Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Construction of the Tetracyclic Ring System of Diterpene Alkaloids via Cationic [5+2] Cycloaddition

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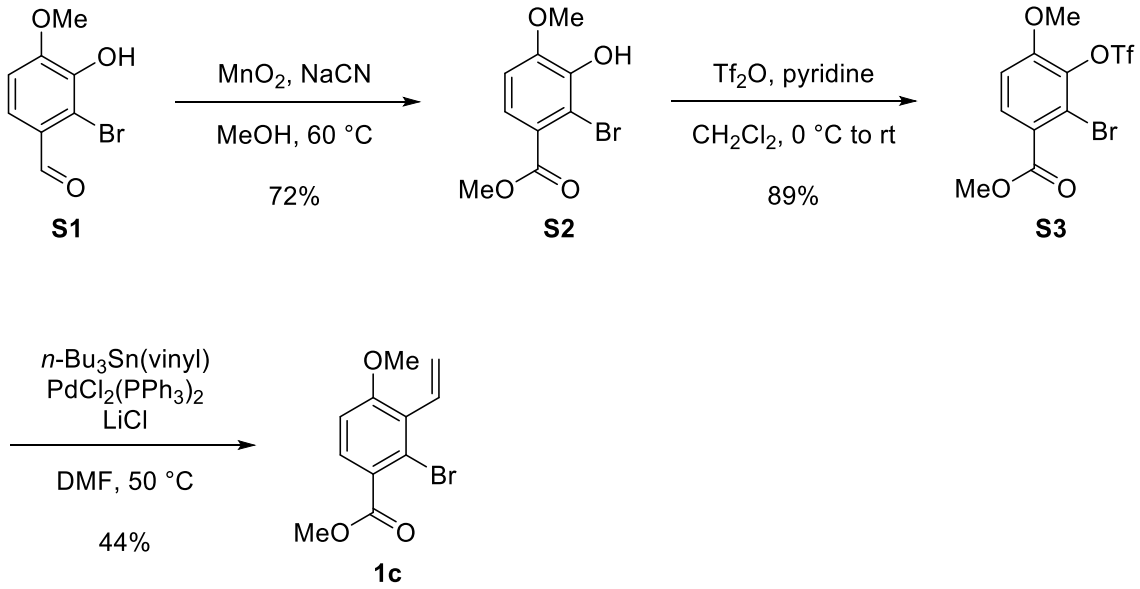
General Remarks

Nuclear magnetic resonance (NMR) spectra were determined on a JEOL-ECS400 or JEOL-ECZ400 instrument. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) downfields from tetramethylsilane as the internal standard, and coupling constants are in hertz (Hz). The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, m = multiplet. Chemical shifts for ^{13}C NMR are reported in ppm relative to the center line of a triplet at 77.0 ppm for deuteriochloroform. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 Fourier Transform Infrared Spectrophotometer and are reported in wavenumbers (cm^{-1}). High resolution mass spectra (HRMS) were obtained on a Bruker Daltonics compact in positive electrospray ionization (ESI) method, using ESI tuning mix as the internal standard. Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel 60 F254. Preparative TLC separations were performed on Merck analytical plates (0.25 or 0.50 mm thick) precoated with silica gel 60 F254. Flash chromatography separations were performed on KANTO CHEMICAL Silica Gel 60 (spherical, 40-100 mesh) or on KANTO CHEMICAL Silica Gel 60 (spherical, NH2, 40-50 mesh). Reagents were commercial grades and were used without any purification. Dehydrated tetrahydrofuran and dichloromethane were purchased from FUJIFILM Wako Pure Chemical Corporation. Dehydrated ethanol and acetonitrile were purchased from FUJIFILM Wako Pure Chemical Industries and stored over activated MS3A. All reactions sensitive to oxygen or moisture were conducted under an argon atmosphere. **S1**[1], **S6**[2], **S8**[3], **2**[4], and **1b**[5] were prepared according to the literature.

Synthesis of styrene 1c



To a stirred solution of **S1** (78.8 mg, 0.341 mmol) in MeOH (1.7 mL) were added NaCN (50.1 mg, 1.02 mmol) and MnO_2 (208 mg, 2.39 mmol) at rt. After stirring for 24 h at 60 °C, the resulting mixture was filtered through a pad of celite, and the filter cake was washed with CH_2Cl_2 and 1N HCl. The resulting mixture was extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-40% ethyl acetate/hexane) to give **S2** (63.8 mg, 0.245 mmol, 72.0 %) as a yellow solid.

^{1}H NMR ($CDCl_3$): 7.50 (d, *J* = 8.7 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 3.96 (s, 3H), 3.91 (s, 3H)

^{13}C NMR ($CDCl_3$): 166.1 (C), 149.7 (C), 143.6 (C), 124.1 (C), 123.7 (CH), 108.9 (C), 108.7 (CH), 56.4 (CH_3), 52.2 (CH_3)

IR (film, cm^{-1}): 2924, 1720, 1596, 1489, 1436, 1285, 1220, 1139, 1030, 622

HRMS (ESI-QTOF) calcd for $C_9H_9BrNaO_4^+$ [M+Na^+] 282.9576, found 282.9577

mp: 156-160 °C

To a stirred solution of **S2** (104 mg, 0.398 mmol) in CH_2Cl_2 (4.0 mL) were added pyridine (96 µL, 1.2 mmol) and Tf_2O (114 µl, 0.797 mmol) at 0 °C. After stirring for 1 h at rt, the resulting mixture was quenched with 1N HCl at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-40% ethyl acetate/hexane) to give **S3** (138 mg, 0.353 mmol, 88.6%) as a yellow oil.

^{1}H NMR ($CDCl_3$): 7.90 (d, *J* = 8.9 Hz, 1H), 7.02 (d, *J* = 8.9 Hz, 1H), 3.98 (s, 3H), 3.93 (s, 3H)

^{13}C NMR ($CDCl_3$): 165.0 (C), 154.7 (C), 137.7 (C), 131.8 (CH), 125.1 (C), 118.5 (CF_3, q, *J* = 319.4 Hz), 118.2 (C), 110.9 (CH), 56.6 (CH_3), 52.6 (CH_3)

IR (film, cm^{-1}): 2952, 1731, 1598, 1489, 1030, 999, 913, 849, 748, 592

HRMS (ESI-QTOF) calcd for $C_{10}H_8BrF_3NaO_6S^+$ [M+Na^+] 414.9069, found 414.9055

To a stirred solution of **S3** (87.8 mg, 0.223 mmol) in DMF (1.5 mL) were added tributylvinyltin (72.1 µL, 0.246 mmol), LiCl (28.4 mg, 0.670 mmol), and $PdCl_2(PPh_3)_2$ (7.8 mg, 0.011 mmol) at rt. After stirring for 12 h at 50 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel and K_2CO_3 (5% w/w) (10-20% ethyl acetate/hexane) to give **1c** (26.5 mg, 43.8 %) as a clear oil.

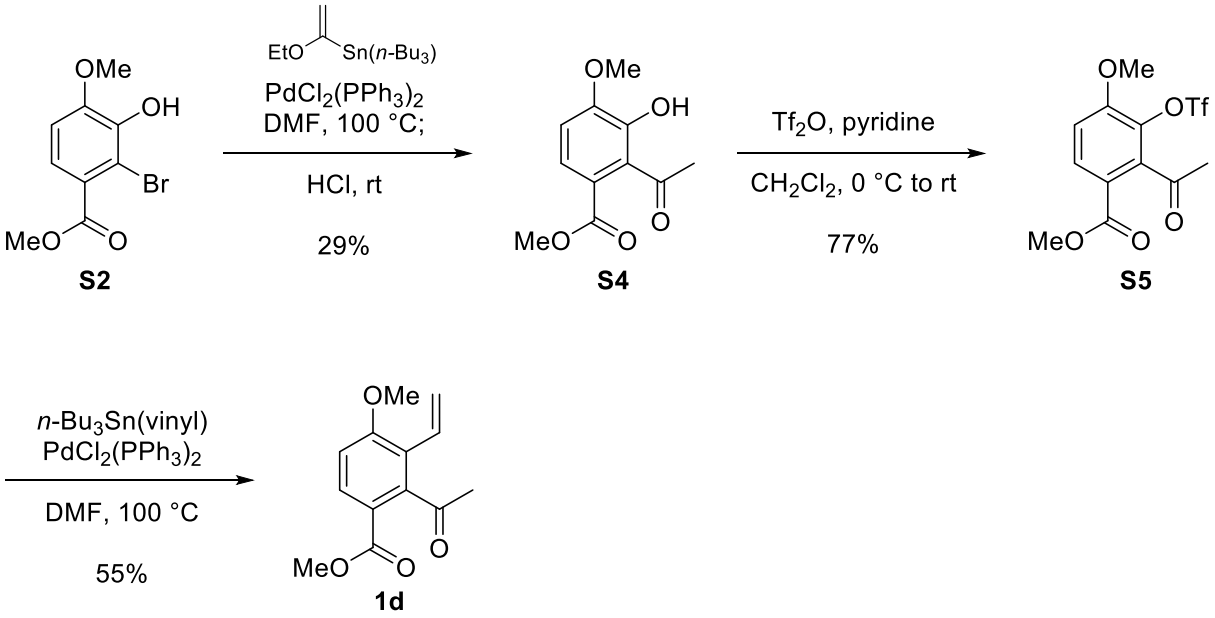
^{1}H NMR ($CDCl_3$): 7.63 (d, *J* = 8.7 Hz, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.77 (dd, *J* = 17.9, 11.7 Hz, 1H), 5.81 (dd, *J* = 17.9, 1.8 Hz, 1H), 5.64 (dd, *J* = 11.7, 1.8 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H)

^{13}C NMR ($CDCl_3$): 167.2 (C), 160.1 (C), 131.8 (CH), 130.5 (CH), 128.5 (C), 125.8 (C), 123.8 (C), 122.0 (CH_2), 109.2 (CH), 56.0 (CH_3), 52.3 (CH_3)

IR (film, cm^{-1}): 2922, 1728, 1579, 1433, 1362, 1263, 1189, 1139, 1029, 818

HRMS (ESI-QTOF) calcd for $C_{11}H_{11}BrNaO_3^+$ [M+Na^+] 292.9784, found 292.9786

Synthesis of styrene 1d



To a stirred solution of **S2** (127 mg, 0.486 mmol) in DMF (2.0 mL) were added (1-ethoxyvinyl)tri-*n*-butylstannane (181 µL, 0.535 mmol) and $PdCl_2(PPh_3)_2$ (34.0 mg, 0.0486 mmol) at rt. After stirring for 12 h at 100 °C, 2 M HCl (2 mL) was added to the reaction solution at rt. After stirring for 1 h at rt, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel and K_2CO_3 (5% w/w) (20-35% ethyl acetate/hexane) to give **S4** (31.3 mg, 0.140 mmol, 28.7%) as an orange solid.

^{1}H NMR ($CDCl_3$): 7.52 (d, *J* = 8.2 Hz, 1H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.67 (s, 1H), 3.96 (s, 3H), 3.85 (s, 3H), 2.56 (s, 3H)
^{13}C NMR ($CDCl_3$): 203.2 (C), 166.4 (C), 150.4 (C), 142.9 (C), 129.3 (C), 123.0 (CH), 120.8 (C), 110.2 (CH), 56.3 (CH_3), 52.3 (CH_3), 31.3 (CH_3)
IR (film, cm^{-1}): 3397, 2361, 1710, 1606, 1437, 1349, 1282, 1133, 1042, 846
HRMS (ESI-QTOF) calcd for $C_{11}H_{12}NaO_5^+$ [M+Na$^+$] 247.0577, found 247.0583
mp: 93-98 °C

To a stirred solution of **S4** (22.8 mg, 0.102 mmol) in CH_2Cl_2 (1.0 mL) were added pyridine (16.4 µL, 0.203 mmol) and Tf_2O (21.8 µL, 0.153 mmol) at 0 °C. After stirring for 15 h at rt, the resulting mixture was quenched with 1N HCl at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-40% ethylacetate/hexane) to give **S5** (28.0 mg, 0.0786 mmol, 77.1%) as a yellow oil.

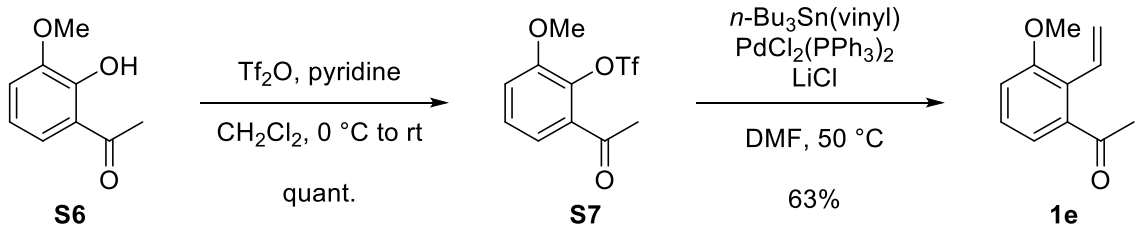
^{1}H NMR ($CDCl_3$): 8.02 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 8.7 Hz, 1H), 4.00 (s, 3H), 3.88 (s, 3H), 2.58 (s, 3H)
^{13}C NMR ($CDCl_3$): 198.7 (C), 164.7 (C), 154.6 (C), 139.3 (C), 133.9 (C), 131.7 (CH), 120.0 (C), 118.6 (CF_3, q, *J* = 319.4 Hz), 112.2 (CH), 56.6 (CH_3), 52.6 (CH_3), 31.6 (CH_3)
IR (film, cm^{-1}): 1720, 1606, 1421, 1285, 1225, 1131, 990, 915, 861, 602

HRMS (ESI-QTOF) calcd for $C_{12}H_{11}F_3NaO_7S^+$ [M+Na^+] 379.0070, found 379.0070

To a stirred solution of **S5** (14.1 mg, 0.0396 mmol) in DMF (200 µL) were added tributylvinyltin (12.8 µL, 0.0435 mmol) and $PdCl_2(PPh_3)_2$ (2.8 mg, 0.0040 mmol) at rt. After stirring for 12 h at 100 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel and K_2CO_3 (5% w/w) (15-30% ethyl acetate/hexane) to give **1d** (5.1 mg, 0.022 mmol, 55%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$): 7.93 (d, *J* = 8.7 Hz, 1H), 6.90 (d, *J* = 8.7 Hz, 1H), 6.64 (dd, *J* = 17.8, 11.8 Hz, 1H), 5.67 (dd, *J* = 17.8, 1.6 Hz, 1H), 5.51 (dd, *J* = 11.8, 1.6 Hz, 1H), 3.92 (s, 3H), 3.85 (s, 3H), 2.49 (s, 3H)
^{13}C NMR ($CDCl_3$): 205.6 (C), 166.1 (C), 160.8 (C), 145.4 (C), 131.4 (CH), 129.2 (CH), 123.3 (C), 122.3 (CH_2), 118.9 (C), 109.7 (CH), 55.9 (CH_3), 52.2 (CH_3), 31.9 (CH_3)
IR (film, cm^{-1}): 2923, 2362, 1713, 1573, 1435, 1269, 1196, 1149, 1041, 986
HRMS (ESI-QTOF) calcd for $C_{13}H_{14}NaO_4$ [M+Na^+] 257.0784, found 257.0788

Synthesis of styrene 1e



To a stirred solution of **S6** (93.4 mg, 0.562 mmol) in CH_2Cl_2 (5.6 mL) were added pyridine (90.5 µL, 1.12 mmol) and Tf_2O (120 µL, 0.844 mmol) at 0 °C. After stirring for 150 min at rt, the resulting mixture was quenched with 1N HCl at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-35% ethyl acetate/hexane) to give **S7** (175 mg, quant.) as a yellow oil.

^{1}H NMR ($CDCl_3$): 7.40 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.27 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.19 (dd, *J* = 8.4, 1.5Hz, 1H), 3.93 (s, 3H), 2.61 (s, 3H)

^{13}C NMR ($CDCl_3$): 197.2 (C), 151.8 (C), 135.8 (C), 133.8 (C), 128.8 (CH), 121.0 (CH), 118.6 (CF_3, q, *J* = 318.5 Hz), 116.2 (CH), 56.4 (CH_3), 29.6 (CH_3)

IR (film, cm^{-1}): 1698, 1577, 1420, 1286, 1204, 1134, 1044, 885, 784, 598

HRMS (ESI-QTOF) calcd for $C_{10}H_9F_3NaO_5S^+$ [M+Na^+] 321.0015, found 321.0029

To a stirred solution of **S7** (18.6 mg, 0.0624 mmol) in DMF (250 µl) were added tributylvinyltin (22.0 µl, 0.0748 mmol), LiCl (7.9 mg, 0.187 mmol), and $PdCl_2(PPh_3)_2$ (4.4 mg, 0.0063 mmol) at rt. After stirring for 13 h at 50 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel and K_2CO_3 (5% w/w) (10-25% ethyl acetate/hexane) to give **1e** (6.9 mg, 0.039 mmol, 63%) as a pale yellow oil.

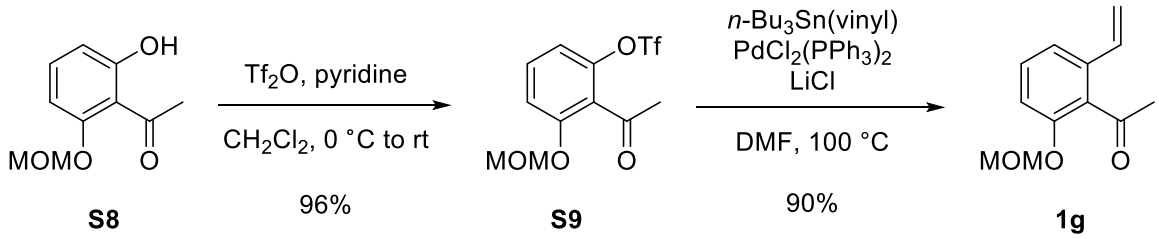
^{1}H NMR ($CDCl_3$): 7.28 (dd, *J* = 7.6, 7.1 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.1 Hz, 1H), 6.96 (dd, *J* = 17.4, 11.8 Hz, 1H), 5.48 (dd, *J* = 11.8, 1.5 Hz, 1H), 5.45 (dd, *J* = 17.4, 1.5 Hz, 1H), 3.86 (s, 3H), 2.46 (s, 3H)

^{13}C NMR ($CDCl_3$): 205.3 (C), 157.2 (C), 142.3 (C), 131.1 (CH), 128.4 (CH), 125.4 (C), 121.1 (CH_2), 119.2 (CH), 112.3 (CH), 55.8 (CH_3), 31.0 (CH_3)

IR (film, cm^{-1}): 2925, 2360, 1691, 1575, 1458, 1353, 1264, 1047, 924, 754

HRMS (ESI-QTOF) calcd for $C_{11}H_{12}NaO_2^+$ [M+Na^+] 199.0730, found 199.0730

Synthesis of styrene 1g



To a stirred solution of **S8** (6.04 g, 30.8 mmol) in CH_2Cl_2 (92 mL) were added pyridine (4.96 mL, 61.6 mmol) and Tf_2O (6.20 mL, 37.0 mmol) at 0 °C. After stirring for 2 h at rt, the resulting mixture was quenched with 1N HCl at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (10-20% ethyl acetate/hexane) to give **S9** (9.72 g, 29.6 mmol, 96.1 %) as a yellow oil.

^{1}H NMR ($CDCl_3$): 7.40 (dd, *J* = 8.7, 8.2 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.99 (d, *J* = 8.7 Hz, 1H), 5.24 (s, 2H), 3.49 (s, 3H), 2.59 (s, 3H)

^{13}C NMR ($CDCl_3$): 198.2 (C), 155.4 (C), 145.3 (C), 131.5 (CH), 125.6 (C), 118.4 (CF_3, q, *J* = 318.5 Hz), 114.9 (CH), 114.5 (CH), 94.6 (CH_2), 56.6 (CH_3), 32.0 (CH_3)

IR (film, cm^{-1}): 1707, 1608, 1425, 1216, 1145, 1026, 926, 831, 741, 596

HRMS (ESI-QTOF) calcd for $C_{11}H_{11}F_3NaO_6S^+$ [M+Na^+] 351.0121, found 351.0125

To a stirred solution of **S9** (9.70 g, 29.6 mmol) in DMF (90 mL) were added tri-*n*-butylvinyltin (8.69 mL, 29.6 mmol), LiCl (3.14 g, 74.1 mmol) and $PdCl_2(PPh_3)_2$ (415 mg, 0.593 mmol) at rt. After stirring for 1 h at 100 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on a mixture of silica gel and K_2CO_3 (5% w/w) (5-30% ethyl acetate/hexane) to give **1g** (5.50 g, 26.7 mmol, 90.1 %) as a yellow oil.

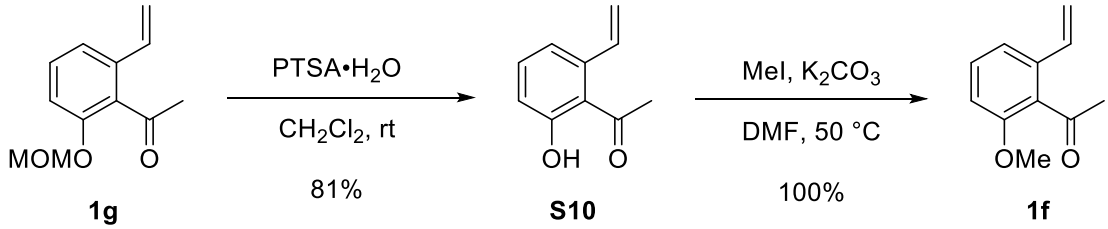
^{1}H NMR ($CDCl_3$): 7.28 (dd, *J* = 8.2, 7.3 Hz, 1H), 7.22 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.05 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.65 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.70 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.31 (dd, *J* = 11.0, 0.9 Hz, 1H), 5.18 (s, 2H), 3.46 (s, 3H), 2.52 (s, 3H)

^{13}C NMR ($CDCl_3$): 205.0 (C), 153.4 (C), 135.4 (C), 133.2 (CH), 131.2 (C), 129.9 (CH), 119.1 (CH), 117.2 (CH_2), 113.5 (CH), 94.5 (CH_2), 56.2 (CH_3), 32.6 (CH_3)

IR (film, cm^{-1}): 2912, 1700, 1568, 1464, 1353, 1249, 1155, 995, 920, 802

HRMS (ESI-QTOF) calcd for $C_{12}H_{14}NaO_3^+$ [M + Na^+] 229.0835, found 229.0844

Synthesis of styrene 1f



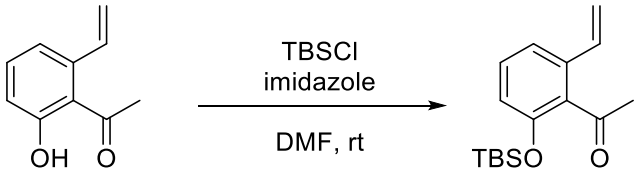
To a stirred solution of **1g** (5.50 g, 26.7 mmol) in CH_2Cl_2 (107 mL) was added PTSA·H_2O (1.02 g, 5.35 mmol) at rt. After stirring for 2 h at rt, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (5-15% ethyl acetate/hexane) to give **S10** (3.50 g, 21.6 mmol, 80.8 %) as a yellow oil.

^{1}H NMR ($CDCl_3$): 12.09 (s, 1H), 7.37 (dd, *J* = 8.4, 7.8 Hz, 1H), 7.04 (dd, *J* = 17.1, 10.9 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 5.57 (dd, *J* = 17.1, 0.9 Hz, 1H), 5.41 (dd, *J* = 10.9, 0.9 Hz, 1H), 2.60 (s, 3H)
^{13}C NMR ($CDCl_3$): 206.1 (C), 161.8 (C), 141.5 (C), 138.1 (CH), 134.7 (CH), 120.2 (CH), 119.9 (C), 118.1 (CH_2), 117.7 (CH), 33.0 (CH_3)
IR (film, cm^{-1}): 2920, 1627, 1444, 1331, 1248, 1215, 1007, 930, 806, 742
HRMS (ESI-QTOF) calcd for $C_{10}H_{10}NaO_2^+$ [M + Na^+] 185.0573 , found 185.0574

To a stirred solution of **S10** (37.2 mg, 0.229 mmol) in DMF (1.1 mL) were added K_2CO_3 (95.1 mg, 0.688 mmol) and MeI (21.4 µL, 0.344 mmol) at rt. After stirring for 2 h at 50 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (10-20% ethyl acetate/hexane) to give **1f** (40.2 mg, 0.228 mmol, 99.6%) as a pale yellow oil.

^{1}H NMR ($CDCl_3$): 7.30 (dd, *J* = 8.3, 7.8 Hz, 1H), 7.17 (d, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 8.3 Hz, 1H), 6.66 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.70 (d, *J* = 17.4 Hz, 1H), 5.30 (d, *J* = 11.0 Hz, 1H), 3.83 (s, 3H), 2.50 (s, 3H)
^{13}C NMR ($CDCl_3$): 205.3 (C), 156.0 (C), 135.4 (C), 133.3 (CH), 130.5 (C), 130.0 (CH), 118.0 (CH), 117.2 (CH_2), 109.9 (CH), 55.7 (CH_3), 32.5 (CH_3)
IR (film, cm^{-1}): 2923, 1698, 1568, 1465, 1351, 1262, 1071, 919, 798, 744
HRMS (ESI-QTOF) calcd for $C_{11}H_{12}NaO_2^+$ [M+Na^+] 199.0730, found 199.0736

Synthesis of styrene 1h



S10 **1h**

To a stirred solution of **S10** (3.40 g, 21.0 mmol) in DMF (63 mL) were added imidazole (2.85 g, 41.9 mmol) and TBSCl (3.79 g, 25.2 mmol) at rt. After stirring for 4 h at rt, the resulting mixture was quenched with H_2O at the same temperature and extracted three times with a 1:1 mixture of ethyl acetate and hexane. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (0-15% ethyl acetate/hexane) to give **1h** (5.16 g, 18.7 mmol, 89.0 %) as a pale yellow oil.

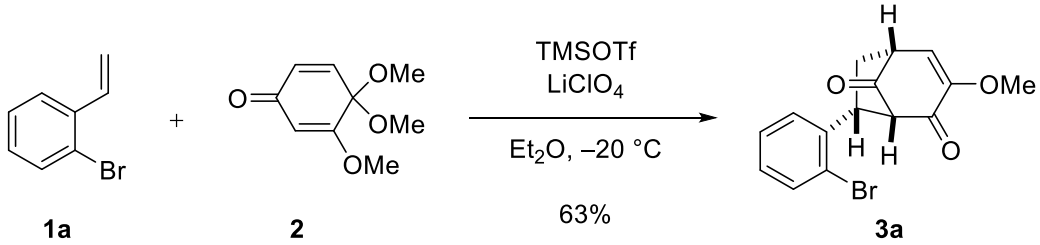
^{1}H NMR ($CDCl_3$): 7.20 (dd, *J* = 7.9, 7.6 Hz, 1H), 7.16 (dd, *J* = 7.9, 1.6 Hz, 1H), 6.75 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.63 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.68 (dd, *J* = 17.4, 0.9 Hz, 1H), 5.28 (dd, *J* = 10.8, 0.9 Hz, 1H), 2.49 (s, 3H), 0.96 (s, 9H), 0.21 (s, 6H)

^{13}C NMR ($CDCl_3$): 205.4 (C), 151.8 (C), 135.6 (C), 133.4 (CH), 133.2 (C), 129.6 (CH), 118.4 (CH), 118.1 (CH), 116.9 (CH), 32.6 (CH_3), 25.6 (CH_3), 18.1 (C), −4.3 (CH_3)

IR (film, cm^{-1}): 2934, 2860, 1705, 1569, 1465, 1354, 1278, 977, 838, 745

HRMS (ESI-QTOF) calcd for $C_{16}H_{24}NaO_2Si^+$ [M + Na^+] 299.1438, found 299.1437

Synthesis of compound 3a

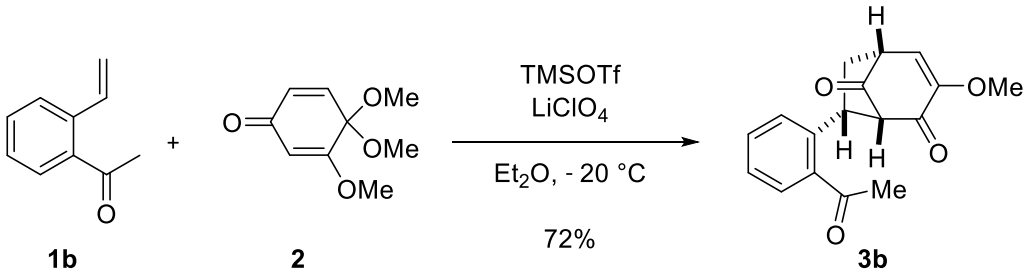


1a **2** **3a**

To a stirred solution of **1a** (70.5 mg, 0.385 mmol) in Et_2O (1.0 mL) were added **2** (35.4 mg, 0.193 mmol), $LiClO_4$ (307 mg, 2.89 mmol), and TMSOTf (38 µL, 0.21 mmol) at −20 °C. After stirring for 10 min at −20 °C, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted four times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel twice (30-60% ethyl acetate/hexane) (100% CH_2Cl_2) to give **3a** (39.2 mg, 0.122 mmol, 63.2%) as an orange foam.

^{1}H NMR ($CDCl_3$): 7.55 (d, *J* = 8.0 Hz, 1H), 7.21 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.07 (dd, *J* = 8.0, 7.8 Hz, 1H), 6.93 (7.8 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 4.35 (ddd, *J* = 10.7, 7.1, 4.6 Hz, 1H), 3.98 (dd, *J* = 7.1, 2.1 Hz, 1H), 3.70 (s, 3H), 3.44 (ddd, *J* = 8.4, 6.3, 2.1 Hz, 1H), 2.72 (ddd, *J* = 13.5, 10.7, 6.3 Hz, 1H), 2.24 (dd, *J* = 13.5, 4.6 Hz, 1H)
^{13}C NMR ($CDCl_3$): 200.3 (C), 198.6 (C), 155.2 (C), 137.6 (C), 133.2 (CH), 128.9 (CH), 128.0 (CH), 127.7 (CH), 126.1 (C), 118.0 (CH), 66.8 (CH), 55.8 (CH_3), 46.5 (CH), 38.3 (CH), 32.6 (CH_3)
IR (film, cm^{-1}): 2936, 1764, 1688, 1605, 1465, 1362, 1217, 1122, 1023, 756
HRMS (ESI-QTOF) calcd for $C_{15}H_{13}BrNaO_3^+$ [M+Na$^+$] 342.9940, found 342.9936

Synthesis of compound 3b



1b **2** **3b**

To a stirred solution of **1b** (90.6 mg, 0.620 mmol) in Et_2O (1.6 mL) were added **2** (57.0 mg, 0.310 mmol), $LiClO_4$ (485 mg, 4.65 mmol), and TMSOTf (61.6 µL, 0.341 mmol) at −20 °C. After stirring for 10 min at −20 °C, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted four times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (40-60% ethyl acetate/hexane) to give **3b** (63.6 mg, 0.224 mmol, 72.2%) as a red foam.

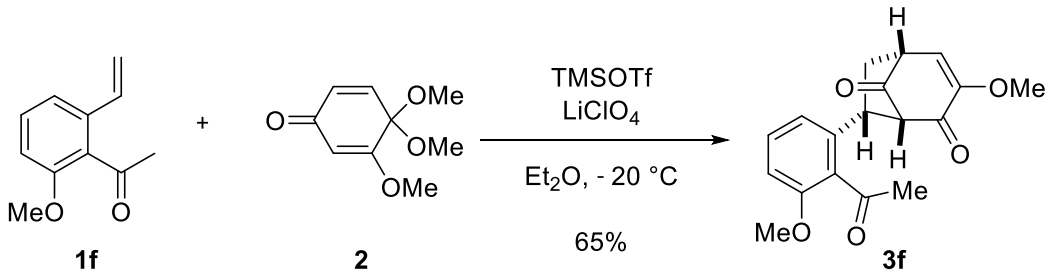
^{1}H NMR ($CDCl_3$): 7.68 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.39 (ddd, *J* = 7.7, 7.6, 1.4 Hz, 1H), 7.30 (ddd, *J* = 7.7, 7.7, 1.1 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.47 (d, *J* = 8.2 Hz, 1H), 4.74 (ddd, *J* = 10.9, 6.9, 6.2 Hz, 1H), 3.96 (dd, *J* = 6.9, 1.9 Hz, 1H), 3.71 (s, 3H), 3.42 (ddd, *J* = 8.2, 6.4, 1.9 Hz, 1H), 2.69 (ddd, *J* = 13.7, 10.9, 6.4 Hz, 1H), 2.63 (s, 3H), 2.26 (dd, *J* = 13.7, 6.2 Hz, 1H)

^{13}C NMR ($CDCl_3$): 202.3 (C), 200.6 (C), 190.1 (C), 155.3 (C), 138.9 (C), 138.2 (C), 131.7 (CH), 129.6 (CH), 128.0 (CH), 127.1 (CH), 118.1 (CH), 68.7 (CH), 55.8 (CH_3), 46.8 (CH), 34.7 (CH), 33.1 (CH_2), 30.0 (CH_3)

IR (film, cm^{-1}): 2360, 1764, 1685, 1604, 1456, 1360, 1248, 1122, 760, 675

HRMS (ESI-QTOF) calcd for $C_{17}H_{16}NaO_4^+$ [M+Na^+] 307.0941, found 307.0951

Synthesis of compound 3f



To a stirred solution of **1f** (33.2 mg, 0.188 mmol) in Et_2O (470 µL) were added **2** (17.3 mg, 0.0942 mmol), $LiClO_4$ (150 mg, 1.41 mmol), and TMSOTf (18.7 µL, 0.104 mmol) at −20 °C. After stirring for 10 min at −20 °C, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted four times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (30-60% ethyl acetate/hexane) to give **3f** (19.2 mg, 0.0611 mmol, 64.8%) as an orange foam.

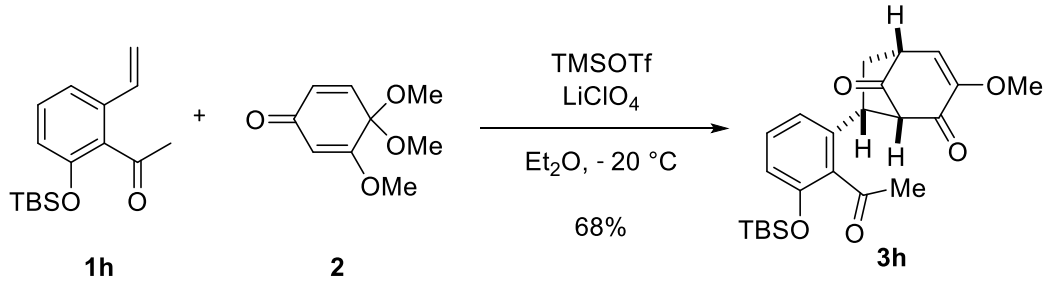
^{1}H NMR ($CDCl_3$): 7.24 (dd, *J* = 8.3, 8.2 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 8.2 Hz, 1H), 6.45 (d, *J* = 8.3 Hz, 1H), 3.97 (ddd, *J* = 10.7, 6.8, 6.1 Hz, 1H), 3.81 (s, 3H), 3.72 (s, 3H), 3.69 (dd, *J* = 6.8, 1.8 Hz, 1H), 3.38 (ddd, *J* = 8.3, 6.4, 1.8 Hz, 1H), 2.68 (ddd, *J* = 13.7, 10.7, 6.4 Hz, 1H), 2.58 (s, 3H), 2.20 (dd, *J* = 13.7, 6.1 Hz, 1H)

^{13}C NMR ($CDCl_3$): 205.8 (C), 200.1 (C), 189.8 (C), 156.4 (C), 155.3 (C), 136,2 (C), 132.2 (C), 130.5 (CH), 119.2 (CH), 118.0 (CH), 110.0 (CH), 68.8 (CH), 55.8 (CH_3), 55.6 (CH_3), 46.4 (CH), 34.8 (CH), 33.2 (CH_2), 32.5 (CH_3)

IR (film, cm^{-1}): 2943, 1763, 1689, 1602, 1466, 1358, 1264, 1078, 1002, 749

HRMS (ESI-QTOF) calcd for $C_{18}H_{18}NaO_5^+$ [M+Na^+] 337.1046, found 337.1043

Synthesis of compound 3h



1h **2** **3h**

To a stirred solution of **1h** (5.26 g, 19.0 mmol) in Et_2O (48 mL) were added **2** (1.75 g, 9.52 mmol), $LiClO_4$ (15.2 g, 143 mmol) and TMSOTf (1.89 mL, 10.5 mmol) at −20 °C. After stirring for 10 min at −20 °C, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted four times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (30-60% ethyl acetate/hexane) to give **3h** (2.69 g, 6.49 mmol, 68.2 %) as a red foam.

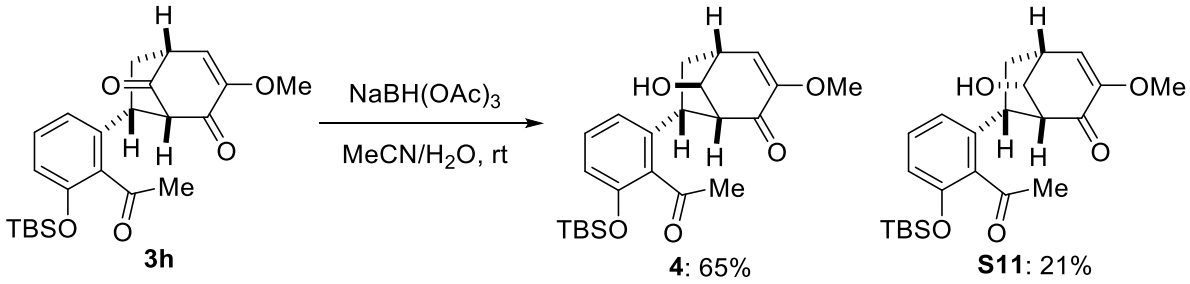
^{1}H NMR ($CDCl_3$): 7.13 (dd, *J* = 8.2, 8.0 Hz, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 6.43 (d, 8.2 Hz, 1H), 3.93 (ddd, *J* = 10.8, 7.3, 5.5 Hz, 1H), 3.71 (s, 3H), 3.67 (dd, *J* = 7.3, 1.8 Hz, 1H), 3.38 (ddd, *J* = 8.2, 6.4, 1.8 Hz, 1H), 2.67 (ddd, *J* = 13.6, 10.8, 6.4 Hz, 1H), 2.54 (s, 3H), 2.20 (dd, *J* = 13.6, 5.5 Hz, 1H), 0.97 (s, 9H), 0.21 (s, 6H)

^{13}C NMR ($CDCl_3$): 206.2 (C), 200.2 (C), 189.7 (C), 155.3 (C), 152.4 (C), 136.3 (C), 135.0 (C), 130.0 (CH), 119.7 (CH), 118.2 (CH), 117.9 (CH), 68.8 (CH), 55.8 (CH_3), 46.5 (CH), 34.8 (CH), 33.2 (CH_2), 32.8 (CH_3), 25.6 (CH_3), 18.1 (C), −4.2 (CH_3), −4.4 (CH_3)

IR (film, cm^{-1}): 2934, 2360, 1765, 1692, 1601, 1463, 1259, 1126, 889, 834

HRMS (ESI-QTOF) calcd for $C_{23}H_{30}NaO_5Si^+$ [M + Na^+] 437.1755, found 437.1743

Synthesis of alcohols 4 and S11



To a stirred solution of **3h** (2.68 g, 6.46 mmol) in MeCN (123.5 mL) and H_2O (6.5 mL) was added $NaBH(OAc)_3$ (4.11 g, 19.4 mmol) at rt. After stirring for 12 h at rt, the resulting mixture was quenched with H_2O at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (50-70% ethyl acetate/hexane) to give **4** (1.75 g, 4.20 mmol, 65.0 %) as a pink foam and its diastereomer **S11** (573 mg, 1.37 mmol, 21.3%) as a pink foam, respectively.

