Supporting Information

Total Syntheses of *ent*-Aogacillin A and Aogacillin B

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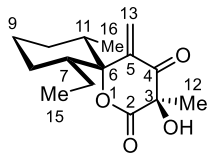
General Information

Reactions were carried out in oven-dried glassware under a nitrogen atmosphere unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as an indicator. Dichloromethane (CH_2Cl_2) was freshly distilled before use from calcium hydride (CaH_2). All other anhydrous solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck precoated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Yantai Xin Nuo. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ^{1}H and 77.16 ppm for ^{13}C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal; *J*, coupling constants in Hertz. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter. High resolution mass spectra were measured at the Hong Kong University of Science and Technology Mass Spectrometry Service Centre on either an Agilent GC/MS 5975C System or an API QSTAR XL System. HPLC (Agilent technologies, 1260 Infinity) was used to determine enantiomeric excess of chiral compounds with eluents of petroleum ether/*i*-PrOH. For X-ray Diffraction Analysis, a suitable crystal of the sample was selected and analysed on a SuperNova, Dual, Cu at zero, Atlas diffractometer. The crystal was kept at 99.99(10) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using

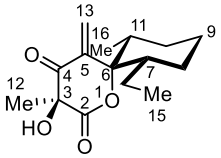
Intrinsic Phasing and refined with the olex2.refine refinement package using Levenberg-Marquardt minimisation.

NMR Comparison of Natural Products and Synthetic Samples

Table S1 NMR comparison of natural aogacillin A and synthetic *ent*-aogacillin A



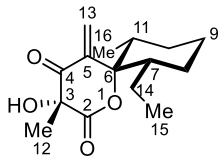
ent-aogacillin A (*ent*-**1a**)



aogacillin A (**1a**)

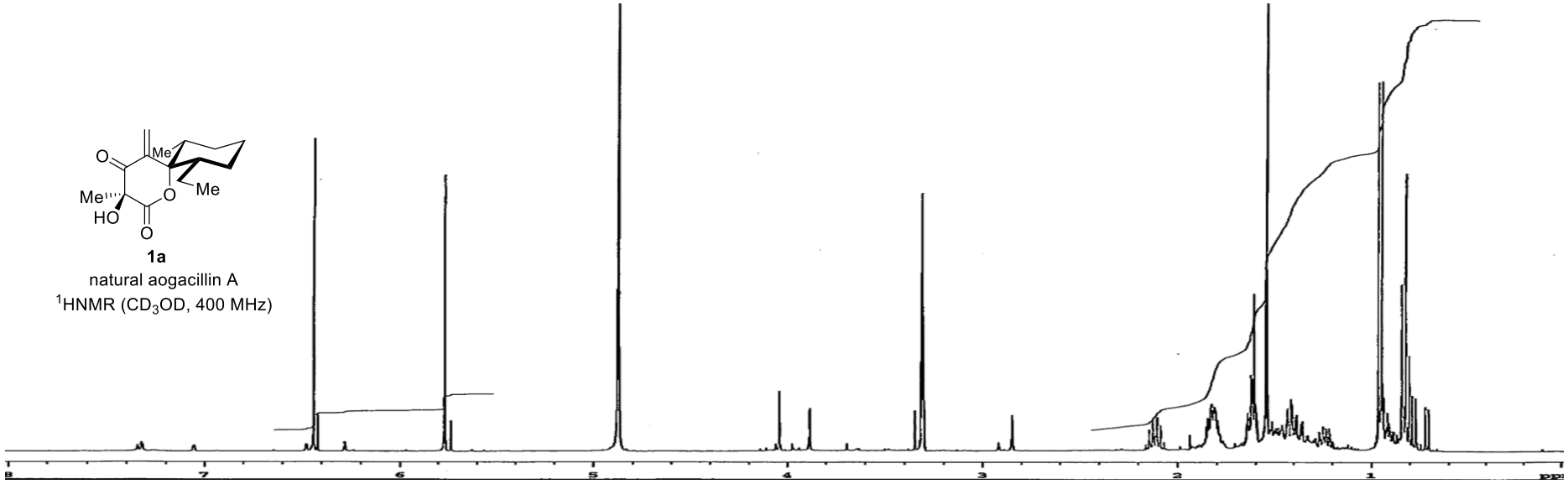
C No.	^{13}C NMR (CD_3OD, 101 MHz)			^{1}H NMR (CD_3OD, 400 MHz)	
	Natural aogacillin A	Synthetic *ent*-aogacillinA	δ (MHz)	Natural aogacillin A	Synthetic *ent*-aogacillin A
2	174.9	174.9	0	-	-
3	77.8	77.8	0	-	-
4	197.4	197.4	0	-	-
5	145.5	145.5	0	-	-
6	91.6	91.6	0	-	-
7	54.6	54.6	0	1.42 (m)	1.42 (m)
8a	27.3	27.3	0	1.38 (m)	1.38 (m)
8b				1.81 (m)	1.81 (m)
9a	26.2	26.2	0	1.45 (m)	1.46 (m)
9b				1.83 (m)	1.82 (m)
10a	30.2	30.6	-0.4	1.50 (dddd, 14.0, 8.8, 8.8, 6.2)	1.50 (m)
10b				1.62 (dddd,14.0, 6.4, 2.2, 2.2)	1.62 (m)
11	42.4	42.4	0	2.21 (dqd, 8.8, 7.2, 5.4)	2.12 (m)
12	27.2	27.2	0	1.54 (s)	1.54 (s)
13a	125.5	125.5	0	5.77 (s)	5.77 (s)
13b				6.44 (s)	6.44 (s)
14a	23.9	23.9	0	0.92 (m)	0.92 (m)
14b				1.24 (m)	1.24 (m)
15	12.3	12.3	0	0.82 (t, 7.2)	0.82 (t, 7.4)
16	17.2	17.2	0	0.95 (d, 7.2)	0.95 (d, 7.4)

Table S2 NMR comparison of natural aogacillin B and synthetic aogacillin B

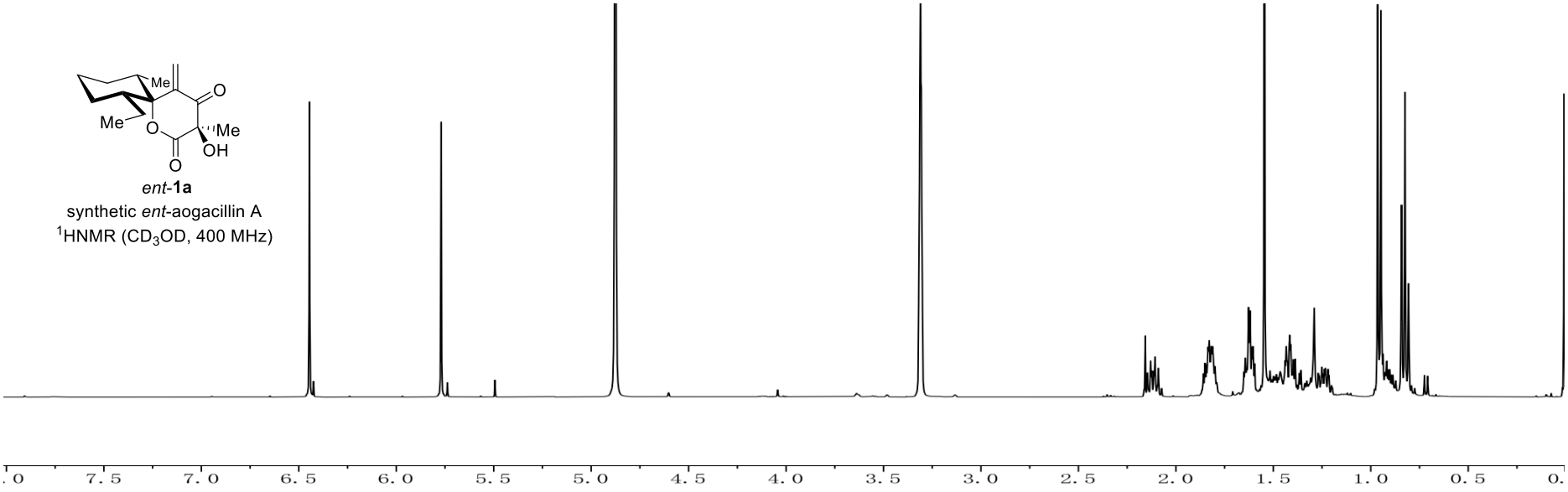


aogacillin B (**1b**)

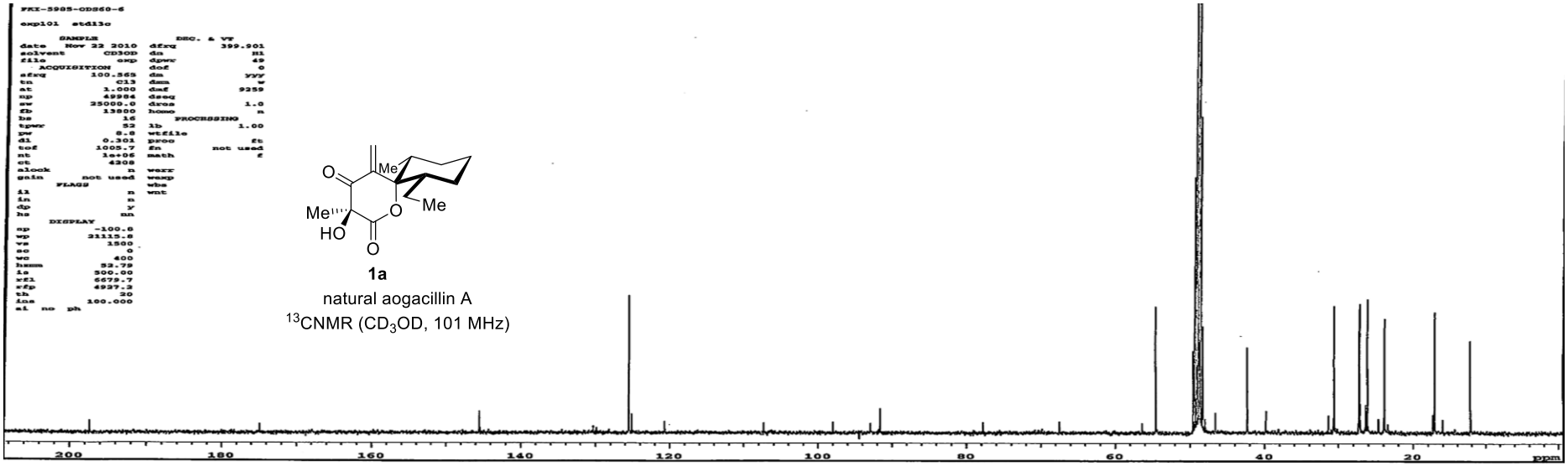
C No.	^{13}C NMR (CD_3OD, 101 MHz)			^{1}H NMR (CD_3OD, 400 MHz)	
	Natural Aogacillin B	Synthetic Aogacillin B	δ (MHz)	Natural Aogacillin B	Synthetic Aogacillin B
2	175.0	175.0	0	-	-
3	77.9	77.9	0	-	-
4	197.6	197.6	0	-	-
5	145.6	145.6	0	-	-
6	91.9	91.9	0	-	-
7	48.7	48.6	0.1	1.84 (m)	1.84 (m)
8a	26.4	26.4	0	1.36 (m)	1.34 (m)
8b				1.91 (m)	1.91 (m)
9a	26.2	26.2	0	1.46 (m)	1.46 (m)
9b				1.84 (m)	1.84 (m)
10a	31.5	31.5	0	1.52 (m, 2H)	1.53 (m, 2H)
10b					
11	48.1	48.1	0	1.68 (m)	1.68 (m)
12	27.3	27.3	0	1.55 (s)	1.55 (s)
13a	125.1	125.1	0	5.73 (s)	5.73 (s)
13b				6.42 (s)	6.42 (s)
14a	24.7	24.7	0	1.14 (m)	1.14 (m)
14b				1.66 (m)	1.66 (m)
15	12.3	12.3	0	0.94 (t, 7.2)	0.94 (t, 7.4)
16	16.1	16.1	0	0.71 (d, 7.2)	0.71 (d, 6.6)



1a
natural aogacillin A
^{1}HNMR (CD_3OD, 400 MHz)



ent-**1a**
synthetic *ent*-aogacillin A
^{1}HNMR (CD_3OD, 400 MHz)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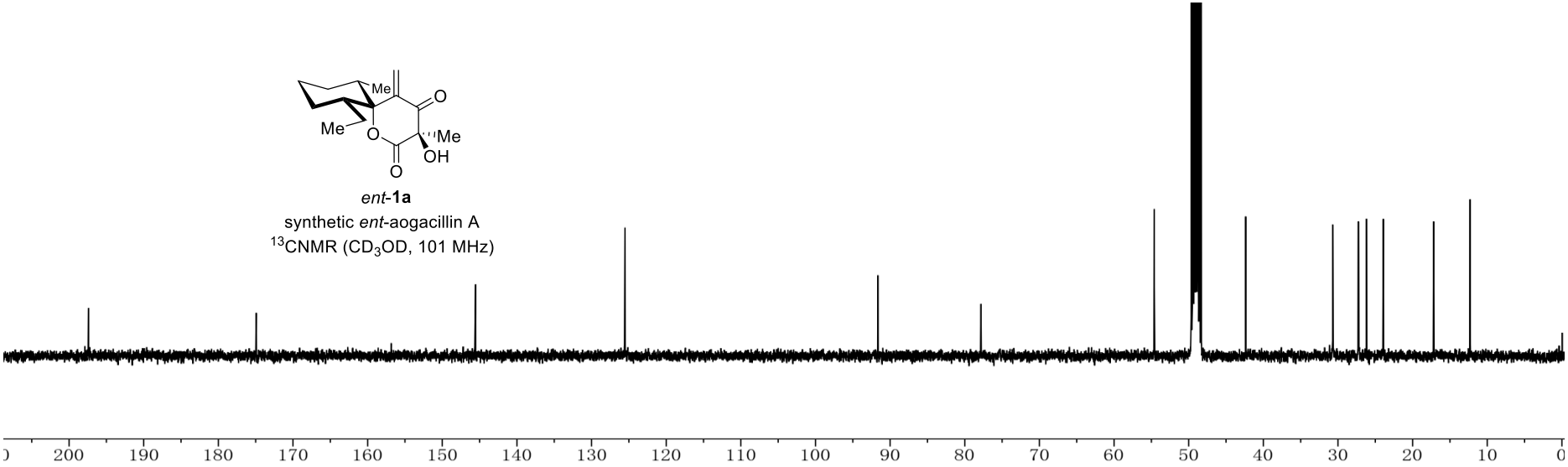
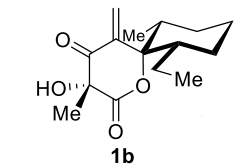
exp101 std13c
SAMPLE
date Nov 22 2010
solvent CD3OD
file exp
ACQUISITION
sfrq 100.569
tn C13
at 1.000
np 49984
sw 25000.0
fb 13800
bs 16
tpwr 52
pw 8.8
d1 0.301
tof 1005.7
nt 1e+06
ct 4208
alock n
gain not used
FLAGS
il n
in n
dp y
hs nn
DISPLAY
sp -100.6
wp 21115.8
vs 1500
sc 0
wc 400
hzmm 52.79
is 500.00
rfl 6679.7
rfp 4927.2
th 20
lna 100.000
at no ph
DEC. & VT
dfrq 399.901
dn H1
dpwr 42
dof 0
dm yyy
dmm w
dmf 9259
decq
decs 1.0
homo n
PROCESSING
lb 1.00
wtfile
proc ft
fn not used
math f
werr
wexp
wbs
wnt
O
Me
Me
O
Me
HO
O
1a
natural aogacillin A
13CNMR (CD3OD, 101 MHz)
200
180
160
140
120
100
80
60
40
20
ppm

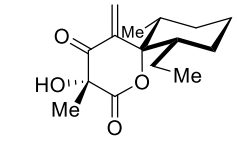

Me
O
Me
O
Me
OH
O
ent-1a
synthetic ent-aogacillin A
13CNMR (CD3OD, 101 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



1b

natural aogacillin B

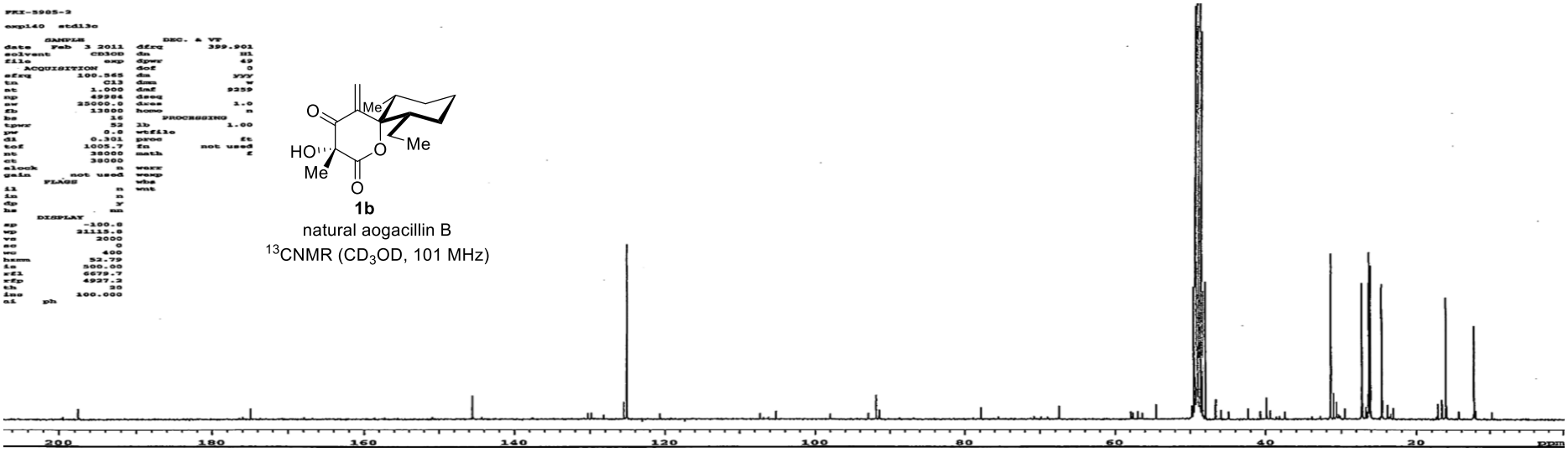
^{1}HNMR (CD_3OD, 400 MHz)

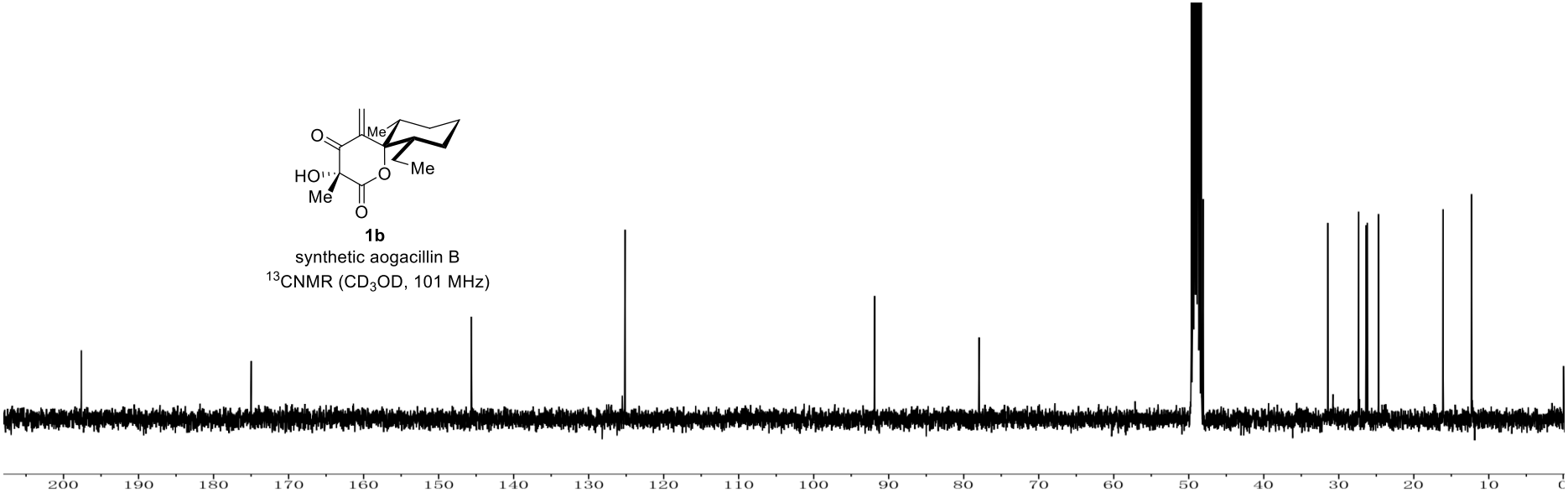


1b

synthetic aogacillin B

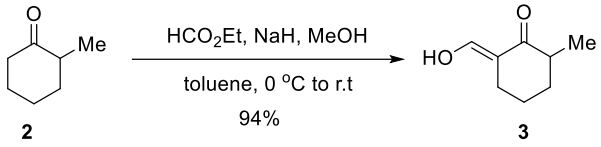
^{1}HNMR (CD_3OD, 400 MHz)


1b
natural aogacillin B
13CNMR (CD3OD, 101 MHz)


1b
synthetic aogacillin B
13CNMR (CD3OD, 101 MHz)

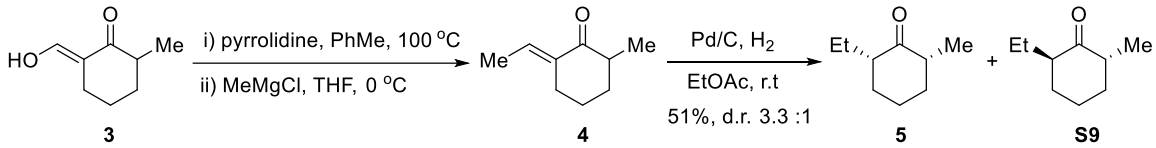
Experiment Procedure and Characterization Data

Preparation of 2-(hydroxymethylene)-6-methylcyclohexanone 3



To a stirred suspension of 60% NaH (35.7 g, 893mmol) in dry toluene (600 mL) at 0°C was added ethyl formate (24.8 g, 2676 mmol). A solution of 2-methylcyclohexanone, **2** (50.0 g, 446 mmol) and MeOH (17.5 mL, 446 mmol) was added dropwise. The mixture was stirred overnight and then quenched with ice water. The organic layer was collected and the aqueous layer was washed with EtOAc followed by acidification with conc. HCl to pH 1~2. Then the aqueous phase was extracted with EtOAc (2 x 500 mL) and the combined organic fractions were washed with H_2O (2 x 300 mL), brine (300 mL), dried over $NaSO_4$, and concentrated under reduced pressure. The residue could be used for the next step without further purification (58.7 g, 94%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 14.56 (s, 1H), 8.58 (s, 1H), 2.43–2.46 (m, 1H), 2.30–2.33 (m, 2H), 1.84–1.88 (m, 1H), 1.77–1.75 (m, 1H), 1.58–1.55 (m, 1H), 1.42–1.36 (m, 1H) 1.20 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 188.5, 187.0, 108.2, 35.8, 29.9, 23.7, 20.9, 17.4.[1]

Preparation of *cis*-2-ethyl-6-methylcyclohexanone 5

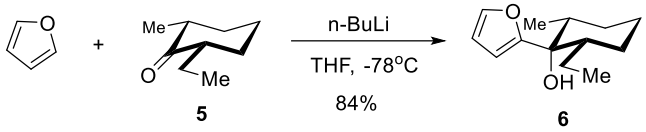


To a stirred solution of **3** (60.0 g, 428.6 mmol) in dry toluene (500 mL) at 0°C was added pyrrolidine (45.6 g, 642.8 mmol). The reaction mixture was heated to 100 °C for 6 h and then the solvent was evaporated directly in vacuo. The residue was dissolved in dry THF (500 mL), and methyl magnesium chloride solution (3.0 M in THF, 171 mL, 514.3 mmol) was added slowly at 0°C. The reaction mixture was stirred at 0°C for 1 h and then quenched by addition of *aq. satd.* NH_4Cl (500 mL). The organic layer was collected and the aqueous layer was extracted with EtOAc (2 x 500 mL). The combined organic fractions were washed with H_2O (2 x 300 mL), brine (300 mL), dried over $NaSO_4$, and concentrated under reduced pressure. The crude **4** was used for the next step directly. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.58 (q, *J* = 7.26 Hz, 1H), 2.70−2.60 (m, 1H), 2.37−2.22 (m, 2H), 2.05−1.95 (m, 1H), 1.91−1.81 (m, 1H), 1.72−1.57 (m, 4H), 1.55−1.42 (m, 1H), 1.11 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 204.0, 137.6, 133.2, 44.1, 32.0, 26.9, 22.7, 16.3, 13.7.[2]

To a stirred solution of the crude **4** in dry EtOAc (150 mL) at room temperature was added palladium on carbon (10 wt%, 4.5 g). The reaction mixture was stirred under H_2 atmosphere (1.0 atm, balloon) at room temperature for 4 h, and then filtered through a pad of Celite. The filtrate was concentrated under reduced pressure to give a residue, which was purified by silica gel column chromatography using eluents (EtOAc/petroleum ether = 1/20) to afford *cis*-2-ethyl-6-methylcyclohexanone **5** (2.5 g, 4%) and a mixture of *cis*-2-ethyl-6-methylcyclohexanone **5** and *trans*-2-ethyl-6-methylcyclohexanone **S9** (28.2 g, 47%, cis:trans = 3:1), which could be further separated by several times of silica gel column chromatography. The mixture of **5** and **S9** could also be subjected to the next step directly, because the products were easier to separate.

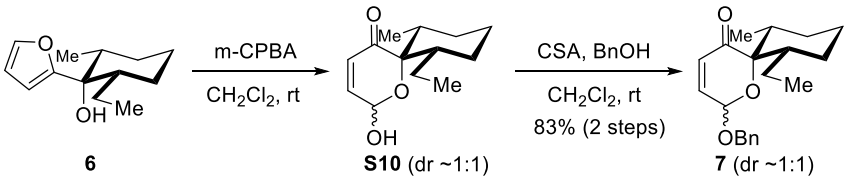
cis-2-ethyl-6-methylcyclohexanone **5**: **^{1}H NMR** (400 MHz, $CDCl_3$) δ 2.30−2.45 (m, 1H), 2.10−2.21 (m, 2H), 2.01−2.10 (m, 1H),1.63−1.88 (m, 3H),1.09−1.37 (m, 3H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.86 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 214.5, 52.5, 45.8, 37.6, 34.9, 25.7, 22.3, 14.7, 12.0.[3]

Preparation of furfuryl alcohol 6



To a solution of furan (10.3 mL, 142.8 mmol) in dry THF (30ml) at -78°C was added n-Butyllithium (2.5 M, 28.6 mL, 71.4 mmol) dropwise. The reaction mixture was stirred at -10 °C for 1 h, then **5** (5.0 g, 35.7 mmol) in THF (20 mL) was added slowly at this temperature. After completion of the addition, the reaction mixture was allowed to stir for additional 1 h at the same temperature. Sat. aqueous NH_4Cl (50 mL) was added to quench the reaction. The organic layer was collected and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic phase was washed with H_2O (2 x 50 mL), brine (50 mL), dried over $NaSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/30) to afford **6** (6.2 g, 84%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (s, 1H), 6.34−6.27 (m, 1H), 6.22−6.14 (m, 1H), 1.94−1.81 (m, 1H), 1.81−1.71 (m, 2H), 1.68 (s, 1H), 1.65−1.50 (m, 2H), 1.47−1.32 (m, 2H), 1.31−1.19 (m, 1H), 1.19−1.07 (m, 1H), 1.07−0.95 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H), 0.65 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.5, 140.7, 110.0, 105.6, 77.5, 47.2, 40.4, 29.9, 26.1, 25.8, 23.2, 16.0, 12.4. **HRMS** (Cl^+): *m/z* calcd. for $C_{13}H_{20}O_2$ $[M]^+$ 208.1463, found 208.1466.

Preparation of Benzylated Pyranone 7

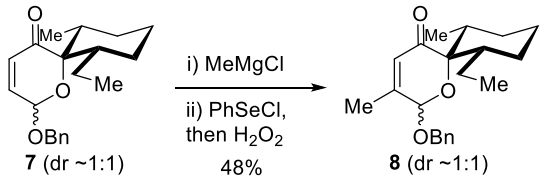


To a stirred solution of **6** (27 g, 129.8 mmol) in CH_2Cl_2 (250 mL) at 0 °C was added 3-chloroperbenzoic acid (26.8 g, 155.8 mmol). The reaction mixture was allowed to warm to room temperature and stirred for 2 h. The reaction was then quenched by addition of Sat. aqueous $NaHCO_3$ (300 mL) and Sat. aqueous $Na_2S_2O_3$ (300 mL) and the resulting reaction mixture was extracted with EtOAc (3 x 200 mL). The combined organic fractions were washed with H_2O (2 x 200 mL), brine (200 mL), dried over $NaSO_4$, and concentrated under reduced pressure. The crude **S10** was used for the next step directly. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.78 (d, *J* = 8.0 Hz, 1H), 6.21 (q, *J* = 4.0 Hz, 1H), 5.89 (d, *J* = 8.0 Hz, 1H), 1.91−1.82 (m, 1H), 1.68−1.63 (m, 3H), 1.46−1.10 (m, 6H), 0.81 (t, *J* = 7.2 Hz, 3H), 0.77 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.68, 200.61, 145.32, 144.96, 129.38, 129.35, 88.18, 88.16, 88.03, 87.83, 48.51, 46.64, 41.64, 40.01, 29.38, 29.07, 25.36, 25.05, 24.78, 24.52, 24.32, 16.95, 16.84, 12.35, 12.20. **HRMS** (Cl^+): *m/z* calcd. for $C_{13}H_{20}O_3$ $[M]^+$ 224.1412, found 224.1497.

To a stirred solution of the above crude **S10** in dry CH_2Cl_2 (250 mL) was added (-)-camphorsulfonic acid (3.0 g, 13.0 mmol) and benzyl alcohol (21.0 g, 194.7 mmol). The reaction mixture was stirred at room temperature for 4 h. Solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/30) to afford **7** (33.8 g, 83% from **6**) as a light colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46−7.27 (m, *5*H), 6.79−6.67 (m, 1H), 6.28−6.14 (m, 1H), 5.63−5.50 (m, 1H), 5.03−4.88 (m, 1H), 4.75−4.63 (m, 1H), 1.99−1.83 (m,

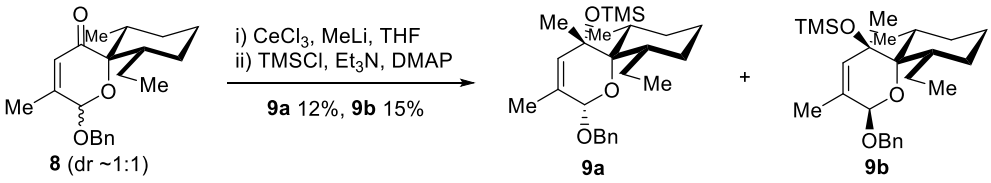
1H), 1.81−1.62 (m, 3H), 1.58−1.05 (m, 6H), 0.92−0.69 (m, 6H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.80, 200.77, 143.92, 143.67, 137.45, 137.43, 129.69, 129.64, 128.59, 128.35, 128.32, 128.03, 92.08, 92.05, 87.90, 87.87, 69.97, 69.90, 48.57, 47.24, 41.85, 40.49, 29.61, 25.66, 25.30, 25.22, 24.36, 24.30, 16.95, 16.90, 12.43, 12.34. **HRMS** (ESI): *m/z* calcd. for $C_{20}H_{26}O_3$ $[M+H]^+$ 315.1955, found 315.1966

Preparation of Enone 8



To a stirred solution of **7** (6.0 g, 19.1 mmol) in dry Et_2O (60 mL) at 0°C was added methyl magnesium chloride solution (3.0 M in THF, 8.3 mL, 24.8 mmol) slowly. The reaction mixture was stirred at 0°C for 1 h. Then the temperature was decreased to -78°C and phenylselenenyl chloride (5.8 g, 30.6 mmol) in Et_2O (30 mL) was added slowly. After completion of the addition, the reaction mixture was allowed to stir for additional 1 h at 0 °C. Then pyridine (3.8 mL, 47.8 mmol) and 30% H_2O_2 (7.6 mL, 66.8 mmol) were added successively. The reaction mixture was allowed to warm to room temperature and stirred for 2 h. Sat. aqueous $NaHSO_3$ was added to quench the reaction, and the organic layer was separated. The aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic fractions were washed with H_2O (2 x 100 mL), brine (100 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/30) to afford **8** (3.0 g, 48%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39−7.32 (m, *5*H), 6.05 (s, 1H), 5.34 (s, 1H), 4.95 (t, *J* = 12.0 Hz, 1H), 4.70 (d, *J* = 6.0 Hz, 1H), 1.95 (s, 3H), 1.89−1.85 (m, 1H), 1.76−1.67 (m, 3H), 1.42−1.15 (m, 7H), 0.84−0.68 (m, 6H), **^{13}C NMR** (101 MHz, $CDCl_3$) δ 200.25, 200.17, 155.21, 155.01, 137.14, 137.39, 128.46, 128.28, 128.19, 127.89, 127.86, 127.02, 127.00, 94.76, 94.72, 87.20, 87.04, 69.79, 69.75, 48.32, 46.93, 41.64, 40.08, 29.63, 29.59, 25.61, 25.24, 24.08, 24.04, 19.87, 19.82, 16.75, 16.70, 12.40, 12.12. **HRMS** (Cl^+): *m/z* calcd. for $C_{21}H_{29}O_3$ $[M+H]^+$ 329.2111, found 329.2119.

Preparation of Tertiary Alcohol 9



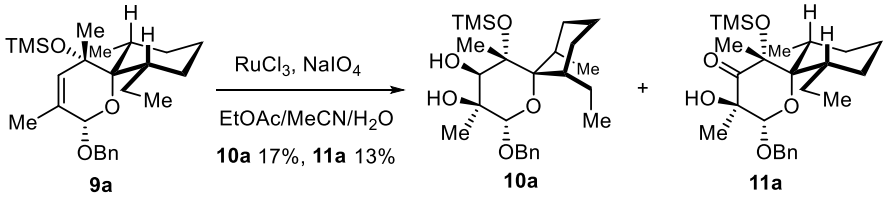
A 250-mL flask was charged with anhydrous cerium trichloride (8.4 g, 34.2 mmol). The flask was heated to 140 °C for 2 h under high vacuum to remove trace of water and moisture. After cooling to room temperature under nitrogen atmosphere, THF (50 mL) was added using a syringe and the reaction mixture was stirred at room temperature for 2 h. The resulting suspension was cooled to -78 °C and MeLi (1.6 M in Et_2O, 15.9 mL, 25.5 mmol) was added dropwise with vigorous stirring. After being stirred at -78 °C for 30 min, enone **8** (2.8 g, 8.5 mmol) in THF (20 mL) was added slowly. The reaction mixture was allowed to warm to 0°C for 1 h and then quenched with Sat. aqueous $NaHCO_3$ (100 mL). The organic layer was collected and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic fractions were washed with H_2O (2 x 100 mL), brine (100 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was dissolved in dry DMF (60 mL), and 4-(dimethylamino)pyridine (330 mg, 0.85 mmol) and triethylamine (Et_3N, 5.9 mL, 42.5 mmol) were

added to this solution. The mixture was stirred at 0°C for 10 min, and trimethylsilyl chloride (3.2 mL, 25.5 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature for 12 h. The reaction mixture was quenched with Sat. aqueous $NaHCO_3$ (100 mL). The organic layer was collected and the aqueous layer was extracted with EtOAc (2 x 100 mL). The combined organic fractions were washed with H_2O (2 x 100 mL), brine (100 mL), dried over $NaSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/100 – 1/50 – 1/30) to afford **9a** (425 mg, 12%) and **9b** (530 mg, 15%) both as colorless oil.

9a R_f = 0.45 (EtOAc /petroleum ether = 1/80). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46−7.23 (m, 5H), 5.59 (s, 1H), 4.97 (s, 1H), 4.82 (d, *J* = 12.0 Hz, 1H), 4.66 (d, *J* = 12.0 Hz, 1H), 2.28−2.16 (m, 1H), 1.98−1.86 (m, 2H), 1.84−1.75 (m, 1H), 1.72−1.64 (m, 4H), 1.58−1.50 (m, 1H), 1.48−1.36 (m, 2H), 1.33−1.24 (m, 4H), 1.20−1.09 (m, 4H), 0.87 (d, *J* =7.2 Hz, 3H), 0.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.77, 133.86, 130.89, 128.24, 127.83, 127.30, 95.43, 81.88, 76.68, 68.80, 43.55, 34.80, 31.56, 26.37, 25.15, 23.17, 19.45, 18.56, 17.97, 14.29, 2.82. **HRMS** (Cl^+): *m/z* calcd. for $C_{25}H_{40}O_3Si$ $[M]^+$ 416.2747, found 416.2762.

9b R_f = 0.55 (EtOAc /petroleum ether = 1/80). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46−7.22 (m, *5*H), 5.60 (s, 1H), 5.00 (s, 1H), 4.83 (d, *J* = 12.0 Hz, 1H), 4.65 (d, *J* = 12.0 Hz, 1H), 2.14−1.77 (m, 5H), 1.71 (s, 3H), 1.49−1.35 (m, 3H), 1.33 (s, 3H), 1.26−1.13 (m, 2H), 1.04 (d, *J* = 7.2 Hz, 3H), 0.81 (t, *J* =7.2 Hz, 3H), 0.18 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.94, 133.67, 131.13, 128.30, 127.93, 127.37, 95.84, 81.95, 77.25, 69.15, 42.48, 34.44, 29.86, 26.67, 26.50, 24.26, 18.21, 18.11, 17.34, 14.49, 2.85. **HRMS** (Cl^+): *m/z* calcd. for $C_{25}H_{40}O_3Si$ $[M-H]^+$ 415.2663, found 415.2766.

Preparation of Diol-10a

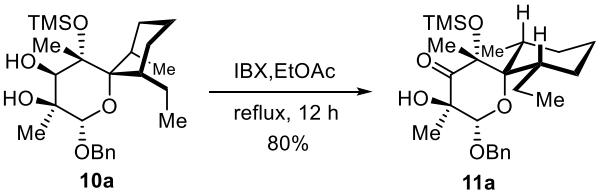


To a stirred solution of protected tertiary alcohol **9a** (107 mg, 0.26 mmol) in EtOAc/MeCN/H_2O (3:3:1, 1.5: 1.5: 0.5 mL) at 0°C was added ruthenium (III) chloride (5 mg, 0.026 mmol). After all the solid was dissolved, the reaction mixture was added sodium periodate (110 mg, 0.51 mmol) in one portion and stirred at the same temperature for 2 h. Sat. aqueous $Na_2S_2O_3$ (10 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 10 mL), brine (10 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/10) to afford **10a** (20 mg, 17%) as a white solid and **11a** (15 mg, 13%) as a white solid.

10a R_f = 0.3 (EtOAc /petroleum ether = 1/6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.27 (m, 5H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.74 (s, 1H), 4.58 (d, *J* = 12.0 Hz, 1H), 3.47 (s, 1H), 3.12 (br, 1H), 2.53–2.36 (m, 2H), 2.13 (br, 1H), 1.92–1.80 (m, 1H), 1.79–1.69 (m, 2H), 1.65 (s, 3H), 1.55–1.47 (m, 1H), 1.47–1.37 (m, 4H), 1.37–1.23 (m, 3H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.85 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.47, 128.50, 127.64, 127.44, 96.27, 84.81, 83.48, 80.41, 72.12, 70.40, 38.16, 32.85, 30.02, 27.58, 25.72, 22.15, 21.82, 17.45, 15.20, 14.82, 2.89. **HRMS** (Cl^+): *m/z* calcd. for $C_{25}H_{46}NO_5Si$ $[M+NH_4]^+$ 468.3140, found 468.3081.

