Supporting Information

InI_3-Catalyzed Polyene Cyclization of Allenes and Its Application in the Total Synthesis of Seven Abietane-Type Diterpenoids

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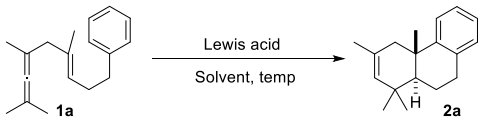
1. General information

All reactions under standard conditions were carried out in anhydrous solvent under argon atmosphere and monitored by TLC on gel F_{254} plates. All products were purified through silica gel chromatography (200~300 mesh). Solvents were dried by standard methods and distilled. All other chemical reagents were purchased from Energy Chemical and Leyan. **^{1}H NMR** and **^{13}C NMR** spectra were obtained on Bruker AVANCE III HD 400, Bruker AVANCE NEO 600 and JEOL JNM-ECS 400 instruments, in $CDCl_3$, DMSO-d_6, CCl_4 and Acetone-d_6 solution. High-resolution mass spectral analysis (**HRMS**) data were measured on the Agilent 6560 Ion Mobility Quadrupole Time of Flight Mass Spectrometer with ESI/APCI resource and Thermo Scientific Q Exactive GC with EI resource. **IR** spectra data were recorded on a Nicolet FT-170SX spectrometer. **X-ray** diffraction data were collected on a XtaLAB Synergy R-DW, HyPix-6000HE diffractometer. Melting points were measured on a melting point apparatus and were uncorrected.

2. Optimization of Experimental Conditions

Table S1. Optimization studies with Lewis acid, solvents and temperature[a]



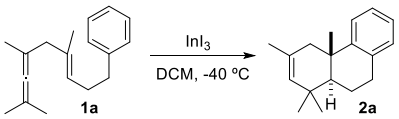
Entry	Lewis acid	equiv	Solvent	Temp (°C)	Time/hour	Yield (%)[b]
1	$InBr_3$	0.2	DCM	r.t.	1	40
2	BF_3•OEt_2	3.0	DCM	-60	18	40
3	$SnCl_4$	0.9	DCM	-78	0.5	15
4	$TiCl_4$	0.9	DCM	-78	20	25
5	$FeCl_3$	1.5	DCM	-20	6	30
6	$InCl_3$	0.2	DCM	r.t.	1	40
7	InI_3	0.2	DCM	-20	4	63
8	$AlCl_3$	0.2	DCM	-40	6	20
9	$ZnCl_2$	0.2	DCM	r.t.	120	NR[c]
10	$ZnBr_2$	0.2	DCM	r.t.	120	20
11	Al $(OTf)_3$	0.2	DCM	r.t.	2	NR[c]
12	In $(OTf)_3$	0.2	DCM	r.t.	18	10
13	Sn $(OTf)_2$	0.2	DCM	0	1	NR[c]

14	$Zn(OTf)_2$	0.2	DCM	r.t.	120	NR[c]
15	$Mg(OTf)_2$	0.2	DCM	r.t.	120	NR[c]
16	AgOTf	0.2	DCM	r.t.	24	NR[c]
17	$Cu(OTf)_2$	0.2	DCM	0	0.5	NR[c]
18	InI_3	0.2	CH_3OH	r.t.	120	NR[c]
19	InI_3	0.2	DMF	r.t.	120	NR[c]
20	InI_3	0.2	DCE	-20	3	45
21	InI_3	0.2	Toluene	-20	3	20
22	InI_3	0.2	CH_3CN	r.t.	120	NR[c]
23	InI_3	0.2	THF	r.t.	120	NR[c]
24	InI_3	0.2	DCM	r.t.	0.5	45
25	InI_3	0.2	DCM	0	1.5	54
27	InI_3	0.2	DCM	-40	6	71
28	InI_3	0.2	DCM	-60	27	60

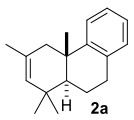
[a]Unless specified, all reactions were carried out with **1a** (0.1 mmol, 1.0 equiv) and solvent (2 mL) in reaction tubes. [b]Isolated yield of product **2a**. [c]No Reaction.

3. Experimental details for the synthesis of compounds (2a-2t)

General procedure (using 2a as an example, the syntheses of 2a-2t follows the same procedure):



A solution of InI_3 (0.02 mmol, 20 mol%) in dry DCM (1 mL) was stirred at -40 °C for 30 min. Then a solution of **1a** (24.0 mg, 0.10 mmol, 1.0 equiv) in dry DCM (1mL) was added. The reaction mixture was stirred at this temperature until the compound **1a** was consumed (monitored by TLC). The reaction mixture was quenched with $NaHCO_3$ (sat. aq., 2 mL) and the organic layer was separated, extracted with DCM (3 × 10 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The crude mixture was purified by column chromatography (PE/EA = 200/1)) to give the desired product **2a.**

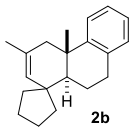


1,1,3,4a-Tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2a)

Compound **2a** (17.0 mg, 71%) was prepared from **1a** (24.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.0 Hz, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.06 - 7.12 (m, 2H), 5.21 (s, 1H), 2.81 -

2.97 (m, 2H), 2.37 (d, *J* = 16.4 Hz, 1H), 2.11 (d, *J* = 16.4 Hz, 1H), 1.88 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.75 (s, 3H), 1.59 - 1.71 (m, 1H), 1.55 - 1.57 (m, 1H), 1.24 (s, 3H), 1.03 (s, 3H), 0.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 135.5, 132.0, 128.9, 128.8, 126.0, 125.9, 125.2, 47.5, 44.7, 37.6, 35.0, 32.2, 31.2, 25.4, 24.4, 22.7, 19.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}$ 241.1951; Found 241.1946; **IR** (KBr, cm^{-1}): *v* 3058, 2959, 1576, 1489, 1448, 757, 726.

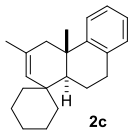


2b

3',4a'-Dimethyl-4a',9',10',10a'-tetrahydro-4'*H*-spiro[cyclopentane-1,1'-phenanthrene] (2b)

Compound **2b** (12.2 mg, 45%) was prepared from **1b** (27.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.6 Hz, 1H), 7.14 - 7.18 (m, 1H), 7.04 - 7.11 (m, 2H), 5.41 (s, 1H), 2.78 - 2.93 (m, 2H), 2.33 (d, *J* = 16.8 Hz, 1H), 2.08 (d, *J* = 16.8 Hz, 1H), 1.57 - 1.81 (m, 12H), 1.42 - 1.48 (m, 1H), 1.32 - 1.38 (m, 1H), 1.16 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 135.6, 131.3, 128.9, 126.7, 126.3, 125.9, 125.2, 46.8, 45.8, 45.1, 41.0, 37.5, 32.9, 31.4, 27.2, 25.3, 24.4, 24.3, 19.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}$ 267.2108; Found 267.2106; **IR** (KBr, cm^{-1}): *v* 3057, 2939, 1577, 1489, 1444, 756, 726.

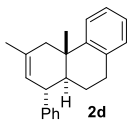


2c

3',4a'-Dimethyl-4a',9',10',10a'-tetrahydro-4'*H*-spiro[cyclohexane-1,1'-phenanthrene] (2c)

Compound **2c** (11.5 mg, 41%) was prepared from **1c** (28.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.0 Hz,, 1H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.04 - 7.10 (m, 2H), 5.92 (s, 1H), 2.93 (dd, *J* = 16.6, 4.6 Hz, 1H), 2.76 - 2.85 (m, 1H), 2.40 (d, *J* = 16.8 Hz, 1H), 2.09 (d, *J* = 16.4 Hz, 1H), 1.91 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.78 (s, 3H), 1.50 - 1.74 (m, 9H), 1.26 - 1.40 (m, 3H), 1.22 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.2, 135.6, 129.8, 128.8, 126.1, 125.9, 125.5, 125.2, 49.4, 45.2, 38.4, 37.8, 37.3, 31.7, 31.0, 26.5, 26.1, 25.1, 22.3, 21.8, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{29}$ 281.2264; Found 281.2261; **IR** (KBr, cm^{-1}): *v* 3056, 2926, 1489, 1447, 763, 725.

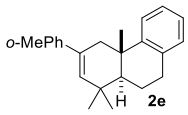


2d

3,4a-Dimethyl-1-phenyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2d)

Compound **2d** (14.5 mg, 50%) was prepared from **1d** (29.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a white soild; mp 114.5 - 116.4 °C.

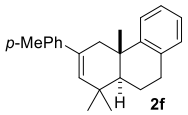
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.38 (m, 3H), 7.17 - 7.25 (m, 4H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 - 7.03 (m, 1H), 5.38 (s, 1H), 3.05 - 3.08 (m, 1H), 2.58 - 2.76 (m, 2H), 2.48 (d, *J* = 16.8 Hz, 1H), 2.33 (d, *J* = 17.2 Hz, 1H), 1.80 (s, 3H), 1.72 - 1.78 (m, 1H), 1.51 - 1.57 (m, 2H), 1.25 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 145.4, 135.5, 132.7, 129.0, 128.8, 128.2, 126.2, 125.8 (two signals overlap), 125.4, 124.8, 46.7, 45.7, 44.7, 36.8, 30.0, 24.1, 23.5, 21.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}$ 289.1951; Found 289.1938; **IR** (KBr, cm^{-1}): *v* 3062, 2963, 2924, 2868, 1492, 1448, 758, 703.



1,1,4a-Trimethyl-3-(*o*-tolyl)-1,4,4a,9,10,10a-hexahydrophenanthrene (2e)

Compound **2e** (12.7 mg, 40%) was prepared from **1e** (31.8 mg) and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil.

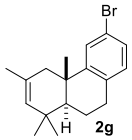
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 - 7.28 (m, 8H), 5.40 (d, *J* = 2.8 Hz, 1H), 2.87 - 3.00 (m, 2H), 2.66 (d, *J* = 16.4 Hz, 1H), 2.46 (dd, *J* = 16.6, 2.2 Hz, 1H), 2.33 (s, 3H), 1.89 - 1.96 (m, 1H), 1.73 - 1.79 (m, 2H), 1.40 (s, 3H), 1.13 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.4, 144.2, 136.4, 135.5, 135.1, 133.6, 130.1, 129.0, 128.4, 126.5, 126.03, 125.96, 125.6, 125.4, 47.7, 44.7, 37.7, 35.3, 32.0, 31.2, 25.3, 22.6, 19.94, 19.85; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2264; **IR** (KBr, cm^{-1}): *v* 3058, 3014, 2960, 1600, 1488, 1447, 727.



1,1,4a-Trimethyl-3-(*p*-tolyl)-1,4,4a,9,10,10a-hexahydrophenanthrene (2f)

Compound **2f** (16.5 mg, 50%) was prepared from **1f** (33.0 mg) and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil.

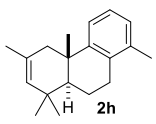
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 - 7.40 (m, 3H), 7.08 - 7.21 (m, 5H), 5.83 (d, *J* = 2.4 Hz, 1H), 2.85 - 2.98 (m, 3H), 2.52 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H), 1.86 - 1.94 (m, 1H), 1.70 - 1.79 (m, 2H), 1.29 (s, 3H), 1.13 (s, 3H), 1.08 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.6, 140.3, 136.3, 135.6, 134.7, 131.9, 129.0, 128.9 (two signals overlap), 126.03, 125.99, 125.4, 125.3 (two signals overlap), 47.7, 42.4, 37.7, 35.5, 32.0, 31.2, 25.1, 22.8, 21.0, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2256; **IR** (KBr, cm^{-1}): *v* 3062, 2977, 2904, 1600, 1496, 753, 691.



6-Bromo-1,1,3,4a-tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2g)

Compound **2g** (10.9 mg, 34%) was prepared from **1g** (32.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

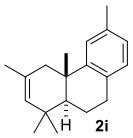
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 5.20 (s, 1H), 2.87 (dd, *J* = 17.2, 4.8 Hz, 1H), 2.70 - 2.79 (m, 1H), 2.29 (d, *J* = 16.4 Hz, 1H), 2.08 (d, *J* = 16.4 Hz, 1H), 1.86 (dd, *J* = 13.0, 6.2 Hz, 1H), 1.73 (s, 3H), 1.59 - 1.70 (m, 1H), 1.50 - 1.54 (m, 1H), 1.20 (s, 3H), 1.01 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 150.3, 134.5, 132.0, 130.6, 129.0, 128.5, 128.3, 119.5, 47.3, 44.6, 37.8, 35.0, 32.1, 30.7, 25.4, 24.3, 22.7, 19.6; **HRMS** (EI) m/z: $[M]^+$ Calcd for $C_{18}H_{23}{}^{79}Br$ 318.0983; Found 318.0980; **IR** (KBr, cm^{-1}): *v* 2959, 1587, 1482, 918, 839, 625.



1,1,3,4a,8-Pentamethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2h)

Compound **2h** (20.7 mg, 82%) was prepared from **1h** (25.2 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.2 Hz, 1H), 5.21 (s, 1H), 2.86 (dd, *J* = 17.2, 5.6 Hz, 1H), 2.55 - 2.64 (m, 1H), 2.37 (d, *J* = 16.4 Hz, 1H), 2.24 (s, 3H), 2.08 (d, *J* = 16.4 Hz, 1H), 1.93 - 1.98 (m, 1H), 1.74 (s, 3H), 1.63 - 1.71 (m, 1H), 1.53 - 1.57 (m, 1H), 1.25 (s, 3H), 1.03 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 136.1, 134.2, 131.9, 128.9, 126.8, 125.6, 123.8, 46.9, 45.2, 37.7, 35.0, 32.1, 28.6, 25.3, 24.4, 22.8, 19.9, 19.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}$ 255.2108; Found 255.2094; **IR** (KBr, cm^{-1}): *ν* 2960, 2928, 1585, 1469, 781, 724.

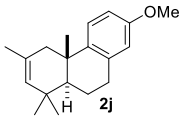


2i

1,1,3,4a,6-Pentamethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2i)

Compound **2i** (19.6 mg, 78%) was prepared from **1i** (25.1 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.91 - 6.97 (m, 2H), 5.20 (s, 1H), 2.75 - 2.92 (m, 2H), 2.30 - 2.38 (m, 4H), 2.09 (d, *J* = 16.0 Hz, 1H), 1.85 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.74 (s, 3H), 1.61 - 1.71 (m, 1H), 1.54 - 1.57 (m, 1H), 1.22 (s, 3H), 1.02 (s, 3H), 0.96 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 135.1, 132.4, 132.0, 128.81, 128.78, 126.5, 126.2, 47.7, 44.7, 37.5, 35.1, 32.2, 30.8, 25.4, 24.4, 22.7, 21.2, 20.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}$ 255.2108; Found 255.2097; **IR** (KBr, cm^{-1}): *ν* 2933, 1613, 1501, 1451, 891, 839, 808.

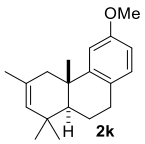


2j

7-Methoxy-1,1,3,4a-tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2j)

Compound **2j** (15.0 mg, 56%) was prepared from **1j** (26.7 mg) and purified by silica gel column chromatography (PE/EA = 20/1) as a white soild; mp 74.9 - 76.8 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.8 Hz, 1H), 6.74 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.57 (d, *J* = 2.8 Hz, 1H), 5.19 (s, 1H), 3.78 (s, 3H), 2.78 - 2.92 (m, 2H), 2.32 (d, *J* = 16.4 Hz, 1H), 2.06 (d, *J* = 16.4 Hz, 1H), 1.83 - 1.87 (m, 1H), 1.72 (s, 3H), 1.62 - 1.69 (m, 1H), 1.52 - 1.56 (m, 1H), 1.19 (s, 3H), 1.01 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 140.4, 136.8, 132.0, 128.8, 127.0, 112.8, 112.5, 55.1, 47.8, 45.0, 37.0, 35.0, 32.2, 31.5, 25.4, 24.4, 22.7, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O$ 271.2057; Found 271.2053; **IR** (KBr, cm^{-1}): *ν* 2909, 2833, 1609, 1500, 1252, 1039, 844, 803.



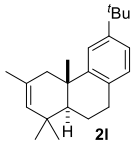
2k

6-Methoxy-1,1,3,4a-tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2k)

Compound **2k** (22.5 mg, 85%) was prepared from **1k** (26.5 mg) and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H), 6.69 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.20 (s, 1H), 3.80 (s, 3H), 2.84 - 2.89 (m, 1H), 2.72 - 2.80 (m, 1H), 2.30 (d, *J* = 16.4 Hz, 1H), 2.10 (d, *J* = 16.4 Hz, 1H), 1.85 (dd,

J = 12.8, 6.0 Hz, 1H), 1.73 (s, 3H), 1.60 - 1.67 (m, 1H), 1.52 - 1.56 (m, 1H), 1.22 (s, 3H), 1.01 (s, 3H), 0.95 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 149.2, 132.0, 129.7, 128.7, 127.8, 111.3, 111.1, 55.3, 47.5, 44.7, 37.8, 35.1, 32.2, 30.4, 25.3, 24.4, 22.7, 20.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O$ 271.2057; Found 271.2057; **IR** (KBr, cm^{-1}): *v* 2958, 2833, 1610, 1502, 1243, 1046, 802, 705.

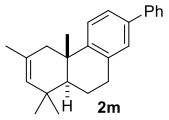


2l

6-(*tert*-Butyl)-1,1,3,4a-tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2l)

Compound **2l** (22.1 mg, 74%) was prepared from **1l** (29.8 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 5.22 (s, 1H), 2.77 - 2.93 (m, 2H), 2.38 (d, *J* = 16.4 Hz, 1H), 2.11 (d, *J* = 16.0 Hz, 1H), 1.86 (dd, *J* = 12.6, 5.8 Hz, 1H), 1.76 (s, 3H), 1.62 - 1.70 (m, 1H), 1.56 - 1.60 (m, 1H), 1.34 (s, 9H), 1.24 (s, 3H), 1.02 (s, 3H), 0.97 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.5, 147.3, 132.6, 132.1, 128.8, 128.4, 122.6, 122.5, 47.7, 44.7, 37.8, 35.1, 34.5, 32.2, 31.5, 30.7, 25.5, 24.5, 22.7, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{33}$ 297.2577; Found 297.2566; **IR** (KBr, cm^{-1}): *v* 2905, 1609, 1500, 1464, 827, 734.

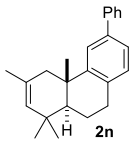


2m

1,1,3,4a-Tetramethyl-7-phenyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2m)

Compound **2m** (19.8 mg, 65%) was prepared from **1m** (30.5 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 - 7.60 (m, 2H), 7.37 - 7.44 (m, 4H), 7.30 - 7.34 (m, 2H), 5.22 (s, 1H), 2.86 - 3.03 (m, 2H), 2.40 (d, *J* = 16.4 Hz, 1H), 2.14 (d, *J* = 16.4 Hz, 1H), 1.91 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.75 (s, 3H), 1.66 - 1.73 (m, 1H), 1.59 - 1.62 (m, 1H), 1.26 (s, 3H), 1.04 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.2, 141.1, 138.1, 135.9, 132.1, 128.7, 128.6, 127.5, 127.0, 126.9, 126.5, 124.8, 47.6, 44.7, 37.5, 35.1, 32.2, 31.3, 25.4, 24.4, 22.7, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2272; **IR** (KBr, cm^{-1}): *v* 3029, 2958, 2935, 1600, 1484, 827, 738, 697.



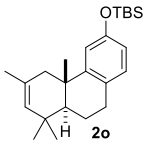
2n

1,1,3,4a-Tetramethyl-6-phenyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2n)

Compound **2n** (21.8 mg, 70%) was prepared from **1n** (31.2 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.52 (d, *J* = 1.6 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.32 - 7.35 (m, 2H), 7.14 (d, *J* = 7.6 Hz, 1H), 5.22 (s, 1H), 2.83 - 3.00 (m, 2H), 2.43 (d, *J* = 16.4 Hz, 1H), 2.16 (d, *J* = 16.4 Hz, 1H), 1.90 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.75 (s, 3H), 1.66 - 1.73 (m, 1H), 1.59 - 1.62 (m, 1H), 1.28 (s, 3H), 1.04 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.3, 141.7, 139.0, 134.8, 132.1, 129.3, 128.7, 128.6, 127.1, 126.9, 124.9, 124.2, 47.6, 44.7, 37.8, 35.1, 32.2, 30.9, 25.5, 24.4, 22.7, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found

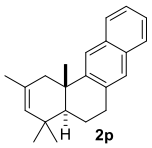
317.2271; **IR** (KBr, cm^{-1}): *v* 3028, 2958, 2935, 1602, 1482, 825, 734, 697.



***tert*-Butyldimethyl((4b,6,8,8-tetramethyl-4b,5,8,8a,9,10-hexahydrophenanthren-3-yl)oxy)silane (2o)**

Compound **2o** (29.1 mg, 81%) was prepared from **1o** (35.9 mg) and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil.

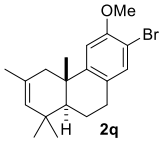
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 8.0 Hz, 1H), 6.74 (d, *J* = 2.4 Hz, 1H), 6.58 (dd, *J* = 8.2, 2.6 Hz, 1H), 5.19 (s, 1H), 2.70 - 2.87 (m, 2H), 2.25 (d, *J* = 16.4 Hz, 1H), 2.07 (d, *J* = 16.4 Hz, 1H), 1.83 (dd, *J* = 12.6, 6.2 Hz, 1H), 1.73 (s, 3H), 1.58 - 1.69 (m, 1H), 1.51 - 1.54 (m, 1H), 1.19 (s, 3H), 1.01 (s, 3H), 0.99 (s, 9H), 0.94 (s, 3H), 0.19 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 153.6, 149.1, 132.1, 129.5, 128.7, 128.2, 117.4, 117.2, 47.5, 44.7, 37.6, 35.1, 32.2, 30.5, 25.8, 25.3, 24.4, 22.7, 20.0, 18.3, -4.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{39}OSi$ 371.2765; Found 371.2774; **IR** (KBr, cm^{-1}): *v* 2932, 2859, 1607, 1493, 1267, 1059, 839, 780, 690.



2,4,4,12b-Tetramethyl-1,4,4a,5,6,12b-hexahydrotetraphene (2p)

Compound **2p** (19.3 mg, 70%) was prepared from **1p** (27.6 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil.

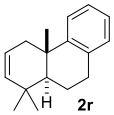
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.78 (m, 3H), 7.55 (s, 1H), 7.33 - 7.39 (m, 2H), 5.24 (s, 1H), 3.19 (dd, *J* = 16.8, 4.8 Hz, 1H), 3.00 - 3.08 (m, 1H), 2.57 (d, *J* = 16.4 Hz, 1H), 2.26 (d, *J* = 16.4 Hz, 1H), 1.95 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.79 (s, 3H), 1.66 - 1.78 (m, 2H), 1.32 (s, 3H), 1.06 (s, 3H), 1.01 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 134.7, 132.4, 132.0, 131.6, 128.8, 127.4, 126.7, 126.6, 125.1, 124.7, 124.5, 47.8, 45.2, 38.1, 35.2, 32.2, 31.6, 26.2, 24.4, 22.9, 20.1; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}$ 291.2108; Found 291.2114; **IR** (KBr, cm^{-1}): *v* 3052, 2935, 1594, 1499, 886, 869, 743.



7-Bromo-6-methoxy-1,1,3,4a-tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2q)

Compound **2q** (15.4 mg, 44%) was prepared from **1q** (35.0 mg) and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 6.79 (s, 1H), 5.20 (s, 1H), 3.88 (s, 3H), 2.69 - 2.85 (m, 2H), 2.28 (d, *J* = 16.4 Hz, 1H), 2.09 (d, *J* = 16.4 Hz, 1H), 1.84 (dd, *J* = 12.8, 6.0 Hz, 1H), 1.74 (s, 3H), 1.58 - 1.68 (m, 1H), 1.49 - 1.53 (m, 1H), 1.21 (s, 3H), 1.01 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 154.0, 148.4, 133.1, 132.2, 129.6, 128.3, 109.6, 108.7, 56.4, 47.4, 44.7, 37.9, 35.1, 32.1, 30.1, 25.3, 24.4, 22.7, 19.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}{}^{79}BrO$ 349.1162; Found 349.1170; **IR** (KBr, cm^{-1}): *v* 2960, 1595, 1489, 1260, 1045, 801, 750.

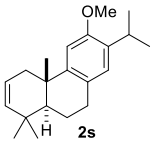


2r

1,1,4a-Trimethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2r)

Compound **2r** (9.6 mg, 41%) was prepared from **1r** (23.5 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a white soild; mp 53.7 - 55.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 7.6 Hz, 1H), 7.16 (t, *J* = 7.2 Hz, 1H), 7.05 - 7.11 (m, 2H), 5.59 - 5.64 (m, 1H), 5.49 - 5.52 (m, 1H), 2.81 - 2.95 (m, 2H), 2.54 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.12 (d, *J* = 16.8 Hz, 1H), 1.85 - 1.89 (m, 1H), 1.65 - 1.76 (m, 2H), 1.27 (s, 3H), 1.06 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.9, 138.1, 135.4, 128.9, 126.0, 125.9, 125.3, 121.8, 48.0, 39.7, 37.0, 35.1, 31.8, 31.1, 25.3, 22.4, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}$ 227.1795; Found 227.1798; **IR** (KBr, cm^{-1}): *v* 3011, 2959, 2935, 1489, 783, 729.

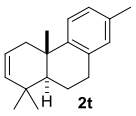


2s

7-Isopropyl-6-methoxy-1,1,4a-trimethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2s)

Compound **2s** (28.6 mg, 95%) was prepared from **1s** (30.1 mg) and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.73 (s, 1H), 5.59 - 5.64 (m, 1H), 5.49 - 5.52 (m, 1H), 3.81 (s, 3H), 3.24 (hept., *J* = 6.8 Hz, 1H), 2.73 - 2.88 (m, 2H), 2.51 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.16 (d, *J* = 16.8 Hz, 1H), 1.81 - 1.88 (m, 1H), 1.62 - 1.73 (m, 2H), 1.28 (s, 3H), 1.21 (t, *J* = 6.6 Hz, 6H), 1.05 (s, 3H), 1.00 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.3, 145.7, 138.2, 134.5, 127.2, 126.3, 121.8, 107.8, 55.6, 48.2, 39.9, 37.1, 35.1, 31.9, 30.5, 26.5, 25.1, 22.9, 22.7, 22.4, 20.2; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{31}O$ 299.2370; Found 299.2376; **IR** (KBr, cm^{-1}): *v* 3009, 2865, 1613, 1501, 1245, 1050, 725.



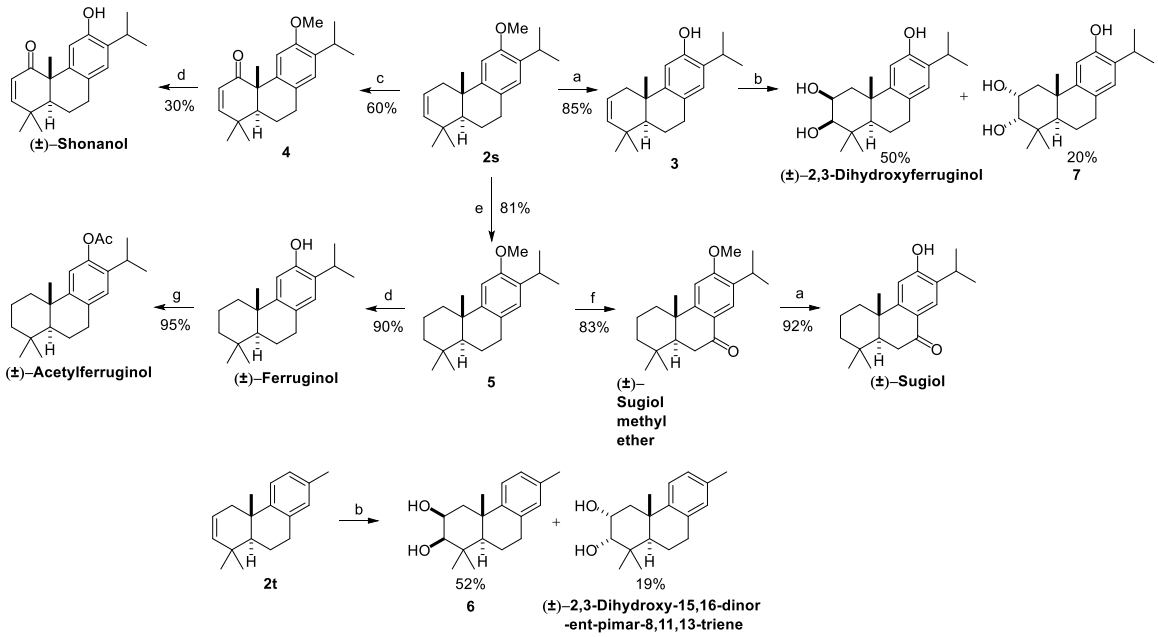
2t

1,1,4a,7-Tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2t)

Compound **2t** (19.9 mg, 83%) was prepared from **1t** (24.0 mg) and purified by silica gel column chromatography (PE/EA = 200/1) as a white soild; mp 31.8 - 33.6 °C.

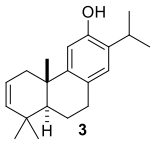
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 5.58 - 5.62 (m, 1H), 5.47 - 5.50 (m, 1H), 2.76 - 2.90 (m, 2H), 2.51 (dd, *J* = 16.6, 6.2 Hz, 1H), 2.28 (s, 3H), 2.09 (d, *J* = 16.8 Hz, 1H), 1.83 - 1.87 (m, 1H), 1.62 - 1.74 (m, 2H), 1.24 (s, 3H), 1.04 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.0, 138.1, 135.3, 134.7, 129.4, 126.8, 125.9, 121.9, 48.2, 39.8, 36.7, 35.1, 31.8, 31.1, 25.3, 22.3, 20.8, 19.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}$ 241.1951; Found 241.1959; **IR** (KBr, cm^{-1}): *v* 3009, 2934, 2863, 1615, 1470, 814, 723.

4. Synthetic applications



Scheme S1. Synthetic Applications.

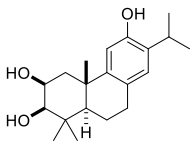
(a) NaSEt, DMF, 140 °C; (b) OsO_4, NMO, citric acid, t-BuOH/acetone/H_2O = 1:1:1; (c) SeO_2, 1,4-dioxane, 100 °C, then DMP, DCM, r.t.; (d) BBr_3, DCM, -20 °C; (e) H_2, Pd/C, CH_3OH, r.t.; (f) CrO_3, AcOH, r.t.; (g) Ac_2O, Et_3N, DMAP, DCM, r.t..



2-Isopropyl-4b,8,8-trimethyl-4b,5,8,8a,9,10-hexahydrophenanthren-3-ol (3)[1]

To a suspension of sodium hydride (60% dissolved in mineral oil, 161 mg, 4.02 mmol, 30.0 equiv) in DMF (2.0 mL) at 0 °C, ethanethiol (298 μL, 4.02 mmol, 30.0 equiv) was added dropwise. The resulting mixture was stirred for 30 min. while warming to room temperature, then a solution of **2s** (40.0 mg, 0.13 mmol, 1.0 equiv) in DMF (2.0 mL) was added and the mixture was heated to 140 °C. After stirring for 12 h, the mixture was cooled to room temperature, diluted with Et_2O (5 mL) and HCl (1M, 5 mL) was added. After stirring vigorously for another 15 min, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL), then brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 8/1) to give compound **3** as a colorless oil (32.4 mg, 0.11 mmol, 85% yield).

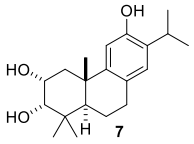
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.64 (s, 1H), 5.57 - 5.62 (m, 1H), 5.47 - 5.50 (m, 1H), 4.50 - 4.54 (m, 1H), 3.13 (hept., *J* = 6.8 Hz, 1H), 2.71 - 2.87 (m, 2H), 2.42 (dd, *J* = 16.8, 6.0 Hz, 1H), 2.11 (d, *J* = 16.4 Hz, 1H), 1.83 - 1.86 (m, 1H), 1.60 - 1.69 (m, 2H), 1.24 - 1.27 (m, 9H), 1.04 (s, 3H), 0.98 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.9, 146.3, 138.1, 131.7, 127.6, 126.5, 121.8, 112.3, 48.0, 39.7, 36.7, 35.1, 31.8, 30.4, 26.8, 25.2, 22.7, 22.5, 22.3, 20.2; **HRMS** (APCI) m/z: $[M-H]^-$ Calcd for $C_{20}H_{27}O$ 283.2067; Found 283.2058; **IR** (KBr, cm^{-1}): *ν* 3451, 2959, 2872, 1465, 1280, 1075, 744.



(±)- 2,3-Dihydroxyferruginol[2]

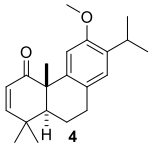
To a solution of **3** (28.9 mg, 0.10 mmol, 1.0 equiv) in acetone/t-BuOH (1:1, 1.0 mL) was added 4-Methylmorpholine *N*-oxide (52 μL, 0.51 mmol, 5.0 equiv), citric acid (98 mg, 0.51 mmol, 5.0 equiv), and osmium(VIII) oxide (10 mg / mL in water, 500 μL, 0.02 mmol, 0.2 equiv). Then the reaction was heated to 35 °C and stirred for 6 h. Upon cooling to room temperature, HCl (1M, 5 mL) was added and the mixture was stirred for 30 min. $Na_2S_2O_3$ (sat. aq., 5 mL) was added to quench, then $NaHCO_3$ (sat. aq., 10 mL) was added to adjust pH to neutral. The reaction mixture was extracted with EtOAc (3 × 20 mL). Combined organic layers were washed with brine (100 mL), dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (PE/EA = 2/1) to give compound **(±)-2,3-dihydroxyferruginol** as a white solid (16.2 mg, 0.05 mmol, 50% yield), mp 213.0 - 214.4 °C and **7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-2,3,6-triol** as a colorless oil (6.5 mg, 0.02 mmol, 20% yield).

^{1}H NMR (400 MHz, Acetone-d_6) δ 7.82 (brs, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 4.12 (hept., J = 3.2 Hz, 1H), 3.57 - 3.69 (m, 2H), 3.15 - 3.26 (m, 2H), 2.81 - 2.82 (m, 1H), 2.67 - 2.76 (m, 1H), 2.56 (dd, J = 14.4, 3.2 Hz, 1H), 1.85 - 1.91 (m, 1H), 1.74 - 1.83 (m, 1H), 1.61 (dd, J = 14.2, 3.4 Hz, 1H), 1.40 (s, 3H), 1.34 (dd, J = 12.0, 2.4 Hz, 1H), 1.17 (t, J = 6.4 Hz, 6H), 1.07 (d, J = 10.0 Hz, 6H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 153.2, 149.3, 132.6, 127.1, 125.7, 111.7, 78.4, 71.9, 50.9, 43.7, 39.1, 37.6, 30.8, 27.4, 27.3, 23.0, 22.9, 19.6, 17.6; **IR** (KBr, cm^{-1}): v 3420, 2961, 1507, 1417, 1034, 794.



7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-2,3,6-triol (7)

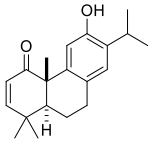
^{1}H NMR (400 MHz, Acetone-d_6) δ 7.73 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 4.04 - 4.11 (m, 1H), 3.55 (d, J = 6.8 Hz, 1H), 3.40 - 3.41 (m, 1H), 3.35 - 3.36 (m, 1H), 3.21 (hept., J = 7.0 Hz, 1H), 2.70 - 2.82 (m, 3H), 1.66 - 1.79 (m, 4H), 1.16 - 1.19 (m, 9H), 1.06 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (100 MHz, Acetone-d_6) δ 153.0, 148.5, 132.6, 127.1, 126.0, 111.1, 79.1, 66.7, 43.8, 41.1, 39.1, 30.3, 30.1, 29.0, 27.4, 26.0, 23.0, 22.9, 22.1, 19.3; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{20}H_{30}NaO_3$ 341.2087; Found 341.2077.



7-Isopropyl-6-methoxy-1,1,4a-trimethyl-4a,9,10,10a-tetrahydrophenanthren-4(1*H*)-one (4)

A mixture of **2s** (42.9 mg, 0.14 mmol, 1.0 equiv) and selenium dioxide (47.8 mg, 0.43 mmol, 3.0 equiv) was stirred in 1,4-dioxane (4 mL) under argon at 100 °C for 24 h. The mixture was filtered by sodium sulfate to remove insoluble substances in the system and concentrated in vacuo. Next, to a stirred solution of the residue in DCM (4 mL), DMP (122.0 mg, 0.29 mmol, 2.0 equiv) was added at room temperature. After the reaction mixture was stirred for 8 h, the reaction was diluted with DCM, quenched by $Na_2S_2O_3$ (sat. aq., 10 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **4** as a colorless oil (26.9 mg, 0.09 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.85 (s, 1H), 6.51 (d, J = 10.0 Hz, 1H), 5.91 (d, J = 10.0 Hz, 1H), 3.87 (s, 3H), 3.25 (hept., J = 6.8 Hz, 1H), 2.73 - 2.86 (m, 2H), 2.07 (dd, J = 12.4, 1.6 Hz, 1H), 1.89 - 1.94 (m, 1H), 1.72 - 1.83 (m, 1H), 1.55 (s, 3H), 1.18 - 1.22 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.7, 155.8, 154.3, 137.0, 135.3, 127.9, 125.9, 125.0, 113.3, 55.6, 48.8, 47.8, 36.6, 31.2, 30.6, 26.5, 26.3, 22.8, 22.5, 21.4, 20.0; **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{29}O_2$ 313.2162; Found 313.2156; **IR** (KBr, cm^{-1}): v 2959, 2916, 2848, 1683, 1501, 1464, 1252, 1065, 800.

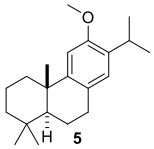


(±)-Shonanol

A solution of **4** (25.9 mg, 0.09 mmol, 1.0 equiv) in DCM (2 mL) was cooled to -20 ℃, BBr_3 (1 M in DCM, 0.9 mL, 0.9 mmol, 10.0 equiv) was slowly added. After the solution was stirred for 6 h. Then the reaction was quenched with $NaHCO_3$ (sat. aq., 5 mL). The aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 6/1) to give compound **(±)-shonanol** as a white solid (7.7 mg, 0.02 mmol, 30% yield), mp 213.1 - 214.7 ℃.

^{1}H NMR (600 MHz, CCl_4) δ 7.25 (s, 1H), 6.67 (s, 1H), 6.47 (d, *J* = 10.2 Hz, 1H), 5.99 (s, 1H), 5.92 (d, *J* = 10.2 Hz, 1H), 3.17 - 3.19 (m, 1H), 2.76 - 2.77 (m, 2H), 2.07 (d, *J* = 12.0 Hz, 1H), 1.86 - 1.87 (m, 1H), 1.75 - 1.78 (m, 1H), 1.48 (s, 3H), 1.18 - 1.25 (m, 12H).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 6.85 (s, 1H), 6.54 (d, *J* = 10.0 Hz, 1H), 6.10 (br s, 1H), 5.97 (d, *J* = 10.0 Hz, 1H), 3.22 (hept., *J* = 6.8 Hz, 1H), 2.73 - 2.86 (m, 2H), 2.09 (d, *J* = 12.0 Hz, 1H), 1.90 - 1.92 (m, 1H), 1.73 - 1.83 (m, 1H), 1.53 (s, 3H), 1.21 - 1.26 (m, 6H), 1.18 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.8, 156.6, 150.7, 137.0, 133.2, 127.7, 126.3, 124.8, 117.3, 48.6, 47.6, 36.6, 31.1, 30.6, 26.8, 26.6, 22.7, 22.4, 21.4, 20.0; **IR** (KBr, cm^{-1}): *ν* 3359, 2960, 1669, 1619, 1511, 1418, 1264, 1022, 882, 737.

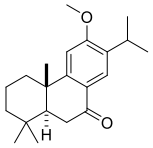


5

7-Isopropyl-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (5)

A mixture of **2s** (148 mg, 0.5 mmol, 1.0 equiv), Pd (10%)/C (5.3 mg) was stirred in CH_3OH (20 mL) under H_2 atmosphere at room temperature for 24 h and concentrated directly in vacuum. The produced residue was purified by column chromatography on silica gel (PE/EA = 200/1) to give compound **5** as a colorless oil (121 mg, 0.40 mmol, 81% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (s, 1H), 6.74 (s, 1H), 3.81 (s, 3H), 3.23 (hept., *J* = 6.8 Hz, 1H), 2.75 - 2.91 (m, 2H), 2.27 (d, *J* = 12.8 Hz, 1H), 1.26 - 1.90 (m, 8H), 1.18 - 1.22 (m, 9H), 0.96 (s, 3H), 0.94 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 148.1, 134.1, 126.9, 126.4, 106.5, 55.6, 50.5, 41.7, 38.9, 37.8, 33.4, 33.3, 29.8, 26.4, 24.8, 22.9, 22.7, 21.6, 19.3, 19.2; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{33}O$ 301.2526; Found 301.2523; **IR** (KBr, cm^{-1}): *ν* 2958, 2866, 1500, 1463, 1249, 1044, 764, 750.

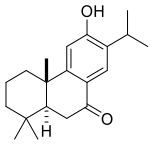


(±)-Sugiol methyl ether

To a stirred solution of **5** (35.3 mg, 0.12 mmol, 1.0 equiv) in AcOH (2 mL) and CrO_3 (14.1 mg, 0.14 mmol, 1.2 equiv) was added at room temperature. After the reaction mixture was stirred for 4 h, it was quenched by $Na_2S_2O_3$ (sat. aq., 5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 20 mL). Then the combined

organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **(±)-sugiol methyl ether** as a white soild (30.7 mg, 0.10 mmol, 83% yield), mp 123.1 - 124.6 °C.

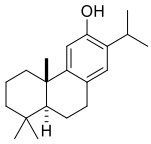
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 6.75 (s, 1H), 3.89 (s, 3H), 3.24 (hept, *J* = 6.8 Hz, 1H), 2.55 - 2.71 (m, 2H), 2.30 (d, *J* = 12.4 Hz, 1H), 1.87 (dd, *J* = 13.4, 3.8 Hz, 1H), 1.78 (tt, *J* = 13.6, 3.2 Hz, 1H), 1.65 - 1.71 (m, 1H), 1.52 - 1.61 (m, 2H), 1.26 - 1.31 (m, 1H), 1.25 (s, 3H), 1.22 (d, *J* = 7.2 Hz, 3H), 1.19 (d, *J* = 6.8 Hz, 3H), 1.00 (s, 3H), 0.93 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 198.5, 161.6, 156.4, 135.2, 125.6, 124.1, 104.4, 55.4, 49.6, 41.4, 38.3, 38.0, 36.0, 33.3, 32.6, 26.5, 23.2, 22.5, 22.4, 21.4, 18.9; **IR** (KBr, cm^{-1}): *v* 2960, 2920, 1673, 1600, 1563, 1495, 1259, 1037, 908, 850.



(±)-Sugiol

To a suspension of sodium hydride (60% in mineral oil, 111 mg, 2.77 mmol, 30.0 equiv) in DMF (2.0 mL), ethanethiol (205 μL, 2.77 mmol, 30.0 equiv) was added dropwise at 0 °C. After the resulting mixture was stirred for 30 min and warmed to room temperature, a solution of **(±)-sugiol methyl ether** (29.0 mg, 0.09 mmol, 1.0 equiv) in DMF (1.5 mL) was added and the mixture was heated to 140 °C and stirred for 12 h, the mixture was cooled to room temperature, diluted with Et_2O (5 mL) and HCl (1M, 5 mL) was added. After stirring vigorously for 15 min, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 20 mL), then brine (50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 6/1) to give compound **(±)-sugiol** as a white solid (25.5 mg, 0.08 mmol, 92% yield), mp 244.6 - 245.3 °C.

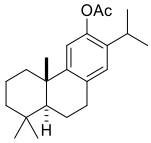
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.26 (s, 1H), 7.65 (s, 1H), 6.78 (s, 1H), 3.13 (hept., *J* = 6.8 Hz, 1H), 2.42 - 2.58 (m, 2H), 2.15 (d, *J* = 12.4 Hz, 1H), 1.68 - 1.79 (m, 2H), 1.58 - 1.62 (m, 1H), 1.38 - 1.47 (m, 2H), 1.22 (td, *J* = 13.2, 3.2 Hz, 1H), 1.12 - 1.16 (m, 9H), 0.94 (s, 3H), 0.88 (s, 3H); **^{13}C NMR** (125 MHz, DMSO-d_6) δ 196.5, 160.1, 155.8, 132.5, 125.0, 122.6, 109.3, 49.1, 40.8, 40.1, 37.5, 35.5, 32.9, 32.3, 26.1, 23.0, 22.4, 22.2, 21.1, 18.5; **IR** (KBr, cm^{-1}): *v* 2960, 2935, 1650, 1594, 1303, 1267, 1027, 749.



(±)-Ferruginol

A solution of **5** (17.7 mg, 0.06 mmol, 1.0 equiv) in DCM (2 mL) was cooled to -20 °C, BBr_3 (1 M in DCM, 0.6 mL, 0.6 mmol, 10.0 equiv) was slowly added. After the solution was stirred for 12 h, it was quenched with $NaHCO_3$ (sat. aq., 5 mL). The aqueous layer was extracted with DCM (3 × 20 mL). Then the combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 10/1) to give compound **(±)-ferruginol** as a yellow oil (15.2 mg, 0.05 mmol, 90% yield).

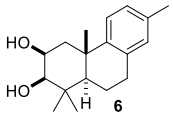
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 (s, 1H), 6.63 (s, 1H), 4.46 (s, 1H), 3.11 (hept., *J* = 6.8 Hz, 1H), 2.83 - 2.89 (m, 1H), 2.73 - 2.81 (m, 1H), 2.17 (d, *J* = 12.8 Hz, 1H), 1.86 (ddt, *J* = 13.4, 7.4, 2.4 Hz, 1H), 1.71 - 1.80 (m, 1H), 1.63 - 1.69 (m, 1H), 1.57 - 1.62 (m, 1H), 1.45 - 1.49 (m, 1H), 1.38 (td, *J* = 13.2, 4.0 Hz, 1H), 1.32 (dd, *J* = 12.4, 2.4 Hz, 1H), 1.24 (t, *J* = 6.6 Hz, 6H), 1.20 - 1.21 (m, 1H), 1.17 (s, 3H), 0.94 (s, 3H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.6, 148.7, 131.4, 127.3, 126.6, 111.0, 50.4, 41.7, 38.9, 37.5, 33.4, 33.3, 29.8, 26.8, 24.8, 22.7, 22.6, 21.6, 19.3, 19.2; **IR** (KBr, cm^{-1}): *v* 3440, 2960, 2925, 2867, 1507, 1417, 1260, 1039, 892, 750.



(±)-Acetylferruginol

To a stirred solution of **(±)-ferruginol** (15.2 mg, 0.05 mmol, 1.0 equiv), Et_3N (22.1 μL, 0.16 mmol, 3.0 equiv) and DMAP (1.3 mg, 0.01 mmol, 0.2 equiv) in DCM (2 mL), Ac_2O (7.5 μL, 0.08 mmol, 1.5 equiv) was added at room temperature. The reaction mixture was stirred for 3 h and then quenched by $NaHCO_3$ (sat. aq., 5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **(±)-acetylferruginol** as a yellow oil (16.6 mg, 0.05 mmol, 95% yield).

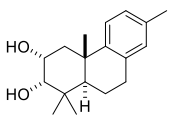
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.94 (s, 1H), 6.83 (s, 1H), 2.78 - 2.94 (m, 3H), 2.30 (s, 3H), 2.16 (d, *J* = 12.4 Hz, 1H), 1.85 - 1.90 (m, 1H), 1.65 - 1.78 (m, 2H), 1.54 - 1.60 (m, 2H), 1.37 - 1.48 (m, 2H), 1.33 (d, *J* = 12.4 Hz, 1H), 1.16 - 1.20 (m, 9H), 0.94 (s, 3H), 0.92 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.0, 148.8, 146.1, 136.6, 133.1, 126.9, 117.9, 50.0, 41.7, 38.8, 37.6, 33.4, 33.3, 30.0, 27.2, 24.8, 23.1, 23.0, 21.6, 21.0, 19.2, 19.0; **IR** (KBr, cm^{-1}): *v* 2961, 2929, 1760, 1496, 1459, 1206, 1016, 914.



(±)-2,3-Dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene (6)

To a solution of **2t** (12.6 mg, 0.05 mmol, 1.0 equiv) in acetone/t-BuOH (1:1, 1.0 mL) was added 4-Methylmorpholine N-oxide (27 μL, 0.26 mmol, 5.0 equiv), citric acid (50.3 mg, 0.26 mmol, 5.0 equiv), and osmium(VIII) oxide (10 mg/mL in water, 500 μL, 0.02 mmol, 0.4 equiv) The reaction was heated to 35 °C and stirred for 6 h. After the reaction mixture was cooled to room temperature, HCl (1M, 5 mL) was added and the mixture was stirred for 30 minutes. $Na_2S_2O_3$ (sat. aq., 5 mL) was added to quench, then $NaHCO_3$ (sat. aq., 10 mL) was added to adjust pH to neutral. Reaction mixture was extracted with EtOAc (3 × 20 mL). Combined organic layers were washed with brine (20 mL), dried over Na_2SO_4. The residue was purified by column chromatography on silica gel (PE/EA = 2/1) to give compound **7** as a white solid (7.5 mg, 0.03 mmol, 52% yield); mp 150.2 -151.6 °C and **(±)-2,3-dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene** as a colorless oil (2.7 mg, 0.01 mmol, 19% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, *J* = 8.4 Hz, 1H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 4.24 (q, *J* = 3.2 Hz, 1H), 3.27 (s, 1H), 2.79 - 2.97 (m, 2H), 2.71 (dd, *J* = 14.4, 3.2 Hz, 1H), 2.27 (s, 3H), 2.20 (s, 2H), 1.80 - 1.94 (m, 2H), 1.72 (dd, *J* = 14.4, 3.6 Hz, 1H), 1.44 (s, 3H), 1.40 (dd, *J* = 11.6, 2.8 Hz, 1H), 1.11 (s, 3H), 1.09 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 134.8, 134.3, 129.6, 126.7, 124.6, 78.2, 71.3, 49.8, 42.7, 38.3, 36.7, 30.5, 29.8, 26.9, 20.8, 18.5, 17.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{26}O_2Na$ 297.1825; Found 297.1817; **IR** (KBr, cm^{-1}): *v* 3418, 2962, 2919, 1612, 1497, 1231, 1072, 748.

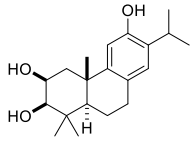


(±)-2,3-Dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene-epimer

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.0 Hz, 1H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.87 (s, 1H), 4.18 (d, *J* = 11.6 Hz, 1H), 3.52 (d, *J* = 2.4 Hz, 1H), 2.81 - 2.94 (m, 2H), 2.27 - 2.30 (m, 1H), 2.27 (s, 3H), 1.95 - 2.05 (m, 2H), 1.72 - 1.81 (m, 4H),

1.21 (s, 3H), 1.09 (s, 3H), 0.97 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 146.1, 134.9, 134.6, 129.6, 126.6, 124.0, 78.8, 67.0, 42.9, 40.2, 38.5, 38.3, 30.0, 28.3, 25.6, 21.6, 20.8, 18.4.

5. NMR data comparisons between the natural products and synthetic ones

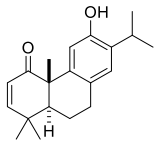


(±)-2,3-Dihydroxyferruginol

^{1}H NMR (in Acetone-d_6, 400 MHz)		
Natural product[3]	**Current work**	**Δδ**
6. 69 (s, 1H)	6.78 (s, 1H)	-0.09
6. 65 (s, 1H)	6.73 (s, 1H)	-0.08
4.50 (br s, 1H)	7.82 (br s, 1H)	Active hydrogen
not provided	4.12 (hept., *J* = 3.2 Hz, 1H)	/
not provided	3.57 - 3.69 (m, 2H)	/
3.20 (d, *J* = 3.5 Hz, 1H)	3.15 - 3.26 (m, 2H)	/
3.06 (m, 1H)		
2.81 (dd, *J* = 16.5, 5.5 Hz, 1H)	2.81 - 2.82 (m, 1H)	/
2.70 (m, 1H)	2.67 - 2.76 (m, 1H)	/
2.56 (dd, *J* = 14.5, 3.0 Hz, 1H)	2.56 (dd, *J* = 14.4, 3.2 Hz, 1H)	0
1.81 (dt, *J* = 12.0, 6.0 Hz, 1H)	1.85 - 1.91 (m, 1H)	/
1.74 (m, 1H)	1.74 - 1.83 (m, 1H)	/
1.66 (dd, *J* = 14.0, 3.0 Hz, 1H)	1.61 (dd, *J* = 14.2, 3.4 Hz, 1H)	+0.05
1.36 (s, 3H)	1.40 (s, 3H)	-0.04
not provided	1.34 (dd, *J* = 12.0, 2.4 Hz, 1H)	/
1.14 (dd, *J* = 10.5, 6.5 Hz, 6H)	1.17 (t, *J* = 6.4 Hz, 6H)	-0.03
1.01 (d, *J* = 13.5 Hz, 6H)	1.07 (d, *J* = 10.0 Hz, 6H)	-0.06

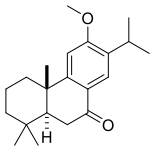
^{13}C NMR (in Acetone-d_6, 100 MHz)					
Natural product	**Current work**	**Δδ**	**Natural product**	**Current work**	**Δδ**
151.0	153.2	-2.2	38.3	39.1	-0.8
148.6	149.3	-0.7	36.8	37.6	-0.8

131.9	132.6	-0.7	31.0	30.8	+0.2
124.1	127.1	-3.0	29.9	27.4	+2.5
126.6	125.7	+0.9	29.8	27.3	+2.5
111.2	111.7	-0.5	26.8		
78.2	78.4	-0.2	22.7	23.0	-0.3
71.4	71.9	-0.5	22.5	22.9	-0.4
49.7	50.9	-1.2	18.7	19.6	-0.9
42.6	43.7	-1.1	17.1	17.6	-0.5



(±)-Shonanol

^{1}H NMR (in CCl_4, 600 MHz)		
Natural product[4]	**Current work**	**Δδ**
7.33 (s, 1H)	7.25 (s, 1H)	+0.08
6.74 (s, 1H)	5.99 (s, 1H)	Active hydrogen
6.67 (s, 1H)	6.67 (s, 1H)	0
6.50 (d, *J* = 10.0 Hz, 1H)	6.47 (d, *J* = 10.2 Hz, 1H)	+0.03
5.95 (d, *J* = 10.0 Hz, 1H)	5.92 (d, *J* = 10.2 Hz, 1H)	+0.03
3.18 (m, 1H)	3.17 - 3.19 (m, 1H)	0
not provided	2.76 - 2.77 (m, 2H)	/
not provided	2.07 (d, *J* = 12.0 Hz, 1H)	/
not provided	1.86 - 1.87 (m, 1H)	/
not provided	1.75 - 1.78 (m, 1H)	/
1.49 (s, 3H),	1.48 (s, 3H)	+0.01
1.19 (s, 6H)	1.18 - 1.25 (m, 12H)	/
1.16 and 1.18 (d, *J* = 7.0 Hz, 6H)		

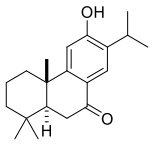


(±)-Sugiol methyl ether

^{1}H NMR (in $CDCl_3$, 400 MHz)		
Natural product[5]	**Current work**	**Δδ**
7.89 (s, 1H)	7.89 (s, 1H)	0
6.75 (s,1H)	6.75 (s, 1H)	0
3.88 (s, 3H),	3.89 (s, 3H)	-0.01
3.25 (sept, *J* = 7.0 Hz, 1H)	3.24 (hept., *J* = 6.8 Hz, 1H)	+0.01
2.56 - 2.71 (m, 2H)	2.55 - 2.71 (m, 2H)	/
1.29 - 2.32 (m, 7H)	2.30 (d, *J* = 12.4 Hz, 1H)	/
	1.87 (dd, *J* = 13.4, 3.8 Hz, 1H)	
	1.78 (tt, *J* = 13.6, 3.2 Hz, 1H)	
	1.65 - 1.71 (m, 1H)	
	1.52 - 1.61 (m, 2H)	
	1.26 - 1.31 (m, 1H)	
1.28 (s, 3H)	1.25 (s, 3H)	+0.03
1.27 (d, *J* = 7.0 Hz, 3H)	1.22 (d, *J* = 7.2 Hz, 3H)	+0.05
1.23 (d, *J* = 7.0 Hz, 3H)	1.19 (d, *J* = 6.8 Hz, 3H)	+0.04
1.00 (s, 3H)	1.00 (s, 3H)	0
0.93 (s, 3H)	0.93 (s, 3H)	0

^{13}C NMR (in $CDCl_3$, 100 MHz)					
Natural product	**Current work**	**Δδ**	**Natural product**	**Current work**	**Δδ**
198.46	198.46	0	37.98	37.98	0
161.63	161.62	+0.01	36.02	36.02	0
156.36	156.36	0	33.29	33.29	0
135.20	135.19	+0.01	32.57	32.56	+0.01
125.59	125.57	+0.02	26.51	26.51	0
124.11	124.09	+0.02	23.24	23.24	0

104.41	104.41	0	22.52	22.51	+0.01
55.37	55.37	0	22.37	22.37	0
49.64	49.64	0	21.35	21.35	0
41.37	41.36	+0.01	18.91	18.90	+0.01
38.26	38.26	0			



(±)-Sugiol

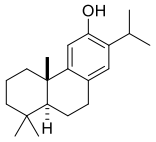
^{1}H NMR (in DMSO-d_6, 400 MHz)

Natural product[5]	**Current work**	**Δδ**
10.23 (s, 1H)	10.26 (s, 1H)	-0.03
7.64 (s,1H)	7.65 (s, 1H)	-0.01
6.78 (s, 1H)	6.78 (s, 1H)	0
3.13 (sept., *J* = 6.8 Hz, 1H)	3.13 (hept., *J* = 6.8 Hz, 1H)	0
2.41 - 2.56 (m, 2H)	2.42 - 2.58 (m, 2H)	/
1.20 - 2.15 (m, 7H)	2.15 (d, *J* = 12.4 Hz, 1H)	/
	1.68 - 1.79 (m, 2H)	
	1.58 - 1.62 (m, 1H)	
	1.38 - 1.47 (m, 2H)	
	1.22 (td, *J* = 13.2, 3.2 Hz, 1H)	
1.15 (d, *J* = 6.8 Hz, 3H)	1.12 - 1.16 (m, 9H)	/
1.13 (s,3H)		
1.11 (d, *J* = 6.8 Hz, 3H)		
0.92 (s, 3H)	0.94 (s, 3H),	-0.02
0.86 (s, 3H)	0.88 (s, 3H)	-0.02

^{13}C NMR (in DMSO-d_6, 125 MHz)

Natural product	**Current work**	**Δδ**	**Natural product**	**Current work**	**Δδ**
196.40	196.54	-0.14	37.41	37.47	-0.06

160.05	160.10	-0.05	35.46	35.52	-0.06
155.75	155.85	-0.10	32.81	32.88	-0.07
132.44	132.51	-0.07	32.24	32.30	-0.06
124.94	125.00	-0.06	26.02	26.06	-0.04
122.53	122.57	-0.04	22.98	23.04	-0.06
109.26	109.33	-0.07	22.32	22.38	-0.06
49.04	49.09	-0.05	22.15	22.21	-0.06
40.80	40.84	-0.04	21.08	21.14	-0.06
39.92	40.07	-0.15	18.43	18.48	-0.05



(±)-Ferruginol

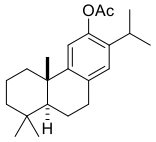
^{1}H NMR (in $CDCl_3$, 400 MHz)

Natural product[6]	**Current work**	**Δδ**
6.83 (s, 1H)	6.83 (s, 1H)	0
6.63 (s, 1H)	6.63 (s, 1H)	0
4.42 (s, 1H)	4.46 (s, 1H)	-0.04
3.11 (hept., *J* = 6.9 Hz, 1H)	3.11 (hept., *J* = 6.8 Hz, 1H)	0
2.91 - 2.82(m,1H)	2.83 - 2.89 (m, 1H)	/
2.81 - 2.72 (m, 1H)	2.73 - 2.81 (m, 1H)	/
2.17 (dtd, *J* = 12.6, 3.3, 1.3 Hz, 1H)	2.17 (d, *J* = 12.8 Hz, 1H),	0
1.86 (ddt, *J* = 12.7, 7.3, 1.8 Hz, 1H)	1.86 (ddt, *J* = 13.4, 7.4, 2.4 Hz, 1H)	0
1.78 - 1.70 (m, 1H)	1.71 - 1.80 (m, 1H)	/
1.69 - 1.62 (m, 1H)	1.63 - 1.69 (m, 1H)	/
1.62 - 1.55 (m, 1H)	1.57 - 1.62 (m, 1H)	/
1.47 (dtd, *J* = 13.2, 3.2, 1.6 Hz, 1H)	1.45 - 1.49 (m, 1H)	0
1.38 (td, *J* = 13.0, 3.6 Hz, 1H)	1.38 (td, *J* = 13.2, 4.0 Hz, 1H)	0
1.32 (dd, *J* = 12.4, 2.3 Hz, 1H)	1.32 (dd, *J* = 12.4, 2.4 Hz, 1H)	0

1.24 (d, *J* = 6.9 Hz, 3H)	1.24 (t, *J* = 6.6 Hz, 6H)	0
1.23 (d, *J* = 6.9 Hz, 3H)		
1.23 - 1.19 (m, 1H)	1.20 - 1.21 (m, 1H),	/
1.17 (s, 3H)	1.17 (s, 3H)	0
0.94 (s, 3H)	0.94 (s, 3H)	0
0.92 (s, 3H)	0.92 (s, 3H)	0

^{13}C NMR (in $CDCl_3$, 100 MHz)

Natural product	Current work	Δδ	Natural product	Current work	Δδ
150.78	150.64	+0.14	33.59	33.44	+0.15
148.83	148.67	+0.16	33.47	33.30	+0.17
131.48	131.36	+0.12	29.91	29.75	+0.16
127.47	127.31	+0.16	26.97	26.82	+0.15
126.77	126.62	+0.15	24.95	24.78	+0.17
111.11	110.97	+0.14	22.89	22.73	+0.16
50.50	50.35	+0.15	22.71	22.55	+0.16
41.84	41.69	+0.15	21.78	21.62	+0.16
39.02	38.87	+0.15	19.47	19.32	+0.15
37.66	37.50	+0.16	19.38	19.23	+0.15

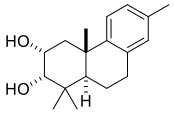


(±)-Acetylferruginol

^{1}H NMR (in $CDCl_3$, 400 MHz)

Natural product[7]	Current work	Δδ
6.94 (s, 1H)	6.94 (s, 1H)	0
6.82 (s, 1H)	6.83 (s, 1H)	-0.01
2.95 - 2.76 (m, 3H)	2.78 - 2.94 (m, 3H)	/
2.30 (s, 3H)	2.30 (s, 3H)	0
2.19 - 2.13 (m, 1H),	2.16 (d, *J* = 12.4 Hz, 1H)	/

1.91 - 1.83 (m, 1H)	1.85 - 1.90 (m, 1H)	/
1.78 - 1.64 (m, 2H)	1.65 - 1.78 (m, 2H)	/
1.61 - 1.54 (m, 2H)	1.54 - 1.60 (m, 2H)	/
1.49 - 1.36 (m, 2H),	1.37 - 1.48 (m, 2H)	/
1.33 (dd, *J* = 12.4, 2.3 Hz, 1H)	1.33 (d, *J* = 12.4 Hz, 1H)	0
1.18 (m, 9H)	1.16 - 1.20 (m, 9H)	/
0.93 (d, *J* = 5.3 Hz, 3H)	0.94 (s, 3H)	-0.01
0.92 (s, 3H).	0.92 (s, 3H)	0



(±)-2,3-Dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene

^{1}H NMR (in $CDCl_3$, 400 MHz)

Natural product[8]	**Current work**	**Δδ**
7.15 (d, *J* = 8.0 Hz, 1H)	7.15 (d, *J* = 8.0 Hz, 1H),	0
6.94 (dd, *J* = 8.0, 1.3 Hz, 1H)	6.95 (d, *J* = 8.0 Hz, 1H)	-0.01
6.87 (s, 1H)	6.87 (s, 1H)	0
4.18 (ddd, *J* = 12.2, 4.4, 2.9 Hz, 1H)	4.18 (d, *J* = 11.6 Hz, 1H)	0
3.52 (d, *J* = 2.9 Hz, 1H)	3.52 (d, *J* = 2.4 Hz, 1H)	0
2.90 (m, 1H)	2.81 - 2.94 (m, 2H)	/
2.85 (m, 1H)		
2.28 (m, 1H)	2.27 - 2.30 (m, 1H)	/
2.26 (s, 3H)	2.27 (s, 3H)	0
not provided	1.95 - 2.05 (m, 2H)	/
1.81 (m, 1H)	1.72 - 1.81 (m, 4H)	/
1.79 (m, 1H)		
1.74 (m, 1H)		
1.73 (m, 1H)		
1.21 (s, 3H)	1.21 (s, 3H)	0

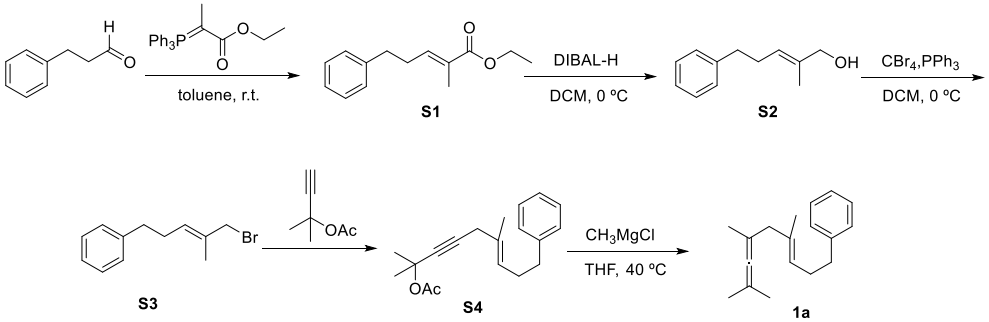
	1.09 (s, 3H)		1.09 (s, 3H)		0
	0.97 (s, 3H)		0.97 (s, 3H)		0

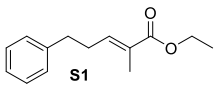
^{13}C NMR (in $CDCl_3$, 125 MHz)

Natural product	Current work	Δδ	Natural product	Current work	Δδ
146.4	146.1	+0.3	40.4	40.2	+0.2
135.1	134.9	+0.2	38.7	38.5	+0.2
134.8	134.6	+0.2	38.5	38.3	+0.2
129.8	129.6	+0.2	30.2	30.0	+0.2
126.8	126.6	+0.2	28.5	28.3	+0.2
124.2	124.0	+0.2	25.8	25.6	+0.2
79.0	78.8	+0.2	21.8	21.6	+0.2
67.2	67.0	+0.2	21.0	20.8	+0.2
43.1	42.9	+0.2	18.6	18.4	+0.2

6. Experimental details for the synthesis of compounds (1a-1t)

General procedure A (using 1a as an example, the syntheses of 1a-1q follows the same procedure):



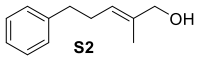


Ethyl (*E*)-2-methyl-5-phenylpent-2-enoate (S1)[9]

A mixture of 3-phenylpropanal (5.0 mL, 37.6 mmol, 1.0 equiv), ethyl 2-(triphenylphosphoranylidene) propionate (15.0 g, 41.4 mmol, 1.1 equiv) in dry toluene (150 mL) was stirred under argon at room temperature for 5 h. Then the reaction mixture was quenched by H_2O (50 mL). Then the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layer was washed with brine (200 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 15/1) to give compound **S1** as a colorless oil (8.1 g, 36.9 mmol, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.30 (m, 2H), 7.18 - 7.21 (m, 3H), 6.81 (td, *J* = 7.2, 1.2 Hz, 1H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.45 - 2.51 (m, 2H), 1.78 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

168.0, 141.2, 140.8, 128.4, 128.3, 128.2, 126.0, 60.4, 34.6, 30.5, 14.2, 12.3; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}O_2Na$ 241.1199; Found 281.1202; **IR** (KBr, cm^{-1}): *v* 3063, 2928, 1709, 1649, 1454, 1266, 1117, 741, 699.

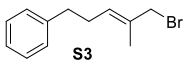


S2

(*E*)-2-Methyl -5-phenylpent-2-en-1-ol (S2)

To a stirred solution of **S1** (8.1 g, 36.9 mmol, 1.0 equiv) in toluene (50 mL), DIBAL-H (1.5 M in toluene, 49.2 mL, 73.8 mmol, 2.0 equiv) was added slowly at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min, it was quenched with HCl (1M, 20 mL) aqueous solution. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 4/1) to give compound **S2** as a colorless oil (5.9 g, 33.2 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 - 7.26 (m, 2H), 7.12 - 7.16 (m, 3H), 5.42 (t, *J* = 6.8 Hz, 1H), 3.90 (s, 2H), 2.91 (br s, 1H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.30 - 2.36 (m, 2H), 1.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.8, 135.2, 128.2, 128.0, 125.6, 124.6, 68.1, 35.5, 29.3, 13.4; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{16}ONa$ 199.1093; Found 199.1095; **IR** (KBr, cm^{-1}): *v* 3343, 3026, 2922, 1603, 1453, 1220, 1004, 747, 699.

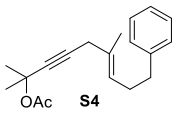


S3

(*E*)-(5-Bromo-4-methylpent-3-en-1-yl) benzene (S3)

To a stirred solution of **S2** (5.9 g, 33.2 mmol, 1.0 equiv) and PPh_3 (10.4 g, 39.8 mmol, 1.2 equiv) in DCM (80 mL), CBr_4 (11.0 g, 33.2 mmol, 1.0 equiv) was added slowly at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min, it was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 50/1) to give compound **S3** as a colorless oil (7.1 g, 29.9 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.26 (m, 2H), 7.14 - 7.16 (m, 3H), 5.60 (t, *J* = 7.0 Hz, 1H), 3.92 (s, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.29 - 2.34 (m, 2H), 1.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.4, 132.6, 130.2, 128.3, 128.2, 125.8, 41.5, 35.1, 30.0, 14.5; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}{}^{79}BrNa$ 261.0249; Found 261.0740; **IR** (KBr, cm^{-1}): *v* 3026, 2922, 1743, 1496, 1453, 749, 699.



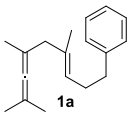
S4

(*E*)-2,6-Dimethyl-9-phenylnon-6-en-3-yn-2-yl acetate (S4)

A mixture of **S3** (7.1 g, 29.9 mmol, 0.6 equiv), 2-methylbut-3-yn-2-yl acetate (6.3 mL, 49.8 mmol, 1.0 equiv), sodium sulfite (3.1 g, 24.9 mmol, 0.5 equiv), copper(I) iodide (1.9 g, 10.0 mmol, 0.2 equiv), potassium carbonate (6.9 g, 49.8 mmol, 1.0 equiv), and DBU (100 μL) was stirred in DMF (60 mL) under argon at room temperature for 2 h, then it was quenched with saturated NH_4Cl (sat. aq., 20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (6 × 50 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified through a silica gel column (PE/EA = 50/1) to give compound **S4** as a colorless oil (5.1 g, 17.9 mmol, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 - 7.22 (m, 2H), 7.08 - 7.13 (m, 3H), 5.38 (t, *J* = 7.0 Hz, 1H), 2.81 (s, 2H), 2.59 (t, *J* = 7.8 Hz, 2H), 2.23 - 2.29 (m, 2H), 1.94 (s, 3H), 1.57 (s, 6H), 1.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.4, 142.1, 130.5, 128.4, 128.2, 125.7, 124.8, 83.8, 81.9, 72.4, 35.8, 29.9, 29.2, 28.6, 22.1, 16.0; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd

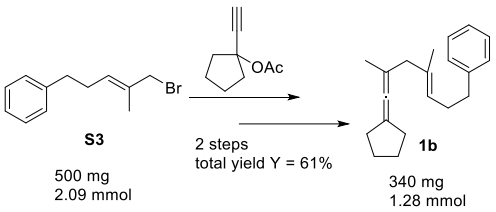
for $C_{19}H_{24}O_2Na$ 307.1669; Found 307.1671; **IR** (KBr, cm^{-1}): *v* 3063, 2925, 2861, 2245, 1745, 1454, 1243, 1134, 1016, 700.



(*E*)-(4,6,8-Trimethylnona-3,6,7-trien-1-yl) benzene (1a)[10]

To a stirred solution of lithium bromide (851 mg, 9.8 mmol, 2.0 equiv) and copper(I) iodide (1.9 g, 9.8 mmol, 2.0 equiv) was stirred in THF (60 mL), methylmagnesium chloride (3.0 M in THF, 3.3 mL, 9.8 mmol, 2.0 equiv) was added slowly at 0 °C under argon. The mixture was stirred for 0.5 h, then **S4** (1.4 g, 4.9 mmol, 1.0 equiv) was added and stirred 1 h at 40 °C. The reaction mixture was quenched by saturated NH_4Cl (sat. aq., 20 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE) to give compound **1a** as a colorless oil (942 mg, 3.9 mmol, 80% yield).

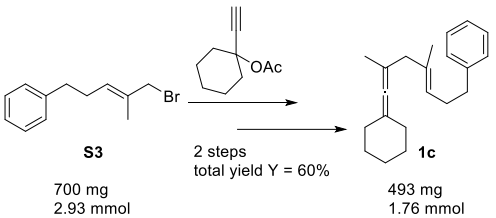
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 - 7.33 (m, 2H), 7.20 - 7.24 (m, 3H), 5.27 (t, *J* = 7.0 Hz, 1H), 2.69 (t, *J* = 8.0 Hz, 2H), 2.62 (s, 2H), 2.34 - 2.40 (m, 2H), 1.69 (s, 6H), 1.59 (s, 3H), 1.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 142.3, 133.8, 128.4, 128.2, 125.7, 125.2, 94.8, 92.7, 45.9, 36.1, 30.0, 20.9, 18.3, 15.4. **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}$ 241.1951; Found 241.1955; **IR** (KBr, cm^{-1}): *v* 3027, 2977, 1940, 1604, 1453, 746, 698.



(*E*)-(7-Cyclopentylidene-4,6-dimethylhepta-3,6-dien-1-yl) benzene (1b)

1b was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (340 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.30 (m, 2H), 7.16 - 7.21 (m, 3H), 5.24 (t, *J* = 7.0 Hz, 1H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 2H), 2.24 - 2.36 (m, 6H), 1.63 - 1.66 (m, 4H), 1.52 - 1.56 (m, 6H) ; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5, 142.4, 133.8, 128.4, 128.2, 125.7, 125.2, 101.7, 97.6, 46.0, 36.1, 31.0, 30.1, 27.0, 18.6, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{20}H_{27}$ 267.2108; Found 267.2113; **IR** (KBr, cm^{-1}): *v* 3026, 2953, 2864, 1604, 1453, 749, 698.

