Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Bioinspired total synthesis of (-)-gymnothelignan L

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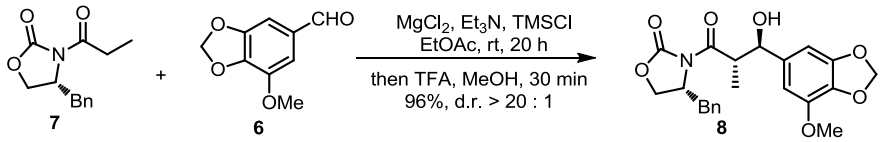
1. General information

Solvents were purified and dried by standard methods prior to use. All commercially available reagents were used without further purification unless otherwise noted. Oxygen- and moisture-sensitive reactions were carried out under argon atmosphere. Column chromatography was generally performed on silica gel (200-300 mesh) and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates with UV light to visualize the course of reaction.

Optical rotations were measured on a precision automated polarimeter. Infrared spectra were recorded on a 670 FT-IR spectrometer. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker APEXII mass spectrometer by means of the electrospray ionization (ESI) technique. ^{1}H NMR and ^{13}C NMR spectra were recorded on 300MHz, 400 MHz and 600 MHz spectrometers. Chemical shifts are reported as δ values relative to internal chloroform (δ 7.27 for ^{1}H NMR and 77.0 for ^{13}C NMR) or acetone-*d*6. Melting points were measured on a melting point apparatus and are uncorrected.

Experimental Procedures



Compound (8). To a solution of (R)-4-benzyl-3-propionyloxazolidin-2-one **7** (1.50 g, 6.44 mmol, 1.1 equiv.) in EtOAc (20 ml) were successively added aldehyde **6** (1.05 g, 5.85 mmol, 1.0 equiv.), $MgCl_2$ (56 mg, 0.59 mmol, 0.1 equiv.), Et_3N (1.62 mL, 11.7 mmol, 2.0 equiv.) and TMSCl (1.48 ml, 11.7 mmol, 2.0 equiv.) under argon atmosphere. The mixture was stirred at room temperature for 20 h. The mixture was diluted with EtOAc followed by filtration through a thin pad of silica gel with EtOAc rinse. The filtrate was concentrated under reduced pressure. To a solution of the mixture in CH_3OH (60 ml) was added three drops TFA. The reaction was allowed to stir for 30 min at room temperature, then concentrated under reduced pressure and purified by flash chromatography (PE : EtOAc, 2 : 1) to afford the product **8** as a white solid (2.32 g, 96%, d.r.> 20 : 1).

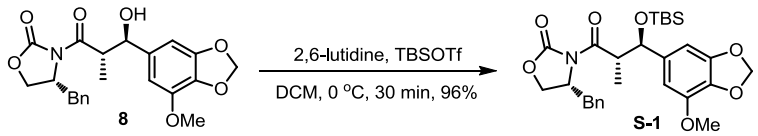
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.28 (m, 3H), 7.19-7.17 (d, *J* = 6.8 Hz, 2H), 6.64 (s, 1H), 6.63 (s, 1H), 5.96 (d, *J* = 1.2 Hz, 2 H), 4.73-4.68 (m, 2H), 4.30-4.27 (m, 1H), 4.20-4.15 (m, 2H), 3.91 (s, 3H), 3.24 (dd, *J* = 13.6 Hz, 3.2 Hz, 1H), 3.04 (br, 1H), 2.74 (dd, *J* = 13.6 Hz, 9.2 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 153.6, 149.0, 143.6, 136.9, 135.2, 134.9, 129.5, 129.0, 127.3, 106.2, 101.5, 100.8, 77.5, 66.0, 56.6, 55.4, 44.3, 37.6, 14.9;

IR (neat) ν_{max} 3493, 2980, 2937, 1779, 1734, 1696, 1634, 1610, 1511, 1498, 1453, 1432, 1386, 1353, 1317, 1290, 1250, 1211, 1121, 1090, 1045, 969, 928, 843, 761, 732, 705, 688, 405 cm^{-1}.

HRMS (ESIMS): calcd for $C_{22}H_{27}N_2O_7$ $[M+NH_4]^+$ 431.1813, found 431.1812;

$[\alpha]_D^{13}$ = +3.0 (c = 1.0, $CHCl_3$); m.p. 145-147 ℃.



Compound (S-1). Alcohol **8** (2.87 g, 6.95 mmol) was dissolved in anhydrous DCM (100 mL) under argon atmosphere and cooled to 0 °C. 2, 6-lutidine (1.60 mL, 2.0 equiv.) and TBSOTf (3.20 mL, 2.0 equiv.) were added dropwise. 30 min later, the reaction was quenched with saturated aq. NH_4Cl, and evaporated DCM. The aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 10 : 1 to 5 : 1) to afford the product **S-1** as a white solid (3.52 g, 96%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.35 (m, 2H), 7.32-7.28 (m, 3H), 6.62 (s, 1H), 6.59 (s, 1H), 5.99 (s, 2H), 4.85 (d, *J* = 9.2 Hz, 1H), 4.74-4.68 (m, 1H), 4.22-4.14 (m, 3H), 3.93 (s, 3H), 3.49 (dd, *J* = 13.2 Hz, 3.2 Hz, 1H), 2.71 (dd, *J* = 13.2 Hz, 10.4 Hz, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.84 (s,

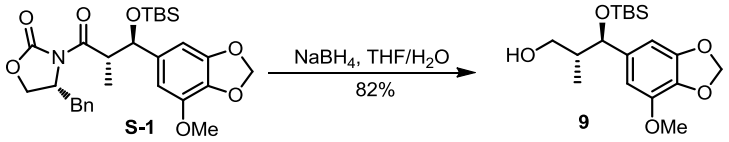
9H), 0.03 (s, 3H), -0.19 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 153.1, 148.5, 143.3, 137.2, 135.6, 134.6, 129.3, 128.9, 127.2, 106.7, 101.7, 101.4, 77.5, 65.8, 56.5, 55.5, 46.4, 38.3, 25.8, 18.0, 14.7, -4.6, -5.0;

IR (neat) ν_{max} 3537, 3372, 3064, 2956, 2932, 2888, 2857, 2779, 2257, 1781, 1700, 1636, 1610, 1510, 1453, 1432, 1384, 1347, 1316, 1289, 1257, 1210, 1128, 1080, 1043, 1019, 971, 910, 857, 838, 779, 734, 704, 683, 650, 506 cm^{-1}.

HRMS (ESIMS): calcd for $C_{28}H_{37}NO_7SiNa$ $[M+Na]^+$ 550.2232, found 550.2234;

$[\alpha]_D^{13}$ = +34.0 (c = 1.0, $CHCl_3$); m.p. 175–177 ℃.



Alcohol (9). Compound **S-1** (6.59 g, 12.49 mmol) was dissolved in a solution of THF/H_2O (100/20 mL) and cooled to 0 ^oC. $NaBH_4$ (1.46 g, 3.0 equiv.) was slowly added, warmed to room temperature and kept stirring overnight. The reaction was cooled to 0 ^oC again and quenched with saturated aq. NH_4Cl, and evaporated THF. The aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 5 : 1) to afford the product **9** as a colorless oil (3.63 g, 82%).

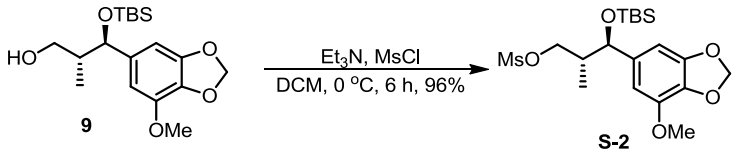
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 1H), 6.48 (s, 1H), 5.97 (s, 2H), 4.46 (d, *J* = 6.8 Hz, 1H), 3.90 (s, 3H), 3.67 (dd, *J* = 10.8 Hz, 3.2 Hz, 1H), 3.59 (dd, J = 10.8 Hz, 6.0 Hz, 1H), 1.91-1.85 (m, 1 H), 0.90 (s, 9H), 0.84 (d, *J* = 7.2 Hz, 3H), 0.06 (s, 3H), -0.18 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 143.3, 138.5, 134.2, 105.8, 101.4, 100.9, 80.8, 66.3, 56.5, 43.3, 25.8, 18.0, 14.3, -4.5, -5.2;

IR (neat) ν_{max} 3372, 2955, 2931, 2888, 2857, 1739, 1635, 1612, 1509, 1464, 1452, 1430, 1376, 1359, 1341, 1317, 1286, 1254, 1233, 1195, 1129, 1078, 1043, 935, 863, 837, 777, 674 cm^{-1}.

HRMS (ESIMS): calcd for $C_{18}H_{30}O_5SiNa$ $[M+Na]^+$ 377.1755, found 377.1754;

$[\alpha]_D^{13}$ = +58.0 (c = 1.0, $CHCl_3$);



Mesylate (S-2). To a solution of alcohol **9** (1.33 g, 3.75 mmol) in anhydrous DCM (30 mL) at 0 ^oC was added Et_3N (1.04 mL, 2.0 equiv.), catalytic amount of DMAP and MsCl (0.35mL, 1.2 equiv.). The reaction was warmed to room temperature and stirred overnight (6 h) and quenched with saturated aq. $NaHCO_3$. The DCM was evaporated and the aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 5 : 1) to afford the product

S-2 as a colorless oil (1.56 g, 96%).

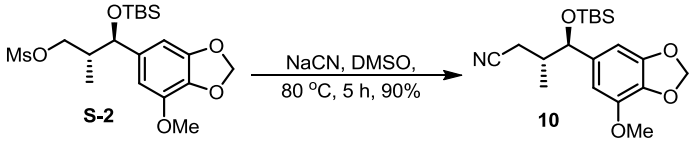
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.46 (d, *J* = 1.6 Hz, 2H), 5.97 (s, 2H), 4.41 (d, *J* = 7.2 Hz, 1H), 4.27 (d, J = 5.2 Hz, 2H), 3.89 (s, 3H), 2.99 (s, 3H), 2.14-2.04 (m, 1H), 0.88 (s, 9H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.04 (s, 3H), -0.20 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 143.2, 137.4, 134.3, 105.9, 101.4, 100.8, 75.8, 71.7, 56.5, 41.7, 37.1, 25.7, 18.0, 13.4, -4.6, -5.3;

IR (neat) ν_{max} 3312, 2954, 2934, 2892, 2857, 1737, 1636, 1510, 1464, 1454, 1432, 1357, 1253, 1196, 1176, 1134, 1080, 1043, 963, 935, 838, 778, 739, 691, 529 cm^{-1}.

HRMS (ESIMS): calcd for $C_{19}H_{32}O_5SSiNa$ $[M+Na]^+$ 455.1530, found 455.1524;

$[\alpha]_D^{13}$ = +34.0 (c = 1.0, $CHCl_3$);



Cyanide (10). To a solution of mesylate **S-2** (2.92 g, 6.75 mmol) in anhydrous DMSO (80 mL) was added NaCN (0.99 g, 3.0 equiv.) and the reaction was warmed to 80 °C and stirred for 5 h, when TLC indicated the reaction was completed, the mixture was cooled to room temperature, and extracted with EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 50 : 1) to afford the product **10** as a colorless oil (2.21 g, 90%).

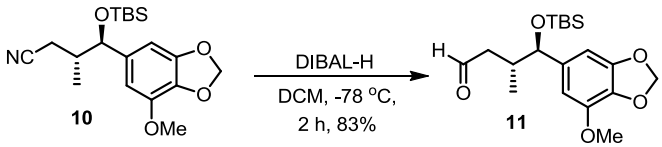
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.45 (s, 1H), 6.44 (s, 1H), 5.97 (s, 2H), 4.34 (d, *J* = 7.2 Hz, 1H), 3.89 (s, 3H), 2.51-2.43 (m, 2H), 2.05-1.99 (m, 1H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.89 (s, 9H), 0.06 (s, 3H), -0.20 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.7, 143.3, 137.4, 134.5, 119.1, 105.8, 101.4, 100.6, 77.7, 56.5, 39.1, 25.7, 20.3, 18.0, 16.3, -4.6, -5.3;

IR (neat) ν_{max} 3308, 2956, 2932, 2886, 2857, 2779, 2246, 1636, 1612, 1510, 1453, 1431, 1381, 1360, 1341, 1287, 1255, 1231, 1196, 1128, 1079, 1044, 1007, 934, 905, 880, 855, 838, 778, 695, 674 cm^{-1}.

HRMS (ESIMS): calcd for $C_{19}H_{33}N_2O_4Si$ $[M+NH_4]^+$ 381.2204, found381.2210;

$[\alpha]_D^{13}$ = +38.0 (c = 1.0, $CHCl_3$);



Compound (11). To a solution of cyanide **10** (4.07 g, 11.20 mmol) in anhydrous DCM (120 mL) at -78 °C was added DIBAL-H (11.20 mL, 1.5 equiv., 1.5 M solution in toluene) and stirred for 2 h. The reaction mixture was quenched with MeOH and saturated sodium potassium tartrate and stirred at room temperature for another 6 h. The solvent DCM was evaporated and the aqueous

solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 20 : 1) to afford the product **11** as a colorless oil (3.41 g, 83%).

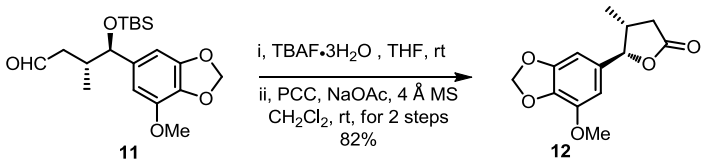
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (s, 1H), 6.47 (s, 1H), 6.44 (s, 1H), 5.95 (s, 2H), 4.35 (d, *J* = 5.2 Hz, 1H), 3.88 (s, 3H), 2.56 (d, *J* = 12.8 Hz, 1H), 2.30-2.20 (m, 2H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.88 (s, 9H), 0.02 (s, 3H), -0.20 (s, 3H);

^{13}C NMR (100 MHz, $CDCl_3$) δ 202.7, 148.5, 143.2, 138.3, 134.1, 105.8, 101.3, 100.7, 78.8, 56.4, 46.3, 37.4, 25.8, 18.1, 17.3, -4.6, -5.2;

IR (neat) ν_{max} 3351, 2956, 2931, 2886, 2857, 2716, 1724, 1635, 1612, 1509, 1463, 1452, 1430, 1402, 1378, 1361, 1340, 1318, 1255, 1230, 1195, 1130, 1083, 1044, 1007, 970, 935, 857, 837, 777, 738, 669, 516 cm^{-1}.

HRMS (ESIMS): calcd for $C_{19}H_{30}O_5SiNa$ $[M+Na]^+$ 389.1755, found 389.1758;

$[\alpha]_D^{13}$ = +38.0 (c = 1.0, $CHCl_3$);



Compound (12). To a solution of compound **11** (3.75 g, 10.25 mmol) in anhydrous THF (100 mL) at 0 ^oC was added TBAF • $3H_2O$ (6.5 g, 2.0 equiv., solution in 25 ml THF). The reaction was warmed to room temperature and stirred for 2 h and quenched with saturated aq. NH_4Cl. The THF was evaporated and the aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 3 : 1) to afford the corresponding hemiacetal as a colorless oil (2.60 g, 100%). The hemiacetal was dissolved in CH_2Cl_2 (100 mL) at 0 ^oC and sequentially added NaOAc (2.55 g, 3.0 equiv.), 4 Å MS (2.55 g) and PCC (3.35 g, 1.5 equiv.). The reaction was warmed to room temperature and stirred overnight (6 h) and ether was added, filtered through a pad of silica gel and washed with EtOAc. The combined organic phase was washed with saturated $CuSO_4$ solution, and dried over $NaSO_4$, concentrated under reduced pressure, purified by flash chromatography (PE : EtOAc, 10 : 1 to 5 : 1) to afford the lactone product **12** as a colorless oil (2.10 g, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (s, 2H), 5.97 (s, 2H), 4.80 (d, *J* = 8.5 Hz, 1H), 3.89 (s, 3H), 2.76 (dd, *J* = 16.8, 7.5 Hz, 1H), 2.43 (ddd, *J* = 14.7, 10.6, 7.8 Hz, 1H), 2.30 (dd, *J* = 16.8, 10.7 Hz, 1H), 1.16 (d, *J* = 6.5 Hz, 3H).

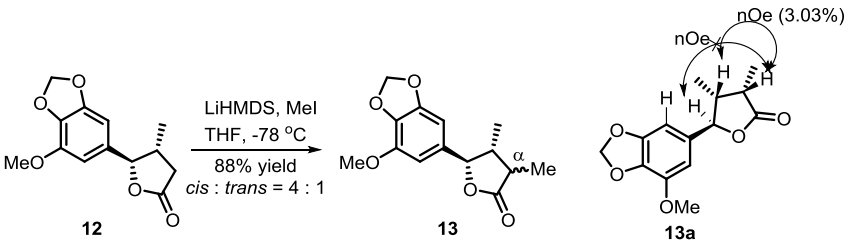
^{13}C NMR (100 MHz, $CDCl_3$) δ 175.8, 149.0, 143.6, 135.4, 132.2, 105.8, 101.6, 100.2, 88.1, 56.6, 39.7, 37.1, 16.3.

IR (neat) ν_{max} 3387, 2964, 2925, 1777, 1636, 1552, 1513, 1453, 1435, 1402, 1384, 1361, 1346,

1322, 1282, 1235, 1208, 1146, 1133, 1093, 1045, 1010, 982, 966, 937, 829, 812, 754, 723, 681,636,592,521,404 cm^{-1}.

HRMS (ESIMS): calcd for $C_{13}H_{14}O_5H$ $[M+H]^+$ 251.0914, found 251.0918;

$[\alpha]_D^{17}$ = -26.0 (c = 1.0, $CHCl_3$);



Compound (13). To a solution of lactone **12** (0.28 g, 1.12 mmol) in THF (10 ml) at -78 °C was added LiHMDS (1.34 ml, 1.2 equiv., 1.0 M solution in THF), and 30 min later, MeI (0.09 mL, 1.5 equiv.) was added. The reaction was allowed to stirred for 2 h and quenched with saturated aq. NH_4Cl, and evaporated THF. The aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 10:1 to 7:1) to afford the product **13** as a colorless oil (0.26 g, *cis* : *trans* = 4 : 1, inseparable, 88%).

NOTE: The relative stereochemistry of **13a** was established by nOe experiments. We did nOe experiment on **13a**, and found that the γ-H has no correlation with the α-H and the β-H. And we found that the α-H only has correlation with the β-H (3.03%) instead of the γ-H. Then we found that the β-H has correlation with the γ-H (0.88%) and with α-H (2.77%), indicating that the two methyl groups in **13a** are *cis*.

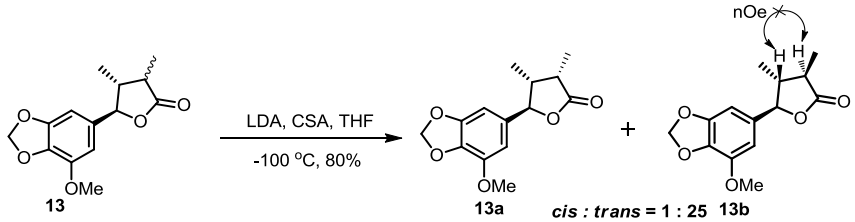
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.49 (s, 2H), 5.99 (s, 2H), 4.94 (d, *J* = 6.8 Hz, 1H), 3.91 (s, 3H), 2.80-2.76 (m, 1H), 2.53 – 2.48 (m, 1H), 1.22 (d, *J* = 7.6 Hz, 3H), 1.09 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.5, 149.1, 143.7, 135.2, 132.8, 105.3, 101.7, 99.9, 85.6, 56.7, 42.3, 38.3, 12.5, 10.2.

IR (neat) ν_{max} 3522, 3018, 2969, 2934, 2882, 2781, 2410, 2345, 2281, 2185, 2100, 2020, 1771, 1670, 1636, 1613, 1514, 1453, 1435, 1387, 1324, 1280, 1262, 1201, 1172, 1137, 1094, 1046, 1003, 977, 968, 931, 899, 863, 826, 788, 758, 683, 67, 639, 585, 532, 504, 438, 403 cm^{-1}.