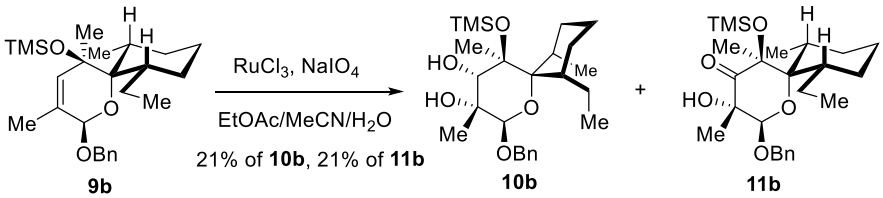
11a R_f = 0.6 (EtOAc /petroleum ether = 1/6). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47–7.39 (m, 2H), 7.34 (t, *J* = 8.0 Hz, 2H), 7.30–7.22 (m, 1H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.85 (s, 1H), 4.75 (d, *J* = 12.0 Hz, 1H), 3.65 (s, 1H), 1.98–1.87 (m, 1H), 1.72– 1.65 (m, 1H), 1.63–1.55 (m, 5H), 1.53–1.46 (m, 1H), 1.45 (s, 3H), 1.35–1.28 (m, 3H), 1.23–1.21 (m, 1H), 1.20–1.17 (m, 3H), 1.13–1.08 (m, 1H), 0.79–0.73 (m, 3H), 0.13 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.34, 138.33, 128.36, 127.55, 127.44, 99.71, 83.32, 81.63, 77.80, 70.73, 46.74, 38.18, 33.50, 29.85, 26.82, 25.99, 23.60, 20.23, 20.11, 14.65, 2.17. **HRMS** (Cl^+): *m/z* calcd. for $C_{25}H_{41}O_5Si$ $[M+H]^+$ 449.2718, found 449.2707.

Preparation of Hydroxyl Ketone-11a



To a stirred solution of **10a** (20 mg, 0.044 mmol) in EtOAc (1 mL) was added 2-Iodoxybenzoic acid (37 mg, 0.133 mmol). The reaction mixture was reflexed for 12 h and then filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/10) to afford **11a** (16 mg, 80%) as a white solid.

Preparation of Diol-10b



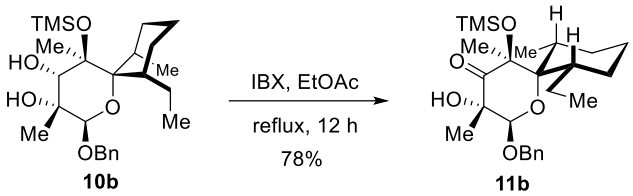
To a stirred solution of protected tertiary alcohol **9b** (81 mg, 0.20 mmol) in EtOAc/MeCN/H_2O (3:3:1, 1.5: 1.5: 0.5 mL) at 0^{o}C was added ruthenium (III) chloride (4 mg, 0.019 mmol). After all the solid was dissolved, the reaction mixture was added sodium periodate (83 mg, 0.39 mmol) in one portion and stirred at the same temperature for 2 h. Sat. aqueous $Na_2S_2O_3$ (10 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (3 x 10 mL). The combined organic phase was washed with H_2O (2 x 10 mL), brine (10 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/10) to afford **10b** (18 mg, 21%) as a white solid and **11b** (18 mg, 21 %) as a white solid.

10b R_f = 0.2 (EtOAc /petroleum ether = 1/8). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.27 (m, 5H), 5.01 (d, *J* = 12.0 Hz, 1H), 4.91 (s, 1H), 4.59 (d, *J* = 12.0 Hz, 1H), 3.48 (s, 1H), 3.11 (br, 1H), 2.95–2.81 (m, 1H), 2.18–2.06 (m, 1H), 2.02–1.93 (m, 1H), 1.89–1.76 (m, 1H), 1.71–1.64 (m, 1H), 1.62 (s, 3H), 1.57– 1.49 (m, 2H), 1.43 (s, 3H), 1.41–1.31 (m, 2H), 1.19–1.12 (m, 4H), 0.87 (t, *J* = 7.2 Hz, 3H), 0.16 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 138.77, 128.47, 127.62, 127.49, 96.45, 84.58, 83.74, 80.57, 72.11, 70.32, 41.08, 30.13, 29.43, 27.39, 25.19, 22.83, 21.76, 17.67, 15.47, 14.59, 2.82. **HRMS** (Cl^+) *m/z* calcd. for $C_{25}H_{45}NO_5Si$ $[M+NH_3]^+$ 467.3067, found 467.3083.

11b R_f = 0.4 (EtOAc /petroleum ether = 1/8). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42–7.28 (m, 5H), 4.99–4.96 (m, 2H), 4.73 (d, *J* = 12.0 Hz, 1H), 3.75 (s, 1H), 2.26–2.16 (m, 1H), 1.71–1.65 (m, 3H), 1.58 (s, 3H), 1.56–

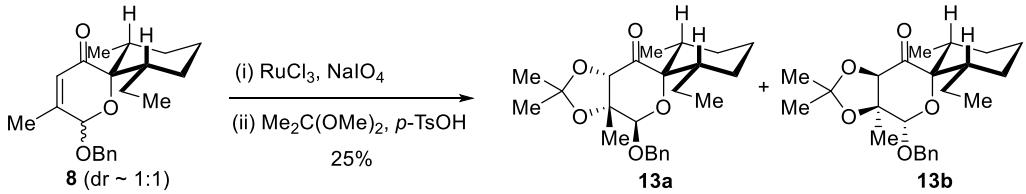
1.53 (m, 1H), 1.44 (s, 3H), 1.41–1.23 (m, 5H), 0.90 (t, *J* = 7.2 Hz, 3H), 0.82 (d, *J* = 7.2 Hz, 3H), 0.14 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 210.75, 138.32, 128.36, 127.54, 127.47, 100.46, 83.44, 82.01, 78.08, 70.50, 43.16, 35.33, 29.85, 29.36, 23.86, 23.37, 20.69, 20.39, 19.84, 13.42, 2.08. **HRMS** (CI^+): *m*/*z* calcd. for $C_{25}H_{41}O_5Si$ $[M+H]^+$ 449.2718, found 449.2713.

Preparation of Hydroxyl Ketone-11b



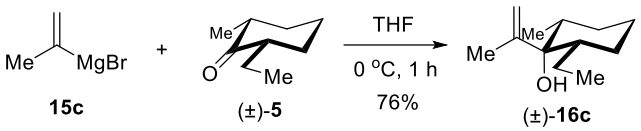
To a stirred solution of **10b** (18 mg, 0.04 mmol) in EtOAc (1 mL) was added 2-Iodoxybenzoic acid (34 mg, 0.12 mmol). The reaction mixture was reflexed for 12 h and then filtered through a pad of Celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/10) to afford **11b** (14 mg, 78%) as a white solid.

Preparation of Diol Acetonide-13a and 13b



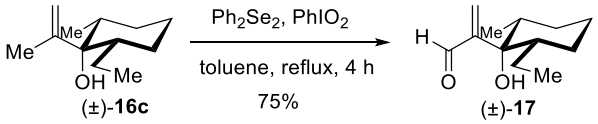
To a stirred solution of enone **8** (200 mg, 0.61 mmol) in EtOAc/MeCN/H_2O (3:3:1, 4.5: 4.5: 1.5 mL) at 0°C was added ruthenium (III) chloride (13 mg, 0.06 mmol). After all the solid was dissolved, the reaction mixture was added sodium periodate (260 mg, 1.22 mmol) in one portion and stirred at the same temperature for 2 h. Sat. aqueous $Na_2S_2O_3$ (10 mL) was added to quench the reaction. The reaction mixture was extracted with EtOAc (2 x 10 mL). The combined organic phase was washed with H_2O (2 x 10 mL), brine (10 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (2 mL). To this solution was added *p*-toluenesulfonic acid (10 mg, 0.06 mmol) and 2,2-dimethoxypropane (0.37 mL, 3.05 mmol). The reaction mixture was reflexed for 3 h and then quenched with Sat. aqueous $NaHCO_3$ (5 mL). The reaction mixture was extracted with EtOAc (2 x 10 mL). The combined organic phase was washed with H_2O (2 x 10 mL), brine (10 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/25) to afford **13a** and **13b** as an inseparable mixture (61 mg, 25%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.45−7.37 (m, 2H), 7.37−7.30 (m, 2H), 7.29−7.21 (m, 1H), 5.05−4.95 (m, 2H), 4.87−4.71 (m, 1H), 4.11−3.98 (m, 1H), 2.06−1.94 (m, 1H), 1.78−1.66 (m, 2H), 1.63−1.56 (m, 1H), 1.55 (s, 3H), 1.51−1.44 (m, 2H), 1.44−1.37 (m, 4H), 1.37−1.34 (m, 1H), 1.33 (s, 3H), 1.31−1.21 (m, 2H), 0.88−0.74 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 211.65, 137.72, 128.38, 128.34, 127.73, 127.48, 110.50, 110.28, 99.84, 99.70, 90.27, 90.07, 83.56, 83.21, 81.36, 81.06, 70.14, 70.00, 50.03, 48.94, 42.84, 41.25, 29.84, 27.83, 27.71, 26.80, 26.70, 25.86, 25.75, 25.39, 25.30, 25.05, 19.76, 18.77, 18.28, 18.01, 13.76, 12.38. **HRMS** (ESI): *m*/*z* calcd. for $C_{24}H_{35}O_5$ $[M+H]^+$ 403.2479, found 403.2481.

Preparation of Tertiary Alcohol (±)-16c



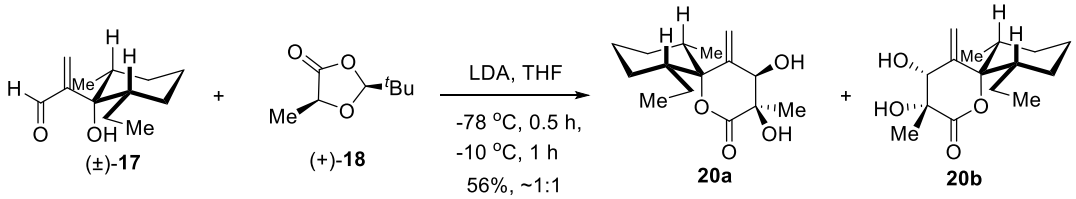
To a stirred solution of (±)-**5** (1.3 g, 9.3 mmol) in THF (15 mL) was added isopropenyl magnesium bromide **15c** (1.0 M in THF, 18.6 mmol) at 0 °C. the reaction mixture was stirred at this temperature for 1 h. Sat. aqueous NH_4Cl (20 mL) was added to quench the reaction. The mixture was extracted with EtOAc (2 x 20 mL). The combined organic phase was washed with H_2O (2 x 20 mL), brine (20 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/40) to afford (±)-**16c** (1.3 g, 76%) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.01 (br, 1H), 4.91 (s, 1H), 1.79−1.68 (m, 2H), 1.66 (s, 3H), 1.63−1.54 (m, 1H), 1.51−1.42 (m, 1H), 1.42−1.22 (m, 4H), 1.01−0.89 (m, 1H), 0.84 (t, *J* = 8.0 Hz, 3H), 0.71 (t, *J* = 8.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 148.38, 111.30, 79.59, 43.89, 36.79, 30.08, 26.00, 25.97, 22.45, 19.47, 15.59, 12.65. **HRMS (ESI)**: m/z Calcd. for $C_{12}H_{23}O$, $[M+H]^+$ 183.1743; Found: 183.1623.

Preparation of Aldehyde (±)-17



To a stirred solution of (±)-**16c** (500 mg, 2.7 mmol) in toluene (25 mL) was added $PhIO_2$ (3 g, 13.7 mmol), Ph_2Se_2 (1.7 g, 5.5 mmol) and pyridine (10.2 mL, 46.3 mmol). The reaction mixture was refluxed for 4 h, and then cooled to room temperature. EtOAc (30 mL) was added, and the organic phase was washed with H_2O (2 x 20 mL), brine (20 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/20) to afford (±)-**17** (406 mg, 75%) as a yellow oil. **^{1}H NMR** (400 MHz, $CDCl_3$): δ 9.57 (s, 1H), 6.68 (s, 1H), 6.18 (s, 1H), 2.25−2.09 (m, 1H), 1.98−1.86 (m, 1H), 1.79−1.65 (m, 2H), 1.56−1.47 (m, 1H), 1.36−1.23 (m, 2H), 1.21−1.10 (m, 2H), 1.03−0.90 (m, 1H), 0.83−0.74 (m, 3H), 0.64 (d, *J* = 10.8 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 193.62, 153.38, 138.24, 77.36, 43.12, 36.38, 29.81, 25.78, 25.46, 23.00, 15.91, 12.37. **HRMS (ESI)**: m/z Calcd. for $C_{12}H_{21}O_2$, $[M+H]^+$ 197.1536; Found: 197.1771.

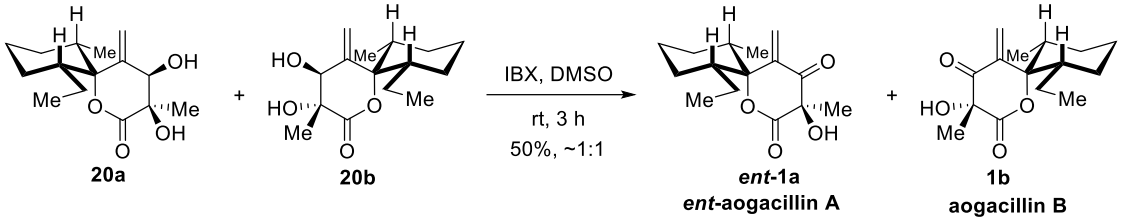
Preparation of Lactones 20a and 20b



To a stirred solution of (+)-**18** (200 mg, 1.3 mmol) in THF (1.0 mL) was added lithium diisopropylamide (2.0 M in THF, 1.0 mL, 2 mmol) dropwise at -78 °C. After stirring for 0.5 h, (±)-**17** (130 mg, 0.7 mmol) in THF (0.5 mL) was added at the same temperature. The reaction mixture was warmed to -10 °C and stirred for 1 h. Sat. aqueous NH_4Cl (5 mL) was added to quench the reaction and the organic phase was collected. The aqueous phase was extracted with EtOAc (2×10 mL). The combined organic phase was washed with H_2O (2 x 10 mL), brine (10 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/1) to afford an inseparable mixture of **20a** and

20b (100 mg, 56%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 5.59−5.53 (m, 1H), 5.19−5.12 (m, 1H), 4.25−4.15 (m, 1H), 2.87−2.65 (m, 1H), 2.55−2.40 (m, 1H), 1.95−1.67 (m, 3H), 1.65−1.54 (m, 5H), 1.54−1.30 (m, 5H), 0.90−0.79 (m, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 173.67, 173.60, 146.07, 145.86, 110.77, 110.11, 92.56, 92.45, 77.36, 74.03, 73.66, 72.10, 52.51, 49.36, 46.19, 42.85, 30.30, 30.08, 25.67, 25.08, 24.31, 24.19, 23.91, 23.18, 22.92, 17.08, 12.63, 12.08. **HRMS (ESI)**: m/z Calcd. for $C_{15}H_{24}O_4Na$, $[M+Na]^+$ 291.1567; Found: 291.2729.

Preparation of *ent*-aogacillin A and aogacillin B

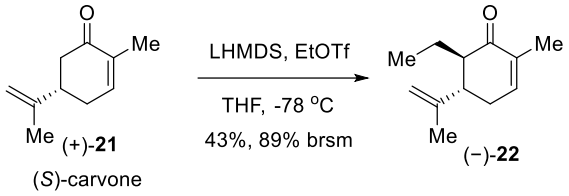


To a stirred solution of **20a** and **20b** (100 mg, 0.4 mmol) in DMSO (1 mL) was added 2-Iodoxybenzoic acid (336 mg, 1.2 mmol). The reaction mixture was stirred at room temperature for 3 h and water (3 mL) was added. The mixture was extracted with EtOAc (2×3 mL). The organic phase was washed with (5×3 mL), brine (3 mL), dried over $NaSO_4$ and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using eluents (EtOAc/petroleum ether = 1/5) to afford a mixture of ***ent*-1a** and **1b** (50 mg, 50%) as a yellow syrup. This mixture was further purified by HPLC on Prep-C18 column (Agilent InfinityLab ZORBAX Eclipse Plus C18 21.2 x250 mm, 5 um) detected at UV 254 nm. The mobile phase (MeCN:H_2O): 0~35 min, 20:80 to 60:40 at 7.0 mL/minute; 35~42 min, 60:40 to 75:25 at 5.0 mL/minute; 42~45 min, 75:25 at 5.0 mL/minute. The retention times of *ent*-aogacillins A (***ent*-1a**) and aogacillins B (**1b**) were 42.044 and 42.443 minutes respectively. 40 mg of the mixture was divided into 6 injections for purification. The combined fractions were lyophilized to give *ent*-aogacillin A (5.8 mg) as a yellow syrup and aogacillin B (4 mg) as a white solid.

***ent*-aogacillin A** $[\alpha]_D^{24}$ = −28.0 (*c* 0.1, MeOH). (Lit[4] $[\alpha]_D^{26.9}$ = +71.6 (*c* 0.1, MeOH).) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.49 (s, 1H), 5.60 (s, 1H), 3.54 (br, 1H), 2.05−1.94 (m, 1H), 1.87−1.75 (m, 2H), 1.73−1.66 (m, 1H), 1.65−1.57 (m, 4H), 1.49−1.34 (m, 2H), 1.34−1.27 (m, 1H), 1.18−1.07 (m, 1H), 1.98 (d, *J* = 6.8 Hz, 3H), 0.96−0.86 (m, 1H), 0.79 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 195.88, 172.51, 143.65, 124.76, 90.73, 77.10, 54.22, 41.05, 29.39, 28.10, 26.02, 25.28, 22.64, 16.93, 12.14. **^{1}H NMR** (400 MHz, CD_3OD): δ 6.45 (s, 1H), 5.77 (s, 1H), 2.17−2.06 (m, 1H), 1.86−1.77 (m, 2H), 1.65−1.58 (m, 2H), 1.54 (s, 3H), 1.51−1.44(m, 1H), 1.44−1.35 (m, 2H), 1.34−1.27 (m, 1H), 1.27−1.18 (m, 1H), 0.95 (d, *J* = 7.4 Hz, 3H), 0.82 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD): δ 197.39, 174.92, 145.54, 125.52, 91.64, 77.84, 54.61, 42.36, 30.70, 27.29, 27.23, 26.18, 23.92, 17.18, 12.31. **HRMS (ESI)**: m/z Calcd. for $C_{15}H_{22}O_4Na$, $[M+Na]^+$ 289.1410; Found: 289.1414.

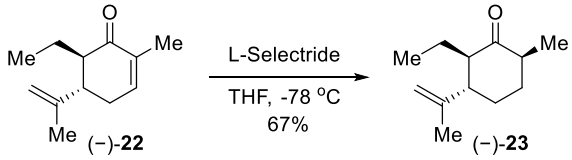
Aogacillin B $[\alpha]_D^{24}$ = +3.0 (*c* 0.1, MeOH). (Lit[4] $[\alpha]_D^{26.9}$ = +38.7 (*c* 0.1, MeOH).) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.46 (s, 1H), 5.57 (s, 1H), 3.53 (br, 1H), 1.94−1.80 (m, 2H), 1.74−1.64 (m, 2H), 1.63−1.60 (m, 3H), 1.60−1.48 (m, 4H), 1.44−1.31 (m, 1H), 1.24−1.14 (m, 1H), 0.92 (t, *J* = 7.4 Hz, 3H), 0.70 (d, *J* = 6.0 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 196.22, 172.52, 143.80, 124.31, 90.93, 77.36, 47.72, 47.46, 30.36, 28.18, 25.32, 25.05, 23.59, 15.67, 12.33. **^{1}H NMR** (400 MHz, CD_3OD): δ 6.42 (s, 1H), 5.74 (s, 1H), 1.94−1.78 (m, 3H), 1.73−1.59 (m, 2H), 1.54 (s, 3H), 1.53−1.40 (m, 3H), 1.33−1.27 (m, 1H), 1.18−1.07 (m, 1H), 0.94 (d, *J* = 7.4 Hz, 3H), 0.72 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (101 MHz, CD_3OD): δ 197.63, 174.98, 145.64, 125.14, 91.87, 77.95, 48.73, 48.08, 31.46, 27.35, 26.38, 26.20, 24.71, 16.10, 12.30. **HRMS (ESI)**: m/z Calcd. for $C_{15}H_{22}O_4Na$, $[M+Na]^+$ 289.1410; Found: 289.1415.

Preparation of Enone (−)-22



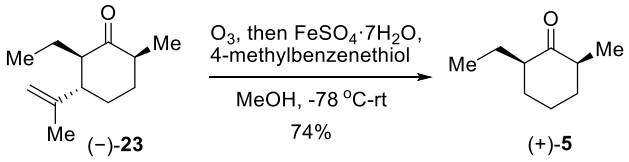
To a solution of (*S*)-Carvone (+)-**21** (20 g, 133.1 mmol) in dry THF (200 mL) was carefully added LHMDS (1.0 M in THF, 173.1 mL, 173.1 mmol) at −78 °C under nitrogen atmosphere, and the reaction mixture was stirred at this temperature for 1h. Then ethyl triflate (118.6 g, 81.2 mL, 665.7 mmol) was added to the solution slowly via syringe, and the reaction mixture was warmed to −20 °C and stirred for 4 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (30 mL). The mixture was extracted with EtOAc (3 × 100 mL). The combined organic extracts were washed with water (2 × 100 mL) and brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by silica gel column chromatography (EtOAc/petroleum ether = 1/400) to give compound (−)-**22** (10.1 g, 43% yield, 89% brsm yield) as colorless oil and (+)-**21** (10.4 g, 52%) was recovered. R_f = 0.8 (EtOAc/petroleum ether = 1/50). $[\alpha]_D^{25}$ = −29.3 (*c* 0.19, $CHCl_3$). (Lit[5] (+)-**22** $[\alpha]_D$ = +9.95 (*c* 0.46, $CHCl_3$).) **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.64 (s, 1H), 4.81 (d, *J* = 7.9 Hz, 2H), 2.75−2.65 (m, 1H), 2.48−2.36 (m, 1H), 2.36−2.25 (m, 2H), 1.87−1.78 (m, 1H), 1.76 (s, 3H), 1.71 (s, 3H), 1.53−1.39 (m, 1H), 0.87 (t, *J* = 7.9 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 203.59, 145.94, 142.97, 135.39, 113.19, 50.28, 46.79, 30.72, 20.41, 18.97, 16.22, 10.91. **HRMS (ESI)**: m/z Calcd. for $C_{12}H_{18}ONa$, $[M+Na]^+$ 201.12499; Found: 201.12497.

Preparation of Ketone (−)-23



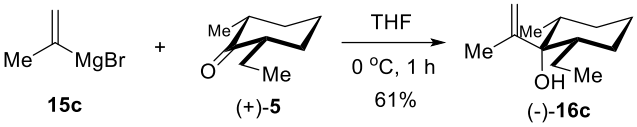
To a dry THF solution (10 mL) of (−)-**22** (1.0 g, 5.6 mmol) under nitrogen at −78 °C was added L-Selectride (1.0 M in THF, 5.6 mL, 5.6 mmol). Then the mixture was stirred for 1h at −78 °C. Addition of 10% NaOH solution (16 mL) and 30% H_2O_2 (12 mL) sufficed to oxidize the trialkylborane by-product after stirring for 3 h at room temperature. Then the reaction was extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with water (2 × 20 mL) and brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/petroleum ether = 1/400) to give compound (−)-**23** (675 mg, 67%) as colorless oil. R_f = 0.8 (EtOAc/petroleum ether = 1/50). $[\alpha]_D^{25}$ = −10.3 (*c* 0.15, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 4.76 (s, 1H), 4.72 (s, 1H), 2.47−2.33 (m, 1H), 2.26−2.12 (m, 2H), 2.12−1.99 (m, 1H), 1.89−1.76 (m, 1H), 1.76−1.70 (m, 1H), 1.69 (s, 3H), 1.62−1.46 (m, 1H), 1.41−1.21 (m, 2H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$): δ 213.49, 146.48, 112.29, 54.70, 54.05, 45.76, 35.89, 31.84, 19.52, 18.26, 14.67, 12.55. **HRMS (ESI)**: m/z Calcd. for $C_{12}H_{20}ONa$, $[M+H]^+$ 203.14064; Found: 203.14052.

Preparation of (+)-*cis*-2-ethyl-6-methylcyclohexanone (+)-5



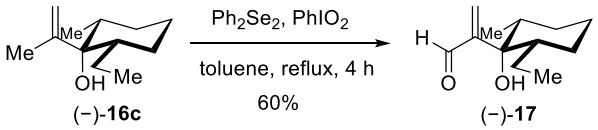
A solution of (−)-**23** (5.7 g, 31.3 mmol) in MeOH/CH_2Cl_2 (3/1, 500 mL) was cooled to −78 °C while open to the air. Ozone was bubbled through the solution for 2 h, until TLC showed consumption of the starting material. The solution was then sparged with nitrogen for 15 min to expel the excess ozone. 4-Methylbenzenethiol (5.8 g, 47.0 mmol) was then added by syringe, followed by the portion-wise addition of ferrous sulfate heptahydrate (10.5 g, 37.6 mmol). The green heterogeneous mixture was stirred at −78 °C for 15 min before the cooling bath was removed. After warming to room temperature, the reaction was stirred for an additional 2 h until TLC showed complete consumption of the peroxide intermediate. Water (63 mL) was added, and the reaction was extracted with CH_2Cl_2 (3 × 200 mL). The combined organic extracts were washed with brine (200 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum. The residue was purified by column chromatography (EtOAc/petroleum ether = 1/50) to give compound (+)-**5** (3.3 g, 74%) as a yellow oil. R_f = 0.7 (EtOAc/petroleum ether = 1/20). $[\alpha]_D^{25}$ = +3.75 (*c* 0.32, $CHCl_3$). The ^{1}HNMR and ^{13}CNMR matches those of racemic **5**.

Preparation of Tertiary Alcohol (−)-16c



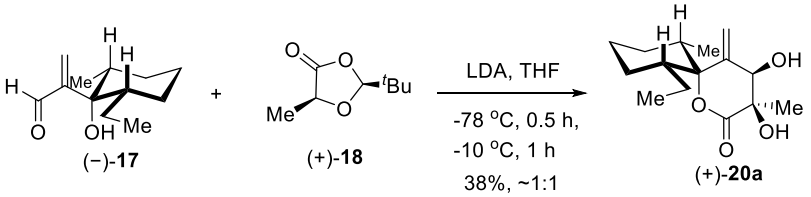
According to the procedure for preparing racemic (±)-**16c**, (−)-**16c** (2.6 g, 14.4 mmol, 61% yield) was prepared as a colorless oil from **15c** (1.0 M, 35.6 mL, 35.6 mmol) and (+)-**5** (3.3 g, 23.6 mmol). $[\alpha]_D^{25}$ = -5.63 (*c* 0.32, $CHCl_3$). The ^{1}H NMR and ^{13}C NMR are the same as those of racemic (±)-**16c**.

Preparation of Aldehyde (−)-17



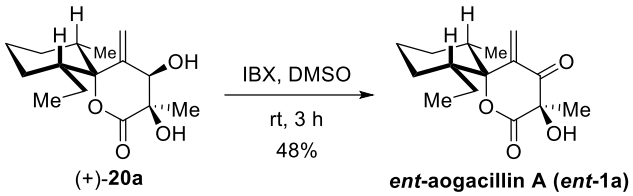
According to the procedure for preparing racemic (±)-**17**, (−)-**17** (1.3 g, 6.6 mmol, 60% yield) was prepared as a yellow oil from (−)-**16c** (2.0 g, 11.0 mmol). $[\alpha]_D^{25}$ = -17.14 (*c* 0.28, $CHCl_3$). The ^{1}H NMR and ^{13}C NMR are the same as those of racemic (±)-**17**.

Preparation of Lactones (+)-20a



According to the procedure for preparing mixture of **20a** and **20b**, (+)-**20** (52 mg, 0.19 mmol) was prepared as a colorless solid from (−)-**17** (100 mg, 0.5 mmol) and (+)-**18** (322 mg, 2.0 mmol). $[\alpha]_D^{25}$ = +81.67 (*c* 0.06, $CHCl_3$). **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.57 (d, *J* = 2.5 Hz, 1H), 5.15 (d, *J* = 2.5 Hz, 1H), 4.21 (d, *J* = 10.5 Hz, 1H), 2.72−2.62 (m, 1H), 2.49−2.42 (m, 1H), 1.86−1.75 (m, 3H), 1.74−1.67 (m, 1H), 1.64 (s, 3H), 1.62−1.53 (m, 3H), 1.49−1.32 (m, 3H), 0.88 (d, *J* = 5.5 Hz, 3H), 0.83−0.80 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 173.61, 146.08, 110.12, 92.53, 73.67, 72.11, 49.37, 46.19, 30.30, 25.66, 25.65, 24.35, 23.17, 17.08, 12.64.

Preparation of *ent*-aogacillin A



(+)-**20a** ***ent*-aogacillin A (*ent*-1a)**

According to the procedure for preparing the mixture of *ent*-aogacillin A and aogacillin B, *ent*-aogacillin A ***ent*-1a** (9.5 mg, 0.036 mmol, 48% yield) was prepared from (+)-**20a** (20 mg, 0.075 mmol).

References

[1] S. Chakraborty and C. Saha, *Eur. J. Org. Chem*. 2013, **2013**, 5731–5736.

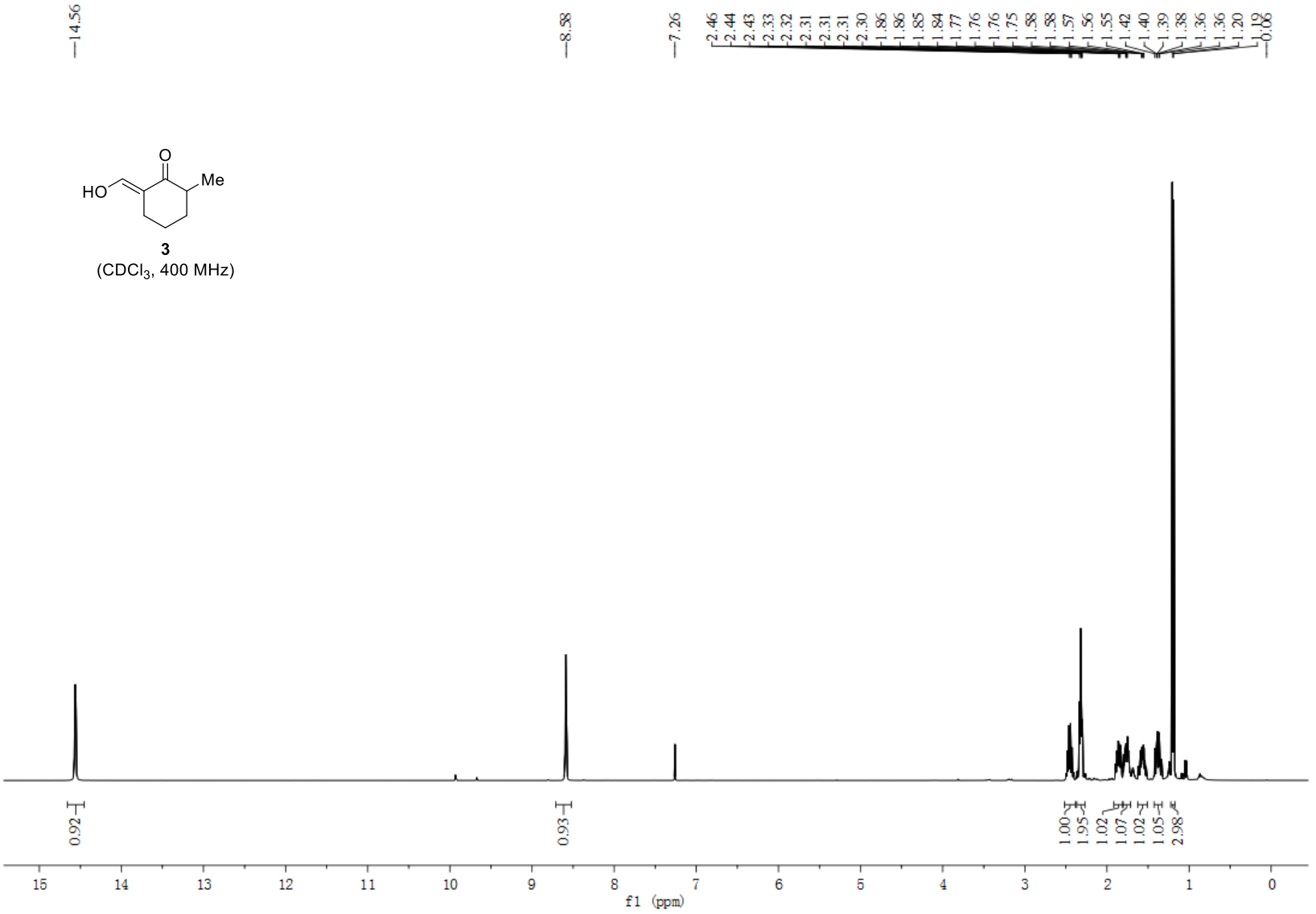
[2] R. E. Ireland and P. W. Schiess, *J. Org. Chem.* 1963, **28**, 6–16.

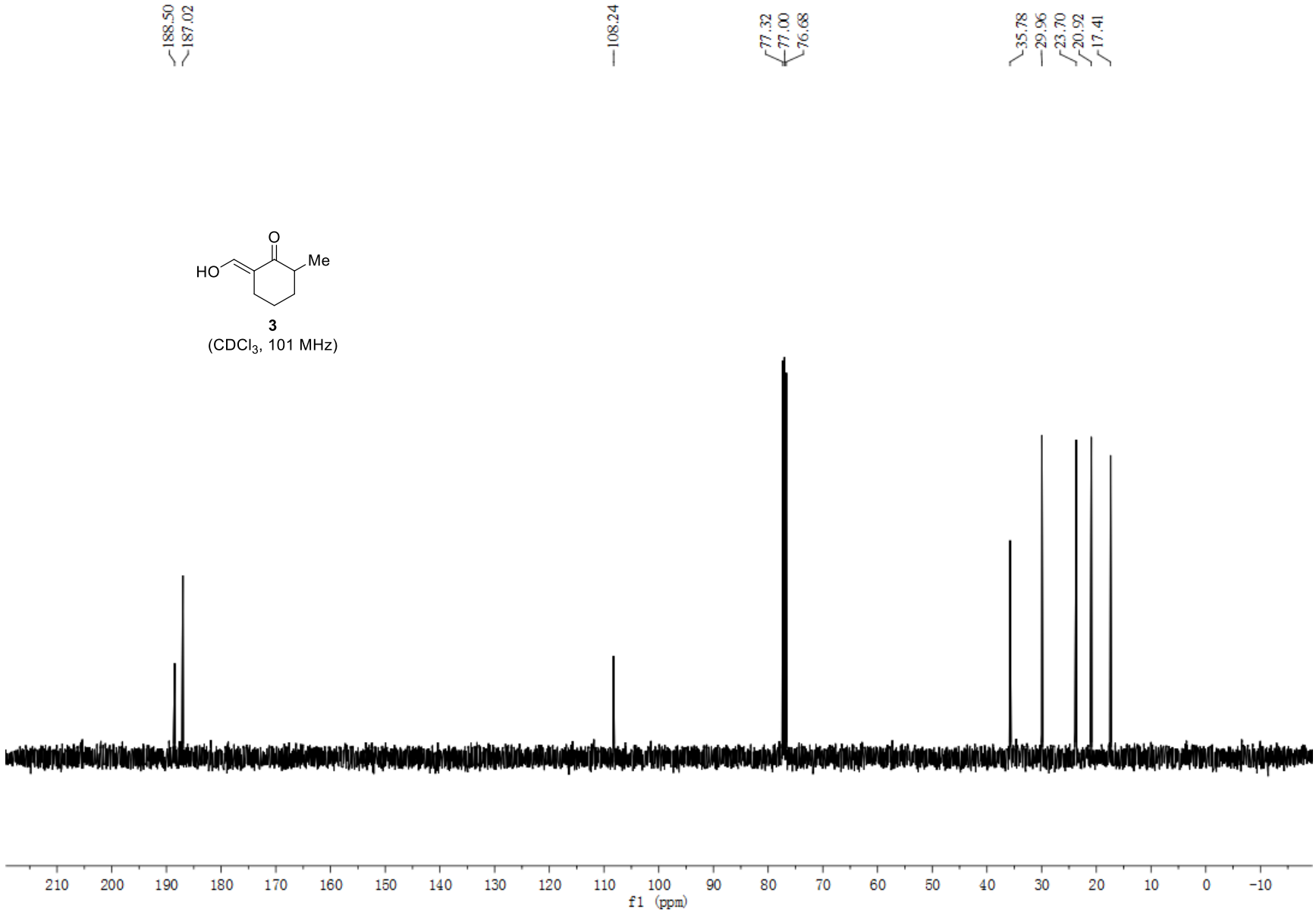
[3] T. Miyoshi, T. Miyakawa, M. Ueda and O. Miyata, *Angew. Chem. Int. Ed.* 2011, **50**, 928–931.

[4] K. Takata, IM. watsuki, T. Yamamoto, T. Shirahata, K. Nonaka, R. Masuma, Y. Hayakawa, H. Hanaki, Y. Kobayashi, G. A. Peterson, S. Omura and K. Shiomi, *Org. Lett.* 2013, ***15***, 4678–4681.

[5] J. P. Gesson, J. C. Jacquesy and B. Renoux, *Tetrahedron* 1989, **45**, 5853–5866.

