

Supporting Information

Stereoselective Construction of the Highly Congested Tricyclic Core Structure in Leucosceptroid H

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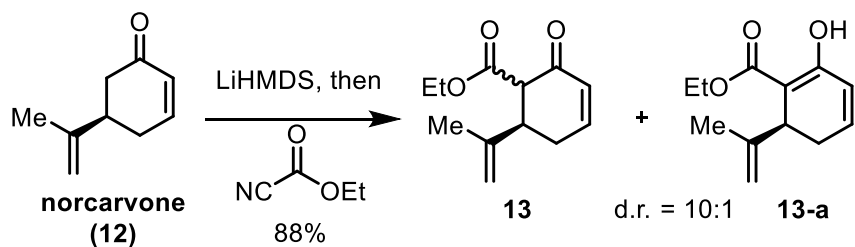
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1. General information

All air and moisture sensitive reactions were performed under an atmosphere of argon. Reagents obtained from Acros, Aldrich, J&K, and Aladdin were used without further purification. THF, Et₂O and toluene were dried by distillation over Na/benzophenone. MeCN, CH₂Cl₂. TLC inspections were on silica gel GF254 plates. Column chromatography was performed on silica gel (200-300 mesh).

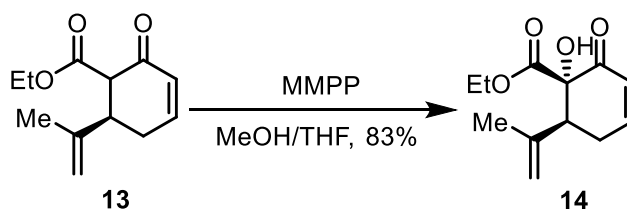
¹H NMR and ¹³C NMR spectra were recorded on a Bruker AVANCE AV400 (400 MHz and 100 MHz). Signal positions were recorded in ppm with the abbreviations s, d, t, and m denoting singlet, doublet, triplet, and multiplet respectively. All NMR chemical shifts were referenced to residual solvent peaks or to Si(CH₃)₄ as an internal standard, spectra recorded in CDCl₃ were referenced to residual CHCl₃ at 7.26 ppm for ¹H NMR or 77.16 ppm for ¹³C NMR, spectra recorded in CD₃OD were referenced to residual CD₂HOD at 3.31 ppm for ¹H NMR or 49.00 ppm for ¹³C NMR. All coupling constants *J* are quoted in Hz. FTIR spectra were obtained with a Bruker Tensor 27 instrument. All IR samples were prepared as thin film and reported in wave numbers (cm⁻¹). High resolution mass spectra (HRMS) were obtained on an IonSpec QFT mass spectrometer with ESI ionization. Optical rotations were recorded on a Perkin–Elmer 341 polarimeter (using the sodium D line; 589 nm). Heating mantle was used as the heat source, when reactions required heating.

2. Experimental details for new compounds

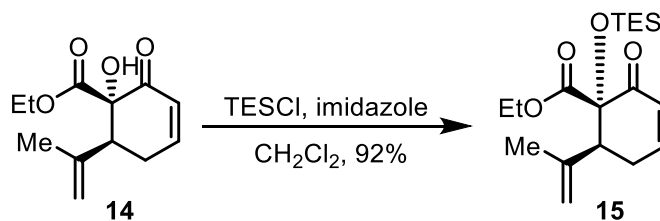


To a stirred solution of lithium *bis*(trimethylsilyl)amide (LHMDS; 400.0 mL, 1.0 M in THF, 400.00 mmol, 1.3 eq.) in anhydrous THF (400.0 mL) at -78 °C under argon was added norcarvone (42.0 g, 309.00 mmol, 1.0 eq.) dropwise for 1.5 h. The mixture was stirred at that temperature for 1 hour, after which ethylcyanoformate (36.7 mL, 371.00 mmol, 1.2 eq.) was added dropwise over 45 min at -78 °C. After stirring for an additional 1.5 h at -60 °C, the

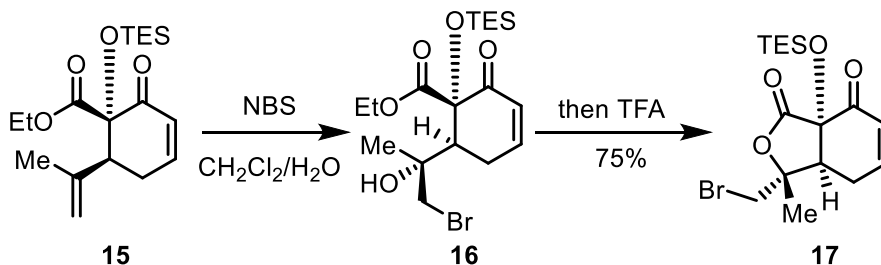
solution was poured into saturated aqueous NH_4Cl (500 mL) and extracted with EtOAc (3×300 mL). The combined organic layers were washed with brine (500 mL) and dried over MgSO_4 . The organic solvents were removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give product **13** (56.3 g, 272.00 mmol, 88%) as a light yellow oil. Data for **13**: R_f 0.35 (8:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.15 – 6.95 (m, 1H), 6.20 – 5.91 (m, 1H), 4.96 – 4.67 (m, 2H), 4.29 – 4.03 (m, 2H), 3.47 (dd, J = 12.8, 2.4 Hz, 1H), 3.28 – 3.07 (m, 1H), 2.58 – 2.46 (m, 1H), 2.43 – 2.27 (m, 1H), 1.84 – 1.68 (m, 3H), 1.34 – 1.15 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 194.5, 169.5, 149.7, 144.4, 128.8, 113.3, 61.1, 58.5, 45.4, 30.8, 19.7, 14.2; IR (thin film) ν_{max} 3460, 3079, 2979, 2933, 1739, 1679, 1447, 1380, 1305, 1256, 1176, 1140, 1093, 1036, 903, 734, 527; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{16}\text{NaO}_3$: 231.0992, found: 231.0995.



To a stirred solution of **13** (57.0 g, 274.00 mmol, 1.0 eq.) in THF (1.0 L) and MeOH (100.0 mL) was added 80% magnesium monoperoxyphthalate hexahydrate (MMPP; 118.1 g, 192.00 mmol, 0.7 eq.) at 0 °C, the resultant mixture was stirred for 3 h at room temperature, then petroleum ether (500 mL) was added. The precipitation was filtered through a pad of Celite, washed with Et₂O (200 mL×3). The combined filtrate was washed with NaHSO_3 (500 mL), NaHCO_3 (500 mL), brine (500 mL), and dried over MgSO_4 . The organic solvents were removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give product **14** (50.9 g, 227.00 mmol, 83%) as a light yellow oil. Data for **14**: R_f 0.35 (8:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.19 (dd, J = 10.2, 2.2 Hz, 1H), 6.16 (dd, J = 10.0, 2.9, 1H), 4.99 (s, 1H), 4.89 (t, J = 2.7 Hz, 1H), 4.23 – 4.13 (m, 3H), 3.14 – 2.99 (m, 1H), 2.92 (dd, J = 11.7, 4.8 Hz, 1H), 2.55 – 2.45 (m, 1H), 1.90 – 1.79 (m, 3H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.5, 169.4, 153.7, 143.2, 126.2, 114.3, 80.8, 62.3, 50.4, 30.7, 23.1, 14.1; IR (thin film) ν_{max} 3484, 3083, 3041, 2978, 2926, 1740, 1679, 1449, 1383, 1321, 1212, 1123, 1089, 1054, 1021, 946, 898, 862, 811, 708, 651, 567, 472; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{16}\text{NaO}_4$: 247.0941, found: 247.0946.

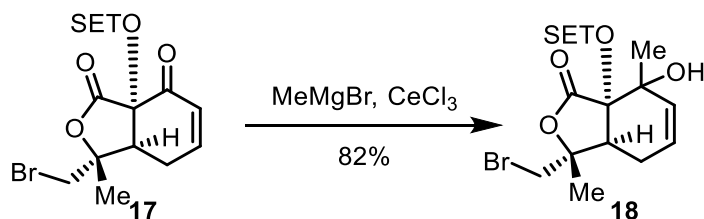


To a stirred solution of compound **14** (26.0 g, 116.00 mmol, 1.0 eq.) in CH_2Cl_2 (150.0 mL) was added imidazole (16.0 g, 232.00 mmol, 2.0 eq.) and TESCl (23.5 mL, 139.00 mmol, 1.2 eq.) sequentially at 0 °C. The mixture was warmed to room temperature and stirred overnight, before it was quenched with sat. NH_4Cl (100 mL). The mixture was extracted with CH_2Cl_2 (3 x 200 mL) and the combined organic phases were washed with brine (2 x 200 mL), dried over MgSO_4 . The organic solvents were removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 30:1) to give product **15** (36.0 g, 106.00 mmol, 92%) as a light yellow oil. Data for **15**: R_f 0.85 (8:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 7.10 – 6.99 (m, 1H), 6.09 (d, J = 10.0 Hz, 1H), 4.92 (s, 1H), 4.75 (s, 1H), 4.11 (q, J = 7.0 Hz, 2H), 2.90 – 2.73 (m, 2H), 2.45 – 2.29 (m, 1H), 1.81 (s, 3H), 1.24 (t, J = 7.1, 3H), 0.95 – 0.88 (m, 9H), 0.74 – 0.54 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 195.6, 169.3, 151.5, 144.1, 127.6, 113.5, 84.2, 61.4, 53.1, 30.8, 23.8, 14.1, 7.3, 6.7; IR (thin film) ν_{max} 3082, 2954, 2922, 2877, 1750, 1729, 1685, 1589, 1457, 1418, 1374, 1315, 1293, 1227, 1179, 1104, 1080, 1012, 964, 892, 842, 783, 731, 585; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{30}\text{NaO}_4\text{Si}$: 361.1806, found: 361.1815.



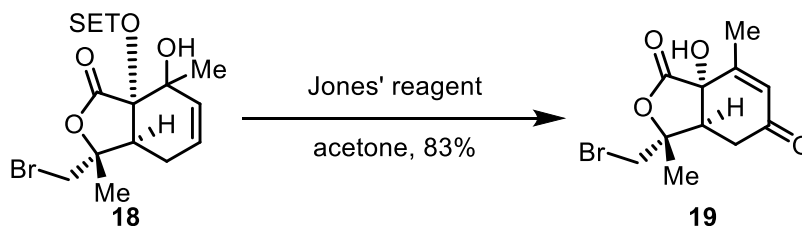
To a stirred solution of compound **15** (31.5g, 93.00 mmol, 1.0 eq.) in CH_2Cl_2 (450.0 mL) and H_2O (45.0 mL) at room temperature was added NBS (33.0 g, 186.00 mmol, 2.0 eq.). After 4 h, TLC showed the consumption of the starting material, TFA (3.0 mL) add added. The mixture was stirred overnight, before it was quenched with saturated aqueous NaHSO_3 (200 mL) and

extracted with CH₂Cl₂ (200 mL×3). The combined organic extracts were washed with saturated aqueous NaHCO₃ (200 mL), brine (200 mL), and dried over MgSO₄. The organic solvents were removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give product **17** (27.1 g, 70.00 mmol, 75%) as a light yellow oil. Data for **17**: R_f 0.52 (3:1, petroleum ether: ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 6.99 – 6.91 (m, 1H), 6.21 (d, *J* = 10.5 Hz, 1H), 3.57 (d, *J* = 11.1 Hz, 1H), 3.49 (d, *J* = 11.1 Hz, 1H), 3.15 (d, *J* = 7.5 Hz, 1H), 2.83 – 2.71 (m, 1H), 2.54 (dd, *J* = 21.0, 5.3 Hz, 1H), 1.38 (s, 3H), 0.91 (t, *J* = 7.9 Hz, 9H), 0.78 – 0.57 (m, *J* = 7.4 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 189.8, 170.2, 148.1, 128.1, 81.8, 77.6, 48.7, 39.9, 22.9, 20.7, 6.9, 5.9; IR (thin film) *v*_{max} 2956, 2912, 2876, 1795, 1681, 1458, 1422, 1320, 1275, 1245, 1203, 1171, 1142, 1064, 1017, 959, 892, 865, 865, 747, 693, 651, 596, 478; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₆H₂₅BrNaO₄Si: 411.0598, found: 411.0602.

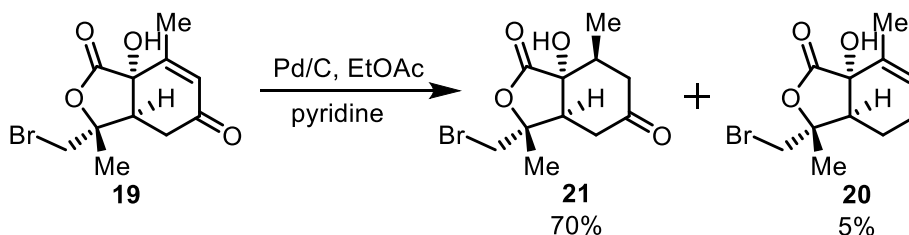


To a suspension of anhydrous CeCl₃, which was dried at 250 °C under vacuum for 30 min prior to use, (39.0 g, 159.00 mmol, 2.0 eq.) in anhydrous THF (400.0 mL) stirred for overnight. To a stirred solution of the mixture at 0 °C was added CH₃MgBr (240.0 mL, 3.0 M in THF, 240.00 mmol, 3.0 eq.) and the mixture was stirred for 1 h at 0 °C and treated dropwise with a solution of enone **17** (31.0 g, 79.70 mmol, 1.0 eq.) in THF (50.0 mL). The reaction mixture was stirred for additional 30 min 0 °C. The reaction was quenched by the addition of saturated aqueous NH₄Cl (300 mL). The phases were separated and the aqueous layer was extracted with EtOAc (100 mL×3). The combined organic layers were washed with saturated aqueous NaCl (200 mL) and dried over MgSO₄. The solvents were removed under reduced pressure and the crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **18** (26.6 g, 66.00 mmol, 82%) as a light yellow oil. Data for **18**: R_f 0.92 (3:1, petroleum ether: ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 5.85 – 5.74 (m, 2H), 3.52 (d, *J* = 10.3 Hz, 1H), 3.41 (d, *J* = 10.1 Hz, 1H), 3.28 (s, 1H), 2.76 (dd, *J* = 9.2, 5.6 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.13 – 2.04 (m, 1H), 1.52 (s, 3H), 1.24 (s, 3H), 0.98 – 0.89 (m, 9H), 0.73 – 0.60 (m, 6H);

^{13}C NMR (100 MHz, CDCl_3) δ 173.6, 135.7, 125.2, 83.4, 83.0, 70.8, 48.0, 42.1, 23.3, 22.7, 21.1, 6.9, 6.07; IR (thin film) ν_{max} 2955, 2912, 2876, 1777, 1457, 1417, 1382, 1338, 1273, 1238, 1205, 1107, 1057, 1042, 1009, 936, 899, 876, 840, 822, 744, 730, 679, 637; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{29}\text{BrNaO}_4\text{Si}$: 427.0911, found: 427.0915.



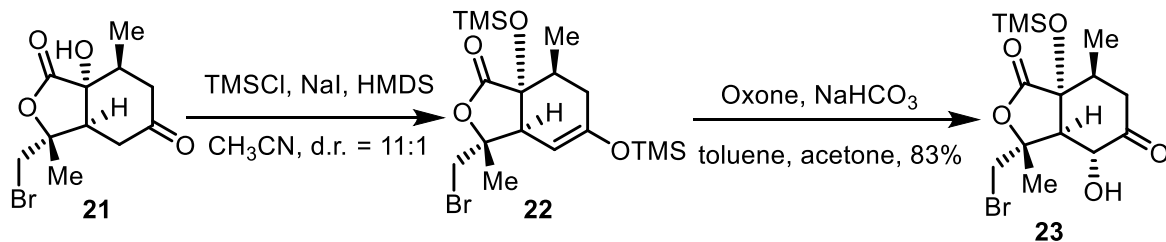
To a stirred solution of **18** (1.5 g, 3.70 mmol, 1.0 eq.) in acetone (37.0 mL) was added Jones' reagent (2.5 mL, 3.0 M in H_2O , 7.40 mmol, 2.0 eq.) at 0 °C. The mixture stirred for 2 h 0 °C, before it was quenched with saturated aqueous NaHSO_3 (100 mL) and extracted with Et_2O (50 mL \times 3). The combined organic extracts were washed with saturated aqueous NaHCO_3 (200 mL), brine (200 mL), and dried over MgSO_4 . The organic solvents were removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to give product **19** (888.0 mg, 3.07 mmol, 83%) as a white solid. Data for **19**: R_f 0.18 (4:1, petroleum ether: ethyl acetate); mp = 105–107 °C; ^1H NMR (400 MHz, acetone) δ 6.11 (s, 1H), 5.90 (s, 1H), 3.97 – 3.84 (m, 2H), 3.33 (t, J = 9.9 Hz, 1H), 2.85 – 2.75 (m, 1H), 2.74 – 2.65 (m, 1H), 2.20 – 2.11 (m, 3H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, acetone) δ 194.8, 172.5, 154.2, 129.9, 82.7, 73.5, 47.0, 40.2, 32.6, 19.5, 17.6; IR (thin film) ν_{max} 3436, 2986, 2924, 2853, 1731, 1627, 1535, 1461, 1378, 1268, 1142, 1042, 893, 757; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{11}\text{H}_{14}\text{BrO}_4$: 289.0070, found: 289.0091.



A mixture of **19** (824.0 mg, 2.85 mmol, 1.0 eq.) and Pd on active carbon (10% Wt.%, 82.0 mg) in EtOAc (30.0 mL) and pyridine (2.2 μL , 28.50 μmol , 0.01 eq.) was stirred under a hydrogen atmosphere (with a hydrogen balloon) at room temperature for 6 h. TLC showed the complete

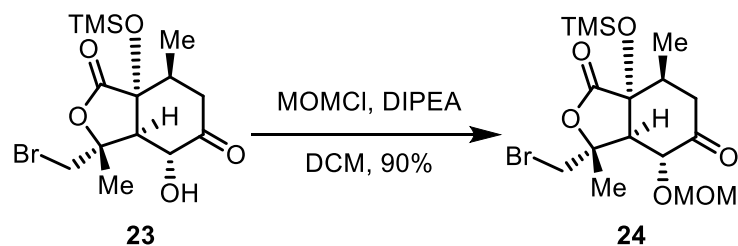
conversion of the starting material. The catalyst was filtered, and the solvent was removed under reduced pressure to give the crude product. The crude product was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give product **21** (580.0 mg, 2.00 mmol, 70%) as a white solid, and product **20** (39.0 mg, 0.14 mmol, 5%) as a light yellow oil. Data for **21**: R_f 0.55 (3:1, petroleum ether: ethyl acetate); mp = 132–134 °C; ^1H NMR (400 MHz, CDCl_3) δ 3.63 (d, J = 10.3 Hz, 1H), 3.54 (d, J = 10.3 Hz, 1H), 3.11 (s, 1H), 3.08 – 3.02 (m, 1H), 2.79 – 2.69 (m, 1H), 2.62 – 2.55 (m, 1H), 2.49 – 2.40 (m, 2H), 2.13 – 2.03 (dd, J = 19.2, 10.7 Hz, 1H), 1.48 (s, 3H), 1.23 (d, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 208.8, 174.8, 84.8, 78.3, 46.6, 42.1, 41.1, 38.3, 36.3, 21.4, 14.5; IR (thin film) ν_{max} 2967, 2854, 2699, 1770, 1714, 1462, 1383, 1288, 1131, 1099, 1048, 916, 759; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{11}\text{H}_{15}\text{BrNaO}_4$: 313.0040, found: 313.0054.

Data for **20**: R_f 0.65 (3:2, petroleum ether: ethyl acetate); mp = 122–124 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.87 – 5.78 (m, 1H), 3.79 (d, J = 10.5 Hz, 1H), 3.60 (d, J = 10.5 Hz, 1H), 2.98 (s, 1H), 2.75 – 2.68 (m, 1H), 2.17 – 2.09 (m, 2H), 1.95 – 1.86 (m, 4H), 1.71 – 1.60 (m, 1H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 130.4, 129.8, 84.5, 77.5, 74.9, 46.8, 40.4, 23.1, 20.7, 20.4, 17.2; IR (thin film) ν_{max} 3445, 2923, 1763, 1440, 1382, 1288, 1161, 1060, 1009, 976, 917, 683; HRMS (ESI) m/z : $[\text{M} + \text{NH}_4]^+$ Calcd for $\text{C}_{11}\text{H}_{19}\text{BrNO}_3$: 292.0543, found: 292.0542.



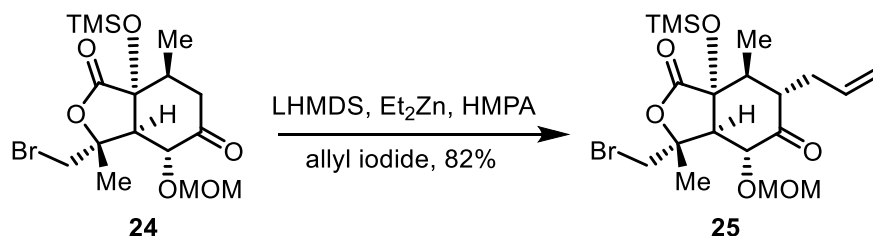
To a stirred solution of **21** (4.2 g, 14.40 mmol, 1.0) and HMDS (10.5 mL, 50.50 mmol, 3.5 eq.) in CH_3CN (100.0 mL) was added NaI (6.5 g, 43.20 mmol, 3.0 eq.) and TMSCl (5.5 mL, 43.20 mmol, 3.0 eq.) at 0 °C under argon. After 30 min, the mixture was warmed to room temperature and stirred overnight, before it was quenched with sat. NaHCO_3 (100 mL). The mixture was extracted with petroleum ether (3 x 100 mL) and the combined organic phases were washed with brine (2 x 200 mL), dried over MgSO_4 . The solvent was removed under reduced pressure to afford silyl enol ethers **22** as a colorless oil which was used in the next step without further purification.

To a solution of silyl enol ethers **22** in toluene (100.0 mL), acetone (20.0 mL) and H₂O (50.0 mL) was added NaHCO₃ (24.0 g, 288.00 mmol, 20.0 eq.) and 43% purity of Oxone (25.0 g, 72.00 mmol, 5.0 eq.) at 0°C. The resulting mixture was stirred for 30 min at the same temperature. After TLC showed the consumption of the starting material, the reaction was quenched with a saturated solution of NaHSO₃ (50 mL), and the mixture was extracted with Et₂O (50 mL×3). The combined organic layers were washed with brine (100 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 5:1) to give product **23** (4.5 g, 11.90 mmol, 83%) as a light yellow oil. Data for **23**: R_f 0.38 (3:1, petroleum ether: ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 4.44 (dd, *J* = 10.6, 3.3 Hz, 1H), 3.73 – 3.64 (m, 2H), 3.52 (d, *J* = 11.2 Hz, 1H), 2.99 – 2.92 (m, 1H), 2.76 (dd, *J* = 10.6, 1.1 Hz, 1H), 2.59 – 2.49 (m, 1H), 2.38 – 2.31 (m, 1H), 1.70 (s, 3H), 1.20 (d, *J* = 7.8 Hz, 3H), 0.18 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 209.6, 173.9, 83.0, 81.2, 70.8, 58.1, 42.2, 38.8, 35.9, 21.8, 17.6, 1.8; IR (thin film) *v*_{max} 3471, 2958, 1778, 1724, 1458, 1388, 1336, 1257, 1181, 1116, 1082, 1050, 961, 877, 844, 756, 697, 622, 586, 547, 513; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₂₃BrNaO₅Si: 401.0390, found: 401.0395.

