Supporting Information

Total synthesis of 14-membered ring β-resorcylic acid lactone (+)-monocillin II

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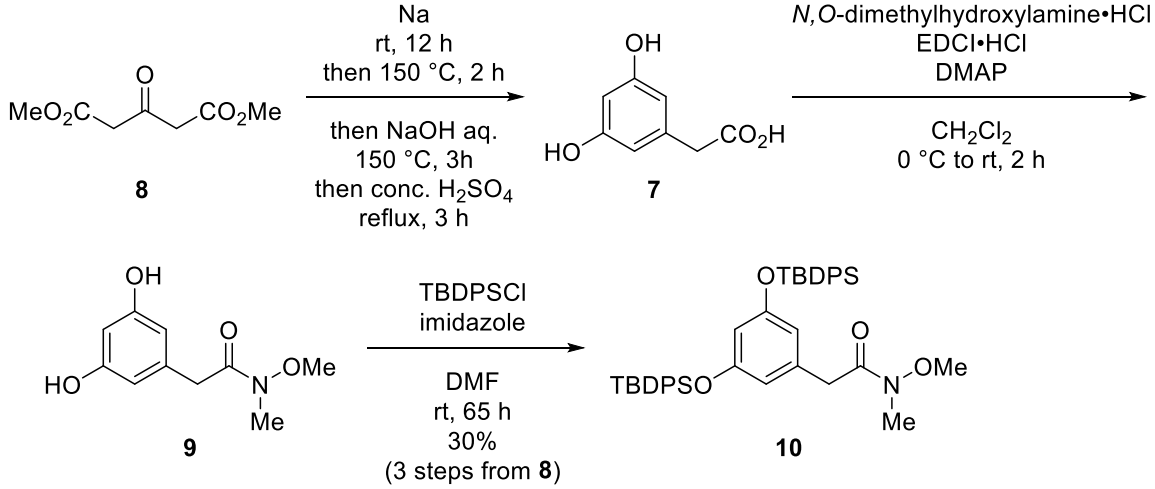
1. General

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 ($CDCl_3$ (0.03% TMS): 0.00 ppm or 7.26 ppm for ^{1}H and 77.00 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.

2. Experimental Procedures

2-(3,5-bis((*tert*-butyldiphenylsilyl)oxy)phenyl)-*N*-methoxy-*N*-methylacetamide (10)



Compound **7** was prepared according to the literature procedure[S1].

To a stirred dimethyl 1,3-acetonedicarboxylate (**8**, 6.0 mL, 41.7 mmol) was added sodium (75 mg, 3.26 mmol) at rt. After being stirred for 12 h at rt, the mixture was heated at 150 °C and stirred for further 2 h. The reaction mixture was cooled to rt and 12% NaOH aq. (38.5 mL) was added. The solution was heated at 150 °C (external temperature) under ambient atmosphere over 3 h. Then, conc. H_2SO_4 was added to the residue at rt (Caution: Evolution of gas) and the mixture was refluxed for further 3 h. The mixture was cooled to rt and diluted with 1 M HCl aq. and 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 crude **7** as black oil, which was used next reaction without purification.

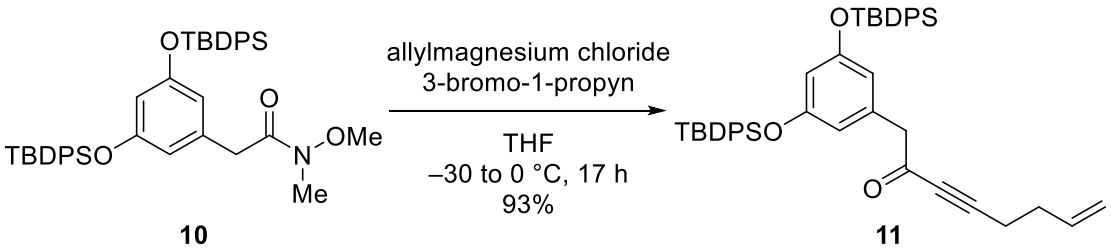
To a solution of crude **7** (prepared above) in CH_2Cl_2 (29 mL) was added *N*,*O*-dimethylhydroxylamine

hydrochloride (2.25 g, 23.1 mmol), EDCI•HCl (5.51 g, 28.7 mmol), and DMAP (421 mg, 3.45 mmol) at 0 °C. The mixture 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 crude **9** as yellow solid, which was used next reaction without further purification.

