Supporting Information

Total Synthesis and Absolute Stereochemistry of Pentenocin B, a Novel Interleukin-1 β Converting Enzyme Inhibitor

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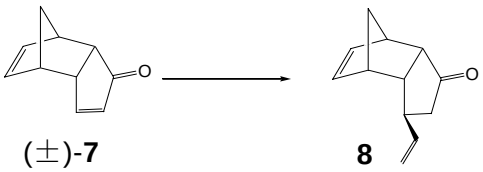
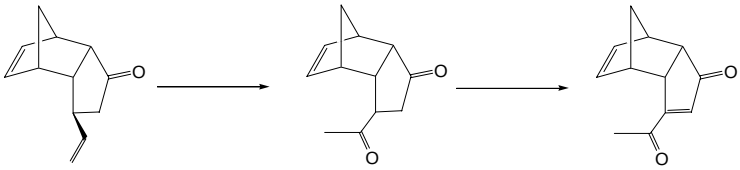
General Procedures. NMR spectra were recorded on a 400 MHz or 600 MHz spectrometer. Chemical shifts were reported in the δ scale relative to tetramethylsilane (TMS) as 0.00 ppm for ^{1}H ($CDCl_3$) and residual $CHCl_3$ (7.26 ppm for ^{1}H and 77.0 ppm for ^{13}C), DMS O (2.49 ppm for ^{1}H and 39.5 ppm for ^{13}C) as internal reference. Mass spectra (MS) were recorded by electron ionization or fast atom bombardment. Melting points were uncorrected. Column chromatography was carried out with silica gel 60 particle size 0.063-0.210 mm. All reactions were stirred magnetically, under an argon atmosphere, unless otherwise noted, and monitored with analytical TLC.

<u>Synthesis of (±)-3</u> : Transformations from (±)–7 to (±)–3 shown in Scheme 1



(±)-**7** **8**

To a stirred suspension of dry copper(I) iodide (13.4 g, 70.6 mmol) in THF (205 mL) was added vinylmagnesium bromide (1.0 M in THF, 118 mL, 118 mmol) dropwise over a 30 min period at –78 ℃. Then, (±)-ketodicyclopentadiene (KDP) (**7**) (5.72 g, 39.2 mmol) in THF (25 mL) was added dropwise over a 10 min period to the solution at –35 ℃. The mixture was stirred at –35 ℃ for 30 min, and saturated aqueous NH_4Cl solution was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 10 min and filtered through Celite®. The filtrate was extracted with ether, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 20) to give **8** (6.2 g, 35.7 mmol, 91%) as a colorless oil. **8** : IR (neat): 1730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 5.88 (ddd, 1H, *J* = 16.6, 10.5, 7.3 Hz), 4.98 (ddd, 1H, *J* = 7.1, 1.2, 1.0 Hz), 4.94 (d, 1H, *J* = 1.2 Hz), 3.19-3.17 (m, 1H), 3.09-3.07 (m, 1H), 2.96 (ddd 1H, *J* = 9.5, 4.6, 1.5 Hz), 2.79 (ddd, 1H, *J* = 9.8, 4.6, 4.4 Hz), 2.40-2.33 (m, 1H), 2.26 (dd, 1H, *J* = 18.3, 8.7 Hz), 2.18 (ddd, 1H, *J* = 18.1, 8.1, 1.7 Hz), 1.59 (d, 1H, *J* = 8.3 Hz), 1.44 (d, 1H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 219.1, 142.2, 136.3, 135.0, 112.8, 54.4, 52.4, 48.5, 47.3, 46.3, 45.9, 40.7; MS (EI) *m/z* 174 (M^{+}), 66 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{14}O$ 174.1044, found 174.1063.



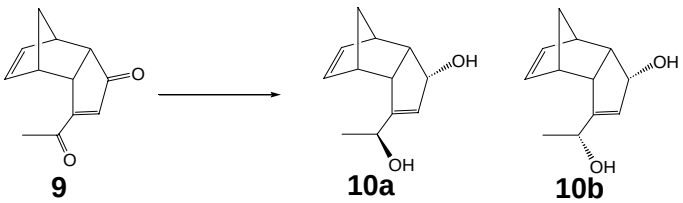
8 **9**

A mixture of copper(I) chloride (137 mg, 1.38 mmol), palladium(II) chloride (40 mg, 0.23 mmol) in DMF (4 mL) and H_2O (0.4 mL) was stirred under oxygen atmosphere at room temperature for 30 min. To the solution was added **8** (200 mg, 1.15 mmol) in DMF (1.5 mL). The reaction mixture was stirred at 45 ℃ for 18 hr and filtered through Celite®. The filtrate was extracted with ether, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 8) to give the diketone (211 mg, 1.11 mmol, 97%) as a colorless oil.

The diketone : IR (neat): 1730, 1712 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.23 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.20 (dd, 1H, *J* = 5.4, 2.8 Hz), 3.22-3.20 (m, 1H), 3.19-3.17 (m, 1H), 3.03 (ddd, 1H, *J* = 9.5, 5.1, 4.2 Hz), 2.96 (ddd, 1H, *J* = 9.5, 4.4, 1.2 Hz), 2.73 (ddd, 1H, *J* = 9.5, 6.8, 4.4 Hz), 2.63 (ddd, 1H, *J* = 18.8, 7.1, 1.8 Hz), 2.26 (s, 3H), 2.12 (dd, 1H, *J* = 18.8, 9.5 Hz), 1.64 (d, 1H, *J* = 8.5 Hz), 1.50 (d, 1H, *J* = 8.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 217.7, 207.7, 136.9, 134.0, 54.1, 52.1, 49.4, 46.9, 46.0, 44.3, 42.3, 28.5; MS (EI) *m/z* 190 (M^+), 66 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{14}O_2$ 190.0993, found 190.1014; Anal. Calcd for $C_{12}H_{14}O_2$ C, 75.76; H, 7.42. Found: C, 75.82; H, 7.44.

A mixture of the diketone (385 mg, 2.03 mmol), anhydrous *p*-toluenesulfonic acid (404 mg, 2.35 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (460 mg, 2.03 mmol) in dioxane (15 mL) was heated at reflux for 20 hr. To the reaction mixture was added H_2O and filtered through Celite®. The filtrate was extracted with EtOAc, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 10) to give **9** (278 mg, 1.48 mmol, 73%) as a colorless crystal.

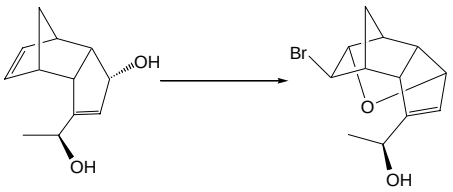
9 : mp 95-96 ℃ (recrystallized from hexane); IR (Nujol): 1698, 1672 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 5.97 (dd, 1H, *J* = 5.4, 2.9 Hz), 5.71 (dd, 1H, *J* = 5.1, 2.9 Hz), 3.59 (dd, 1H, *J* = 4.6, 4.6 Hz), 3.24 (brs, 1H), 3.21 (brs, 1H), 2.95 (dd, 1H, *J* = 5.1, 5.1 Hz), 2.40 (s, 3H), 1.76 (d, 1H, *J* = 8.5 Hz), 1.63 (d, 1H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 209.7, 196.6, 168.0, 138.4, 132.5, 132.2, 52.0, 51.3, 45.4, 44.5, 44.0, 27.3; MS (EI) *m/z* 188 (M^+), 66 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{12}O_2$ 188.0837, found 188.0846; Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.58; H, 6.56.



To a stirred solution of **9** (584 mg, 3.11 mmol) in THF (24 mL) was added a solution of diisobutylaluminum hydride (DIBALH) (1.5 M in toluene, 8.3 mL, 12.4 mmol) dropwise at –78 ℃. The reaction mixture was stirred for 15 min, and then quenched by addition of saturated aqueous NH_4Cl solution. The mixture was stirred at room temperature for 20 min, poured into saturated aqueous potassium sodium tartrate (Rochelle salt) solution, and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 1) to give **10a** (496 mg, 2.58 mmol, 83%) and as a colorless crystal and **10b** (83 mg, 0.43 mmol, 14%) as a colorless crystal.

10a : mp 145-146 ℃ (recrystallized from $CHCl_3$); IR (Nujol): 3270 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.6, 2.9 Hz), 5.85 (dd, 1H, *J* = 5.6, 3.2 Hz), 5.48 (s, 1H), 4.67 (d, 1H, *J* = 8.5 Hz), 4.19 (q, 1H, *J* = 6.6 Hz), 3.21 (dd, 1H, *J* = 8.1, 4.1 Hz), 3.02 (ddd, 1H, *J* = 8.5, 8.3, 4.1 Hz), 2.95-2.93 (m, 2H), 1.59 (d, 1H, *J* = 8.1 Hz), 1.42 (d, 1H, *J* = 8.5 Hz), 1.31 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 134.3, 133.5, 127.8, 75.1, 66.7, 53.2, 52.3, 47.7, 46.6, 44.3, 22.5; MS (EI) *m/z* 192 (M^+), 174 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{16}O_2$ 192.1149, found: 192.1113; Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.27.

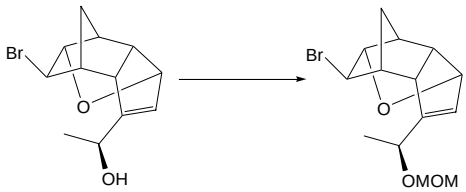
10b : mp 150-151 ℃ (recrystallized from $CHCl_3$); IR (Nujol): 3296 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.4, 2.7 Hz), 5.84 (dd, 1H, *J* = 5.6, 3.2 Hz), 5.46 (s, 1H), 4.65 (dd, 1H, *J* = 9.3, 8.8 Hz), 4.24 (qd, 1H, *J* = 6.6, 5.4 Hz), 3.36 (dd, 1H, *J* = 7.8, 4.1 Hz), 3.04-2.99 (m, 2H), 2.93 (brs, 1H), 1.60 (d, 1H, *J* = 8.3 Hz), 1.45 (d, 1H, *J* = 8.3 Hz), 1.32 (d, 3H, *J* = 6.3 Hz), 1.23 (d, 1H, *J* = 9.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 134.3, 133.5, 127.8, 75.1, 66.7, 53.2, 52.3, 47.7, 46.6, 44.3, 22.5; MS (EI) *m/z* 174 (M^+-H_2O), 156 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{14}O$ 174.1044, found 174.1048.; Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.32.



10a **22a**

To a stirred solution of **10a** (223 mg, 1.16 mmol) in THF (5 mL) was added *N*-bromosuccinimide (248 mg, 1.39 mmol) at –15 ℃. The reaction mixture was stirred at –15 ℃ under dark for 15 min, quenched by addition of saturated aqueous $Na_2S_2O_3$ solution and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **22a** (240 mg, 0.89 mmol, 76%) as a colorless oil.

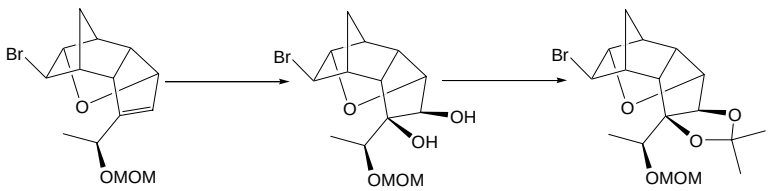
22a : IR (neat): 3390 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.68 (dd, 1H, *J* = 5.6, 2.4 Hz), 4.62 (d, 1H, *J* = 4.9 Hz), 4.36 (q, 1H, *J* = 6.6 Hz), 3.97 (d, 1H, *J* = 2.2 Hz), 3.13 (ddd, 1H, *J* = 8.8, 5.4, 5.3 Hz), 3.03 (dd, 1H, *J* = 8.8, 3.9 Hz), 2.72-2.69 (m, 1H), 2.50 (s, 1H), 2.40 (d, 1H, *J* = 11.0 Hz), 1.96 (d, 1H, *J* = 11.0 Hz), 1.33 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.4, 127.9, 91.0, 84.9, 66.7, 55.0, 51.8, 50.3, 47.9, 47.2, 40.2, 22.0; MS (EI) *m/z* 191 (M^+-Br), 43 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}O_2$ 191.1071, found 191.1052.



22a **11a**

To a stirred solution of **22a** (130 mg, 0.48 mmol) and ^{i}Pr$_2$NEt (0.50 mL, 2.88 mmol) in CH_2Cl_2 (1.6 mL) was added MOMCl (0.11 mL, 1.44 mmol) at 0 ℃. The reaction mixture was stirred at room temperature for 10 hr, and then poured into water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give **11a** (126 mg, 0.40 mmol, 83%) as a colorless oil.

11a : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.85 (d, 1H, *J* = 2.2 Hz), 4.66 (dd, 1H, *J* = 5.9, 2.4 Hz), 4.62 (d, 1H, *J* = 4.9 Hz), 4.59 (s, 2H), 4.29 (q, 1H, *J* = 6.6 Hz), 3.96 (d, 1H, *J* = 2.2 Hz), 3.37 (s, 3H), 3.12 (ddd, 1H, *J* = 8.8, 5.6, 5.4 Hz), 3.01 (dd, 1H, *J* = 8.8, 3.9 Hz), 2.69 (ddd, 1H, *J* = 5.1, 5.1, 1.2 Hz), 2.50-2.49 (m, 1H), 2.44 (d, 1H, *J* = 10.7 Hz), 1.95 (dd, 1H, *J* = 10.7, 1.5 Hz), 1.29 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 130.3, 94.2, 91.0, 84.7, 70.5, 55.4, 55.0, 51.3, 50.3, 48.2, 47.1, 40.2, 19.6; MS (EI) *m/z* 314 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{19}BrO_3$ 314.0517, found 314.0529; Anal. Calcd for $C_{14}H_{19}BrO_3$: C, 53.35; H, 6.08; Br, 25.35. Found: C, 53.43; H, 6.12; Br, 25.42.



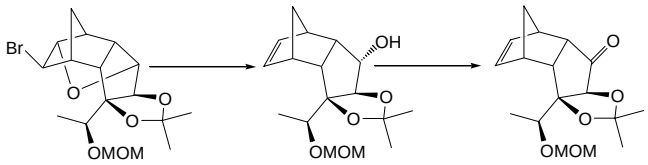
11a **12a**

To a stirred solution of **11a** (424 mg, 1.35 mmol) and 4-methylmolpholine *N*-oxide (237 mg, 2.02 mmol) in THF (7.5 mL) and H_2O (2.5 mL) was added OsO_4 (0.197M in THF, 1.37 mL, 0.269 mmol) at room temperature. The mixture was stirred at room temperature for 4 days, and quenched by addition of saturated aqueous $Na_2S_2O_3$ solution, and extracted with $CHCl_3$. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 1) to give the diol (376 mg, 1.08 mmol, 80%) as a colorless oil.

The diol : IR (neat): 3450 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.73 (d, 1H, *J* = 6.3 Hz), 4.63 (d, 1H, *J* = 6.3 Hz), 4.62 (d, 1H, *J* = 4.4 Hz), 4.33 (d, 1H, *J* = 6.6 Hz), 4.22 (d, 1H, *J* = 3.4 Hz), 3.81(d, 1H, *J* = 2.0 Hz), 3.68 (q, 1H, *J* = 6.3 Hz), 3.40 (s, 3H), 3.37 (s, 1H), 3.15-3.10 (m, 1H), 2.75 (brs, 2H), 2.51 (dd, 1H, *J* = 9.5, 3.9 Hz), 2.34 (s, 1H), 2.30 (d, 1H, *J* = 11.0 Hz), 1.70 (d, 1H, *J* = 10.5 Hz), 1.30 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 95.0, 90.4, 89.4, 86.9, 81.7, 78.1, 56.7, 55.8, 54.7, 48.1, 46.2, 44.7, 37.8, 14.8; MS (EI) *m/z* 207 (M^+-MOM-OH-Br), 45 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}O_3$ 207.1020, found 207.0993.

A mixture of the diol (376 mg, 1.08 mmol), anhydrous *p*-toluenesulfonic acid (19 mg, 0.108 mmol) and 2,2-dimethoxypropane (0.20 mL) in CH_2Cl_2 (5 mL) was stirred at room temperature for 15 hr. To the reaction mixture was added saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **12a** (386 mg, 0.99 mmol, 92%) as a colorless crystal.

12a : mp 93 ℃ (recrystallized from hexane); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.76 (d, 1H, *J* = 6.8 Hz), 4.62 (d, 1H, *J* = 6.8 Hz), 4.57 (s, 1H), 4.56 (d, 1H, *J* = 6.1 Hz), 4.36 (d, 1H, *J* = 5.9 Hz), 3.68 (q, 1H, *J* = 6.3 Hz), 3.61 (d, 1H, *J* = 2.2 Hz), 3.35 (s, 3H), 3.16 (ddd, 1H, *J* = 9.3, 5.9, 5.4 Hz), 2.87-2.78 (m, 1H), 2.64 (dd, 1H, *J* = 9.5, 4.0 Hz), 2.32 (d, 1H, *J* = 3.2 Hz), 2.28 (d, 1H, *J* = 10.7 Hz), 1.71 (d, 1H, *J* = 11.7 Hz), 1.46 (s, 3H), 1.37 (s, 3H), 1.29 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 111.1, 95.4, 95.1, 92.2, 90.6, 89.2, 75.0, 56.3, 55.7, 55.0, 48.4, 47.8, 45.1, 37.6, 29.1, 27.2, 15.9; MS (EI) *m/z* 373 (M^+-Me), 299 (100%); HRMS (EI) *m/z* calcd for $C_{16}H_{22}BrO_5$ 373.0650, found 373.0626; Anal. Calcd for $C_{17}H_{25}BrO_5$: C, 52.45; H, 6.47; Br, 20.53. Found: C, 52.25; H, 6.47; Br, 20.81.



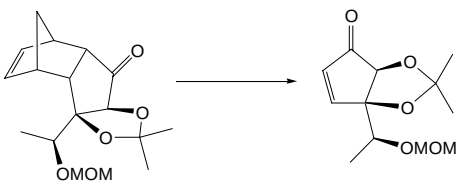
12a **13a**

A mixture of **12a** (100 mg, 0.26 mmol) and activated Zn (230 mg, 3.52 mmol) in MeOH (1.2 mL) and AcOH (0.12 mL) was stirred at 80 ℃ for 3.5 hr, and then filtered through Celite®. The filtrate was poured into saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the alcohol (80 mg, 0.258 mmol, 100%) as a colorless crystal.

The alcohol : mp 71-72 ℃ (recrystallized from hexane); IR (Nujol): 3368 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, 1H, *J* = 5.6, 2.9 Hz), 6.07 (dd, 1H, *J* = 5.4, 2.0 Hz), 4.69 (d, 1H, *J* = 7.1 Hz), 4.56 (d, 1H, *J* = 7.1 Hz), 4.44 (dd, 1H, *J* = 9.8, 4.4 Hz), 4.09 (d, 1H, *J* = 4.4 Hz), 3.80 (q, 1H, *J* = 6.1 Hz), 3.37 (s, 3H), 3.18 (ddd, 1H, *J* = 9.8, 9.3, 4.4 Hz), 2.91 (s, 1H), 2.84-2.81 (m, 2H), 2.29 (brs, 1H), 1.49-1.48 (m, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.30-1.29 (m, 1H), 1.30 (d, 3H, *J* = 6.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.0, 132.6, 110.2, 95.0, 93.1, 93.0, 79.7, 74.4, 55.7, 55.5, 51.2, 49.8, 45.1, 44.4, 30.1, 27.6, 15.4; MS (EI) *m/z* 295 (M^+-Me), 45 (100%); HRMS (EI) *m/z* calcd for $C_{16}H_{23}O_5$ 295.1544, found 295.1534.

To a stirred solution of the alcohol (269 mg, 0.868 mmol) in CH_2Cl_2 (4 mL) was added pyridinium dichromate (490 mg, 1.30 mmol). The reaction mixture was stirred at room temperature for 10 hr, filtered through Celite®, and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **13a** (198 mg, 0.64 mmol, 74%) as a colorless crystal.

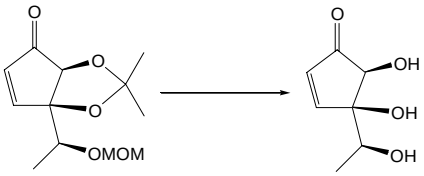
13a : mp 79-80 ℃ (recrystallized from hexane); IR (Nujol): 1748 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.6, 2.9 Hz), 6.15 (dd, 1H, *J* = 5.6, 2.4 Hz), 4.72 (d, 1H, *J* = 7.1 Hz), 4.55 (d, 1H, *J* = 6.8 Hz), 3.85 (s, 1H), 3.75 (q, 1H, *J* = 6.3 Hz), 3.37 (s, 3H), 3.24 (brs, 1H), 3.20-3.17 (m, 1H), 3.04 (brs, 1H), 2.97 (dd, 1H, *J* = 8.5, 3.7 Hz), 1.62 (d, 1H, *J* = 8.3 Hz), 1.49 (d, 1H, *J* = 8.3 Hz), 1.47 (s, 3H), 1.37 (d, 3H, *J* = 6.3 Hz), 1.25 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 219.0, 138.4, 133.9, 111.1, 95.0, 90.2, 83.8, 74.8, 55.7, 53.2, 52.0, 48.9, 46.1, 45.0, 29.1, 26.6, 15.0 ; MS (EI) *m/z* 308 (M^+), 153 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{24}O_5$ 308.1622, found 308.1646; Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.07; H, 7.70.



13a **14a**

A mixture of **13a** (70 mg, 0.227 mmol) in Ph_2O (1 mL) was heated at reflux for 15 min. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give **14a** (51 mg, 0.211 mmol, 93%) as a colorless oil.

14a : IR (neat): 1728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H, *J* = 5.9 Hz), 6.27 (d, 1H, *J* = 6.1 Hz), 4.71 (d, 1H, *J* = 6.8 Hz), 4.63 (d, 1H, *J* = 7.1 Hz), 4.28 (s, 1H), 4.05 (q, 1H, *J* = 6.3 Hz), 3.35 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 1.23 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0, 161.8, 134.1, 115.6, 95.3, 90.9, 78.4, 73.9, 55.7, 28.3, 28.2, 15.8; MS (EI) *m/z* 227 (M^+-Me), 45 (100%); HRMS (EI) *m/z* calcd for $C_{11}H_{15}O_5$ 227.0919, found 227.0917.



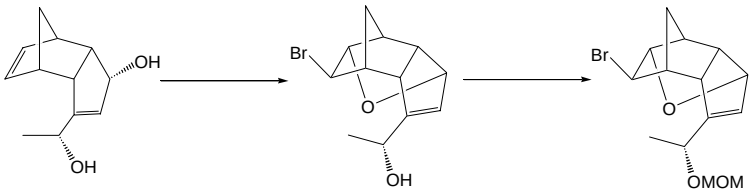
14a (±)-**3**

A mixture of **14a** (40 mg, 0.165 mmol), trifluoroacetic acid (0.3 mL) and H_2O (0.03 mL) was stirred at 0 ℃ for 2 hr. The mixture was concentrated in vacuo and purified by silica gel column chromatography (EtOAc-MeOH = 9 : 1) to give (±)-**3** (7.8 mg, 0.049 mmol, 30%) as a colorless resin.

(±)-**3** : IR (neat): 3386, 1678 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.48 (d, 1H, *J* = 6.1 Hz), 6.15 (d, 1H, *J* = 6.1 Hz), 5.32 (d, 1H, *J* = 7.3 Hz), 4.90 (s, 1H), 4.83 (d, 1H, *J* = 5.1 Hz), 3.91 (d, 1H, *J* = 7.3 Hz), 3.69 (qd, 1H, *J* = 6.3, 5.6 Hz), 1.12 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 208.1, 165.3, 131.6, 78.8, 70.7, 69.2, 18.0; MS (FAB) *m/z* 159 (MH^+), 191 ($M+Na^+$).

<u>Synthesis of (±)-4</u> : Transformations from 10b to (±)-4 shown in Scheme 1

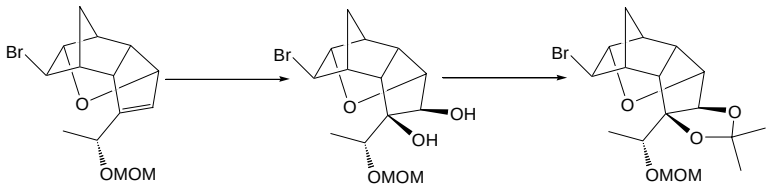
All the reactions were conducted as described above as those for **10a** to (±)-**3**.



10b **11b**

The minor bromoether : 98% yield; mp 81-82 ℃ (recrystallized from CH_2Cl_2-hexane); IR (Nujor): 3418 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.82 (s, 1H), 4.67 (dd, 1H, *J* = 5.6, 2.4 Hz), 4.62 (d, 1H, *J* = 4.6 Hz), 4.35 (q, 1H, *J* = 6.3 Hz), 3.97 (d, 1H, *J* = 1.7 Hz), 3.13-3.07 (m, 2H), 2.70 (dd, 1H, *J* = 4.9, 4.6 Hz), 2.52 (s, 1H), 2.44 (d, 1H, *J* = 10.7 Hz), 2.04 (s, 1H), 1.96 (d, 1H, *J* = 10.7 Hz), 1.34 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 150.9, 128.2, 91.0, 84.8, 66.3, 55.1, 51.5, 50.3, 48.0, 47.3, 40.1, 22.0; MS (EI) *m/z* 270 (M^+), 191 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}O_2$ 191.1071, found 191.1045; Anal. Calcd for $C_{12}H_{15}BrO_2$: C, 53.15; H, 5.58; Br, 29.47. Found: C, 53.05; H, 5.49; Br, 29.26.

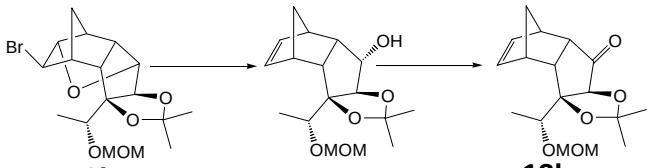
11b : 92% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.83 (s, 1H), 4.67-4.60 (m, 4H), 4.27 (q, 1H, *J* = 6.6 Hz), 3.94 (s, 1H), 3.38 (s, 3H), 3.14-3.09 (m, 1H), 3.06 (dd, 1H, *J* = 8.5, 3.7 Hz), 2.70 (dd, 1H, *J* = 5.1, 4.9 Hz), 2.50 (m, 1H), 2.43 (d, 1H, *J* = 11.0 Hz), 1.95 (d, 1H, *J* = 11.0 Hz), 1.31 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.5, 129.5, 94.4, 90.9, 84.8, 70.4, 55.5, 55.2, 51.5, 50.2, 48.0, 47.3, 40.1, 19.5; MS (EI) *m/z* 314 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{19}BrO_3$ 314.0517, found 314.0517.



11b **12b**

The diol : 95% yield; mp 134-135 ℃ (recrystallized from CH_2Cl_2-hexane); IR (Nujor): 3430 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.77 (d, 1H, *J* = 6.8 Hz), 4.66 (d, 1H, *J* = 6.8 Hz), 4.58 (d, 1H, *J* = 4.9 Hz), 4.33 (d, 1H, *J* = 6.6 Hz), 4.08 (d, 1H, *J* = 6.3 Hz), 3.94 (s, 1H), 3.67 (q, 1H, *J* = 6.3 Hz), 3.46 (d, 1H, *J* = 6.3 Hz), 3.42 (s, 3H), 3.17 (s, 1H), 3.13-3.08 (m, 1H), 2.73 (dd, 1H, *J* = 5.4, 5.1 Hz), 2.61 (dd, 1H, *J* = 9.5, 3.7 Hz), 2.55 (s, 1H), 2.27 (d, 1H, *J* = 11.0 Hz), 1.68 (d, 1H, *J* = 10.7 Hz), 1.30 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 95.1, 91.8, 89.1, 83.2, 82.4, 75.5, 56.7, 56.1, 55.4, 48.0, 46.0, 45.2, 37.6, 14.6; MS (EI) *m/z* 348 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}O_3$ 207.1020, found 207.1028.; Anal. Calcd for $C_{14}H_{21}BrO_5$: C, 48.15; H, 6.06; Br, 22.88. Found: C, 47.85; H, 5.99; Br, 22.85.

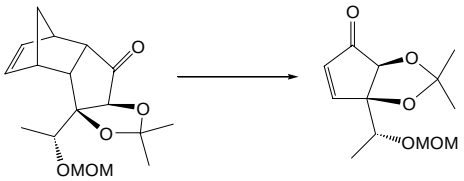
12b : 97% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.79 (d, 1H, *J* = 6.8 Hz), 4.65 (d, 1H, *J* = 6.8 Hz), 4.54-4.53 (m, 1H), 4.53 (s, 1H), 4.36 (d, 1H, *J* = 6.1 Hz), 4.16 (d, 1H, *J* = 2.2 Hz), 3.80 (q, 1H, *J* = 6.3 Hz), 3.43 (s, 3H), 3.15-3.09 (m, 1H), 2.76-2.73 (m, 2H), 2.54 (d, 1H, *J* = 2.9 Hz), 2.26 (d, 1H, *J* = 10.7 Hz), 1.66 (d, 1H, *J* = 10.7 Hz), 1.38 (s, 3H), 1.36 (s, 3H), 1.29 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 110.2, 95.6, 94.6, 91.4, 89.8, 88.9, 74.2, 56.5, 56.1, 54.0, 47.9, 47.5, 45.7, 37.7, 29.3, 28.5, 15.5; MS (EI) *m/z* 373 (M^+-Me), 45 (100%); HRMS (EI) *m/z* calcd for $C_{16}H_{22}BrO_5$ 373.0650, found 373.0657; Anal. Calcd for $C_{17}H_{25}BrO_5$: C, 52.45; H, 6.47; Br, 20.53. Found: C, 52.39; H, 6.18; Br, 20.23.



12b **13b**

The alcohol : 96% yield; mp 65-66 ℃ (recrystallized from hexane); IR (Nujol): 3464 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.29 (dd, 1H, *J* = 5.4, 3.2 Hz), 6.10 (dd, 1H, *J* = 5.1, 2.9 Hz), 4.77 (d, 1H, *J* = 7.1 Hz), 4.67 (d, 1H, *J* = 6.8 Hz), 4.42 (ddd, 1H, *J* = 9.5, 6.8, 3.2 Hz), 4.00 (d, 1H, *J* = 3.2 Hz), 3.80 (q, 1H, *J* = 6.3 Hz), 3.42 (s, 3H), 3.18 (ddd, 1H, *J* = 9.5, 9.5, 4.4 Hz), 3.15 (s, 1H), 3.07 (dd, 1H, *J* = 9.5, 3.7 Hz), 2.88-2.87 (m, 1H), 1.51 (d, 1H, *J* = 8.1 Hz), 1.47 (s, 3H), 1.42 (s, 3H), 1.35 (d, 1H, *J* = 8.1 Hz), 1.32 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.1, 135.2, 110.0, 95.7, 94.4, 92.8, 78.7, 74.9, 56.0, 53.2, 50.0, 45.6, 44.2, 29.2, 28.5, 15.5; MS (EI) *m/z* 310 (M^+), 155 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{26}O_5$ 310.1779, found 310.1760; Anal. Calcd for $C_{17}H_{26}O_5$: C, 65.78; H, 8.44. Found: C, 65.57; H, 8.25.

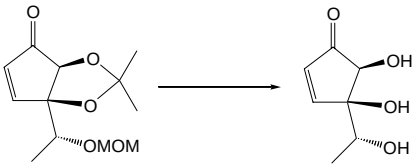
13b : 93% yield; mp 49-50 ℃ (recrystallized from hexane); IR (Nujol): 1745 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.12 (dd, 1H, *J* = 5.6, 2.9 Hz), 6.07 (dd, 1H, *J* = 5.6, 2.2 Hz), 4.77 (d, 1H, *J* = 6.8 Hz), 4.66 (d, 1H, *J* = 6.8 Hz), 3.82 (s, 1H), 3.81 (q, 1H, *J* = 6.6 Hz), 3.41 (s, 3H), 3.28 (brs, 1H), 3.17 (s, 1H), 3.17-3.10 (m, 2H), 1.62 (d, 1H, *J* = 8.5 Hz), 1.48 (d, 1H, *J* = 8.3 Hz), 1.42 (s, 3H), 1.40 (d, 3H, *J* = 6.6 Hz), 1.24 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 218.9, 136.4, 136.0, 110.3, 95.6, 89.6, 82.3, 73.6, 55.8, 52.7, 52.5, 46.7, 45.4, 45.1, 28.8, 28.5, 14.7; MS (EI) *m/z* 308 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{24}O_5$ 308.1622, found 308.1588; Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 65.94; H, 7.75.



13b **14b**

14b : 85% yield; IR (neat): 1722 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.61 (d, 1H, *J* = 5.9 Hz), 6.27 (d, 1H, *J* = 6.1 Hz), 4.73 (d, 1H, *J* = 7.1 Hz), 4.63 (d, 1H, *J* = 7.1 Hz), 4.28 (s, 1H), 3.97 (q, 1H, *J* = 6.3 Hz), 3.36 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.30 (d, 3H, *J* = 6.3 Hz);

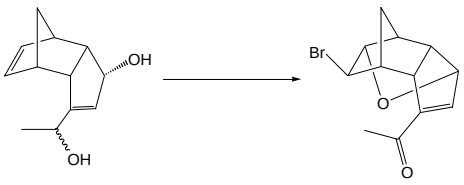
^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.4, 160.1, 134.1, 115.7, 95.4, 90.9, 79.8, 74.5, 55.8, 28.22, 28.19, 15.7; MS (EI) *m/z* 242 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{18}O_5$ 242.1153, found 242.1181; Anal. Calcd for $C_{12}H_{18}O_5$: C, 59.49; H, 7.49. Found: C, 59.36; H, 7.28



14b (±)-**4**

(±)-4 : 32% yield; IR (neat): 3410, 1716 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.58 (d, 1H, J = 6.1 Hz), 6.20 (d, 1H, J = 6.1 Hz), 5.44 (brs, 1H), 4.82 (brs, 2H), 3.90 (s, 1H), 3.65 (q, 1H, J = 5.9 Hz), 1.14 (d, 3H, J = 6.3 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 207.3, 162.0, 132.8, 79.0, 72.7, 68.7, 17.7; MS (FAB) *m/z* 159 (MH^+)

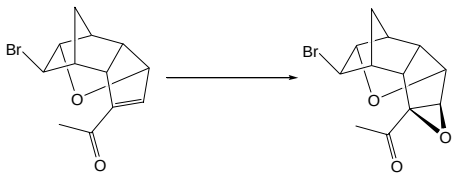
<u>Synthesis of (±)-5</u> : Transformations from 10a,b to (±)-5 shown in scheme 2



10a,b **15**

To a stirred solution of (±)-**10a,b** (1.5 g, 7.81 mmol) in THF (50 mL) was added *N*-bromosuccinimide (1.7 g, 9.55 mmol) at –15 ℃, and the mixture was stirred at –15 ℃ under dark for 15 min. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ solution, and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the bromoether as a colorless oil. To a stirred solution of the bromoether in CH_2Cl_2 (50 mL) was added MnO_2 (15 g, 172 mmol) at room temperature. The reaction mixture was stirred at room temperature for 12 hr, filtered through Celite®, and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **15** (1.54 g, 5.73 mmol, 73% for two steps) as a colorless crystal.

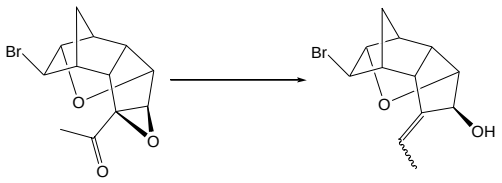
15 : mp 92-93 ℃ (recrystallized from hexane); IR (Nujor): 1666 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.75 (d, 1H, *J* = 2.4 Hz), 4.81 (dd, 1H, *J* = 5.9, 2.4 Hz), 4.64 (d, 1H, *J* = 5.1 Hz), 3.78 (d, 1H, *J* = 2.2 Hz), 3.34 (dd, 1H, *J* = 9.0, 4.1 Hz), 3.16 (ddd, 1H, *J* = 8.8, 5.6, 5.4 Hz), 2.77-2.74 (m, 1H), 2.64-2.63 (m, 1H), 2.43 (d, 1H, *J* = 11.0 Hz), 2.35 (s, 3H), 2.03-2.00 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.5, 146.1, 143.2, 91.4, 84.6, 54.3, 50.8, 49.4, 47.4, 47.2, 40.2, 26.8; MS (EI) *m/z* 268 (M^+), 43 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0077; Anal. Calcd for $C_{12}H_{13}BrO_2$: C, 53.55; H, 4.87; Br, 29.69. Found: C, 53.40; H, 4.84; Br, 29.85.



15 **16**

To a stirred solution of **15** (802 mg, 2.99 mmol) and hydrogen peroxide (30% in H_2O, 1.15 mL, 11.9 mmol) in MeOH (15 mL) was added benzyltrimethylammonium hydroxide (40% in MeOH, 0.678 mL, 1.49 mmol) at 0 ℃. The reaction mixture was stirred at 0 ℃ for 15 min, quenched by addition of saturated aqueous $Na_2S_2O_3$ solution and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **16** (824 mg, 2.90 mmol, 97%) as a colorless crystal.

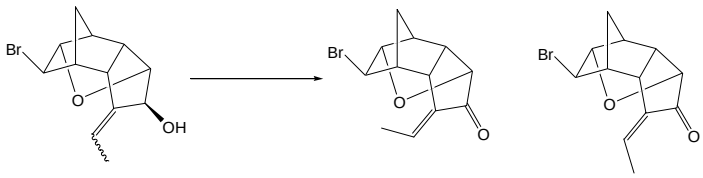
16 : mp 86-87 ℃ (recrystallized from hexane); IR (Nujor): 1691 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.60 (d, 1H, *J* = 4.4 Hz), 4.55 (d, 1H, *J* = 5.4 Hz), 3.84 (s, 1H), 3.62 (d, 1H, *J* = 2.0 Hz), 3.03 (brs, 1H), 2.80 (dd, 1H, *J* = 8.8, 4.1 Hz), 2.77-2.74 (m, 1H), 2.65-2.60 (m, 1H), 2.25 (d, 1H, *J* = 11.0 Hz), 2.12 (s, 3H), 1.70 (d, 1H, *J* = 11.2 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 203.8, 90.1, 81.9, 67.5, 64.9, 54.9, 47.2, 46.5, 46.1, 46.0, 37.0, 25.3; MS (EI) *m/z* 284 (M^+), 123 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{13}BrO_3$ 284.0048, found 284.0051; Anal. Calcd for $C_{12}H_{13}BrO_3$: C, 50.55; H, 4.60; Br, 28.02. Found: C, 50.36; H, 4.54; Br, 27.99.



16 **17a, b**

A mixture of **16** (209 mg, 0.73 mmol) and hydrazine monohydrate (0.18 mL, 3.65 mmol) in THF (1.5 mL) and MeOH (1.5 mL) was stirred at reflux for 2.5 hr. The reaction mixture was poured into H_2O, and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **17a,b** (189 mg, 0.7 mmol, 95%) as a colorless oil.

17a,b : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.93 (qd, 0.54H, *J* = 6.8, 2.4 Hz), 5.71 (q, 0.46H, *J* = 5.7 Hz), 4.68 (s, 0.46H), 4.51 (d, 0.54H, *J* = 4.9 Hz), 4.51 (s, 0.46H), 4.36 (s, 0.54H), 4.20 (d, 0.46H, *J* = 4.6 Hz), 4.15 (d, 0.54H, *J* = 4.4 Hz), 3.70 (d, 0.46H, *J* = 2.0 Hz), 3.66 (d, 0.54H, *J* = 1.7 Hz), 3.39-3.27 (m, 1H), 3.14 (ddd, 0.54H, *J* = 5.1, 5.1, 4.6 Hz), 3.07 (ddd, 0.46H, *J* = 5.4, 5.1, 4.6 Hz), 2.84-2.81 (m, 1H), 2.62 (d, 0.54H, *J* = 3.9 Hz), 2.43 (d, 0.46H, *J* = 3.9 Hz), 2.32 (d, 0.54H, *J* = 11.0 Hz), 2.30 (d, 0.46H, *J* = 11.2 Hz), 1.88-1.81 (m, 1H), 1.82 (dd, 1.38H, *J* = 7.1, 2.0 Hz), 1.73 (dd, 1.62H, *J* = 6.8, 1.5 Hz)

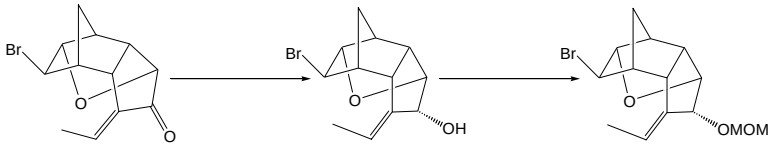


17a, b **18a** **18b**

To a stirred solution of **17a,b** (487 mg, 1.80 mmol) in CH_2Cl_2 (10 mL) was added Dess-Martin periodinane (1.14 g, 2.69 mmol) at 0 ℃. The reaction mixture was stirred at room temperature for 1 hr, and the reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution. The mixture was extracted with ether, and the organic extract was washed with saturated aqueous $NaHCO_3$ solution, brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **18a** (221 mg, 0.82 mmol, 46%) as a colorless crystal and **18b** (167 mg, 0.62 mmol, 35%) as a colorless crystal.

18a : mp 137-140 ℃; IR (Nujor): 1718 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.92 (qdd, 1H, *J* = 7.3, 2.2, 2.0 Hz), 4.66 (d, 1H, *J* = 4.9 Hz), 4.11 (dd, 1H, *J* = 5.4, 2.0 Hz), 3.56 (d, 1H, *J* = 2.0 Hz), 3.39-3.36 (m, 1H), 2.99-2.97 (m, 1H), 2.92 (ddd, 1H, *J* = 10.0, 5.1, 4.9 Hz), 2.68 (d, 1H, *J* = 3.9 Hz), 2.40 (d, 1H, *J* = 11.2 Hz), 1.95-1.91 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 196.5, 146.1, 143.2, 91.4, 84.6, 54.3, 50.8, 49.4, 47.4, 47.2, 40.2, 26.8; MS (EI) *m/z* 268 (M^+), 189 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0081.

18b : mp 88-90 ℃; IR (Nujor): 1712 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.36 (qd, 1H, *J* = 7.3, 1.7 Hz), 4.66 (d, 1H, *J* = 4.6 Hz), 4.03 (d, 1H, *J* = 5.4 Hz), 3.68 (d, 1H, *J* = 2.0 Hz), 3.28-3.24 (m, 1H), 2.95-2.93 (m, 1H), 2.90-2.85 (m, 1H), 2.56 (s, 1H), 2.36 (d, 1H, *J* = 11.0 Hz), 2.21 (dd, 1H, *J* = 7.3, 1.5 Hz), 1.88 (d, 1H, *J* = 11.0 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.3, 142.4, 134.2, 90.0, 83.9, 54.6, 48.7, 48.6, 47.2, 42.4, 37.2, 15.1; MS (EI) *m/z* 268 (M^+), 189 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0080.