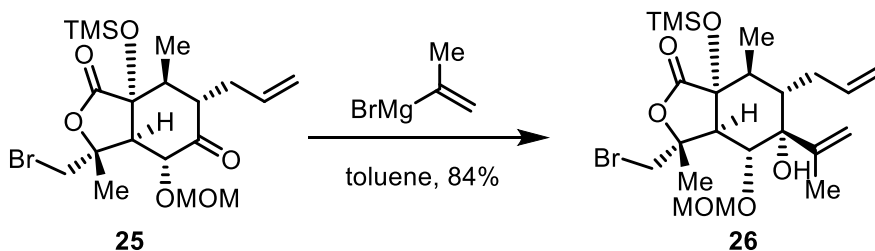


To a stirred solution of **23** (100.0 mg, 0.26 mmol, 1.0 eq.) in CH₂Cl₂ (3.0 mL) was added DIPEA (262 μL, 1.58 mmol, 6.0 eq.) and MOMCl (88 μL, 1.05 mmol, 4.0 eq.) at 0°C. After 30 min, the mixture was warmed to 40 °C and stirred overnight, before it was quenched with a saturated solution of NH₄Cl (10 mL), and the mixture was extracted with EtOAc (10 mL×3). The combined organic extract was washed with brine (10 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give product **24** (99.0 mg, 0.24 mmol, 90%) as a light yellow oil. Data for **24**: R_f 0.48 (3:1, petroleum ether: ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 4.79 (d, *J* = 7.2 Hz, 1H), 4.71 (d, *J* = 7.2 Hz, 1H), 4.43 (d, *J* = 9.5 Hz, 1H), 3.68 (d, *J* = 11.0 Hz, 1H), 3.48 (d, *J* = 11.0 Hz, 1H), 3.41 (s, 3H), 3.02 (d, *J* = 9.4 Hz, 1H), 2.90 – 2.83 (m,

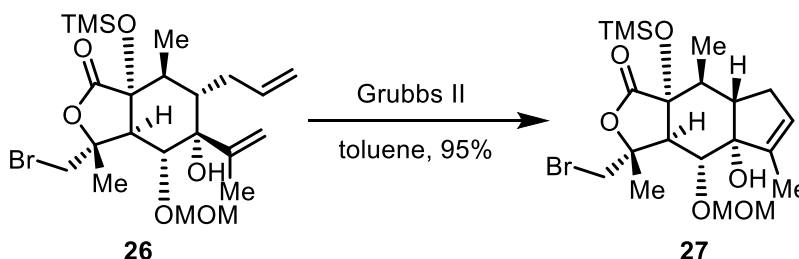
1H), 2.65 – 2.58 (m, 1H), 2.23 – 2.16 (m, 1H), 1.65 (s, 3H), 1.23 (d, $J = 7.5$ Hz, 3H), 0.18 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.0, 173.6, 96.8, 82.6, 81.2, 75.9, 56.9, 55.9, 42.2, 40.8, 35.8, 21.3, 17.5, 1.8; IR (thin film) ν_{max} 3006, 2989, 2903, 1779, 1731, 1457, 1417, 1387, 1276, 1261, 1212, 1179, 1103, 1078, 1035, 964, 922, 881, 844, 763, 746, 706; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{27}\text{BrNaO}_6\text{Si}$: 445.0652, found: 445.0655.



To a stirred solution of lithium *bis*(trimethylsilyl)amide (LHMDs; 1.9 mL, 1.0 M in THF, 2.53 mmol, 1.2 eq.) in anhydrous THF (2.0 mL) at -78°C under argon was added compound **24** (892.0 mg, 2.11 mmol, 1.0 eq.) in THF (2.0 mL) dropwise for 60 min. The mixture was stirred at that temperature for 1 hour, after which Et_2Zn (2.1 mL, 1.0 M in hexane, 2.11 mmol, 1.0 eq.), HMPA (490 μL , 2.74 mmol, 1.3 eq.) and allyl iodide (394 μL , 4.22 mmol, 2.0 eq.) was added. The mixture was slowly warmed to 0°C , and TLC showed the consumption of the starting material, then the reaction was quenched with a saturated solution of NH_4Cl (20 mL) and the mixture was extracted with Et_2O (20 mL \times 3). The combined organic layers were washed with brine (20 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give product **25** (796.0 mg, 1.72 mmol, 82%) as a light yellow oil. Data for **25**: R_f 0.56 (3:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 5.75 (q, $J = 8.5$ Hz, 1H), 5.19 – 5.04 (m, 2H), 4.77 – 4.63 (m, 2H), 4.51 (d, $J = 9.8$ Hz, 1H), 3.66 (d, $J = 11.0$ Hz, 1H), 3.47 (d, $J = 11.0$ Hz, 1H), 3.42 (d, $J = 1.3$ Hz, 3H), 3.02 (d, $J = 9.7$ Hz, 1H), 2.92 – 2.85 (m, 1H), 2.60 – 2.45 (m, 1H), 2.28 – 2.17 (m, 1H), 2.16 – 2.04 (m, 1H), 1.66 (s, 3H), 1.28 (d, $J = 7.8$ Hz, 3H), 0.22 – 0.15 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 207.5, 173.6, 135.5, 117.6, 96.1, 82.2, 81.1, 74.7, 57.4, 56.9, 52.3, 42.4, 42.3, 35.1, 21.3, 19.5, 1.9; IR (thin film) ν_{max} 2995, 2925, 2853, 1771, 1376, 1246, 1101, 1050, 1019, 845; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{31}\text{BrNaO}_6\text{Si}$: 485.0965, found: 485.0970.

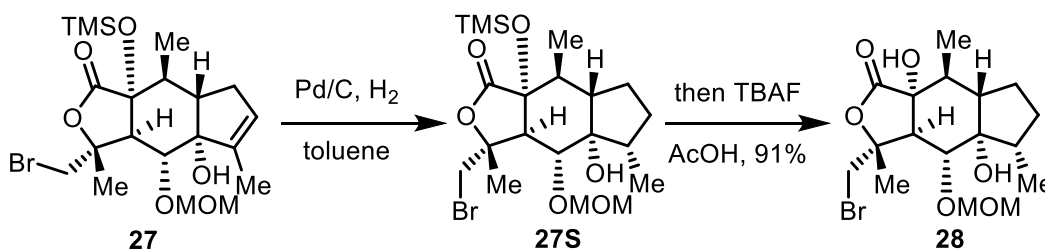


To a stirred solution of **25** (262.0 mg, 0.56 mmol, 1.0 eq.) in toluene (5.0 mL) at 0°C under argon was added isopropenylmagnesium bromide (1.4 mL, 0.5 M in THF, 0.85 mmol, 1.2 eq.). The resultant mixture was then stirred at the same temperature for 15 min. The reaction was quenched by addition of a saturated solution of NH₄Cl (10 mL), and the mixture was extracted with EtOAc (3×5 mL). The combined organic extracts were washed with brine (5 mL), and dried over Na₂SO₄. The solvent was removed under vacuum, and residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give product **26** (239.0 mg, 0.47 mmol, 84%, single isomer) as a white solid. Data for **26**: *R_f* 0.78 (4:1, petroleum ether: ethyl acetate); mp = 156–158 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.80 – 5.70 (m, 1H), 5.42 (s, 1H), 5.18 – 5.10 (m, 2H), 5.06 – 5.03 (m, 1H), 4.67 (s, 2H), 4.34 (s, 1H), 3.92 (s, 1H), 3.81 (d, *J* = 11.0 Hz, 1H), 3.57 (d, *J* = 11.0 Hz, 1H), 3.35 (s, 3H), 3.22 (d, *J* = 9.9 Hz, 1H), 2.33 – 2.26 (m, 1H), 2.21 – 2.16 (m, 1H), 2.12 – 2.03 (m, 1H), 1.83 (s, 3H), 1.70 (s, 3H), 1.24 (s, 1H), 1.00 (d, *J* = 7.6 Hz, 3H), 0.27 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 225.4, 173.6, 143.9, 136.8, 123.3, 117.0, 83.6, 83.1, 79.8, 77.3, 76.9, 56.6, 52.8, 52.5, 43.1, 38.0, 35.3, 21.7, 20.4, 1.8; IR (thin film) *ν*_{max} 3463, 3441, 2955, 1778, 1636, 1279, 1255, 1069, 1029, 916, 848, 756, 712, 668, 534, 493, 451; HRMS (ESI) *m/z*: [M + H]⁺ Calcd for C₂₂H₃₈BrO₆Si: 505.1616, found: 505.1610.



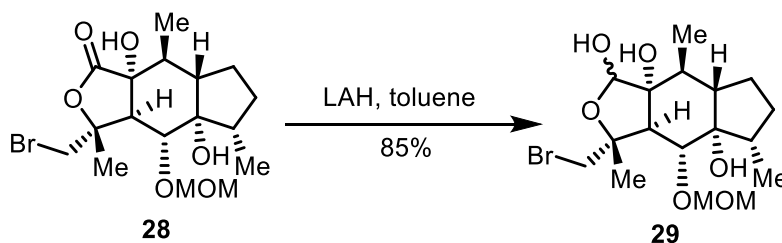
To a stirred solution of **26** (191.0 mg, 0.38 mmol, 1.0 eq.) in toluene (5.0 mL) was added Grubbs II catalyst (32.0 mg, 0.04 mmol, 0.1 eq.) at 50 °C for 5 h. The reaction was cooled back to room temperature, quenched with a saturated solution of NaHCO₃ (5 mL), and the mixture was extracted with EtOAc (10 mL×3). The combined organic extract was washed with brine (10 mL),

and dried over Na₂SO₄. The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give product **27** (172.0 mg, 0.36 mmol, 95%) as a white solid. Data for **27**: *R_f* 0.58 (8:1, petroleum ether: ethyl acetate); mp = 142–144 °C; ¹H NMR (400 MHz, CDCl₃) δ 5.60 (q, *J* = 2.0 Hz, 1H), 5.05 (d, *J* = 7.2 Hz, 1H), 4.76 (d, *J* = 7.2 Hz, 1H), 4.09 (d, *J* = 10.2 Hz, 1H), 3.81 (d, *J* = 8.2 Hz, 1H), 3.75 (s, 1H), 3.60 (d, *J* = 10.2 Hz, 1H), 3.46 (s, 3H), 3.18 (d, *J* = 8.1 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.16 (dd, *J* = 8.2, 2.1 Hz, 2H), 1.87 (q, *J* = 2.0 Hz, 3H), 1.62 (s, 3H), 1.42 – 1.31 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.28 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 172.8, 144.6, 130.3, 93.8, 83.8, 83.7, 81.8, 79.1, 56.9, 51.5, 49.8, 41.0, 37.5, 32.0, 22.7, 14.7, 13.3, 1.8; IR (thin film) *ν*_{max} 2955, 2960, 1770, 1758, 1374, 1245, 1049, 939, 847, 734, 703, 634, 609; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₀H₃₃BrNaO₆Si: 499.1122, found: 499.1126.

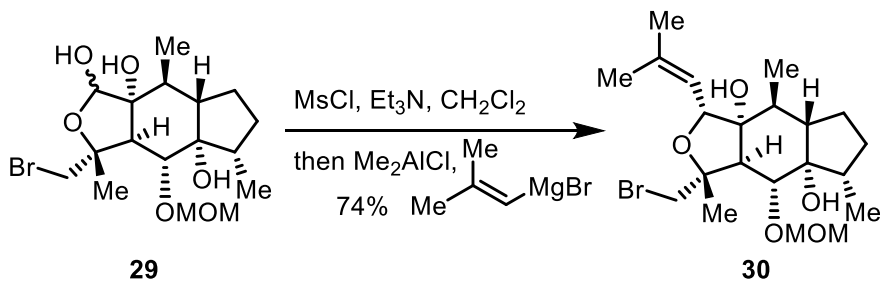


A mixture of **27** (146.0 mg, 0.31 mmol, 1.0 eq.) and Pd on active carbon (10% Wt.%, 15.0 mg) in toluene (5.0 mL) was stirred under a hydrogen atmosphere (with a hydrogen balloon) at room temperature for 5 h. TLC showed the complete conversion of the starting material, AcOH (86 μL, 1.44 mmol, 3.0 eq.) and TBAF (0.9 mL, 1.0 M in THF, 0.96 mmol, 2.0 eq.) was added, and the mixture was stirred for another 2 h. The catalyst was filtered through a pad of Celite, washed with Et₂O (10 mL). The combined filtrate was washed with NaHCO₃ (10 mL), brine (10 mL), and dried over MgSO₄. The organic solvents were removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 6:1) to give product **28** (115.0 mg, 0.28 mmol, 91%) as a white solid. Data for **28**: *R_f* 0.43 (4:1, petroleum ether: ethyl acetate); mp = 161–163 °C; ¹H NMR (400 MHz, CDCl₃) δ 4.79 (d, *J* = 7.0 Hz, 1H), 4.70 (d, *J* = 7.0 Hz, 1H), 4.33 (s, 1H), 3.96 (d, *J* = 10.8 Hz, 1H), 3.66 (d, *J* = 10.9 Hz, 1H), 3.55 (d, *J* = 6.0 Hz, 1H), 3.41 (s, 3H), 3.09 (d, *J* = 6.1 Hz, 1H), 2.26 – 2.15 (m, 1H), 1.95 – 1.69 (m, 4H), 1.54 (s, 3H), 1.45 – 1.32 (m, 2H), 1.22 (d, *J* = 2.6 Hz, 1H), 1.10 (d, *J* = 7.4 Hz, 3H), 1.04 (d, *J* = 6.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 173.6, 95.3, 82.8, 80.5, 80.3, 80.1, 56.8,

54.4, 50.1, 43.3, 41.1, 41.1, 31.4, 26.9, 22.7, 15.0, 14.6; IR (thin film) ν_{\max} 3410, 2988, 2950, 1765, 1457, 1377, 1243, 1155, 1053, 931, 740, 631; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{17}H_{27}BrNaO_6$: 429.0883, found: 429.0888.



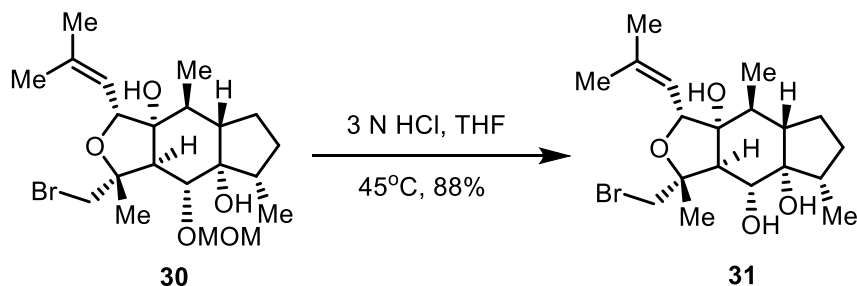
To a stirred solution of compound **28** (20.0 mg, 0.04 mmol, 1.0 eq.) in anhydrous toluene (0.5 mL) at $-78\text{ }^{\circ}\text{C}$ under argon was added LAH (35 μL , 2.4 M in THF, 0.08 mmol, 2.0 eq.) slowly. The mixture was stirred for 30 min, after which the reaction was quenched by addition of ethyl acetate (2 mL) at $-78\text{ }^{\circ}\text{C}$ followed by addition of a saturated sodium potassium tartrate solution (10 mL). The resulting suspension was allowed to warm to room temperature with vigorous stirring for 2 h. The organic layer was collected, and the aqueous layer was extracted with Et_2O (20 mL \times 3). The combined organic layers were washed with brine (20 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by a flash column chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) to give product **29** (15.0 mg, 0.04 mmol, 85%, d.r. > 20:1) as a white solid. Data for **29**: R_f 0.15 (4:1, petroleum ether: ethyl acetate); mp = 168–170 $^{\circ}\text{C}$; ^1H NMR (400 MHz, acetone- d_6) δ 5.27 (d, J = 3.2 Hz, 1H), 5.04 (d, J = 3.2 Hz, 1H), 4.94 (d, J = 5.8 Hz, 1H), 4.76 (d, J = 5.8 Hz, 1H), 3.88 (d, J = 10.2 Hz, 1H), 3.82 – 3.75 (m, 2H), 3.40 (d, J = 6.9 Hz, 3H), 3.01 (s, 1H), 2.51 (d, J = 10.2 Hz, 1H), 2.12 – 2.01 (m, 3H), 1.99 – 1.90 (m, 1H), 1.61 (s, 3H), 1.45 – 1.40 (m, 1H), 1.38 – 1.28 (m, 2H), 1.13 – 1.04 (m, 6H), 0.90 (d, J = 7.0 Hz, 1H); ^{13}C NMR (100 MHz, acetone) δ 103.4, 96.7, 86.7, 85.8, 83.1, 81.4, 56.5, 55.5, 50.3, 45.9, 42.7, 40.0, 33.1, 26.6, 24.4, 16.0, 12.6; IR (thin film) ν_{\max} 3457, 2955, 2923, 1774, 1637, 1455, 1379, 1269, 1203, 1147, 1082, 1032, 1010, 923, 755; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{17}H_{29}BrNaO_6$: 431.1040, found: 431.1045.



To a stirred solution of compound **29** (200.0 mg, 0.49 mmol, 1.0 eq.) in anhydrous CH_2Cl_2 (1.0 mL) was added Et_3N (0.5 mL, 3.65 mmol, 7.5 eq.) and MsCl (120 μL , 1.47 mmol, 3.0 eq.) at room temperature. The resultant mixture was then stirred at room temperature for 1 h. The reaction was quenched with a saturated solution of NH_4Cl (5 mL), and the mixture was extracted with CH_2Cl_2 (5 mL \times 3). The combined organic extract was washed with brine (5 mL), dried over MgSO_4 . The solvent was removed under vacuum to afford the crude unstable methanesulfonate ester product as a colorless oil which was used in the next step without further purification.

To a stirred solution of 2-methyl-1-propenylmagnesium bromide (7.8 mL, 0.5 M in THF, 3.92 mmol, 8.0 eq.) was added Me_2AlCl (4.4 mL, 0.9 M in toluene, 3.92 mmol, 8.0 eq.) at 0 °C under argon. The resultant mixture was stirred for 1 h at the same temperature. Next, to the above reaction mixture was added the solution of crude methanesulfonate ester product in anhydrous CH_2Cl_2 (2.0 mL) at 0 °C. The reaction mixture was stirred for 30 min before it was quenched with a saturated sodium potassium tartrate solution (20 mL). The resulting suspension was allowed to warm to room temperature with vigorous stirring for 2 h. The organic layer was collected, and the aqueous layer was extracted with Et_2O (20 mL \times 3). The combined organic layers were washed with brine (20 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to give product **30** ((159.0 mg, 0.36 mmol, 74%, single isomer) as a colorless oil. Data for **30**: R_f 0.85 (3:1, petroleum ether: ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 5.46 (d, J = 9.3 Hz, 1H), 4.98 (d, J = 6.4 Hz, 1H), 4.65 (d, J = 6.3 Hz, 1H), 4.43 (d, J = 9.3 Hz, 1H), 4.20 (d, J = 9.7 Hz, 1H), 3.65 (d, J = 10.3 Hz, 1H), 3.42 (d, J = 7.4 Hz, 4H), 3.24 (s, 1H), 2.81 (d, J = 10.3 Hz, 1H), 2.36 (s, 1H), 2.16 – 2.07 (m, 1H), 2.01 – 1.79 (m, 3H), 1.73 (s, 3H), 1.67 (s, 3H), 1.65 – 1.59 (m, 1H), 1.48 (s, 3H), 1.40 – 1.30 (m, 2H), 1.06 (d, J = 6.4 Hz, 3H), 0.76 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.5, 121.6, 94.7, 86.0, 83.3, 82.9, 79.4, 76.7, 56.8, 54.9, 49.6, 43.4, 43.2, 38.6, 31.9, 26.4, 25.7, 22.9, 18.7, 15.7, 13.2; IR (thin film) ν_{max} 3006, 2989, 2693, 2348, 1774, 1458, 1377, 1276, 1261, 1155, 1108, 1049, 1012, 899, 767,

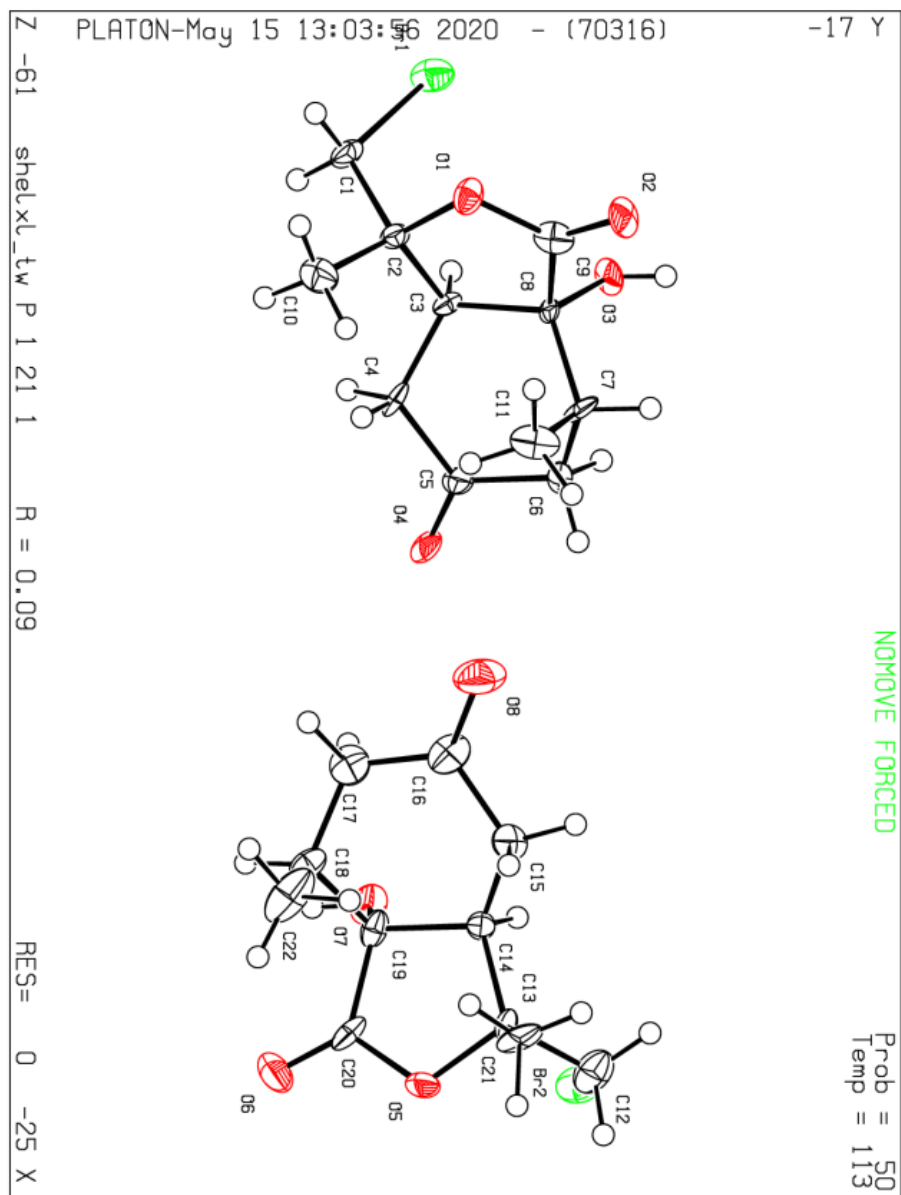
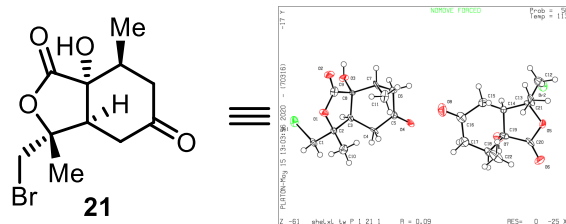
760, 746, 707; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{35}BrNaO_5$: 469.1560, found: 469.1563.



To a stirred solution of **30** (30.0 mg, 0.07 mmol, 1.0 eq.) in THF (1.2 mL) was added 3 N HCl (0.3 mL) at 45 °C. The reaction mixture was stirred for 30 min, before it was quenched with saturated NaHCO_3 (1 mL). The mixture was extracted with Et_2O (3×3 mL). The combined organic layers were washed with brine (2 mL), and dried over Na_2SO_4 . The solvent was removed under vacuum, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 8:1) to give product **31** (23.0 mg, 0.06 mmol, 88%) as a white solid. Data for **31**: R_f 0.65 (3:1, petroleum ether: ethyl acetate); mp = 182–184 °C; ^1H NMR (400 MHz, CDCl_3) δ 5.49 – 5.38 (m, 1H), 4.45 (d, J = 9.4 Hz, 1H), 4.12 (d, J = 9.3 Hz, 1H), 3.63 (dd, J = 9.9, 6.6 Hz, 1H), 3.41 (d, J = 9.3 Hz, 1H), 2.48 (d, J = 9.8 Hz, 1H), 2.30 – 2.20 (m, 2H), 2.08 – 2.03 (m, 1H), 1.98 – 1.92 (m, 1H), 1.90 – 1.85 (m, 2H), 1.75 – 1.67 (m, 7H), 1.55 (s, 3H), 1.45 – 1.35 (m, 3H), 1.10 (d, J = 6.4 Hz, 3H), 0.78 (d, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.6, 121.2, 85.3, 83.2, 79.8, 77.2, 74.9, 59.1, 48.9, 43.5, 43.4, 39.1, 30.9, 26.2, 25.6, 22.5, 18.6, 15.2, 12.9; IR (thin film) ν_{max} 3457, 2956, 2926, 2874, 1719, 1669, 1635, 1455, 1377, 1296, 1239, 1147, 1104, 1047, 1007, 960, 898, 784, 727, 656; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{19}H_{31}BrNaO_4$: 425.1298, found: 425.1302.

