Supporting Information

Total Syntheses of *Ganoderma*-derived Meroterpenoids, (−)-Oregonensin A, (−)-Chizhine E, (−)-Applanatumol U, and (−)-*ent*-Fornicin A

Kazuki Hori, Shogo Kamo*, and Kazuyuki Sugita*

Department of Synthetic Medicinal Chemistry, Faculty of Pharmaceutical Sciences, Hoshi University, 2-4-41 Ebara, Shinagawa-ku, Tokyo 142-8501, Japan

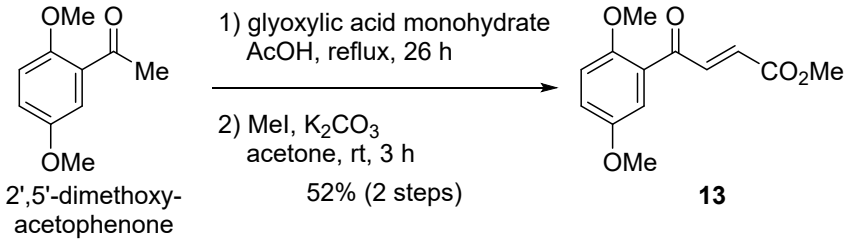
Index

1. General

All reactions were carried out in a round-bottom flask or a test tube fitted with a 3-way glass stopcock under an Ar atmosphere unless otherwise stated. Reagents were purchased from commercial suppliers and used as received unless otherwise noted. All work-up and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Analytical thin layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 F_{254}, 0.25 mm). Flash chromatography was performed using silica gel CHROMATOREX PSQ60B (neutral, 60 μm; Fuji Silysia Chemical LTD.). Melting point (Mp) data were determined using a Yanaco MP apparatus and were uncorrected. Optical rotation was measured on JASCO P-2200. IR spectra were recorded on a JASCO FT/IR 4100 spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on JEOL ECA-600 spectrometers. Chemical shift values are reported in δ (ppm) relative to residual solvent signals ($CDCl_3$: 7.26 ppm for ^{1}H and 77.00 ppm for ^{13}C, acetone-d_6: 2.04 ppm for ^{1}H and 29.8 ppm for ^{13}C, CD_3OD: 3.30 ppm for ^{1}H and 49.0 ppm for ^{13}C). NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, quin: quintet, m: multiplet, br: broad signal), coupling constant, and integration. High-resolution mass spectra (ESI-TOF) were measured on JEOL JMS-T100LP. Analytical chiral HPLC was performed by LC-NetII/ADC system (JASCO, pump: PU-4180; UV detector: MD4017) with CHIRAL ART Cellulose-SB (YMC, 4.6 mm × 250 mm).

2. Experimental Procedures

Known compound 13



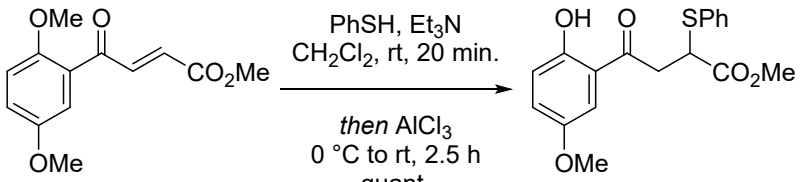
Compound **13** was prepared according to the literature reported by Wang and co-workers with slight modification[S1].

2',5'-dimethoxyacetophenone (2.50 g, 13.9 mmol) and glyoxylic acid monohydrate (1.35 g, 14.7 mmol) were dissolved in acetic acid (28 mL) at rt. After the mixture was refluxed for 26 h, the reaction mixture was cooled to rt and concentrated to give a crude carboxylic acid which was used next reaction without further purification.

To a suspension of the crude carboxylic acid (prepared above) and K_2CO_3 (9.63g, 69.7 mmol) in acetone (46 mL) was added MeI (2.2 mL, 35.3 mmol) at rt. The mixture was stirred for 3 h at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 9/1 to 7/3) to give **13** (1.79 g, 7.15 mmol, 52%) as an orange solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, J = 15.6 Hz, 1H), 7.23 (d, J = 3.6 Hz, 1H), 7.08 (dd, J = 9.0, 3.6 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 6.76 (d, J = 15.6 Hz, 1H), 3.87 (s, 3H), 3.82 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.7, 166.4, 153.60, 153.56, 141.1, 129.4, 127.6, 121.2, 114.1, 113.3, 56.2, 55.8, 52.1.

methyl 4-(2-hydroxy-5-methoxyphenyl)-4-oxo-2-(phenylthio)butanoate (14)

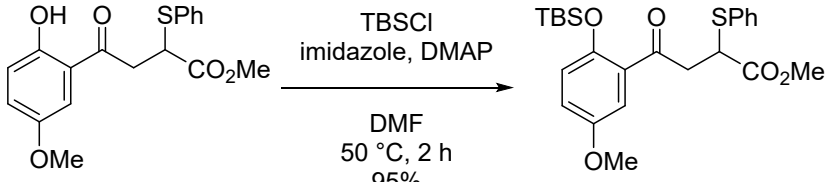


13 **14**

To a solution of **13** (1.70 g, 6.79 mmol) in CH_2Cl_2 (68 mL) was added Et_3N (94.2 μL, 680 μmol) and PhSH (728 μL, 7.14 mmol) at rt. The mixture was stirred for 20 min at rt and then cooled to 0 °C. To the solution was added $AlCl_3$ (3.21 g, 24.1 mmol) and the resulting mixture was stirred for further 2.5 h at rt. The reaction mixture was poured into ice cold 1 M HCl aq. (100 mL) and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give **14** (2.39 g, 6.90 mmol, quant.) as a yellow solid.

Mp = 50–53 °C; IR (KBr) ν_{max} = 3451, 2948, 2912, 2842, 1735, 1647, 1485, 1341, 1272, 1232, 1164, cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 11.48 (s, 1H), 7.54-7.51 (m, 2H), 7.36-7.34 (m, 3H), 7.13-7.11 (m, 2H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 4.22 (dd, *J* = 9.6, 4.2 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.69 (dd, *J* = 18.0, 9.6 Hz, 1H), 3.41 (dd, *J* = 18.0, 4.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 201.9, 171.8, 156.8, 151.8, 133.8 (2C), 132.0, 129.1 (2C), 128.8, 124.8, 119.5, 118.3, 112.1, 56.0, 52.6, 44.9, 40.7; HRMS (ESI) *m*/*z* calcd. for $C_{18}H_{19}O_5S$ ($[M+H]^+$) 347.0948, found 347.0953.

methyl 4-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-4-oxo-2-(phenylthio)butanoate (12)

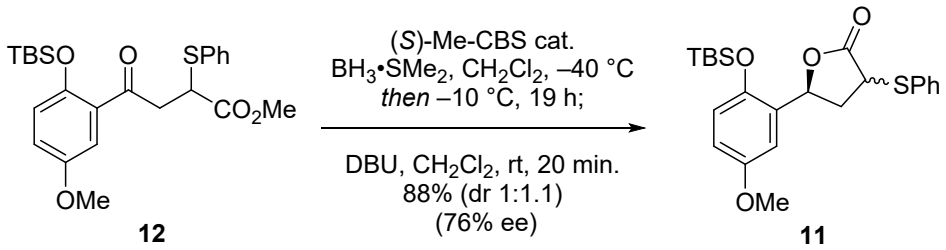


14 **12**

To a solution of **14** (2.35 g, 6.78 mmol) in DMF (22.5 mL) was added imidazole (1.15 g, 16.9 mmol), DMAP (82.7 mg, 677 μmol), and TBSCl (1.25 g, 8.29 mmol) at rt. The mixture was stirred for 2 h at 50 °C. The reaction mixture was cooled to rt and quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 9/1 to 4/1) to give **12** (2.98 g, 6.47 mmol, 95%) as a yellow solid.

Mp = 57–59 °C; IR (KBr) ν_{max} = 2952, 2933, 2891, 2858, 1730, 1663, 1489, 1419, 1321, 1274, 1224, 1153, 1019, 915, 839, 788, 751 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.49-7.47 (m, 2H), 7.31-7.29 (m, 3H), 7.17 (d, *J* = 3.0 Hz, 1H), 6.94 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.80 (d, *J* = 9.0 Hz, 1H), 4.20 (dd, *J* = 9.6, 4.8 Hz, 1H), 3.76 (s, 3H), 3.70 (dd, *J* = 18.6, 9.6 Hz, 1H), 3.68 (s, 3H), 3.51 (dd, *J* = 10.6, 4.8 Hz, 1H), 0.99 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 198.7, 172.2, 153.6, 149.3, 133.2 (2C), 132.8, 129.2, 129.0 (2C), 128.2, 121.2, 120.9, 112.9, 55.7, 52.3, 45.9, 45.7, 26.0 (3C), 18.5, −3.9 (2C); HRMS (ESI) *m*/*z* calcd. for $C_{24}H_{33}O_5SSi$ ($[M+H]^+$) 461.18120, found 461.1802.

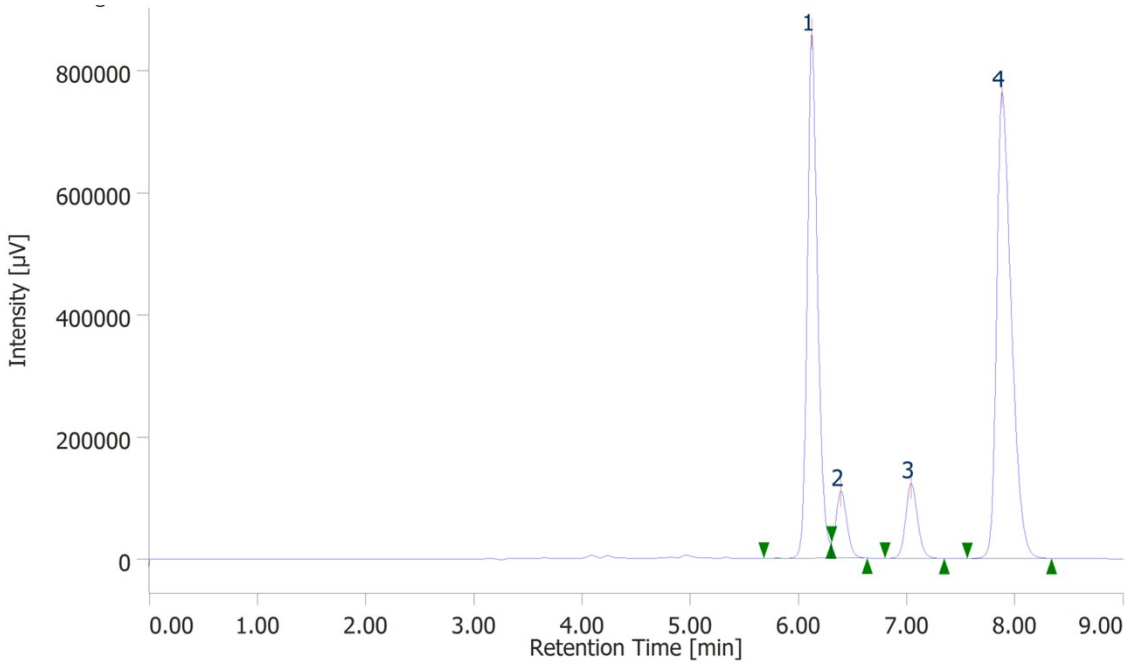
(5*S*)-5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-3-(phenylthio)dihydrofuran-2(3*H*)-one (11)



To a solution of **11** (465.3 mg, 1.01 mmol) and in CH_2Cl_2 (10.0 mL) was added (*S*)-Me-CBS catalyst (1 M in toluene, 400 μL, 400 μmol) at rt. After the mixture was cooled to −40 °C, BH_3•SMe_2 (90%, 120 μL, 1.14 mmol) was added dropwise via syringe. The solution was stirred for 19 h at −10 °C. The reaction mixture was quenched by the addition of MeOH and concentrated to give a crude alcohol. To a solution of the crude alcohol in CH_2Cl_2 (10.0 mL) was added DBU (30 μL, 201 μmol) at rt. After being stirred for 20 min at rt, the solution was concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 17/3) to give **11** (382.5 mg, 888 μmol, 88%, dr = 1:1.1) as a yellow oil.

$[\alpha]_D^{24}$ −8.3 (*c* 0.40, $CHCl_3$); IR (neat) ν_{max} = 2953, 2934, 2895, 2858, 1779, 1497, 1437, 1270, 1175, 1041, 904, 840 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, diastereomer mixture, dr = 1:1.1) δ 7.58-7.54 (m, 4.2H), 7.36-7.31 (m, 6.3H), 6.84 (brd, *J* = 2.4 Hz, 1H), 6.74-6.69 (m, 4.2H), 6.66 (brd, *J* = 1.2 Hz, 1.1H), 5.78 (dd, *J* = 7.8, 6.6 Hz, 1H), 5.65 (dd, *J* = 9.0, 6.0 Hz, 1.1H), 4.06 (dd, *J* = 10.8, 9.0 Hz, 1H), 3.97 (dd, *J* = 8.4, 4.8 Hz, 1.1H), 3.75 (s, 3H), 3.70 (s, 3.3H), 3.05-3.00 (m, 1.1H), 2.72-2.68 (m, 1H), 2.53-2.48 (m, 1H), 2.12-2.06 (m, 1.1H), 1.00 (s, 9H), 0.98 (s, 9.9H), 0.25 (s, 3H), 0.23 (s, 3H), 0.22 (s, 3.3H), 0.20 (s, 3.3H); ^{13}C NMR (150 MHz, CD_3OD, diastereomer mixture, dr = 1:1.1) δ 176.9, 176.4, 155.7, 155.6, 147.4, 147.3, 134.6 (2C), 133.9 (2C), 133.6, 133.5, 131.2, 131.1, 130.4 (2C), 130.3 (2C), 129.6, 129.5, 120.5, 120.4, 115.6, 115.4, 112.3, 112.1, 77.3, 76.2, 56.13, 56.10, 47.1, 46.3, 38.5, 38.2, 26.40 (3C), 26.37 (3C), 19.1 (2C), -3.85, -3.90, -4.1, -4.2; HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{30}O_4SSiNa$ ($[M+Na]^+$) 453.1526, found 453.1538.

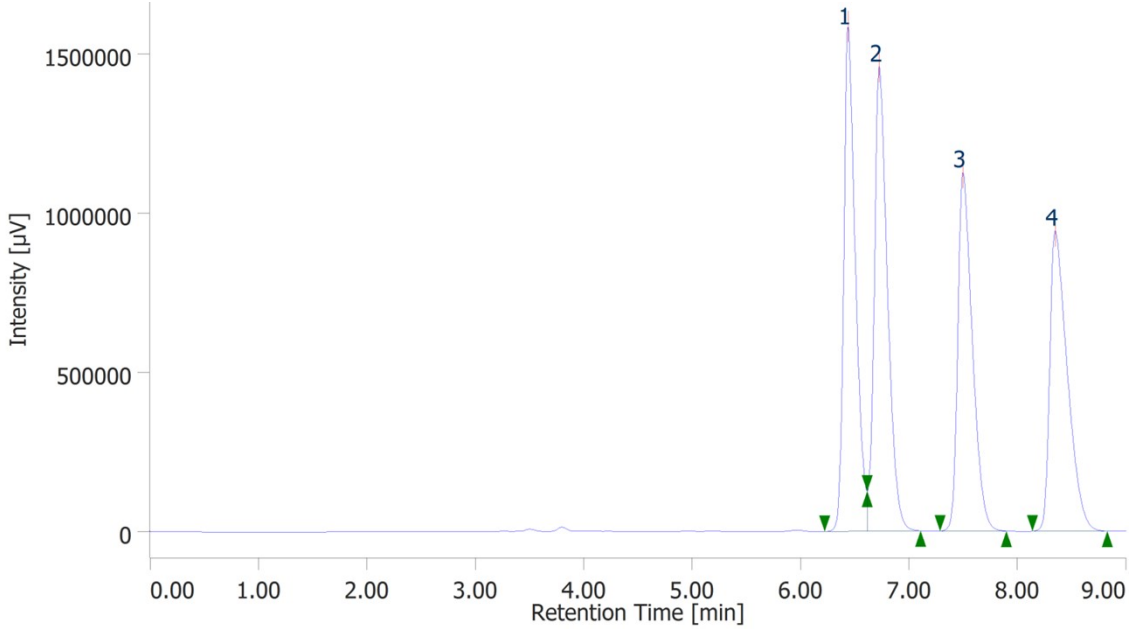
The enantiomeric excess of (−)-**11** was determined by chiral HPLC analysis [CHIRAL ART Cellulose-SB (4.6 × 250 mm), hexane/2-propanol = 90/10 v/v, 1.0 mL/min, UV 254 nm, RT, t_{R1} = 6.1 min (39.0%), t_{R2} = 6.4 min (5.3%), t_{R3} = 7.0 min (6.4%), t_{R4} = 7.9 min (49.2%)] to be 76% ee.



Peak Information

#	tR [min]	Area [μV·sec]	Area%	Height%	Symmetry Factor
1	6.120	5697023	38.999	46.267	1.247
2	6.390	779728	5.338	5.922	N/A
3	7.040	939959	6.435	6.637	1.108
4	7.877	7191331	49.229	41.174	1.489

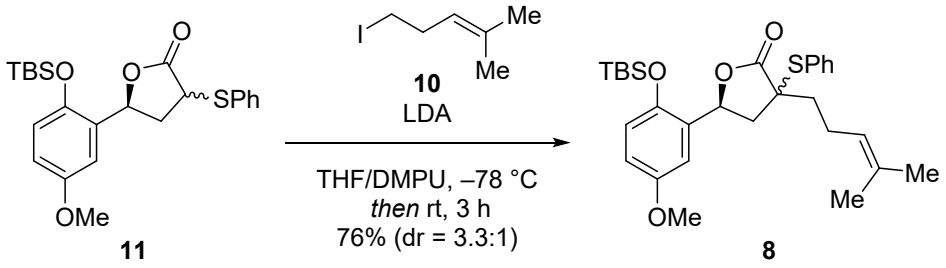
Racemic **11** was preparade from compound **12** *via* reduction of ketone using $NaBH_4$ and subsequent lactonization mediated by DBU.



Peak Info.

#	tR [min]	Area [μV·sec]	Area%	Height%	Symmetry Factor
1	6.433	11845166	26.147	31.004	N/A
2	6.723	12330734	27.219	28.519	N/A
3	7.493	10481107	23.136	22.029	1.530
4	8.343	10644853	23.498	18.448	1.812

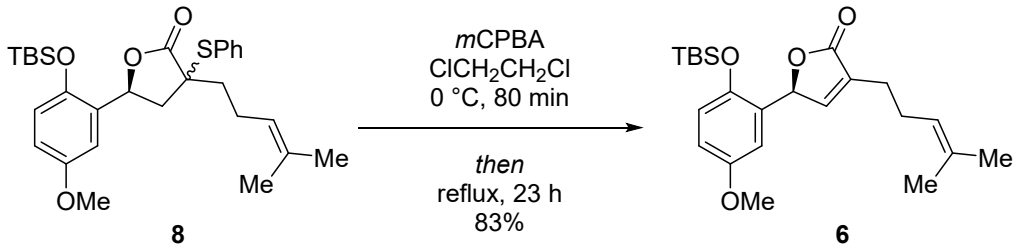
(5*S*)-5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-3-(4-methylpent-3-en-1-yl)-3-(phenylthio)dihydrofuran-2(3*H*)-one (8)



To a solution of **11** (210.5 mg, 489 μmol) in THF (2.4 mL) was added LDA (2.0 M in THF, prepared from iPr$_2$NH and nBuLi, 320 μL, 640 μmol) dropwise via syringe at −78 °C. The mixture was stirred for 30 min at 0 °C, and then cooled to −78 °C. To the reaction mixture was added a solution of **10**[S2] (345 μL, 2.46 mmol) in DMPU (1.9 mL) dropwise via syringe at −78 °C. The solution was stirred for 3 h at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1 to 9/1) to give **8** (191.3 mg, 373 μmol, 76%, dr = 3.3:1) as a yellow oil.

$[\alpha]_D^{23}$ −25.4 (*c* 0.50, $CHCl_3$); IR (neat) ν_{max} = 3059, 2954, 2933, 2858, 1771, 1496, 1469, 1438, 1268, 1177, 1038, 916, 887, 839, 809 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, diastereomer mixture, dr = 3.3:1) δ 7.58-7.54 (m, 2.6H), 7.44-7.31 (m, 3.9H), 6.92 (d, *J* = 3.0 Hz, 1H), 6.76-6.72 (m, 2H), 6.67 (s, 0.3H), 6.668 (brs, 0.3H), 6.43 (brs, 0.3H), 5.94 (dd, *J* = 10.2, 6.0 Hz, 1H), 5.62 (dd, *J* = 7.8, 8.4 Hz, 0.3H), 5.09-5.07 (m, 0.3H), 5.04-5.01 (m, 1H), 3.76 (s, 3H), 3.65 (s, 0.9H), 2.81 (dd, *J* = 13.8, 7.8Hz, 0.3H), 2.69 (dd, *J* = 13.8, 6.0 Hz, 1H), 2.37-2.31 (m, 1.3H), 2.25-2.13 (m, 1.6H), 2.02-1.95 (m, 1H), 1.94-1.81 (m, 1.6H), 1.70 (s, 0.9H), 1.70-1.65 (m, 1H), 1.65 (s, 3H), 1.63 (s, 0.9H), 1.58 (s, 3H), 1.05 (s, 9H), 0.99 (s, 2.7H), 0.27 (s, 3H), 0.25 (s, 3H), 0.23 (s, 0.9H), 0.19 (s, 0.9H); ^{13}C NMR (150 MHz, $CDCl_3$, diastereomer mixture, dr = 3.3:1) δ 176.8, 174.9, 154.2, 153.9, 146.0, 145.6, 137.1 (2C), 137.0 (2C), 133.2, 132.6, 130.4, 130.2, 129.9, 129.7, 129.2 (2C), 129.0, 128.9 (3C), 122.7, 122.3, 119.1, 118.7, 114.8, 114.3, 110.7, 110.4, 74.1, 73.1, 56.3, 55.8, 55.7, 55.6, 42.4, 40.7, 36.2, 34.2, 25.9 (3C), 25.8, 25.7, 25.6 (3C), 23.5, 23.2, 18.2, 18.2, 17.76, 17.74, -3.9, -4.0, -4.3, -4.4; HRMS (ESI) *m*/*z* calcd. for $C_{29}H_{41}O_4SSi$ ([M+H]$^+$) 513.2489, found 513.2494.

(*S*)-5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-3-(4-methylpent-3-en-1-yl)furan-2(5*H*)-one (6)

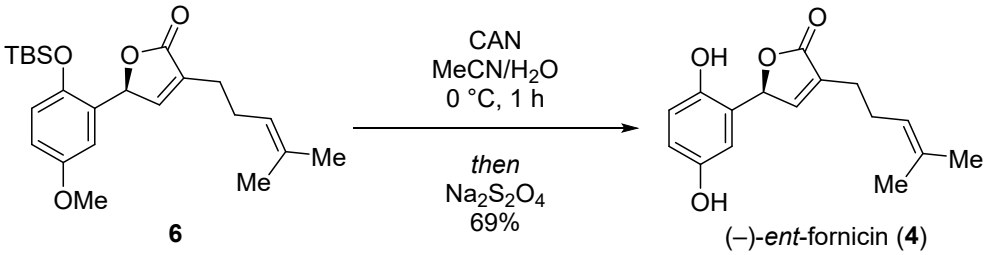


To a solution of **8** (129.0 mg, 252 μmol) in dichloroethane (2.5 mL) was added *m*CPBA (65%, 70.2 mg, 264 μmol) at 0 °C. After being stirred for 80 min at 0 °C, the solution was refluxed for further 23 h. The reaction mixture was cooled to rt and quenched by the addition of sat. $NaHCO_3$ aq. and diluted with CH_2Cl_2. The aqueous layer was

extracted with CH_2Cl_2. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1 to 9/1) to give **6** (84.3 mg, 209 μmol, 83%) as a yellow oil.

$[\alpha]_D^{23}$ −35.4 (*c* 0.40, $CHCl_3$); IR (neat) ν_{max} = 2954, 2932, 2859, 1764, 1496, 1469, 1431, 1269, 1216, 1049, 936, 904, 842, 810, 783 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.13 (brd *J* = 1.2 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.74 (dd, *J* = 8.4, 3.0 Hz, 1H), 6.65 (d, *J* 3.0 Hz, 1H), 6.19 (brd, *J* = 1.2 Hz, 1H), 5.10-5.07 (m, 1H), 3.73 (s, 3H), 2.40-2.32 (m, 2H), 2.31-2.22 (m, 2H), 1.67 (d, *J* = 1.2 Hz, 3H), 1.58 (s, 3H), 1.01 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.4, 154.3, 148.0, 146.6, 133.2, 132.9, 126.6, 122.8, 119.2, 114.9, 111.3, 77.8, 55.8, 25.9 (4C), 25.7, 25.4, 18.3, 17.9, -3.9, -4.3; HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{35}O_4Si$ ($[M+H]^+$) 403.2299, found 403.2316.

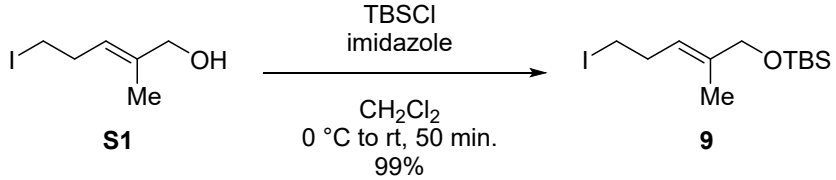
***ent*-fornicin A (*ent*-4)**



To a solution of **6** (61.5 mg, 153 μmol) in a mixture of MeCN/H_2O (2:1 v/v, 1.5 mL) was added CAN (180.1 mg, 329 μmol) at 0 °C. The mixture was stirred for 1 h at 0 °C. The reaction mixture was quenched by the addition of H_2O and sat. $Na_2S_2O_4$ aq., and then diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 9/1 to 1/1) to give *ent*-**4** (28.8 mg, 105 μmol, 69%) as a yellow oil.

$[\alpha]_D^{24}$ −36.2 (*c* 0.71, MeOH); IR (neat) ν_{max} = 3364, 2968, 2920, 2855, 1733, 1507, 1455, 1357, 1302, 1200, 815 cm^{-1}; ^1H NMR (600 MHz, acetone-d_6) δ 8.26 (s, 1H), 7.80 (s, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.53 (d, *J* = 2.4 Hz, 1H), 5.13 (brt, *J* = 7.2 Hz, 1H), 2.33-2.30 (m, 2H), 2.29-2.25 (brm, 2H), 1.64 (d, *J* = 1.2 Hz, 3H), 1.58 (s, 3H); ^{13}C NMR (150 MHz, acetone-d_6) δ 174.4, 151.5, 149.4, 148.2, 133.2, 132.8, 124.0, 123.8, 117.1, 116.8, 113.2, 78.2, 26.7, 26.0, 25.7, 17.7; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{18}O_4Na$ ($[M+Na]^+$) 297.1097, found 297.1106.

(*E*)-*tert*-butyl((5-iodo-2-methylpent-2-en-1-yl)oxy)dimethylsilane (9)

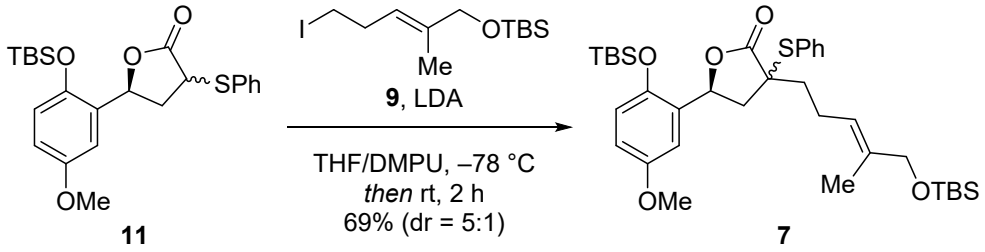


To a solution of **S1**[S3] (1.01 g, 4.47 mmol) and imidazole (662.6 mg, 9.37 mmol) in CH_2Cl_2 (8.9 mL) was added TBSCl (734.8 mg, 4.88 mmol) at 0 °C. The mixture was stirred for 50 min at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The

combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 97/3) to give **9** (1.50 g, 4.41 mmol, 99%) as a colorless oil.