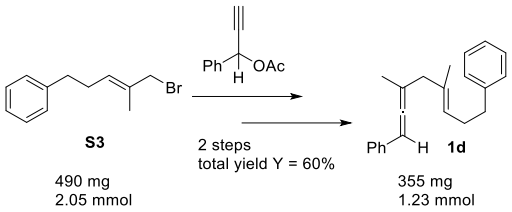


(*E*)-(7-Cyclohexylidene-4,6-dimethylhepta-3,6-dien-1-yl) benzene (1c)

1c was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (493 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.30 (m, 2H), 7.17 - 7.21 (m, 3H), 5.24 (t, *J* = 7.2 Hz, 1H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 2H), 2.31 - 2.36 (m, 2H), 2.01 - 2.10 (m, 4H), 1.47 - 1.63 (m, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 142.4,

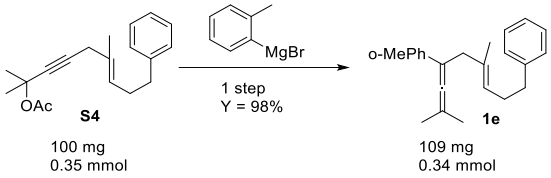
133.9, 128.4, 128.2, 125.6, 125.1, 100.6, 94.7, 46.1, 36.1, 32.0, 30.1, 27.8, 26.3, 18.8, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{29}$ 281.2264; Found 281.2272; **IR** (KBr, cm^{-1}): *v* 3026, 2924, 1958, 1445, 749, 698.



(*E*)-(7-Cyclohexylidene-4,6-dimethylhepta-3,6-dien-1-yl)benzene (1d)

1d was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (355 mg, 60% yield).

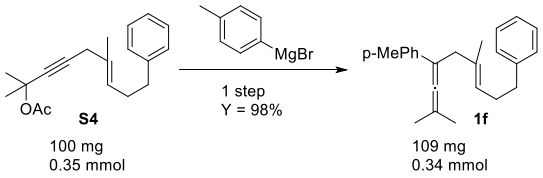
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 - 7.30 (m, 6H), 7.14 - 7.19 (m, 4H), 6.02 (sextet., *J* = 2.8 Hz, 1H), 5.30 (t, *J* = 7.2 Hz, 1H), 2.75 (s, 2H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.31 - 2.37 (m, 2H), 1.69 (d, *J* = 3.2 Hz, 3H), 1.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 203.5, 142.2, 135.8, 132.8, 128.5, 128.4, 128.2, 126.6, 126.4, 126.2, 125.7, 101.5, 92.9, 45.2, 36.0, 30.0, 17.8, 15.7; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{25}$ 289.1951; Found 289.1958; **IR** (KBr, cm^{-1}): *v* 3027, 2918, 1951, 1599, 1453, 749, 694.



(*E*)-1-(2,6-Dimethyl-9-phenylnona-2,3,6-trien-4-yl)-2-methylbenzene (1e)

1e was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil (109 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 - 7.29 (m, 2H), 7.11 - 7.21 (m, 7H), 5.21 (t, *J* = 7.0 Hz, 1H), 2.98 (s, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.35 (d, *J* = 1.6 Hz, 3H), 2.27 - 2.33 (m, 2H), 1.73 (d, *J* = 2.0 Hz, 6H), 1.65 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 142.3, 138.6, 135.8, 133.4, 130.3, 128.4, 128.2, 128.1, 126.3, 125.8, 125.6, 125.5, 100.1, 94.6, 45.1, 36.0, 30.0, 20.7, 20.4, 15.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2271; **IR** (KBr, cm^{-1}): *v* 3025, 2976, 2927, 1959, 1602, 1453, 755, 727, 699.

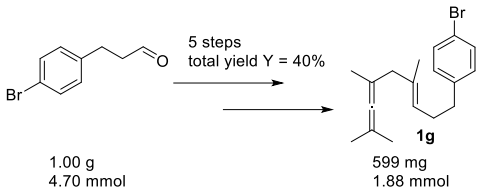


(*E*)-1-(2,6-Dimethyl-9-phenylnona-2,3,6-trien-4-yl)-4-methylbenzene (1f)

1f was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil (109 mg, 98% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 - 7.33 (m, 4H), 7.20 - 7.24 (m, 3H), 7.14 - 7.16 (m, 2H), 5.14 (t, *J* = 7.2 Hz, 1H), 3.13 (s, 2H), 2.68 (t, *J* = 7.6 Hz, 2H), 2.35 - 2.41 (m, 5H), 1.84 (s, 3H), 1.83 (s, 3H), 1.67 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.7, 142.3, 135.6, 135.3, 133.7, 128.8, 128.4, 128.2, 126.1, 125.6, 125.4, 101.1, 97.1, 41.4, 36.0, 30.1, 21.0, 20.3, 16.0; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2274; **IR** (KBr, cm^{-1}): *v* 3026, 2974,

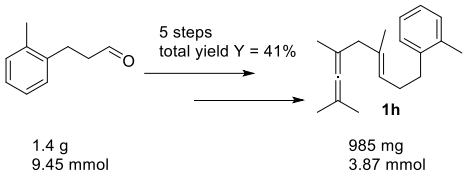
2925, 1950, 1606, 1453, 817, 750.



(*E*)-1-Bromo-4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1g)

1g was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (600 mg, 40% yield).

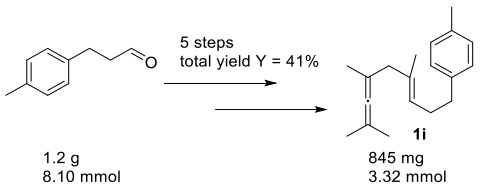
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 5.19 (t, *J* = 7.0 Hz, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.57 (s, 2H), 2.27 - 2.33 (m, 2H), 1.65 (s, 6H), 1.53 (s, 3H), 1.52 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 141.2, 134.2, 131.2, 130.2, 124.7, 119.4, 94.7, 92.8, 45.8, 35.4, 29.8, 20.9, 18.4, 15.5; **HRMS** (EI) m/z: $[M-CH_3]^-$ Calcd for $C_{17}H_{20}{}^{79}Br$ 303.0754; Found 303.0742; **IR** (KBr, cm^{-1}): *v* 2925, 2856, 1959, 1433, 814, 750.



(*E*)-1-Methyl-2-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1h)

1h was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (985 mg, 41% yield).

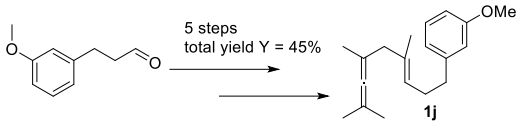
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 - 7.19 (m, 4H), 5.30 (t, *J* = 7.0 Hz, 1H), 2.66 (t, *J* = 8.0 Hz, 2H), 2.61 (s, 2H), 2.35 (s, 3H), 2.28 - 2.32 (m, 2H), 1.68 - 1.68 (m, 6H), 1.58 - 1.59 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 140.5, 135.8, 133.7, 130.1, 128.8, 125.9, 125.8, 125.4, 94.8, 92.8, 45.8, 33.4, 28.8, 20.9, 19.3, 18.4, 15.4; **HRMS** (APCI) m/z: [M+H]+ Calcd for $C_{19}H_{27}$ 255.2108; Found 255.2108; **IR** (KBr, cm^{-1}): *v* 3016, 2976, 2864, 1605, 1443, 741.



(*E*)-1-Methyl-4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1i)

1i was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (845 mg, 41% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (s, 4H), 5.25 (t, *J* = 7.2 Hz, 1H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 2H), 2.29 - 2.35 (m, 5H), 1.67 (s, 3H), 1.67 (s, 3H), 1.57 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 139.3, 135.0, 133.6, 128.9, 128.3, 125.3, 94.8, 92.7, 45.9, 35.7, 30.2, 21.0, 20.9, 18.4, 15.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}$ 255.2108; Found 255.2106; **IR** (KBr, cm^{-1}): *v* 3047, 2977, 2857, 1515, 1443, 807.



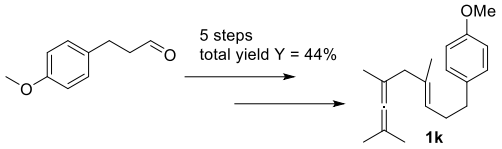
1.5 g
9.13 mmol

1.1 g
4.11 mmol

(*E*)-1-Methoxy-3-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1j)

1j was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil (1.1 g, 45% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.8 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 6.73 - 6.76 (m, 2H), 5.24 (t, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 2.64 (t, *J* = 7.8 Hz, 2H), 2.59 (s, 2H), 2.31 - 2.37 (m, 2H), 1.66 (s, 6H), 1.57 (s, 3H), 1.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 159.6, 144.0, 133.8, 129.2, 125.2, 120.9, 114.2, 111.0, 94.8, 92.8, 55.1, 45.8, 36.1, 29.9, 20.9, 18.3, 15.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O$ 271.2057; Found 271.2061; **IR** (KBr, cm^{-1}): *v* 2976, 2930, 2857, 1970, 1601, 1453, 1261, 1053, 779, 695.



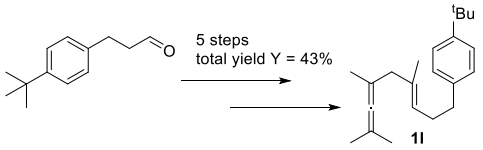
1.0 g
6.09 mmol

725 mg
2.68 mmol

(*E*)-1-Methoxy-4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1k)

1k was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil (725 mg, 44% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 - 7.13 (m, 2H), 6.81 - 6.85 (m, 2H), 5.22 (t, *J* = 7.0 Hz, 1H), 3.79 (s, 3H), 2.57 - 2.62 (m, 4H), 2.27 - 2.33 (m, 2H), 1.65 (s, 6H), 1.55 (s, 3H), 1.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 157.7, 134.5, 133.7, 129.3, 125.3, 113.6, 94.8, 92.7, 55.2, 45.9, 35.2, 30.3, 20.9, 18.4, 15.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{27}O$ 271.2057; Found 271.2061; **IR** (KBr, cm^{-1}): *v* 2976, 2930, 2857, 1612, 1442, 1246, 1040, 824.



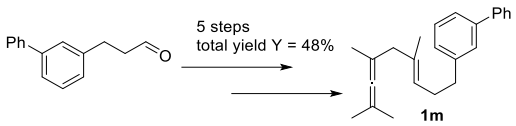
940 mg
4.94 mmol

630 mg
2.12 mmol

(*E*)-1-(*tert*-Butyl)-4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1l)

1l was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (630 mg, 43% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 5.26 (t, *J* = 7.0 Hz, 1H), 2.64 (t, *J* = 8.0 Hz, 2H), 2.59 (s, 2H), 2.31 - 2.37 (m, 2H), 1.66 (s, 6H), 1.57 (s, 3H), 1.54 (s, 3H), 1.33 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 148.4, 139.3, 133.6, 128.0, 125.4, 125.1, 94.8, 92.8, 45.8, 35.5, 34.3, 31.4, 30.0, 20.9, 18.4, 15.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{33}$ 297.2577; Found 297.2560; **IR** (KBr, cm^{-1}): *v* 2906, 2868, 1608, 1513, 1445, 825, 750.



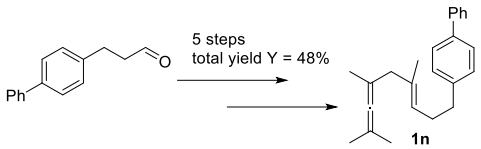
990 mg
4.71 mmol

715 mg
2.26 mmol

(*E*)-3-(4,6,8-Trimethylnona-3,6,7-trien-1-yl)-1,1'-biphenyl (1m)

1m was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (715 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.63 (m, 2H), 7.42 - 7.47 (m, 4H), 7.34 - 7.39 (m, 2H), 7.20 - 7.22 (m, 1H), 5.28 (t, *J* = 7.0 Hz, 1H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.60 (s, 2H), 2.38 - 2.43 (m, 2H), 1.67 (s, 6H), 1.58 (s, 3H), 1.54 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 142.8, 141.4, 141.2, 133.9, 128.7 (three signals overlap), 127.4 (two signals overlap), 127.2, 127.1, 125.1, 124.6, 94.7, 92.7, 45.9, 36.2, 30.1, 20.9, 18.3, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 317.2275; **IR** (KBr, cm^{-1}): *v* 3031, 2976, 2927, 1959, 1599, 1442, 797, 700.



880 mg
4.18 mmol

636 mg
2.01 mmol

(*E*)-4-(4,6,8-Trimethylnona-3,6,7-trien-1-yl)-1,1'-biphenyl (1n)

1n was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (636 mg, 48% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 - 7.62 (m, 2H), 7.52 - 7.54 (m, 2H), 7.43 - 7.46 (m, 2H), 7.28 - 7.36 (m, 3H), 5.28 (t, *J* = 7.0 Hz, 1H), 2.72 (t, *J* = 7.8 Hz, 2H), 2.61 (s, 2H), 2.36 - 2.42 (m, 2H), 1.67 (s, 6H), 1.59 (s, 3H), 1.56 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.0, 141.5, 141.2, 138.6, 133.9, 128.8, 128.7, 127.0 (five signals overlap), 125.1, 94.7, 92.8, 45.9, 35.7, 30.0, 20.9, 18.4, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{29}$ 317.2264; Found 371.2270; **IR** (KBr, cm^{-1}): *v* 3027, 2975, 2926, 1601, 1486, 1442, 761, 697.

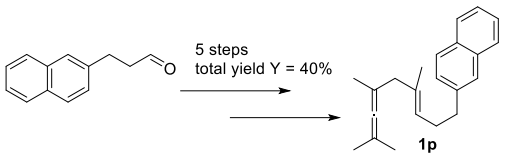
1.6 g
6.05 mmol

897 mg
2.42 mmol

(*E*)-*tert*-Butyldimethyl(4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)phenoxy)silane (1o)

1o was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 100/1) as a colorless oil (897 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, *J* = 8.4 Hz, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.22 (t, *J* = 7.2 Hz, 1H), 2.57 - 2.60 (m, 4H), 2.26 - 2.32 (m, 2H), 1.65 (s, 6H), 1.53 (s, 6H), 0.99 (s, 9H), 0.19 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 153.5, 135.1, 133.6, 129.2, 125.3, 119.7, 94.8, 92.7, 45.9, 35.2, 30.2, 25.7, 20.9, 18.3, 18.2, 15.4, -4.4; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{39}OSi$ 371.2765; Found 371.2776; **IR** (KBr, cm^{-1}): *v* 3028, 2957, 2929, 1609, 1443, 1254, 1101, 917, 839, 780.



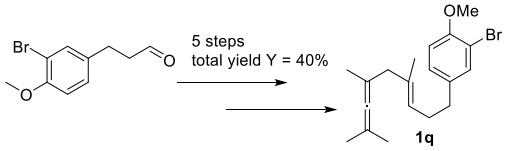
620 mg
3.37 mmol

391 mg
1.35 mmol

(*E*)-2-(4,6,8-Trimethylnona-3,6,7-trien-1-yl)naphthalene (1p)

1p was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 200/1) as a colorless oil (391 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 - 7.83 (m, 3H), 7.65 (s, 1H), 7.37 - 7.48 (m, 3H), 5.30 (t, *J* = 6.6 Hz, 1H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 2H), 2.42 - 2.48 (m, 2H), 1.67 (s, 6H), 1.59 (s, 3H), 1.55 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 139.9, 133.9, 133.6, 132.0, 127.7, 127.6, 127.4 (two signals overlap), 126.4, 125.8, 125.2, 125.0, 94.8, 92.8, 45.9, 36.3, 29.9, 20.9, 18.4, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{27}$ 291.2108; Found 291.2113; **IR** (KBr, cm^{-1}): *v* 3052, 2976, 2855, 1601, 1442, 852, 815, 743.



780 mg
3.21 mmol

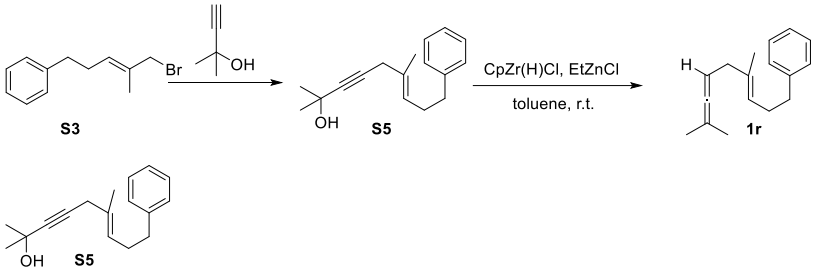
448 mg
1.28 mmol

(*E*)-2-Bromo-1-methoxy-4-(4,6,8-trimethylnona-3,6,7-trien-1-yl)benzene (1q)

1q was prepared according to general procedure A and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil (448 mg, 40% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.0 Hz, 1H), 7.08 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.81 (d, *J* = 8.4 Hz, 1H), 5.19 (t, *J* = 7.2 Hz, 1H), 3.87 (s, 3H), 2.55 - 2.59 (m, 4H), 2.26 - 2.32 (m, 2H), 1.65 (s, 6H), 1.54 (s, 3H), 1.53 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.1, 153.9, 136.1, 134.1, 133.2, 128.3, 124.7, 111.8, 111.3, 94.7, 92.8, 56.3, 45.8, 34.8, 30.0, 20.9, 18.3, 15.5; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{19}H_{26}{}^{79}BrO$ 349.1162; Found 349.1174; **IR** (KBr, cm^{-1}): *v* 2974, 2929, 2856, 1603, 1441, 1256, 1057, 808, 673.

General procedure B (using 1r as an example, the syntheses of 1s-1t follows the same procedure):

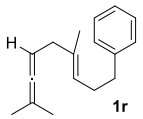


(*E*)-2,6-Dimethyl-9-phenylnon-6-en-3-yn-2-ol (S5)

A mixture of **S3** (2.0 g, 8.4 mmol, 0.6 equiv), 3-Methyl butynol (1.4 mL, 13.9 mmol, 1.0 equiv), sodium sulfite (882 mg, 7.0 mmol, 0.5 equiv), copper(I) iodide (530 mg, 2.8 mmol, 0.2 equiv), potassium carbonate (1.9 g, 13.9 mmol, 1.0 equiv), and DBU (50 μL) was stirred in DMF (30 mL) under argon at room temperature for 2 h, and then quenched by NH_4Cl (sat. aq., 20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 50 mL). The combined organic layer was washed with brine (6 × 50 mL), dried over Na_2SO_4 and concentrated under vacuum. The

residue was purified through a silica gel column (PE/EA = 5/1) to give compound **S5** as a colorless oil (1.2 g, 5.0mmol, 60% yield).

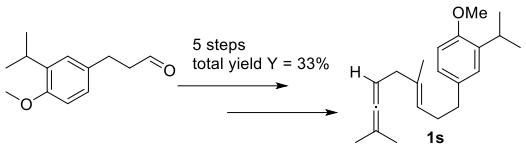
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.31 (m, 2H), 7.17 - 7.21 (m, 3H), 5.45 (t, *J* = 7.0 Hz, 1H), 2.87 (s, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.32 - 2.38 (m, 2H), 1.94 (br s, 1H), 1.62 (s, 3H), 1.51 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.1, 130.6, 128.5, 128.2, 125.7, 124.8, 87.3, 79.9, 65.3, 35.8, 31.6, 29.8, 28.5, 16.0; **HRMS** (APCI) m/z: $[M-H]^-$ Calcd for $C_{17}H_{21}O$ 241.1598; Found 241.1580; **IR** (KBr, cm^{-1}): *v* 3348, 3027, 2931, 2235, 1603, 1454, 1242, 1030, 948, 750, 700.



(*E*)-(4,8-Dimethylnona-3,6,7-trien-1-yl)benzene (1r)[11]

A mixture of zinc chloride (1.0 M in THF, 4.1 mL, 4.1 mmol, 2.0 equiv), diethylzinc (1.0 M in toluene, 4.1 mg, 4.1 mmol, 2.0 equiv) was stirred under argon at room temperature for 0.5 h, and then 2 mL toluene was added. A solution of **S5** (500 mg, 2.1 mmol, 1.0 equiv) in 20 mL toluene was added into the alkyl zinc solution at 0 °C. The mixture was stirred for 20 min before the addition of Schwartz reagent (2.1 g, 8.3 mmol, 4.0 equiv) in one portion under nitrogen atmosphere. The reaction was stirred vigorously for 12 to 24 h and quenched by $NaHCO_3$ (sat. aq., 20 mL). The aqueous phase was extracted by ether (3 × 50 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE) to give compound **1r** as a colorless oil (327 mg, 1.4 mmol, 70% yield).

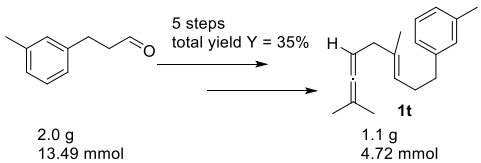
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.30 (m, 2H), 7.17 - 7.21 (m, 3H), 5.26 (t, *J* = 7.2 Hz, 1H), 4.84 - 4.91 (m, 1H), 2.60 - 2.67 (m, 4H), 2.29 - 2.35 (m, 2H), 1.69 (s, 3H), 1.69 (s, 3H), 1.58 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 142.3, 134.8, 128.5, 128.2, 125.7, 124.2, 94.6, 87.2, 40.1, 36.1, 30.0, 29.7, 20.7, 15.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{17}H_{23}$ 227.1795; Found 227.1790; **IR** (KBr, cm^{-1}): *v* 3027, 2978, 2933, 1968, 1604, 1454, 750.



4-(4,8-Dimethylnona-6,7-dien-1-yl)-2-isopropyl-1-methoxybenzene (1s)

1s was prepared according to general procedure B and purified by silica gel column chromatography (PE/EA = 20/1) as a colorless oil (1.8 g, 33% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, *J* = 2.4 Hz, 1H), 6.97 (dd, *J* = 8.2, 2.2 Hz, 1H), 6.76 (d, *J* = 8.4 Hz, 1H), 5.25 (t, *J* = 7.2 Hz, 1H), 4.84 - 4.90 (m, 1H), 3.80 (s, 3H), 3.29 (hept, *J* = 7.2 Hz, 1H), 2.56 - 2.61 (m, 4H), 2.26 - 2.31 (m, 2H), 1.68 (s, 3H), 1.68 (s, 3H), 1.57 (s, 3H), 1.20 (d, *J* = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 154.9, 136.7, 134.6, 134.3, 126.2, 126.1, 124.5, 110.3, 94.5, 87.3, 55.5, 40.1, 35.4, 30.3, 26.7, 22.8, 20.7, 15.9; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{31}O$ 299.2370; Found 299.2378; **IR** (KBr, cm^{-1}): *v* 2960, 2932, 2868, 1608, 1498, 1362, 1247, 1035, 810.



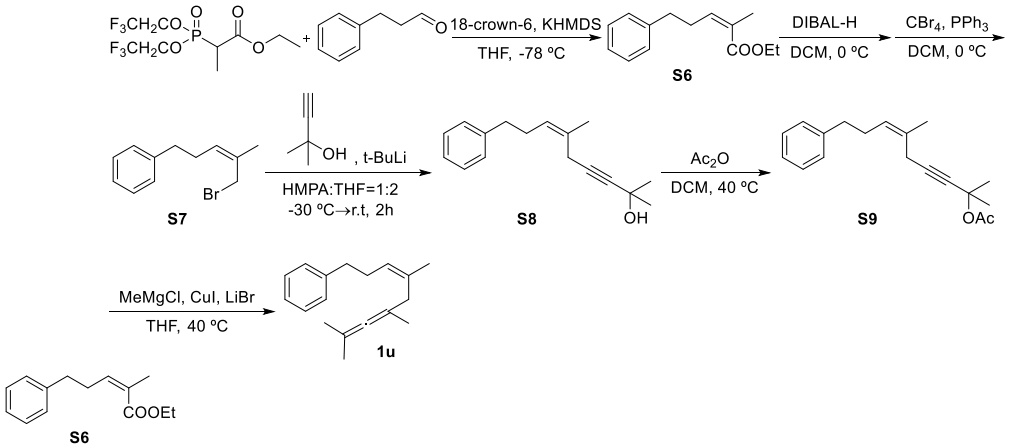
(*E*)-1-(4,8-Dimethylnona-3,6,7-trien-1-yl)-3-methylbenzene (1t)

1t was prepared according to general procedure B and purified by silica gel column chromatography (PE/EA = 200/1) as

a colorless oil (1.1 g, 35% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.4 Hz, 1H), 7.00 - 7.02 (m, 3H), 5.27 (t, *J* = 7.2 Hz, 1H), 4.85 - 4.92 (m, 1H), 2.60 - 2.63 (m, 4H), 2.28 - 2.34 (m, 6H), 1.69 - 1.74 (m, 7H), 1.57 - 1.59 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.4, 142.3, 137.7, 134.8, 129.3, 128.1, 126.4, 125.4, 124.3, 94.5, 87.3, 40.1, 36.0, 30.1, 21.4, 20.7, 15.8; **HRMS** (APCI) m/z: $[M+H]^+$ Calcd for $C_{18}H_{25}$ 241.1951; Found 241.1955; **IR** (KBr, cm^{-1}): *v* 2961, 2924, 2855, 1609, 1447, 800.

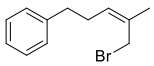
7. Experimental details for the synthesis of 1u and 2u



Ethyl (*Z*)-2-methyl-5-phenylpent-2-enoate (S6)

A solution of $(CF_3CH_2O)_2POCHMeCO_2Et$[12] (3.0 g, 8.67 mmol, 1.05 equiv) and 18-crown-6 (2.5 g, 9.49 mmol, 1.15 equiv) in dry THF (40 mL) was cooled to -78 °C, and KHMDS (1.0 M solution in THF, 8.7 mL, 8.67 mmol, 1.05 equiv) was added, followed by 3-phenylpropanal (1.1 g, 8.26 mmol, 1.0 equiv). After stirring at -78 °C for 30 min, the reaction mixture was poured into a rapidly stirring NH_4Cl (sat. aq., 20 mL), After stirring vigorously for 15 min, the organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 50 mL), then brine (100 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **S6** as a yellow oil (1.3 g, 5.78 mmol, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 - 7.30 (m, 2H), 7.17 - 7.21 (m, 3H), 5.96 (td, *J* = 7.2, 1.2 Hz, 1H), 4.19 (q, *J* = 7.2 Hz, 2H), 2.70 - 2.82 (m, 4H), 1.89 (d, *J* = 1.6 Hz, 3H), 1.30 (t, *J* = 7.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 141.5, 128.4, 128.3, 127.8, 125.9, 60.1, 35.5, 31.1, 20.6, 14.3; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{14}H_{18}NaO_2$ 241.1199; Found 241.1200.



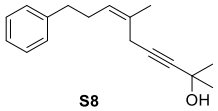
S7

(*Z*)-(5-Bromo-4-methylpent-3-en-1-yl)benzene (S7)

To a stirred solution of **S6** (1.3 g, 5.78 mmol, 1.0 equiv) in dry DCM (20 mL), DIBAL-H (1.5 M in toluene, 7.7 mL, 11.56 mmol, 2.0 equiv) was added slowly at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min, it was quenched with HCl (1M, 5 mL) aqueous solution. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 × 30 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. To a stirred solution of the residue and PPh_3 (1.8 g, 6.94 mmol, 1.2 equiv) in DCM (40 mL), CBr_4 (2.3 g, 6.94 mmol, 1.2 equiv) was added slowly at 0 °C. After the reaction mixture was stirred at 0 °C for 10 min, it was concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 50/1) to give compound **S7** as a colorless oil (1.2 g, 5.20 mmol, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 - 7.32 (m, 2H), 7.19 - 7.22 (m, 3H), 5.44 (td, *J* = 7.4, 1.2 Hz, 1H), 3.90 (s, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.37 - 2.43 (m, 2H), 1.84 (d, *J* = 1.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.5, 132.3, 130.5,

128.4, 128.3, 125.9, 35.4, 32.1, 29.9, 21.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{12}H_{15}BrNa$ 261.0249; Found 261.0238.

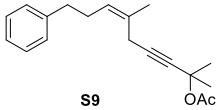


S8

(*Z*)-2,6-Dimethyl-9-phenylnon-6-en-3-yn-2-ol (S8)

To a solution of the appropriate alcohol (28 mg, 0.33 mmol, 1.0 equiv) in THF (1.0 mL) and HMPA (0.5 mL, 2.0 mmol, 6.0 equiv) at -78 °C, under argon atmosphere and magnetic stirring, was added n-butyl lithium (0.27 mL, 2.5 M in hexane, 0.67 mmol, 2.0 equiv). The temperature was progressively raised to -30 °C and maintained for 45 min. The appropriate bromide **S7** (80 mg, 0.33 mmol, 1.0 equiv) was added dropwise at -30 °C. After this the solution was stirred at room temperature for 2 h. The solution was diluted by NH_4Cl (sat. aq., 2 mL) and extracted with EtOAc (3 × 20 mL), then brine (50 mL), dried over Na_2SO_4, filtered and concentrated in vacuo. The residue was purified by column chromatography on silica gel (PE/EA = 6/1) to give compound **S8** as a yellow oil (4.0 mg, 0.02 mmol, 5% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 - 7.30 (m, 5H), 5.25 (td, *J* = 7.2, 1.2 Hz, 1H), 2.85 (s, 2H), 2.66 (t, *J* = 7.8 Hz, 2H), 2.30 - 2.35 (m, 2H), 1.82 (s, 1H), 1.78 (d, *J* = 1.2 Hz, 3H), 1.49 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.0, 131.1, 128.4, 128.3, 125.8, 125.5, 85.1, 80.1, 65.3, 35.9, 31.7, 29.8, 23.0, 21.2; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{17}H_{22}NaO$ 265.1563; Found 265.1549.

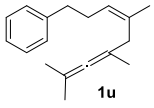


S9

(*Z*)-2,6-Dimethyl-9-phenylnon-6-en-3-yn-2-yl acetate (S9)

To a stirred solution of **S8** (60.0 mg, 0.25 mmol, 1.0 equiv), Et_3N (103 μL, 0.74 mmol, 3.0 equiv) and DMAP (6.1 mg, 0.05 mmol, 0.2 equiv) in DCM (4 mL), Ac_2O (74.2 μL, 0.74 mmol, 3.0 equiv) was added at room temperature. The reaction mixture was stirred for 3 h and then quenched by $NaHCO_3$ (sat. aq., 5 mL). The organic layer was separated and the aqueous layer was extracted with DCM (3 × 20 mL). The combined organic layer was washed with brine (20 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE/EA = 20/1) to give compound **S9** as a colorless oil (70.9 mg, 0.24 mmol, 95% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.29 (m, 2H), 7.16 - 7.19 (m, 3H), 5.24 (td, *J* = 7.2, 1.2 Hz, 1H), 2.88 (s, 2H), 2.65 (t, *J* = 7.8 Hz, 2H), 2.28 - 2.34 (m, 2H), 2.00 (s, 3H), 1.79 (d, *J* = 1.2 Hz, 3H), 1.63 (s, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.3, 142.0, 131.1, 128.4, 128.2, 125.8, 125.4, 82.2, 81.6, 72.5, 35.9, 29.8, 29.2, 23.0, 22.0, 21.4; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{24}NaO_2$ 307.1669; Found 307.1667.



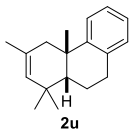
1u

(*Z*)-(4,6,8-Trimethylnona-3,6,7-trien-1-yl)benzene (1u)

To a stirred solution of lithium bromide (175 mg, 2.01 mmol, 10.0 equiv) and copper(I) iodide (384 mg, 2.01 mmol, 10.0 equiv) was stirred in THF (20 mL), methylmagnesium chloride (3.0 M in THF, 0.67 mL, 2.01 mmol, 10.0 equiv) was added slowly at 0 °C under argon. The mixture was stirred for 0.5 h, then **S9** (60.1 mg, 0.20 mmol, 1.0 equiv) was added and stirred 1 h at 40 °C. The reaction mixture was quenched by saturated NH_4Cl (sat. aq., 20 mL) at 0 °C. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20 mL). The combined organic layer was washed with brine (100 mL), dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by column chromatography on silica gel (PE) to give compound 1a as a colorless oil (38.5 mg, 0.16 mmol, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 - 7.30 (m, 2H), 7.20 - 7.24 (m, 3H), 5.27 (t, *J* = 7.2 Hz, 1H), 2.62 - 2.66 (m, 4H), 2.29 - 2.35 (m, 2H), 1.68 (s, 3H), 1.65 (s, 6H), 1.57 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 142.4, 133.9, 128.4,

128.2, 125.7, 125.4, 94.7, 93.4, 37.4, 36.4, 30.0, 23.3, 20.8, 18.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{24}Na$ 263.1770; Found 263.1759.



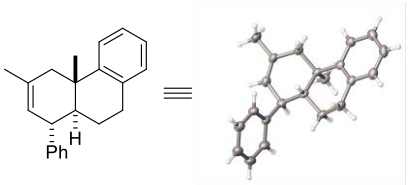
2u

Compound **2u** (6.0 mg, 25%) was prepared according to general procedure from **1u** (24.0 mg) and purified by silica gel column chromatography (PE) as a colorless oil.

7-Isopropyl-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-2,3,6-triol (2u) and 1,1,3,4a-Tetramethyl-1,4,4a,9,10,10a-hexahydrophenanthrene (2a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.01 - 7.31 (m, 8H), 5.20 (s, 1H), 5.01 (s, 1H), 2.79 - 2.95 (m, 4H), 2.34 - 2.41 (m, 2H), 2.07 - 2.17 (m, 2H), 1.82 - 1.97 (m, 4H), 1.67 - 1.81 (m, 8H), 1.31 (s, 3H), 1.22 (s, 3H), 1.06 (s, 3H), 1.02 (s, 3H), 0.96 (s, 3H), 0.59 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.0, 144.8, 137.2, 135.5, 132.1, 132.0, 131.8, 131.7, 128.9, 128.8, 128.6, 128.3, 126.0, 125.9, 125.3, 125.2, 47.9, 47.6, 44.8, 41.4, 37.9, 37.6, 35.7, 35.1, 32.4, 32.2, 31.2, 30.1, 28.7, 27.3, 25.4, 24.4, 23.8, 22.7, 20.8, 19.9; **HRMS** (ESI) m/z: $[M+Na]^+$ Calcd for $C_{18}H_{24}Na$ 263.1770; Found 263.1764.

8. Crystal of 2d (CCDC: 2171065), (±)-2,3-dihydroxyferruginol (CCDC: 2171067) and (±)-shonanol (CCDC: 2171063)

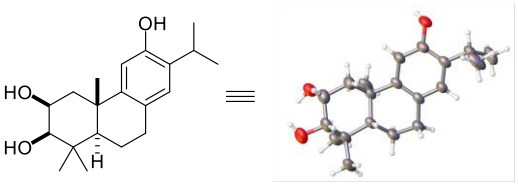


Crystal of 2d was obtained by slow evaporation of a solution containing 2d in the mixture of petroleum ether and diethyl ether at room temperature. CCDC number 2171065. The crystal mounted on a XtaLAB Synergy R-DW, HyPix-6000HE diffractometer. The crystal was kept at 149.99(10) K during data collection.

Table S2. Crystal data and structure refinement for 2d.

Identification code	2171065
Empirical formula	$C_{22}H_{24}$
Formula weight	288.41
Temperature/K	149.99(10)
Crystal system	hexagonal
Space group	$P6_1$
a/Å	17.4778(4)
b/Å	17.4778(4)
c/Å	9.9640(2)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	2635.95(13)
Z	6
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	0.454

F(000)	936.0
Crystal size/mm^3	0.11 × 0.03 × 0.02
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	5.838 to 154.22
Index ranges	-21 ≤ h ≤ 21, -21 ≤ k ≤ 21, -8 ≤ l ≤ 12
Reflections collected	14286
Independent reflections	2980 [R_{int} = 0.0594, R_{sigma} = 0.0449]
Data/restraints/parameters	2980/1/201
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0408, wR_2 = 0.1093
Final R indexes [all data]	R_1 = 0.0446, wR_2 = 0.1125
Largest diff. peak/hole / e Å^{-3}	0.13/-0.14
Flack parameter	-0.3(10)

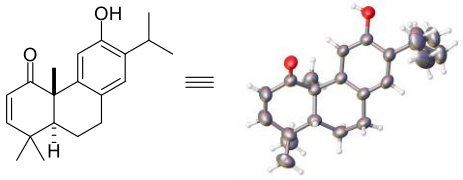


Crystal of (±)-2,3-dihydroxyferruginol was obtained by slow evaporation of a solution containing (±)-2,3-dihydroxyferruginol in the mixture of petroleum ether and ethyl acetate at room temperature. CCDC number 2171067. The crystal mounted on a XtaLAB Synergy R-DW, HyPix-6000HE diffractometer. The crystal was kept at 150.00(10) K during data collection.

Table S3. Crystal data and structure refinement for (±)-2,3-dihydroxyferruginol.

Identification code	2171067
Empirical formula	$C_{20}H_{30}O_3$
Formula weight	318.44
Temperature/K	150.00(10)
Crystal system	monoclinic
Space group	C2/c
a/Å	24.7444(7)
b/Å	6.0960(2)
c/Å	22.9960(6)
α/°	90
β/°	95.293(2)
γ/°	90
Volume/Å^3	3453.97(18)
Z	8
ρ_{calc}g/cm^3	1.225
μ/mm^{-1}	0.632
F(000)	1392.0
Crystal size/mm^3	0.23 × 0.21 × 0.17
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.176 to 133.192

Index ranges	$-29 \le h \le 29, -7 \le k \le 6, -27 \le l \le 27$
Reflections collected	10868
Independent reflections	3023 [R_{int} = 0.0447, R_{sigma} = 0.0419]
Data/restraints/parameters	3023/1/216
Goodness-of-fit on F^2	1.231
Final R indexes [I>=2σ (I)]	R_1 = 0.0943, wR_2 = 0.2859
Final R indexes [all data]	R_1 = 0.1083, wR_2 = 0.3056
Largest diff. peak/hole / e $Å^{-3}$	0.97/-0.38



Crystal of (±)-shonanol was obtained by slow evaporation of a solution containing (±)-shonanol in the mixture of petroleum ether and acetone at room temperature. CCDC number 2171063. The crystal mounted on a XtaLAB Synergy R-DW, HyPix - 6000HE diffractometer. The crystal was kept at 301.82(11) K during data collection.

Table S4. Crystal data and structure refinement for (±)-shonanol.

Identification code	2171063
Empirical formula	$C_{20}H_{26}O_2$
Formula weight	298.41
Temperature/K	301.82(11)
Crystal system	monoclinic
Space group	C2/c
a/Å	20.2191(2)
b/Å	11.57240(10)
c/Å	14.8457(2)
α/°	90
β/°	92.8010(10)
γ/°	90
Volume/$Å^3$	3469.50(7)
Z	8
$\rho_{calc}g/cm^3$	1.143
μ/mm^{-1}	0.559
F(000)	1296.0
Crystal size/mm^3	0.09 × 0.07 × 0.05
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.758 to 152.458
Index ranges	$-25 \le h \le 25, -14 \le k \le 14, -18 \le l \le 17$
Reflections collected	53861
Independent reflections	3559 [R_{int} = 0.0362, R_{sigma} = 0.0136]
Data/restraints/parameters	3559/24/225
Goodness-of-fit on F^2	1.083
Final R indexes [I>=2σ (I)]	R_1 = 0.0448, wR_2 = 0.1272

Final R indexes [all data]	R_1 = 0.0495, wR_2 = 0.1319
Largest diff. peak/hole / e Å^{-3}	0.20/-0.18

9. Reference

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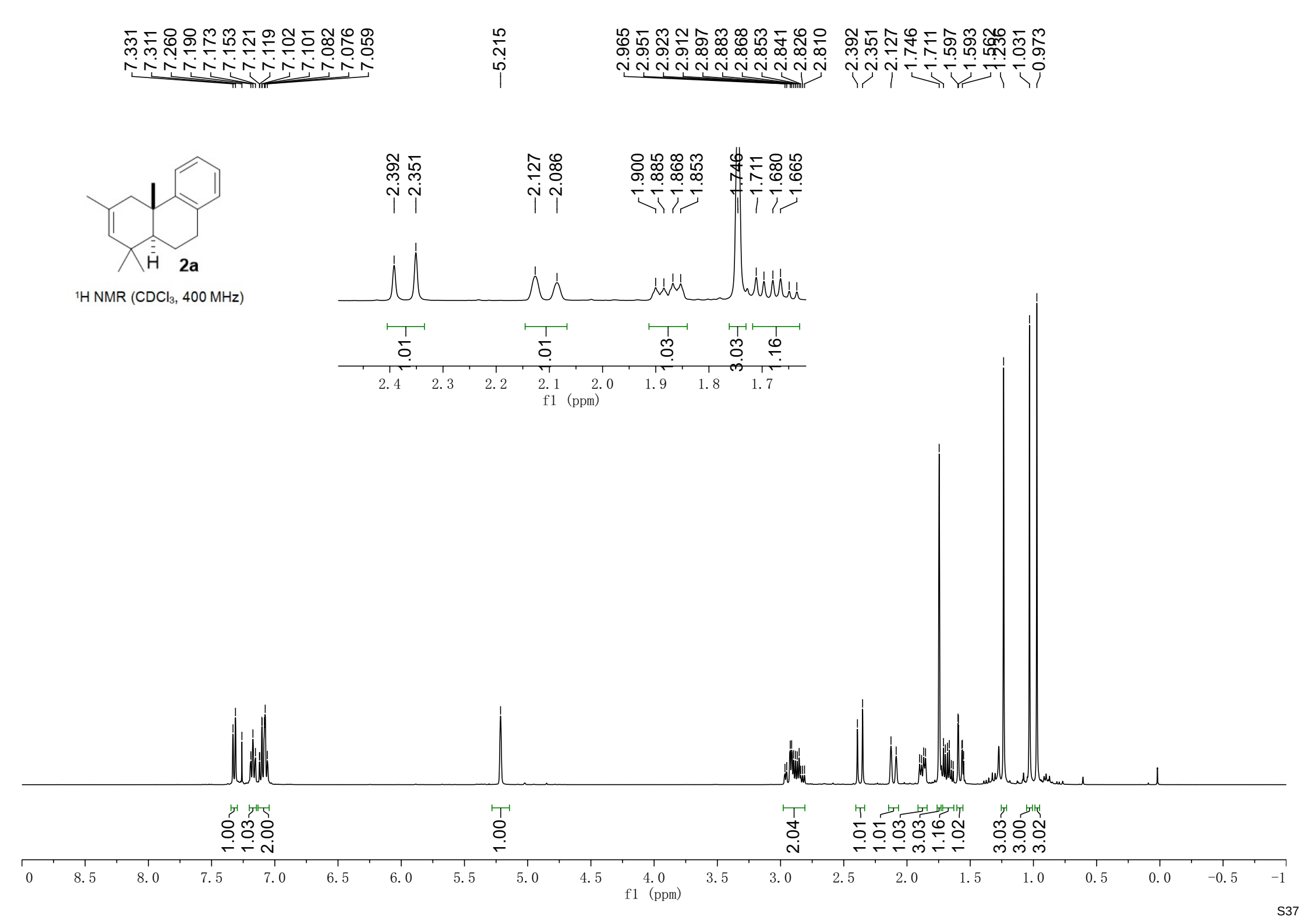
10. NMR spectra of new compounds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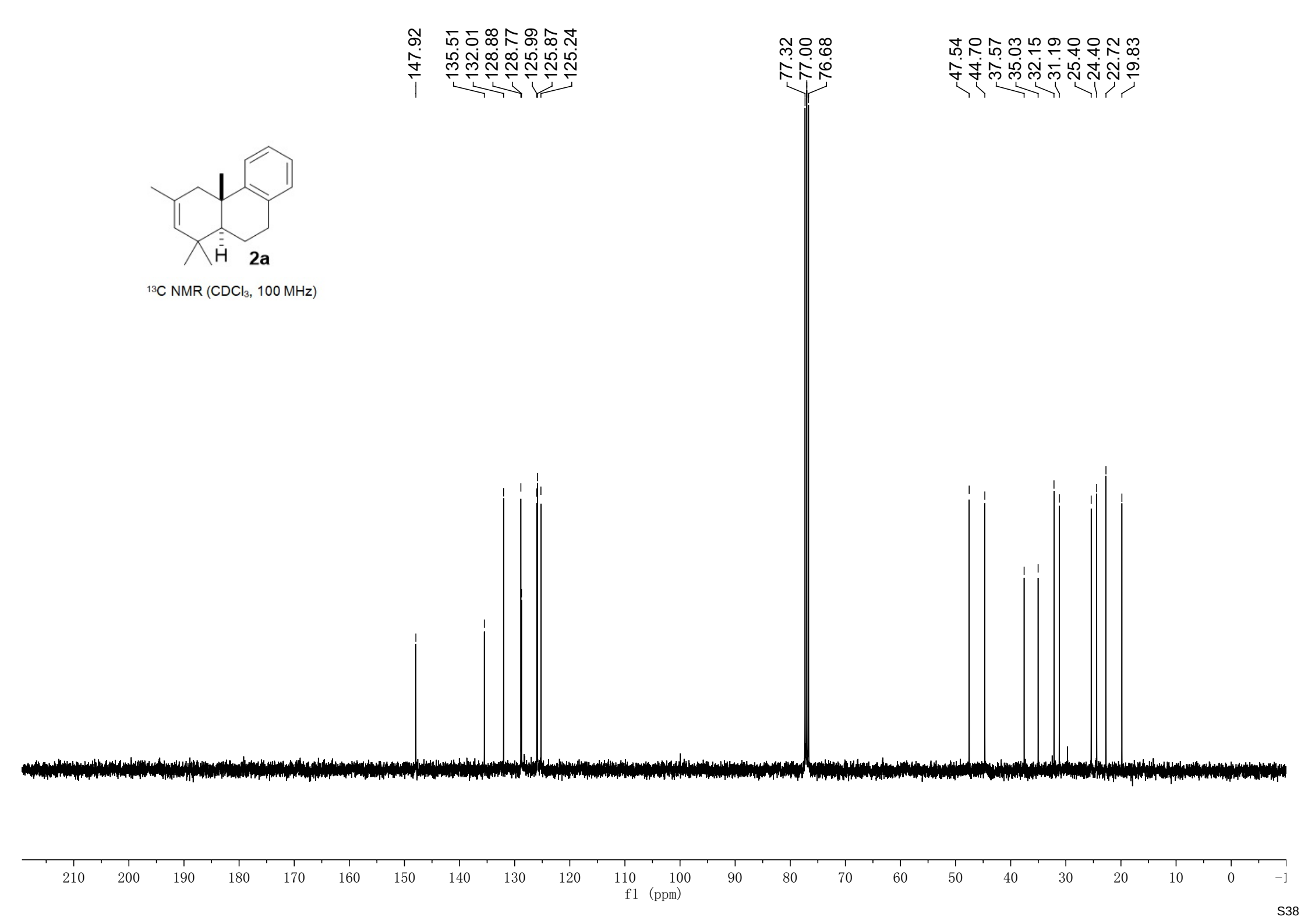
7.260
7.190
7.173
7.153
7.121
7.119
7.102
7.101
7.082
7.076
7.059
5.215
2.965
2.951
2.923
2.912
2.897
2.883
2.868
2.853
2.841
2.826
2.810
2.392
2.351
2.127
1.746
1.711
1.597
1.593
1.562
1.236
1.031
0.973
H
2a
1H NMR (CDCl3, 400 MHz)
2.392
2.351
2.127
2.086
1.900
1.885
1.868
1.853
1.746
1.711
1.680
1.665
1.01
1.01
1.03
3.03
1.16
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
f1 (ppm)
1.00
1.03
2.00
1.00
2.04
1.01
1.01
1.03
3.03
1.16
1.02
3.03
3.00
3.02
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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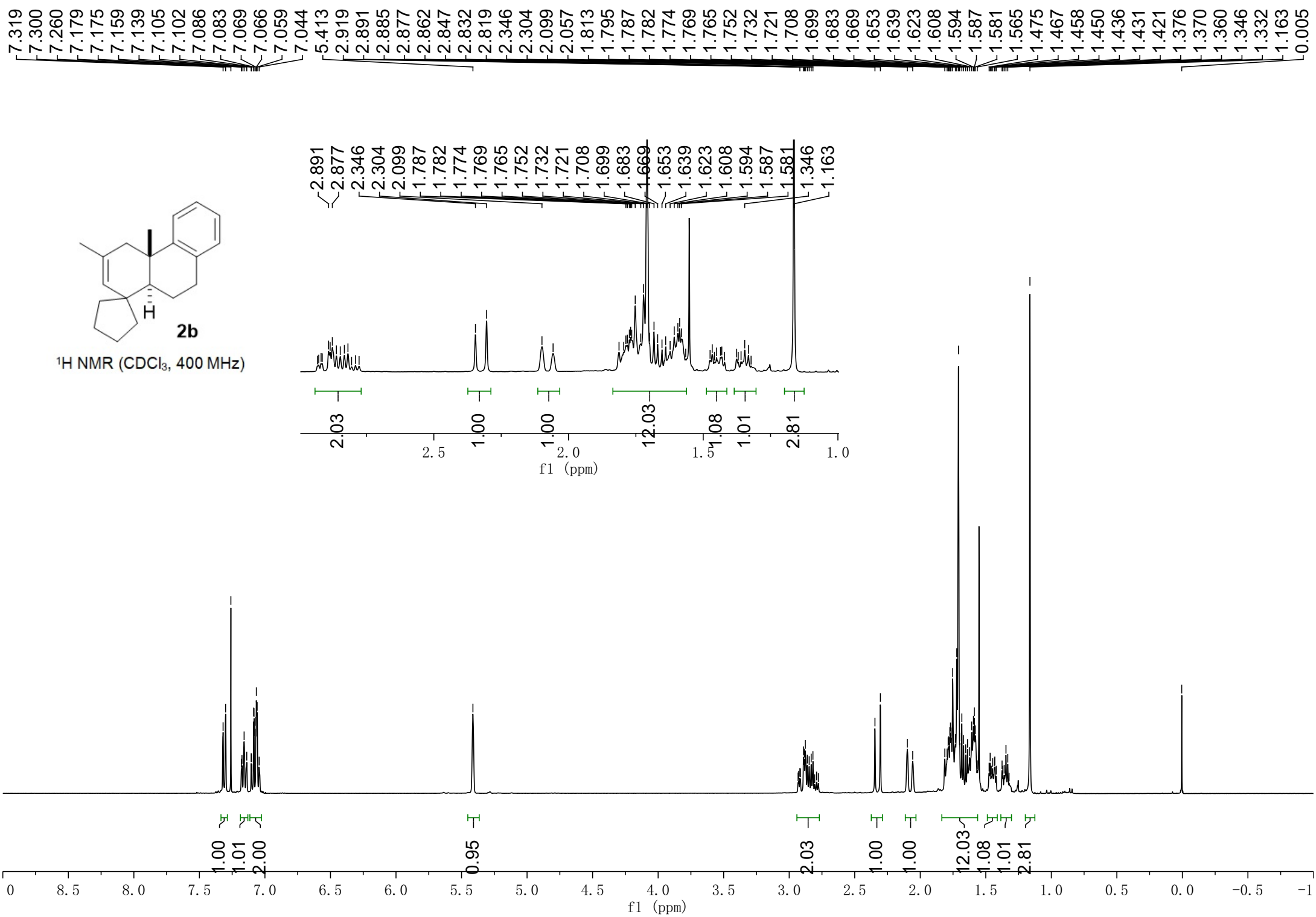
135.51
132.01
128.88
128.77
125.99
125.87
125.24
77.32
77.00
76.68
47.54
44.70
37.57
35.03
32.15
31.19
25.40
24.40
22.72
19.83
H
2a
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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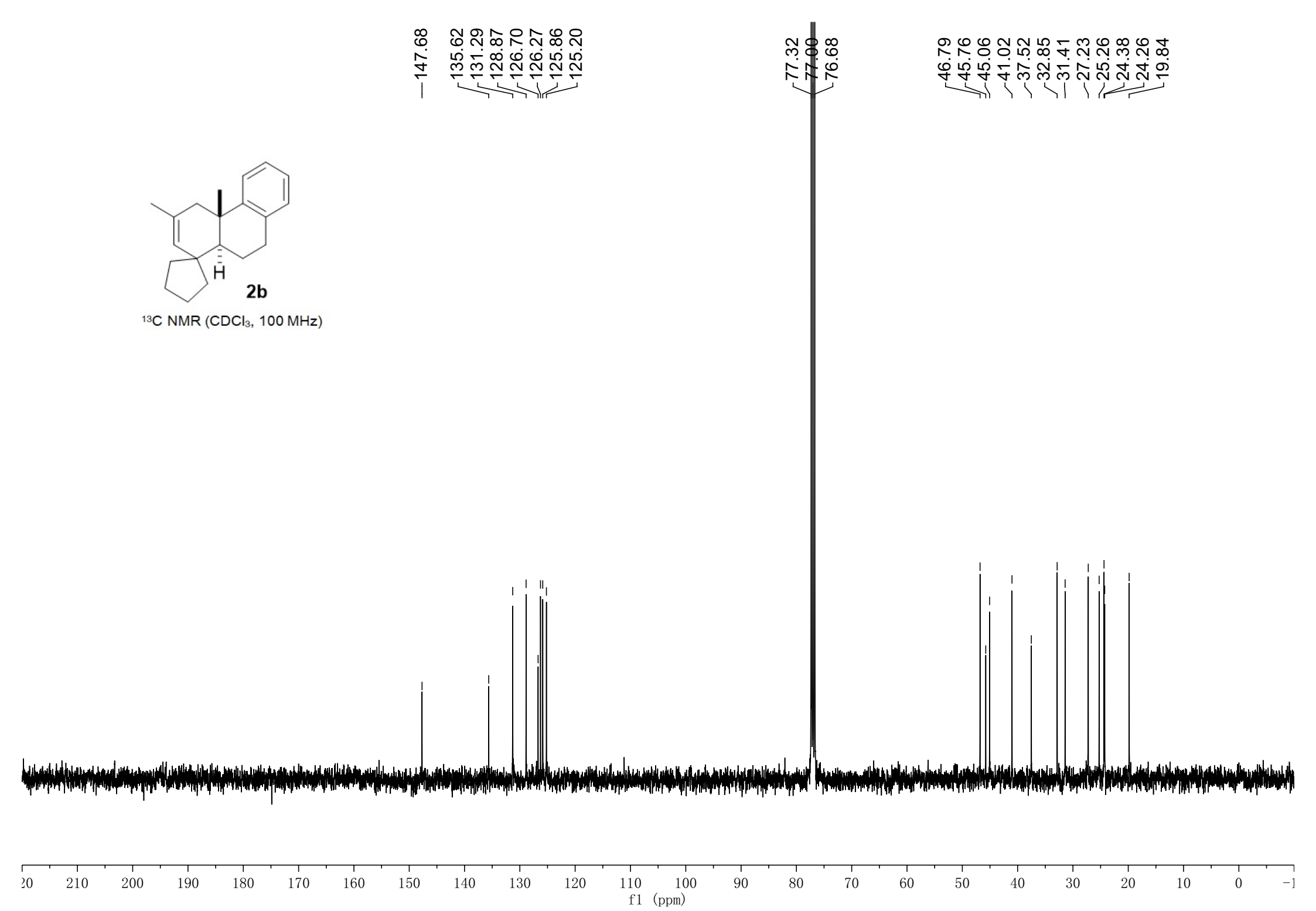
5.413 2.919 2.891 2.885 2.877 2.862 2.847 2.832 2.819 2.346 2.304 2.099 2.057 1.813 1.795 1.787 1.782 1.774 1.769 1.765 1.752 1.732 1.721 1.708 1.699 1.683 1.669 1.653 1.639 1.623 1.608 1.594 1.587 1.581 1.565 1.475 1.467 1.458 1.450 1.436 1.431 1.421 1.376 1.370 1.360 1.346 1.332 1.163 0.005
2b
1H NMR (CDCl3, 400 MHz)
2.891 2.877 2.346 2.304 2.099 1.787 1.782 1.774 1.769 1.765 1.752 1.732 1.721 1.708 1.699 1.683 1.669 1.653 1.639 1.623 1.608 1.594 1.587 1.581 1.346 1.163
2.03 1.00 1.00 12.03 1.08 1.01 2.81
2.5 2.0 1.5 1.0
f1 (ppm)
1.00 1.01 2.00 0.95 2.03 1.00 1.00 12.03 1.08 1.01 2.81
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)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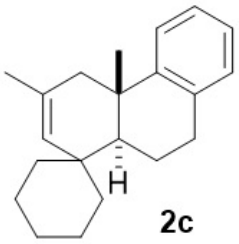
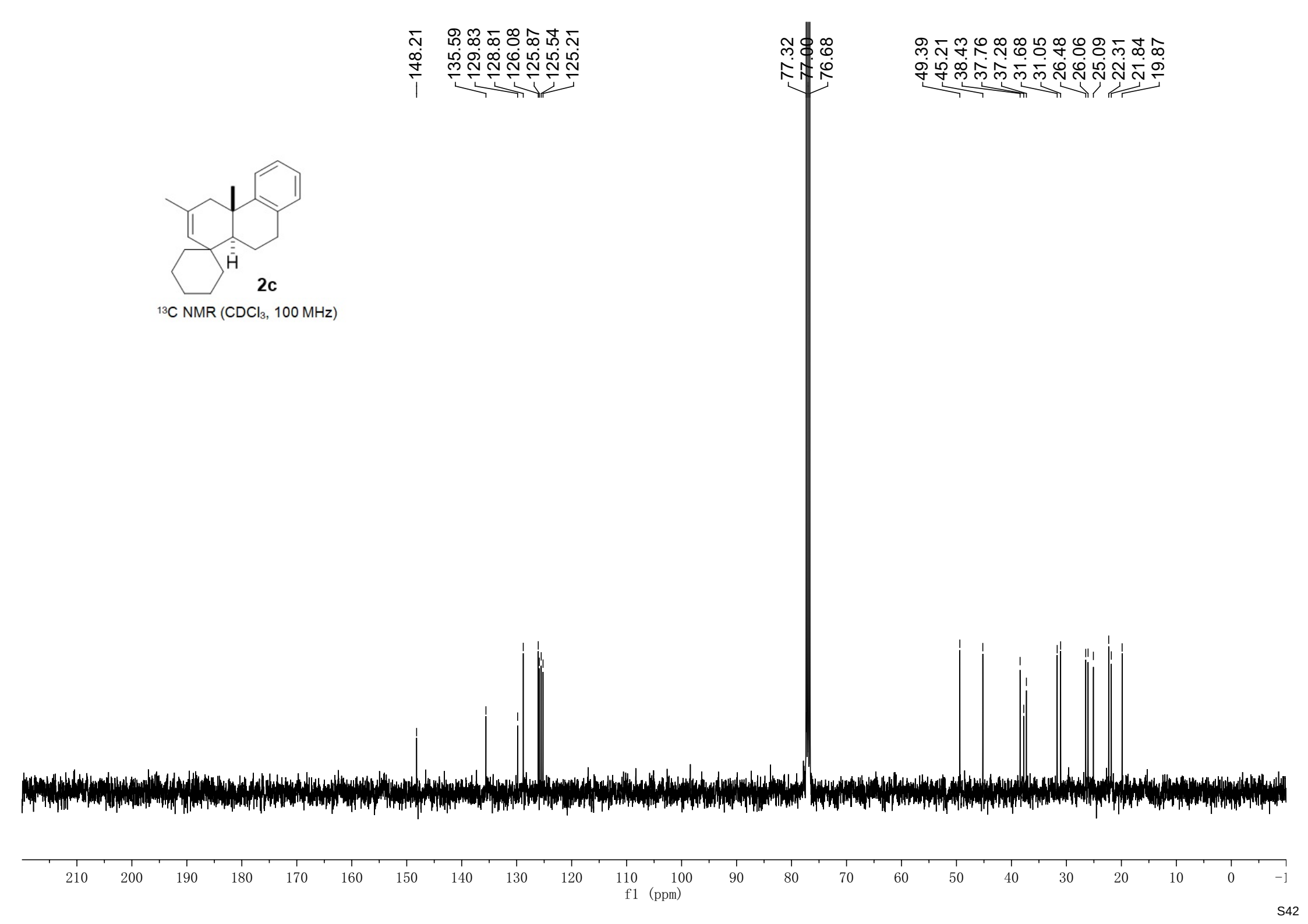
131.29
128.87
126.70
126.27
125.86
125.20
77.32
77.00
76.68
46.79
45.76
45.06
41.02
37.52
32.85
31.41
27.23
25.26
24.38
24.26
19.84
H
2b
13C NMR (CDCl3, 100 MHz)
f1 (ppm)