18a **19a**

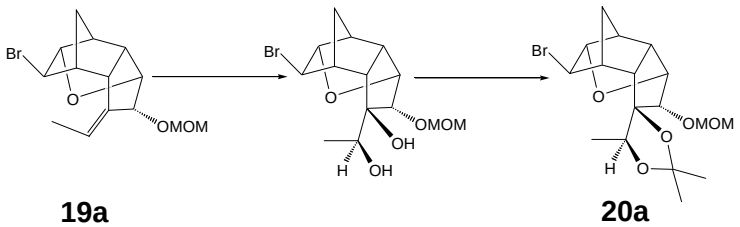
To a stirred solution of **18a** (221 mg, 0.82 mmol) in THF (5 mL) was added a solution of diisobutylaluminum hydride (DIBALH) (1.5 M in toluene, 0.66 mL, 0.99 mmol) dropwise at –78 ℃. After stirring for 5 min, the reaction mixture was quenched by addition of saturated aqueous NH_4Cl solution. The mixture was warmed to room temperature, and stirred for 20 min, and poured into saturated aqueous potassium sodium tartrate (Rochelle salt) solution. The mixture was extracted with ether, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the *endo*-allyl alcohol (210 mg, 0.78 mmol, 94%) as a colorless crystal.

The *endo*-allyl alcohol : mp 93-94 ℃; IR (Nujor): 3284 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.81 (qdd, 1H, *J* = 7.1, 2.7, 2.4 Hz), 4.54 (d, 1H, *J* = 4.9 Hz), 4.33-4.30 (m, 1H), 4.24 (dd, 1H, *J* = 4.2, 4.1 Hz), 3.72 (d, 1H, *J* = 2.0 Hz), 3.09-3.07 (m, 1H), 2.90-2.87 (m, 1H), 2.74-2.68 (m, 2H), 2.33 (d, 1H, *J* = 11.0 Hz), 2.31 (d, 1H, *J* = 11.0 Hz), 1.78 (d, 1H, *J* = 11.0 Hz), 1.71 (ddd, 3H, *J* = 7.1, 2.4, 1.7 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 141.7, 122.6, 88.7, 83.8, 78.9, 56.1, 47.2, 45.5, 45.4, 45.0, 37.4, 14.9; MS (EI) *m/z* 270 (M^+), 191 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}BrO_2$ 270.0255, found 270.0267.

To a stirred solution of the *endo*-(*E*)-allyl alcohol (210 mg, 0.78mmol) and $^{i}Pr_2NEt$ (0.68 mL, 3.88 mmol) in CH_2Cl_2 (6 mL) was added MOMCl (0.18 mL, 2.33 mmol) at 0 ℃. After stirring the mixture for 10 hr at room temperature, the mixture was poured into water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography

(EtOAc-hexane = 1 : 4) to give **19a** (223 mg, 0.71 mmol, 91%) as a colorless oil.

19a : ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.76 (qdd, 1H, *J* = 6.8, 2.7, 2.4 Hz), 4.82 (d, 1H, *J* = 6.6 Hz), 4.74 (d, 1H, *J* = 6.6 Hz), 4.54 (d, 1H, *J* = 5.1 Hz), 4.36 (dd, 1H, *J* = 4.1, 3.7 Hz), 4.29 (d, 1H, *J* = 2.2 Hz), 3.85 (d, 1H, *J* = 1.2 Hz), 3.44 (s, 3H), 3.05-3.03 (m, 1H), 2.86-2.84 (m, 1H), 2.74-2.69 (m, 2H), 2.31 (d, 1H, *J* = 11.0 Hz), 1.77 (dd, 1H, *J* = 11.0, 0.7 Hz), 1.72 (ddd, 3H, *J* = 7.1, 2.4, 1.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.3, 121.7, 96.4, 89.1, 83.7, 82.2, 56.0, 55.6, 46.7, 45.6, 45.5, 44.6, 37.3, 14.7; MS (EI) *m/z* 314 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{19}BrO_3$ 314.0517, found 314.0507.



19a **20a**

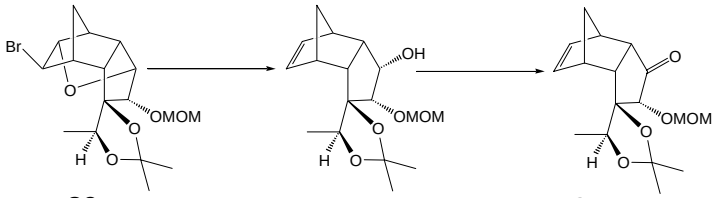
To a stirred solution of **19a** (223 mg, 0.71 mmol) and 4-methylmolpholine *N*-oxide (249 mg, 2.13 mmol) in THF (2.5 mL) and H_2O (2.5 mL) was added OsO_4 (0.197M in THF, 1.08 mL, 0.21 mmol) at room temperature, and the mixture was stirred at room temperature for 9 hr. The reaction was quenched by addition of saturated aqueous $Na_2S_2O_3$ solution and extracted with $CHCl_3$. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 1) to give the diol (246 mg, 0.71 mmol, 100%) as a colorless crystal.

The diol : mp 93-94 ℃; IR (Nujor): 3432 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.75 (d, 1H, *J* = 5.9 Hz), 4.69 (d, 1H, *J* = 6.1 Hz), 4.66 (dd, 1H, *J* = 6.1, 5.1 Hz), 4.61 (d, 1H, *J* = 4.9 Hz), 4.31 (d, 1H, *J* = 2.4 Hz), 4.10 (qd, 1H, *J* = 6.6, 2.9 Hz), 4.05 (dd, 1H, *J* = 6.3, 1.2 Hz), 3.44 (s, 3H), 3.22 (d, 1H, *J* = 2.4 Hz), 3.15 (ddd, 1H, *J* = 9.3, 6.1, 5.9 Hz), 2.82-2.80 (m, 1H), 2.71 (s, 1H), 2.39 (brs, 1H), 2.25 (d, 1H, *J* = 11.0 Hz), 2.25-2.22 (m, 1H), 1.66 (dd, 1H, *J* = 11.0, 1.5 Hz), 1.25 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 96.7, 89.7, 88.5, 85.0, 82.6, 67.7, 56.5, 55.1, 53.0, 48.4, 47.8, 44.9, 37.9, 16.4; MS (EI) *m/z* 349 (M^++H), 163 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{22}BrO_5$ 349.0650, found 349.0651.

A mixture of the diol (246 mg, 0.71 mmol), 2,2-dimethoxypropane (0.44 mL, 3.54 mmol) and *p*-toluenesulfonic acid (12 mg, 0.070 mmol) in CH_2Cl_2 (5 mL) was stirred at room temperature for 1.5 hr. To the reaction mixture was added saturated aqueous $NaHCO_3$ solution, extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **20a** (233 mg, 0.60 mmol, 85%) as a colorless crystal.

20a : mp 59-60 ℃; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.71 (d, 1H, *J* = 6.8 Hz), 4.65 (d, 1H, *J* = 6.8 Hz), 4.62 (d, 1H, *J* = 8.5 Hz), 4.60 (d, 1H, *J* = 6.6 Hz), 4.55 (q, 1H, *J* = 6.6 Hz), 4.24 (d, 1H, *J* = 2.2 Hz), 4.20 (dd, 1H, *J* = 6.3, 1.2 Hz), 3.43 (s, 3H), 3.08 (ddd, 1H, *J* = 9.3, 6.1, 5.9

Hz), 2.78 (ddd, 1H, *J* = 5.9, 4.4, 1.2 Hz), 2.66 (d, 1H, *J* = 3.4 Hz), 2.49 (ddd, 1H, *J* = 9.3, 3.9, 1.0 Hz), 2.24 (d, 1H, *J* = 11.0 Hz), 1.64 (dd, 1H, *J* = 10.7, 1.5 Hz), 1.44 (d, 3H, *J* = 6.6 Hz), 1.42 (s, 3H), 1.37 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 107.4, 95.6, 92.6, 89.9, 85.3, 82.5, 74.0, 56.0, 55.1, 53.1, 48.7, 47.2, 46.1, 37.7, 29.2, 26.8, 17.7; MS (EI) *m/z* 388 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{25}BrO_5$ 388.0884, found 388.0872.



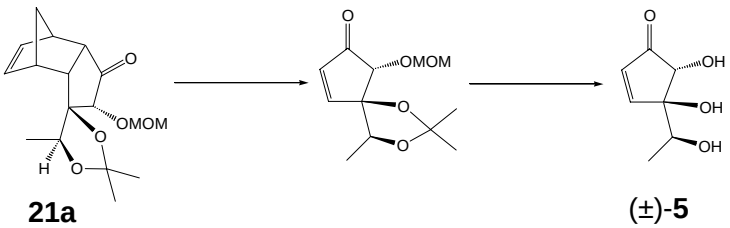
20a **21a**

A mixture of **20a** (233 mg, 0.60 mmol), activated Zn (1.18 g, 18 mmol) in MeOH (3 mL) and AcOH (0.6 mL) was stired at 50 ℃ for 3 hr, and filtered through Celite®. The filtrate was poured into saturated aqueous $NaHCO_3$ solution, and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the alcohol (162 mg, 0.52 mmol, 87%) as a colorless oil.

The alcohol : IR (neat): 3488 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.02 (dd, 1H, *J* = 5.4, 2.9 Hz), 5.83 (dd, 1H, *J* = 5.4, 2.7 Hz), 4.66 (d, 1H, *J* = 6.1 Hz), 4.57 (d, 1H, *J* = 6.1 Hz), 4.42 (ddd, 1H, *J* = 9.5, 9.3, 7.1 Hz), 4.35 (q, 1H, *J* = 6.6 Hz), 3.78 (d, 1H, *J* = 6.8 Hz), 3.40 (s, 3H), 3.14 (ddd, 1H, *J* = 9.3, 9.0, 4.2 Hz), 3.09 (s, 1H), 2.94 (s, 1H), 2.78 (dd, 1H, *J* = 8.8, 3.9 Hz), 2.23 (d, 1H, *J* = 9.3 Hz), 1.49-1.45 (m, 1H), 1.49 (d, 3H, *J* = 6.6 Hz), 1.45 (s, 3H), 1.38 (s, 3H), 1.30 (d, 1H, *J* = 7.8 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 135.7, 133.8, 107.9, 98.7, 92.0, 86.7, 74.5, 71.1, 56.5, 53.9, 52.9, 50.4, 46.0, 44.0, 30.0, 28.0, 19.1; MS (EI) *m/z* 310 (M^+), 86 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{26}O_5$ 310.1779, found 310.1797.

To a stirred solution of the alcohol (162 mg, 0.52 mmol) in CH_2Cl_2 (3 mL) was added pyridinium dichromate (786 mg, 2.09 mmol). The reaction mixture was stirred at room temperature for 10 hr, filtered through Celite®, and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give **21a** (144 mg, 0.47 mmol, 89%) as a colorless crystal.

21a : mp 73-74 ℃; IR (Nujor): 1734 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, 1H, *J* = 5.6, 2.7 Hz), 5.87 (dd, 1H, *J* = 5.6, 2.7 Hz), 4.82 (d, 1H, *J* = 6.6 Hz), 4.52 (d, 1H, *J* = 6.3 Hz), 4.49 (q, 1H, *J* = 6.6 Hz), 3.63 (s,1H), 3.39-3.34 (m, 1H), 3.37 (s, 3H), 3.20-3.15 (m, 2H), 3.07 (dd, 1H, *J* = 8.3, 3.7 Hz), 1.56 (d, 3H, *J* = 6.8 Hz), 1.55-1.53 (m, 1H), 1.49 (s, 3H), 1.40-1.37 (m, 1H), 1.37 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 218.2, 136.0, 133.6, 108.3, 95.2, 89.0, 80.9, 73.8, 55.8, 53.4, 52.8, 50.0, 46.4, 45.1, 29.8, 27.2, 18.7; MS (EI) *m/z* 308 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{24}O_5$ 308.1622, found 308.1600.



21a (±)-**5**

A mixture of **21a** (28 mg, 0.09 mmol) in Ph_2O (0.2 mL) was heated at reflux for 15 min. After cooling at room temperature, the reaction mixture was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the enone (22 mg, 0.09 mmol, 100%) as a colorless oil.

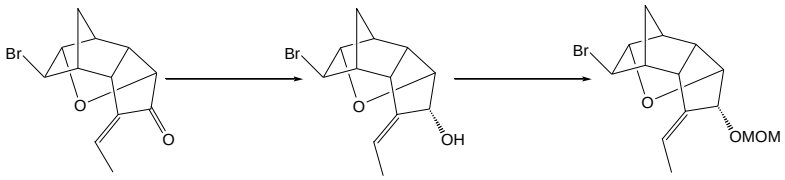
The enone : IR (neat): 1731 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.29 (d, 1H, *J* = 6.3 Hz), 6.29 (d, 1H, *J* = 6.3 Hz), 5.06 (d, 1H, *J* = 6.1 Hz), 4.82 (d, 1H, *J* = 6.3 Hz), 4.55 (q, 1H, *J* = 6.3 Hz), 4.47 (s,1H), 3.49 (s, 3H), 1.54 (s, 3H), 1.47 (s, 3H), 1.08 (d, 1H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 201.7, 159.4, 132.6, 108.3, 96.7, 88.6, 78.7, 73.6, 56.0, 28.6, 26.3, 15.4; MS (EI) *m/z* 242 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{18}O_5$ 242.1153, found 242.1158.

A mixture of the enone (22 mg, 0.09mmol), trifluoroacetic acid (0.2 mL) and H_2O (0.02 mL) was stirred at 0 ℃ for 3 hr. The mixture was concentrated in vacuo and purified by silica gel column chromatography (EtOAc-MeOH = 9 : 1) to give (±)-**5** (4.8 mg, 0.03 mmol, 35%) as a light yellow oil.

(±)-5 : IR (neat): 3386, 1720 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.29 (d, 1H, *J* = 6.3 Hz), 6.28 (d, 1H, *J* = 6.3 Hz), 5.91 (d, 1H), 5.41 (s, 1H), 4.65 (d, 1H, *J* = 4.4 Hz), 4.04 (d, 1H, *J* = 5.9 Hz), 3.77 (qd, 1H, *J* = 6.3, 4.6 Hz), 0.79 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 203.9, 161.3, 131.4, 82.4, 81.3, 69.6, 18.4

<u>Synthesis of (±)-6</u> : Transformations from 10b to (±)-6 shown in Scheme 2

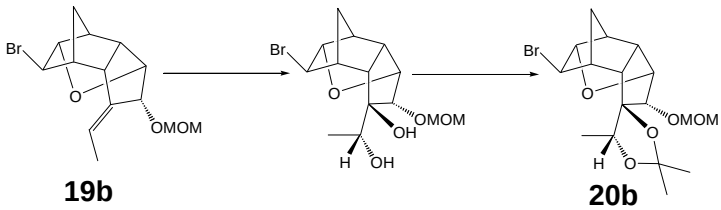
The reactions were conducted as described above as those for **18a** to (±)-**5**.



18b **19b**

The *endo*-(*Z*)-Allyl alcohol : 75% yield; mp 65-66 ℃; IR (Nujor): 3468 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.66 (qdd, 1H, *J* = 7.1, 2.4, 2.0 Hz), 4.64-4.60 (m, 1H), 4.57 (d, 1H, *J* = 5.1 Hz), 4.31 (dd, 1H, *J* = 4.9, 4.6 Hz), 3.81 (d, 1H, *J* = 2.2 Hz), 3.01-2.98 (m, 1H), 2.90 (ddd, 1H, *J* = 5.1, 4.9, 1.2 Hz), 2.69 (ddd, 1H, *J* = 10.0, 5.1, 4.9 Hz), 2.62 (d, 1H, *J* = 10.5 Hz), 2.44 (d, 1H, *J* = 4.1 Hz), 2.27 (d, 1H, *J* = 11.0 Hz), 1.85 (ddd, 3H, *J* = 7.1, 2.0, 1.7 Hz), 1.75 (dd, 1H, *J* = 11.0, 1.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.7, 125.8, 88.5, 84.4, 77.4, 56.3, 49.2, 48.4, 47.9, 44.6, 37.1, 13.9; MS (EI) *m/z* 270 (M^+), 191 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{15}BrO_2$ 270.0255, found 270.0269.

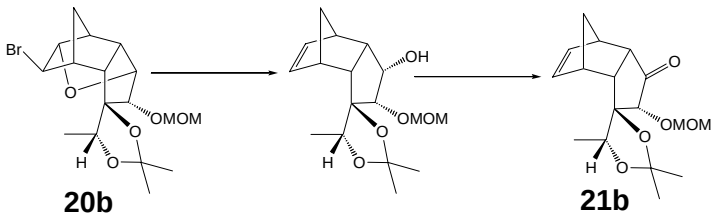
19b : 98% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.67-5.61 (m, 1H), 4.81 (d, 1H, *J* = 6.6 Hz), 4.76 (d, 1H, *J* = 6.6 Hz), 4.56-4.55 (m, 1H), 4.55 (s, 1H), 4.43 (dd, 1H, *J* = 4.6, 4.4 Hz), 3.98 (d, 1H, *J* = 2.2 Hz), 3.47 (s, 3H), 2.97-2.94 (m, 1H), 2.85 (ddd, 1H, *J* = 5.1, 4.9, 1.2 Hz), 2.66 (ddd, 1H, *J* = 10.0, 5.1, 4.9 Hz), 2.47 (d, 1H, *J* = 4.9 Hz), 2.27 (d, 1H, *J* = 10.7 Hz), 1.80 (ddd, 3H, *J* = 7.1, 2.0, 1.7 Hz), 1.74-1.71 (m, 1H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 138.0, 124.9, 96.2, 88.9, 82.93, 82.88, 56.3, 56.1, 48.4, 48.0, 47.8, 45.0, 37.2, 13.7; MS (EI) *m/z* 314 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{19}BrO_3$ 314.0517, found 314.0507.



19b **20b**

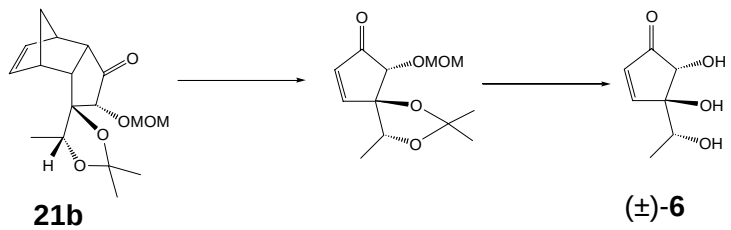
The diol : 100% yield; mp 121-122 ℃; IR (Nujor): 3412 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.69 (d, 1H, *J* = 6.6 Hz), 4.67 (dd, 1H, *J* = 6.3, 6.1 Hz), 4.62 (d, 1H, *J* = 6.6 Hz), 4.61 (d, 1H, *J* = 4.9 Hz), 4.43 (d, 1H, *J* = 2.2 Hz), 3.99-3.97 (m, 2H), 3.44 (s, 3H), 3.09 (ddd, 1H, *J* = 9.3, 6.1, 5.9 Hz), 2.82-2.79 (m, 1H), 2.63-2.62 (m, 1H), 2.36 (ddd, 1H, *J* = 9.3, 3.9, 1.2 Hz), 2.26 (d, 1H, *J* = 11.0 Hz), 1.85-1.81 (m, 2H), 1.67-1.64 (m, 2H), 1.35 (d, 3H, *J* = 6.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 96.4, 89.8, 85.5, 85.2, 83.8, 69.5, 58.2, 57.1, 53.5, 48.1, 47.3, 45.5, 37.8, 18.0; MS (EI) *m/z* 349 (M^++H), 163 (100%); HRMS (EI) *m/z* calcd for $C_{14}H_{22}BrO_5$ 349.0650, found 349.0633.

20b : 91% yield; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.67 (d, 1H, *J* = 6.6 Hz), 4.65 (d, 1H, *J* = 6.6 Hz), 4.62-4.59 (m, 2H), 4.48 (dd, 1H, *J* = 6.6, 1.2 Hz), 4.32 (d, 1H, *J* = 2.2 Hz), 4.26 (q, 1H, *J* = 6.6 Hz), 3.45 (s, 3H), 2.99 (ddd, 1H, *J* = 9.3, 5.9, 5.9 Hz), 2.82 (ddd, 1H, *J* = 5.4, 5.1, 1.2 Hz), 2.48-2.47 (m, 1H), 2.40 (dd, 1H, *J* = 9.5, 4.2 Hz), 2.27 (d, 1H, *J* = 10.7 Hz), 1.66-1.63 (m, 1H), 1.62 (d, 3H, *J* = 6.6 Hz), 1.48 (s, 3H), 1.34 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 106.9, 95.2, 90.3, 89.4, 85.9, 83.2, 76.7, 56.9, 56.1, 53.3, 47.8, 46.5, 44.9, 37.5, 28.0, 26.9, 15.4; MS (EI) *m/z* 388 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{25}BrO_5$ 388.0884, found 388.0860.



The alcohol : 82% yield; IR (neat): 3498 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.15 (dd, 1H, *J* = 5.6, 2.7 Hz), 5.90 (dd, 1H, *J* = 5.6, 2.9 Hz), 4.68 (d, 1H, *J* = 6.1 Hz), 4.61 (d, 1H, *J* = 6.1 Hz), 4.29 (ddd, 1H, *J* = 7.1, 5.6, 5.1 Hz), 4.22 (q, 1H, *J* = 6.6 Hz), 3.89 (d, 1H, *J* = 5.6 Hz), 3.41 (s, 3H), 2.97-2.92 (m, 3H), 2.83 (dd, 1H, *J* = 9.9, 3.8 Hz), 2.20 (d, 1H, *J* = 4.9 Hz), 1.54-1.51 (m, 1H), 1.44 (d, 3H, *J* = 6.6 Hz), 1.42 (s, 3H), 1.40 (s, 3H), 1.34 (d, 1H, *J* = 8.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 137.3, 132.5, 105.9, 98.6, 90.4, 90.1, 76.3, 71.3, 56.2, 55.3, 54.0, 47.3, 44.4, 44.2, 28.3, 26.6, 16.8; MS (EI) *m/z* 310 (M^+), 86 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{26}O_5$ 310.1779, found 310.1793.

21b : 43% yield; mp 68-70 ℃; IR (Nujor): 1758 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.01 (dd, 1H, *J* = 5.9, 2.8 Hz), 4.76 (d, 1H, *J* = 6.3 Hz), 4.72 (d, 1H, *J* = 6.6 Hz), 4.59 (s, 1H), 4.11 (q, 1H, *J* = 6.3 Hz), 3.42 (s, 3H), 3.28-3.27 (m, 2H), 3.21 (brs, 1H), 3.12 (brs, 1H), 1.64 (ddd, 1H, *J* = 8.3, 1.7, 1.7 Hz), 1.48 (s, 3H), 1.45 (s, 3H), 1.40 (d, 3H, *J* = 8.1 Hz), 1.33 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 209.8, 136.5, 134.8, 106.0, 96.2, 88.3, 86.5, 77.0, 56.0, 52.9, 50.0, 49.6, 44.6, 42.2, 27.2, 25.6, 15.5; MS (EI) *m/z* 308 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{17}H_{24}O_5$ 308.1622, found 308.1613.

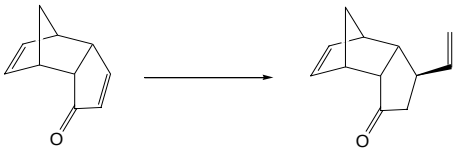


The enone : 61% yield; IR (neat): 1728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 1H, *J* = 6.6 Hz), 6.27 (d, 1H, *J* = 6.6 Hz), 4.97 (d, 1H, *J* = 6.3 Hz), 4.88 (d, 1H, *J* = 6.6 Hz), 4.41 (s, 1H), 4.25 (q, 1H, *J* = 6.6 Hz), 3.52 (s, 3H), 1.56 (s, 3H), 1.46 (s, 3H), 1.36 (d, 3H, *J* = 6.6 Hz);

^{13}C-NMR (100 MHz, $CDCl_3$) δ 200.8, 157.8, 132.8, 109.0, 97.1, 86.9, 85.8, 77.0, 56.4, 27.2, 25.9, 12.0; MS (EI) *m/z* 242 (M^+), 45 (100%); HRMS (EI) *m/z* calcd for $C_{12}H_{18}O_5$ 242.1153, found 242.1144.

(±)-6 : IR (neat) : 56% yield; 3406, 1680 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.24 (d, 1H, *J* = 6.3 Hz), 6.27 (d, 1H, *J* = 6.3 Hz), 5.63 (s, 1H), 5.30 (d, 1H, *J* = 7.3 Hz), 4.30 (d, 1H, *J* = 5.6 Hz), 3.90 (d, 1H, *J* = 7.3 Hz), 3.80 (qd, 1H, *J* = 6.3, 6.1 Hz), 1.09 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 202.9, 158.9, 132.4, 82.7, 82.3, 67.8, 18.2

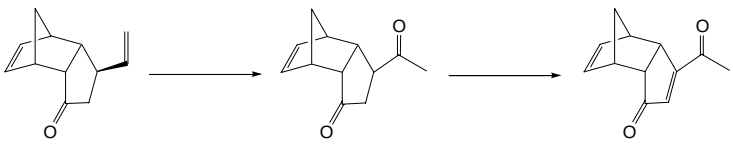
<u>Synthesis of (+)-3</u> : Transformations from (-)-7 to (+)-3 shown in Scheme 3



(-)-**7** (-)-**8**

To a stirred suspension of dry copper(I) iodide (1.64 g, 8.64 mmol) in THF (25 mL) was added vinylmagnesium bromide (1.0 M in THF, 14.4 mL, 14.4 mmol) dropwise over a 30 min period at –78 ℃. Then, (-)-ketodicyclopentadiene (KDP) (**7**) (0.7 g, 4.79 mmol) in THF (3 mL) was added dropwise over a 10 min period to the solution at –35 ℃. The mixture was stirred at –35 ℃ for 30 min, and saturated aqueous NH_4Cl solution was added dropwise to the reaction mixture. The mixture was stirred at room temperature for 10 min and filtered through Celite®. The filtrate was extracted with ether, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 20) to give (-)-**8** (759 mg, 4.36 mmol, 91%) as a colorless oil.

(-)-**8** : $[\alpha]_D^{29}$ –138.5° (*c* 0.74, $CHCl_3$); IR (neat): 1730 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.18 (s, 2H), 5.88 (ddd, 1H, *J* = 16.6, 10.5, 7.3 Hz), 4.98 (ddd, 1H, *J* = 7.1, 1.2, 1.0 Hz), 4.94 (d, 1H, *J* = 1.2 Hz), 3.19-3.17 (m, 1H), 3.09-3.07 (m, 1H), 2.96 (ddd 1H, *J* = 9.5, 4.6, 1.5 Hz), 2.79 (ddd, 1H, *J* = 9.8, 4.6, 4.4 Hz), 2.40-2.33 (m, 1H), 2.26 (dd, 1H, *J* = 18.3, 8.7 Hz), 2.18 (ddd, 1H, *J* = 18.1, 8.1, 1.7 Hz), 1.59 (d, 1H, *J* = 8.3 Hz), 1.44 (d, 1H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 219.1, 142.2, 136.3, 135.0, 112.8, 54.4, 52.4, 48.5, 47.3, 46.3, 45.9, 40.7; MS (EI) m/z 174 (M^+), 66 (100%); HRMS (EI) m/z calcd for $C_{12}H_{14}O$ 174.1044, found 174.1063.



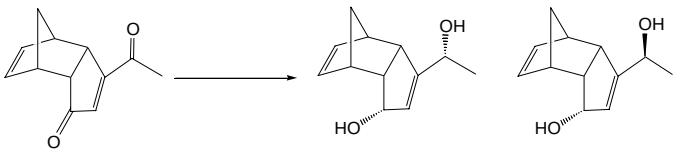
(-)-**8** (+)-**9**

A mixture of copper(I) chloride (31.4 mg, 0.317 mmol), palladium(II) chloride (9.4 mg, 0.053 mmol) in DMF (1 mL) and H_2O (0.1 mL) was stirred under oxygen atmosphere at room temperature for 30 min. To the solution was added (-)-**8** (46 mg, 0.264 mmol) in DMF (1 mL). The reaction mixture was stirred at 50 ℃ for 10 hr and filtered through Celite®. The filtrate was extracted with ether, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 8) to give the diketone (42 mg, 0.221 mmol, 84%) as a colorless oil.

The diketone : $[\alpha]_D^{22}$ –106.2° (*c* 0.48, $CHCl_3$); IR (neat): 1730, 1712 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.23 (dd, 1H, *J* = 5.6, 3.2 Hz), 6.20 (dd, 1H, *J* = 5.4, 2.8 Hz), 3.22-3.20 (m, 1H), 3.19-3.17 (m, 1H), 3.03 (ddd, 1H, *J* = 9.5, 5.1, 4.2 Hz), 2.96 (ddd, 1H, *J* = 9.5, 4.4, 1.2 Hz), 2.73 (ddd, 1H, *J* = 9.5, 6.8, 4.4 Hz), 2.63 (ddd, 1H, *J* = 18.8, 7.1, 1.8 Hz), 2.26 (s, 3H), 2.12 (dd, 1H, *J* = 18.8, 9.5 Hz), 1.64 (d, 1H, *J* = 8.5 Hz), 1.50 (d, 1H, *J* = 8.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 217.7, 207.7, 136.9, 134.0, 54.1, 52.1, 49.4, 46.9, 46.0, 44.3, 42.3, 28.5; MS (EI) m/z 190 (M^+), 66 (100%); HRMS (EI) m/z calcd for $C_{12}H_{14}O_2$ 190.0993, found 190.1014. Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.82; H, 7.44.

A mixture of the diketone (75 mg, 0.395 mmol), anhydrous *p*-toluenesulfonic acid (79 mg, 0.459 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) (161 mg, 0.711 mmol) in dioxane (3 mL) was heated at reflux for 20 hr. To the reaction mixture was added H_2O and filtered through Celite®. The filtrate was extracted with EtOAc, and the organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 10) to give (+)-**9** (54 mg, 0.287 mmol, 73%) as a colorless crystal.

(+)-**9** : mp 95-96 ℃ (recrystallized from hexane); $[\alpha]_D^{23}$ ＋22.1° (*c* 0.40, $CHCl_3$); IR (Nujol): 1698, 1672 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.35 (s, 1H), 5.97 (dd, 1H, *J* = 5.4, 2.9 Hz), 5.71 (dd, 1H, *J* = 5.1, 2.9 Hz), 3.59 (dd, 1H, *J* = 4.6, 4.6 Hz), 3.24 (brs, 1H), 3.21 (brs, 1H), 2.95 (dd, 1H, *J* = 5.1, 5.1 Hz), 2.40 (s, 3H), 1.76 (d, 1H, *J* = 8.5 Hz), 1.63 (d, 1H, *J* = 8.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 209.7, 196.6, 168.0, 138.4, 132.5, 132.2, 52.0, 51.3, 45.4, 44.5, 44.0, 27.3; MS (EI) m/z 188 (M^+), 66 (100%); HRMS (EI) m/z calcd for $C_{12}H_{12}O_2$ 188.0837. found 188.0846. Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43. Found: C, 76.58; H, 6.56.

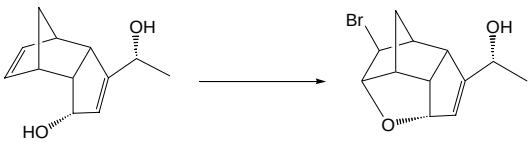


(+)-**9** (+)-**10a** (+)-**10b**

To a stirred solution of (+)-**9** (1.69 g, 8.99 mmol) in THF (45 mL) was added a solution of diisobutylaluminum hydride (DIBALH) (1.5 M in toluene, 13.2 mL, 19.8 mmol) dropwise at –78 ℃. The reaction mixture was stirred for 15 min, and then quenched by addition of saturated aqueous NH_4Cl solution. After stirring for 20 min at room temperature, the mixture was poured into saturated aqueous potassium sodium tartrate (Rochelle salt) solution, and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 1) to give (+)-**10a** (1.13 g, 5.89 mmol, 66%) and as a colorless crystal and (+)-**10b** (191 mg, 0.99 mmol, 11%) as a colorless crystal.

(+)-**10a** : mp 145-146 ℃ (recrystallized from $CHCl_3$); $[\alpha]_D^{28}$ +154.2° (*c* 0.15, $CHCl_3$); IR (Nujol): 3270 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.6, 2.9 Hz), 5.85 (dd, 1H, *J* = 5.6, 3.2 Hz), 5.48 (s, 1H), 4.67 (d, 1H, *J* = 8.5 Hz), 4.19 (q, 1H, *J* = 6.6 Hz), 3.21 (dd, 1H, *J* = 8.1, 4.1 Hz), 3.02 (ddd, 1H, *J* = 8.5, 8.3, 4.1 Hz), 2.95-2.93 (m, 2H), 1.59 (d, 1H, *J* = 8.1 Hz), 1.42 (d, 1H, *J* = 8.5 Hz), 1.31 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 134.3, 133.5, 127.8, 75.1, 66.7, 53.2, 52.3, 47.7, 46.6, 44.3, 22.5; MS (EI) m/z 192 (M^+), 174 (100%); HRMS (EI) m/z calcd for $C_{12}H_{16}O_2$ 192.1149. found 192.1113. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.68; H, 8.27.

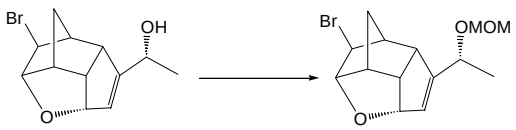
(+)-**10b** : mp 150-151 ℃ (recrystallized from $CHCl_3$); $[\alpha]_D^{26}$ +146.5° (*c* 0.14, $CHCl_3$); IR (Nujol): 3296 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.4, 2.7 Hz), 5.84 (dd, 1H, *J* = 5.6, 3.2 Hz), 5.46 (s, 1H), 4.65 (dd, 1H, *J* = 9.3, 8.8 Hz), 4.24 (qd, 1H, *J* = 6.6, 5.4 Hz), 3.36 (dd, 1H, *J* = 7.8, 4.1 Hz), 3.04-2.99 (m, 2H), 2.93 (brs, 1H), 1.60 (d, 1H, *J* = 8.3 Hz), 1.45 (d, 1H, *J* = 8.3 Hz), 1.32 (d, 3H, *J* = 6.3 Hz), 1.23 (d, 1H, *J* = 9.5 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 152.2, 134.3, 133.5, 127.8, 75.1, 66.7, 53.2, 52.3, 47.7, 46.6, 44.3, 22.5; MS (EI) m/z 174 (M^+-H_2O), 156 (100%); HRMS (EI) m/z calcd for $C_{12}H_{14}O$ 174.1044. found 174.1048. Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 74.85; H, 8.32.



(+)-**10a** (+)-**22a**

To a stirred solution of (+)-**10a** (201 mg, 1.05 mmol) in THF (5 mL) was added *N*-bromosuccinimide (280 mg, 1.57 mmol) at –15 ℃, and the mixture was stirred at –15 ℃ under dark for 15 min. The reaction was then quenched by addition of saturated aqueous $Na_2S_2O_3$ solution and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give (+)-**22a** (274 mg, 1.01 mmol, 97%) as a colorless oil.

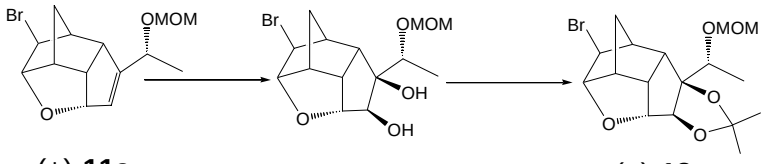
(+)-**22a** : $[\alpha]_D^{27}$ +87.7° (*c* 0.59, $CHCl_3$); IR (neat): 3390 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.84 (s, 1H), 4.68 (dd, 1H, *J* = 5.6, 2.4 Hz), 4.62 (d, 1H, *J* = 4.9 Hz), 4.36 (q, 1H, *J* = 6.6 Hz), 3.97 (d, 1H, *J* = 2.2 Hz), 3.13 (ddd, 1H, *J* = 8.8, 5.4, 5.3 Hz), 3.03 (dd, 1H, *J* = 8.8, 3.9 Hz), 2.72-2.69 (m, 1H), 2.50 (s, 1H), 2.40 (d, 1H, *J* = 11.0 Hz), 1.96 (d, 1H, *J* = 11.0 Hz), 1.33 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 151.4, 127.9, 91.0, 84.9, 66.7, 55.0, 51.8, 50.3, 47.9, 47.2, 40.2, 22.0; MS (EI) m/z 191 (M^+-Br), 43 (100%); HRMS (EI) m/z calcd for $C_{12}H_{15}O_2$ 191.1071. found 191.1052.



(+)-**22a** (+)-**11a**

To a stirred solution of (+)-**22a** (274 mg, 1.01 mmol) and $^{i}Pr_2NEt$ (0.88 mL, 5.05 mmol) in CH_2Cl_2 (5 mL) was added MOMCl (0.23 mL, 3.03 mmol) at 0 ℃. The reaction mixture was stirred at room temperature for 10 hr, and then poured into water and extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give (+)-**11a** (290 mg, 0.92 mmol, 91%) as a colorless oil.

(+)-**11a** : $[\alpha]_D^{30}$ ＋145.0° (*c* 0.17, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.85 (d, 1H, *J* = 2.2 Hz), 4.66 (dd, 1H, *J* = 5.9, 2.4 Hz), 4.62 (d, 1H, *J* = 4.9 Hz), 4.59 (s, 2H), 4.29 (q, 1H, *J* = 6.6 Hz), 3.96 (d, 1H, *J* = 2.2 Hz), 3.37 (s, 3H), 3.12 (ddd, 1H, *J* = 8.8, 5.6, 5.4 Hz), 3.01 (dd, 1H, *J* = 8.8, 3.9 Hz), 2.69 (ddd, 1H, *J* = 5.1, 5.1, 1.2 Hz), 2.50-2.49 (m, 1H), 2.44 (d, 1H, *J* = 10.7 Hz), 1.95 (dd, 1H, *J* = 10.7, 1.5 Hz), 1.29 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 148.4, 130.3, 94.2, 91.0, 84.7, 70.5, 55.4, 55.0, 51.3, 50.3, 48.2, 47.1, 40.2, 19.6; MS (EI) m/z 314 (M^+), 45 (100%); HRMS (EI) m/z calcd for $C_{14}H_{19}BrO_3$ 314.0517. found 314.0529. Anal. Calcd for $C_{14}H_{19}BrO_3$: C, 53.35; H, 6.08; Br, 25.35. Found: C, 53.43; H, 6.12; Br, 25.42.



(+)-**11a** (+)-**12a**

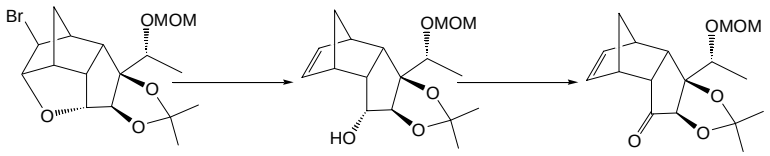
To a stirred solution of (+)-**11a** (70 mg, 0.223mmol) and 4-methylmolpholine *N*-oxide (39 mg, 0.334 mmol) in THF (1.5 mL) and H_2O (0.5 mL) was added OsO_4 (0.197M in THF, 0.227 mL, 0.045 mmol) at room temperature. The mixture was stirred at room temperature for 4 days, and quenched by addition of saturated aqueous $Na_2S_2O_3$ solution, and extracted with $CHCl_3$. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 1) to give the diol (47 mg, 0.135 mmol, 61%) as a colorless oil.

The diol : $[\alpha]_D^{27}$ ＋108.5° (*c* 0.53, $CHCl_3$); IR (neat): 3450 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.73 (d, 1H, *J* = 6.3 Hz), 4.63 (d, 1H, *J* = 6.3 Hz), 4.62 (d, 1H, *J* = 4.4 Hz), 4.33 (d, 1H, *J* = 6.6 Hz), 4.22 (d, 1H, *J* = 3.4 Hz), 3.81(d, 1H, *J* = 2.0 Hz), 3.68 (q, 1H, *J* = 6.3 Hz), 3.40 (s, 3H), 3.37 (s, 1H), 3.15-3.10 (m, 1H), 2.75 (brs, 2H), 2.51 (dd, 1H, *J* = 9.5, 3.9 Hz), 2.34 (s, 1H), 2.30 (d, 1H, *J* = 11.0 Hz), 1.70 (d, 1H, *J* = 10.5 Hz), 1.30 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 95.0, 90.4, 89.4, 86.9, 81.7, 78.1, 56.7, 55.8, 54.7, 48.1,

46.2, 44.7, 37.8, 14.8; MS (EI) m/z 207 (M^+-MOM-OH-Br), 45 (100%); HRMS (EI) m/z calcd for $C_{12}H_{15}O_3$ 207.1020. found 207.0993.

A mixture of the diol (43 mg, 0.123 mmol) and anhydrous *p*-toluenesulfonic acid (2.3 mg, 0.013 mmol) in 2,2-dimethoxypropane (0.5 mL) was stirred at room temperature for 17 hr. To the reaction mixture was added saturated aqueous $NaHCO_3$ solution, extracted with ether. Organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give (+)-**12a** (36 mg, 0.093 mmol, 75%) as a colorless crystal.

(+)-**12a** : mp 93 ℃ (recrystallized from hexane); $[\alpha]_D^{27}$ +4.6° (*c* 1.02, $CHCl_3$); ^{1}H-NMR (400 MHz, $CDCl_3$) δ 4.76 (d, 1H, *J* = 6.8 Hz), 4.62 (d, 1H, *J* = 6.8 Hz), 4.57 (s, 1H), 4.56 (d, 1H, *J* = 6.1 Hz), 4.36 (d, 1H, *J* = 5.9 Hz), 3.68 (q, 1H, *J* = 6.3 Hz), 3.61 (d, 1H, *J* = 2.2 Hz), 3.35 (s, 3H), 3.16 (ddd, 1H, *J* = 9.3, 5.9, 5.4 Hz), 2.87-2.78 (m, 1H), 2.64 (dd, 1H, *J* = 9.5, 4.0 Hz), 2.32 (d, 1H, *J* = 3.2 Hz), 2.28 (d, 1H, *J* = 10.7 Hz), 1.71 (d, 1H, *J* = 11.7 Hz), 1.46 (s, 3H), 1.37 (s, 3H), 1.29 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 111.1, 95.4, 95.1, 92.2, 90.6, 89.2, 75.0, 56.3, 55.7, 55.0, 48.4, 47.8, 45.1, 37.6, 29.1, 27.2, 15.9; MS (EI) m/z 373 (M^+-Me), 299 (100%); HRMS (EI) m/z calcd for $C_{16}H_{22}BrO_5$ 373.0650. found 373.0626. Anal. Calcd for $C_{17}H_{25}BrO_5$: C, 52.45; H, 6.47; Br, 20.53. Found: C, 52.25; H, 6.47; Br, 20.81.



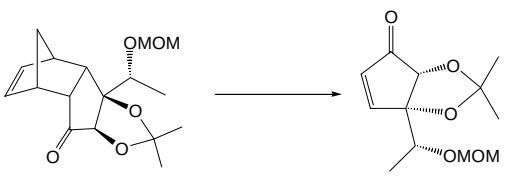
(+)-**12a** (-)-**13a**

A mixture of (+)-**12a** (89 mg, 0.229 mmol) and activated Zn (375 mg, 5.73 mmol) in MeOH (2 mL) and AcOH (0.2 mL) was stirred at 50 ℃ for 1 hr, and then filtered through Celite®. The filtrate was poured into saturated aqueous $NaHCO_3$ solution, and the mixture was extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give the alcohol (71 mg, 0.229 mmol, 100%) as a colorless crystal.