IR (neat) ν_{max} = 2953, 2930, 2892, 2856, 1466, 1254, 1115, 1071, 839.8, 777 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 5.38 (tdd, *J* = 7.2, 1.2, 1.2 Hz, 1H), 4.00 (br s, 2H), 3.13 (t, *J* = 7.2 Hz, 2H), 2.63 (q, *J* = 7.2 Hz, 2H), 1.60 (br s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.1, 122.4, 68.0, 31.9, 25.9 (3C), 18.4, 13.6, 5.4, -5.3 (2C); HRMS (ESI) *m*/*z* calcd. for $C_{12}H_{25}IOSiNa$ ([M+Na]$^+$) 363.0612, found 363.0607.

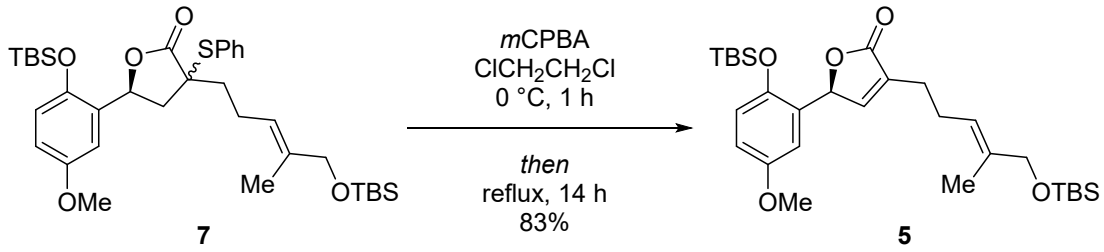
(5*S*)-3-((*E*)-5-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-3-en-1-yl)-5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-3-(phenylthio)dihydrofuran-2(3*H*)-one (7)



To a solution of **11** (90.0 mg, 209 μmol) in THF (2.0 mL) was added LDA (2.0 M in THF, prepared from *i*Pr_2NH and *n*BuLi, 135 μL, 270 μmol) dropwise via syringe at −78 °C. The mixture was stirred for 30 min at 0 °C, and then cooled to −78 °C. To the reaction mixture was added a solution of **9** (145.2 mg, 427 μmol) in DMPU (1.6 mL) dropwise via syringe at −78 °C. The solution was stirred for 2 h at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1 to 9/1) to give **7** (93.3 mg, 145 μmol, 69%, dr = 5:1) as a yellow oil.

$[\alpha]_D^{26}$ −18.7 (*c* 0.20, $CHCl_3$); IR (neat) ν_{max} = 2953, 2933, 2895, 2857, 1773, 1497, 1469, 1258, 1177, 1112, 1044, 917, 839, 779 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, diastereomer mixture, dr = 5:1) δ 7.59-7.52 (m, 2.4H), 7.44-7.31 (m, 3.6H), 6.91 (d, *J* = 2.4 Hz, 1H), 6.75 (d, *J* = 9.0 Hz, 1H), 6.73 (dd, *J* = 9.0, 2.4 Hz, 1H), 6.671 (br s, 0.2H), 6.669 (br s, 0.2H), 6.43 (s, 0.2H), 5.95 (dd, *J* = 10.2, 5.4 Hz, 1H), 5.63 (t, *J* = 7.8 Hz, 0.2H), 5.36 (td, *J* = 7.8, 1.2 Hz, 0.2H), 5.31 (td, *J* = 7.8, 1.2 Hz, 1H), 4.01 (br s, 0.4H), 3,96 (br s, 2H), 3.76 (s, 3H), 3.65 (s, 0.6H), 3.79 (dd, *J* = 13.8, 7.8 Hz, 0.2H), 2.70 (dd, *J* = 14.4, 5.4 Hz, 1H), 2.45-2.29 (m, 1.4H), 2.26-2.18 (m, 1.2H), 2.06-2.00 (m, 1H), 1.96-1.83 (m, 1.2H), 1.72-1.66 (m, 1H), 1.64-1.56 (m, 0.2H), 1.61 (s, 0.6H), 1.57 (s, 3H), 1.05 (s, 9H), 0.98 (s, 1.8H), 0.91 (1.8H), 0.88 (s, 9H), 0.27 (s, 3H), 0.25 (s, 3H), 0.23 (s, 0.6H), 0.19 (s, 0.6H), 0.06 (s, 1.2H), 0.02 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$, diastereomer mixture, dr = 5:1) δ 176.4, 174.8, 154.2, 153.9, 146.0, 145.6, 137.1 (2C), 136.9 (2C), 136.0, 135.5, 130.3, 130.1, 130.0, 129.7, 129.1, 129.0 (2C), 128.9 (3C), 122.4, 121.8, 119.1, 118.7, 114.8, 114.3, 110.7, 110.3, 74.1, 73.1, 68.2, 68.1, 56.3, 55.8, 55.7, 55.5, 42.5, 40.8, 35.9, 34.0, 25.9 (6C), 25.7 (6C), 23.0, 22.6, 18.39, 18.36, 18.2, 18.1, 13.5 (2C), -3.9, -4.0, -4.3, -4.4, -5.28 (2C), -5.32 (2C); HRMS (ESI) *m*/*z* calcd. for $C_{35}H_{54}O_5SSi_2Na$ ([M+Na]$^+$) 665.3123, found 665.3100.

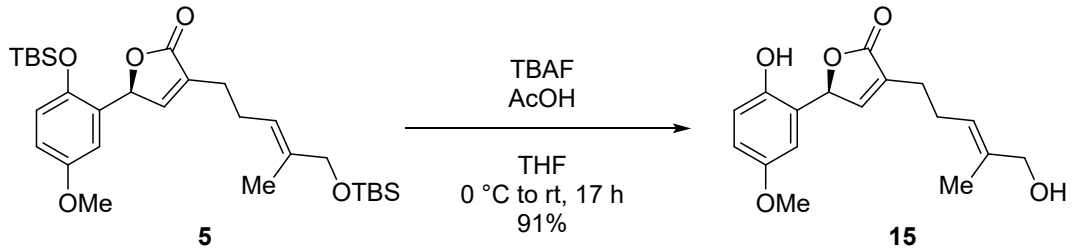
(*S*,*E*)-3-(5-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-3-en-1-yl)-5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)furan-2(5*H*)-one (5)



To a solution of **7** (87.1 mg, 135 μmol) in dichloroethane (1.4 mL) was added *m*CPBA (65%, 38.5 mg, 145 μmol) at 0 °C. The mixture was stirred for 1 h at 0 °C, and then refluxed for further 14 h. The reaction mixture was cooled to rt and quenched by the addition of sat. $NaHCO_3$ aq. and diluted with CH_2Cl_2. The aqueous layer was extracted with CH_2Cl_2. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 99/1 to 9/1) to give **5** (59.9 mg, 112 μmol, 83%) as a yellow oil.

$[\alpha]_D^{26}$ −18.7 (*c* 0.25, $CHCl_3$); IR (neat) ν_{max} = 2953, 2933, 2896, 2858, 1765, 1496, 1468, 1259, 1109, 1056, 904, 840, 780 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.14 (d, *J* = 1.8 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 6.74 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 6.19 (d, *J* = 1.8 Hz, 1H), 5.38 (tdd, *J* = 6.0, 1.2, 1.2 Hz, 1H), 3.97 (br s, 2H), 3.72 (s, 3H), 2.39 (td, *J* = 7.8 Hz, 1.2 Hz, 2H), 2.32 (dd, *J* = 14.4, 7.8 Hz, 2H), 1.58 (br s, 3H), 1.01 (s, 9H), 0.89 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H), 0.031 (s, 3H), 0.038 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.2, 154.1, 147.9, 146.5, 135.9, 132.8, 126.4, 122.3, 119.2, 114.8, 111.2, 77.7, 68.2, 55.7, 25.9 (3C), 25.8 (3C), 25.3, 25.2, 18.4, 18.2, 13.5, -4.0, -4.4, -5.3 (2C); HRMS (ESI) *m/z* calcd. for $C_{29}H_{48}O_5Si_2Na$ ($[M+Na]^+$) 555.2932, found 555.2929.

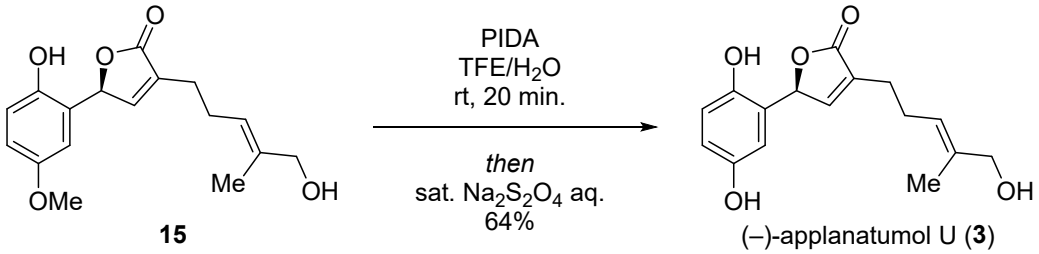
(*S*,*E*)-3-(5-hydroxy-4-methylpent-3-en-1-yl)-5-(2-hydroxy-5-methoxyphenyl)furan-2(5*H*)-one (15)



To a solution of **5** (100.2 mg, 188 μmol) in THF (625 μL) was added AcOH (33.0 μL, 577 μmol) and TBAF (1.0 M in THF, 565 μL, 565 μmol) at 0 °C. The mixture was stirred for 17 h at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 7/3 to 1/4) to give **15** (52.1 mg, 171 μmol, 91%) as a yellow oil.

$[\alpha]_D^{23}$ −12.1 (*c* 0.30, $CHCl_3$); IR (neat) ν_{max} = 3400, 2935, 2865, 1737, 1508, 1435, 1278, 1208, 1043, 815 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.36 (d, *J* = 2.4 Hz, 1H), 6.76 (d, 9.0 Hz, 1H), 6.74 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.54 (d, *J* = 3.0 Hz, 1H), 6.23 (d, *J* = 2.4 HZ, 1H), 5.39 (br td, *J* = 7.2, 1.2 Hz, 1H), 3.88 (br s, 2H), 3.68 (s, 3H), 2.38-2.36 (m, 2H), 2.35-2.29 (m, 2H), 1.60 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.8, 153.5, 148.9, 147.5, 136.0, 132.3, 124.3, 122.6, 116.7, 114.8, 112.0, 78.6, 68.5, 55.8, 25.3, 24.9, 13.7; HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}O_5Na$ ($[M+Na]^+$) 327.1203, found 327.1196.

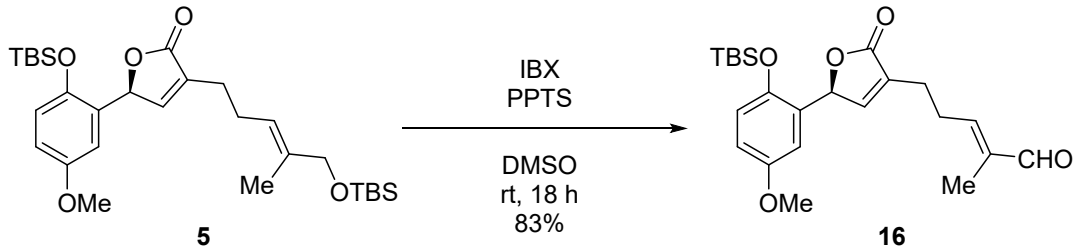
(−)-applanatumol U (3)



To a solution of **15** (45.0 mg, 148 μmol) in a mixture of 2,2,2-trifluoroethanol (TFE)/H_2O (5:3 v/v, 1.5 mL) was added iodobenzenediacetate (PIDA, 71.4 mg, 222 μmol) at rt. The mixture was stirred for 20 min at rt. The reaction mixture was quenched by the addition of sat. $Na_2S_2O_4$ aq. and H_2O, and then diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 7/3 to 1/4) to give (−)-**3** (27.3 mg, 94.0 μmol, 64%) as a yellow oil.

$[\alpha]_D^{23}$ −18.5 (*c* 0.23, MeOH); IR (neat) ν_{max} = 3314, 2925, 2857, 1733, 1508, 1456, 1358, 1303, 1203, 1052, 815 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.35 (d, *J* = 1.2 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 1H), 6.60 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.44 (d, *J* = 3.0 Hz, 1H), 6.24 (d, *J* = 1.2Hz, 1H), 5.40 (br t, *J* = 7.2 Hz, 1H), 3.90 (s, 2H), 2.40-2.30 (m, 4H), 1.61 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 176.7, 151.5, 151.2, 149.0, 137.6, 133.1, 124.8, 123.4, 117.3, 117.2, 113.4, 79.7, 68.6, 26.5, 26.0, 13.8; HRMS (ESI) *m/z* calcd. for $C_{16}H_{18}O_5Na$ ($[M+Na]^+$) 313.1046, found 313.1054.

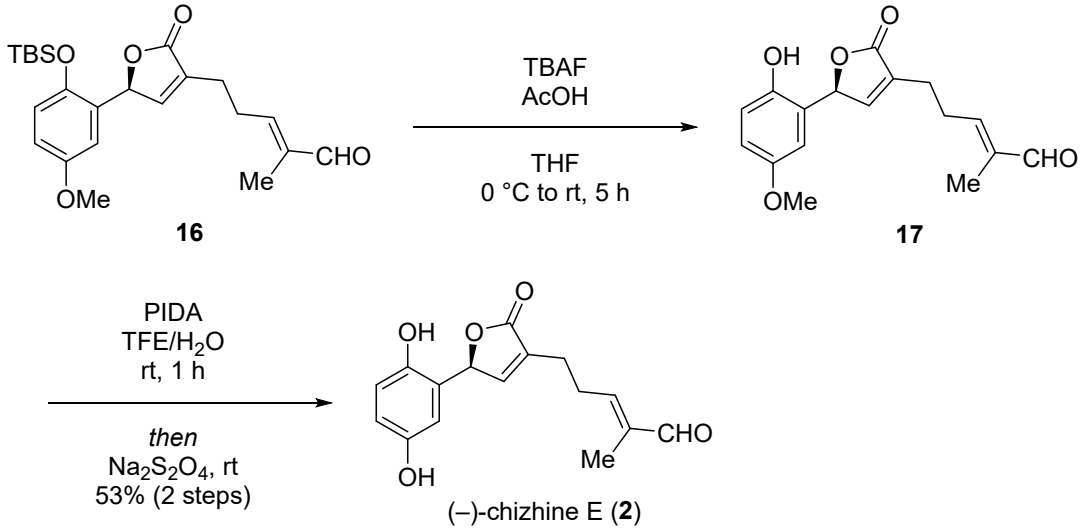
(*S*,*E*)-5-(5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-yl)-2-methylpent-2-enal (16)



To a solution of **5** (95.1 mg, 178 μmol) in DMSO (1.8 mL) was added PPTS (45.2 mg, 180 μmol) and IBX (74.8 mg, 267 μmol) at rt. The mixture was stirred for 18 h at rt. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 19/1 to 4/1) to give **16** (61.5 mg, 148 μmol, 83%) as a yellow oil.

$[\alpha]_D^{23}$ −26.8 (*c* 0.30, $CHCl_3$); IR (neat) ν_{max} = 2953, 2933, 2858, 1762, 1686, 1497, 1270, 1216, 1049, 905, 842, 782 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.39 (s, 1H), 7.20 (d, *J* = 1.2 Hz, 1H), 6.78 (d, *J* = 9.0 Hz, 1H), 6.75 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 6.44 (td, *J* = 7.2, 1.8 Hz, 1H), 6.21 (d, *J* = 1.2 Hz, 1H), 3.72 (s, 3H), 2.70-2.63 (m, 2H), 2.60-2.51 (m, 2H), 1.74 (d, *J* = 1.8 Hz, 1H), 1.00 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.8, 173.7, 154.2, 151.7, 148.6, 146.5, 140.4, 131.7, 126.0, 119.2, 114.9, 111.1, 77.9, 55.8, 26.7, 25.8 (3C), 24.1, 18.2, 9.3, -3.9, -4.4; HRMS (ESI) *m/z* calcd. for $C_{23}H_{32}O_5SiNa$ ($[M+Na]^+$) 439.1911, found 439.1921.

(−)-chizhine E (2)

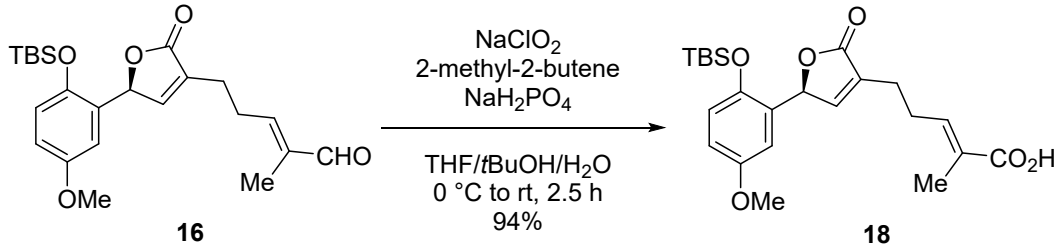


To a solution of **16** (24.8 mg, 59.5 μmol) in THF (600 μL) was added AcOH (5.5 μL, 96 μmol) and TBAF (1.0 M in THF, 90 μL, 90 μmol) at 0 °C. The mixture was stirred for 5 h at rt. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a crude **17**, which was used next reaction without further purification.

To a solution of crude **17** (prepared above, 59.5 μmol) in a mixture of TFE/H_2O (5:3 v/v, 600 μL) was added PIDA (38.4 mg, 119 μmol) at rt. The mixture was stirred for 1 h at rt. The reaction mixture was quenched by the addition of sat. $Na_2S_2O_4$ aq. and H_2O, and then diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 7/3 to 1/4) to give (−)-**2** (9.2 mg, 31.7 μmol, 53% over two steps from **16**) as a yellow oil.

$[\alpha]_D^{23}$ −25.0 (*c* 0.04, MeOH); IR (neat) ν_{max} = 3363, 2923, 2851, 1735, 1670, 1508, 1455, 1359, 1303, 1202, 1052, 816 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 9.35 (s, 1H), 7.44 (d, *J* = 1.2 Hz, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.8 Hz, 1H), 6.61-6.59 (m, 1H), 6.45 (d, *J* = 1.8 Hz, 1H), 6.23 (d, *J* = 1.2 Hz, 1H), 2.68 (dd, *J* = 14.4, 7.8 Hz, 2H), 2.54 (td, *J* = 7.8, 1.2 Hz, 2H), 1.71 (d, *J* = 1.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 196.9, 176.4, 154.5, 151.7, 151.5, 149.0, 141.4, 132.3, 123.2, 117.3, 117.2, 113.3, 80.1, 27.9, 24.8, 9.2; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}O_5Na$ ($[M+Na]^+$) 311.0890, found 311.0898.

(*S*,*E*)-5-(5-(2-((*tert*-butyldimethylsilyl)oxy)-5-methoxyphenyl)-2-oxo-2,5-dihydrofuran-3-yl)-2-methylpent-2-enoic acid (18)

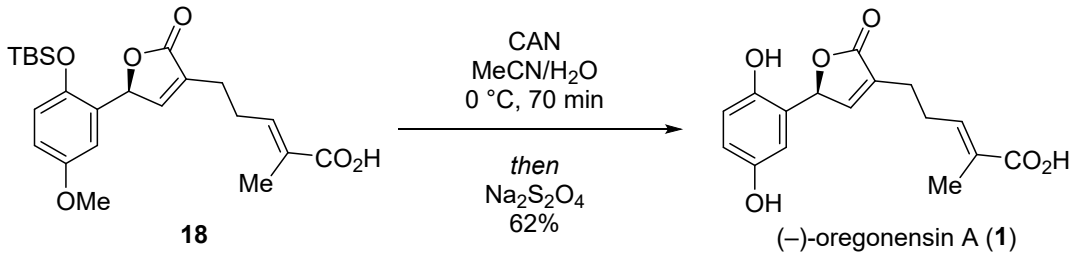


To a solution of **16** (51.1 mg, 123 μmol) and NaH_2PO_4 (304.2 mg, 2.54 mmol) in THF (570 μL) and *t*BuOH (570

μL) was added 2-methyl-2-butene (720 μL, 6.78 mmol) and a solution of $NaClO_2$ (192.1 mg, 1.70 mmol) in H_2O (570 μL) at 0 °C. The mixture was stirred for 2.5 h at rt. The reaction mixture was quenched by the addition of H_2O and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography ($CHCl_3$/MeOH = 99/1 to 97/3) to give **18** (50.0 mg, 115 μmol, 94%) as a yellow oil.

$[\alpha]_D^{23}$ −34.7 (*c* 0.20, $CHCl_3$); IR (neat) ν_{max} = 2953, 2934, 2859, 1762, 1688, 1496, 1273, 1216, 1048, 904, 842, 783 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.18 (d, *J* = 1.8 Hz, 1H), 6.84 (br t, *J* = 6.6 Hz, 1H), 6.77 (d, *J* = 9.0 Hz, 1H), 6.75 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.64 (d, *J* = 3.0 Hz, 1H), 6.21 (d, *J* = 1.8 Hz, 1H), 3.72 (s, 3H), 2.54-2.48 (m, 4H), 2.84 (s, 3H), 1.00 (s, 9H), 0.28 (s, 3H), 0.24 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 173.8, 172.9, 154.2, 148.5, 146.5, 142.5, 131.9, 128.5, 126.0, 119.2, 115.0, 111.0, 77.9, 55.7, 26.5, 25.7 (3C), 24.2, 18.2, 12.1, -4.0, -4.4; HRMS (ESI) *m*/*z* calcd. for $C_{23}H_{32}O_6SiNa$ ($[M+Na]^+$) 455.1860, found 455.1840.

(−)-oregonensin A (1)



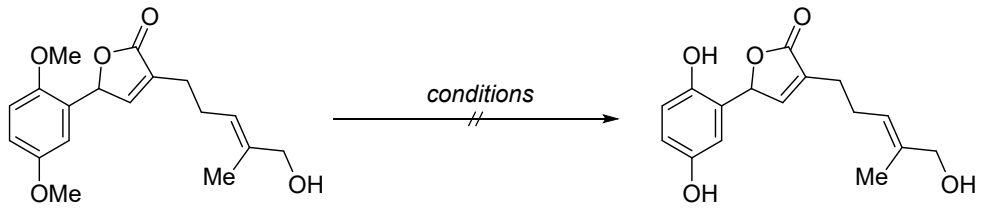
To a solution of **18** (33.0 mg, 76.3 μmol) in a mixture of MeCN/H_2O (760 μL) was added CAN (62.8 mg, 115 μmol) at 0 °C. The mixture was stirred for 70 min at 0 °C. The reaction mixture was quenched by the addition of sat. $Na_2S_2O_4$ aq. and H_2O, and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic solution was washed with brine, dried over Na_2SO_4, filtered, and concentrated to give a residue. The residue was purified by flash column chromatography ($CHCl_3$/MeOH = 99/1 to 9/1) to give **1** (14.3 mg, 47.0 μmol, 62%) as a yellow oil.

$[\alpha]_D^{23}$ −11.2 (*c* 0.18, $CHCl_3$); IR (neat) ν_{max} = 3345, 2959, 2928, 2857, 1735, 1646, 1507, 1455, 1263, 1201, 1095, 1052, 811 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 7.40 (d, *J* = 1.2 Hz, 1H), 6.76 (td, *J* = 7.2, 1.2 Hz, 1H), 6.67 (d, *J* = 9.0 Hz, 1H), 6.60 (dd, *J* = 9.0, 3.0 Hz, 1H), 6.46 (d, *J* = 3.0 Hz, 1H), 6.24 (d, *J* = 1.2 Hz, 1H), 2.51-2.45 (m, 4H), 1.80 (s, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 176.4, 171.5, 151.5, 151.4, 149.0, 141.8, 132.6, 130.3, 123.3, 117.3, 117.2, 113.3, 80.0, 27.6, 25.1, 12.5; HRMS (ESI) *m*/*z* calcd. for $C_{16}H_{16}O_6Na$ ($[M+Na]^+$) 327.0839, found 327.0844.

3. Additional Results

Our preliminary experiments are shown in Table S1 and Scheme S1. Our efforts to deprotect two methyl groups were unsuccessful due to the high reactivity of benzylic and allylic positions.

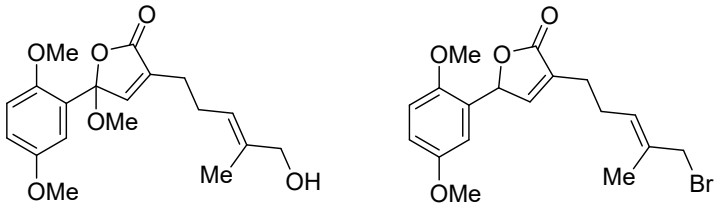
Table S1. Attempts for removal of two methyl group of S2.



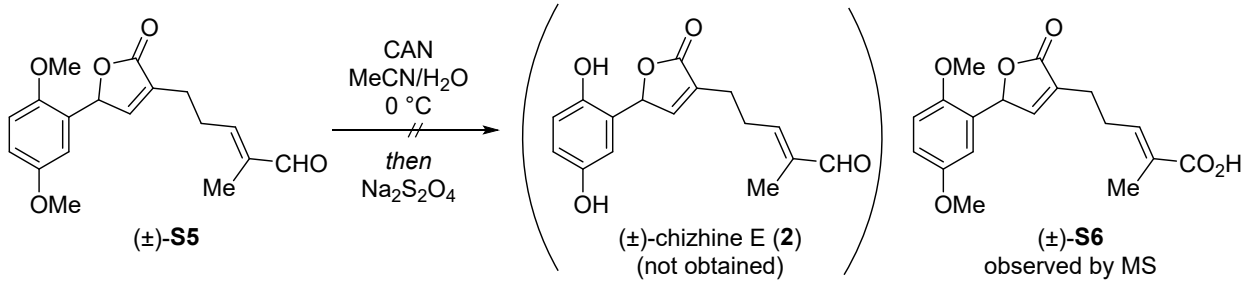
(±)-**S2** (±)-applanatumol U (**3**) (not obtained)

entry	reagent	solvent	temp (°C)	results
1[a]	CAN	MeCN/H_2O	0	complex mixture
2[a]	CAN	MeOH/DCM	–78 to –30	**S3** was observed by ^{1}H NMR and MS.
3[a]	PIDA	TFE/H_2O	rt	no reaction
4[a]	PIFA	TFE/H_2O	rt to 50	complex mixture
5	BBr_3	DCM	–78 to rt	**S4** was observed by MS.

[a]Reaction mixture was treated with $Na_2S_2O_4$ aq. as work up.



(±)-**S3** (±)-**S4**

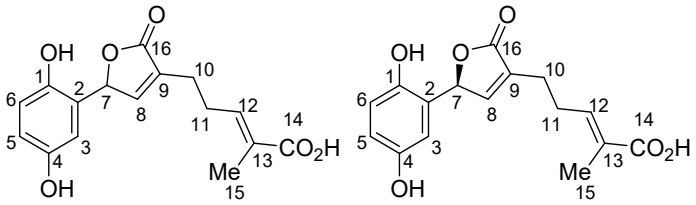


(±)-**S5** (±)-chizhine E (**2**) (not obtained) (±)-**S6** observed by MS

Scheme S1. Attempt for demethylation of dimethyl protected substrate S5.

4. ^{1}H and ^{13}C NMR spectroscopic data

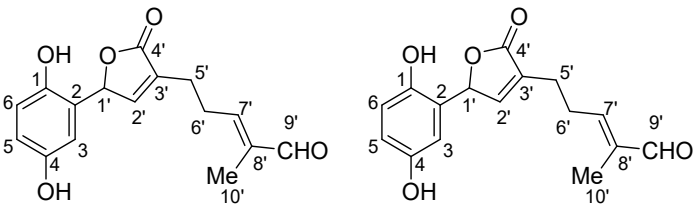
Table S2. NMR spectroscopic data (CD_3OD) for natural oregonensin A (1) and synthetic (−)-oregonensin A (1).



natural (±)-oregonensin A (**1**) synthetic (–)-oregonensin A (**1**)

	Natural (±)-**1**		Synthetic (−)-**1**	
No.	δ_C	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)
1	149.1		149.0	
2	123.4		123.3	
3	113.4	6.46 (d, 3.4)	113.3	6.46 (d, 3.0)
4	151.5		151.4	
5	117.4	6.61 (dd, 8.7, 3.4)	117.3	6.60 (dd, 9.0, 3.0)
6	117.3	6.67 (d, 8.7)	117.2	6.67 (d, 9.0)
7	80.1	6.24 (br s)	80.0	6.24 (d, 1.2)
8	151.6	7.41 (d, 1.4)	151.5	7.40 (d, 1.2)
9	132.8		132.6	
10	25.2	2.46 (m)	25.1	2.51-2.45 (m)
11	27.7	2.47 (m)	27.6	2.51-2.45 (m)
12	141.8	6.76 (t, 6.4)	141.8	6.76 (td, 7.2, 1.2)
13	130.5		130.3	
14	171.7		171.5	
15	12.7	1.80 (s)	12.5	1.80 (s)
16	176.5		176.4	

Table S3. NMR spectroscopic data (CD_3OD) for natural chizhine E (2) and synthetic (−)-chizhine E (2).

