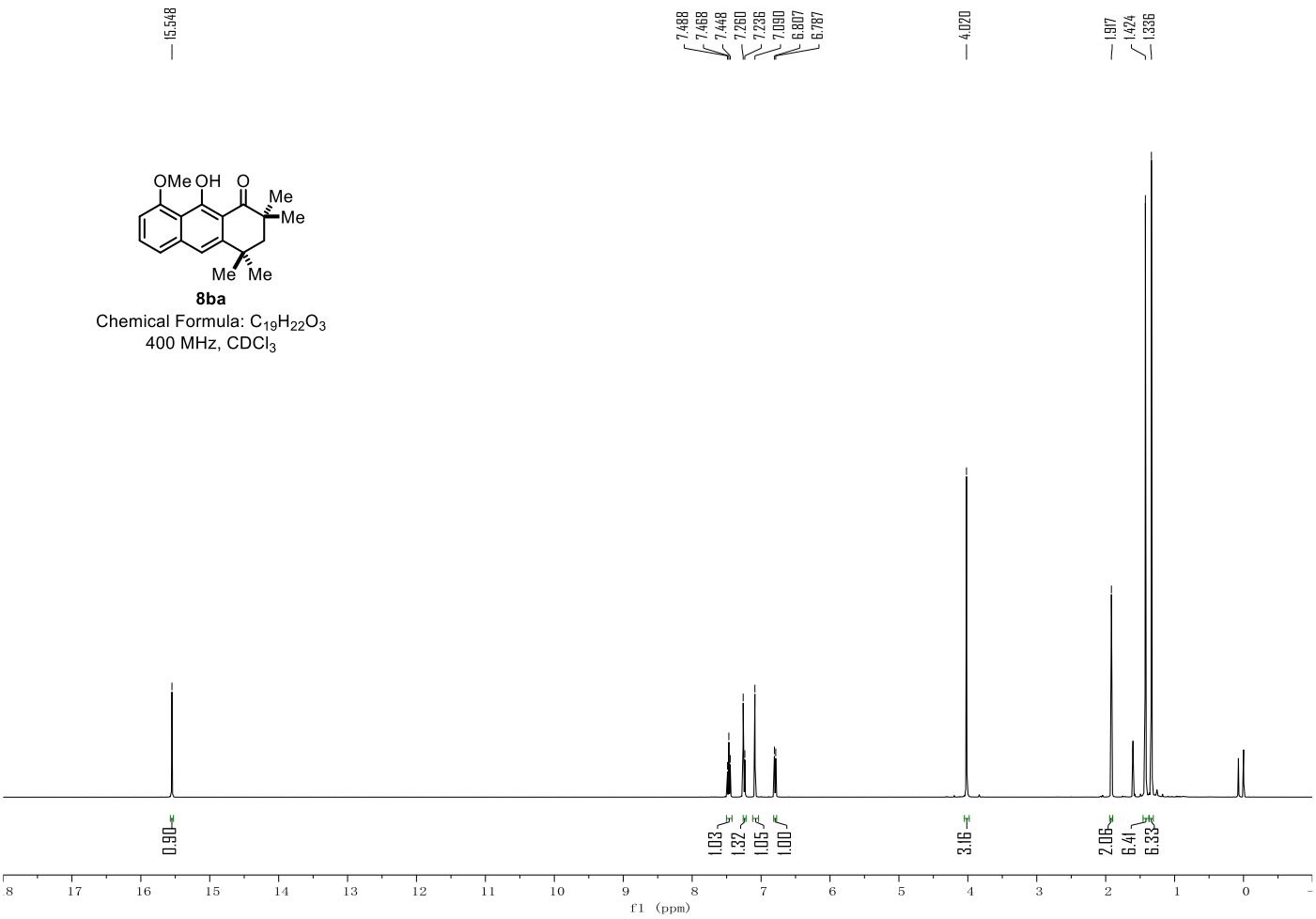
400 MHz, $CDCl_3$



12ba

Chemical Formula: $C_{19}H_{24}O_3$

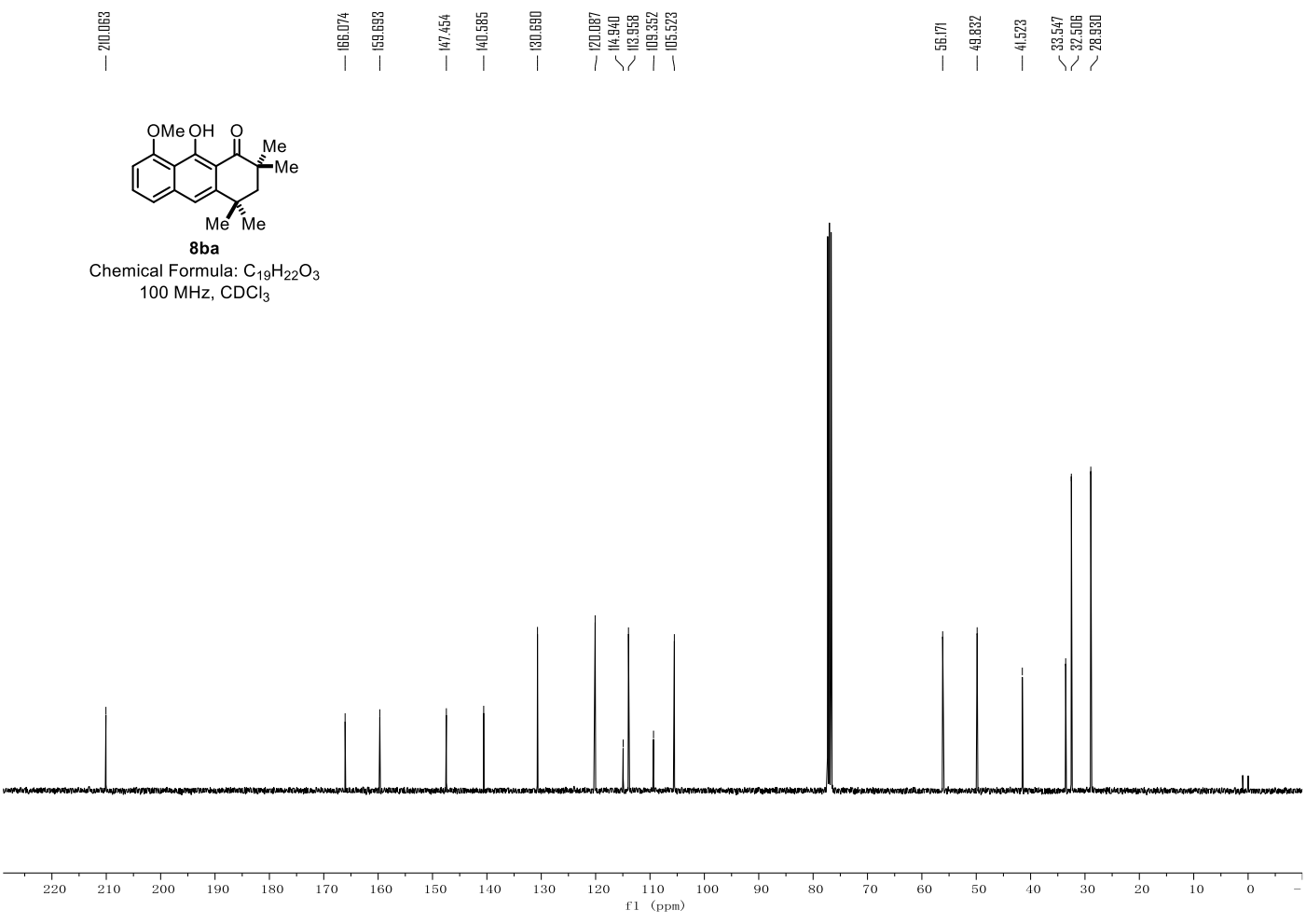
100 MHz, $CDCl_3$



8ba

Chemical Formula: $C_{19}H_{22}O_3$

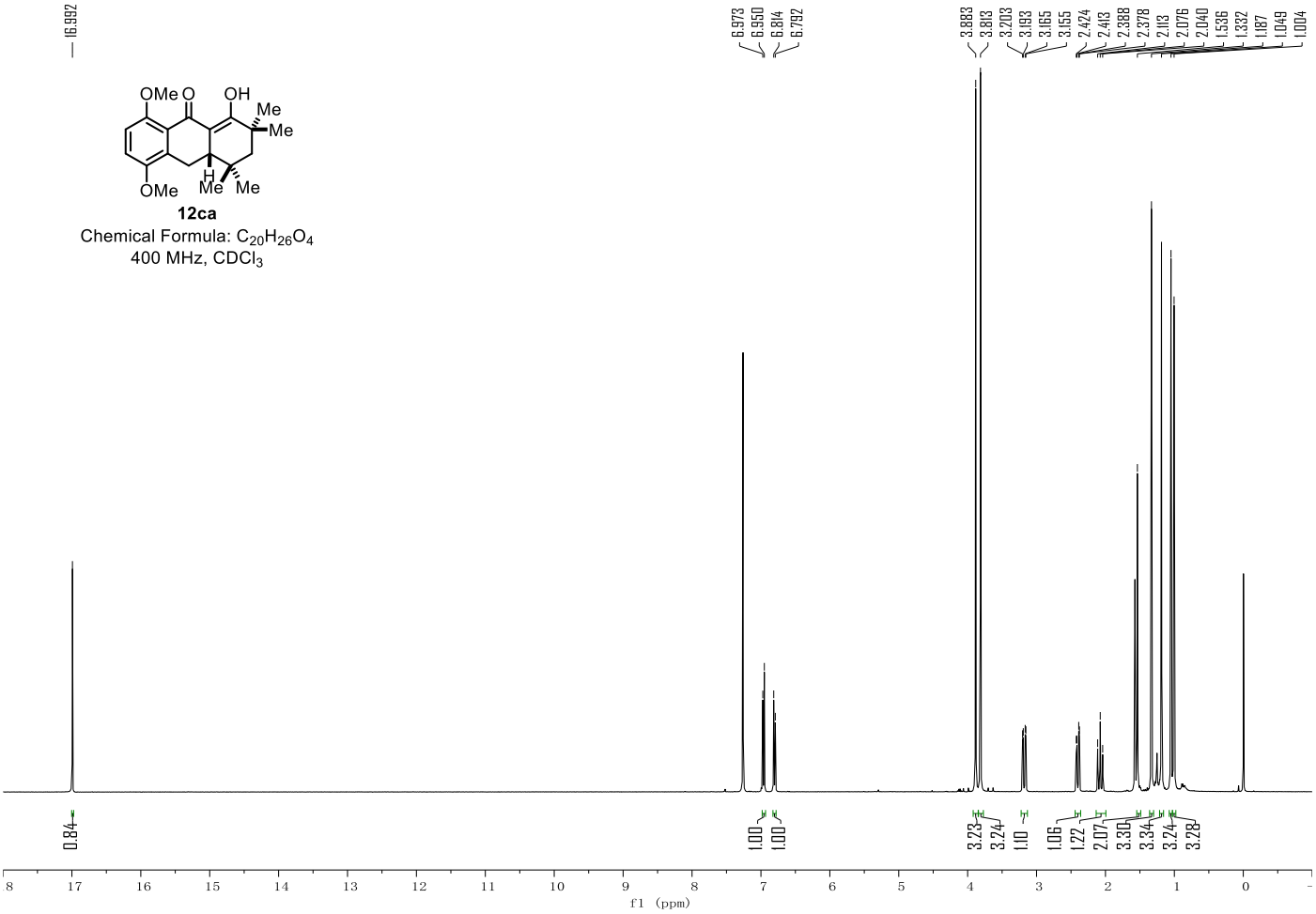
400 MHz, $CDCl_3$

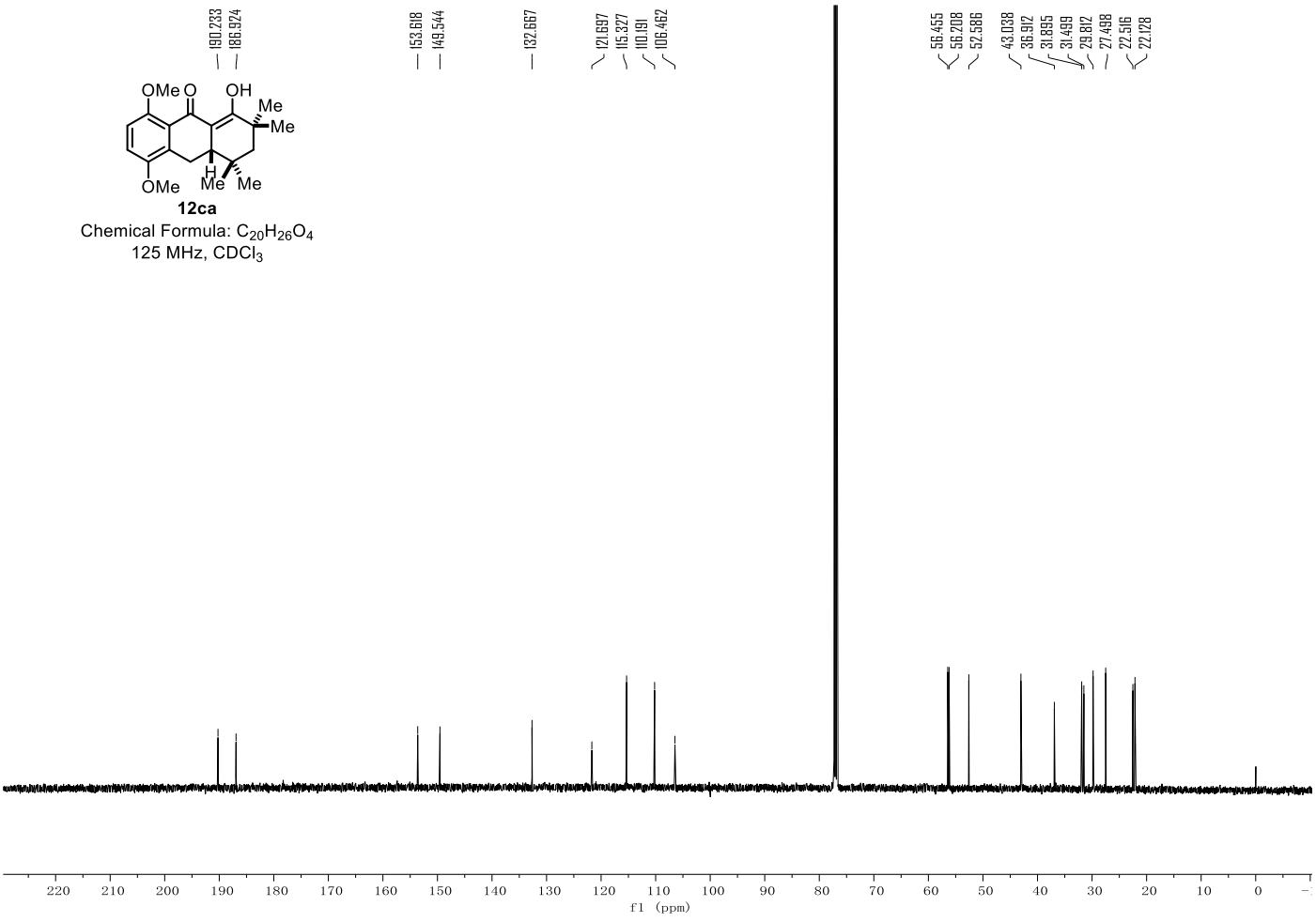


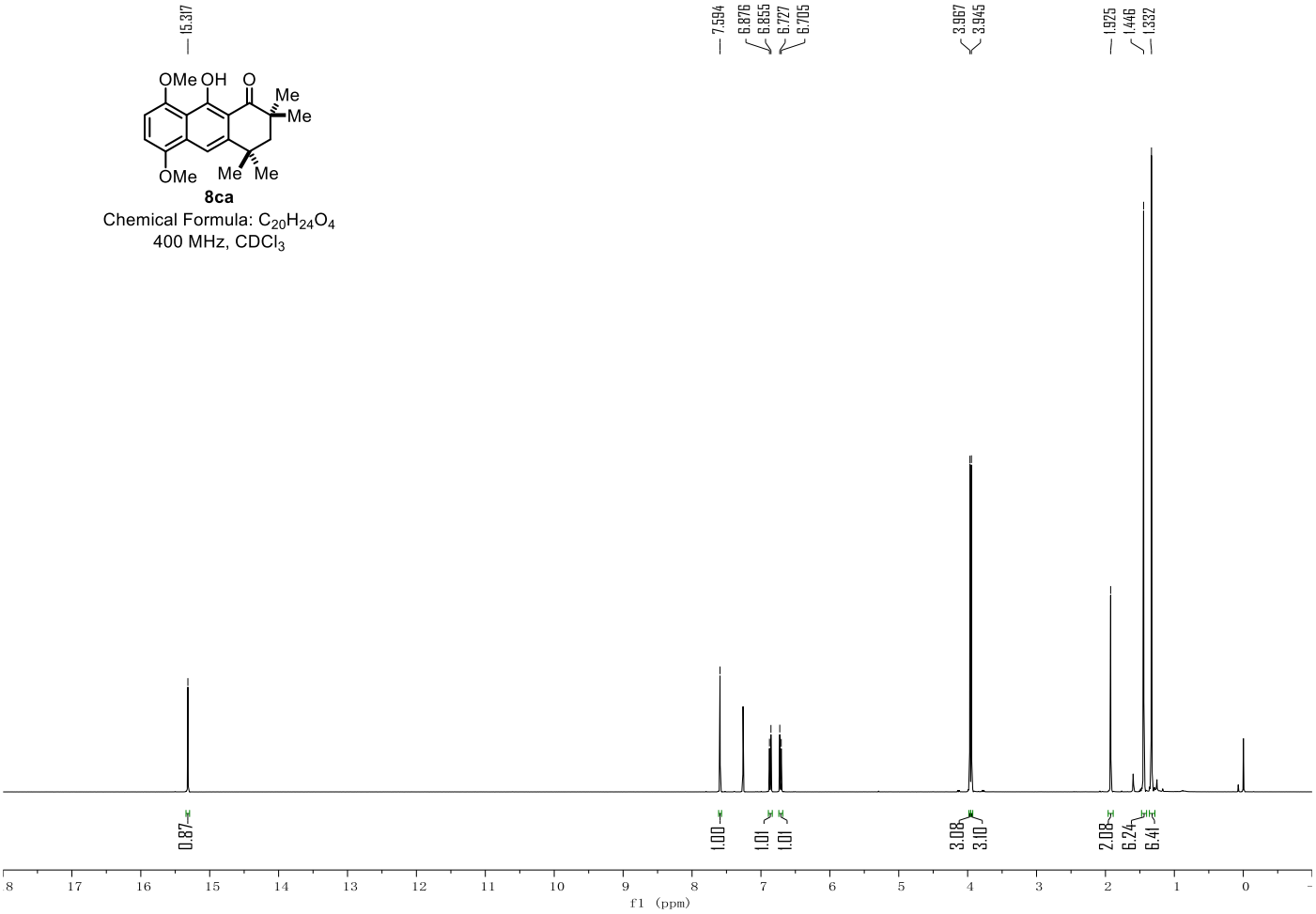
8ba

Chemical Formula: $C_{19}H_{22}O_3$

100 MHz, $CDCl_3$


16.992
6.973
6.950
6.814
6.792
3.883
3.813
3.203
3.193
3.165
3.155
2.424
2.413
2.388
2.378
2.113
2.076
2.040
1.536
1.332
1.187
1.049
1.004
OMe O
OH
Me
Me
H
Me Me
OMe
12ca
Chemical Formula: C20H26O4
400 MHz, CDCl3
0.84
1.00
1.00
3.23
3.24
1.10
1.06
1.22
2.07
3.30
3.34
3.24
3.28
f1 (ppm)

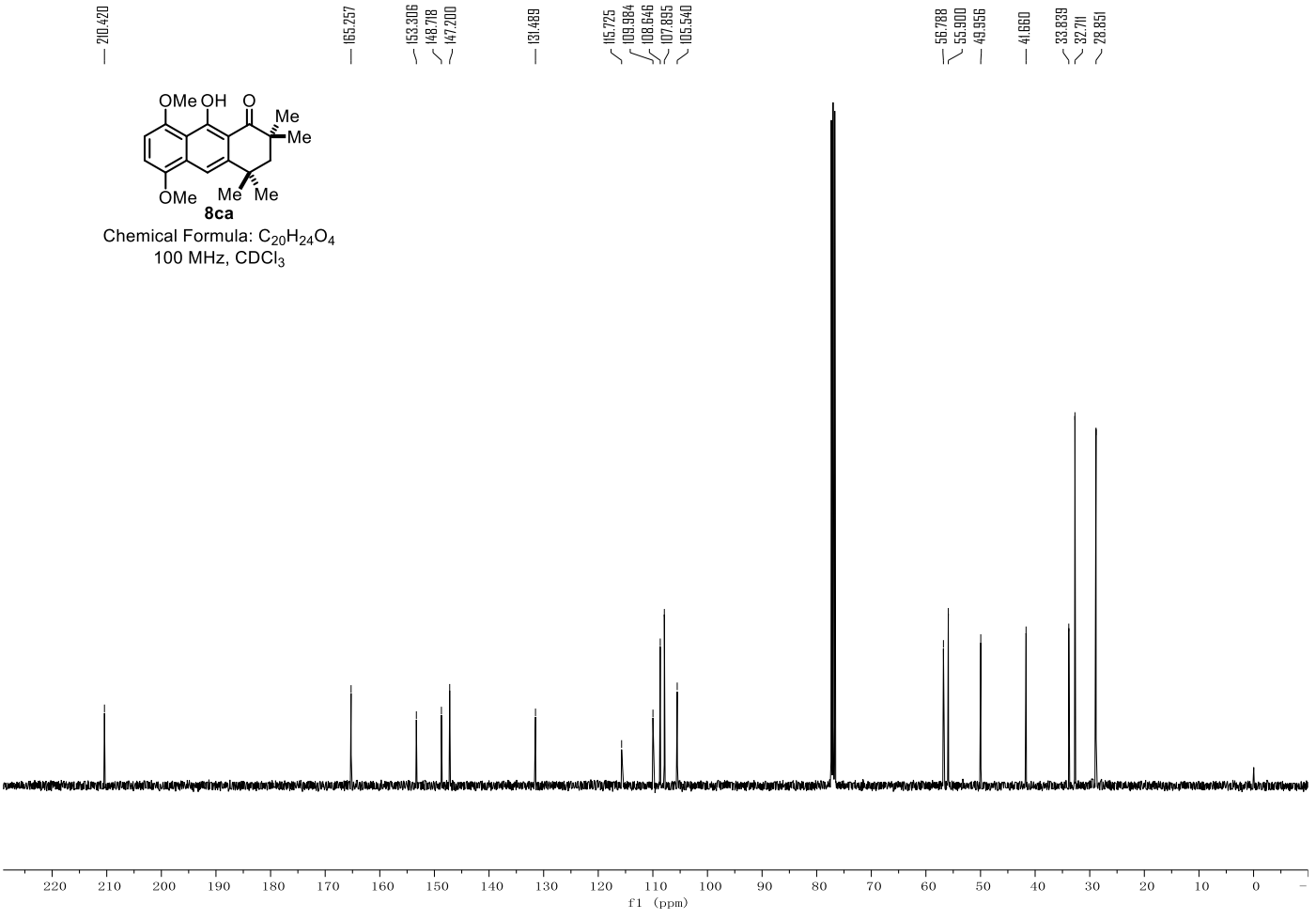

190.233
186.974
153.818
149.544
132.667
121.697
115.327
110.191
106.462
56.455
56.208
52.586
43.038
36.912
31.895
31.499
29.812
27.498
22.516
22.128
OMe O
OH
Me
Me
H
Me Me
OMe
12ca
Chemical Formula: C20H26O4
125 MHz, CDCl3
f1 (ppm)



8ca

Chemical Formula: $C_{20}H_{24}O_4$

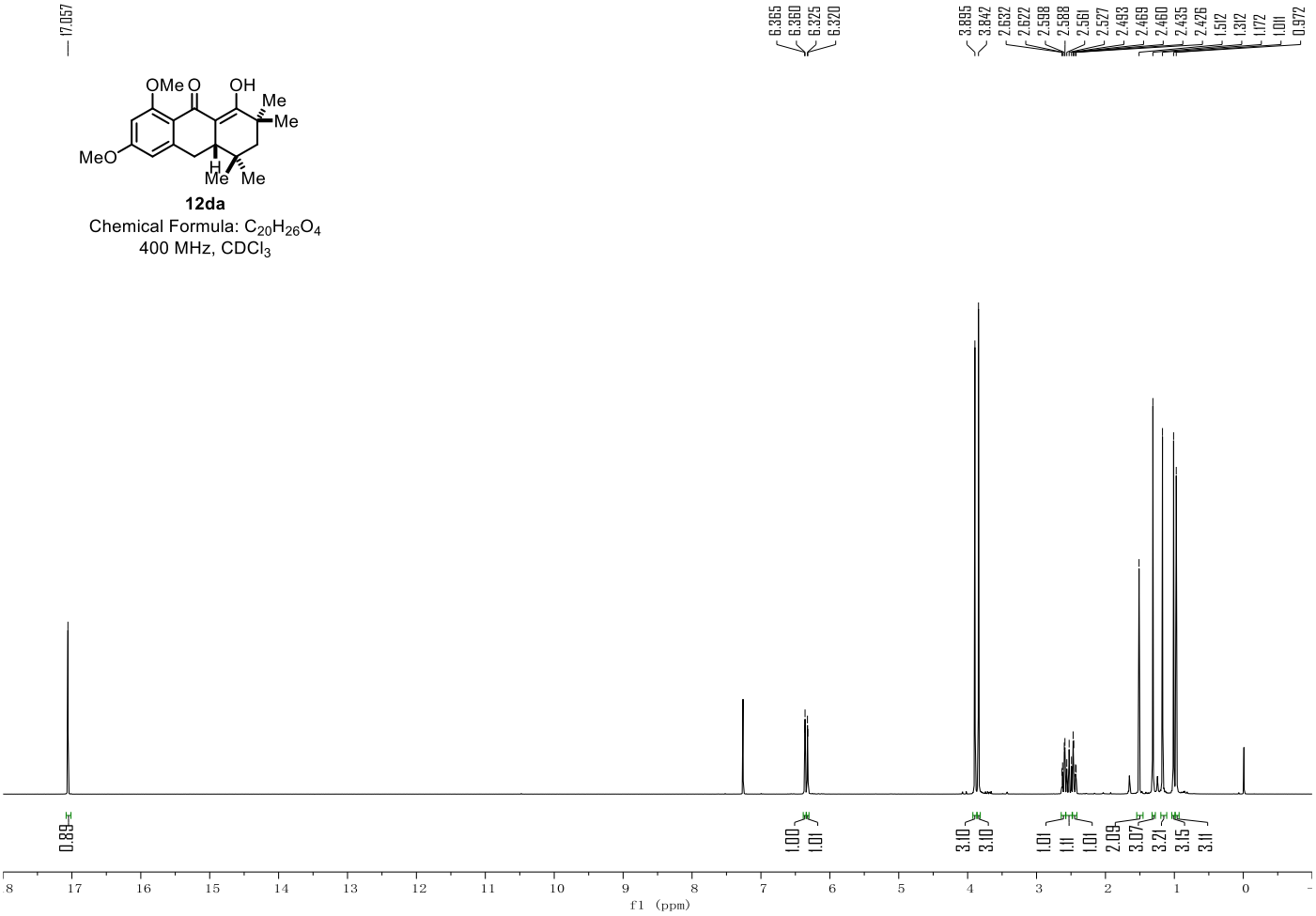
400 MHz, $CDCl_3$



8ca

Chemical Formula: $C_{20}H_{24}O_4$

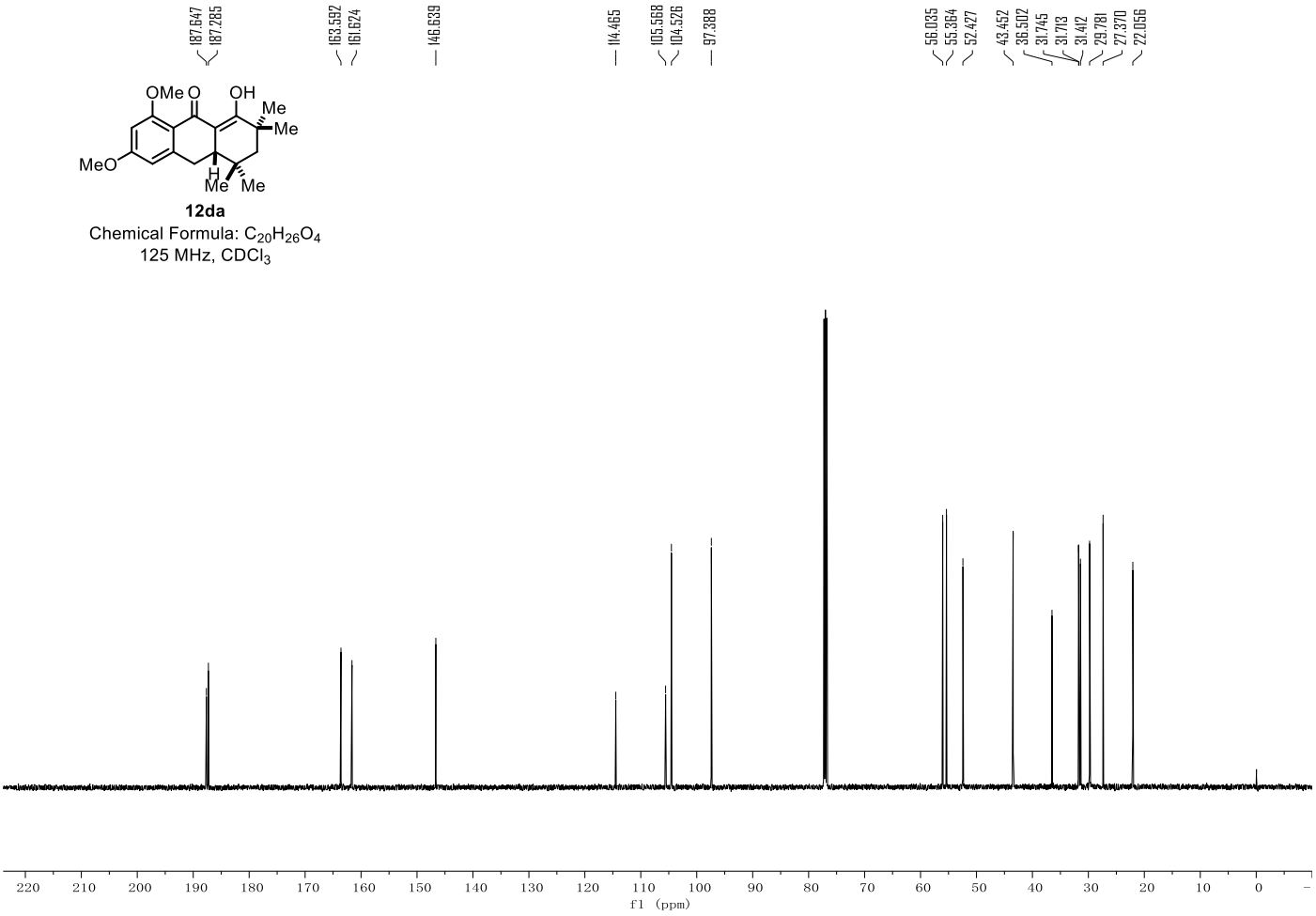
100 MHz, $CDCl_3$



12da

Chemical Formula: $C_{20}H_{26}O_4$

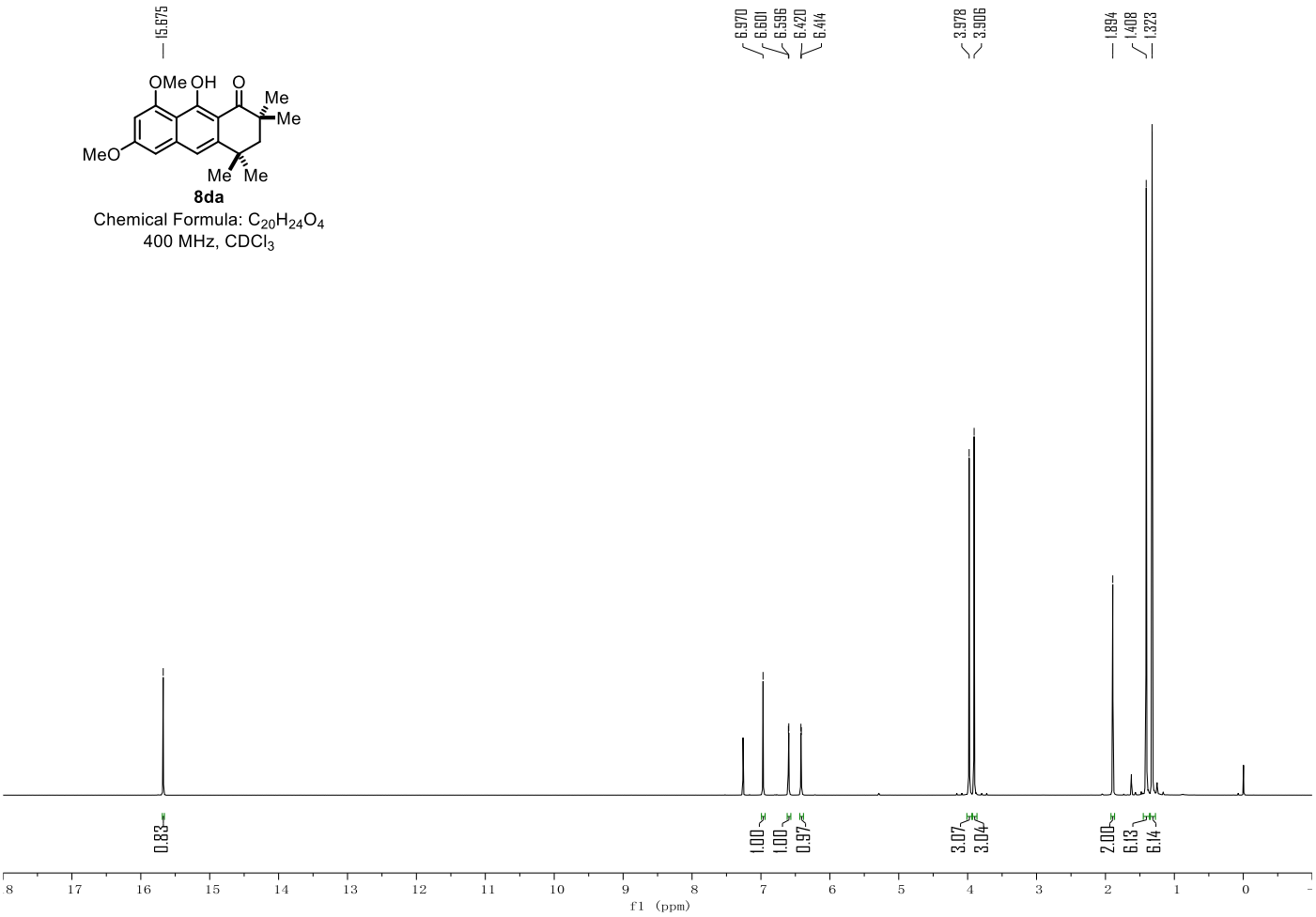
400 MHz, $CDCl_3$



12da

Chemical Formula: $C_{20}H_{26}O_4$

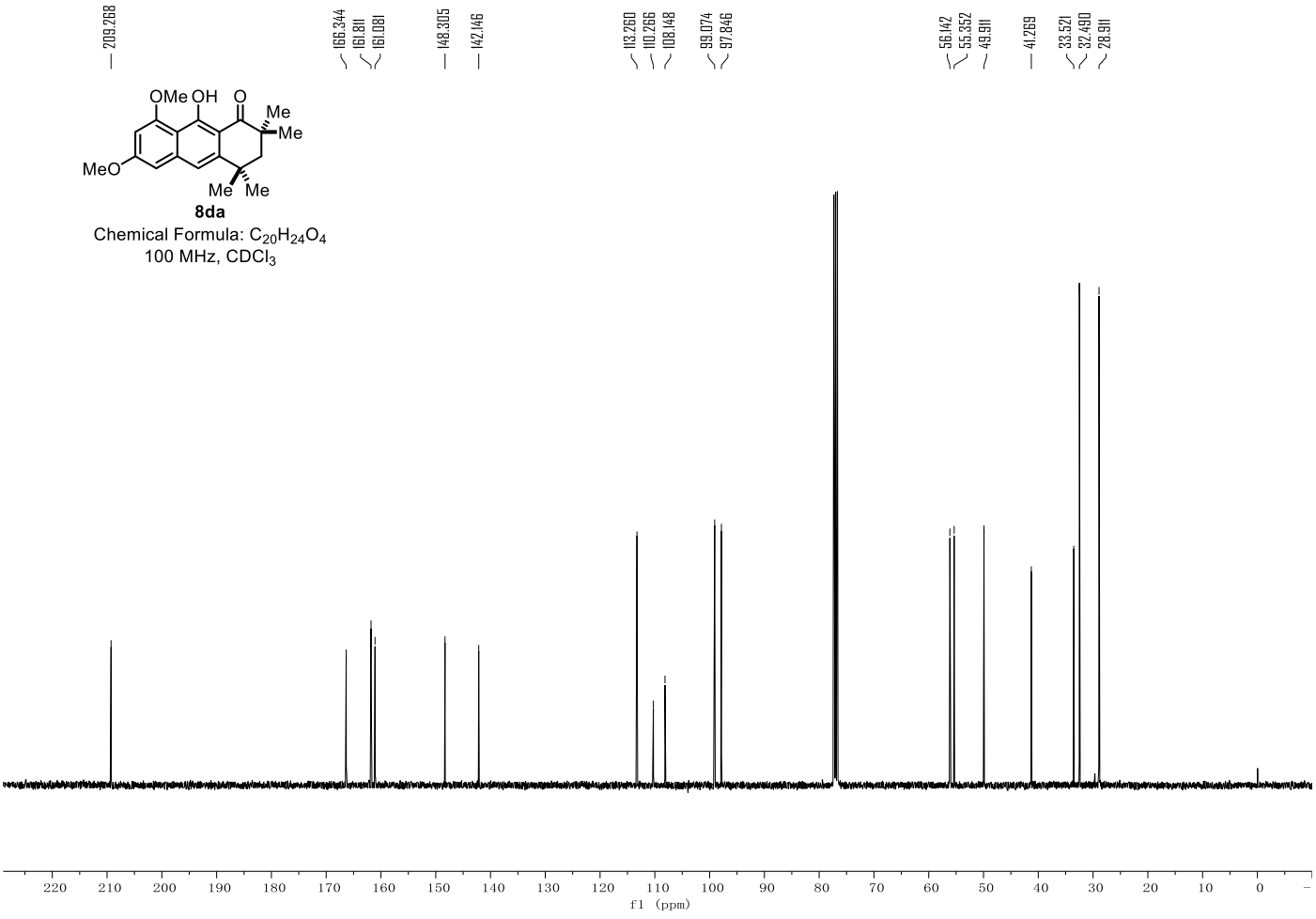
125 MHz, $CDCl_3$



8da

Chemical Formula: $C_{20}H_{24}O_4$

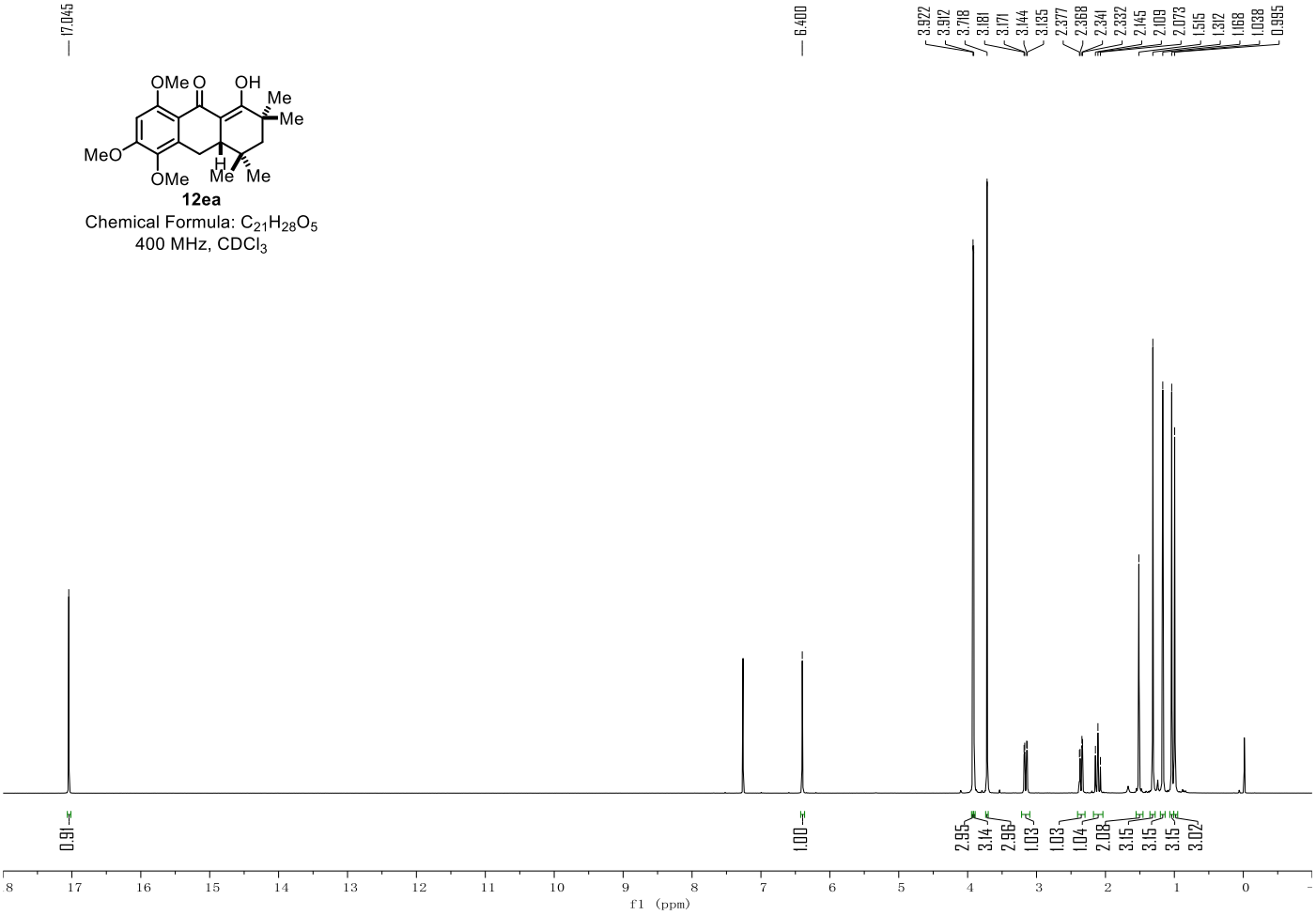
400 MHz, $CDCl_3$



8da

Chemical Formula: $C_{20}H_{24}O_4$

100 MHz, $CDCl_3$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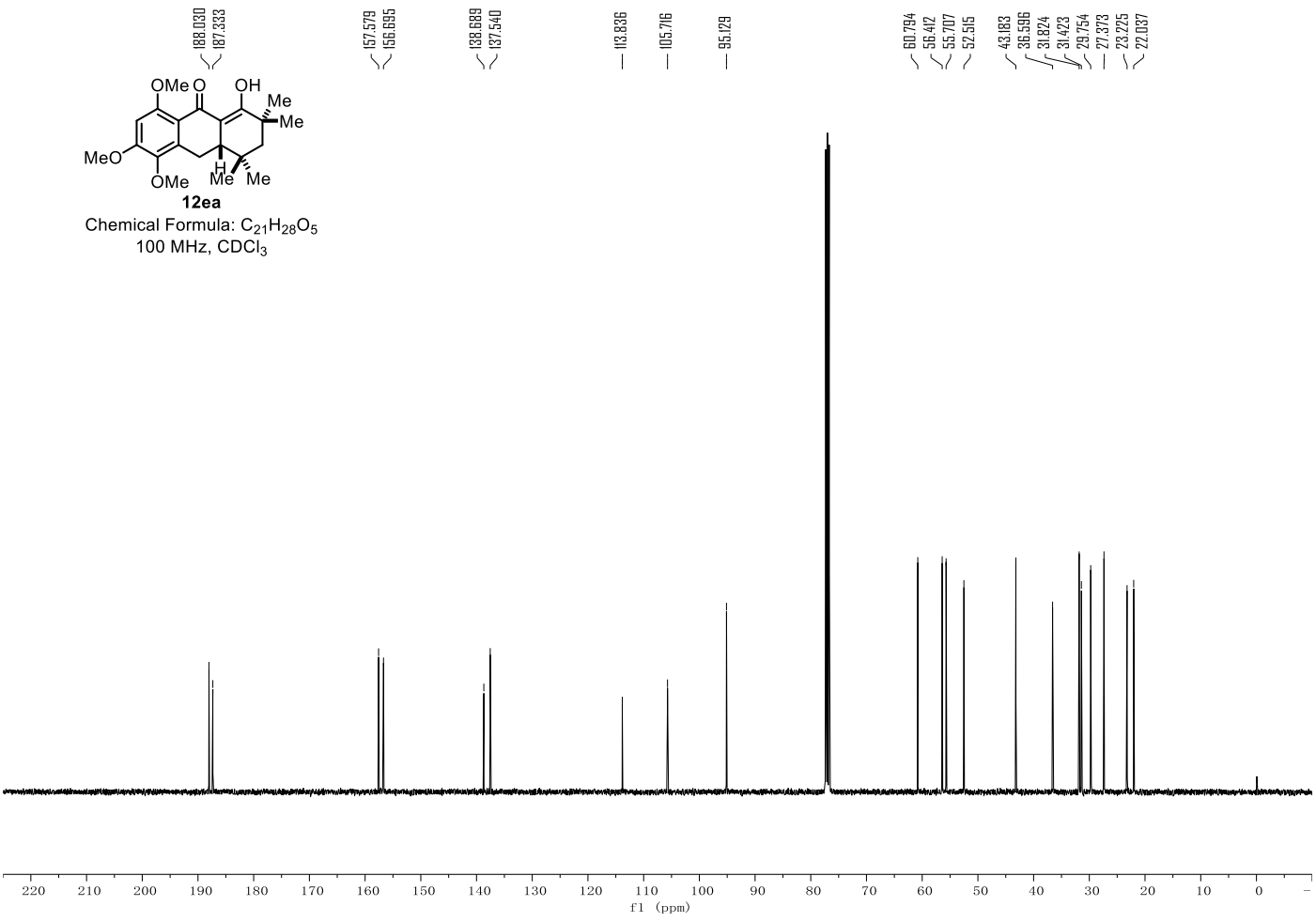
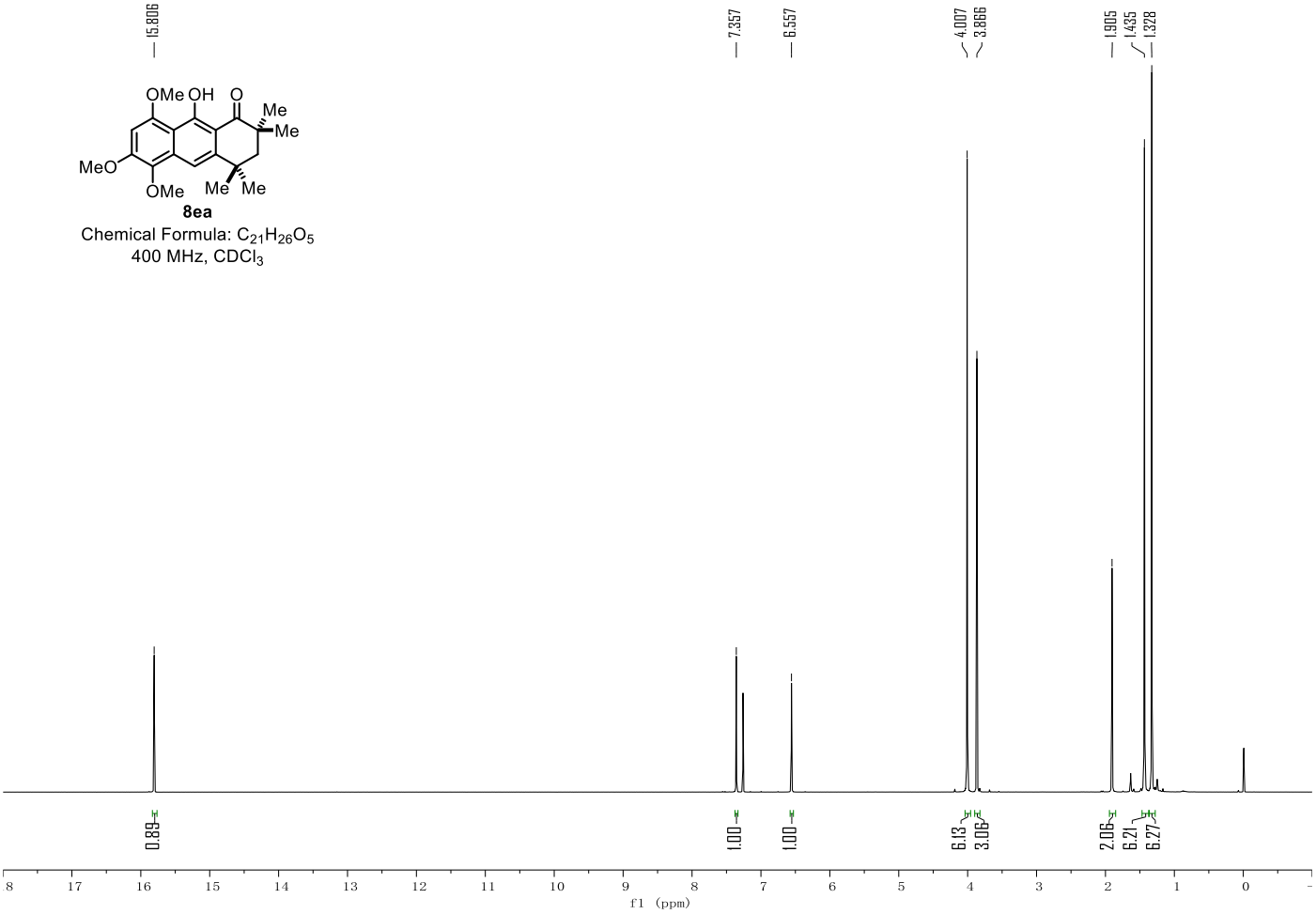
6.400
3.922
3.912
3.718
3.181
3.171
3.144
3.135
2.377
2.368
2.341
2.332
2.145
2.109
2.073
1.515
1.312
1.168
1.038
0.995
OMe O
OH
Me
Me
MeO
OMe
H
Me Me
12ea
Chemical Formula: C21H28O5
400 MHz, CDCl3
0.91
1.00
2.95
3.14
2.96
1.03
1.03
1.04
2.08
3.15
3.15
3.15
3.02
f1 (ppm)


188.030
187.333
157.579
156.695
138.689
137.540
113.836
105.716
95.129
60.794
56.412
55.707
52.515
43.183
36.596
31.824
31.423
29.754
27.373
23.225
22.037
OMe O
OH
Me
Me
MeO
OMe
H
Me Me
12ea
Chemical Formula: C21H28O5
100 MHz, CDCl3
f1 (ppm)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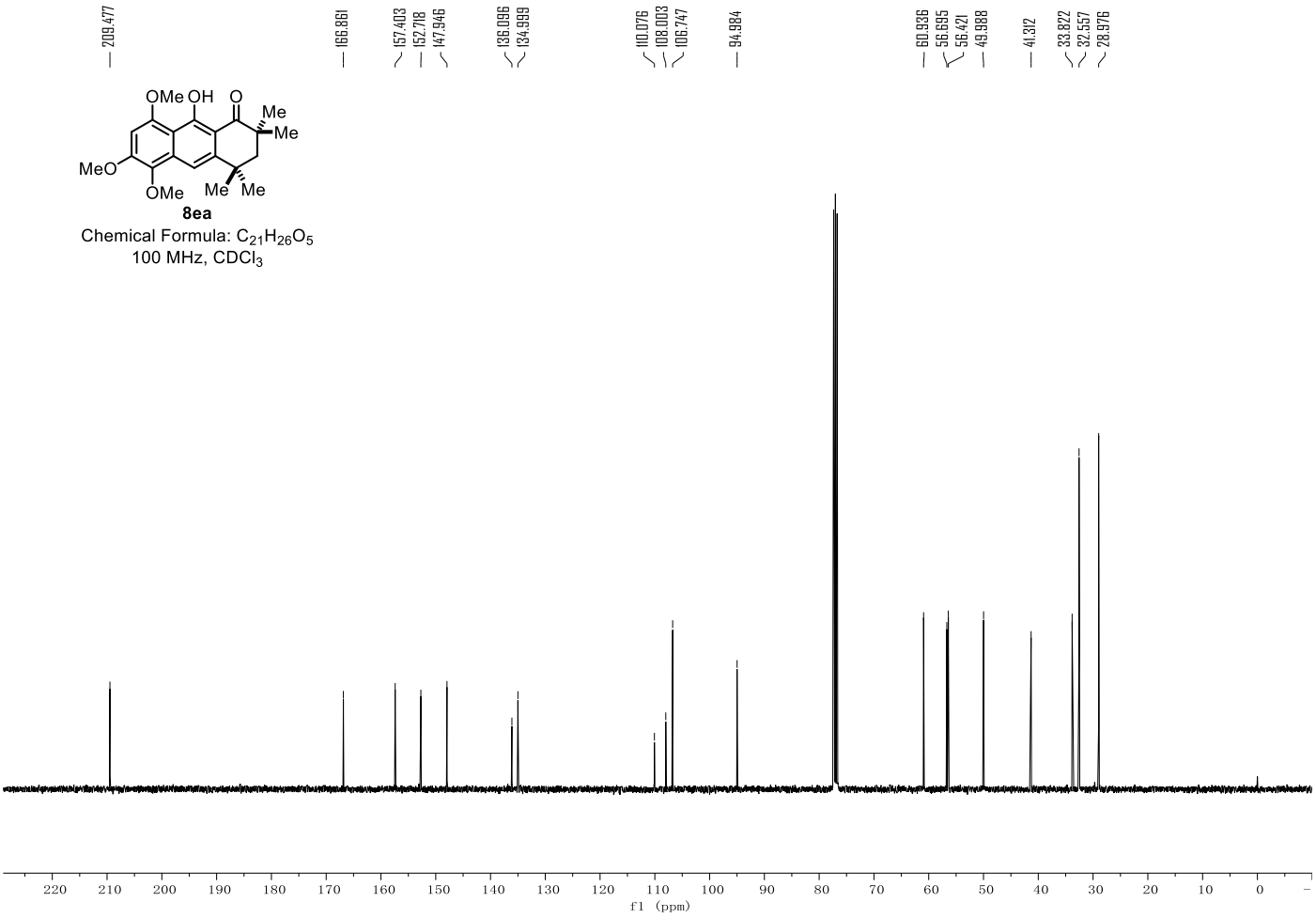
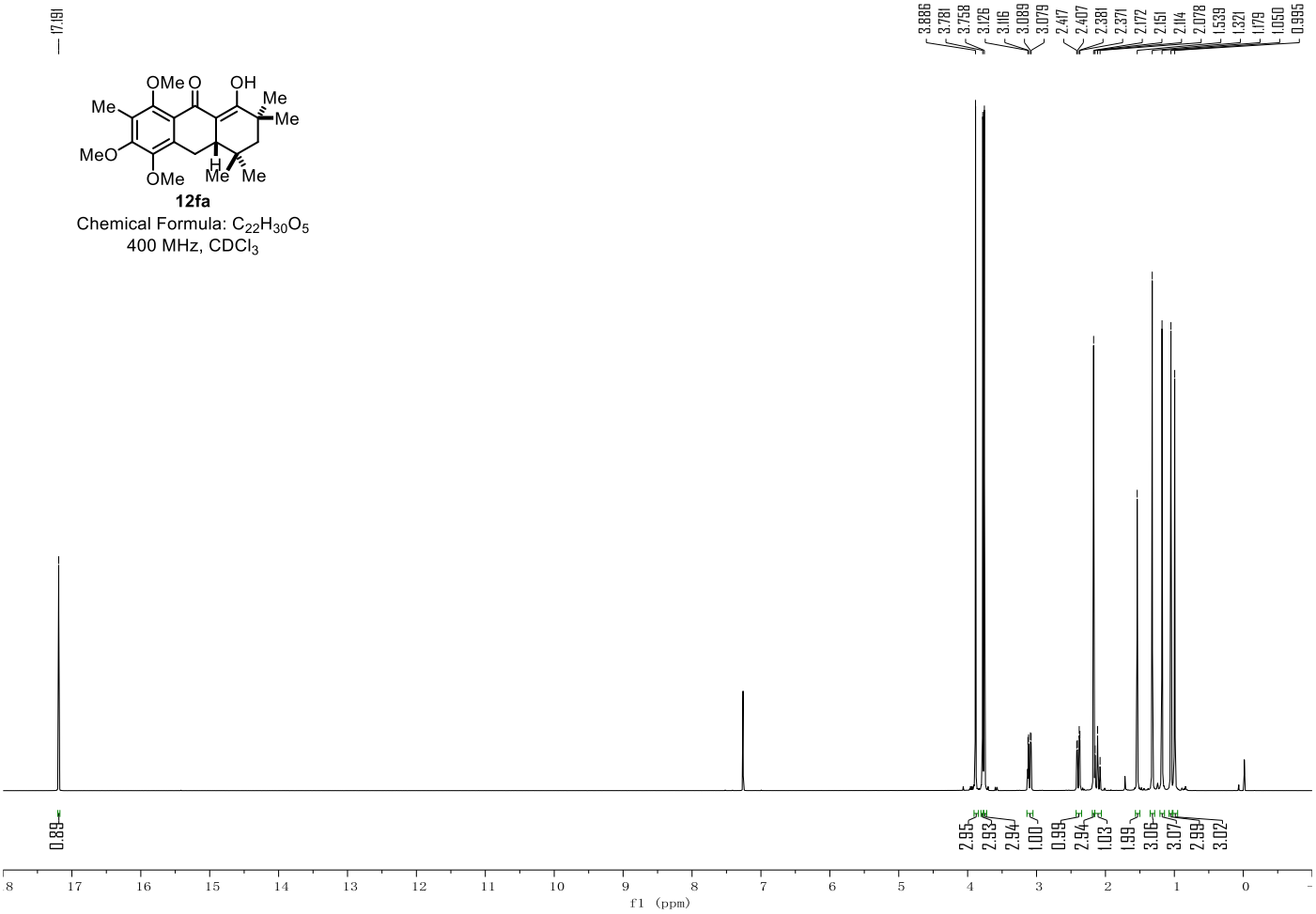
7.357
6.557
4.007
3.866
1.905
1.435
1.328
OMe OH O
Me
Me
MeO
OMe
Me Me
8ea
Chemical Formula: C21H26O5
400 MHz, CDCl3
0.89
1.00
1.00
6.13
3.06
2.06
6.21
6.27
f1 (ppm)

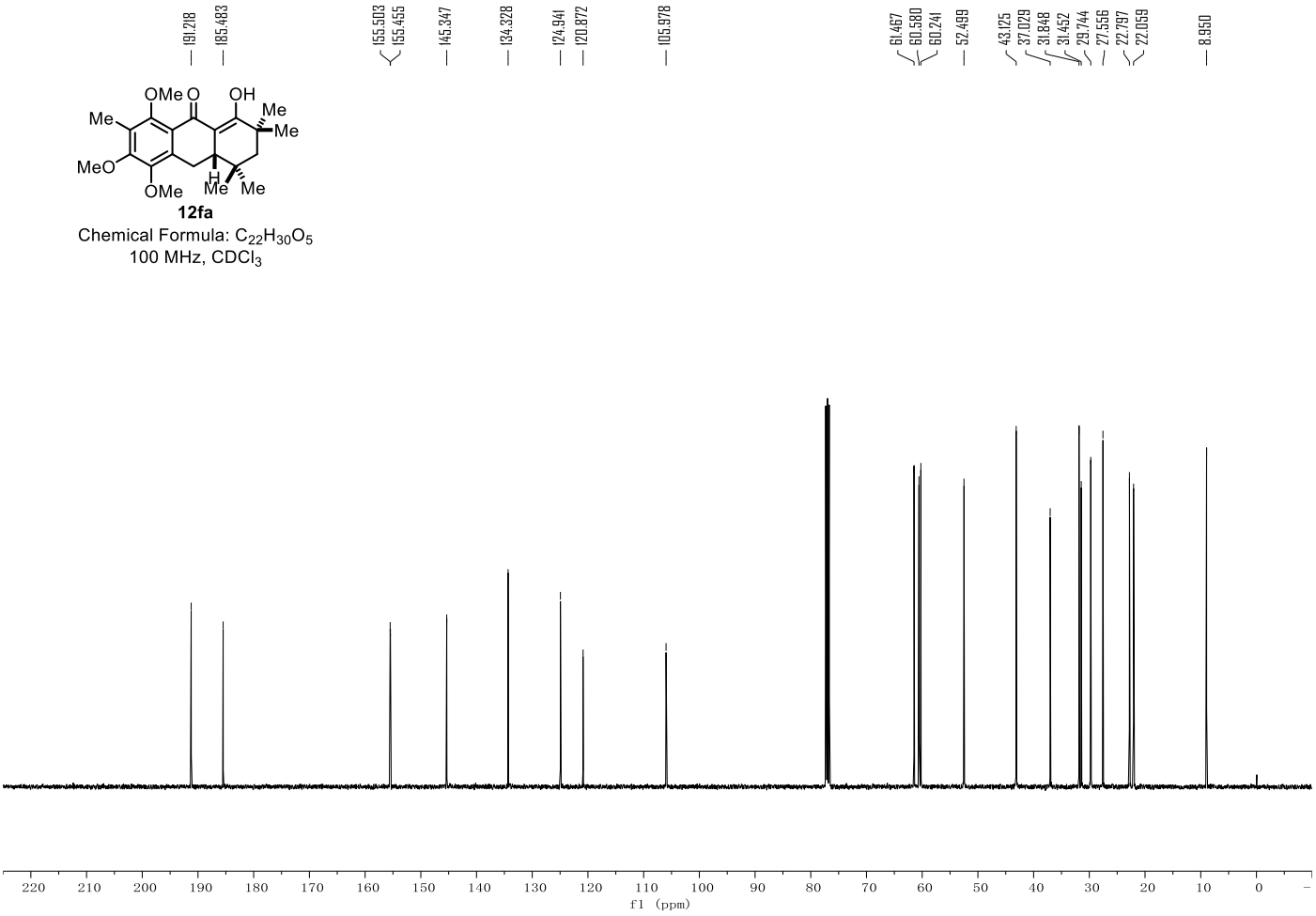

209.477
166.861
157.403
152.718
147.946
136.096
134.999
110.076
108.003
106.747
94.984
60.936
56.695
56.421
49.988
41.312
33.822
32.557
28.976
OMe OH O
Me
Me
MeO
OMe
Me Me
8ea
Chemical Formula: C21H26O5
100 MHz, CDCl3
f1 (ppm)



12fa

Chemical Formula: $C_{22}H_{30}O_5$

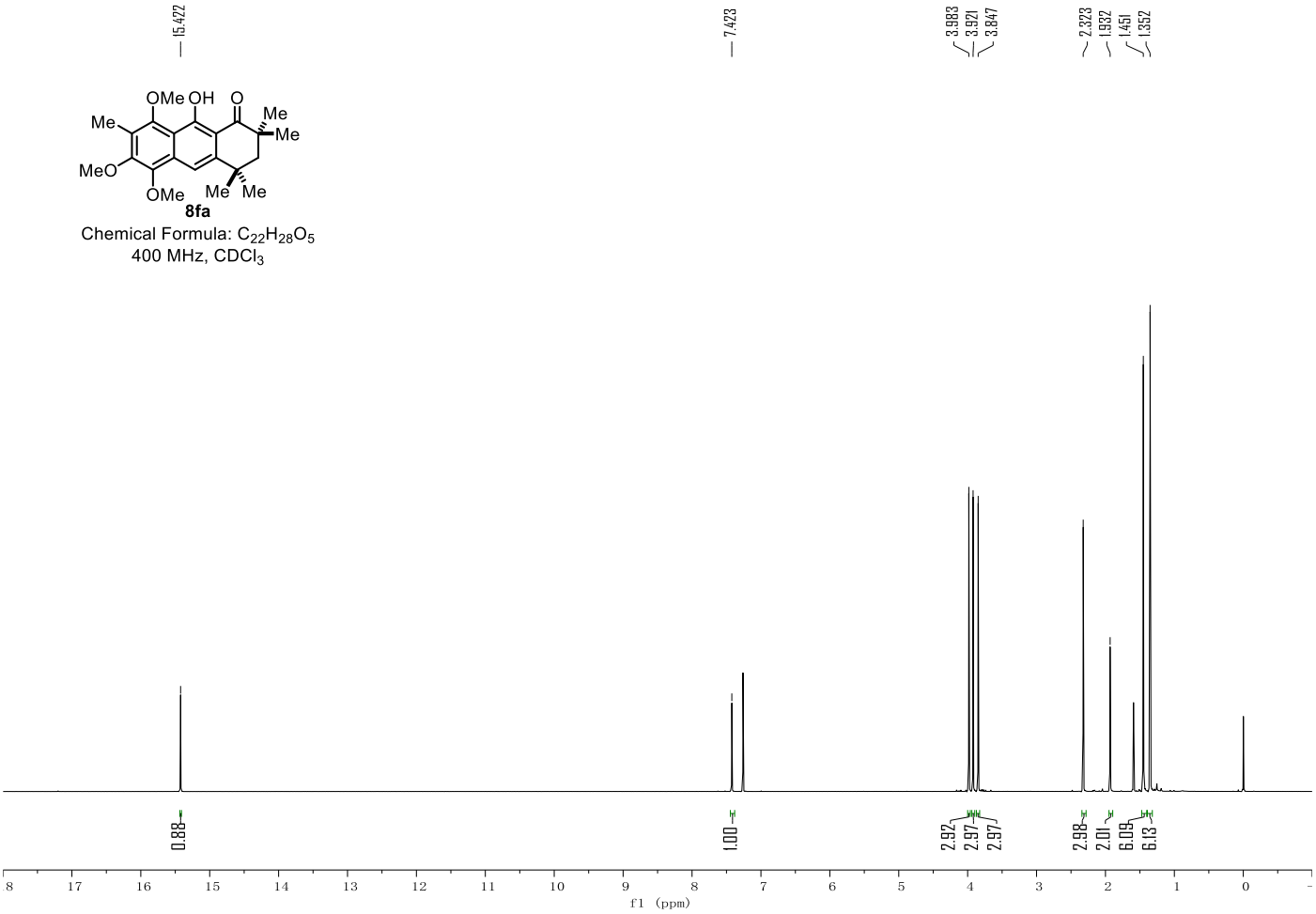
400 MHz, $CDCl_3$



12fa

Chemical Formula: $C_{22}H_{30}O_5$

100 MHz, $CDCl_3$


15.422
7.423
3.983
3.921
3.847
2.323
1.932
1.451
1.352
OMe OH O
Me
Me
Me
MeO
OMe
Me Me
8fa
Chemical Formula: C22H28O5
400 MHz, CDCl3
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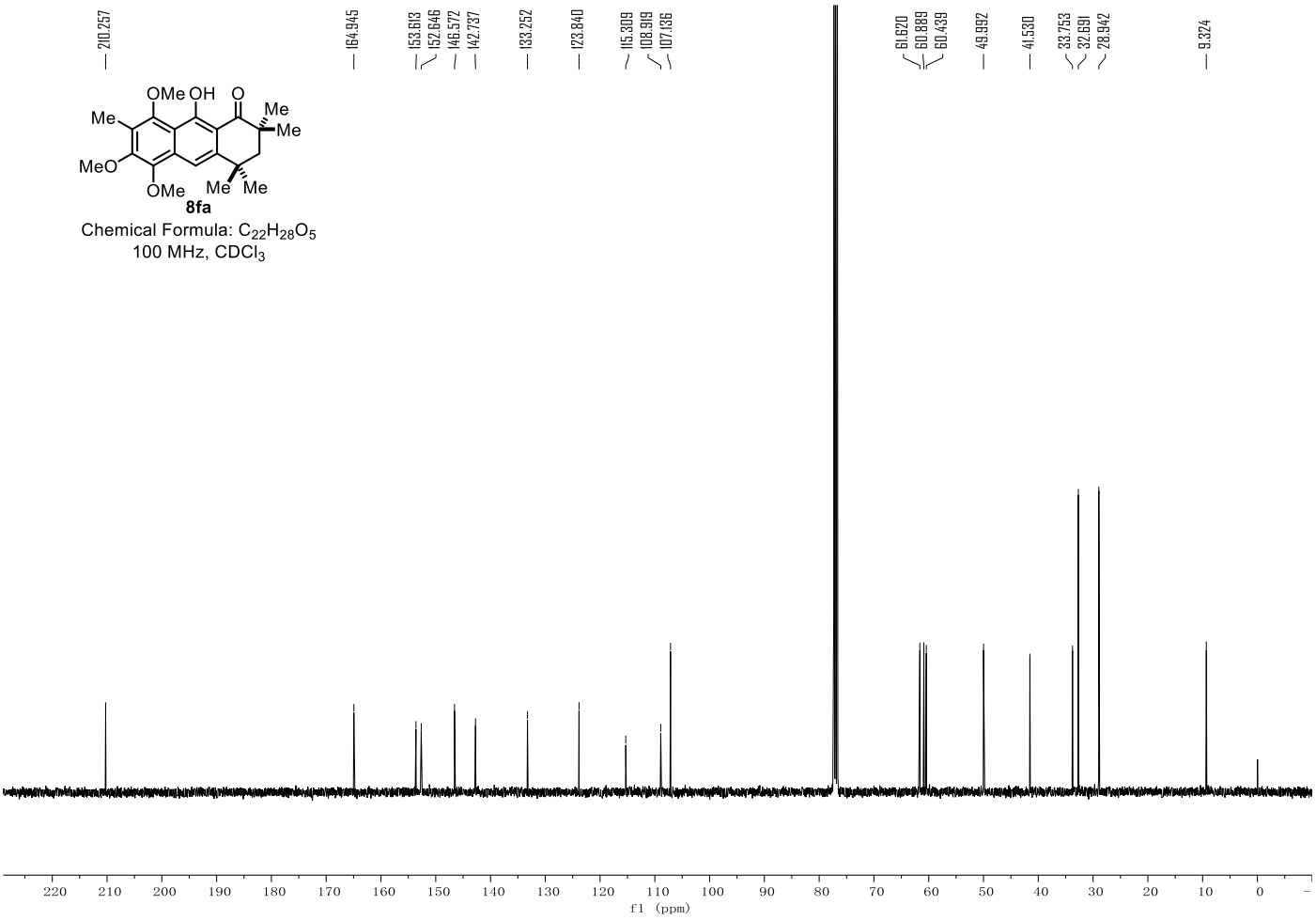
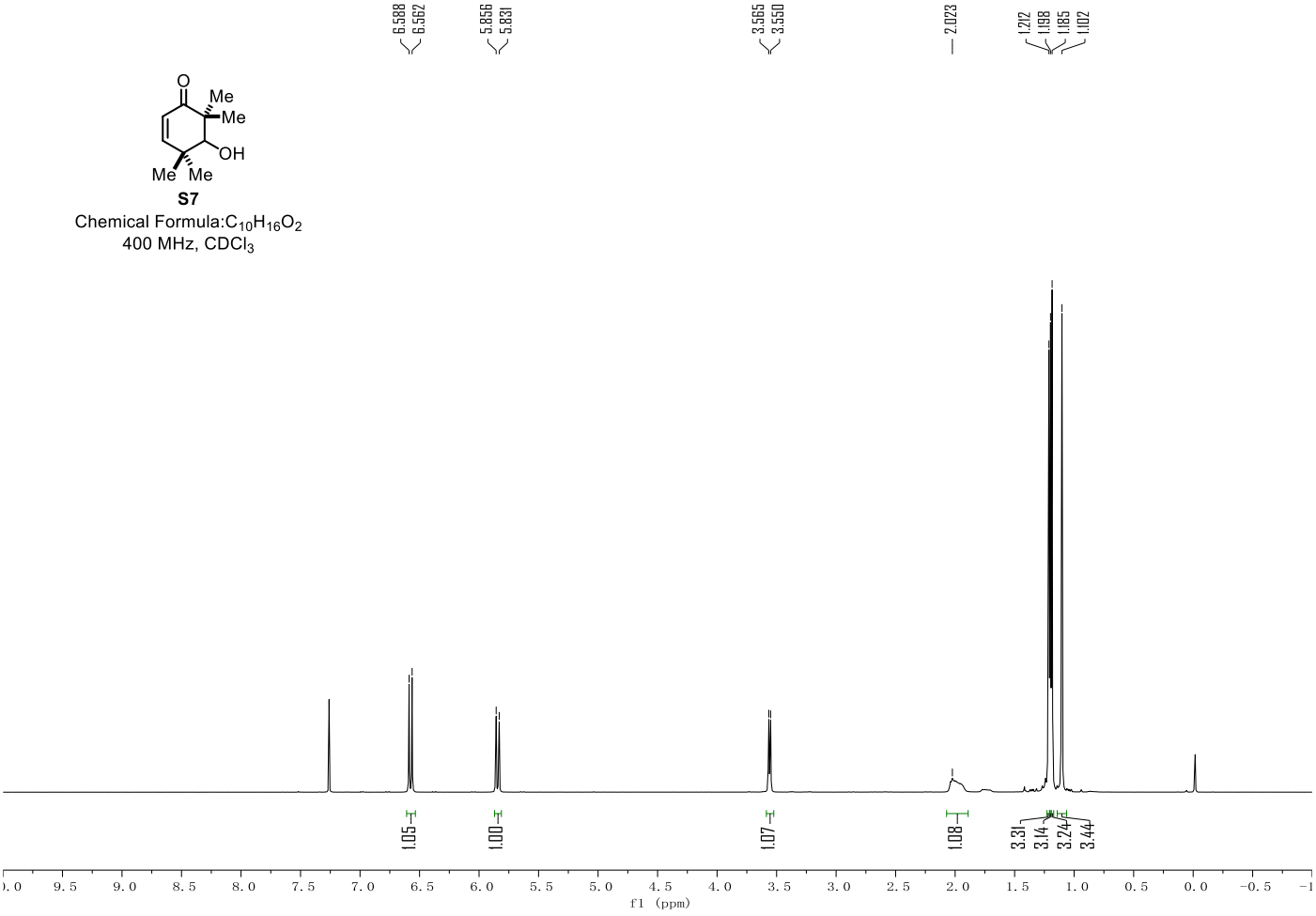
1.00
2.92
2.97
2.97
2.98
2.01
6.09
6.13
f1 (ppm)