The alcohol : mp 71-72 ℃ (recrystallized from hexane); $[\alpha]_D^{26}$ –16.3° (*c* 0.68, $CHCl_3$); IR (Nujol): 3368 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.39 (dd, 1H, *J* = 5.6, 2.9 Hz), 6.07 (dd, 1H, *J* = 5.4, 2.0 Hz), 4.69 (d, 1H, *J* = 7.1 Hz), 4.56 (d, 1H, *J* = 7.1 Hz), 4.44 (dd, 1H, *J* = 9.8, 4.4 Hz), 4.09 (d, 1H, *J* = 4.4 Hz), 3.80 (q, 1H, *J* = 6.1 Hz), 3.37 (s, 3H), 3.18 (ddd, 1H, *J* = 9.8, 9.3, 4.4 Hz), 2.91 (s, 1H), 2.84-2.81 (m, 2H), 2.29 (brs, 1H), 1.49-1.48 (m, 1H), 1.49 (s, 3H), 1.48 (s, 3H), 1.30-1.29 (m, 1H), 1.30 (d, 3H, *J* = 6.1 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 140.0, 132.6, 110.2, 95.0, 93.1, 93.0, 79.7, 74.4, 55.7, 55.5, 51.2, 49.8, 45.1, 44.4, 30.1, 27.6, 15.4; MS (EI) m/z 295 (M^+-Me), 45 (100%); HRMS (EI) m/z calcd for $C_{16}H_{23}O_5$ 295.1544. found 295.1534.

To a stirred solution of oxalyl chloride (0.10 mL, 1.16 mmol) in CH_2Cl_2 (2 mL) was added DMSO (0.165 mL, 2.32 mmol) dropwise at –78 ℃. After 10 min, the alcohol (60 mg, 0.194 mmol) in CH_2Cl_2 (1 mL) was added to the solution. The mixture was stirred at –78 ℃ for 30 min, and triethylamine (0.486 mL, 3.48 mmol) was added dropwise to the reaction mixture. The mixture was allowed to warm to room temperature, and then extracted with ether. The organic extract was washed with brine, dried ($MgSO_4$), and concentrated. The residue was purified by silica gel column chromatography (EtOAc-hexane = 1 : 2) to give (-)-**13a** (59 mg, 0.192 mmol, 99%) as a colorless crystal.

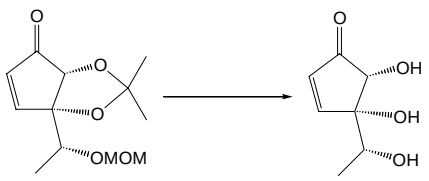
(-)-**13a** : mp 79-80 ℃ (recrystallized from hexane); $[\alpha]_D^{27}$ –228.1° (*c* 0.56, $CHCl_3$); IR (Nujol): 1748 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.21 (dd, 1H, *J* = 5.6, 2.9 Hz), 6.15 (dd, 1H, *J* = 5.6, 2.4 Hz), 4.72 (d, 1H, *J* = 7.1 Hz), 4.55 (d, 1H, *J* = 6.8 Hz), 3.85 (s, 1H), 3.75 (q, 1H, *J* = 6.3 Hz), 3.37 (s, 3H), 3.24 (brs, 1H), 3.20-3.17 (m, 1H), 3.04 (brs, 1H), 2.97 (dd, 1H, *J* = 8.5, 3.7 Hz), 1.62 (d, 1H, *J* = 8.3 Hz), 1.49 (d, 1H, *J* = 8.3 Hz), 1.47 (s, 3H), 1.37 (d, 3H, *J* = 6.3 Hz), 1.25 (s, 3H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 219.0, 138.4, 133.9, 111.1, 95.0, 90.2, 83.8, 74.8, 55.7, 53.2, 52.0, 48.9, 46.1, 45.0, 29.1, 26.6, 15.0 ; MS (EI) m/z 308 (M^+), 153 (100%); HRMS (EI) m/z calcd for $C_{17}H_{24}O_5$ 308.1622. found 308.1646. Anal. Calcd for $C_{17}H_{24}O_5$: C, 66.21; H, 7.84. Found: C, 66.07; H, 7.70.



(-)-**13a** (-)-**14a**

A mixture of (-)-**13a** (35 mg, 0.114 mmol) in Ph_2O (1 mL) was heated at reflux for 15 min. After cooling to room temperature, the reaction mixture was directly purified by silica gel column chromatography (EtOAc-hexane = 1 : 4) to give (-)-**14a** (27 mg, 0.112 mmol, 98%) as a colorless oil.

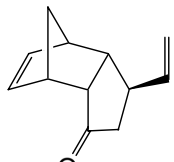
(-)-**14a** : $[\alpha]_D^{26}$ +10.9° (*c* 0.90, $CHCl_3$); IR (neat): 1728 cm^{-1}; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 7.56 (d, 1H, *J* = 5.9 Hz), 6.27 (d, 1H, *J* = 6.1 Hz), 4.71 (d, 1H, *J* = 6.8 Hz), 4.63 (d, 1H, *J* = 7.1 Hz), 4.28 (s, 1H), 4.05 (q, 1H, *J* = 6.3 Hz), 3.35 (s, 3H), 1.46 (s, 3H), 1.33 (s, 3H), 1.23 (d, 3H, *J* = 6.6 Hz); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 204.0, 161.8, 134.1, 115.6, 95.3, 90.9, 78.4, 73.9, 55.7, 28.3, 28.2, 15.8; MS (EI) m/z 227 (M^+-Me), 45 (100%); HRMS (EI) m/z calcd for $C_{11}H_{15}O_5$ 227.0919. found 227.0917.



(-)-**14a** (+)-pentenocin B (**3**)

A mixture of (-)-**14a** (33 mg, 0.136 mmol), trifluoroacetic acid (0.2 mL) and H_2O (0.02 mL) was stirred at 0 ℃ for 2 hr. The mixture was concentrated in vacuo, and purified by silica gel column chromatography (EtOAc-MeOH = 9 : 1) to give (+)-**3** (9.1 mg, 0.058 mmol, 42%) as a colorless resin.

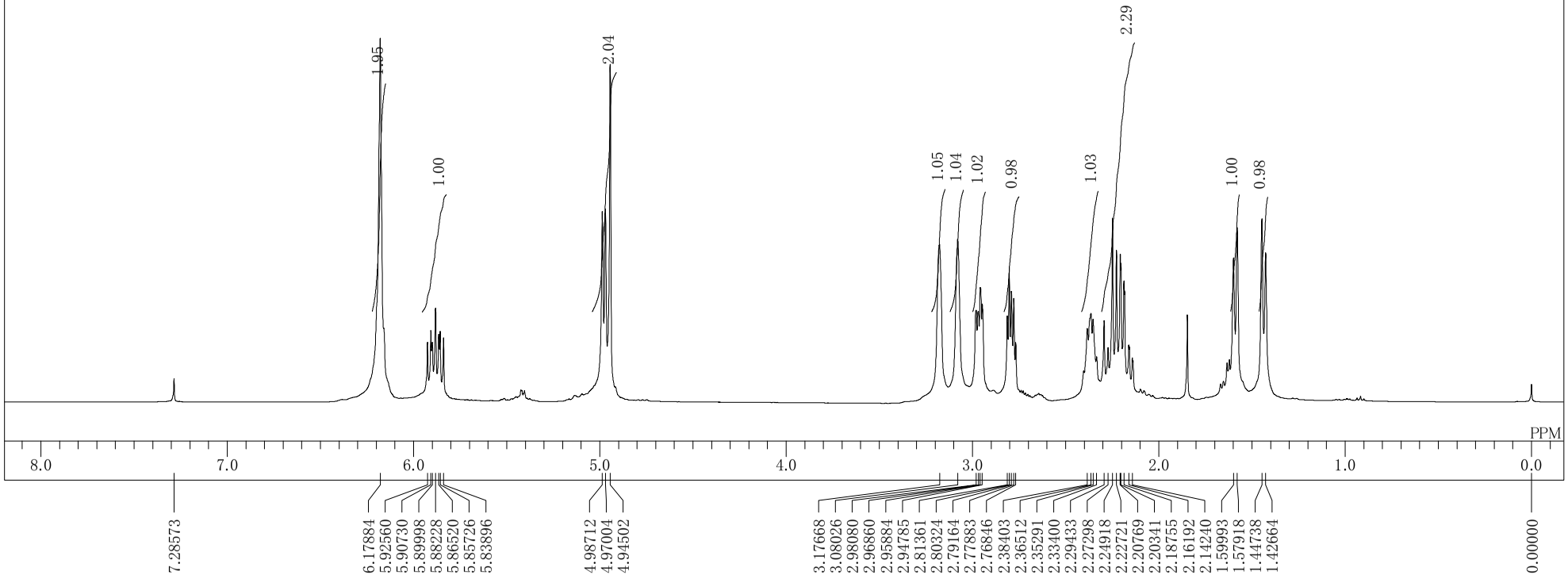
(+)-**3** : $[\alpha]_D^{30}$ +100.8° (*c* 1.0, H_2O) {lit. $[\alpha]_D$ +76° (*c* 1.0, H_2O)}; IR (neat): 3386, 1678 cm^{-1}; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 7.48 (d, 1H, *J* = 6.1 Hz), 6.15 (d, 1H, *J* = 6.1 Hz), 5.32 (d, 1H, *J* = 7.3 Hz), 4.90 (s, 1H), 4.83 (d, 1H, *J* = 5.1 Hz), 3.91 (d, 1H, *J* = 7.3 Hz), 3.69 (qd, 1H, *J* = 6.3, 5.6 Hz), 1.12 (d, 3H, *J* = 6.3 Hz); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 208.1, 165.3, 131.6, 78.8, 70.7, 69.2, 18.0; MS (FAB) m/z 159 (M^++H).

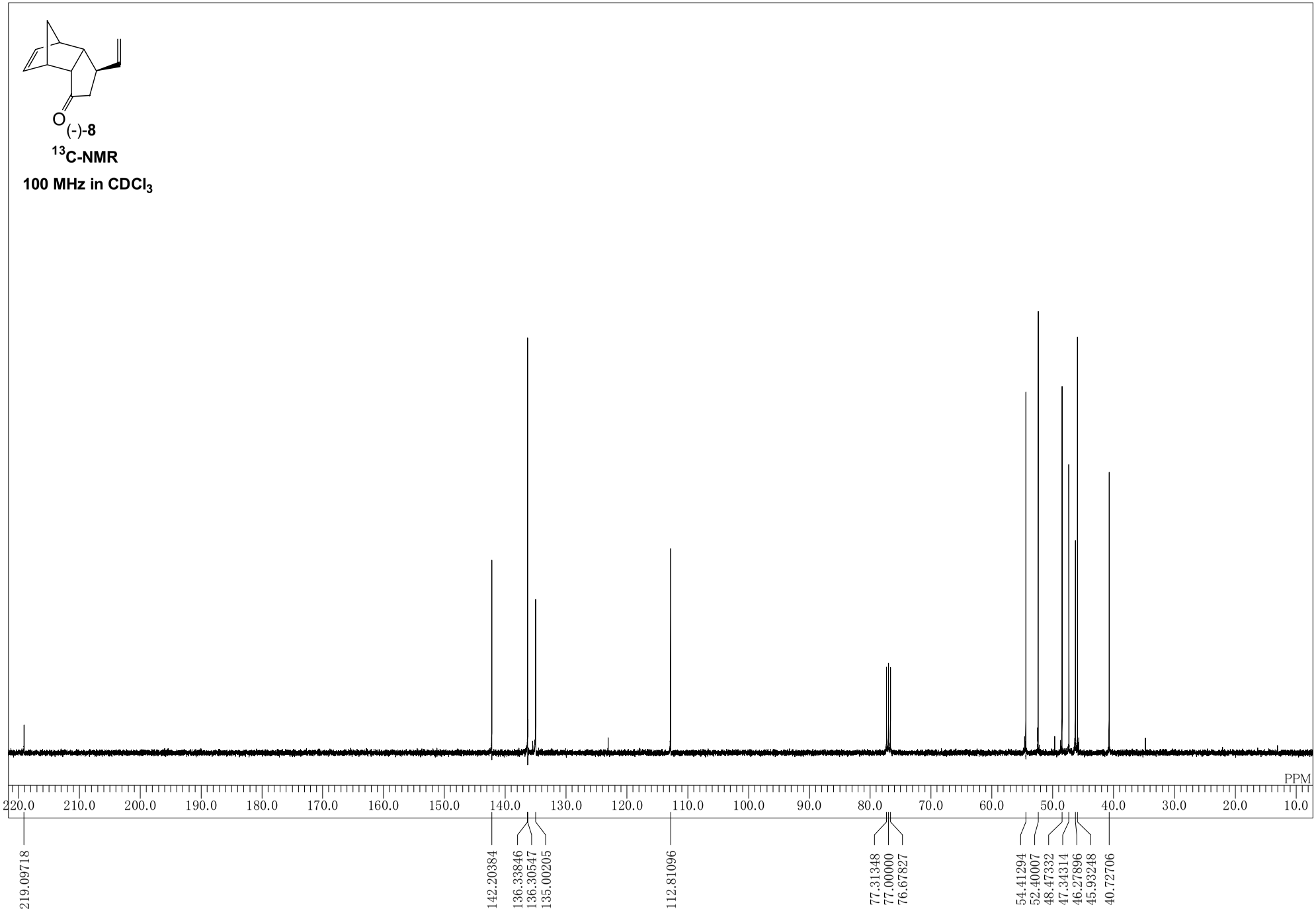


(-)-8

^{1}H-NMR

400 MHz in $CDCl_3$




(-)-8
13C-NMR
100 MHz in CDCl3
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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
219.09718
142.20384
136.33846
136.30547
135.00205
112.81096
77.31348
77.00000
76.67827
54.41294
52.40007
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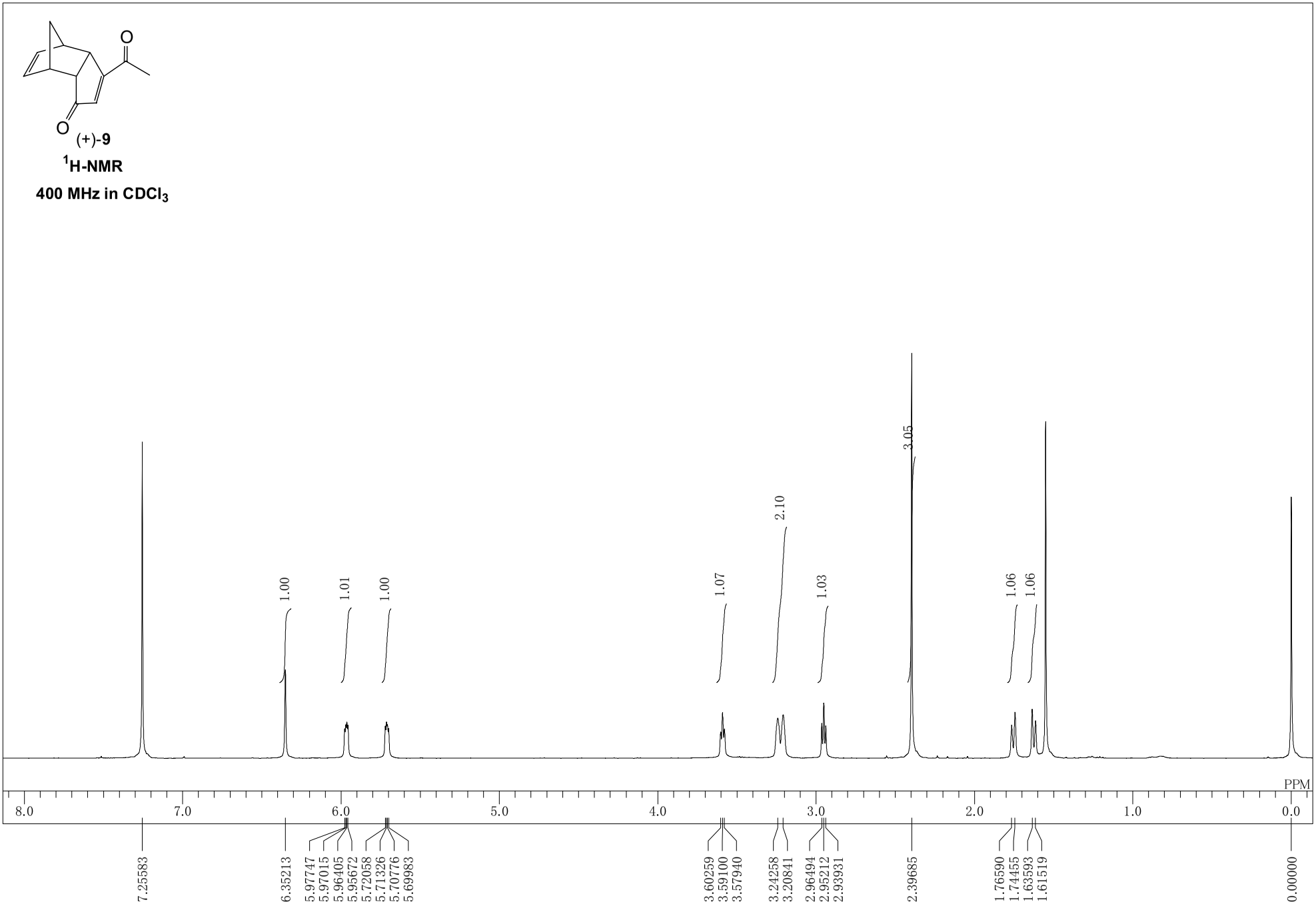
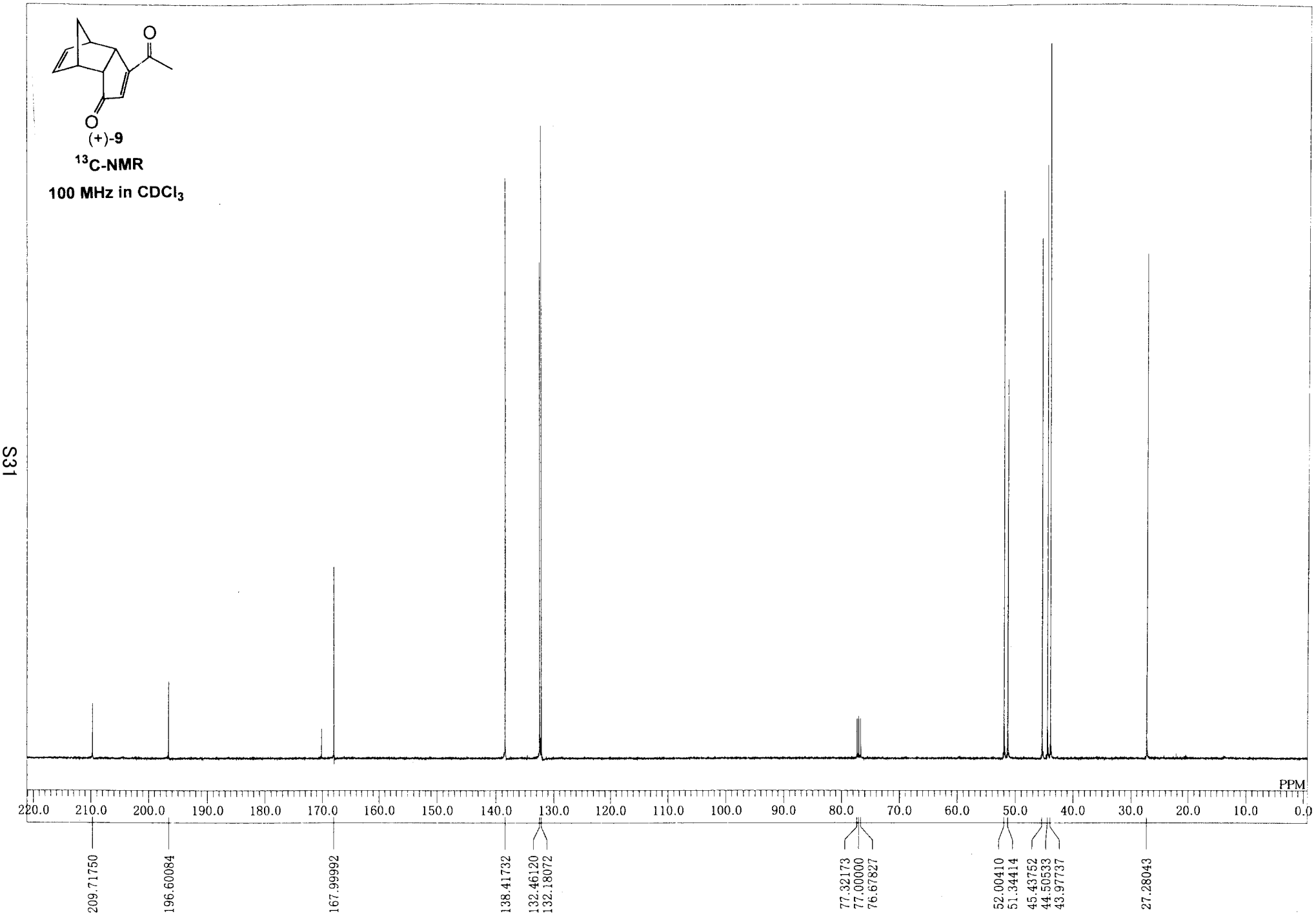
46.27896
45.93248
40.72706

(+)-**9**

^{1}H-NMR

400 MHz in $CDCl_3$




(+)-9
^{13}C-NMR
100 MHz in $CDCl_3$
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200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
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196.60084
167.99992
138.41732
132.46120
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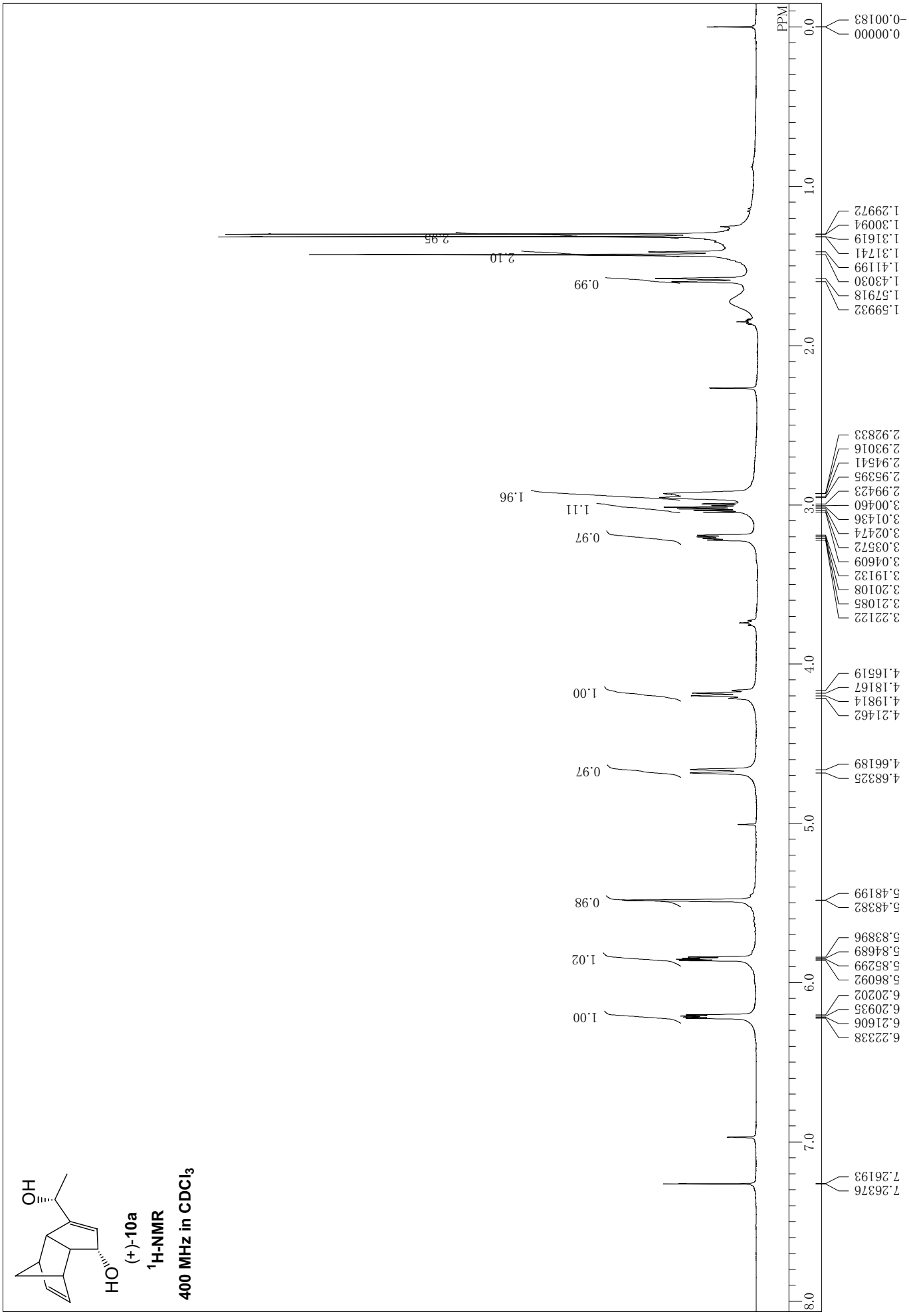
43.97737
27.28043


OH
HO
(+)-10a
1H-NMR
400 MHz in CDCl3
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1.41199
1.31741
1.31619
1.30094
1.29972
2.92833
2.93016
2.94541
2.95395
2.99423
3.00460
3.01436
3.02474
3.03572
3.04609
3.19132
3.20108
3.21085
3.22122
4.16519
4.18167
4.19814
4.21462
4.66189
4.68325
5.48199
5.48382
5.83896
5.84689
5.85299
5.86092
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6.20935
6.21606
6.22338
7.26193
7.26376
1.00
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0.97
1.00
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2.95
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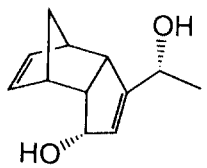
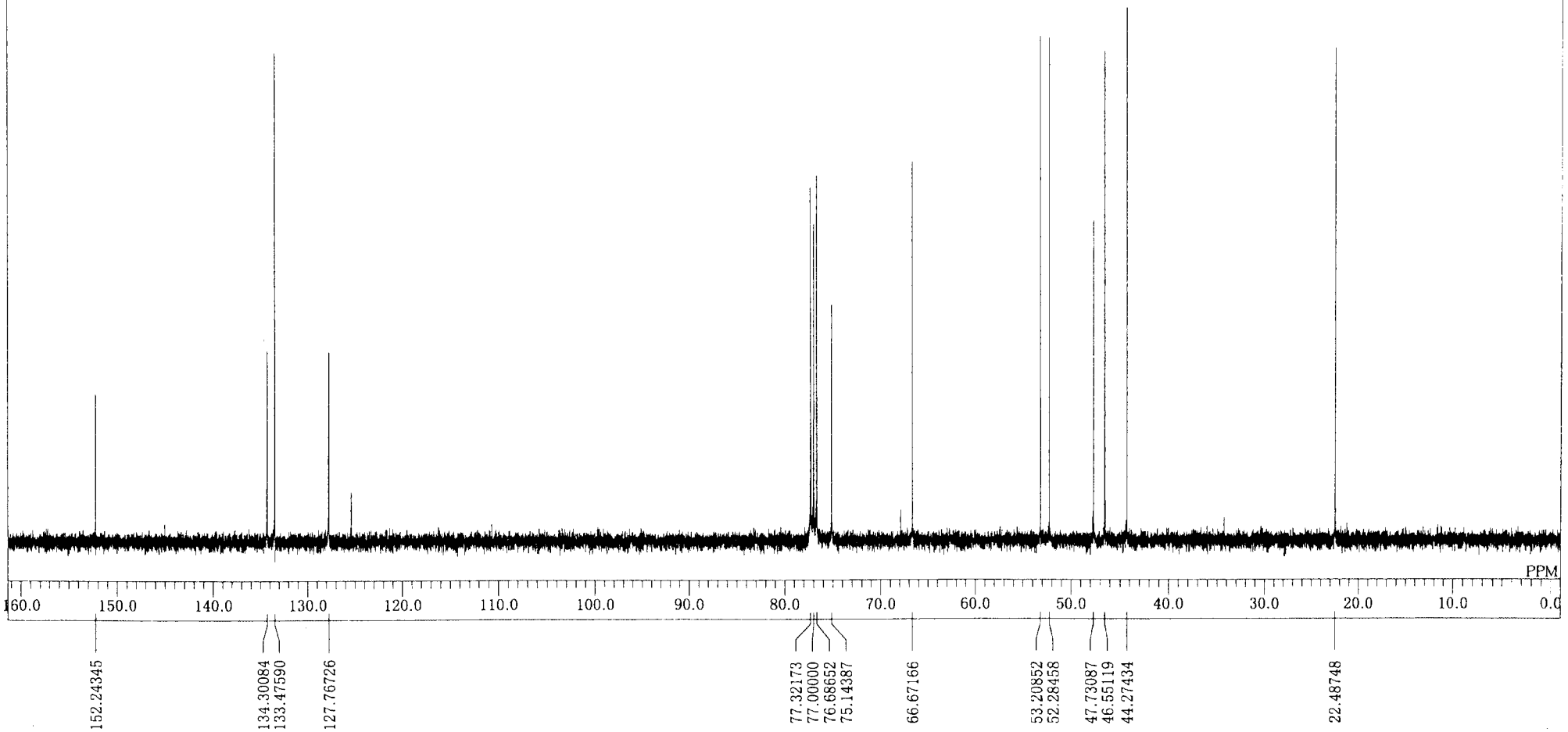
1.11
0.97
1.00