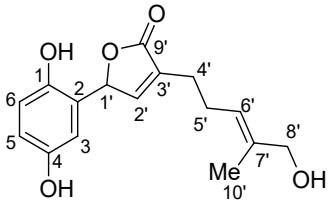


natural (±)-chizhine E (**2**) synthetic (–)-chizhine E (**2**)

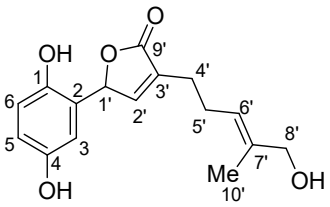
	Natural (±)-**2**		Synthetic (−)-**2**	
No.	δ_C	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)
1	148.9		149.0	
2	123.2		123.2	

3	113.5	6.46 (d, 2.9)	113.3	6.45 (d, 1.8)
4	151.5		151.5	
5	117.2	6.61 (dd, 8.6, 2.9)	117.2	6.61 (dd, 7.8, 1.8)
6	117.3	6.68 (d, 8.6)	117.3	6.66 (d, 7.8)
1′	80.1	6.24 (d, 1.5)	80.1	6.23 (d, 1.2)
2′	151.7	7.44 (d, 1.5)	151.7	7.44 (d, 1.2)
3′	132.3		132.3	
4′	176.4		176.4	
5′	24.8	2.54 (m)	24.8	2.54 (td, 7.8, 1.2)
6′	27.9	2.68 (m)	27.9	2.68 (dd, 14.4, 7.8)
7′	154.5	6.59 (overlap)	154.5	6.61-6.59 (m)
8′	141.4		141.4	
9′	196.9	9.34 (s)	196.9	9.35 (s)
10′	9.2	1.71 (s)	9.2	1.71 (d, 1.2)

Table S4. NMR spectroscopic data (CD_3OD) for natural applanatumol U (3) and synthetic (−)-applanatumol U (3).



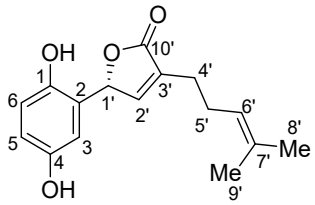
natural
(±)-applanatumol U (**3**)



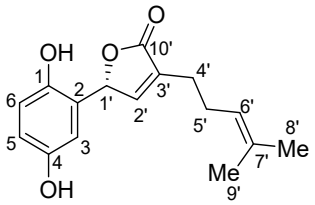
synthetic
(−)-applanatumol U (**3**)

	Natural (±)-**3**		Synthetic (−)-**3**	
No.	δ_C	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)
1	149.0		149.0	
2	123.4		123.4	
3	113.4	6.46 (d, 2.9)	113.4	6.44 (d, 3.0)
4	151.5		151.5	
5	117.2	6.62 (dd, 8.9, 2.9)	117.2	6.60 (dd, 9.0, 3.0)
6	117.3	6.68 (d, 8.9)	117.3	6.67 (d, 9.0)
1′	79.7	6.25 (br s)	79.7	6.24 (d, 1.2)
2′	151.2	7.35 (br s)	151.2	7.35 (d, 1.2)
3′	133.1		133.1	
4′	25.9	2.37 (overlap)	26.0	2.40-2.30 (m)
5′	26.5	2.37 (overlap)	26.5	2.40-2.30 (m)
6′	124.8	5.41 (t, 7.1)	124.8	5.40 (br t, 7.2)
7′	137.5		137.6	
8′	68.6	3.91 (s)	68.6	3.90 (s)
9′	176.7		176.7	
10′	13.8	1.62 (s)	13.8	1.61 (s)

Table S5. NMR spectroscopic data (acetone-d_6) for natural (+)-fornicin A (4) and synthetic (−)-*ent*-fornicin (*ent*-4).



natural
(+)-fornicin A (**4**)



synthetic
(–)-*ent*-fornicin A (**4**)

	Natural (+)-**4**		Synthetic (−)-**4**	
No.	δ_C	δ_H (mult, *J* in Hz)	δ_C	δ_H (mult, *J* in Hz)
1	148.2		148.2	
2	123.6		123.8	
3	113.2	6.53 8d, 2.9)	113.2	6.53 (d, 2.4)
4	151.3		151.5	
5	116.8	6.65 (dd, 8.6, 2.9)	116.8	6.65 (dd, 9.0, 2.4)
6	117.0	6.76 (d, 8.6)	117.1	6.75 (d, 9.0)
1′	78.3	6.20 (d, 1.4)	78.2	
2′	149.5	7.35 (d, 1.4)	149.4	7.35 (d, 1.8)
3′	132.7		132.8	
4′	26.6	2.30 (m)	26.7	2.33-2.30 (m)
5′	25.9	2.28 (m)	26.0	2.29-2.25 (brm)
6′	123.9	5.12 (br t, 6.9)	124.0	5.13 (brt, 7.2)
7′	133.1		133.2	
8′	25.7	1.64 (s)	25.7	1.64 (d, 1.2)
9′	17.7	1.57 (s)	17.7	1.58 (s)
10′	174.6		174.4	
PhOH				8.26 (s) 7.80 (s)

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 13.

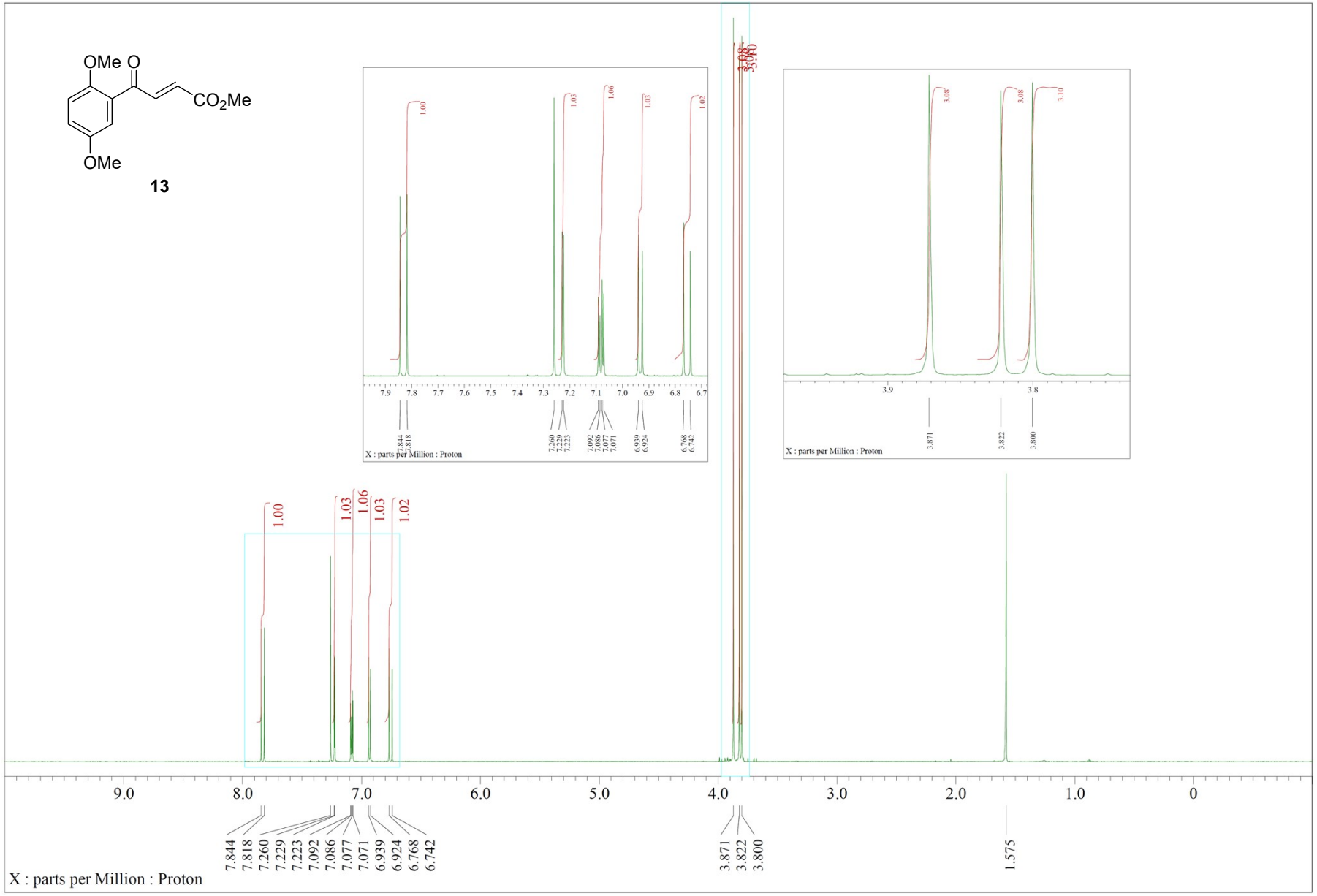


Figure S2. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 13.

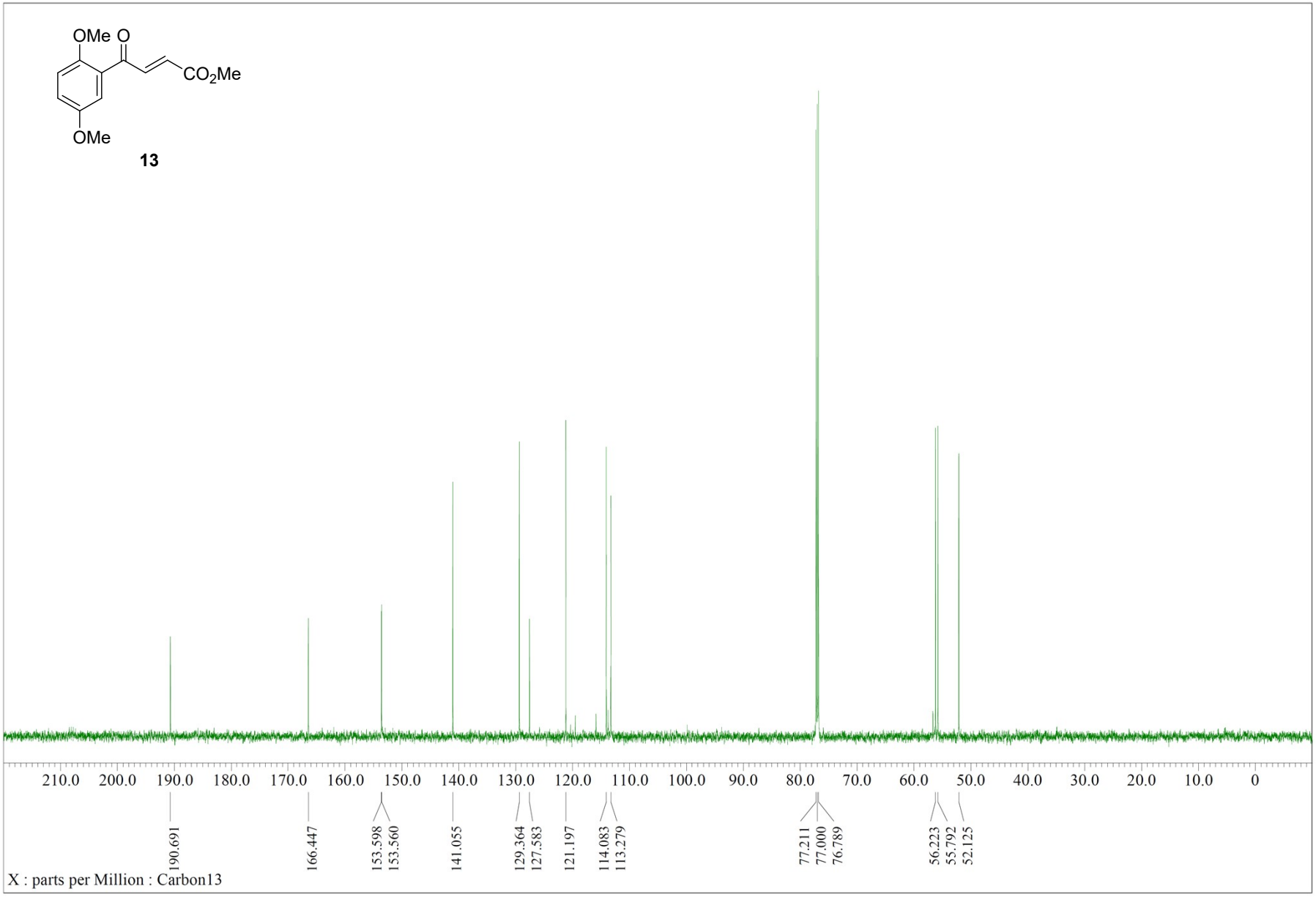


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 14.

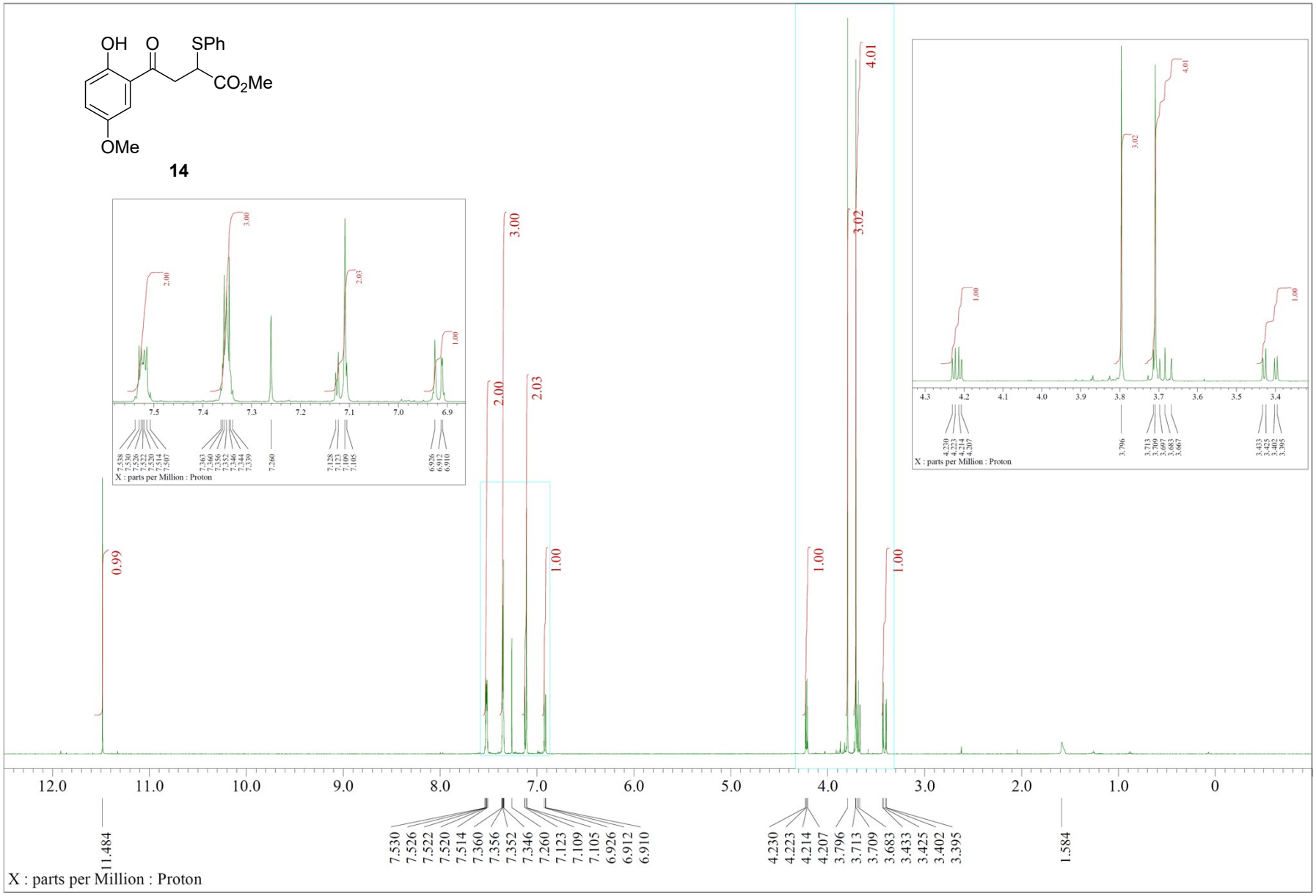


Figure S4. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 14.

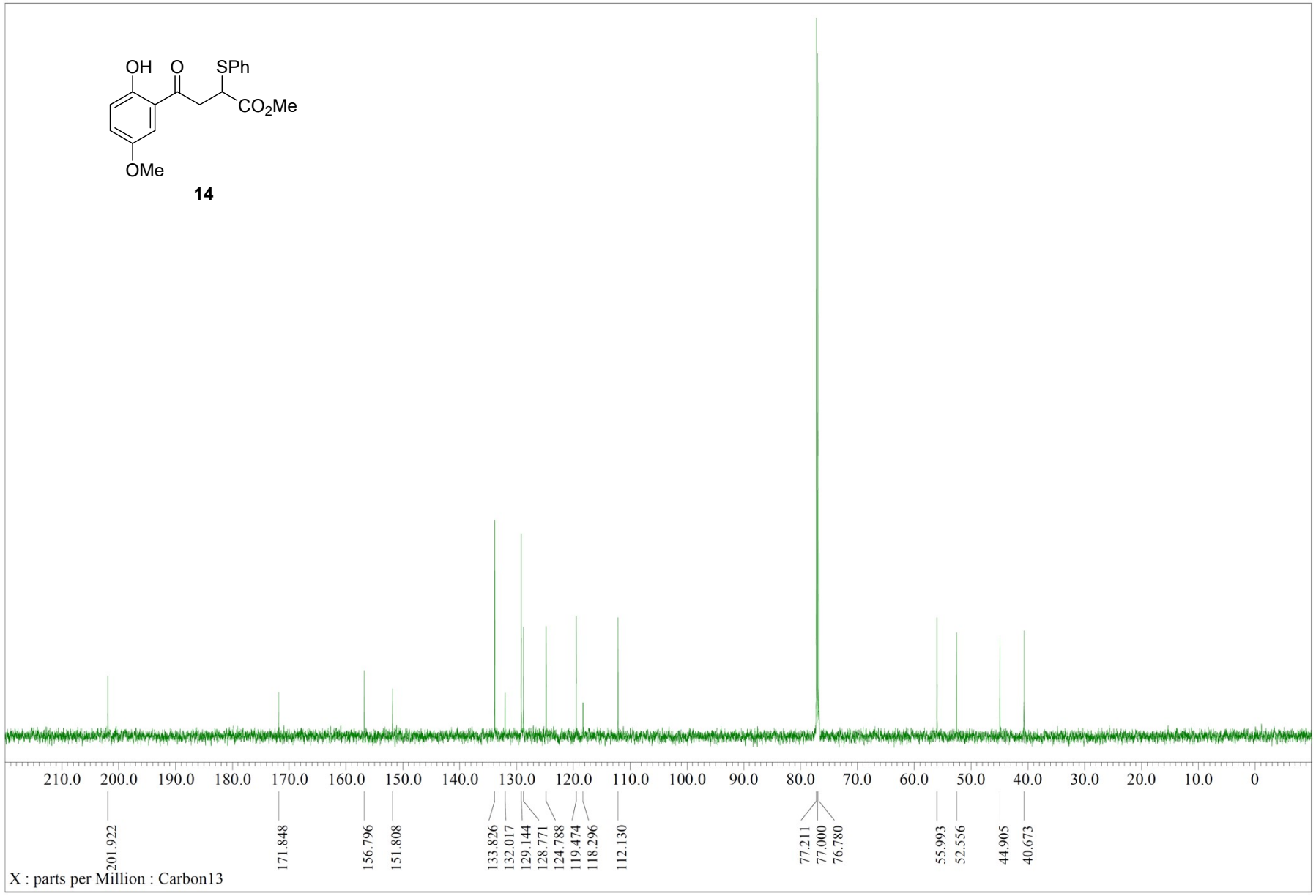


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 12.

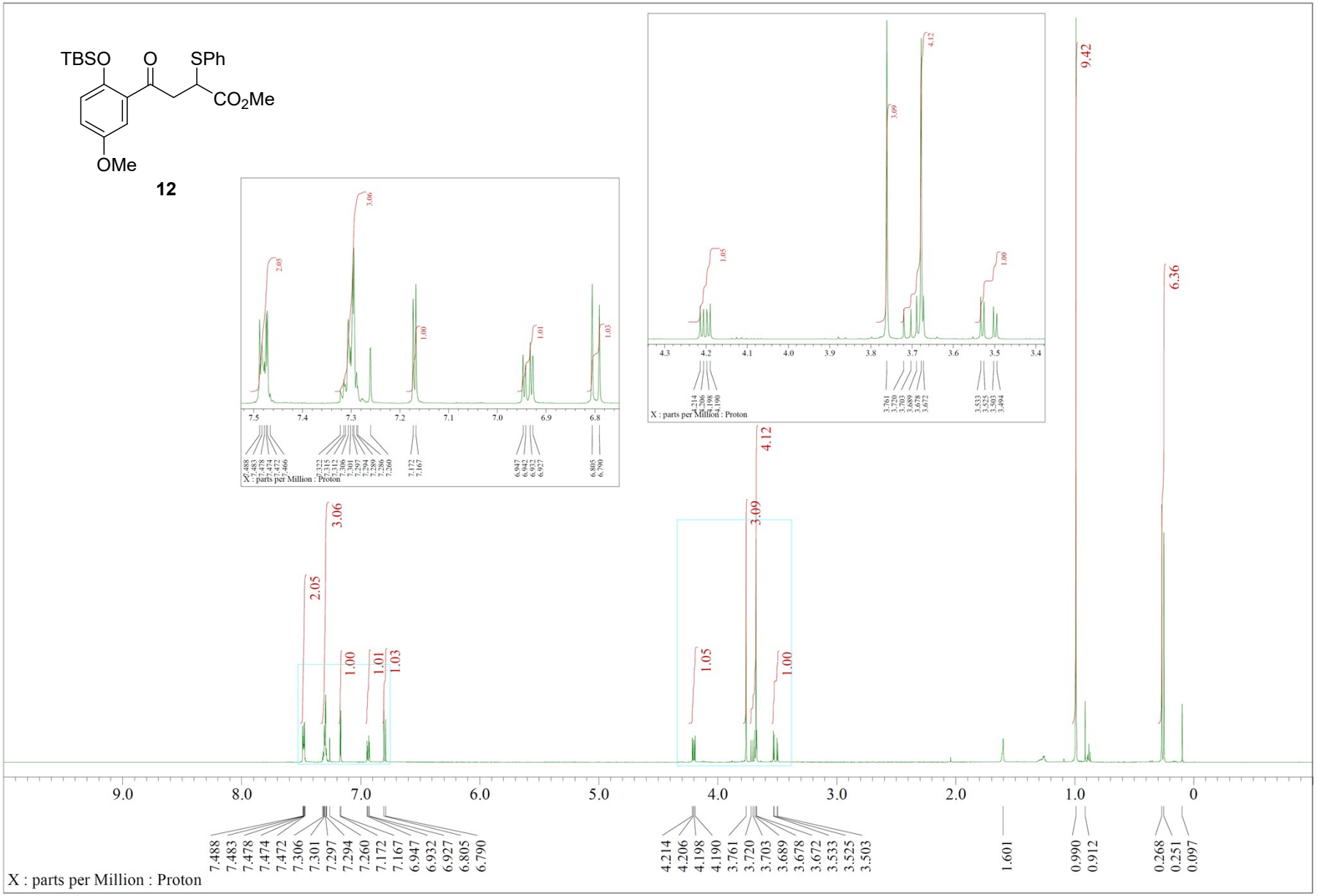


Figure S6. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 12.

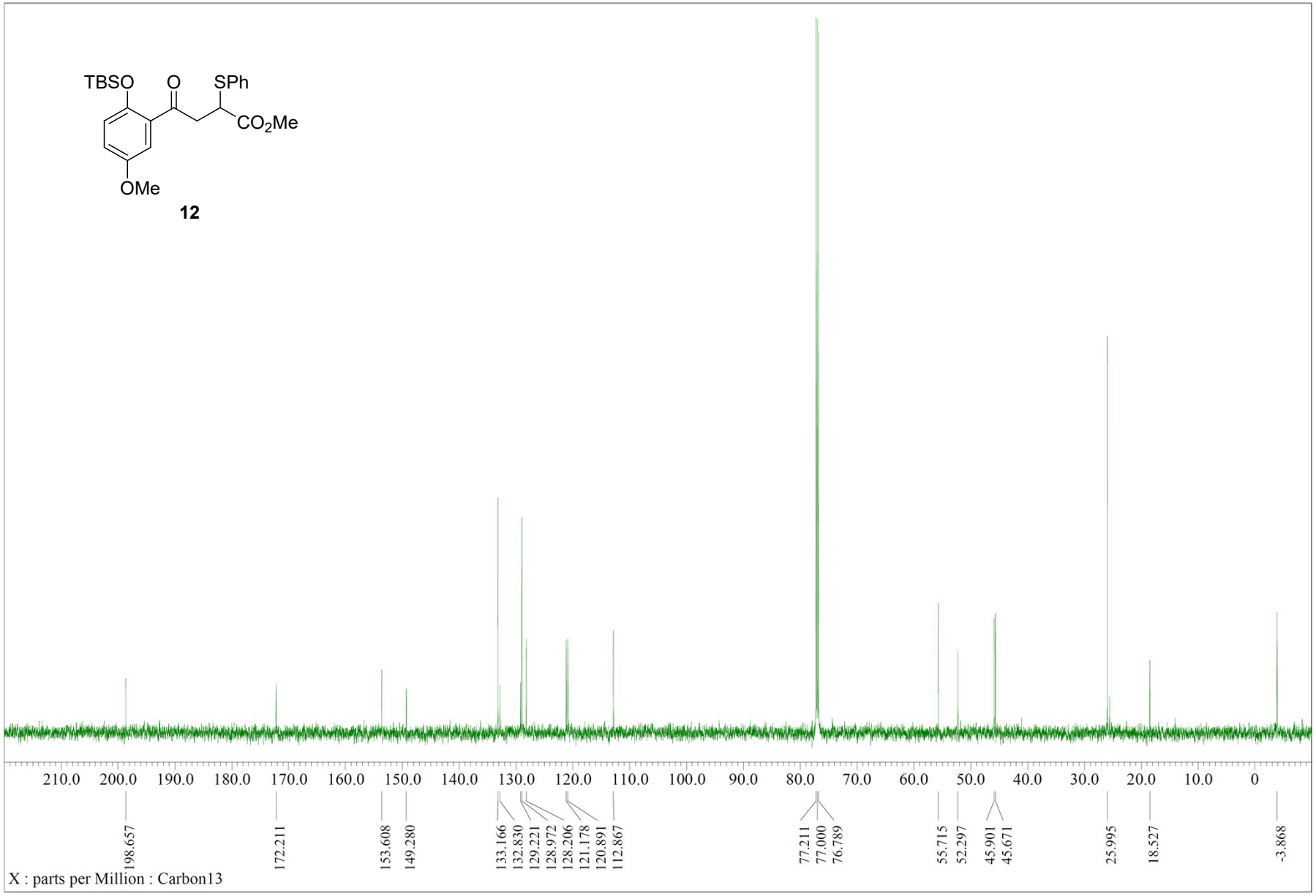


Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, dr = 1:1.1) of compound 11.

