Divergent Synthesis of Multi-Substituted Phenanthrenes via Internal Redox Reaction/Ring Expansion Sequence

Ryosei Koyama,[†] Masahiro Anada,[‡§] Shunsuke Sueki,[‡§] Kosho Makino,[‡§] Tatsuhiro Kojima,[#] Tomoko Kawasaki-Takasuka,[†]and Keiji Mori[†]*

[†] *Department of Applied Chemistry, Graduate School of Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan.*

[‡] *Faculty of Pharmacy, Musashino University, Nishitokyo, Tokyo 202-8585, Japan.*

[§] *Research Institute of Pharmaceutical Sciences, Musashino University, Nishitokyo, Tokyo 202-8585, Japan.*

[#] *Department of Applied Chemistry, Kobe City College of Technology (KCCT) 8-3, Gakuen-Higashimachi, Nishi-ku, Kobe, 651-2194, Japan*

k_mori@cc.tuat.ac.jp

Supporting Information

General experimental procedures

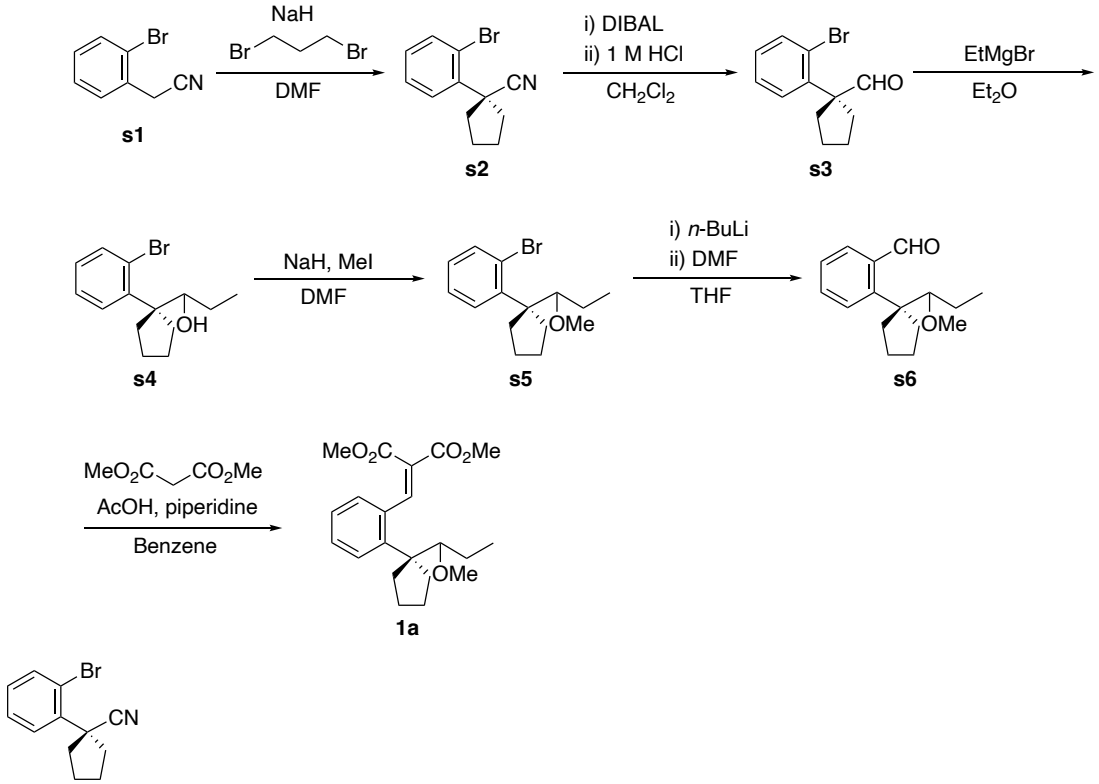
All reactions utilizing air- and moisture-sensitive reagents were performed in dried glassware under an atmosphere of dry nitrogen. Anhydrous ethereal solvents (THF, Et_2O) were purchased from Kanto Chemical Co., INC., and used directly. Dichloromethane and 1,2-dichloroethane were distilled over CaH_2. Benzene and toluene were distilled over CaH_2, and stored over 4A molecular sieves. *N*,*N*-Dimethylformamide (DMF) was distilled over CaH_2, and stored over 4A molecular sieves.

For thin-layer chromatography (TLC) analysis, Merck pre-coated plates (silica gel 60 F_{254}, Art 5715, 0.25 mm) were used. Column chromatography and preparative TLC (PTLC) were performed on Silica Gel 60N (spherical, neutral), Kanto Chemical Ltd. and Wakogel B-5F, Wako Pure Chemical Industries, respectively.

Melting point (mp) determinations were performed by using a AS ONE ATM-01 instrument and are uncorrected. ^{1}H NMR, ^{13}C NMR NMR were measured on a AL-300 MR (JEOL Ltd., 300 MHz) and ECX-400 (JEOL Ltd., 400 MHz) spectrometers. Chemical shifts are expressed in parts per million (ppm) downfield from internal standard (tetramethylsilane for ^{1}H, 0.00 ppm, C_6F_6 for ^{19}F, –163.00 ppm), and coupling constants are reported as hertz (Hz). Splitting patterns are indicated as follows: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; sep, septet; m, multiplet. Infrared (IR) spectra were recorded on a FTIR-8600PC instrument (Shimadzu Co.). Elemental analysis (EA) was carried out on Flash2000 instrument (Amco Inc.).

1. Preparation of starting materials.

Scheme S1. Preparation of starting materials **1**. Preparation of **1a** was shown as a representative example.[1]



Synthesis of 1-(2-bromophenyl)cyclopentane-1-carbonitrile (s2):[1]

To a solution of benzyl cyanide **s1** (3.16 g, 16.1 mmol) in DMF (95.0 mL) were successively added NaH (60% oil, 2.58 g, 64.6 mmol) and 1,4-dibromoethane (2.3 ml, 19.4 mmol) at 0 °C. After being stirred for 1.5 h at 50 °C, the reaction was quenched by adding H_2O at 0 °C. The crude mixture was extracted with EtOAc (x4) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 10/1) to give **s2** (2.48 g, 61%) as colorless oil.

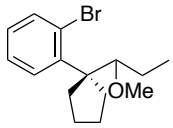
IR (neat) 3066, 2960, 2876, 2231, 1586, 1567, 1469, 1454, 1436, 1319, 1284, 1275, 1228, 1167, 1057, 1038, 1024 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.67 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.42 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.32 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.19 (ddd, 1H, *J* = 7.8, 7.8 1.5 Hz), 2.79-2.71 (m, 2H), 2.28-2.14 (m, 2H), 2.11-1.97 (m, 2H), 1.96-1.82 (m, 4H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 137.2, 134.7, 129.3, 127.4, 127.3, 123.3, 122.6, 47.2, 37.8,

23.3.

Anal. Calcd for $C_{12}H_{12}ON$: C, 57.62; H, 4.84; N, 5.60. Found: C, 59.55; H, 6.60; N, 5.83.



Synthesis of 1-bromo-2-(1-(1-methoxypropyl)cyclopentyl)benzene (s5):

To a solution of **s2** (3.82 g, 15.3 mmol) in CH_2Cl_2 (61.1 mL) was slowly added DIBAL (1.0 M in toluene, 18.5 mL, 18.6 mmol) at –78 °C. After being stirred for 3 h at –78 C, the reaction was quenched by addition of 1 M HCl (61.1 mL). After being stirred for 17.5 h at room temperature, the crude mixture was extracted with CH_2Cl_2 (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give crude **s3** (3.83 g) as colorless oil. This crude material was used for next reaction without further purification.

To a solution of crude **s3** in Et_2O (50.9 mL) was added EtMgBr, prepared from Mg (0.94 mg, 38.6 mmol) and EtBr (1.94 mL, 26.0 mmol), at 0 °C. After being stirred for 2 h at room temperature, the reaction was stopped by adding saturated aqueous NH_4Cl at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo to give alcohol **s4** (4.29 g) as colorless oil. This crude material was used for next reaction without further purification.

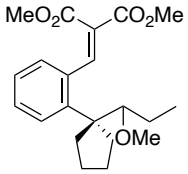
To a solution of crude **s4** in DMF (51.0 mL) were successively added NaH (60 % oil, 1.24 g, 31.1 mmol) and MeI (1.33 mL, 21.4 mmol). After being stirred for 24 h at room temperature, the reaction was quenched by addition of saturated aqueous NH_4Cl at 0 °C. The crude mixture was extracted with mixed solvent (EtOAc:Hexane = 1:4, x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 20/1) to give **s5** (4.06 g, 89% from **s2**) as pale yellow oil.

IR (neat) 2962, 2872, 2825, 1455, 1433, 1370, 1354, 1192, 1146, 1105, 1090, 1016 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.38 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.23 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.03 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 4.08 (dd, 1H, *J* = 9.6, 2.7 Hz), 3.45 (s, 3H), 2.40-2.19 (m, 4H), 1.77-1.10 (m, 6H), 0.86 (t, 3H, *J* =

7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 135.6, 129.9, 127.5, 126.9, 123.1, 85.3, 61.2, 57.6, 34.2, 31.8, 25.8, 24.9, 23.8, 11.8.

Anal. Calcd for $C_{14}H_{19}BrO$: C, 59.37; H, 6.76. Found: C, 59.55; H, 6.56.



Synthesis of dimethyl 2-(2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (3a)[1]

To a solution of **s5** (4.06 mg, 13.7 mmol) in THF (45.5 mL) was added *n*-BuLi (1.60 M in hexane, 11.1 mL, 17.8 mmol) at –78 °C. The reaction mixture was stirred for 0.5 min at –78 °C, to which DMF (2.1 mL, 27.3 mmol) was added. After being stirred for 1.5 h, the reaction was quenched by addition of saturated aqueous NH_4Cl at –78 °C. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo to give crude **s6** (3.79 g) as colorless oil. This crude material was used for next reaction without further purification. To a solution of crude **s6** (3.79 g) in benzene (68.3 mL) were successively added dimethyl malonate (1.52 mL, 13.3 mmol), piperidine (1.35 mL, 13.7 mmol), and AcOH (0.78 mL, 13.7 mmol) at room temperature, and then heated to reflux. After being stirred for 24 h at refluxing temperature, the reaction was quenched by addition of saturated aqueous $NaHCO_3$ at 0 °C. The crude mixture was extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 20/1) to afford **3a** (2.77 g, 56%) as white solid.

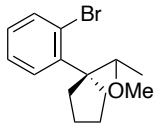
Mp. 81–82 °C.

IR (KBr) 3104, 2966, 2945, 2926, 2872, 2829, 1733, 1713, 1627, 1597, 1431, 1368, 1294, 1250, 1216, 1178, 1125, 1092, 1068 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.39-7.10 (m, 4H), 3.87 (s, 3H), 3.64 (s, 3H), 3.53 (s, 3H), 3.23 (dd, 1H, J = 9.6, 1.8 Hz), 2.31-2.10 (m, 2H), 2.07-1.89 (m, 2H), 1.86-1.56 (m, 4H), 1.49-1.34 (m, 1H), 1.21-1.03 (m, 1H), 0.89 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ166.8, 164.6, 149.4, 145.8, 133.9, 129.3, 129.3, 128.9, 126.0, 125.3, 88.9, 61.8, 57.5, 52.5, 52.2, 37.0, 34.5, 25.6, 23.8, 11.7.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.45; H, 7.33.



1-Bromo-2-(1-(1-methoxyethyl)cyclopentyl)benzene (**s7**).

Pale yellow crystal (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

Yield: 97% (1.22 g, synthesized from **s2**).

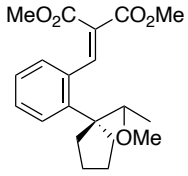
Mp. 75–77 °C.

IR (KBr) 3092, 2966, 2876, 2826, 1628, 1597, 1429, 1374, 1298, 1218, 1178, 1115, 1088, 1066 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59 (d, 1H, *J* = 7.8 Hz), 7.41 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.24 (dd, 1H, *J* = 7.8, 7.8 Hz), 7.03 (ddd, 1H, *J* = 7.8, 7.8, 1.2 Hz), 4.25 (q, 1H, *J* = 6.3 Hz), 3.34 (s, 3H), 2.42-2.19 (m, 2H), 2.19-2.09 (m, 2H), 1.81-1.62 (m, 2H), 1.59-1.43 (m, 2H), 0.89 (d, 3H, *J* = 6.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.9, 135.5, 129.9, 127.4, 126.7, 123.1, 78.8, 57.5, 57.2, 34.6, 31.7, 25.4, 24.3, 15.0.

Anal. Calcd for $C_{14}H_{19}BrO$: C, 59.37; H, 6.76. Found: C, 59.58; H, 6.54.



Dimethyl 2-(2-(1-(1-methoxypentyl)cyclopentyl)benzylidene)malonate (**4b**).

Colorless crystal (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

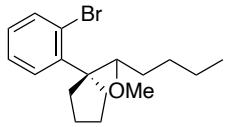
Yield: 92% (1.10 g, synthesized from **s7**).

Mp. 77–79 °C.

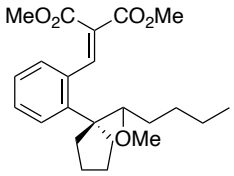
IR (KBr) 3092, 2966, 2875, 2826, 1735, 1708, 1628, 1597, 1429, 1372, 1298, 1252, 1114, 1066 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.34 (d, 1H, *J* = 8.1, 1.2 Hz), 7.29-7.24 (m,

1H), 7.21-7.11 (m, 2H), 3.86 (s, 3H), 3.64 (s, 3H), 3.43 (q, 1H, J = 6.3 Hz), 3.35 (s, 3H), 2.40-2.30 (m, 1H), 2.22-2.13 (m, 1H), 1.98-1.61 (m, 6H), 0.94 (d, 3H, J = 6.3 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 164.6, 150.0, 145.4, 134.3, 129.8, 129.1, 128.7, 125.9, 125.1, 81.8, 57.6, 57.0, 52.4, 52.1, 37.3, 34.7, 24.0, 23.8, 14.3.
Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.10; H, 7.34.

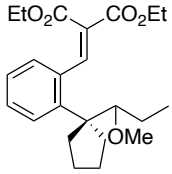


1-Bromo-2-(1-(1-methoxypentyl)cyclopentyl)benzene (**s8**).
Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).
Yield: 93% (763.7 mg, synthesized from **s2**).
IR (neat) 2954, 2871, 2825, 1465, 1455, 1432, 1377, 1188, 1144, 1117, 1094, 1017 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, 1H, J = 7.8 Hz), 7.38 (d, 1H, J = 7.8 Hz), 7.23 (dd, 1H, J = 7.8, 7.8 Hz), 7.03 (dd, 1H, J = 7.8 Hz), 4.17 (d, 1H, J = 9.0 Hz), 3.43 (s, 3H), 2.42-1.99 (m, 4H), 1.78-1.60 (m, 2H), 1.57-1.10 (m, 8H), 0.79 (t, 3H, J = 6.6 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 144.6, 135.7, 130.0, 127.6, 127.0, 123.2, 83.6, 61.1, 57.7, 34.1, 32.7, 31.8, 29.4, 24.9, 23.8, 22.7, 14.0.
Anal. Calcd for $C_{17}H_{25}BrO$: C, 62.77; H, 7.75. Found: C, 62.59; H, 7.52.

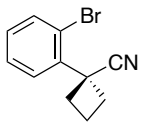


Dimethyl 2-(2-(1-(1-methoxypentyl)cyclopentyl)benzylidene)malonate (**4c**).
Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).
Yield: 79% (529 mg, synthesized from **s8**).
IR (neat) 2953, 2872, 1738, 1727, 1626, 1436, 1363, 1257, 1215, 1093, 1070 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.33 (dd, 1H, J = 8.1, 1.2 Hz), 7.29-7.23 (m, 1H), 7.22-7.11 (m, 2H), 3.87 (s, 3H), 3.64 (s, 3H), 3.51 (s, 3H), 3.29 (d, 1H, J = 9.0 Hz), 2.30-2.10 (m, 2H), 2.02-1.90 (m, 2H), 1.82-1.61 (m, 4H), 1.45-1.05 (m, 6H), 0.85-0.81 (t, 3H, J = 6.9 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 164.3, 149.1, 145.6, 133.7, 129.1, 129.1, 128.7,

125.8, 125.0, 87.1, 61.3, 57.3, 52.2, 51.9, 36.8, 34.4, 32.4, 29.2, 23.6, 22.7, 13.8.
Anal. Calcd for $C_{23}H_{32}O_5$: C, 71.11; H, 8.30. Found: C, 71.35; H, 8.16.



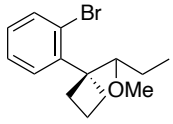
Diethyl 2-(2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (**4d**).
Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 30/1).
Yield: 76% (371 mg, synthesized from **s2**).
IR (neat) 2963, 2875, 1736, 1723, 1626, 1462, 1374, 1349, 1252, 1206, 1100, 1092, 1068, 1024 cm^{-1}.
^1H NMR (300 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.32 (d, 1H, *J* = 7.8, 1.2 Hz), 7.29-7.20 (m, 2H), 7.13 (ddd, 1H, *J* = 7.8, 7.8, 1.2 Hz), 4.32 (qd, 2H, *J* = 7.2, 1.8 Hz), 4.12 (q, 2H, *J* = 7.2 Hz), 3.54 (s, 3H), 3.26 (dd, 1H, *J* = 9.6, 2.1 Hz), 2.28-2.11 (m, 2H), 2.08-1.88 (m, 2H), 1.83-1.55 (m, 4H), 1.48-1.35 (m, 1H), 1.35 (t, 3H, *J* = 7.2 Hz), 1.20-1.08 (m, 1H), 1.05 (t, 3H, *J* = 7.2 Hz), 0.88 (t, 3H, *J* = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 164.0, 148.4, 145.3, 133.9, 129.5, 128.8, 128.7, 126.0, 125.8, 88.7, 61.6, 61.2, 60.9, 57.3, 36.7, 34.0, 25.5, 23.7, 23.6, 14.0, 13.5, 11.6.
Anal. Calcd for $C_{23}H_{32}O_5$: C, 71.11; H, 8.30. Found: C, 71.01; H, 8.37.



1-(2-Bromophenyl)cyclobutane-1-carbonitrile (**s9**).
Yellow solid (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).
Yield: 60% (1.09 g, synthesized from **s1**).
Mp. 76–78 °C.
IR (KBr) 3054, 3006, 2986, 2954, 2893, 2873, 2224, 1591, 1569, 1468, 1436, 1285, 1267, 1249, 1178, 1127, 1032, 1017 cm^{-1}
^1H NMR (300 MHz, $CDCl_3$) δ 7.60 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.35 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.25 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.19 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 3.04-2.92 (m, 2H), 2.72-2.58 (m, 2H), 2.57-2.39 (m, 1H), 2.01-1.88 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.3, 133.9, 129.5, 127.7, 127.5, 122.8, 122.4, 41.4, 34.0, 16.9.

Anal. Calcd for $C_{11}H_{10}BrN$: C, 55.96; H, 4.27; N, 5.93. Found: C, 55.75; H, 4.05; N, 6.17.



1-Bromo-2-(1-(1-methoxypropyl)cyclobutyl)benzene (**s10**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 50/1).

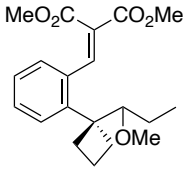
Yield: 53% (644.4 mg, synthesized from **s9**).

IR (neat) 3061, 2972, 2938, 2874, 2824, 1588, 1561, 1466, 1434, 1363, 1345, 1297, 1272, 1255, 1244, 1192, 1140, 1090, 1018 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$, 50 deg) δ 7.49 (dd 1H, *J* = 7.6, 1.2 Hz,), 7.26-7.18 (m, 2H), 7.02 (ddd, 1H, *J* = 7.6, 7.6, 2.0 Hz), 3.58 (dd, 1H, *J* = 6.0, 6.0 Hz), 3.43 (brs, 3H), 2.64 (brs, 1H), 2.58-2.42 (m, 4H), 2.05-1.91 (m, 1H), 1.78-1.67 (m, 1H), 1.39 (brs, 1H), 0.89 (brs, 3H).

^{13}C NMR (100 MHz, $CDCl_3$, 50 deg) δ 146.3, 134.0, 130.2, 127.4, 126.6, 122.2, 86.3, 61.1, 53.3, 32.0, 29.5, 24.2, 16.6, 11.2.

Anal. Calcd for $C_{14}H_{19}BrO$: C, 59.37; H, 6.76. Found: C, 59.62; H, 6.98.



Dimethyl 2-(2-(1-(1-methoxypropyl)cyclobutyl)benzylidene)malonate (**4e**).

White solid (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

Yield: 63% (401 mg, synthesized from **s10**).

Mp. 46–48 °C.

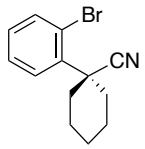
IR (KBr) 3067, 2976, 2941, 2872, 2828, 1731, 1713, 1620, 1598, 1443, 1431, 1369, 1287, 1259, 1212, 1198, 1137, 1090, 1072 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (brs, 1H), 7.29 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.24 (d, 1H, *J* = 7.8 Hz), 7.15 (d, 1H, *J* = 7.8, 1.2 Hz), 7.09 (d, 1H, *J* = 7.8 Hz), 3.85 (s, 3H), 3.70 (s, 3H), 3.55 (s, 3H), 3.41 (d, 1H, *J* = 9.3 Hz), 2.52-2.30 (m, 4H), 2.18-2.01 (m, 1H), 1.90-

1.75 (m, 1H), 1.49 (brs, 1H), 1.30-1.11 (m, 1H), 0.93 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.5, 164.1, 147.2, 145.9, 131.9, 128.8, 128.2, 127.9, 125.6, 125.1, 88.7, 61.5, 52.0, 51.8, 51.5, 32.4, 31.0, 24.0, 16.7, 11.1.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.17; H, 7.80.



1-(2-Bromophenyl)cyclohexane-1-carbonitrile (**s11**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

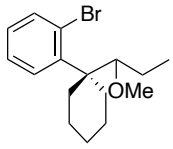
Yield: 47% (791 mg, synthesized from **s1**).

IR (neat) 2936, 2860, 2230, 1567, 1469, 1453, 1432, 1350, 1286, 1272, 1200, 1052, 1038, 1025, 1009 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, 1H, *J* = 7.8, 1.2 Hz), 7.45 (d, 1H, *J* = 7.8, 1.2 Hz), 7.35 (dd, 1H, *J* = 7.8, 7.8 Hz), 7.19 (ddd, 1H, *J* = 7.8, 7.8, 1.2 Hz), 2.57 (d, 2H, *J* = 10.8 Hz), 1.98-1.72 (m, 7H), 1.38-1.19 (m, 1H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 138.0, 135.3, 129.1, 127.6, 127.1, 122.6, 120.6, 43.3, 34.6, 24.6, 22.9.

Anal. Calcd for $C_{13}H_{14}BrN$: C, 59.11; H, 5.34; N, 5.30. Found: C, 59.24; H, 5.55; N, 5.45.



1-Bromo-2-(1-(1-methoxypropyl)cyclohexyl)benzene (**s12**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 69 % (652 mg, synthesized from **s11**).

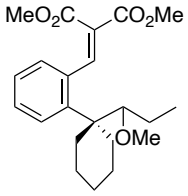
IR (neat) 2928, 2855, 2826, 1466, 1456, 1421, 1371, 1360, 1305, 1177, 1128, 1102, 1088, 1057, 1046, 1013 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.44 (dd, 1H, *J* = 7.8, 1.5 Hz), 7.26 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 7.03 (ddd, 1H, *J* = 7.8, 7.8, 1.5 Hz), 3.75 (d, 1H, *J* = 9.9 Hz), 3.40 (brs, 3H), 3.18 (brs, 1H), 2.52 (brs, 1H), 1.75-1.00 (m, 10H), 0.87 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.4, 136.4, 133.5, 127.5, 126.8, 122.6, 87.3, 61.6, 50.6,

30.6, 29.2, 26.8, 23.9, 22.5, 22.4, 11.8.

Anal. Calcd for $C_{16}H_{23}BrO$: C, 61.74; H, 7.45. Found: C, 61.68; H, 7.27.



Dimethyl 2-(2-(1-(1-methoxypropyl)cyclohexyl)benzylidene)malonate (**4f**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 4/1).

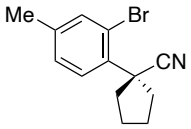
Yield: 99% (647 mg, synthesized from **s12**).

IR (neat) 3058, 2932, 2860, 1726, 1626, 1436, 1359, 1270, 1251, 1213, 1148, 1129, 1071 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.36 (d, 1H, J = 7.8 Hz), 7.35-7.26 (m, 1H), 7.19-7.12 (m, 2H), 3.86 (s, 3H), 3.64 (s, 3H), 3.42 (s, 3H), 3.01 (d, 1H, J = 9.9 Hz), 2.55-2.32 (m, 2H), 1.67-1.05 (m, 10H), 0.88 (t, 3H, J = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 164.6, 150.1, 141.5, 134.8, 131.1, 130.0, 128.8, 125.9, 124.7, 92.2, 61.7, 52.4, 52.0, 50.1, 34.3, 33.8, 26.6, 24.1, 21.8, 21.7, 11.4.

Anal. Calcd for $C_{22}H_{30}O_5$: C, 70.56; H, 8.08. Found: C, 70.33; H, 8.32.



1-(2-Bromo-4-methylphenyl)cyclopentane-1-carbonitrile (**s13**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

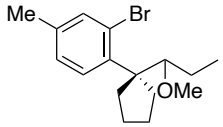
Yield: 81% (589 mg, synthesized from 2-(2-bromo-4-methylphenyl)acetonitrile[2]).

IR (neat) 2957, 2921, 2875, 2230, 1605, 1486, 1452, 1386, 1319, 1286, 1213, 1052, 1038 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.28 (d, 1H, J = 7.2 Hz), 7.10 (d, 1H, J = 7.2 Hz), 2.78-2.69 (m, 2H), 2.32 (s, 3H), 2.22-2.13 (m, 2H), 2.10-1.96 (m, 2H), 1.94-1.85 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 139.4, 135.1, 134.1, 128.0, 127.1, 122.9, 122.6, 46.8, 37.9, 23.2, 20.0.

Anal. Calcd for $C_{13}H_{14}BrN$: C, 59.11; H, 5.34; N, 5.30. Found: C, 59.34; H, 5.50; N, 5.53.



2-Bromo-1-(1-(1-methoxypropyl)cyclopentyl)-4-methylbenzene (**s14**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 40/1).

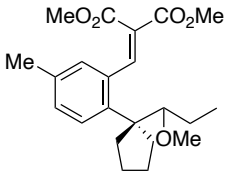
Yield: 46% (196 mg, synthesized from **s13**).

IR (neat) 2962, 2872, 2825, 1605, 1483, 1462, 1455, 1382, 1354, 1193, 1141, 1092, 1036 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.25 (d, 1H, *J* = 9.0 Hz), 7.03 (d, 1H, *J* = 9.0 Hz), 4.05 (dd, 1H, *J* = 9.0, 2.4 Hz), 3.46 (s, 3H), 2.28 (s, 3H), 2.38-1.97 (m, 4H), 1.78-1.59 (m, 2H), 1.58-1.44 (m, 2H), 1.31-1.15 (m, 2H), 0.86 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 137.4, 136.1, 129.6, 127.7, 122.9, 85.4, 61.3, 57.3, 34.3, 31.7, 25.8, 24.8, 23.7, 20.1, 11.8.

Anal. Calcd for $C_{16}H_{23}BrO$: C, 61.74; H, 7.45. Found: C, 61.50; H, 7.67.



Dimethyl 2-(2-(1-(1-methoxypropyl)cyclopentyl)-5-methylbenzylidene)malonate (**4g**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

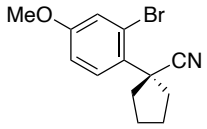
Yield: 53% (206 mg, synthesized from **s14**).

IR (neat) 2953, 2875, 2829, 1738, 1726, 1626, 1436, 1363, 1256, 1229, 1188, 1141, 1095, 1071 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.20 (d, 1H, *J* = 8.1 Hz), 7.07 (d, 1H, *J* = 8.1 Hz), 7.01 (s, 1H), 3.87 (s, 3H), 3.65 (s, 3H), 3.53 (s, 3H), 3.21 (d, 1H, *J* = 8.4 Hz), 2.26 (s, 3H), 2.31-2.11 (m, 2H), 2.02-1.85 (m, 2H), 1.82-1.62 (m, 2H), 1.48-1.33 (m, 1H), 1.20-1.05 (m, 1H), 0.88 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 164.4, 149.3, 142.6, 135.3, 133.5, 129.7, 129.5, 129.1, 124.9, 88.7, 61.6, 56.9, 52.3, 51.9, 36.9, 34.4, 25.5, 23.6, 20.4, 11.6.

Anal. Calcd for $C_{22}H_{30}O_5$: C, 70.56; H, 8.08. Found: C, 70.32; H, 7.97.



1-(2-Bromo-4-methoxyphenyl)cyclopentane-1-carbonitrile (**s15**).

Yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

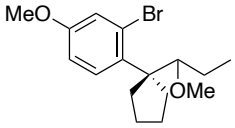
Yield: 50% (459 mg, synthesized from 2-(2-bromo-4-methoxyphenyl)acetonitrile[2]).

IR (neat) 2960, 2919, 2876, 2838, 2230, 1602, 1564, 1491, 1458, 1439, 1296, 1241, 1028 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.30 (d, 1H, *J* = 8.7 Hz), 7.22 (d, 1H, *J* = 2.7 Hz), 6.83 (dd, 1H *J* = 8.7, 2.7 Hz), 3.81 (s, 3H), 2.75-2.69 (m, 2H), 2.19-2.11 (m, 2H), 2.06-1.95 (m, 2H), 1.95-1.86 (m, 2H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4, 129.5, 128.2, 123.9, 123.1, 120.3, 112.9, 55.4, 46.8, 38.3, 23.5.

Anal. Calcd for $C_{13}H_{14}BrNO$: C, 55.73; H, 5.04; N, 5.00. Found: C, 55.52; H, 5.17; N, 5.18.



2-Bromo-4-methoxy-1-(1-(1-methoxypropyl)cyclopentyl)benzene (**s16**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 30/1).

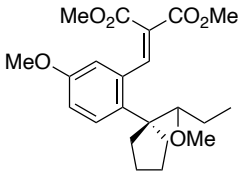
Yield: 69% (570 mg, synthesized from **s15**).

IR (neat) 2959, 2872, 2833, 1601, 1561, 1488, 1463, 1438, 1290, 1266, 1228, 1183, 1138, 1091, 1041, 1024 cm^{-1}.

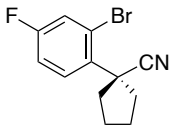
^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (d, 1H, *J* = 8.4 Hz), 7.15 (d, 1H, *J* = 2.7 Hz), 6.78 (dd, 1H, *J* = 8.7, 2.7 Hz), 4.01 (dd, 1H, *J* = 9.0, 3.3 Hz), 3.78 (s, 3H), 3.46 (s, 3H), 2.39-2.12 (m, 2H), 2.10-1.97 (m, 2H), 1.78-1.59 (m, 2H), 1.59-1.45 (m, 2H), 1.33-1.15 (m, 2H), 0.86 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.8, 136.2, 130.1, 123.0, 120.7, 112.4, 85.4, 61.1, 56.8, 55.1, 34.3, 31.8, 25.6, 24.7, 23.6, 11.7.

Anal. Calcd for $C_{16}H_{23}BrO_2$: C, 58.72; H, 7.08. Found: C, 58.95; H, 6.91.

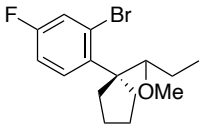


Dimethyl 2-(5-methoxy-2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (**4h**).
Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).
Yield: 75% (510 mg, synthesized from **s16**).
IR (neat) 2954, 2875, 1729, 1626, 1604, 1568, 1489, 1459, 1436, 1362, 1236, 1143, 1091, 1072, 1040 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (s, 1H), 7.22 (d, 1H, J = 8.4 Hz), 6.84-6.76 (m, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 3.68 (s, 3H), 3.54 (s, 3H), 3.18 (dd, 1H, J = 9.3, 3.3 Hz), 2.28-2.05 (m, 2H), 1.97-1.81 (m, 2H), 1.80-1.58 (m, 2H), 1.48-1.34 (m, 1H), 1.19-1.03 (m, 1H), 0.89 (t, 3H, J = 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 164.4, 157.2, 149.0, 137.6, 134.6, 130.4, 125.3, 114.5, 113.9, 88.8, 61.6, 56.6, 55.0, 52.3, 52.1, 37.1, 34.7, 25.4, 23.6, 11.6.
Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.92; H, 7.54.



1-(2-Bromo-4-fluorophenyl)cyclopentane-1-carbonitrile (**s17**).
White solid (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).
Yield: 43% (450 mg, synthesized from 2-(2-bromo-4-fluorophenyl)acetonitrile[3]).
Mp. 52–54 °C.
IR (KBr) 3107, 3077, 3047, 2965, 2880, 2229, 1598, 1583, 1485, 1453, 1384, 1327, 1299, 1282, 1237, 1204, 1161, 1039 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 (dd, 1H, J = 8.4, 3.0 Hz), 7.39 (dd, 1H, J = 8.4, 5.4 Hz), 7.04 (ddd, 1H, J = 8.4, 7.5, 2.7 Hz), 2.81-2.70 (m, 2H), 2.22-1.83 (m, 6H).
^{13}C NMR (75 MHz, $CDCl_3$) δ 161.0 (d, J_{C-F} = 250.4 Hz), 133.2 (d, J_{C-F} = 3.1 Hz), 128.5 (d, J_{C-F} = 8.0 Hz), 123.3 (d, J_{C-F} = 8.7 Hz), 121.9, 121.5 (d, J_{C-F} = 24.1 Hz), 113.9 (d, J_{C-F} = 20.3 Hz), 46.4, 37.7, 22.9.
^{19}F NMR (283 MHz, $CDCl_3$) δ -113.60 (m).
Anal. Calcd for $C_{12}H_{11}BrFN$: C, 53.75; H, 4.14; N, 5.22. Found: C, 53.70; H, 4.34; N,

5.46.



2-Bromo-4-fluoro-1-(1-(1-methoxypropyl)cyclopentyl)benzene (**s18**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 78% (737 mg, synthesized from **s17**).

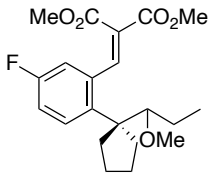
IR (neat) 3076, 2962, 2874, 2826, 1597, 1580, 1480, 1463, 1380, 1276, 1205, 1147, 1133, 1091, 1031 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.37-7.32 (m, 2H), 6.95 (ddd, 1H, J = 9.0, 7.5, 2.7 Hz), 3.99 (dd, 1H, J = 9.0, 2.4 Hz), 3.44 (s, 3H), 2.36-2.16 (m, 2H), 2.13-2.04 (m, 2H), 1.79-1.38 (m, 4H), 1.35-1.15 (m, 2H), 0.87 (t, 3H, J = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 160.4 (d, $J_{C–F}$ = 247.3 Hz), 140.6, 130.9 (d, $J_{C–F}$ = 8.0 Hz), 122.8 (d, $J_{C–F}$ = 9.2 Hz), 122.5 (d, $J_{C–F}$ = 23.4 Hz), 113.7 (d, $J_{C–F}$ = 19.7 Hz), 85.5, 61.3, 57.3, 34.4, 32.3, 25.7, 24.8, 23.7, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.58 (s).

Anal. Calcd for $C_{15}H_{20}BrFO$: C, 57.15; H, 6.40. Found: C, 57.28; H, 6.32.



Dimethyl 2-(5-fluoro-2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (**4i**).

Yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 73 % (573 mg, synthesized from **s18**).

IR (neat) 3062, 2955, 2877, 2828, 1731, 1631, 1606, 1581, 1484, 1456, 1436, 1361, 1258, 1226, 1174, 1071, 997 cm^{-1}.

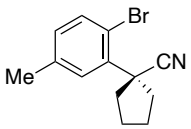
^1H NMR (300 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.26 (dd, 1H, J = 9.3, 7.6 Hz), 6.99-6.89 (m, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 3.53 (s, 3H), 3.16 (dd, J = 9.6, 2.4 Hz, 1H), 2.33-2.22 (m, 1H), 2.18-2.07 (m, 1H), 1.96-1.60 (m, 6H), 1.51-1.37 (m, 1H), 1.18-1.01 (m, 1H), 0.90 (t, 3H, J = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 164.1, 160.3 (d, $J_{C–F}$ = 244.1 Hz), 147.8, 141.4 (d,

$J_{C–F}$ = 3.8 Hz), 135.6 (d, $J_{C–F}$ = 7.4 Hz), 131.1 (d, $J_{C–F}$ = 8.0 Hz), 126.0, 115.6 (d, $J_{C–F}$ = 22.2 Hz), 115.0 (d, $J_{C–F}$ = 19.7 Hz), 88.5, 61.6, 57.0, 52.4, 52.1, 37.2, 34.9, 25.4, 23.5, 23.3, 11.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -118.69 (s).

Anal. Calcd for $C_{21}H_{27}FO_5$: C, 66.65; H, 7.19. Found: C, 66.56; H, 7.26.



1-(2-Bromo-5-methylphenyl)cyclopentane-1-carbonitrile (**s19**).

Pink oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

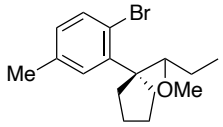
Yield: 50% (487 mg, synthesized from 2-(2-bromo-5-methylphenyl)acetonitrile[2]).

IR (neat) 2957, 2922, 2876, 2231, 1471, 1154, 1394, 1319, 1288, 1202, 1025 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, 1H, J = 8.4 Hz), 7.22 (d, 1H, J = 1.6 Hz), 7.00 (dd, 1H, J = 8.4, 1.6 Hz), 2.76-2.68 (m, 2H), 2.32 (s, 3H), 2.25-2.17 (m, 2H), 2.08-1.97 (m, 2H), 1.96-1.87 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 137.3, 136.9, 134.6, 130.1, 128.4, 122.9, 119.9, 47.4, 38.0, 23.5, 20.9.

Anal. Calcd for $C_{13}H_{14}BrN$: C, 59.11; H, 5.34; N, 5.30. Found: C, 59.02; H, 5.23; N, 5.44.



2-Bromo-2-(1-(1-methoxypropyl)cyclopentyl)-4-methylbenzene (**s20**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

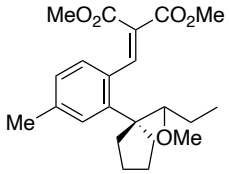
Yield: 80% (352 mg, synthesized from **s19**).

IR (neat) 2961, 2872, 2825, 1455, 1386, 1371, 1354, 1191, 1127, 1092, 1062, 1018 cm^{-1}.

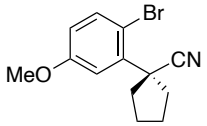
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, 1H, J = 7.8 Hz), 7.16 (s, 1H), 6.84 (d, 1H, J = 7.8 Hz), 4.07 (d, 1H, J = 9.3 Hz), 3.46 (s, 3H), 2.29 (s, 3H), 2.41-1.94 (m, 4H), 1.79-1.38 (m, 4H), 1.36-1.15 (m, 2H), 0.86 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 144.2, 136.4, 135.3, 130.6, 128.3, 119.8, 85.4, 61.2, 57.5, 34.3, 31.6, 25.8, 24.9, 23.8, 21.1, 11.8.

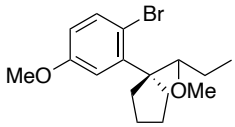
Anal. Calcd for $C_{16}H_{23}BrO$: C, 61.74; H, 7.45. Found: C, 61.98; H, 7.58.



Dimethyl 2-(2-(1-(1-methoxypropyl)cyclopentyl)-4-methylbenzylidene)malonate (**4j**).
Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 15/1).
Yield: 89% (369 mg, synthesized from **s20**).
IR (neat) 2953, 2875, 1731, 1625, 1606, 1455, 1436, 1364, 1256, 1215, 1097, 1069 cm^{-1}.
^1H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H), 7.11 (s, 1H), 7.09 (d, 1H, *J* = 7.5 Hz), 6.95 (d, 1H, *J* = 7.5 Hz), 3.86 (s, 3H), 3.66 (s, 3H), 3.53 (s, 3H), 3.24 (dd, 1H, *J* = 9.9, 1.8 Hz), 2.33 (s, 3H), 2.26-2.10 (m, 2H), 2.04-1.86 (m, 2H), 1.82-1.50 (m, 4H), 1.45-1.30 (m, 1H), 1.23-1.06 (m, 1H), 0.88 (t, 3H, *J* = 7.2 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 164.4, 148.9, 145.7, 138.7, 130.7, 129.8, 129.1, 126.5, 124.4, 88.7, 61.6, 57.1, 52.2, 51.9, 36.8, 34.1, 25.4, 23.8, 23.7, 21.3, 11.5.
Anal. Calcd for $C_{22}H_{30}O_5$: C, 70.56; H, 8.08. Found: C, 70.37; H, 7.97.



1-(2-Bromo-5-methoxyphenyl)cyclopentane-1-carbonitrile (**s21**).
Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).
Yield: 64% (650 mg, synthesized from 2-(2-bromo-5-methoxyphenyl)acetonitrile[2]).
IR (neat) 3075, 2961, 2877, 2838, 2232, 1593, 1572, 1465, 1443, 1410, 1292, 1244, 1182, 1162, 1138, 1059, 1040, 1017 cm^{-1}.
^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, 1H, *J* = 8.8 Hz), 6.98 (d, 1H, *J* = 2.8 Hz), 6.73 (dd, 1H, *J* = 8.8, 2.8 Hz), 3.80 (s, 3H), 2.78-2.69 (m, 2H), 2.25-2.16 (m, 2H), 2.07-2.00 (m, 2H), 1.95-1.87 (m, 2H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7, 138.3, 135.5, 122.7, 114.9, 113.7, 113.5, 55.4, 47.4, 38.0, 23.5.
Anal. Calcd for $C_{13}H_{14}BrNO$: C, 55.73; H, 5.04; N, 5.00. Found: C, 55.63; H, 5.17; N, 4.79.



2-Bromo-4-methoxy-2-(1-(1-methoxypropyl)cyclopentyl)benzene (**s22**).

Colorless oil (purified by silica gel column chromatography, Hexane/EtOAc = 15/1).

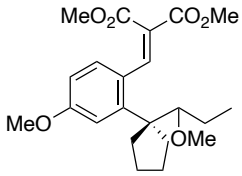
Yield: 92% (545 mg, synthesized from **s21**).

IR (neat) 2954, 2872, 2832, 1592, 1567, 1463, 1456, 1439, 1402, 1389, 1284, 1234, 1182, 1146, 1104, 1064, 1014 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.25 (d, 1H, *J* = 8.7 Hz), 7.28-7.24 (m, 1H), 6.95 (d, 1H, *J* = 3.0 Hz), 6.60 (dd, 1H, *J* = 8.7, 3.0 Hz), 4.09 (dd, 1H, *J* = 9.0, 2.4 Hz), 3.78 (s, 3H), 3.47 (s, 3H), 2.38-2.15 (m, 2H), 2.14-2.02 (m, 2H), 1.78-1.41 (m, 4H), 1.30-1.19 (m, 2H), 0.87 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4, 145.7, 136.0, 116.8, 113.4, 111.8, 85.1, 61.2, 57.6, 55.1, 34.1, 31.6, 25.7, 24.8, 23.7, 11.7.

Anal. Calcd for $C_{16}H_{23}BrO_2$: C, 58.72; H, 7.08. Found: C, 58.78; H, 7.32.



Dimethyl 2-(4-methoxy-2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (**4k**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 15/1).

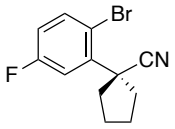
Yield: 96% (495 mg, synthesized from **s22**).

IR (neat) 2953, 2875, 2833, 1737, 1601, 1566, 1458, 1436, 1366, 1296, 1241, 1218, 1099, 1069 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.20 (d, 1H, *J* = 8.4 Hz), 6.89 (d, 1H, *J* = 2.7 Hz), 6.67 (dd, 1H, *J* = 8.4, 2.7 Hz), 4.09 (dd, 1H, J = 9.0, 2.4 Hz), 3.85 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H), 3.53 (s, 3H), 3.26 (dd, 1H, *J* = 9.3, 1.8 Hz), 2.27-2.10 (m, 2H), 2.03-1.87 (m, 2H), 1.81-1.55 (m, 2H), 1.44-1.32 (m, 1H), 1.21-1.09 (m, 1H), 0.88 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 167.0, 164.5, 159.9, 148.2, 148.0, 130.8, 126.0, 123.6, 116.1, 109.6, 88.6, 61.6, 57.3, 54.9, 52.2, 52.0, 36.7, 33.9, 25.5, 23.9, 23.7, 11.5.

Anal. Calcd for $C_{22}H_{30}O_6$: C, 67.67; H, 7.74. Found: C, 67.90; H, 7.54.



1-(2-Bromo-5-fluorophenyl)cyclopentane-1-carbonitrile (**s23**).

White solid (purified by silica gel column chromatography, Hexane/EtOAc = 10/1).

Yield: 76% (760 mg, synthesized from 2-(2-bromo-5-fluorophenyl)acetonitrile[2]).

Mp. 85–87 °C.

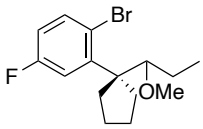
IR (KBr) 3099, 3077, 2957, 2877, 2234, 1600, 1579, 1461, 1399, 1322, 1271, 1234, 1161, 1114, 1080, 1031 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (dd, 1H, J = 8.7, 5.7 Hz), 7.15 (dd, 1H, J = 10.2, 3.0 Hz), 6.98-6.91 (m, 1H), 2.80-2.71 (m, 2H), 2.23-1.86 (m, 6H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1 (d, $J_{C–F}$ = 246.0 Hz), 139.2 (d, $J_{C–F}$ = 6.8 Hz), 135.8 (d, $J_{C–F}$ = 8.0 Hz), 121.6, 117.2 (d, $J_{C–F}$ = 3.1 Hz), 116.1 (d, $J_{C–F}$ = 21.6 Hz), 115.0 (d, $J_{C–F}$ = 17.2 Hz), 46.9 (d, $J_{C–F}$ = 1.8 Hz), 37.5, 23.0.

^{19}F NMR (283 MHz, $CDCl_3$) δ -114.60 (m).

Anal. Calcd for $C_{12}H_{11}BrFN$: C, 53.75; H, 4.14; N, 5.22. Found: C, 53.56; H, 4.26; N, 5.42.



2-Bromo-4-fluoro-2-(1-(1-methoxypropyl)cyclopentyl)benzene (**s24**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 63% (906 mg, synthesized from **s23**).

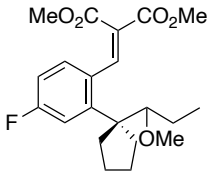
IR (neat) 2962, 2874, 2827, 1602, 1576, 1455, 1390, 1267, 1227, 1211, 1145, 1101, 1060, 1023, 1101, 1090, 1060, 1023 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, 1H, J = 8.8, 6.0 Hz), 7.11 (dd, 1H, J = 11.4, 3.0 Hz), 6.82-6.74 (m, 1H), 4.05 (dd, 1H, J = 9.3, 2.7 Hz), 3.45 (s, 3H), 2.35-2.18 (m, 2H), 2.12-2.03 (m, 2H), 1.78-1.14 (m, 6H), 0.88 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 161.7 (d, $J_{C–F}$ = 244.1 Hz), 147.4 (d, $J_{C–F}$ = 7.9 Hz), 136.6 (d, $J_{C–F}$ = 8.0 Hz), 117.3 (d, $J_{C–F}$ = 24.1 Hz), 117.0 (d, $J_{C–F}$ = 3.2 Hz), 114.5 (d, $J_{C–F}$ = 21.6 Hz), 85.1, 61.3, 57.9, 34.1, 32.0, 25.8, 24.9, 23.8, 11.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -116.48 (s).

Anal. Calcd for $C_{15}H_{20}BrFO$: C, 57.15; H, 6.40. Found: C, 57.34; H, 6.58.



Dimethyl 2-(4-fluoro-2-(1-(1-methoxypropyl)cyclopentyl)benzylidene)malonate (**4l**).

Yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 55% (541 mg, synthesized from **s24**).

IR (neat) 2954, 2877, 2833, 1738, 1629, 1604, 1579, 1484, 1437, 1363, 1275, 1217, 1101, 1070 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.64 (s, 1H), 7.19 (dd, 1H, J = 8.4, 6.3 Hz), 7.04 (dd, 1H, J = 11.4, 2.7 Hz), 6.88-6.82 (ddd, 1H, J = 8.4, 8.4, 2.7 Hz), 3.87 (s, 3H), 3.66 (s, 3H), 3.53 (s, 3H), 3.22 (dd, 1H, J = 9.9, 2.4 Hz), 2.29-2.08 (m, 2H), 1.96-1.61 (m, 6H), 1.20-1.05 (m, 1H), 1.45-1.35 (m, 1H), 0.90 (t, 3H, J = 7.3 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 164.2, 162.6 (d, $J_{C–F}$ = 246.6 Hz), 148.9 (d, $J_{C–F}$ = 6.8 Hz), 147.8, 130.9 (d, $J_{C–F}$ = 8.6 Hz), 129.8 (d, $J_{C–F}$ = 3.1 Hz), 125.4, 116.5 (d, $J_{C–F}$ = 22.2 Hz), 112.6 (d, $J_{C–F}$ = 21.0 Hz), 88.3, 61.6, 57.4, 57.4, 52.3, 52.0, 36.8, 34.3, 25.5, 23.6, 11.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.91 (s).

Anal. Calcd for $C_{21}H_{27}FO_5$: C, 66.65; H, 7.19. Found: C, 66.87; H, 7.03.

2. Synthesis of fused-phenanthrene derivatives.

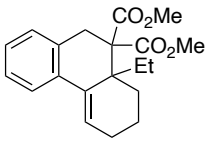
General Procedure of the formation of fused-phenanthrene derivatives.

To a solution of malonate **4** (0.10 mmol) in $ClCH_2CH_2Cl$ or toluene (1.0 mL) was added BF_3•OEt_2 or $Bi(OTf)_3$ (0.010–0.030 mmol, 10–30 mol%), and the mixture was heated at reflux (heat block). After completion of the reaction, the reaction was stopped by adding saturated aqueous $NaHCO_3$. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by preparative TLC to give phenanthrene derivatives **6** or **7**.

General Procedure of the formation of fused-phenanthrene derivatives 6 and 7 (1 mmol-scale reaction).

To a solution of malonate **4a** (362 mg, 0.10 mmol) in $ClCH_2CH_2Cl$ (10.1 mL) was added BF_3•OEt_2 (14.2 mg, 0.010 mmol, 10 mol%), and the mixture was heated at reflux (oil bath). After completion of the reaction, the reaction was stopped by adding saturated aqueous $NaHCO_3$. The crude products were extracted with EtOAc (x3), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 20/1) to give **6a** (277 mg, 84%) as colorless oil.

To a solution of malonate **4a** (363 mg, 0.10 mmol) in $ClCH_2CH_2Cl$ (1.0 mL) was added $Bi(OTf)_3$ (66.3 mg, 0.010 mmol, 10 mol%), and the mixture was heated at reflux (oil bath). After completion of the reaction, the reaction was stopped by adding saturated aqueous $NaHCO_3$. The crude products were extracted with EtOAc (x3), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 20:1) to give **7a** (218 mg, 66%) as colorless oil.



Dimethyl 8a-ethyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6a**).

Pale yellow oil (purified by silica gel column chromatography, Hexane/EtOAc = 20/1).

Yield: 94% (29.3 mg, with 10 mol% of BF_3•OEt_2).

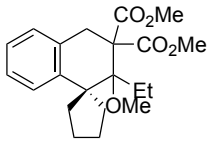
IR (neat) 2951, 2875, 1752, 1732, 1455, 1433, 1256, 1228, 1171, 1123, 1111, 1055 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.40 (m, 1H), 7.17-7.10 (m, 2H), 7.09-7.02 (m, 1H),

6.42 (dd, 1H, *J* = 5.1, 3.6 Hz), 3.76 (s, 3H), 3.56 (s, 3H), 3.50 (d, H, *J* = 18.0 Hz), 3.42 (d, H, *J* = 18.0 Hz), 2.56-2.45 (m, 1H), 2.29-2.10 (m, 2H), 1.91 (ddd, 1H, *J* = 14.1, 5.6, 5.6 Hz), 1.77-1.50 (m, 4H), 0.76 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 171.1, 136.1, 135.3, 132.0, 128.1, 126.8, 126.6, 126.2, 124.5, 61.5, 52.2, 52.1, 41.5, 34.3, 29.4, 28.4, 25.3, 20.2, 9.9.

Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 73.32; H, 7.16.



Dimethyl 2'-ethyl-2'-methoxy-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-3',3'(4'*H*)-dicarboxylate (**5a**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

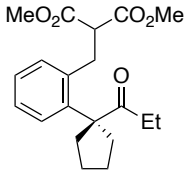
Yield: 98% (33.7 mg, with 30 mol% of $Mg(OTf)_2$).

IR (neat) 2950, 2876, 2837, 1733, 1491, 1451, 1433, 1226, 1136, 1090, 1059 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19-7.11 (m, 4H), 6.42 (dd, 1H, *J* = 5.1, 3.6 Hz), 3.70 (s, 3H), 3.70 (s, 3H), 3.66 (d, 1H, *J* = 16.4 Hz), 3.38 (s, 3H), 3.20 (d, 1H, *J* = 16.4 Hz), 2.45-2.22 (m, 4H), 1.80-1.65 (m, 6H), 0.77 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 171.3, 145.8, 133.5, 127.8, 126.1, 125.6, 125.1, 85.4, 62.9, 58.7, 53.0, 52.5, 52.3, 37.5, 35.6, 25.9, 23.8, 10.7.

Anal. Calcd for $C_{21}H_{28}O_5$: C, 69.98; H, 7.83. Found: C, 70.18; H, 7.63.



Dimethyl 2-(2-(1-propionylcyclopentyl)benzyl)malonate (**8**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 46% (17.5 mg, with 30 mol% of $TiCl_4$).

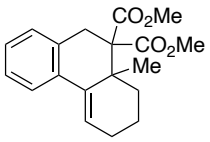
IR (neat) 2953, 2874, 1754, 1738, 1703, 1487, 1451, 1436, 1342, 1240, 1200, 1154, 1055, 1023 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (d, 1H, *J* = 7.6 Hz), 7.25 (ddd, 1H, *J* = 7.6, 7.6, 1.6 Hz), 7.20 (ddd, 1H, *J* = 7.6, 7.6, 1.6 Hz), 7.09 (d, 1H, *J* = 7.6 Hz), 3.72 (s, 6H), 3.69 (t,

1H, *J* = 7.6 Hz), 3.10 (d, 2H, *J* = 7.6 Hz), 2.54-2.47 (m, 2H), 1.98-1.90 (m, 2H), 2.16 (q, 2H, *J* = 7.6 Hz), 1.71-1.65 (m, 4H), 0.94 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 169.3, 142.5, 136.9, 129.1, 127.1, 127.0, 64.8, 52.7, 51.9, 35.4, 31.1, 31.0, 24.4, 8.7.

Anal. Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.40; H, 7.34.



Dimethyl 8a-methyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6b**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

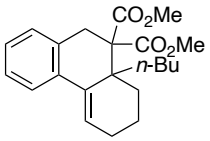
Yield: 93% (28.0 mg, with 10 mol% of BF_3•OEt_2 in toluene).

IR (neat) 2987, 2952, 2874, 1785, 1730, 1456, 1435, 1266, 1236, 1182, 1121, 1057 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57-7.50 (m, 1H), 7.18-7.04 (m, 3H), 6.42 (dd, 1H, *J* = 5.7, 2.7 Hz), 3.77 (s, 3H), 3.62 (d, 1H *J* = 17.4 Hz), 3.55 (s, 3H), 3.37 (d, *J* = 17.4 Hz, 1H), 2.54-2.42 (m, 1H), 2.41-2.17 (m, 2H), 1.84-1.52 (m, 3H), 1.15 (s, 3H).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.7, 137.0, 133.7, 131.2, 128.7, 126.6, 126.3, 124.2, 123.6, 61.0, 52.2, 52.0, 38.7, 34.2, 31.8, 25.9, 22.3, 19.0.

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.37; H, 6.88.



Dimethyl 8a-butyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6c**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 82% (29.6 mg, with 10 mol% of BF_3•OEt_2).

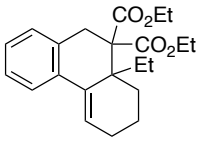
IR (neat) 3026, 2953, 2871, 2836, 1753, 1731, 1488, 1455, 1433, 1262, 1232, 1170, 1126, 1112, 1060 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.41 (m, 1H), 7.15-7.03 (m, 3H), 6.38 (dd, 1H, *J* = 5.1, 3.6 Hz), 3.76 (s, 3H), 3.55 (s, 3H), 3.52 (d, 1H, *J* = 18.0 Hz), 3.40 (d, 1H, *J* = 18.0 Hz), 2.56-2.43 (m, 1H), 2.30-2.10 (m, 2H), 1.94 (ddd, 1H, *J* = 14.1, 4.2, 4.2 Hz), 1.76-1.60 (m, 3H), 1.52-1.42 (m, 1H), 1.33-0.98 (m, 4H), 0.73 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 171.0, 136.5, 135.1, 131.8, 128.0, 126.5, 126.2,

124.4, 61.4, 52.2, 52.1, 41.3, 35.8, 34.3, 29.8, 27.4, 25.3, 23.5, 20.1, 13.9.

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.26; H, 7.70.



Diethyl 8a-ethyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6d**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

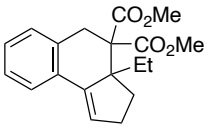
Yield: 70% (722.8 mg, with 10 mol% of BF_3•OEt_2).

IR (neat) 2979, 2936, 2874, 2836, 1749, 1730, 1455, 1365, 1255, 1226, 1175, 1111, 1095, 1054 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.49-7.44 (m, 1H), 7.16-7.04 (m, 3H), 6.42 (dd, 1H, *J* = 5.1, 3.3 Hz), 4.23 (q, 1H, *J* = 7.2 Hz), 4.22 (q, 1H, *J* = 7.2 Hz), 4.03 (q, 1H, *J* = 7.2 Hz), 4.02 (q, 1H, *J* = 7.2 Hz), 3.50 (d, 1H, *J* = 18.0 Hz), 3.40 (d, 1H, *J* = 18.0 Hz), 2.60-2.47 (m, 1H), 2.32-2.10 (m, 2H), 1.93 (ddd, 1H, *J* = 14.1, 4.2, 4.2 Hz), 1.79-1.50 (m, 4H), 1.30 (t, 3H, *J* = 7.2 Hz), 1.10 (t, 3H, *J* = 7.2 Hz), 0.77 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.6, 136.1, 135.2, 132.1, 128.1, 126.6, 126.5, 126.1, 124.4, 61.3, 61.1, 60.8, 41.4, 34.4, 29.3, 28.5, 25.3, 20.2, 14.1, 13.8, 10.0.

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.03; H, 8.14.



Dimethyl 3a-ethyl-2,3,3a,5-tetrahydro-4*H*-cyclopenta[*a*]naphthalene-4,4-dicarboxylate (**6e**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

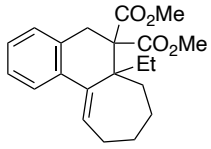
Yield: 94% (28.4 mg, with 10 mol% of BF_3•OEt_2).

IR (neat) 2953, 1732, 1456, 1435, 1264, 1231, 1175, 1059 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.61-7.54 (m, 1H), 7.18-7.11 (m, 1H), 6.20 (dd, 1H, *J* = 2.1, 2.1 Hz), 3.79 (s, 3H), 3.63 (d, 1H, *J* = 17.7 Hz), 3.57 (s, 3H), 3.27 (d, 1H, *J* = 17.7 Hz), 2.59-2.42 (m, 3H), 2.14-1.98 (m, 1H), 1.52-1.31 (m, 2H), 0.78 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.6, 170.8, 140.7, 132.1, 131.0, 128.5, 127.1, 126.2, 125.0, 124.5, 60.7, 54.0, 52.3, 52.1, 34.3, 32.4, 32.3, 27.9, 7.9.

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.72; H, 6.84.



Dimethyl 6a-ethyl-5,6a,7,8,9,10-hexahydro-6*H*-cyclohepta[*a*]naphthalene-6,6-dicarboxylate (**6f**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

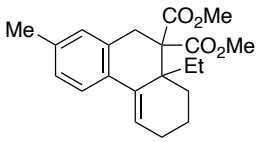
Yield: 58% (19.8 mg with 10 mol% of BF_3•OEt_2).

IR (neat) 2948, 2932, 2864, 1732, 1487, 1455, 1433, 1252, 1223, 1166, 1054 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.45-7.38 (m, 1H), 7.15-7.09 (m, 2H), 7.06-7.01 (m, 1H), 6.38 (dd, 1H, *J* = 8.0, 5.2 Hz), 3.77 (s, 3H), 3.55 (d, 1H, *J* = 17.6 Hz), 3.55 (s, 3H), 3.44 (d, 1H, *J* = 17.6 Hz), 2.88-2.78 (m, 1H), 2.63-2.53 (m, 1H), 2.27-2.18 (m, 1H), 1.94 (ddd, 1H, *J* = 15.2, 4.0, 4.0 Hz), 1.86-1.62 (m, 6H), 0.79 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 171.2, 140.4, 137.9, 132.3, 129.9, 127.8, 126.5, 126.2, 125.6, 62.5, 52.3, 52.2, 49.0, 35.4, 29.8, 27.4, 26.1, 26.1, 23.1, 10.2.

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.87; H, 7.88.



Dimethyl 8a-ethyl-2-methyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6g**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

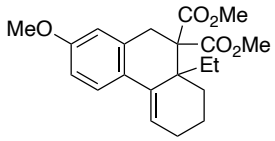
Yield: 88% (31.5 mg, with 10 mol% of BF_3•OEt_2).

IR (neat) 2952, 1782, 1731, 1447, 1434, 1266, 1231, 1173, 1122, 1057 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, 1H, *J* = 7.8 Hz), 6.95 (d, 1H, *J* = 7.8 Hz), 6.88 (s, 1H), 6.37 (dd, 1H, *J* = 5.1, 3.6 Hz), 3.76 (s, 3H), 3.56 (s, 3H), 3.47 (d, 1H, *J* = 18.0 Hz), 3.36 (d, 1H, *J* = 18.0 Hz), 2.56-2.45 (m, 1H), 2.29 (s, 3H), 2.25-2.03 (m, 2H), 1.90 (ddd, 1H, *J* = 14.1, 4.2, 4.2 Hz), 1.75-1.50 (m, 4H), 0.76 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 171.2, 136.2, 135.8, 132.5, 131.7, 128.6, 127.2, 125.7, 124.4, 61.5, 52.2, 52.1, 41.6, 34.3, 29.4, 28.4, 25.3, 21.0, 20.2, 9.9.

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.44; H, 7.61.



Dimethyl 8a-ethyl-2-methoxy-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6h**).

White solid (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 82% (27.9 mg, with 10 mol% of BF_3•OEt_2).

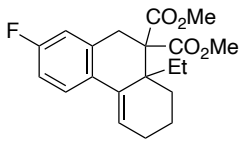
Mp. 111–113 °C.

IR (KBr) 3035, 2978, 2946, 2899, 2875, 2833, 1750, 1716, 1607, 1503, 1455, 1435, 1331, 1291, 1253, 1221, 1172, 1052, 1039 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, 1H, *J* = 8.7 Hz), 6.72 (dd, 1H, *J* = 8.7, 2.1 Hz), 6.59 (d, 1H, *J* = 2.1 Hz), 6.28 (dd, 1H, *J* = 4.2, 4.2 Hz), 3.78 (s, 3H), 3.76 (s, 3H), 3.57 (s, 3H), 3.48 (d, 1H, *J* = 18.0 Hz), 3.36 (d, 1H, *J* = 18.0 Hz), 2.55-2.42 (m, 1H), 2.28-2.09 (m, 2H), 1.90 (ddd, 1H, *J* = 14.1, 4.2, 4.2 Hz), 1.76-1.50 (m, 4H), 0.75 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 171.1, 158.3, 135.5, 133.2, 128.2, 125.8, 124.7, 112.8, 112.3, 61.4, 55.1, 52.2, 52.1, 41.7, 34.6, 29.4, 28.4, 25.2, 20.2, 9.9.

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.19; H, 7.08.



Dimethyl 8a-ethyl-2-fluoro-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6i**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 86% (26.5 mg, with 10 mol% of BF_3•OEt_2).

IR (neat) 2952, 2833, 1731, 1610, 1496, 1434, 1255, 1236, 1169, 1099, 1055 cm^{-1}.

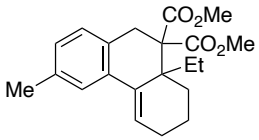
^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, 1H, *J* = 8.7, 5.7 Hz), 6.83 (ddd, 1H, *J* = 8.7, 8.7, 2.4 Hz), 6.76 (dd, 1H, *J* = 9.3, 2.4 Hz), 6.33 (dd, 1H, *J* = 4.8, 3.9 Hz), 3.76 (s, 3H), 3.57 (s, 3H), 3.46 (d, 1H, *J* = 18.0 Hz), 3.37 (d, 1H, *J* = 18.0 Hz), 2.56-2.45 (m, 1H), 2.22-2.08 (m, 2H), 1.93 (ddd, 1H, *J* = 14.4, 4.5, 4.5 Hz), 1.77-1.46 (m, 4H), 0.75 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.8, 161.7 (d, $J_{C–F}$ = 243.5 Hz), 135.2, 134.0 (d, $J_{C–F}$ = 7.4 Hz), 131.5 (d, $J_{C–F}$ = 3.1 Hz), 126.6 (d, $J_{C–F}$ = 1.2 Hz), 126.2 (d, $J_{C–F}$ = 7.4 Hz),

114.1 (d, J_{C-F} = 21.0 Hz), 113.5 (d, J_{C-F} = 21.6 Hz), 61.2, 52.3, 52.2, 41.6, 34.4 (d, J_{C-F} = 1.9 Hz), 29.3, 28.3, 25.3, 20.2, 9.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.92 (s).

Anal. Calcd for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.54; H, 6.56.



Dimethyl 8a-ethyl-3-methyl-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6j**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

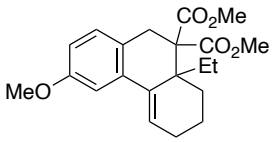
Yield: 99% (32.6 mg, with 10 mol% of BF_3•OEt_2).

IR (neat) 2950, 2875, 2836, 1753, 1732, 1498, 1455, 1433, 1256, 1229, 1169, 1122, 1055 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27 (s, 1H), 6.96 (brs, 2H), 6.42 (dd, 1H, *J* = 4.8, 3.6 Hz), 3.75 (s, 3H), 3.56 (s, 3H), 3.46 (d, 1H, *J* = 17.7 Hz), 3.37 (d, 1H, *J* = 17.7 Hz), 2.55-2.45 (m, 1H), 2.30 (s, 3H), 2.27-2.11 (m, 2H), 1.90 (ddd, 1H, *J* = 14.1, 4.2, 4.2 Hz), 1.76-1.50 (m, 4H), 0.76 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 171.1, 136.1, 135.4, 134.9, 128.9, 128.0, 127.6, 126.5, 124.9, 61.5, 52.2, 52.1, 41.5, 34.0, 29.3, 28.4, 25.3, 21.2, 20.2, 9.9.

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.43; H, 7.42.



Dimethyl 8a-ethyl-3-methoxy-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6k**).

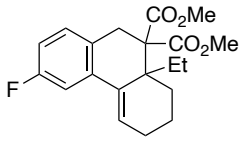
Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 85% (30.9 mg, with 10 mol% of BF_3•OEt_2).

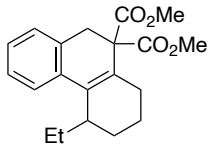
IR (neat) 2952, 1783, 1731, 1611, 1499, 1455, 1434, 1271, 1173, 1123, 1044 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98 (d, 1H, *J* = 8.4, Hz), 6.98 (d, 1H, *J* = 2.4 Hz), 6.73 (dd, 1H, *J* = 8.4, 2.4 Hz), 6.42 (dd, 1H, *J* = 4.8, 3.6 Hz), 3.79 (s, 3H), 3.75 (s, 3H), 3.56 (s, 3H), 3.43 (d, 1H, *J* = 17.7 Hz), 3.35 (d, 1H, *J* = 17.7 Hz), 2.57-2.45 (m, 1H), 2.31-2.11

(m, 2H), 1.90 (ddd, 1H, J = 14.1, 4.2, 4.2 Hz), 1.76-1.51 (m, 4H), 0.77 (t, 3H, J = 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 171.1, 158.0, 136.2, 136.2, 129.1, 126.8, 124.3, 113.3, 108.9, 61.6, 55.2, 52.2, 52.1, 41.5, 33.6, 29.4, 28.5, 25.3, 20.1, 9.9.
Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.58; H, 7.53.



Dimethyl 8a-ethyl-3-fluoro-6,8,8a,10-tetrahydrophenanthrene-9,9(7*H*)-dicarboxylate (**6l**).
Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).
Yield: 74% (26.3 mg, with 10 mol% of BF_3•OEt_2).
IR (neat) 2952, 2878, 1731, 1612, 1495, 1434, 1255, 1230, 1219, 1173, 1123, 1056 cm^{-1}.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.13 (dd, 1H, J = 10.5, 2.7 Hz), 7.02 (dd, 1H, J = 8.4, 6.0 Hz), 6.83 (ddd, 1H, J = 8.4, 8.4, 2.7 Hz), 6.41 (dd, 1H, J = 5.1, 3.6 Hz), 3.76 (s, 3H), 3.57 (s, 3H), 3.45 (d, 1H, J = 18.0 Hz), 3.37 (d, 1H, J = 18.0 Hz), 2.54-2.41 (m, 1H), 2.31-2.11 (m, 2H), 1.92 (ddd, 1H, J = 14.1, 4.2, 4.2 Hz), 1.76-1.46 (m, 4H), 0.76 (t, 3H, J = 7.5 Hz).
^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.9, 161.6 (d, $J_{C–F}$ = 240.4 Hz), 137.1 (d, $J_{C–F}$ = 6.8 Hz), 135.6 (d, $J_{C–F}$ = 2.5 Hz), 129.6 (d, $J_{C–F}$ = 8.6 Hz), 127.8, 127.5 (d, $J_{C–F}$ = 3.1 Hz), 113.7 (d, $J_{C–F}$ = 21.6 Hz), 110.6 (d, $J_{C–F}$ = 21.6 Hz), 61.3, 52.2, 52.1, 41.3, 33.7, 29.2, 28.4, 25.3, 20.0, 9.8.
^{19}F NMR (376 MHz, $CDCl_3$) δ -118.4 (s).
Anal. Calcd for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.27; H, 6.85.

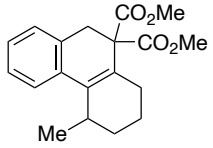


Dimethyl 5-ethyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7a**).
Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).
Yield: 76% (23.6 mg, with 10 mol% of $Bi(OTf)_3$).
IR (neat) 2955, 2875, 1734, 1669, 1603, 1488, 1453, 1435, 1269, 1235, 1178, 1064 cm^{-1}.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25-7.08 (m, 4H), 3.77 (s, 3H), 3.58 (s, 3H), 3.38 (d, 1H, J = 14.4 Hz), 3.31 (d, 1H, J = 14.4 Hz), 2.75 (brs, 1H), 2.43-2.32 (m, 1H), 2.09 (ddd, 1H,

J = 17.2, 4.8, 4.8 Hz), 1.90-1.53 (m, 5H), 1.38-1.22 (m, 1H), 0.90 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.0, 134.9, 133.6, 132.8, 130.8, 127.6, 126.7, 126.4, 122.7, 60.2, 52.7, 52.5, 36.1, 35.0, 28.2, 26.4, 26.2, 19.3, 11.6.

Anal. Calcd for $C_{20}H_{24}O_4$: C, 73.15; H, 7.37. Found: C, 72.94; H, 7.60.



Dimethyl 5-methyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7b**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

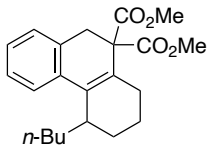
Yield: 53% (15.0 mg, with 30 mol% of $Bi(OTf)_3$ in toluene).

IR (neat) 2951, 2931, 2871, 1732, 1490, 1451, 1433, 1267, 1231, 1173, 1055 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, 1H, *J* = 7.6 Hz), 7.23-7.08 (m, 3H), 3.78 (s, 3H), 3.59 (s, 3H), 3.40 (d, 1H, *J* = 14.8 Hz), 3.32 (d, 1H, *J* = 14.8 Hz), 3.05-2.97 (m, 1H), 2.42-2.32 (m, 1H), 2.10 (ddd, 1H, *J* = 18.0, 5.2, 5.2 Hz), 1.99-1.88 (m, 1H), 1.87-1.76 (m, 1H), 1.69-1.50 (m, 2H), 1.10 (d, 3H, *J* = 6.8 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.4, 171.1, 135.6, 133.4, 132.7, 130.2, 127.6, 126.7, 126.4, 123.0, 60.2, 52.7, 52.6, 36.1, 30.8, 28.4, 28.2, 20.8, 19.3.

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.83; H, 7.27.



Dimethyl 5-butyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7c**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

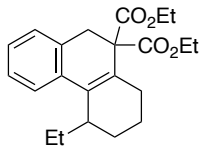
Yield: 70% (25.3 mg, with 10 mol% of $Bi(OTf)_3$).

IR (neat) 2953, 2932, 2871, 2860, 1733, 1665, 1489, 1454, 1434, 1378, 1268, 1233, 1176, 1052 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27-7.07 (m, 4H), 3.77 (s, 3H), 3.58 (s, 3H), 3.38 (d, 1H, *J* = 15.0 Hz), 3.30 (d, 1H, *J* = 15.0 Hz), 2.80 (brs, 1H), 2.44-2.30 (m, 1H), 2.10 (ddd, 1H, *J* = 17.4, 4.8, 4.8 Hz), 1.90-1.47 (m, 5H), 1.44-1.18 (m, 5H), 0.87 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.0, 135.2, 133.6, 132.8, 130.5, 127.6, 126.7, 126.4, 122.7, 60.3, 52.7, 52.5, 36.2, 33.5, 33.5, 29.7, 28.2, 26.7, 22.8, 19.2, 14.1.

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.02; H, 8.16.



Diethyl 5-ethyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7d**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

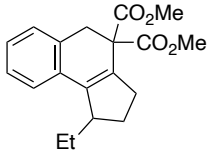
Yield: 60% (19.6 mg, with 10 mol% of $Bi(OTf)_3$ in toluene).

IR (neat) 2960, 2934, 2871, 1731, 1489, 1454, 1365, 1261, 1227, 1190, 1178, 1143, 1095, 1049, 1017 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.06 (m, 4H), 4.32-4.17 (m, 2H), 4.13-3.92 (m, 2H), 3.38 (d, 1H, *J* = 14.7 Hz), 3.30 (d, 1H, *J* = 14.7 Hz), 2.75 (brs, 1H), 2.48-2.33 (m, 1H), 2.14 (ddd, 1H, *J* = 17.4, 4.8, 4.5 Hz), 1.91-1.55 (m, 6H), 1.28 (t, 3H, *J* = 7.2 Hz), 1.10 (t, 3H, *J* = 7.2 Hz), 0.90 (t, 3H, *J* = 7.2 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.9, 170.5, 134.7, 133.7, 132.9, 131.2, 127.6, 126.6, 126.3, 122.7, 61.6, 61.1, 60.1, 36.1, 35.0, 28.2, 26.4, 26.3, 19.4, 14.1, 13.9, 11.6.

Anal. Calcd for $C_{22}H_{28}O_4$: C, 74.13; H, 7.92. Found: C, 74.33; H, 7.71.



Dimethyl 1-ethyl-1,2,3,5-tetrahydro-4*H*-cyclopenta[*a*]naphthalene-4,4-dicarboxylate (**7e**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

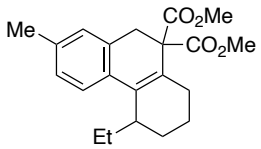
Yield: 91% (26.2 mg, with 10 mol% of $Bi(OTf)_3$).

IR (neat) 2956, 2873, 1739, 1732, 1491, 1454, 1434, 1271, 1243, 1138, 1065, 1049 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.22-7.09 (m, 4H), 3.76 (s, 3H), 3.65 (s, 3H), 3.45 (brs, 2H), 3.17-3.08 (m, 1H), 2.69-2.51 (m, 2H), 2.27-2.11 (m, 1H), 1.85-1.65 (m, 2H), 1.46-1.30 (m, 1H), 0.91 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 170.6, 141.0, 134.0, 132.8, 131.3, 127.6, 126.8, 126.8, 123.1, 56.8, 52.7, 52.6, 44.9, 36.3, 32.5, 28.1, 26.1, 11.3.

Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.51; H, 7.27.



Dimethyl 5-ethyl-2-methyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7g**).

Colorless oil (purified by preparative TLC, hexane/EtOAc = 4/1).

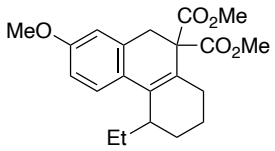
Yield: 82% (26.7 mg, with 10 mol% of $Bi(OTf)_3$).

IR (neat) 2954, 2932, 2872, 1732, 1434, 1266, 1232, 1176, 1062 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, 1H, *J* = 8.1 Hz), 6.99 (d, 1H, *J* = 8.1 Hz), 6.96 (s, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 3.35 (d, 1H, *J* = 14.7 Hz), 3.26 (d, 1H, *J* = 14.7 Hz), 2.73 (brs, 1H), 2.43 (s, 3H), 2.13-2.25 (m, 1H), 2.13-2.01 (m, 1H), 1.92-1.50 (m, 5H), 1.37-1.23 (m, 1H), 0.90 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 172.5, 171.2, 136.1, 134.8, 132.7, 130.9, 129.5, 128.4, 127.3, 122.7, 60.3, 52.7, 52.5, 36.1, 35.0, 28.1, 26.4, 26.1, 21.1, 19.3, 11.7.

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.80; H, 7.82.



Dimethyl 5-ethyl-2-methoxy-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7h**).

Pale yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

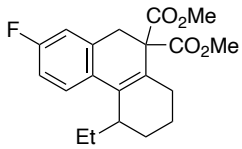
Yield: 53% (18.8 mg, with 10 mol% of $Bi(OTf)_3$ in toluene).

IR (neat) 2953, 2934, 2871, 2838, 1732, 1610, 1500, 1462, 1434, 1256, 1230, 1198, 1141, 1051 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.13 (d, 1H, *J* = 8.1 Hz), 6.72 (d, 1H, *J* = 8.1 Hz), 6.71 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.60 (s, 3H), 3.37 (dd, 1H, *J* = 14.7 Hz), 3.27 (dd, 1H, *J* = 14.7 Hz), 2.69 (brs, 1H), 2.42-2.30 (m, 1H), 2.12-2.20 (m, 1H), 1.86-1.51 (m, 5H), 1.38-1.23 (m, 1H), 0.90 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.2, 158.0, 134.5, 128.2, 126.7, 124.0, 113.4, 111.6, 60.2, 55.2, 52.7, 52.6, 36.4, 35.1, 28.0, 26.4, 26.1, 19.3, 11.7.

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.15; H, 7.51.



Dimethyl 5-ethyl-2-fluoro-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7i**).

Yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 76% (24.1 mg, with 10 mol% of $Bi(OTf)_3$).

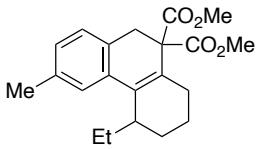
IR (neat) 2955, 2875, 1739, 1731, 1609, 1496, 1435, 1253, 1135, 1112, 1064, 1049 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (dd, 1H, J = 9.3, 5.7 Hz), 6.91-6.80 (m, 2H), 3.78 (s, 3H), 3.60 (s, 3H), 3.37 (d, 1H, J = 15.0 Hz), 3.28 (d, 1H, J = 15.0 Hz), 2.69 (brs, 1H), 2.43-2.28 (m, 1H), 2.13-1.94 (m, 1H), 1.89-1.46 (m, 5H), 1.37-1.20 (m, 1H), 0.89 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.1, 170.8, 161.2 (d, $J_{C–F}$ = 244.7 Hz), 135.3 (d, $J_{C–F}$ = 8.0 Hz), 134.2, 130.2, 129.8 (d, $J_{C–F}$ = 3.1 Hz), 124.4 (d, $J_{C–F}$ = 8.0 Hz), 114.6 (d, $J_{C–F}$ = 21.5 Hz), 113.3 (d, $J_{C–F}$ = 21.0 Hz), 60.1, 52.8, 52.6, 36.1, 35.2, 28.1, 26.3, 26.2, 19.3, 11.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -117.3 (s).

Anal. Calcd for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.08; H, 6.76.



Dimethyl 5-ethyl-3-methyl-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7j**).

Yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

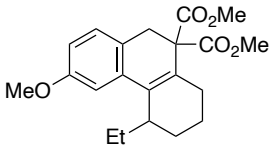
Yield: 55% (19.0 mg, with 30 mol% of $Bi(OEt)_3$).

IR (neat) 2955, 2874, 1733, 1435, 1270, 1235, 1206, 1064, 1048 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (d, 1H, J = 7.5 Hz), 7.02 (s, 1H), 6.92 (d, 1H, J = 7.5 Hz), 3.77 (s, 3H), 3.58 (s, 3H), 3.34 (d, 1H, J = 14.7 Hz), 3.26 (d, 1H, J = 14.7 Hz), 2.76 (brs, 1H), 2.31 (s, 3H), 2.42-2.25 (m, 1H), 2.14-2.02 (m, 1H), 1.90-1.53 (m, 5H), 1.39-1.20 (m, 1H), 0.90 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.5, 171.1, 135.9, 135.0, 133.5, 130.7, 129.7, 127.4, 127.1, 123.6, 60.4, 52.7, 52.5, 35.8, 34.9, 28.2, 26.4, 26.3, 21.6, 19.4, 11.6.

Anal. Calcd for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 73.75; H, 7.80.



Dimethyl 5-ethyl-3-methoxy-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7k**).

Yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

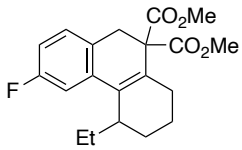
Yield: 54% (19.6 mg, with 30 mol% of $Bi(OTf)_3$).

IR (neat) 2954, 2933, 2872, 1732, 1609, 1573, 1497, 1462, 1434, 1339, 1270, 1236, 1166, 1062, 1043 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, 1H, J = 8.1 Hz), 6.78 (d, 1H, J = 2.4 Hz), 6.66 (dd, 1H, J = 8.1, 2.4 Hz), 3.78 (s, 3H), 3.77 (s, 3H), 3.59 (s, 3H), 3.31 (d, 1H, J = 15.0 Hz), 3.25 (d, 1H, J = 15.0 Hz), 2.70 (brs, 1H), 2.42-2.31 (m, 1H), 2.15-2.03 (m, 1H), 1.89-1.52 (m, 5H), 1.40-1.25 (m, 1H), 0.91 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 172.4, 171.1, 158.5, 134.9, 134.8, 131.5, 128.2, 125.0, 110.9, 109.6, 60.6, 55.2, 52.7, 52.5, 35.4, 35.1, 28.3, 26.4, 26.3, 19.3, 11.7.

Anal. Calcd for $C_{21}H_{26}O_5$: C, 70.37; H, 7.31. Found: C, 70.14; H, 7.39.



Dimethyl 5-ethyl-3-fluoro-6,7,8,10-tetrahydrophenanthrene-9,9(5*H*)-dicarboxylate (**7l**).

Yellow oil (purified by preparative TLC, hexane/EtOAc = 4/1).

Yield: 53% (17.4 mg, with 30 mol% of $Bi(OTf)_3$).

IR (neat) 2955, 2937, 2873, 1733, 1611, 1580, 1494, 1457, 1434, 1265, 1234, 1062, 1046 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.10 (dd, 1H, J = 8.4, 6.0 Hz), 6.91 (dd, 1H, J = 10.8, 2.4 Hz), 6.81 (ddd, 1H, J = 8.4, 8.4, 2.4 Hz), 3.78 (s, 3H), 3.59 (s, 3H), 3.31 (brs, 2H), 2.65 (brs, 1H), 2.38 (td, 1H, J = 12.0, 6.0 Hz), 2.42-2.34 (m, 1H), 2.09 (ddd, 1H, J = 14.0, 4.4, 4.4 Hz), 1.88-1.52 (m, 5H), 1.36-1.24 (m, 1H), 0.91 (t, 3H, J = 7.6 Hz).

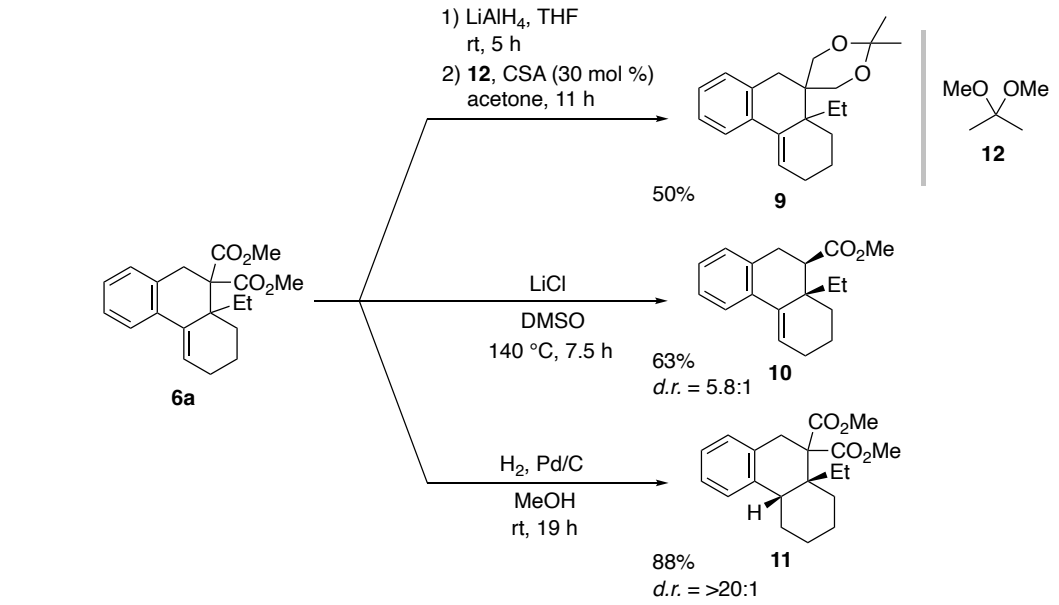
^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1, 170.8, 161.5 (d, $J_{C–F}$ = 240.3 Hz), 135.6 (d, $J_{C–F}$ = 7.6 Hz), 134.4 (d, $J_{C–F}$ = 1.9 Hz), 132.3, 128.7 (d, $J_{C–F}$ = 7.6 Hz), 128.2 (d, $J_{C–F}$ = 2.8 Hz), 112.9 (d, $J_{C–F}$ = 21.0 Hz), 110.0 (d, $J_{C–F}$ = 22.9 Hz), 60.3, 52.8, 52.6, 35.4, 35.1, 28.2, 26.2, 26.1, 19.2, 11.6.

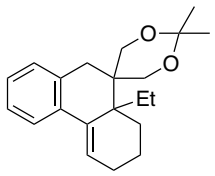
^{19}F NMR (376 MHz, $CDCl_3$) δ -117.2 (s).

Anal. Calcd for $C_{20}H_{23}FO_4$: C, 69.35; H, 6.69. Found: C, 69.18; H, 6.90.

3. Derivatization from the adduct.

Scheme S3. Further derivatization from **6a**.





Synthesis of 8a-ethyl-2',2'-dimethyl-6,8,8a,10-tetrahydro-7H-spiro[phenanthrene-9,5'-[1,3]dioxane] (9):

To a solution of **6a** (41.5 mg, 0.126 mmol) in THF (1.3 mL) was added $LiAlH_4$ (9.7 mg, 0.26 mmol) at 0 °C. After being stirred for 5 h at room temperature, the reaction was stopped by adding Na_2SO_4•$10H_2O$. The crude material was filtered through Celite® pad and the resulting filtrate was concentrated in vacuo to give crude diol (37.3 mg). The crude material was used for the next reaction without further purification.

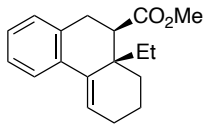
To a solution of diol in acetone (2.50 mL) were successively added acetone dimethylacetal (24.0 μL, 0.20 mmol), and CSA (7.6 mg, 0.033 mmol) at room temperature. After being stirred for 11 h, the reaction was stopped by adding of saturated aqueous $NaHCO_3$ at 0 °C. The crude products were extracted with EtOAc (x3) and the combined organic extracts were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by preparative TLC (silica gel, hexane/EtOAc = 4/1) to give **9** (19.7 mg, 50% from **6a**) as colorless oil.

IR (neat) 3017, 2959, 2937, 2876, 2831, 1454, 1378, 1369, 1262, 1244, 1227, 1200, 1091, 1059, 1027 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$) δ 7.44-7.39 (m, 1H), 7.17-7.09 (m, 3H), 6.33 (t, 1H, *J* = 4.0 Hz), 4.14 (d, 1H, *J* = 11.6 Hz), 3.86 (dd, 1H, *J* = 11.6, 2.0 Hz), 3.59 (dd, 1H, *J* = 11.6, 1.2 Hz), 3.42 (d, 1H, *J* = 18.0 Hz), 3.22 (d, 1H, *J* = 11.6, 1.2 Hz), 2.78 (d, 1H, *J* = 18.0 Hz), 2.19-2.15 (m, 2H), 2.12-2.03 (m, 1H), 1.83-1.64 (m, 3H), 1.58-1.46 (m, 1H), 1.42 (s, 3H), 1.38 (s, 3H), 1.39-1.28 (m, 1H), 0.78 (t, 3H, *J* = 7.6 Hz).

^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.8, 133.5, 129.4, 126.7, 126.0, 125.9, 124.7, 98.4, 65.2, 63.8, 40.7, 40.0, 34.7, 28.1, 27.3, 26.8, 25.6, 21.1, 20.4, 10.4.

Anal. Calcd for $C_{21}H_{28}O_2$: C, 80.73; H, 9.03. Found: C, 80.60; H, 9.25.



Synthesis of methyl (8a,9)-8a-ethyl-6,7,8,8a,9,10-hexahydrophenanthrene-9-carboxylate (10):

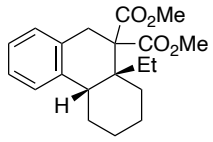
To a solution of **6a** (113 mg, 0.343 mmol) in DMSO (3.4 mL) was added LiCl (145 mg, 3.41 mmol), and then heated at 140 °C. After being stirred for 7.5 h, the reaction was quenched by addition of H_2O. The crude mixture was extracted with EtOAc (x3), dried (Na_2SO_4) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, hexane/EtOAc = 30/1) to give **10** (58.7 mg, 63% *d.r.* = 5.8:1) as pale yellow oil.

IR (neat) 3022, 2948, 2882, 1731, 1672, 1657, 1592, 1490, 1454, 1436, 1372, 1325, 1268, 1224, 1193, 1167, 1111, 1025 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$) δ 7.42-7.36 (m, 1H), 7.18-7.11 (m, 2H), 7.10-7.04 (m, 1H), 6.17 (t, 1H, *J* = 4.2 Hz), 3.72 (s, 3H), 3.31 (ddd, 1H, *J* = 15.6, 15.6, 5.1 Hz), 2.99-2.86 (m, 2H), 2.23-2.15 (m, 2H), 1.91-1.82 (m, 1H), 1.72-1.51 (m, 5H), 0.73 (t, 3H, *J* = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 174.7, 139.1, 136.0, 133.3, 128.3, 126.6, 126.2, 125.1, 124.8, 51.3, 50.3, 38.4, 33.0, 29.4, 26.1, 24.9, 19.2, 9.9.

Anal. Calcd for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 80.20; H, 8.36.



Synthesis of dimethyl (4bS,8aR)-8a-ethyl-4b,6,7,8,8a,10-hexahydrophenanthrene-9,9(5H)-dicarboxylate (11):

To a solution of **6a** (108.8 mg, 0.331 mmol) in MeOH (3.3 mL) was added 10% Pd/C (11.7 mg). After being stirred under H_2 (1 atm) at room temperature for 19 h, the reaction mixture was filtered through Celite® pad and concentrated in vacuo to give **11** (96.3 mg, 88%) as colorless crystal, which was subjected to X-ray analysis.

Mp. 104–106 °C.

IR (KBr) 3060, 2949, 2885, 2864, 1730, 1495, 1474, 1453, 1433, 1263, 1236, 1214, 1169, 1076, 1055, 1033, 1014 cm^{-1}.

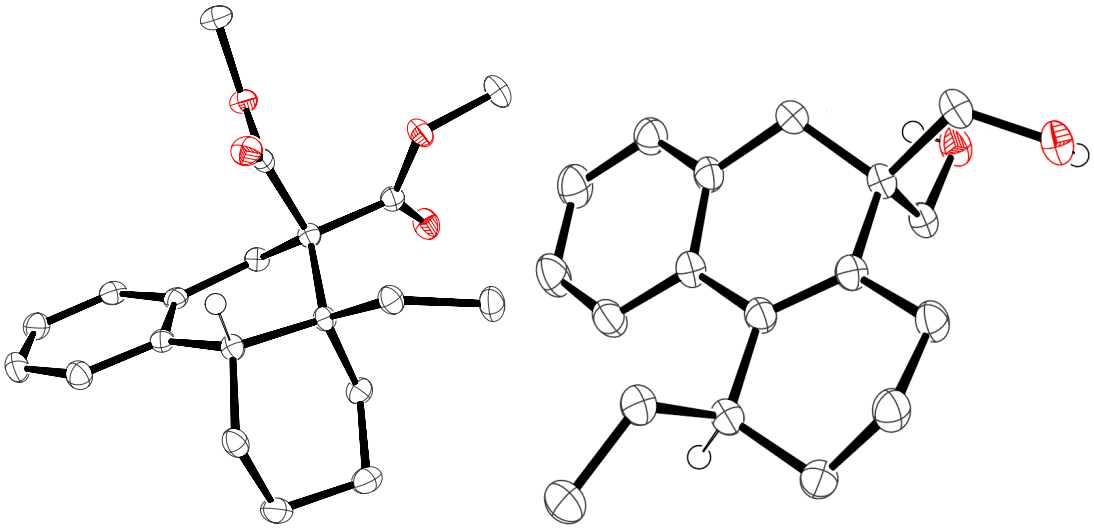
^1H NMR (300 MHz, $CDCl_3$) δ 7.34 (d, 1H, J = 7.8 Hz), 7.18-7.04 (m, 3H), 3.74 (s, 3H), 3.64 (d, 1H, J = 17.4 Hz), 3.54 (s, 3H), 3.33 (brs, 1H), 3.25 (d, 1H, J = 17.4 Hz), 2.52-2.38 (m, 1H), 2.29-2.20 (m, 1H), 2.19-2.00 (m, 2H), 1.77-1.71 (m, 1H), 1.58-1.35 (m, 4H), 1.07-0.92 (m, 1H), 0.80 (t, 3H, J = 7.5 Hz).

^{13}C NMR (75 MHz, $CDCl_3$) δ 171.8, 171.2, 138.1, 133.6, 128.6, 127.2, 126.4, 125.2, 59.6, 52.3, 51.9, 41.0, 39.6, 35.1, 26.3, 25.9, 24.2, 21.9, 20.6, 8.6.

Anal. Calcd for $C_{20}H_{26}O_4$: C, 72.70; H, 7.93. Found: C, 72.61; H, 7.78.

4. Structural determination.

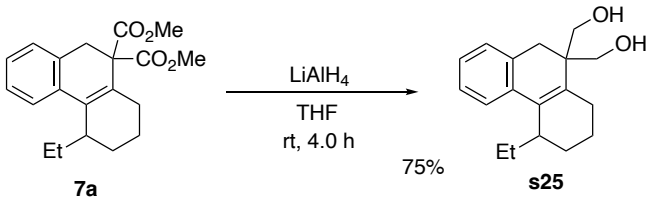
The structure of **6** was confirmed by X-ray analysis of analogue **11** (CCDC-2324188). Although we could not obtain good crystals from compound **7** itself, the corresponding diol **s25**, which was synthesized from **7** by the treatment of $LiAlH_4$, gave high quality crystals, which allowed us the structural determination (CCDC-2338653).



compound **11** compound **s25**

Figure S1. X-ray structures of **11** and **s25** (All hydrogens except for methine proton were omitted for clarity).

Scheme S4. Synthesis of **s25**.



Synthesis of (5-ethyl-5,6,7,8,9,10-hexahydrophenanthrene-9,9-diyl)dimethanol (s25): To a solution of **7a** (28.0 mg, 0.0852 mmol) in THF (1.0 mL) was added $LiAlH_4$ (9.7 mg, 0.26 mmol) at 0 °C. After being stirred for 4 h at room temperature, the reaction was stopped by adding $Na_2SO_4 \cdot 10H_2O$. The crude material was filtered through Celite® pad and the resulting filtrate was concentrated in vacuo. The residue was purified by preparative TLC (silica gel, hexane/EtOAc = 1/1) to give **s25** (17.4 mg, 75%) as colorless oil, which was crystallized in hexane/CH_2Cl_2 at –10 °C.

Mp. 111‑113 °C.

IR (KBr) 3353, 2931, 2871, 1717, 1488, 1453, 1429, 1377, 1257, 1046, 1029 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21-7.16 (m, 3H), 7.15-7.08 (m, 1H), 4.01 (d, 1H, *J* = 11.2 Hz), 3.74 (d, 1H, *J* = 11.2 Hz), 3.63 (d, 1H, *J* = 10.0 Hz), 3.35 (d, 1H, *J* = 10.0 Hz), 2.98 (d, 1H, *J* = 15.6 Hz), 2.78 (d, 1H, *J* = 15.6 Hz), 2.66 (d, 1H, *J* = 6.8 Hz), 2.25-2.14 (m, 2H), 1.99 (brs, 2H), 1.77-1.52 (m, 4H), 1.32-1.21 (m, 2H), 0.91 (t, 3H, *J* = 7.6 Hz).
3.54 (s, 3H), 3.33 (brs, 1H), 3.25 (d, 1H, *J* = 17.4 Hz), 2.52-2.38 (m, 1H), 2.29-2.20 (m, 1H), 2.19-2.00 (m, 2H), 1.77-1.71 (m, 1H),

^{13}C NMR (100 MHz, $CDCl_3$) δ 135.1, 134.6, 134.4, 134.2, 128.3, 126.2, 126.1, 122.4, 68.1, 65.1, 43.3, 34.9, 33.1, 26.4, 25.9, 25.7, 19.1, 11.8.

Anal. Calcd for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.16; H, 9.01.

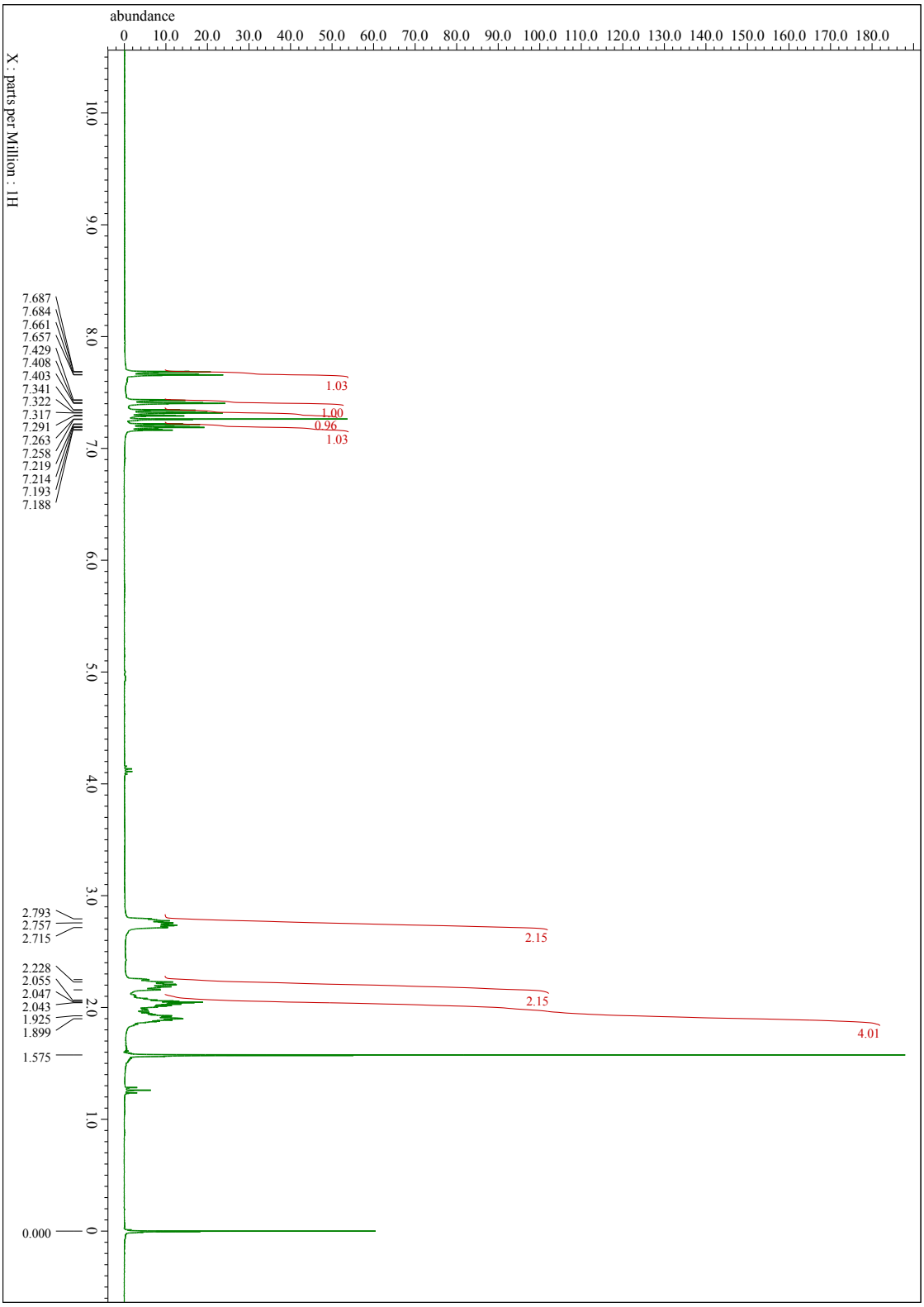
References

1) Hsieh, J.-C.; Cheng, A.-Y.; Fu, J.-H.; Kang, T.-W. *J. Am. Chem. Soc*. **2018**, *140*, 6404.

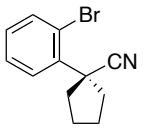
2) Yokoo, K.; Mori, K. *Chem. Chemmun*. **2011**, *54*, 6927.

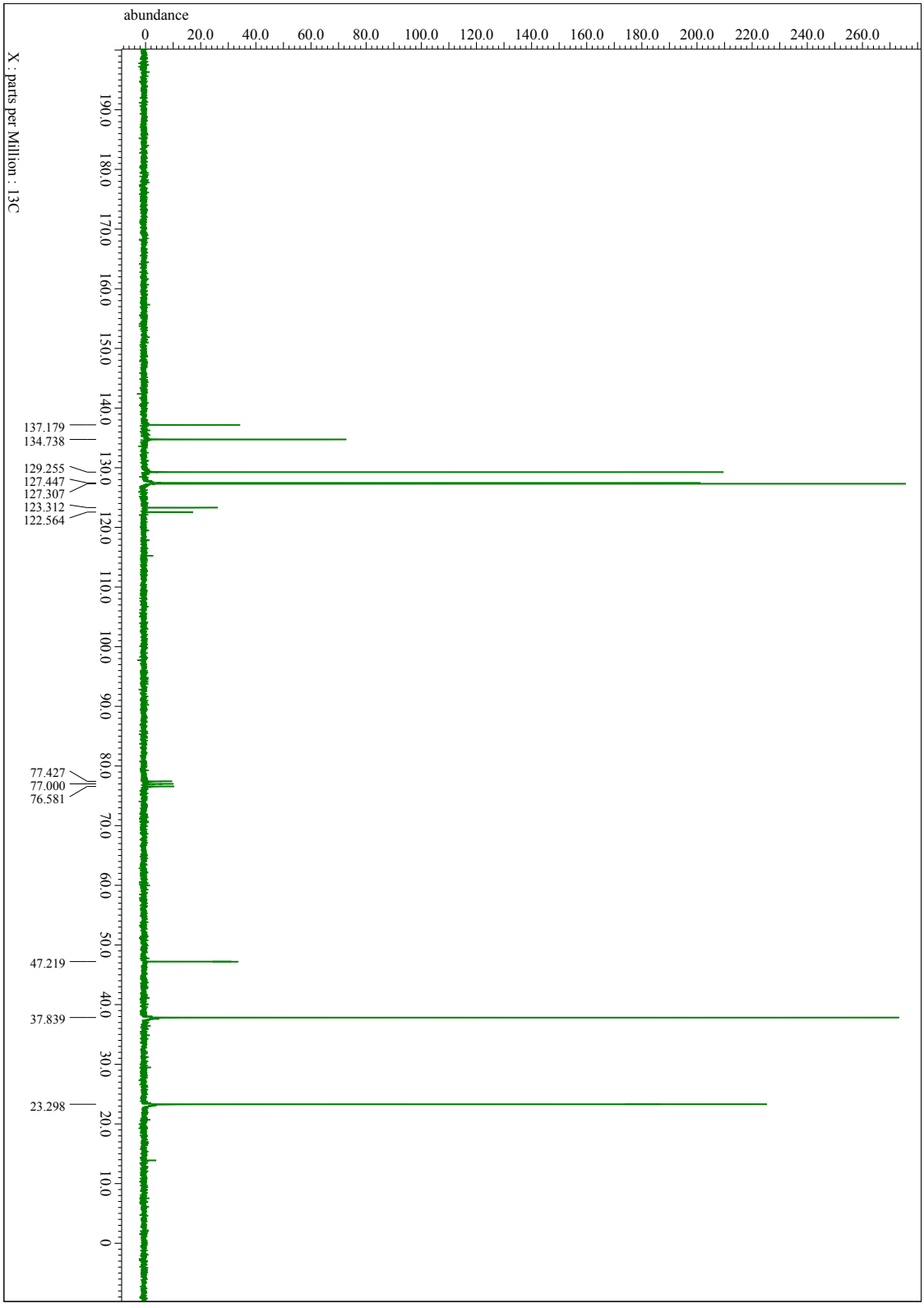
3) Mori, K.; Isogai, R.; Kamei, Y.; Yamanaka, M.; Akiyama, T. *J. Am. Chem. Soc.* **2018**, *140*, 6203–6207.

^{1}H NMR spectrum of **s2** ($CDCl_3$, 300 MHz).

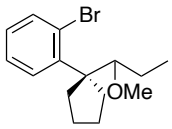


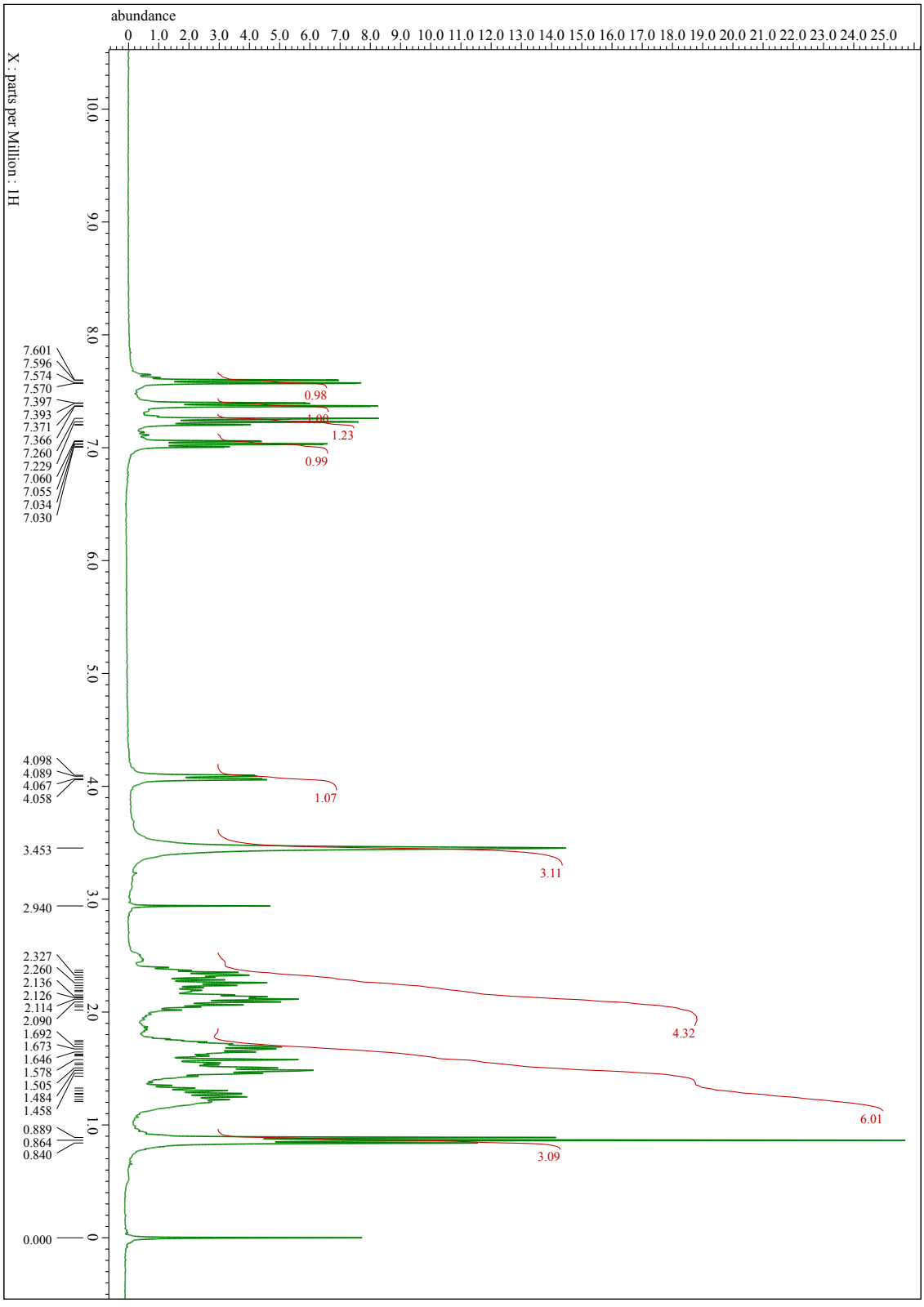
^{13}C NMR spectrum of **s2** ($CDCl_3$, 75 MHz).



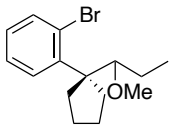


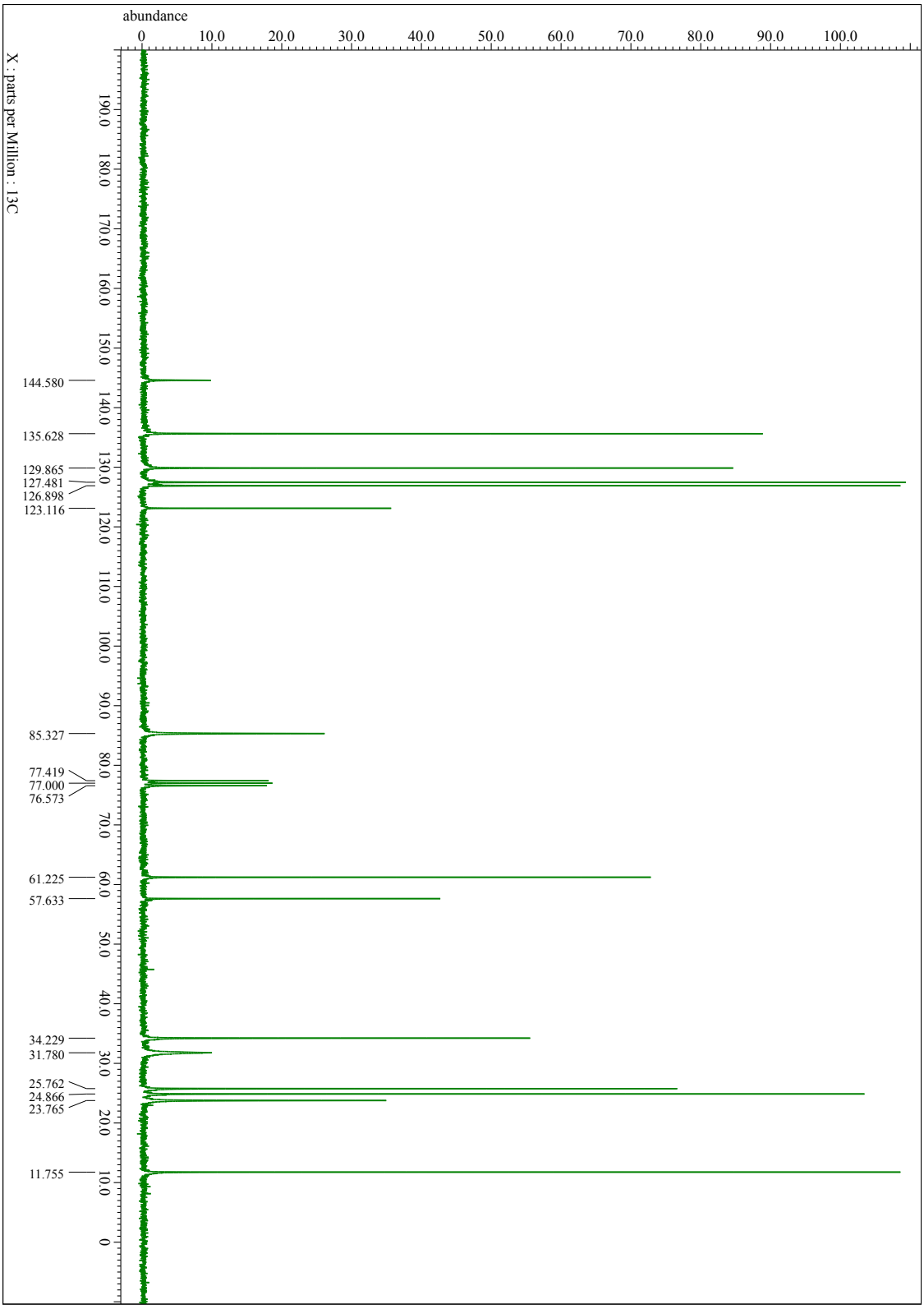
^{1}H NMR spectrum of **s5** ($CDCl_3$, 300 MHz).



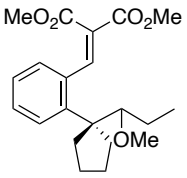


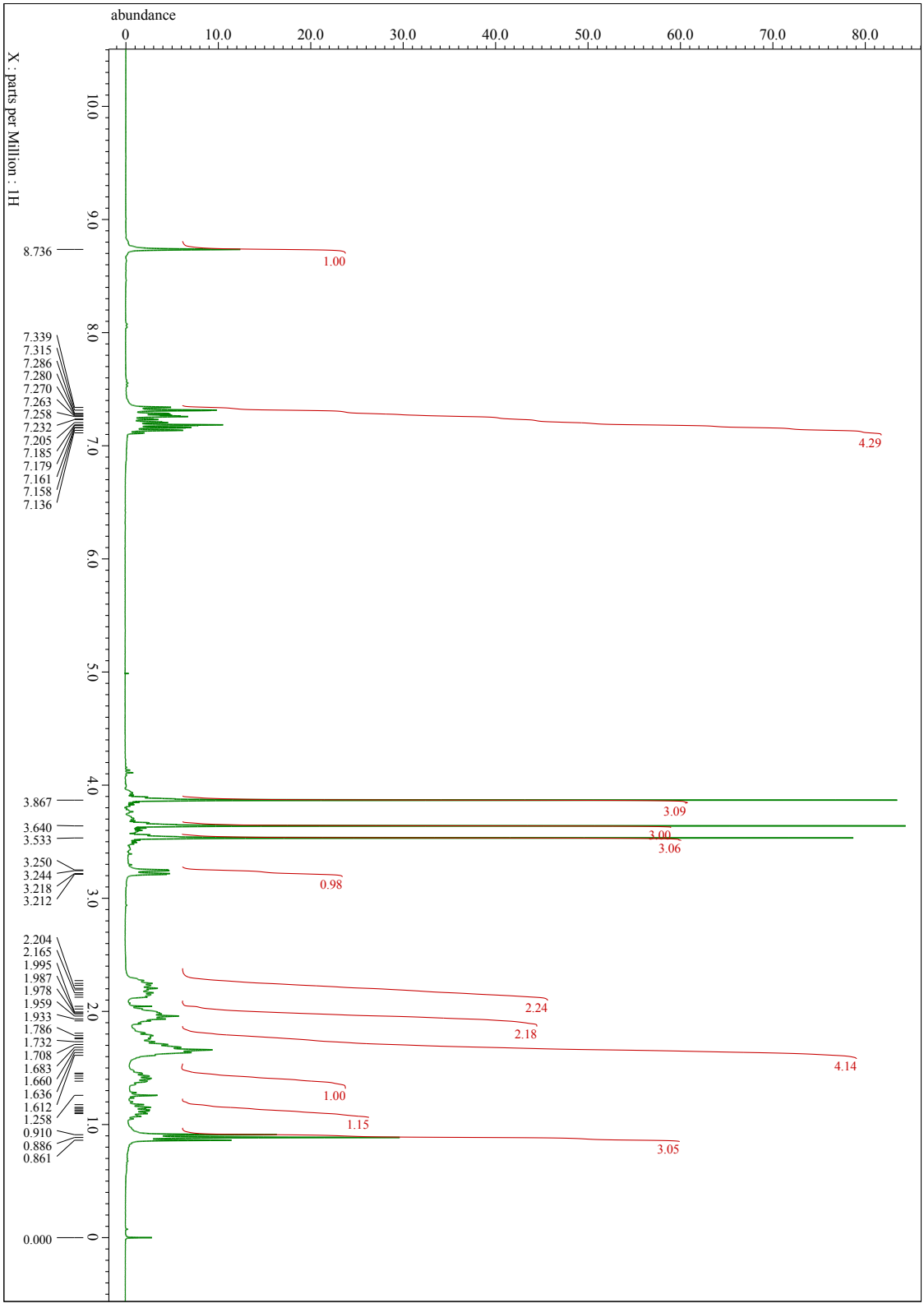
^{13}C NMR spectrum of **s5** ($CDCl_3$, 75 MHz).



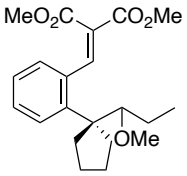


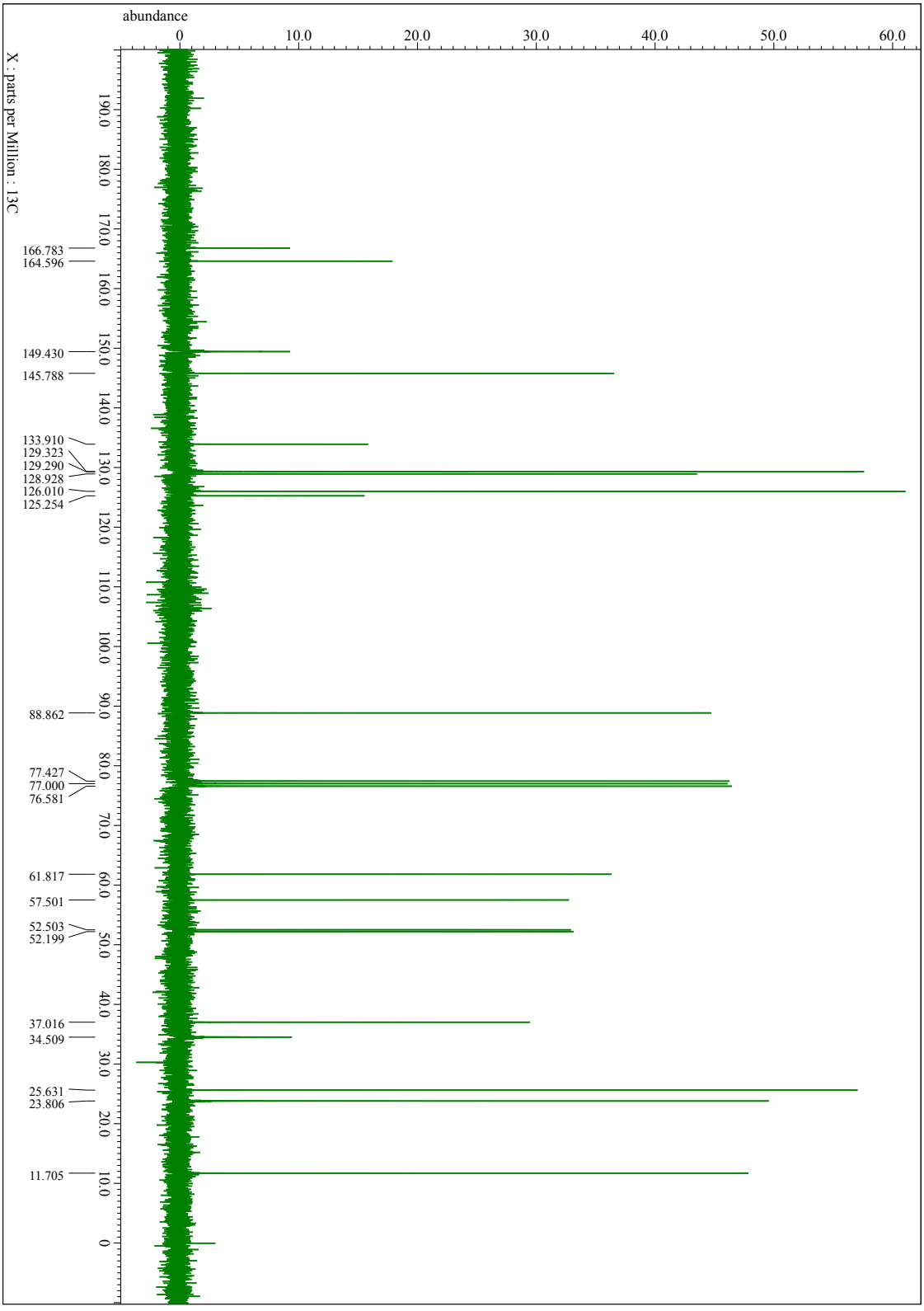
^{1}H NMR spectrum of **3a** ($CDCl_3$, 300 MHz).



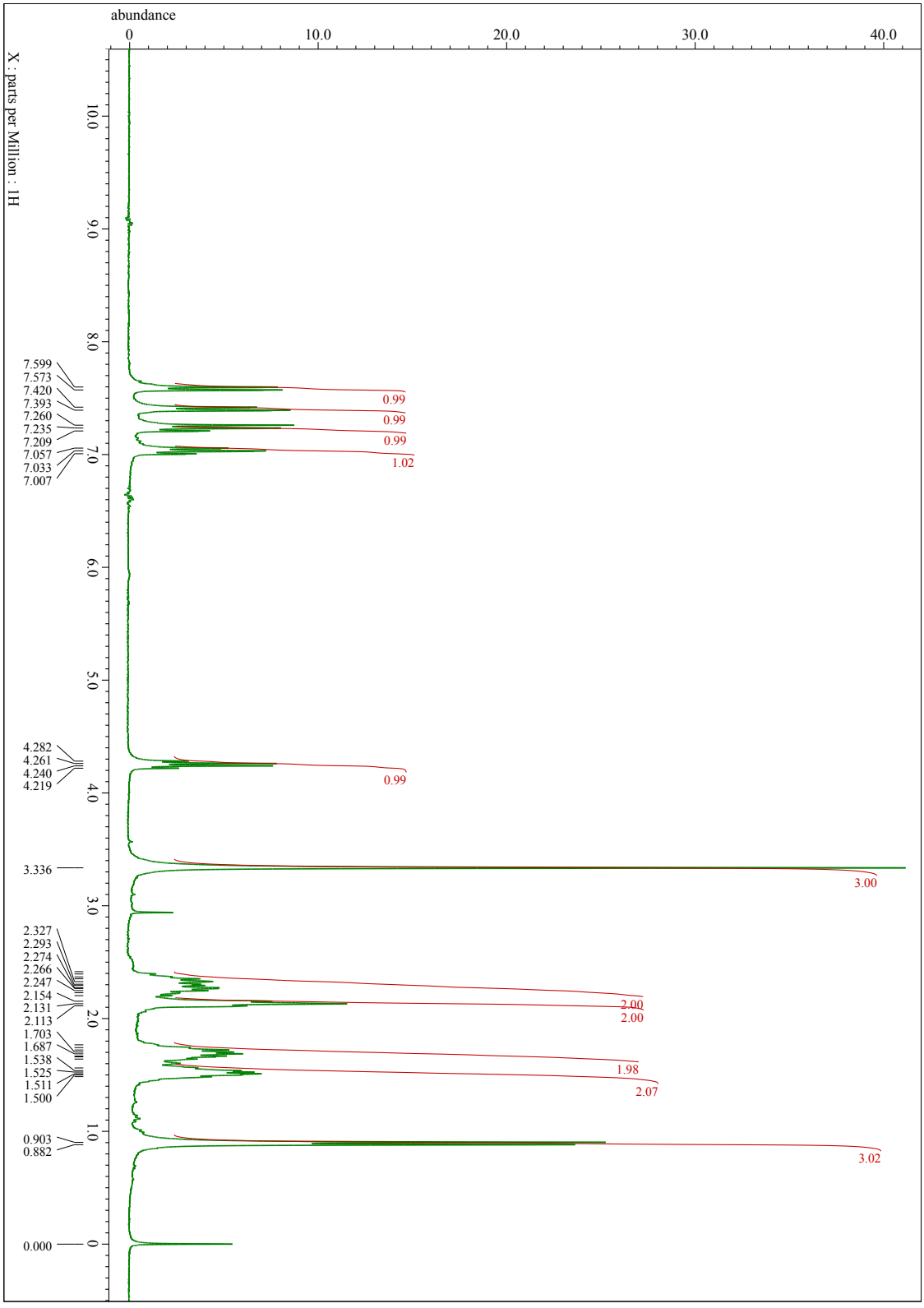


^{13}C NMR spectrum of **3a** ($CDCl_3$, 75 MHz).

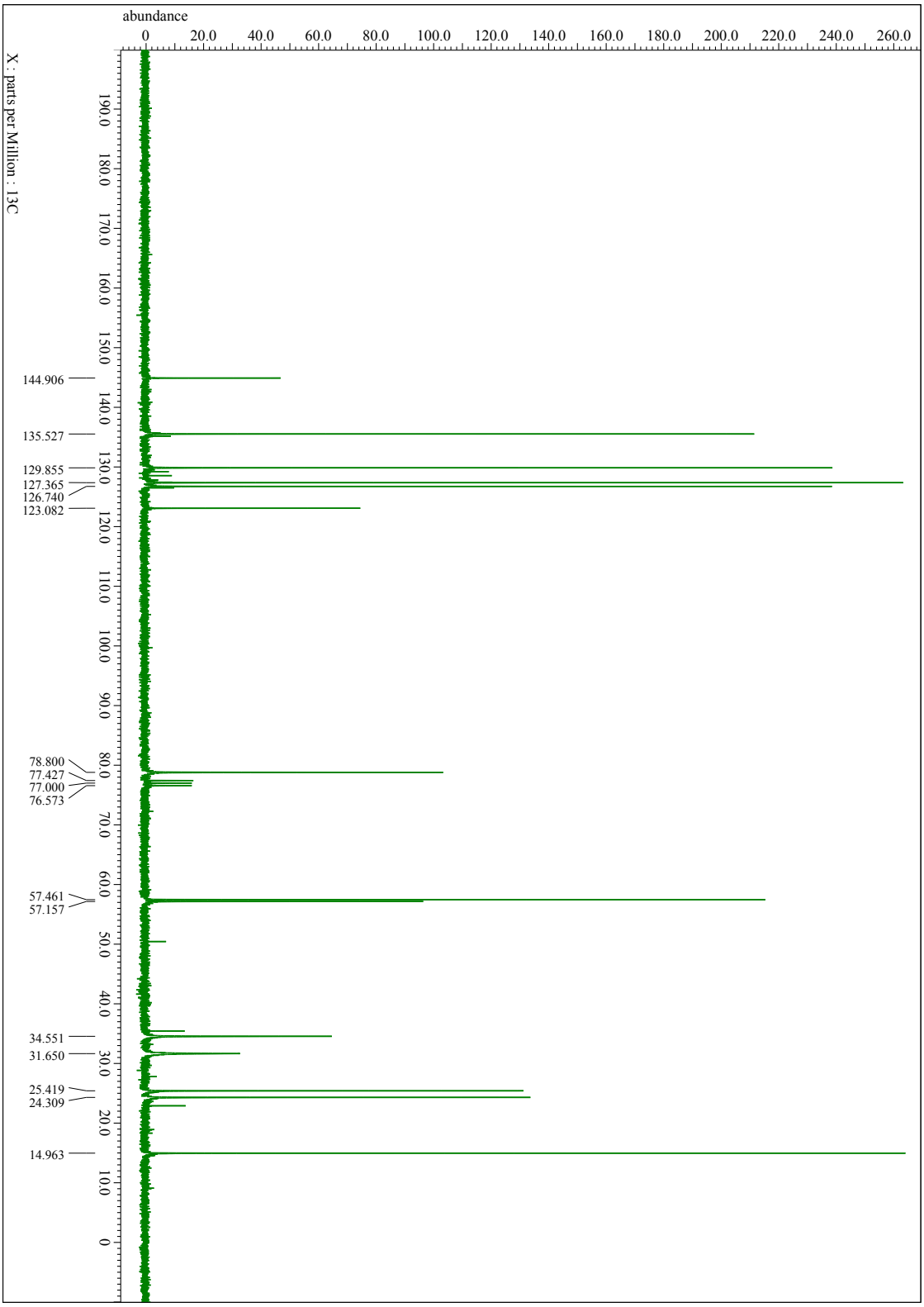




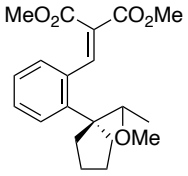
^{1}H NMR spectrum of **s7** ($CDCl_3$, 300 MHz).

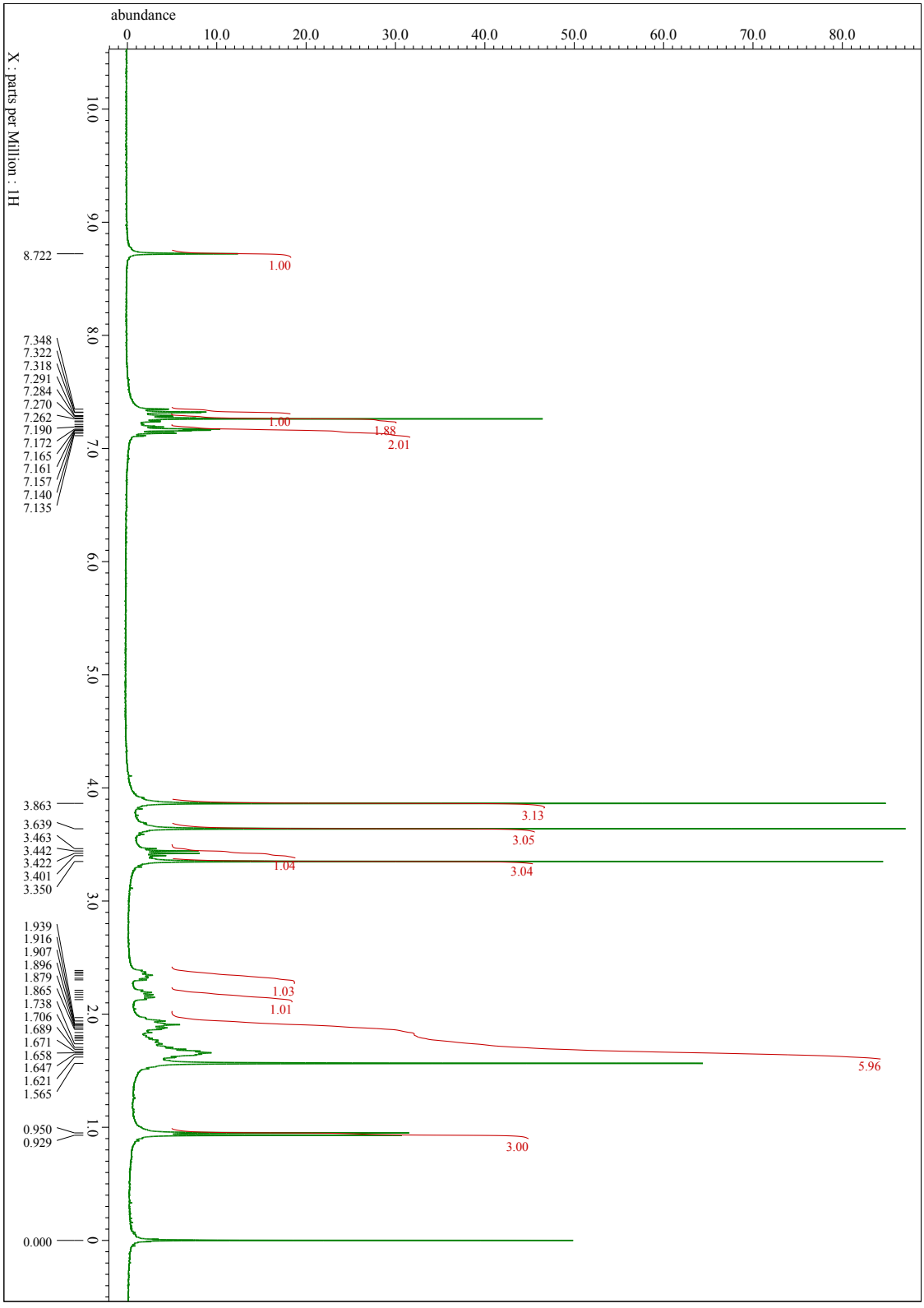


^{13}C NMR spectrum of **s7** ($CDCl_3$, 75 MHz).

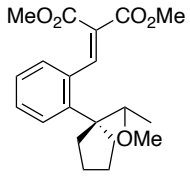


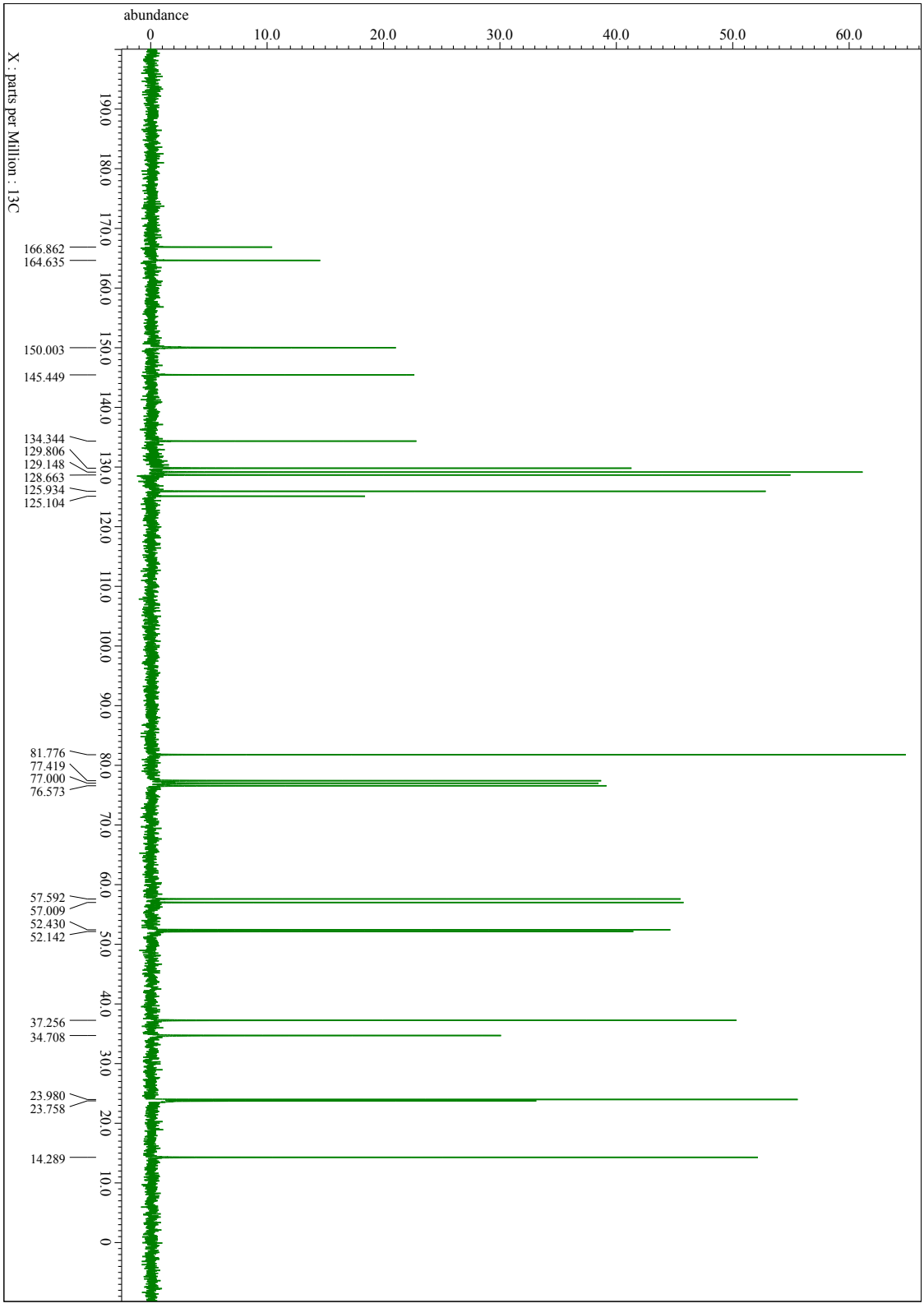
^{1}H NMR spectrum of **4b** ($CDCl_3$, 300 MHz).



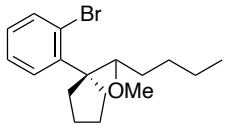


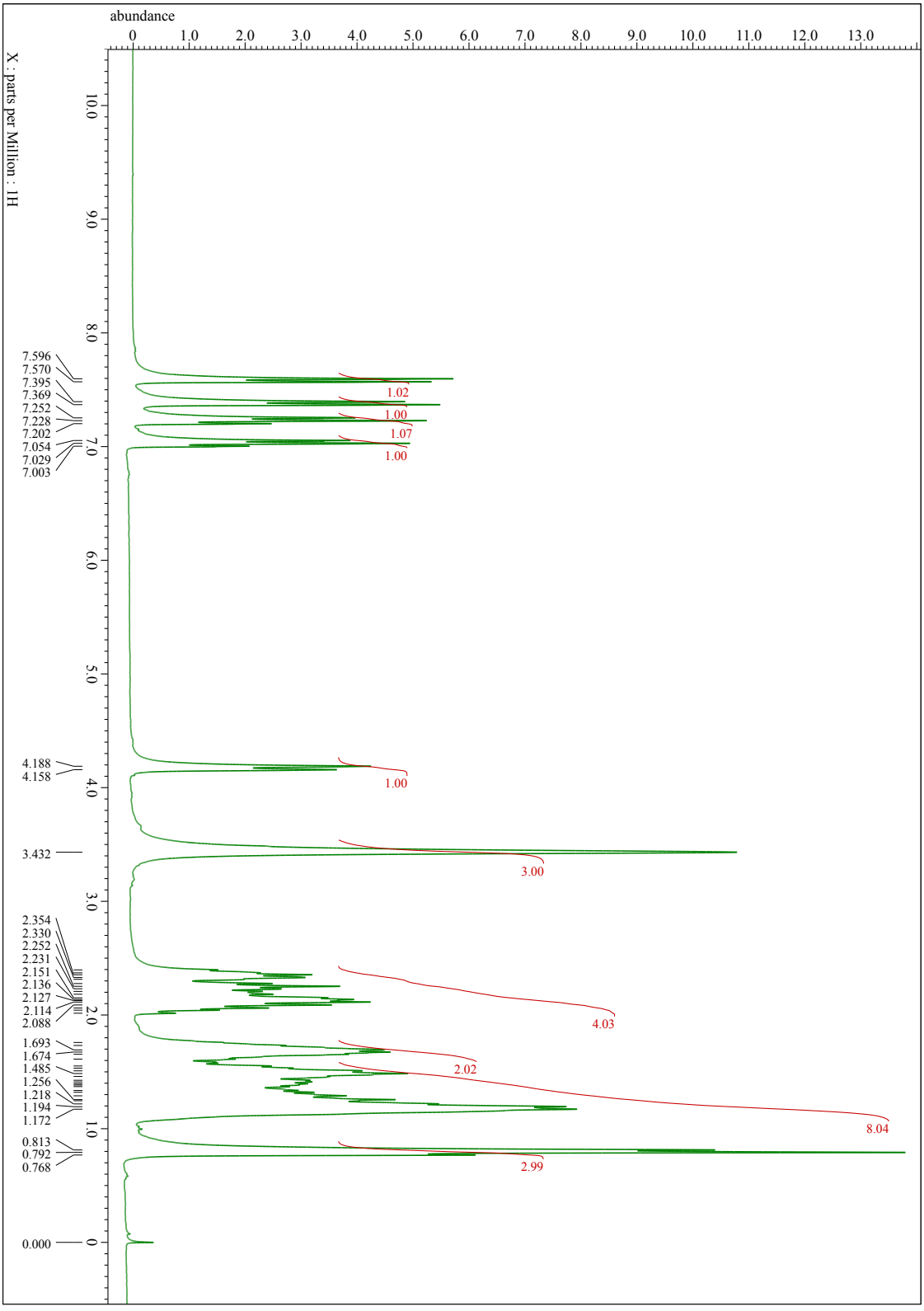
^{13}C NMR spectrum of **4b** ($CDCl_3$, 75 MHz).



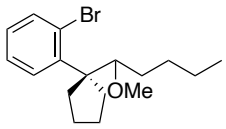


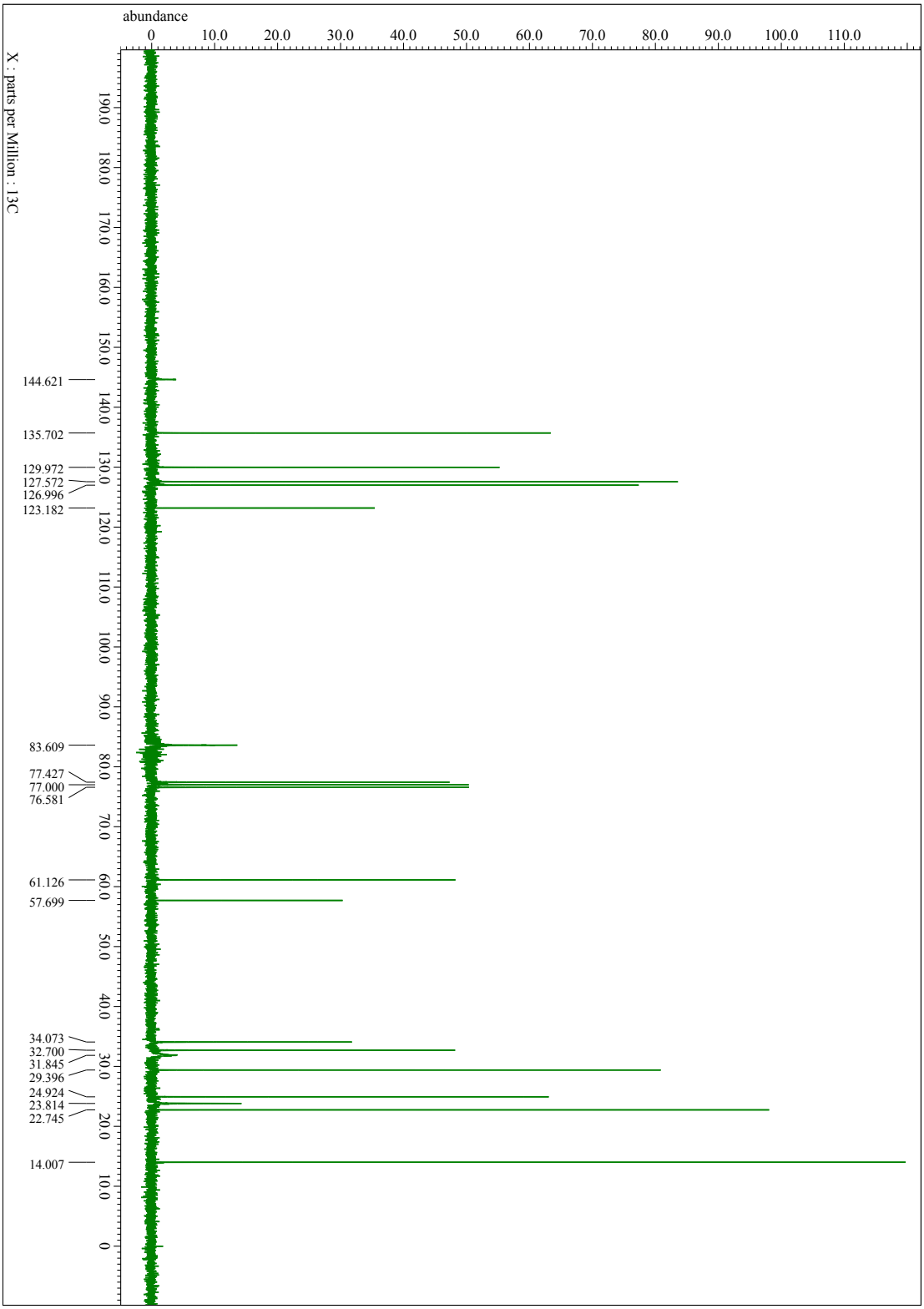
^{1}H NMR spectrum of **s8** ($CDCl_3$, 300 MHz).



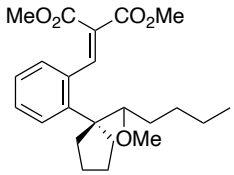


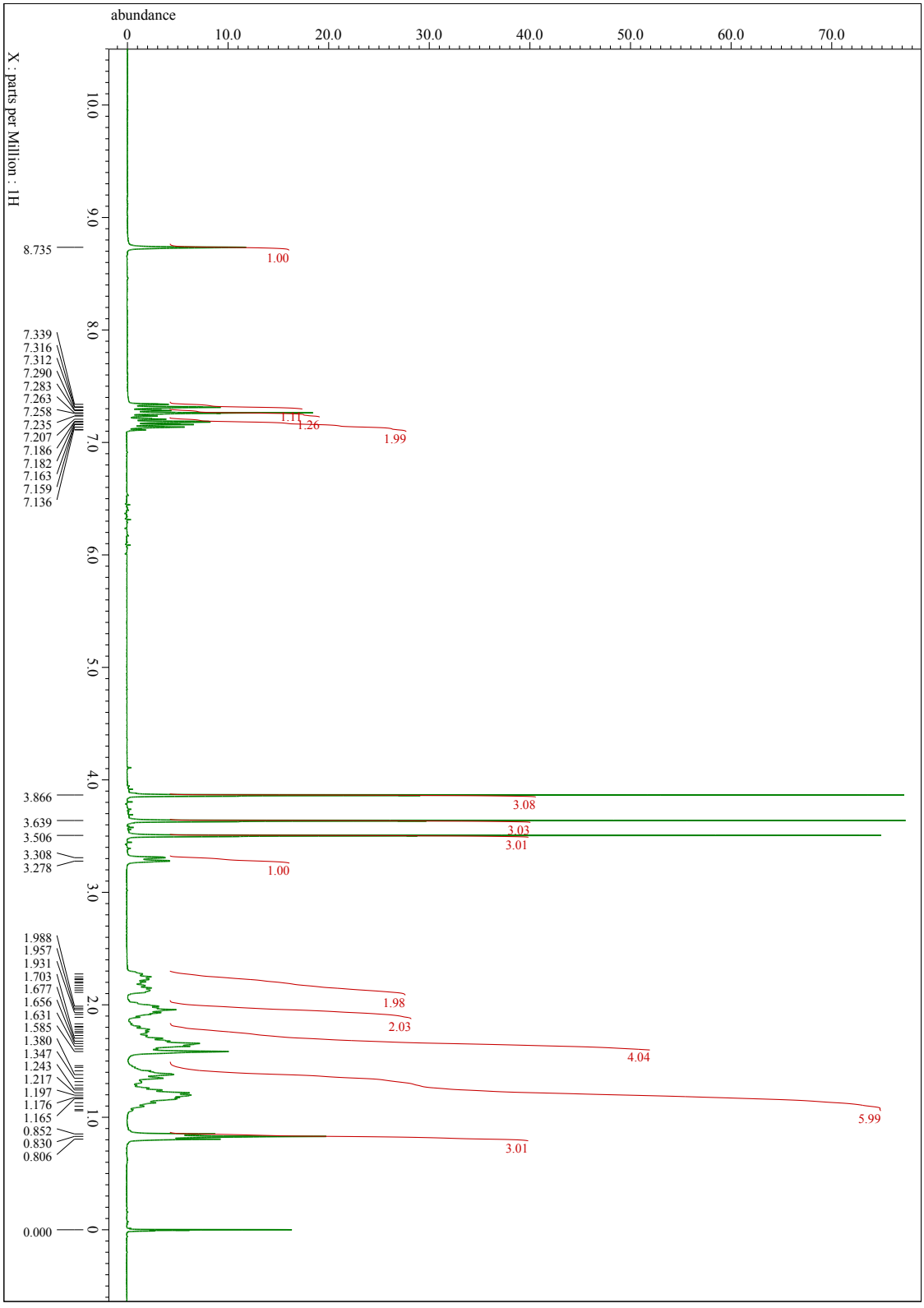
^{13}C NMR spectrum of **s8** ($CDCl_3$, 75 MHz).



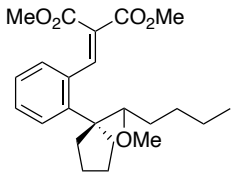


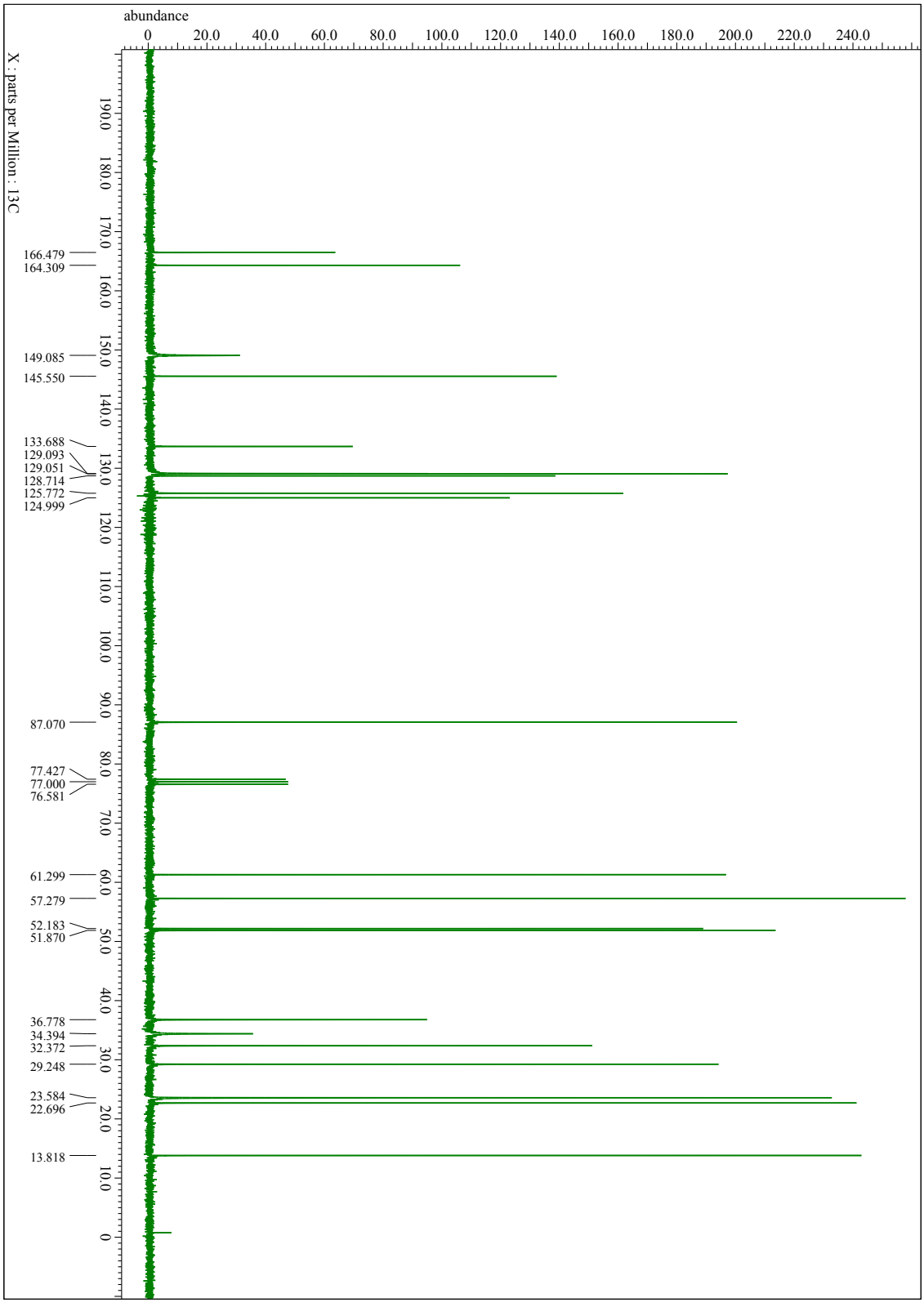
^{1}H NMR spectrum of **4c** ($CDCl_3$, 300 MHz).