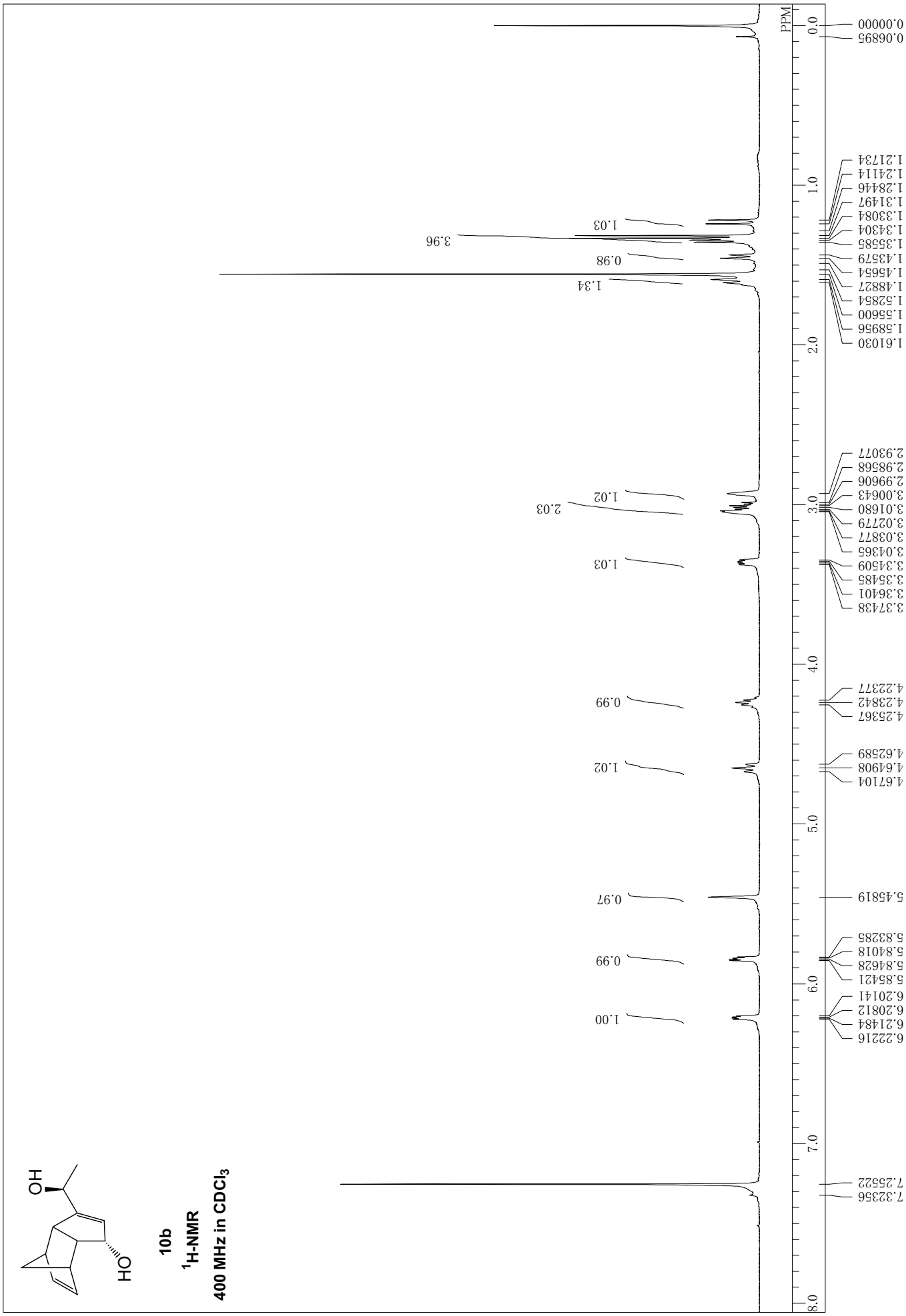


(+)-**10a**

^{13}C-NMR

100 MHz in $CDCl_3$

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HO
10b
1H-NMR
400 MHz in CDCl3
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1.45654
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1.61030
2.93077
2.98568
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3.00643
3.01680
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3.03877
3.04365
3.34509
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3.36401
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6.22216
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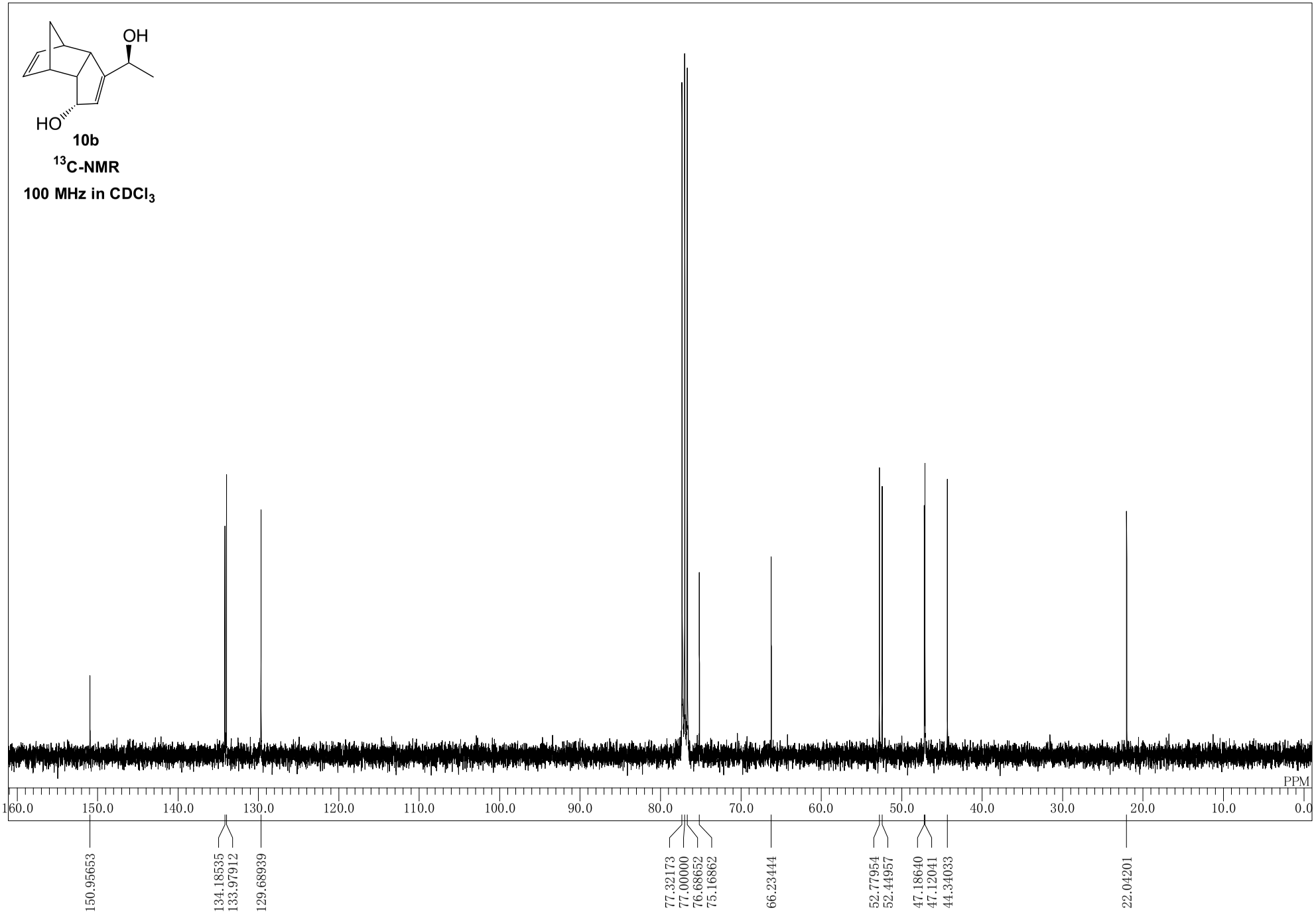
1.00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10b
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100 MHz in CDCl3
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30.0
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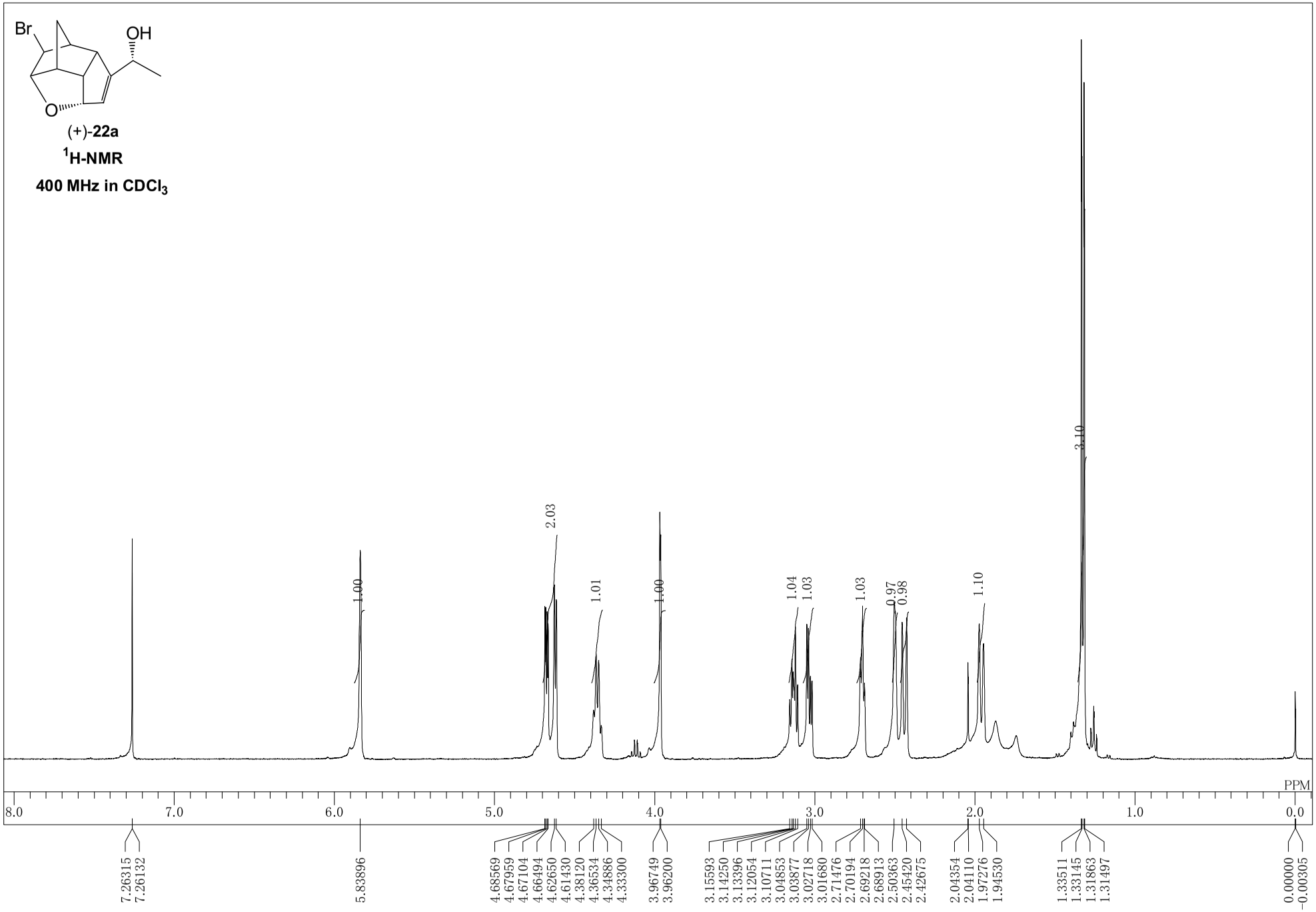
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OH
O
(+)-22a
1H-NMR
400 MHz in CDCl3
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1.00
1.04
1.03
1.03
0.97
0.98
1.10
3.10
PPM
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7.0
6.0
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4.0
3.0
2.0
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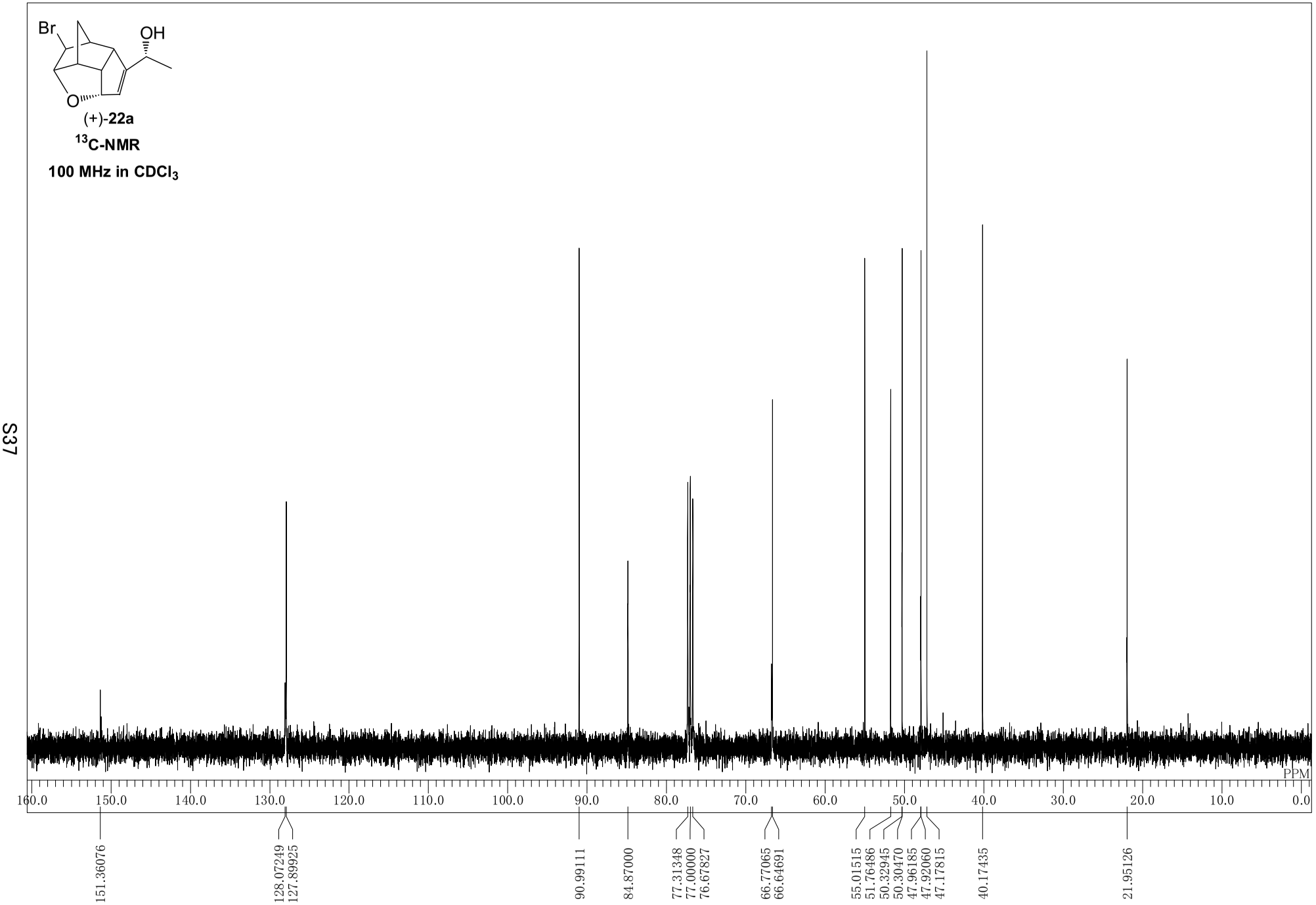
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OH
O
(+)-22a
13C-NMR
100 MHz in CDCl3
PPM
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150.0
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120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
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20.0
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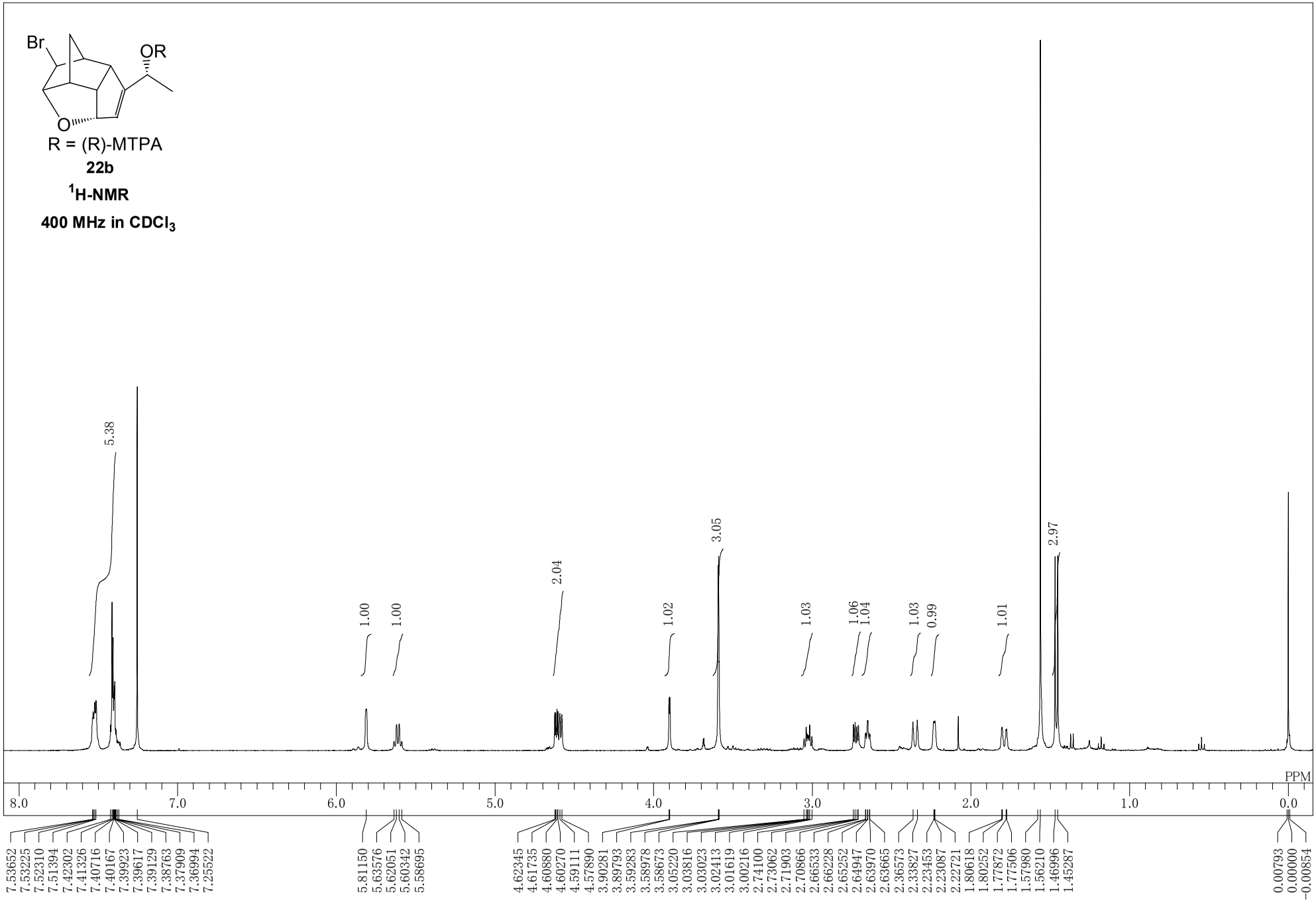
Br
OR
O
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22b
1H-NMR
400 MHz in CDCl3
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1.02
3.05
1.03
1.06
1.04
1.03
0.99
1.01
2.97
PPM
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7.0
6.0
5.0
4.0
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2.0
1.0
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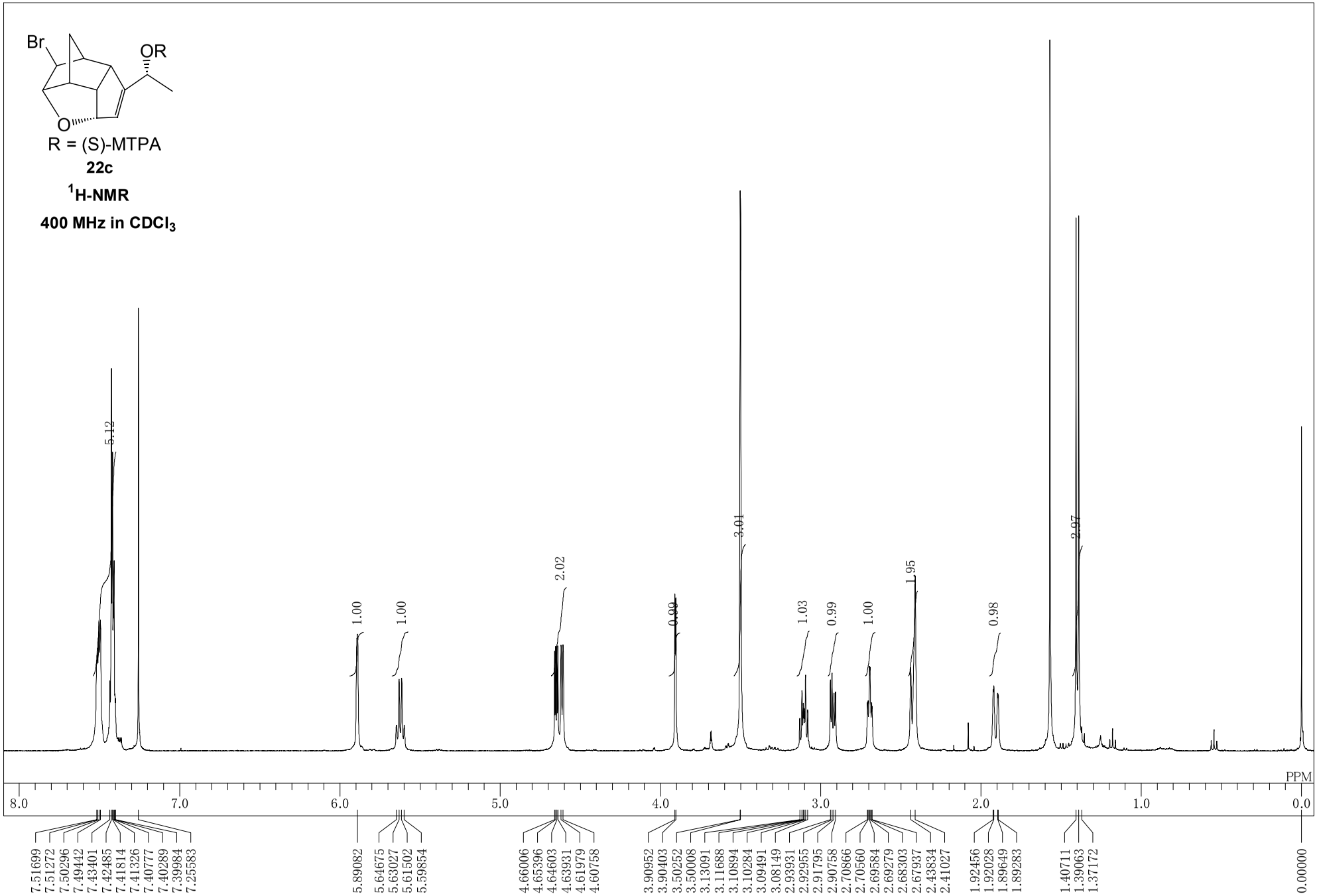
Br
OR
O
R = (S)-MTPA
22c
1H-NMR
400 MHz in CDCl3
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0.99
3.01
1.03
0.99
1.00
1.95
0.98
2.97
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
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7.51272
7.50296
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7.42485
7.41814
7.41326
7.40777
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4.61979
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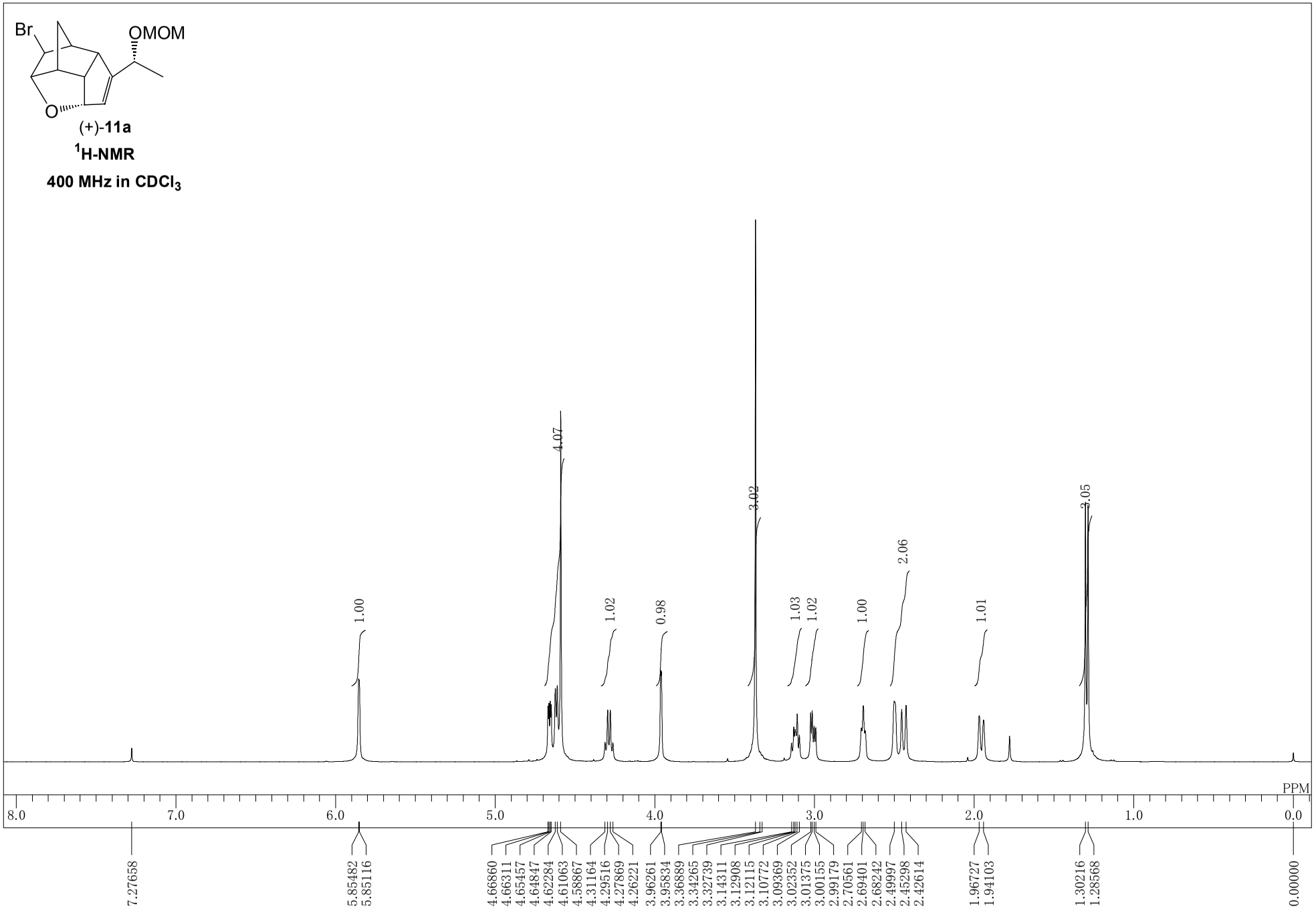
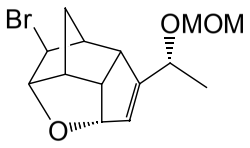
1.89649
1.89283
1.40711
1.39063
1.37172
0.00000

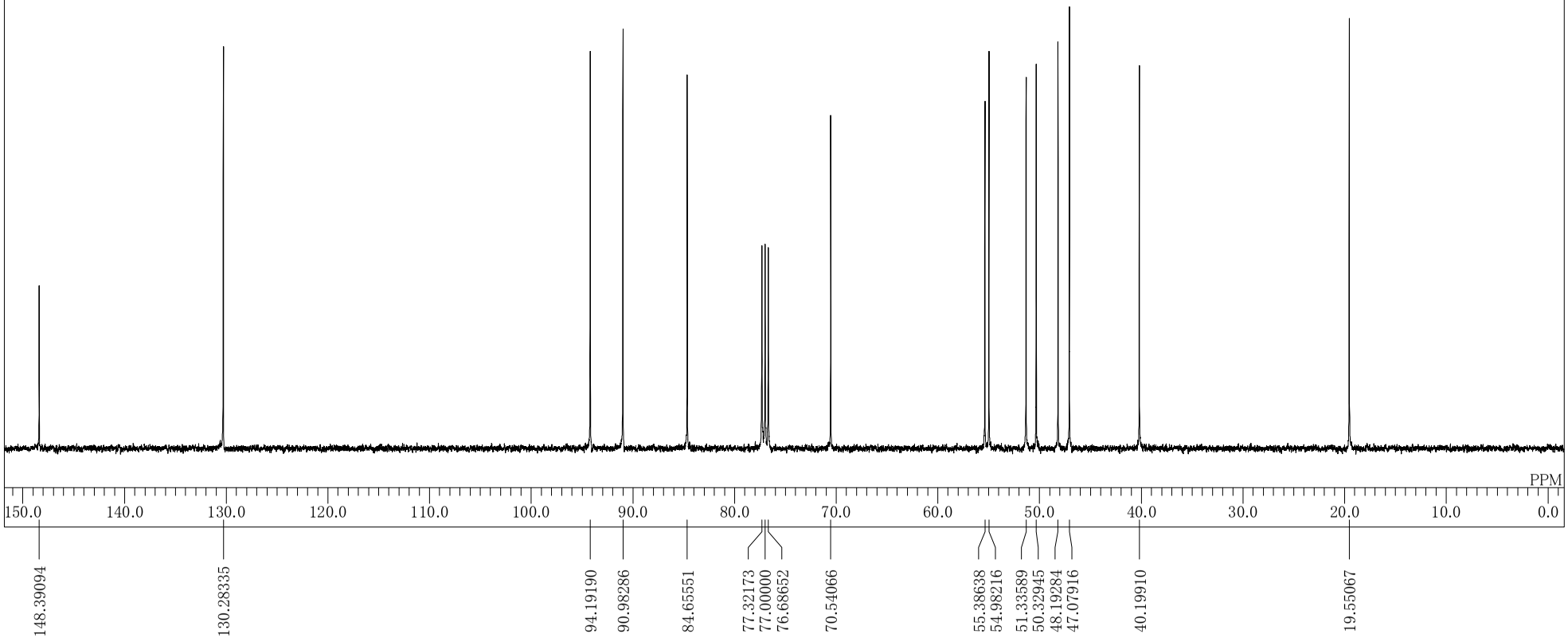

Br
OMOM
O
(+)-11a
1H-NMR
400 MHz in CDCl3
1.00
4.07
1.02
0.98
3.02
1.03
1.02
1.00
2.06
1.01
3.05
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.27658
5.85482
5.85116
4.66860
4.66311
4.65457
4.64847
4.62284
4.61063
4.58867
4.31164
4.29516
4.27869
4.26221
3.96261
3.95834
3.36889
3.34265
3.32739
3.14311
3.12908
3.12115
3.10772
3.09369
3.02352
3.01375
3.00155
2.99179
2.70561
2.69401
2.68242
2.49997
2.45298
2.42614
1.96727
1.94103
1.30216
1.28568
0.00000

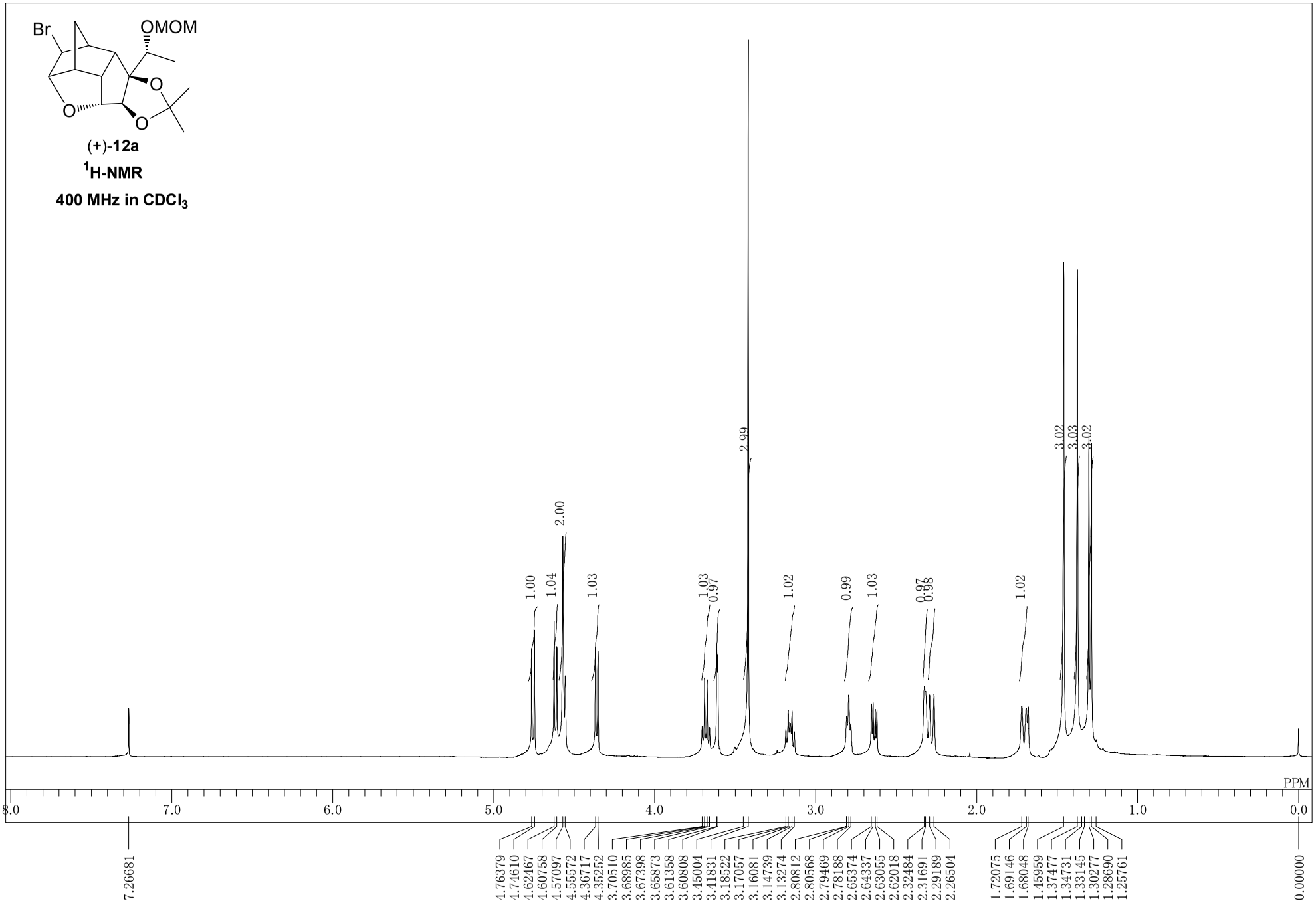


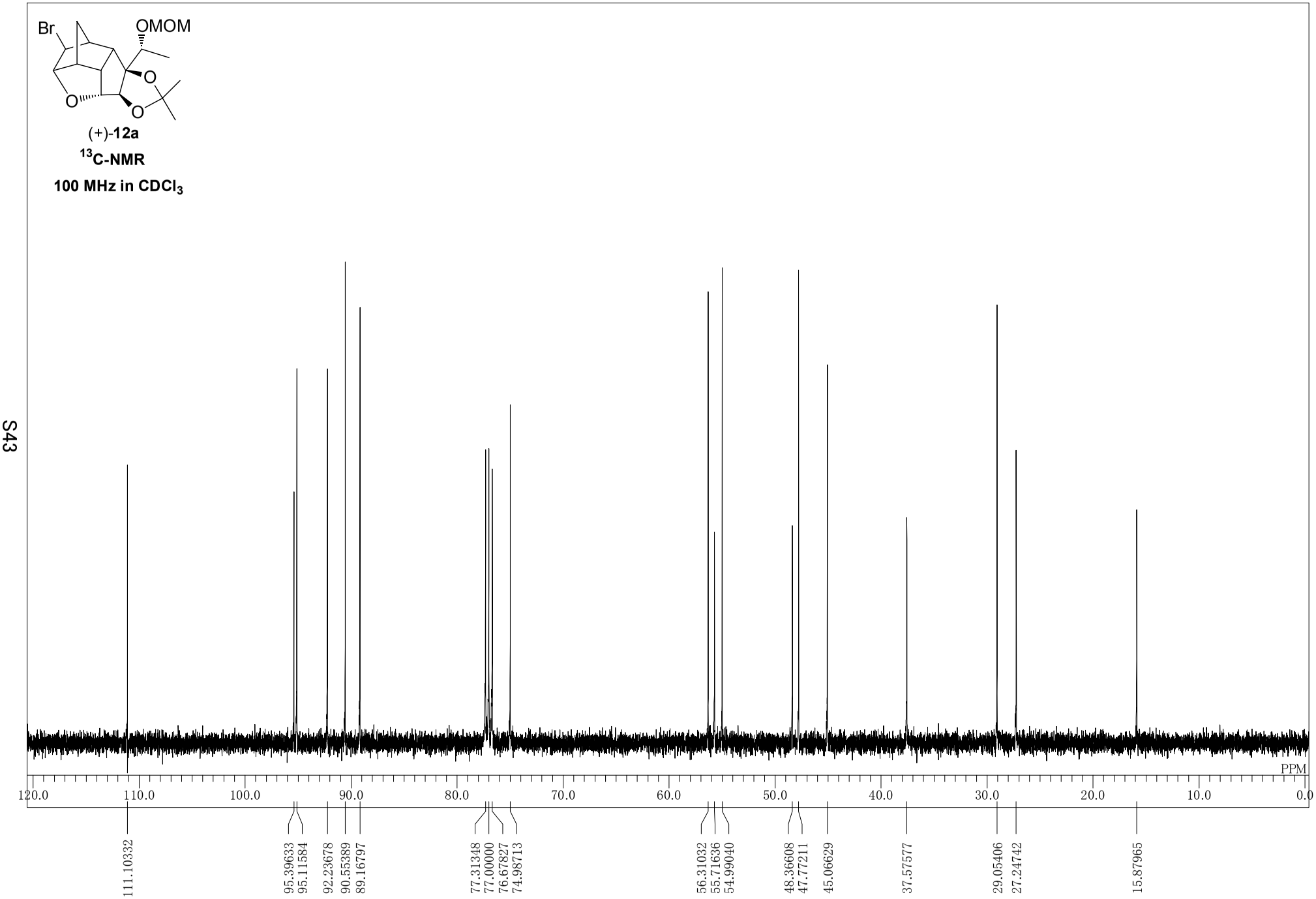
(+)-**11a**

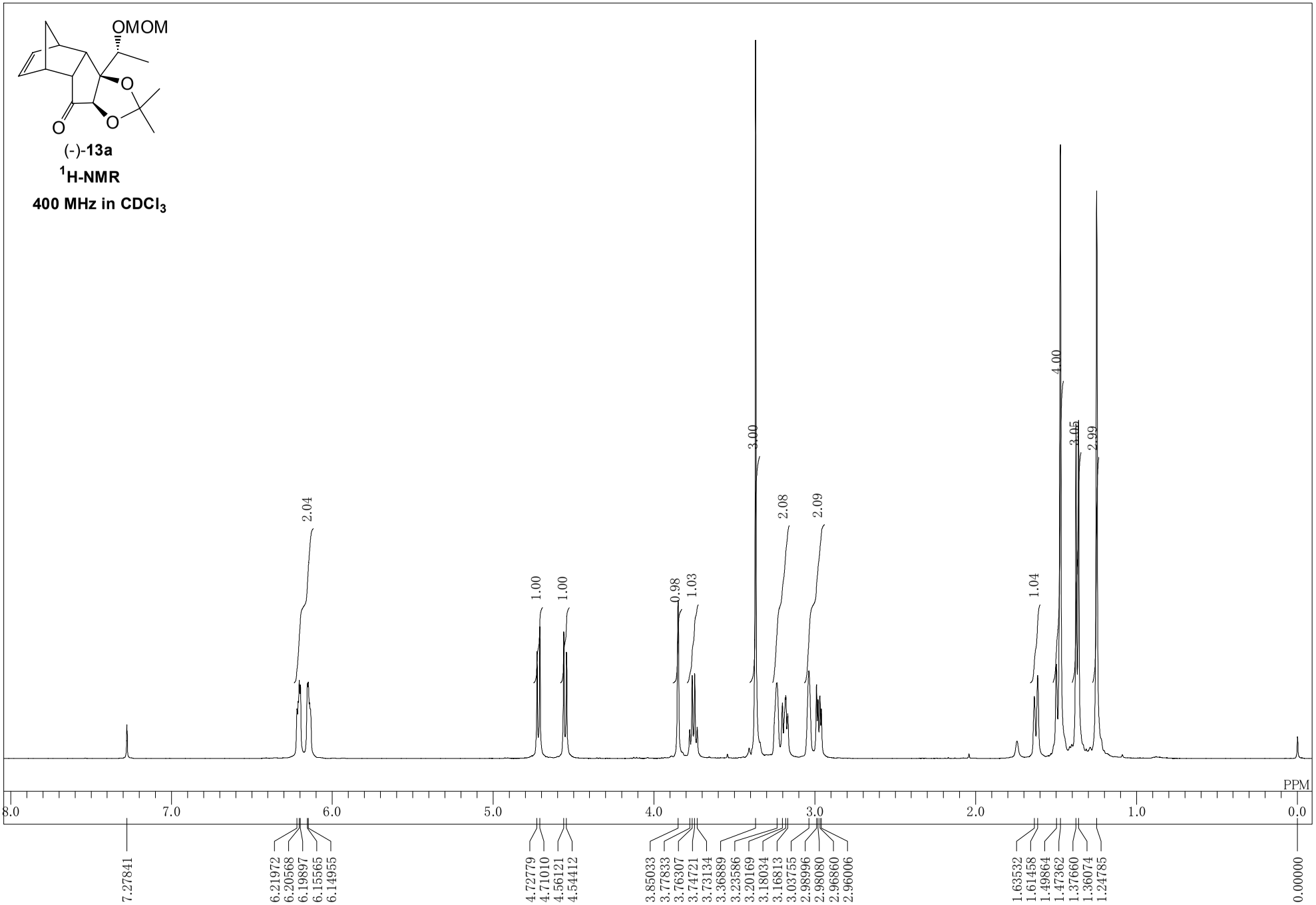
^{13}C-NMR

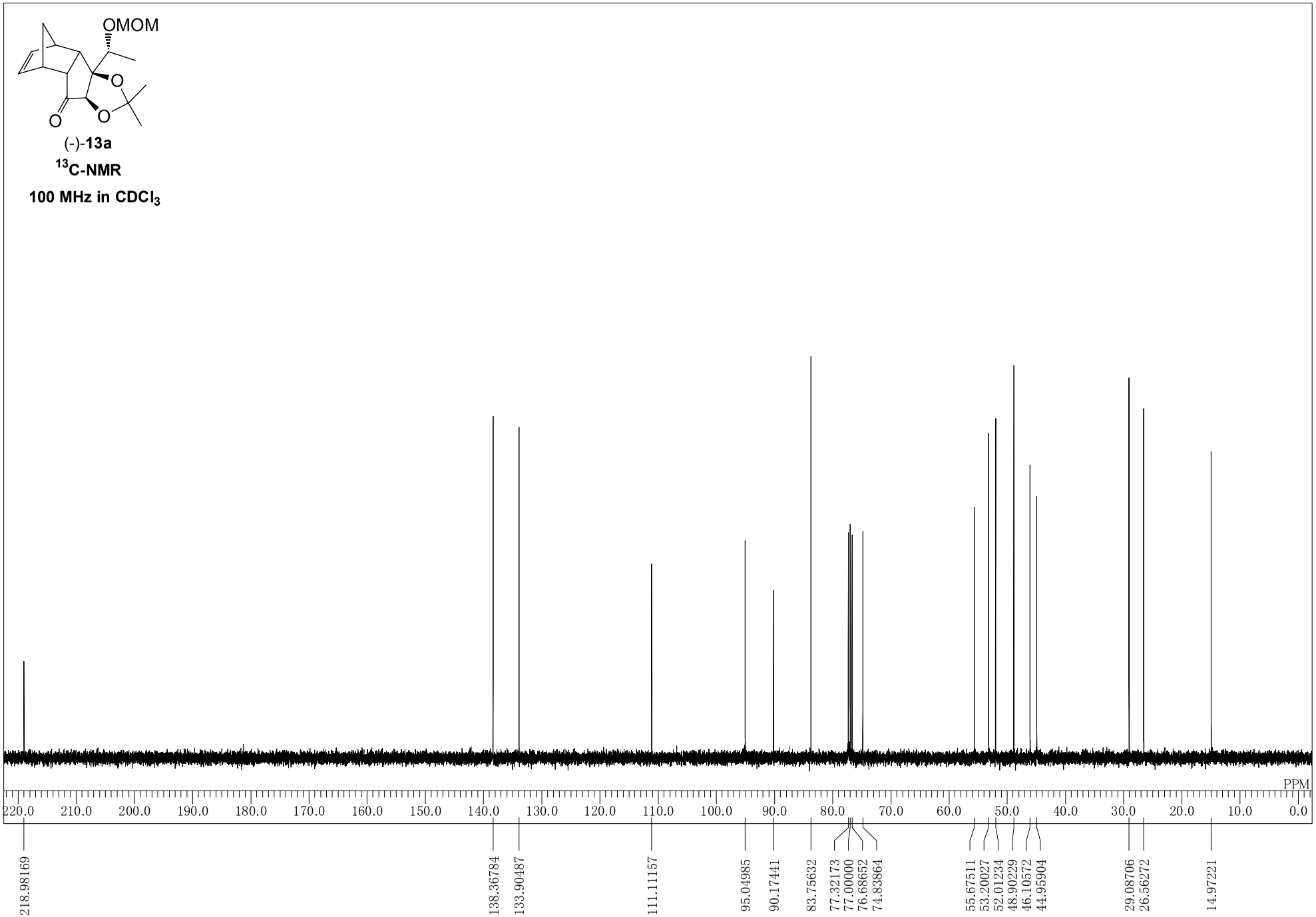
100 MHz in $CDCl_3$

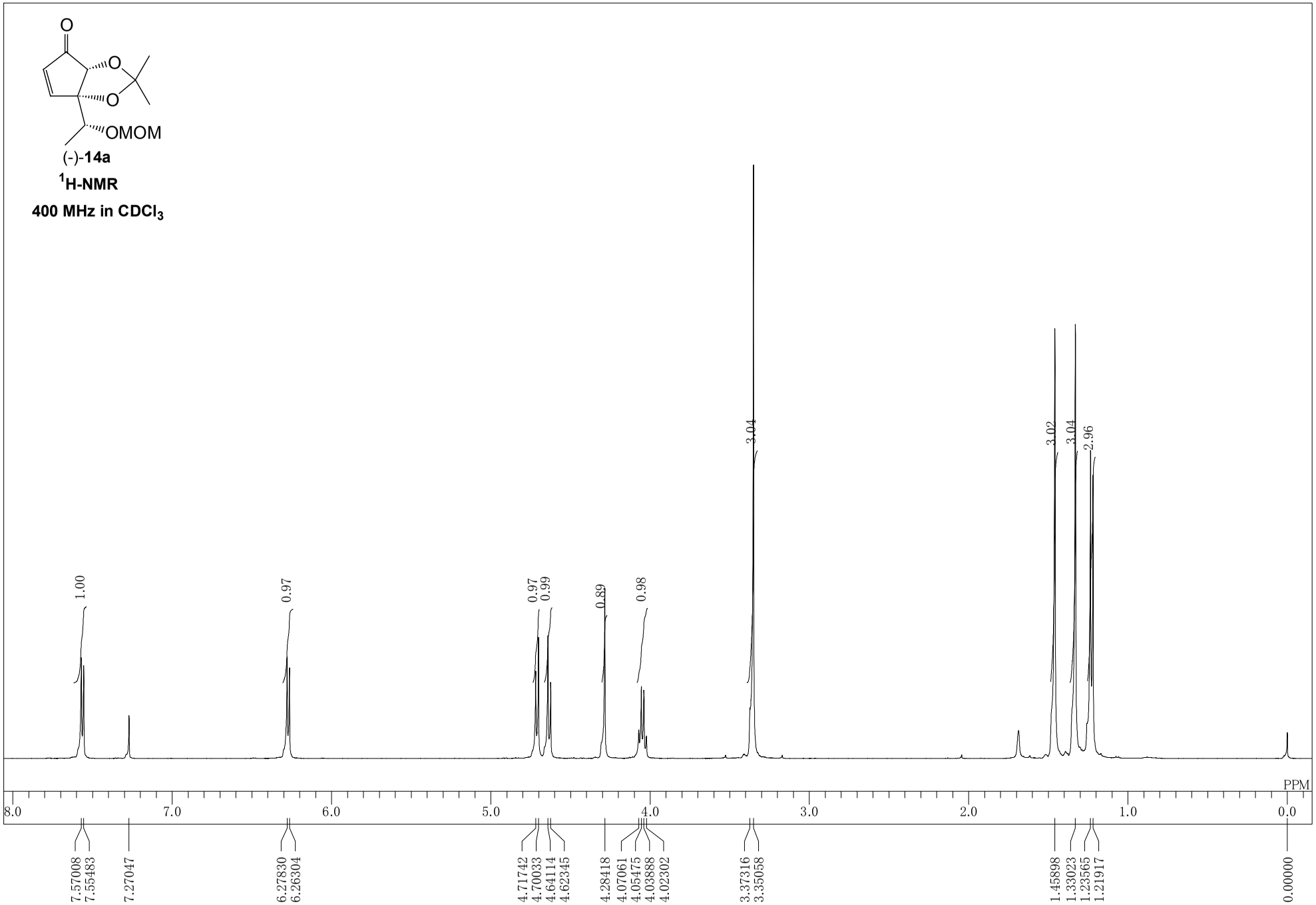


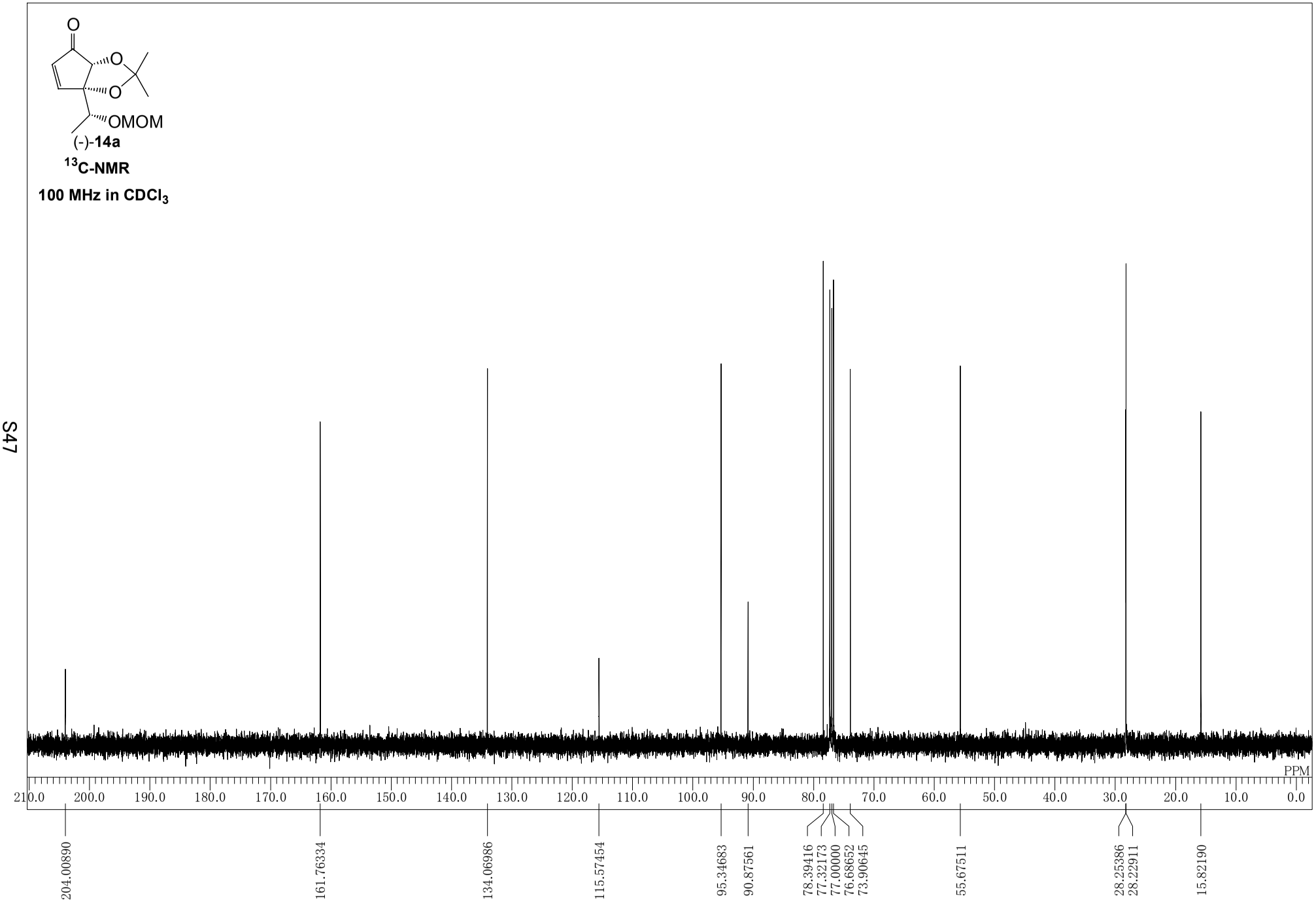

Br
OMOM
O
O
O
(+)-12a
1H-NMR
400 MHz in CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26681
4.76379
4.74610
4.62467
4.60758
4.57097
4.55572
4.36717
4.35252
3.70510
3.68985
3.67398
3.65873
3.61358
3.60808
3.45004
3.41831
3.18522
3.17057
3.16081
3.14739
3.13274
2.80812
2.80568
2.79469
2.78188
2.65374
2.64337
2.63055
2.62018
2.32484
2.31691
2.29189
2.26504
1.72075
1.69146
1.68048
1.45959
1.37477
1.34731
1.33145
1.30277
1.28690
1.25761
0.00000
1.00
1.04
2.00
1.03
1.03
0.97
2.99
1.02
0.99
1.03
0.97
0.98
1.02
3.02
3.03
3.02

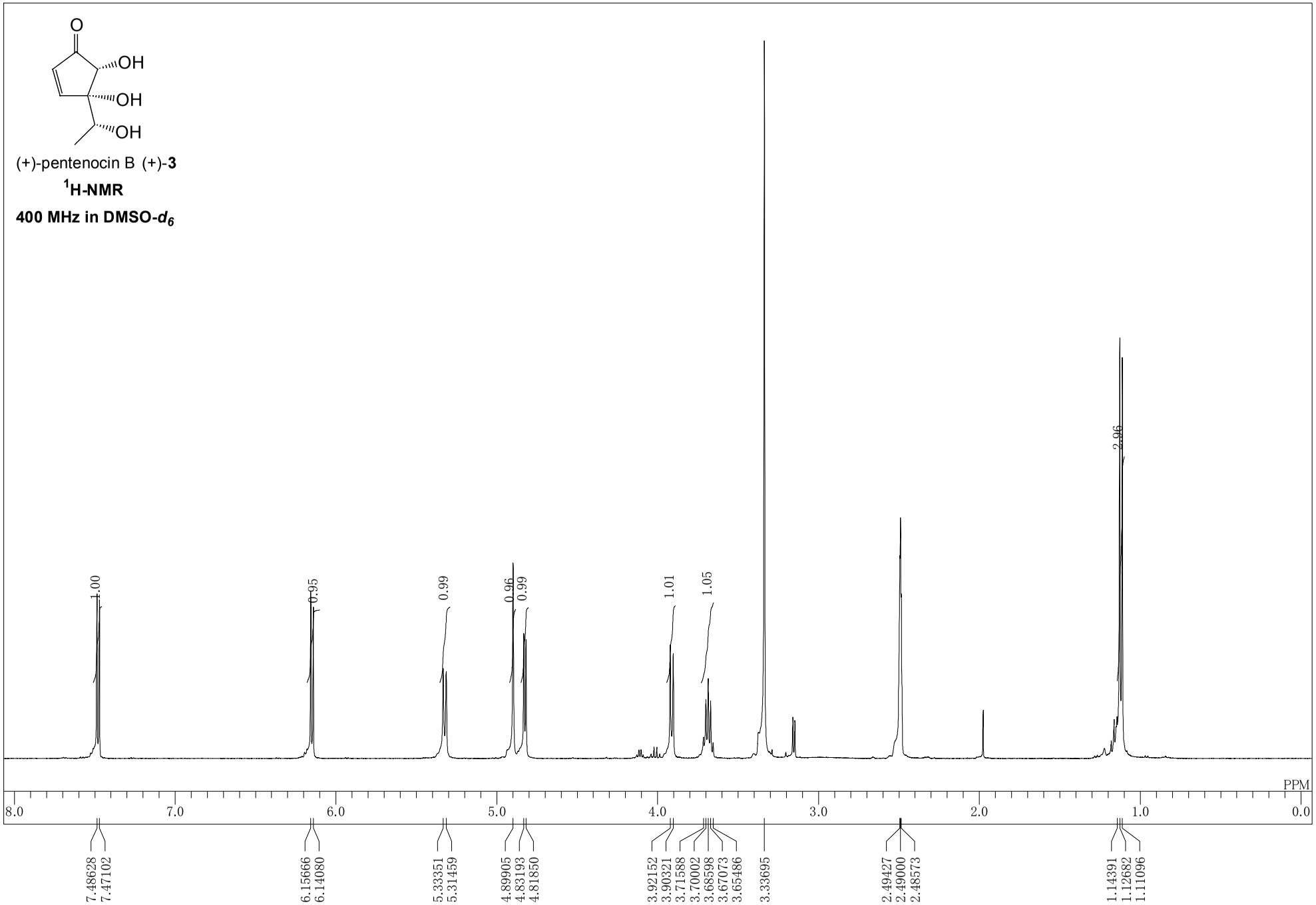

Br
OMOM
O
O
O
(+)-12a
13C-NMR
100 MHz in CDCl3
PPM
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
111.10332
95.39633
95.11584
92.23678
90.55389
89.16797
77.31348
77.00000
76.67827
74.98713
56.31032
55.71636
54.99040
48.36608
47.77211
45.06629
37.57577
29.05406
27.24742
15.87965