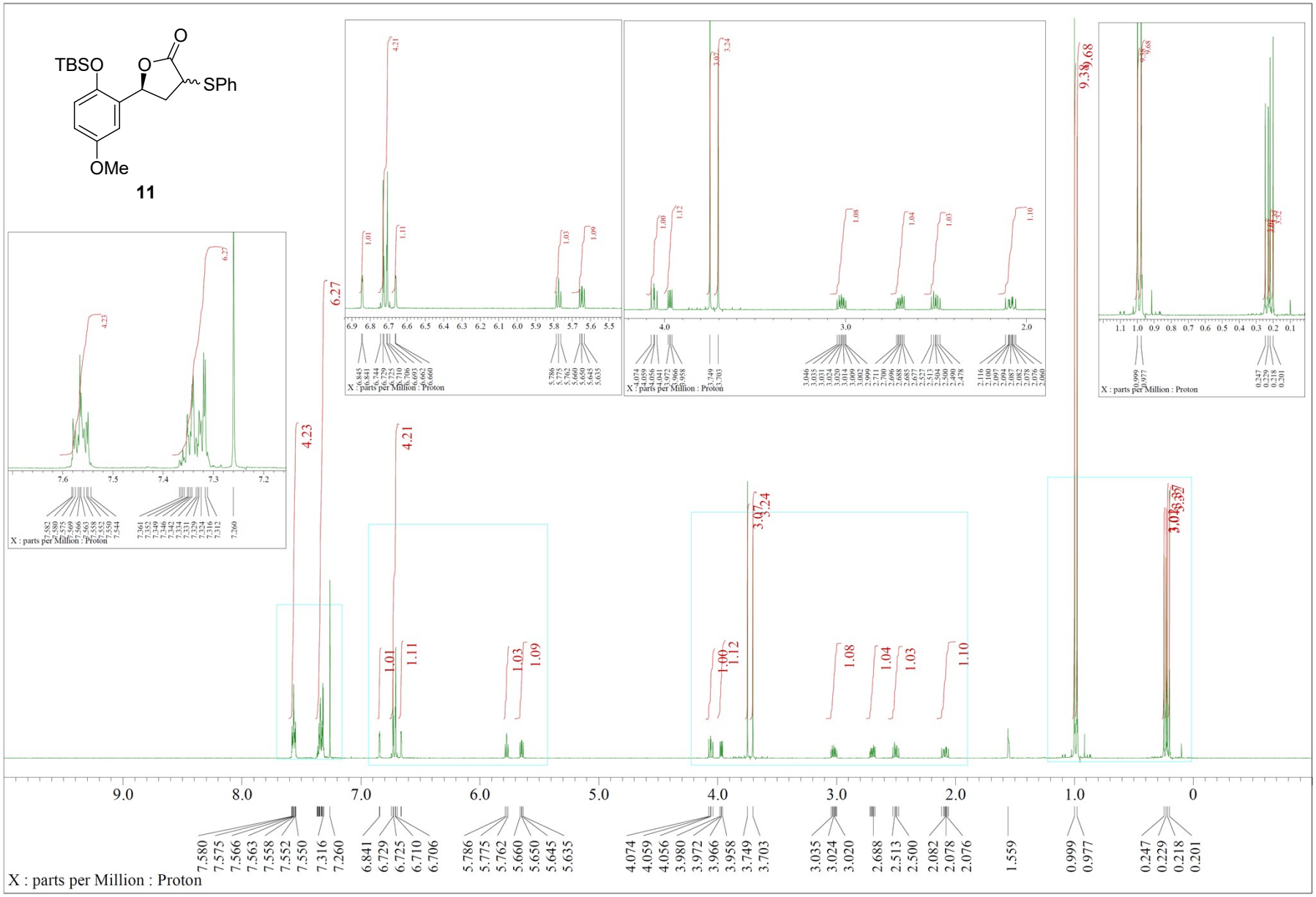


Figure S8. ^{13}C NMR spectrum (150 MHz, CD_3OD, dr = 1:1.1) of compound 11.

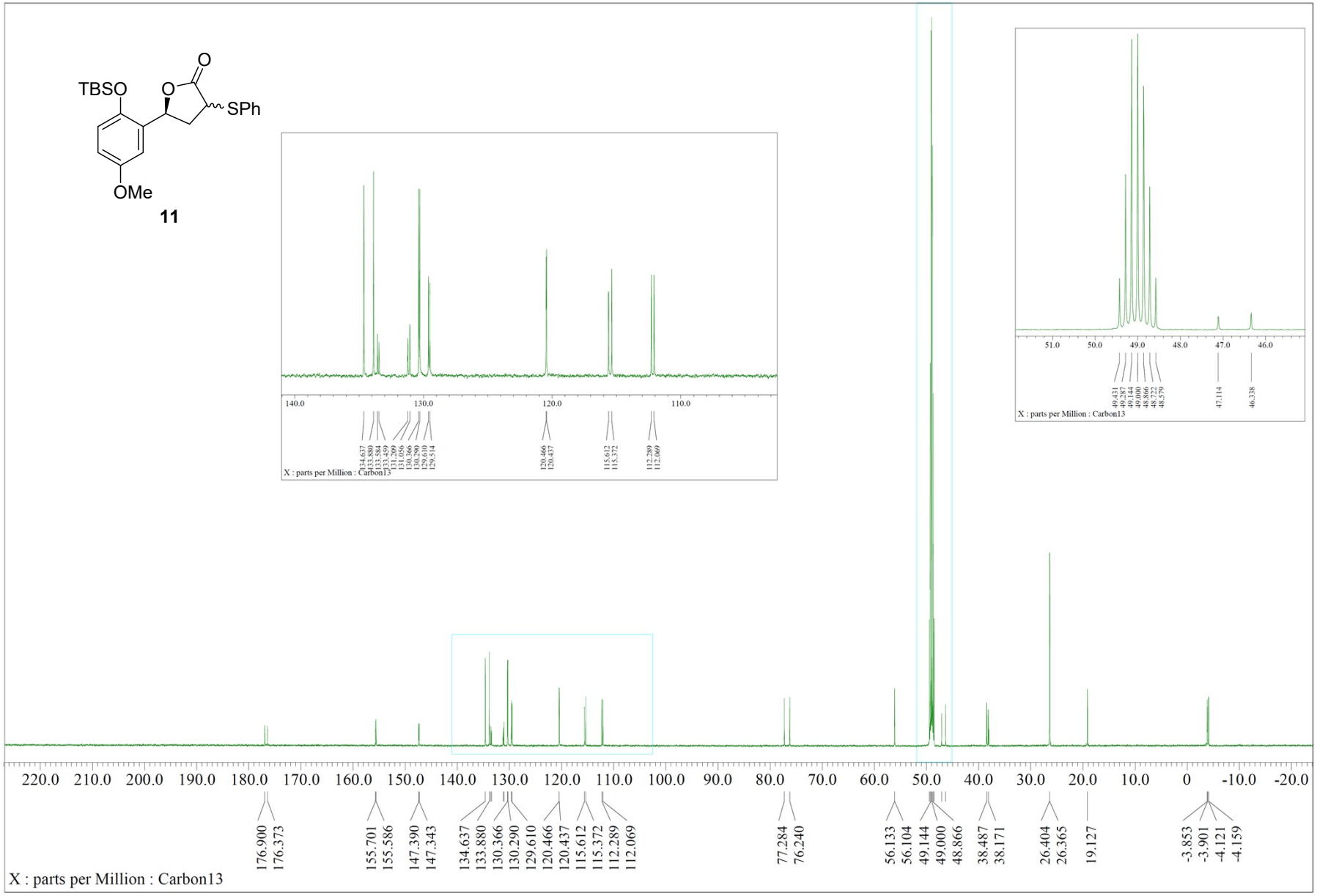


Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, dr = 3.3:1) of compound 8.

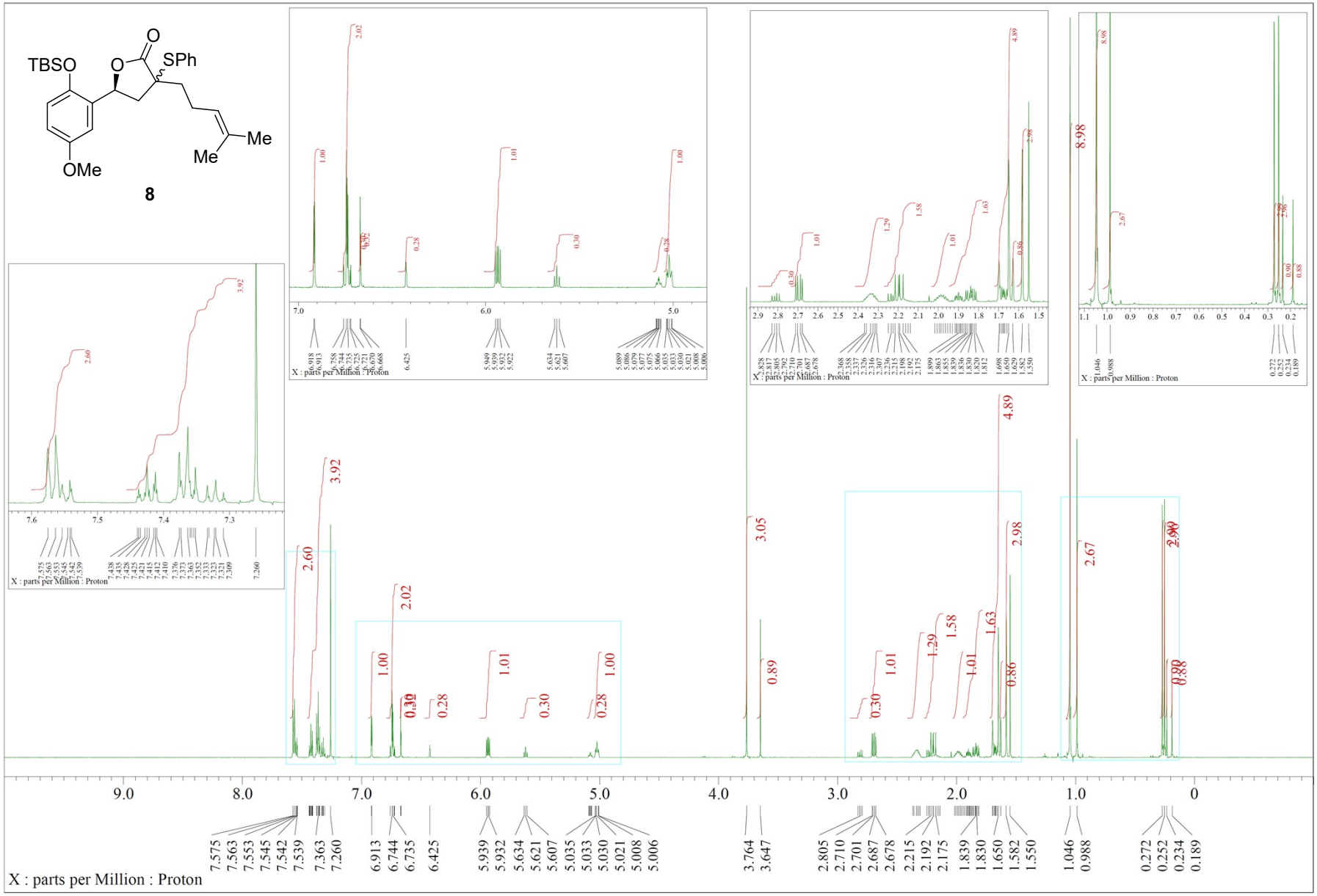


Figure S10. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, dr = 3.3:1) of compound 8.

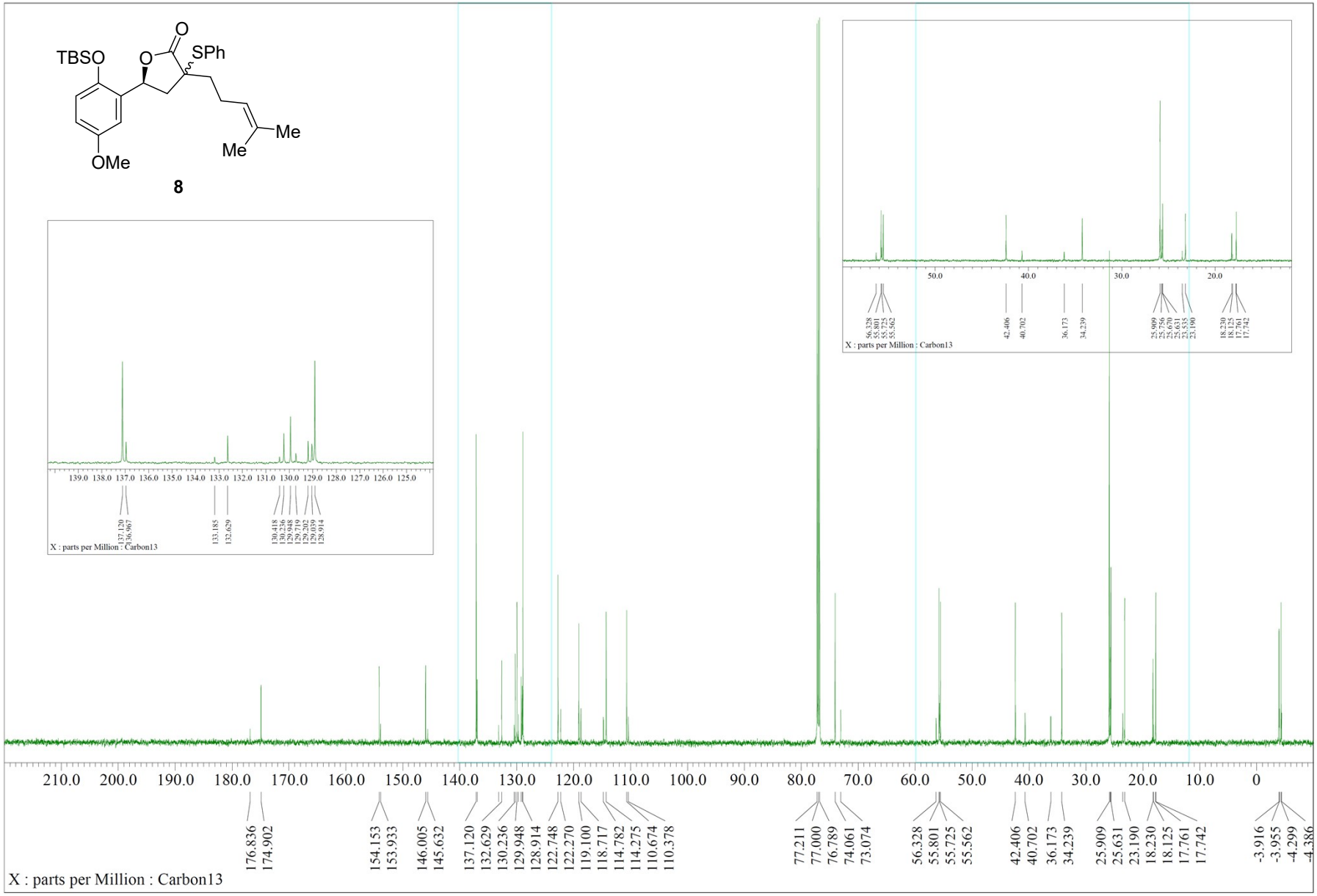


Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 6.

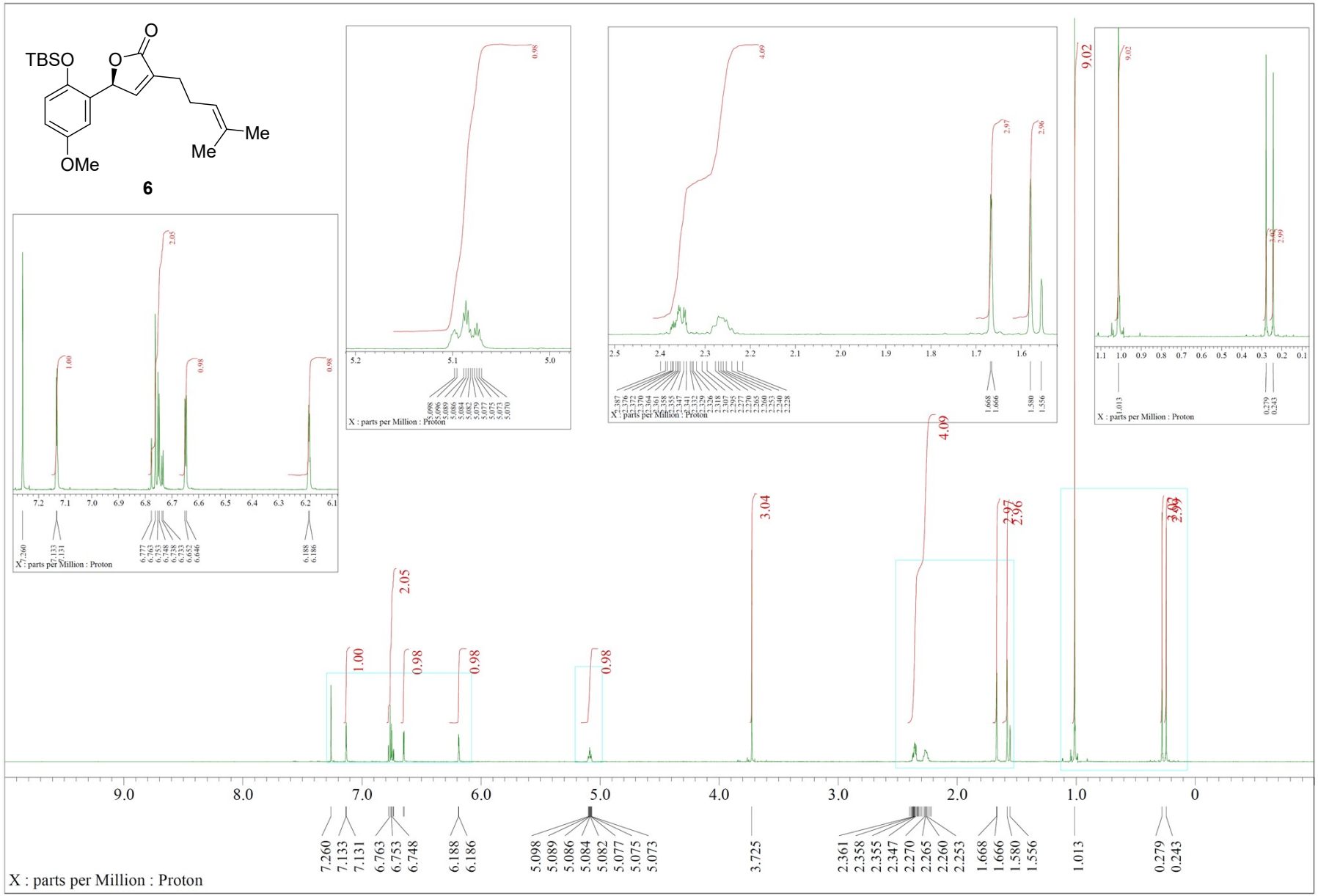


Figure S12. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 6.

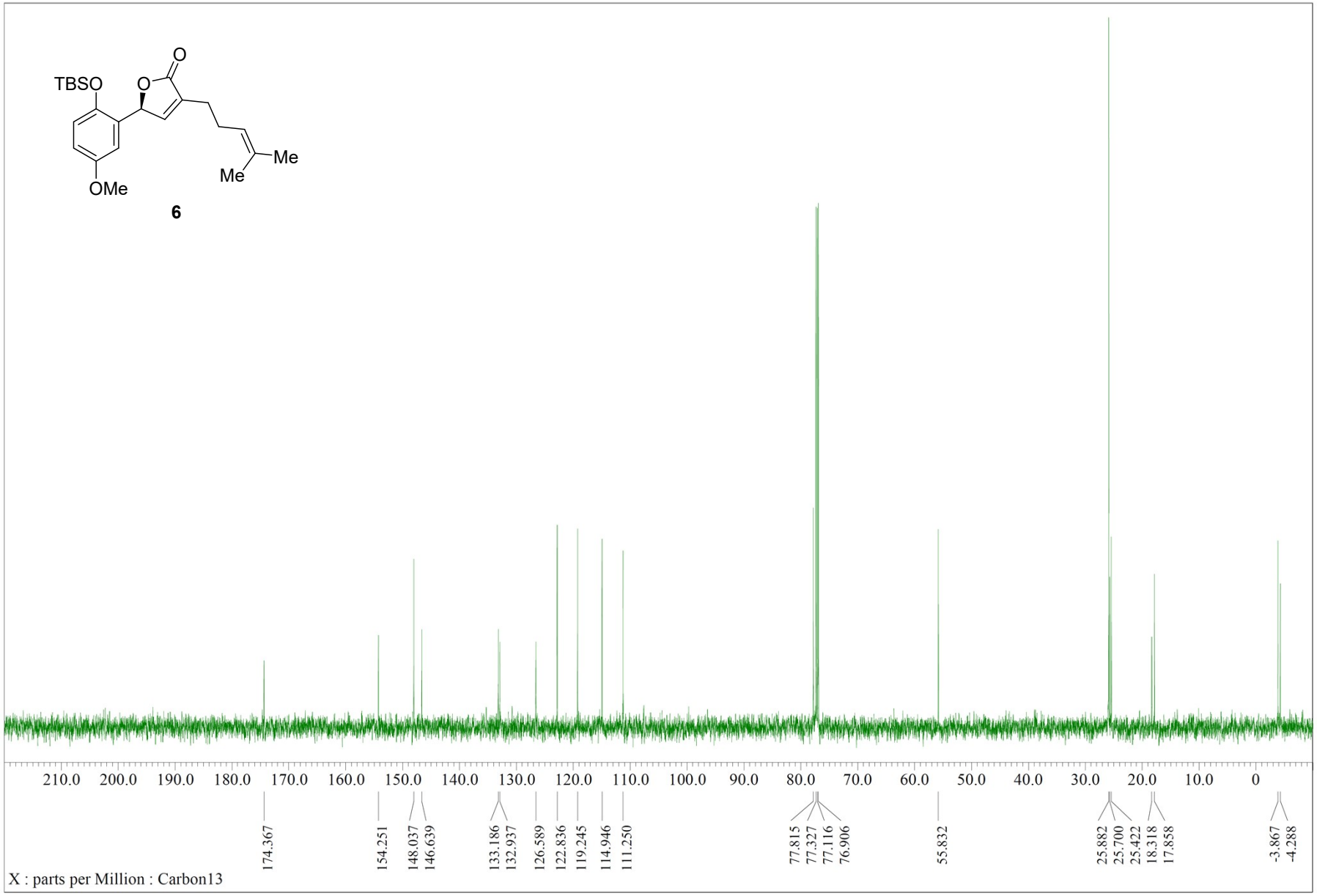


Figure S13. ^{1}H NMR spectrum (600 MHz, acetone-d_6) of (−)-*ent*-fornicin A (*ent*-4).

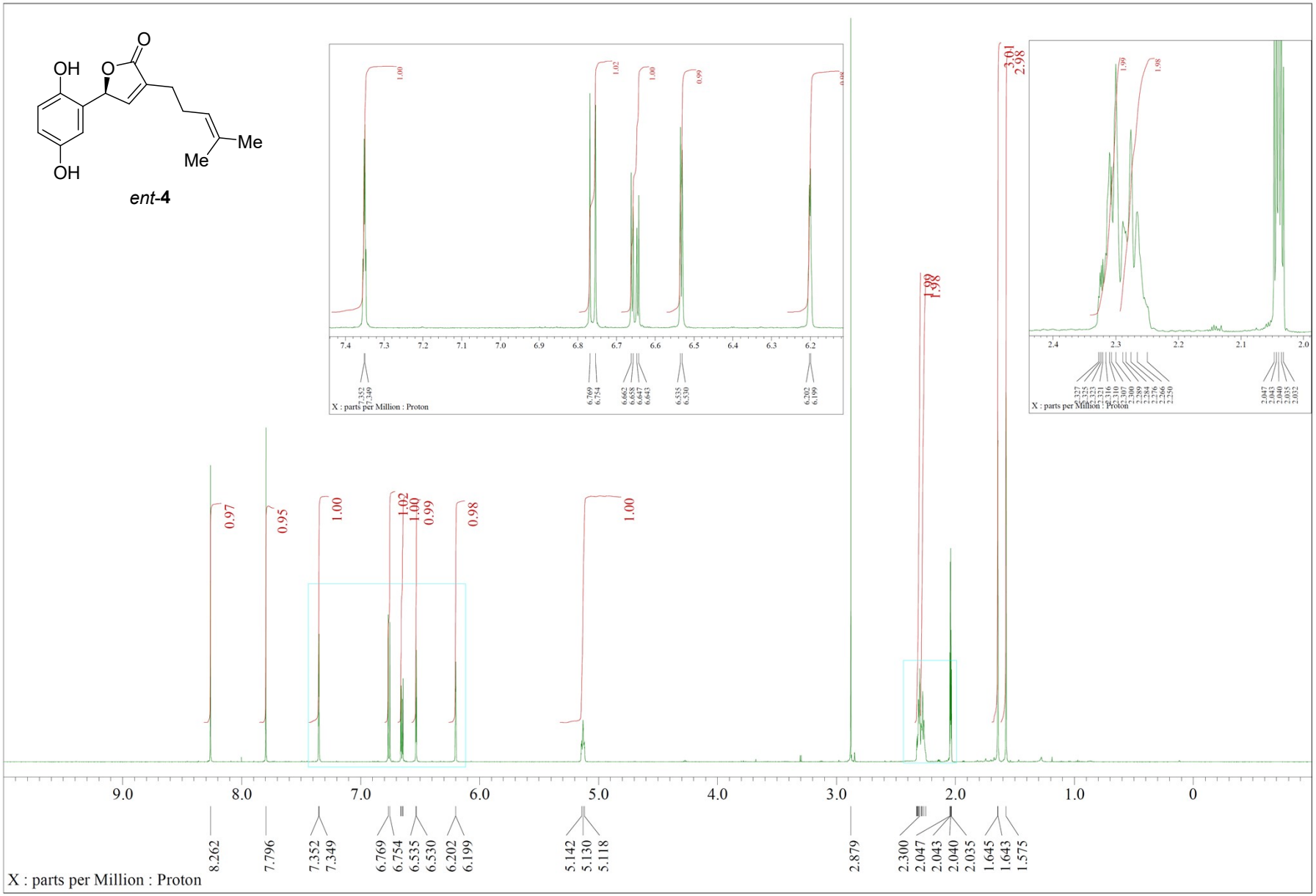


Figure S14. ^{13}C NMR spectrum (150 MHz, acetone-d_6) of (−)-*ent*-fornicin A (*ent*-4).

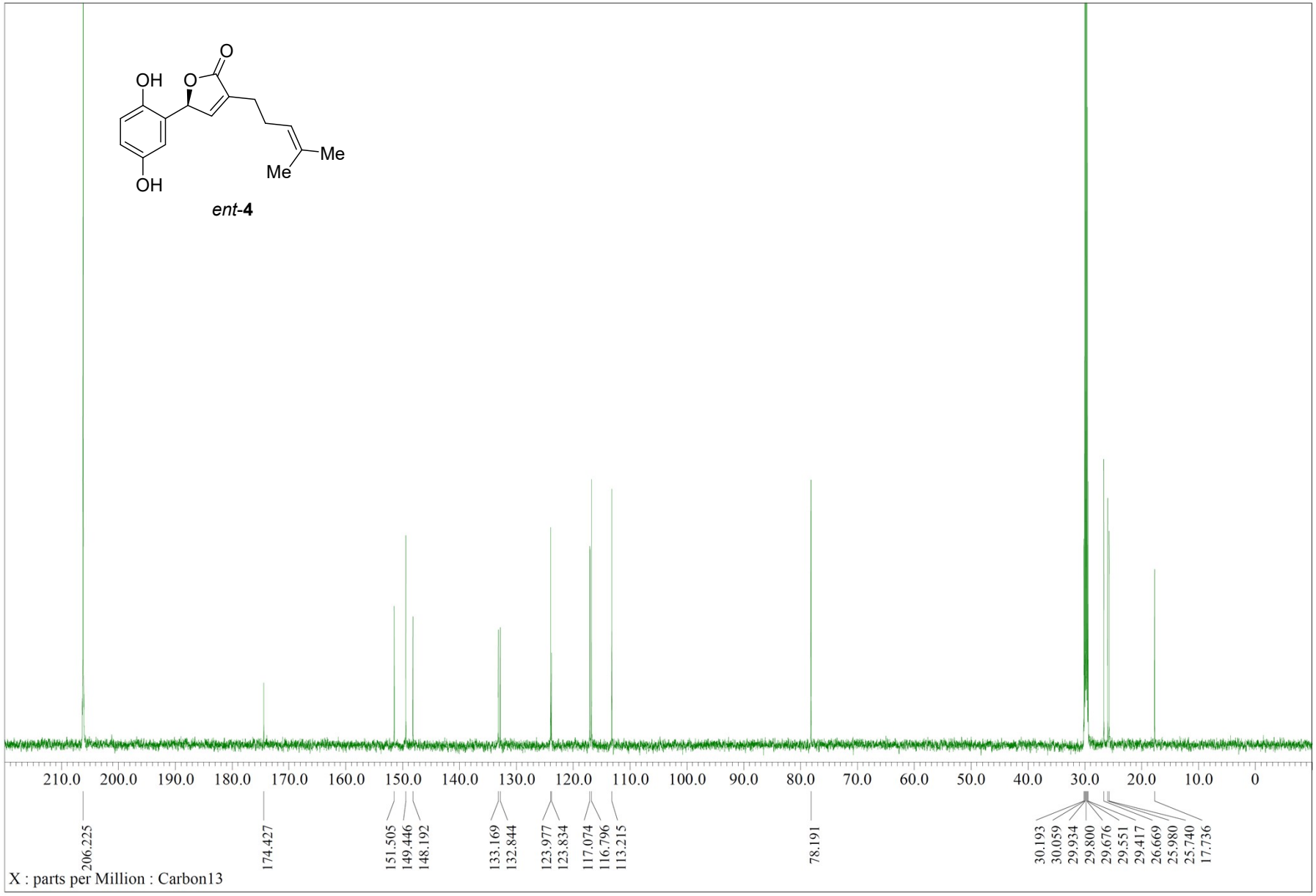


Figure S15. COSY spectrum of (−)-*ent*-fornicin A (*ent*-4).