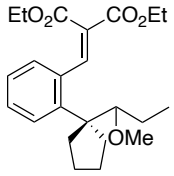


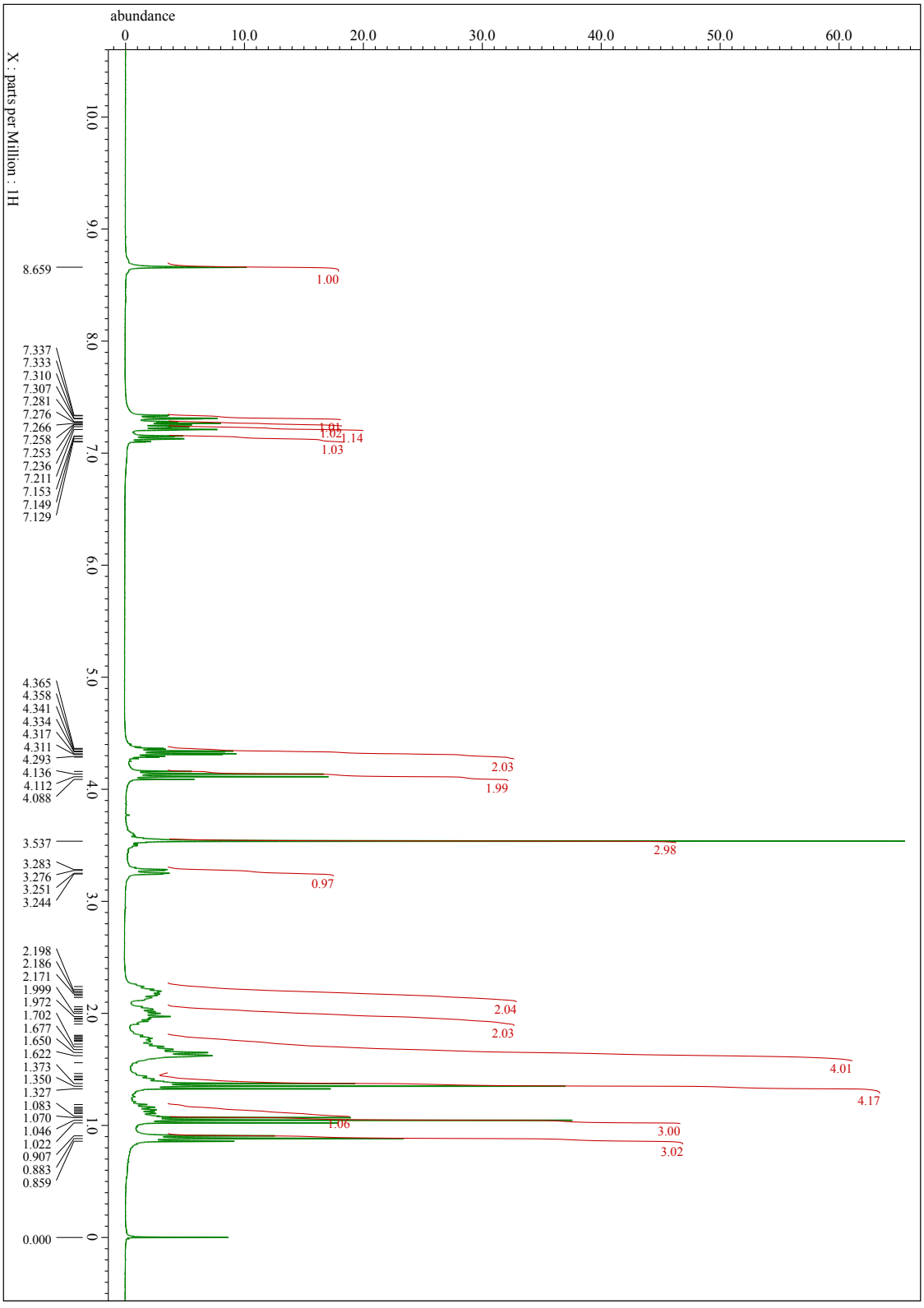
^{13}C NMR spectrum of **4c** ($CDCl_3$, 75 MHz).



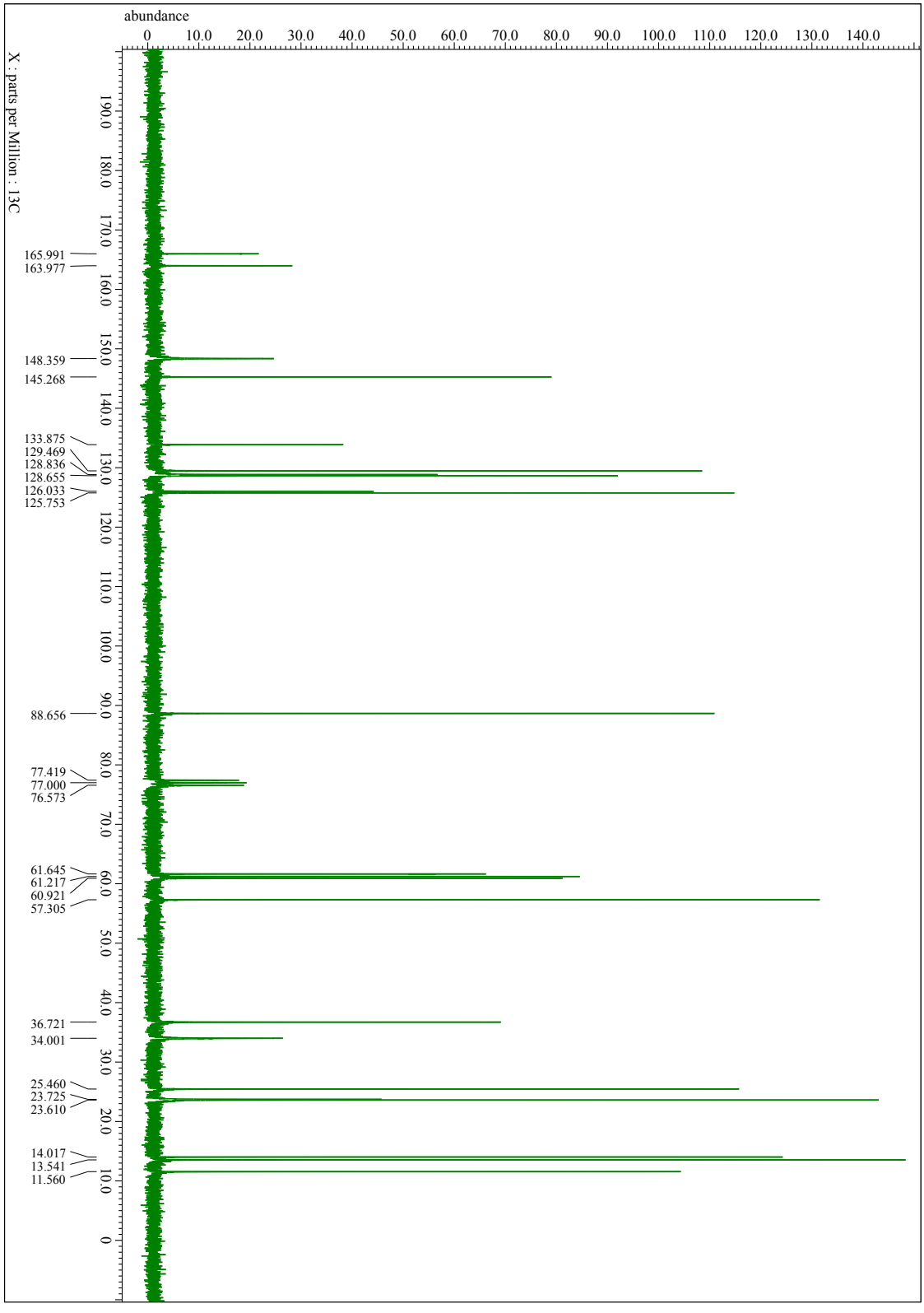


^{1}H NMR spectrum of **4d** ($CDCl_3$, 300 MHz).

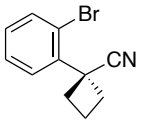


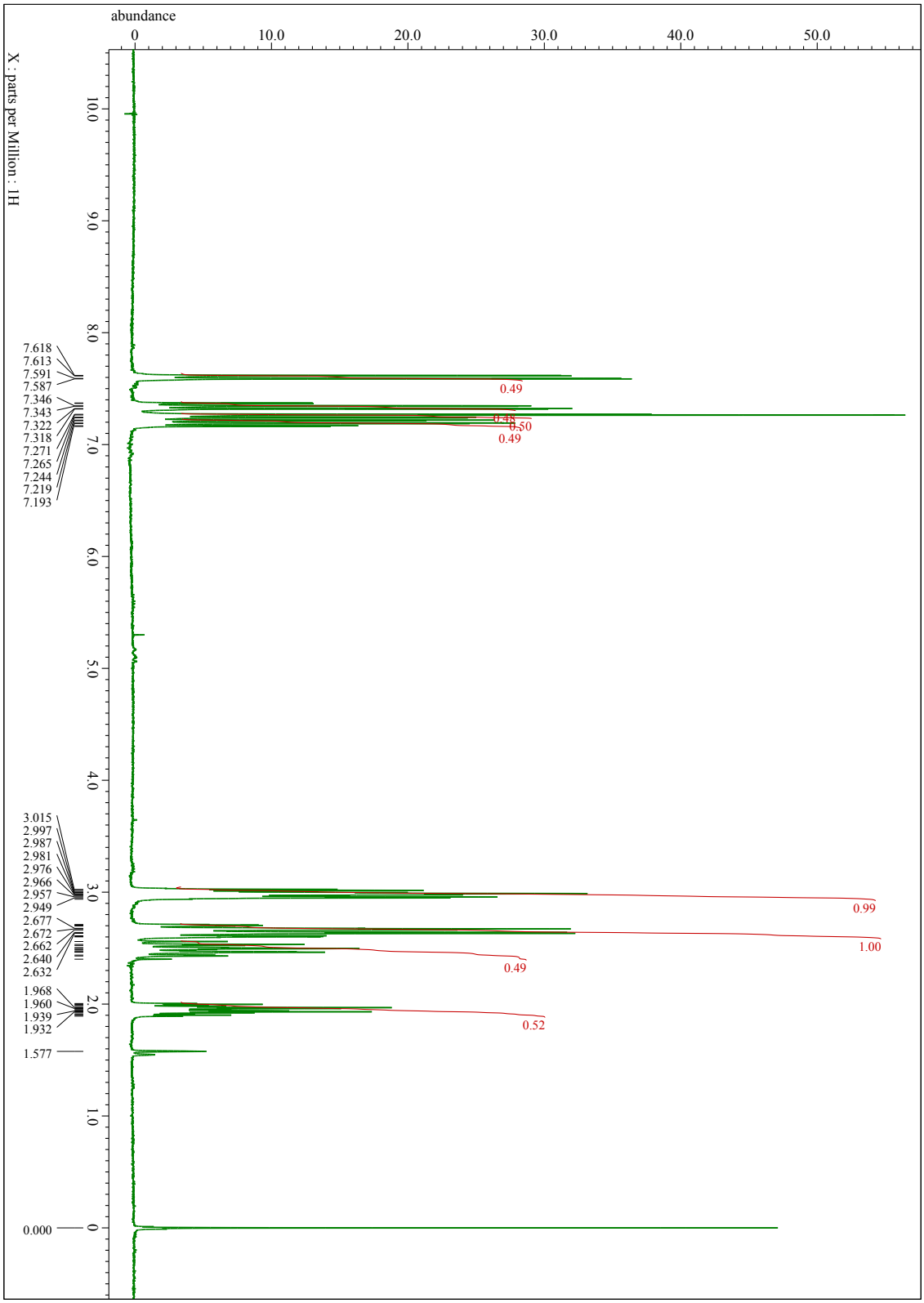


^{13}C NMR spectrum of **4d** ($CDCl_3$, 75 MHz).

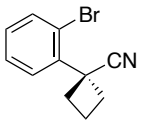


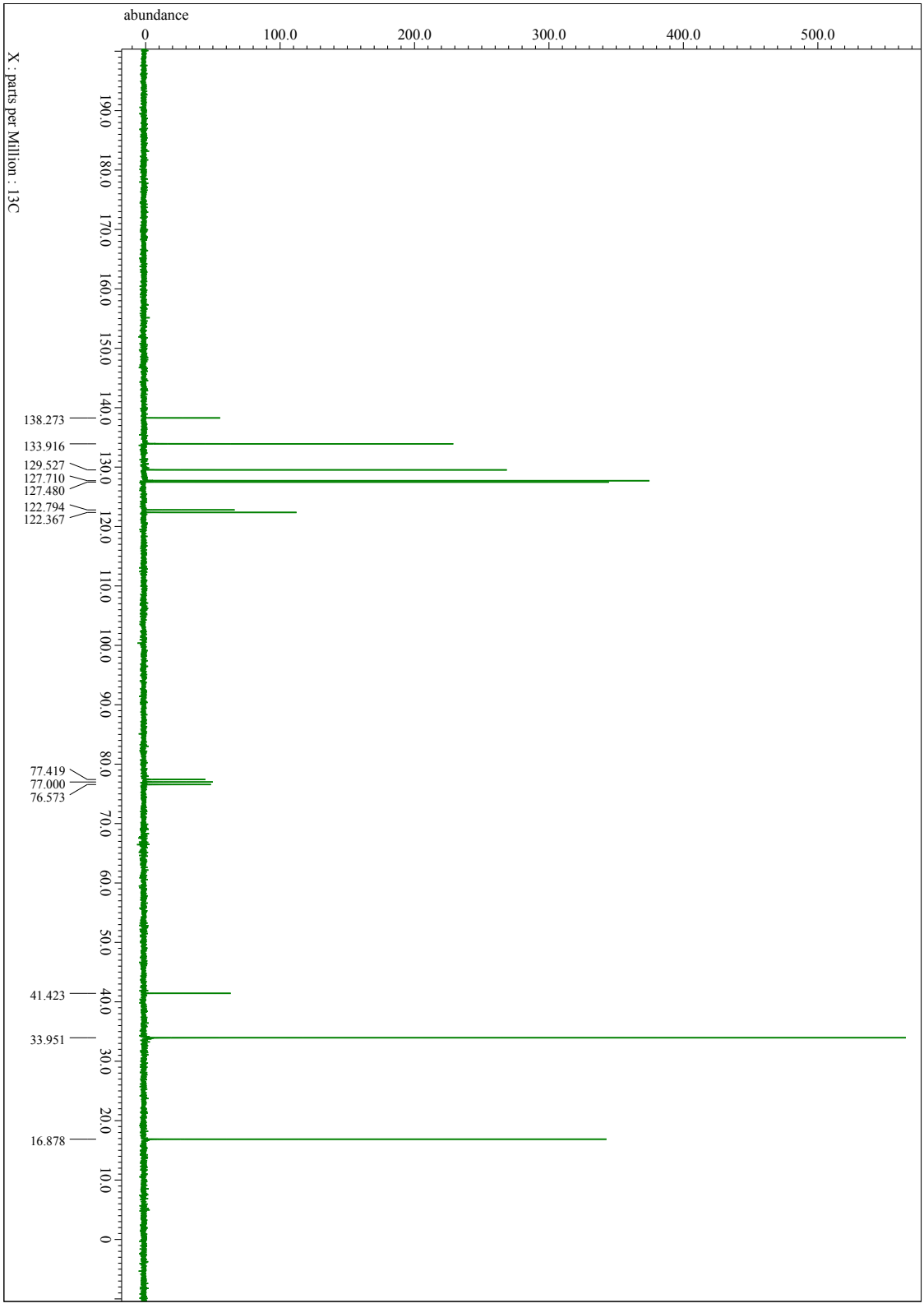
^{1}H NMR spectrum of **s9** ($CDCl_3$, 300 MHz).



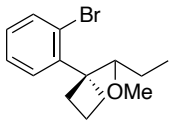


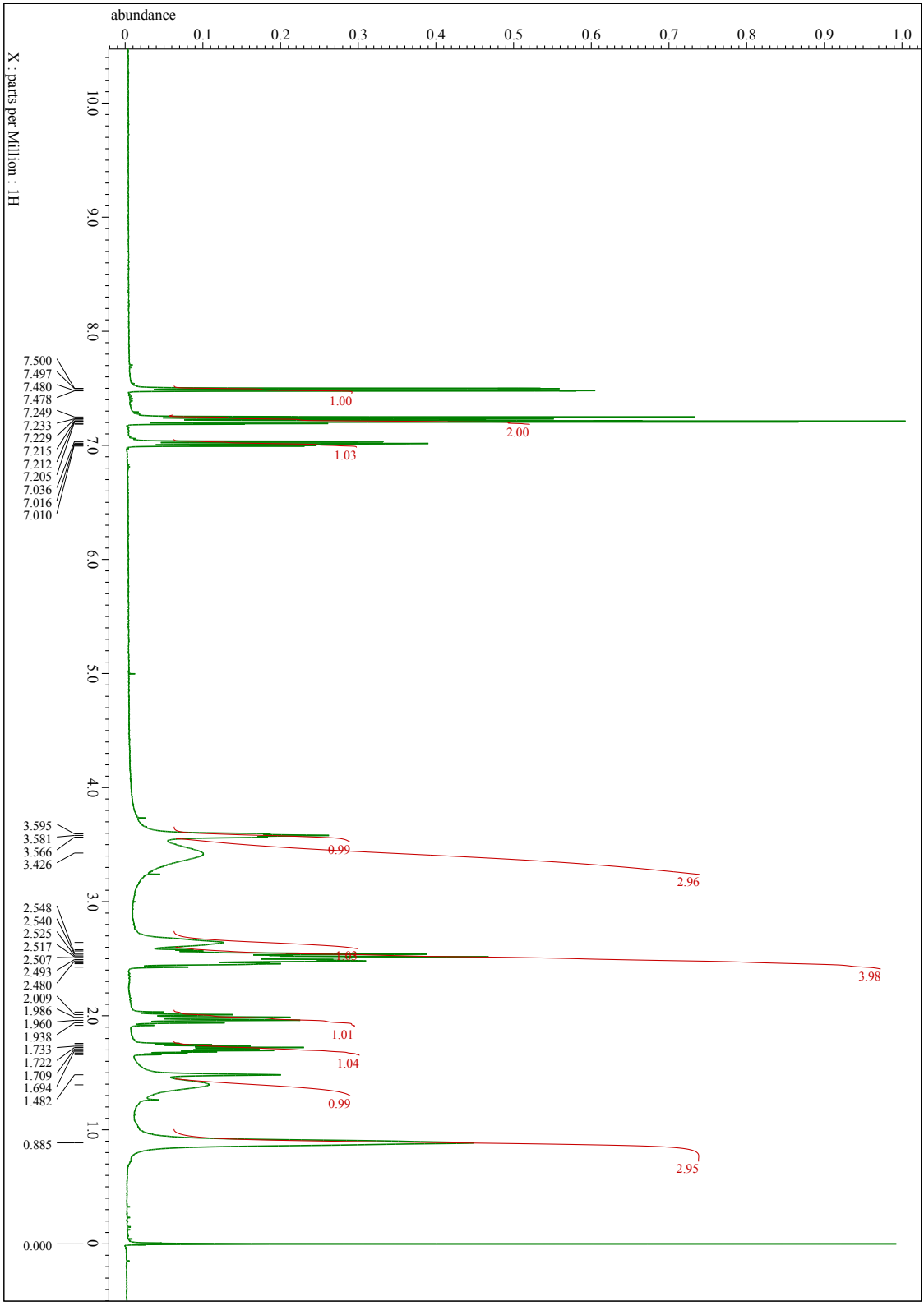
^{13}C NMR spectrum of **s9** ($CDCl_3$, 75 MHz).



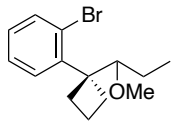


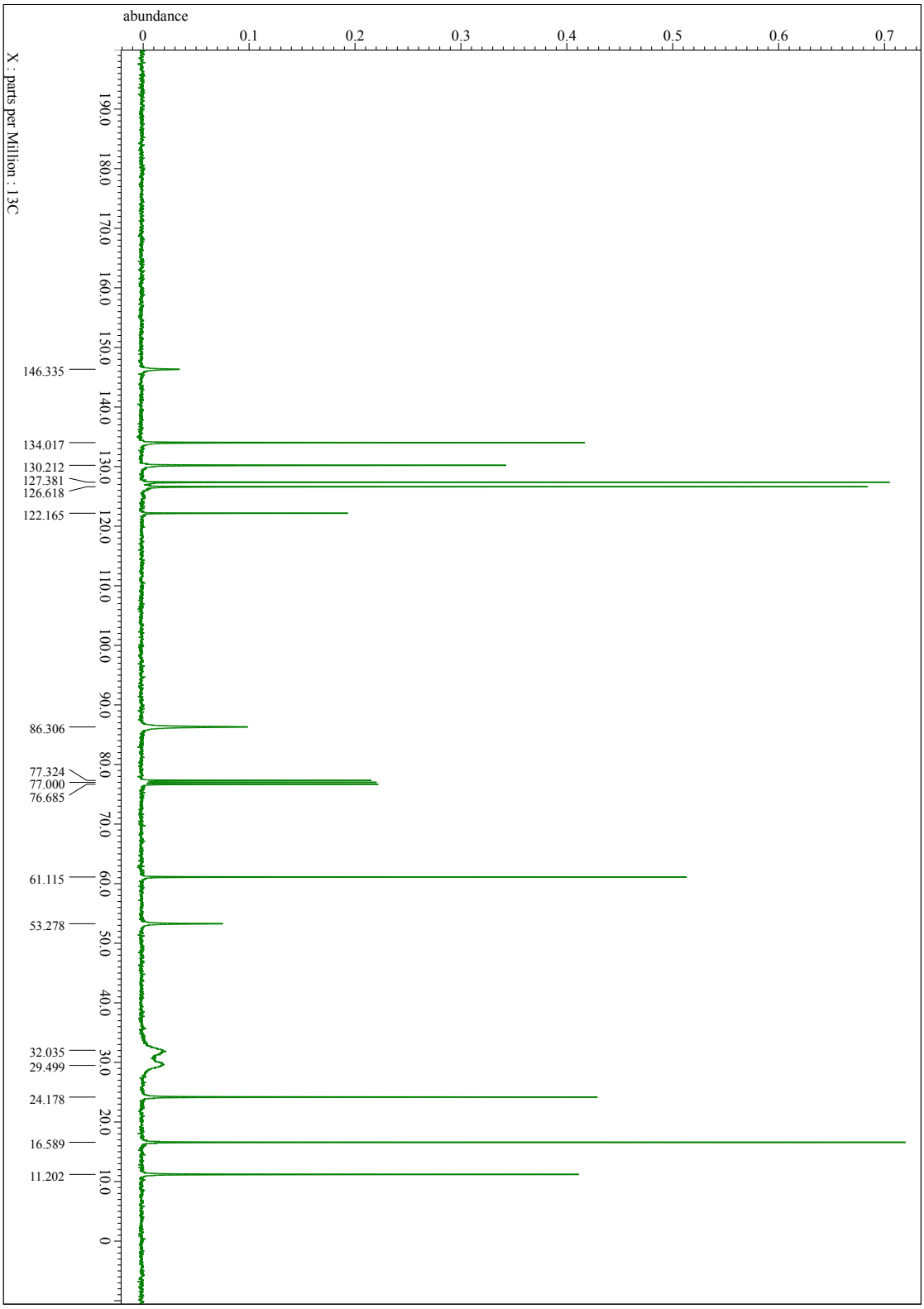
^{1}H NMR spectrum of **s10** ($CDCl_3$, 400 MHz).



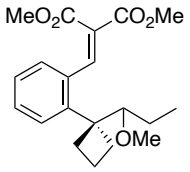


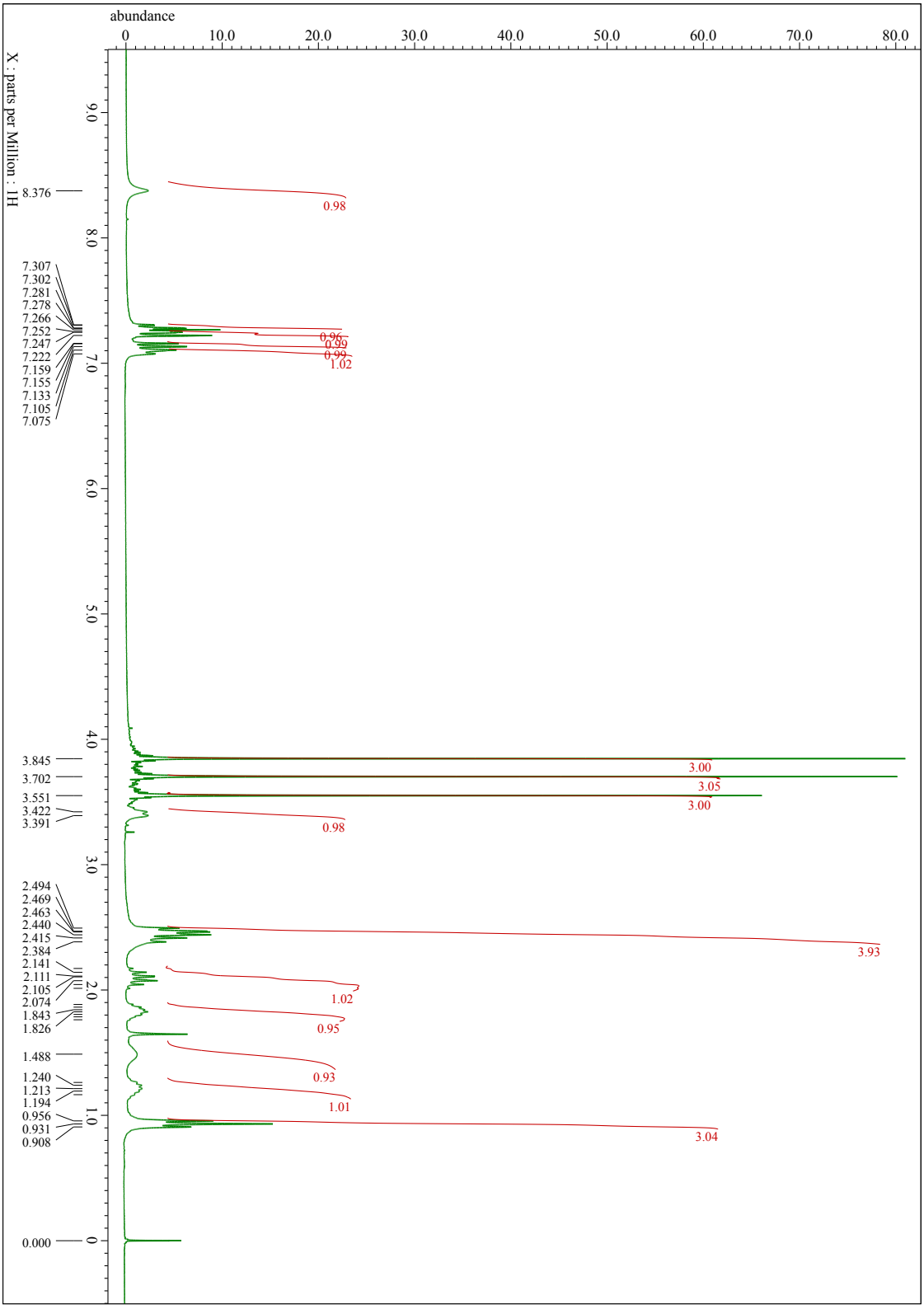
^{13}C NMR spectrum of **s10** ($CDCl_3$, 100 MHz).



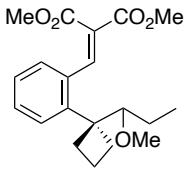


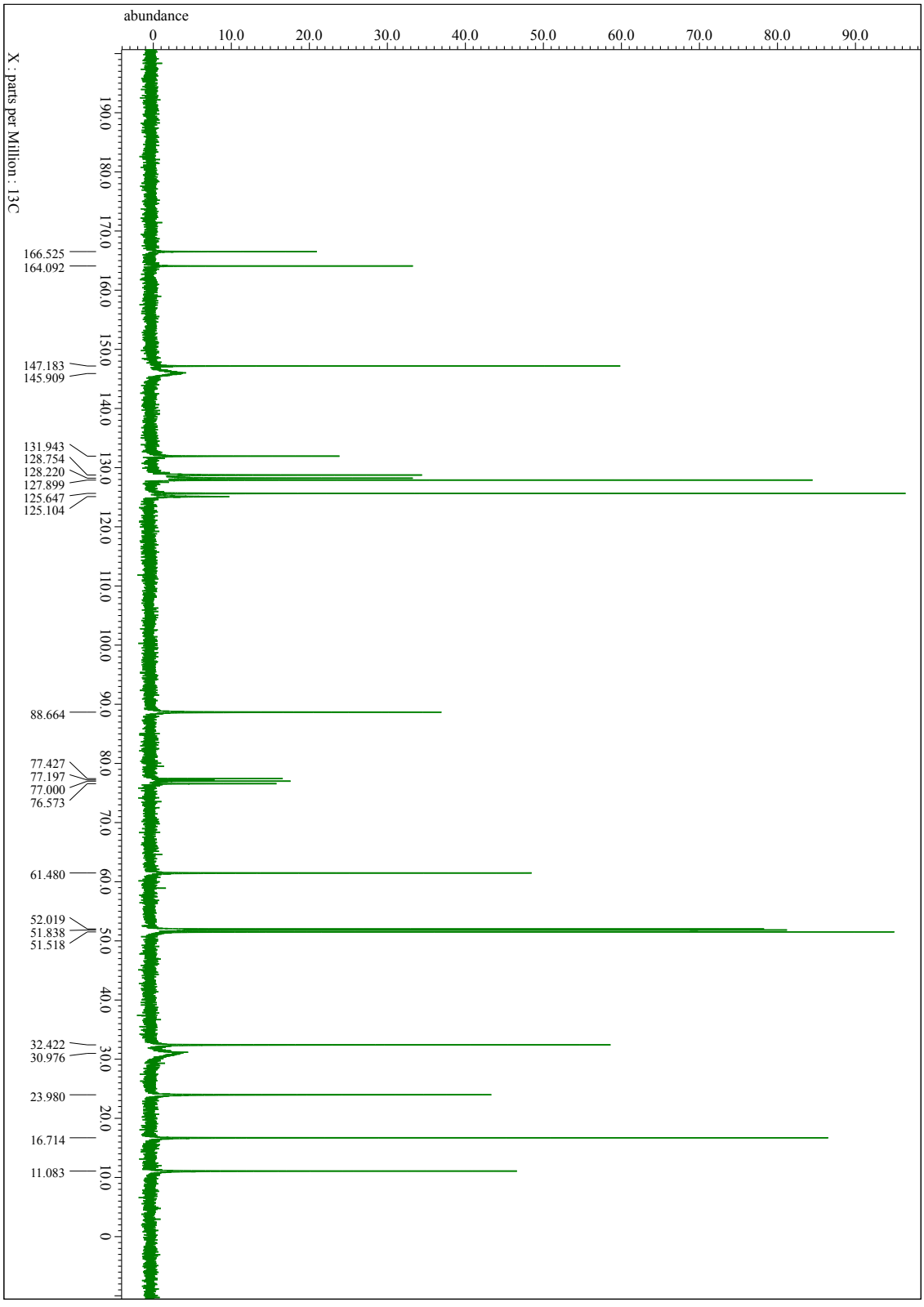
^{1}H NMR spectrum of **4e** ($CDCl_3$, 300 MHz).



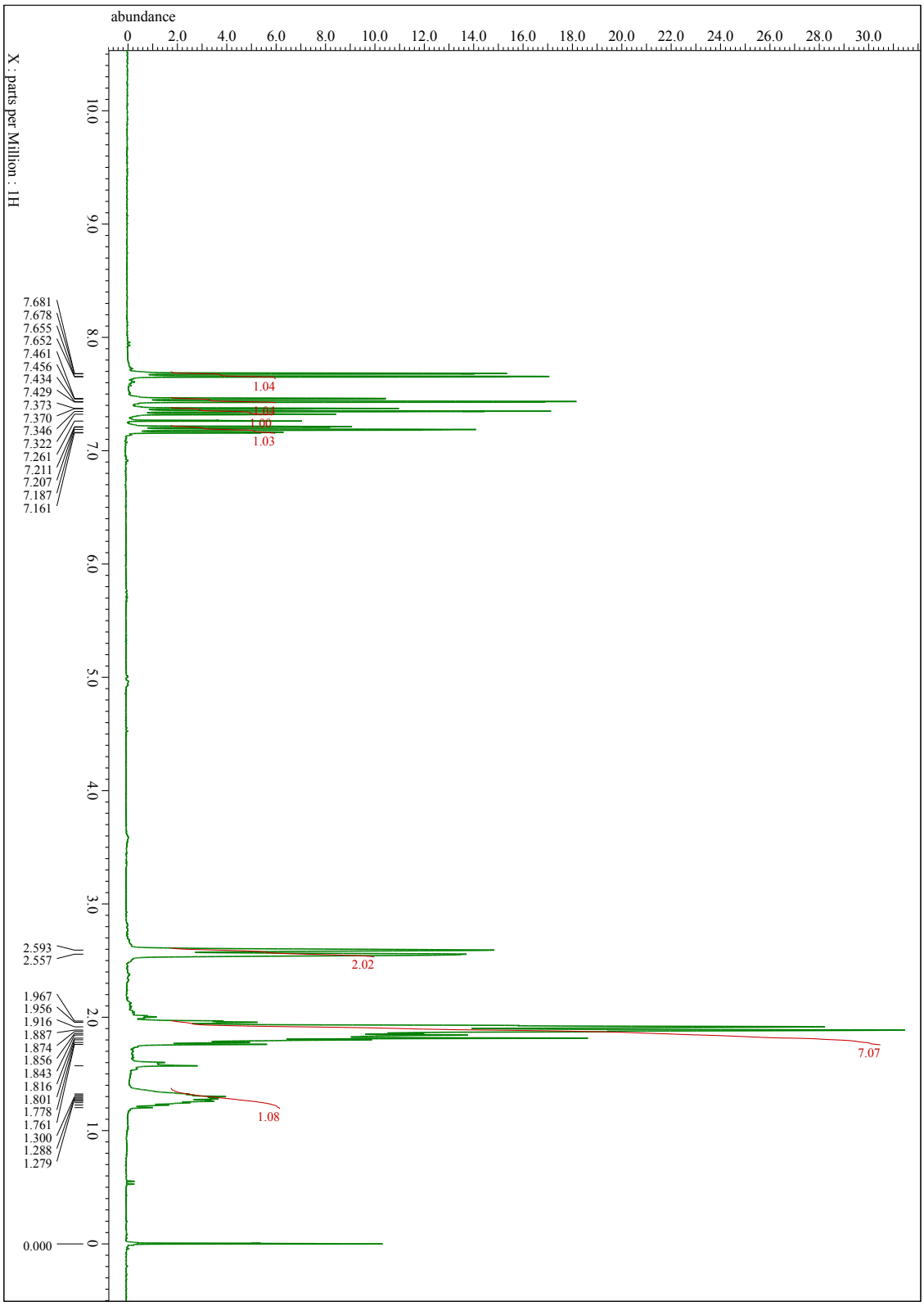


^{13}C NMR spectrum of **4e** ($CDCl_3$, 75 MHz).

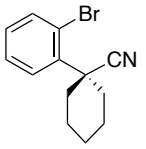


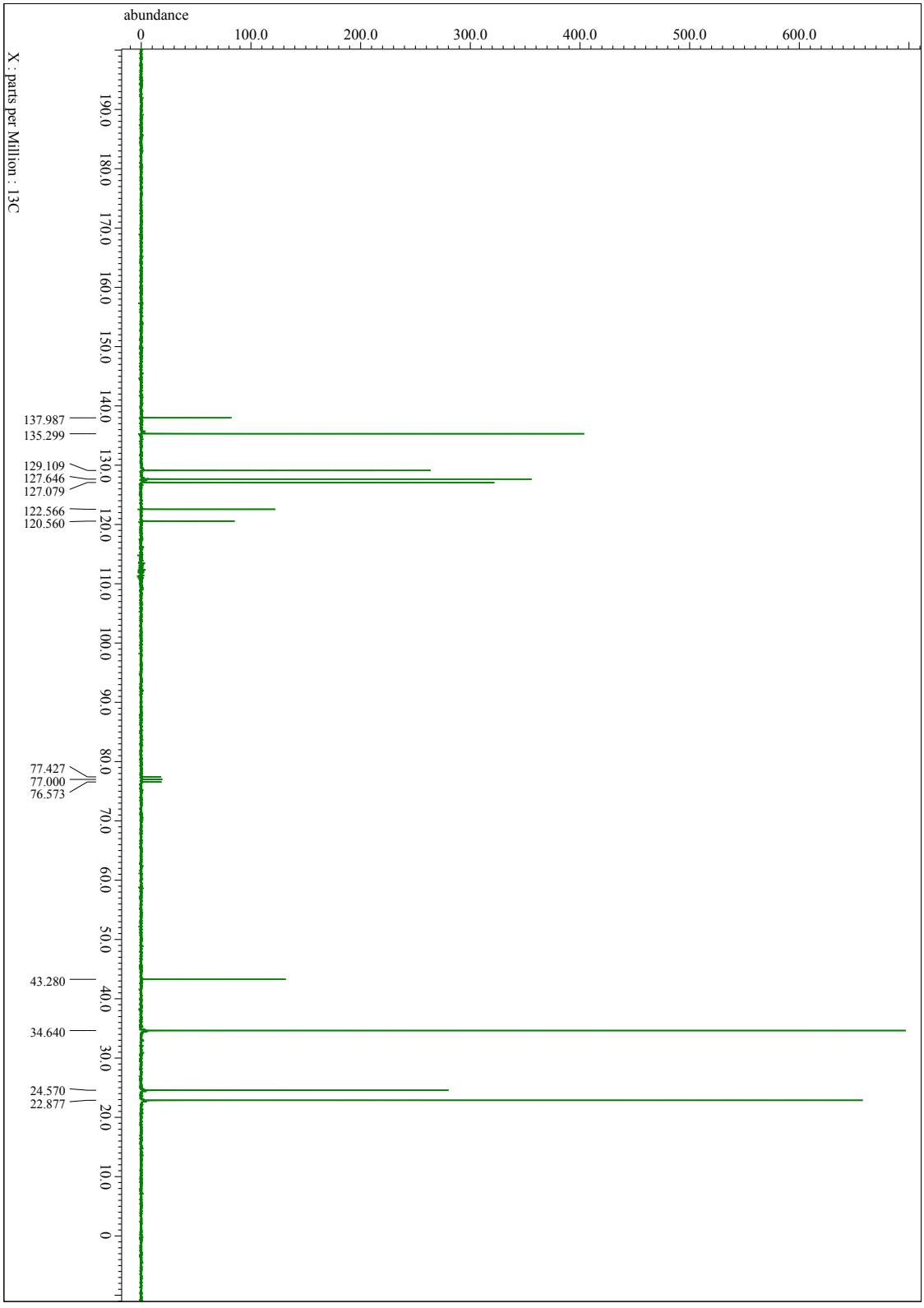


^{1}H NMR spectrum of **s11** ($CDCl_3$, 300 MHz).

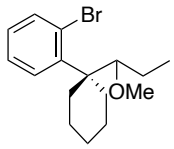


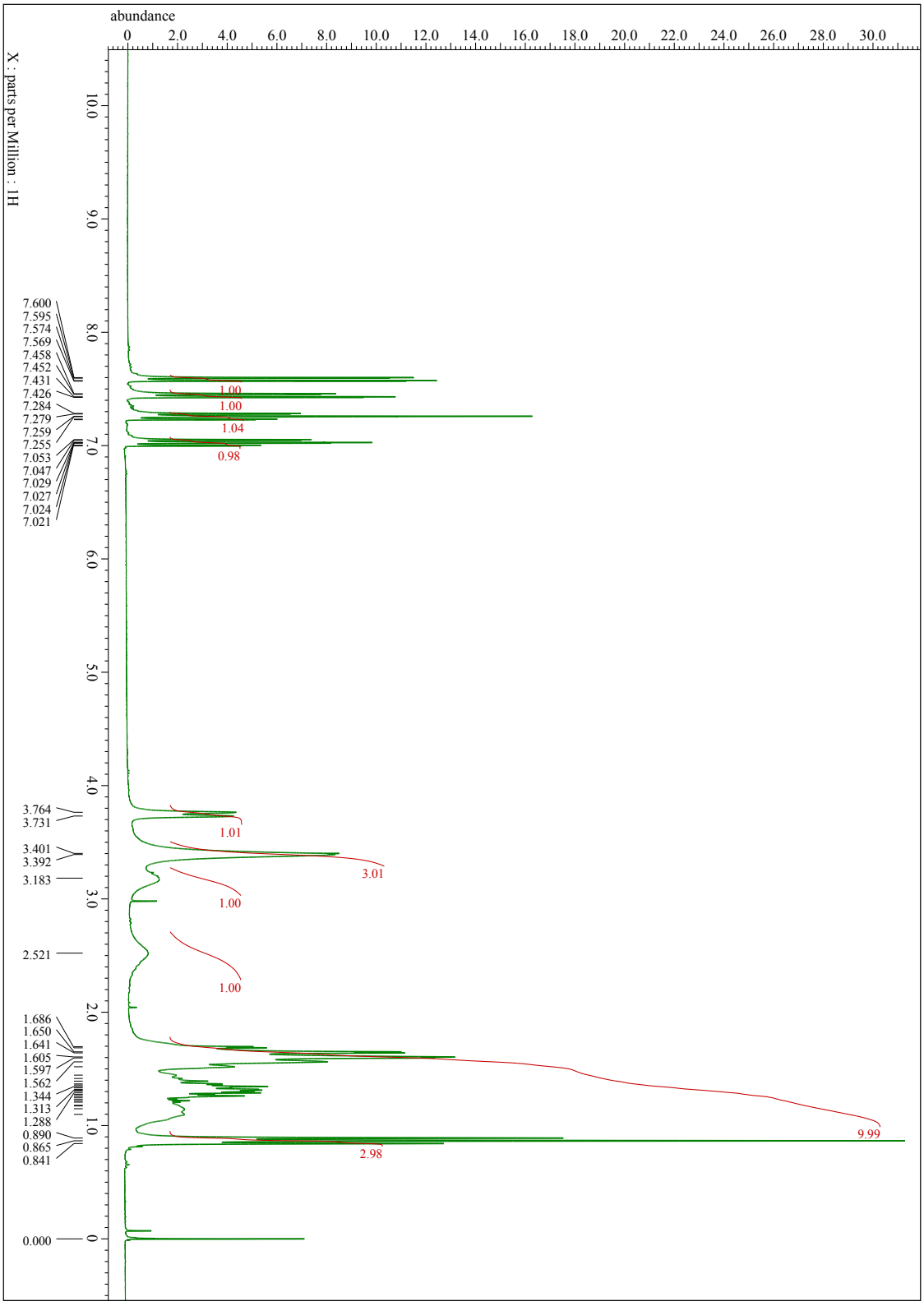
^{13}C NMR spectrum of **s11** ($CDCl_3$, 75 MHz).



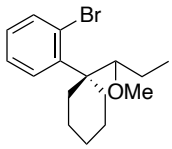


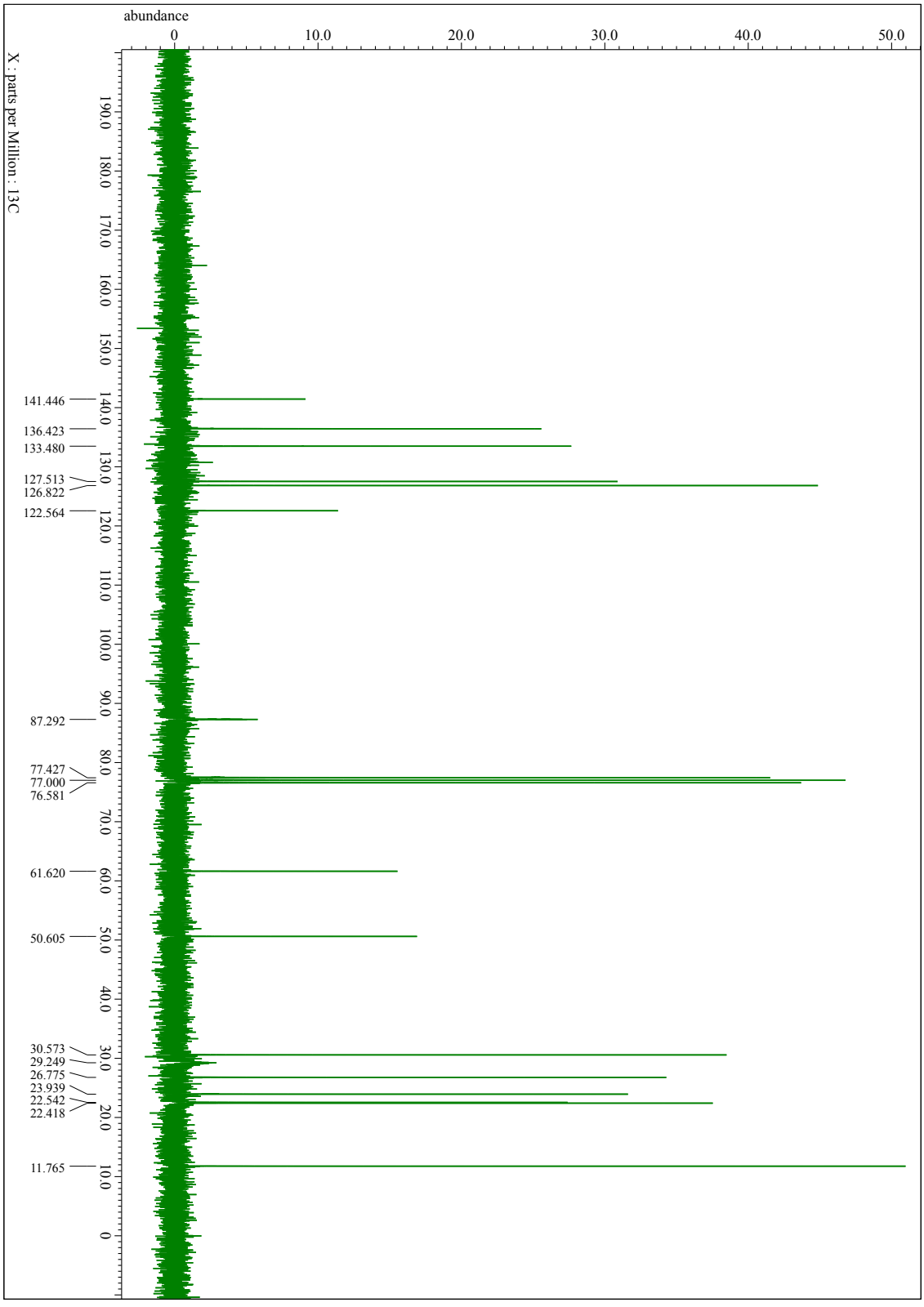
^{1}H NMR spectrum of **s12** ($CDCl_3$, 300 MHz).



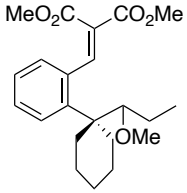


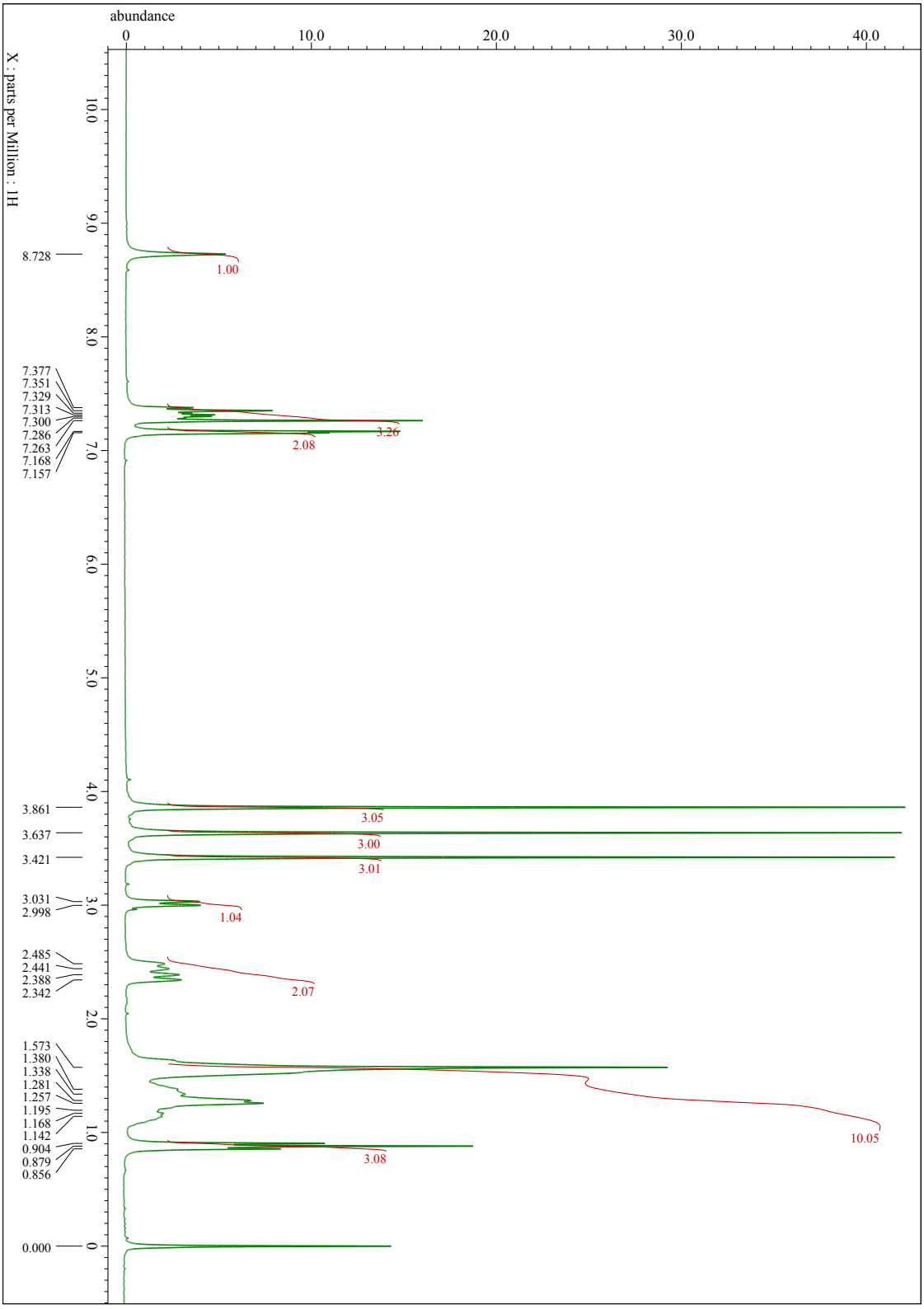
^{13}C NMR spectrum of **s12** ($CDCl_3$, 75 MHz).



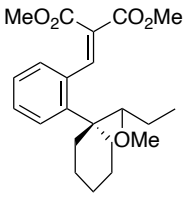


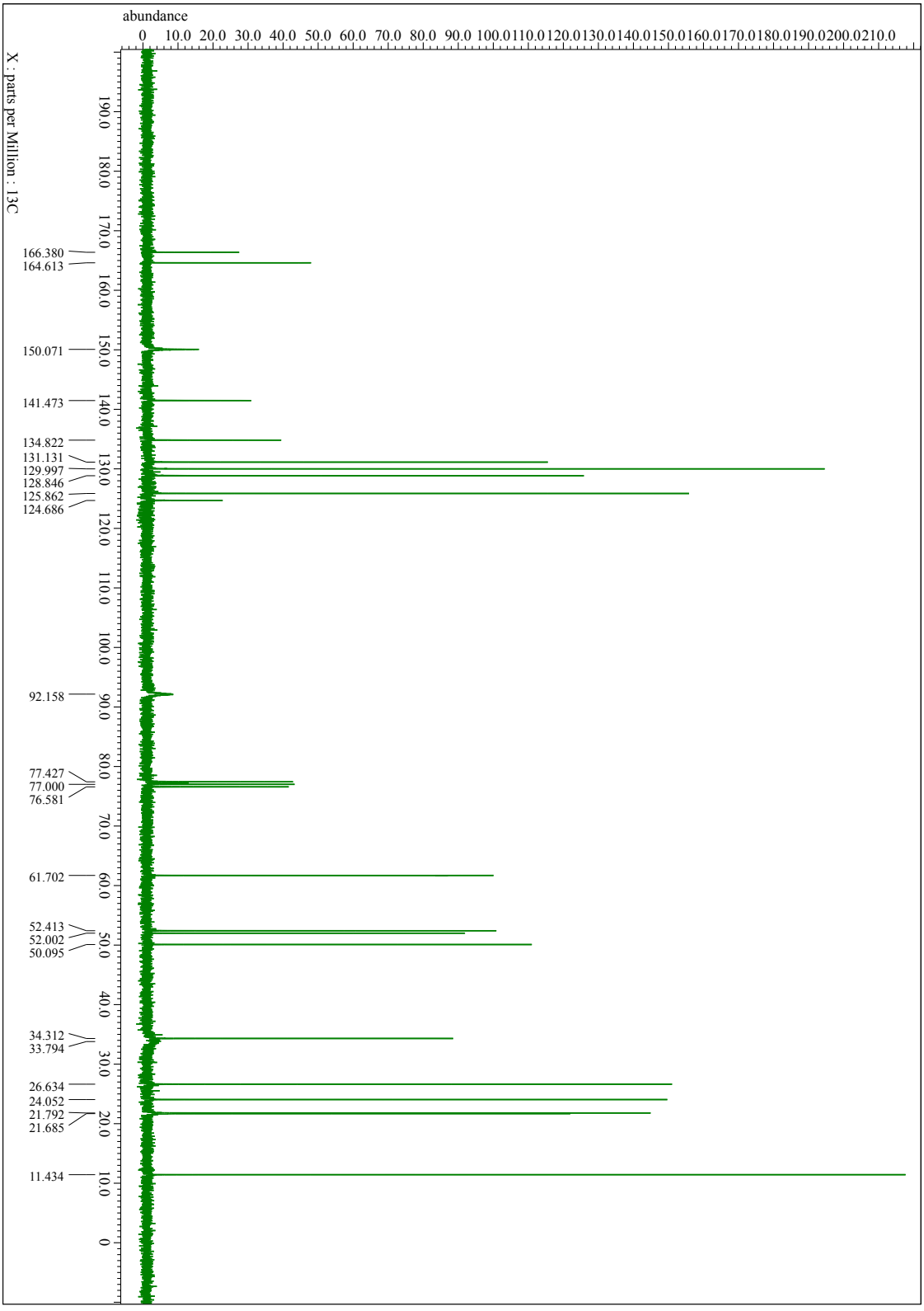
^{1}H NMR spectrum of **4f** ($CDCl_3$, 300 MHz).



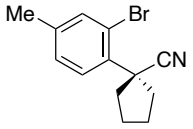


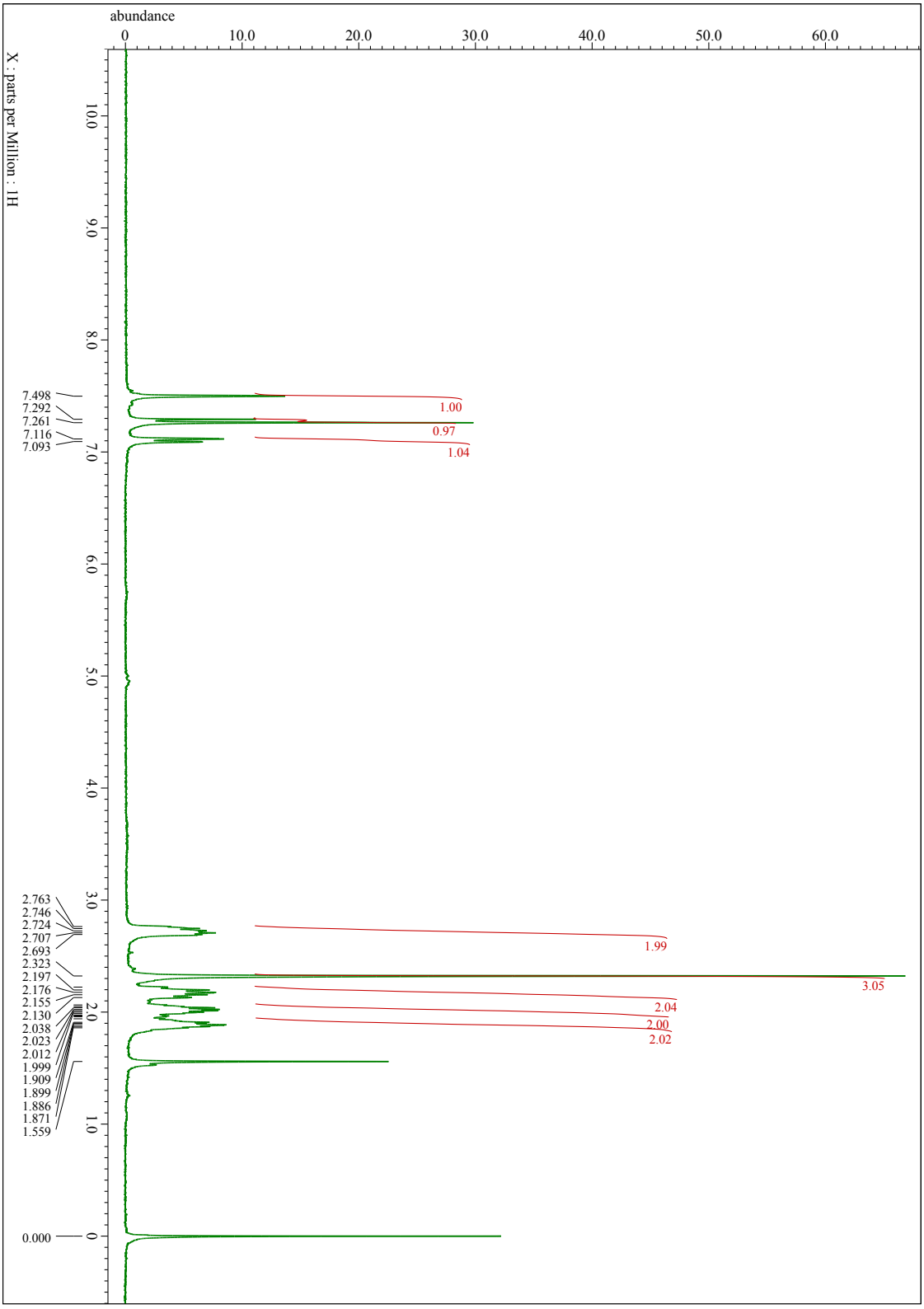
^{13}C NMR spectrum of **4f** ($CDCl_3$, 75 MHz).



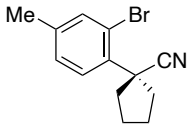


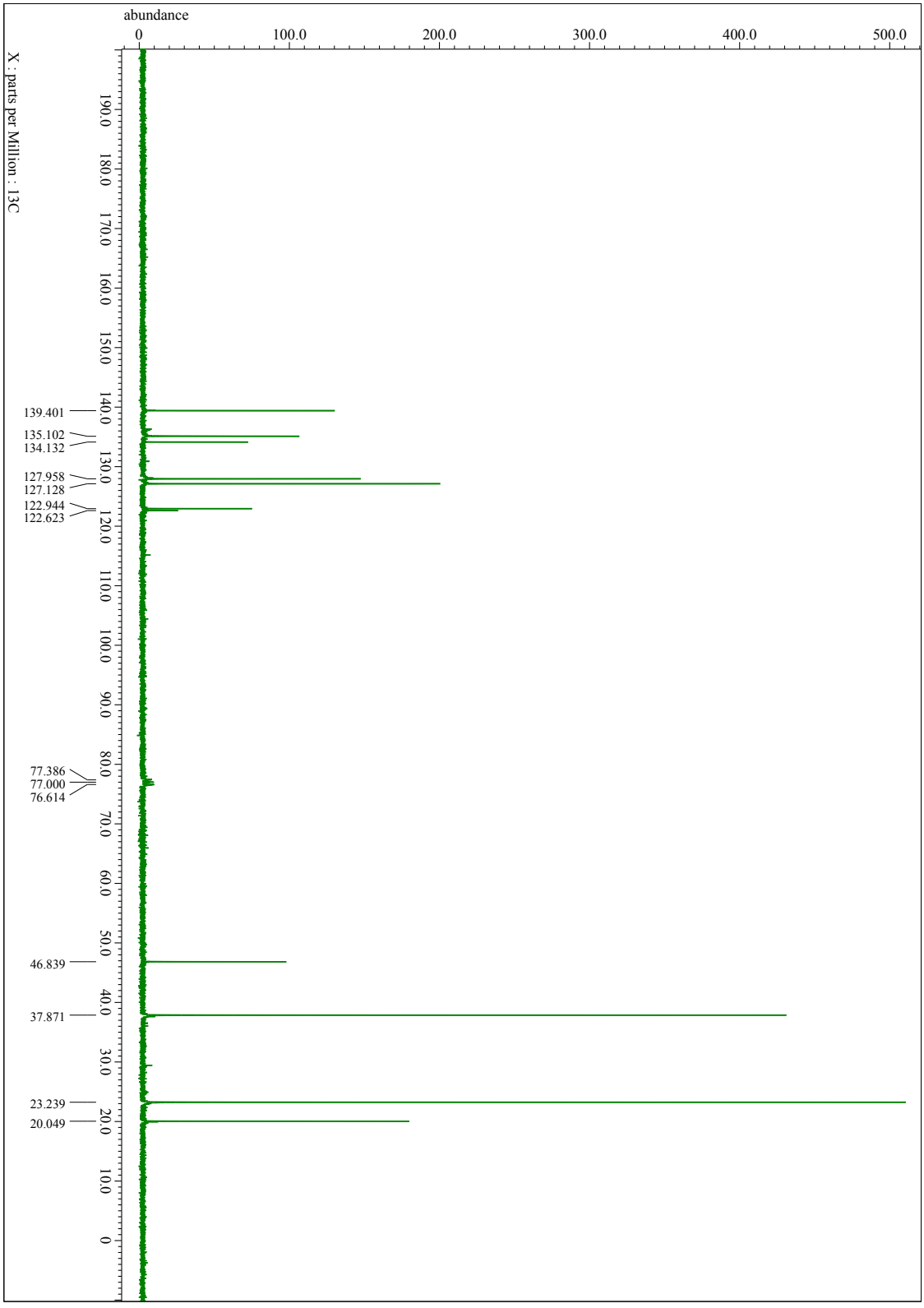
^{1}H NMR spectrum of **s13** ($CDCl_3$, 300 MHz).



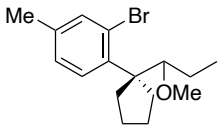


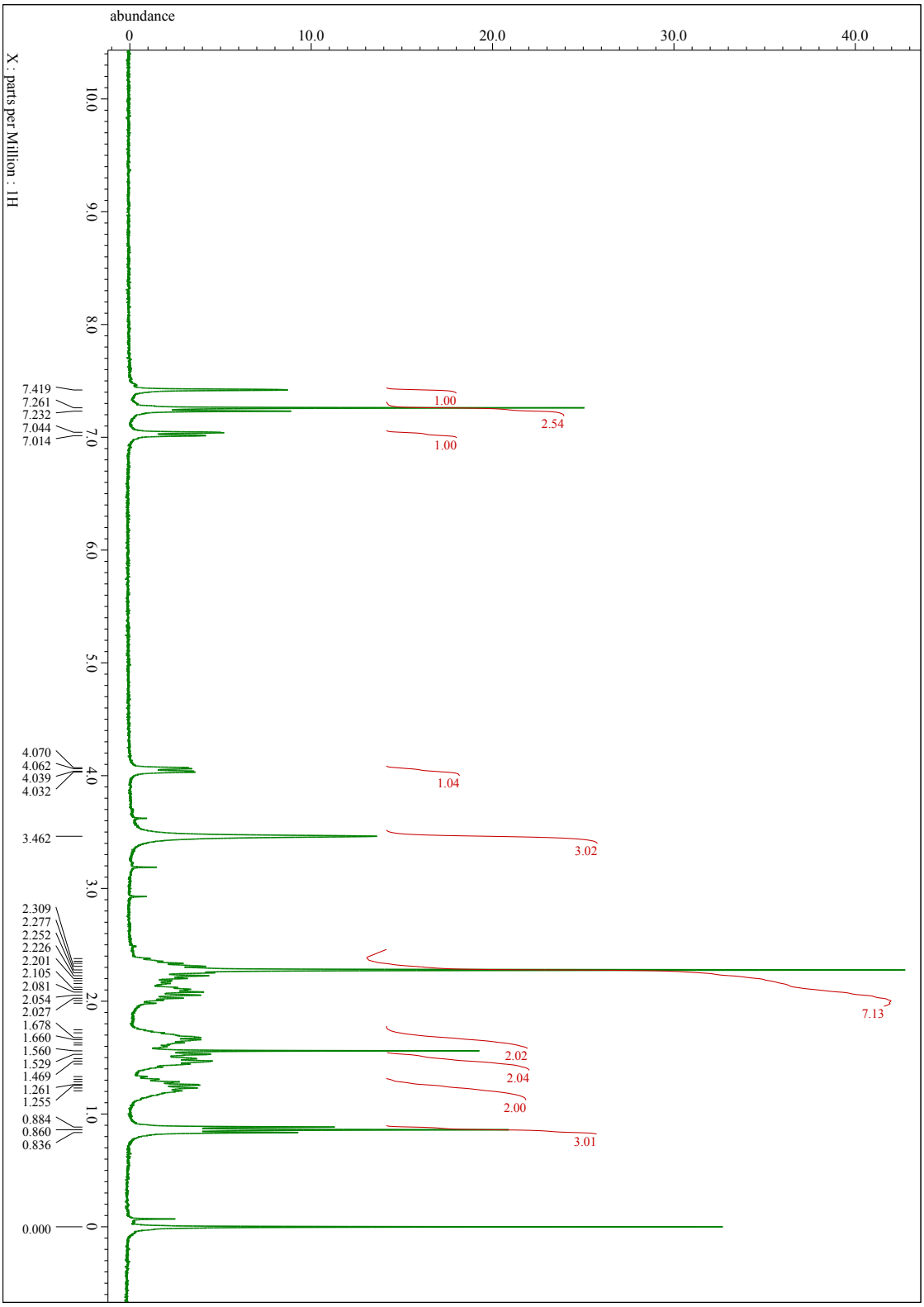
^{13}C NMR spectrum of **s13** ($CDCl_3$, 75 MHz).



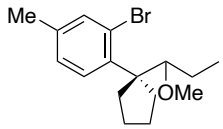


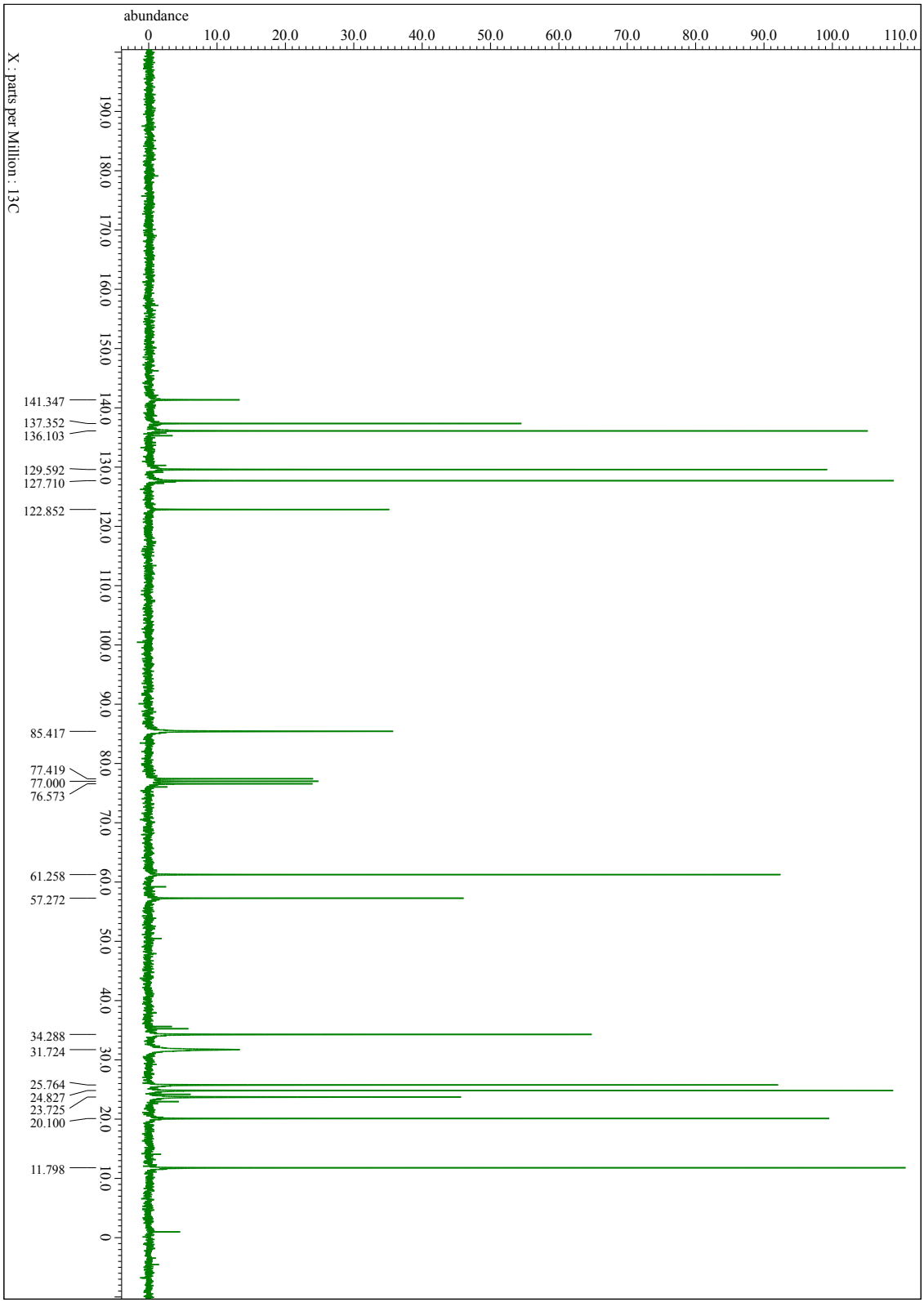
^{1}H NMR spectrum of **s14** ($CDCl_3$, 300 MHz).



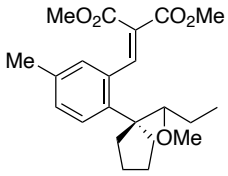


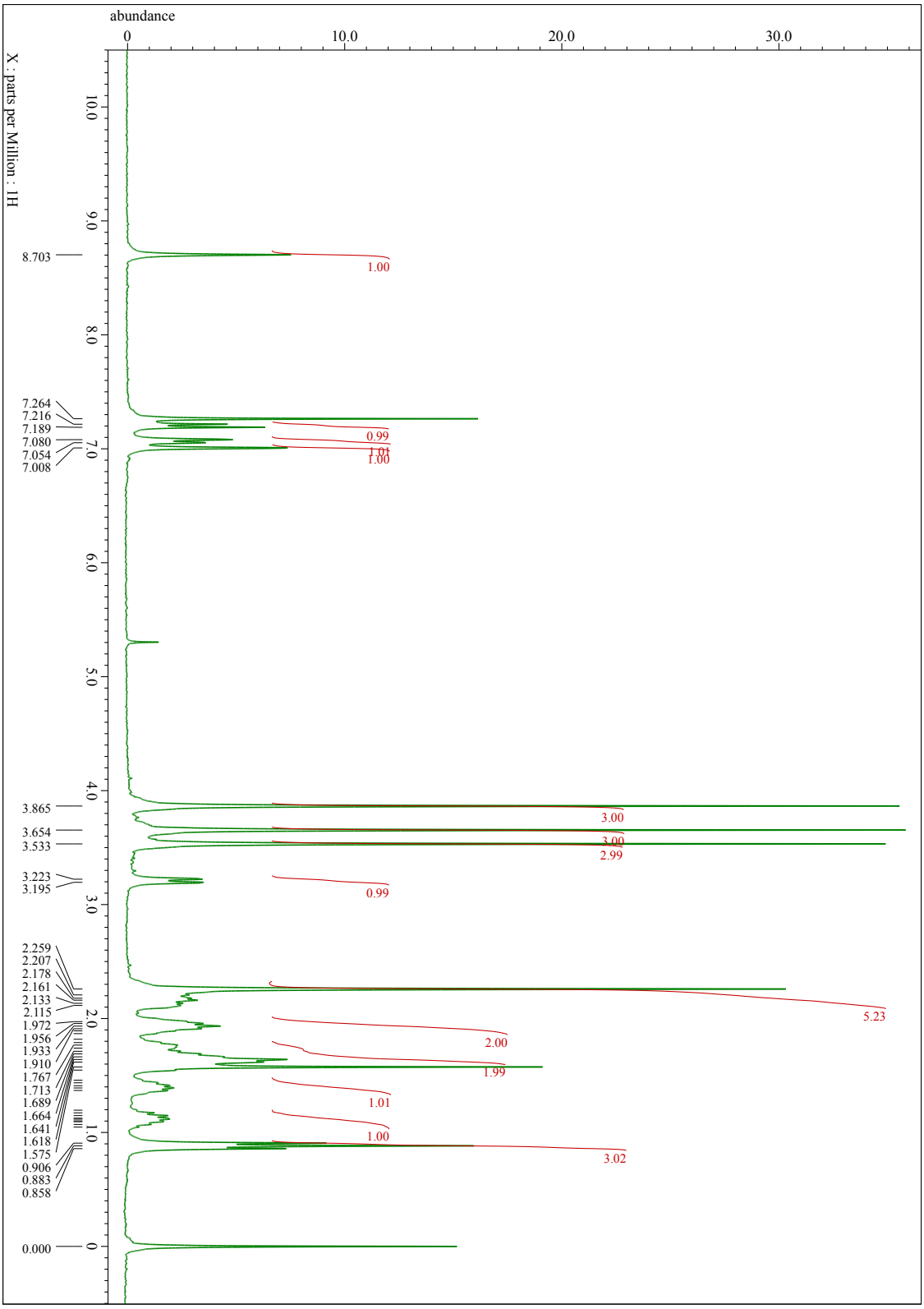
^{13}C NMR spectrum of **s14** ($CDCl_3$, 75 MHz).



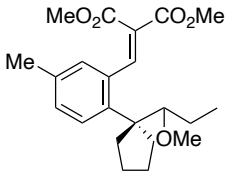


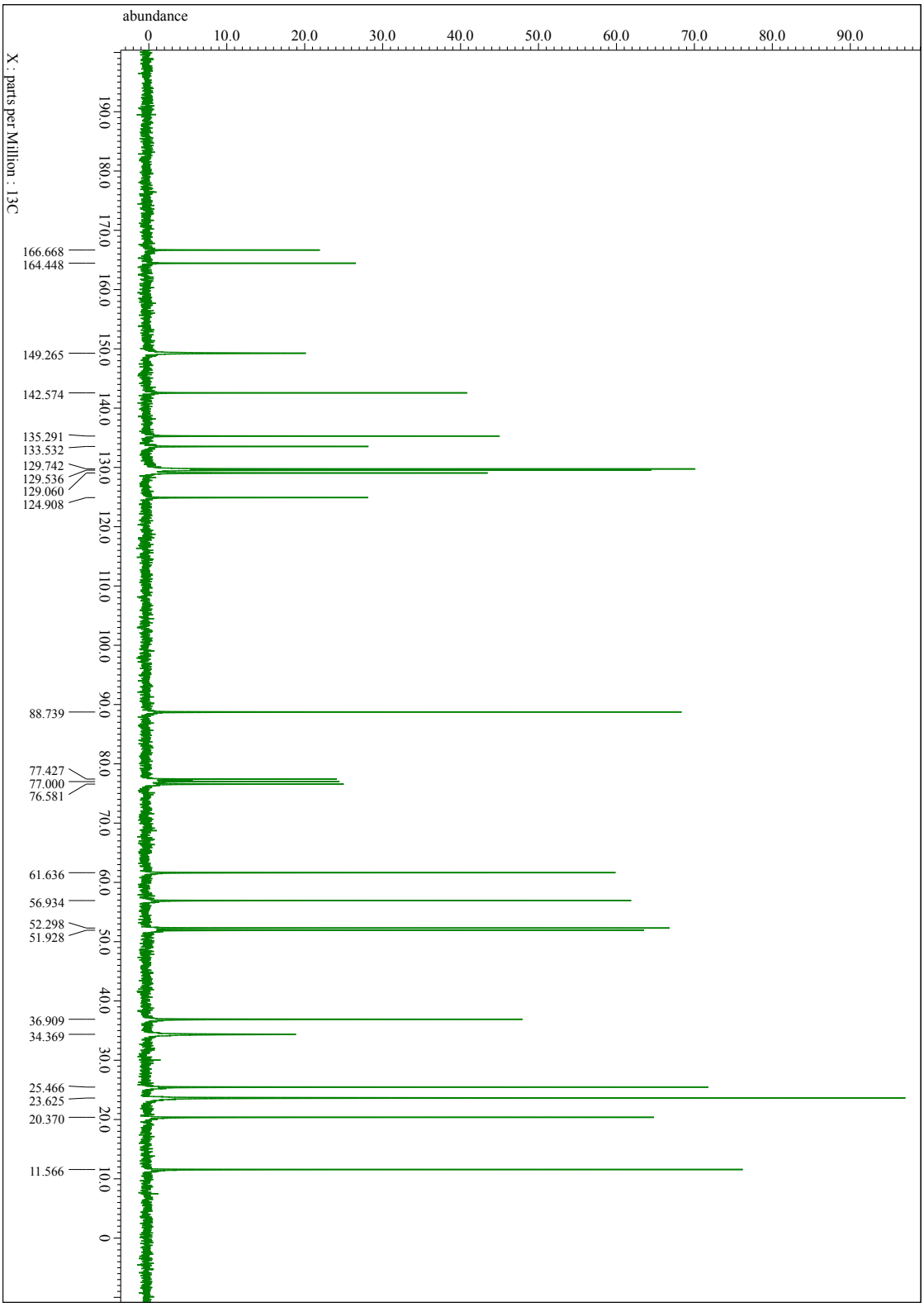
^{1}H NMR spectrum of **4g** ($CDCl_3$, 300 MHz).