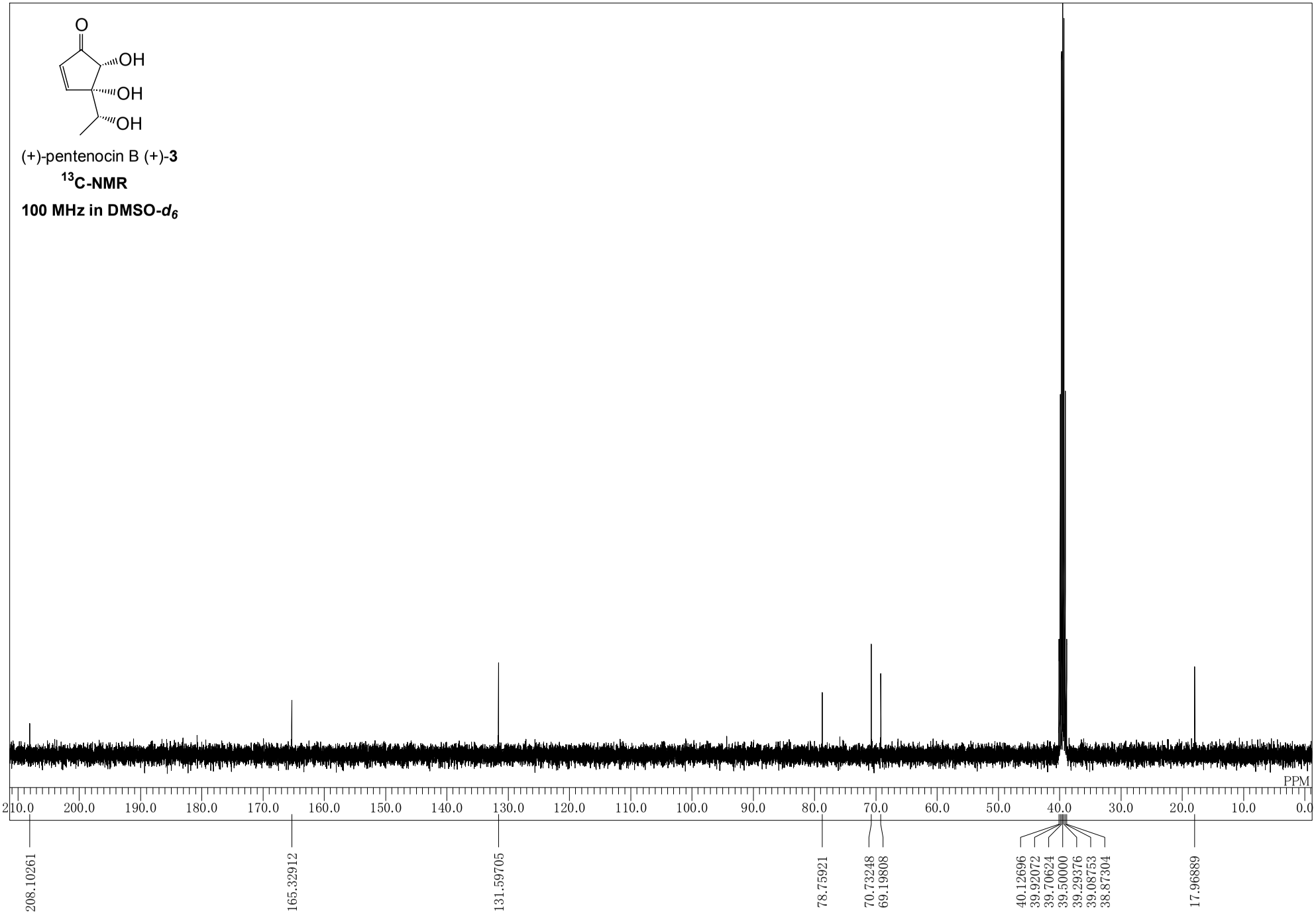

OMOM
O
O
O
(-)-13a
1H-NMR
400 MHz in CDCl3
2.04
1.00
1.00
0.98
1.03
3.00
2.08
2.09
1.04
4.00
3.05
2.99
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.27841
6.21972
6.20568
6.19897
6.15565
6.14955
4.72779
4.71010
4.56121
4.54412
3.85033
3.77833
3.76307
3.74721
3.73134
3.36889
3.23586
3.20169
3.18034
3.16813
3.03755
2.98996
2.98080
2.96860
2.96006
1.63532
1.61458
1.49864
1.47362
1.37660
1.36074
1.24785
0.00000

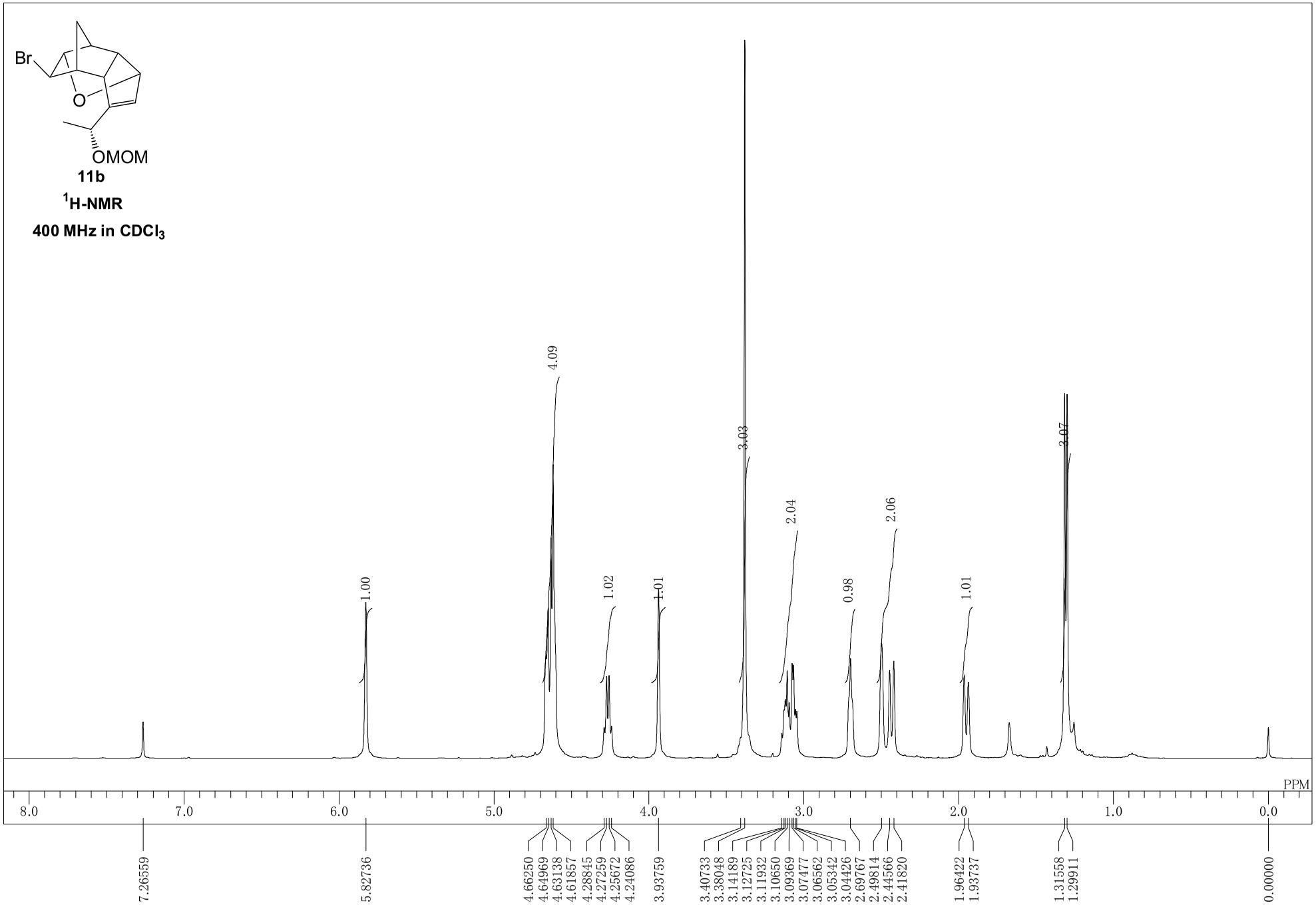

OMOM
O
O
O
(-)-13a
13C-NMR
100 MHz in CDCl3
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
218.98169
138.36784
133.90487
111.11157
95.04985
90.17441
83.75632
77.32173
77.00000
76.68652
74.83864
55.67511
53.20027
52.01234
48.90229
46.10572
44.95904
29.08706
26.56272
14.97221

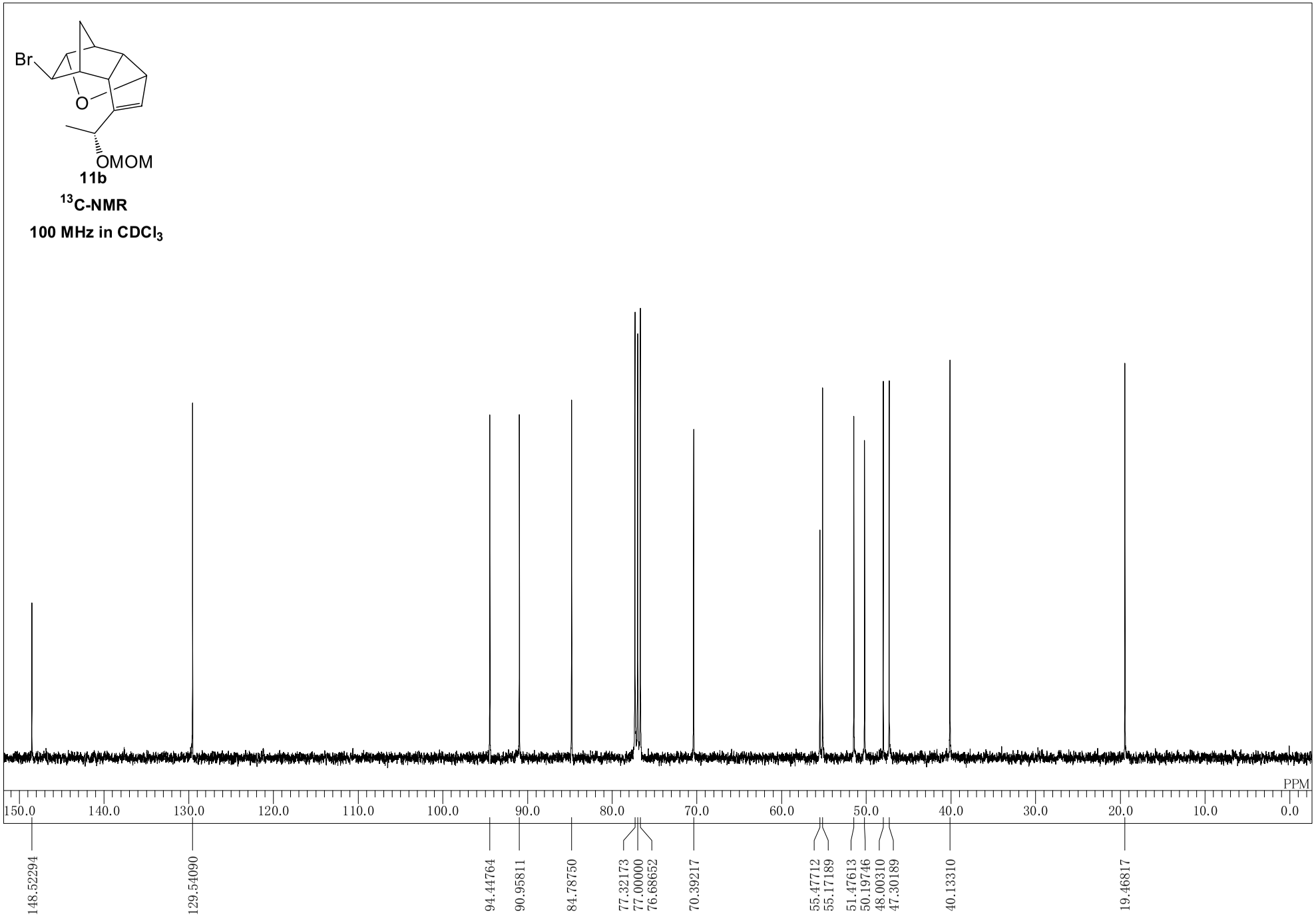

O
O
O
OMOM
(-)-14a
1H-NMR
400 MHz in CDCl3
1.00
0.97
0.97
0.99
0.89
0.98
3.04
3.02
3.04
2.96
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.57008
7.55483
7.27047
6.27830
6.26304
4.71742
4.70033
4.64114
4.62345
4.28418
4.07061
4.05475
4.03888
4.02302
3.37316
3.35058
1.45898
1.33023
1.23565
1.21917
0.00000

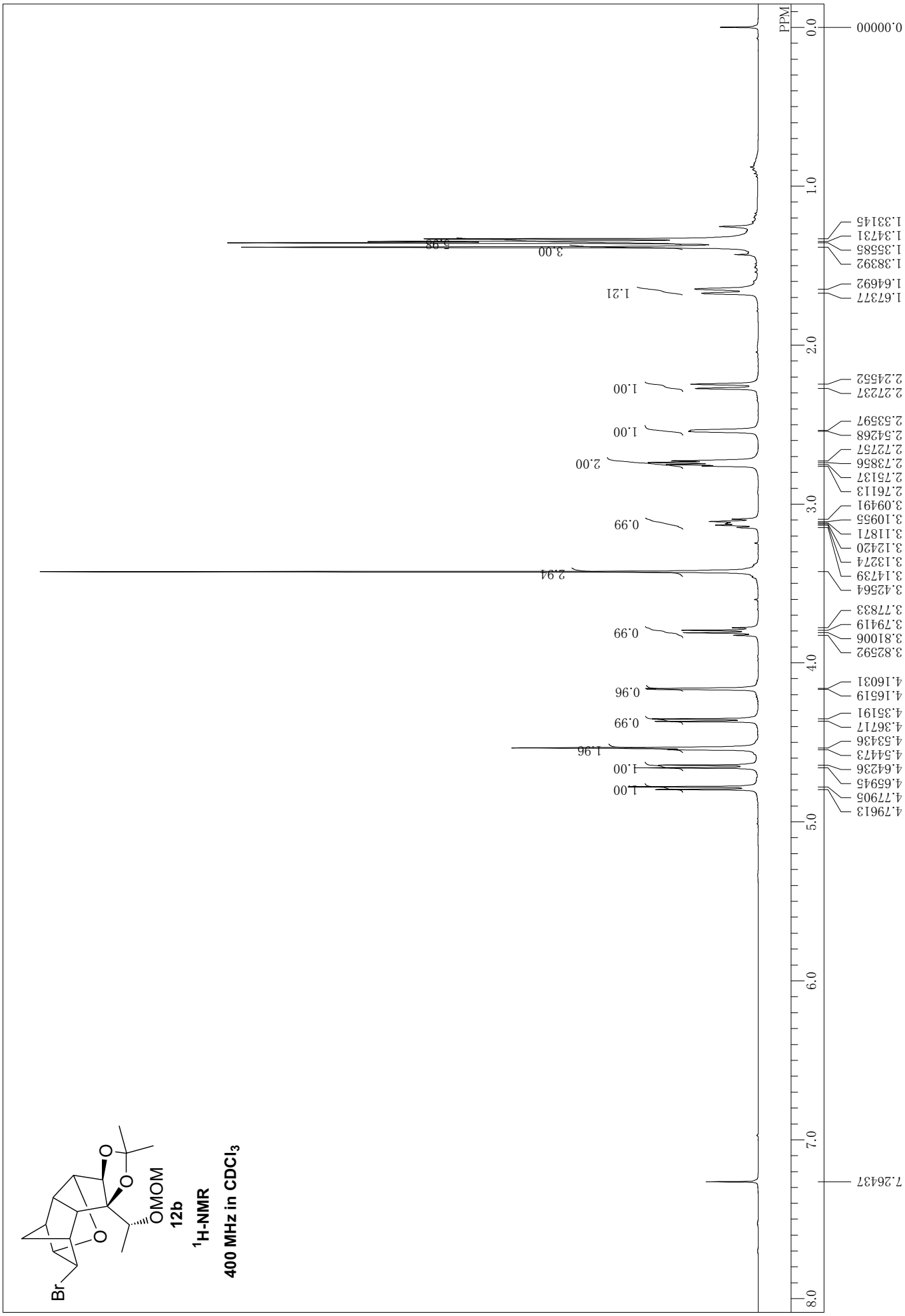

O
O
O
OMOM
(-)-14a
13C-NMR
100 MHz in CDCl3
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
204.00890
161.76334
134.06986
115.57454
95.34683
90.87561
78.39416
77.32173
77.00000
76.68652
73.90645
55.67511
28.25386
28.22911
15.82190

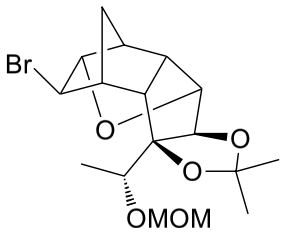

O
OH
OH
OH
(+)-pentenocin B (+)-3
1H-NMR
400 MHz in DMSO-d6
1.00
0.95
0.99
0.96
0.99
1.01
1.05
2.96
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.48628
7.47102
6.15666
6.14080
5.33351
5.31459
4.89905
4.83193
4.81850
3.92152
3.90321
3.71588
3.70002
3.68598
3.67073
3.65486
3.33695
2.49427
2.49000
2.48573
1.14391
1.12682
1.11096


O
OH
OH
OH
(+)-pentenocin B (+)-3
13C-NMR
100 MHz in DMSO-d6
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
208.10261
165.32912
131.59705
78.75921
70.73248
69.19808
40.12696
39.92072
39.70624
39.50000
39.29376
39.08753
38.87304
17.96889


Br
O
OMOM
11b
1H-NMR
400 MHz in CDCl3
1.00
4.09
1.02
1.01
3.03
2.04
0.98
2.06
1.01
3.07
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26559
5.82736
4.66250
4.64969
4.63138
4.61857
4.28845
4.27259
4.25672
4.24086
3.93759
3.40733
3.38048
3.14189
3.12725
3.11932
3.10650
3.09369
3.07477
3.06562
3.05342
3.04426
2.69767
2.49814
2.44566
2.41820
1.96422
1.93737
1.31558
1.29911
0.00000


Br
O
OMOM
11b
13C-NMR
100 MHz in CDCl3
PPM
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
148.52294
129.54090
94.44764
90.95811
84.78750
77.32173
77.00000
76.68652
70.39217
55.47712
55.17189
51.47613
50.19746
48.00310
47.30189
40.13310
19.46817

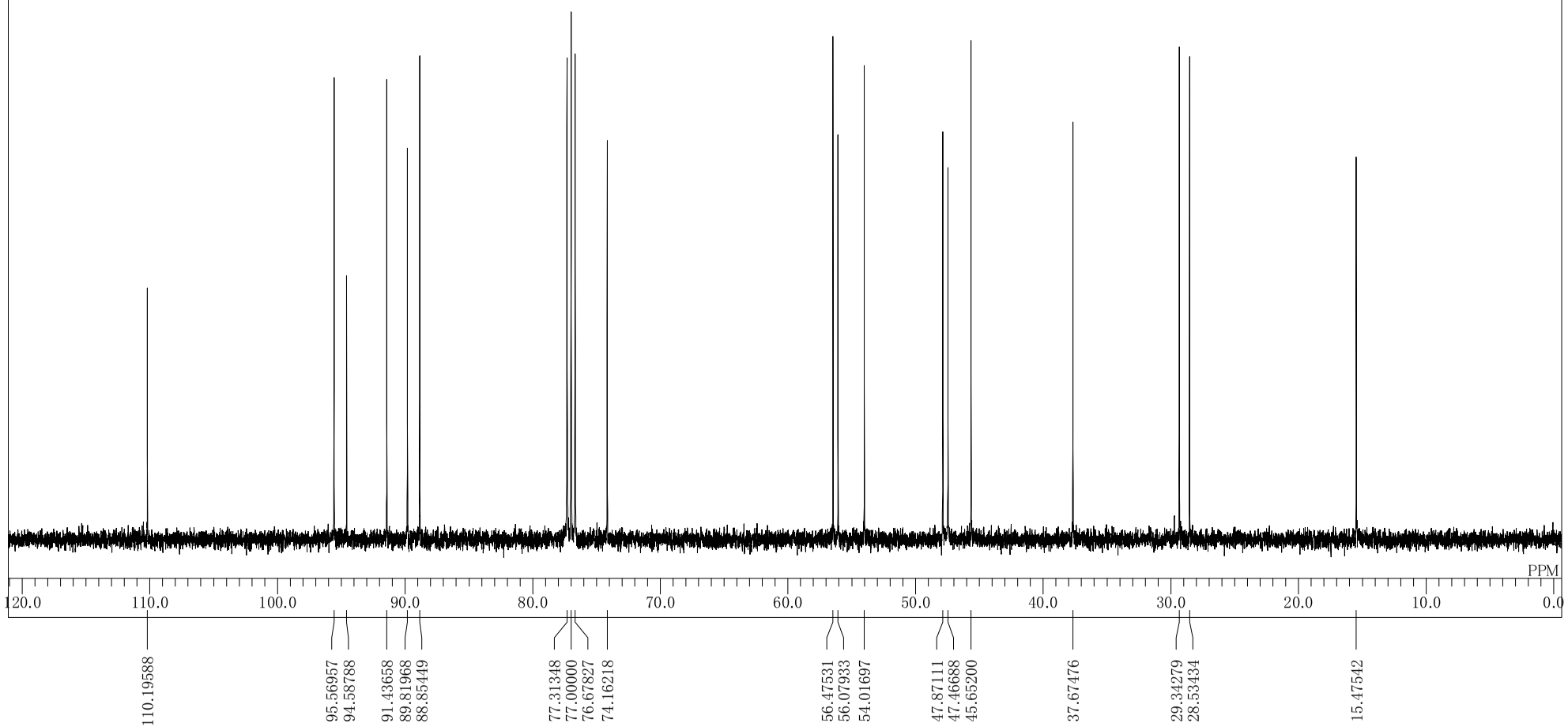

Br
O
O
O
OMOM
12b
1H-NMR
400 MHz in CDCl3
PPM
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0.00000
1.33145
1.34731
1.35585
1.38392
1.64692
1.67377
2.24552
2.27237
2.53597
2.54268
2.72757
2.73856
2.75137
2.76113
3.09491
3.10955
3.11871
3.12420
3.13274
3.14739
3.42564
3.77833
3.79419
3.81006
3.82592
4.16031
4.16519
4.35191
4.36717
4.53436
4.54473
4.64236
4.65945
4.77905
4.79613
7.26437
1.00
1.00
1.96
0.99
0.96
0.99
1.00
2.94
0.99
2.00
1.00
1.00
1.21
3.00
5.98

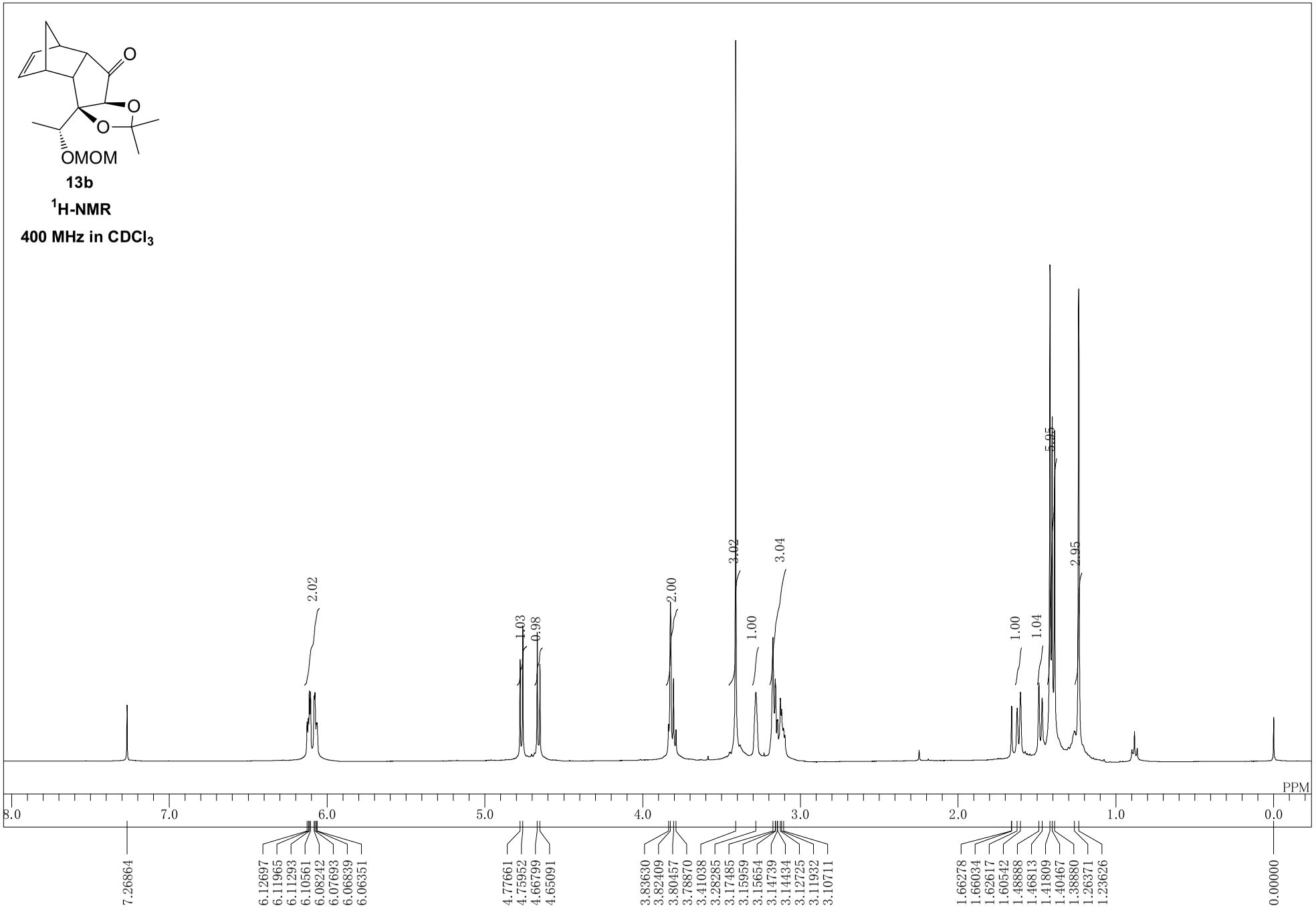


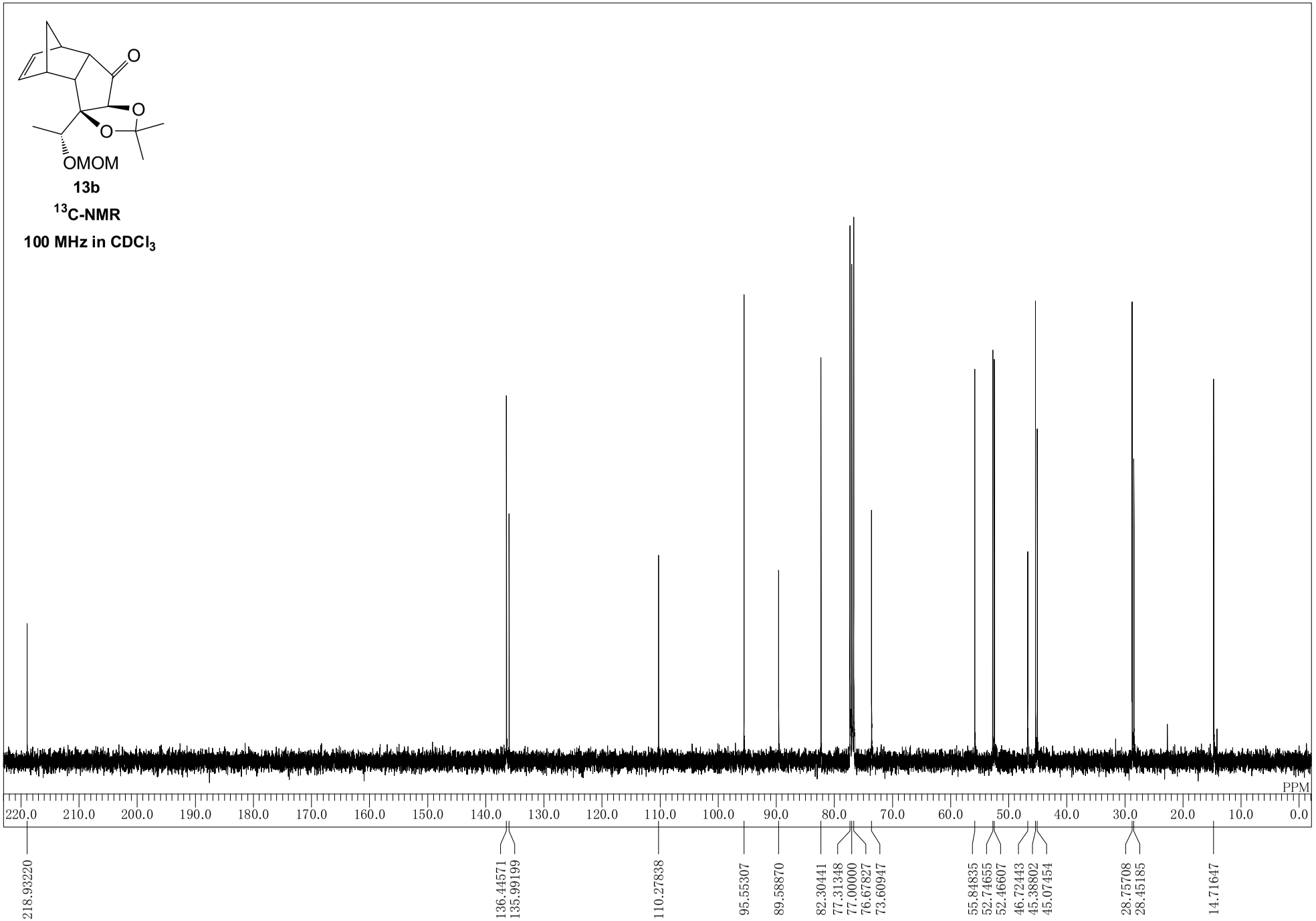
12b

^{13}C-NMR

100 MHz in $CDCl_3$




OMOM
13b
1H-NMR
400 MHz in CDCl3
2.02
1.03
0.98
2.00
3.02
1.00
3.04
1.00
1.04
5.95
2.95
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26864
6.12697
6.11965
6.11293
6.10561
6.08242
6.07693
6.06839
6.06351
4.77661
4.75952
4.66799
4.65091
3.83630
3.82409
3.80457
3.78870
3.41038
3.28285
3.17485
3.15959
3.15654
3.14739
3.14434
3.12725
3.11932
3.10711
1.66278
1.66034
1.62617
1.60542
1.48888
1.46813
1.41809
1.40467
1.38880
1.26371
1.23626
0.00000


OMOM
13b
13C-NMR
100 MHz in CDCl3
PPM
220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
218.93220
136.44571
135.99199
110.27838
95.55307
89.58870
82.30441
77.31348
77.00000
76.67827
73.60947
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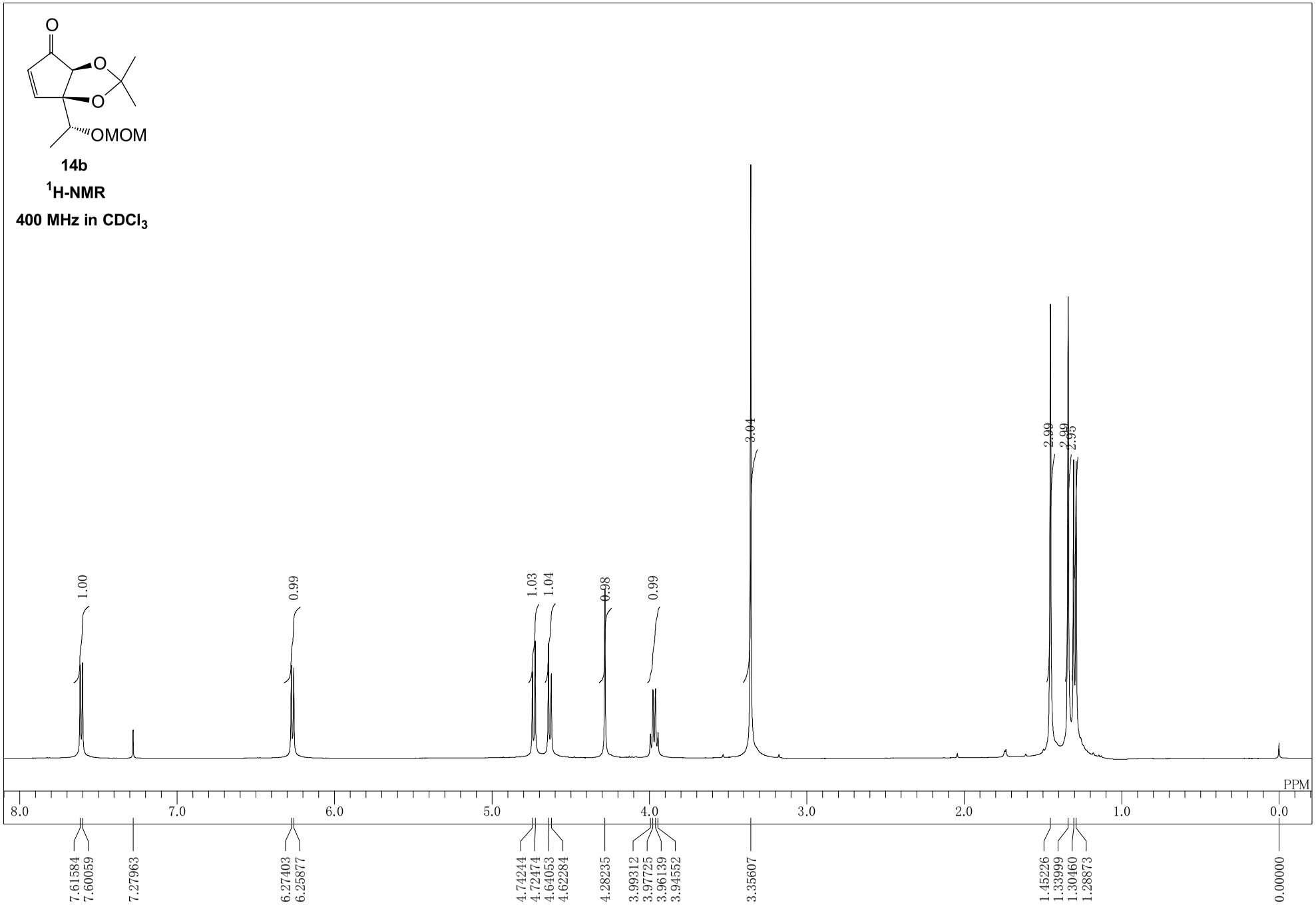
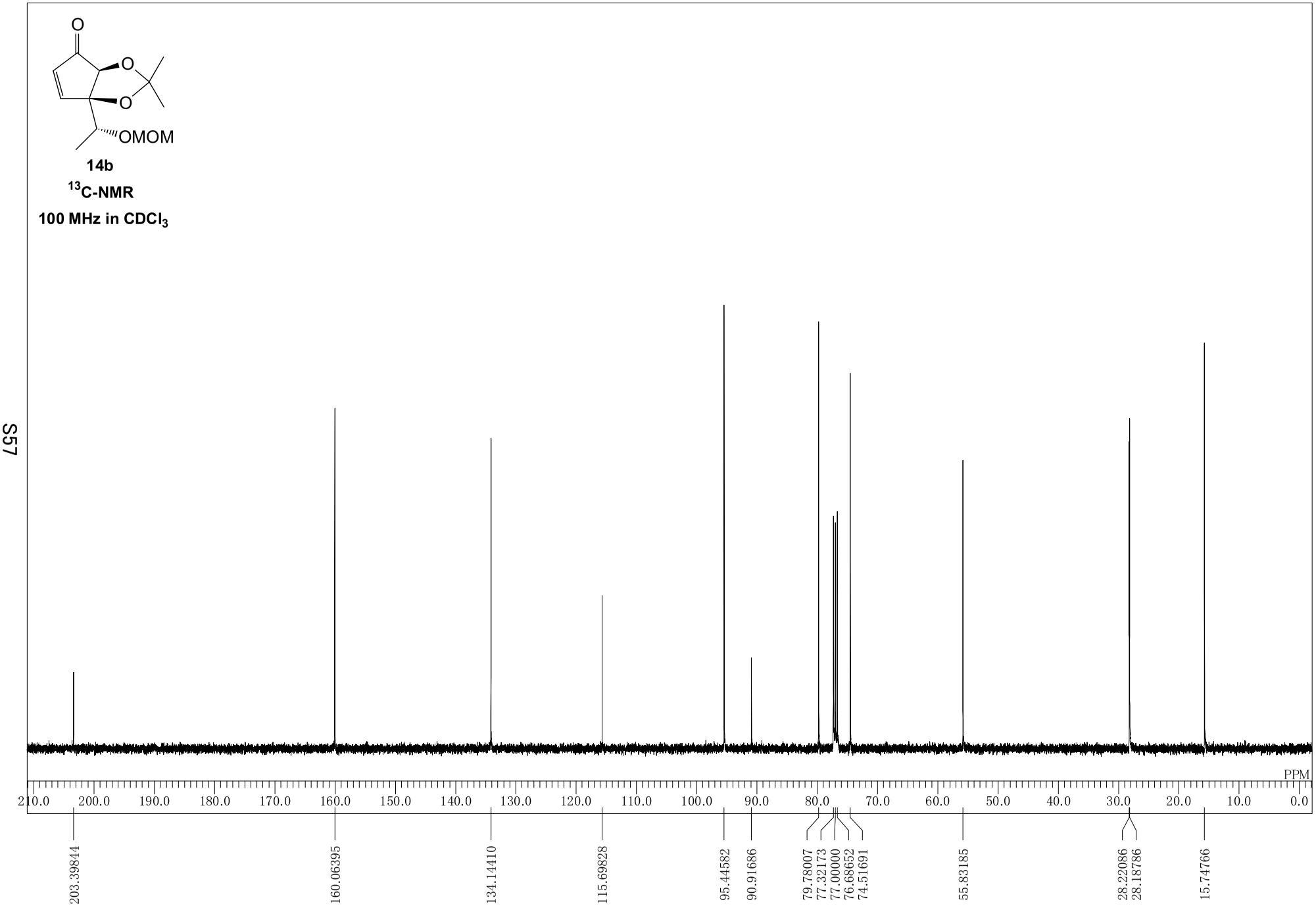
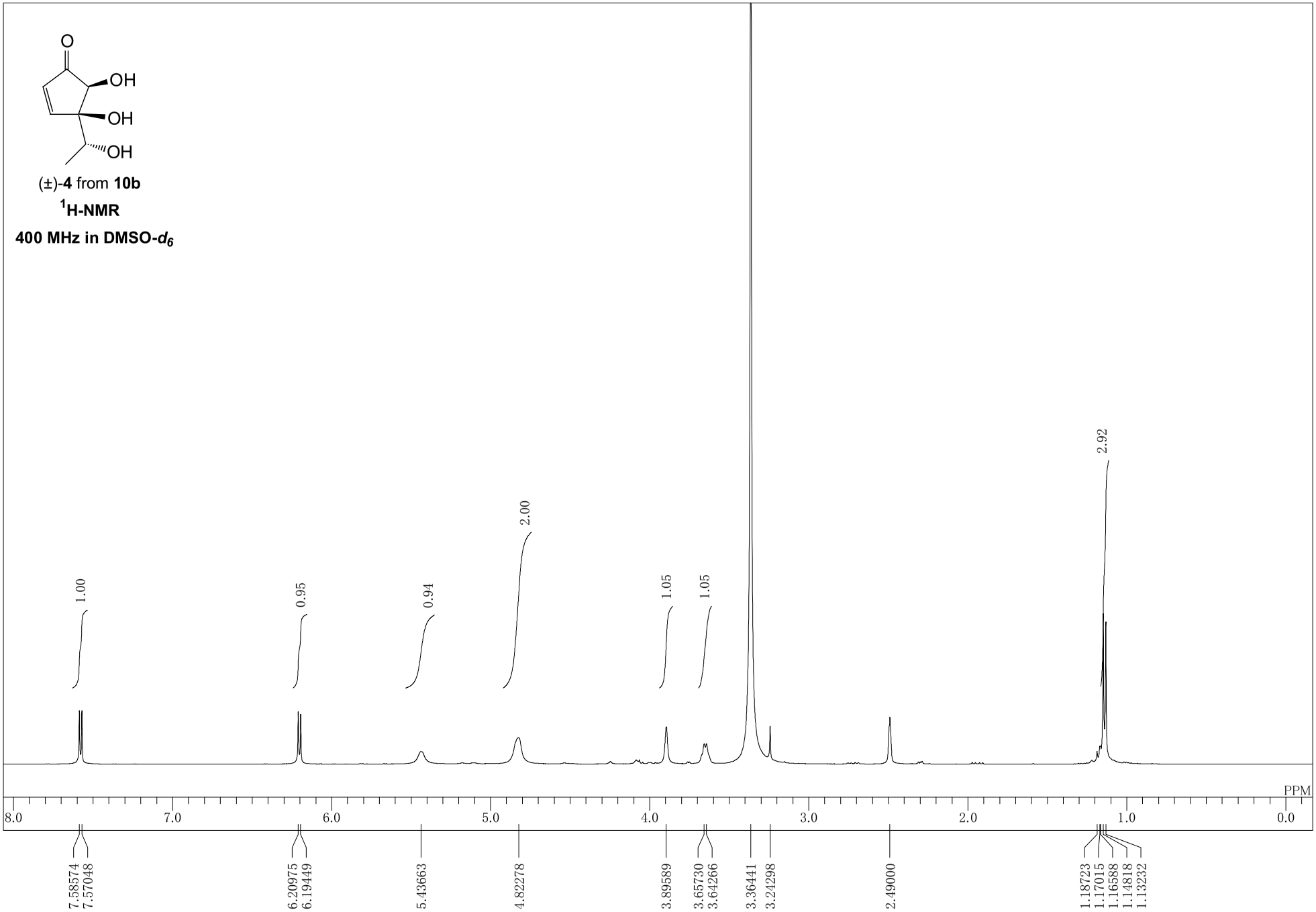
52.74655
52.46607
46.72443
45.38802
45.07454
28.75708
28.45185
14.71647