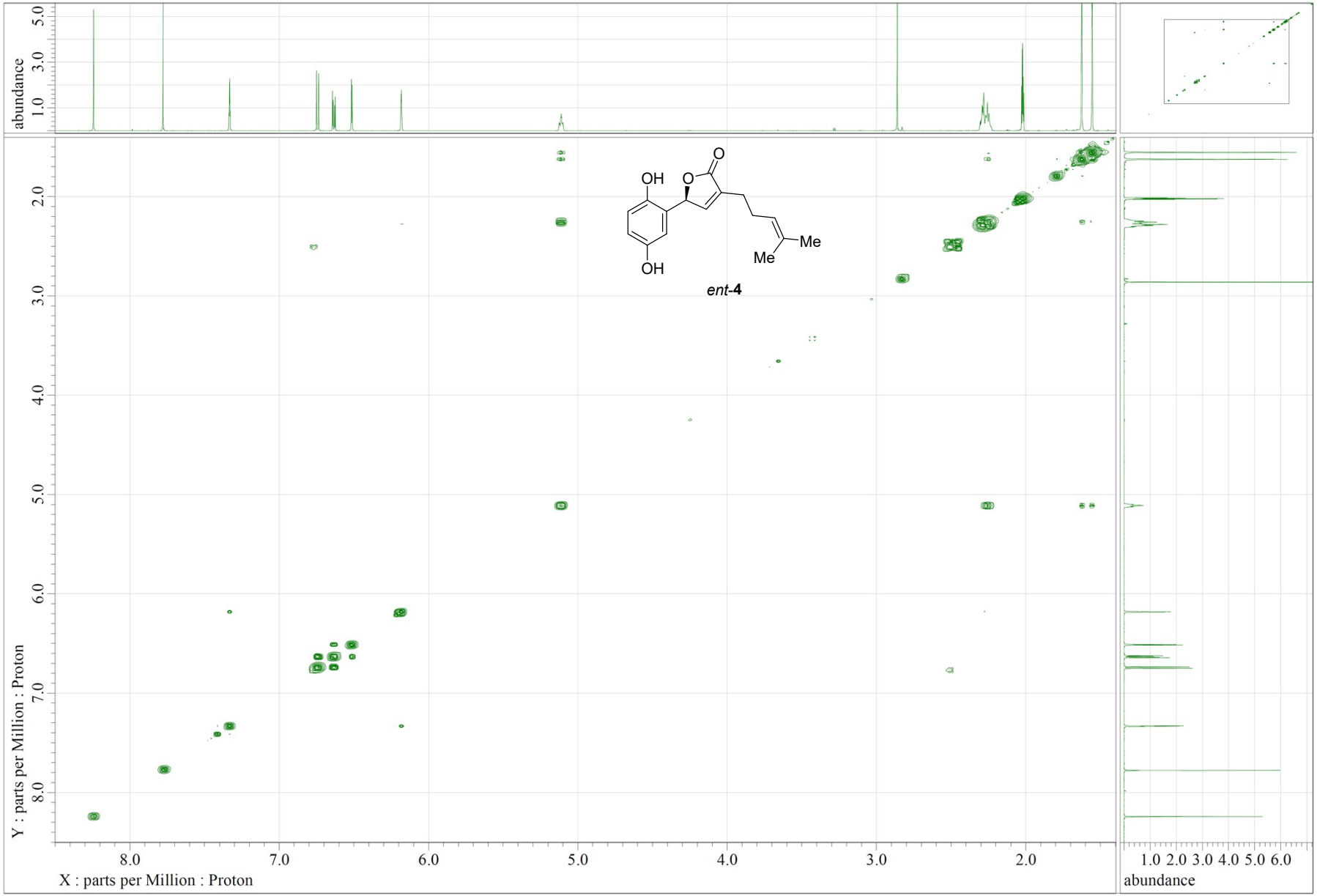


Figure S16. HMQC spectrum of (−)-*ent*-fornicin A (*ent*-4).

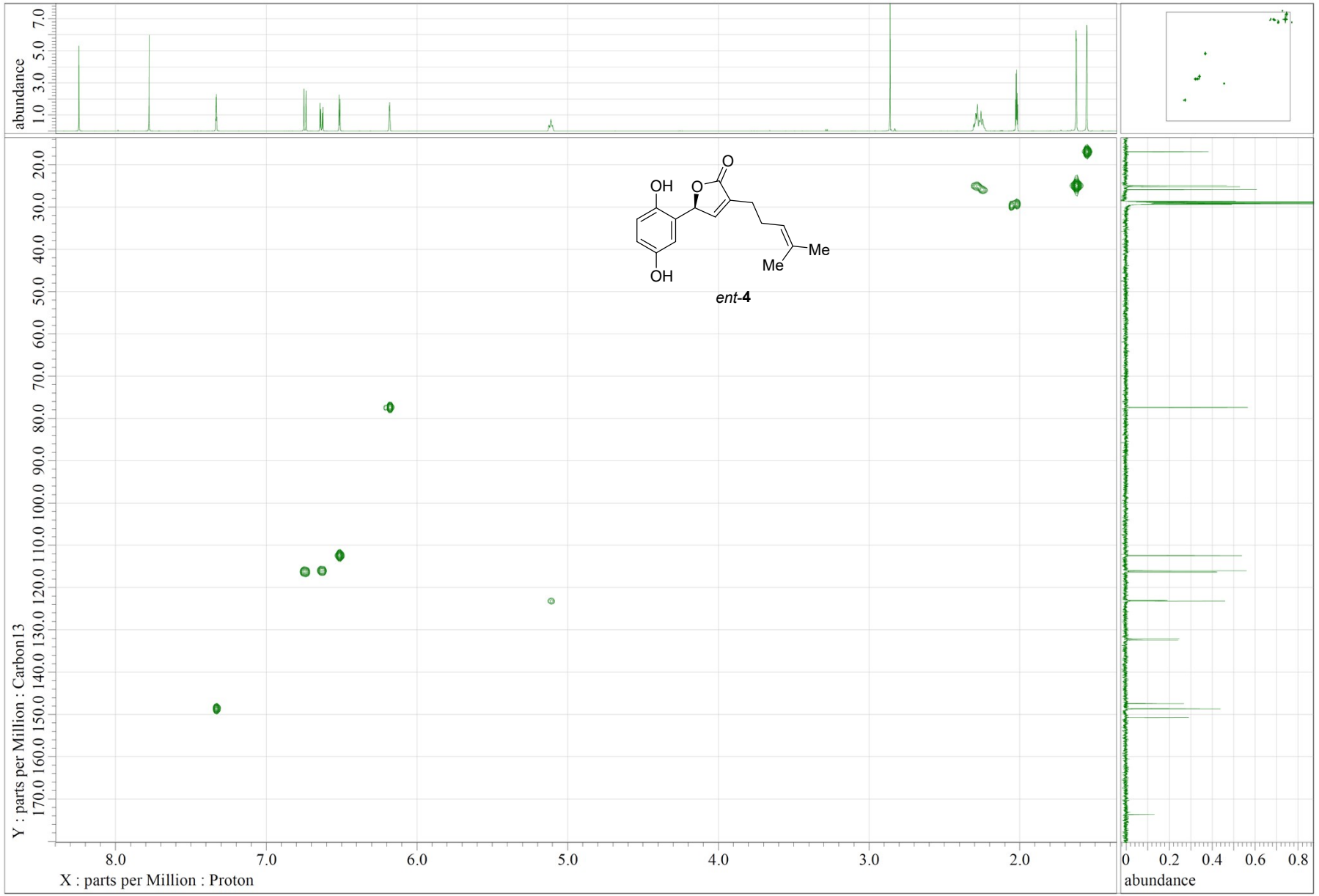


Figure S17. HMBC spectrum of (−)-*ent*-fornicin A (*ent*-4).

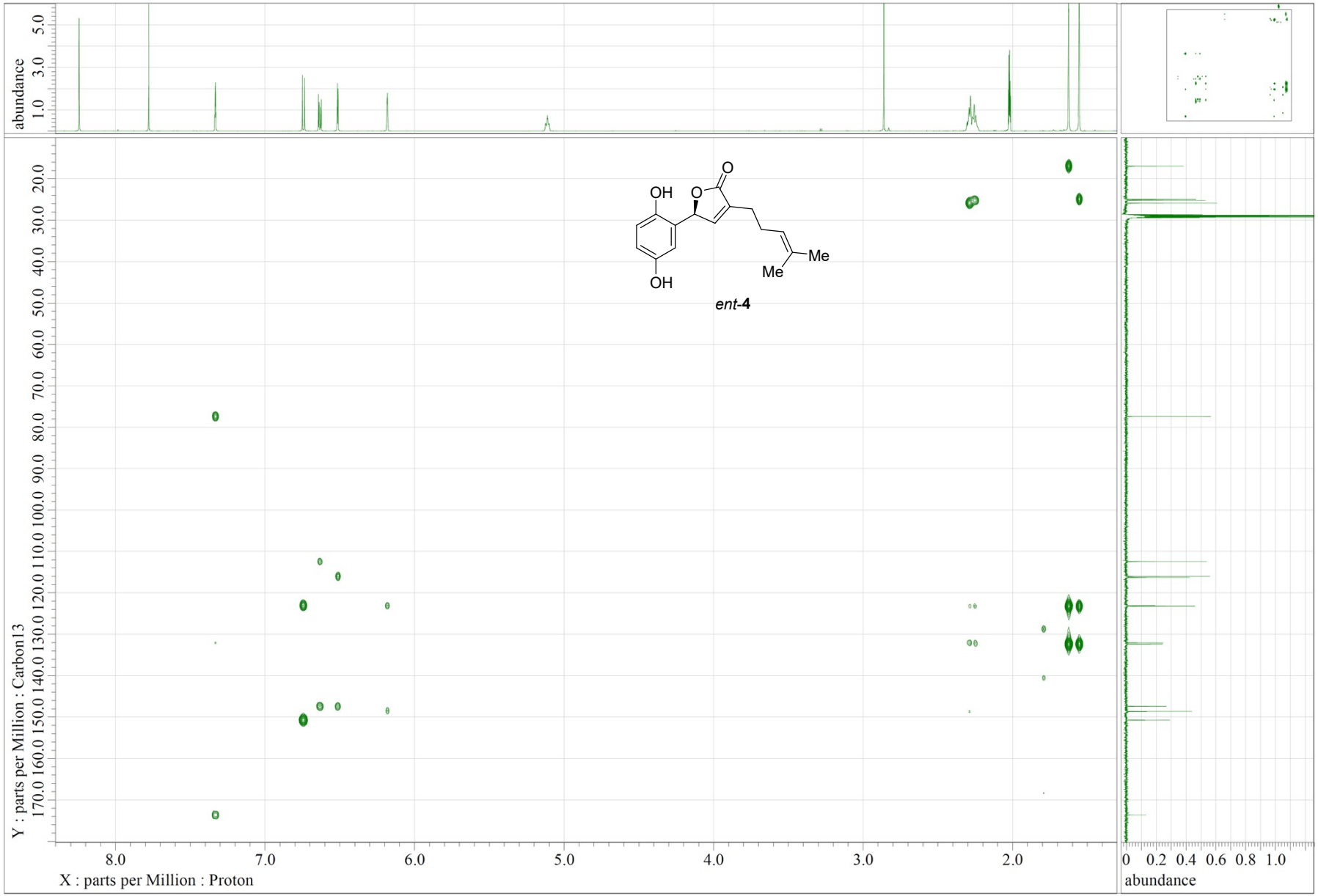


Figure S18 ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 9.

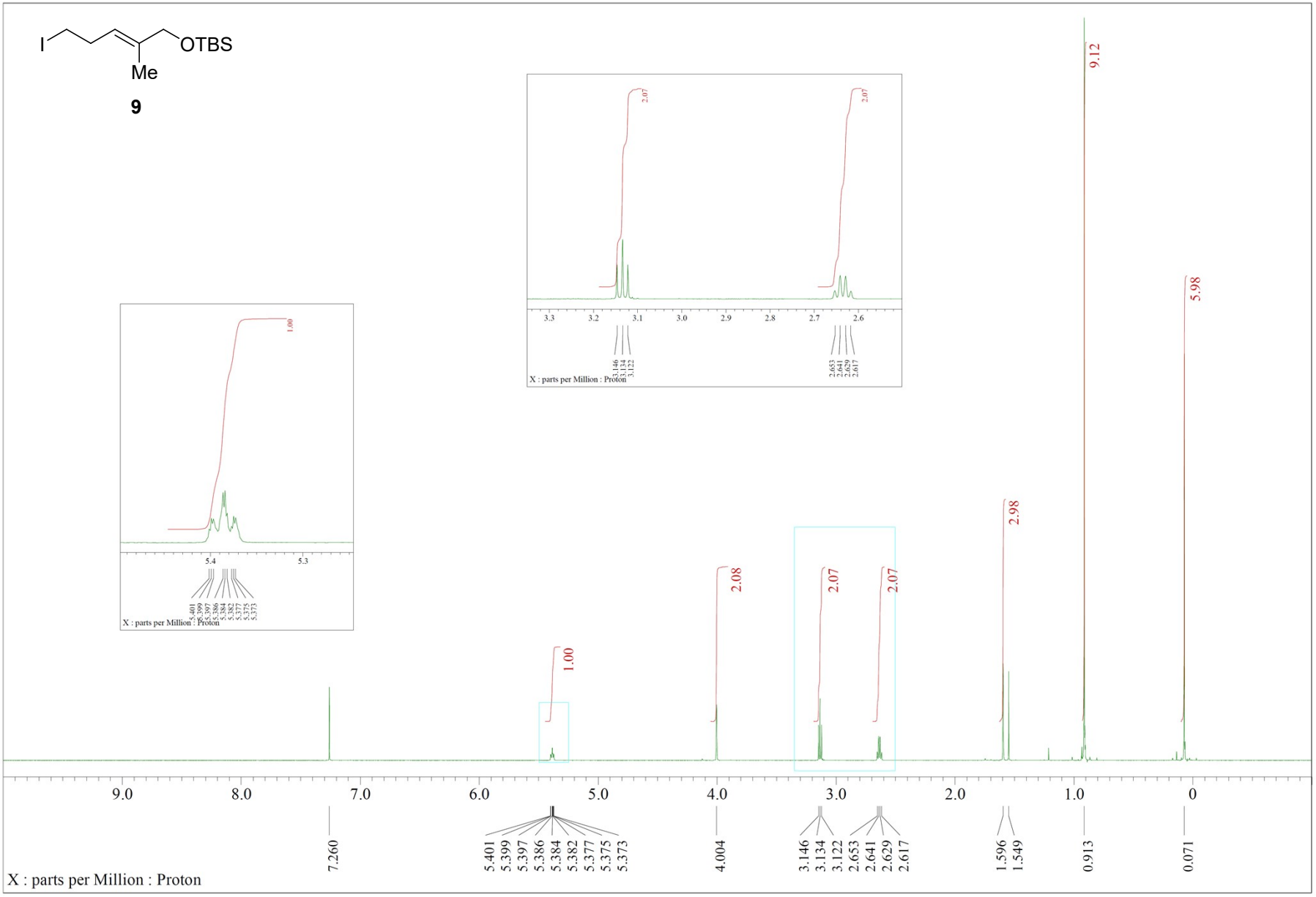


Figure S19. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 9.

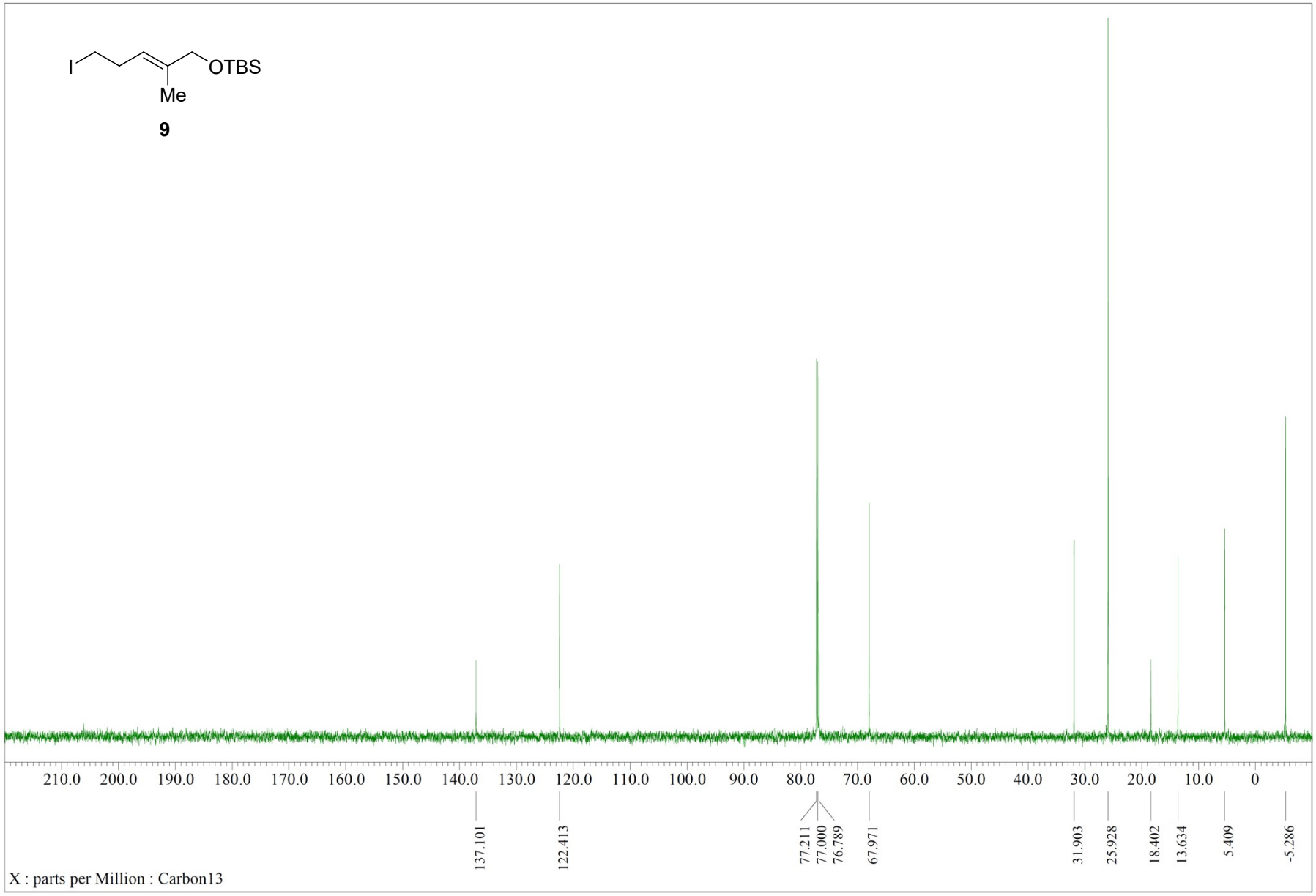


Figure S20. ^{1}H NMR spectrum (600 MHz, $CDCl_3$, dr = 5:1) of compound 7.

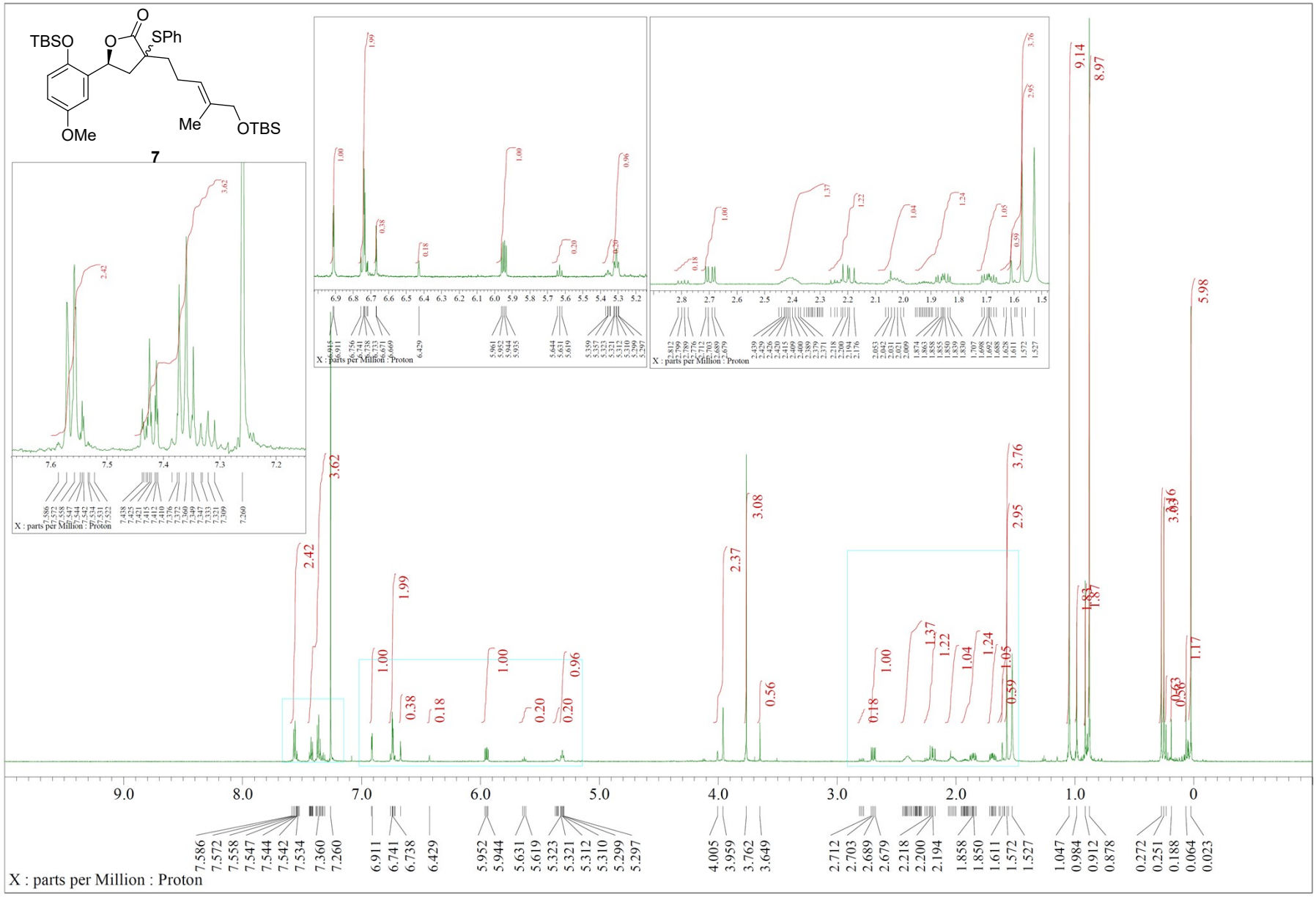


Figure S21. ^{13}C NMR spectrum (150 MHz, $CDCl_3$, dr = 5:1) of compound 7.

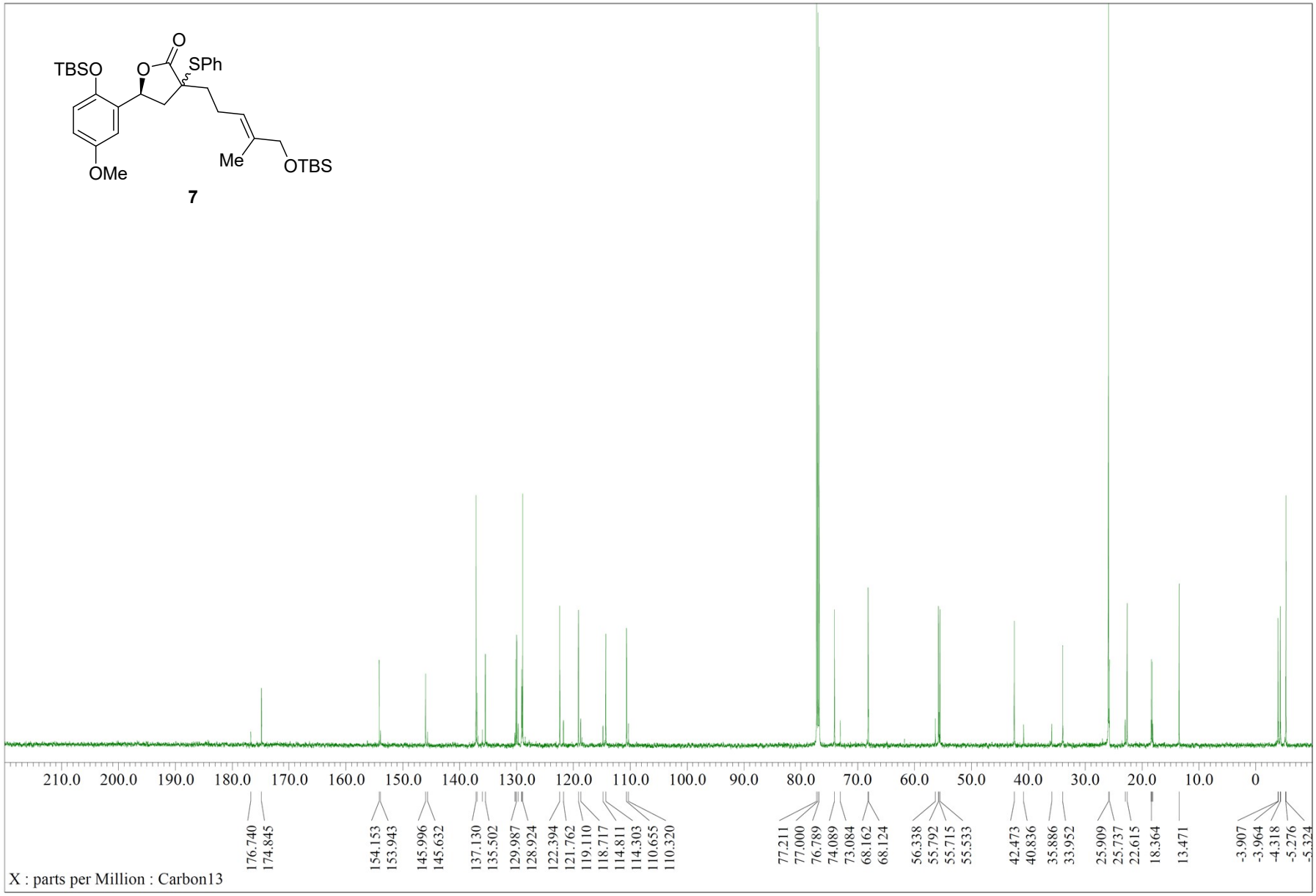


Figure S22. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 5.