2c

^{1}H NMR ($CDCl_3$, 400 MHz)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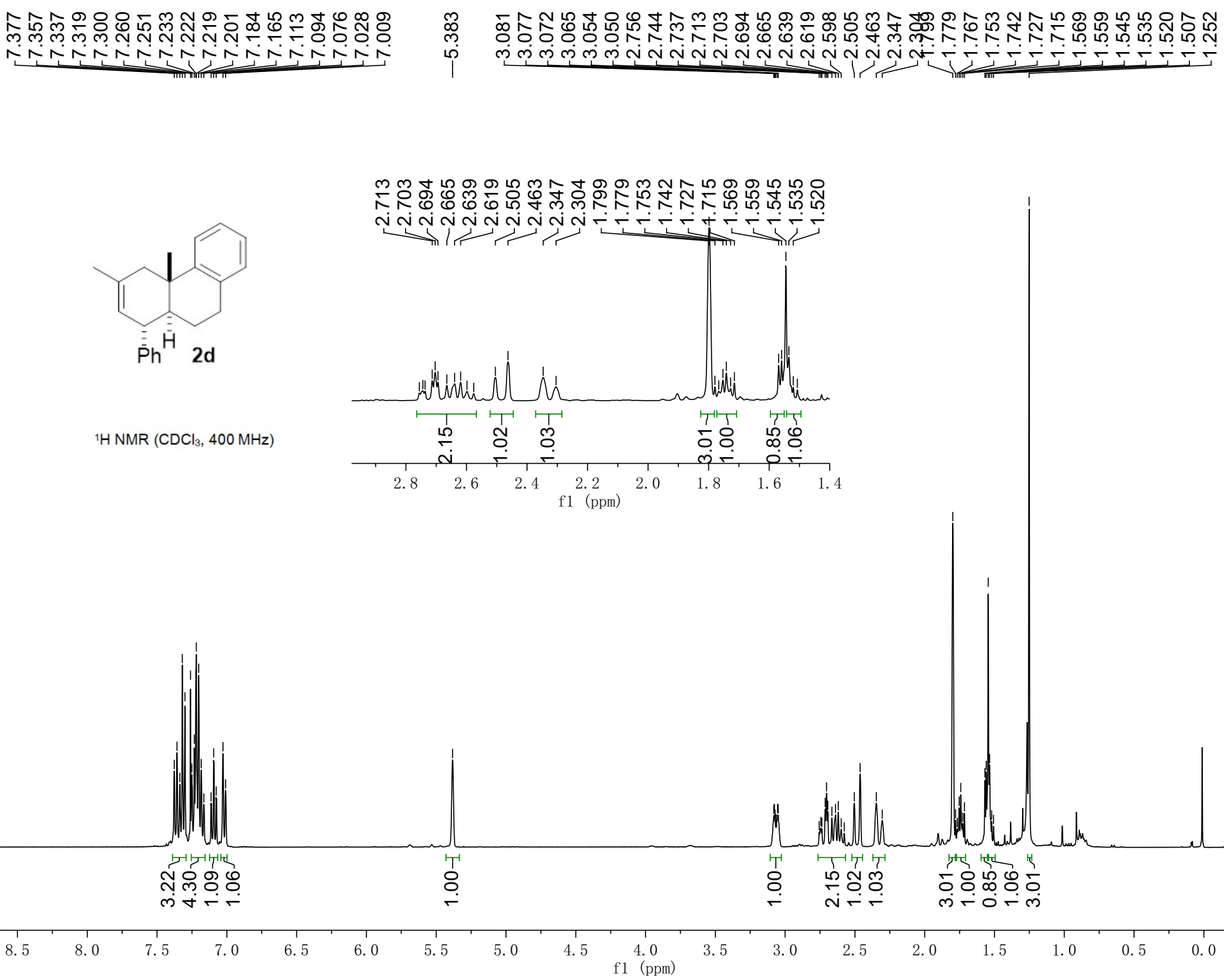
129.83
128.81
126.08
125.87
125.54
125.21
77.32
77.00
76.68
49.39
45.21
38.43
37.76
37.28
31.68
31.05
26.48
26.06
25.09
22.31
21.84
19.87
H
2c
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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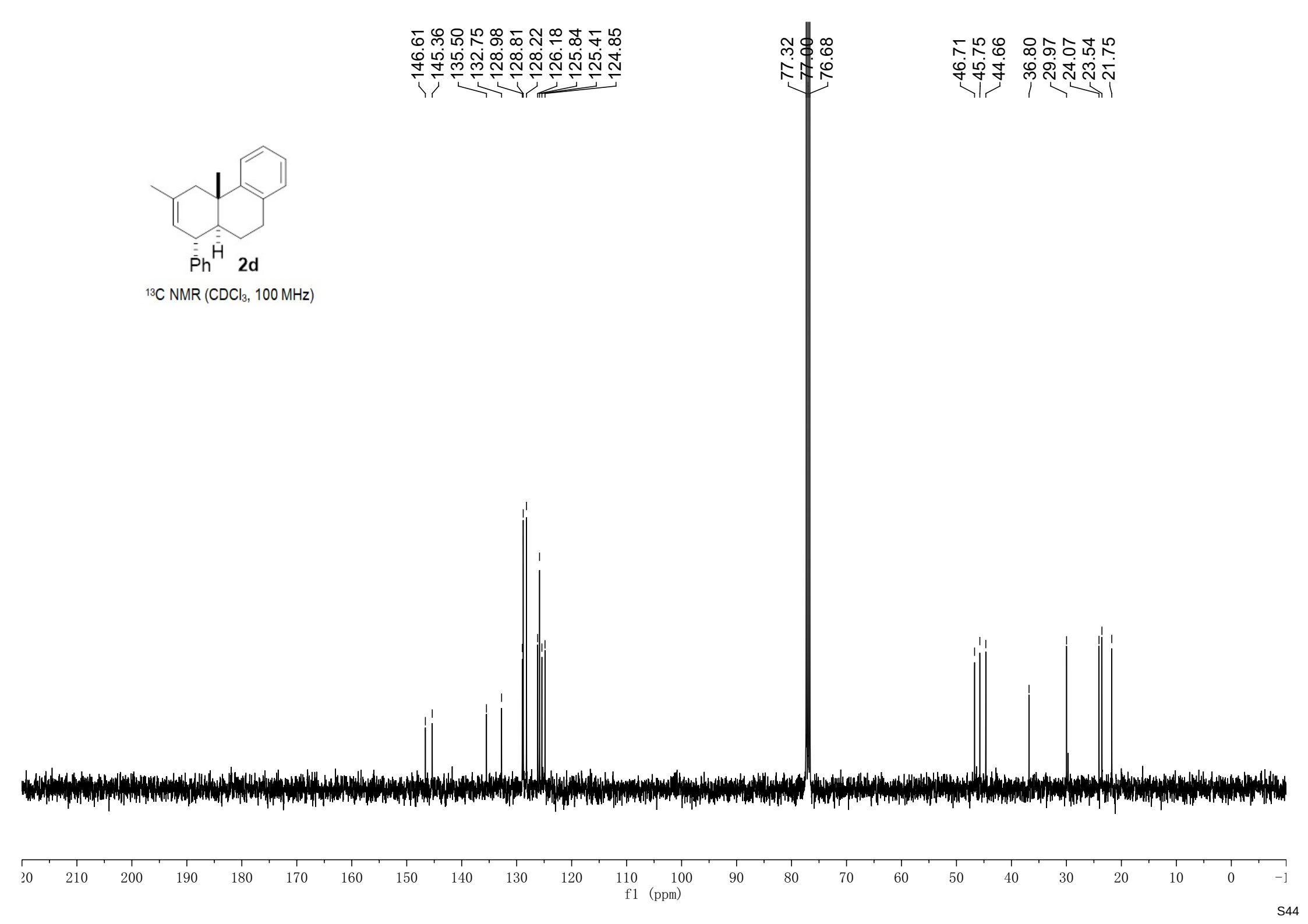
7.165
7.113
7.094
7.076
7.028
7.009
5.383
3.081
3.077
3.072
3.065
3.054
3.050
2.756
2.744
2.737
2.713
2.703
2.694
2.665
2.639
2.619
2.598
2.505
2.463
2.347
2.304
1.799
1.779
1.767
1.753
1.742
1.727
1.715
1.569
1.559
1.545
1.535
1.520
1.507
1.252
Ph
H
2d
¹H NMR (CDCl₃, 400 MHz)
2.15
1.02
1.03
3.01
1.00
0.85
1.06
f1 (ppm)
3.22
4.30
1.09
1.06
1.00
1.00
2.15
1.02
1.03
3.01
1.00
0.85
1.06
3.01
f1 (ppm)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128.98
128.81
128.22
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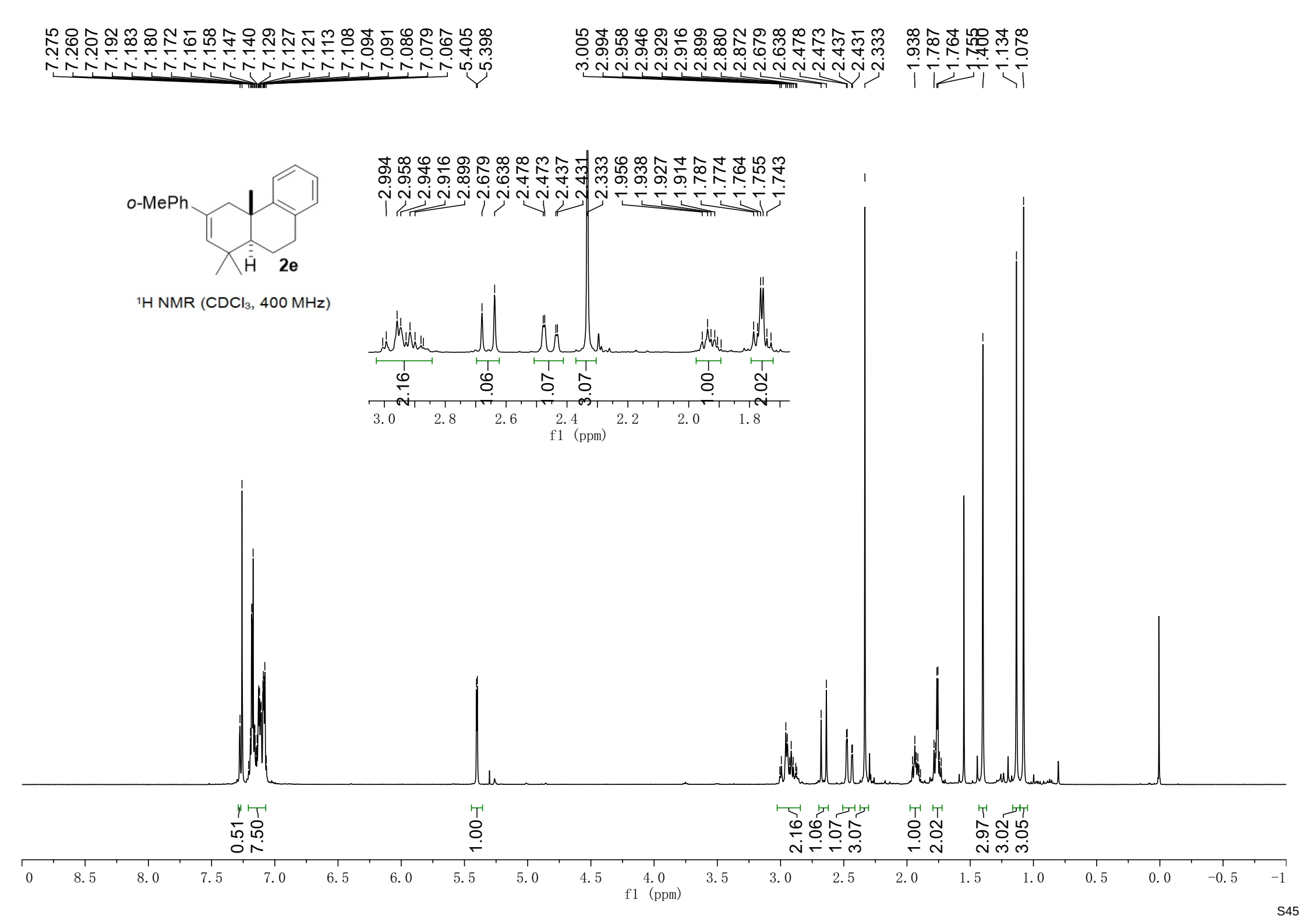
125.84
125.41
124.85
77.32
77.00
76.68
46.71
45.75
44.66
36.80
29.97
24.07
23.54
21.75
Ph
H
2d
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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7.183
7.180
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7.161
7.158
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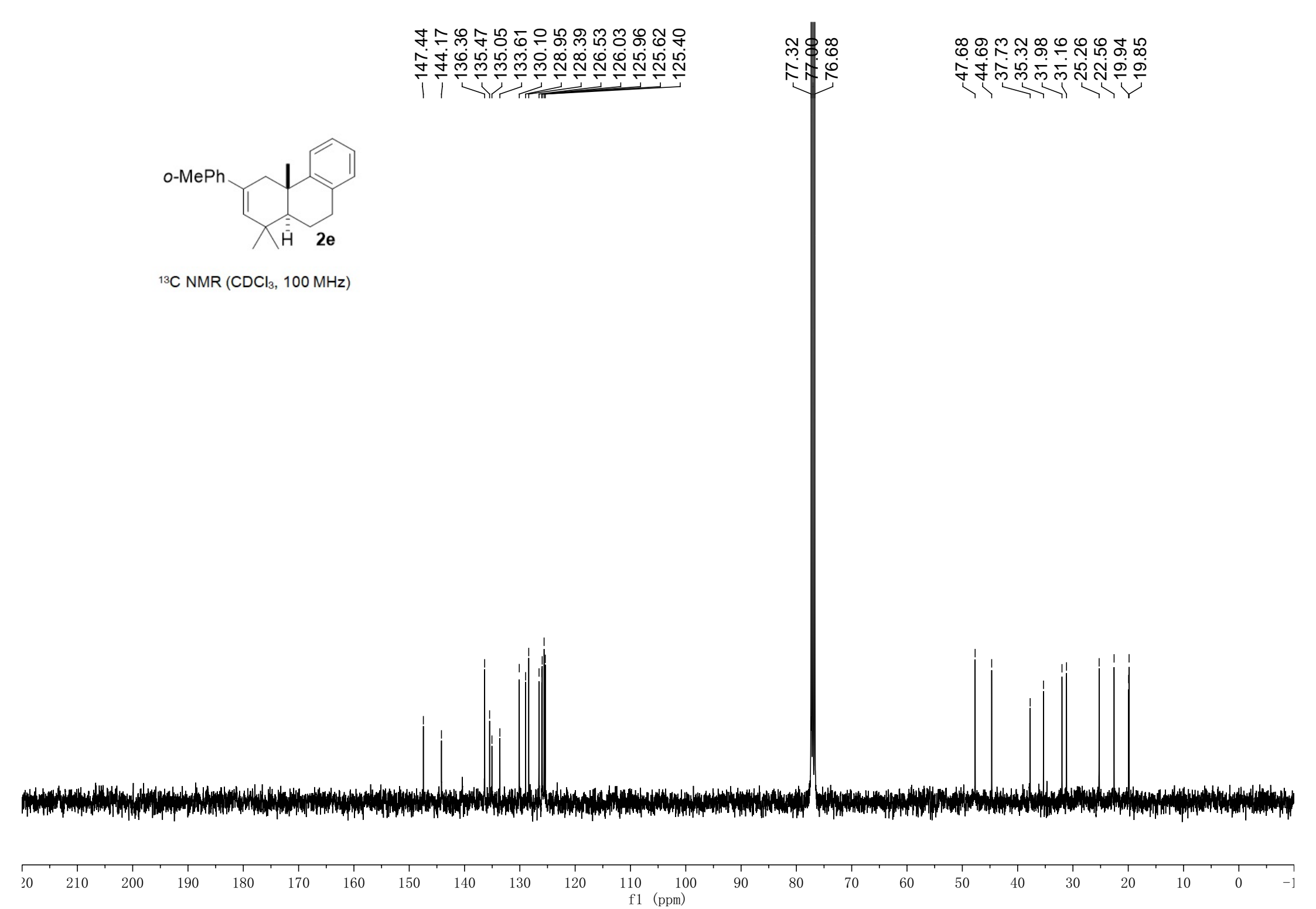
7.140
7.129
7.127
7.121
7.113
7.108
7.094
7.091
7.086
7.079
7.067
5.405
5.398
3.005
2.994
2.958
2.946
2.929
2.916
2.899
2.880
2.872
2.679
2.638
2.478
2.473
2.437
2.431
2.333
1.938
1.787
1.764
1.755
1.400
1.134
1.078
o-MePh
H
2e
1H NMR (CDCl3, 400 MHz)
2.994
2.958
2.946
2.916
2.899
2.679
2.638
2.478
2.473
2.437
2.431
2.333
1.956
1.938
1.927
1.914
1.787
1.774
1.764
1.755
1.743
2.16
1.06
1.07
3.07
1.00
2.02
3.0
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)
0.51
7.50
1.00
2.16
1.06
1.07
3.07
1.00
2.02
2.97
3.02
3.05
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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35.32
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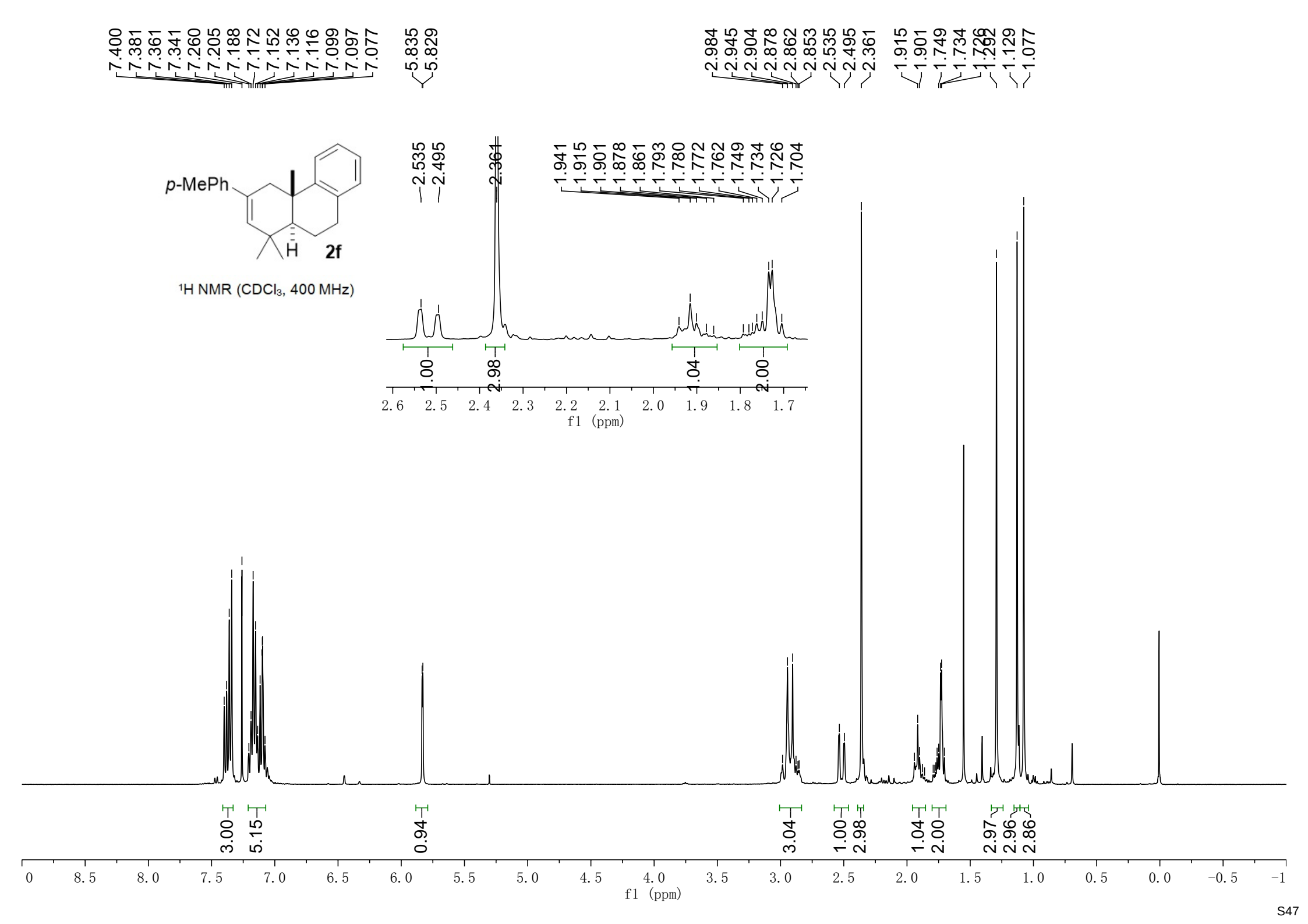
H
2e
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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7.136
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7.097
7.077
5.835
5.829
2.984
2.945
2.904
2.878
2.862
2.853
2.535
2.495
2.361
1.915
1.901
1.749
1.734
1.726
1.292
1.129
1.077
p-MePh
H
2f
1H NMR (CDCl3, 400 MHz)
2.535
2.495
2.361
1.941
1.915
1.901
1.878
1.861
1.793
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1.772
1.762
1.749
1.734
1.726
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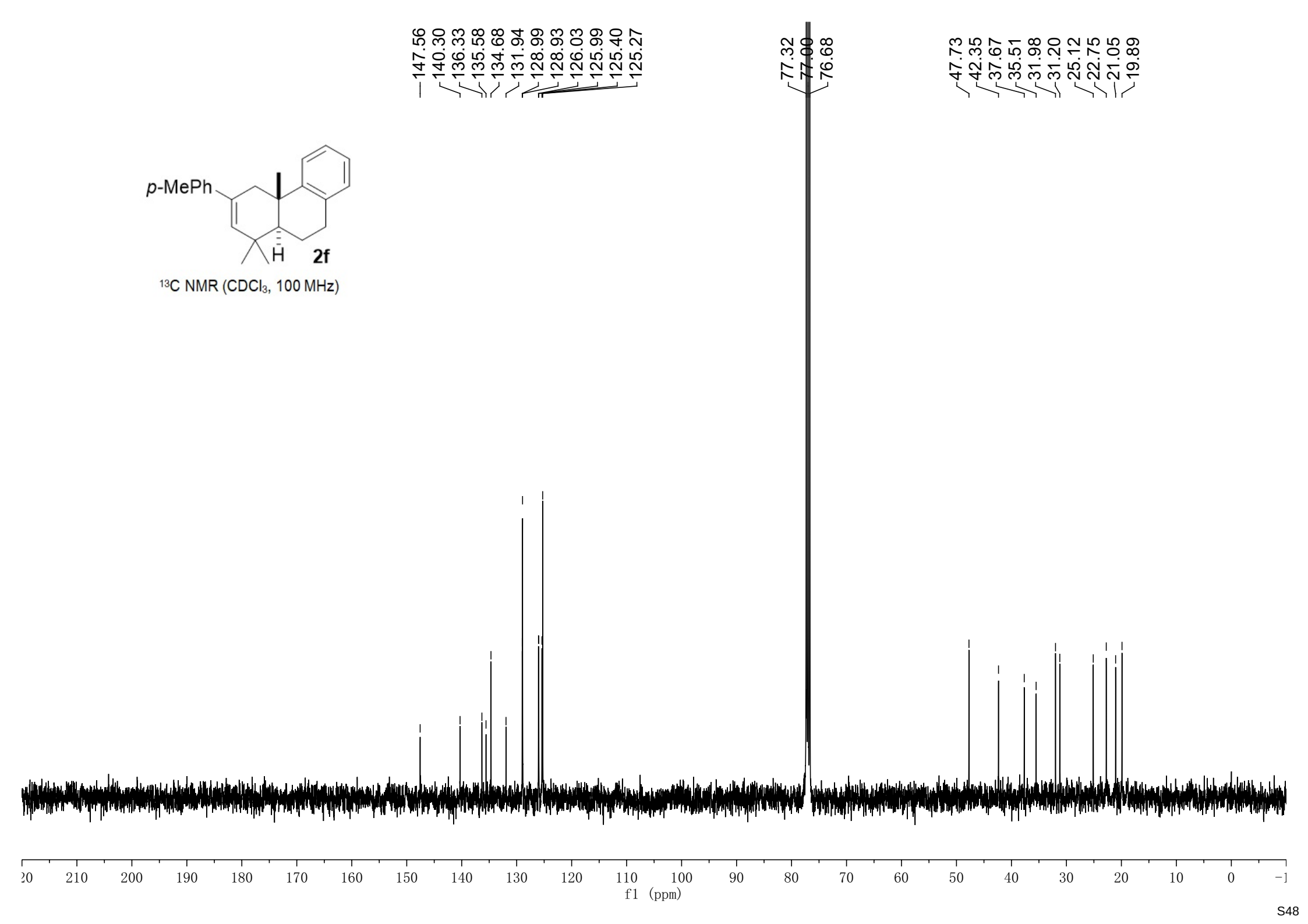
2.5
2.4
2.3
2.2
2.1
2.0
1.9
1.8
1.7
f1 (ppm)
3.00
5.15
0.94
3.04
1.00
2.98
1.04
2.00
2.97
2.96
2.86
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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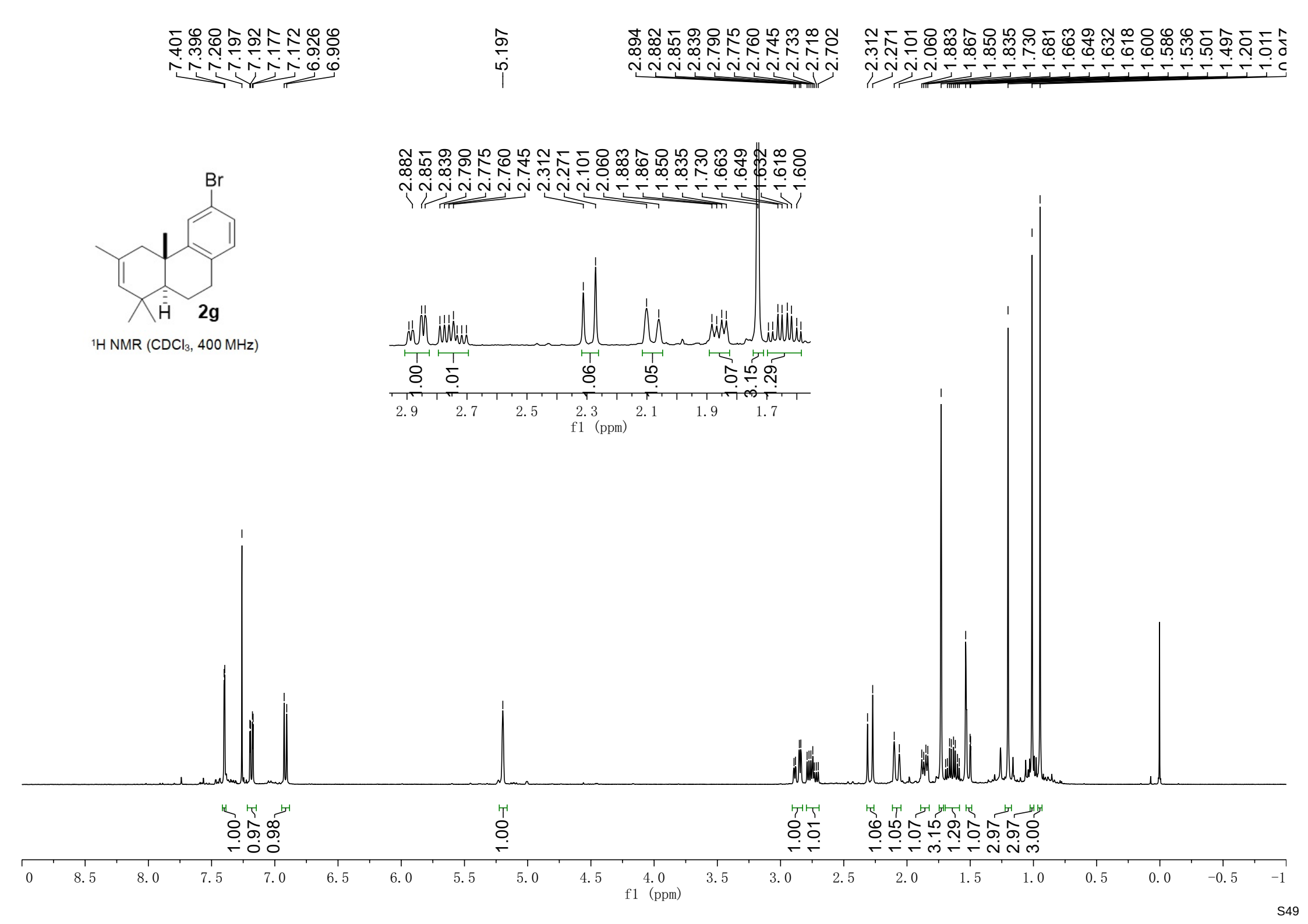
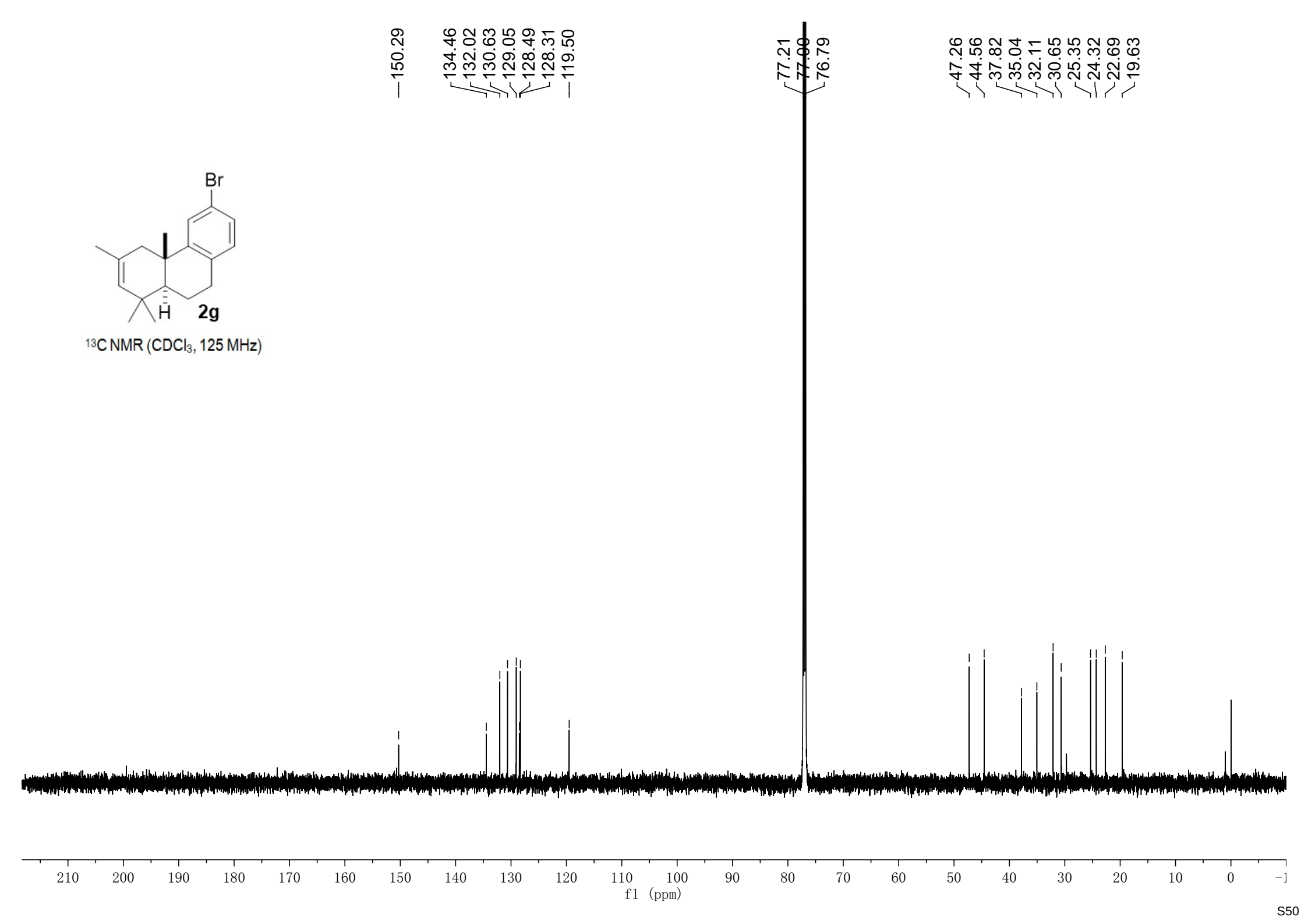
140.30
136.33
135.58
134.68
131.94
128.99
128.93
126.03
125.99
125.40
125.27
77.32
77.00
76.68
47.73
42.35
37.67
35.51
31.98
31.20
25.12
22.75
21.05
19.89
p-MePh
H
2f
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


Br
H
2g
1H NMR (CDCl3, 400 MHz)
f1 (ppm)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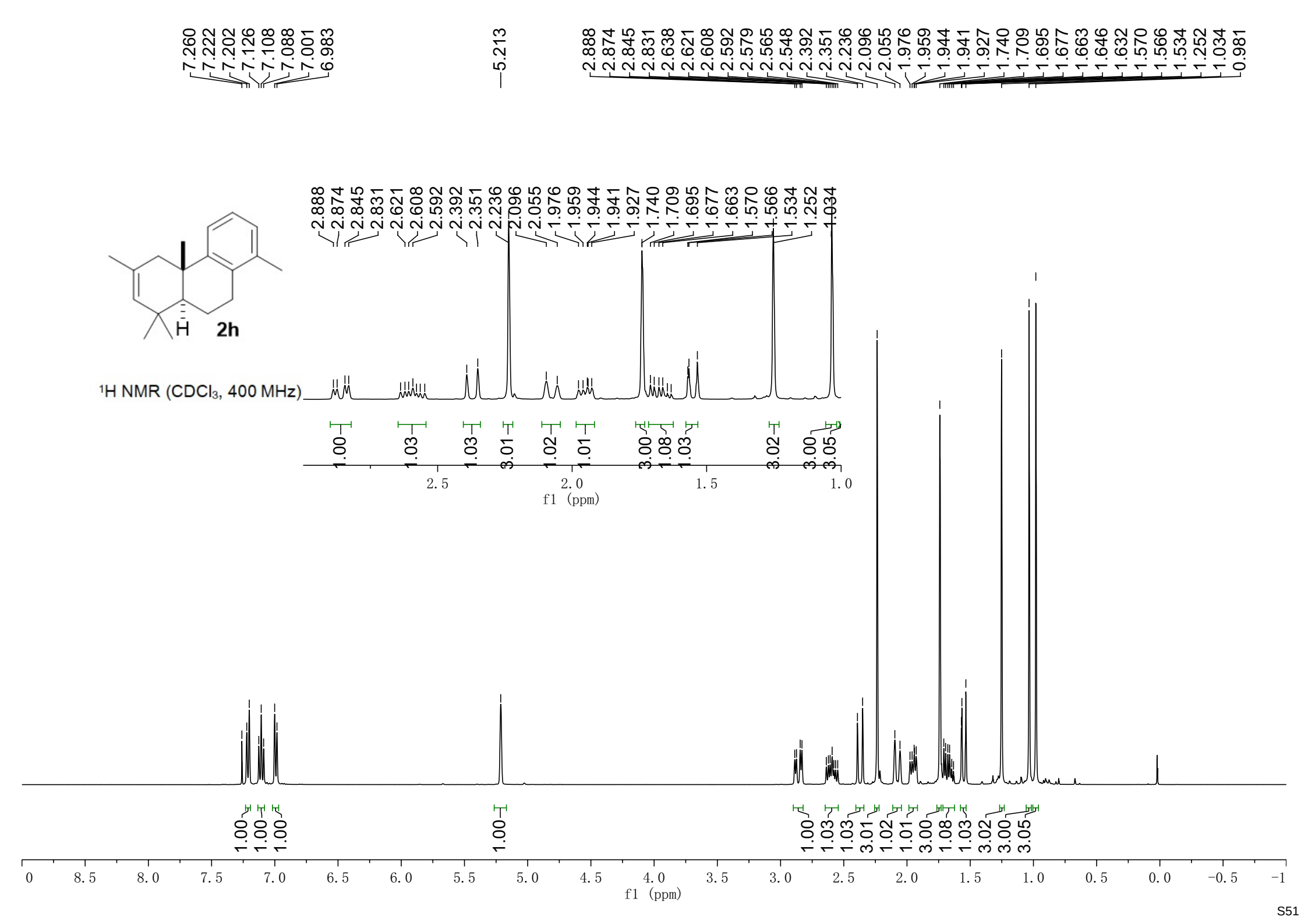
134.46
132.02
130.63
129.05
128.49
128.31
119.50
77.21
77.00
76.79
47.26
44.56
37.82
35.04
32.11
30.65
25.35
24.32
22.69
19.63
Br
H
2g
13C NMR (CDCl3, 125 MHz)
f1 (ppm)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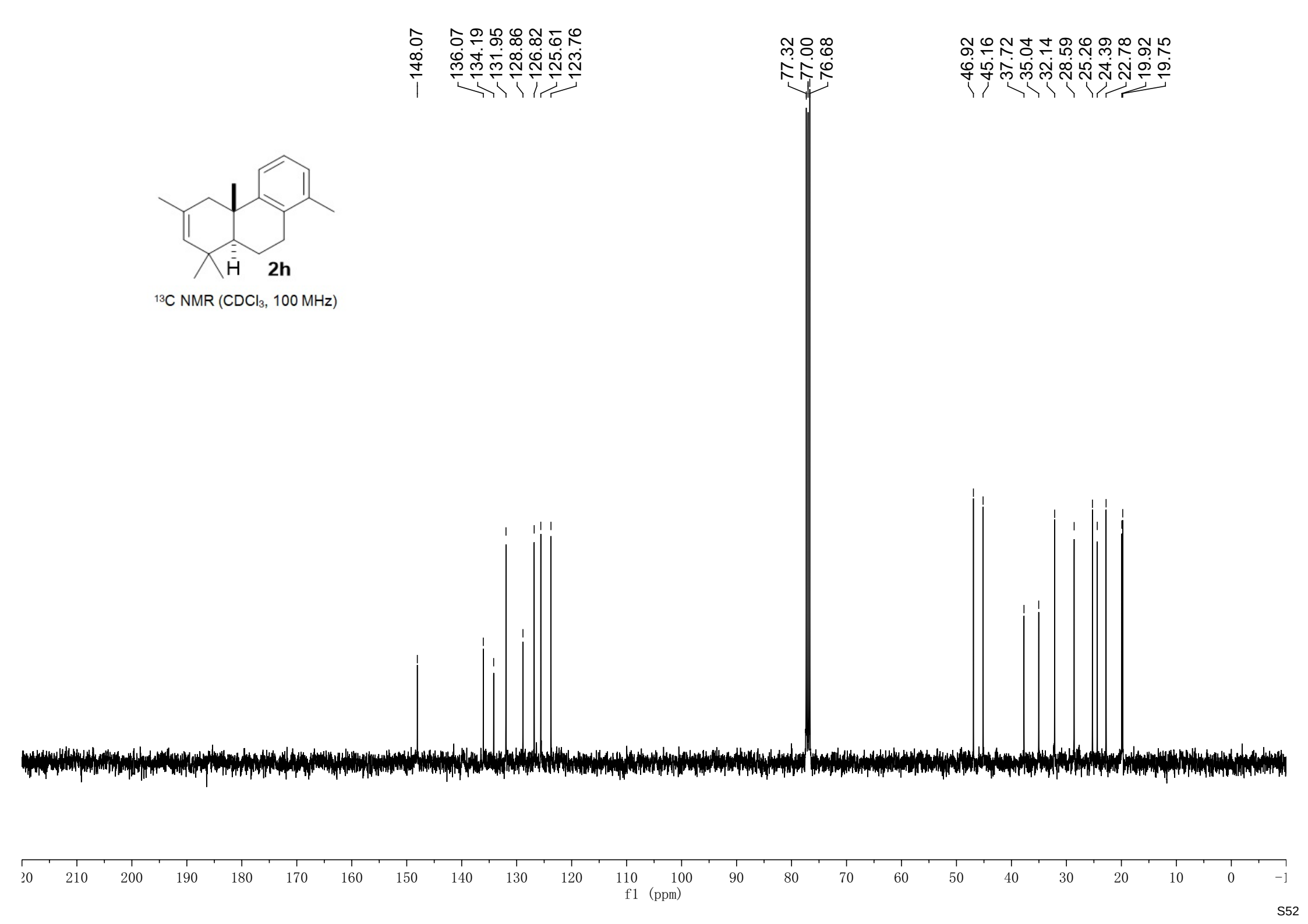
7.222
7.202
7.126
7.108
7.088
7.001
6.983
5.213
2.888
2.874
2.845
2.831
2.638
2.621
2.608
2.592
2.579
2.565
2.548
2.392
2.351
2.236
2.096
2.055
1.976
1.959
1.944
1.941
1.927
1.740
1.709
1.695
1.677
1.663
1.646
1.632
1.570
1.566
1.534
1.252
1.034
0.981
H
2h
1H NMR (CDCl3, 400 MHz)
1.00
1.03
1.03
3.01
1.02
1.01
3.00
1.08
1.03
3.02
3.00
3.05
2.5
2.0
1.5
1.0
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
1.03
1.03
3.01
1.02
1.01
3.00
1.08
1.03
3.02
3.00
3.05
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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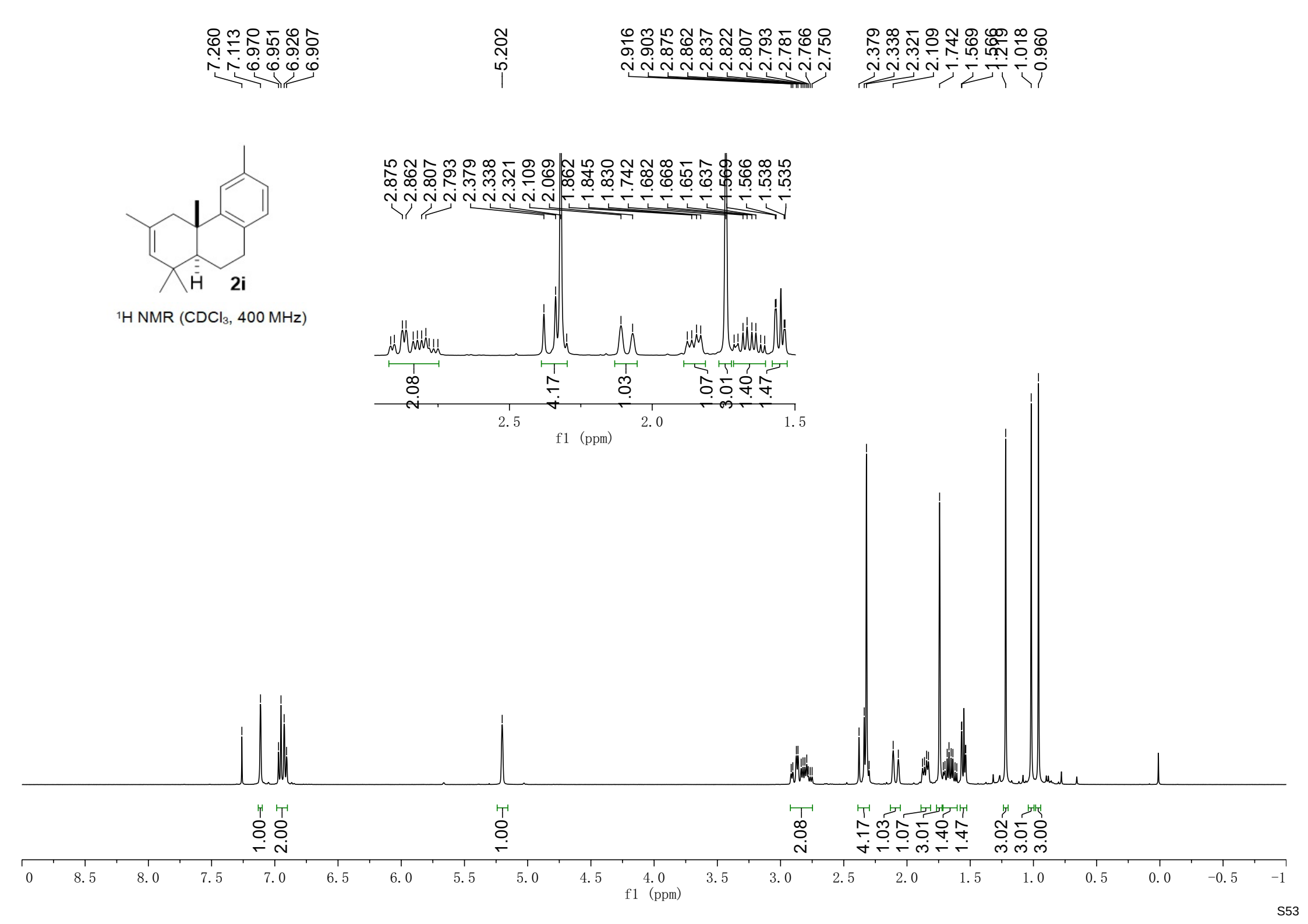
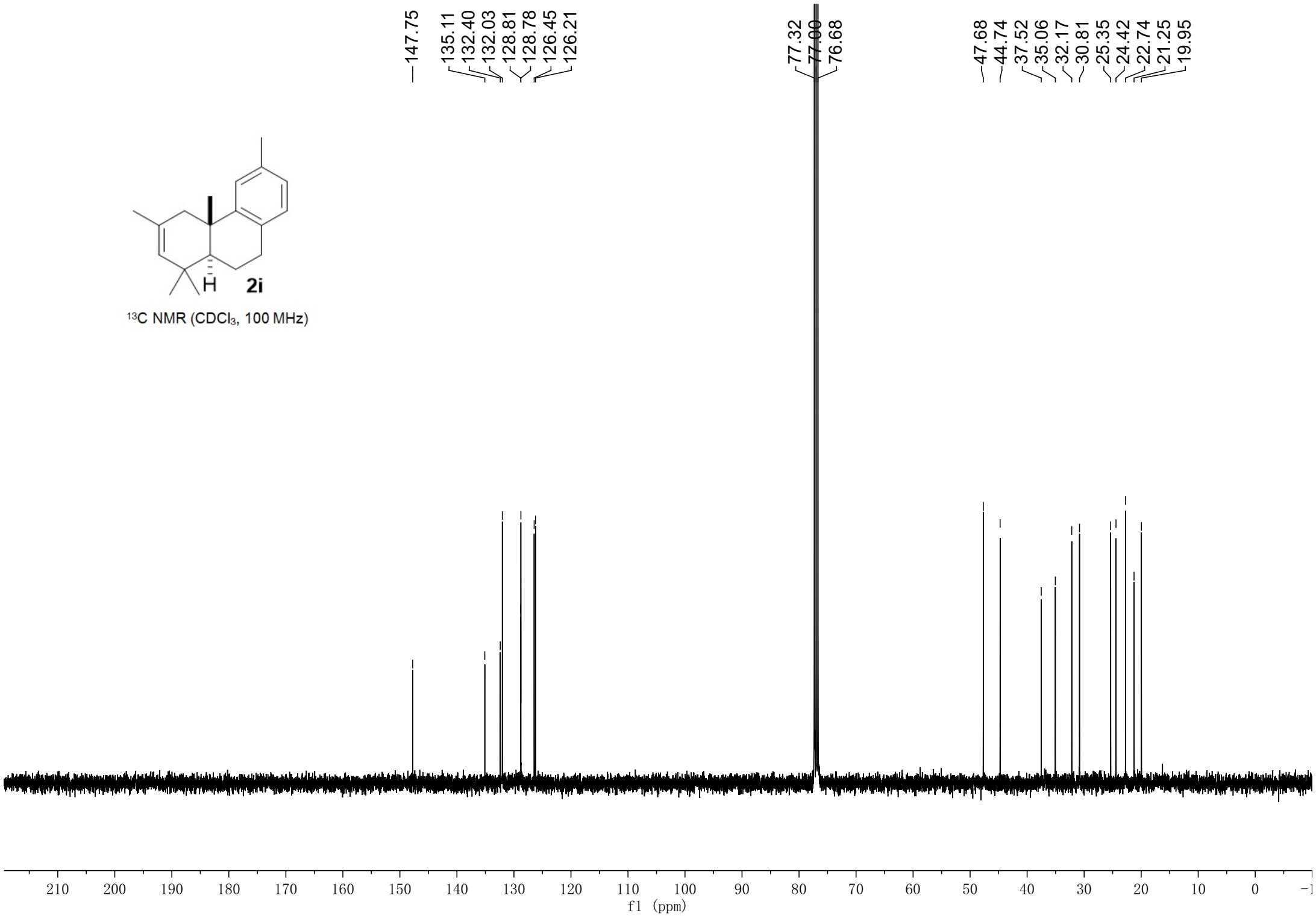
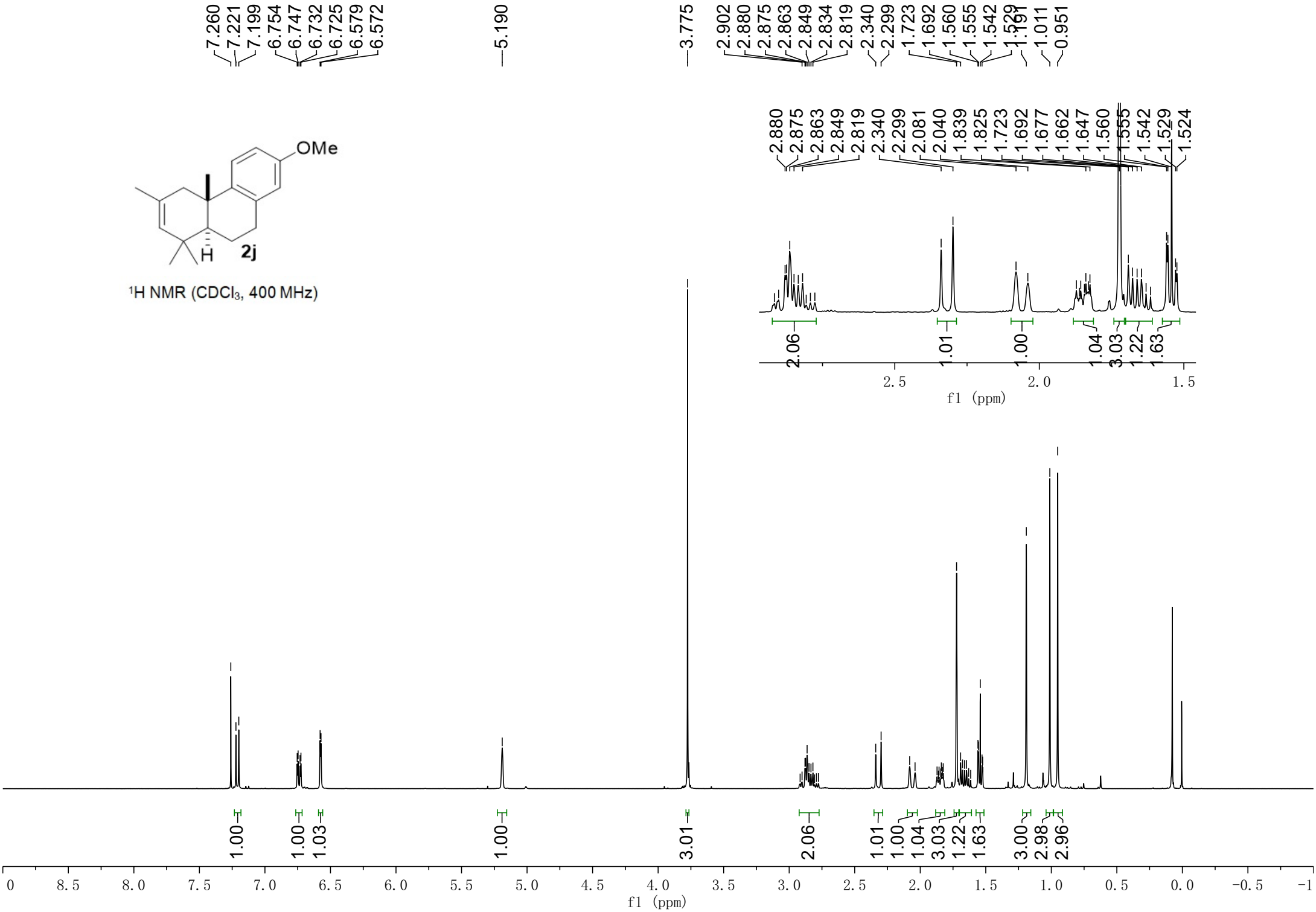
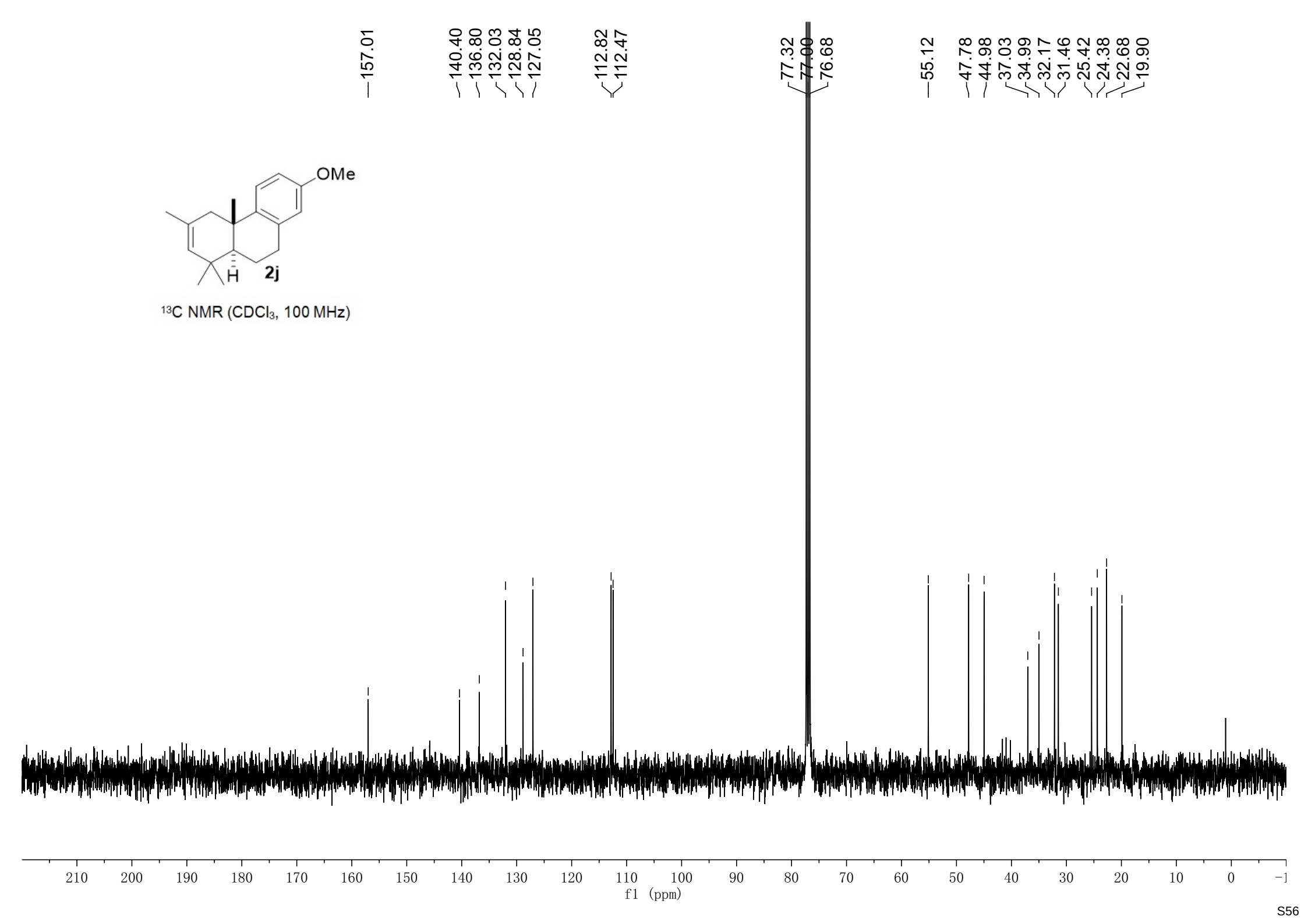
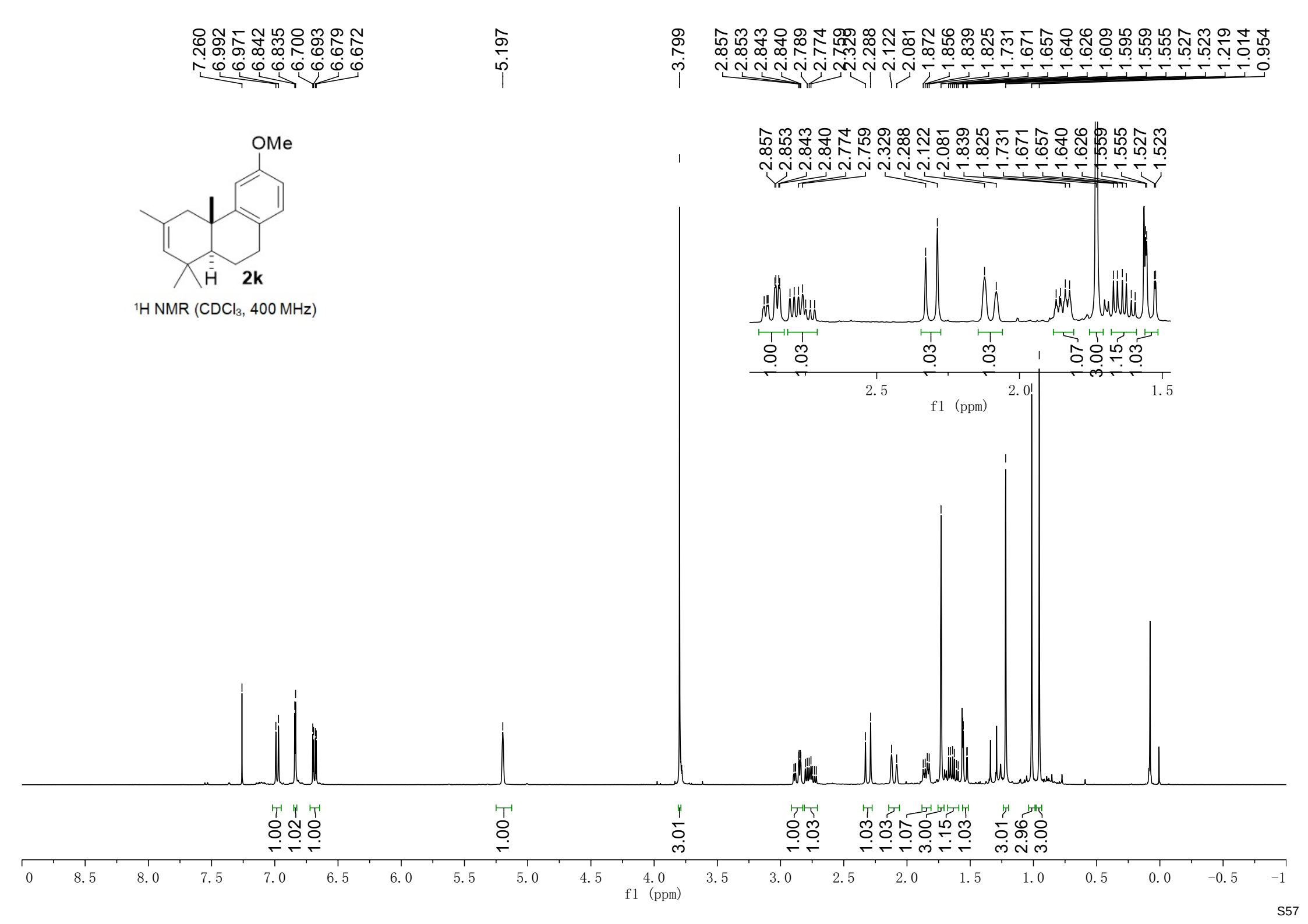
136.07
134.19
131.95
128.86
126.82
125.61
123.76
77.32
77.00
76.68
46.92
45.16
37.72
35.04
32.14
28.59
25.26
24.39
22.78
19.92
19.75
H
2h
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

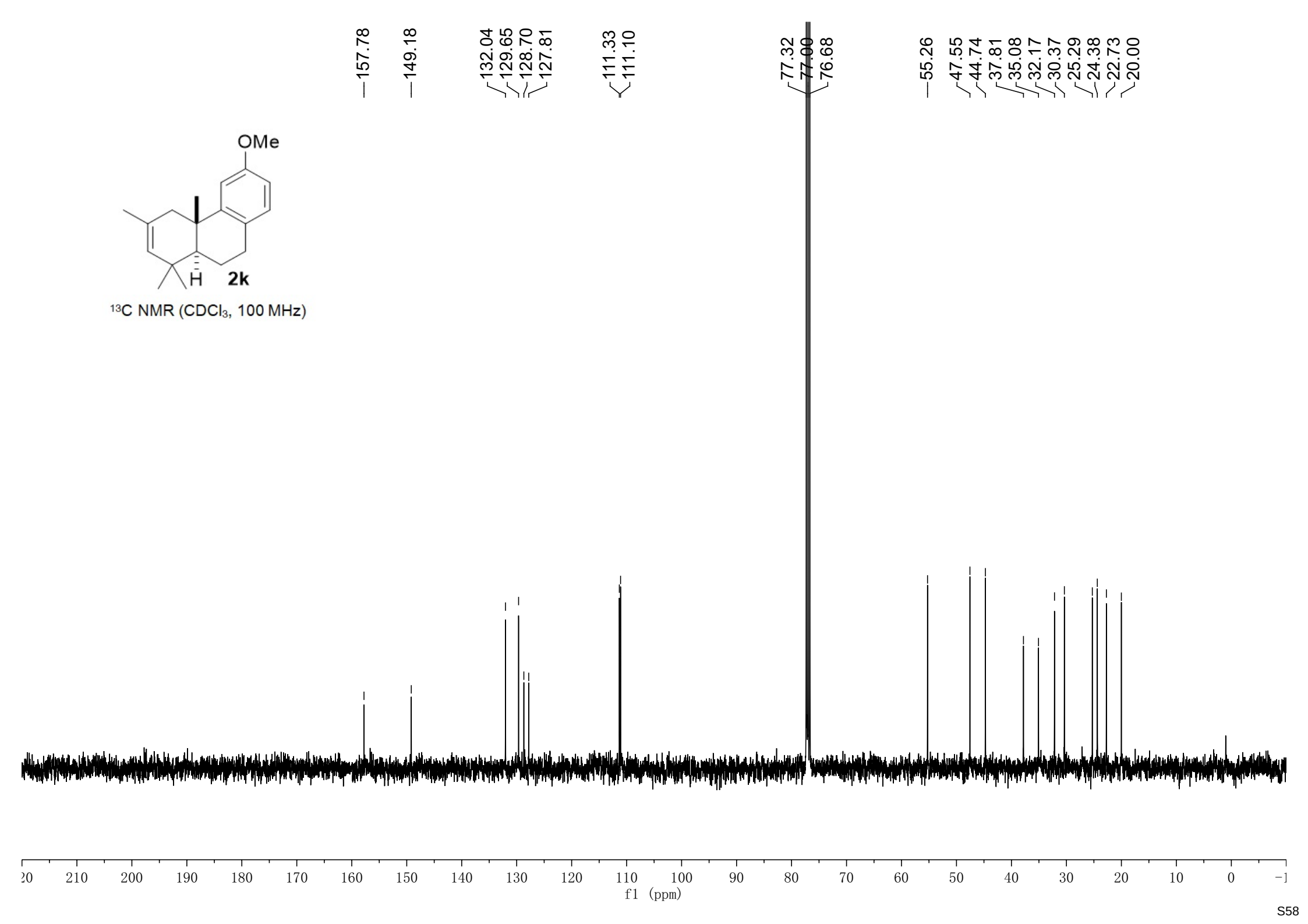

7.260
7.113
6.970
6.951
6.926
6.907
5.202
2.916
2.903
2.875
2.862
2.837
2.822
2.807
2.793
2.781
2.766
2.750
2.379
2.338
2.321
2.109
1.742
1.569
1.566
1.219
1.018
0.960
H
2i
1H NMR (CDCl3, 400 MHz)
2.875
2.862
2.807
2.793
2.379
2.338
2.321
2.109
2.069
1.862
1.845
1.830
1.742
1.682
1.668
1.651
1.637
1.569
1.566
1.538
1.535
2.08
4.17
1.03
1.07
3.01
1.40
1.47
2.5
2.0
1.5
f1 (ppm)
1.00
2.00
1.00
2.08
4.17
1.03
1.07
3.01
1.40
1.47
3.02
3.01
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

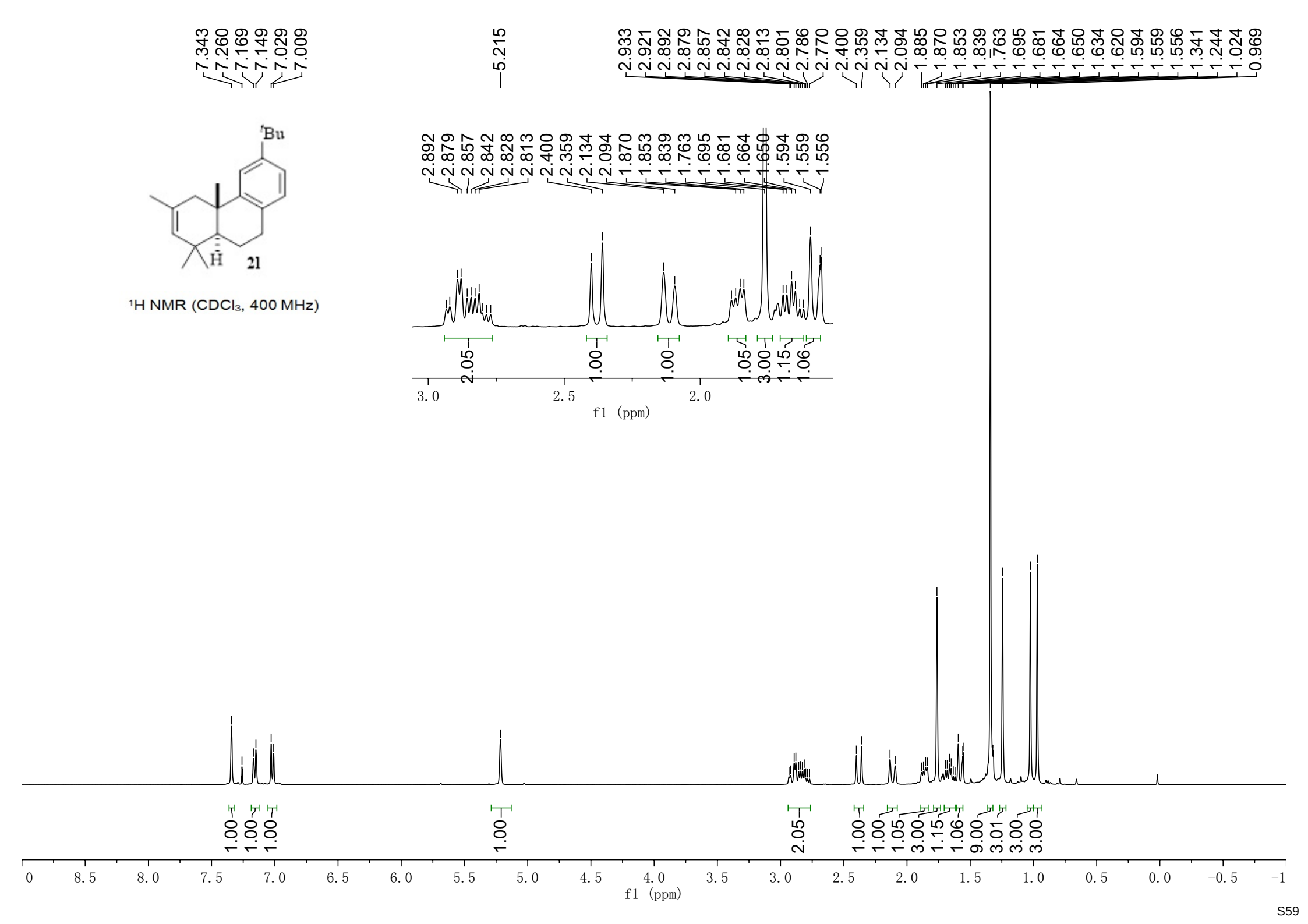

147.75
135.11
132.40
132.03
128.81
128.78
126.45
126.21
77.32
77.00
76.68
47.68
44.74
37.52
35.06
32.17
30.81
25.35
24.42
22.74
21.25
19.95
H
2i
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
7.221
7.199
6.754
6.747
6.732
6.725
6.579
6.572
5.190
3.775
2.902
2.880
2.875
2.863
2.849
2.834
2.819
2.340
2.299
1.723
1.692
1.560
1.555
1.542
1.529
1.191
1.011
0.951
OMe
H
2j
1H NMR (CDCl3, 400 MHz)
2.880
2.875
2.863
2.849
2.819
2.340
2.299
2.081
2.040
1.839
1.825
1.723
1.692
1.677
1.662
1.647
1.560
1.555
1.542
1.529
1.524
2.06
1.01
1.00
1.04
3.03
1.22
1.63
2.5
2.0
1.5
f1 (ppm)
1.00
1.00
1.03
1.00
3.01
2.06
1.01
1.00
1.04
3.03
1.22
1.63
3.00
2.98
2.96
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


157.01
140.40
136.80
132.03
128.84
127.05
112.82
112.47
77.32
77.00
76.68
55.12
47.78
44.98
37.03
34.99
32.17
31.46
25.42
24.38
22.68
19.90
OMe
H
2j
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.260
6.992
6.971
6.842
6.835
6.700
6.693
6.679
6.672
5.197
3.799
2.857
2.853
2.843
2.840
2.789
2.774
2.759
2.329
2.288
2.122
2.081
1.872
1.856
1.839
1.825
1.731
1.671
1.657
1.640
1.626
1.609
1.595
1.559
1.555
1.527
1.523
1.219
1.014
0.954
OMe
H
2k
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
S57


157.78
149.18
132.04
129.65
128.70
127.81
111.33
111.10
77.32
77.00
76.68
55.26
47.55
44.74
37.81
35.08
32.17
30.37
25.29
24.38
22.73
20.00
OMe
H
2k
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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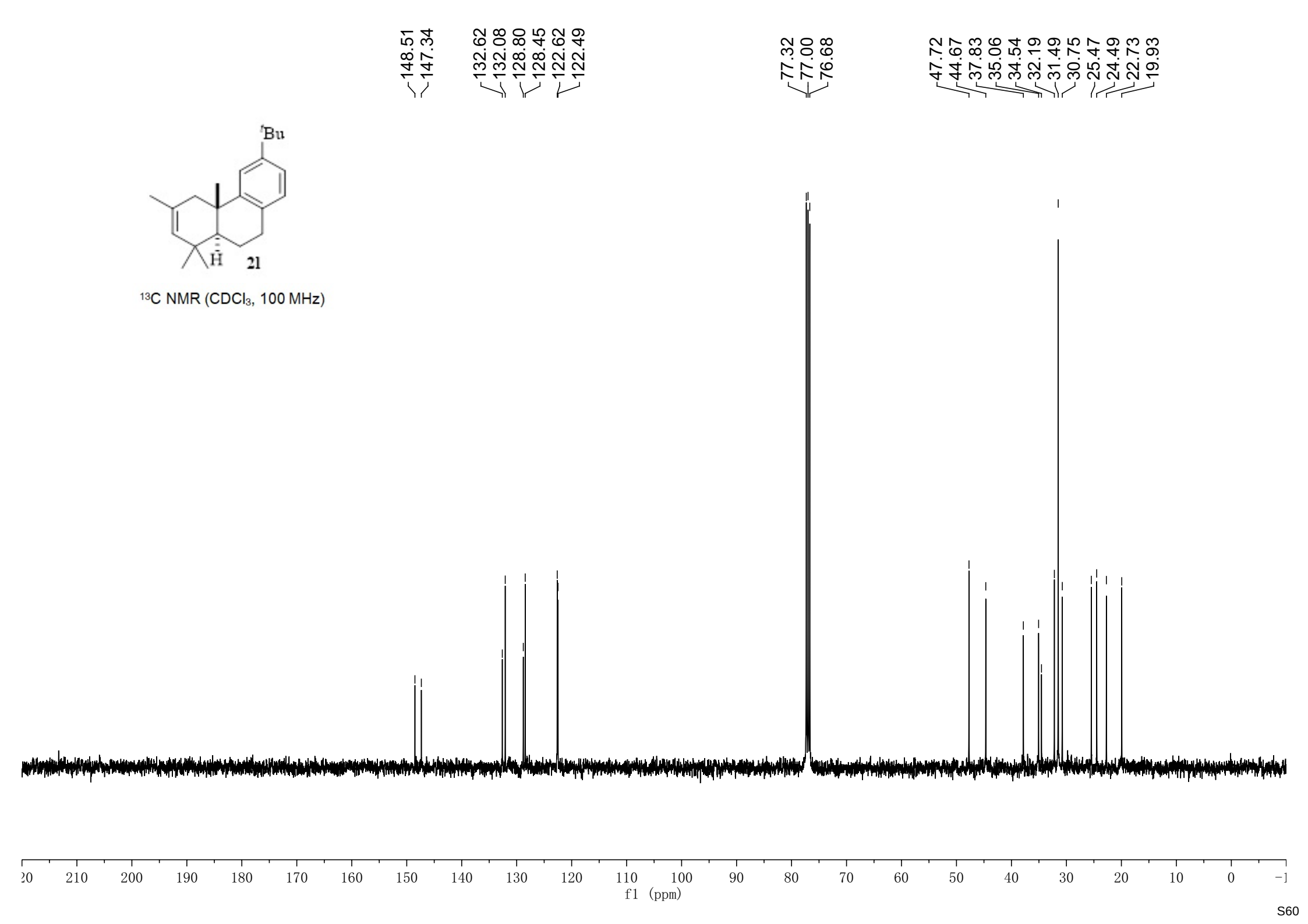
7.260
7.169
7.149
7.029
7.009
5.215
2.933
2.921
2.892
2.879
2.857
2.842
2.828
2.813
2.801
2.786
2.770
2.400
2.359
2.134
2.094
1.885
1.870
1.853
1.839
1.763
1.695
1.681
1.664
1.650
1.634
1.620
1.594
1.559
1.556
1.341
1.244
1.024
0.969
tBu
H
21
1H NMR (CDCl3, 400 MHz)
2.892
2.879
2.857
2.842
2.828
2.813
2.400
2.359
2.134
2.094
1.870
1.853
1.839
1.763
1.695
1.681
1.664
1.650
1.594
1.559
1.556
2.05
1.00
1.00
1.05
3.00
1.15
1.06
3.0
2.5
2.0
f1 (ppm)
1.00
1.00
1.00
1.00
2.05
1.00
1.00
1.05
3.00
1.15
1.06
9.00
3.01
3.00
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)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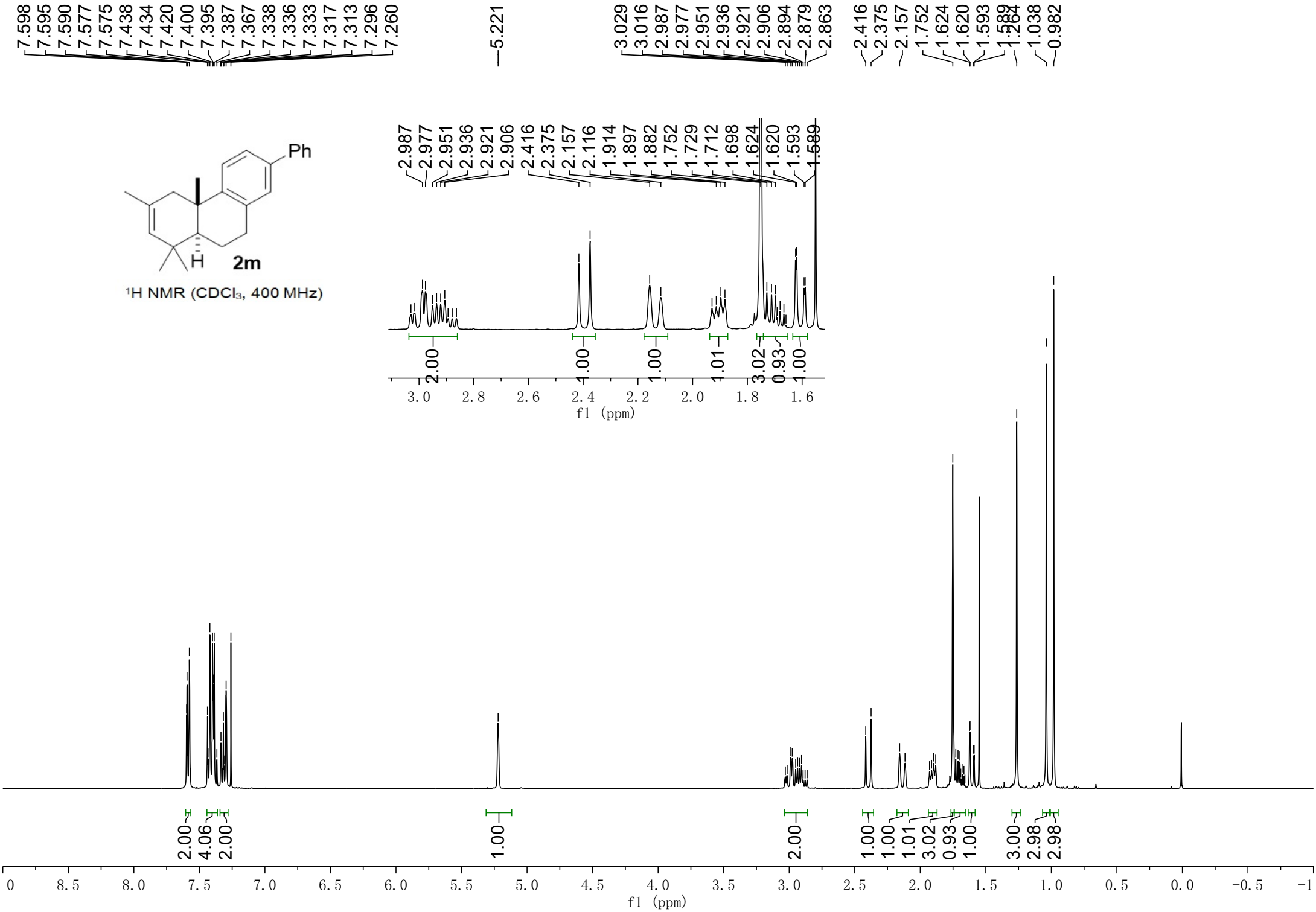
132.62
132.08
128.80
128.45
122.62
122.49
77.32
77.00
76.68
47.72
44.67
37.83
35.06
34.54
32.19
31.49
30.75
25.47
24.49
22.73
19.93
tBu
H
21
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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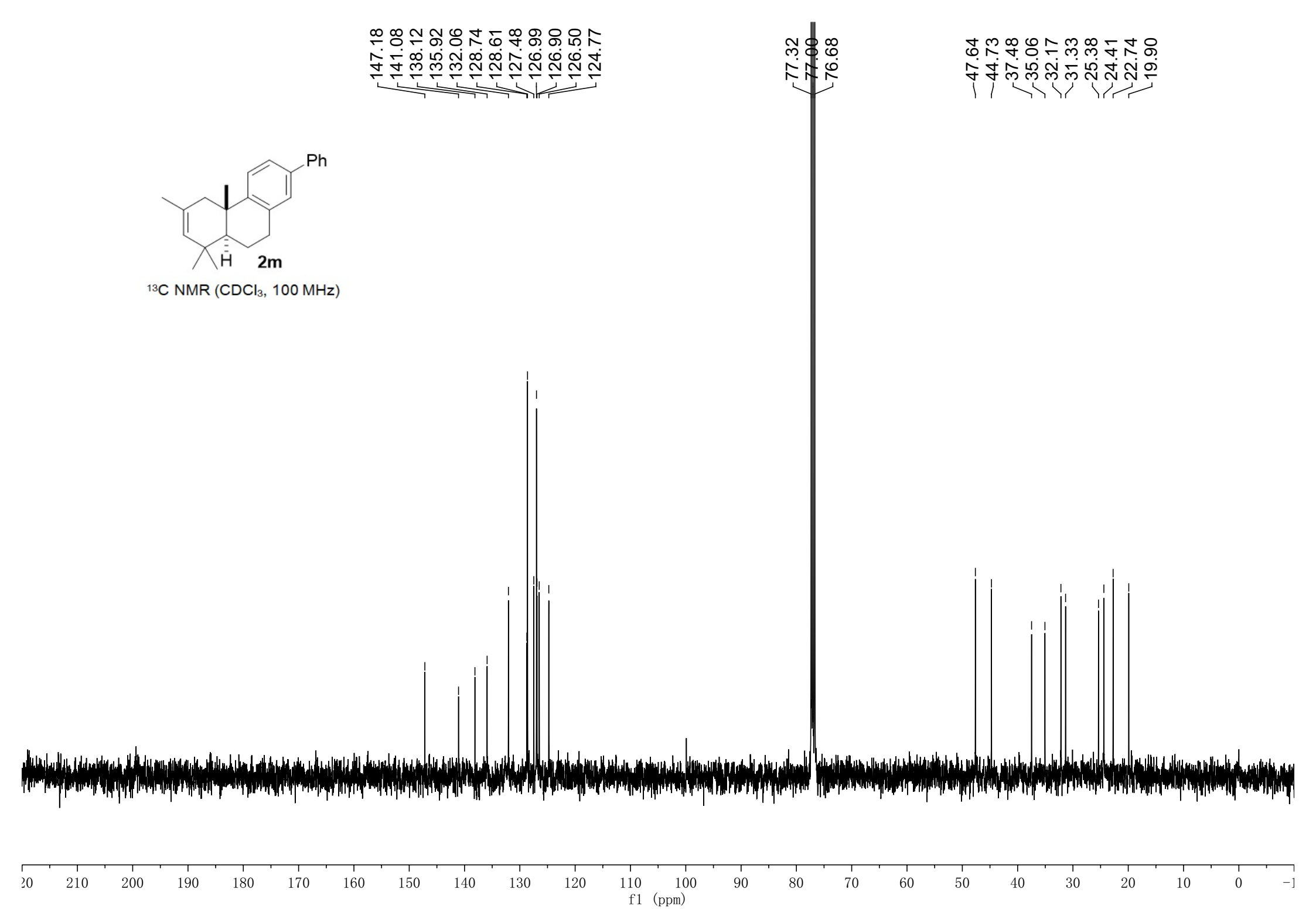
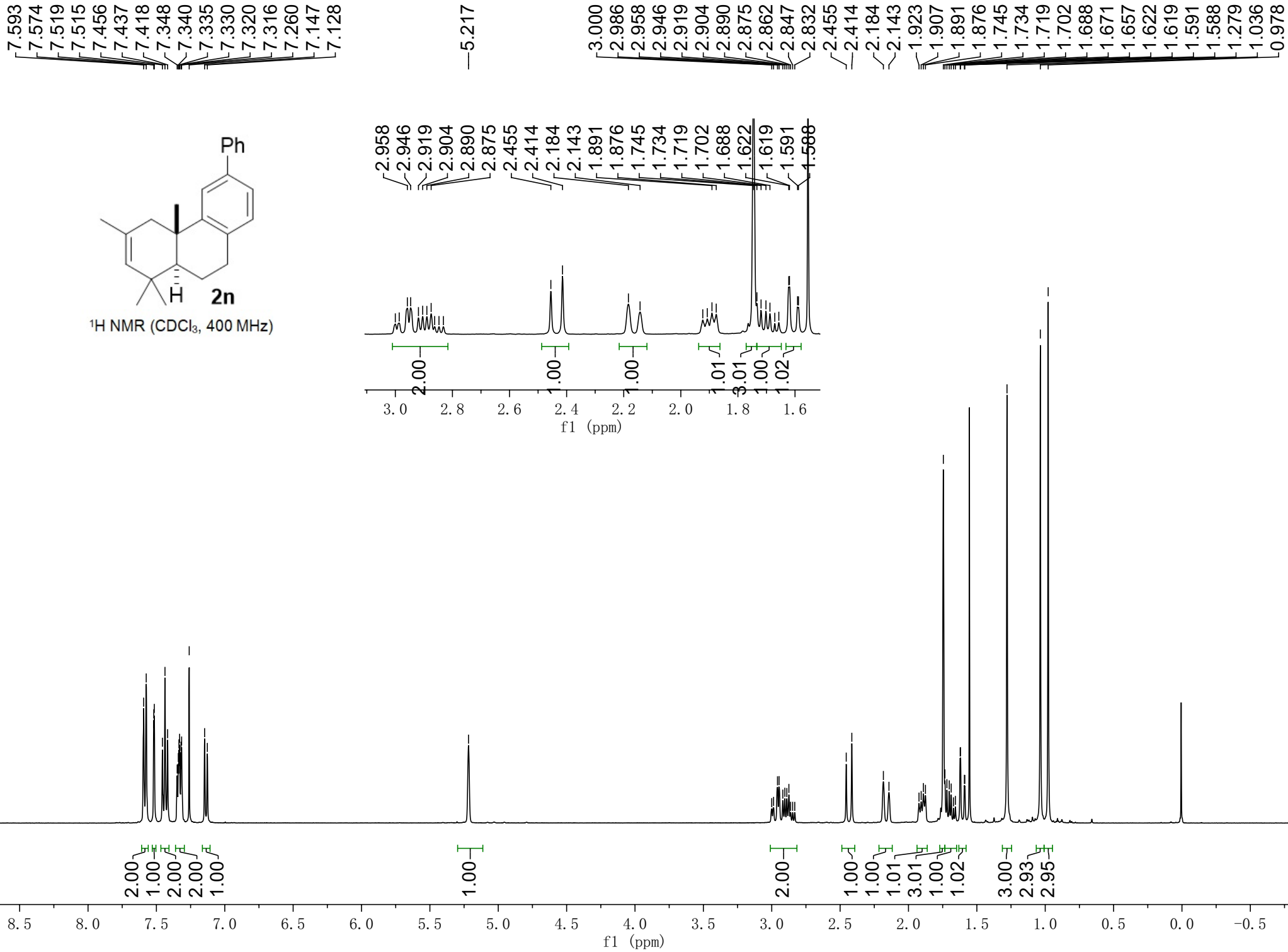
7.595
7.590
7.577
7.575
7.438
7.434
7.420
7.400
7.395
7.387
7.367
7.338
7.336
7.333
7.317
7.313
7.296
7.260
5.221
3.029
3.016
2.987
2.977
2.951
2.936
2.921
2.906
2.894
2.879
2.863
2.416
2.375
2.157
1.752
1.624
1.620
1.593
1.589
1.264
1.038
0.982
Ph
H
2m
1H NMR (CDCl3, 400 MHz)
2.987
2.977
2.951
2.936
2.921
2.906
2.416
2.375
2.157
2.116
1.914
1.897
1.882
1.752
1.729
1.712
1.698
1.624
1.620
1.593
1.589
2.00
1.00
1.00
1.01
3.02
0.93
1.00
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)
2.00
4.06
2.00
1.00
2.00
1.00
1.00
1.01
3.02
0.93
1.00
3.00
2.98
2.98
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