3. X-ray Crystallography

3.1 X-ray Crystallography of compound **21** (CCDC 1935896)

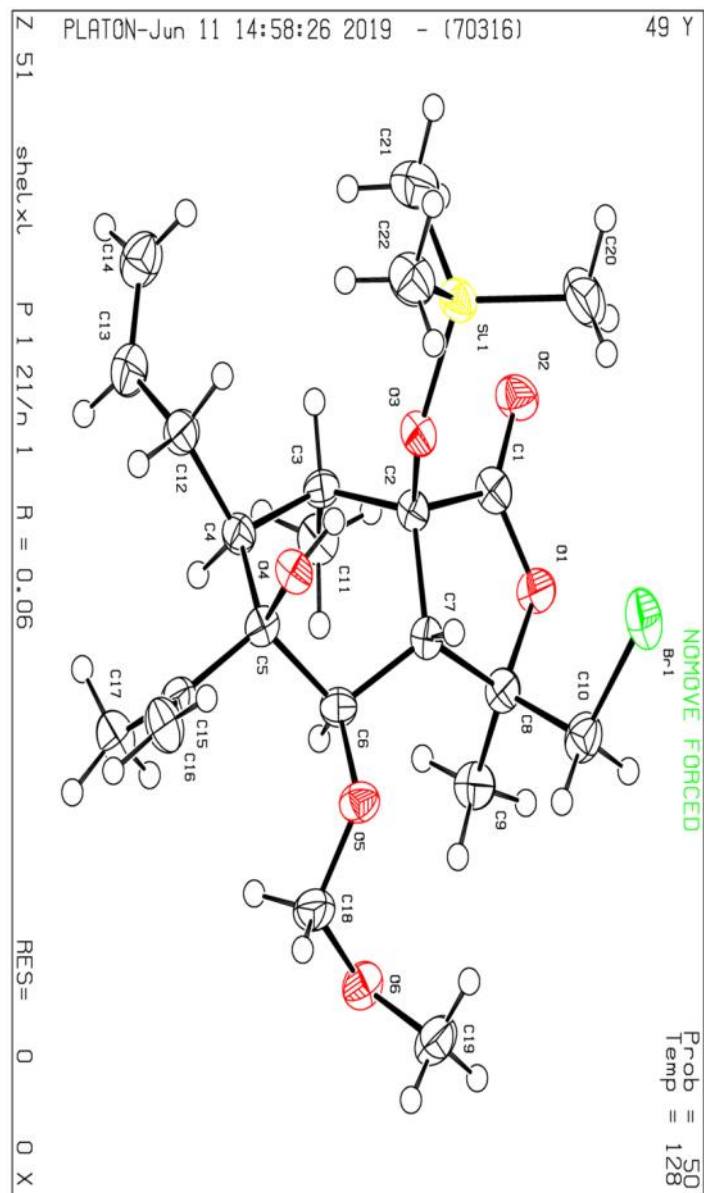
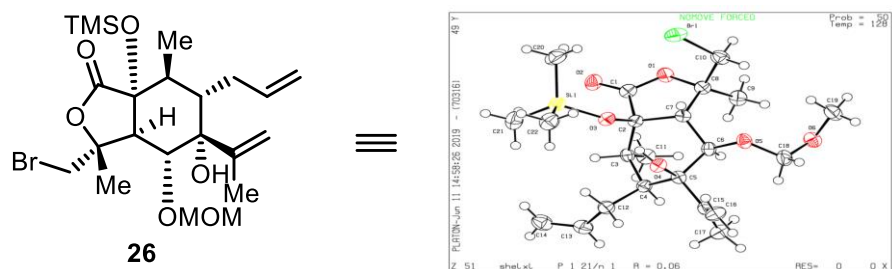


Displacement ellipsoids are drawn at the 50% probability level.

A colorless block shaped crystal of **21** for X-ray diffraction was obtained by slow evaporation from MeOH. The X-ray intensity data were measured at 113.15 K on a Rigaku Saturn 70 CCD diffractometer with helios mx multilayer monochromator Co K α radiation ($\lambda = 0.71073$ Å). The supplementary crystallographic data has been deposited in The Cambridge Crystallographic Data Centre. CCDC **1935896**.

Empirical formula	C ₂₂ H ₃₀ Br ₂ O ₈
Formula weight	582.28
TemperatureK	113.15 K
Crystal system	monoclinic
Wavelength	0.71073 Å
Space group	P 21/n
Unit cell dimensions	a = 9.3701(19) Å $\alpha = 90^\circ$
	b = 11.387(2) Å $\beta = 112.33(3)^\circ$
	c = 12.151(2) Å $\gamma = 90^\circ$
Volume	1199.3(5) Å ³
Z	2
ρ_{calc}	1.612 g/cm ³
μ	3.424 mm ⁻¹
F(000)	592.0
Crystal size	0.2 × 0.18 × 0.12 mm ³
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	3.624 to 50.06°
Limiting indices	-11 ≤ h ≤ 10, -13 ≤ k ≤ 13, -12 ≤ l ≤ 14
Reflections collected	4231
Data/restraints/parameters	4231/13/296
Goodness-of-fit on F ²	1.053
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0869, wR ₂ = 0.2272
Final R indexes [all data]	R ₁ = 0.0958, wR ₂ = 0.2324
Largest diff. peak/hole	3.52/-1.95 e Å ⁻³

3.2 X-ray Crystallography of compound **26** (CCDC 1922328)

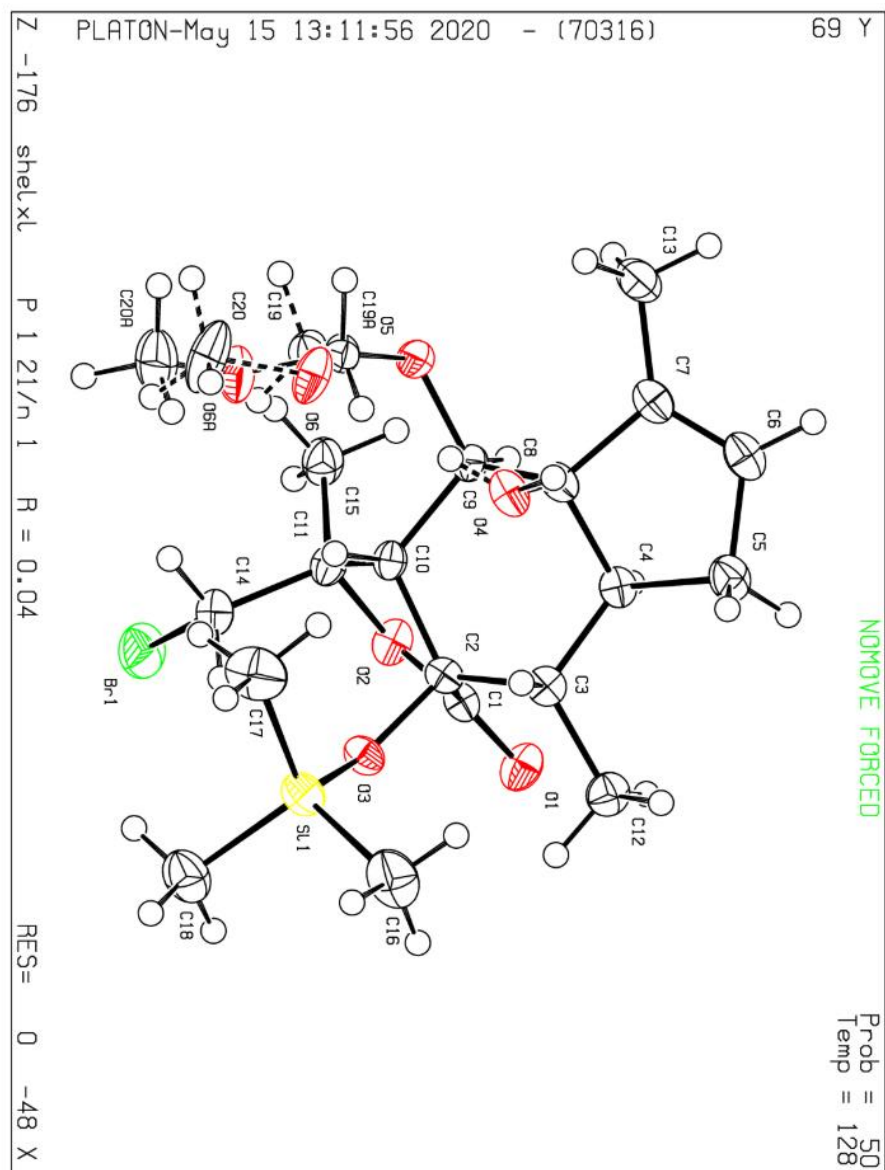
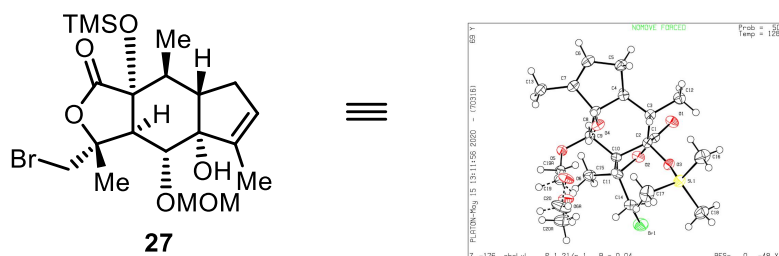


Displacement ellipsoids are drawn at the 50% probability level.

A colorless block shaped crystal of **26** for X-ray diffraction was obtained by slow evaporation from MeOH. The X-ray intensity data were measured at 128.15 K on a Rigaku Saturn 70 CCD diffractometer with helios mx multilayer monochromator Co K α radiation ($\lambda = 0.71073$ Å). The supplementary crystallographic data has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1922328.

Empirical formula	C ₂₂ H ₃₇ BrO ₆ Si
Formula weight	505.51
TemperatureK	128.15 K
Crystal system	monoclinic
Wavelength	0.71073 Å
Space group	P 2 ₁ /n
Unit cell dimensions	a = 12.104(2) Å $\alpha = 90^\circ$
	b = 12.203(2) Å $\beta = 106.05(3)^\circ$
	c = 17.634(4) Å $\gamma = 90^\circ$
Volume	2503.1(9) Å ³
Z	4
ρ_{calc}	1.341 g/cm ³
μ	1.723 mm ⁻¹
F(000)	1064.0
Crystal size	0.2 × 0.18 × 0.12 mm ³
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	4.114 to 55.786°
Limiting indices	-15 ≤ h ≤ 15, -16 ≤ k ≤ 16, -23 ≤ l ≤ 23
Reflections collected	23261
Data/restraints/parameters	5930/0/280
Goodness-of-fit on F ²	0.969
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0557, wR ₂ = 0.1206
Final R indexes [all data]	R ₁ = 0.0855, wR ₂ = 0.1357
Largest diff. peak/hole	0.93/-0.74 e Å ⁻³

3.3 X-ray Crystallography of compound **27** (CCDC 1922331)

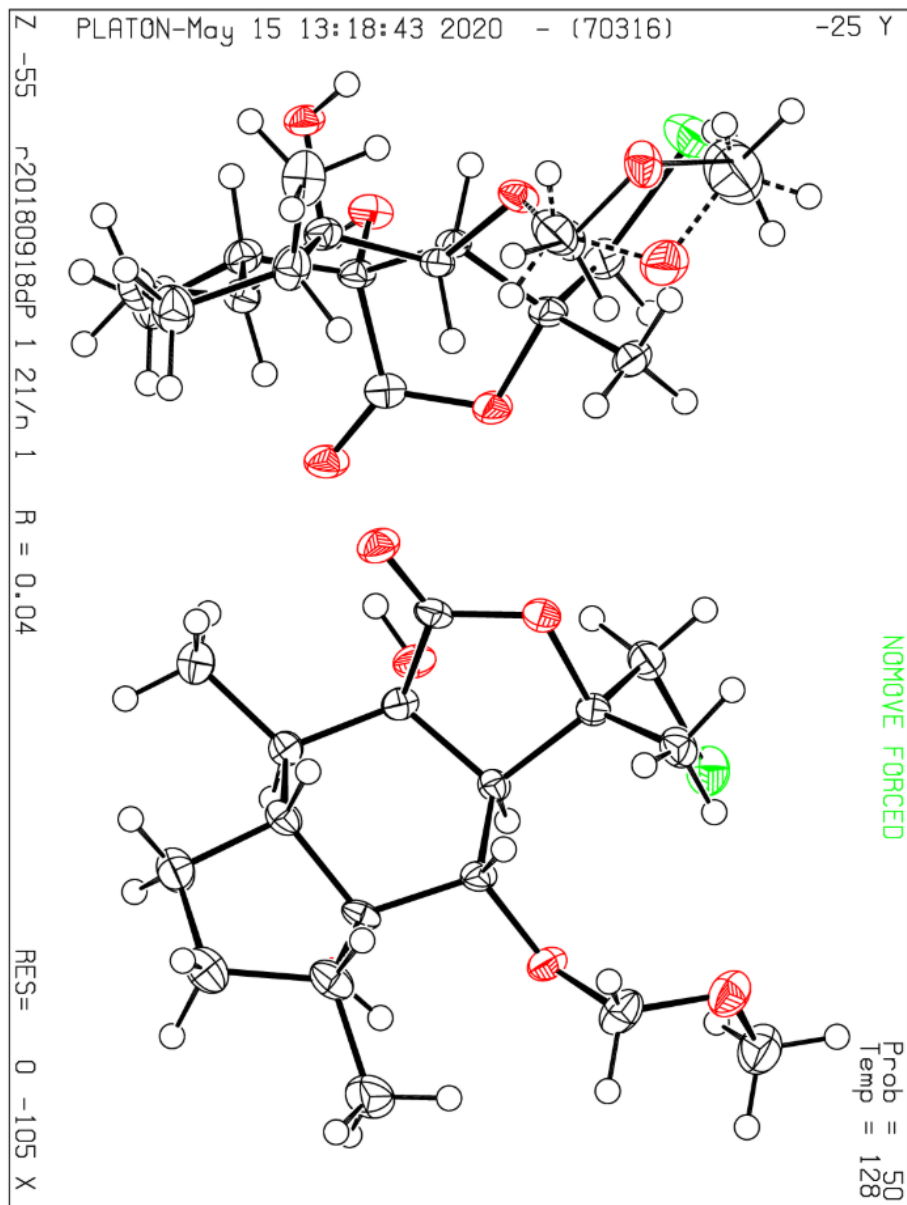
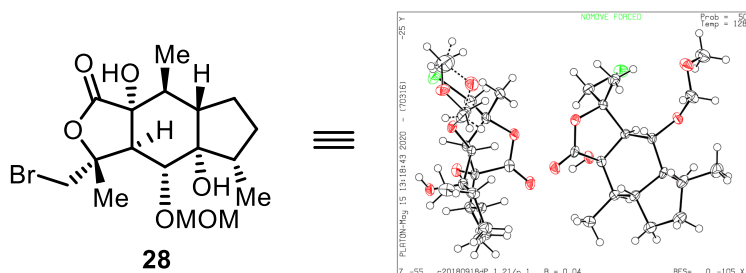


Displacement ellipsoids are drawn at the 50% probability level.

A colorless block shaped crystal of **27** for X-ray diffraction was obtained by slow evaporation from MeOH. The X-ray intensity data were measured at 128.15 K on a Rigaku Saturn 70 CCD diffractometer with helios mx multilayer monochromator Co K α radiation ($\lambda = 0.71073$ Å). The supplementary crystallographic data has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1922331.

Empirical formula	C ₂₀ H ₃₃ BrO ₆ Si
Formula weight	477.46
TemperatureK	128.15 K
Crystal system	monoclinic
Space group	P 21/n
Unit cell dimensions	a = 12.523(3) Å $\alpha = 90^\circ$
	b = 11.072(2) Å $\beta = 91.20(3)^\circ$
	c = 16.050(3) Å $\gamma = 90^\circ$
Volume	2224.9(8) Å ³
Z	4
ρ_{calc}	1.425 g/cm ³
μ	1.934 mm ⁻¹
F(000)	1000.0
Crystal size	0.22 × 0.18 × 0.16 mm ³
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	4.168 to 55.72°
Limiting indices	-16 ≤ h ≤ 16, -14 ≤ k ≤ 13, -21 ≤ l ≤ 17
Reflections collected	21900
Data/restraints/parameters	5293/10/298
Goodness-of-fit on F ²	1.041
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0443, wR ₂ = 0.0895
Final R indexes [all data]	R ₁ = 0.0643, wR ₂ = 0.0983
Largest diff. peak/hole	0.74/-0.89 e Å ⁻³

3.4 X-ray Crystallography of compound **28** (CCDC 1922334)

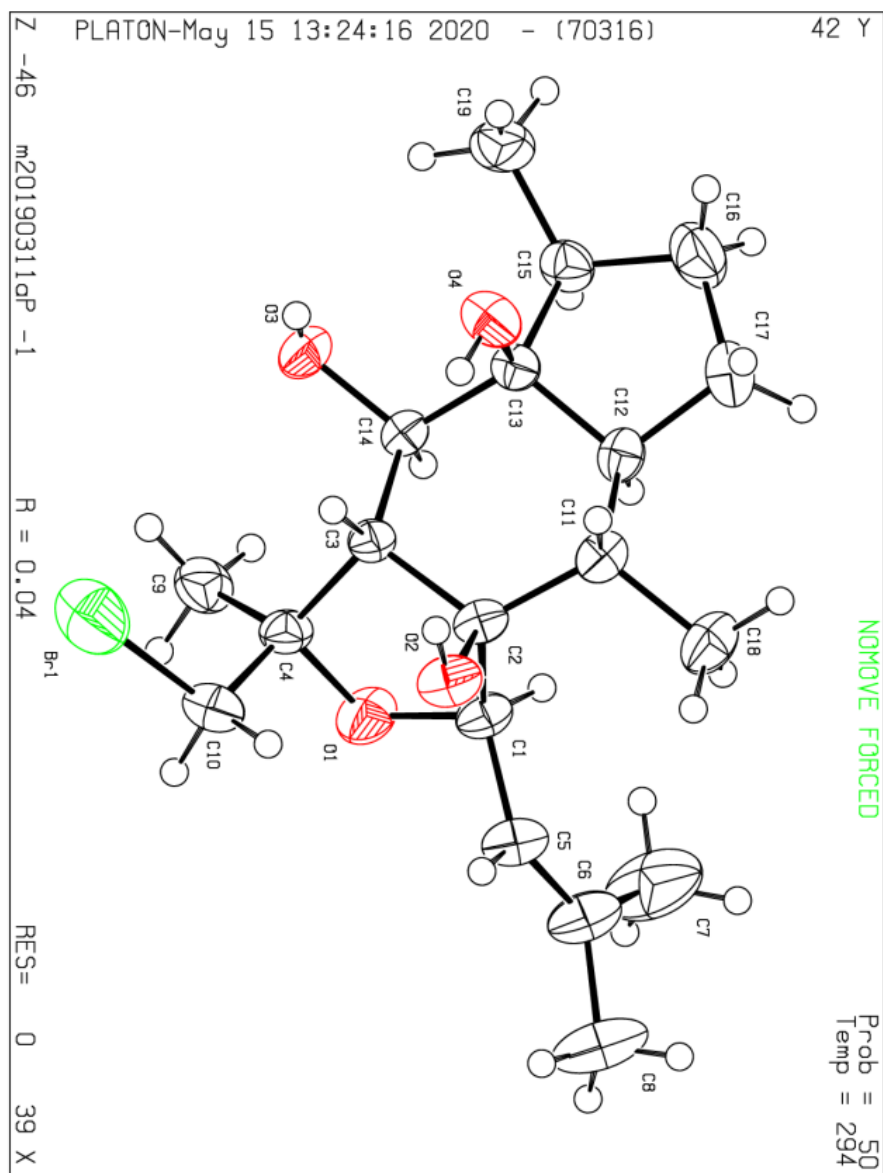
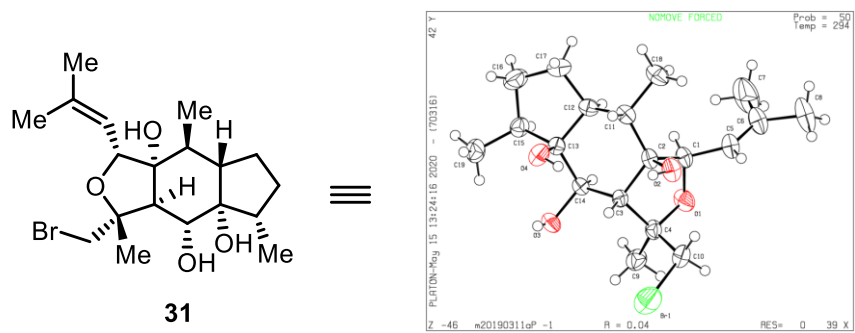


Displacement ellipsoids are drawn at the 50% probability level.

A colorless block shaped crystal of **28** for X-ray diffraction was obtained by slow evaporation from MeOH. The X-ray intensity data were measured at 128.15 K on a Rigaku Saturn 70 CCD diffractometer with helios mx multilayer monochromator Co K α radiation ($\lambda = 0.71073$ Å). The supplementary crystallographic data has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1922334.

Empirical formula	C ₁₇ H ₂₇ BrO ₆
Formula weight	407.29
TemperatureK	128.15 K
Crystal system	monoclinic
Space group	P 2 ₁ /n
Unit cell dimensions	a = 22.3206(14) Å $\alpha = 90^\circ$
	b = 7.4453(3) Å $\beta = 114.968(7)^\circ$
	c = 23.6226(15) Å $\gamma = 90^\circ$
Volume	3558.8(4) Å ³
Z	8
ρ_{calc}	1.520 g/cm ³
μ	2.340 mm ⁻¹
F(000)	1696.0
Crystal size	0.26 × 0.24 × 0.14 mm ³
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection	3.302 to 52.742°
Limiting indices	-27 ≤ h ≤ 27, -9 ≤ k ≤ 9, -29 ≤ l ≤ 29
Reflections collected	36852
Independent reflections	7292 [R _{int} = 0.0707, R _{sigma} = 0.0501]
Data/restraints/parameters	7292/33/474
Goodness-of-fit on F ²	1.025
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0401, wR ₂ = 0.0829
Final R indexes [all data]	R ₁ = 0.0608, wR ₂ = 0.0909
Largest diff. peak/hole	0.58/-0.74 e Å ⁻³

3.5 X-ray Crystallography of compound **31** (CCDC 1935895)

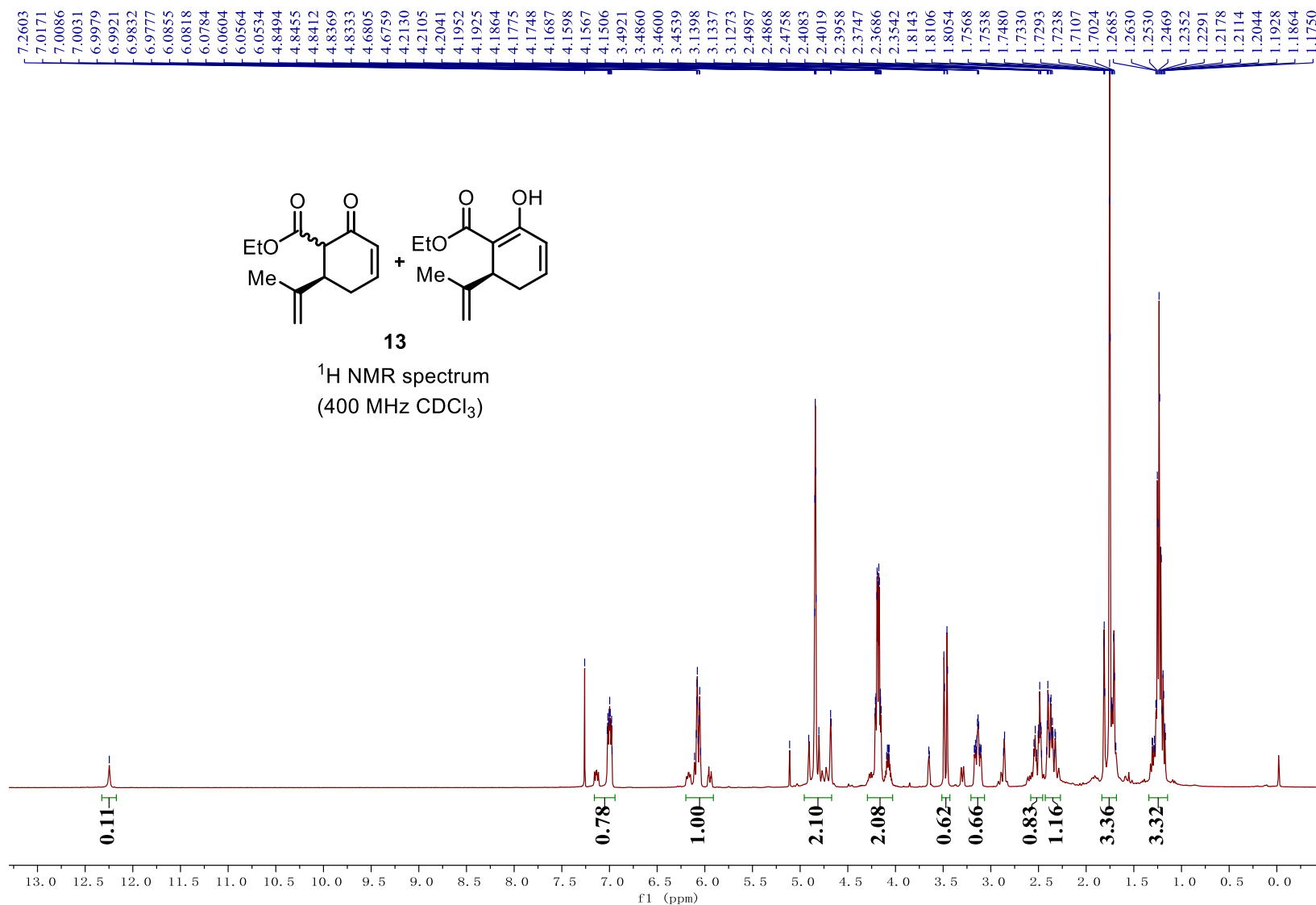


Displacement ellipsoids are drawn at the 50% probability level.