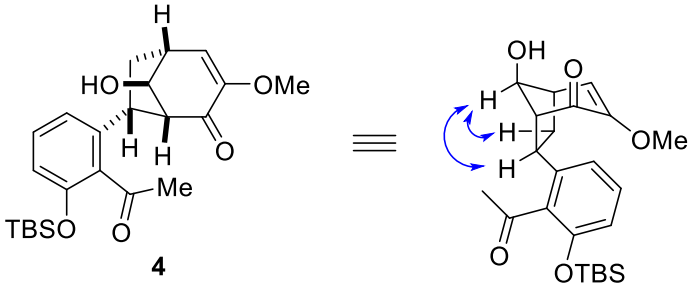
Data for alcohol **4**

^{1}H NMR ($CDCl_3$): 7.08 (dd, *J* = 8.0, 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 6.57 (d, *J* = 8.0 Hz, 1H), 5.98 (dd *J* = 7.3, 1.1 Hz, 1H), 4.35 (ddd, *J* = 6.6, 4.5, 1.1 Hz, 1H), 3.81 (ddd, *J* = 10.5, 5.0, 4.8 Hz, 1H), 3.68 (s, 3H), 3.16 (ddd, *J* = 6.6, 4.8, 1.4 Hz, 1H), 3.06 (dddd, *J* = 7.3, 5.9, 4.5, 1.4 Hz, 1H), 2.59 (s, 3H), 2.49 (ddd, *J* = 13.7, 10.5, 5.9 Hz, 1H), 2.08 (dd, *J* = 13.7, 5.0 Hz, 1H), 0.95 (s, 9H), 0.20 (s, 3H), 0.16 (s, 3H)

^{13}C NMR ($CDCl_3$): 207.0 (C), 193.2 (C), 154.1 (C), 152.0 (C), 137.4 (C), 134.5 (C), 129.7 (CH), 119.7 (CH), 117.5 (CH), 114.8 (CH), 79.7 (CH), 62.2 (CH), 55.1 (CH_3), 40.6 (CH), 36.5 (CH), 34.2 (CH_2), 32.9 (CH_3), 25.6 (CH_3), 18.1 (C), −4.2 (CH_3), −4.4 (CH_3)

IR (film, cm^{-1}): 3445, 2954, 2361, 1691, 1577, 1464, 1259, 1128, 897, 838

HRMS (ESI-QTOF) calcd for $C_{23}H_{32}NaO_5Si^+$ [M + Na^+] 439.1911, found 439.1905



Selected NOESY correlation of **4**

Data for alcohol **S11**

^{1}H NMR ($CDCl_3$): 7.06 (dd, *J* = 8.2, 7.8 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.21 (d, *J* = 7.8 Hz, 1H), 4.14 (m, 1H), 4.00 (ddd, *J* = 10.5, 6.7, 4.4 Hz, 1H), 3.64 (s, 3H), 3.21 (d, *J* = 6.7 Hz, 1H), 2.98 (dd, *J* = 7.8, 6.1 Hz, 1H), 2.71 (ddd, *J* = 13.2, 10.5, 6.1 Hz, 1H), 2.59 (s, 3H), 2.49 (br, 1H), 2.00 (dd, *J* = 13.2, 4.4 Hz, 1H), 0.95 (s, 9H),

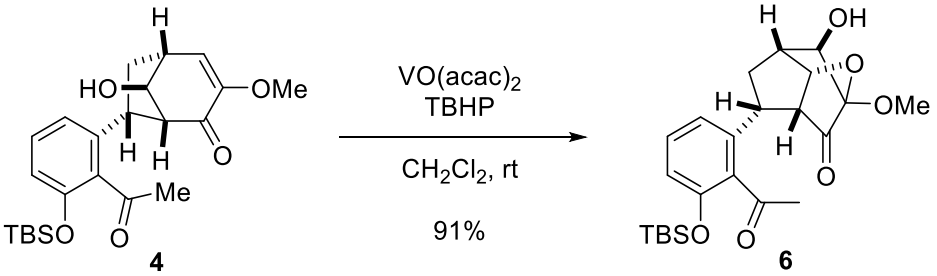
0.19 (s, 3H), 0.18 (s, 3H)

^{13}C NMR ($CDCl_3$): 206.8 (C), 194.3 (C), 154.3 (C), 151.9 (C), 137.6 (C), 134.8 (C), 129.6 (CH), 120.1 (CH), 119.8 (CH), 117.2 (CH), 79.0 (CH), 65.2 (CH), 55.3 (CH_3), 42.9 (CH), 38.1 (CH), 34.2 (CH_2), 32.9 (CH_3), 25.6 (CH_3), 18.1 (C), −4.3 (CH_3), −4.4 (CH_3)

IR (film, cm^{-1}): 3449, 2954, 1691, 1615, 1463, 1257, 1126, 1057, 896, 835

HRMS (ESI-QTOF) calcd for $C_{23}H_{32}NaO_5Si^+$ [M+Na^+] 439.1911, found 439.1926

Synthesis of alcohol 6



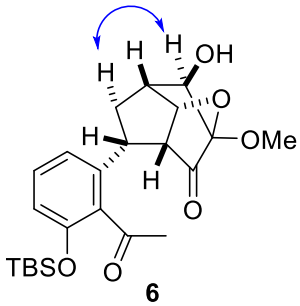
To a stirred solution of **4** (1.69 g, 4.06 mmol) in CH_2Cl_2 (41 mL) were added $VO(acac)_2$ (108 mg, 0.406 mmol) and 70% TBHP solution in H_2O (783 mL, 6.09 mmol) at rt. After stirring for 3 h at rt, the resulting mixture was quenched with aqueous $Na_2S_2O_3$ at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (40-60% ethyl acetate/hexane) to give **6** (1.60 g, 3.70 mmol, 91.1 %) as a yellow foam.

^{1}H NMR ($CDCl_3$): 7.20 (dd, *J* = 8.2, 8.0 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 5.15 (dd, *J* = 6.2, 5.5 Hz, 1H), 3.73 (d, *J* = 3.2 Hz, 1H), 3.51 (s, 3H), 3.43 (ddd, *J* = 10.9, 8.4, 7.4 Hz, 1H), 2.77 (dd *J* = 7.4, 5.5 Hz, 1H), 2.72 (dd, *J* = 8.3, 6.2 Hz, 1H), 2.52 (s, 3H), 2.47 (m, 1H), 2.26 (d, *J* = 3.2 Hz, 1H), 2.11 (dd, *J* = 14.7, 8.4 Hz, 1H), 0.96 (s, 9H), 0.22 (s, 3H), 0.21 (s, 3H)

^{13}C NMR ($CDCl_3$): 208.3 (C), 206.5 (C), 152.0 (C), 136.3 (C), 134.2 (C), 129.3 (CH), 120.3 (CH), 117.7 (CH), 108.2 (C), 80.2 (CH), 77.2 (CH), 55.4 (CH), 54.6 (CH_3), 49.5 (CH), 41.4 (CH), 33.8 (CH_2), 32.8 (CH_3), 25.6 (CH_3), 18.1 (C), −4.3 (CH_3)

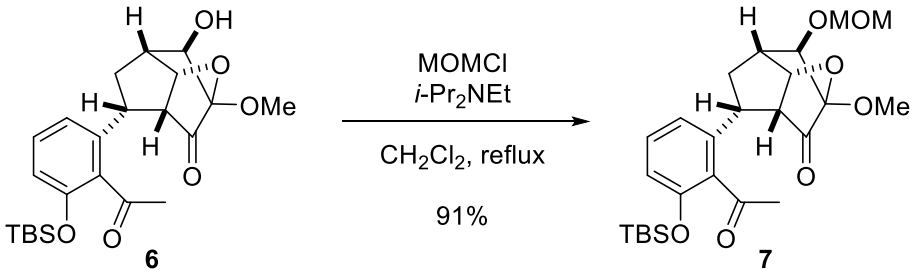
IR (film, cm^{-1}): 2954, 2360, 1766, 1696, 1578, 1464, 1278, 1154, 995, 834

HRMS (ESI-QTOF) calcd for $C_{23}H_{32}NaO_6Si^+$ [M + Na^+] 455.1860, found 455.1860



Selected NOESY correlation of **6**

Synthesis of MOM ether 7



To a stirred solution of **6** (1.56 g, 3.61 mmol) in CH_2Cl_2 (14.5 mL) were added *i*-Pr_2NEt (1.26 mL, 7.21 mmol) and MOMCl (411 μL, 5.41 mmol) at rt. After stirring for 8 h at reflux, the resulting mixture was quenched with H_2O at rt and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-50% ethyl acetate/hexane) to give **7** (1.56 g, 3.27 mmol, 90.7 %) as a yellow foam.

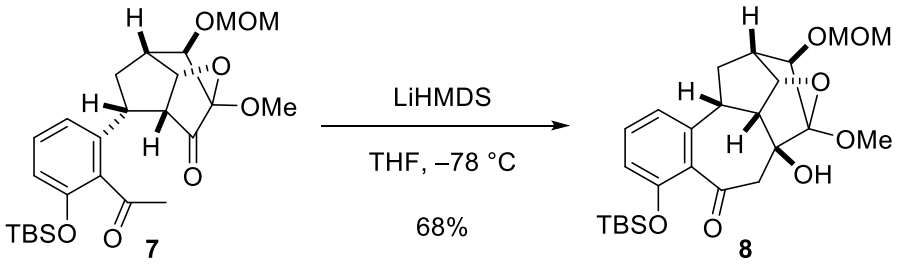
^{1}H NMR ($CDCl_3$): 7.21 (dd, *J* = 8.5, 8.0 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 8.0 Hz, 1H), 5.16 (dd, *J* = 6.2, 5.7 Hz, 1H), 4.85 (d, *J* = 6.7 Hz, 1H), 4.72 (d, *J* = 6.7 Hz, 1H), 3.72 (s, 1H), 3.48 (s, 3H), 3.46 (m, 1H), 3.41 (s, 3H), 2.77 (dd, *J* = 8.7, 6.2 Hz, 1H), 2.72 (dd, *J* = 7.3, 5.7 Hz, 1H), 2.51 (s, 3H), 2.49 (m, 1H), 2.13 (dd, *J* = 14.9, 8.9 Hz, 1H), 0.96 (s, 9H), 0.22 (s, 6H)

^{13}C NMR ($CDCl_3$): 208.9 (C), 206.5 (C), 152.0 (C), 136.3 (C), 134.1 (C), 129.4 (CH), 120.4 (CH), 117.7 (CH), 108.7 (C), 95.9 (CH_2), 80.1 (CH), 79.9 (CH), 55.7 (CH_3), 55.3 (CH), 54.5 (CH_3), 48.9 (CH), 41.7 (CH), 34.0 (CH_2), 32.8 (CH_3), 25.6 (CH_3), 18.1 (C), −4.3 (CH_3)

IR (film, cm^{-1}): 2952, 1767, 1697, 1577, 1464, 1279, 1152, 1103, 1029, 834

HRMS (ESI-QTOF) calcd for $C_{25}H_{36}NaO_7Si^+$ [M + Na^+] 499.2123, found 499.2108

Synthesis of β-hydroxyketone 8



To a stirred solution of **7** (273 mg, 0.573 mmol) in THF (5.7 mL) was added LiHMDS (0.72 M in THF, 2.39 mL, 1.72 mmol) at −78 °C. After stirring for 12 h at −78 °C, the resulting mixture was quenched with aqueous NH_4Cl at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (40-60% ethyl acetate/hexane) to give **8** (186 mg, 0.390 mmol, 68.1 %) as a yellow foam.

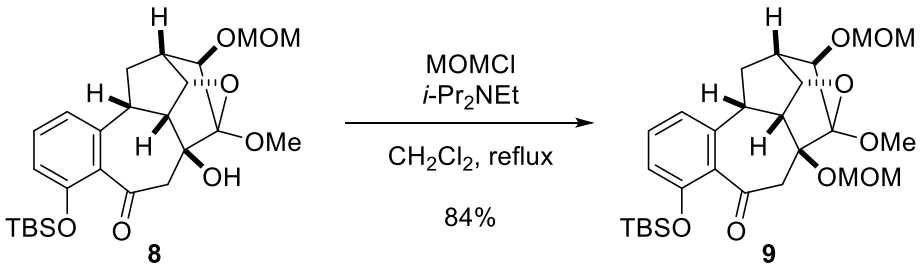
^{1}H NMR ($CDCl_3$): 7.17 (dd, *J* = 8.2, 7.8 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 4.86 (dd, *J* = 5.5, 5.0 Hz, 1H), 4.74 (d, *J* = 6.9 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 3.84 (s, 3H), 3.81 (s, 1H), 3.48 (ddd, *J* = 11.1, 9.9, 5.5 Hz, 1H), 3.38 (s, 3H), 3.17 (d, *J* = 11.5 Hz, 1H), 2.79 (s, 1H), 2.72 (dd, *J* = 5.5, 5.0 Hz, 1H), 2.65 (d, *J* = 11.5 Hz, 1H), 2.62-2.51 (m, 2H), 1.85 (dd, *J* = 13.5, 11.1 Hz), 0.96 (s, 9H), 0.26 (s, 3H), 0.18 (s, 3H)

^{13}C NMR ($CDCl_3$): 197.4 (C), 153.4 (C), 141.4 (C), 131.3 (CH), 130.6 (C), 123.1 (CH), 118.8 (CH), 110.4 (C), 95.1 (CH_2), 82.8 (CH), 80.1 (CH), 78.0 (C), 56.0 (CH_3), 55.7 (CH), 55.6 (CH_3), 49.3 (CH_2), 47.9 (CH), 44.9 (CH), 36.7 (CH_2), 25.7 (CH_3), 18.2 (C), −4.4 (CH_3), −4.4 (CH_3)

IR (film, cm^{-1}): 2952, 1695, 1583, 1457, 1285, 1151, 1034, 890, 837, 785

HRMS (ESI-QTOF) calcd for $C_{25}H_{37}NaO_7Si^+$ [M + Na^+] 499.2123, found 499.2105

Synthesis of MOM ether 9



To a stirred solution of **8** (130 mg, 0.273 mmol) in CH_2Cl_2 (2.4 mL) were added MOMCl (83.0 µL, 1.09 mmol) and *i*-Pr_2NEt (190 µL, 1.09 mmol) at rt. After stirring for 14 h at reflux, the resulting mixture was quenched with H_2O at rt and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (30-40% ethyl acetate/hexane) to give **9** (120 mg, 0.230 mmol, 84.4 %) as a yellow foam.

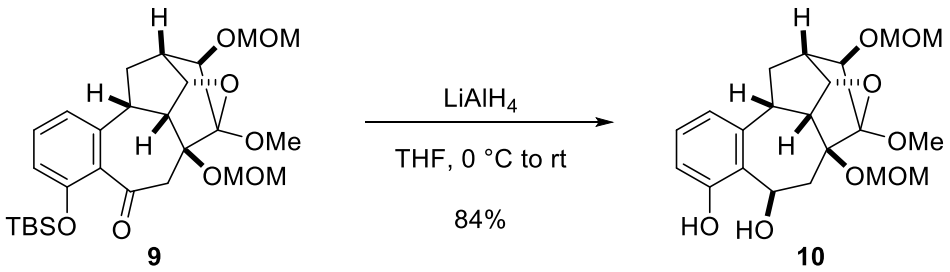
^{1}H NMR ($CDCl_3$): 7.17 (dd, *J* = 8.1, 7.5 Hz, 1H), 6.75 (dd, *J* = 8.1, 0.9 Hz, 1H), 6.72 (d, *J* = 7.5 Hz, 1H), 5.17 (d, *J* = 7.3 Hz, 1H), 4.85 (dd, *J* = 5.5, 5.5 Hz, 1H), 4.80 (d, *J* = 7.3 Hz, 1H), 4.77 (d, *J* = 6.8 Hz, 1H), 4.67 (d, *J* = 6.8 Hz, 1H), 3.77 (s, 3H), 3.74 (s, 1H), 3.49 (ddd, *J* = 10.1, 5.5, 5.5 Hz, 1H), 3.37 (s, 3H), 3.35 (s, 3H), 3.22 (dd, *J* = 5.5, 5.5 Hz, 1H), 3.12 (d, *J* = 12.1 Hz, 1H), 3.01 (d, *J* = 12.1 Hz, 1H), 2.58-2.46 (m, 2H), 1.81 (dd, *J* = 13.7, 10.1 Hz, 1H), 0.98 (s, 9H), 0.22 (s, 3H), 0.18 (s, 3H)

^{13}C NMR ($CDCl_3$): 197.0 (C), 153.3 (C), 141.1 (C), 131.1 (CH), 131.1 (C), 123.1 (CH), 119.3 (CH), 112.3 (C), 95.6 (CH_2), 92.9 (CH_2), 82.6 (C), 82.5 (CH), 80.1 (CH), 55.8 (CH_3), 55.6 (CH_3), 55.2 (CH_3), 52.4 (CH), 48.2 (CH), 47.9 (CH_2), 45.7 (CH), 36.9 (CH_2), 25.7 (CH_3), 18.2 (C), −4.3 (CH_3), −4.4 (CH_3)

IR (film, cm^{-1}): 2951, 1696, 1584, 1464, 1286, 1152, 1027, 891, 837, 785

HRMS (ESI-QTOF) calcd for $C_{27}H_{40}NaO_8Si^+$ [M + Na^+] 543.2385, found 543.2373

Synthesis of alcohol 10



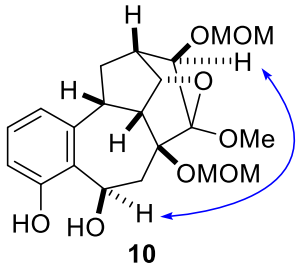
To a stirred solution of **9** (694 mg, 1.33 mmol) in THF (13.3 mL) was added $LiAlH_4$ (101 mg, 2.67 mmol) at 0 °C. After stirring for 90 min at rt, the resulting mixture was quenched with aqueous Rochel salt at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (40-70% ethyl acetate/hexane) to give **10** (456 mg, 1.12 mmol, 83.9 %) as a pale yellow foam.

^{1}H NMR ($CDCl_3$): 7.46 (s, 1H), 7.09 (dd, *J* = 8.1, 7.6 Hz, 1H), 6.83 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.60 (d, *J* = 7.6 Hz, 1H), 5.19 (m, 1H), 5.17 (d, *J* = 6.7 Hz, 1H), 5.09 (d, *J* = 8.2 Hz, 1H), 4.96 (d, *J* = 6.7 Hz, 1H), 4.80 (dd, *J* = 5.5, 5.5 Hz, 1H), 4.74 (d, *J* = 6.9 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 3.85 (s, 1H), 3.79 (s, 3H), 3.40 (s, 3H), 3.38 (s, 3H), 3.34 (m, 1H), 3.16 (dd, *J* = 5.5, 5.0 Hz, 1H), 2.66 (dd, *J* = 15.6, 5.0 Hz, 1H), 2.56-2.46 (m, 2H), 2.29 (dd, *J* = 15.6, 2.7 Hz, 1H), 1.80 (dd, *J* = 12.8, 10.0 Hz, 1H)

^{13}C NMR ($CDCl_3$):157.7 (C), 137.6 (C), 128.7 (CH), 126.9 (C), 123.7 (CH), 115.3 (CH), 111.6 (C), 94.9 (CH_2), 92.9 (CH_2), 84.5 (C), 82.8 (CH), 79.3 (CH), 68.1 (CH), 56.5 (CH_3), 55.7 (CH_3), 55.0 (CH_3), 53.9 (CH), 47.4 (CH), 45.1 (CH), 35.7 (CH_2), 33.2 (CH_2)

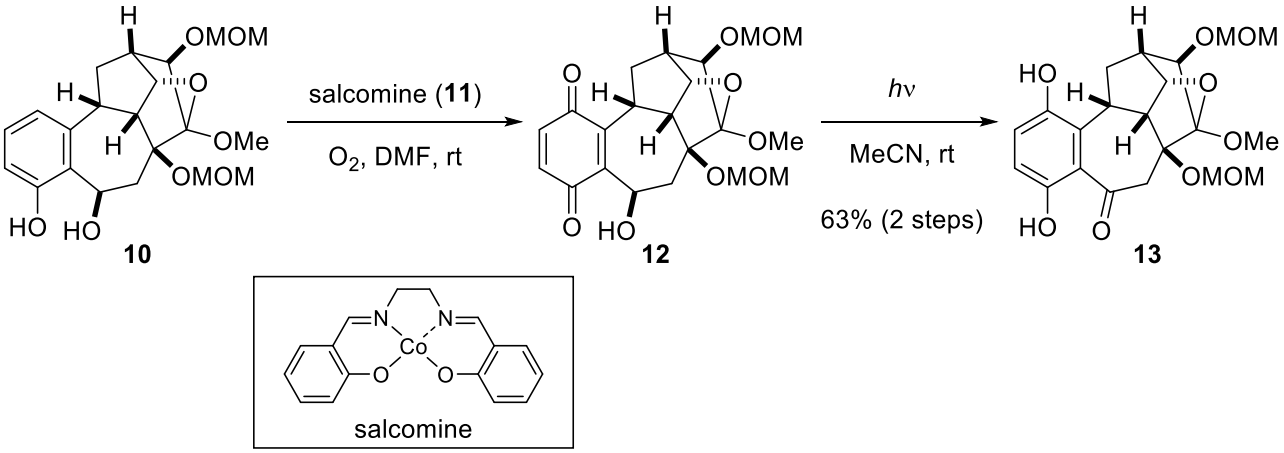
IR (film, cm^{-1}): 3415, 2950, 2361, 1585, 1459, 1281, 1151, 1018, 921, 753

HRMS (ESI-QTOF) calcd for $C_{21}H_{28}NaO_8^+$ [M + Na^+] 431.1676, found 431.1663



Selected NOESY correlation of **10**

Synthesis of hydroquinone 13

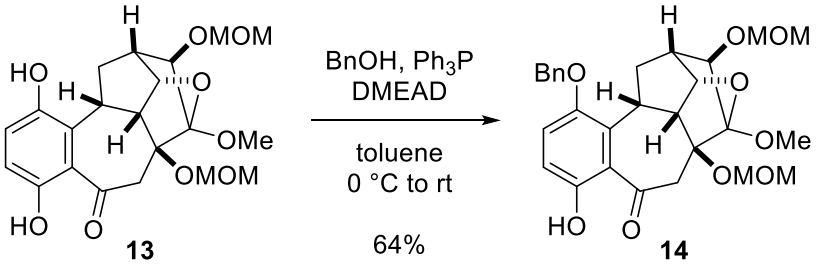


To a stirred solution of **10** (1.14 g, 2.79 mmol) in DMF (14 mL) was added salcomine **11** (227 mg, 0.698 mmol) and then oxygen gas was purged at rt. After stirring for 13 h at rt, the resulting mixture was quenched with H_2O at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated to give the crude product of **12**. This was used for the next reaction without further purification.

A solution of the residue in MeCN (280 mL) was irradiated with a Hg lamp at rt. After stirring for 3 h, the solution was concentrated. The residue was purified by flash column chromatography on silica gel (40-70% ethyl acetate/hexane) to give **13** (744 mg, 1.76 mmol, 63.1 %) as a yellow foam.

^{1}H NMR ($CDCl_3$): 12.01 (s, 1H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.77 (d, *J* = 8.7 Hz, 1H), 5.28 (d, *J* = 6.9 Hz, 1H), 5.22 (br, 1H), 4.82 (dd, *J* = 6.4, 5.5 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 3.82 (ddd, *J* = 11.6, 10.8, 4.6 Hz, 1H), 3.78 (s, 3H), 3.70 (s, 1H), 3.41 (s, 3H), 3.31 (s, 3H), 3.22 (dd, *J* = 5.5, 4.6 Hz, 1H), 3.03 (d, *J* = 12.2 Hz, 1H), 2.95 (d, *J* = 12.2 Hz, 1H), 2.81 (ddd, *J* = 14.1, 11.6, 9.1 Hz, 1H), 2.54 (dd, *J* = 6.4, 9.1 Hz, 1H), 1.71 (dd, *J* = 14.1, 10.8 Hz, 1H)
^{13}C NMR ($CDCl_3$): 202.7 (C), 156.3 (C), 146.6 (C), 127.9 (C), 123.3 (CH), 120.5 (C), 117.2 (CH), 111.7 (C), 95.0 (CH_2), 92.7 (CH_2), 83.0 (C), 82.8 (CH), 79.3 (CH), 55.7 (CH_3), 55.7 (CH_3), 55.2 (CH_3), 52.2 (CH), 47.6 (CH_2), 47.6 (CH), 38.6 (CH), 33.4 (CH_2)
IR (film, cm^{-1}): 3363, 2953, 1637, 1462, 1291, 1205, 1150, 1025, 919, 756
HRMS (ESI-QTOF) calcd for $C_{21}H_{26}NaO_9^+$ [M + Na^+] 445.1469, found 445.1451

Synthesis of benzyl ether 14



To a stirred solution of **13** (440 mg, 1.04 mmol) in toluene (10.5 mL) were added BnOH (130 µL, 1.25 mmol), PPh_3 (328 mg, 1.25 mmol) and DMEAD (293 mg, 1.25 mmol) at 0 °C. After stirring for 1.5 h at rt, the resulting mixture was quenched with H_2O at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (20-50% ethyl acetate/hexane) to give **14** (340 mg, 0.663 mmol, 63.7 %) as a yellow foam.

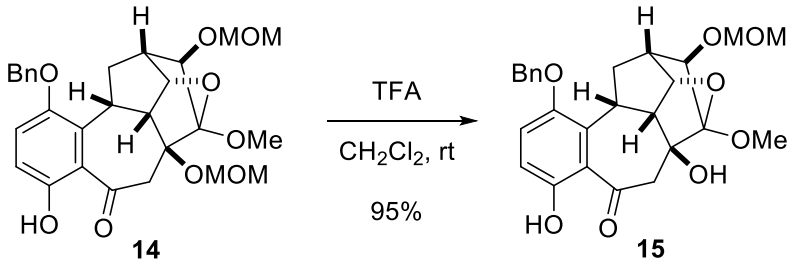
^{1}H NMR ($CDCl_3$): 12.03 (s, 1H), 7.43-7.34 (m, 5H), 7.10 (d, *J* = 9.2 Hz, 1H), 6.85 (d, *J* = 9.2 Hz, 1H), 5.28 (d, *J* = 7.3 Hz, 1H), 5.08 (d, *J* = 11.7 Hz, 1H), 4.99 (d, *J* = 11.7 Hz, 1H), 4.80 (dd, *J* = 6.7, 5.5 Hz, 1H), 4.77 (d, *J* = 6.9 Hz, 1H), 4.75 (d, *J* = 7.3 Hz, 1H), 4.67 (d, *J* = 6.9 Hz, 1H), 3.93 (ddd, *J* = 11.6, 10.5, 5.6 Hz, 1H), 3.77 (s, 3H), 3.72 (s, 1H), 3.38 (s, 3H), 3.29 (s, 3H), 3.22 (dd, *J* = 5.6, 5.5 Hz, 1H), 3.13 (d, *J* = 11.9 Hz, 1H), 2.99 (d, *J* = 11.9 Hz, 1H), 2.79 (ddd, *J* = 14.3, 11.6, 8.8 Hz, 1H), 2.52 (dd, *J* = 8.8, 6.7 Hz, 1H), 1.79 (dd, *J* = 14.3, 10.5 Hz, 1H)

^{13}C NMR ($CDCl_3$): 203.0 (C), 156.3 (C), 149.6 (C), 136.8 (C), 130.9 (CH), 128.7 (CH), 128.1 (CH), 127.3 (CH), 120.8 (C), 120.7 (CH), 116.9 (CH), 111.8 (C), 95.2 (CH_2), 92.8 (CH_2), 82.8 (C), 82.7 (CH), 79.2 (CH), 71.4 (CH_2), 55.6 (CH_3), 55.6 (CH_3), 55.3 (CH_3), 52.3 (CH), 47.7 (CH), 47.7 (CH_2), 38.7 (CH), 33.6 (CH_2)

IR (film, cm^{-1}): 2952, 1640, 1457, 1380, 1290, 1214, 1150, 1027, 916, 750

HRMS (ESI-QTOF) calcd for $C_{28}H_{32}NaO_9^+$ [M + Na^+] 535.1939, found 535.1935

Synthesis of alcohol 15



To a stirred solution of **14** (307 mg, 0.599 mmol) in CH_2Cl_2 (5.7 mL) was added TFA (300 µL) at rt. After stirring for 30 min, the resulting mixture was quenched with aqueous $NaHCO_3$ at the same temperature and extracted three times with CH_2Cl_2. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (30-60% ethyl acetate/hexane) to give **15** (266 mg, 0.568 mmol, 94.8 %) as a yellow foam.

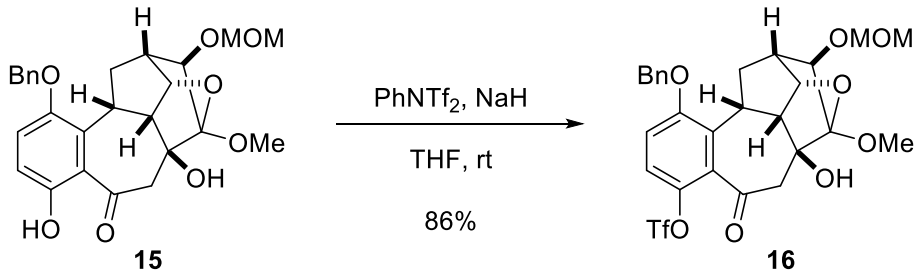
^{1}H NMR ($CDCl_3$): 11.79 (s, 1H), 7.43-7.34 (m, 5H), 7.10 (d, *J* = 9.1 Hz, 1H), 6.85 (d, *J* = 9.1 Hz, 1H), 5.07 (d, *J* = 11.7 Hz, 1H), 4.99 (d, *J* = 11.7 Hz, 1H), 4.83 (dd, *J* = 6.9, 5.0 Hz, 1H), 4.72 (d, *J* = 6.8 Hz, 1H), 4.70 (d, *J* = 6.8 Hz, 1H), 3.85 (s, 3H), 3.82 (s, 1H), 3.81 (m, 1H), 3.40 (s, 3H), 3.21 (d, *J* = 11.7 Hz, 1H), 2.81 (ddd, *J* = 14.5, 11.4, 8.9 Hz, 1H), 2.76 (s, 1H), 2.71 (d, *J* = 11.7 Hz, 1H), 2.62 (dd, *J* = 5.0, 5.0 Hz, 1H), 2.56 (dd, *J* = 8.9, 6.9 Hz, 1H), 1.79 (dd, *J* = 14.5, 10.3 Hz, 1H)

^{13}C NMR ($CDCl_3$): 203.0 (C), 155.9 (C), 149.6 (C), 136.8 (C), 130.7 (C), 128.7 (C), 128.2 (CH), 127.3 (CH), 121.0 (C), 120.7 (CH), 117.0 (CH), 109.9 (C), 94.7 (CH_2), 82.9 (CH), 79.5 (CH), 78.3 (C), 71.5 (CH_2), 56.0 (CH_3), 55.7 (CH_3), 55.5 (CH), 49.4 (CH_2), 47.7 (CH), 38.1 (CH), 33.3 (CH_2)

IR (film, cm^{-1}): 3489, 2952, 1640, 1457, 1288, 1217, 1145, 1029, 749, 547

HRMS (ESI-QTOF) calcd for $C_{26}H_{28}NaO_8^+$ [M + Na^+] 491.1676, found 491.1670

Synthesis of triflate 16



To a stirred solution of **15** (243 mg, 0.517 mmol) in THF (5.2 mL) were added $PhNTf_2$ (278 mg 0.778 mmol) and NaH (55%, dispersion in paraffin liquid, 27.2 mg, 0.622 mmol) at rt. After stirring for 2 h at rt, the resulting mixture was quenched with 1N HCl at the same temperature and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel (30-60% ethyl acetate/hexane) to give **16** (267 mg, 0.445 mmol, 86.0 %) as a pale yellow foam.

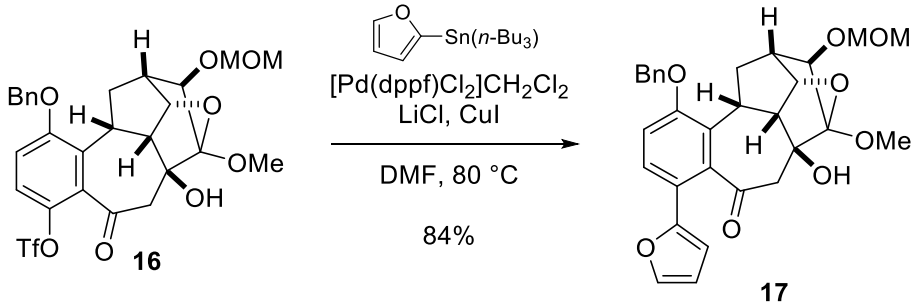
^{1}H NMR ($CDCl_3$): 7.46-7.36 (m, 5H), 7.13 (d, *J* = 9.2 Hz, 1H), 7.00 (d, *J* = 9.2 Hz, 1H), 5.13 (d, *J* = 11.9 Hz, 1H), 5.08 (d, *J* = 11.9 Hz, 1H), 4.87 (dd, *J* = 6.8, 5.0 Hz, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.69 (d, *J* = 6.9 Hz, 1H), 3.87 (m, 1H), 3.84 (s, 3H), 3.81 (s, 1H), 3.39 (s, 3H), 3.21 (d, *J* = 11.2 Hz, 1H), 2.83 (ddd, *J* = 14.2, 11.3, 9.2 Hz, 1H), 2.74-2.69 (m, 2H), 2.72 (d, 11.2 Hz, 1H), 2.54 (dd, *J* = 9.2, 6.8 Hz, 1H), 1.71 (dd, *J* = 14.2, 10.7 Hz, 1H)

^{13}C NMR ($CDCl_3$): 195.1 (C), 155.9 (C), 139.2 (C), 135.6 (C), 132.9 (C), 131.6 (C), 128.9 (CH), 128.6 (CH), 127.4 (CH), 121.7 (CH),118.6 (CF_3, q, *J* = 318.5 Hz) 114.1 (CH), 110.1 (C), 94.8 (CH_2), 82.7 (CH), 79.8 (CH), 78.2 (C), 71.1 (CH_2), 56.0 (CH_3), 55.7 (CH_3), 55.3 (CH), 48.9 (CH_2), 47.7 (CH), 38.0 (CH), 33.8 (CH_2)

IR (film, cm^{-1}): 2953, 1703, 1597, 1423, 1213, 1142, 1030, 873, 753, 591

HRMS (ESI-QTOF) calcd for $C_{27}H_{27}F_3NaO_{10}^+$ [M + Na^+] 623.1169, found 623.1144

Synthesis of furan 17



To a stirred solution of **16** (245 mg, 0.408 mmol) in DMF (2.1 mL) were added tributyl(2-furyl)tin (190 µL, 0.612 mmol), LiCl (52.0 mg, 1.22 mmol), CuI (117 mg, 0.612 mmol) and $[Pd(dppf)Cl_2]CH_2Cl_2$ (66.6 mg, 0.0816 mmol) at rt. After stirring for 1 h at 80 °C, the resulting mixture was quenched with H_2O at rt and extracted three times with ethyl acetate. The combined organic layer was dried over Na_2SO_4, filtrated, and concentrated. The residue was purified by flash column chromatography on silica gel and K_2CO_3 (40-70% ethyl acetate/hexane) to give **17** (179 mg, 0.344 mmol, 84.4 %) as an orange foam.

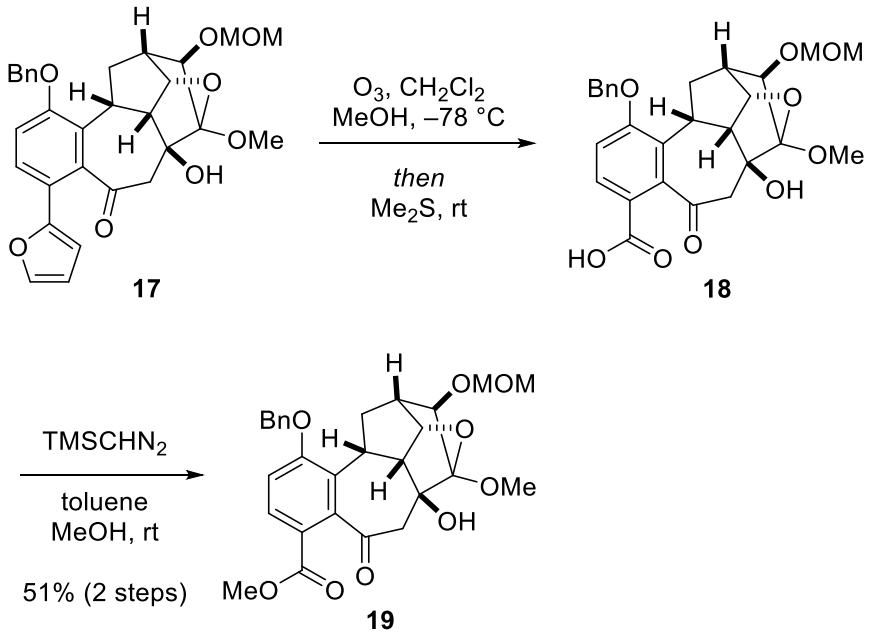
^{1}H NMR ($CDCl_3$): 7.44-7.33 (m, 7H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.41-6.38 (m, 2H), 5.13 (d, *J* = 11.9 Hz, 1H), 5.09 (d, *J* = 11.9 H, 1H), 4.86 (dd, *J* = 6.4, 5.3 Hz, 1H), 4.74 (d, *J* = 6.6 Hz, 1H), 4.69 (d, *J* = 6.6 Hz, 1H), 3.94 (ddd, *J* = 11.3, 10.5, 5.7 Hz, 1H), 3.86 (s, 1H), 3.84 (s, 3H), 3.40 (d, *J* = 11.2 Hz, 1H), 3.38 (s, 3H), 2.87 (s, 1H), 2.82 (d, *J* = 11.2 Hz, 1H), 2.77 (ddd, *J* = 14.3, 11.3, 9.0 Hz, 1H), 2.65 (dd, *J* = 5.7, 5.3 Hz, 1H), 2.52 (dd, *J* = 9.0, 6.4 Hz, 1H), 1.69 (dd, *J* = 14.3, 10.5 Hz, 1H)

^{13}C NMR ($CDCl_3$): 201.2 (C), 156.0 (C), 153.1 (C), 141.9 (CH), 139.0 (C), 126.3 (C), 129.2 (CH), 128.8 (C), 128.8 (CH), 128.2 (CH), 127.3 (CH), 122.2 (C), 113.2 (CH), 111.2 (CH), 110.5 (C), 107.1 (CH), 95.0 (CH_2), 82.7 (CH), 80.0 (CH), 78.1 (C), 70.7 (CH_2), 56.2 (CH), 56.0 (CH_3), 55.6 (CH_3), 48.2 (CH_2), 48.0 (CH), 37.2 (CH), 34.4 (CH_2)

IR (film, cm^{-1}): 2952, 1699, 1573, 1450, 1284, 1150, 1030, 914, 815, 749

HRMS (ESI-QTOF) calcd for $C_{30}H_{30}NaO_8^+$ [M + Na^+] 541.1833, found 541.1823

Synthesis of methyl ester 19



A stirred solution of **17** (28.8 mg, 0.0555 mmol) in CH_2Cl_2 (420 µL) and MeOH (140 µL) was bubbled with ozone gas at −78 °C. After the starting material was consumed completely, argon gas was then passed through the mixture until the disappearance of the blue color. Then the reaction mixture was added to Me_2S (20.5 µL, 0.278 mmol) at −78 °C. After stirring for 1 h at rt, the resulting mixture was concentrated to give the crude product of **18**. This was used for the next reaction without further purification.

To a stirred solution of the residue in toluene (330 µL) and MeOH (220 µL) was added $TMSCHN_2$ (0.6 M in hexane, 185 µL, 0.111 mmol) at rt. After stirring for 40 min at rt, the resulting mixture was quenched with AcOH at the same temperature and concentrated. The residue was purified by pTLC (60% ethyl acetate/hexane) to give **19** (14.4 mg, 0.0282 mmol, 50.8%) as a yellow foam.

^{1}H NMR ($CDCl_3$): 7.49 (d, *J* = 8.3 Hz, 1H), 7.44-7.36 (m, 5H), 6.96 (d, *J* = 8.3 Hz, 1H), 5.14 (d, *J* = 11.9 Hz, 1H), 5.09 (d, *J* = 11.9 Hz, 1H), 4.86 (dd, *J* = 6.2, 5.5 Hz, 1H), 4.73 (d, *J* = 6.9 Hz, 1H), 4.69 (d, *J* = 6.9 Hz, 1H), 3.90 (m, 1H), 3.87 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.39 (s, 3H), 3.37 (d, *J* = 11.4 Hz, 1H), 2.81 (d, *J* = 11.4 Hz, 1H), 2.81 (s, 1H), 2.74 (ddd, *J* = 14.1, 11.6, 9.0 Hz, 1H), 2.64 (dd, *J* = 5.5, 5.0 Hz, 1H), 2.53 (dd, *J* = 9.0, 6.2 Hz, 1H), 1.69 (dd, *J* = 14.1, 10.5 Hz, 1H)

^{13}C NMR ($CDCl_3$): 199.6 (C), 160.1 (C), 158.0 (C), 140.7 (C), 135.8 (C), 129.2 (C), 128.9 (CH), 128.8 (CH), 128.4 (CH), 127.4 (CH), 124.9 (C), 112.6 (CH), 110.4 (C), 94.9 (CH_2), 82.7 (CH), 79.9 (CH), 77.9 (C), 70.8 (CH_2), 56.0 (CH_3), 56.0 (CH), 55.7 (CH_3), 52.5 (CH_3), 48.0 (CH), 47.8 (CH_2), 37.0 (CH), 34.1 (CH_2)

IR (film, cm^{-1}): 2951, 2361, 1724, 1579, 1457, 1236, 1146, 1031, 914, 751

HRMS (ESI-QTOF) calcd for $C_{28}H_{30}NaO_9^+$ [M + Na^+] 533.1782, found 533.1771

References for Supporting Information

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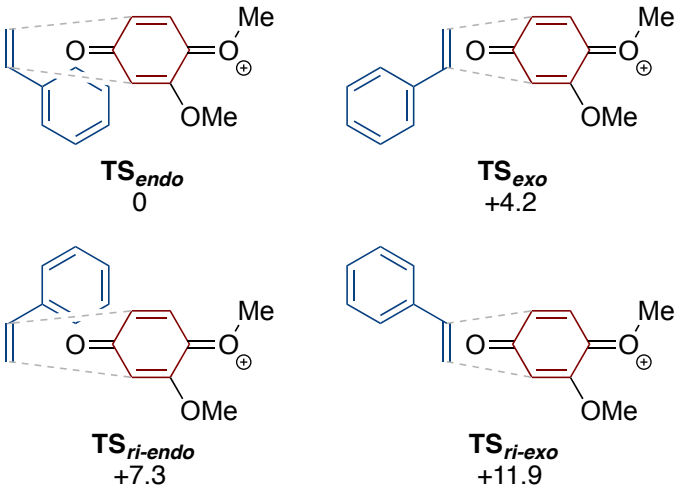
4. Tamura, Y.; Yakura, T.; Haruta, J.; Kita, Y. *J*. *Org*. *Chem*. **1987**, *17*, 3927.