To a solution of the crude amide **9** (prepared above) in DMF (15 mL) was added imidazole (2.07 g, 30.4 mmol) and TBDPSCl (4.1 mL, 16 mmol) at rt. After being stirred for 1 h, imidazole (1.00 g, 14.7 mmol) and TBDPSCl (2.0 mL, 7.8 mmol) was added to the mixture. The mixture was stirred for 64 h at rt. The reaction mixture was quenched by the addition of water 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 = 2/1) to give **10** (4.25 g, 6.18 mmol, 30% over 3 steps) as a colorless oil.

IR (neat) ν_{max} = 3071, 3050, 2958, 2934, 2894, 2859, 1668, 1591, 1454, 1429, 1340, 1169, 1113, 1037, 704 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 17.53 (dd, *J* = 7.2, 12. Hz, 8H), 7.37-7.34 (m, 4H), 7.27-7.24 (m, 8H), 6.31 (br s, 2H), 6.06 (br s, 1H), 3.42 (br s, 2H), 3.19 (br s, 3H), 3.04 (br s, 3H), 0.98 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.0, 156.1 (2C), 136.5, 135.4 (8C), 132.7 (4C), 129.6 (4C), 127.5 (8C), 113.9 (2C), 110.0, 60.9, 39.4, 32.0, 26.5 (6C), 19.3 (2C), ; HRMS (ESI) *m*/*z* calcd. for $C_{42}H_{50}NO_4Si_2$ ($[M+H]^+$) 688.3273, found 688.3287.

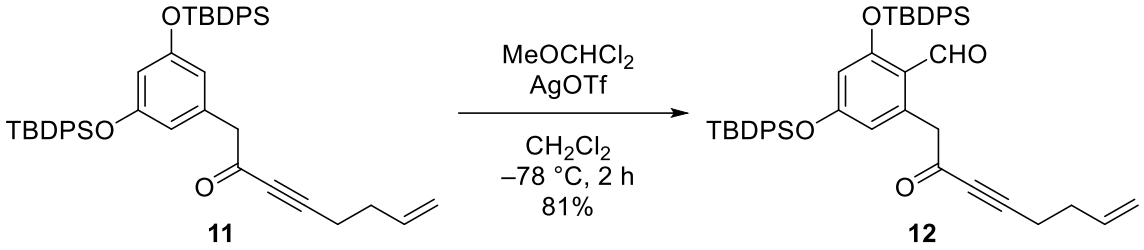
1-(3,5-bis((*tert*-butyldiphenylsilyl)oxy)phenyl)oct-7-en-3-yn-2-one (11)



To a solution of 3-bromo-1-propyn (427 μL, 4.95 mmol) in THF (5.0 mL) was added allylmagnesium chloride (2 M in THF, 4.95 mL, 9.90 mmol) at 0 °C. The mixture was stirred for 5 h at 30 °C and then cooled to −30 °C. To the solution was added a solution of **10** (1.70 g, 2.47 mmol) in THF (20 mL) dropwise via syringe over 30 min. at −30 °C and the resulting mixture was stirred for further 15 h at 0 °C. 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 9/1) to give **11** (1.63 g, 2.31 mmol, 93%) as a colorless oil.

IR (neat) ν_{max} = 3072, 3051, 2957, 2934, 2895, 2859, 2213, 1675, 1590, 1453, 1340, 1172, 1112, 1038, 703 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 8H), 7.42 (dd, *J* = 7.8, 7.2 Hz, 4H), 7.32 (dd, *J* = 7.8, 7.2 Hz, 8H), 6.39 (s, 2H), 6.17 (s, 1H), 5.84-5.78 (m, 1H), 5.13-5.09 (m, 2H), 3.54 (s, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 2.27 (dd, *J* = 13.8, 7.2 Hz, 2H), 1.07 (s, 18H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.7, 156.2 (2C), 135.7, 135.3 (8C), 134.5, 132.6 (4C), 129.6 (4C), 127.5 (8C), 116.3, 114.6 (2C), 110.4, 94.9, 80.8, 77.2, 51.9, 31.6, 26.4 (6C), 19.3 (2C), 18.6; HRMS (ESI) *m*/*z* calcd. for $C_{46}H_{51}O_3Si_2$ ($[M+H]^+$) 707.3371, found 707.3385.