HRMS (ESIMS): calcd for $C_{14}H_{16}O_5H$ $[M+H]^+$ 265.1071, found 265.1077;

$[\alpha]_D^{17}$ = -13.0 (c = 1.0, $CHCl_3$);



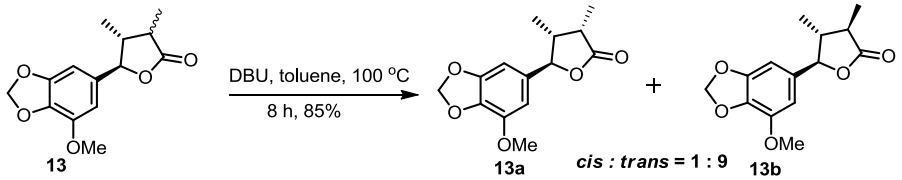
kinetic reprotonation. To a solution of LDA (0.06 ml, 2.0 equiv., Diisopropylamine and 0.16 ml of 2.5 M *n*-BuLi in hexane) in THF (2 ml) cooled at -78 °C was added lactone **13** (58 mg, 0.22 mmol, **13a** : **13b** = 4 : 1). The solution was stirred at -78 °C for 20 min and then warmed up to 0 °C. This solution was added to camphorsulfonic acid (CSA, 150 mg, 3.0 equiv.) at -100 °C. The

reaction mixture was stirred and warmed from -100 °C to room temperature, and then saturated $NaHCO_3$ (2 mL) was added with vigorous stirring. The aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 7 : 1) to afford the product **13b** as a colorless oil (46 mg, *cis* : *trans* = 1 : 25, inseparable, 80%).

NOTE: The major product **13b** was determined as *trans* methyl by nOe experiment. It is already clear that the γ-H and β-H are *trans* substitution, and they don't have nOe correlation. Then we found that the α-H only has correlation with the γ-H (1.9%) instead of the β-H. Thus we think that the two methyl groups in **13b** are *trans*.

^{1}H NMR (600 MHz, $CDCl_3$) δ 6.51 (s, 2H), 5.98 (s, 2H), 4.70 (d, *J* = 9.9 Hz, 1H), 3.91 (s, 3H), 2.35 – 2.31 (m, 1H), 1.97 – 1.95 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H).

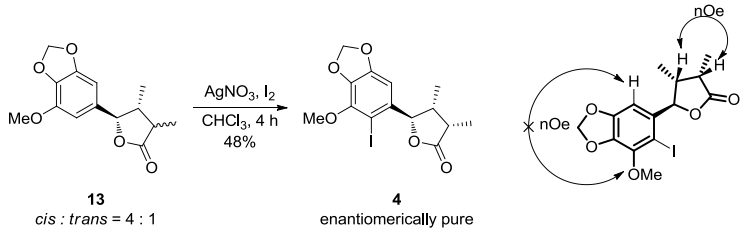
^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 149.1, 143.7, 135.6, 131.9, 106.0, 101.7, 100.6, 86.3, 56.7, 47.9, 43.3, 14.4, 12.9.



Thermodynamic reprotonation. To a solution of lactone **13** (47 mg, 0.18 mmol, **13a** : **13b** = 4 : 1) in toluene (4 ml) was added DBU (0.05 ml, 2.0 equiv.). The reaction was allowed to stir for 10 min at room temperature and was heated at 100 ℃ with vigorous stirring for 8 h. Cooled to room temperature, the mixture was concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 7 : 1) to afford the product **13b** as a colorless oil (38 mg, *cis* : *trans* = 1 : 9, inseparable, 80%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (s, 2H), 5.99 (s, 2H), 4.71 (d, *J* = 9.9 Hz, 1H), 3.91 (s, 3H), 2.36 - 2.31 (m, 1H), 1.97 – 1.93 (m, 1H), 1.29 (d, *J* = 7.0 Hz, 3H), 1.13 (d, *J* = 6.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 178.4, 148.9, 143.6, 135.4, 131.8, 105.8, 101.7, 100.5, 86.2, 56.6, 47.8, 43.3, 14.3, 12.9.



Compound (4). To a solution of lactone **13 (**168 mg, 0.64 mmol) in $CHCl_3$ (10 ml) at 0 °C was added $AgNO_3$ (162 mg, 1.5 equiv.), and 5 min later, added I_2 (242mg, 1.5 equiv., a solution in 5 ml $CHCl_3$). The reaction was warmed to room temperature and stirred for 2 h and quenched with saturated aq. Na_2SO_3, and evaporated $CHCl_3$. The aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 10 : 1 to 8 : 1) to afford the product **4** as a colorless oil (111 mg, 48%). The product **4** was determined by nOe experiment that iodination at the *ortho* position of methoxyl group.

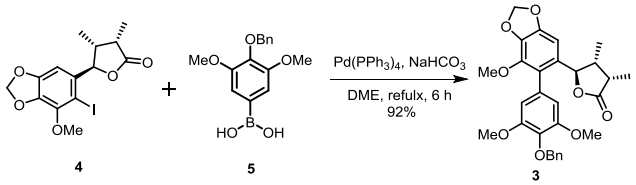
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.54 (d, *J* = 0.8 Hz, 1H), 5.98 (dd, *J* = 5.2, 0.8 Hz, 2H), 5.24 (d, *J* = 1.6 Hz, 1H), 4.03 (d, *J* = 1.2 Hz, 3H), 2.74-2.70 (m, 1H), 2.52 – 2.48 (m, 1H), 1.26 (d, *J* = 7.2, 3H), 1.16 (d, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 150.4, 142.3, 135.8, 135.6, 101.8, 101.1, 87.7, 82.1, 59.9, 41.3, 36.3, 14.4, 9.5.

IR (neat) ν_{max} 3384, 3018, 2962, 2927, 1776, 1688, 1655, 1601, 1562, 1500, 1476, 1449, 1404, 1392, 1371, 1345, 1331, 1314, 1273, 1236, 1216, 1172, 1109, 1085, 1050, 1029, 1000, 980, 962, 935, 910, 829, 794, 758, 667, 633, 595, 517 cm^{-1}.

HRMS (ESIMS): calcd for $C_{14}H_{19}IO_5N$ $[M+NH_4]^+$ 408.0302, found 408.0300;

$[\alpha]_D^{17}$ = +18.0 (c = 1.0, $CHCl_3$);



Compound (3). To a solution of compound **4** (99 mg, 0.25 mmol), $NaHCO_3$ (84 mg, 4.0 equiv.) and boronic acid **5**[2] (144 mg, 2.0 equiv.) in DME (4 ml) was added $Pd(PPh_3)_4$ (30 mg, 0.1 equiv.). The reaction was allowed to stir for 10 min at room temperature and was heated at 95 ℃ with vigorous stirring for 4 h. Cooled to room temperature, the mixture was diluted with Et_2O followed by filtration through a thin pad of silica gel with Et_2O rinse. Solvent evaporation followed by flash chromatography (PE : EtOAc, 8 : 1 to 5 : 1) to afford the product **3** as a colorless oil (116 mg, 92%).

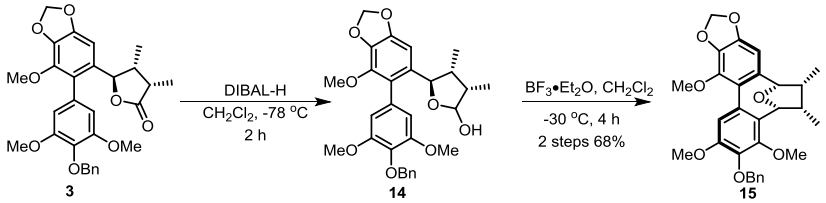
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.51 (m, 2H), 7.37 – 7.30 (m, 3H), 6.60 (s, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 6.36 (d, *J* = 1.6 Hz, 1H), 6.00 (dd, *J* = 2.8 Hz, 1.2 Hz, 2H), 5.11 (s, 2H), 4.90 (d, *J* = 4.8 H, 1H), 3.84 (s, 3H), 3.83 (s, 3H), 3.80 (s, 3H), 2.80-2.72 (m, 1H), 2.40 – 2.35 (m, 1H), 1.06 (d, *J* = 7.6 Hz, 3H), 0.63 (d, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 179.7, 153.5, 153.3, 148.9, 141.1, 137.7, 136.8, 135.9, 131.4, 131.0, 128.5, 128.1, 127.9, 127.6, 108.2, 106.8, 101.4, 99.7, 82.9, 74.9, 60.0, 56.2, 56.2, 41.6, 37.3, 13.2, 9.9.

IR (neat) ν_{max} 3373, 3062, 3013, 2963, 2931, 2855, 2587, 2431, 2150, 1958, 1871, 1773, 1656, 1618, 1583, 1502, 1479, 1462, 1426, 1410, 1384, 1375, 1350, 1312, 1275, 1234, 1200, 1176, 1127, 1084, 1051, 1021, 994, 979, 930, 838, 819, 798, 756, 698, 666, 637, 600, 524 cm^{-1}.

HRMS (ESIMS): calcd for $C_{29}H_{34}O_8N$ $[M+NH_4]^+$ 524.2279, found 524.2281;

$[\alpha]_D^{17}$ = -67.0 (c = 1.0, $CHCl_3$);



Compound (15). To a solution of compound **3** (120 mg, 0.24 mmol) in anhydrous CH_2Cl_2 (4 mL) at -78 °C was added DIBAL-H (0.24 mL, 1.5 equiv., 1.5 M solution in toluene) and stirred for 2 h. The reaction mixture was quenched with MeOH (1 ml) and saturated sodium potassium tartrate (20 ml) and stirred at room temperature for another 2 h. The CH_2Cl_2 was evaporated and the

aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 3 : 1) to afford the hemiacetal **14** as a colorless oil. To a solution of hemiacetal **14** in anhydrous CH_2Cl_2 (2 mL) at -78 ^oC was added $BF_3 \cdot Et_2O$ (0.06 mL, 2.0 equiv.). The reaction was allowed to stir for 4 h at -30 ^oC. The reaction mixture was quenched with 1 ml H_2O. The CH_2Cl_2 was evaporated and the aqueous solution was extracted by EtOAc. The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by flash chromatography (PE : EtOAc, 5 : 1) to afford the product **15** as a colorless oil (79 mg for 2 steps, 68%).

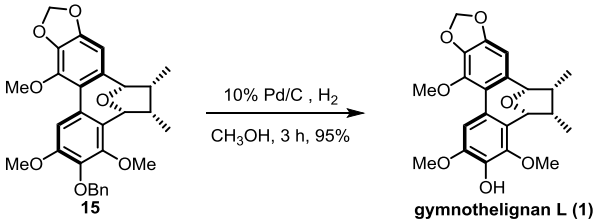
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2H), 7.38 – 7.30 (m, 4H), 6.45 (s, 1H), 6.03 (d, *J* = 1.6 Hz, 1H), 5.97 (d, *J* = 1.6 Hz, 1H), 5.19 (d, *J* = 1.6 Hz, 1H), 5.14-5.05 (m, 2H), 4.49 (d, *J* = 6.0 Hz, 1H), 3.91 (s, 3H), 3.82 (d, *J* = 7.8 Hz, 3H), 3.64 (s, 3H), 2.42-2.38 (m, 1H), 2.26 – 2.22 (m, 1H), 1.10 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 149.8, 147.0, 143.3, 140.3, 139.3, 138.9, 137.7, 129.6, 128.3, 128.2, 127.8, 127.8, 123.5, 112.8, 103.4, 101.5, 90.3, 84.8, 74.8, 61.1, 60.4, 55.9, 49.0, 41.8, 13.8, 13.7.

IR (neat) ν_{max} 3570, 3375, 3006, 2963, 2934, 2874, 2779, 1720, 1710, 1618, 1595, 1565, 1499, 1478, 1450, 1423, 1397, 1372, 1348, 1334, 1308, 1278, 1261, 1249, 1213, 1195, 1106, 1082, 1044, 1026, 1013, 984, 960, 936, 845, 754, 698, 633, 545, 403 cm^{-1}.

HRMS (ESIMS): calcd for $C_{29}H_{31}O_7$ $[M+H]^+$ 491.2064 found 491.2072;

$[\alpha]_D^{17}$ = -28.0 (c = 1.0, $CHCl_3$);



15 **gymnothelignan L (1)**

Gymnothelignan L (1). The compound **15** (20 mg) was dissolved in CH_3OH (2 mL), and 10% Pd/C (20 mg, excess) was added. The reaction was stirred under hydrogen atmosphere (balloon) for 3 h, and filtered through a pad of celite, concentrated under reduced pressure and purified by flash chromatography (PE : EtOAc, 3 : 1) to afford the natural product **1** as a yellow solid (16 mg, 95%). The physical data of the synthetic gymnothelignan L was in agreement with those reported by Xu and Zhou.[1]

^{1}H NMR (600 MHz, acetone-d_6): δ 7.24 (s, 1H), 6.49 (s, 1H), 6.02 (d，*J* = 1.1 Hz, 1H), 5.96 (d, *J* = 1.1 Hz, 1H), 5.08 (d, *J* = 1.9 Hz, 1H), 4.47 (d, *J* = 5.5 Hz, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.68 (s, 3H), 2.35 – 2.32 (m, 1H), 2.23 – 2.21 (m, 1H), 1.03 (d, *J* = 7.4 Hz, 3H),1.01 (d, *J* = 7.5 Hz, 3H).

^{13}C NMR (150 MHz, acetone-d_6): δ 147.6, 146.5, 144.5, 143.8, 140.9, 139.4, 138.8, 130.8, 124.7, 123.9, 113.2, 103.7, 102.2, 90.6, 85.3, 60.3, 60.2, 56.4, 49.5, 42.6, 13.9, 13.7.

IR (neat) ν_{max} 3430, 2963, 2928, 1624, 1508, 1478, 1448, 1425, 1369, 1301, 1254, 1208, 1101, 1046, 931, 670 cm^{-1}.

HRMS (ESIMS): calcd for $C_{22}H_{25}O_7$ $[M+H]^+$ 401.1595 found 401.1597;

$[\alpha]_D^{17}$ = -5.0 (c = 1.0, Me_2CO);

Comparison of the data of our synthetic samples with those reported by literature.

Gymnothelignan L:

^{1}H NMR, 600 M NMR, acetone-d_6

Natural sample		Synthetic sample	
δ (ppm)	*J* (Hz)	δ (ppm)	*J* (Hz)
7.24 s	-,1H	7.24 (s, 1H)	-,1H
6.50 s	-,1H	6.49 (s, 1H)	-,1H
6.02d	1.0, 1H	6.02 d	1.1, 1H
5.96d	1.0, 1H	5.96 d	1.1, 1H
5.09 d	1.9, 1H	5.08 d	1.9, 1H
4.48 d	5.5, 1H	4.47 d	5.5, 1H
3.85 s	-,3H	3.85 s	-,3H
3.81 s	-,3H	3.81 s	-,3H
3.68 s	-,3H	3.68 s	-,3H
2.33 m	-,1H	2.33 m	-,1H
2.22 m	-,1H	2.22 m	-,1H
1.03 d	7.1, 1H	1.03 d	7.4, 3H
1.01 d	7.1, 1H	1.01 d	7.5, 3H

^{13}C NMR, 150 M NMR, acetone-d_6

Natural sample	Synthetic sample
δ (ppm)	δ (ppm)
147.6	147.6
146.6	146.5
144.5	144.5
143.7	143.8
140.6	140.9
139.4	139.4
138.8	138.8
130.6	130.8
124.6	124.7
123.7	123.9
113.4	113.2
103.7	103.7
102.2	102.2
90.6	90.6
85.2	85.3
60.4	60.3
60.2	60.2
56.4	56.4
49.4	49.5
42.6	42.6
13.9	13.9
13.7	13.7

Natural sample: IR (KBr) ν_{max} 3429, 2961, 2934, 1616, 1479, 1101 cm^{-1}
Synthetic sample: IR (neat) ν_{max} 3430, 2963, 2928, 1624, 1508, 1101 cm^{-1}

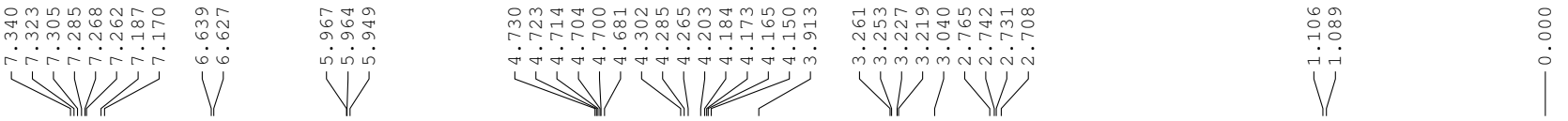
Natural sample: HRESIMS: calcd for $C_{22}H_{25}O_7$ $[M+H]^+$ 401.1594, found 401.1595
Synthetic sample: HRMS (ESIMS): calcd for $C_{22}H_{25}O_7$ $[M+H]^+$ 401.1595, found 401.1597;

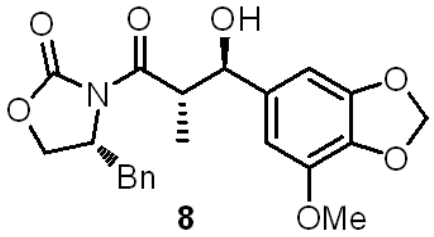
Optical rotation: Natural sample: $[\alpha]_D^{20}$ = -10 (c = 0.20, Me_2CO);
Synthetic sample: $[\alpha]_D^{20}$ = -2 (c = 0.20, Me_2CO);

References:

(1) D. He, L. Ding, H. Xu, X. Lei, H. Xiao and Y. Zhou, *J. Org. Chem.*, 2012, **77**, 8435.

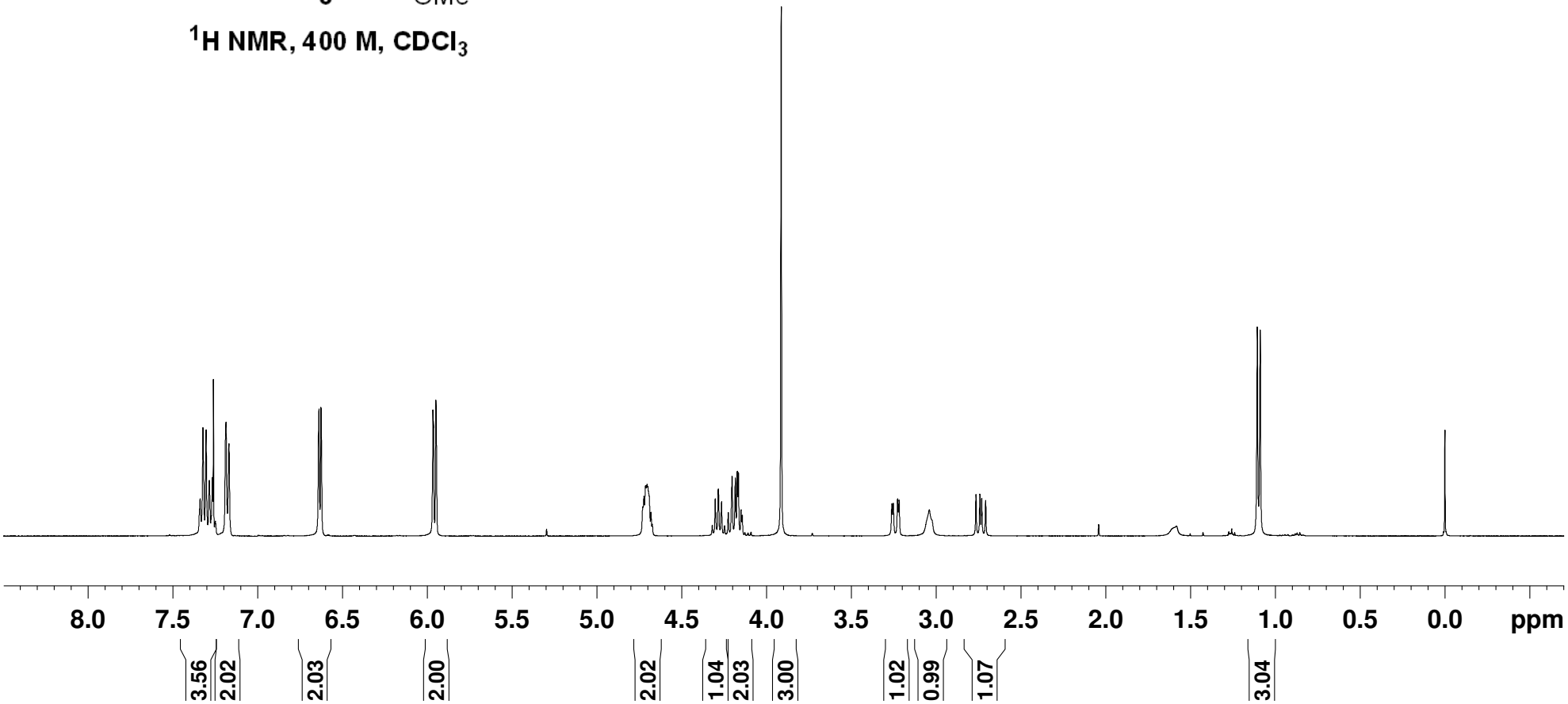
(2) B. M. Rosen, D. A. Wilson, C. J. Wilson, M. Peterca, B. C. Won, L. R. Lipski, X. Zeng, G. Ungar, P. A. Heiney and V. Percec, *J. Am. Chem. Soc.*, 2009, **131**, 17500.