Copies of ^{1}H- and ^{13}C-NMR Spectra

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187.02
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77.32
77.00
76.68
35.78
29.96
23.70
20.92
17.41
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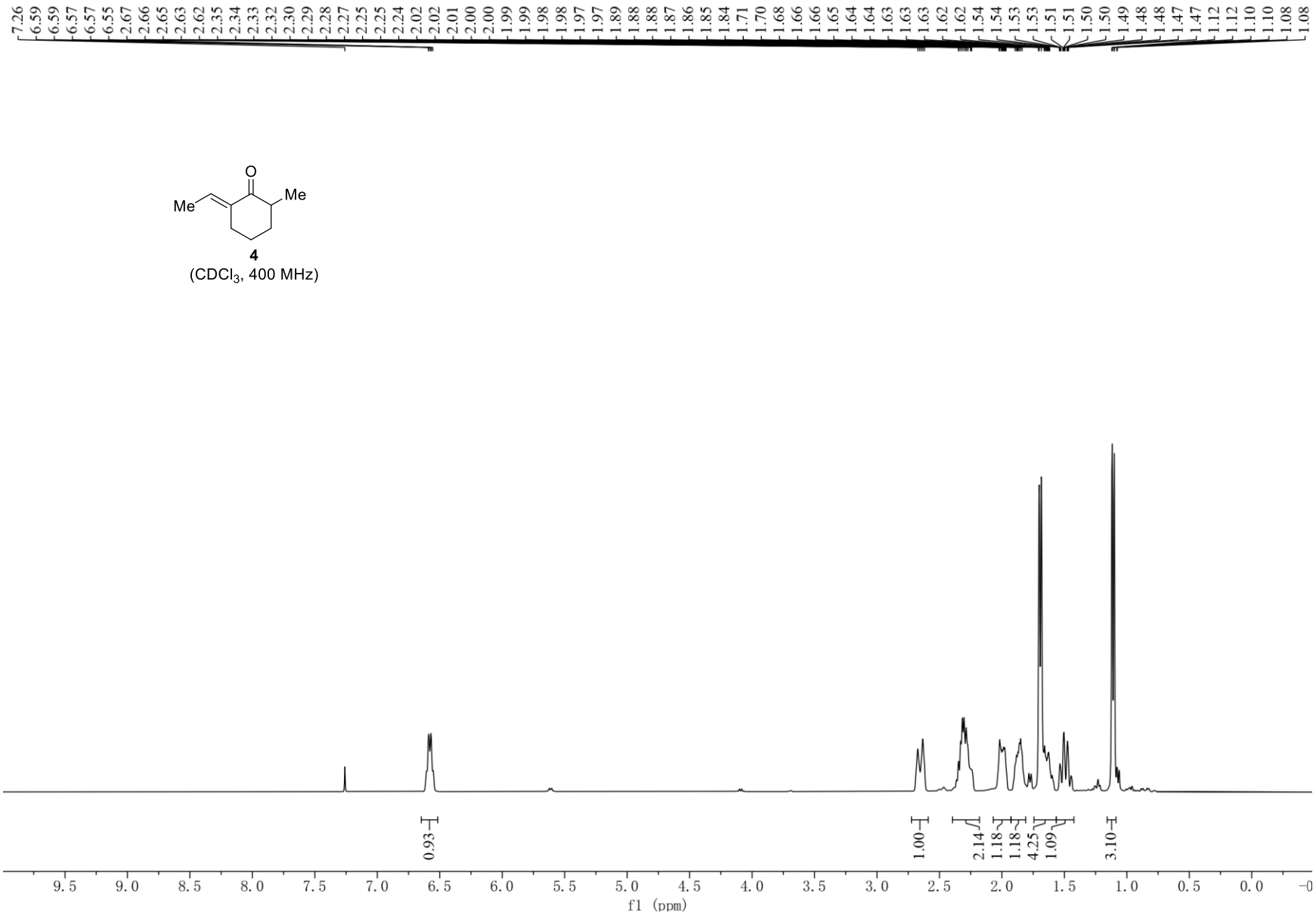
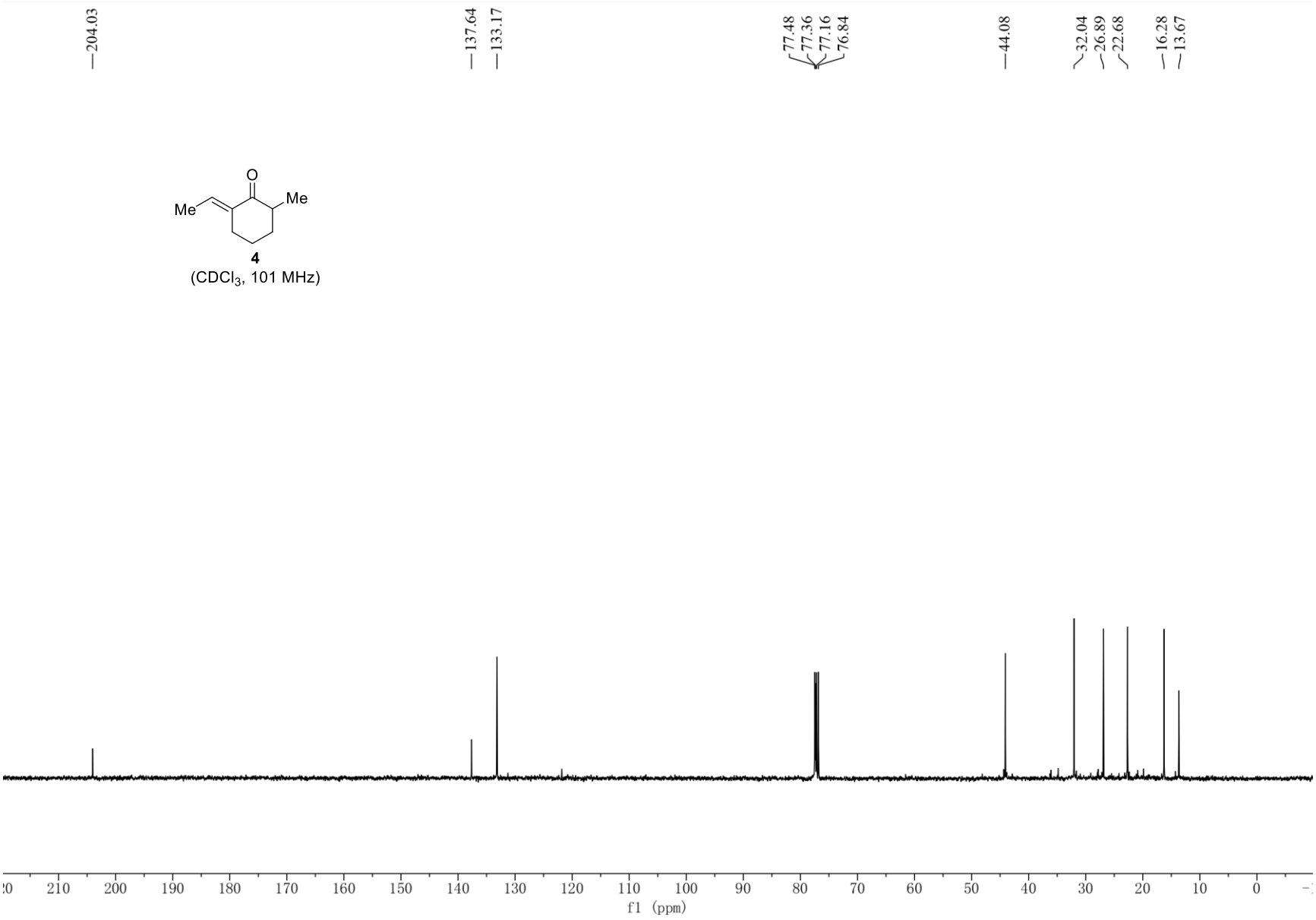
HO
Me
3
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4

($CDCl_3$, 400 MHz)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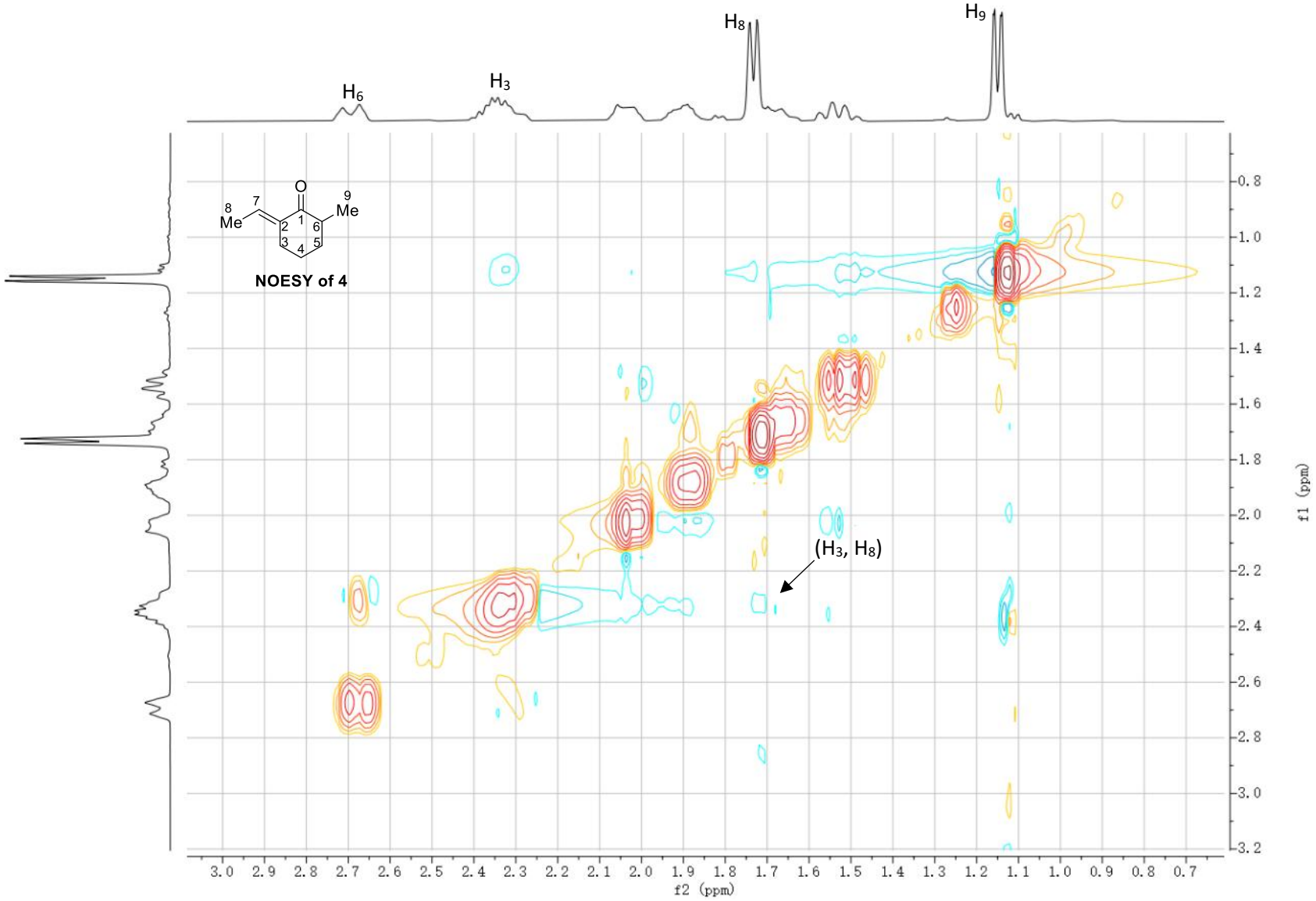
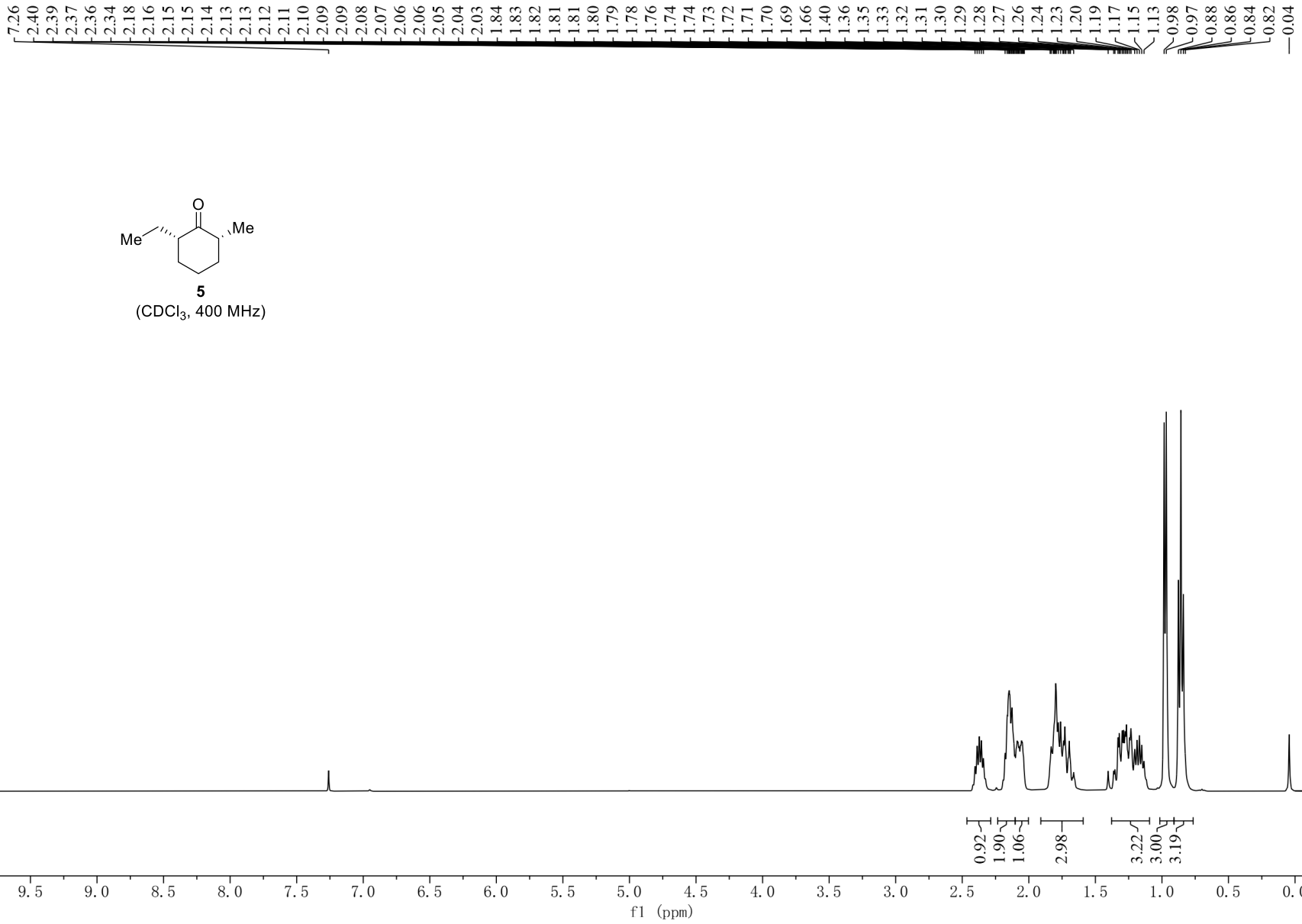
137.64
133.17
77.48
77.36
77.16
76.84
44.08
32.04
26.89
22.68
16.28
13.67
O
Me
Me
4
(CDCl3, 101 MHz)
f1 (ppm)


H6
H3
H8
H9
O
1
2
3
4
5
6
7
8
9
Me
Me
NOESY of 4
(H3, H8)
f2 (ppm)
f1 (ppm)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2.40
2.39
2.37
2.36
2.34
2.18
2.16
2.15
2.15
2.14
2.13
2.13
2.12
2.11
2.10
2.09
2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.03
1.84
1.83
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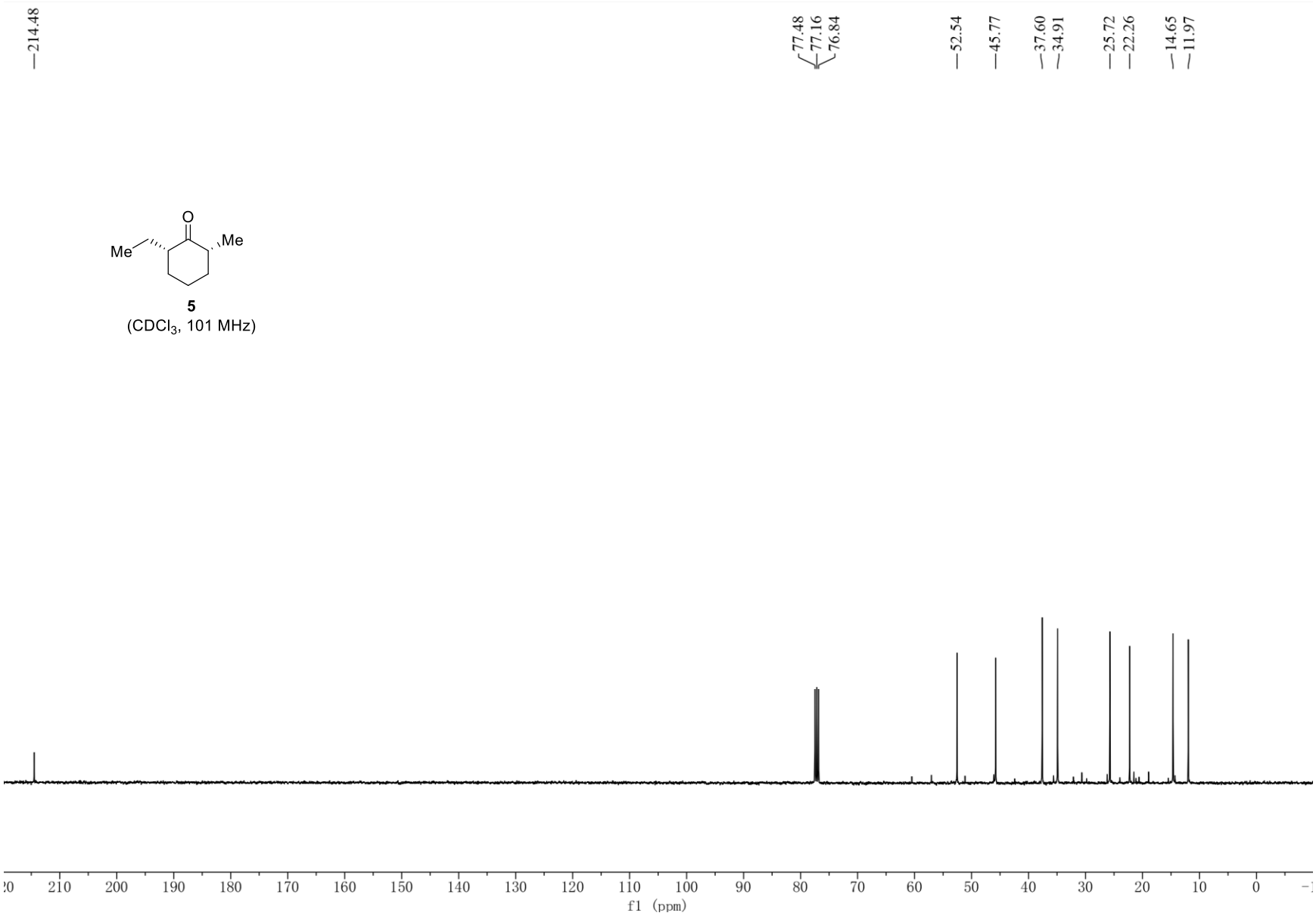
1.24
1.23
1.20
1.19
1.17
1.15
1.13
0.98
0.97
0.88
0.86
0.84
0.82
0.04
O
Me
Me
5
(CDCl3, 400 MHz)
0.92
1.90
1.06
2.98
3.22
3.00
3.19
0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0
f1 (ppm)



5

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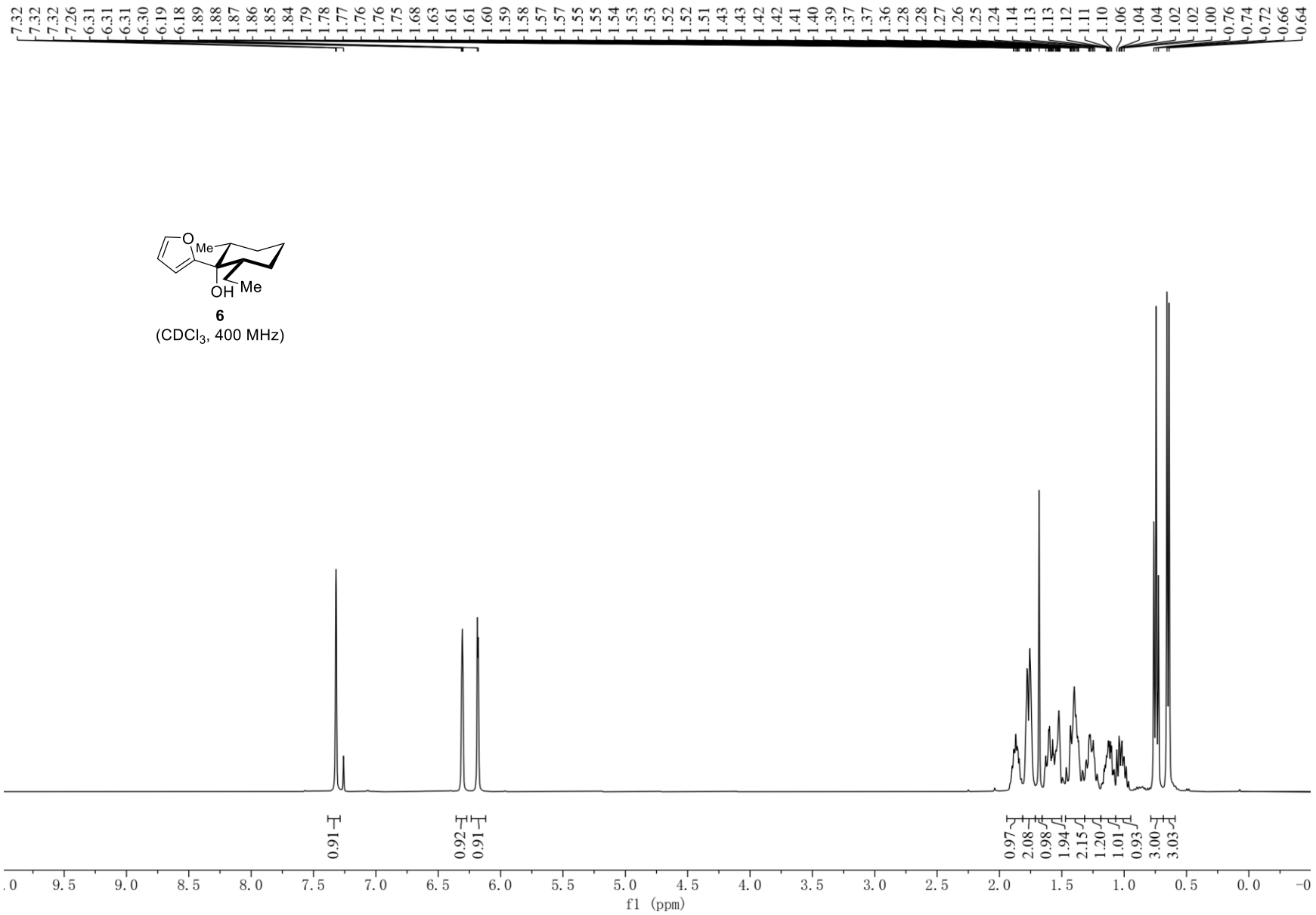
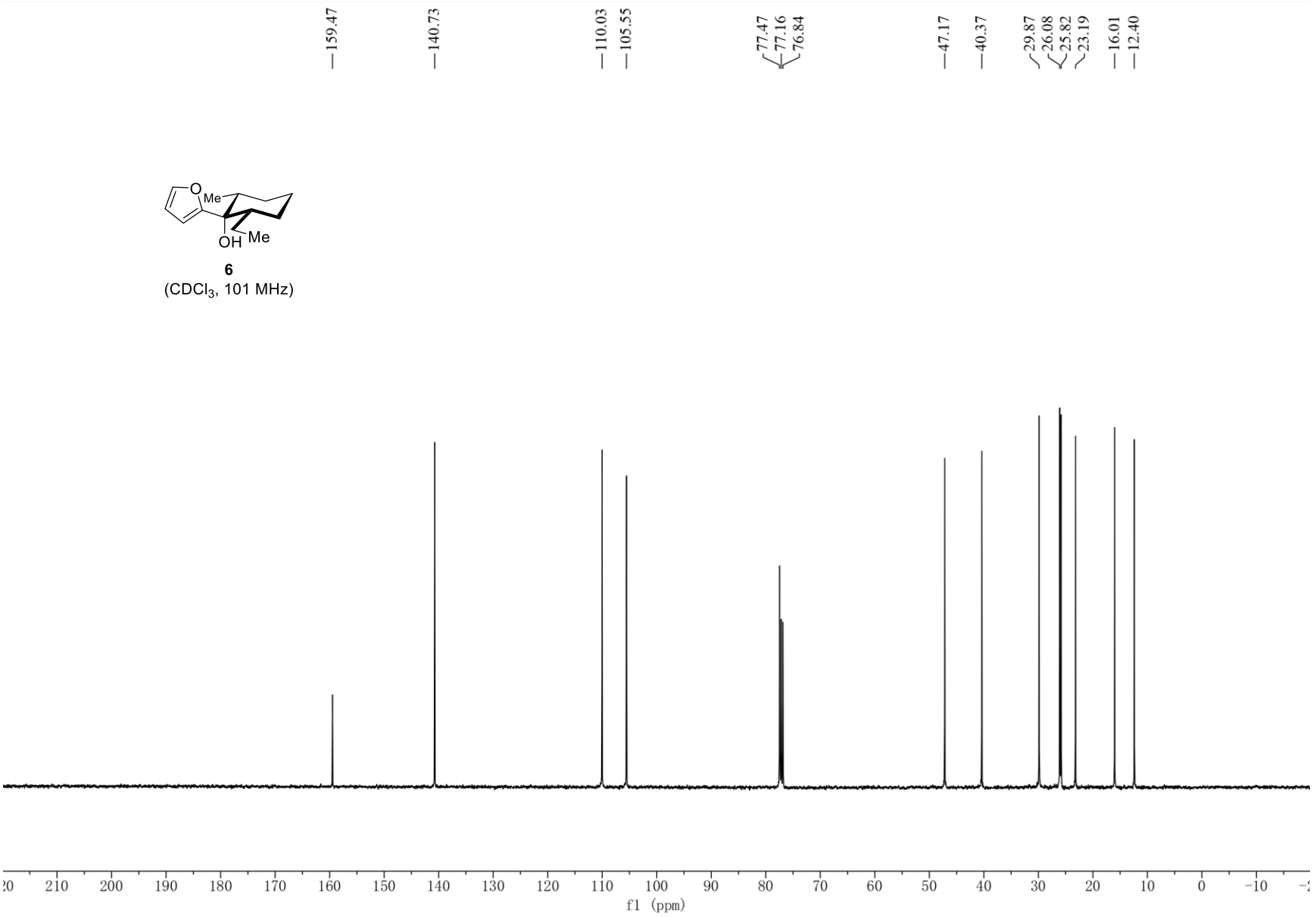


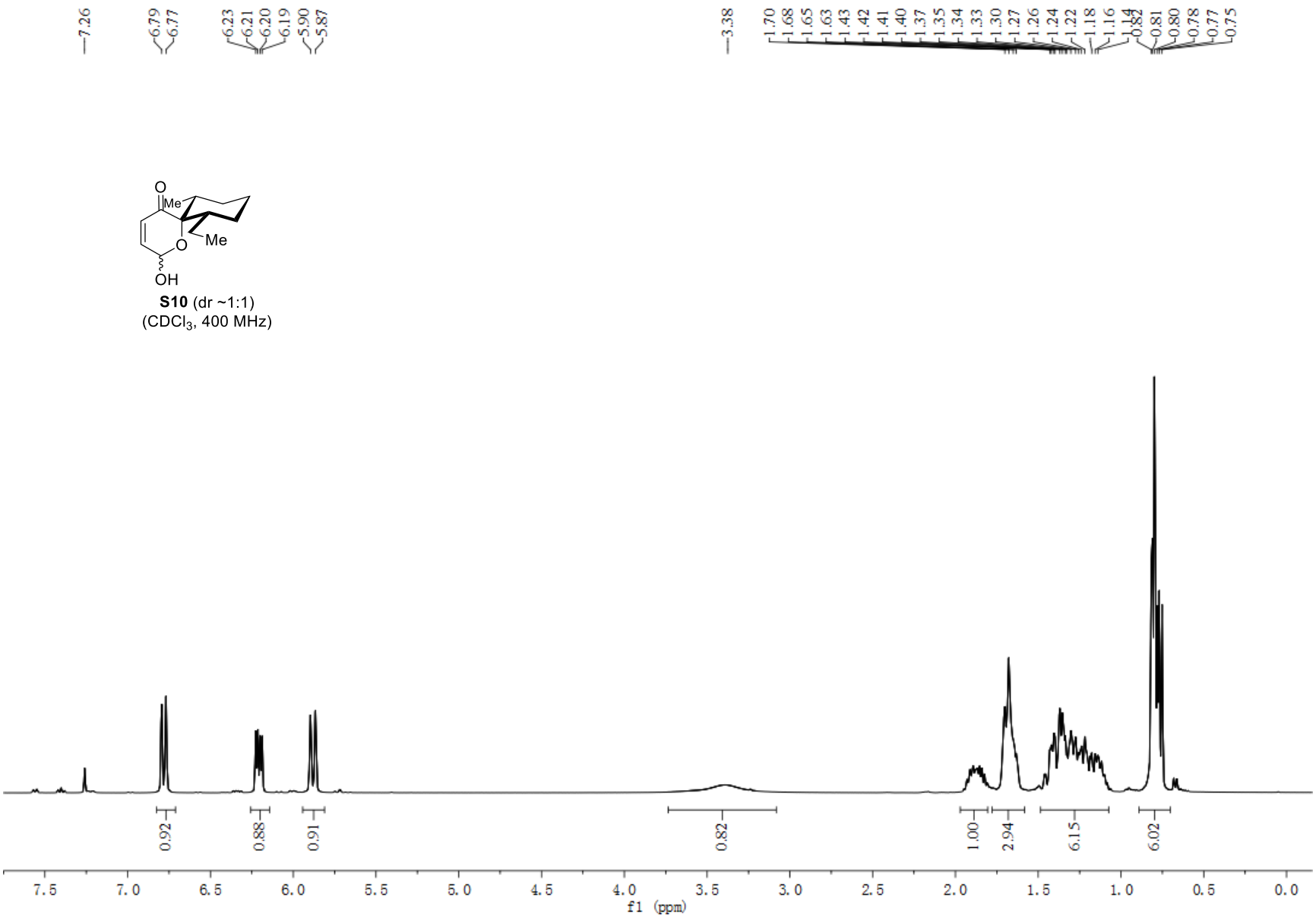
6

($CDCl_3$, 400 MHz)

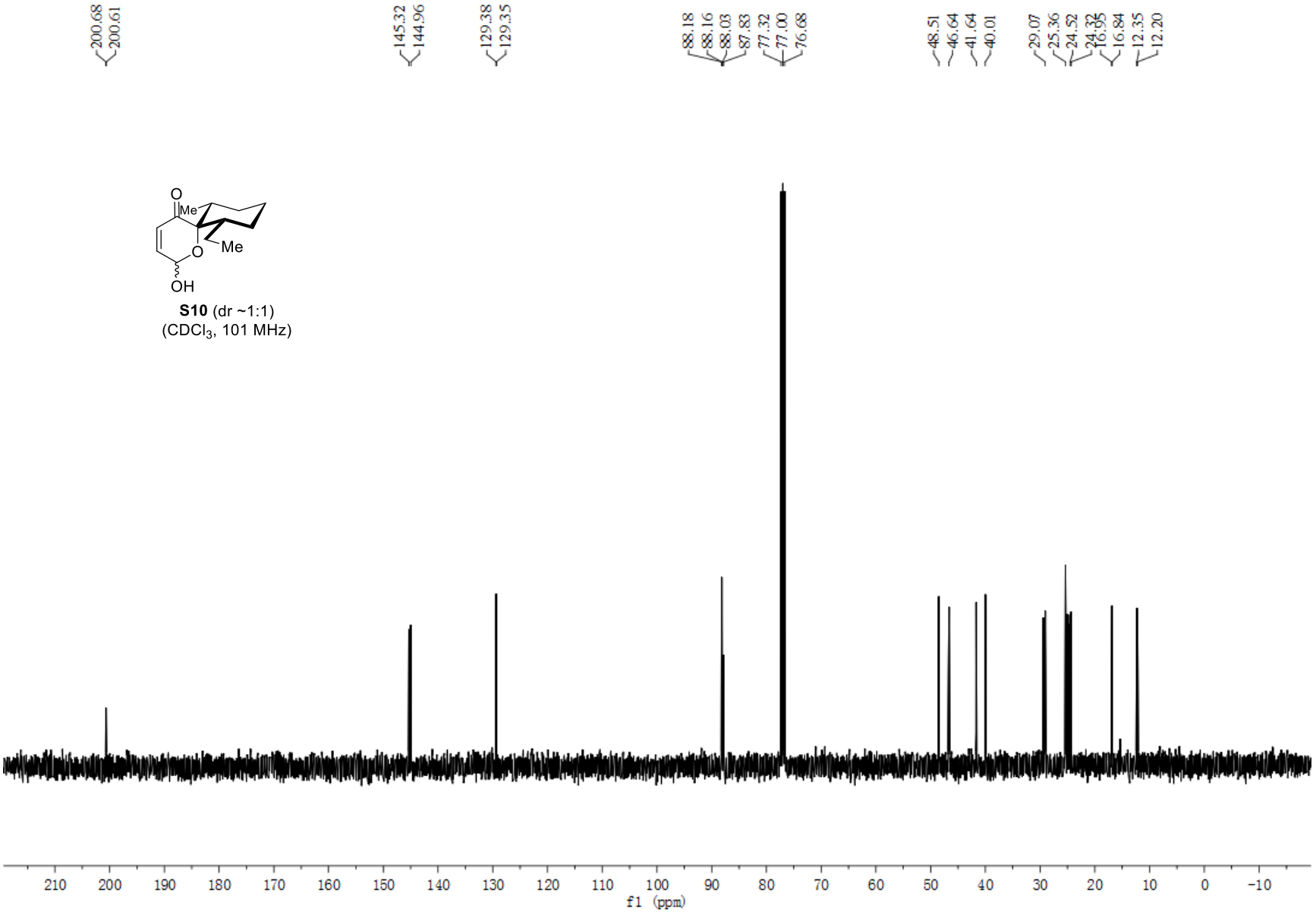


6

($CDCl_3$, 101 MHz)