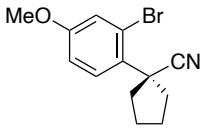


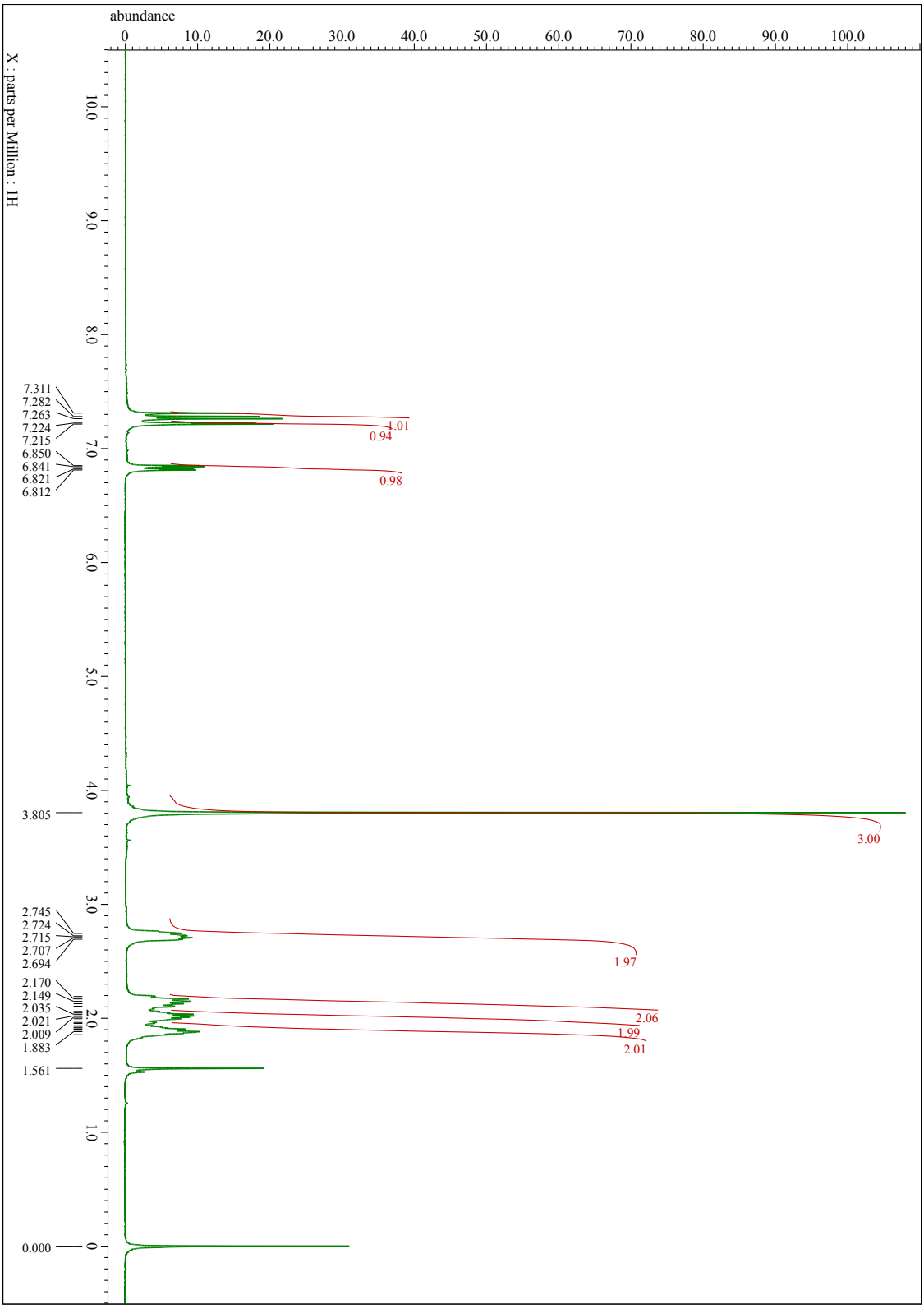
^{13}C NMR spectrum of **4g** ($CDCl_3$, 75 MHz).



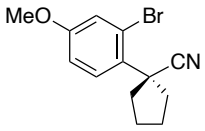


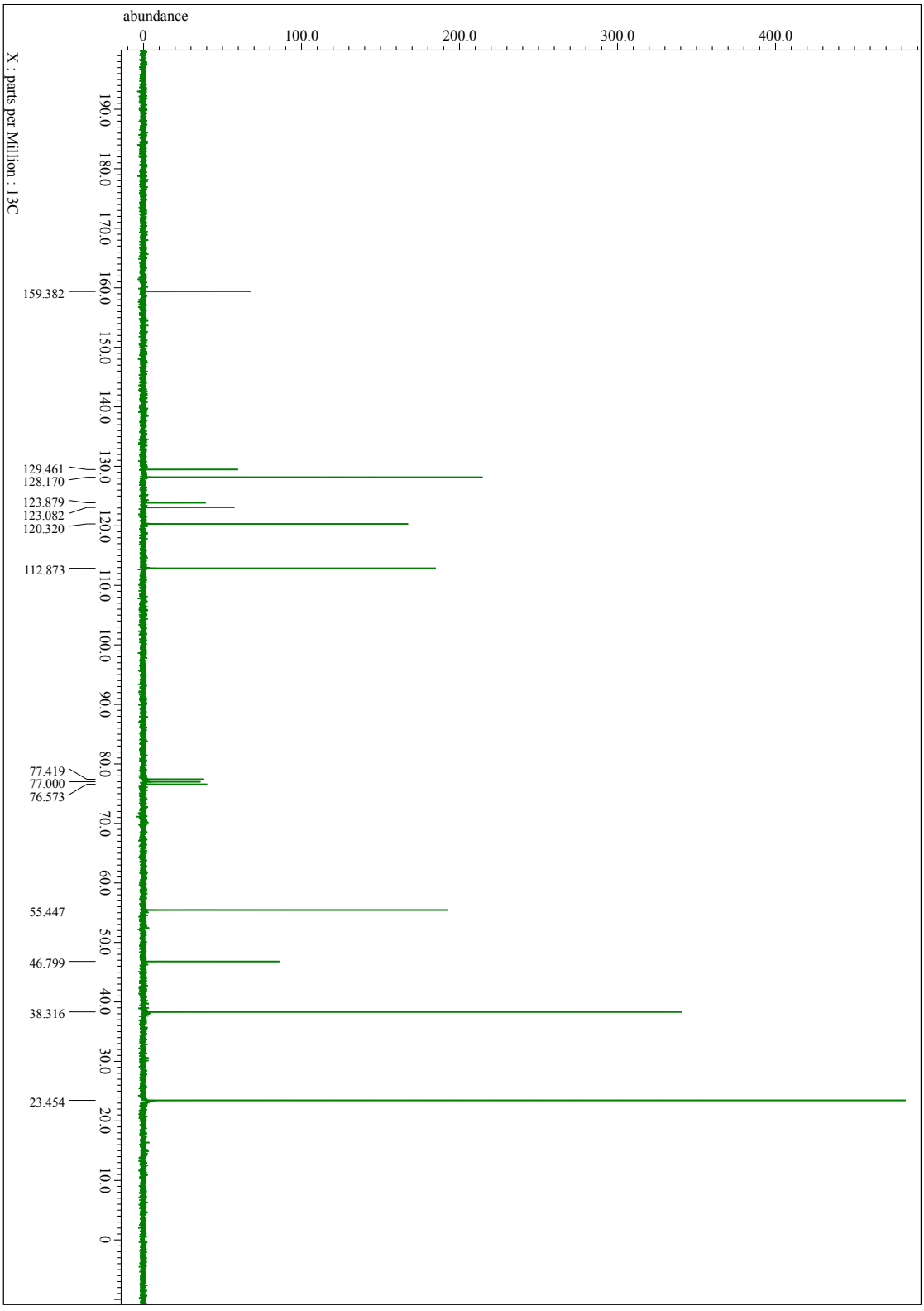
^{1}H NMR spectrum of **s15** ($CDCl_3$, 300 MHz).



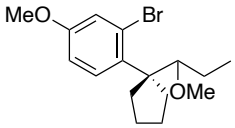


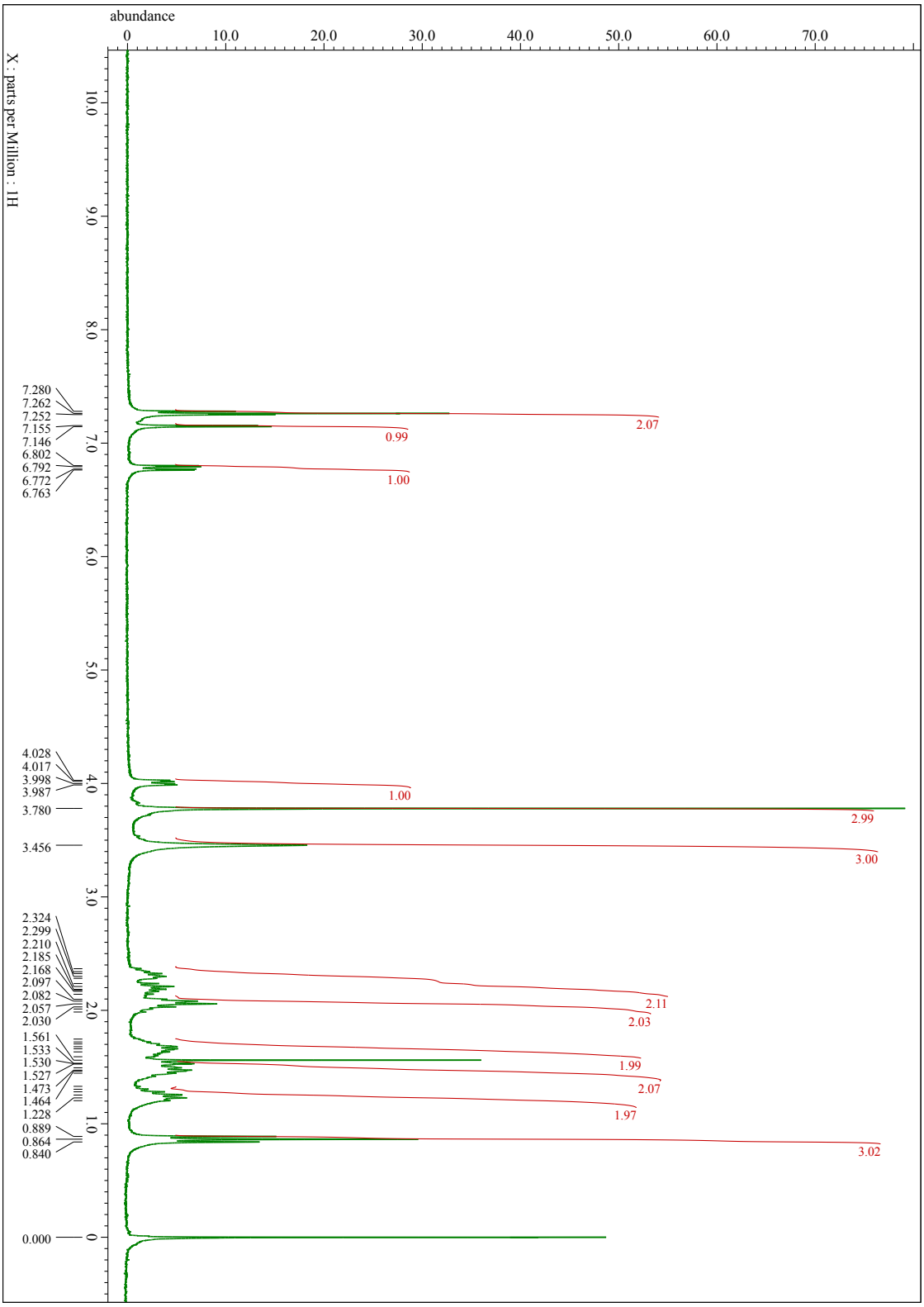
^{13}C NMR spectrum of **s15** ($CDCl_3$, 75 MHz).



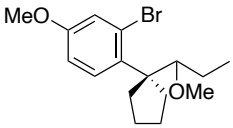


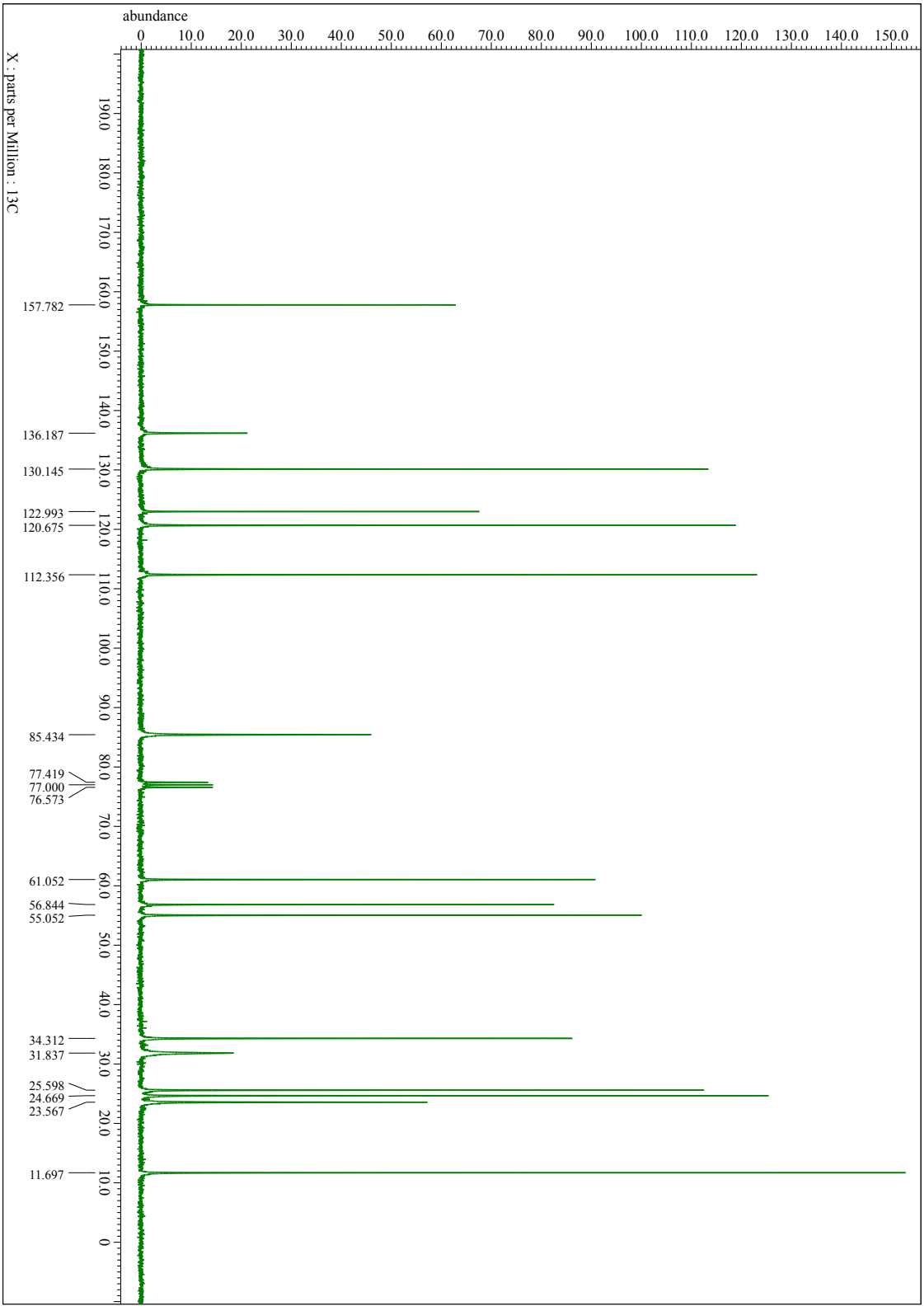
^{1}H NMR spectrum of **s16** ($CDCl_3$, 300 MHz).



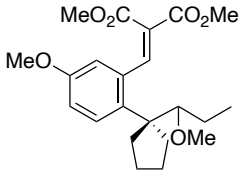


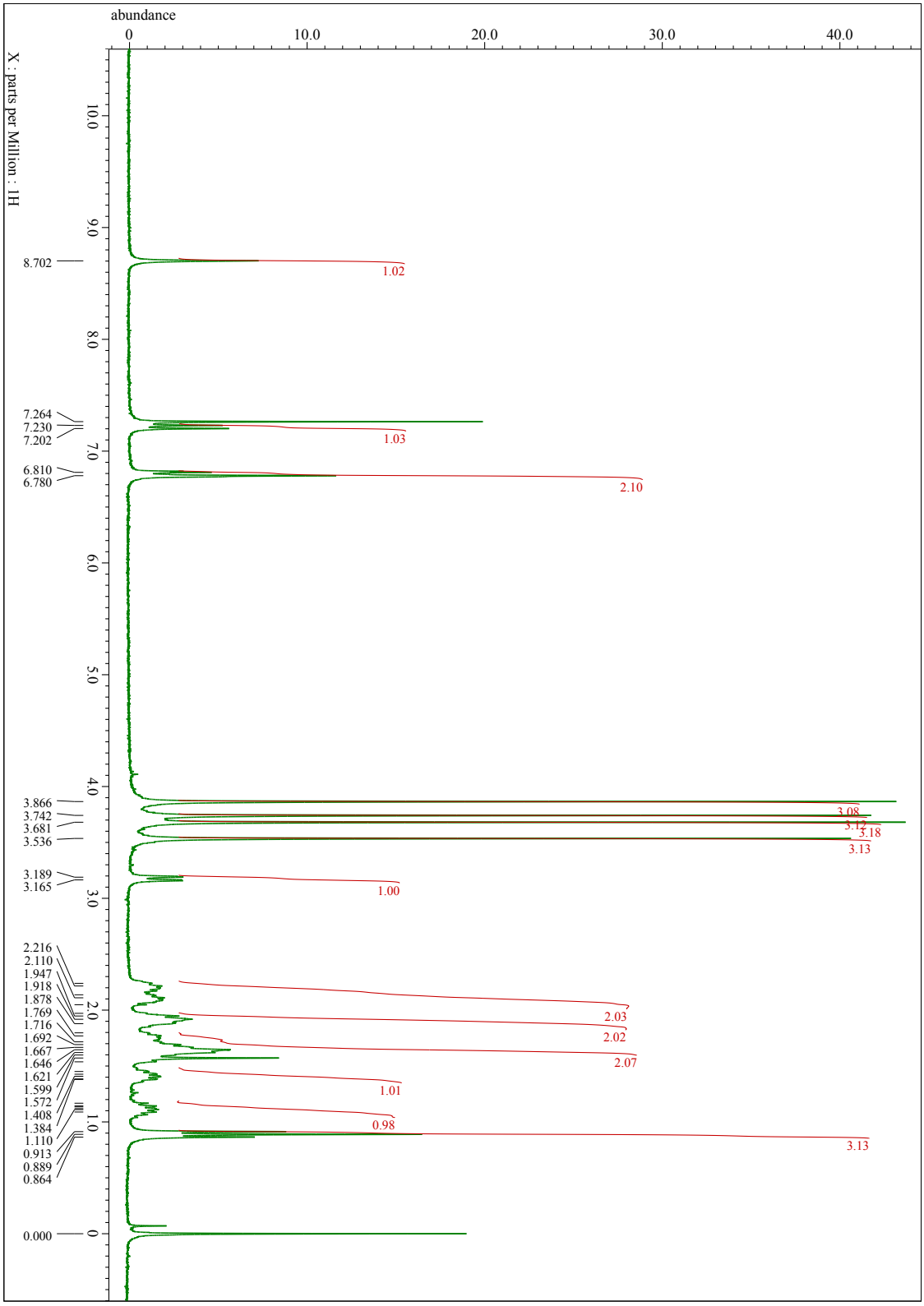
^{13}C NMR spectrum of **s16** ($CDCl_3$, 75 MHz).



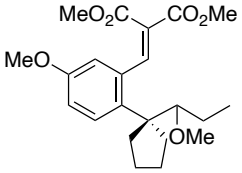


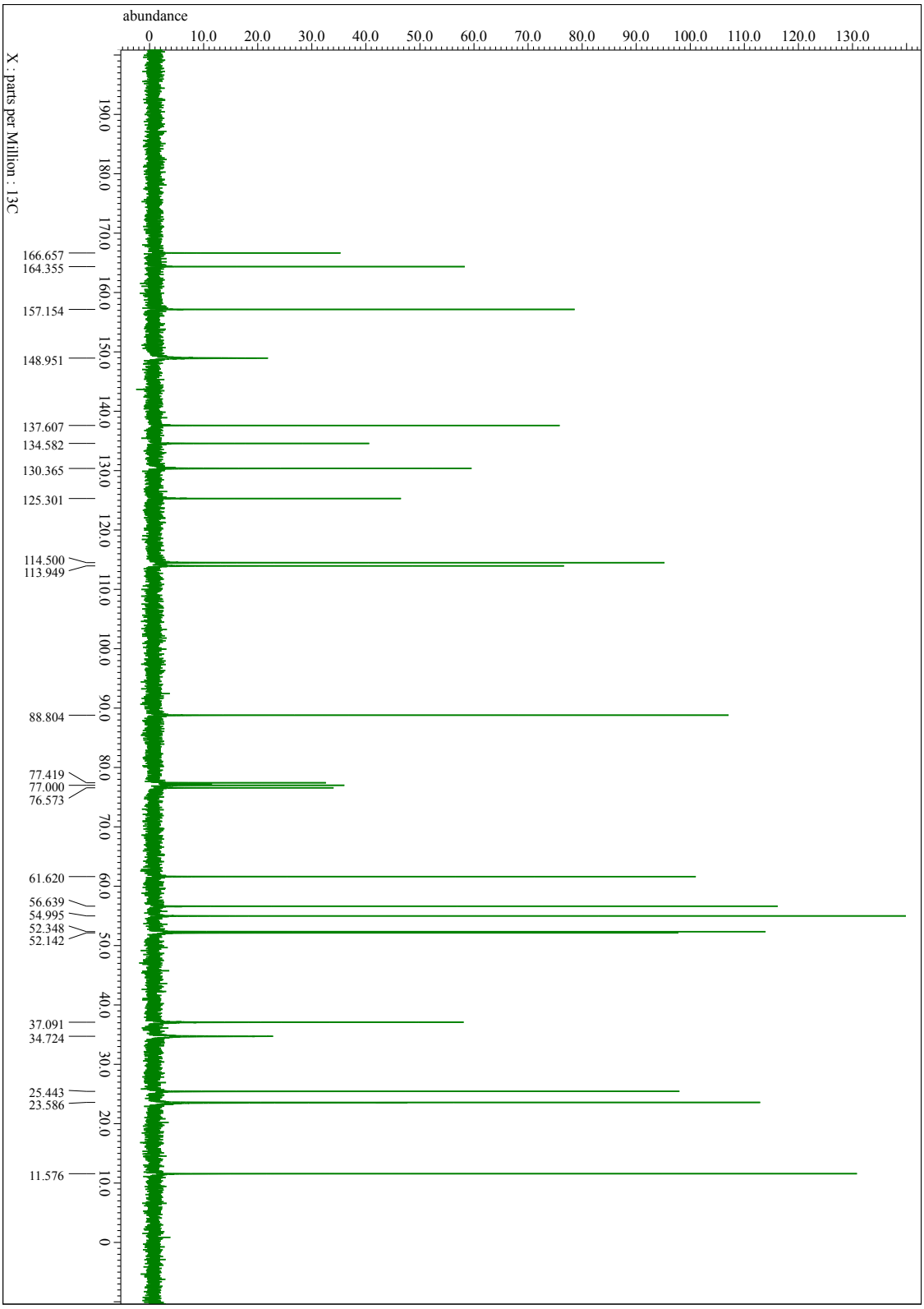
^{1}H NMR spectrum of **4h** ($CDCl_3$, 300 MHz).



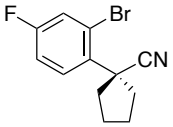


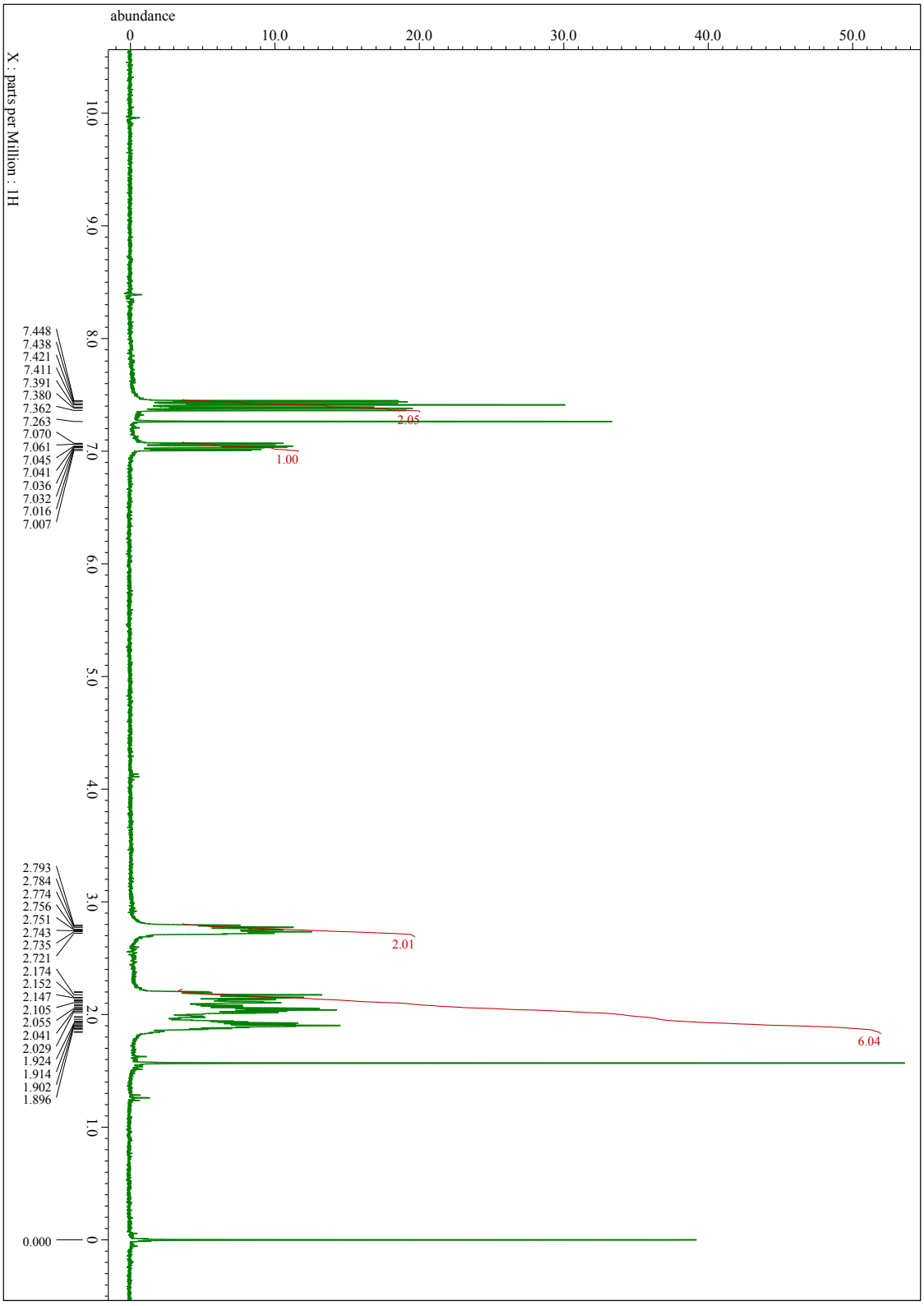
^{13}C NMR spectrum of **4h** ($CDCl_3$, 75 MHz).



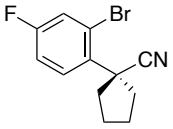


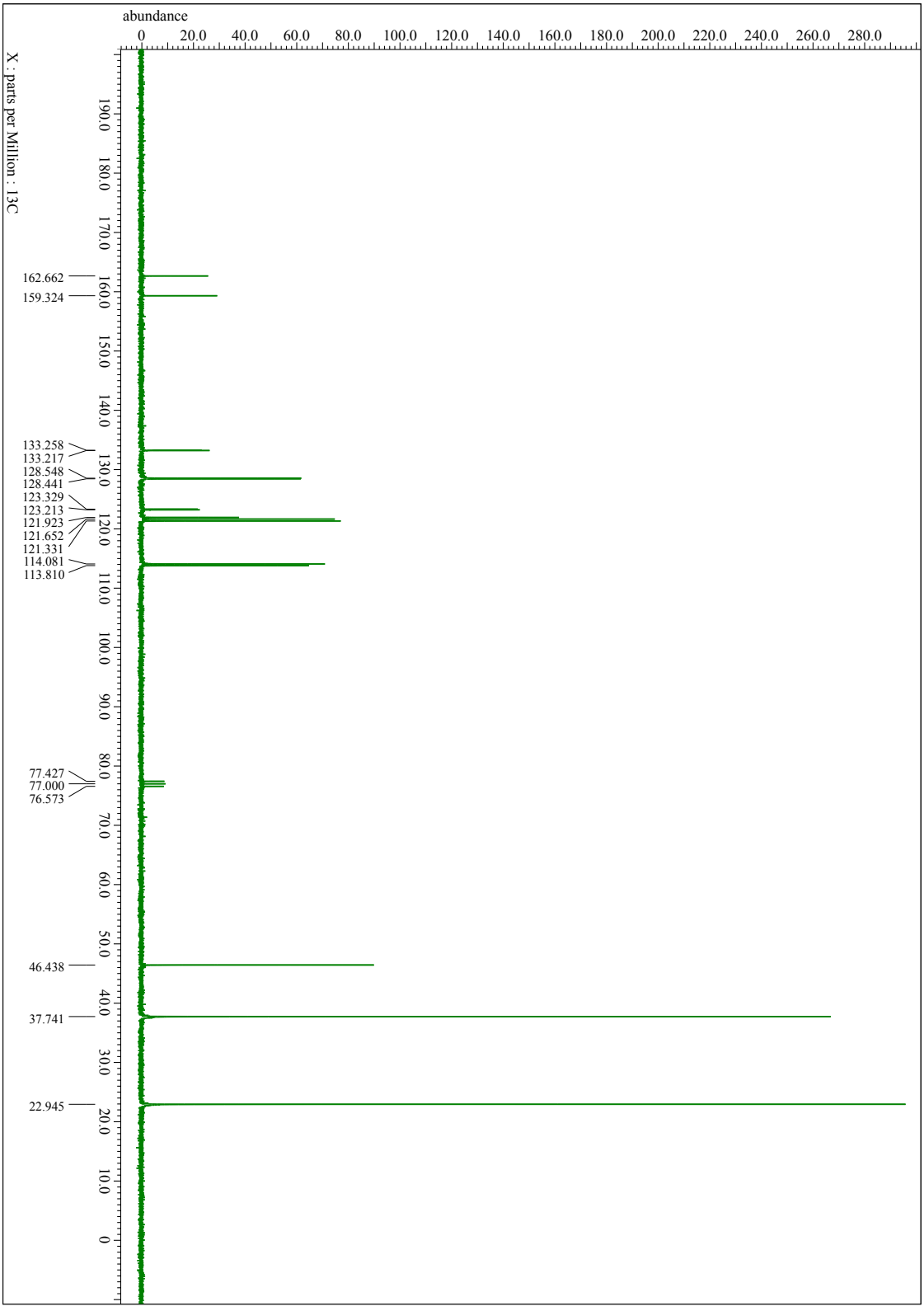
^{1}H NMR spectrum of **s17** ($CDCl_3$, 300 MHz).



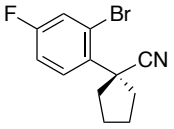


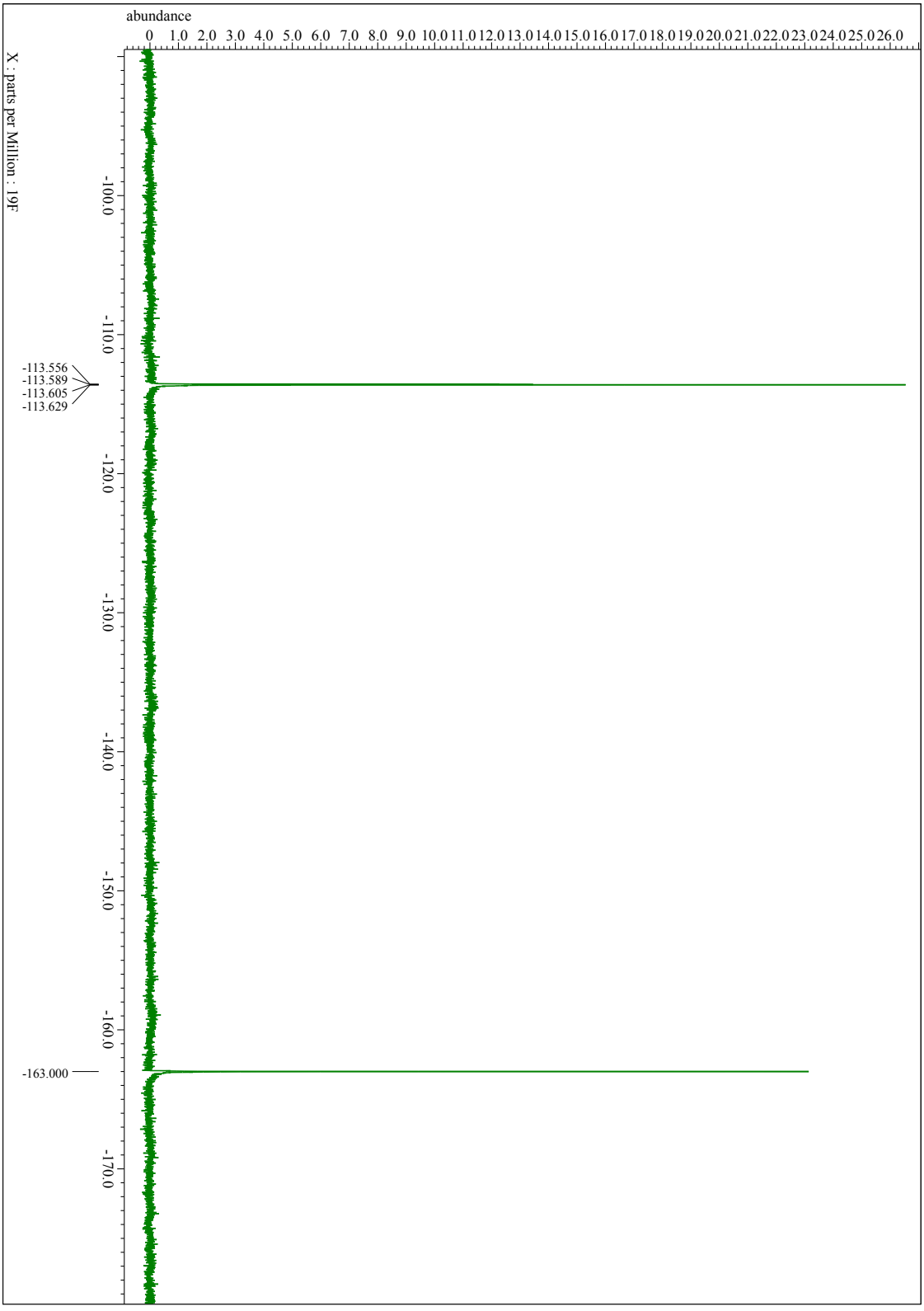
^{13}C NMR spectrum of **s17** ($CDCl_3$, 75 MHz).



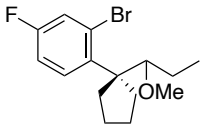


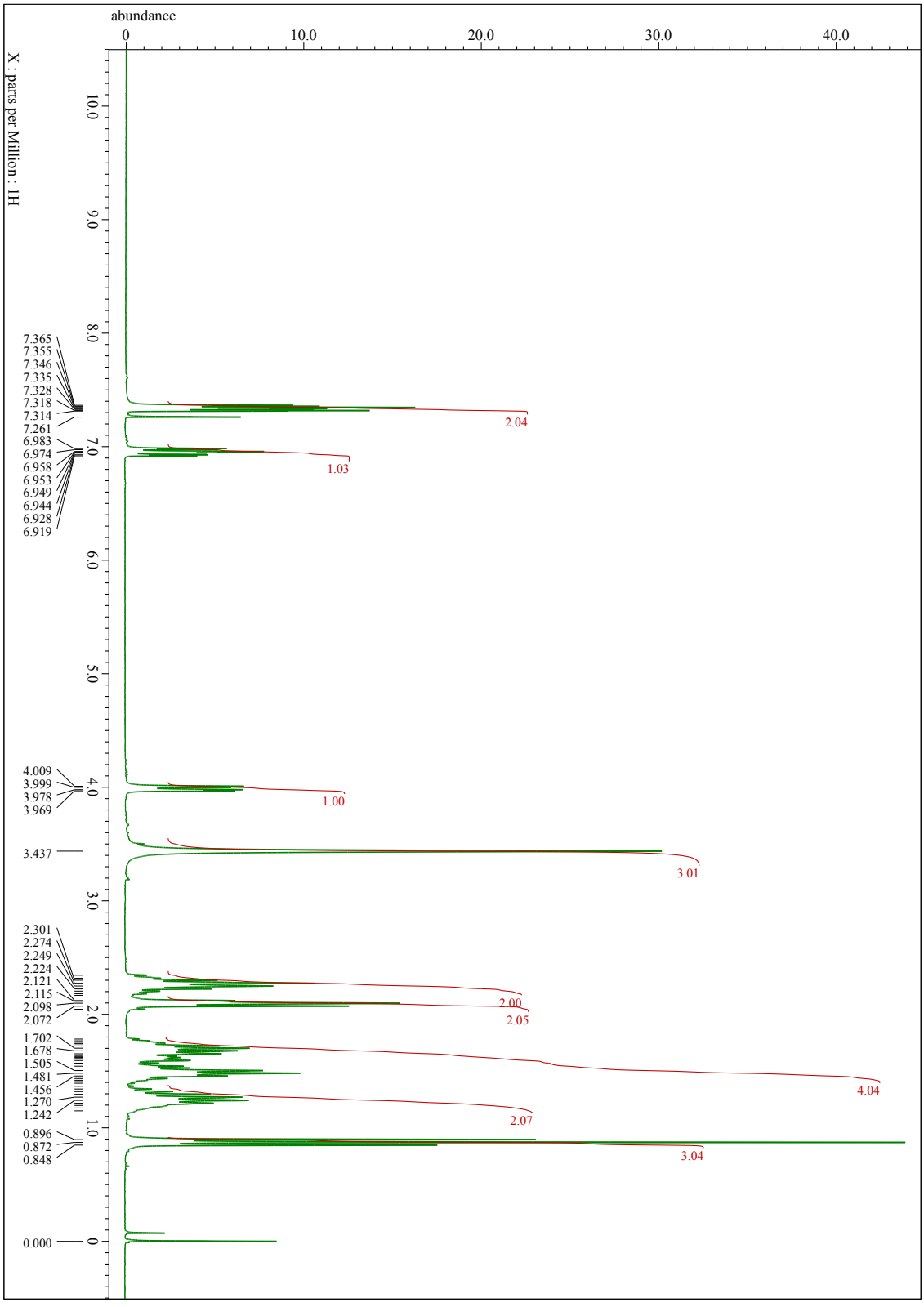
^{19}F NMR spectrum of **s17** ($CDCl_3$, 283 MHz).



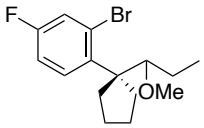


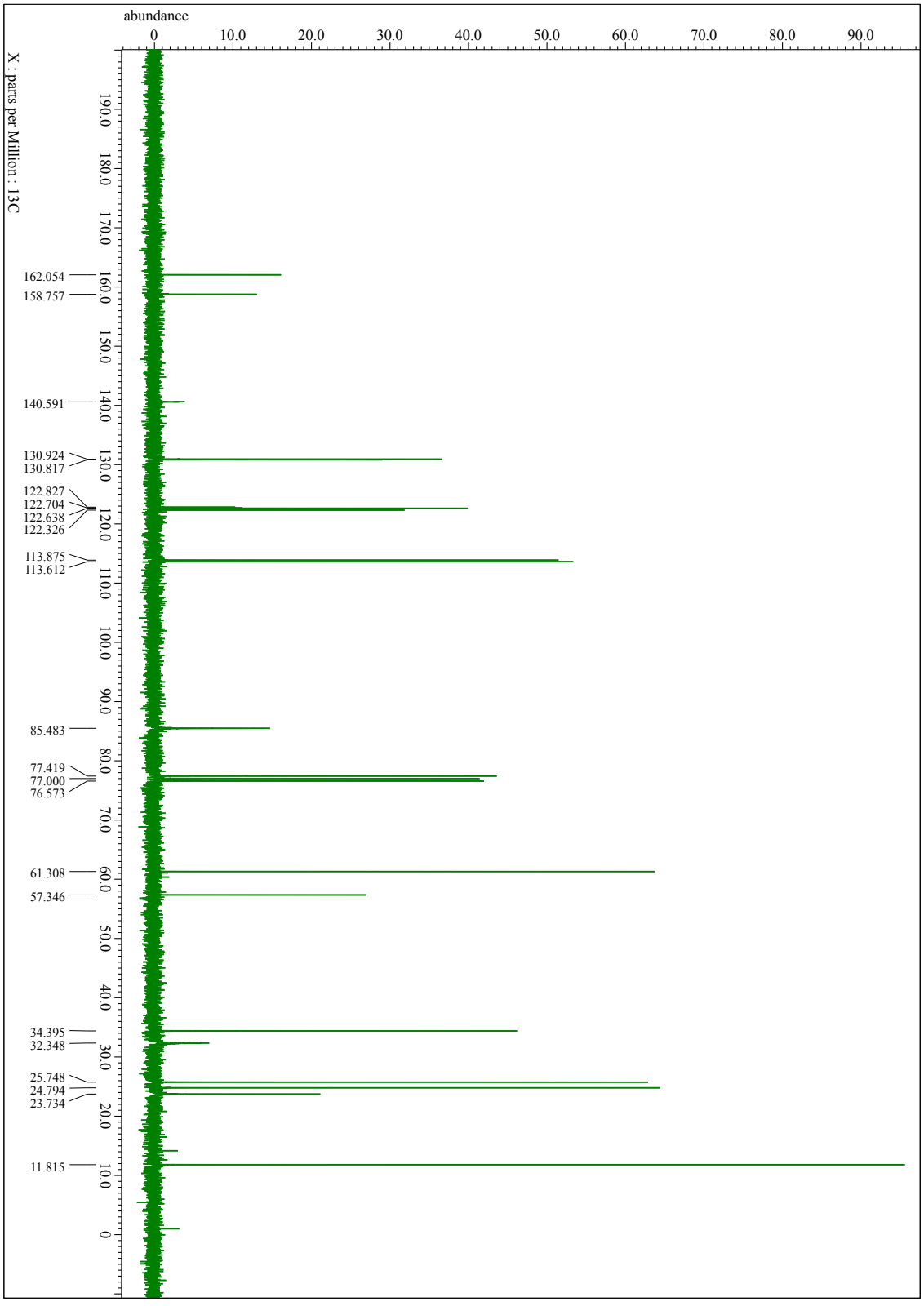
^{1}H NMR spectrum of **s18** ($CDCl_3$, 300 MHz).



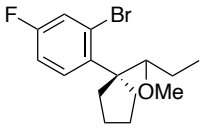


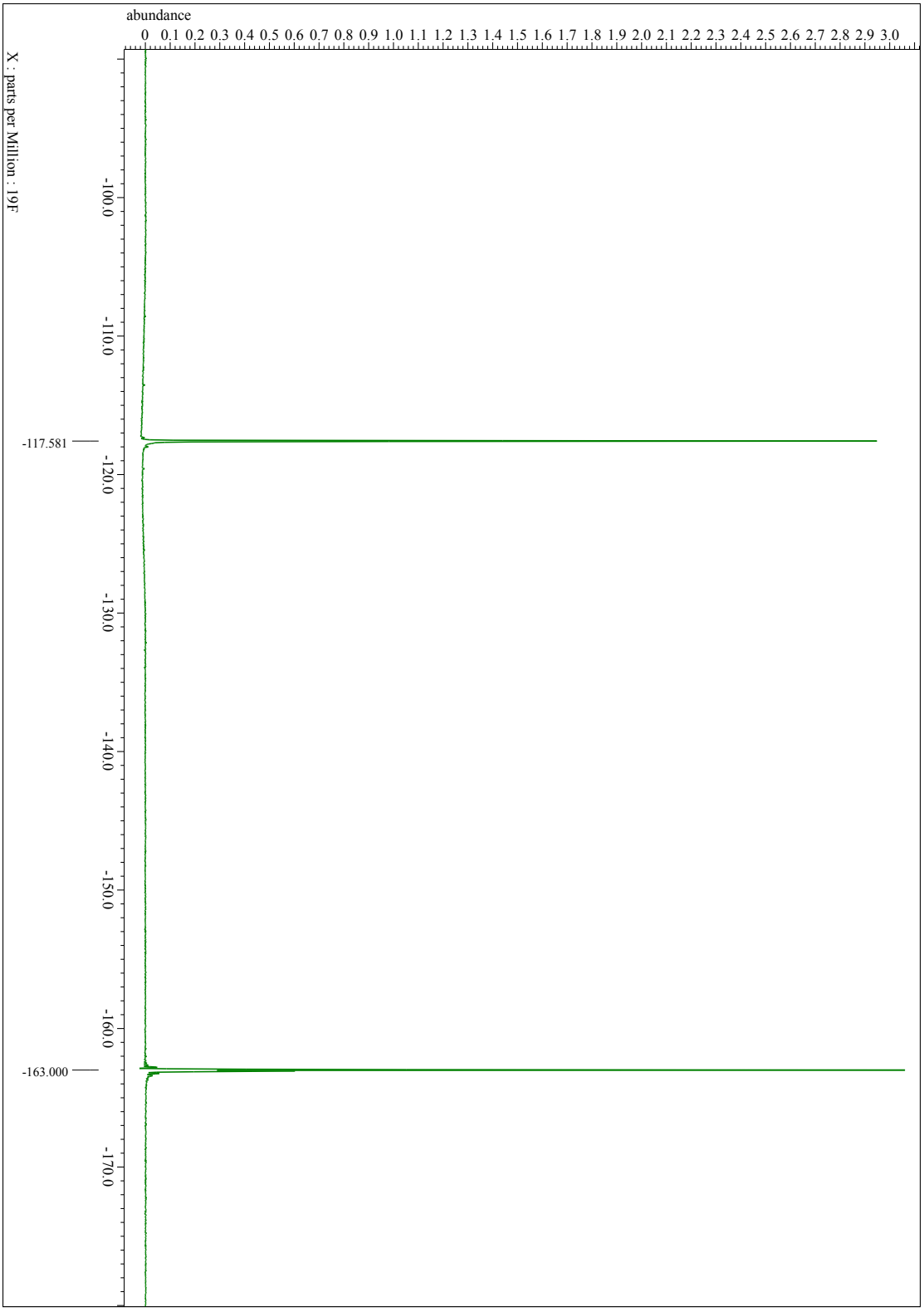
^{13}C NMR spectrum of **s18** ($CDCl_3$, 75 MHz).



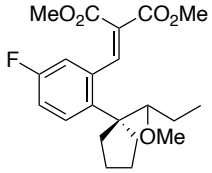


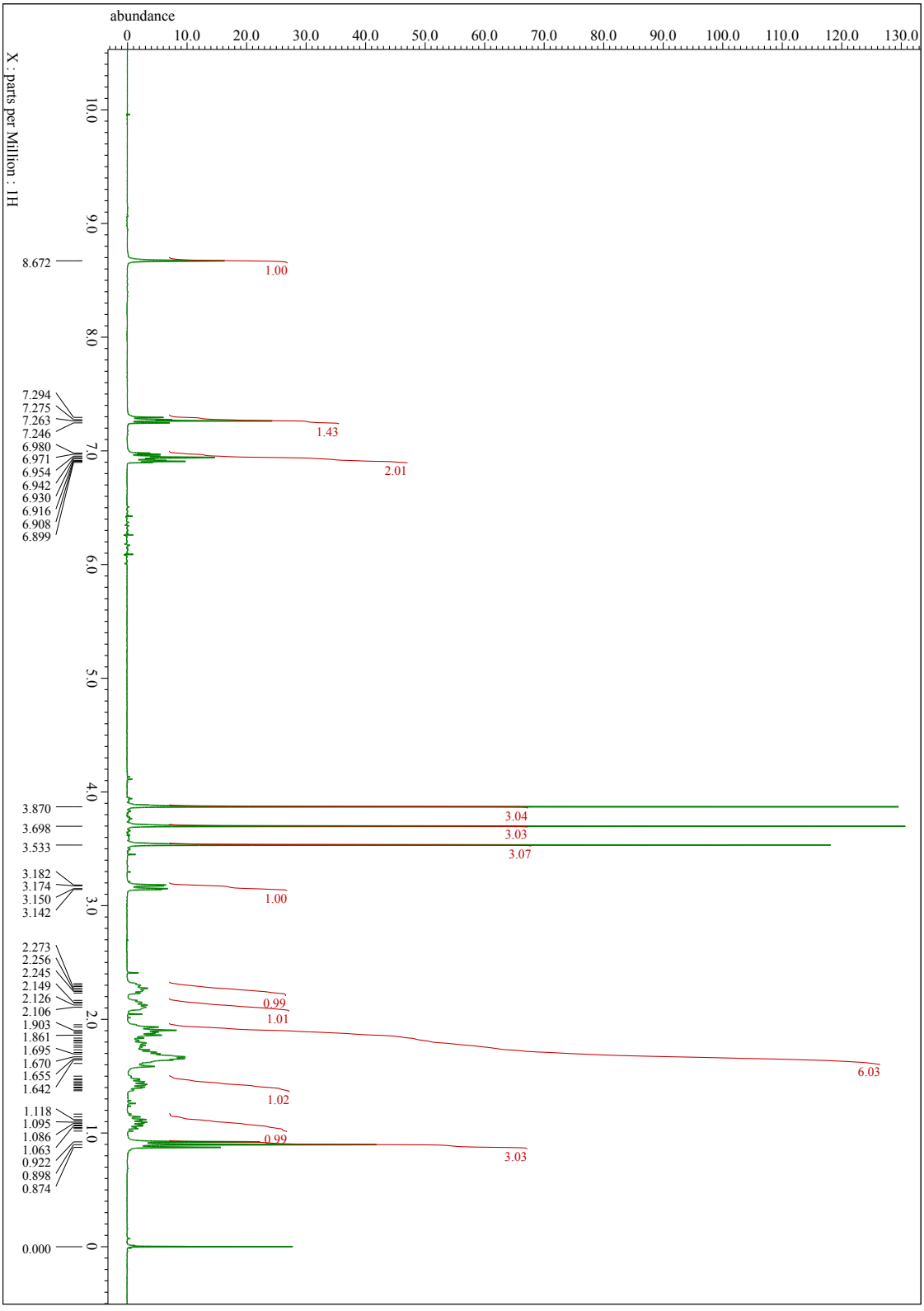
^{19}F NMR spectrum of **s18** ($CDCl_3$, 283 MHz).



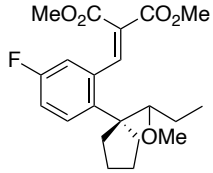


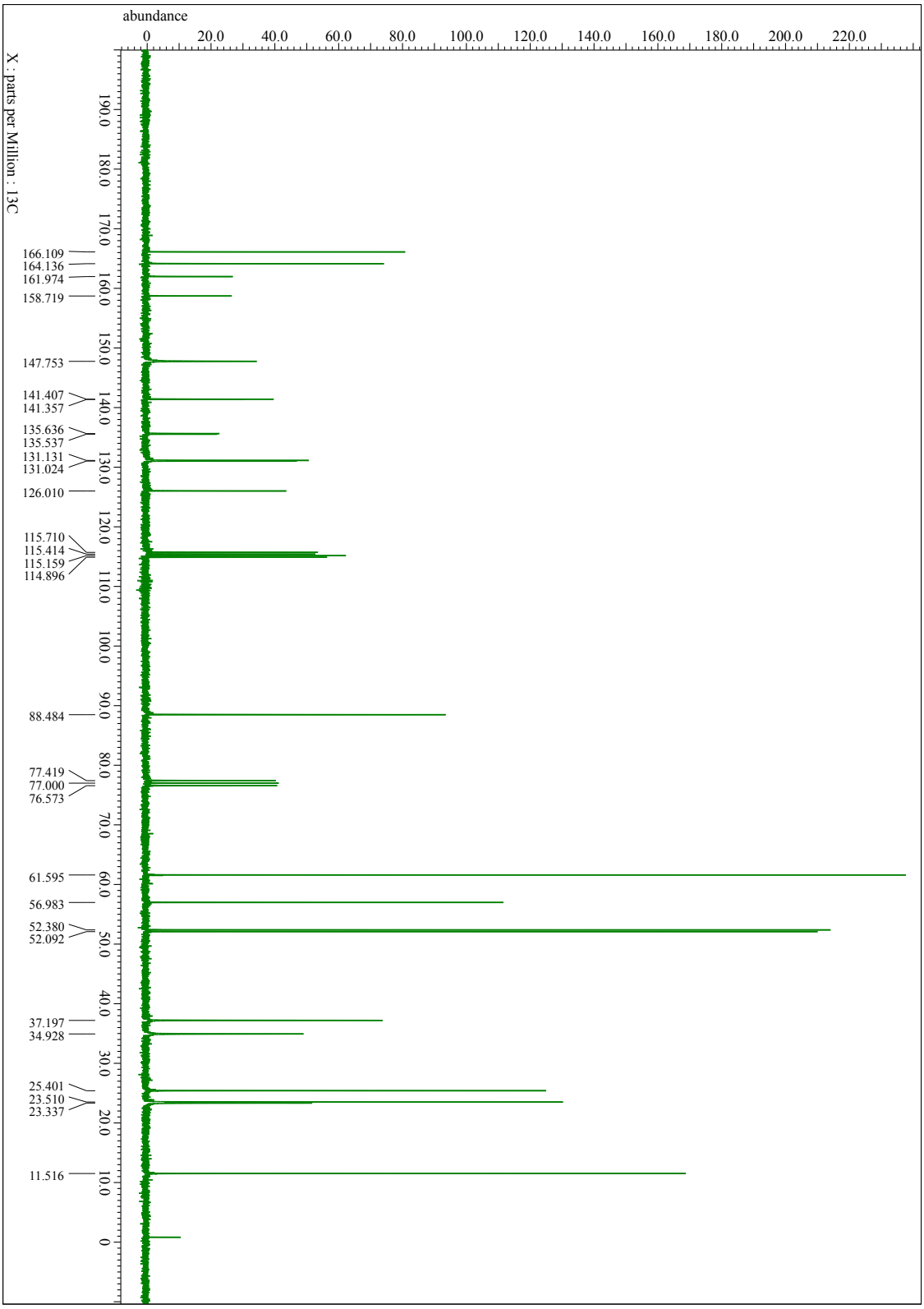
^{1}H NMR spectrum of **4i** ($CDCl_3$, 300 MHz).



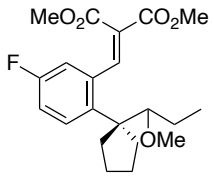


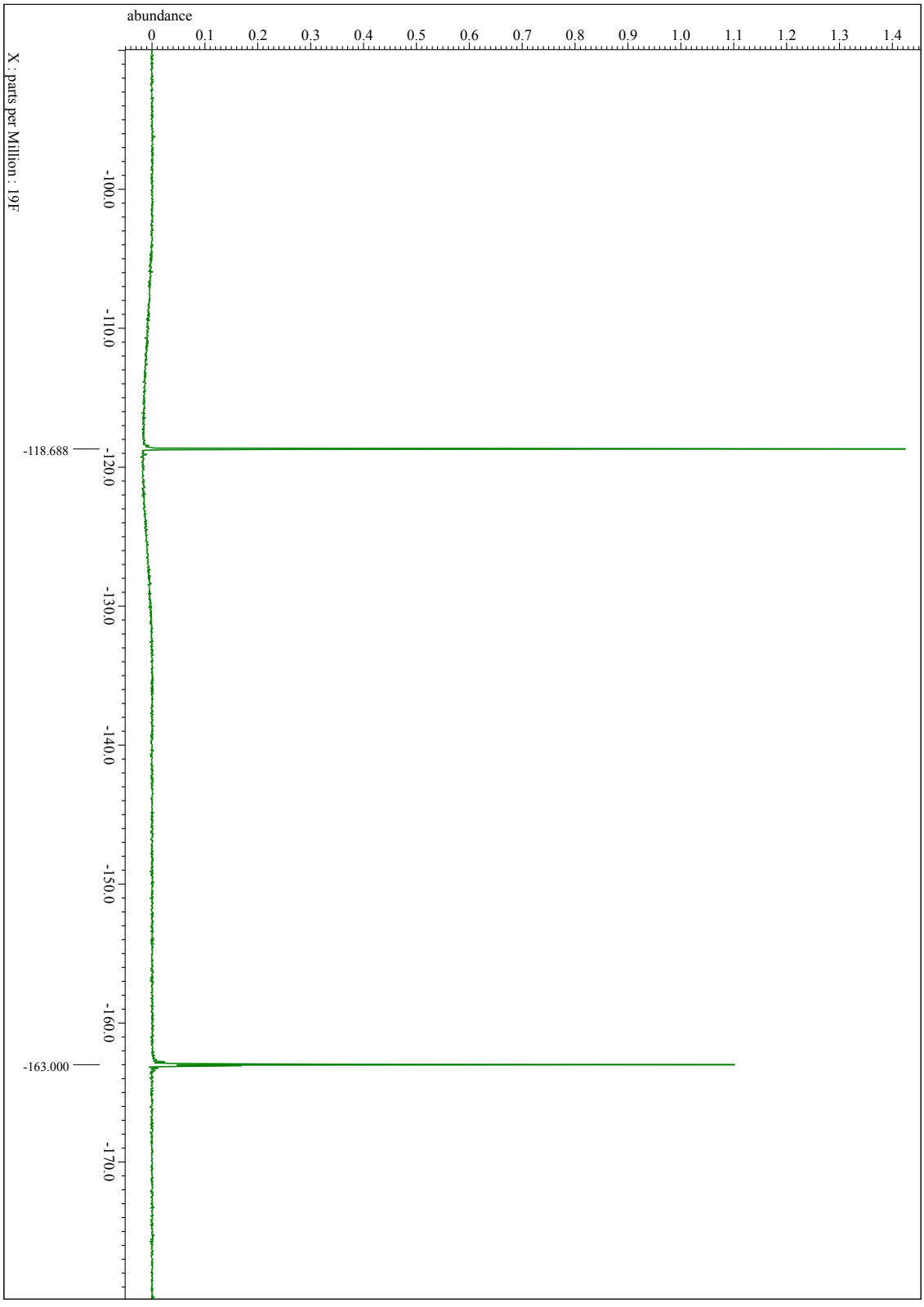
^{13}C NMR spectrum of **4i** ($CDCl_3$, 75 MHz).



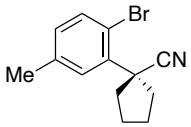


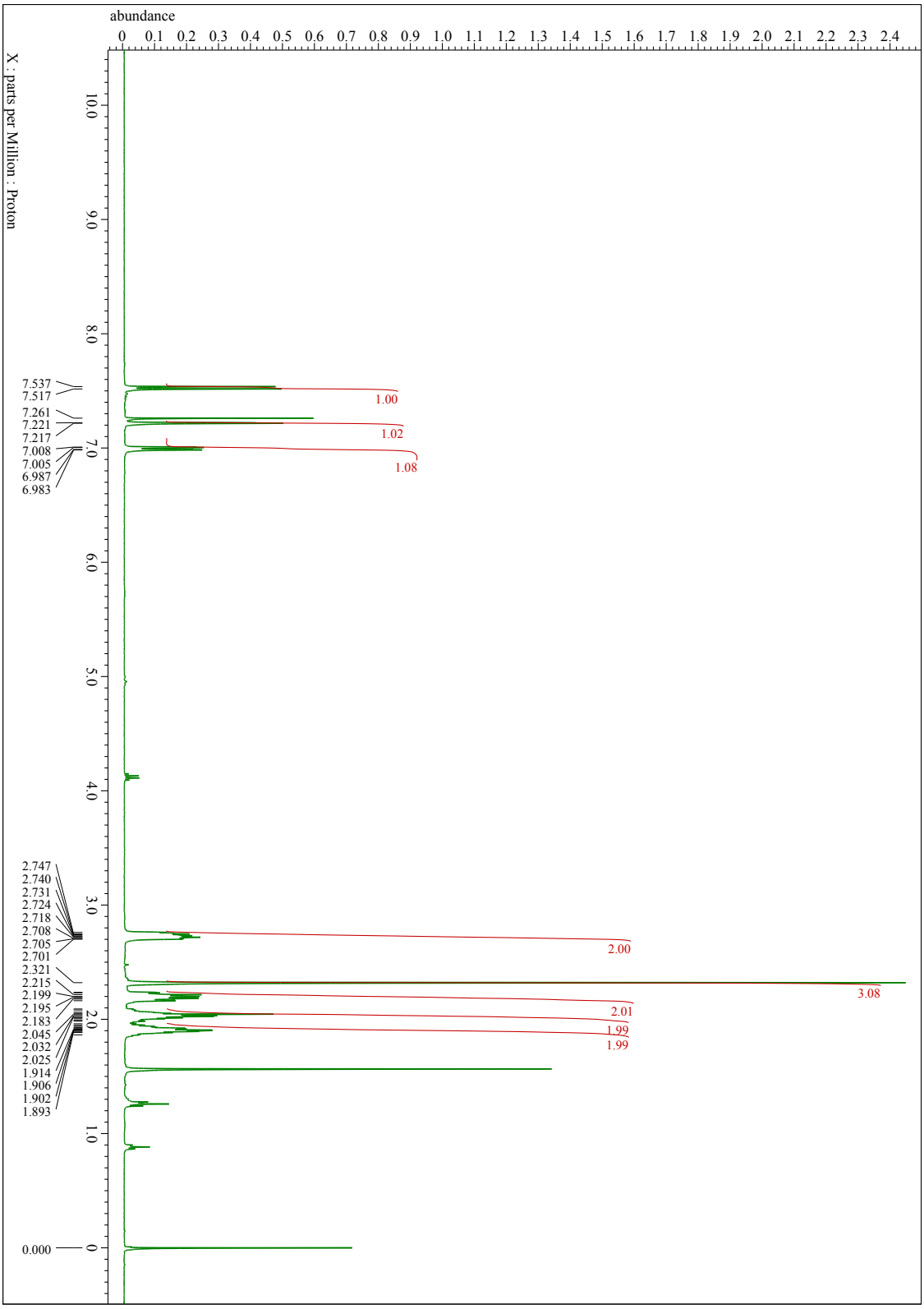
^{19}F NMR spectrum of **4i** ($CDCl_3$, 376 MHz).



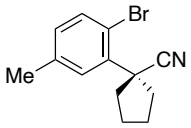


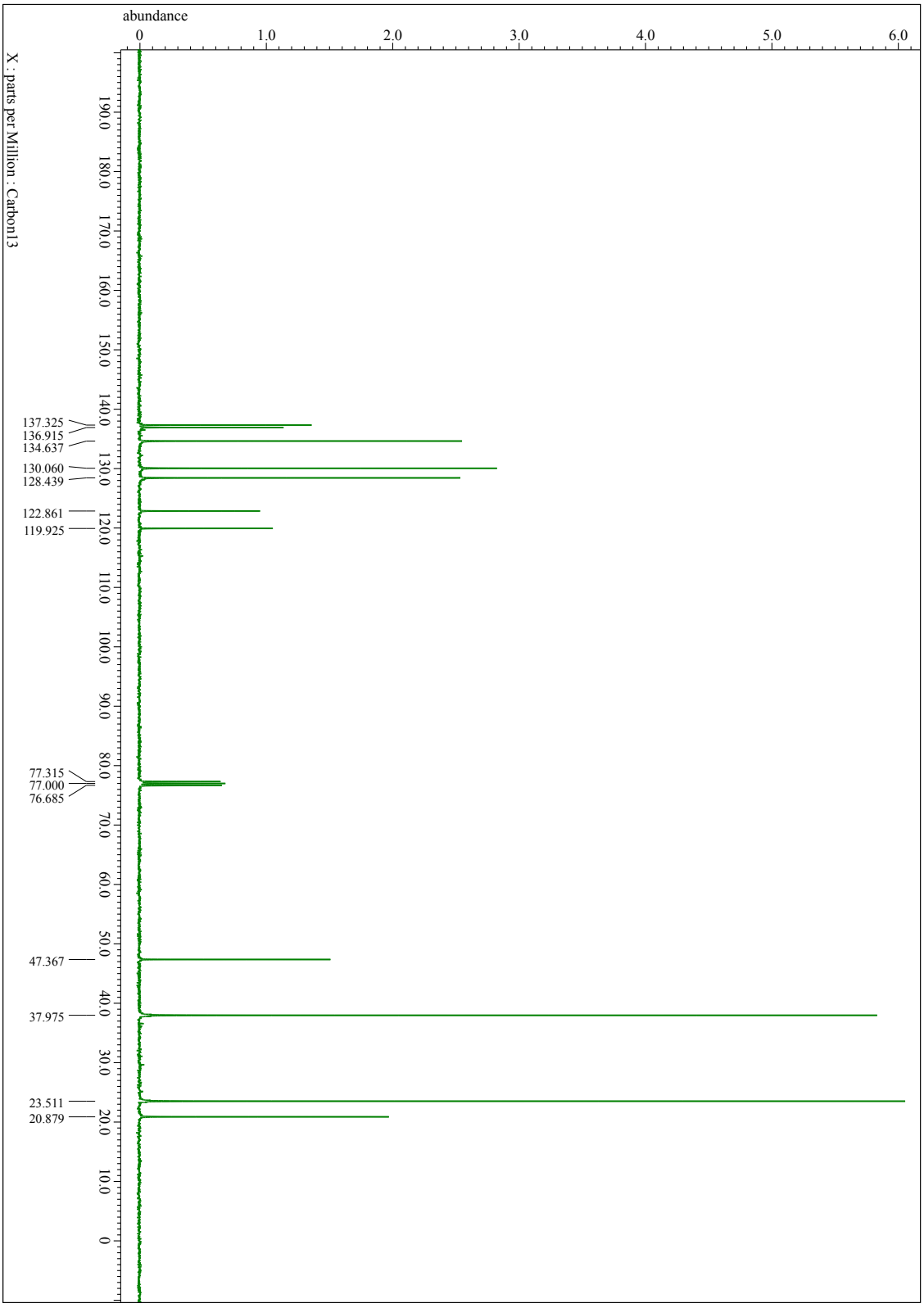
^{1}H NMR spectrum of **s19** ($CDCl_3$, 400 MHz).



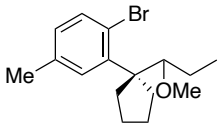


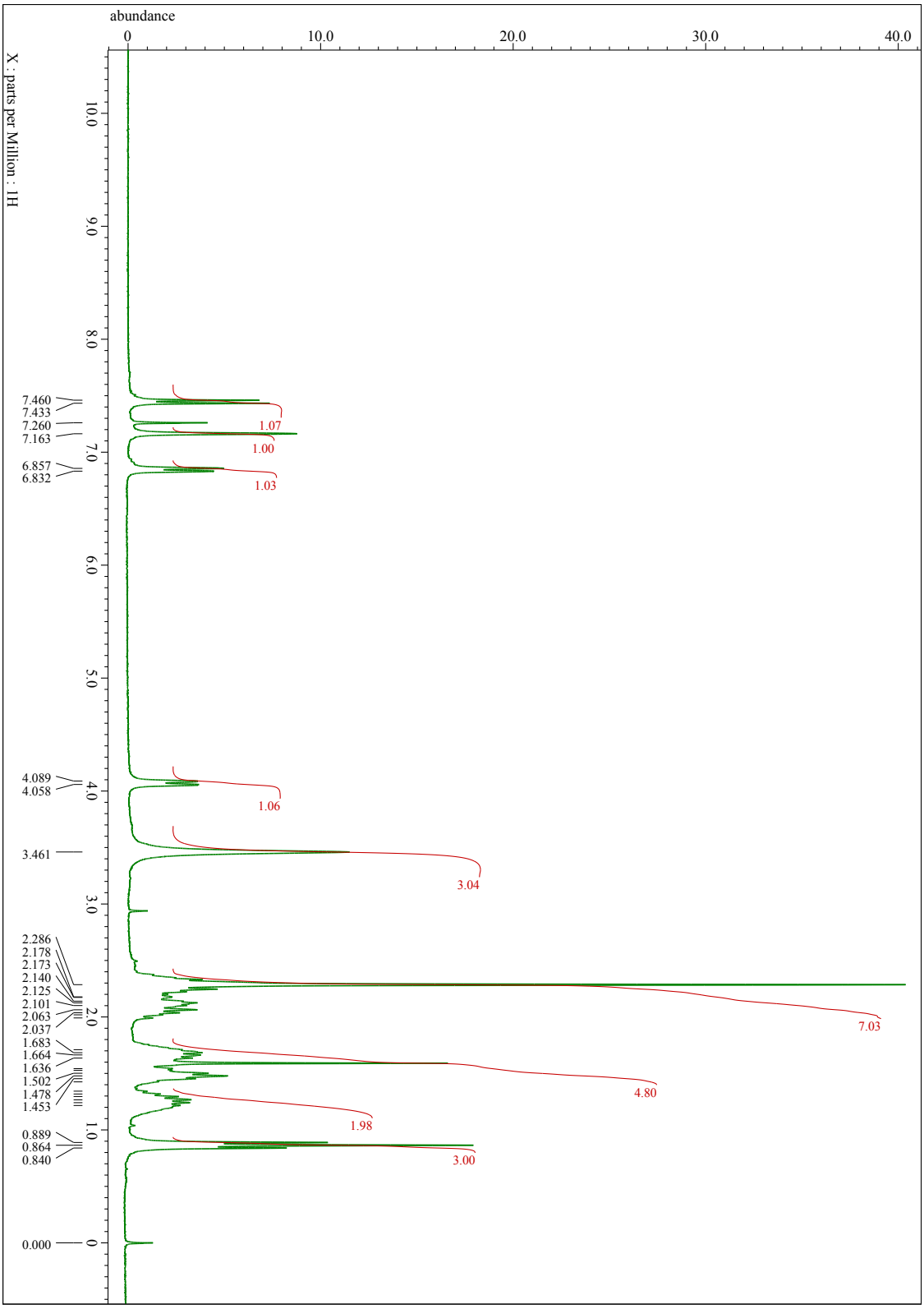
^{13}C NMR spectrum of **s19** ($CDCl_3$, 100 MHz).



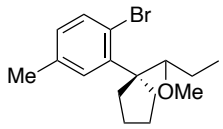


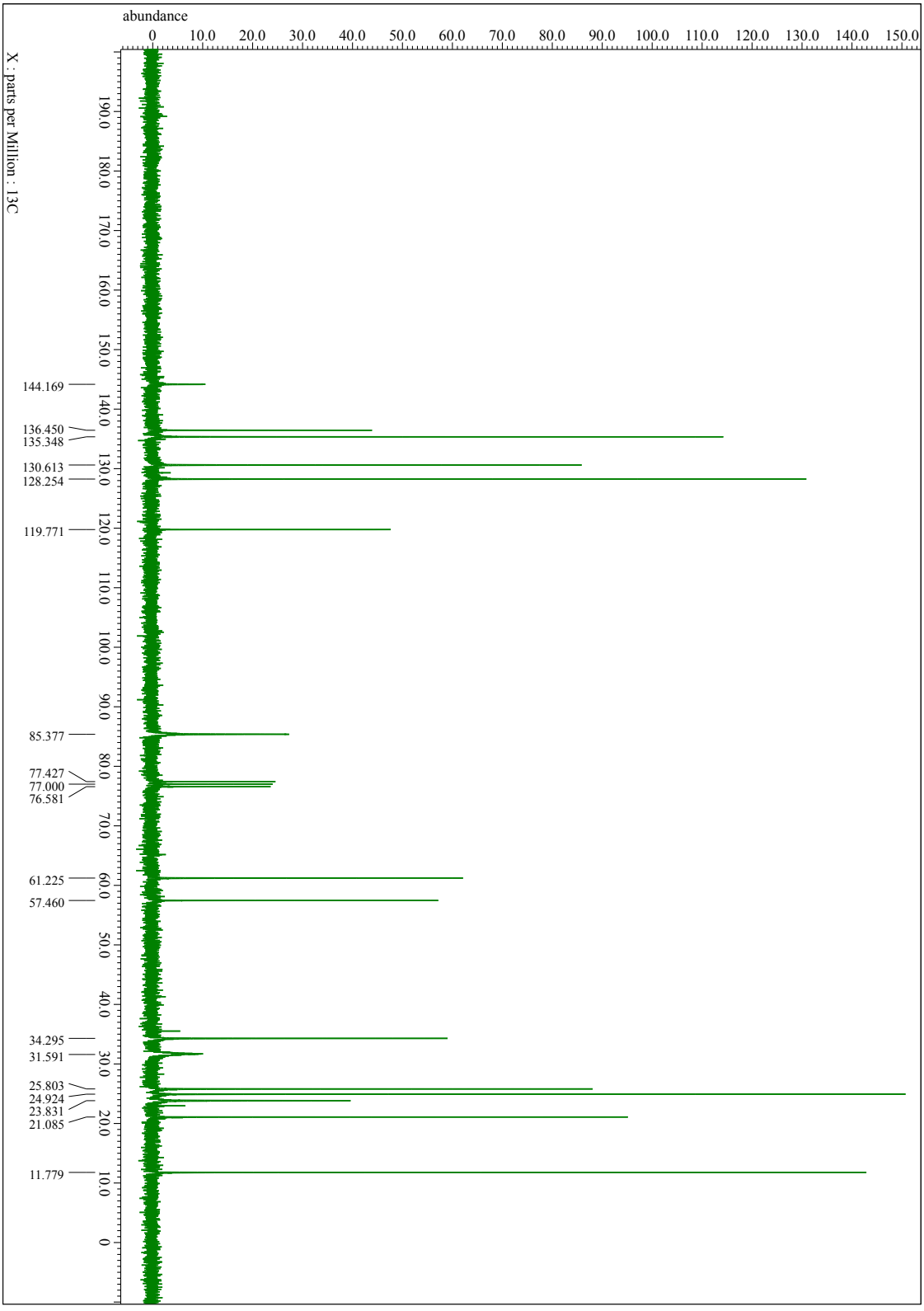
^{1}H NMR spectrum of **s20** ($CDCl_3$, 300 MHz).