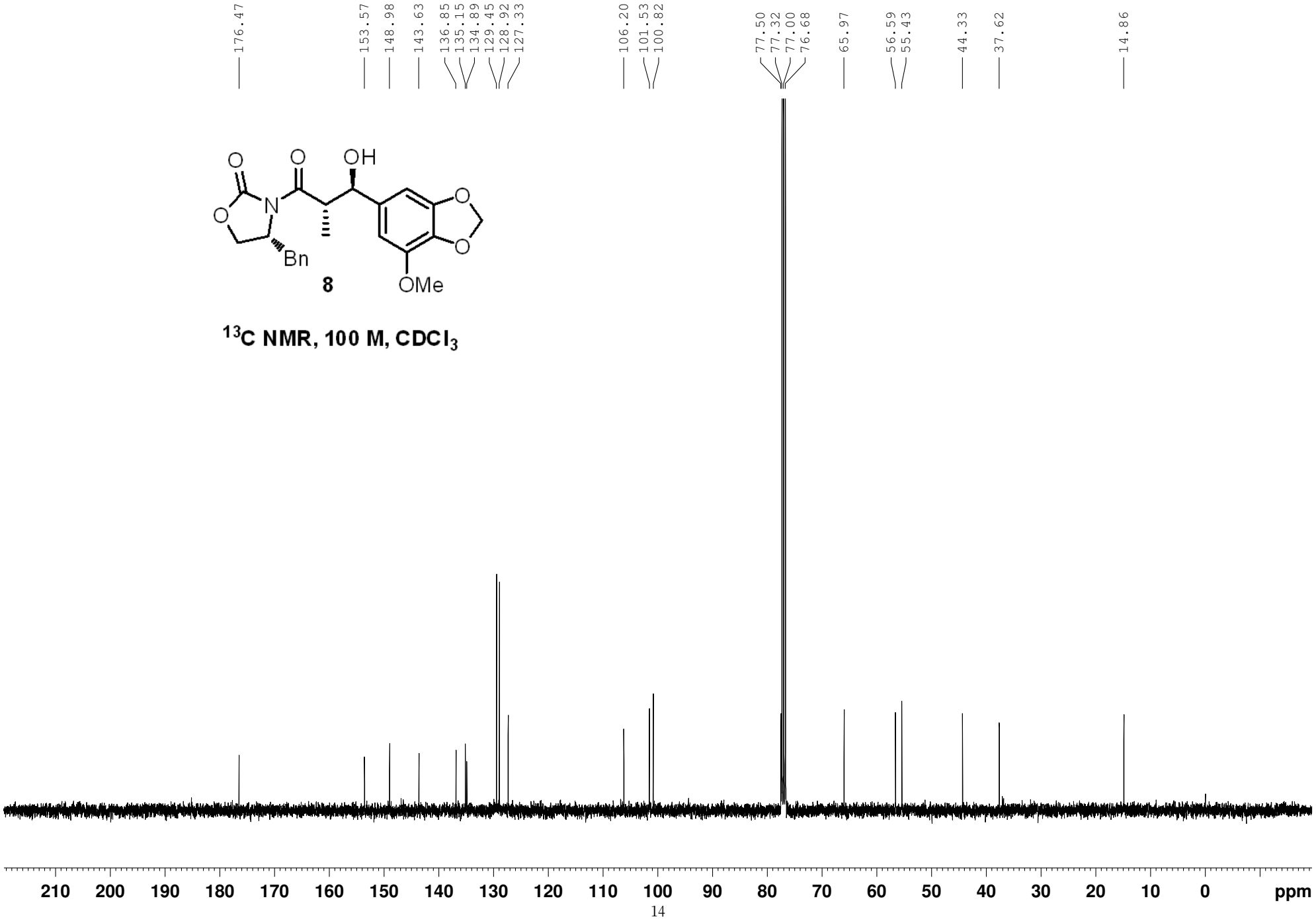




8

^{1}H NMR, 400 M, $CDCl_3$

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129.45
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127.33
106.20
101.53
100.82
77.50
77.32
77.00
76.68
65.97
56.59
55.43
44.33
37.62
14.86
O
O
OH
N
O
O
O
Bn
OMe
8
13C NMR, 100 M, CDCl3
210
200
190
180
170
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130
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70
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20
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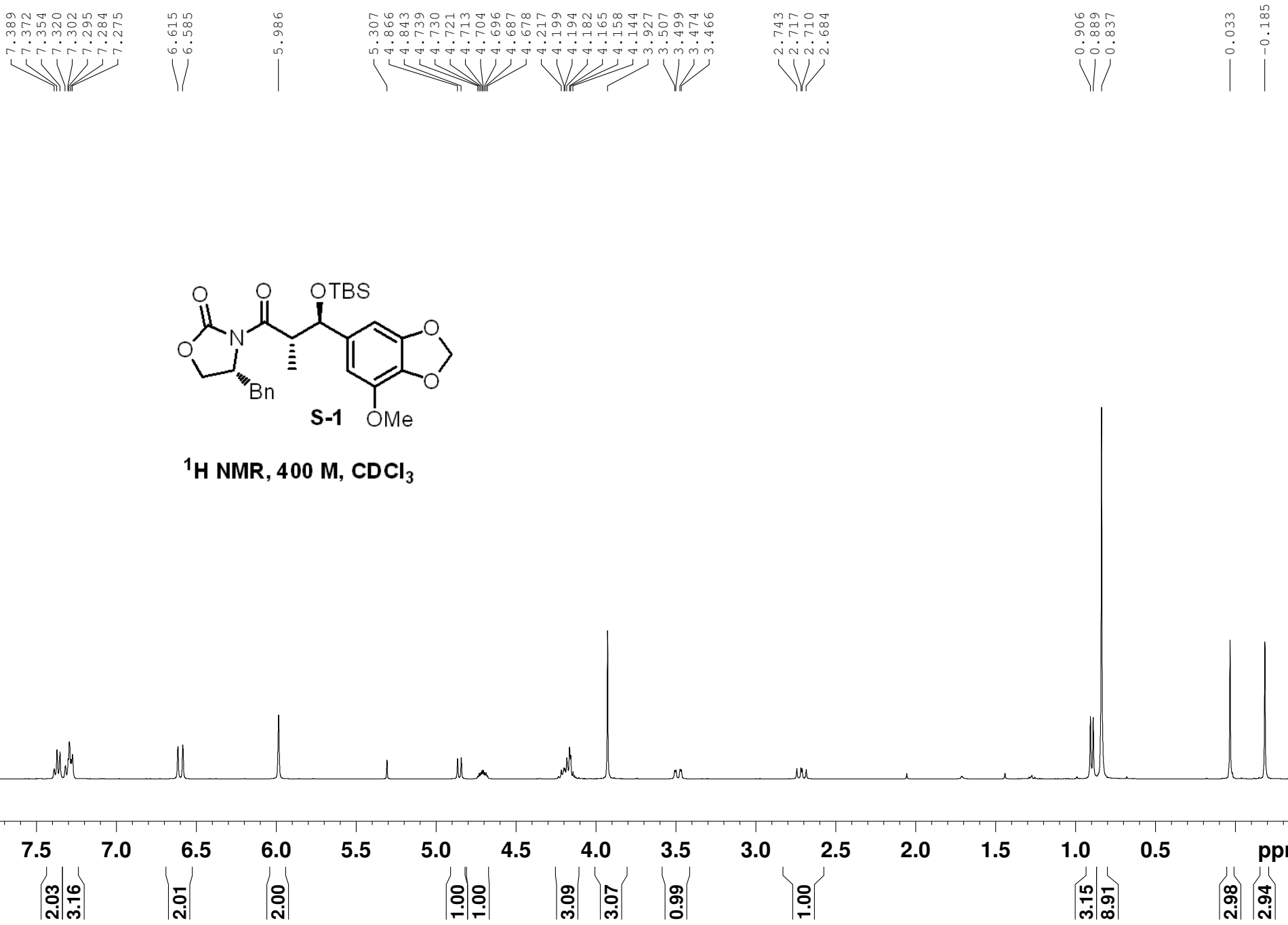
ppm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7.320
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7.295
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4.843
4.739
4.730
4.721
4.713
4.704
4.696
4.687
4.678
4.217
4.199
4.194
4.182
4.165
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4.144
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3.499
3.474
3.466
2.743
2.717
2.710
2.684
0.906
0.889
0.837
0.033
-0.185
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O
OTBS
N
O
O
O
Bn
S-1
OMe
1H NMR, 400 M, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
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1.5
1.0
0.5
ppm
2.03
3.16
2.01
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1.00
1.00
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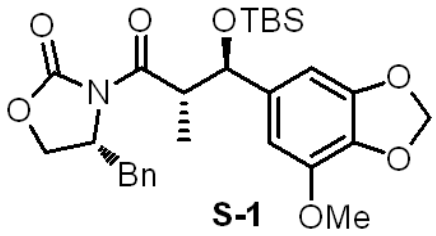
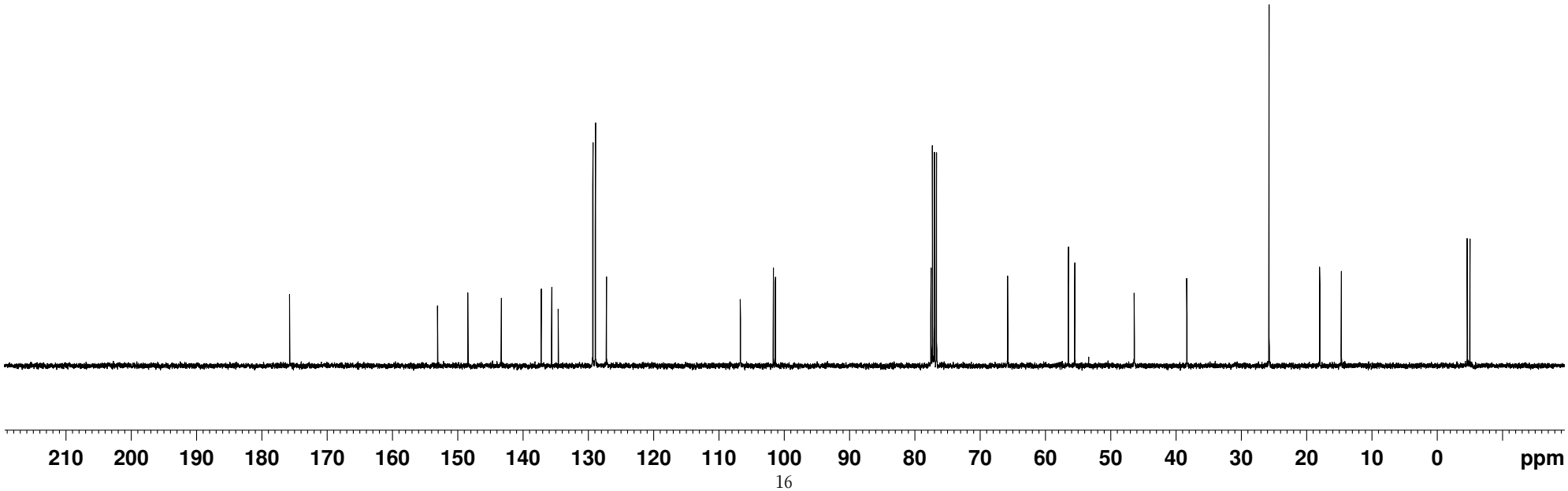
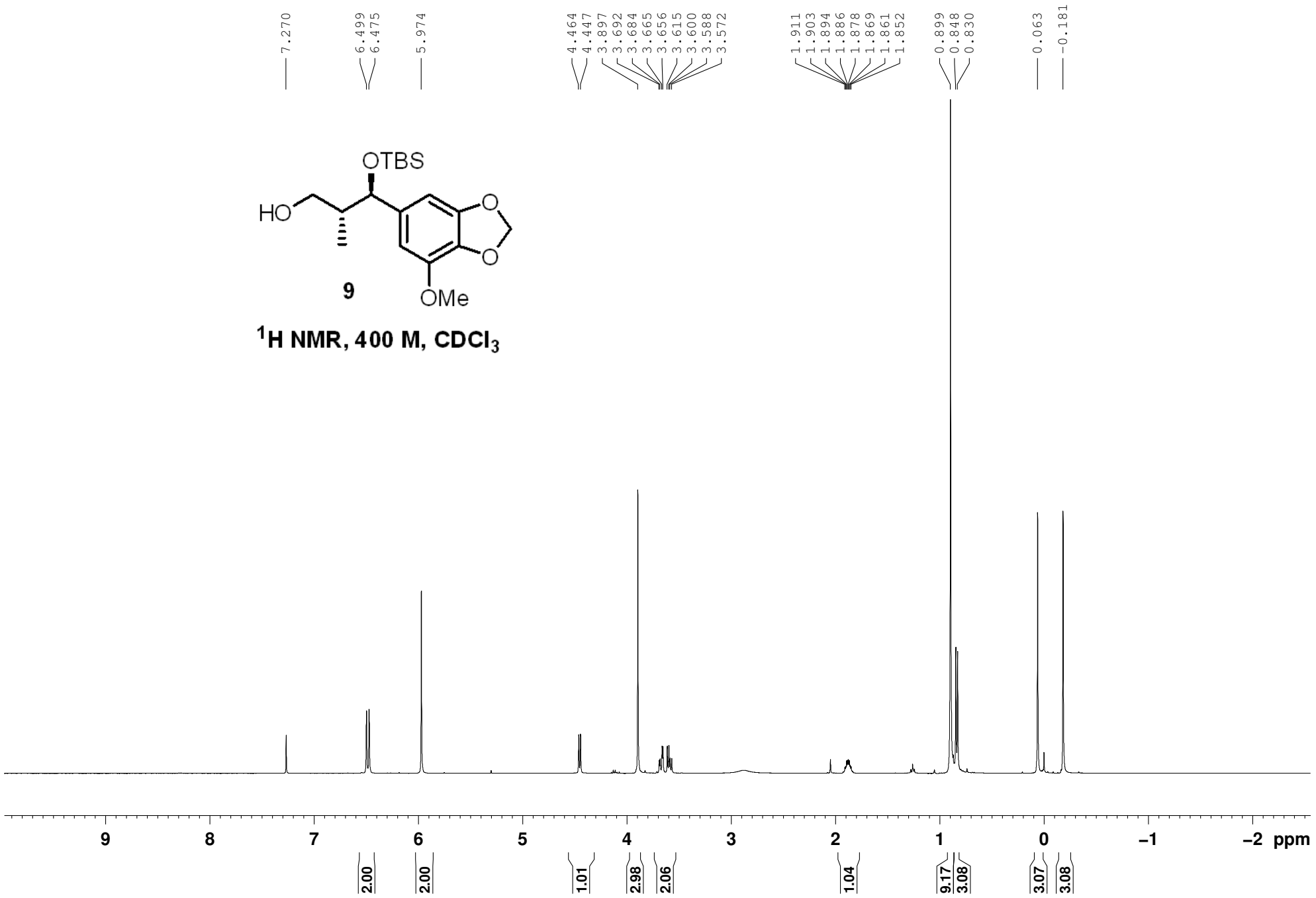
3.07
0.99
1.00
3.15
8.91
2.98
2.94



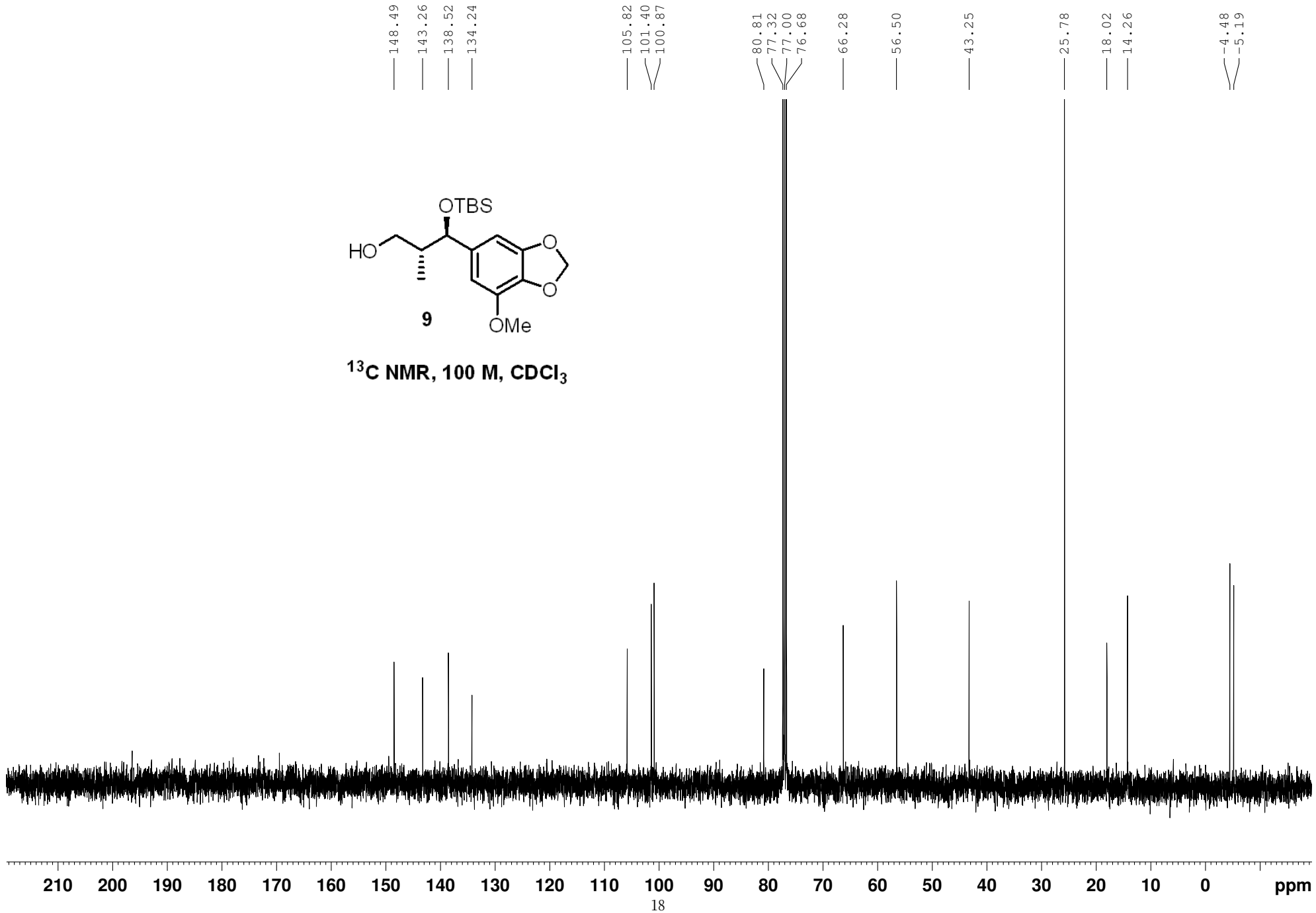
S-1

^{13}C NMR, 100 M, $CDCl_3$





^{1}H NMR, 400 M, $CDCl_3$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101.40
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77.00
76.68
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56.50
43.25
25.78
18.02
14.26
-4.48
-5.19
OTBS
HO
O
O
OMe
9
13C NMR, 100 M, CDCl3
210
200
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140
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120
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100
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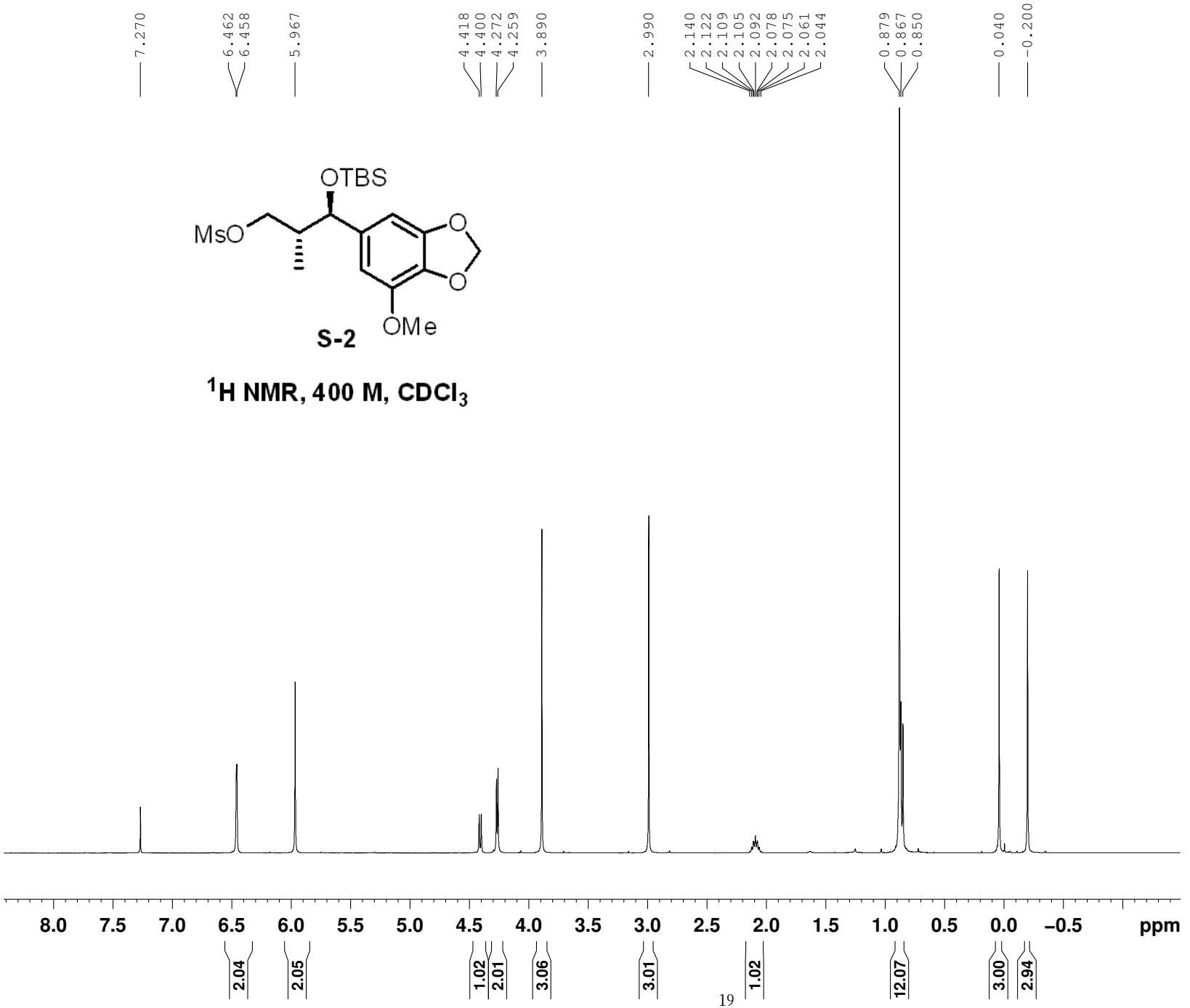
ppm