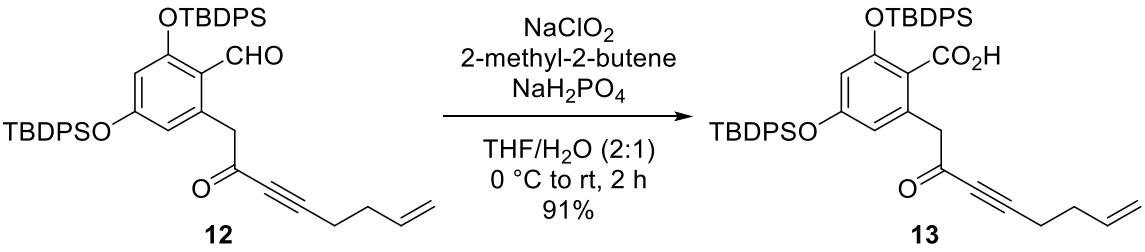
2,4-bis((*tert*-butyldiphenylsilyl)oxy)-6-(2-oxooct-7-en-3-yn-1-yl)benzaldehyde (12)



To a solution of **11** (140.0 mg, 198 μmol) in CH_2Cl_2 (8 mL) was added AgOTf (210.4 mg, 819 μmol) at −78 °C. To the mixture was added a solution of dichloromethyl methyl ether ($MeOCHCl_2$, 35.9 μL, 397 μmol) CH_2Cl_2 (2 mL) dropwise via syringe at −78 °C. The mixture was stirred for 2 h at the same temperature. The reaction mixture was 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 = 49/1 to 4/1) to give **12** (118.2 mg, 161 μmol, 81%) as a colorless oil.

IR (neat) ν_{max} = 3072, 2956, 2933, 2894, 2859, 2216, 1679, 1595, 1565, 1430, 1341, 1164, 1113, 744, 702 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.68 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 4H), 7.38-7.33 (m, 8H), 7.24 (dd, *J* = 7.8, 7.2 Hz, 4H), 7.19 (dd, *J* = 7.8, 7.2 Hz, 4H), 6.22 (br s, 1H), 5.93 (d, *J* = 1.8 Hz, 1H), 5.87-5.80 (m, 1H), 5.10 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.07 (d, *J* = 10.2 Hz, 1H), 4.06 (s, 2H), 2.44 (t, *J* = 6.6 Hz, 2H), 2.31 (dd, *J* = 13.8, 6.6 Hz, 2H), 0.99 (s, 9H), 0.89 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 190.1, 183.9, 161.8, 160.5, 137.7, 135.9, 135.1 (4C), 135.0 (4C), 131.5 (2C), 131.1 (2C), 130.0 (2C), 129.8 (2C), 127.8 (4C), 127.7 (4C), 119.3, 118.4, 116.2, 110.3, 93.0, 81.1, 50.4, 31.7, 26.4 (3C), 26.2 (3C), 19.5, 19.2, 18.8; HRMS (ESI) *m*/*z* calcd. for $C_{47}H_{50}O_4Si_2Na$ ($[M+Na]^+$) 757.3140, found 757.3155.

2,4-bis((*tert*-butyldiphenylsilyl)oxy)-6-(2-oxooct-7-en-3-yn-1-yl)benzoic acid (13)

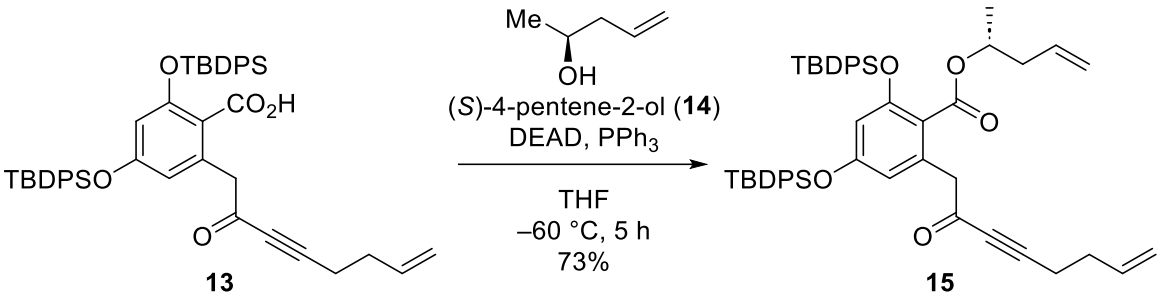


To a suspension of **12** (245.8 mg, 334 μmol), 2-methyl-2-butene (1.7 mL, 16.0 mmol), and NaH_2PO_4 (401.8 mg, 3.35 mmol) in THF (3.3 mL) was added a solution of $NaClO_2$ (303.5 mg, 3.36 mmol) in H_2O (1.7 mL) at 0 °C. The mixture was stirred for 2 h at rt. The reaction mixture was quenched by the addition of water 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** (228.1 mg, 304 μmol, 91%) as a colorless oil.