147.18
141.08
138.12
135.92
132.06
128.74
128.61
127.48
126.99
126.90
126.50
124.77
77.32
77.00
76.68
47.64
44.73
37.48
35.06
32.17
31.33
25.38
24.41
22.74
19.90
Ph
H
2m
13C NMR (CDCl3, 100 MHz)
f1 (ppm)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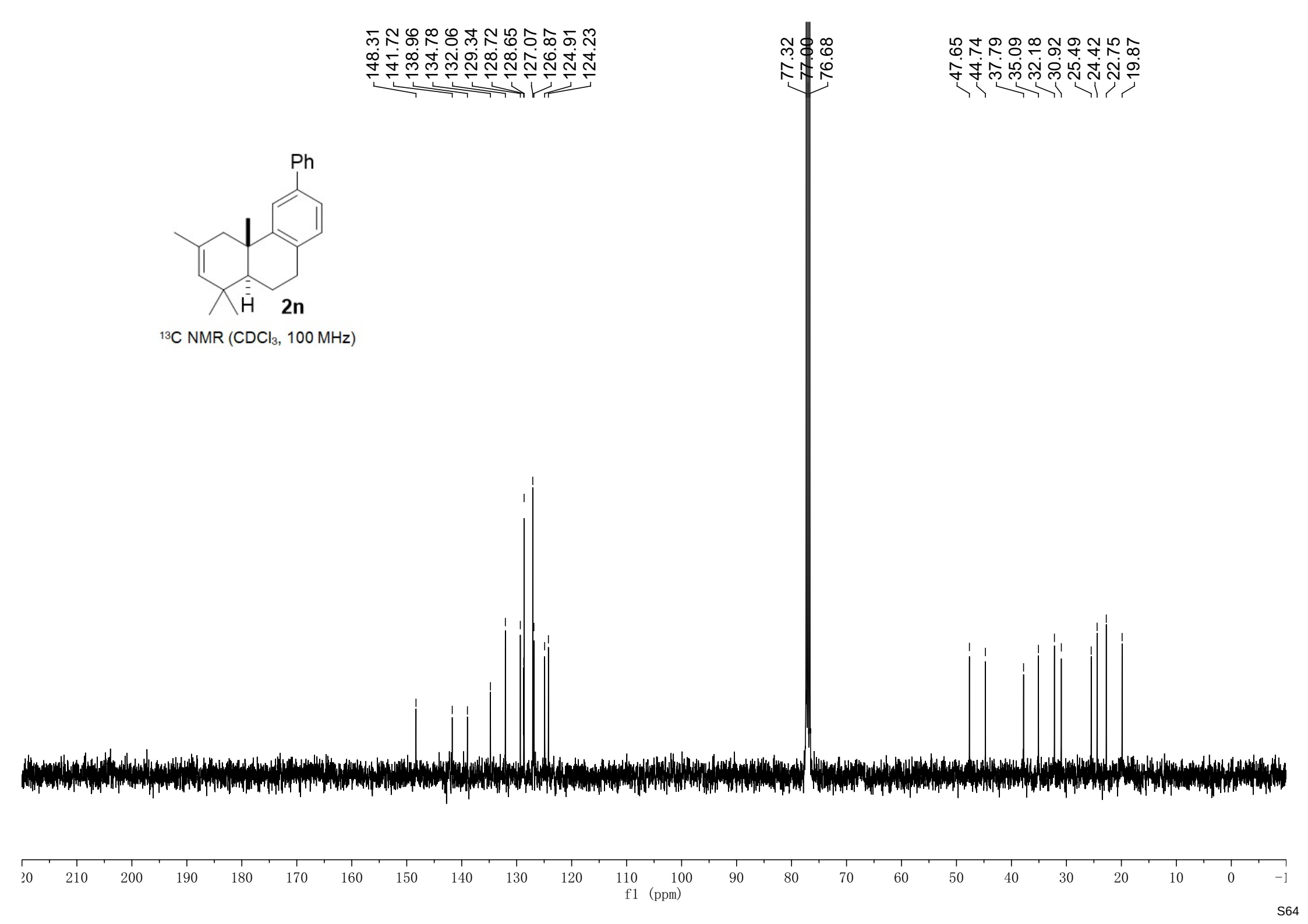
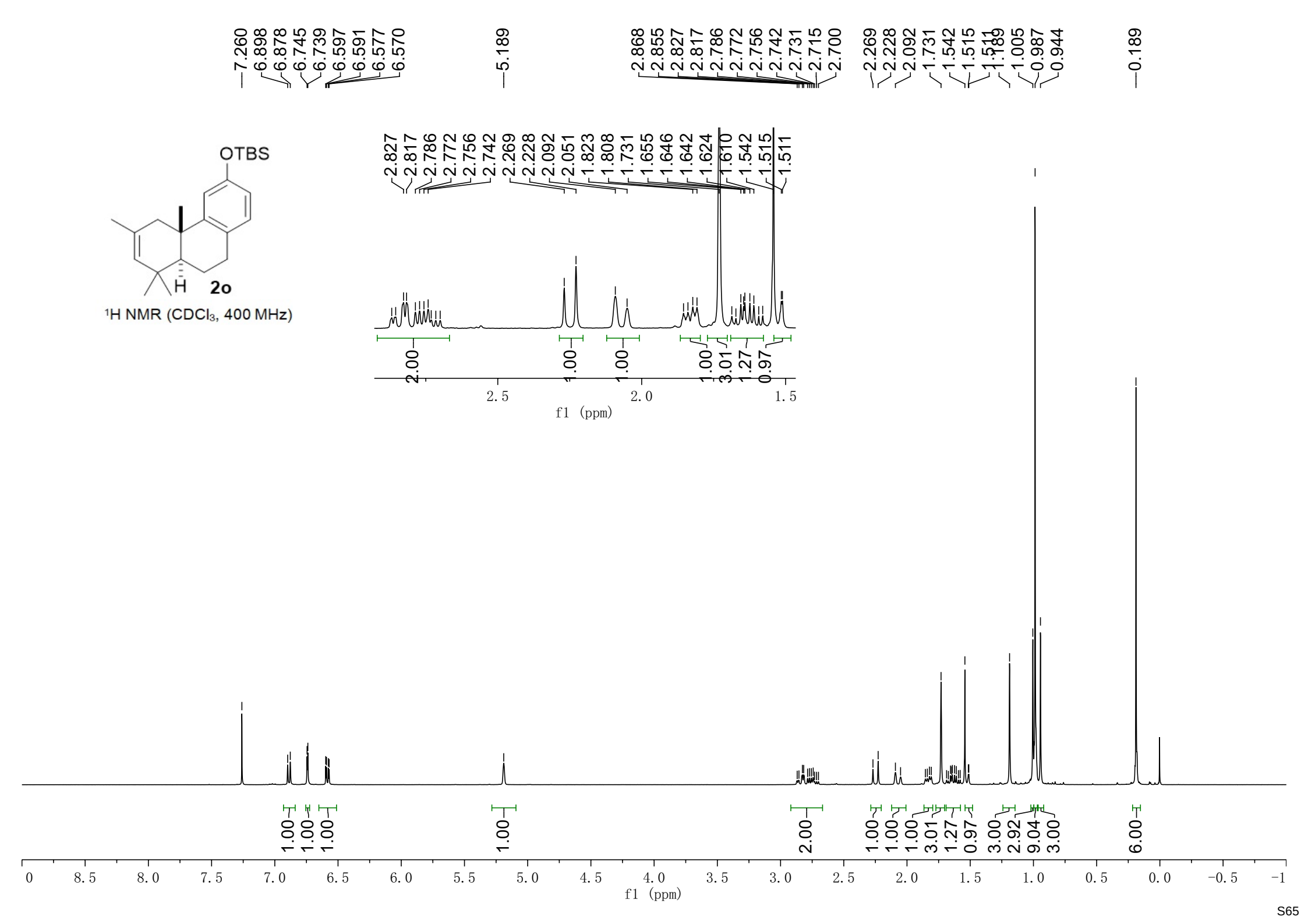
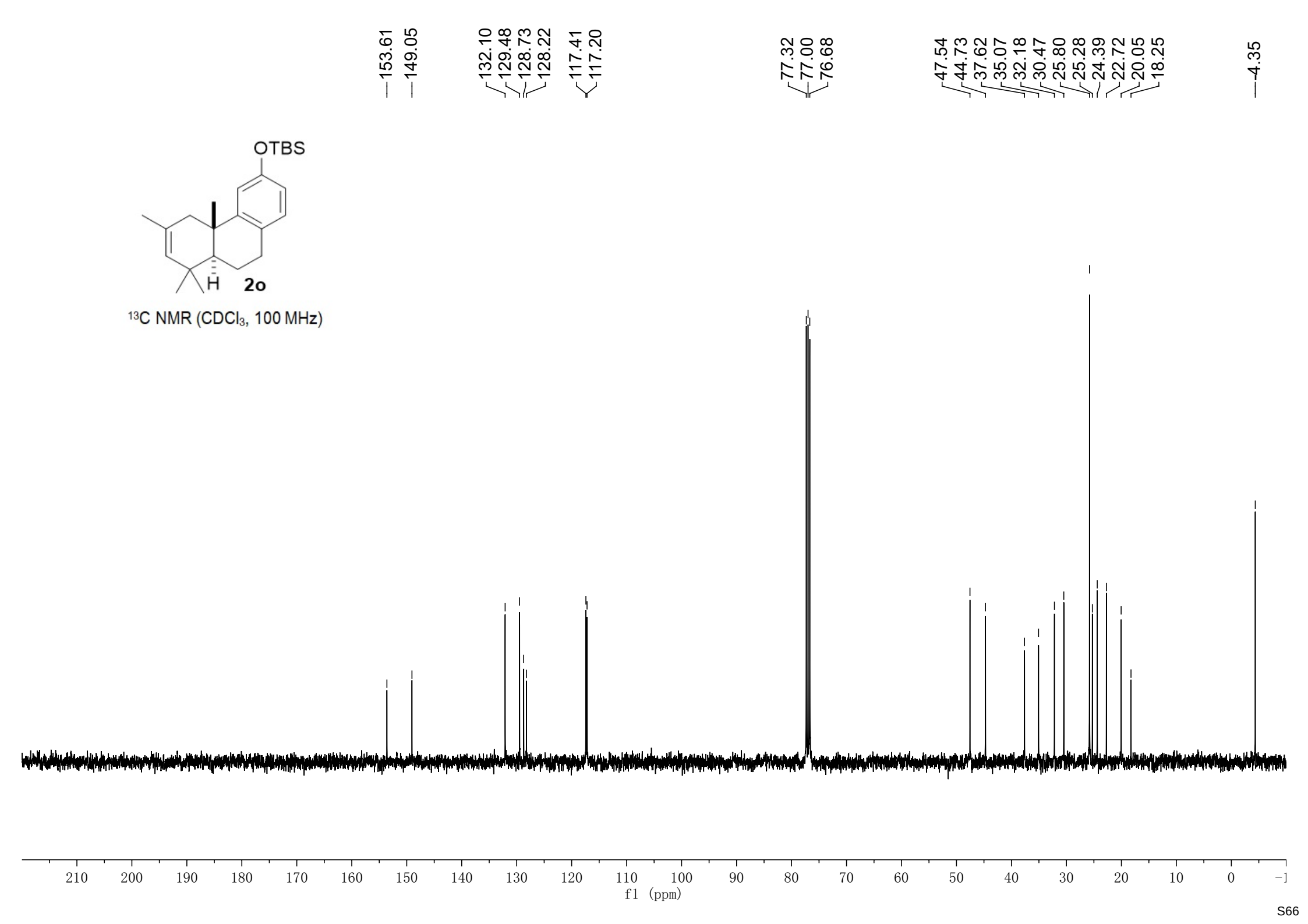
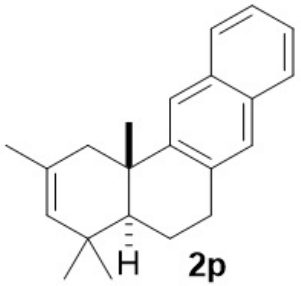
7.515
7.456
7.437
7.418
7.348
7.340
7.335
7.330
7.320
7.316
7.260
7.147
7.128
5.217
3.000
2.986
2.958
2.946
2.919
2.904
2.890
2.875
2.862
2.847
2.832
2.455
2.414
2.184
2.143
1.923
1.907
1.891
1.876
1.745
1.734
1.719
1.702
1.688
1.671
1.657
1.622
1.619
1.591
1.588
1.279
1.036
0.978
Ph
H
2n
1H NMR (CDCl3, 400 MHz)
f1 (ppm)
f1 (ppm)


148.31
141.72
138.96
134.78
132.06
129.34
128.72
128.65
127.07
126.87
124.91
124.23
77.32
77.00
76.68
47.65
44.74
37.79
35.09
32.18
30.92
25.49
24.42
22.75
19.87
Ph
H
2n
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

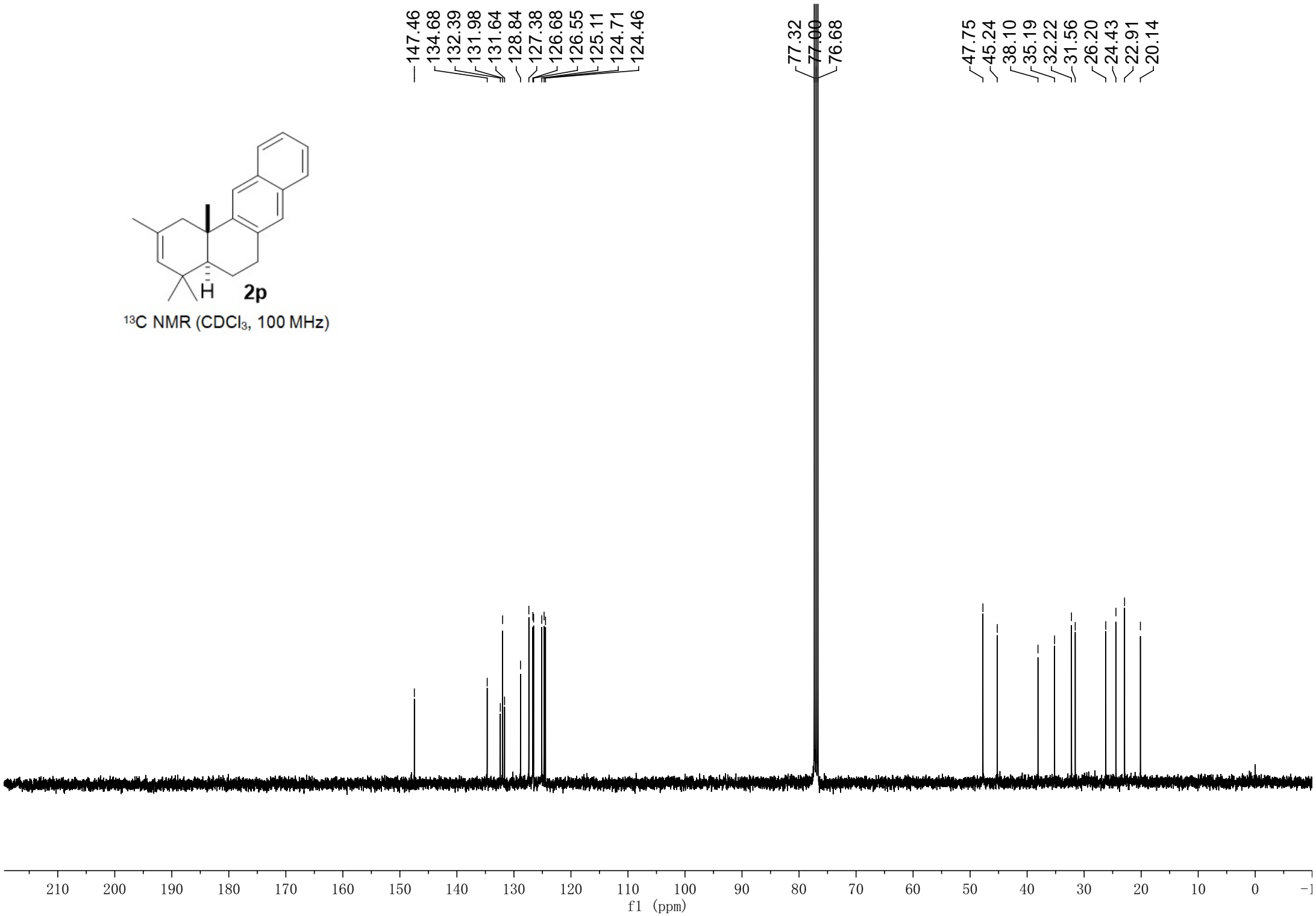

OTBS
H
2o
1H NMR (CDCl3, 400 MHz)
f1 (ppm)

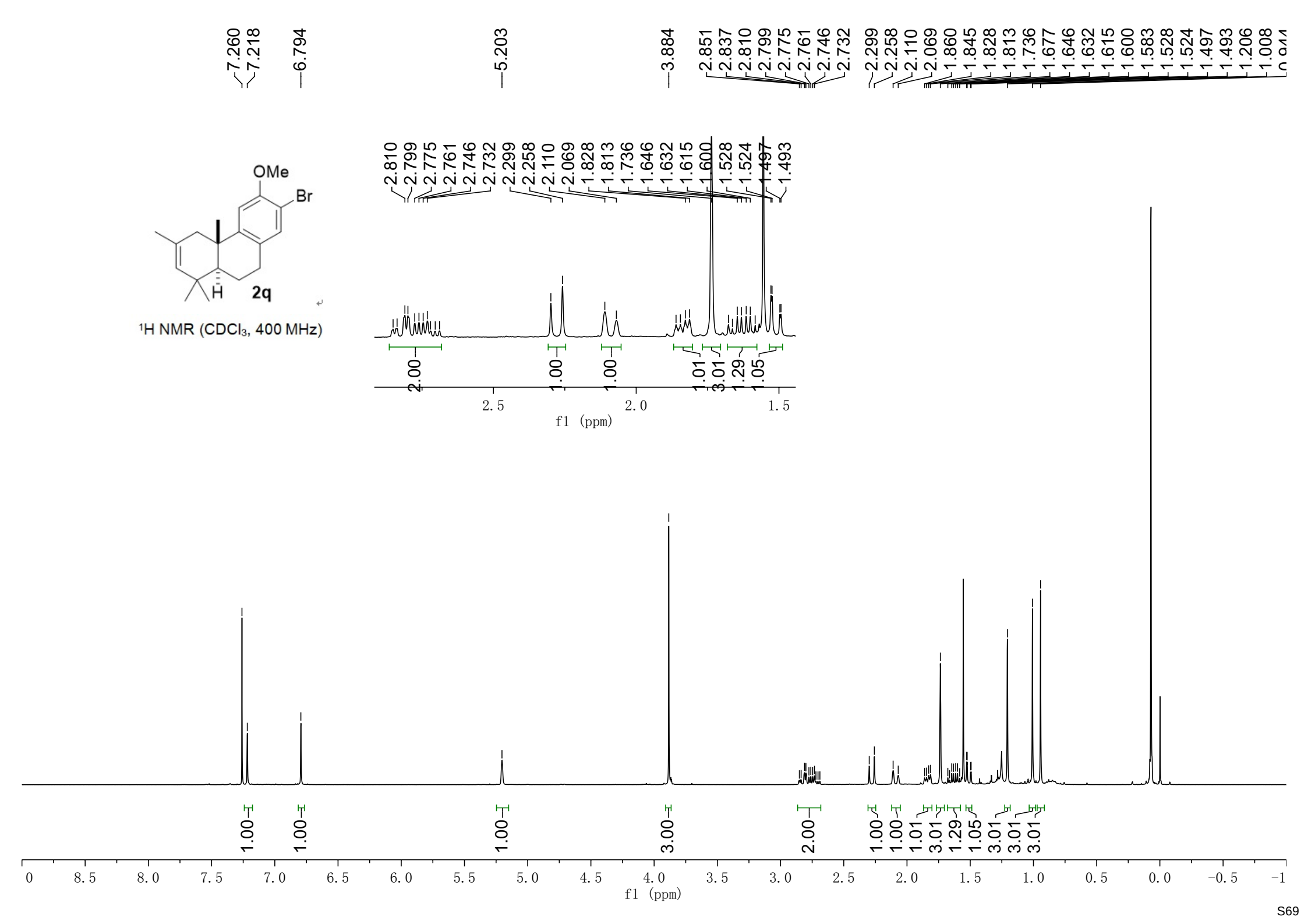

153.61
149.05
132.10
129.48
128.73
128.22
117.41
117.20
77.32
77.00
76.68
47.54
44.73
37.62
35.07
32.18
30.47
25.80
25.28
24.39
22.72
20.05
18.25
4.35
OTBS
H
2o
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

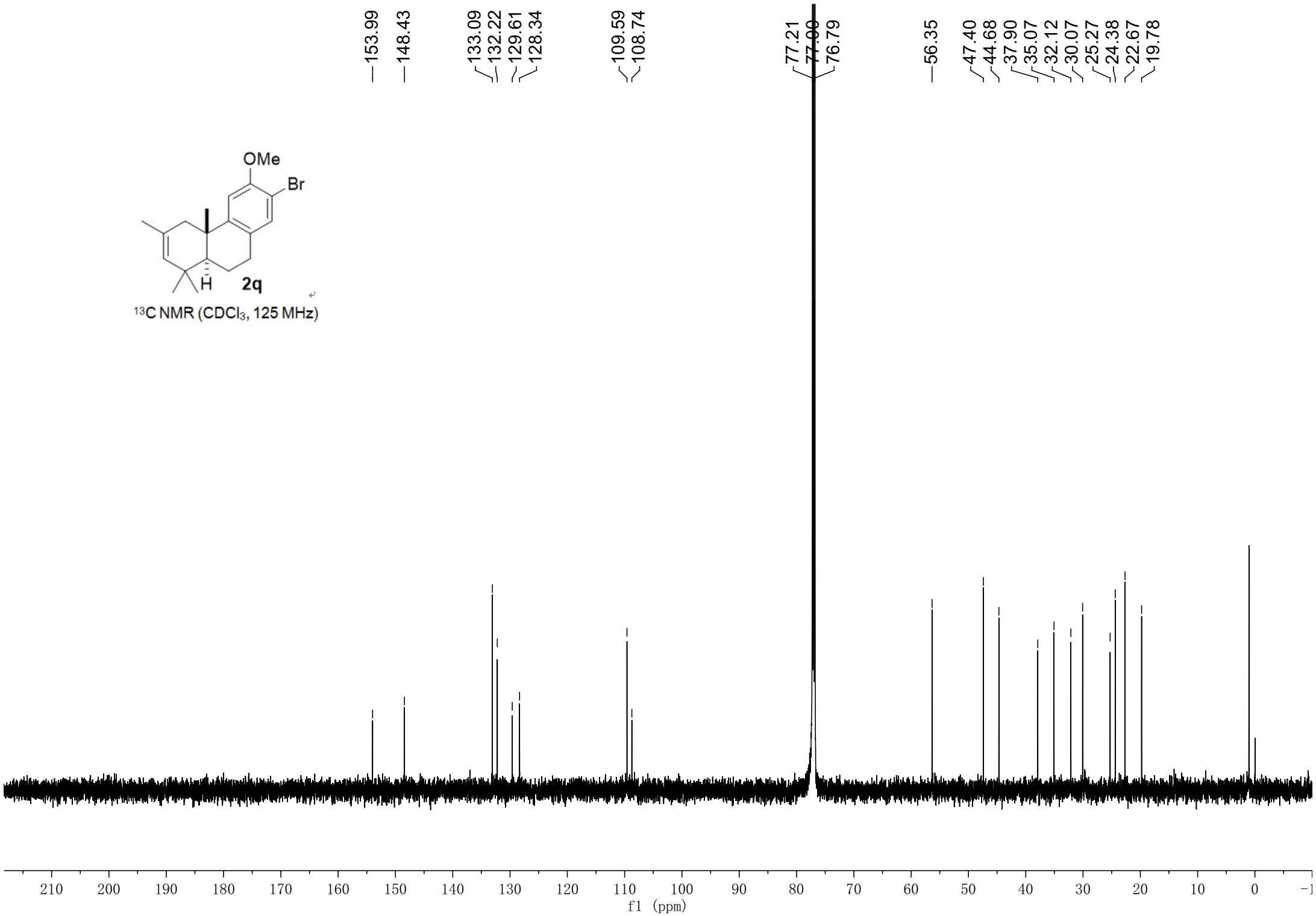


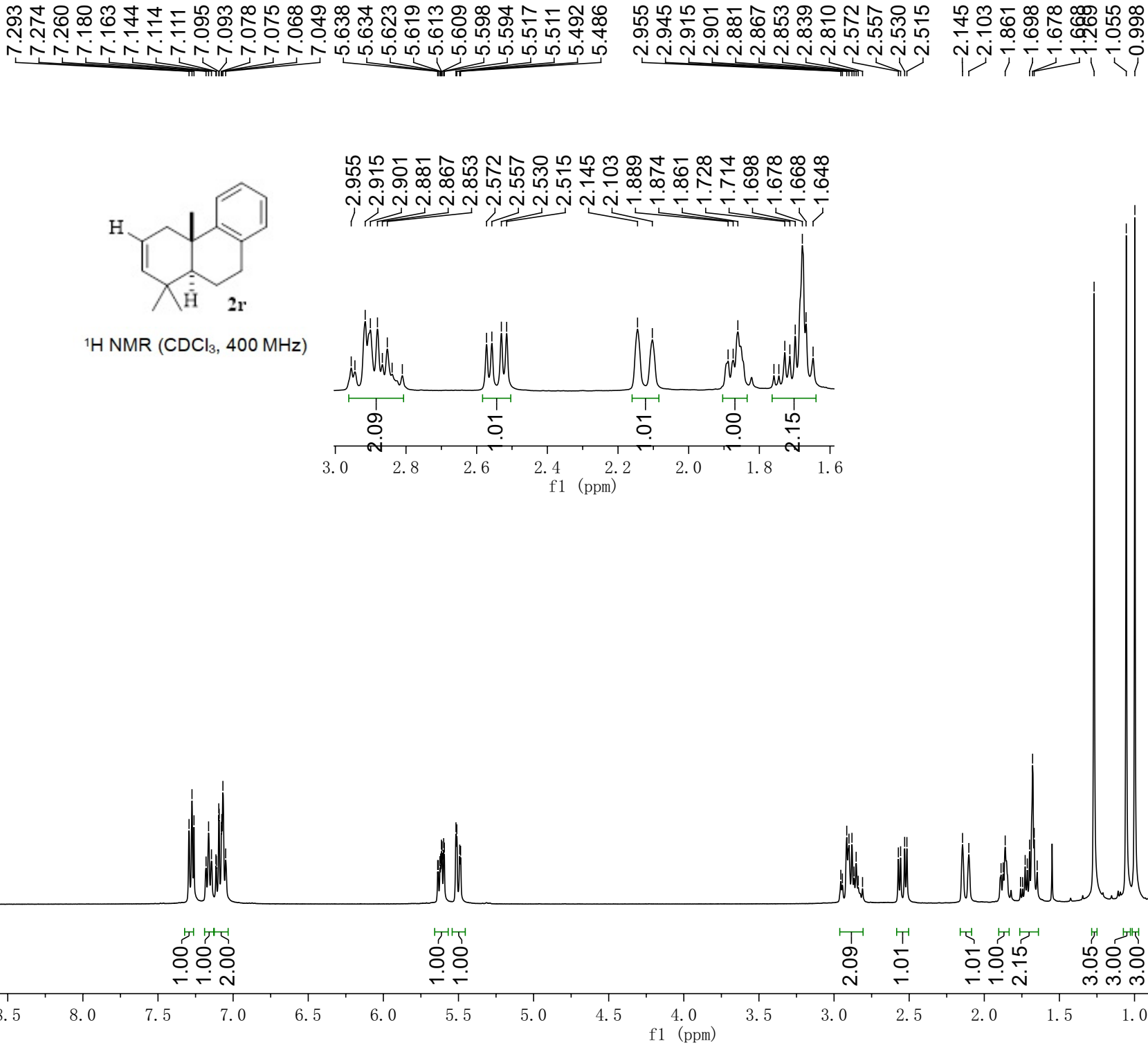
2p

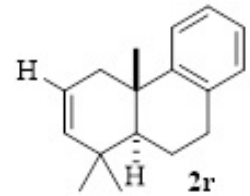
^{1}H NMR ($CDCl_3$, 400 MHz)


147.46
134.68
132.39
131.98
131.64
128.84
127.38
126.68
126.55
125.11
124.71
124.46
77.32
77.00
76.68
47.75
45.24
38.10
35.19
32.22
31.56
26.20
24.43
22.91
20.14
H
2p
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
7.218
6.794
5.203
3.884
2.851
2.837
2.810
2.799
2.775
2.761
2.746
2.732
2.299
2.258
2.110
2.069
1.860
1.845
1.828
1.813
1.736
1.677
1.646
1.632
1.615
1.600
1.583
1.528
1.524
1.497
1.493
1.206
1.008
OMe
Br
H
2q
1H NMR (CDCl3, 400 MHz)
2.810
2.799
2.775
2.761
2.746
2.732
2.299
2.258
2.110
2.069
1.828
1.813
1.736
1.646
1.632
1.615
1.600
1.528
1.524
1.497
1.493
2.00
1.00
1.00
1.01
3.01
1.29
1.05
2.5
2.0
1.5
f1 (ppm)
1.00
1.00
1.00
3.00
2.00
1.00
1.00
1.01
3.01
1.29
1.05
3.01
3.01
3.01
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


153.99
148.43
133.09
132.22
129.61
128.34
109.59
108.74
77.21
77.00
76.79
56.35
47.40
44.68
37.90
35.07
32.12
30.07
25.27
24.38
22.67
19.78
OMe
Br
H
2q
13C NMR (CDCl3, 125 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.293
7.274
7.260
7.180
7.163
7.144
7.114
7.111
7.095
7.093
7.078
7.075
7.068
7.049
5.638
5.634
5.623
5.619
5.613
5.609
5.598
5.594
5.517
5.511
5.492
5.486
2.955
2.945
2.915
2.901
2.881
2.867
2.853
2.839
2.810
2.572
2.557
2.530
2.515
2.145
2.103
1.861
1.698
1.678
1.055
0.998
H
H
2r
1H NMR (CDCl3, 400 MHz)
2.955
2.915
2.901
2.881
2.867
2.853
2.572
2.557
2.530
2.515
2.145
2.103
1.889
1.874
1.861
1.728
1.714
1.698
1.678
1.668
1.648
2.09
1.01
1.01
1.00
2.15
3.0
2.8
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)
1.00
1.00
2.00
1.00
1.00
2.09
1.01
1.01
1.00
2.15
3.05
3.00
3.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



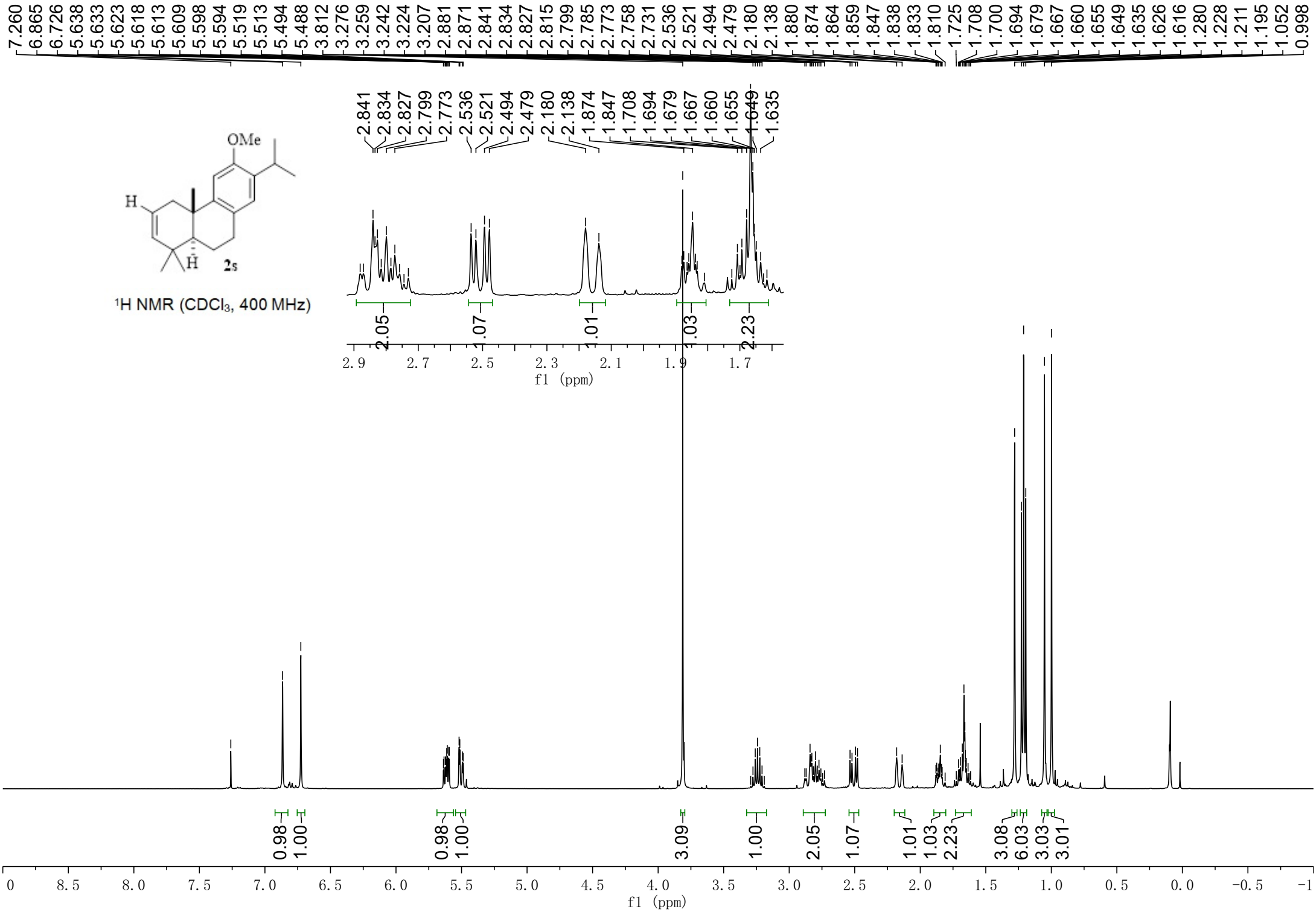
2r

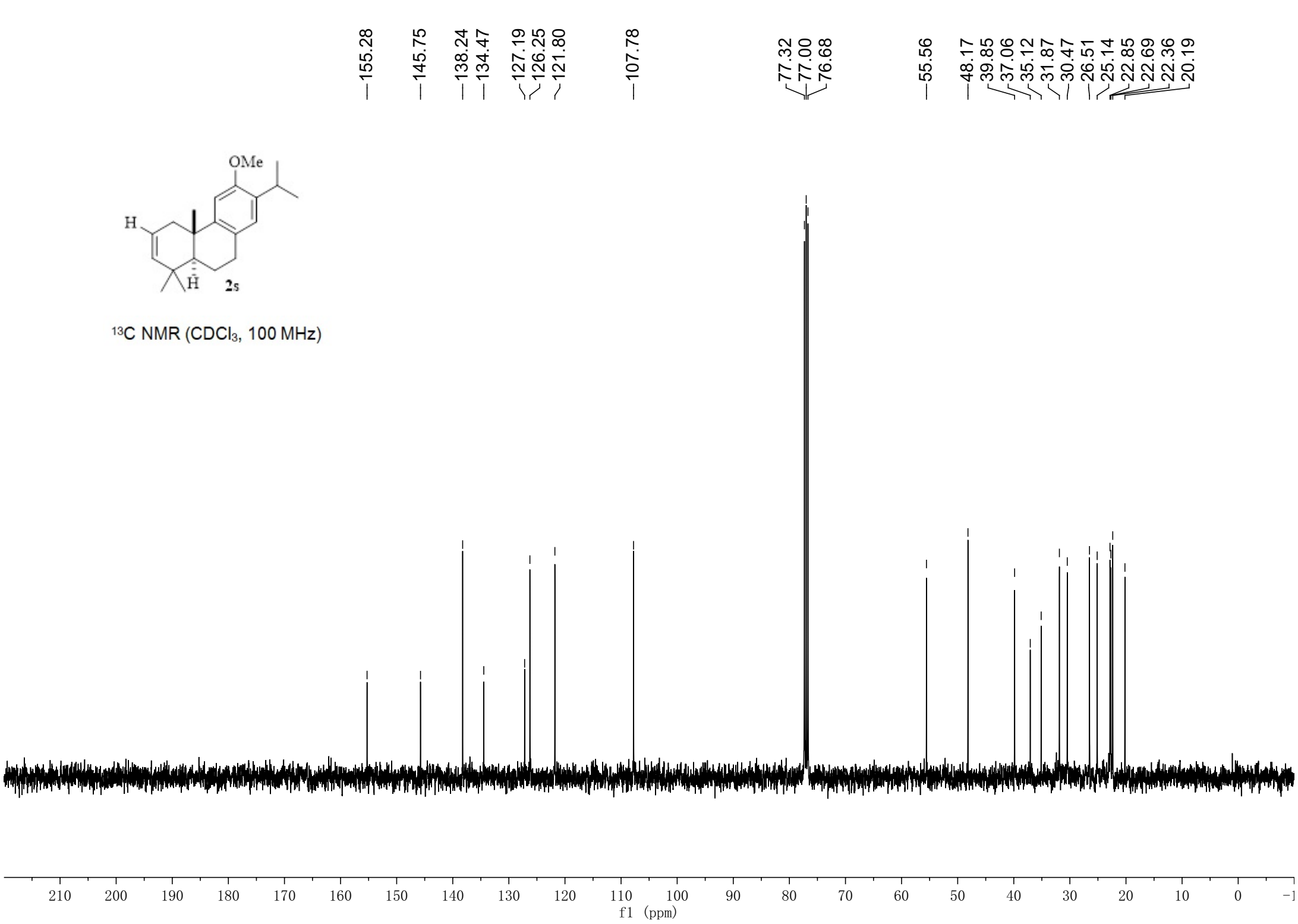
^{13}C NMR ($CDCl_3$, 100 MHz)

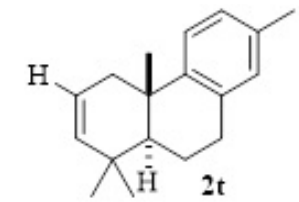
147.87
138.08
135.44
128.88
126.01
125.91
125.27
121.83
77.32
77.00
76.68
48.02
39.68
37.00
35.08
31.82
31.13
25.26
22.36
19.90

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

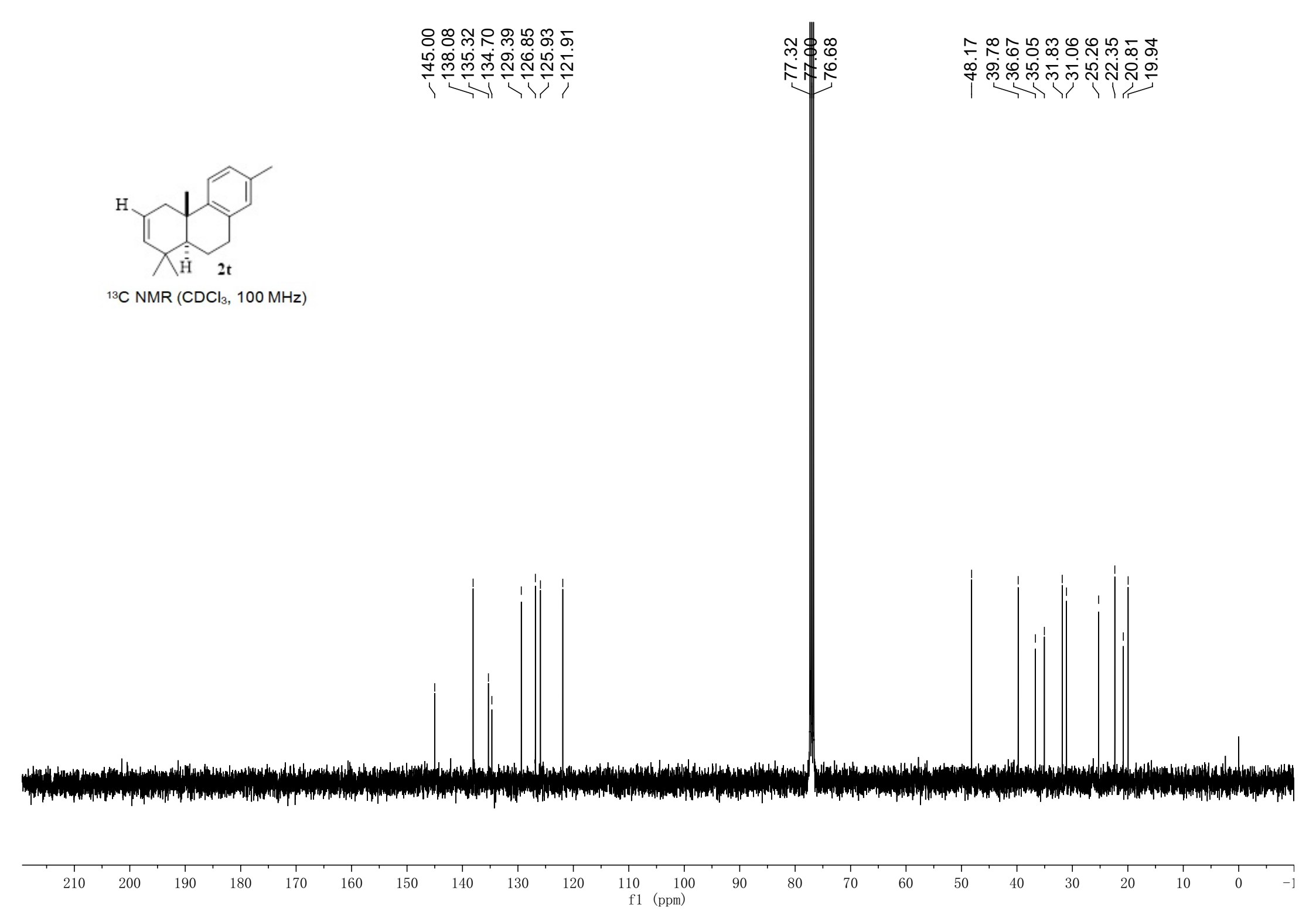
f1 (ppm)

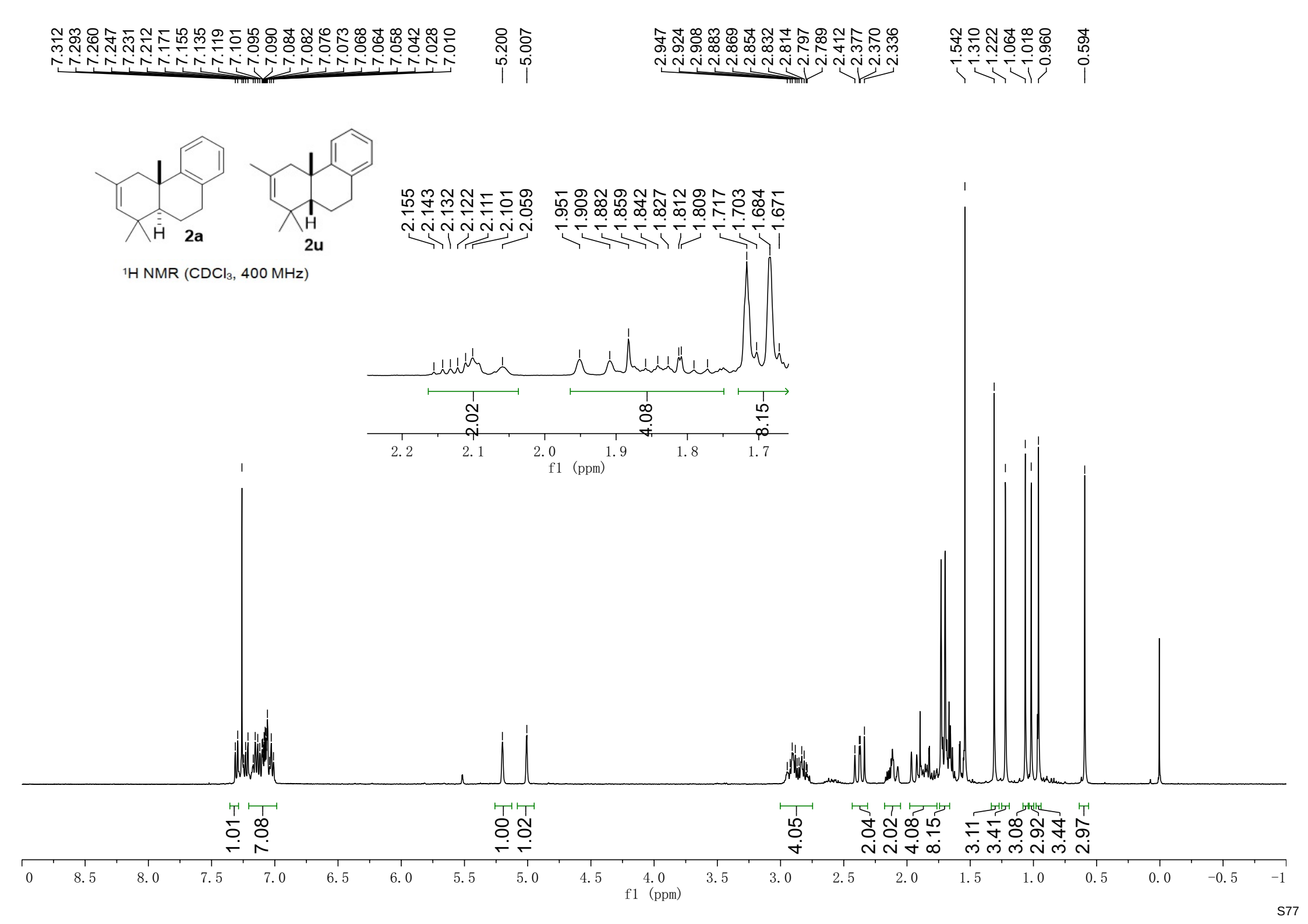

OMe
H
H
2s
¹H NMR (CDCl₃, 400 MHz)
f1 (ppm)
f1 (ppm)

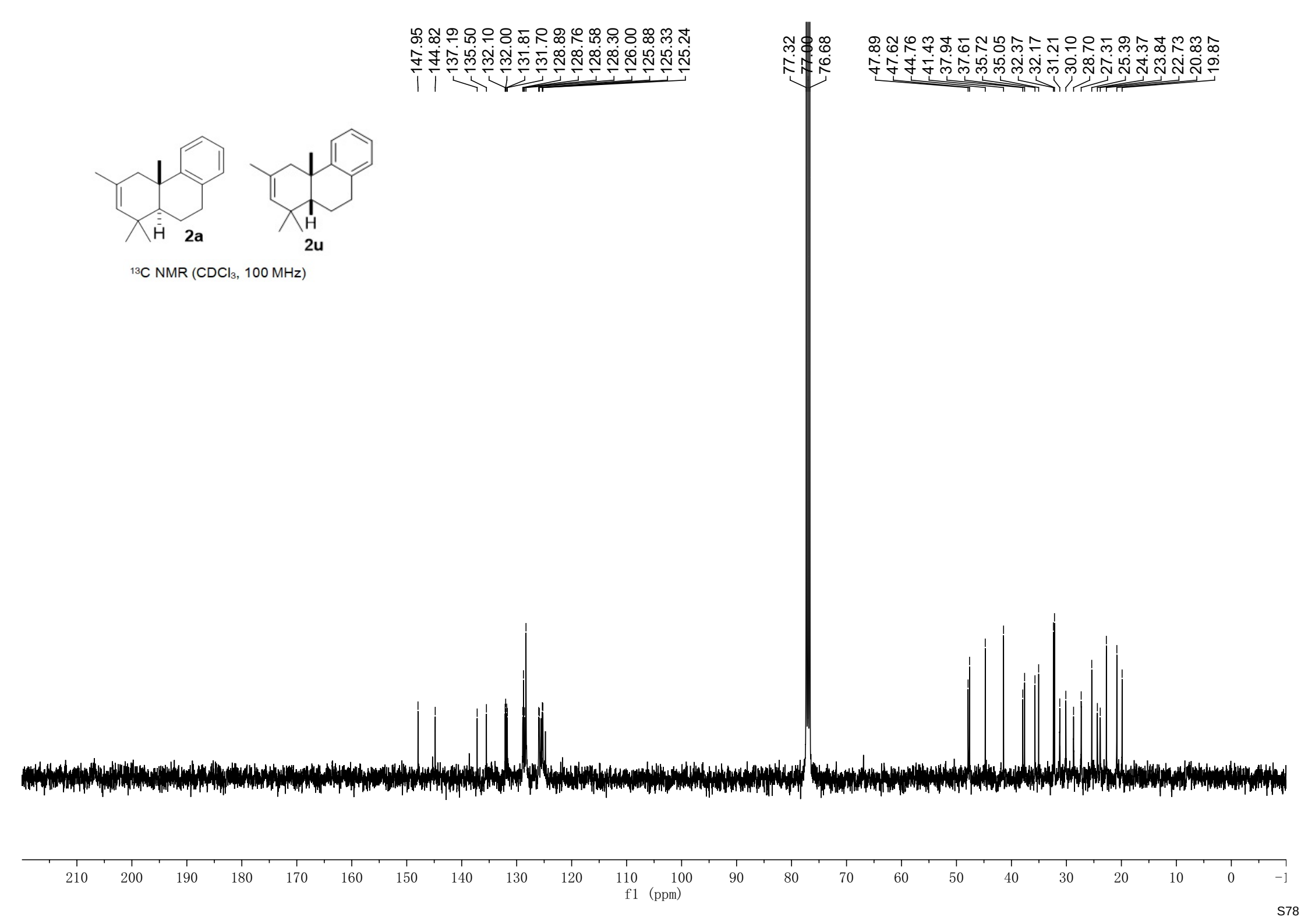

155.28
145.75
138.24
134.47
127.19
126.25
121.80
107.78
77.32
77.00
76.68
55.56
48.17
39.85
37.06
35.12
31.87
30.47
26.51
25.14
22.85
22.69
22.36
20.19
OMe
H
H
2s
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

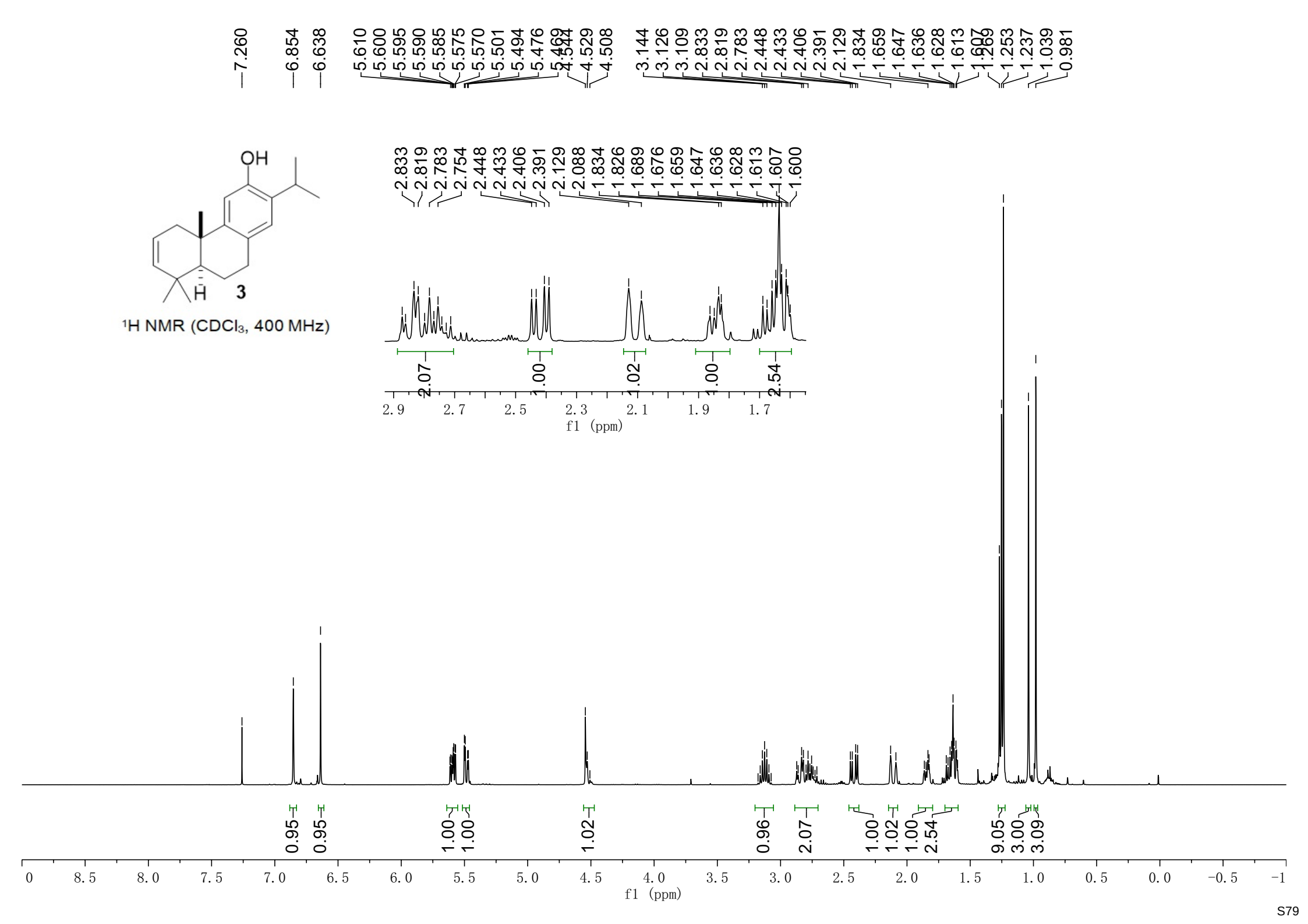


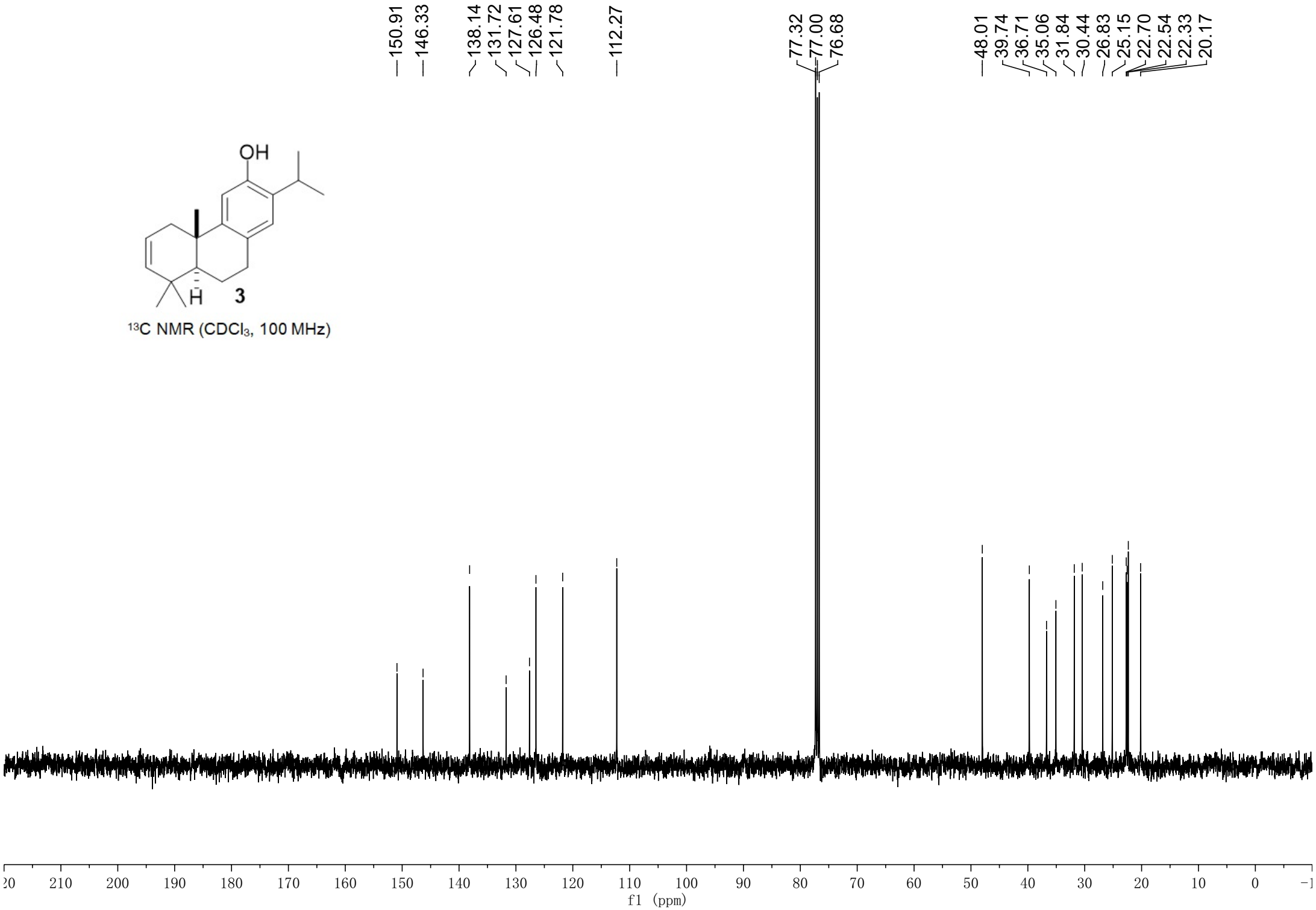
^{1}H NMR ($CDCl_3$, 400 MHz)

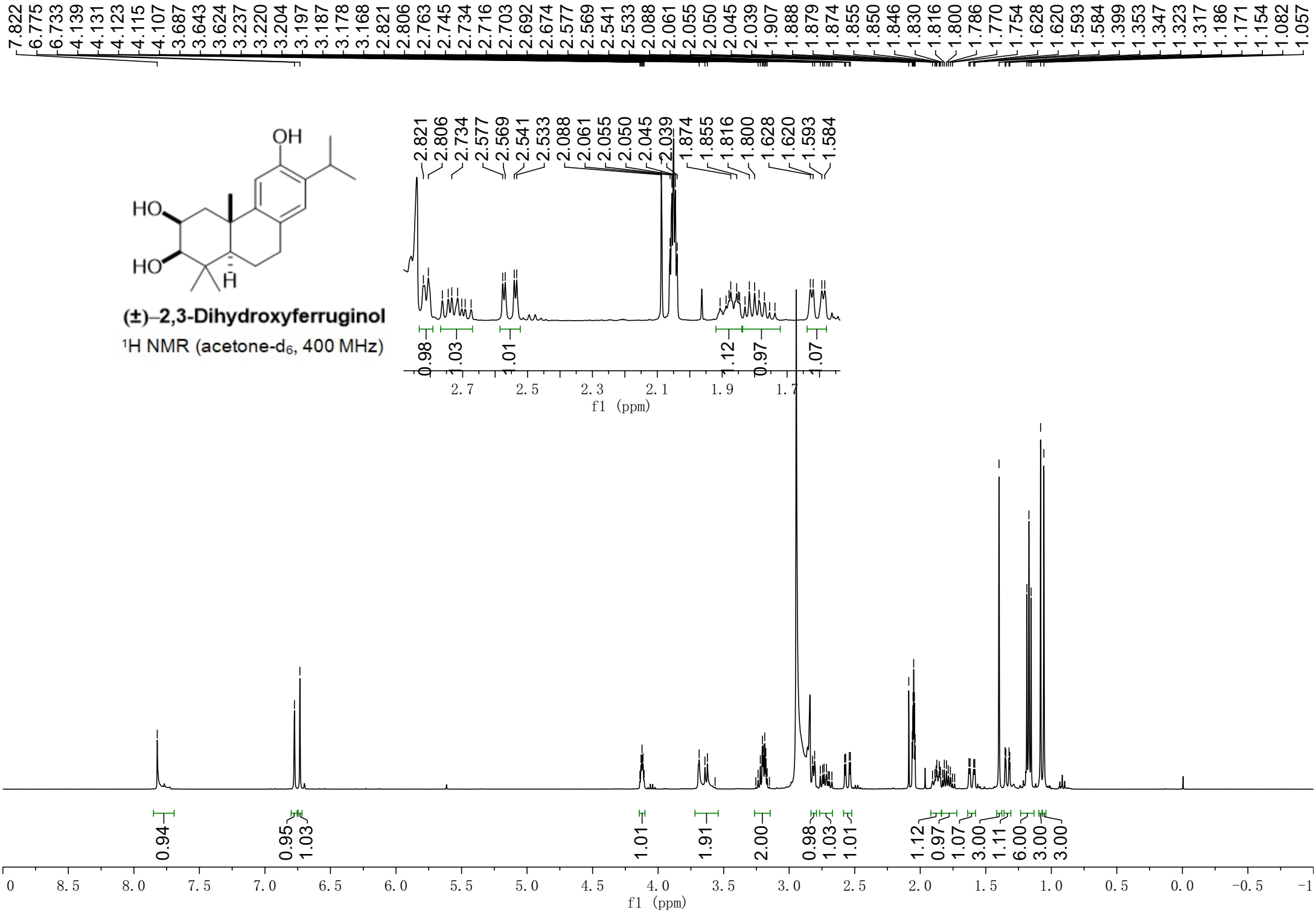

145.00
138.08
135.32
134.70
129.39
126.85
125.93
121.91
77.32
77.00
76.68
48.17
39.78
36.67
35.05
31.83
31.06
25.26
22.35
20.81
19.94
H
H
2t
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

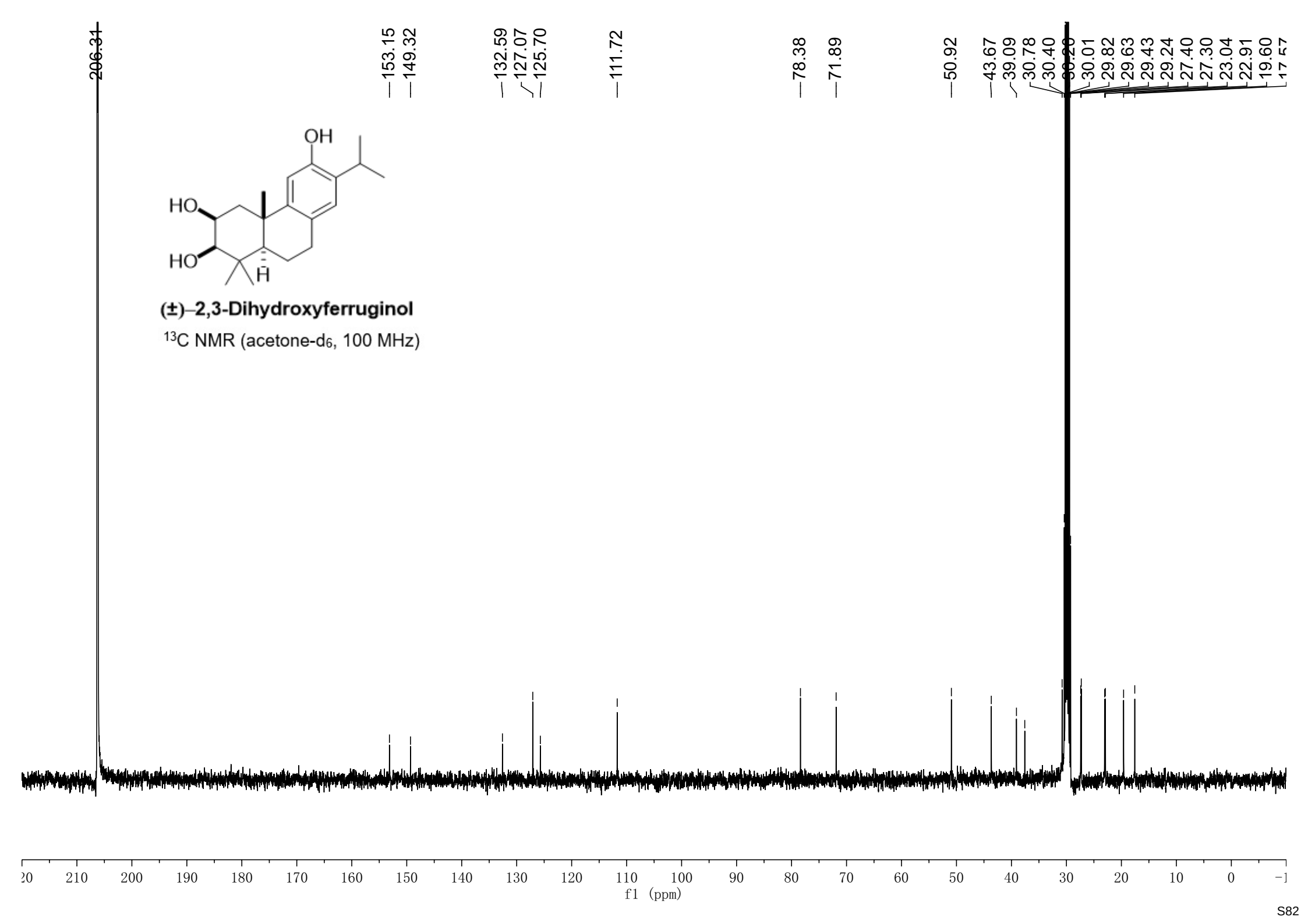

7.312
7.293
7.260
7.247
7.231
7.212
7.171
7.155
7.135
7.119
7.101
7.095
7.090
7.084
7.082
7.076
7.073
7.068
7.064
7.058
7.042
7.028
7.010
5.200
5.007
2.947
2.924
2.908
2.883
2.869
2.854
2.832
2.814
2.797
2.789
2.412
2.377
2.370
2.336
1.542
1.310
1.222
1.064
1.018
0.960
0.594
2a
2u
1H NMR (CDCl3, 400 MHz)
2.155
2.143
2.132
2.122
2.111
2.101
2.059
1.951
1.909
1.882
1.859
1.842
1.827
1.812
1.809
1.717
1.703
1.684
1.671
2.02
4.08
8.15
2.2
2.1
2.0
1.9
1.8
1.7
f1 (ppm)
1.01
7.08
1.00
1.02
4.05
2.04
2.02
4.08
8.15
3.11
3.41
3.08
2.92
3.44
2.97
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

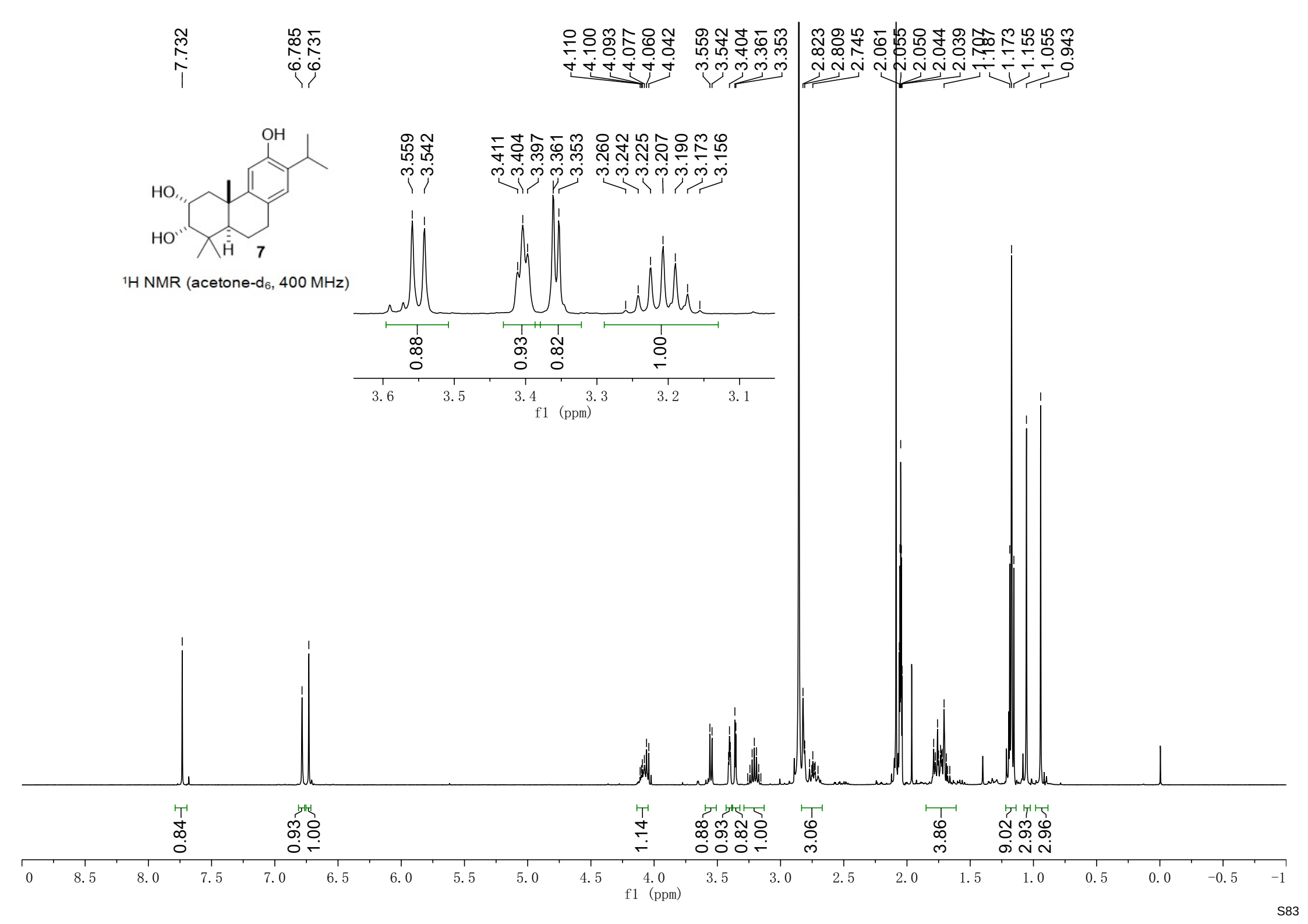

147.95
144.82
137.19
135.50
132.10
132.00
131.81
131.70
128.89
128.76
128.58
128.30
126.00
125.88
125.33
125.24
77.32
77.00
76.68
47.89
47.62
44.76
41.43
37.94
37.61
35.72
35.05
32.37
32.17
31.21
30.10
28.70
27.31
25.39
24.37
23.84
22.73
20.83
19.87
H
2a
H
2u
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

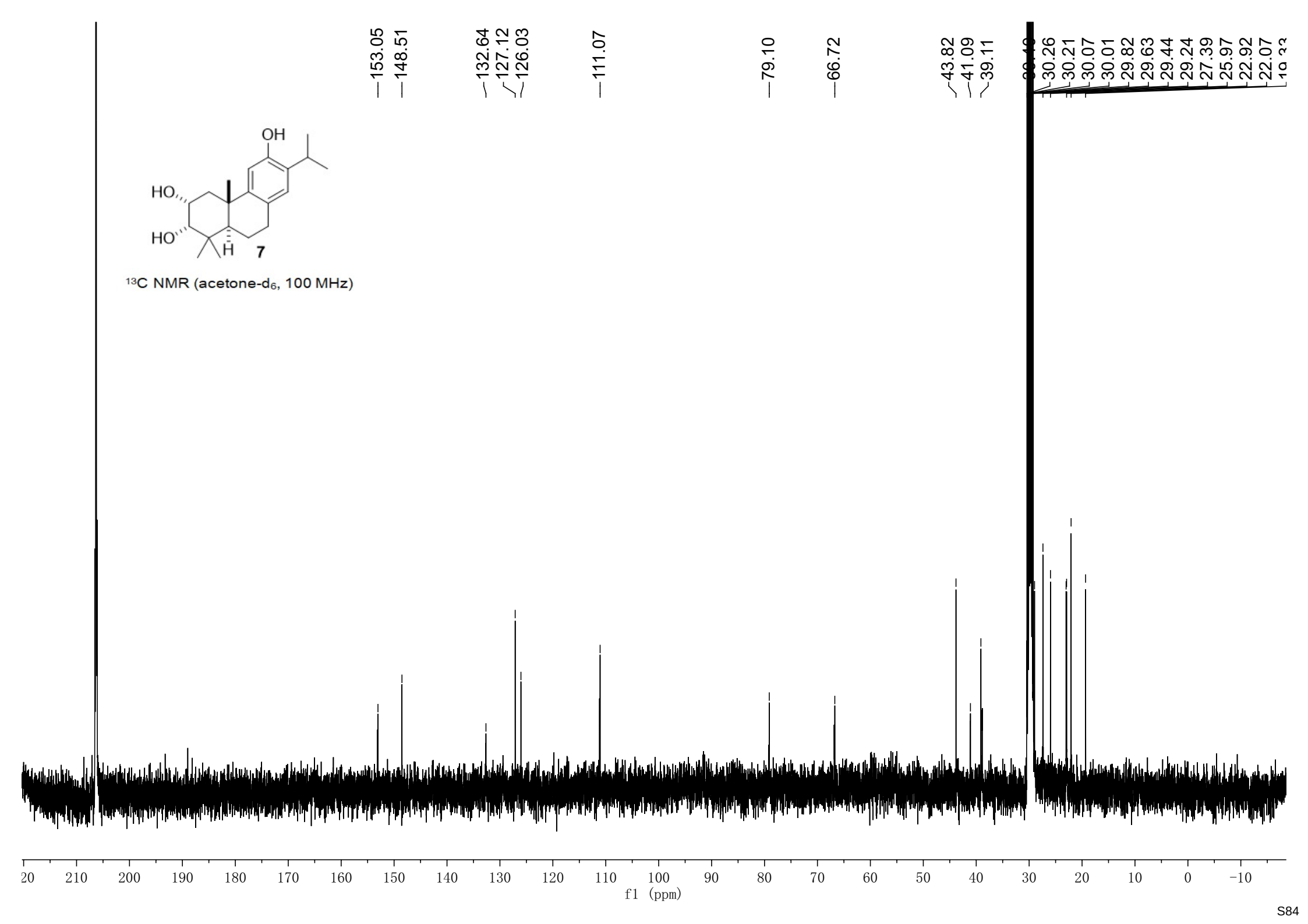

7.260
6.854
6.638
5.610
5.600
5.595
5.590
5.585
5.575
5.570
5.501
5.494
5.476
5.469
4.544
4.529
4.508
3.144
3.126
3.109
2.833
2.819
2.783
2.448
2.433
2.406
2.391
2.129
1.834
1.659
1.647
1.636
1.628
1.613
1.607
1.600
1.269
1.253
1.237
1.039
0.981
OH
H
3
1H NMR (CDCl3, 400 MHz)
2.833
2.819
2.783
2.754
2.448
2.433
2.406
2.391
2.129
2.088
1.834
1.826
1.689
1.676
1.659
1.647
1.636
1.628
1.613
1.607
1.600
2.07
1.00
1.02
1.00
2.54
2.9
2.7
2.5
2.3
2.1
1.9
1.7
f1 (ppm)
0.95
0.95
1.00
1.00
1.02
0.96
2.07
1.00
1.02
1.00
2.54
9.05
3.00
3.09
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

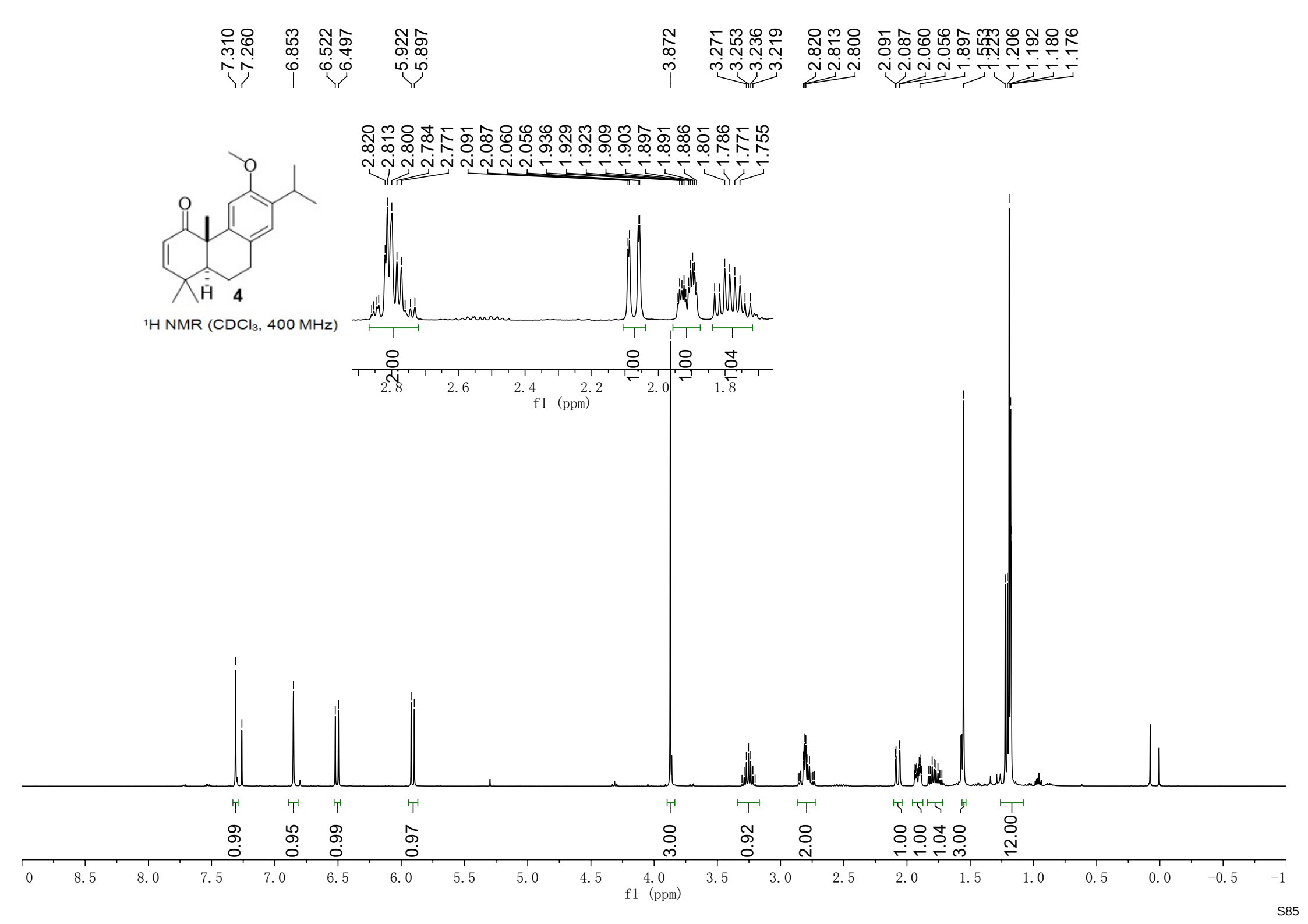

150.91
146.33
138.14
131.72
127.61
126.48
121.78
112.27
77.32
77.00
76.68
48.01
39.74
36.71
35.06
31.84
30.44
26.83
25.15
22.70
22.54
22.33
20.17
OH
H
3
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