14b
1H-NMR
400 MHz in CDCl3
OMOM
1.00
0.99
1.03
1.04
0.98
0.99
3.04
2.99
2.99
2.95
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.61584
7.60059
7.27963
6.27403
6.25877
4.74244
4.72474
4.64053
4.62284
4.28235
3.99312
3.97725
3.96139
3.94552
3.35607
1.45226
1.33999
1.30460
1.28873
0.00000


O
O
O
OMOM
14b
13C-NMR
100 MHz in CDCl3
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
203.39844
160.06395
134.14410
115.69828
95.44582
90.91686
79.78007
77.32173
77.00000
76.68652
74.51691
55.83185
28.22086
28.18786
15.74766


O
OH
OH
OH
(±)-4 from 10b
1H-NMR
400 MHz in DMSO-d6
1.00
0.95
0.94
2.00
1.05
1.05
2.92
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.58574
7.57048
6.20975
6.19449
5.43663
4.82278
3.89589
3.65730
3.64266
3.36441
3.24298
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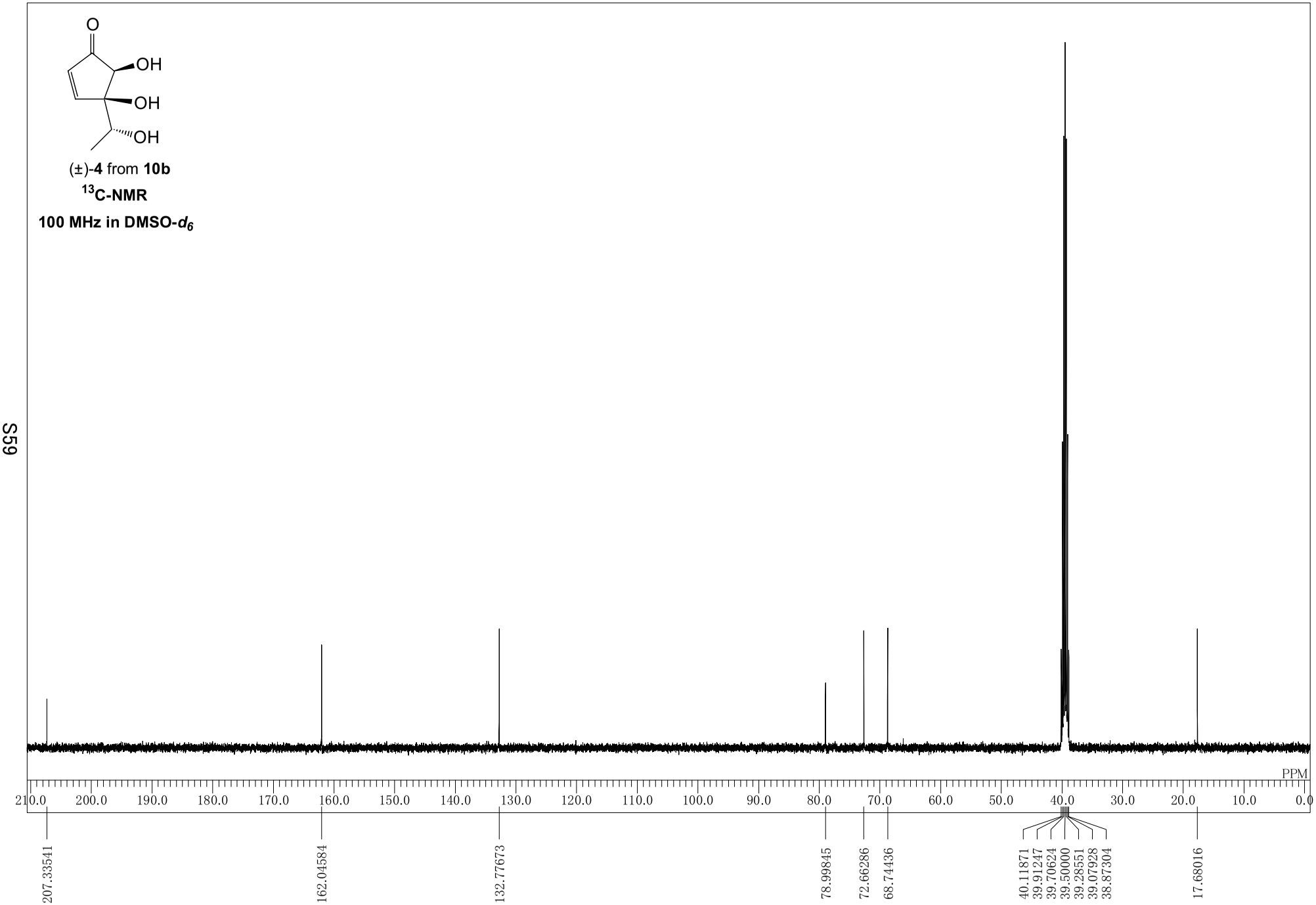
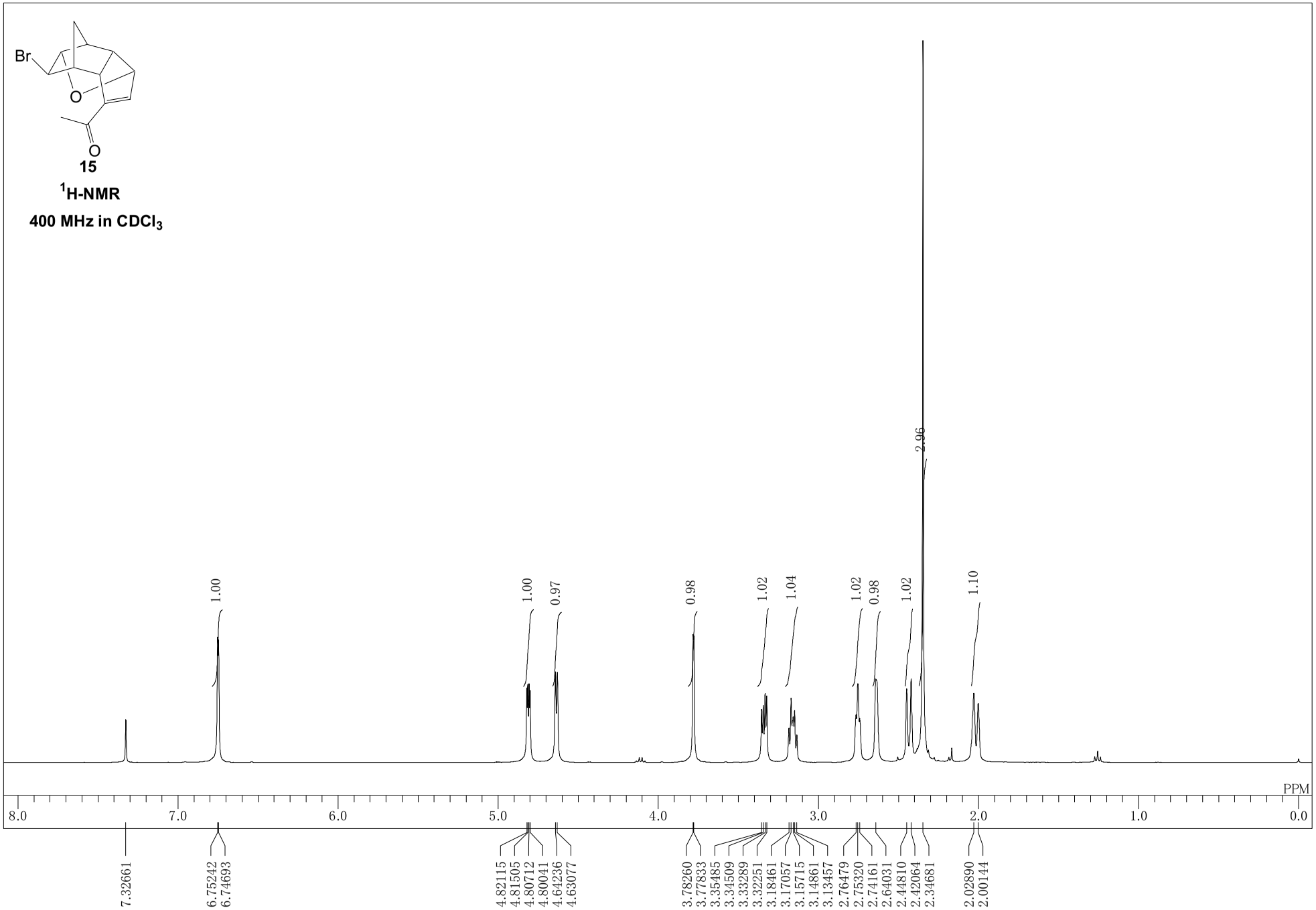
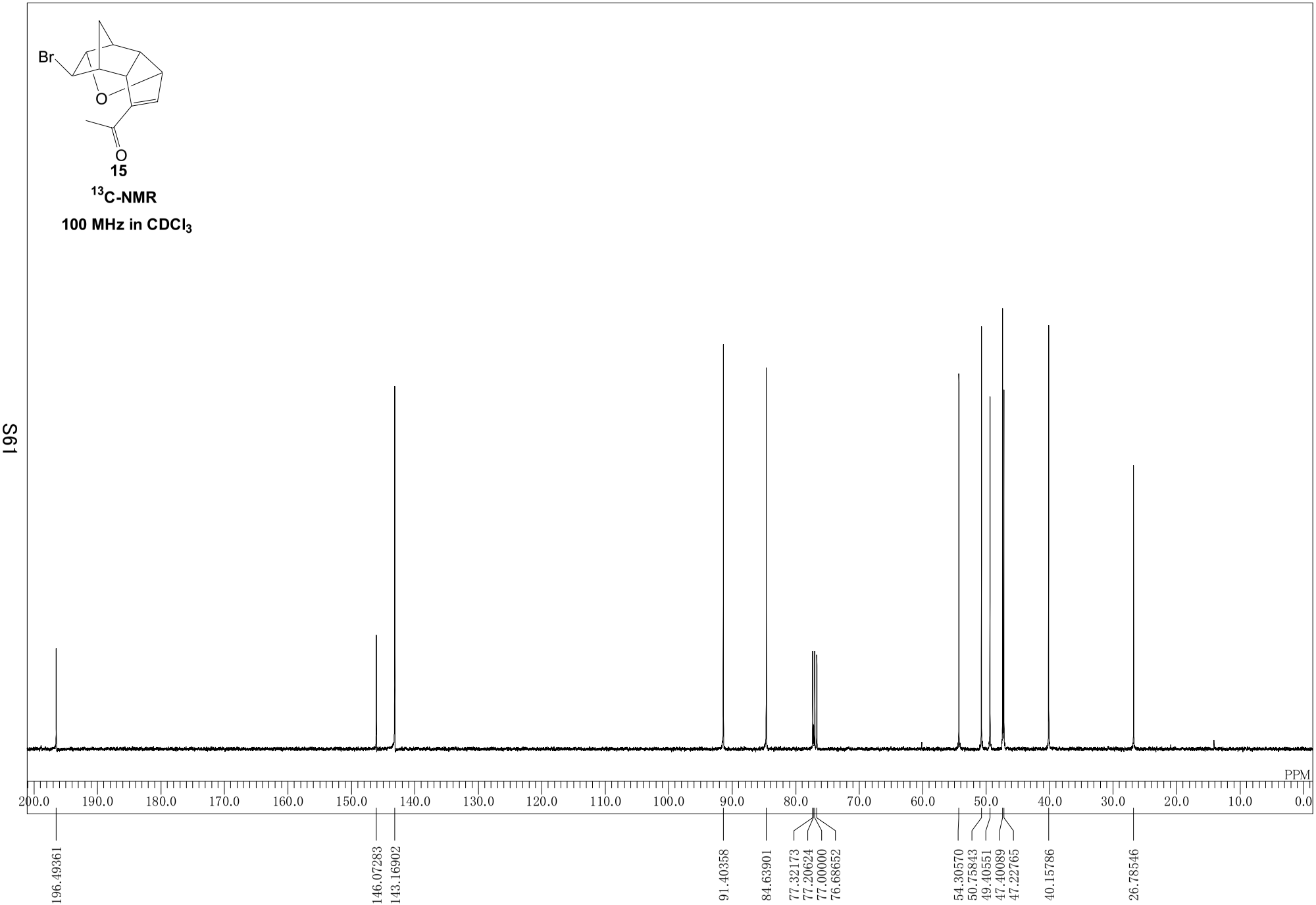
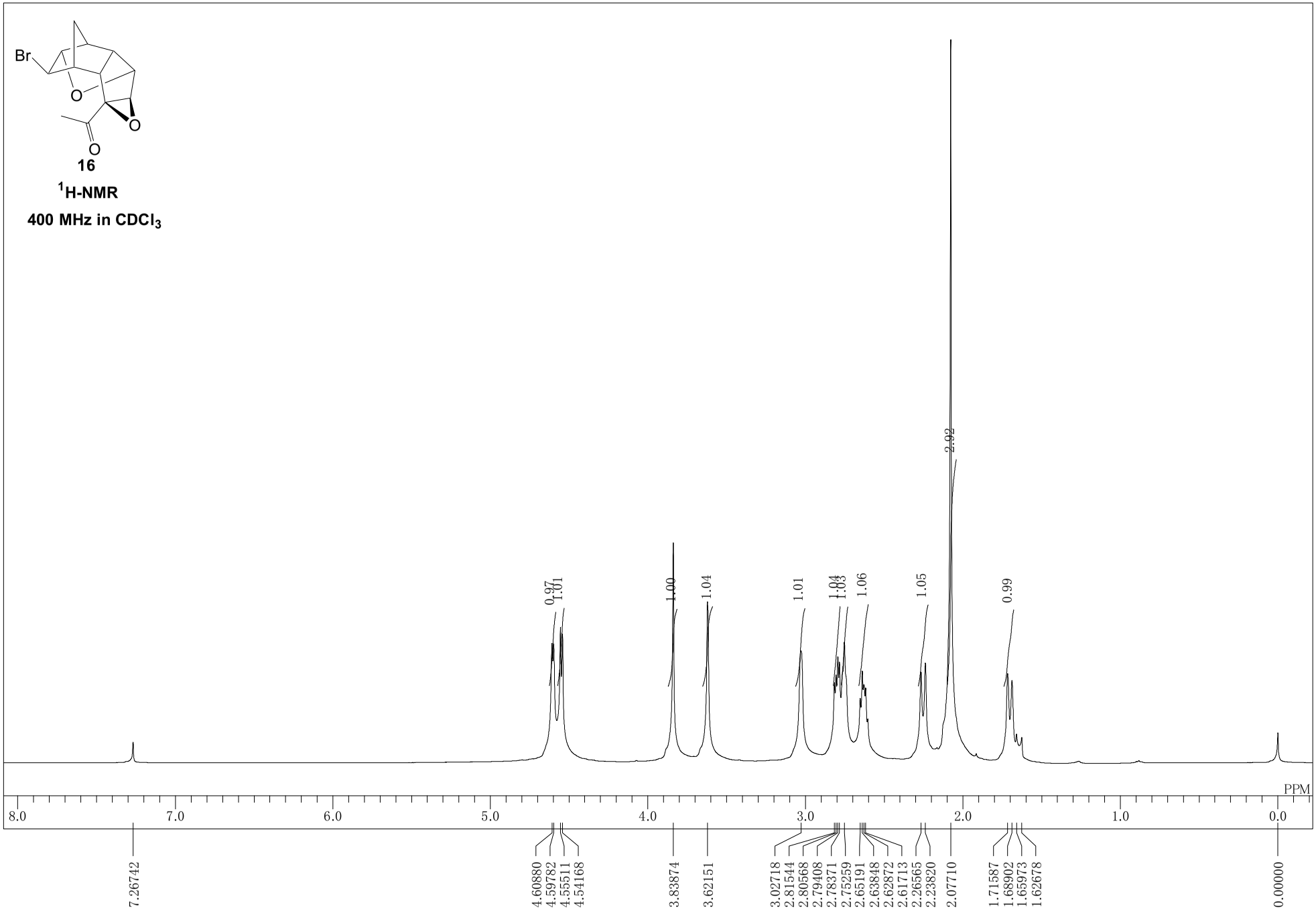
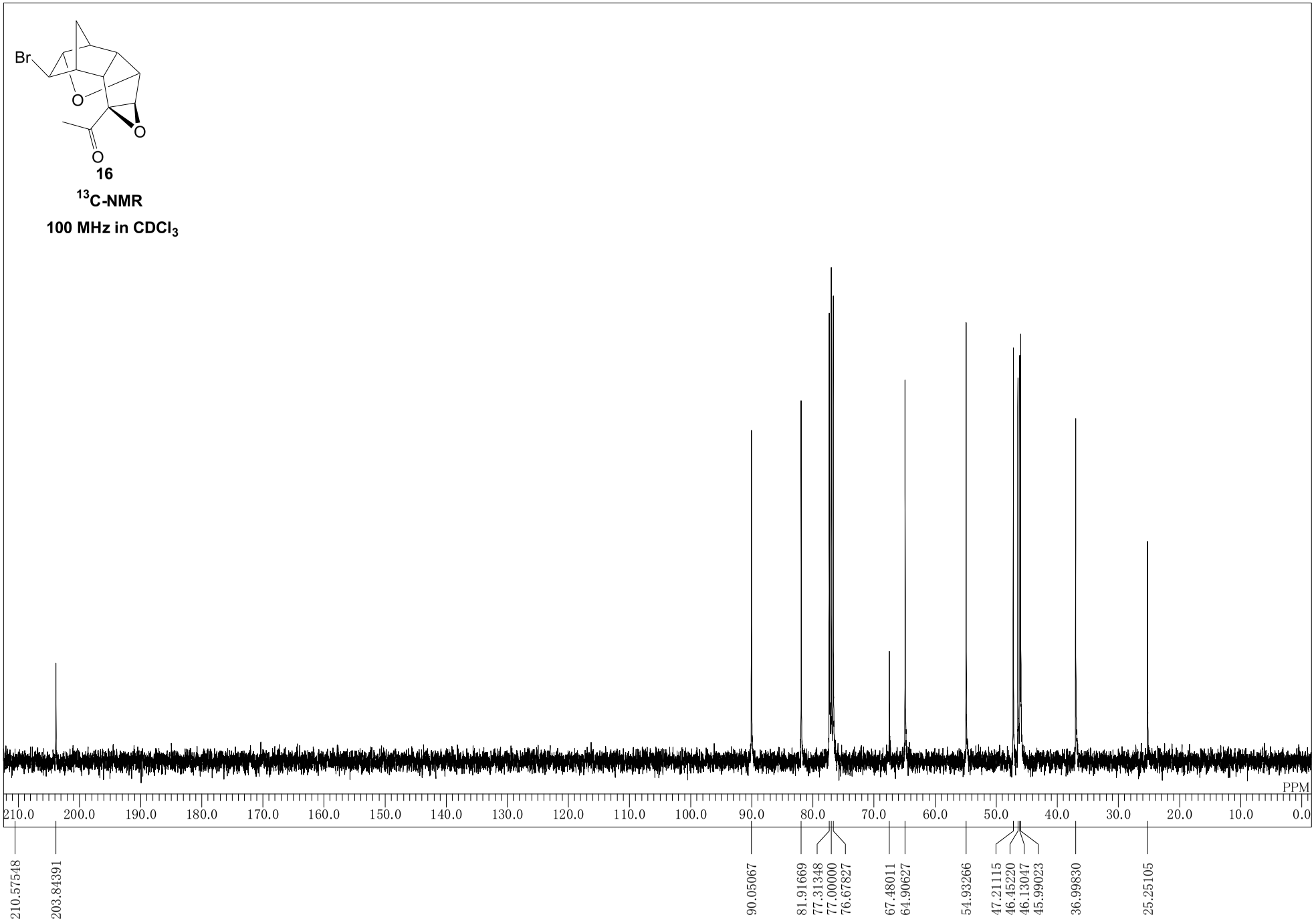
1.18723
1.17015
1.16588
1.14818
1.13232

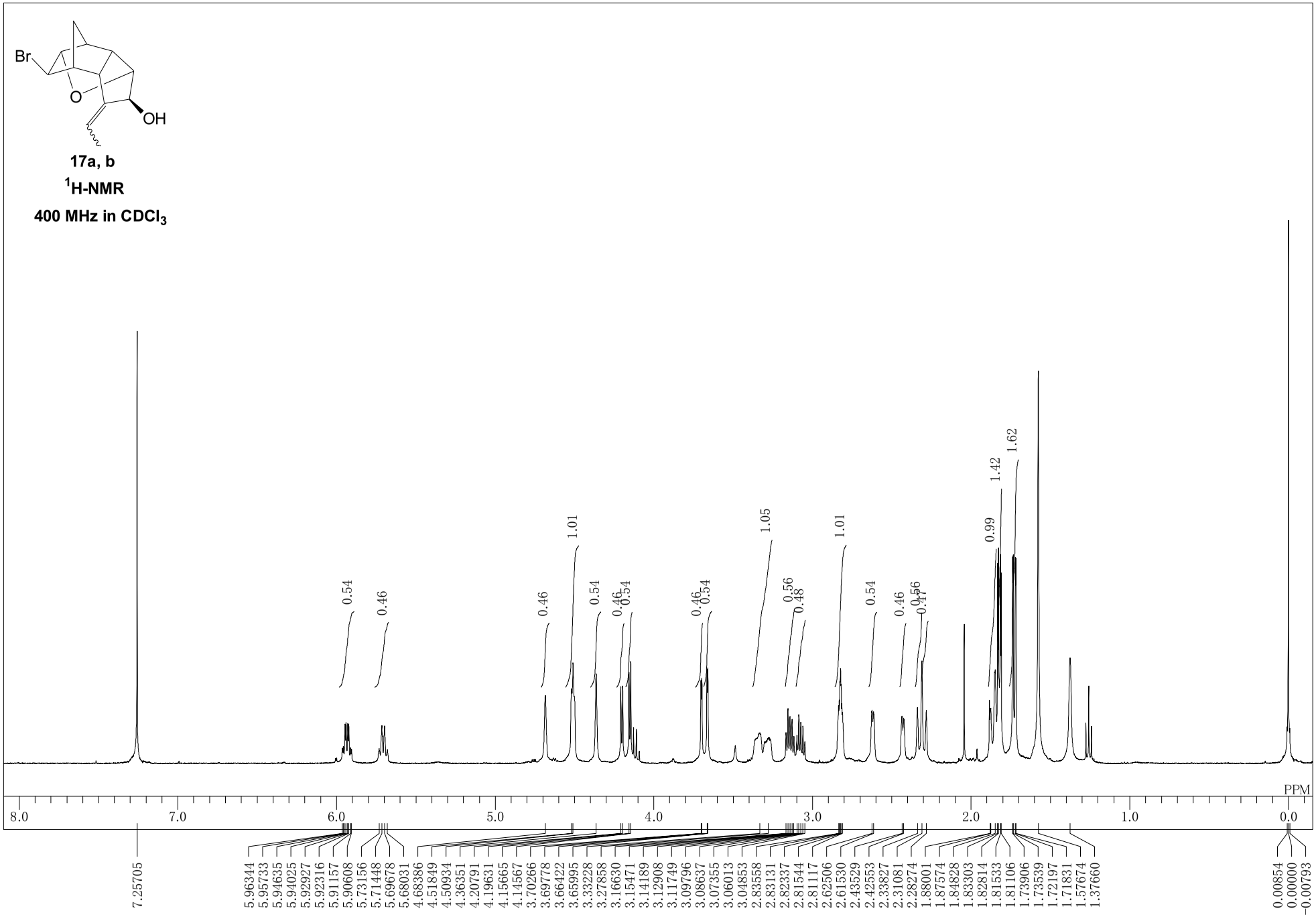

O
OH
OH
OH
(±)-4 from 10b
13C-NMR
100 MHz in DMSO-d6
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
207.33541
162.04584
132.77673
78.99845
72.66286
68.74436
40.11871
39.91247
39.70624
39.50000
39.28551
39.07928
38.87304
17.68016


Br
O
O
15
1H-NMR
400 MHz in CDCl3
1.00
1.00
0.97
0.98
1.02
1.04
1.02
0.98
1.02
2.96
1.10
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.32661
6.75242
6.74693
4.82115
4.81505
4.80712
4.80041
4.64236
4.63077
3.78260
3.77833
3.35485
3.34509
3.33289
3.32251
3.18461
3.17057
3.15715
3.14861
3.13457
2.76479
2.75320
2.74161
2.64031
2.44810
2.42064
2.34681
2.02890
2.00144


Br
O
O
15
13C-NMR
100 MHz in CDCl3
PPM
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
196.49361
146.07283
143.16902
91.40358
84.63901
77.32173
77.20624
77.00000
76.68652
54.30570
50.75843
49.40551
47.40089
47.22765
40.15786
26.78546


Br
O
O
O
16
1H-NMR
400 MHz in CDCl3
0.97
1.01
1.00
1.04
1.01
1.04
1.03
1.06
1.05
2.92
0.99
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26742
4.60880
4.59782
4.55511
4.54168
3.83874
3.62151
3.02718
2.81544
2.80568
2.79408
2.78371
2.75259
2.65191
2.63848
2.62872
2.61713
2.26565
2.23820
2.07710
1.71587
1.68902
1.65973
1.62678
0.00000

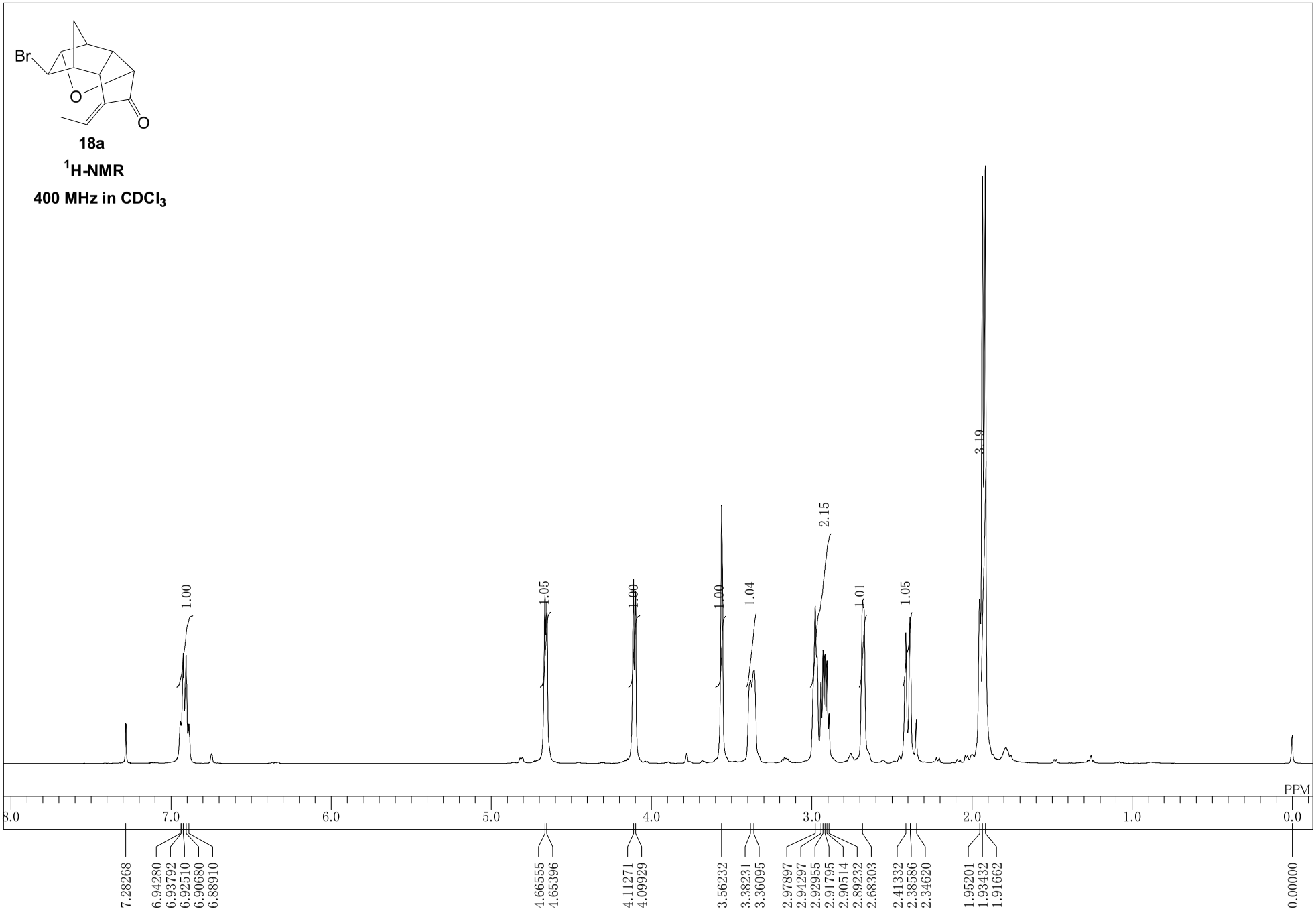

Br
O
O
O
16
13C-NMR
100 MHz in CDCl3
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
210.57548
203.84391
90.05067
81.91669
77.31348
77.00000
76.67827
67.48011
64.90627
54.93266
47.21115
46.45220
46.13047
45.99023
36.99830
25.25105

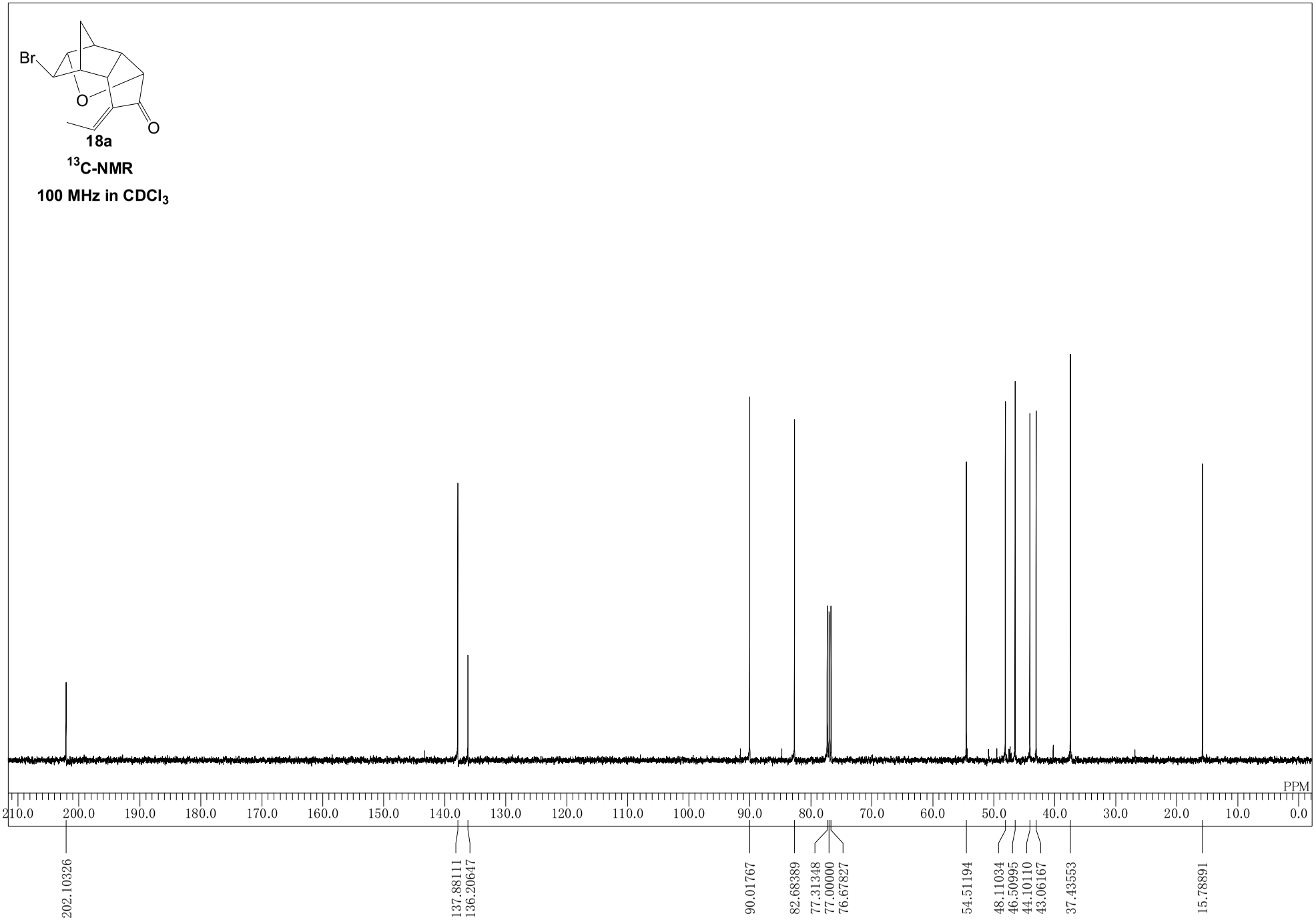

Br
O
OH
17a, b
1H-NMR
400 MHz in CDCl3
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
0.54
0.46
0.46
1.01
0.54
0.46
0.54
0.46
0.54
1.05
0.56
0.48
1.01
0.54
0.46
0.56
0.47
0.99
1.42
1.62
7.25705
5.96344
5.95733
5.94635
5.94025
5.92927
5.92316
5.91157
5.90608
5.73156
5.71448
5.69678
5.68031
4.68386
4.51849
4.50934
4.36351
4.20791
4.19631
4.15665
4.14567
3.70266
3.69778
3.66422
3.65995
3.33228
3.27858
3.16630
3.15471
3.14189
3.12908
3.11749
3.09796
3.08637
3.07355
3.06013
3.04853
2.83558
2.83131
2.82337
2.81544
2.81117
2.62506
2.61530
2.43529
2.42553
2.33827
2.31081
2.28274
1.88001
1.87574
1.84828
1.83303
1.82814
1.81533
1.81106
1.73906
1.73539
1.72197
1.71831
1.57674
1.37660
0.00854
0.00000
−0.00793