5. Jarrige, L.; Carboni, A.; Dagousset, G.; Levitre, G,; Magnier, E,; Masson, G. *Org*. *Lett*. **2016**, *18*, 2906.

Procedure for calculations. The geometries of the stationary points and transition states were optimized using ωB97X-D and the 6-31G(d) basis set with Spartan '16. The vibrational frequencies were calculated at the same level of theory. Intrinsic reaction coordinate (IRC) calculations from the transition state were performed at the same level of theory.

Structure	Gibbs free energy / au (298.15 K)	Number of imaginary frequency
TS*endo*	–844.756214	1
TS*exo*	–844.749535	1
TS*ri-endo*	–844.744644	1
TS*ri-exo*	–844.737279	1

Figure S1. Relative Gibbs free energies of transition states at 298.15 K (kcal/mol). *ri* = regioisomeric.

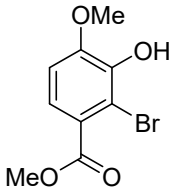


Cartesian coordinates

TS_{endo}				**TS_{exo}**			
H	0.107939	2.317740	-3.115774	H	-1.412883	1.480500	-2.466513
C	-0.466300	1.877884	-2.306558	C	-1.752291	1.164973	-1.484621
H	-1.459687	1.522751	-2.561811	H	-2.750619	0.745465	-1.426680
C	-0.091989	2.102765	-1.009556	C	-1.108117	1.547599	-0.346422
H	0.845510	2.627948	-0.837824	C	0.917076	-0.931923	-0.101600
C	2.232602	-0.085556	-0.838068	H	1.851634	-0.489851	0.219988
H	3.222513	0.274314	-0.586118	C	-0.873275	-1.088214	-1.867453
C	0.358601	-0.226617	-2.523774	H	-1.156525	-0.896541	-2.896790
H	0.085645	-0.153886	-3.572018	C	-1.565351	-2.001958	-1.102832
C	-0.350278	-1.061949	-1.675032	H	-2.488816	-2.435034	-1.466418
H	-1.295971	-1.485701	-1.988558	C	-1.065821	-2.348087	0.160219
C	0.155011	-1.325589	-0.399771	C	0.178182	-1.747783	0.687557
C	1.469006	-0.792390	0.029460	C	0.493993	-0.631709	-1.468004
C	1.778784	0.160640	-2.207546	O	1.196337	-0.035438	-2.263231
O	2.479854	0.661171	-3.062813	O	-1.614257	-3.198200	0.969338
O	-0.403570	-2.094120	0.487296	O	0.435724	-2.109981	1.935275
O	1.760200	-1.107978	1.282284	C	-2.824303	-3.890438	0.613306
C	-1.632881	-2.770356	0.190491	H	-3.633914	-3.172464	0.462547
H	-2.416918	-2.042225	-0.029299	H	-3.041541	-4.531275	1.464249
H	-1.876228	-3.326311	1.092887	H	-2.657671	-4.491966	-0.283163
H	-1.486840	-3.455441	-0.648488	C	1.616996	-1.592140	2.545105
C	3.012929	-0.675081	1.805083	H	2.506159	-1.930242	2.003422
H	3.839155	-1.110504	1.233807	H	1.622309	-1.990966	3.557319
H	3.041718	-1.033911	2.832246	H	1.584825	-0.497463	2.570372
H	3.078516	0.418604	1.786612	C	0.134065	2.288169	-0.241029
C	-0.768302	1.603345	0.160370	C	2.572749	3.621702	0.074839
C	-1.926529	0.512947	2.465462	C	0.657533	2.533191	1.042826
C	-2.029113	0.973374	0.101944	C	0.854637	2.734513	-1.363602
C	-0.115047	1.688733	1.408268	C	2.066408	3.393078	-1.201501
C	-0.681069	1.140864	2.544720	C	1.863803	3.194319	1.200446
C	-2.604668	0.445645	1.250076	H	0.100542	2.204357	1.916997
H	-2.580777	0.940191	-0.832281	H	0.470672	2.574484	-2.364758
H	0.851070	2.183214	1.465465	H	2.615279	3.730874	-2.073843
H	-0.165052	1.206506	3.496326	H	2.254337	3.385933	2.194532
H	-3.590093	-0.007100	1.202459	H	3.517672	4.141521	0.196865
H	-2.377739	0.096080	3.360032	H	-1.565514	1.269754	0.602779

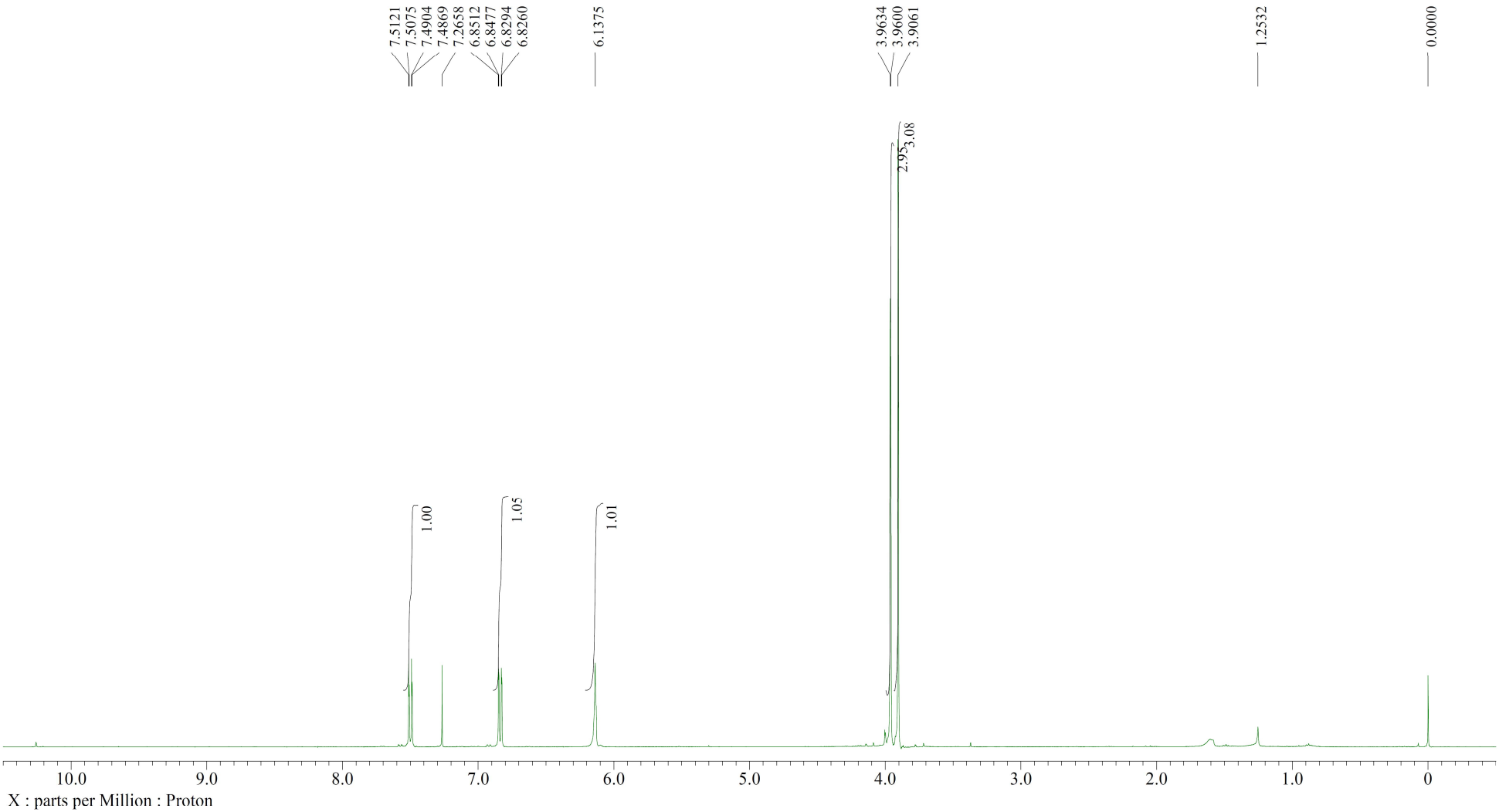
$TS_{ri\text{-}endo}$			
H	0.423858	2.181414	-2.091463
C	0.219746	1.959474	-1.045879
C	1.201575	2.255419	-0.115637
H	2.077494	2.808008	-0.441742
H	0.942206	2.365284	0.932992
C	2.249298	0.425392	0.255980
H	3.045416	0.925770	0.798062
C	1.516503	-0.552193	-1.942670
H	1.595207	-0.577440	-3.024036
C	0.616794	-1.301736	-1.271044
H	-0.083386	-1.922061	-1.817876
C	0.555954	-1.303520	0.172461
C	1.389182	-0.443101	0.929488
C	2.537446	0.216094	-1.200446
O	3.527900	0.675604	-1.722668
O	-0.206555	-2.115091	0.863145
O	1.212462	-0.482356	2.255346
C	-1.079987	-3.042815	0.206619
H	-1.812157	-2.506692	-0.402754
H	-1.583966	-3.572500	1.012466
H	-0.504265	-3.749277	-0.397396
C	2.178133	0.151101	3.091123
H	3.181010	-0.241556	2.893455
H	1.883945	-0.092057	4.110458
H	2.166984	1.238610	2.960591
C	-1.046589	1.354879	-0.743392
C	-3.489690	0.075323	-0.250357
C	-1.955857	1.101933	-1.796841
C	-1.392882	0.942912	0.560187
C	-2.605221	0.303444	0.798795
C	-3.162981	0.477058	-1.552579
H	-1.698152	1.412539	-2.805853
H	-0.733827	1.137825	1.399470
H	-2.862021	-0.001857	1.807546
H	-3.860502	0.303996	-2.365706
H	-4.443072	-0.407825	-0.059845

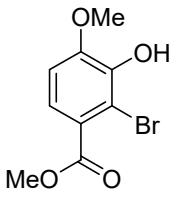
$TS_{ri\text{-}exo}$			
C	-0.880421	1.293665	-0.205508
H	-1.851494	0.803743	-0.215189
C	-0.182065	1.296852	0.999451
H	0.625931	2.007284	1.143832
H	-0.710687	1.006987	1.900269
C	1.191077	-0.378989	1.067797
H	2.040178	0.176598	1.450929
C	0.008299	-1.269244	-0.948260
H	-0.189191	-1.210262	-2.013055
C	-0.636554	-2.148889	-0.139441
H	-1.402912	-2.795140	-0.552508
C	-0.330069	-2.250618	1.257246
C	0.579498	-1.352507	1.862534
C	1.147837	-0.498402	-0.419281
O	1.976297	0.034284	-1.127882
O	-0.877921	-3.131889	2.062942
O	0.705538	-1.462621	3.186736
C	-1.757250	-4.144474	1.561924
H	-2.674079	-3.697523	1.166827
H	-1.993877	-4.764271	2.424128
H	-1.256026	-4.745163	0.797914
C	1.708621	-0.695616	3.844827
H	2.702235	-0.928663	3.447037
H	1.656455	-0.986977	4.892179
H	1.507802	0.377871	3.755885
C	-0.491087	1.954528	-1.423549
C	0.176205	3.193388	-3.839588
C	0.746916	2.613122	-1.573571
C	-1.383487	1.927886	-2.516443
C	-1.055698	2.546049	-3.709120
C	1.073771	3.223682	-2.774749
H	1.456152	2.649618	-0.754198
H	-2.341044	1.424386	-2.410847
H	-1.751786	2.528476	-4.540903
H	2.029335	3.725096	-2.882258
H	0.433503	3.677734	-4.776106



S2

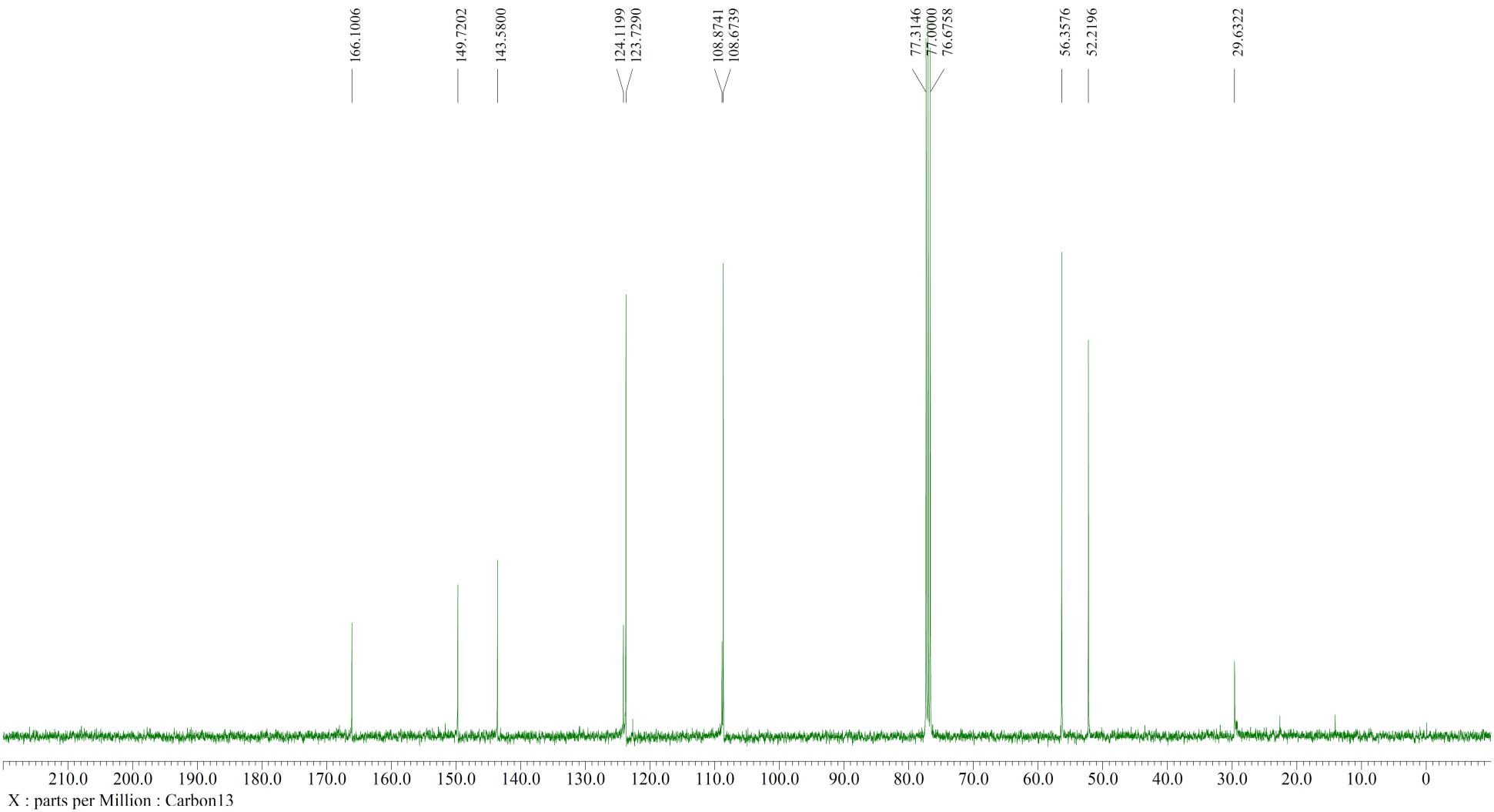
^{1}H-NMR (400 MHz, $CDCl_3$)

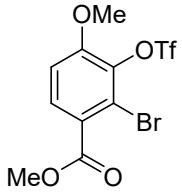




S2

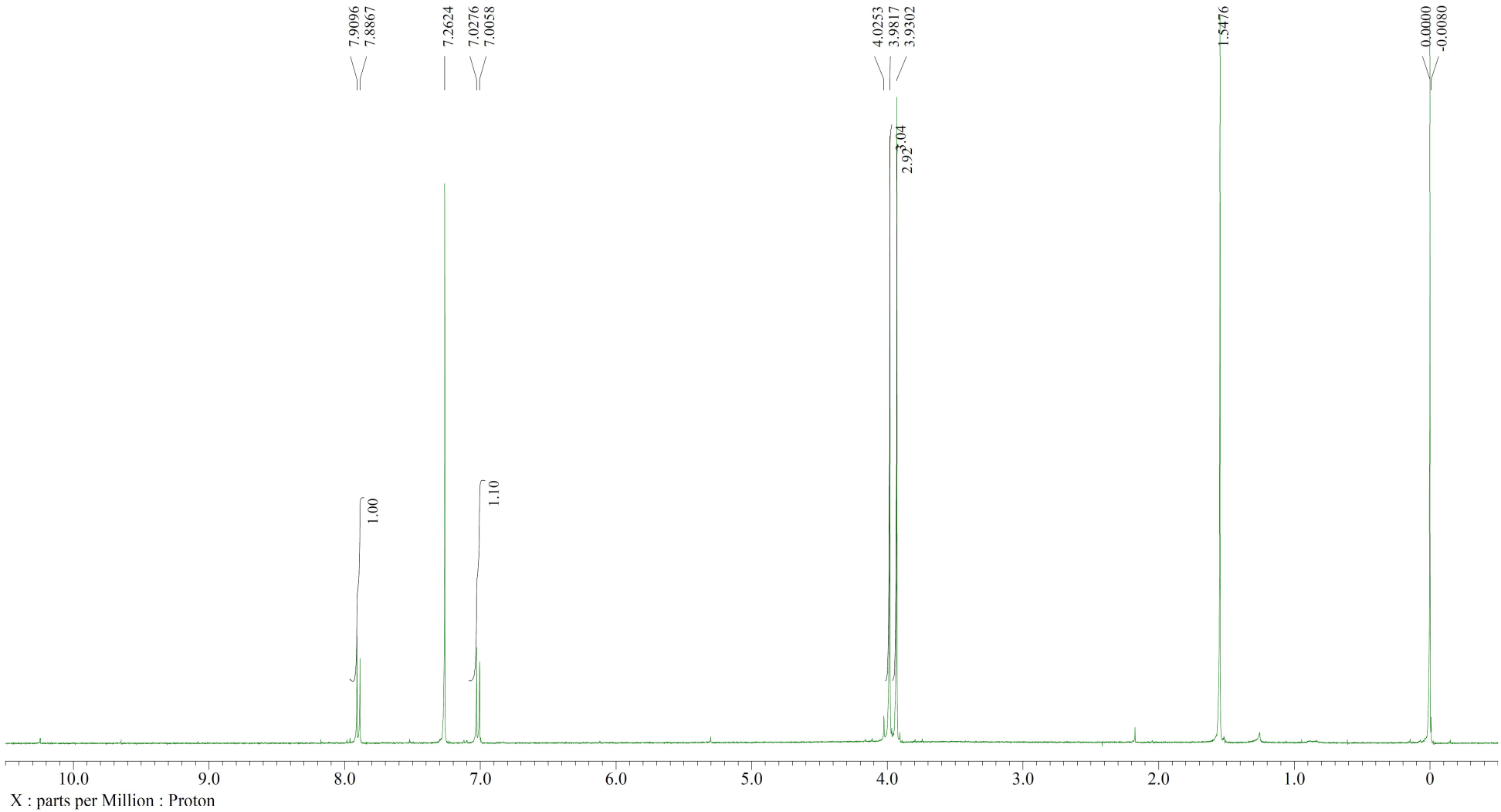
^{13}C-NMR (100 MHz, $CDCl_3$)

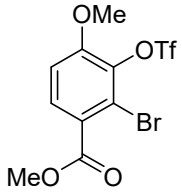




S3

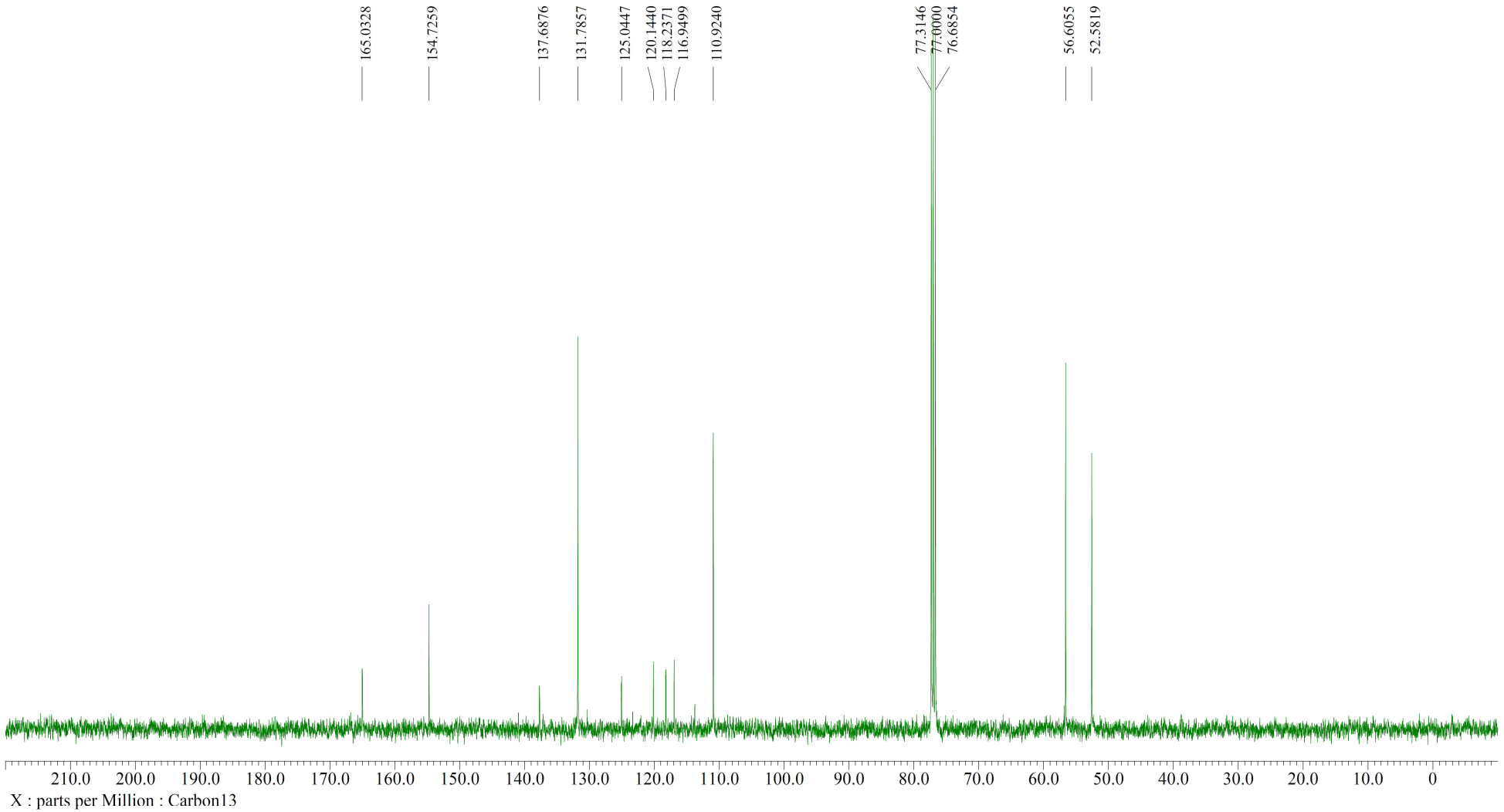
^{1}H-NMR (400 MHz, $CDCl_3$)

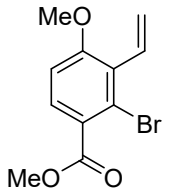




S3

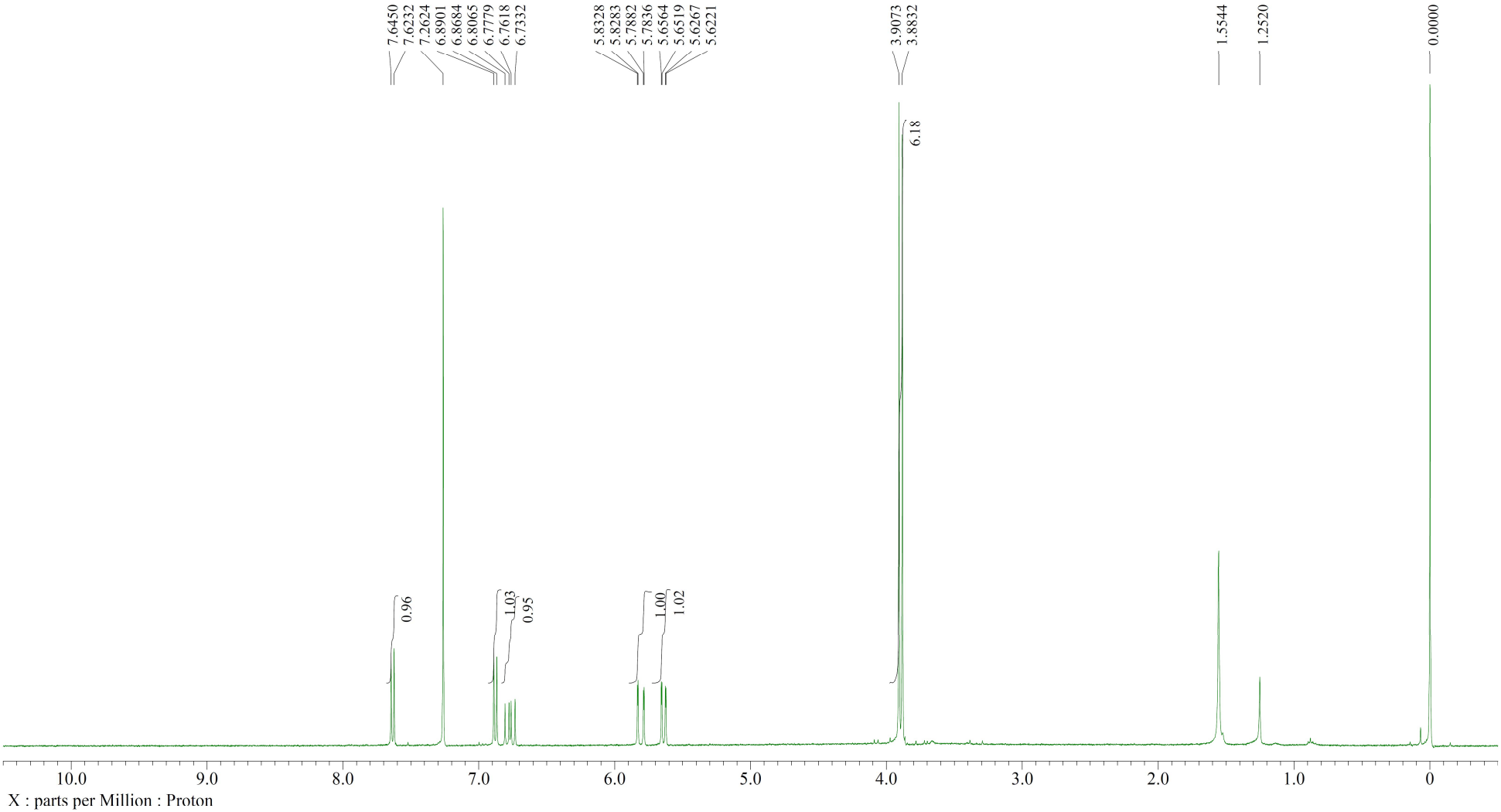
^{13}C-NMR (100 MHz, $CDCl_3$)

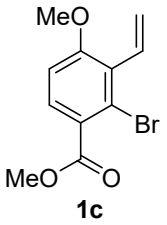




1c

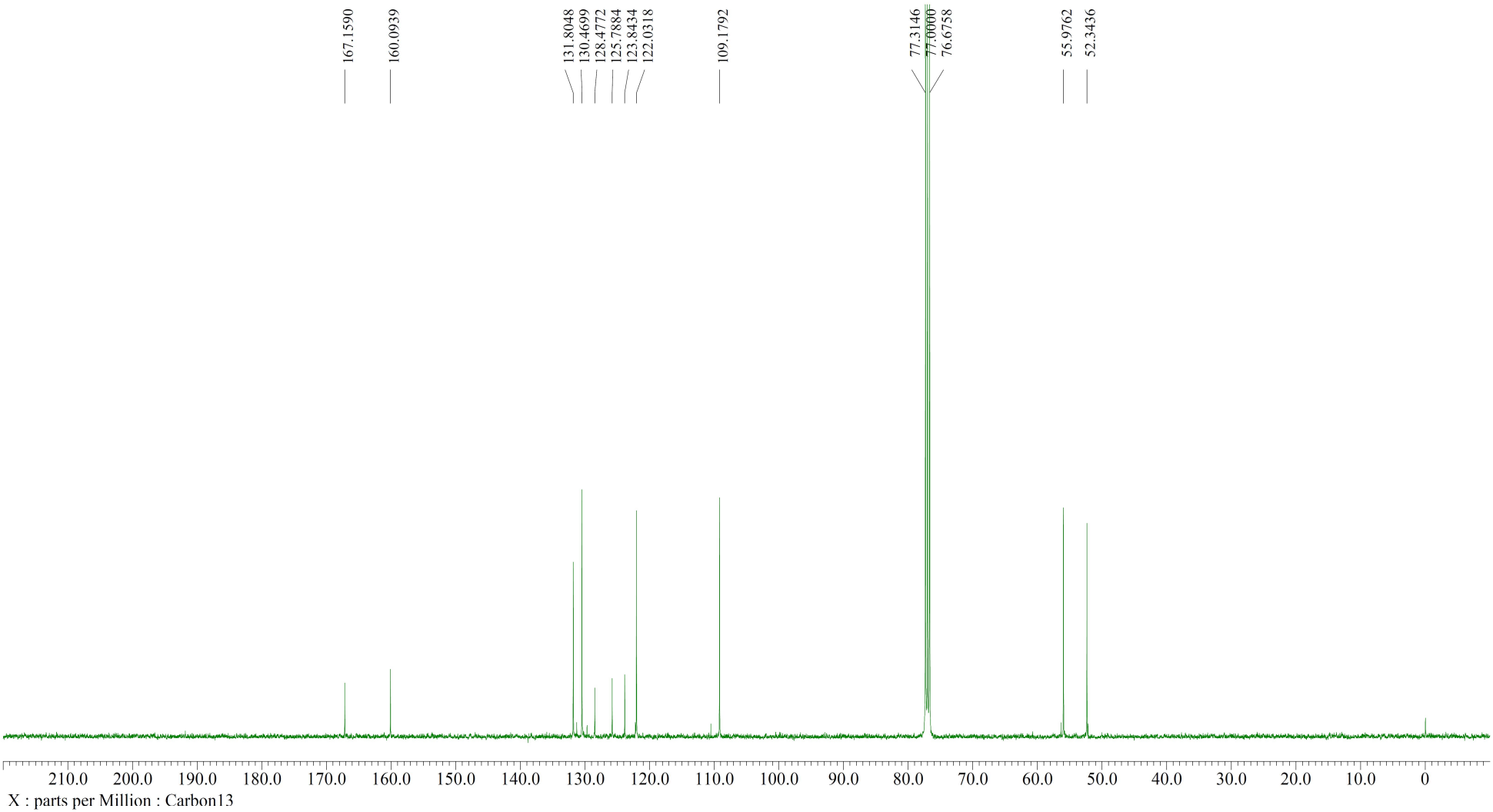
^{1}H-NMR (400 MHz, $CDCl_3$)

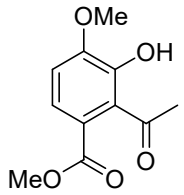




1c

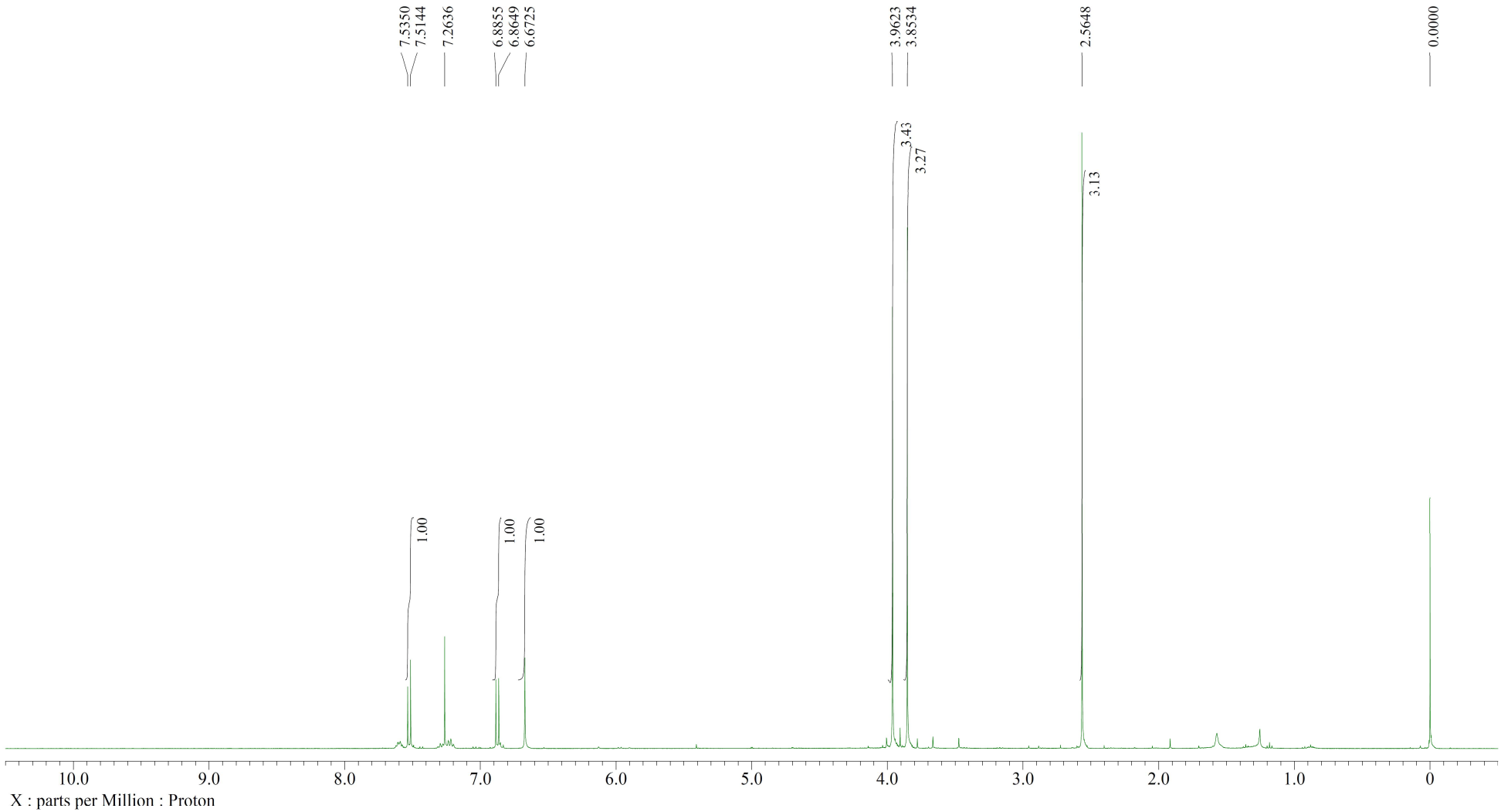
^{13}C-NMR (100 MHz, $CDCl_3$)

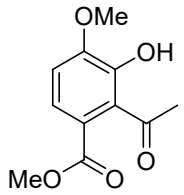




S4

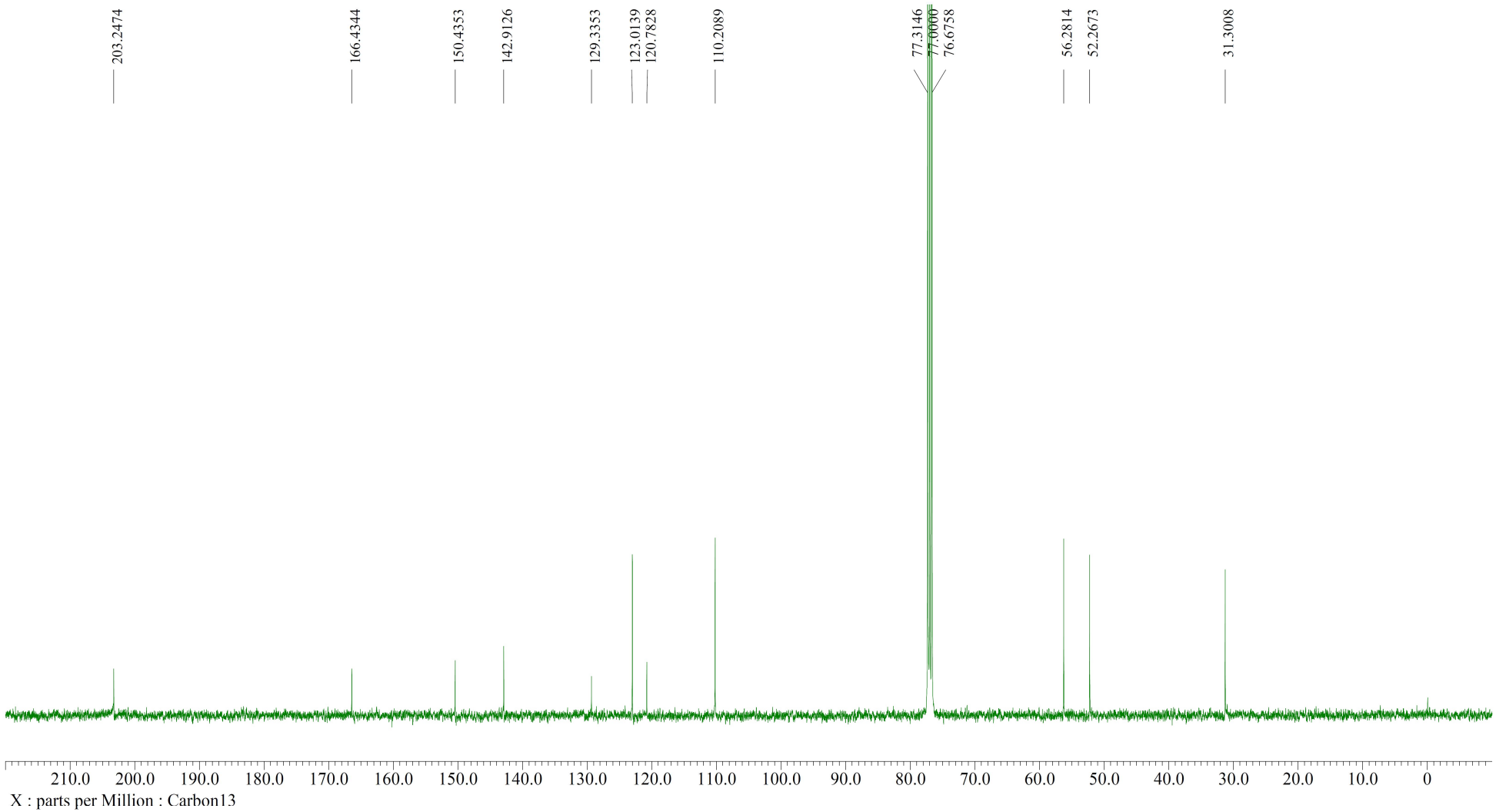
^{1}H-NMR (400 MHz, $CDCl_3$)