S10 (dr ~1:1)
($CDCl_3$, 400 MHz)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200.61
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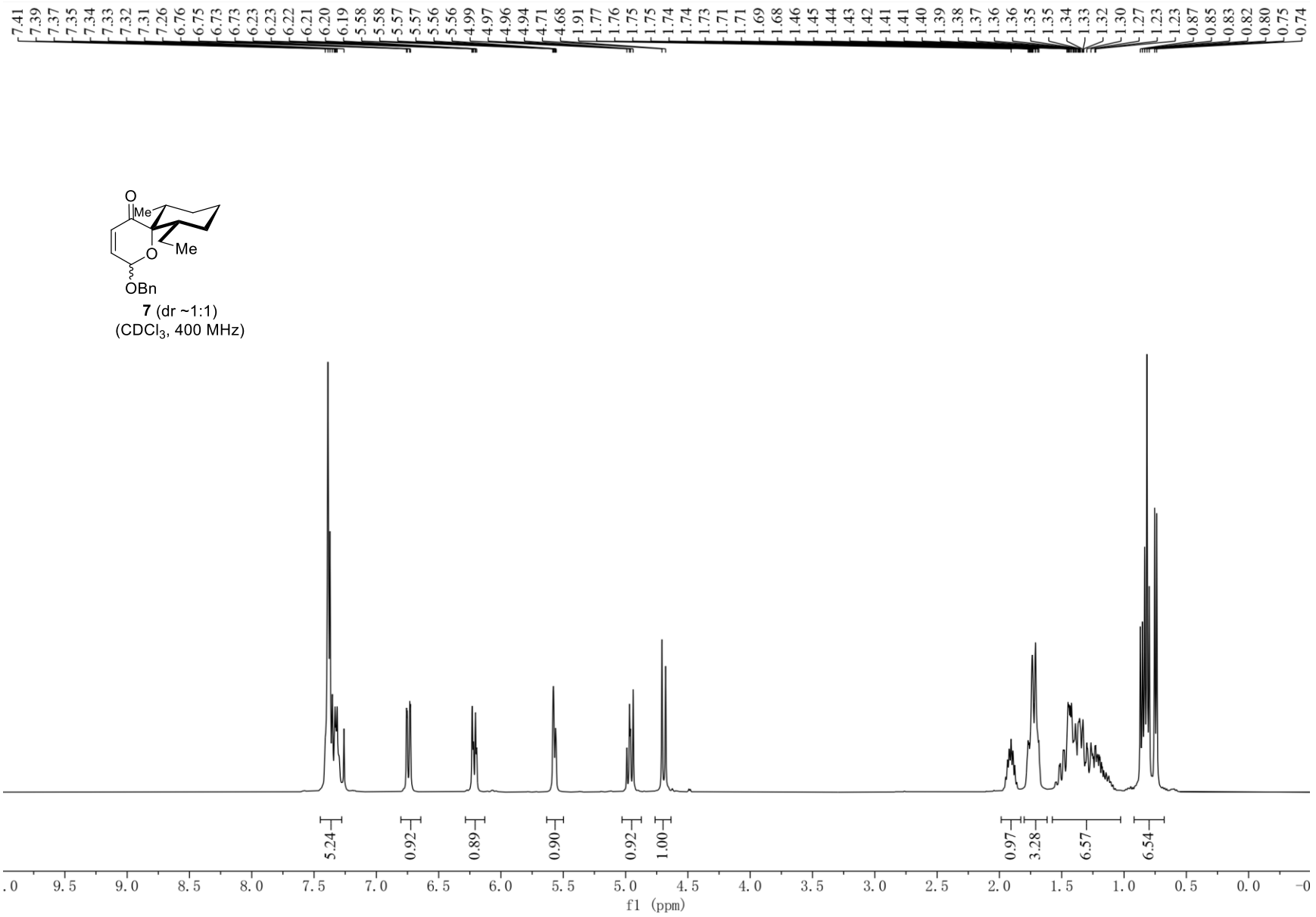
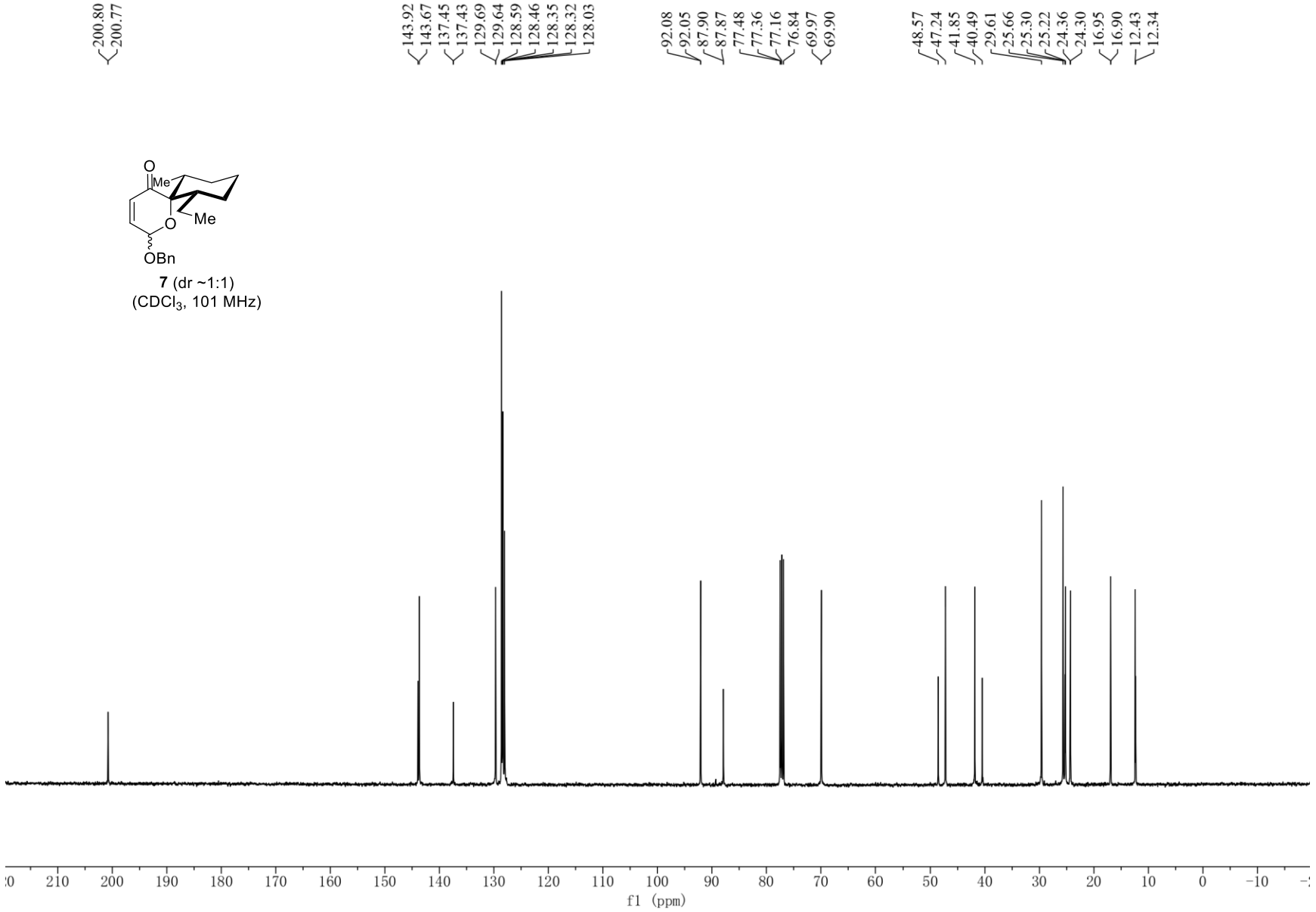
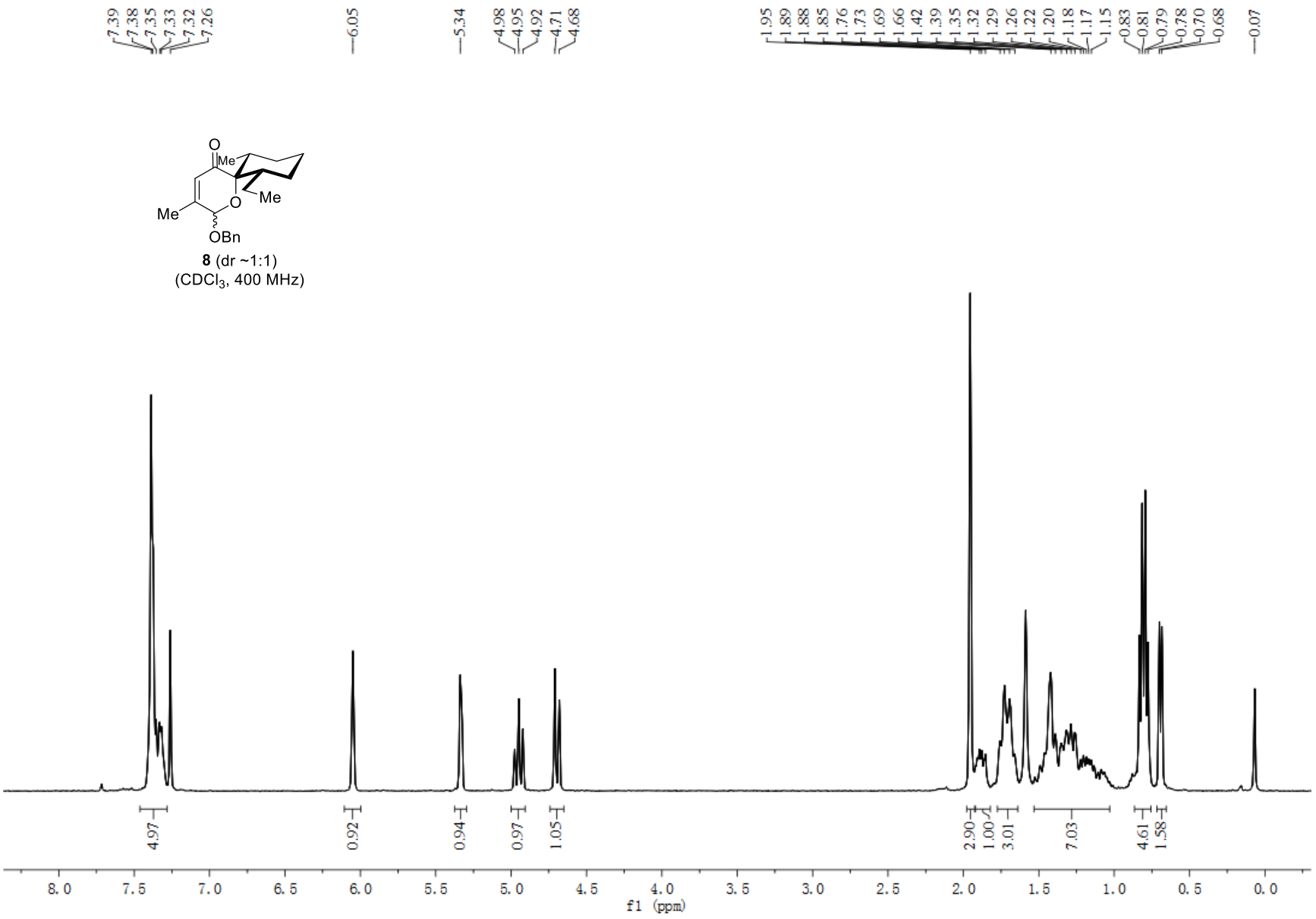
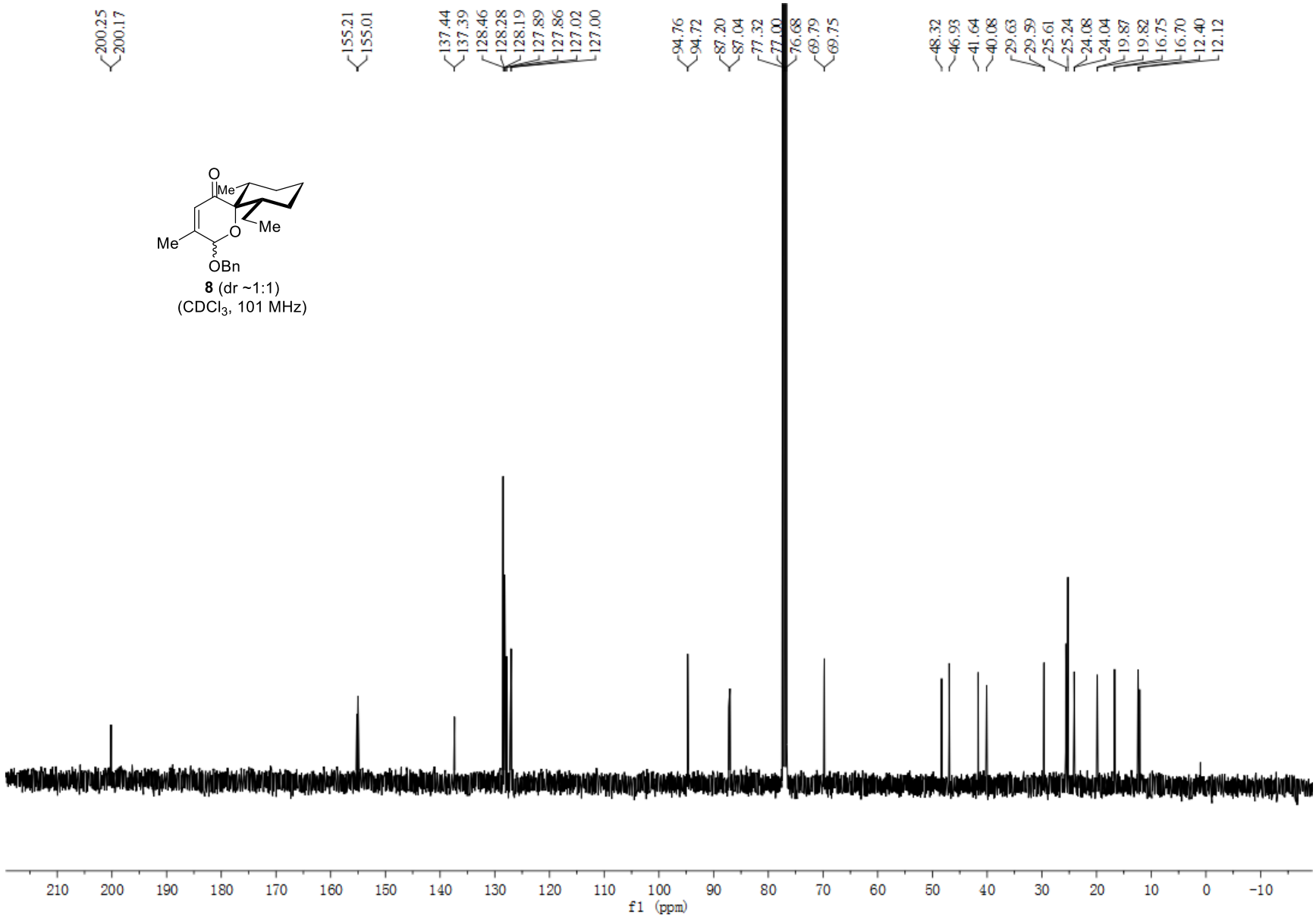
144.96
129.38
129.35
88.18
88.16
88.03
87.83
77.32
77.00
76.68
48.51
46.64
41.64
40.01
29.07
25.36
24.52
24.32
16.95
16.84
12.35
12.20
O
Me
Me
O
OH
S10 (dr ~1:1)
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.41 7.39 7.37 7.35 7.34 7.33 7.32 7.31 7.26 6.76 6.75 6.73 6.73 6.23 6.23 6.22 6.21 6.20 6.19 5.58 5.58 5.57 5.57 5.56 5.56 4.99 4.97 4.96 4.94 4.71 4.68 1.91 1.77 1.76 1.75 1.75 1.74 1.74 1.73 1.71 1.71 1.69 1.68 1.46 1.45 1.44 1.43 1.42 1.41 1.41 1.40 1.39 1.38 1.37 1.36 1.36 1.35 1.35 1.34 1.33 1.32 1.30 1.27 1.23 1.23 0.87 0.85 0.83 0.82 0.80 0.75 0.74
O
Me
O
Me
OBn
7 (dr ~1:1)
(CDCl3, 400 MHz)
5.24
0.92
0.89
0.90
0.92
1.00
0.97
3.28
6.57
6.54
f1 (ppm)

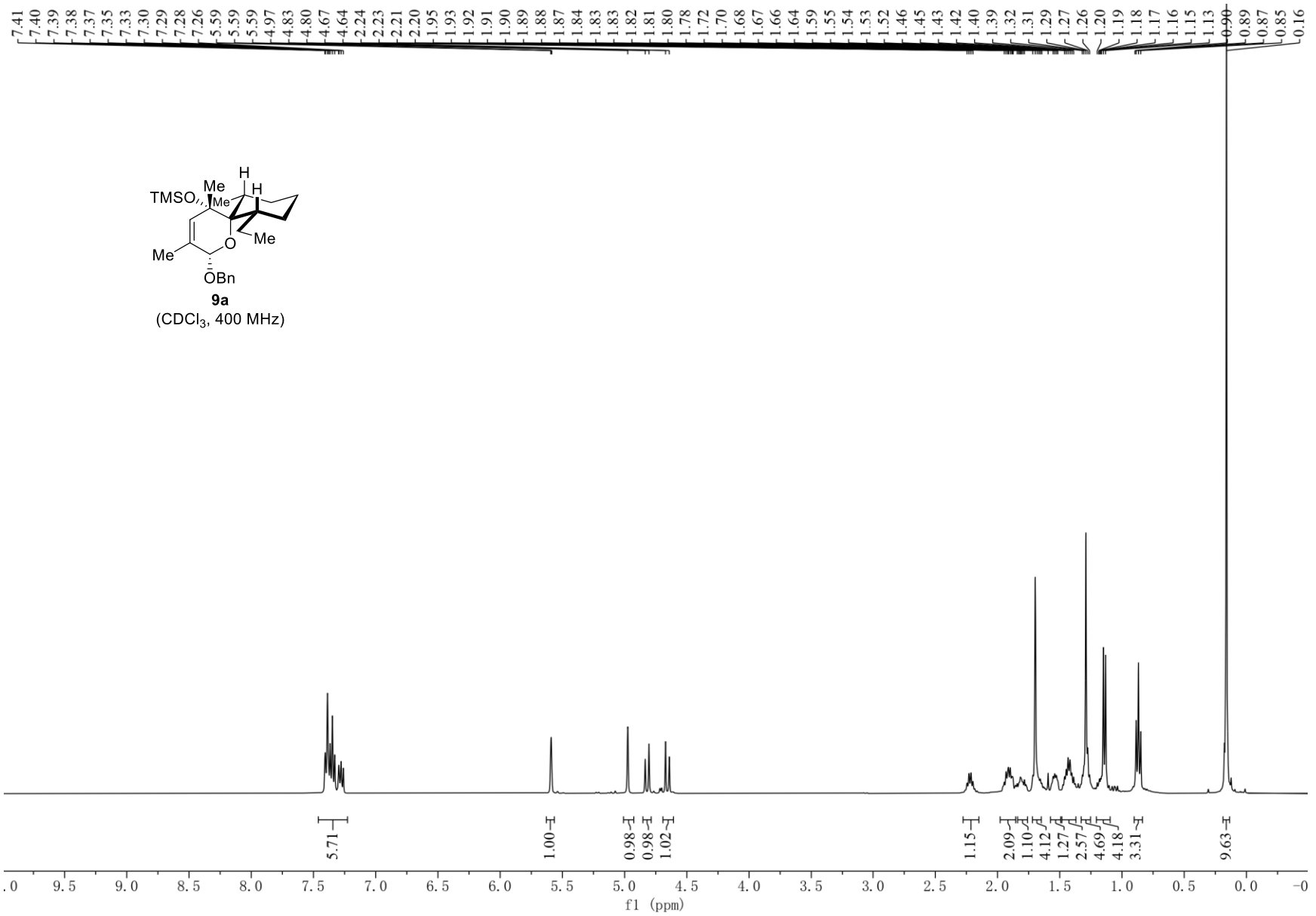

200.80
200.77
143.92
143.67
137.45
137.43
129.69
129.64
128.59
128.46
128.35
128.32
128.03
92.08
92.05
87.90
87.87
77.48
77.36
77.16
76.84
69.97
69.90
48.57
47.24
41.85
40.49
29.61
25.66
25.30
25.22
24.36
24.30
16.95
16.90
12.43
12.34
O
Me
O
Me
OBn
7 (dr ~1:1)
(CDCl3, 101 MHz)
f1 (ppm)



8 (dr ~1:1)
($CDCl_3$, 400 MHz)

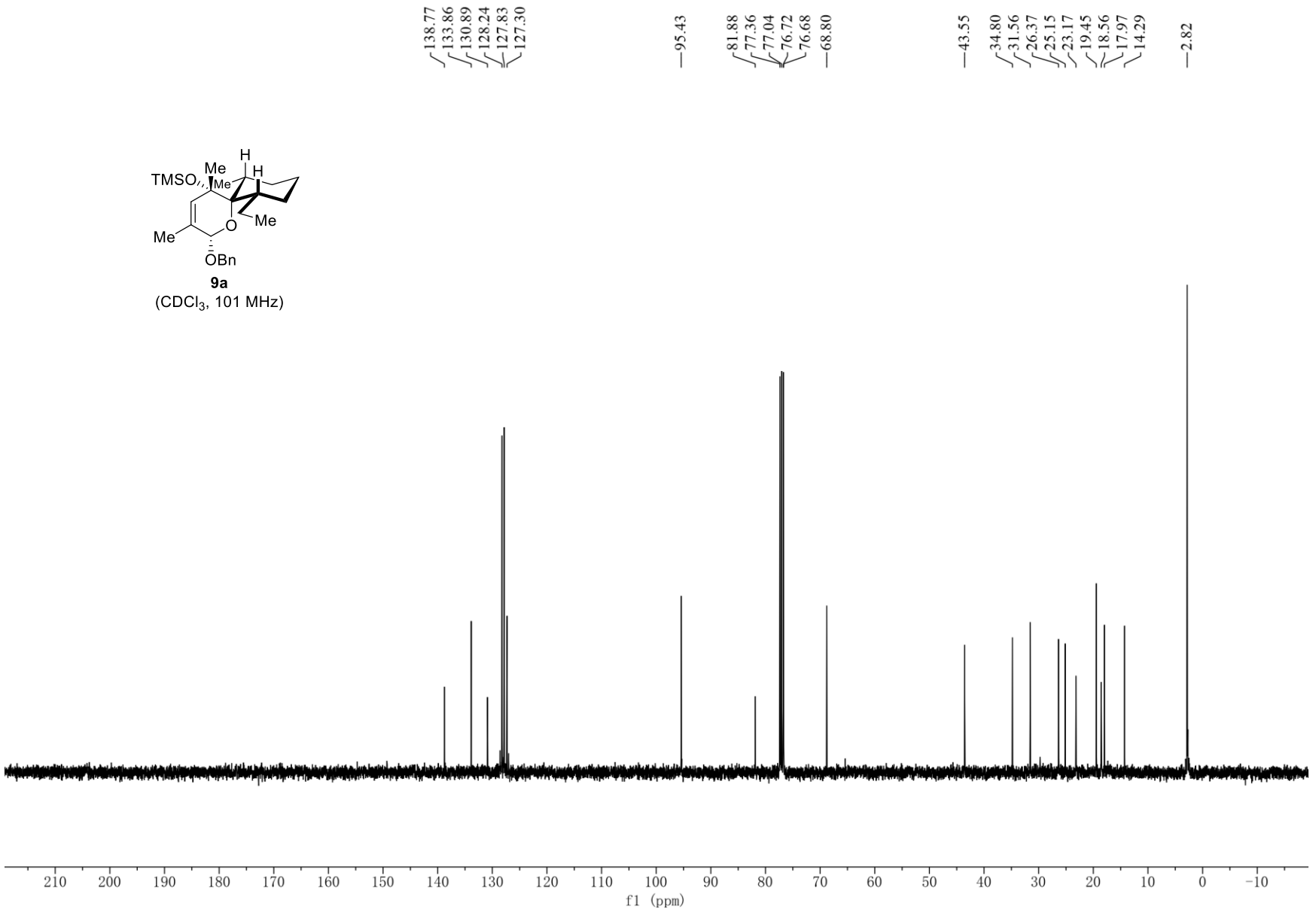


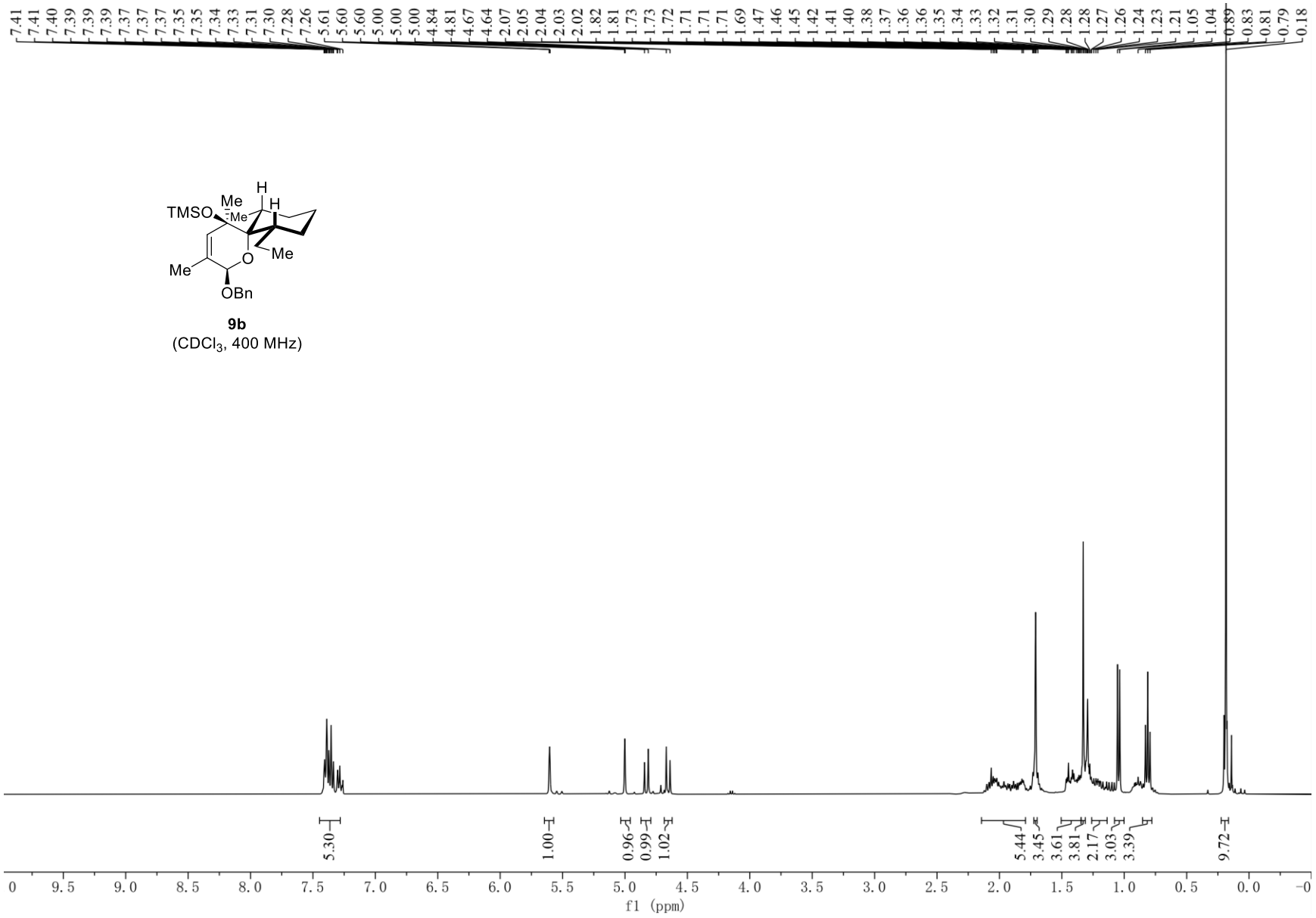
8 (dr ~1:1)
($CDCl_3$, 101 MHz)



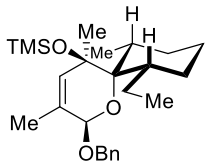
9a

($CDCl_3$, 400 MHz)

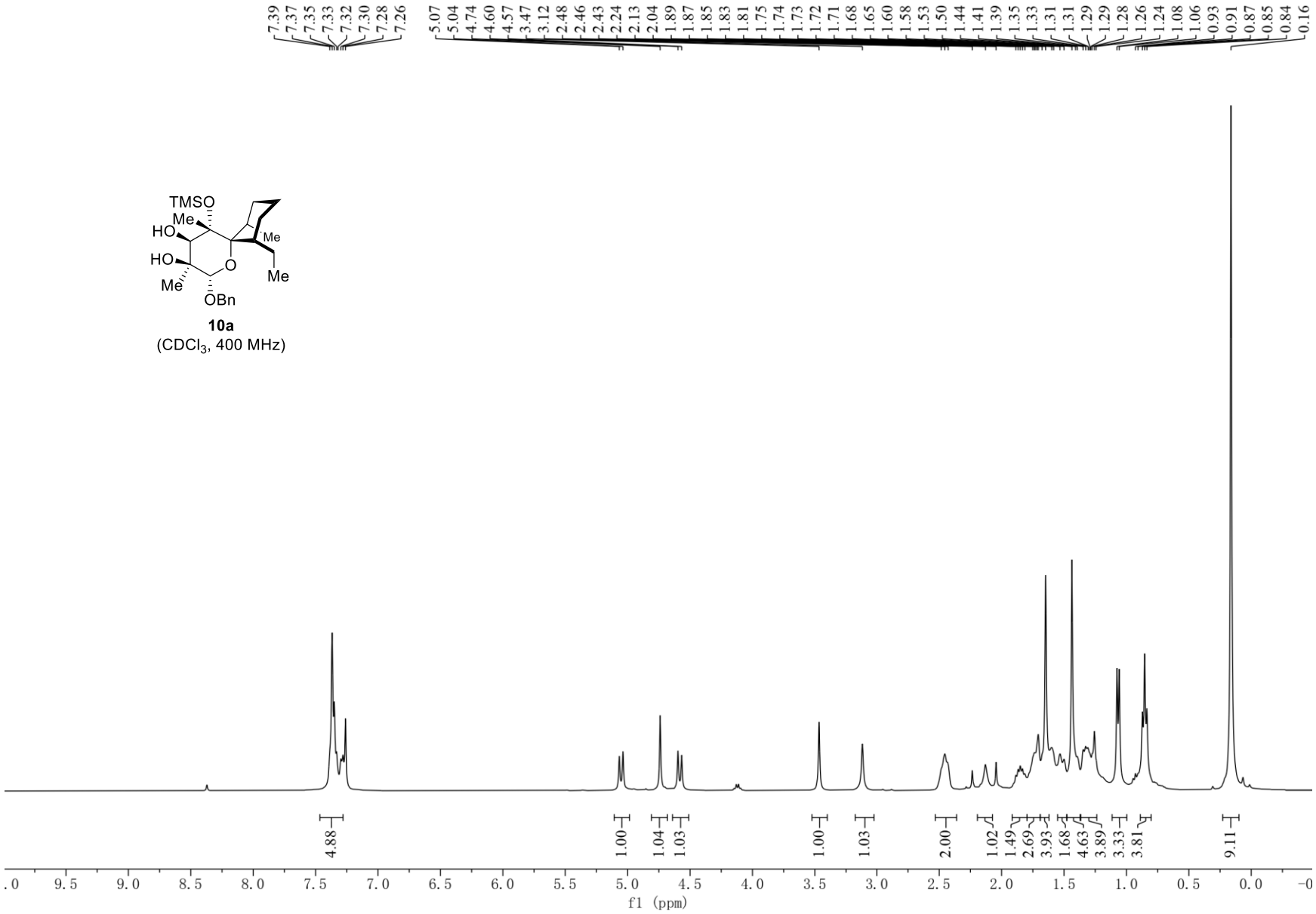

138.77
133.86
130.89
128.24
127.83
127.30
95.43
81.88
77.36
77.04
76.72
76.68
68.80
43.55
34.80
31.56
26.37
25.15
23.17
19.45
18.56
17.97
14.29
2.82
TMSO
Me
Me
H
H
Me
Me
O
OBn
9a
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



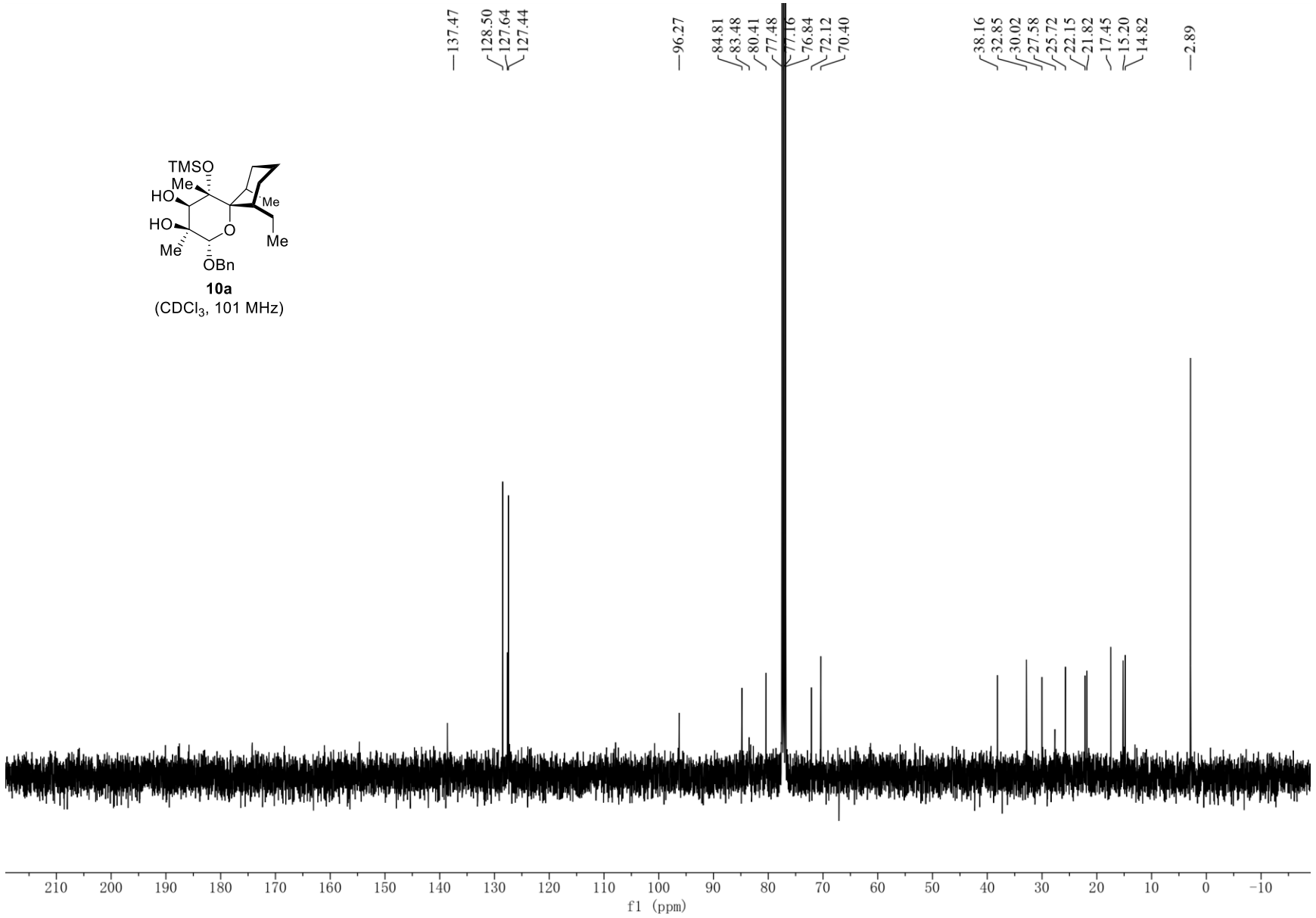
9b
($CDCl_3$, 400 MHz)

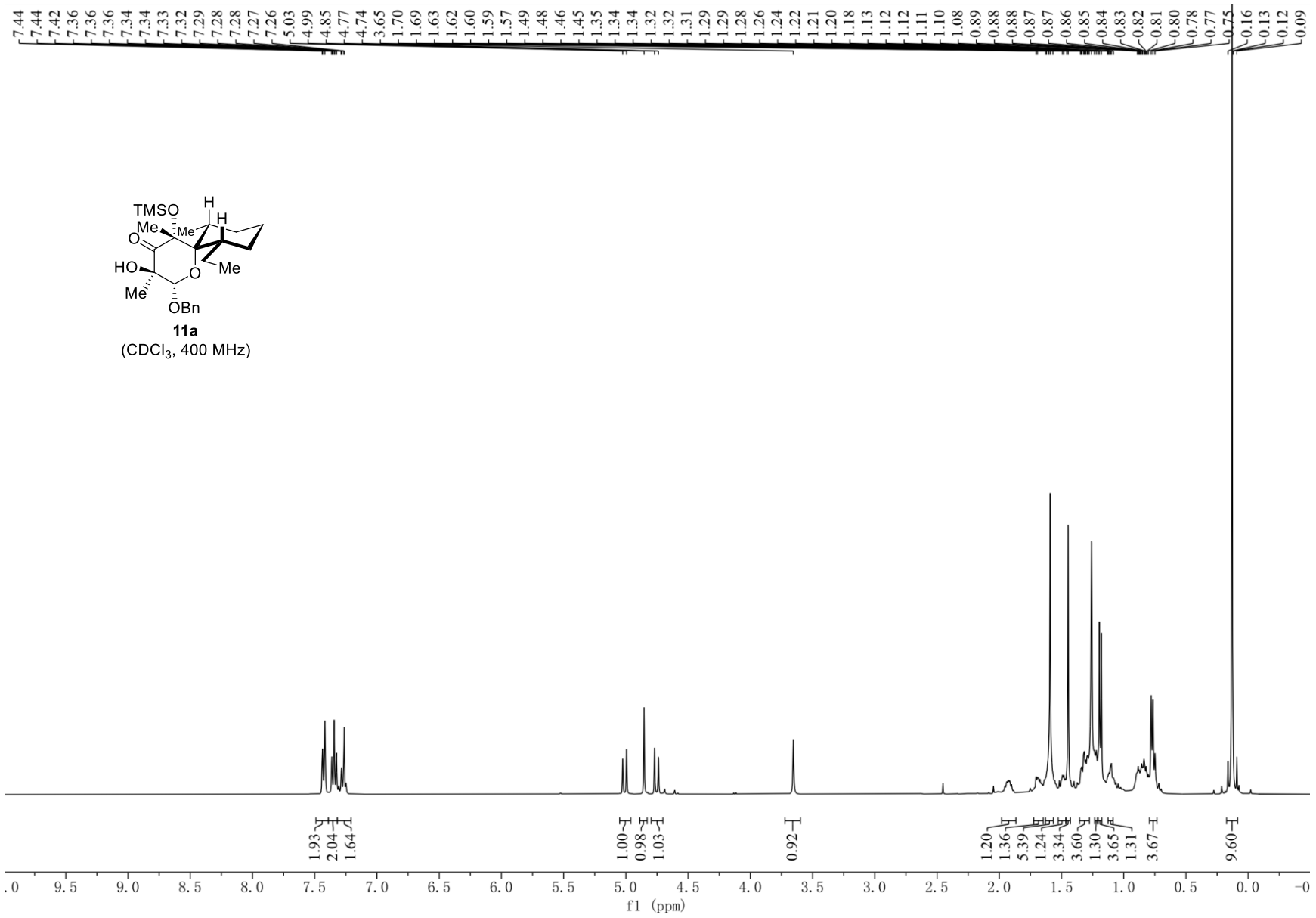


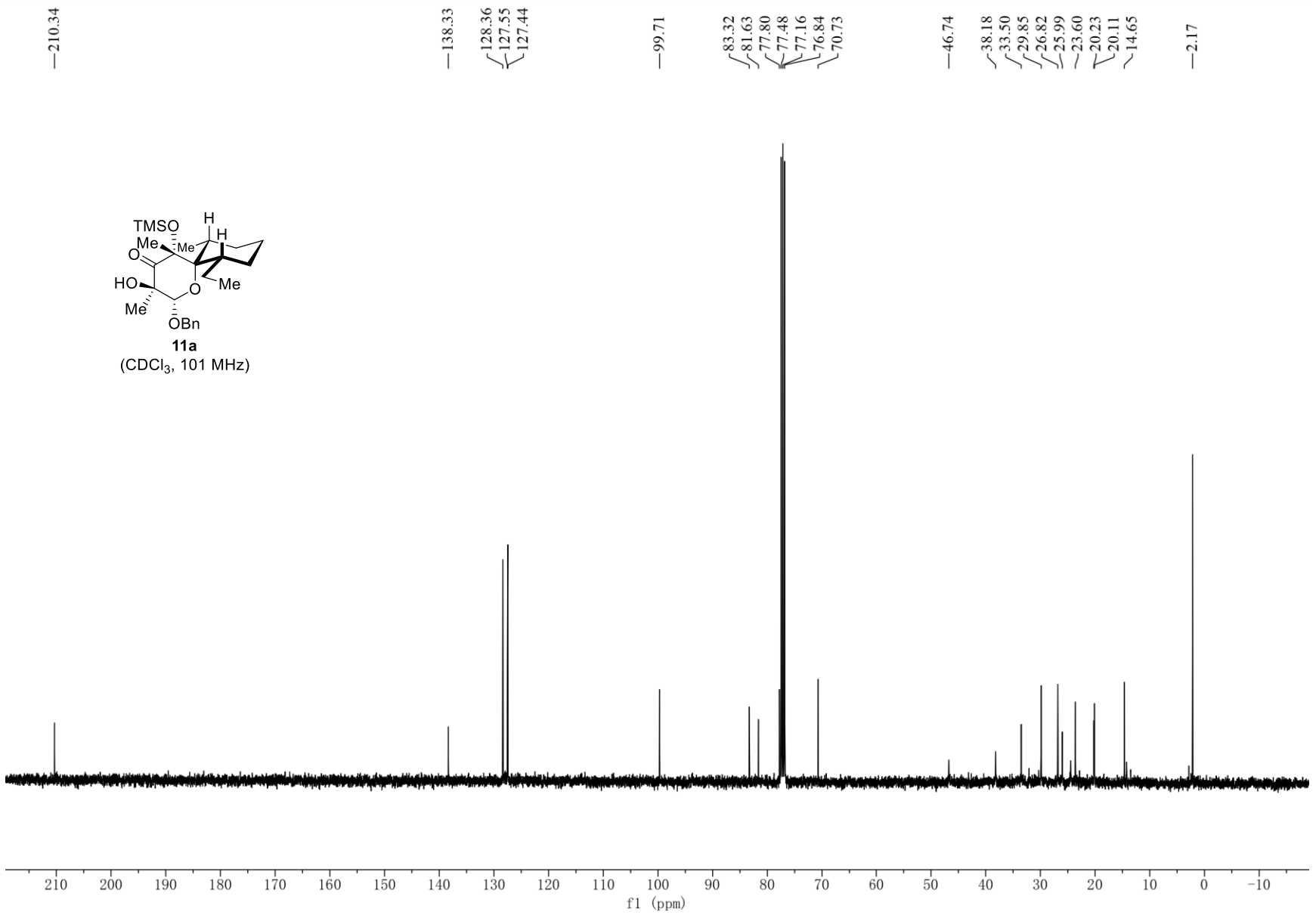
9b
($CDCl_3$, 101 MHz)