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PROCNO                  1
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PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8012.820 Hz
FIDRES           0.122266 Hz
AQ               4.0894966 sec
RG                    128
DW                 62.400 usec
DE                  6.50 usec
TE                 292.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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NUC1                   1H
P1                  10.79 usec
SI                  65536
SF           400.1300058 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
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148.55
143.23
137.44
134.33
105.92
101.39
100.75
77.32
77.20
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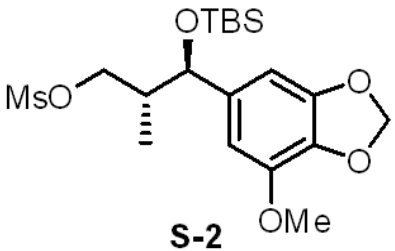
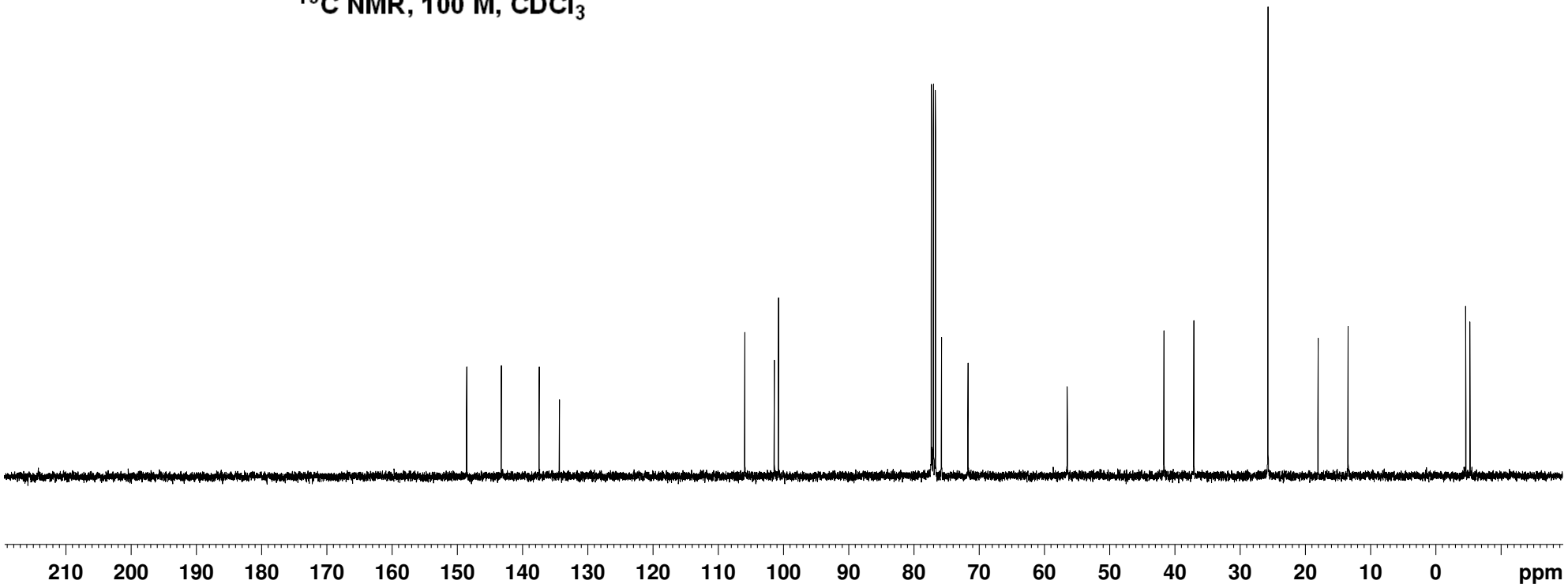
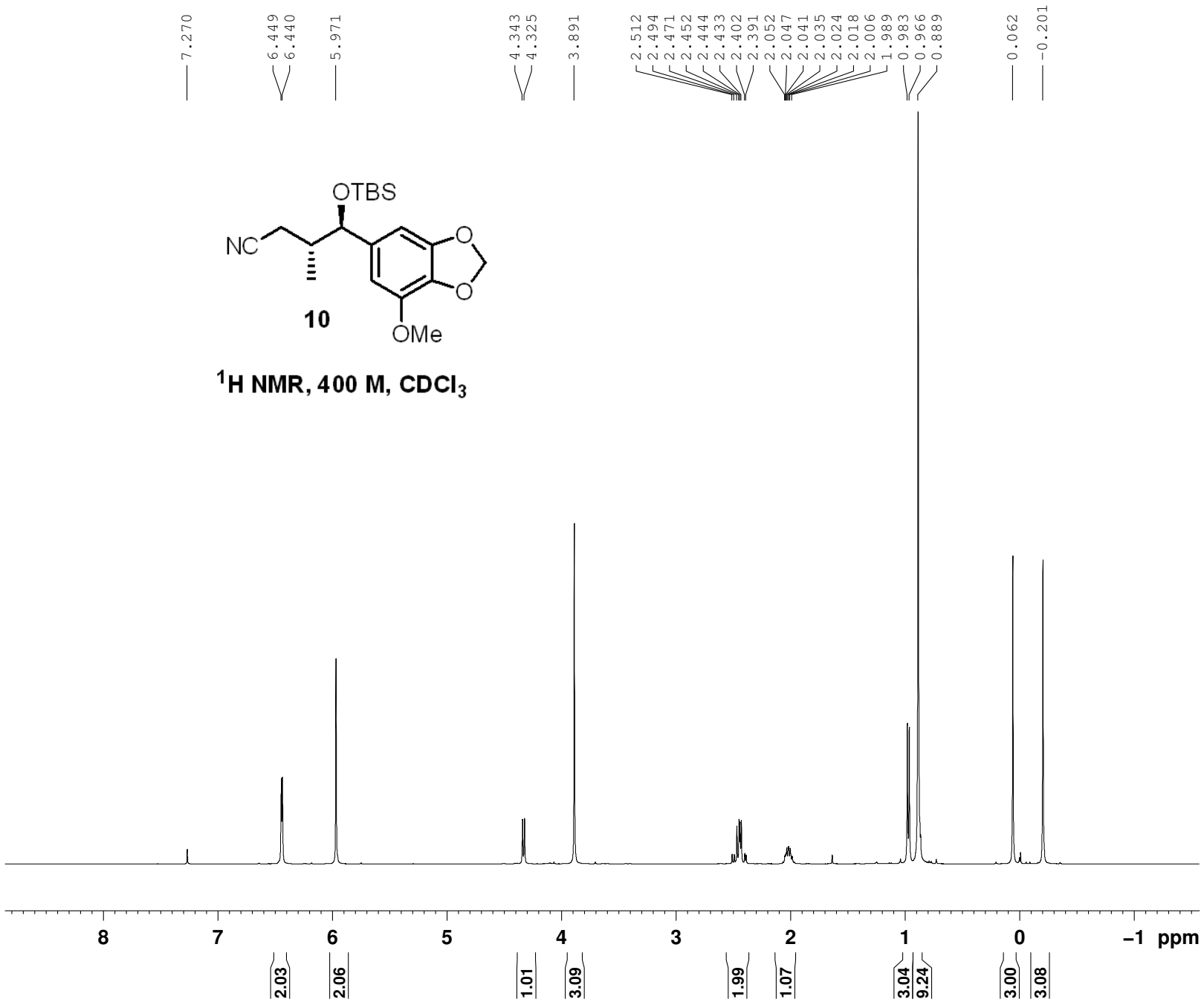


S-2

^{13}C NMR, 100 M, $CDCl_3$



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SOLVENT             CDCl3
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DS                      2
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RG                   71.8
DW                 62.400 usec
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TE                 291.3 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
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NUC1                   1H
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PC                   1.00
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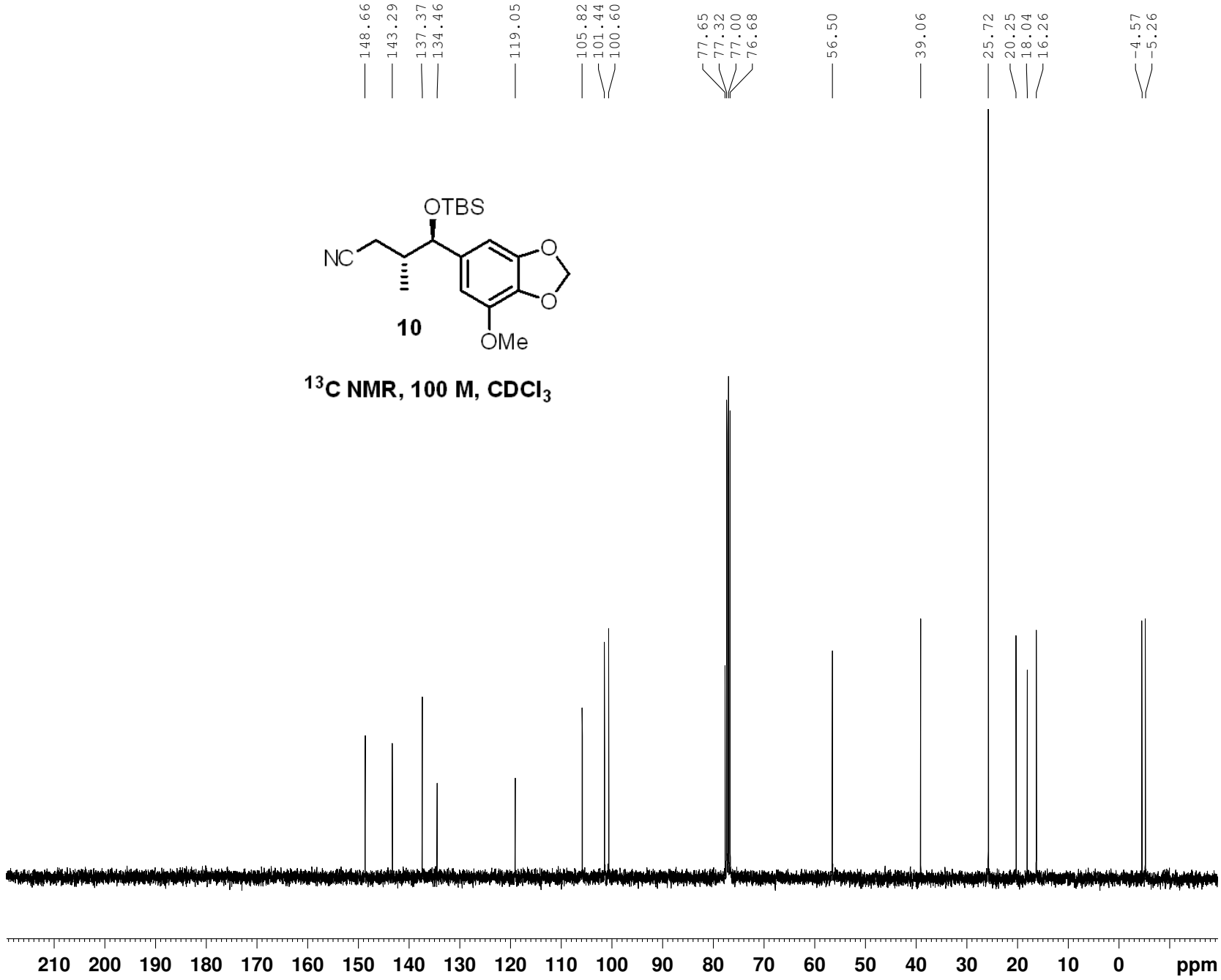

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FIDRES	0.366798 Hz
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TE	292.1 K
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TD0	1
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SI	32768
SF	100.6127756 MHz
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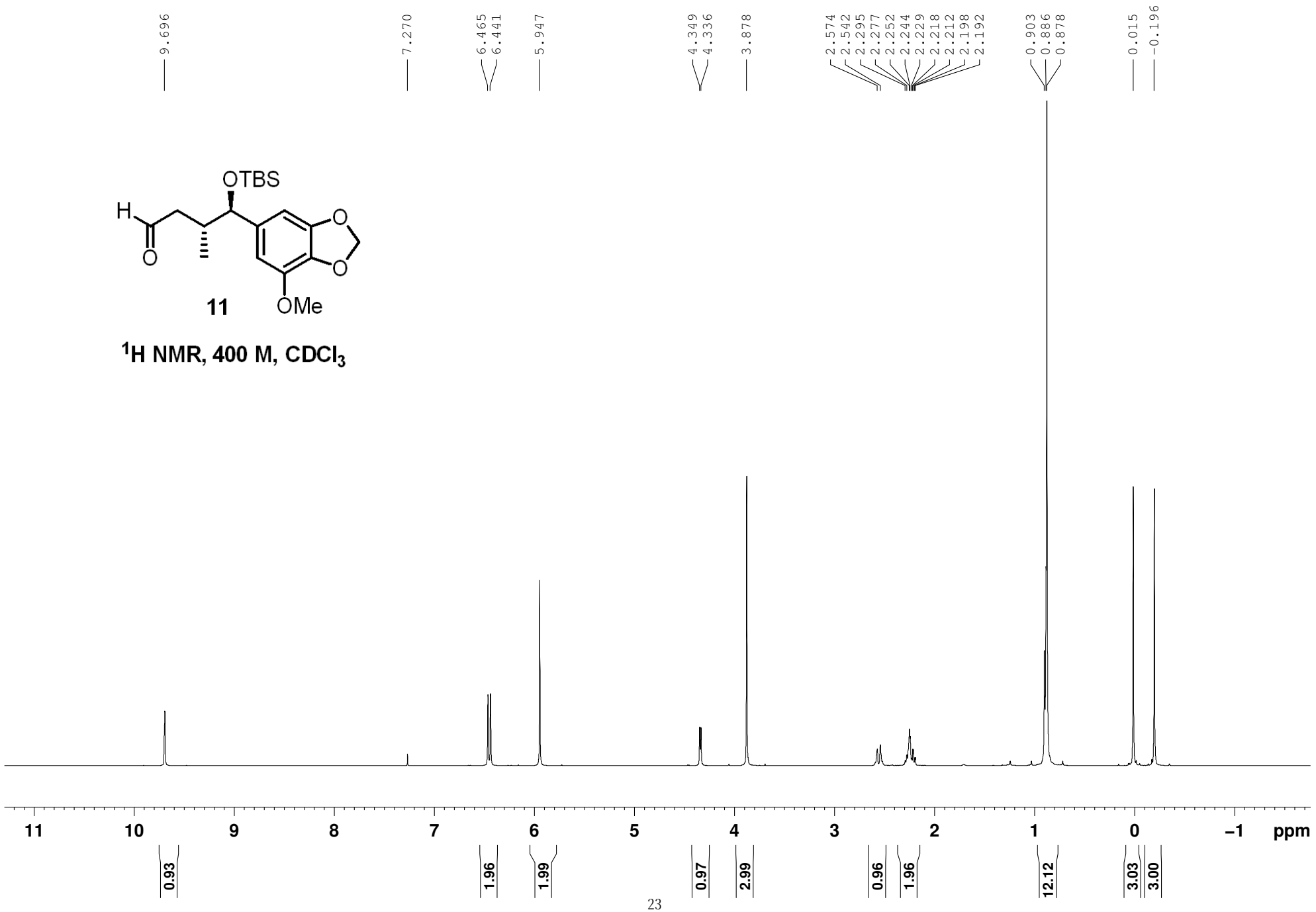
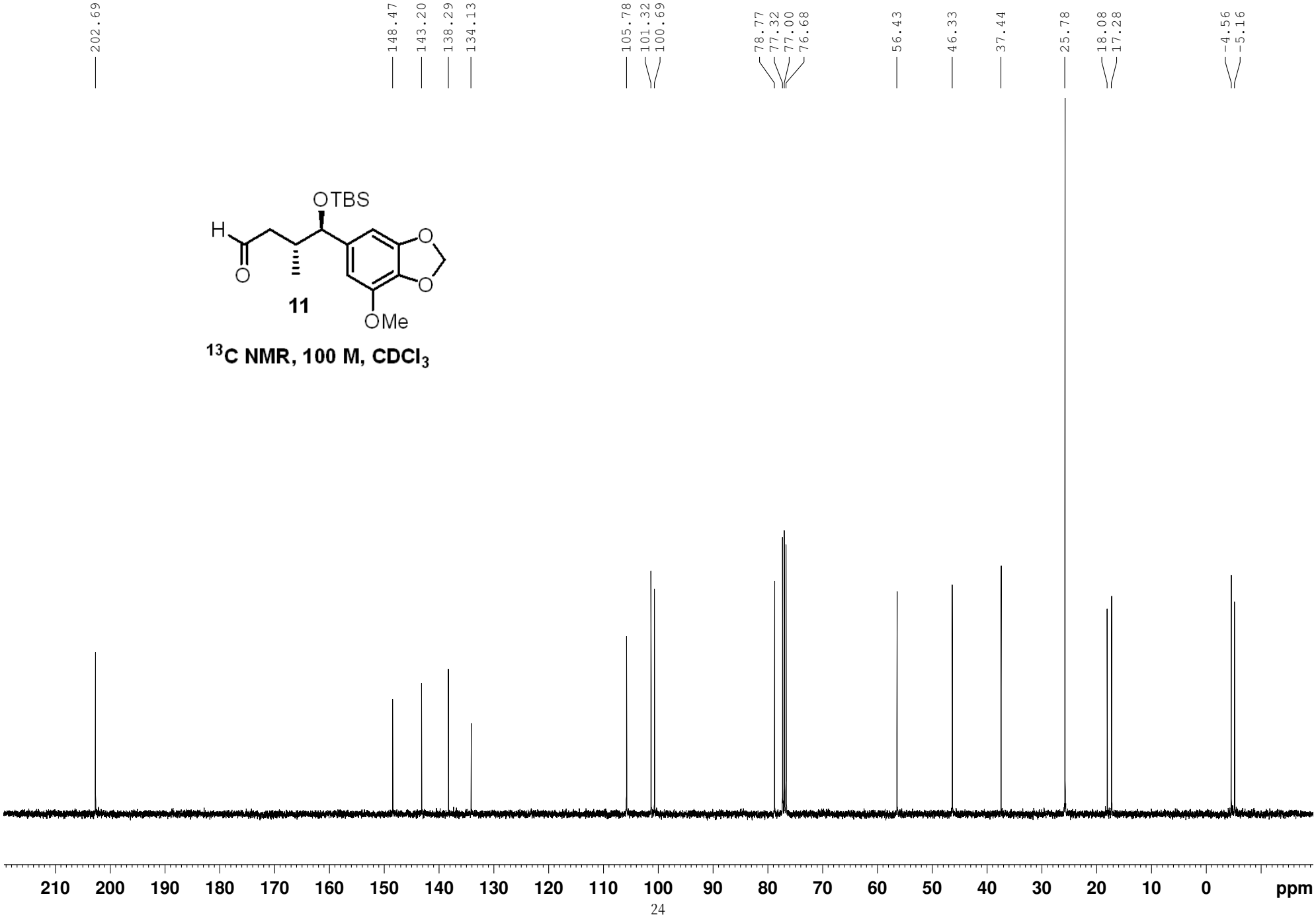
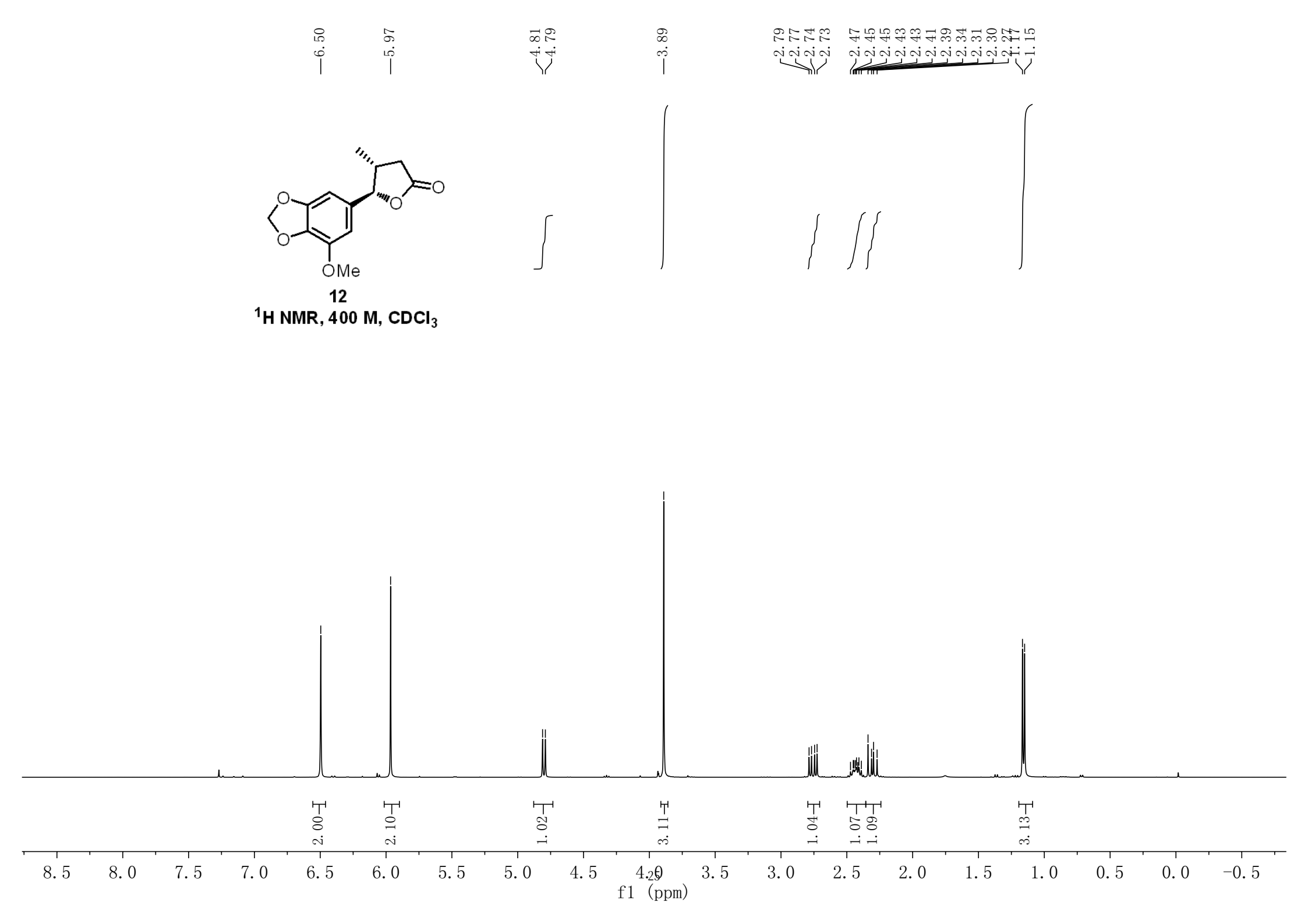
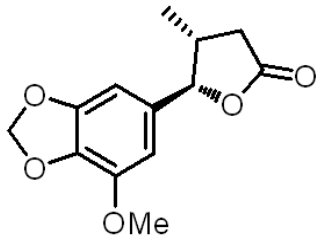
GB	0
PC	1.40