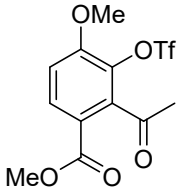




S4

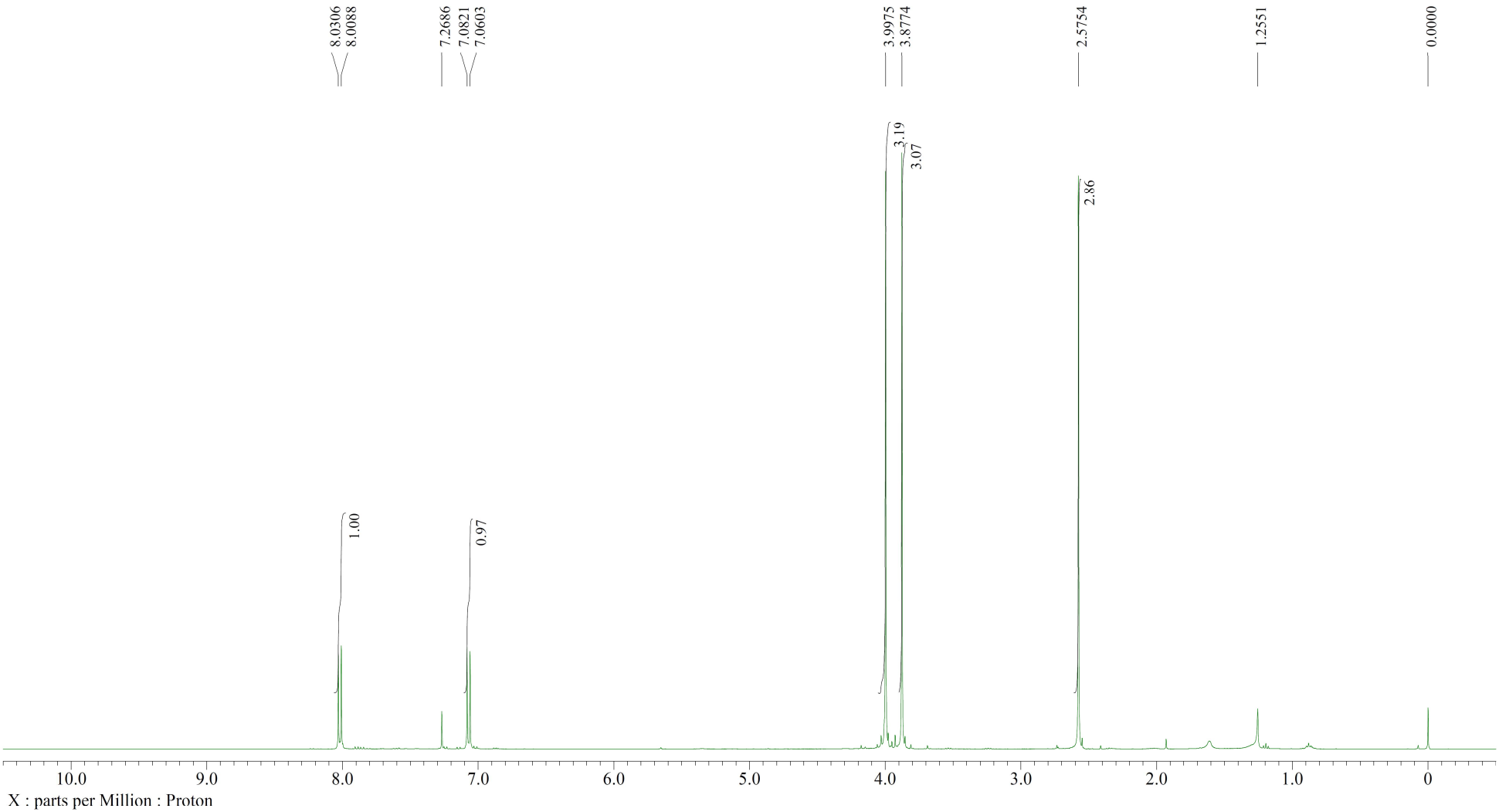
^{13}C-NMR (100 MHz, $CDCl_3$)

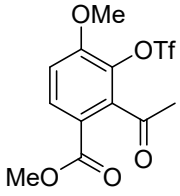




S5

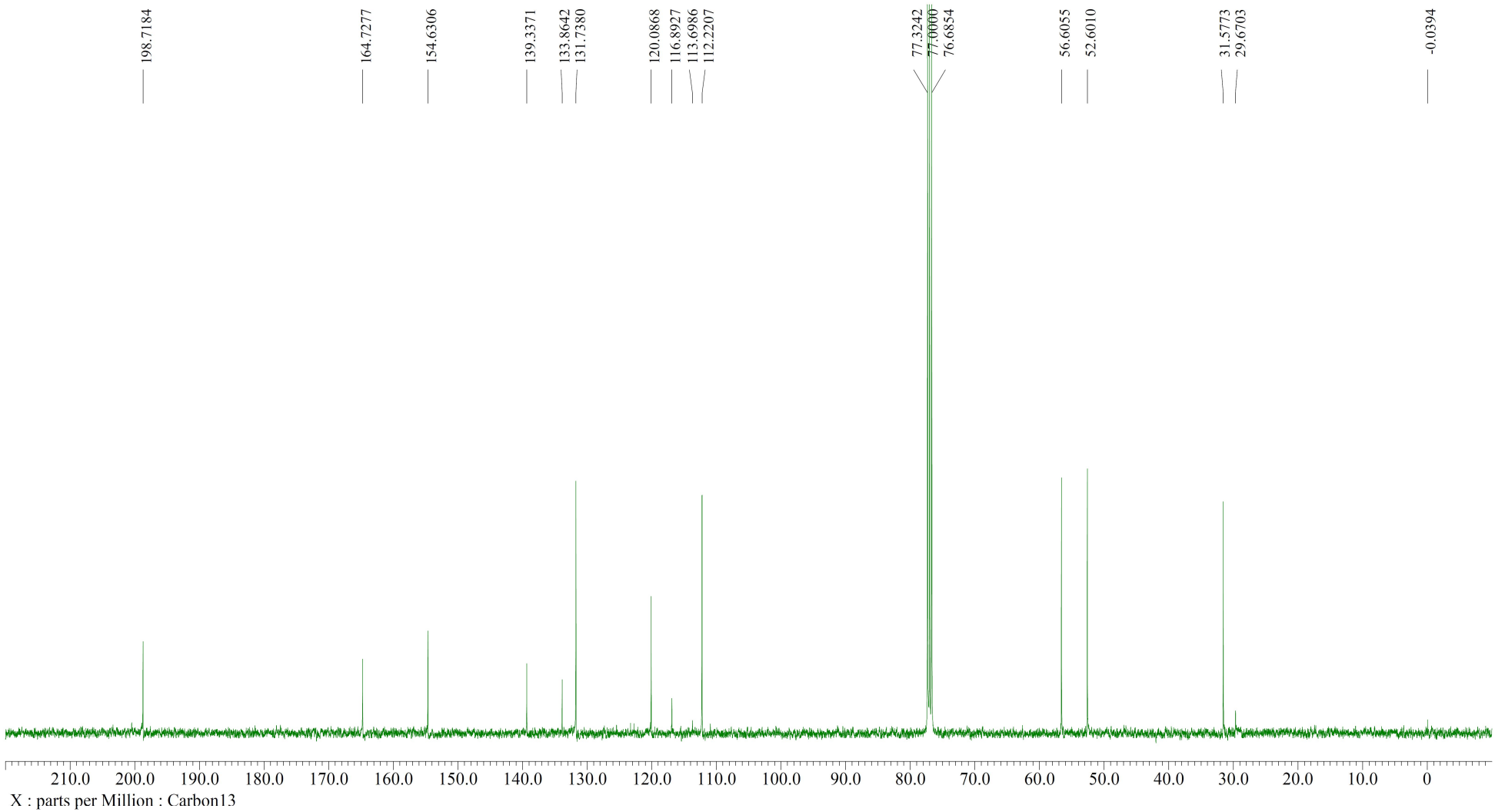
^{1}H-NMR (400 MHz, $CDCl_3$)

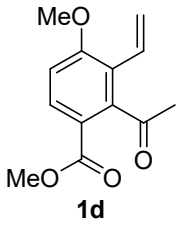




S5

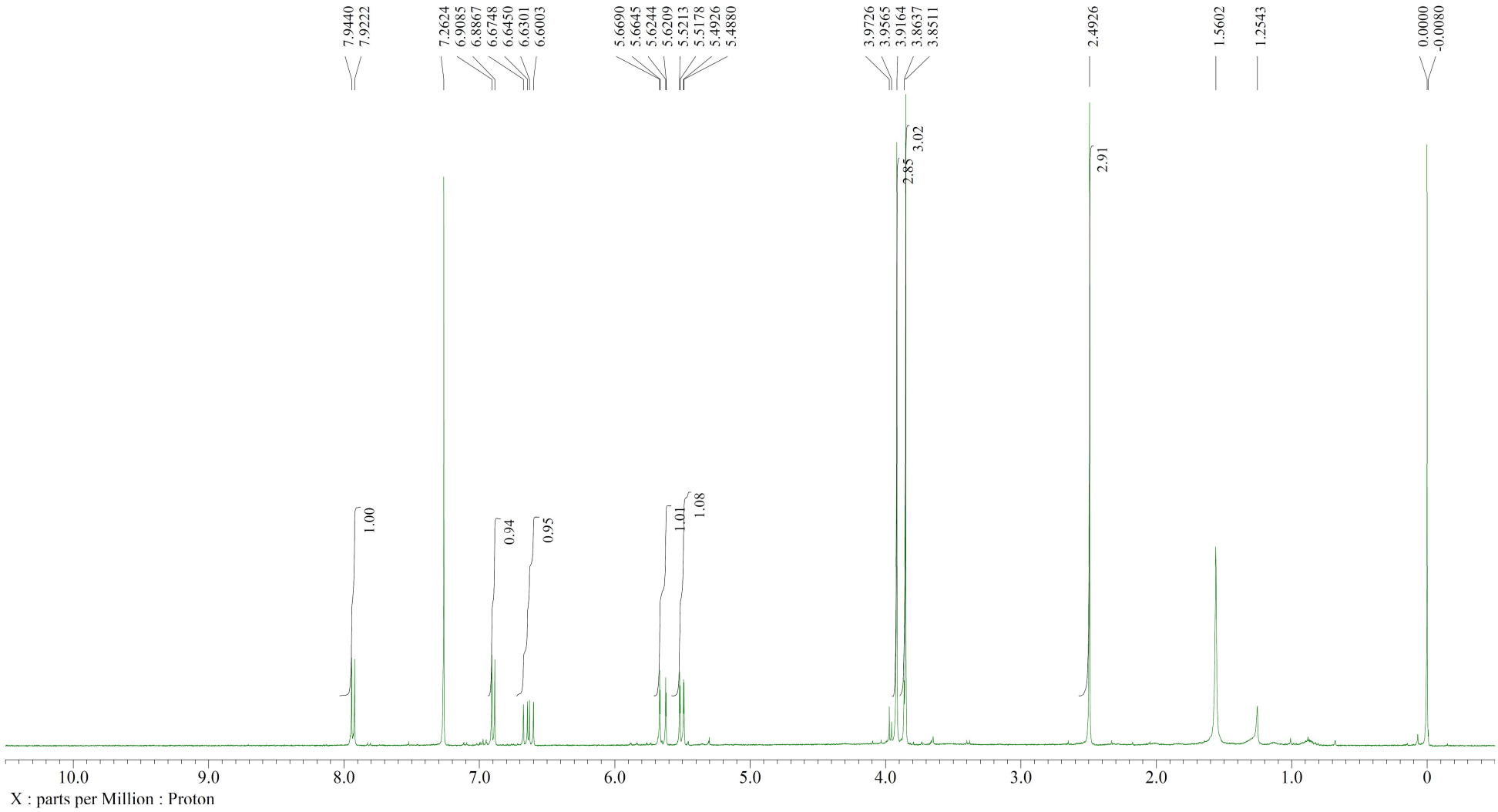
^{13}C-NMR (100 MHz, $CDCl_3$)

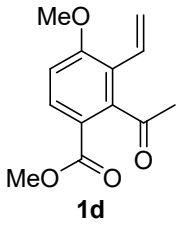




1d

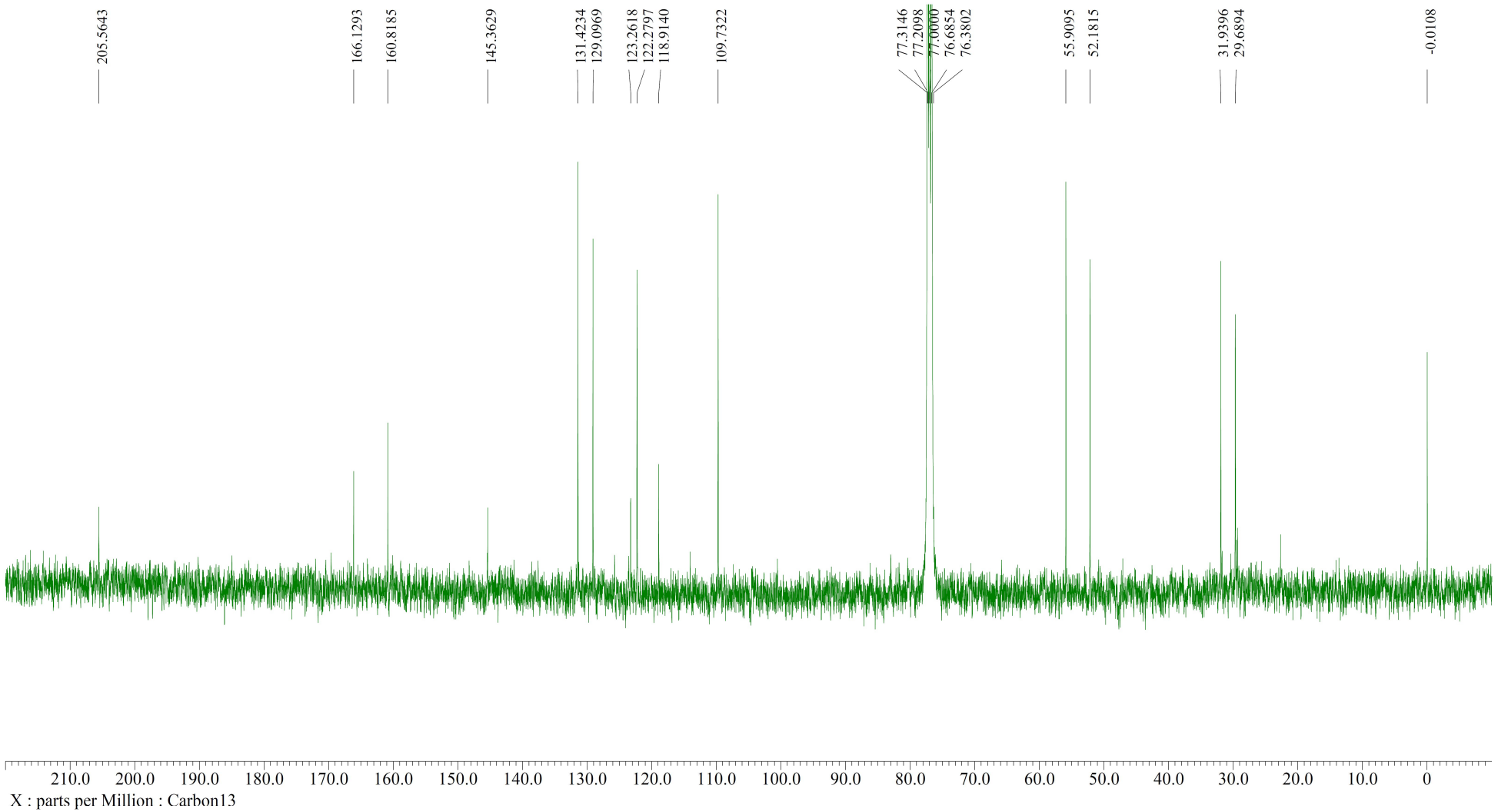
^{1}H-NMR (400 MHz, $CDCl_3$)

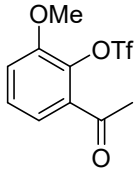




1d

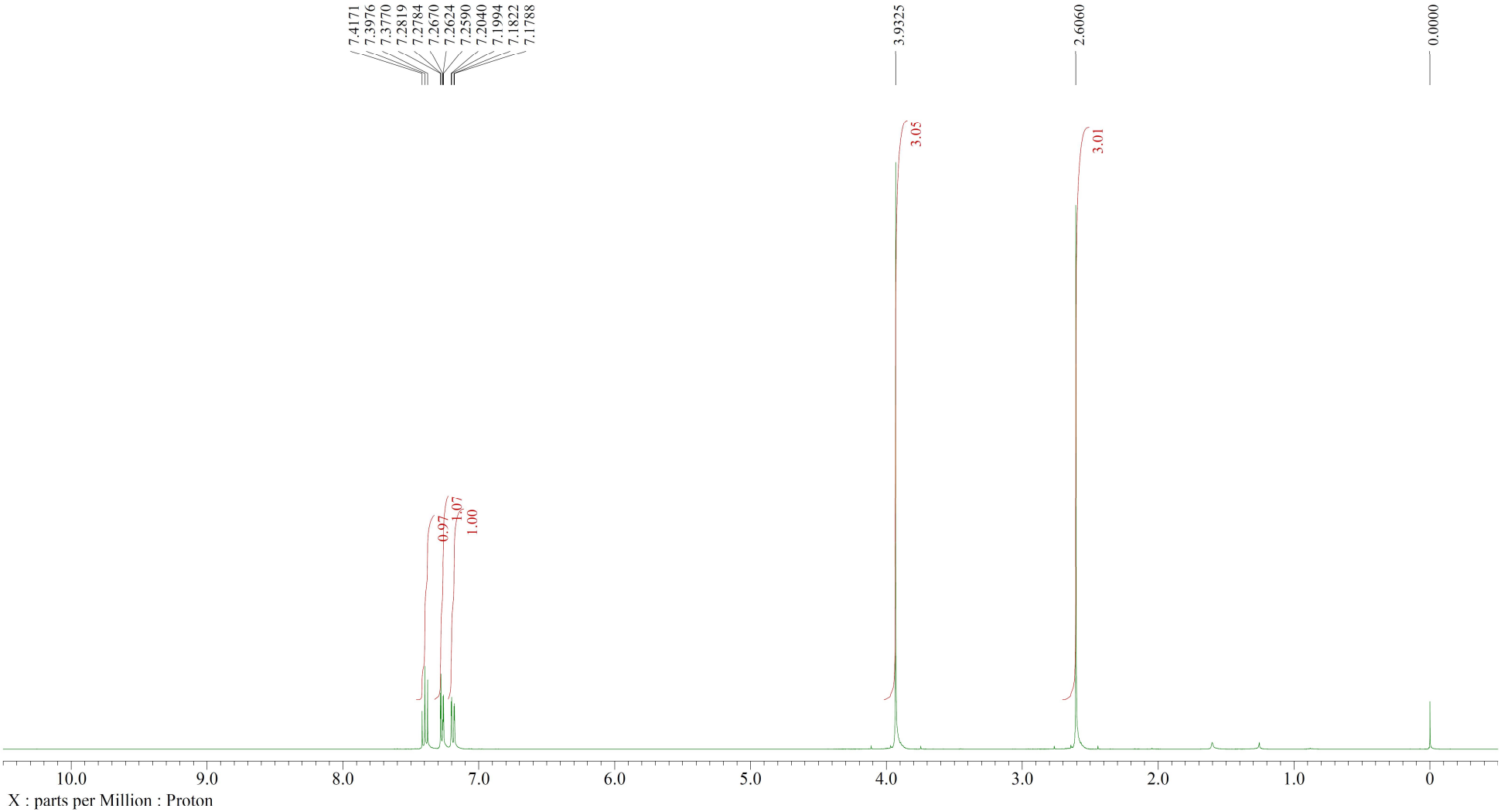
^{13}C-NMR (100 MHz, $CDCl_3$)

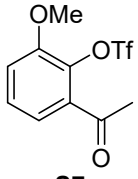




S7

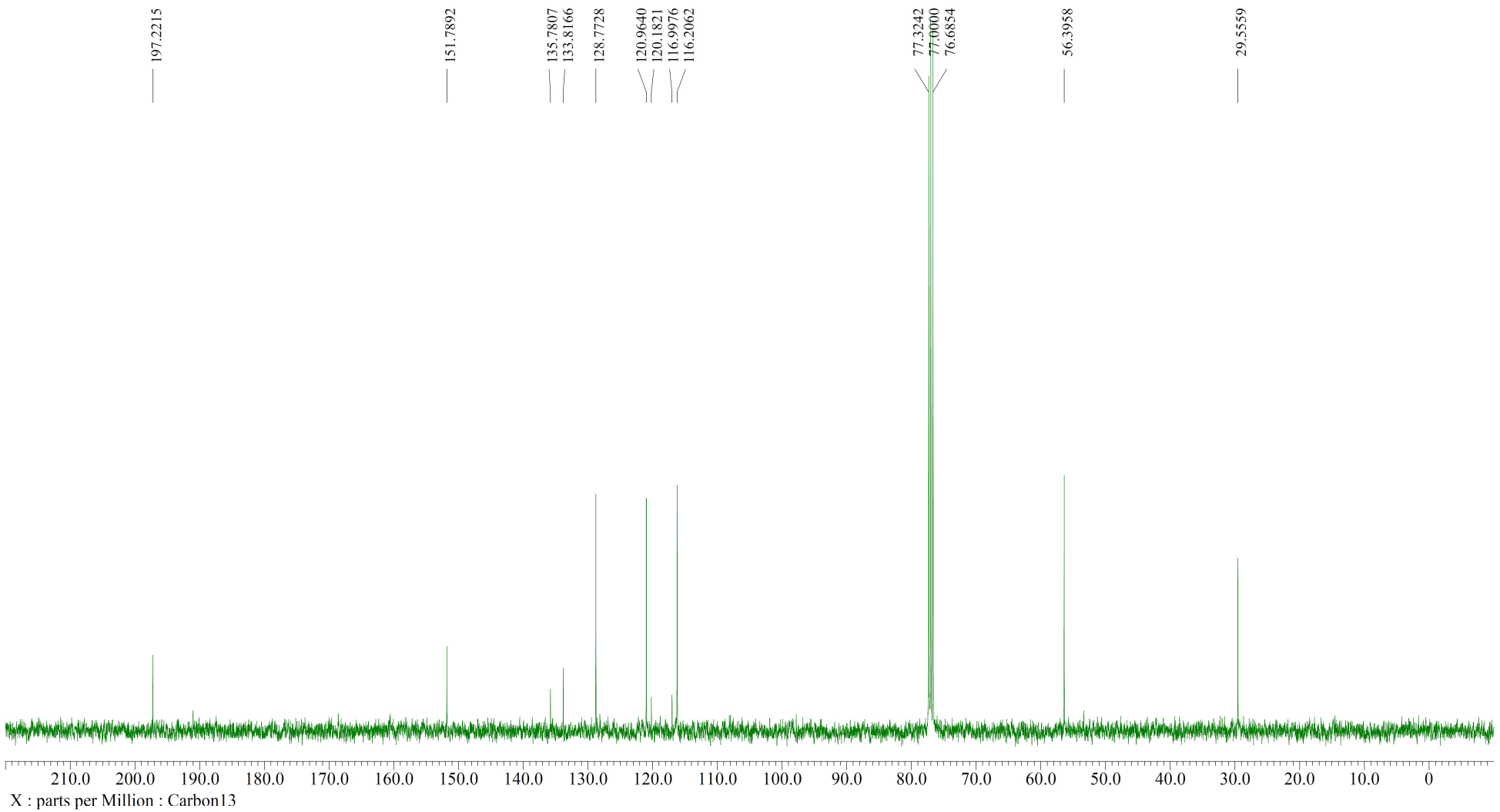
^{1}H-NMR (400 MHz, $CDCl_3$)

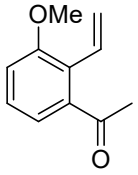




S7

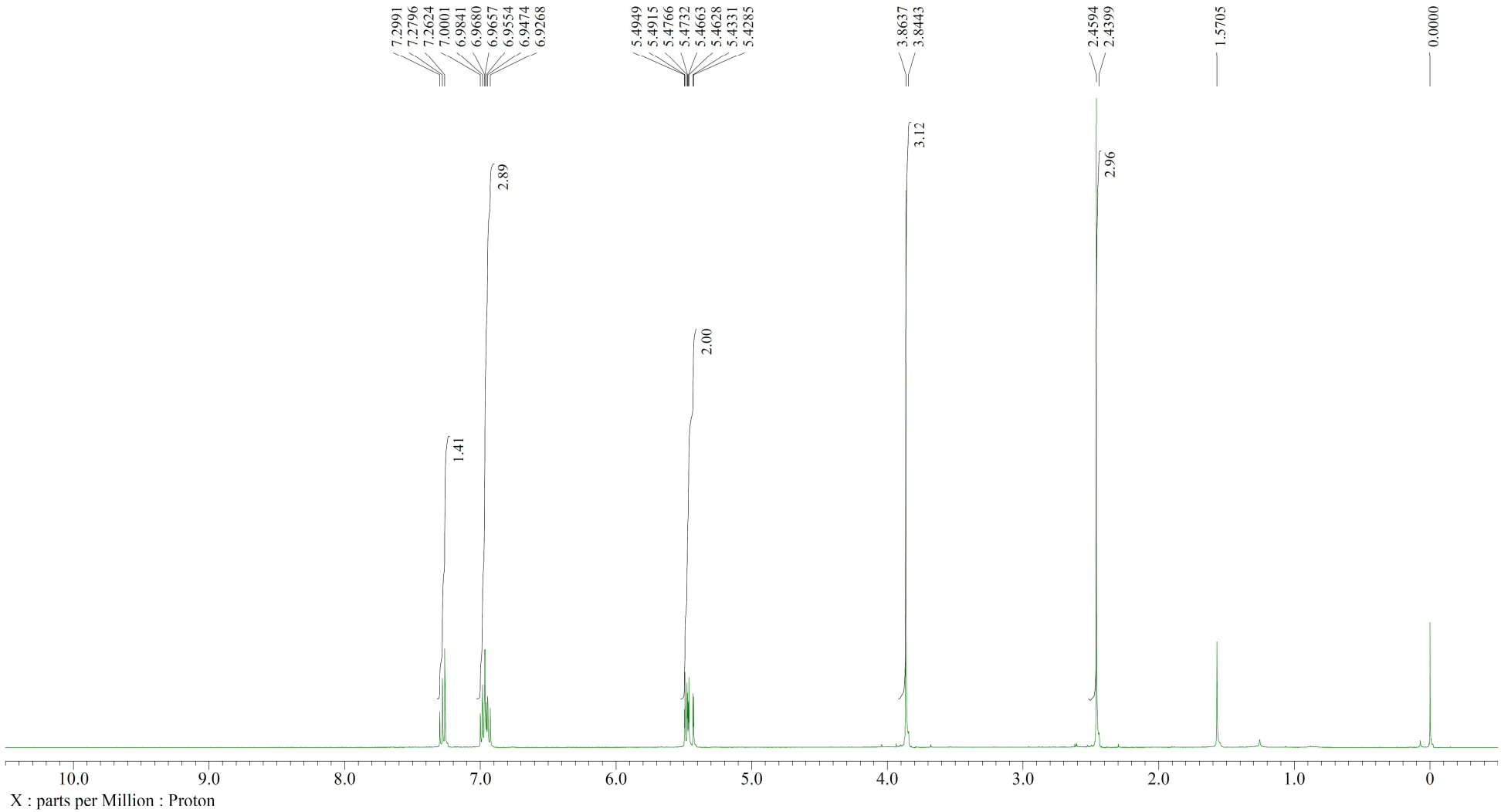
^{13}C-NMR (100 MHz, $CDCl_3$)

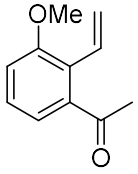




1e

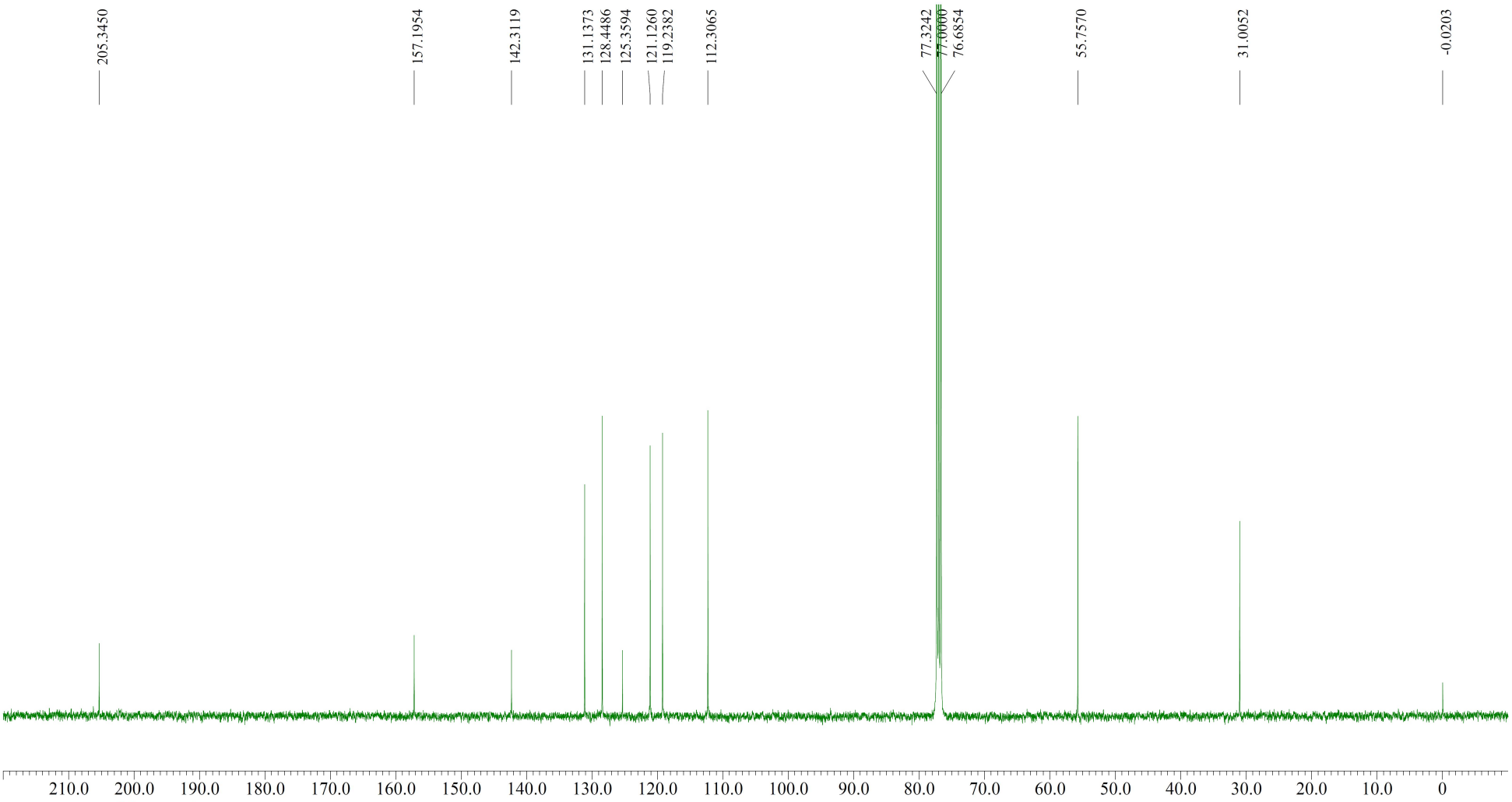
^{1}H-NMR (400 MHz, $CDCl_3$)

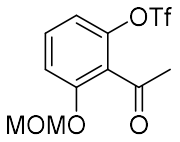




1e

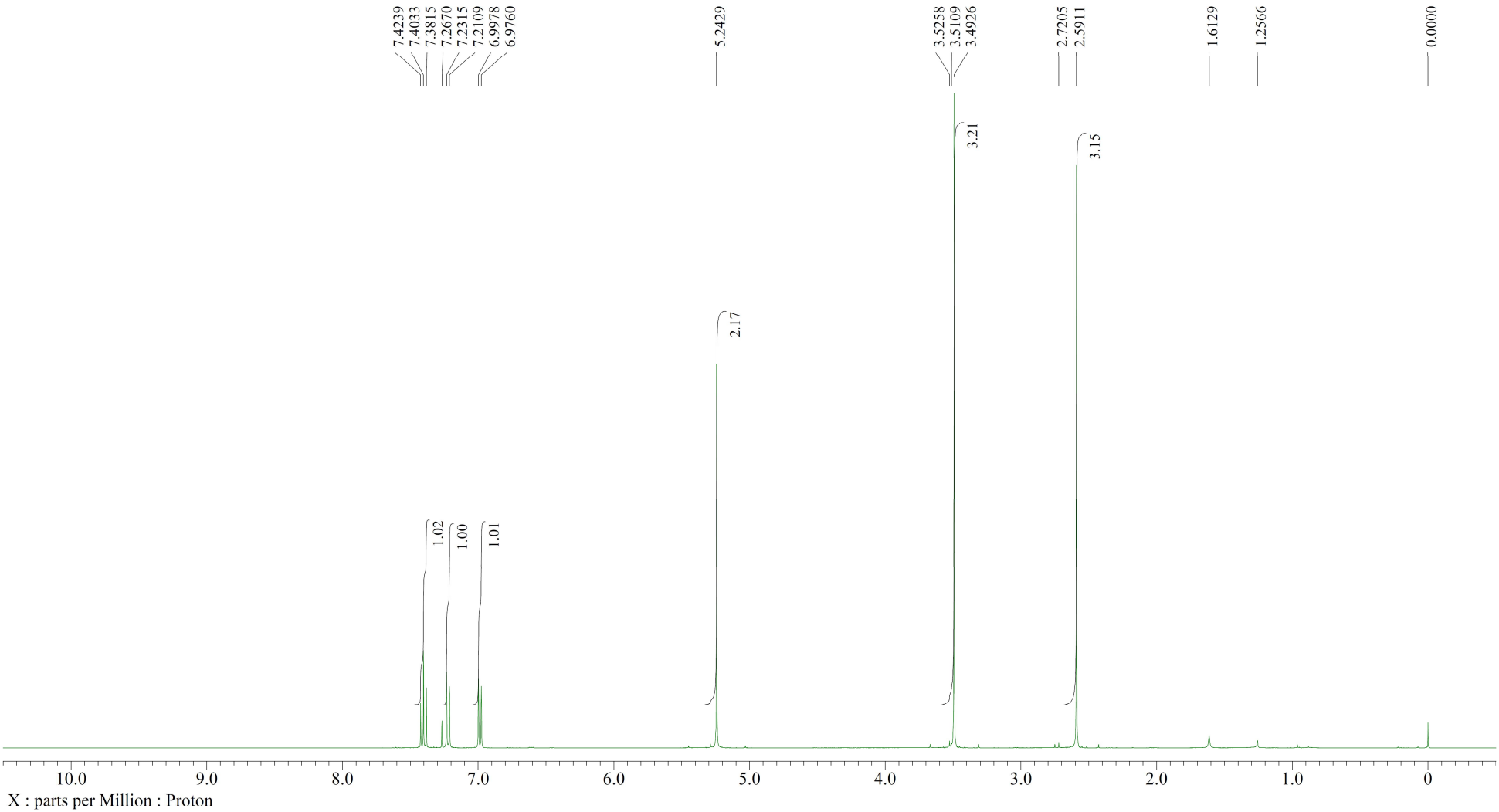
^{13}C-NMR (100 MHz, $CDCl_3$)

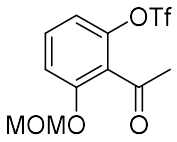




S9

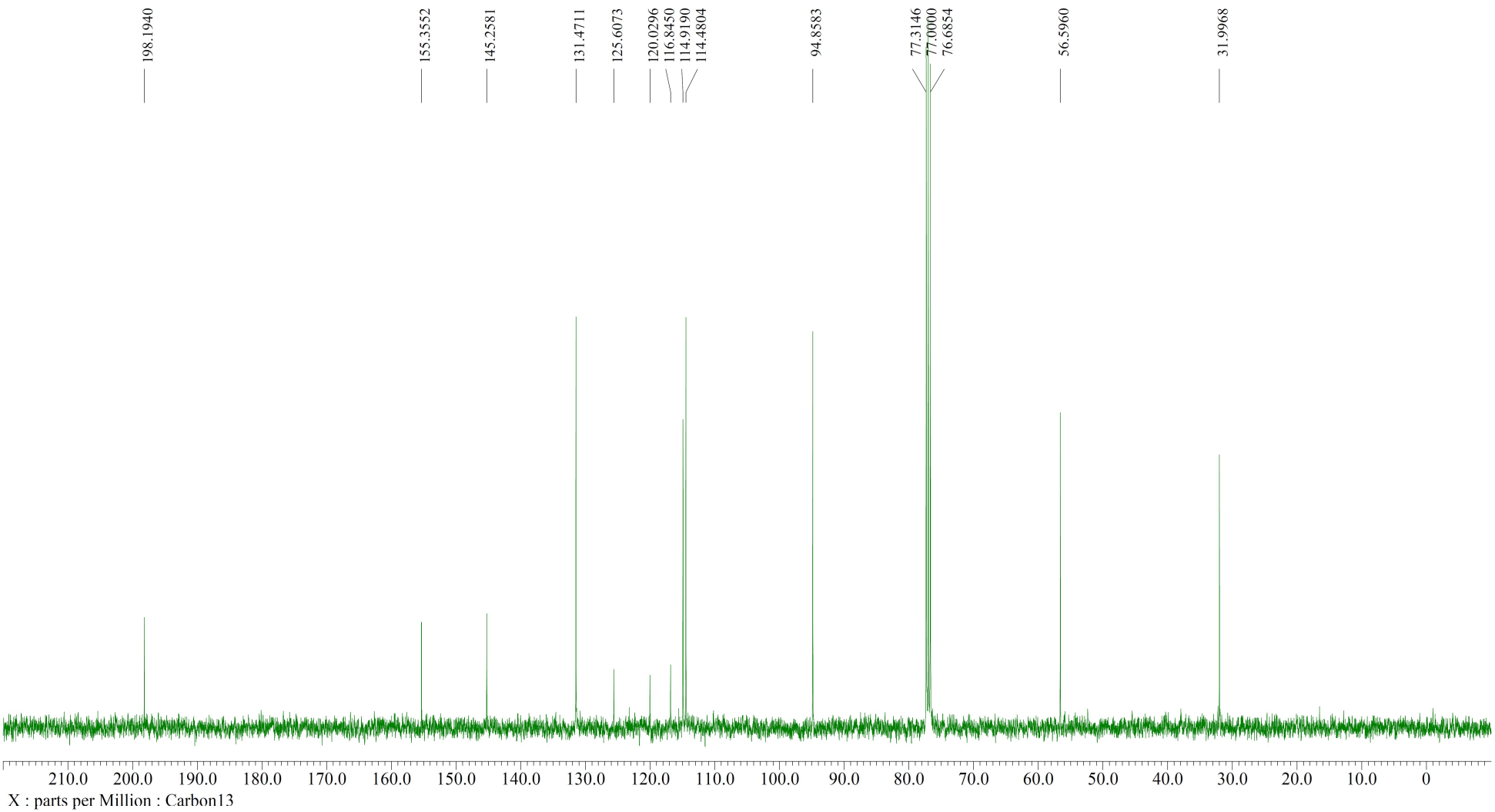
^{1}H-NMR (400 MHz, $CDCl_3$)

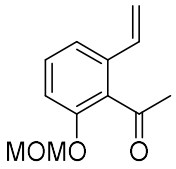




S9

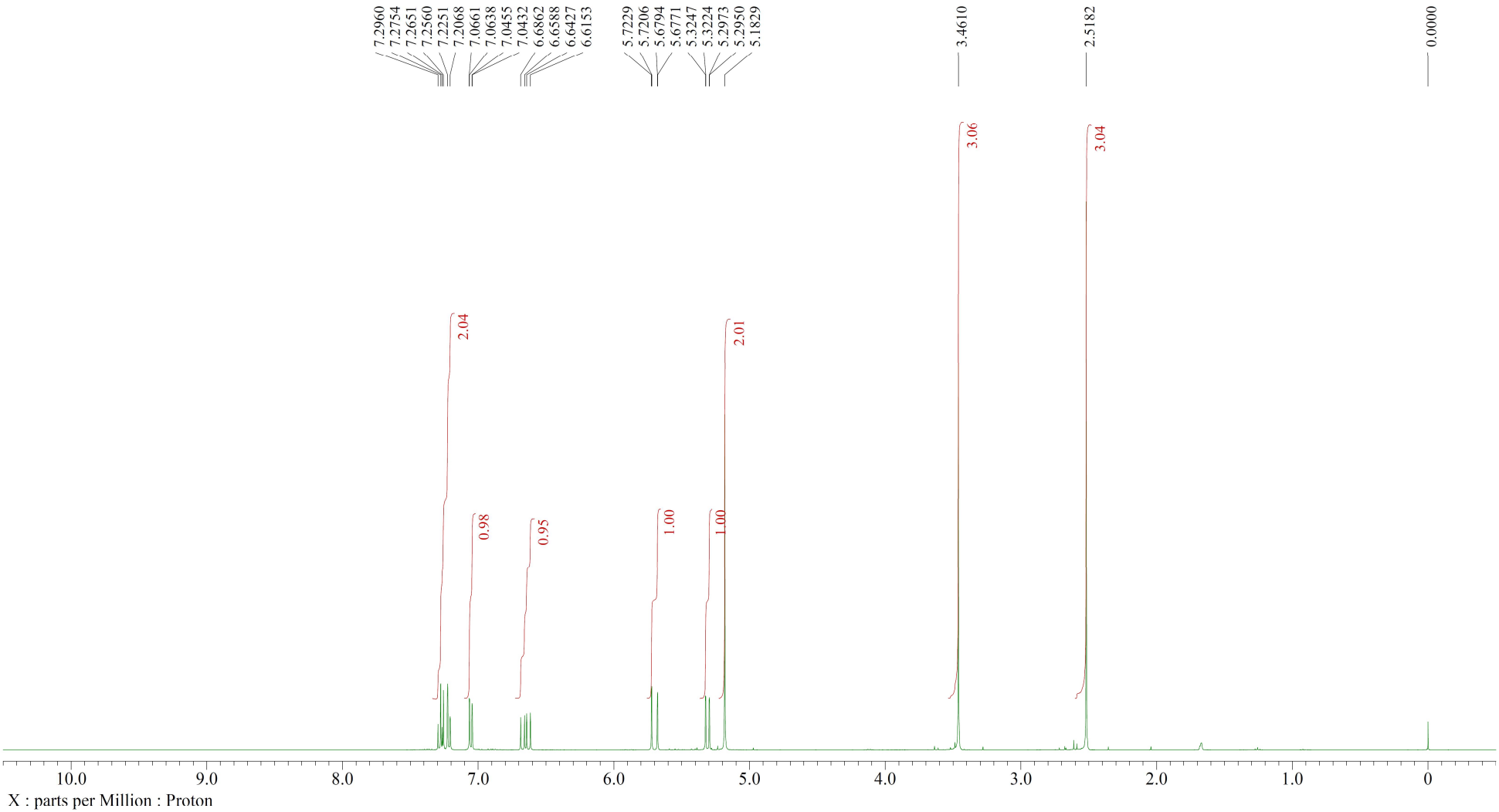
^{13}C-NMR (100 MHz, $CDCl_3$)