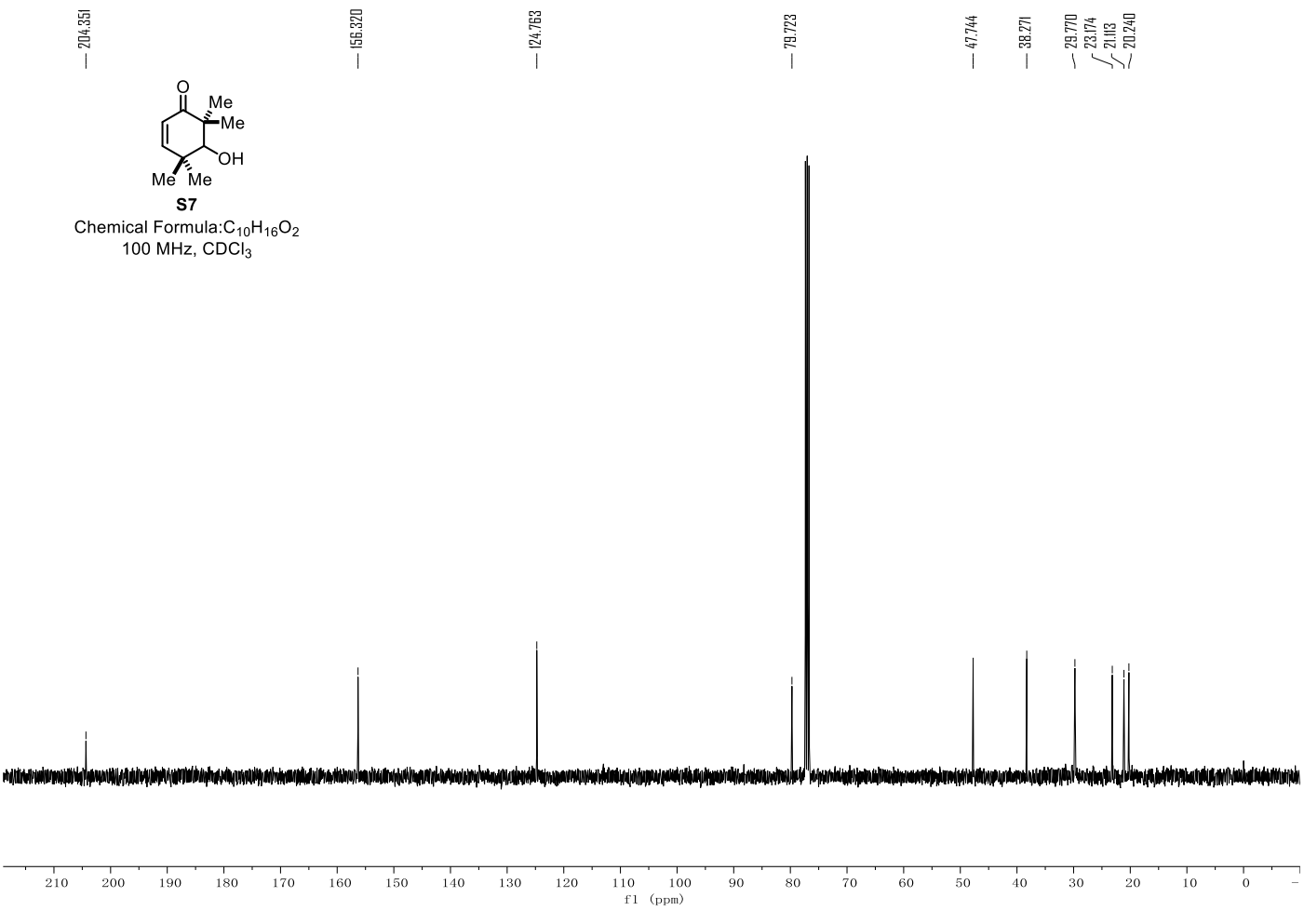

210.257
164.945
153.613
152.646
146.572
142.737
133.252
123.840
115.309
108.919
107.136
61.620
60.889
60.439
49.992
41.580
33.753
32.691
28.942
9.324
OMe OH O
Me
Me
Me
MeO
OMe
Me Me
8fa
Chemical Formula: C22H28O5
100 MHz, CDCl3
f1 (ppm)



S7

Chemical Formula:$C_{10}H_{16}O_2$

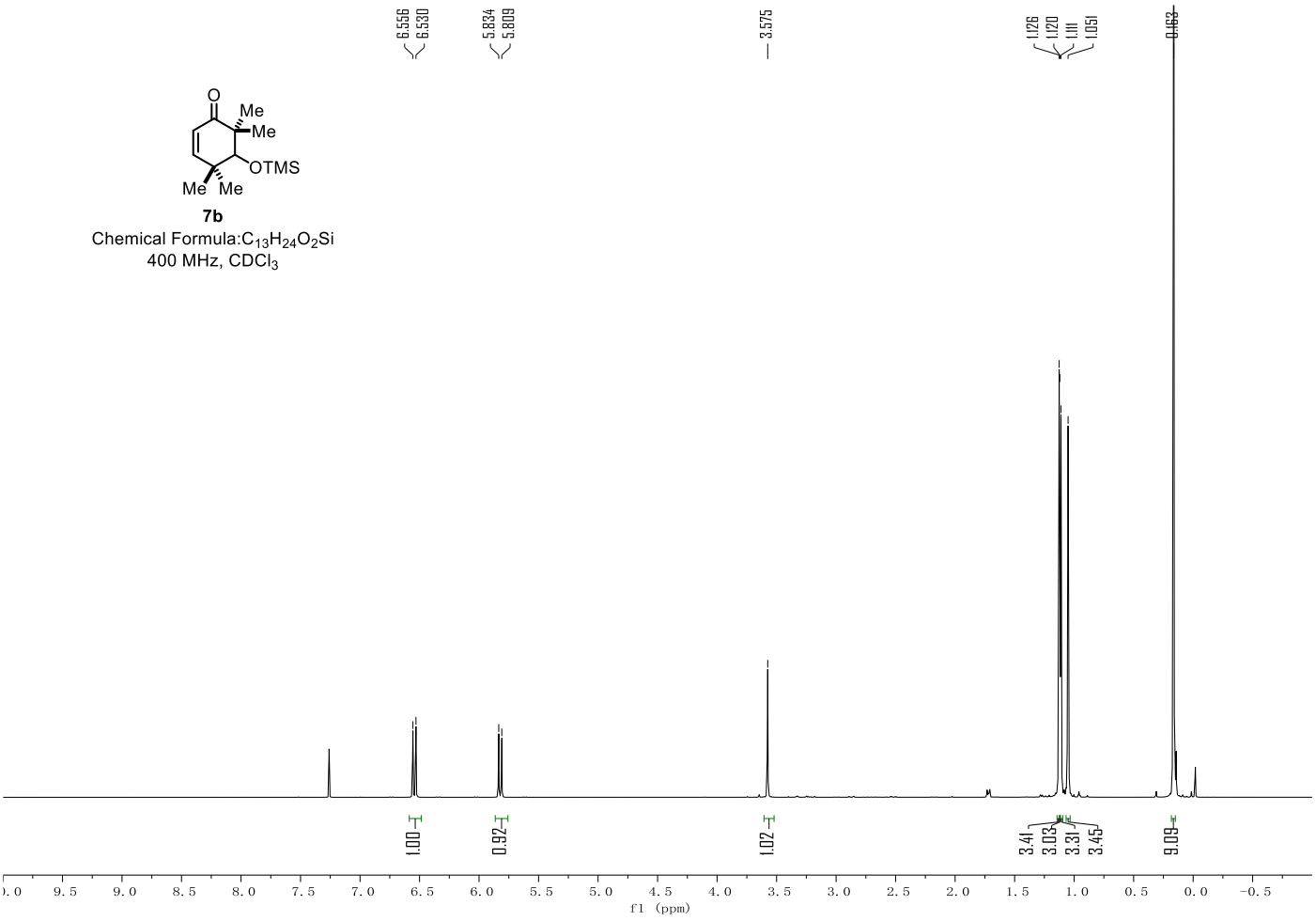
400 MHz, $CDCl_3$



S7

Chemical Formula:$C_{10}H_{16}O_2$

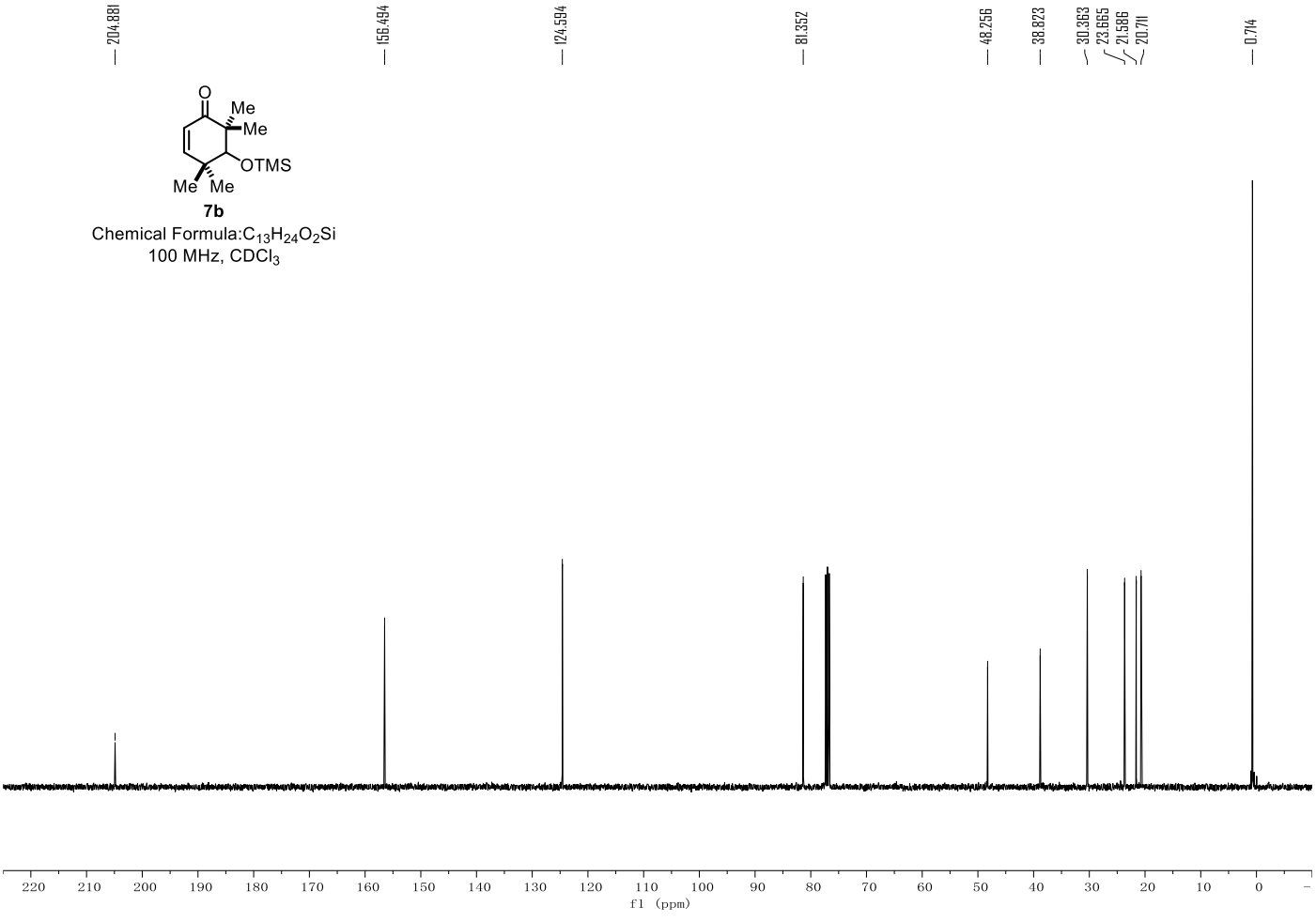
100 MHz, $CDCl_3$



7b

Chemical Formula:$C_{13}H_{24}O_2Si$

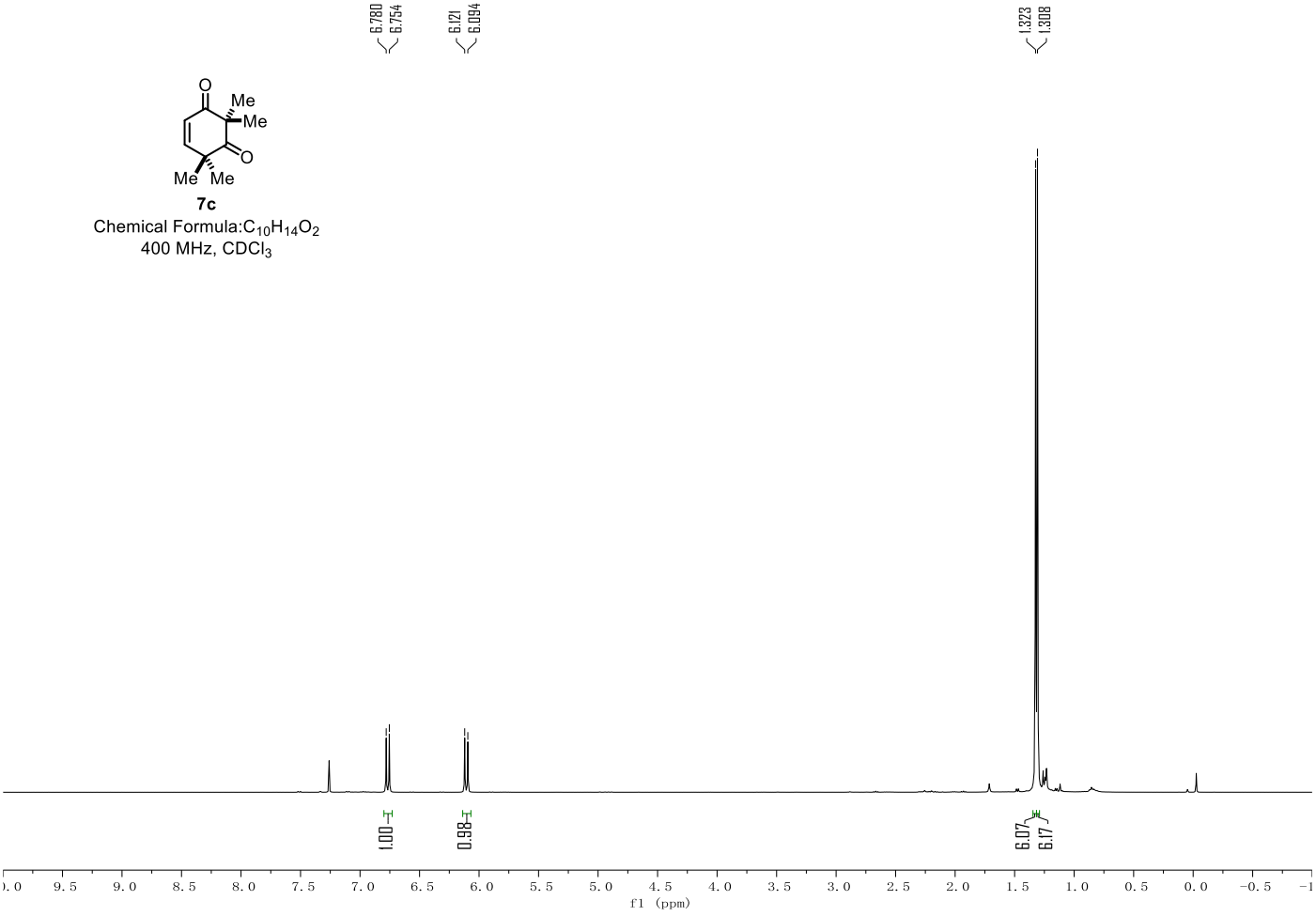
400 MHz, $CDCl_3$

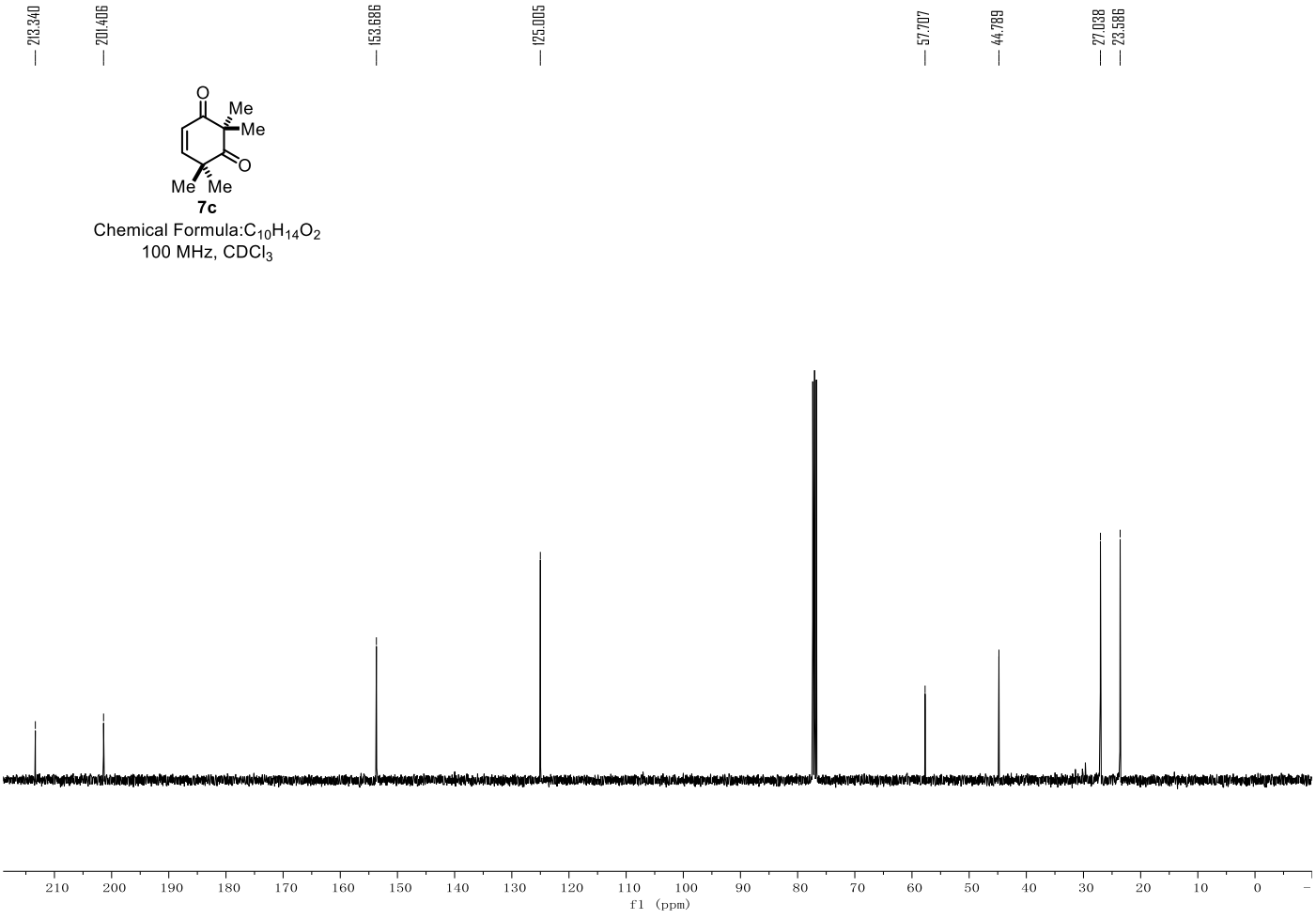


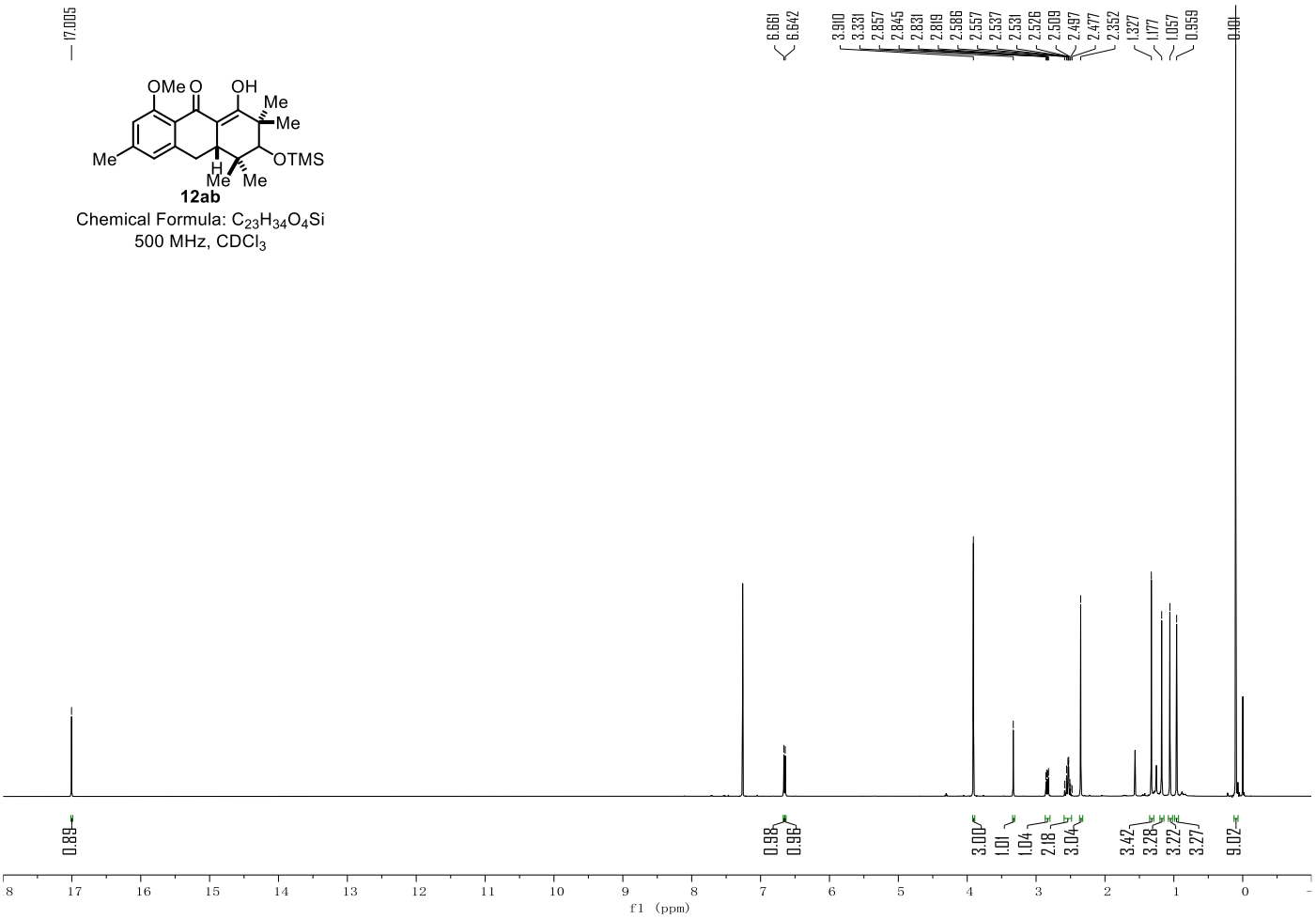
7b

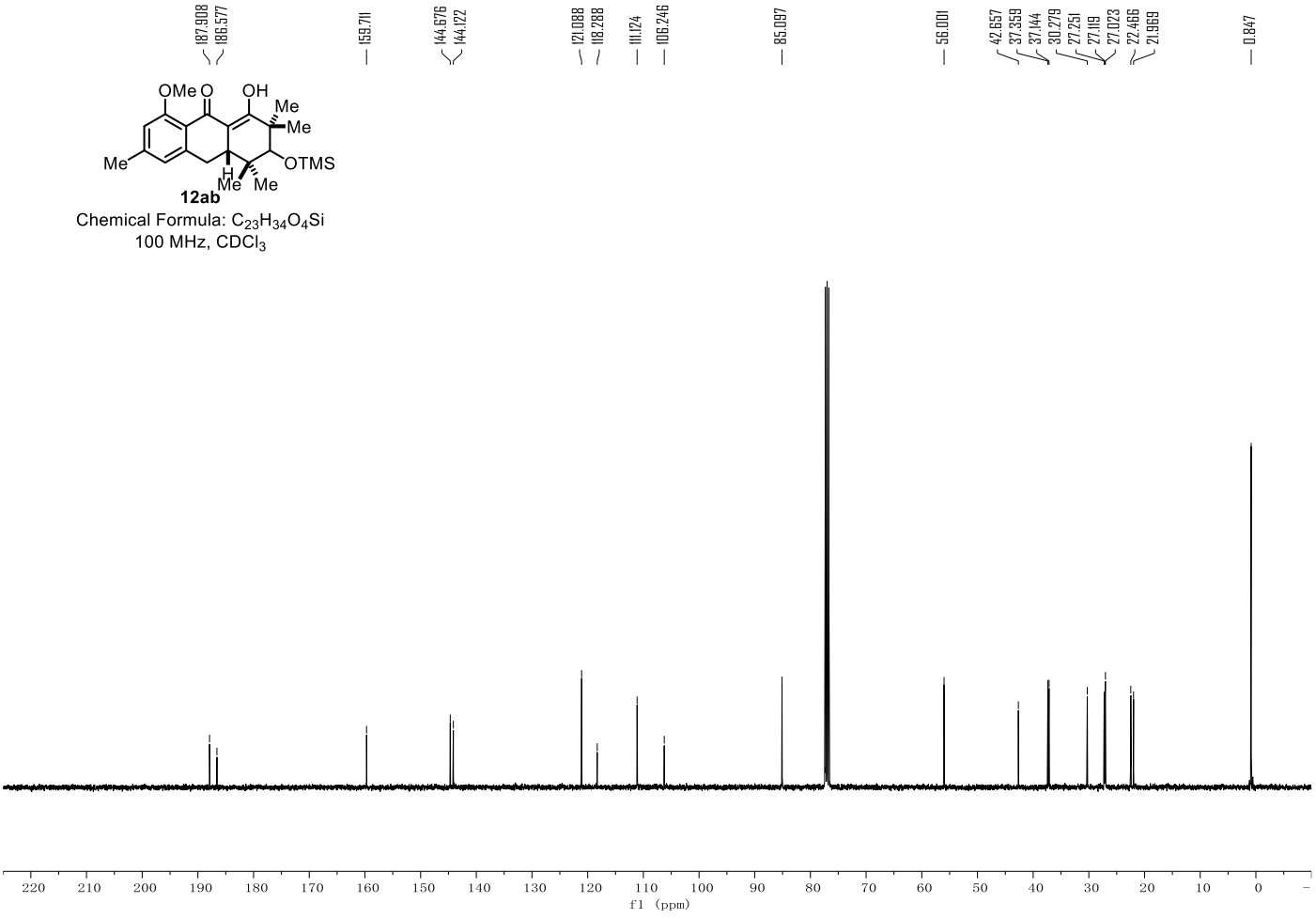
Chemical Formula:$C_{13}H_{24}O_2Si$

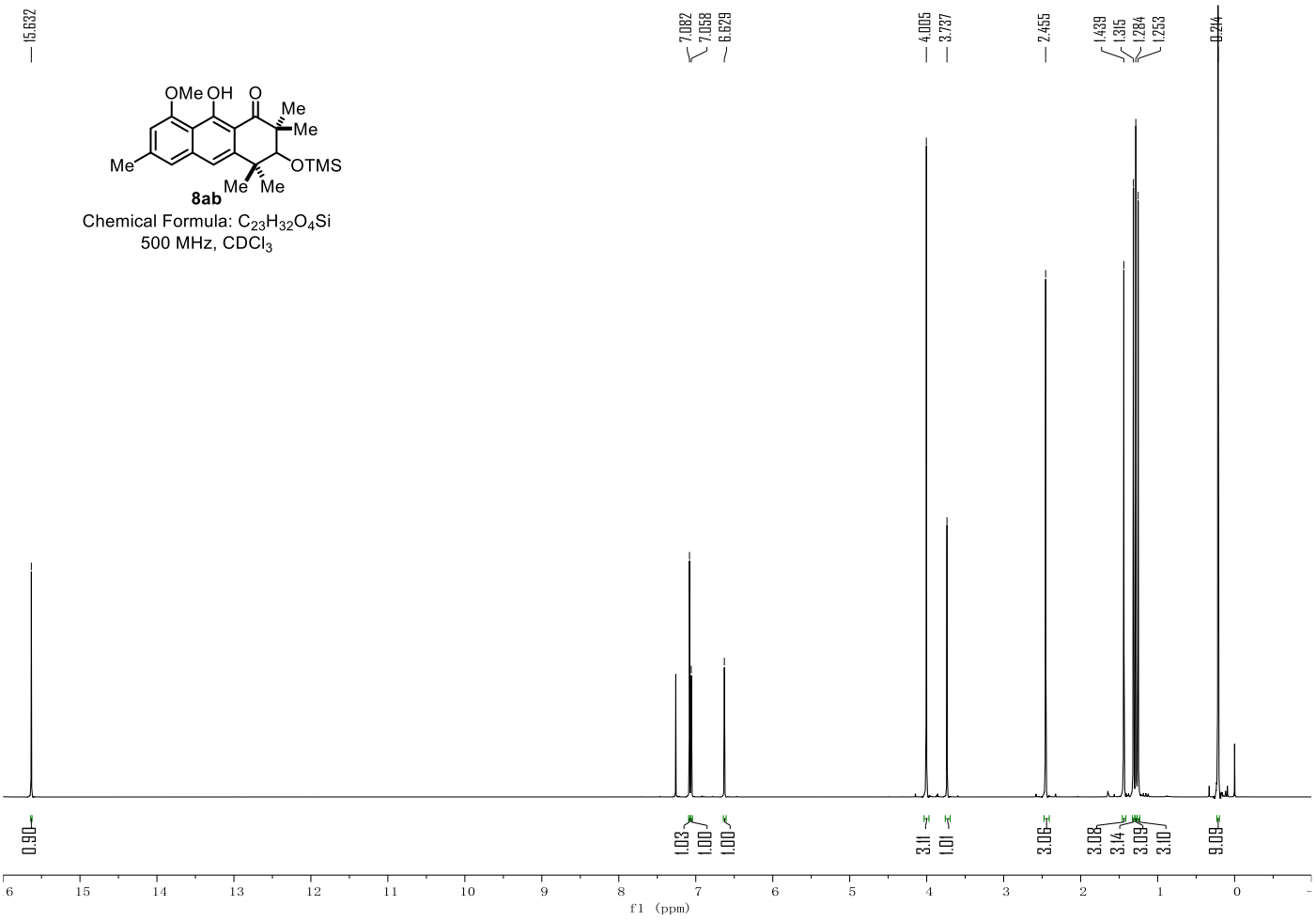
100 MHz, $CDCl_3$

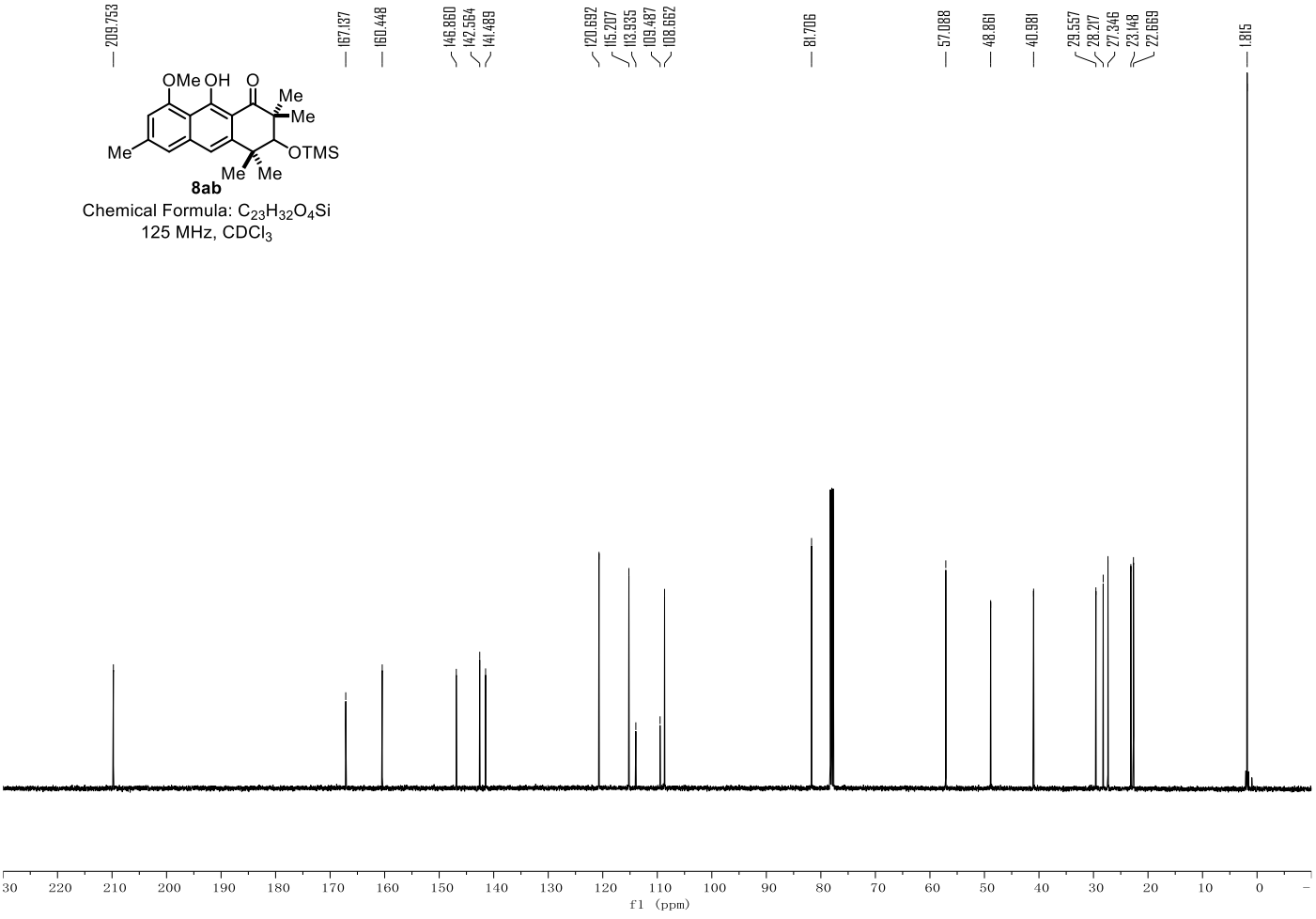

6.780
6.754
6.121
6.094
1.323
1.308
Me
Me
Me
Me
O
O
7c
Chemical Formula:C10H14O2
400 MHz, CDCl3
1.00
0.98
6.07
6.17
f1 (ppm)

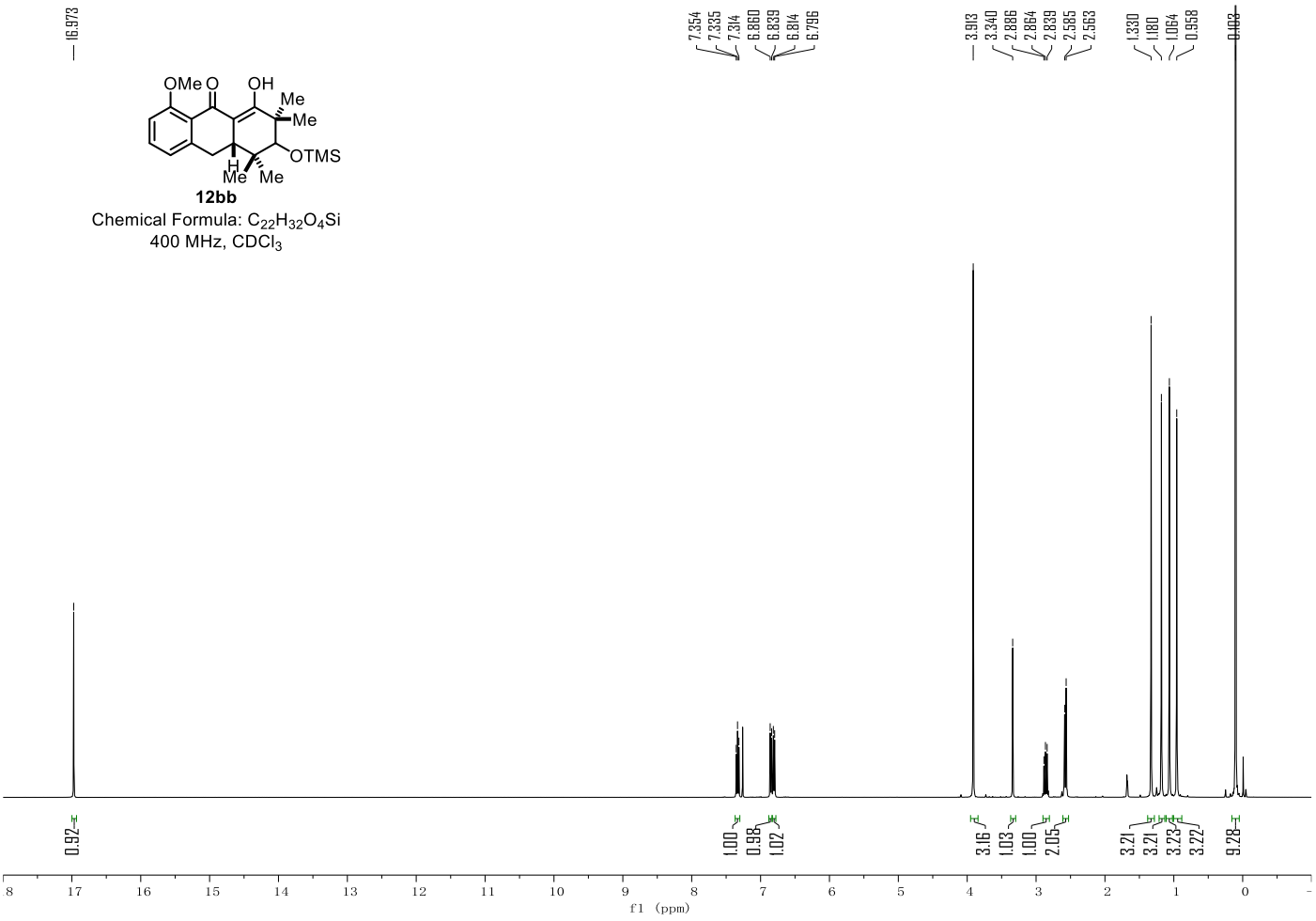

213.340
201.406
153.686
125.005
57.707
44.789
27.038
23.586
Me
Me
Me
Me
O
O
7c
Chemical Formula:C10H14O2
100 MHz, CDCl3
f1 (ppm)


17.005
6.661
6.642
3.910
3.331
2.857
2.845
2.831
2.819
2.586
2.557
2.537
2.531
2.526
2.509
2.497
2.477
2.352
1.327
1.177
1.057
0.959
0.101
OMe
O
OH
Me
Me
Me
OTMS
H
Me
Me
12ab
Chemical Formula: C23H34O4Si
500 MHz, CDCl3
0.89
0.98
0.96
3.00
1.01
1.04
2.18
3.04
3.42
3.28
3.22
3.27
9.02
f1 (ppm)


187.908
186.577
159.711
144.676
144.122
121.088
118.288
111.124
106.246
85.087
56.001
42.657
37.359
37.144
30.279
27.251
27.119
27.023
22.466
21.969
0.847
OMe
O
OH
Me
Me
Me
OTMS
H
Me
Me
12ab
Chemical Formula: C23H34O4Si
100 MHz, CDCl3
f1 (ppm)


15.632
7.082
7.058
6.629
4.005
3.737
2.455
1.439
1.315
1.284
1.253
0.244
OMe OH O
Me
Me
Me
OTMS
Me Me
8ab
Chemical Formula: C23H32O4Si
500 MHz, CDCl3
0.90
1.03
1.00
1.00
3.11
1.01
3.06
3.08
3.14
3.09
3.10
9.09
f1 (ppm)

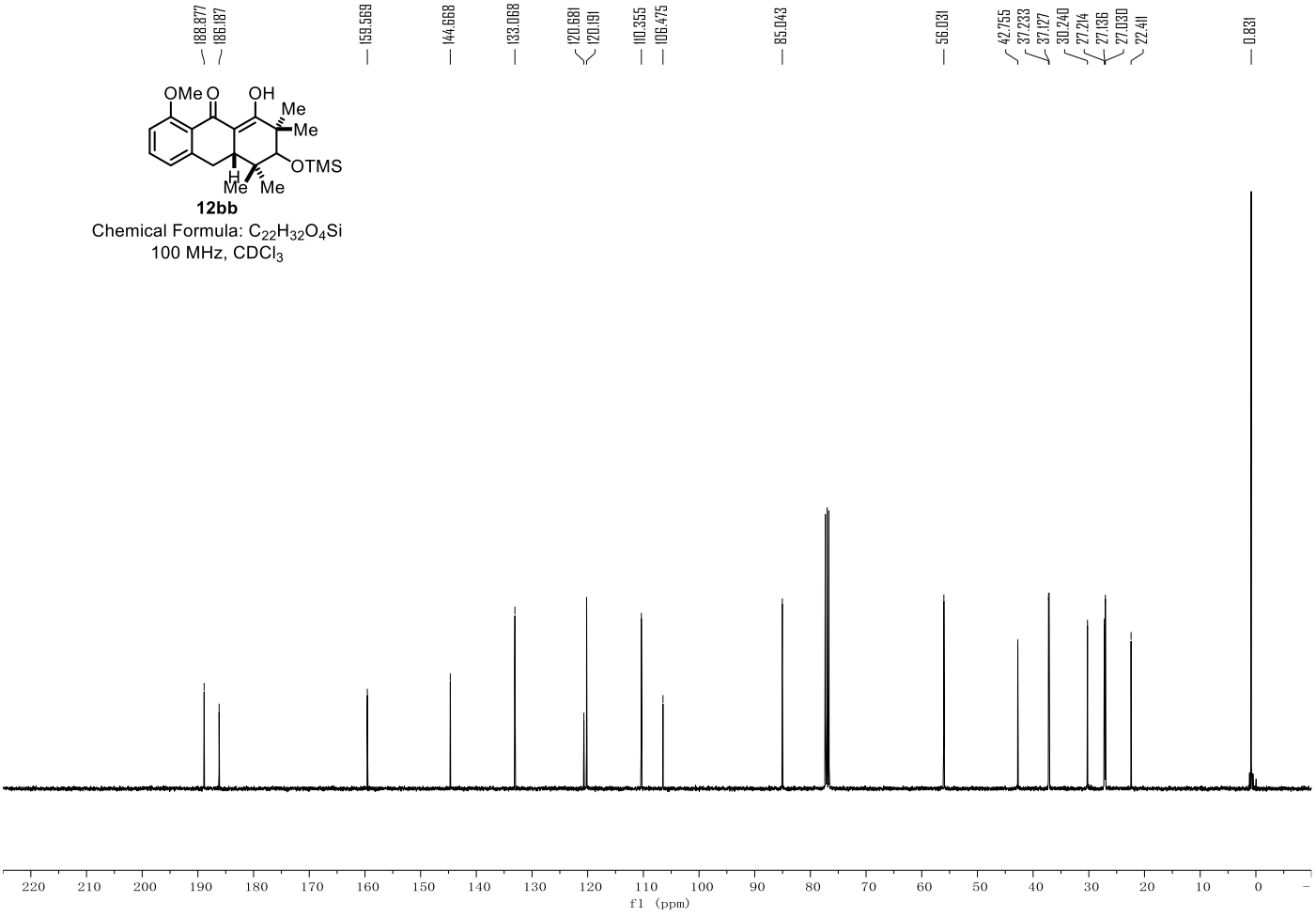

209.753
167.137
160.448
146.860
142.564
141.493
120.692
115.207
113.935
109.487
108.662
81.706
57.088
48.861
40.981
29.557
28.217
27.346
23.148
22.669
1.815
OMe OH O
Me
Me
Me
OTMS
Me Me
8ab
Chemical Formula: C23H32O4Si
125 MHz, CDCl3
f1 (ppm)



12bb

Chemical Formula: $C_{22}H_{32}O_4Si$

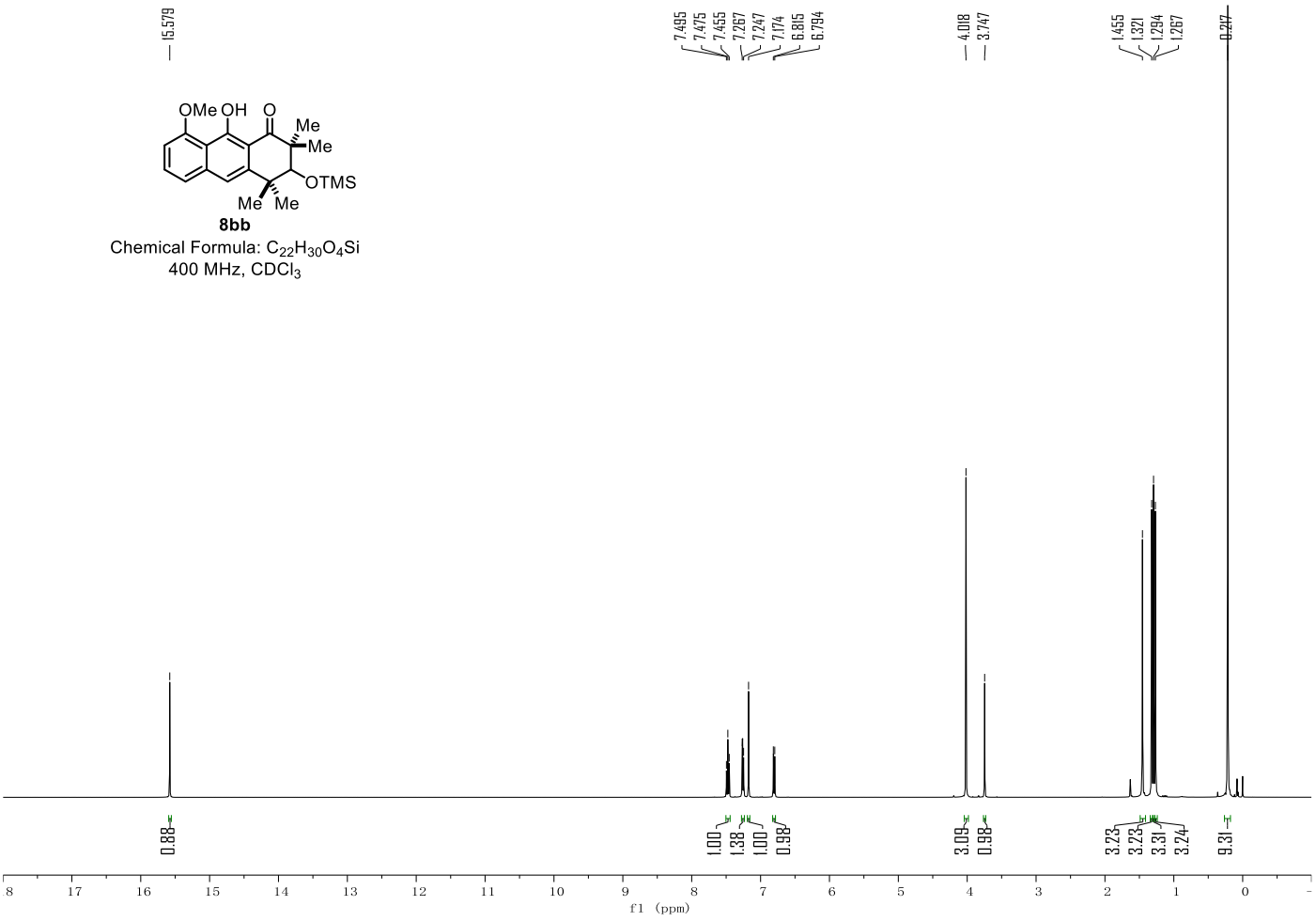
400 MHz, $CDCl_3$



12bb

Chemical Formula: $C_{22}H_{32}O_4Si$

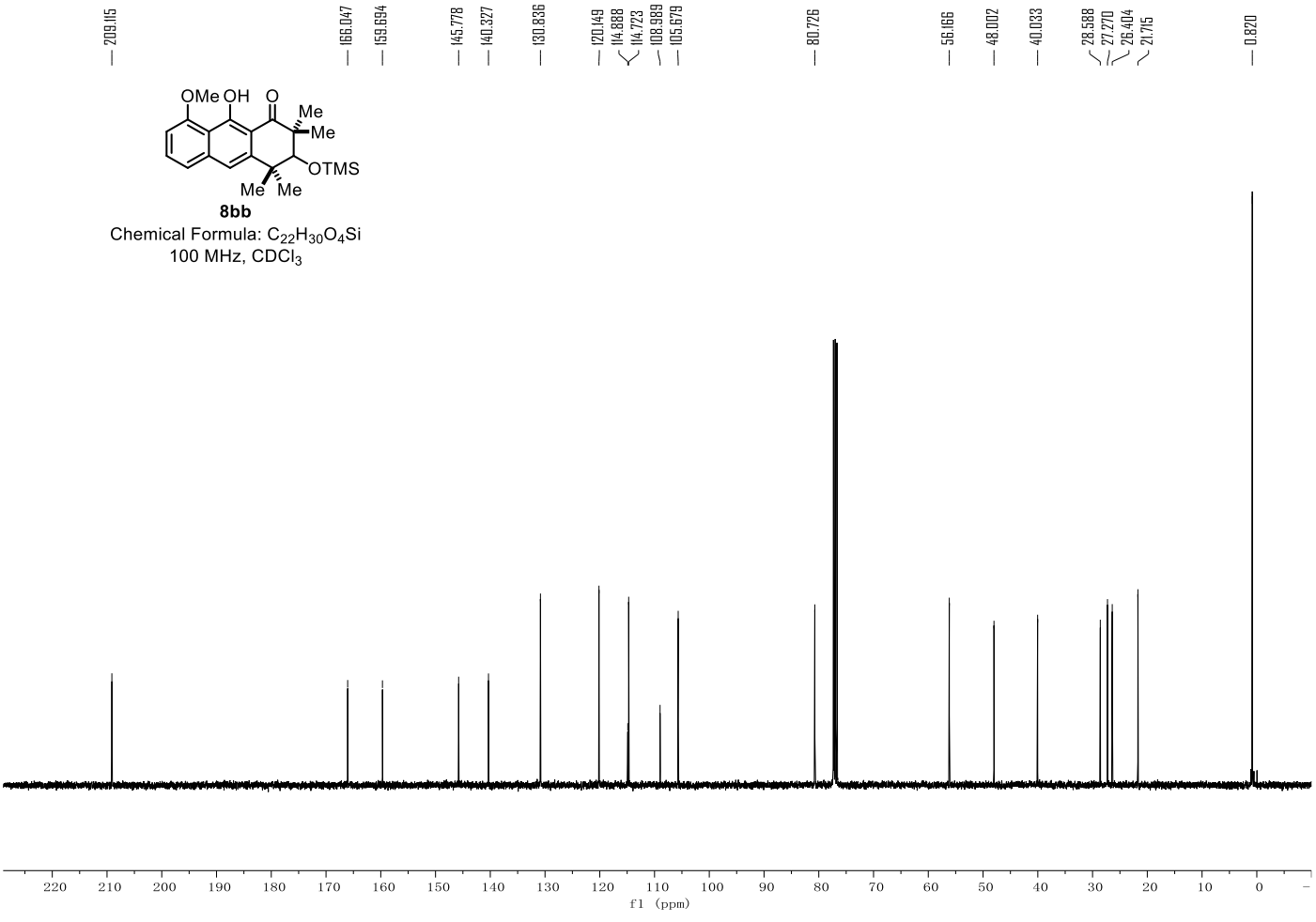
100 MHz, $CDCl_3$



8bb

Chemical Formula: $C_{22}H_{30}O_4Si$

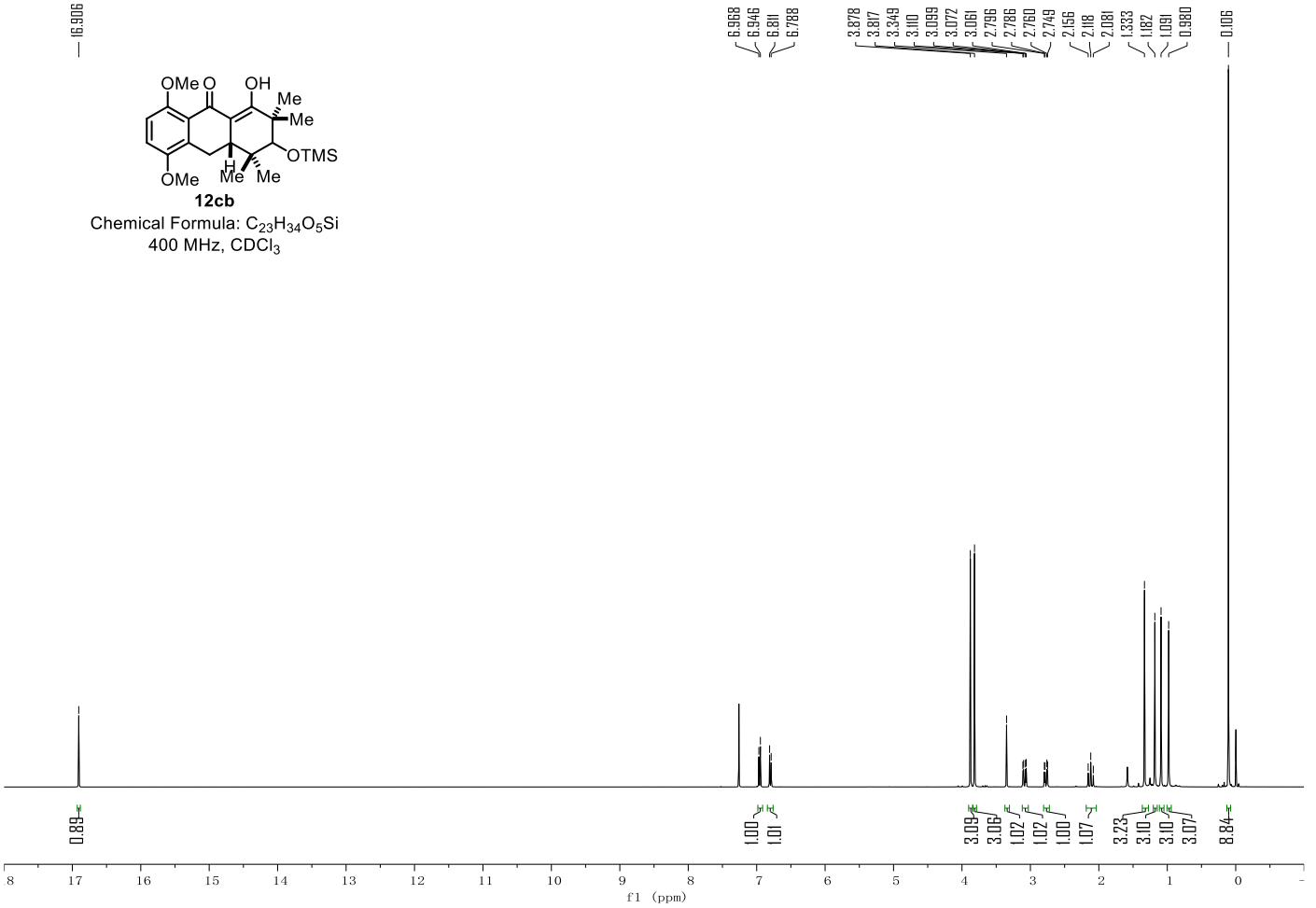
400 MHz, $CDCl_3$

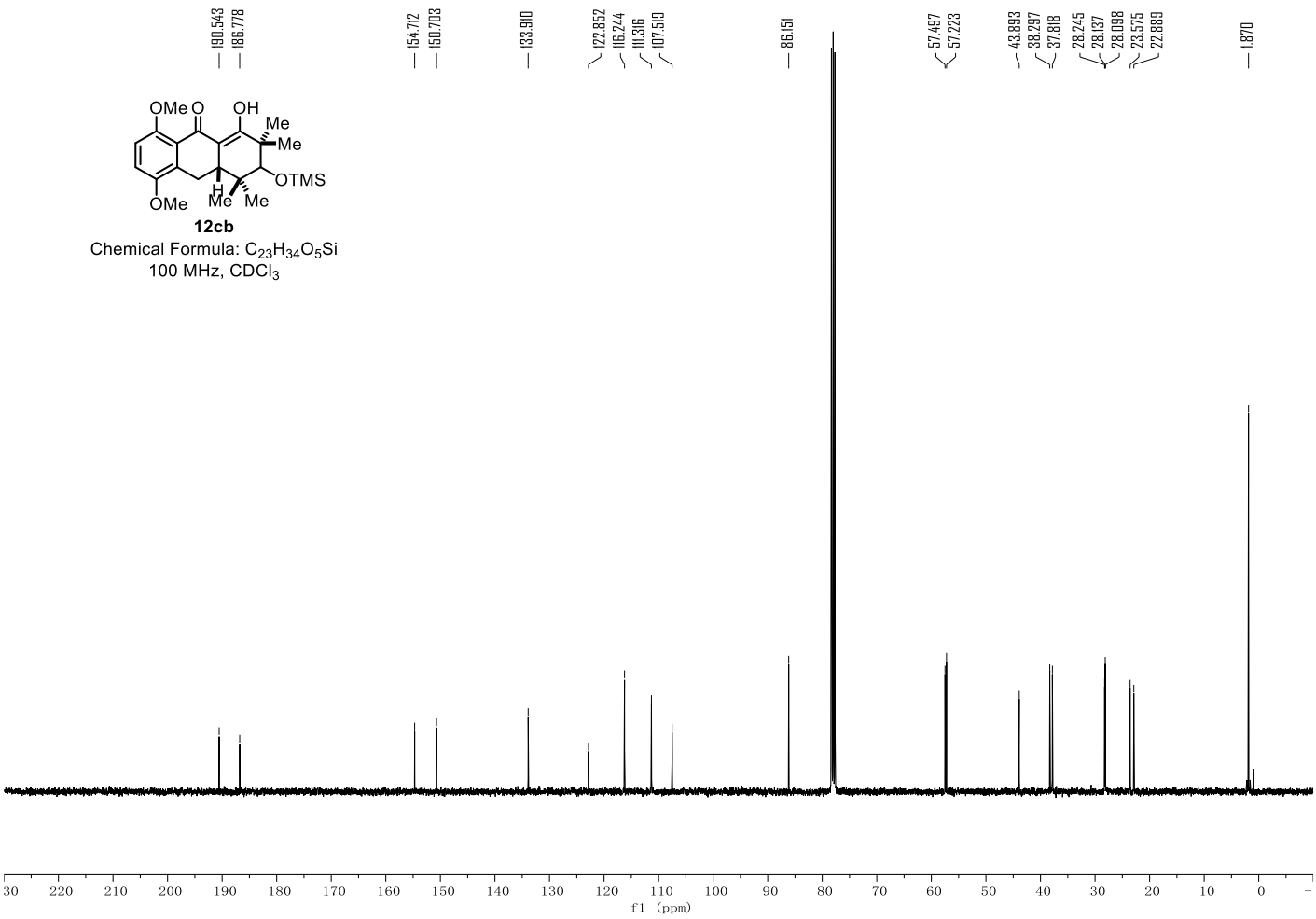


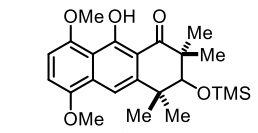
8bb

Chemical Formula: $C_{22}H_{30}O_4Si$

100 MHz, $CDCl_3$


16.906
6.968
6.946
6.811
6.788
3.878
3.817
3.349
3.110
3.099
3.072
3.061
2.796
2.786
2.760
2.749
2.156
2.118
2.081
1.333
1.182
1.091
0.980
0.106
OMe O OH
Me
Me
OTMS
H
Me Me
OMe
12cb
Chemical Formula: C23H34O5Si
400 MHz, CDCl3
0.89
1.00
1.01
3.09
3.06
1.02
1.02
1.00
1.07
3.23
3.10
3.10
3.07
8.84
f1 (ppm)

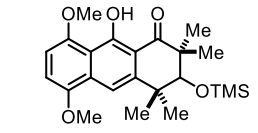

190.543
186.778
154.712
150.703
133.910
127.852
116.744
111.316
107.519
86.151
57.497
57.223
43.893
38.297
37.818
28.245
28.137
28.098
23.575
22.889
1.870
OMe O OH
Me
Me
OTMS
H
Me Me
OMe
12cb
Chemical Formula: C23H34O5Si
100 MHz, CDCl3
f1 (ppm)