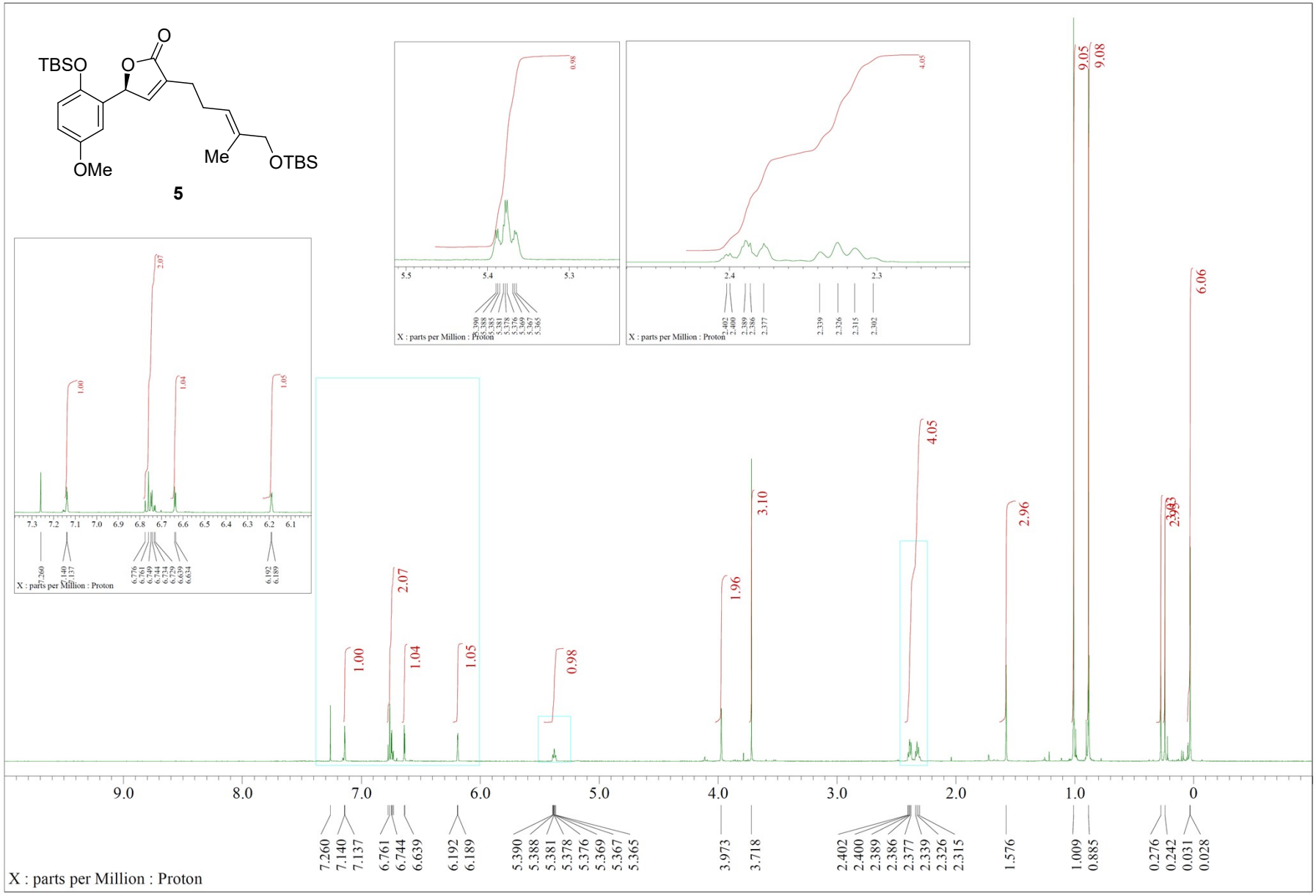


Figure S23. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 5.

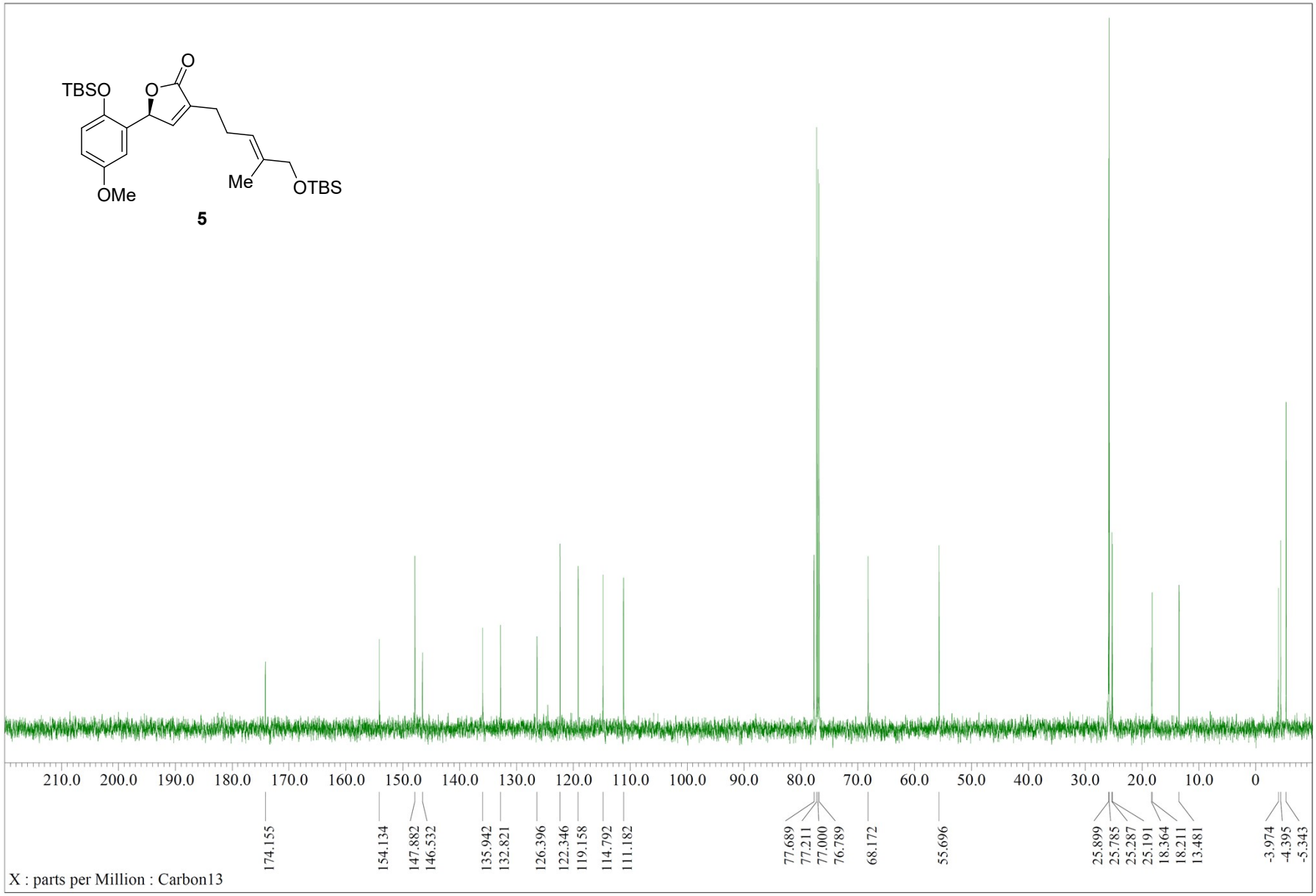


Figure S24. ^{1}H NMR spectrum (600 MHz, CD_3OD) of compound 15.

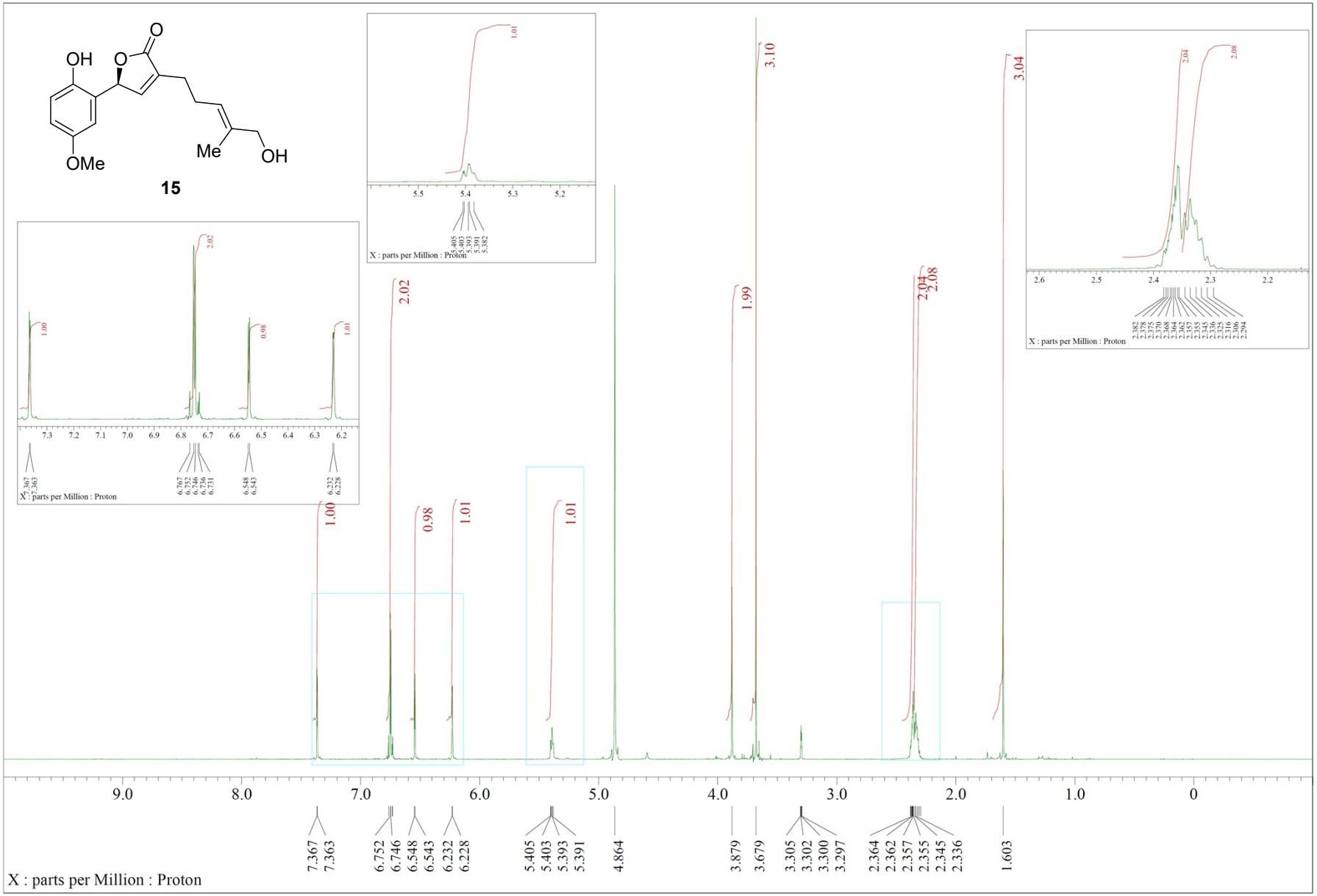


Figure S25. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 15.

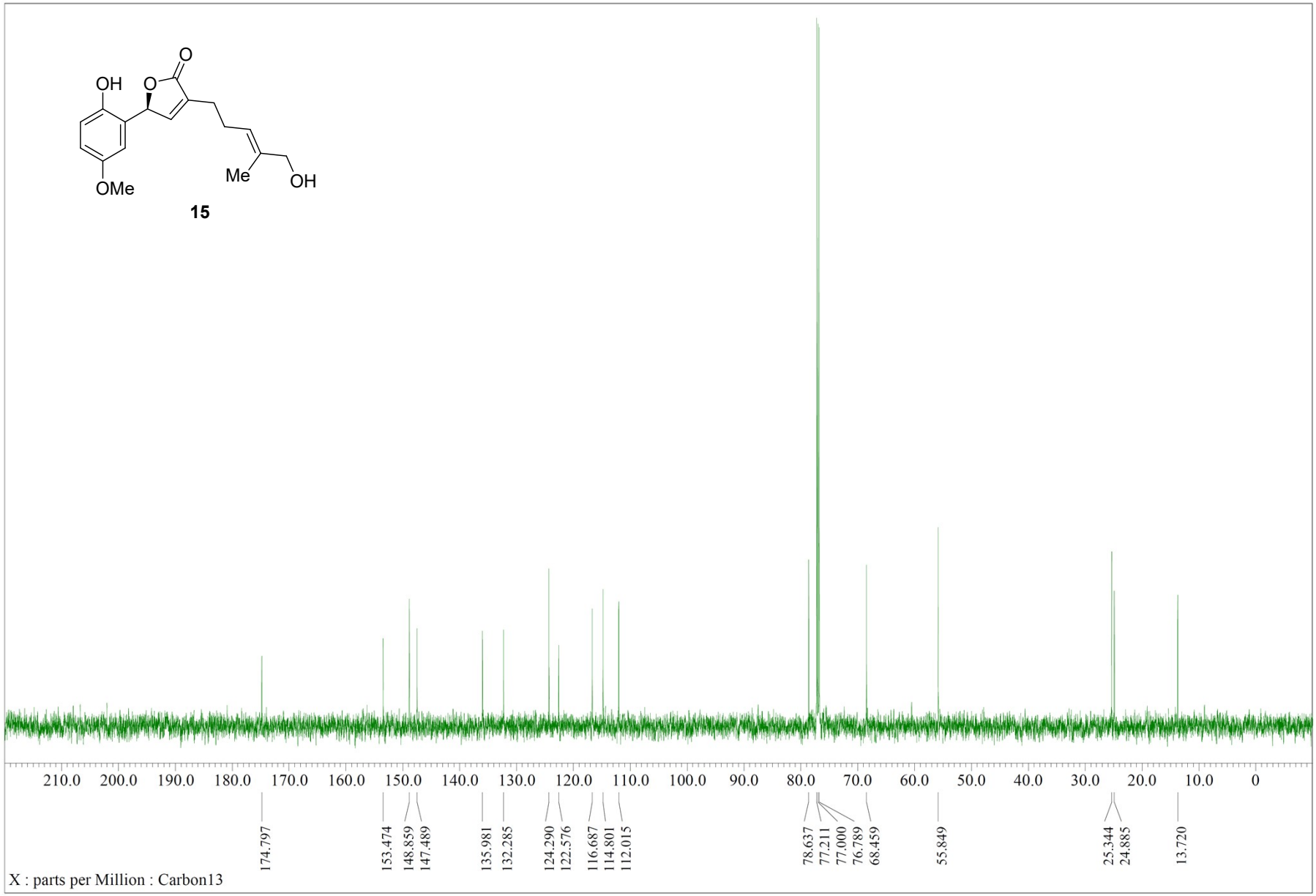


Figure S26. ^{1}H NMR spectrum (600 MHz, CD_3OD) of (−)-applanatumol U (3).

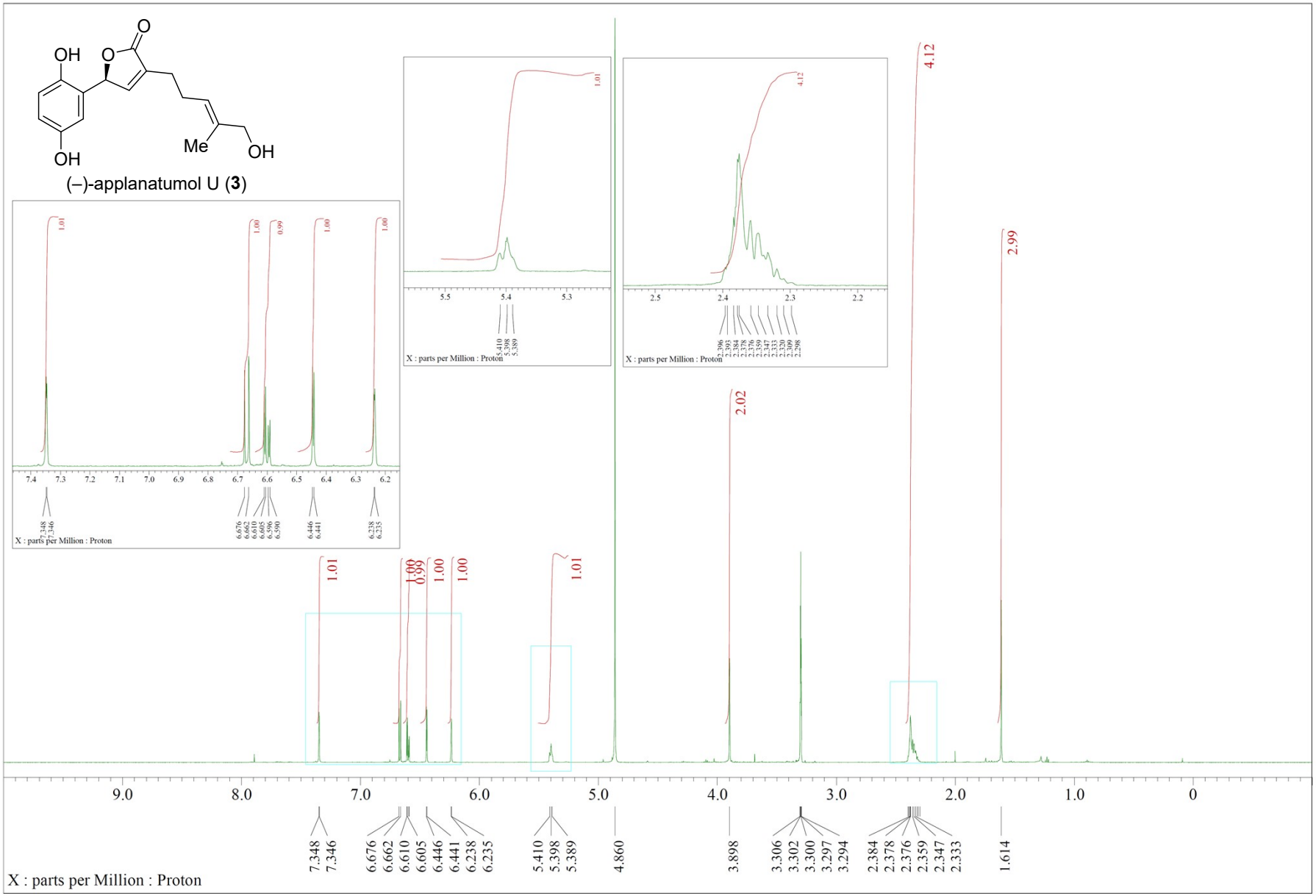


Figure S27. ^{13}C NMR spectrum (150 MHz, CD_3OD) of (−)-applanatumol U (3).

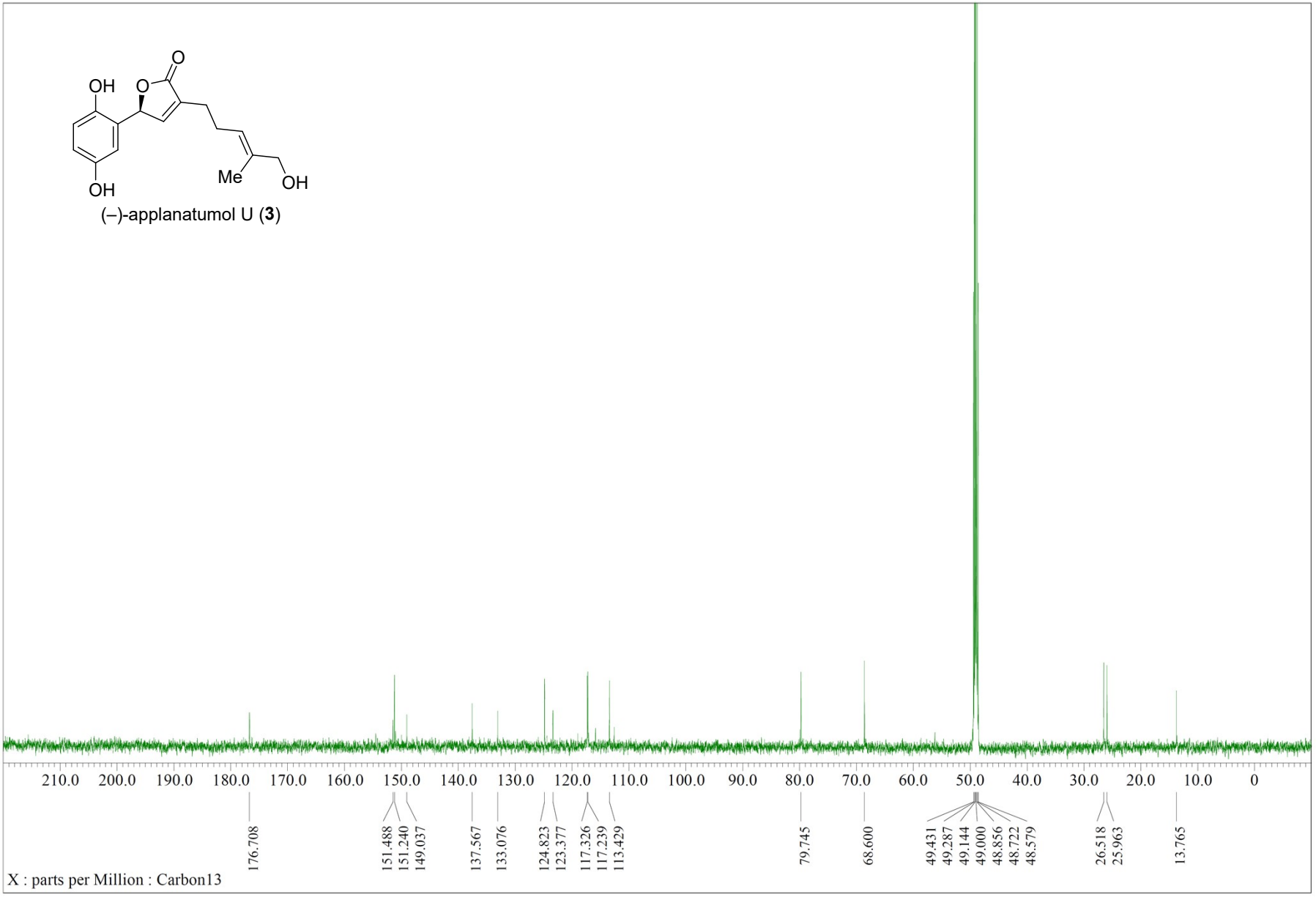


Figure S28. COSY spectrum of (−)-applanatumol U (3).

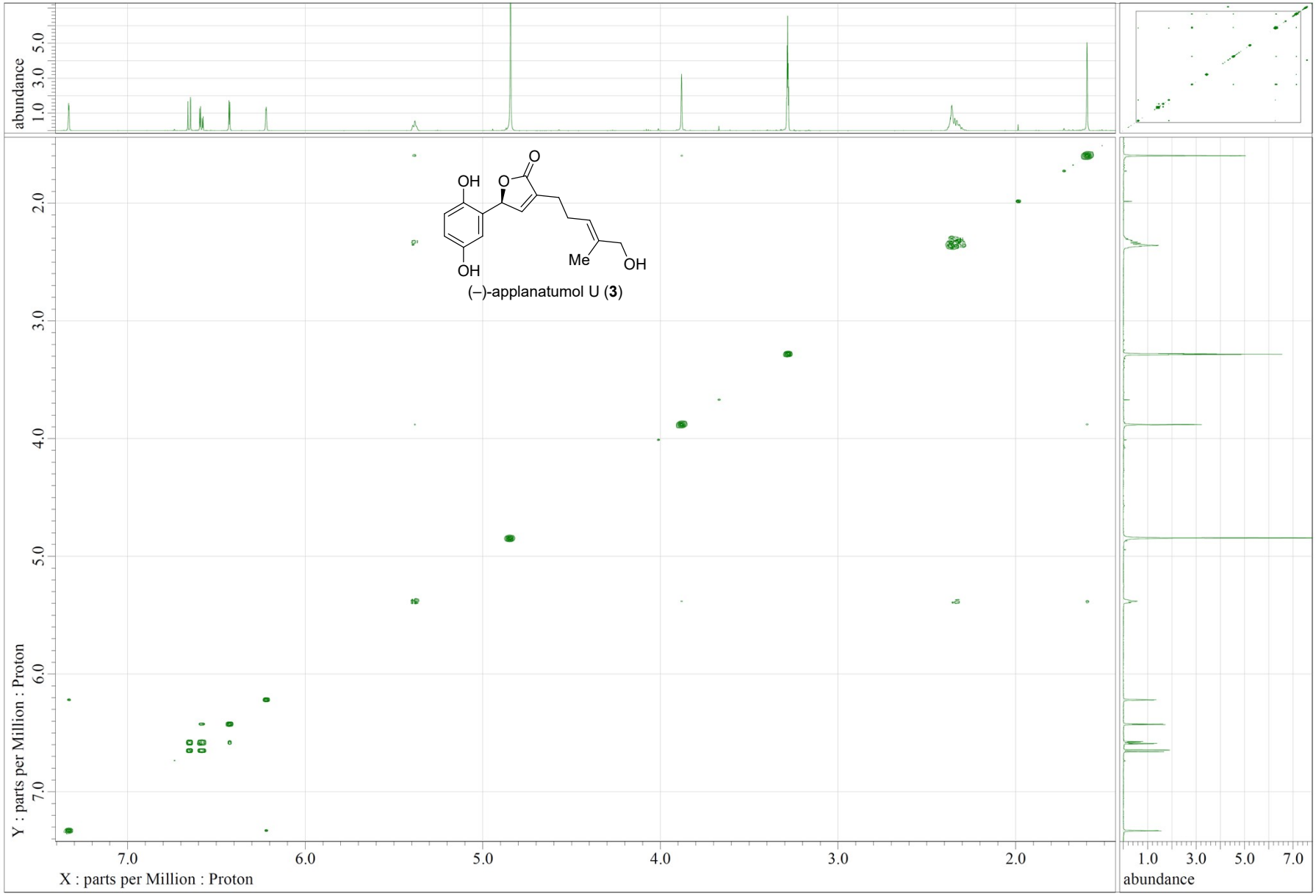


Figure S29. HMQC spectrum of (−)-applanatumol U (3).

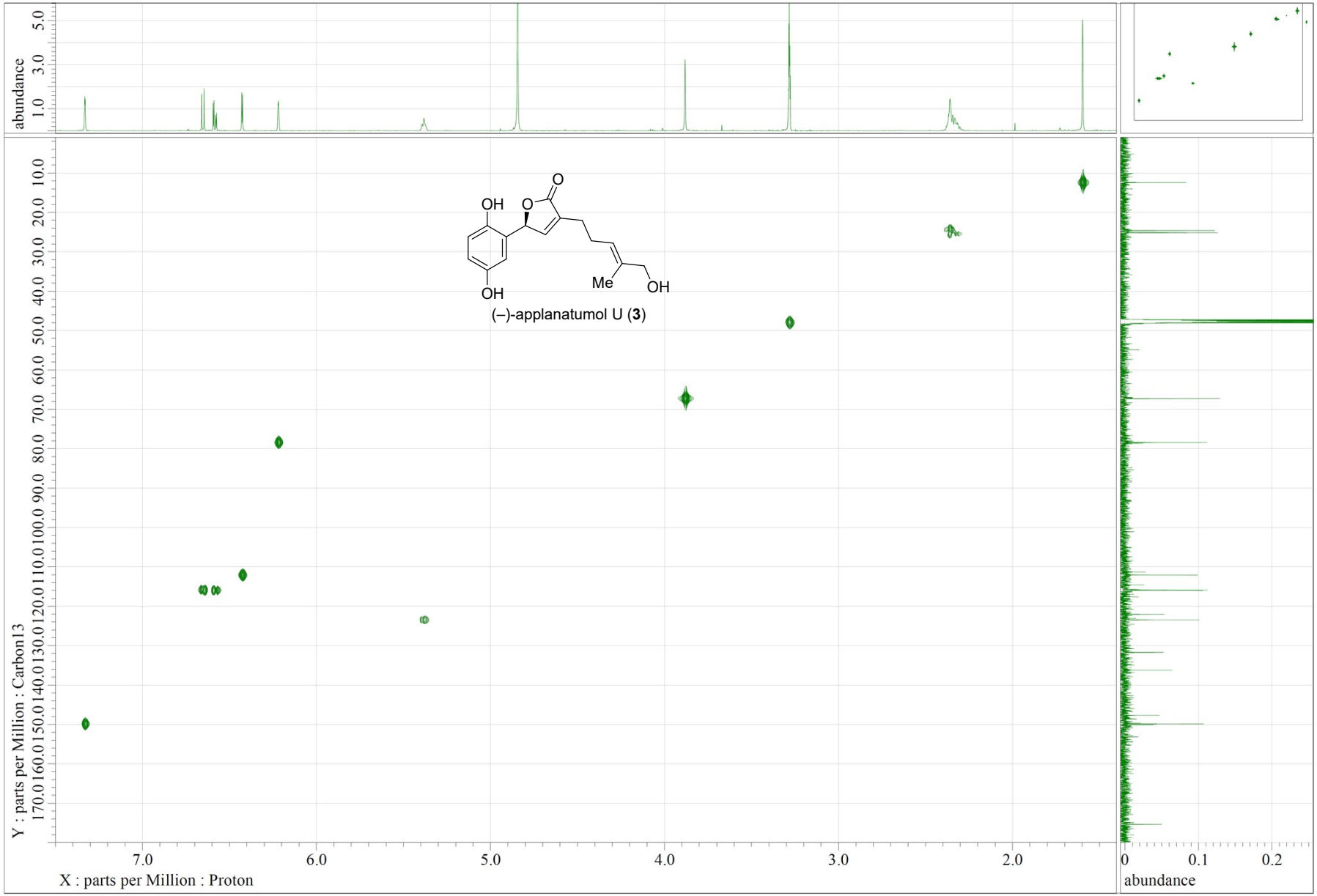


Figure S30. HMBC spectrum of (−)-applanatumol U (3).