A colorless block shaped crystal of **31** for X-ray diffraction was obtained by slow evaporation from MeOH. The X-ray intensity data were measured at 294.15 K on a XtaLAB AFC10 (RCD3): fixed-chi single diffractometer with helios mx multilayer monochromator Co K α radiation (λ = 0.71073 Å). The supplementary crystallographic data has been deposited in The Cambridge Crystallographic Data Centre. CCDC 1935895.

Empirical formula	C ₁₉ H ₃₁ BrO ₄
Formula weight	403.35
TemperatureK	294.15 K
Crystal system	triclinic
Space group	P-1
Unit cell dimensions	a = 7.5394(2) Å α = 71.454(2)°
	b = 10.5904(2) Å β = 79.781(2)°
	c = 12.8713(3) Å γ = 85.245(2)°
Volume	958.50(4) Å ³
Z	2
ρ_{calc}	1.398 g/cm ³
μ	2.163 mm ⁻¹
F(000)	424.0
Crystal size	0.24 × 0.22 × 0.18 mm ³
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection	6.738 to 56.548°
Limiting indices	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -17 ≤ l ≤ 16
Reflections collected	24599
Independent reflections	4713 [R _{int} = 0.0389, R _{sigma} = 0.0284]
Data/restraints/parameters	4713/0/225
Goodness-of-fit on F ²	1.032
Final R indexes [$I \geq 2\sigma(I)$]	R ₁ = 0.0355, wR ₂ = 0.0902
Final R indexes [all data]	R ₁ = 0.0494, wR ₂ = 0.0962
Largest diff. peak/hole	0.43/-0.33 e Å ⁻³

4. ^1H and ^{13}C NMR Spectra of Compounds



— 194.3662

— 169.3883

— 149.5655

— 144.3054

— 128.7228

— 113.1773

77.3701
77.0486
76.7334

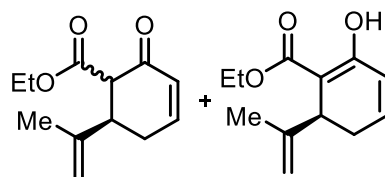
— 60.9592
— 58.4311

— 45.2901

— 30.7212

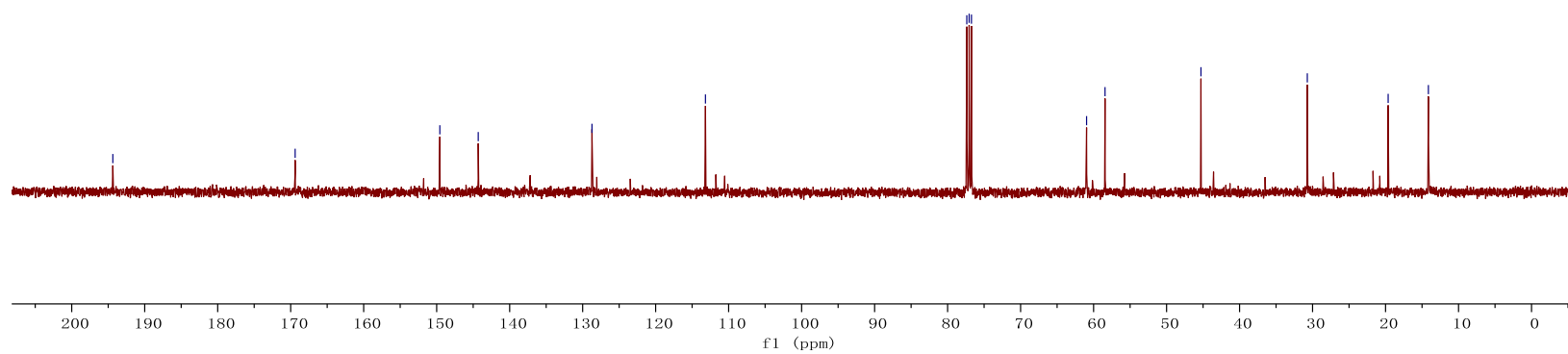
— 19.6446

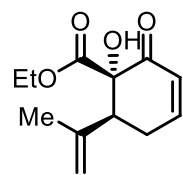
— 14.1310



13

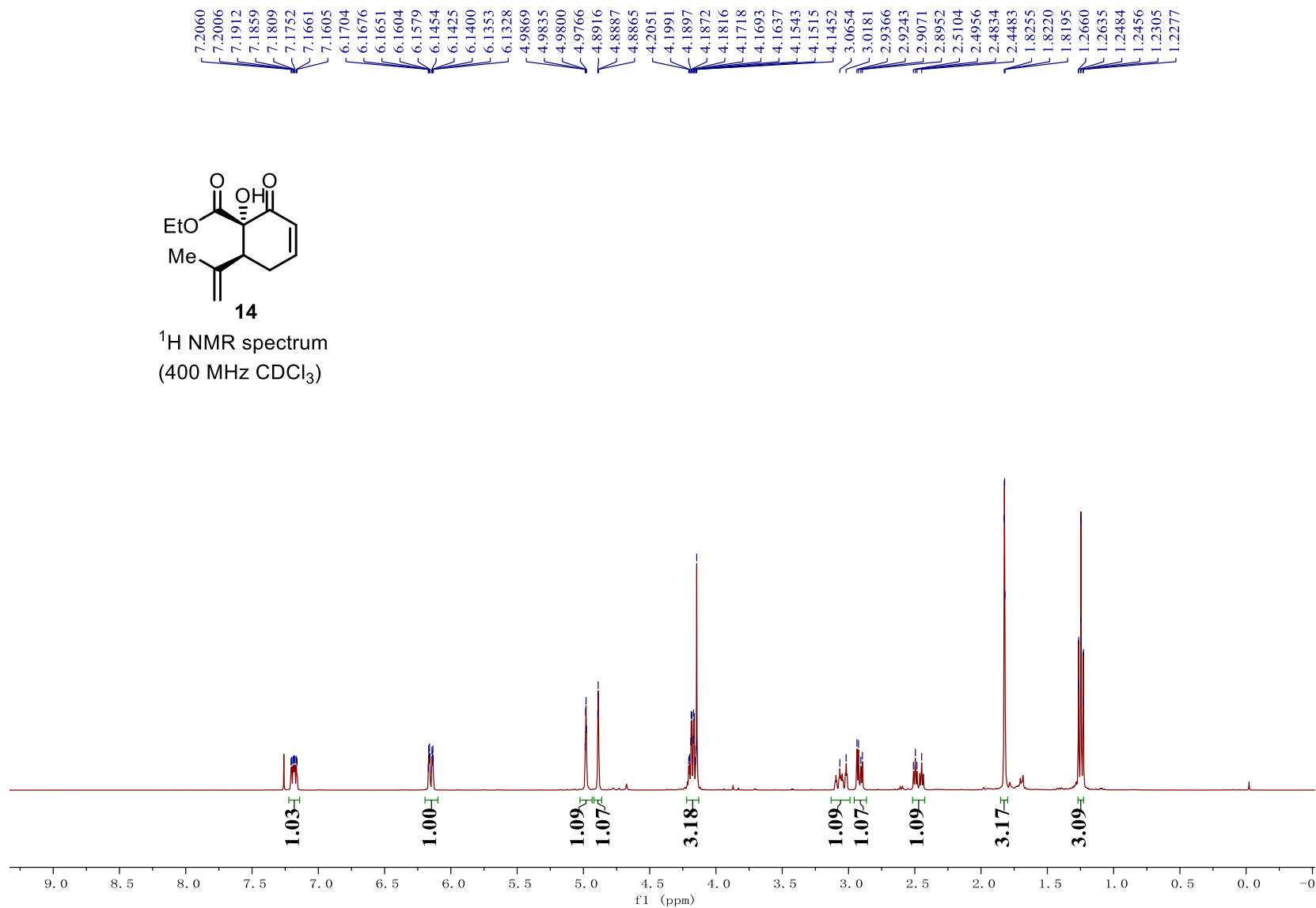
¹³C NMR spectrum
(100 MHz CDCl₃)

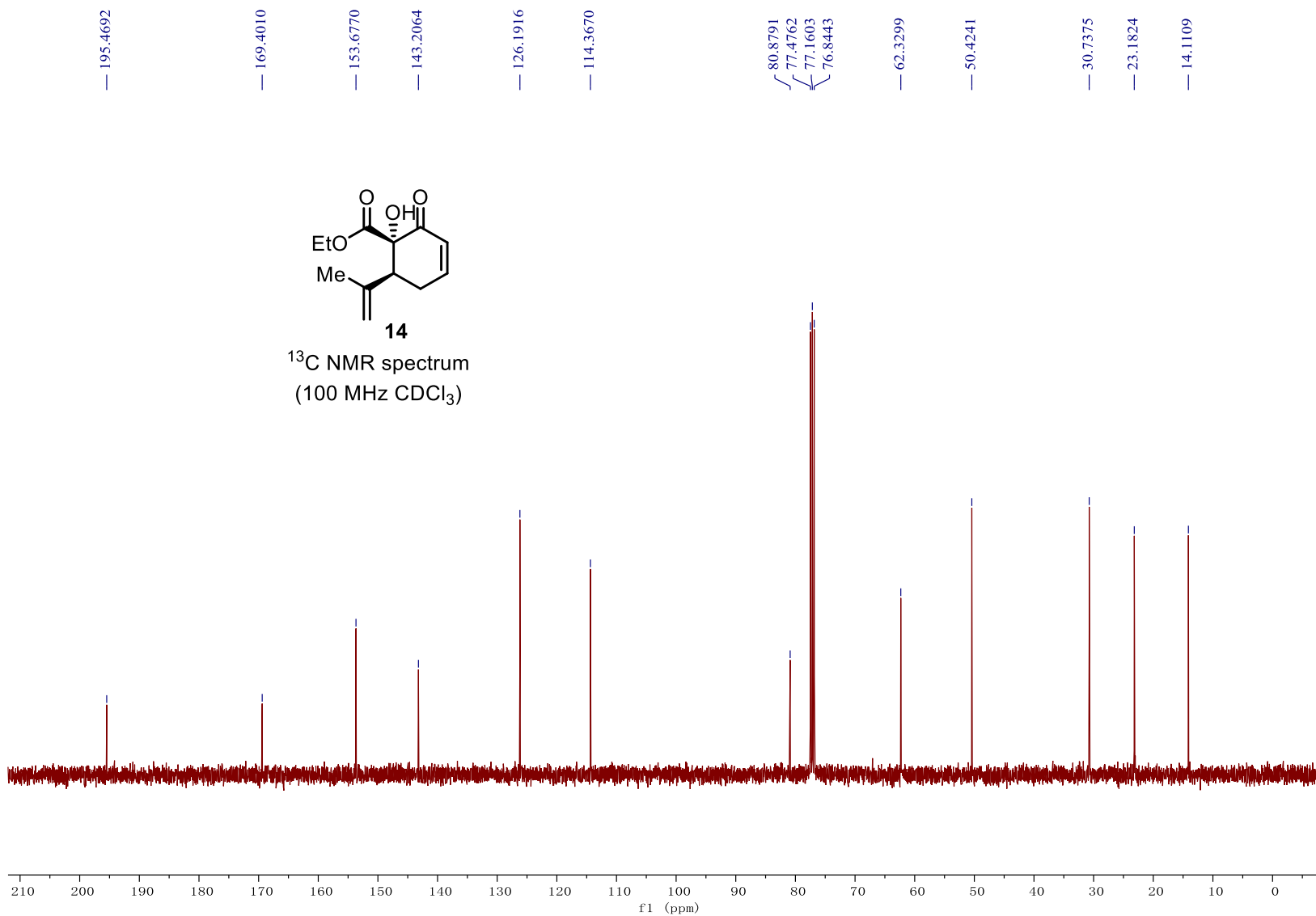


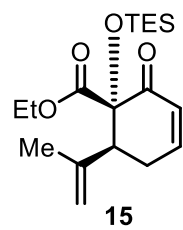


14

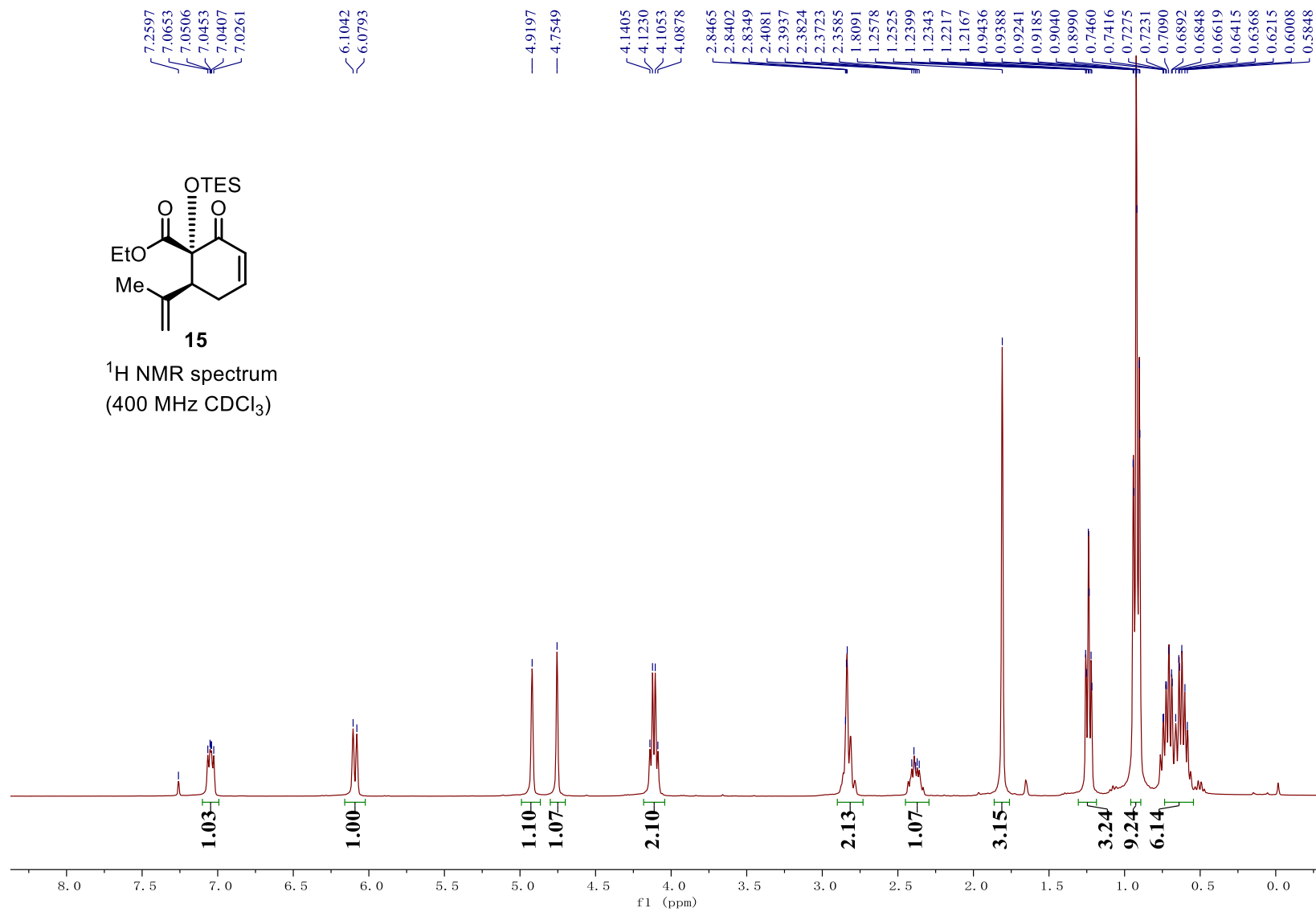
^1H NMR spectrum
(400 MHz CDCl_3)

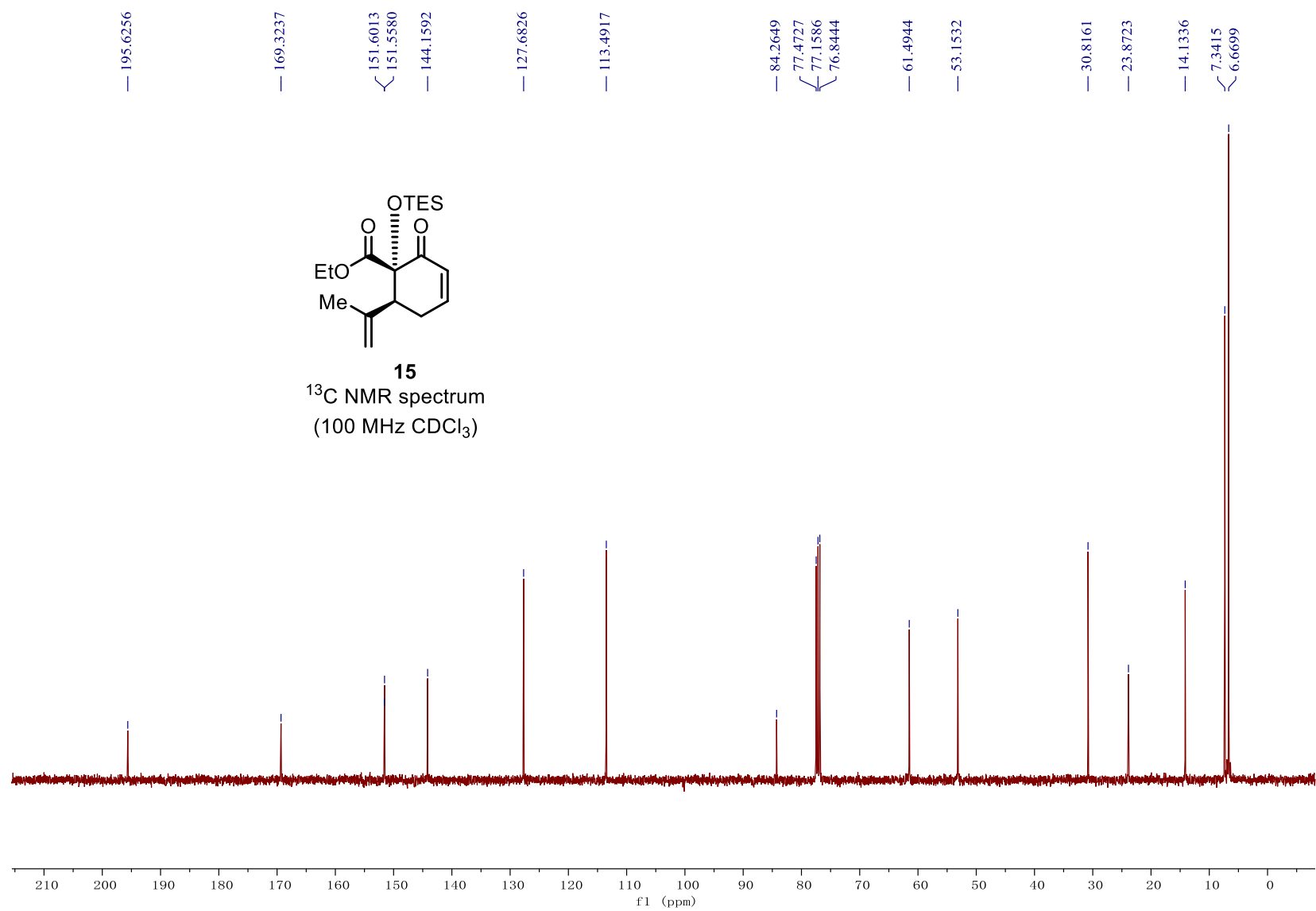






^1H NMR spectrum
(400 MHz CDCl_3)



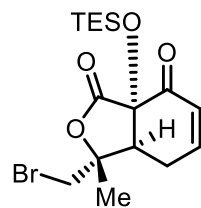


7.2605
6.9757
6.9650
6.9497
6.9387
6.9293

6.2194
6.1932

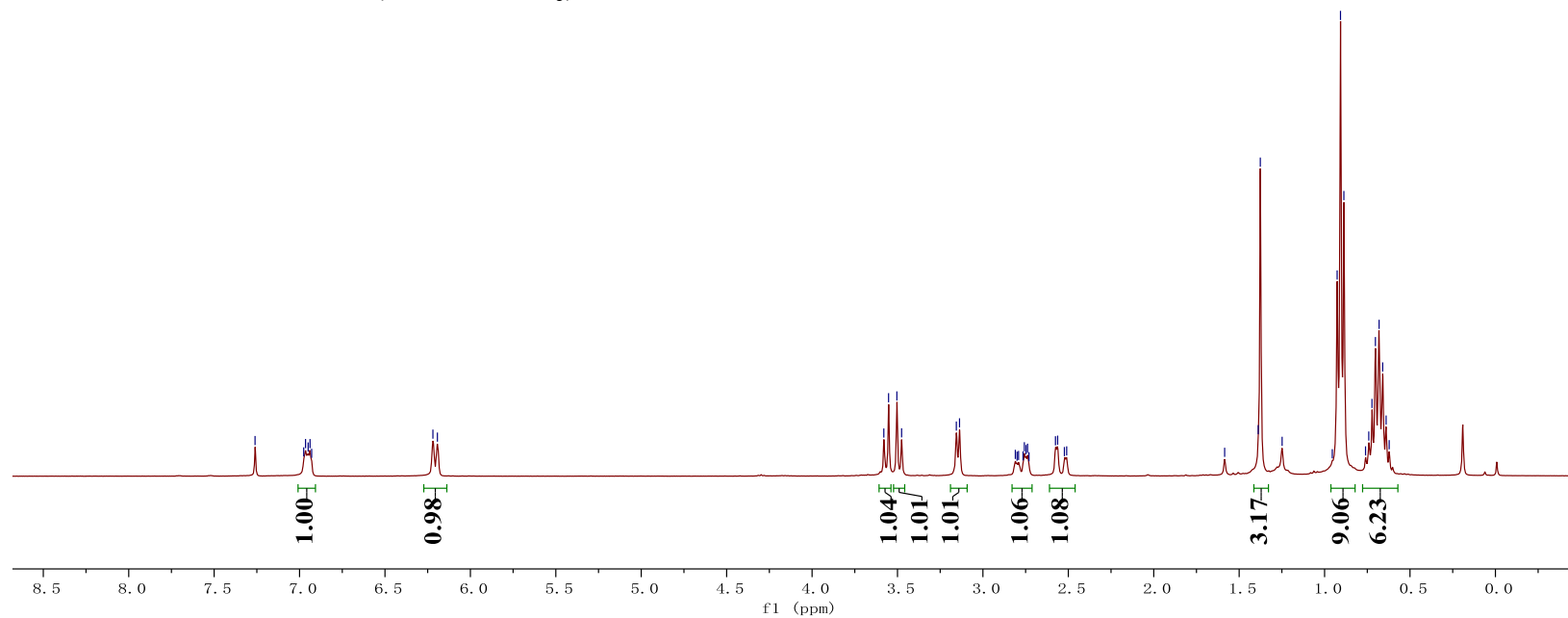
3.5800
3.5522
3.5036
3.4758
3.1556
3.1369