8cb

Chemical Formula: $C_{23}H_{32}O_5Si$

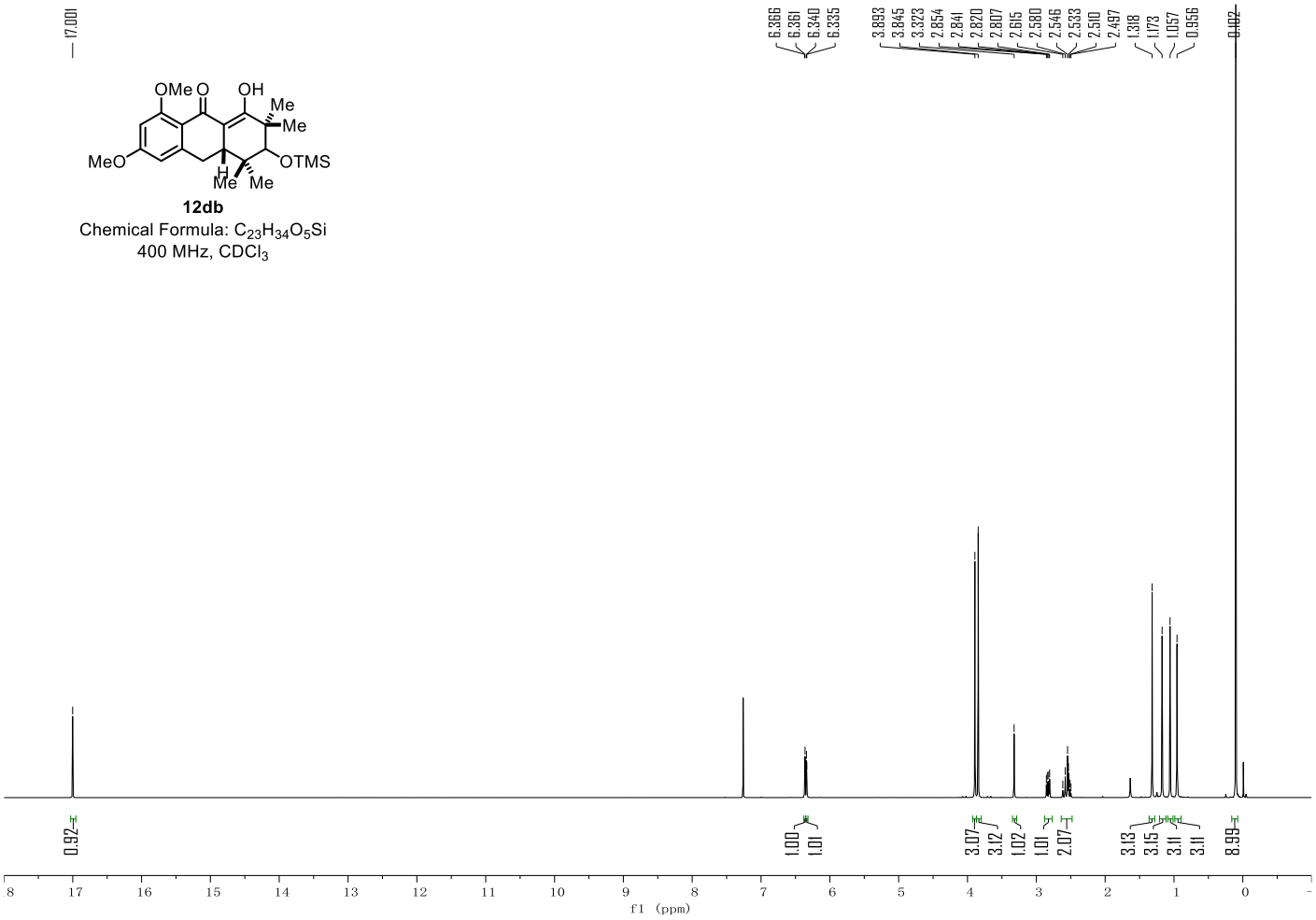
400 MHz, $CDCl_3$



8cb

Chemical Formula: $C_{23}H_{32}O_5Si$

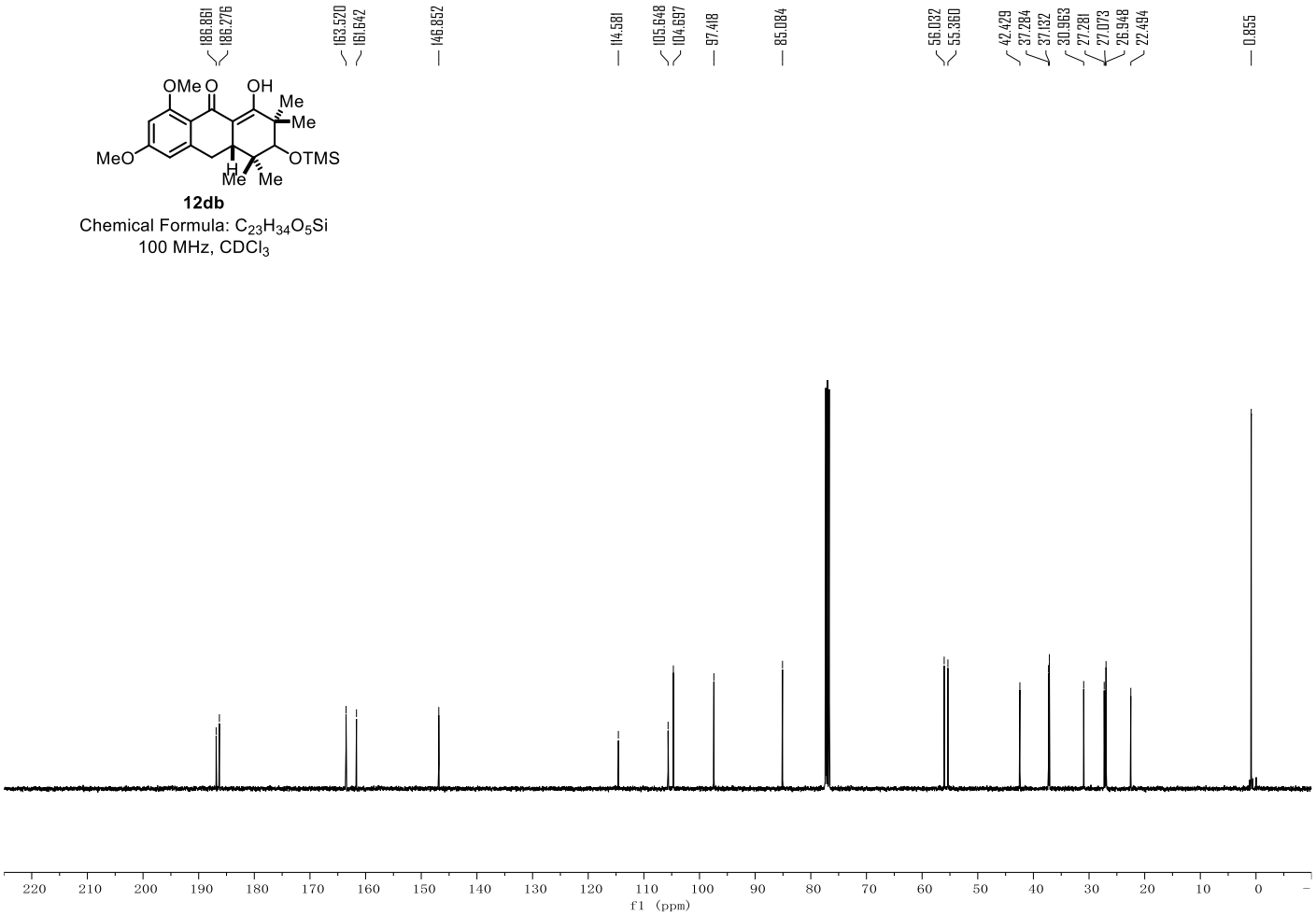
100 MHz, $CDCl_3$



12db

Chemical Formula: $C_{23}H_{34}O_5Si$

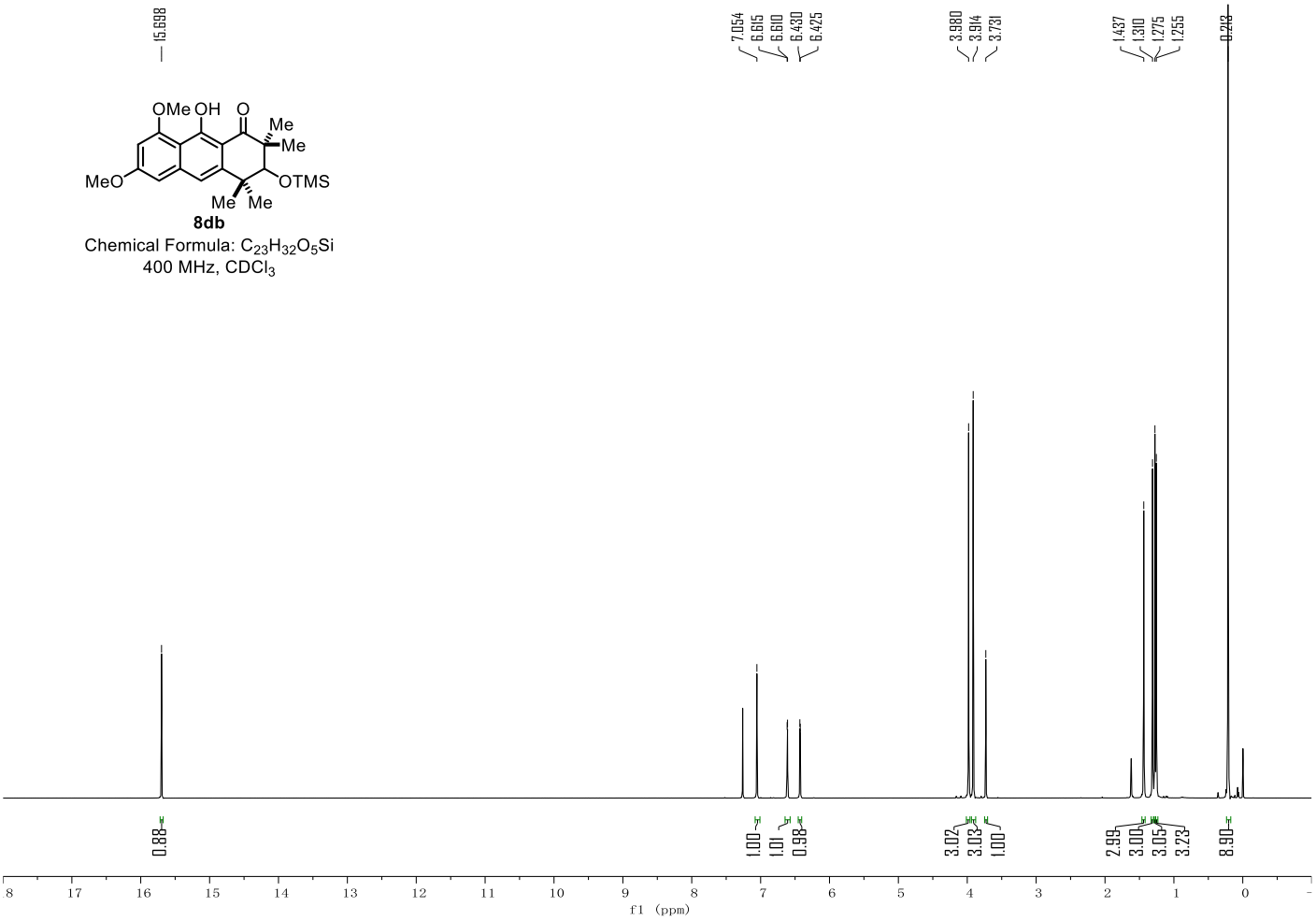
400 MHz, $CDCl_3$



12db

Chemical Formula: $C_{23}H_{34}O_5Si$

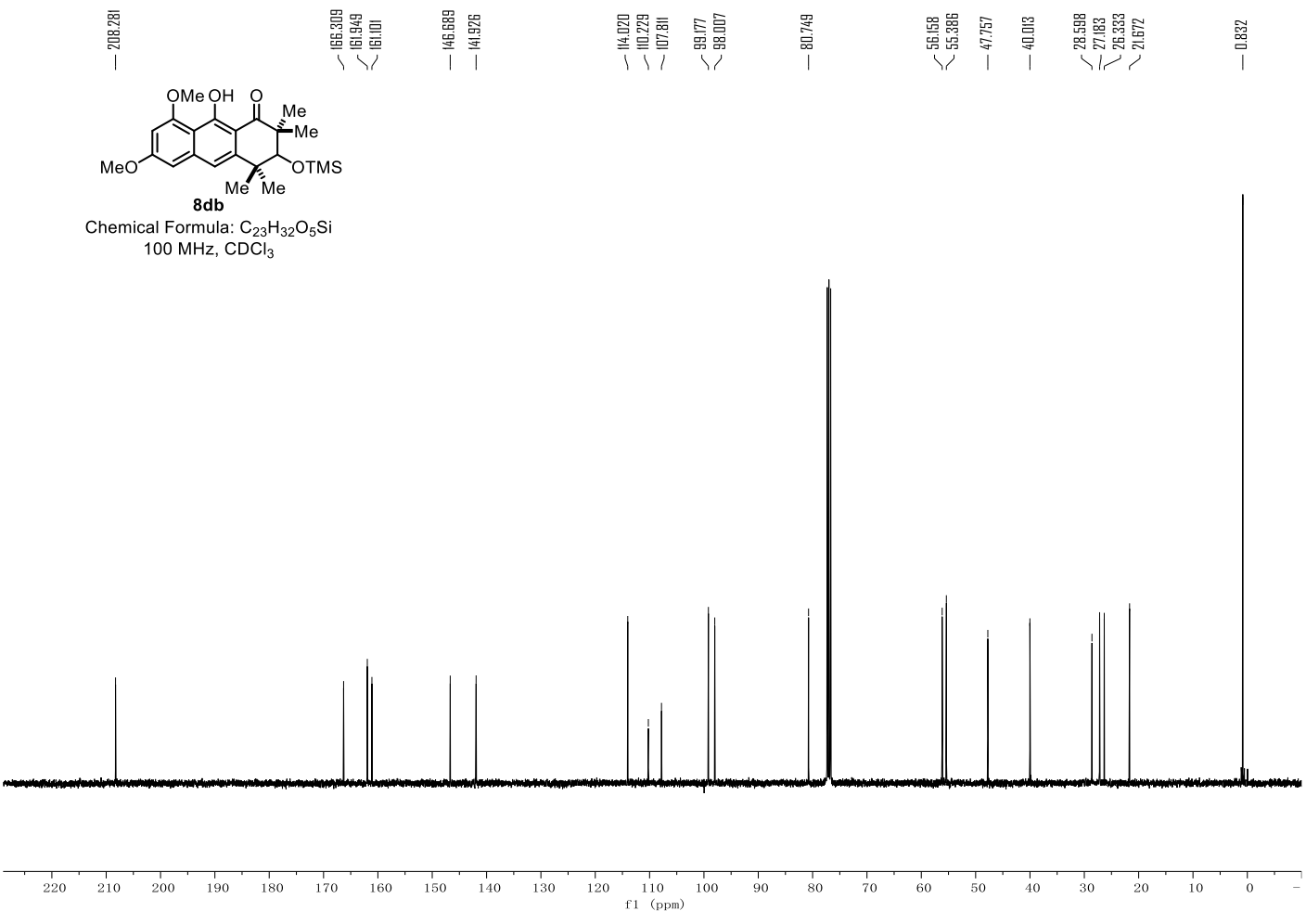
100 MHz, $CDCl_3$



8db

Chemical Formula: $C_{23}H_{32}O_5Si$

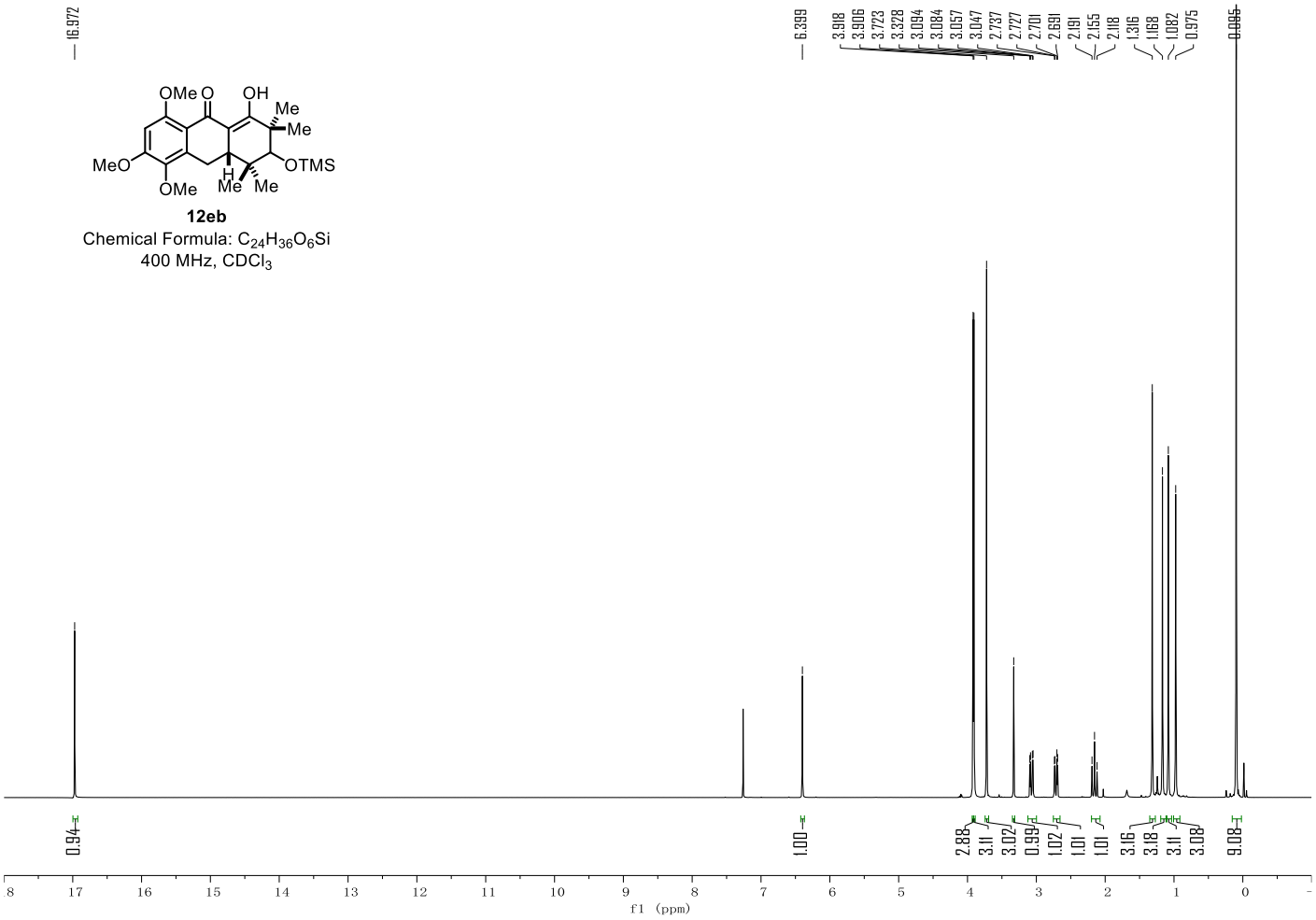
400 MHz, $CDCl_3$

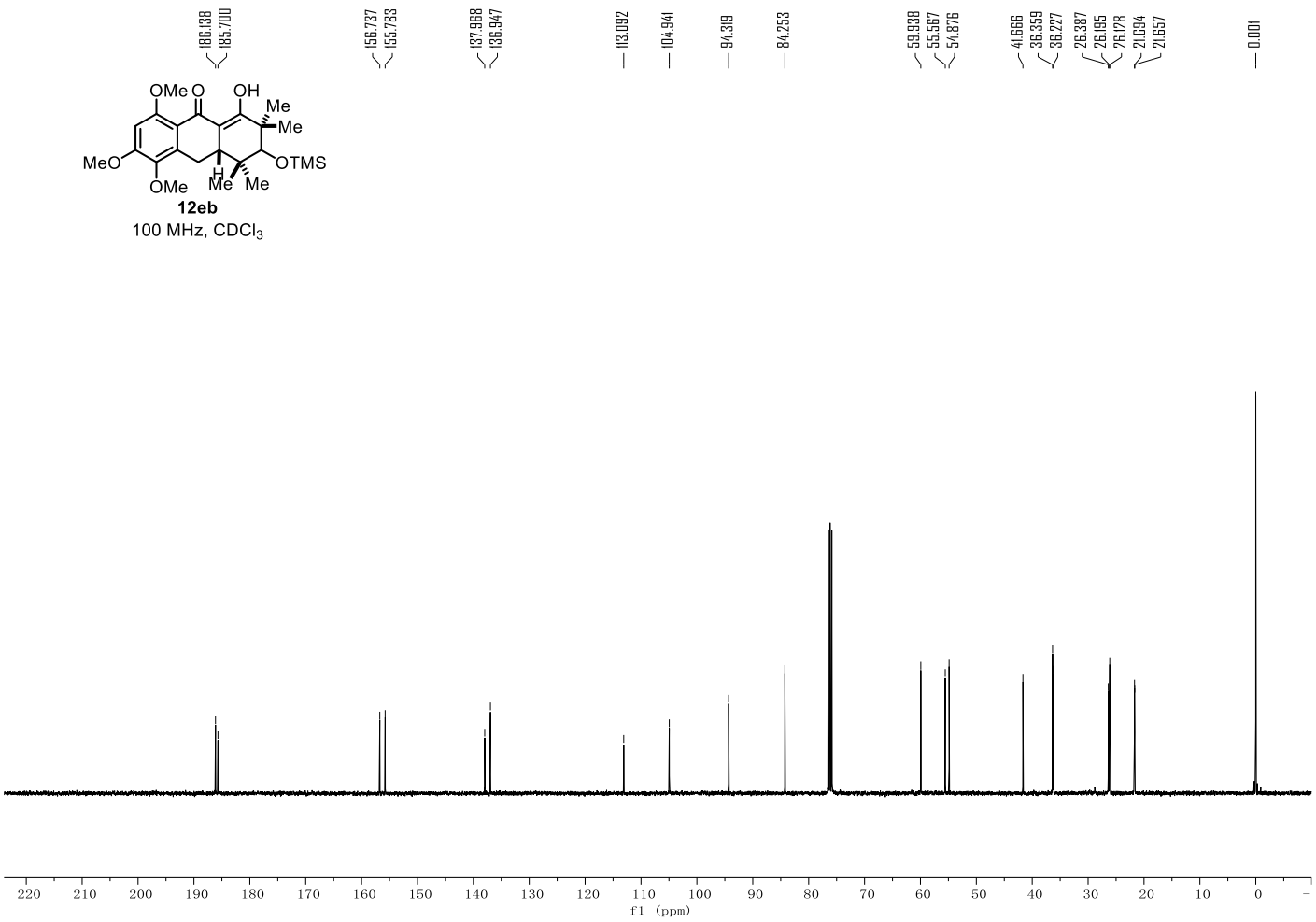


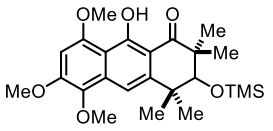
8db

Chemical Formula: $C_{23}H_{32}O_5Si$

100 MHz, $CDCl_3$


16.972
6.399
3.918
3.906
3.723
3.328
3.094
3.084
3.057
3.047
2.737
2.727
2.701
2.691
2.191
2.155
2.118
1.316
1.168
1.082
0.975
0.995
OMe O OH
Me
Me
MeO
OTMS
H
Me Me
OMe
12eb
Chemical Formula: C24H36O6Si
400 MHz, CDCl3
0.94
1.00
2.88
3.11
3.02
0.99
1.02
1.01
1.01
3.16
3.18
3.11
3.08
9.08
f1 (ppm)

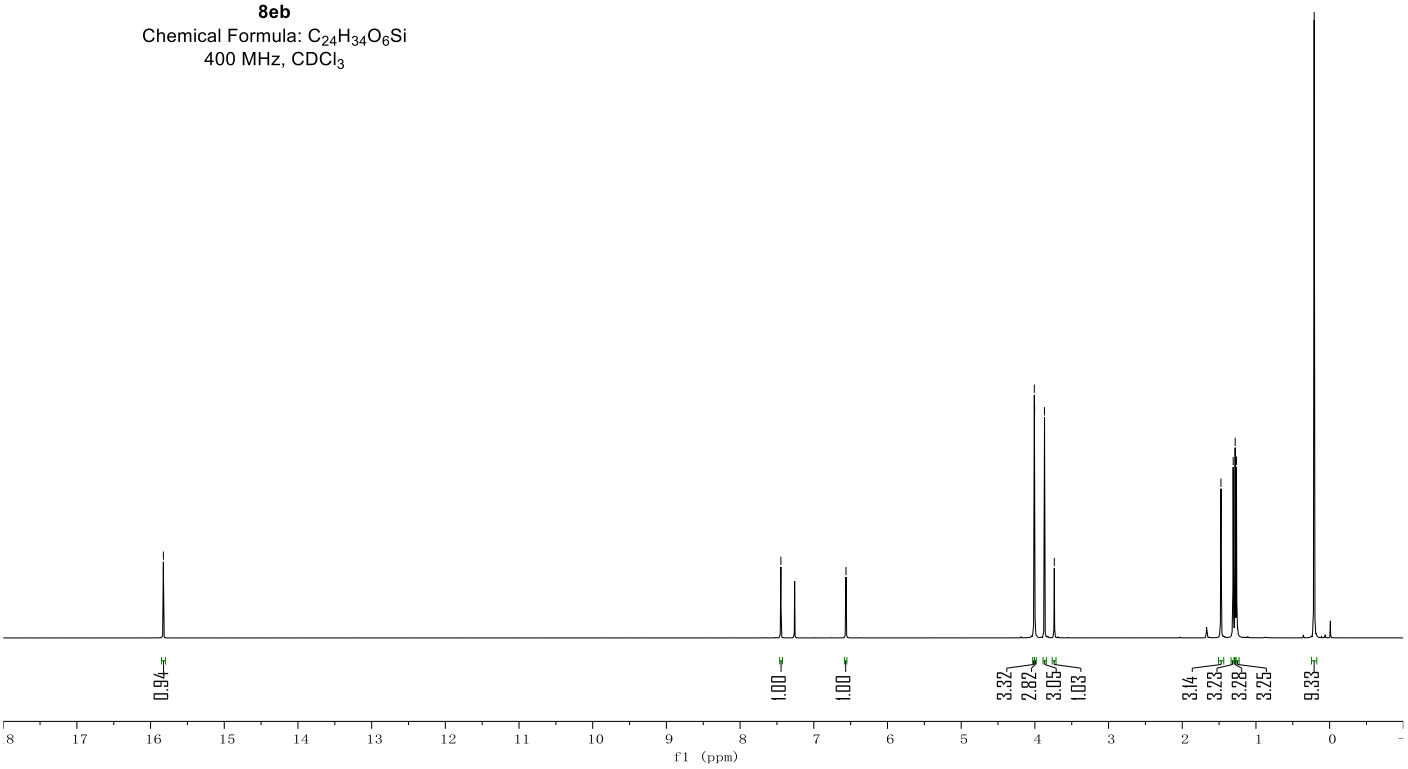

186.138
185.700
156.737
155.783
137.968
136.947
113.092
104.941
94.319
84.253
59.938
55.567
54.876
41.666
36.359
36.227
26.387
26.195
26.128
21.694
21.657
0.001
OMe O OH
Me
Me
MeO
OTMS
H
Me Me
OMe
12eb
100 MHz, CDCl3
f1 (ppm)

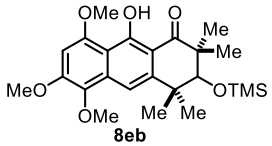


8eb

Chemical Formula: $C_{24}H_{34}O_6Si$

400 MHz, $CDCl_3$

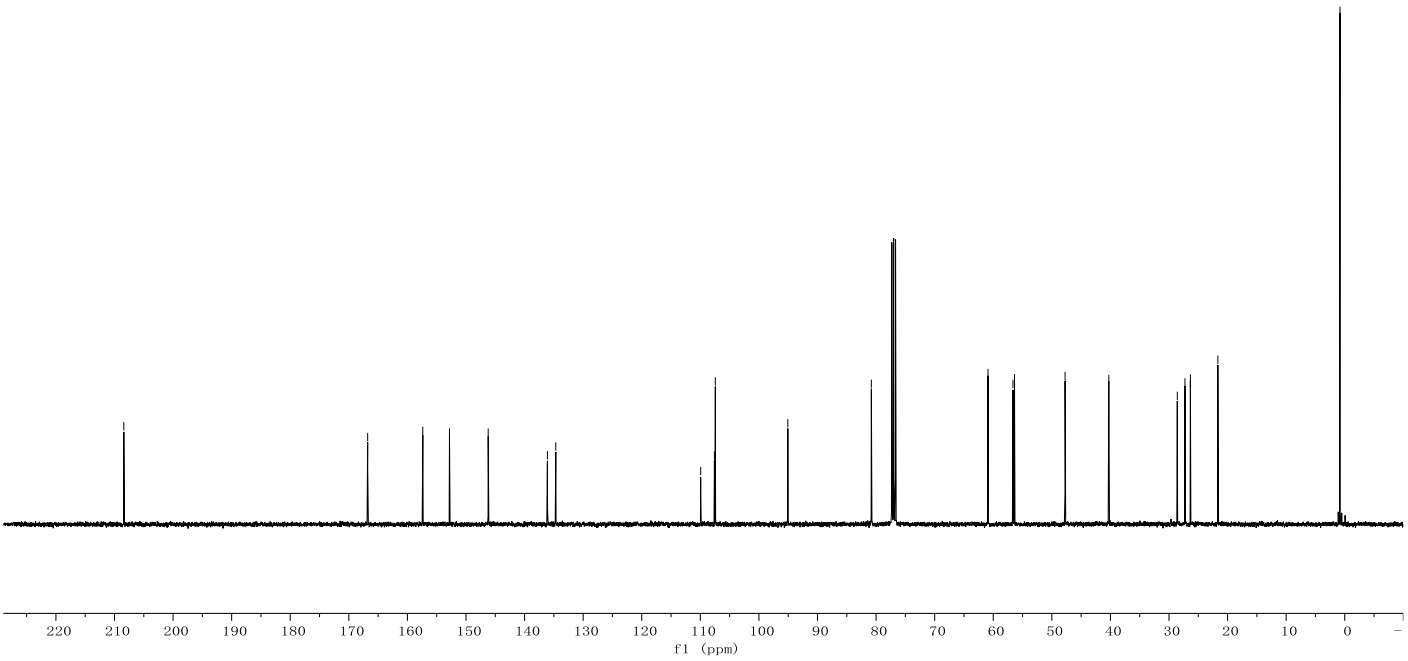


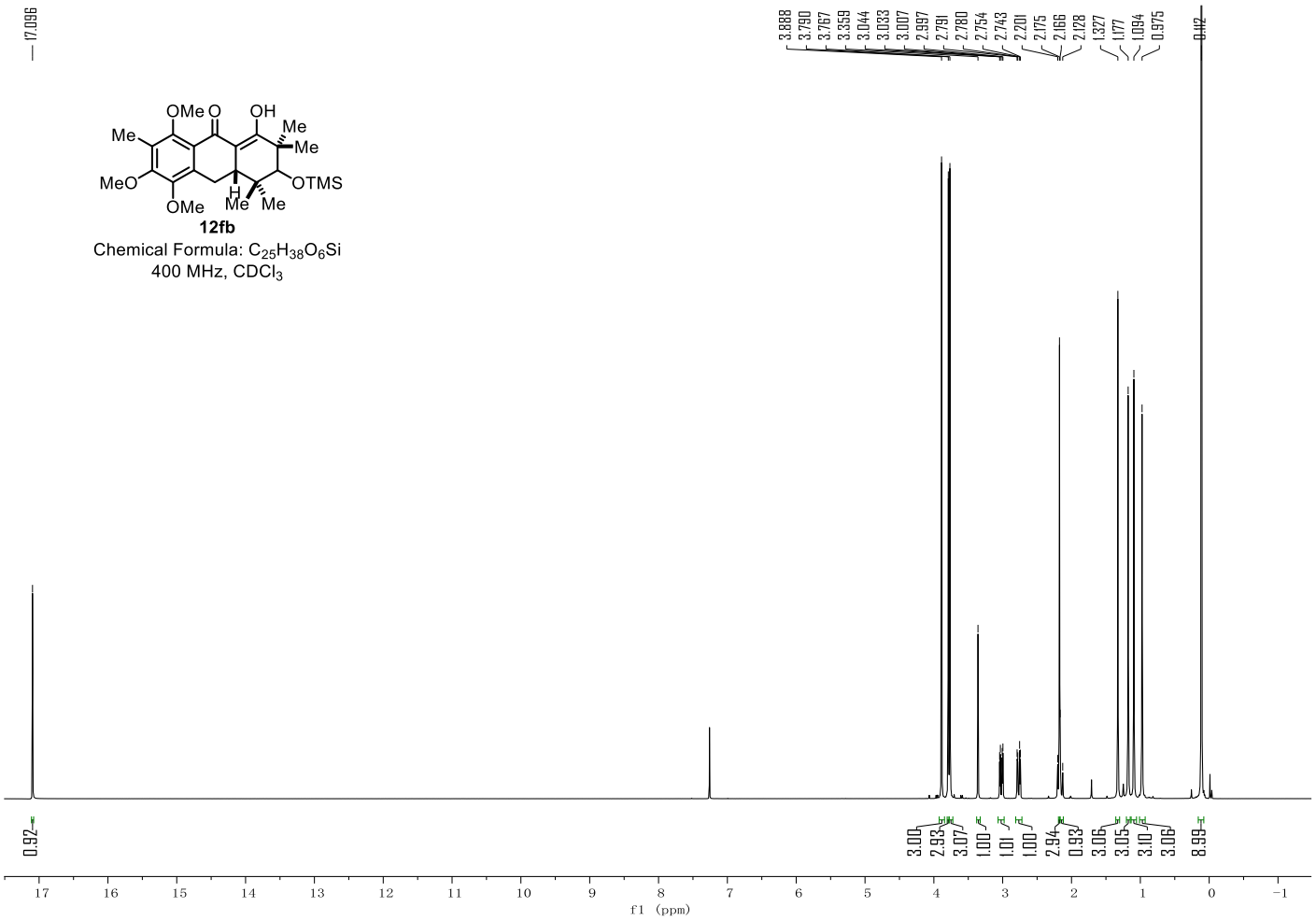


8eb

Chemical Formula: $C_{24}H_{34}O_6Si$

100 MHz, $CDCl_3$

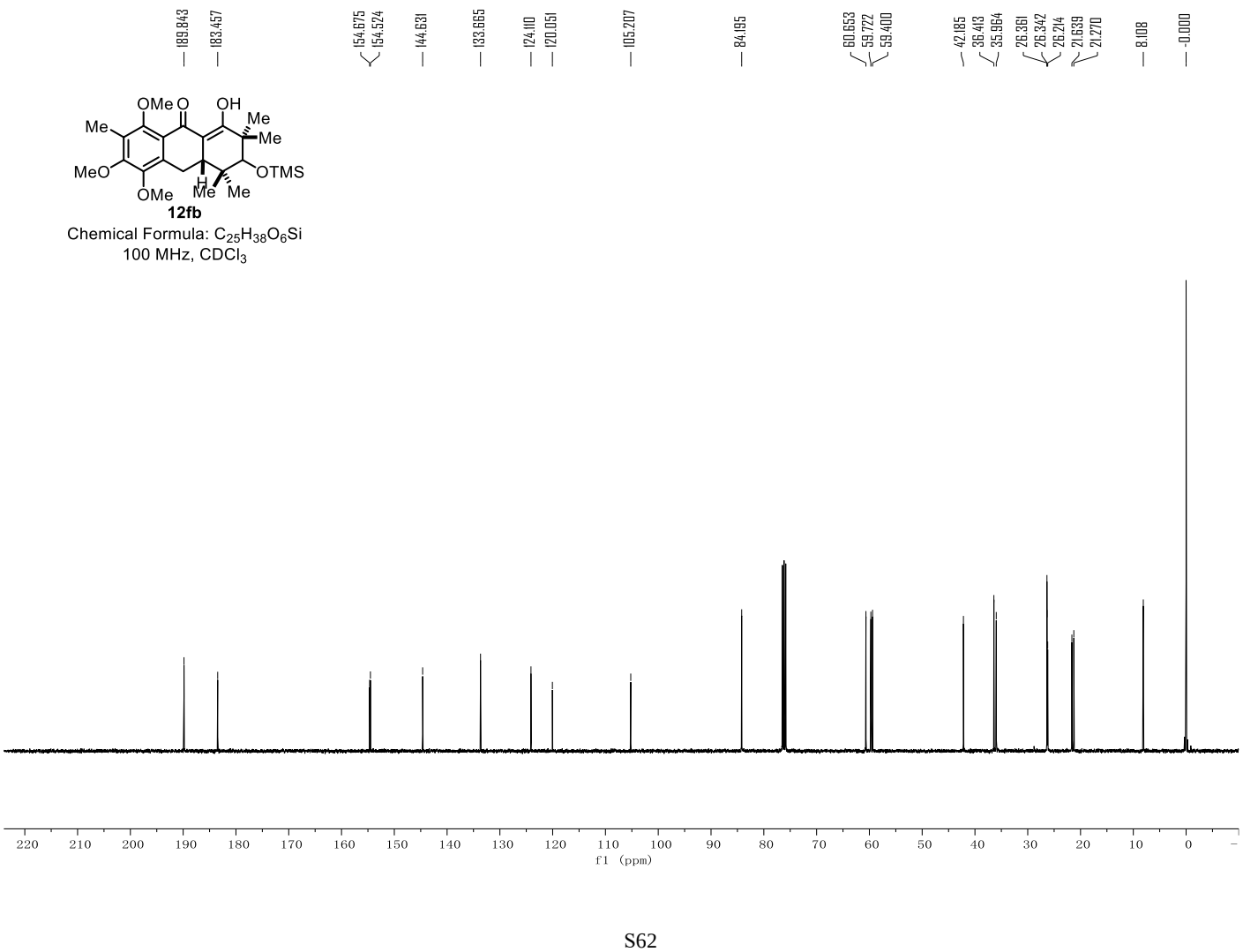




12fb

Chemical Formula: $C_{25}H_{38}O_6Si$

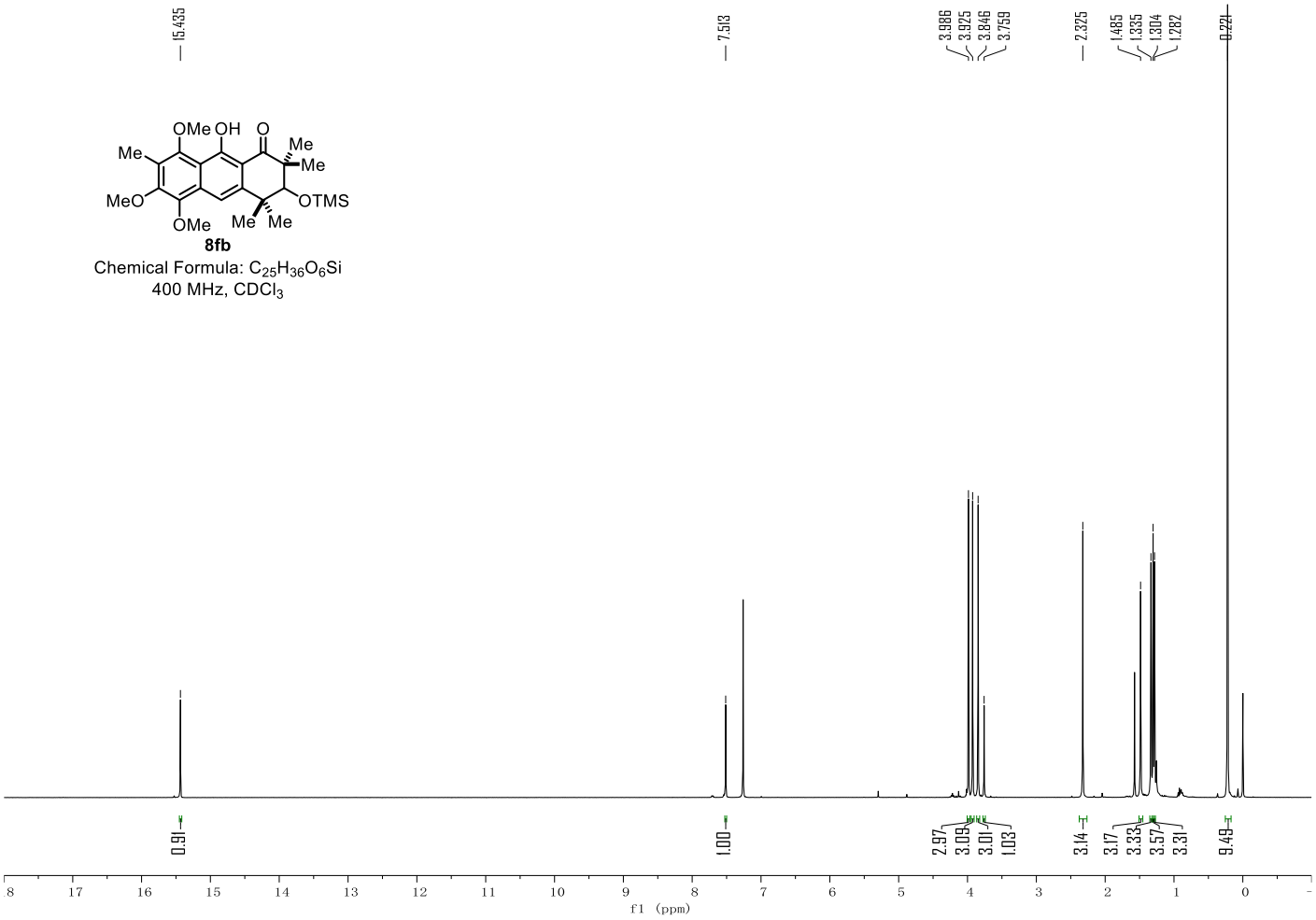
400 MHz, $CDCl_3$

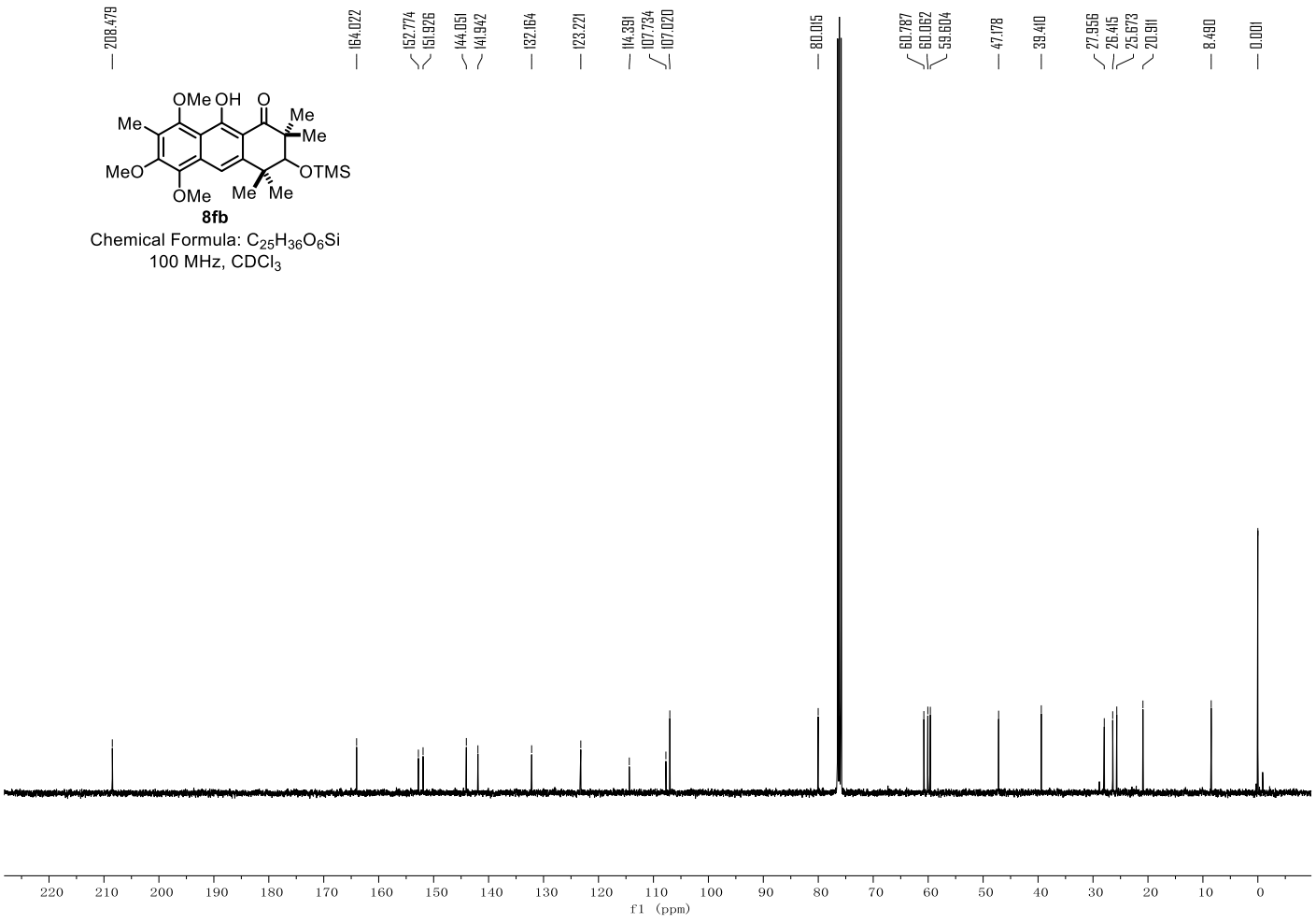


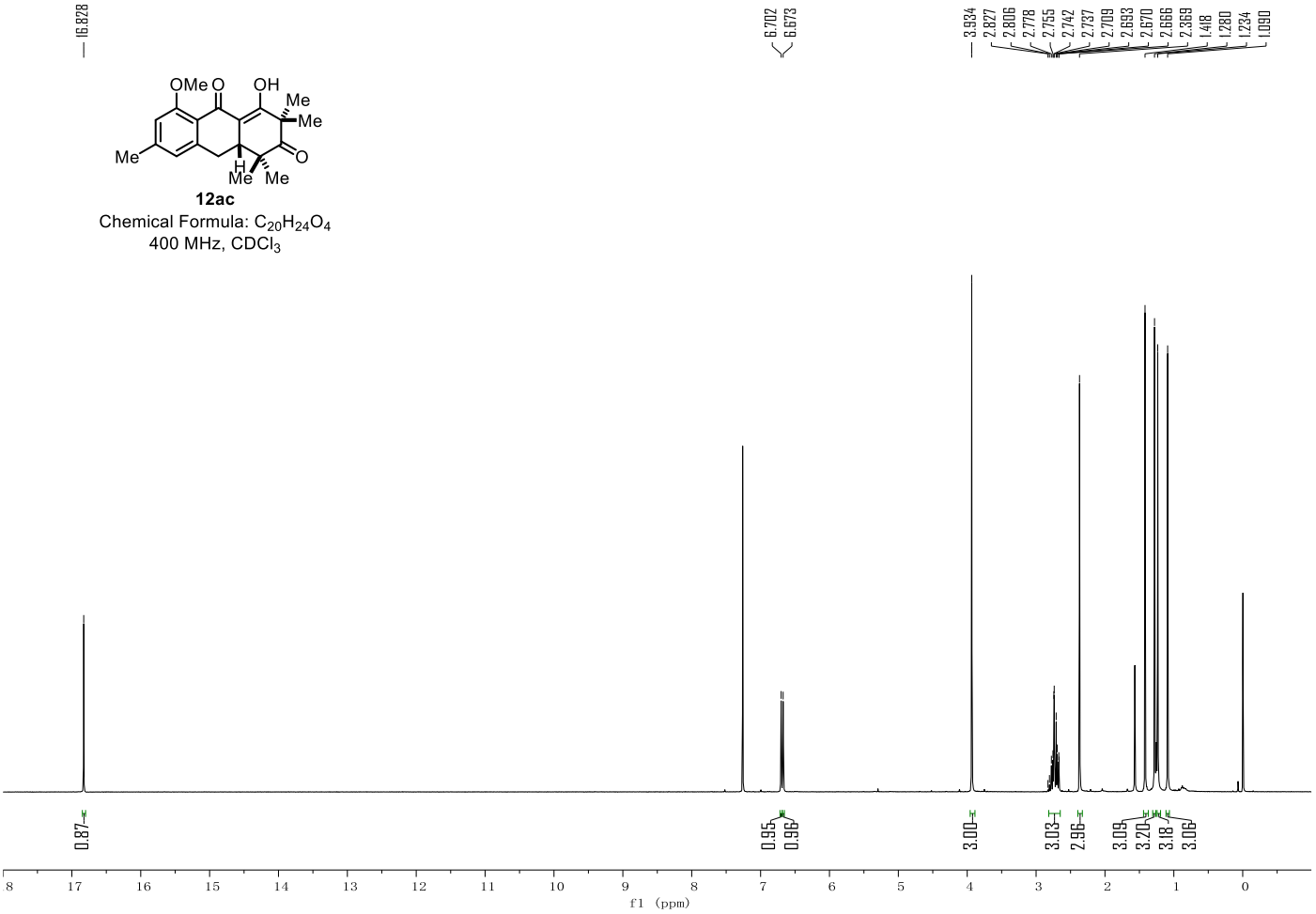
12fb

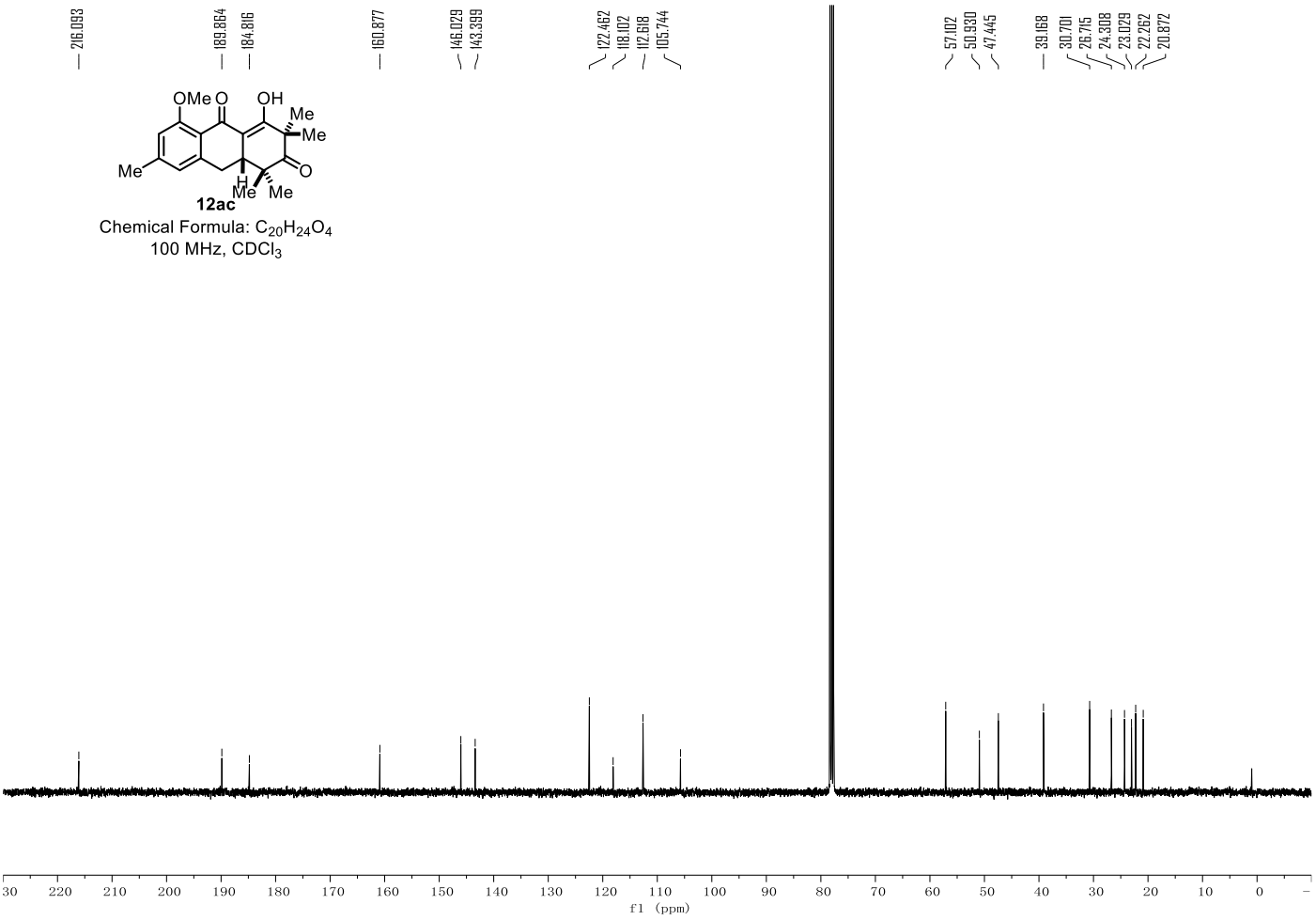
Chemical Formula: $C_{25}H_{38}O_6Si$

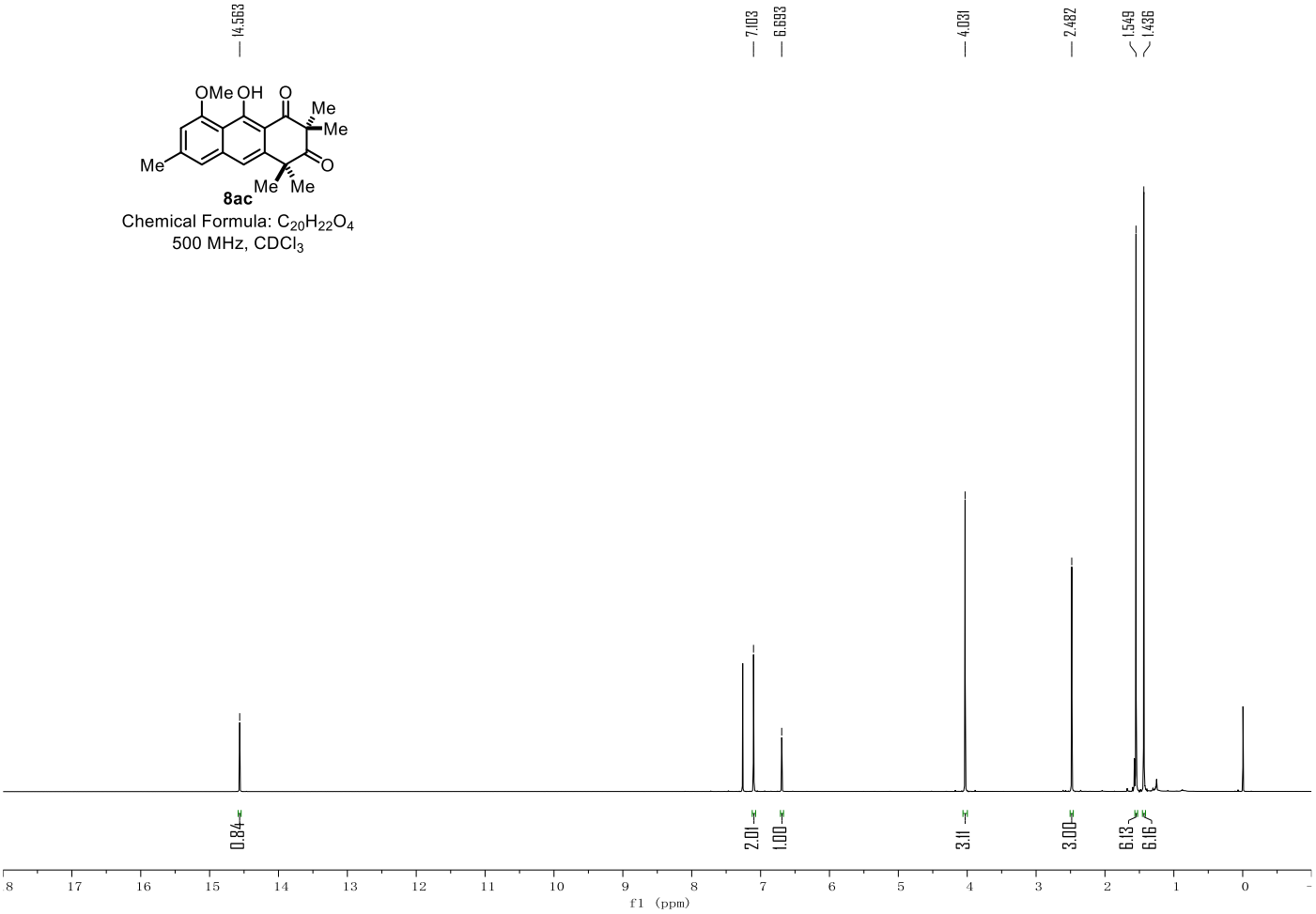
100 MHz, $CDCl_3$

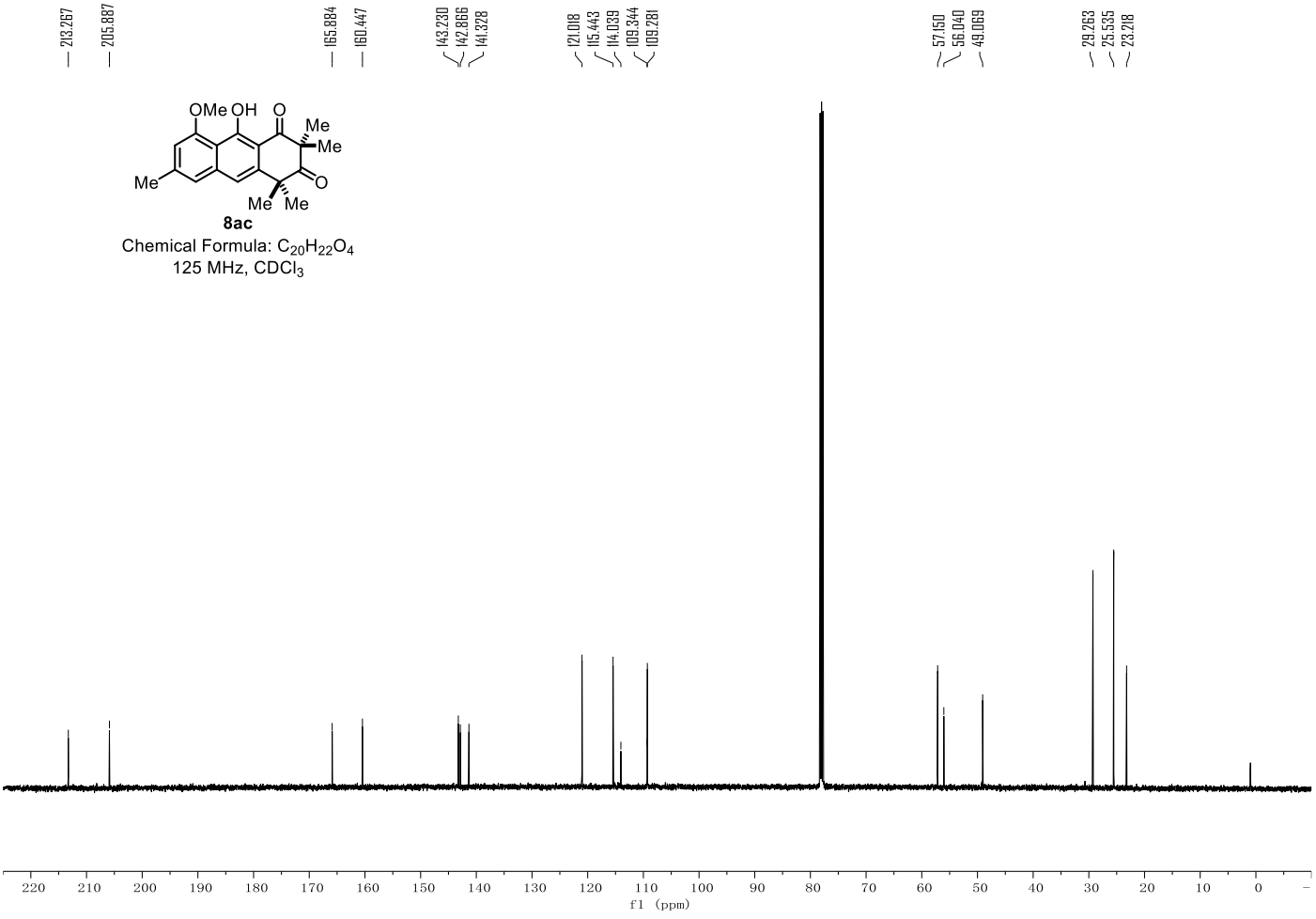

15.435
7.513
3.986
3.925
3.846
3.759
2.325
1.485
1.335
1.304
1.282
0.221
OMe OH O
Me
Me
Me
MeO
OTMS
OMe
Me Me
8fb
Chemical Formula: C25H36O6Si
400 MHz, CDCl3
0.91
1.00
2.97
3.09
3.01
1.03
3.14
3.17
3.33
3.57
3.31
9.49
f1 (ppm)

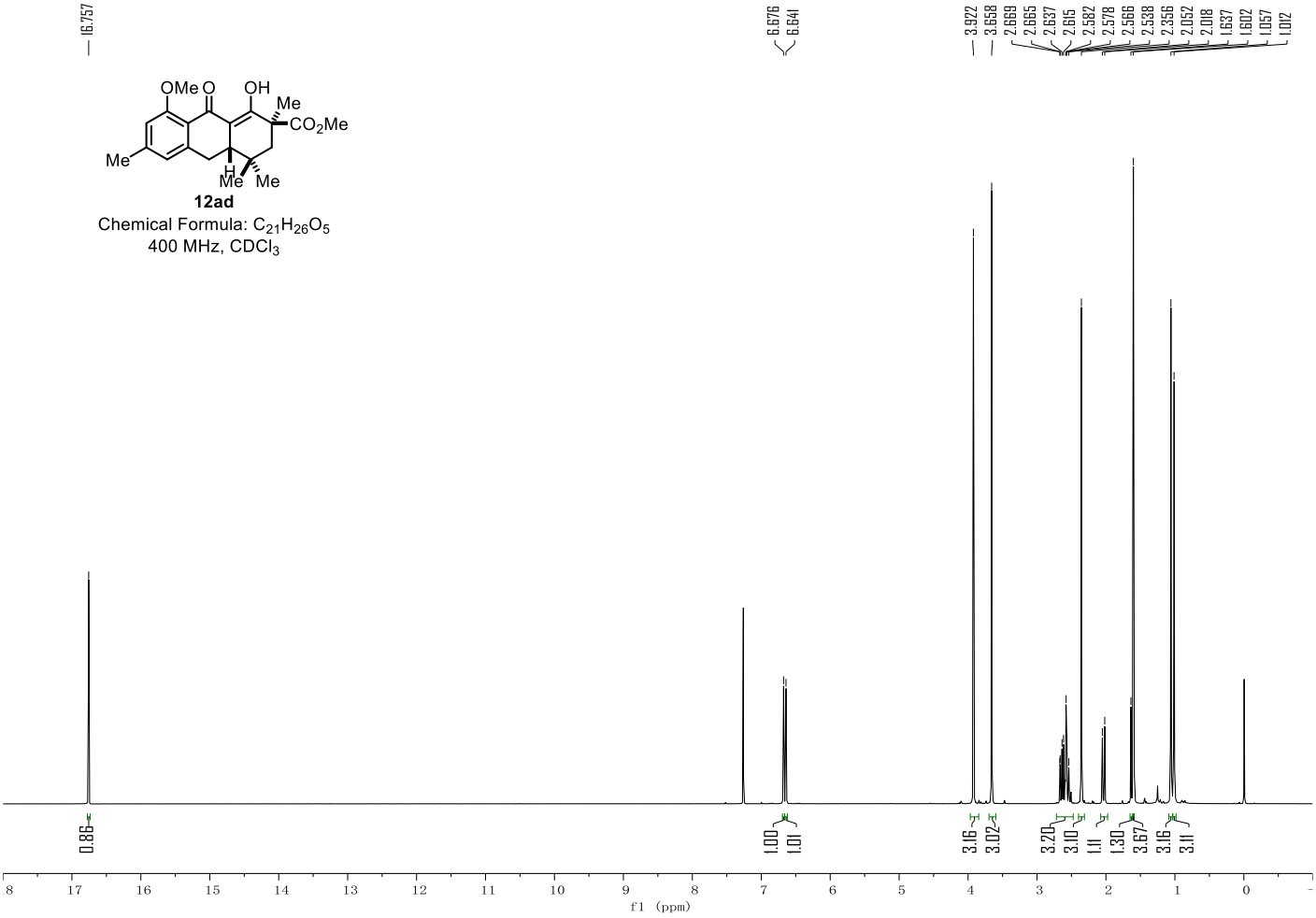

208.479
164.022
152.774
151.926
144.051
141.942
132.164
123.221
114.391
107.734
107.020
80.015
60.787
60.062
59.604
47.178
39.410
27.956
26.415
25.673
20.911
8.490
0.001
OMe OH O
Me
Me
Me
MeO
OTMS
OMe
Me Me
8fb
Chemical Formula: C25H36O6Si
100 MHz, CDCl3
f1 (ppm)

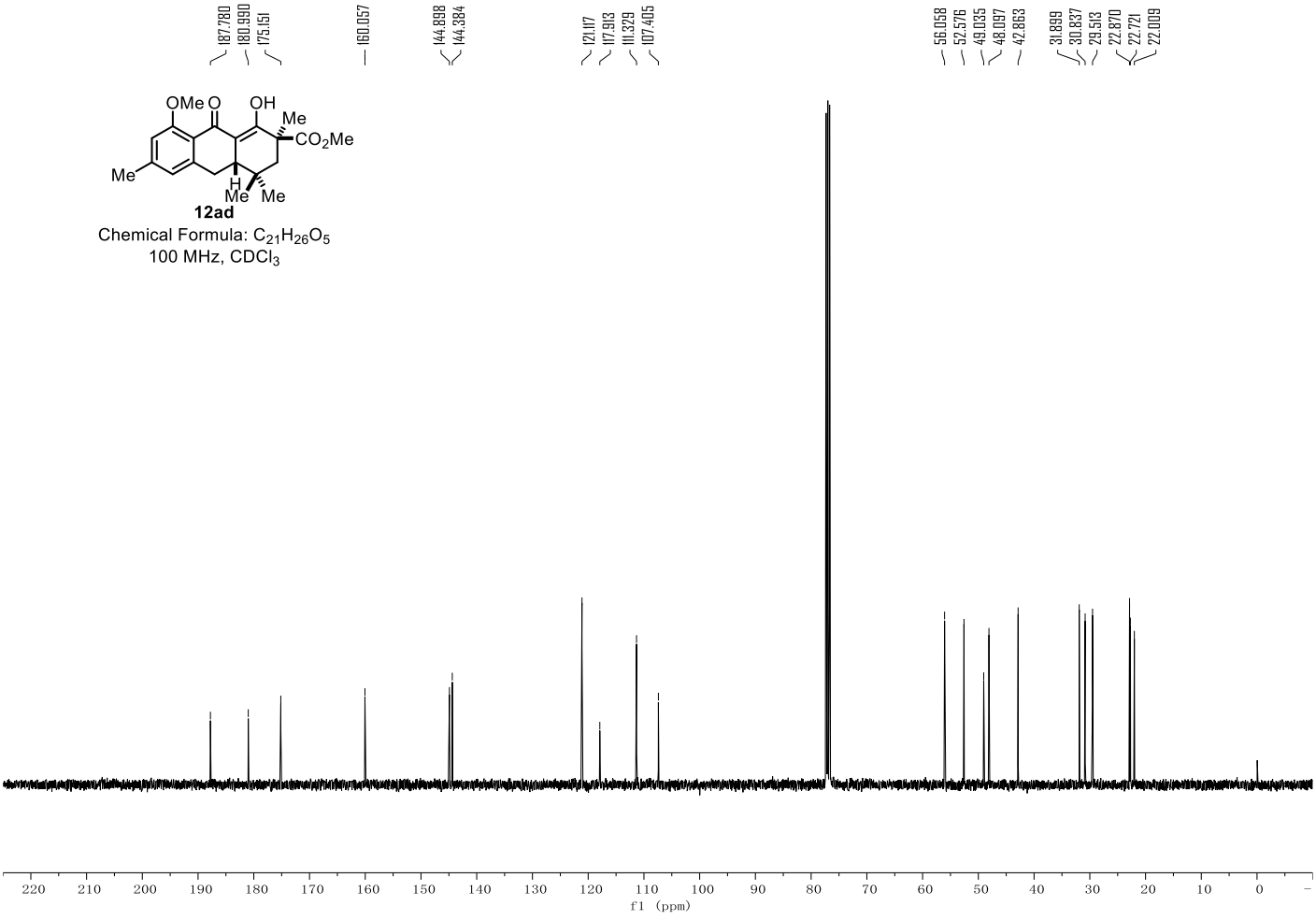

16.828
6.702
6.673
3.934
2.827
2.806
2.778
2.755
2.742
2.737
2.709
2.693
2.670
2.666
2.389
1.418
1.280
1.234
1.090
OMe O
OH
Me
Me
Me
O
H
Me
Me
12ac
Chemical Formula: C20H24O4
400 MHz, CDCl3
0.87
0.95
0.96
3.00
3.03
2.96
3.09
3.20
3.18
3.06
f1 (ppm)

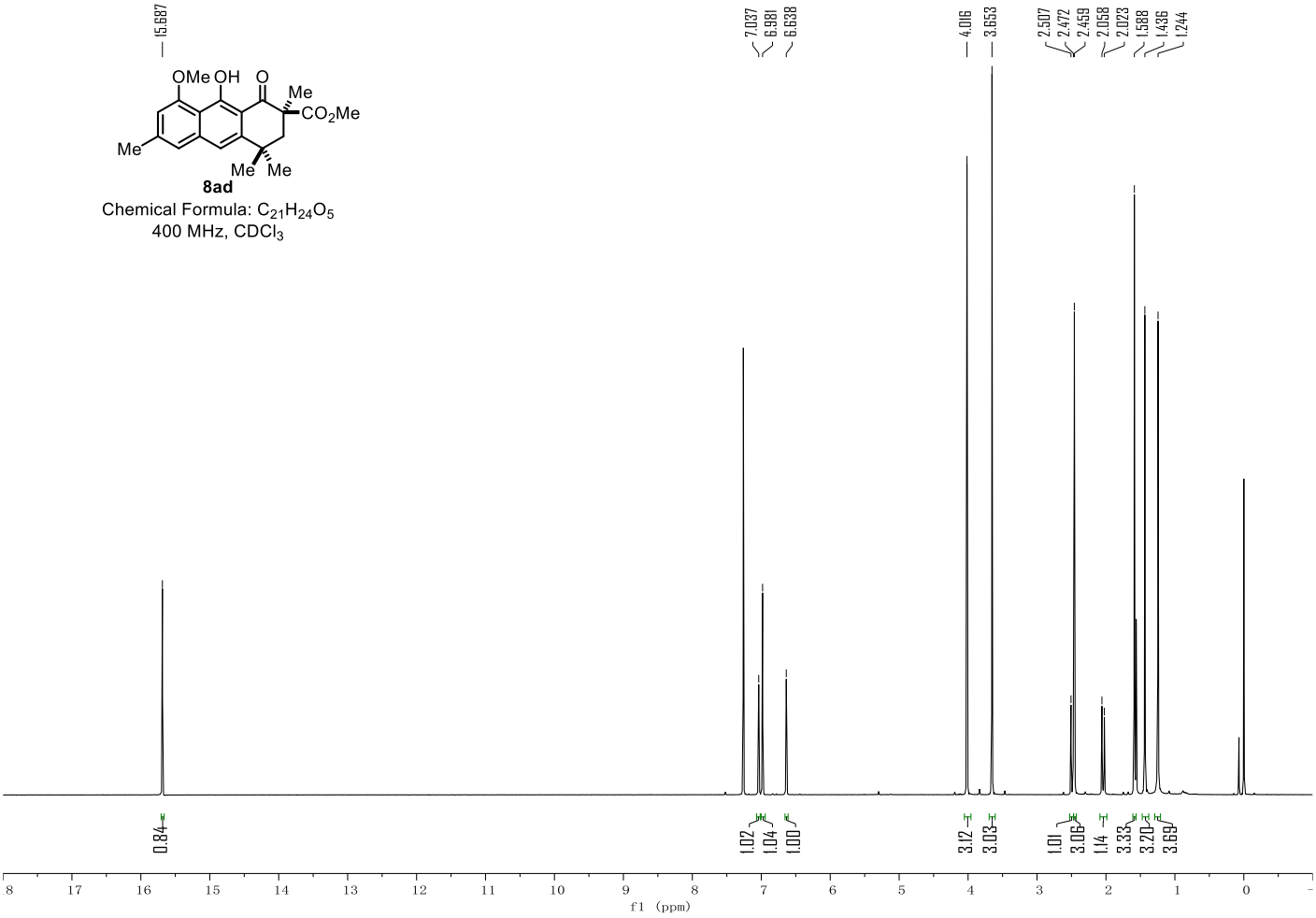

216.093
189.864
184.816
160.877
146.029
143.399
122.462
118.102
112.618
105.744
57.102
50.930
47.445
39.168
30.701
26.715
24.308
23.029
22.262
20.872
OMe O
OH
Me
Me
Me
O
H
Me
Me
12ac
Chemical Formula: C20H24O4
100 MHz, CDCl3
f1 (ppm)

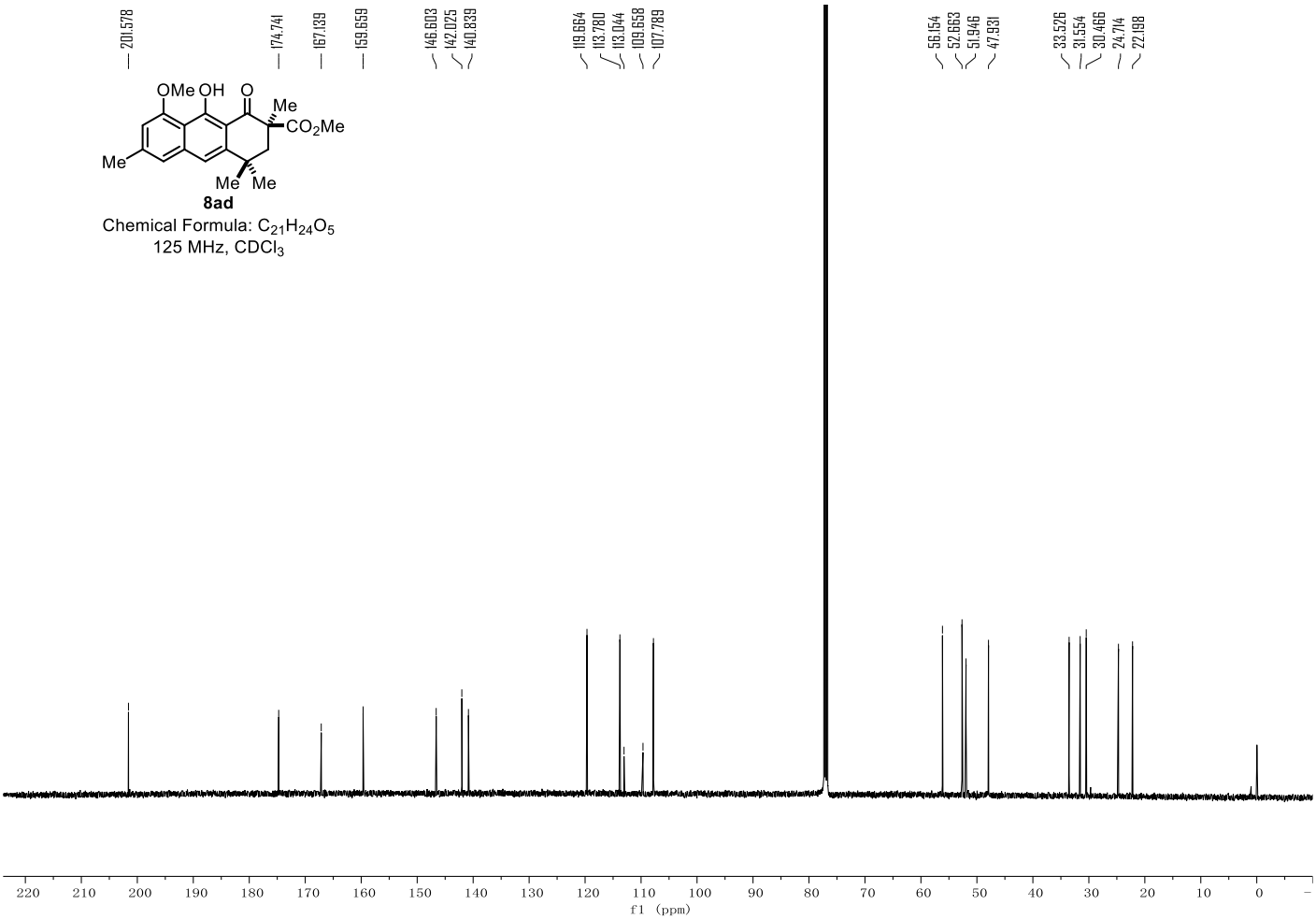

14.563
7.103
6.893
4.031
2.482
1.549
1.436
OMe OH O
Me
Me
Me
O
Me Me
8ac
Chemical Formula: C20H22O4
500 MHz, CDCl3
0.84
2.01
1.00
3.11
3.00
6.13
6.16
f1 (ppm)

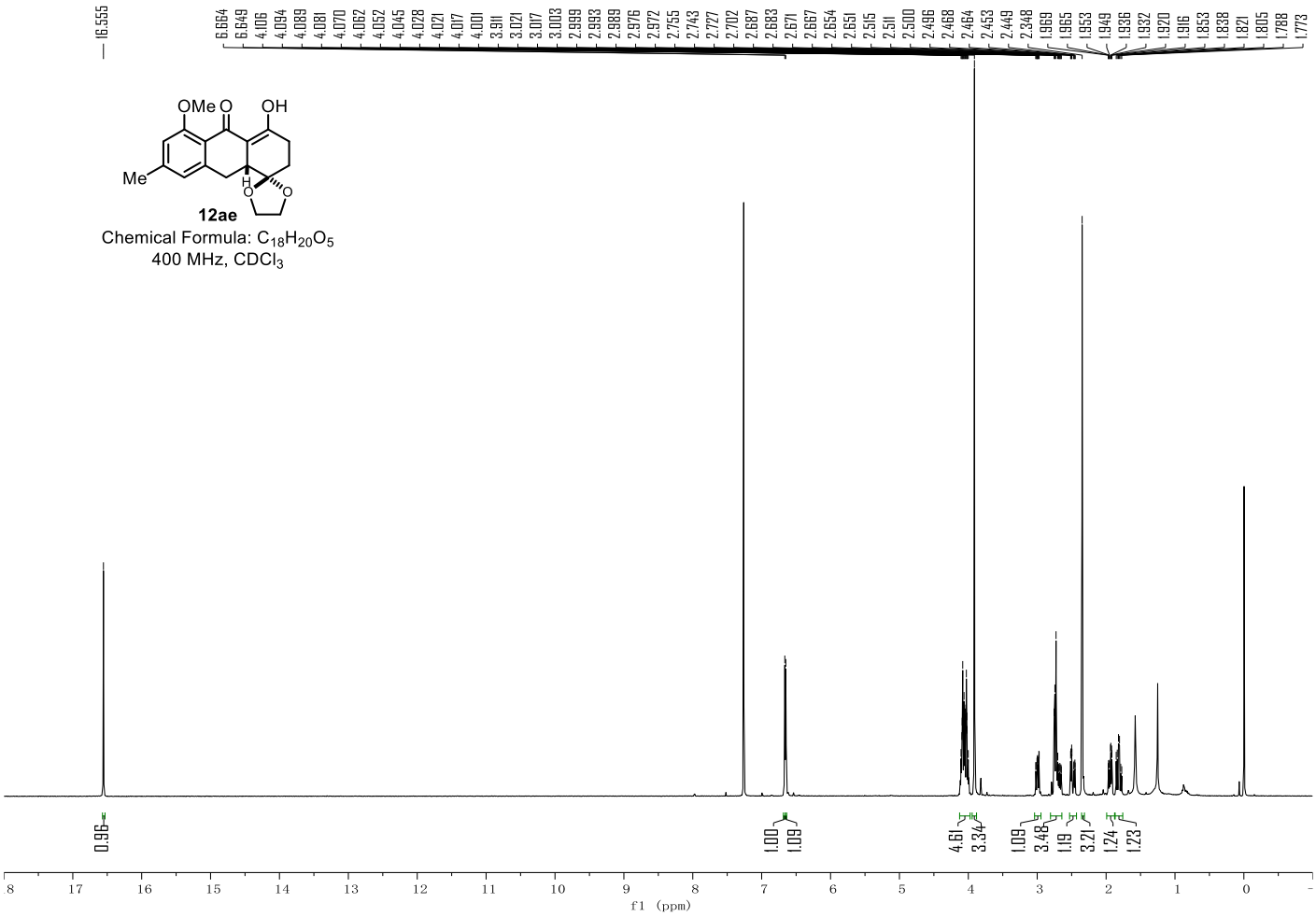

218.267
205.887
165.884
160.447
143.230
142.866
141.328
121.018
115.443
114.039
109.344
109.281
57.150
56.040
49.069
29.263
25.535
23.218
OMe OH O
Me
Me
Me
O
Me Me
8ac
Chemical Formula: C20H22O4
125 MHz, CDCl3
f1 (ppm)

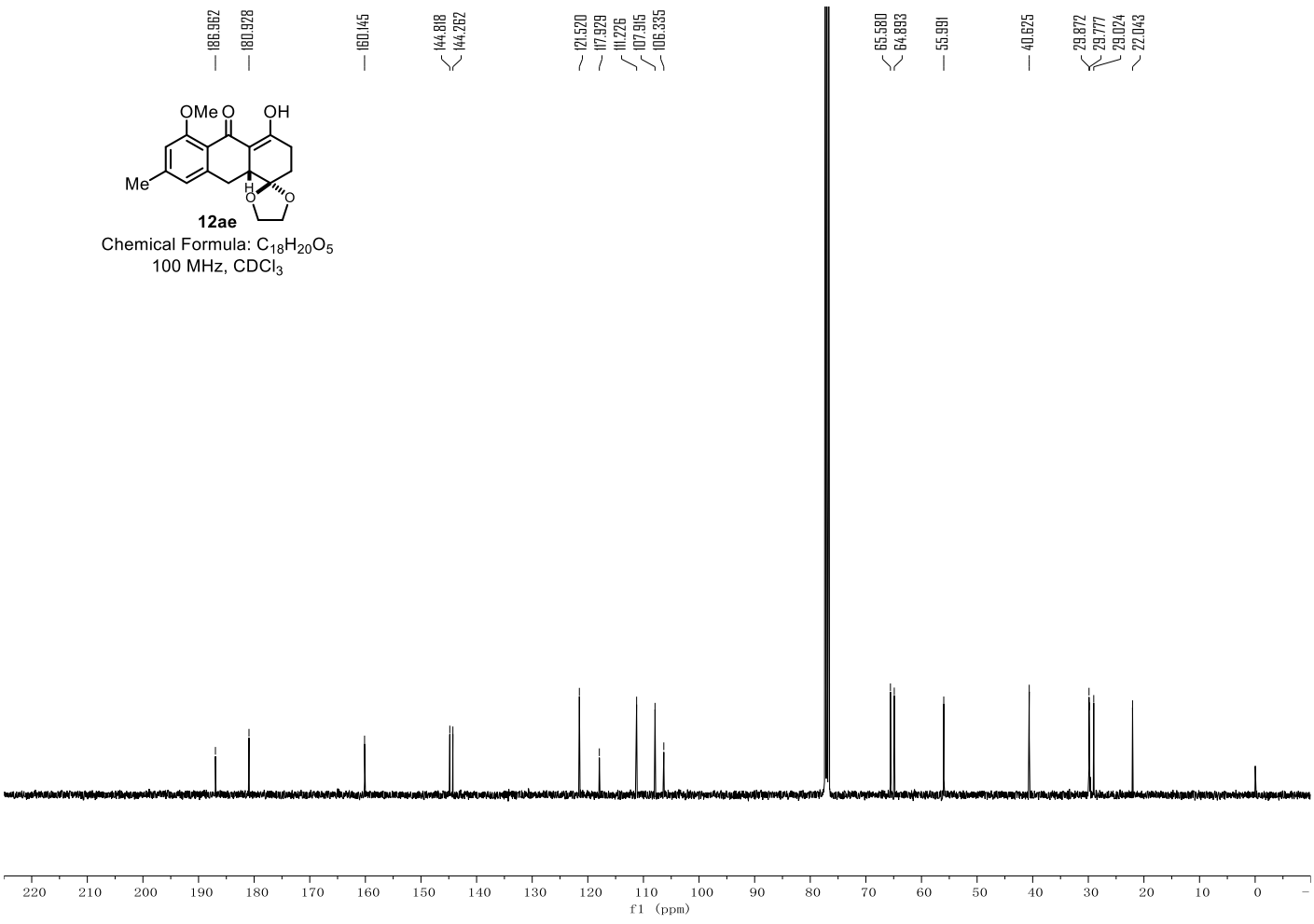

16.757
6.676
6.641
3.922
3.658
2.669
2.665
2.637
2.615
2.582
2.578
2.566
2.538
2.356
2.052
2.018
1.637
1.602
1.057
1.012
OMe O
OH
Me
CO2Me
Me
H
Me Me
12ad
Chemical Formula: C21H26O5
400 MHz, CDCl3
0.86
1.00
1.01
3.16
3.02
3.20
3.10
1.11
1.30
3.67
3.16
3.11
f1 (ppm)