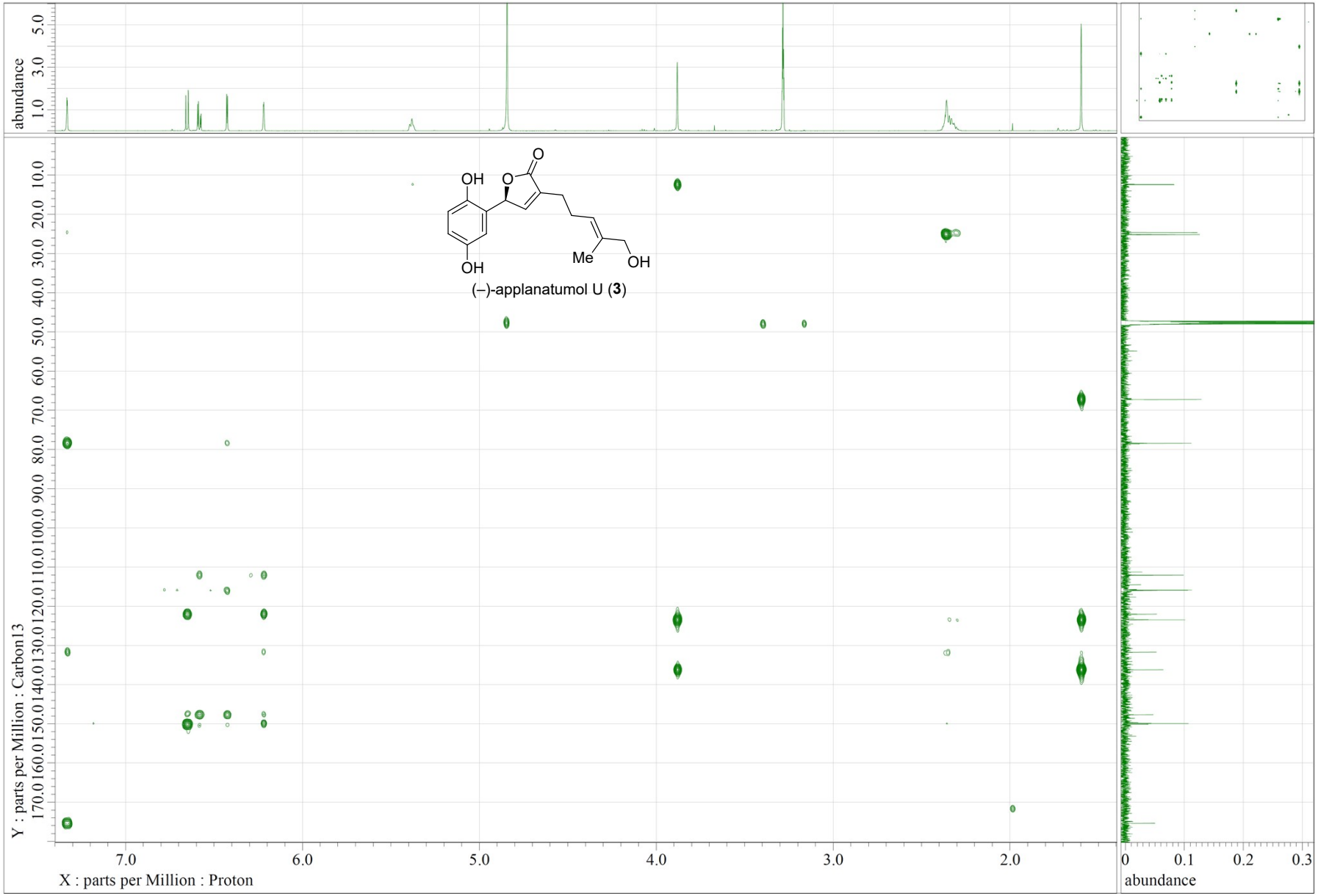


Figure S31. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 16.

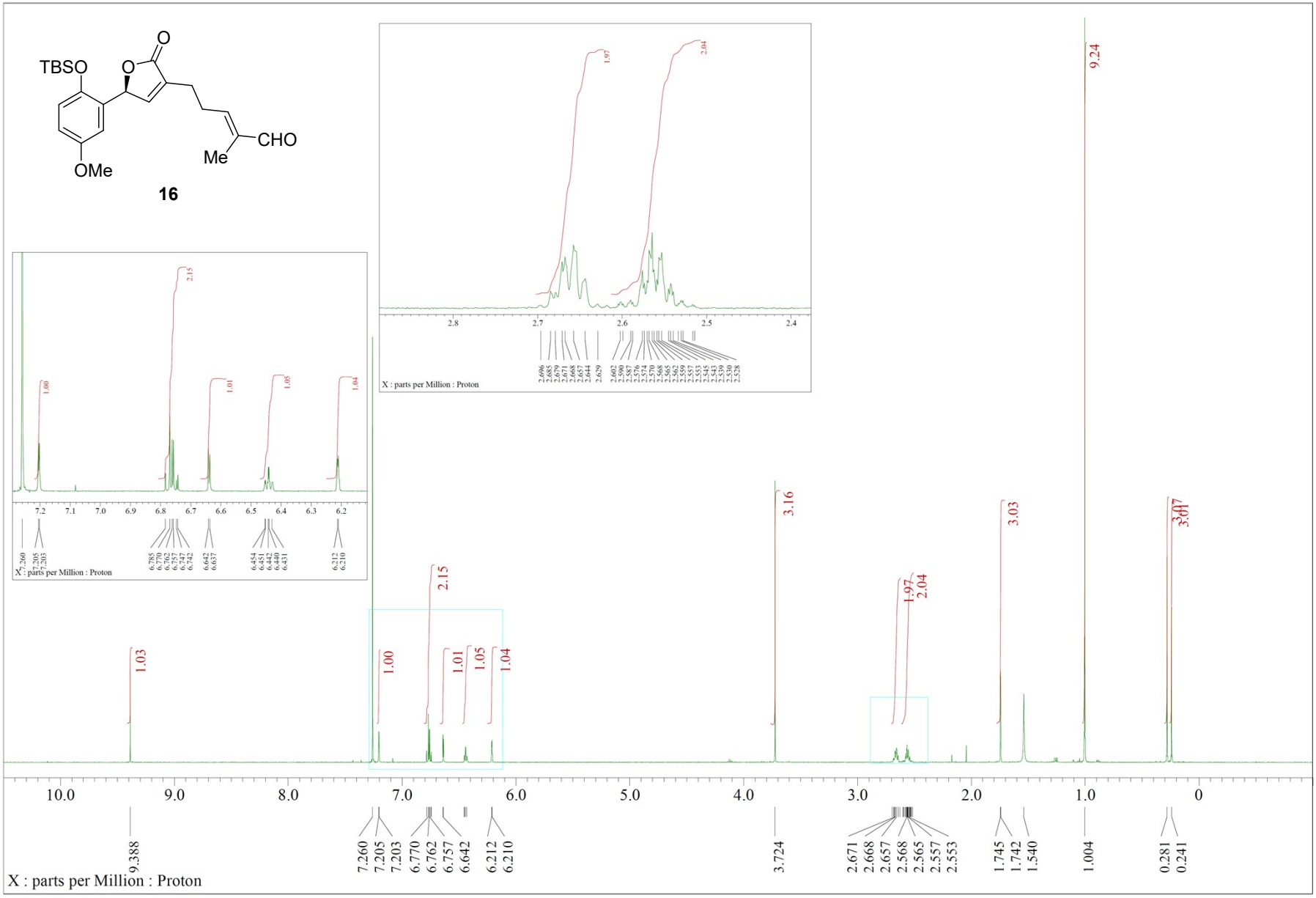


Figure S32. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 16.

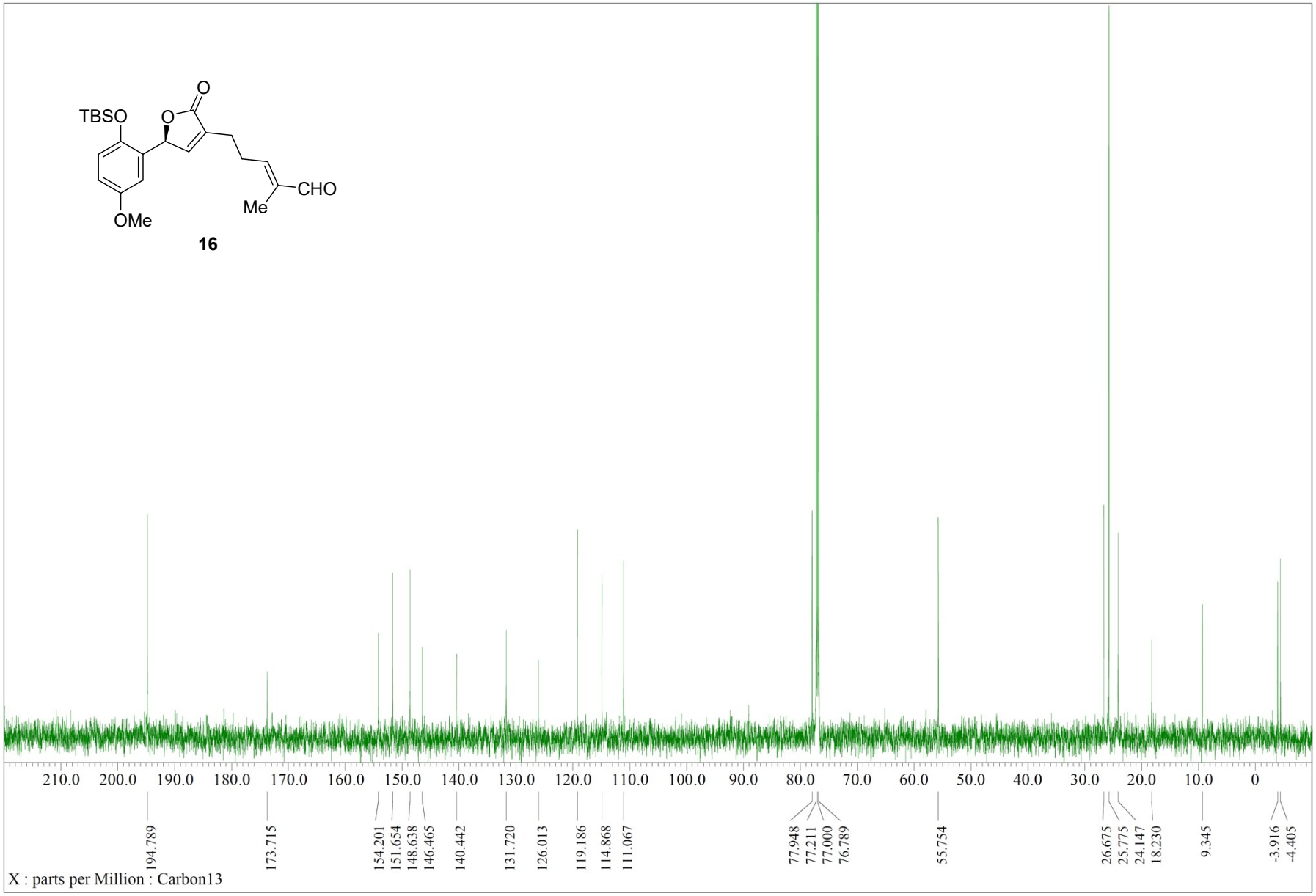


Figure S33. ^{1}H NMR spectrum (600 MHz, CD_3OD) of (−)-chizhine E (2).

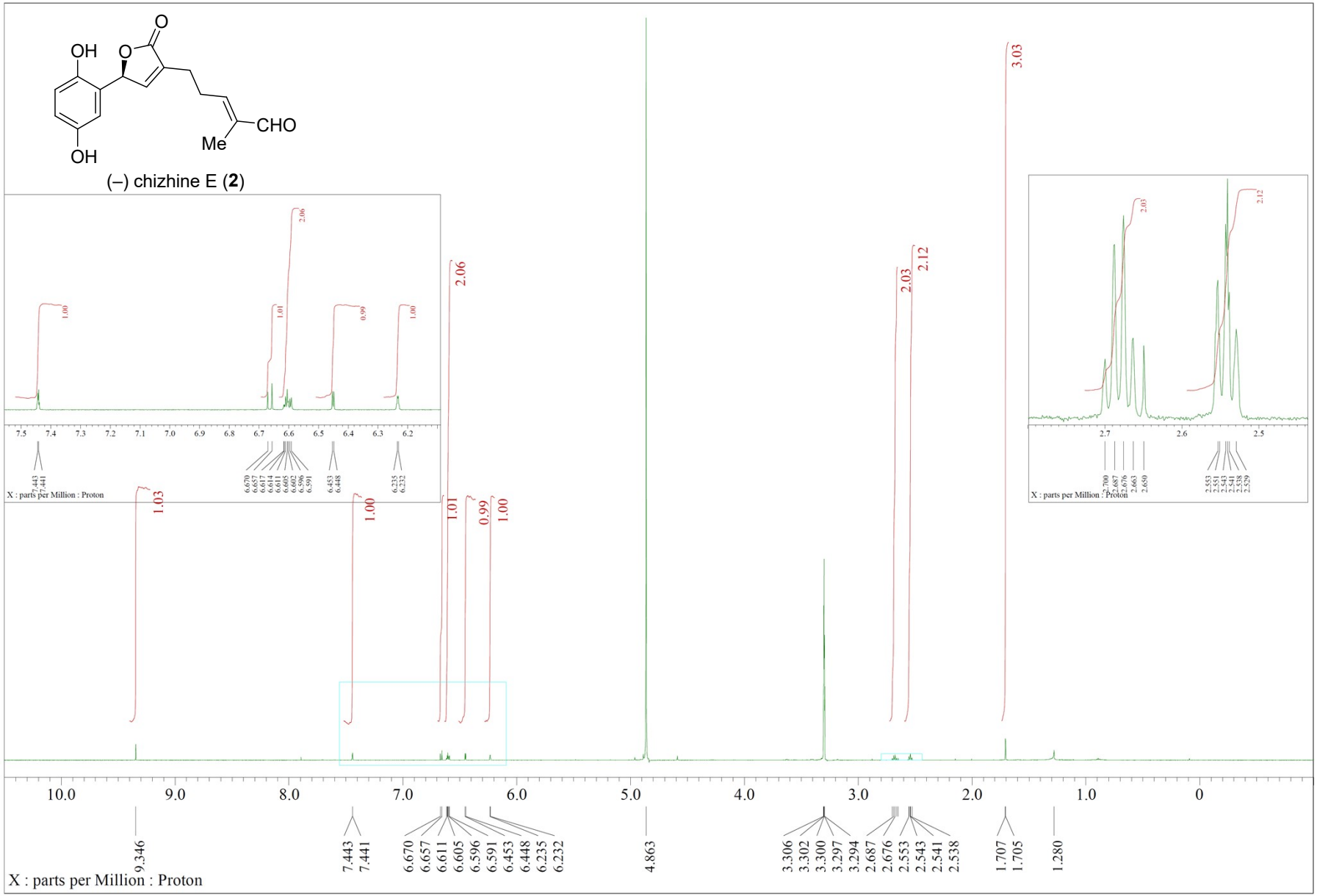


Figure S34. ^{13}C NMR spectrum (150 MHz, CD_3OD) of (−)-chizhine E (2).

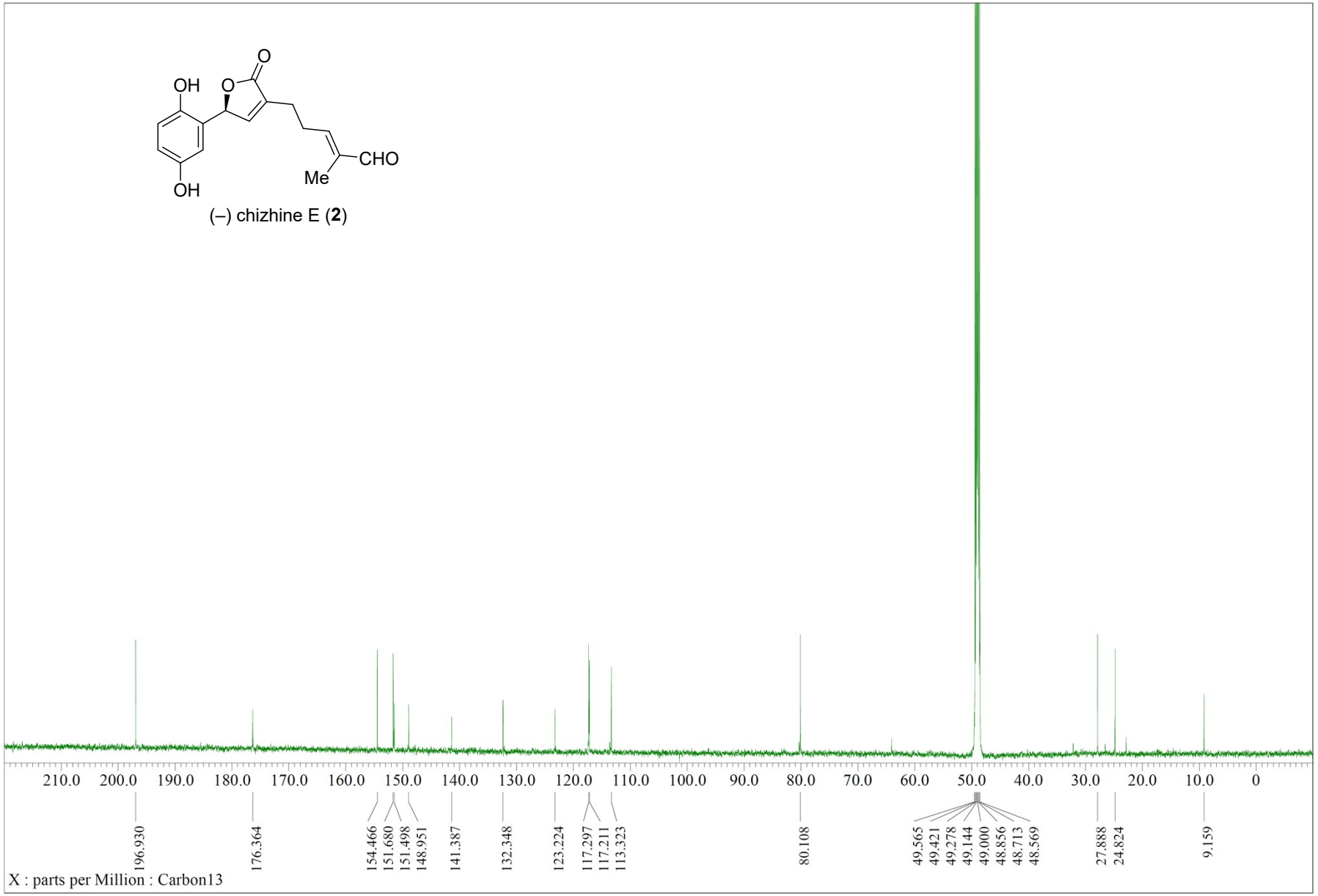


Figure S35. COSY spectrum of (−)-chizhine E (2).

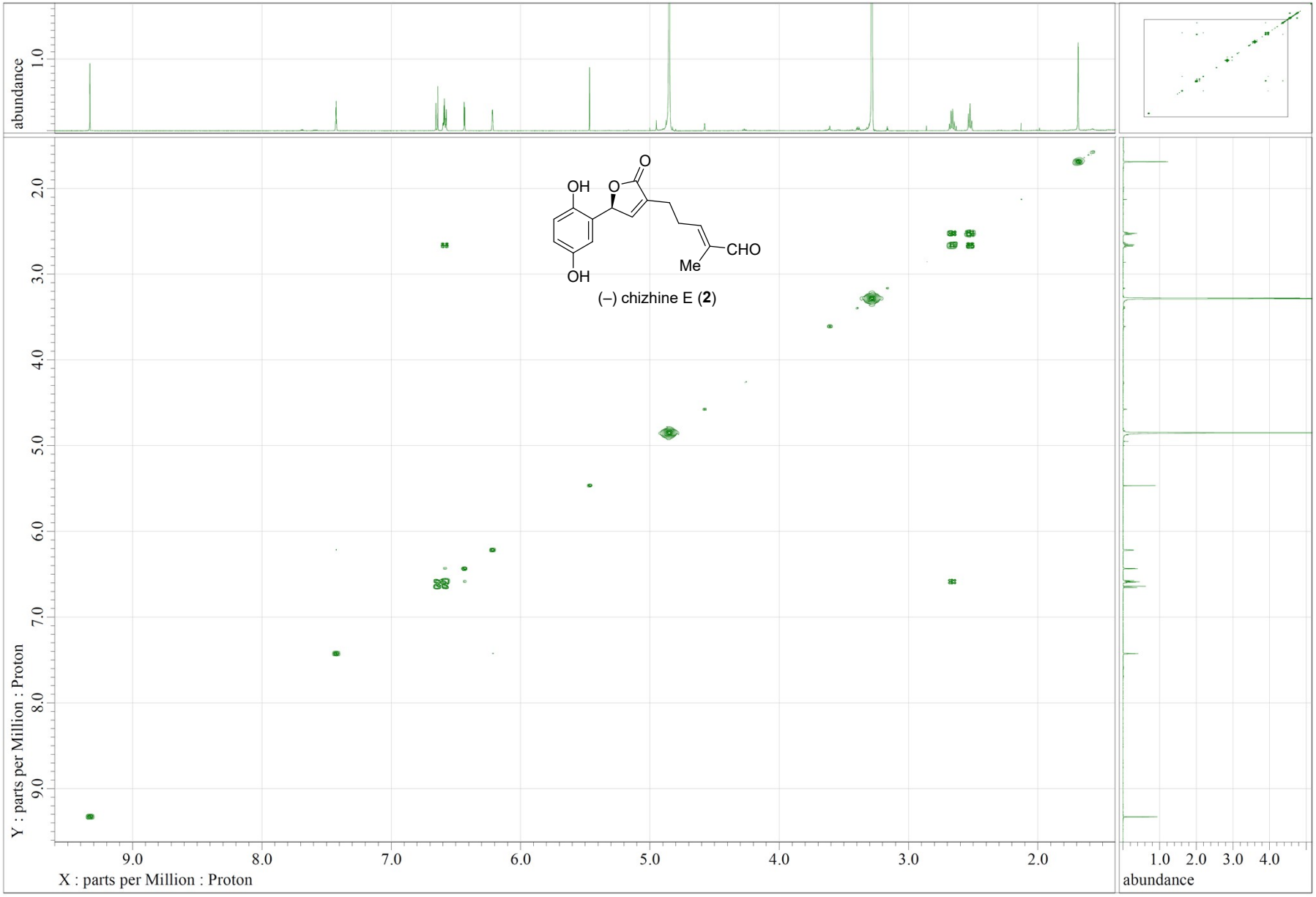


Figure S36. HMQC spectrum of (−)-chizhine E (2).

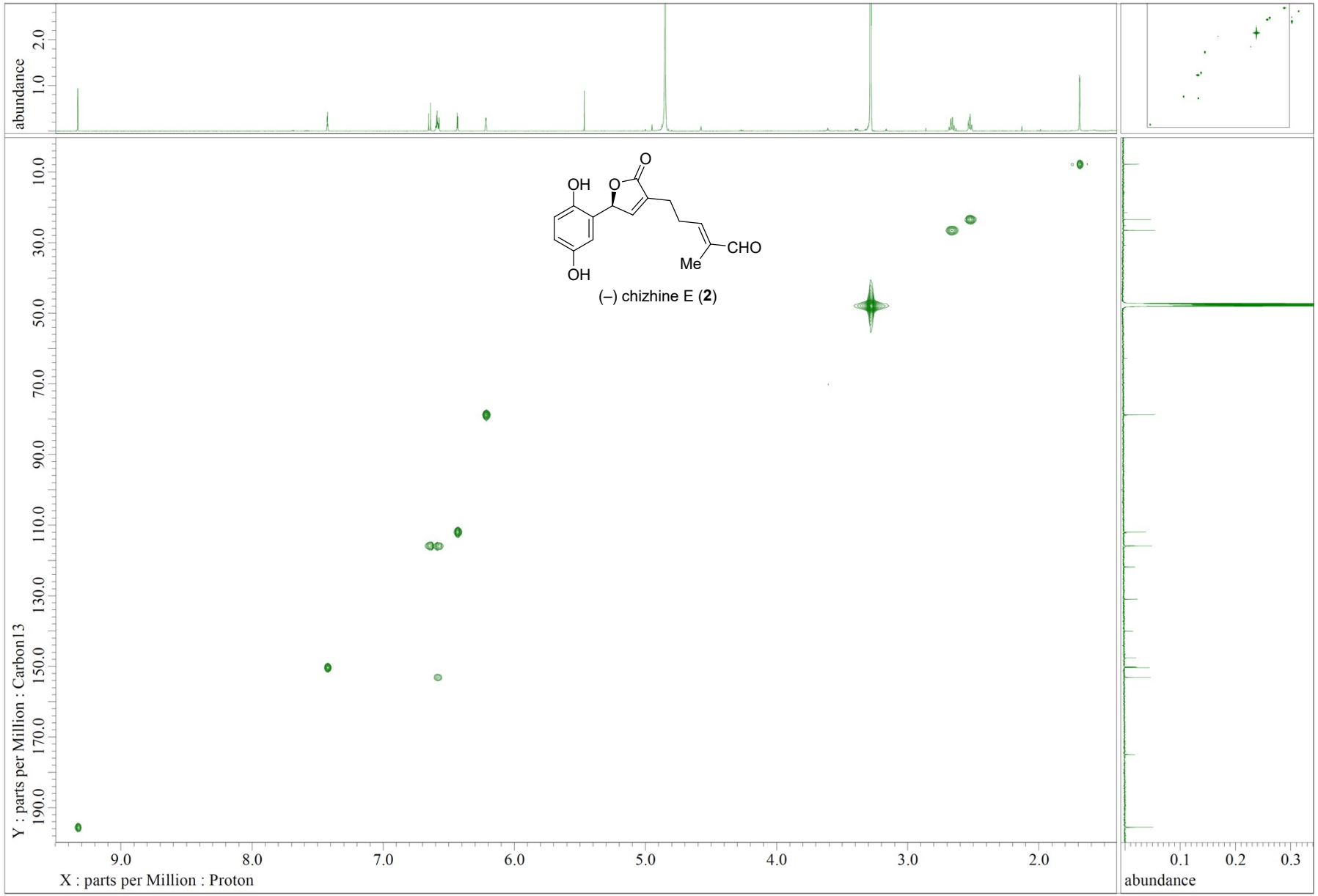


Figure S37. HMBC spectrum of (−)-chizhine E (2).

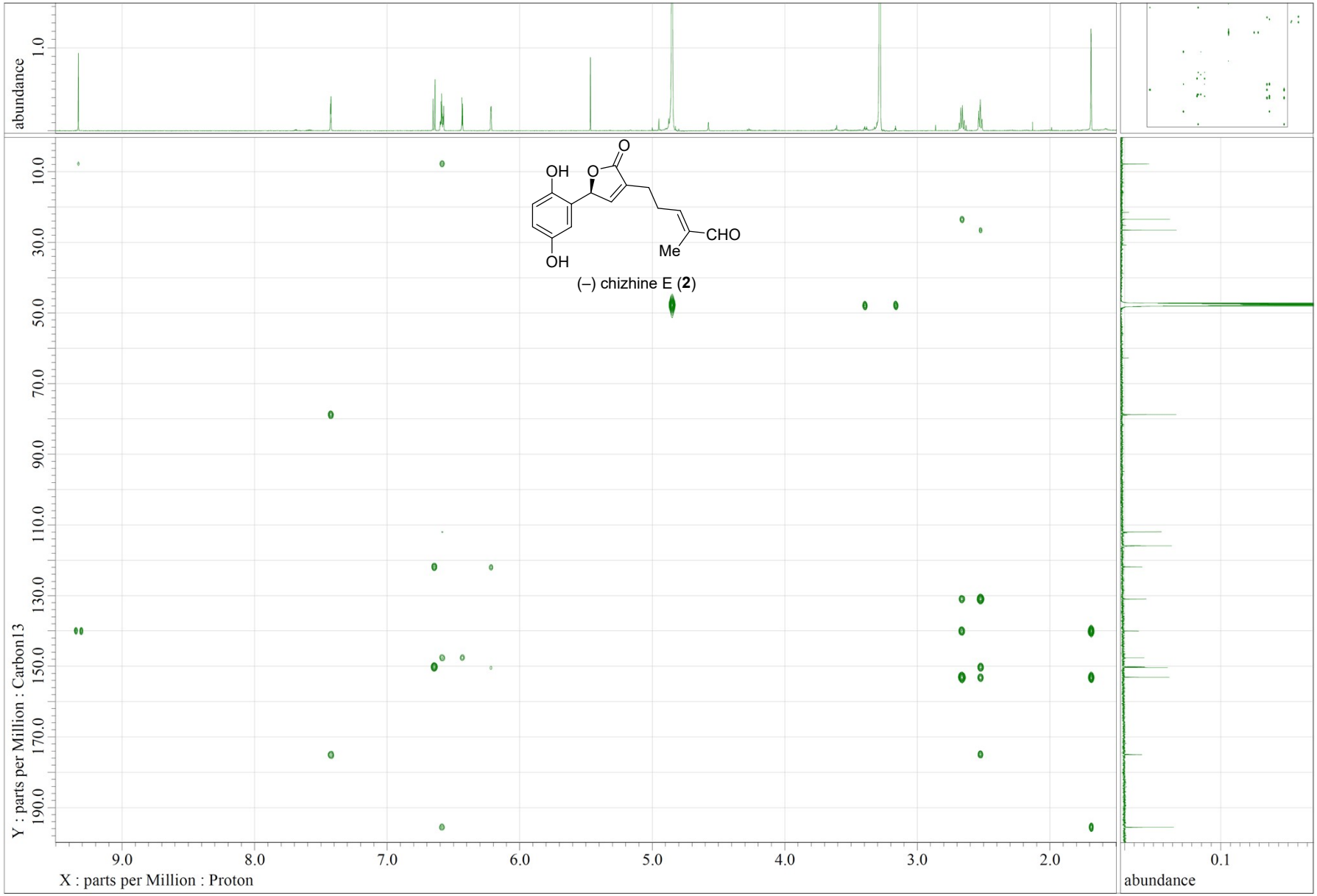


Figure S38. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 18.