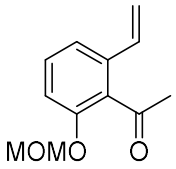




1g

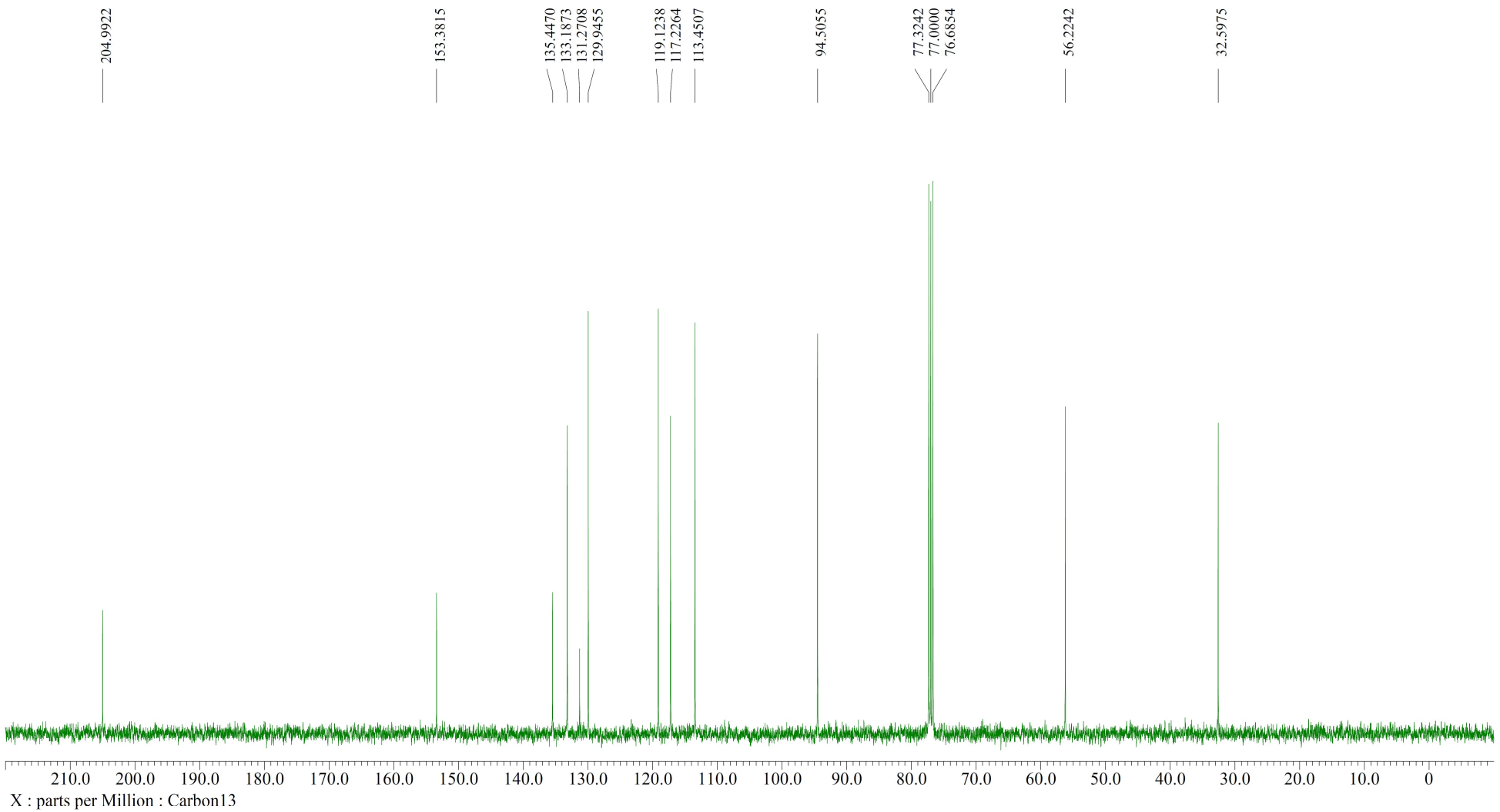
^{1}H-NMR (400 MHz, $CDCl_3$)

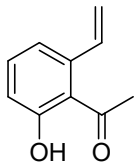




1g

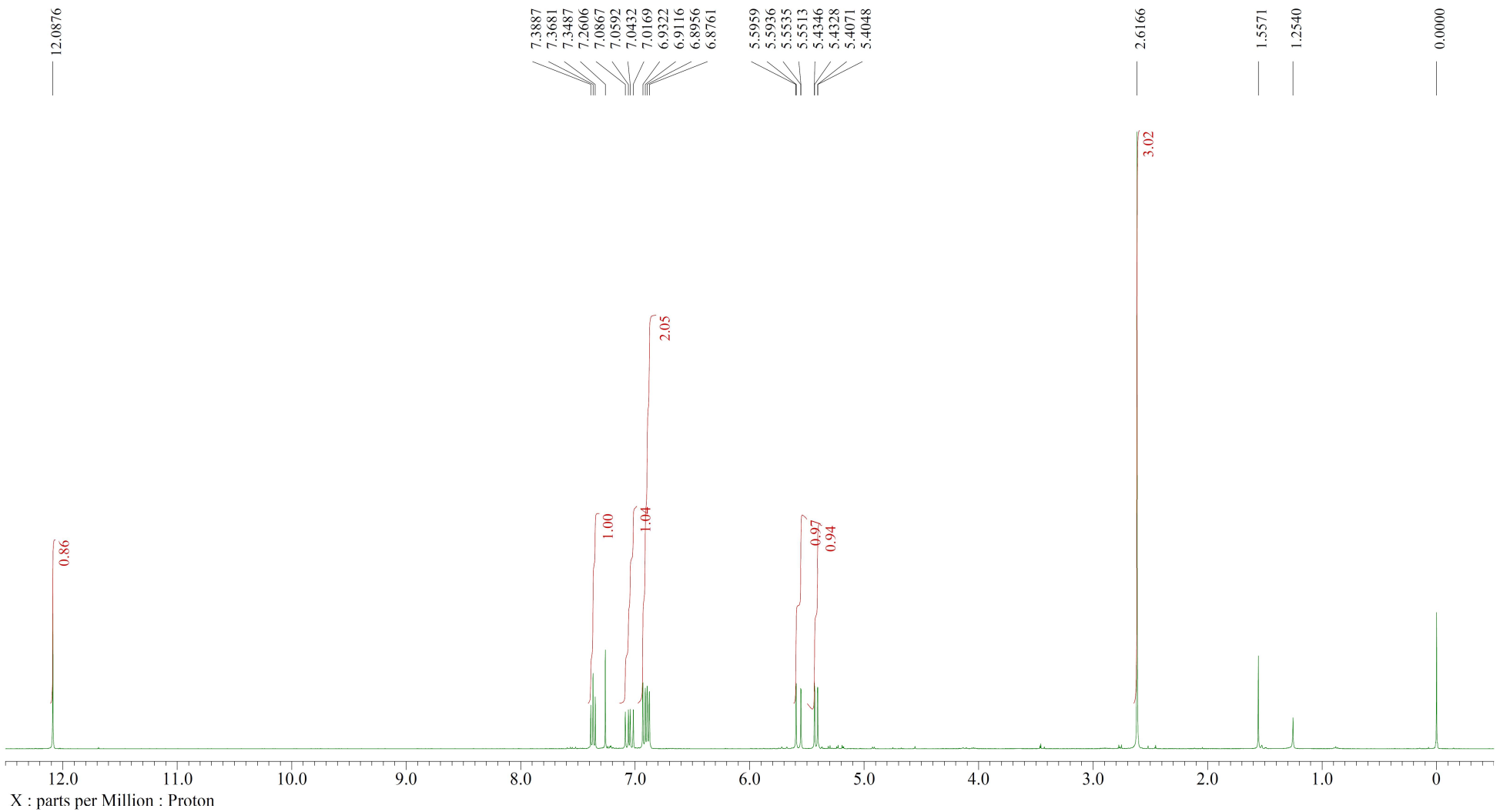
^{13}C-NMR (100 MHz, $CDCl_3$)

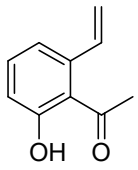




S10

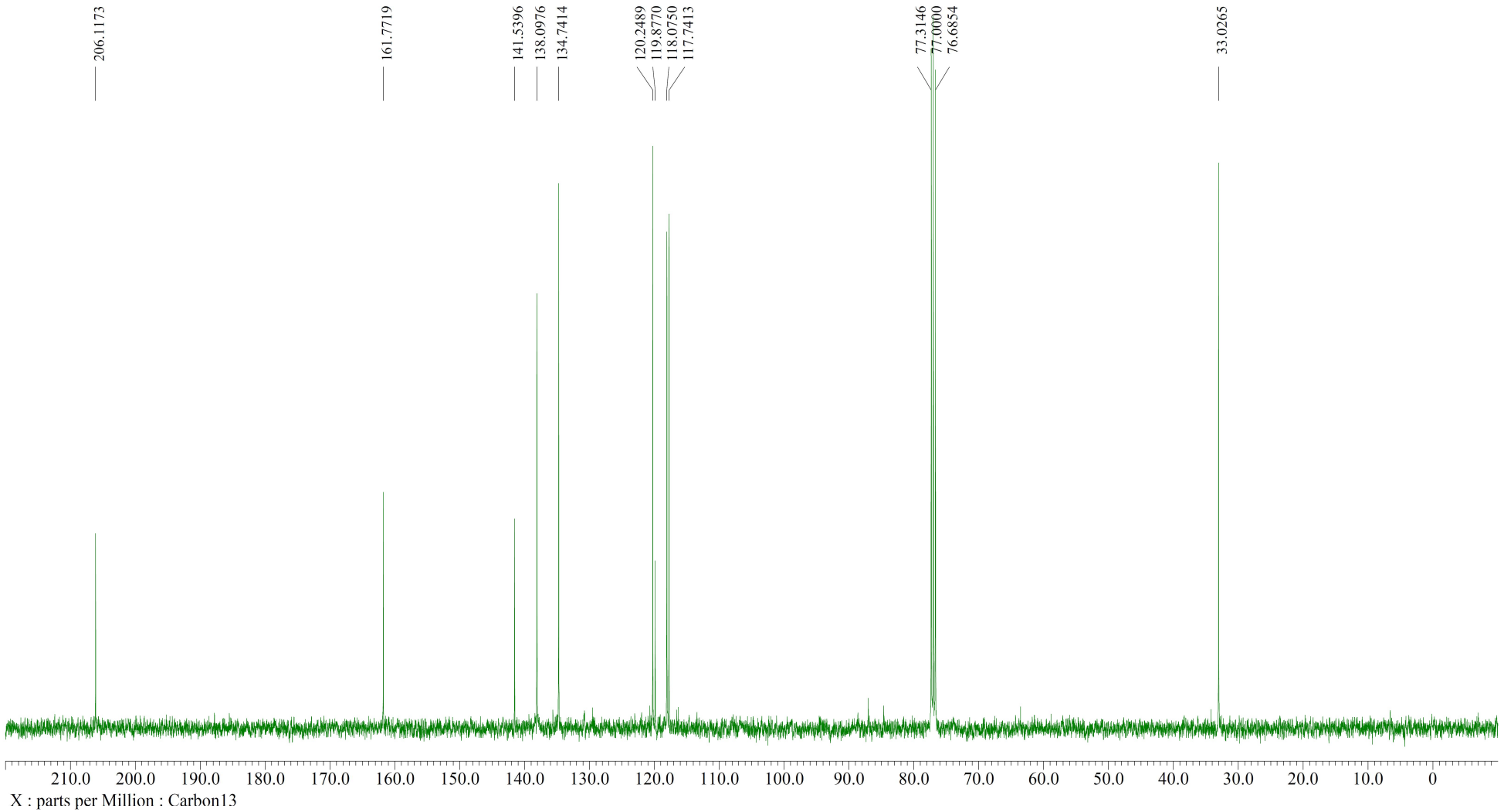
^{1}H-NMR (400 MHz, $CDCl_3$)

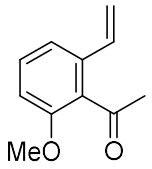




S10

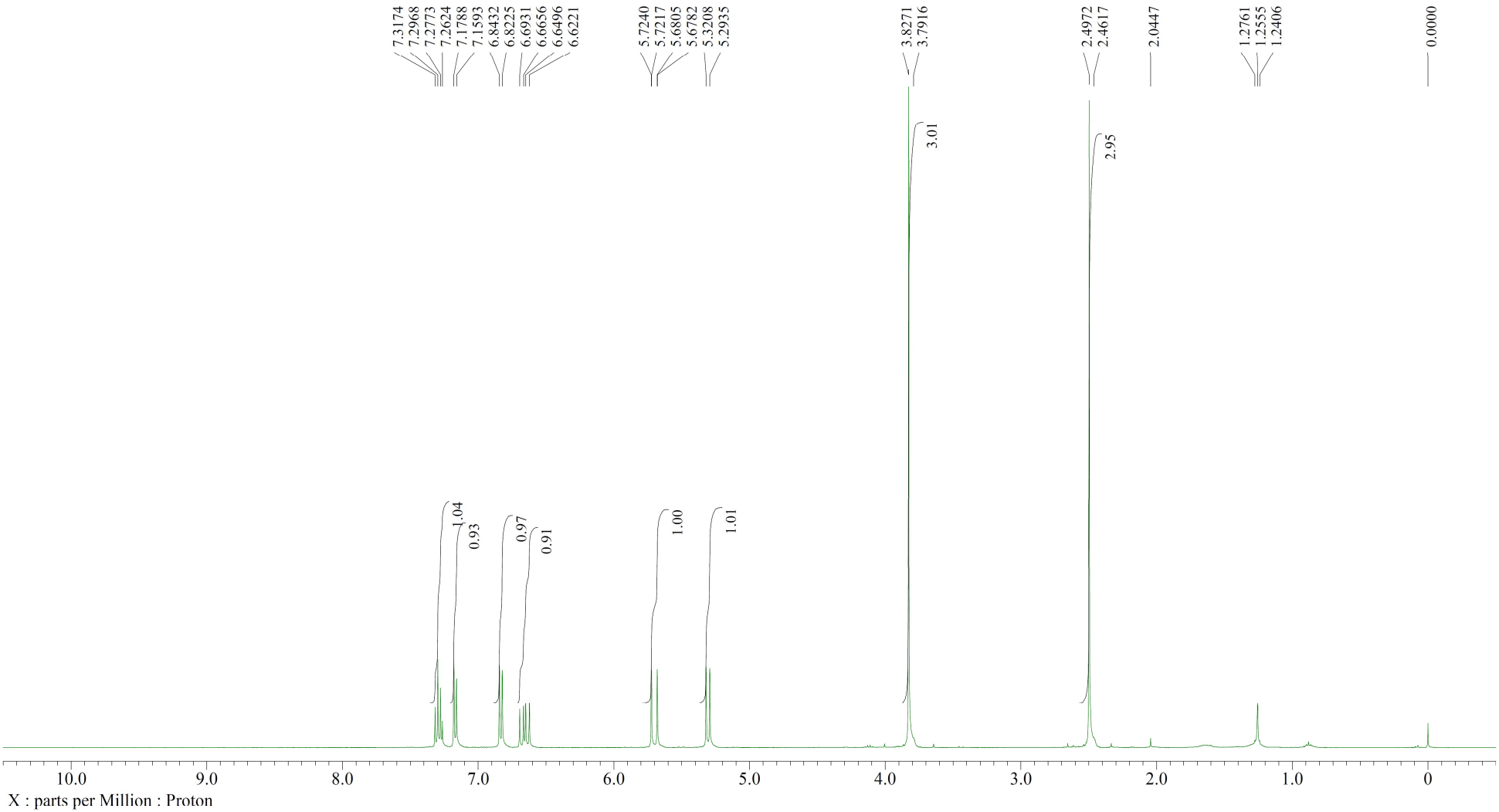
^{13}C-NMR (100 MHz, $CDCl_3$)

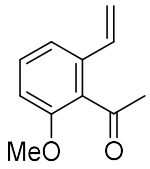




1f

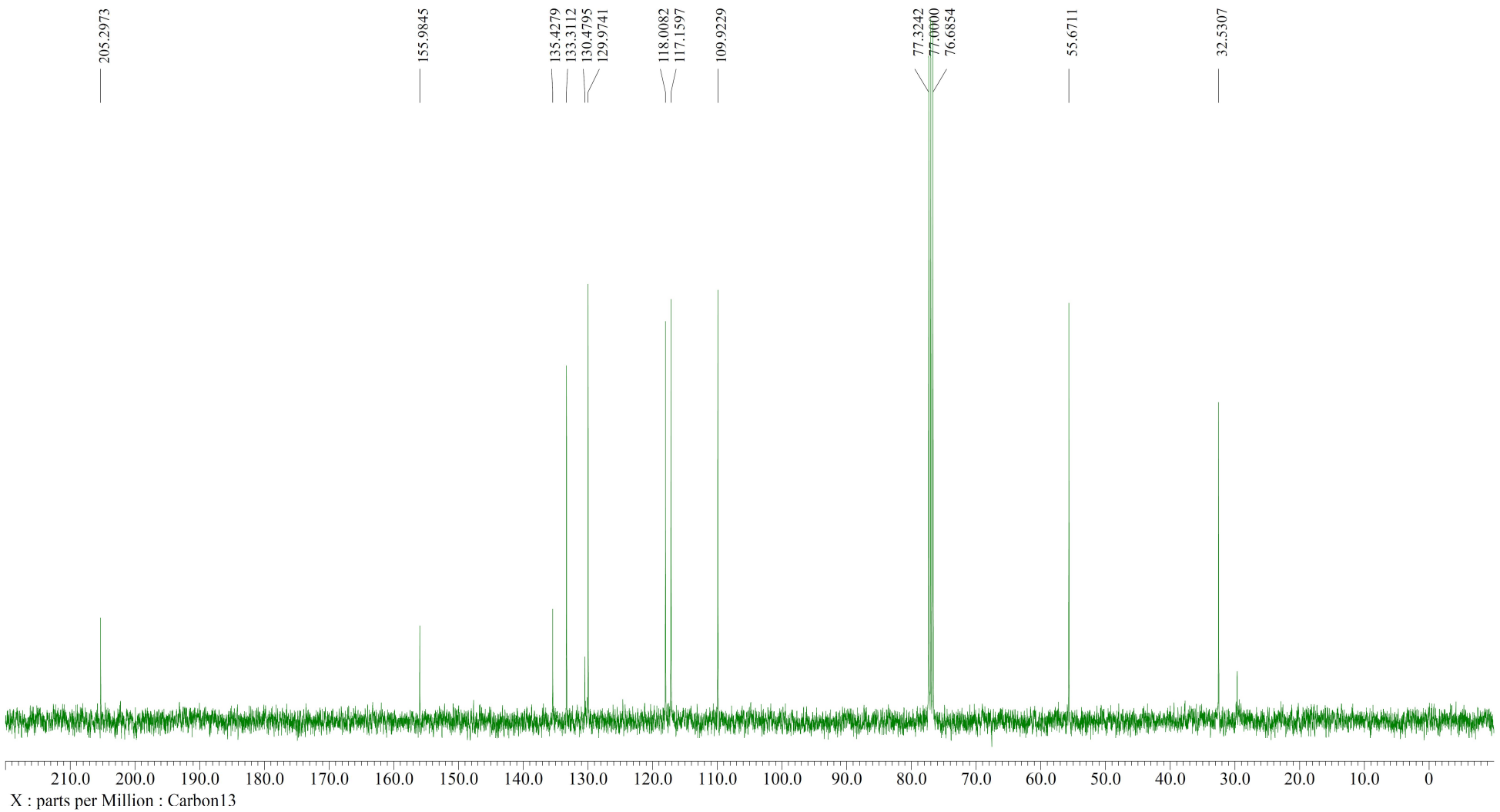
^{1}H-NMR (400 MHz, $CDCl_3$)

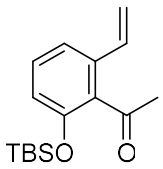




1f

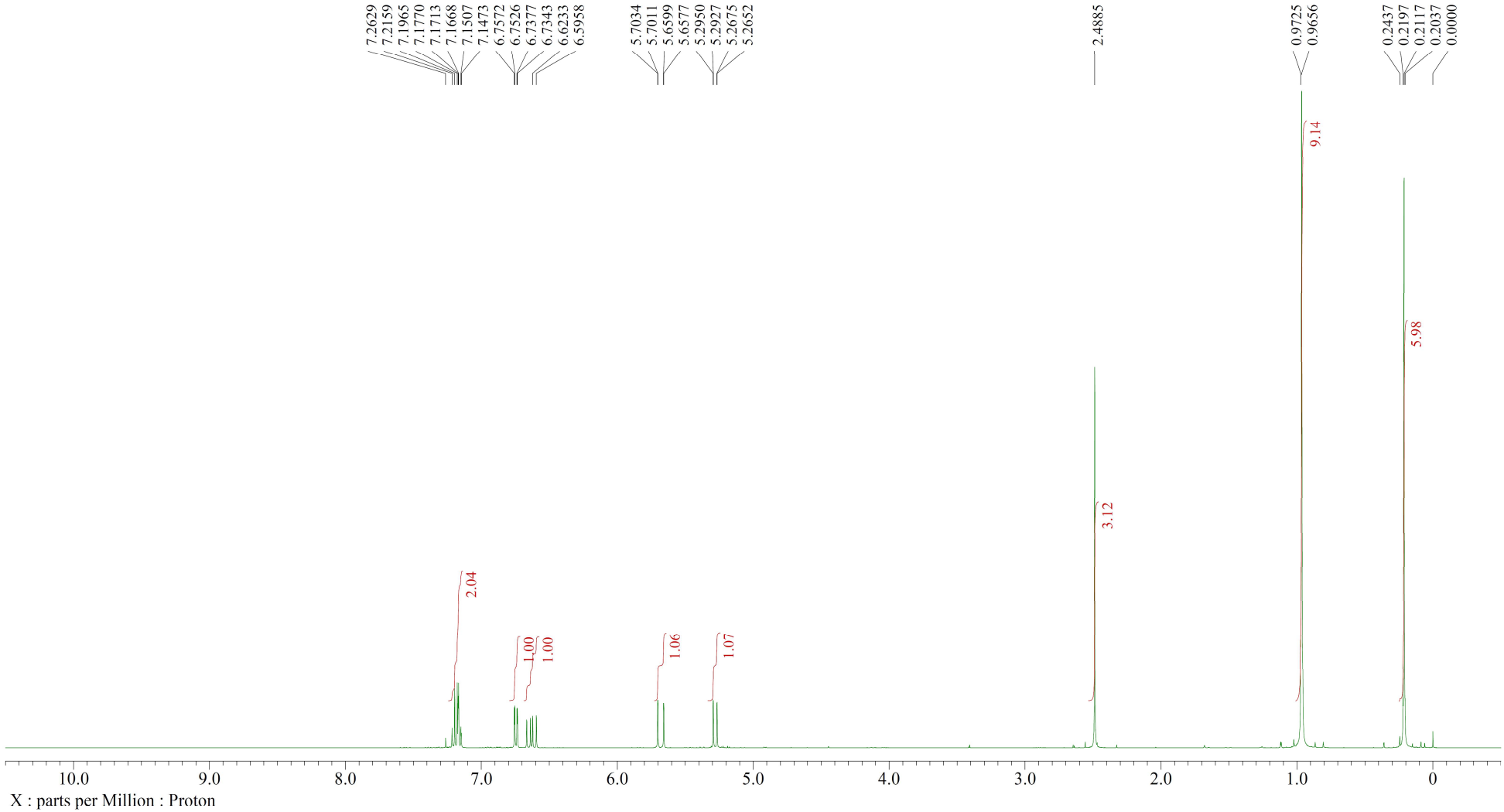
^{13}C-NMR (100 MHz, $CDCl_3$)

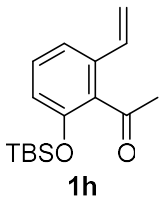




1h

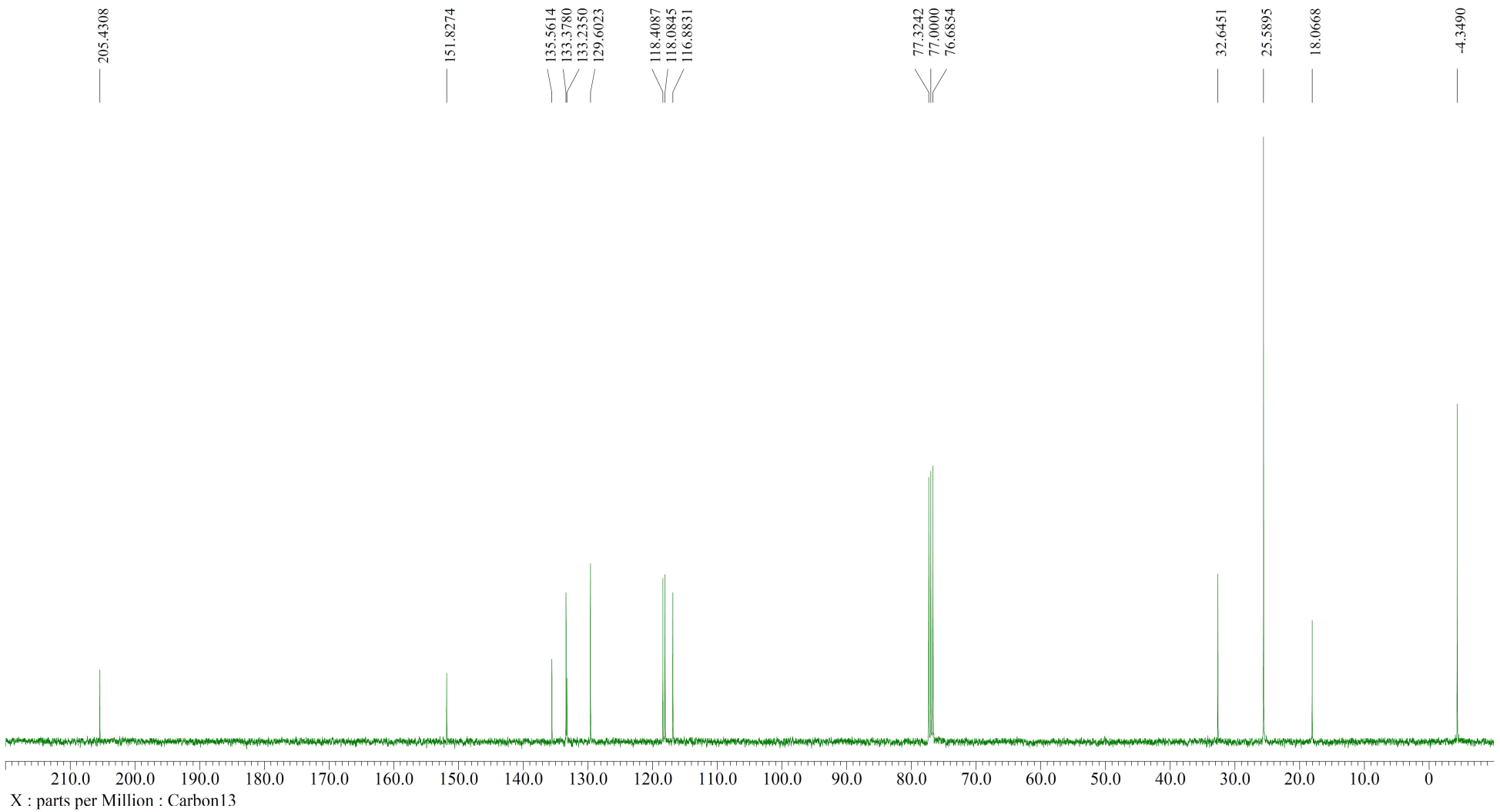
^{1}H-NMR (400 MHz, $CDCl_3$)

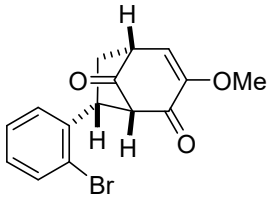




1h

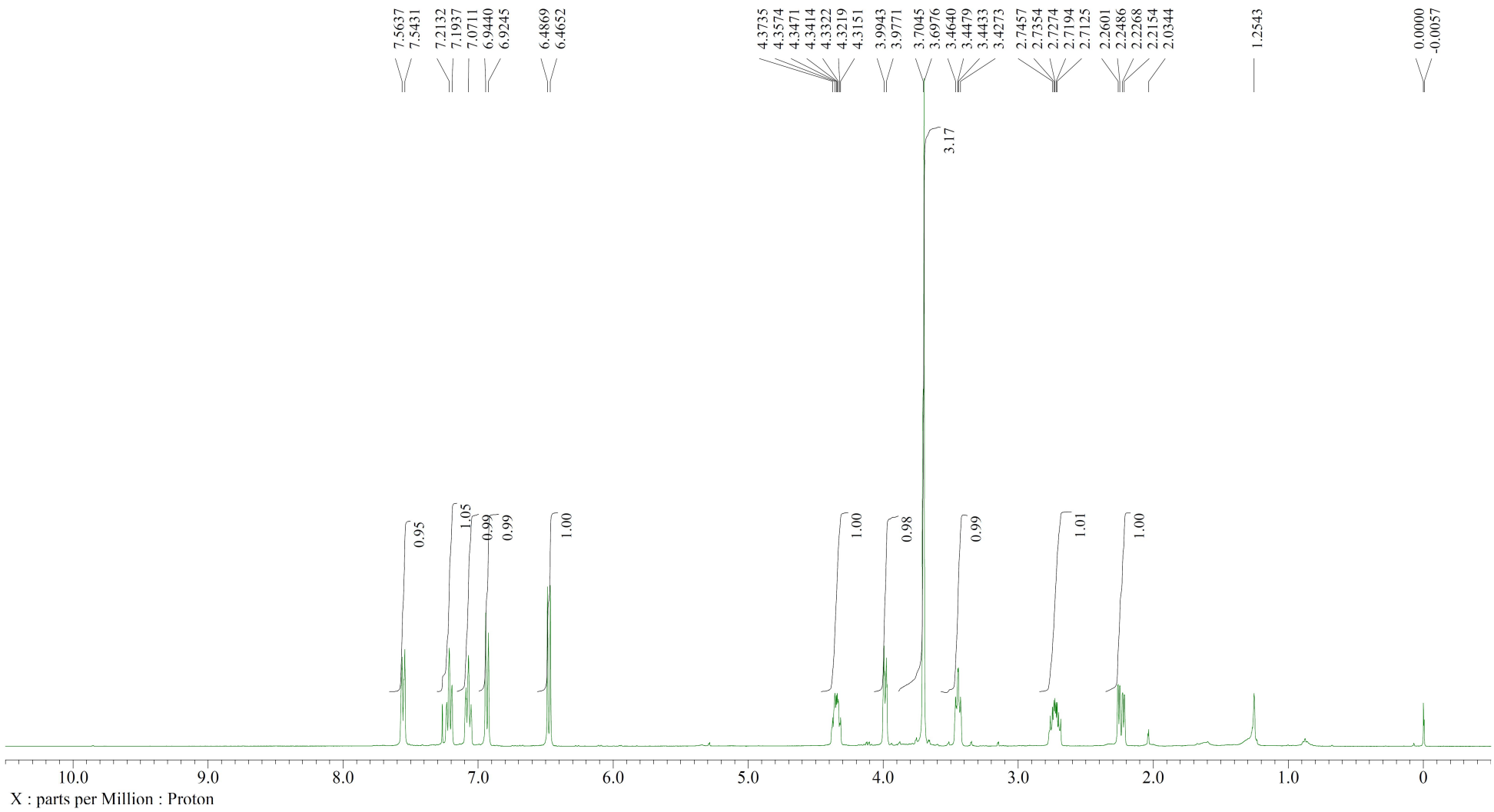
^{13}C-NMR (100 MHz, $CDCl_3$)

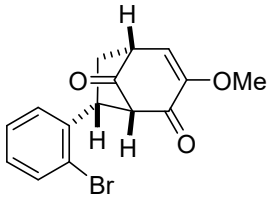




3a

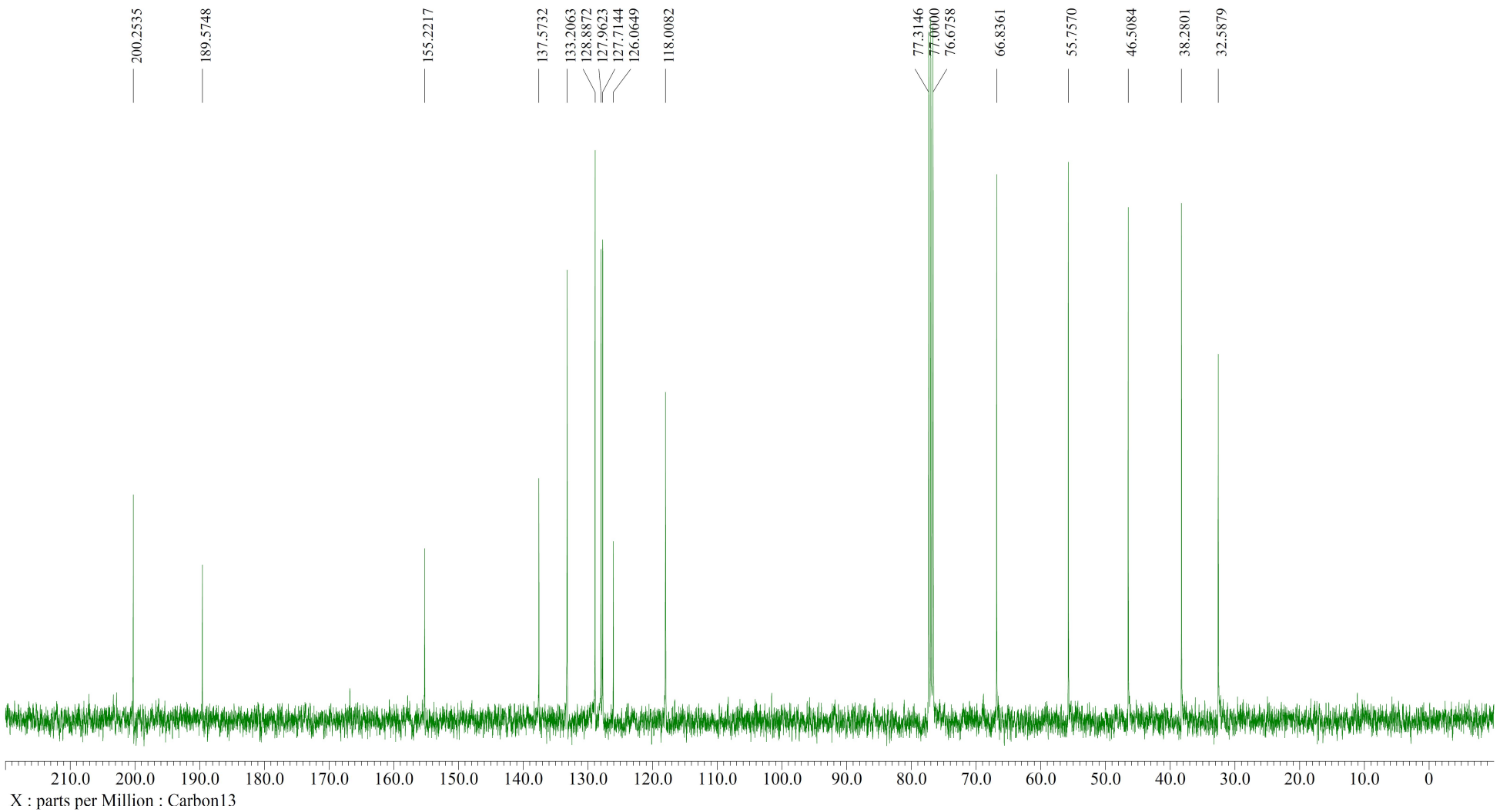
^{1}H-NMR (400 MHz, $CDCl_3$)

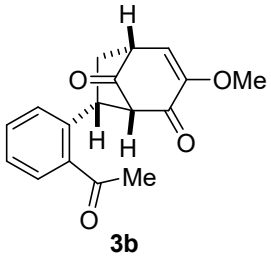




3a

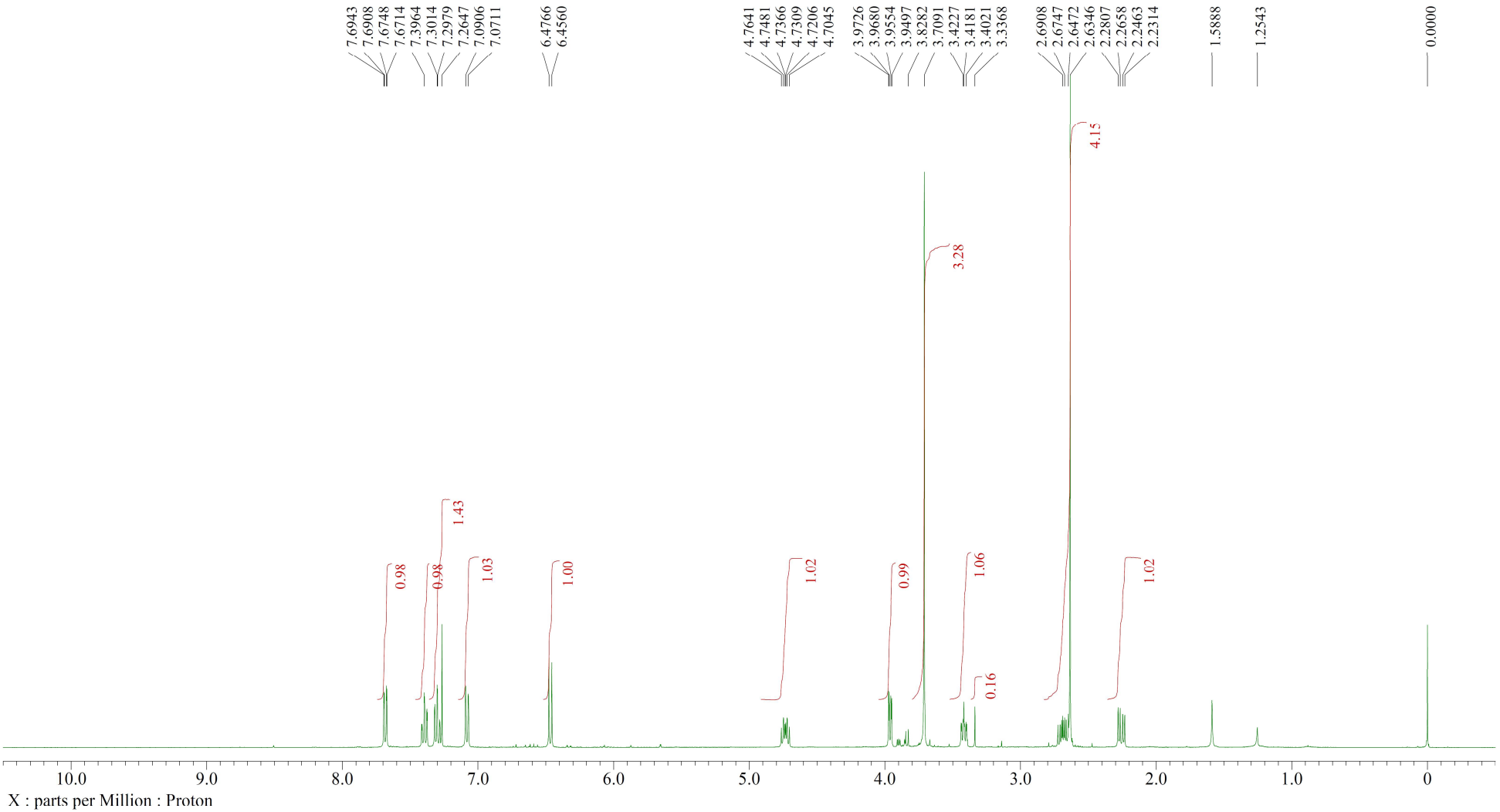
^{13}C-NMR (100 MHz, $CDCl_3$)