IR (neat) ν_{max} = 3072, 3051, 3017, 2955, 2934, 2896, 2860, 2215, 1689, 1597, 1430, 1348, 1179, 1113, 846, 745, 703 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 10.70 (br s, 1H), 7.49 (d, *J* = 6.6 Hz, 4H), 7.39 (dd, *J* = 7.2, 7.8 Hz, 2H), 7.34 (dd, *J* = 7.8, 6.6 Hz, 2H), 7.29-7.25 (m, 8H), 7.17 (dd, *J* = 7.8, 7.2 Hz, 4H), 6.23 (d, *J* = 1.8 Hz, 1H), 6.00 (d, *J* = 1.8 Hz, 1H), 5.84-5.80 (m, 1H), 5.09 (dd, *J* = 16.8, 1.8 Hz, 1H), 5.07 (dd, *J* = 10.2, 1.8 Hz, 1H), 4.02 (d, *J* = 2.4

Hz, 2H), 2.41 (t, J = 7.8 Hz, 2H), 2.28 (dd, J = 13.8, 7.8 Hz, 2H), 0.99 (s, 9H), 0.84 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.1, 169.2, 157.9, 155.8, 137.3, 135.9, 135.2 (4C), 135.0 (4C), 131.7 (2C), 130.8 (2C), 130.1 (2C), 129.8 (2C), 127.8 (4C), 127.6 (4C), 117.8, 116.2, 115.2, 110.5, 94.2, 80.7, 50.9, 31.6, 26.2 (3C), 26.1 (3C), 19.23, 19.17, 18.7; HRMS (ESI) m/z calcd. for $C_{47}H_{50}O_5Si_2Na$ ([M+Na]$^+$) 773.3088, found 773.3105.

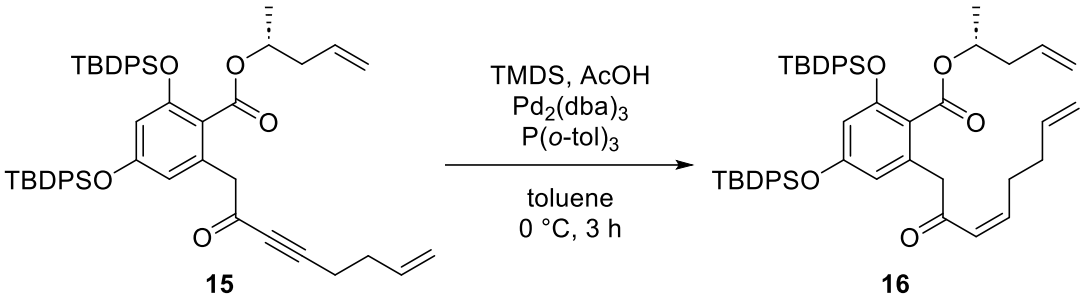
(*R*)-pent-4-en-2-yl 2,4-bis((*tert*-butyldiphenylsilyl)oxy)-6-(2-oxooct-7-en-3-yn-1-yl)benzoate (15)

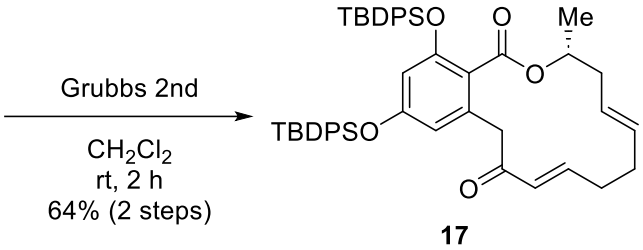


To a suspension of PPh_3 (175.0 mg, 667 μmol) in THF (1.0 mL) was added DEAD (40% in toluene, 306 μL, 667 μmol) at 0 °C. The mixture was stirred for 30 min. at rt and then cooled to −60 °C. To the mixture was added a solution of **13** (50.0 mg, 66.6 μmol) and (*S*)-4-pentene-2-ol (**14**, 10.3 μL, 100 μmol) in THF (0.3 mL) dropwise via syringe at −60 °C. The solution was stirred for 5 h at the same temperature. The reaction mixture was quenched by the addition of sat. $NaHCO_3$ 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 9/1) to give **15** (39.9 mg, 48.7 μmol, 73%) as a colorless oil.