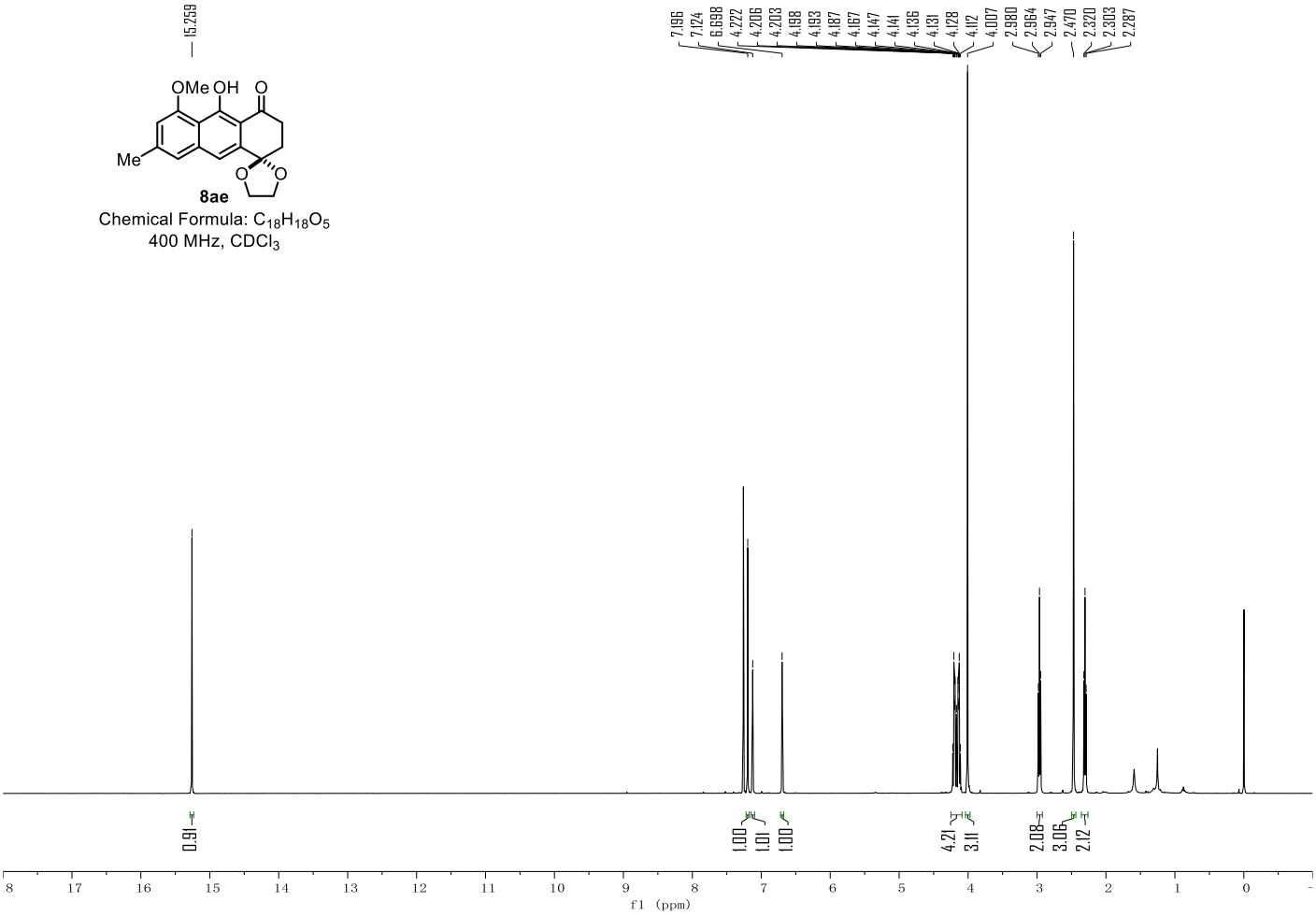

187.780
180.990
175.151
160.057
144.898
144.384
121.117
117.913
111.329
107.405
56.058
52.576
49.035
48.097
42.863
31.899
30.837
29.513
22.870
22.721
22.009
OMe O
OH
Me
CO2Me
Me
H
Me Me
12ad
Chemical Formula: C21H26O5
100 MHz, CDCl3
f1 (ppm)

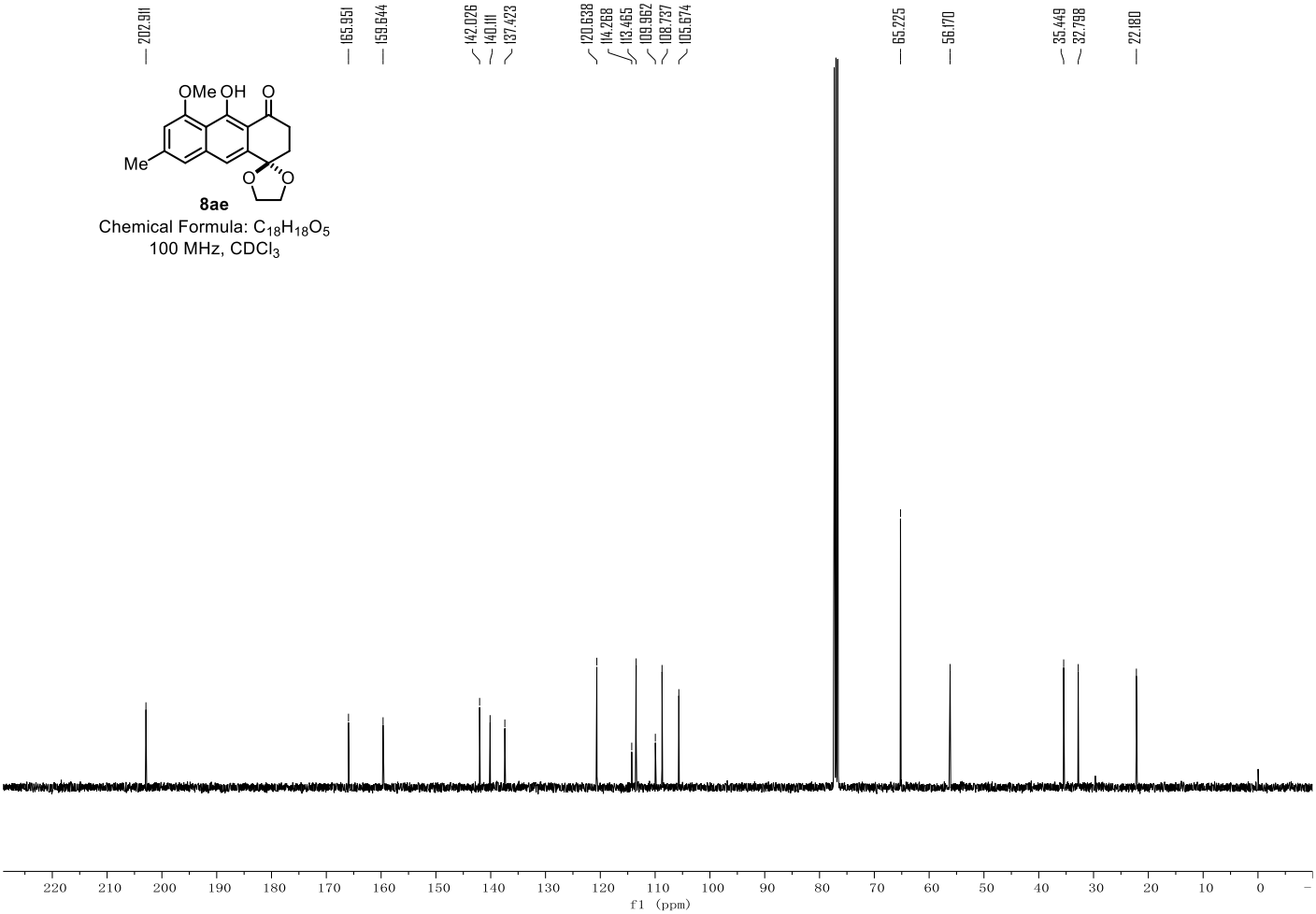

15.687
7.037
6.981
6.638
4.016
3.653
2.507
2.472
2.459
2.058
2.023
1.588
1.436
1.244
OMe OH O
Me
CO2Me
Me
Me Me
8ad
Chemical Formula: C21H24O5
400 MHz, CDCl3
0.84
1.02
1.04
1.00
3.12
3.03
1.01
3.06
1.14
3.33
3.20
3.69
f1 (ppm)

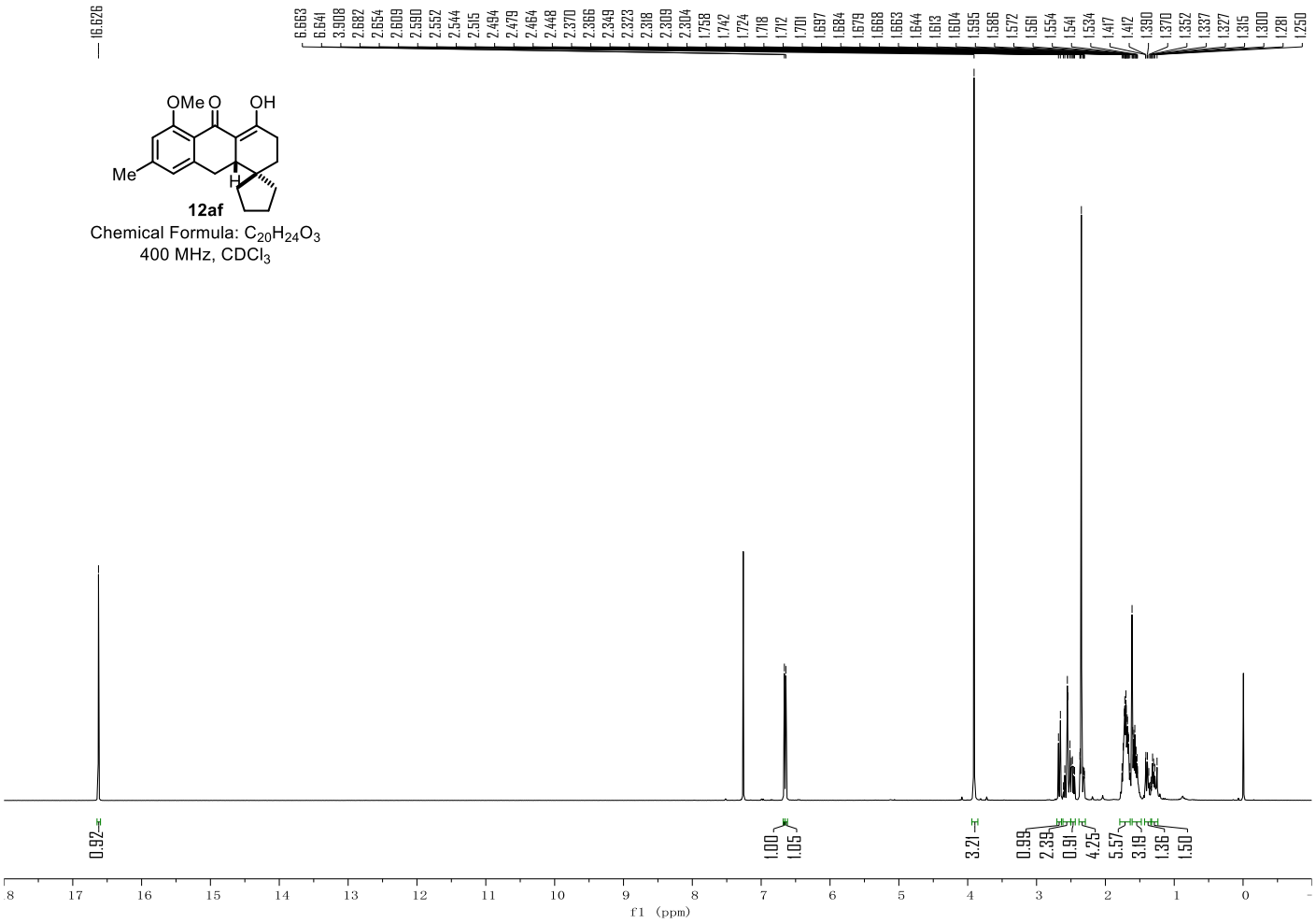

201.578
174.741
167.139
159.659
146.603
142.025
140.839
119.664
113.780
113.044
109.658
107.789
56.154
52.663
51.946
47.831
33.526
31.554
30.466
24.714
22.198
OMe OH O
Me
CO2Me
Me
Me Me
8ad
Chemical Formula: C21H24O5
125 MHz, CDCl3
f1 (ppm)

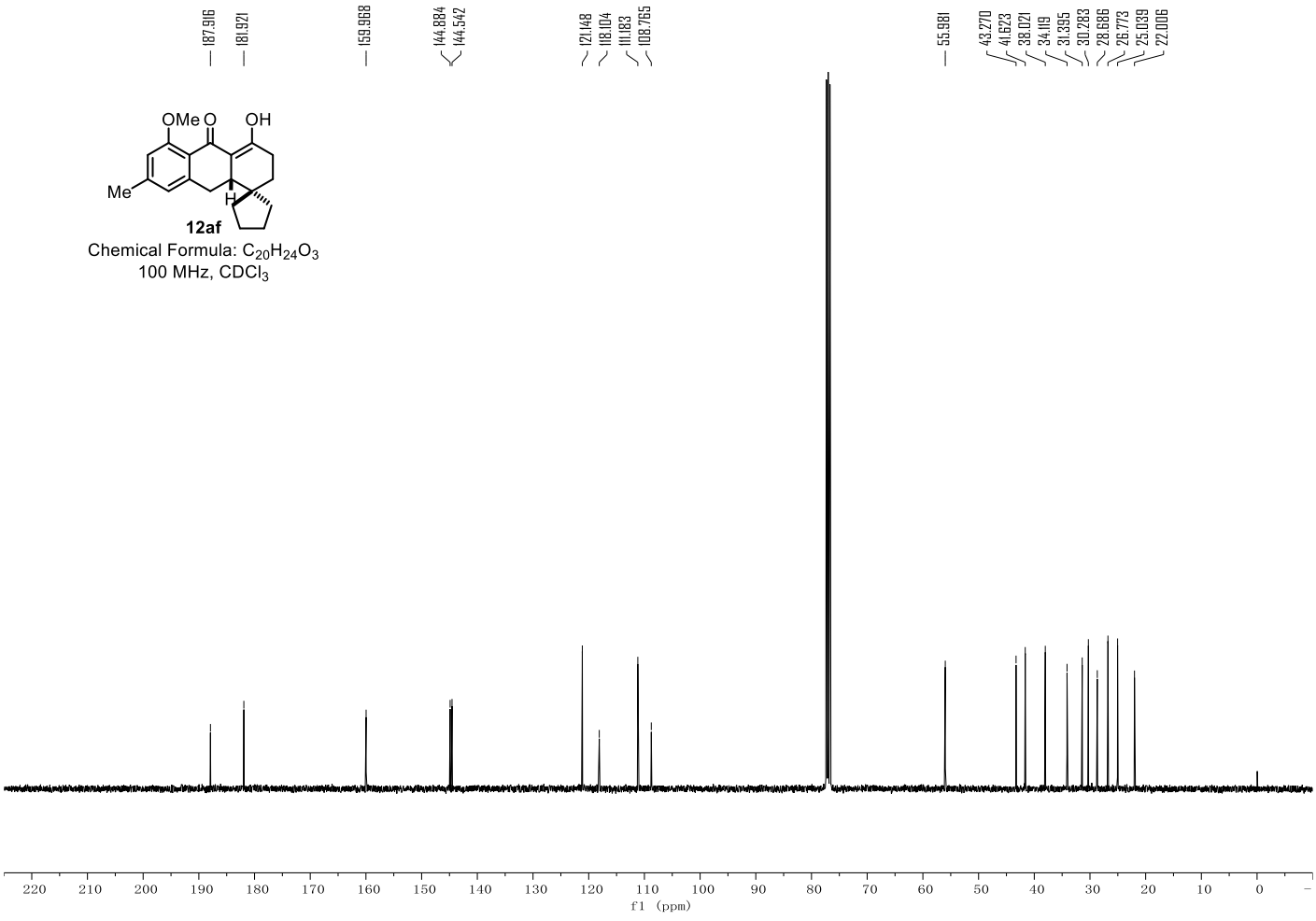

16.555
6.664
6.649
4.106
4.094
4.089
4.081
4.070
4.062
4.052
4.045
4.028
4.021
4.017
4.001
3.911
3.021
3.017
3.003
2.999
2.993
2.983
2.976
2.972
2.755
2.743
2.727
2.702
2.687
2.683
2.671
2.667
2.654
2.651
2.515
2.511
2.500
2.496
2.468
2.464
2.453
2.449
2.348
1.969
1.965
1.953
1.949
1.936
1.932
1.920
1.916
1.853
1.838
1.821
1.805
1.788
1.773
OMe O
OH
Me
H
O
O
12ae
Chemical Formula: C18H20O5
400 MHz, CDCl3
0.96
1.00
1.09
4.61
3.34
1.09
3.48
1.19
3.21
1.24
1.23
f1 (ppm)

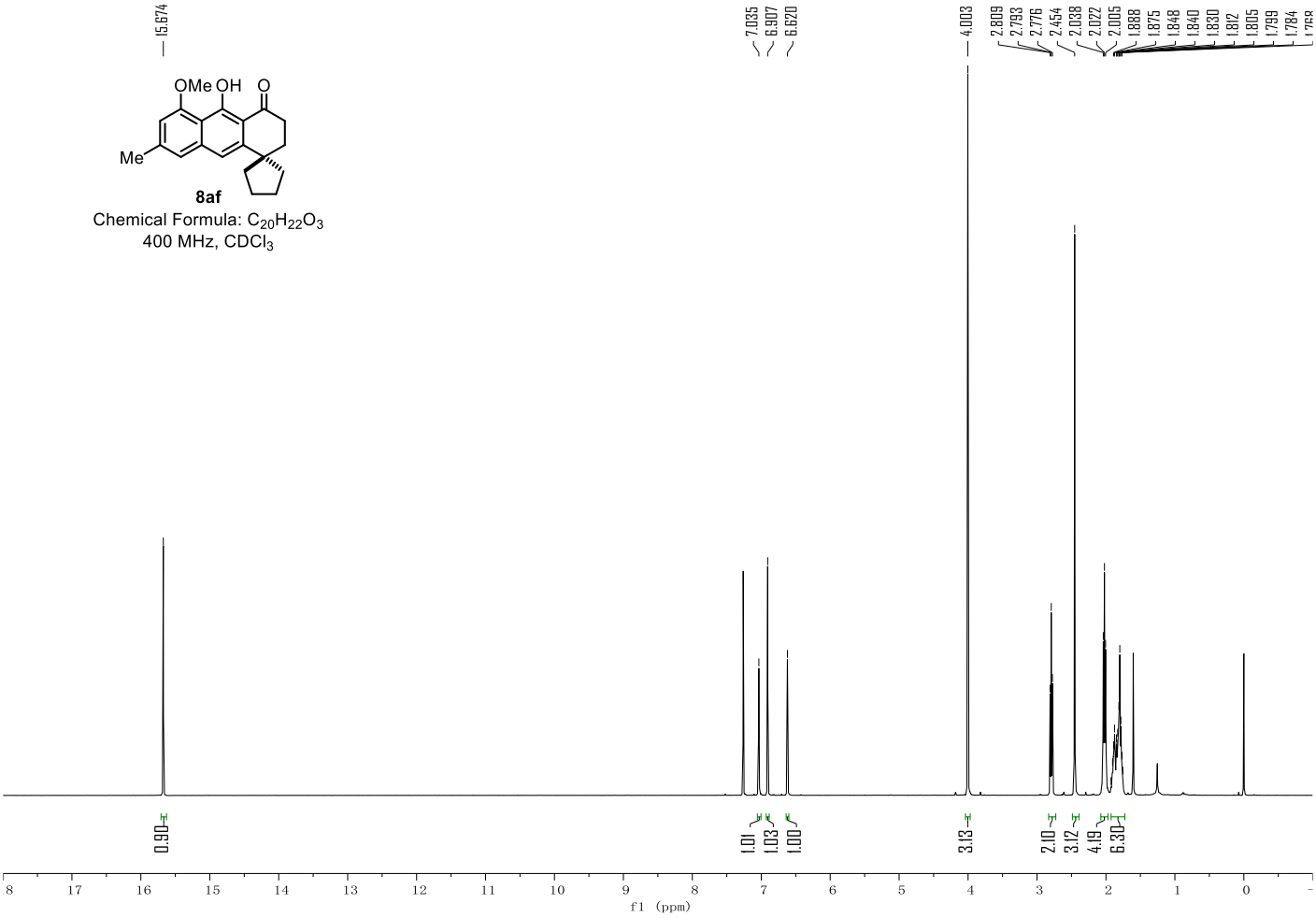

186.962
180.928
160.145
144.818
144.282
121.520
117.829
111.226
107.915
106.335
65.580
64.883
55.991
40.625
29.872
29.777
29.024
22.043
OMe O
OH
Me
H
O
O
12ae
Chemical Formula: C18H20O5
100 MHz, CDCl3
f1 (ppm)


15.259
7.196
7.124
6.698
4.222
4.206
4.203
4.198
4.193
4.187
4.167
4.147
4.141
4.136
4.131
4.128
4.112
4.007
2.980
2.964
2.947
2.470
2.320
2.303
2.287
OMe OH O
Me
O
O
8ae
Chemical Formula: C18H18O5
400 MHz, CDCl3
0.91
1.00
1.01
1.00
4.21
3.11
2.08
3.06
2.12
f1 (ppm)


202.911
165.951
159.644
142.026
140.111
137.423
120.638
114.268
113.465
109.962
108.737
105.674
65.225
56.170
35.449
32.798
22.180
OMe OH O
Me
O
O
8ae
Chemical Formula: C18H18O5
100 MHz, CDCl3
f1 (ppm)


16.626
6.663
6.641
3.908
2.682
2.654
2.609
2.590
2.552
2.544
2.515
2.494
2.479
2.464
2.448
2.370
2.366
2.349
2.323
2.318
2.309
2.304
1.758
1.742
1.724
1.718
1.712
1.701
1.697
1.684
1.679
1.668
1.663
1.644
1.613
1.604
1.595
1.588
1.572
1.561
1.554
1.541
1.534
1.417
1.412
1.390
1.370
1.352
1.337
1.327
1.315
1.300
1.281
1.250
OMe O
OH
Me
H
12af
Chemical Formula: C20H24O3
400 MHz, CDCl3
0.92
1.00
1.05
3.21
0.99
2.38
0.91
4.25
5.57
3.19
1.36
1.50
f1 (ppm)

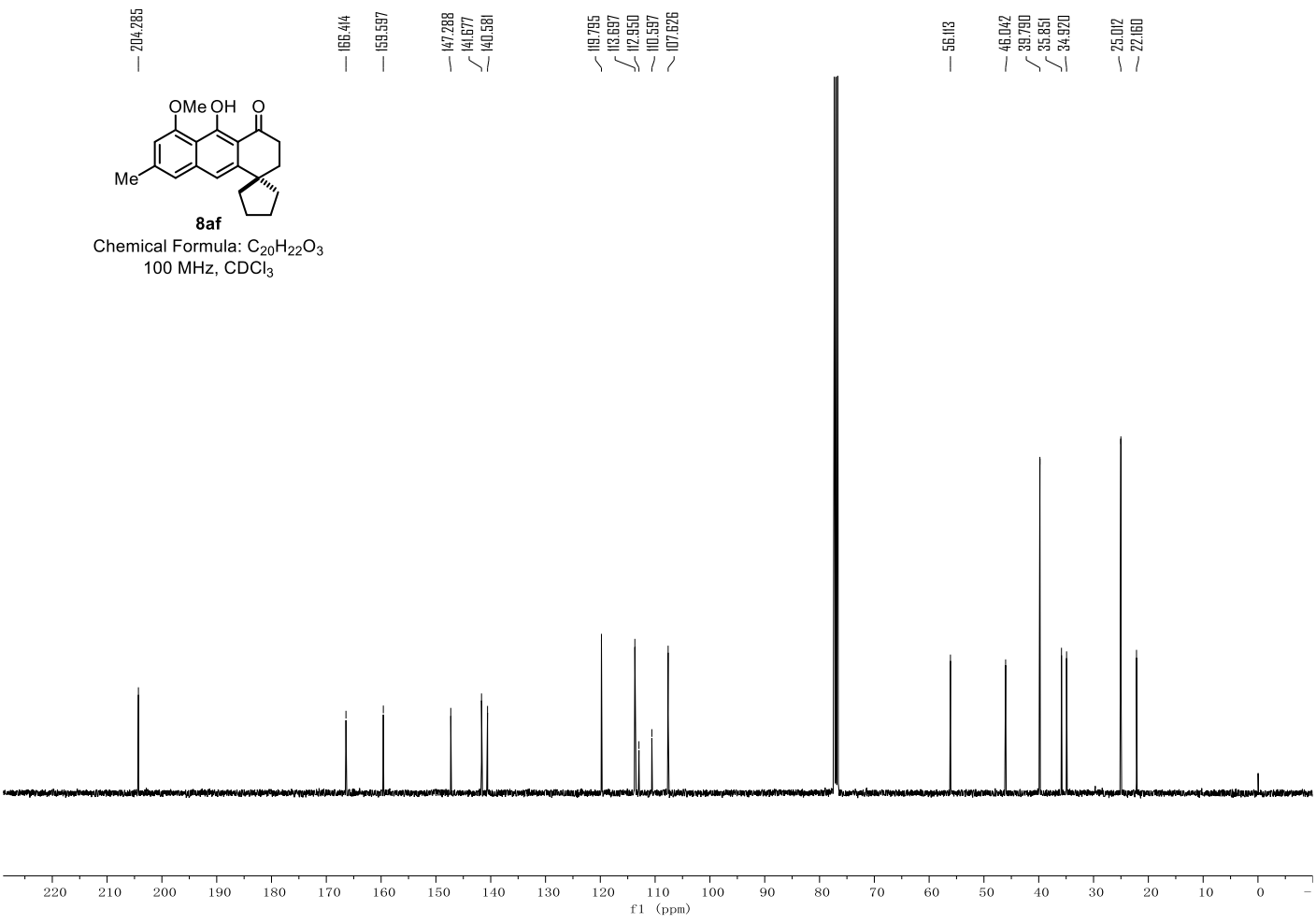

187.916
181.921
159.968
144.884
144.542
121.148
118.104
111.183
108.765
55.981
43.270
41.623
38.021
34.119
31.395
30.283
28.686
26.773
25.039
22.006
OMe O
OH
Me
H
12af
Chemical Formula: C20H24O3
100 MHz, CDCl3
f1 (ppm)



8af

Chemical Formula: $C_{20}H_{22}O_3$

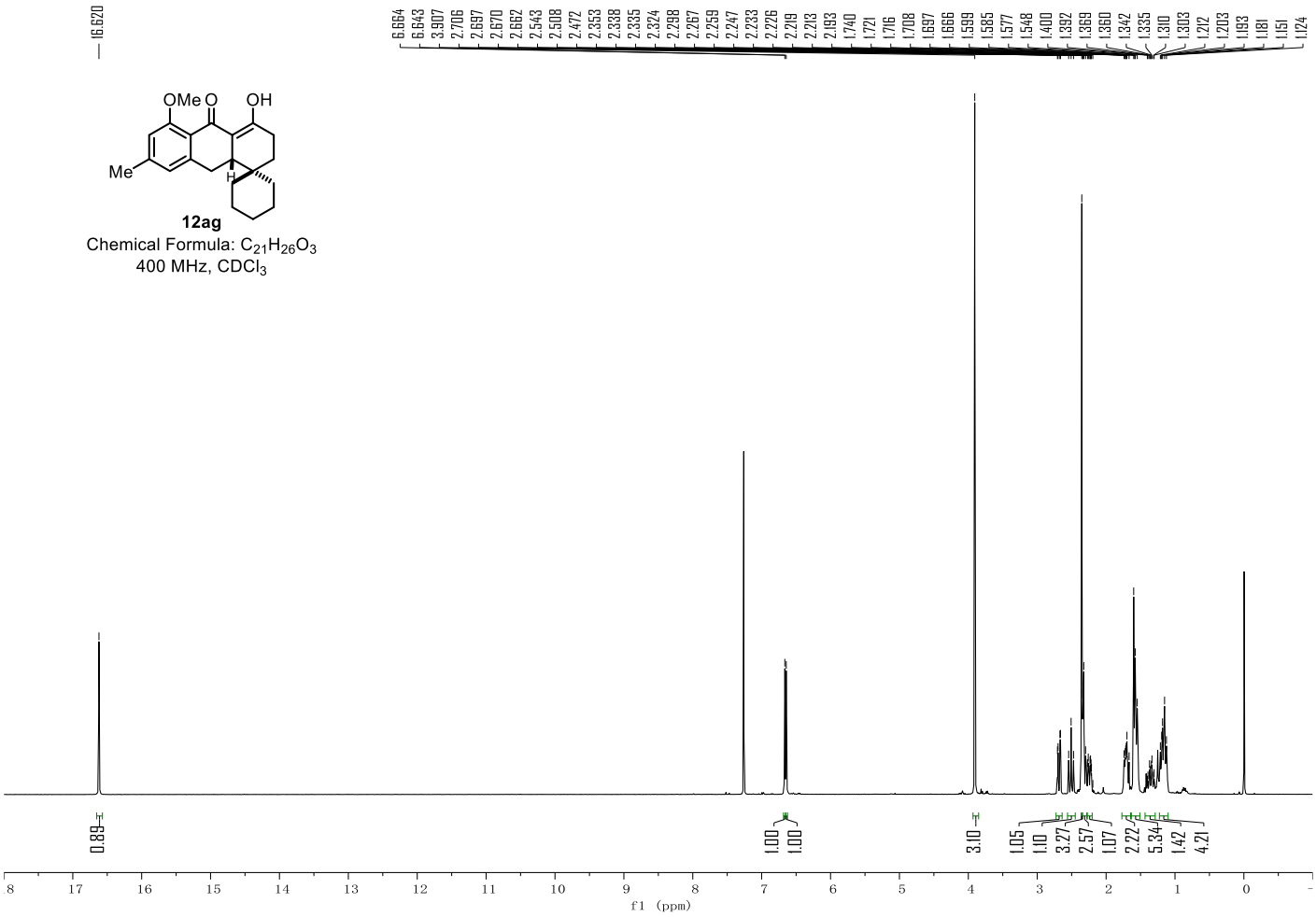
400 MHz, $CDCl_3$

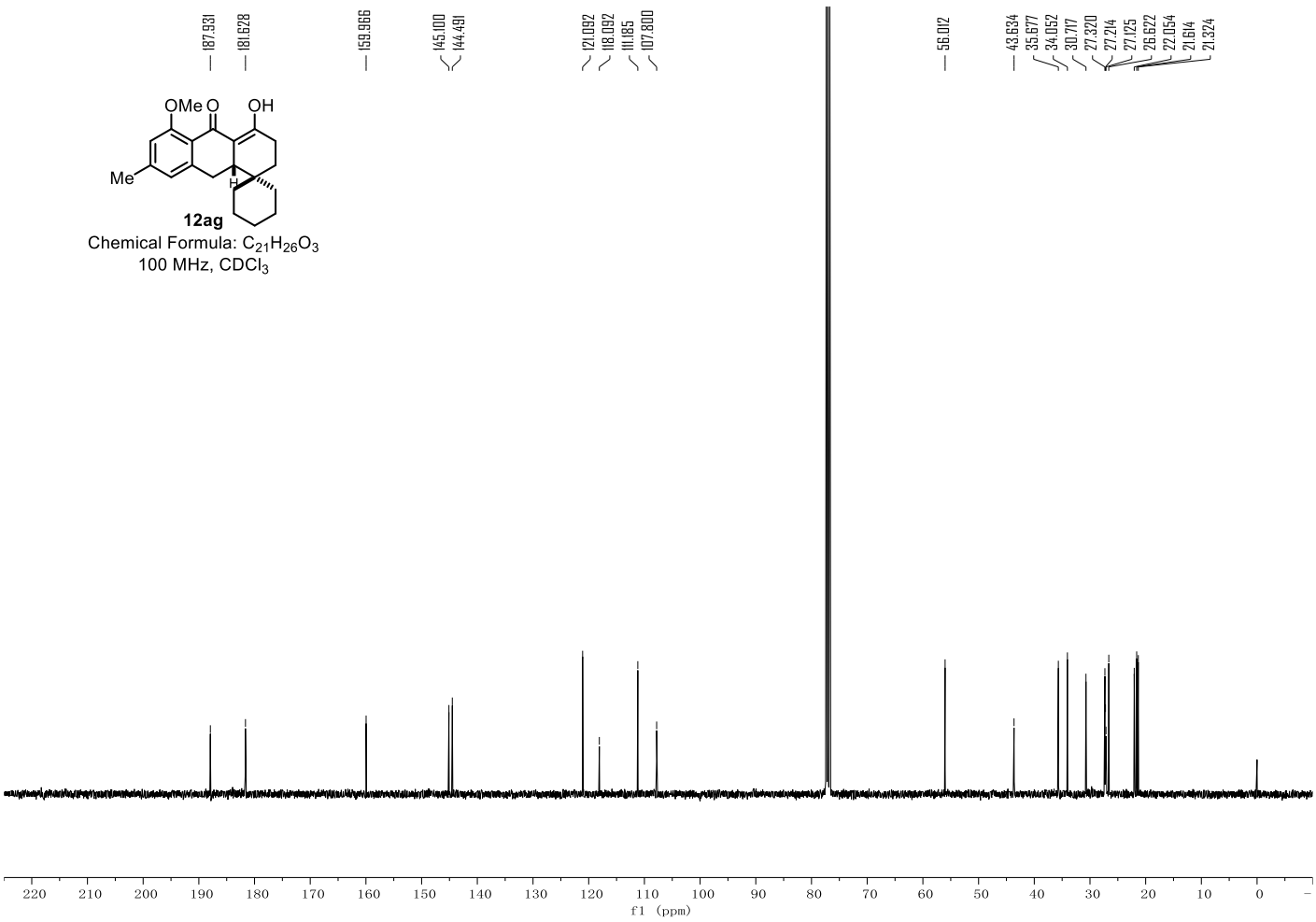


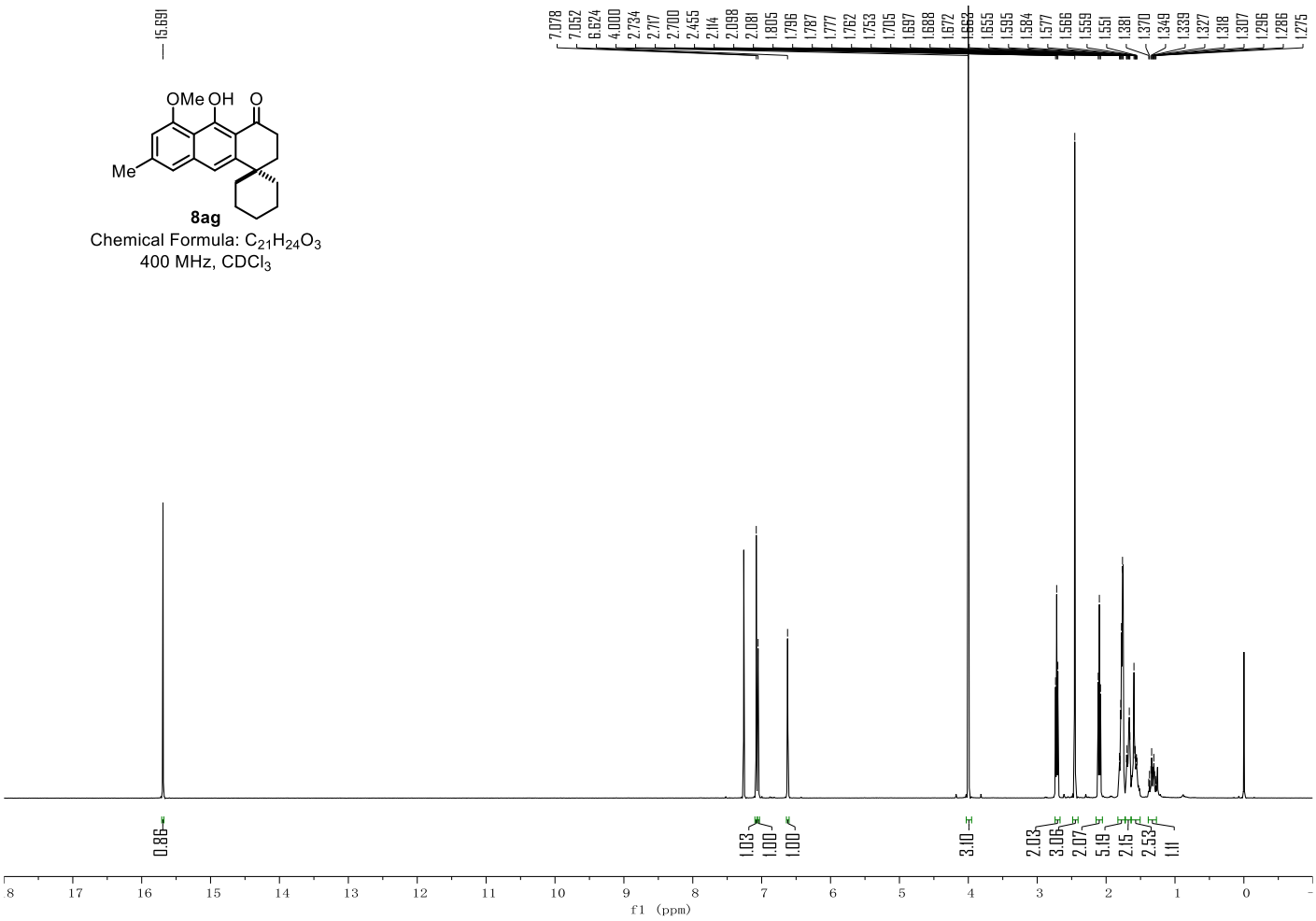
8af

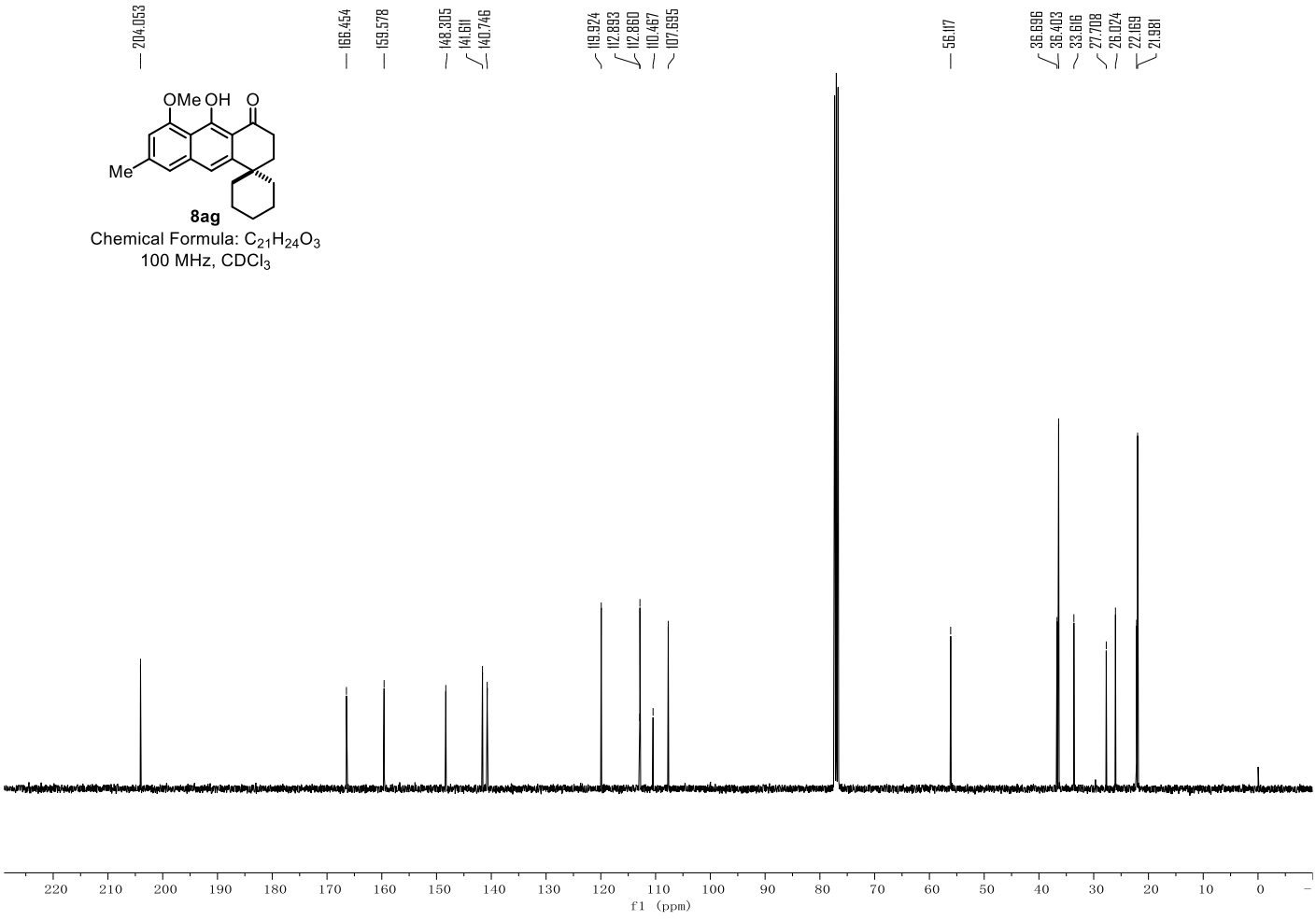
Chemical Formula: $C_{20}H_{22}O_3$

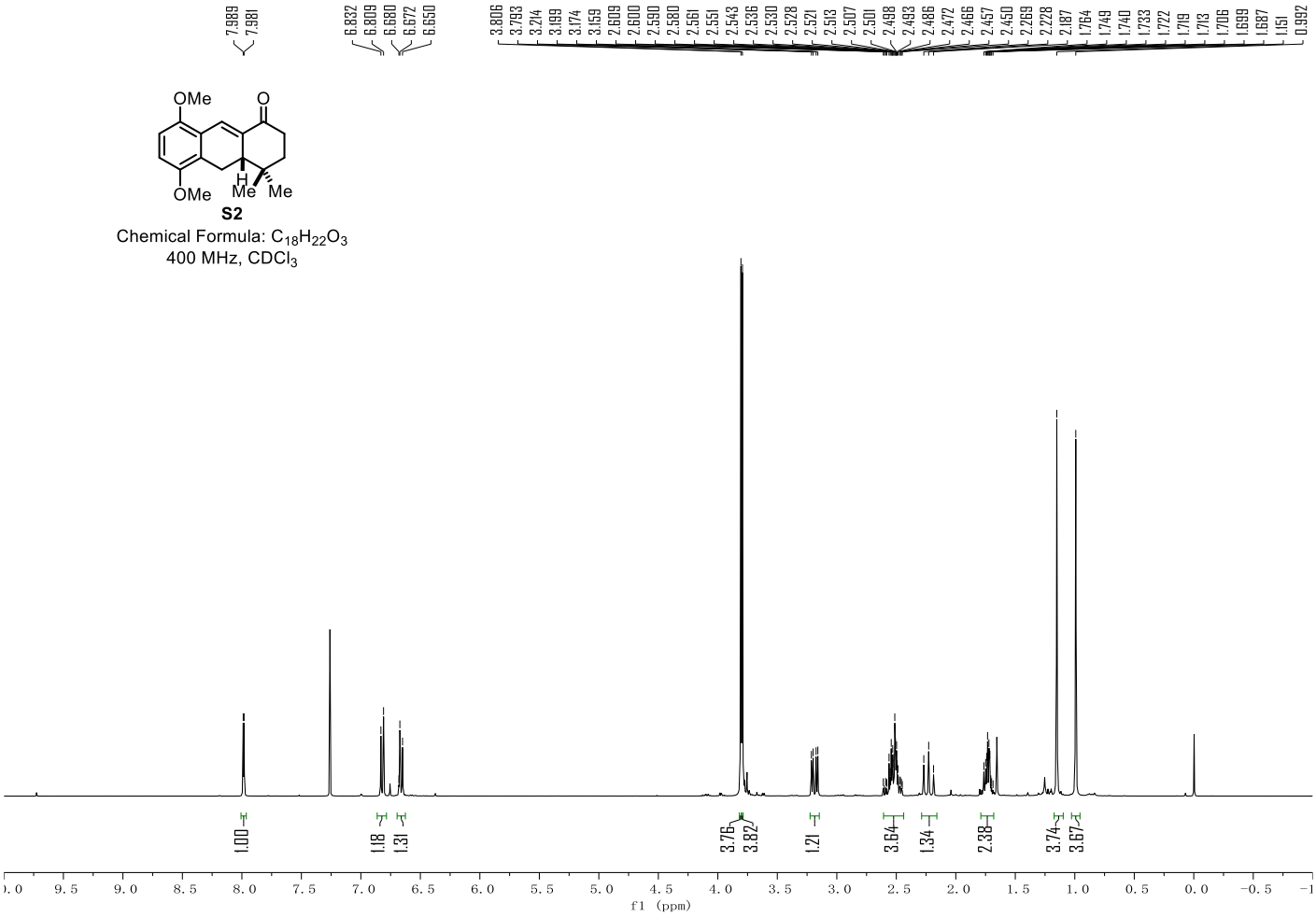
100 MHz, $CDCl_3$

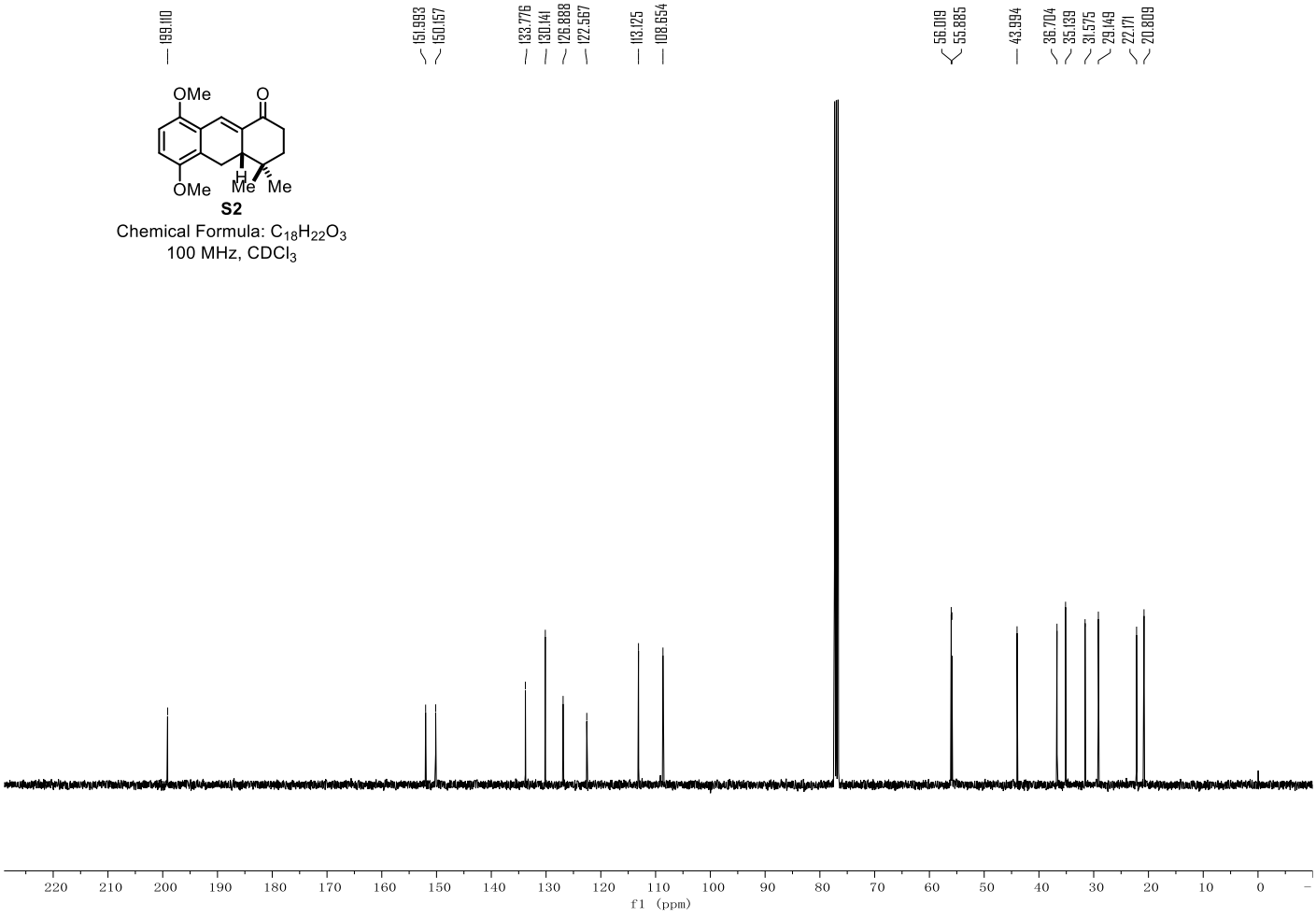

16.620
6.664
6.643
3.907
2.706
2.697
2.670
2.662
2.543
2.508
2.472
2.353
2.338
2.335
2.324
2.298
2.267
2.259
2.247
2.233
2.226
2.219
2.213
2.193
1.740
1.721
1.716
1.708
1.697
1.666
1.599
1.585
1.577
1.548
1.400
1.392
1.369
1.360
1.342
1.335
1.310
1.303
1.212
1.203
1.193
1.181
1.151
1.124
OMe O
OH
Me
H
12ag
Chemical Formula: C21H26O3
400 MHz, CDCl3
0.89
1.00
1.00
3.10
1.05
1.10
3.27
2.57
1.07
2.22
5.34
1.42
4.21
f1 (ppm)

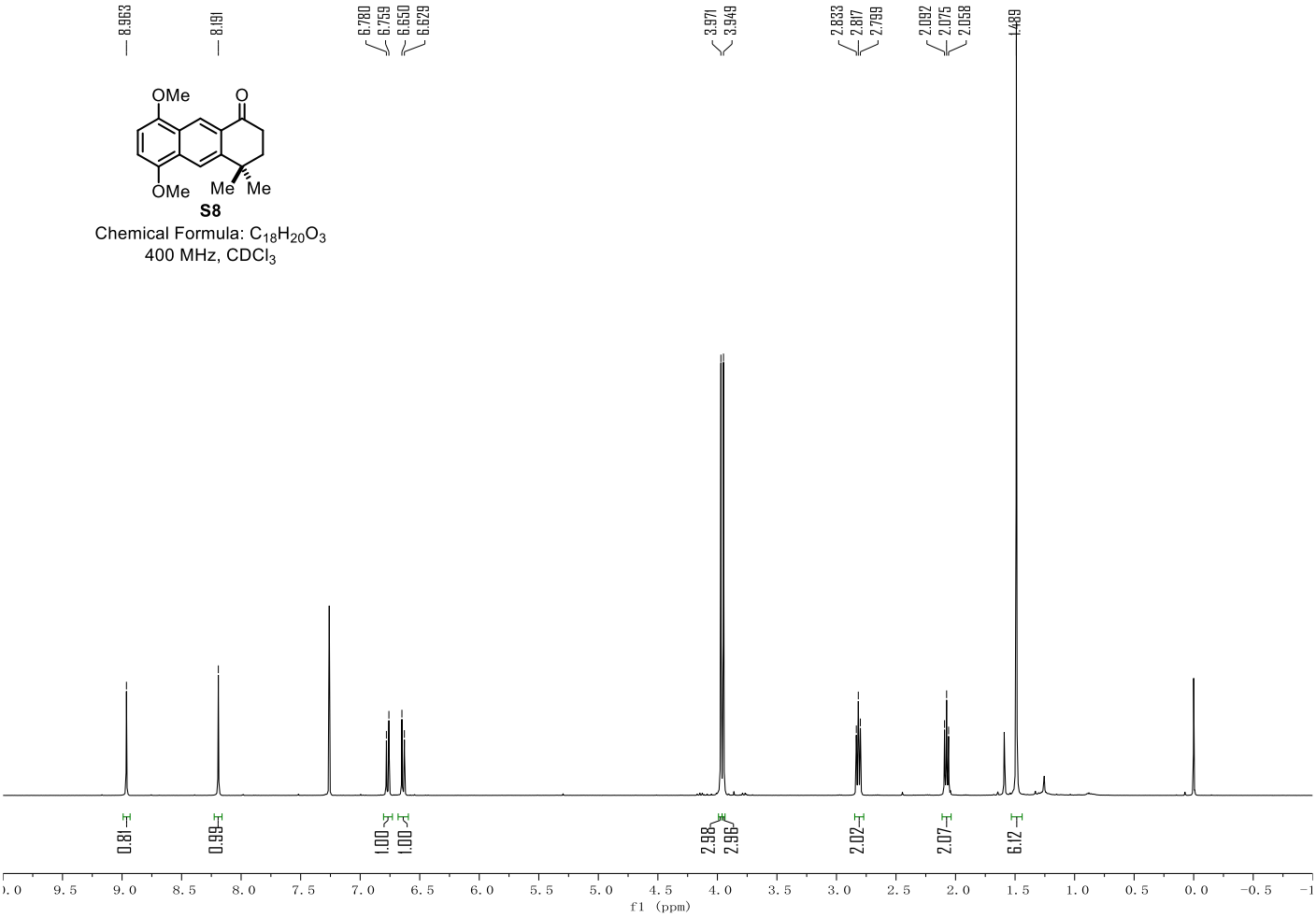

187.931
181.628
159.986
145.100
144.491
121.092
118.092
111.185
107.800
56.012
43.634
35.677
34.052
30.717
27.320
27.214
27.125
26.622
22.054
21.614
21.324
OMe O
OH
Me
H
12ag
Chemical Formula: C21H26O3
100 MHz, CDCl3
f1 (ppm)


15.691
7.078
7.052
6.624
4.000
2.734
2.717
2.700
2.455
2.114
2.098
2.081
1.805
1.796
1.787
1.777
1.762
1.753
1.705
1.697
1.688
1.672
1.663
1.655
1.595
1.584
1.577
1.566
1.559
1.551
1.381
1.370
1.349
1.339
1.327
1.318
1.307
1.296
1.286
1.275
OMe OH O
Me
8ag
Chemical Formula: C21H24O3
400 MHz, CDCl3
0.86
1.03
1.00
1.00
3.10
2.03
3.06
2.07
5.19
2.15
2.53
1.11
f1 (ppm)


204.053
166.454
159.578
148.305
141.611
140.746
119.924
112.893
112.860
110.467
107.695
56.117
36.696
36.403
33.616
27.708
26.024
22.169
21.981
OMe OH O
Me
8ag
Chemical Formula: C21H24O3
100 MHz, CDCl3
f1 (ppm)


OMe
O
OMe
H
Me
Me
S2
Chemical Formula: C18H22O3
400 MHz, CDCl3
f1 (ppm)

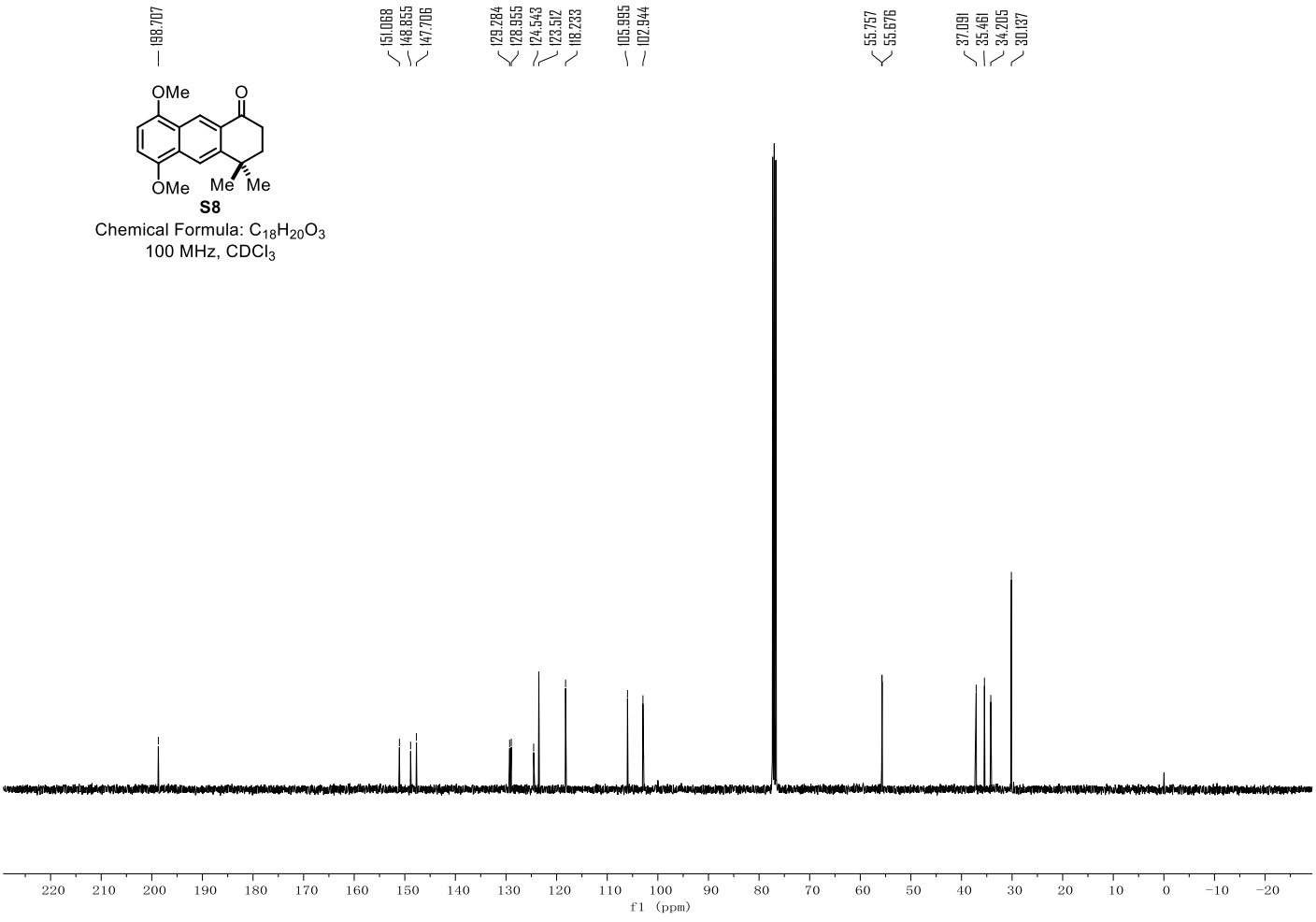

OMe
O
OMe
H
Me
Me
S2
Chemical Formula: C18H22O3
100 MHz, CDCl3
f1 (ppm)



S8

Chemical Formula: $C_{18}H_{20}O_3$

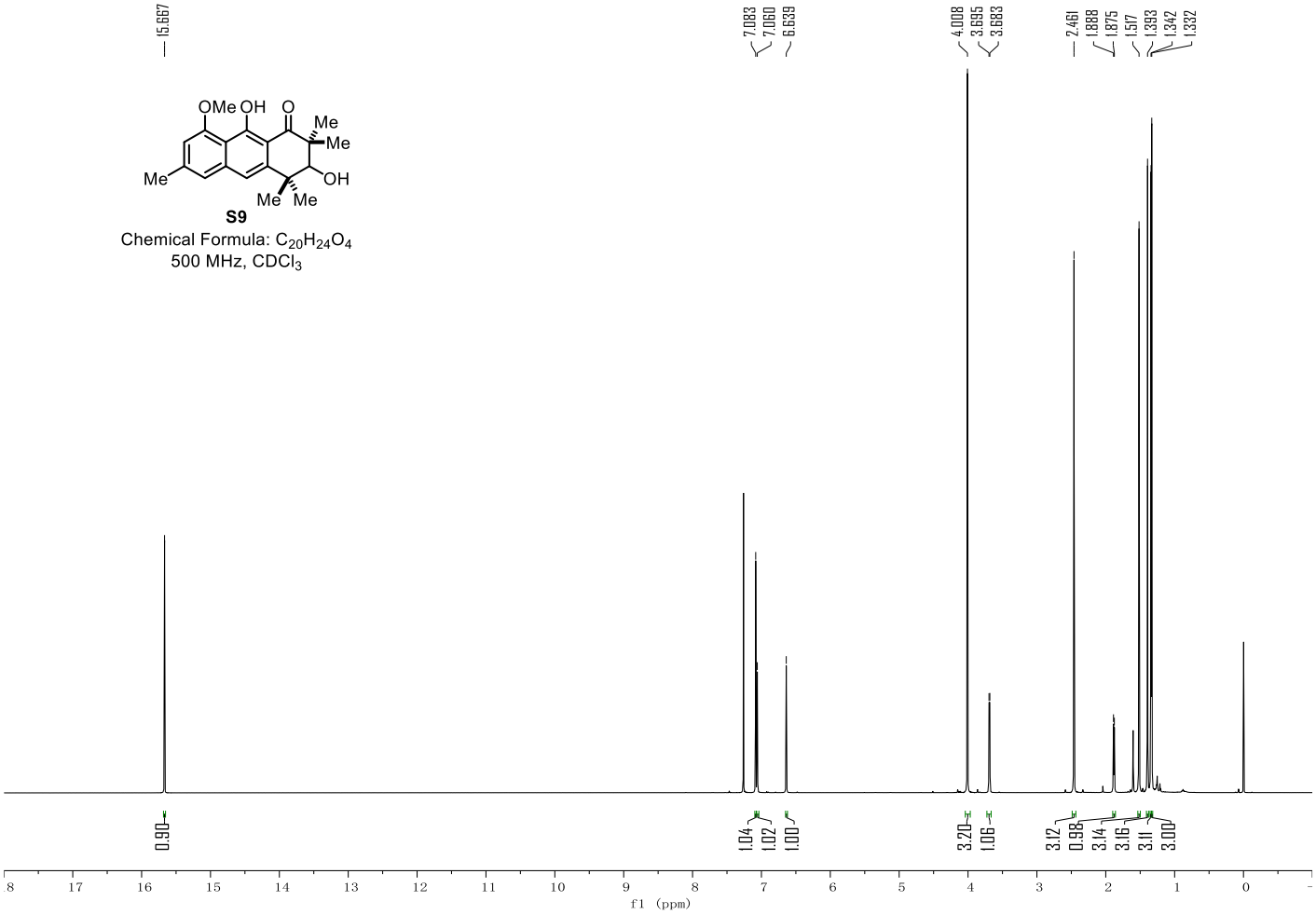
400 MHz, $CDCl_3$



S8

Chemical Formula: $C_{18}H_{20}O_3$

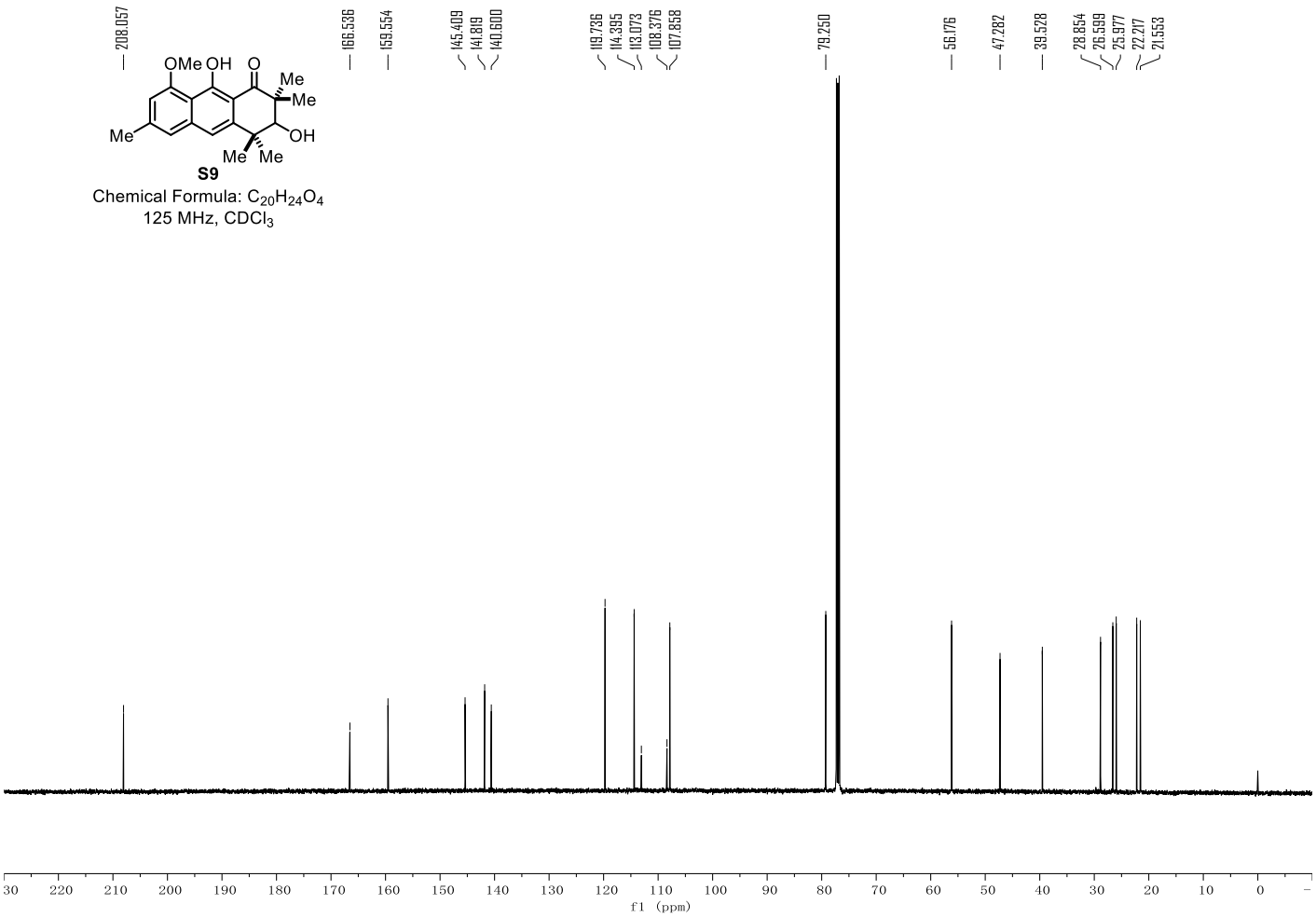
100 MHz, $CDCl_3$



S9

Chemical Formula: $C_{20}H_{24}O_4$

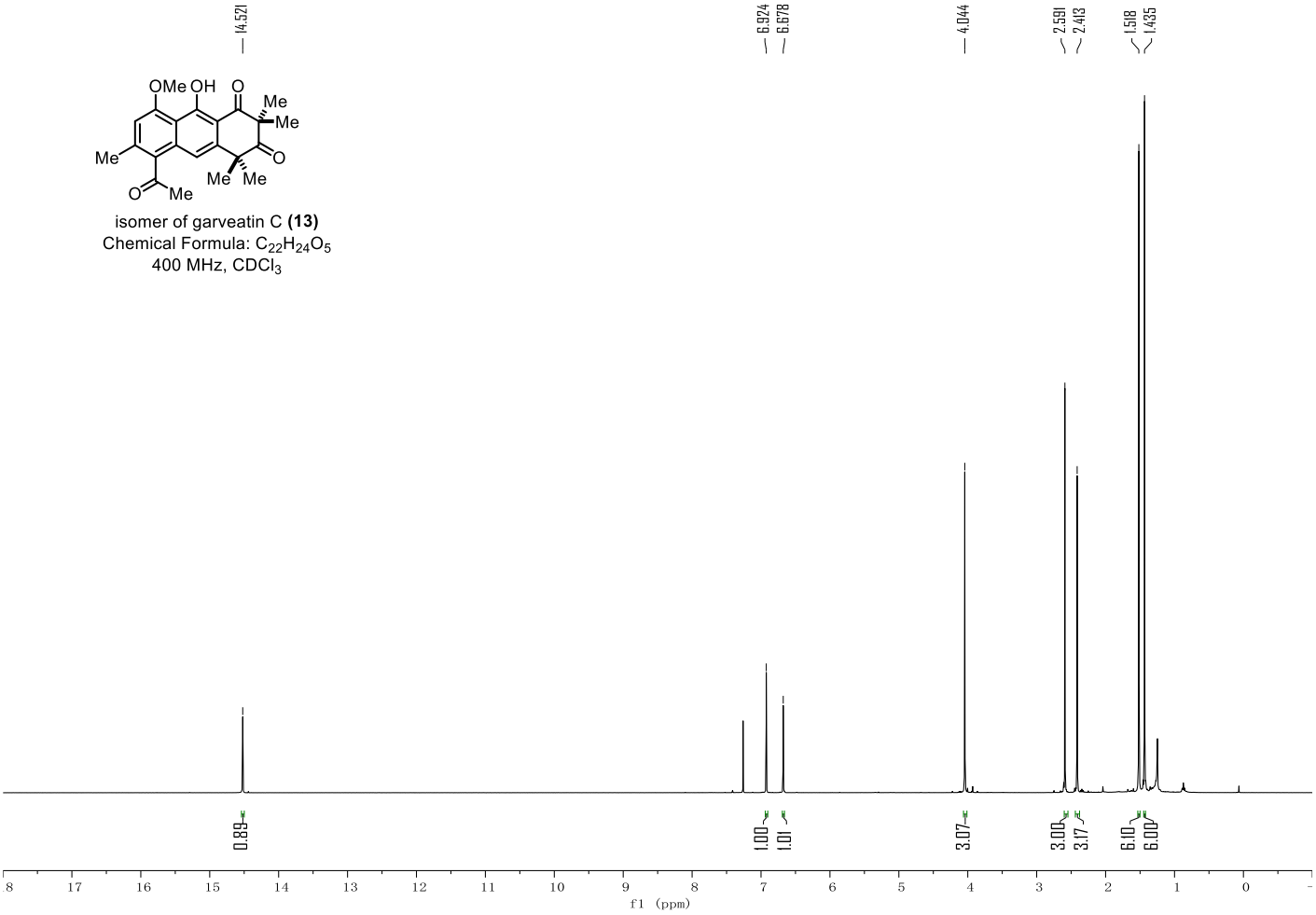
500 MHz, $CDCl_3$



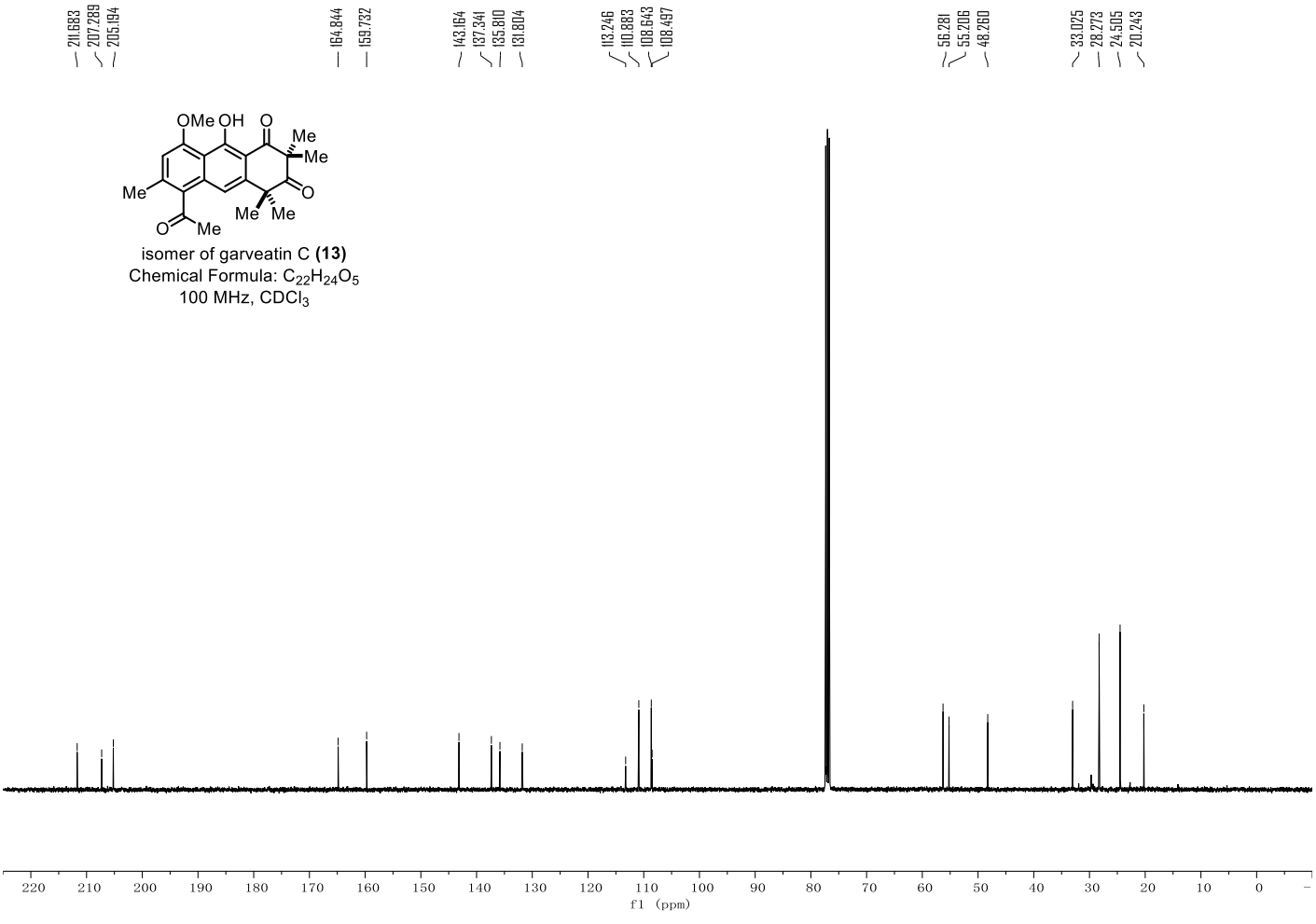
S9

Chemical Formula: $C_{20}H_{24}O_4$

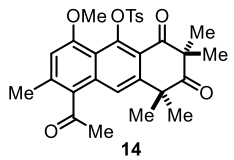
125 MHz, $CDCl_3$



isomer of garveatin C **(13)**
Chemical Formula: $C_{22}H_{24}O_5$
400 MHz, $CDCl_3$