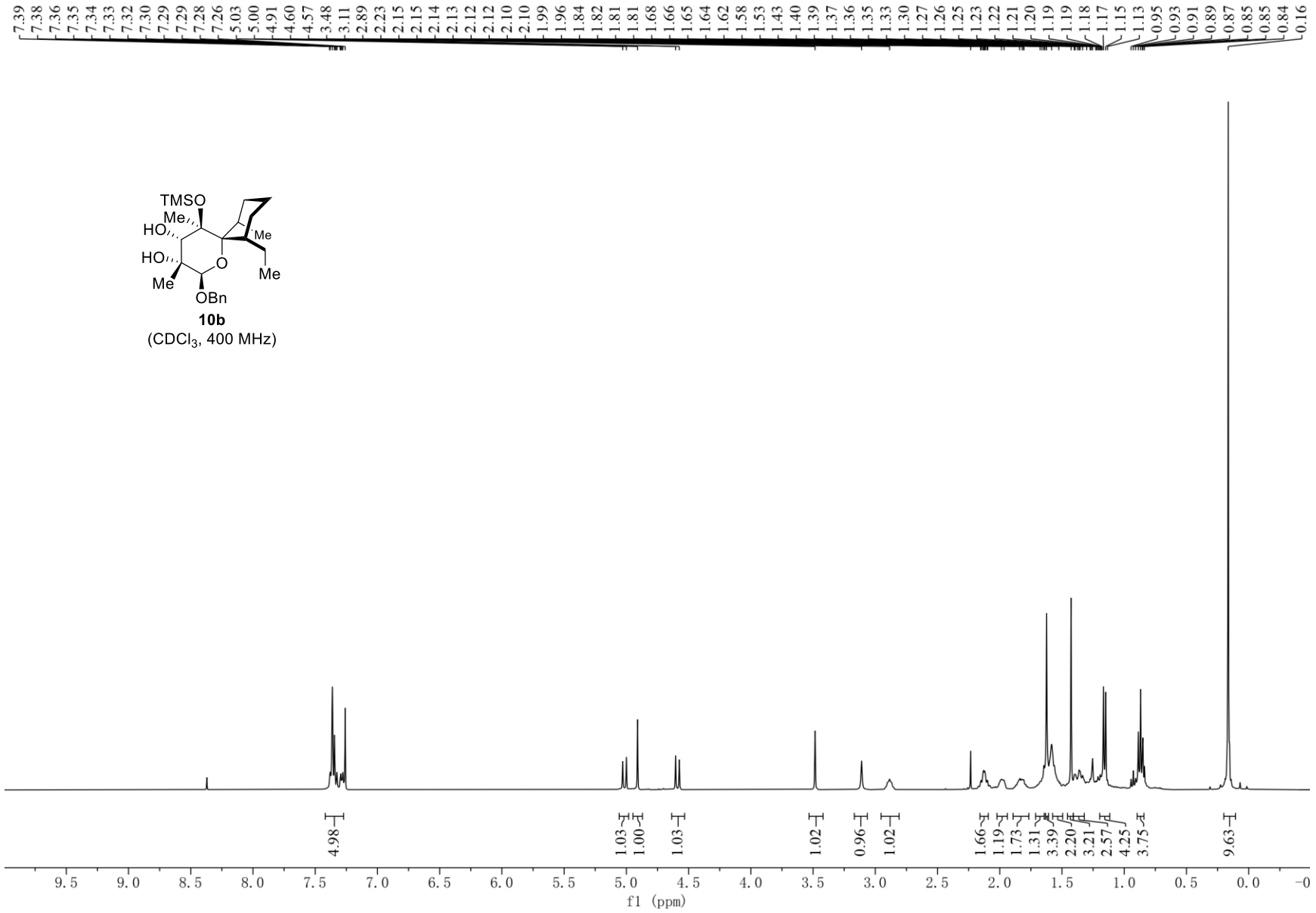


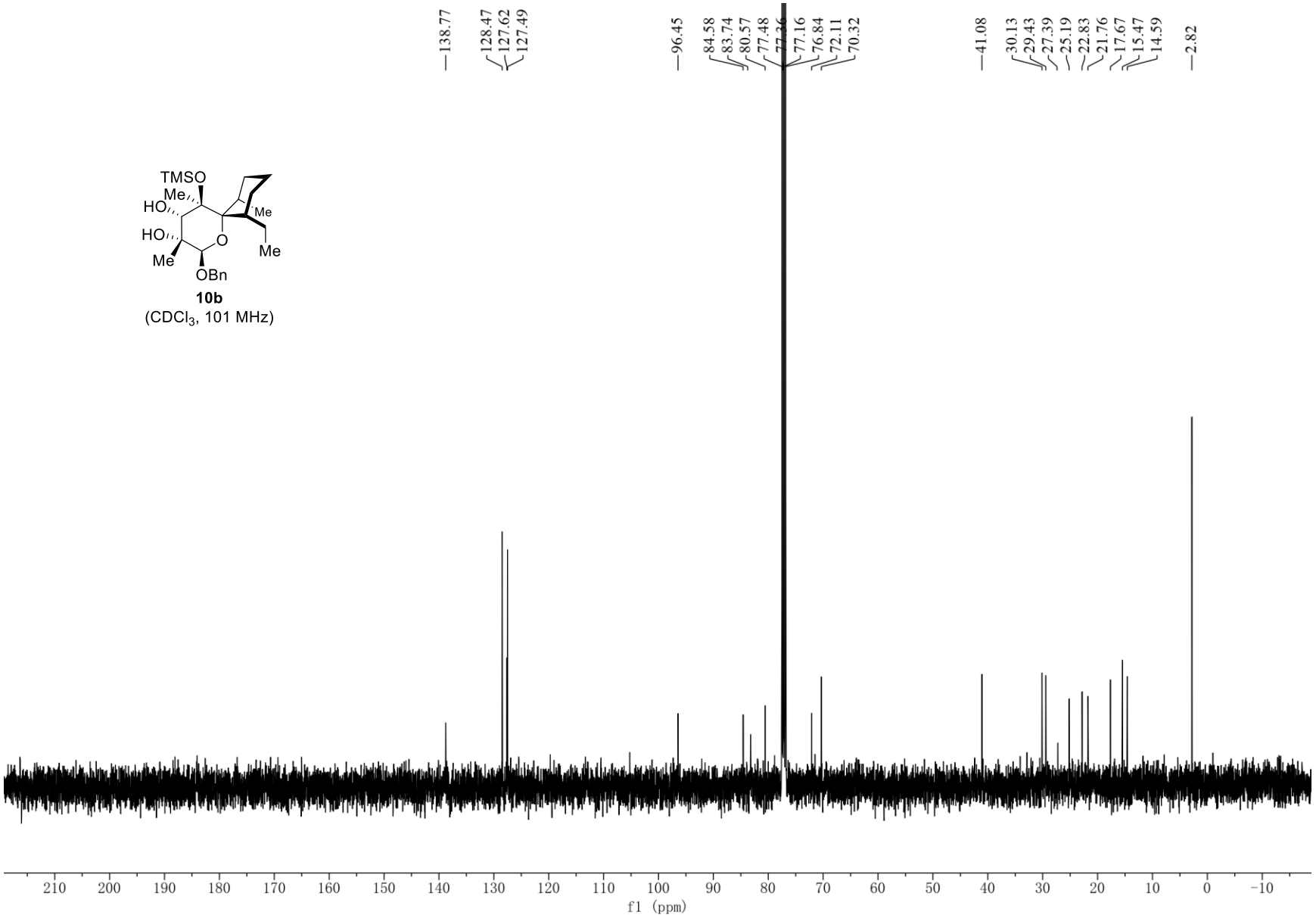
10a
($CDCl_3$, 400 MHz)

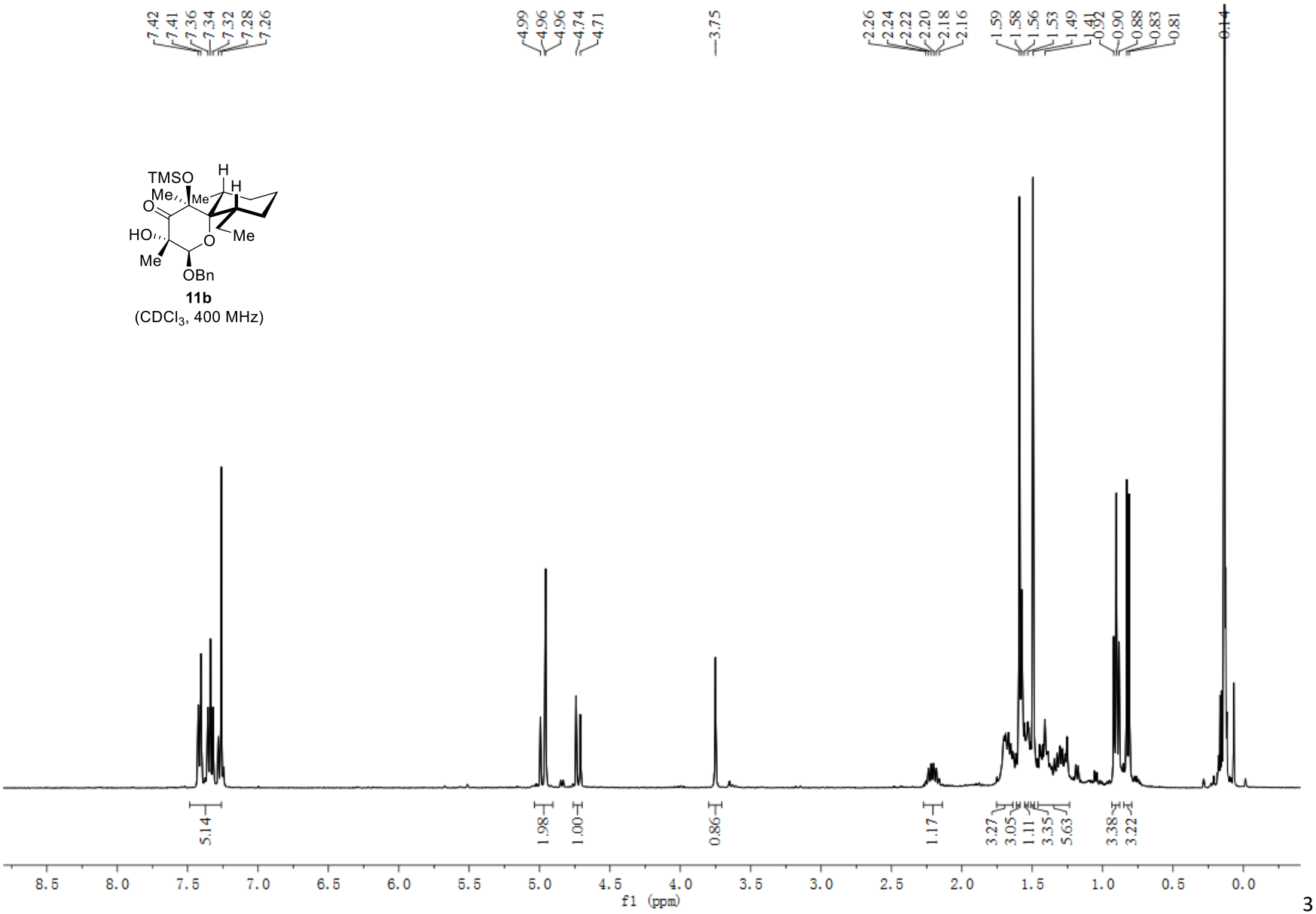

137.47
128.50
127.64
127.44
96.27
84.81
83.48
80.41
77.48
77.16
76.84
72.12
70.40
38.16
32.85
30.02
27.58
25.72
22.15
21.82
17.45
15.20
14.82
2.89
TMSO
Me
HO
HO
Me
OBn
Me
Me
O
10a
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.44 7.44 7.42 7.36 7.36 7.36 7.34 7.34 7.33 7.32 7.29 7.28 7.28 7.27 7.26 5.03 4.99 4.85 4.77 4.74 3.65 1.70 1.69 1.63 1.62 1.60 1.59 1.57 1.49 1.48 1.46 1.45 1.35 1.34 1.34 1.32 1.32 1.31 1.29 1.29 1.28 1.26 1.24 1.22 1.21 1.20 1.18 1.13 1.12 1.12 1.11 1.10 1.08 0.89 0.88 0.88 0.87 0.87 0.86 0.85 0.84 0.83 0.82 0.81 0.80 0.78 0.77 0.75 0.16 0.13 0.12 0.09
TMSO
Me
Me
H
H
O
HO
O
Me
Me
OBn
11a
(CDCl3, 400 MHz)
1.93 2.04 1.64 1.00 0.98 1.03 0.92 1.20 1.36 5.39 1.24 3.34 3.60 1.30 3.65 1.31 3.67 9.60
f1 (ppm)


210.34
138.33
128.36
127.55
127.44
99.71
83.32
81.63
77.80
77.48
77.16
76.84
70.73
46.74
38.18
33.50
29.85
26.82
25.99
23.60
20.23
20.11
14.65
2.17
TMSO
Me
Me
O
HO
Me
Me
O
H
H
OBn
11a
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

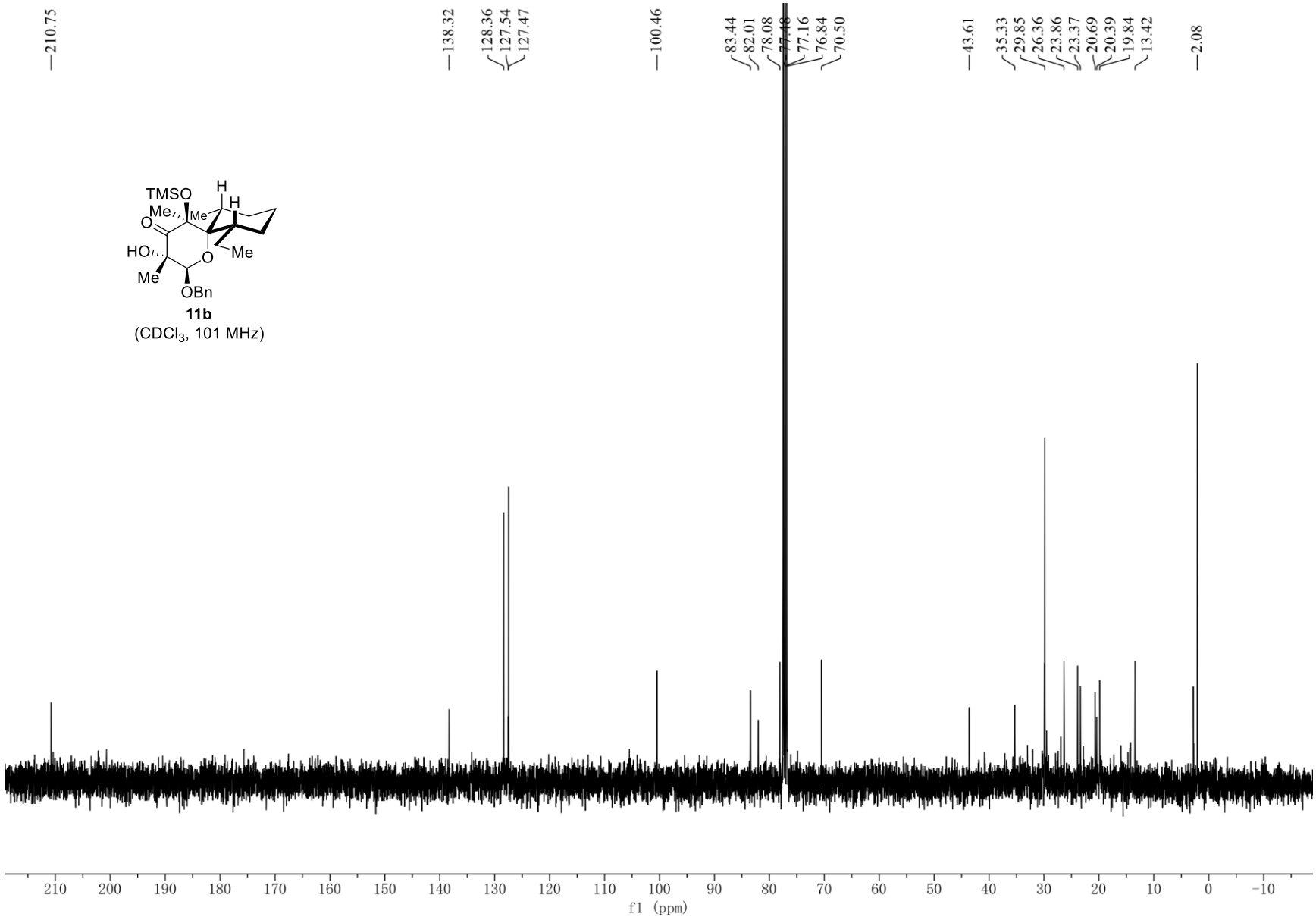

7.39 7.38 7.36 7.35 7.34 7.33 7.32 7.30 7.29 7.29 7.28 7.26 5.03 5.00 4.91 4.60 4.57 3.48 3.11 2.89 2.23 2.15 2.15 2.14 2.13 2.12 2.12 2.10 2.10 1.99 1.96 1.84 1.82 1.81 1.81 1.68 1.66 1.65 1.64 1.62 1.58 1.53 1.43 1.40 1.39 1.37 1.36 1.35 1.33 1.30 1.27 1.26 1.25 1.23 1.22 1.21 1.20 1.19 1.19 1.18 1.17 1.15 1.13 0.95 0.93 0.91 0.89 0.87 0.85 0.85 0.84 0.16
TMSO
Me
HO
HO
Me
O
Me
Me
OBn
10b
(CDCl3, 400 MHz)
4.98
1.03
1.00
1.03
1.02
0.96
1.02
1.66
1.19
1.73
1.31
3.39
2.20
3.21
2.57
4.25
3.75
9.63
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 −0
f1 (ppm)

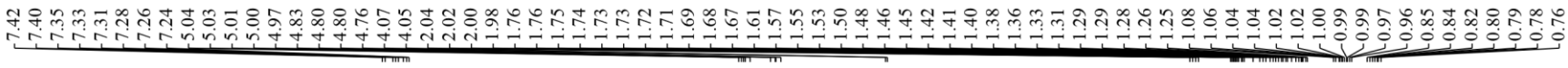

138.77
128.47
127.62
127.49
96.45
84.58
83.74
80.57
77.48
77.16
76.84
72.11
70.32
41.08
30.13
29.43
27.39
25.19
22.83
21.76
17.67
15.47
14.59
2.82
TMSO
Me
HO
HO
Me
Me
Me
OBn
O
10b
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

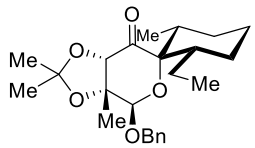


11b
($CDCl_3$, 400 MHz)

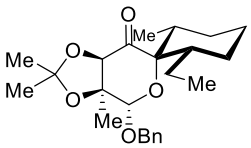
3


210.75
138.32
128.36
127.54
127.47
100.46
83.44
82.01
78.08
77.16
76.84
70.50
43.61
35.33
29.85
26.36
23.86
23.37
20.69
20.39
19.84
13.42
2.08
TMSO
Me
Me
H
H
O
HO
Me
O
Me
Me
OBn
11b
(CDCl3, 101 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)



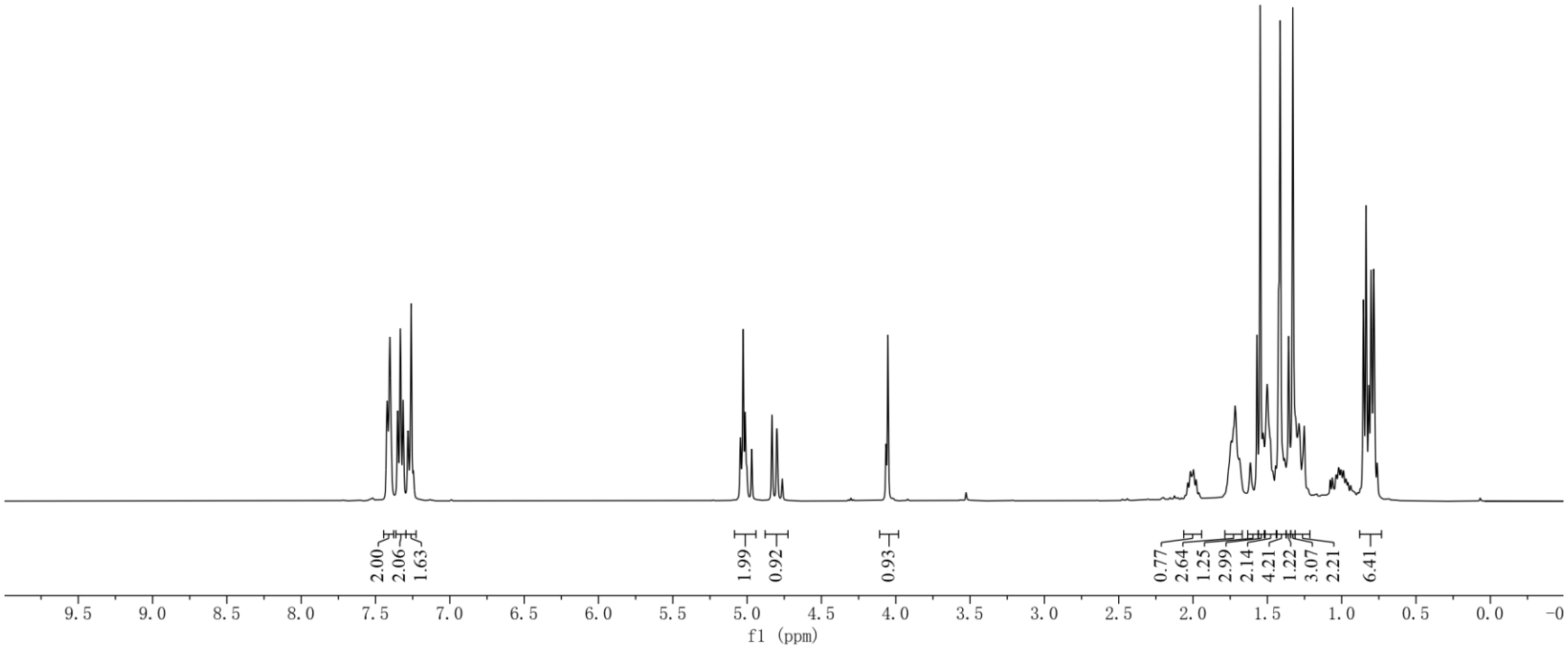


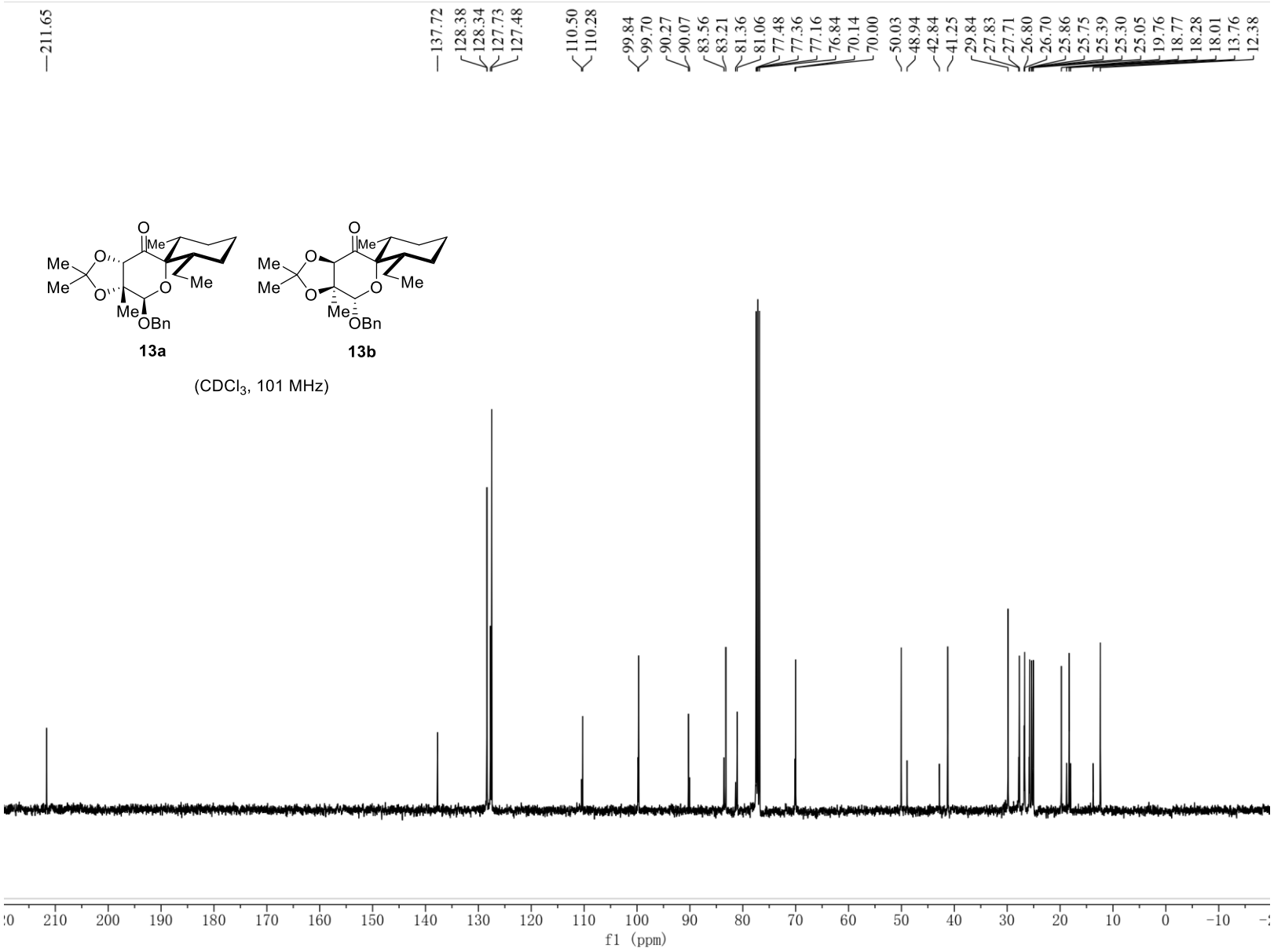
13a

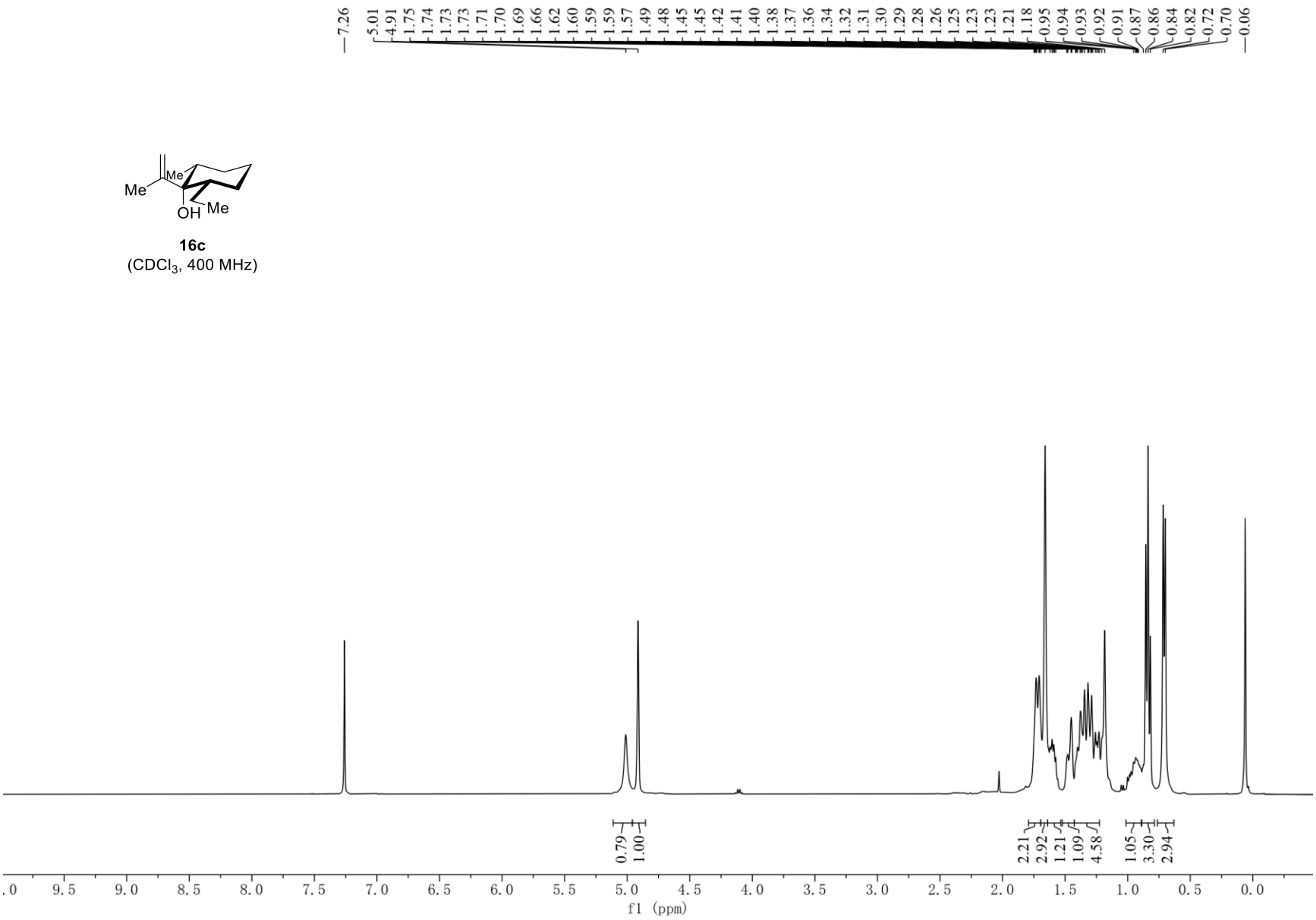


13b

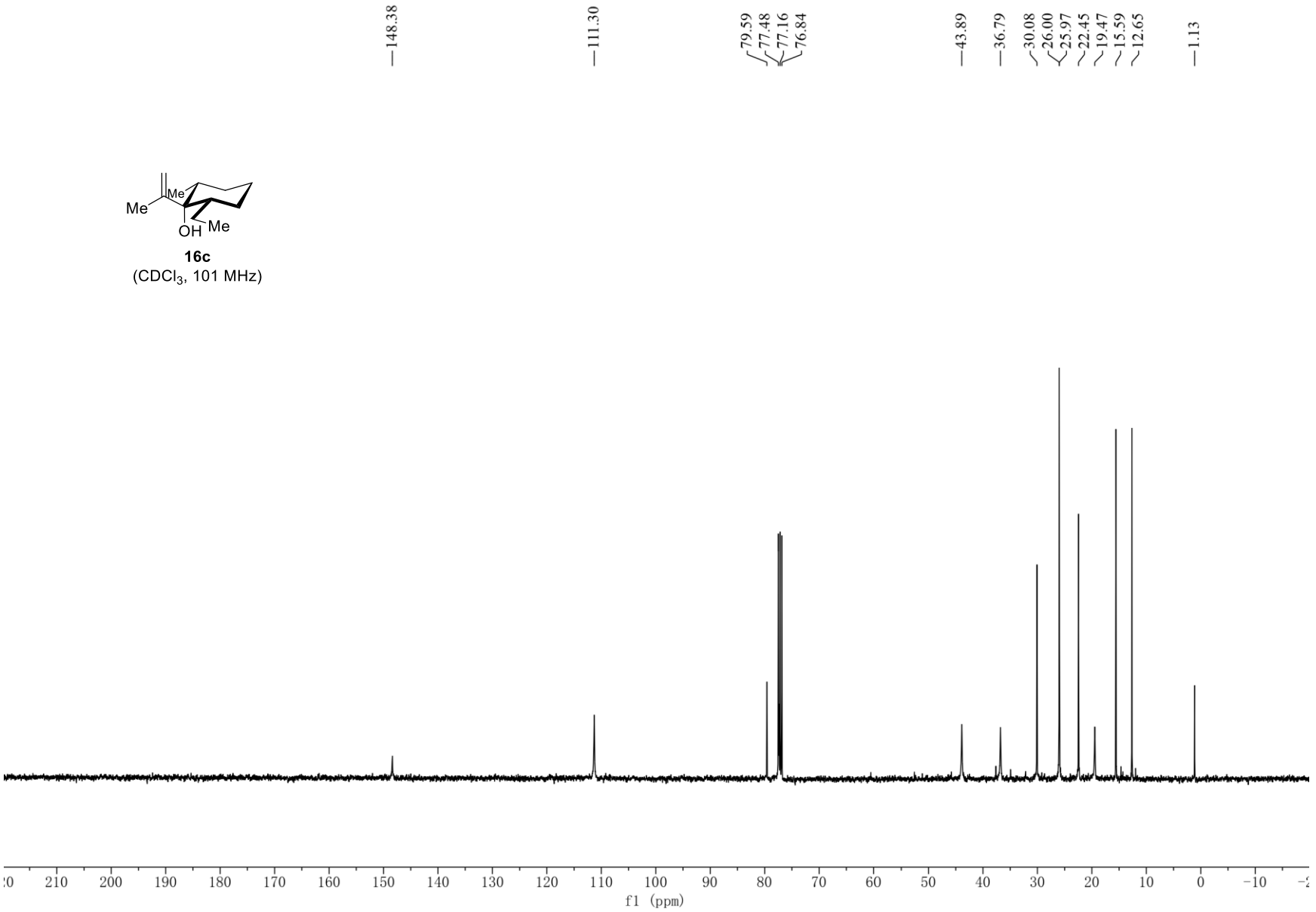
($CDCl_3$, 400 MHz)

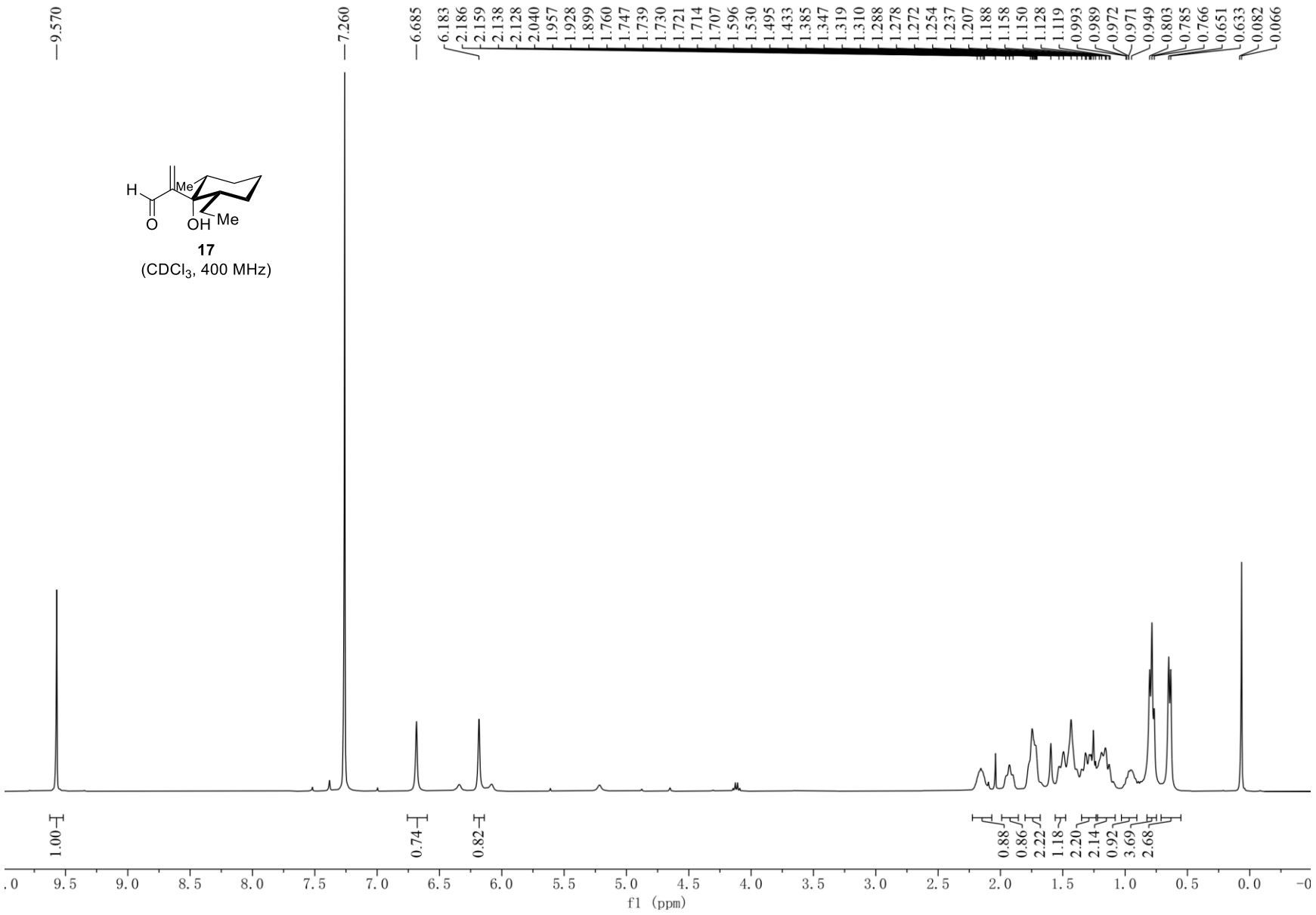


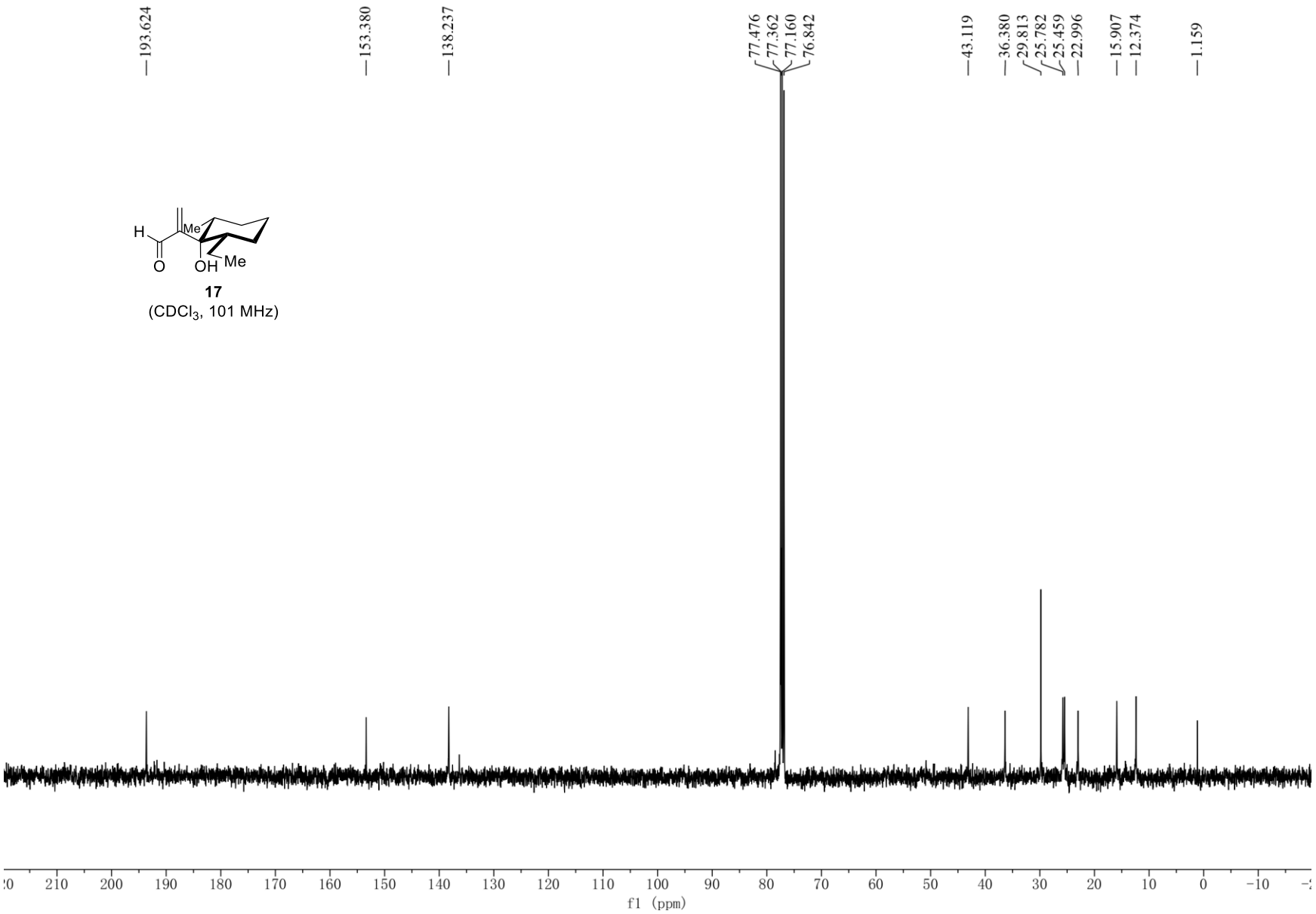

211.65
137.72
128.38
128.34
127.73
127.48
110.50
110.28
99.84
99.70
90.27
90.07
83.56
83.21
81.36
81.06
77.48
77.36
77.16
76.84
70.14
70.00
50.03
48.94
42.84
41.25
29.84
27.83
27.71
26.80
26.70
25.86
25.75
25.39
25.30
25.05
19.76
18.77
18.28
18.01
13.76
12.38
13a
13b
(CDCl3, 101 MHz)
f1 (ppm)