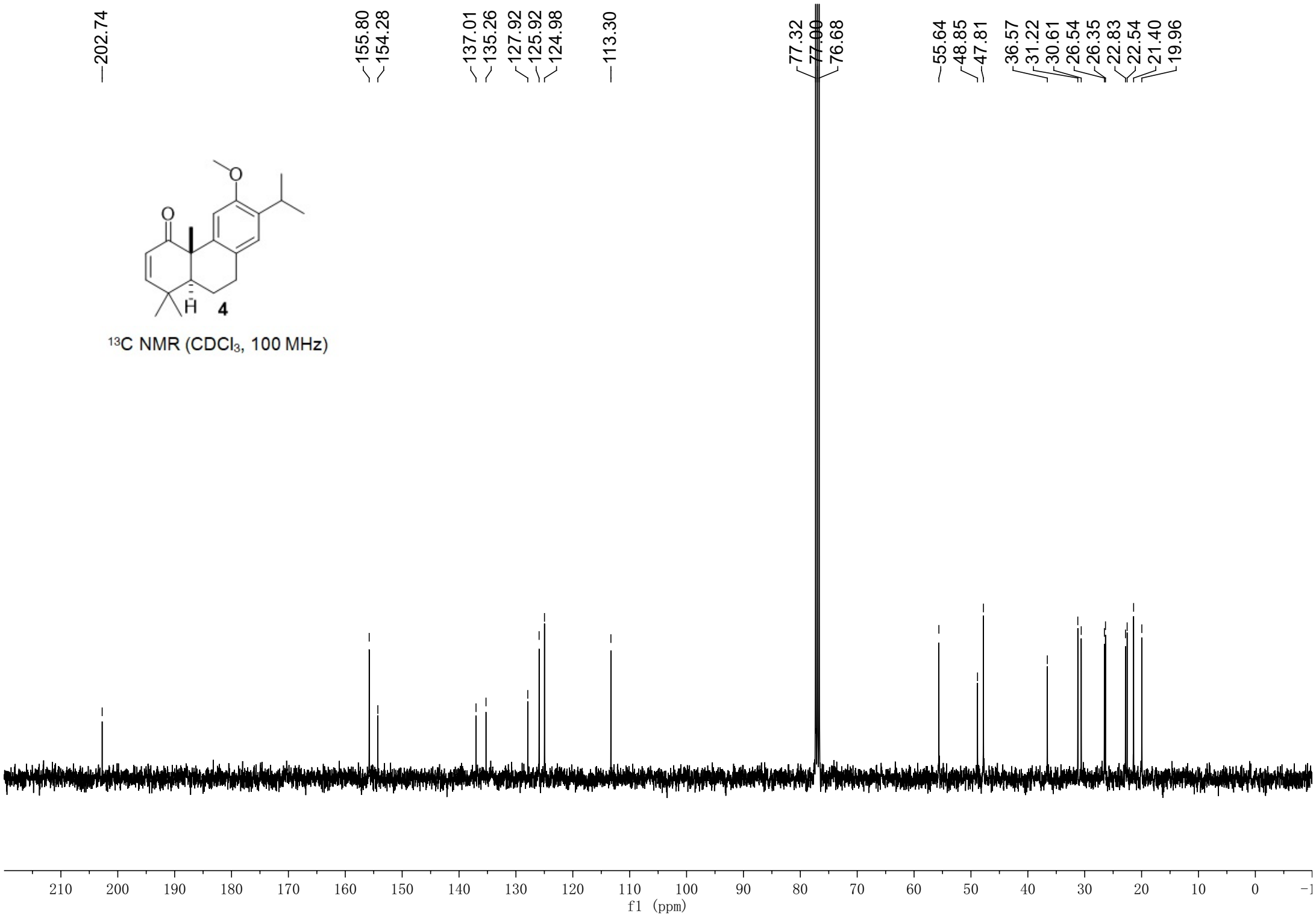

7.822 6.775 6.733 4.139 4.131 4.123 4.115 4.107 3.687 3.643 3.624 3.237 3.220 3.204 3.197 3.187 3.178 3.168 2.821 2.806 2.763 2.745 2.734 2.716 2.703 2.692 2.674 2.577 2.569 2.541 2.533 2.088 2.061 2.055 2.050 2.045 2.039 1.907 1.888 1.879 1.874 1.855 1.850 1.846 1.830 1.816 1.800 1.786 1.770 1.754 1.628 1.620 1.593 1.584 1.399 1.353 1.347 1.323 1.317 1.186 1.171 1.154 1.082 1.057
OH
HO
HO
H
(±)–2,3-Dihydroxyferruginol
1H NMR (acetone-d6, 400 MHz)
2.821 2.806 2.734 2.577 2.569 2.541 2.533 2.088 2.061 2.055 2.050 2.045 2.039 1.874 1.855 1.816 1.800 1.628 1.620 1.593 1.584
0.98 1.03 1.01 1.12 0.97 1.07
2.7 2.5 2.3 2.1 1.9 1.7
f1 (ppm)
0.94 0.95 1.03 1.01 1.91 2.00 0.98 1.03 1.01 1.12 0.97 1.07 3.00 1.11 6.00 3.00 3.00
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5 −1
f1 (ppm)

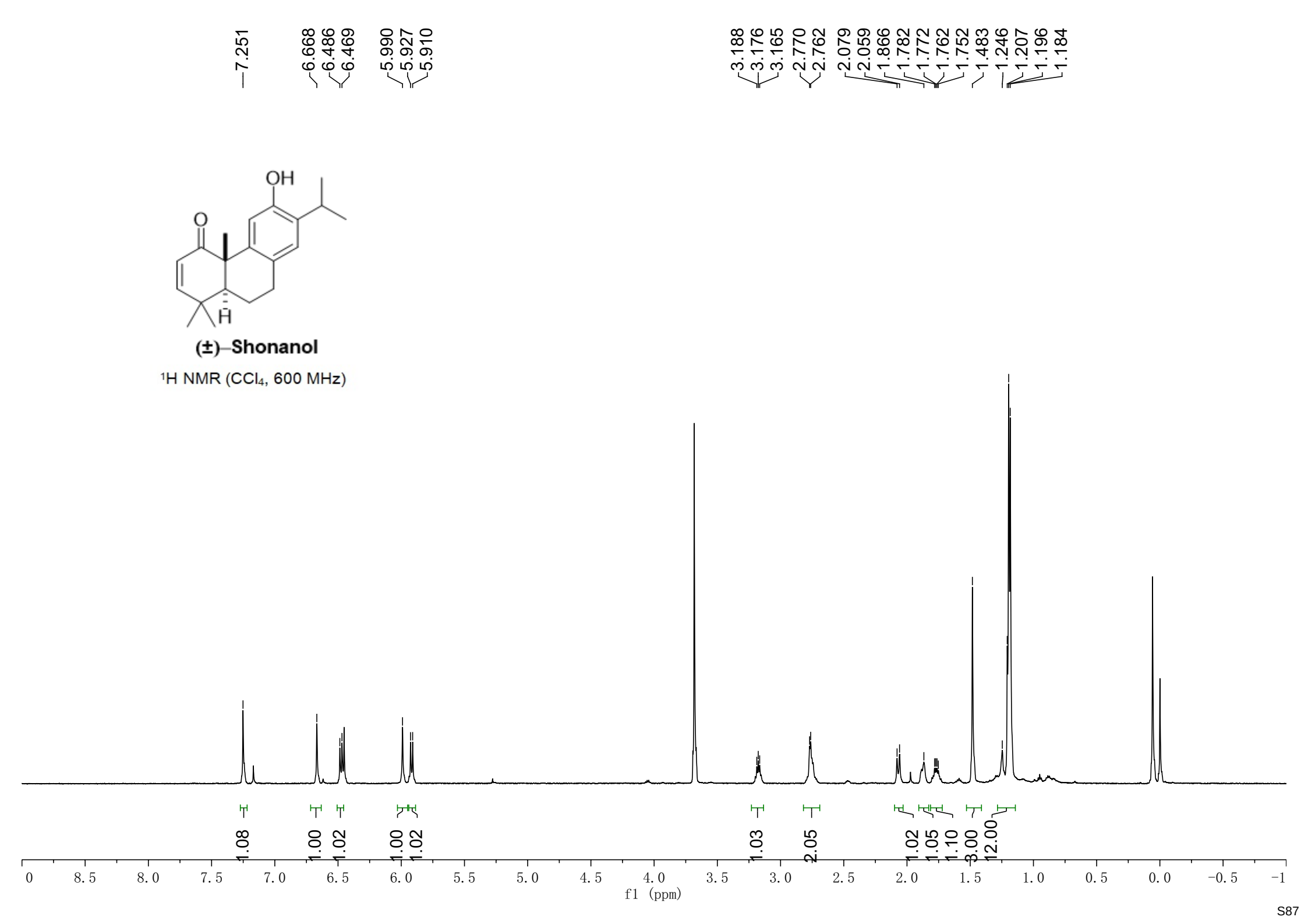

206.34
153.15
149.32
132.59
127.07
125.70
111.72
78.38
71.89
50.92
43.67
39.09
30.78
30.40
30.01
29.82
29.63
29.43
29.24
27.40
27.30
23.04
22.91
19.60
OH
HO
HO
H
(±)–2,3-Dihydroxyferruginol
13C NMR (acetone-d6, 100 MHz)
f1 (ppm)

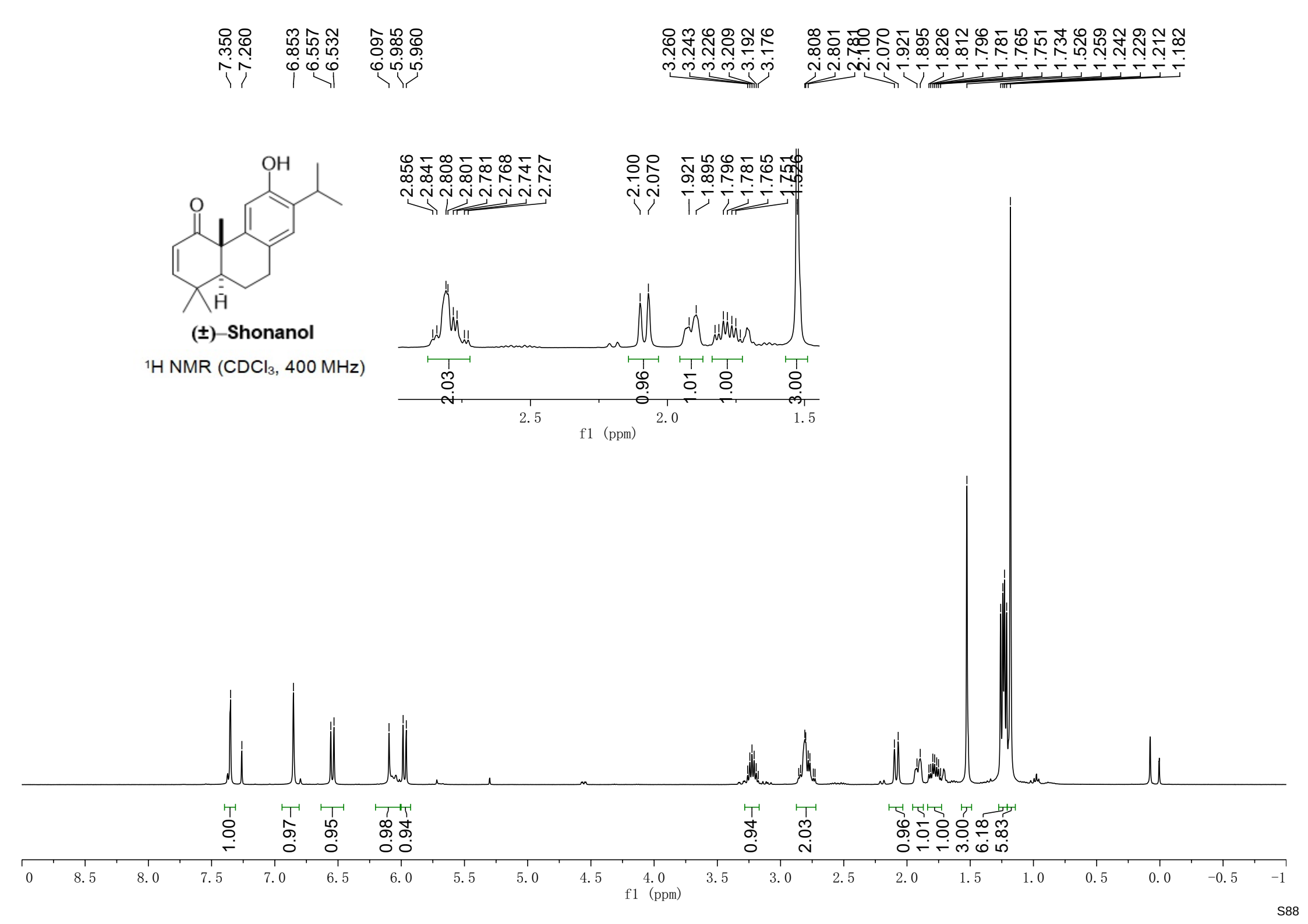

7.732
6.785
6.731
4.110
4.100
4.093
4.077
4.060
4.042
3.559
3.542
3.404
3.361
3.353
2.823
2.809
2.745
2.061
2.055
2.050
2.044
2.039
1.187
1.173
1.155
1.055
0.943
OH
HO
HO
H
7
1H NMR (acetone-d6, 400 MHz)
3.559
3.542
3.411
3.404
3.397
3.361
3.353
3.260
3.242
3.225
3.207
3.190
3.173
3.156
0.88
0.93
0.82
1.00
3.6
3.5
3.4
3.3
3.2
3.1
f1 (ppm)
0.84
0.93
1.00
1.14
0.88
0.93
0.82
1.00
3.06
3.86
9.02
2.93
2.96
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

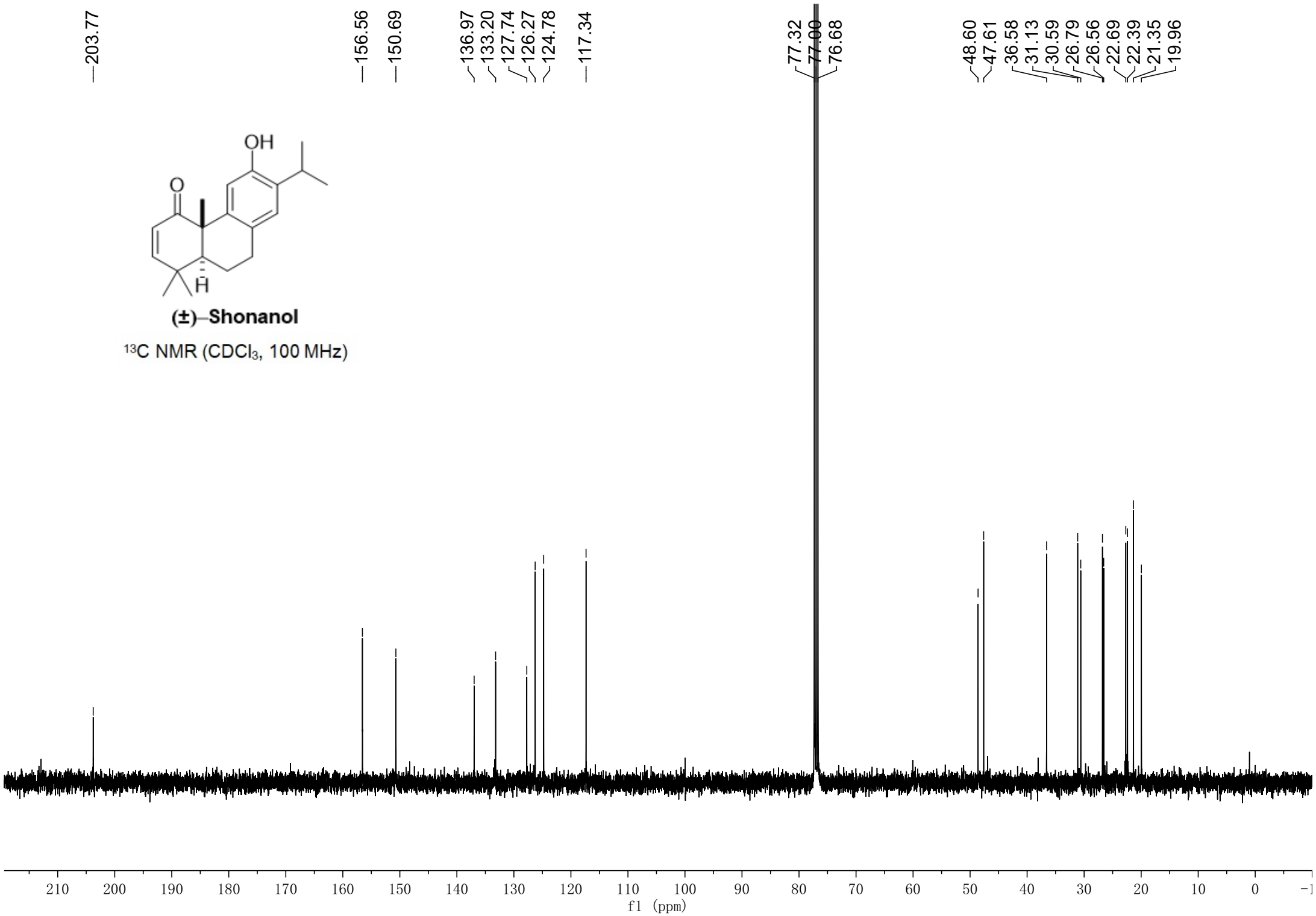

153.05
148.51
132.64
127.12
126.03
111.07
79.10
66.72
43.82
41.09
39.11
30.26
30.21
30.07
30.01
29.82
29.63
29.44
29.24
27.39
25.97
22.92
22.07
OH
HO
HO
H
7
13C NMR (acetone-d6, 100 MHz)
f1 (ppm)

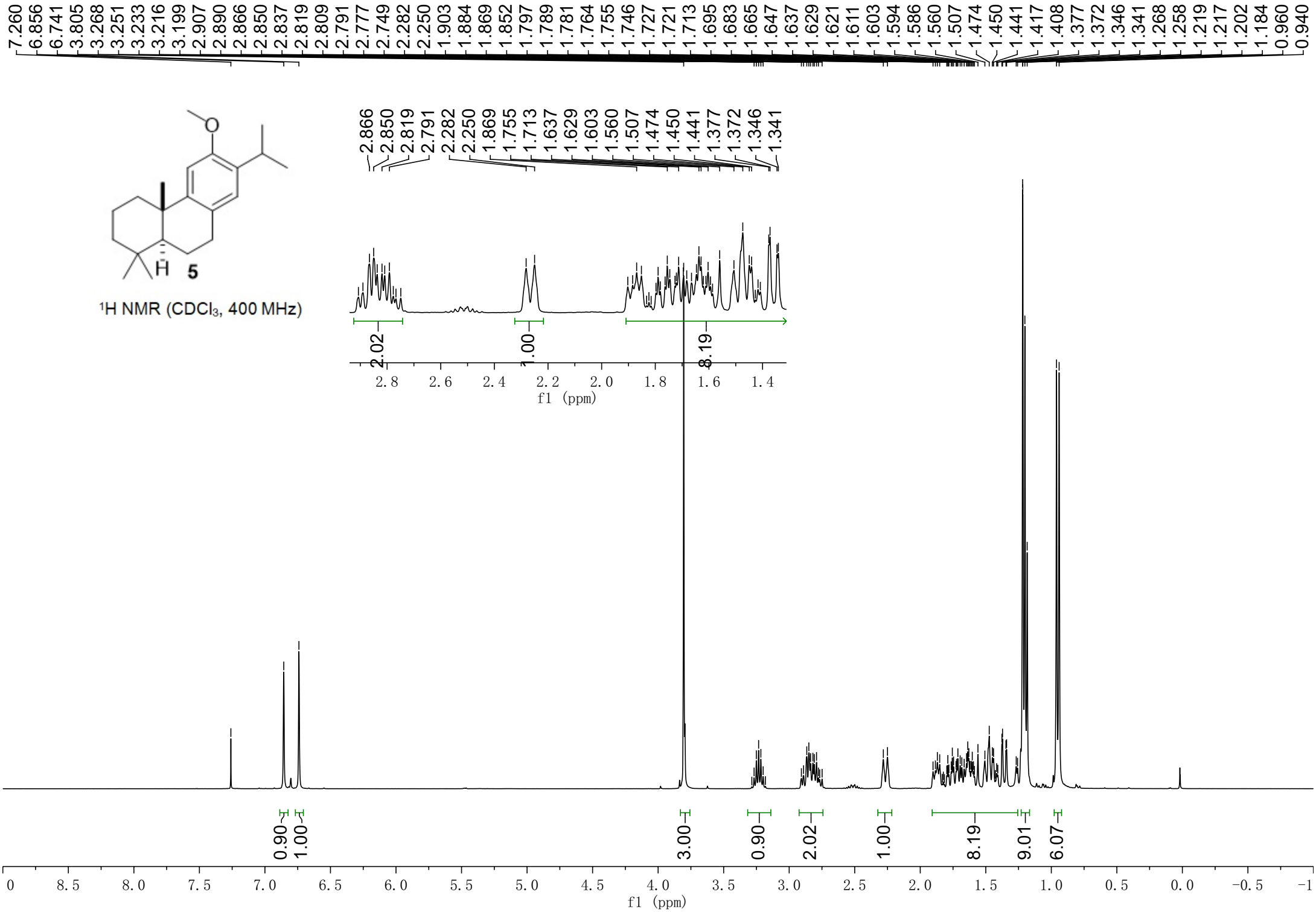

7.310
7.260
6.853
6.522
6.497
5.922
5.897
3.872
3.271
3.253
3.236
3.219
2.820
2.813
2.800
2.091
2.087
2.060
2.056
1.897
1.553
1.223
1.206
1.192
1.180
1.176
2.820
2.813
2.800
2.784
2.771
2.091
2.087
2.060
2.056
1.936
1.929
1.923
1.909
1.903
1.897
1.891
1.886
1.801
1.786
1.771
1.755
O
O
H
4
¹H NMR (CDCl₃, 400 MHz)
2.00
1.00
1.00
1.04
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)
0.99
0.95
0.99
0.97
3.00
0.92
2.00
1.00
1.00
1.04
3.00
12.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

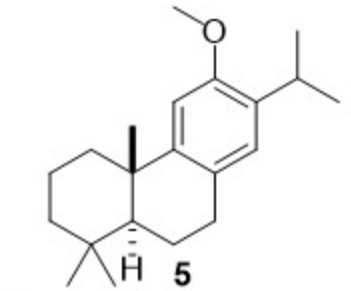

202.74
155.80
154.28
137.01
135.26
127.92
125.92
124.98
113.30
77.32
77.00
76.68
55.64
48.85
47.81
36.57
31.22
30.61
26.54
26.35
22.83
22.54
21.40
19.96
O
O
H
4
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.251
6.668
6.486
6.469
5.990
5.927
5.910
3.188
3.176
3.165
2.770
2.762
2.079
2.059
1.866
1.782
1.772
1.762
1.752
1.483
1.246
1.207
1.196
1.184
OH
O
H
(±)–Shonanol
¹H NMR (CCl₄, 600 MHz)
1.08
1.00
1.02
1.00
1.02
1.03
2.05
1.02
1.05
1.10
3.00
12.00
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


7.350
7.260
6.853
6.557
6.532
6.097
5.985
5.960
3.260
3.243
3.226
3.209
3.192
3.176
2.808
2.801
2.781
2.100
2.070
1.921
1.895
1.826
1.812
1.796
1.781
1.765
1.751
1.734
1.526
1.259
1.242
1.229
1.212
1.182
OH
O
H
(±)–Shonanol
1H NMR (CDCl3, 400 MHz)
2.856
2.841
2.808
2.801
2.781
2.768
2.741
2.727
2.100
2.070
1.921
1.895
1.796
1.781
1.765
1.751
1.526
2.03
0.96
1.01
1.00
3.00
2.5
2.0
1.5
f1 (ppm)
1.00
0.97
0.95
0.98
0.94
0.94
2.03
0.96
1.01
1.00
3.00
6.18
5.83
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


203.77
156.56
150.69
136.97
133.20
127.74
126.27
124.78
117.34
77.32
77.00
76.68
48.60
47.61
36.58
31.13
30.59
26.79
26.56
22.69
22.39
21.35
19.96
OH
O
H
(±)–Shonanol
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260 6.856 6.741 3.805 3.268 3.251 3.233 3.216 3.199 2.907 2.890 2.866 2.850 2.837 2.819 2.809 2.791 2.777 2.749 2.282 2.250 1.903 1.884 1.869 1.852 1.797 1.789 1.781 1.764 1.755 1.746 1.727 1.721 1.713 1.695 1.683 1.665 1.647 1.637 1.629 1.621 1.611 1.603 1.594 1.586 1.560 1.507 1.474 1.450 1.441 1.417 1.408 1.377 1.372 1.346 1.341 1.268 1.258 1.219 1.217 1.202 1.184 0.960 0.940
O
H
5
1H NMR (CDCl3, 400 MHz)
2.866 2.850 2.819 2.791 2.282 2.250 1.869 1.755 1.713 1.637 1.629 1.603 1.560 1.507 1.474 1.450 1.441 1.377 1.372 1.346 1.341
2.02
1.00
8.19
2.8 2.6 2.4 2.2 2.0 1.8 1.6 1.4
f1 (ppm)
0.90
1.00
3.00
0.90
2.02
1.00
8.19
9.01
6.07
0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)



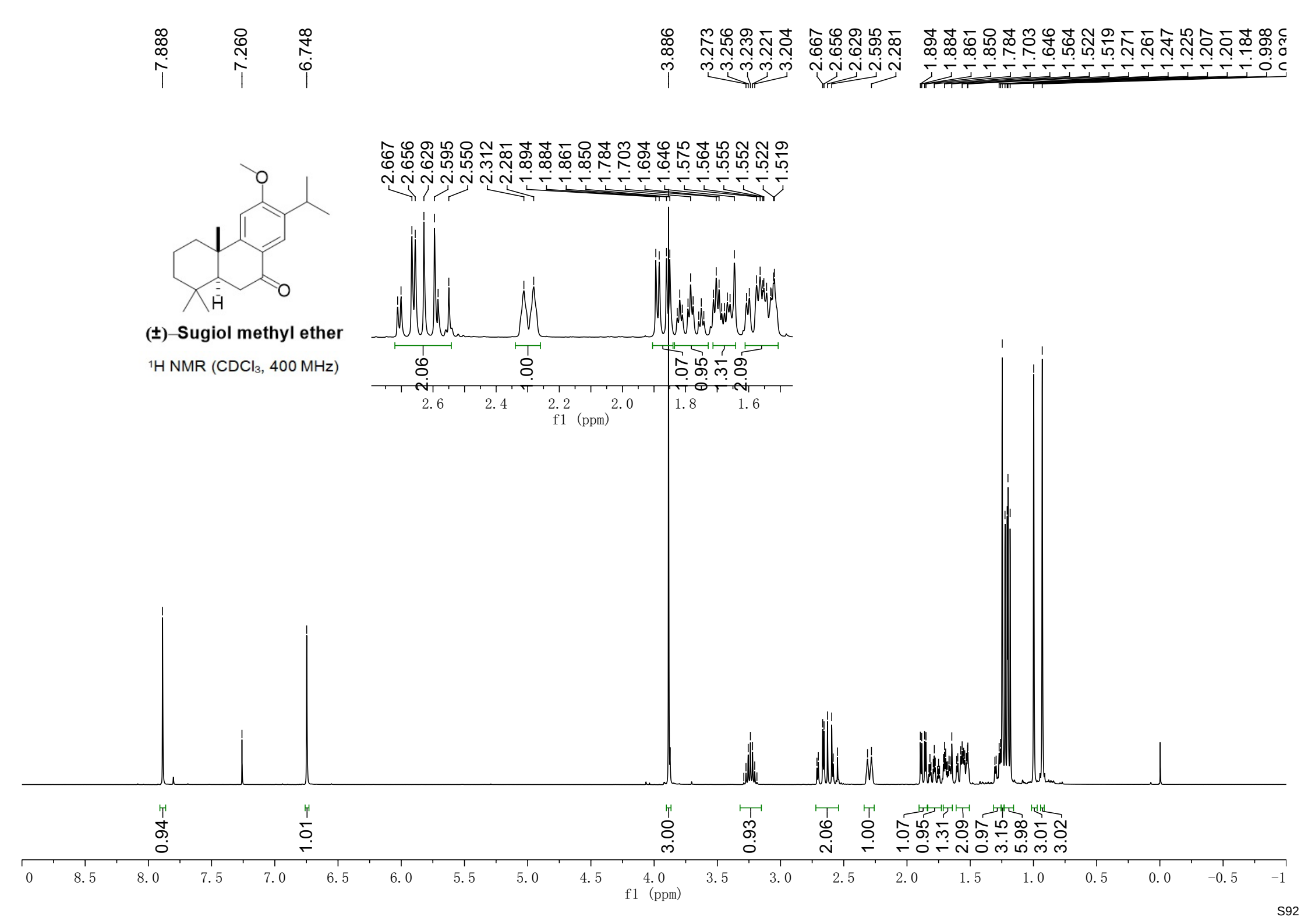
5

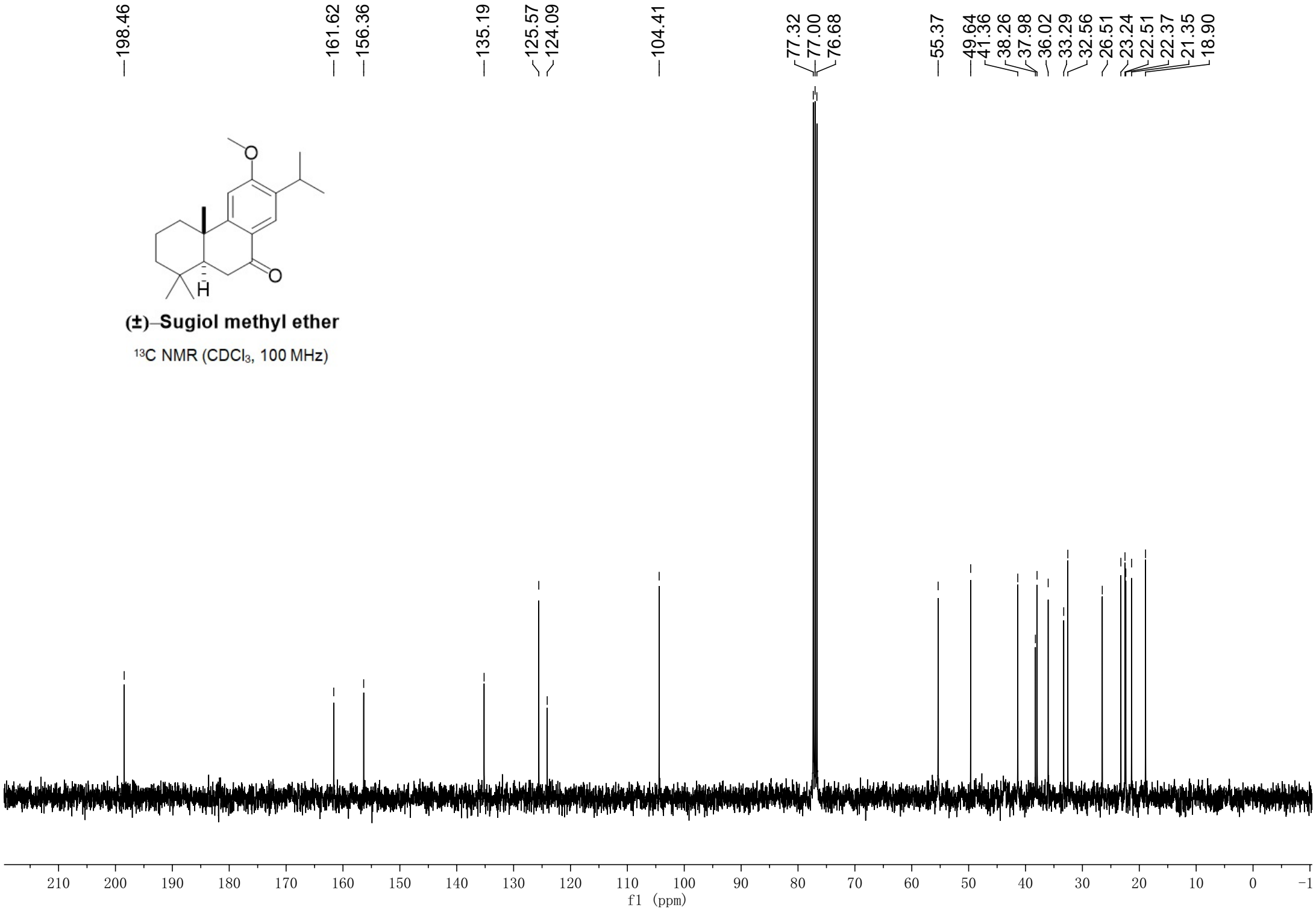
^{13}C NMR ($CDCl_3$, 100 MHz)

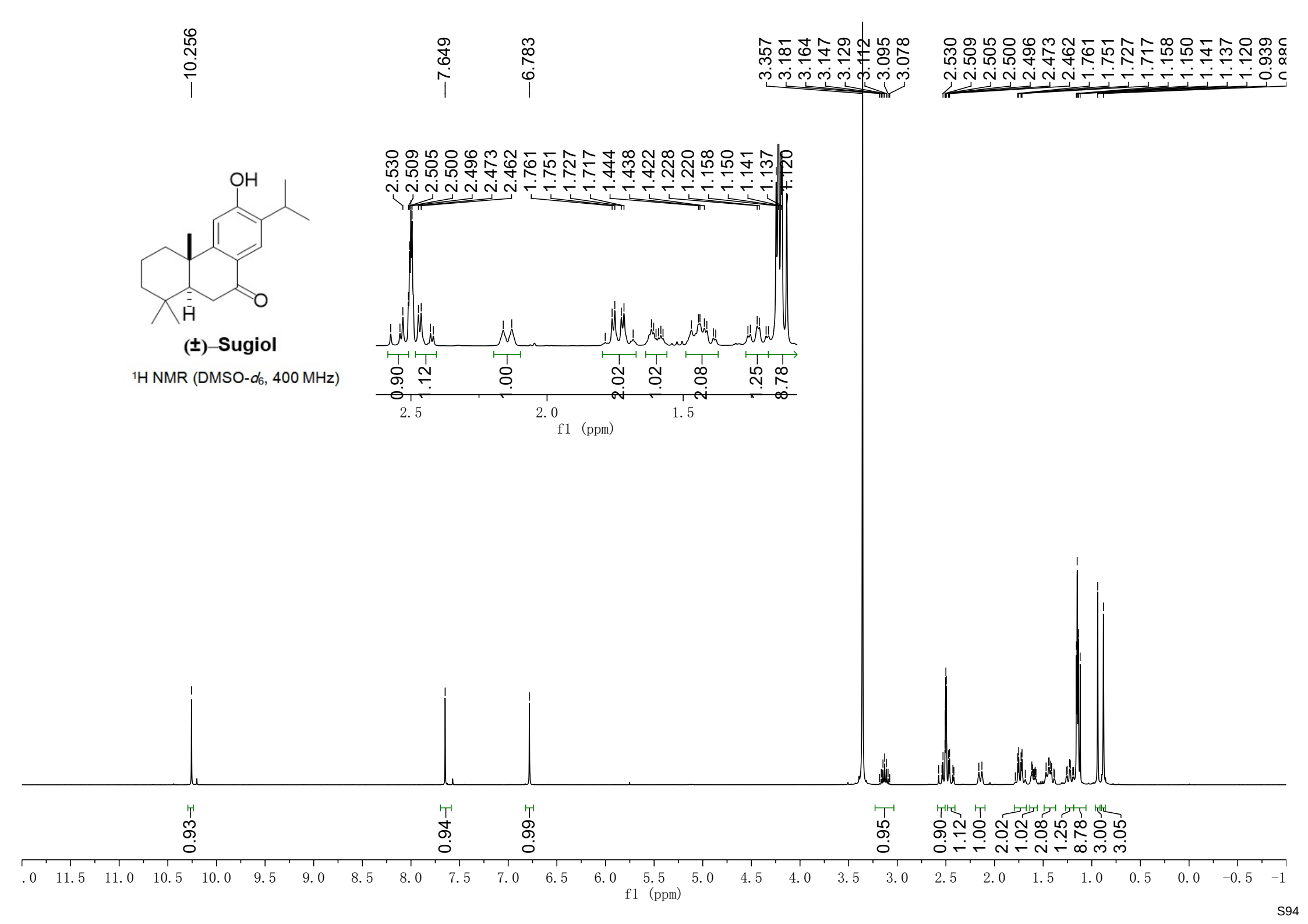
154.97
148.06
134.10
126.86
126.36
106.53
77.32
77.00
76.68
55.56
50.47
41.69
38.91
37.83
33.45
33.33
29.82
26.42
24.81
22.89
22.68
21.62
19.34
19.22

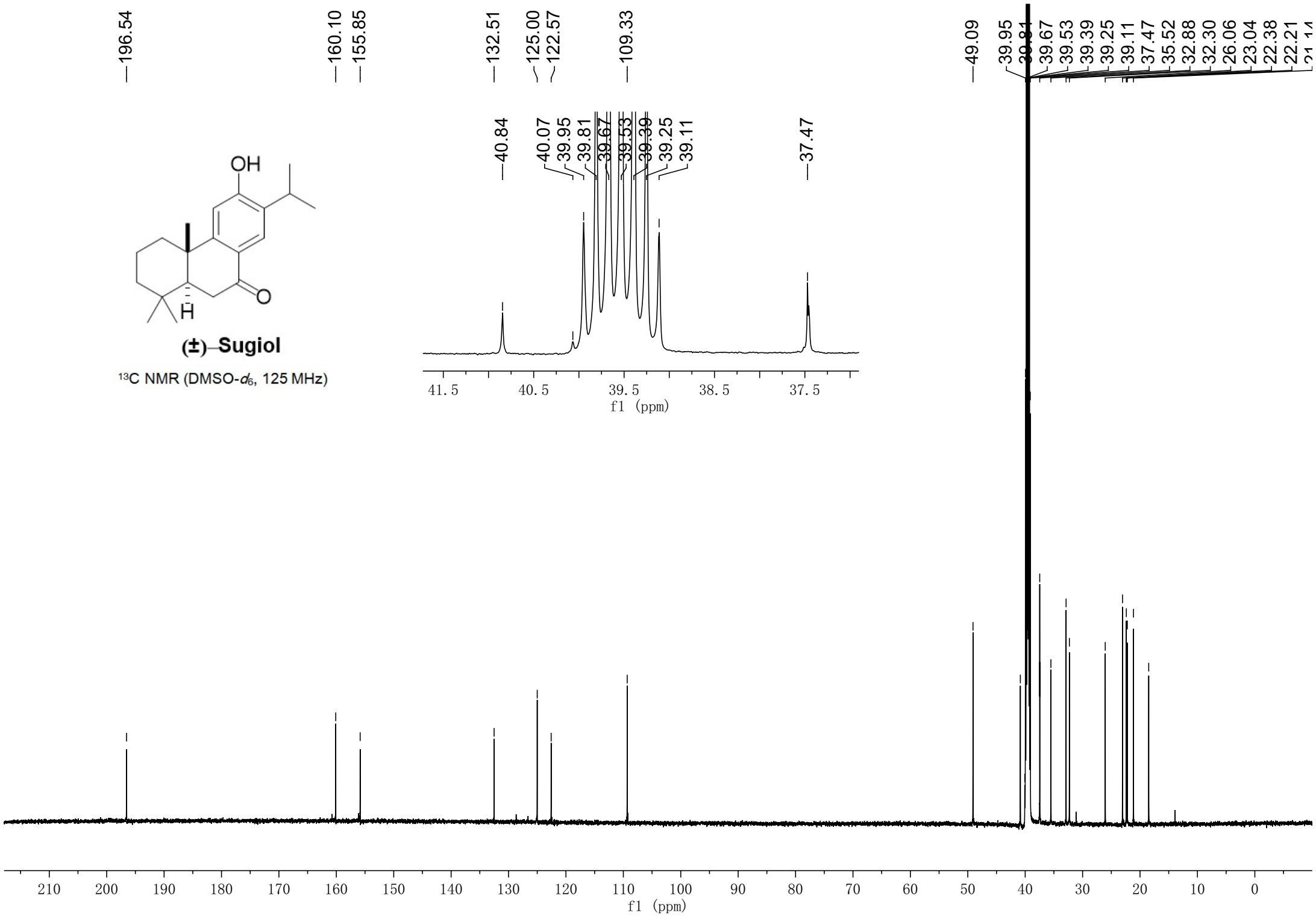
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1

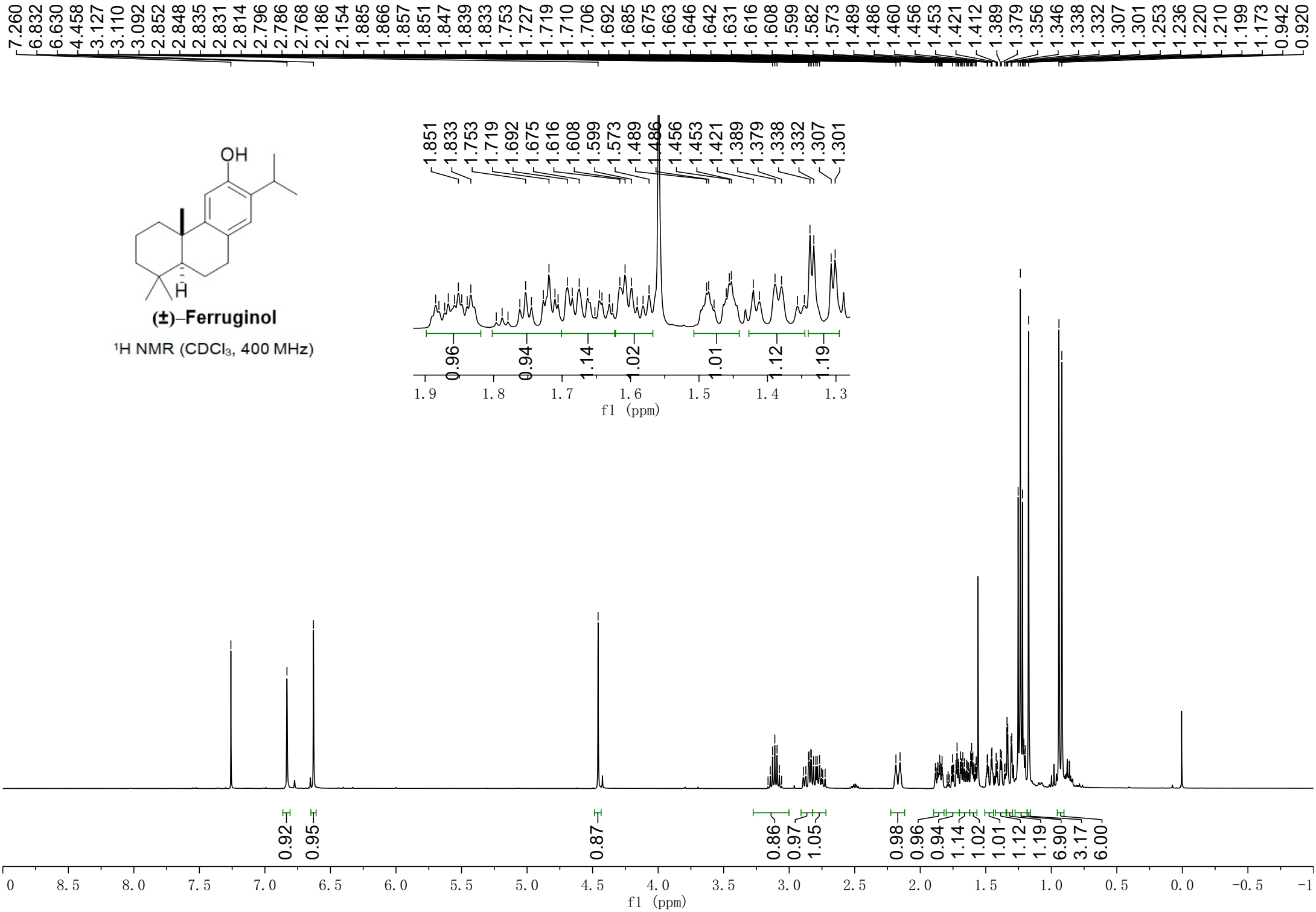
f1 (ppm)

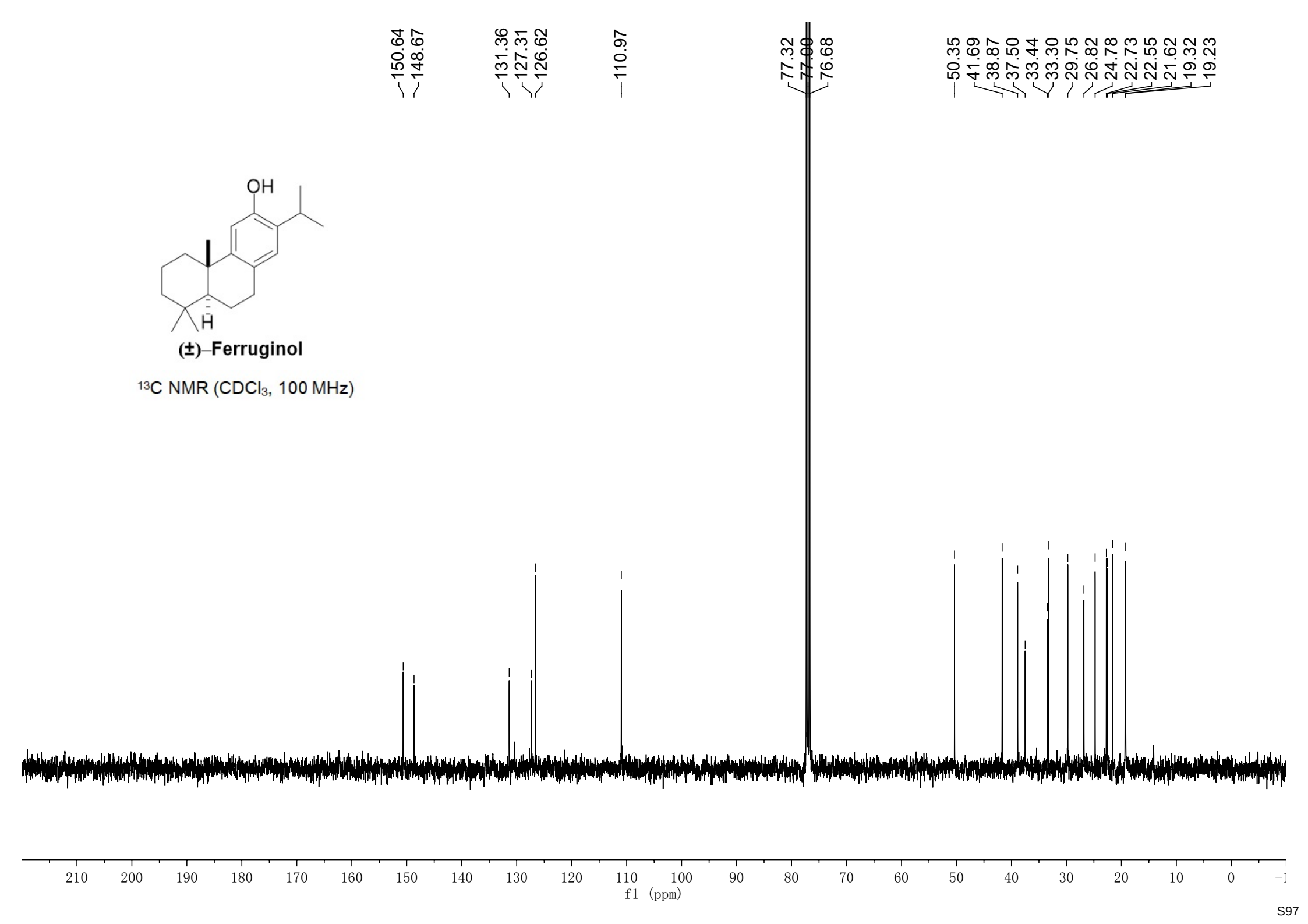

7.888
7.260
6.748
3.886
3.273
3.256
3.239
3.221
3.204
2.667
2.656
2.629
2.595
2.281
1.894
1.884
1.861
1.850
1.784
1.703
1.646
1.564
1.522
1.519
1.271
1.261
1.247
1.225
1.207
1.201
1.184
0.998
(±)–Sugiol methyl ether
¹H NMR (CDCl₃, 400 MHz)
2.667
2.656
2.629
2.595
2.550
2.312
2.281
1.894
1.884
1.861
1.850
1.784
1.703
1.694
1.646
1.575
1.564
1.555
1.552
1.522
1.519
2.06
1.00
1.07
0.95
1.31
2.09
2.6
2.4
2.2
2.0
1.8
1.6
f1 (ppm)
0.94
1.01
3.00
0.93
2.06
1.00
1.07
0.95
1.31
2.09
0.97
3.15
5.98
3.01
3.02
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

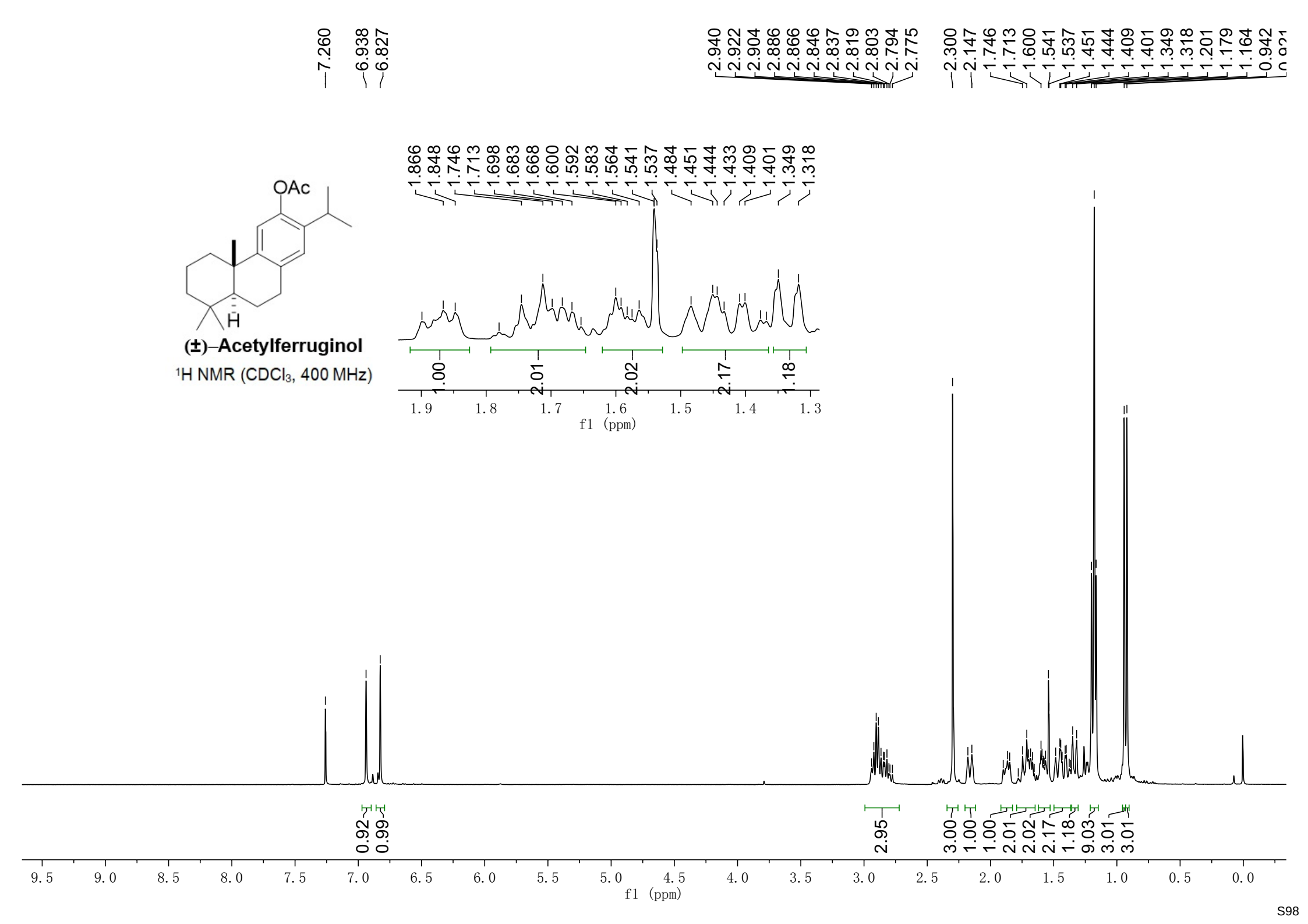

198.46
161.62
156.36
135.19
125.57
124.09
104.41
77.32
77.00
76.68
55.37
49.64
41.36
38.26
37.98
36.02
33.29
32.56
26.51
23.24
22.51
22.37
21.35
18.90
O
O
H
(±)–Sugiol methyl ether
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−1
f1 (ppm)

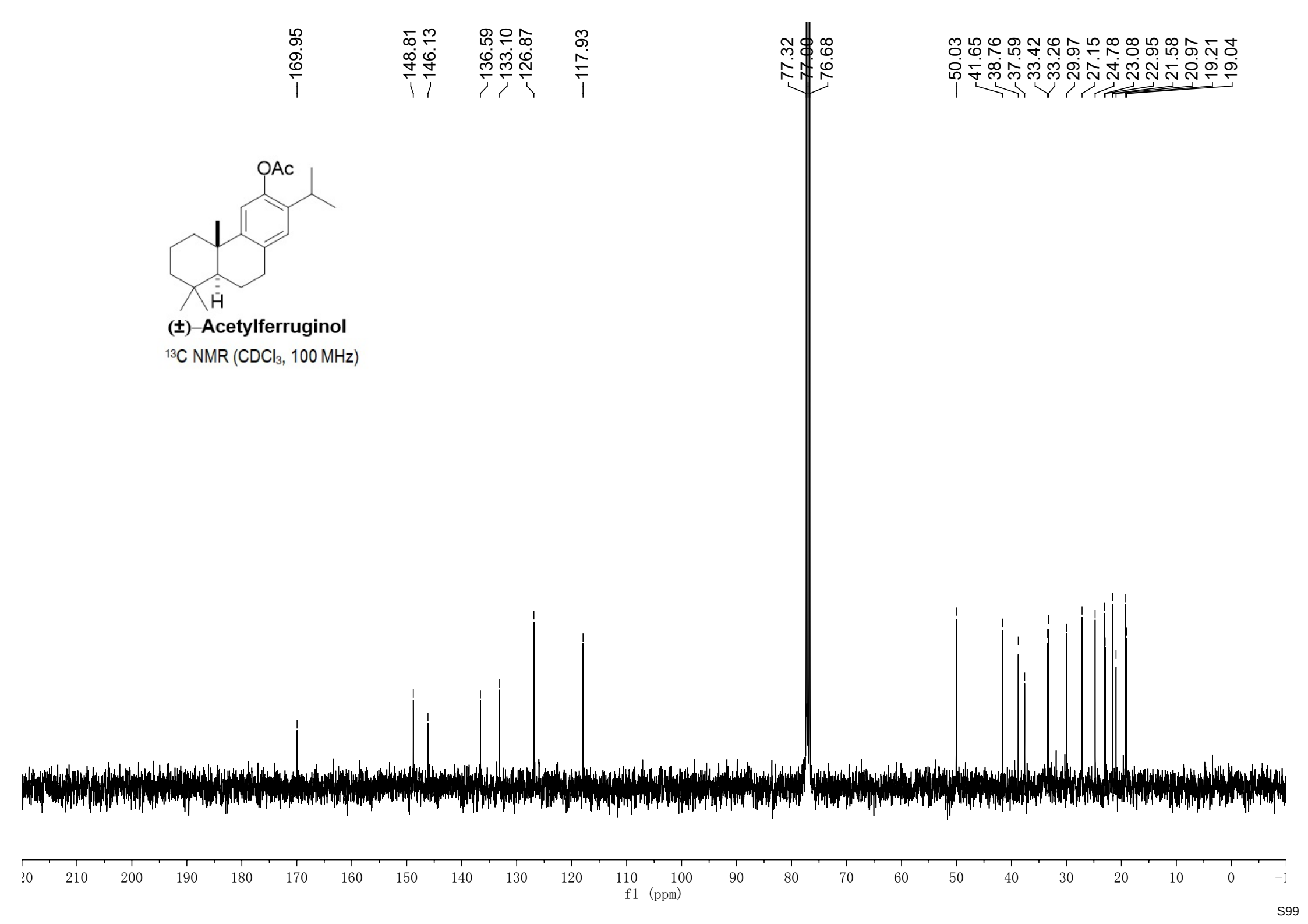

OH
O
H
(±)–Sugiol
¹H NMR (DMSO-d6, 400 MHz)
10.256
7.649
6.783
3.357
3.181
3.164
3.147
3.129
3.112
3.095
3.078
2.530
2.509
2.505
2.500
2.496
2.473
2.462
1.761
1.751
1.727
1.717
1.158
1.150
1.141
1.137
1.120
0.939
2.530
2.509
2.505
2.500
2.496
2.473
2.462
1.761
1.751
1.727
1.717
1.444
1.438
1.422
1.228
1.220
1.158
1.150
1.141
1.137
1.120
0.90
1.12
1.00
2.02
1.02
2.08
1.25
8.78
2.5
2.0
1.5
f1 (ppm)
0.93
0.94
0.99
0.95
0.90
1.12
1.00
2.02
1.02
2.08
1.25
8.78
3.00
3.05
f1 (ppm)

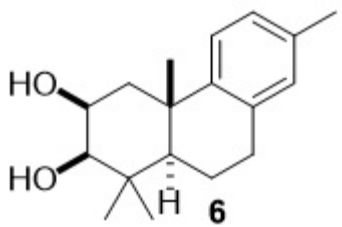

196.54
160.10
155.85
132.51
125.00
122.57
109.33
49.09
39.95
39.67
39.53
39.39
39.25
39.11
37.47
35.52
32.88
32.30
26.06
23.04
22.38
22.21
40.84
40.07
39.95
39.81
39.67
39.53
39.39
39.25
39.11
37.47
OH
O
H
(±)–Sugiol
13C NMR (DMSO-d6, 125 MHz)
41.5
40.5
39.5
38.5
37.5
f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


OH
H
(±)–Ferruginol
¹H NMR (CDCl₃, 400 MHz)
f1 (ppm)


150.64
148.67
131.36
127.31
126.62
110.97
77.32
77.00
76.68
50.35
41.69
38.87
37.50
33.44
33.30
29.75
26.82
24.78
22.73
22.55
21.62
19.32
19.23
OH
H
(±)–Ferruginol
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

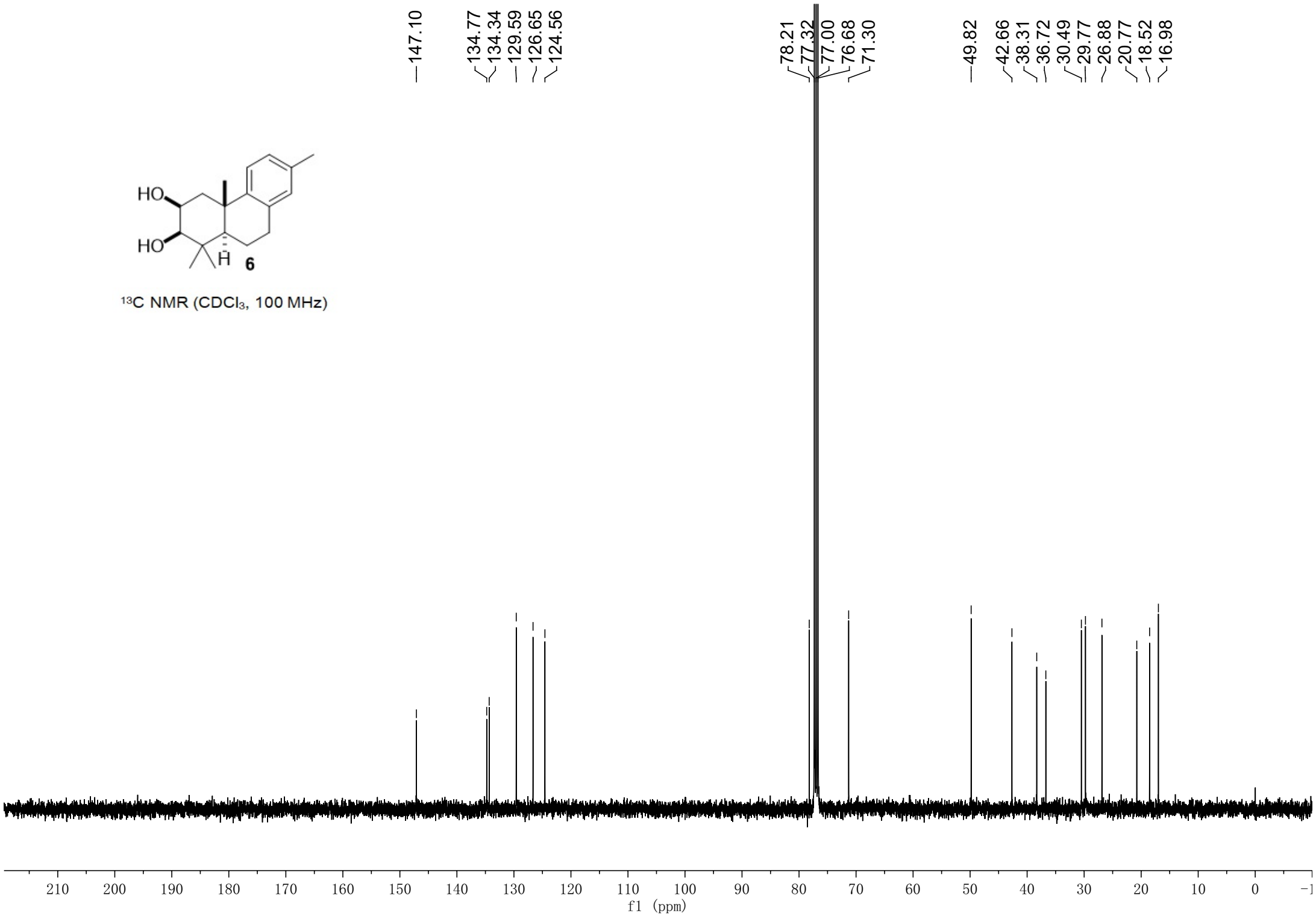

7.260
6.938
6.827
2.940
2.922
2.904
2.886
2.866
2.846
2.837
2.819
2.803
2.794
2.775
2.300
2.147
1.746
1.713
1.600
1.541
1.537
1.451
1.444
1.409
1.401
1.349
1.318
1.201
1.179
1.164
0.942
OAc
H
(±)–Acetylferruginol
¹H NMR (CDCl₃, 400 MHz)
1.866
1.848
1.746
1.713
1.698
1.683
1.668
1.600
1.592
1.583
1.564
1.541
1.537
1.484
1.451
1.444
1.433
1.409
1.401
1.349
1.318
1.00
2.01
2.02
2.17
1.18
1.9
1.8
1.7
1.6
1.5
1.4
1.3
f1 (ppm)
0.92
0.99
2.95
3.00
1.00
1.00
2.01
2.02
2.17
1.18
9.03
3.01
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

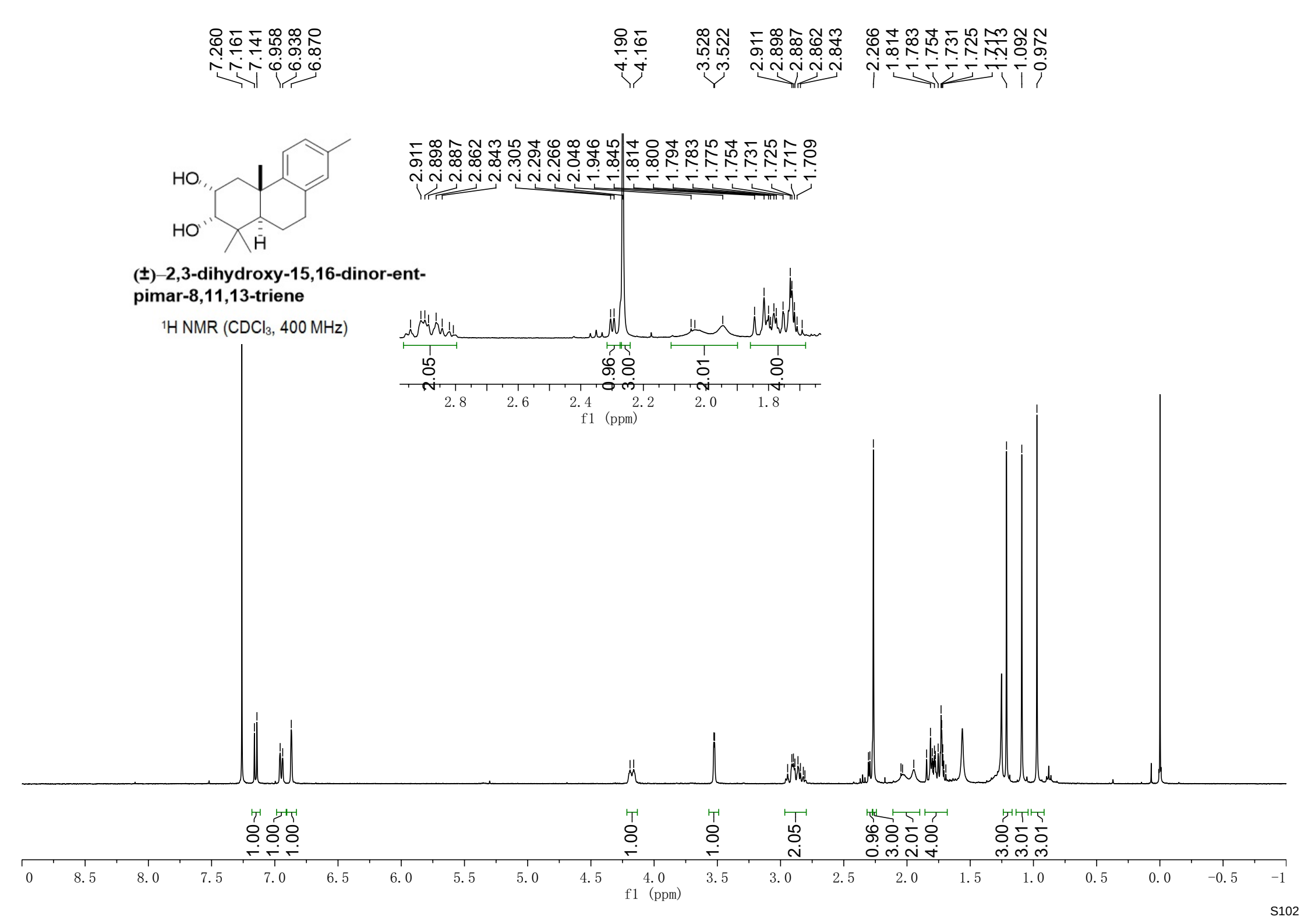

169.95
148.81
146.13
136.59
133.10
126.87
117.93
77.32
77.00
76.68
50.03
41.65
38.76
37.59
33.42
33.26
29.97
27.15
24.78
23.08
22.95
21.58
20.97
19.21
19.04
OAc
H
(±)–Acetylferruginol
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

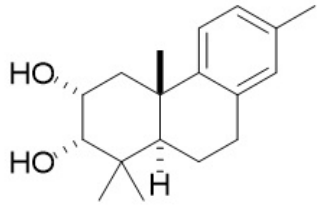


6

^{1}H NMR ($CDCl_3$, 400 MHz)

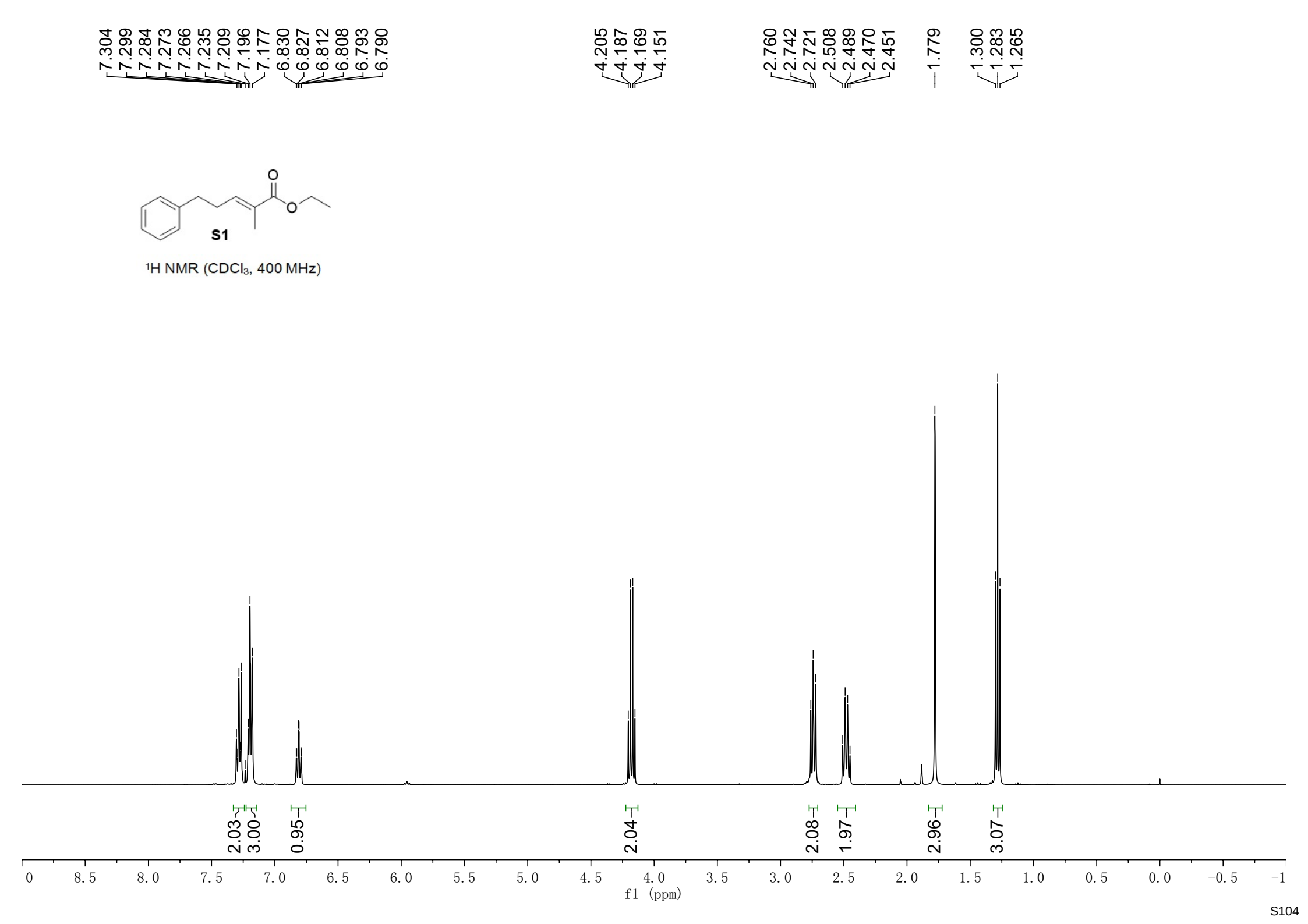

147.10
134.77
134.34
129.59
126.65
124.56
78.21
77.32
77.00
76.68
71.30
49.82
42.66
38.31
36.72
30.49
29.77
26.88
20.77
18.52
16.98
HO
HO
H
6
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

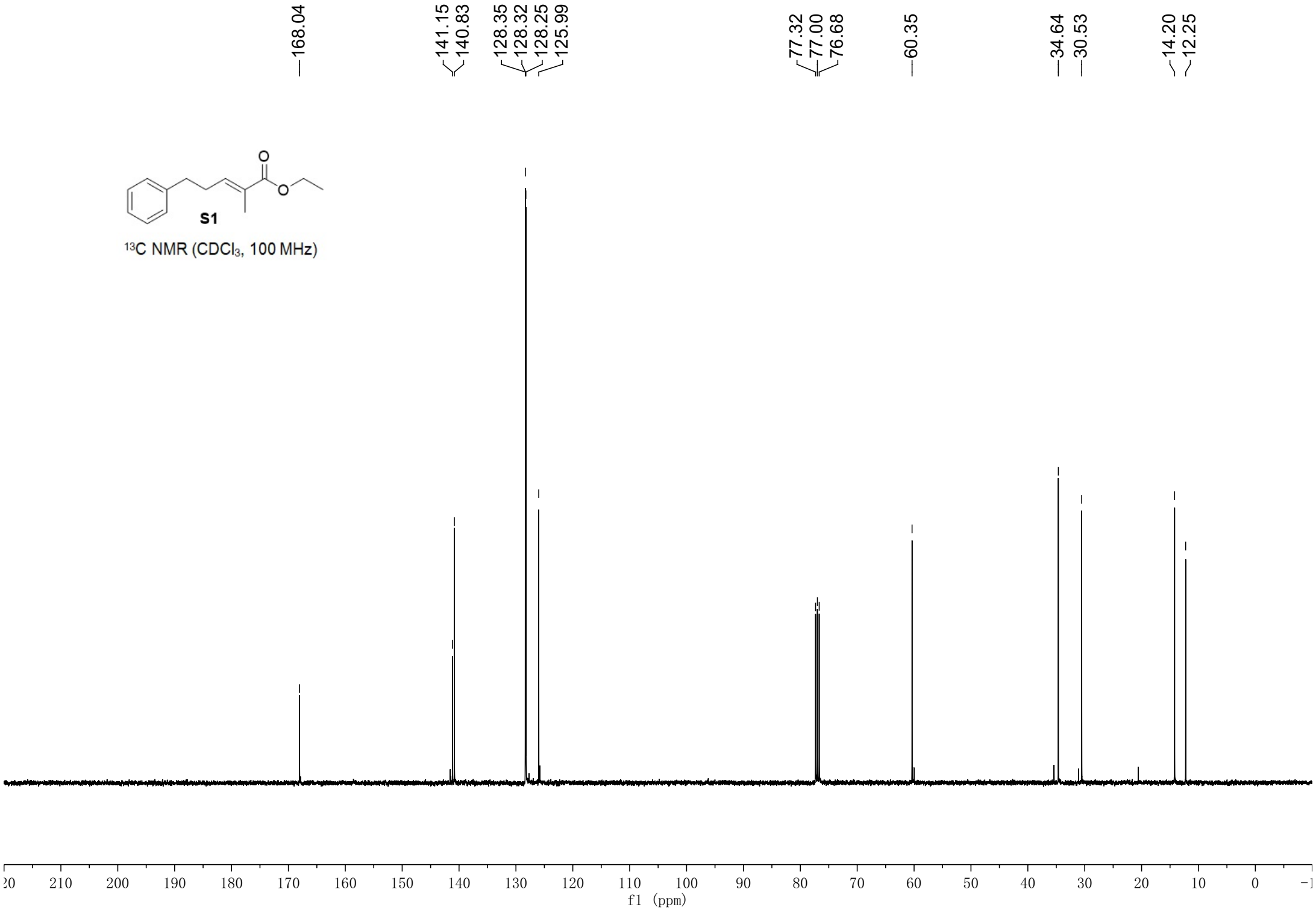

7.260
7.161
7.141
6.958
6.938
6.870
4.190
4.161
3.528
3.522
2.911
2.898
2.887
2.862
2.843
2.266
1.814
1.783
1.754
1.731
1.725
1.717
1.213
1.092
0.972
HO
HO
H
(±)–2,3-dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene
1H NMR (CDCl3, 400 MHz)
2.911
2.898
2.887
2.862
2.843
2.305
2.294
2.266
2.048
1.946
1.845
1.814
1.800
1.794
1.783
1.775
1.754
1.731
1.725
1.717
1.709
2.05
0.96
3.00
2.01
4.00
2.8
2.6
2.4
2.2
2.0
1.8
f1 (ppm)
1.00
1.00
1.00
1.00
1.00
2.05
0.96
3.00
2.01
4.00
3.00
3.01
3.01
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
−1
f1 (ppm)