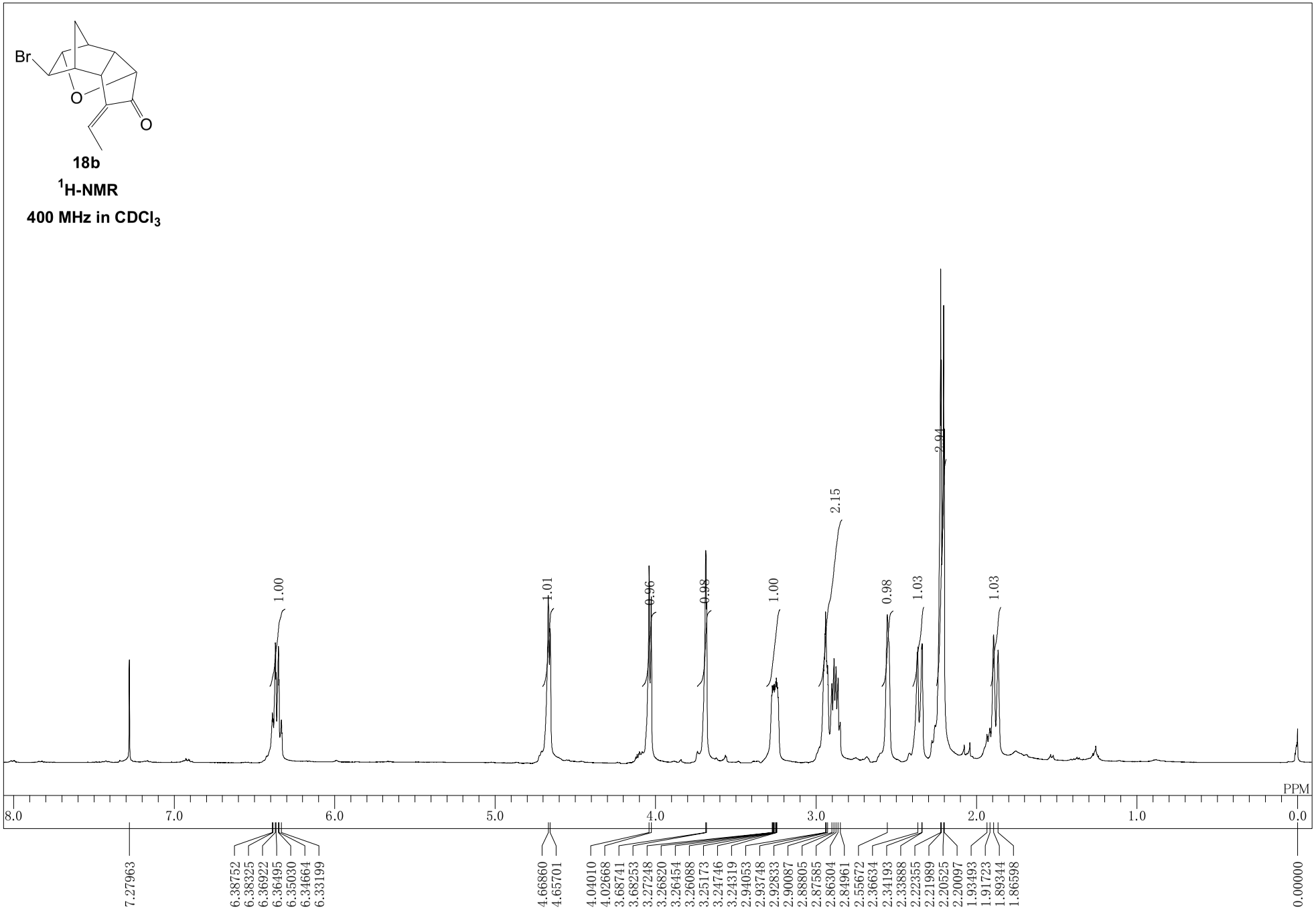
18a

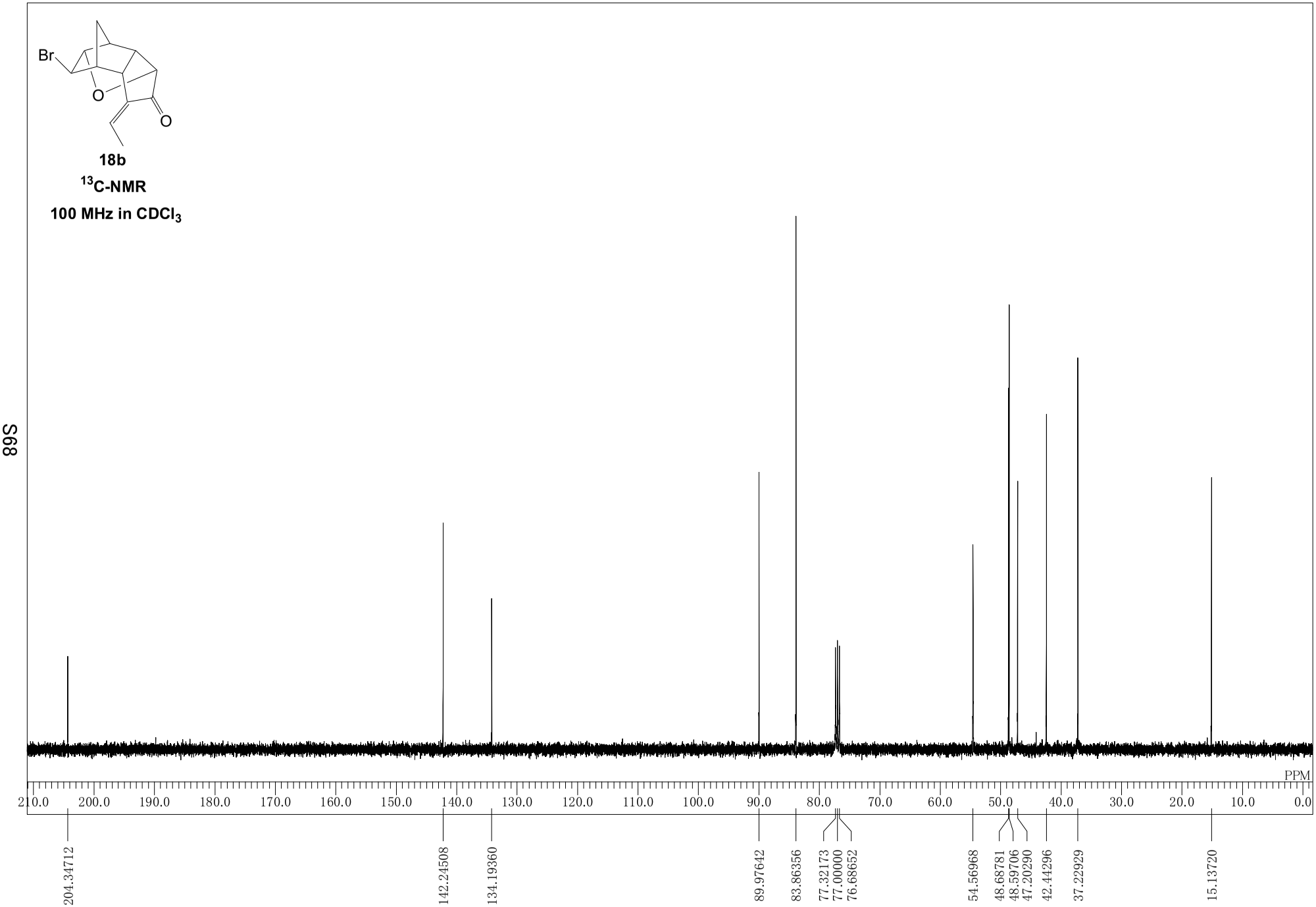
^{1}H-NMR

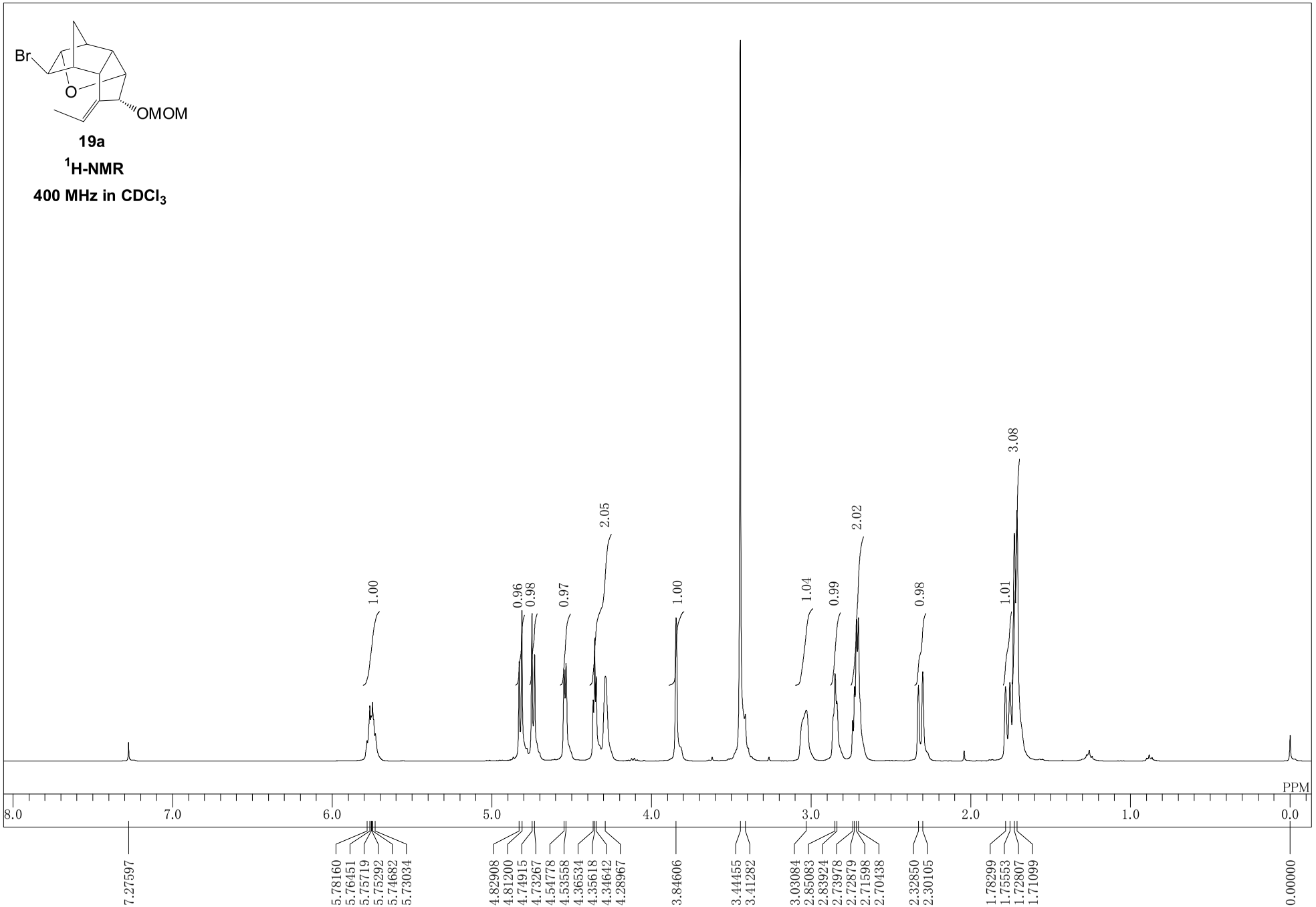
400 MHz in $CDCl_3$

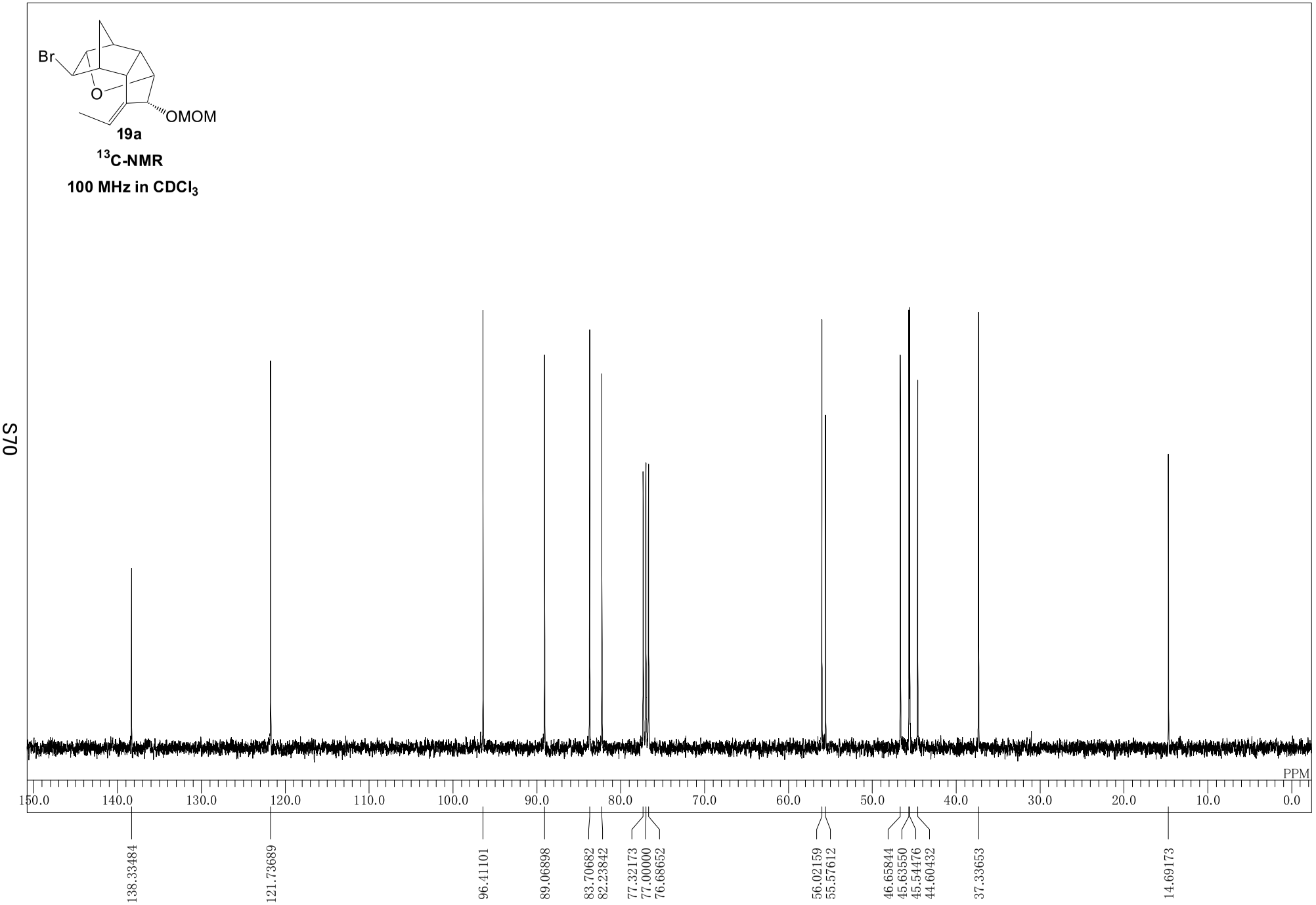



Br
O
O
18a
13C-NMR
100 MHz in CDCl3
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
202.10326
137.88111
136.20647
90.01767
82.68389
77.31348
77.00000
76.67827
54.51194
48.11034
46.50995
44.10110
43.06167
37.43553
15.78891


Br
O
O
18b
1H-NMR
400 MHz in CDCl3
1.00
1.01
0.96
0.98
1.00
2.15
0.98
1.03
2.94
1.03
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.27963
6.38752
6.38325
6.36922
6.36495
6.35030
6.34664
6.33199
4.66860
4.65701
4.04010
4.02668
3.68741
3.68253
3.27248
3.26820
3.26454
3.26088
3.25173
3.24746
3.24319
2.94053
2.93748
2.92833
2.90087
2.88805
2.87585
2.86304
2.84961
2.55672
2.36634
2.34193
2.33888
2.22355
2.21989
2.20525
2.20097
1.93493
1.91723
1.89344
1.86598
0.00000


Br
O
O
18b
13C-NMR
100 MHz in CDCl3
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
204.34712
142.24508
134.19360
89.97642
83.86356
77.32173
77.00000
76.68652
54.56968
48.68781
48.59706
47.20290
42.44296
37.22929
15.13720


Br
O
OMOM
19a
1H-NMR
400 MHz in CDCl3
1.00
0.96
0.98
0.97
2.05
1.00
1.04
0.99
2.02
0.98
1.01
3.08
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.27597
5.78160
5.76451
5.75719
5.75292
5.74682
5.73034
4.82908
4.81200
4.74915
4.73267
4.54778
4.53558
4.36534
4.35618
4.34642
4.28967
3.84606
3.44455
3.41282
3.03084
2.85083
2.83924
2.73978
2.72879
2.71598
2.70438
2.32850
2.30105
1.78299
1.75553
1.72807
1.71099
0.00000


Br
O
OMOM
19a
13C-NMR
100 MHz in CDCl3
PPM
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
138.33484
121.73689
96.41101
89.06898
83.70682
82.23842
77.32173
77.00000
76.68652
56.02159
55.57612
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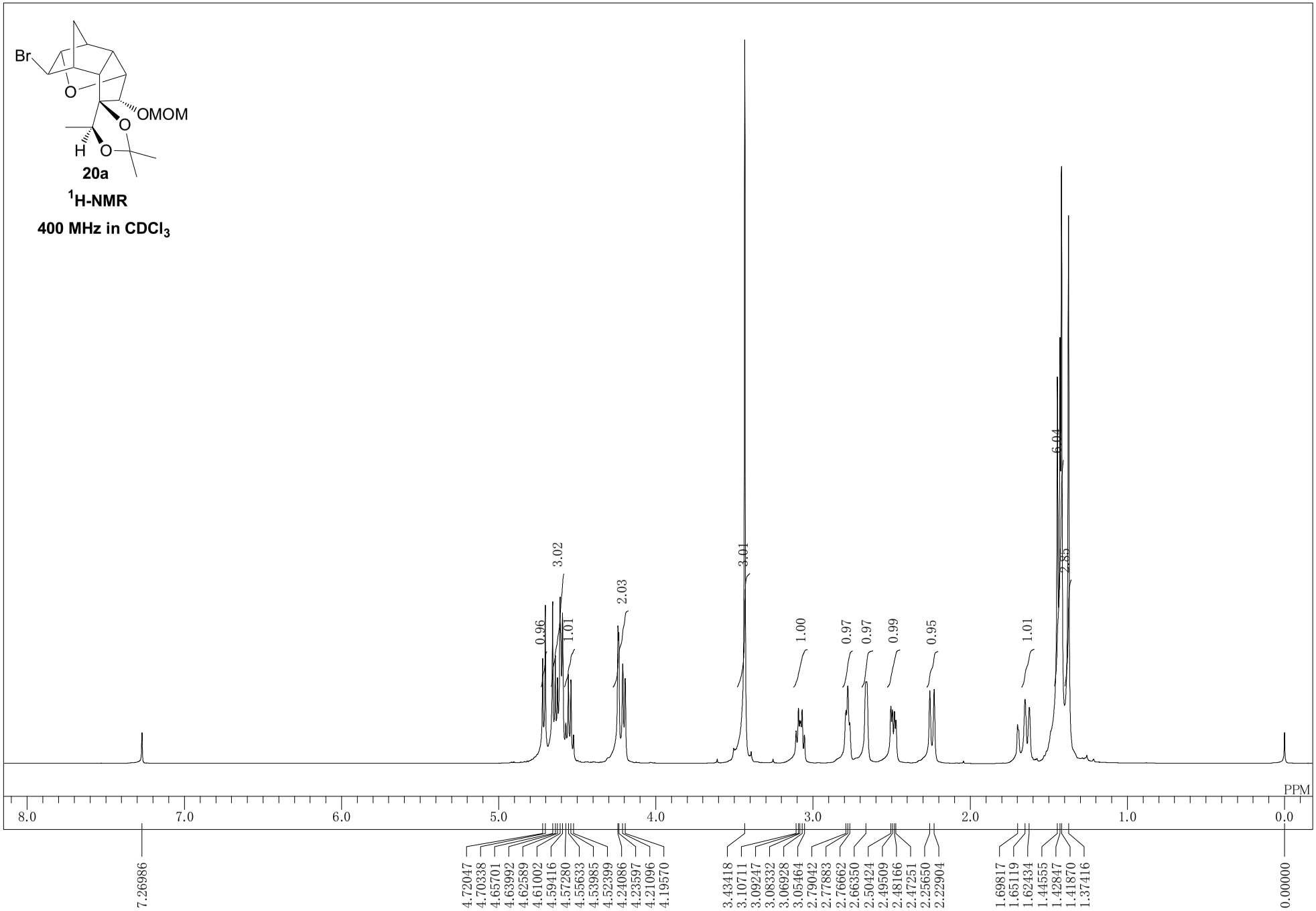
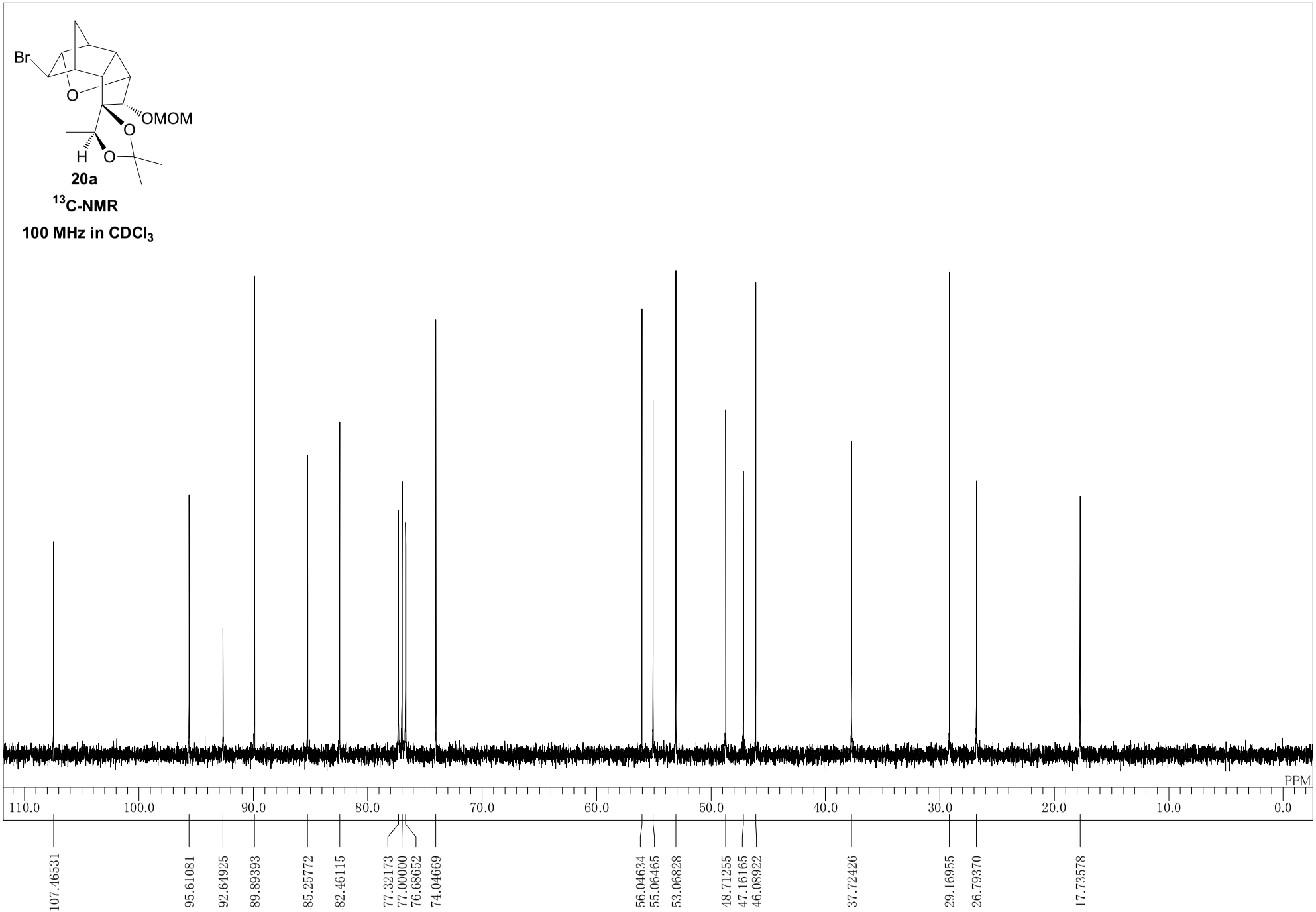
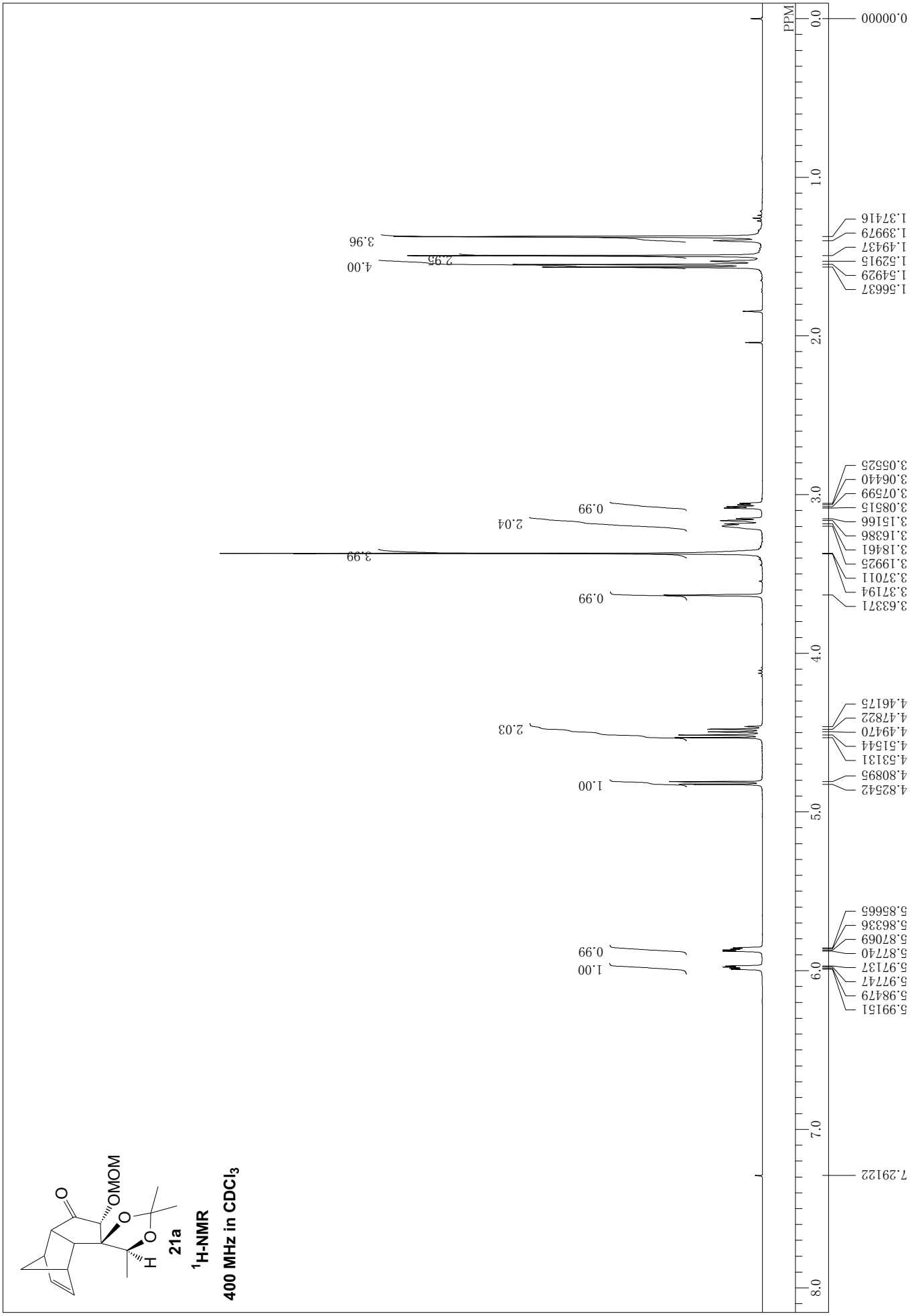
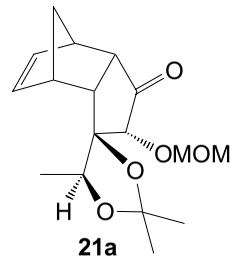
45.63550
45.54476
44.60432
37.33653
14.69173


Br
O
OMOM
O
H
O
20a
1H-NMR
400 MHz in CDCl3
0.96
3.02
1.01
2.03
3.01
1.00
0.97
0.97
0.99
0.95
1.01
6.04
2.85
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26986
4.72047
4.70338
4.65701
4.63992
4.62589
4.61002
4.59416
4.57280
4.55633
4.53985
4.52399
4.24086
4.23597
4.21096
4.19570
3.43418
3.10711
3.09247
3.08332
3.06928
3.05464
2.79042
2.77883
2.76662
2.66350
2.50424
2.49509
2.48166
2.47251
2.25650
2.22904
1.69817
1.65119
1.62434
1.44555
1.42847
1.41870
1.37416
0.00000


Br
O
OMOM
O
H
O
20a
13C-NMR
100 MHz in CDCl3
PPM
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
107.46531
95.61081
92.64925
89.89393
85.25772
82.46115
77.32173
77.00000
76.68652
74.04669
56.04634
55.06465
53.06828
48.71255
47.16165
46.08922
37.72426
29.16955
26.79370
17.73578

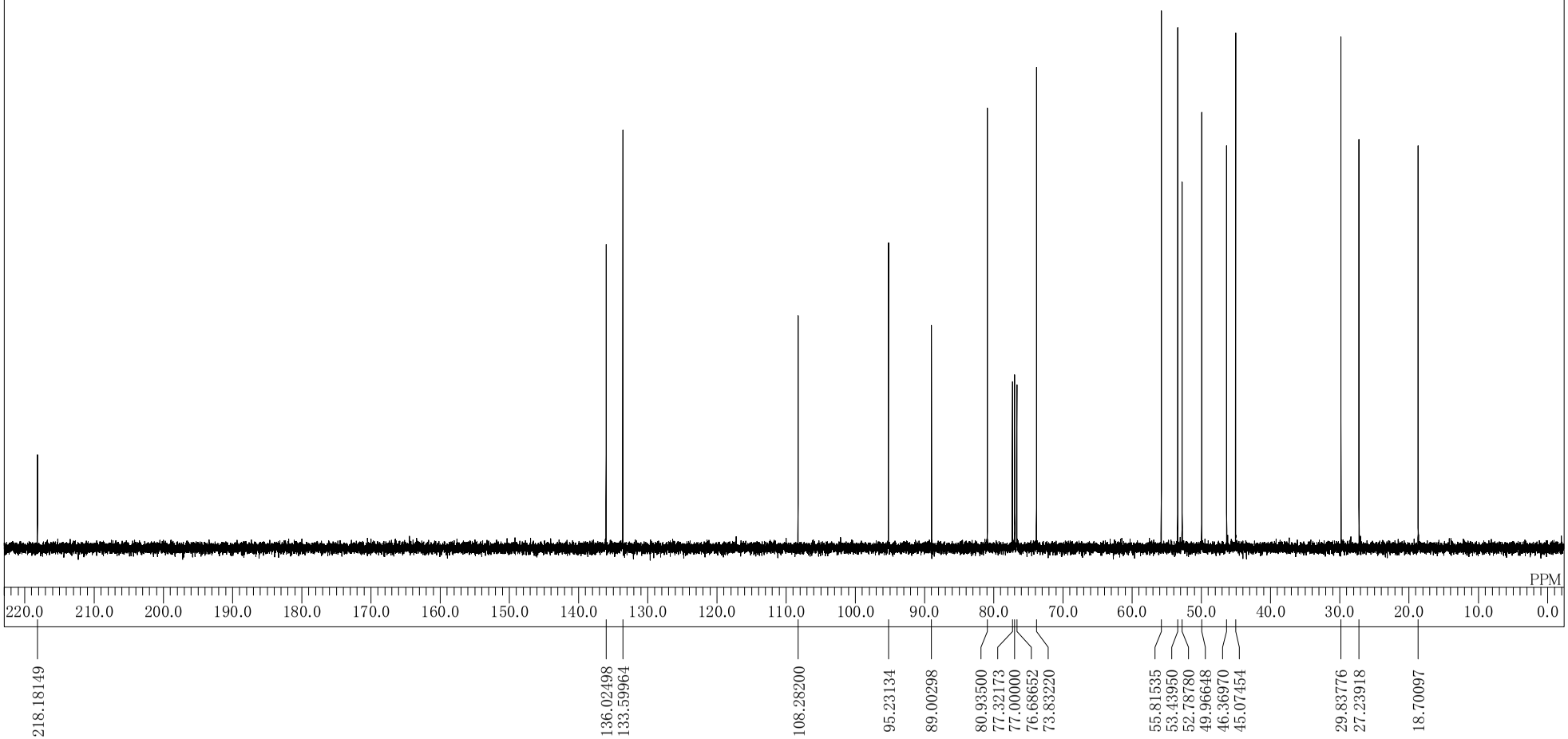

21a
^{1}H-NMR
400 MHz in $CDCl_3$
OMOM
O
O
O
H
PPM
0.00000
1.37416
1.39979
1.49437
1.52915
1.54929
1.56637
3.05525
3.06440
3.07599
3.08515
3.15166
3.16386
3.18461
3.19925
3.37011
3.37194
3.63371
4.46175
4.47822
4.49470
4.51544
4.53131
4.80895
4.82542
5.85665
5.86336
5.87069
5.87740
5.97137
5.97147
5.98479
5.99151
7.29122
0.99
1.00
2.03
1.00
0.99
3.99
2.04
0.99
4.00
2.95
3.96



21a

^{13}C-NMR

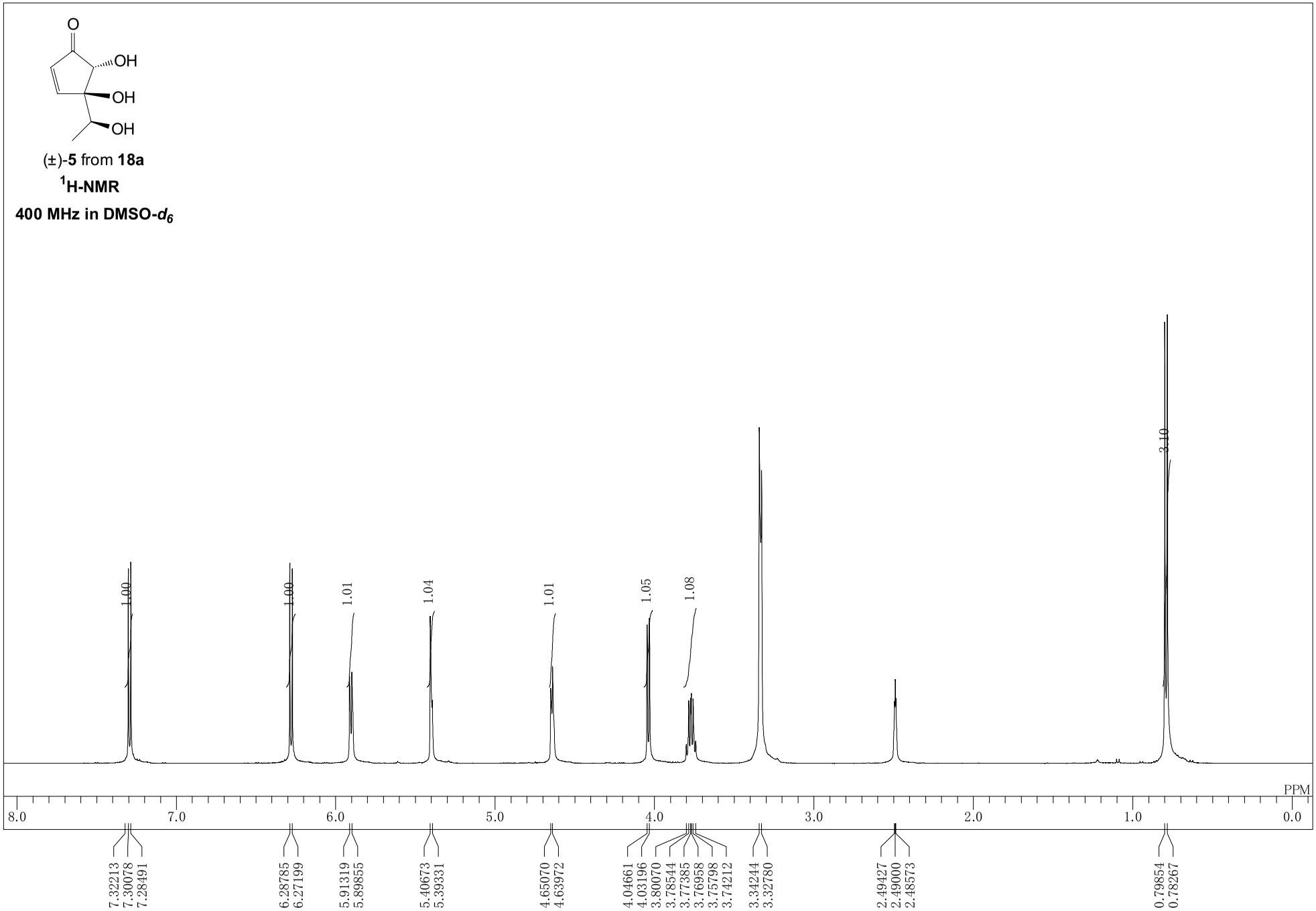
100 MHz in $CDCl_3$

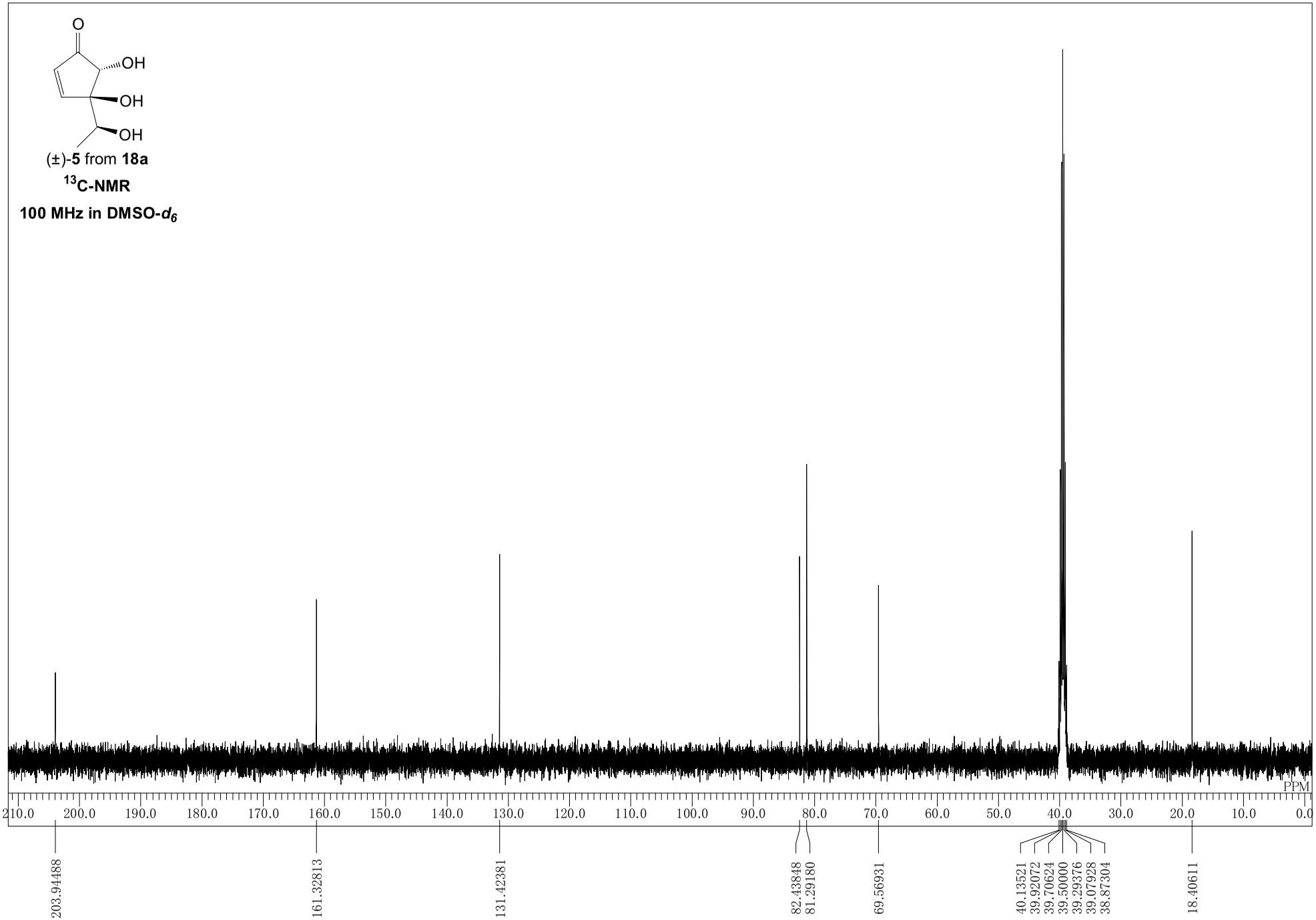


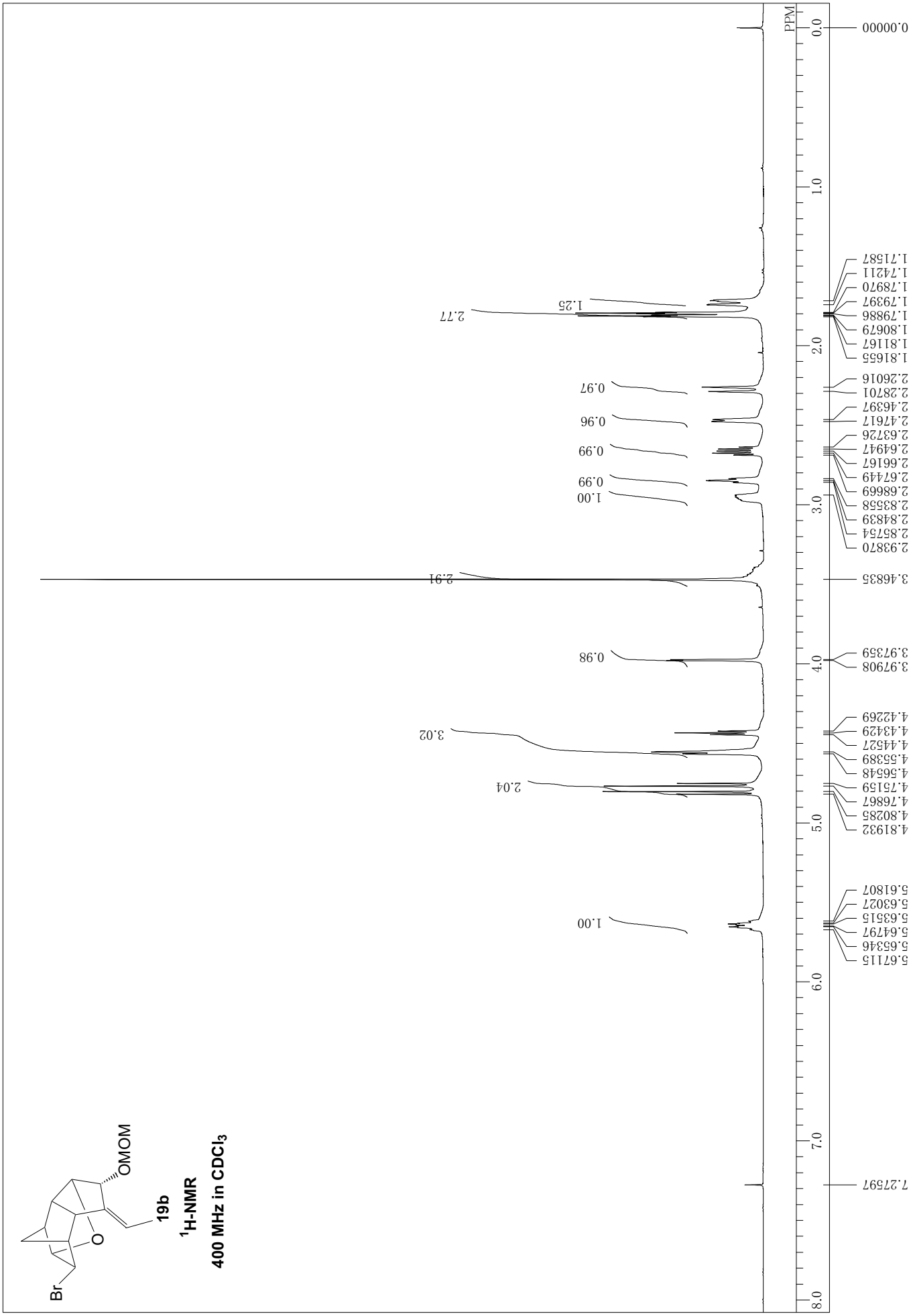
(±)-**5** from **18a**

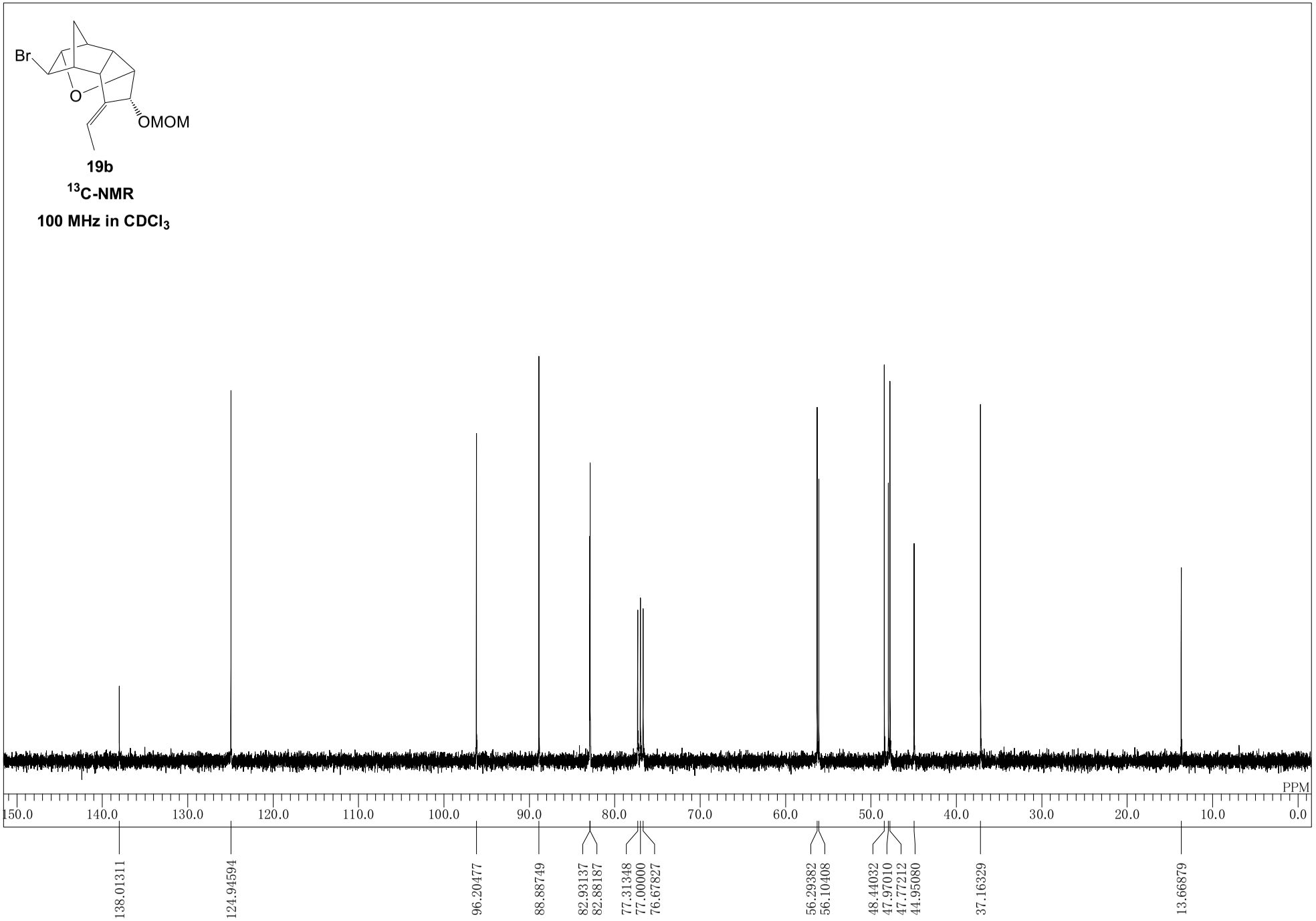
^{1}H-NMR

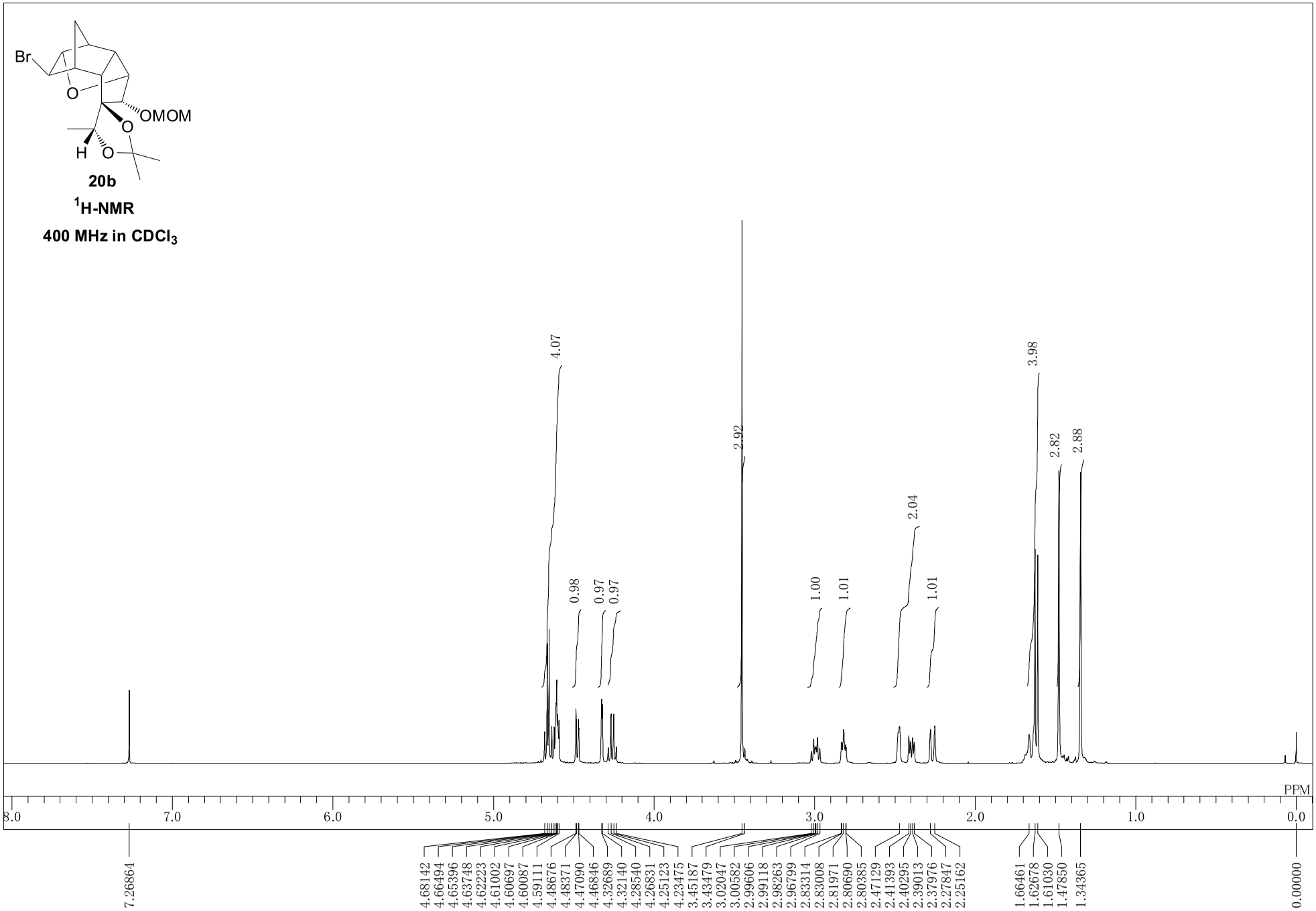
400 MHz in DMSO-d_6




O
OH
OH
OH
(±)-5 from 18a
13C-NMR
100 MHz in DMSO-d6
PPM
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
203.94488
161.32813
131.42381
82.43848
81.29180
69.56931
40.13521
39.92072
39.70624
39.50000
39.29376
39.07928
38.87304
18.40611