^{1}H NMR, 400 M, $CDCl_3$

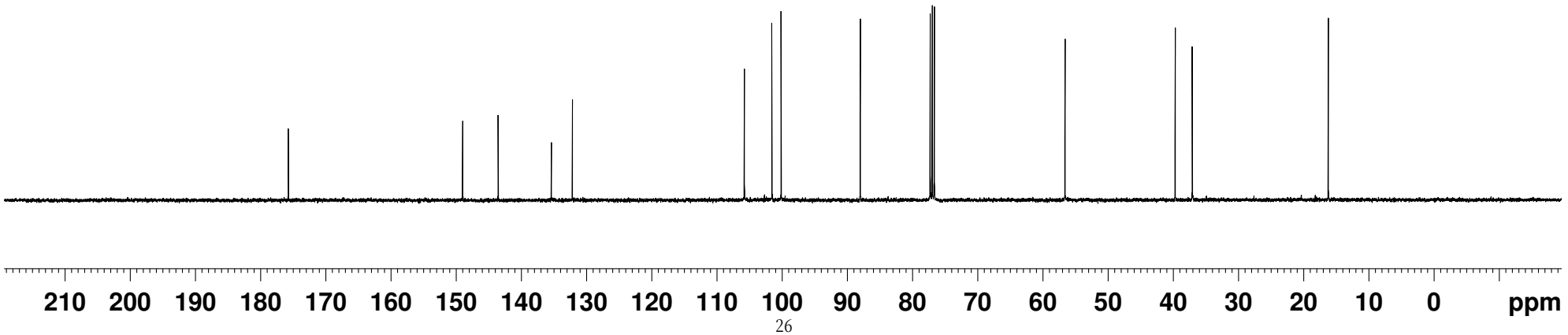

202.69
148.47
143.20
138.29
134.13
105.78
101.32
100.69
78.77
77.32
77.00
76.68
56.43
46.33
37.44
25.78
18.08
17.28
-4.56
-5.16
OTBS
H
O
O
O
11
OMe
13C NMR, 100 M, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

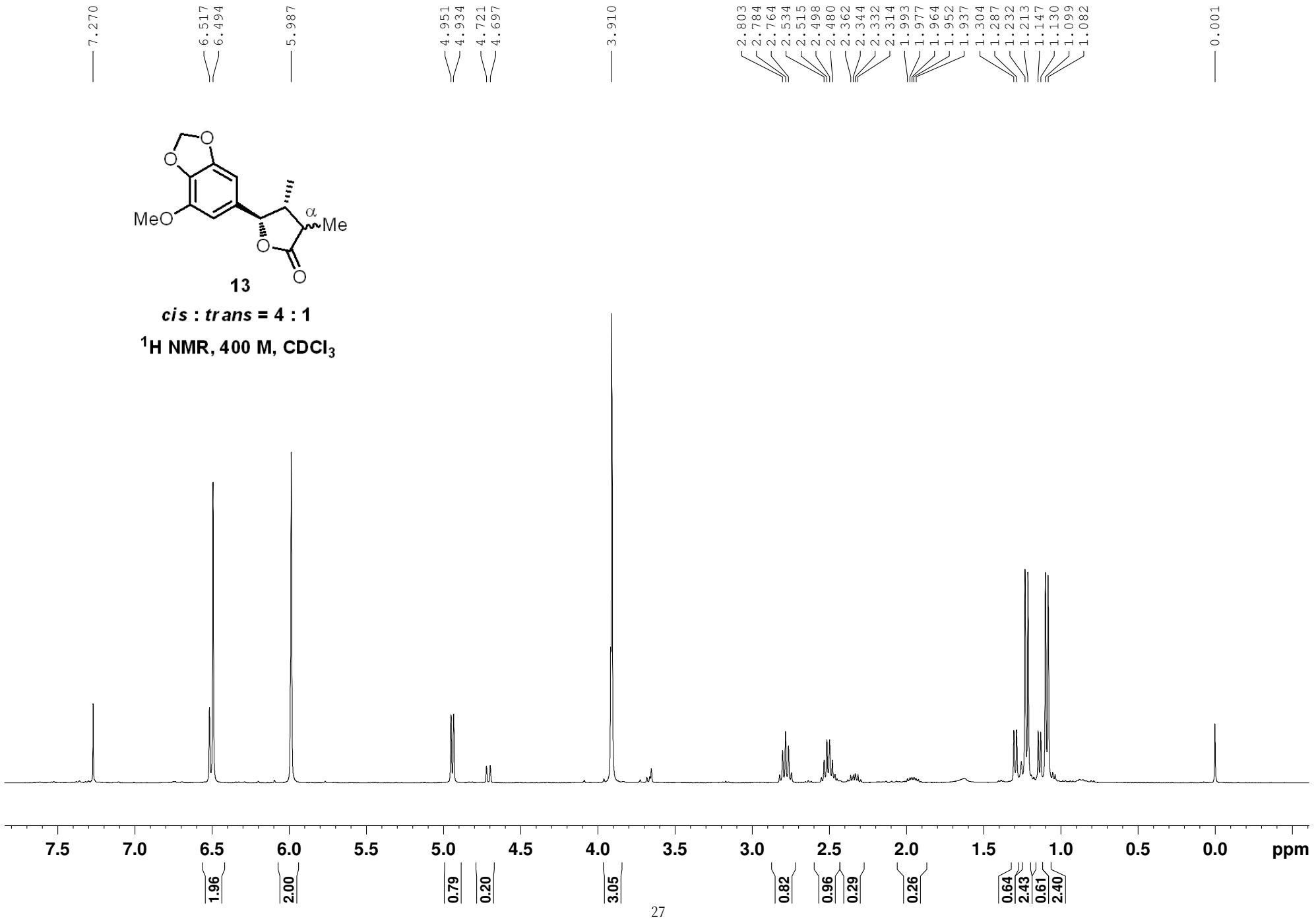

6.50
5.97
4.81
4.79
3.89
2.79
2.77
2.74
2.73
2.47
2.45
2.45
2.43
2.43
2.41
2.39
2.34
2.31
2.30
2.27
2.17
1.15
OMe
12
1H NMR, 400 M, CDCl3
2.00
2.10
1.02
3.11
1.04
1.07
1.09
3.13
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