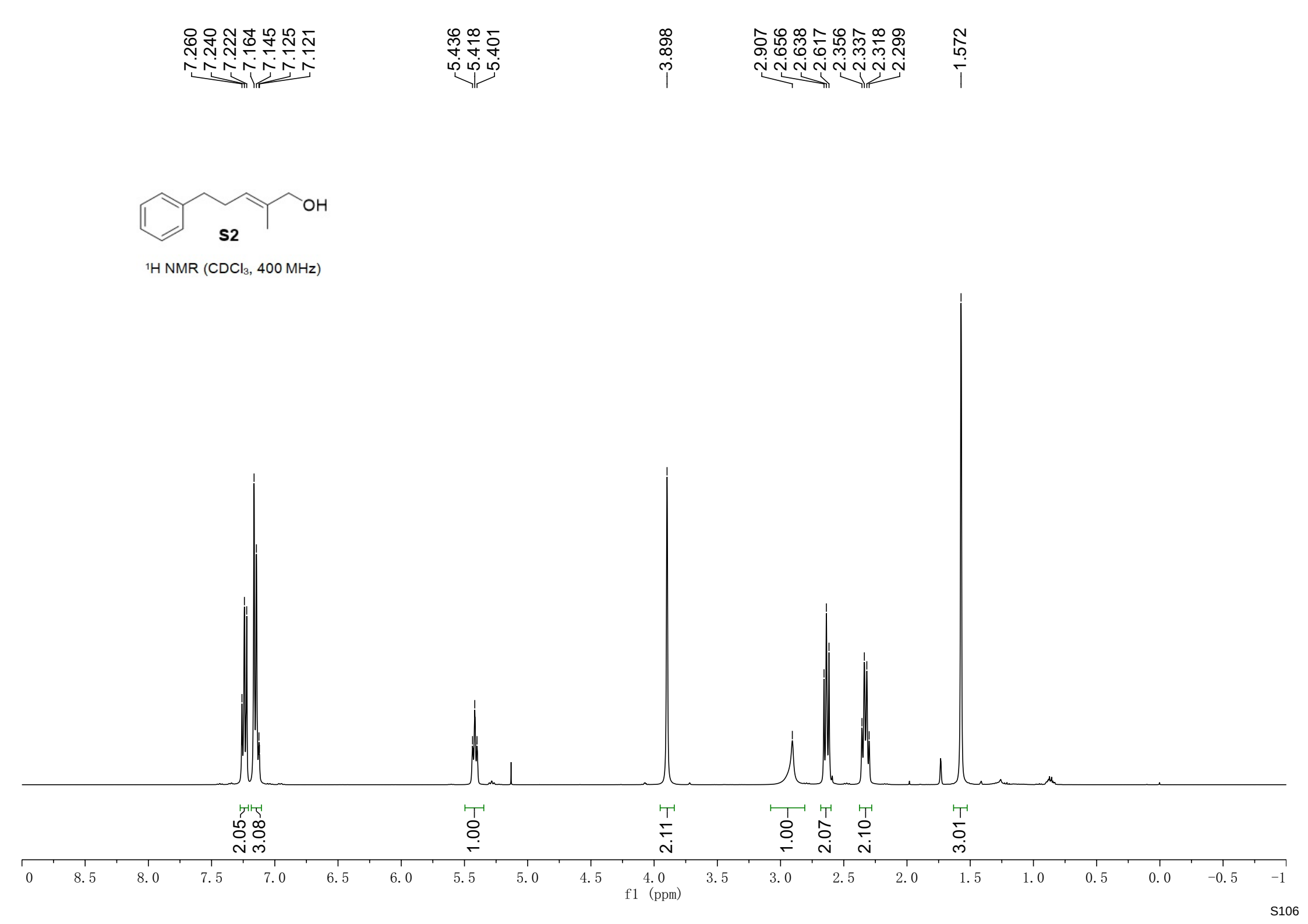


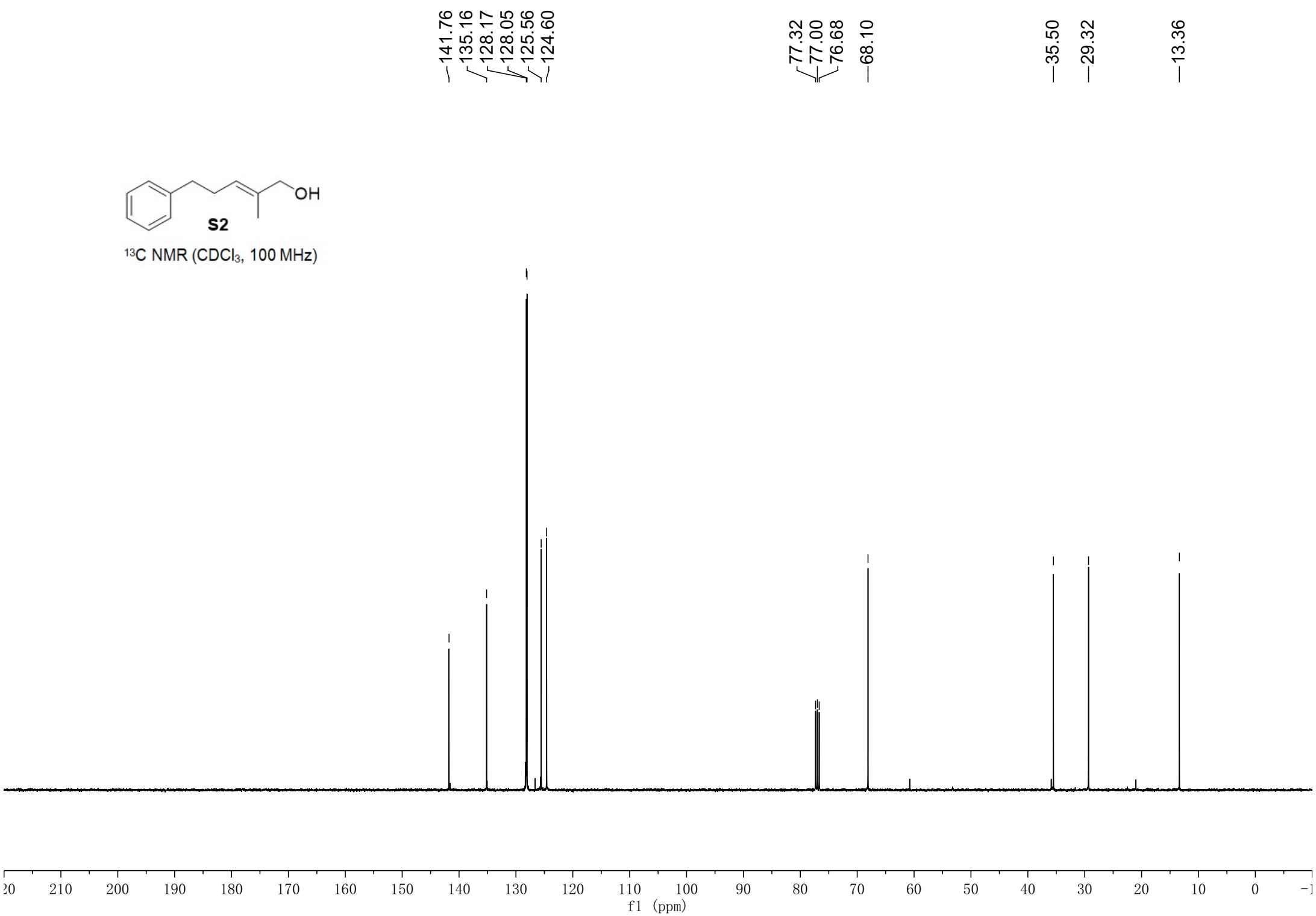
(±)–2,3-dihydroxy-15,16-dinor-ent-pimar-8,11,13-triene

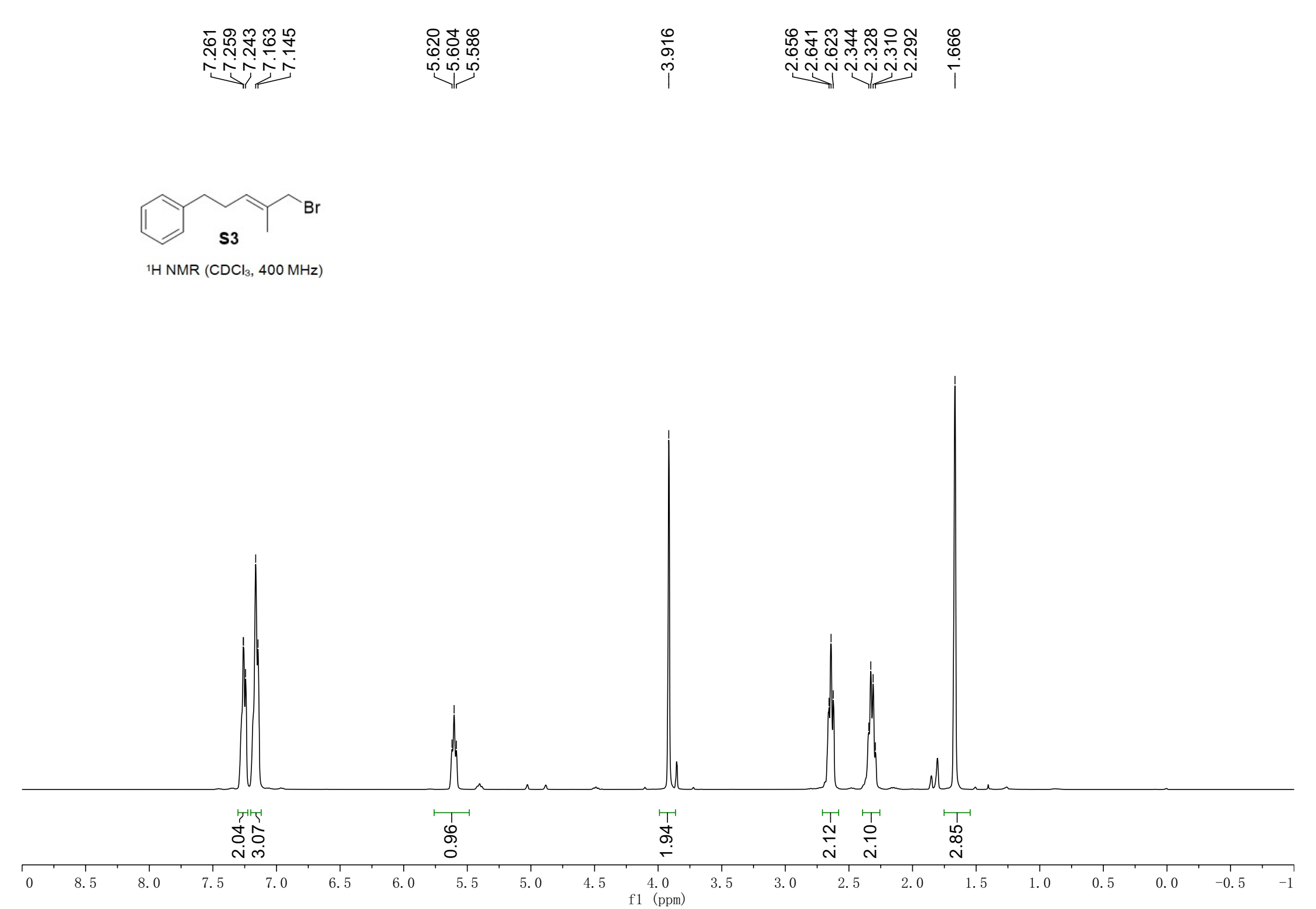
^{13}C NMR ($CDCl_3$, 125 MHz)

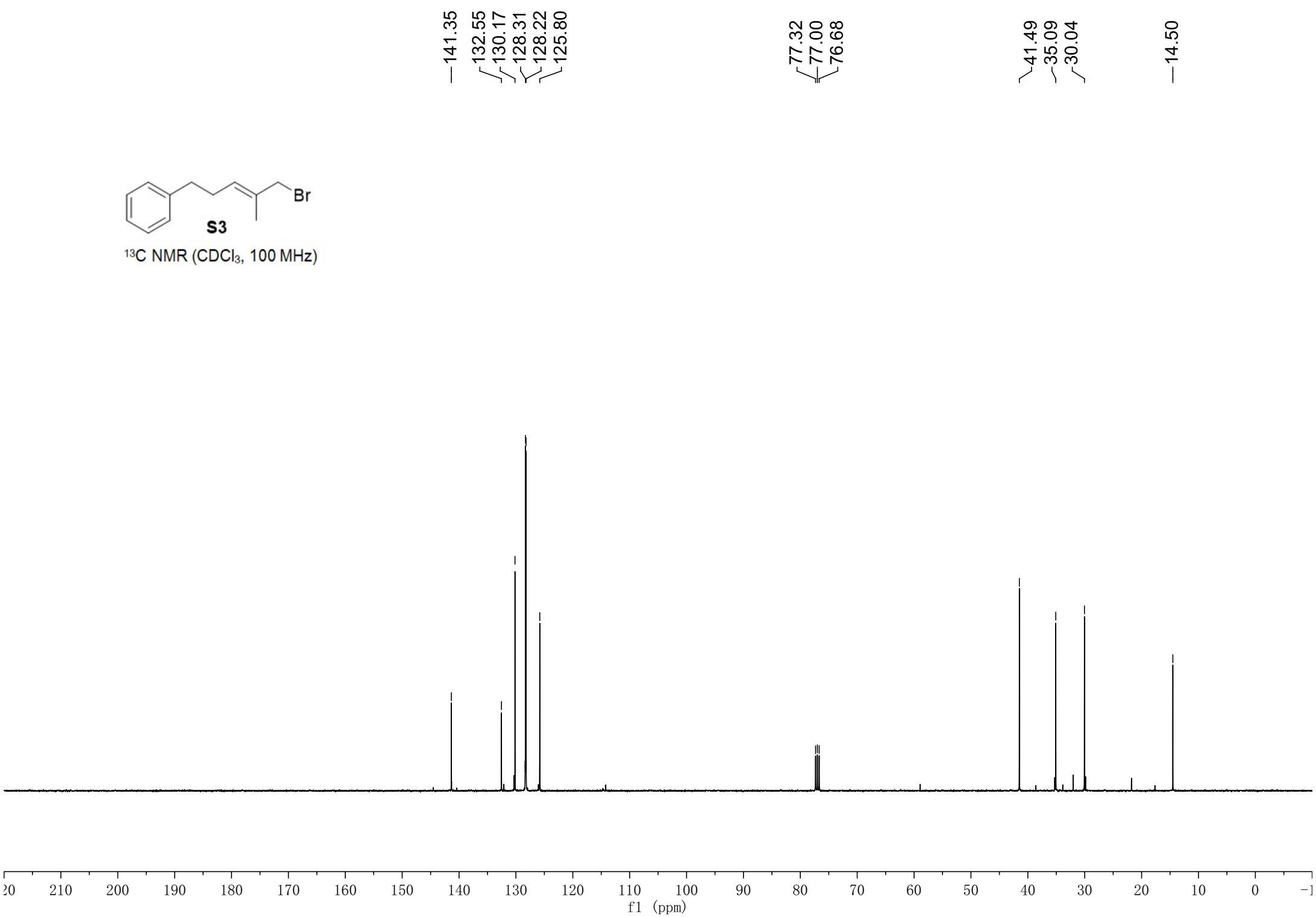

7.304
7.299
7.284
7.273
7.266
7.235
7.209
7.196
7.177
6.830
6.827
6.812
6.808
6.793
6.790
4.205
4.187
4.169
4.151
2.760
2.742
2.721
2.508
2.489
2.470
2.451
1.779
1.300
1.283
1.265
O
O
S1
1H NMR (CDCl3, 400 MHz)
2.03
3.00
0.95
2.04
2.08
1.97
2.96
3.07
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

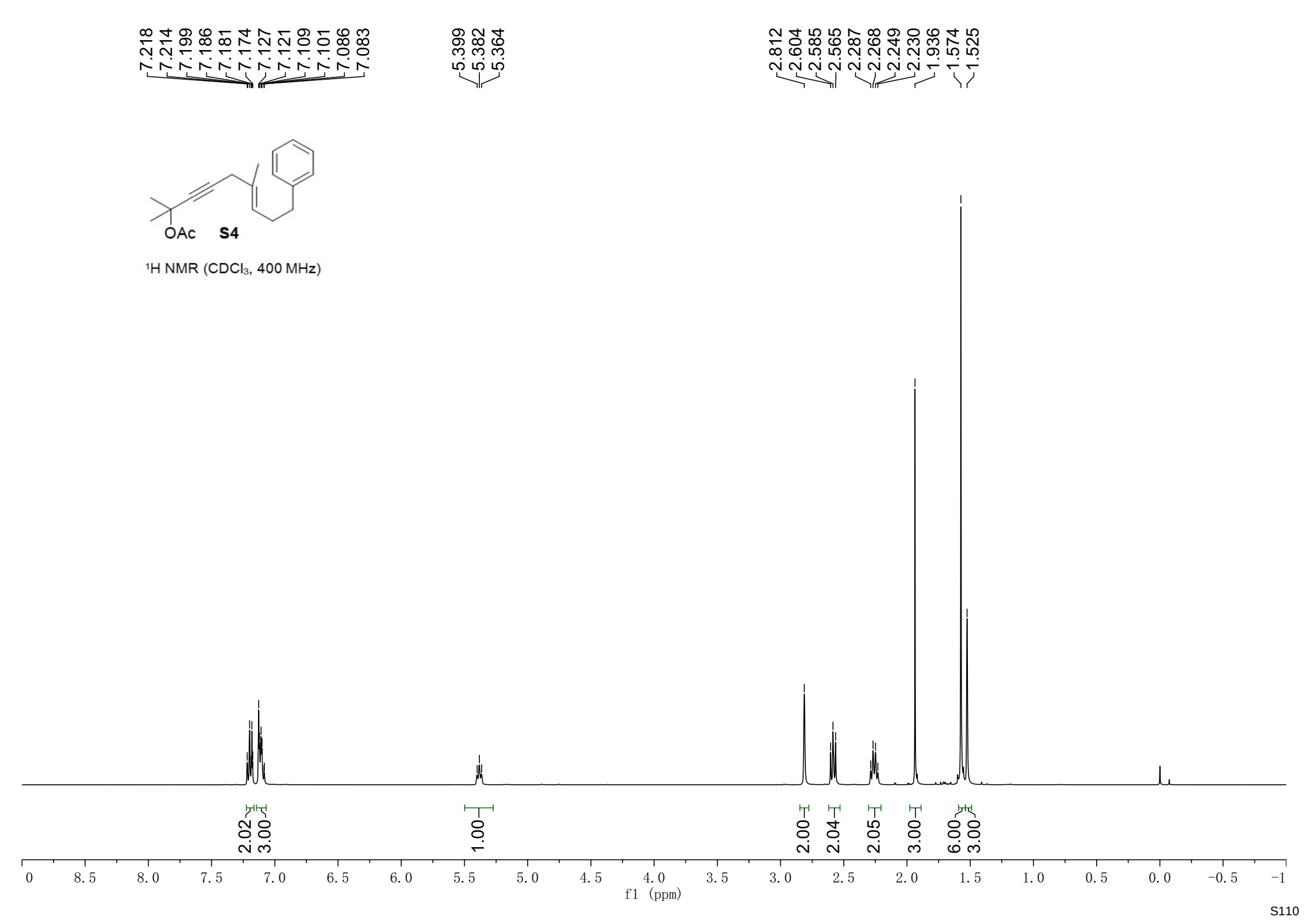

168.04
141.15
140.83
128.35
128.32
128.25
125.99
77.32
77.00
76.68
60.35
34.64
30.53
14.20
12.25
S1
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

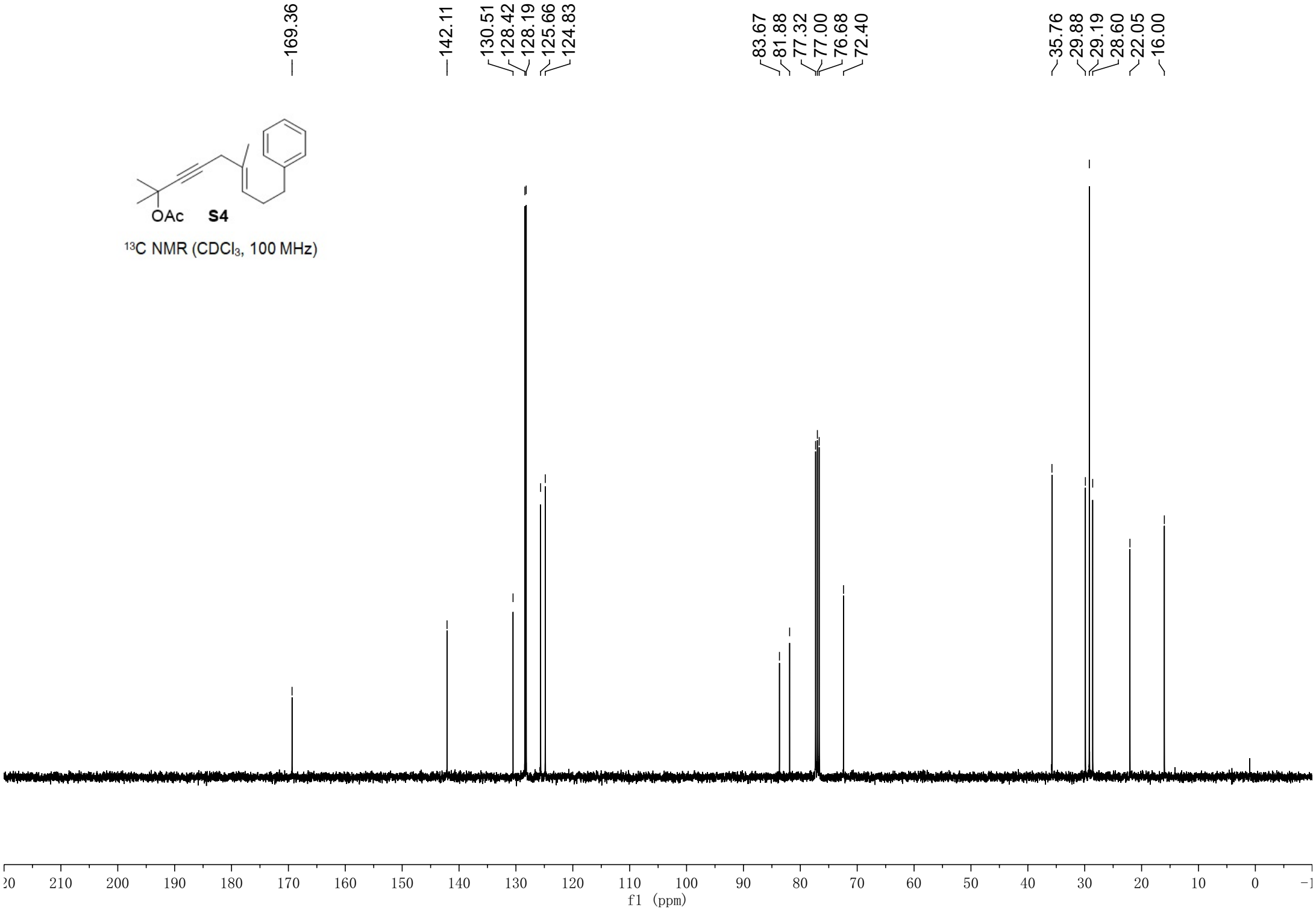

7.260
7.240
7.222
7.164
7.145
7.125
7.121
5.436
5.418
5.401
3.898
2.907
2.656
2.638
2.617
2.356
2.337
2.318
2.299
1.572
OH
S2
¹H NMR (CDCl₃, 400 MHz)
2.05
3.08
1.00
2.11
1.00
2.07
2.10
3.01
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

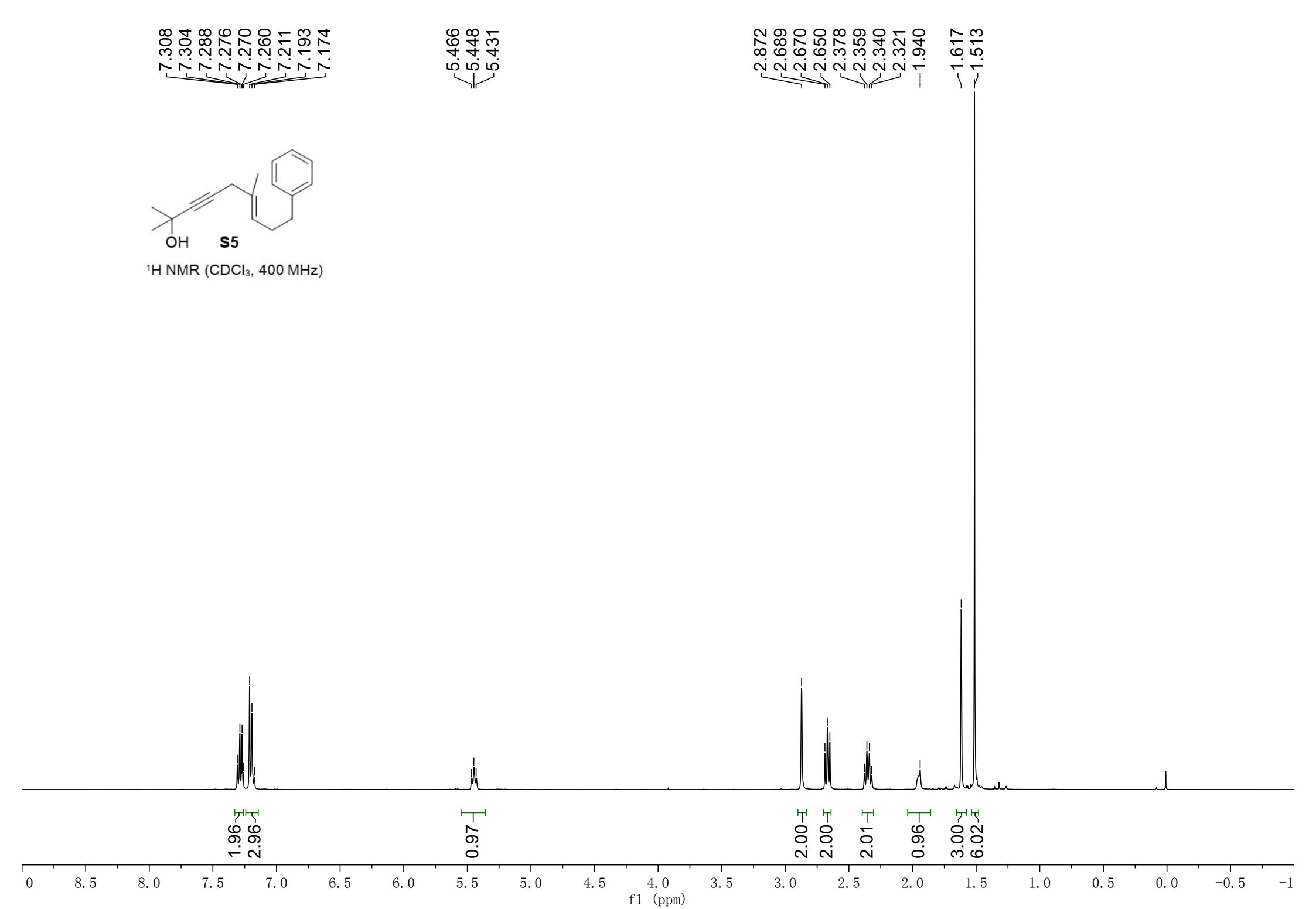

141.76
135.16
128.17
128.05
125.56
124.60
77.32
77.00
76.68
68.10
35.50
29.32
13.36
OH
S2
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

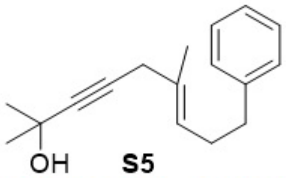

7.261
7.259
7.243
7.163
7.145
5.620
5.604
5.586
3.916
2.656
2.641
2.623
2.344
2.328
2.310
2.292
1.666
Br
S3
1H NMR (CDCl3, 400 MHz)
2.04
3.07
0.96
1.94
2.12
2.10
2.85
f1 (ppm)


141.35
132.55
130.17
128.31
128.22
125.80
77.32
77.00
76.68
41.49
35.09
30.04
14.50
Br
S3
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.218
7.214
7.199
7.186
7.181
7.174
7.127
7.121
7.109
7.101
7.086
7.083
5.399
5.382
5.364
2.812
2.604
2.585
2.565
2.287
2.268
2.249
2.230
1.936
1.574
1.525
OAc
S4
1H NMR (CDCl3, 400 MHz)
2.02
3.00
1.00
2.00
2.04
2.05
3.00
6.00
3.00
f1 (ppm)

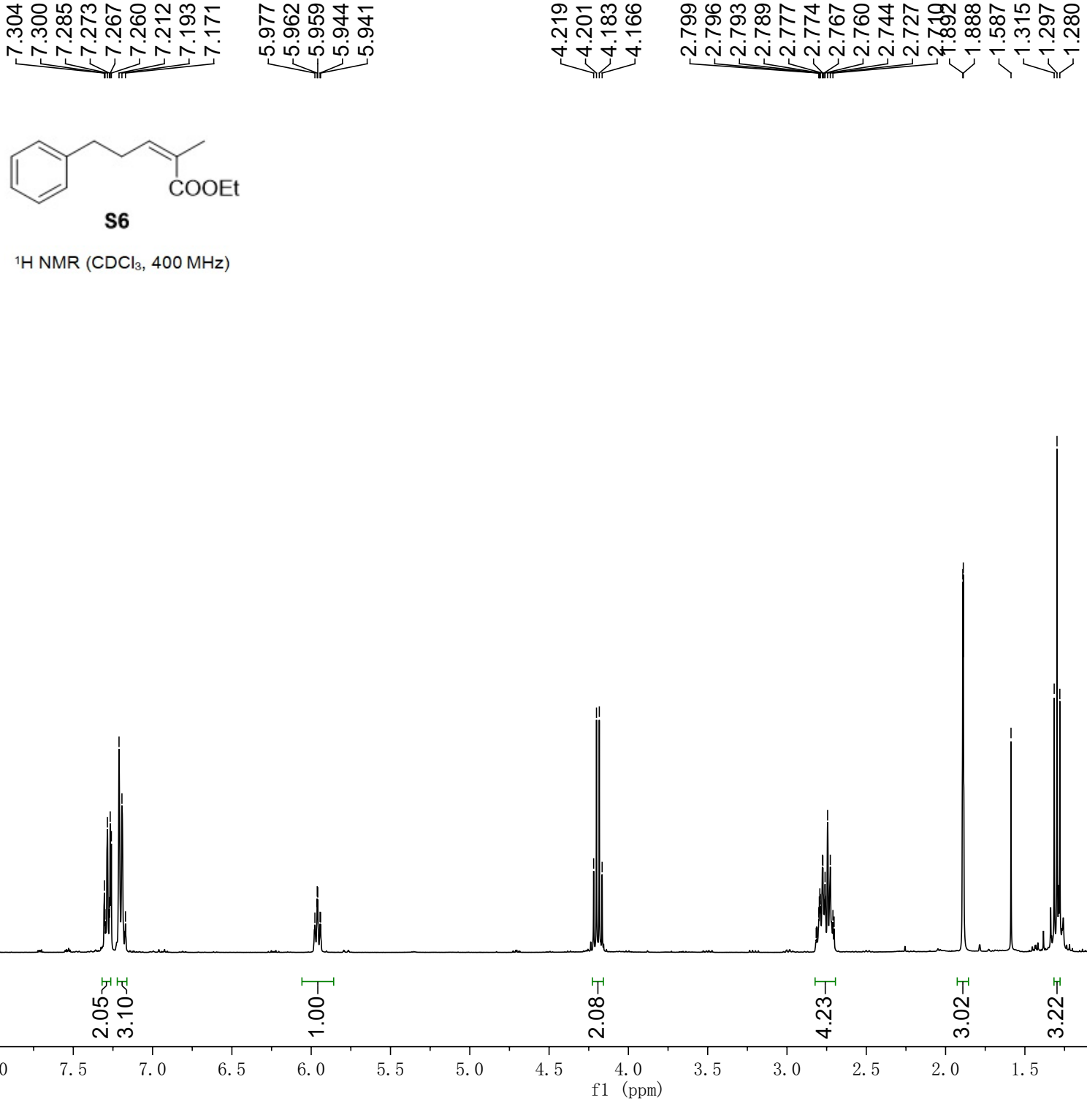

169.36
142.11
130.51
128.42
128.19
125.66
124.83
83.67
81.88
77.32
77.00
76.68
72.40
35.76
29.88
29.19
28.60
22.05
16.00
OAc
S4
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.308
7.304
7.288
7.276
7.270
7.260
7.211
7.193
7.174
5.466
5.448
5.431
2.872
2.689
2.670
2.650
2.378
2.359
2.340
2.321
1.940
1.617
1.513
OH
S5
1H NMR (CDCl3, 400 MHz)
1.96
2.96
0.97
2.00
2.00
2.01
0.96
3.00
6.02
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)



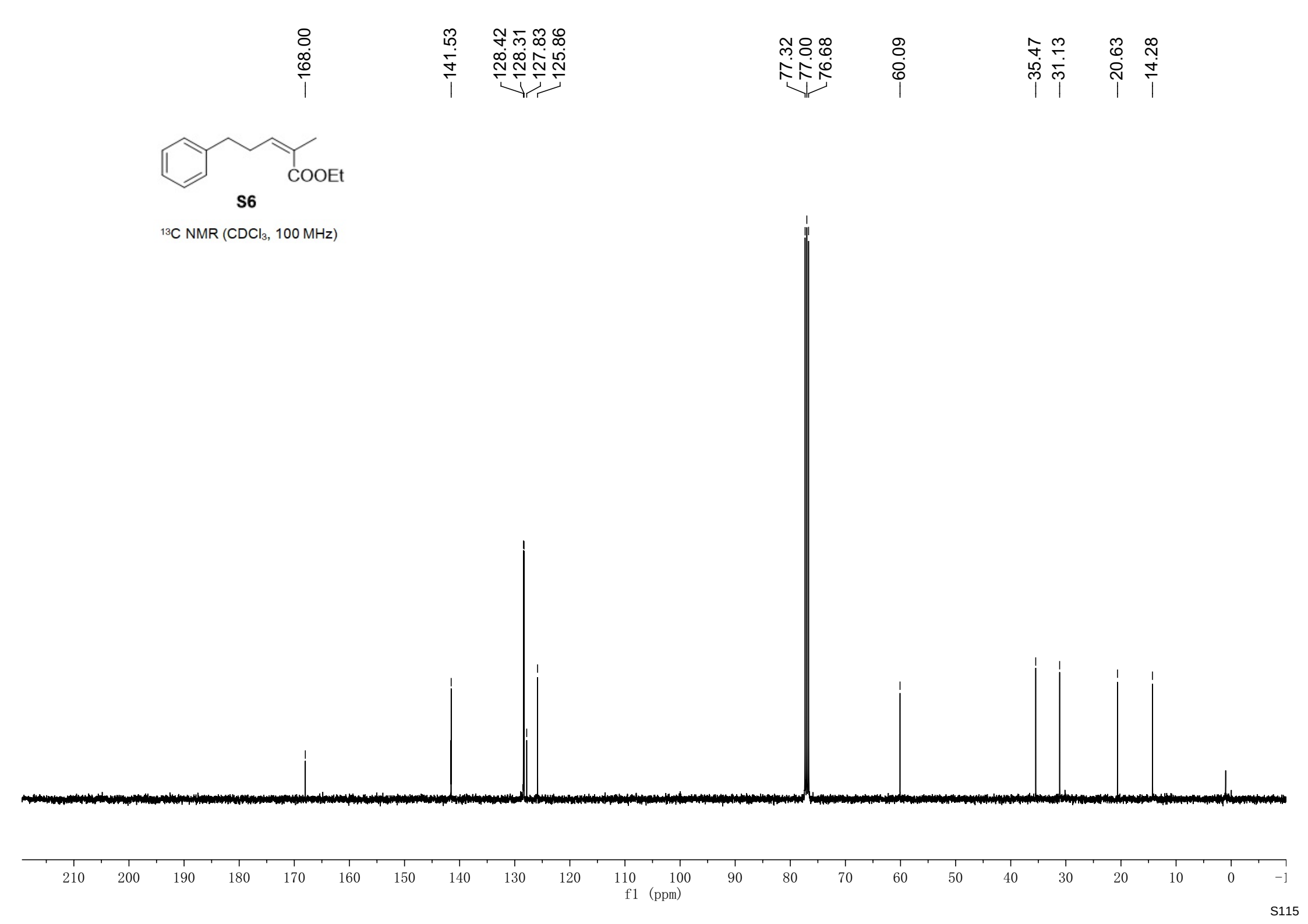
S5

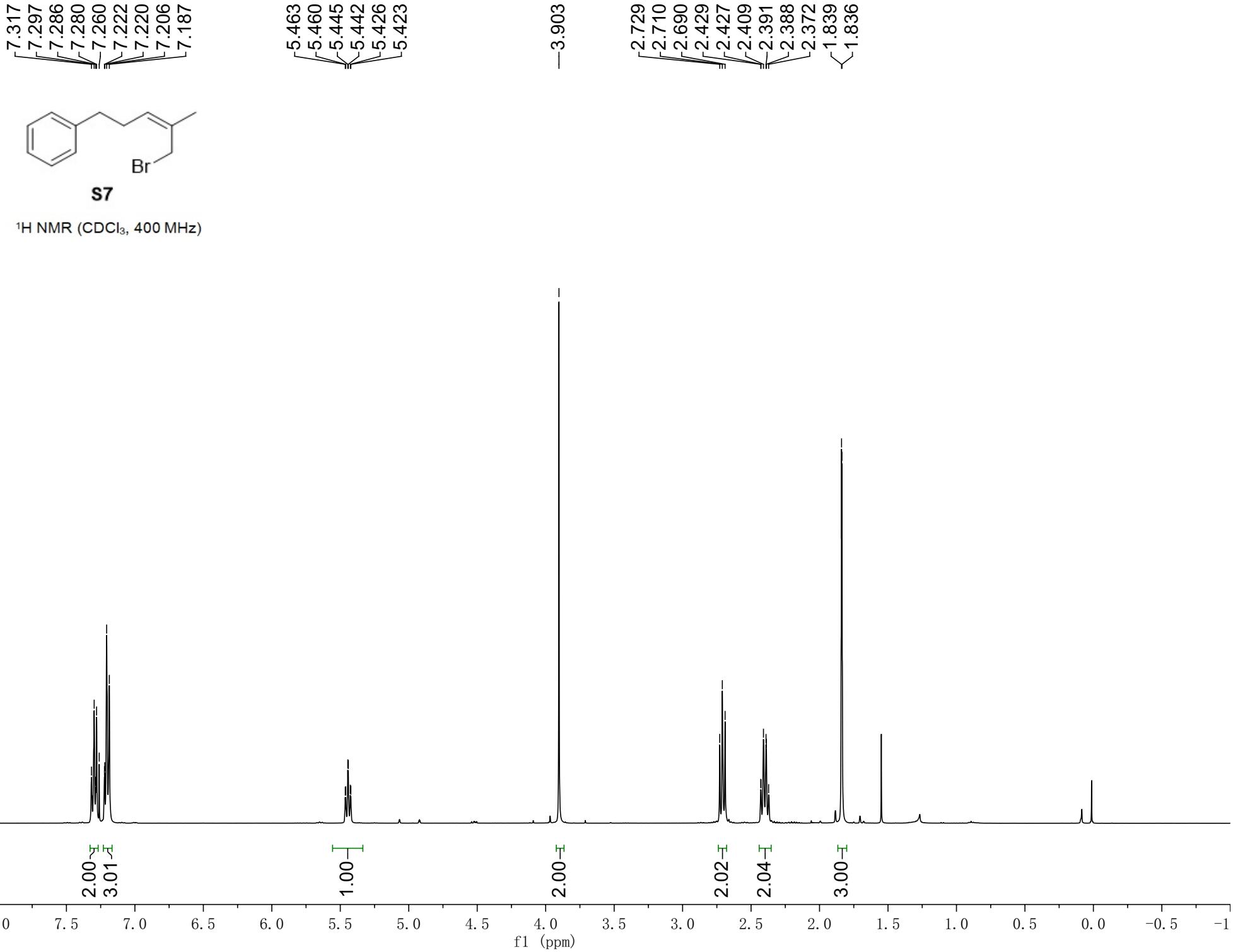
^{13}C NMR ($CDCl_3$, 100 MHz)

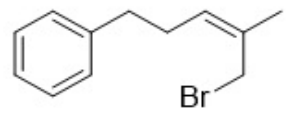


S6

^{1}H NMR ($CDCl_3$, 400 MHz)

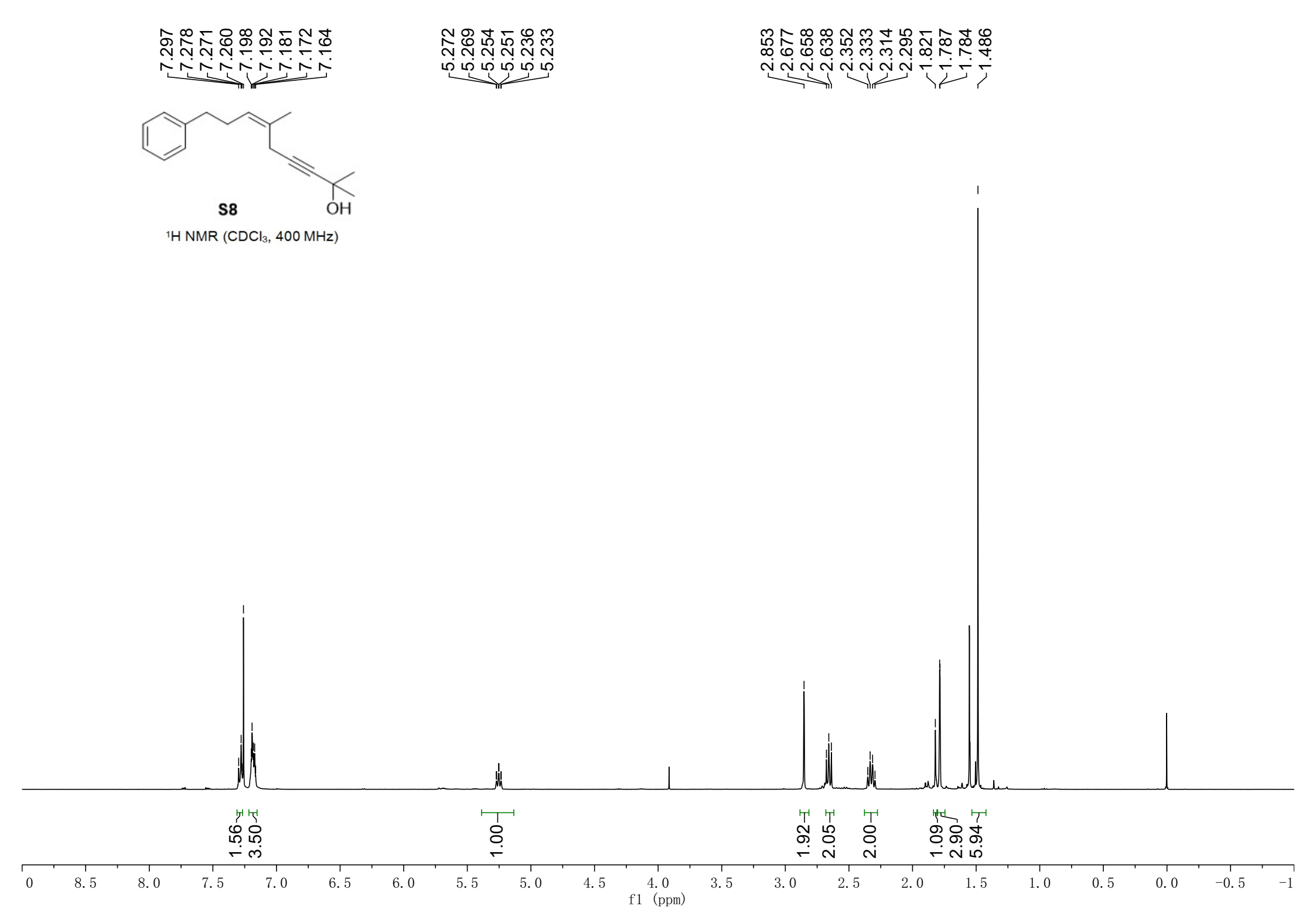

168.00
141.53
128.42
128.31
127.83
125.86
77.32
77.00
76.68
60.09
35.47
31.13
20.63
14.28
COOEt
S6
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.317
7.297
7.286
7.280
7.260
7.222
7.220
7.206
7.187
5.463
5.460
5.445
5.442
5.426
5.423
3.903
2.729
2.710
2.690
2.429
2.427
2.409
2.391
2.388
2.372
1.839
1.836
Br
S7
¹H NMR (CDCl₃, 400 MHz)
2.00
3.01
1.00
2.00
2.02
2.04
3.00
f1 (ppm)



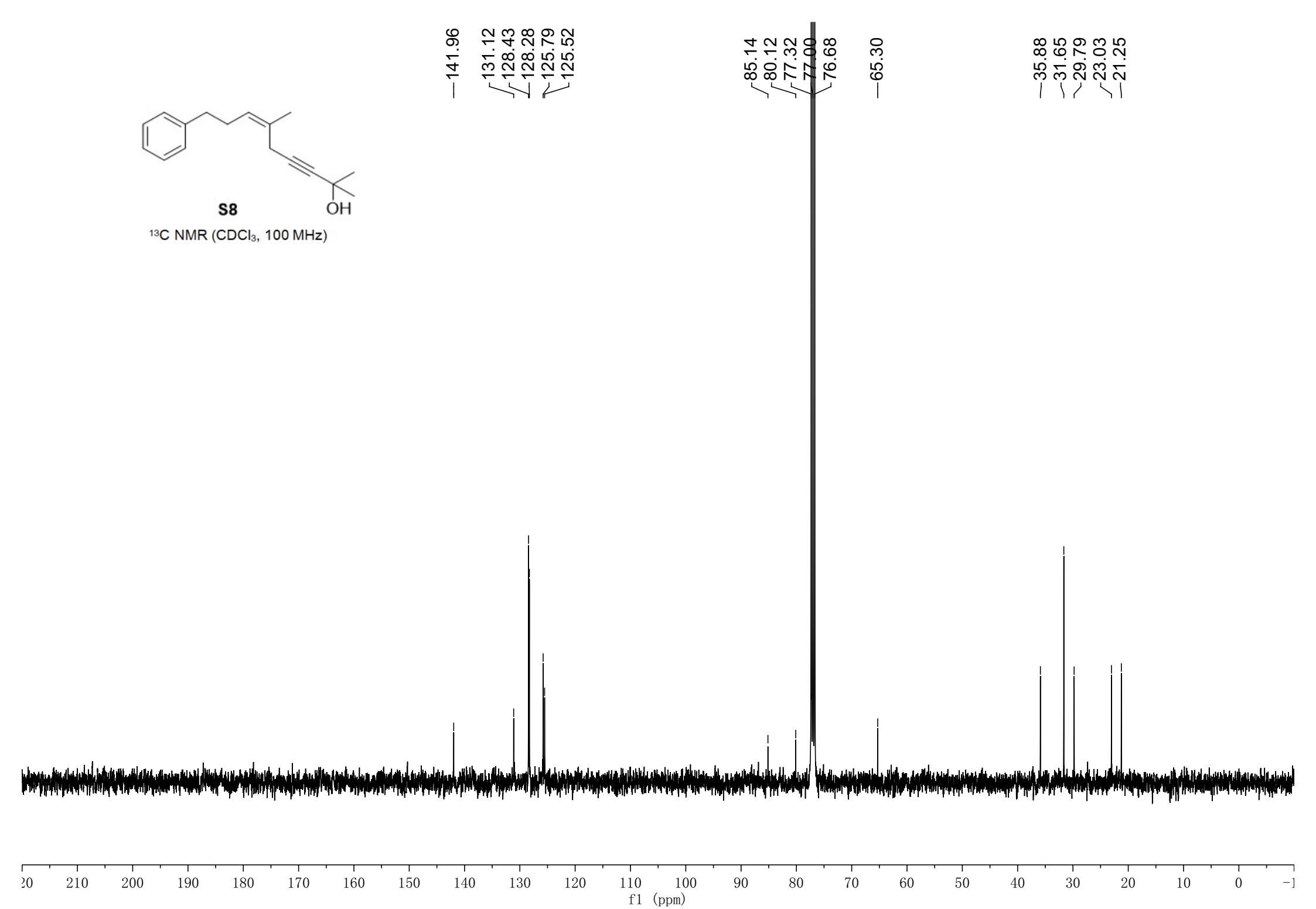
S7

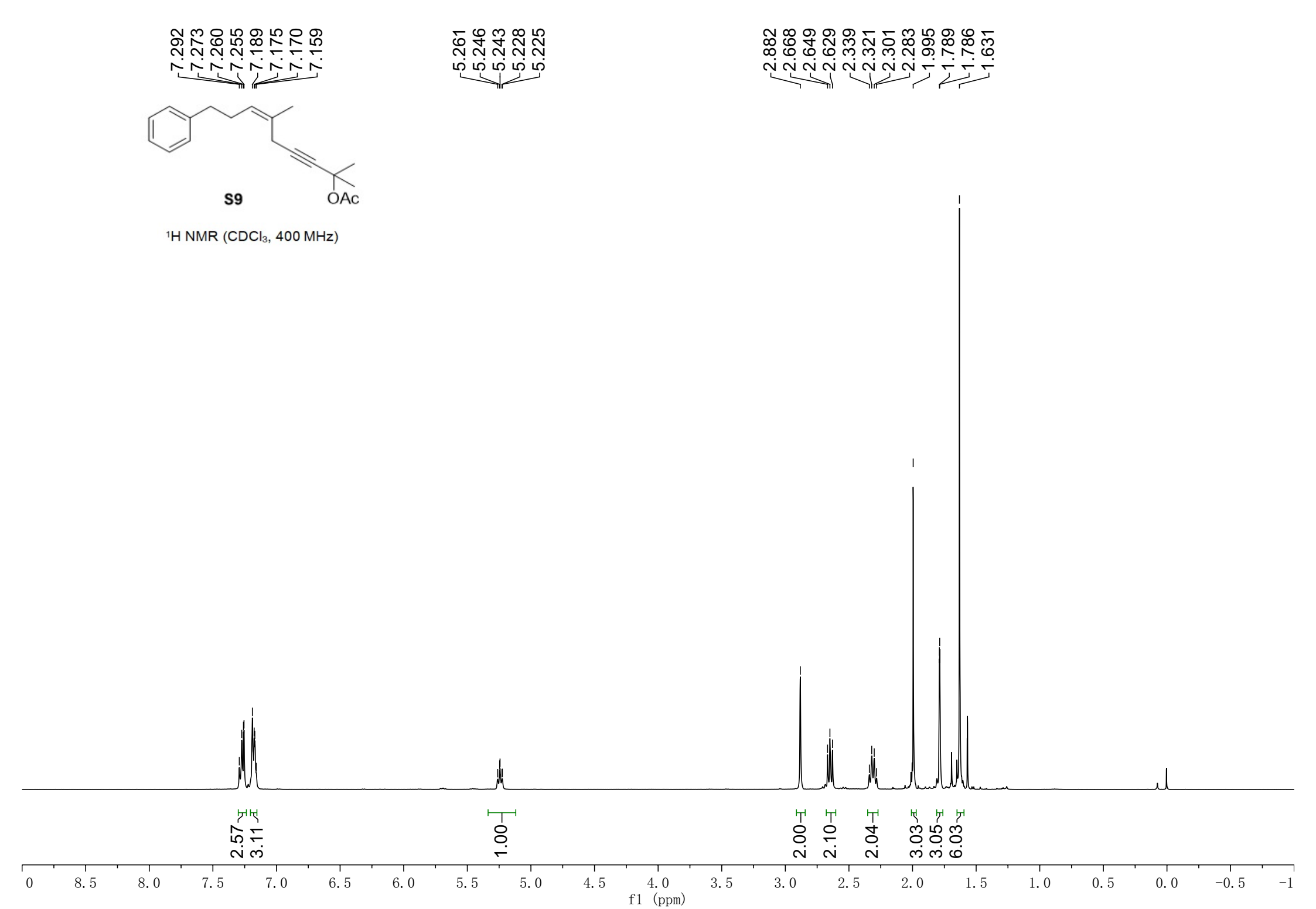
^{13}C NMR ($CDCl_3$, 100 MHz)

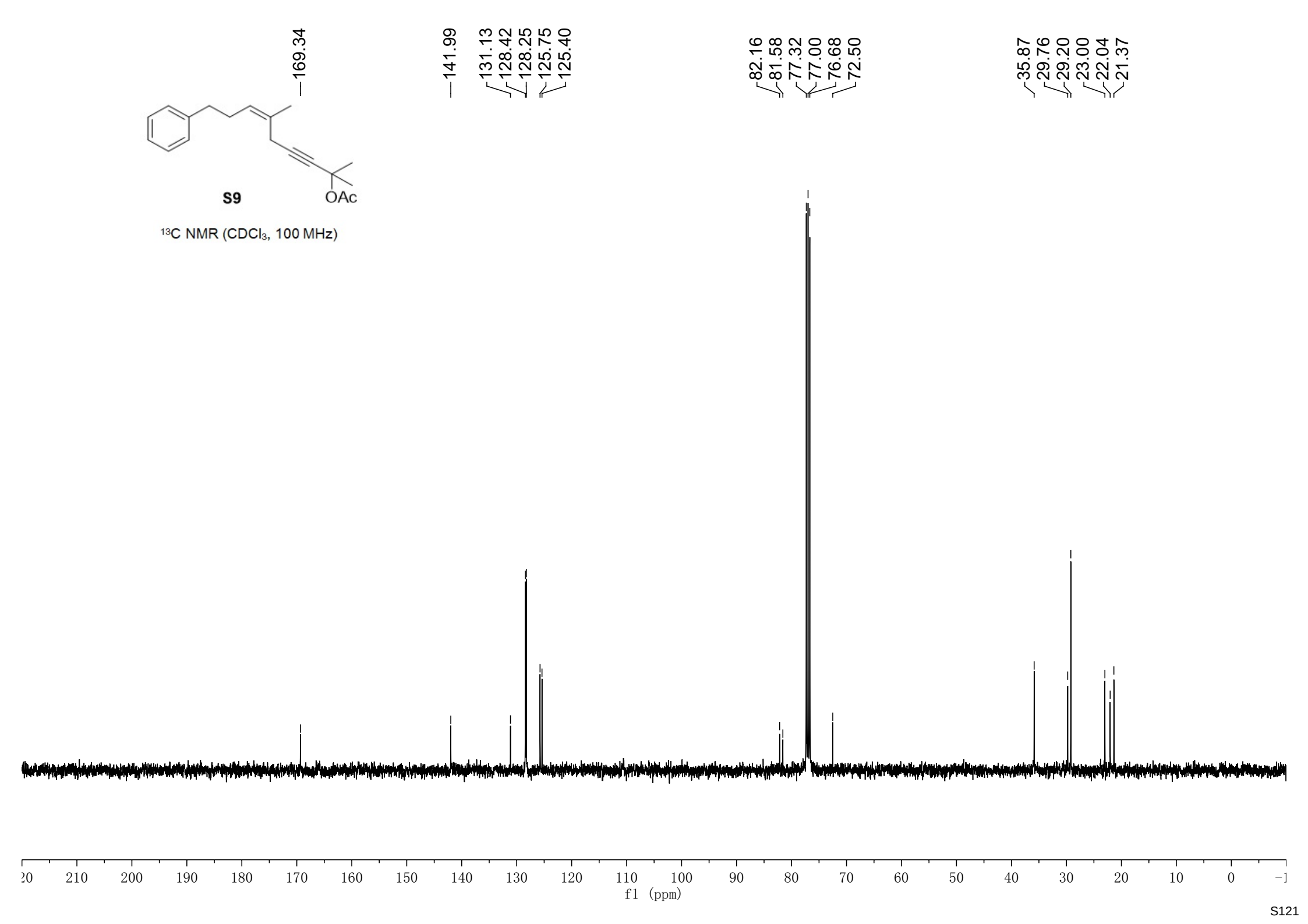


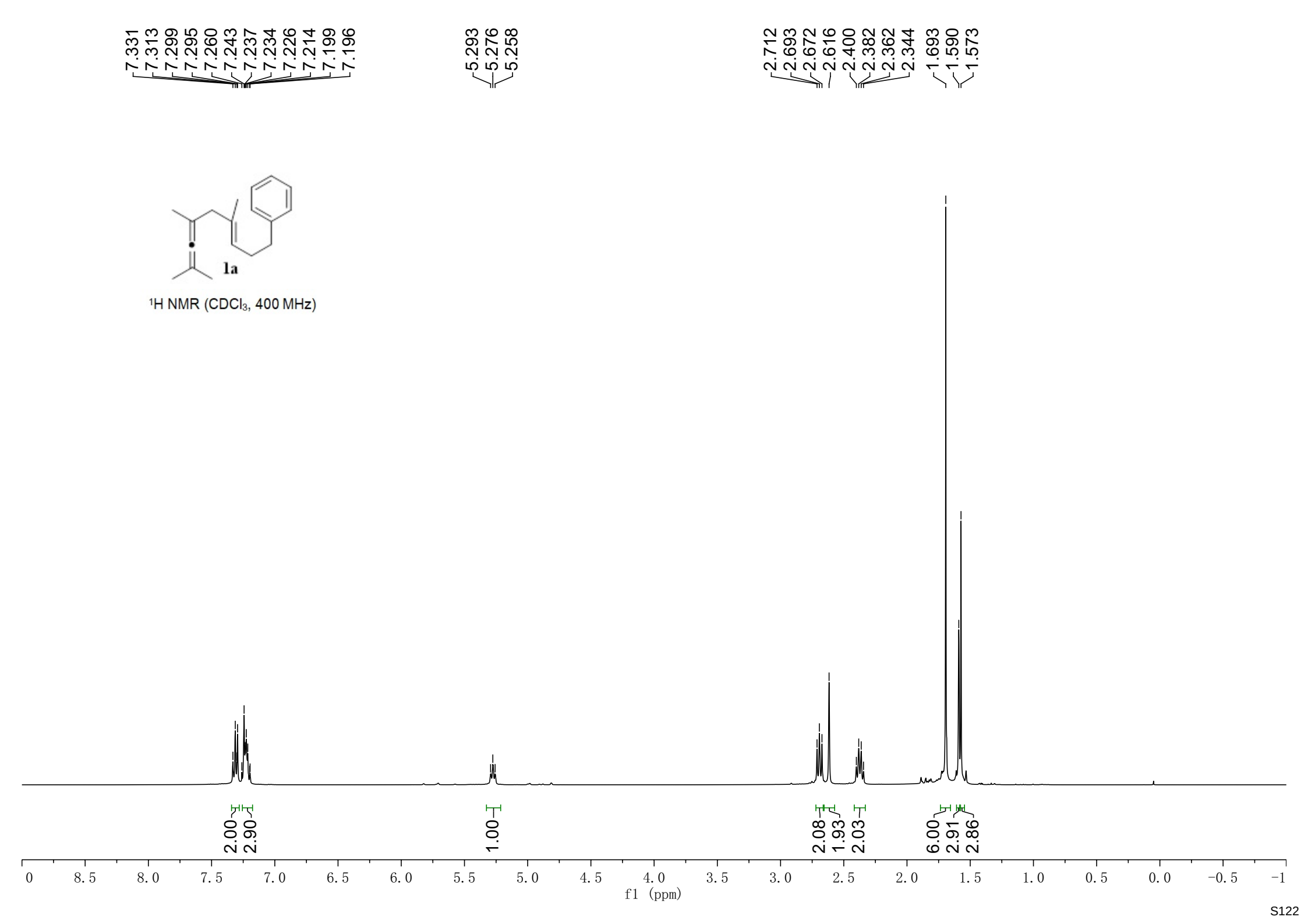
S8

^{1}H NMR ($CDCl_3$, 400 MHz)

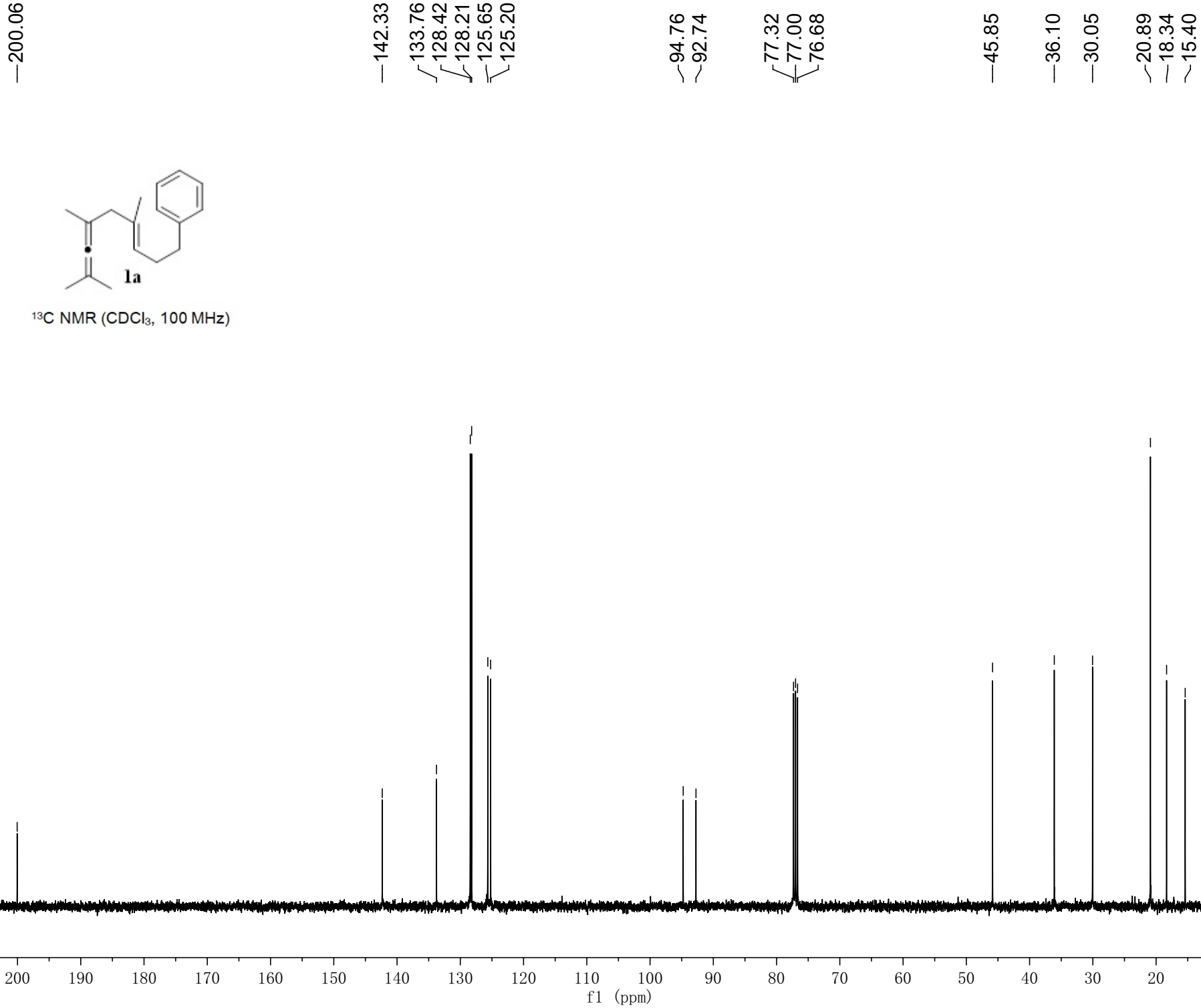

141.96
131.12
128.43
128.28
125.79
125.52
85.14
80.12
77.32
77.00
76.68
65.30
35.88
31.65
29.79
23.03
21.25
OH
S8
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

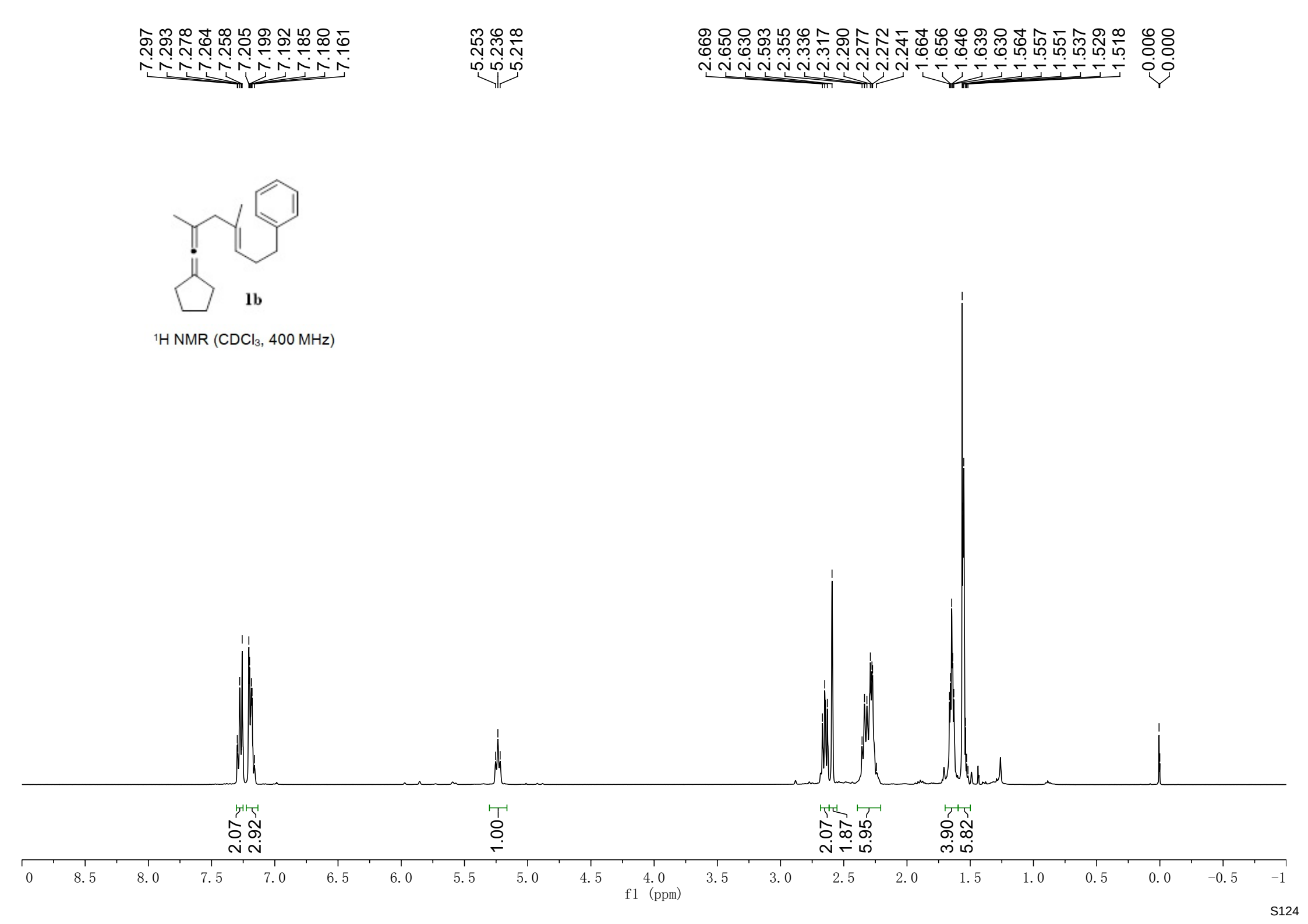

7.292
7.273
7.260
7.255
7.189
7.175
7.170
7.159
5.261
5.246
5.243
5.228
5.225
2.882
2.668
2.649
2.629
2.339
2.321
2.301
2.283
1.995
1.789
1.786
1.631
OAc
S9
1H NMR (CDCl3, 400 MHz)
2.57
3.11
1.00
2.00
2.10
2.04
3.03
3.05
6.03
f1 (ppm)

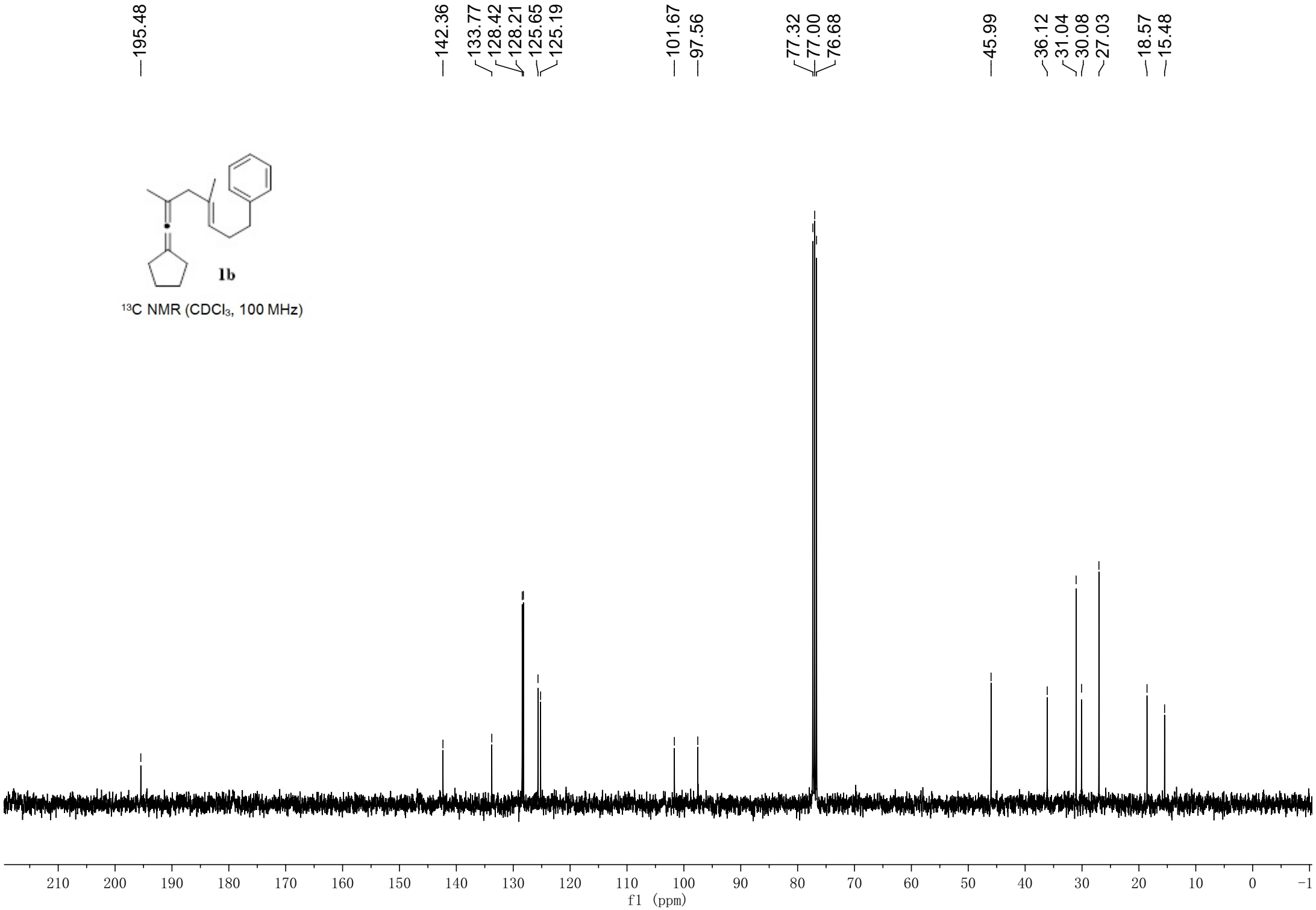

169.34
141.99
131.13
128.42
128.25
125.75
125.40
82.16
81.58
77.32
77.00
76.68
72.50
35.87
29.76
29.20
23.00
22.04
21.37
OAc
S9
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

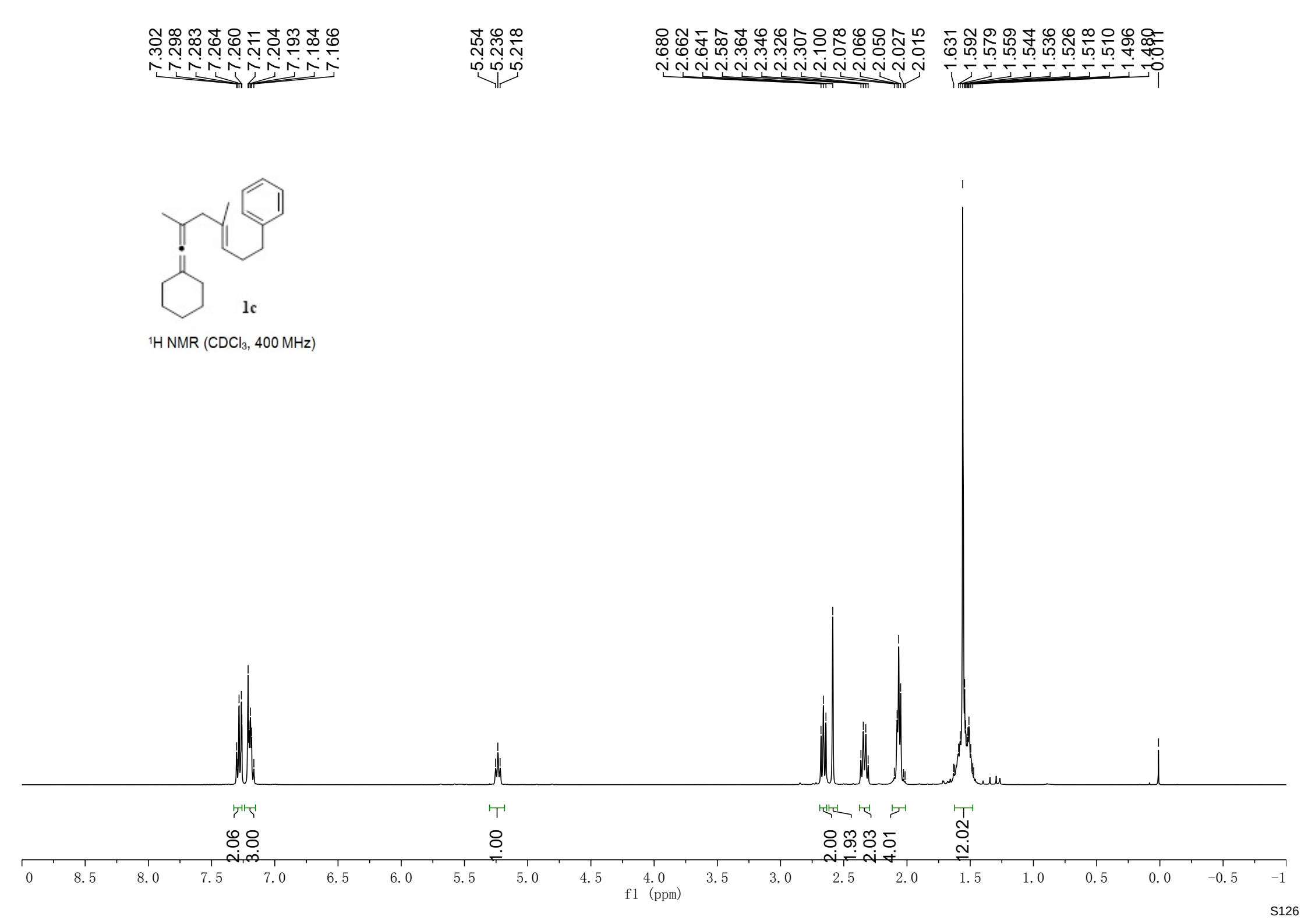


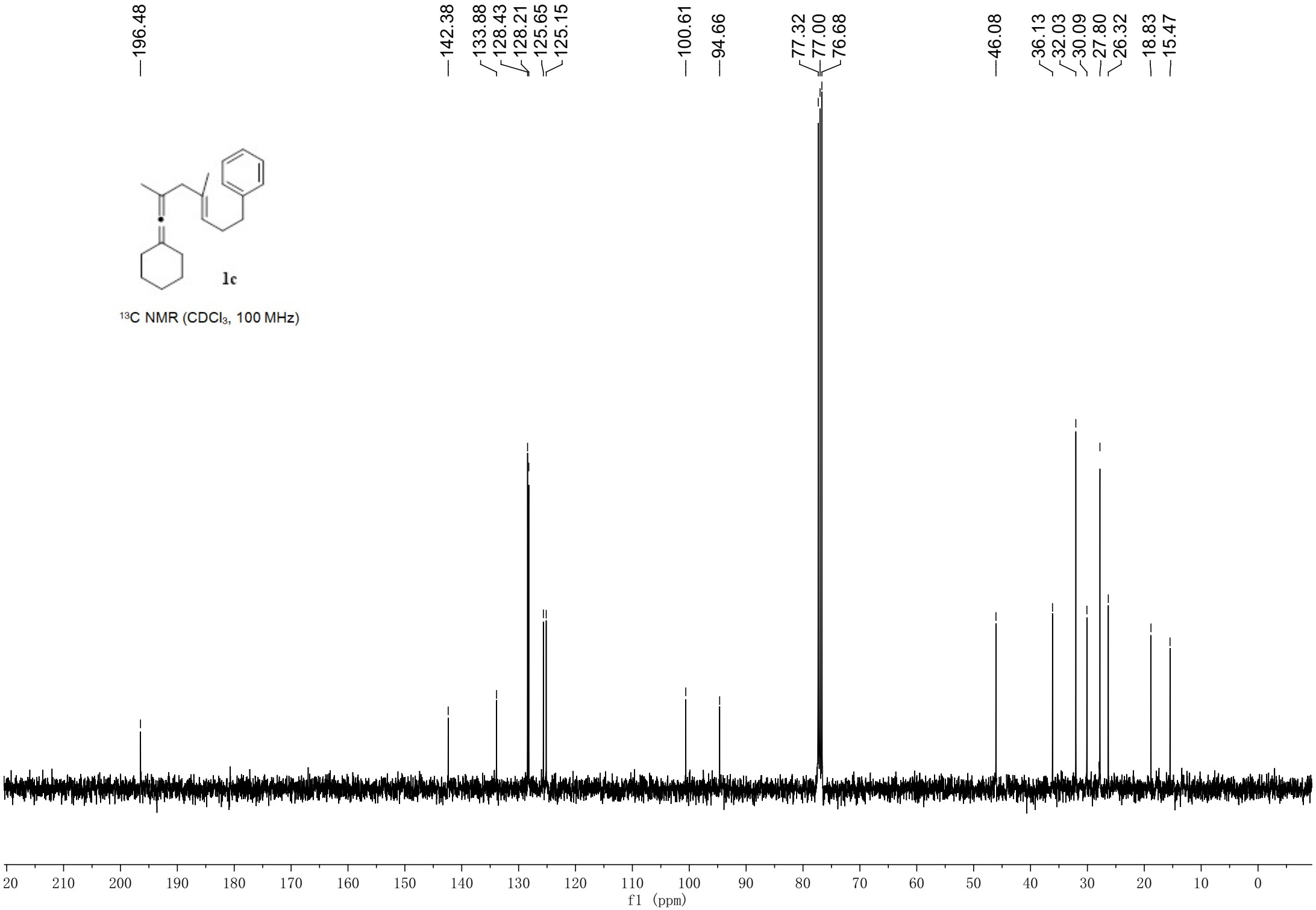
^{1}H NMR ($CDCl_3$, 400 MHz)