Br
O
OMOM
19b
1H-NMR
400 MHz in CDCl3
PPM
0.00000
7.27597
5.67115
5.65346
5.64797
5.63515
5.63027
5.61807
4.81932
4.80285
4.76867
4.75159
4.56548
4.55389
4.44527
4.43429
4.42269
3.97908
3.97359
3.46835
2.93870
2.85754
2.84839
2.83558
2.68669
2.67449
2.66167
2.64947
2.63726
2.47617
2.46397
2.28701
2.26016
1.81655
1.81167
1.80679
1.79886
1.79397
1.78970
1.74211
1.71587
1.25
2.77
0.97
0.96
0.99
0.99
1.00
2.91
0.98
3.02
2.04
1.00


Br
O
OMOM
19b
13C-NMR
100 MHz in CDCl3
PPM
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
138.01311
124.94594
96.20477
88.88749
82.93137
82.88187
77.31348
77.00000
76.67827
56.29382
56.10408
48.44032
47.97010
47.77212
44.95080
37.16329
13.66879


Br
O
OMOM
O
H
O
20b
1H-NMR
400 MHz in CDCl3
4.07
0.98
0.97
0.97
2.92
1.00
1.01
2.04
1.01
3.98
2.82
2.88
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.26864
4.68142
4.66494
4.65396
4.63748
4.62223
4.61002
4.60697
4.60087
4.59111
4.48676
4.48371
4.47090
4.46846
4.32689
4.32140
4.28540
4.26831
4.25123
4.23475
3.45187
3.43479
3.02047
3.00582
2.99606
2.99118
2.98263
2.96799
2.83314
2.83008
2.81971
2.80690
2.80385
2.47129
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2.40295
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1.61030
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1.34365
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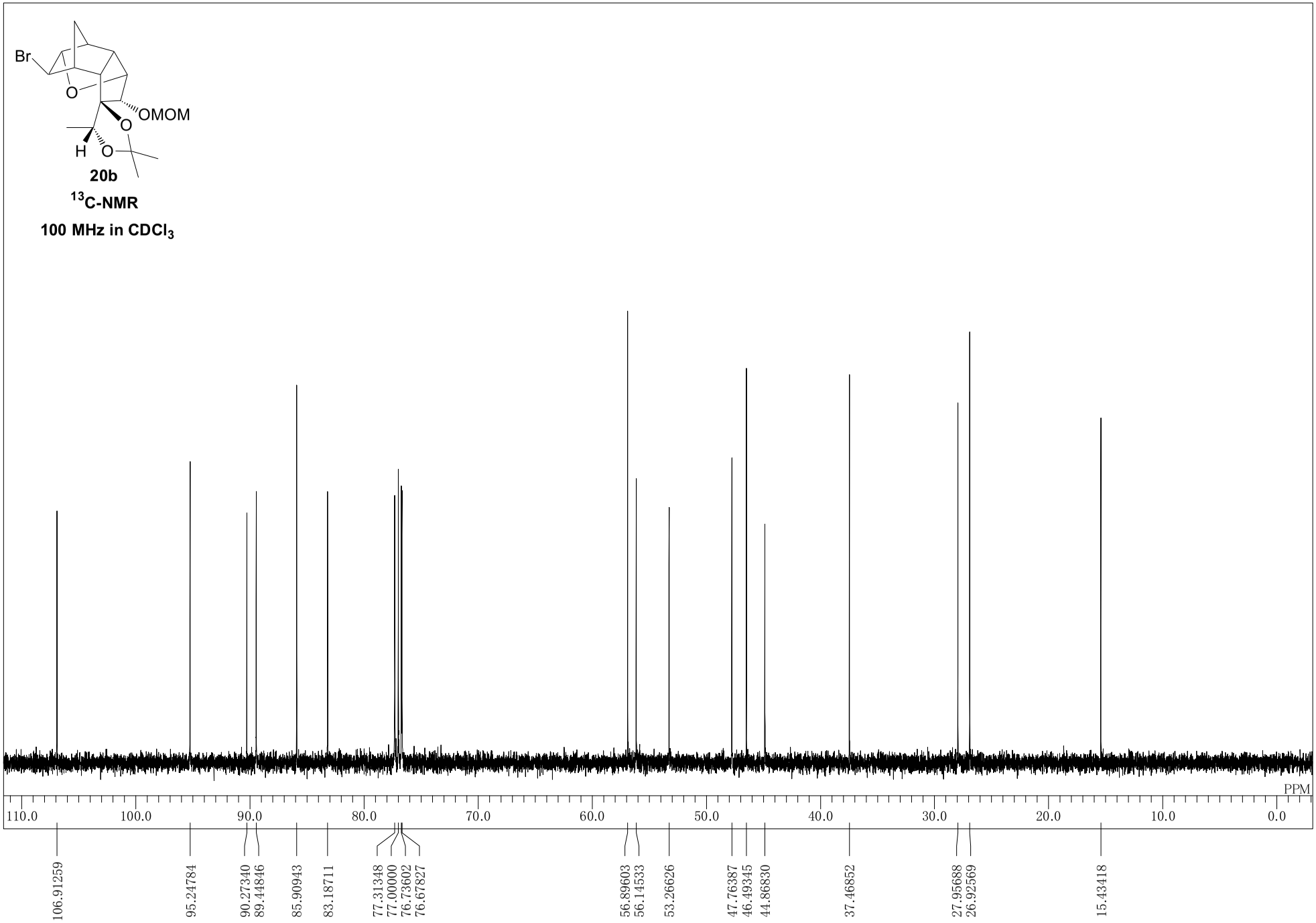
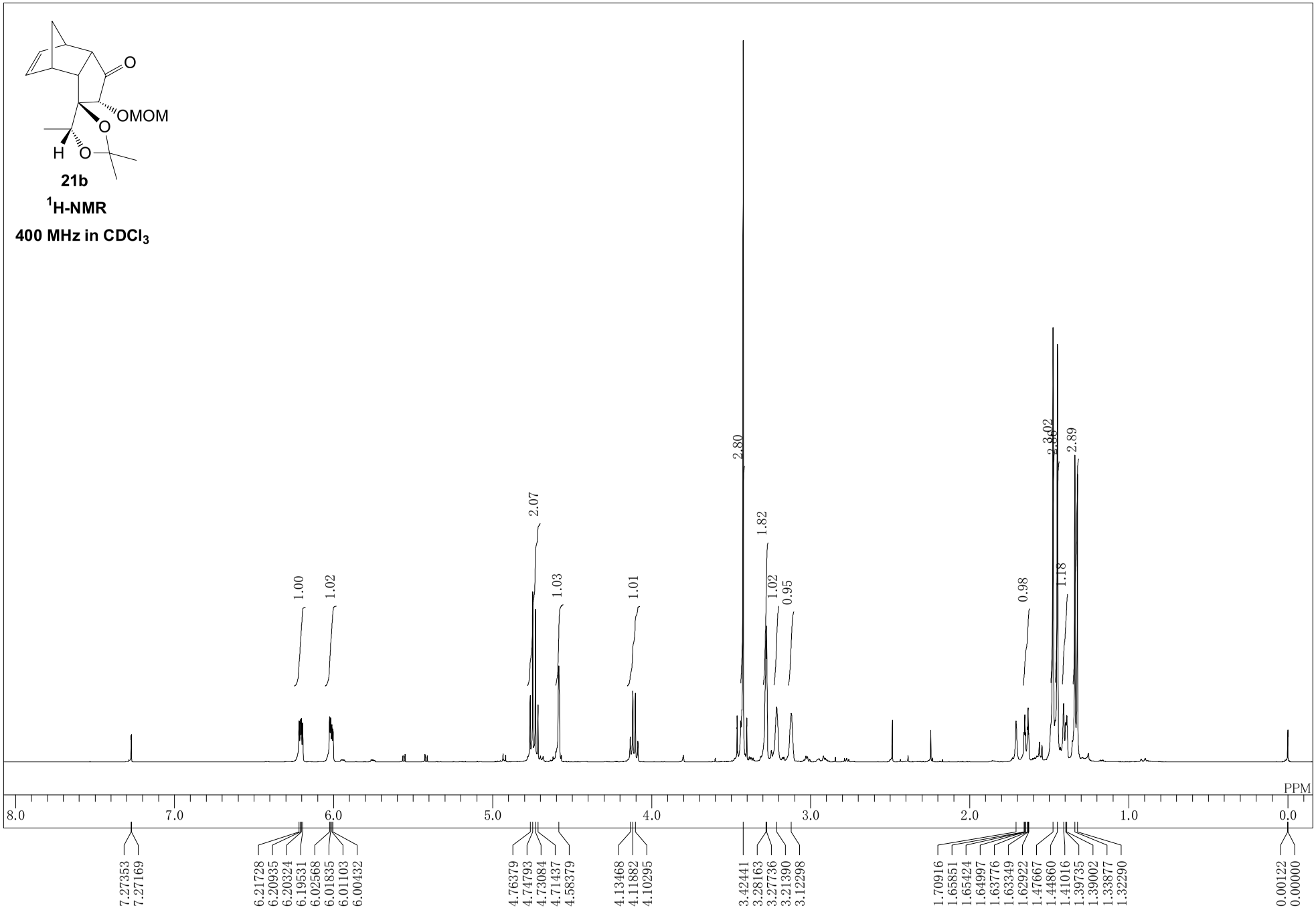

Br
O
OMOM
O
H
O
20b
13C-NMR
100 MHz in CDCl3
PPM
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
106.91259
95.24784
90.27340
89.44846
85.90943
83.18711
77.31348
77.00000
76.73602
76.67827
56.89603
56.14533
53.26626
47.76387
46.49345
44.86830
37.46852
27.95688
26.92569
15.43418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OMOM
O
H
O
21b
1H-NMR
400 MHz in CDCl3
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1.02
2.07
1.03
1.01
2.80
1.82
1.02
0.95
0.98
2.88
3.02
1.18
2.89
PPM
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
7.27353
7.27169
6.21728
6.20935
6.20324
6.19531
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6.00432
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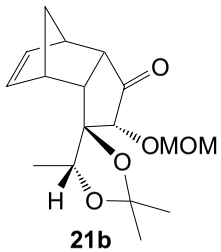
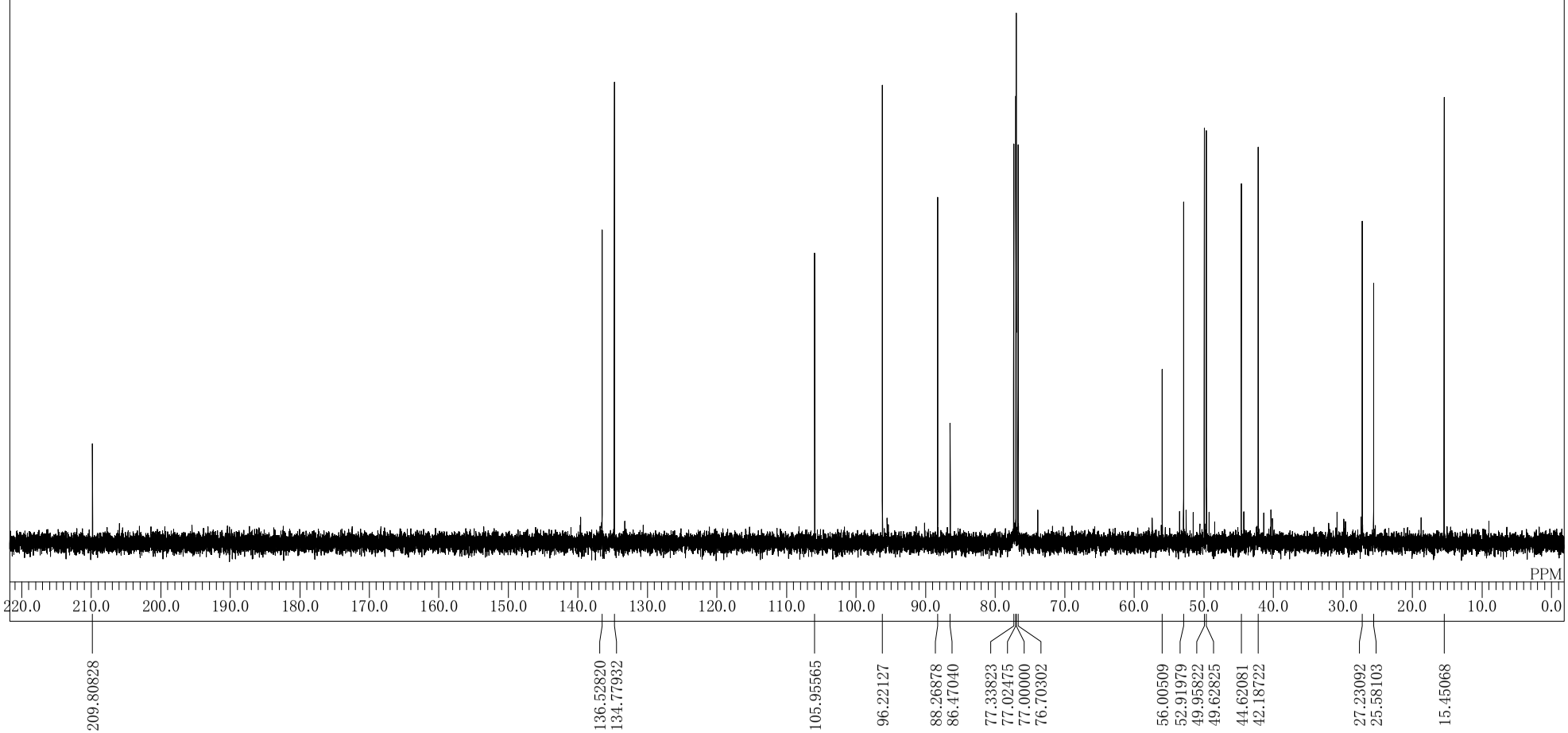
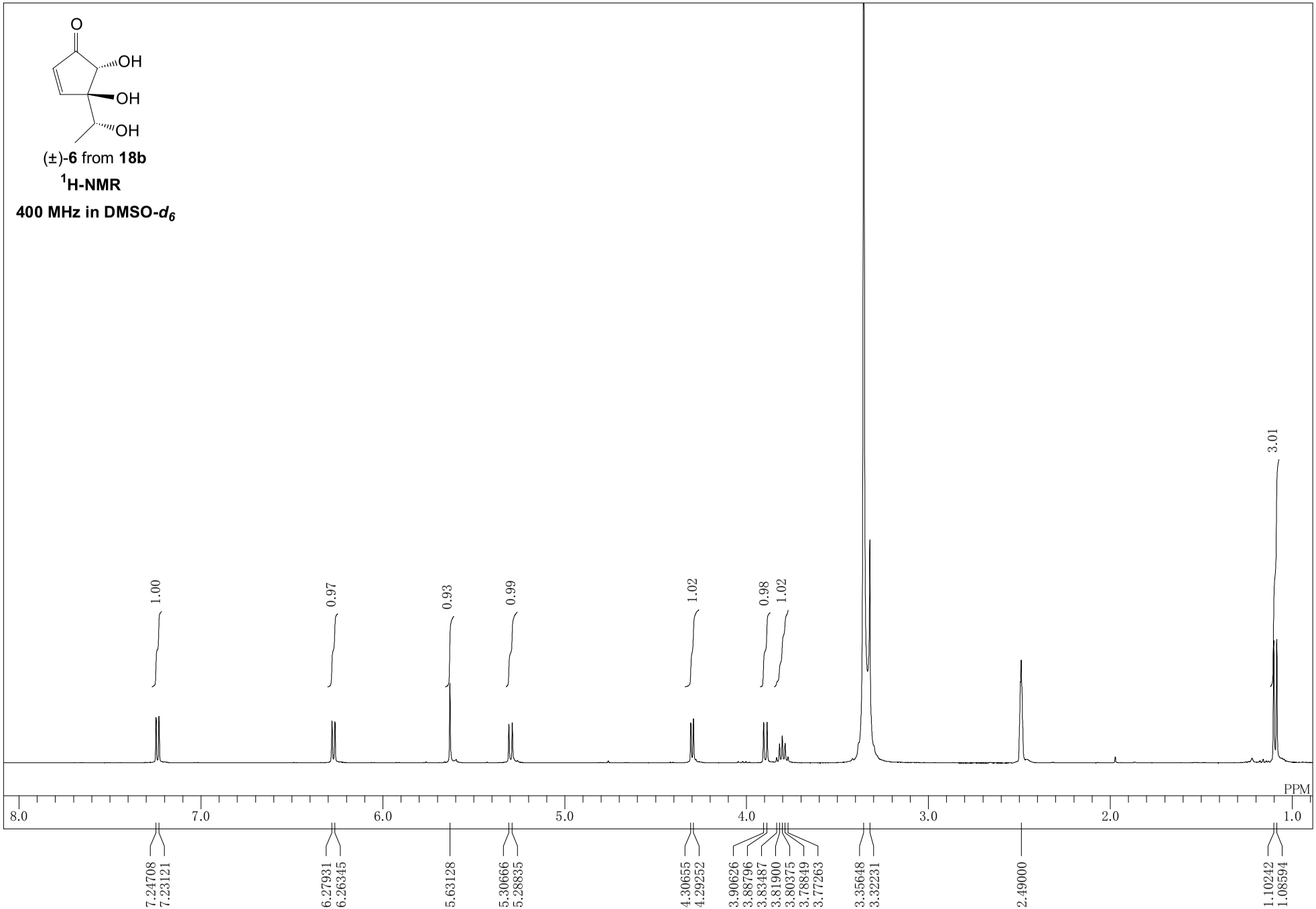


21b

^{13}C-NMR

100 MHz in $CDCl_3$

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OH
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(±)-6 from 18b
1H-NMR
400 MHz in DMSO-d6
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0.93
0.99
1.02
0.98
1.02
3.01
PPM
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
7.24708
7.23121
6.27931
6.26345
5.63128
5.30666
5.28835
4.30655
4.29252
3.90626
3.88796
3.83487
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3.80375
3.78849
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3.32231
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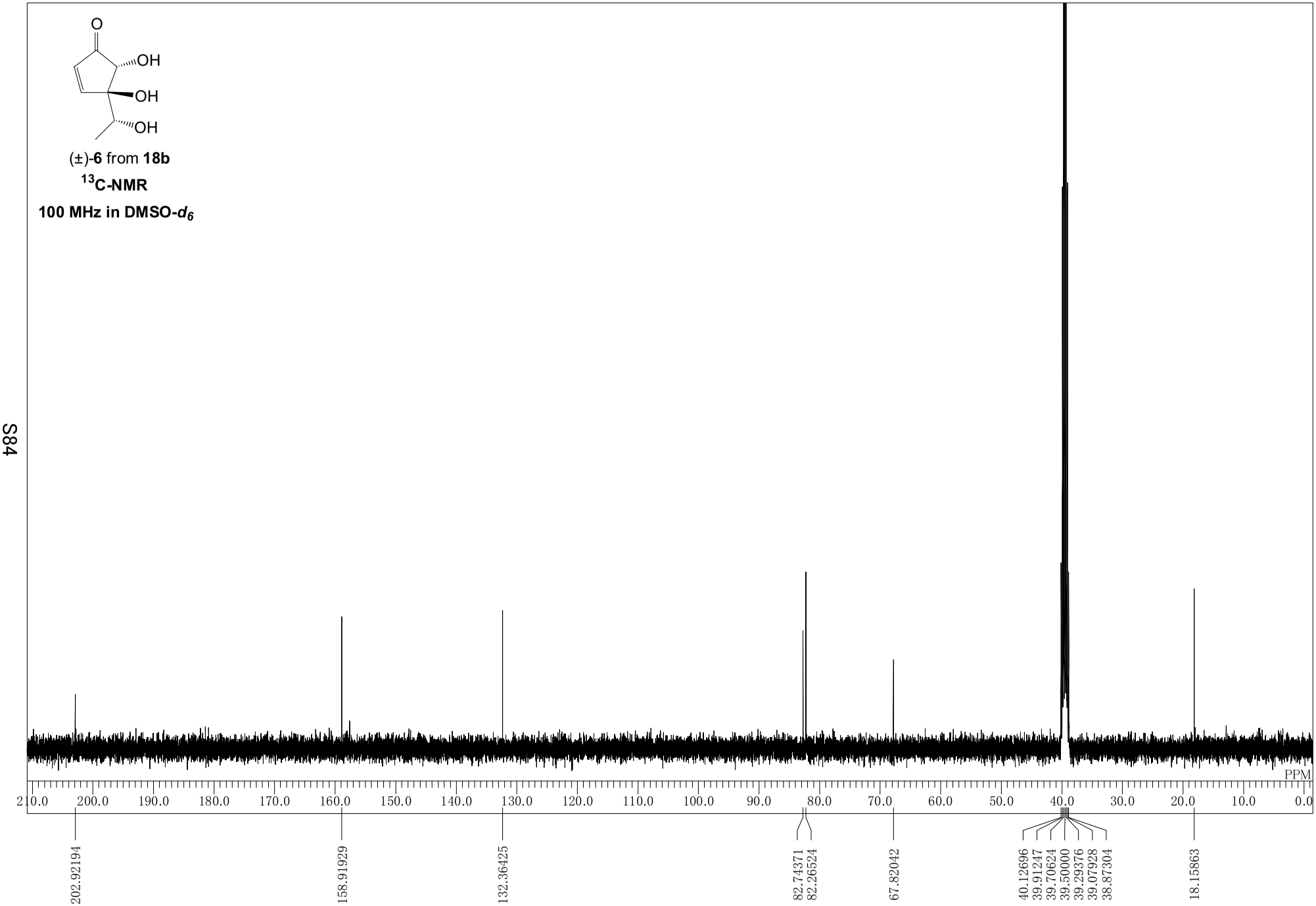
1.08594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OH
OH
(±)-6 from 18b
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100 MHz in DMSO-d6
PPM
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170.0
160.0
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140.0
130.0
120.0
110.0
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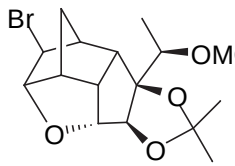
82.26524
67.82042
40.12696
39.91247
39.70624
39.50000
39.29376
39.07928
38.87304
18.15863

X-ray structure of (+)-12a

The structure of (+)-**12a** has been determined by a single-crystal X-ray analysis. A perspective drawing of a molecule of (+)-**12a** is shown in the Figure.



(+)-**12a**

The intensity data were measured on a Mac Science MAXC18 diffractometer with graphite monochromated Cu $K\alpha$ radiation. The size of the crystal used for data collection was approximately 0.3 x 0.2 x 0.15 mm. The data were not corrected for absorption. Of the 1566 independent reflections for θ< 64.68, 1660 were considered observed [I > 3.00σ(I)].

The structure was solved by a multiple-solution procedure (maXus) and was refined by full-matrix least squares. In the final refinment, the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the structure-factor calculations, but their parameters were not refined. The final discrepancy indices are R = 0.034 and Rw = 0.091 for the 1660 observed reflections. The X-ray data are summarized in Table I to V.

Table I. X-ray data for **(+)-12a** at 288 K

Formula	$C_{17}H_{25}O_5Br$
Formular weight	389.29
Crystal Size (mm)	0.3 x 0.2 x 0.15
Crystal color, habit	colorless, plate
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a (Å)	14.383 (3)
b (Å)	16.958 (3)
c (Å)	7.194 (1)
V (Å^3)	1754.6 (6)
Z value	4
d_{calc} (g·cm^{-1})	1.47
μ(Cu $K\alpha$) (mm^{-1})	3.389
μ(Cu $K\alpha$) (Å)	1.5418
Absorption correction	none
Maximum θ (°)	64.68
Unique reflections	1707
Observed reflections [I > 3.00σ(I)]	1660
R	0.034
Rw	0.091
$(\Delta\rho)_{max}$ (e Å^{-3})	0.54
$(\Delta\rho)_{min}$ (e Å^{-3})	–0.41

Table II. Fractional atomic coordinates & U(iso) for (+)-**12a**

Atom	x/a	y/b	z/c	U(iso)
Br(1)	-0.977126(19)	-0.566787(12)	-0.68477(4)	0.06244(13)
C(2)	-0.95595(12)	-0.47524(10)	-0.8461(3)	0.0404(9)
C(3)	-0.86341(14)	-0.48239(11)	-0.9561(3)	0.0413(9)
C(4)	-0.84667(12)	-0.34519(11)	-0.9748(3)	0.0384(9)
C(5)	-0.93659(12)	-0.32713(10)	-0.8609(2)	0.0336(8)
C(6)	-0.94295(12)	-0.39999(10)	-0.7311(2)	0.0365(8)
C(7)	-0.84049(13)	-0.40807(12)	-0.6722(3)	0.0473(10)
C(8)	-0.80407(13)	-0.41658(11)	-0.8718(3)	0.0454(9)
O(9)	-0.87594(10)	-0.46281(7)	-1.14732(19)	0.0458(7)
C(10)	-0.88165(12)	-0.37770(10)	-1.1624(3)	0.0396(9)
C(11)	-0.98333(13)	-0.35136(9)	-1.1863(3)	0.0371(9)
O(12)	-0.99675(10)	-0.29459(7)	-1.32805(18)	0.0488(7)
C(13)	-1.00020(14)	-0.21702(11)	-1.2486(3)	0.0415(8)
O(14)	-1.00361(9)	-0.22841(6)	-1.05242(17)	0.0382(6)
C(15)	-1.01219(12)	-0.31022(9)	-1.0036(2)	0.0310(8)
C(16)	-0.9129(2)	-0.17244(19)	-1.2958(5)	0.0687(16)
C(17)	-1.08660(18)	-0.17576(13)	-1.3165(4)	0.0541(12)
C(18)	-1.11062(13)	-0.32753(10)	-0.9331(3)	0.0378(9)
C(19)	-1.13831(14)	-0.27367(14)	-0.7733(3)	0.0509(11)
O(20)	-1.17727(9)	-0.31798(8)	-1.0795(2)	0.0492(7)
C(21)	-1.23915(17)	-0.38094(16)	-1.1019(4)	0.0646(14)
O(22)	-1.20108(13)	-0.44319(9)	-1.2032(3)	0.0669(10)
C(23)	-1.1920(3)	-0.4254(2)	-1.3951(4)	0.084(2)
H(2)	-1.0050(14)	-0.4750(12)	-0.923(3)	0.045624
H(3)	-0.8409(14)	-0.5380(12)	-0.945(3)	0.046137
H(4)	-0.8047(14)	-0.2974(11)	-0.992(3)	0.043814
H(5)	-0.9288(12)	-0.2822(11)	-0.794(3)	0.038618
H(6)	-0.9879(13)	-0.3963(11)	-0.632(3)	0.041477
H(7A)	-0.8153(15)	-0.3608(13)	-0.620(3)	0.052410
H(7B)	-0.8282(15)	-0.4546(13)	-0.596(3)	0.052410
H(8)	-0.7357(14)	-0.4276(12)	-0.891(3)	0.050873

Atom	x/a	y/b	z/c	U(iso)
H(10)	-0.8438(14)	-0.3591(12)	-1.271(3)	0.044814
H(11)	-1.0170(14)	-0.3917(11)	-1.213(3)	0.042041
H(16A)	-0.9178(19)	-0.1251(15)	-1.258(4)	0.072928
H(16B)	-0.9044(18)	-0.1715(16)	-1.438(4)	0.072928
H(16C)	-0.8621(19)	-0.1975(15)	-1.258(4)	0.072928
H(17A)	-1.0829(16)	-0.1263(14)	-1.273(4)	0.059658
H(17B)	-1.1437(16)	-0.2020(14)	-1.278(4)	0.059658
H(17C)	-1.0824(17)	-0.1693(14)	-1.444(4)	0.059658
H(18)	-1.1138(14)	-0.3827(11)	-0.884(3)	0.042827
H(19A)	-1.0945(15)	-0.2817(13)	-0.685(4)	0.056553
H(19B)	-1.1301(15)	-0.2156(13)	-0.814(4)	0.056553
H(19C)	-1.2022(15)	-0.2819(13)	-0.718(3)	0.056553
H(21A)	-1.2530(17)	-0.3996(15)	-0.981(4)	0.069584
H(21B)	-1.2929(18)	-0.3567(14)	-1.156(4)	0.069584
H(23A)	-1.161(2)	-0.4790(17)	-1.425(5)	0.089378
H(23B)	-1.154(2)	-0.3697(16)	-1.422(4)	0.089378
H(23C)	-1.2506(19)	-0.4351(18)	-1.452(5)	0.089378

Table III. Anisotropic thermal parameters for (+)-**12a**

Atom	U11	U22	U33	U12	U13	U23
Br(1)	0.07850(16)	0.04109(11)	0.06772(15)	0.00500(11)	0.00886(13)	0.01279(11)
C(2)	0.0410(9)	0.0358(8)	0.0446(10)	0.0070(7)	-0.0019(8)	0.0034(8)
C(3)	0.0437(10)	0.0356(8)	0.0446(9)	0.0131(8)	0.0006(9)	-0.0025(8)
C(4)	0.0321(9)	0.0417(9)	0.0415(9)	0.0007(7)	0.0008(8)	-0.0044(8)
C(5)	0.0320(8)	0.0331(7)	0.0357(9)	0.0031(6)	-0.0010(7)	-0.0052(7)
C(6)	0.0371(8)	0.0383(8)	0.0341(8)	0.0057(7)	0.0003(8)	-0.0004(7)
C(7)	0.0443(10)	0.0559(11)	0.0417(10)	0.0088(8)	-0.0121(10)	0.0012(10)
C(8)	0.0338(9)	0.0493(11)	0.0530(11)	0.0059(8)	-0.0037(8)	-0.0032(9)
O(9)	0.0563(8)	0.0393(6)	0.0417(7)	0.0142(6)	0.0033(7)	-0.0074(6)
C(10)	0.0406(9)	0.0391(8)	0.0390(10)	0.0050(7)	0.0018(9)	-0.0030(8)
C(11)	0.0431(8)	0.0337(7)	0.0344(8)	0.0022(7)	-0.0042(9)	-0.0030(7)
O(12)	0.0689(10)	0.0432(6)	0.0344(6)	0.0148(6)	-0.0054(7)	-0.0022(6)
C(13)	0.0493(12)	0.0383(8)	0.0369(8)	-0.0005(7)	-0.0005(7)	0.0023(7)
O(14)	0.0478(8)	0.0301(5)	0.0367(6)	0.0018(5)	-0.0006(6)	-0.0018(5)
C(15)	0.0323(8)	0.0264(7)	0.0343(8)	-0.0001(7)	-0.0012(7)	-0.0034(6)
C(16)	0.0627(14)	0.0749(15)	0.0686(17)	-0.0114(13)	0.0102(14)	0.0129(16)
C(17)	0.0655(13)	0.0448(10)	0.0521(12)	0.0140(9)	-0.0086(12)	0.0044(11)
C(18)	0.0369(9)	0.0343(8)	0.0421(10)	0.0023(7)	-0.0004(8)	-0.0017(8)
C(19)	0.0392(10)	0.0647(13)	0.0488(12)	0.0068(10)	0.0055(9)	-0.0089(10)
O(20)	0.0367(7)	0.0423(7)	0.0687(9)	-0.0014(6)	-0.0153(7)	-0.0050(7)
C(21)	0.0463(12)	0.0659(14)	0.0817(17)	-0.0162(11)	-0.0015(13)	-0.0177(14)
O(22)	0.0839(10)	0.0457(8)	0.0711(10)	-0.0217(8)	-0.0028(10)	-0.0055(9)
C(23)	0.103(2)	0.0811(19)	0.0677(16)	-0.0288(19)	-0.0132(16)	-0.0157(16)

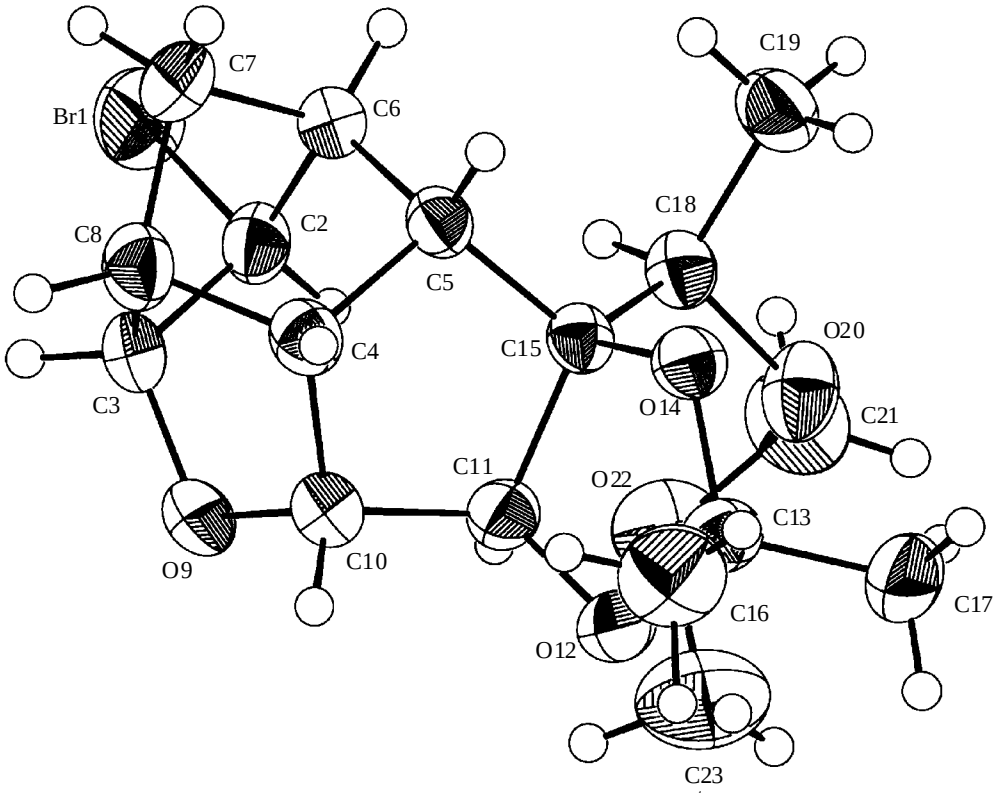
Table IV. Intramolecular bond length (Å) for (+)-**12a**

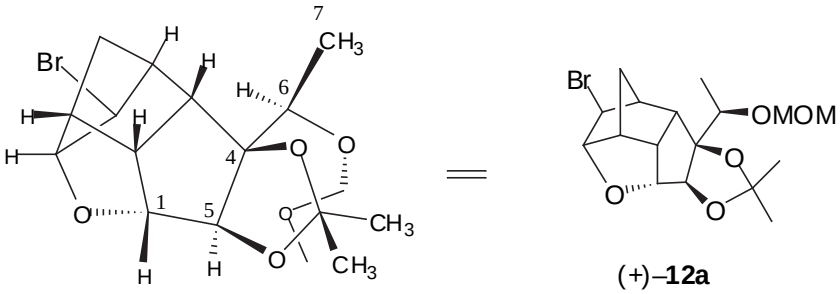
Br(1)-C(2)	1.962(2)	C(2)-C(3)	1.553(3)
C(2)-C(6)	1.532(2)	C(3)-C(8)	1.530(3)
C(3)-O(9)	1.427(2)	C(4)-C(5)	1.561(3)
C(4)-C(8)	1.546(3)	C(4)-C(10)	1.543(3)
C(5)-C(6)	1.552(2)	C(5)-C(15)	1.523(2)
C(6)-C(7)	1.539(3)	C(6)-C(8)	2.257(3)
C(7)-C(8)	1.535(3)	O(9)-C(10)	1.450(2)
C(10)-C(11)	1.539(3)	C(11)-O(12)	1.416(2)
C(11)-C(15)	1.545(2)	O(12)-C(13)	1.435(2)
C(13)-O(14)	1.426(2)	C(13)-C(16)	1.505(4)
C(13)-C(17)	1.507(3)	O(14)-C(15)	1.436(2)
C(15)-C(18)	1.532(3)	C(18)-C(19)	1.522(3)
C(18)-O(20)	1.434(2)	O(20)-C(21)	1.399(3)
C(21)-O(22)	1.395(3)	O(22)-C(23)	1.419(4)

Table V. Intramolecular bond angle for (+)-**12a**

Br(1)-C(2)-C(3)	111.87(12)	Br(1)-C(2)-C(6)	111.00(12)
C(3)-C(2)-C(6)	103.62(14)	C(2)-C(3)-C(8)	102.66(15)
C(2)-C(3)-O(9)	111.4(2)	C(8)-C(3)-O(9)	106.43(15)
C(5)-C(4)-C(8)	103.33(15)	C(5)-C(4)-C(10)	105.01(14)
C(8)-C(4)-C(10)	105.60(15)	C(4)-C(5)-C(6)	102.03(13)
C(4)-C(5)-C(15)	105.96(14)	C(6)-C(5)-C(15)	120.92(14)
C(2)-C(6)-C(5)	110.19(14)	C(2)-C(6)-C(7)	101.02(14)
C(2)-C(6)-C(8)	76.23(11)	C(5)-C(6)-C(7)	100.37(14)
C(5)-C(6)-C(8)	77.12(11)	C(7)-C(6)-C(8)	42.69(11)
C(6)-C(7)-C(8)	94.5(2)	C(3)-C(8)-C(4)	99.2(2)
C(3)-C(8)-C(6)	77.00(11)	C(3)-C(8)-C(7)	104.4(2)
C(4)-C(8)-C(6)	76.50(11)	C(4)-C(8)-C(7)	103.8(2)
C(6)-C(8)-C(7)	42.84(10)	C(3)-O(9)-C(10)	108.14(14)
C(4)-C(10)-O(9)	105.75(15)	C(4)-C(10)-C(11)	107.69(15)
O(9)-C(10)-C(11)	110.56(14)	C(10)-C(11)-O(12)	114.0(2)
C(10)-C(11)-C(15)	106.96(15)	O(12)-C(11)-C(15)	105.61(13)
C(11)-O(12)-C(13)	109.96(13)	O(12)-C(13)-O(14)	105.74(14)
O(12)-C(13)-C(16)	110.0(2)	O(12)-C(13)-C(17)	109.0(2)
O(14)-C(13)-C(16)	108.7(2)	O(14) -C(13) -C(17)	110.8(2)
C(16)-C(13)-C(17)	112.4(2)	C(13)-O(14) -C(15)	112.07(12)
C(5)-C(15)-C(11)	107.26(14)	C(5)-C(15)-O(14)	106.58(13)
C(5)-C(15)-C(18)	113.60(14)	C(11)-C(15)-O(14)	101.84(12)
C(11)-C(15)-C(18)	116.33(14)	O(14)-C(15)-C(18)	110.20(13)
C(15)-C(18)-C(19)	112.16(15)	C(15)-C(18)-O(20)	110.66(15)
C(19)-C(18)-O(20)	108.21(15)	C(18)-O(20)-C(21)	115.1(2)
O(20)-C(21)-O(22)	112.8(2)	C(21)-O(22)-C(23)	112.5(2)

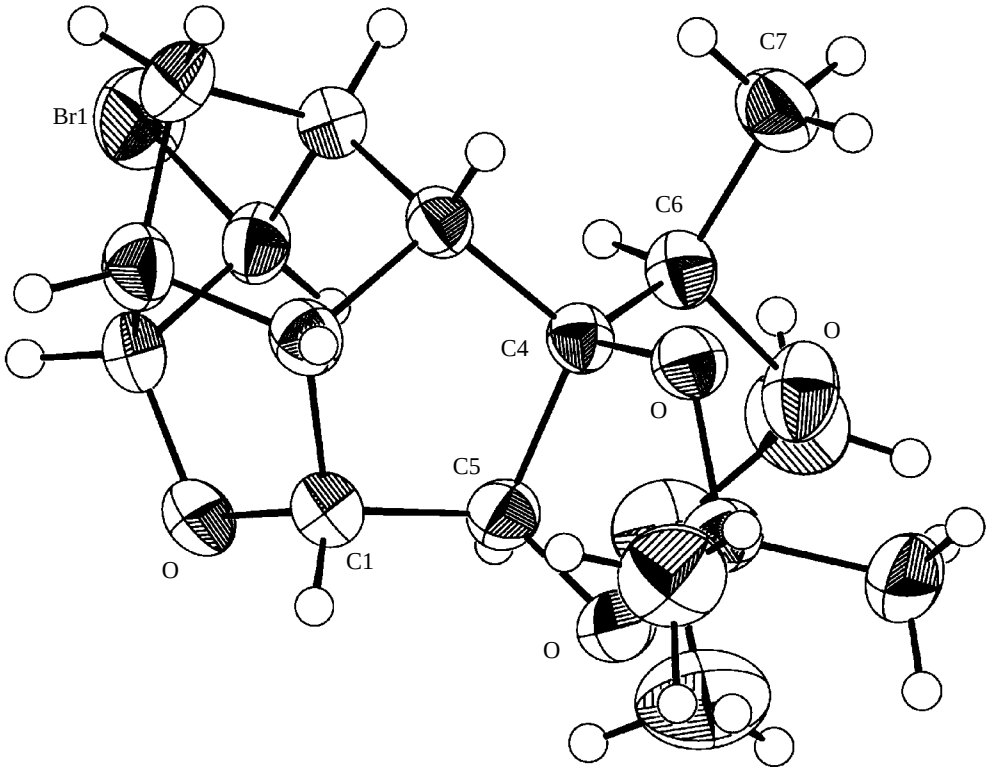
Figure. X-ray structure of (+)-**12a** at 288 K

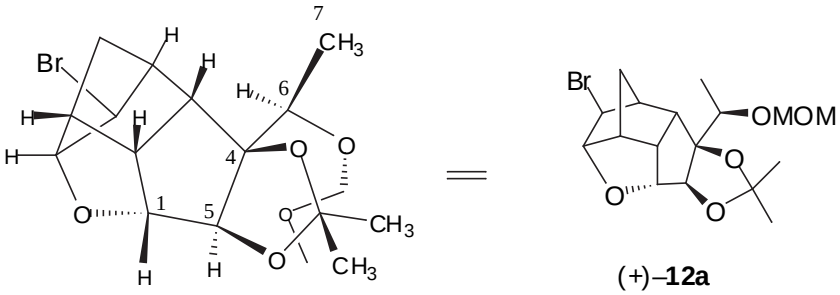




(+)–**12a**

Figure. X-ray structure of (+)-**12a** at 288 K (Showing the Pentenocin number)





(+)–**12a**