$[\alpha]_D^{27}$ −6.75 (*c* 1.50, $CHCl_3$); IR (neat) ν_{max} = 3073, 2955, 2934, 2895, 2859, 2214, 1725, 1675, 1596, 1471, 1427, 1348, 1260, 1177, 1113, 703 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 (dd, J = 7.8, 1.8 Hz, 4H), 7.35-7.29 (m, 8H), 7.23 (d, J = 7.2 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 7.17 (d, J = 7.2 Hz, 2H), 7.15 (d, J = 7.8 Hz, 2H), 6.23 (d, J = 1.2 Hz, 1H), 5.88 (d, J = 1.2 Hz, 1H), 5.82-5.73 (m, 2H), 5.15-5.01 (m, 5H), 3.67 (d, J = 1.8 Hz, 2H), 2.52-2.48 (m, 1H), 2.37-2.31 (m, 3H), 2.23 (dd, J = 13.8, 7.8 Hz, 2H), 1.33 (d, J = 6.0 Hz, 3H), 0.95 (s, 9H), 0.85 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 184.1, 166.8, 156.4, 154.0, 135.8, 135.3 (2C), 135.2 (2C), 135.1 (4C), 135.0, 133.7, 132.7, 132.1 (2C), 131.9, 131.8, 129.6 (4C), 127.6 (4C), 127.5 (4C), 120.1, 117.9, 116.3, 115.5, 110.0, 95.2, 80.7, 71.5, 49.7, 40.2, 31.6, 26.3 (6C), 19.3 (2C), 18.7; HRMS (ESI) m/z calcd. for $C_{52}H_{58}O_5Si_2Na$ ([M+Na]$^+$) 841.3715, found 841.3717.

(*R*,5*E*,9*E*)-14,16-bis((*tert*-butyldiphenylsilyl)oxy)-3-methyl-3,4,7,8-tetrahydro-1*H*-benzo[*c*][1]oxacyclotetradecine-1,11(12*H*)-dione (17)





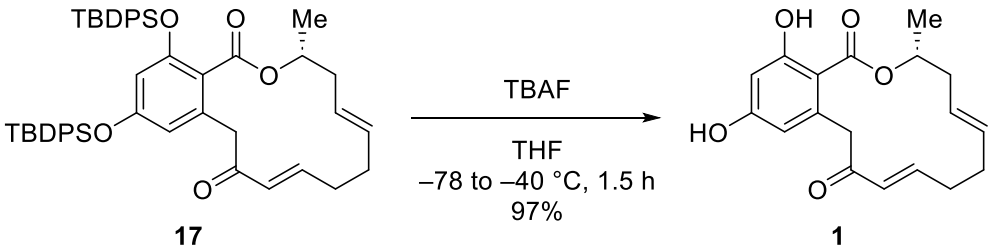
To a suspension of **15** (50.0 mg, 61.0 μmol), 1,1,3,3-tetramethyldisiloxane (TMDS, 10.8 μL, 61.1 μmol), and AcOH (3.5 μL, 61.2 μmol) in toluene (1.2 mL) was added P(*o*-tol)$_3$ (7.6 mg, 25 μmol) and Pd$_2$(dba)$_3$ (5.7 mg, 6.2 μmol) at 0 °C. The mixture was stirred for 3 h at 0 °C. The mixture was concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 97/3 to 9/1) to give (*Z*)-**16** (50.1, 61.0 μmol, quant.) as colorless oil. Product (*Z*)-**16** rapidly isomerized to give an *E*/*Z*-mixture.