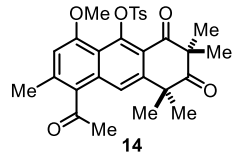


isomer of garveatin C **(13)**
Chemical Formula: $C_{22}H_{24}O_5$
100 MHz, $CDCl_3$



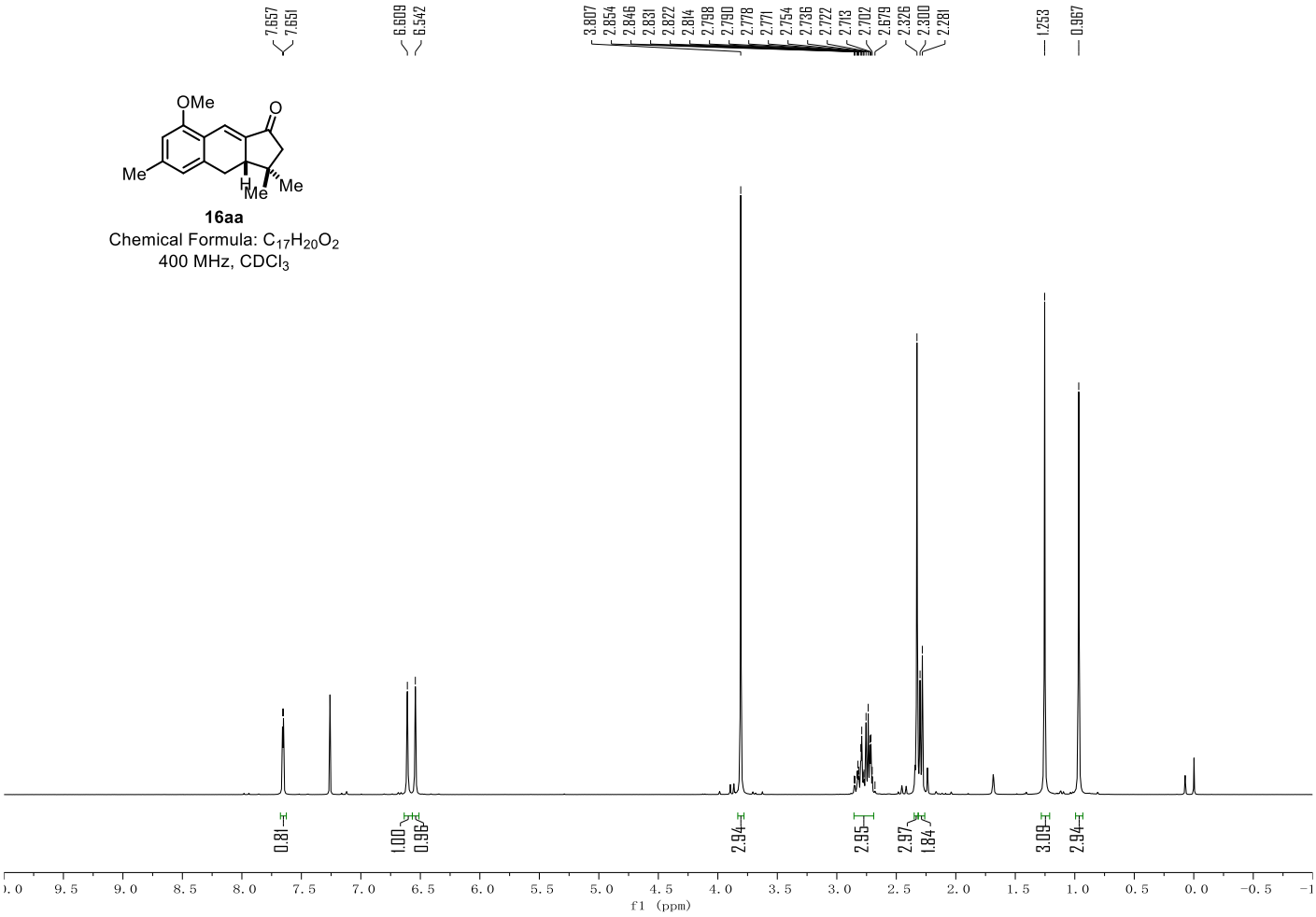
14

Chemical Formula: $C_{29}H_{30}O_7S$
400 MHz, $CDCl_3$

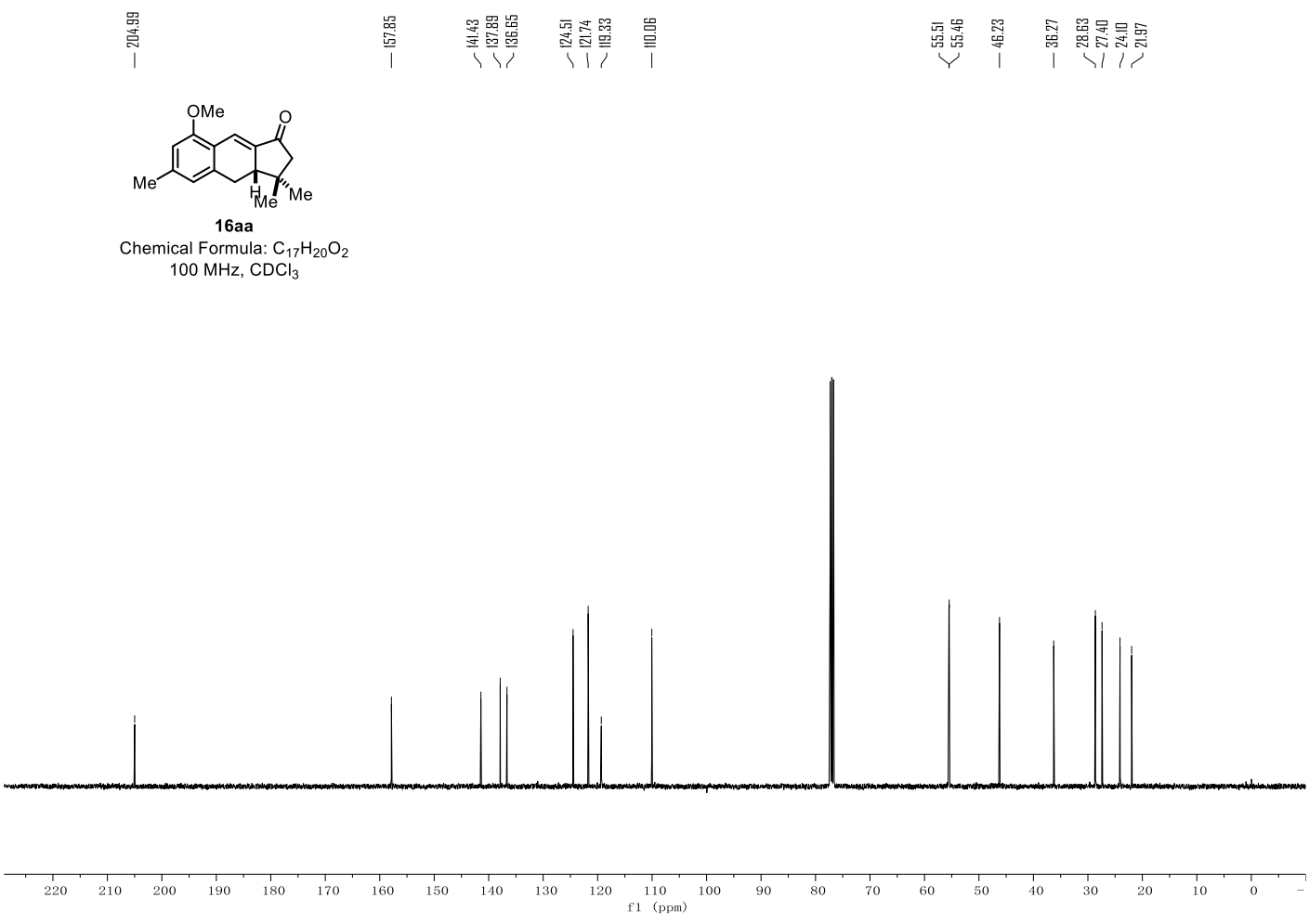


14

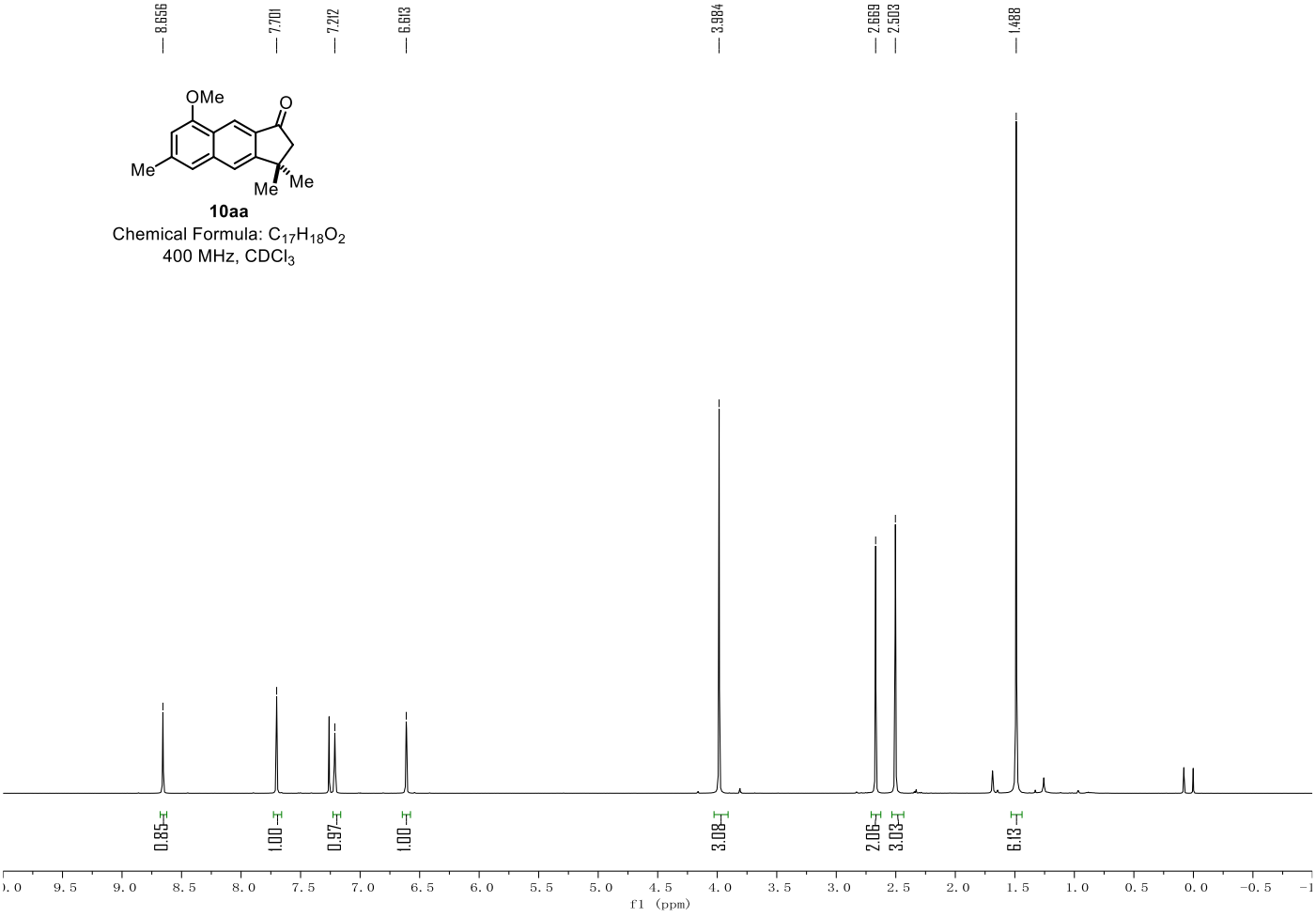
Chemical Formula: $C_{29}H_{30}O_7S$
100 MHz, $CDCl_3$



16aa
Chemical Formula: $C_{17}H_{20}O_2$
400 MHz, $CDCl_3$



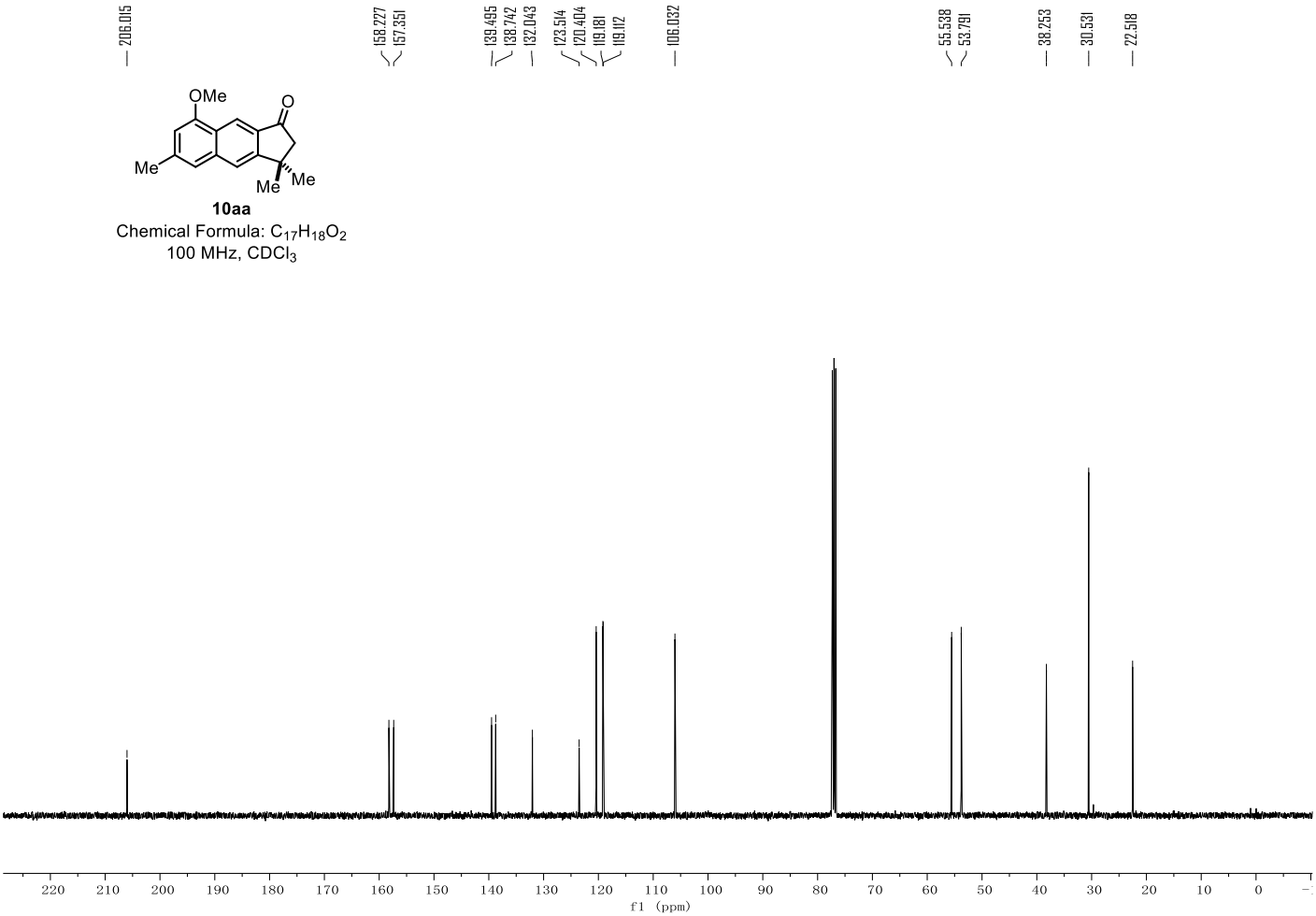
16aa
Chemical Formula: $C_{17}H_{20}O_2$
100 MHz, $CDCl_3$



10aa

Chemical Formula: $C_{17}H_{18}O_2$

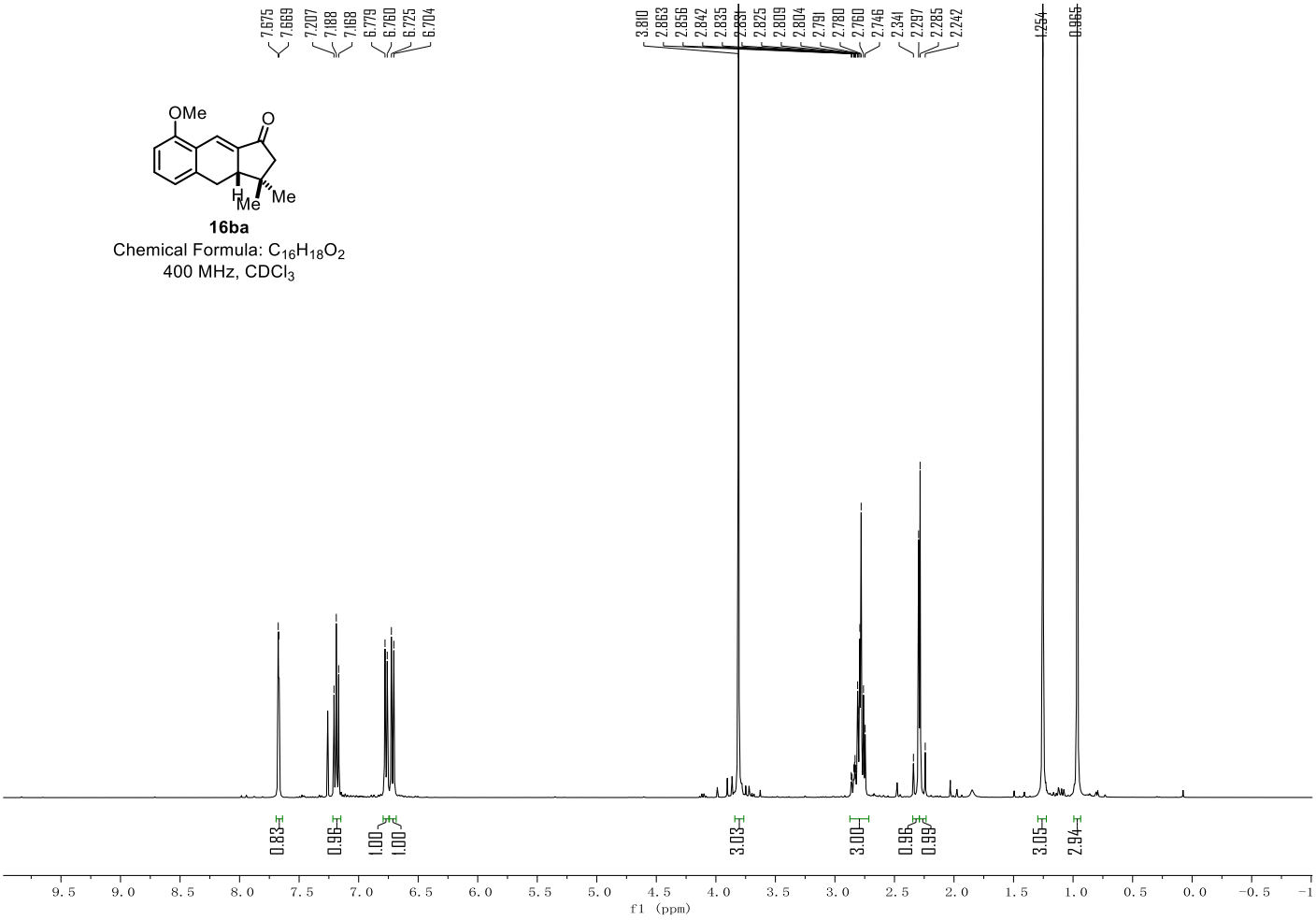
400 MHz, $CDCl_3$



10aa

Chemical Formula: $C_{17}H_{18}O_2$

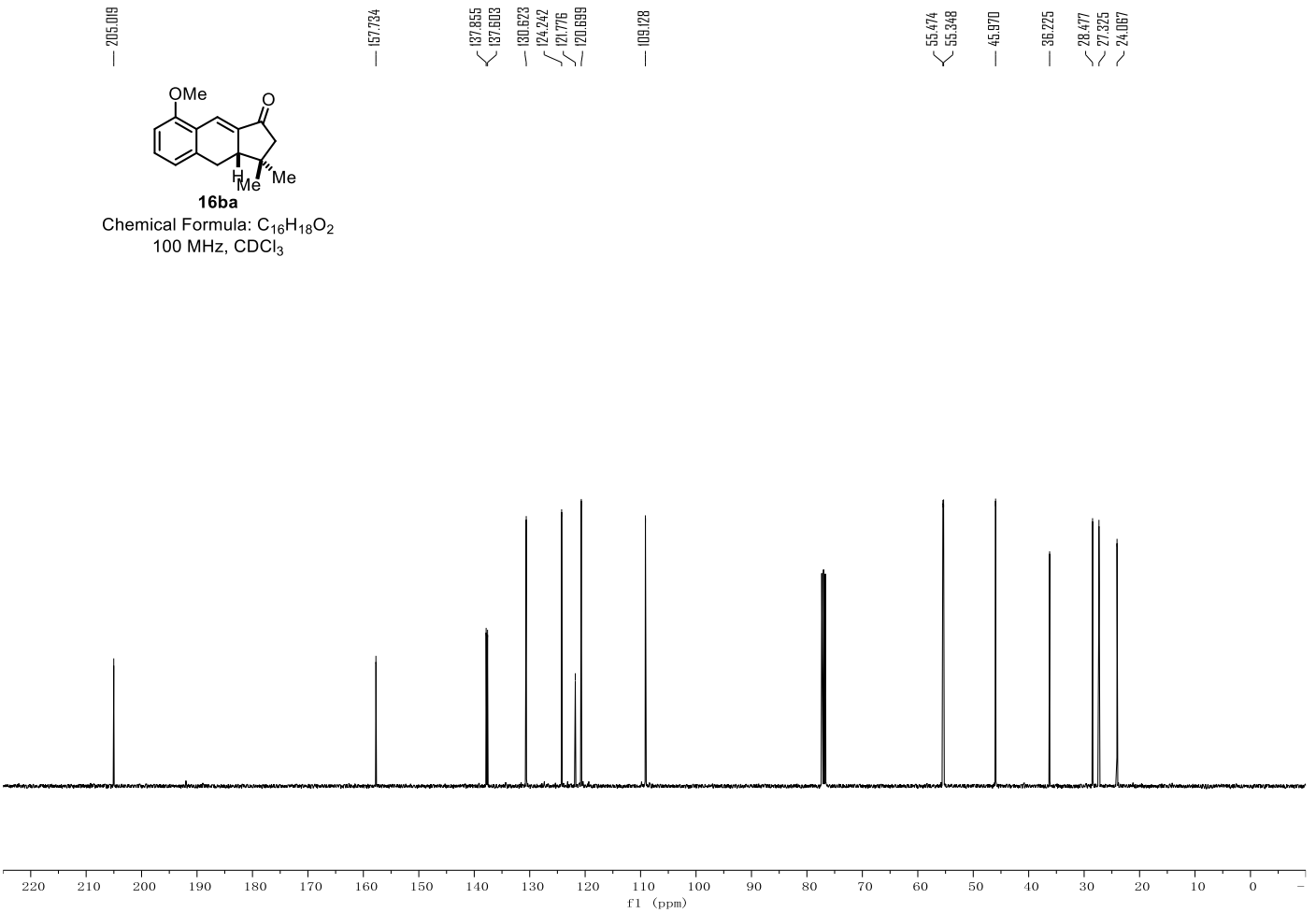
100 MHz, $CDCl_3$



16ba

Chemical Formula: $C_{16}H_{18}O_2$

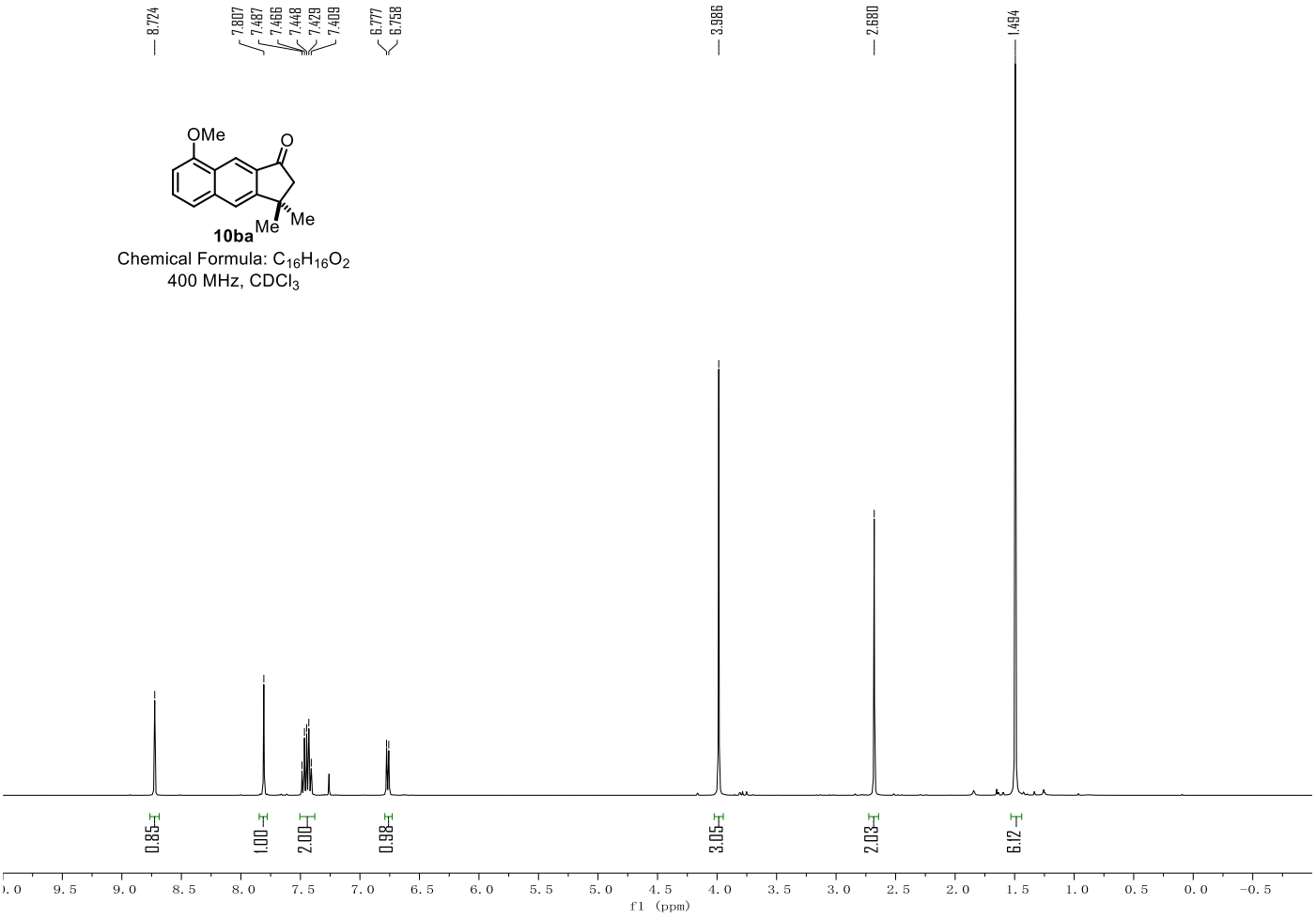
400 MHz, $CDCl_3$



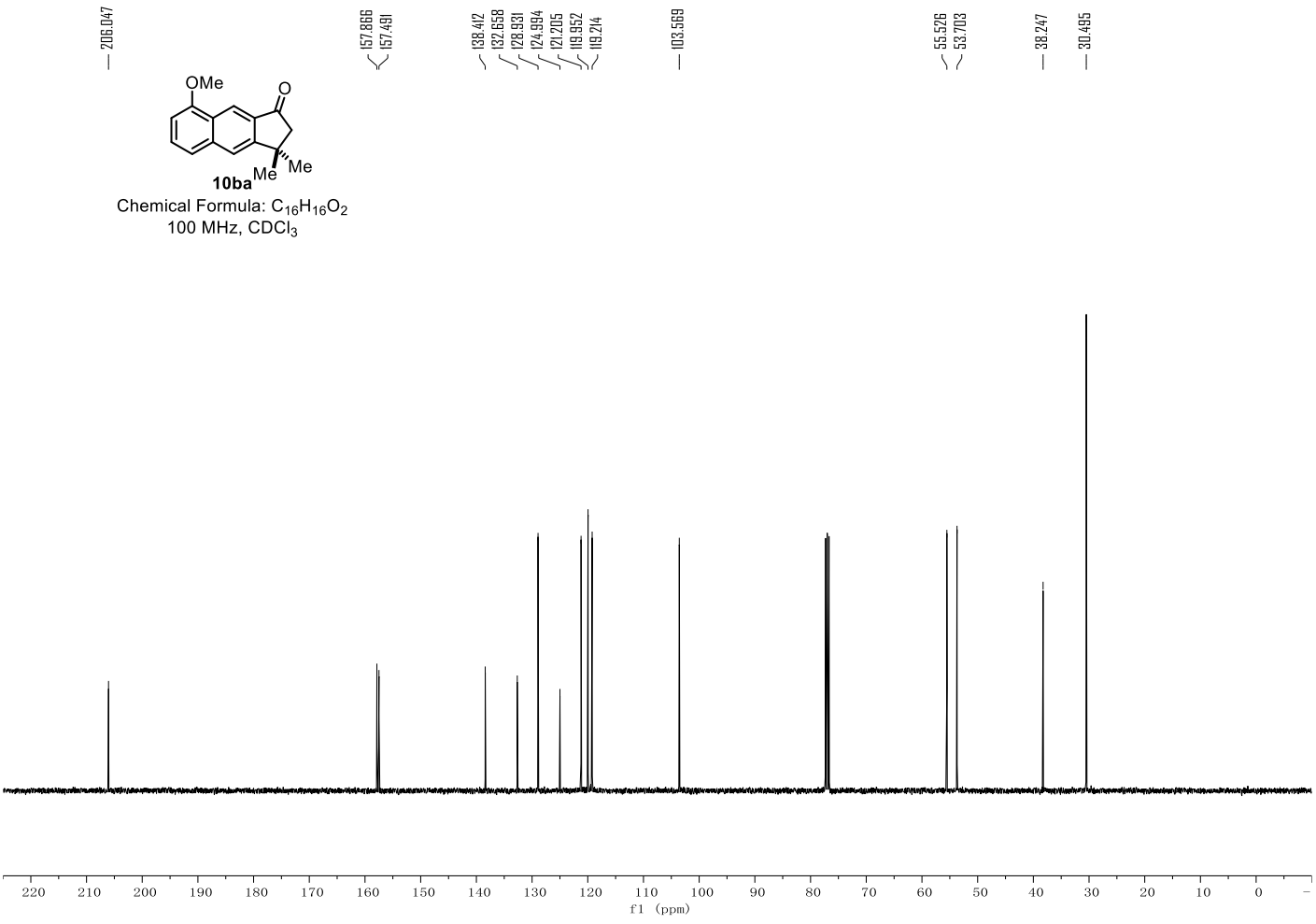
16ba

Chemical Formula: $C_{16}H_{18}O_2$

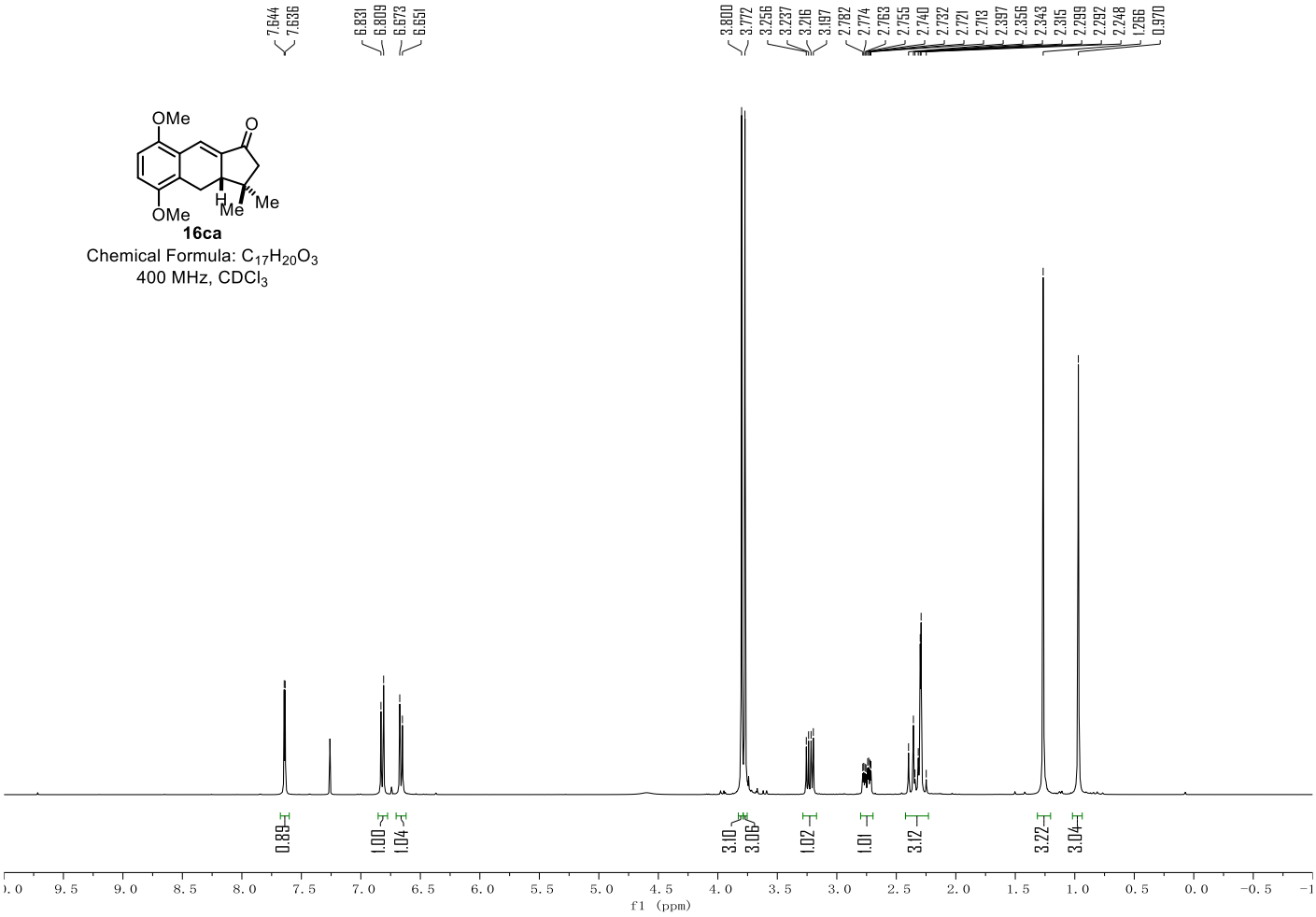
100 MHz, $CDCl_3$

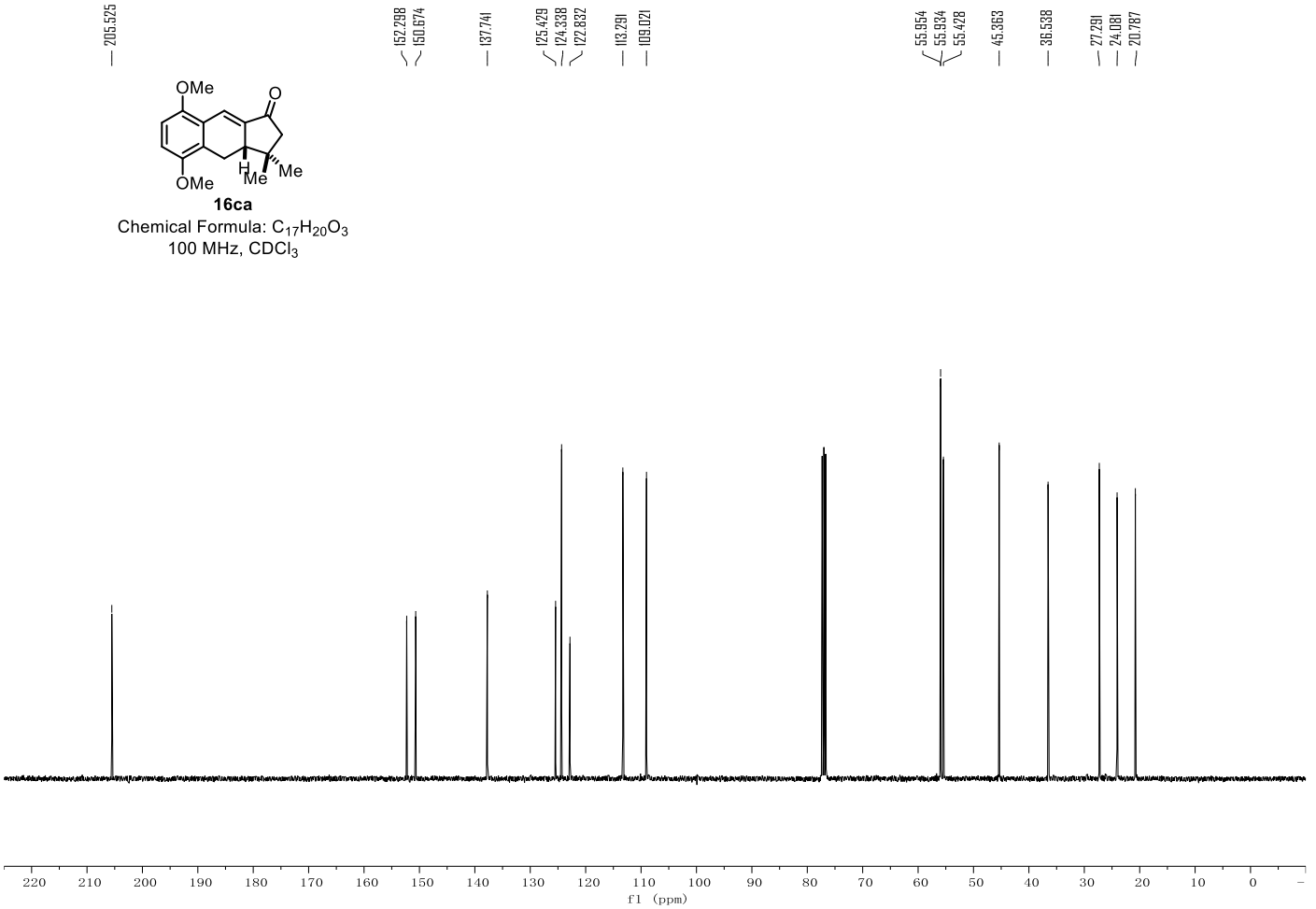


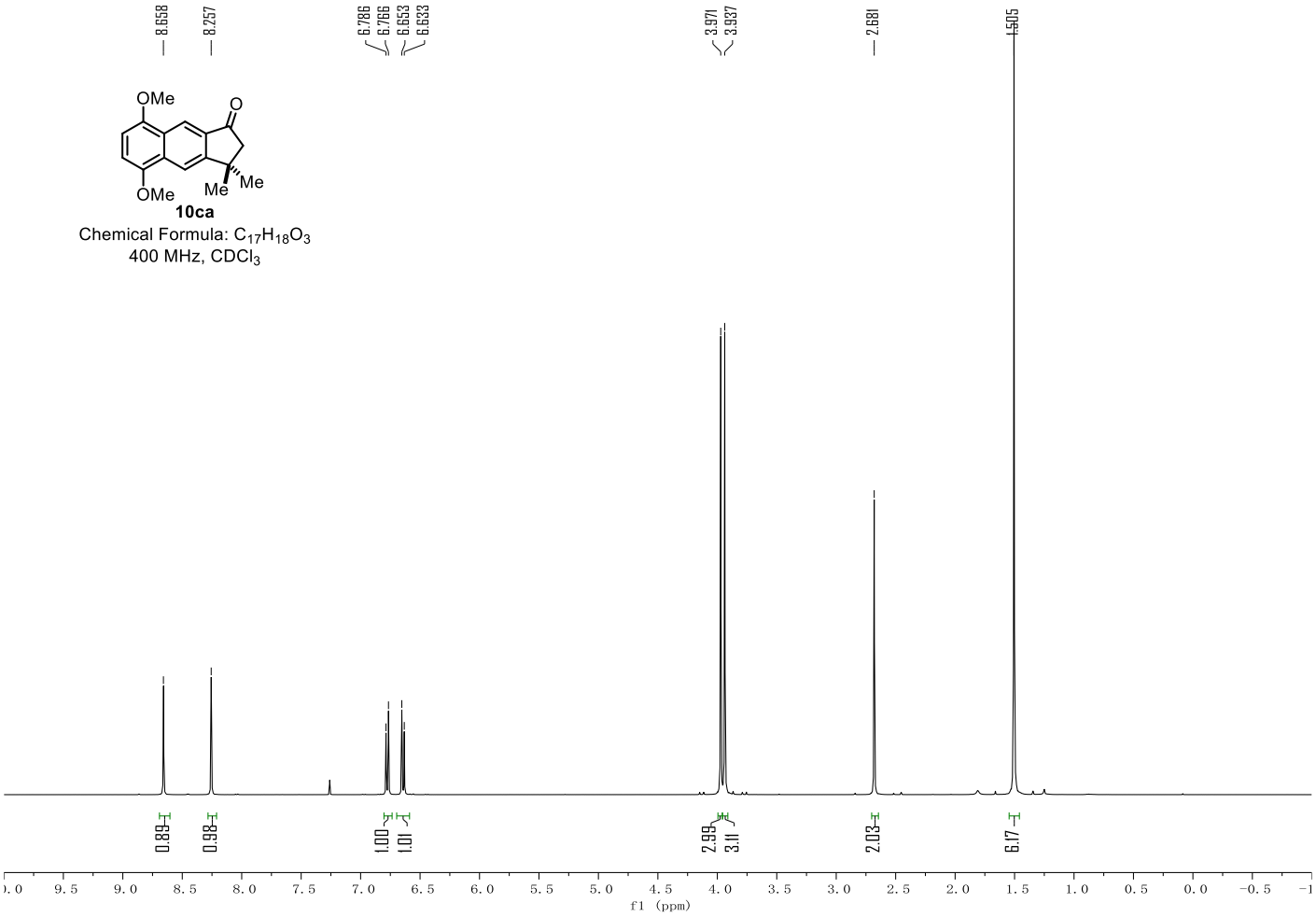
Chemical Formula: $C_{16}H_{16}O_2$
400 MHz, $CDCl_3$

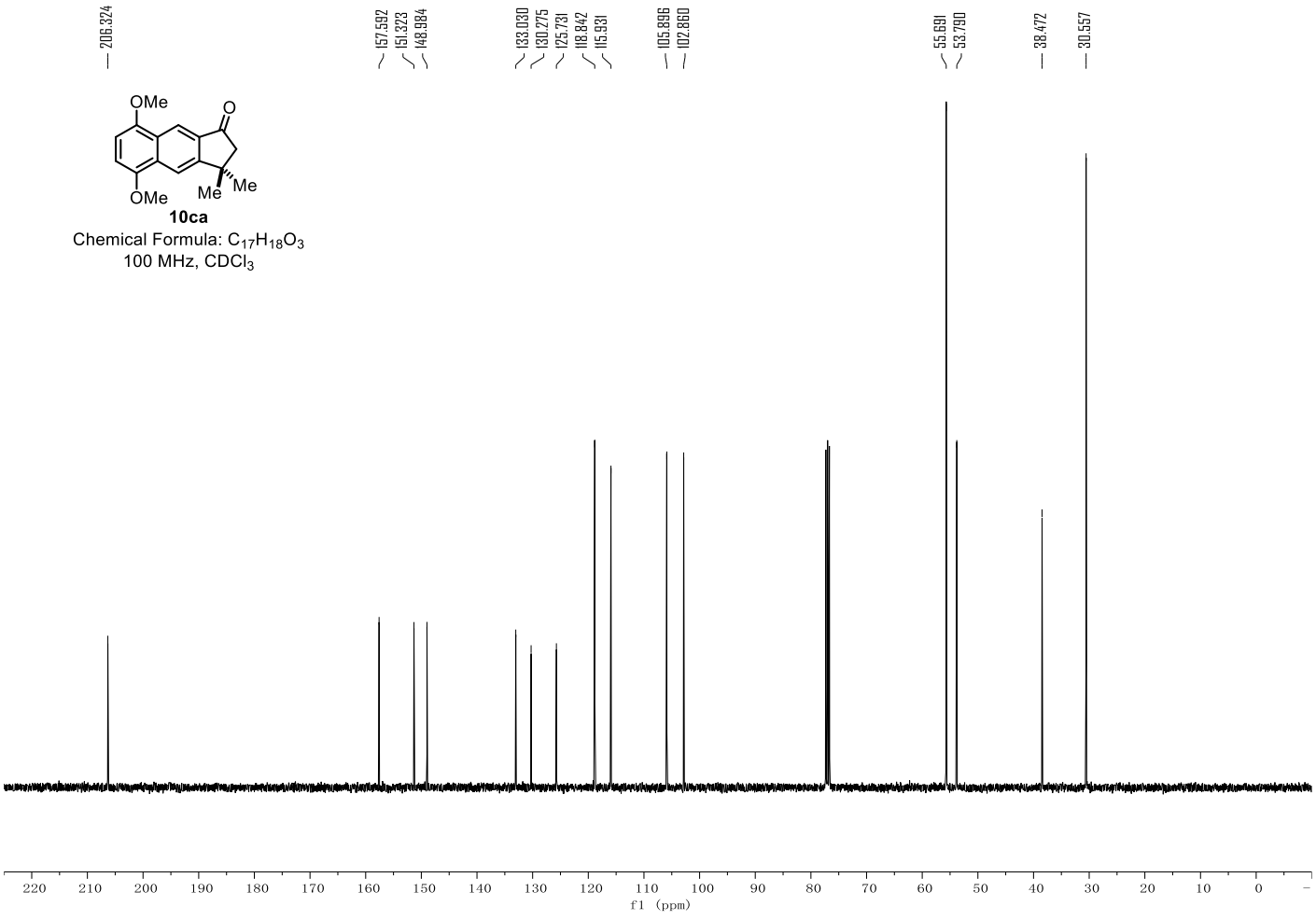


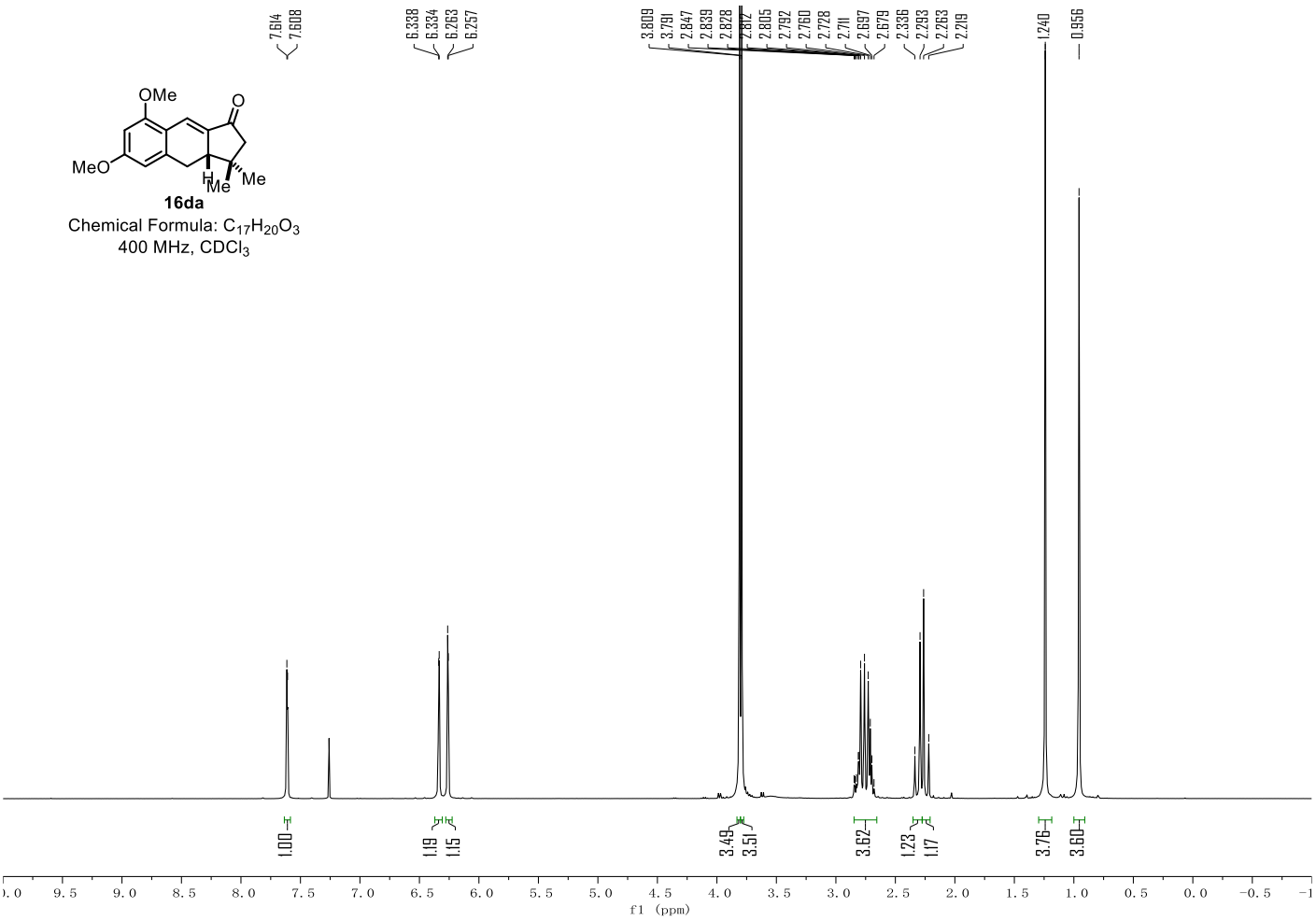
Chemical Formula: $C_{16}H_{16}O_2$
100 MHz, $CDCl_3$


7.644
7.636
6.831
6.809
6.673
6.651
3.800
3.772
3.256
3.237
3.216
3.197
2.782
2.774
2.763
2.755
2.740
2.732
2.721
2.713
2.397
2.356
2.343
2.315
2.299
2.292
2.248
1.266
0.970
OMe
O
OMe
H
Me
Me
16ca
Chemical Formula: C17H20O3
400 MHz, CDCl3
0.89
1.00
1.04
3.10
3.06
1.02
1.01
3.12
3.22
3.04
f1 (ppm)


205.525
152.298
150.674
137.741
125.429
124.338
122.832
113.291
109.021
55.954
55.934
55.428
45.363
38.538
27.291
24.081
20.787
OMe
O
OMe
H
Me
Me
16ca
Chemical Formula: C17H20O3
100 MHz, CDCl3
f1 (ppm)


8.658
8.257
6.788
6.766
6.653
6.633
3.971
3.937
2.681
1.505
OMe
O
OMe
Me
Me
10ca
Chemical Formula: C17H18O3
400 MHz, CDCl3
0.89
0.98
1.00
1.01
2.99
3.11
2.03
6.17
f1 (ppm)

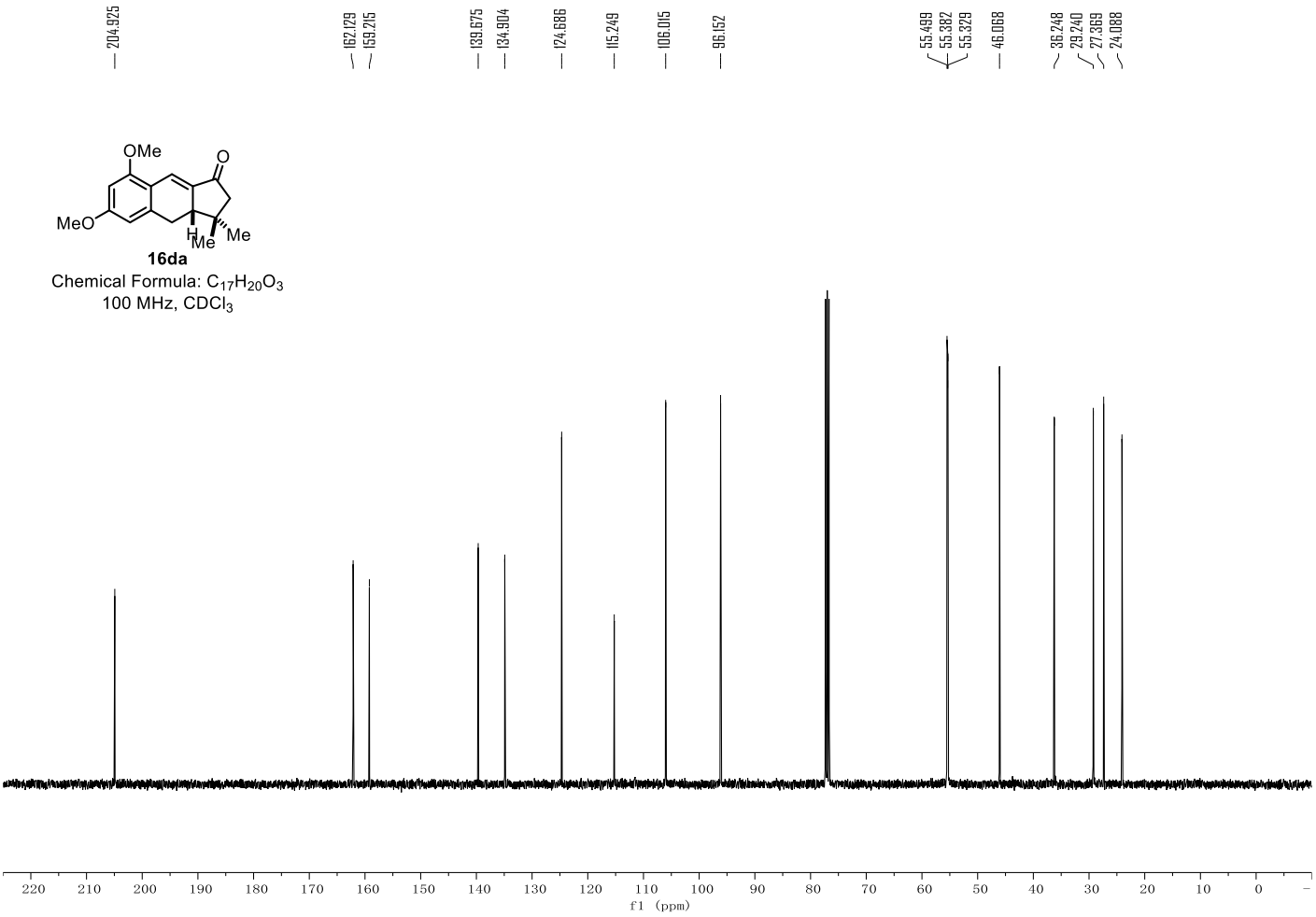

206.324
157.592
151.323
148.984
133.030
130.275
125.731
118.842
115.931
105.896
102.860
55.691
53.790
38.472
30.557
OMe
O
OMe
Me
Me
10ca
Chemical Formula: C17H18O3
100 MHz, CDCl3
f1 (ppm)



16da

Chemical Formula: $C_{17}H_{20}O_3$

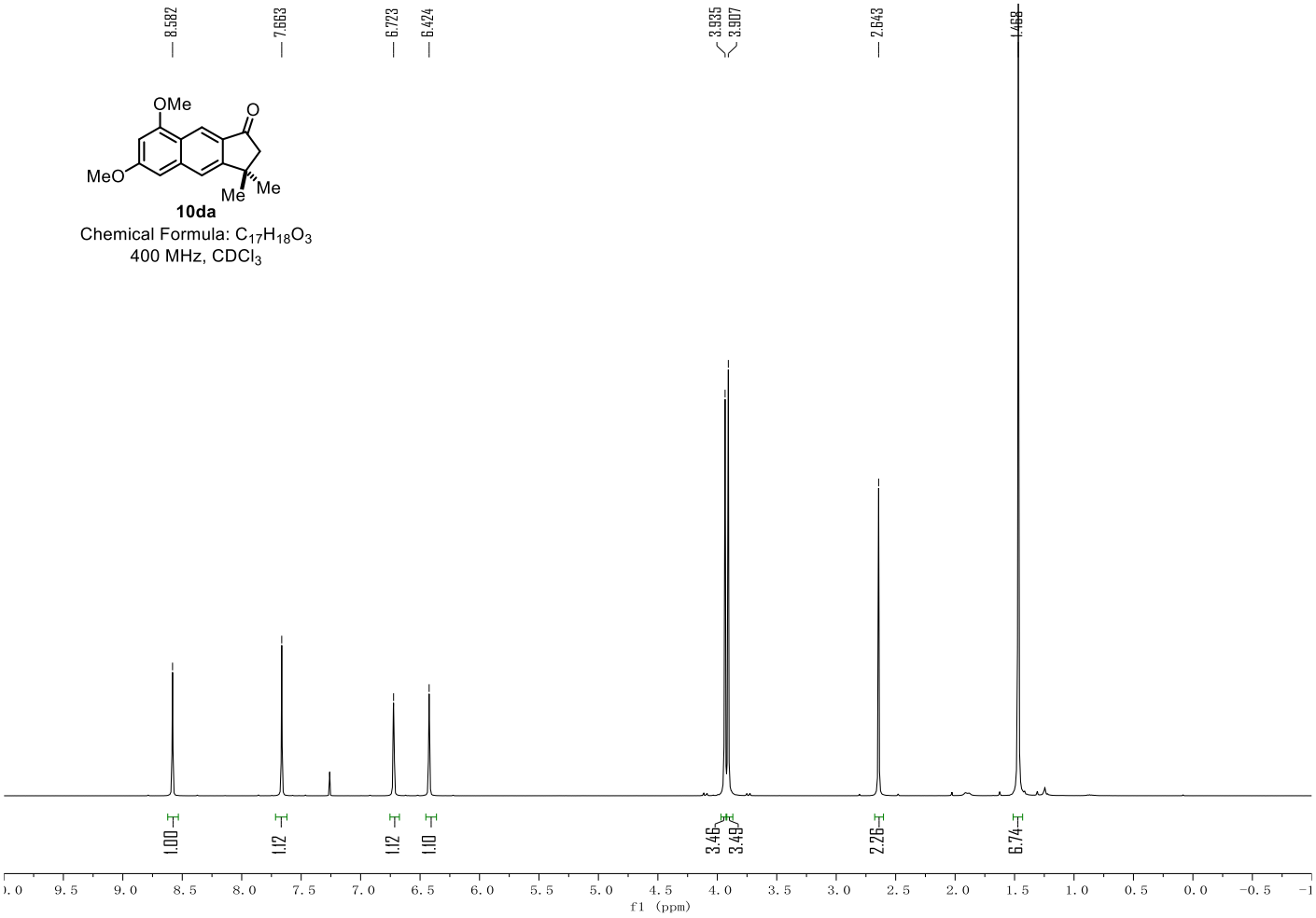
400 MHz, $CDCl_3$

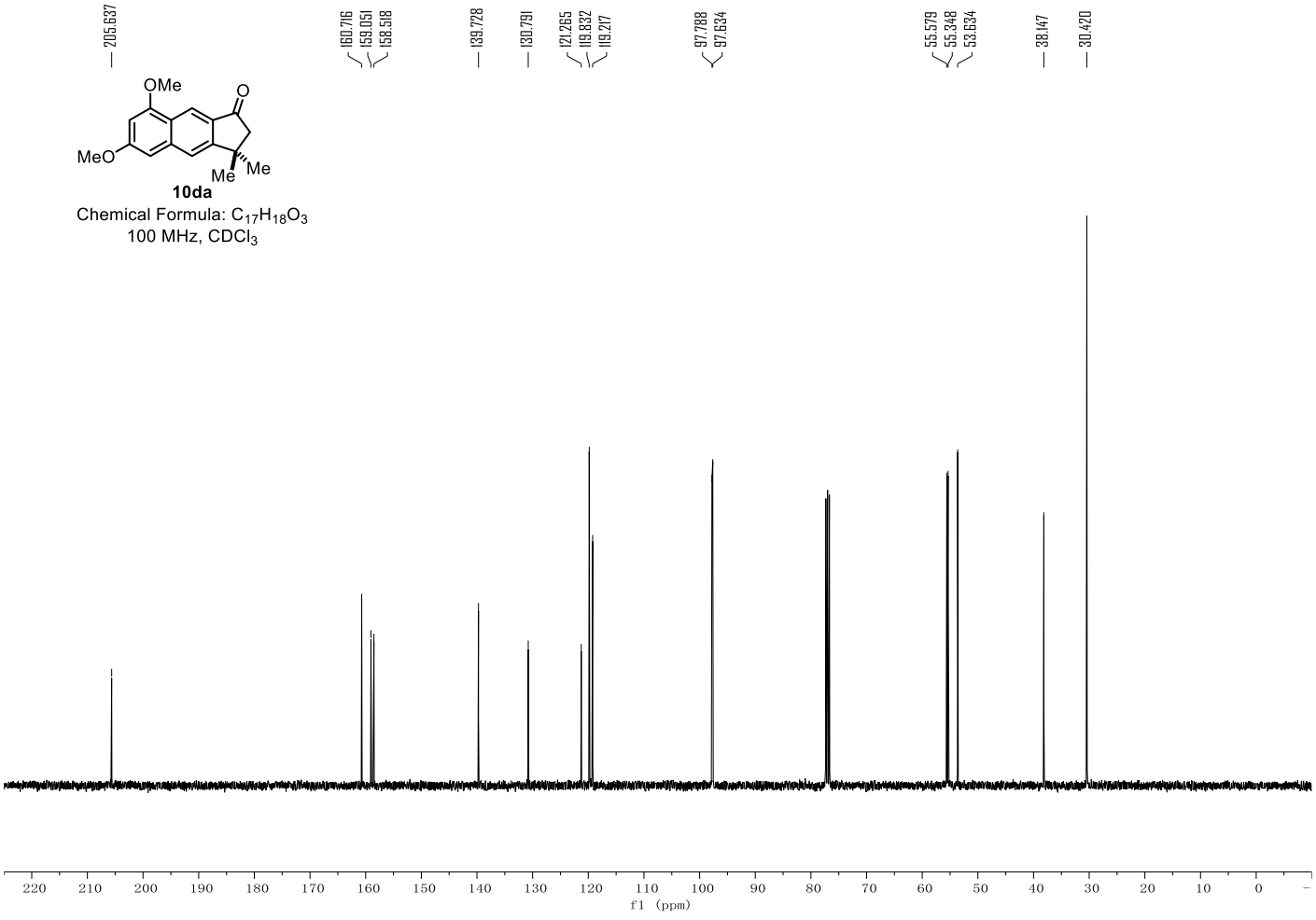


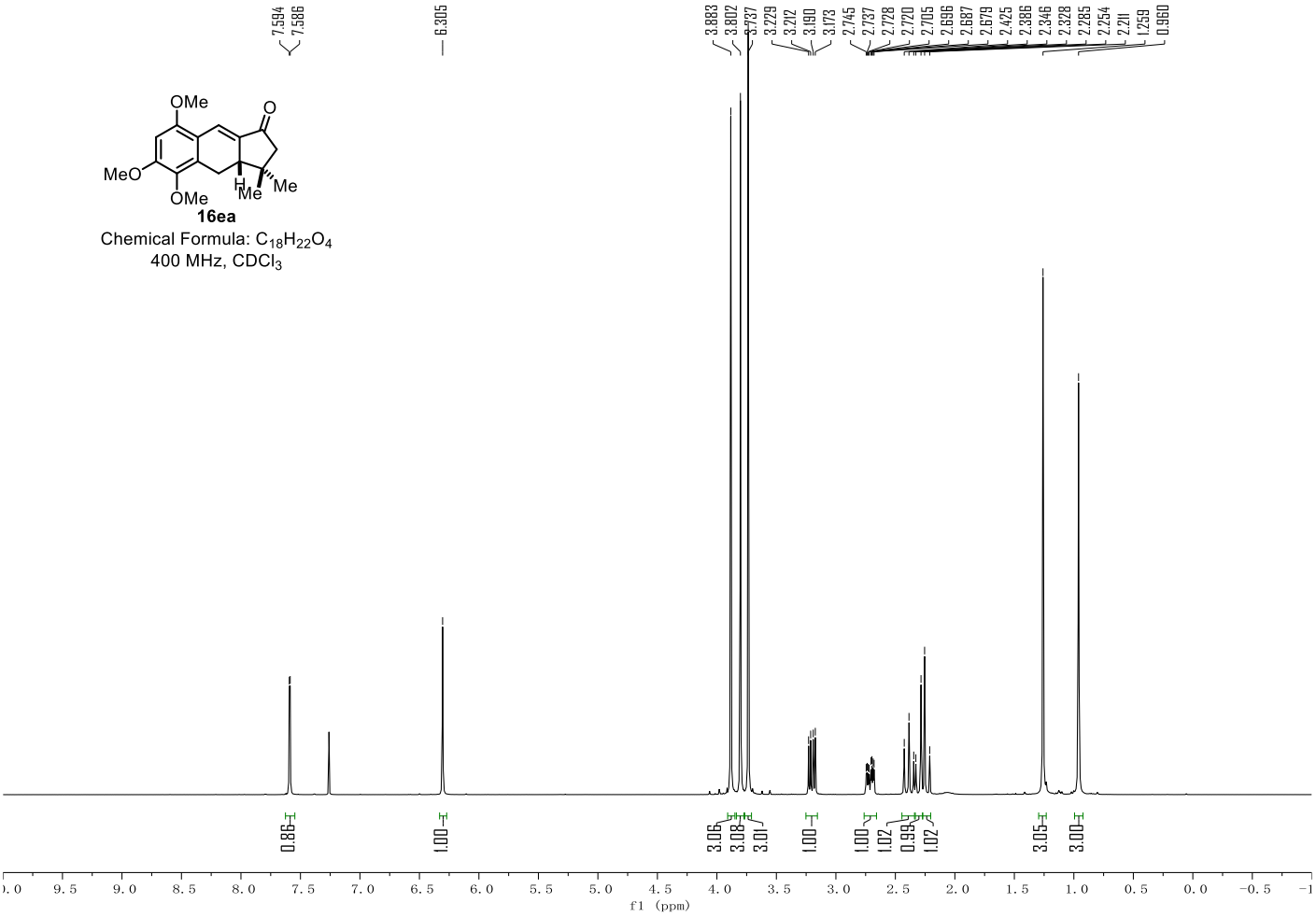
16da

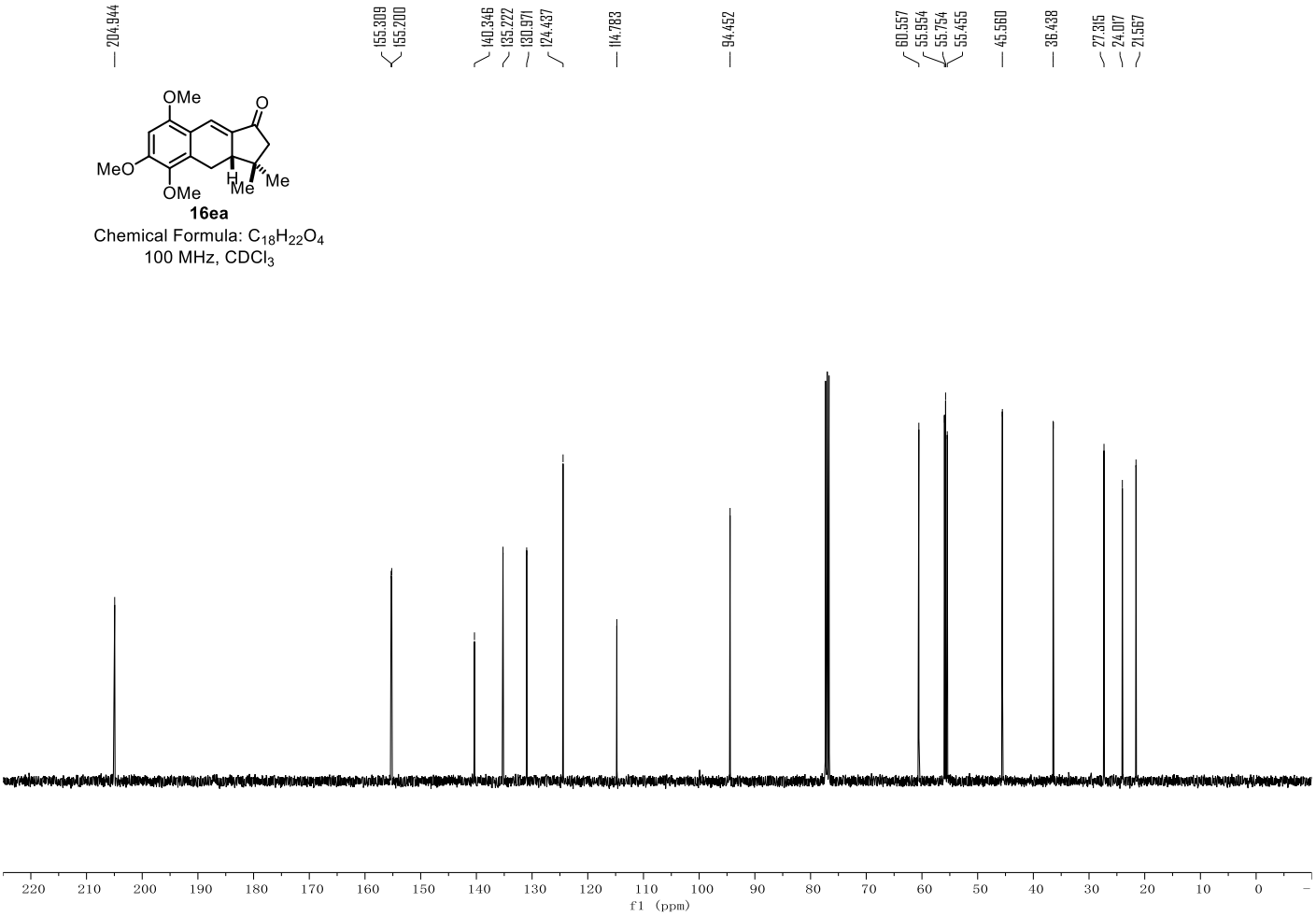
Chemical Formula: $C_{17}H_{20}O_3$

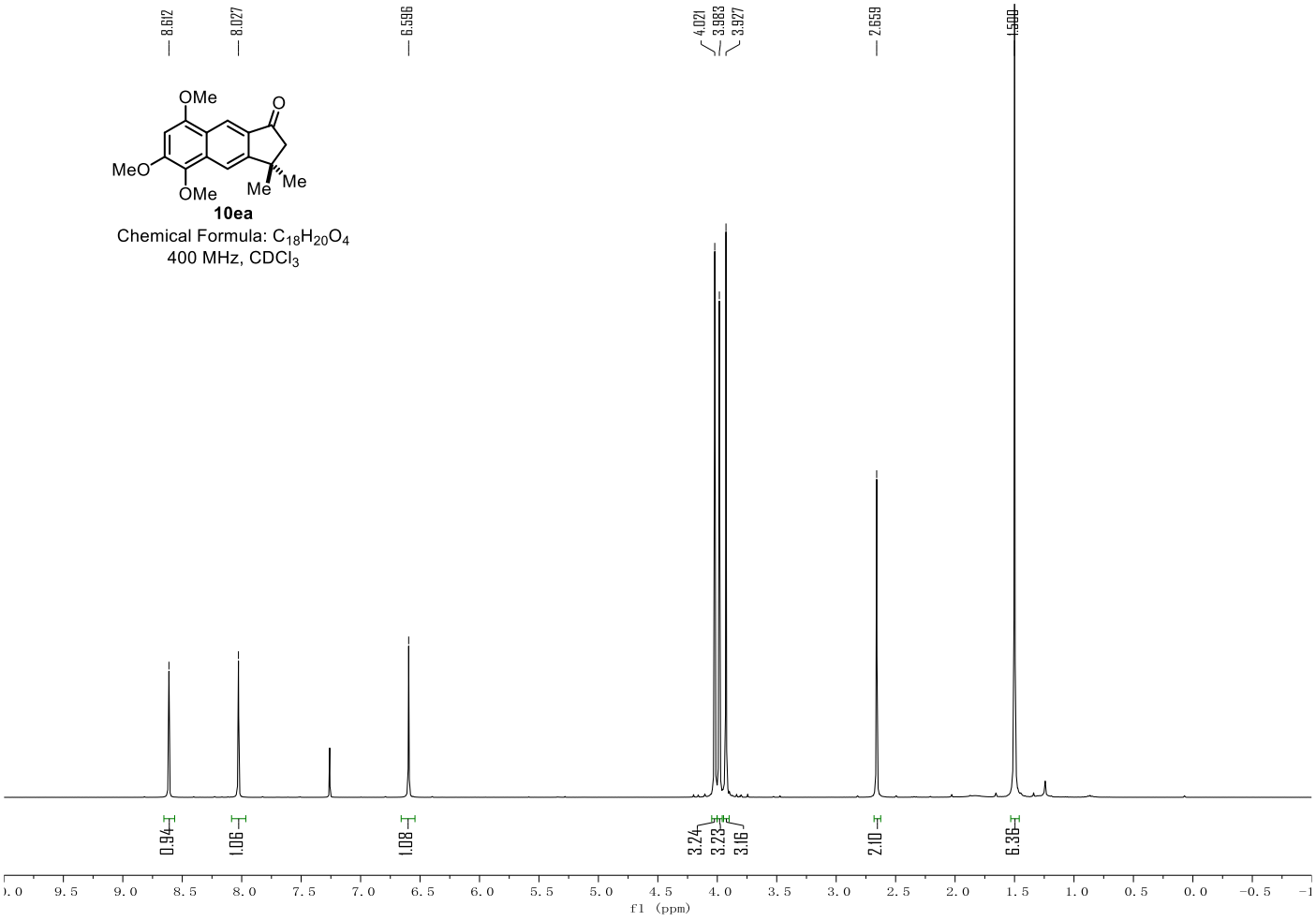
100 MHz, $CDCl_3$

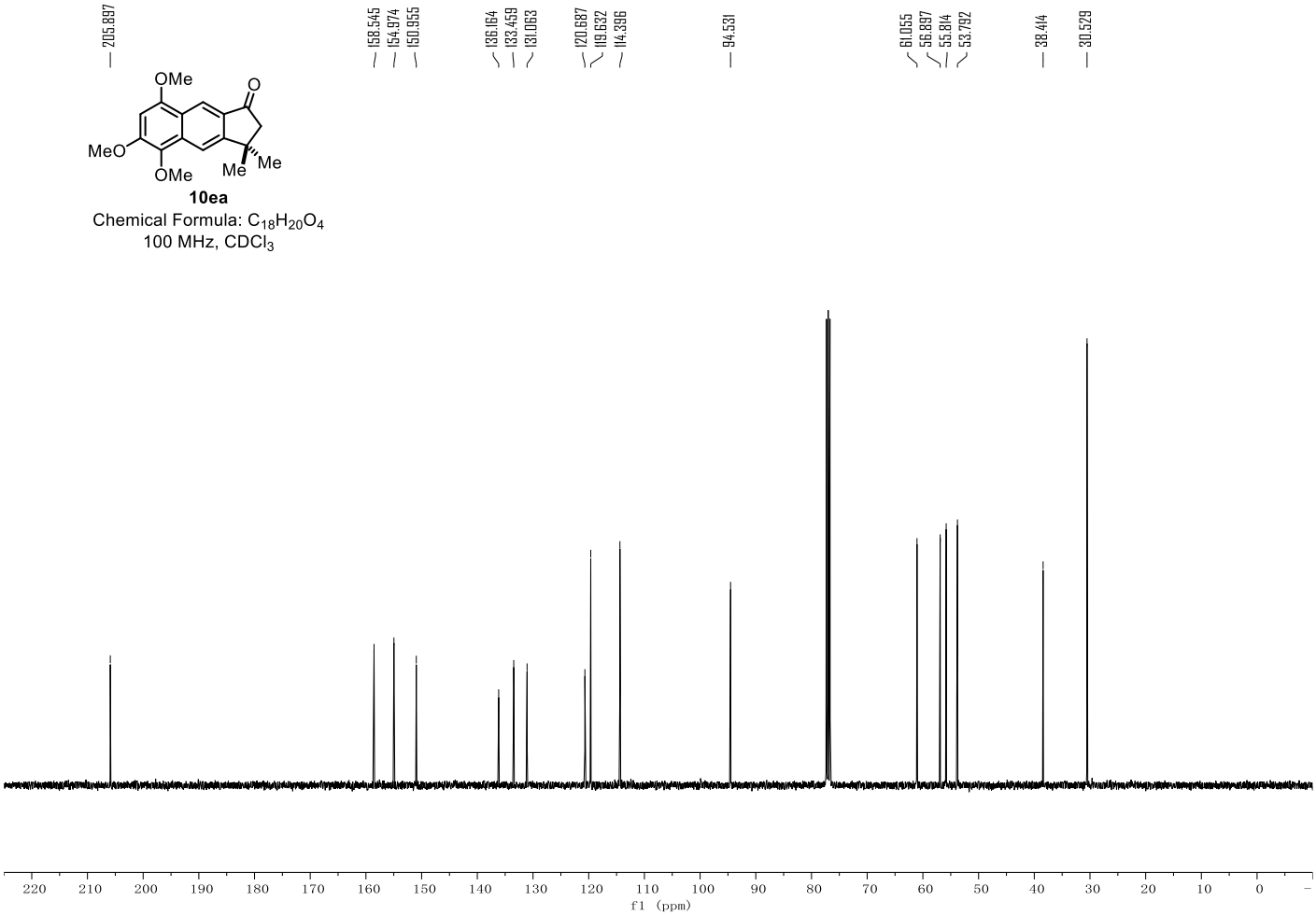

8.582
7.663
6.723
6.424
3.935
3.907
2.643
1.468
OMe
O
MeO
Me
Me
10da
Chemical Formula: C17H18O3
400 MHz, CDCl3
1.00
1.12
1.12
1.10
3.46
3.49
2.26
6.74
f1 (ppm)