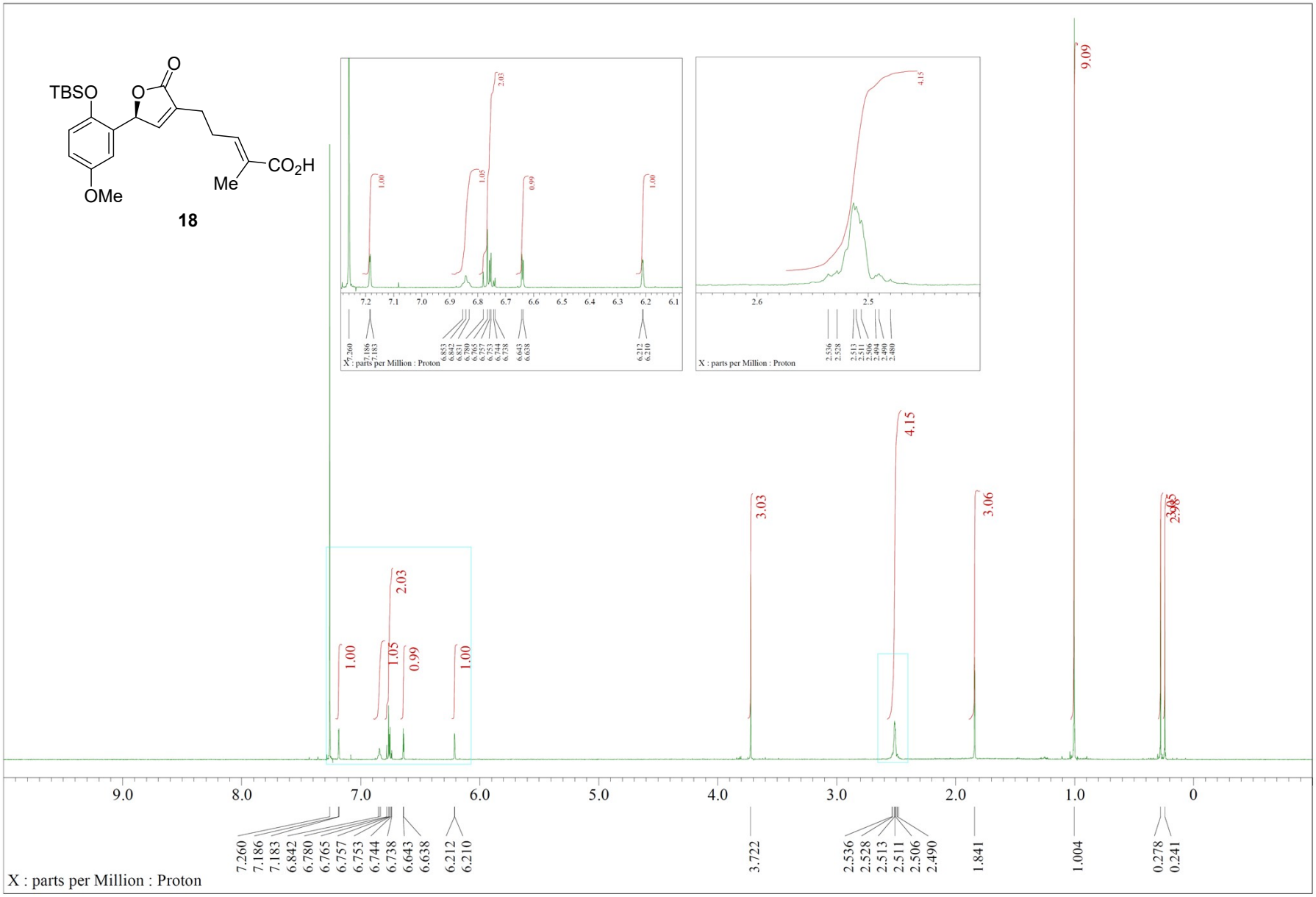


Figure S39. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 18.

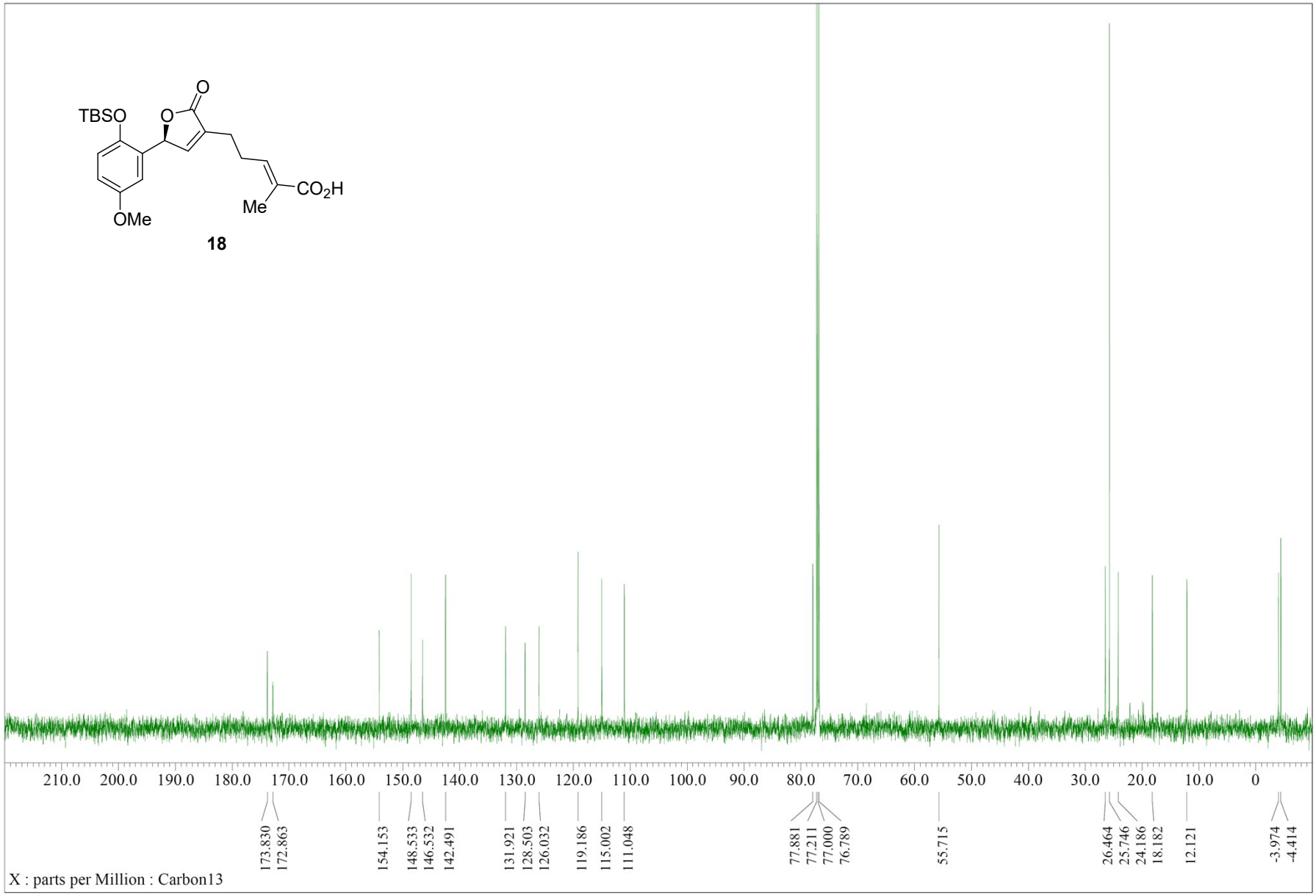


Figure S40. ^{1}H NMR spectrum (600 MHz, CD_3OD) of (−)-oregonensin A (1).

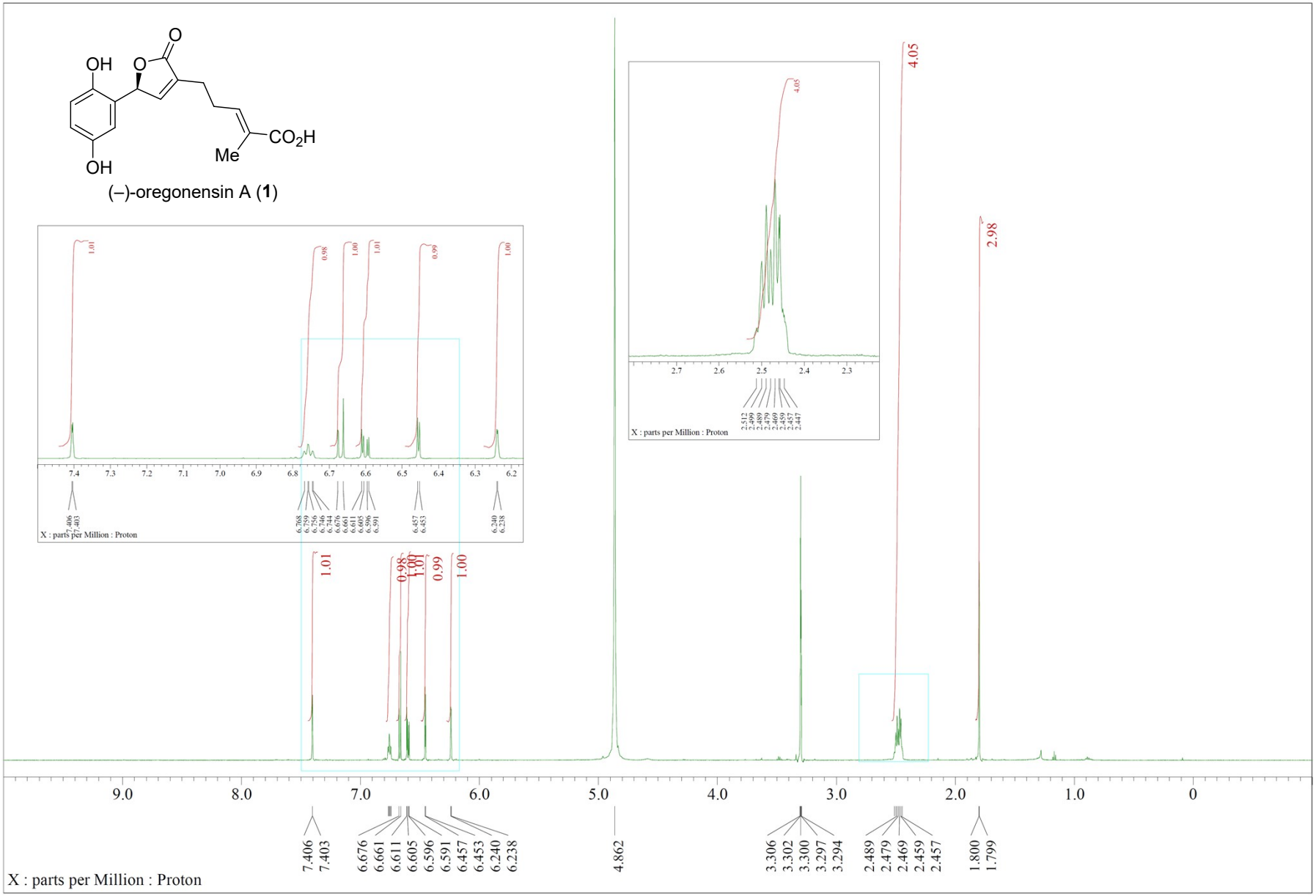


Figure S41. ^{13}C NMR spectrum (150 MHz, CD_3OD) of (−)-oregonensin A (1).

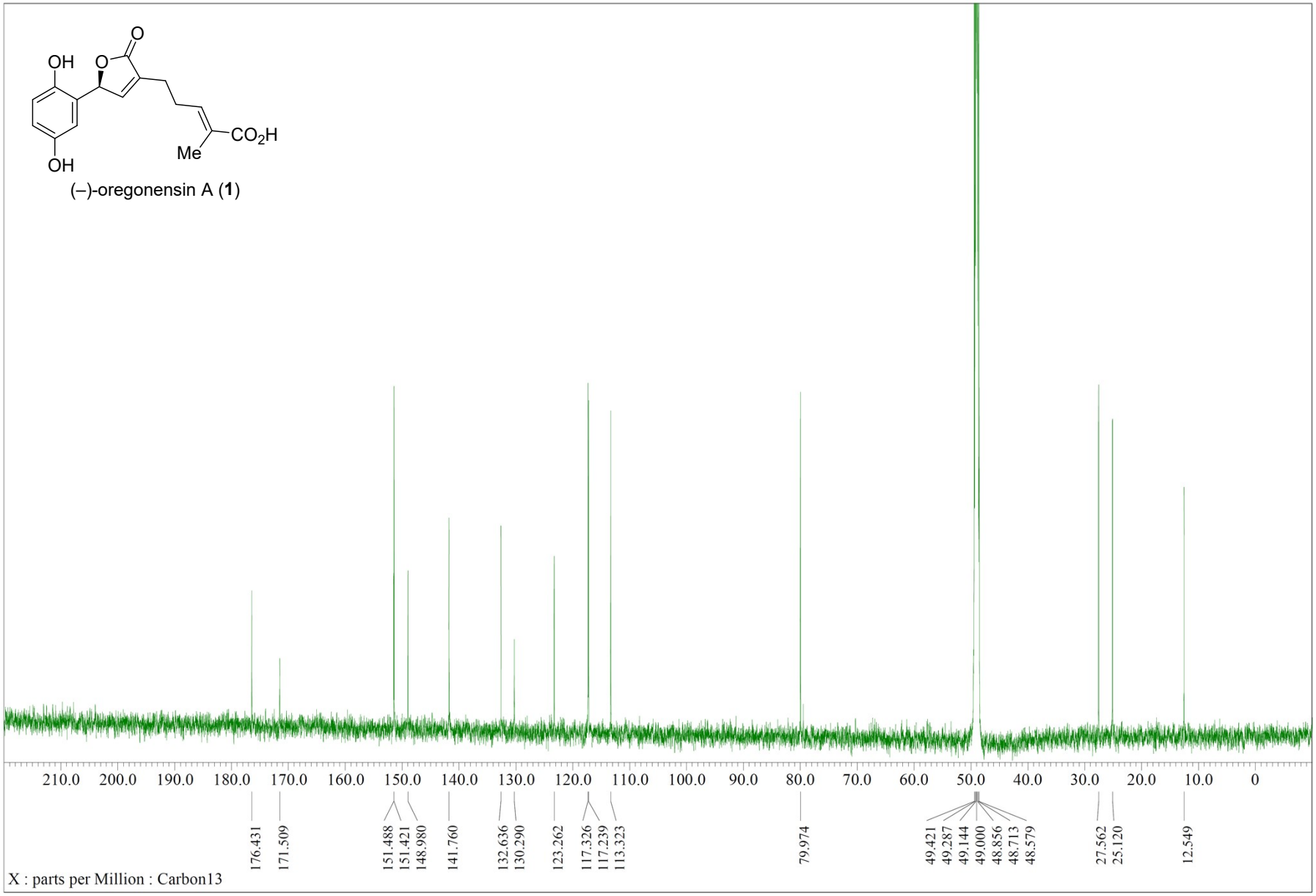


Figure S42. COSY spectrum of (−)-oregonensin A (1).

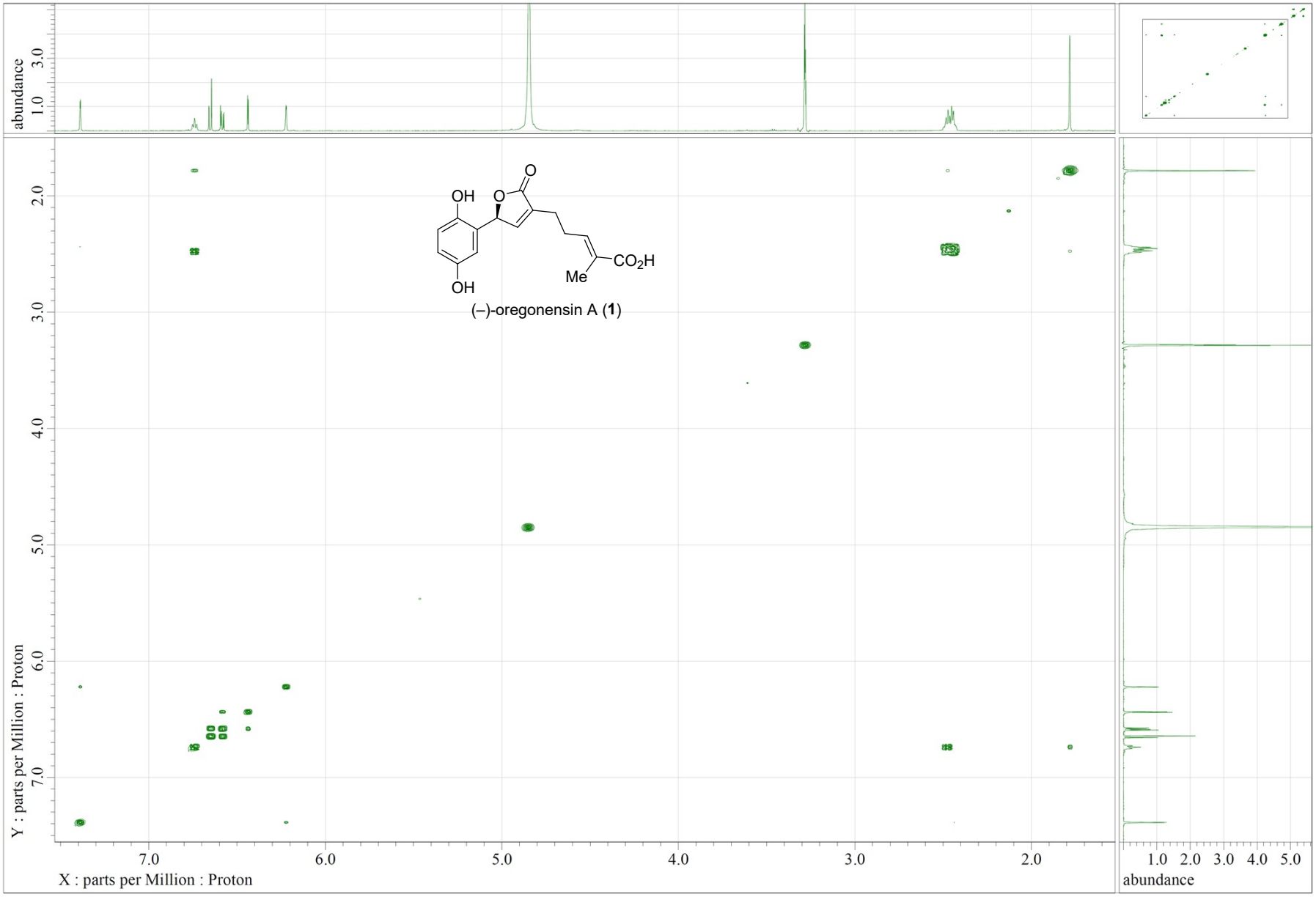


Figure S43. HMQC spectrum of (−)-oregonensin A (1).

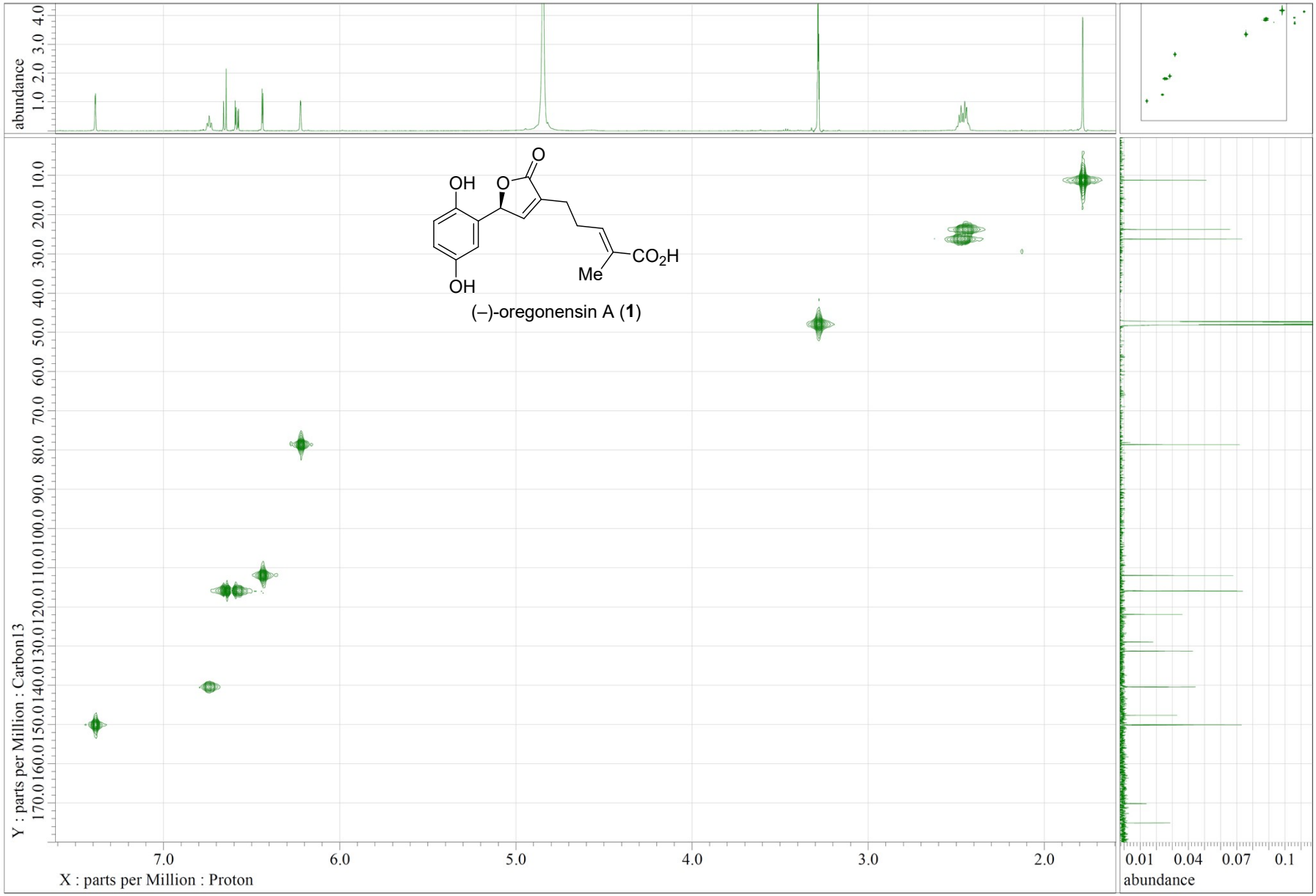
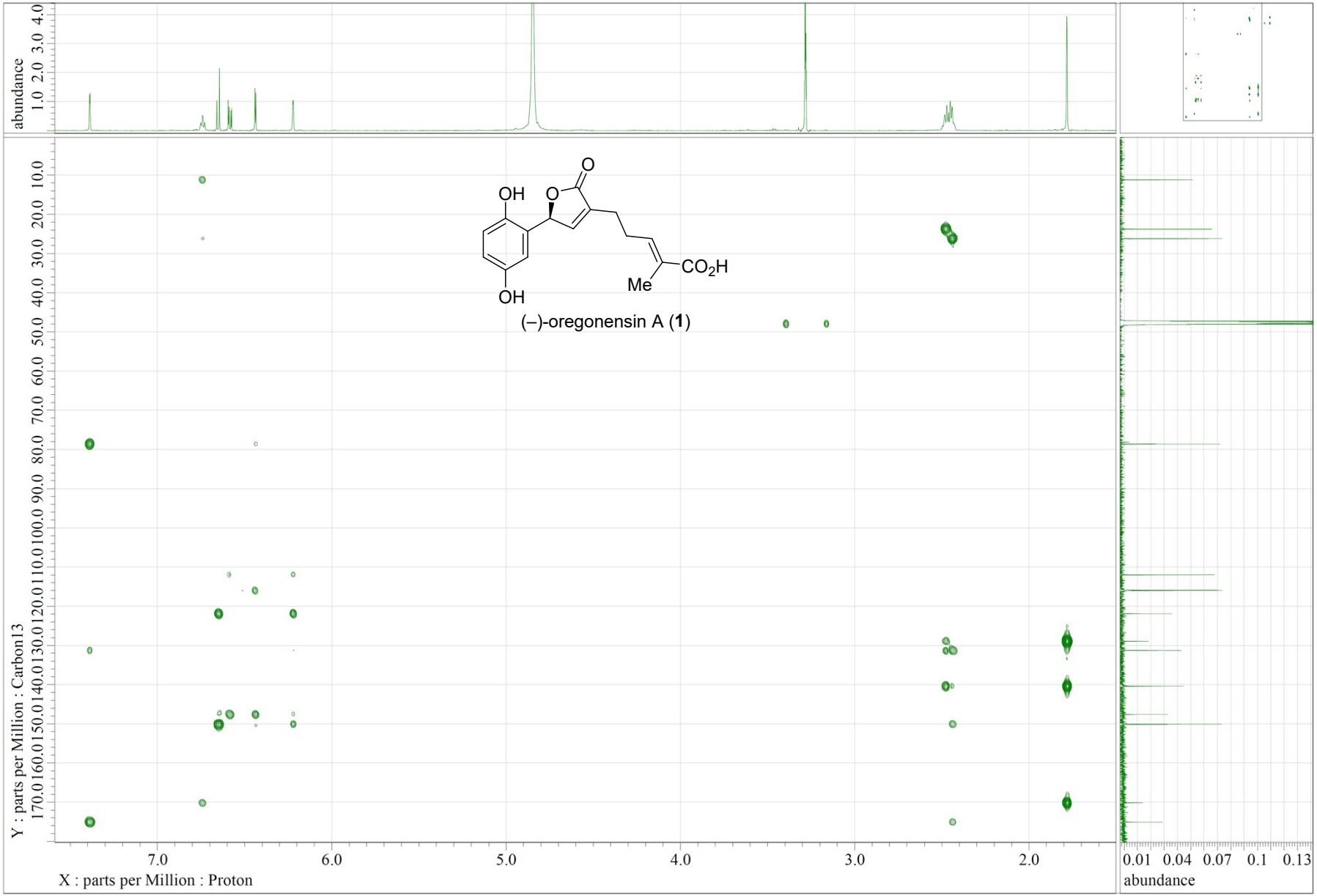


Figure S44. HMBC spectrum of (−)-oregonensin A (1).



5. References

S1) Xu, C.; Bai, X.; Xu, J.; Ren, J.; Xing, Y.; Li, Z.; Wang, J.; Shi, J.; Yu, L.; Wang, Y. *RSC Adv*. **2017**, *7*, 4763–4775.

S2) Guo, X.; Mayr, H. *J. Am. Chem. Soc.* **2013**, *135*, 12377–12387.

S3) (a) Andresen, G.; Eriksen, A. B.; Dalhus, B.; Gundersen L. -L.; Rise, F. *J. Chem. Soc., Perkin Trans. 1* **2001**, 1662–1672. (b) Gaich, T.; Mulzer, J. *Org. Lett.* **2010**, *12*, 272–275.