(*Z*)-**16**: $[\alpha]_D^{27}$ −6.2 (*c* 0.7, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.4, 1.8 Hz, 2H), 7.50 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 6H), 7.28-7.24 (m, 4H), 7.18-7.14 (m, 4H), 6.73-6.68 (m, 1H), 6.11 (d, *J* = 1.8 Hz, 1H), 5.90 (d, *J* = 1.8 Hz, 1H), 5.76 (d, *J* = 16.2 Hz, 1H), 5.39-5.30 (m, 2H), 5.07-5.04 (m, 1H), 3.60 (d, *J* = 15.6 Hz, 1H), 3.48 (d, *J* = 15.6 Hz, 1H), 2.28-2.08 (m, 6H), 1.39 (d, *J* = 6.0 Hz, 3H), 0.98 (s, 9H), 0.84 (s, 9H); HRMS (ESI) *m*/*z* calcd. for $C_{52}H_{60}O_5Si_2Na$ ([M+Na]$^+$) 843.3872, found 843.3882.

To a solution of **16** (prepared above: mainly *Z*-isomer) in CH_2Cl_2 (6.1 mL) was added Grubbs 2nd catalyst (8.6 mg, 9.4 μmol) at rt. The mixture was stirred for 2 h at rt. The reaction mixture was concentrated to give a residue. The residue was purified by flash column chromatography (hexane/EtOAc = 97/3 to 9/1) to give **17** (30.7, 38.7 μmol, 64% over 2 steps) as a colorless oil.

$[\alpha]_D^{28}$ −49.6 (*c* 0.15, $CHCl_3$); IR (neat) ν_{max} = 3071, 3049, 3016, 2933, 2858, 1724, 1622, 1595, 1469, 1428, 1344, 1262, 1176, 1113, 758, 703 cm^{-1};; ^{13}C NMR (150 MHz, $CDCl_3$) δ 197.5, 167.8, 156.6, 153.8, 147.8, 135.3 (4C), 135.21, 135.16 (4C), 134.5, 132.1, 132.00, 131.95, 131.8 (2C), 129.9, 129.8, 129.7, 129.5 127.74 (2C), 127.68 (2C), 127.6 (2C), 127.5 (2C), 120.3, 114.1, 109.9, 95.2, 72.2 (d), 45.7, 38.5, 31.3, 31.0 26.3 (6C), 19.3 (2C), 19.1; HRMS (ESI) *m*/*z* calcd. for $C_{50}H_{57}O_5Si_2$ ([M+H]$^+$) 793.3739, found 793.3753.

Monocillin II (1)



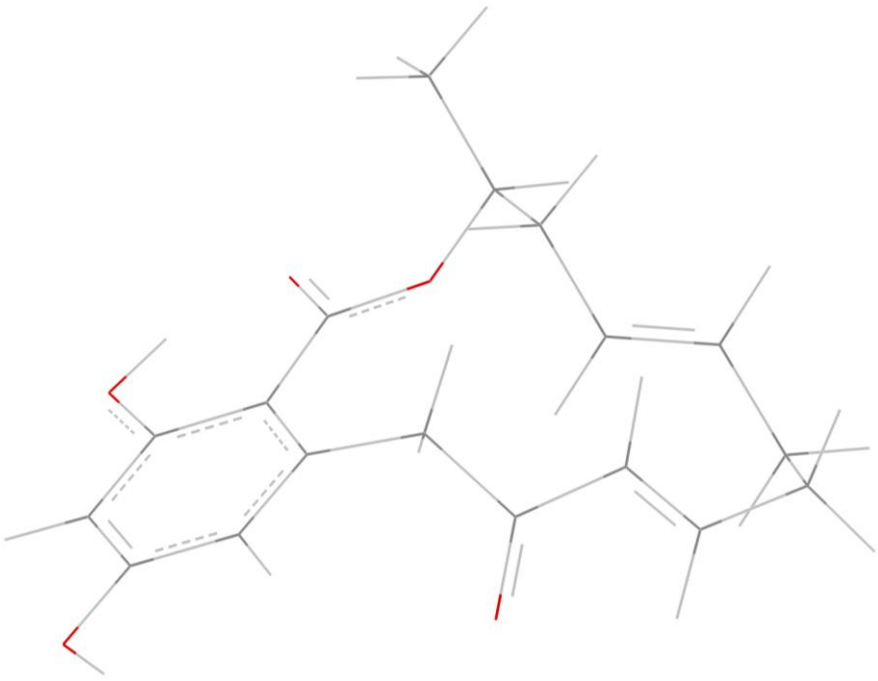
To a suspension of **17** (30.0 mg, 37.8 μmol) in THF (1.9 mL) was added TBAF (1.0 N in THF, 113.4 μL, 113 μmol) at −78 °C. The mixture was stirred for 1.5 h at −40 °C. The reaction mixture was quenched by the addition of sat. NH_4Cl aq. and diluted with EtOAc. The aqueous layer was extracted with EtOAc. 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 = 3/2) to give **1** (11.5 mg, 36.4 μmol, 97%) as a white solid.