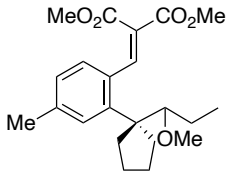


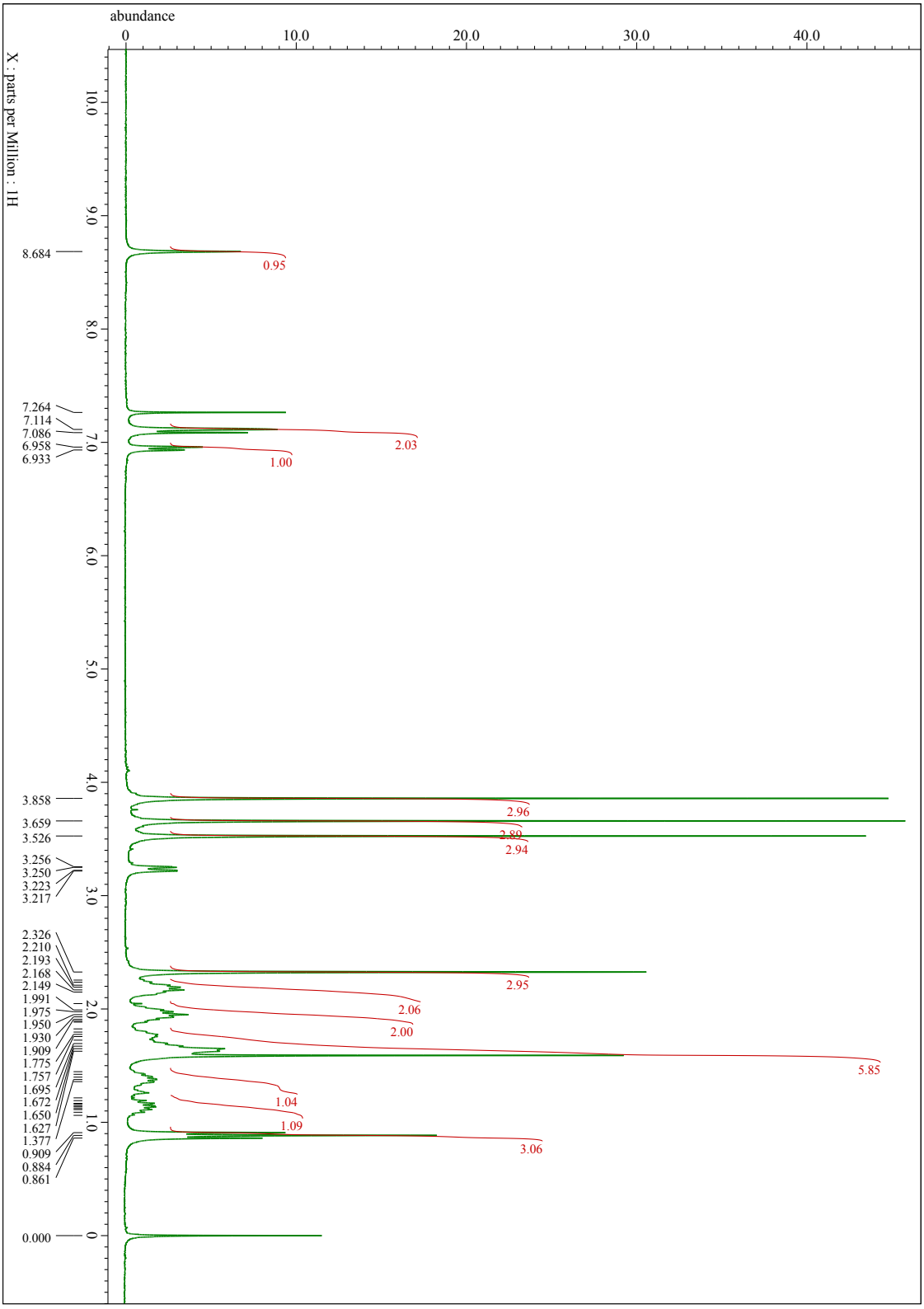
^{13}C NMR spectrum of **s20** ($CDCl_3$, 75 MHz).



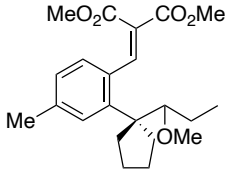


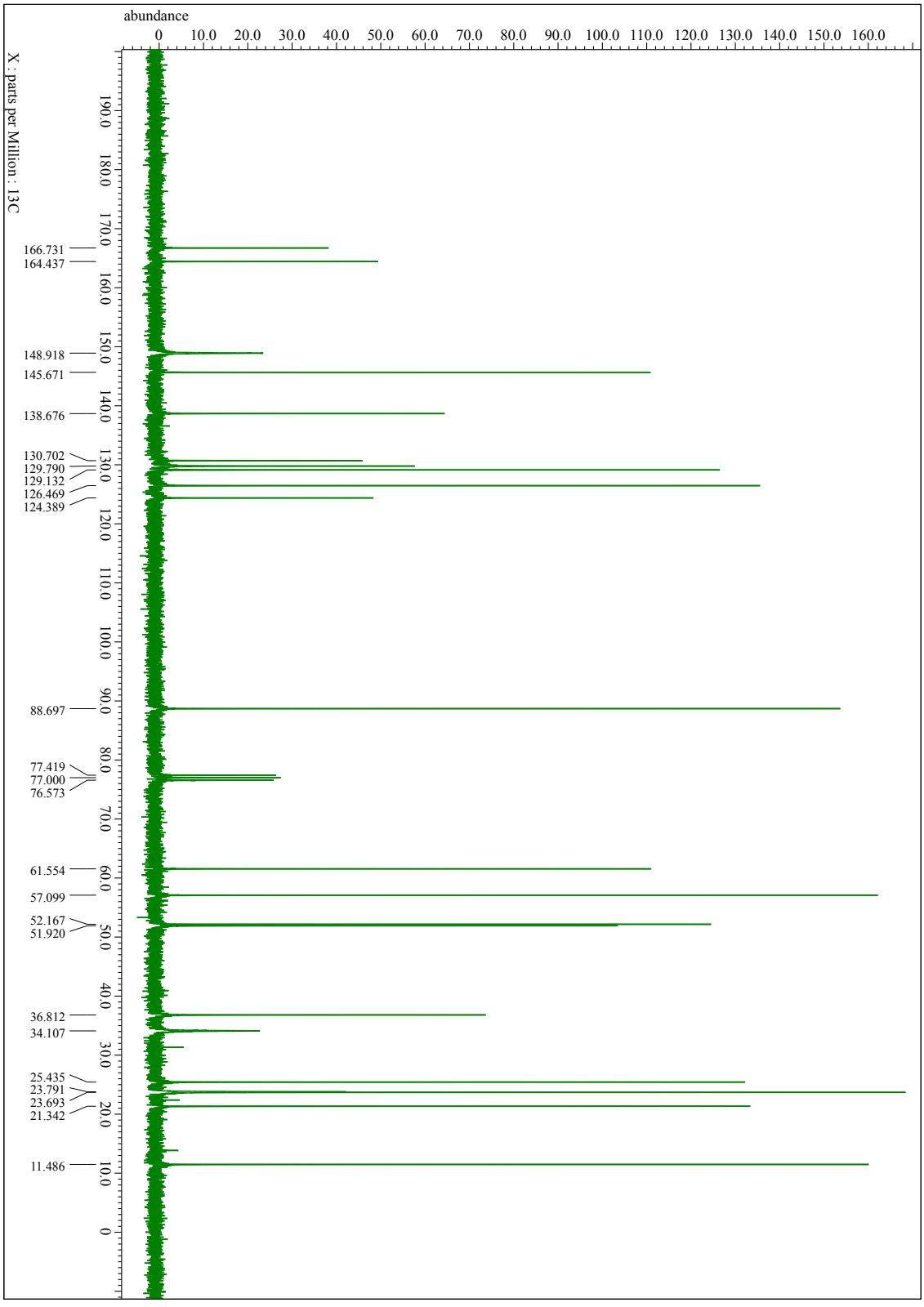
^{1}H NMR spectrum of **4j** ($CDCl_3$, 300 MHz).



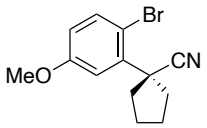


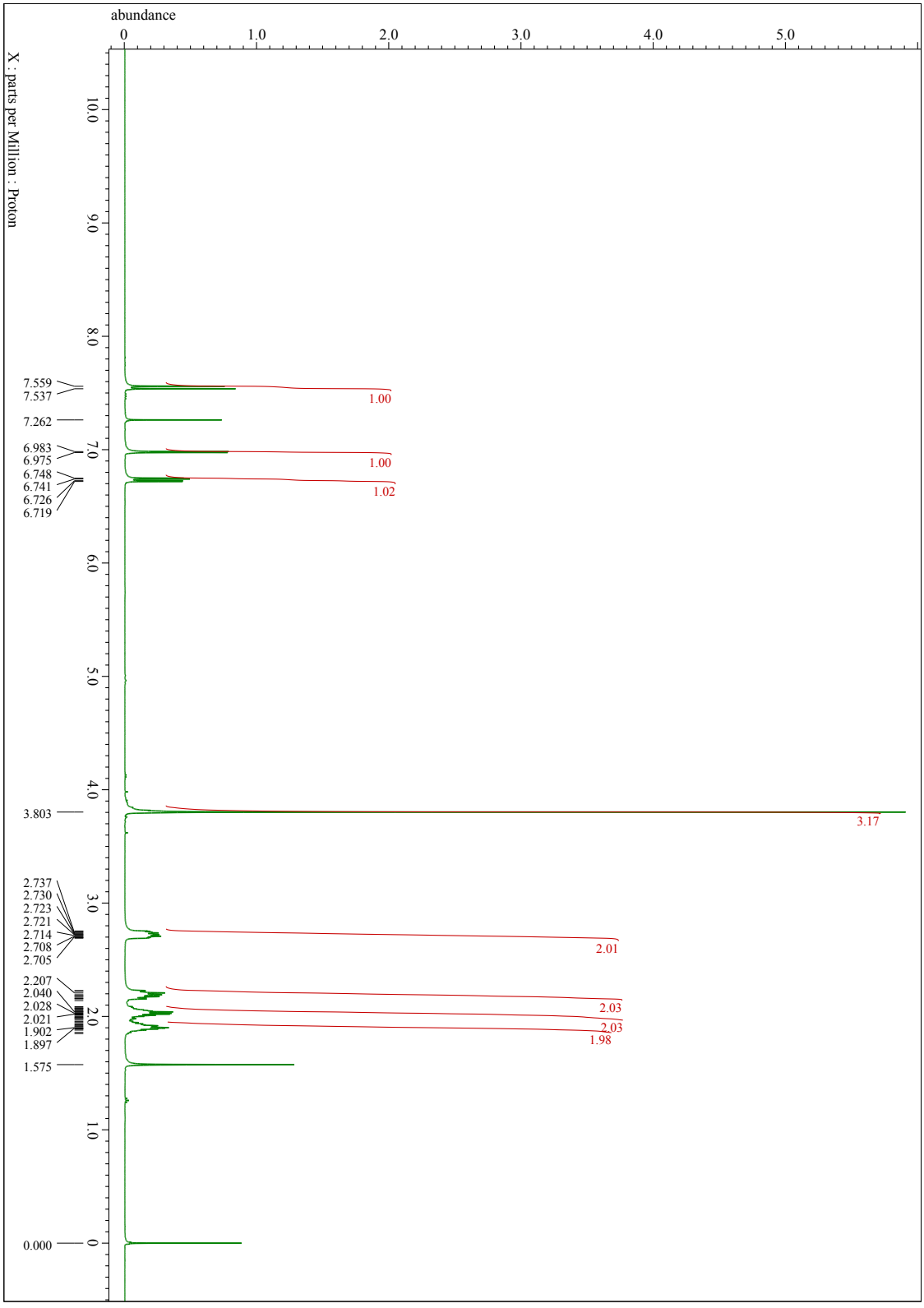
^{13}C NMR spectrum of **4j** ($CDCl_3$, 75 MHz).



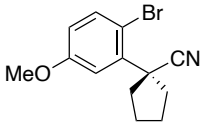


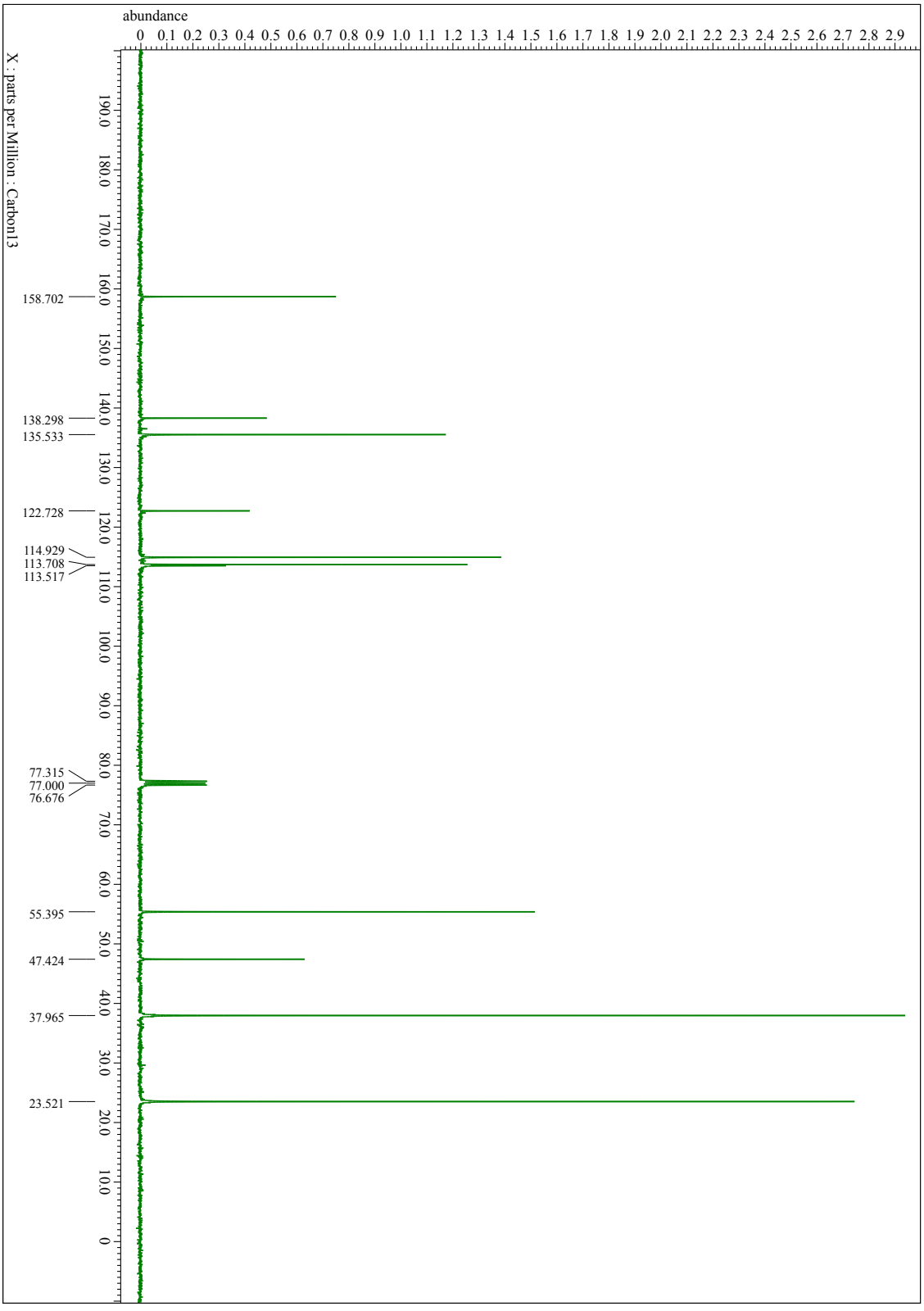
^{1}H NMR spectrum of **s21** ($CDCl_3$, 400 MHz).



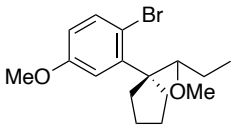


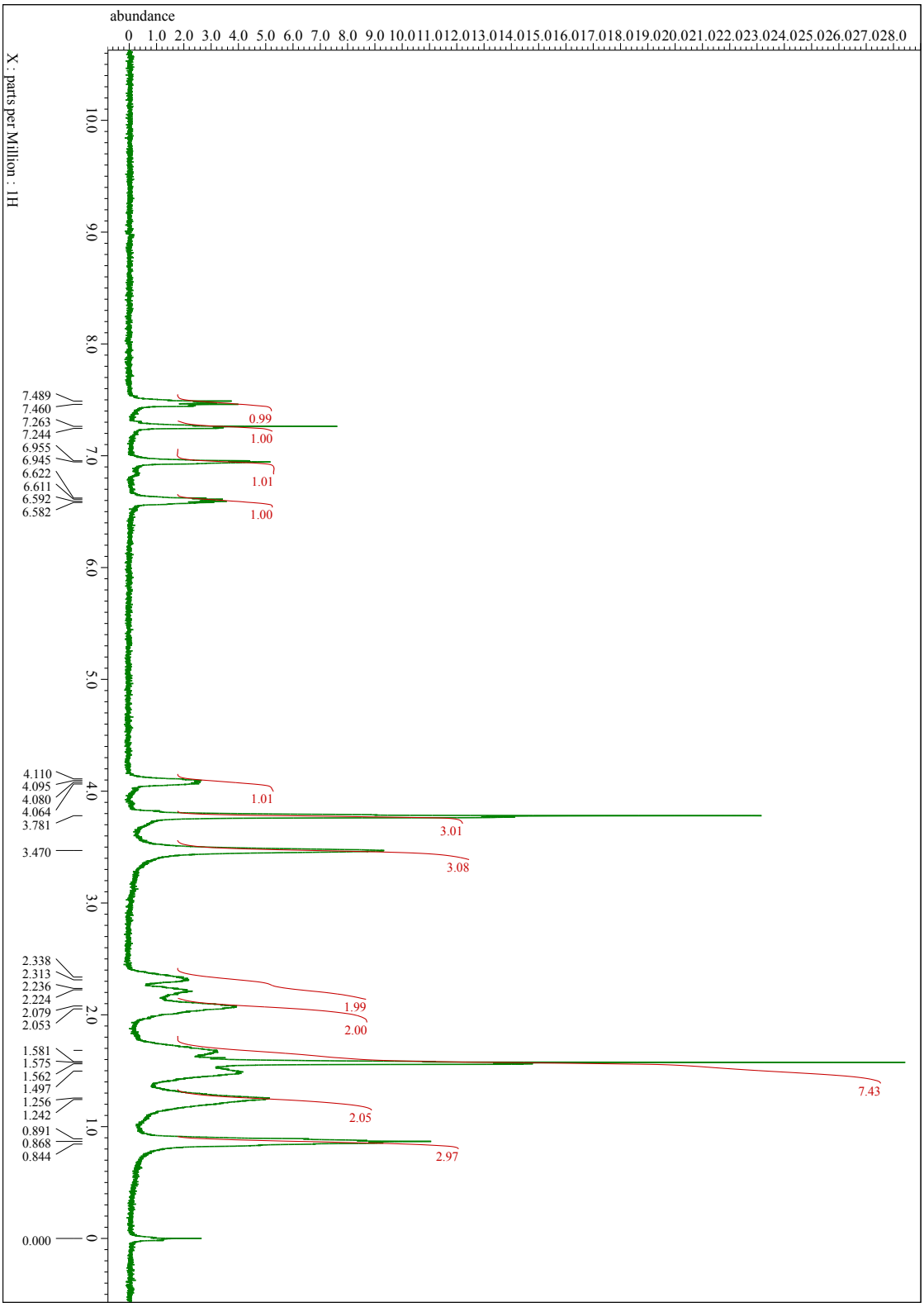
^{13}C NMR spectrum of **s21** ($CDCl_3$, 100 MHz).



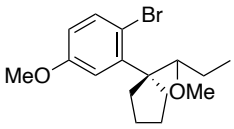


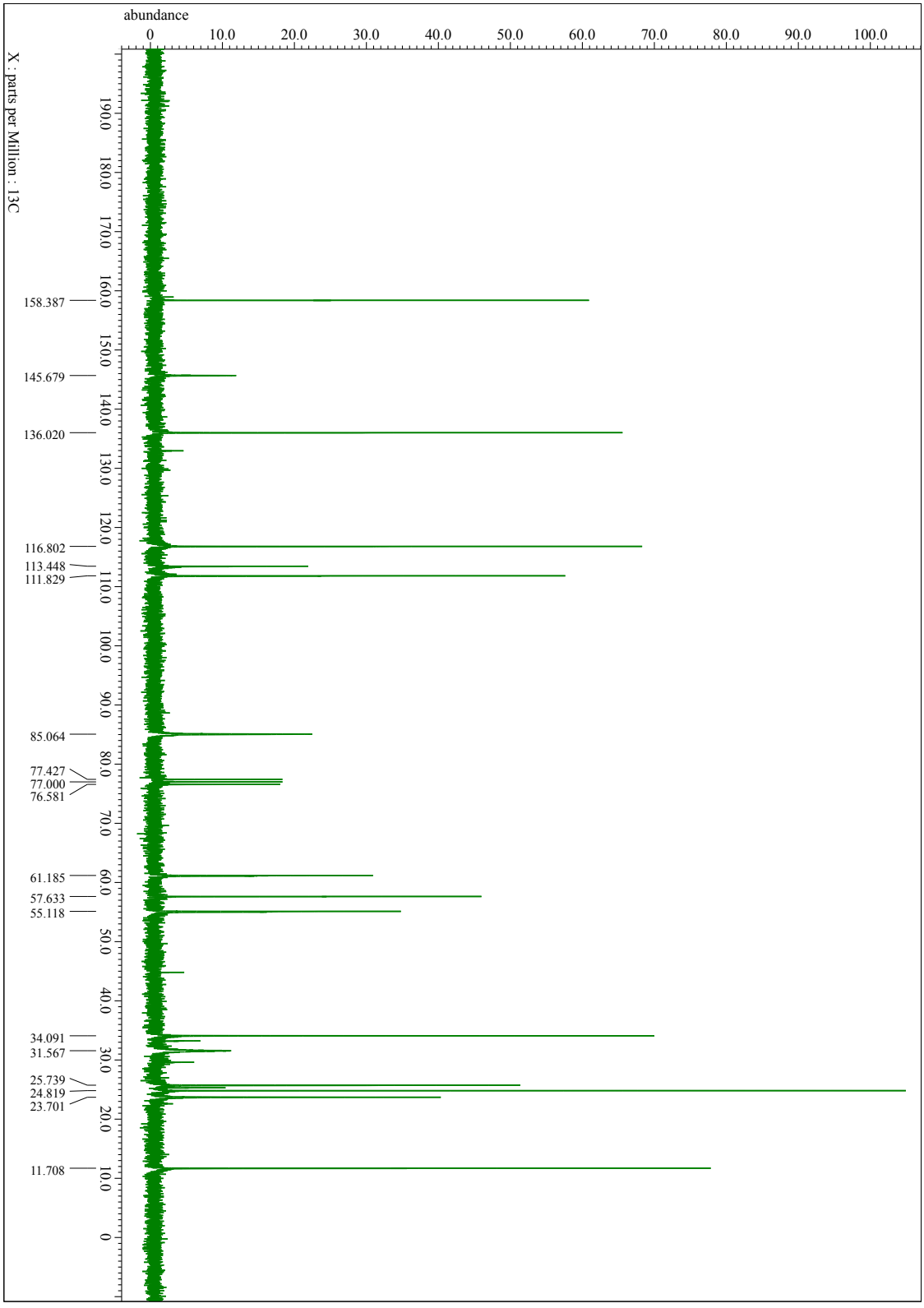
^{1}H NMR spectrum of **s22** ($CDCl_3$, 300 MHz).



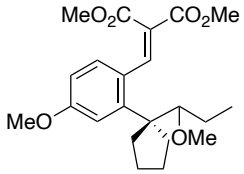


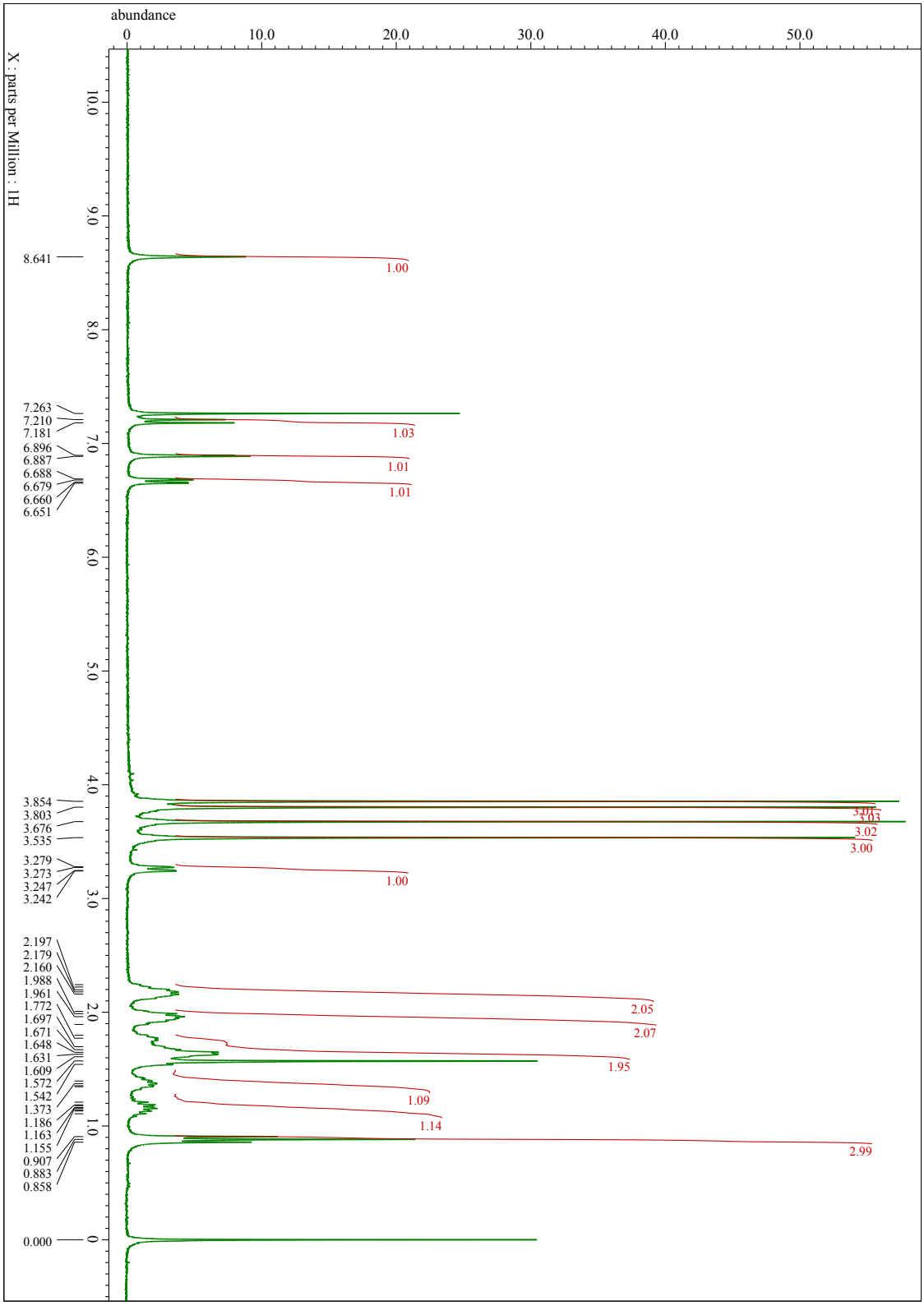
^{13}C NMR spectrum of **s22** ($CDCl_3$, 75 MHz).



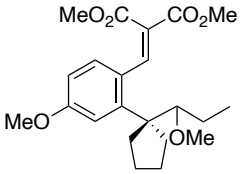


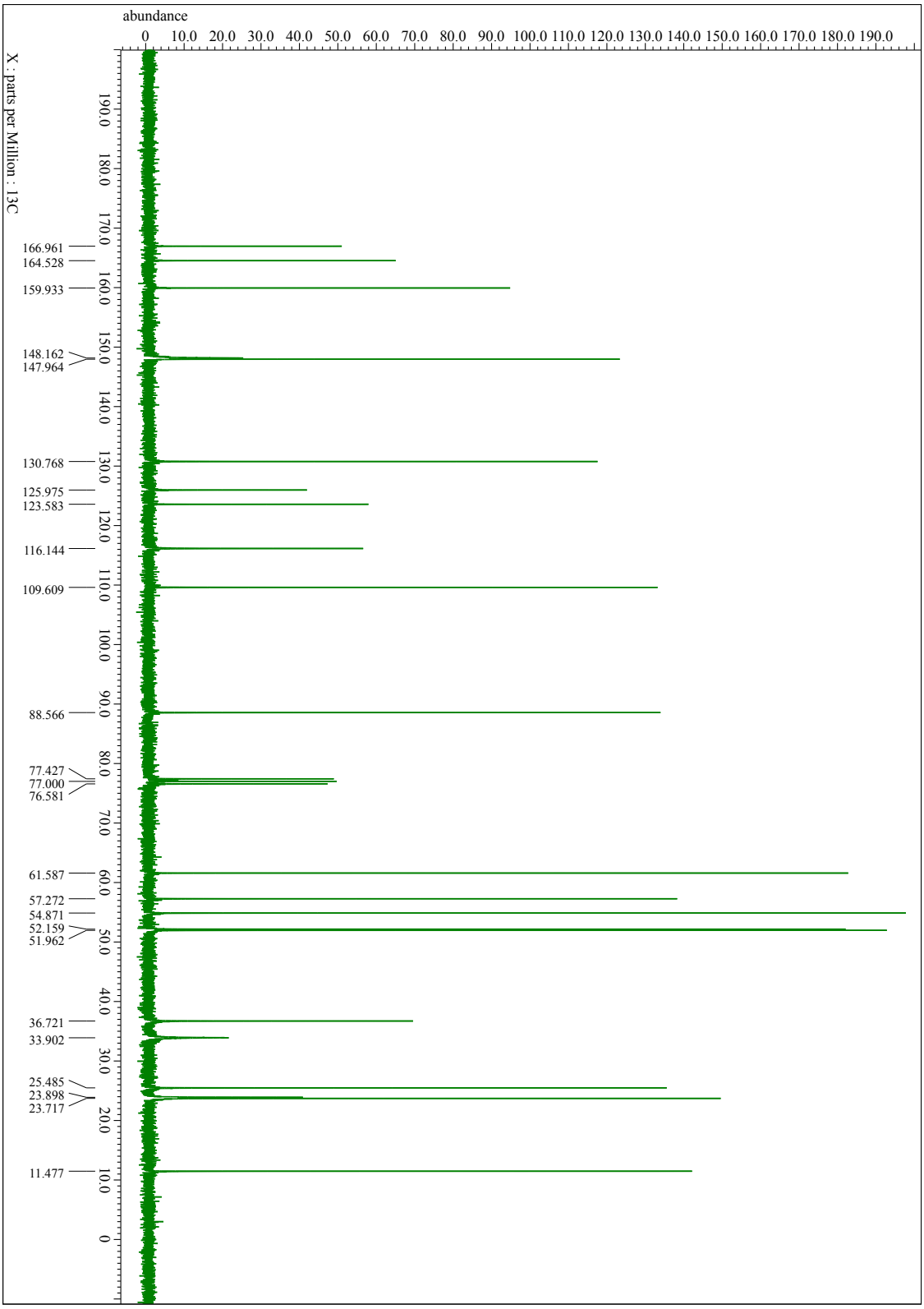
^{1}H NMR spectrum of **4k** ($CDCl_3$, 300 MHz).



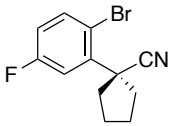


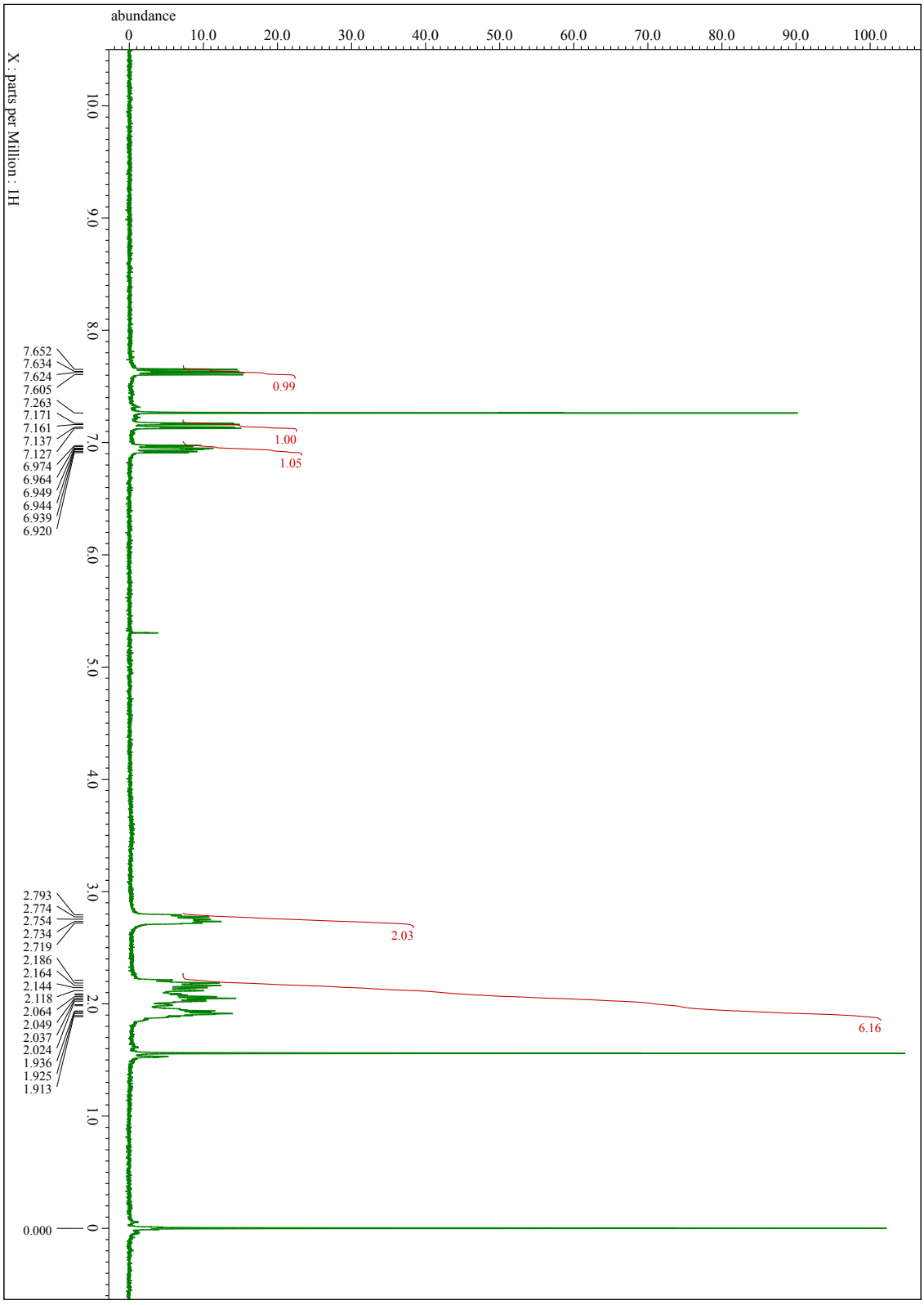
^{13}C NMR spectrum of **4k** ($CDCl_3$, 75 MHz).



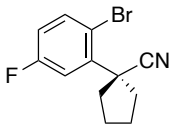


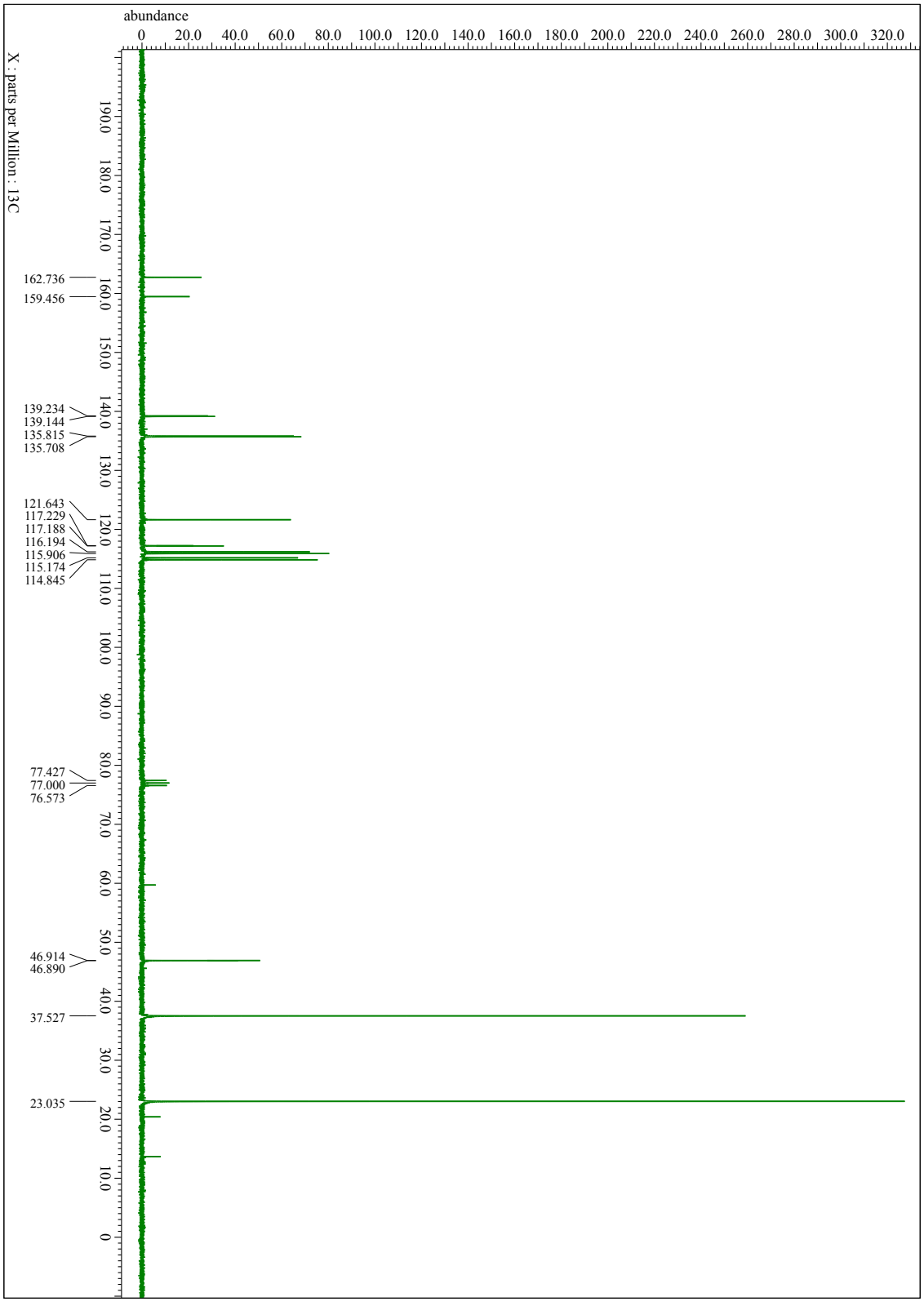
^{1}H NMR spectrum of **s23** ($CDCl_3$, 300 MHz).



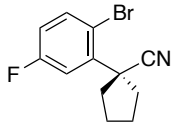


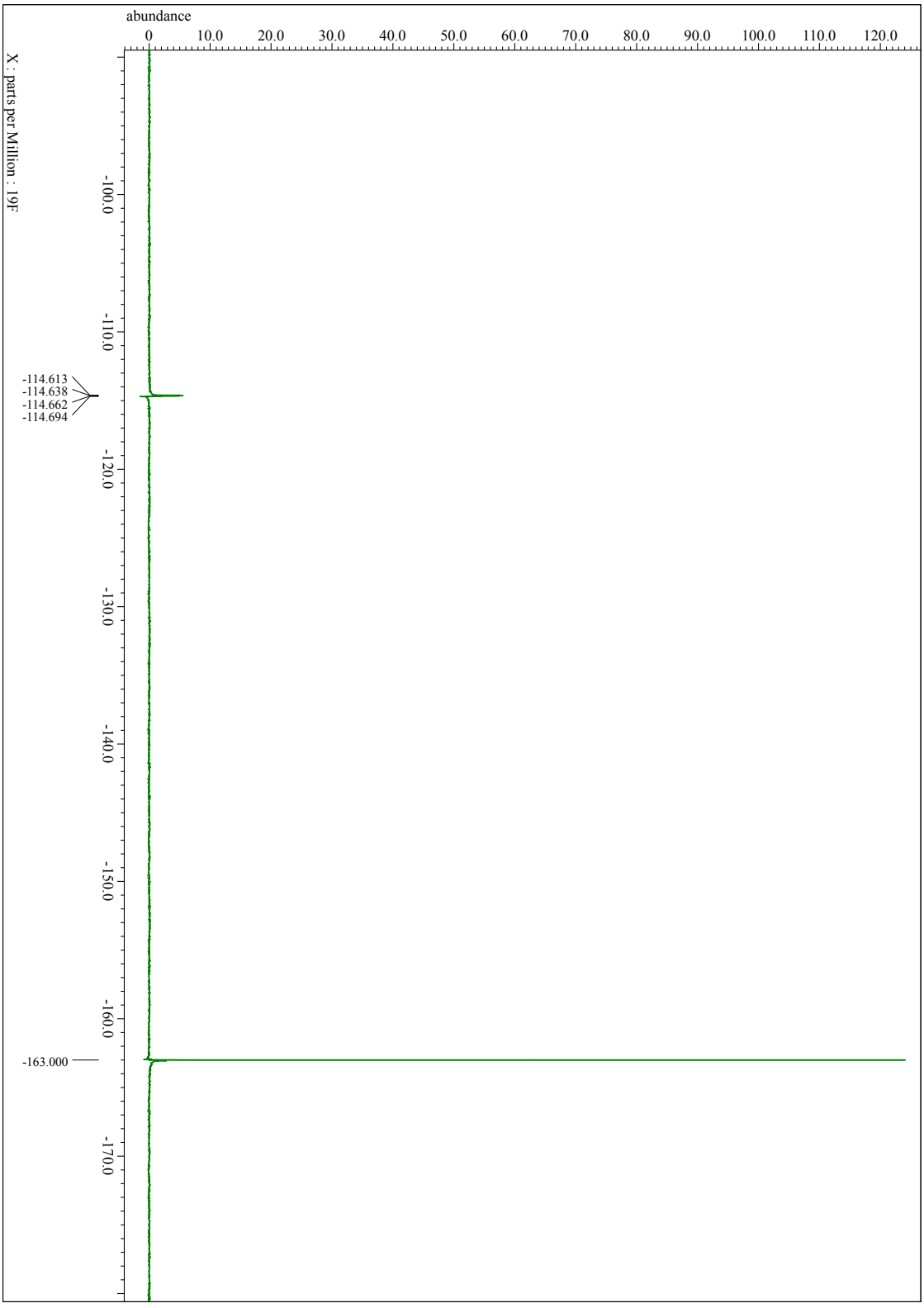
^{13}C NMR spectrum of **s23** ($CDCl_3$, 75 MHz).



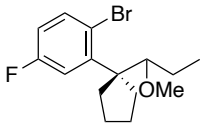


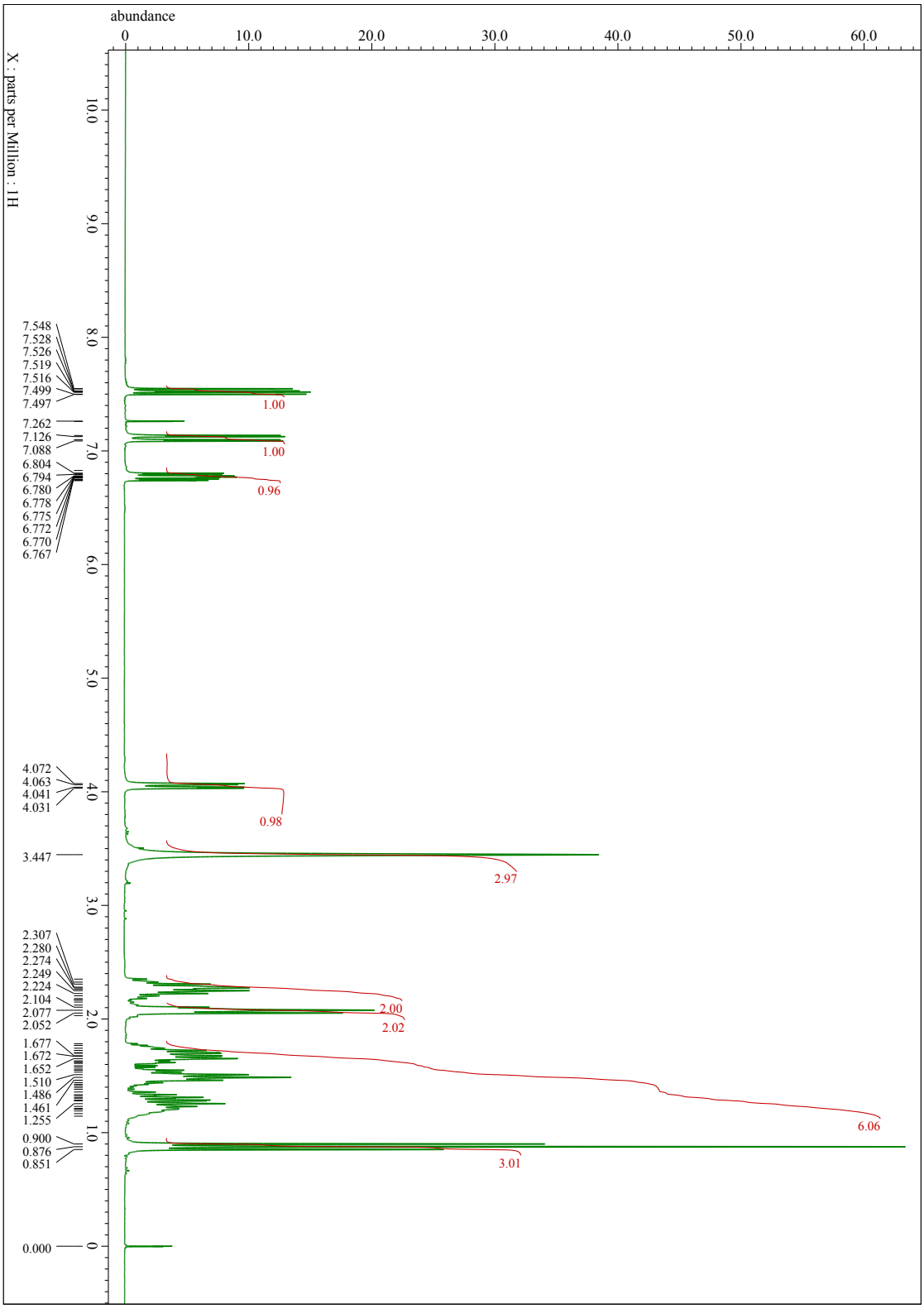
^{19}F NMR spectrum of **s23** ($CDCl_3$, 283 MHz).



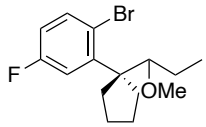


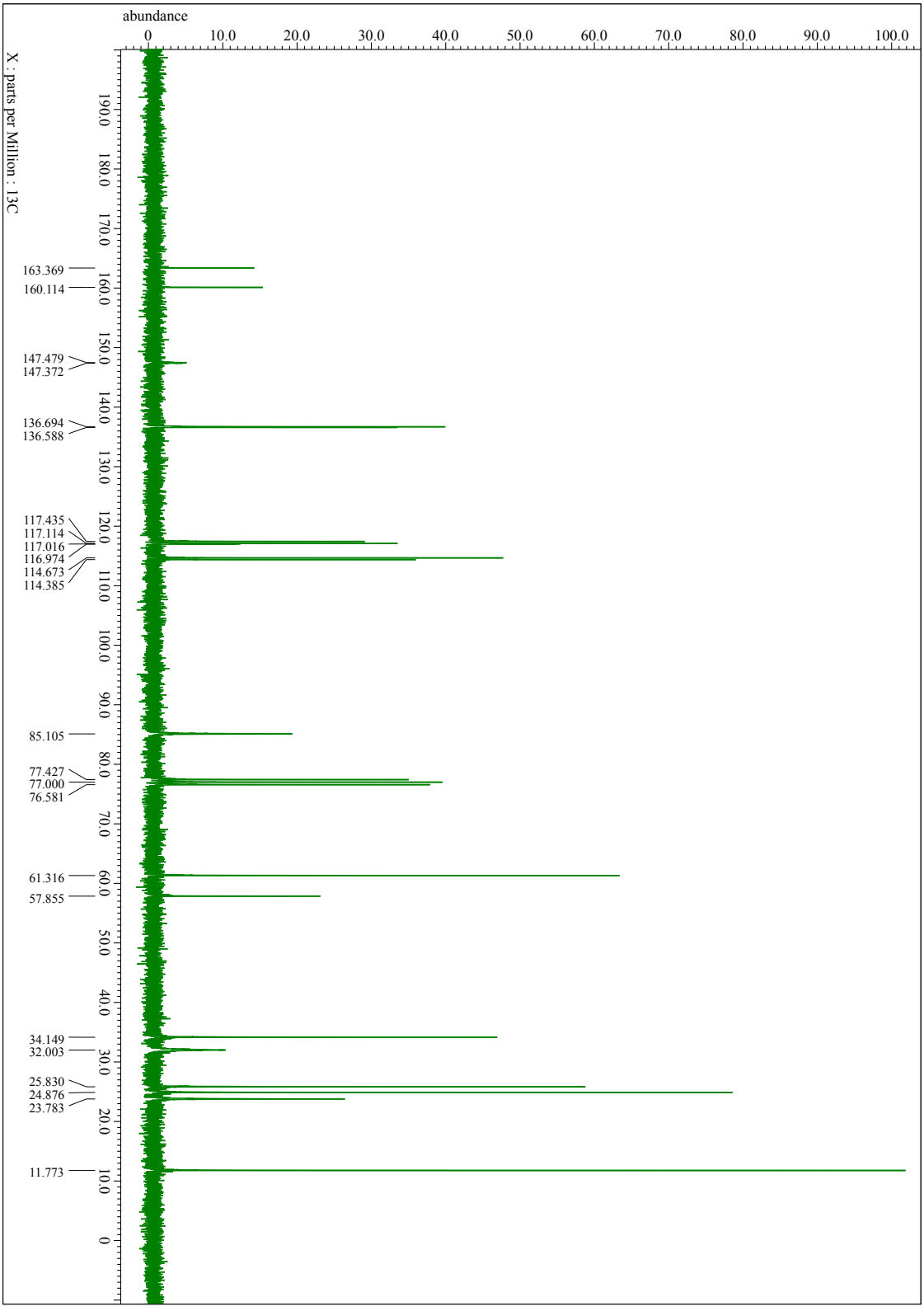
^{1}H NMR spectrum of **s24** ($CDCl_3$, 300 MHz).



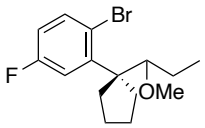


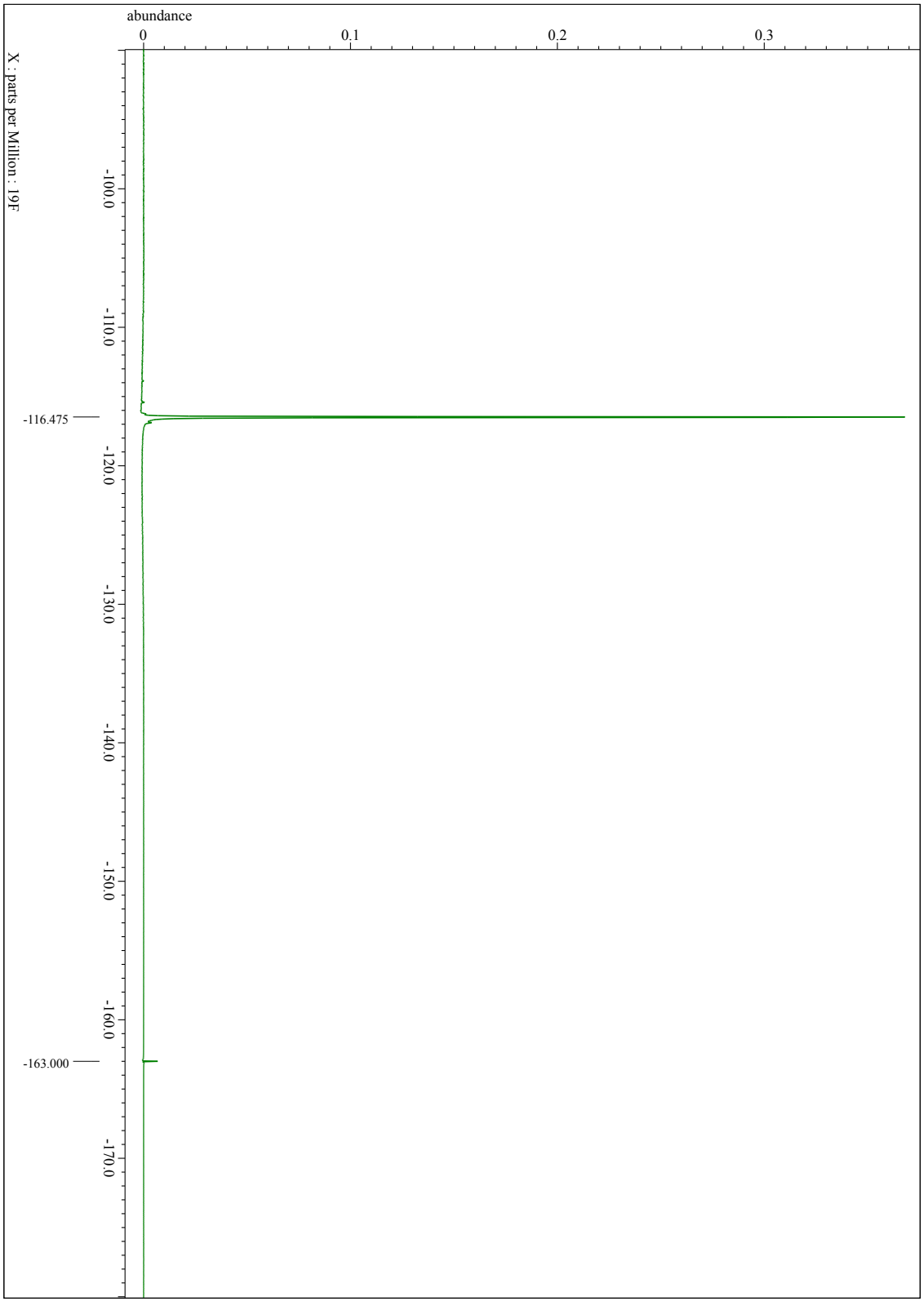
^{13}C NMR spectrum of **s24** ($CDCl_3$, 75 MHz).



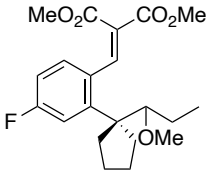


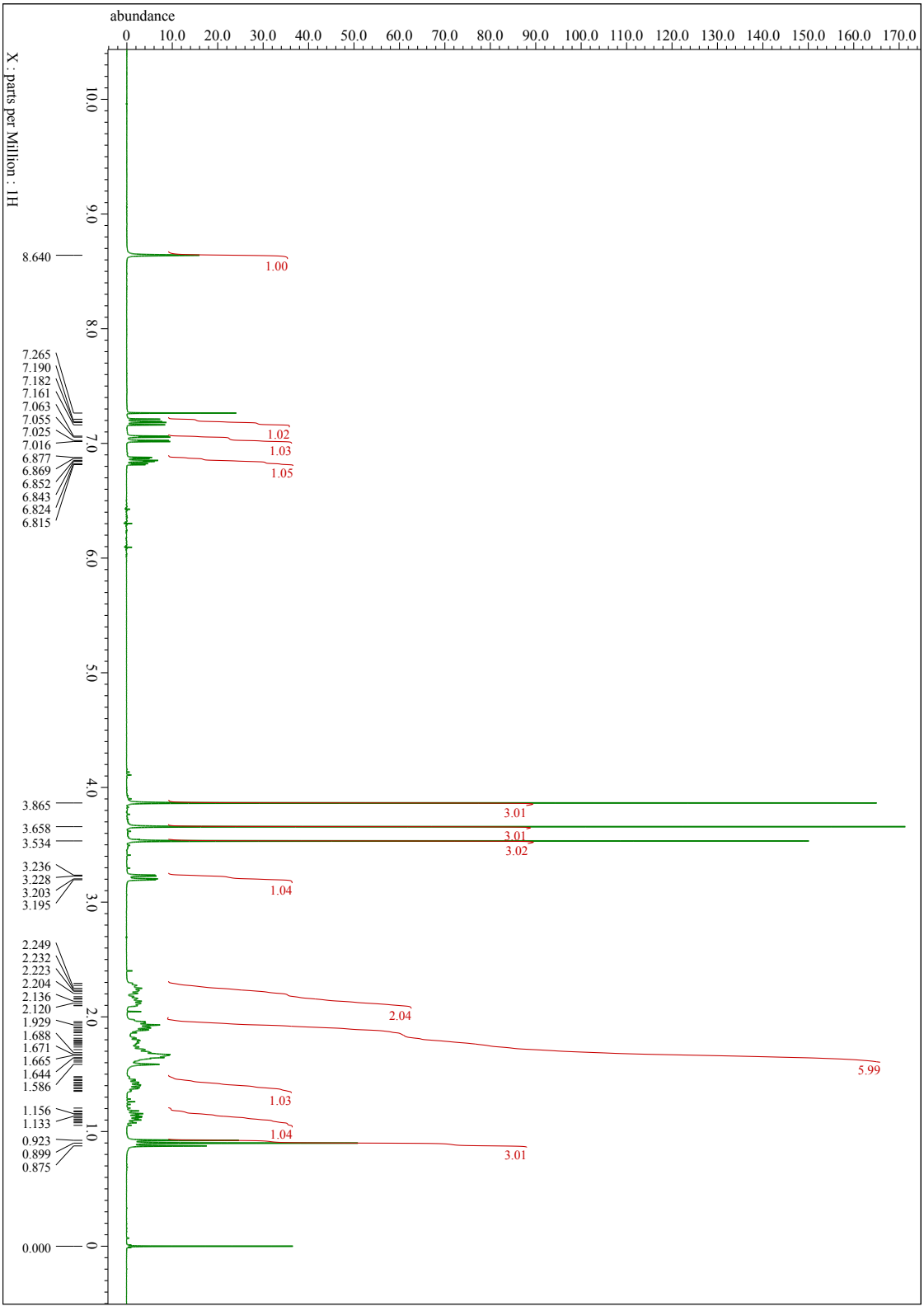
^{19}F NMR spectrum of **s24** ($CDCl_3$, 376 MHz).



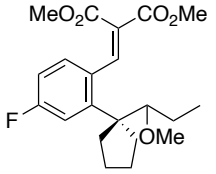


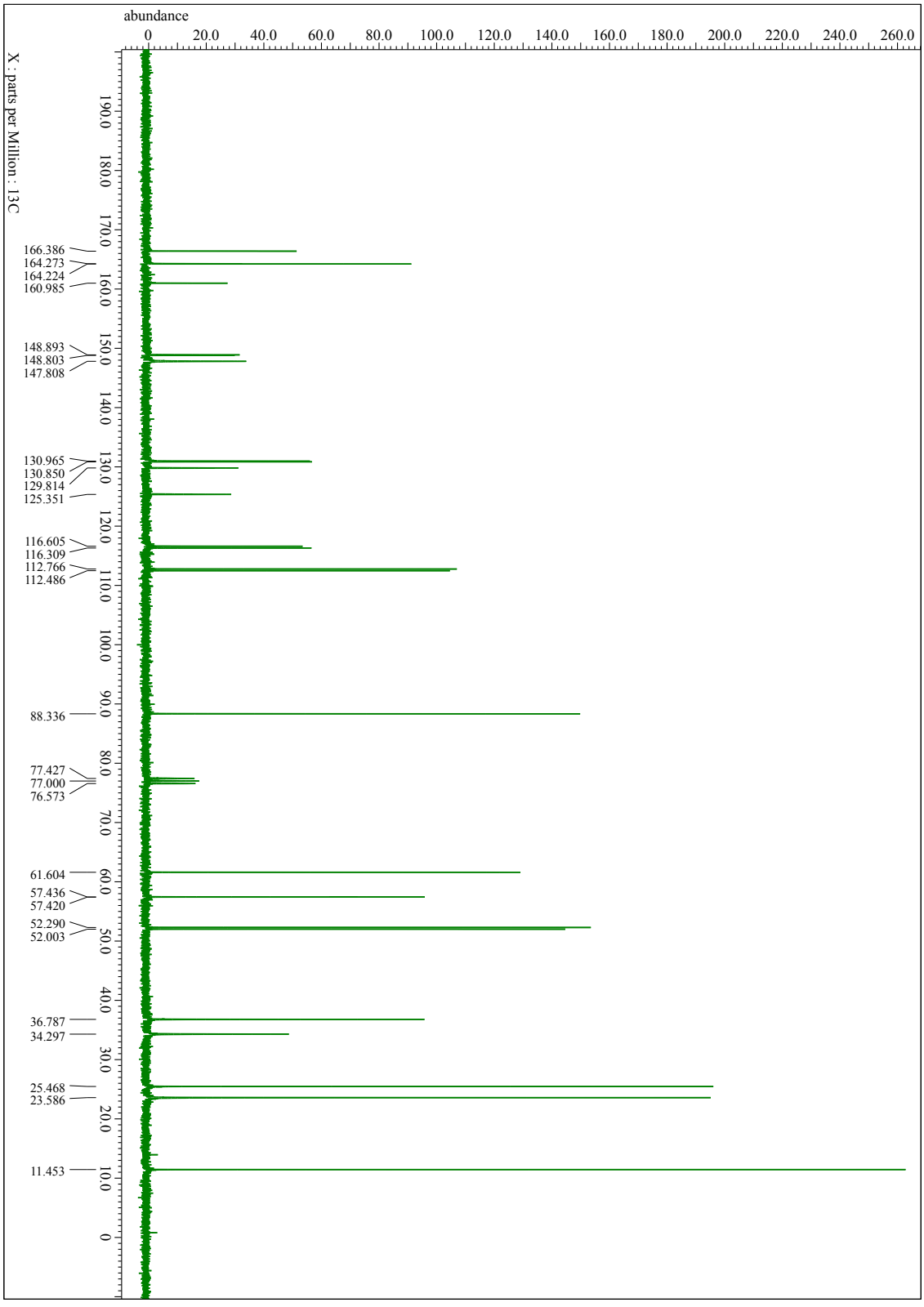
^{1}H NMR spectrum of **4l** ($CDCl_3$, 300 MHz).



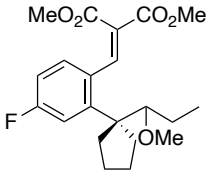


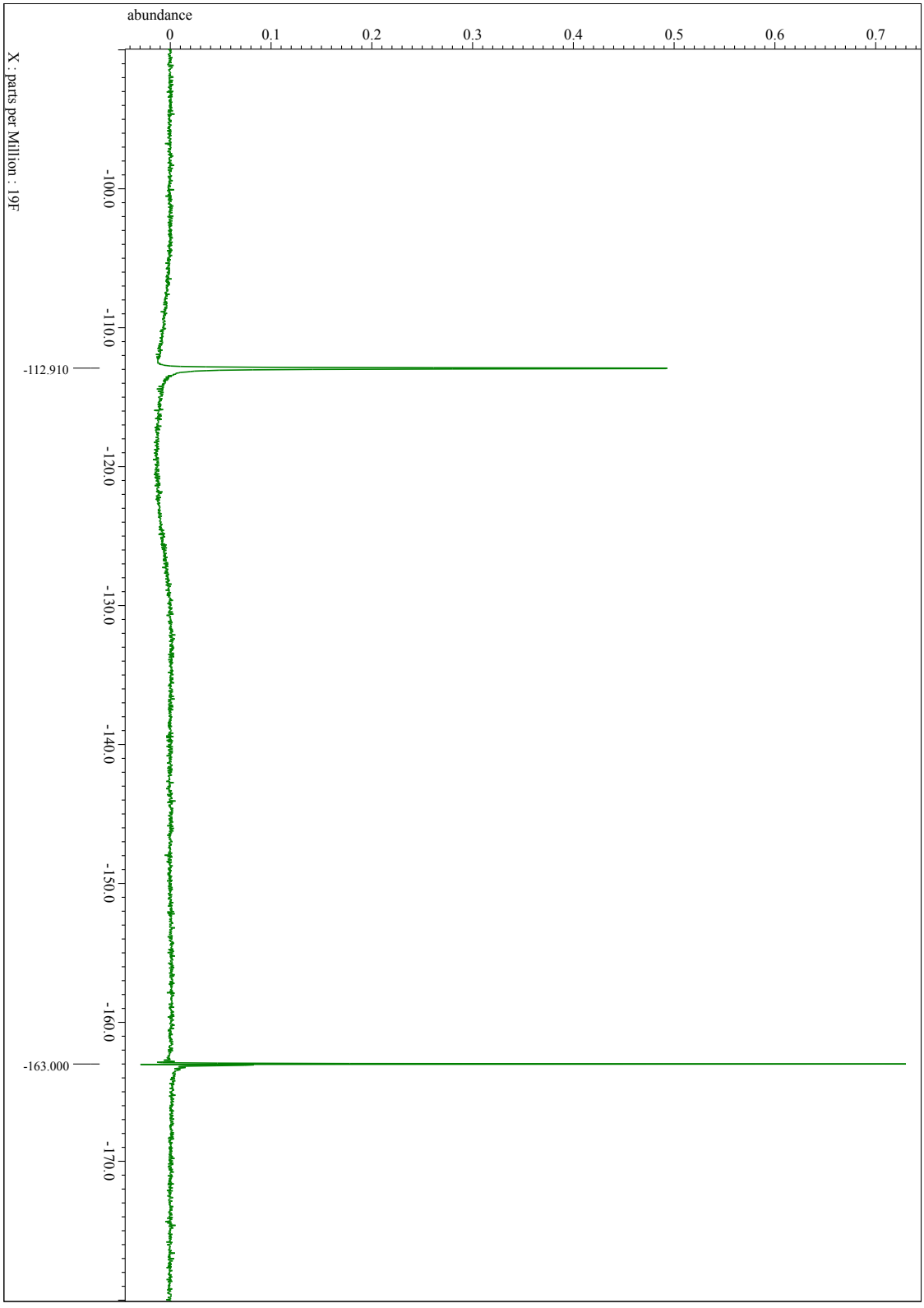
^{13}C NMR spectrum of **4l** ($CDCl_3$, 75 MHz).



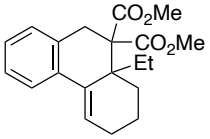


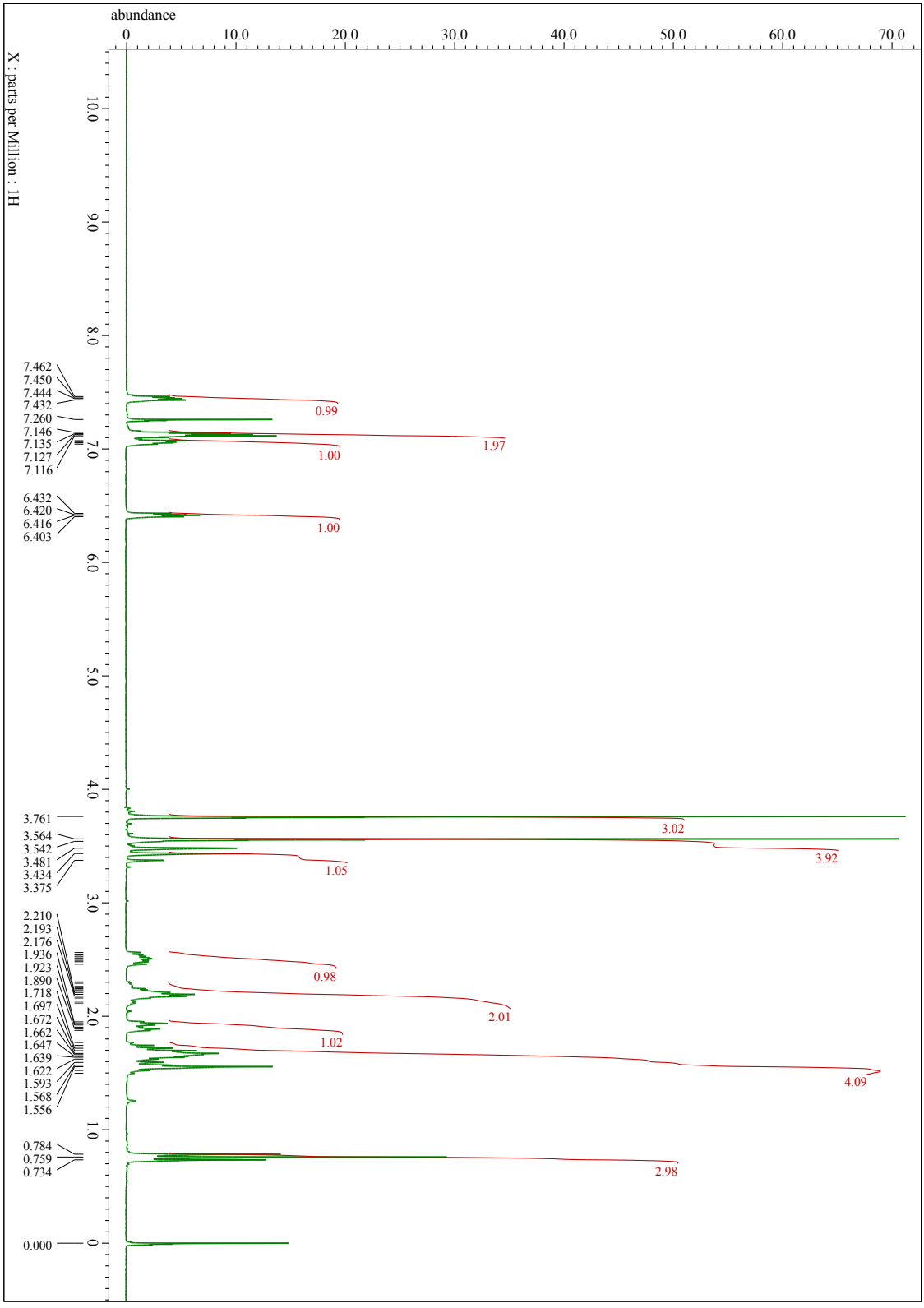
^{19}F NMR spectrum of **4l** ($CDCl_3$, 376 MHz).



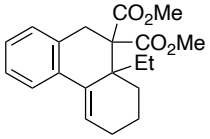


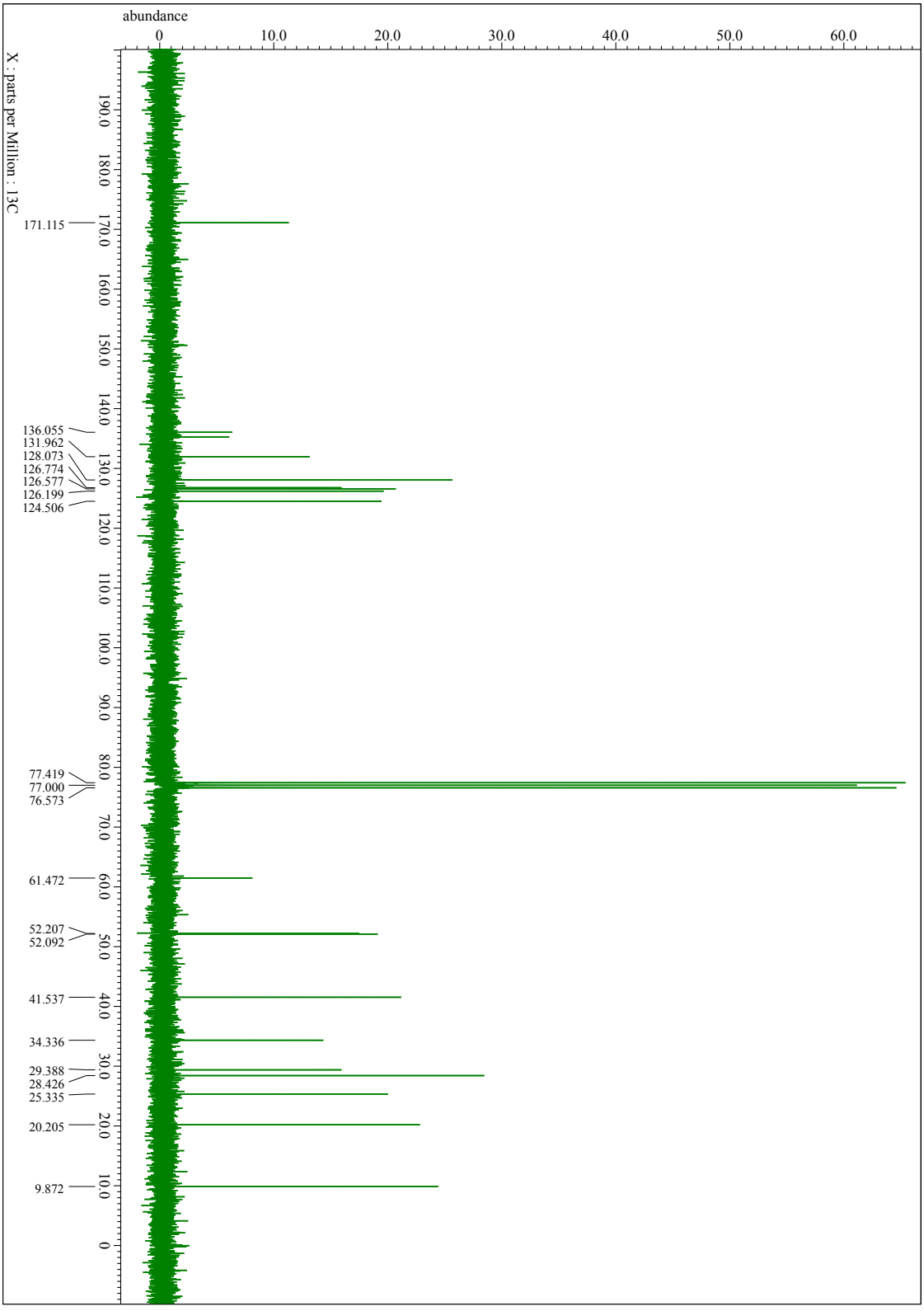
^{1}H NMR spectrum of **6a** ($CDCl_3$, 300 MHz).



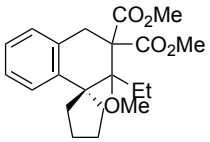


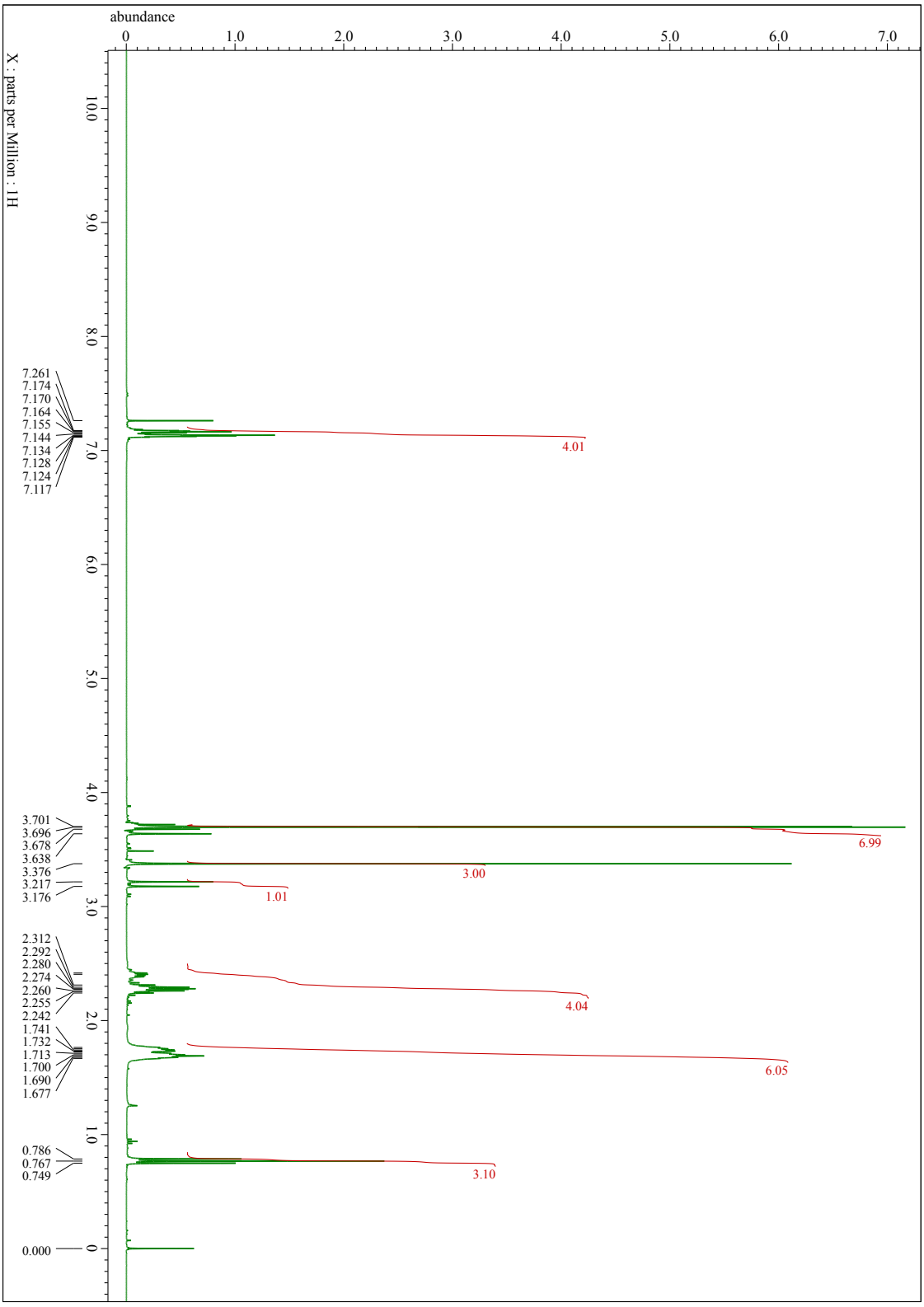
^{13}C NMR spectrum of **6a** ($CDCl_3$, 75 MHz).