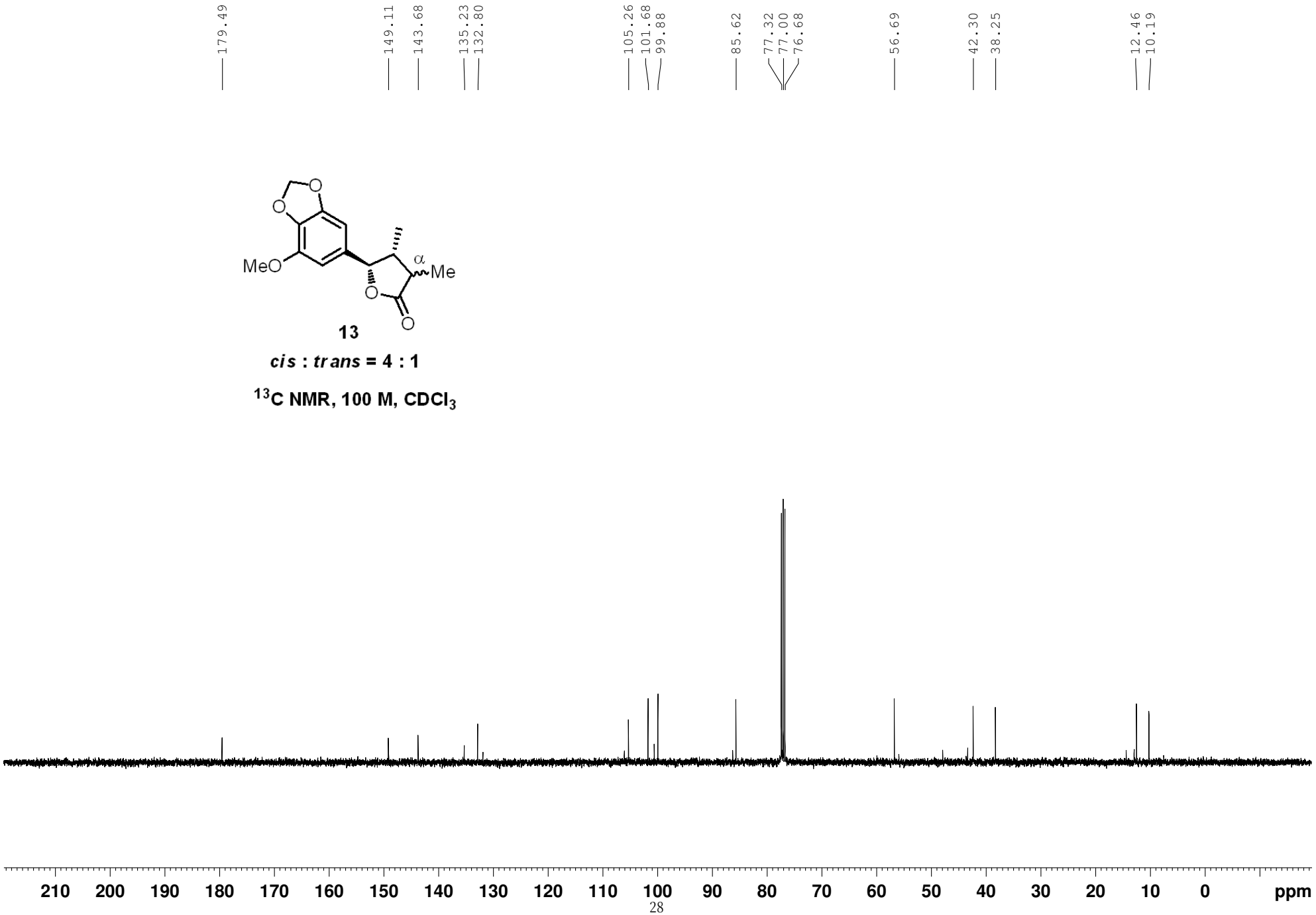


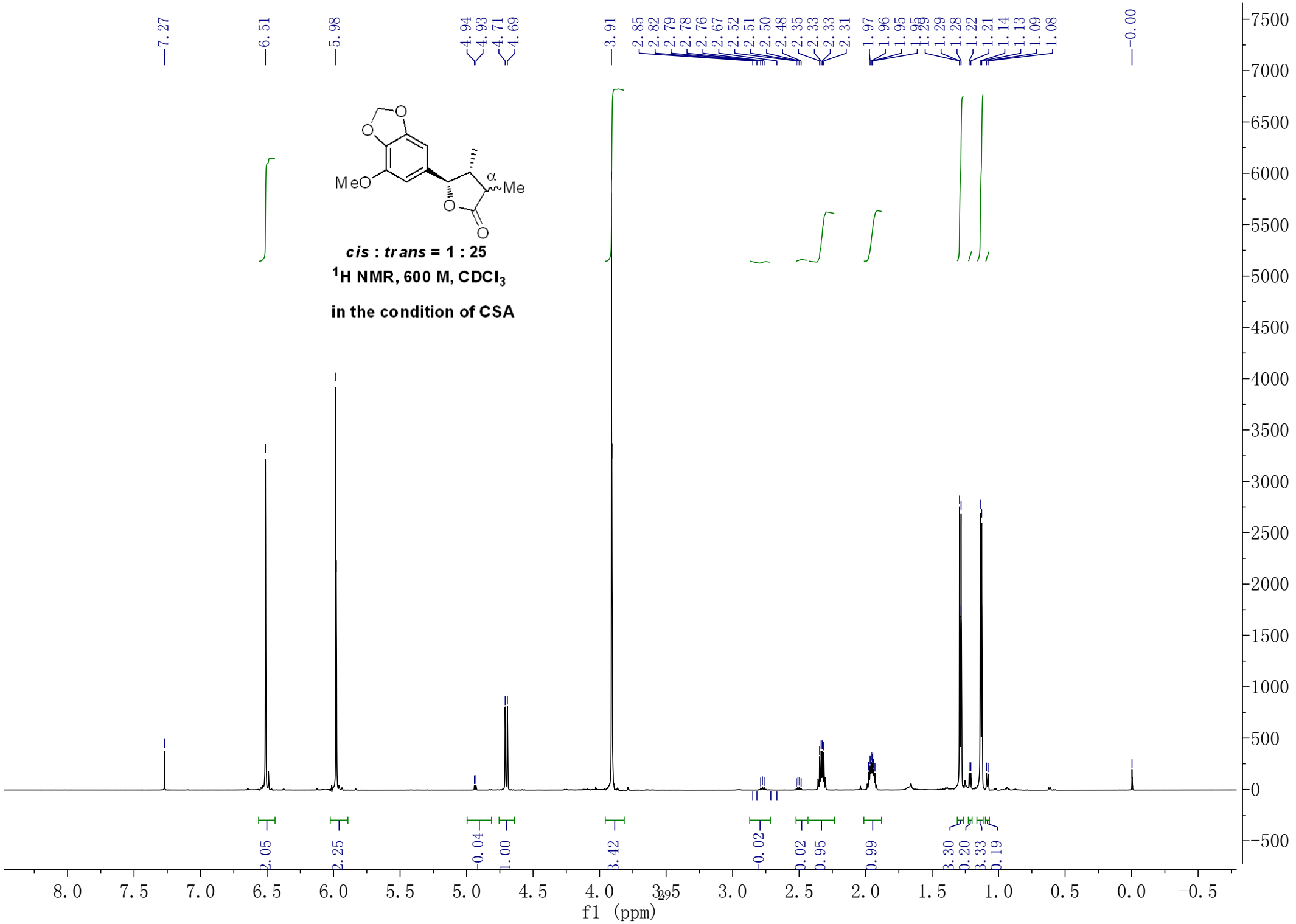
12

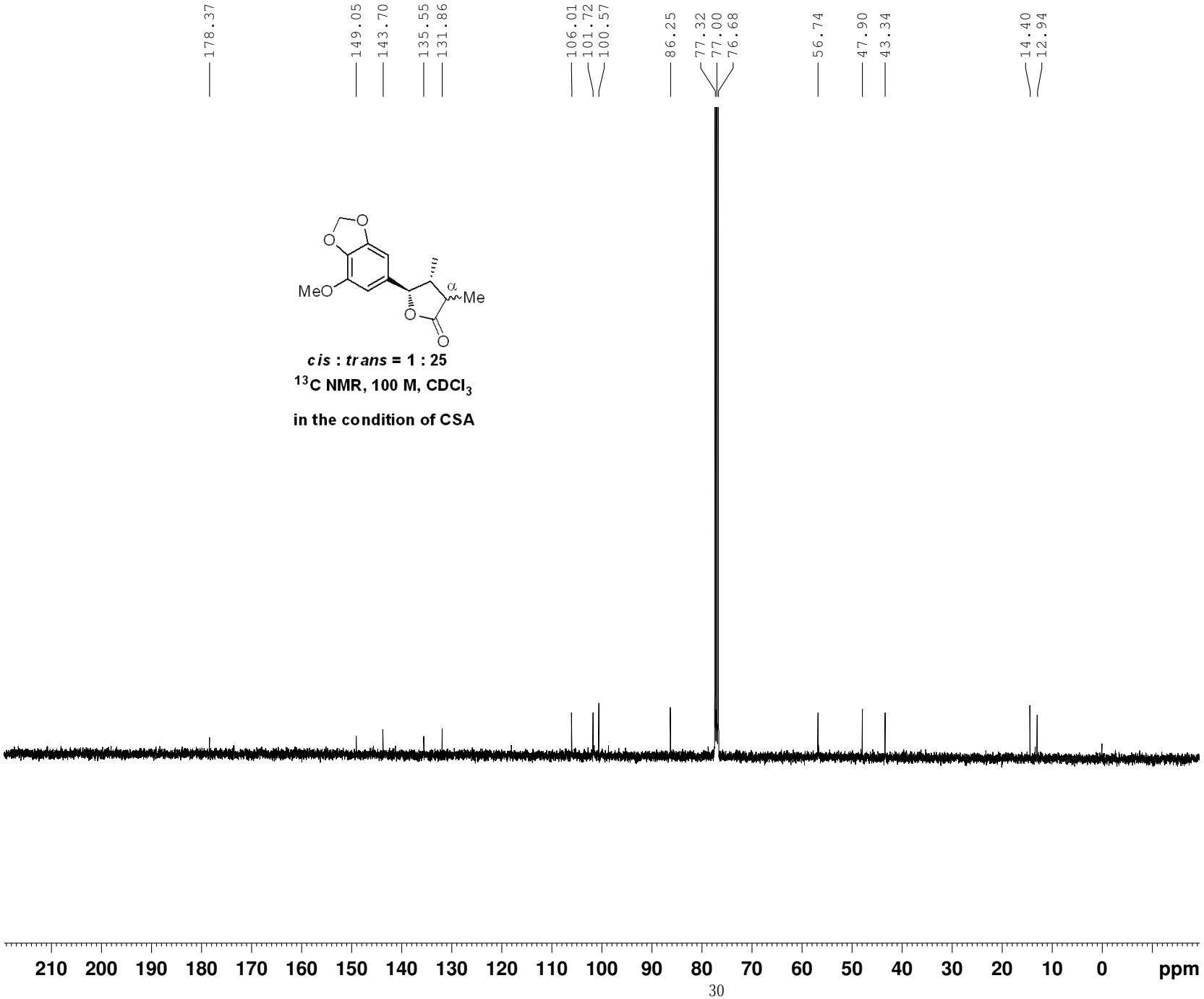
^{13}C NMR, 100 M, $CDCl_3$



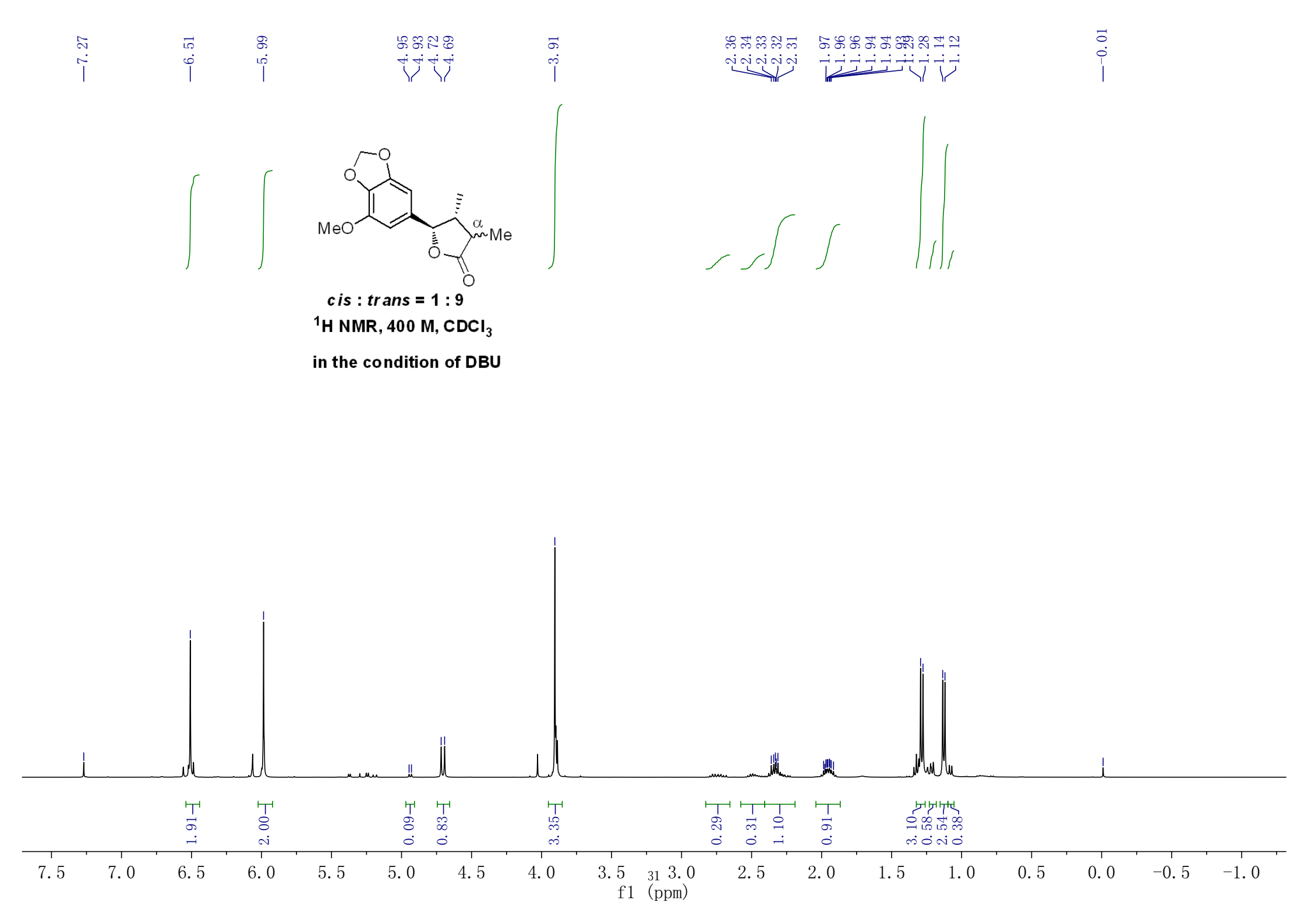

7.270
6.517
6.494
5.987
4.951
4.934
4.721
4.697
3.910
2.803
2.784
2.764
2.534
2.515
2.498
2.480
2.362
2.344
2.332
2.314
1.993
1.977
1.964
1.952
1.937
1.304
1.287
1.232
1.213
1.147
1.130
1.099
1.082
0.001
MeO
α
Me
O
O
O
O
13
cis : trans = 4 : 1
1H NMR, 400 M, CDCl3
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
1.96
2.00
0.79
0.20
3.05
0.82
0.96
0.29
0.26
0.64
2.43
0.61
2.40


179.49
149.11
143.68
135.23
132.80
105.26
101.68
99.88
85.62
77.32
77.00
76.68
56.69
42.30
38.25
12.46
10.19
MeO
α
Me
O
O
O
O
13
cis : trans = 4 : 1
13C NMR, 100 M, CDCl3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

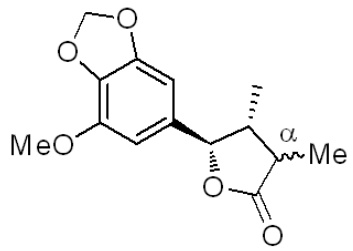

7.27
6.51
5.98
4.94
4.93
4.71
4.69
3.91
2.85
2.82
2.79
2.78
2.76
2.67
2.52
2.51
2.50
2.48
2.35
2.33
2.33
2.31
1.97
1.96
1.95
1.29
1.28
1.22
1.21
1.14
1.13
1.09
1.08
0.00
MeO
α
Me
cis : trans = 1 : 25
1H NMR, 600 M, CDCl3
in the condition of CSA
2.05
2.25
0.04
1.00
3.42
0.02
0.02
0.95
0.99
3.30
0.20
3.33
0.19
f1 (ppm)



NAME	chenp20170119-CAS
EXPNO	13
PROCNO	1
Date_	20170119
Time	0.58
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	560
DS	2
SWH	24038.461 Hz
FIDRES	0.366798 Hz
AQ	1.3631988 sec
RG	1030
DW	20.800 usec
DE	6.50 usec
TE	339.0 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	100.6228298 MHz
NUC1	13C
P1	14.70 usec
SI	32768
SF	100.6127715 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40


7.27
6.51
5.99
4.95
4.93
4.72
4.69
3.91
2.36
2.34
2.33
2.32
2.31
1.97
1.96
1.96
1.94
1.94
1.28
1.14
1.12
0.01
MeO
α
Me
O
O
O
O
cis : trans = 1 : 9
1H NMR, 400 M, CDCl3
in the condition of DBU
1.91
2.00
0.09
0.83
3.35
0.29
0.31
1.10
0.91
3.10
0.58
2.54
0.38
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

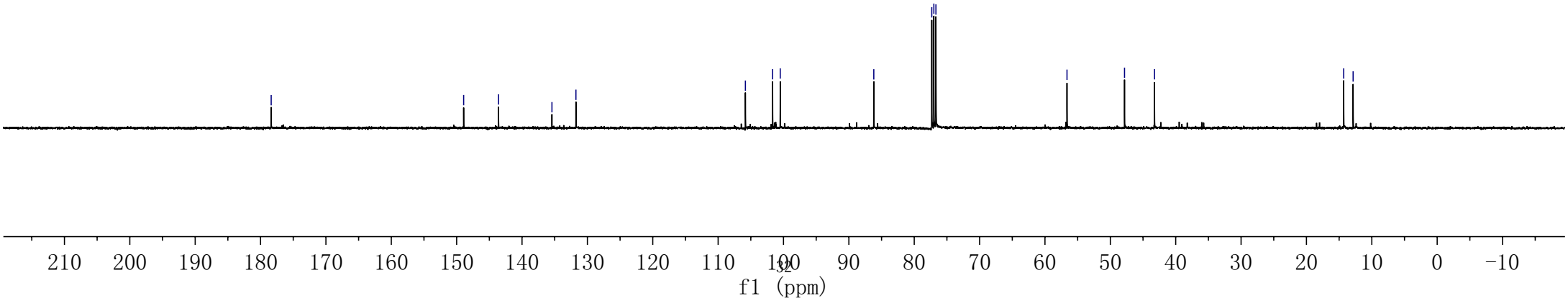
178.37
148.93
143.59
135.42
131.75
105.83
101.67
100.50
86.19
77.32
77.00
76.68
56.63
47.83
43.25
14.30
12.86

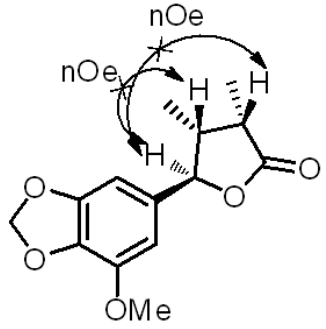


***cis* : *trans* = 1 : 9**

^{13}C NMR, 100 M, $CDCl_3$

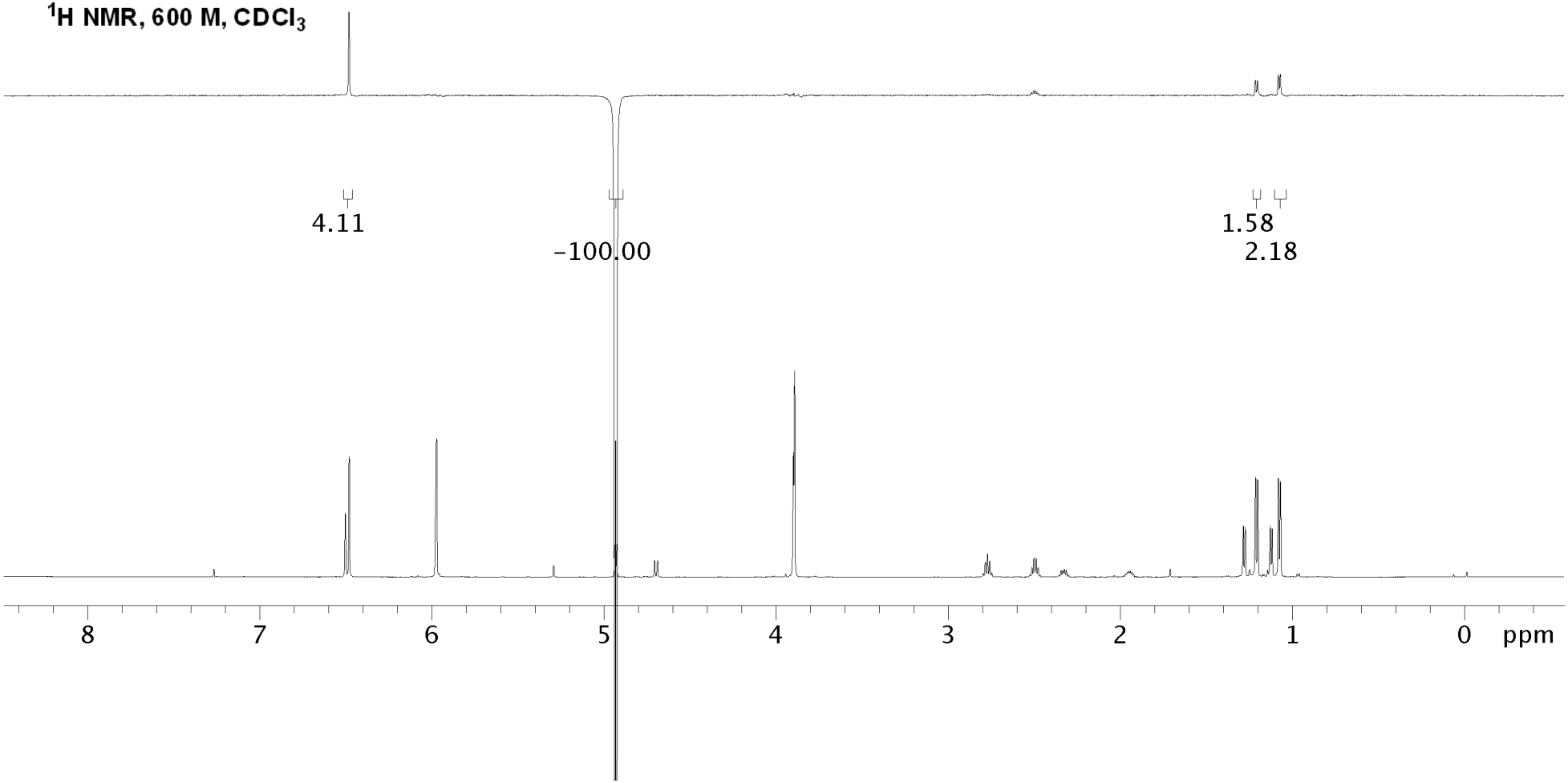
in the condition of DBU

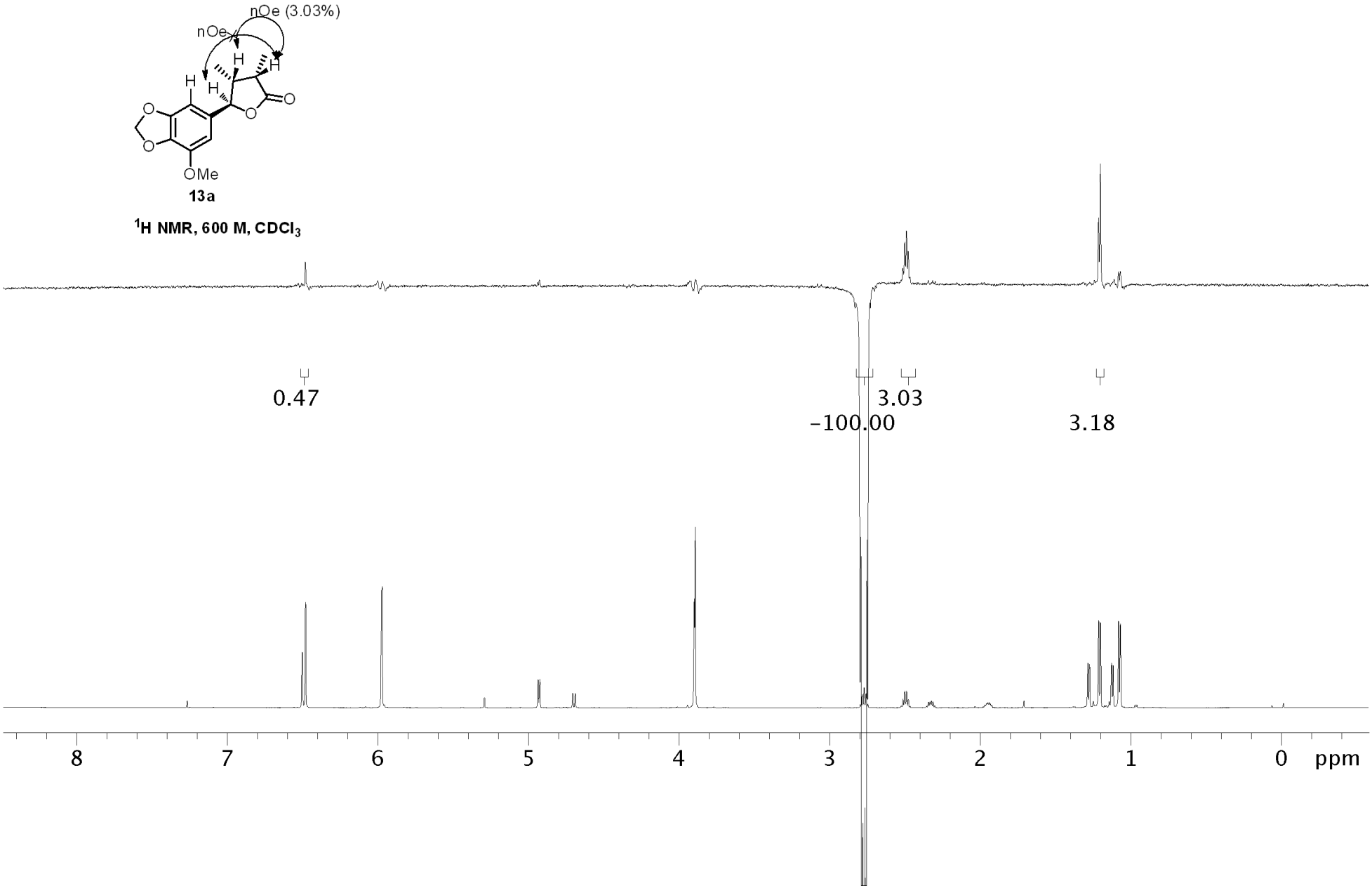


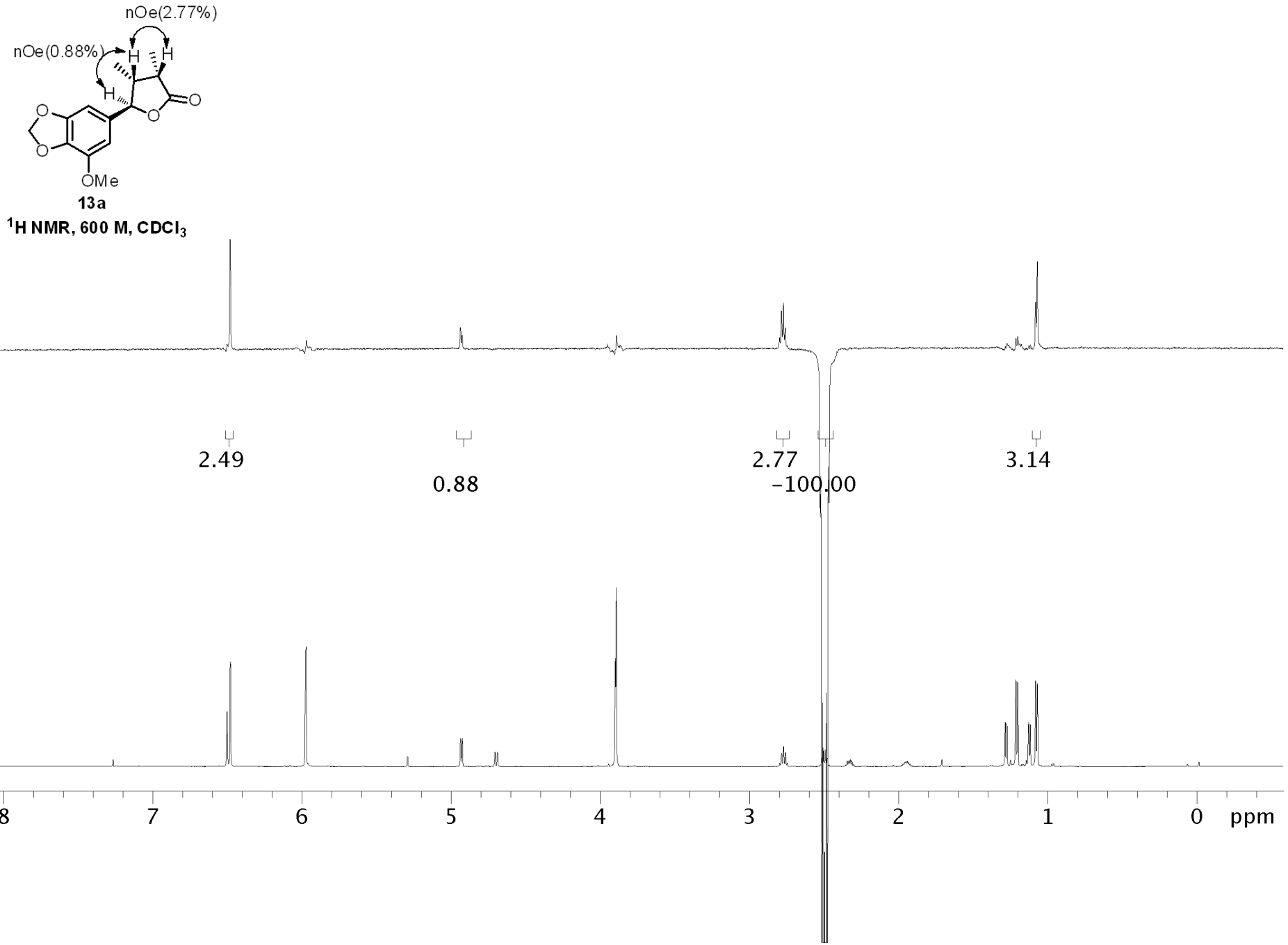


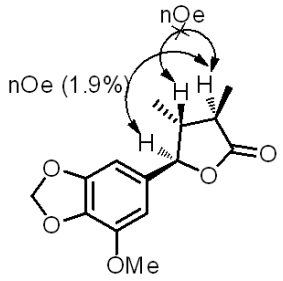
13a

^{1}H NMR, 600 M, $CDCl_3$



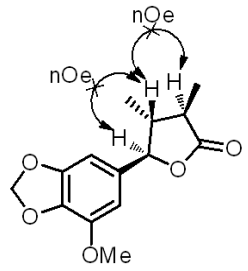

nOe (3.03%)
nOe
H
H
H
H
O
O
O
O
OMe
13a
^{1}H NMR, 600 M, CDCl$_3$
0.47
-100.00
3.03
3.18
8
7
6
5
4
3
2
1
0
ppm


nOe(2.77%)
nOe(0.88%)
H
H
H
O
O
O
O
OMe
13a
1H NMR, 600 M, CDCl3
2.49
0.88
2.77
-100.00
3.14
8
7
6
5
4
3
2
1
0
ppm