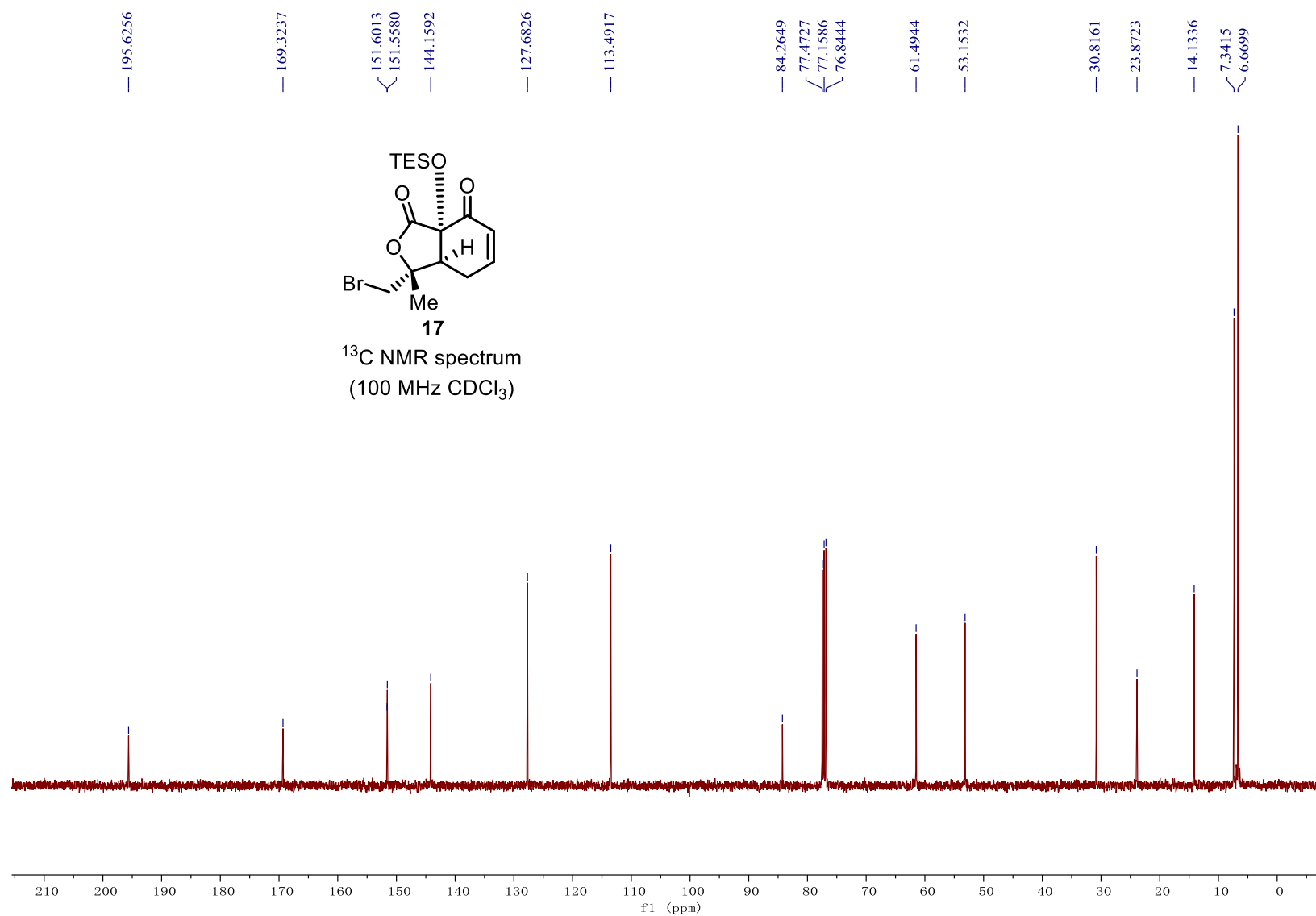
2.8103
2.8002
2.7913
2.7651
2.7574
2.7473
2.7385
2.5753
2.5625
2.5230
2.5096
1.5850
1.3885
1.3763
1.2485
0.9549
0.9265
0.9069
0.8871
0.7602
0.7413
0.7227
0.7025
0.6808
0.6597
0.6399
0.6218

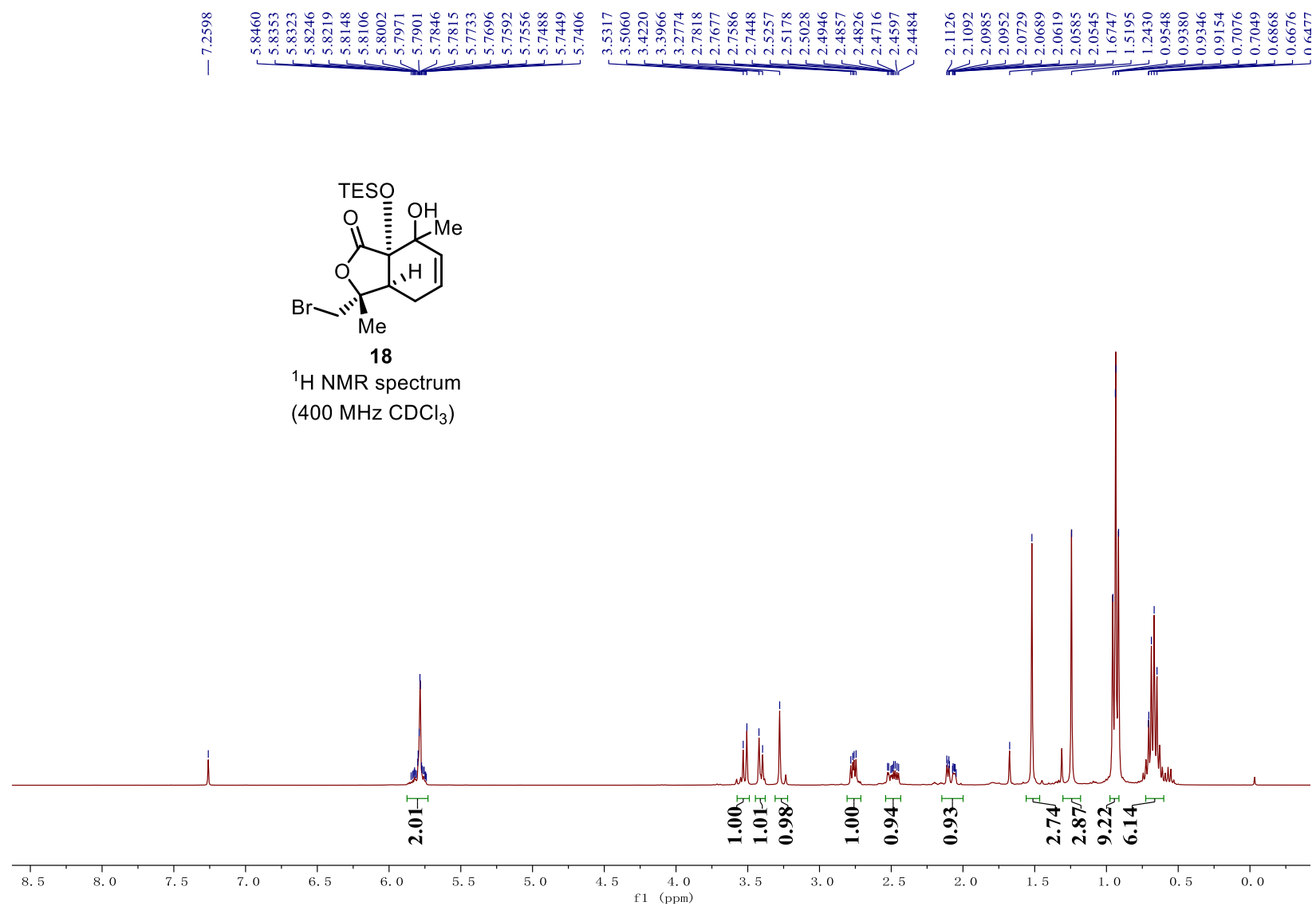


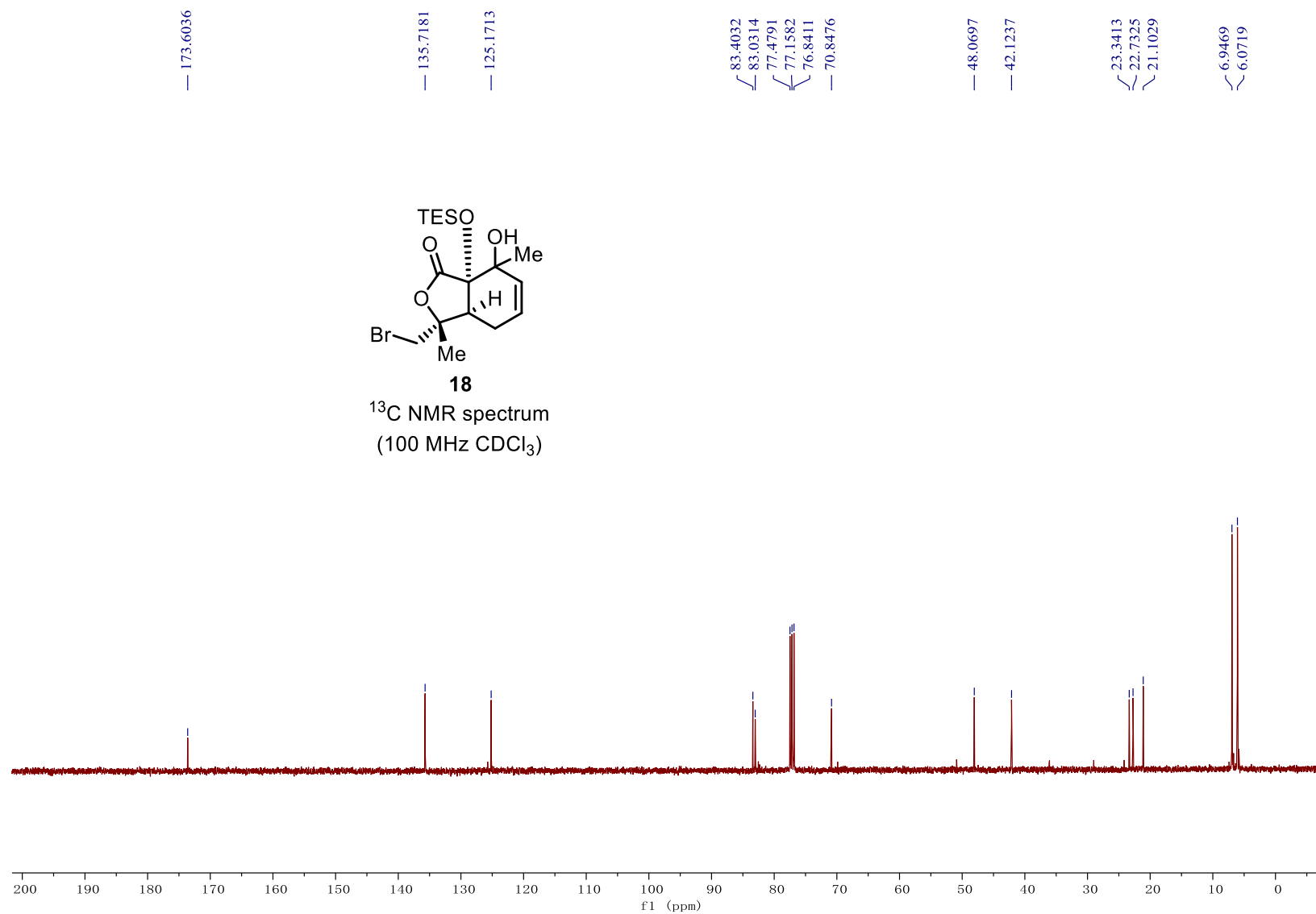
17

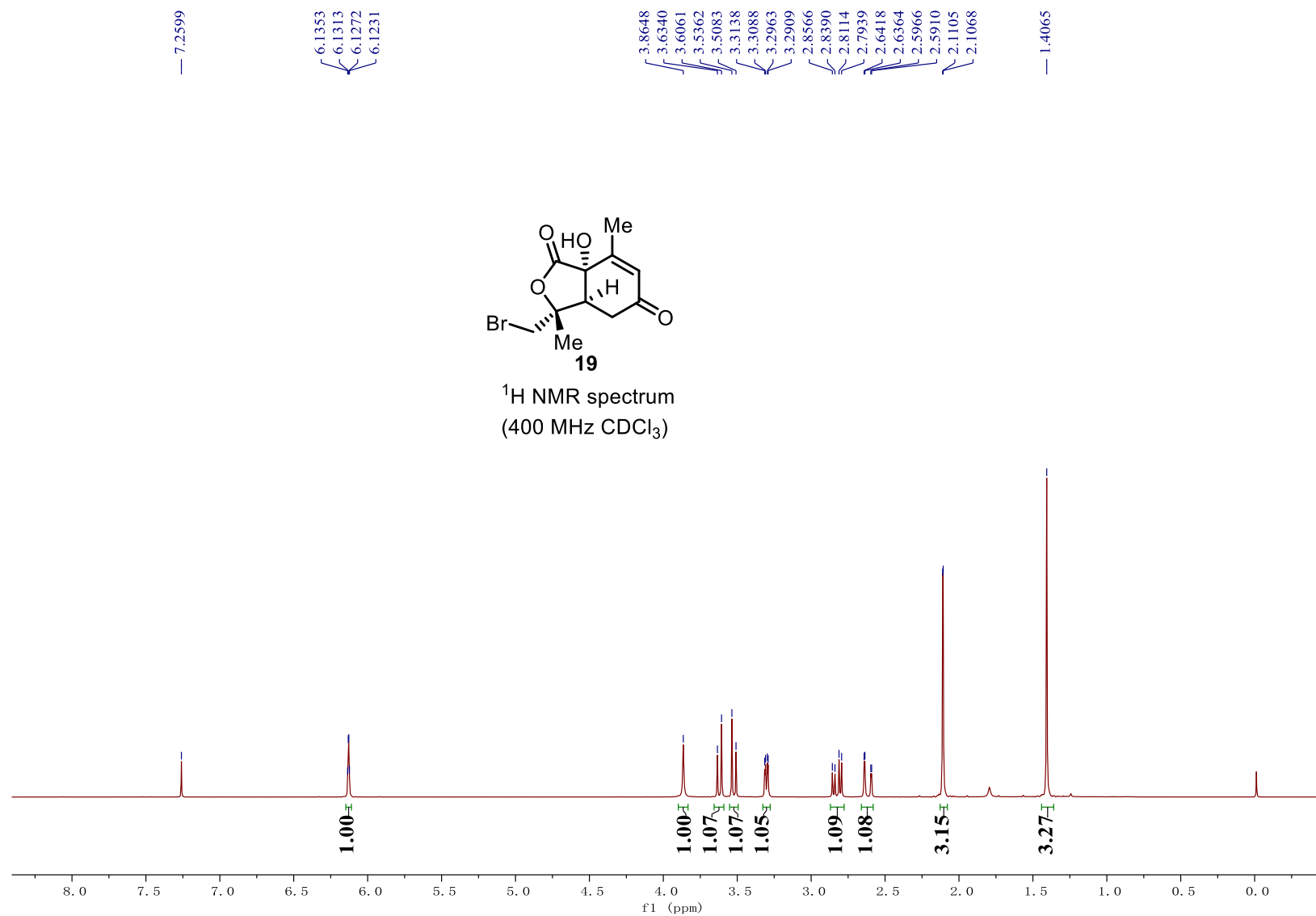
^1H NMR spectrum
(400 MHz CDCl_3)