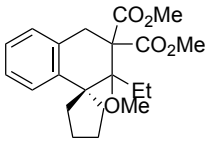


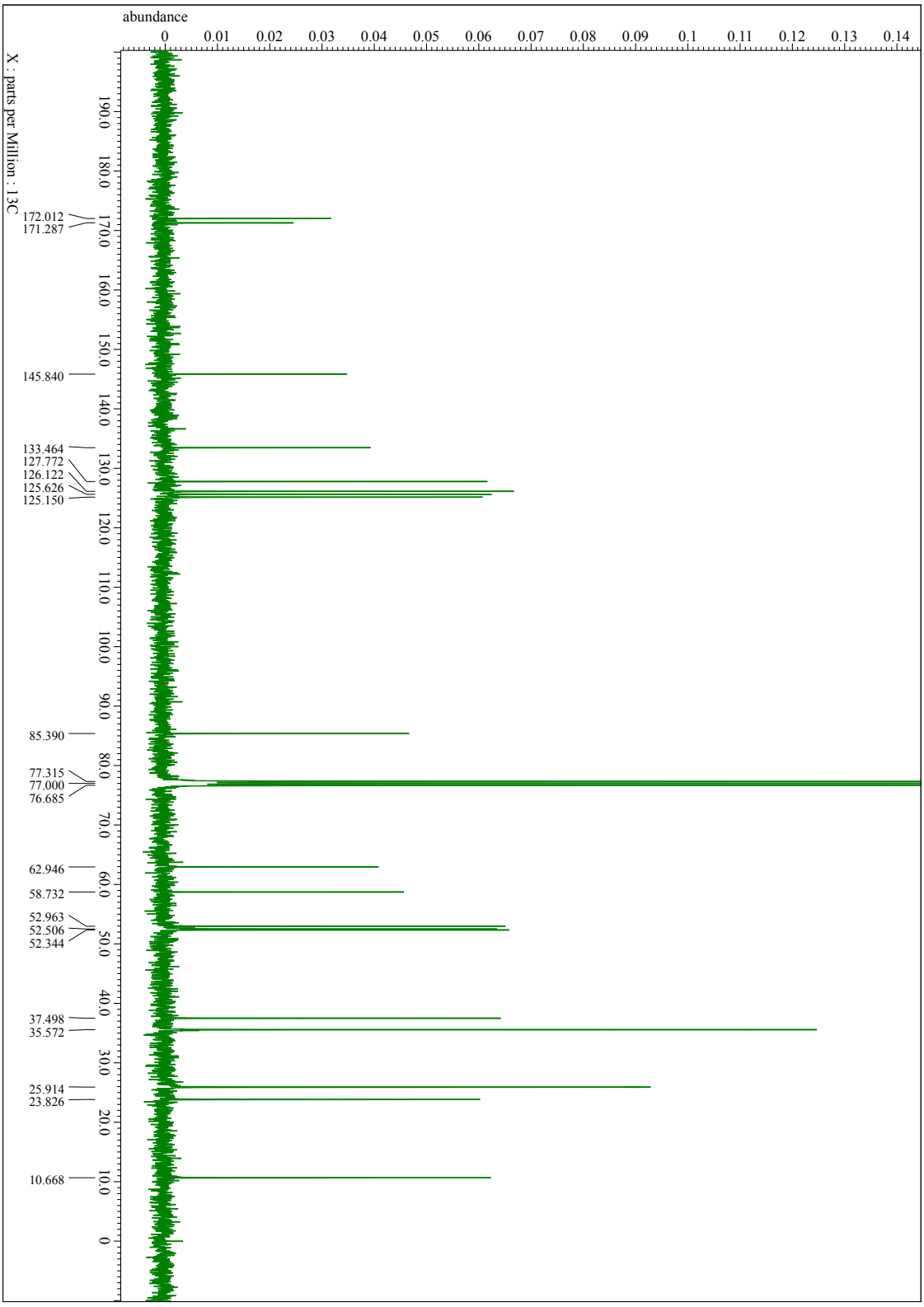
^{1}H NMR spectrum of **5a** ($CDCl_3$, 400 MHz).



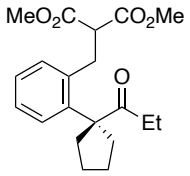


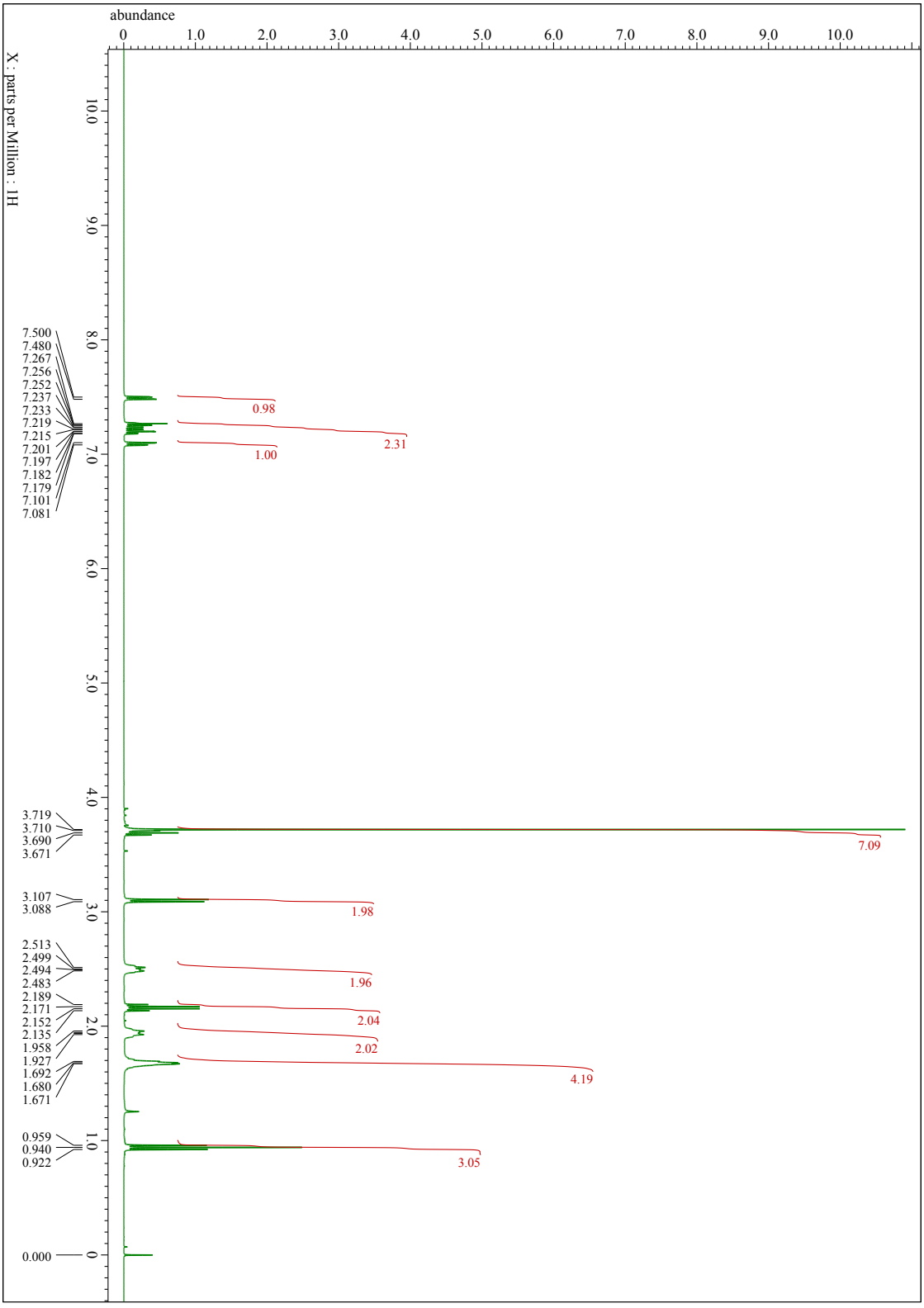
^{13}C NMR spectrum of **5a** ($CDCl_3$, 100 MHz).



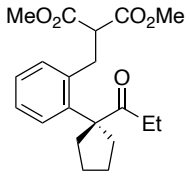


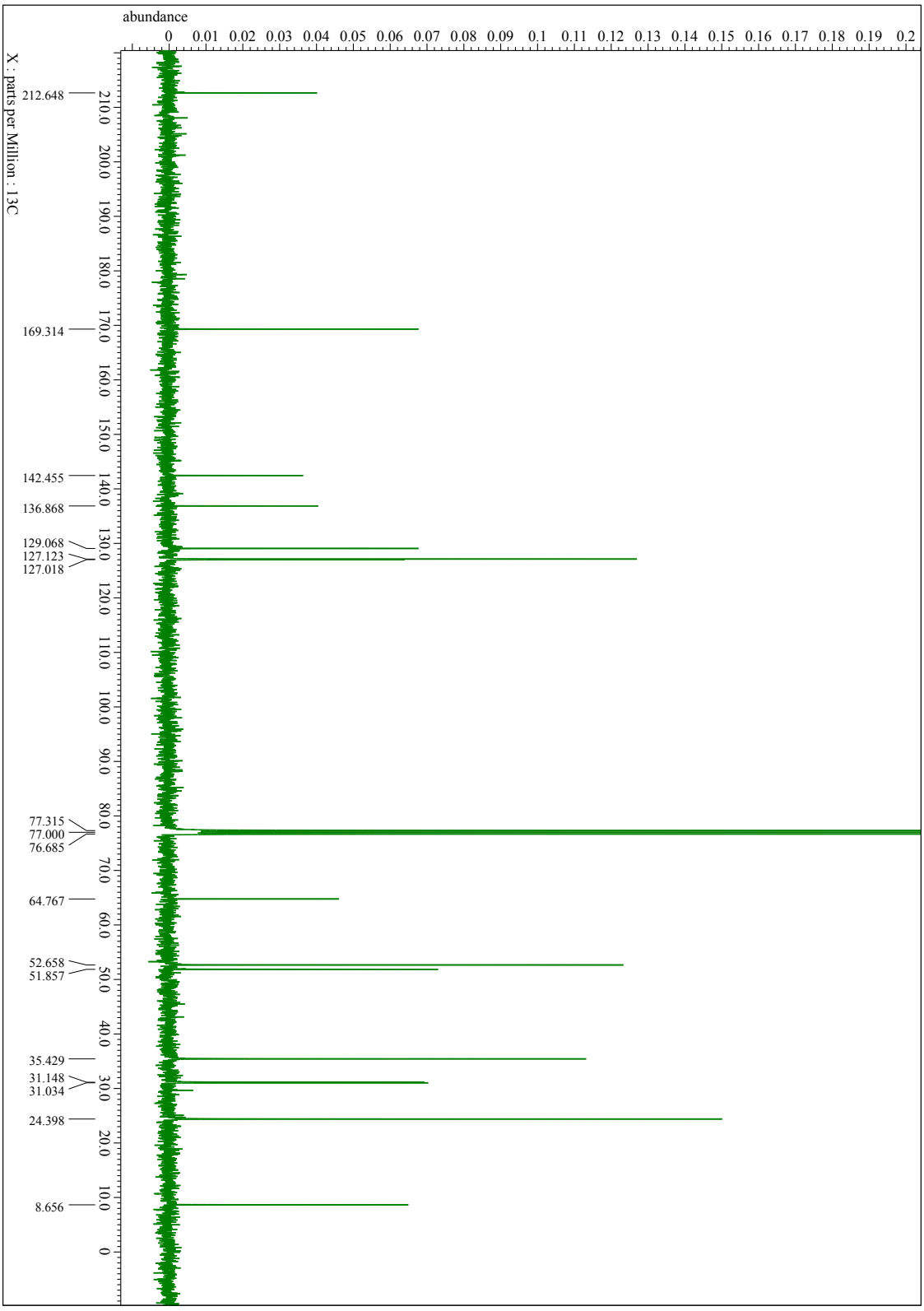
^{1}H NMR spectrum of **8** ($CDCl_3$, 400 MHz).



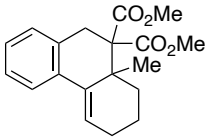


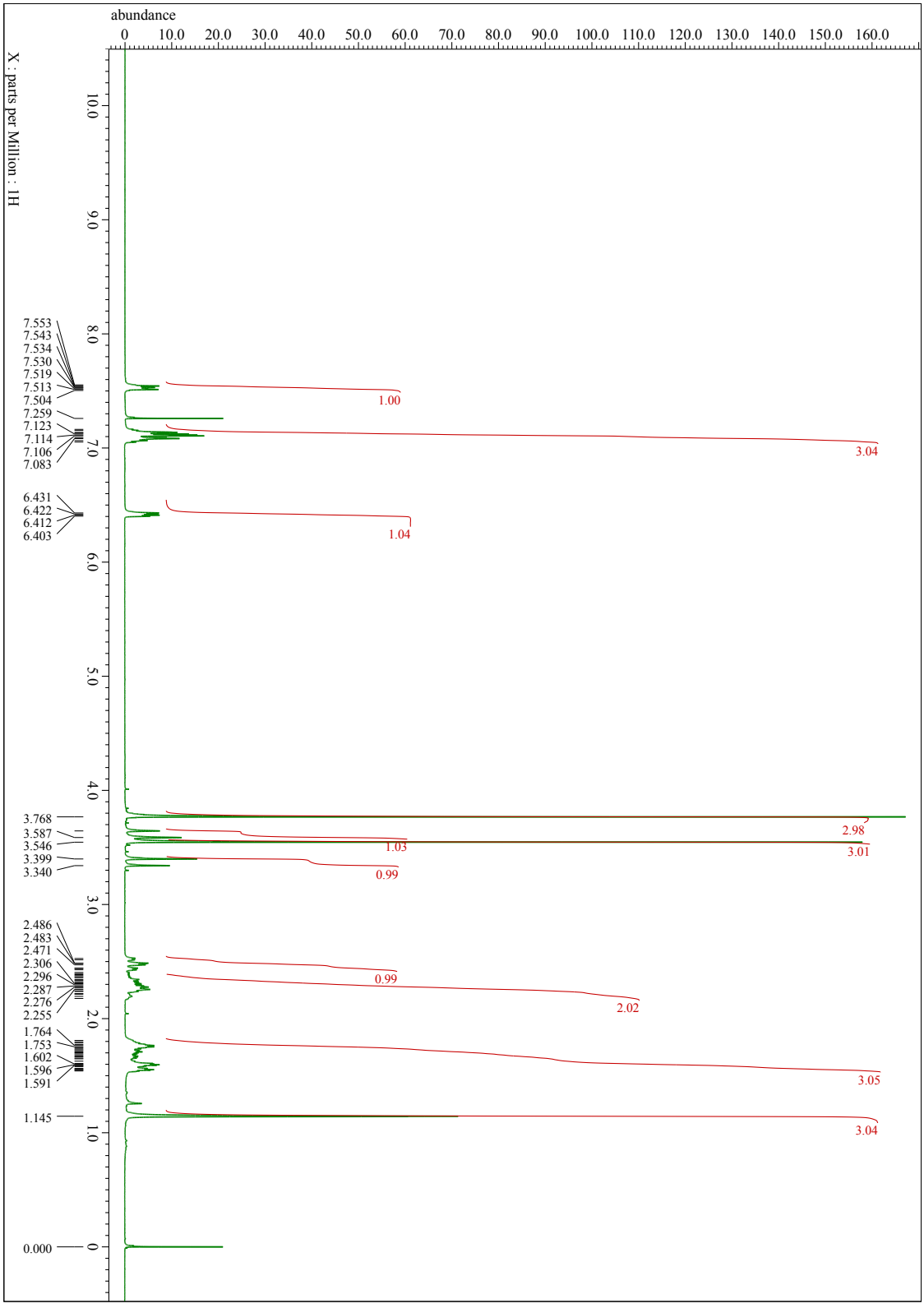
^{13}C NMR spectrum of **8** ($CDCl_3$, 100 MHz).



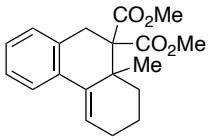


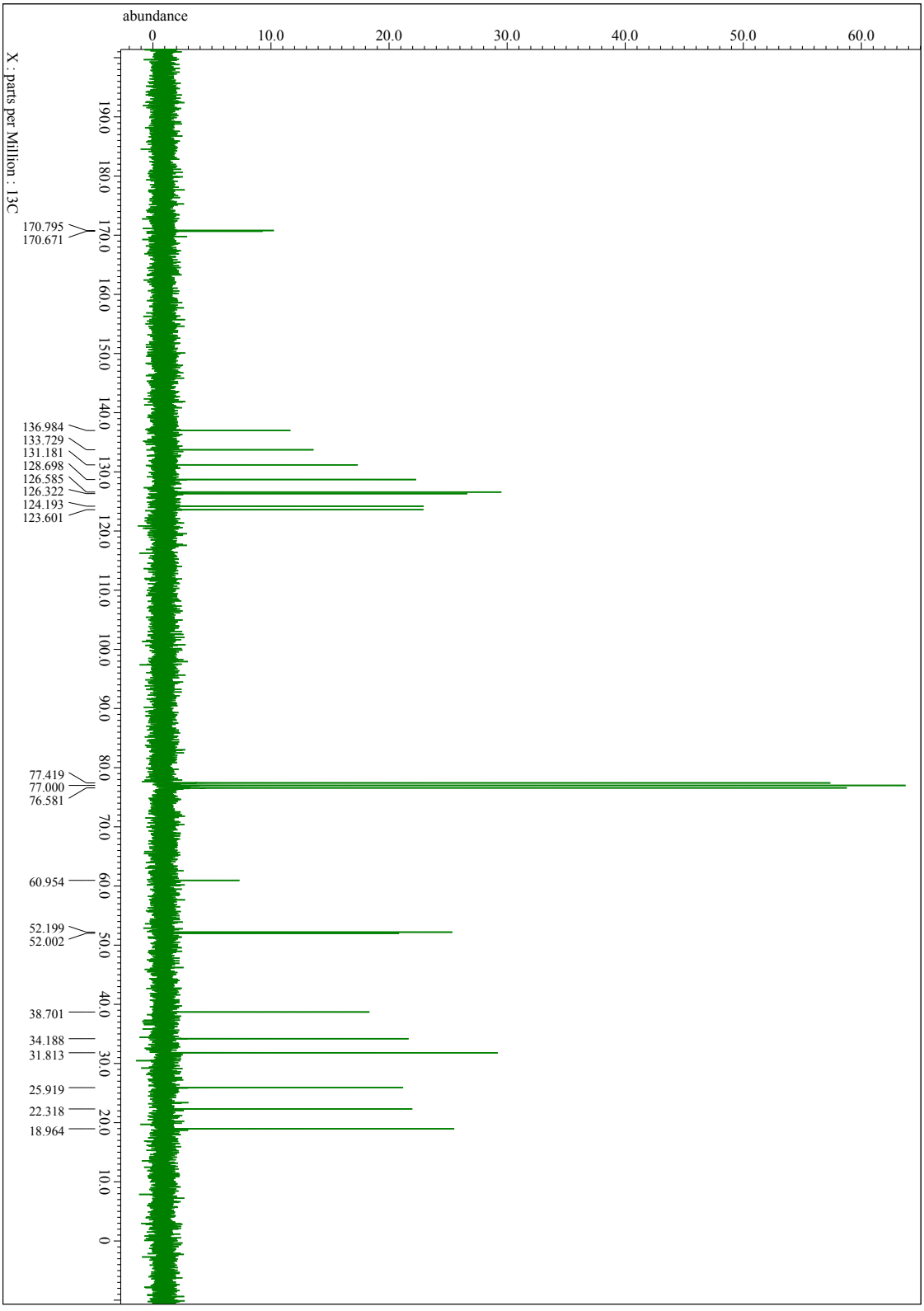
^{1}H NMR spectrum of **6b** ($CDCl_3$, 300 MHz).



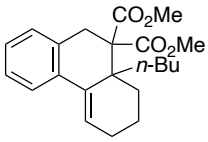


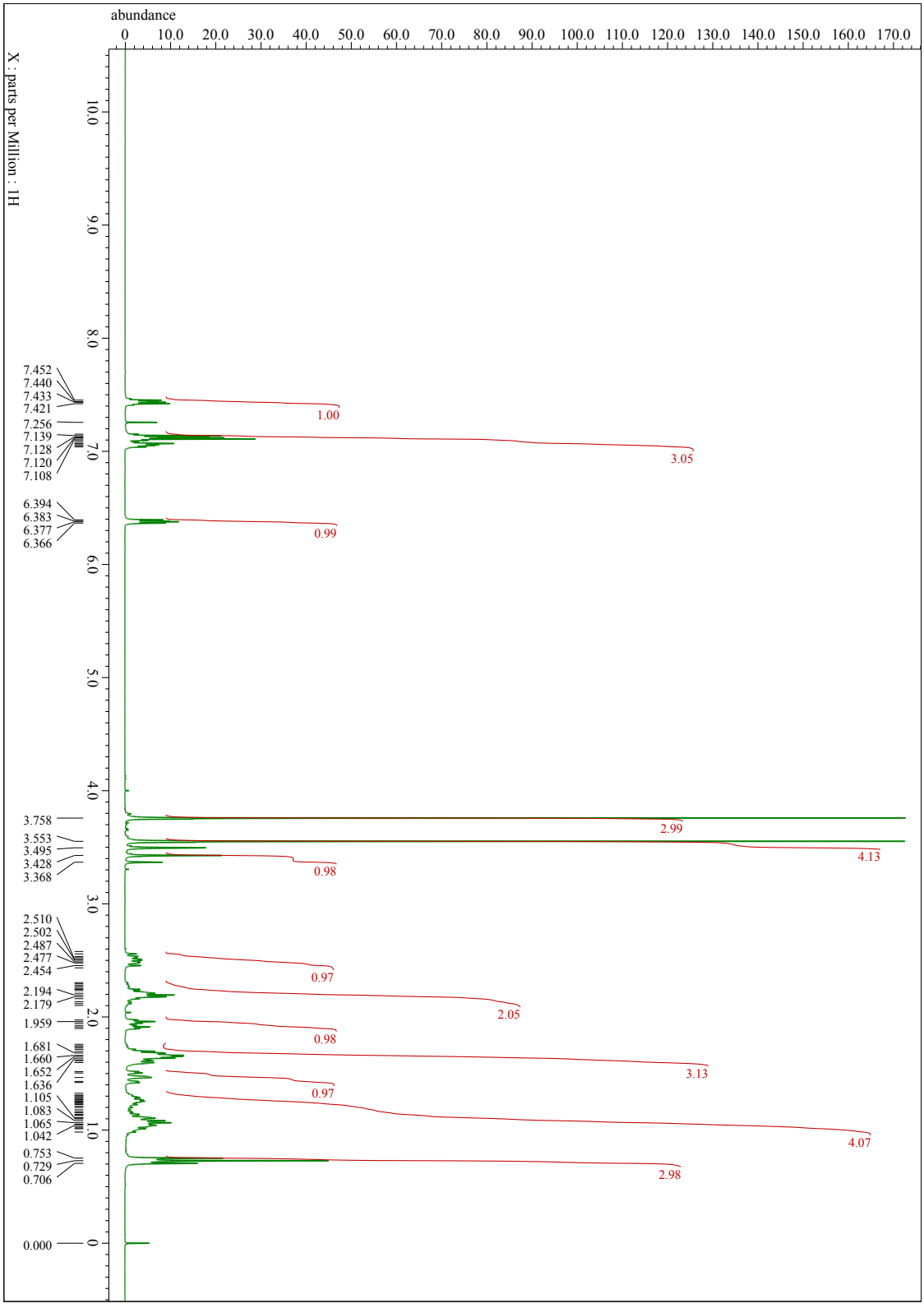
^{13}C NMR spectrum of **6b** ($CDCl_3$, 75 MHz).



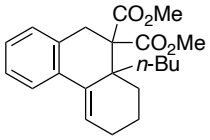


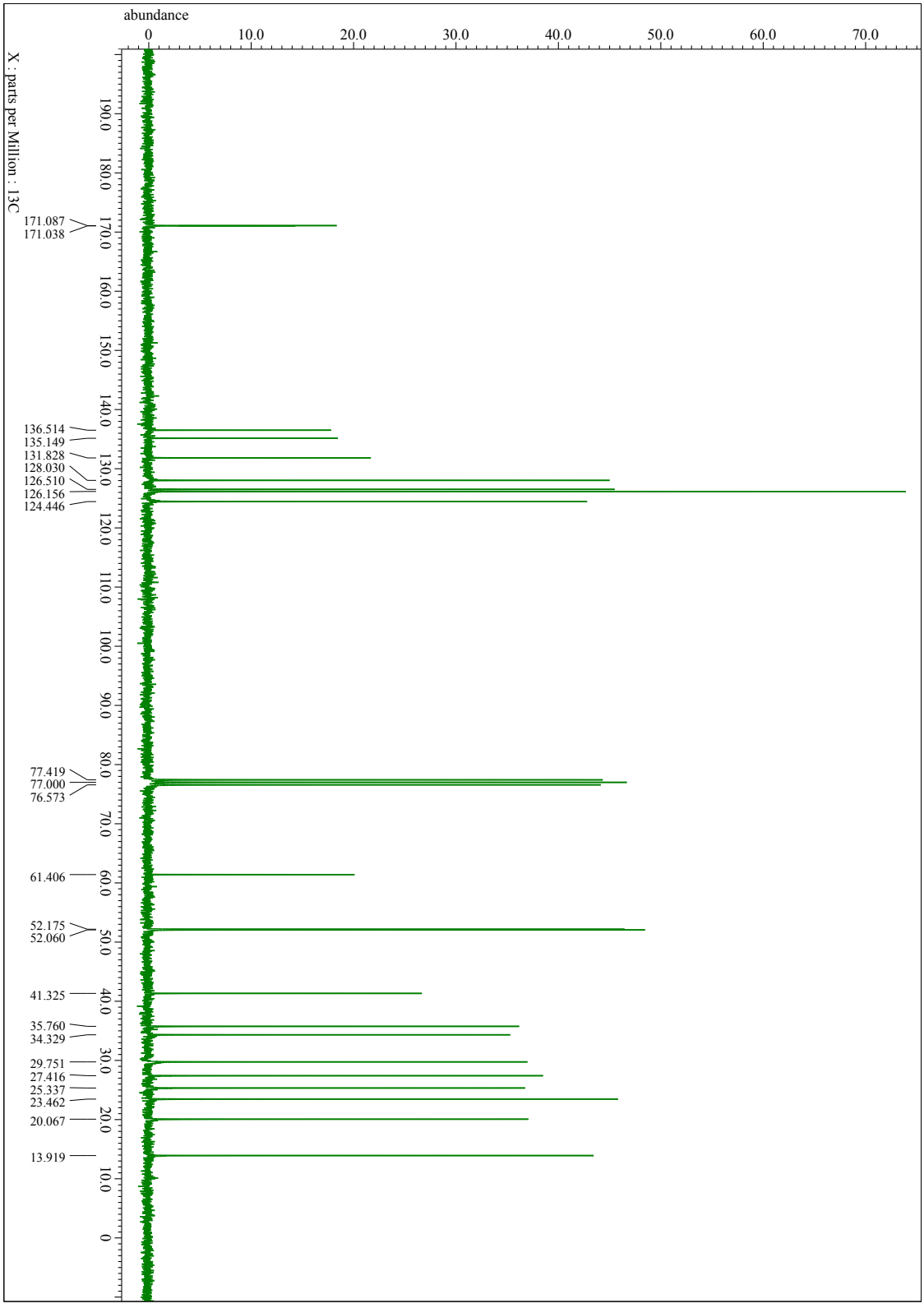
^{1}H NMR spectrum of **6c** ($CDCl_3$, 300 MHz).



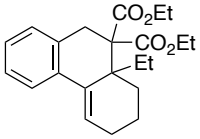


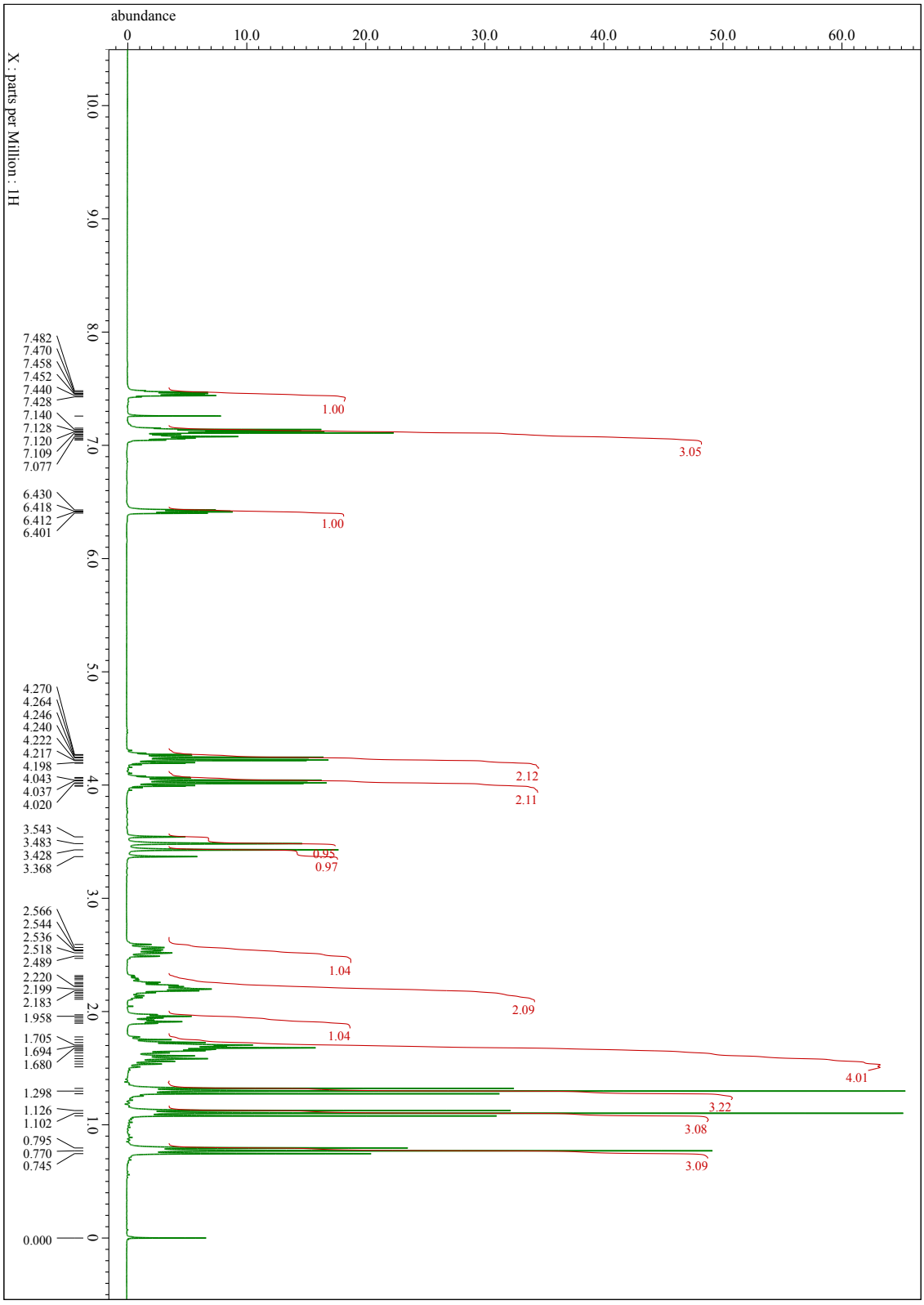
^{13}C NMR spectrum of **6c** ($CDCl_3$, 75 MHz).



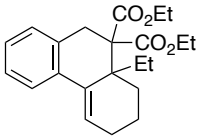


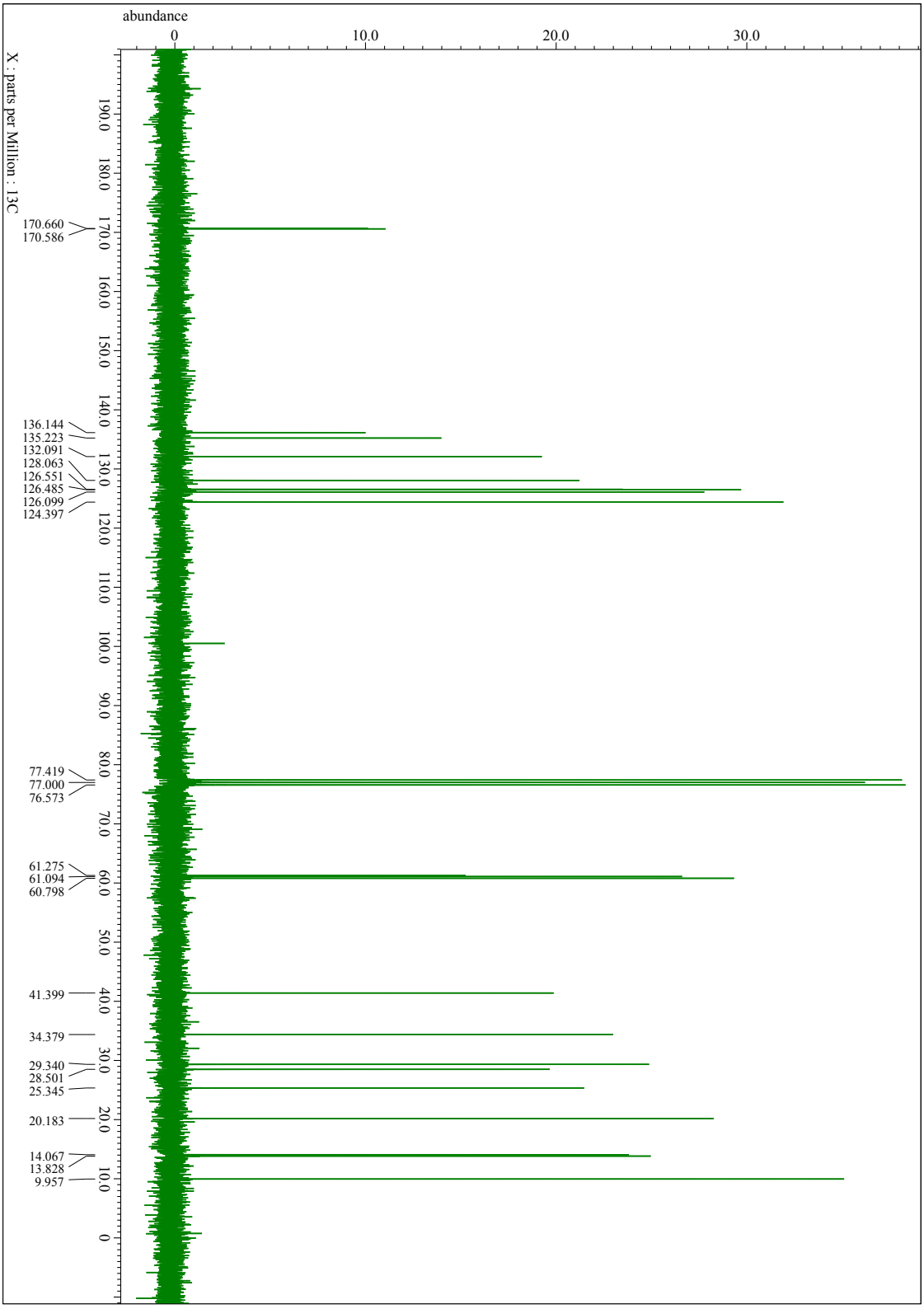
^{1}H NMR spectrum of **6d** ($CDCl_3$, 300 MHz).



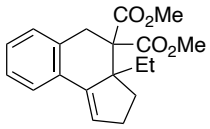


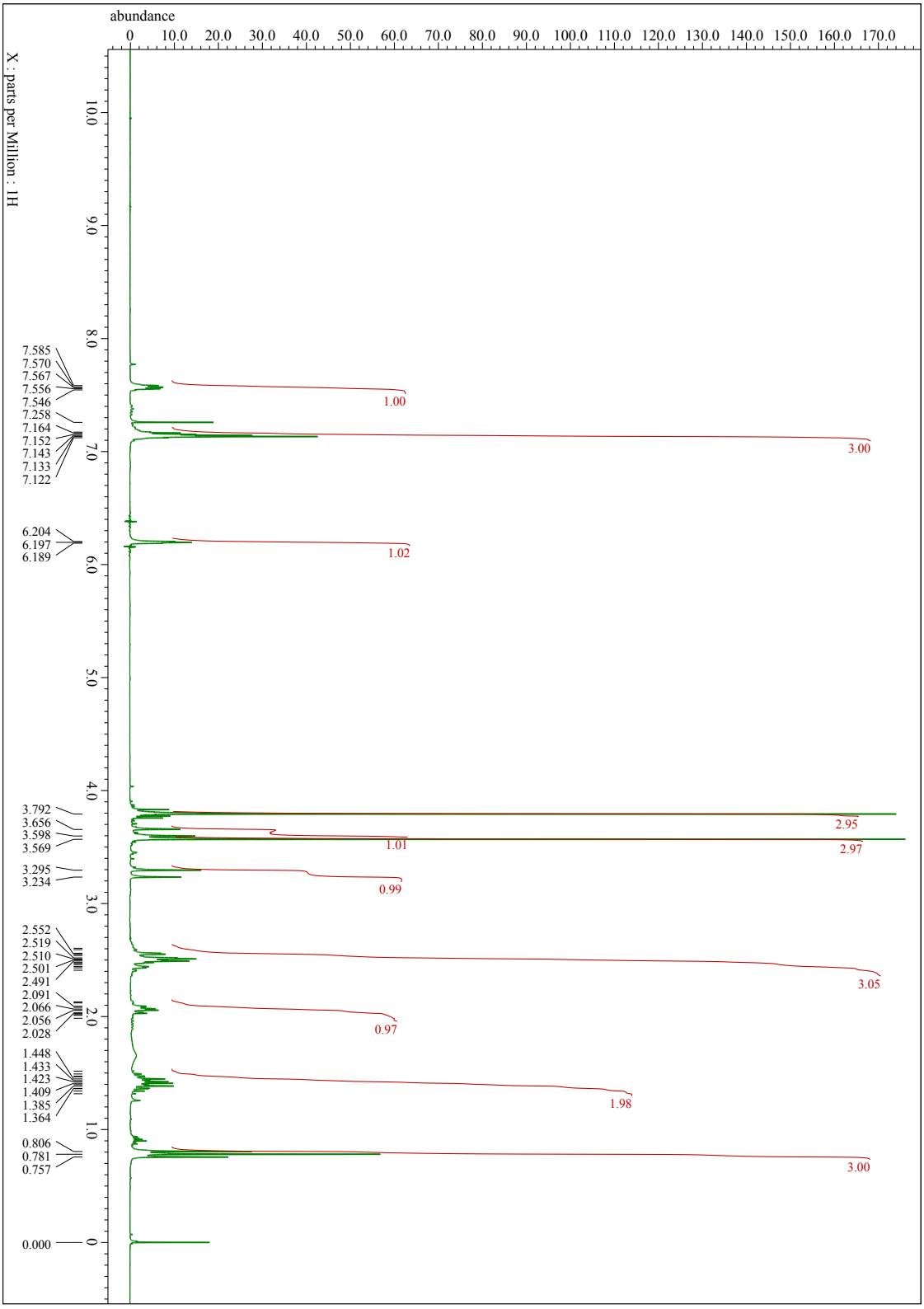
^{13}C NMR spectrum of **6d** ($CDCl_3$, 75 MHz).



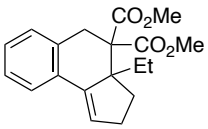


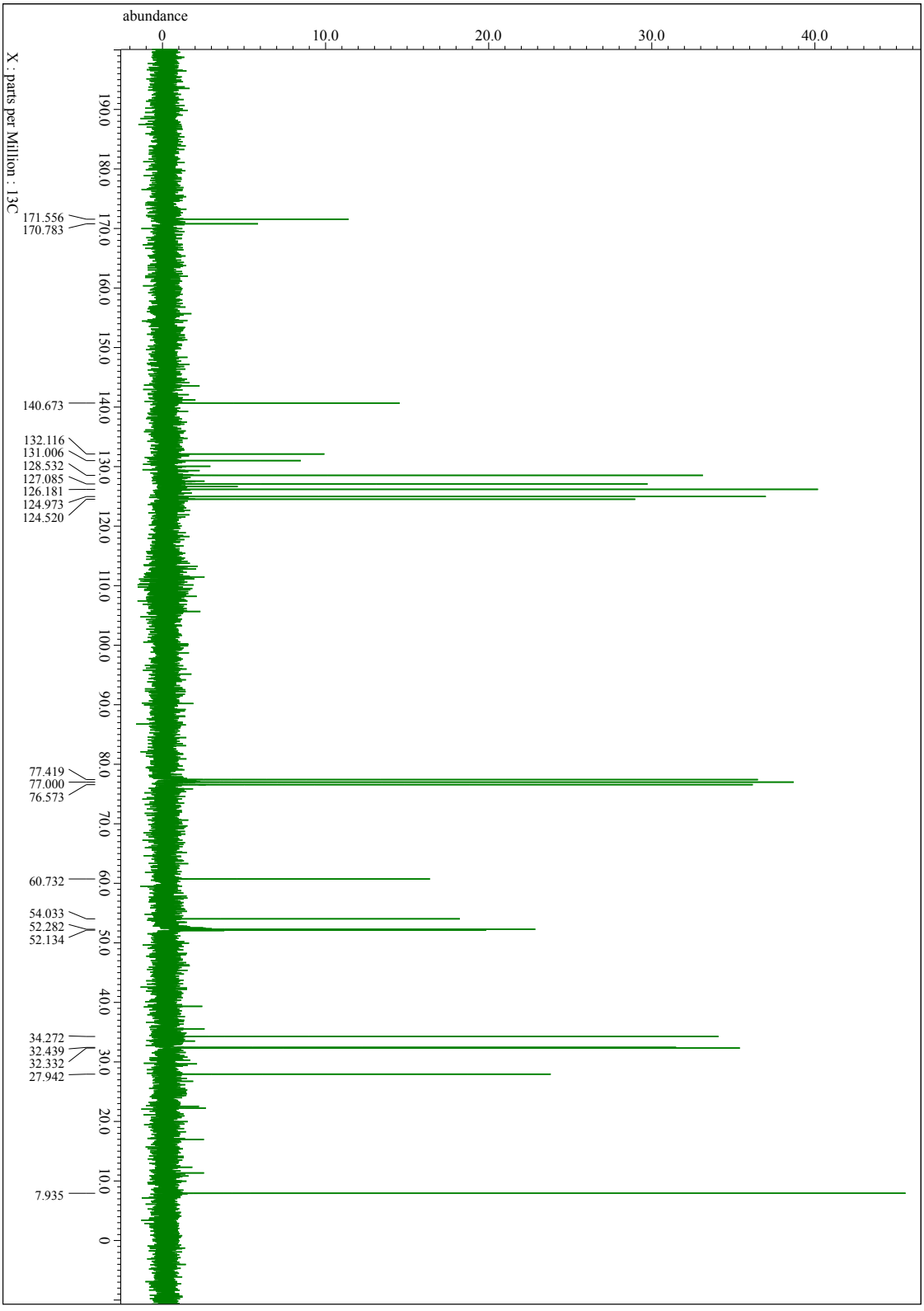
^{1}H NMR spectrum of **6e** ($CDCl_3$, 300 MHz).



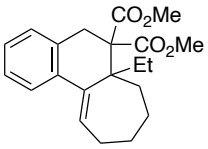


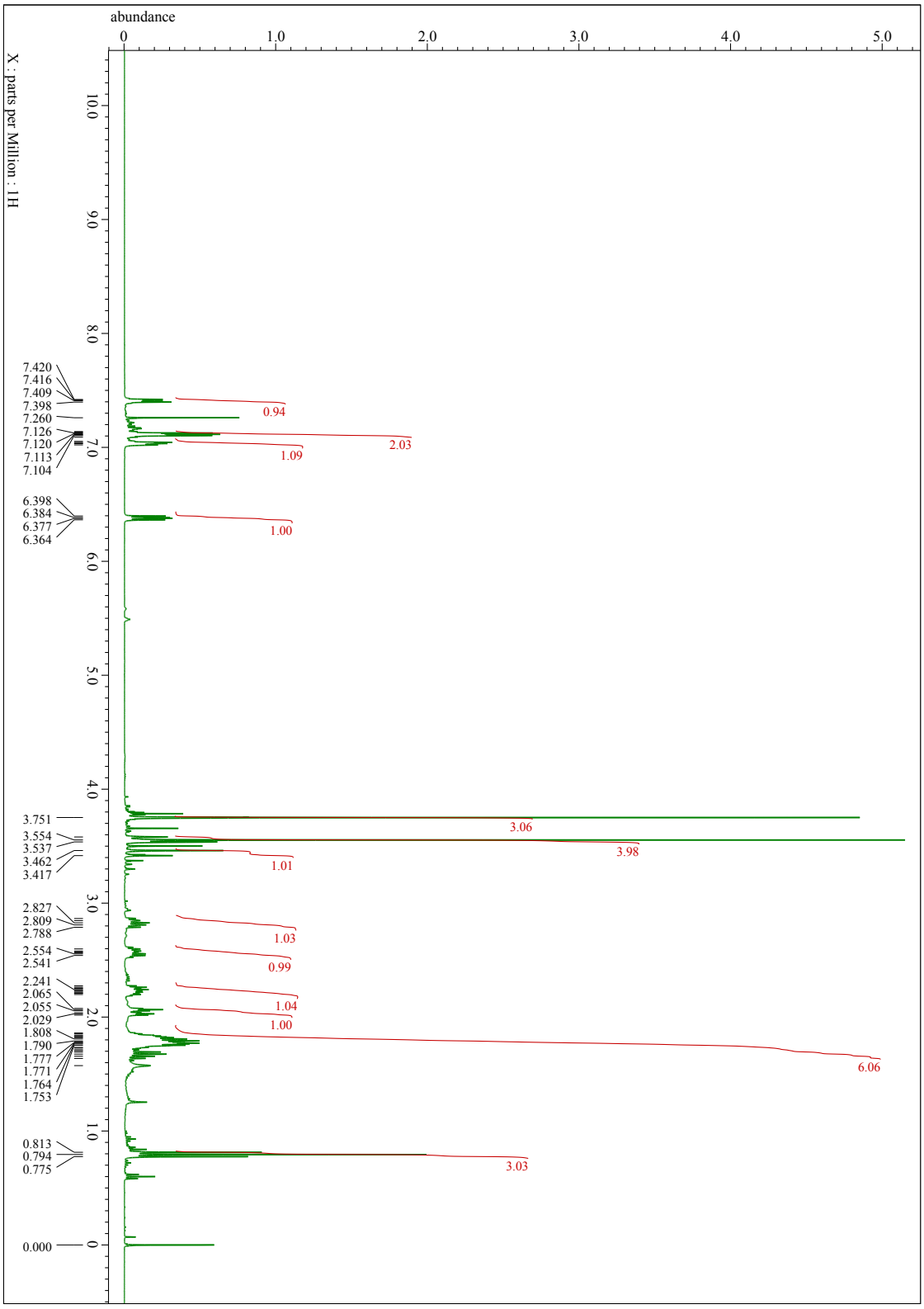
^{13}C NMR spectrum of **6e** ($CDCl_3$, 75 MHz).



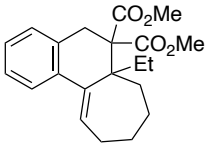


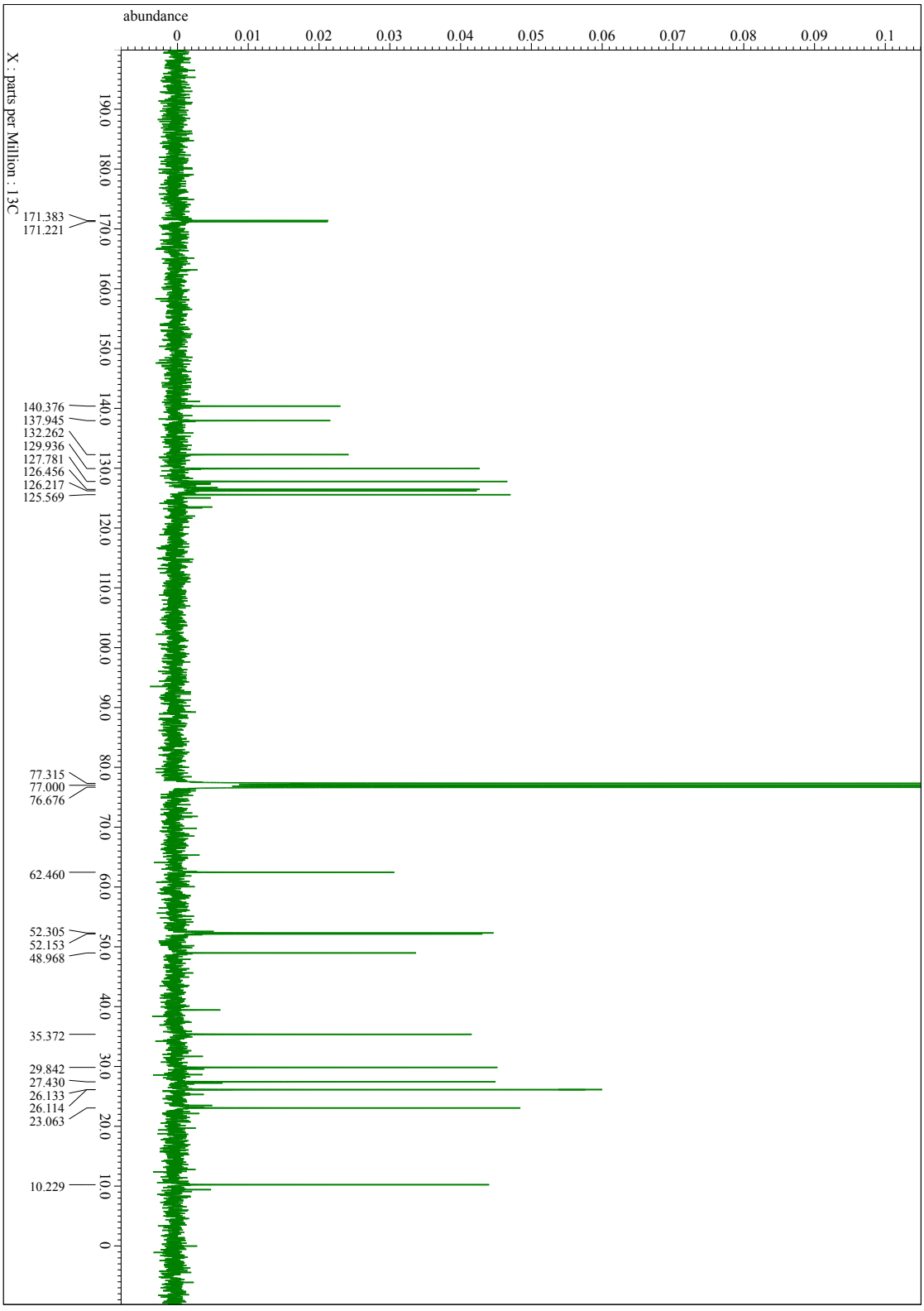
^{1}H NMR spectrum of **6f** ($CDCl_3$, 400 MHz).



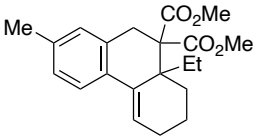


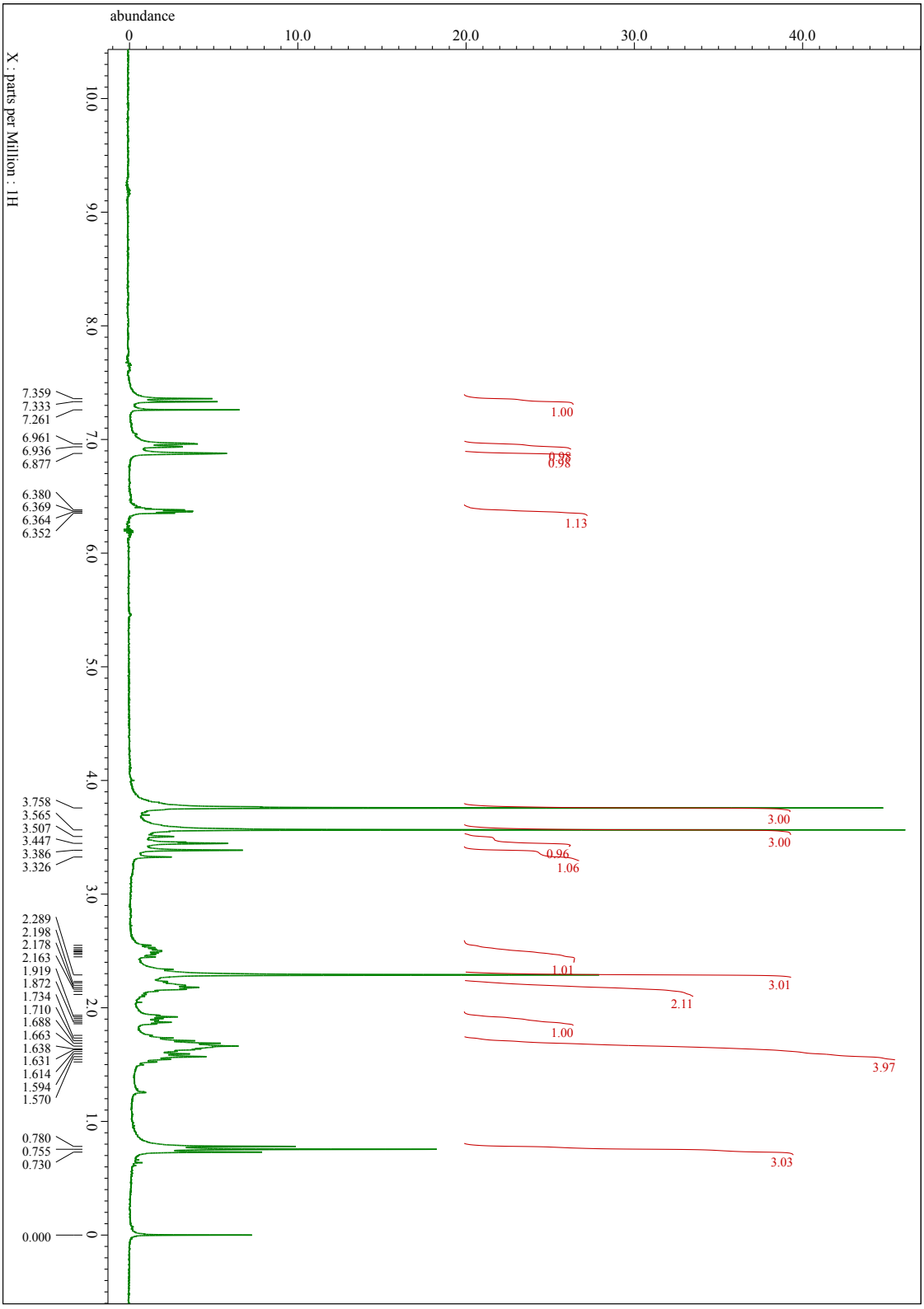
^{13}C NMR spectrum of **6f** ($CDCl_3$, 100 MHz).



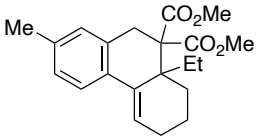


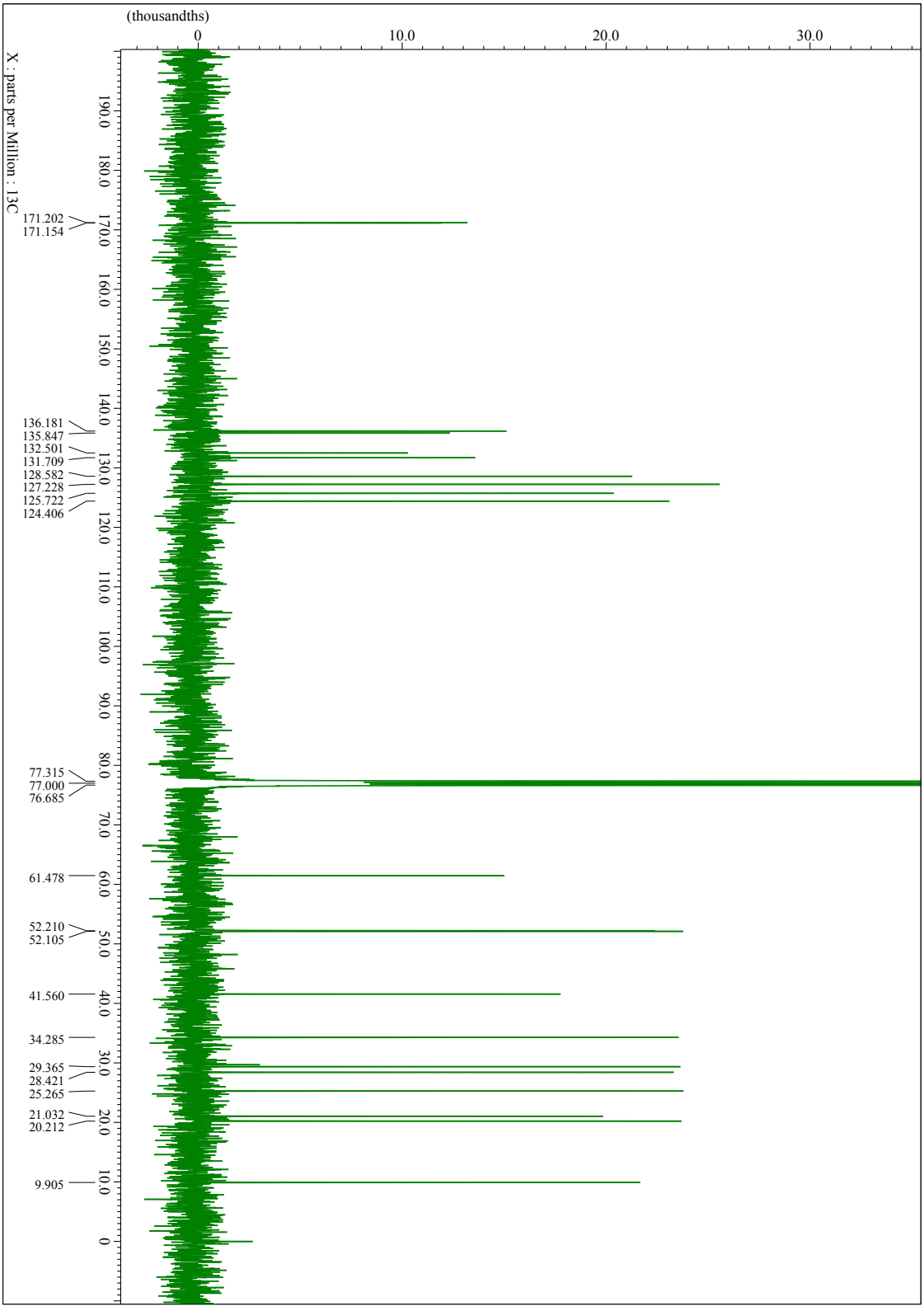
^{1}H NMR spectrum of **6g** ($CDCl_3$, 300 MHz).



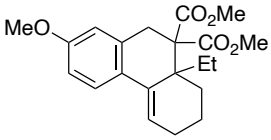


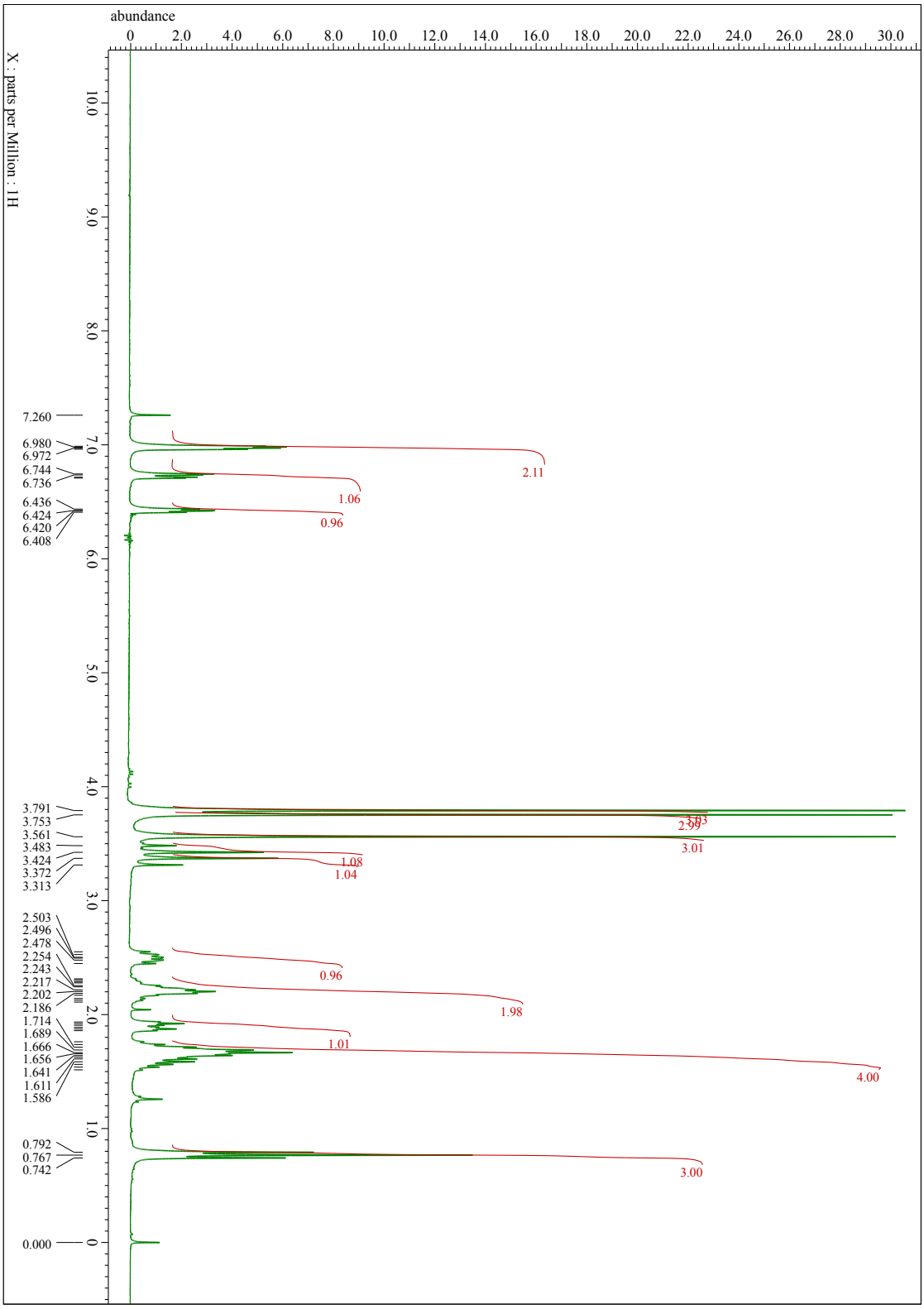
^{13}C NMR spectrum of **6g** ($CDCl_3$, 75 MHz).



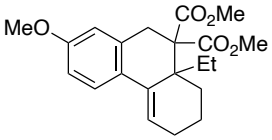


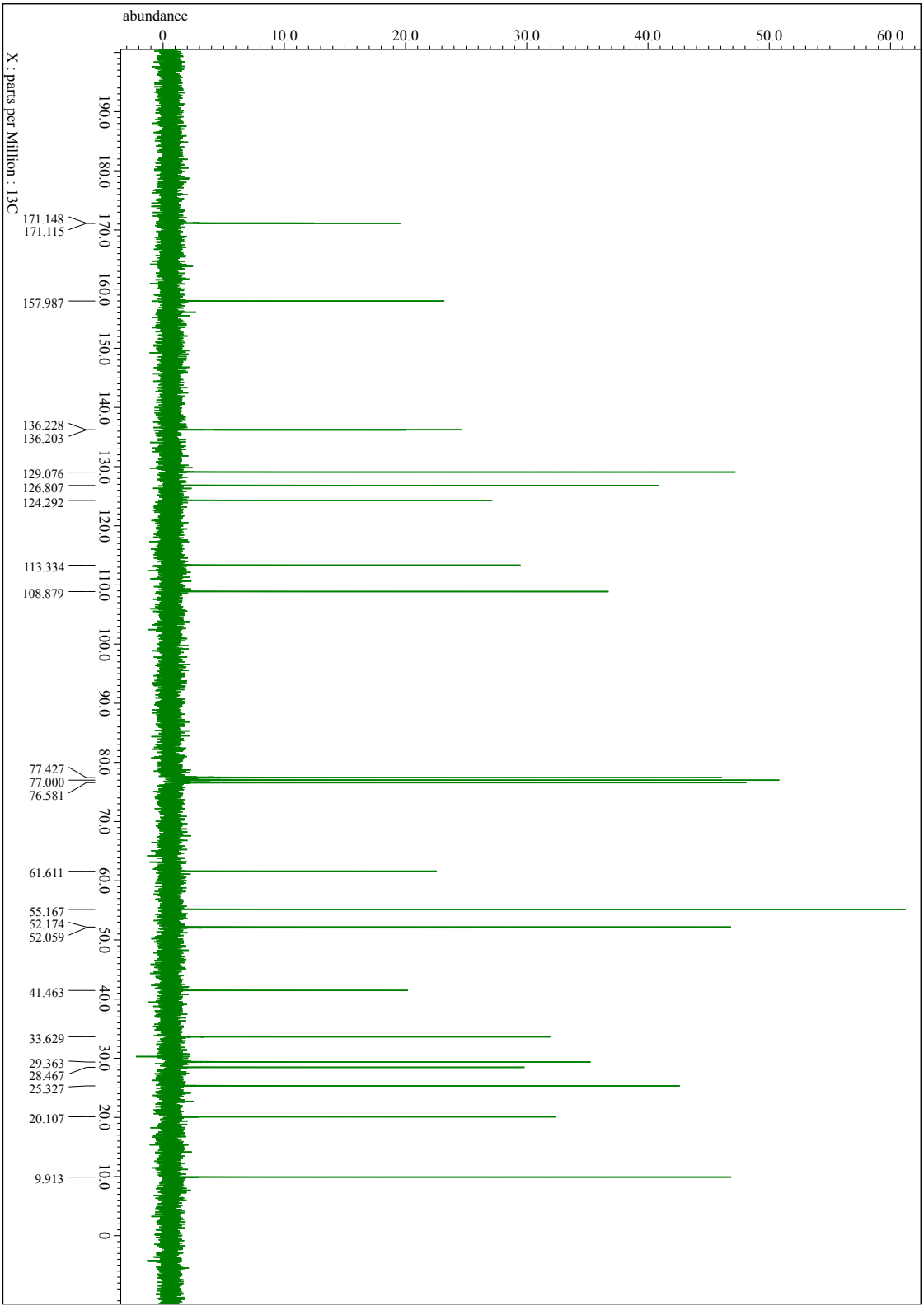
^{1}H NMR spectrum of **6h** ($CDCl_3$, 300 MHz).



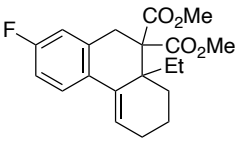


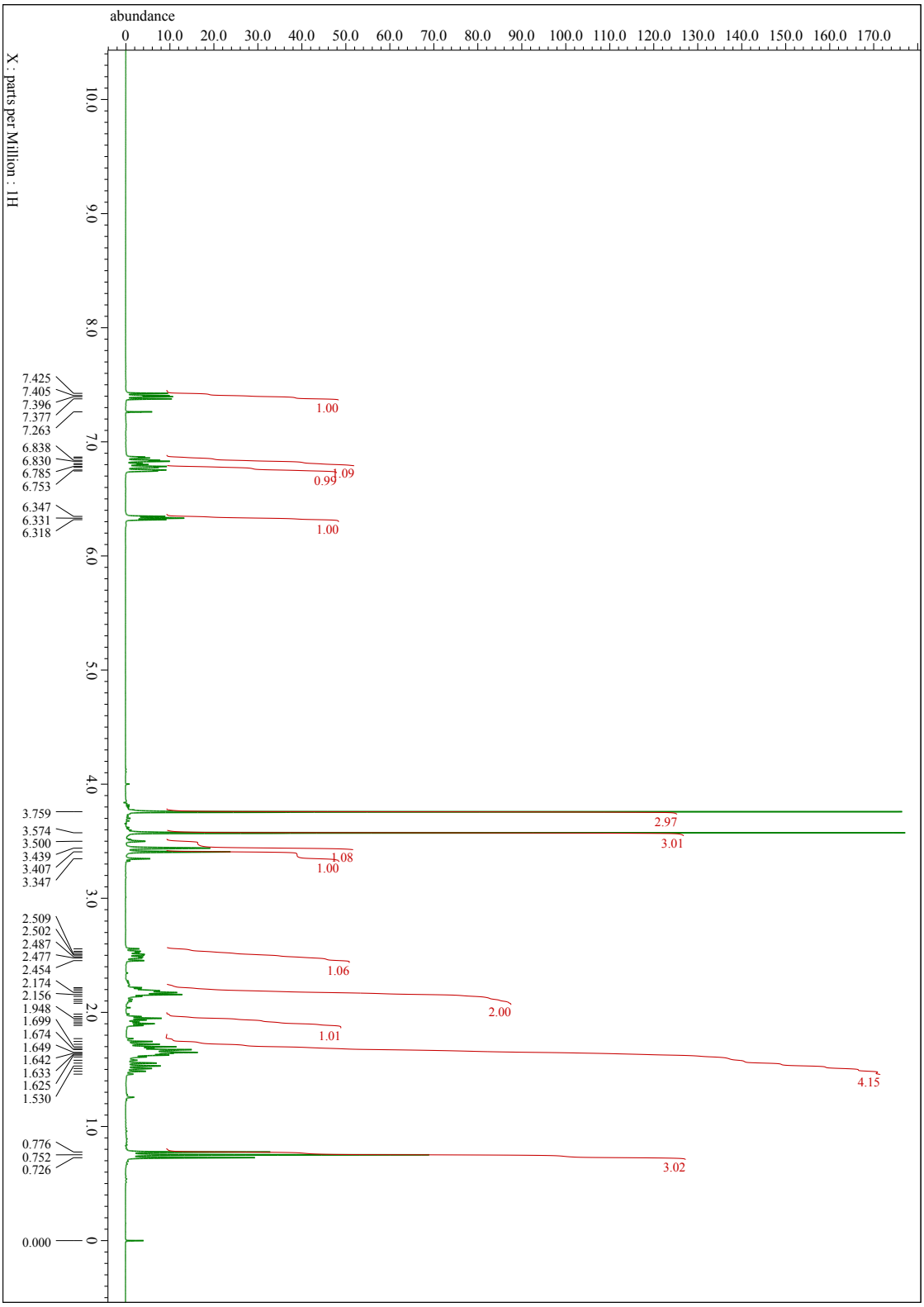
^{13}C NMR spectrum of **6h** ($CDCl_3$, 75 MHz).



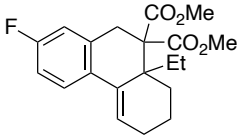


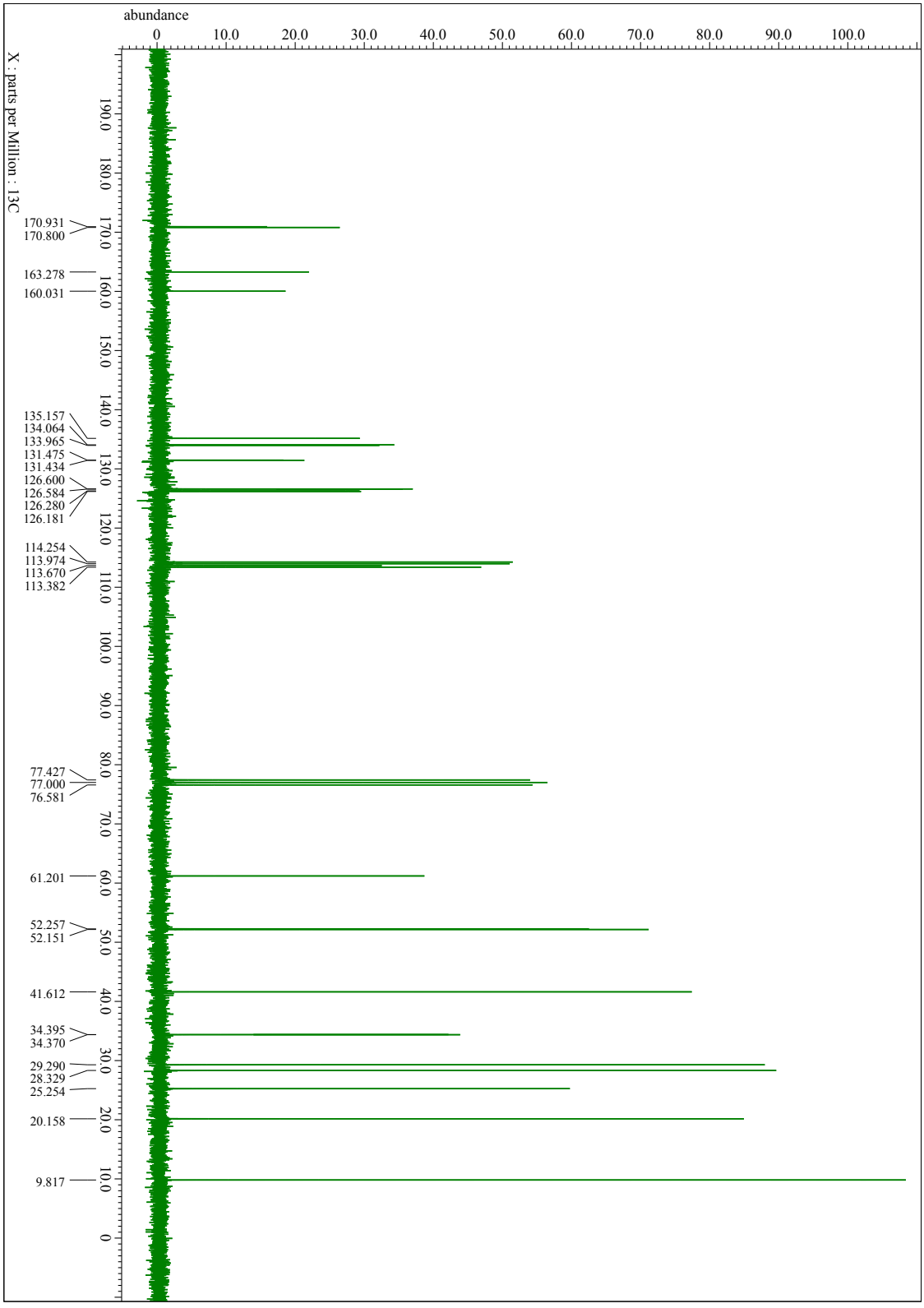
^{1}H NMR spectrum of **6i** ($CDCl_3$, 300 MHz).