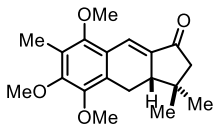

205.637
160.716
159.051
158.518
139.728
130.791
121.265
119.832
119.217
97.788
97.634
55.579
55.348
53.634
38.147
30.420
OMe
O
MeO
Me
Me
10da
Chemical Formula: C17H18O3
100 MHz, CDCl3
f1 (ppm)


7.594
7.586
6.305
3.883
3.802
3.737
3.229
3.212
3.190
3.173
2.745
2.737
2.728
2.720
2.705
2.696
2.687
2.679
2.425
2.386
2.346
2.328
2.285
2.254
2.211
1.259
0.960
OMe
O
MeO
OMe
H
Me
Me
16ea
Chemical Formula: C18H22O4
400 MHz, CDCl3
0.86
1.00
3.06
3.08
3.01
1.00
1.00
1.02
0.99
1.02
3.05
3.00
f1 (ppm)


204.944
155.309
155.200
140.346
135.222
130.971
124.437
114.783
94.452
60.557
55.954
55.754
55.455
45.560
36.438
27.315
24.017
21.567
OMe
O
MeO
OMe
H
Me
Me
16ea
Chemical Formula: C18H22O4
100 MHz, CDCl3
f1 (ppm)


8.612
8.027
6.596
4.021
3.983
3.927
2.659
1.500
OMe
O
MeO
OMe
Me
Me
10ea
Chemical Formula: C18H20O4
400 MHz, CDCl3
0.94
1.06
1.08
3.24
3.23
3.16
2.10
6.36
f1 (ppm)

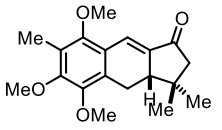

205.897
158.545
154.974
150.955
136.164
133.459
131.063
120.687
119.632
114.396
94.531
61.055
56.897
55.814
53.792
38.414
30.529
OMe
O
MeO
OMe
Me
Me
10ea
Chemical Formula: C18H20O4
100 MHz, CDCl3
f1 (ppm)



16fa

Chemical Formula: $C_{19}H_{24}O_4$

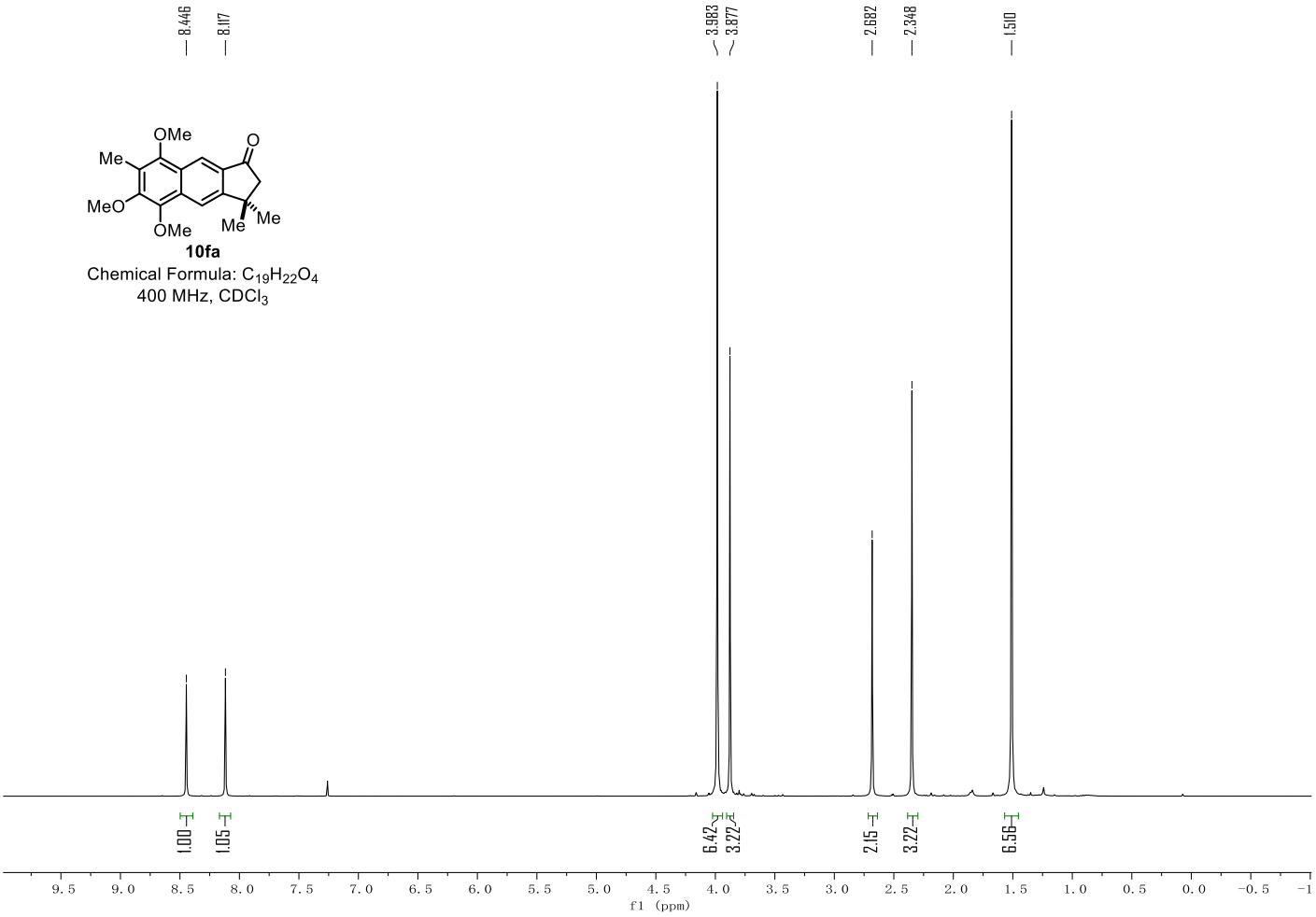
400 MHz, $CDCl_3$

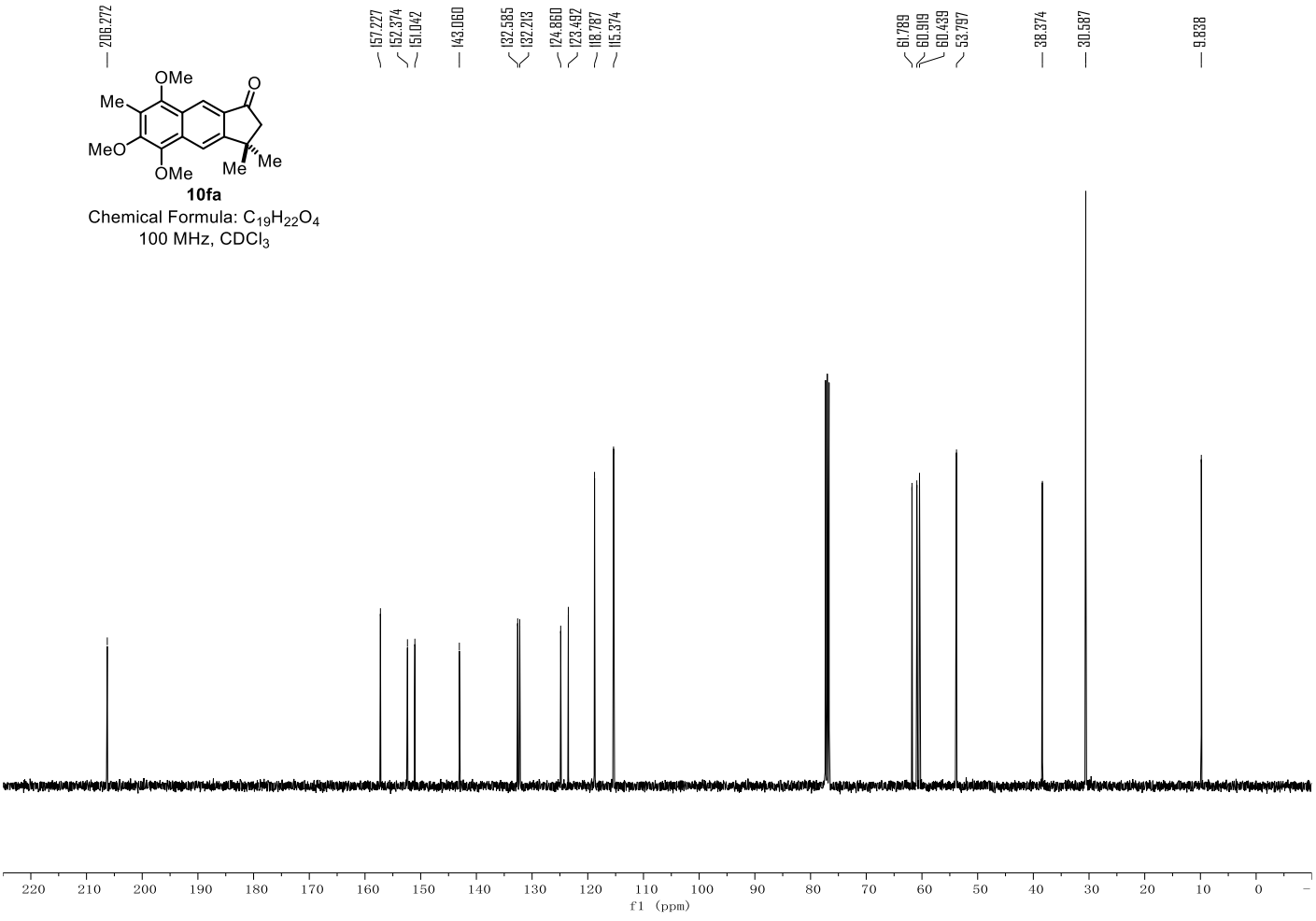


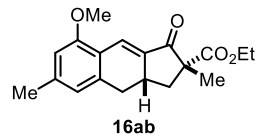
16fa

Chemical Formula: $C_{19}H_{24}O_4$

100 MHz, $CDCl_3$


8.446
8.117
3.983
3.877
2.682
2.348
1.510
OMe
Me
MeO
OMe
O
Me
Me
10fa
Chemical Formula: C19H22O4
400 MHz, CDCl3
1.00
1.05
6.42
3.22
2.15
3.22
6.56
f1 (ppm)

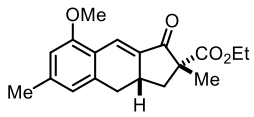

206.272
157.227
152.374
151.042
143.060
132.585
132.213
124.860
123.492
118.787
115.374
61.789
60.918
60.439
53.797
38.374
30.587
9.838
OMe
Me
MeO
OMe
O
Me
Me
10fa
Chemical Formula: C19H22O4
100 MHz, CDCl3
f1 (ppm)



16ab

Chemical Formula: $C_{19}H_{22}O_4$

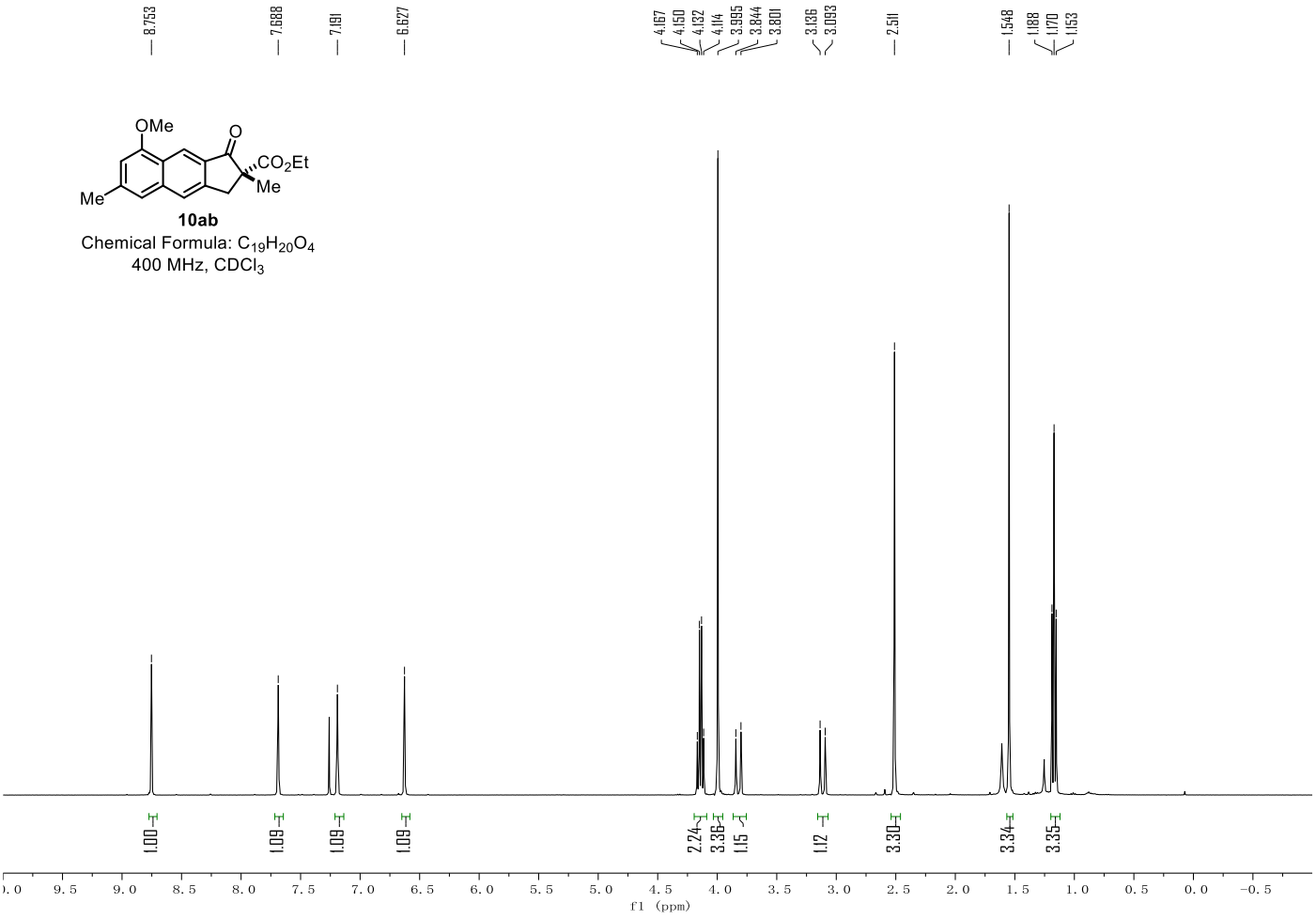
400 MHz, $CDCl_3$

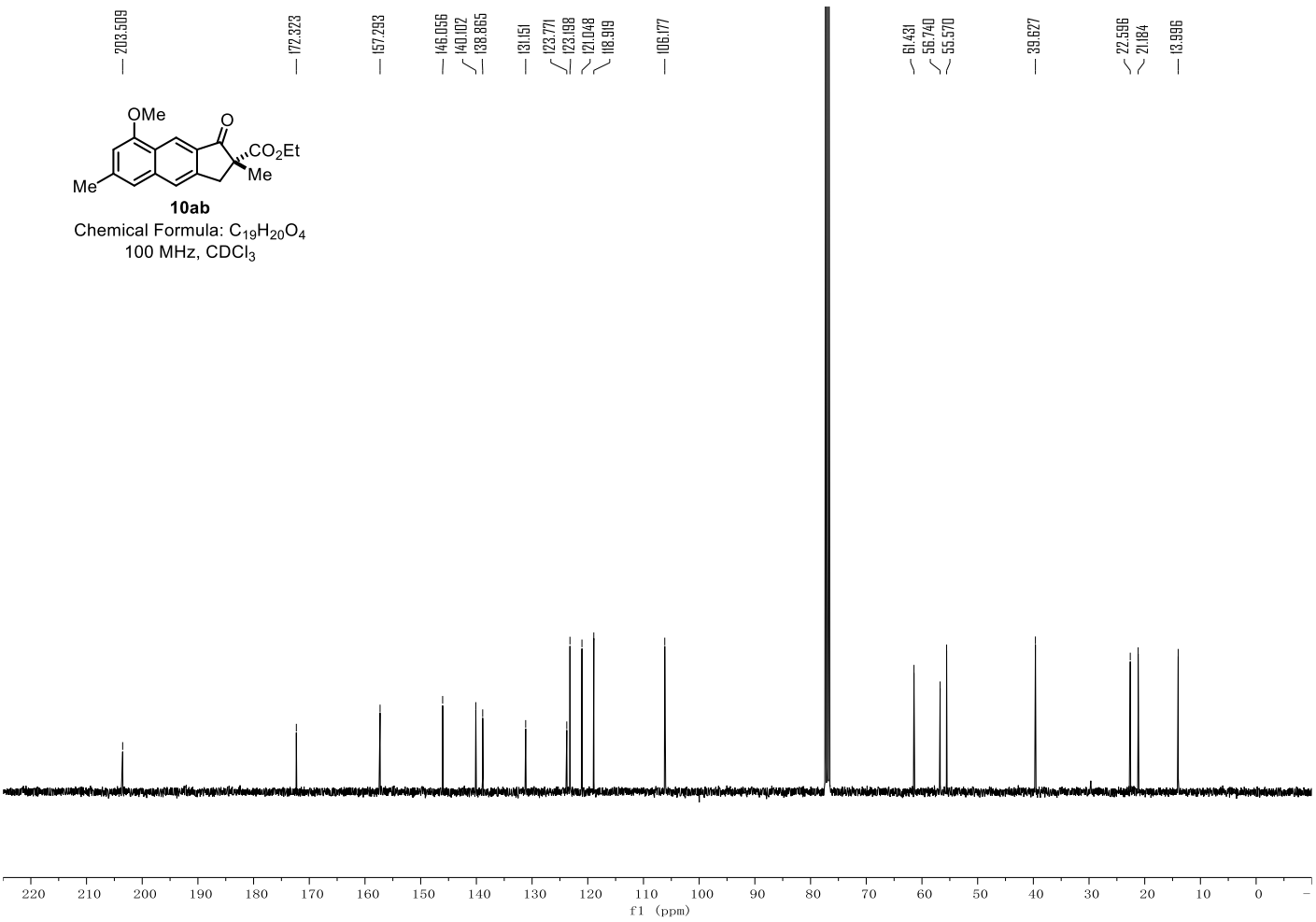


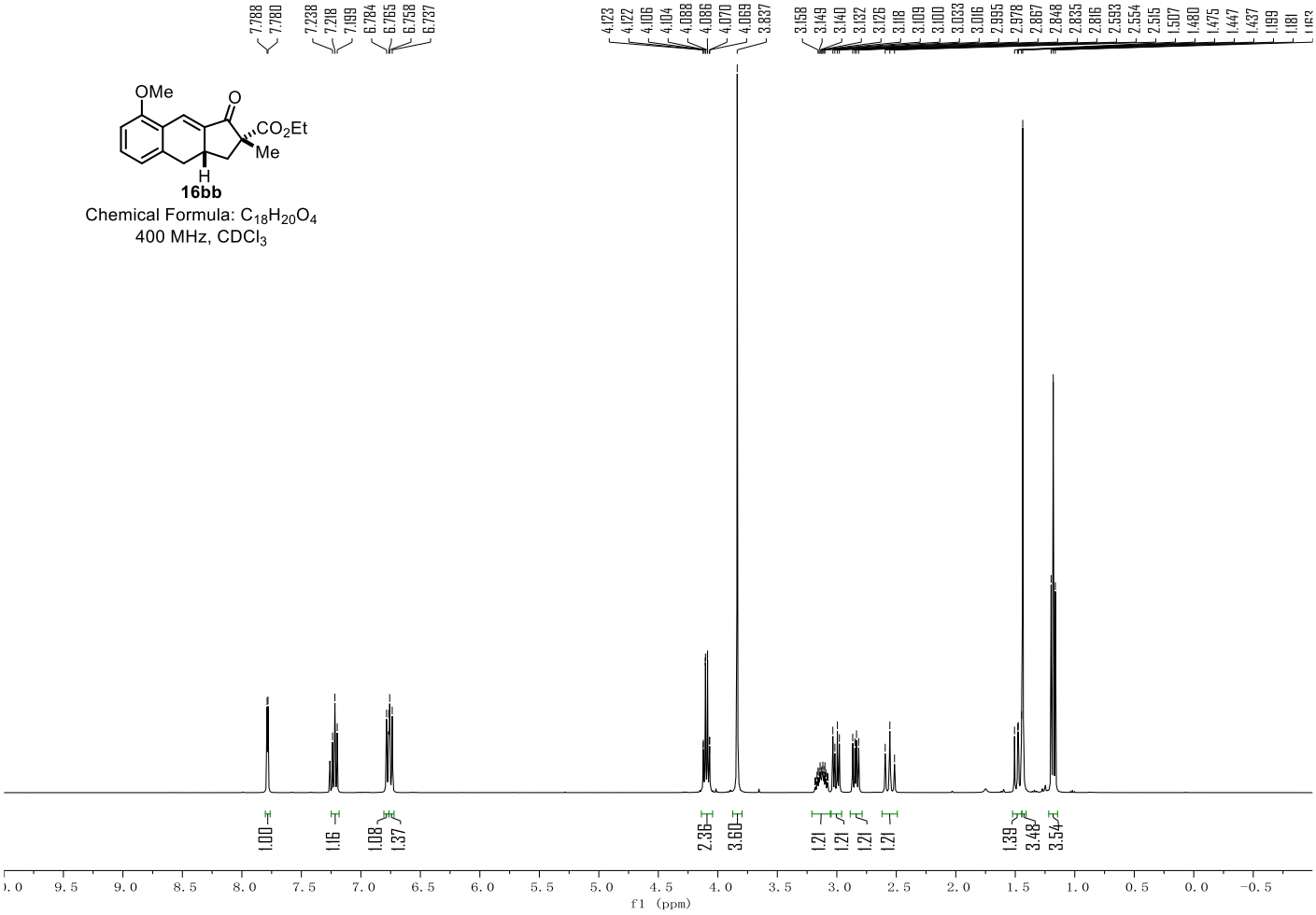
16ab

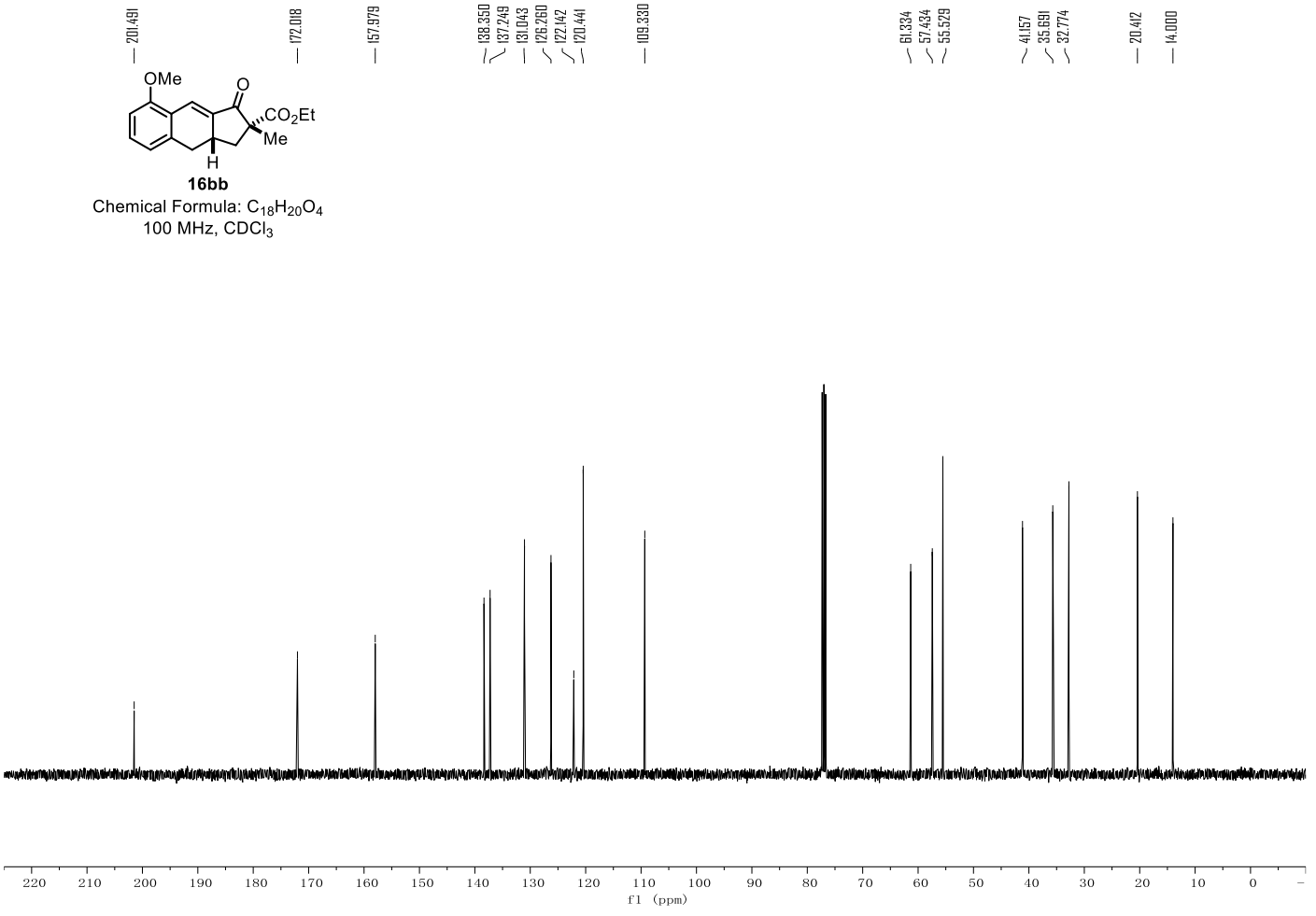
Chemical Formula: $C_{19}H_{22}O_4$

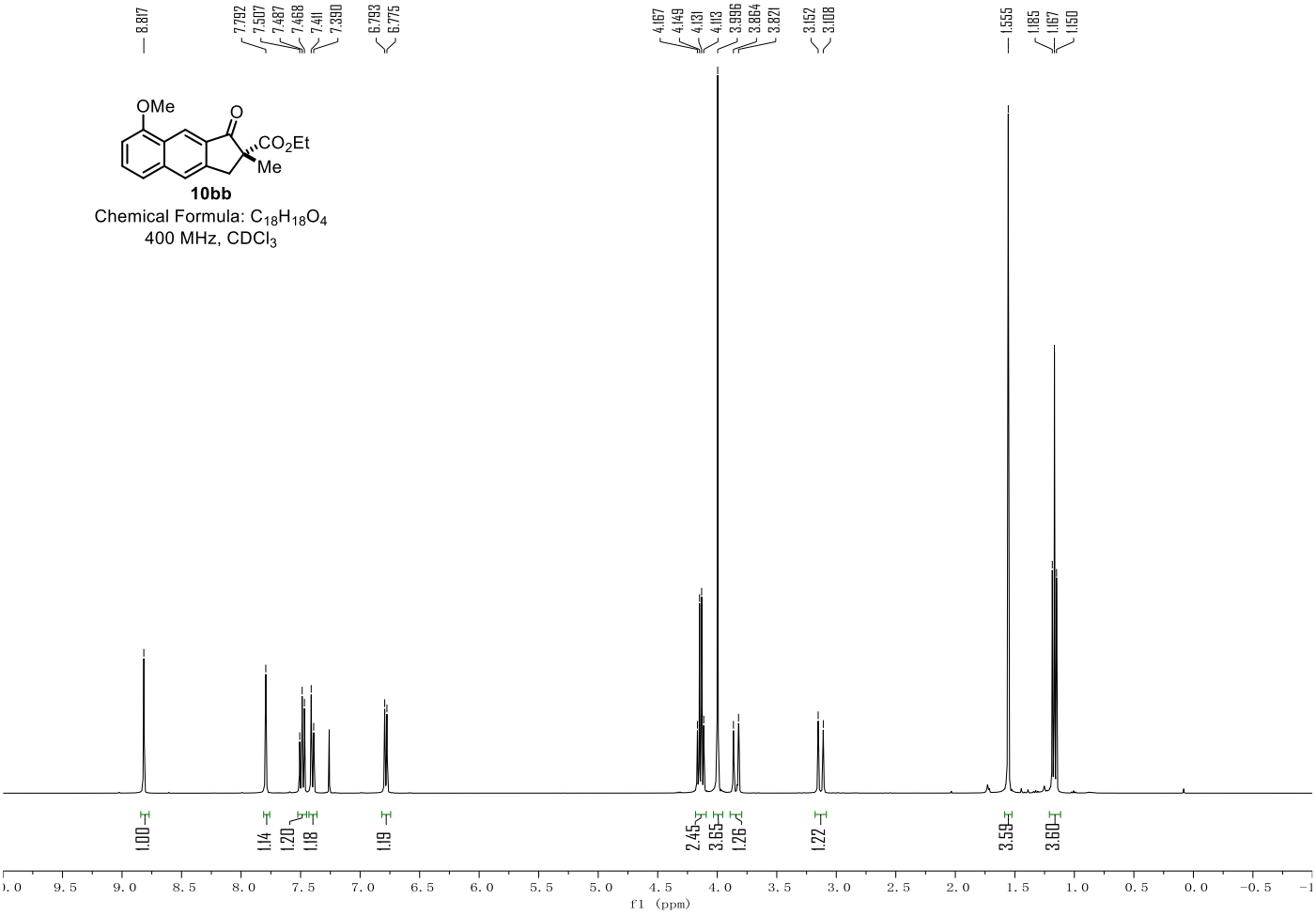
100 MHz, $CDCl_3$

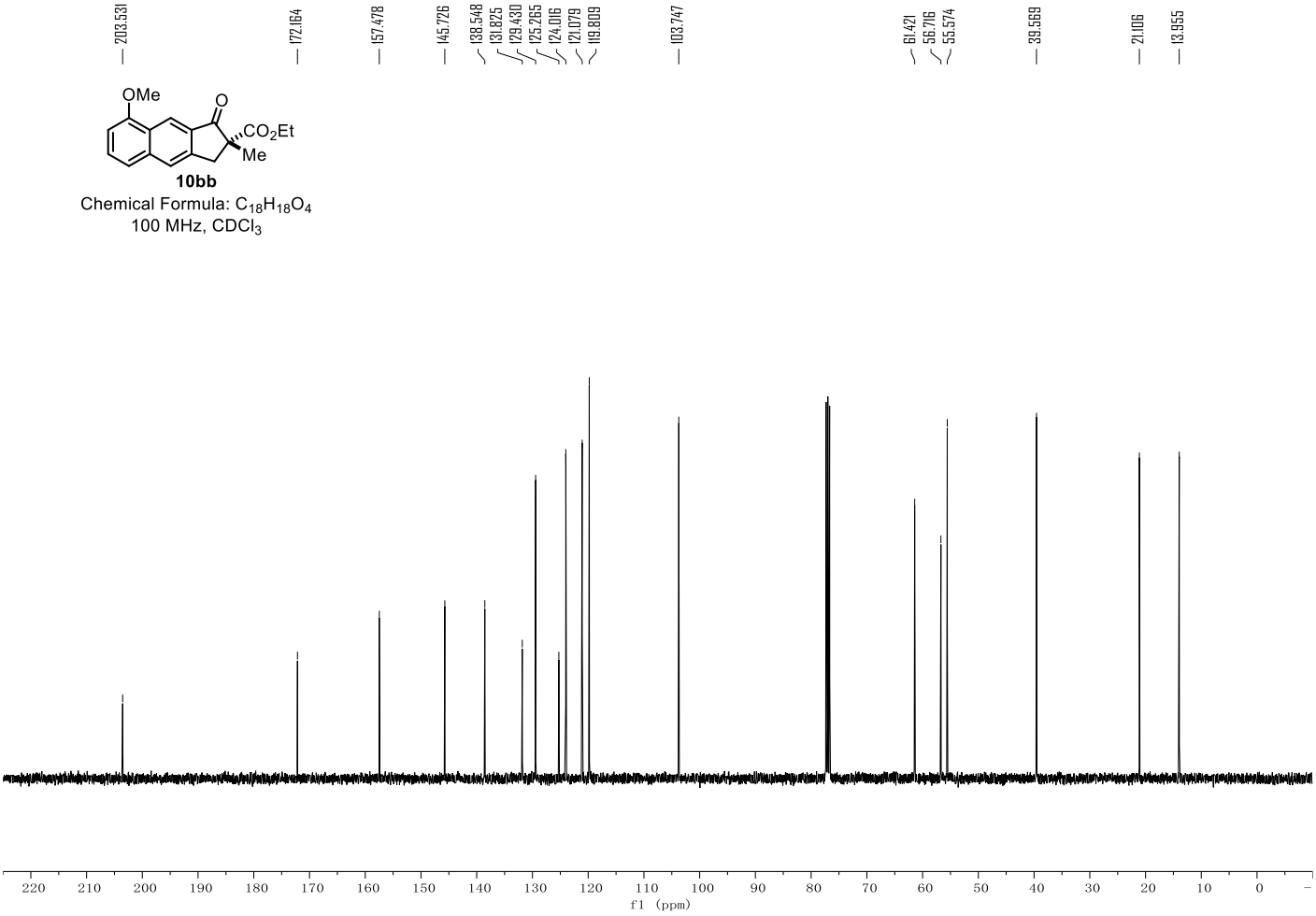

8.753
7.688
7.191
6.627
4.167
4.150
4.132
4.114
3.995
3.844
3.801
3.136
3.093
2.511
1.548
1.188
1.170
1.153
OMe
O
CO2Et
Me
Me
10ab
Chemical Formula: C19H20O4
400 MHz, CDCl3
1.00
1.09
1.09
1.09
2.24
3.36
1.15
1.12
3.30
3.34
3.35
f1 (ppm)

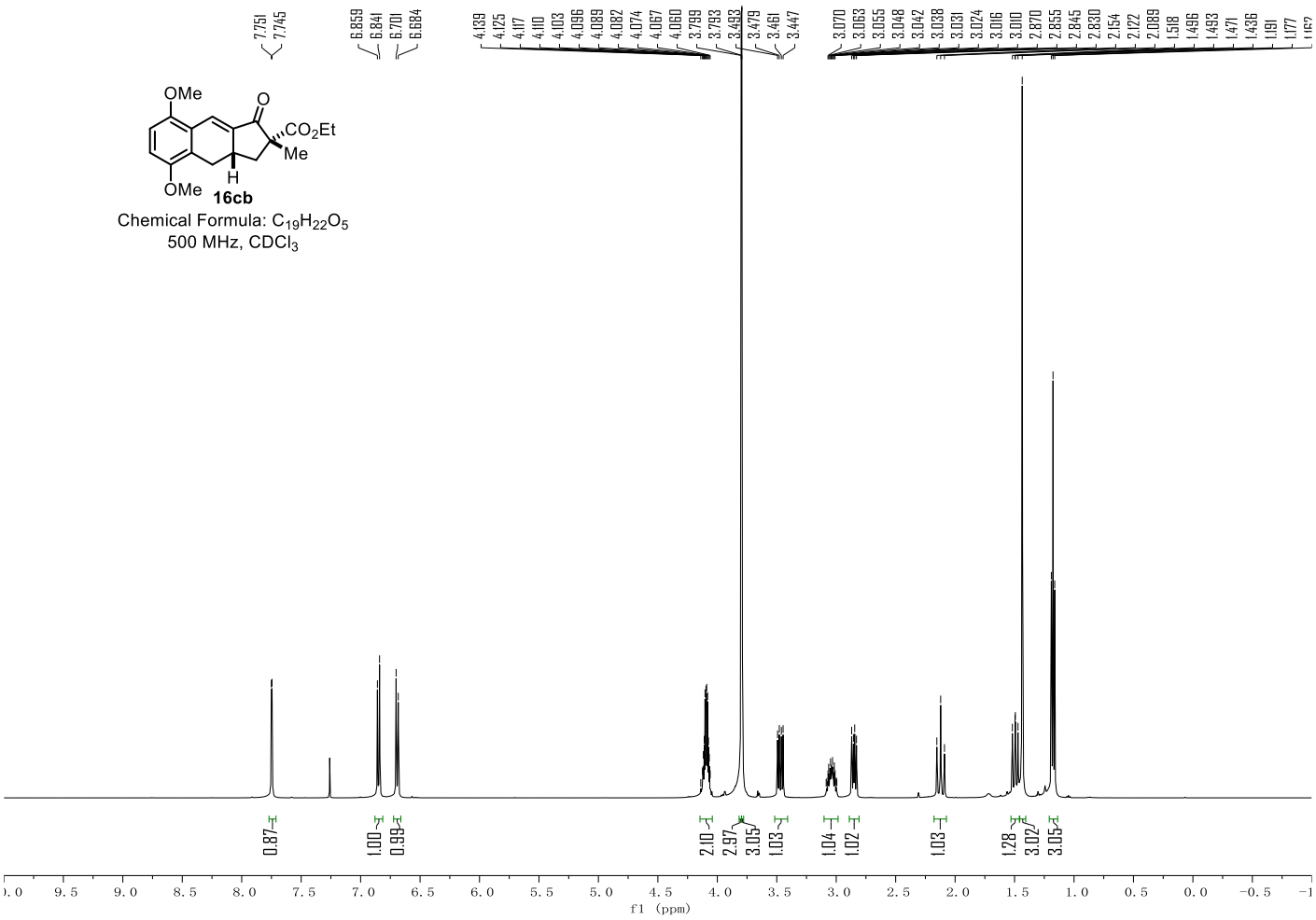

203.509
172.323
157.293
146.056
140.102
138.865
131.151
123.771
123.198
121.048
118.919
106.177
61.431
56.740
55.570
39.627
22.596
21.184
13.996
OMe
O
CO2Et
Me
Me
10ab
Chemical Formula: C19H20O4
100 MHz, CDCl3
f1 (ppm)

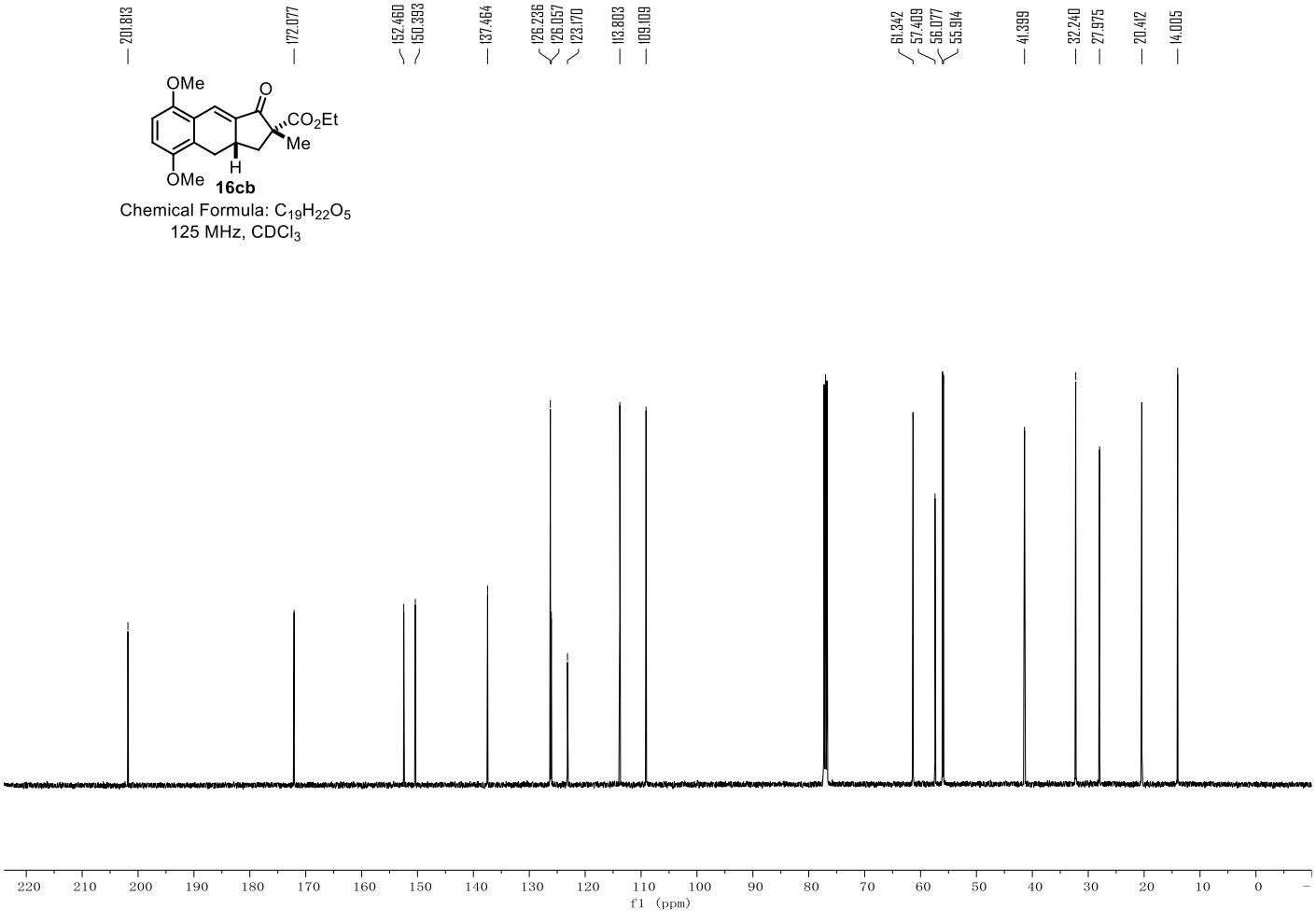

OMe
O
CO2Et
Me
H
16bb
Chemical Formula: C18H20O4
400 MHz, CDCl3
f1 (ppm)

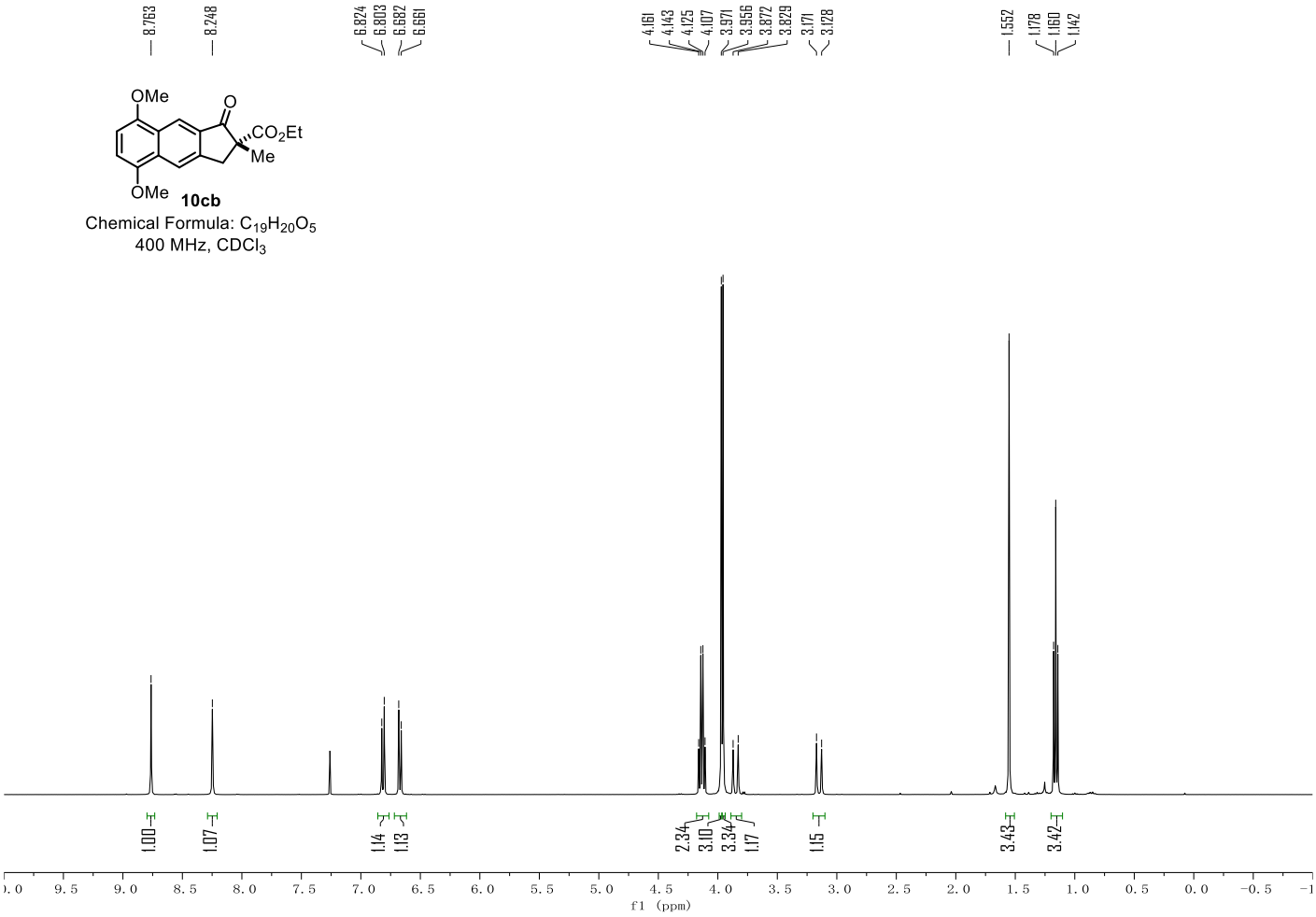

OMe
O
CO2Et
Me
H
16bb
Chemical Formula: C18H20O4
100 MHz, CDCl3
f1 (ppm)

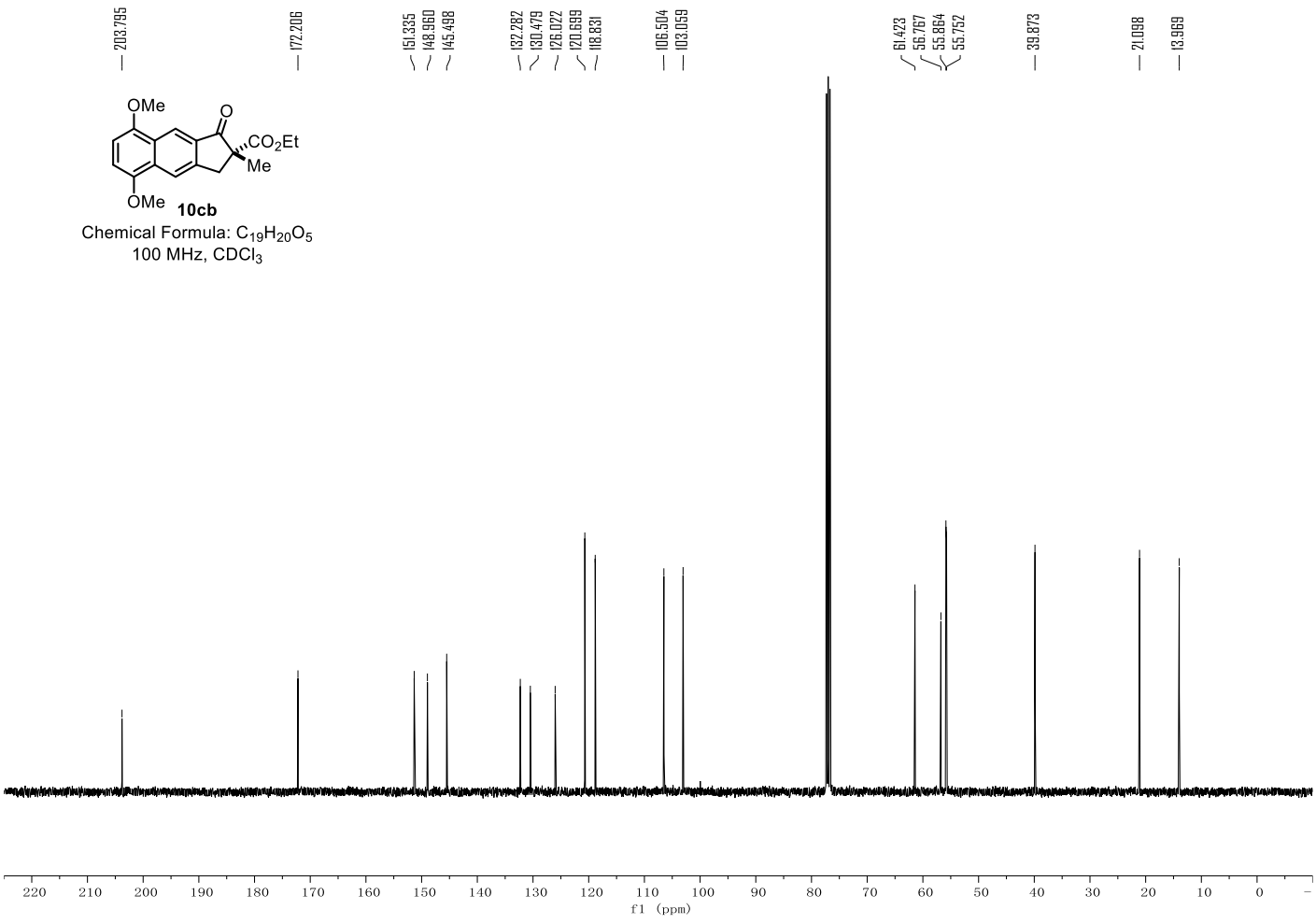

8.817
7.792
7.507
7.487
7.468
7.411
7.390
6.793
6.775
4.167
4.149
4.131
4.113
3.996
3.864
3.821
3.152
3.108
1.555
1.185
1.167
1.150
OMe
O
CO2Et
Me
10bb
Chemical Formula: C18H18O4
400 MHz, CDCl3
1.00
1.14
1.20
1.18
1.19
2.45
3.65
1.26
1.22
3.59
3.60
f1 (ppm)

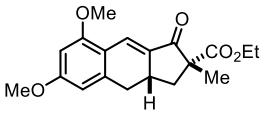

203.531
172.164
157.478
145.726
138.548
131.825
129.430
125.285
124.016
121.079
119.809
103.747
61.421
56.716
55.574
39.589
21.016
13.955
OMe
O
CO2Et
Me
10bb
Chemical Formula: C18H18O4
100 MHz, CDCl3
f1 (ppm)


OMe
O
CO2Et
Me
H
OMe
16cb
Chemical Formula: C19H22O5
500 MHz, CDCl3
f1 (ppm)


OMe
O
CO2Et
Me
H
OMe
16cb
Chemical Formula: C19H22O5
125 MHz, CDCl3
f1 (ppm)


8.763
8.248
6.824
6.803
6.682
6.661
4.161
4.143
4.125
4.107
3.971
3.956
3.872
3.829
3.171
3.128
1.557
1.178
1.160
1.142
OMe
O
CO2Et
Me
OMe
10cb
Chemical Formula: C19H20O5
400 MHz, CDCl3
1.00
1.07
1.14
1.13
2.34
3.10
3.34
1.17
1.15
3.43
3.42
f1 (ppm)

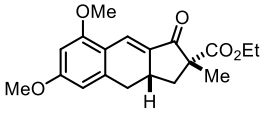

203.795
172.206
151.335
148.960
145.498
132.282
130.479
126.022
120.699
118.831
106.504
103.059
61.423
56.767
55.864
55.752
39.873
21.098
13.969
OMe
O
CO2Et
Me
OMe
10cb
Chemical Formula: C19H20O5
100 MHz, CDCl3
f1 (ppm)



16db

Chemical Formula: $C_{19}H_{22}O_5$

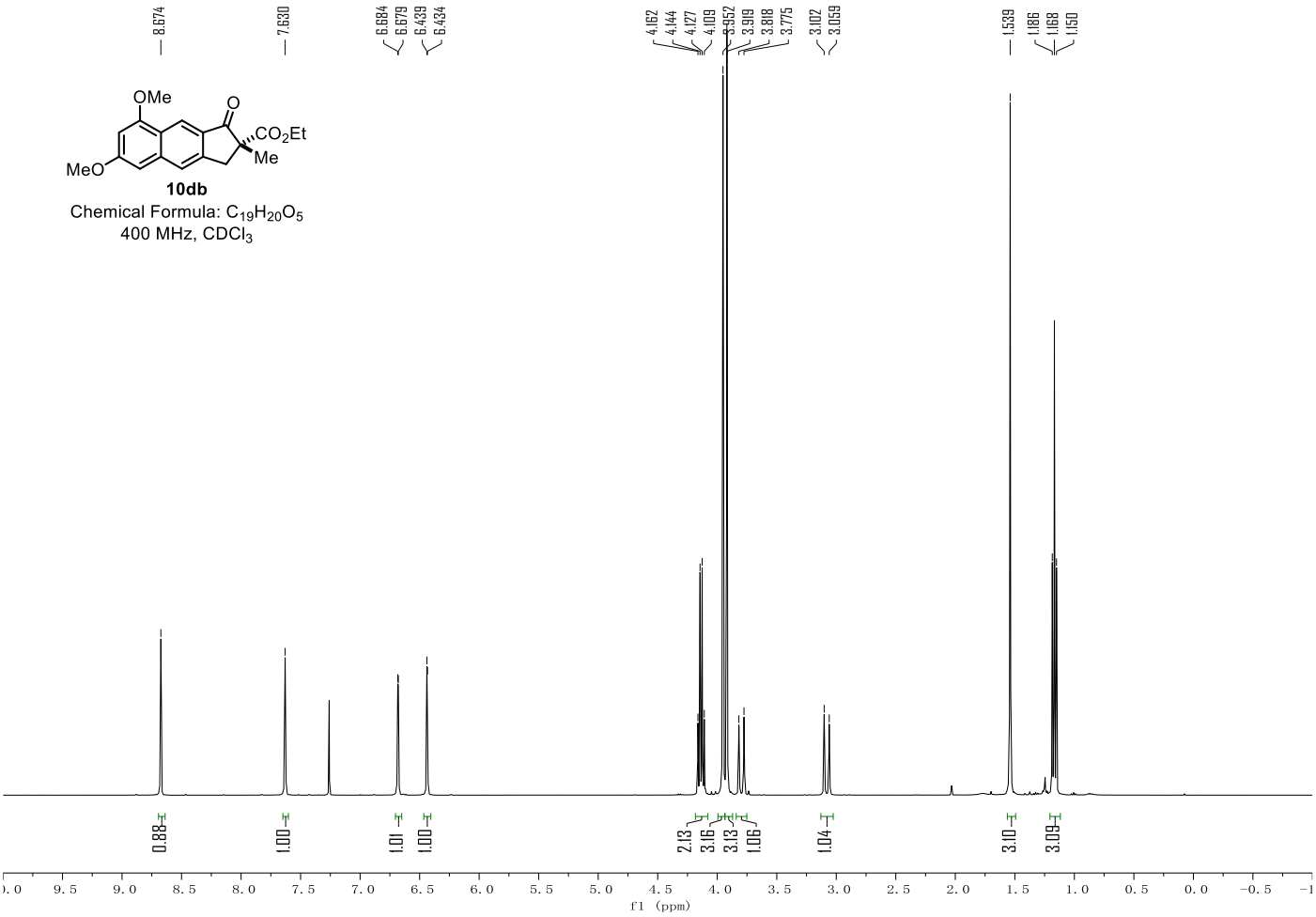
400 MHz, $CDCl_3$

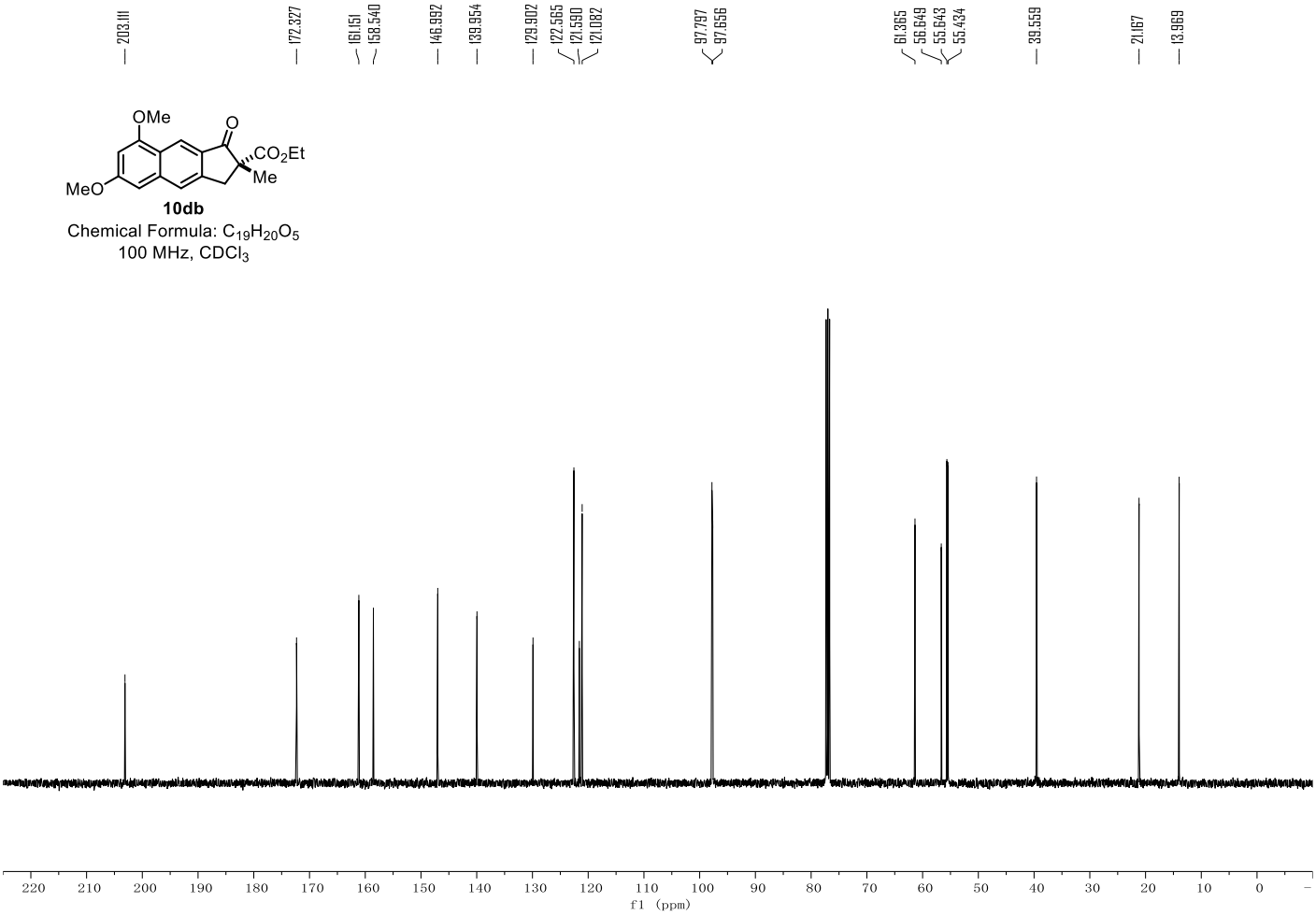


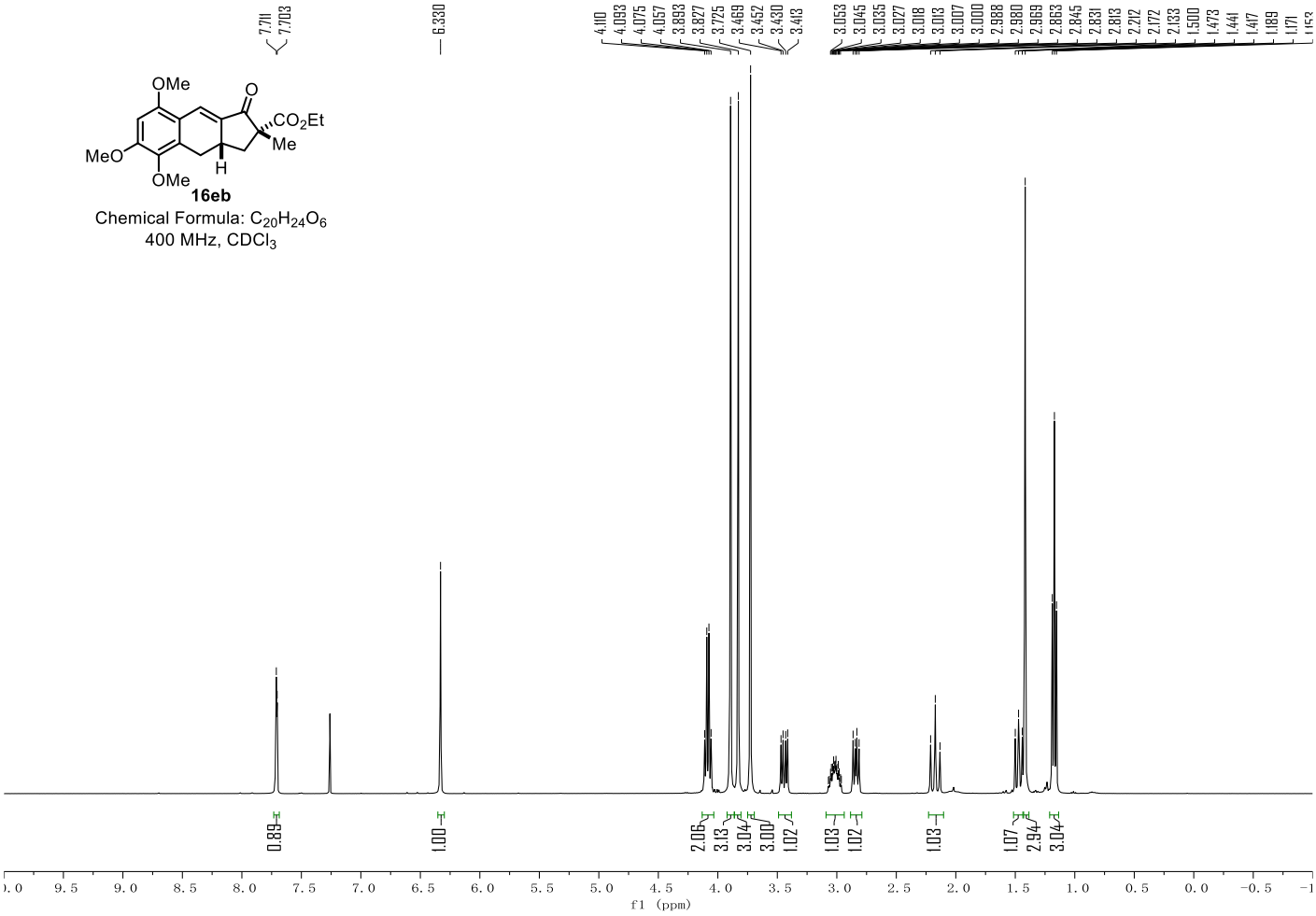
16db

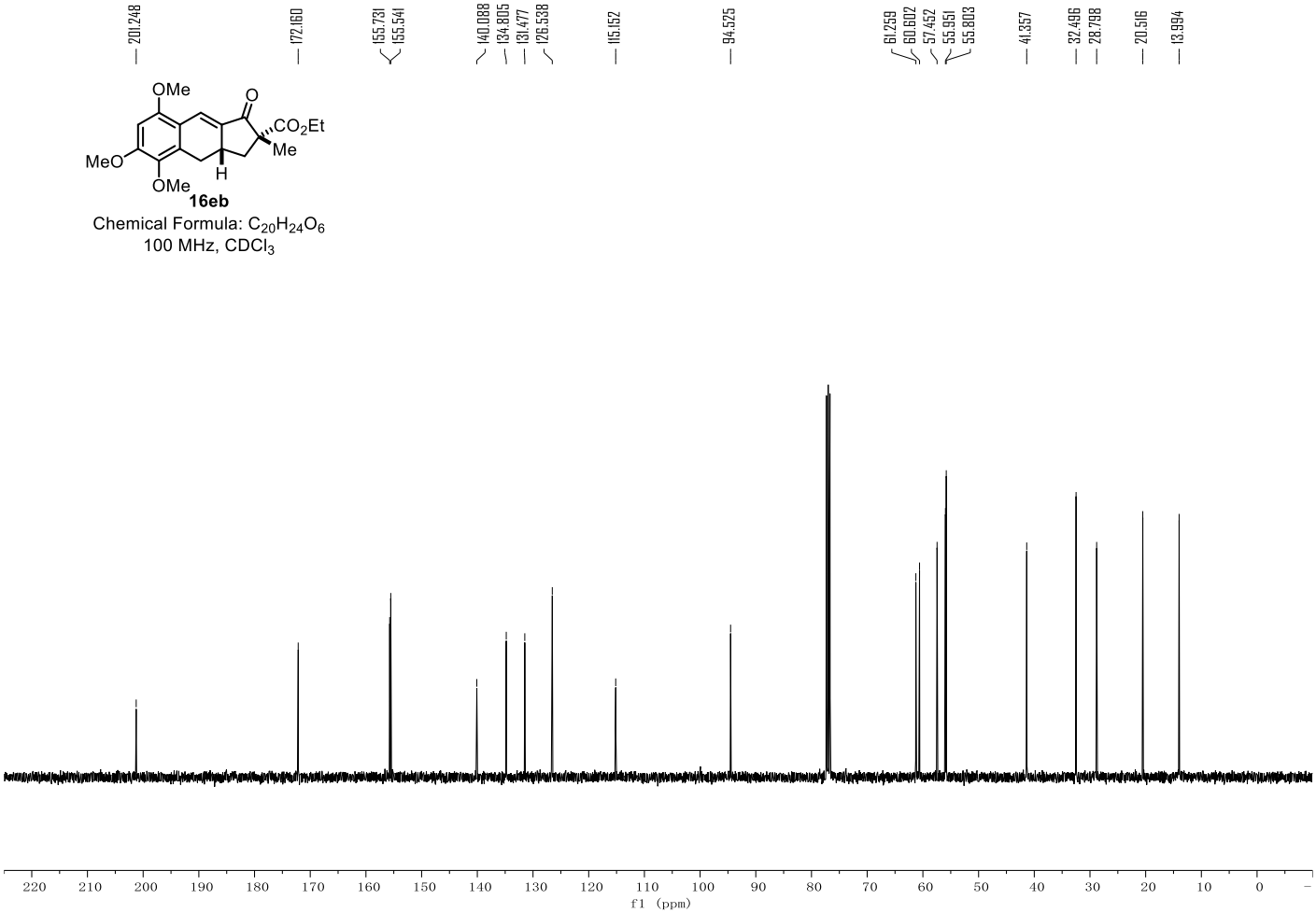
Chemical Formula: $C_{19}H_{22}O_5$

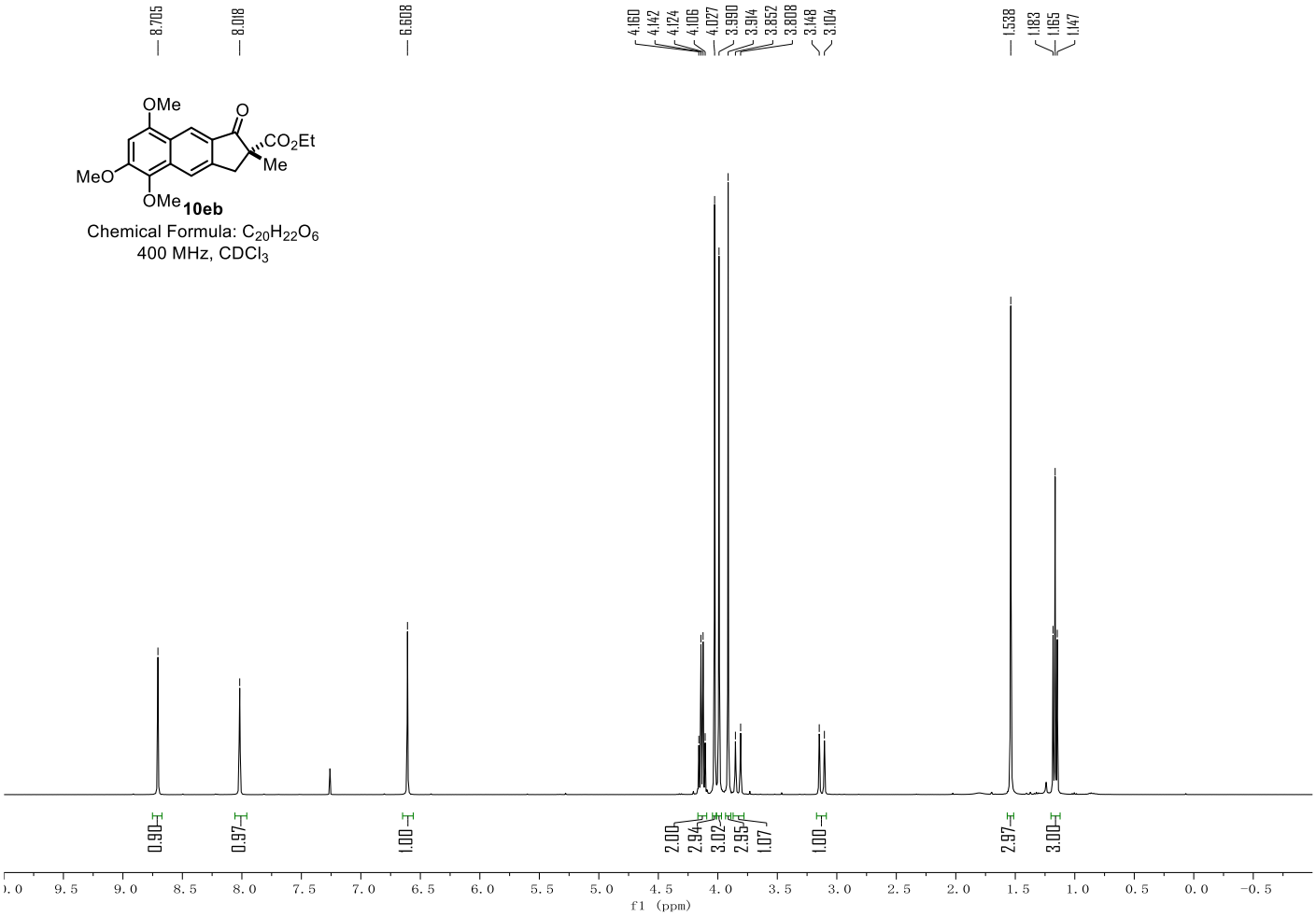
100 MHz, $CDCl_3$

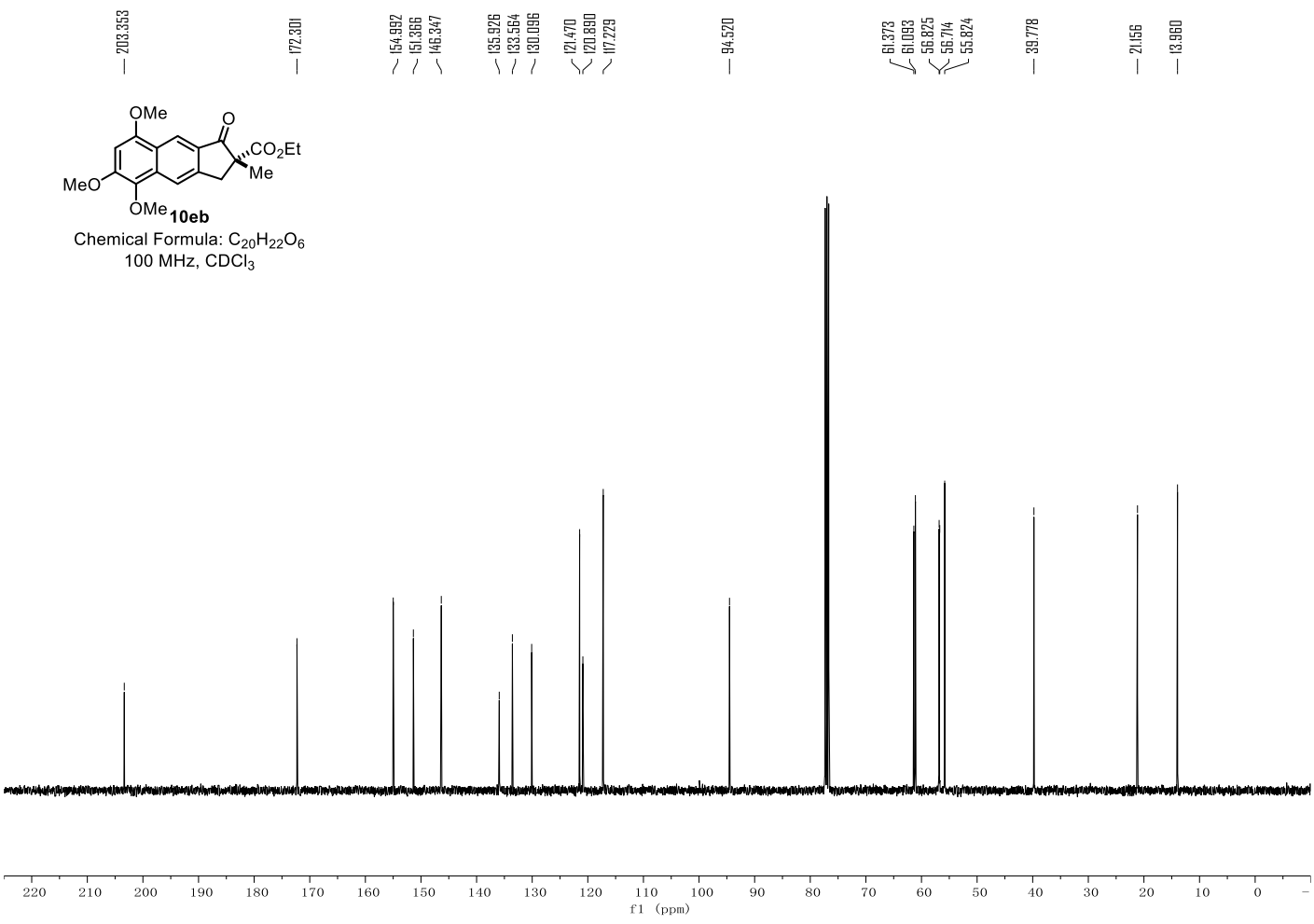

8.674
7.630
6.684
6.679
6.439
6.434
4.162
4.144
4.127
4.109
3.952
3.919
3.818
3.775
3.102
3.059
1.539
1.186
1.168
1.150
OMe
O
CO2Et
Me
MeO
10db
Chemical Formula: C19H20O5
400 MHz, CDCl3
0.88
1.00
1.01
1.00
2.13
3.16
3.13
1.06
1.04
3.10
3.09
f1 (ppm)