Mp. = 193.5–197.0 °C; $[\alpha]_D^{26}$ +45.1 (*c* 0.06, $CHCl_3$); IR (KBr) ν_{max} = 3357, 3073, 2930, 2857, 1723, 1685, 1646, 1619, 1429, 1343, 1313, 1262, 1176, 1112, 703 cm^{-1}; ^1H NMR (600 MHz, CD_3OD) δ 6.74-6.69 (m, 1H), 6.26 (d, *J* = 2.4 Hz, 1H), 6.20 (d, *J* = 2.4 Hz, 1H), 5.84 (d, *J* = 15.6 Hz, 1H), 5.33-5.22 (m, 3H), 3.98 (d, *J* = 17.4 Hz, 1H), 3.90 (d, *J* = 17.4 Hz, 1H), 2.63-2.59 (m, 1H), 2.27-2.17 (m, 5H), 1.29 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, CD_3OD) δ 199.9, 171.3, 165.7, 163.7, 149.8, 140.6, 133.0, 131.0, 128.7, 113.1, 107.3, 103.1, 73.4, 49.4-48.7 (overlap), 38.2, 32.3, 32.1, 18.8; HRMS (ESI) *m/z* calcd. for $C_{18}H_{20}O_5Na$ ($[M+Na]^+$) 339.1203, found 339.1212.

3. Computational Details

Conformation analyses of monocillins II (**1**) and VI (**2**) were performed by BEST method in BIOVIA Discovery Studio 2022 Client. Conformers within 5.25 kcal/mol energy differences were optimized using DFT calculations at the B3LYP/6-31G(d,p) level, implemented in the Gaussian 16 program package. [S2] The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum (no imaginary frequency).

Table S1. **Number of Imaginary Frequencies and Atom Coordinates for Monocillin II (1) Optimized by DFT/B3LYP/6-31G(d,p) Level.** [S2]