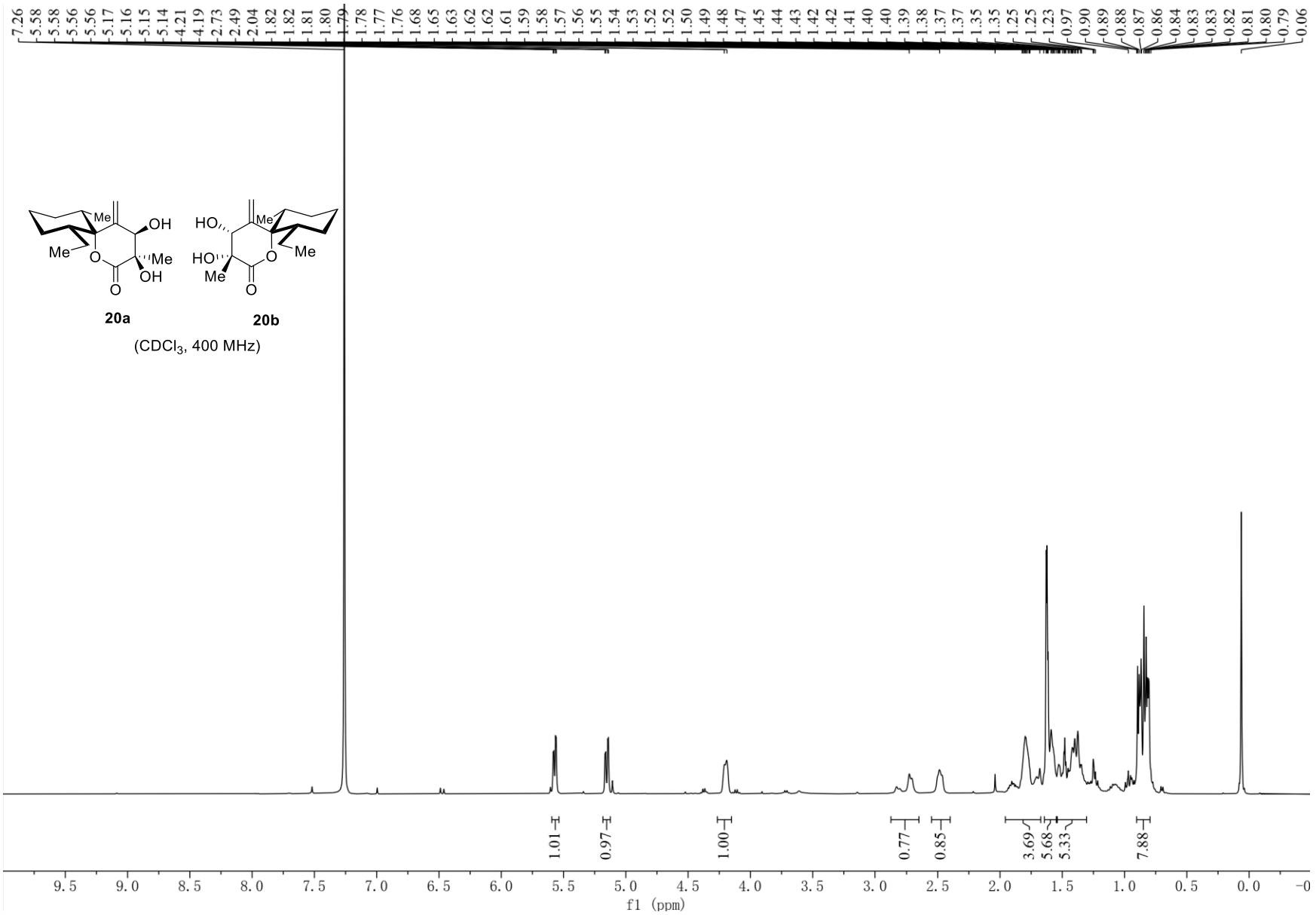


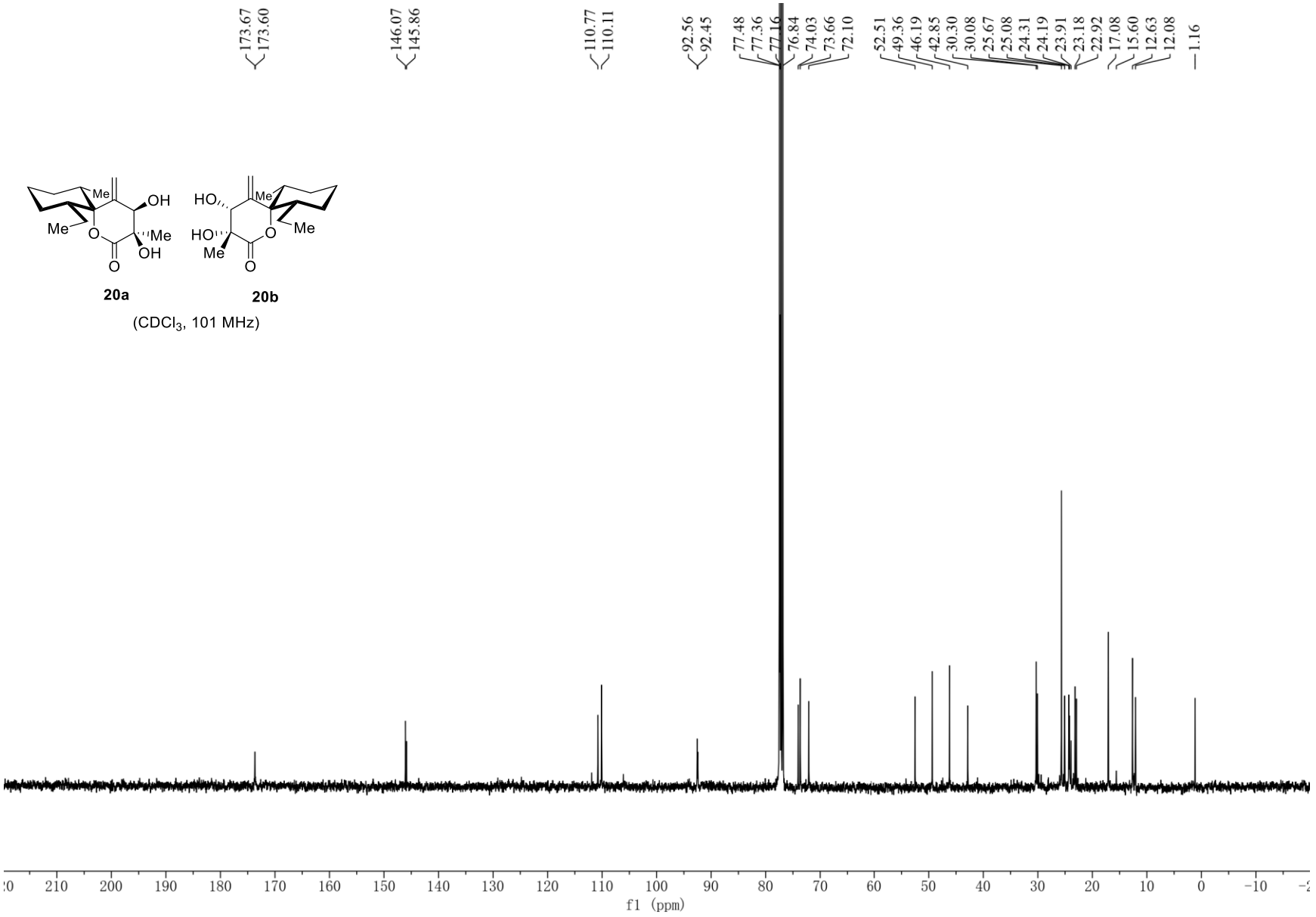
16c
($CDCl_3$, 400 MHz)

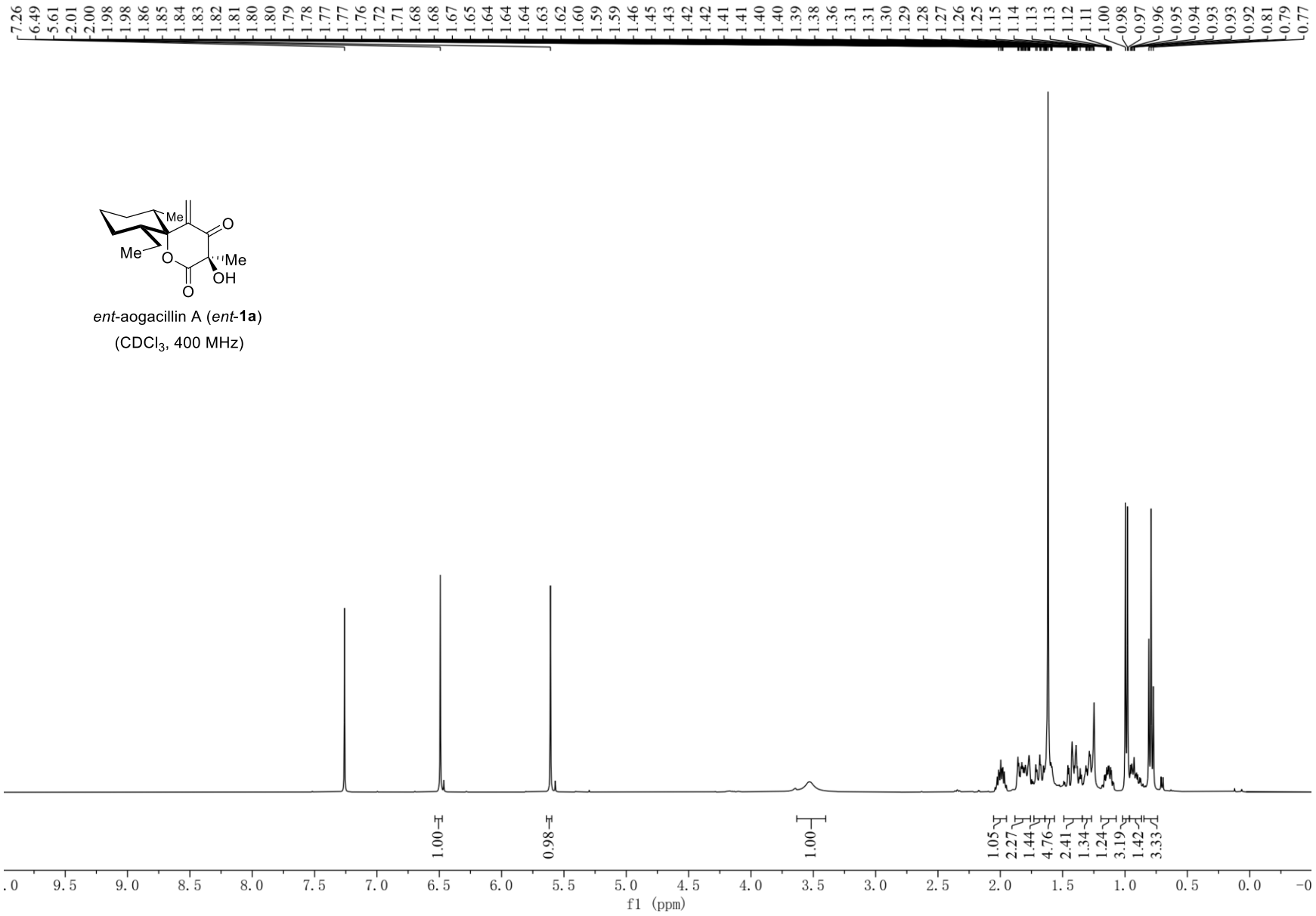

148.38
111.30
79.59
77.48
77.16
76.84
43.89
36.79
30.08
26.00
25.97
22.45
19.47
15.59
12.65
1.13
Me
Me
OH
Me
16c
(CDCl3, 101 MHz)
f1 (ppm)


9.570
7.260
6.685
6.183
2.186
2.159
2.138
2.128
2.040
1.957
1.928
1.899
1.760
1.747
1.739
1.730
1.721
1.714
1.707
1.596
1.530
1.495
1.433
1.385
1.347
1.319
1.310
1.288
1.278
1.272
1.254
1.237
1.207
1.188
1.158
1.150
1.128
1.119
0.993
0.989
0.972
0.971
0.949
0.803
0.785
0.766
0.651
0.633
0.082
0.066
H
O
Me
OH
Me
17
(CDCl3, 400 MHz)
1.00
0.74
0.82
0.88
0.86
2.22
1.18
2.20
2.14
0.92
3.69
2.68
f1 (ppm)


193.624
153.380
138.237
77.476
77.362
77.160
76.842
43.119
36.380
29.813
25.782
25.459
22.996
15.907
12.374
1.159
H
O
Me
OH
Me
17
(CDCl3, 101 MHz)
f1 (ppm)

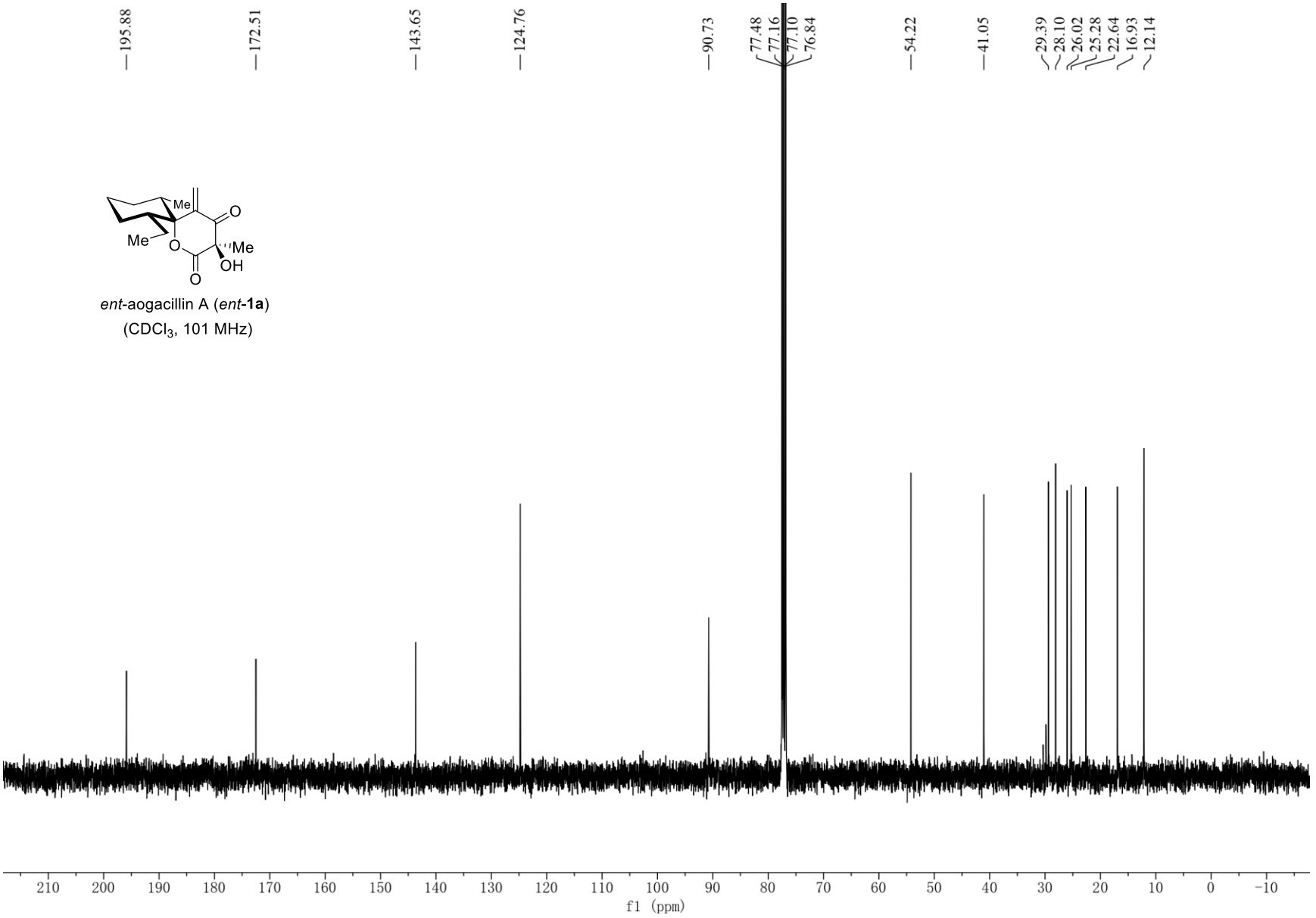

7.26
5.58
5.58
5.56
5.56
5.17
5.16
5.15
5.14
4.21
4.19
2.73
2.49
2.04
1.82
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.68
1.65
1.63
1.62
1.62
1.61
1.59
1.58
1.57
1.56
1.55
1.54
1.53
1.52
1.52
1.50
1.49
1.48
1.47
1.45
1.44
1.43
1.42
1.42
1.41
1.40
1.40
1.39
1.38
1.37
1.37
1.35
1.35
1.25
1.25
1.23
0.97
0.90
0.89
0.88
0.87
0.86
0.84
0.83
0.83
0.82
0.81
0.80
0.79
0.06
Me
OH
Me
O
Me
OH
O
HO
Me
HO
Me
O
Me
O
20a
20b
(CDCl3, 400 MHz)
1.01
0.97
1.00
0.77
0.85
3.69
5.68
5.33
7.88
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)


173.67
173.60
146.07
145.86
110.77
110.11
92.56
92.45
77.48
77.36
77.16
76.84
74.03
73.66
72.10
52.51
49.36
46.19
42.85
30.30
30.08
25.67
25.08
24.31
24.19
23.91
23.18
22.92
17.08
15.60
12.63
12.08
1.16
Me
OH
Me
O
Me
OH
O
HO
Me
HO
Me
O
Me
O
20a
20b
(CDCl3, 101 MHz)
f1 (ppm)

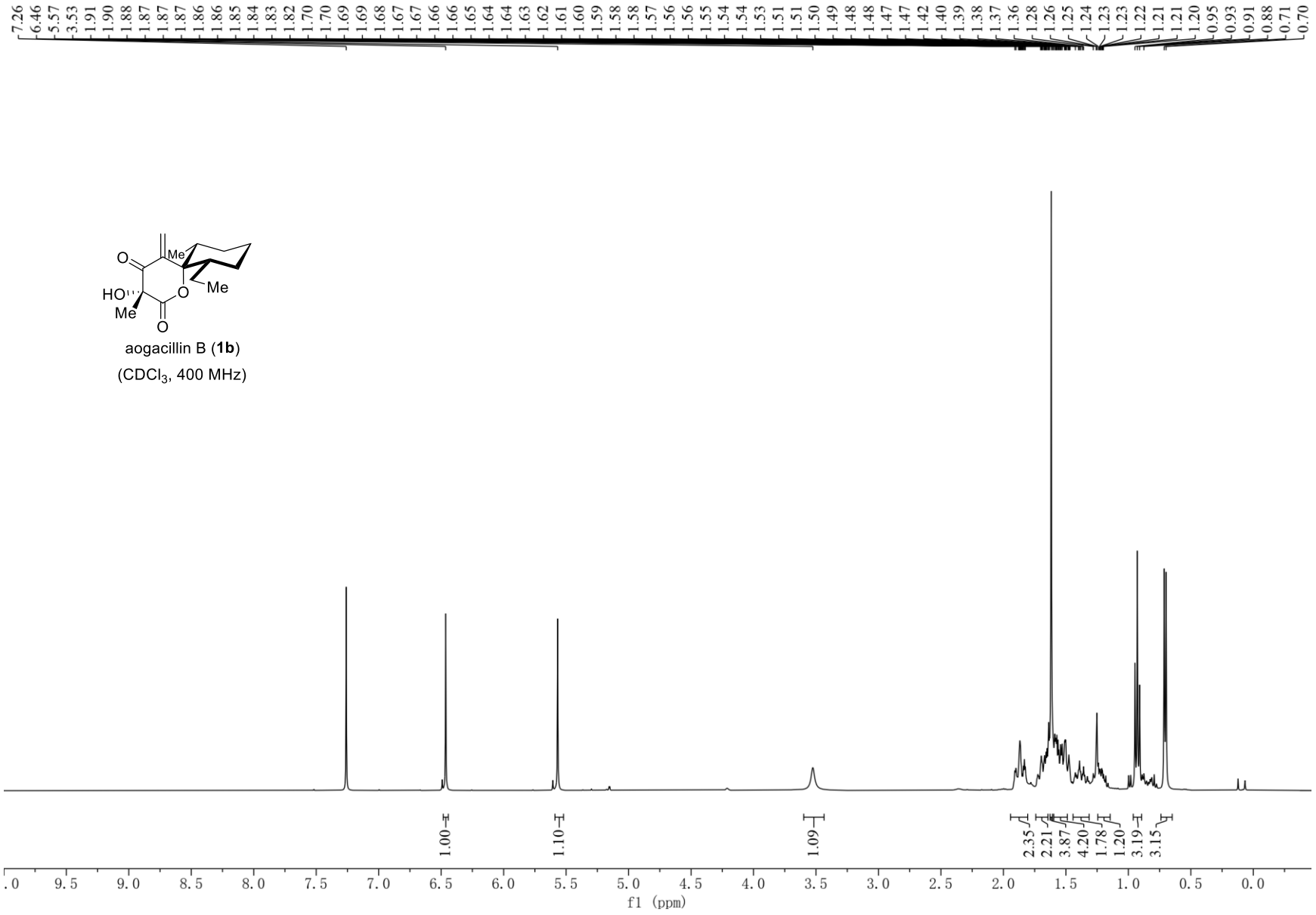


ent-aogacillin A (*ent*-**1a**)

($CDCl_3$, 400 MHz)

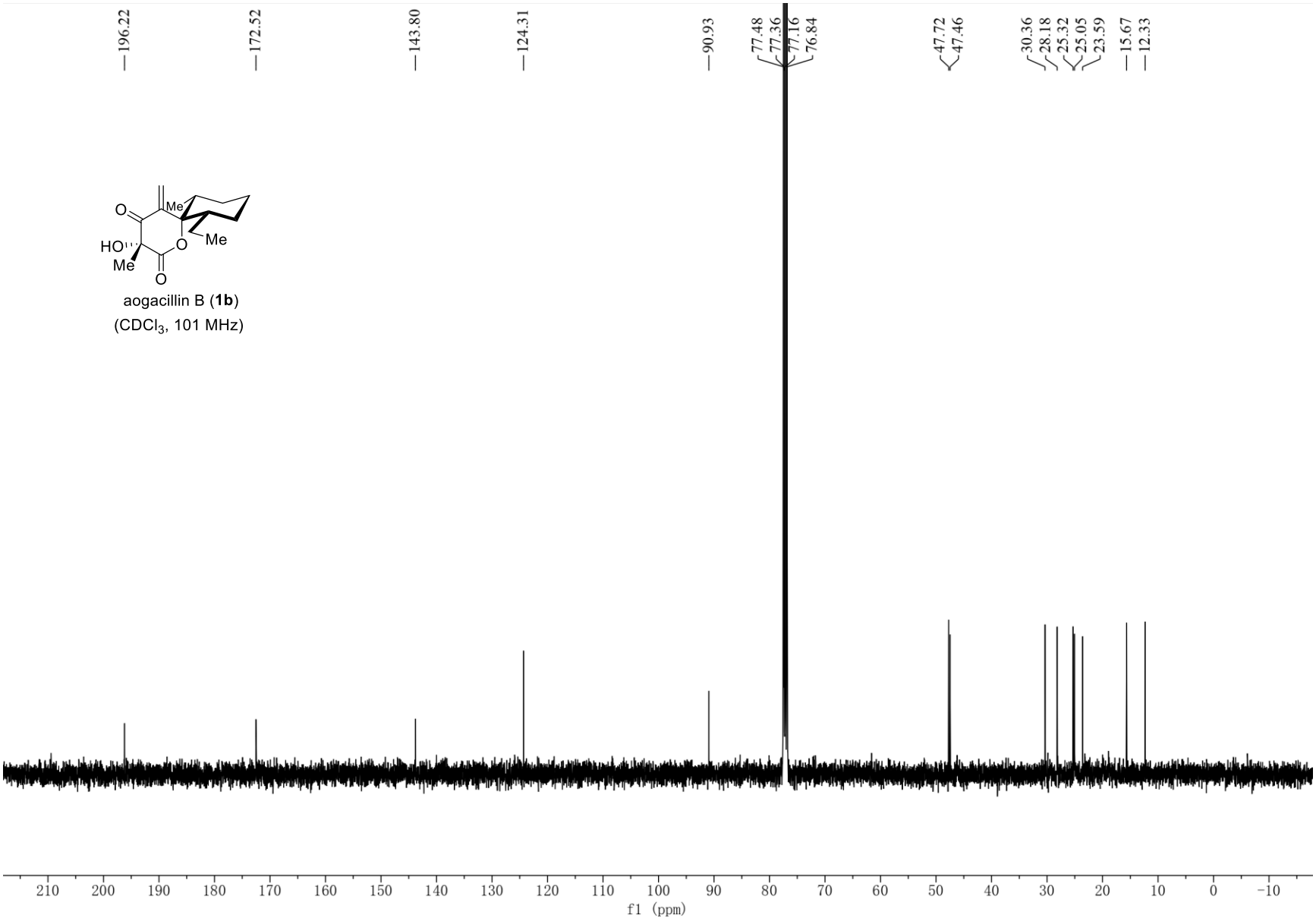


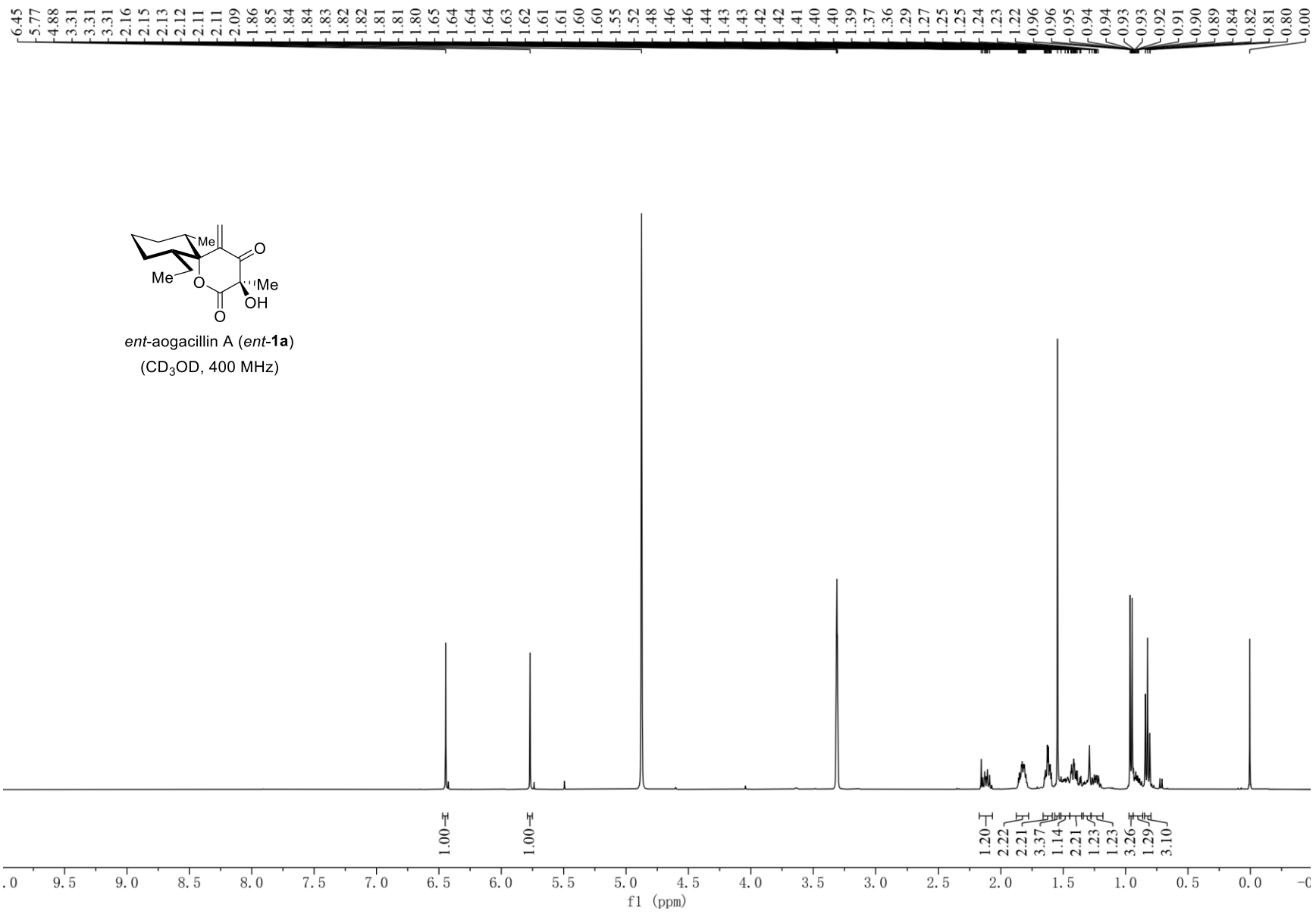
ent-aogacillin A (*ent*-**1a**)
($CDCl_3$, 101 MHz)

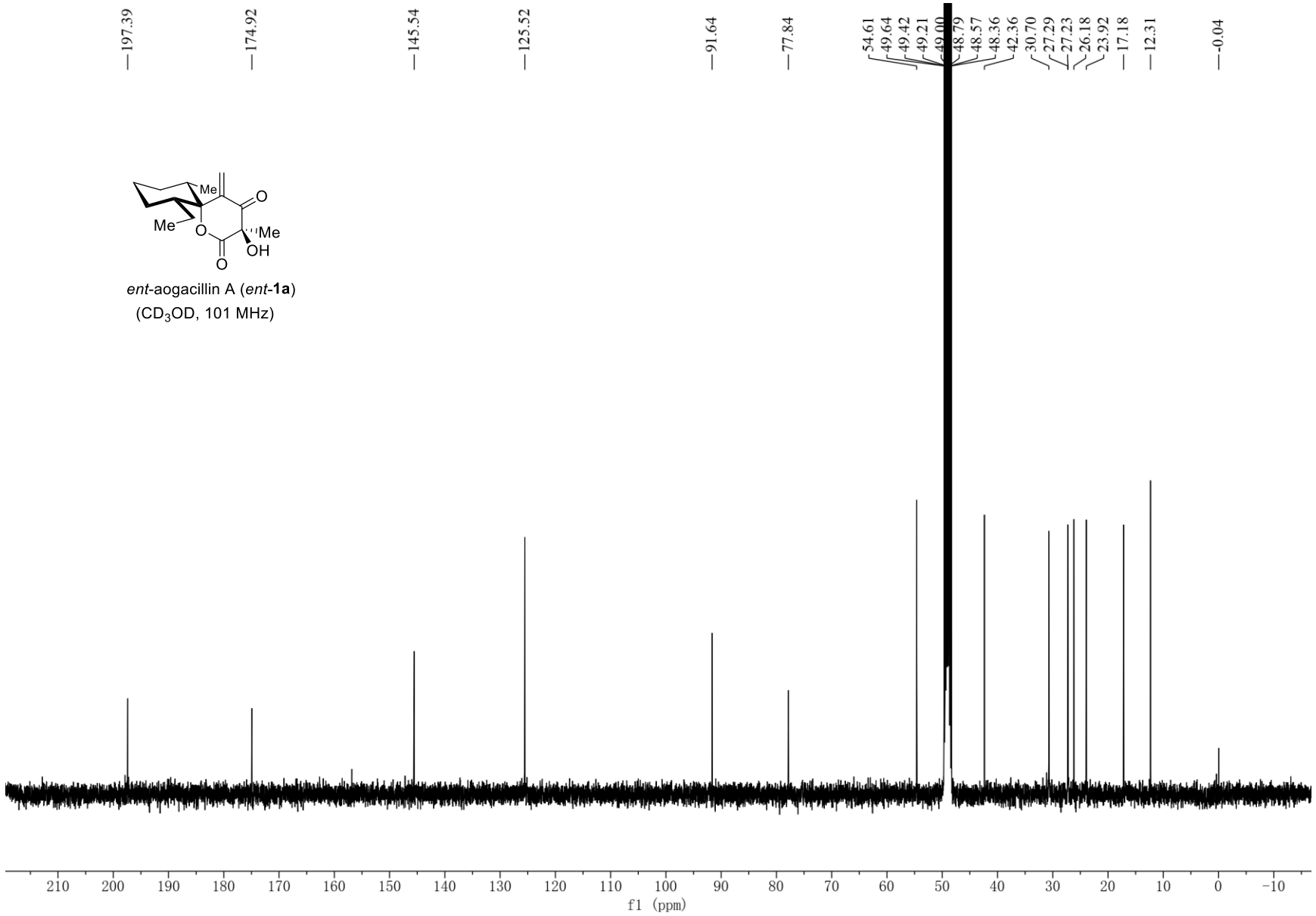


aogacillin B (**1b**)

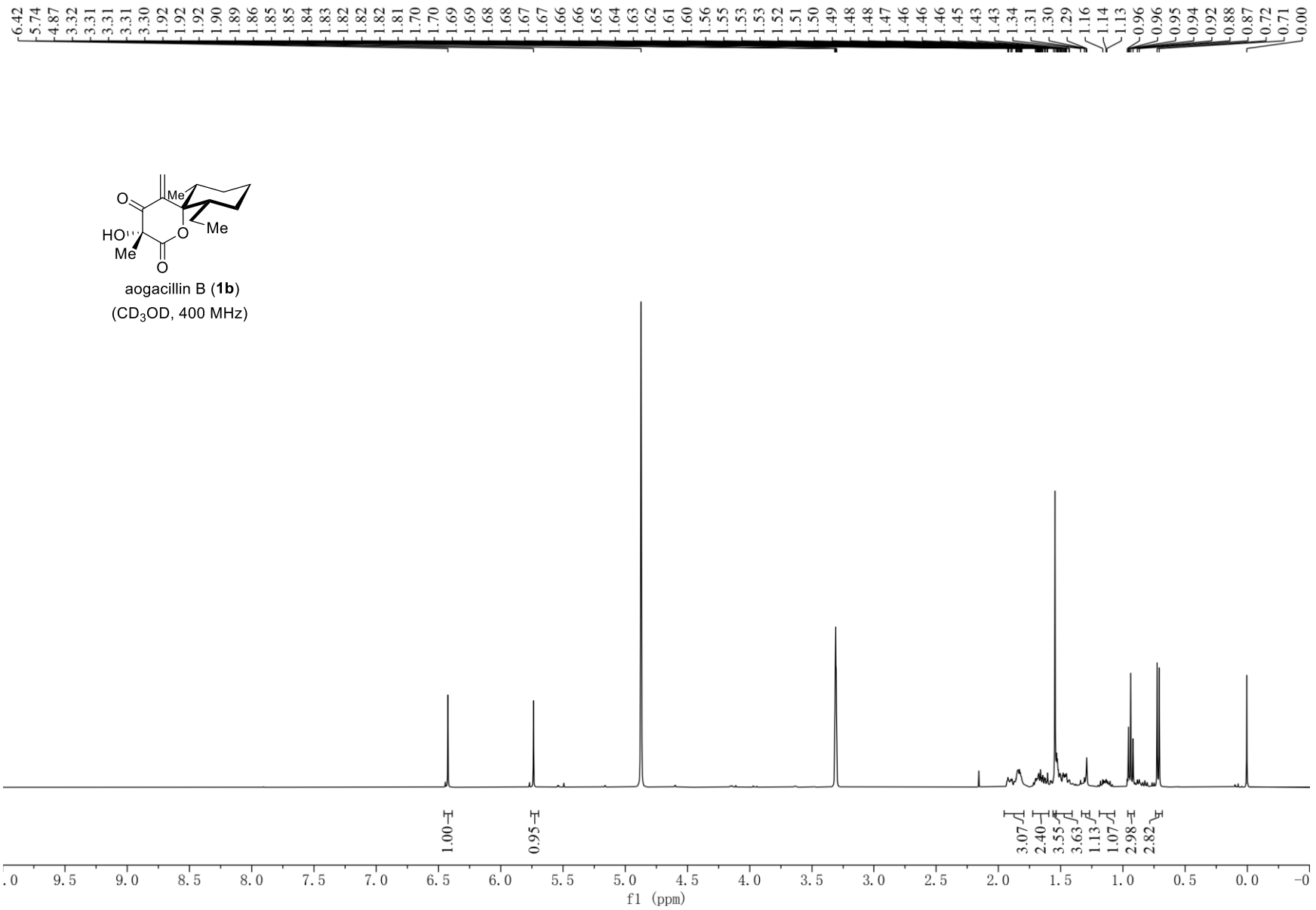
($CDCl_3$, 400 MHz)


196.22
172.52
143.80
124.31
90.93
77.48
77.36
77.16
76.84
47.72
47.46
30.36
28.18
25.32
25.05
23.59
15.67
12.33
O
Me
HO
Me
O
Me
O
aogacillin B (1b)
(CDCl3, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

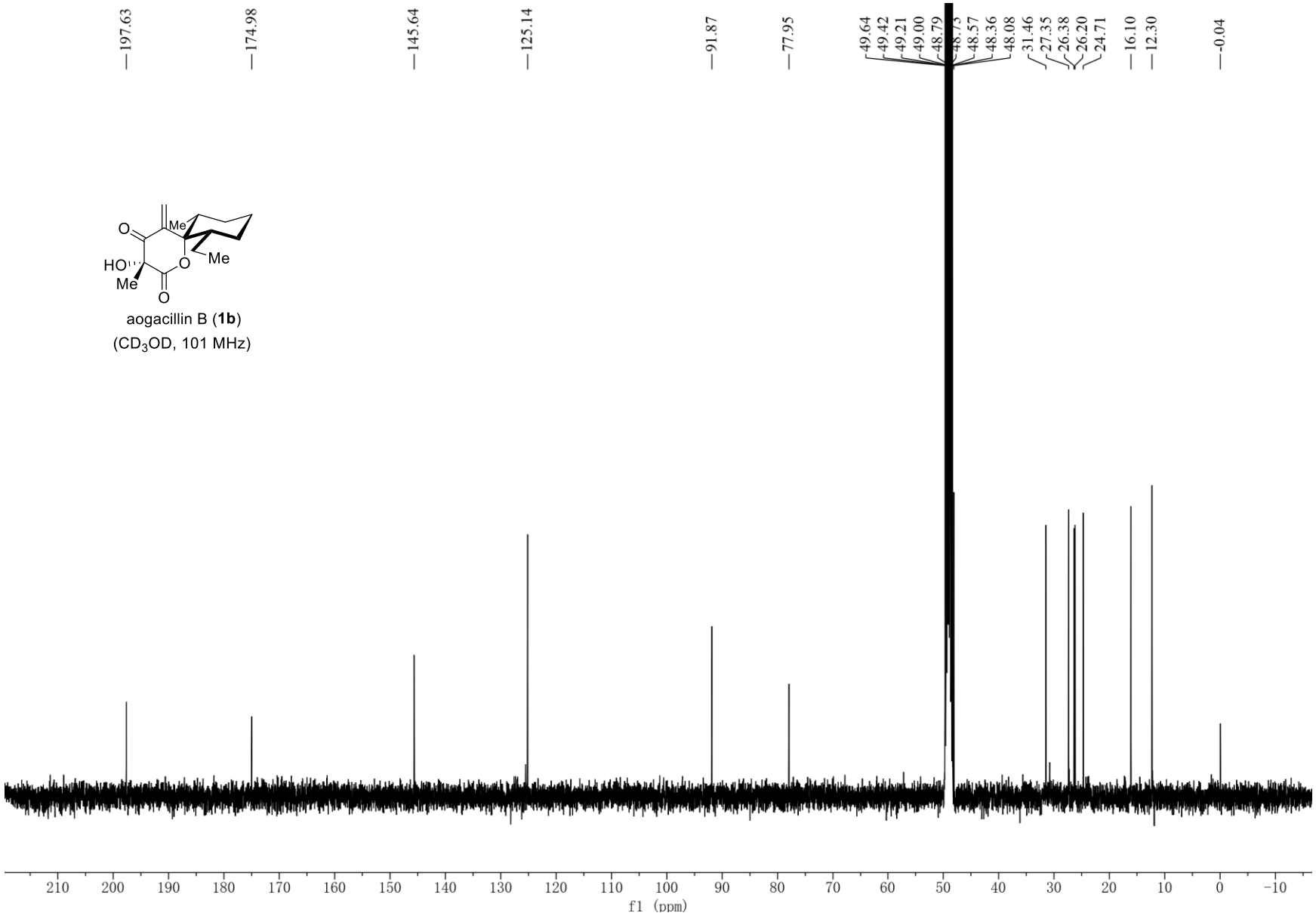

Me
O
Me
O
Me
OH
O
ent-aogacillin A (*ent*-**1a**)
(CD_3OD, 400 MHz)
f1 (ppm)