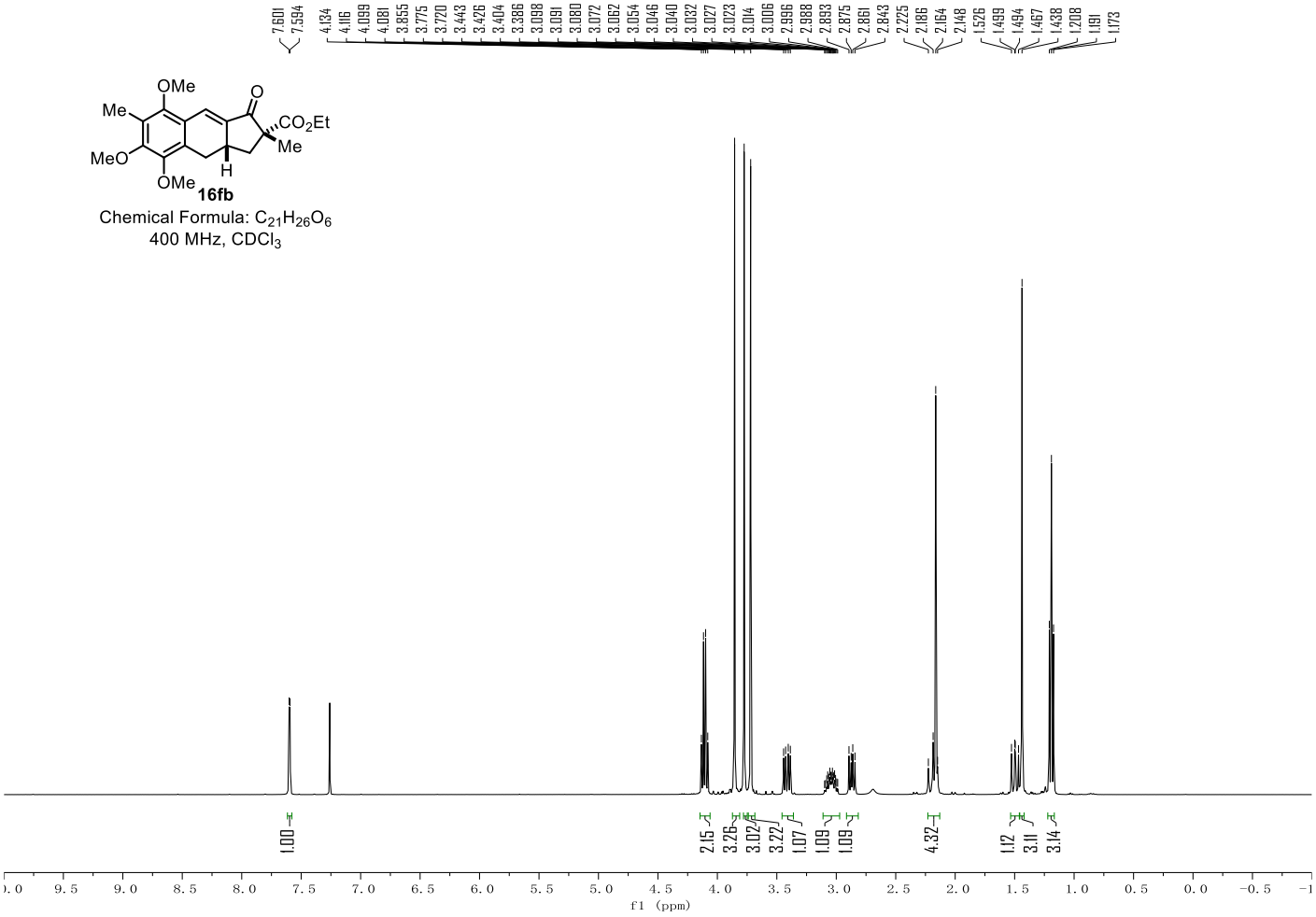

203.111
172.327
161.151
158.540
146.992
139.954
129.902
122.565
121.590
121.082
97.797
97.656
61.365
56.649
55.643
55.434
39.559
21.167
13.969
OMe
O
CO2Et
Me
MeO
10db
Chemical Formula: C19H20O5
100 MHz, CDCl3
f1 (ppm)

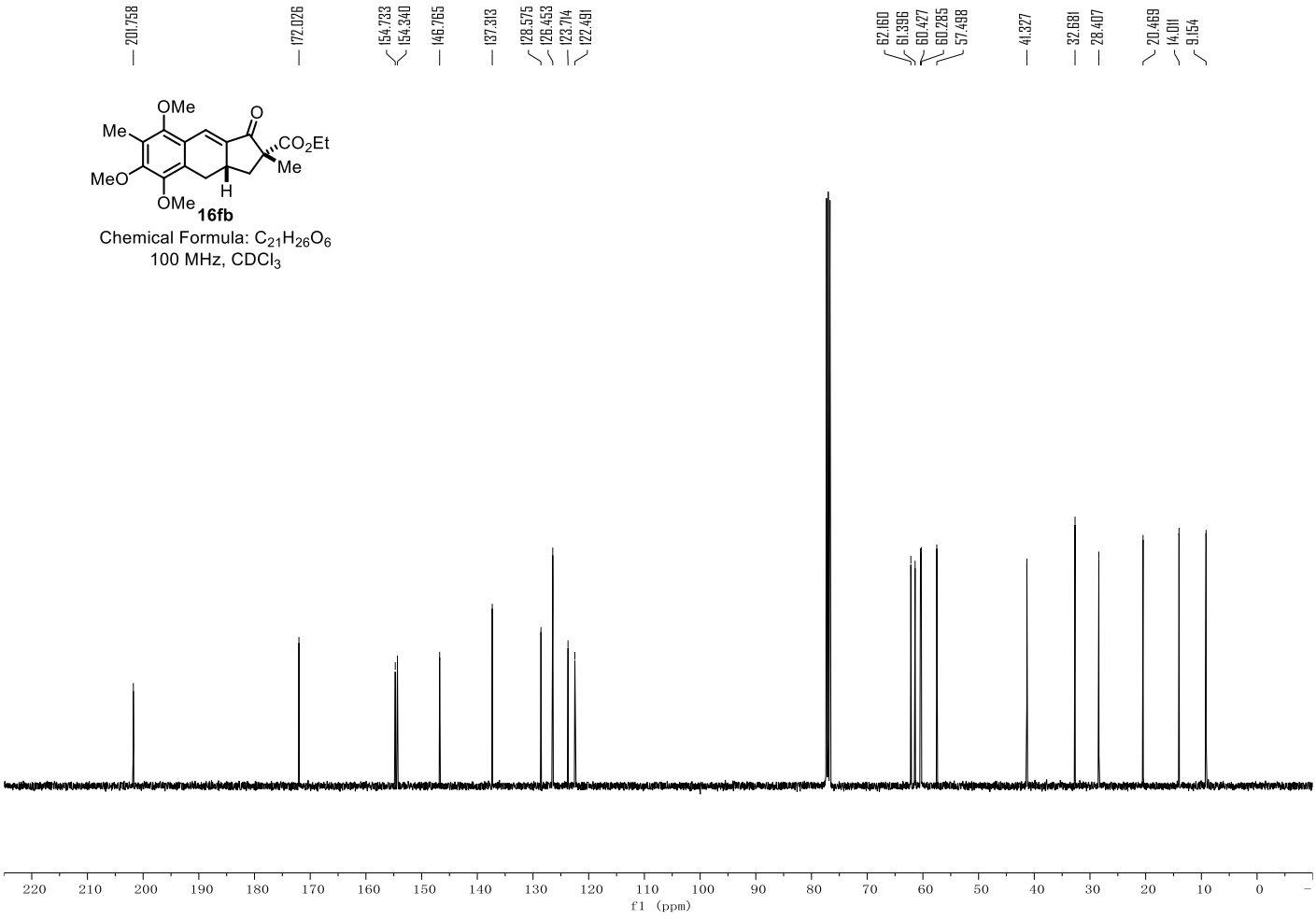

7.711
7.703
6.330
4.110
4.093
4.075
4.057
3.893
3.827
3.725
3.469
3.452
3.430
3.413
3.053
3.045
3.035
3.027
3.018
3.013
3.007
3.000
2.988
2.980
2.969
2.863
2.845
2.831
2.813
2.212
2.172
2.133
1.500
1.473
1.441
1.417
1.189
1.171
OMe
O
CO2Et
Me
MeO
OMe
H
16eb
Chemical Formula: C20H24O6
400 MHz, CDCl3
0.89
1.00
2.06
3.13
3.04
3.00
1.02
1.03
1.02
1.03
1.07
2.94
3.04
f1 (ppm)

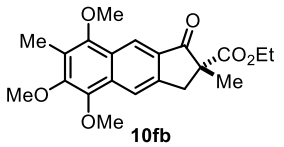

201.248
172.160
155.731
155.541
140.088
134.805
131.477
126.538
115.152
94.525
61.259
60.602
57.452
55.951
55.803
41.357
32.496
28.798
20.516
13.994
OMe
O
CO2Et
Me
MeO
OMe
H
16eb
Chemical Formula: C20H24O6
100 MHz, CDCl3
f1 (ppm)


8.705
8.018
6.608
4.160
4.142
4.124
4.106
4.027
3.990
3.914
3.852
3.808
3.148
3.104
1.538
1.183
1.165
1.147
OMe
O
CO2Et
Me
MeO
OMe
10eb
Chemical Formula: C20H22O6
400 MHz, CDCl3
0.90
0.97
1.00
2.00
2.94
3.02
2.95
1.07
1.00
2.97
3.00
f1 (ppm)


203.353
172.301
154.992
151.366
146.347
135.926
133.564
130.096
121.470
120.890
117.229
94.520
61.373
61.093
56.825
56.714
55.824
39.778
21.156
13.960
OMe
O
CO2Et
Me
MeO
OMe
10eb
Chemical Formula: C20H22O6
100 MHz, CDCl3
f1 (ppm)


7.601
7.594
4.134
4.116
4.099
4.081
3.855
3.775
3.720
3.443
3.426
3.404
3.386
3.098
3.091
3.080
3.072
3.062
3.054
3.046
3.040
3.032
3.027
3.023
3.014
3.006
2.996
2.988
2.893
2.875
2.861
2.843
2.225
2.186
2.164
2.148
1.526
1.499
1.494
1.467
1.438
1.208
1.191
1.173
OMe
Me
MeO
OMe
O
CO2Et
Me
H
16fb
Chemical Formula: C21H26O6
400 MHz, CDCl3
1.00
2.15
3.26
3.02
3.22
1.07
1.09
1.09
4.32
1.12
3.11
3.14
f1 (ppm)

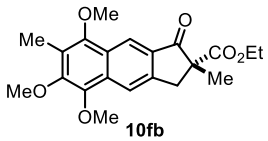

201.758
172.026
154.733
154.340
146.765
137.313
128.575
126.453
123.714
122.491
62.160
61.396
60.427
60.285
57.498
41.327
32.681
28.407
20.469
14.011
9.154
OMe
Me
MeO
OMe
O
CO2Et
Me
H
16fb
Chemical Formula: C21H26O6
100 MHz, CDCl3
f1 (ppm)



10fb

Chemical Formula: $C_{21}H_{24}O_6$

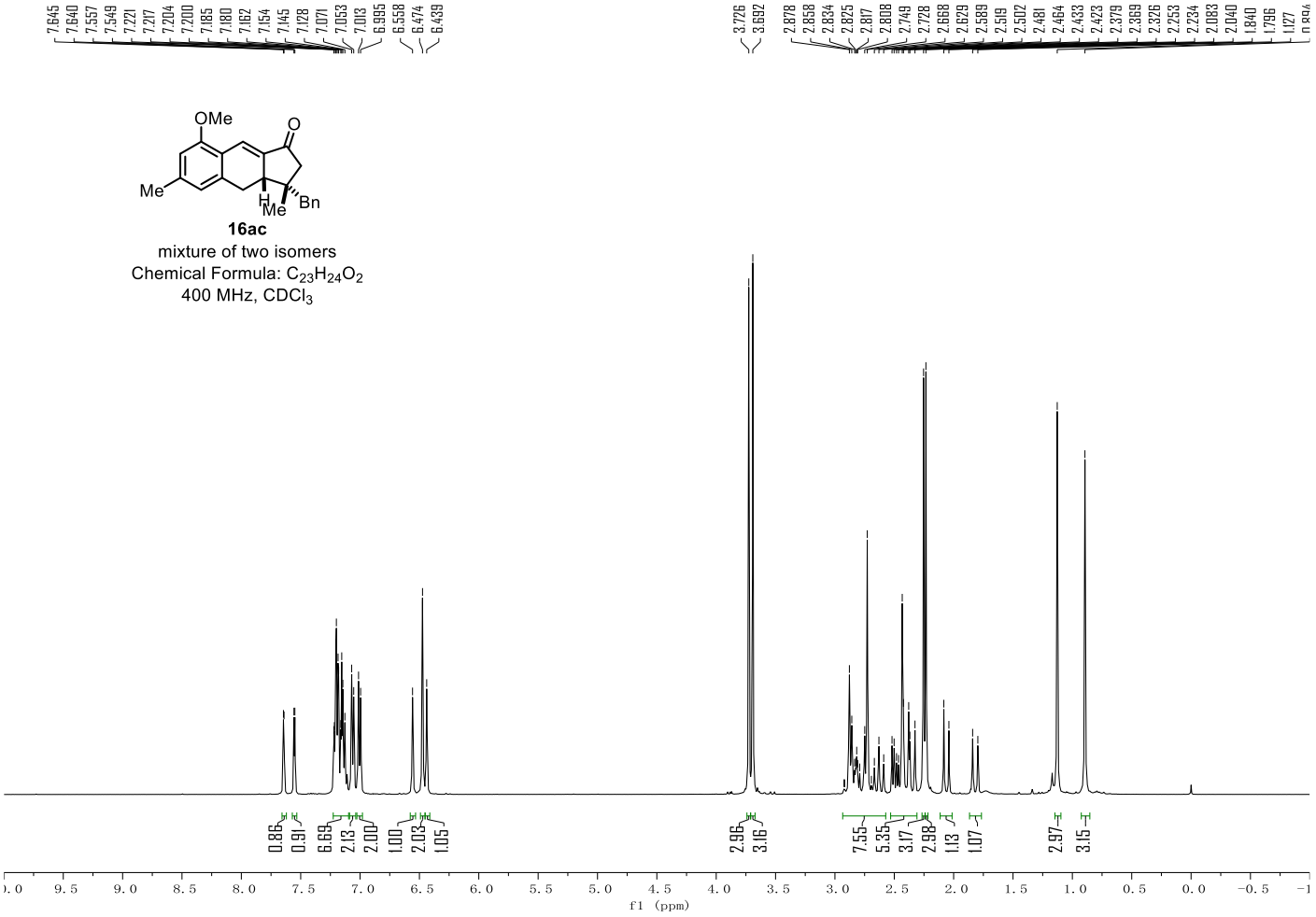
400 MHz, $CDCl_3$

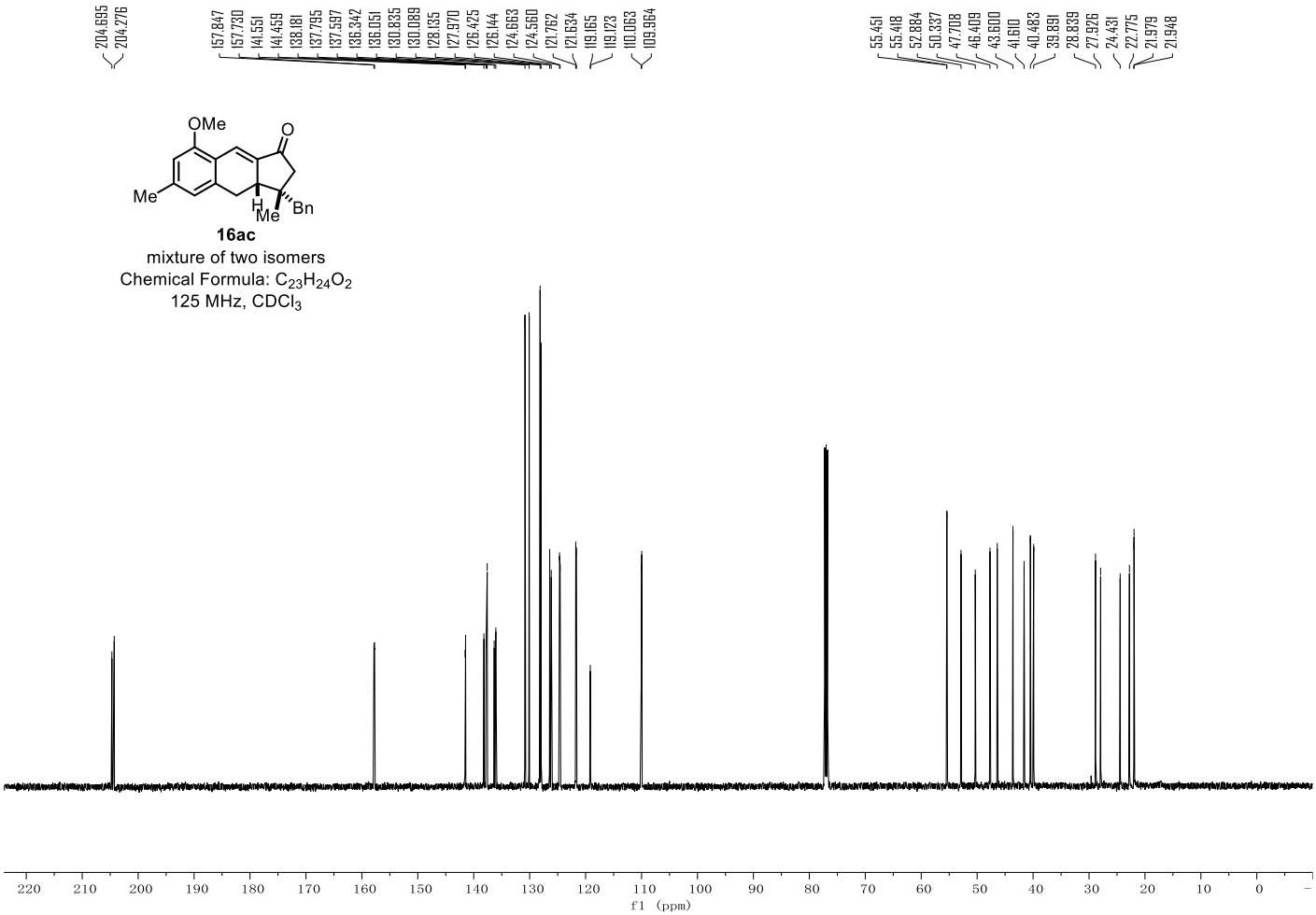


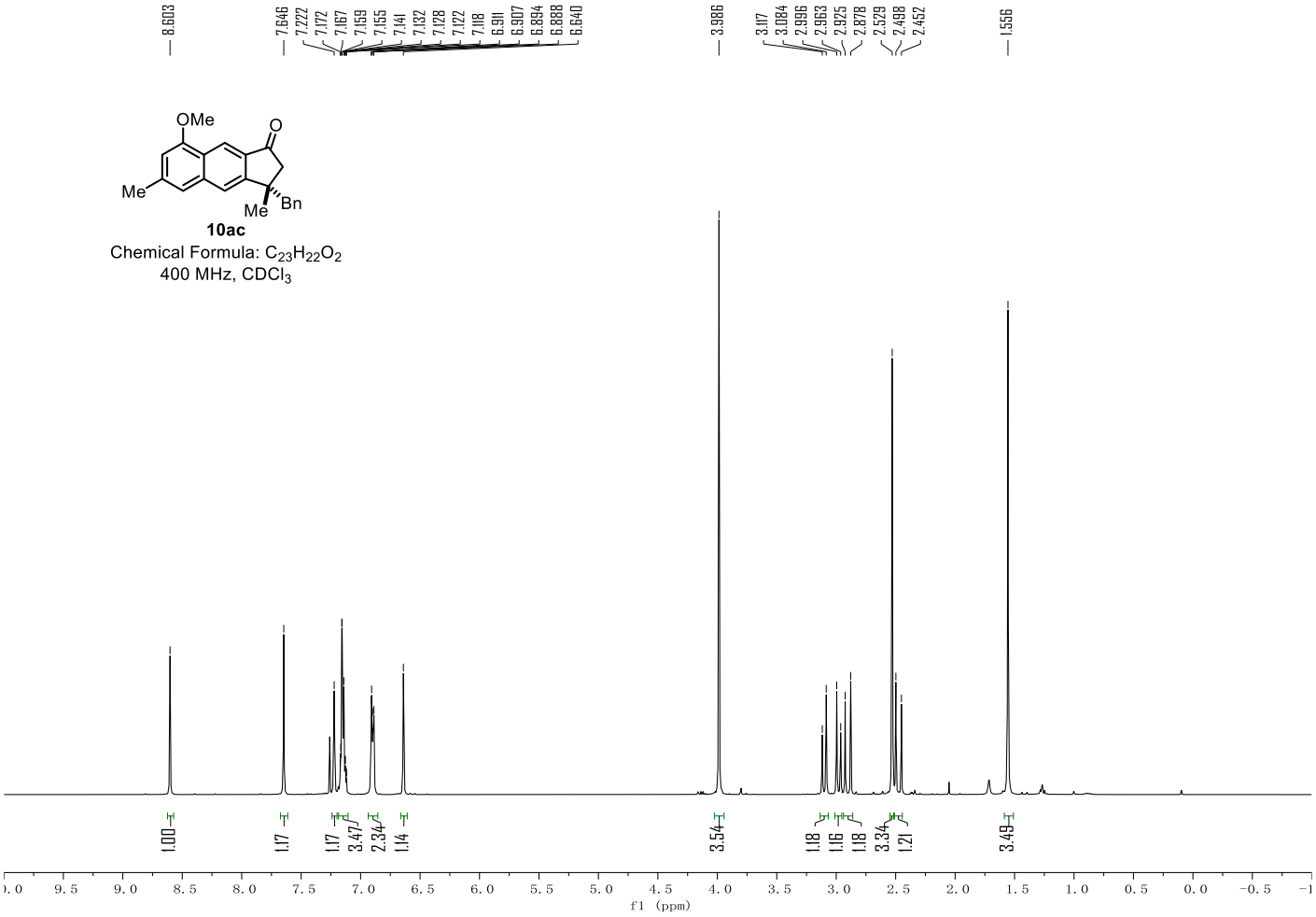
10fb

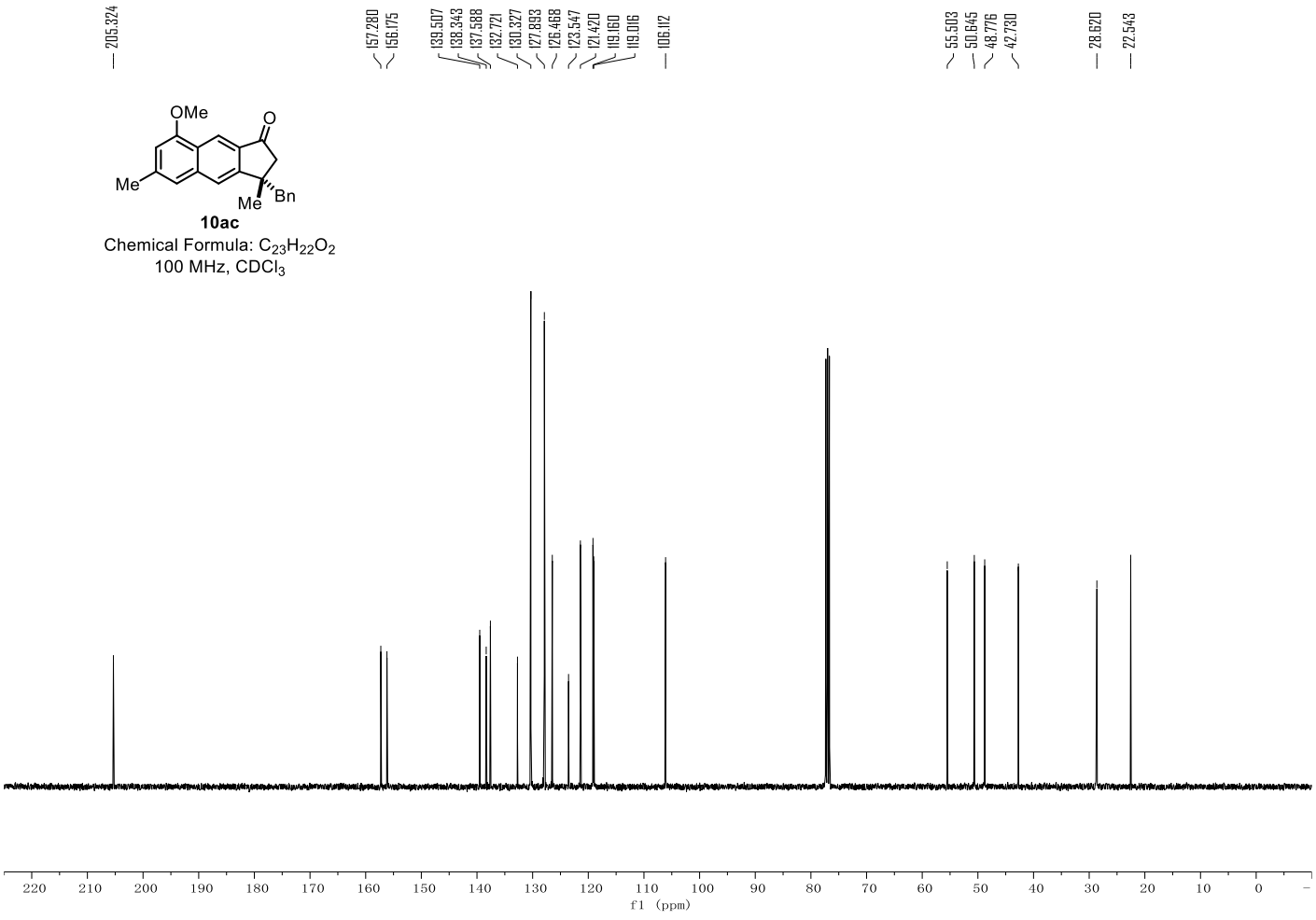
Chemical Formula: $C_{21}H_{24}O_6$

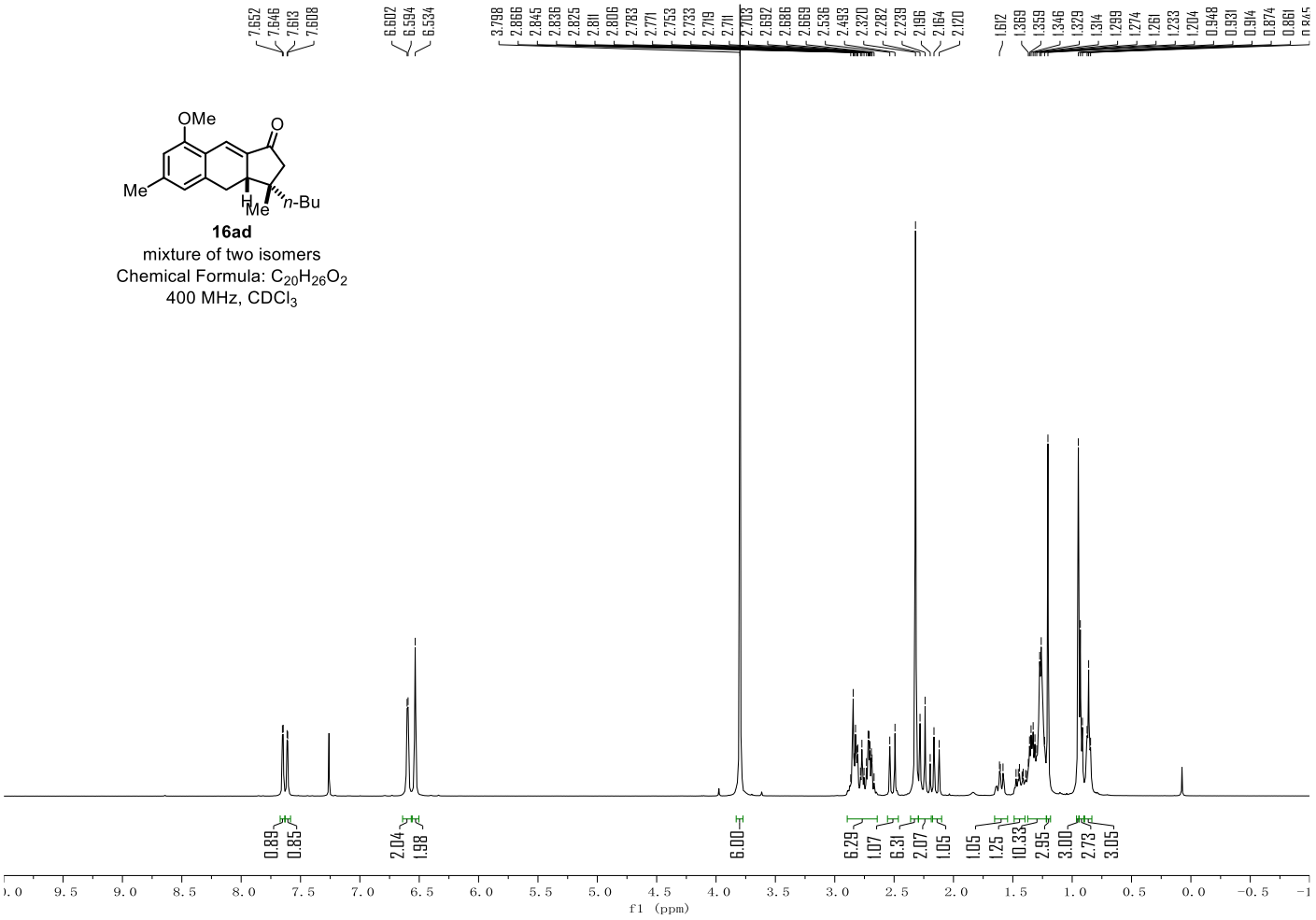
100 MHz, $CDCl_3$


OMe
O
Me
H
Me
Bn
16ac
mixture of two isomers
Chemical Formula: C23H24O2
400 MHz, CDCl3
f1 (ppm)

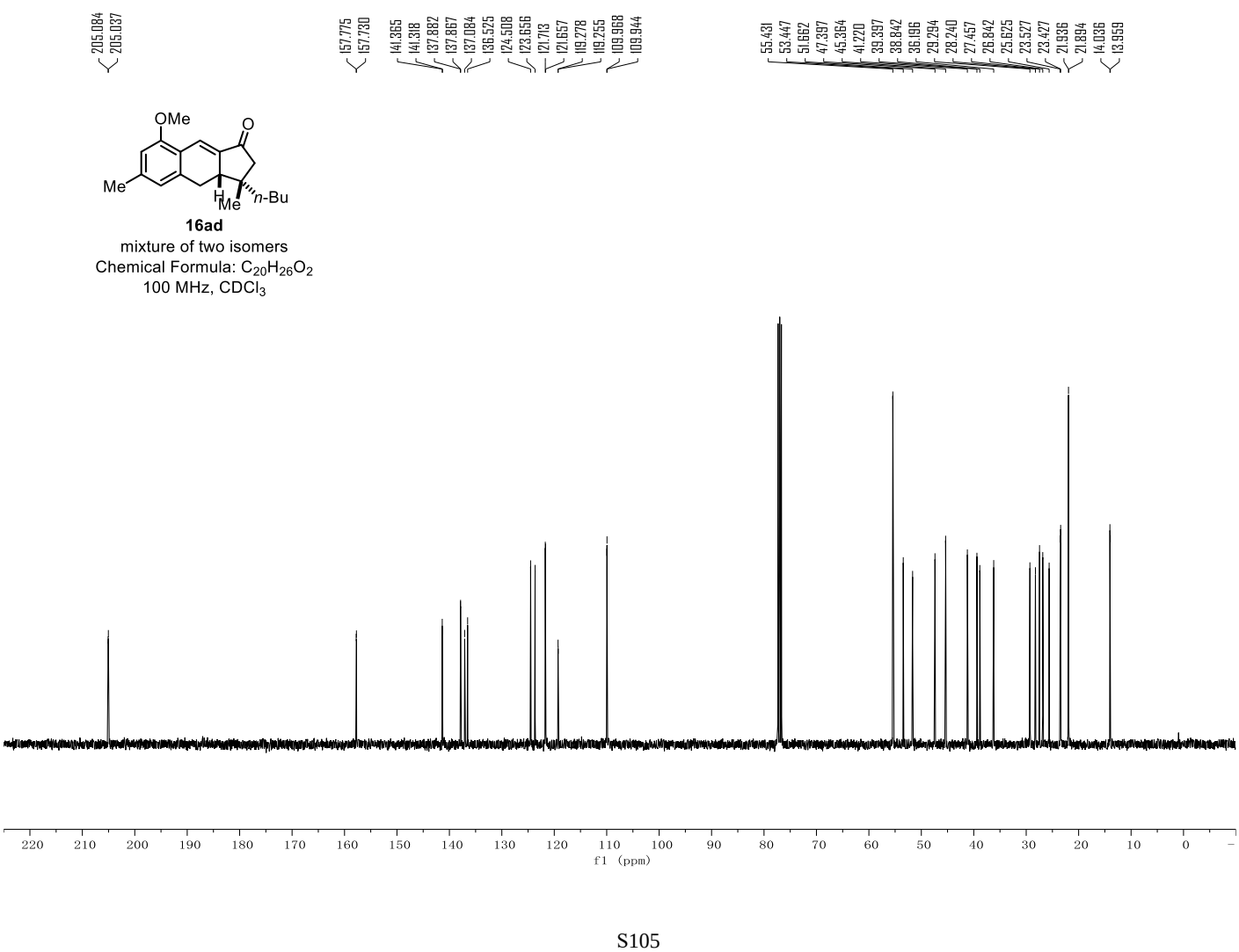

OMe
O
Me
H
Me
Bn
16ac
mixture of two isomers
Chemical Formula: C23H24O2
125 MHz, CDCl3
f1 (ppm)


8.603
7.646
7.222
7.172
7.167
7.159
7.155
7.141
7.132
7.128
7.122
7.118
6.911
6.907
6.894
6.888
6.640
3.986
3.117
3.084
2.996
2.963
2.925
2.878
2.529
2.498
2.452
1.556
OMe
O
Me
Me
Bn
10ac
Chemical Formula: C23H22O2
400 MHz, CDCl3
1.00
1.17
1.17
3.47
2.34
1.14
3.54
1.18
1.16
1.18
3.34
1.21
3.49
f1 (ppm)

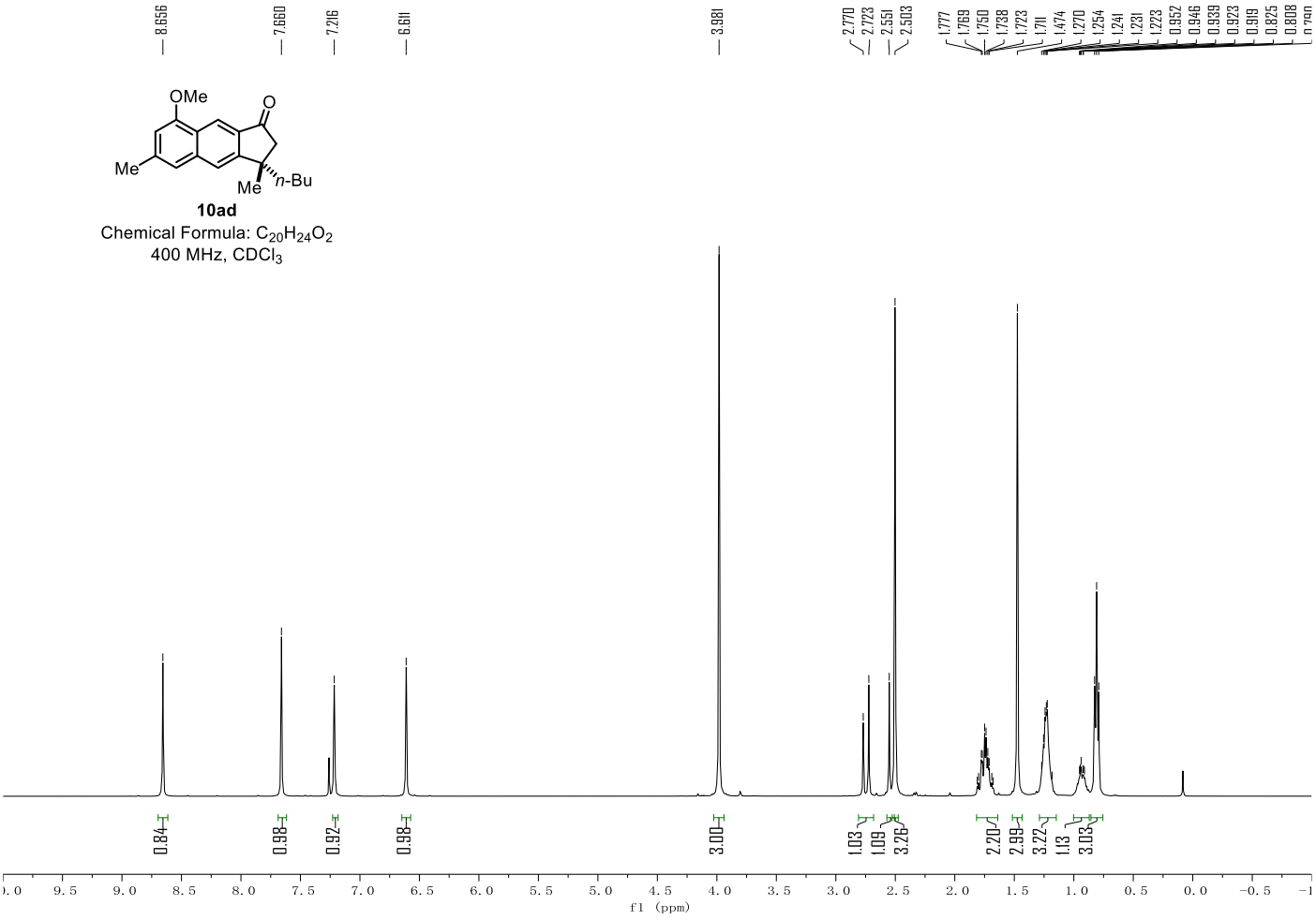

205.324
157.280
156.175
139.507
138.343
137.588
132.721
130.327
127.883
126.468
123.547
121.420
119.160
119.016
106.112
55.503
50.645
48.776
42.730
28.620
22.543
OMe
O
Me
Me
Bn
10ac
Chemical Formula: C23H22O2
100 MHz, CDCl3
f1 (ppm)



16ad
mixture of two isomers
Chemical Formula: $C_{20}H_{26}O_2$
400 MHz, $CDCl_3$



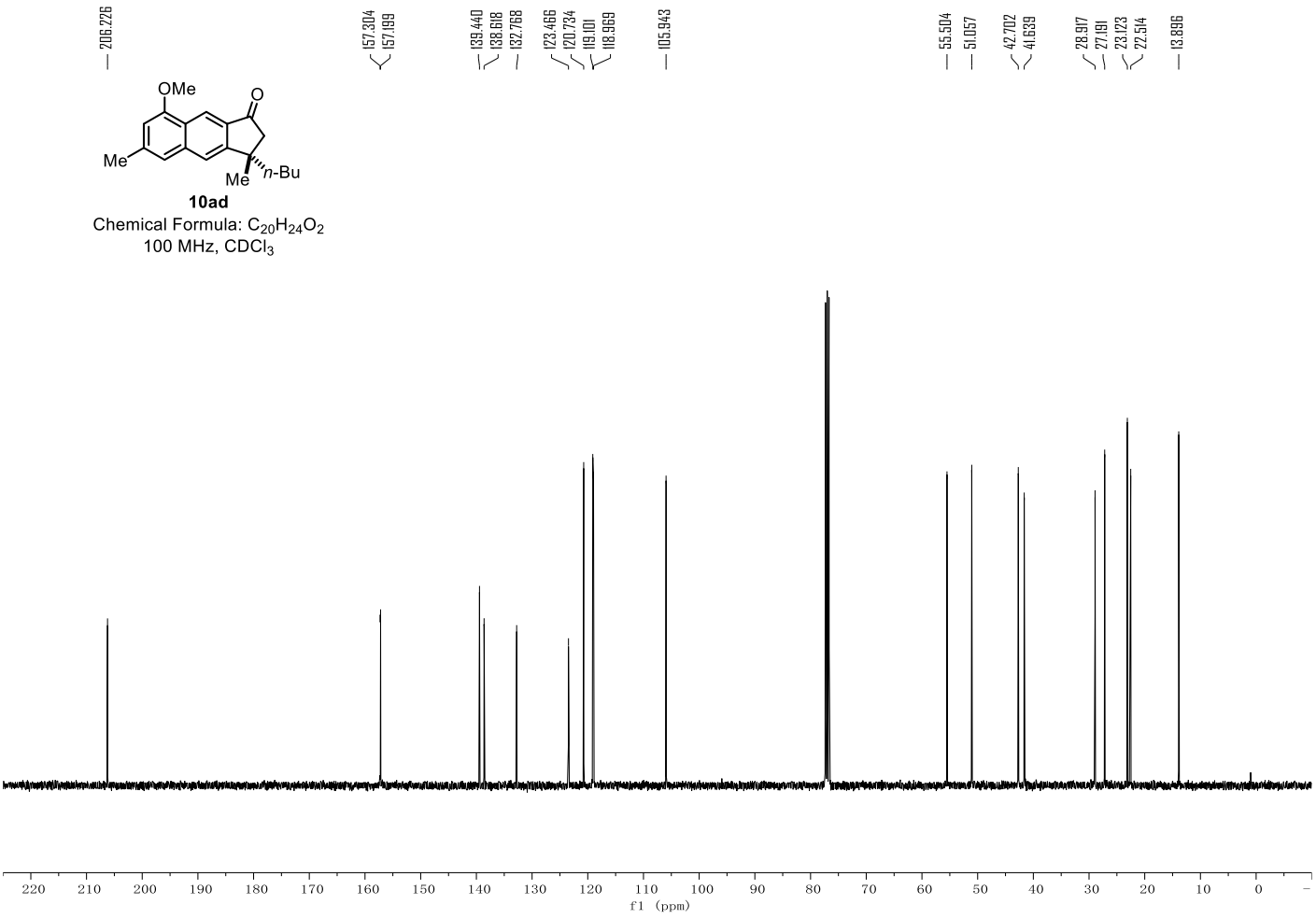
16ad
mixture of two isomers
Chemical Formula: $C_{20}H_{26}O_2$
100 MHz, $CDCl_3$



10ad

Chemical Formula: $C_{20}H_{24}O_2$

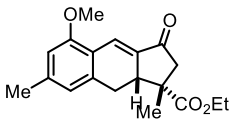
400 MHz, $CDCl_3$



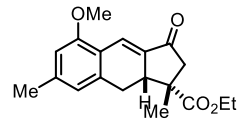
10ad

Chemical Formula: $C_{20}H_{24}O_2$

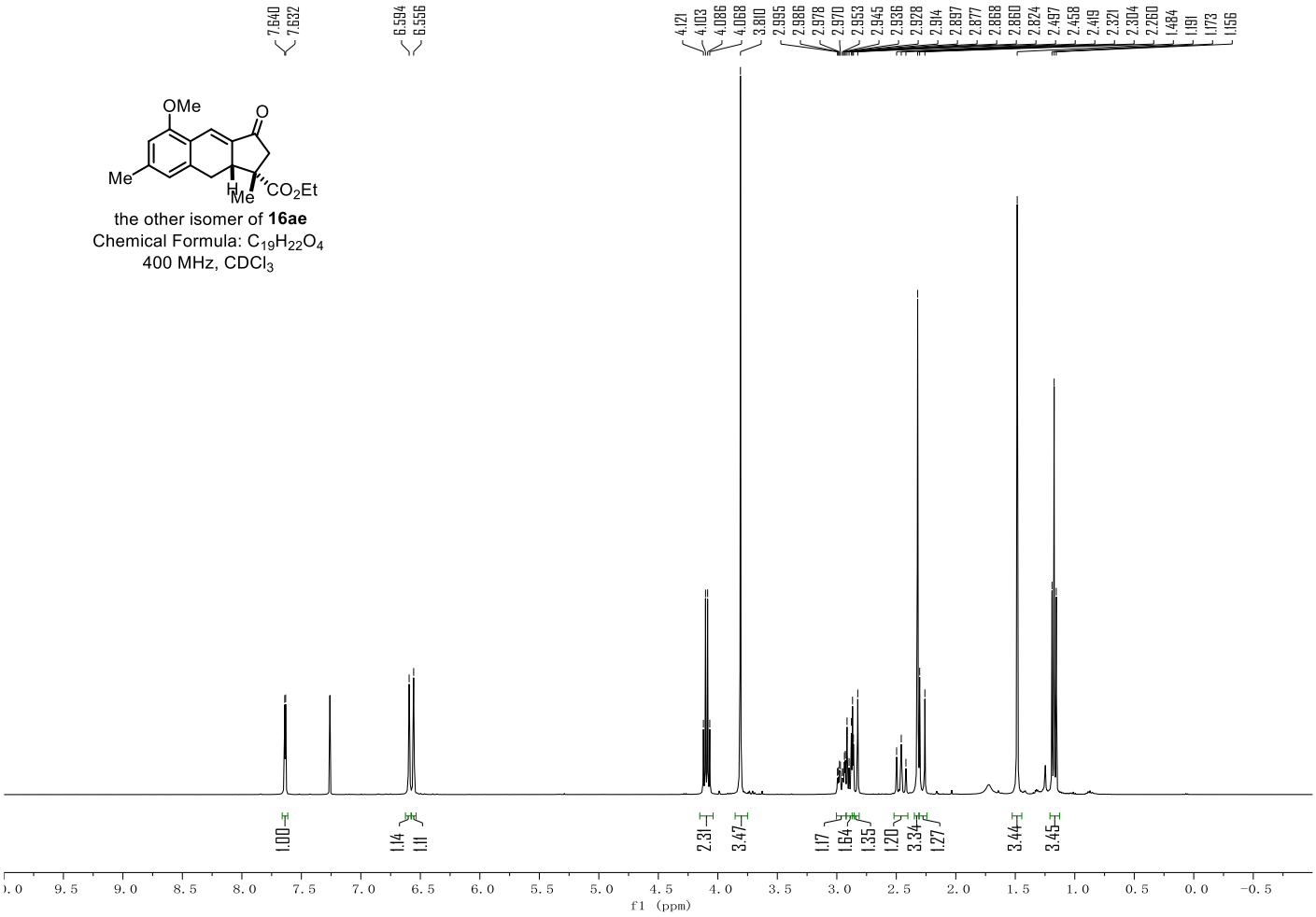
100 MHz, $CDCl_3$



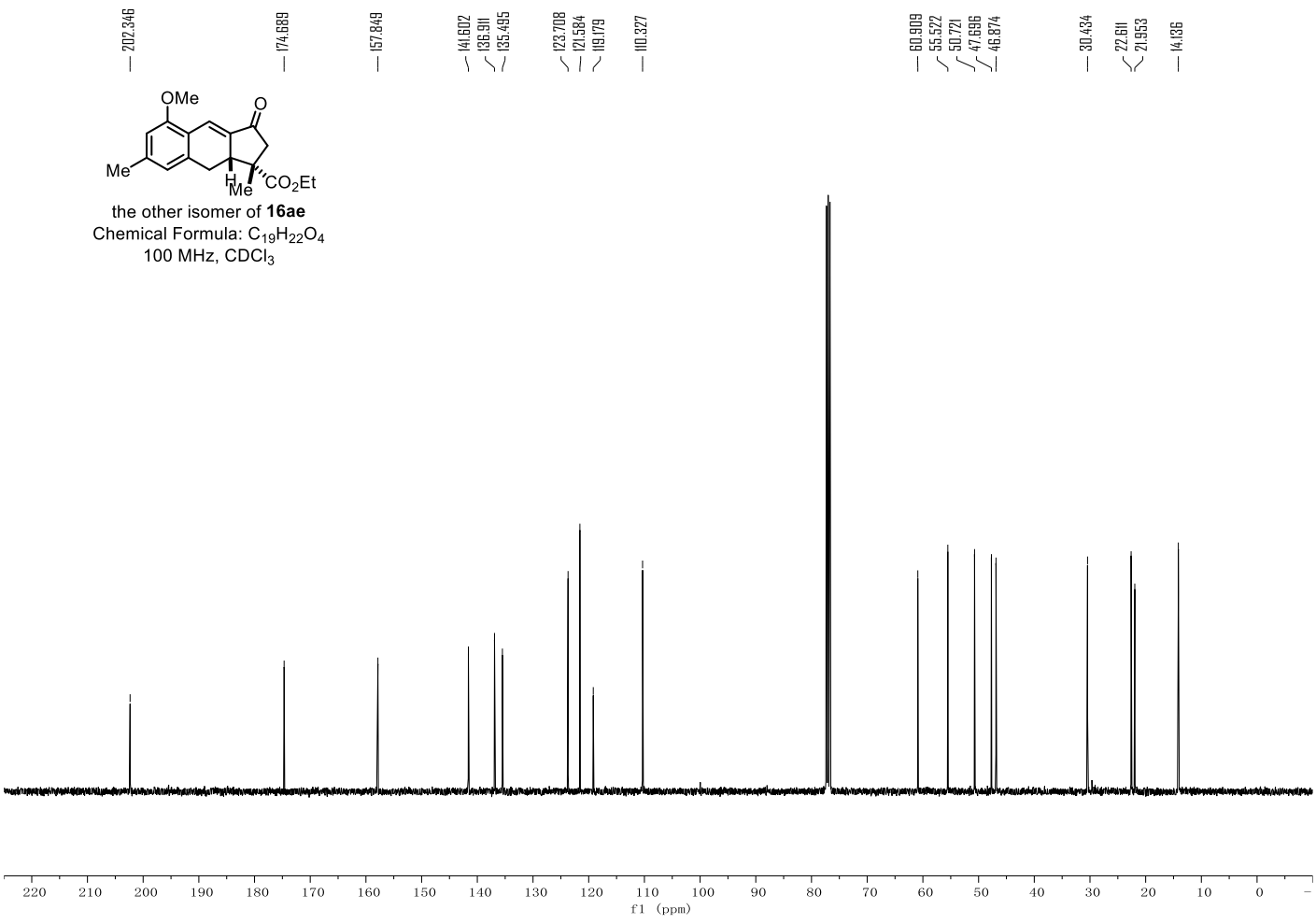
one isomer of **16ae**
Chemical Formula: $C_{19}H_{22}O_4$
400 MHz, $CDCl_3$



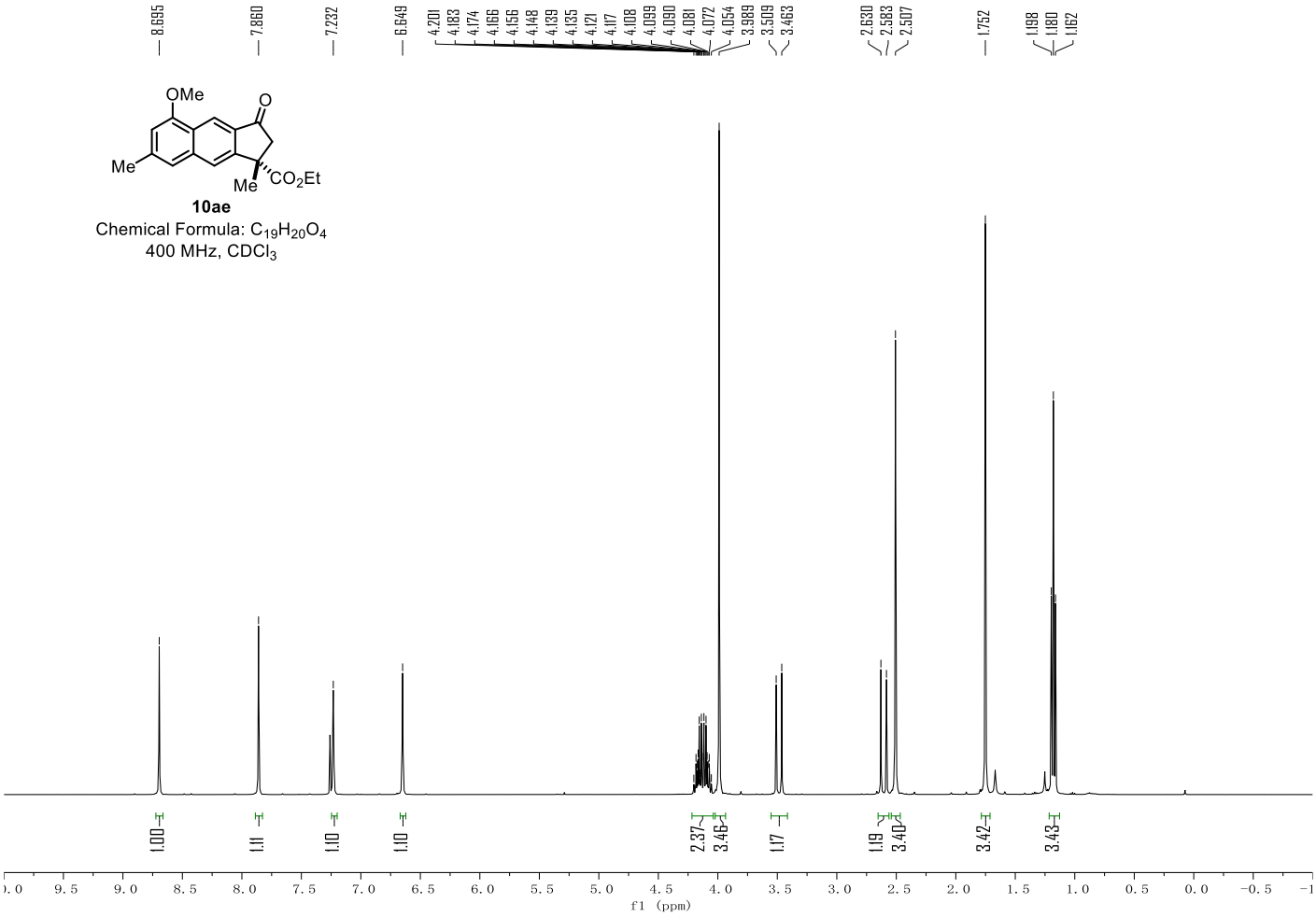
one isomer of **16ae**
Chemical Formula: $C_{19}H_{22}O_4$
100 MHz, $CDCl_3$

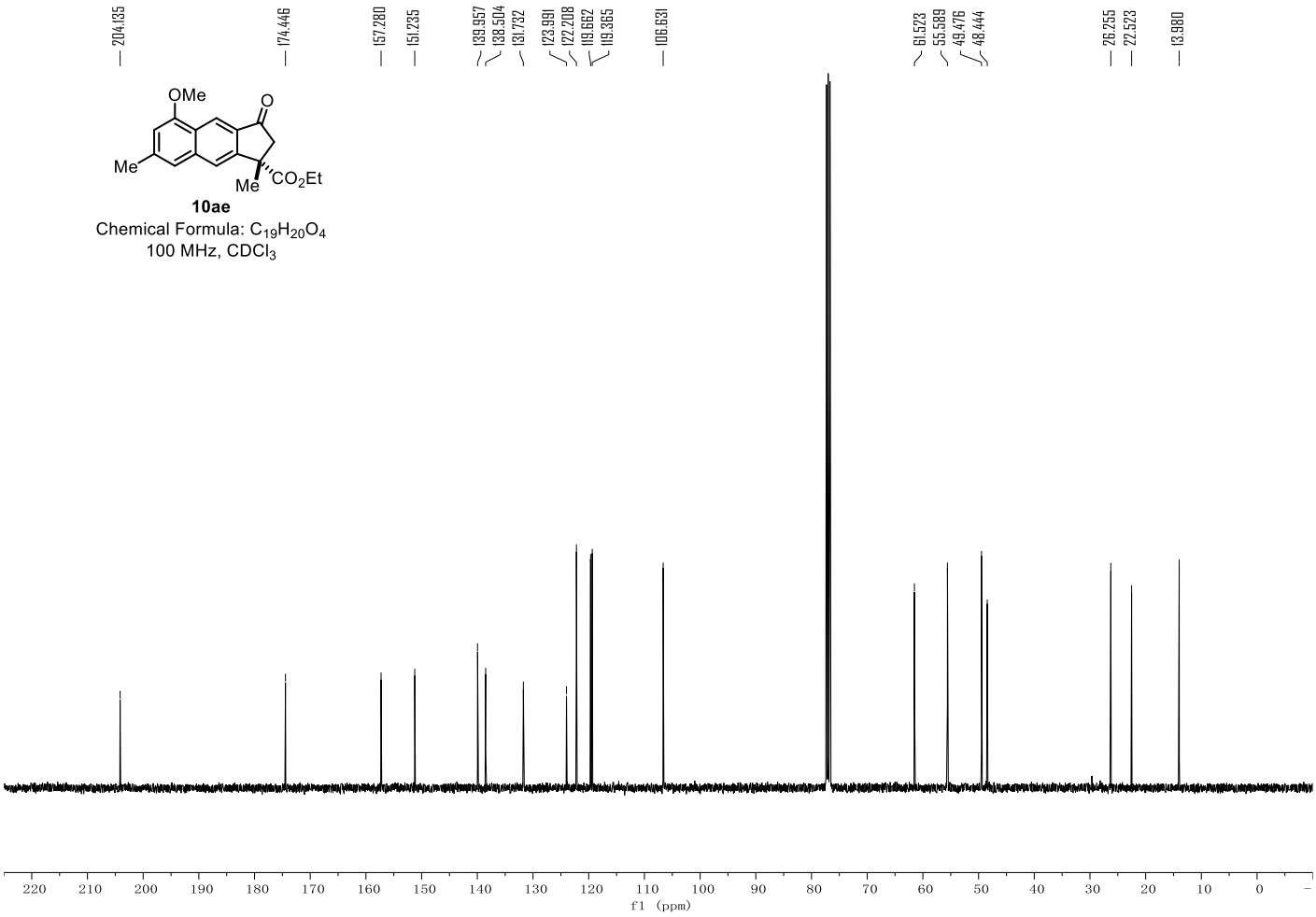


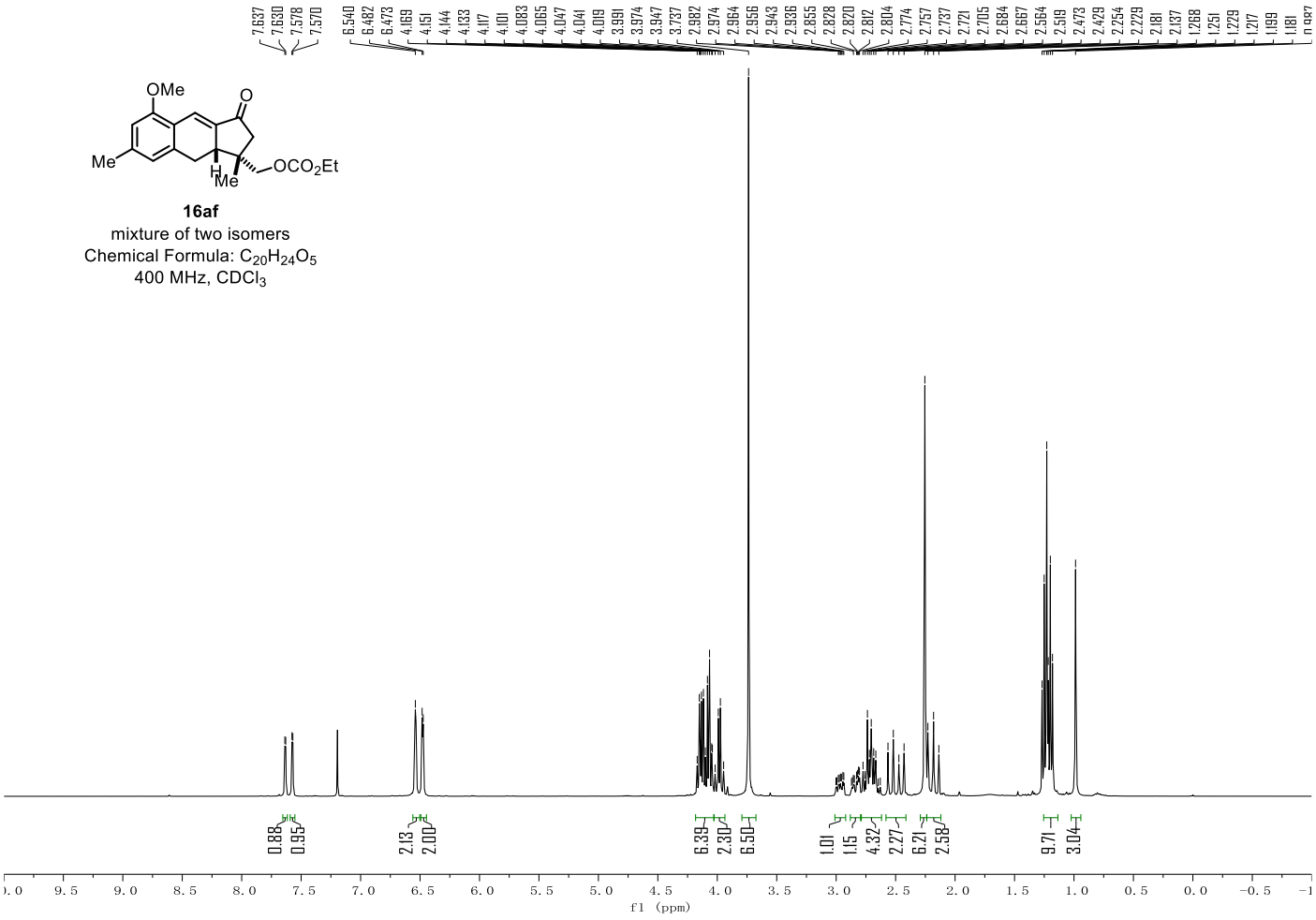
the other isomer of **16ae**
Chemical Formula: $C_{19}H_{22}O_4$
400 MHz, $CDCl_3$



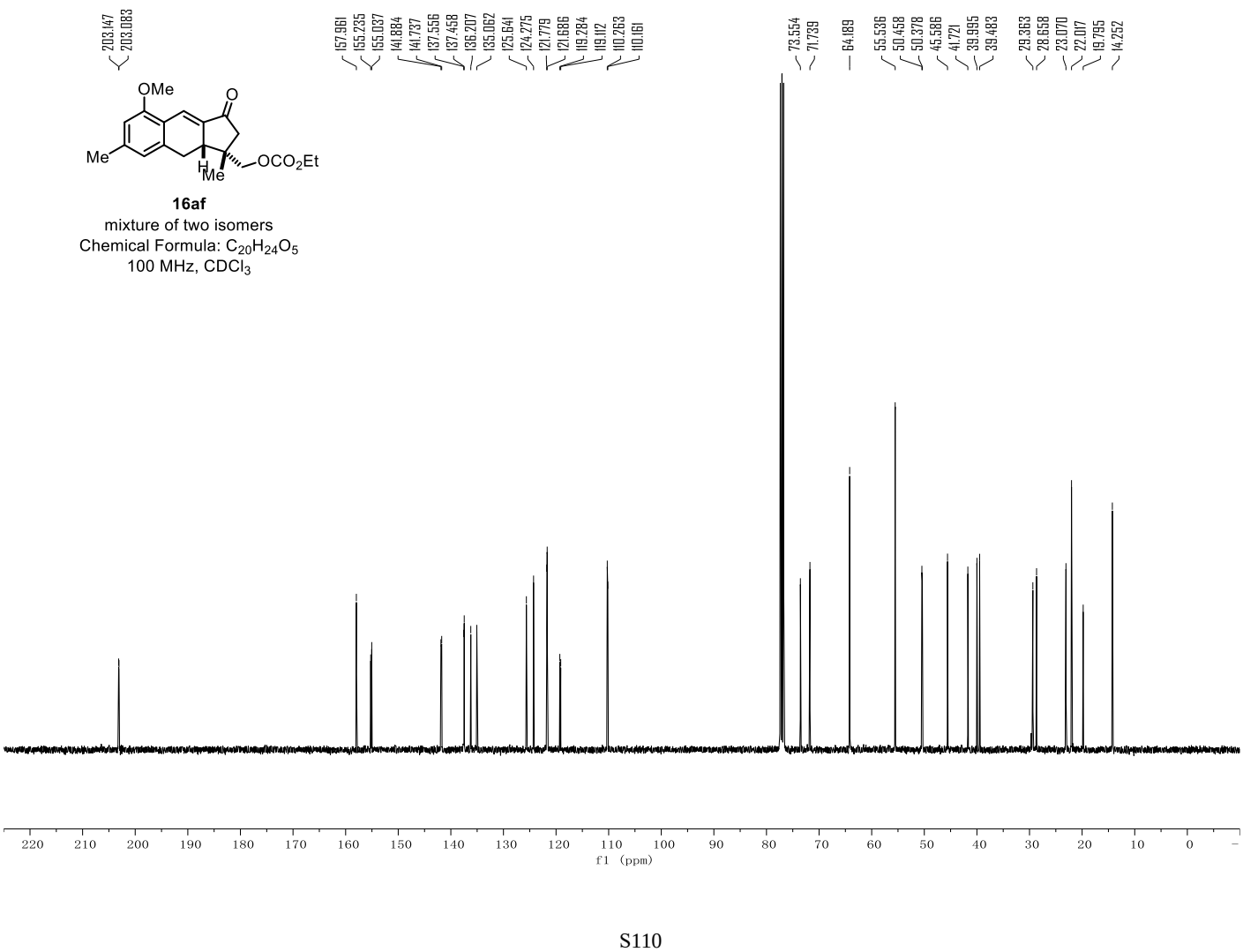
the other isomer of **16ae**
Chemical Formula: $C_{19}H_{22}O_4$
100 MHz, $CDCl_3$