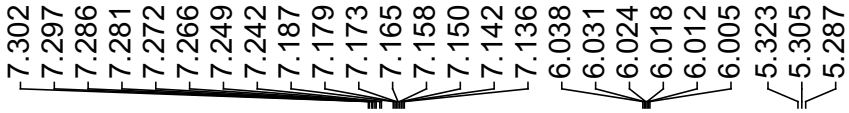

200.06
142.33
133.76
128.42
128.21
125.65
125.20
94.76
92.74
77.32
77.00
76.68
45.85
36.10
30.05
20.89
18.34
15.40
1a
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

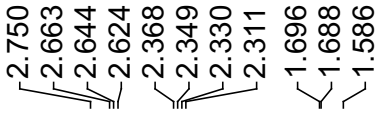

7.297
7.293
7.278
7.264
7.258
7.205
7.199
7.192
7.185
7.180
7.161
5.253
5.236
5.218
2.669
2.650
2.630
2.593
2.355
2.336
2.317
2.290
2.277
2.272
2.241
1.664
1.656
1.646
1.639
1.630
1.564
1.557
1.551
1.537
1.529
1.518
0.006
0.000
1b
1H NMR (CDCl3, 400 MHz)
2.07
2.92
1.00
2.07
1.87
5.95
3.90
5.82
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

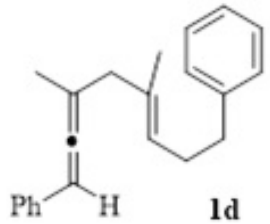

195.48
142.36
133.77
128.42
128.21
125.65
125.19
101.67
97.56
77.32
77.00
76.68
45.99
36.12
31.04
30.08
27.03
18.57
15.48
1b
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)


7.302
7.298
7.283
7.264
7.260
7.211
7.204
7.193
7.184
7.166
5.254
5.236
5.218
2.680
2.662
2.641
2.587
2.364
2.346
2.326
2.307
2.100
2.078
2.066
2.050
2.027
2.015
1.631
1.592
1.579
1.559
1.544
1.536
1.526
1.518
1.510
1.496
1.480
0.011
1c
1H NMR (CDCl3, 400 MHz)
2.06
3.00
1.00
2.00
1.93
2.03
4.01
12.02
f1 (ppm)


196.48
142.38
133.88
128.43
128.21
125.65
125.15
100.61
94.66
77.32
77.00
76.68
46.08
36.13
32.03
30.09
27.80
26.32
18.83
15.47
1c
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

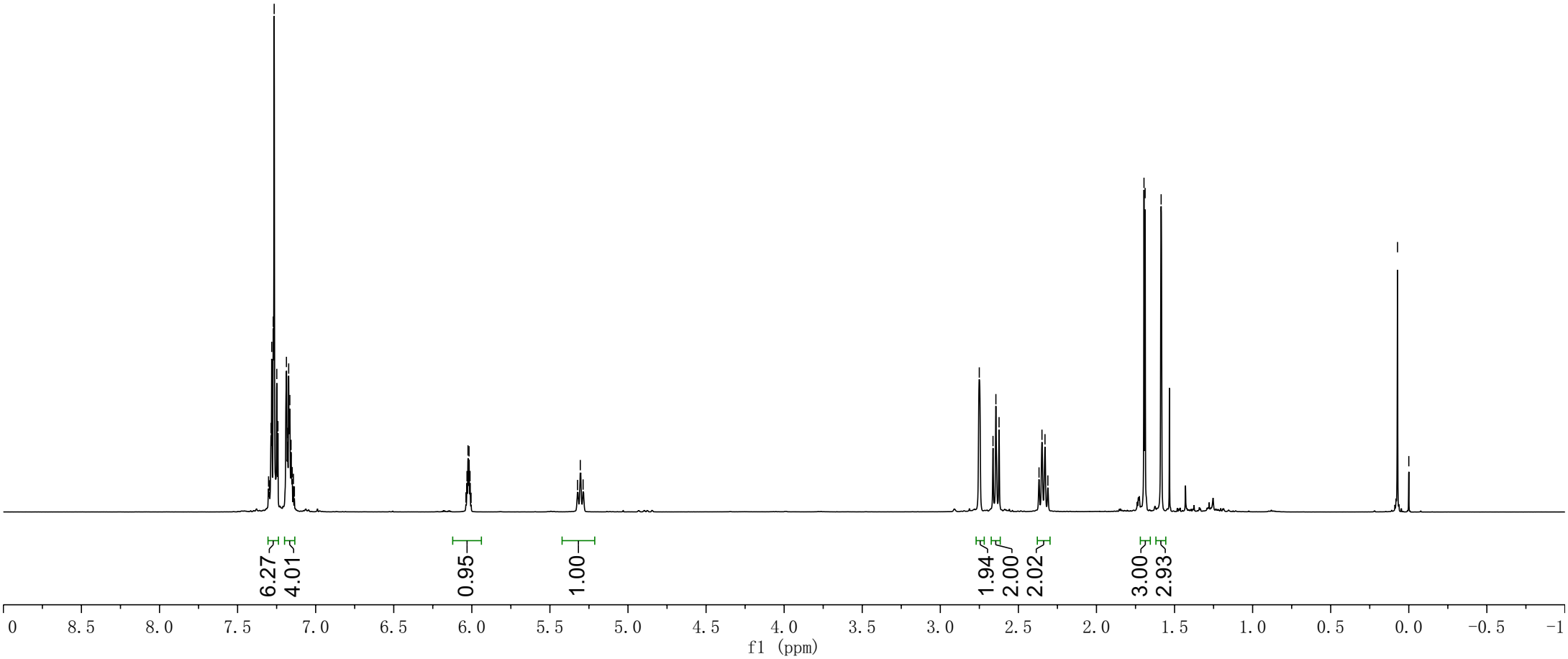


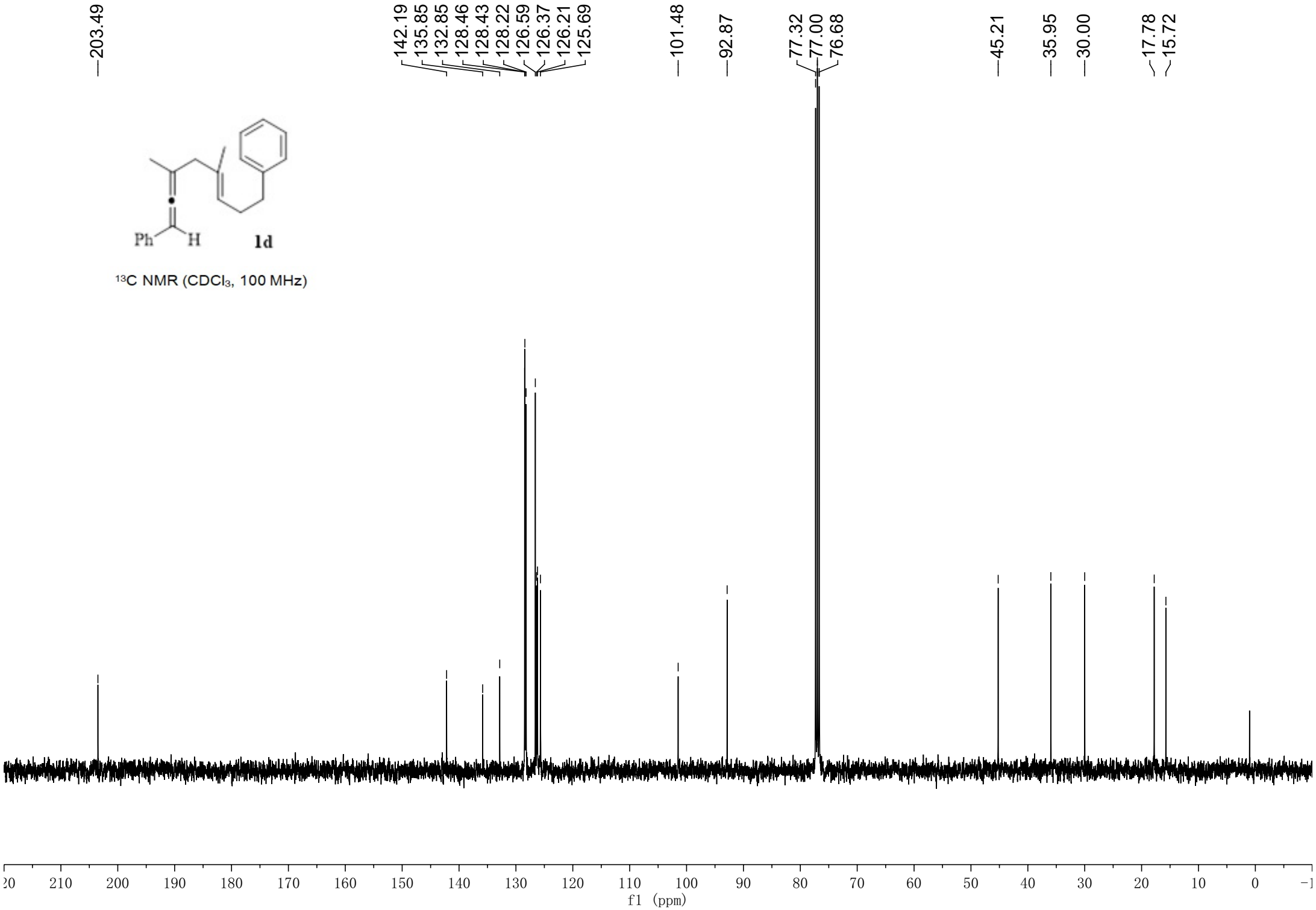




1d

^{1}H NMR ($CDCl_3$, 400 MHz)




203.49
142.19
135.85
132.85
128.46
128.43
128.22
126.59
126.37
126.21
125.69
101.48
92.87
77.32
77.00
76.68
45.21
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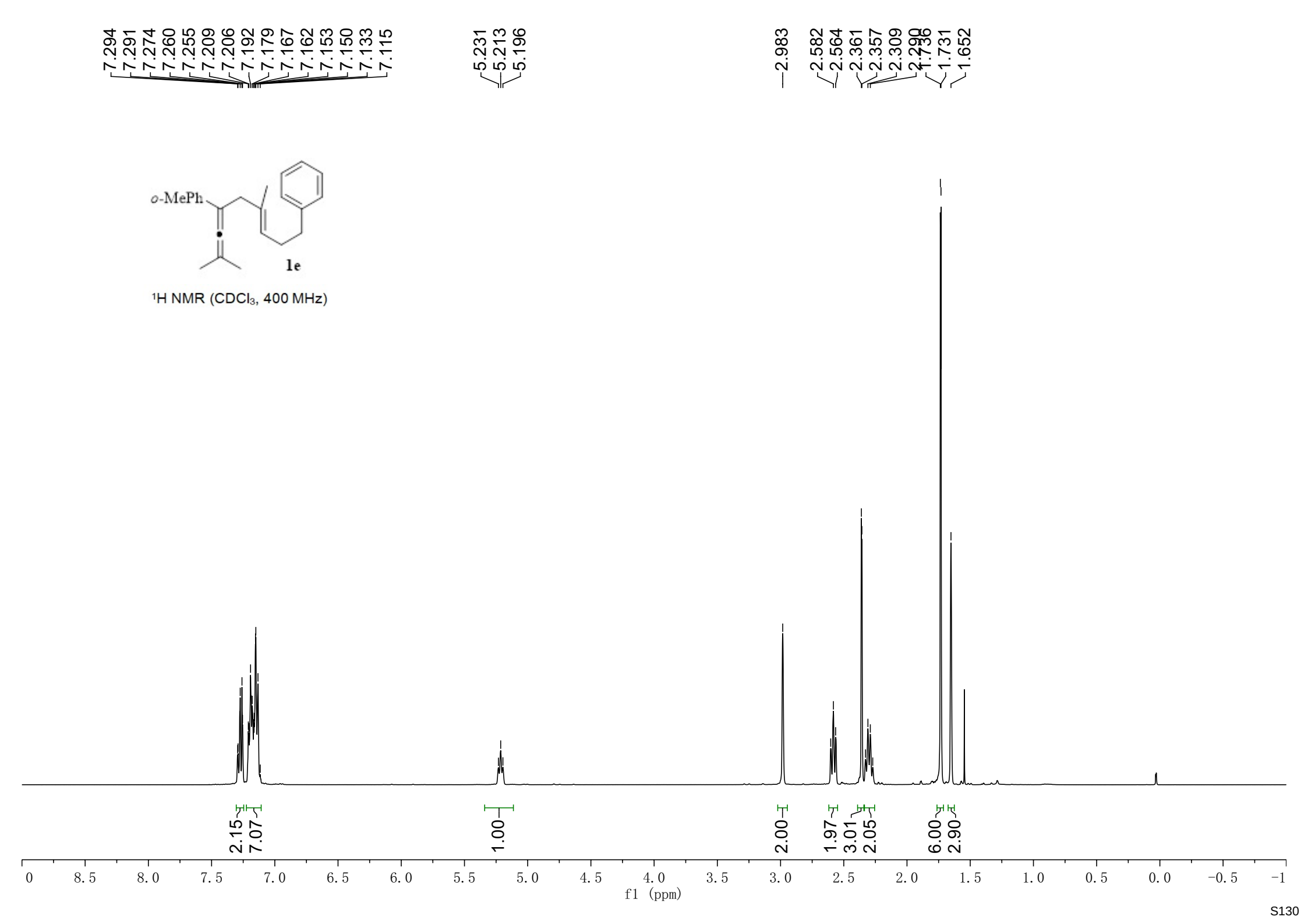
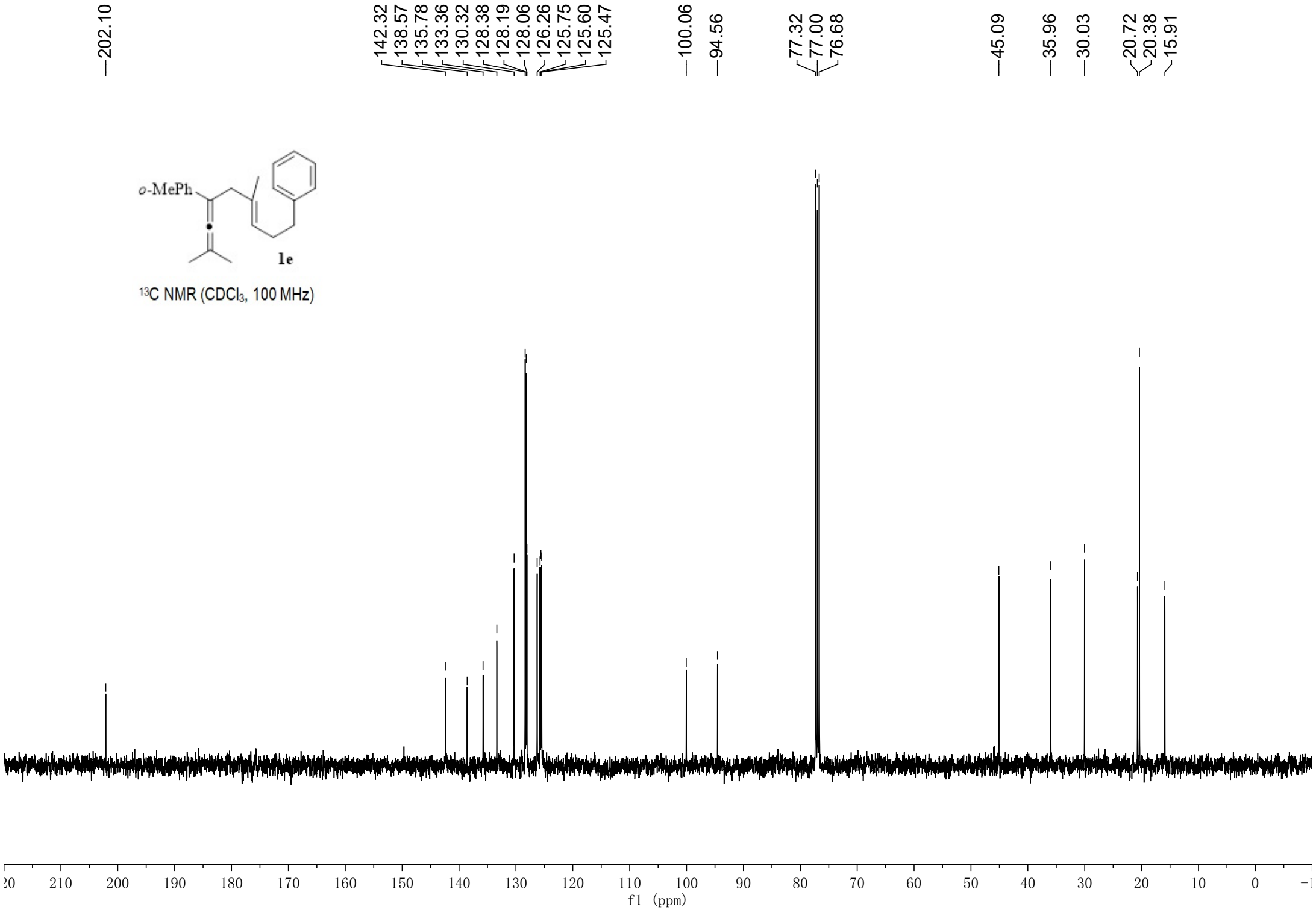
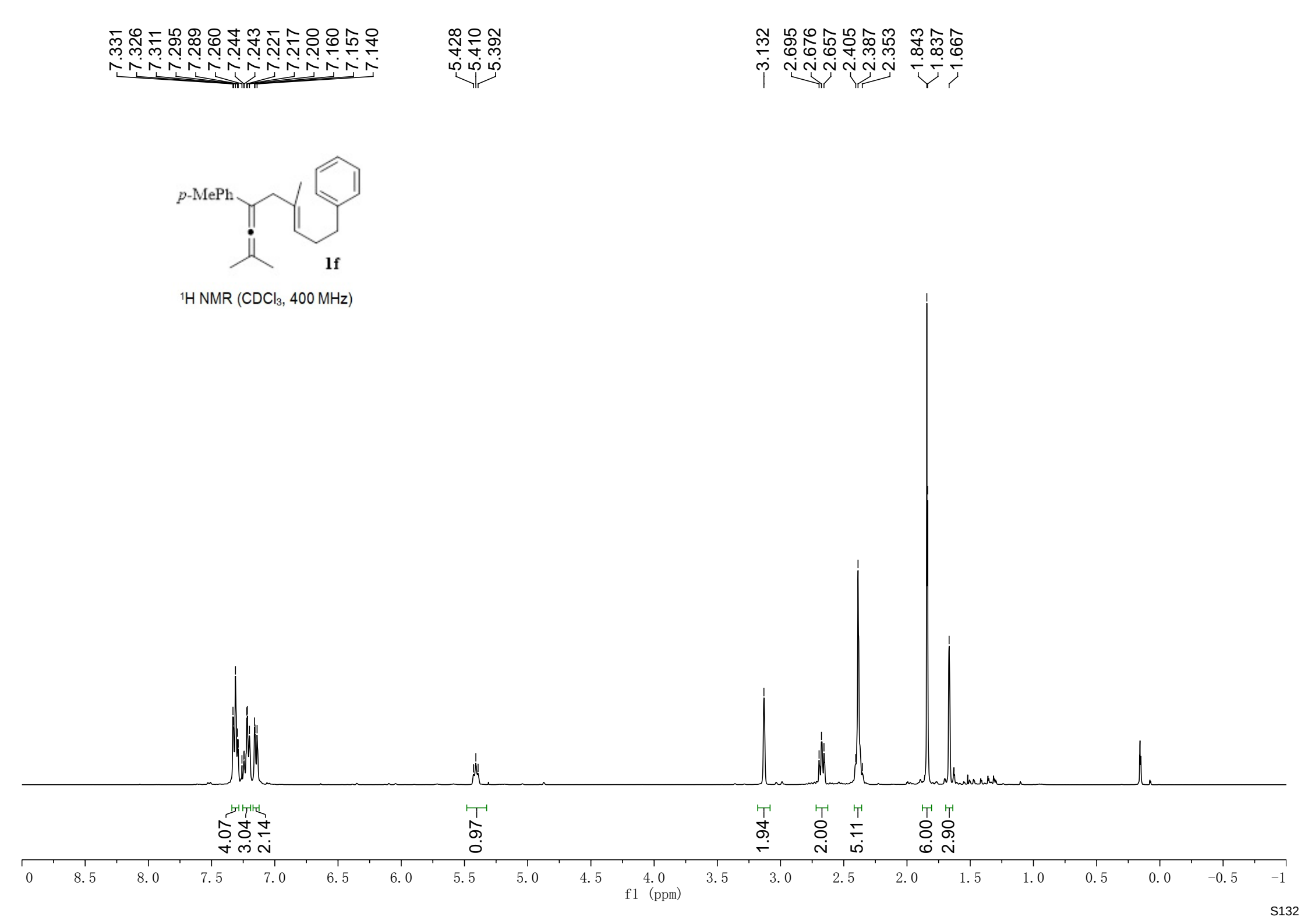
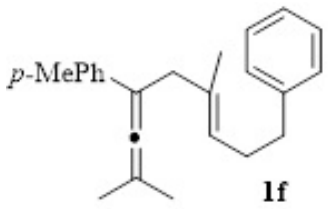
30.00
17.78
15.72
Ph
H
1d
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.294
7.291
7.274
7.260
7.255
7.209
7.206
7.192
7.179
7.167
7.162
7.153
7.150
7.133
7.115
5.231
5.213
5.196
2.983
2.582
2.564
2.361
2.357
2.309
1.736
1.731
1.652
o-MePh
1e
¹H NMR (CDCl₃, 400 MHz)
2.15
7.07
1.00
2.00
1.97
3.01
2.05
6.00
2.90
f1 (ppm)


202.10
142.32
138.57
135.78
133.36
130.32
128.38
128.19
128.06
126.26
125.75
125.60
125.47
100.06
94.56
77.32
77.00
76.68
45.09
35.96
30.03
20.72
20.38
15.91
o-MePh
1e
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

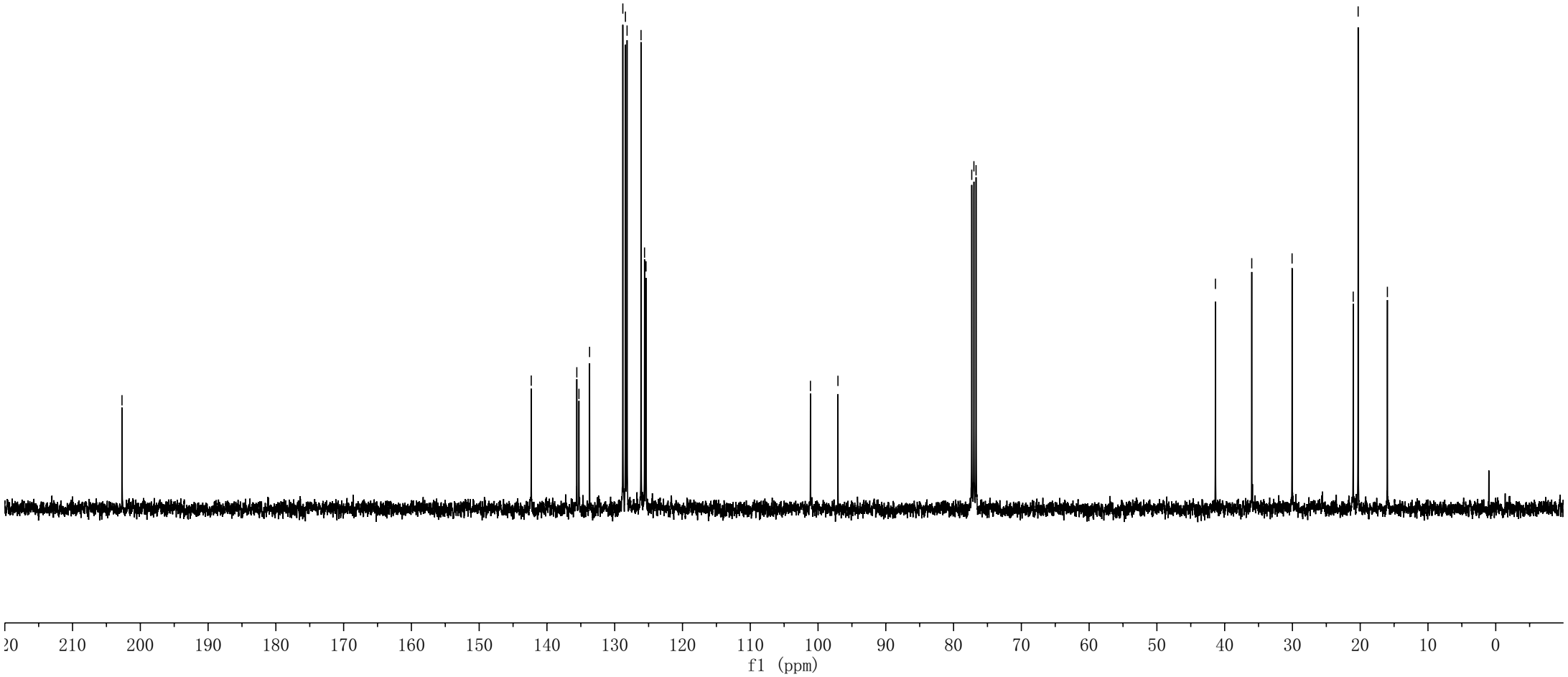

7.331
7.326
7.311
7.295
7.289
7.260
7.244
7.243
7.221
7.217
7.200
7.160
7.157
7.140
5.428
5.410
5.392
3.132
2.695
2.676
2.657
2.405
2.387
2.353
1.843
1.837
1.667
p-MePh
1f
¹H NMR (CDCl₃, 400 MHz)
4.07
3.04
2.14
0.97
1.94
2.00
5.11
6.00
2.90
f1 (ppm)

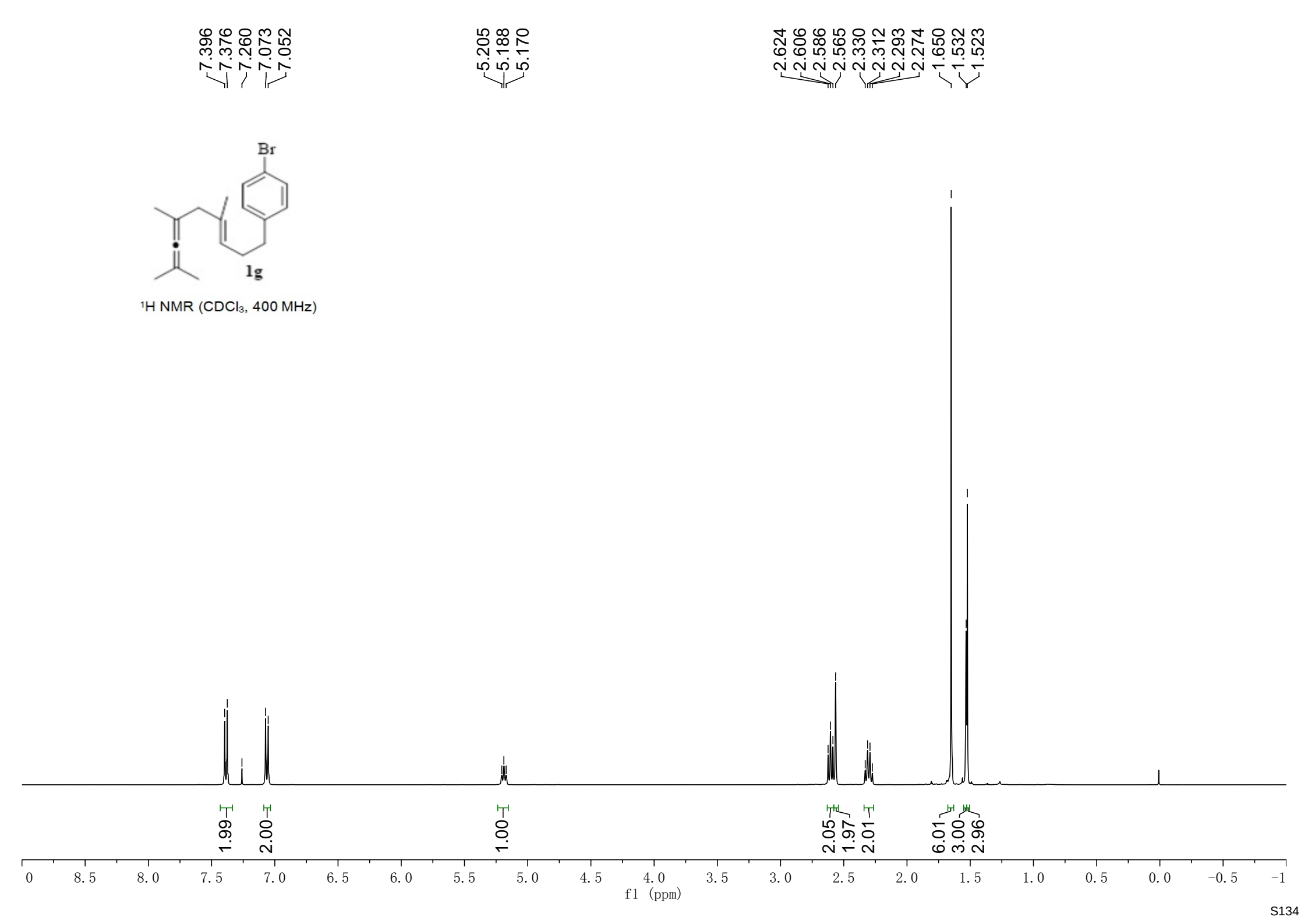
202.70
142.32
135.59
135.28
133.71
128.80
128.42
128.18
126.12
125.60
125.38
101.12
97.06
77.32
77.00
76.68
41.36
36.00
30.05
21.03
20.30
15.99

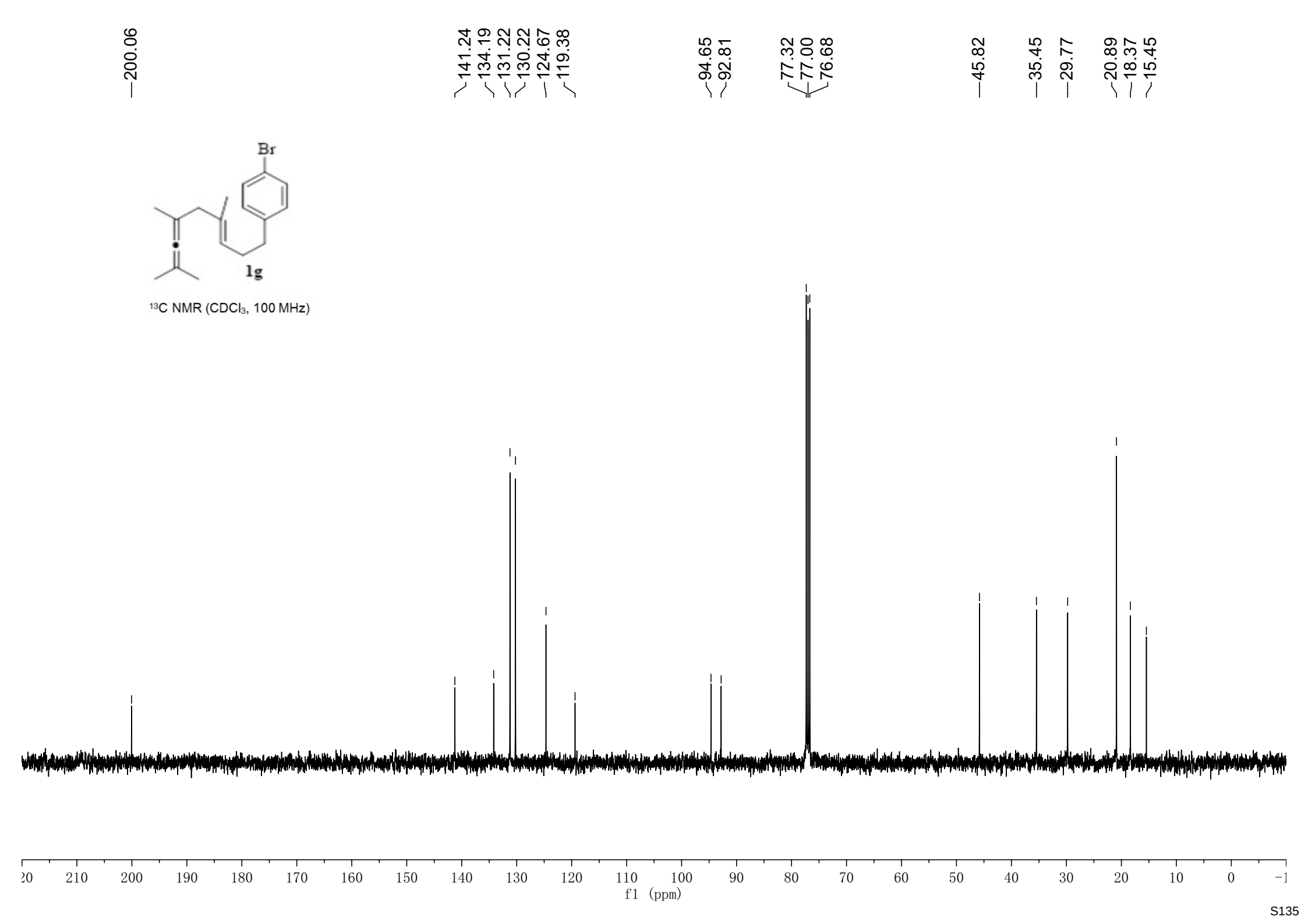


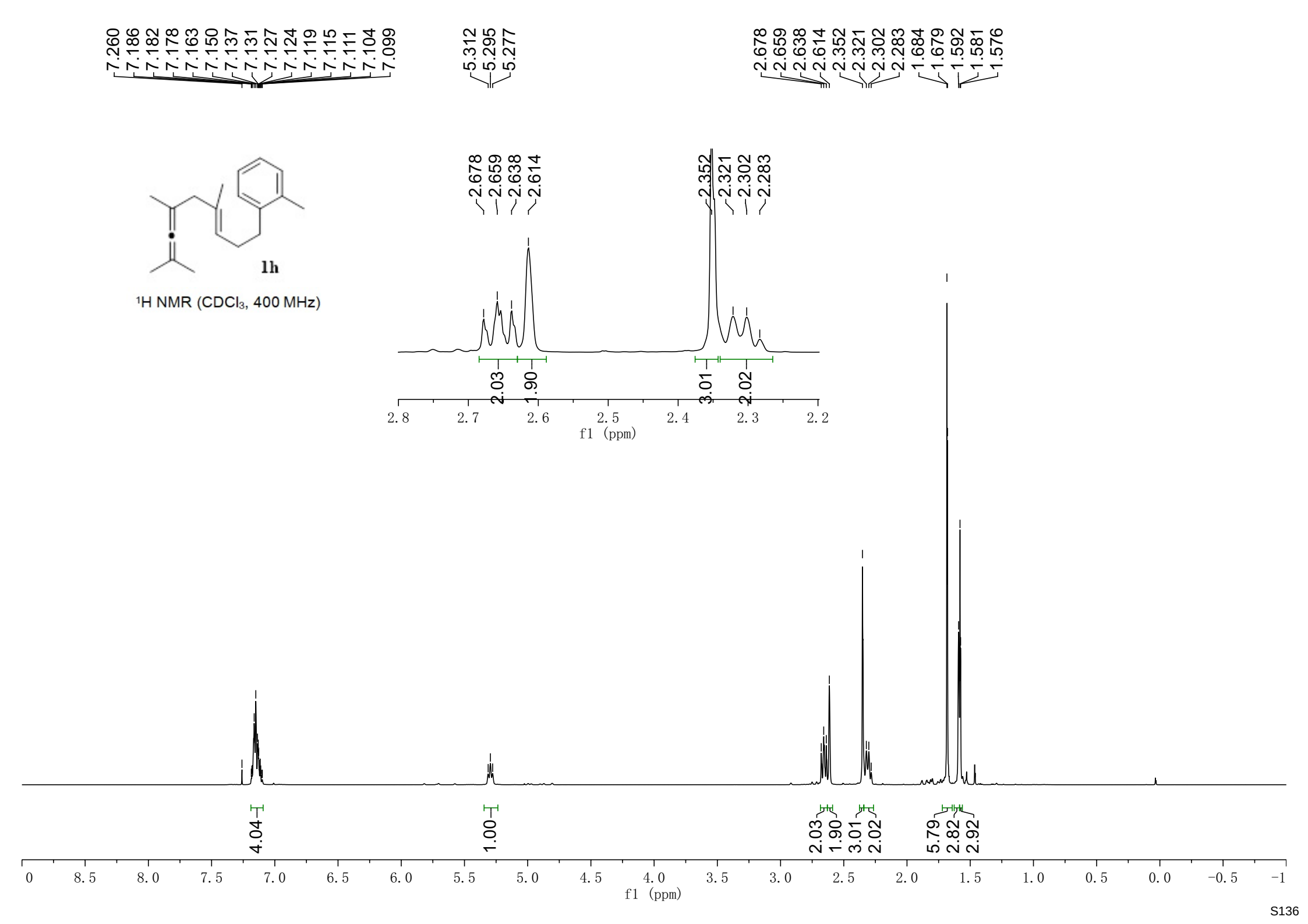
1f

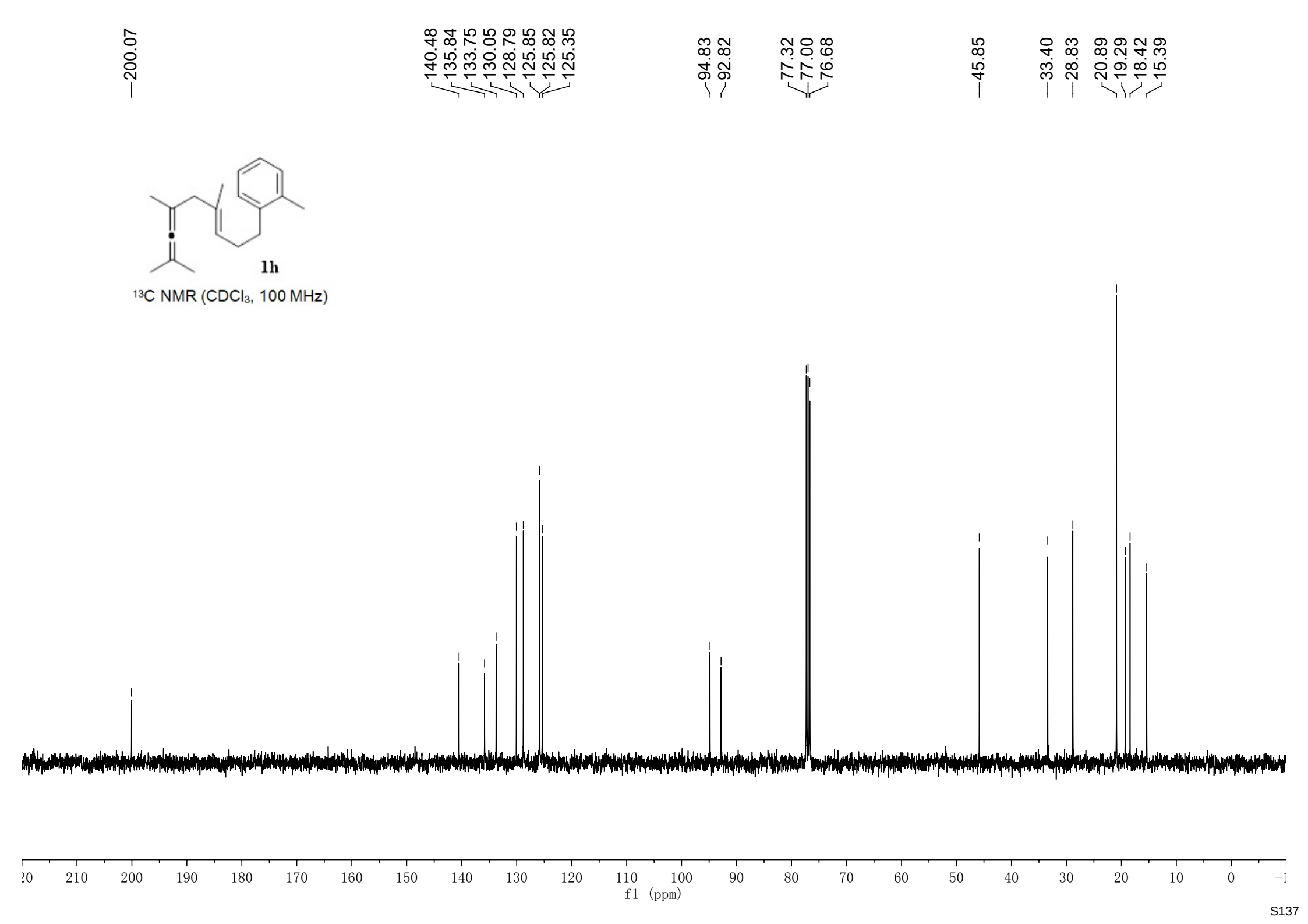
^{13}C NMR ($CDCl_3$, 100 MHz)

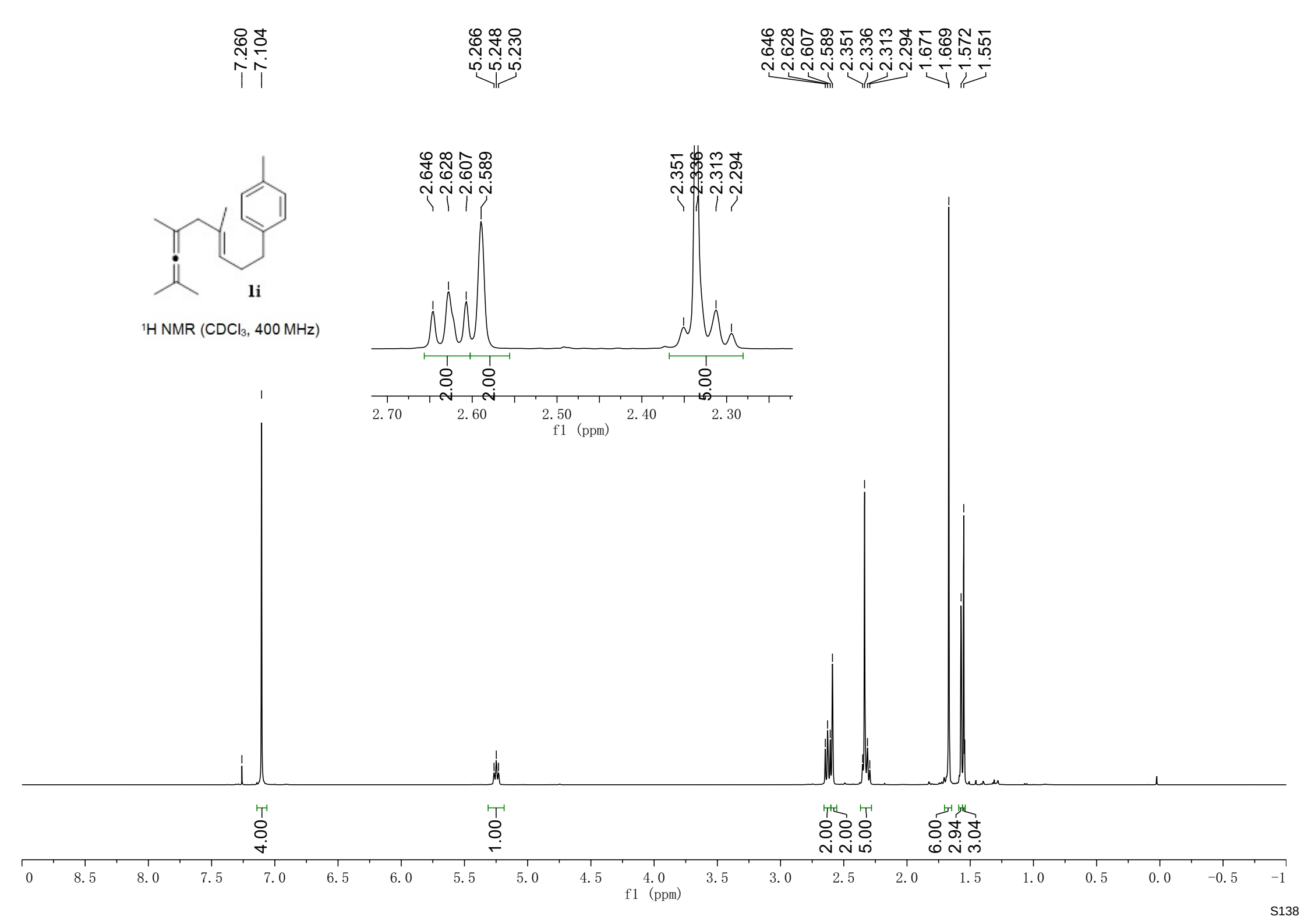


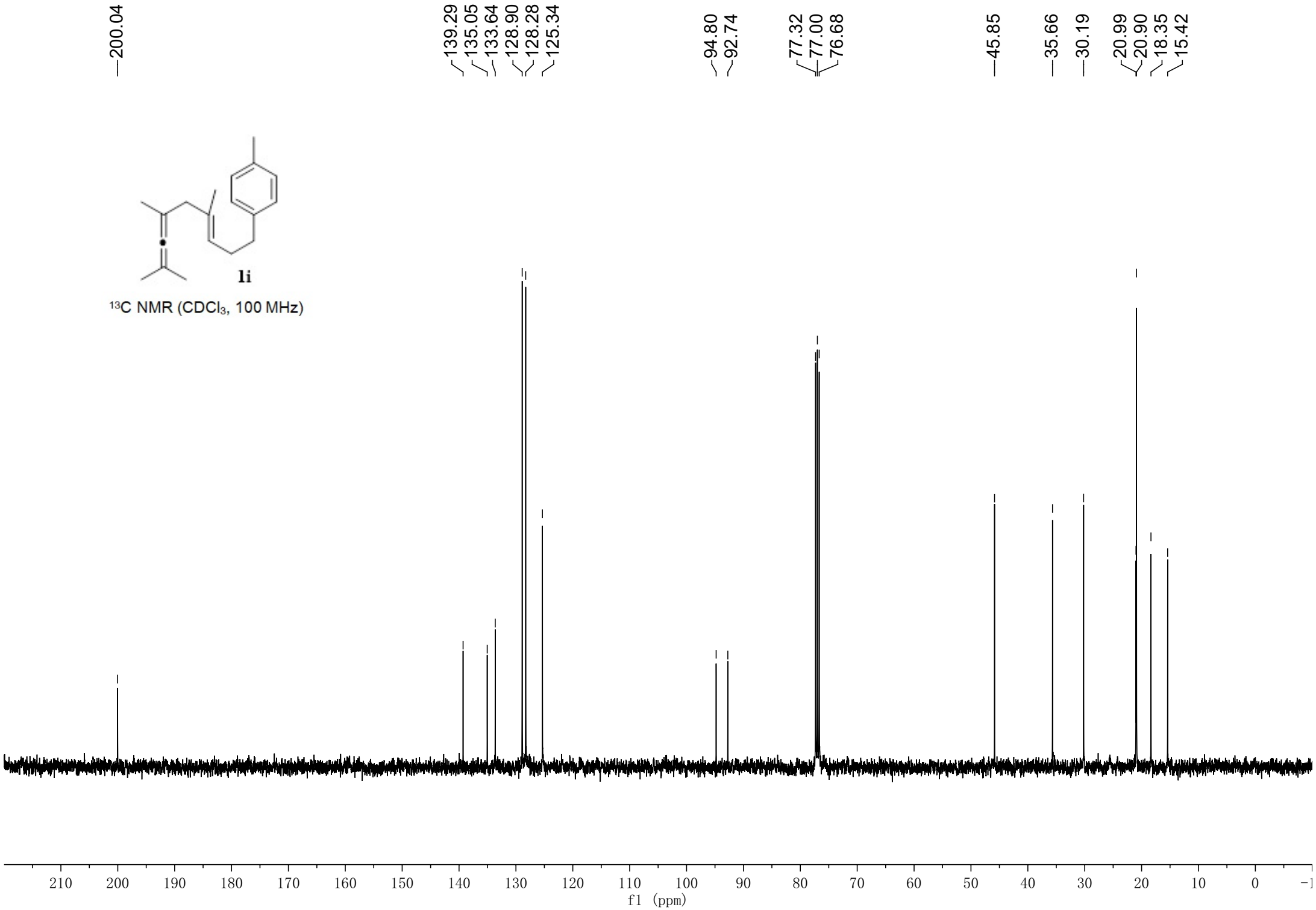

7.396
7.376
7.260
7.073
7.052
5.205
5.188
5.170
2.624
2.606
2.586
2.565
2.330
2.312
2.293
2.274
1.650
1.532
1.523
Br
1g
1H NMR (CDCl3, 400 MHz)
1.99
2.00
1.00
2.05
1.97
2.01
6.01
3.00
2.96
f1 (ppm)

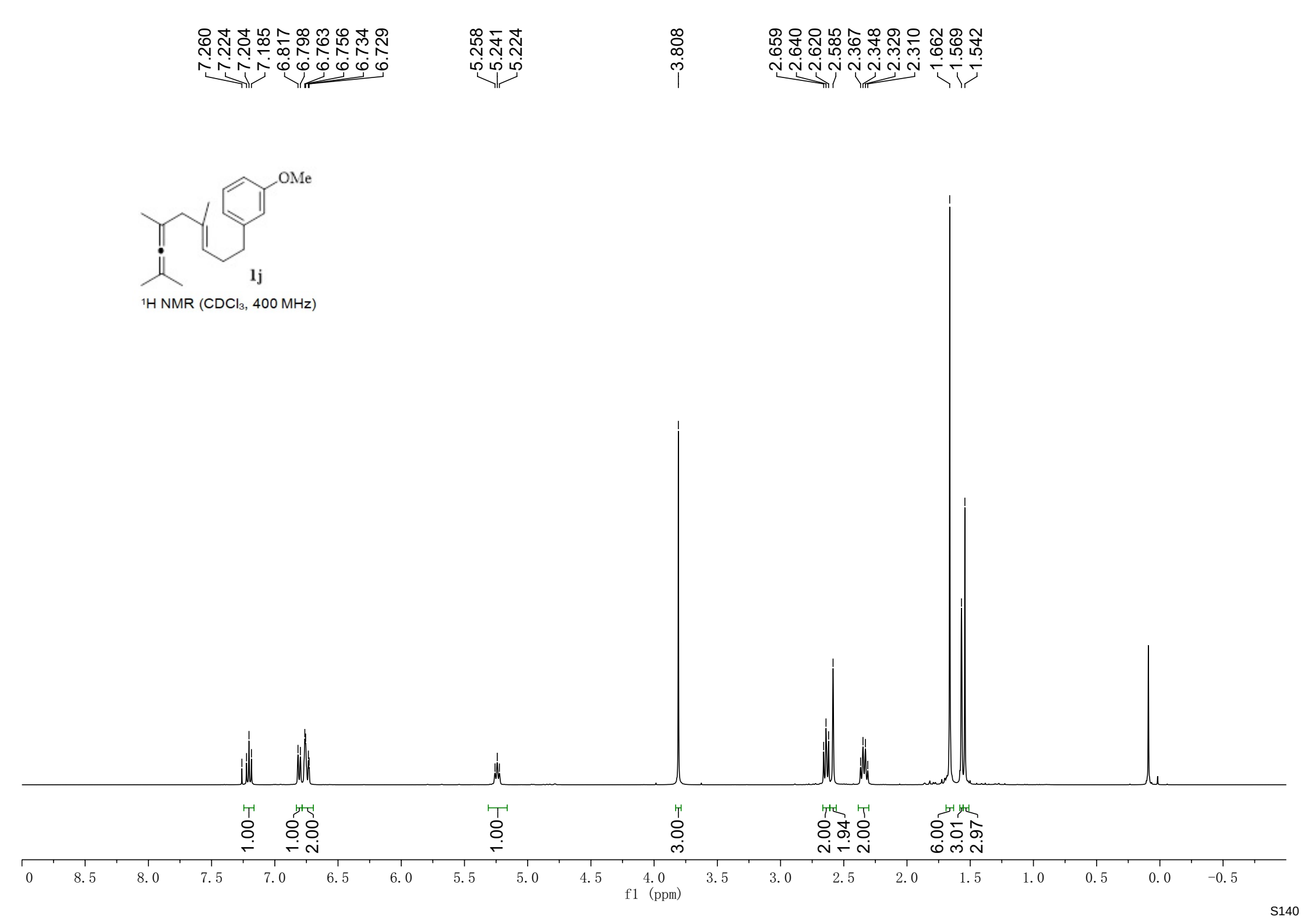

200.06
141.24
134.19
131.22
130.22
124.67
119.38
94.65
92.81
77.32
77.00
76.68
45.82
35.45
29.77
20.89
18.37
15.45
Br
1g
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

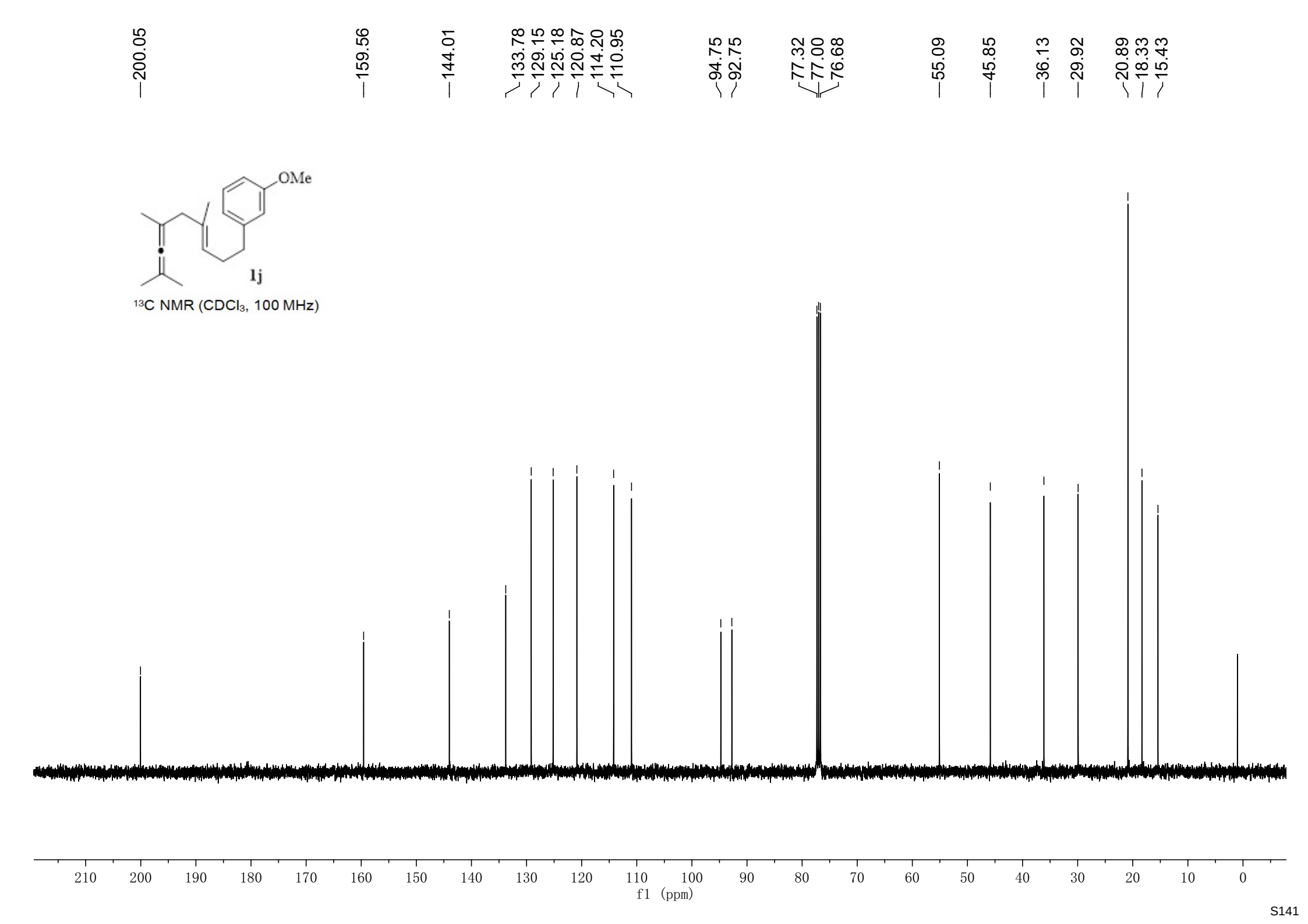

7.260
7.186
7.182
7.178
7.163
7.150
7.137
7.131
7.127
7.124
7.119
7.115
7.111
7.104
7.099
5.312
5.295
5.277
2.678
2.659
2.638
2.614
2.352
2.321
2.302
2.283
1.684
1.679
1.592
1.581
1.576
1h
1H NMR (CDCl3, 400 MHz)
2.03
1.90
3.01
2.02
f1 (ppm)
4.04
1.00
2.03
1.90
3.01
2.02
5.79
2.82
2.92
f1 (ppm)

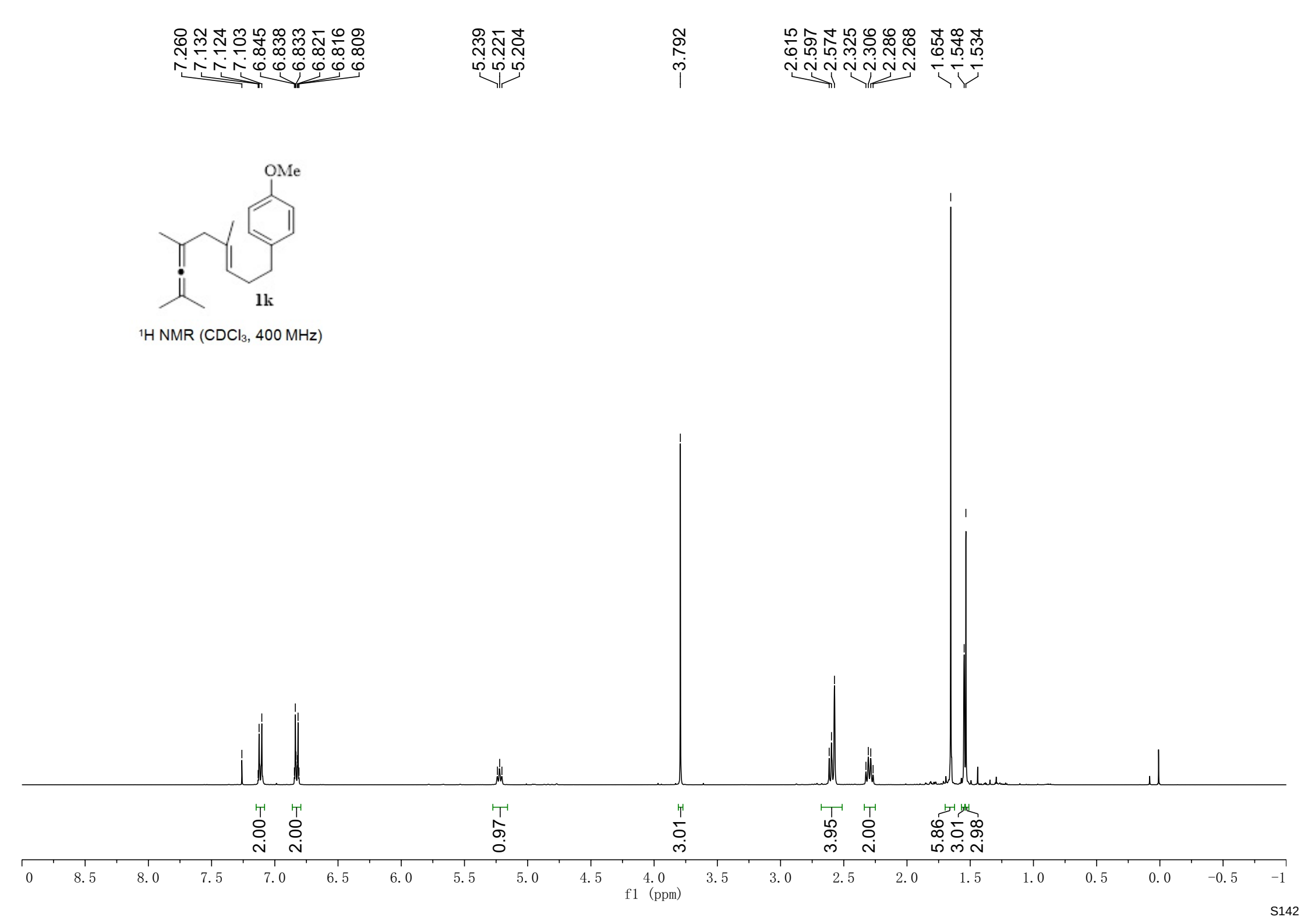

200.07
140.48
135.84
133.75
130.05
128.79
125.85
125.82
125.35
94.83
92.82
77.32
77.00
76.68
45.85
33.40
28.83
20.89
19.29
18.42
15.39
1h
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

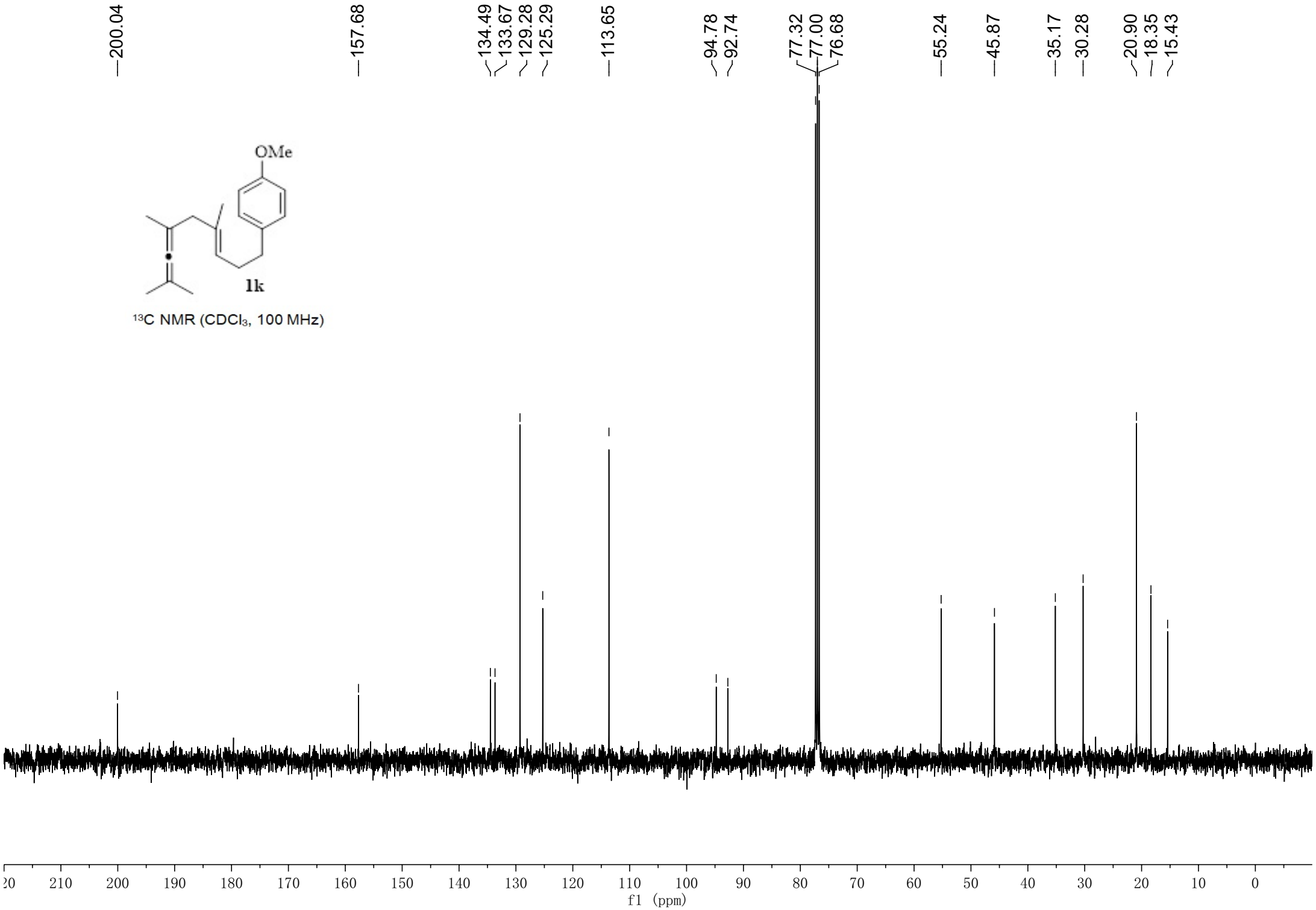

7.260
7.104
5.266
5.248
5.230
2.646
2.628
2.607
2.589
2.351
2.336
2.313
2.294
1.671
1.669
1.572
1.551
1i
^{1}H NMR ($CDCl_3$, 400 MHz)
2.00
2.00
5.00
2.70
2.60
2.50
2.40
2.30
f1 (ppm)
4.00
1.00
2.00
2.00
5.00
6.00
2.94
3.04
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)

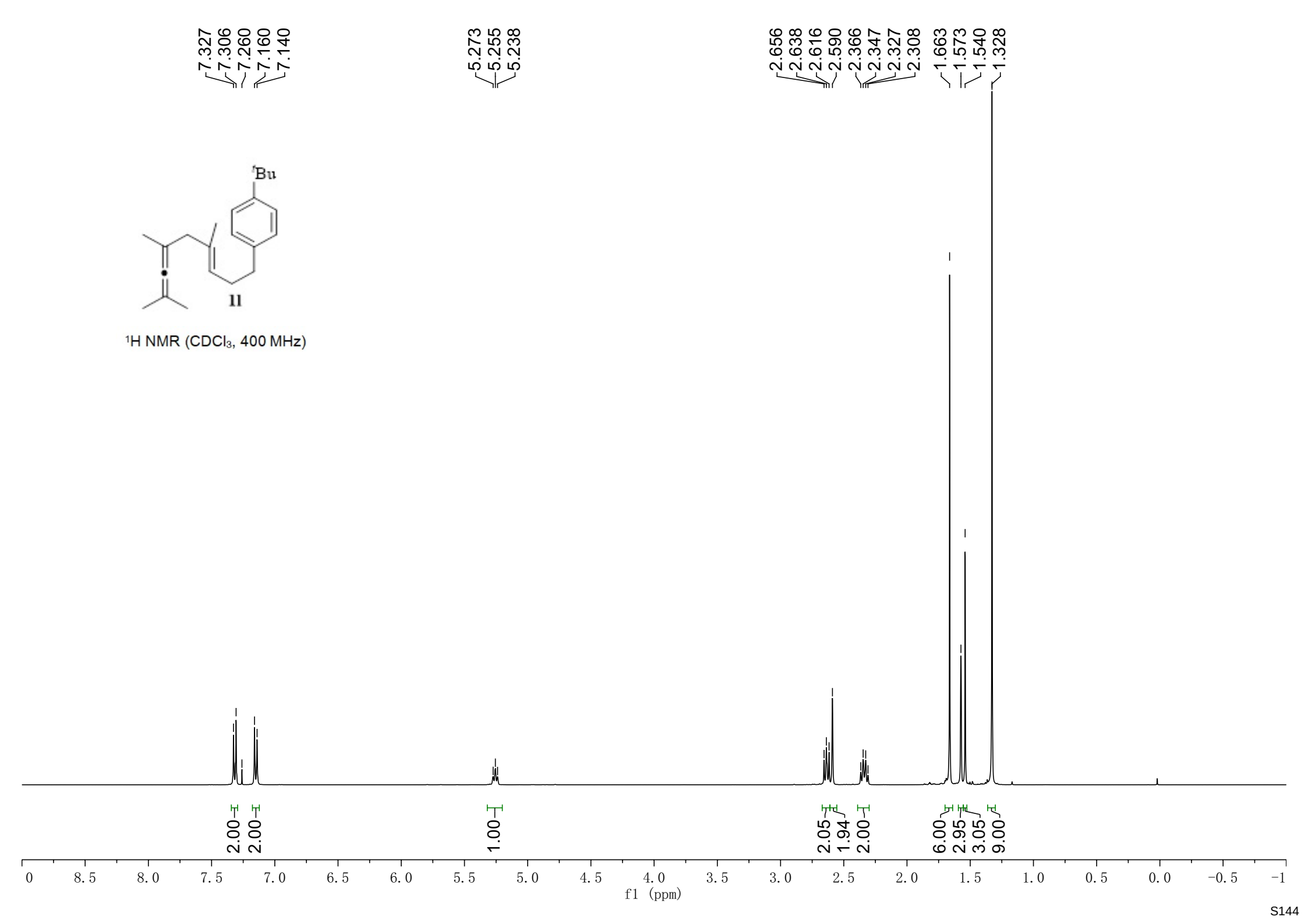

200.04
139.29
135.05
133.64
128.90
128.28
125.34
94.80
92.74
77.32
77.00
76.68
45.85
35.66
30.19
20.99
20.90
18.35
15.42
1i
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

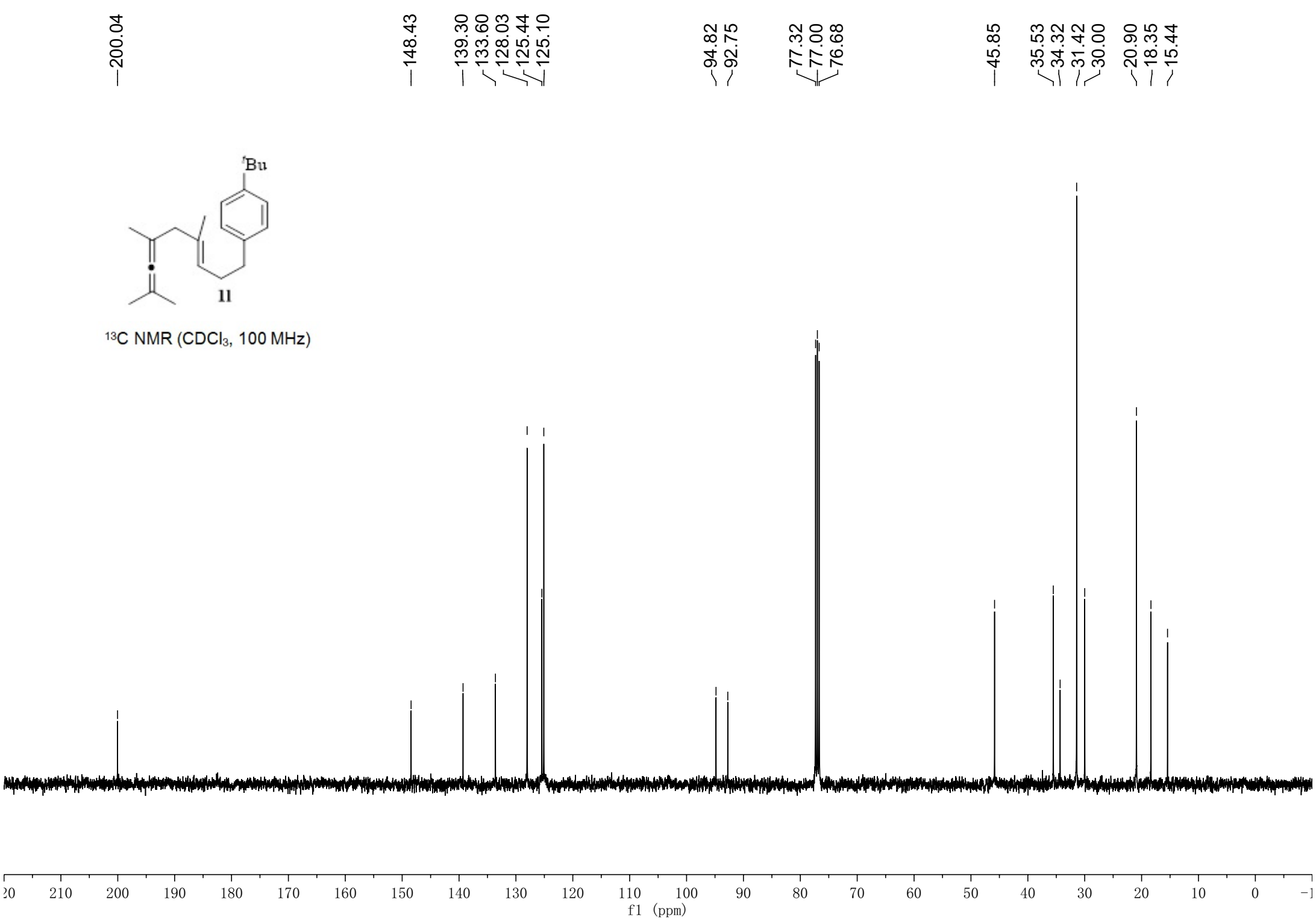

7.260
7.224
7.204
7.185
6.817
6.798
6.763
6.756
6.734
6.729
5.258
5.241
5.224
3.808
2.659
2.640
2.620
2.585
2.367
2.348
2.329
2.310
1.662
1.569
1.542
OMe
1j
1H NMR (CDCl3, 400 MHz)
1.00
1.00
2.00
1.00
3.00
2.00
1.94
2.00
6.00
3.01
2.97
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