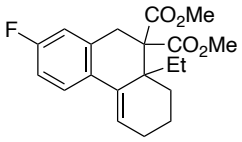


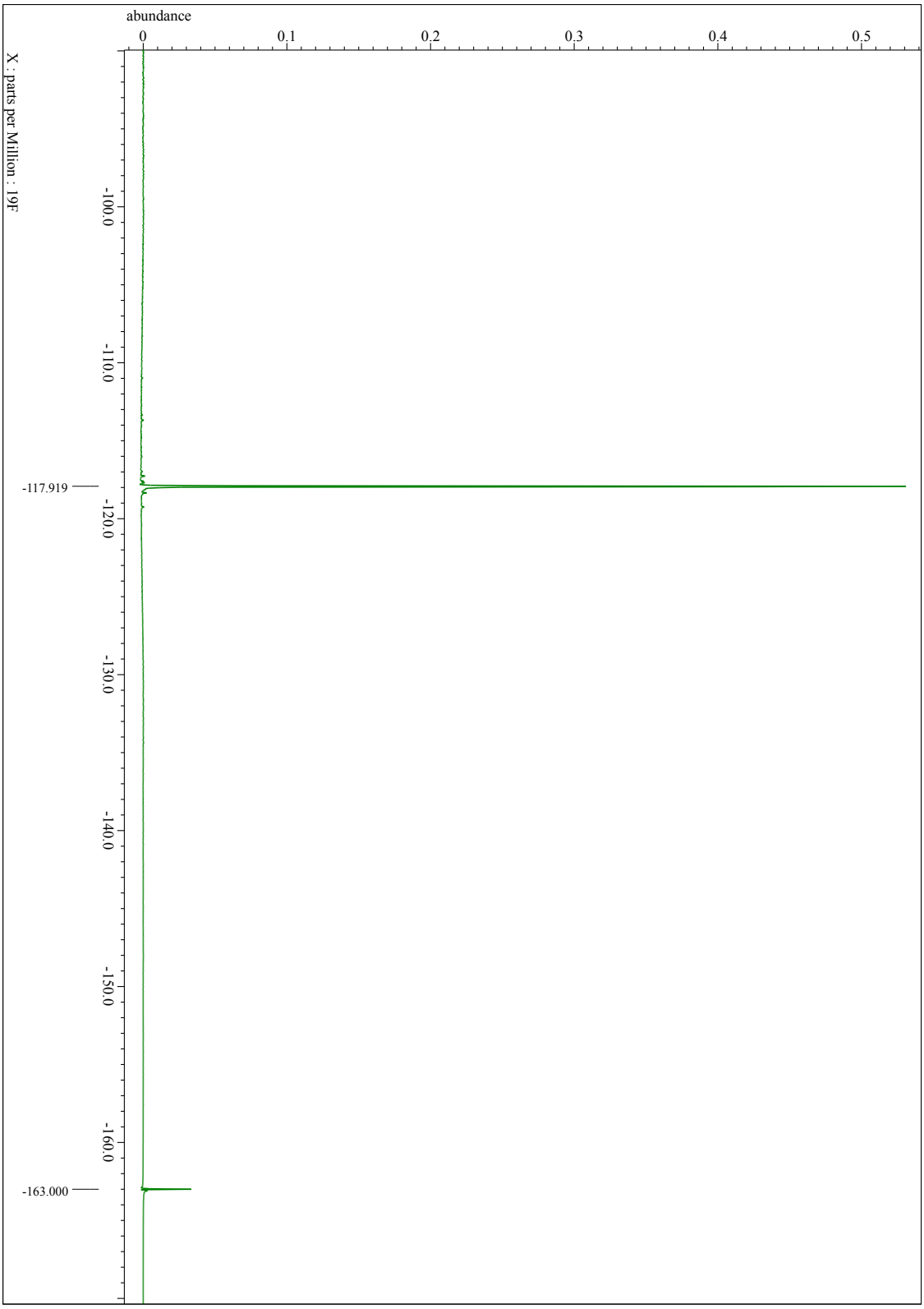
^{13}C NMR spectrum of **6i** ($CDCl_3$, 75 MHz).



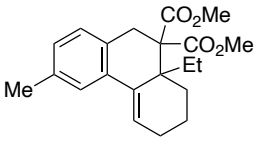


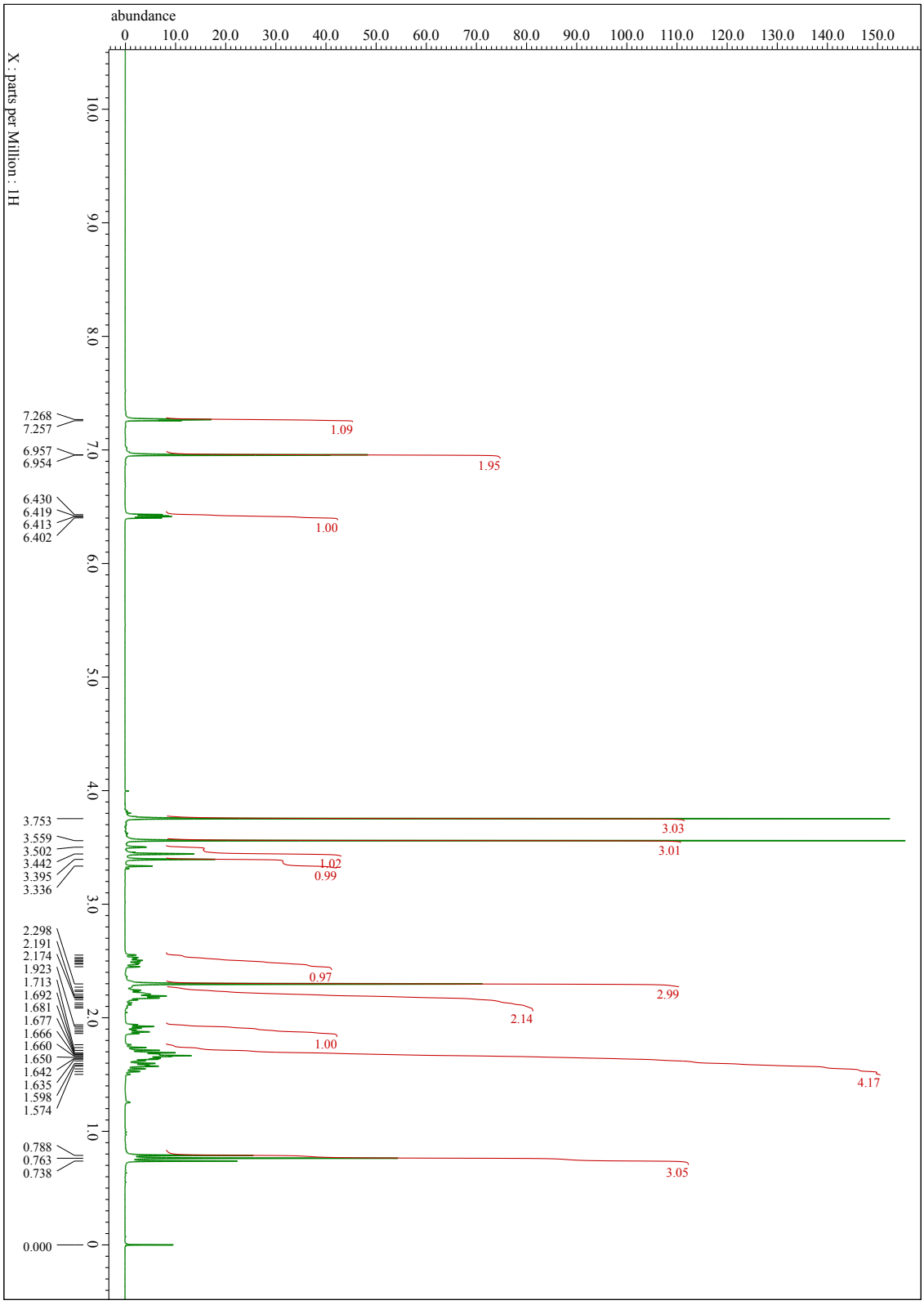
^{19}F NMR spectrum of **6i** ($CDCl_3$, 376 MHz).



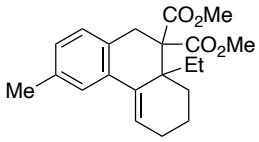


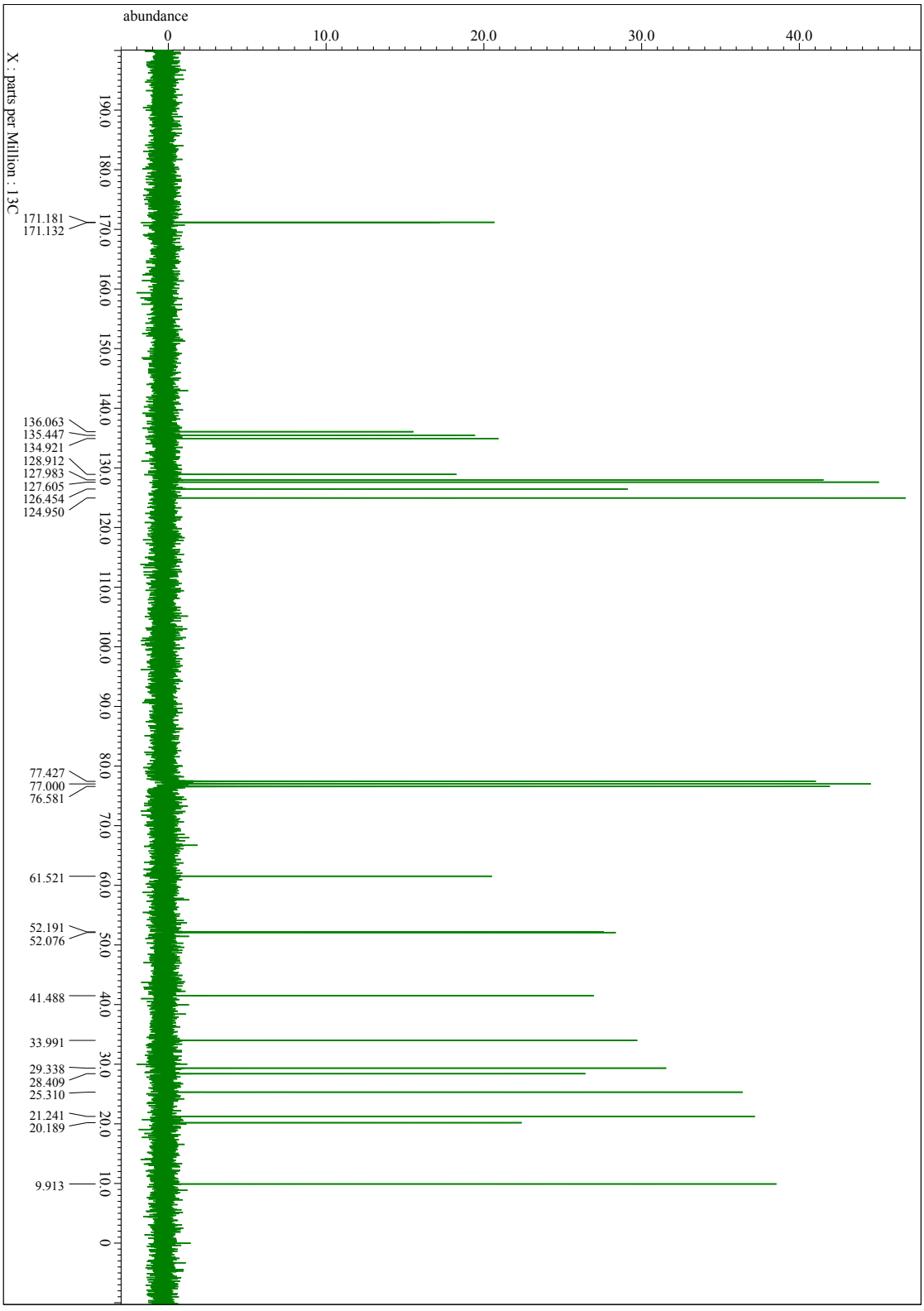
^{1}H NMR spectrum of **6j** ($CDCl_3$, 300 MHz).



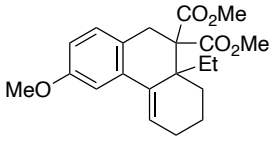


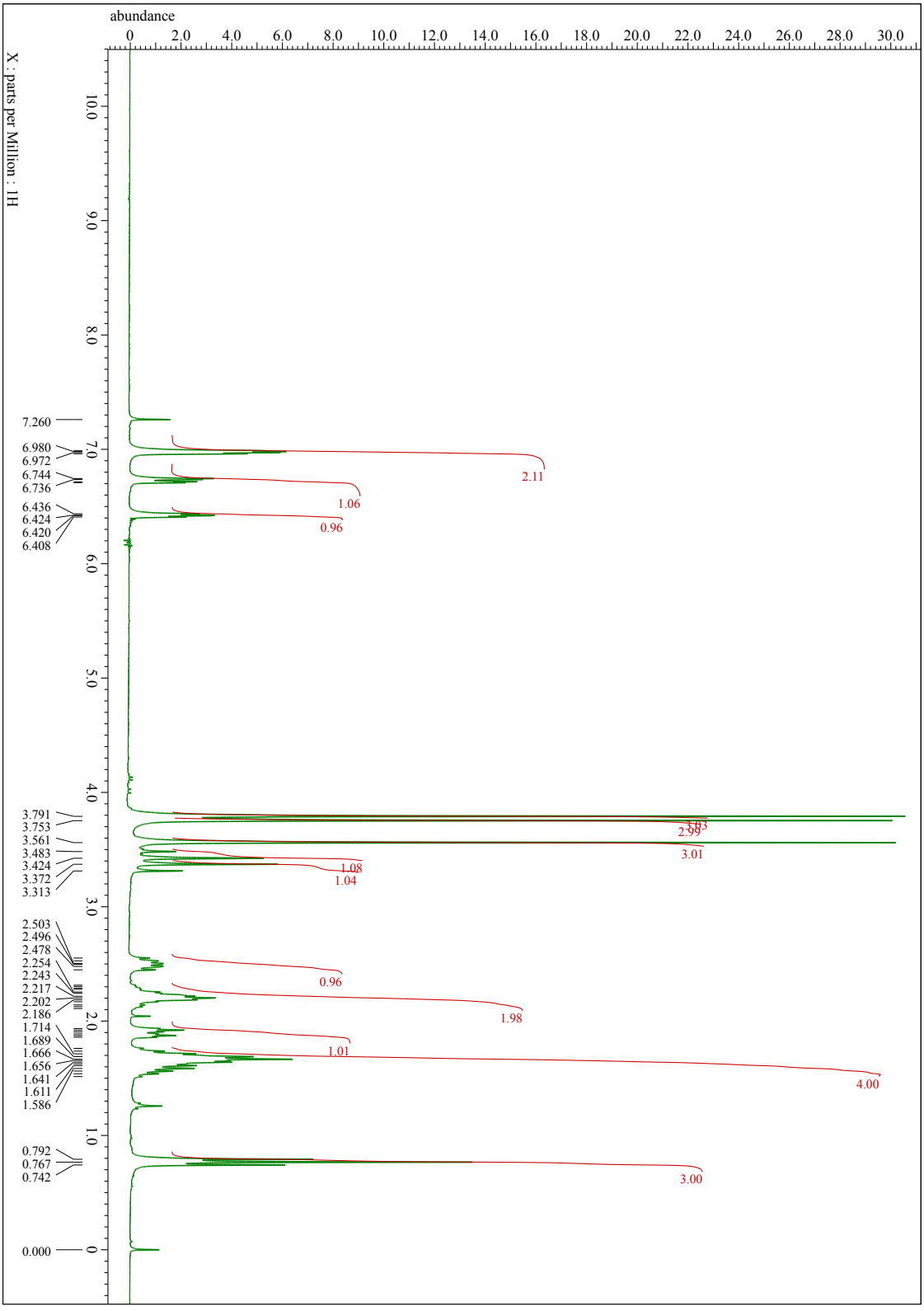
^{13}C NMR spectrum of **6j** ($CDCl_3$, 75 MHz).



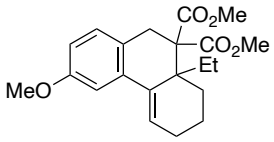


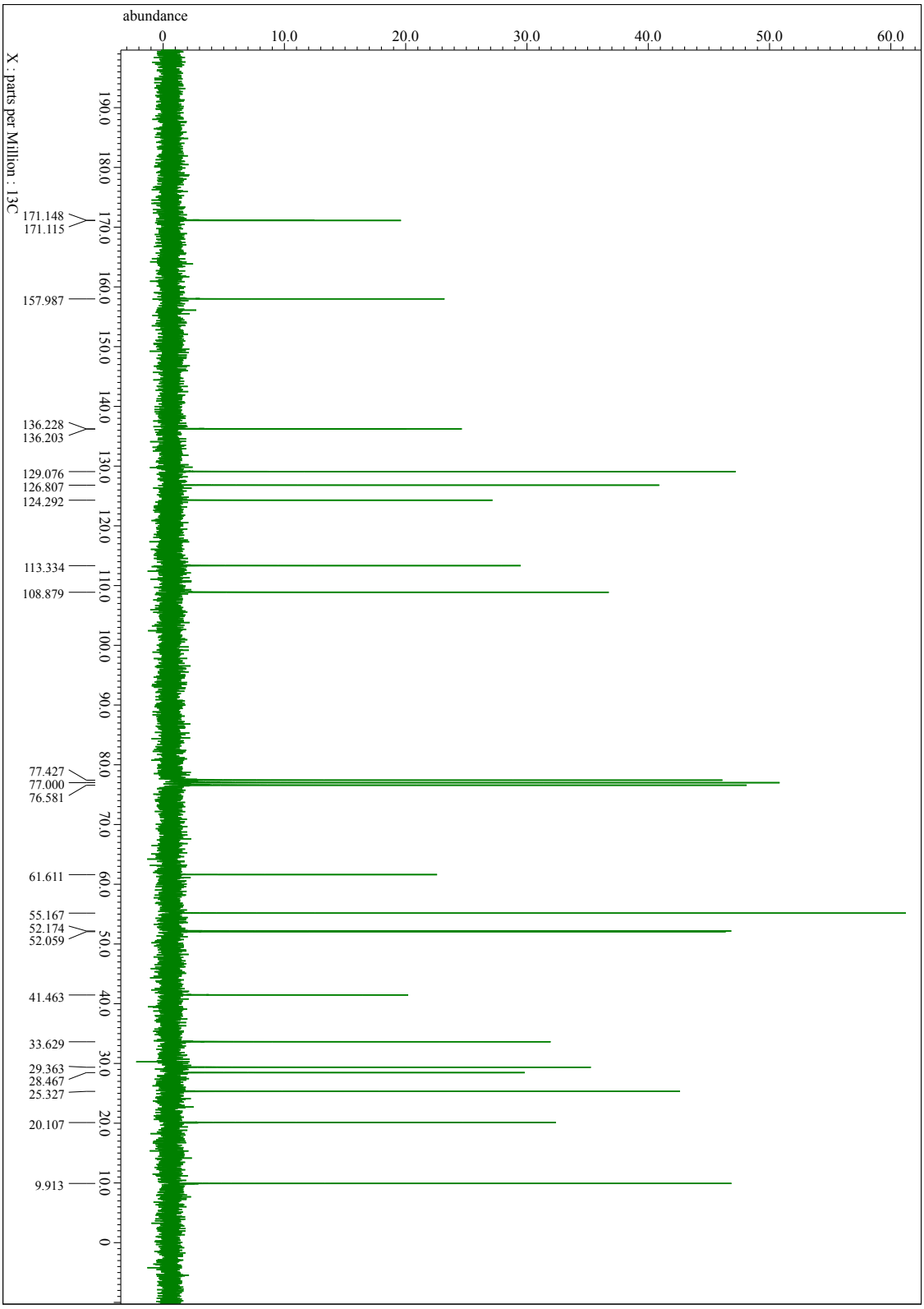
^{1}H NMR spectrum of **6k** ($CDCl_3$, 300 MHz).



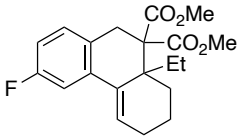


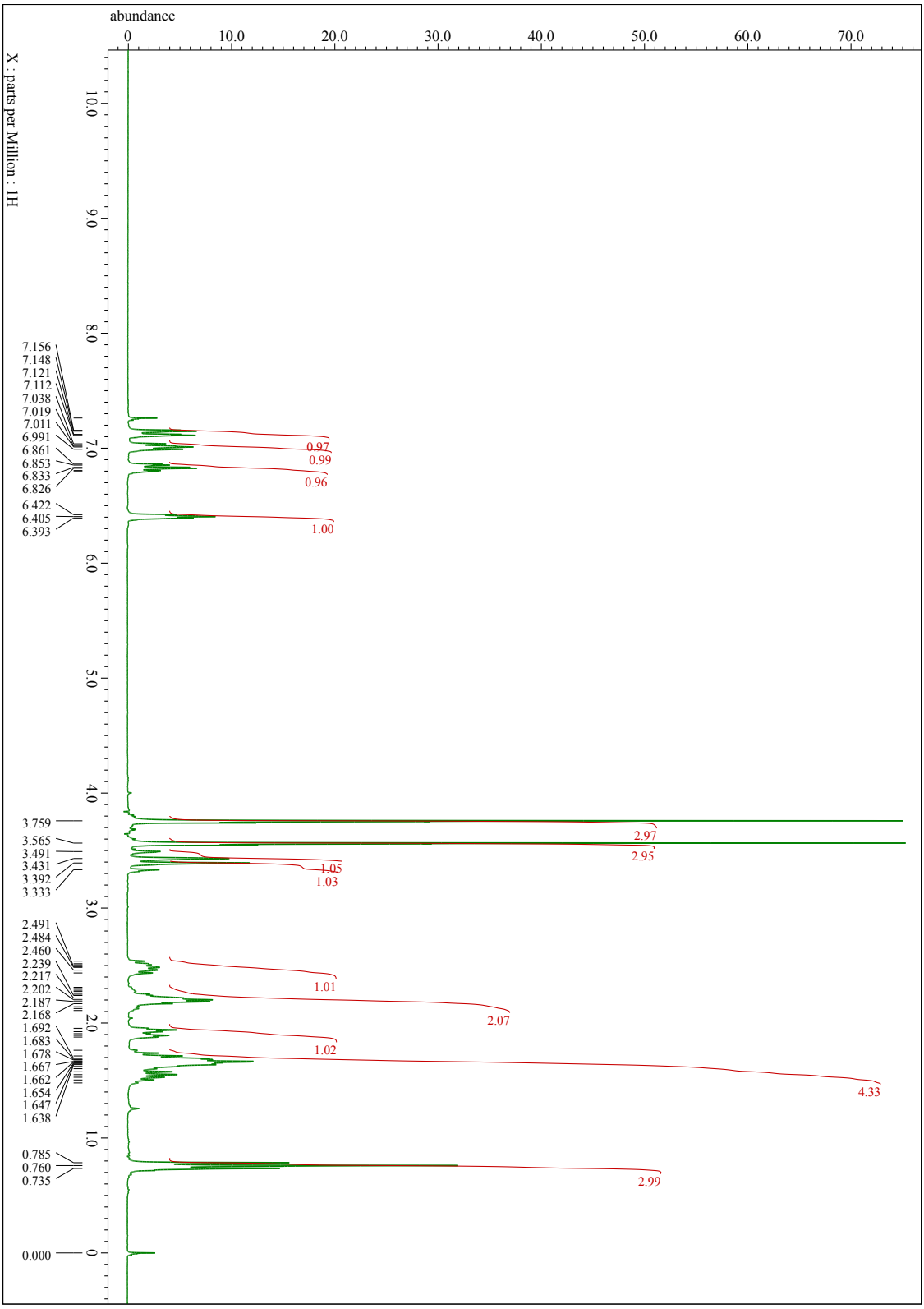
^{13}C NMR spectrum of **6k** ($CDCl_3$, 75 MHz).



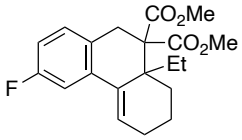


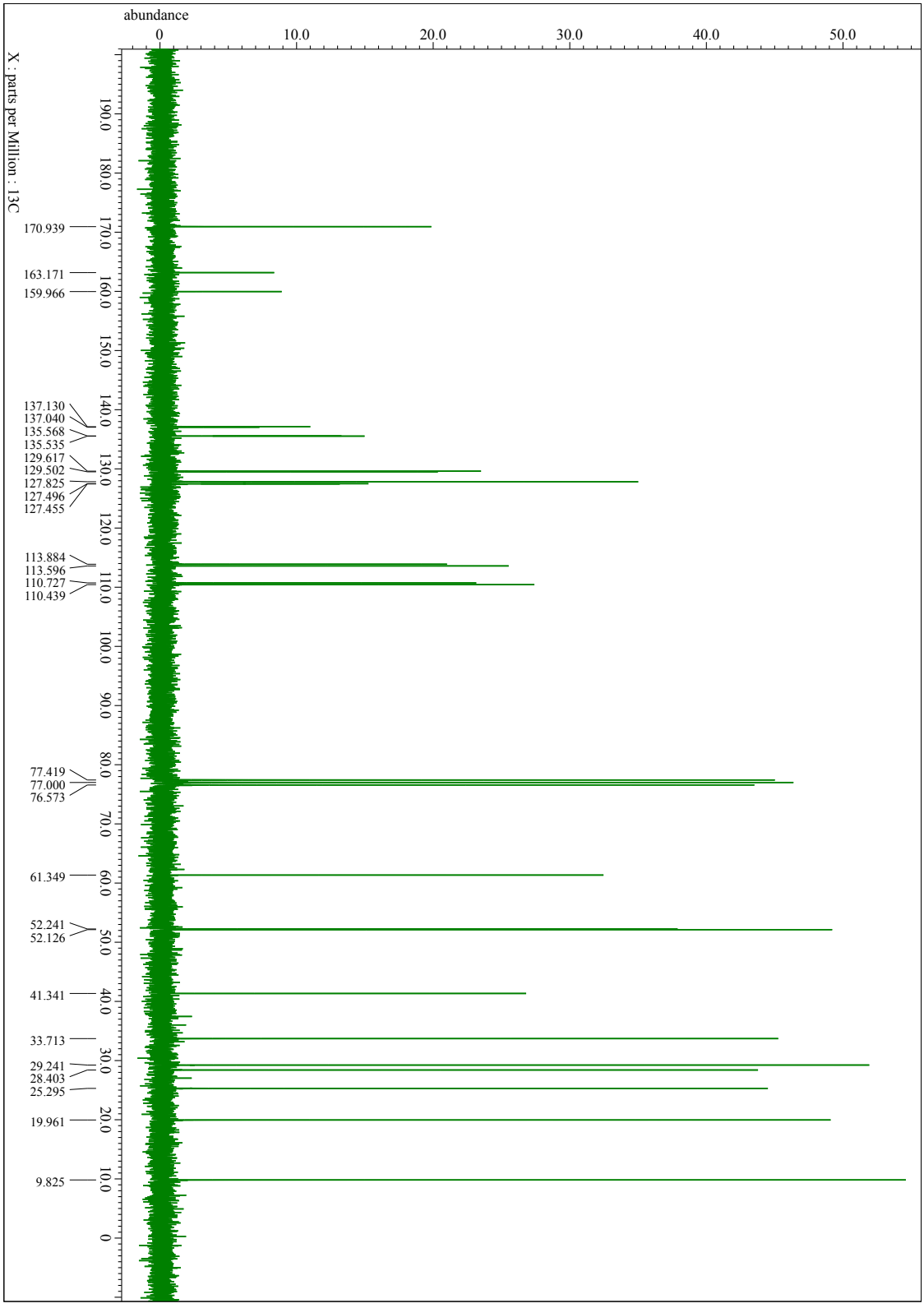
^{1}H NMR spectrum of **6l** ($CDCl_3$, 300 MHz).



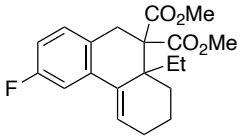


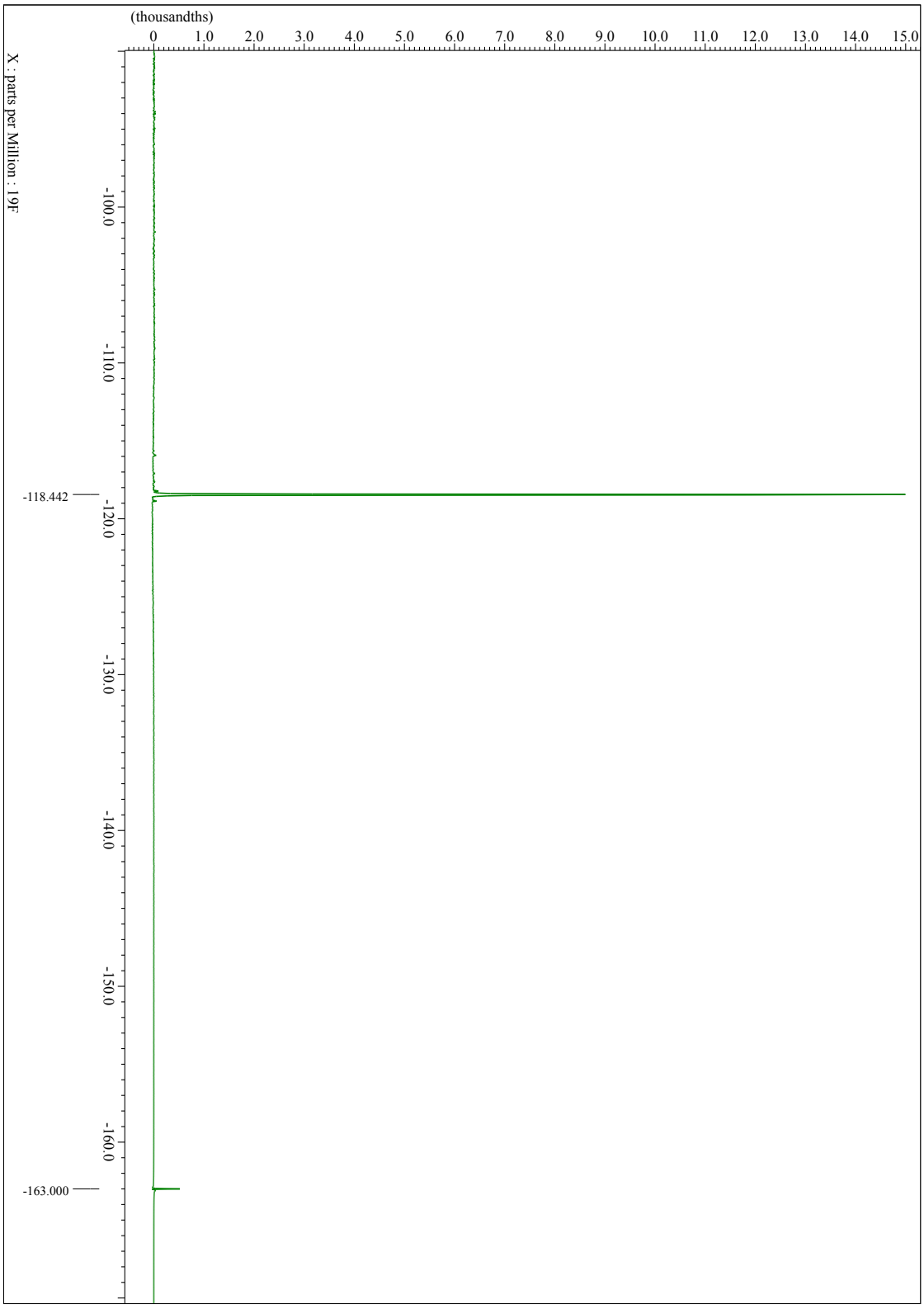
^{13}C NMR spectrum of **6l** ($CDCl_3$, 75 MHz).



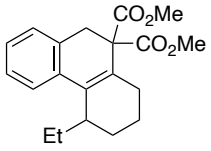


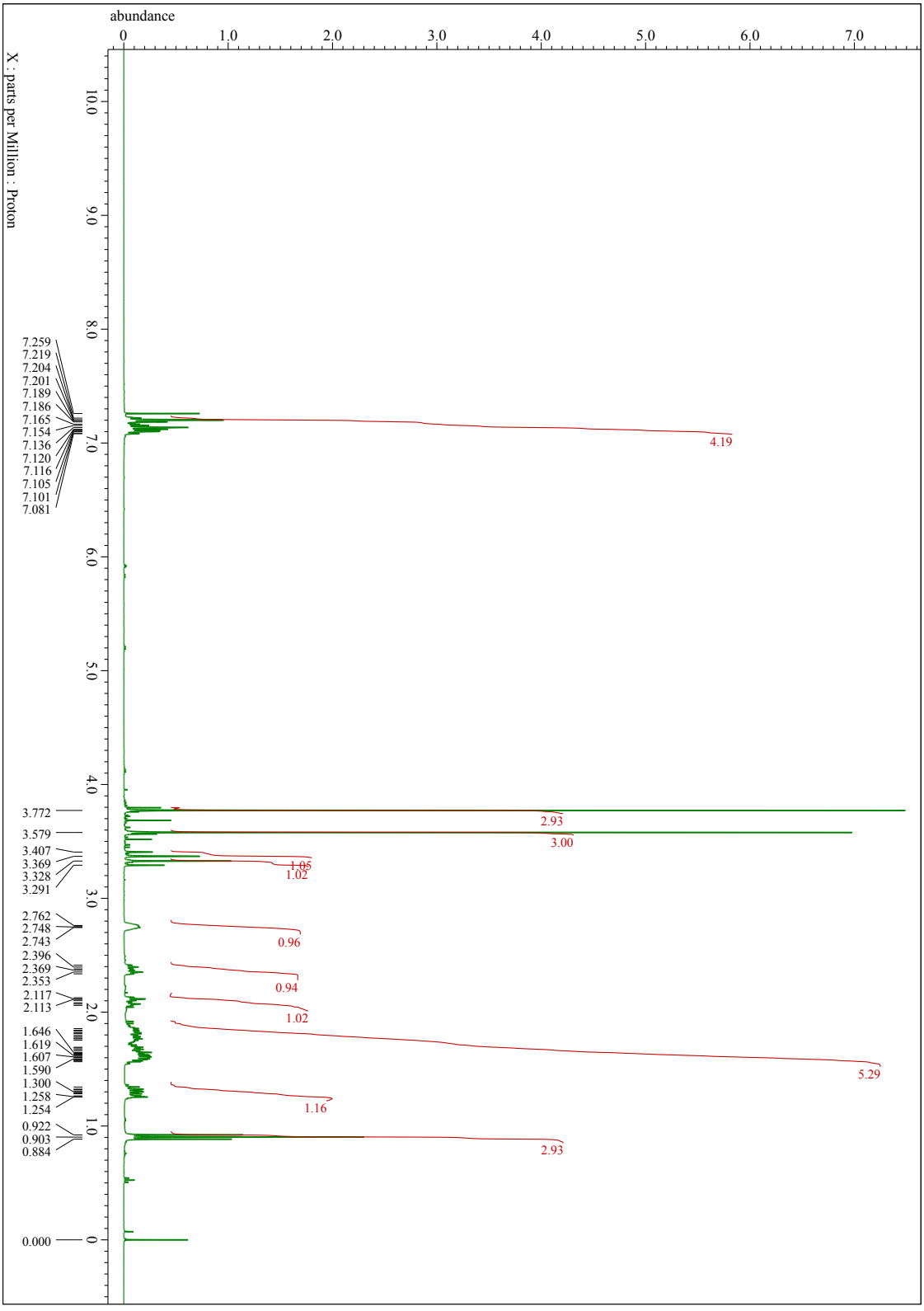
^{19}F NMR spectrum of **6l** ($CDCl_3$, 376 MHz).



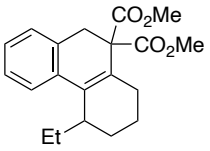


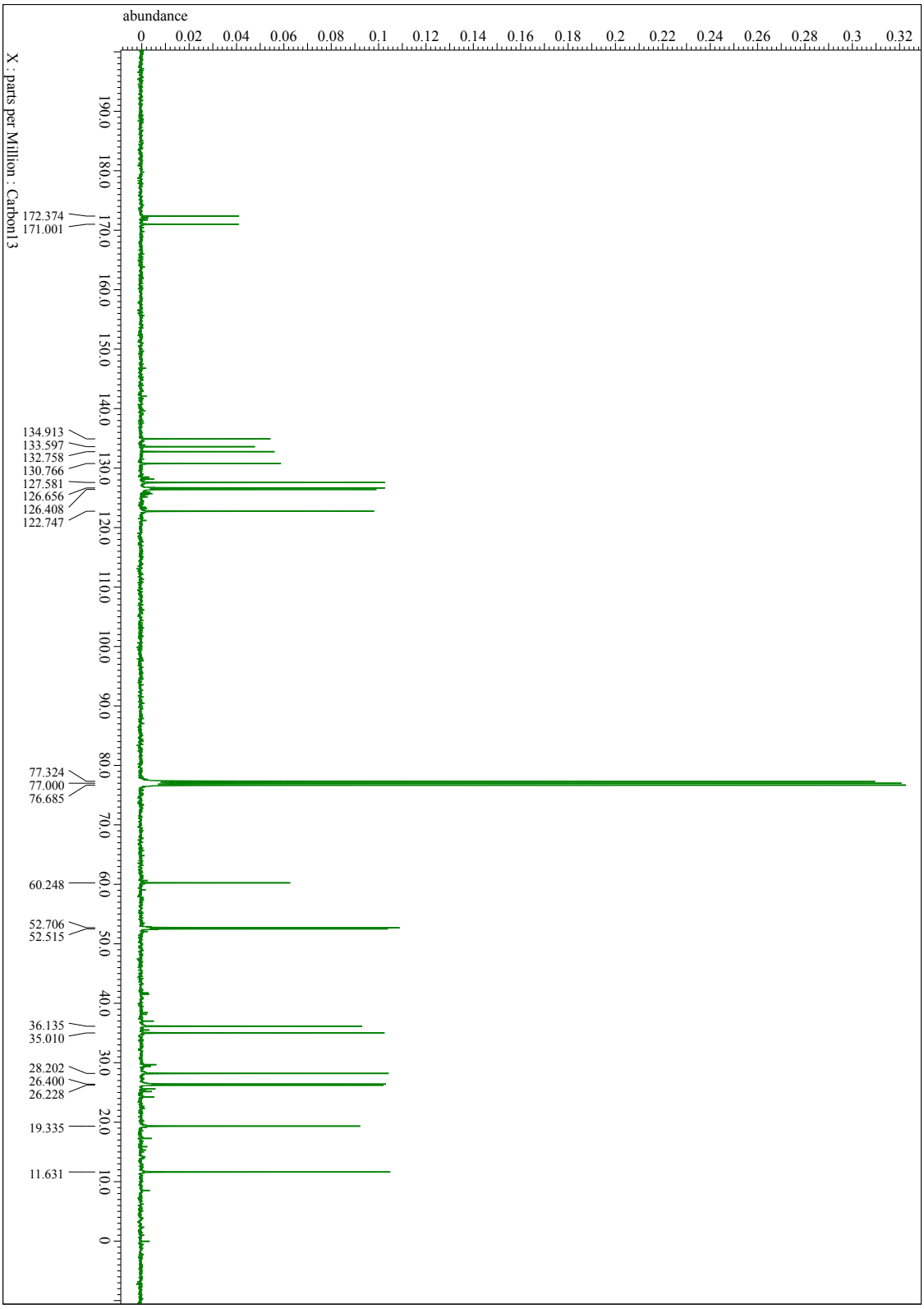
^{1}H NMR spectrum of **7a** ($CDCl_3$, 400 MHz).



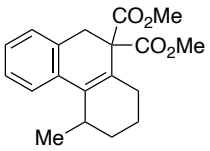


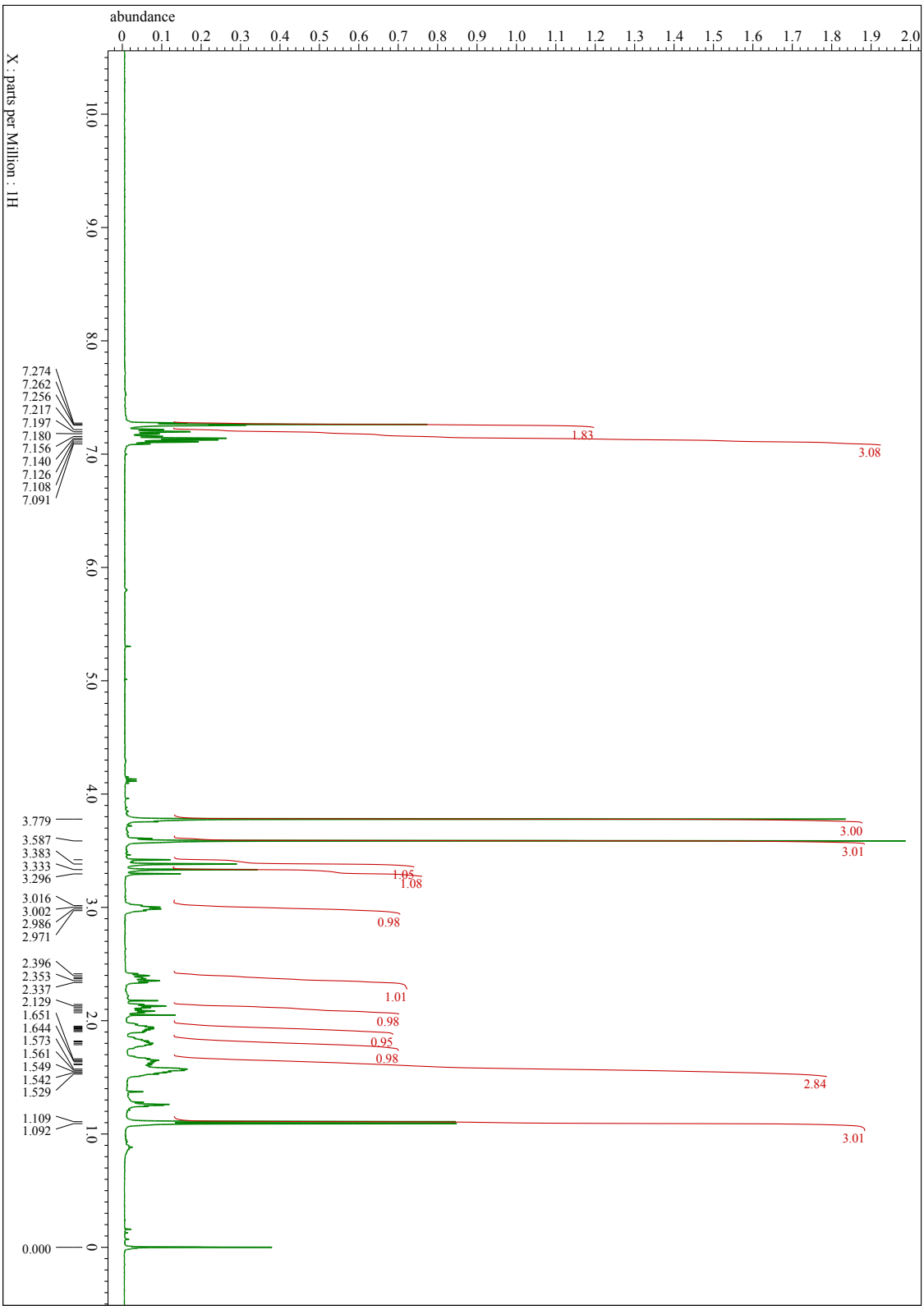
^{13}C NMR spectrum of **7a** ($CDCl_3$, 100 MHz).



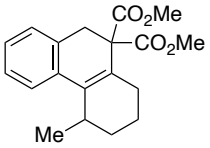


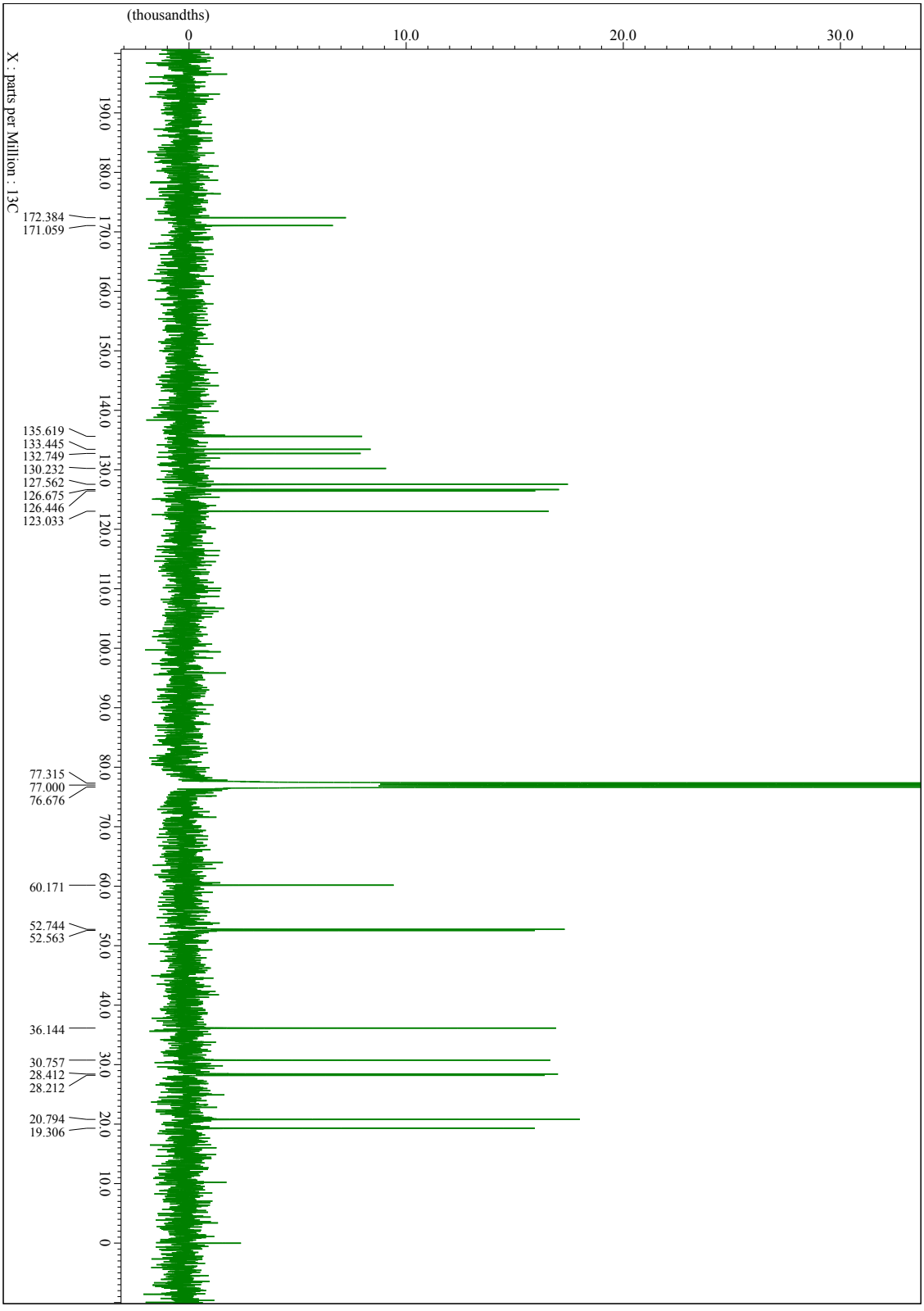
^{1}H NMR spectrum of **7b** ($CDCl_3$, 400 MHz).



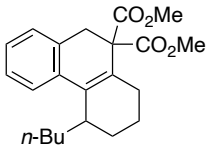


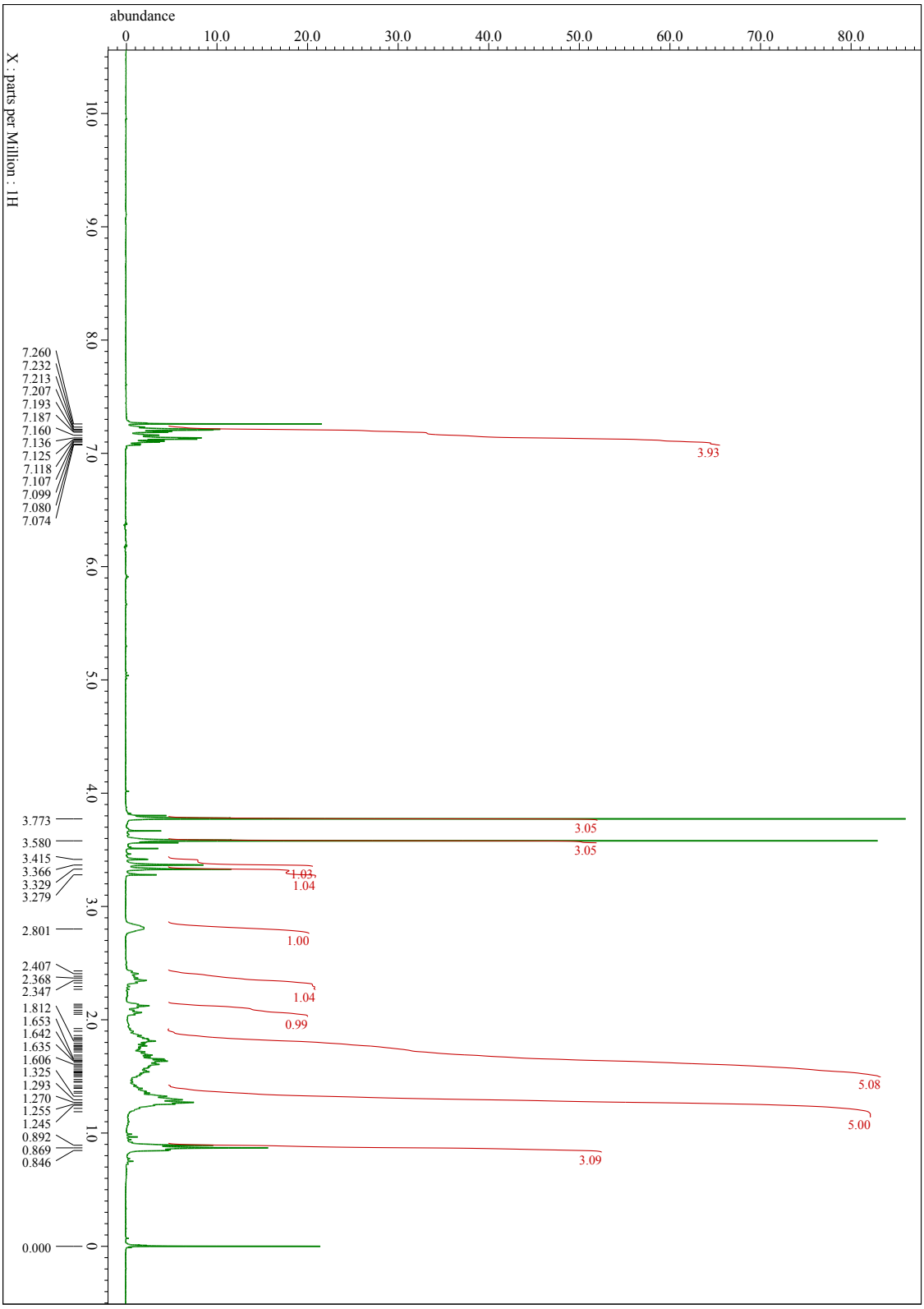
^{13}C NMR spectrum of **7b** ($CDCl_3$, 100 MHz).



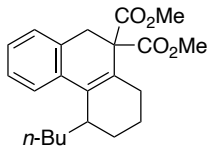


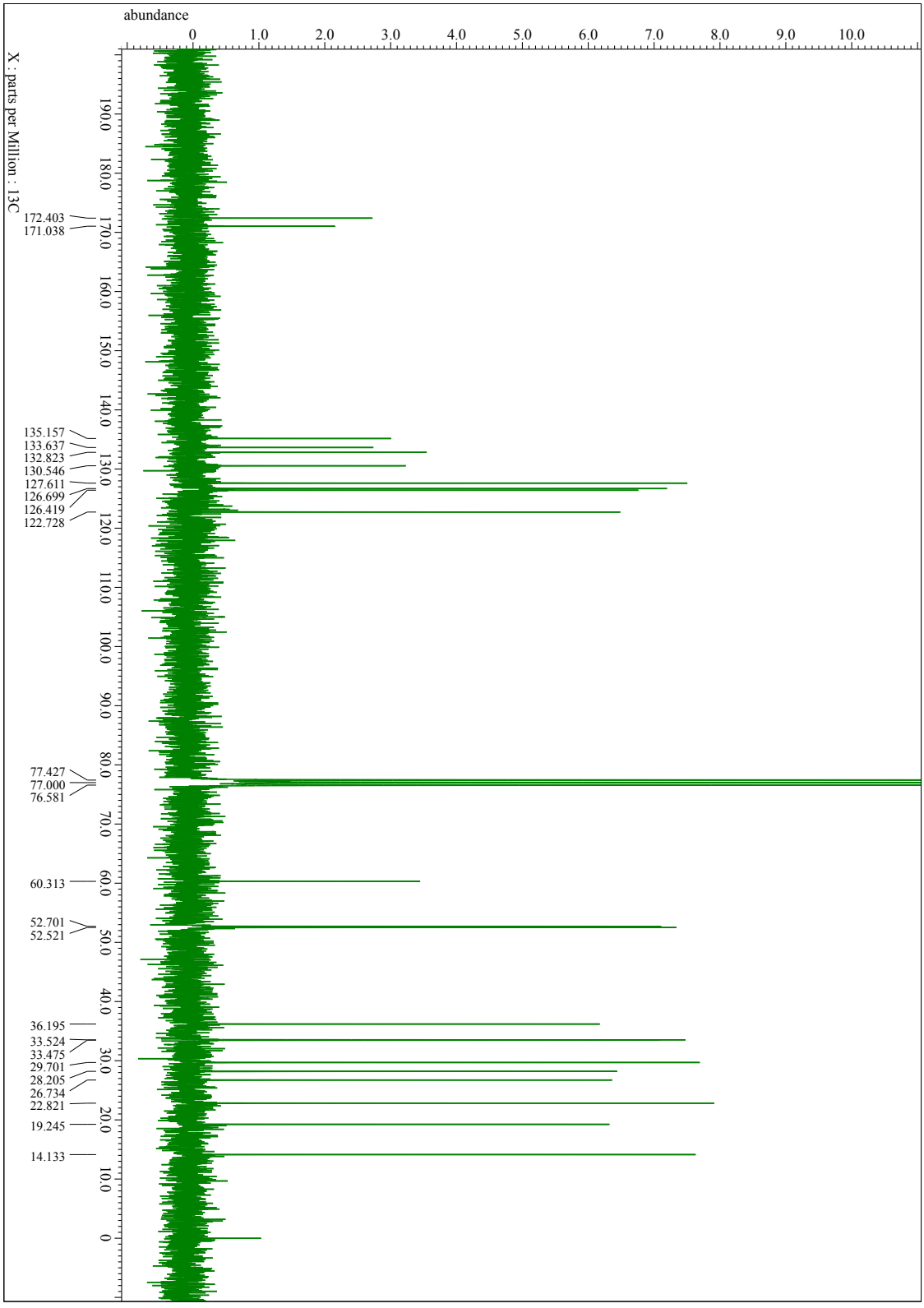
^{1}H NMR spectrum of **7c** ($CDCl_3$, 300 MHz).



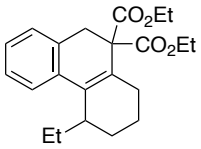


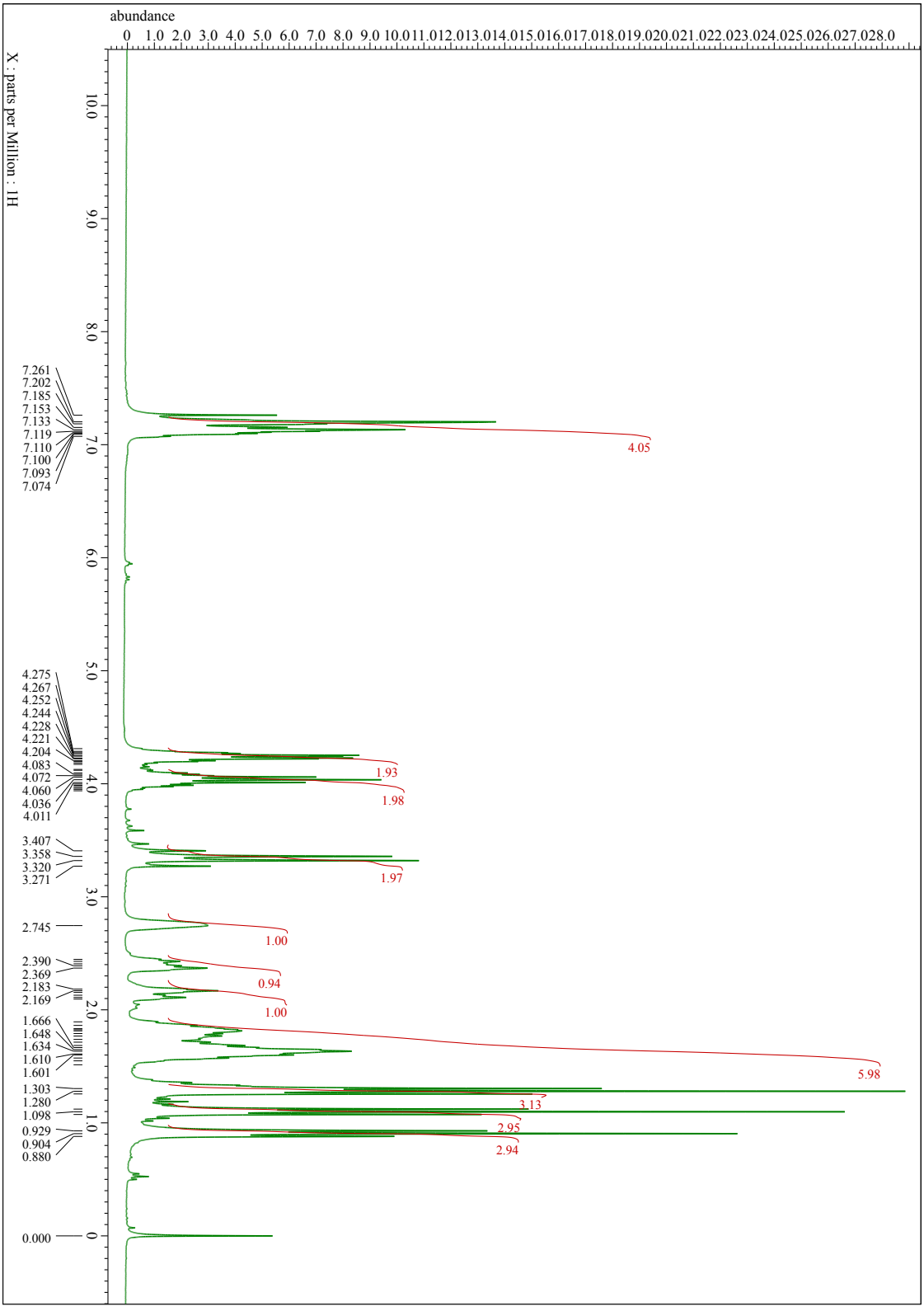
^{13}C NMR spectrum of **7c** ($CDCl_3$, 75 MHz).



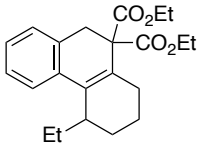


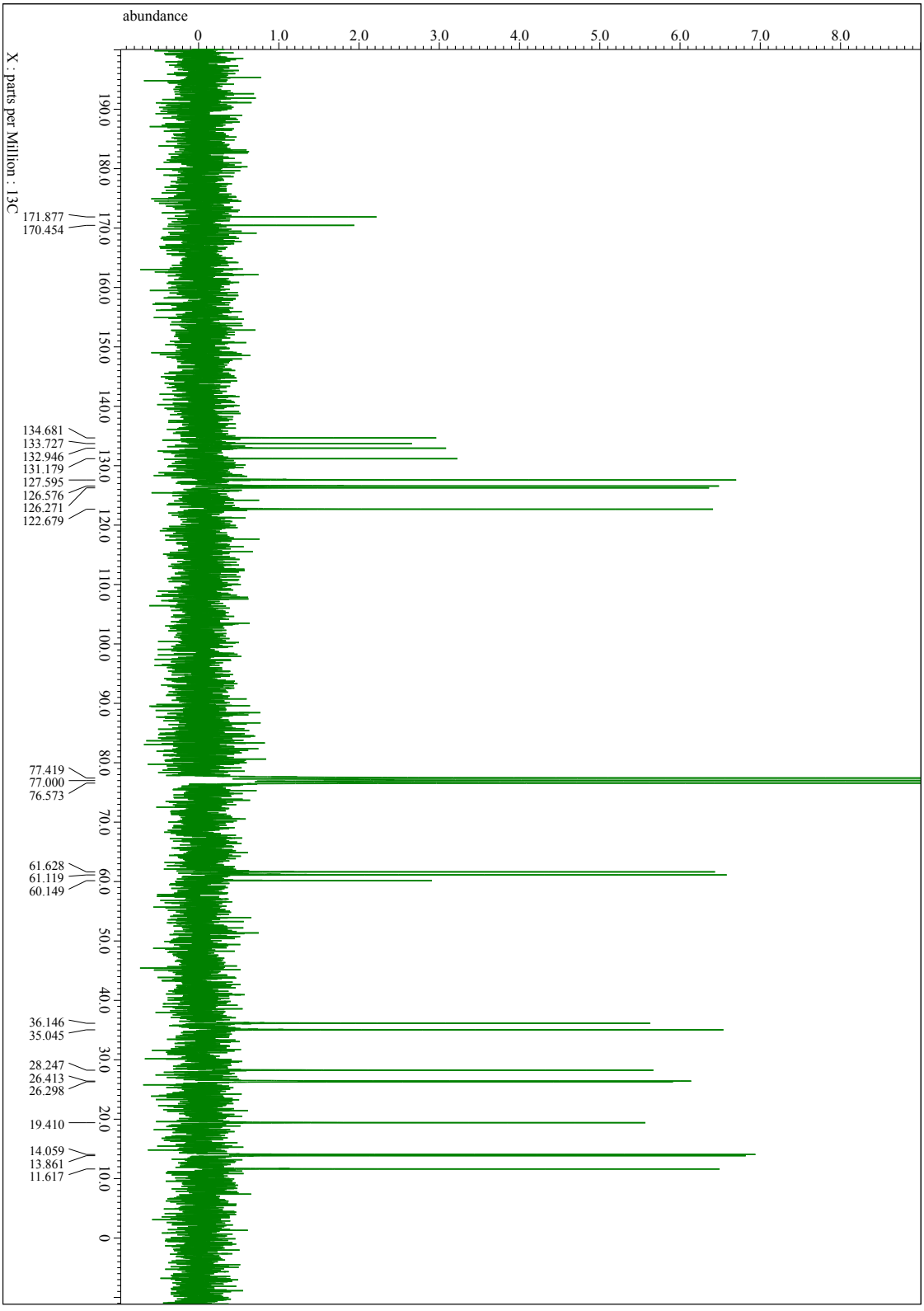
^{1}H NMR spectrum of **7d** ($CDCl_3$, 300 MHz).



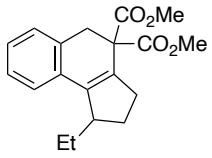


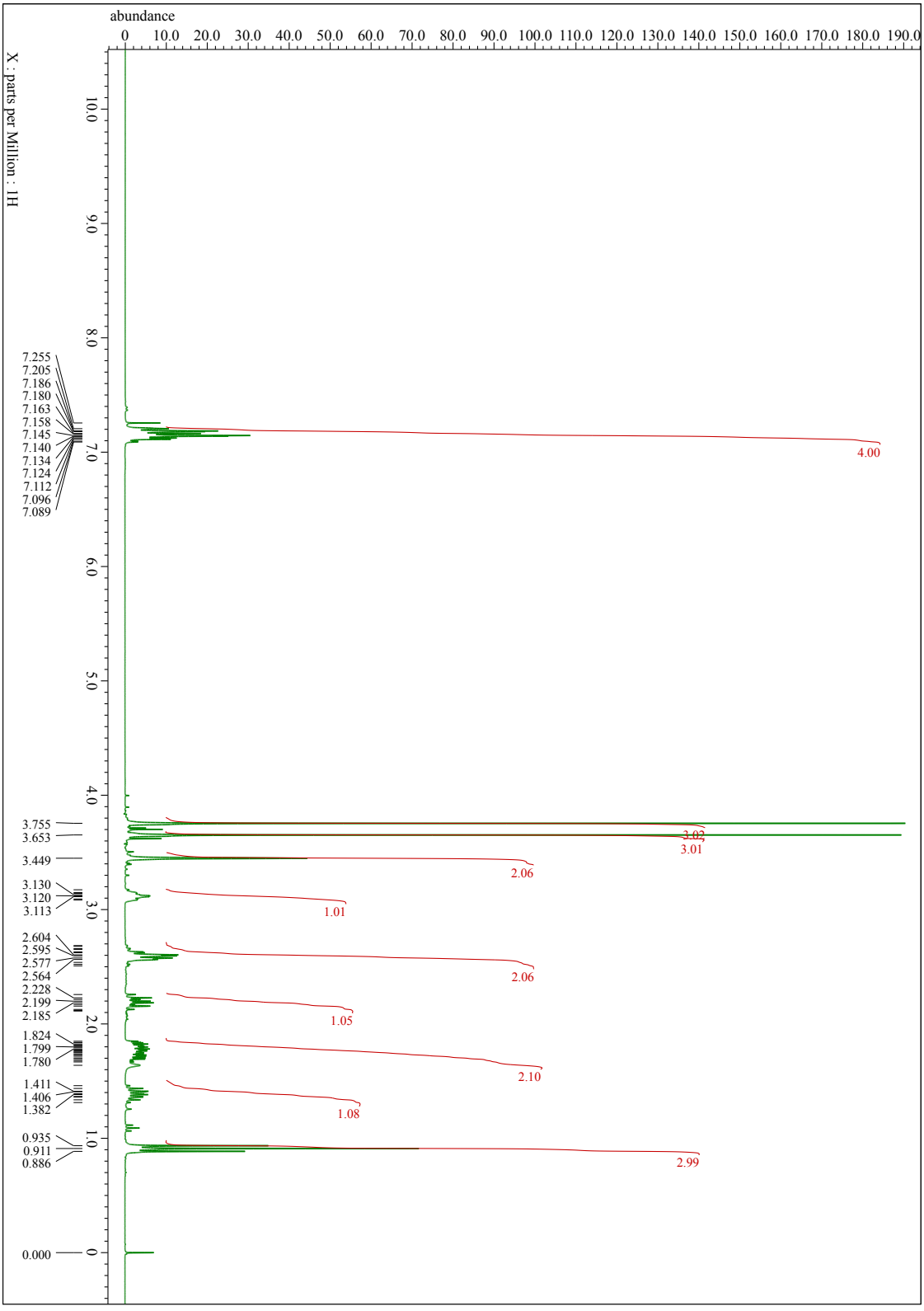
^{13}C NMR spectrum of **7d** ($CDCl_3$, 75 MHz).



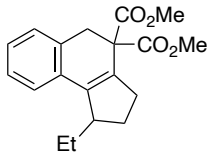


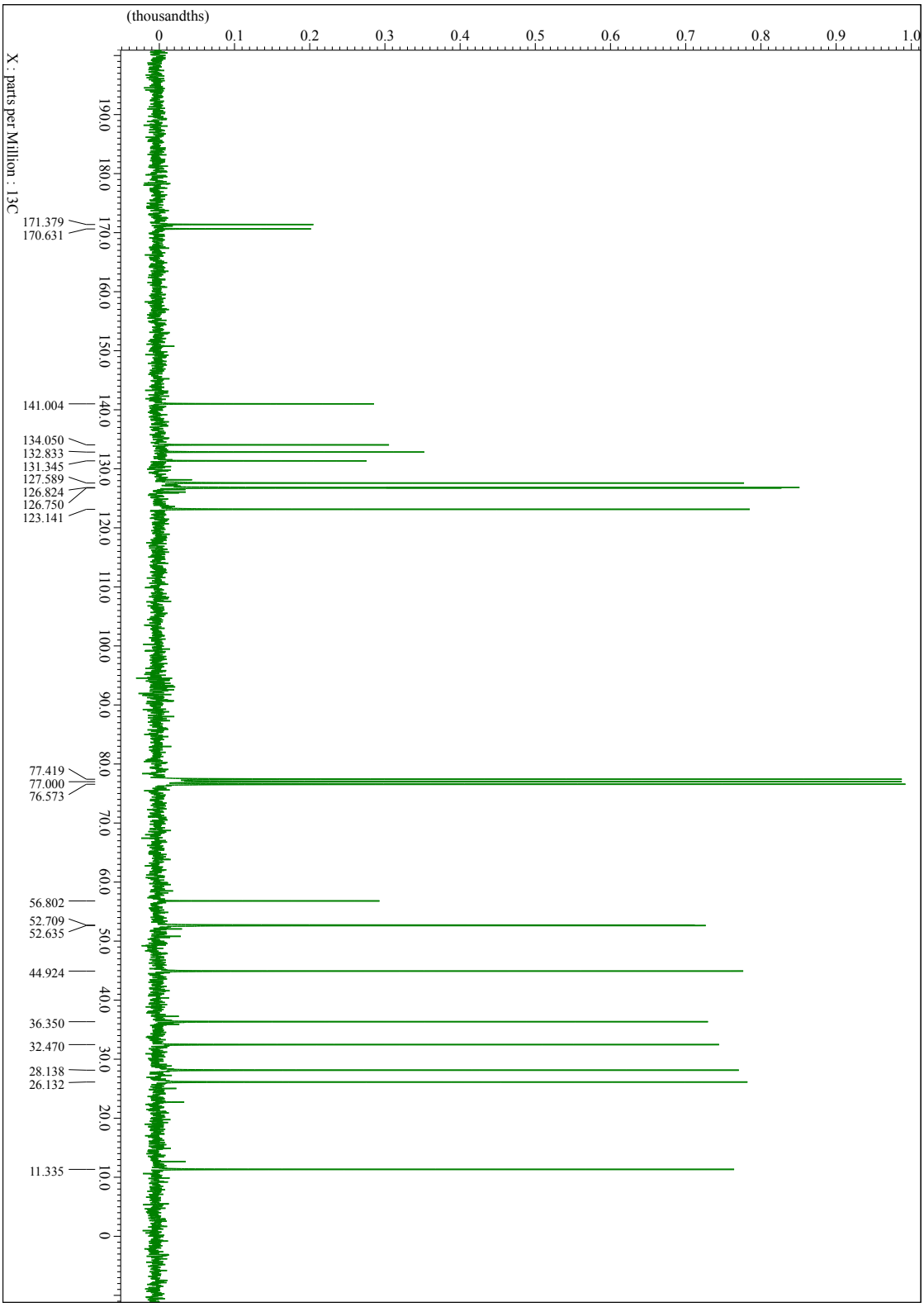
^{1}H NMR spectrum of **7e** ($CDCl_3$, 300 MHz).



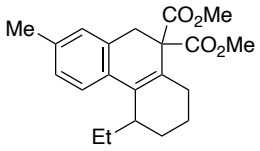


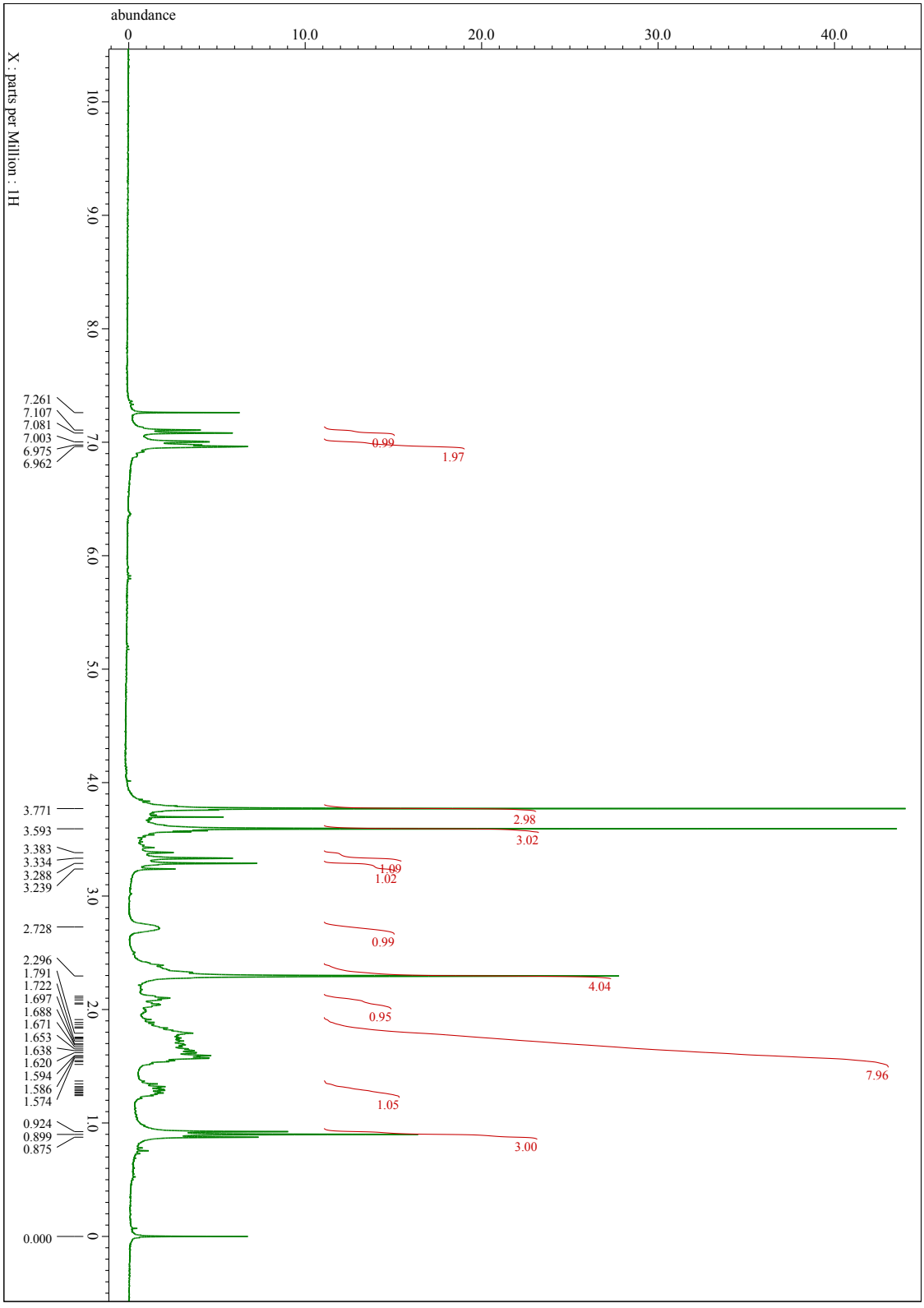
^{13}C NMR spectrum of **7e** ($CDCl_3$, 75 MHz).



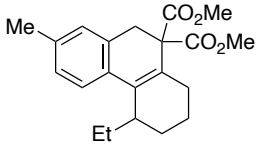


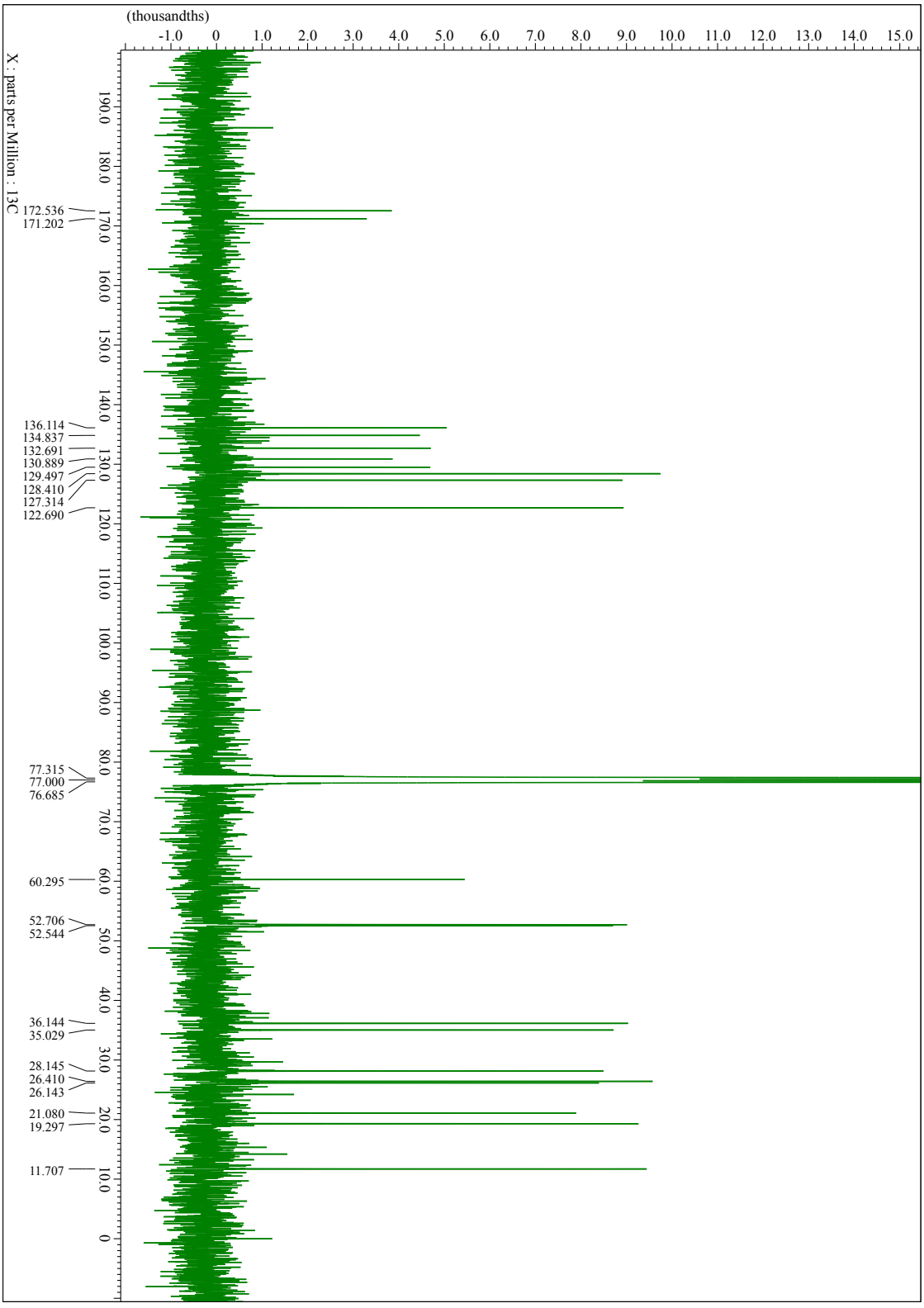
^{1}H NMR spectrum of **7g** ($CDCl_3$, 300 MHz).