8.695
7.860
7.232
6.649
4.201
4.183
4.174
4.166
4.156
4.148
4.139
4.135
4.121
4.117
4.108
4.099
4.090
4.081
4.072
4.054
3.988
3.509
3.463
2.630
2.583
2.507
1.752
1.198
1.180
1.162
OMe
O
Me
CO2Et
Me
10ae
Chemical Formula: C19H20O4
400 MHz, CDCl3
1.00
1.11
1.10
1.10
2.37
3.46
1.17
1.19
3.40
3.42
3.43
f1 (ppm)

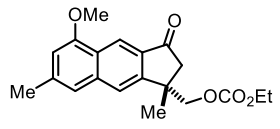

204.135
174.446
157.280
151.235
139.957
138.504
131.732
123.991
122.208
119.662
119.365
106.631
61.523
55.589
49.476
48.444
26.255
22.523
13.980
OMe
O
Me
CO2Et
Me
10ae
Chemical Formula: C19H20O4
100 MHz, CDCl3
f1 (ppm)



16af
mixture of two isomers
Chemical Formula: $C_{20}H_{24}O_5$
400 MHz, $CDCl_3$



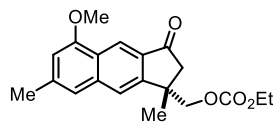
16af
mixture of two isomers
Chemical Formula: $C_{20}H_{24}O_5$
100 MHz, $CDCl_3$



10af

Chemical Formula: $C_{20}H_{22}O_5$

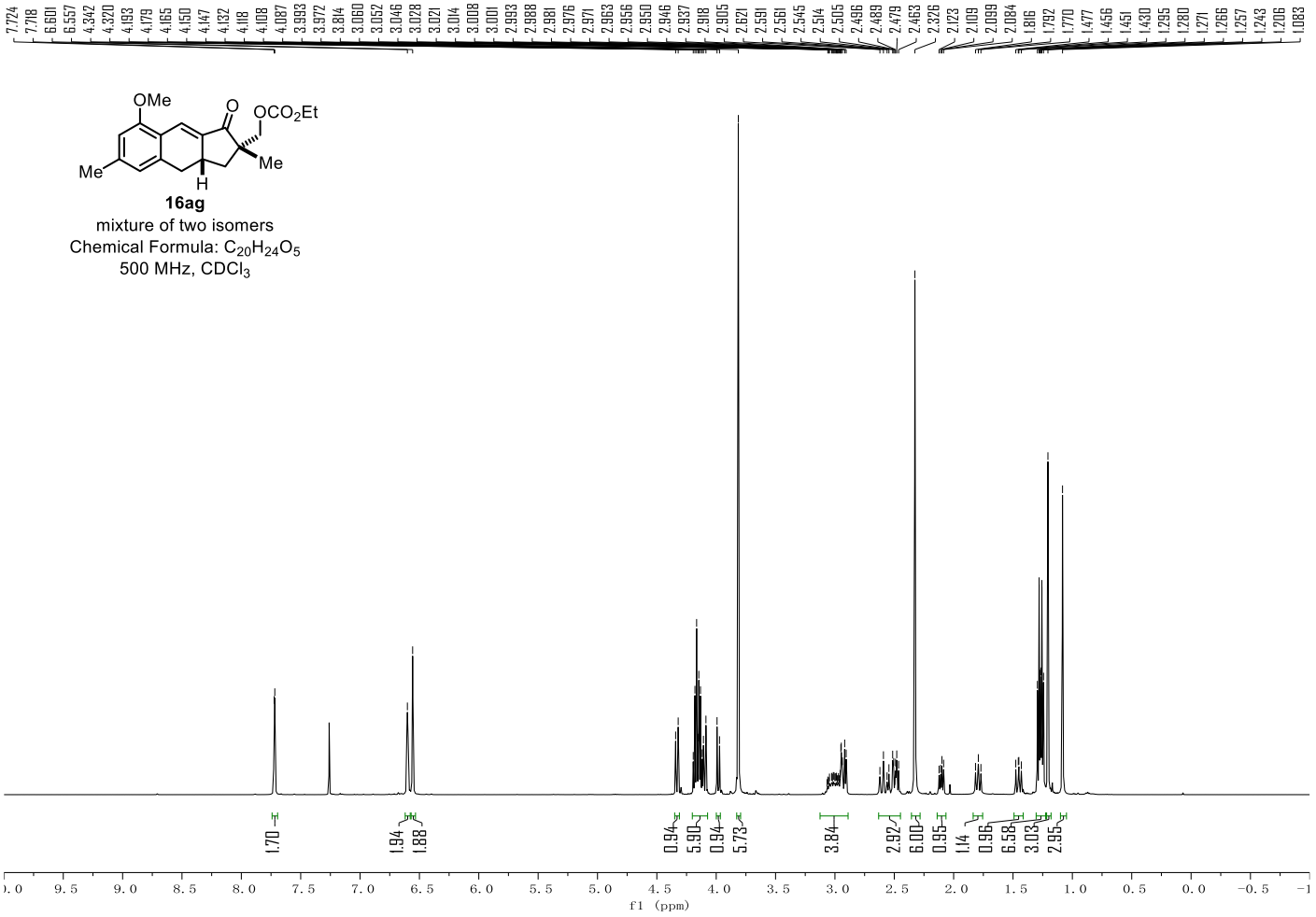
400 MHz, $CDCl_3$

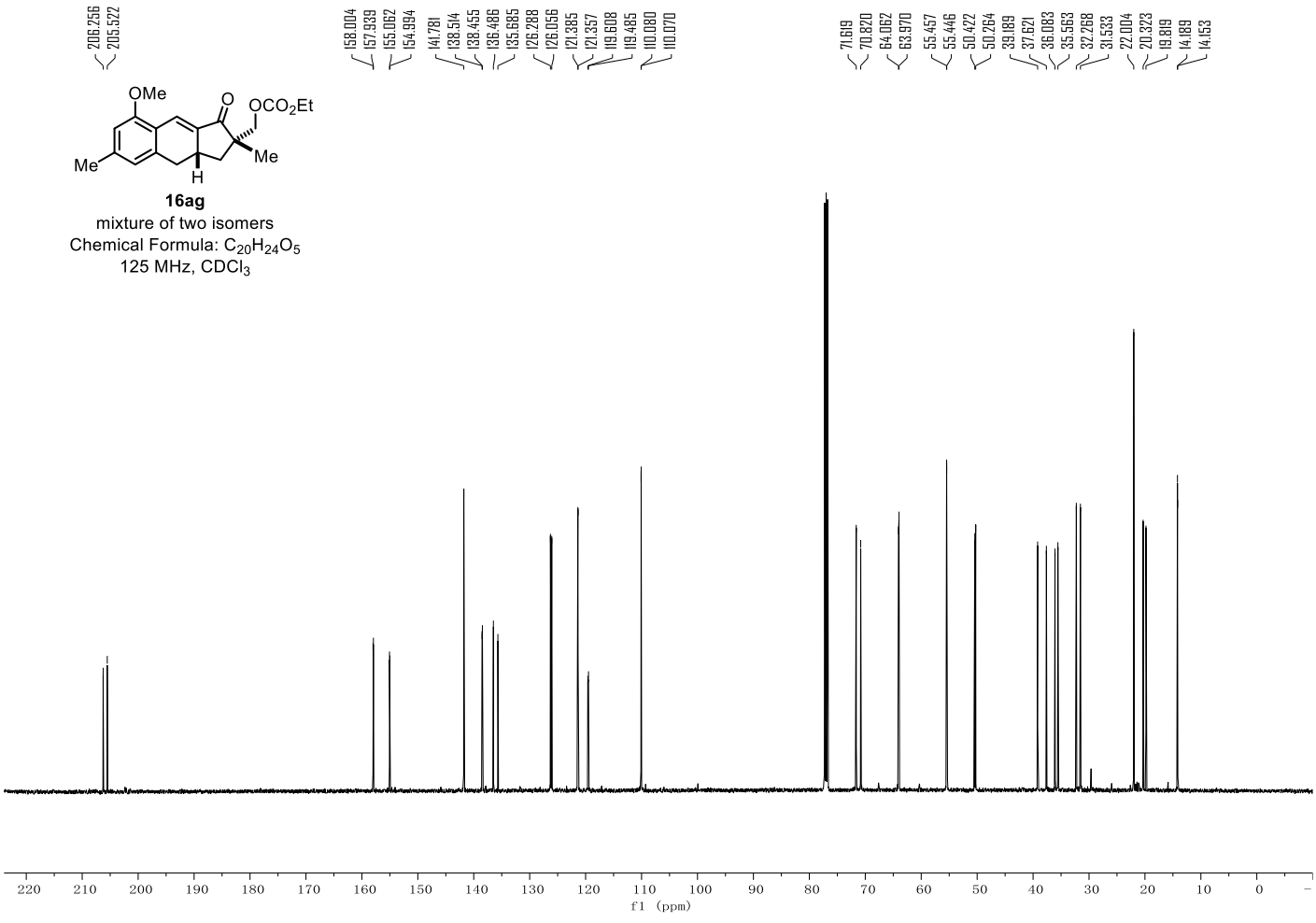


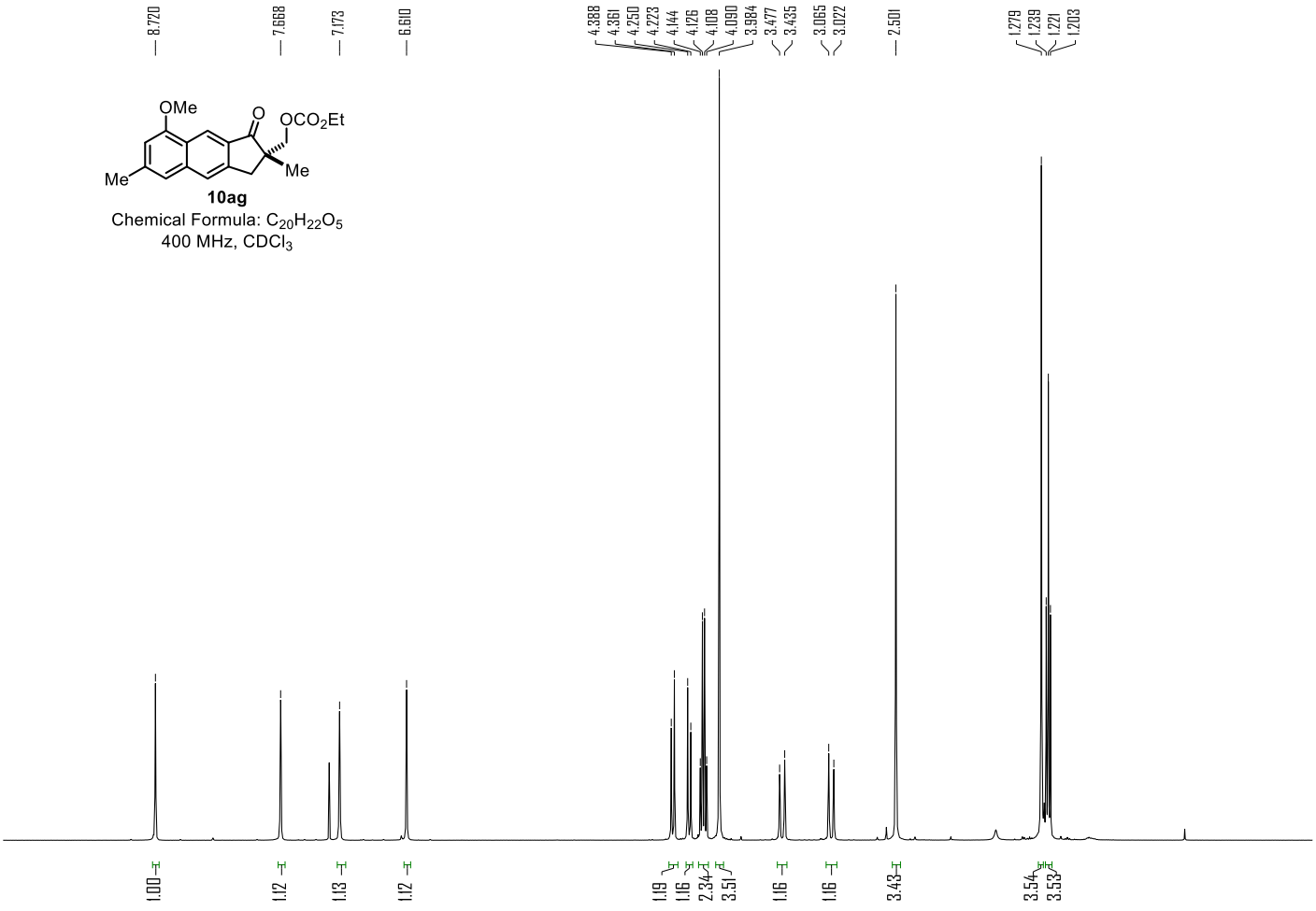
10af

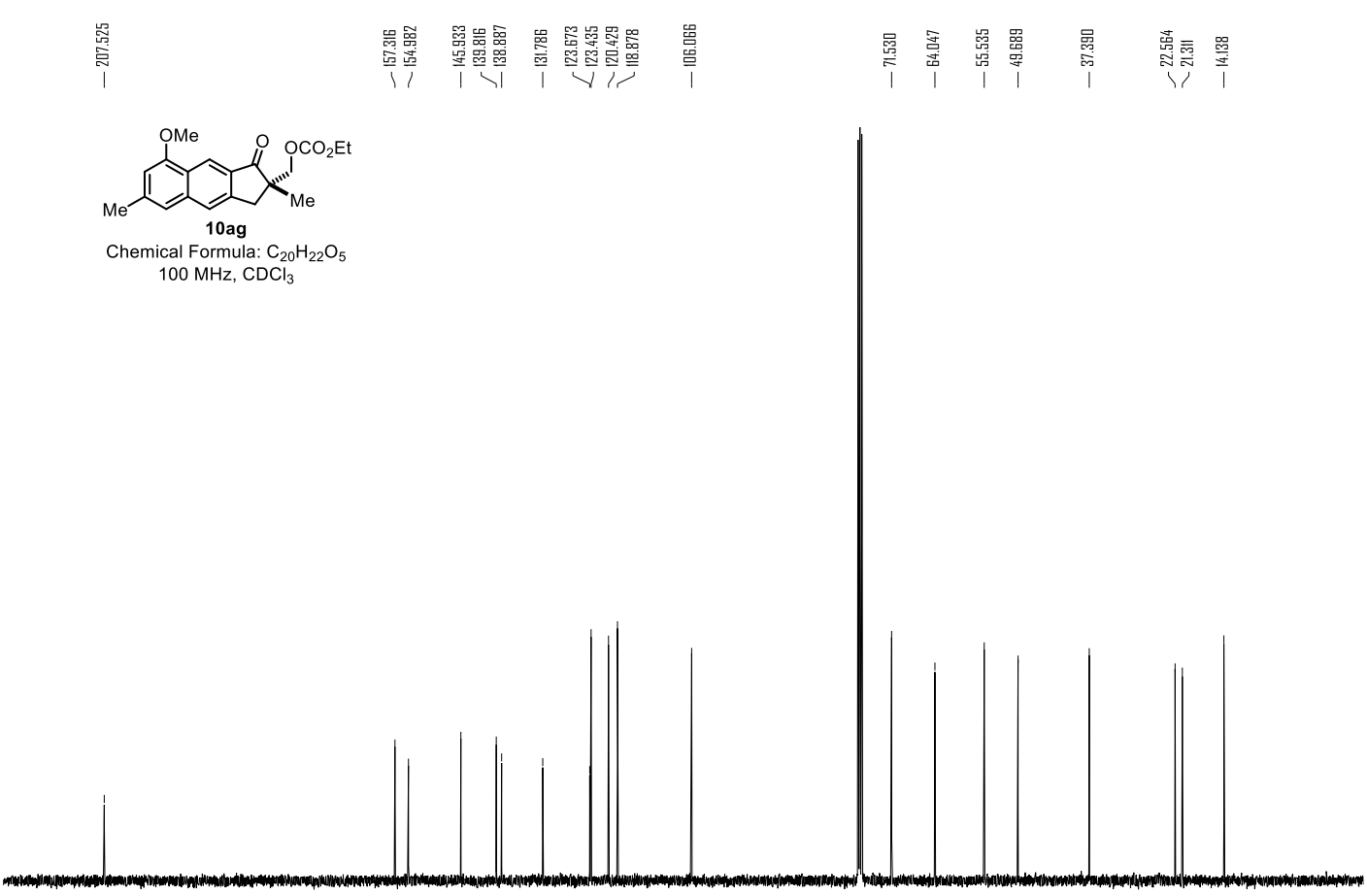
Chemical Formula: $C_{20}H_{22}O_5$

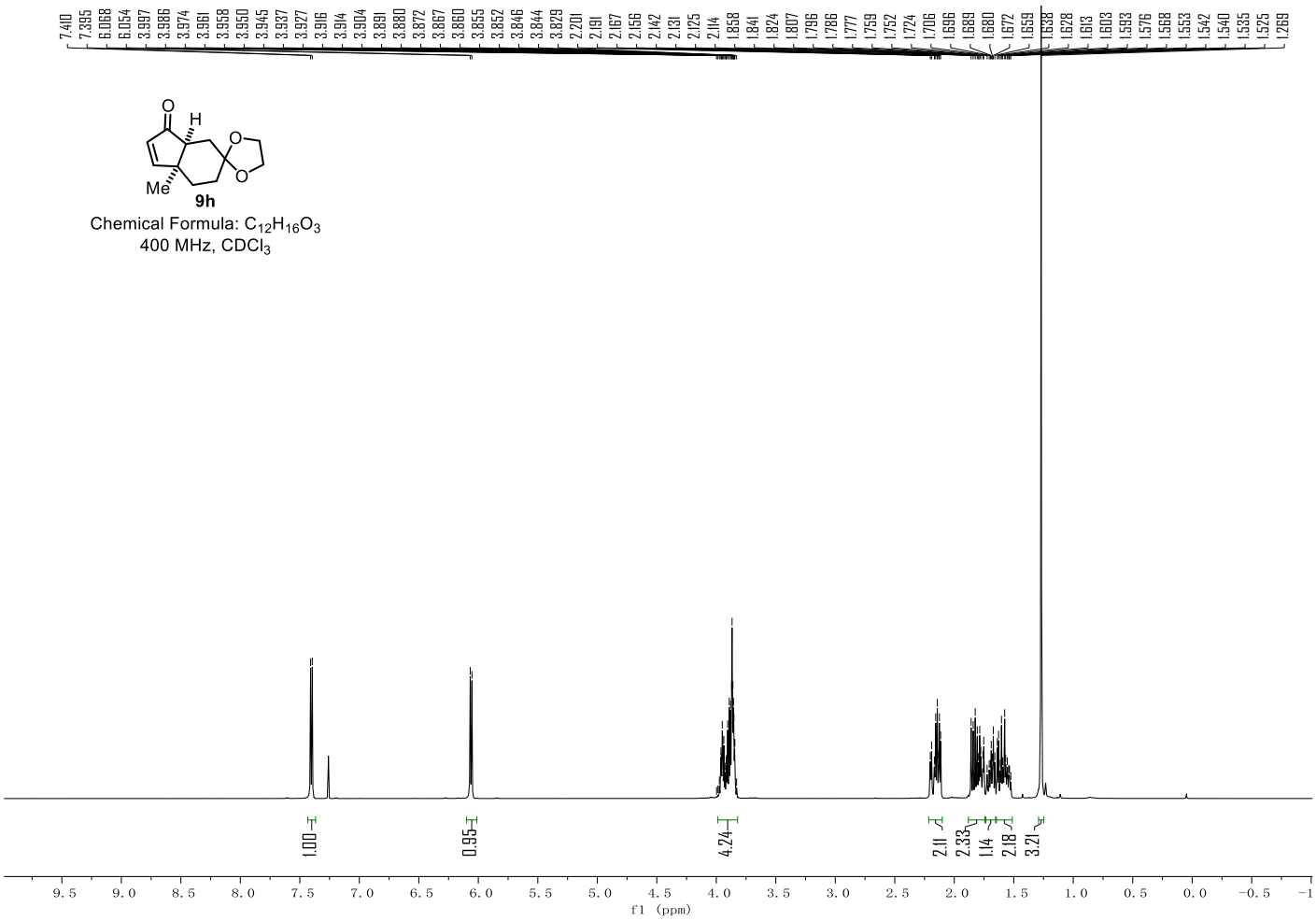
100 MHz, $CDCl_3$

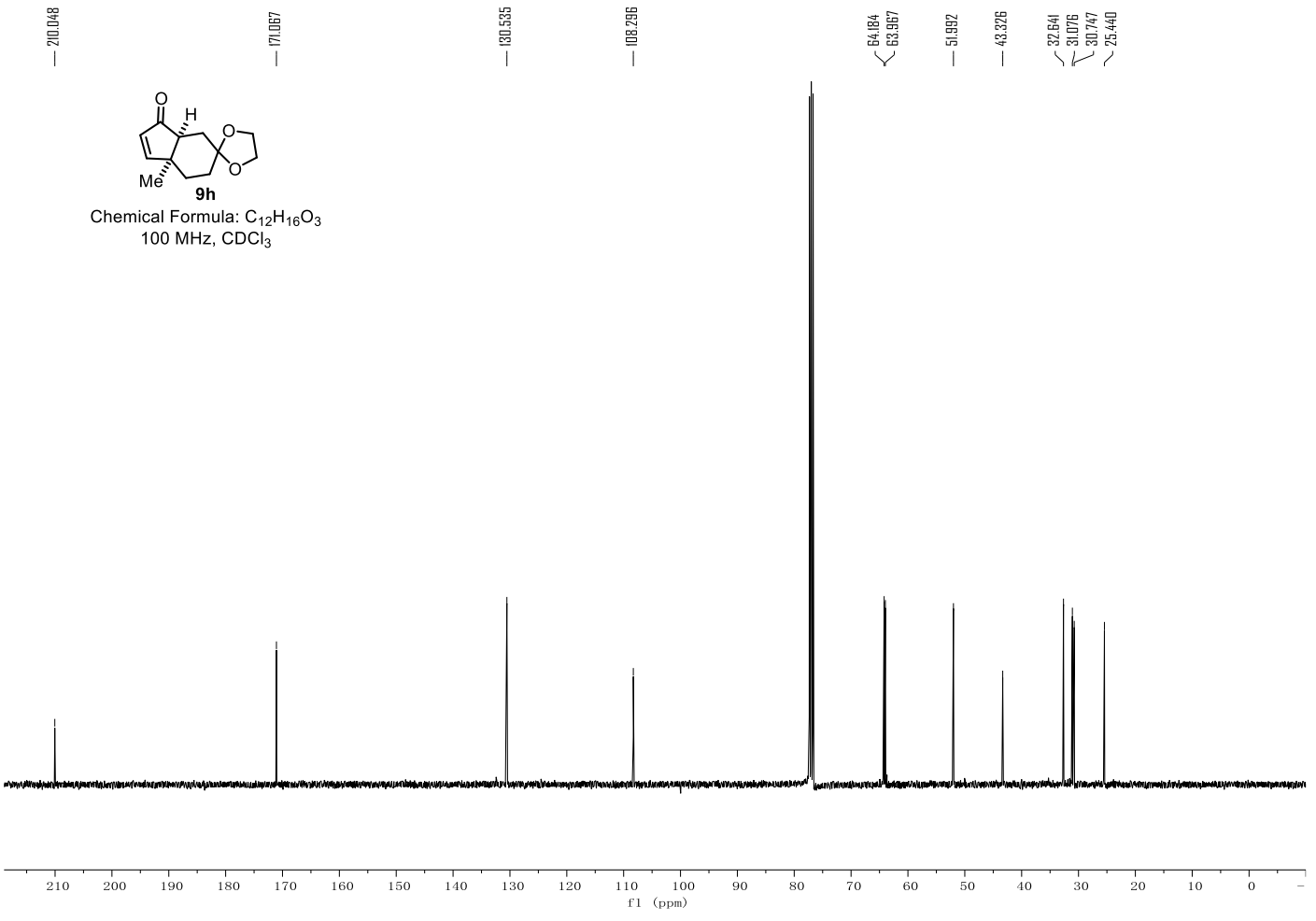

OMe
O
OCO2Et
Me
Me
H
16ag
mixture of two isomers
Chemical Formula: C20H24O5
500 MHz, CDCl3
f1 (ppm)

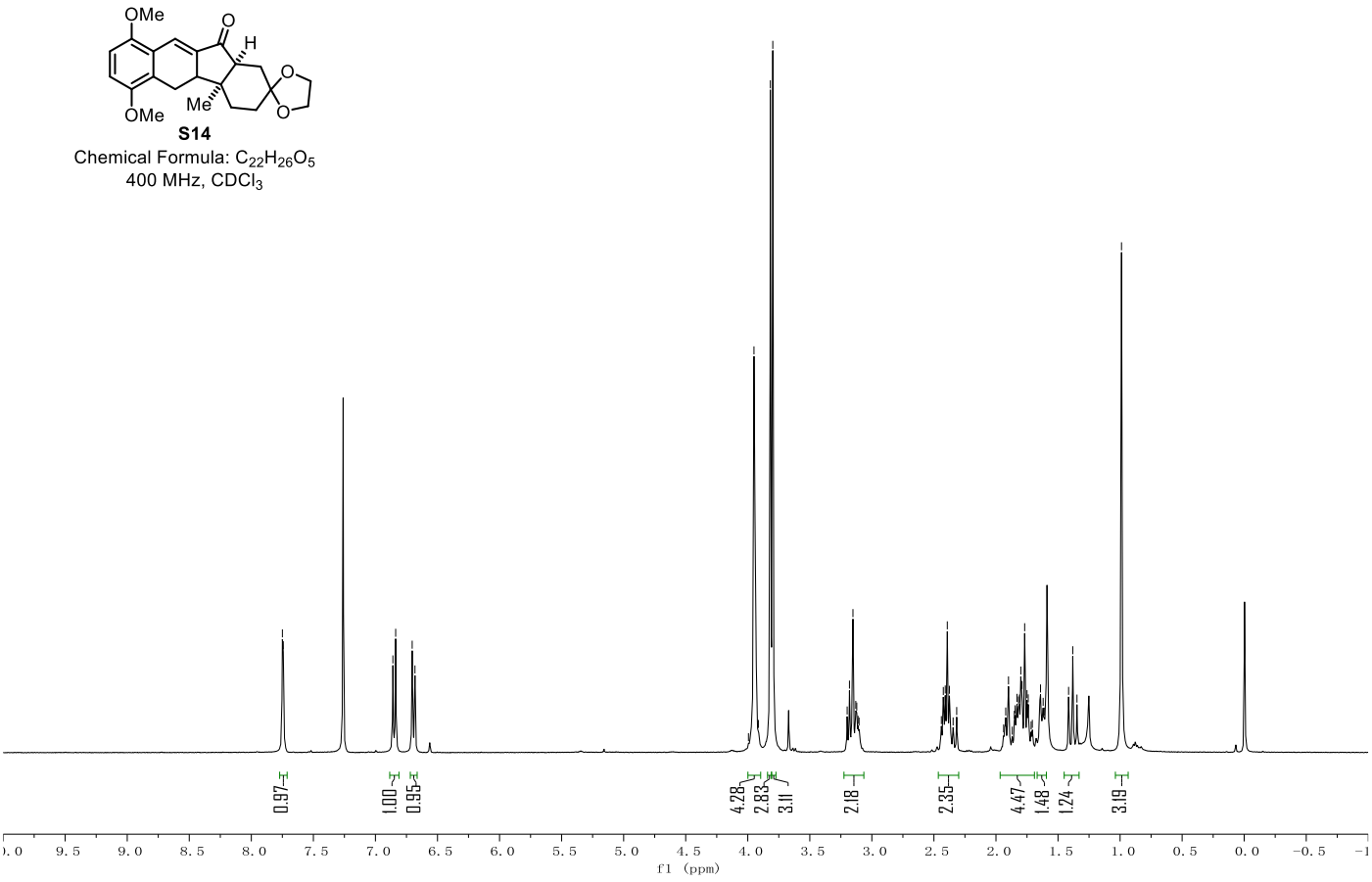

OMe
O
OCO2Et
Me
Me
H
16ag
mixture of two isomers
Chemical Formula: C20H24O5
125 MHz, CDCl3
f1 (ppm)


8.720
7.668
7.173
6.610
4.388
4.361
4.250
4.223
4.144
4.126
4.108
4.090
3.984
3.477
3.435
3.065
3.022
2.501
1.279
1.239
1.221
1.203
OMe
O
OCO2Et
Me
Me
10ag
Chemical Formula: C20H22O5
400 MHz, CDCl3
1.00
1.12
1.13
1.12
1.19
1.16
2.34
3.51
1.16
1.16
3.43
3.54
3.53


207.525
157.316
154.982
145.933
139.816
138.887
131.786
123.673
123.435
120.429
118.878
106.066
71.530
64.047
55.535
49.689
37.390
22.564
21.311
14.138
OMe
O
OCO2Et
Me
Me
10ag
Chemical Formula: C20H22O5
100 MHz, CDCl3


9h
Chemical Formula: C12H16O3
400 MHz, CDCl3
f1 (ppm)

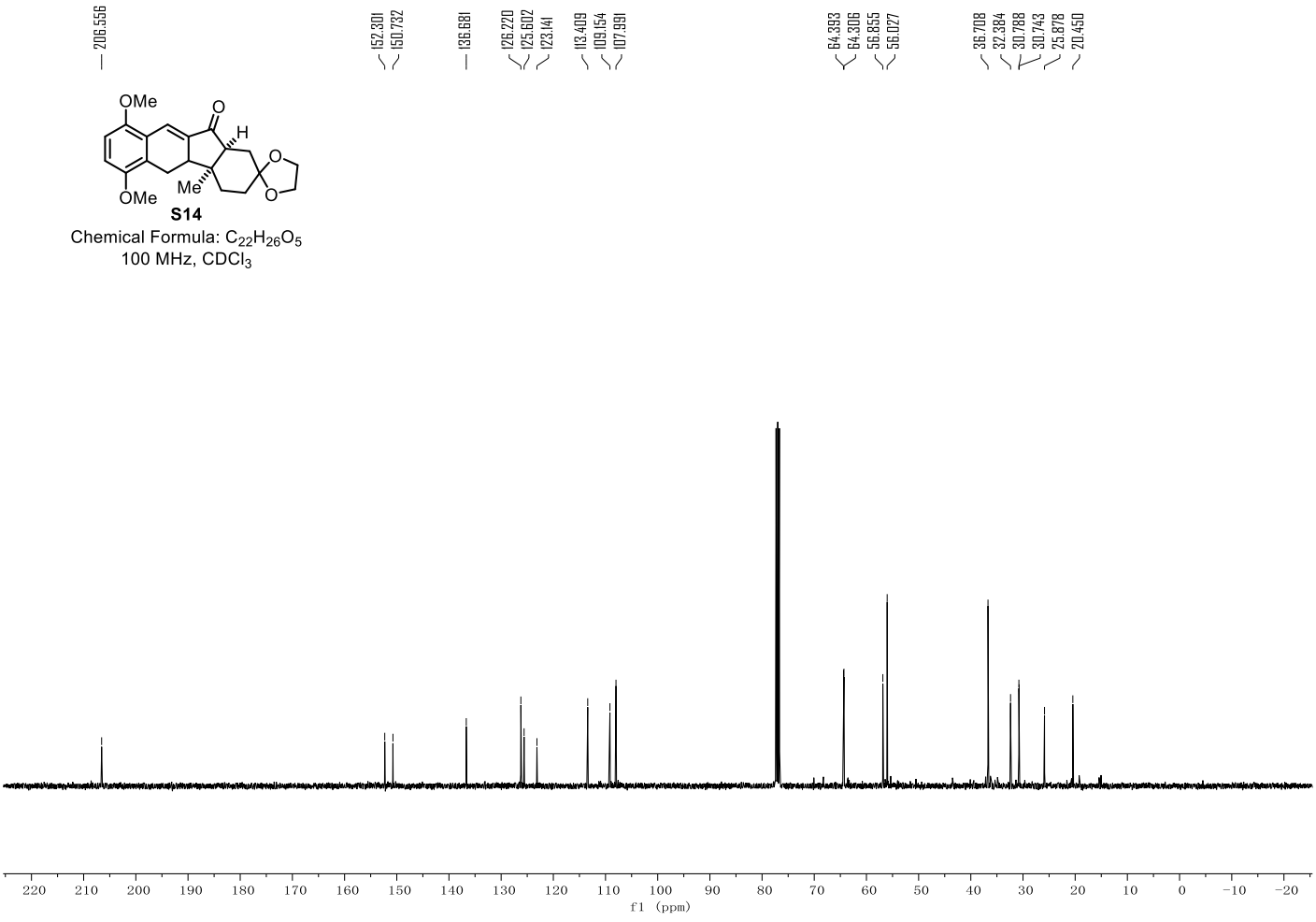

9h
Chemical Formula: C12H16O3
100 MHz, CDCl3
f1 (ppm)



S14

Chemical Formula: $C_{22}H_{26}O_5$

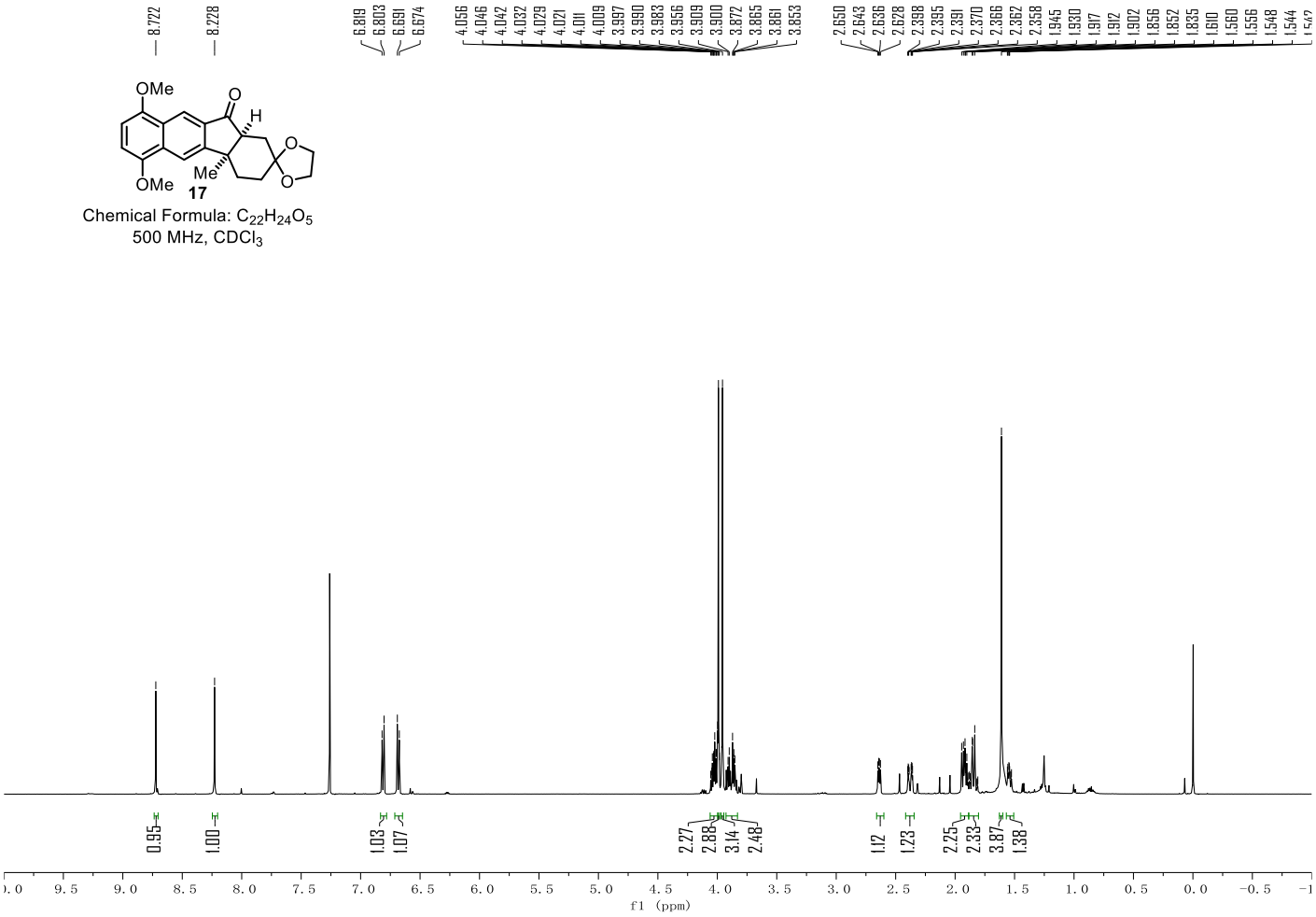
400 MHz, $CDCl_3$



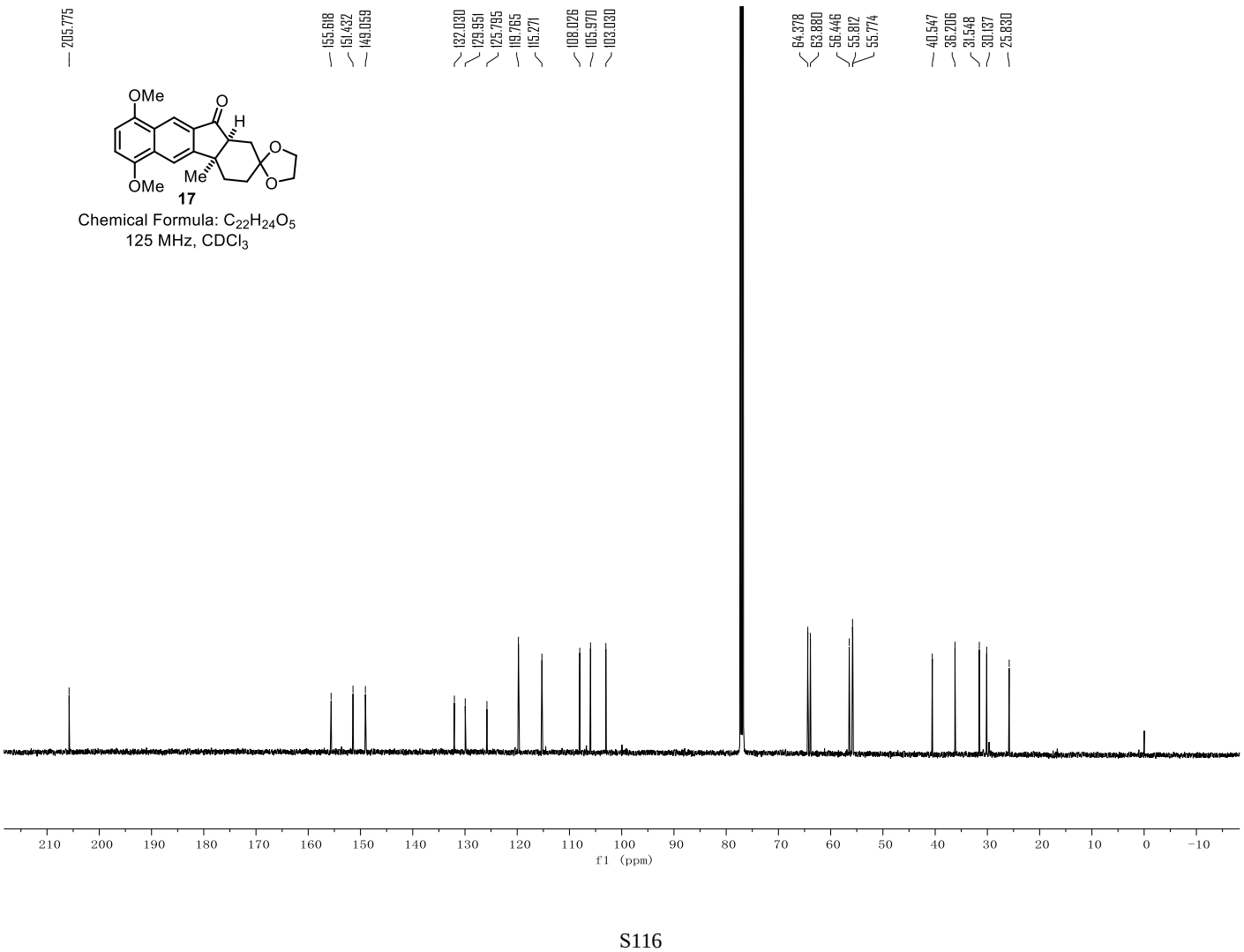
S14

Chemical Formula: $C_{22}H_{26}O_5$

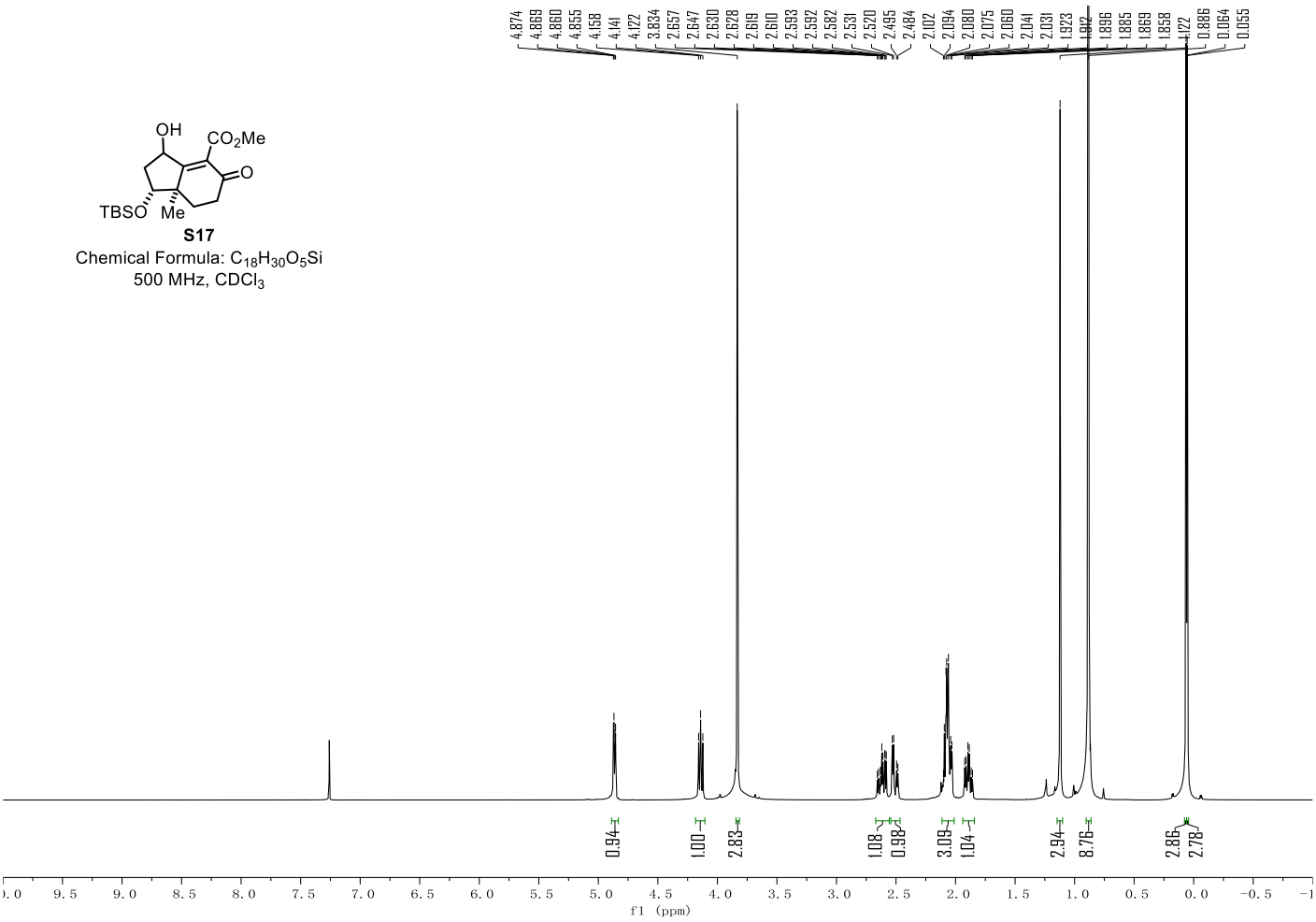
100 MHz, $CDCl_3$



Chemical Formula: $C_{22}H_{24}O_5$
500 MHz, $CDCl_3$



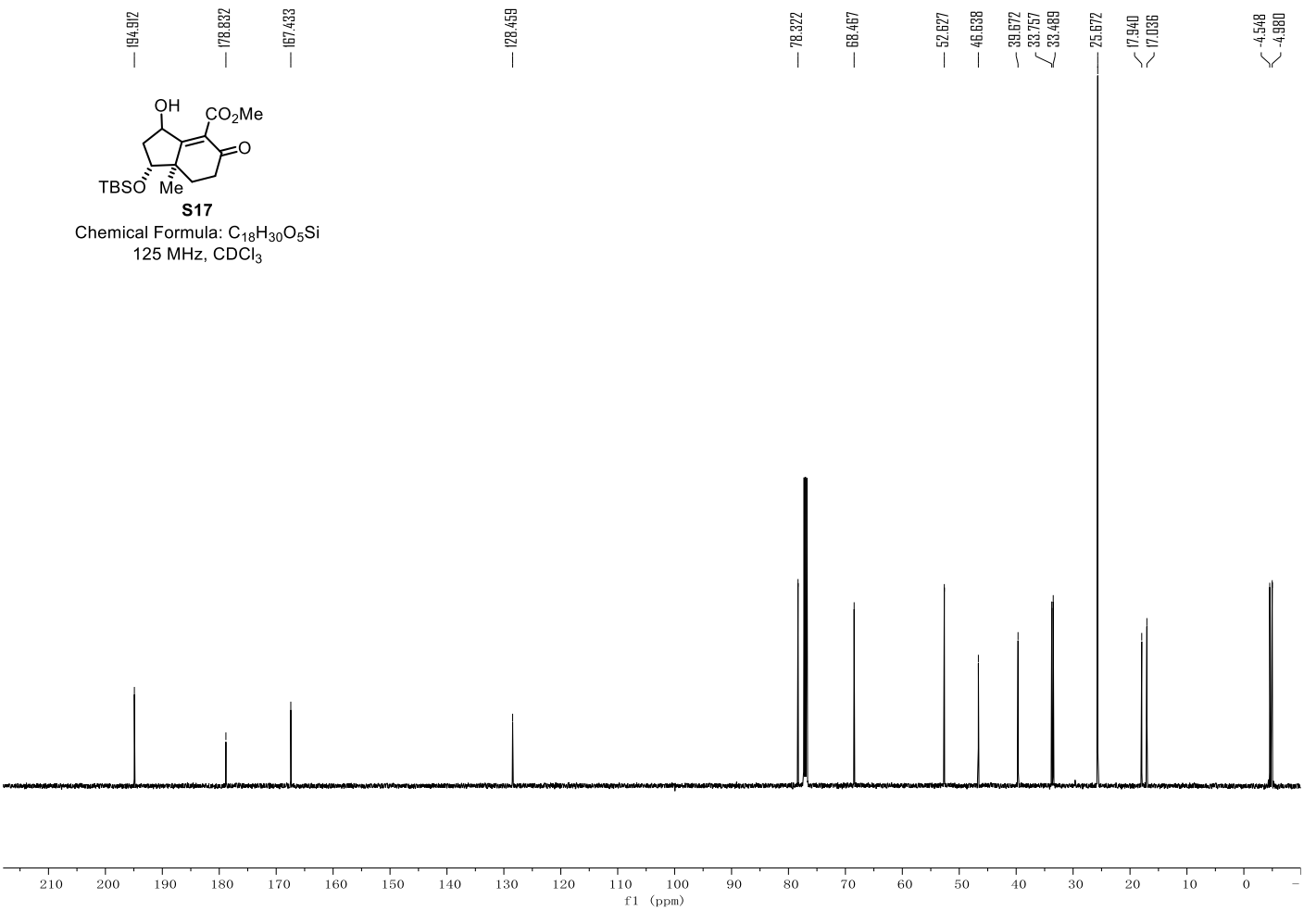
Chemical Formula: $C_{22}H_{24}O_5$
125 MHz, $CDCl_3$



S17

Chemical Formula: $C_{18}H_{30}O_5Si$

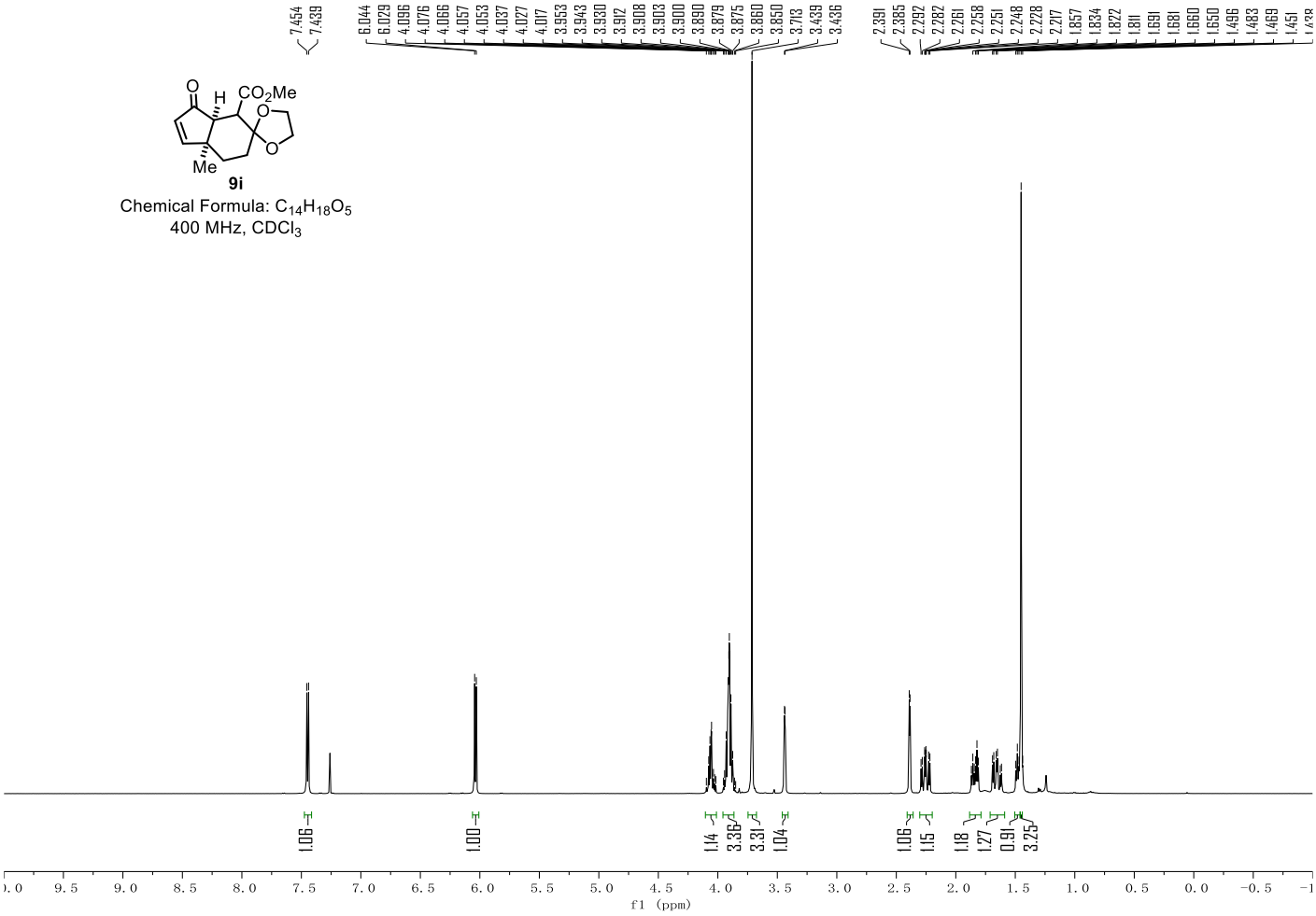
500 MHz, $CDCl_3$



S17

Chemical Formula: $C_{18}H_{30}O_5Si$

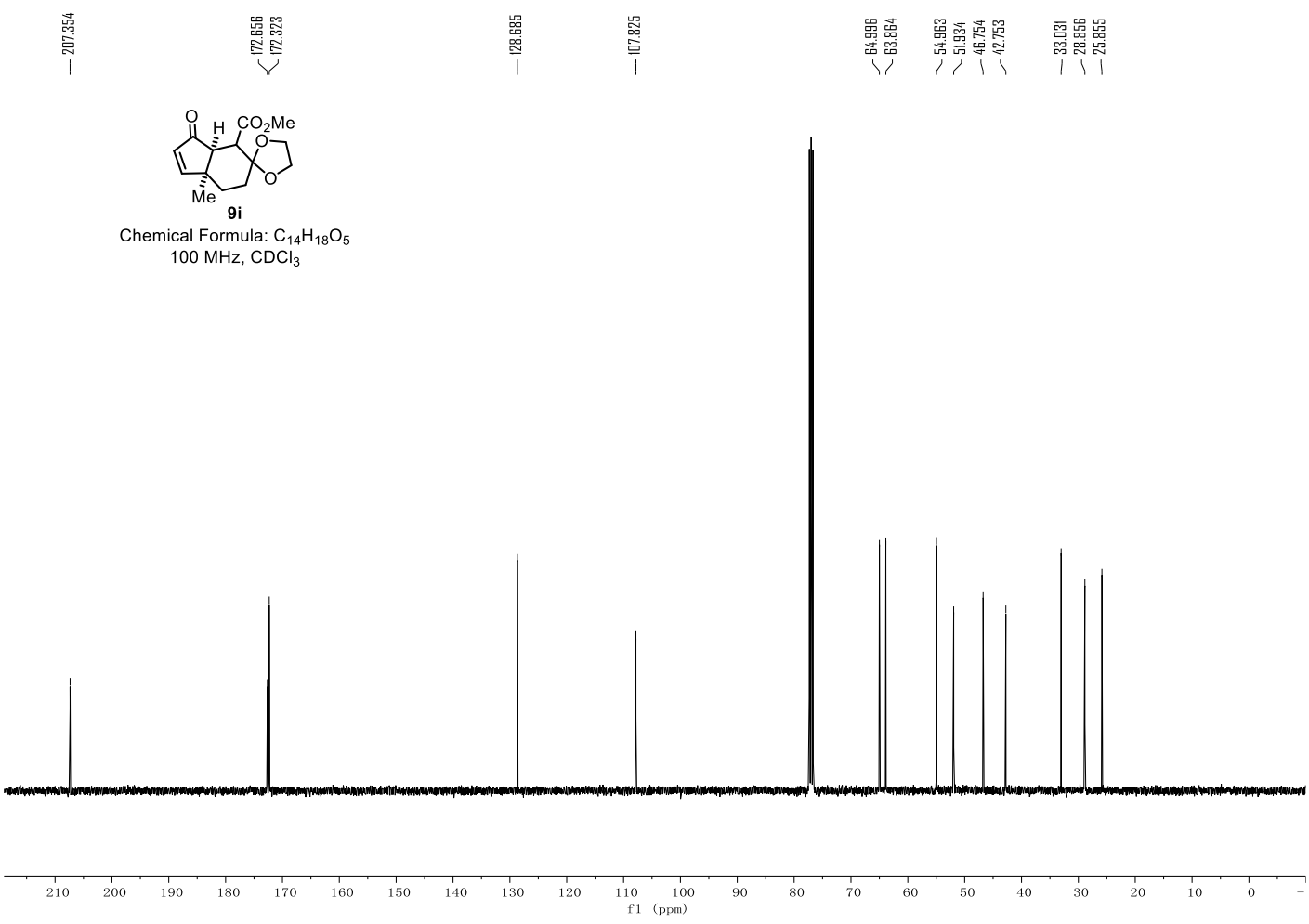
125 MHz, $CDCl_3$



9i

Chemical Formula: $C_{14}H_{18}O_5$

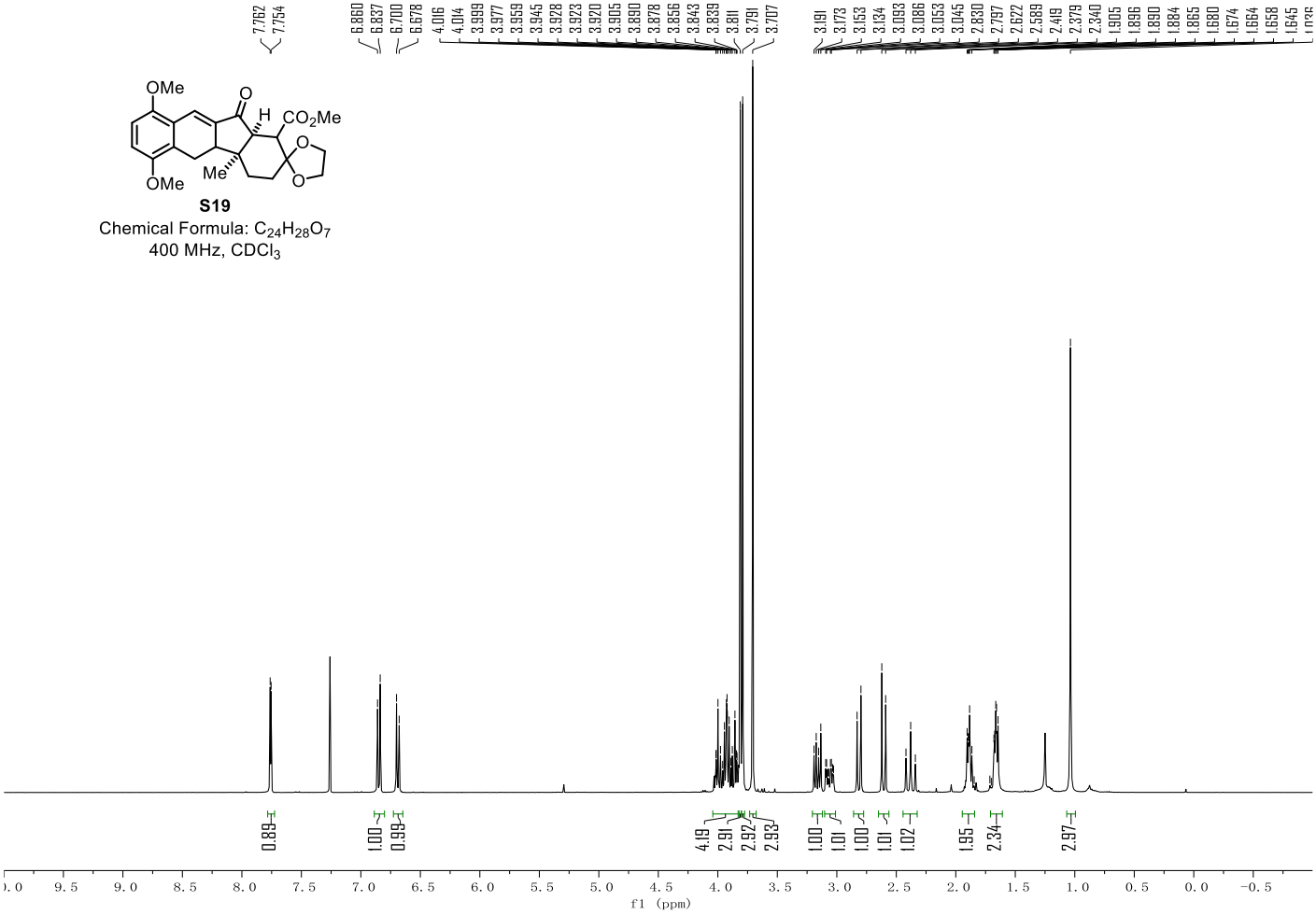
400 MHz, $CDCl_3$

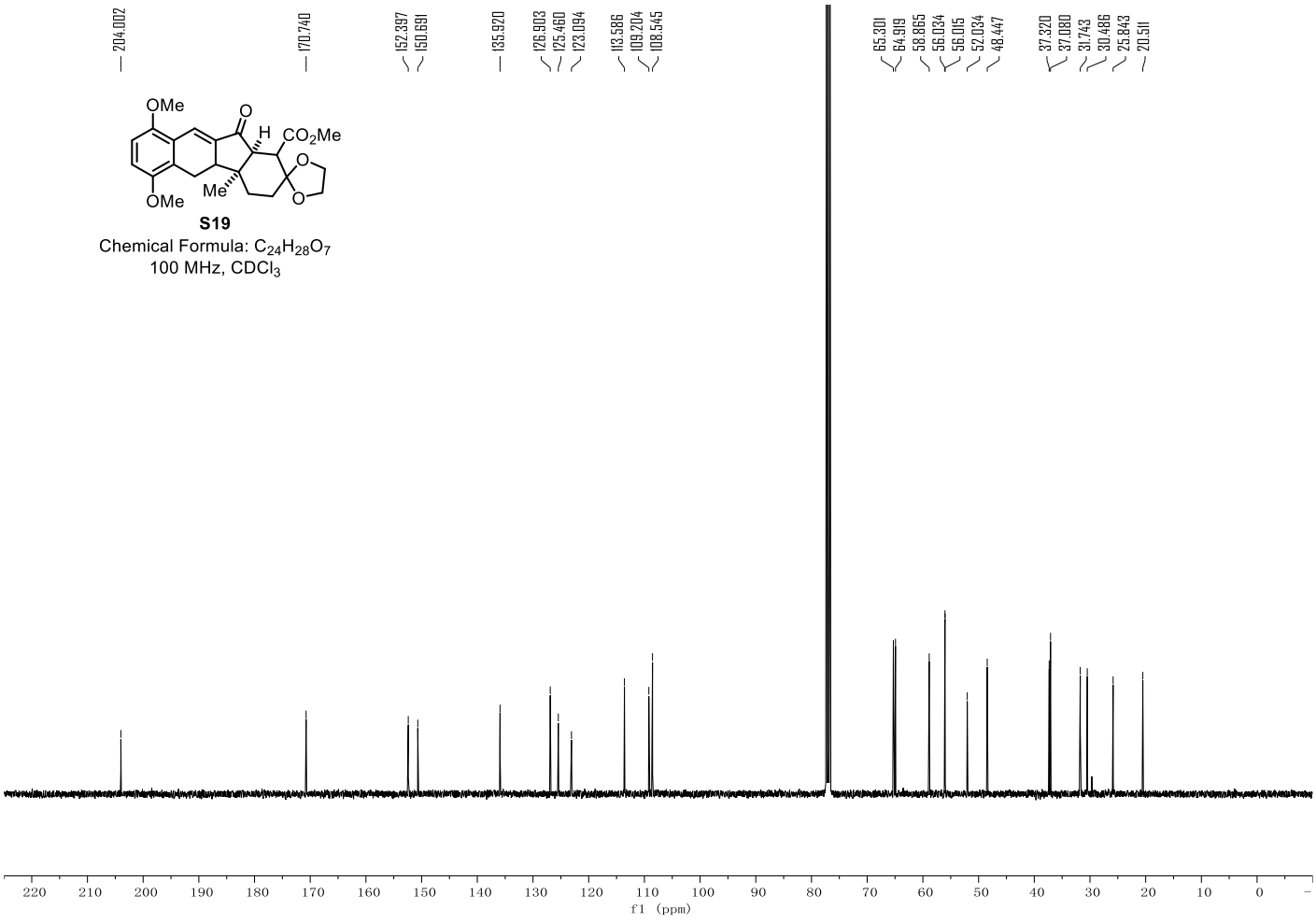


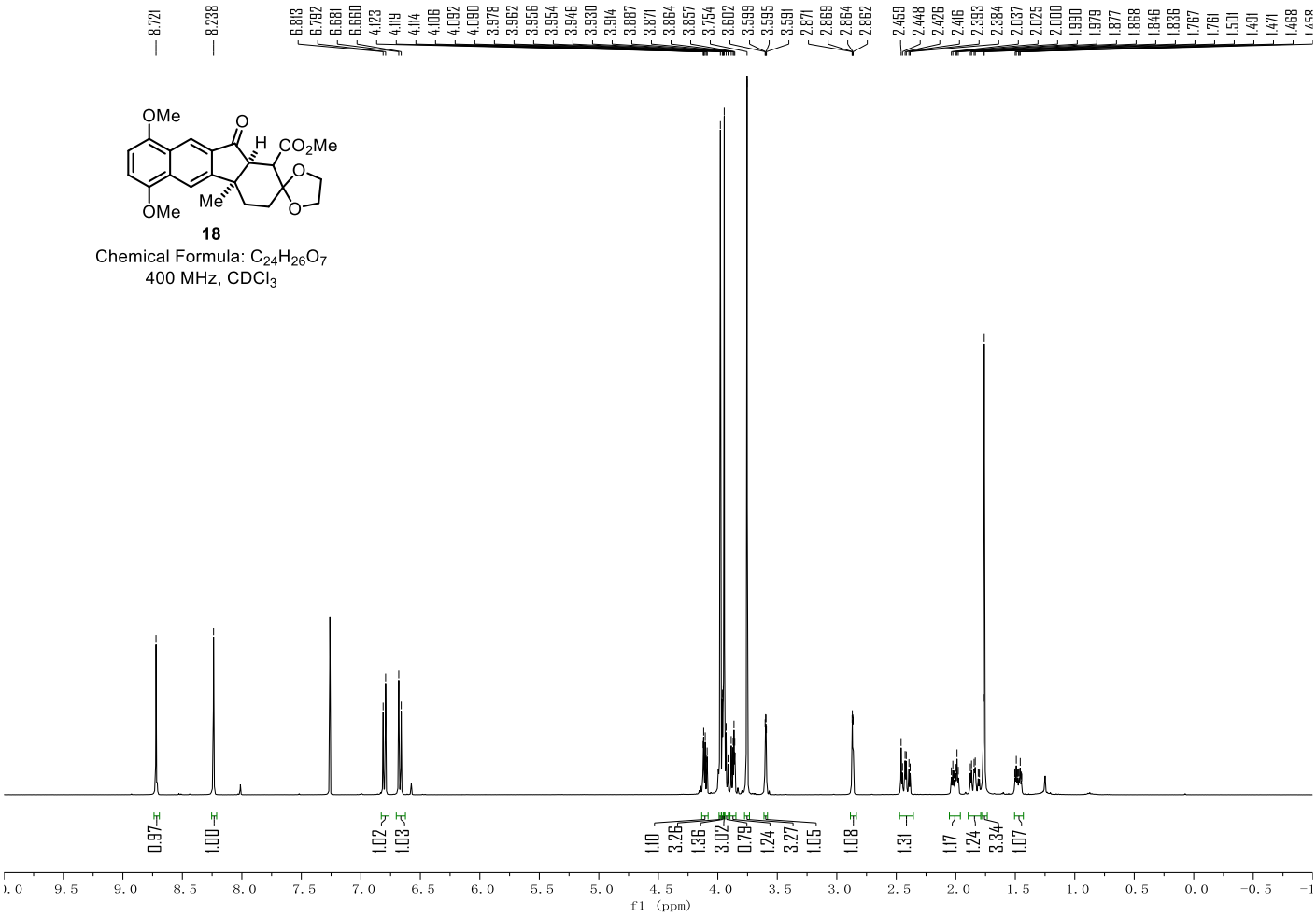
9i

Chemical Formula: $C_{14}H_{18}O_5$

100 MHz, $CDCl_3$


OMe
O
H
CO2Me
Me
OMe
O
O
S19
Chemical Formula: C24H28O7
400 MHz, CDCl3
f1 (ppm)

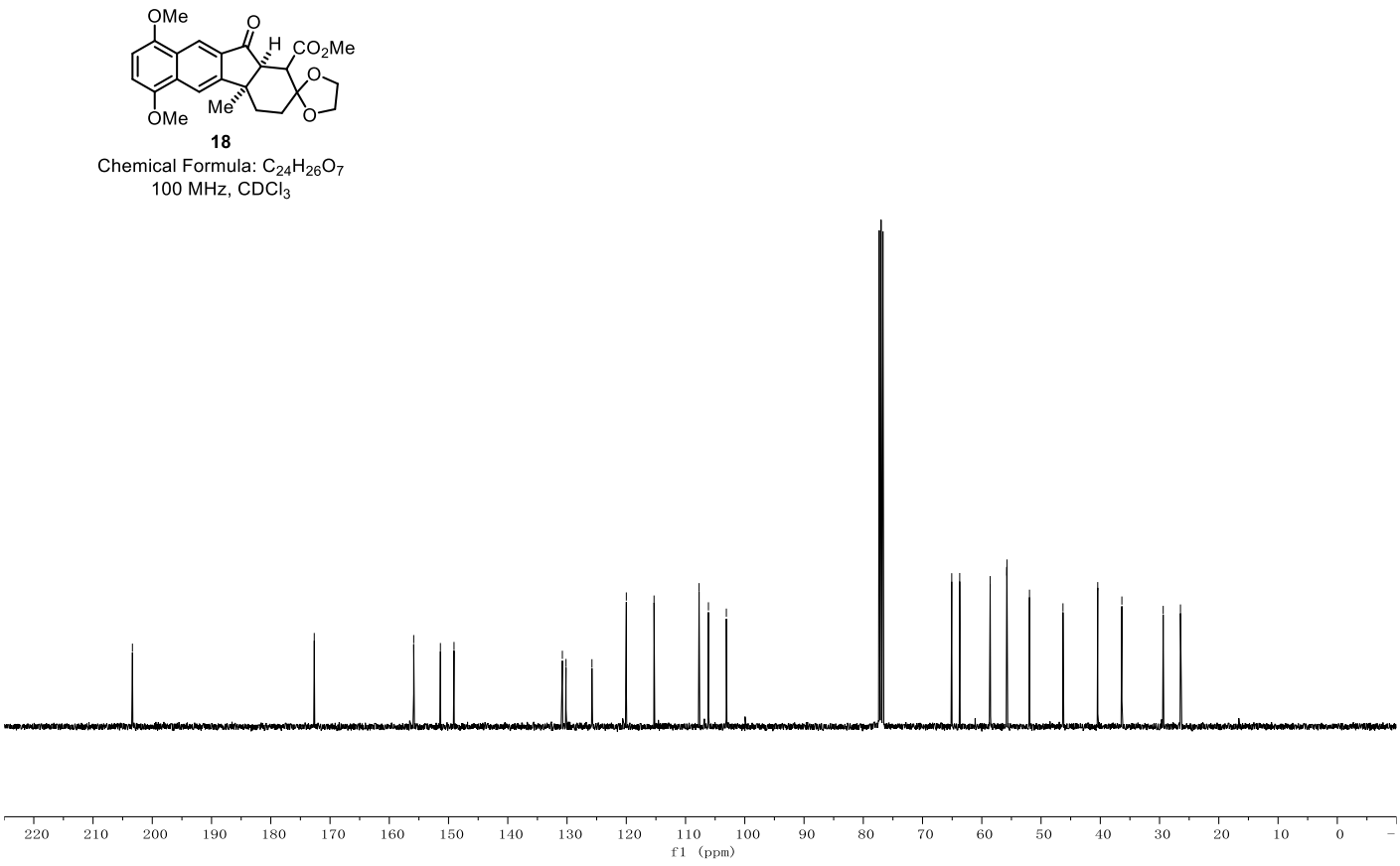

OMe
O
H
CO2Me
Me
OMe
O
O
S19
Chemical Formula: C24H28O7
100 MHz, CDCl3
f1 (ppm)



18

Chemical Formula: $C_{24}H_{26}O_7$

400 MHz, $CDCl_3$



18

Chemical Formula: $C_{24}H_{26}O_7$

100 MHz, $CDCl_3$