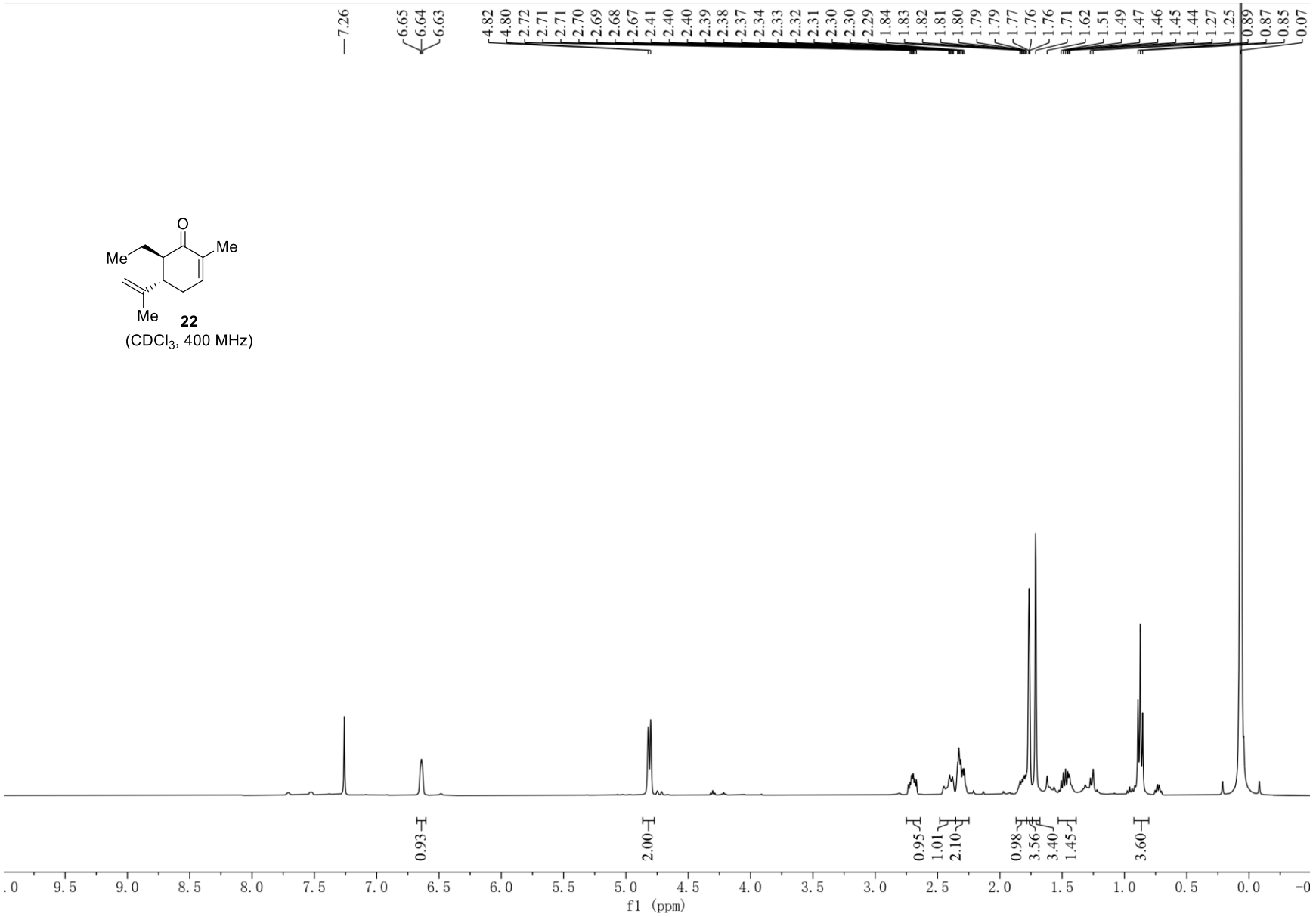


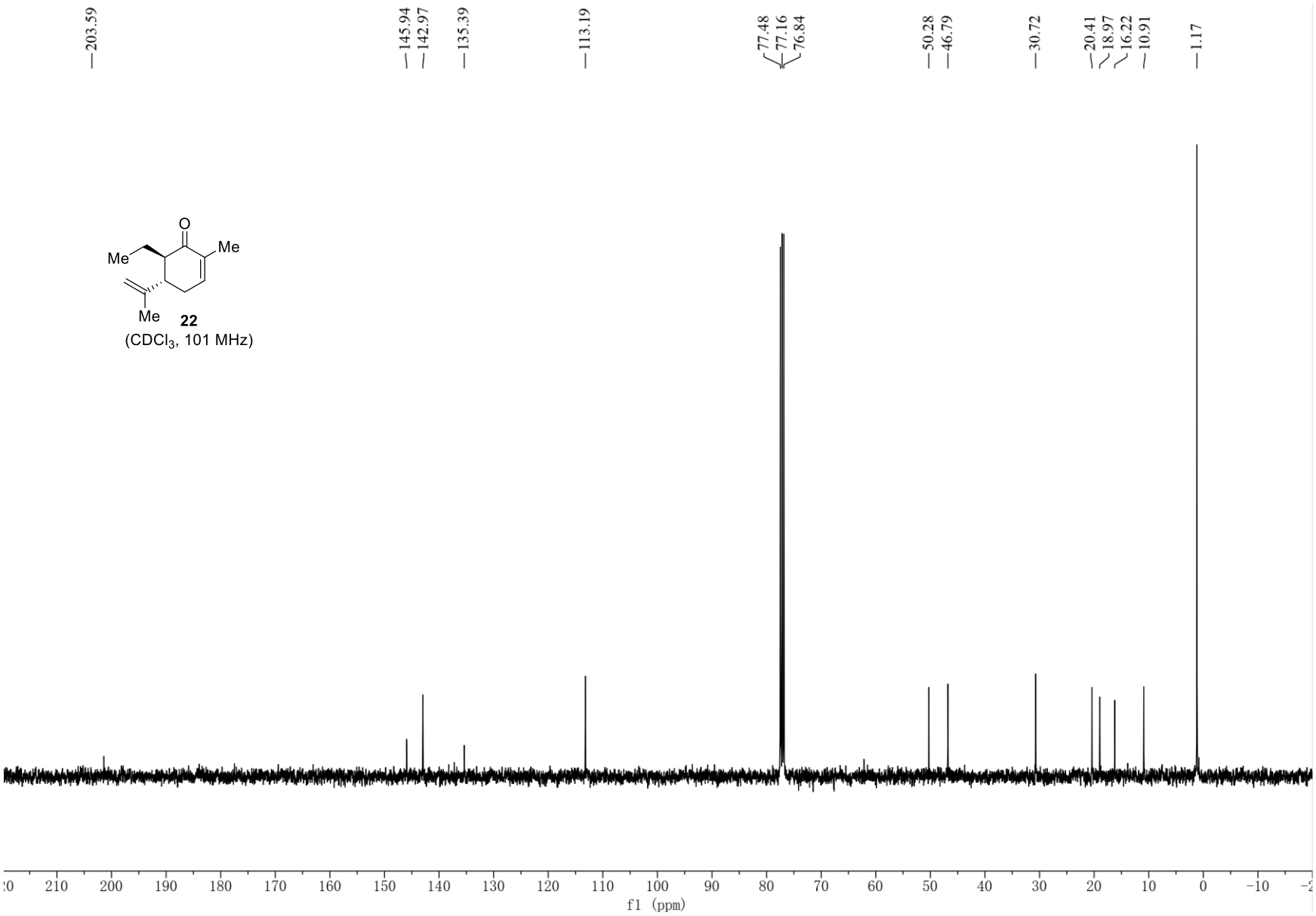
ent-aogacillin A (*ent*-**1a**)
(CD_3OD, 101 MHz)

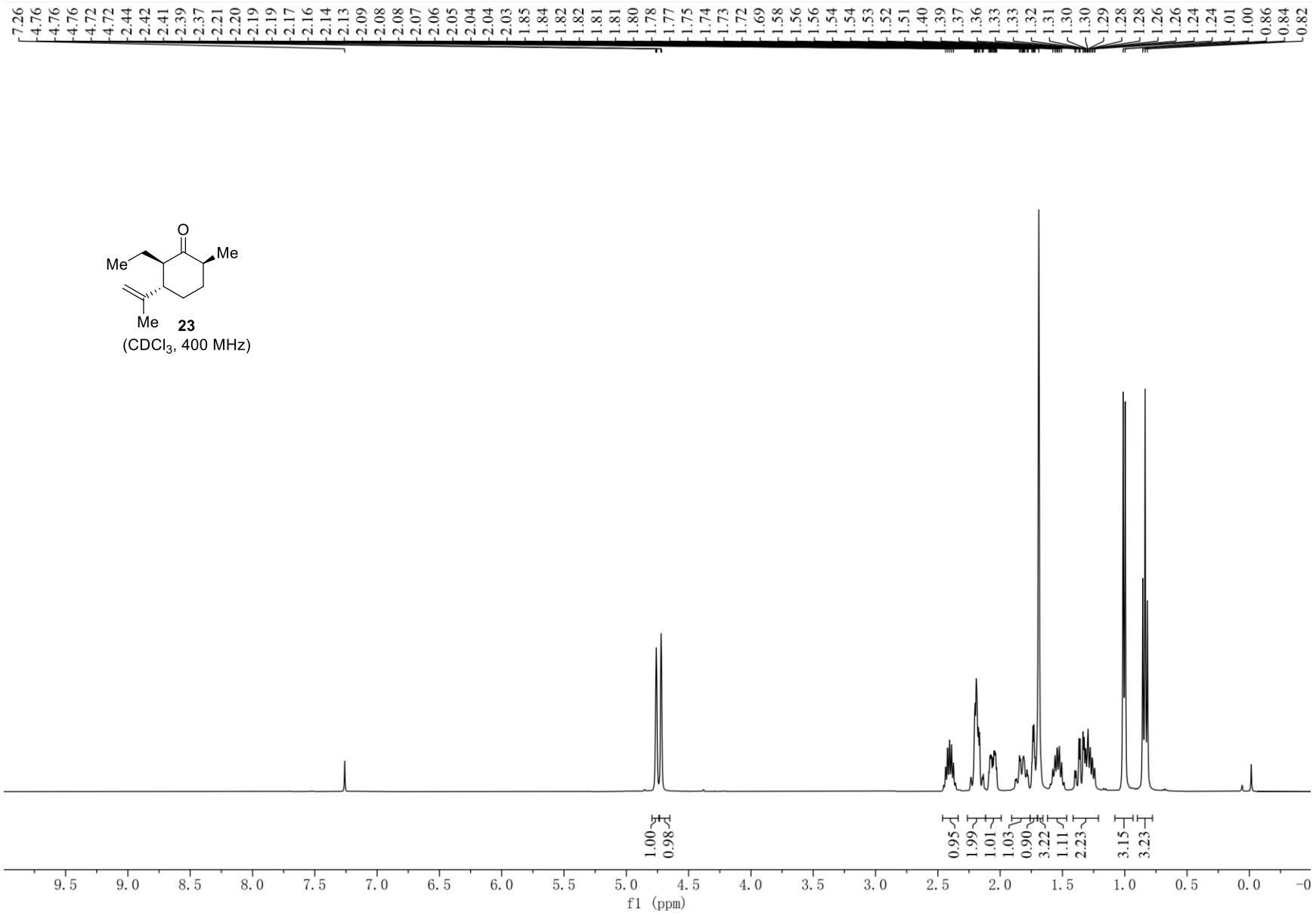


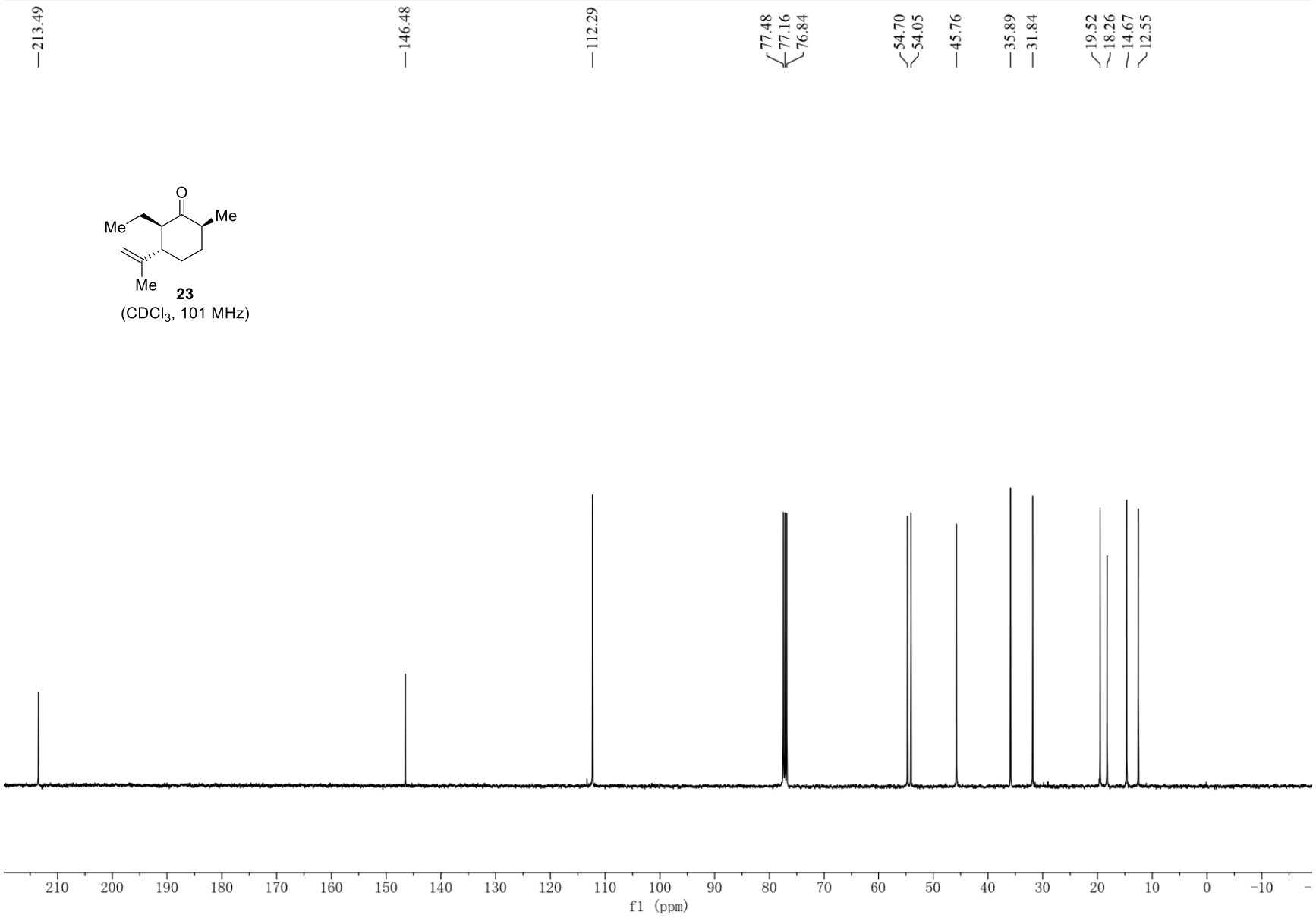
aogacillin B (**1b**)
(CD_3OD, 400 MHz)


197.63
174.98
145.64
125.14
91.87
77.95
49.64
49.42
49.21
49.00
48.79
48.57
48.36
48.08
31.46
27.35
26.38
26.20
24.71
16.10
12.30
-0.04
O
Me
HO
Me
O
Me
O
aogacillin B (1b)
(CD3OD, 101 MHz)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.26
6.65
6.64
6.63
4.82
4.80
2.72
2.71
2.71
2.70
2.69
2.68
2.67
2.41
2.40
2.40
2.39
2.38
2.37
2.34
2.33
2.32
2.31
2.30
2.30
2.29
1.84
1.83
1.82
1.81
1.80
1.79
1.79
1.77
1.76
1.76
1.71
1.62
1.51
1.49
1.47
1.46
1.45
1.44
1.27
1.25
0.89
0.87
0.85
0.07
O
Me
Me
Me
22
(CDCl3, 400 MHz)
0.93
2.00
0.95
1.01
2.10
0.98
3.56
3.40
1.45
3.60
f1 (ppm)

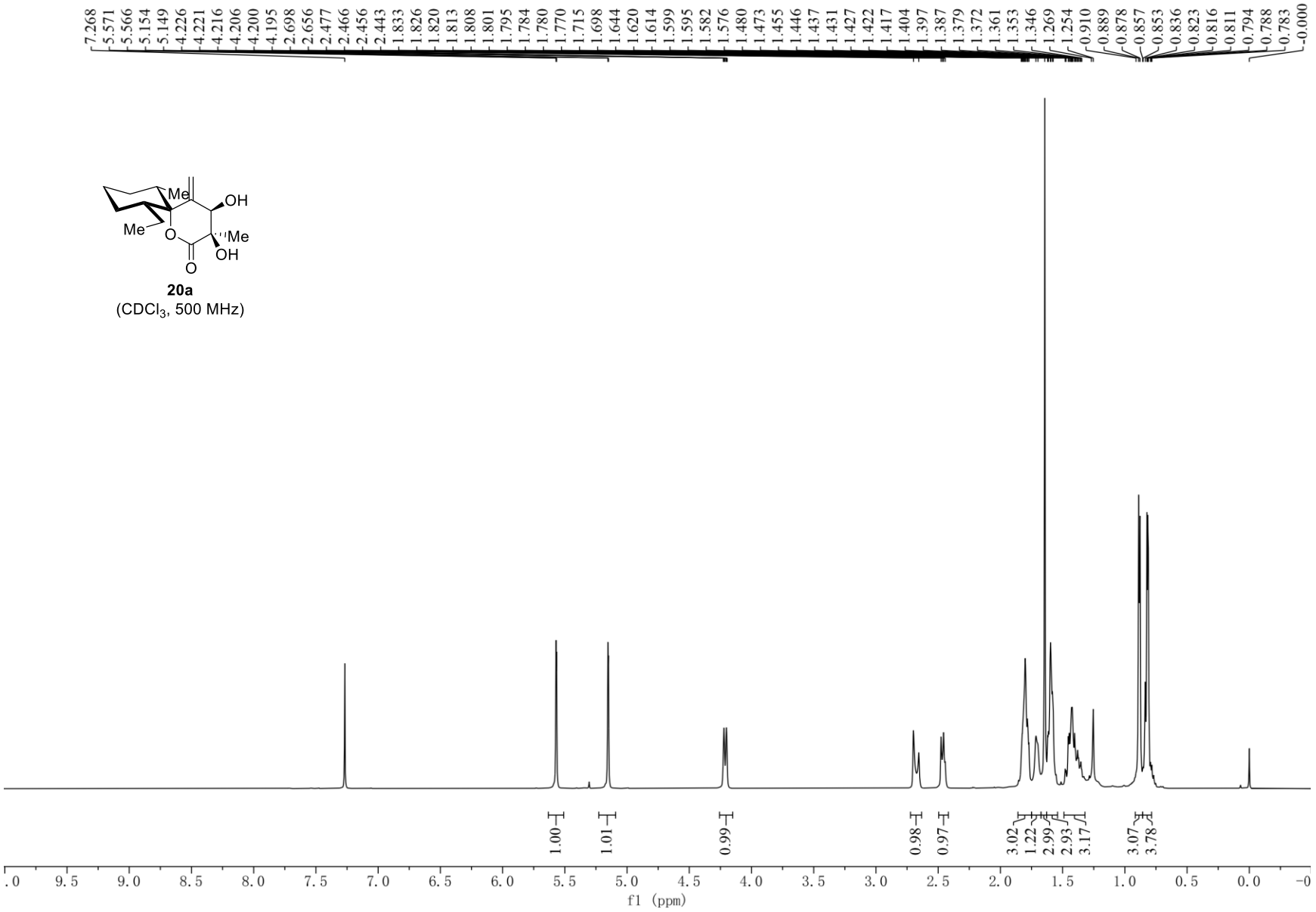

203.59
145.94
142.97
135.39
113.19
77.48
77.16
76.84
50.28
46.79
30.72
20.41
18.97
16.22
10.91
1.17
O
Me
Me
Me
22
(CDCl3, 101 MHz)
f1 (ppm)


7.26
4.76
4.76
4.76
4.72
4.72
2.44
2.42
2.41
2.39
2.37
2.21
2.20
2.19
2.19
2.17
2.16
2.14
2.13
2.09
2.08
2.08
2.07
2.06
2.05
2.04
2.04
2.03
1.85
1.84
1.82
1.82
1.81
1.81
1.80
1.78
1.77
1.75
1.74
1.73
1.72
1.69
1.58
1.56
1.56
1.54
1.54
1.53
1.52
1.51
1.40
1.39
1.37
1.36
1.33
1.33
1.32
1.31
1.30
1.30
1.29
1.28
1.28
1.26
1.26
1.24
1.24
1.01
1.00
0.86
0.84
0.82
O
Me
Me
Me
23
(CDCl3, 400 MHz)
1.00
0.98
0.95
1.99
1.01
1.03
0.90
3.22
1.11
2.23
3.15
3.23
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
−0
f1 (ppm)

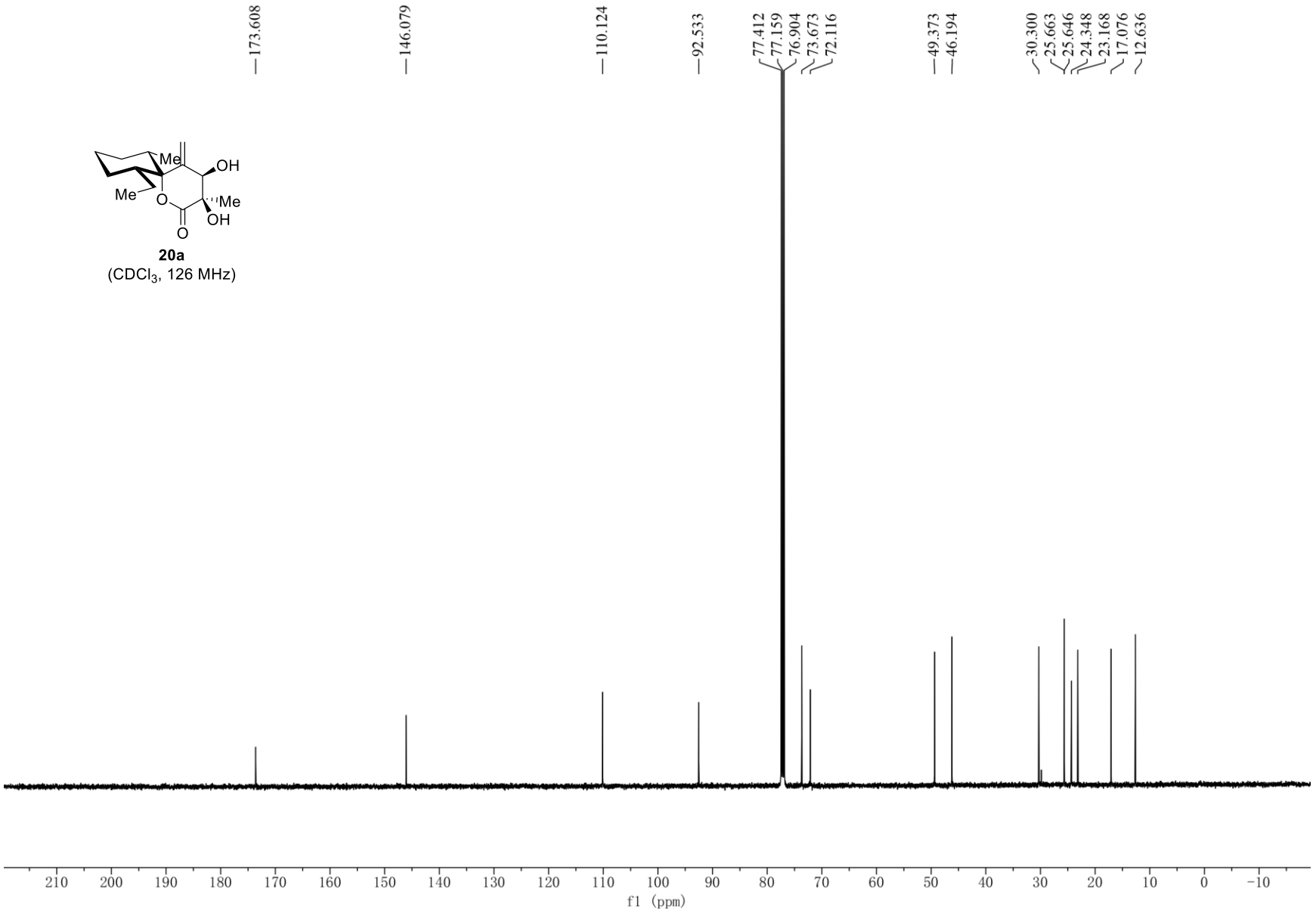


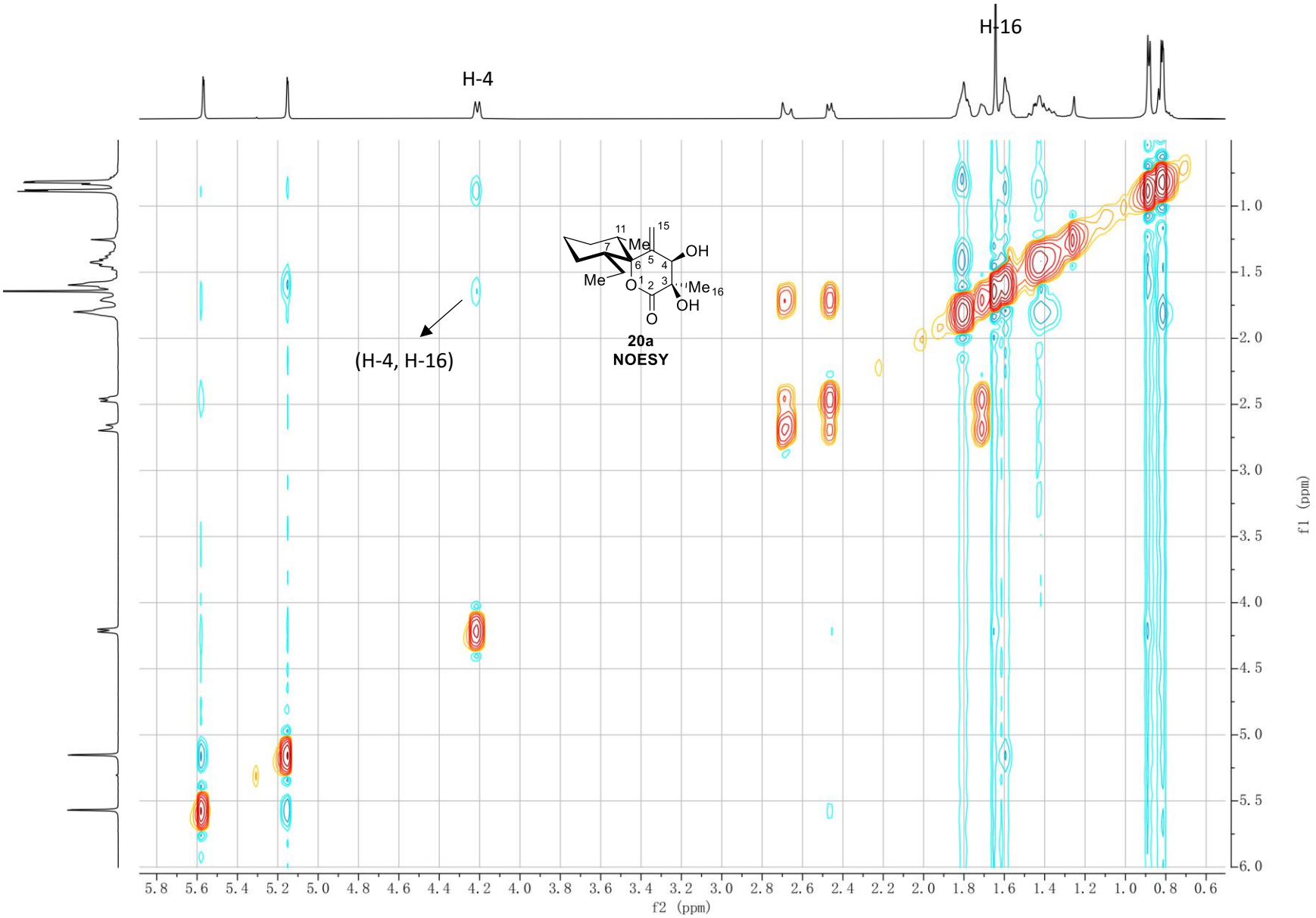
23

($CDCl_3$, 101 MHz)



20a
($CDCl_3$, 500 MHz)


173.608
146.079
110.124
92.533
77.412
77.159
76.904
73.673
72.116
49.373
46.194
30.300
25.663
25.646
24.348
23.168
17.076
12.636
Me
OH
Me
O
Me
OH
O
20a
(CDCl3, 126 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


H-16
H-4
(H-4, H-16)
20a
NOESY
Me
OH
Me
O
Me16
OH
O
11
15
7
6
5
4
1
2
3
f2 (ppm)
f1 (ppm)

HPLC of *ent*-Aogacillin A and Aogacillin B

```
Data File C:\Users\P...on\1\Data\public\TEST 2025-01-07 22-55-40\001-P1-D2-GHX-D26-250MM.D
Sample Name: GHX-D26-250MM

    ======================================================================
    Acq. Operator   : SYSTEM                          Seq. Line :   1
    Acq. Instrument : Perp LC                          Location :   P1-D-02
    Injection Date  : 7/1/2025 10:56:32 pm                  Inj :   1
                                                     Inj Volume : 5.000 µl
    Different Inj Volume from Sample Entry!  Actual Inj Volume : 20.000 µl
    Acq. Method     : C:\Users\Public\Documents\ChemStation\1\Data\public\TEST 2025-01-07 22-55-
                      40\0.2 to 0.6 to 0.7-40-775.M
    Last changed    : 7/1/2025 11:36:53 pm by SYSTEM
                      (modified after loading)
    Analysis Method : C:\Users\Public\Documents\ChemStation\1\Data\public\TEST 2025-01-07 22-55-
                      40\0.2 to 0.6 to 0.7-40-775.M (Sequence Method)
    Last changed    : 7/1/2025 11:41:35 pm by SYSTEM
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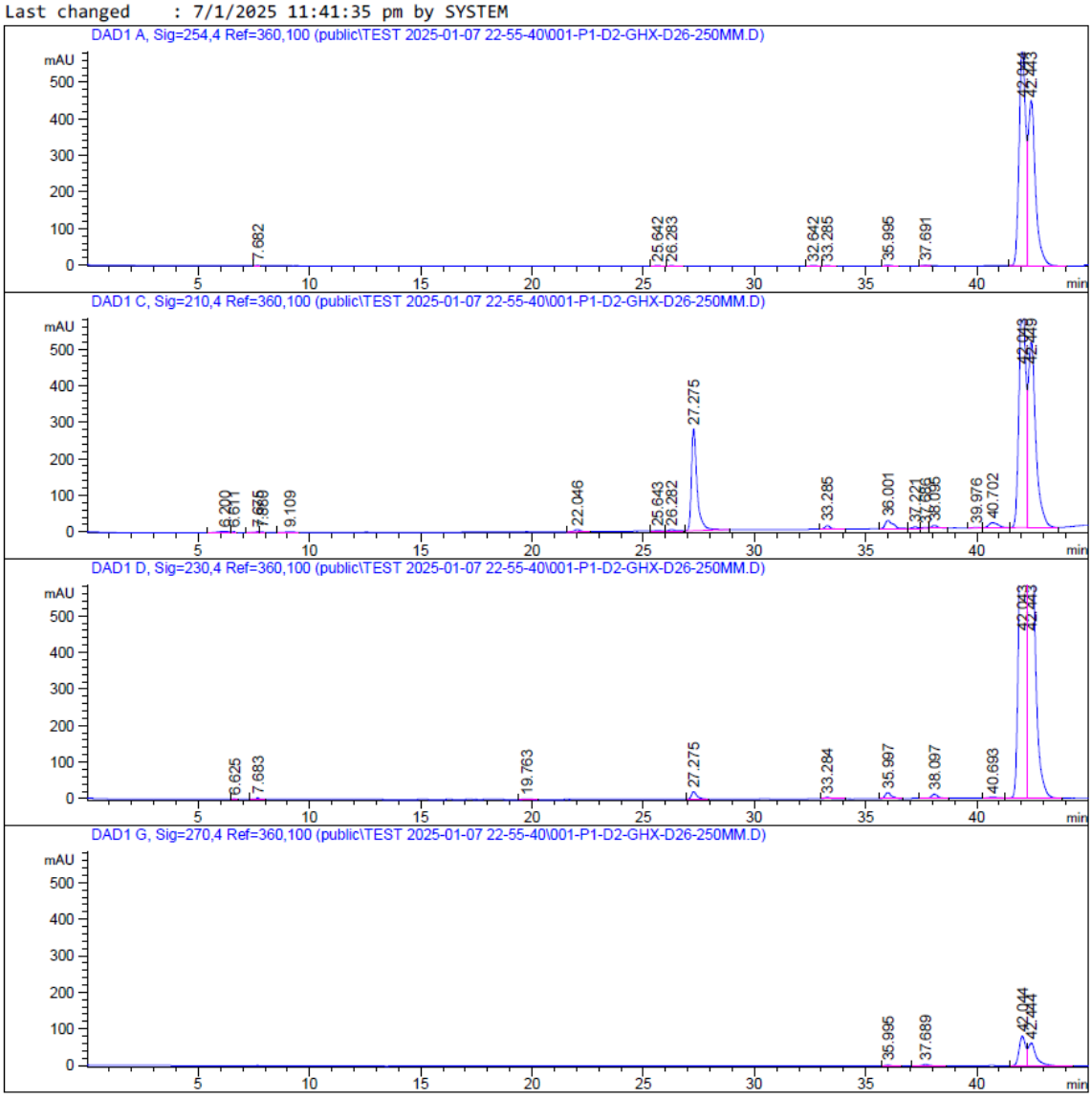


```
    ==============================================================================