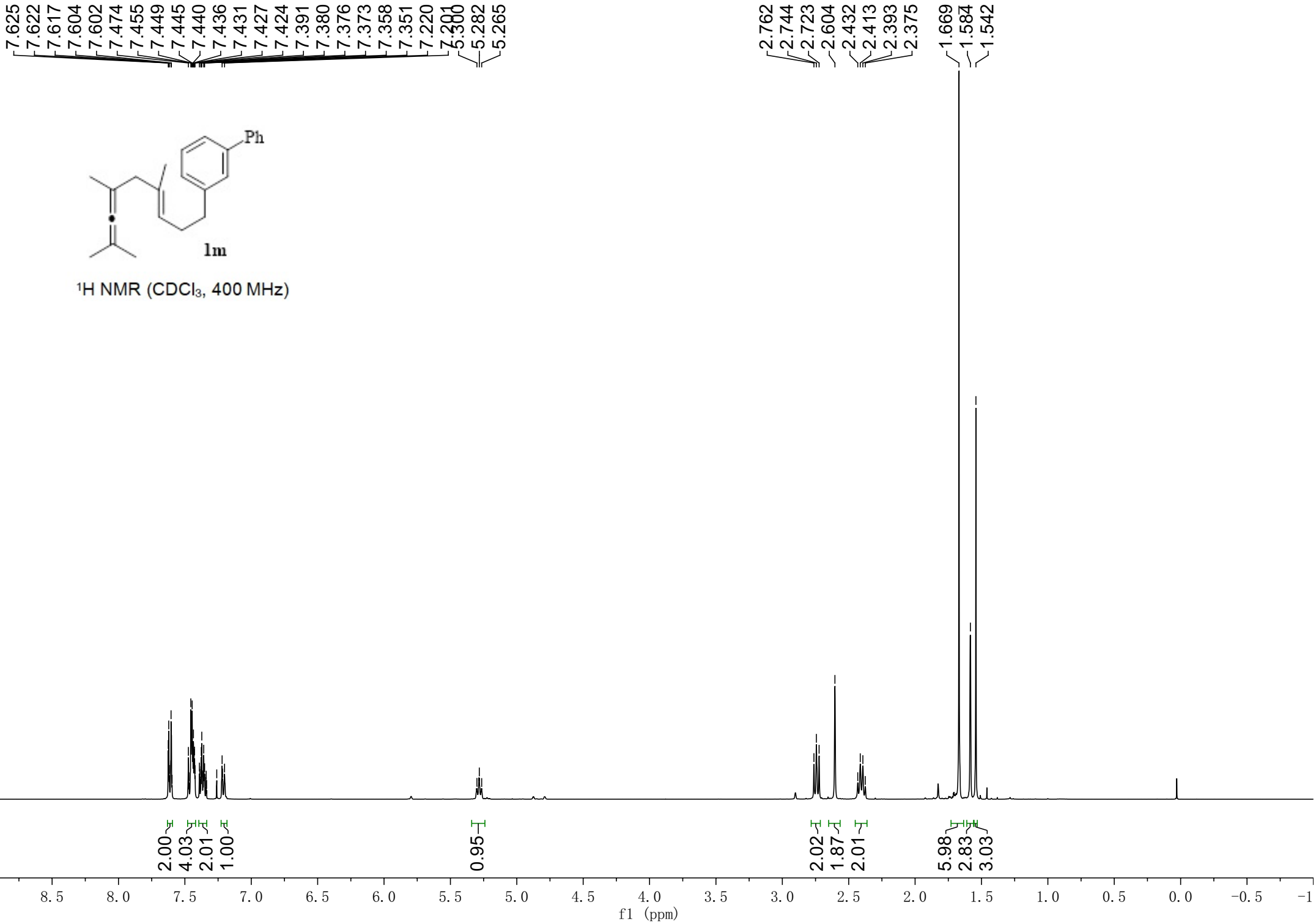

200.05
159.56
144.01
133.78
129.15
125.18
120.87
114.20
110.95
94.75
92.75
77.32
77.00
76.68
55.09
45.85
36.13
29.92
20.89
18.33
15.43
OMe
1j
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.260
7.132
7.124
7.103
6.845
6.838
6.833
6.821
6.816
6.809
5.239
5.221
5.204
3.792
2.615
2.597
2.574
2.325
2.306
2.286
2.268
1.654
1.548
1.534
OMe
1k
¹H NMR (CDCl₃, 400 MHz)
2.00
2.00
0.97
3.01
3.95
2.00
5.86
3.01
2.98
f1 (ppm)

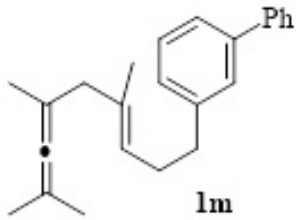

200.04
157.68
134.49
133.67
129.28
125.29
113.65
94.78
92.74
77.32
77.00
76.68
55.24
45.87
35.17
30.28
20.90
18.35
15.43
OMe
1k
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.327
7.306
7.260
7.160
7.140
5.273
5.255
5.238
2.656
2.638
2.616
2.590
2.366
2.347
2.327
2.308
1.663
1.573
1.540
1.328
tBu
11
1H NMR (CDCl3, 400 MHz)
2.00
2.00
1.00
2.05
1.94
2.00
6.00
2.95
3.05
9.00
f1 (ppm)


200.04
148.43
139.30
133.60
128.03
125.44
125.10
94.82
92.75
77.32
77.00
76.68
45.85
35.53
34.32
31.42
30.00
20.90
18.35
15.44
tBu
11
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

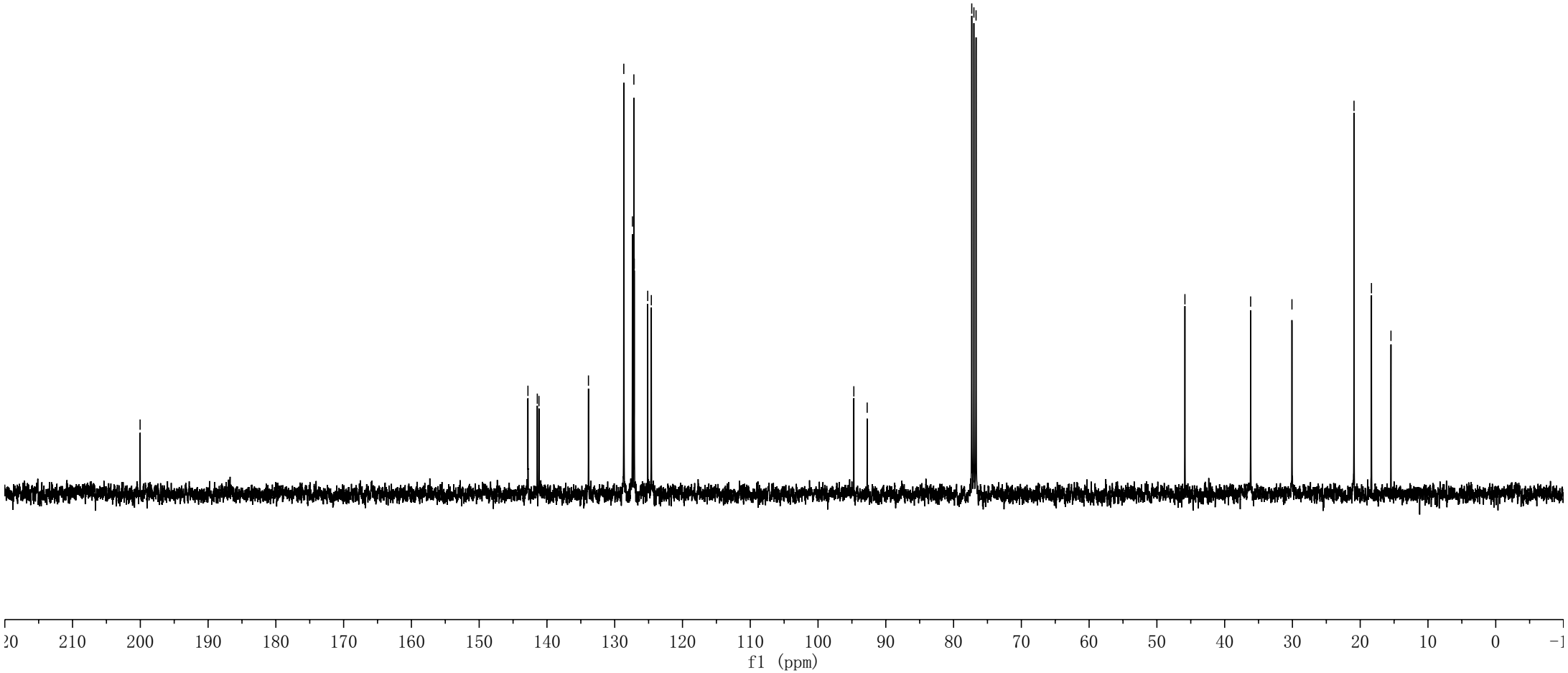

7.625
7.622
7.617
7.604
7.602
7.474
7.455
7.449
7.445
7.440
7.436
7.431
7.427
7.424
7.391
7.380
7.376
7.373
7.358
7.351
7.220
7.201
5.300
5.282
5.265
2.762
2.744
2.723
2.604
2.432
2.413
2.393
2.375
1.669
1.584
1.542
Ph
1m
^{1}H NMR ($CDCl_3$, 400 MHz)
2.00
4.03
2.01
1.00
0.95
2.02
1.87
2.01
5.98
2.83
3.03
f1 (ppm)

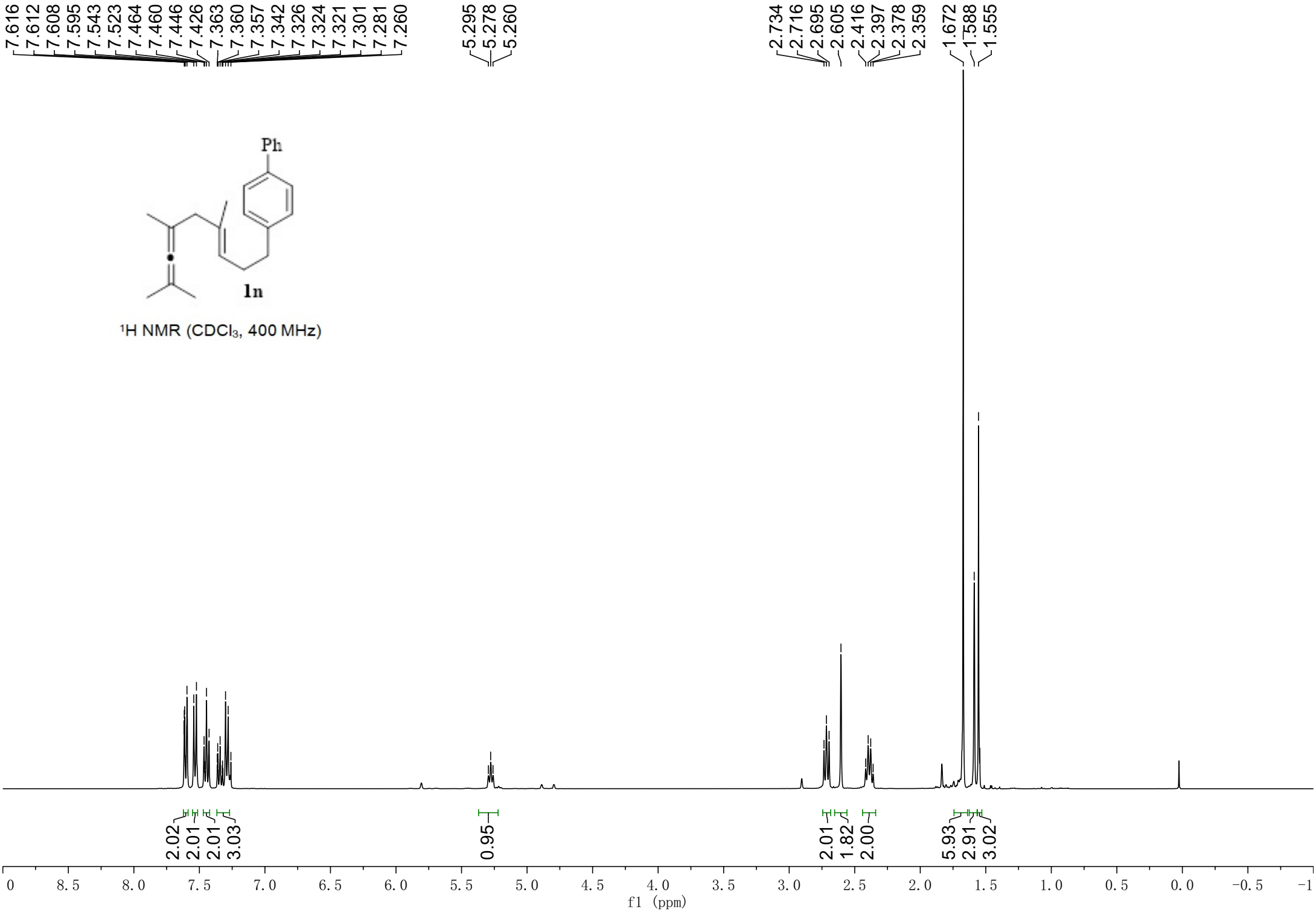
200.03
142.81
141.42
141.18
133.87
128.66
127.39
127.17
127.11
125.13
124.60
94.72
92.75
77.32
77.00
76.68
45.86
36.16
30.07
20.91
18.34
15.46

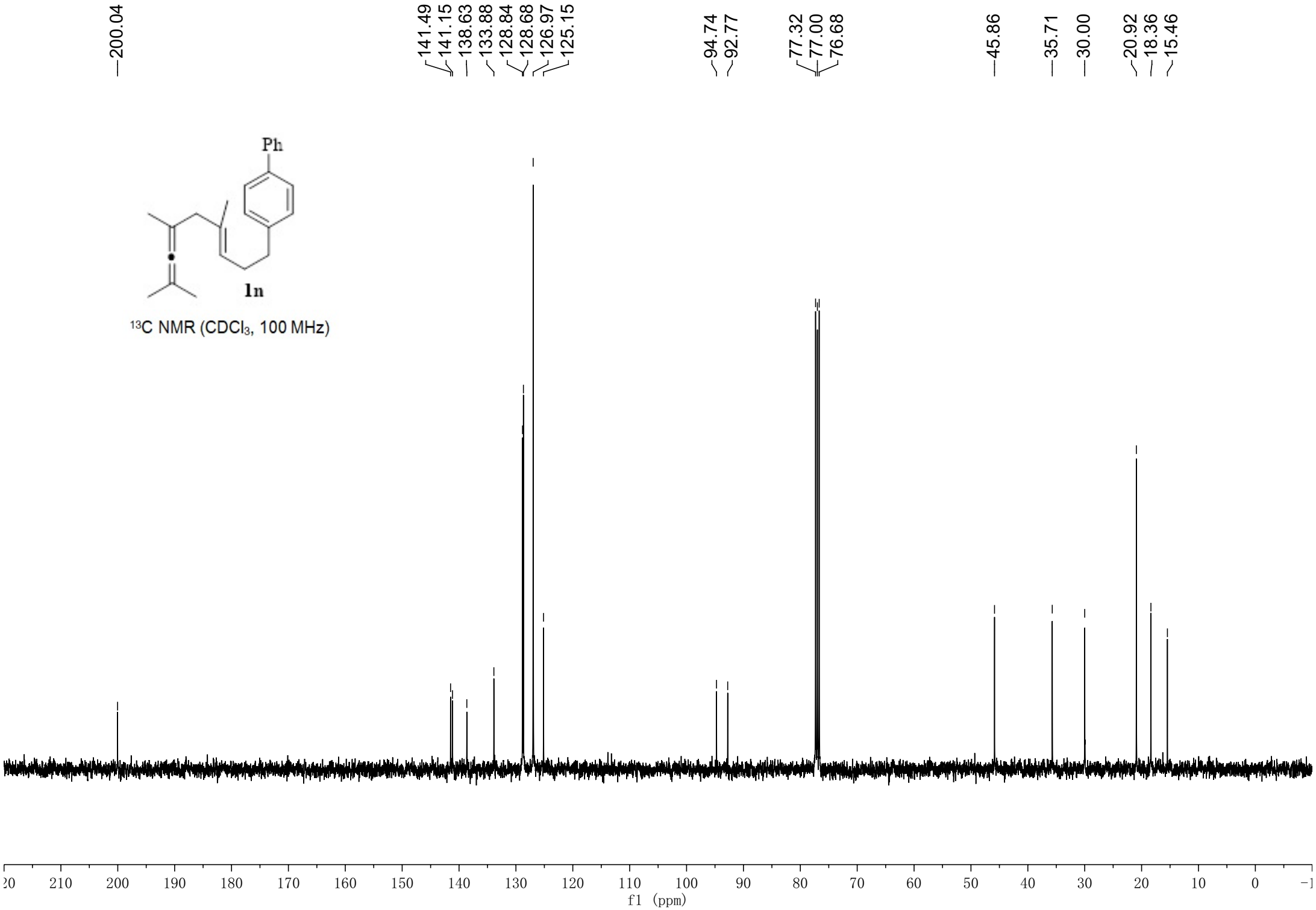


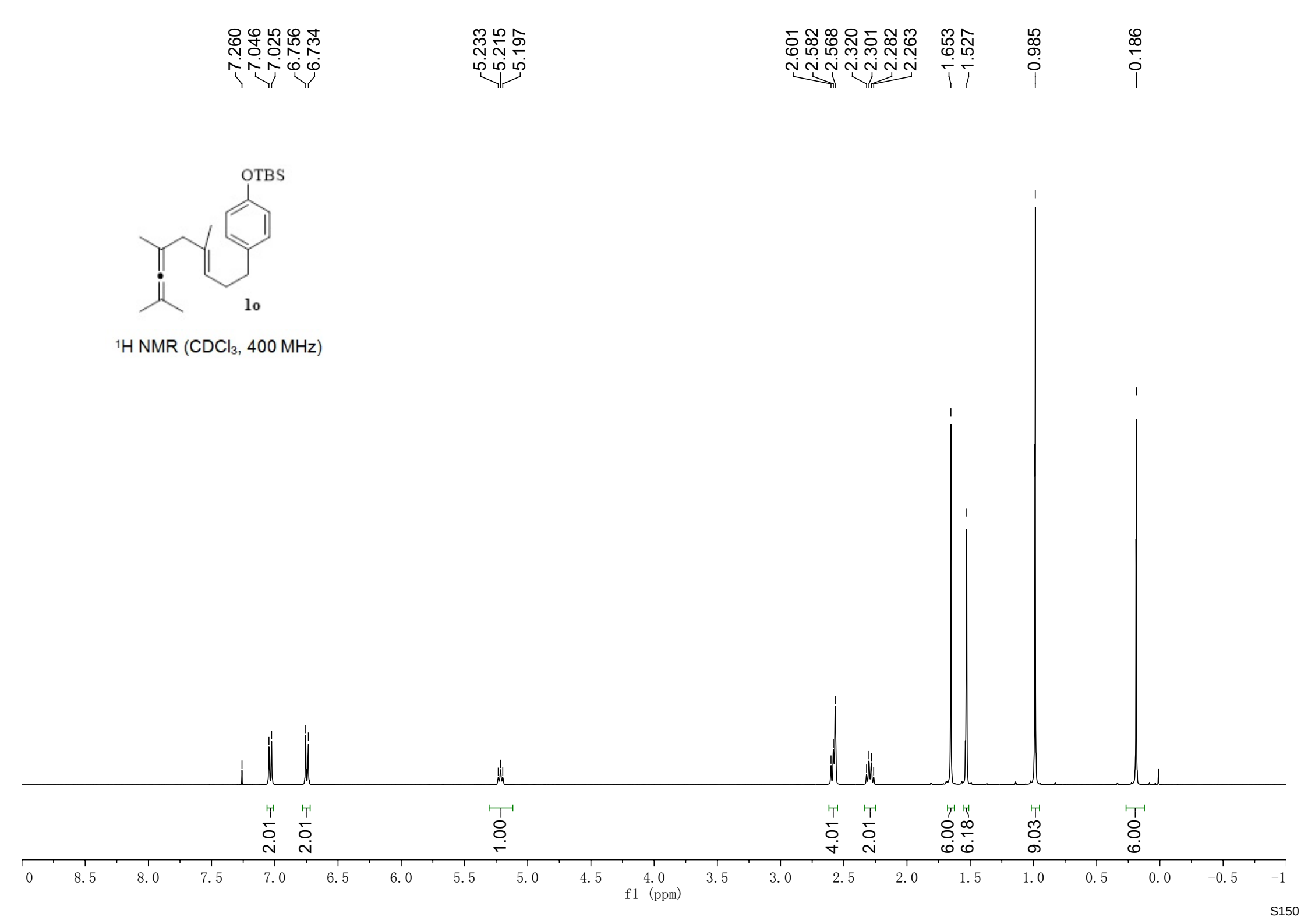
1m

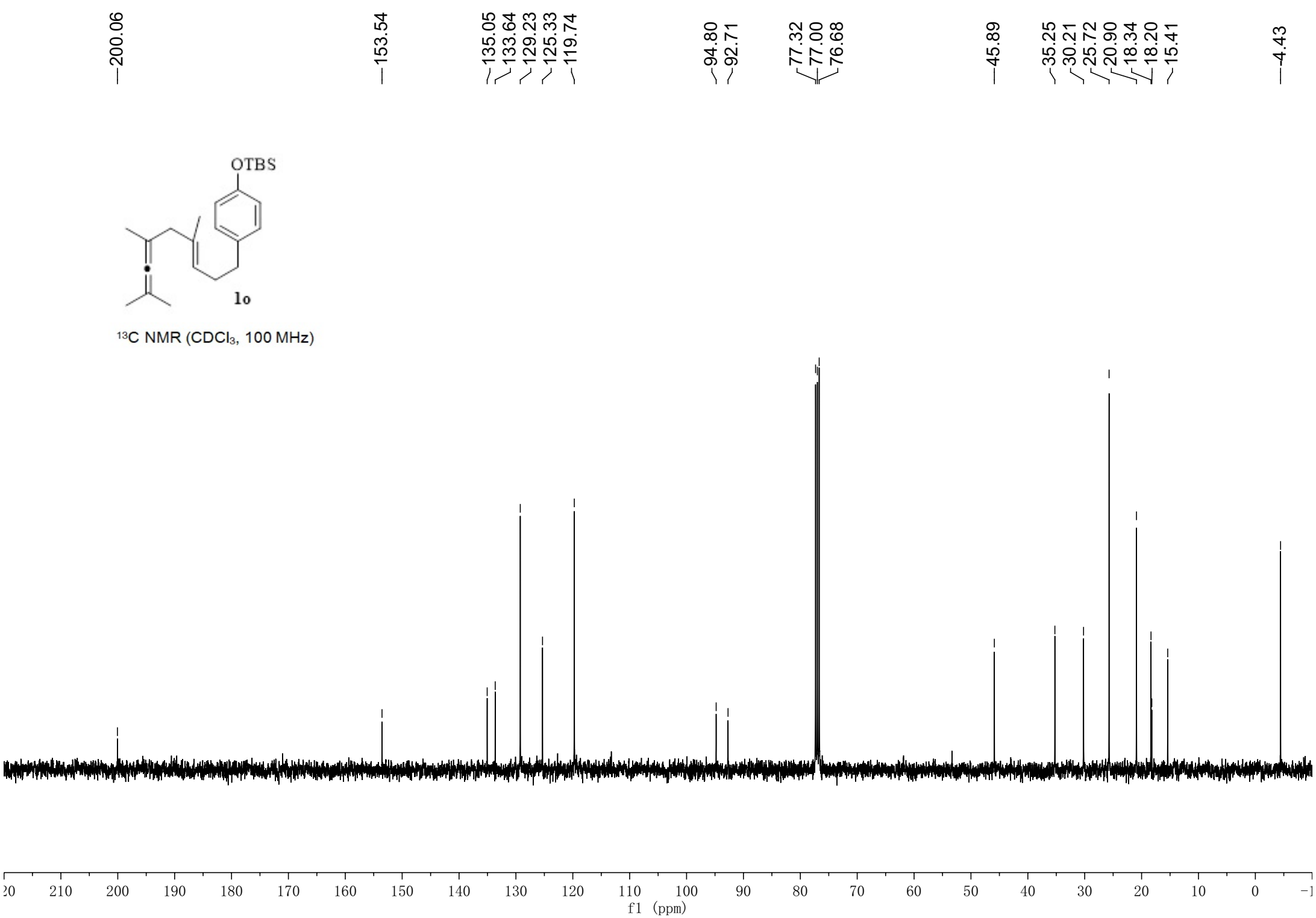
^{13}C NMR ($CDCl_3$, 100 MHz)

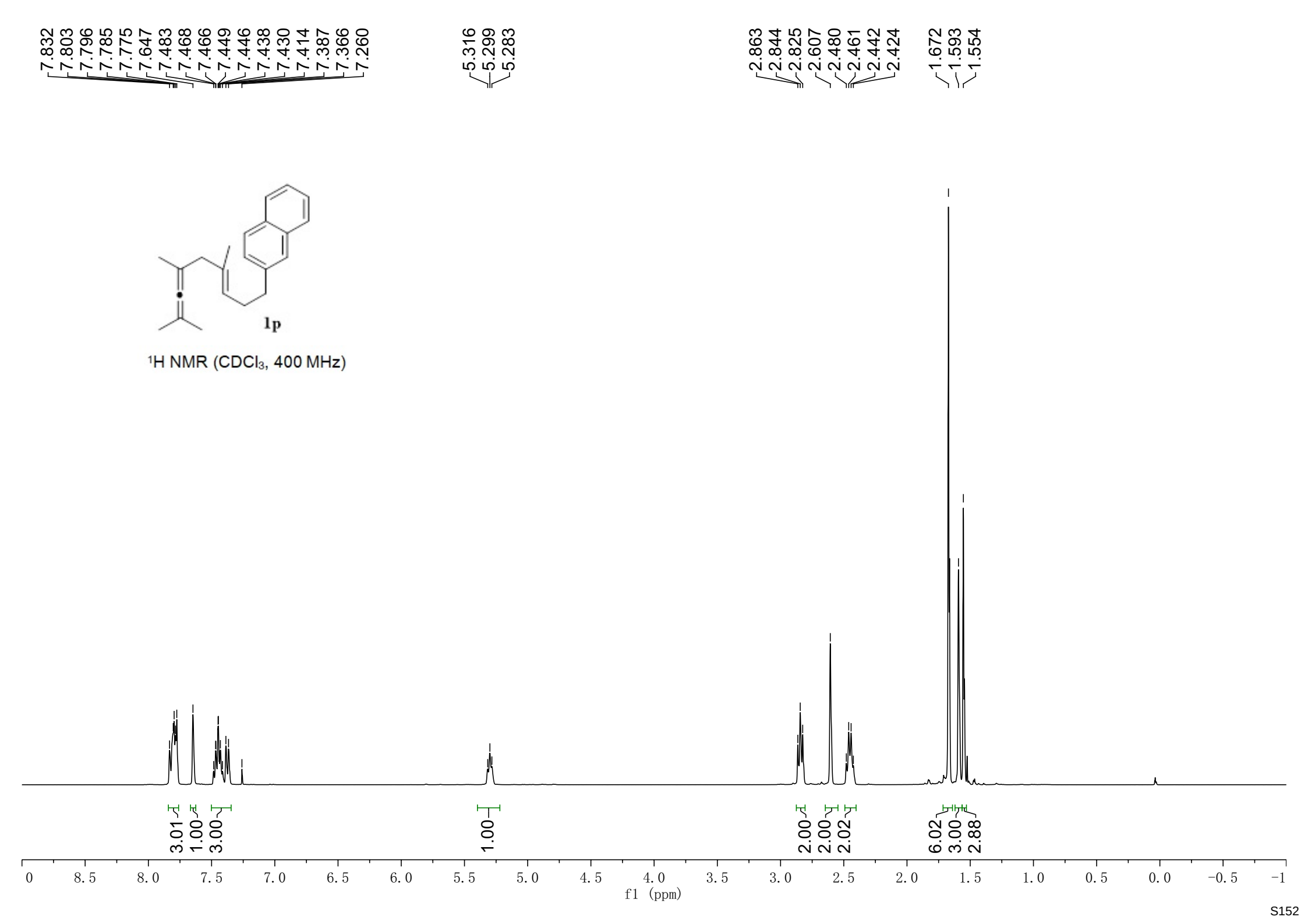


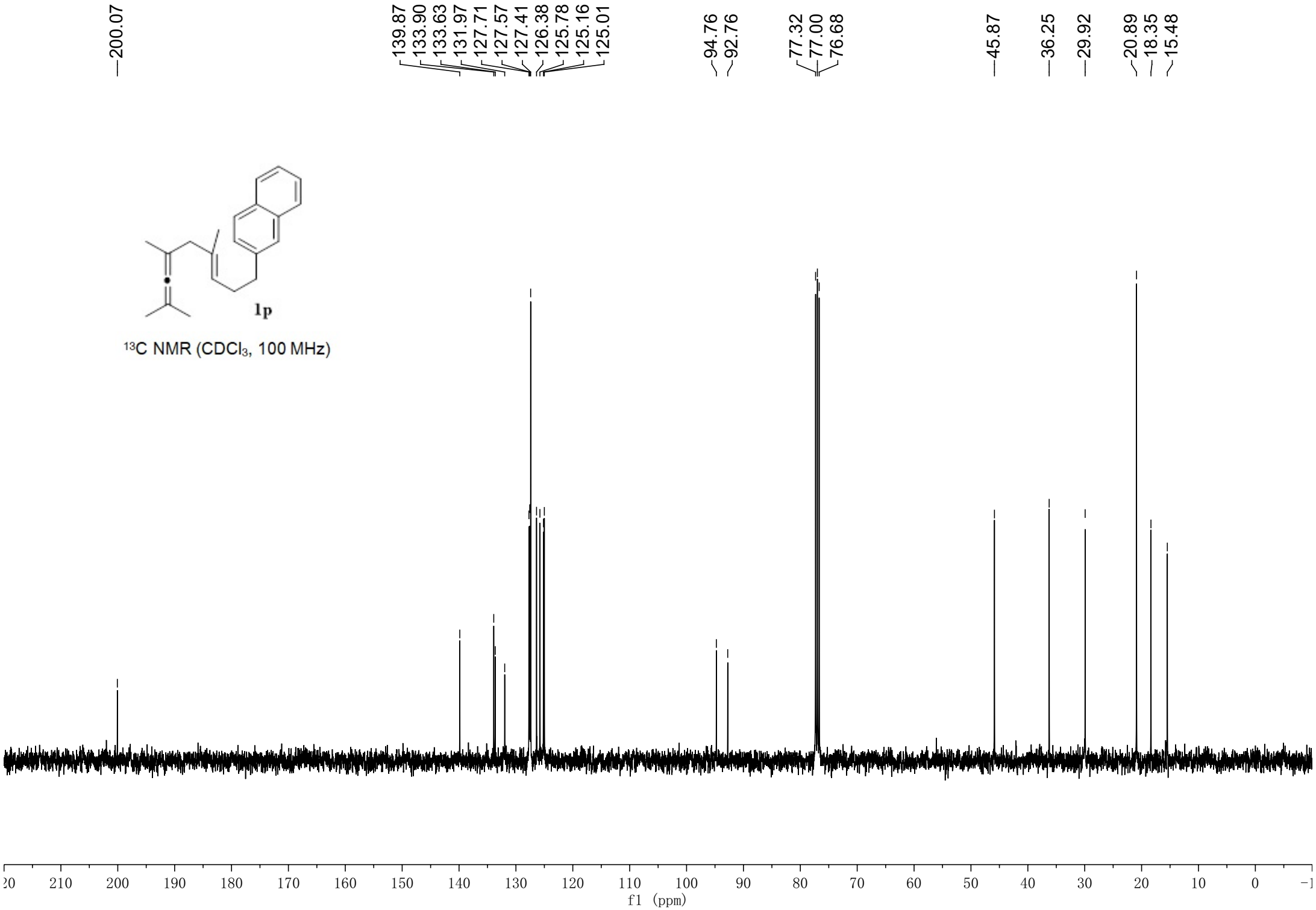

7.616
7.612
7.608
7.595
7.543
7.523
7.464
7.460
7.446
7.426
7.363
7.360
7.357
7.342
7.326
7.324
7.321
7.301
7.281
7.260
5.295
5.278
5.260
2.734
2.716
2.695
2.605
2.416
2.397
2.378
2.359
1.672
1.588
1.555
Ph
1n
¹H NMR (CDCl₃, 400 MHz)
2.02
2.01
2.01
3.03
0.95
2.01
1.82
2.00
5.93
2.91
3.02
f1 (ppm)

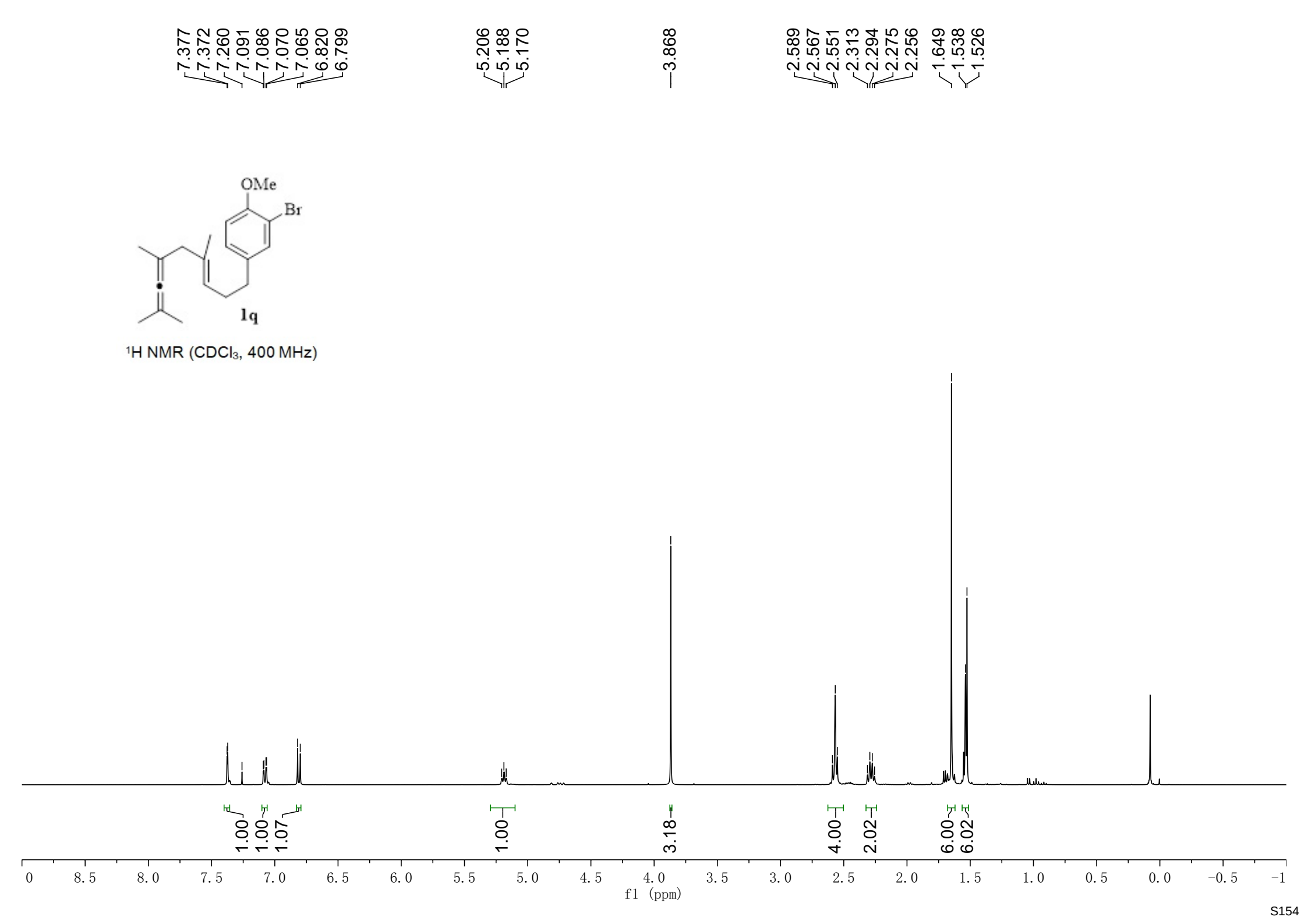

200.04
141.49
141.15
138.63
133.88
128.84
128.68
126.97
125.15
94.74
92.77
77.32
77.00
76.68
45.86
35.71
30.00
20.92
18.36
15.46
Ph
1n
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

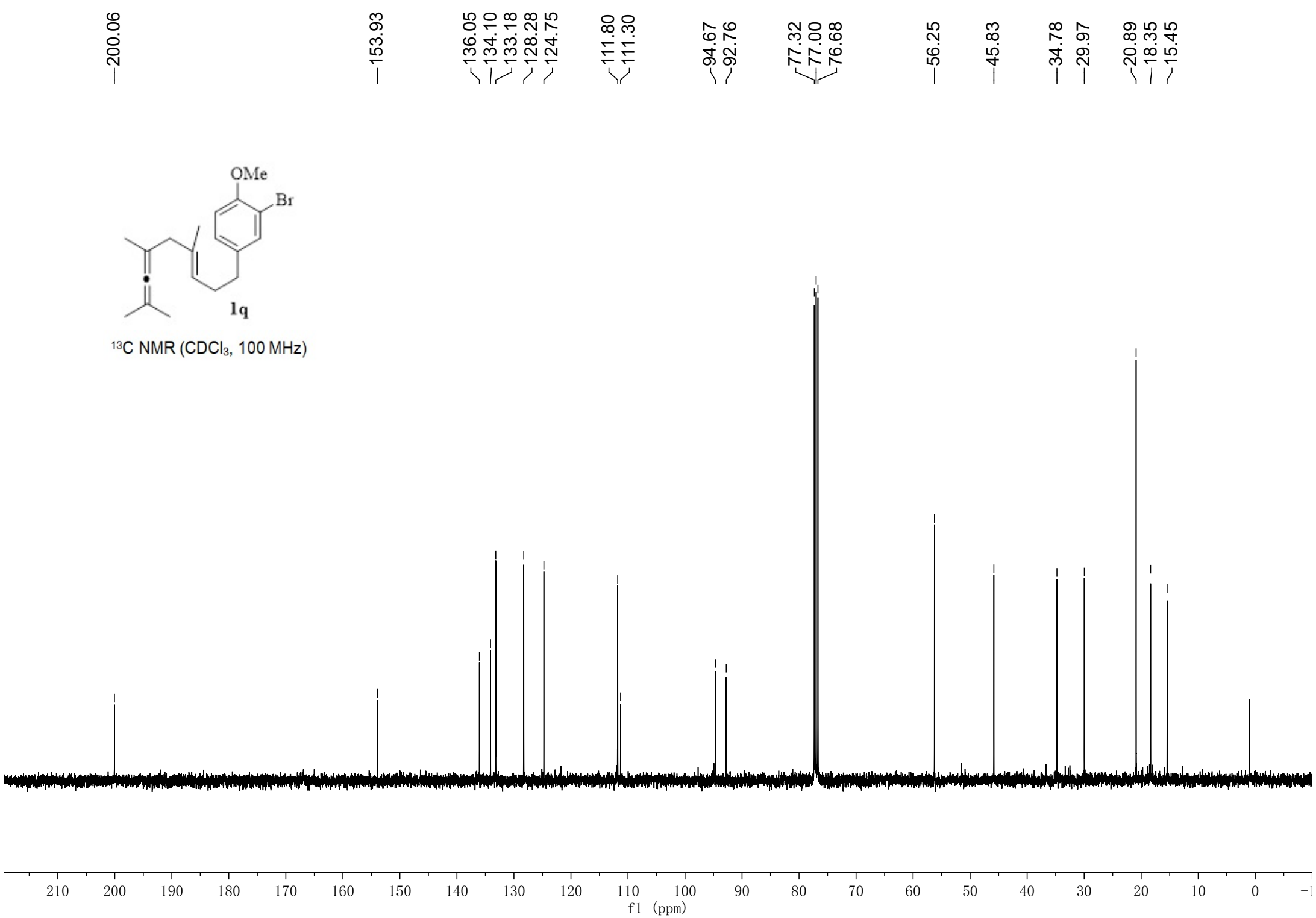

7.260
7.046
7.025
6.756
6.734
5.233
5.215
5.197
2.601
2.582
2.568
2.320
2.301
2.282
2.263
1.653
1.527
0.985
0.186
OTBS
1o
1H NMR (CDCl3, 400 MHz)
2.01
2.01
1.00
4.01
2.01
6.00
6.18
9.03
6.00
f1 (ppm)

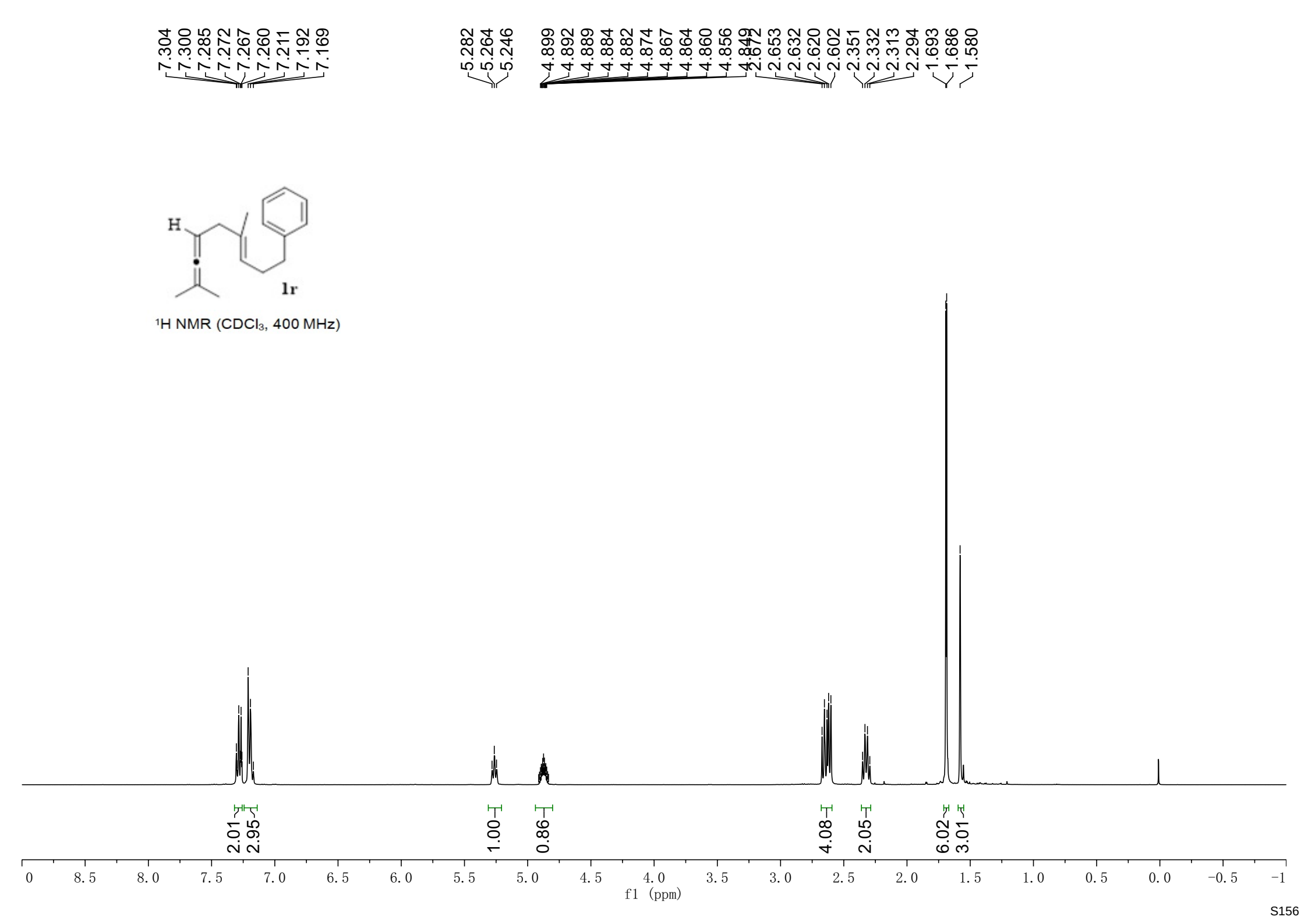

200.06
153.54
135.05
133.64
129.23
125.33
119.74
94.80
92.71
77.32
77.00
76.68
45.89
35.25
30.21
25.72
20.90
18.34
18.20
15.41
4.43
OTBS
1o
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

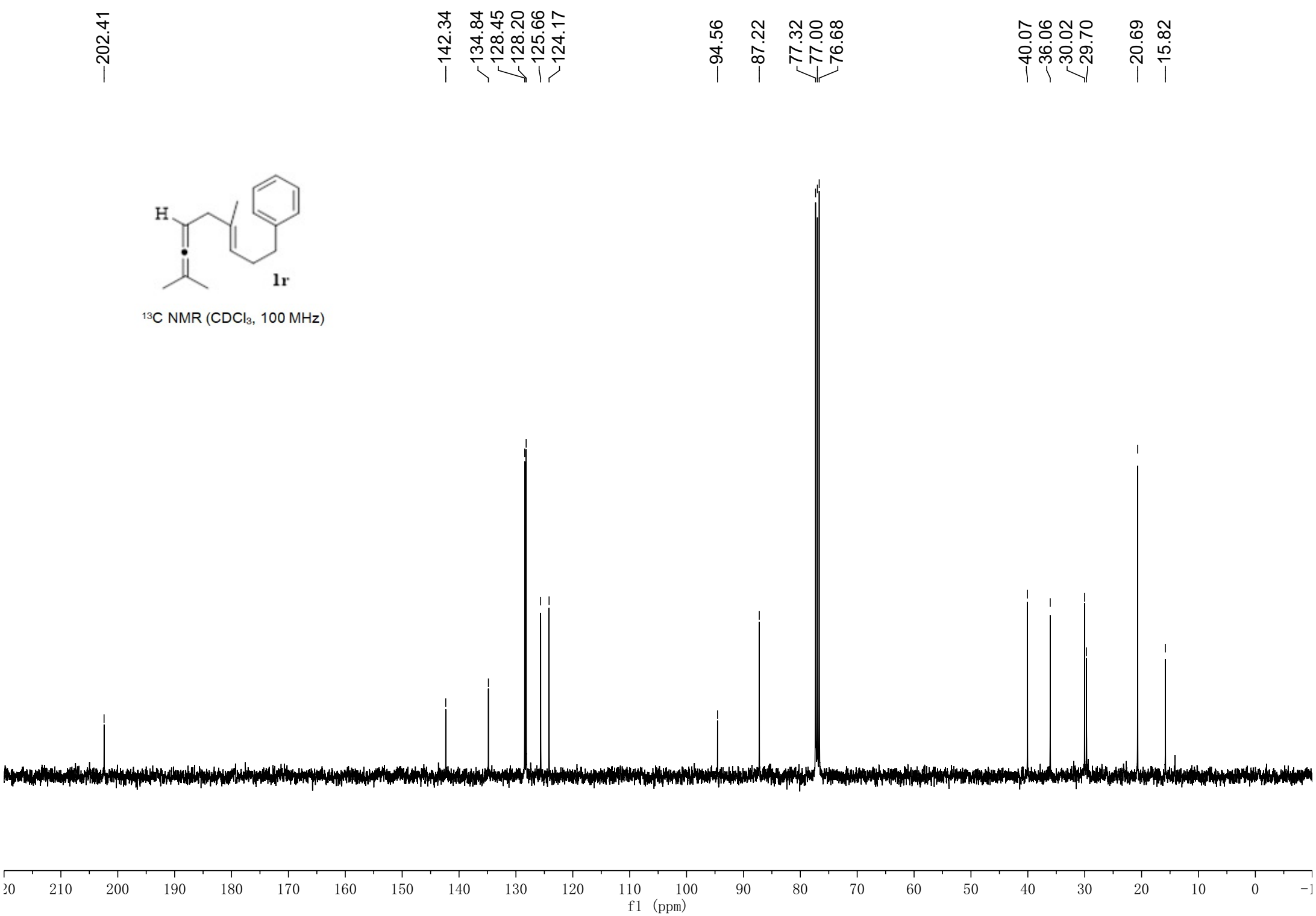

7.832
7.803
7.796
7.785
7.775
7.647
7.483
7.468
7.466
7.449
7.446
7.438
7.430
7.414
7.387
7.366
7.260
5.316
5.299
5.283
2.863
2.844
2.825
2.607
2.480
2.461
2.442
2.424
1.672
1.593
1.554
1p
1H NMR (CDCl3, 400 MHz)
3.01
1.00
3.00
1.00
2.00
2.00
2.02
6.02
3.00
2.88
f1 (ppm)

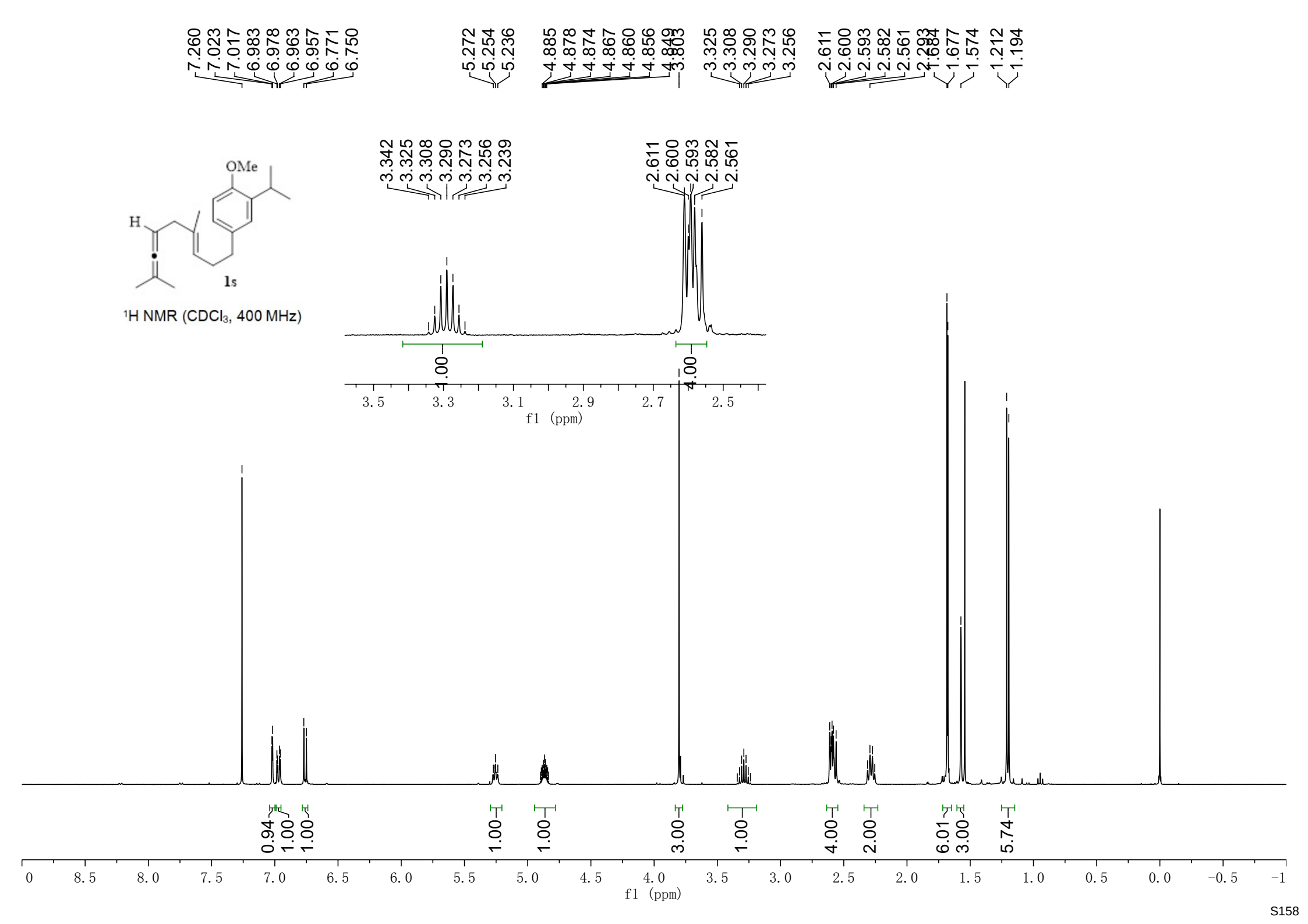

200.07
139.87
133.90
133.63
131.97
127.71
127.57
127.41
126.38
125.78
125.16
125.01
94.76
92.76
77.32
77.00
76.68
45.87
36.25
29.92
20.89
18.35
15.48
1p
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

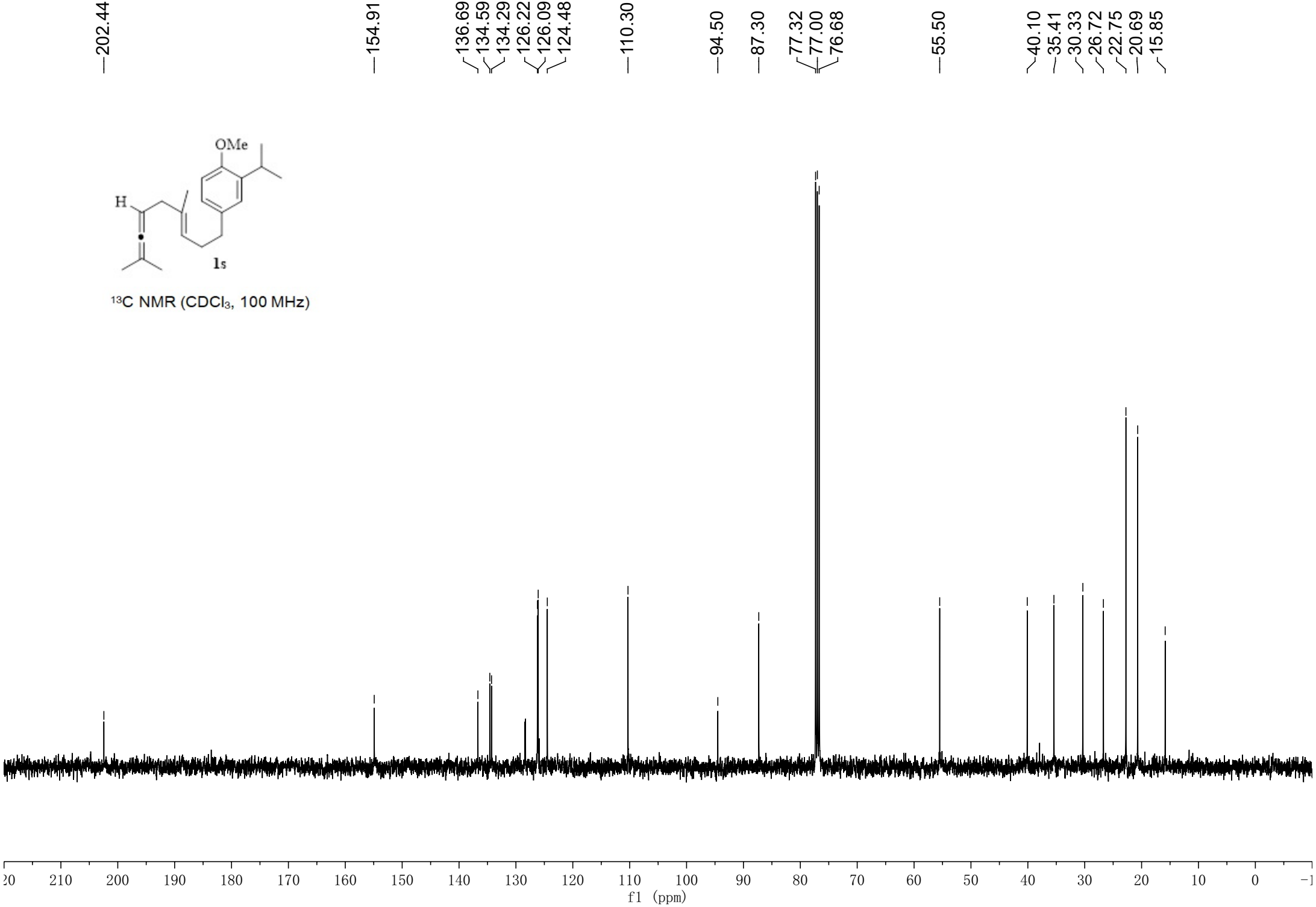

7.377
7.372
7.260
7.091
7.086
7.070
7.065
6.820
6.799
5.206
5.188
5.170
3.868
2.589
2.567
2.551
2.313
2.294
2.275
2.256
1.649
1.538
1.526
OMe
Br
1q
1H NMR (CDCl3, 400 MHz)
1.00
1.00
1.07
1.00
3.18
4.00
2.02
6.00
6.02
f1 (ppm)

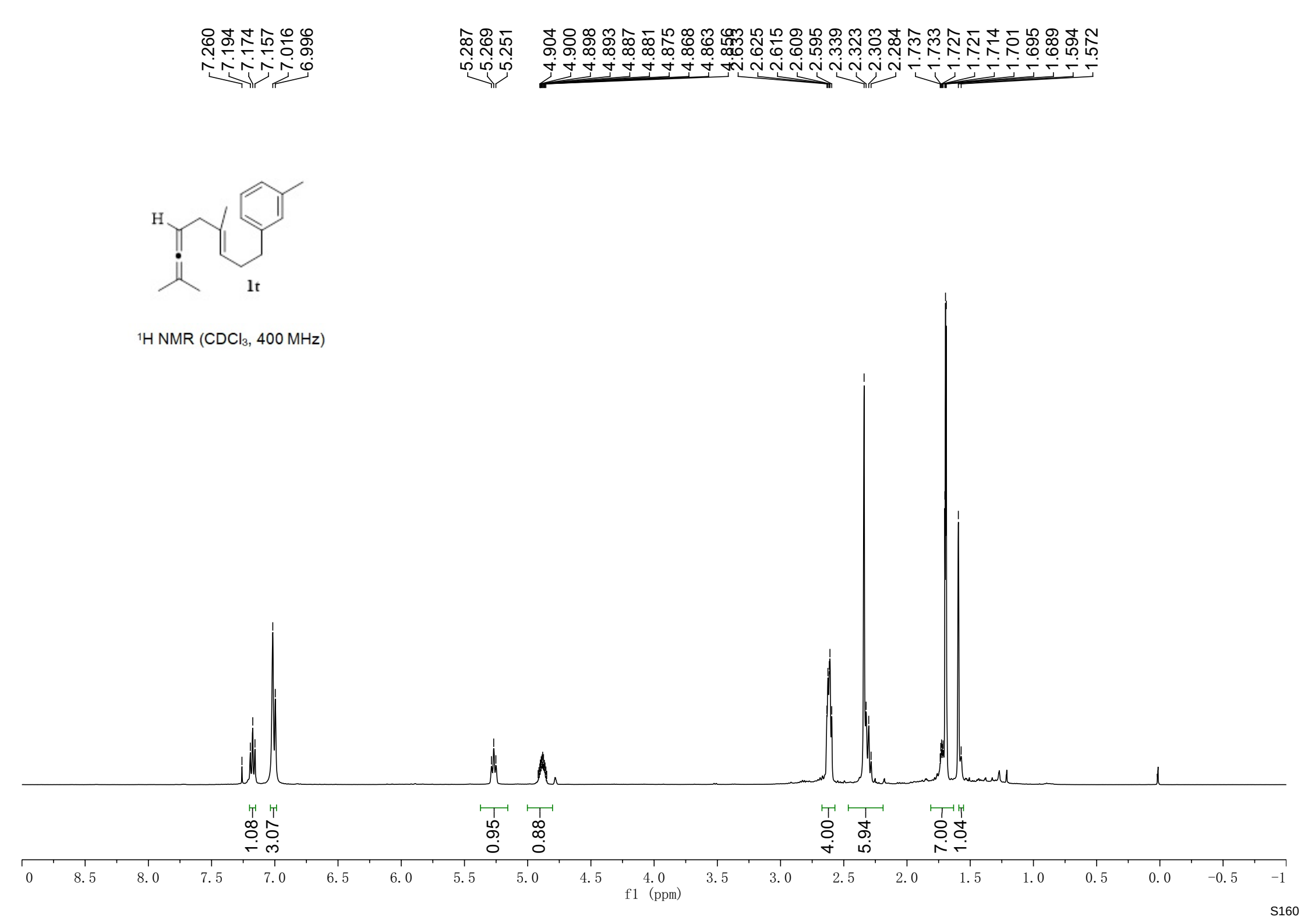

200.06
153.93
136.05
134.10
133.18
128.28
124.75
111.80
111.30
94.67
92.76
77.32
77.00
76.68
56.25
45.83
34.78
29.97
20.89
18.35
15.45
OMe
Br
1q
13C NMR (CDCl3, 100 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

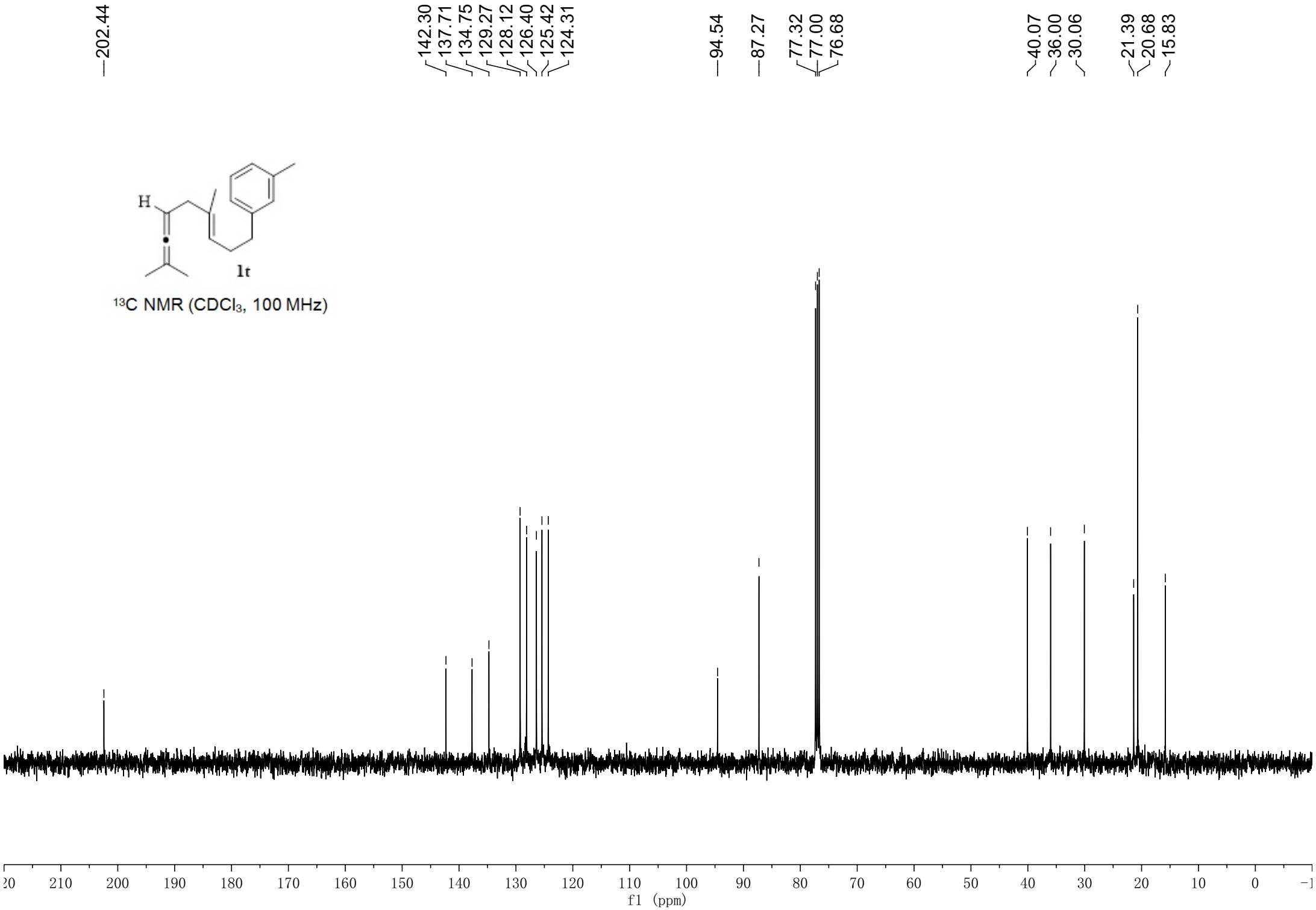

7.304
7.300
7.285
7.272
7.267
7.260
7.211
7.192
7.169
5.282
5.264
5.246
4.899
4.892
4.889
4.884
4.882
4.874
4.867
4.864
4.860
4.856
4.849
2.672
2.653
2.632
2.620
2.602
2.351
2.332
2.313
2.294
1.693
1.686
1.580
H
1r
¹H NMR (CDCl₃, 400 MHz)
2.01
2.95
1.00
0.86
4.08
2.05
6.02
3.01
f1 (ppm)

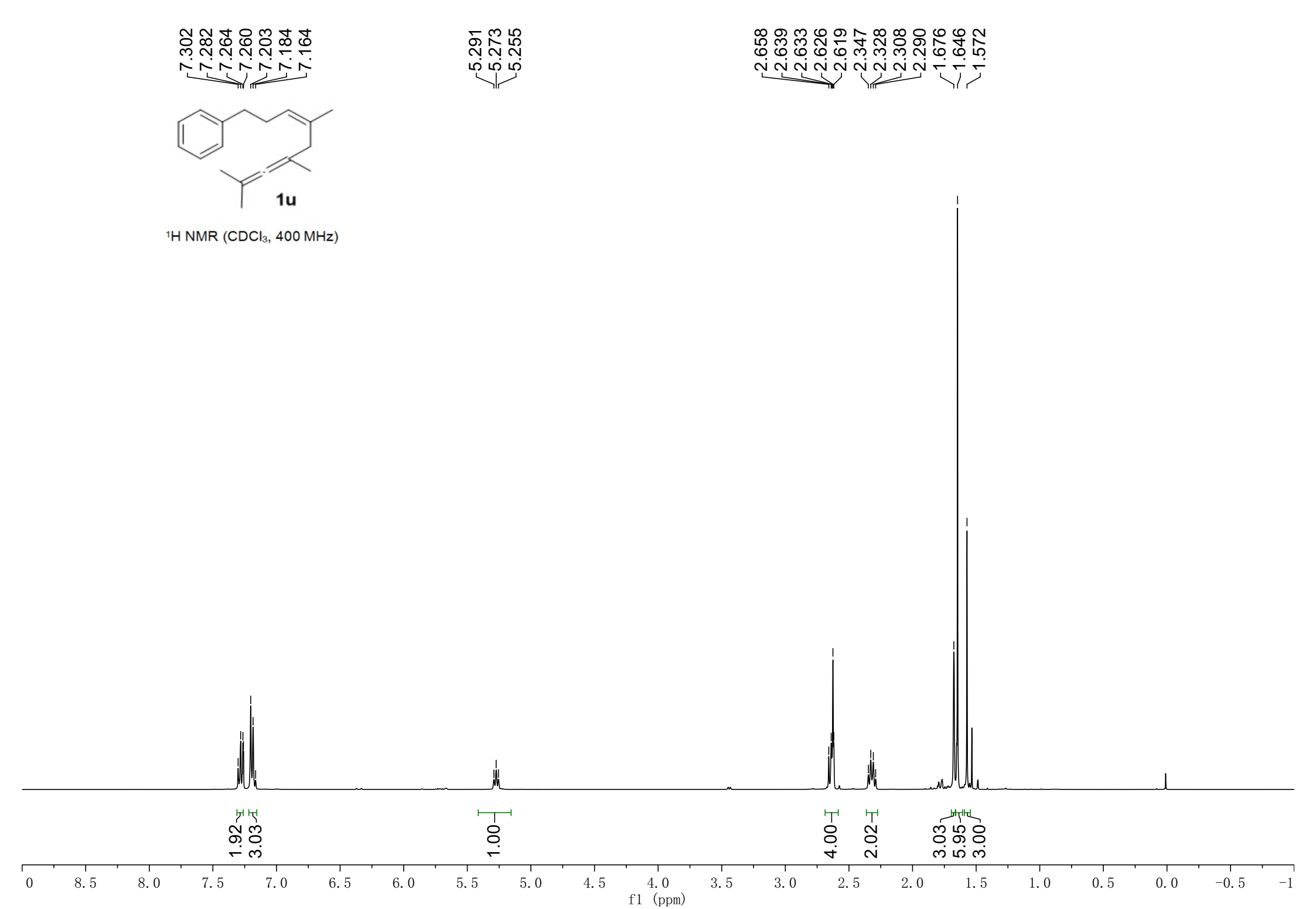

202.41
142.34
134.84
128.45
128.20
125.66
124.17
94.56
87.22
77.32
77.00
76.68
40.07
36.06
30.02
29.70
20.69
15.82
H
1r
13C NMR (CDCl3, 100 MHz)
f1 (ppm)

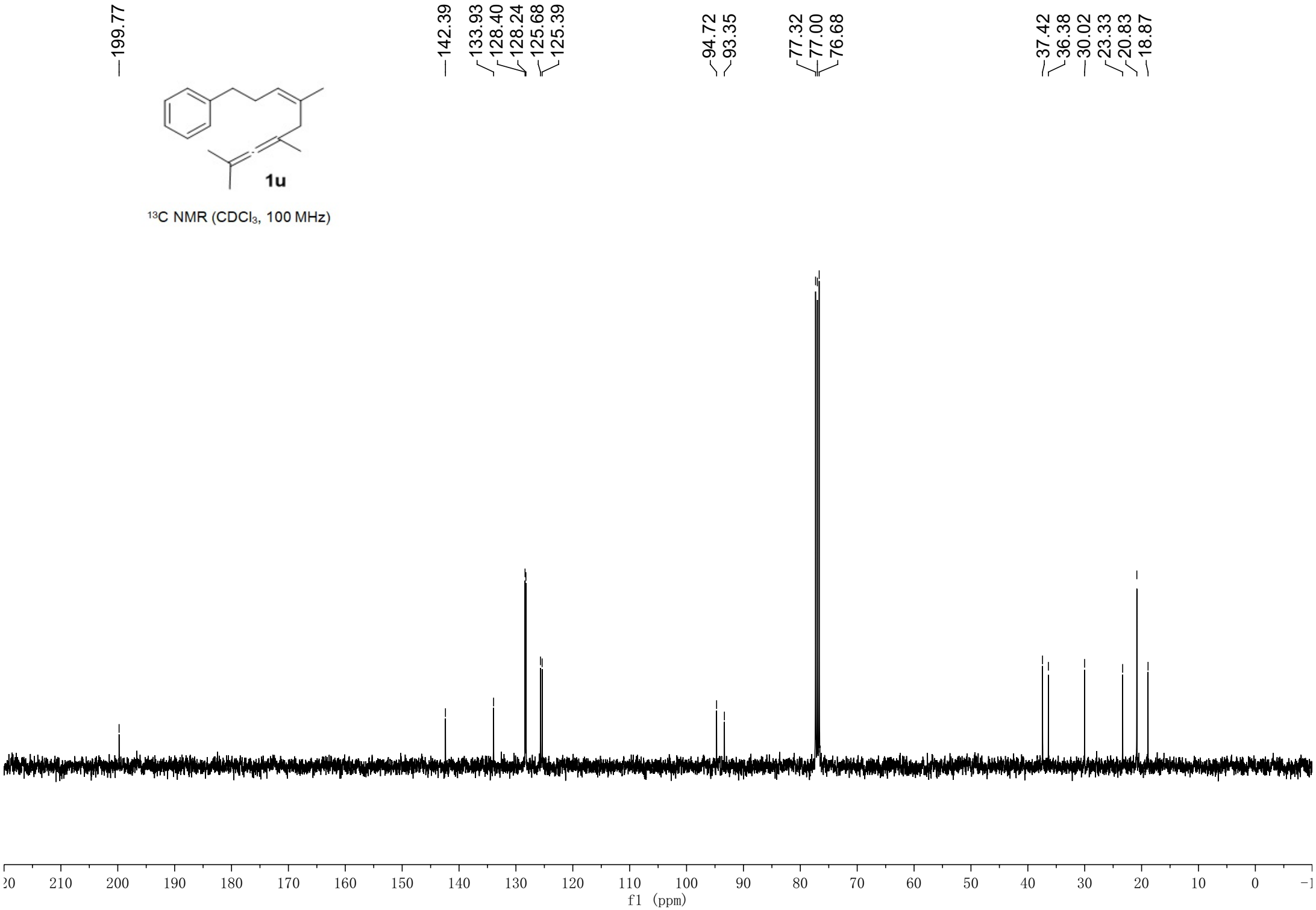

7.260
7.023
7.017
6.983
6.978
6.963
6.957
6.771
6.750
5.272
5.254
5.236
4.885
4.878
4.874
4.867
4.860
4.856
4.849
4.843
3.803
3.325
3.308
3.290
3.273
3.256
2.611
2.600
2.593
2.582
2.561
1.677
1.574
1.212
1.194
OMe
H
1s
1H NMR (CDCl3, 400 MHz)
3.342
3.325
3.308
3.290
3.273
3.256
3.239
2.611
2.600
2.593
2.582
2.561
1.00
4.00
3.5
3.3
3.1
2.9
2.7
2.5
f1 (ppm)
0.94
1.00
1.00
1.00
1.00
3.00
1.00
4.00
2.00
6.01
3.00
5.74
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


202.44
154.91
136.69
134.59
134.29
126.22
126.09
124.48
110.30
94.50
87.30
77.32
77.00
76.68
55.50
40.10
35.41
30.33
26.72
22.75
20.69
15.85
OMe
H
1s
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.260
7.194
7.174
7.157
7.016
6.996
5.287
5.269
5.251
4.904
4.900
4.898
4.893
4.887
4.881
4.875
4.868
4.863
2.633
2.625
2.615
2.609
2.595
2.339
2.323
2.303
2.284
1.737
1.733
1.727
1.721
1.714
1.701
1.695
1.689
1.594
1.572
H
1t
1H NMR (CDCl3, 400 MHz)
1.08
3.07
0.95
0.88
4.00
5.94
7.00
1.04
0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1
f1 (ppm)


202.44
142.30
137.71
134.75
129.27
128.12
126.40
125.42
124.31
94.54
87.27
77.32
77.00
76.68
40.07
36.00
30.06
21.39
20.68
15.83
H
1t
13C NMR (CDCl3, 100 MHz)
f1 (ppm)


7.302
7.282
7.264
7.260
7.203
7.184
7.164
5.291
5.273
5.255
2.658
2.639
2.633
2.626
2.619
2.347
2.328
2.308
2.290
1.676
1.646
1.572
1u
1H NMR (CDCl3, 400 MHz)
1.92
3.03
1.00
4.00
2.02
3.03
5.95
3.00
f1 (ppm)


199.77
142.39
133.93
128.40
128.24
125.68
125.39
94.72
93.35
77.32
77.00
76.68
37.42
36.38
30.02
23.33
20.83
18.87
1u
13C NMR (CDCl3, 100 MHz)
f1 (ppm)