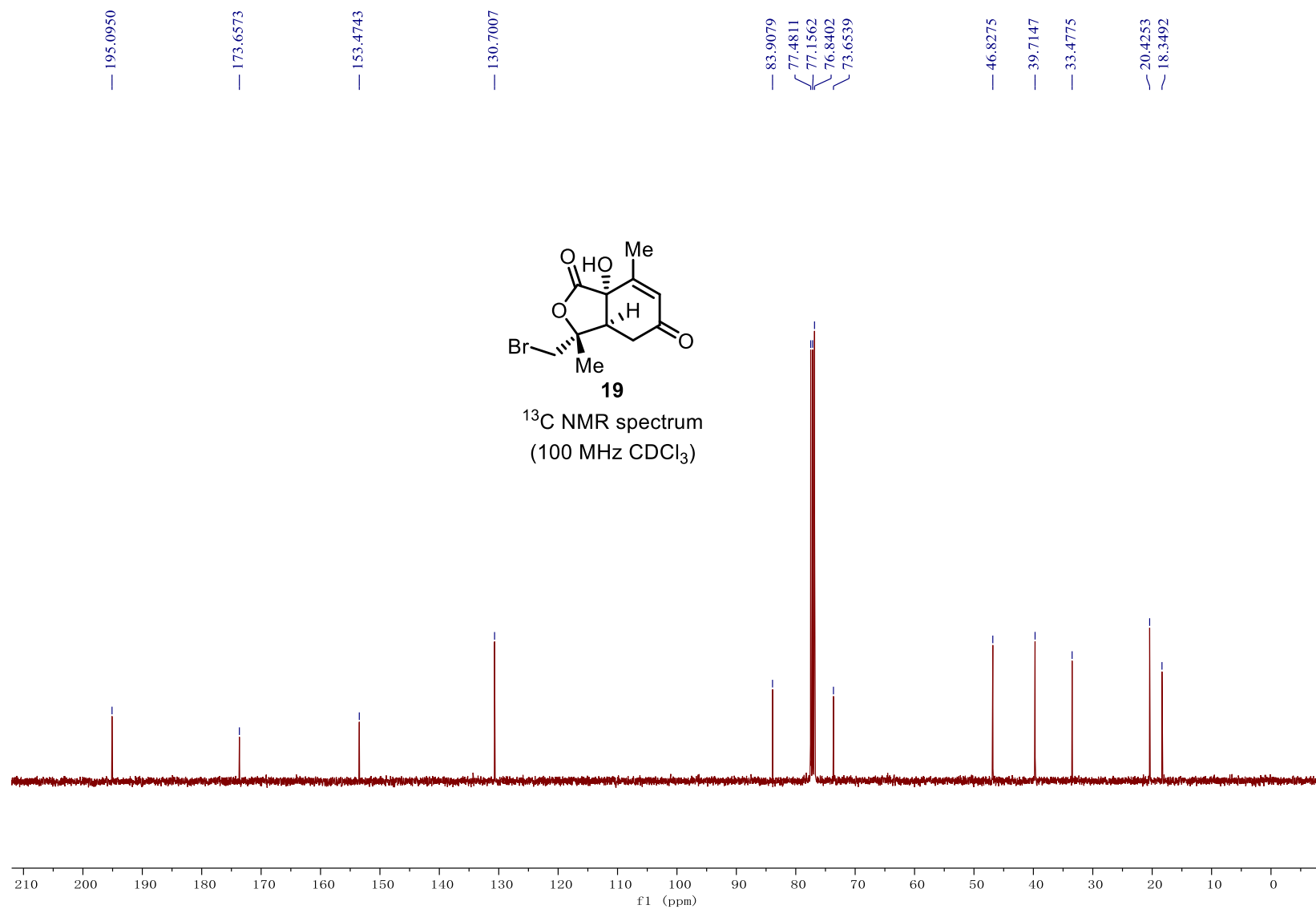


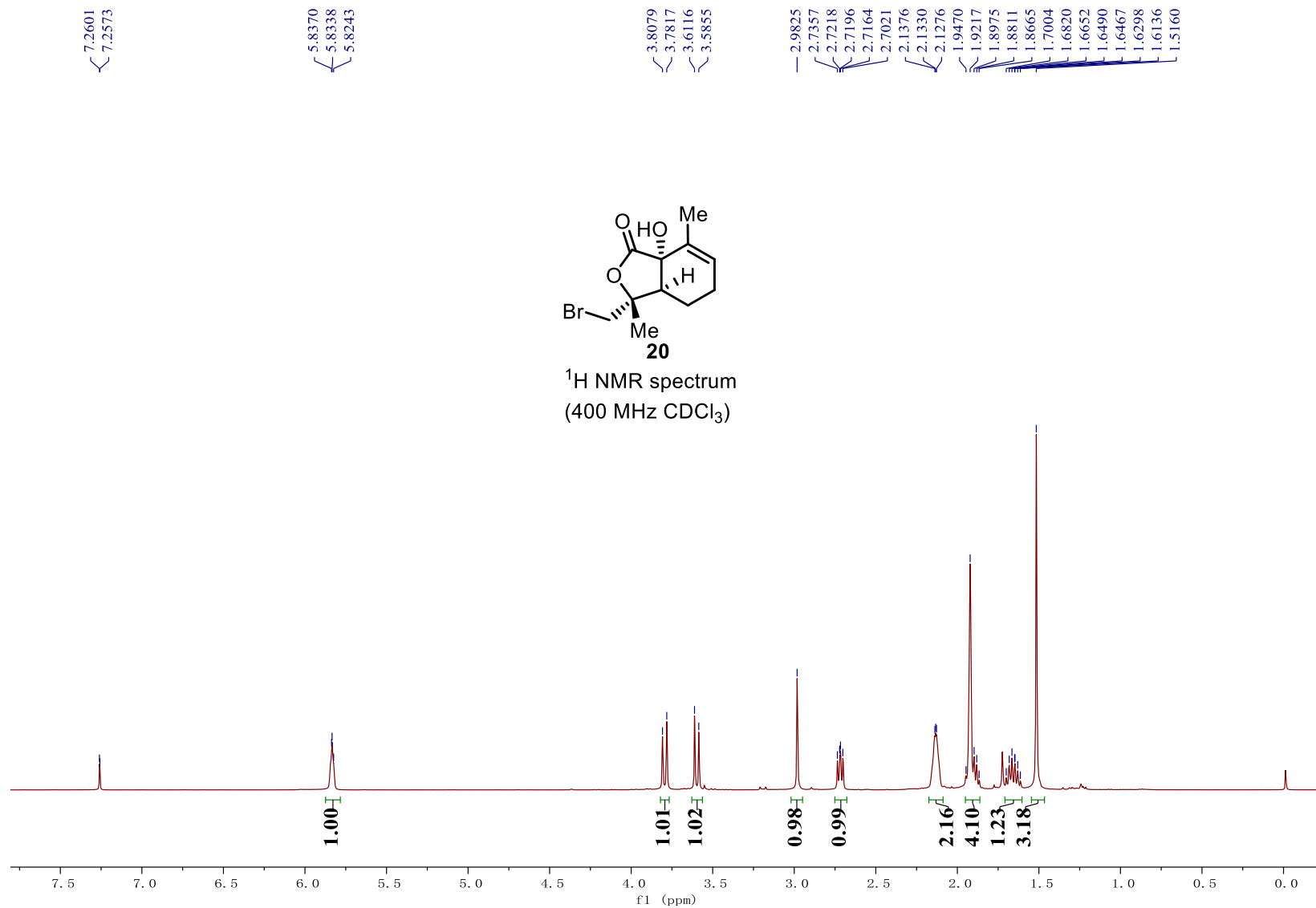


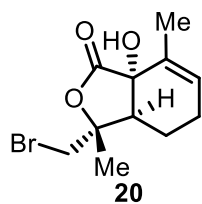




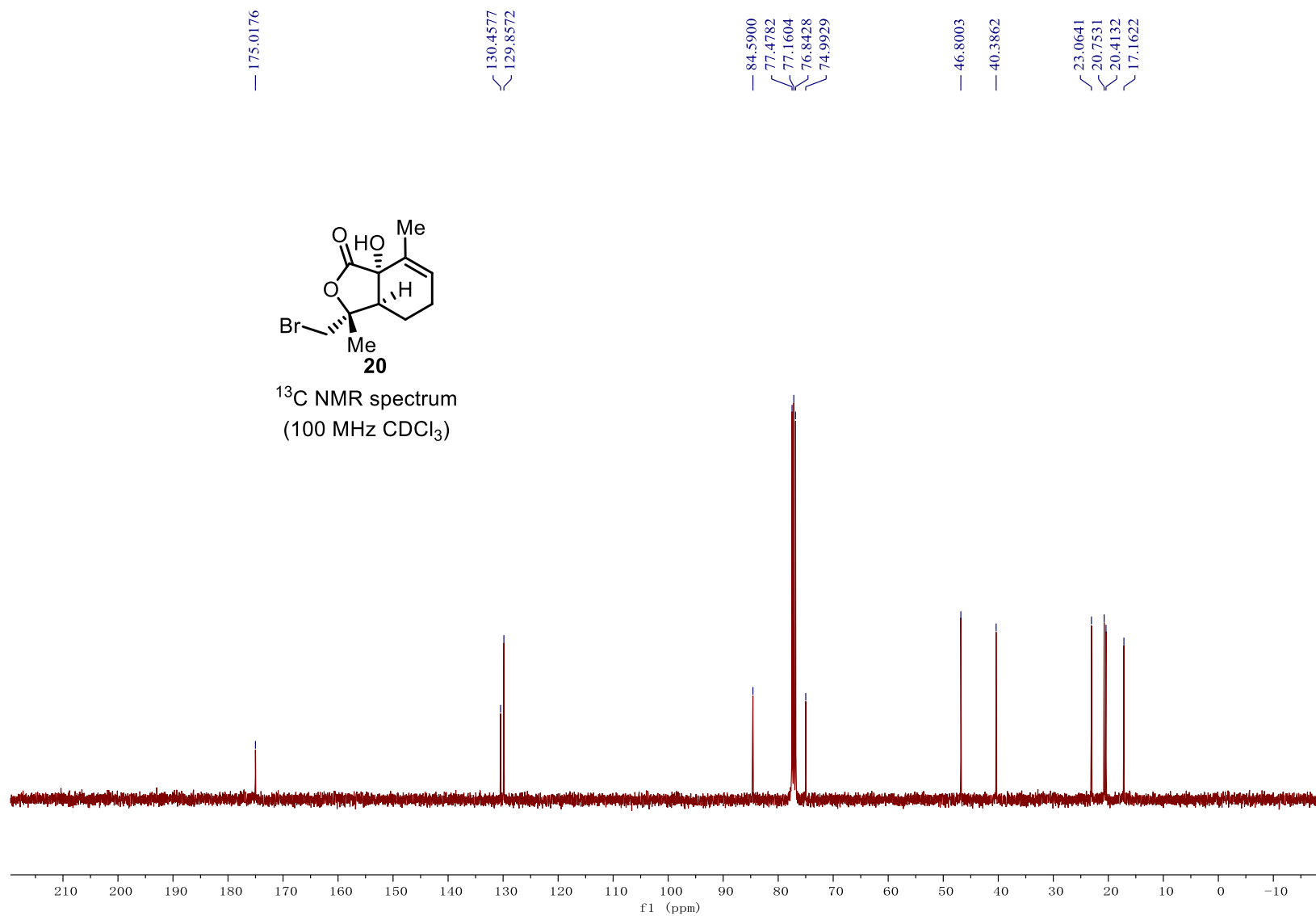


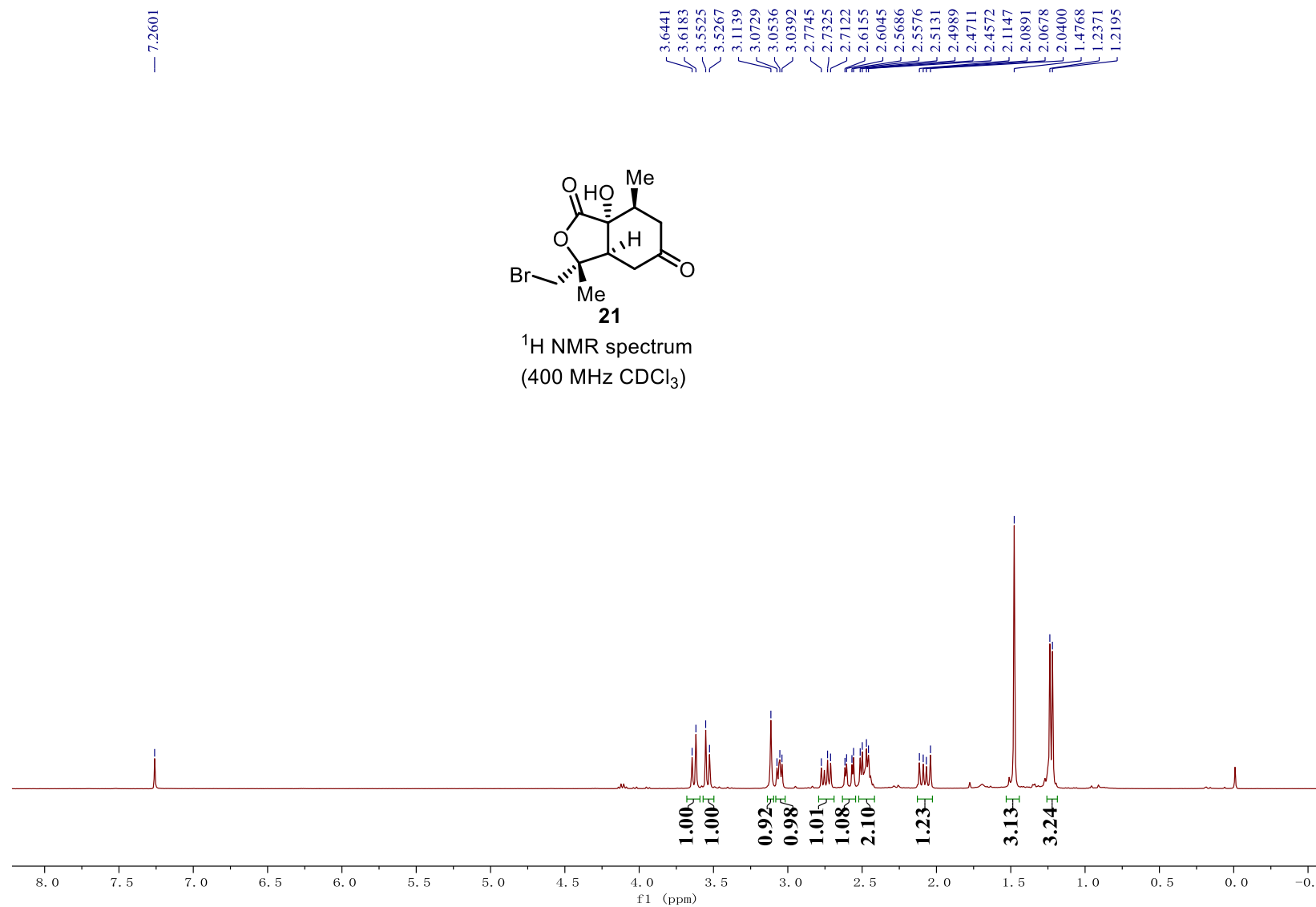


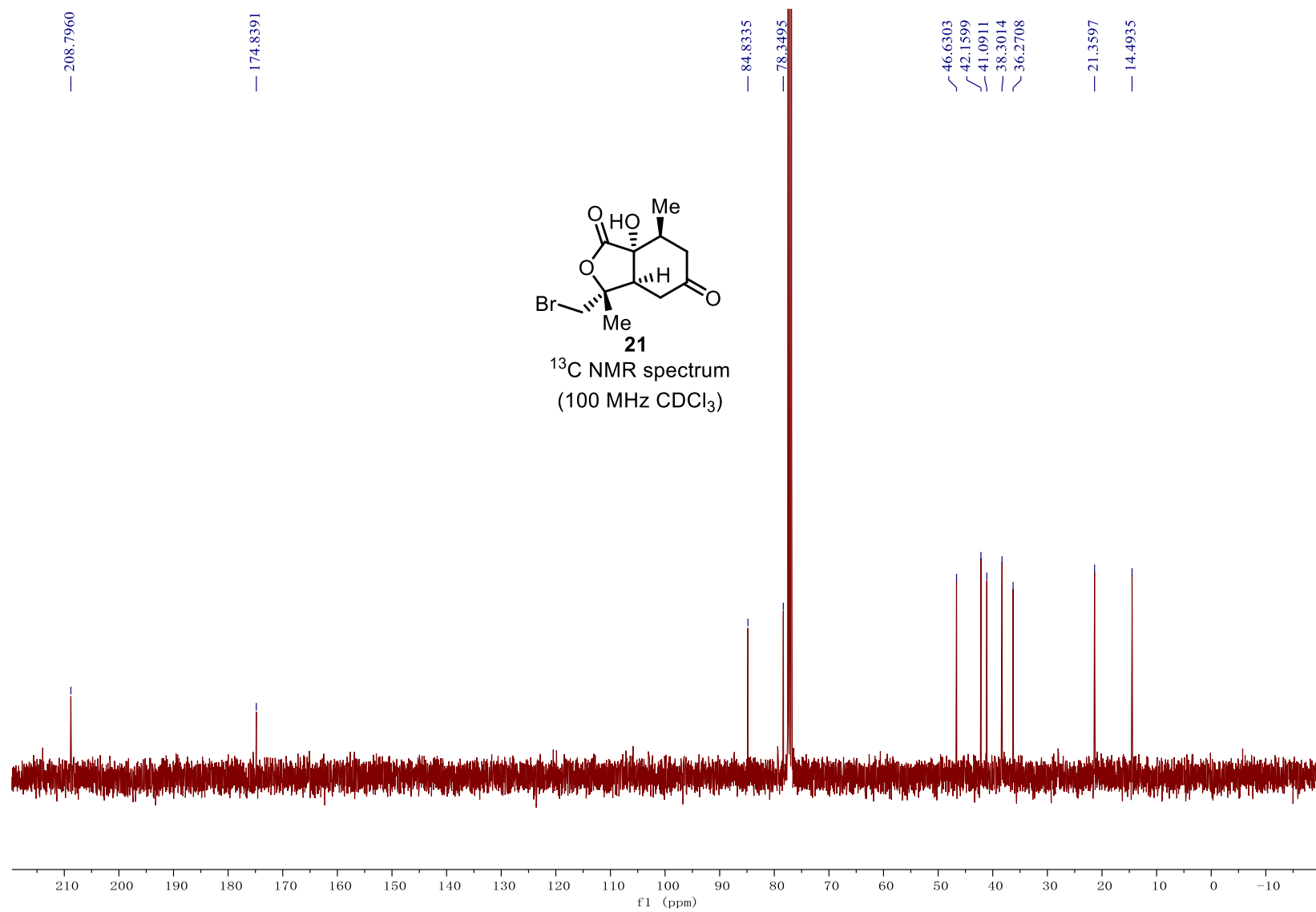


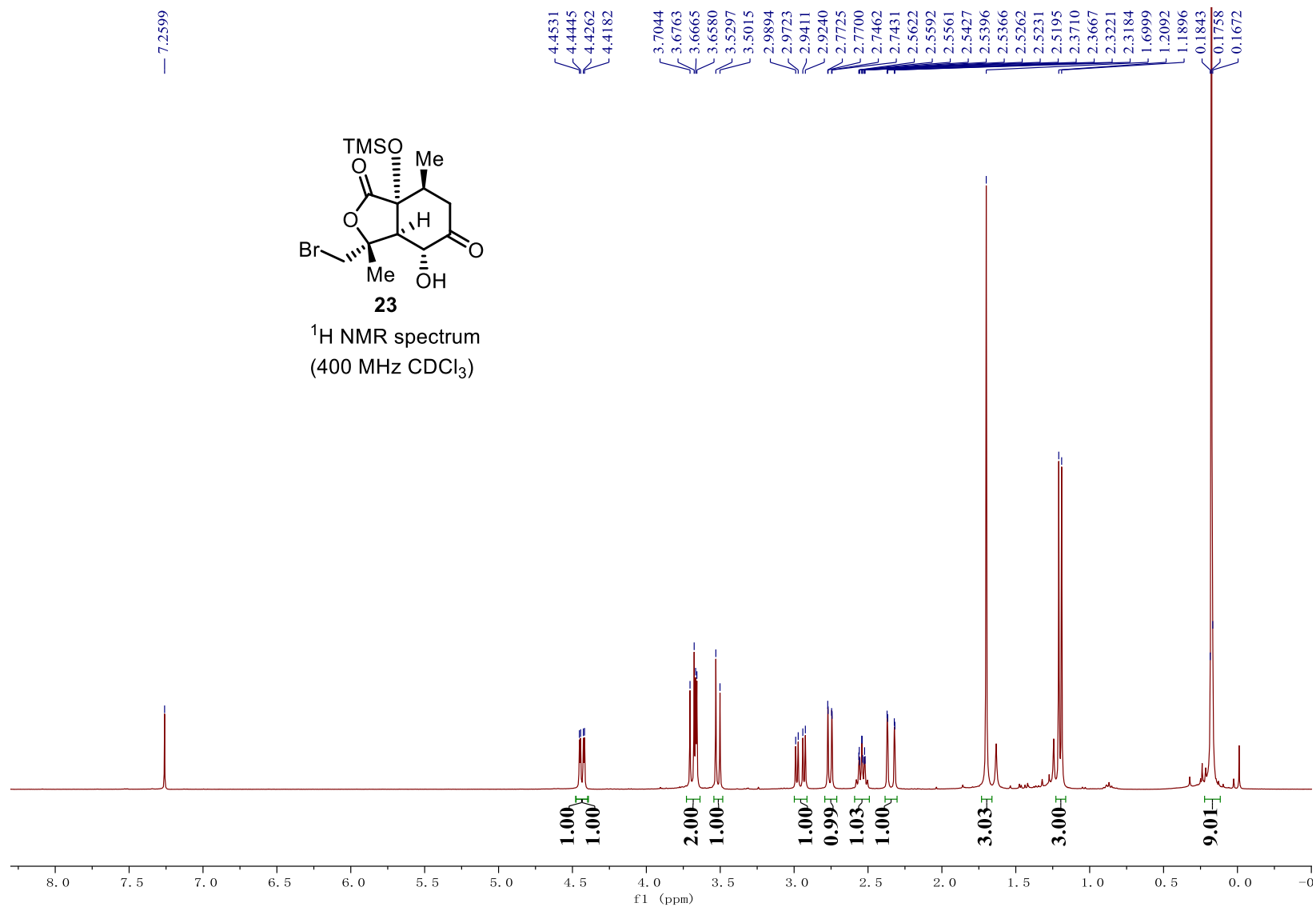


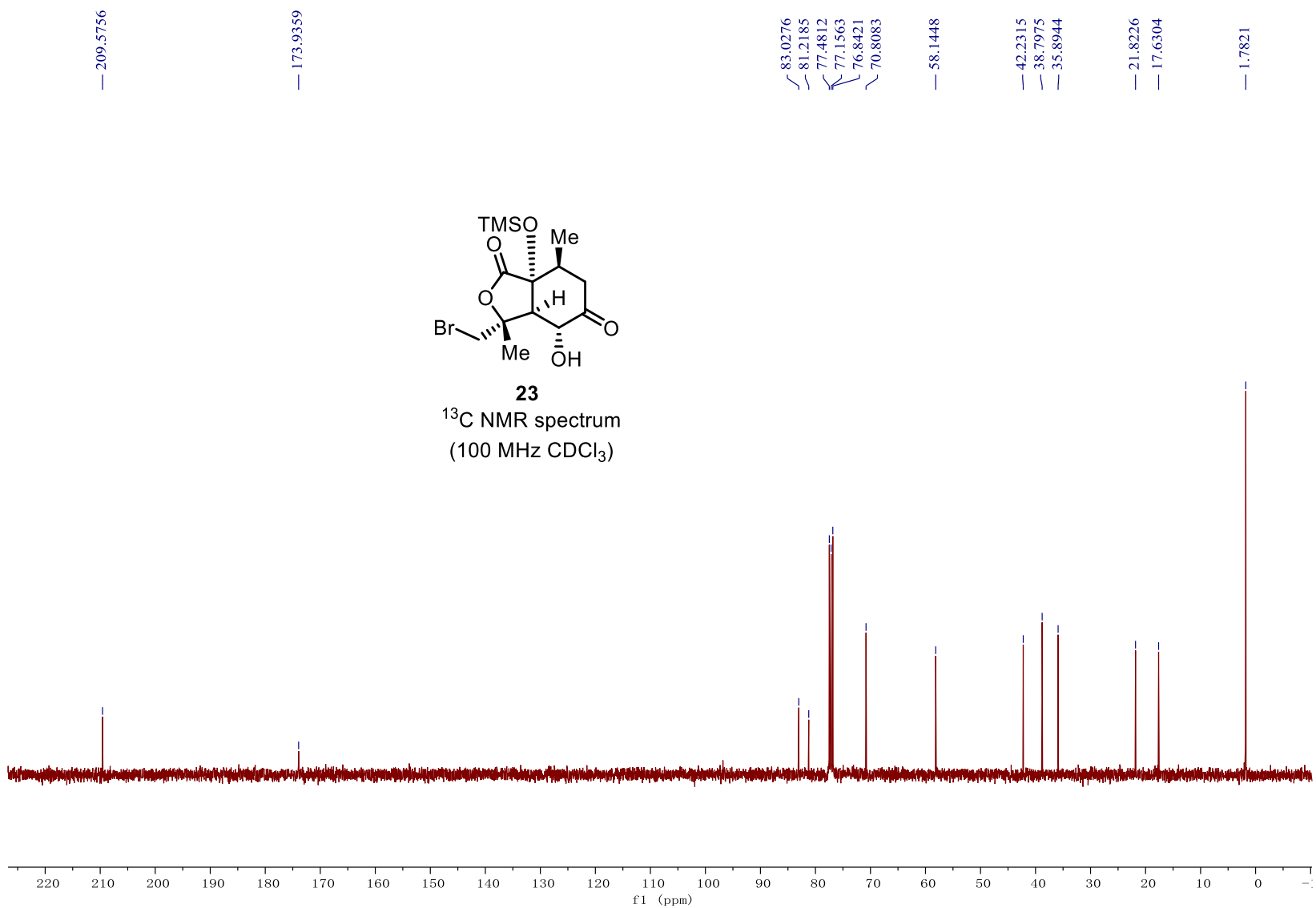
^{13}C NMR spectrum
(100 MHz CDCl_3)