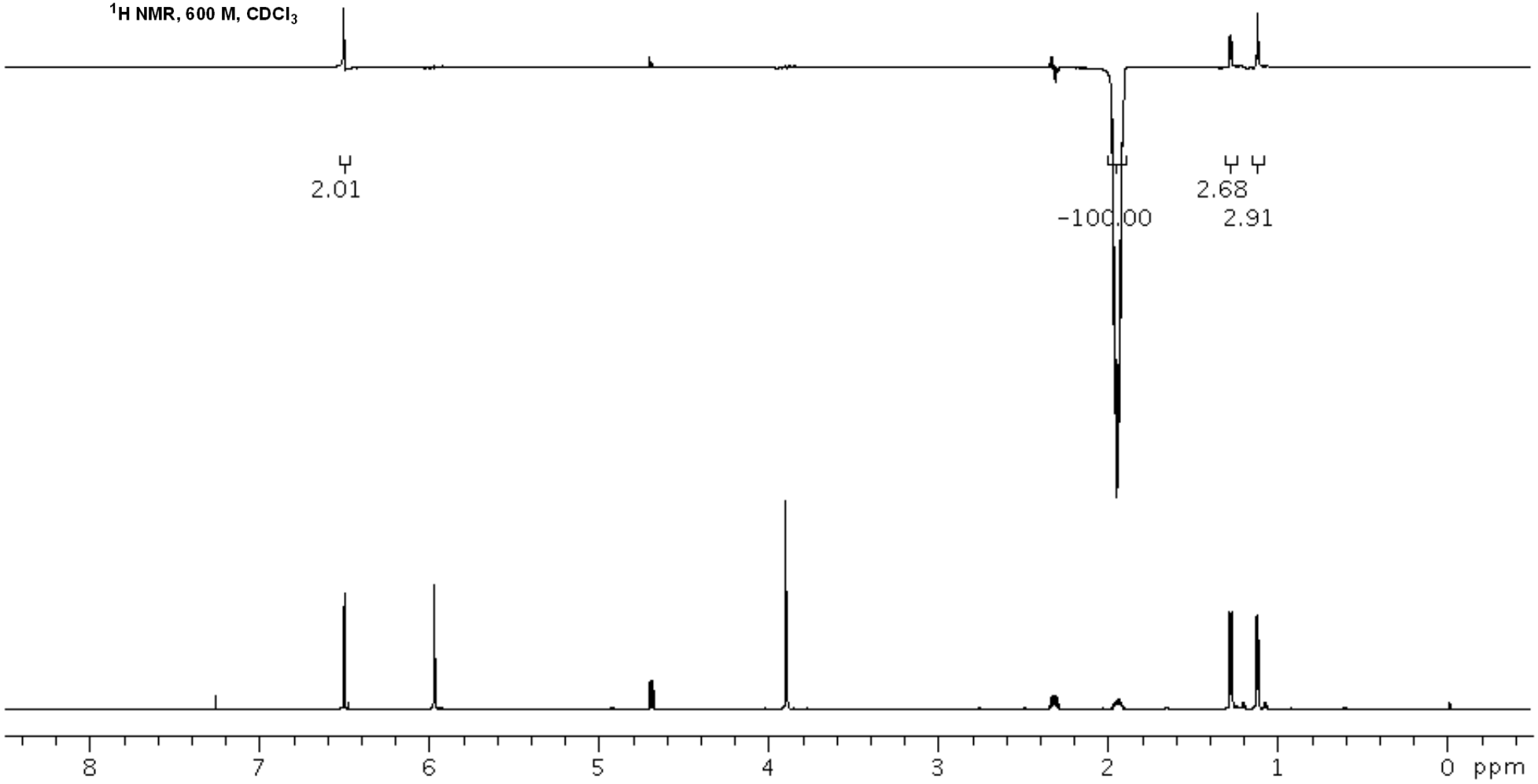
13b

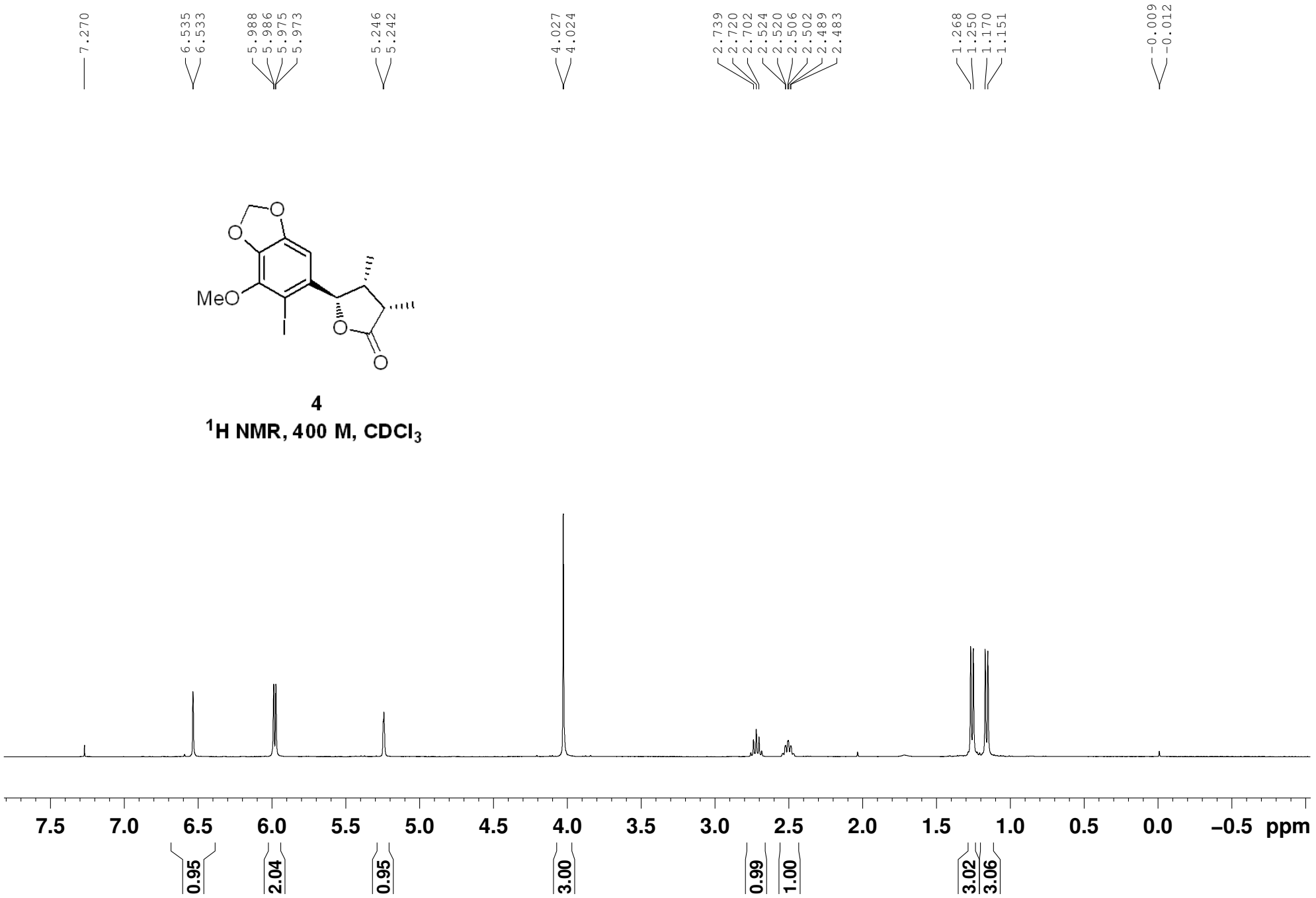
^{1}H NMR, 600 M, $CDCl_3$



13b

^{1}H NMR, 600 M, $CDCl_3$

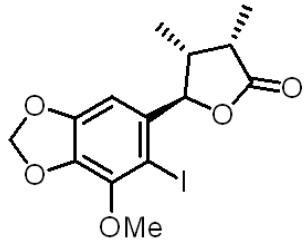




4

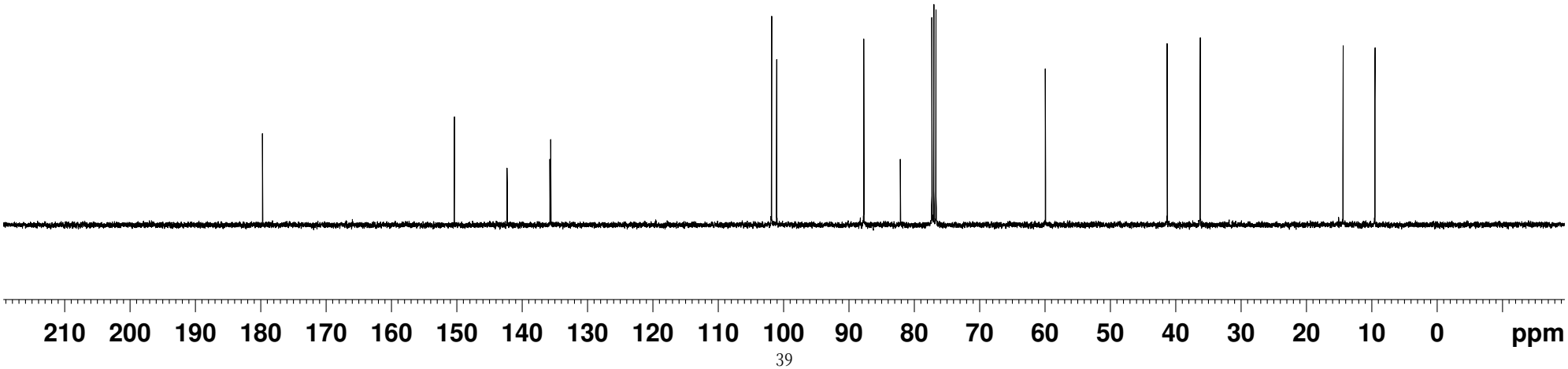
^{1}H NMR, 400 M, $CDCl_3$

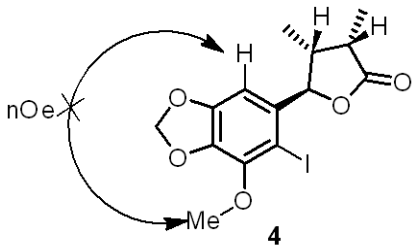
179.74
150.38
142.30
135.77
135.64
101.83
101.06
87.73
82.14
77.32
77.00
76.68
59.94
41.31
36.26
14.40
9.52



4

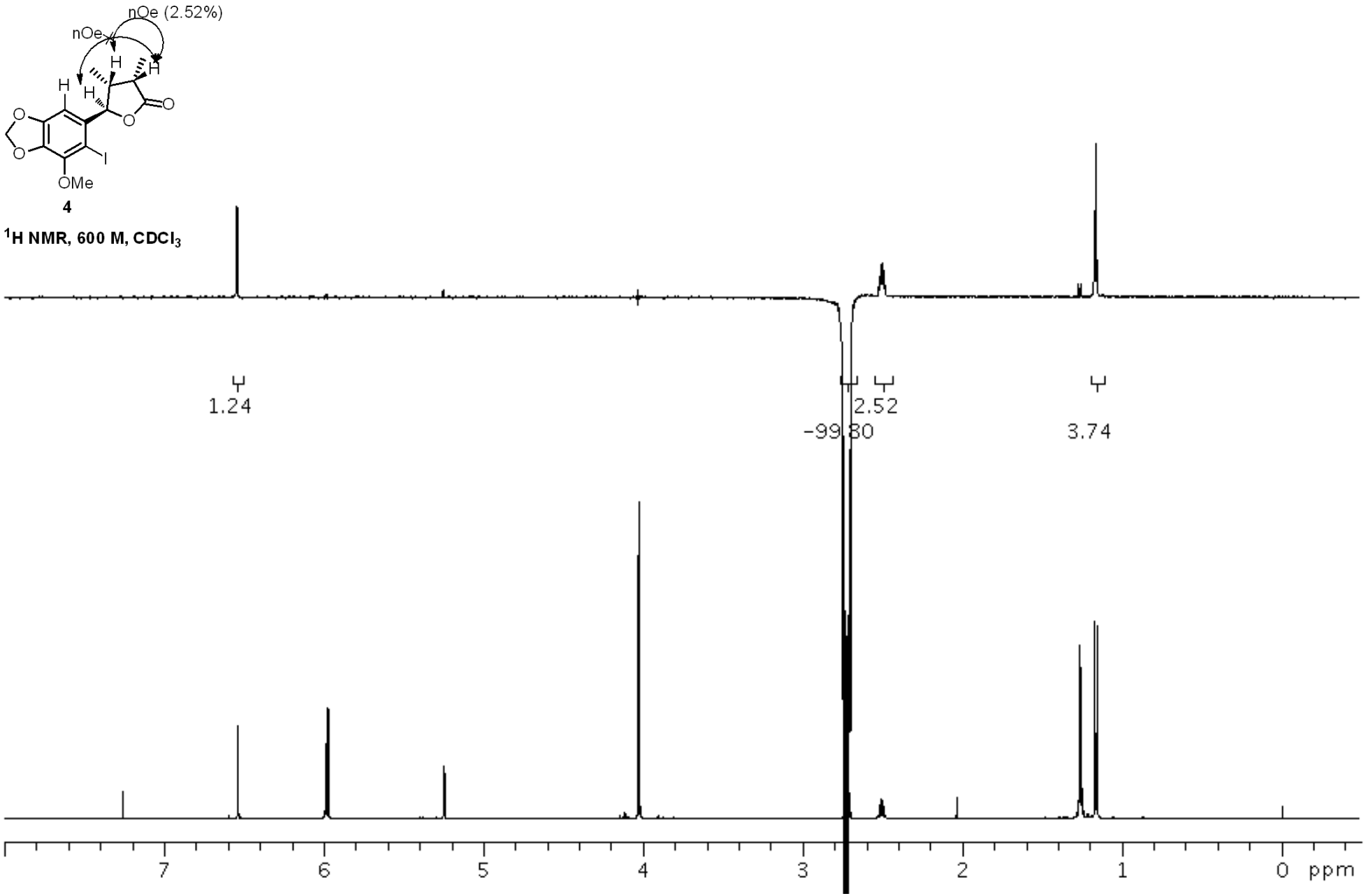
^{13}C NMR, 100 M, $CDCl_3$

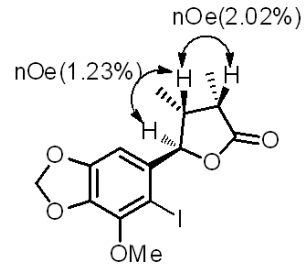




4

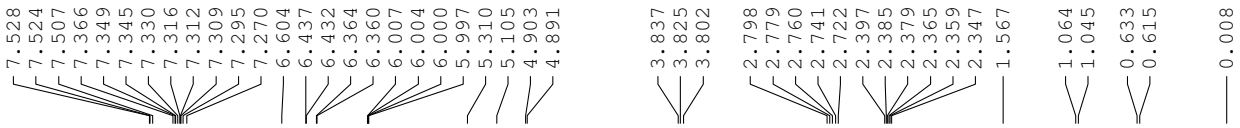
^{1}H NMR, 300 M, $CDCl_3$

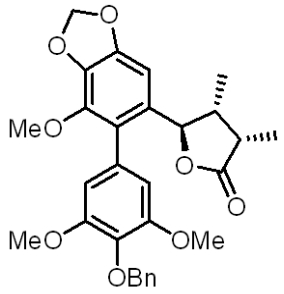

nOe (2.52%)
nOe
H
H
H
O
O
O
O
I
OMe
4
1H NMR, 600 M, CDCl3
1.24
2.52
-99.80
3.74
7
6
5
4
3
2
1
0 ppm