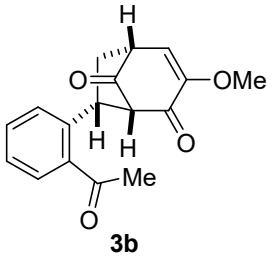




3b

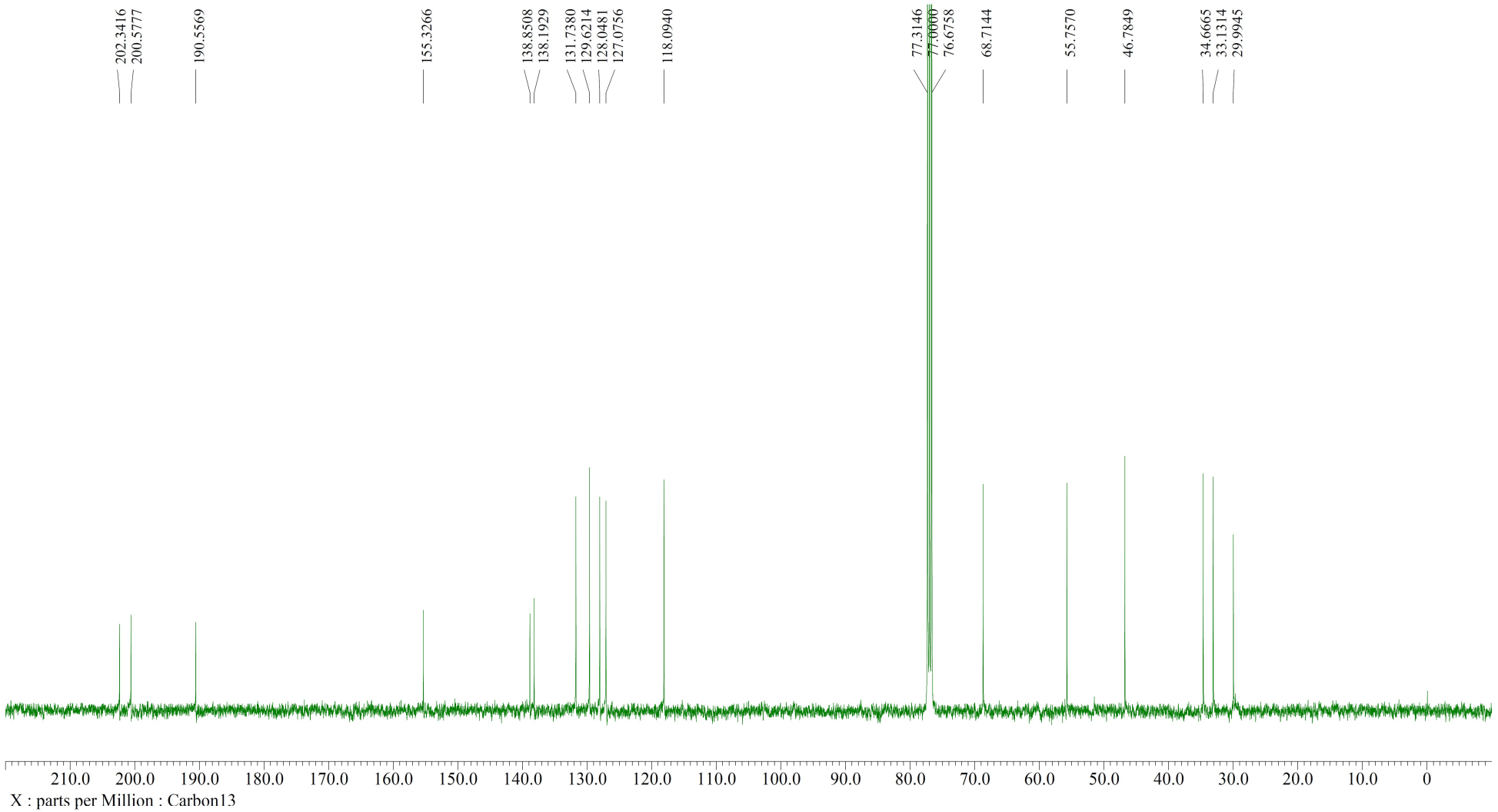
^{1}H-NMR (400 MHz, $CDCl_3$)

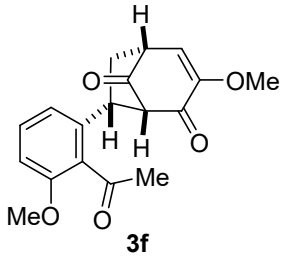




3b

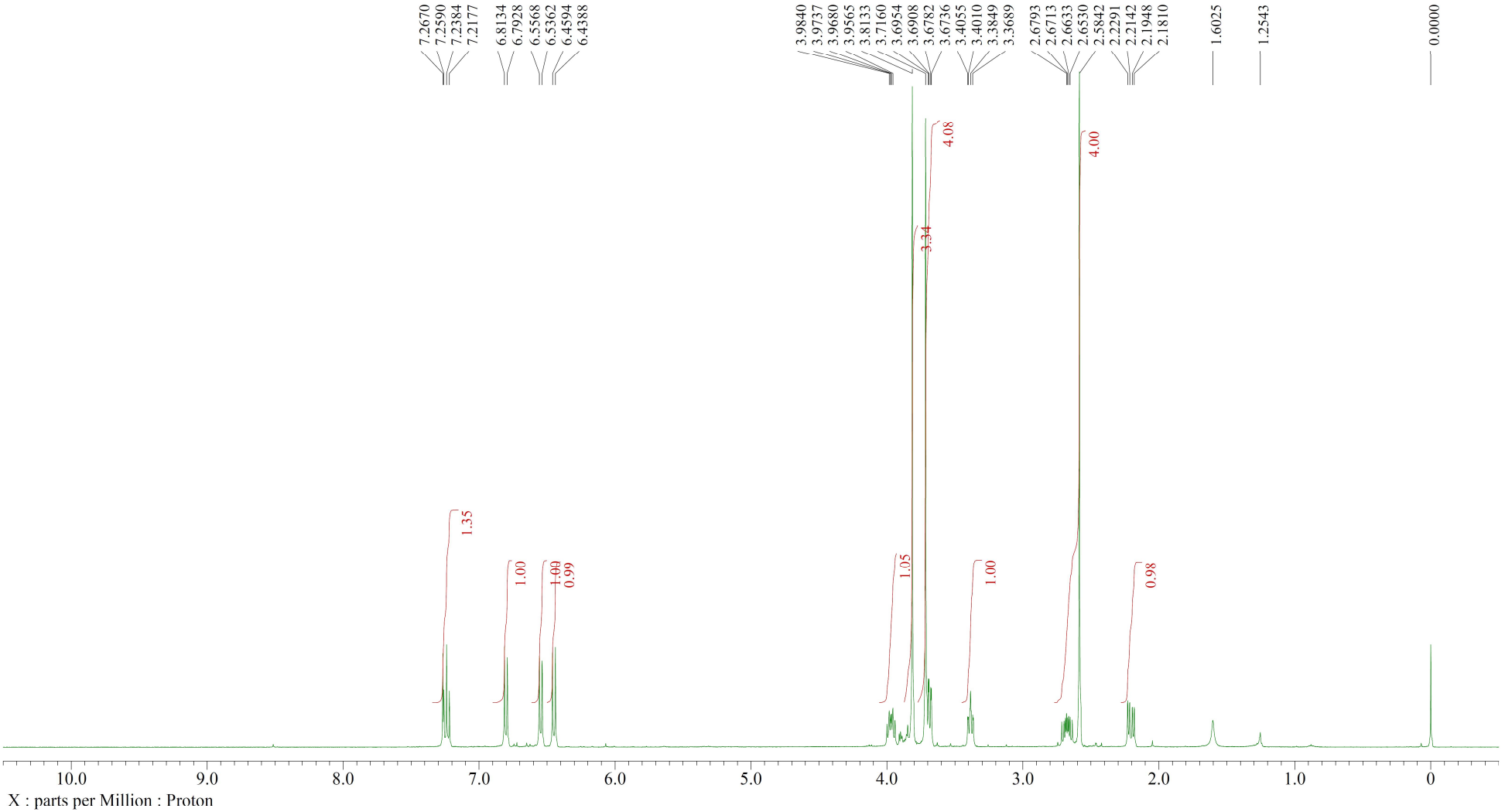
^{13}C-NMR (100 MHz, $CDCl_3$)

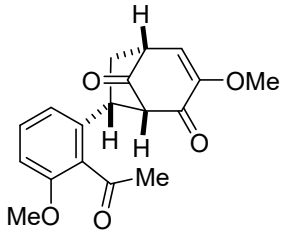




3f

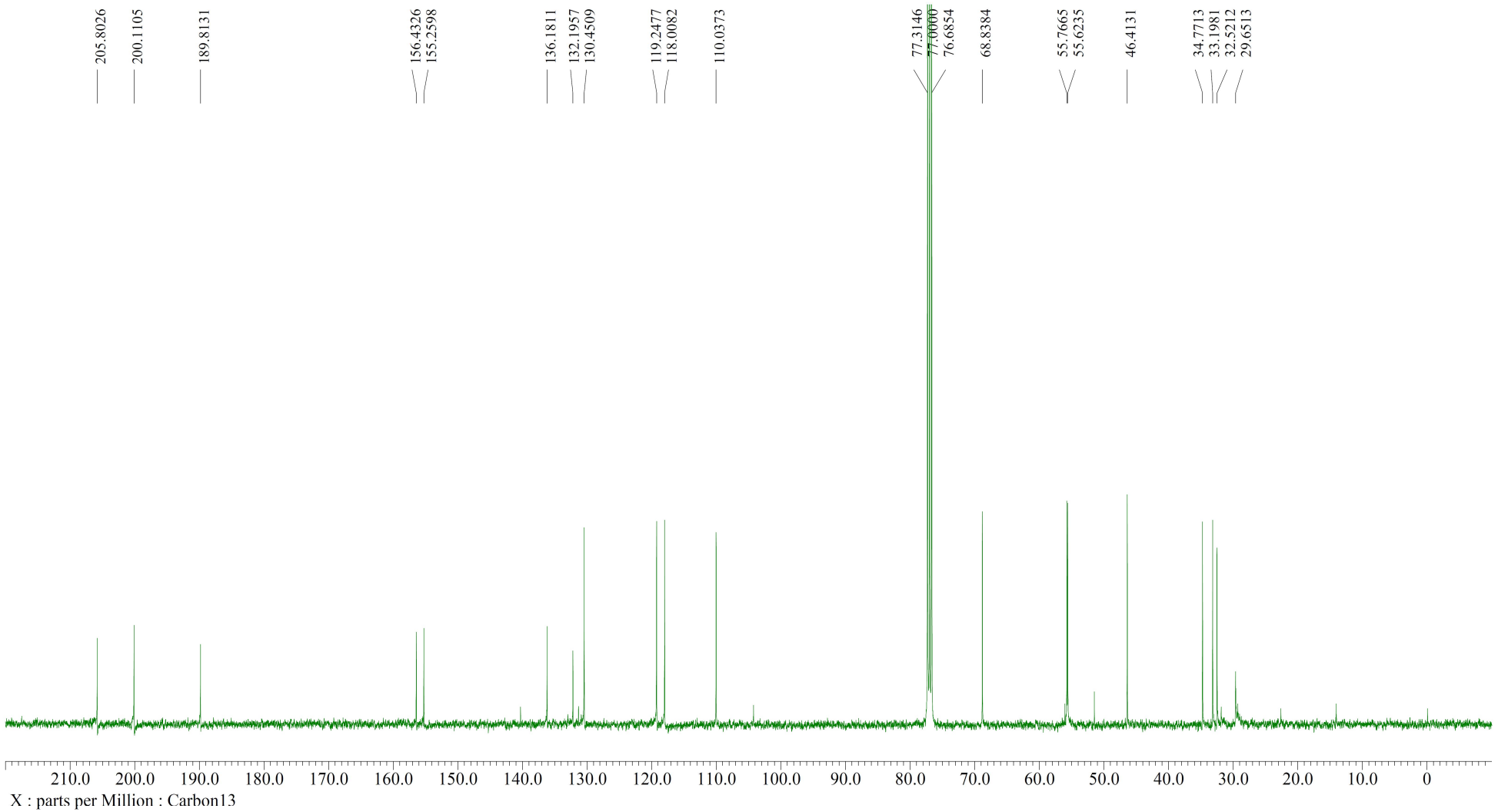
^{1}H-NMR (400 MHz, $CDCl_3$)

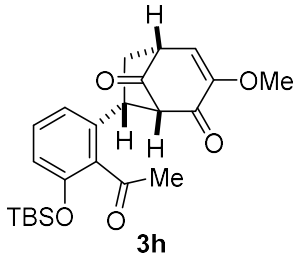




3f

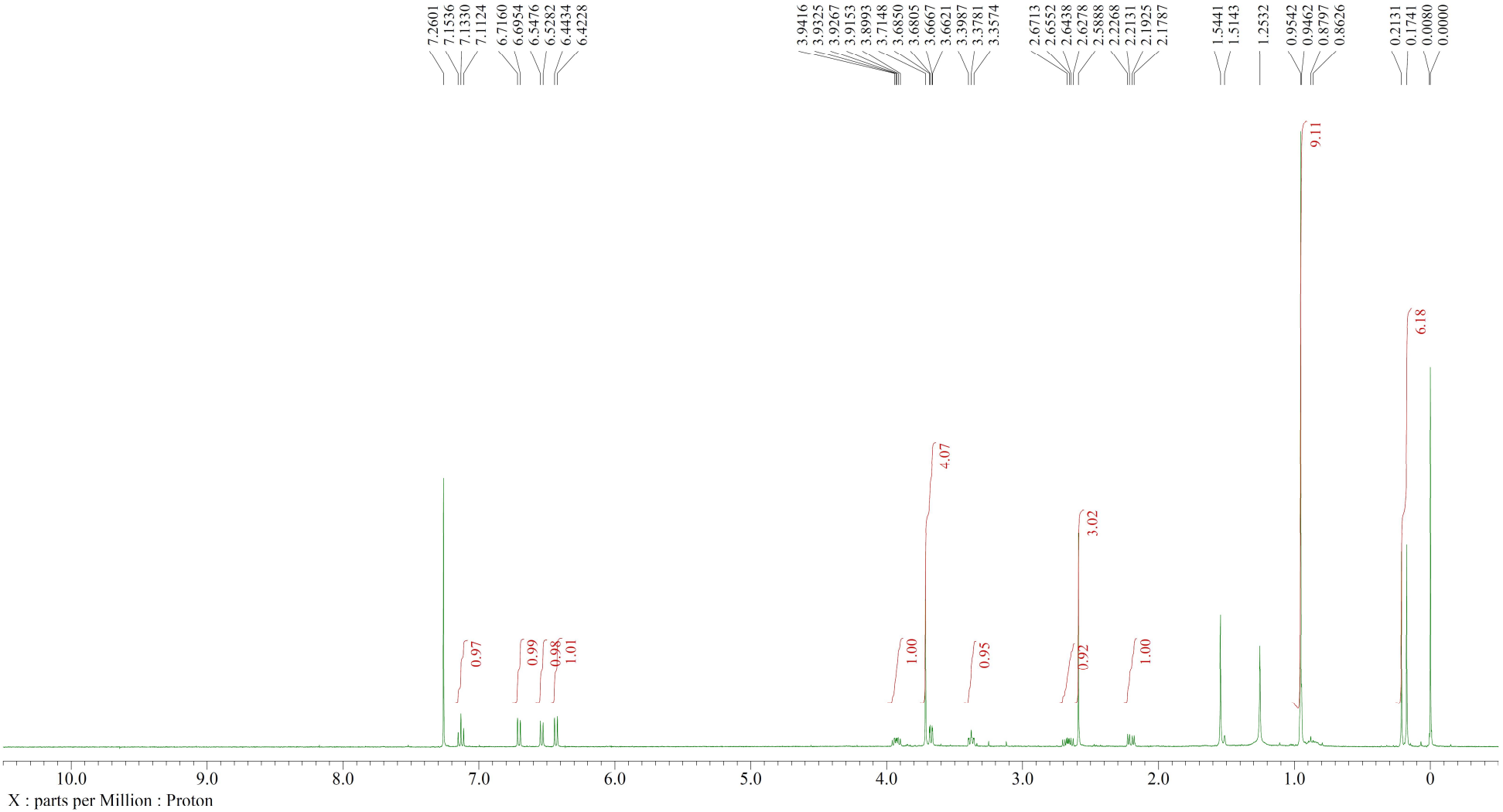
^{13}C-NMR (100 MHz, $CDCl_3$)

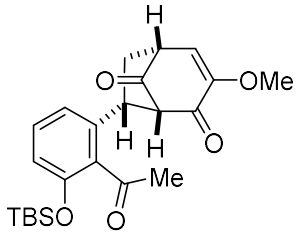




3h

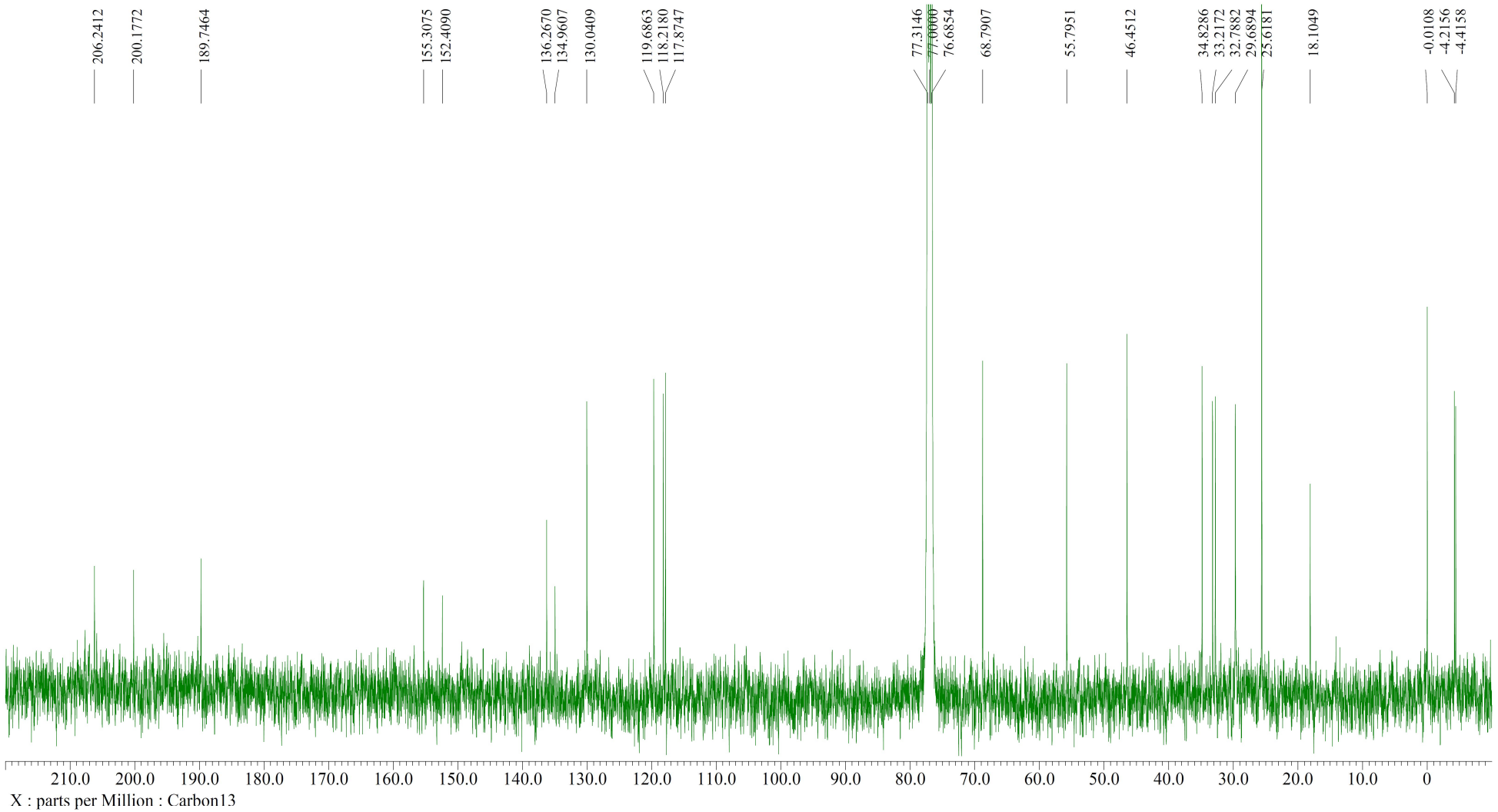
^{1}H-NMR (400 MHz, $CDCl_3$)

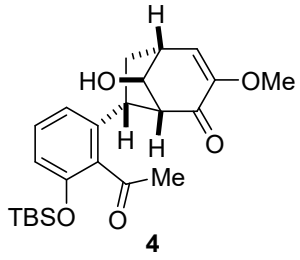




3h

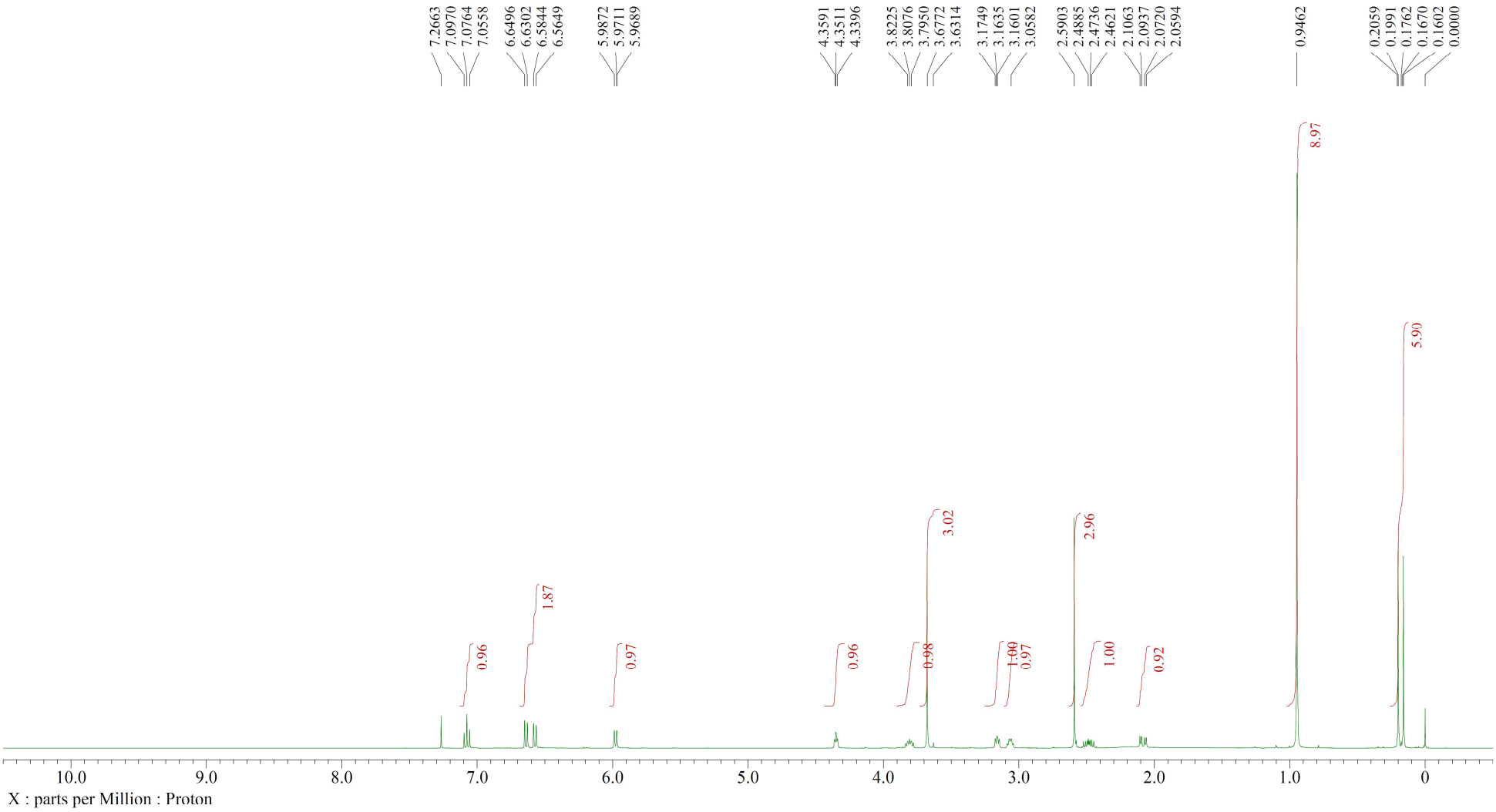
^{13}C-NMR (100 MHz, $CDCl_3$)

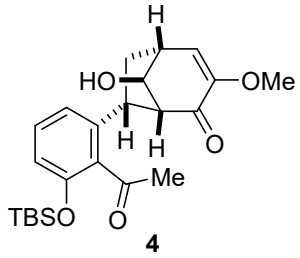




4

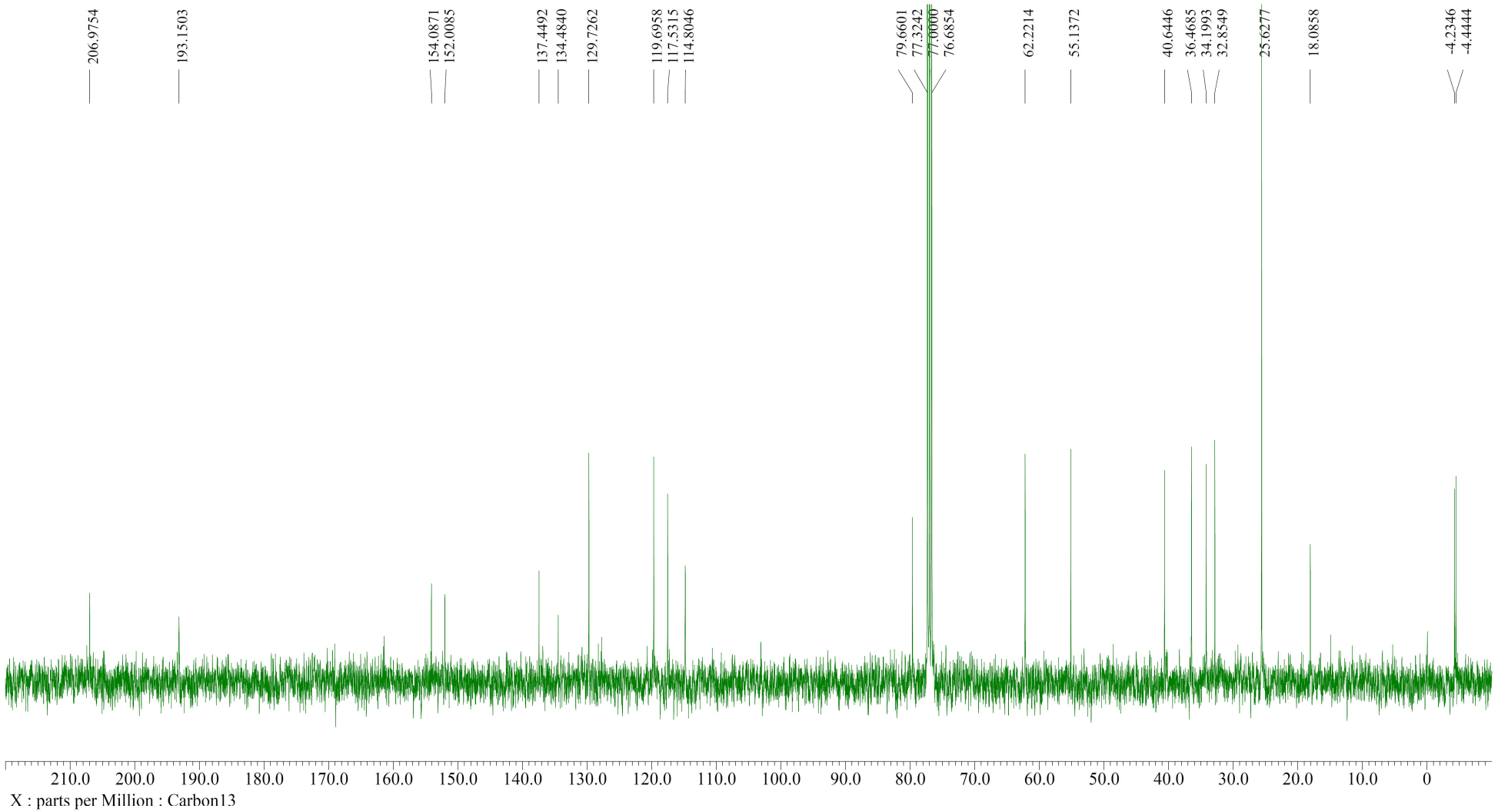
^{1}H-NMR (400 MHz, $CDCl_3$)



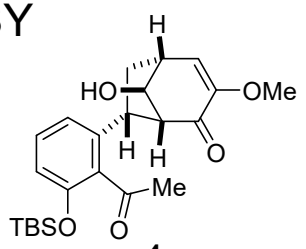


4

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

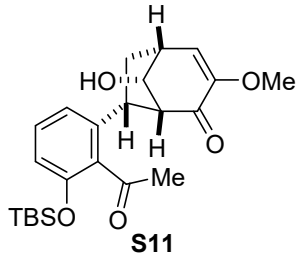


NOESY


H
HO
OMe
H
H
O
Me
TBSO
O

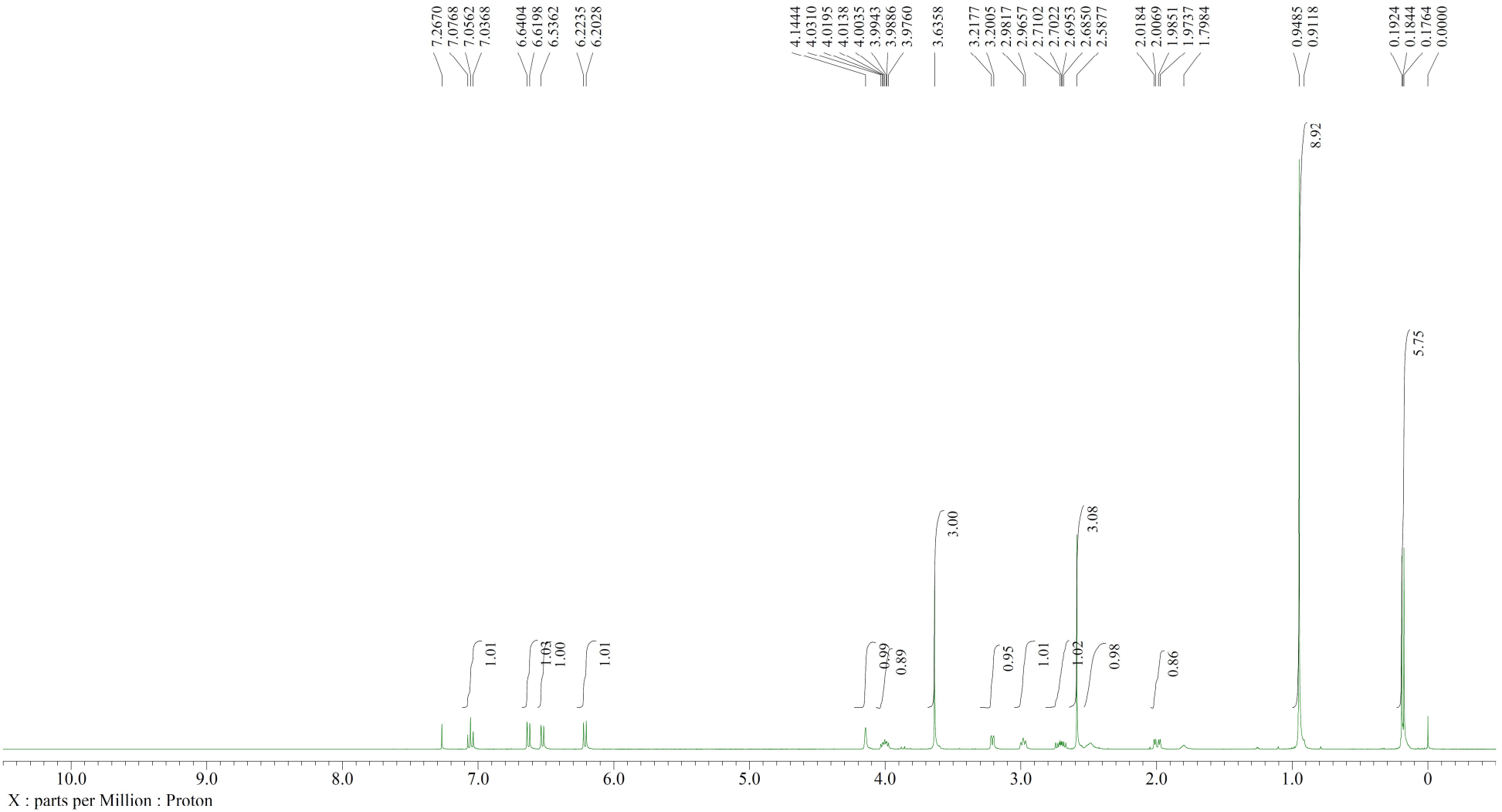
4

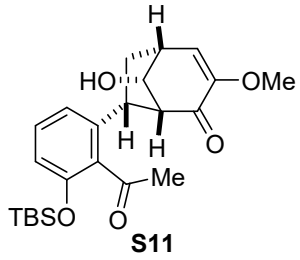
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance



S11

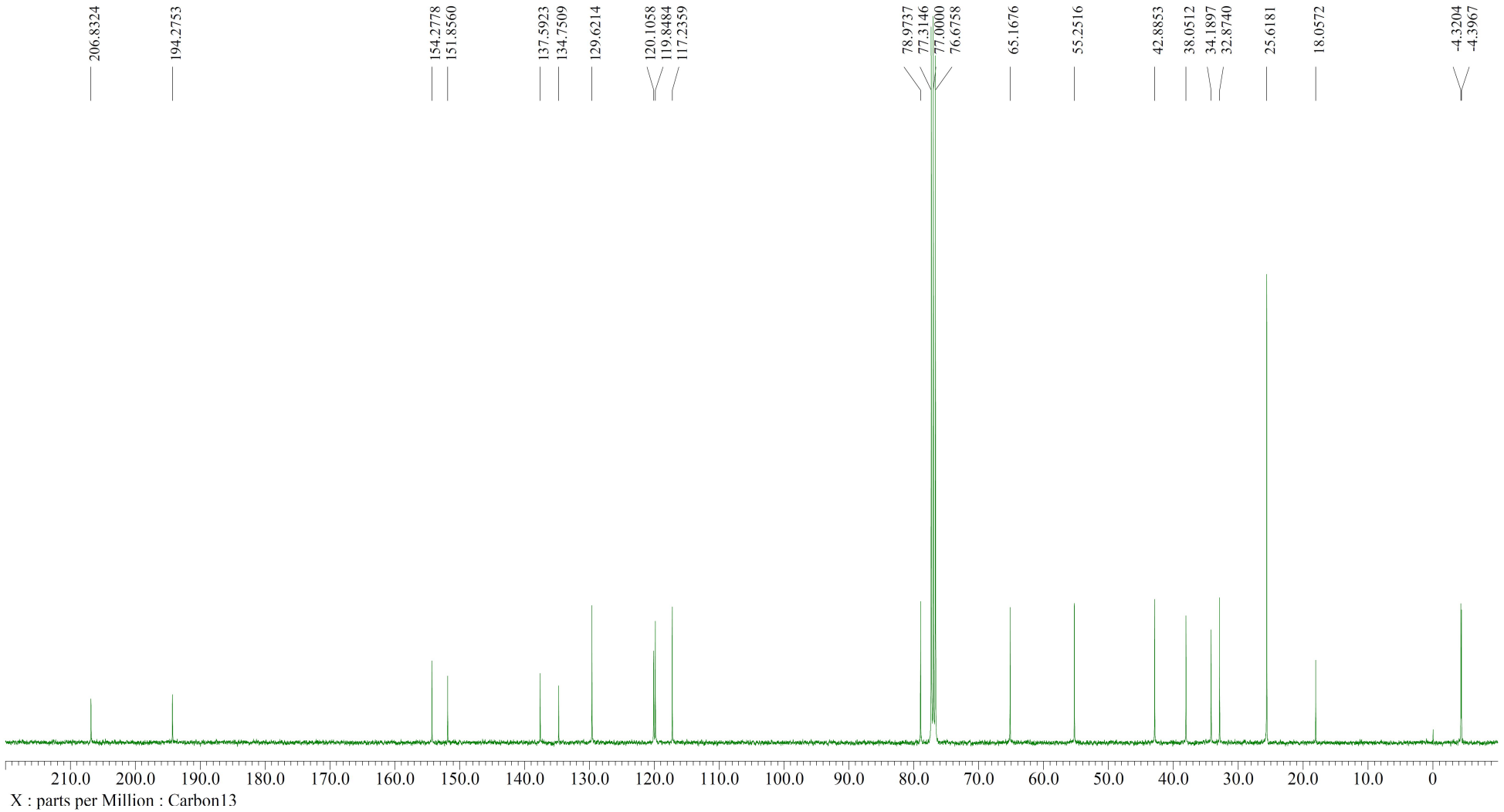
^{1}H-NMR (400 MHz, $CDCl_3$)

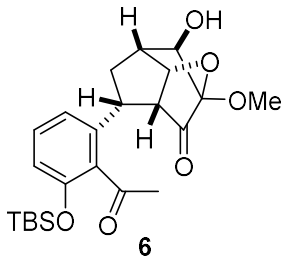




S11

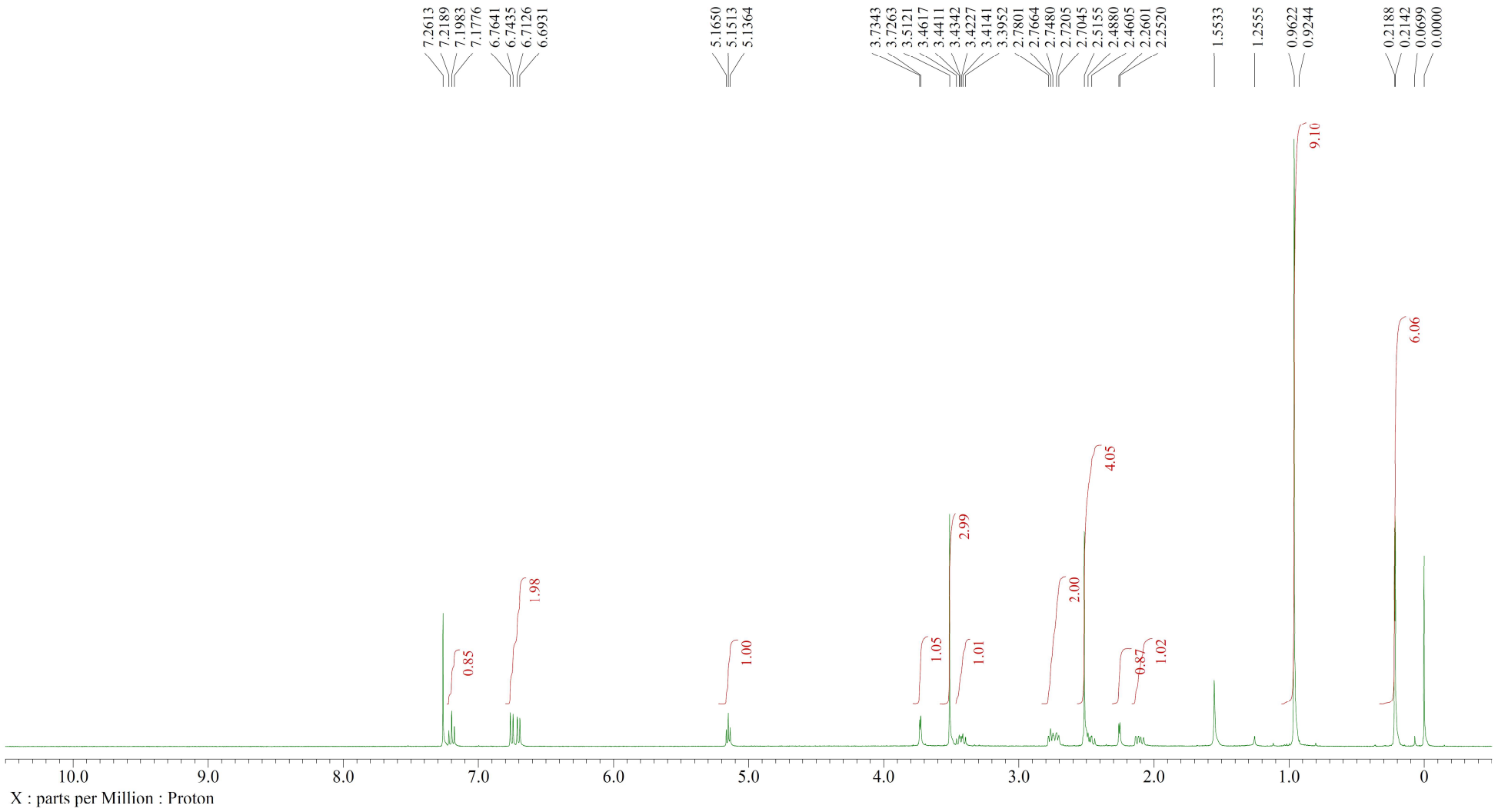
^{13}C-NMR (100 MHz, $CDCl_3$)