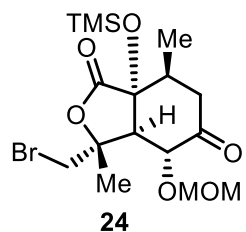




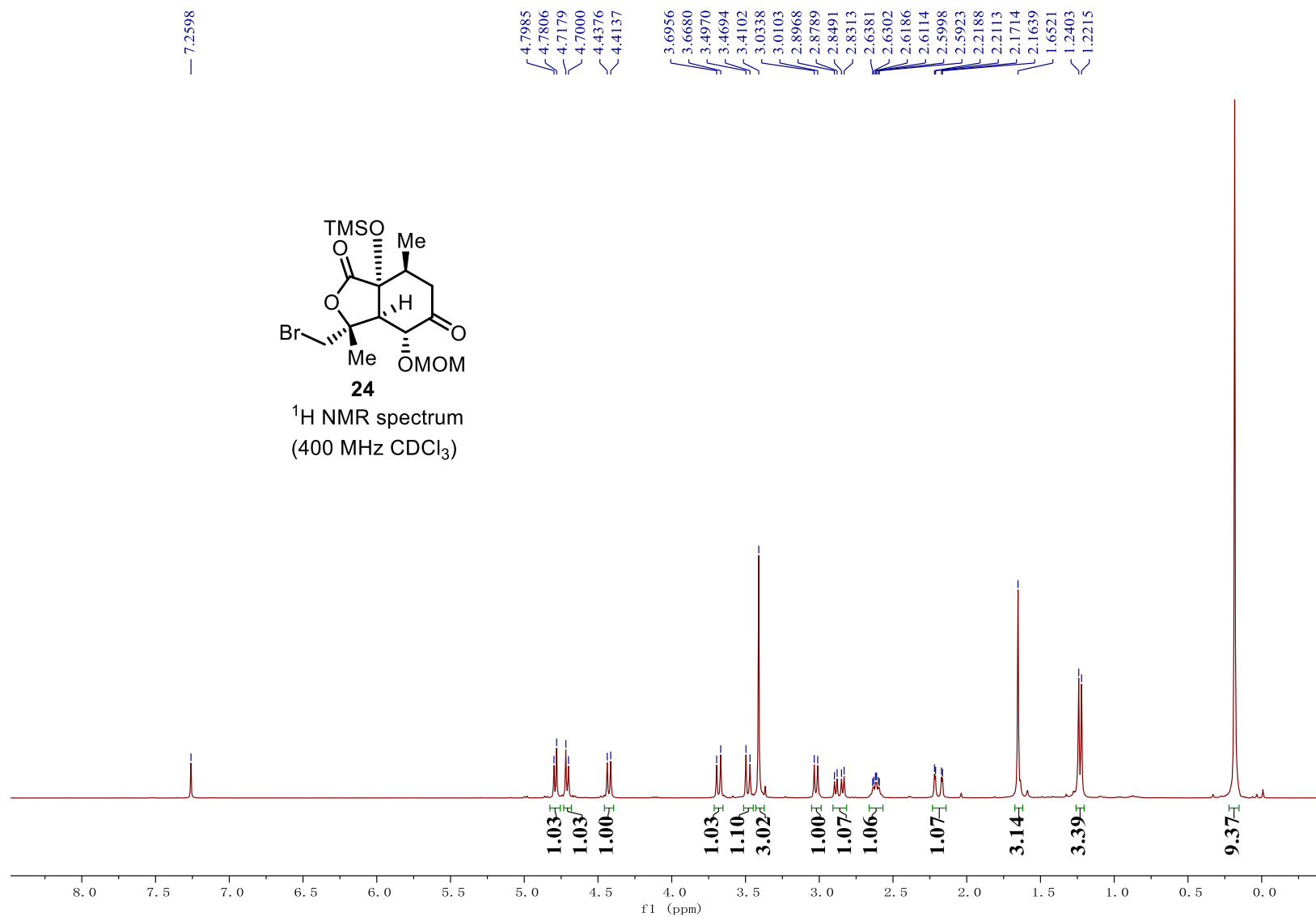


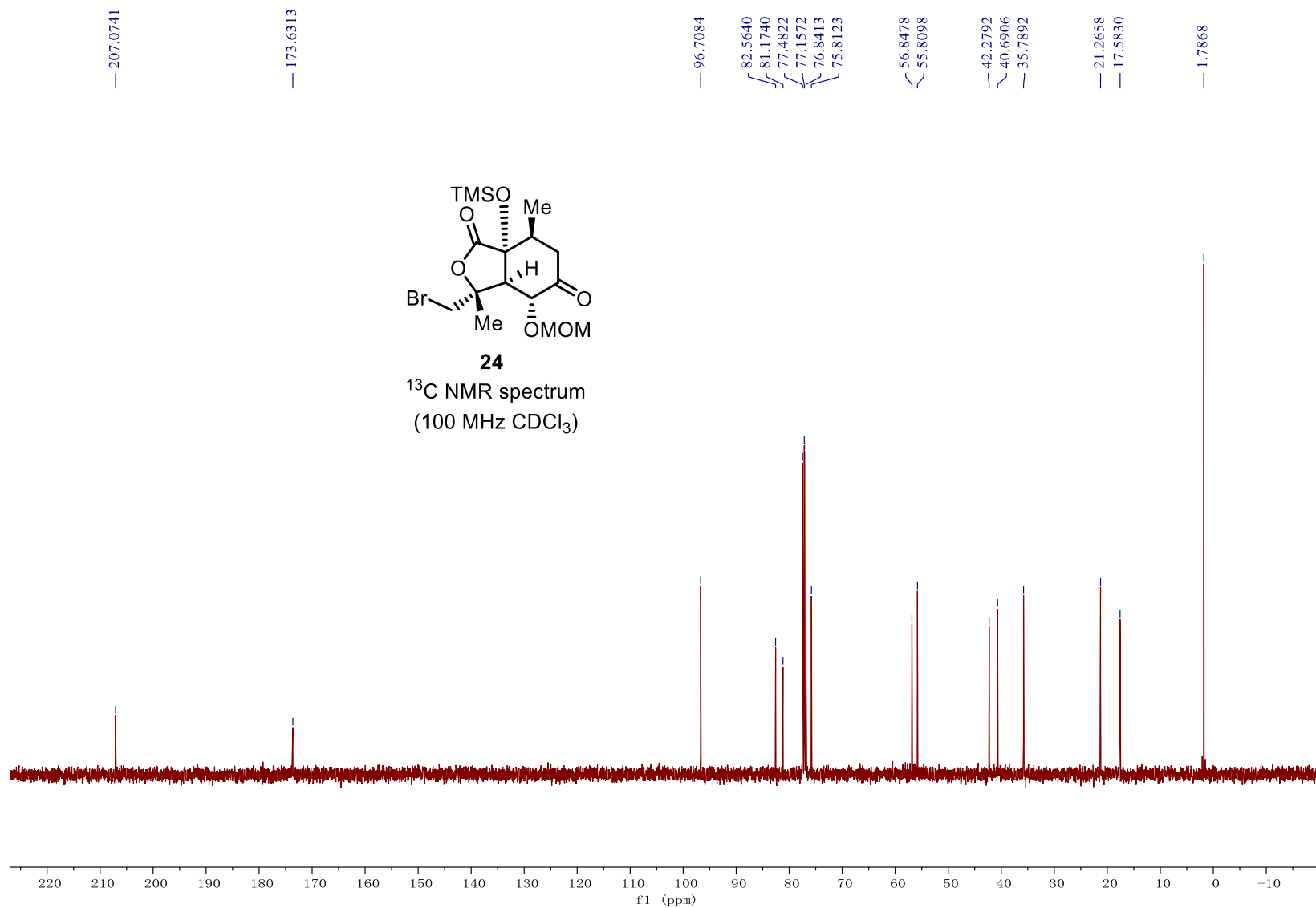


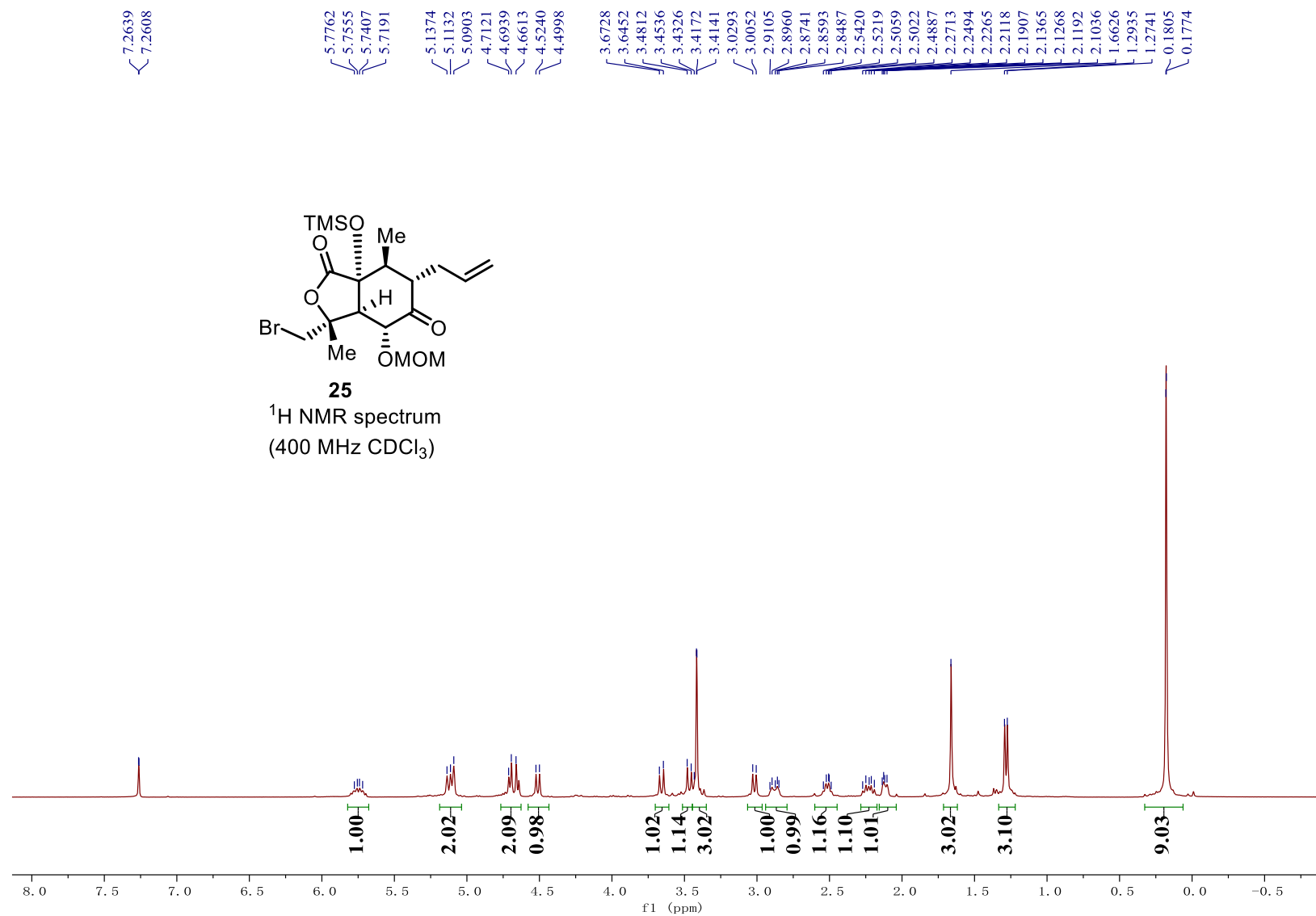


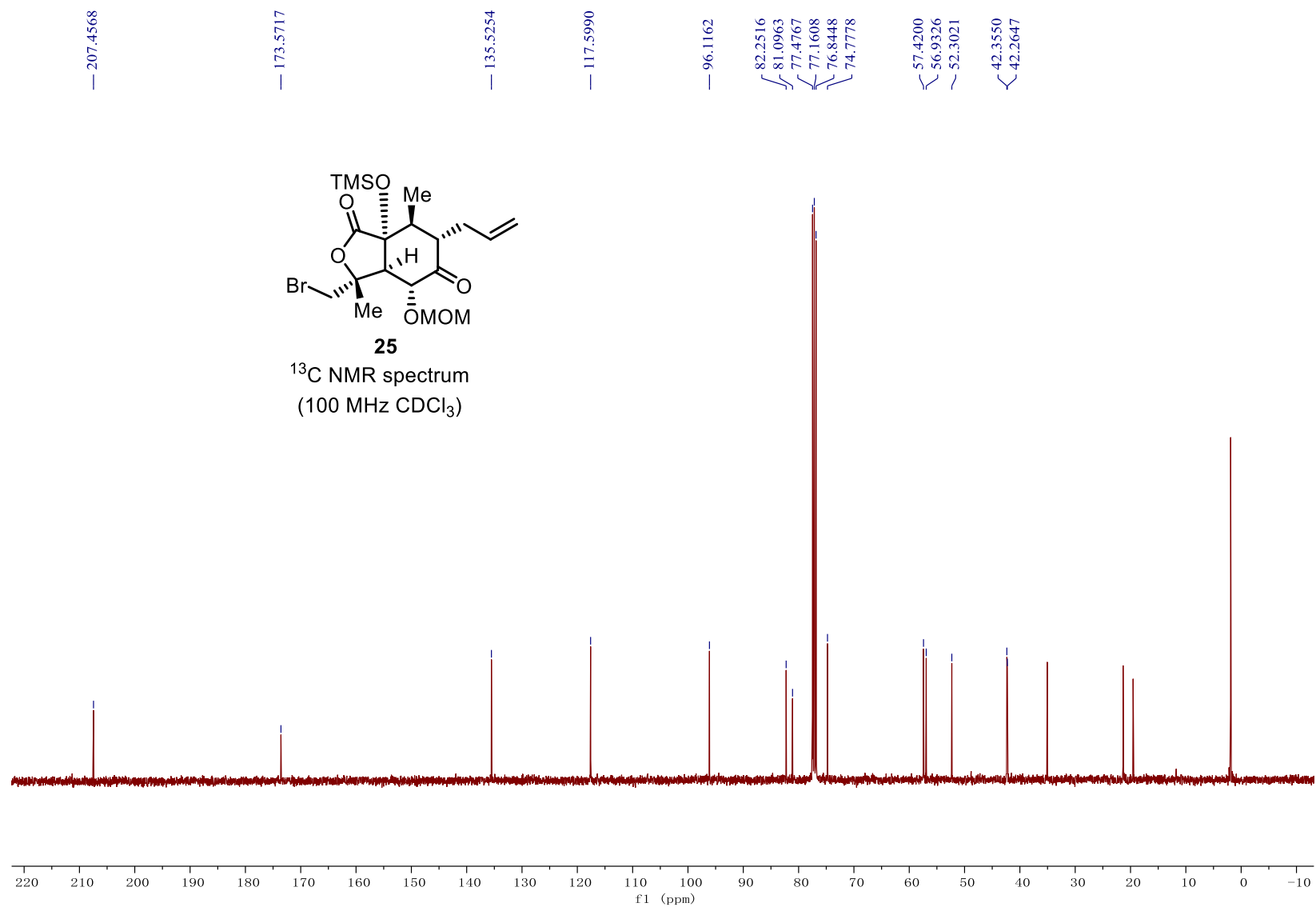


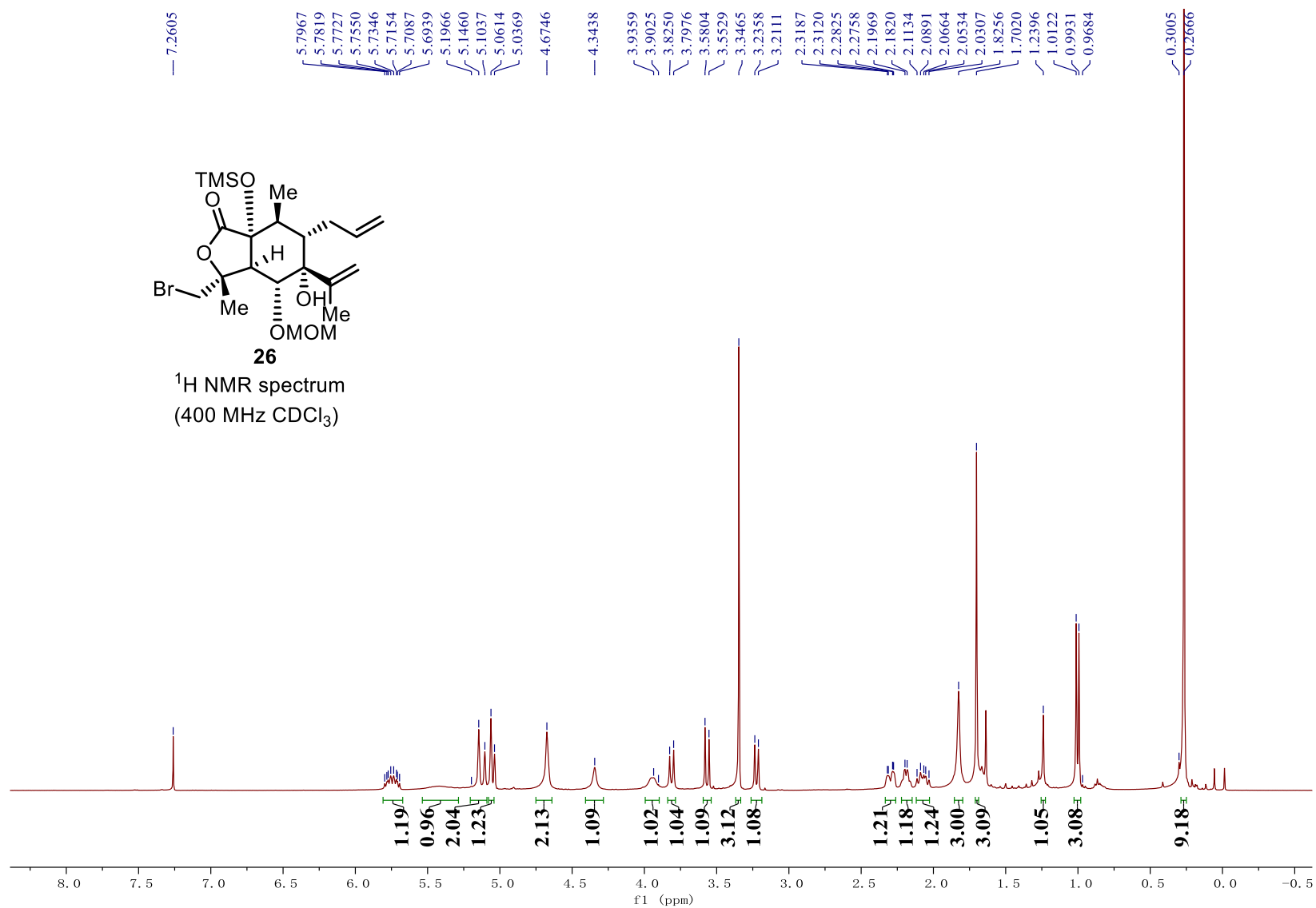
^1H NMR spectrum
(400 MHz CDCl_3)

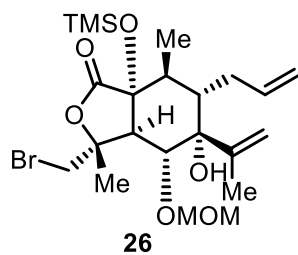




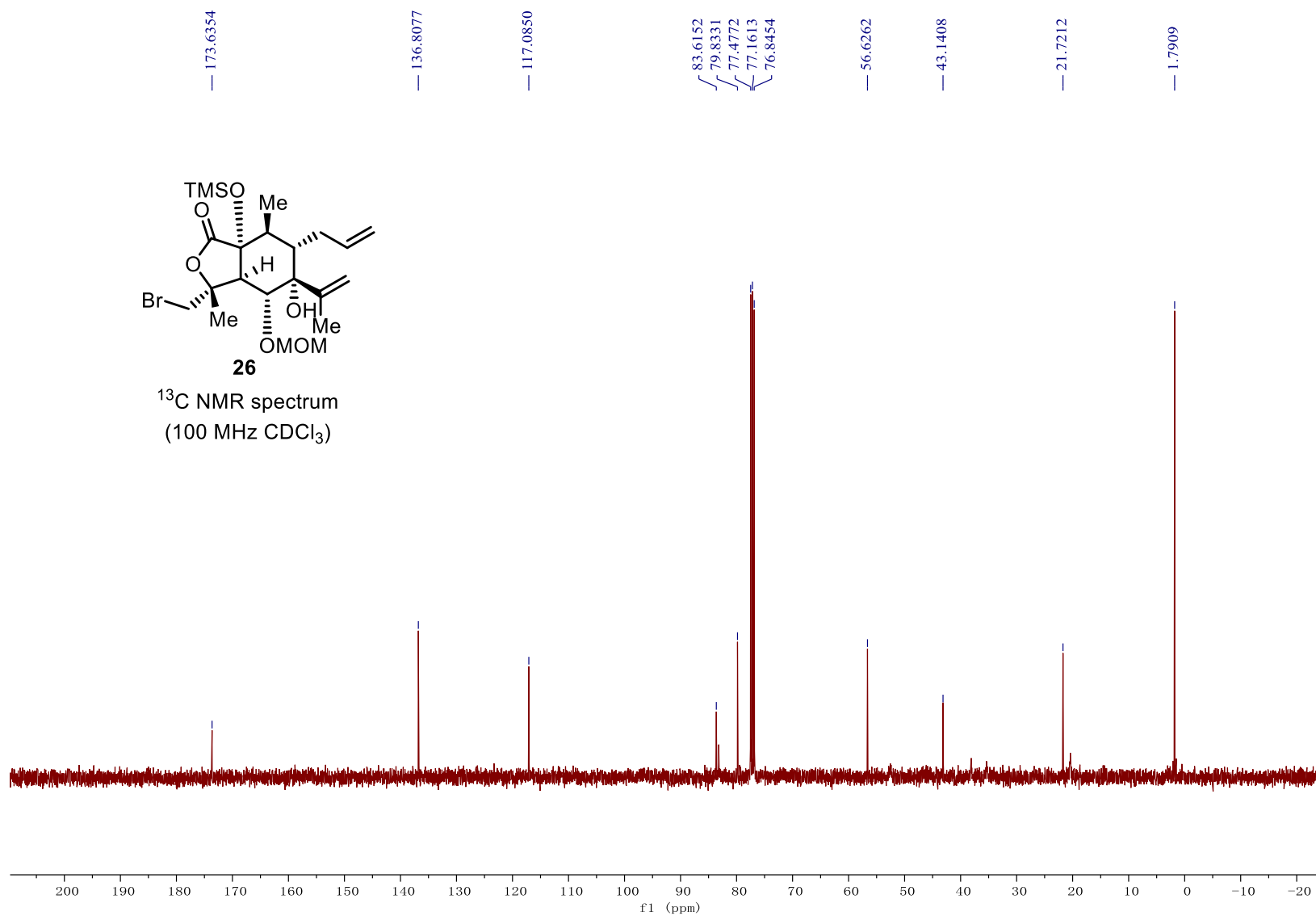


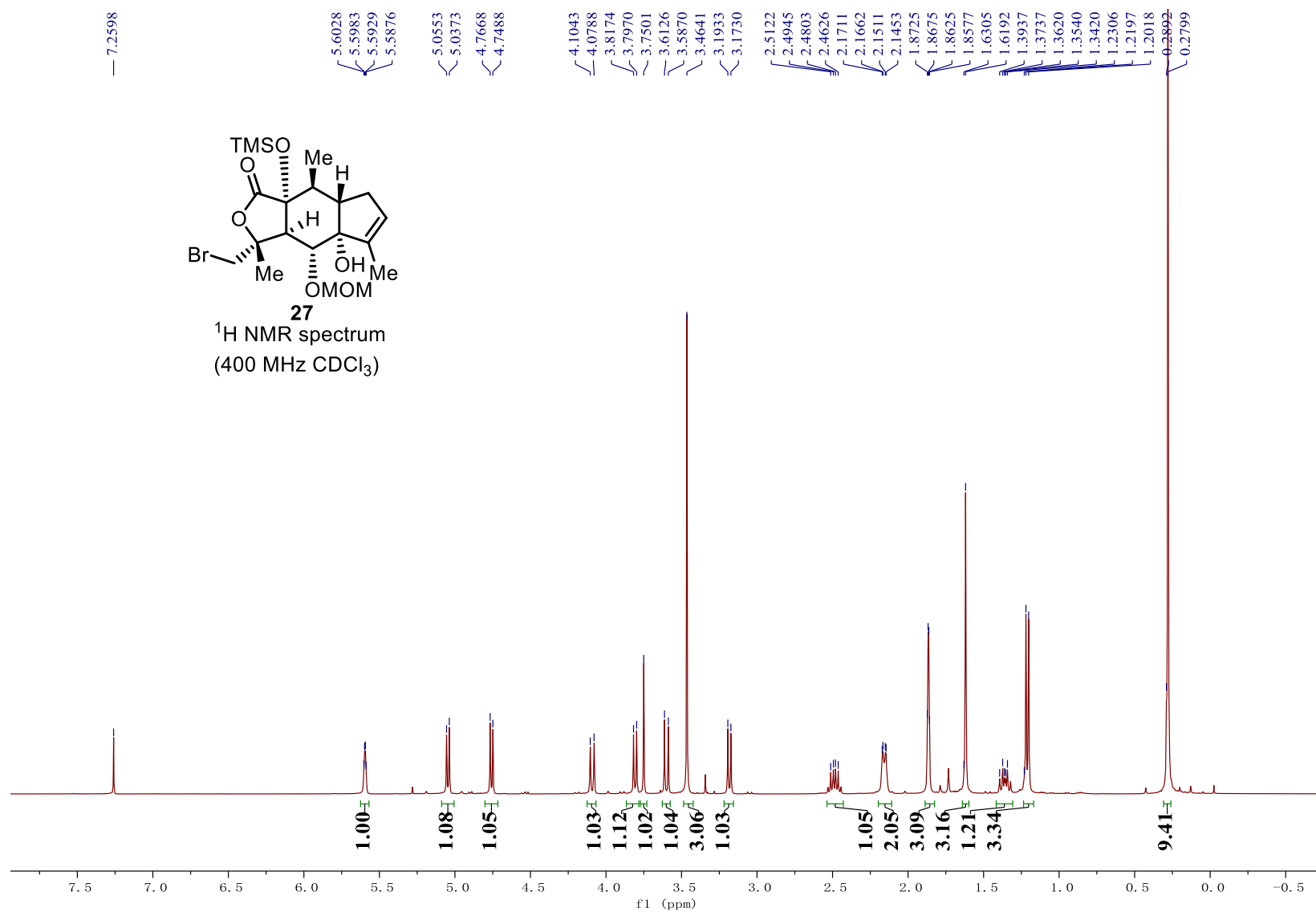


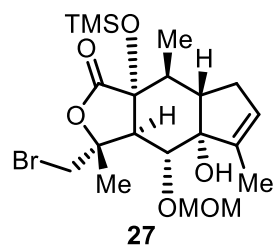




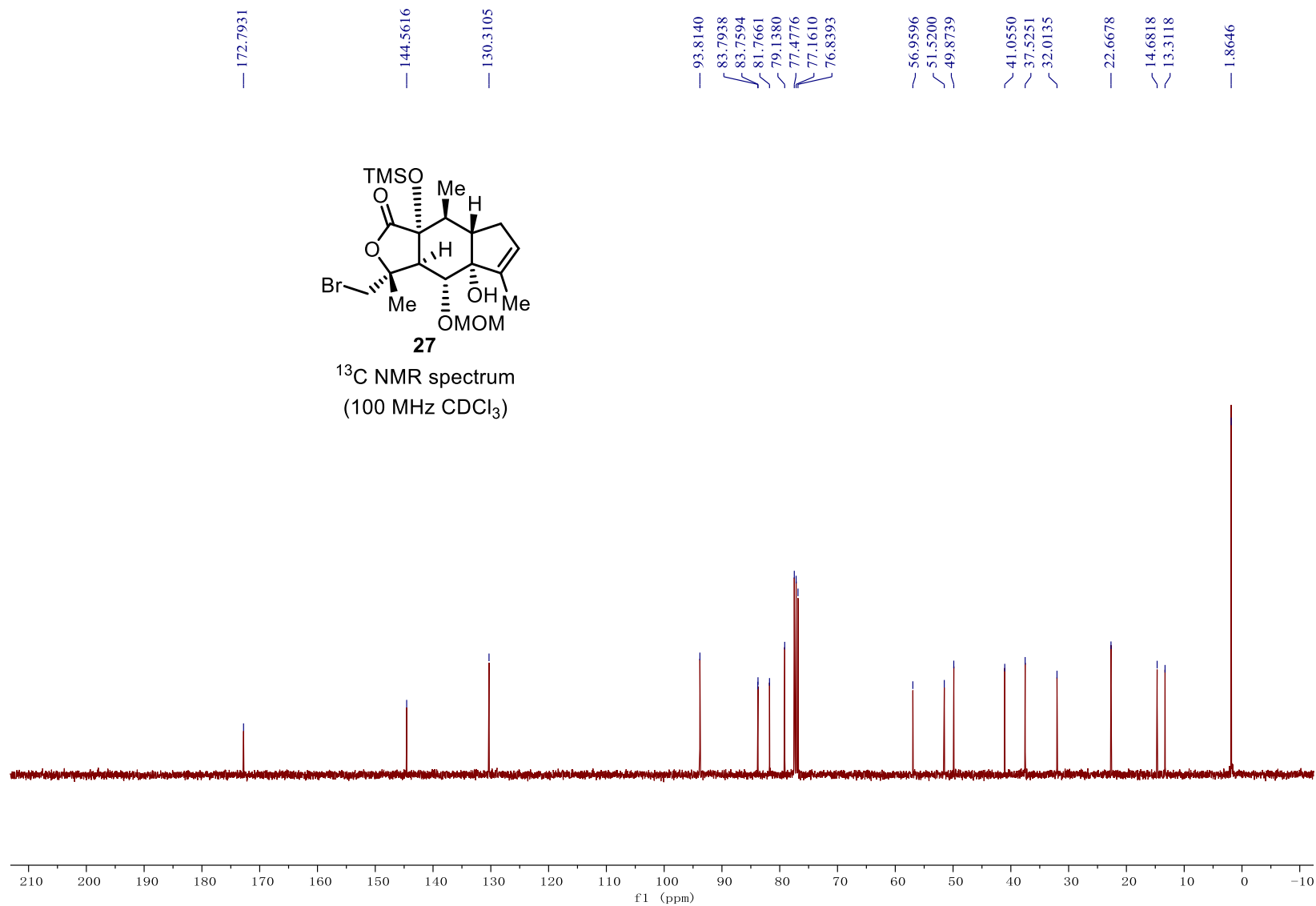
^{13}C NMR spectrum
(100 MHz CDCl_3)