4

^{1}H NMR, 600 M, $CDCl_3$

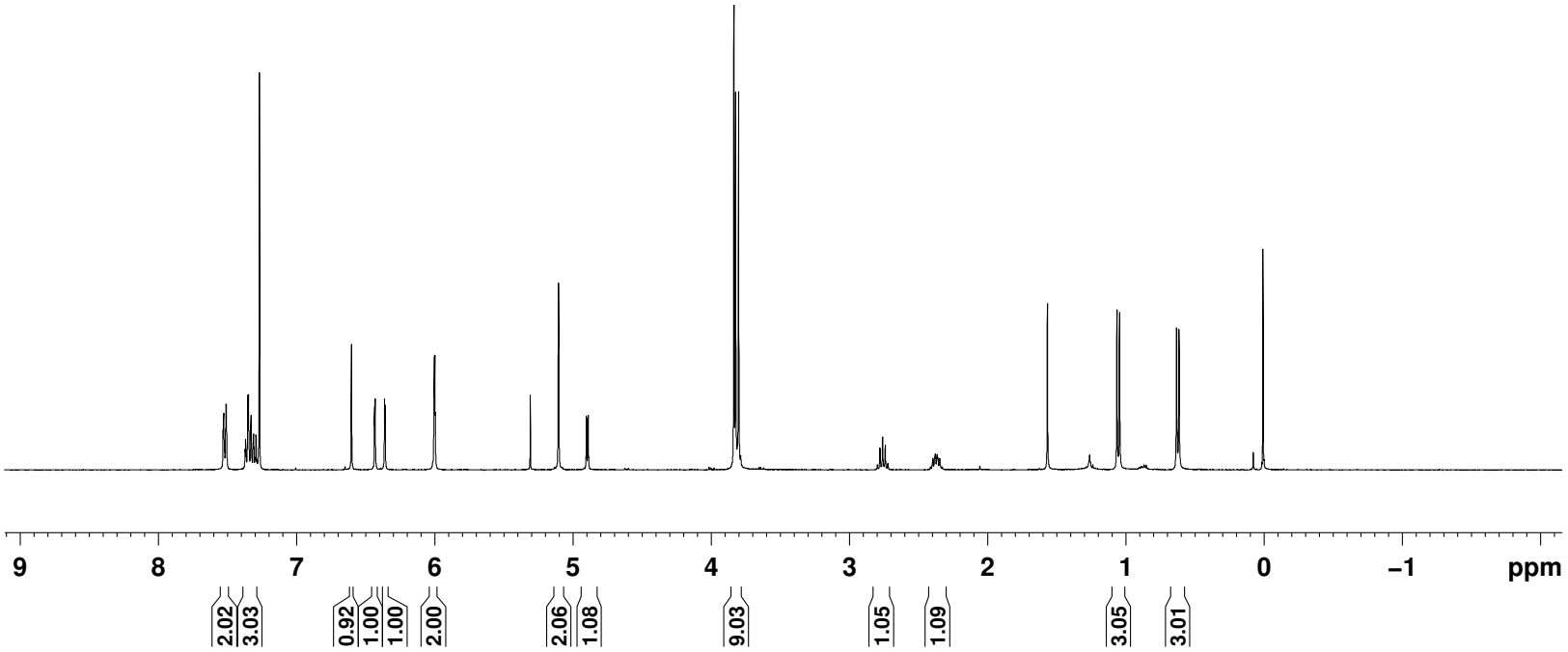


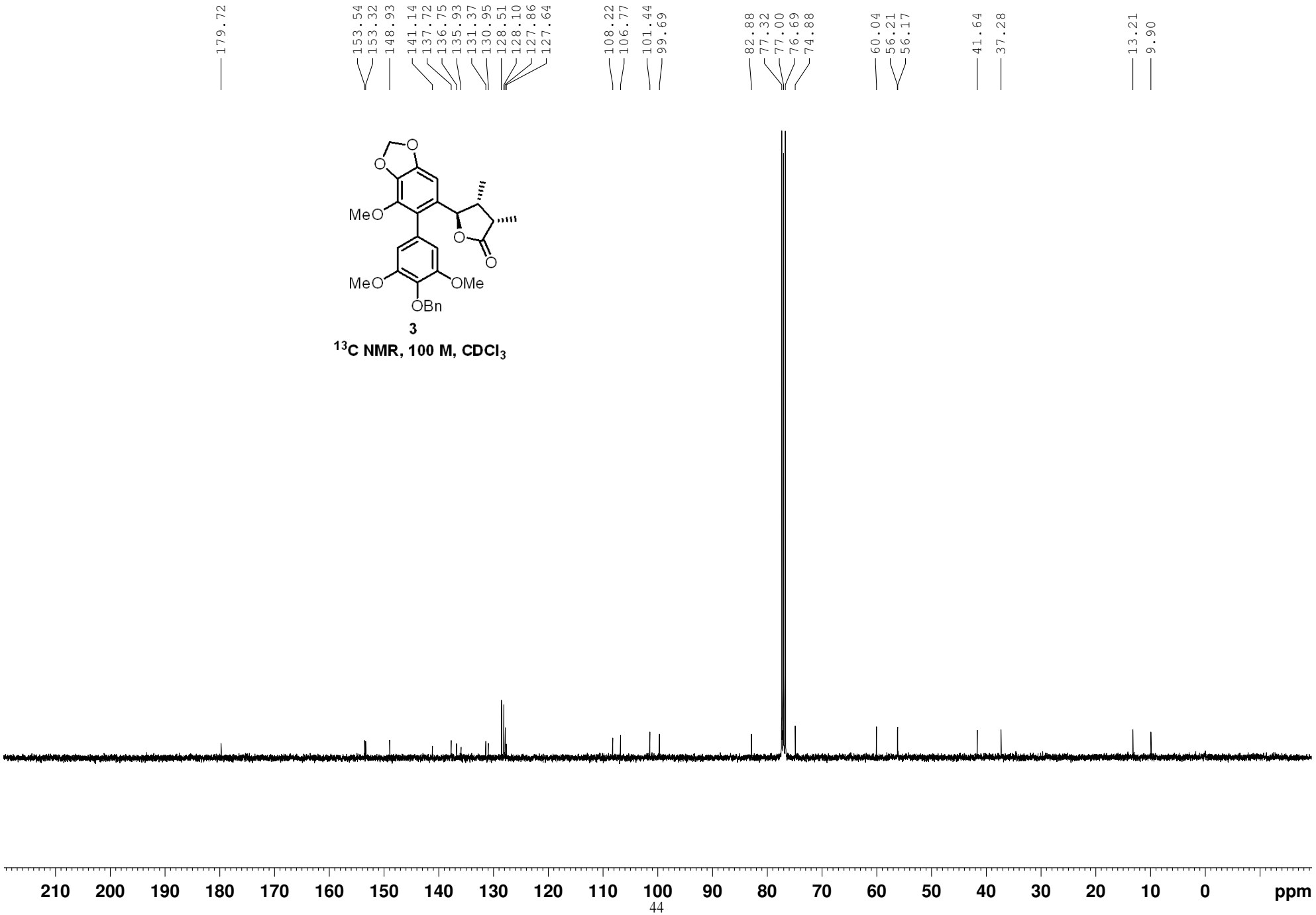


3

^{1}H NMR, 400 M, CDCl$_3$

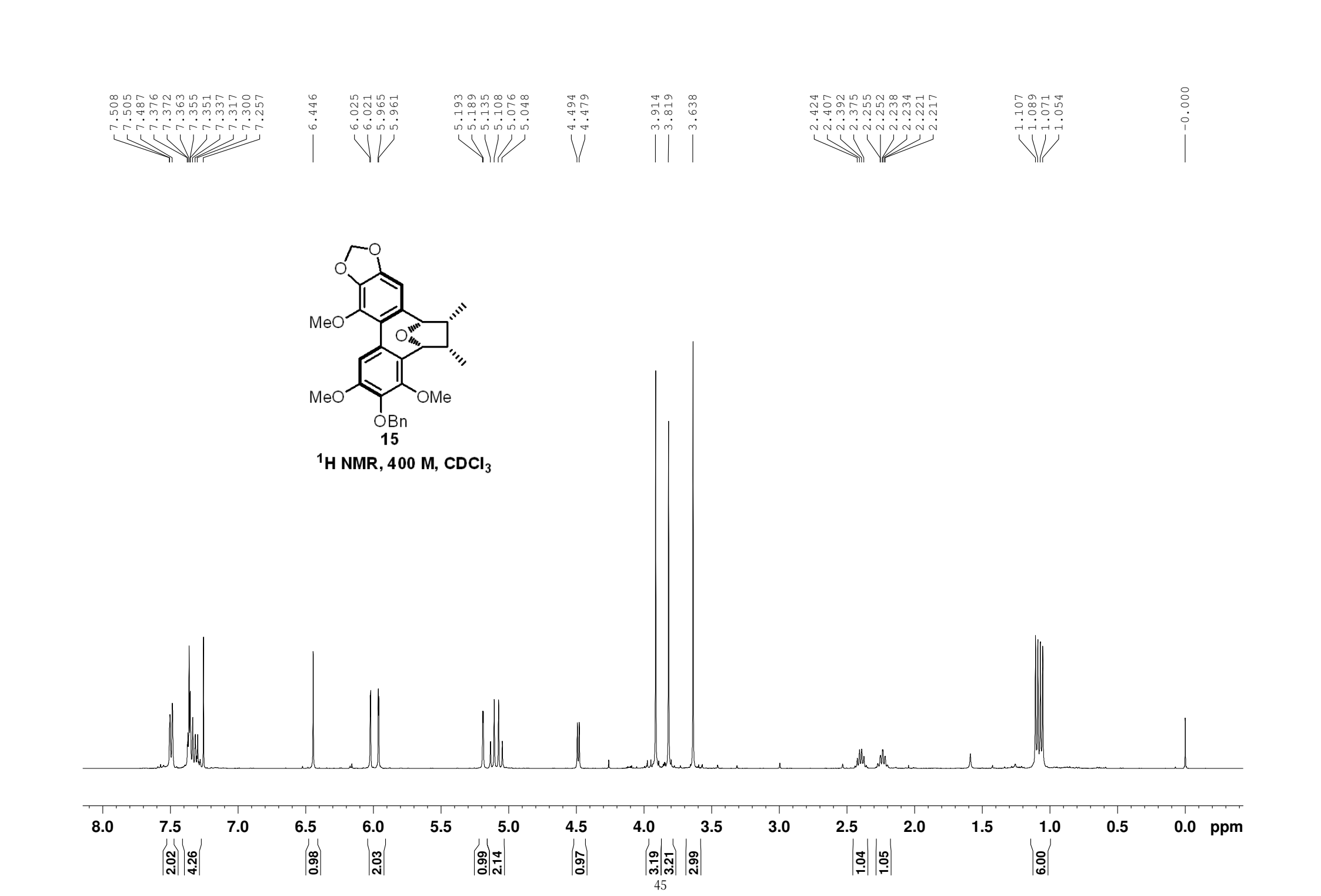
```
NAME                cp
EXPNO               20
PROCNO              1
Date_           20161230
Time               14.43
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8012.820 Hz
FIDRES             0.122266 Hz
AQ              4.0894966 sec
RG                   456
DW                62.400 usec
DE                 6.50 usec
TE                291.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         400.1324710 MHz
NUC1                   1H
P1                 10.92 usec
SI                 65536
SF           400.1300057 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

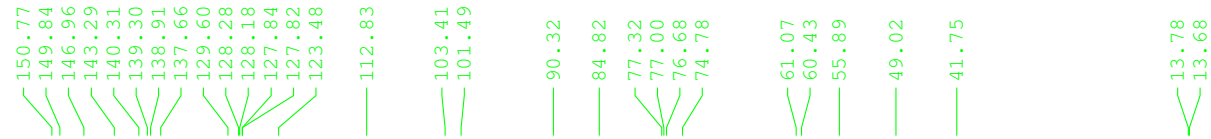


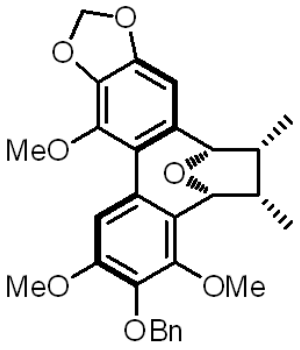


3

^{13}C NMR, 100 M, $CDCl_3$

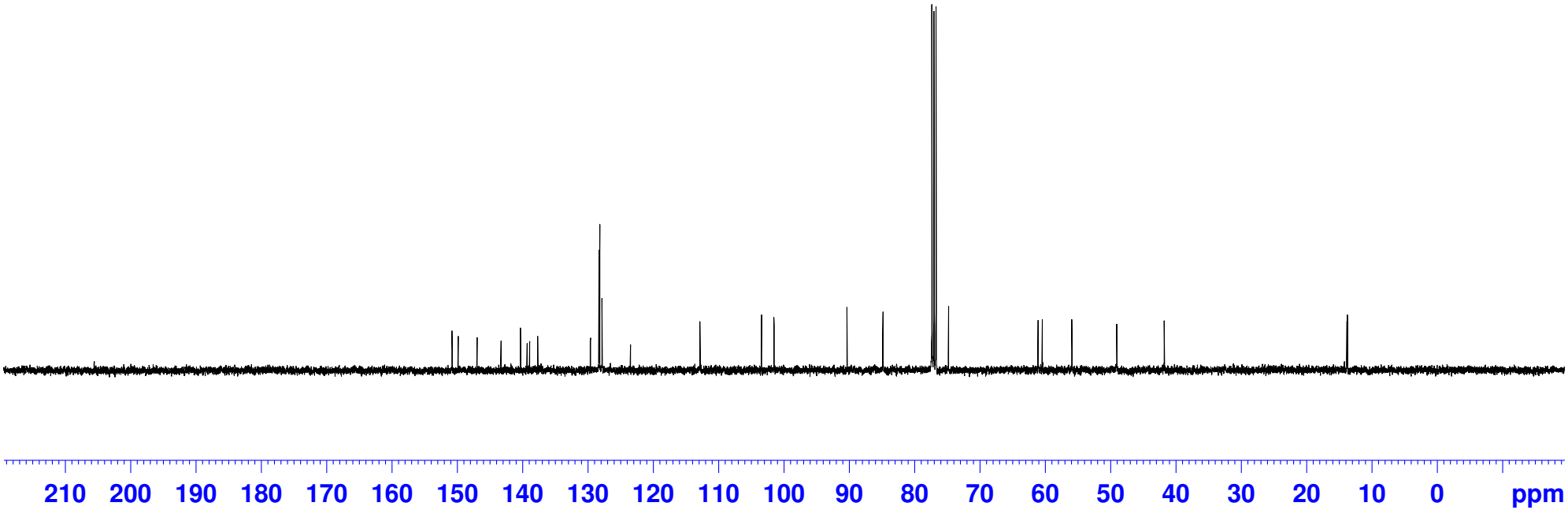

7.508
7.505
7.487
7.376
7.372
7.363
7.355
7.351
7.337
7.317
7.300
7.257
6.446
6.025
6.021
5.965
5.961
5.193
5.189
5.135
5.108
5.076
5.048
4.494
4.479
3.914
3.819
3.638
2.424
2.407
2.392
2.375
2.255
2.252
2.238
2.234
2.221
2.217
1.107
1.089
1.071
1.054
-0.000
MeO
O
MeO
OMe
OBn
15
1H NMR, 400 M, CDCl3
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
2.02
4.26
0.98
2.03
0.99
2.14
0.97
3.19
3.21
2.99
1.04
1.05
6.00

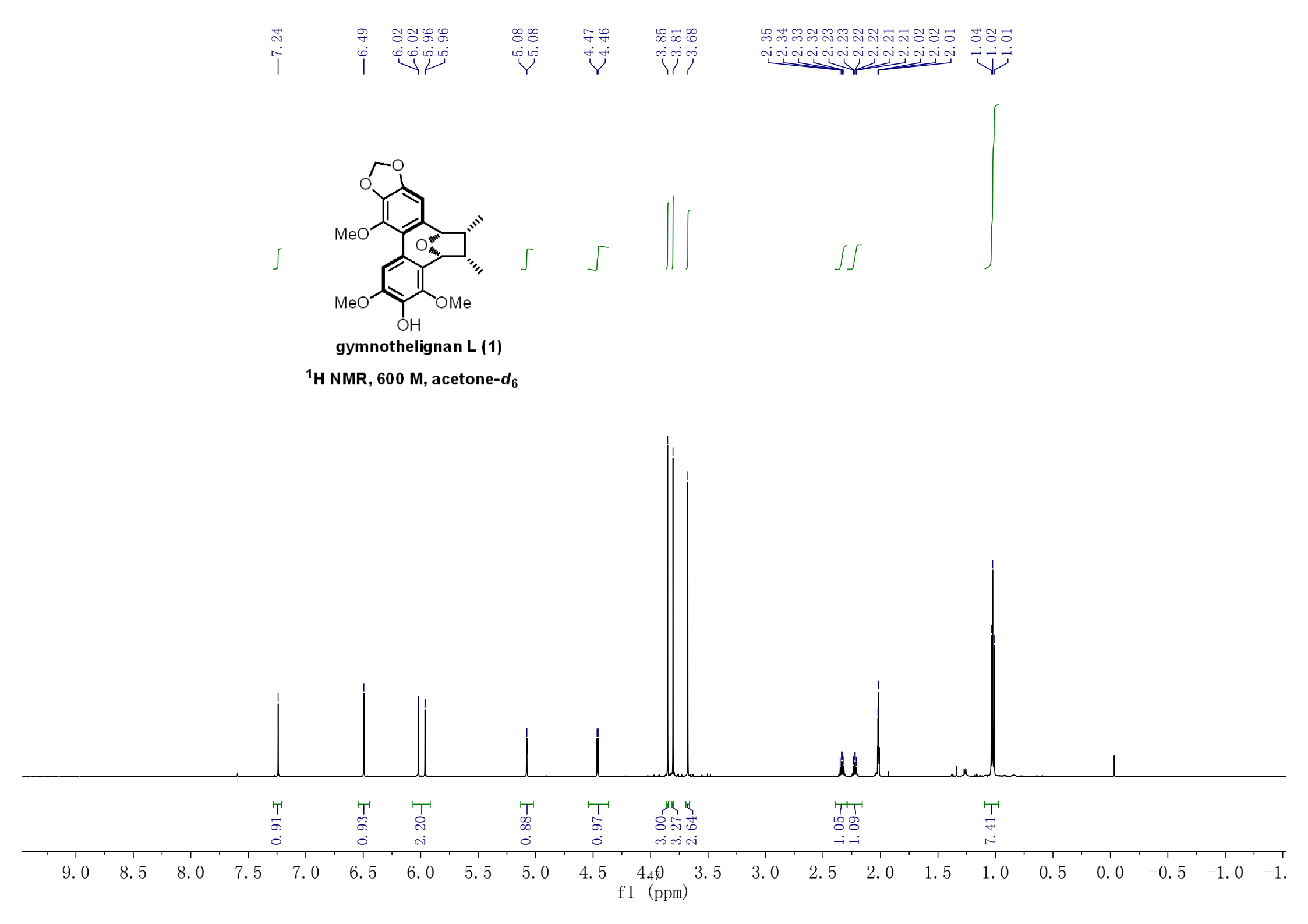




15

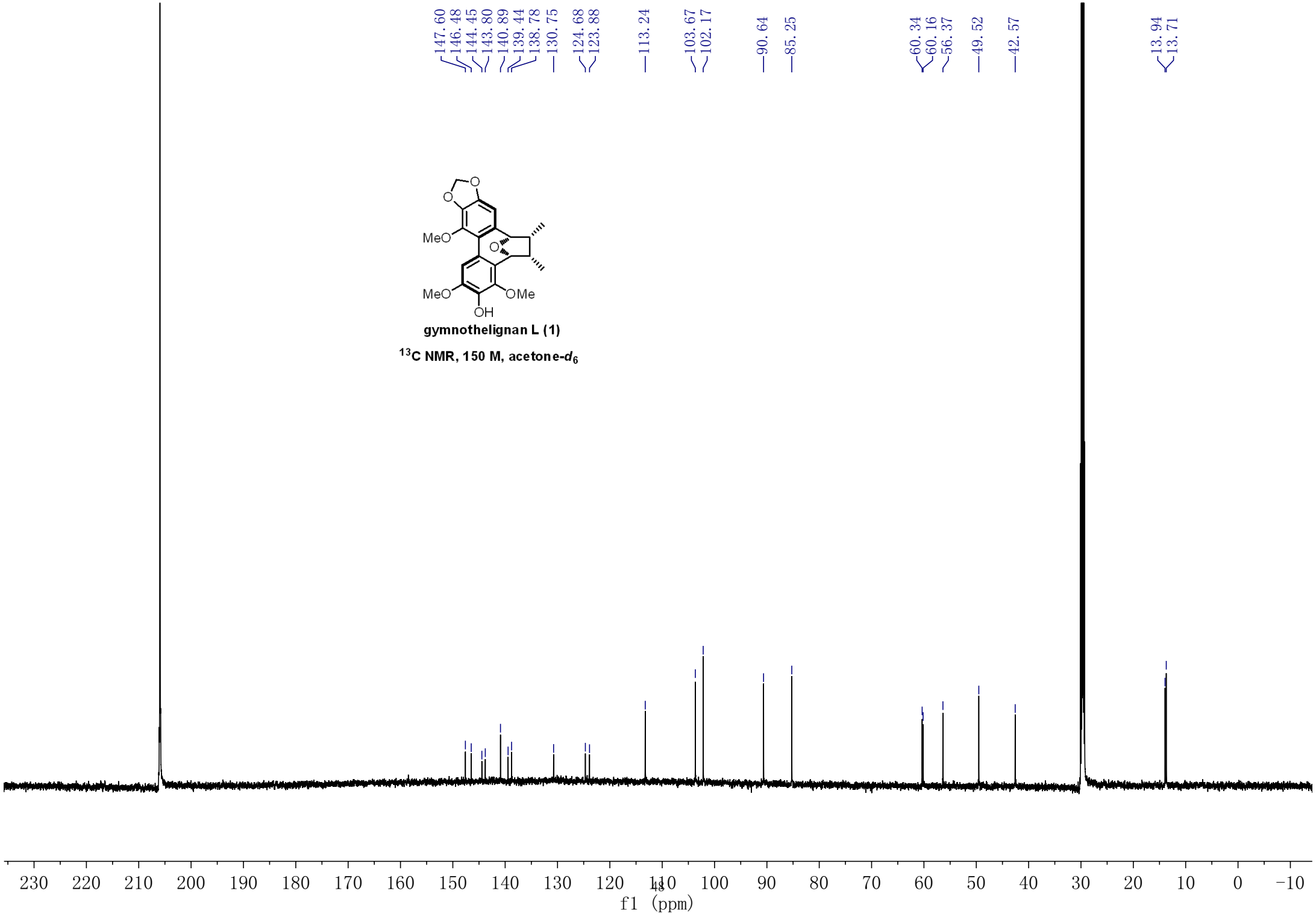
^{13}C NMR, 100 M, $CDCl_3$





gymnothelignan L (1)

^{1}H NMR, 600 M, acetone-d_6



gymnothelignan L (1)

^{13}C NMR, 150 M, acetone-d_6