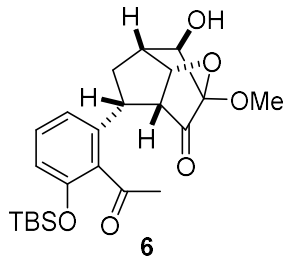




6

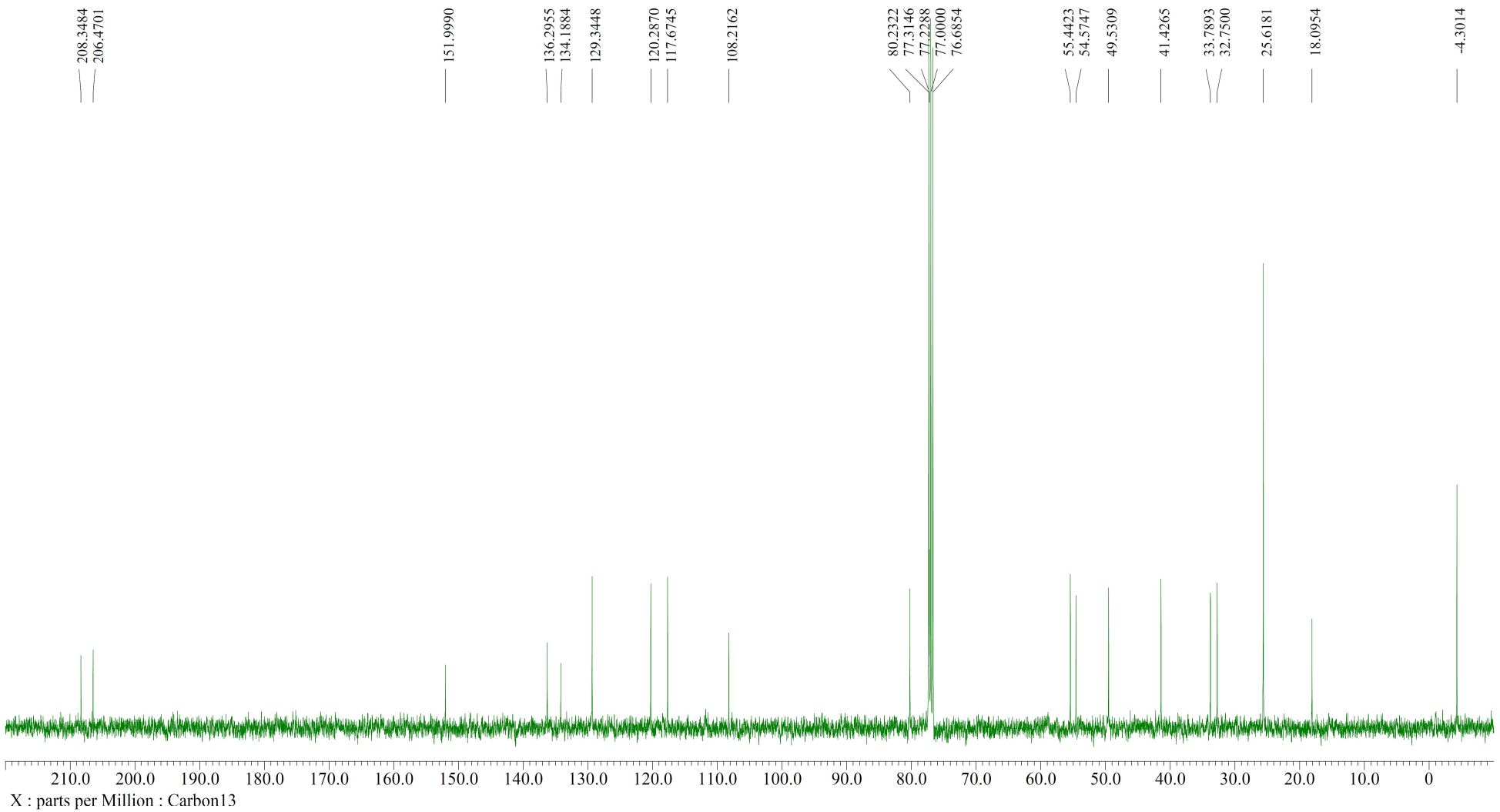
^{1}H-NMR (400 MHz, $CDCl_3$)

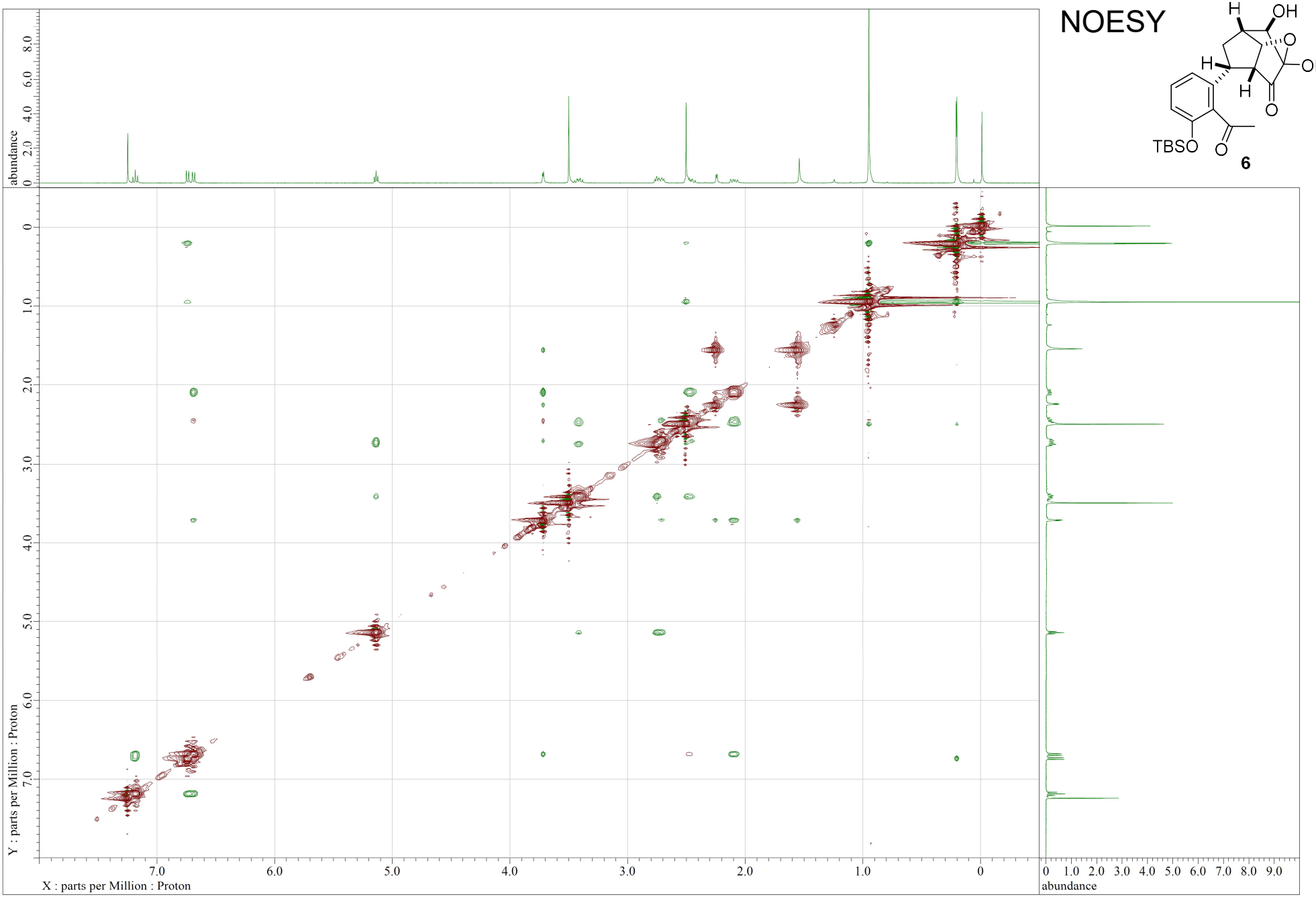


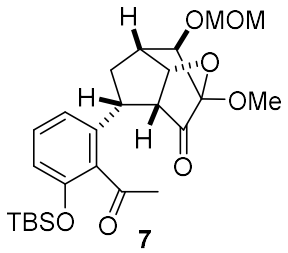


6

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

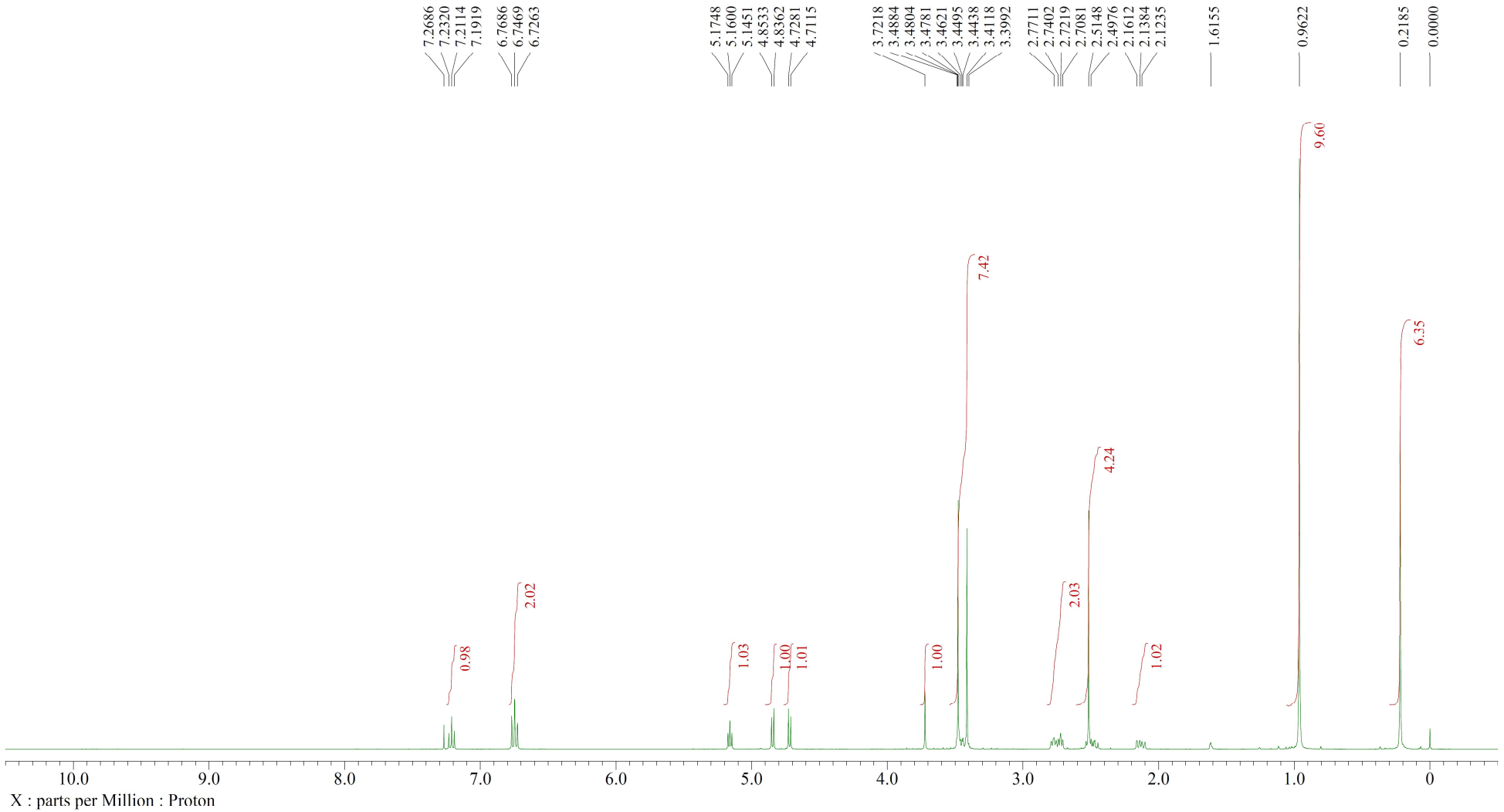


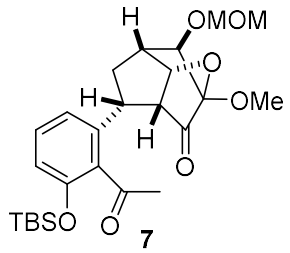

NOESY
H
OH
O
H
OMe
H
O
TBSO
O
6
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance



7

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





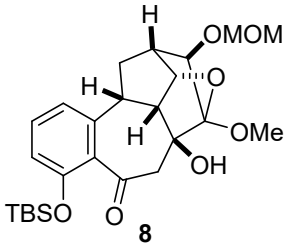
7

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

208.9109
206.4510
151.9799
136.2574
134.1407
129.3639
120.3823
117.6650
108.6834
95.8975
80.0511
79.9367
77.3146
77.0000
76.6854
55.6616
55.2612
54.4507
48.9111
41.6935
34.0276
32.7595
25.6181
18.0954
-4.3014

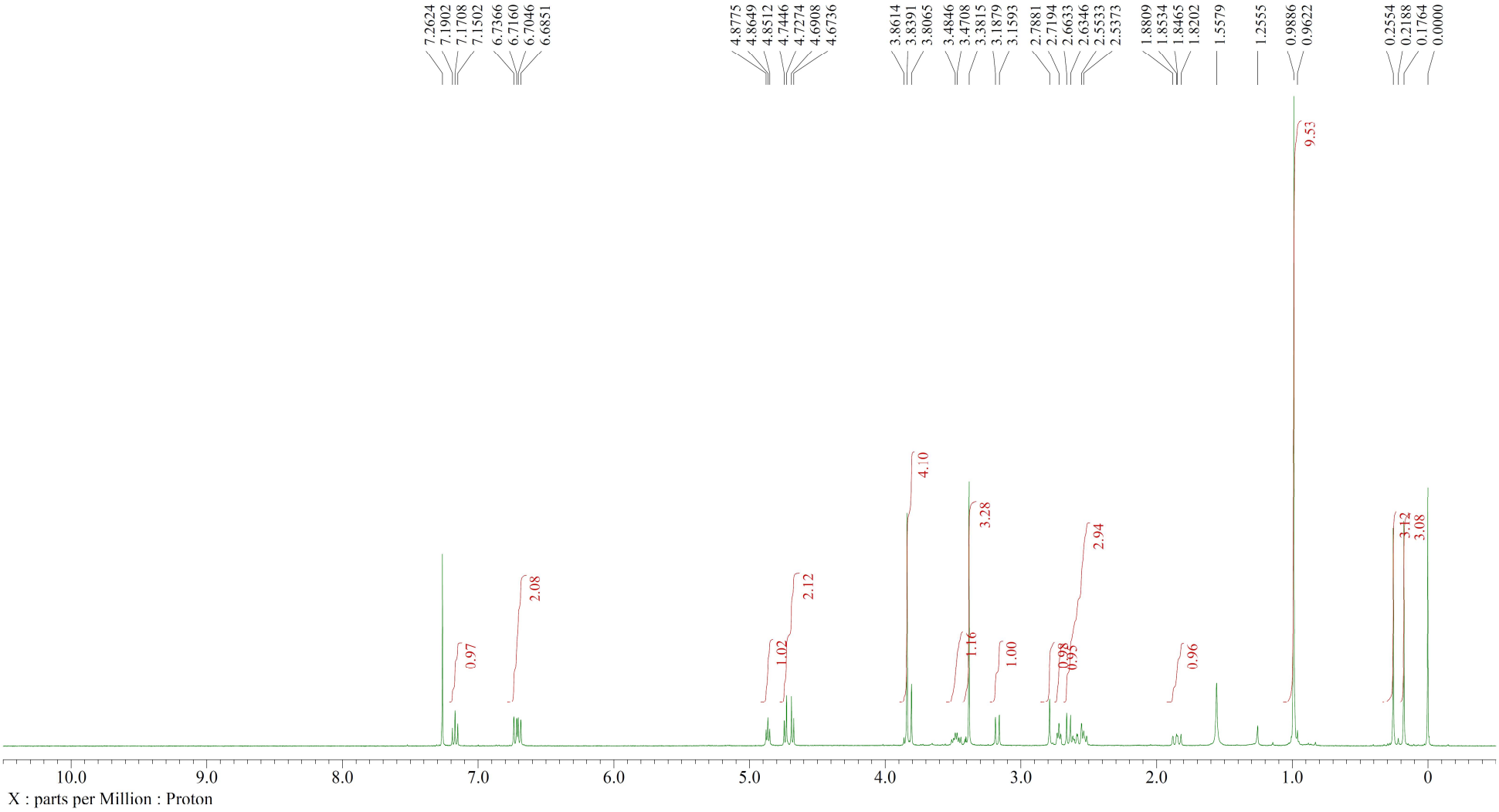
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

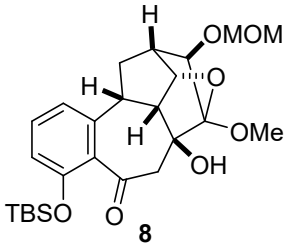
X : parts per Million : Carbon13



8

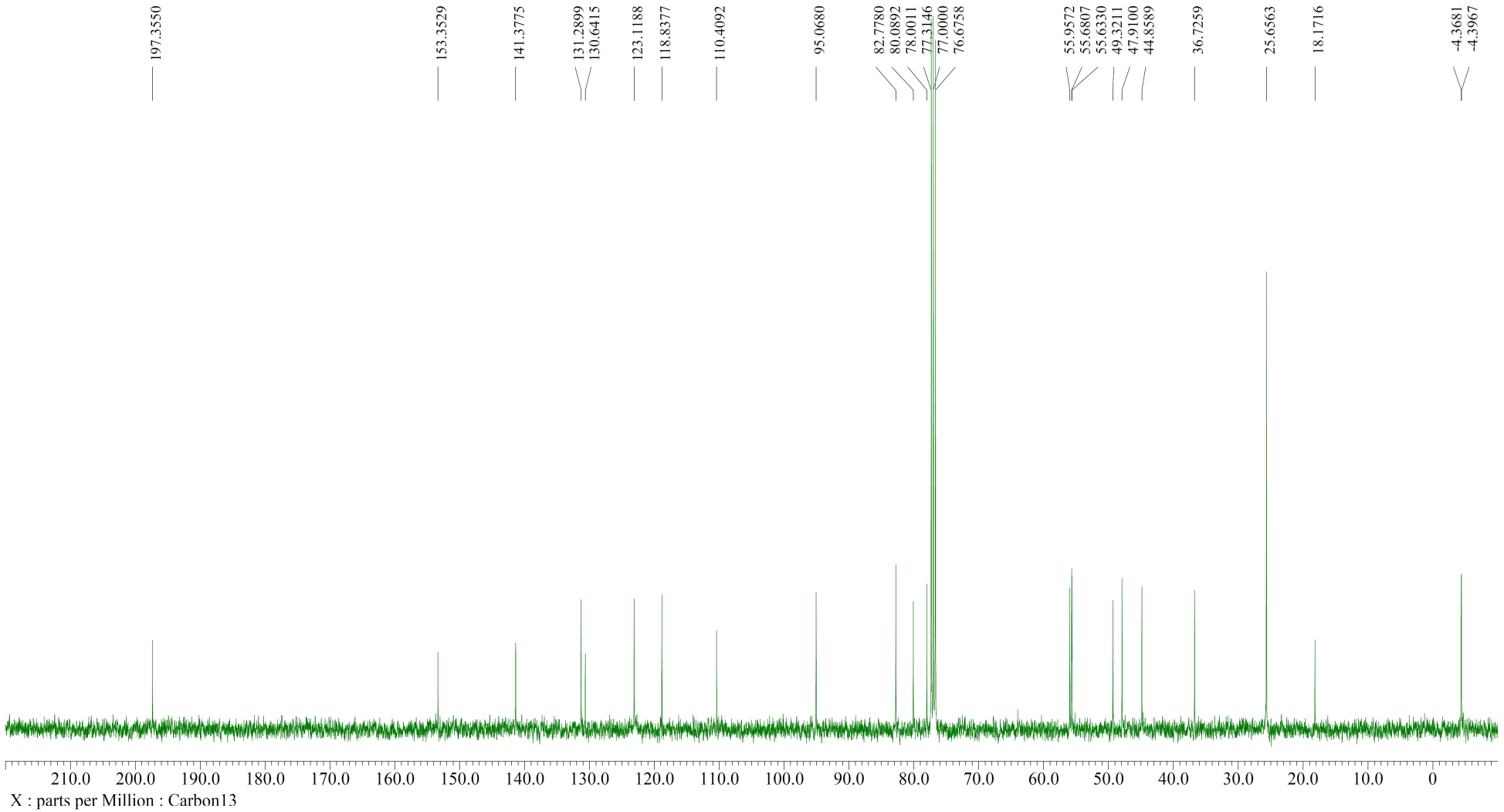
^{1}H-NMR (400 MHz, $CDCl_3$)

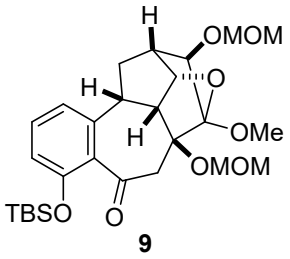




8

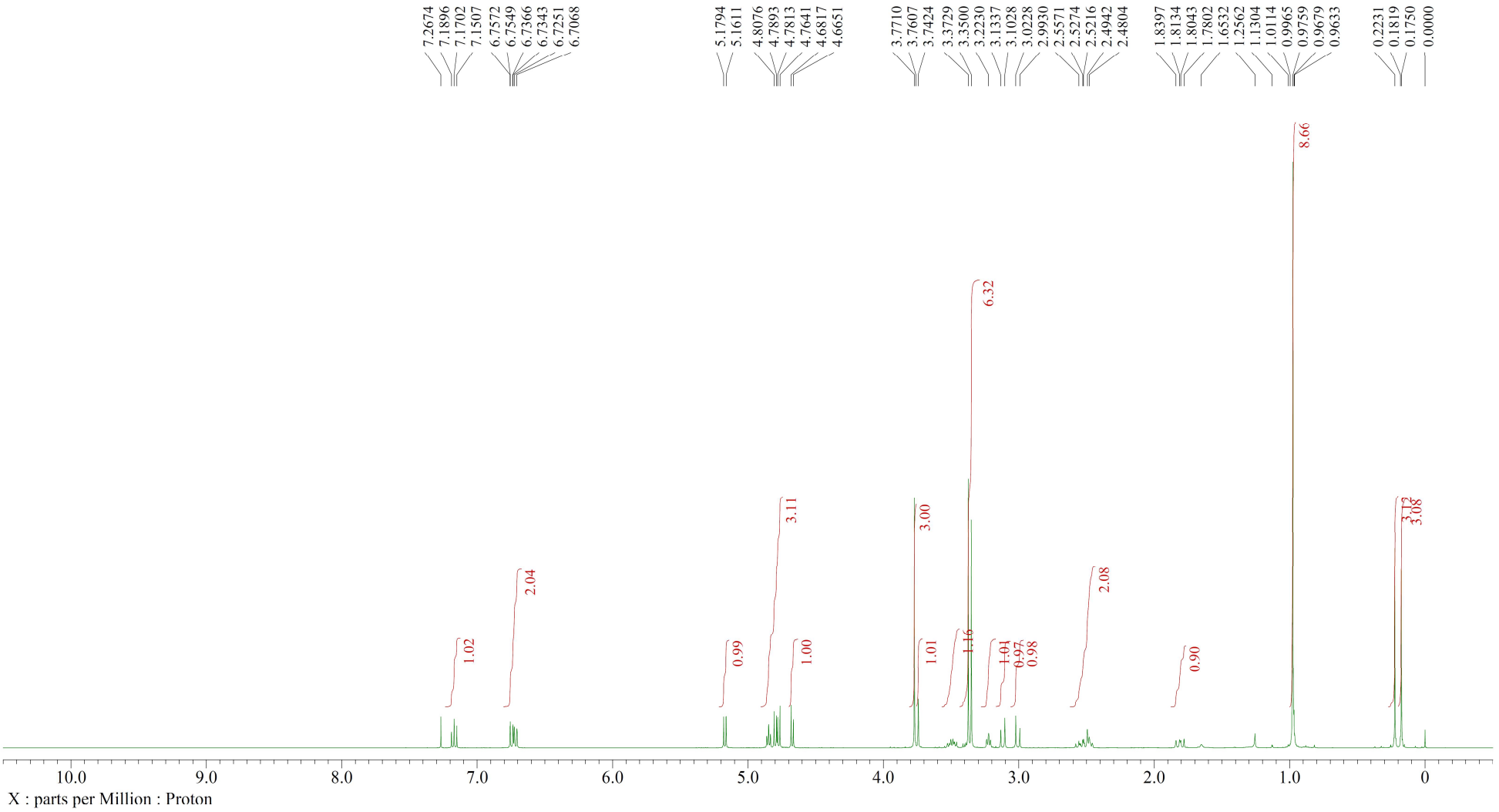
^{13}C-NMR (100 MHz, $CDCl_3$)

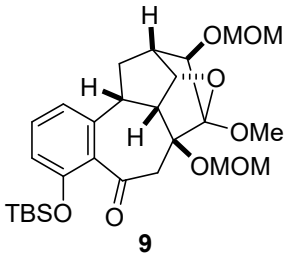




9

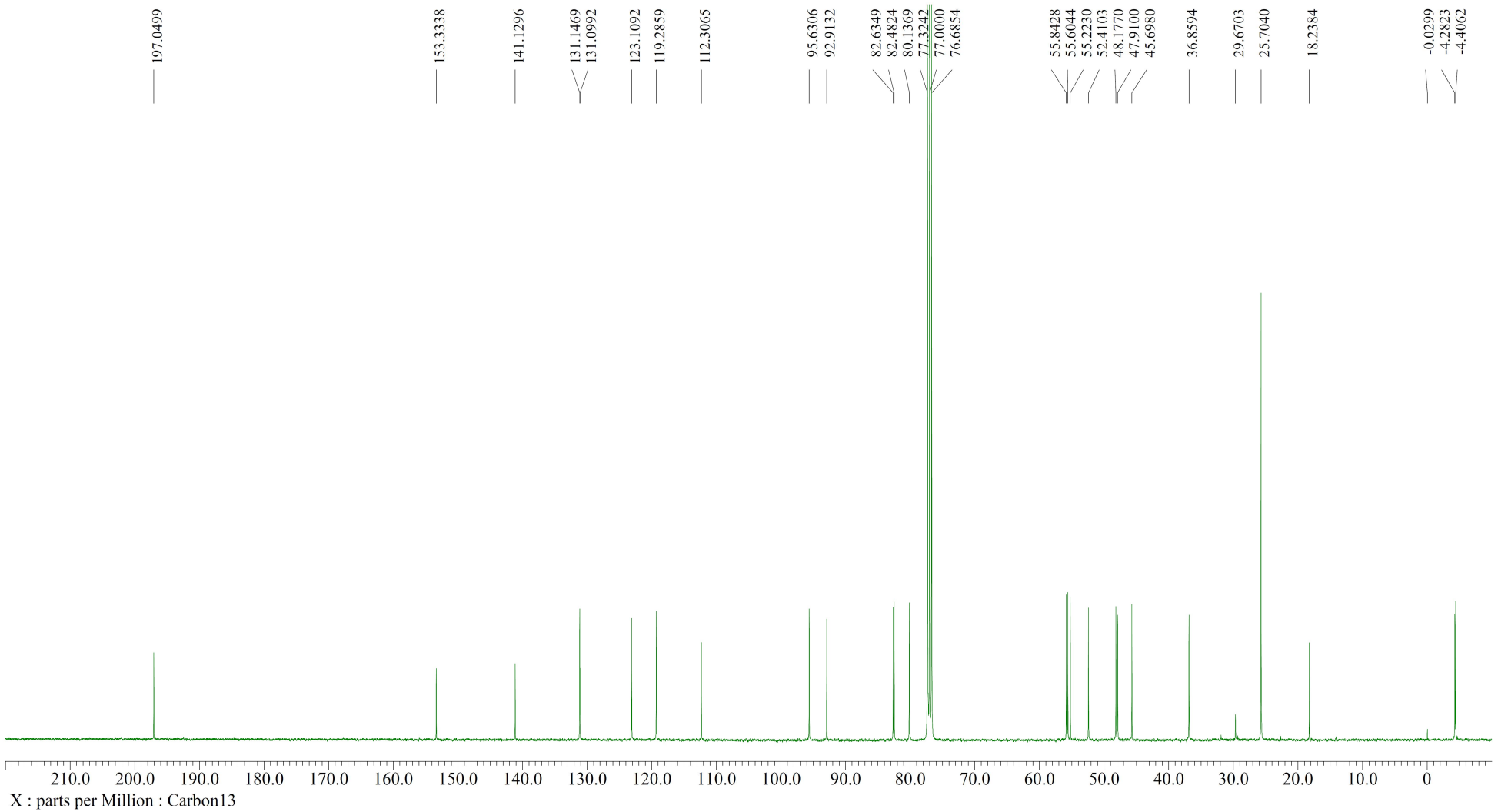
^{1}H-NMR (400 MHz, $CDCl_3$)

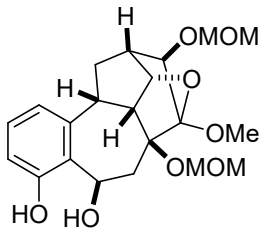




9

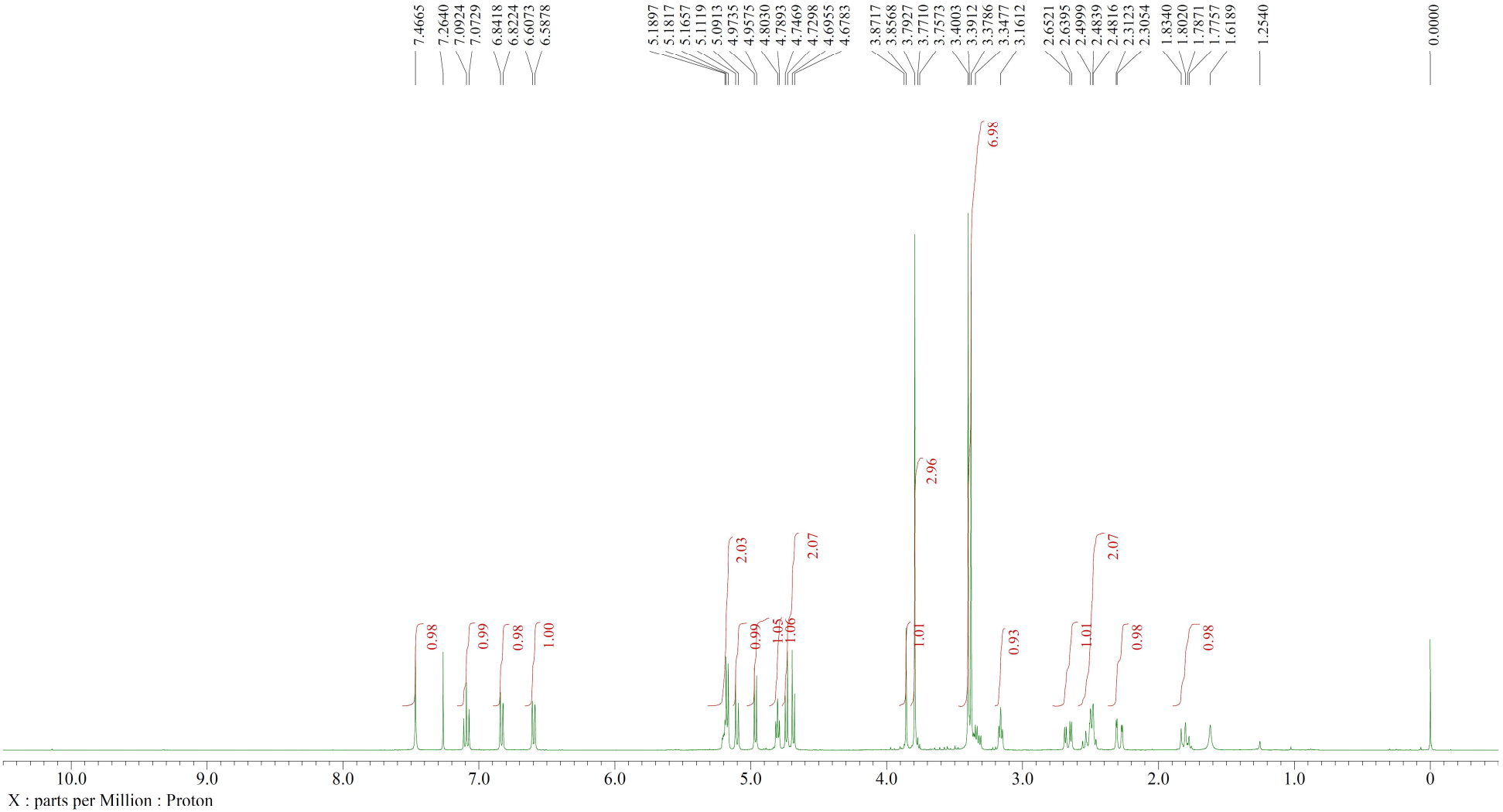
^{13}C-NMR (100 MHz, $CDCl_3$)

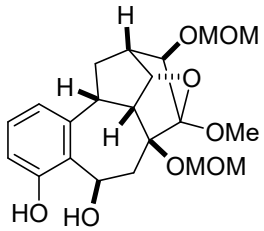




10

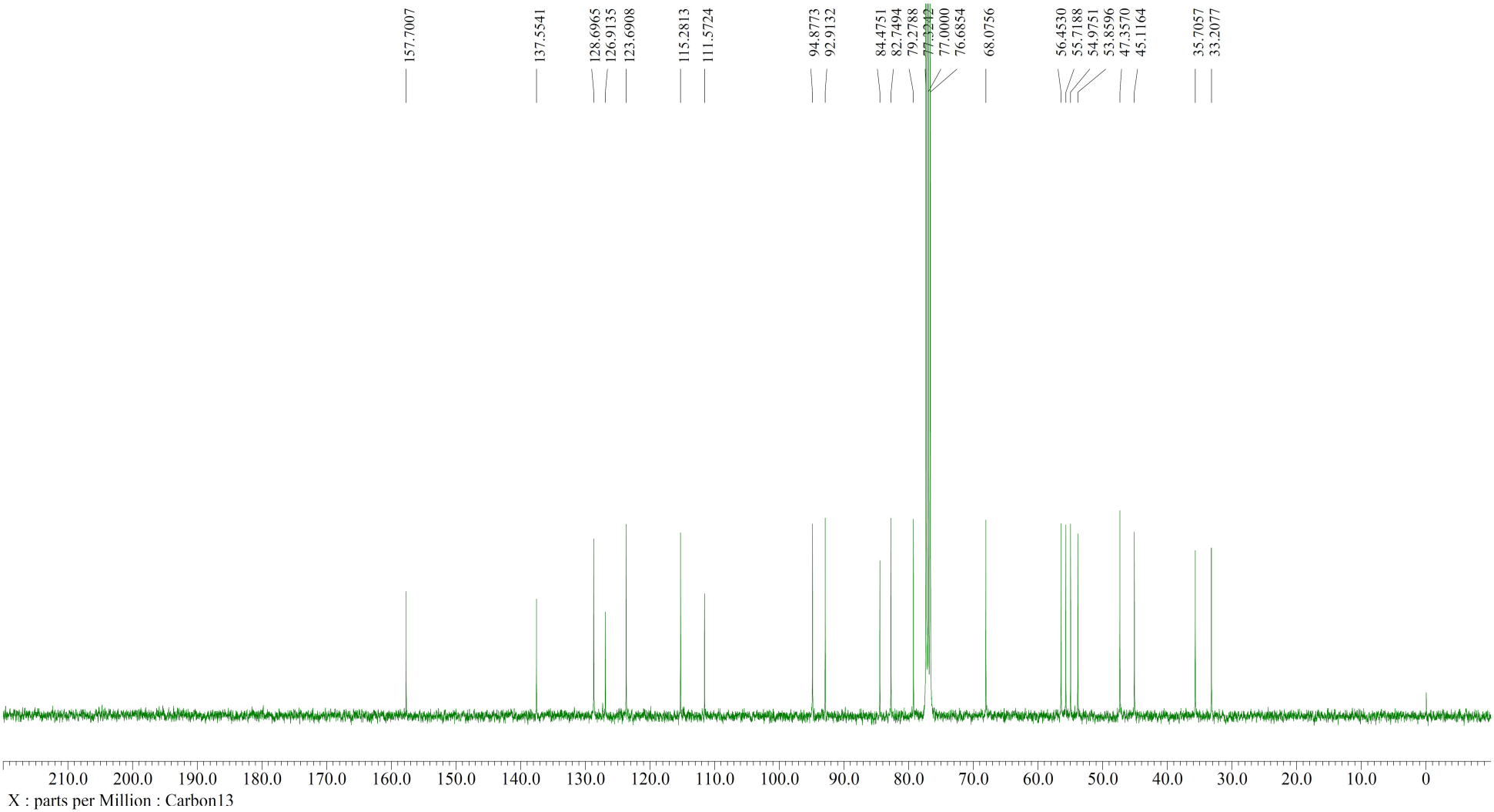
^{1}H-NMR (400 MHz, $CDCl_3$)

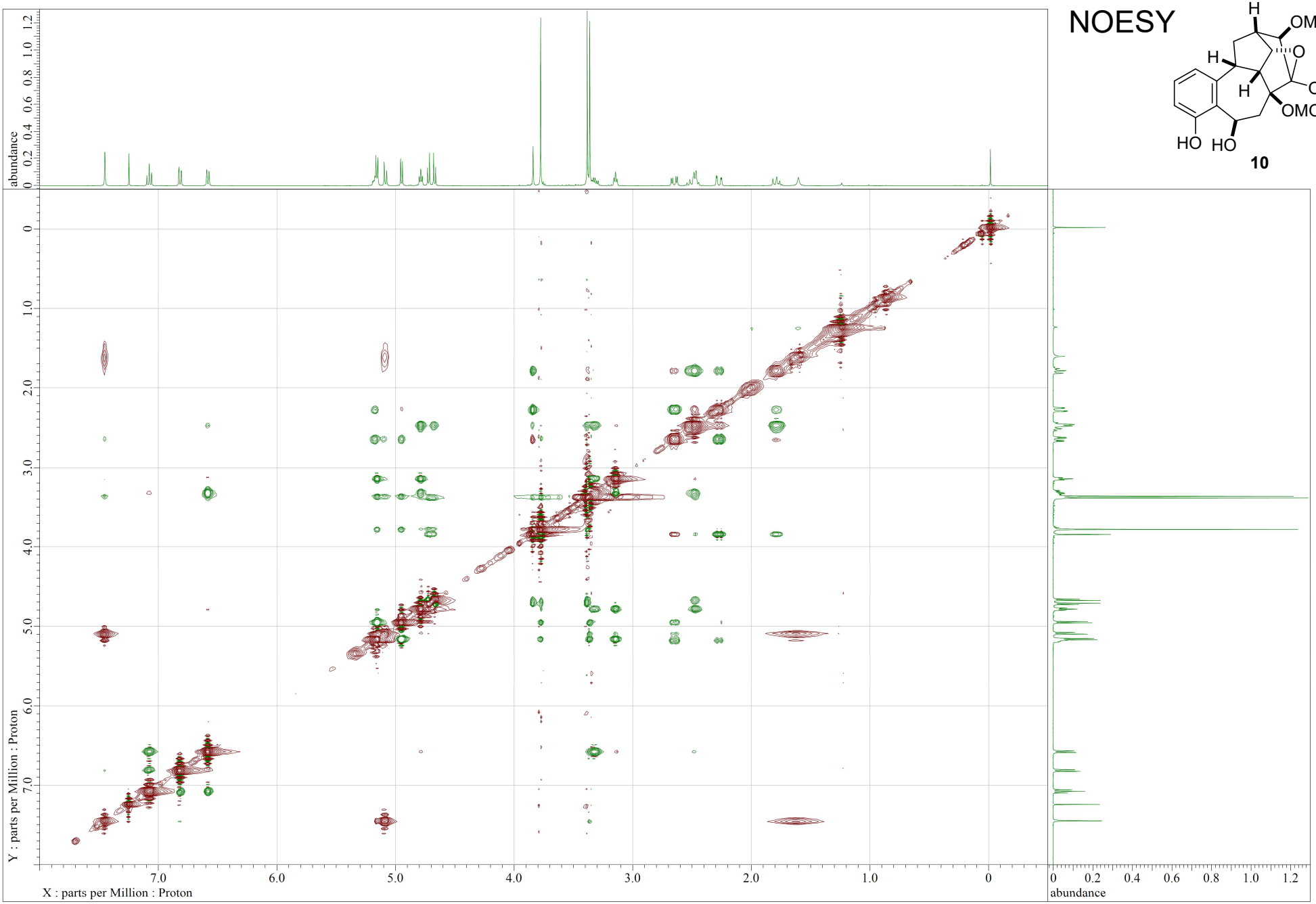


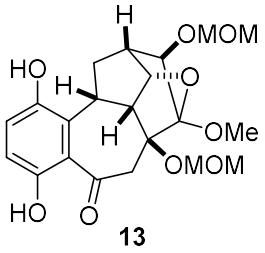


10

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

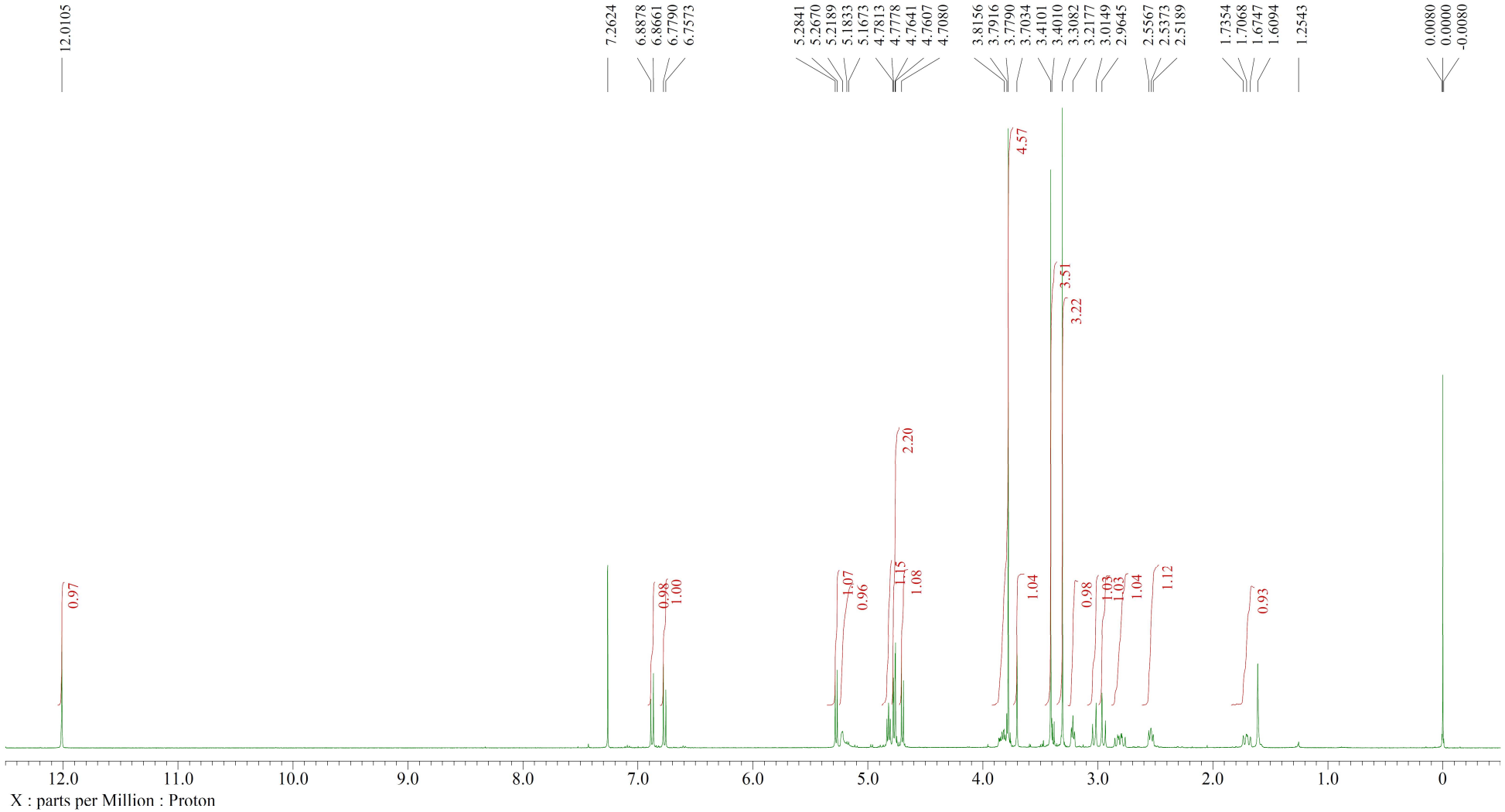


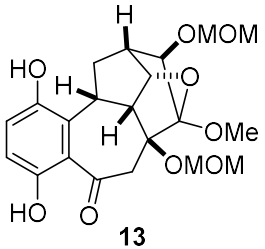

NOESY
H
OMOM
O
H
H
OMe
OMOM
HO
HO
10
abundance
Y : parts per Million : Proton
X : parts per Million : Proton
abundance