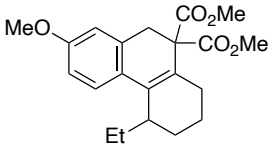


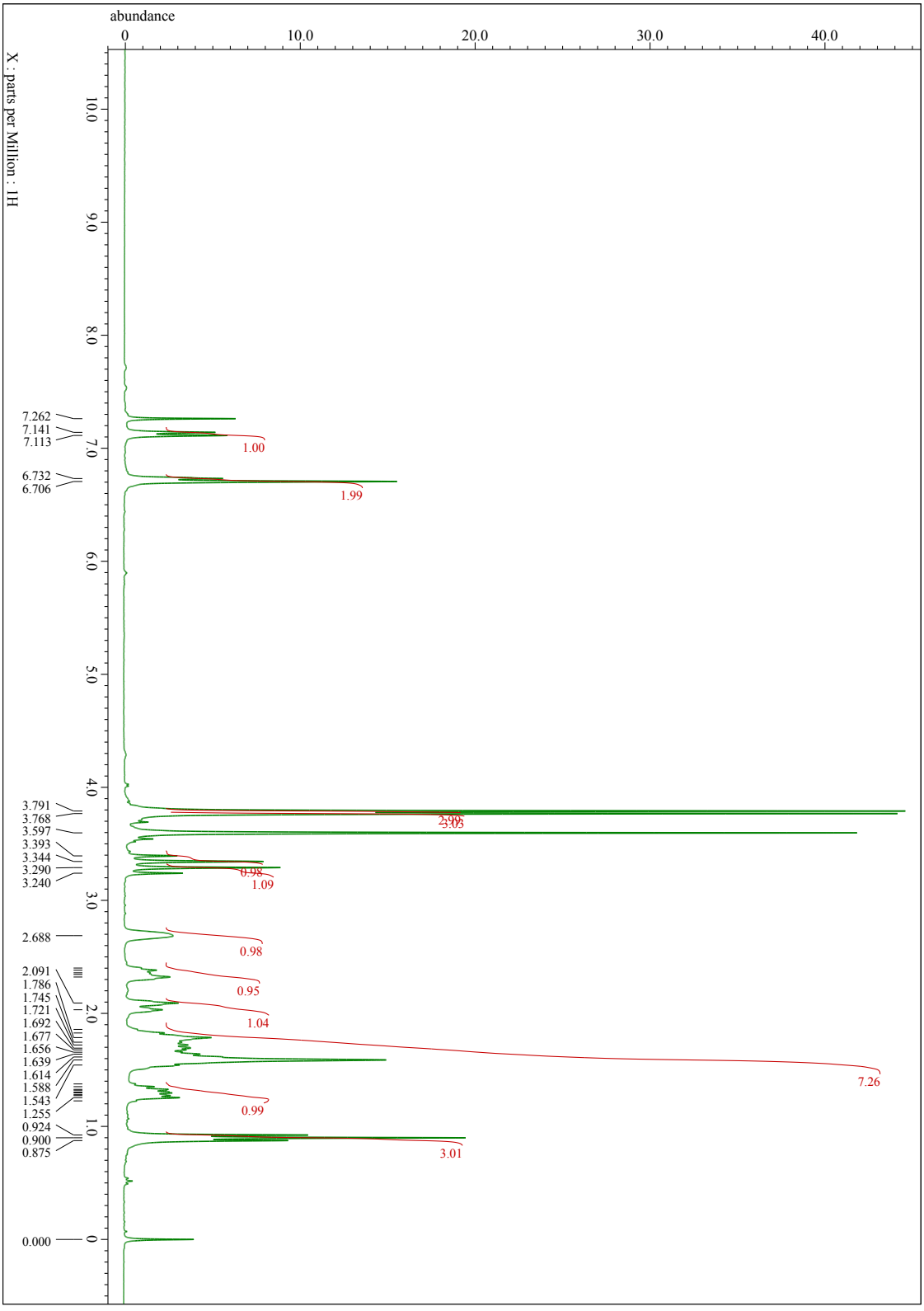
^{13}C NMR spectrum of **7g** ($CDCl_3$, 75 MHz).



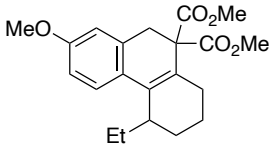


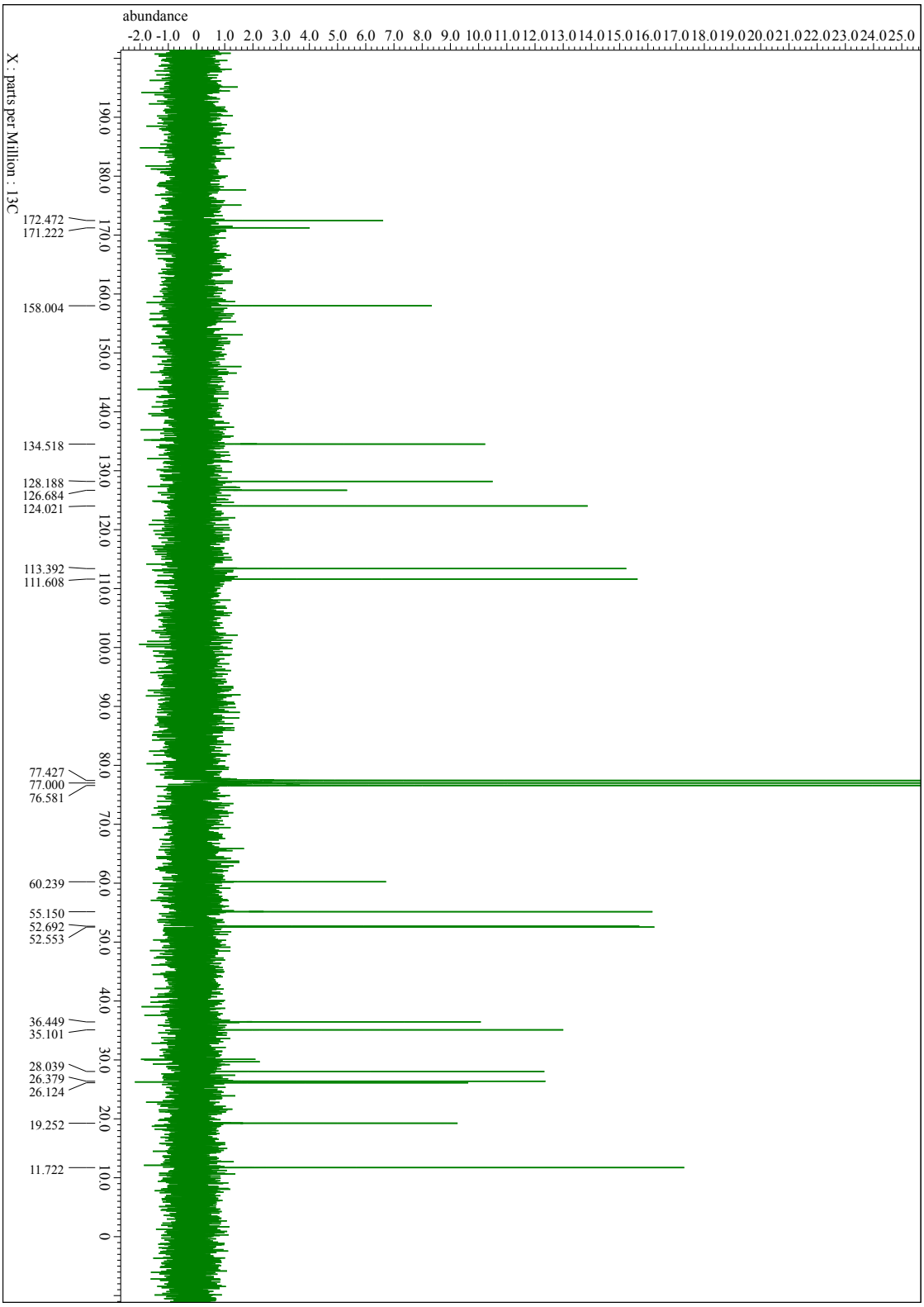
^{1}H NMR spectrum of **7h** ($CDCl_3$, 300 MHz).



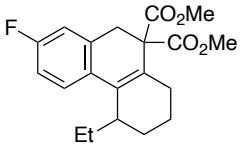


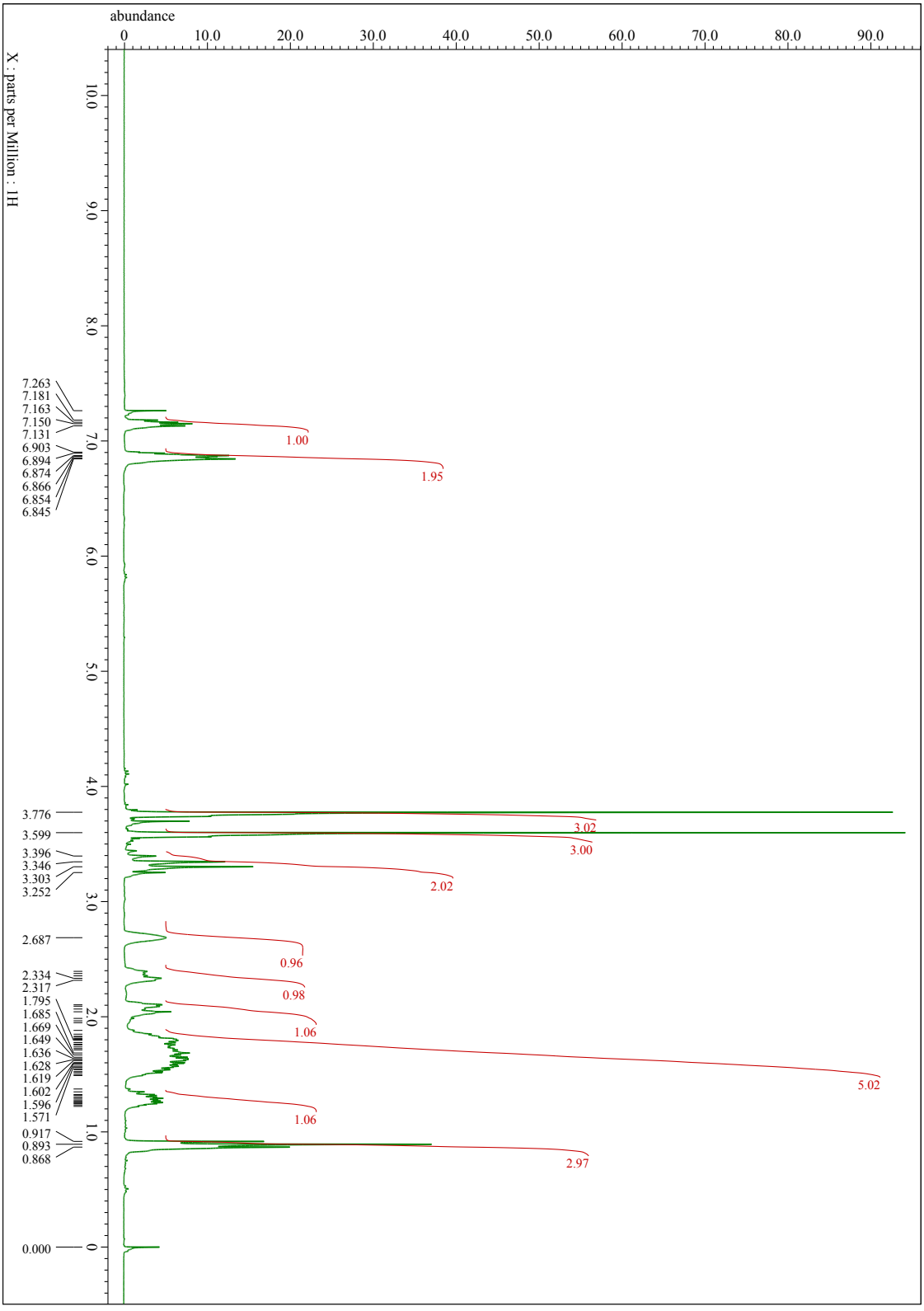
^{13}C NMR spectrum of **7h** ($CDCl_3$, 75 MHz).



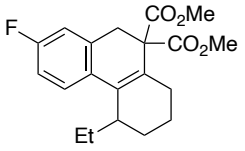


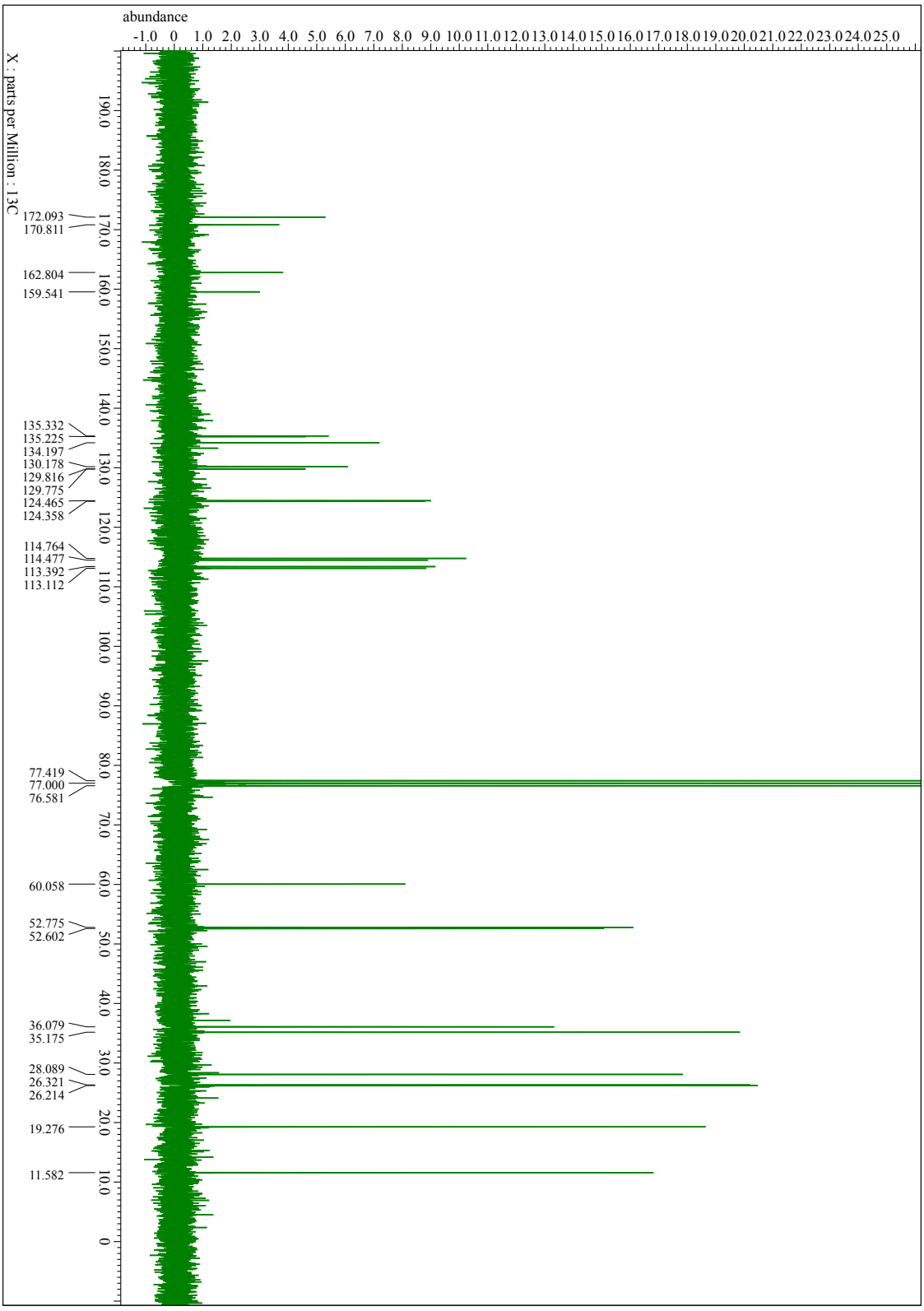
^{1}H NMR spectrum of **7i** ($CDCl_3$, 300 MHz).



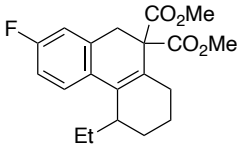


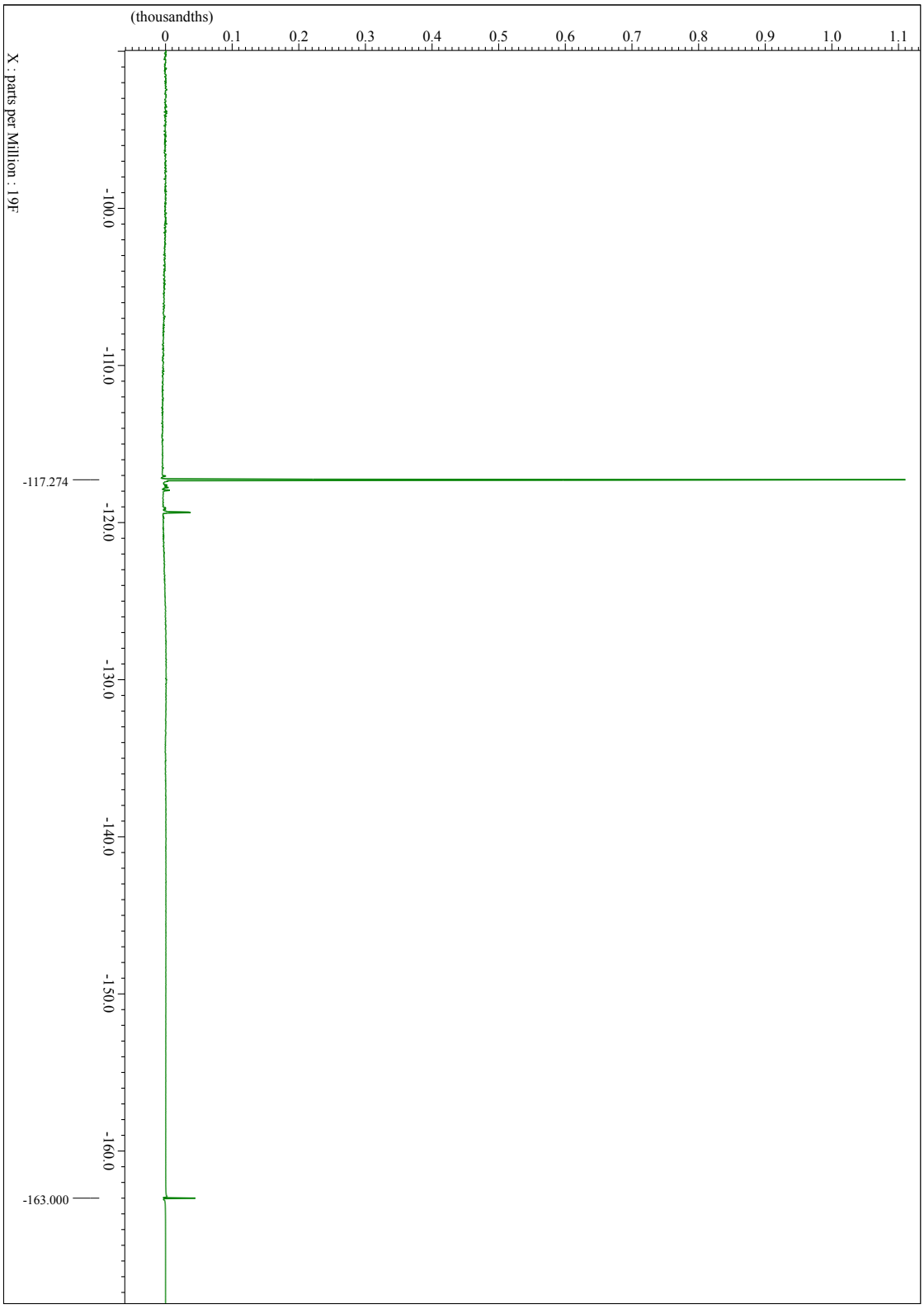
^{13}C NMR spectrum of **7i** ($CDCl_3$, 75 MHz).



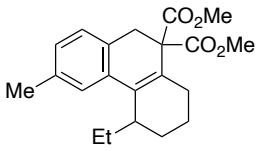


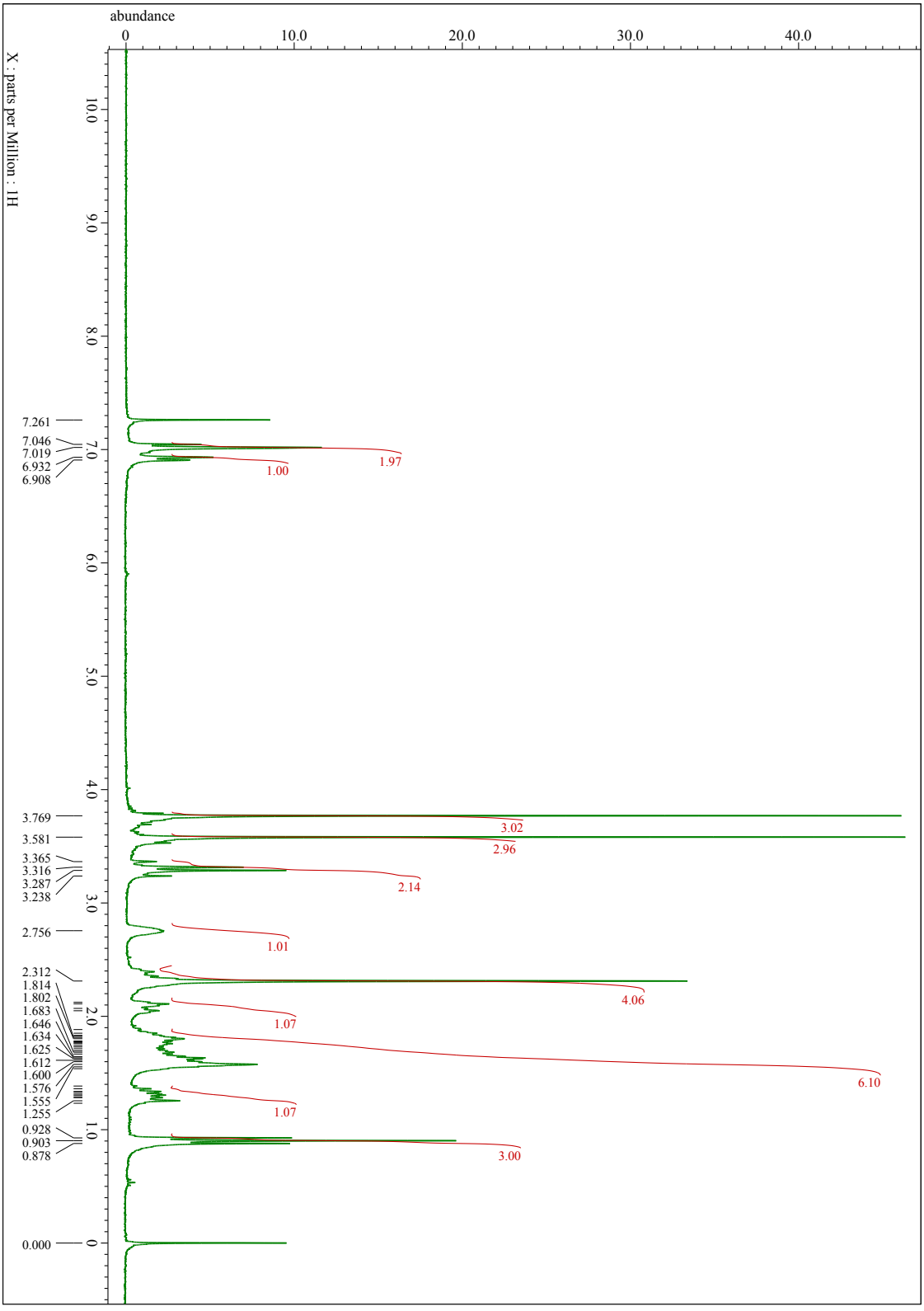
^{19}F NMR spectrum of **7i** ($CDCl_3$, 376 MHz).



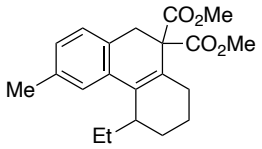


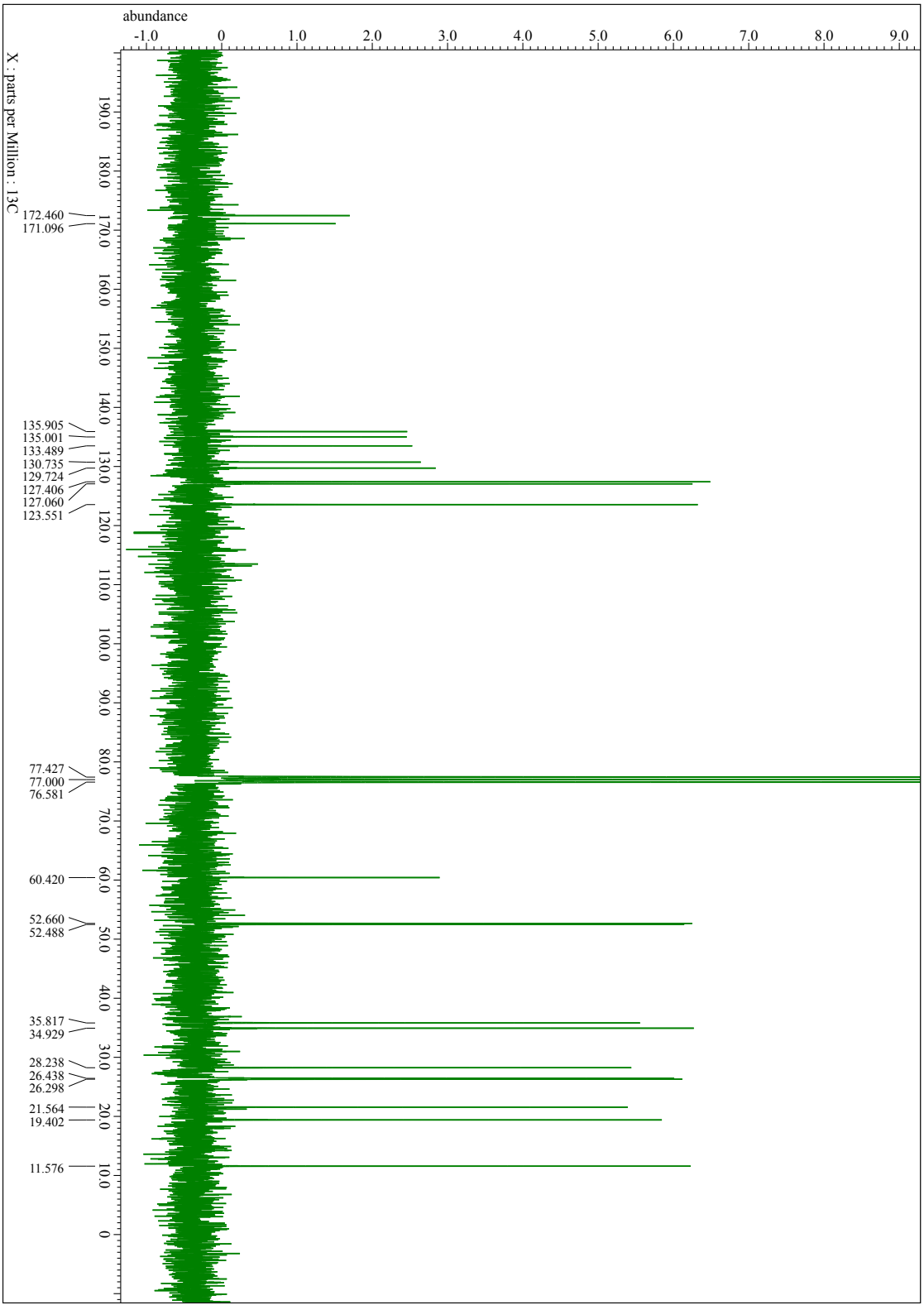
^{1}H NMR spectrum of **7j** ($CDCl_3$, 300 MHz).



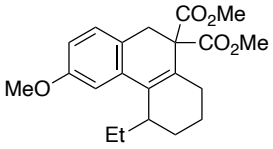


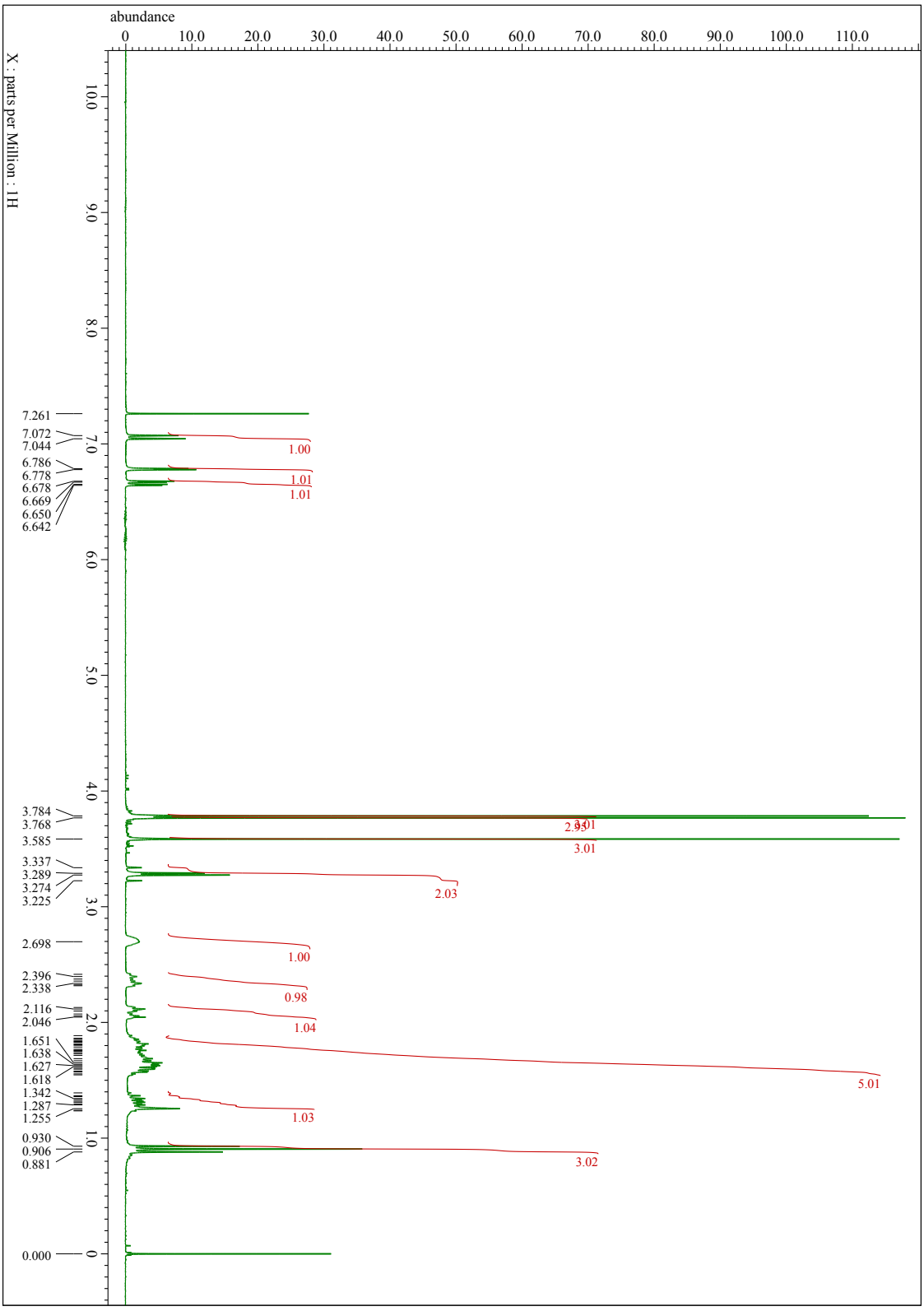
^{13}C NMR spectrum of **7j** ($CDCl_3$, 75 MHz).



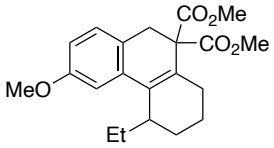


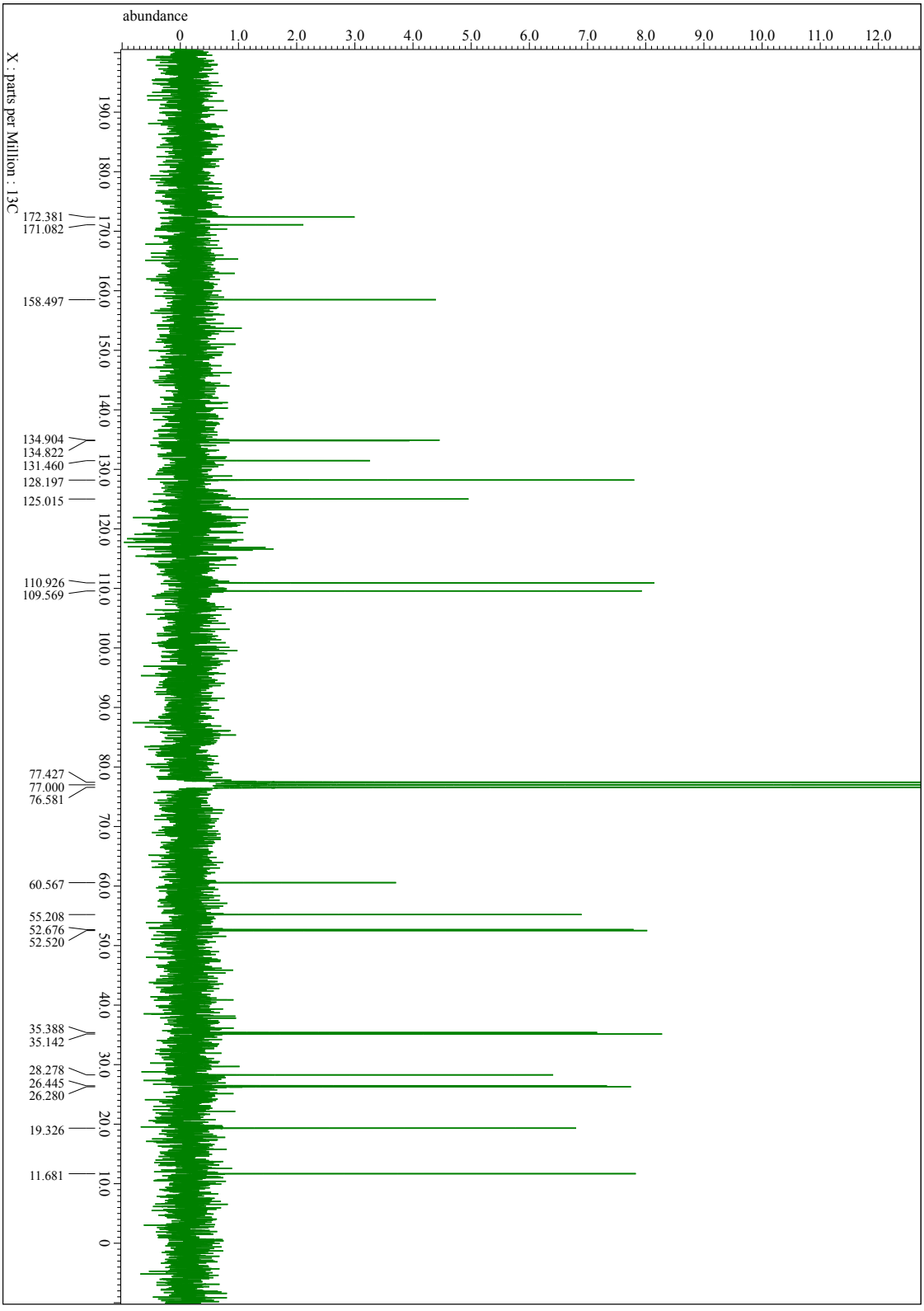
^{1}H NMR spectrum of **7k** ($CDCl_3$, 300 MHz).



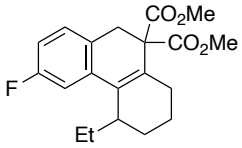


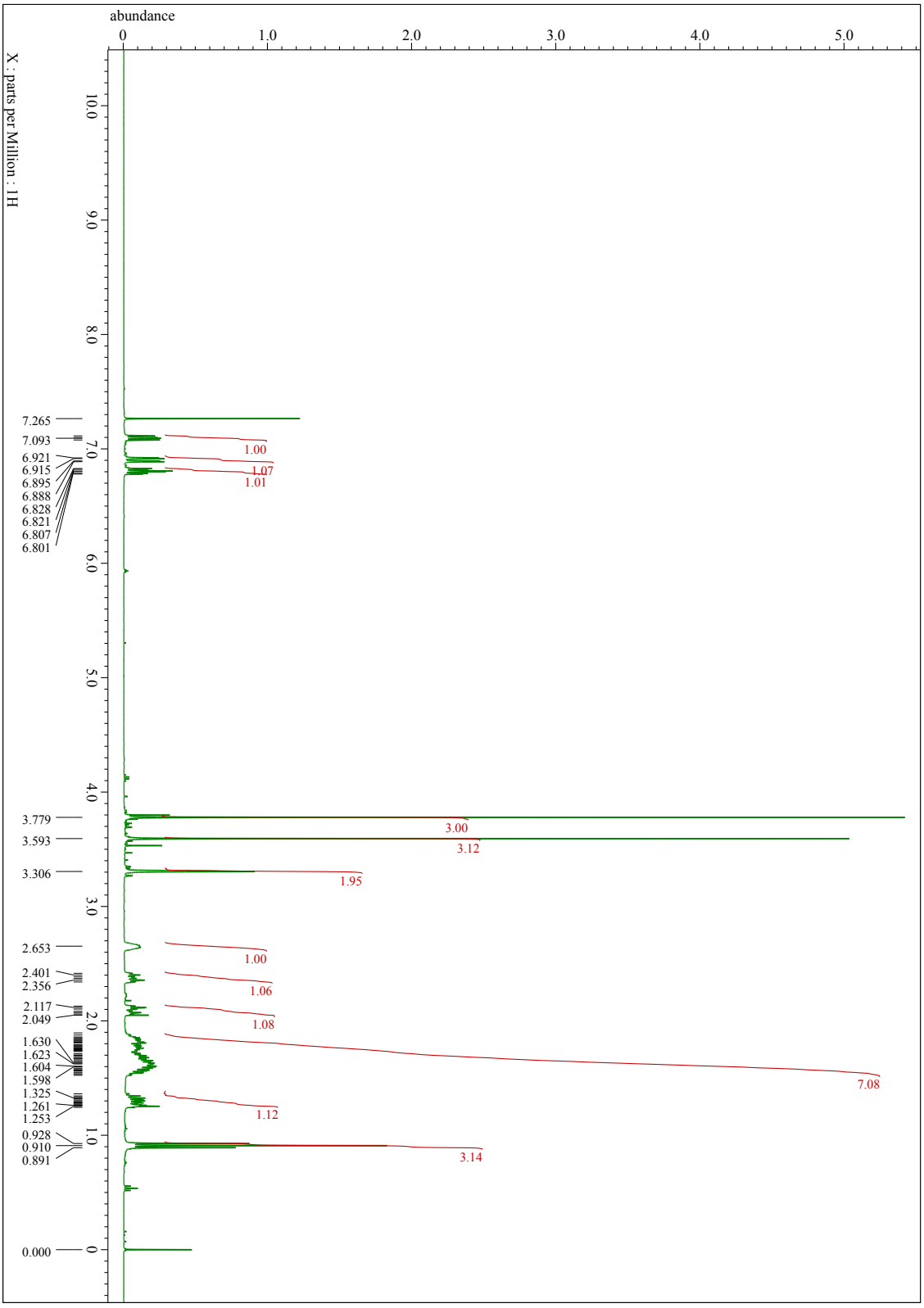
^{13}C NMR spectrum of **7k** ($CDCl_3$, 75 MHz).



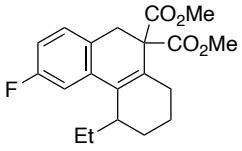


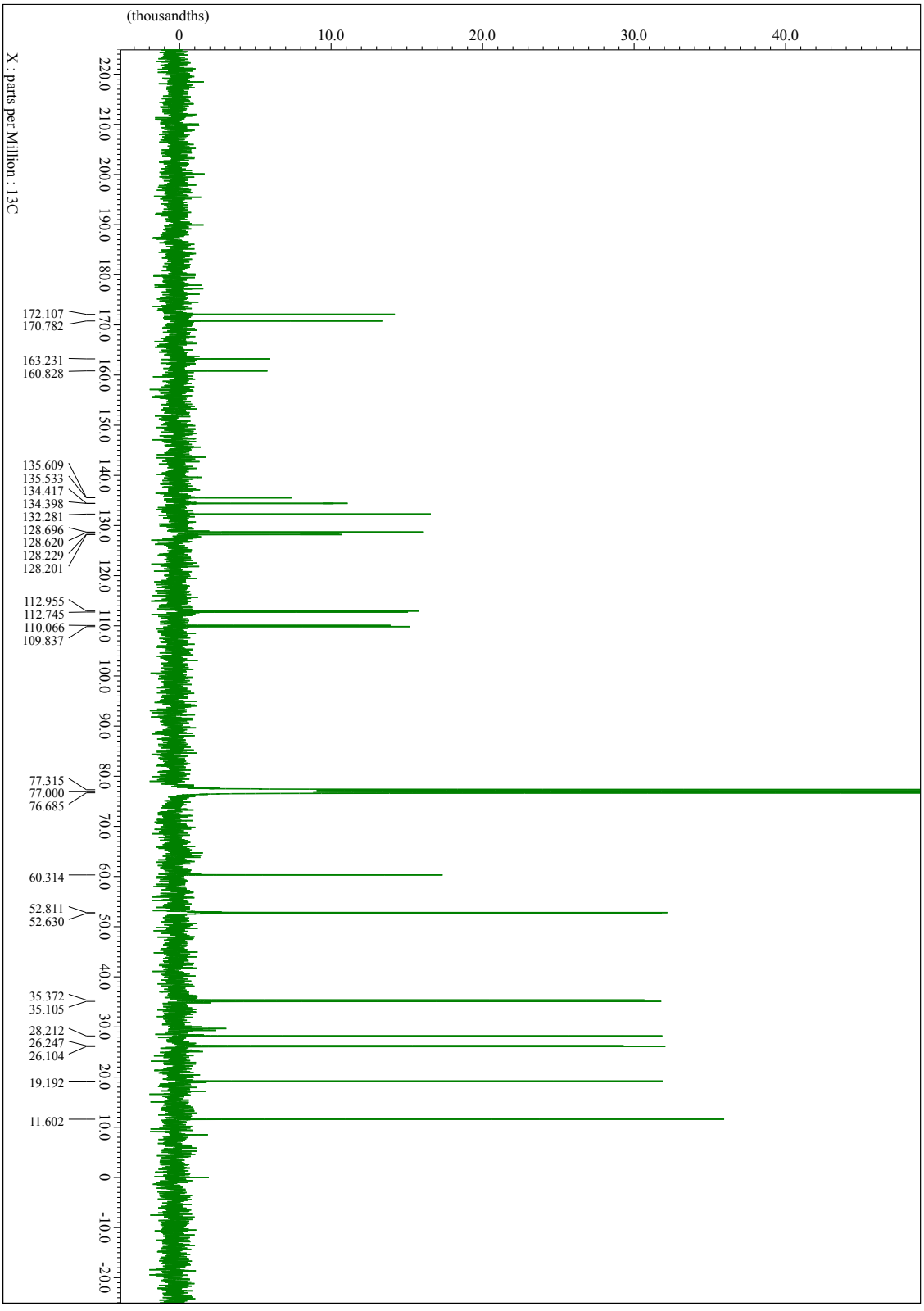
^{1}H NMR spectrum of **7l** ($CDCl_3$, 400 MHz).



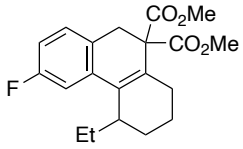


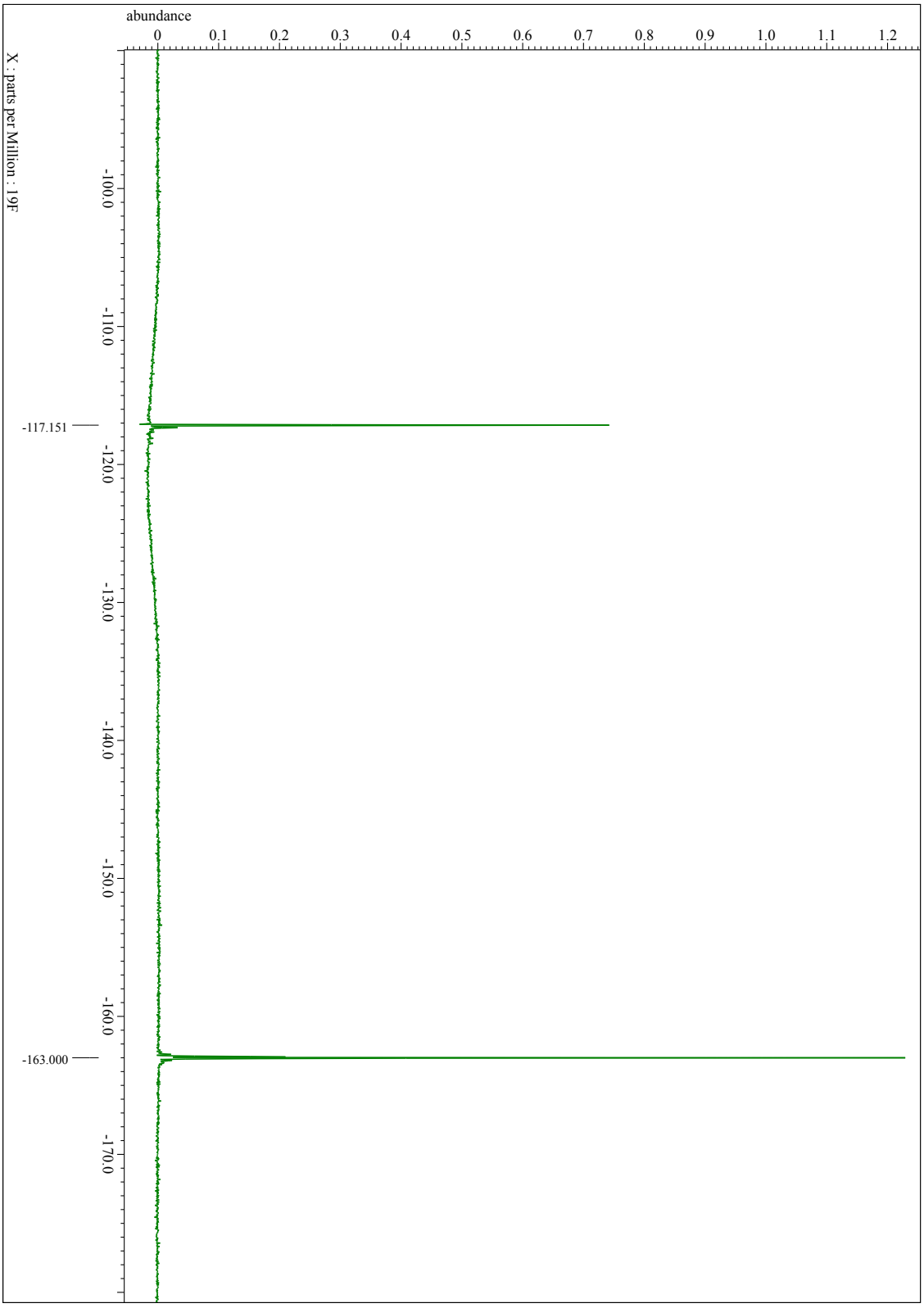
^{13}C NMR spectrum of **7i** ($CDCl_3$, 100 MHz).



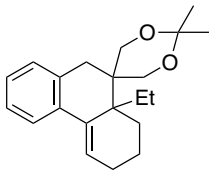


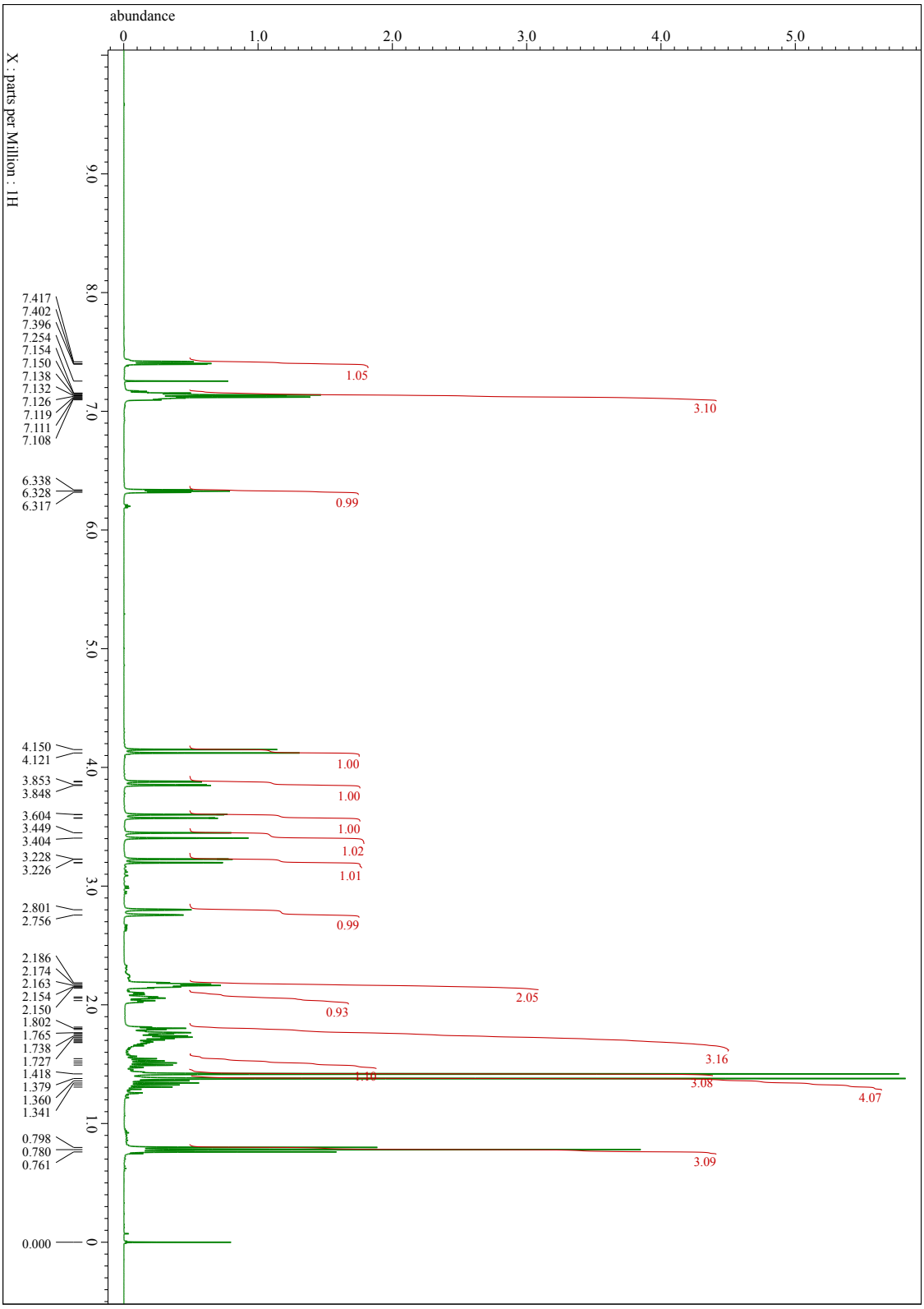
^{19}F NMR spectrum of **7l** ($CDCl_3$, 376 MHz).



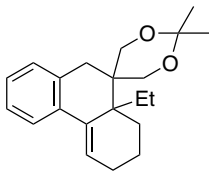


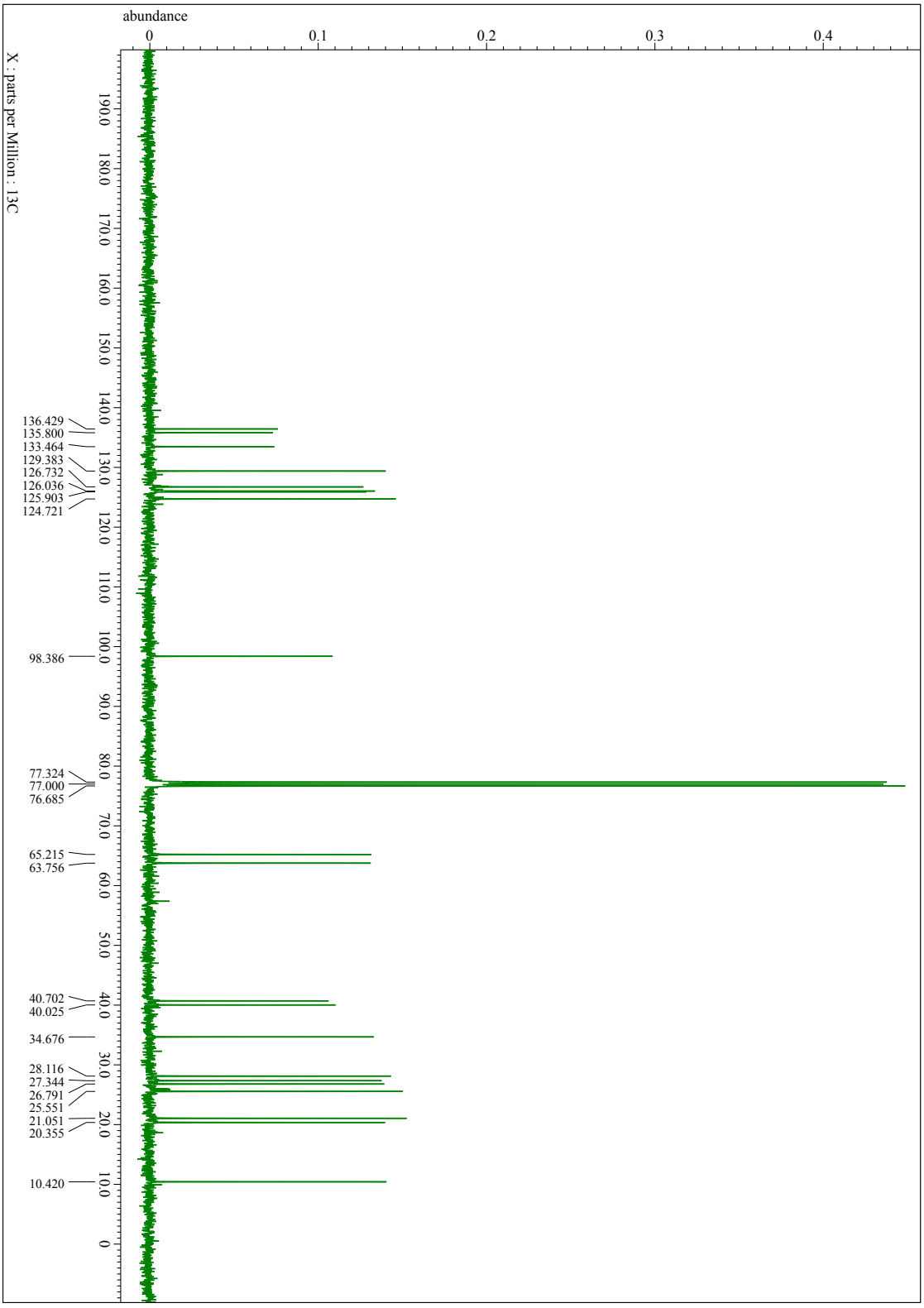
^{1}H NMR spectrum of **9** ($CDCl_3$, 400 MHz).



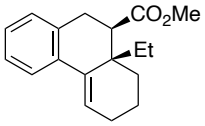


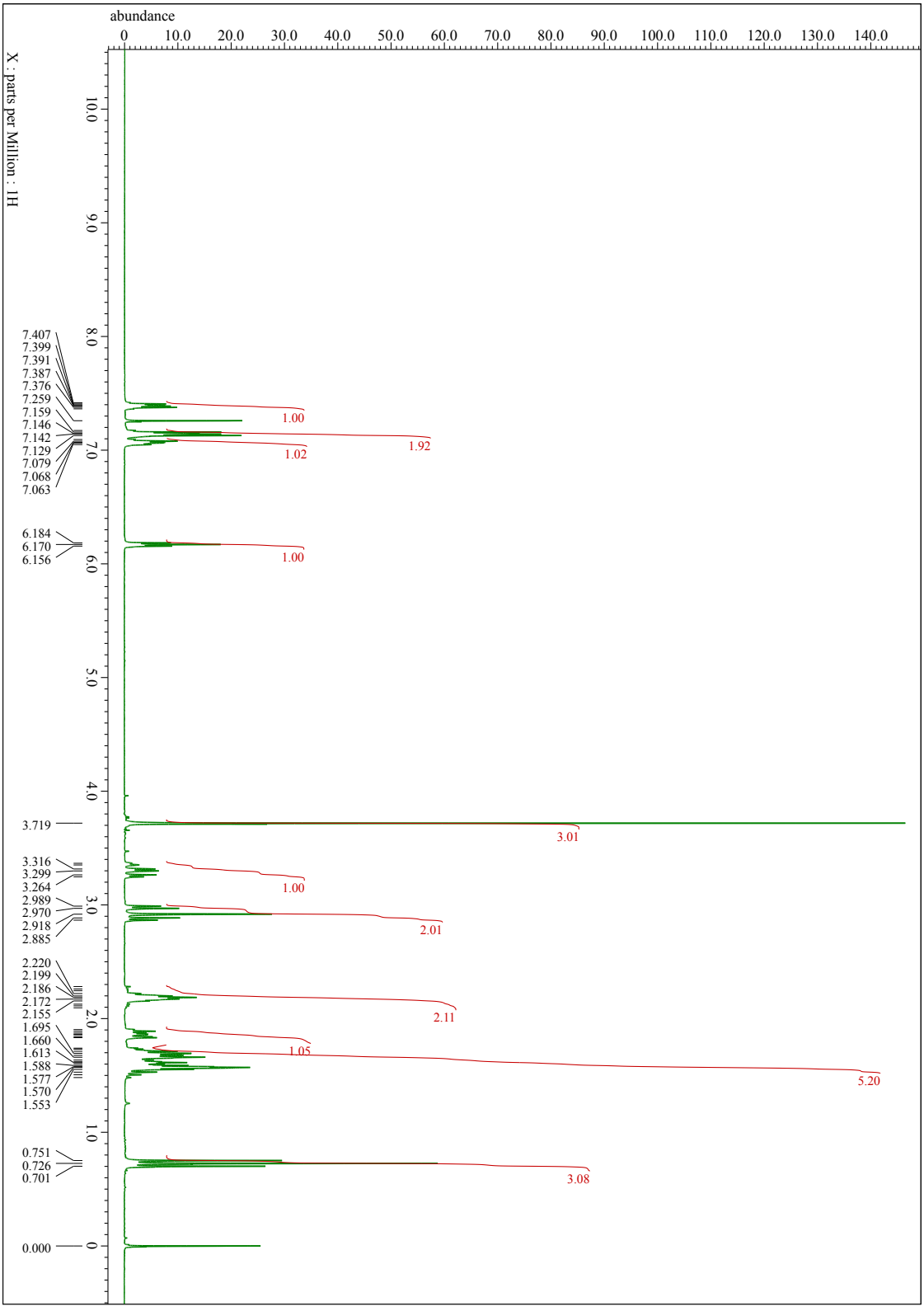
^{13}C NMR spectrum of **9** ($CDCl_3$, 100 MHz).



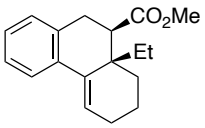


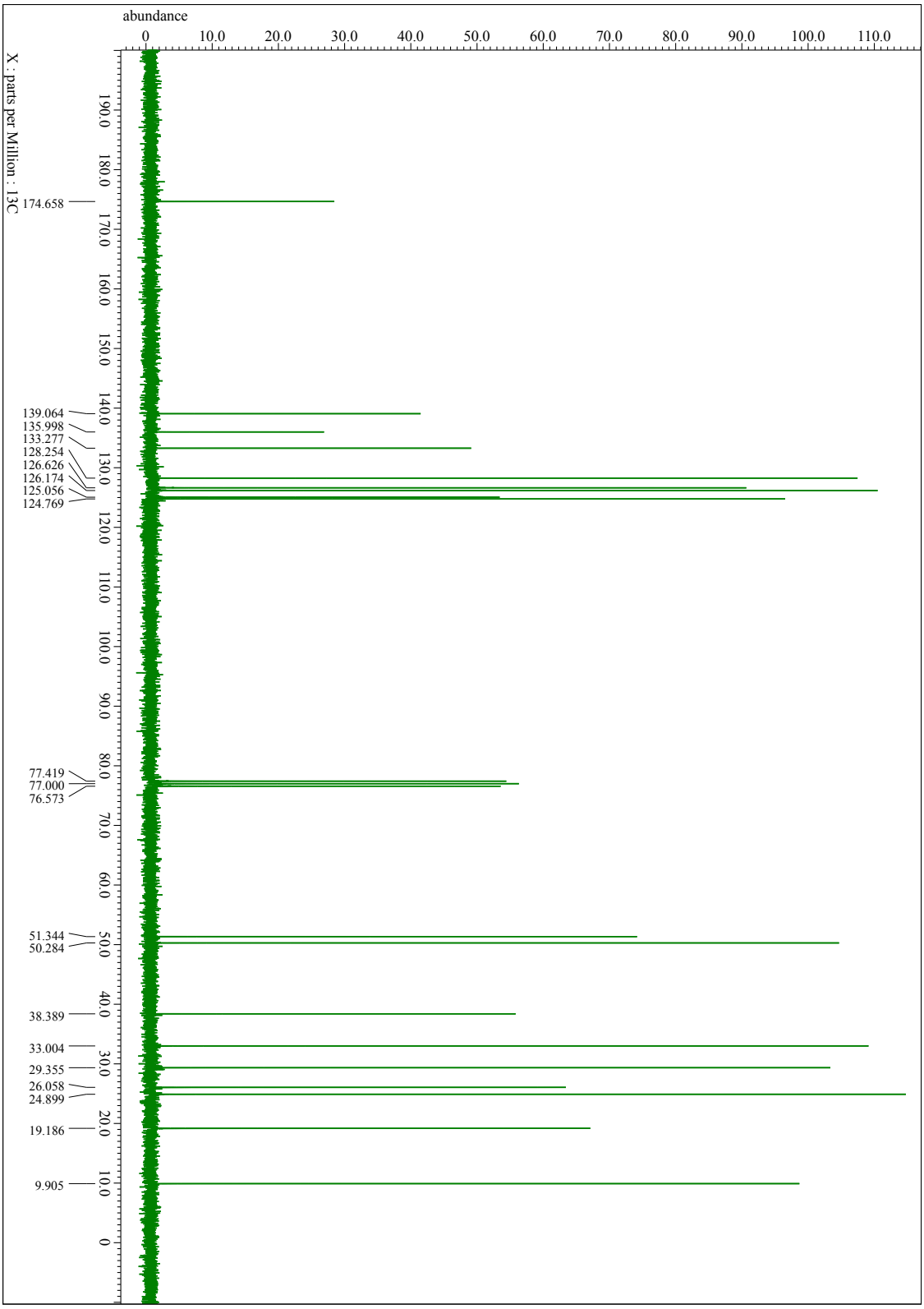
^{1}H NMR spectrum of **10** ($CDCl_3$, 300 MHz).



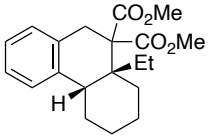


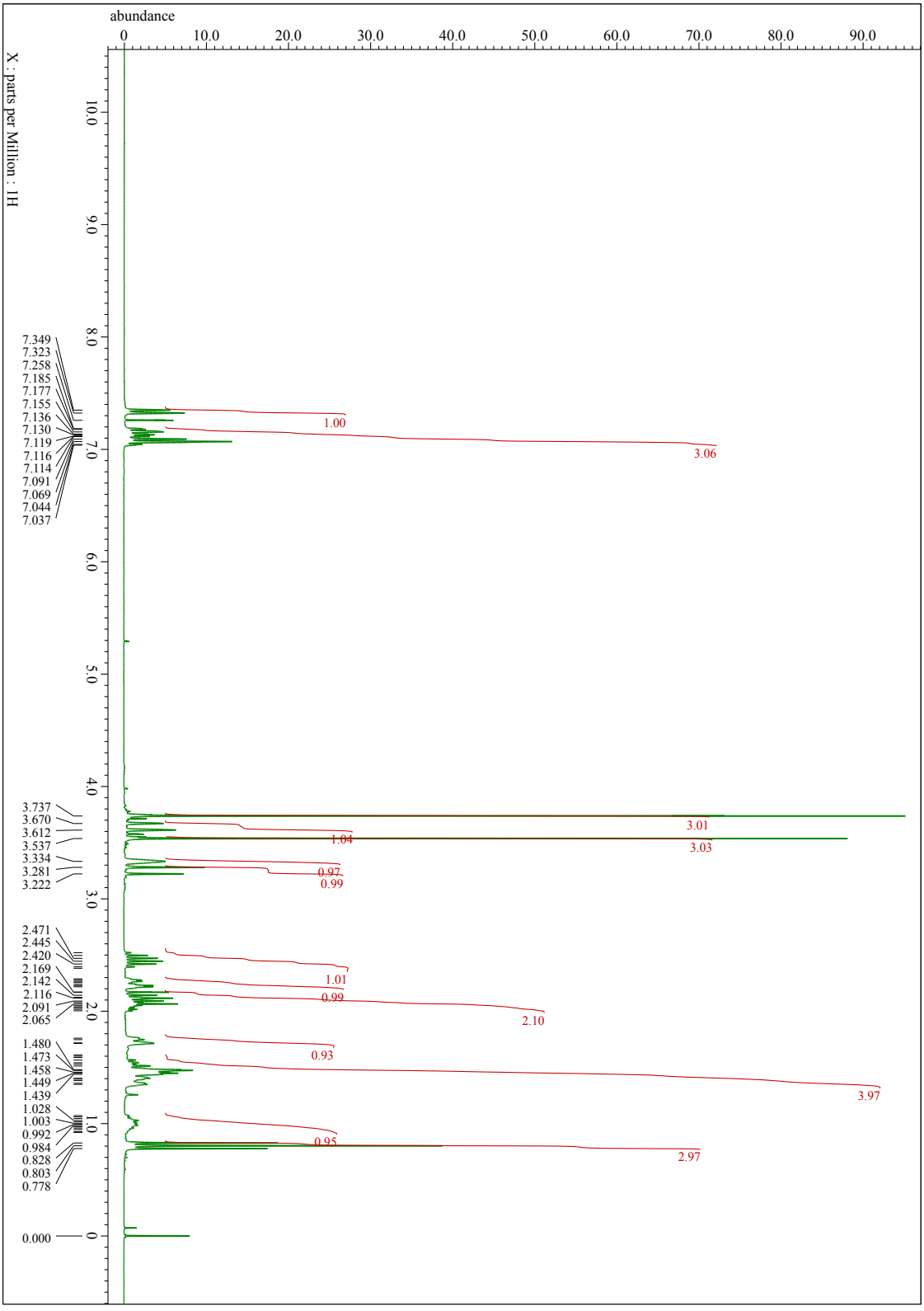
^{13}C NMR spectrum of **10** ($CDCl_3$, 75 MHz).



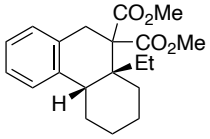


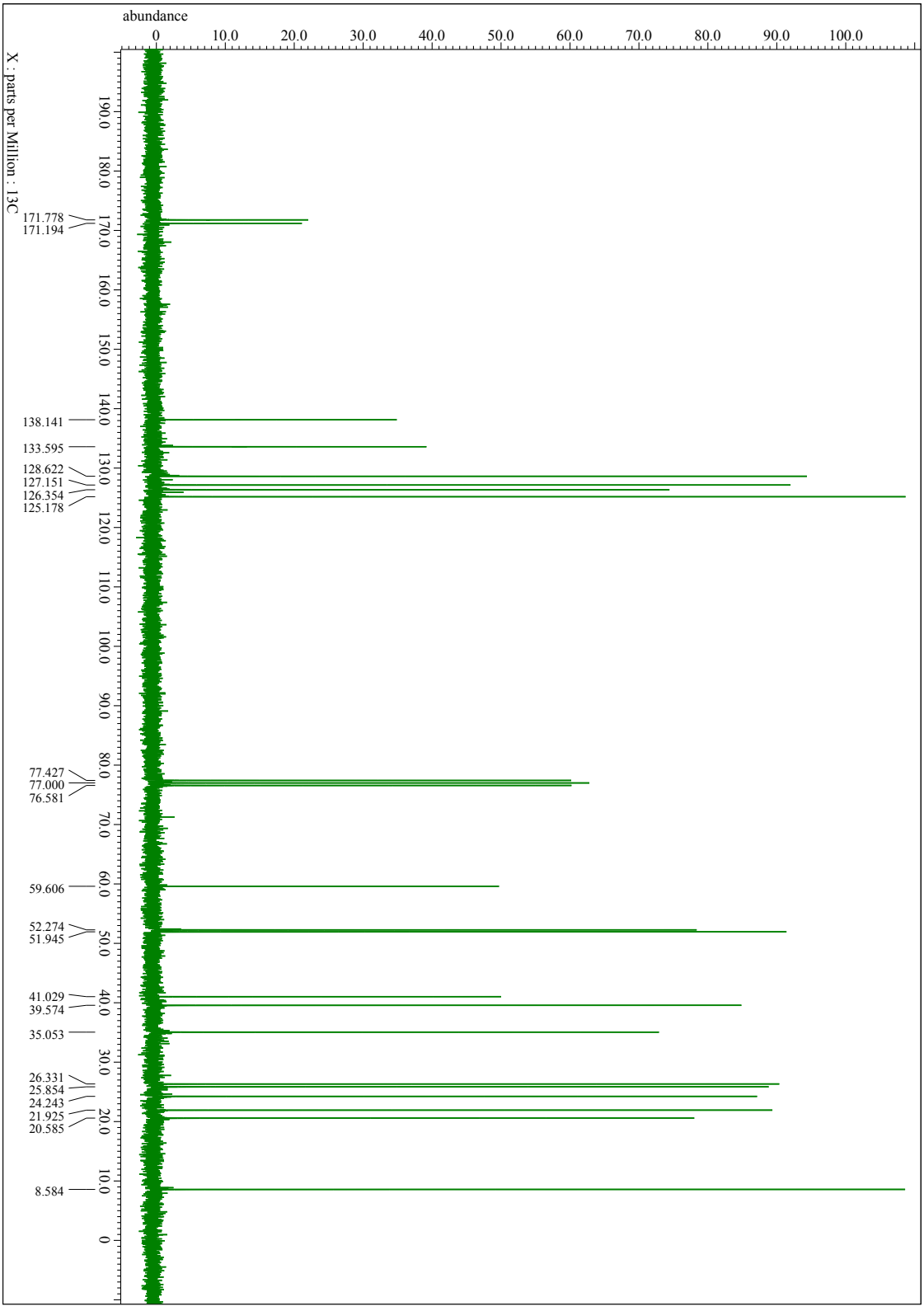
^{1}H NMR spectrum of **11** ($CDCl_3$, 300 MHz).



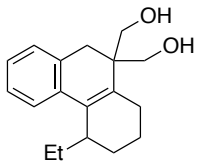


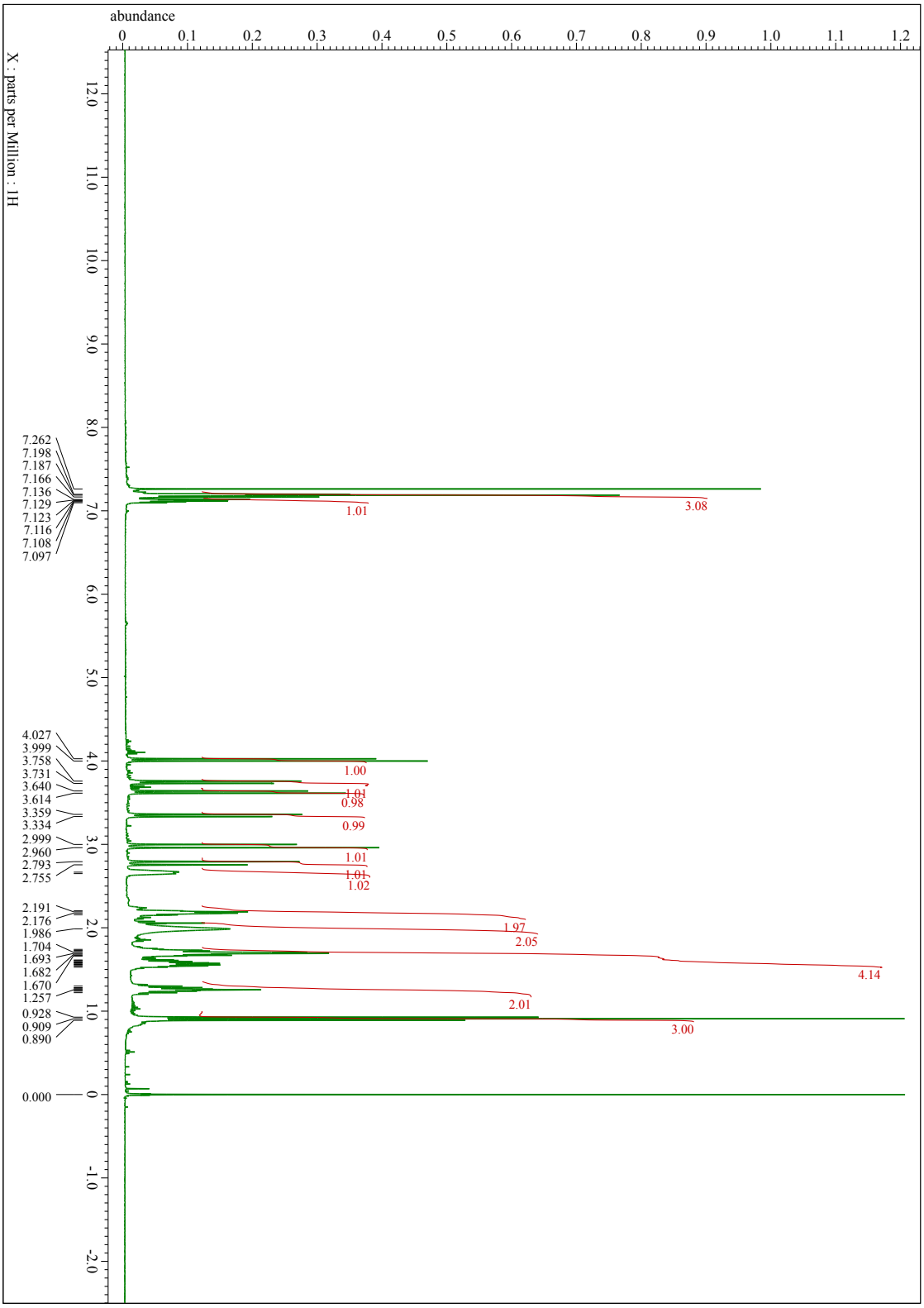
^{13}C NMR spectrum of **11** ($CDCl_3$, 75 MHz).





^{1}H NMR spectrum of **s25** ($CDCl_3$, 400 MHz).





^{13}C NMR spectrum of **s25** ($CDCl_3$, 100 MHz).