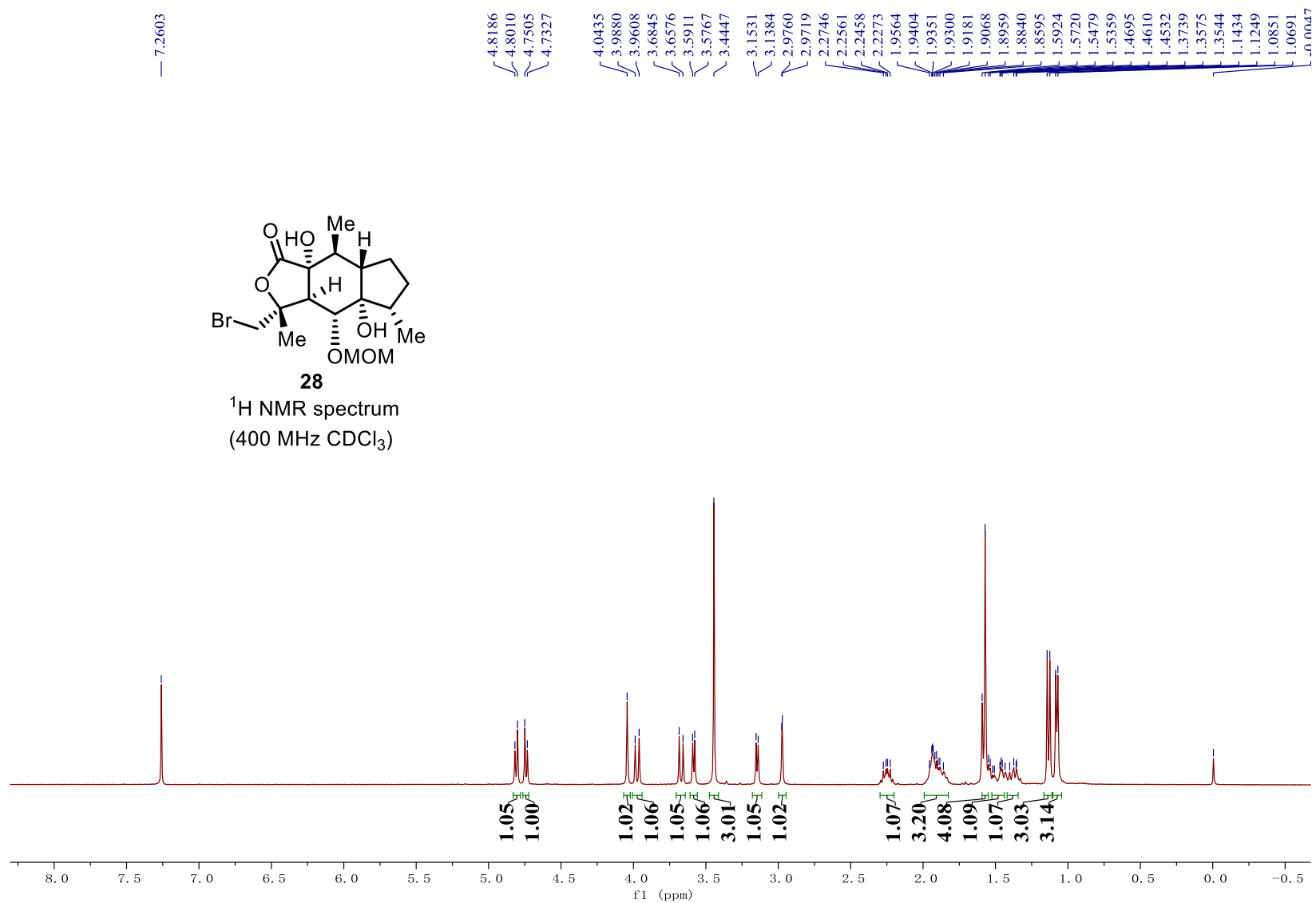


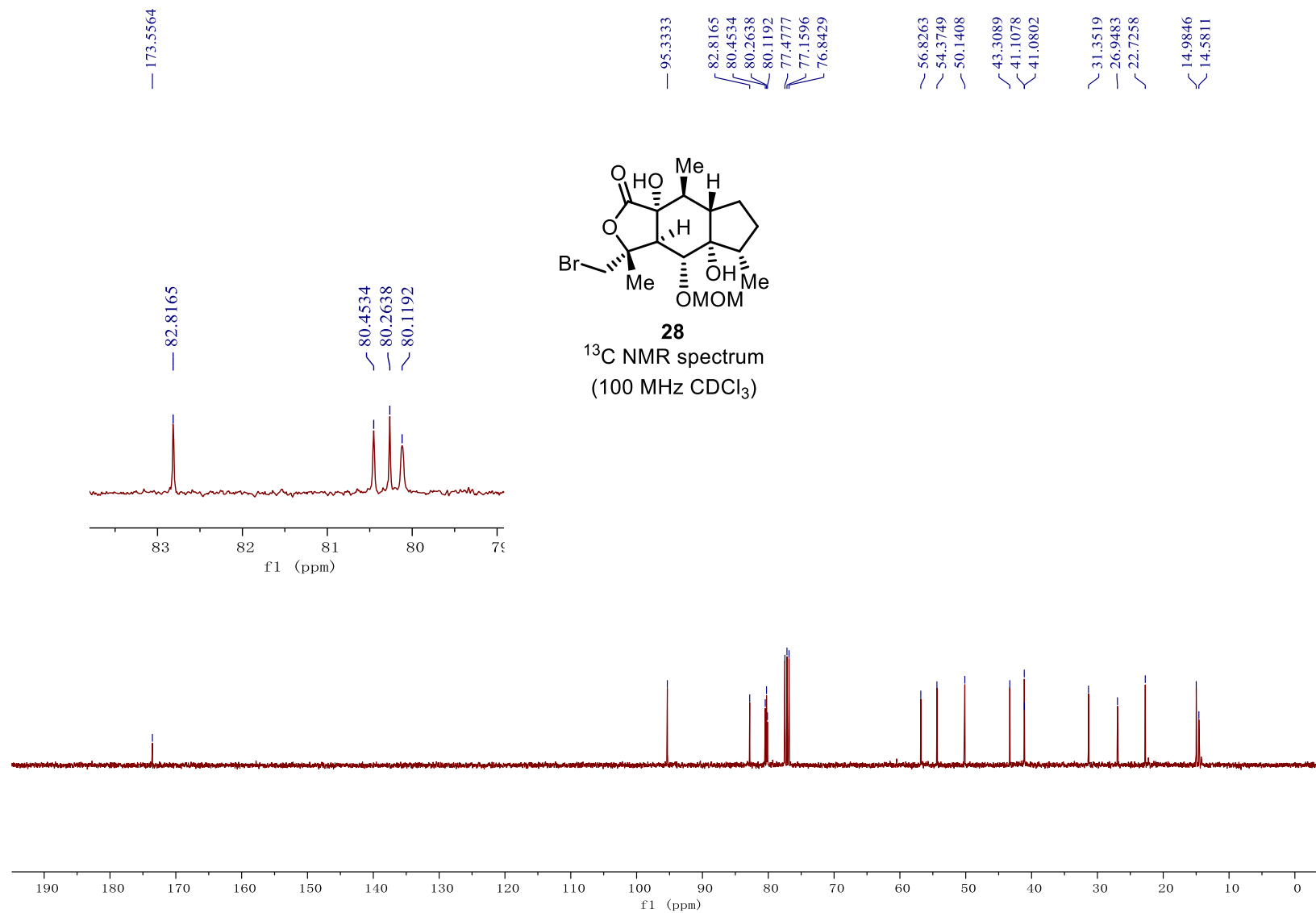


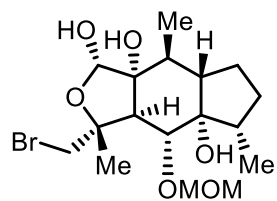


^{13}C NMR spectrum
(100 MHz CDCl_3)



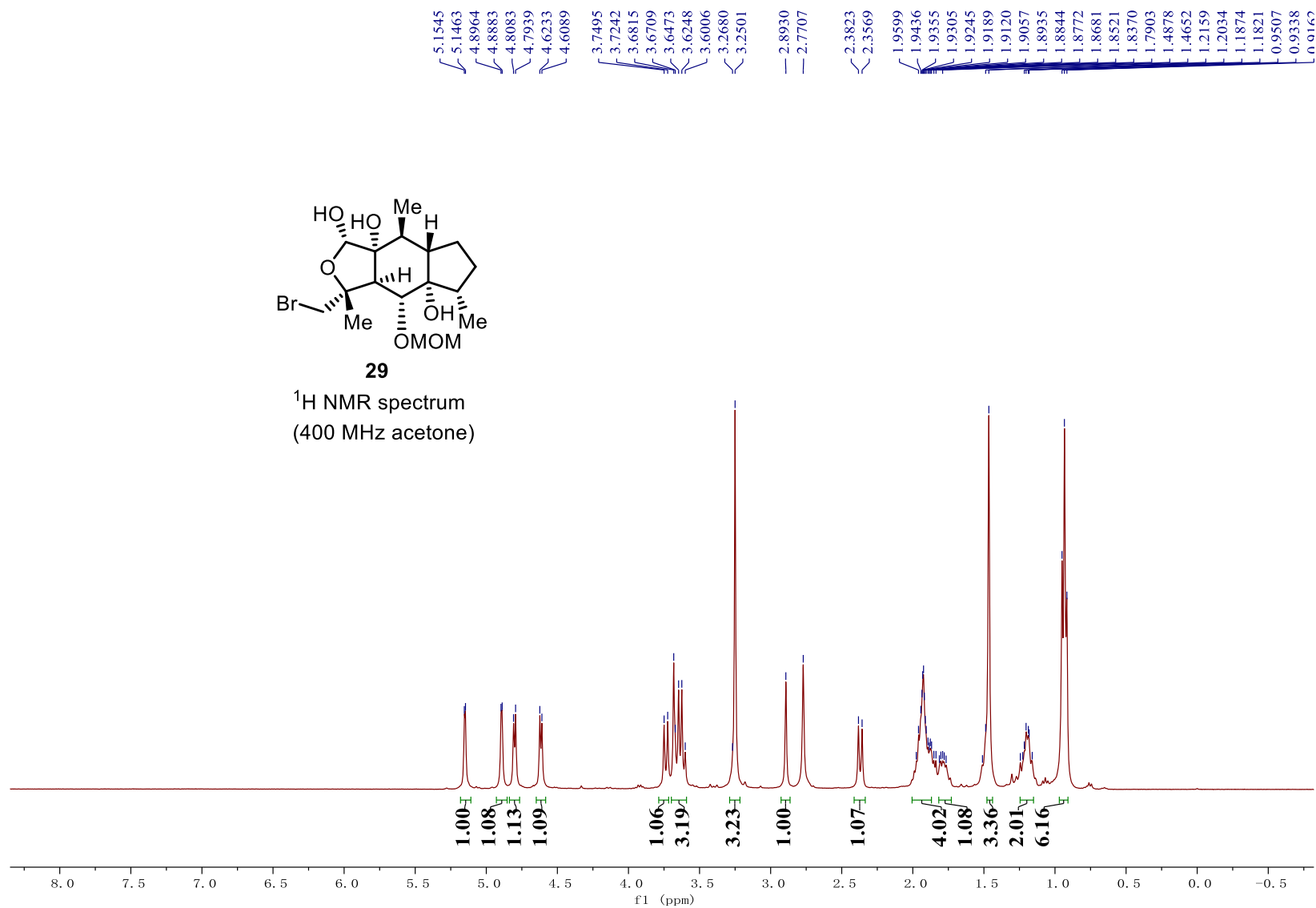


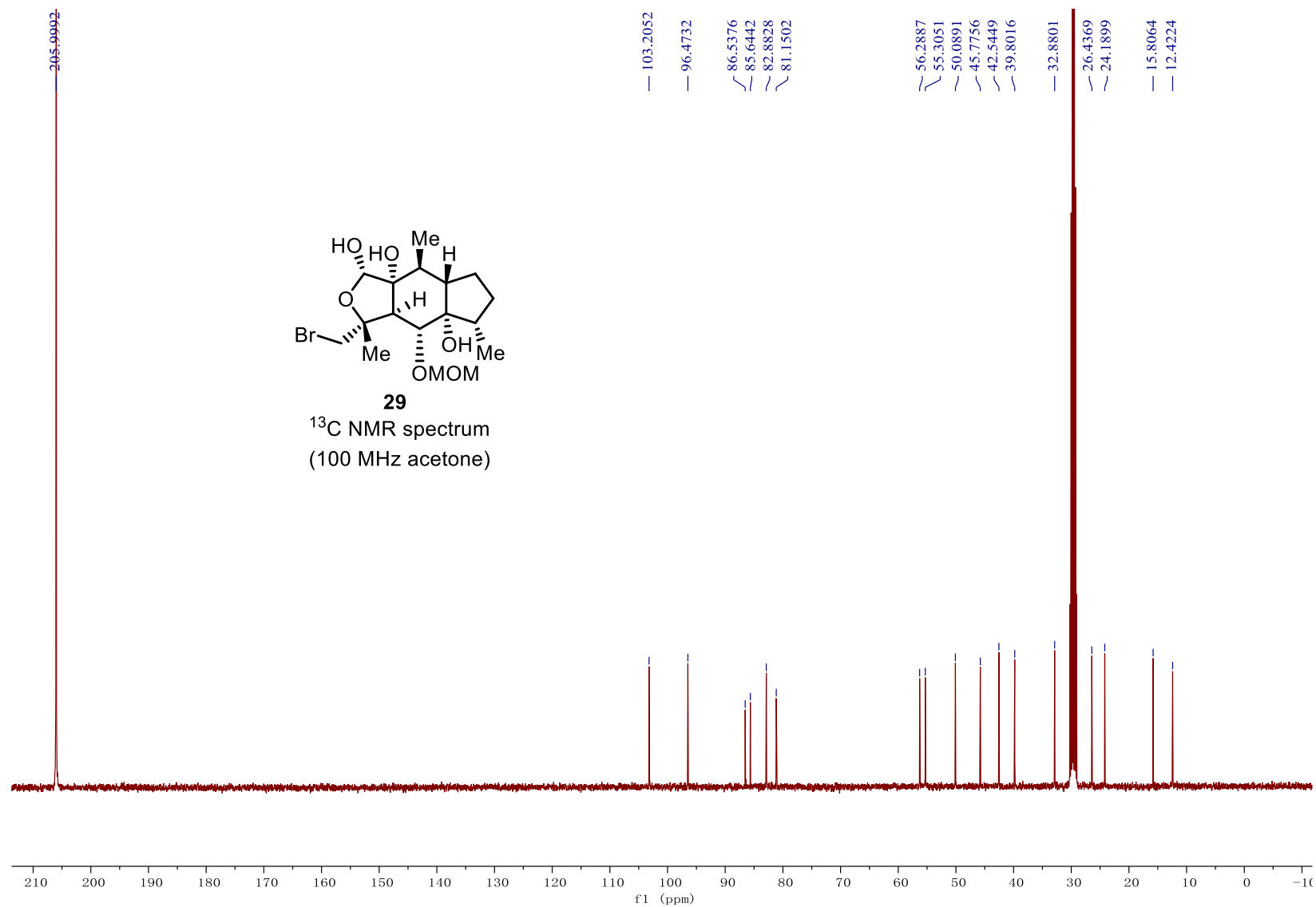


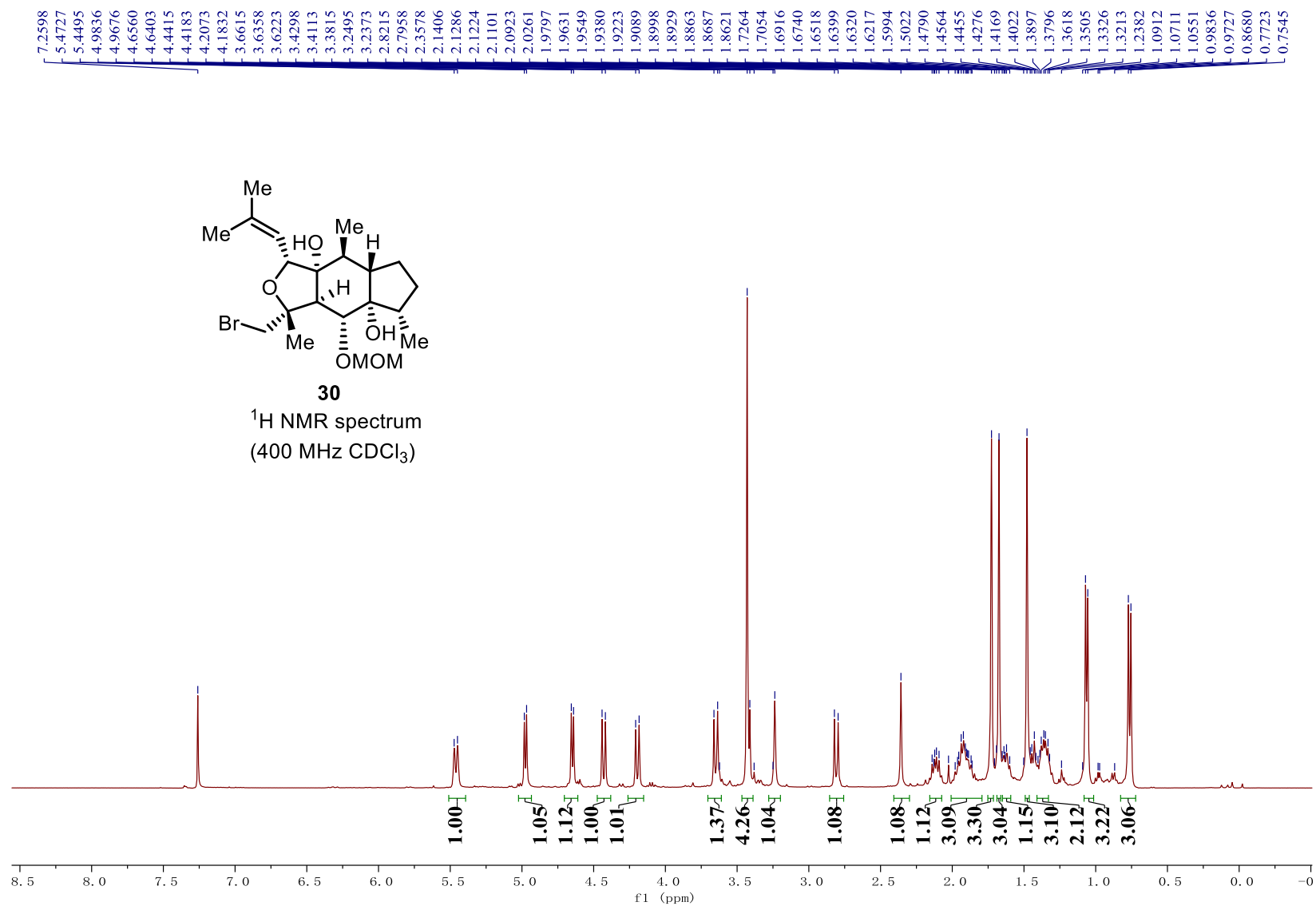


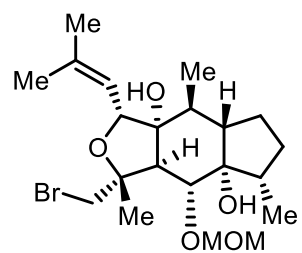
29

¹H NMR spectrum
(400 MHz acetone)



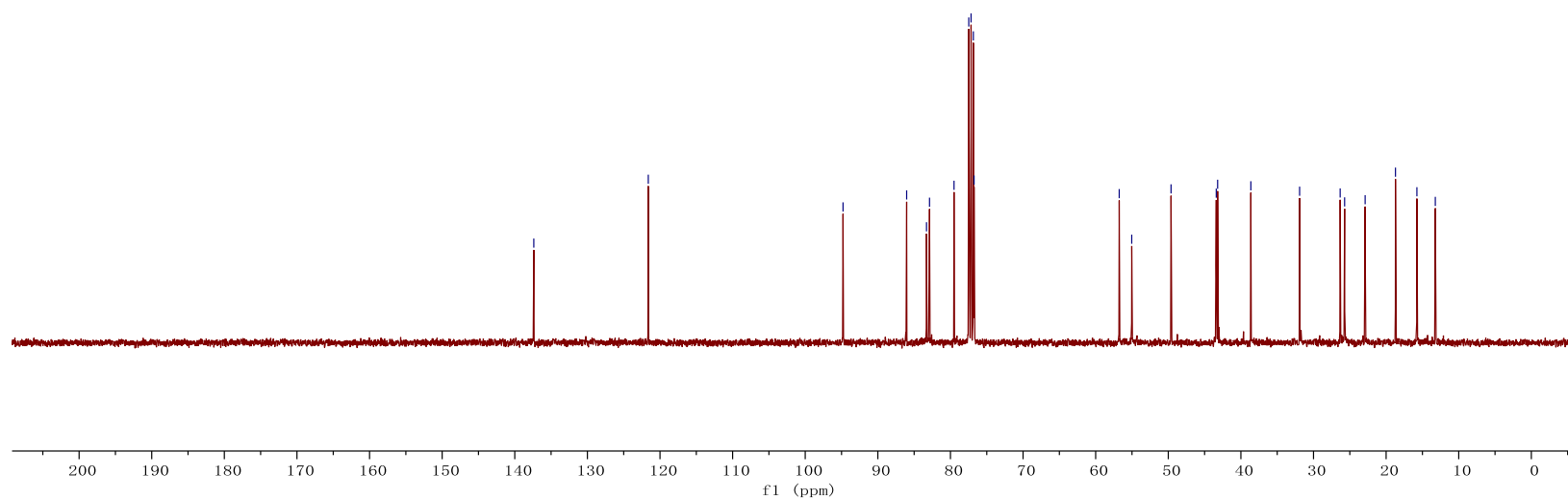


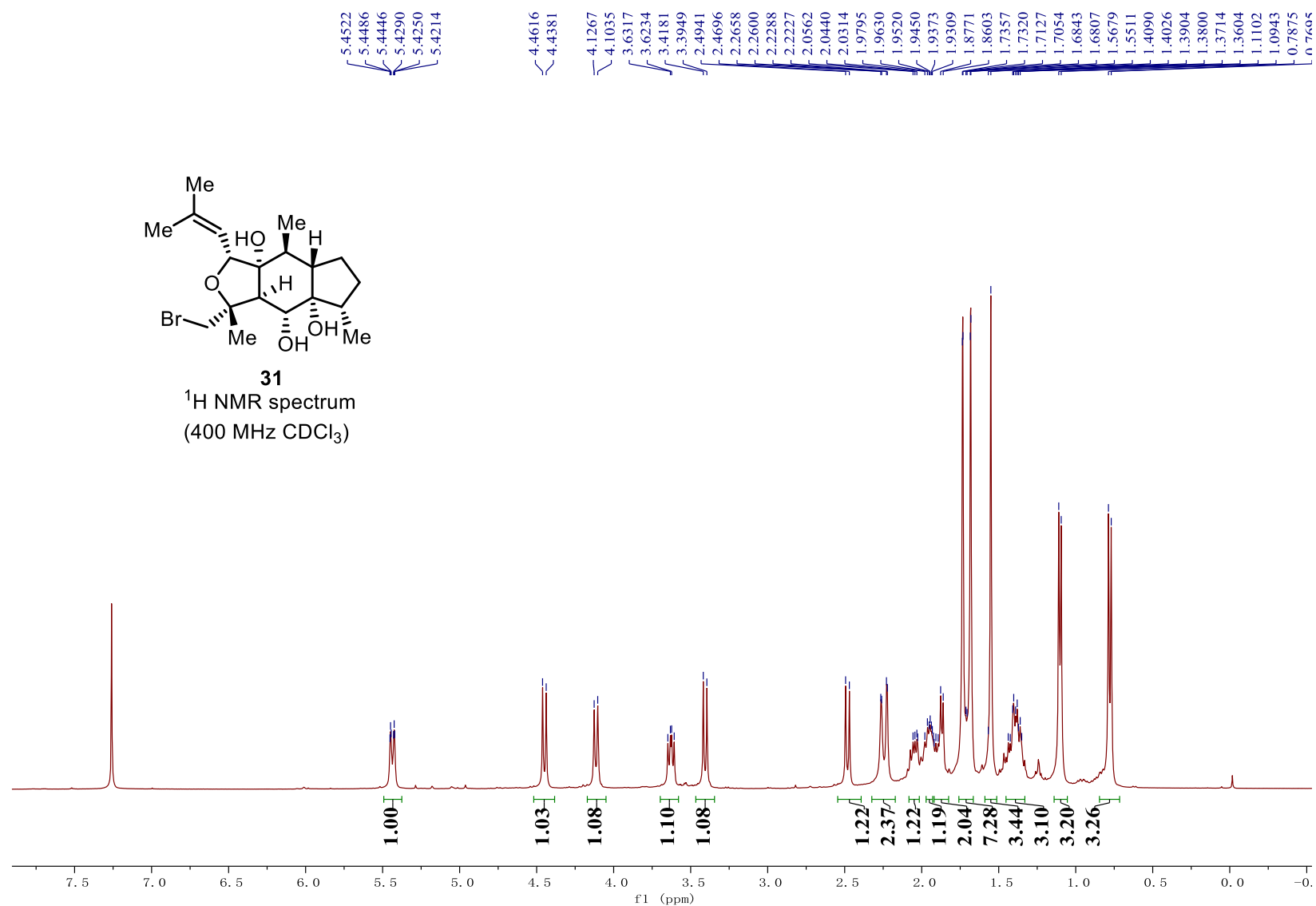


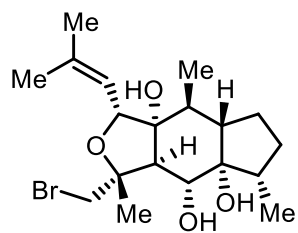


30

^{13}C NMR spectrum
(100 MHz CDCl_3)







31

^{13}C NMR spectrum
(100 MHz CDCl_3)