13

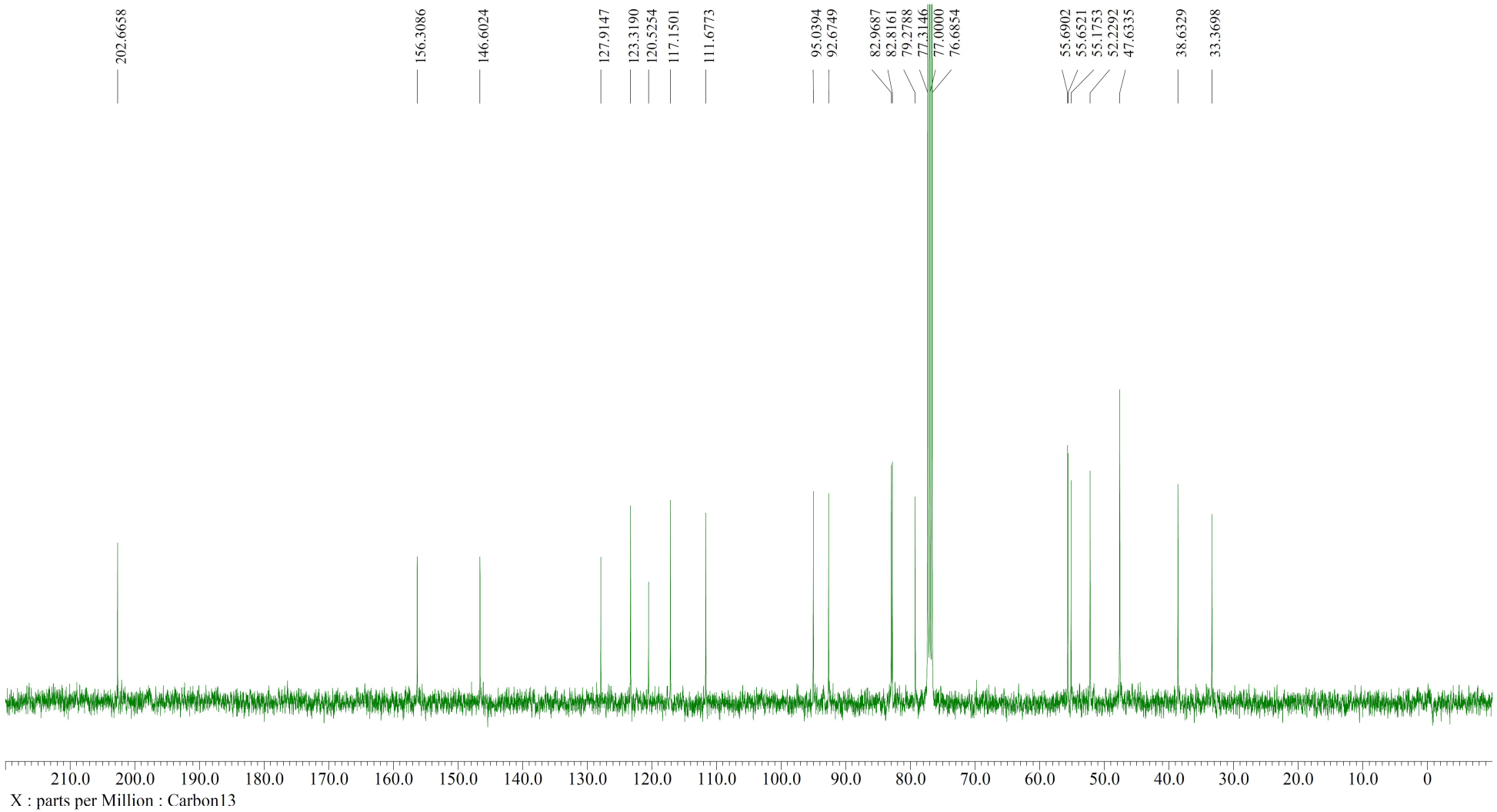
^{1}H-NMR (400 MHz, $CDCl_3$)

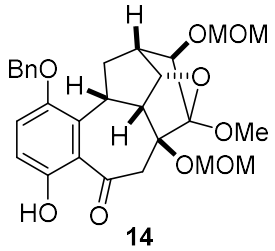




13

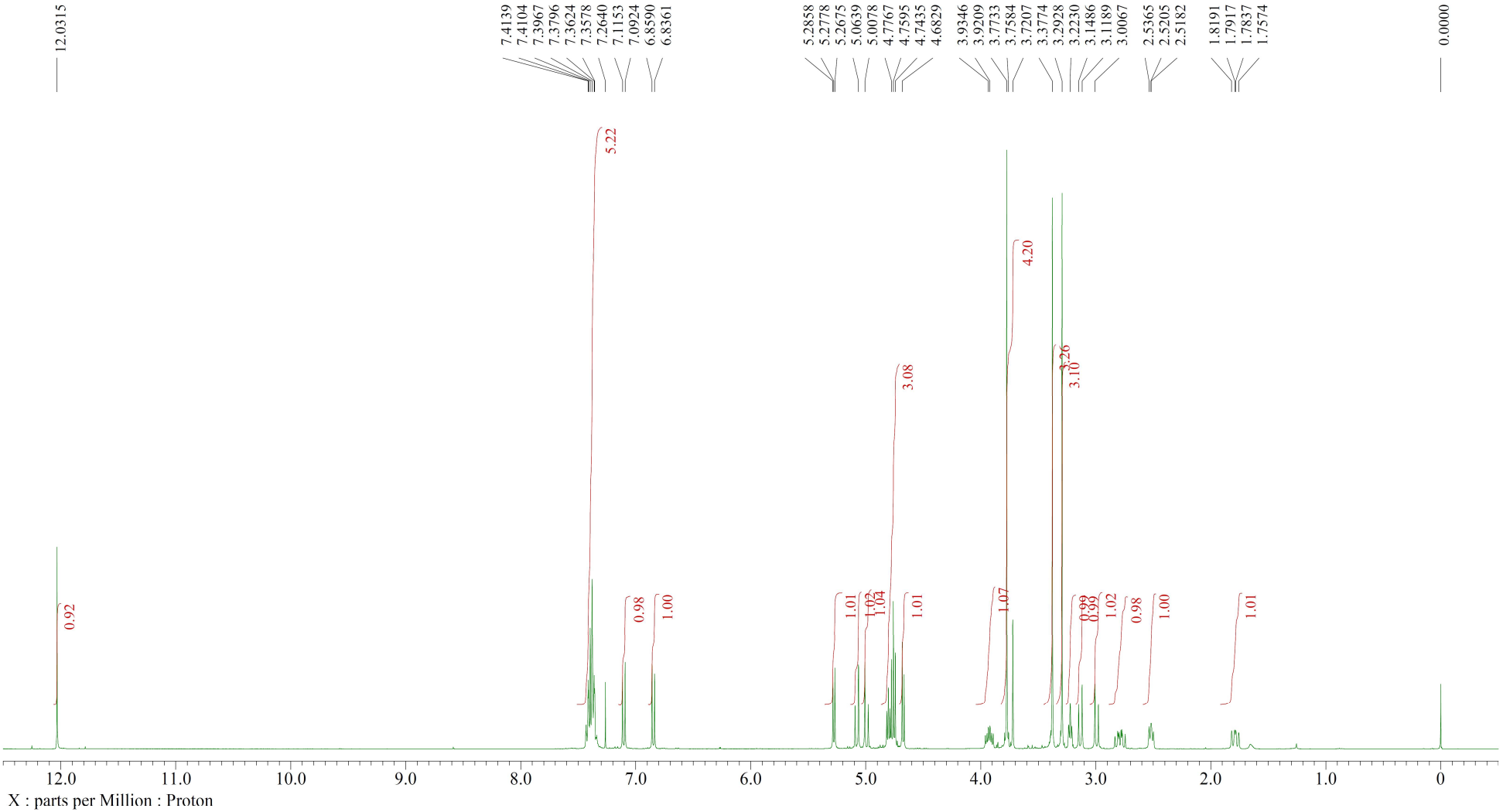
^{13}C-NMR (100 MHz, $CDCl_3$)

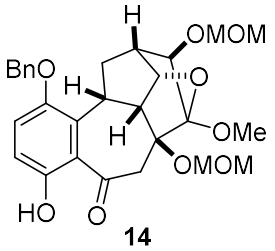




14

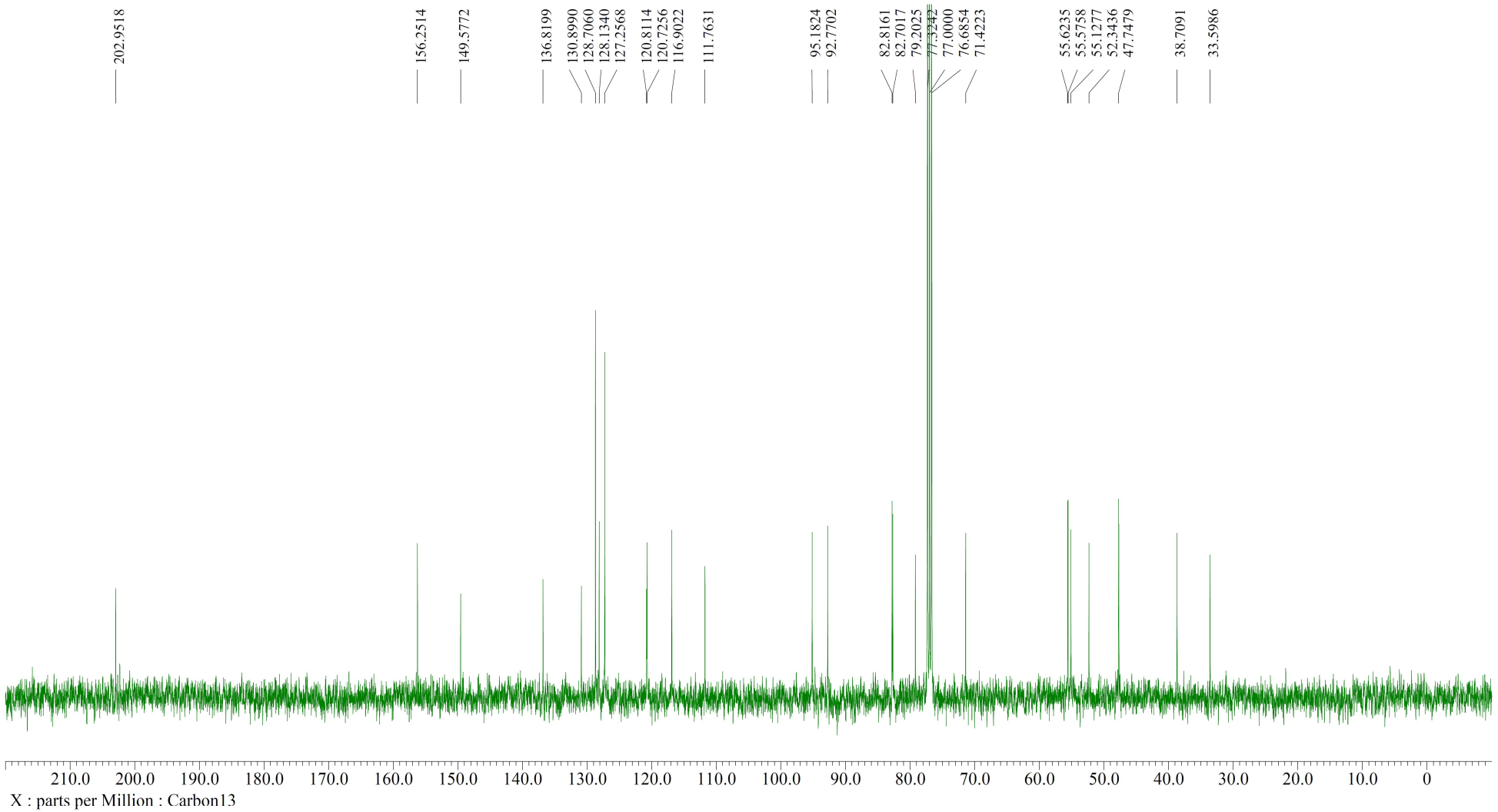
^{1}H-NMR (400 MHz, $CDCl_3$)

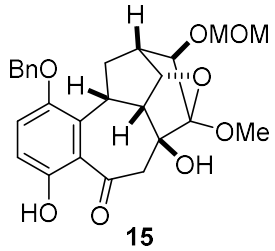




14

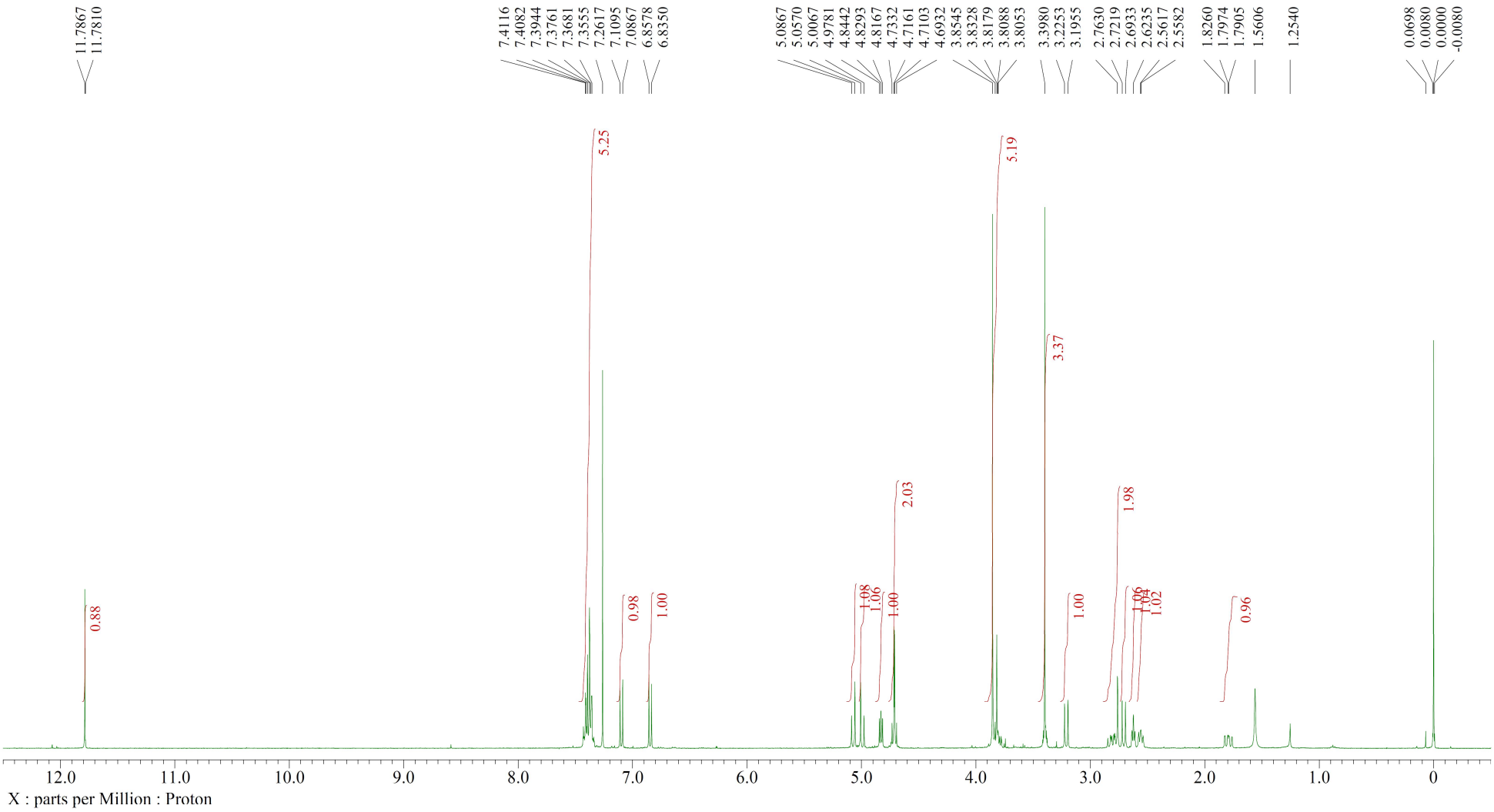
^{13}C-NMR (100 MHz, $CDCl_3$)

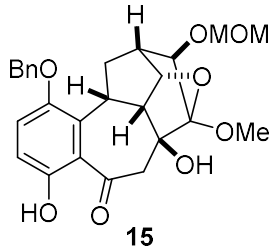




15

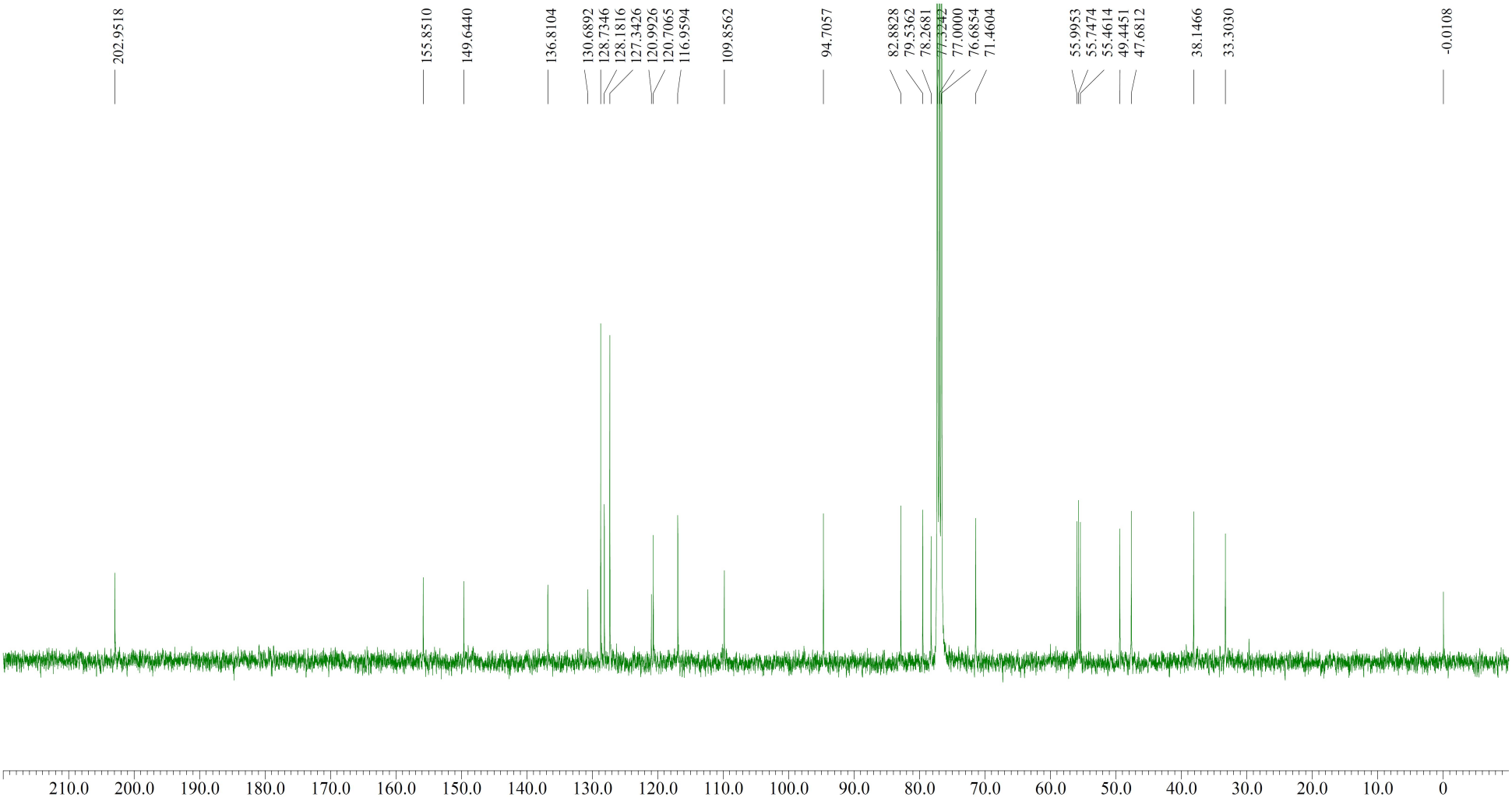
^{1}H-NMR (400 MHz, $CDCl_3$)

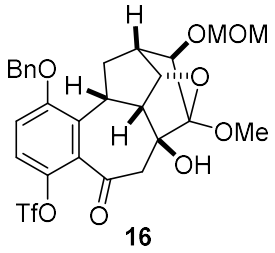




15

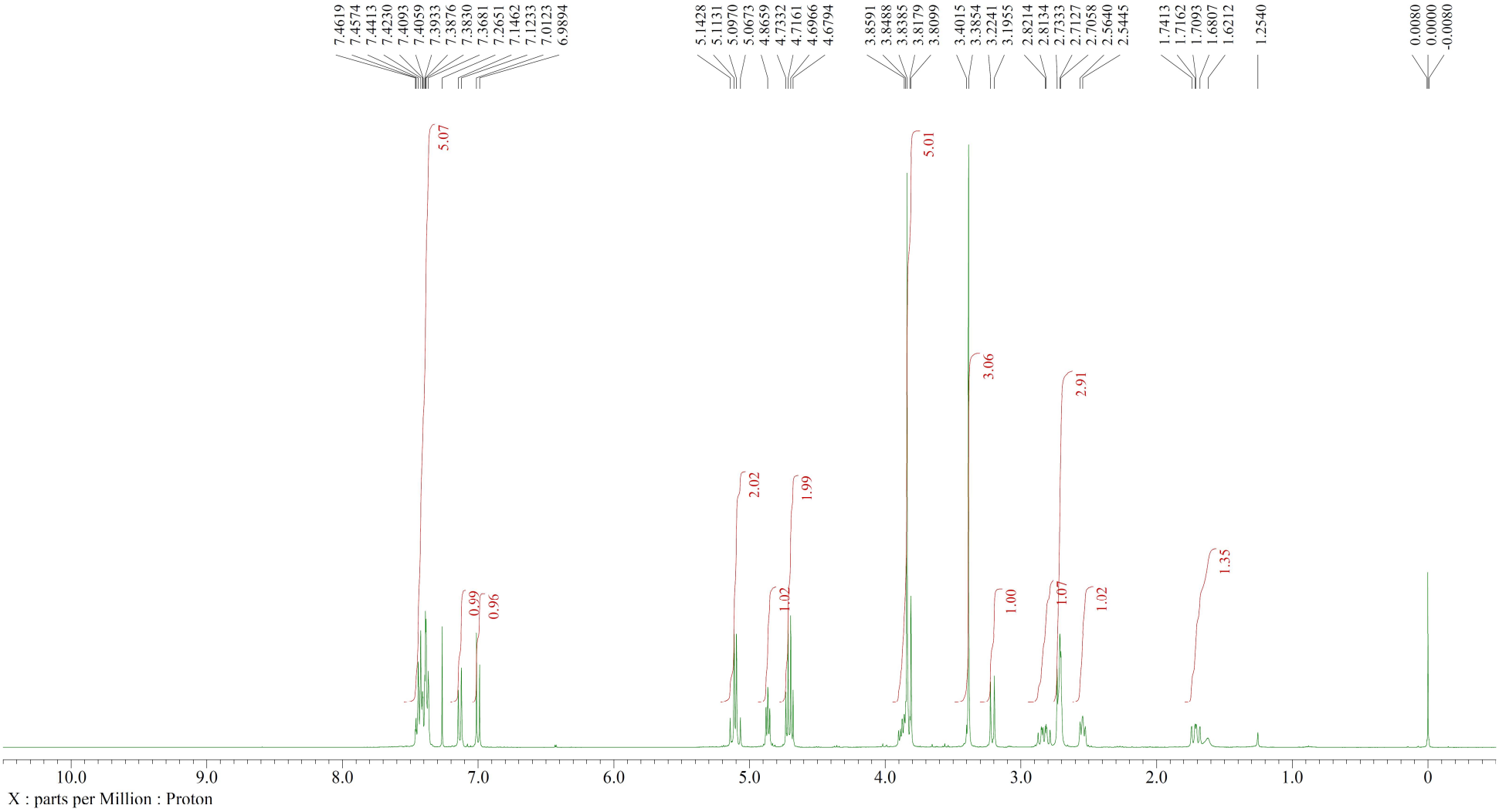
^{13}C-NMR (100 MHz, $CDCl_3$)

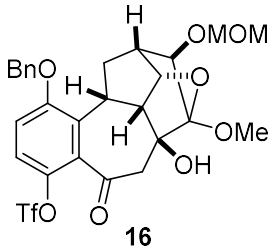




16

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





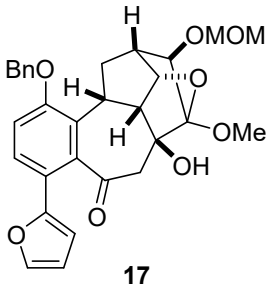
16

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

196.6876
195.0858
155.8700
139.1750
135.5518
132.9012
131.6331
128.9253
128.5535
128.4486
127.6191
127.4189
121.6886
120.1440
116.9594
114.1181
110.1136
94.7915
82.7494
79.7555
78.2204
77.3146
77.0000
76.6854
71.1076
56.0430
55.6902
55.3470
48.9302
47.7288
39.0142
38.0226
33.7511
-0.0299

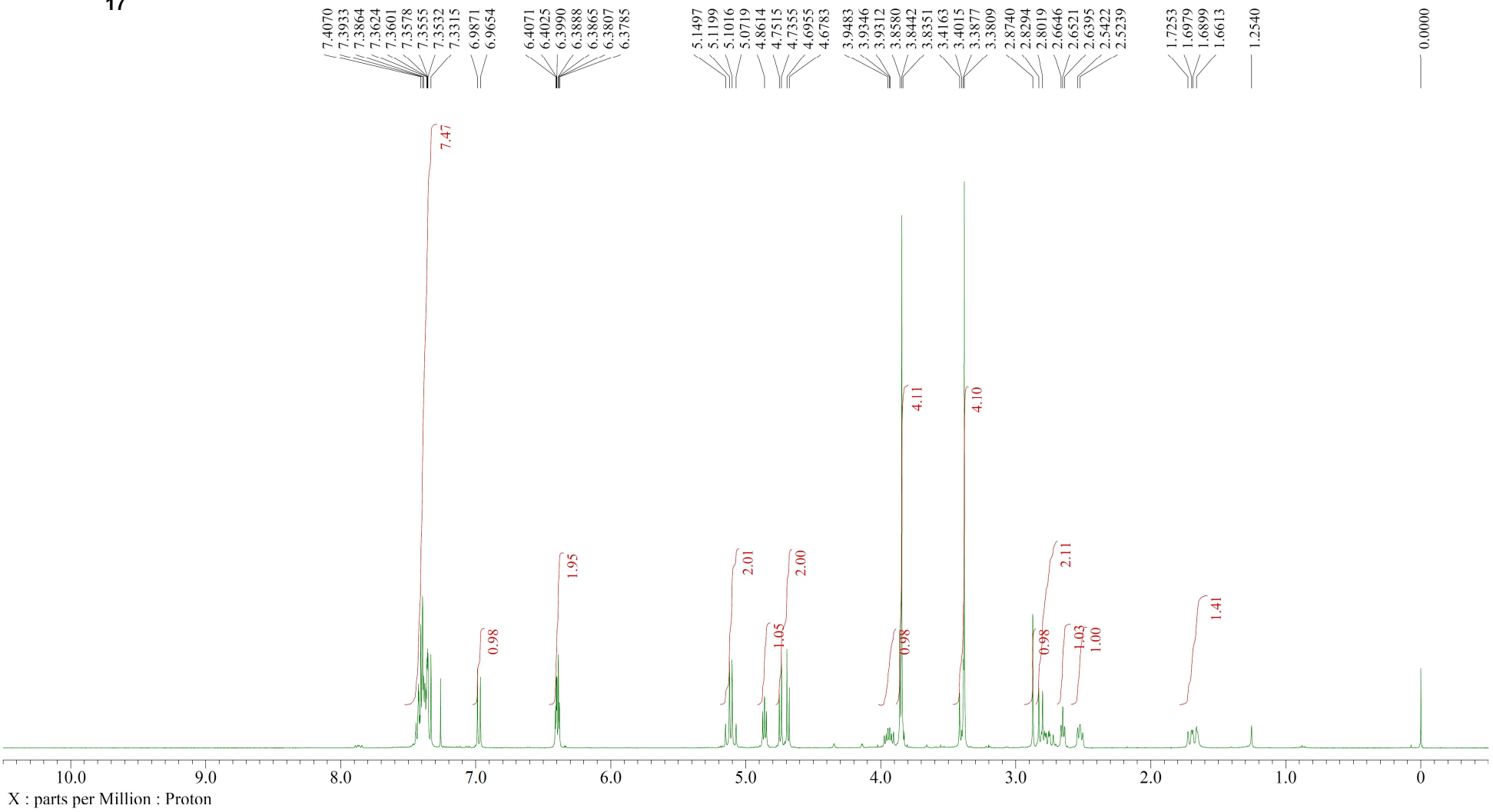
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0

X : parts per Million : Carbon13

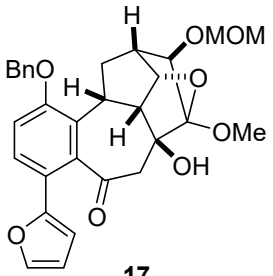


17

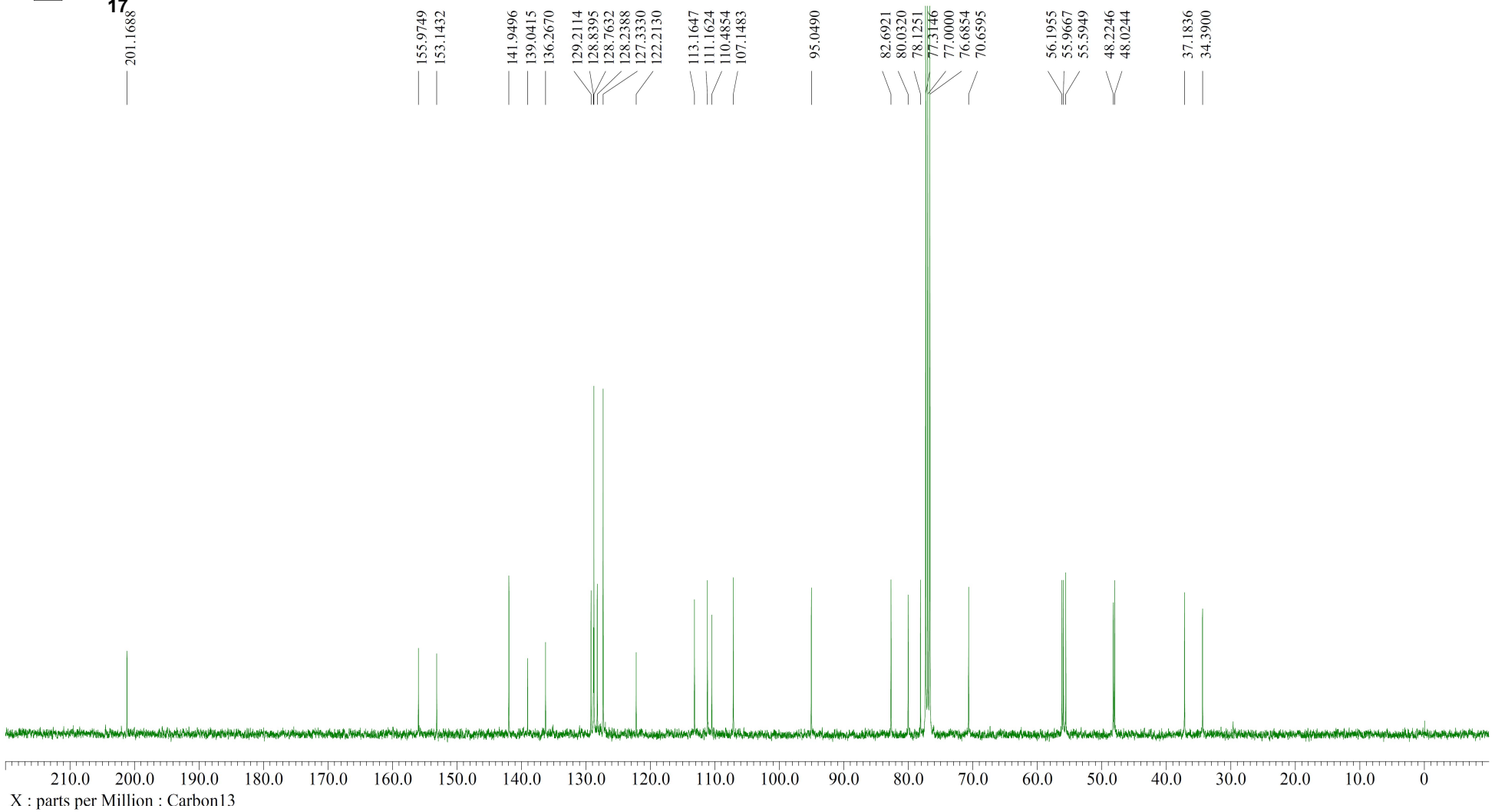
^{1}H-NMR (400 MHz, $CDCl_3$)

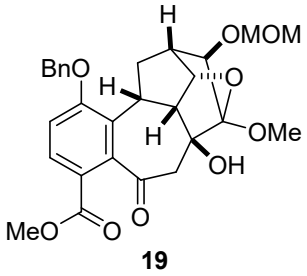


^{13}C-NMR (100 MHz, $CDCl_3$)



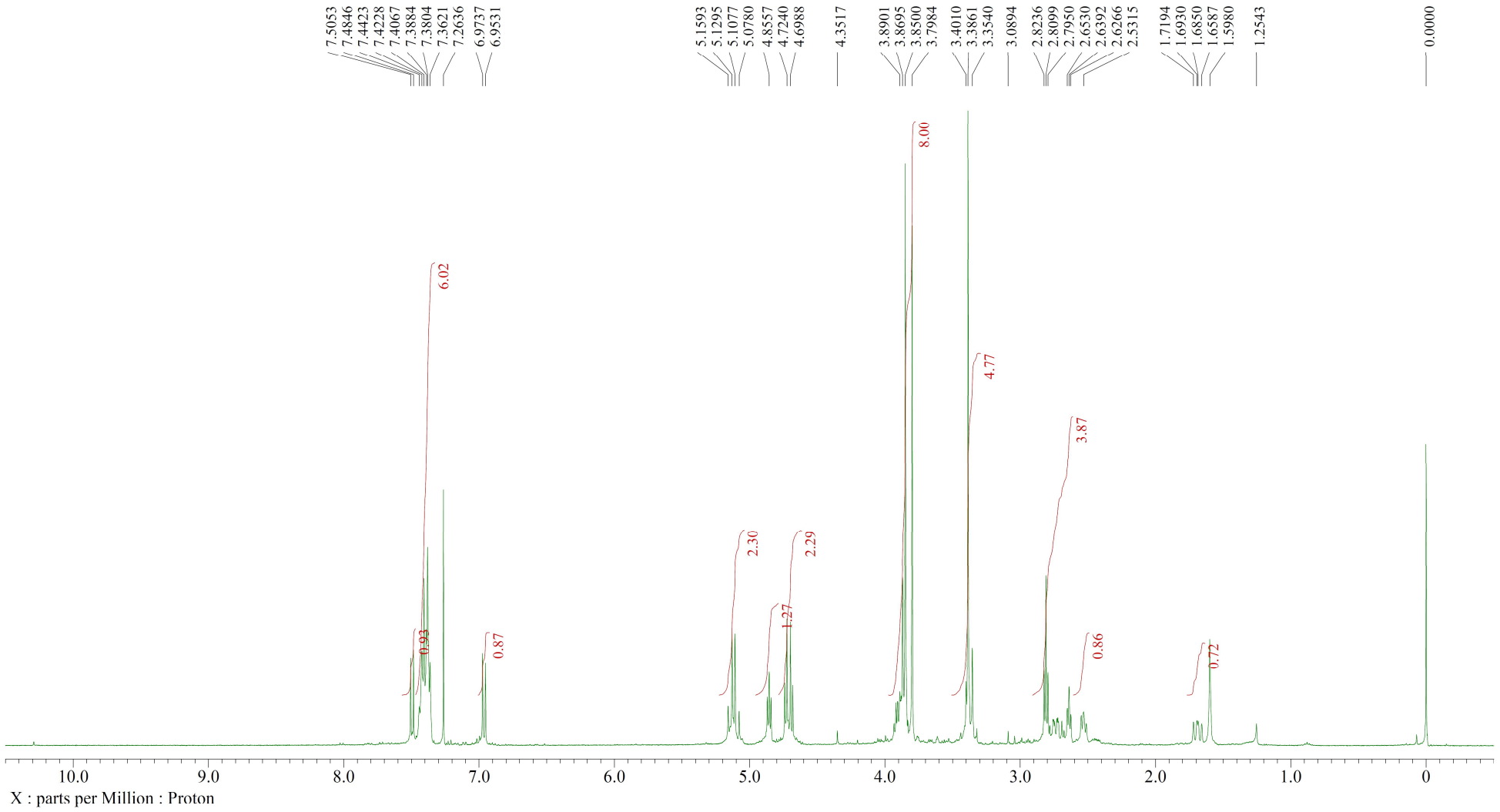
17

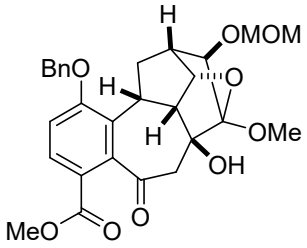




19

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





19

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