Perp LC 8/1/2025 12:08:53 am SYSTEM                          Page   1 of 3
```

Data File C:\Users\P...on\1\Data\public\TEST 2025-01-07 22-55-40\001-P1-D2-GHX-D26-250MM.D
Sample Name: GHX-D26-250MM

Fraction Information

No Fractions found.

Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.682	BB	0.0664	7.73754	1.72115	0.0339
2	25.642	BB	0.2169	27.93059	1.92878	0.1224
3	26.283	BB	0.2158	18.95523	1.36645	0.0831
4	32.642	BB	0.2668	31.40070	1.80647	0.1376
5	33.285	BB	0.2280	25.72269	1.70532	0.1127
6	35.995	BB	0.2554	42.13104	2.51597	0.1846
7	37.691	BB	0.2448	23.59667	1.48995	0.1034
8	42.044	BV	0.3093	1.21659e4	598.08972	53.3046
9	42.443	VB	0.3406	1.04800e4	451.77802	45.9178
Totals :				2.28234e4	1062.40182	

Signal 2: DAD1 C, Sig=210,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.200	BV	0.4959	143.68996	3.99189	0.4420
2	6.611	VB	0.1056	24.70831	3.44967	0.0760
3	7.675	BV	0.0891	17.56317	2.80227	0.0540
4	7.880	VB	0.1292	11.13766	1.36440	0.0343
5	9.109	BB	0.3109	27.44184	1.31810	0.0844
6	22.046	BB	0.2685	97.97961	5.48274	0.3014
7	25.643	BB	0.2111	21.64577	1.52998	0.0666
8	26.282	BB	0.2399	53.46592	3.39130	0.1645
9	27.275	BB	0.2622	4905.75146	277.58978	15.0895
10	33.285	BB	0.2579	163.69524	9.64820	0.5035
11	36.001	BB	0.3379	550.75891	22.95303	1.6941
12	37.221	BV	0.2449	74.04540	4.62290	0.2278
13	37.686	VV	0.2574	58.19829	3.33798	0.1790
14	38.095	VB	0.2984	161.68903	8.18890	0.4973
15	39.976	BB	0.2848	37.32713	2.04676	0.1148
16	40.702	BV	0.4269	394.37692	13.57522	1.2131
17	42.043	VV	0.3091	1.35673e4	667.69354	41.7313

Data File C:\Users\P...on\1\Data\public\TEST 2025-01-07 22-55-40\001-P1-D2-GHX-D26-250MM.D
Sample Name: GHX-D26-250MM

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
Totals :				3.25111e4	1541.17380	

Signal 3: DAD1 D, Sig=230,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.625	BB	0.0668	6.15902	1.36059	0.0148
2	7.683	BB R	0.0850	28.84280	4.74252	0.0693
3	19.763	BB	0.2660	19.96965	1.13113	0.0480
4	27.275	BB	0.2510	337.26599	20.18346	0.8106
5	33.284	BB	0.2630	68.75019	3.98959	0.1652
6	35.997	BB	0.2840	316.93634	16.50882	0.7617
7	38.097	BB	0.3016	226.59802	11.22204	0.5446
8	40.693	BB	0.3896	65.04498	2.33041	0.1563
9	42.043	BV	0.3091	2.17966e4	1072.67627	52.3843
10	42.443	VB	0.3362	1.87428e4	821.45667	45.0451
Totals :				4.16089e4	1955.60148	

Signal 4: DAD1 G, Sig=270,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	35.995	BB	0.2663	41.89453	2.32414	1.2479
2	37.689	BB	0.3132	85.77504	4.11449	2.5550
3	42.044	BV	0.3091	1660.02209	81.66573	49.4466
4	42.444	VB	0.3646	1569.51086	62.15364	46.7506
Totals :				3357.20253	150.25800	

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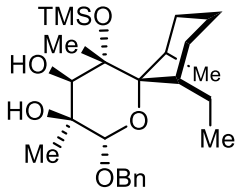
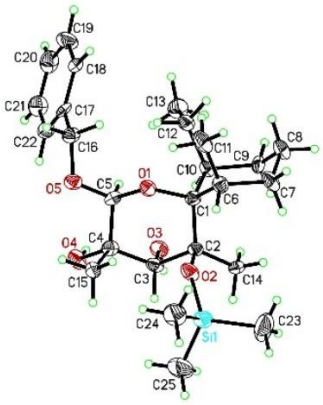
*** End of Report ***

X-Ray Diffraction

X-Ray Data of 10a (CCDC 2464462)



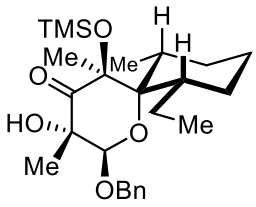
10a



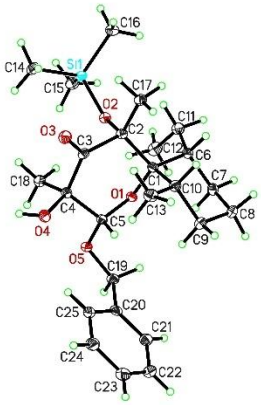
Crystal data and structure refinement for rsang9cult.

Identification code	rsang9cult
Empirical formula	$C_{25}H_{42}O_5Si$
Formula weight	450.67
Temperature/K	99.9(5)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.5417(8)
b/Å	27.4850(16)
c/Å	7.5621(4)
α/°	90
β/°	93.110(6)
γ/°	90
Volume/Å^3	2602.9(3)
Z	4
ρ_{calc}g/cm^3	1.150
μ/mm^{-1}	1.040
F(000)	984.0
Crystal size/mm^3	0.3 × 0.05 × 0.05
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	9.554 to 134.98
Index ranges	-15 ≤ h ≤ 14, -27 ≤ k ≤ 32, -9 ≤ l ≤ 5
Reflections collected	11515
Independent reflections	4592 [R_{int} = 0.1838, R_{sigma} = 0.1875]
Data/restraints/parameters	4592/0/289
Completeness to theta =66.5 °	98.2%
Goodness-of-fit on F^2	1.587
Final R indexes [I>=2σ (I)]	R_1 = 0.2388, wR_2 = 0.4781
Final R indexes [all data]	R_1 = 0.2897, wR_2 = 0.4962
Largest diff. peak/hole / e Å^{-3}	2.10/-0.75

X-Ray Data of 11b (CCDC 2464461)



11b



Crystal data and structure refinement for sang7CuLT.

Identification code	sang7cult	
Empirical formula	C_{25} H_{40} O_5 Si	
Formula weight	448.66	
Temperature	99.9(5) K	
Wavelength	1.54184 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 8.7653(5) Å	a= 87.894(4)°.
	b = 10.9607(6) Å	b= 82.343(5)°.
	c = 12.7961(7) Å	g = 79.763(5)°.
Volume	1198.91(11) $Å^3$	
Z	2	
Density (calculated)	1.243 Mg/m^3	
Absorption coefficient	1.128 mm^{-1}	
F(000)	488	
Crystal size	0.08 x 0.07 x 0.02 mm^3	
Theta range for data collection	4.10 to 67.49°.	
Index ranges	-10<=h<=10, -13<=k<=12, -15<=l<=14	
Reflections collected	6498	
Independent reflections	4245 [R(int) = 0.0293]	
Completeness to theta = 66.50°	98.4 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.76686	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4245 / 0 / 288	
Goodness-of-fit on F^2	1.002	
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0829	
R indices (all data)	R1 = 0.0499, wR2 = 0.0888	
Largest diff. peak and hole	0.273 and -0.249 $e.Å^{-3}$	

Computational Method and Results

DFT Calculations

All the theoretical calculations were carried out with the density-functional theory (DFT) methods in Gaussian 16 package.[1] The geometry optimization of transition states (**TS-I**, **TS-II**, **TS-III**, **TS-IV**) and products (**19a**, **C4-*epi*-19a**, **19b**, **C4-*epi*-19b**) were performed at the B3LYP-D3 method with 6-311g(d,p) basis set in PCM solvent model (THF).

[1] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, et al., Gaussian 16, Revision C.01, Wallingford CT 2019.

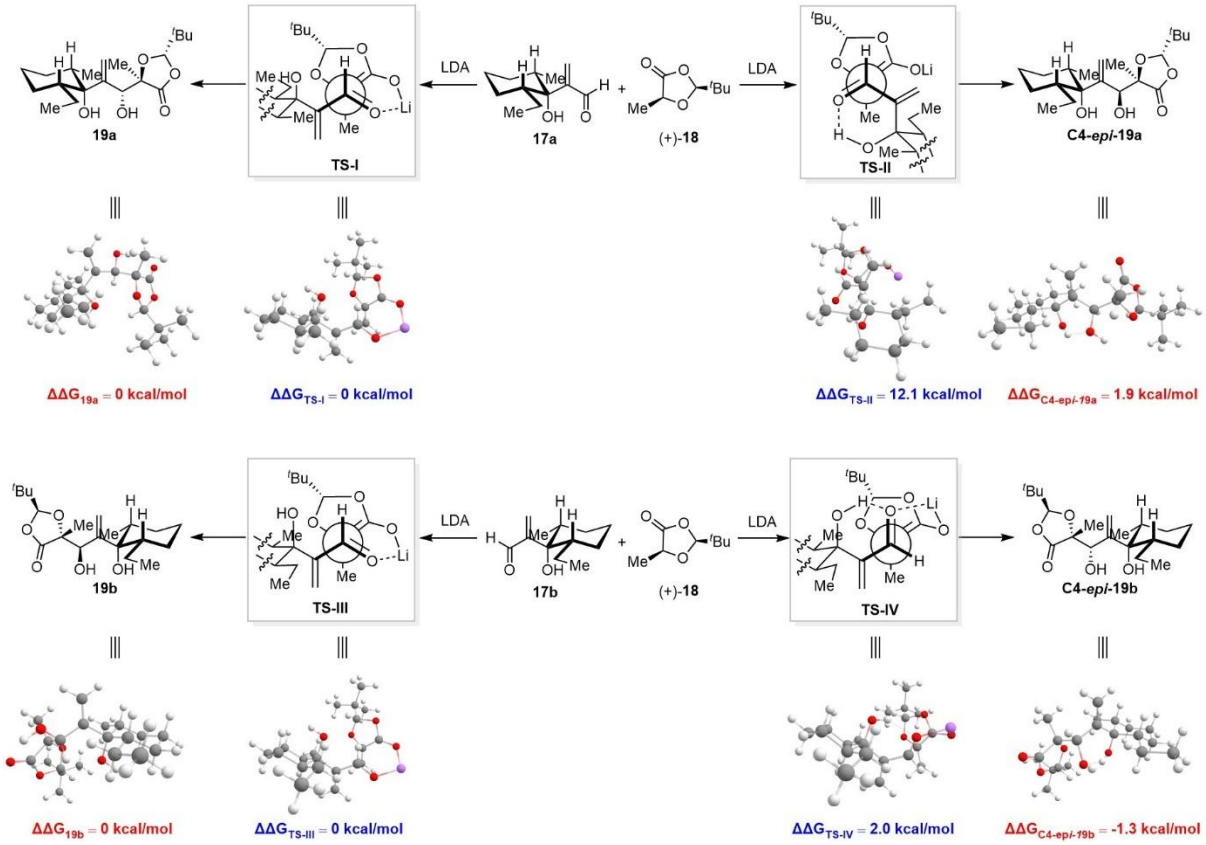
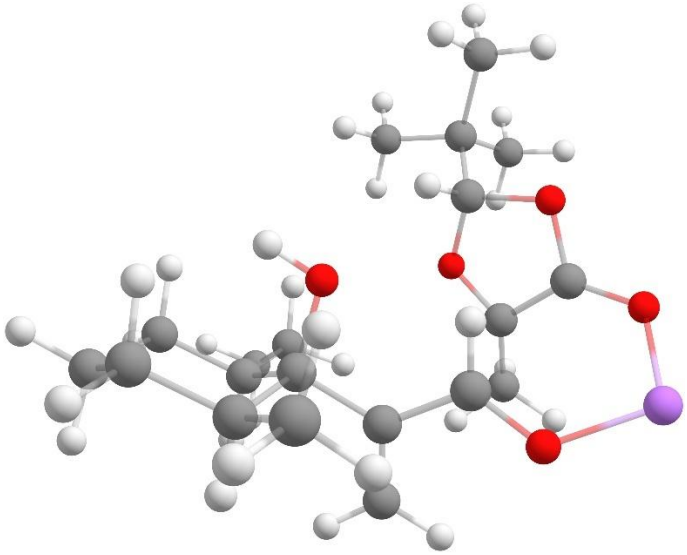


Table S3 Gibbs Free Energy by DFT calculation

	Gibbs Free Energy (a.u.)	ΔΔG (kcal/mol)
TS-I	-1165.659775	0.0
TS-II	-1165.640415	12.1
19a	-1158.676363	0.0
4-*epi*-19a	-1158.67333	1.9
TS-III	-1165.663276	0.0
TS-IV	-1165.6601	2.0
19b	-1158.674443	0.0
4-*epi*-19b	-1158.676512	-1.3

For the aldol condensation of **17a** and **18**, DFT calculations demonstrated that the energy barriers of transition state TS-II leading to C4-*epi*-**19a** is higher than that of TS-I leading to **19a**; the Gibbs free energy of C4-*epi*-**19a** is higher than that of **19a**. This indicates that **19a** is favored both kinetically and thermodynamically. The experimental result is consistent with this calculation result. For the aldol condensation of **17b** and **18**, DFT calculations demonstrated that the energy barriers of transition state TS-IV leading to C4-*epi*-**19b** is higher than that of TS-III leading to **19b**; the Gibbs free energy of C4-*epi*-**19b** is lower than that of **19b**. This indicates that **19b** is favored kinetically and C4-*epi*-**19b** is favored thermodynamically.

Cartesian Coordinates

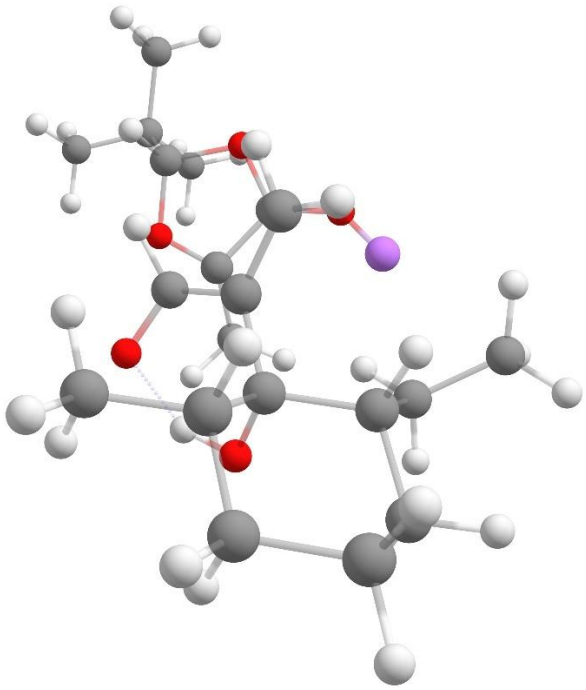


TS-I

C	-2.435446000	-1.011737000	0.787968000
C	-2.040054000	0.136534000	-0.197782000
C	-3.314235000	0.632863000	-0.976971000
C	-4.045573000	-0.527861000	-1.674367000
C	-4.417059000	-1.649433000	-0.704179000
C	-3.183795000	-2.143254000	0.054568000
C	-3.012803000	1.753565000	-1.979971000
C	-1.417628000	1.348785000	0.511786000
C	-0.336833000	2.101793000	-0.167878000
O	-1.057052000	-0.343387000	-1.136217000
C	-1.929633000	1.858745000	1.643474000
C	1.665061000	0.994749000	0.939552000
H	-3.145211000	-0.576096000	1.502635000
H	-3.989086000	1.033617000	-0.210462000

O	-0.110953000	3.317857000	0.110851000
O	1.826560000	-0.393727000	0.755182000
C	2.309206000	-0.550817000	-0.569059000
O	2.919572000	0.708248000	-0.917048000
C	2.464485000	1.638523000	-0.014258000
O	2.760009000	2.846241000	-0.174372000
C	-1.234014000	-1.558710000	1.580255000
C	3.306135000	-1.712113000	-0.686907000
C	2.571617000	-3.007244000	-0.295709000
C	4.508944000	-1.483110000	0.242339000
C	3.772970000	-1.796967000	-2.151401000
C	1.445346000	1.441527000	2.337973000
H	-4.940770000	-0.135291000	-2.167529000
H	-3.418704000	-0.928433000	-2.484678000
H	-4.892411000	-2.477890000	-1.239521000
H	-5.158141000	-1.275593000	0.013518000
H	-3.473814000	-2.910797000	0.776245000
H	-2.496630000	-2.644465000	-0.642947000
H	-2.628032000	2.650083000	-1.491193000
H	-2.277363000	1.427005000	-2.719695000
H	0.005182000	1.686663000	-1.116222000
H	-1.448289000	-1.071320000	-1.628013000
H	-1.530818000	2.784934000	2.036709000
H	-2.749344000	1.399157000	2.180787000
H	1.453277000	-0.693980000	-1.242179000
H	-0.623987000	-0.725888000	1.928058000
H	-0.588442000	-2.126924000	0.905022000
H	1.704356000	-3.181735000	-0.940671000
H	3.241603000	-3.865594000	-0.397741000
H	2.222758000	-2.963679000	0.737807000
H	5.038415000	-0.565215000	-0.021756000
H	5.211776000	-2.317314000	0.161170000

H	4.187097000	-1.406614000	1.282882000
H	2.927269000	-1.951179000	-2.829442000
H	4.286978000	-0.882463000	-2.453891000
H	4.461106000	-2.637192000	-2.280019000
H	0.427988000	1.234693000	2.692355000
H	2.145206000	0.939383000	3.017322000
H	1.613656000	2.516873000	2.414953000
H	-3.925295000	2.033450000	-2.514174000
C	-1.618873000	-2.423874000	2.786156000
H	-2.255660000	-1.870496000	3.484709000
H	-2.154521000	-3.333051000	2.499646000
H	-0.725318000	-2.735352000	3.333883000
Li	1.481051000	4.079023000	-0.162750000



TS-II

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C	-2.448465000	-0.423692000	0.008770000
C	-3.266414000	-1.563744000	-0.713163000

C	-4.698325000	-1.631832000	-0.159923000
C	-5.441263000	-0.304756000	-0.315626000
C	-4.660781000	0.818750000	0.364608000
C	-2.599491000	-2.942067000	-0.637545000
C	-1.034882000	-0.378841000	-0.637801000
C	0.118170000	-1.110029000	0.070044000
O	-2.366359000	-0.648465000	1.402067000
C	-0.846282000	0.101460000	-1.883500000
C	1.489421000	0.181500000	0.768551000
H	-3.259707000	1.166407000	-1.217799000
H	-3.327868000	-1.274473000	-1.771669000
O	-0.163542000	-1.857680000	1.063842000
O	2.680486000	-0.604783000	0.797452000
C	3.378747000	-0.365593000	-0.397499000
O	2.875900000	0.908946000	-0.895347000
C	1.766620000	1.213832000	-0.193206000
O	1.107542000	2.225183000	-0.487776000
C	-2.500345000	2.091885000	0.593976000
C	4.898912000	-0.335072000	-0.190488000
C	5.317648000	-1.721957000	0.332980000
C	5.280602000	0.754124000	0.824663000
C	5.569275000	-0.060086000	-1.548442000
C	1.025026000	0.504238000	2.154739000
H	-5.238995000	-2.432925000	-0.674907000
H	-4.649920000	-1.906098000	0.899061000
H	-6.445977000	-0.374077000	0.113776000
H	-5.572269000	-0.076907000	-1.382210000
H	-5.168382000	1.780565000	0.225024000
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H	-1.639164000	-2.968809000	-1.155085000
H	-2.420466000	-3.237561000	0.397384000
H	0.822624000	-1.506661000	-0.681639000

H	-1.569982000	-1.237545000	1.529165000
H	0.118470000	0.011364000	-2.375411000
H	-1.660218000	0.473847000	-2.499560000
H	3.114671000	-1.111290000	-1.160620000
H	-1.471847000	1.810857000	0.863049000
H	-2.954714000	2.219129000	1.578245000
H	5.052414000	-2.511987000	-0.376710000
H	6.400614000	-1.754680000	0.479098000
H	4.832400000	-1.945472000	1.284580000
H	4.991493000	1.745874000	0.468967000
H	6.362609000	0.755202000	0.981588000
H	4.796895000	0.576602000	1.786969000
H	5.301358000	-0.822640000	-2.286802000
H	5.277472000	0.914780000	-1.944911000
H	6.656907000	-0.072600000	-1.438837000
H	0.603416000	-0.404469000	2.593685000
H	1.859532000	0.851112000	2.771143000
H	0.253061000	1.275313000	2.142838000
H	-3.249389000	-3.689797000	-1.101782000
C	-2.564507000	3.442003000	-0.141653000
H	-2.125312000	3.428316000	-1.154895000
H	-3.603197000	3.738315000	-0.303601000
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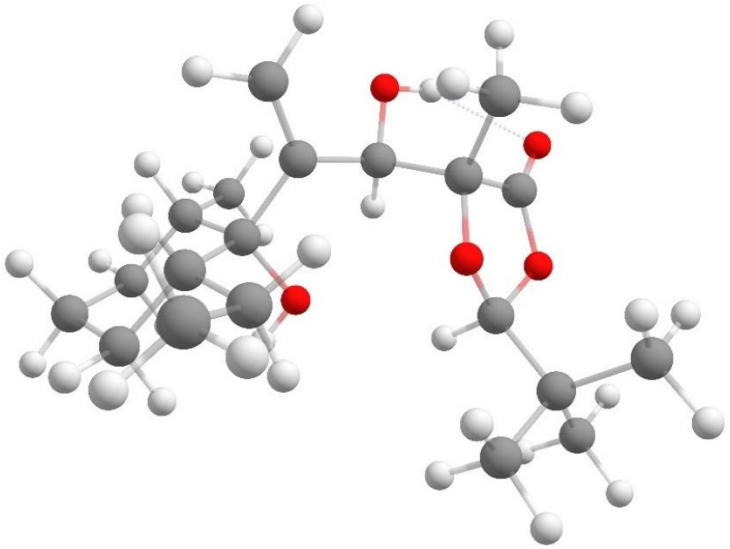
Li	-0.631970000	2.107619000	-0.803772000



19a

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C	-3.105955000	0.978661000	-0.840575000
C	-4.000928000	0.053984000	-1.684327000
C	-4.550821000	-1.121017000	-0.874610000
C	-3.415218000	-1.902716000	-0.210708000
C	-2.622548000	2.173424000	-1.672934000
C	-1.148088000	1.173798000	0.729564000
C	0.126782000	1.789492000	0.169449000
O	-1.023460000	-0.302639000	-1.157273000
C	-1.635114000	1.619576000	1.887629000
C	1.466078000	1.167465000	0.725011000
H	-3.140365000	-0.587072000	1.449464000
H	-3.718841000	1.365645000	-0.017721000
O	0.123308000	3.185754000	0.461837000
O	1.560144000	-0.241495000	0.507562000
C	2.256350000	-0.476916000	-0.696890000
O	3.057193000	0.713220000	-0.924498000
C	2.580811000	1.717267000	-0.166617000
O	2.958639000	2.856772000	-0.244781000
C	-1.405309000	-1.853343000	1.345655000

C	3.141225000	-1.727810000	-0.625207000
C	2.222083000	-2.940421000	-0.389632000
C	4.163038000	-1.606850000	0.516801000
C	3.866077000	-1.878047000	-1.975898000
C	1.716839000	1.459543000	2.198442000
H	-4.818890000	0.646024000	-2.107379000
H	-3.438395000	-0.322837000	-2.551978000
H	-5.145247000	-1.782267000	-1.513459000
H	-5.230335000	-0.740349000	-0.101779000
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H	-2.070771000	2.897597000	-1.071256000
H	-1.975255000	1.844668000	-2.490678000
H	0.127804000	1.630631000	-0.911785000
H	-1.534775000	-0.813251000	-1.791980000
H	-1.131624000	2.407465000	2.431259000
H	-2.563315000	1.251879000	2.308153000
H	1.549684000	-0.545152000	-1.531362000
H	-0.641500000	-1.187058000	1.748167000
H	-0.899709000	-2.456777000	0.585792000
H	1.475220000	-3.032952000	-1.184021000
H	2.814276000	-3.859355000	-0.377524000
H	1.695124000	-2.857015000	0.562208000
H	4.826619000	-0.752266000	0.366309000
H	4.780977000	-2.507679000	0.560505000
H	3.662208000	-1.492274000	1.480011000
H	3.153592000	-1.961714000	-2.802635000
H	4.517266000	-1.024570000	-2.174429000
H	4.478877000	-2.783294000	-1.972408000
H	0.952843000	0.974376000	2.806432000
H	2.694522000	1.073265000	2.491634000
H	1.687806000	2.532601000	2.382052000

H	-3.478892000	2.690454000	-2.115082000
C	-1.919114000	-2.758356000	2.471687000
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H	-2.644711000	-3.496559000	2.119175000
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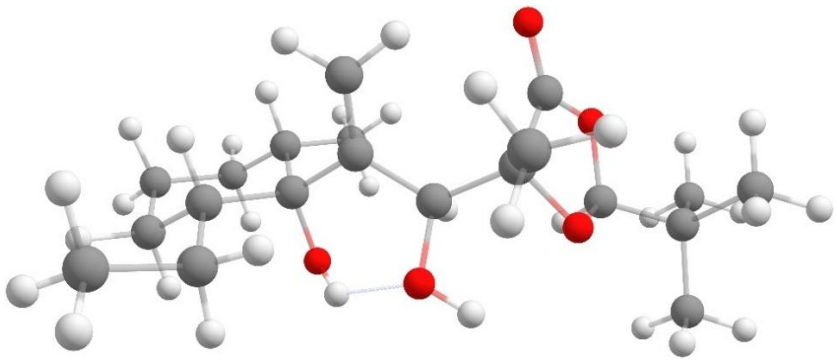
H	0.964790000	3.552168000	0.152996000



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C	3.915150000	-2.376730000	-0.282070000
C	5.124393000	-1.445283000	-0.194043000
C	4.782726000	-0.059850000	-0.745949000
C	1.506304000	-2.775544000	0.355462000
C	1.124744000	0.205281000	0.667276000
C	-0.168054000	0.371277000	-0.112053000
O	1.975238000	-0.600839000	-1.507081000
C	1.233807000	0.445865000	1.973346000
C	-1.477332000	0.863427000	0.582254000
H	3.801072000	0.682501000	1.016142000
H	2.941240000	-1.647385000	1.482753000
O	0.082009000	1.284764000	-1.200130000
O	-2.491329000	0.818973000	-0.455123000

C	-3.163413000	-0.426666000	-0.367871000
O	-3.027839000	-0.840687000	1.002293000
C	-2.044587000	-0.127865000	1.608185000
O	-1.747666000	-0.270387000	2.756745000
C	3.272224000	1.981007000	-0.610053000
C	-4.636354000	-0.311827000	-0.780638000
C	-4.676329000	0.153402000	-2.248389000
C	-5.372567000	0.694862000	0.118065000
C	-5.275731000	-1.707220000	-0.655379000
C	-1.427904000	2.289743000	1.113766000
H	4.150130000	-3.350228000	0.162472000
H	3.665308000	-2.558188000	-1.332647000
H	5.972175000	-1.870407000	-0.741684000
H	5.443755000	-1.355795000	0.853031000
H	5.646582000	0.603490000	-0.646293000
H	4.564374000	-0.140996000	-1.816455000
H	0.654605000	-2.440150000	0.952029000
H	1.180988000	-2.907465000	-0.678835000
H	-0.395258000	-0.612056000	-0.545470000
H	1.535937000	0.197645000	-1.830655000
H	0.408052000	0.768285000	2.588915000
H	2.167080000	0.266993000	2.494839000
H	-2.656673000	-1.182320000	-0.983718000
H	2.295970000	2.319687000	-0.256439000
H	3.196760000	1.922082000	-1.702111000
H	-4.142123000	-0.542558000	-2.903251000
H	-5.711609000	0.204700000	-2.594660000
H	-4.229664000	1.143094000	-2.362579000
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H	-6.418000000	0.772991000	-0.191352000
H	-4.923314000	1.687313000	0.047270000
H	-4.765826000	-2.438819000	-1.290083000

H	-5.240683000	-2.067816000	0.374443000
H	-6.321902000	-1.667652000	-0.969173000
H	-1.072621000	2.957007000	0.329078000
H	-2.426417000	2.600884000	1.424026000
H	-0.755968000	2.368932000	1.965811000
H	1.808885000	-3.752844000	0.742084000
C	4.319613000	3.035255000	-0.231988000
H	4.407260000	3.129751000	0.855263000
H	5.311282000	2.798107000	-0.625297000
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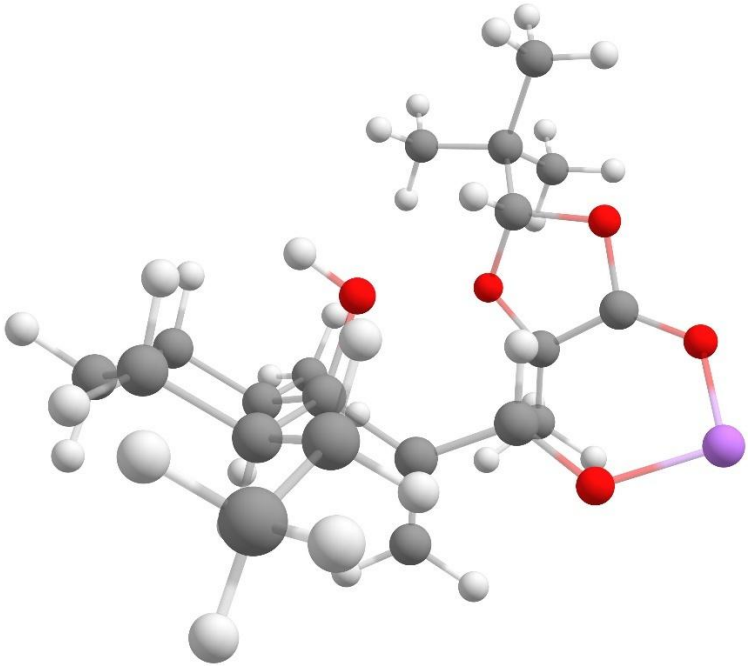
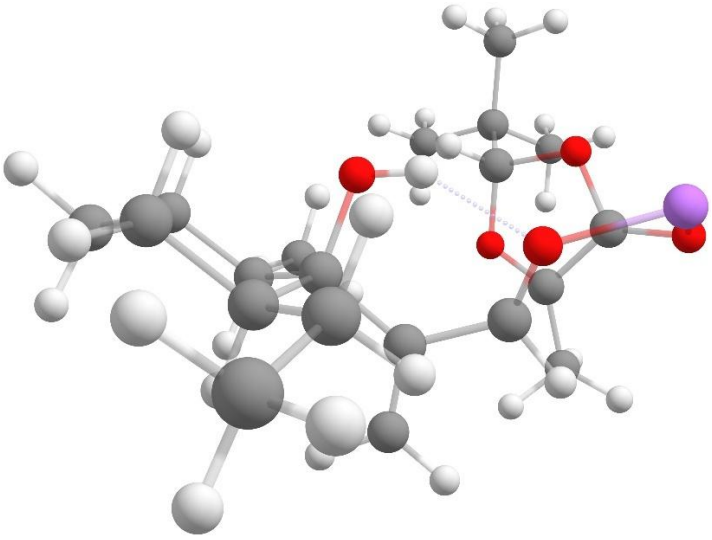


TS-III

C	-2.046290000	-1.303976000	1.403985000
C	-1.900306000	-0.253119000	0.254601000
C	-3.298169000	-0.034969000	-0.440522000
C	-3.896428000	-1.370995000	-0.922929000
C	-3.999819000	-2.412489000	0.193523000
C	-2.650312000	-2.620584000	0.880827000

C	-3.247937000	1.007665000	-1.575171000
C	-1.378546000	1.100803000	0.757604000
C	-0.454894000	1.882399000	-0.097095000
O	-0.947012000	-0.724294000	-0.717812000
C	-1.848288000	1.678873000	1.875078000
C	1.768867000	1.077959000	0.897675000
H	-2.771855000	-0.890497000	2.115097000
H	-3.957407000	0.358856000	0.344519000
O	-0.332807000	3.135244000	0.045473000
O	2.062404000	-0.297126000	0.795893000
C	2.442349000	-0.510495000	-0.554306000
O	2.869223000	0.772683000	-1.051690000
C	2.397054000	1.720889000	-0.175217000
O	2.541124000	2.936239000	-0.449406000
C	-4.613929000	1.366982000	-2.173574000
C	-0.735809000	-1.573532000	2.149754000
C	3.552827000	-1.563008000	-0.681526000
C	3.012262000	-2.890790000	-0.120567000
C	4.799692000	-1.124104000	0.102872000
C	3.891905000	-1.724440000	-2.174418000
C	1.625257000	1.618192000	2.272815000
H	-4.885242000	-1.191932000	-1.351754000
H	-3.289902000	-1.770477000	-1.749827000
H	-4.378654000	-3.359431000	-0.204891000
H	-4.732777000	-2.071453000	0.935532000
H	-2.753843000	-3.316936000	1.718800000
H	-1.945190000	-3.101156000	0.187717000
H	-2.797219000	1.926137000	-1.192376000
H	-2.582507000	0.644596000	-2.365668000
H	-0.152440000	1.406110000	-1.029833000
H	-1.303889000	-1.520674000	-1.121566000
H	-1.530513000	2.682085000	2.128417000

H	-2.558132000	1.196701000	2.535062000
H	1.552996000	-0.802879000	-1.128673000
H	-4.512319000	2.187647000	-2.888919000
H	-5.073769000	0.530768000	-2.705792000
H	-5.313053000	1.693484000	-1.396639000
H	-0.881523000	-2.369967000	2.885910000
H	-0.380715000	-0.689473000	2.678330000
H	0.053669000	-1.875340000	1.461063000
H	2.113780000	-3.211987000	-0.657392000
H	3.763815000	-3.678176000	-0.226580000
H	2.759979000	-2.796293000	0.937370000
H	5.194964000	-0.182848000	-0.284931000
H	5.583250000	-1.882806000	0.020002000
H	4.565155000	-0.988186000	1.160560000
H	3.012689000	-2.031036000	-2.750408000
H	4.263782000	-0.788680000	-2.596473000
H	4.660752000	-2.490977000	-2.306180000
H	2.398639000	1.201893000	2.929753000
H	1.744385000	2.703003000	2.257790000
H	0.649248000	1.393287000	2.720412000
Li	1.141154000	4.025700000	-0.426184000



TS-IV

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C	4.031352000	1.119419000	-0.906640000
C	3.980784000	2.448026000	-0.151503000
C	2.542078000	2.802377000	0.218057000
C	3.541676000	-1.374851000	-0.849734000
C	1.224646000	-0.820176000	1.004937000
C	0.392166000	-1.839249000	0.321944000
O	1.128010000	0.578968000	-1.003075000
C	1.514847000	-1.039963000	2.298733000
C	-1.848785000	-1.300450000	0.967499000
H	2.416865000	1.508375000	1.916712000
H	3.863307000	-0.113828000	0.849442000
O	0.444322000	-2.011131000	-0.953641000
O	-2.199261000	0.061794000	0.975978000
C	-2.389585000	0.440028000	-0.381549000
O	-2.580055000	-0.798325000	-1.105563000
C	-2.259316000	-1.830628000	-0.268603000
O	-2.222433000	-2.992435000	-0.727263000
C	5.000028000	-1.835208000	-0.976288000

C	0.431183000	2.136946000	1.398503000
C	-3.593600000	1.377883000	-0.557353000
C	-3.325375000	2.659471000	0.252470000
C	-4.879542000	0.698847000	-0.058623000
C	-3.717383000	1.722268000	-2.053020000
C	-1.951955000	-1.970166000	2.291356000
H	5.070759000	0.859346000	-1.123477000
H	3.519418000	1.225106000	-1.869502000
H	4.425912000	3.245094000	-0.756742000
H	4.588427000	2.373293000	0.760467000
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H	1.967850000	3.001905000	-0.692629000
H	2.990070000	-2.149547000	-0.313951000
H	3.089415000	-1.314382000	-1.845369000
H	0.167584000	-2.710310000	0.946074000
H	0.895576000	-0.294005000	-1.364206000
H	1.138091000	-1.914887000	2.815982000
H	2.144810000	-0.375704000	2.876384000
H	-1.466324000	0.891315000	-0.764067000
H	5.048789000	-2.839844000	-1.406501000
H	5.593935000	-1.180362000	-1.617833000
H	5.488553000	-1.873322000	0.003129000
H	0.495789000	3.013501000	2.050605000
H	-0.135882000	1.365826000	1.918255000
H	-0.134810000	2.424579000	0.511066000
H	-2.420275000	3.167519000	-0.092134000
H	-4.162316000	3.353925000	0.138094000
H	-3.206121000	2.436882000	1.314484000
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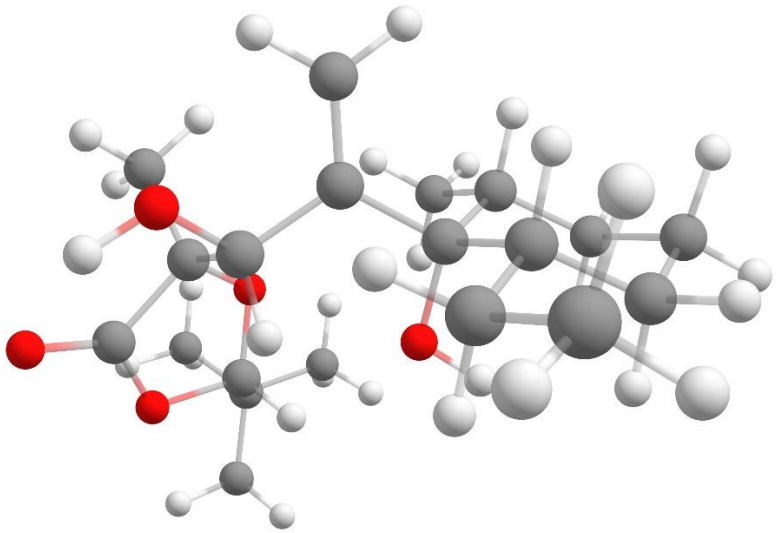
H	-4.797590000	0.436804000	0.998314000
H	-2.804165000	2.194403000	-2.428489000

H	-3.908509000	0.828068000	-2.650020000
H	-4.543402000	2.421306000	-2.210221000
H	-2.920821000	-1.760104000	2.759268000
H	-1.855470000	-3.050999000	2.173787000
H	-1.173316000	-1.617339000	2.976386000
Li	-0.720922000	-3.158130000	-1.716624000



19b

C	-2.001386000	-1.498191000	1.219718000
C	-1.778085000	-0.305658000	0.238790000
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C	-3.907567000	-1.005085000	-1.009546000
C	-4.106437000	-2.174128000	-0.042610000
C	-2.770962000	-2.641036000	0.536068000
C	-2.976327000	1.350619000	-1.336433000
C	-1.112220000	0.889991000	0.935513000
C	-0.011259000	1.633269000	0.200553000
O	-0.899084000	-0.724061000	-0.826714000
C	-1.563349000	1.361412000	2.097457000
C	1.439778000	1.245767000	0.671959000
H	-2.635874000	-1.124199000	2.030614000

H	-3.740407000	0.516697000	0.491154000
O	-0.197774000	3.039111000	0.385105000
O	1.690100000	-0.154002000	0.569336000
C	2.281542000	-0.426229000	-0.680818000
O	2.882467000	0.833146000	-1.110966000
C	2.387184000	1.832567000	-0.370054000
O	2.632152000	2.997526000	-0.565450000
C	-4.293000000	1.953488000	-1.836929000
C	-0.690805000	-2.015717000	1.815061000
C	3.345288000	-1.522316000	-0.585866000
C	2.651083000	-2.810610000	-0.114298000
C	4.441710000	-1.116331000	0.409453000
C	3.941971000	-1.733451000	-1.987260000
C	1.775838000	1.707770000	2.079279000
H	-4.877457000	-0.655090000	-1.370666000
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H	-2.151052000	-3.072582000	-0.261685000
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H	-1.387355000	-1.328130000	-1.395605000
H	-1.149010000	2.263903000	2.527556000
H	-2.374789000	0.888585000	2.638029000
H	1.512017000	-0.673193000	-1.418324000
H	-4.101106000	2.855717000	-2.425588000
H	-4.854743000	1.264196000	-2.472679000
H	-4.938839000	2.237081000	-0.998710000
H	-0.889359000	-2.843137000	2.503705000
H	-0.153689000	-1.237589000	2.358278000

H	-0.032209000	-2.372234000	1.023097000
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H	3.370751000	-3.633777000	-0.097718000
H	2.242350000	-2.691850000	0.890590000
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H	2.820600000	1.481787000	2.300788000
H	1.613517000	2.780437000	2.177349000
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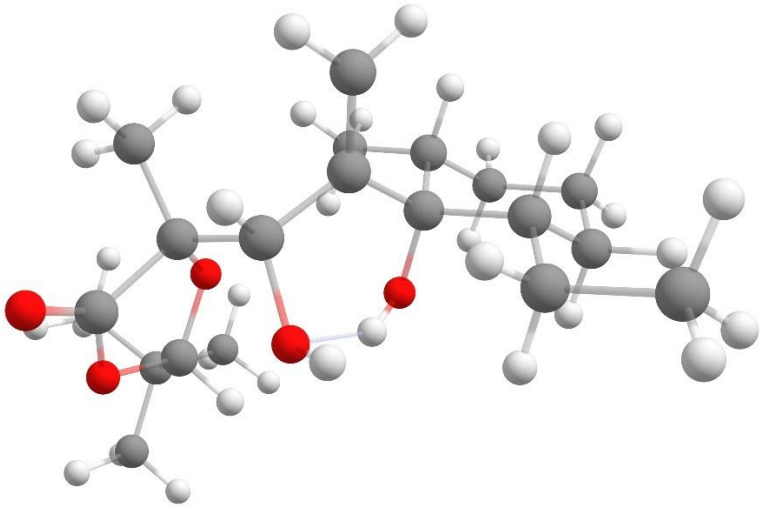

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C	4.230131000	2.101629000	-0.035437000
C	2.911686000	2.546977000	0.595626000

C	3.140498000	-1.422737000	-1.342072000
C	1.209187000	-0.978834000	0.933666000
C	-0.054764000	-1.627918000	0.362518000
O	1.097436000	0.807362000	-0.779368000
C	1.744649000	-1.554225000	2.013760000
C	-1.432513000	-1.087294000	0.841260000
H	2.820102000	0.977631000	2.049030000
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O	-0.105359000	-1.589844000	-1.080951000
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C	-2.530495000	0.220609000	-0.727807000
O	-3.177127000	-1.069423000	-0.718779000
C	-2.513653000	-1.902779000	0.108078000
O	-2.764888000	-3.064434000	0.245021000
C	4.469614000	-2.012173000	-1.831657000
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C	-3.557518000	1.360010000	-0.722288000
C	-2.781261000	2.690120000	-0.721304000
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C	-4.398447000	1.246531000	-2.007747000
C	-1.618906000	-1.206026000	2.350362000
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H	3.409082000	1.294351000	-1.861661000
H	4.708751000	2.941781000	-0.549541000
H	4.925249000	1.783141000	0.753161000
H	3.093359000	3.327333000	1.342569000
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H	2.587643000	-2.227833000	-0.845506000
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H	1.308370000	-2.441799000	2.459799000

H	2.632056000	-1.166412000	2.499013000
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H	4.295427000	-2.907583000	-2.434927000
H	5.032015000	-1.309609000	-2.449748000
H	5.106482000	-2.300385000	-0.989339000
H	1.103741000	2.763958000	2.561177000
H	0.419184000	1.139574000	2.570674000
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H	-2.100147000	2.755864000	-1.575052000
H	-3.480249000	3.528487000	-0.783728000
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H	-5.122163000	2.064477000	-2.054240000
H	-1.553895000	-2.252346000	2.654556000
H	-0.860286000	-0.631967000	2.880668000
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H	0.480823000	-2.269029000	-1.428795000