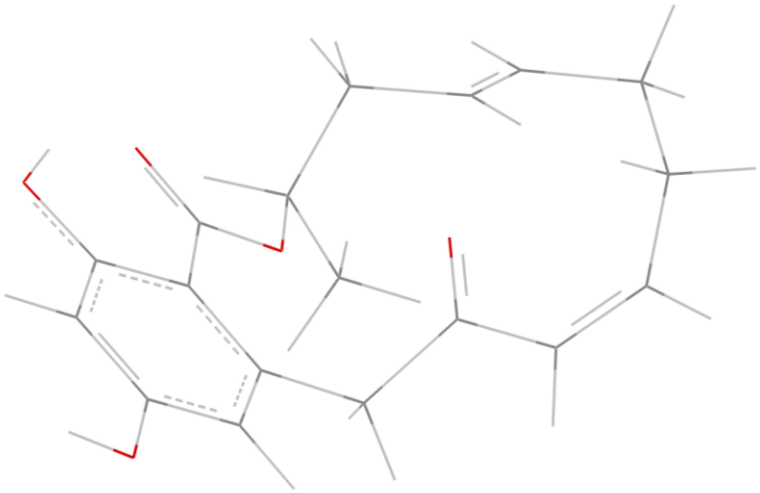


Number of imaginary frequencies = 0.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.973674	0.299786	-0.811045
2	6	0	-4.037692	-0.919174	-0.156678
3	6	0	-2.946837	-1.377910	0.599343
4	6	0	-1.778043	-0.637468	0.708809
5	6	0	-1.675591	0.621180	0.036895
6	6	0	-2.809115	1.067422	-0.726385
7	8	0	-2.823012	2.228836	-1.392241
8	8	0	-5.183127	-1.640689	-0.270963
9	6	0	-0.661813	-1.291535	1.503604
10	6	0	0.237266	-2.169476	0.605917
11	6	0	1.706052	-1.983465	0.717605
12	8	0	-0.262538	-2.980280	-0.158636
13	6	0	2.537822	-2.520995	-0.187536
14	6	0	4.012914	-2.282398	-0.272672
15	6	0	-0.513913	1.524237	0.055868
16	8	0	0.524661	1.136874	0.814394
17	8	0	-0.473003	2.589599	-0.578241
18	6	0	1.693759	2.005270	0.985395
19	6	0	2.508929	2.181203	-0.310878
20	6	0	2.870103	0.873297	-0.965633
21	6	0	4.015650	0.216662	-0.760159
22	6	0	4.342415	-1.148882	-1.299688
23	6	0	1.329569	3.317559	1.673822
24	1	0	-4.808739	0.666113	-1.394989
25	1	0	-3.008970	-2.344367	1.091366
26	1	0	-1.933289	2.646470	-1.254446
27	1	0	-5.078288	-2.478792	0.199215
28	1	0	-1.116005	-1.977874	2.228126
29	1	0	-0.069528	-0.568264	2.056627
30	1	0	2.081613	-1.347532	1.514668
31	1	0	2.083531	-3.117656	-0.978655
32	1	0	4.517545	-3.201196	-0.594459
33	1	0	4.422134	-2.008724	0.706456
34	1	0	2.295544	1.400186	1.670564
35	1	0	1.955100	2.824660	-0.998963
36	1	0	3.422923	2.714763	-0.021006

37	1	0	2.115535	0.428327	-1.612985
38	1	0	4.762988	0.658945	-0.097741
39	1	0	3.789399	-1.337383	-2.226920
40	1	0	5.408781	-1.211268	-1.546105
41	1	0	0.768870	3.976781	1.010938
42	1	0	0.732256	3.123932	2.569699
43	1	0	2.247942	3.826270	1.984619

Table S2. Number of Imaginary Frequencies and Atom Coordinates for Monocillin VI (2) Optimized by DFT/B3LYP/6-31G(d,p) Level. [S2]



Number of imaginary frequencies = 0.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-4.095708	-0.062814	-0.628545
2	6	0	-3.997610	1.174056	-0.011884
3	6	0	-2.809129	1.555300	0.631135
4	6	0	-1.711378	0.709557	0.668715
5	6	0	-1.783937	-0.576378	0.050846
6	6	0	-3.002099	-0.937327	-0.608683
7	8	0	-3.175808	-2.111319	-1.227380
8	8	0	-5.020119	2.069915	0.006429
9	6	0	-0.476457	1.244872	1.354855
10	6	0	0.653359	1.644025	0.394587

11	6	0	1.902369	2.086175	1.067749
12	8	0	0.505149	1.610080	-0.817469
13	6	0	3.056651	2.421135	0.462496
14	6	0	3.377030	2.397375	-1.003445
15	6	0	-0.715621	-1.585931	0.037567
16	8	0	0.397984	-1.295461	0.733635
17	8	0	-0.820154	-2.672561	-0.552053
18	6	0	1.421524	-2.337605	0.827651
19	6	0	2.351538	-2.300667	-0.401723
20	6	0	3.281217	-1.119934	-0.480126
21	6	0	3.175623	-0.122787	-1.361703
22	6	0	4.085733	1.071374	-1.418414
23	6	0	2.117397	-2.113909	2.162624
24	1	0	-4.999340	-0.385170	-1.136949
25	1	0	-2.767271	2.536546	1.090363
26	1	0	-2.318266	-2.606206	-1.135748
27	1	0	-5.773305	1.701778	-0.475104
28	1	0	-0.742789	2.145225	1.923940
29	1	0	-0.067661	0.535208	2.078334
30	1	0	1.860379	2.127606	2.154708
31	1	0	3.884803	2.701691	1.115454
32	1	0	4.055631	3.229304	-1.228311
33	1	0	2.468721	2.517685	-1.593888
34	1	0	0.899377	-3.296958	0.825176
35	1	0	1.725423	-2.359426	-1.296567
36	1	0	2.937638	-3.230483	-0.369104
37	1	0	4.099039	-1.093804	0.241407
38	1	0	2.352882	-0.131030	-2.076032
39	1	0	4.963796	0.906486	-0.781291
40	1	0	4.458245	1.208073	-2.442181
41	1	0	2.568481	-1.119230	2.209749
42	1	0	2.907887	-2.858528	2.300656
43	1	0	1.406908	-2.213111	2.987878

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3. ^{1}H and ^{13}C NMR spectroscopic data

Figure S1. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 10.

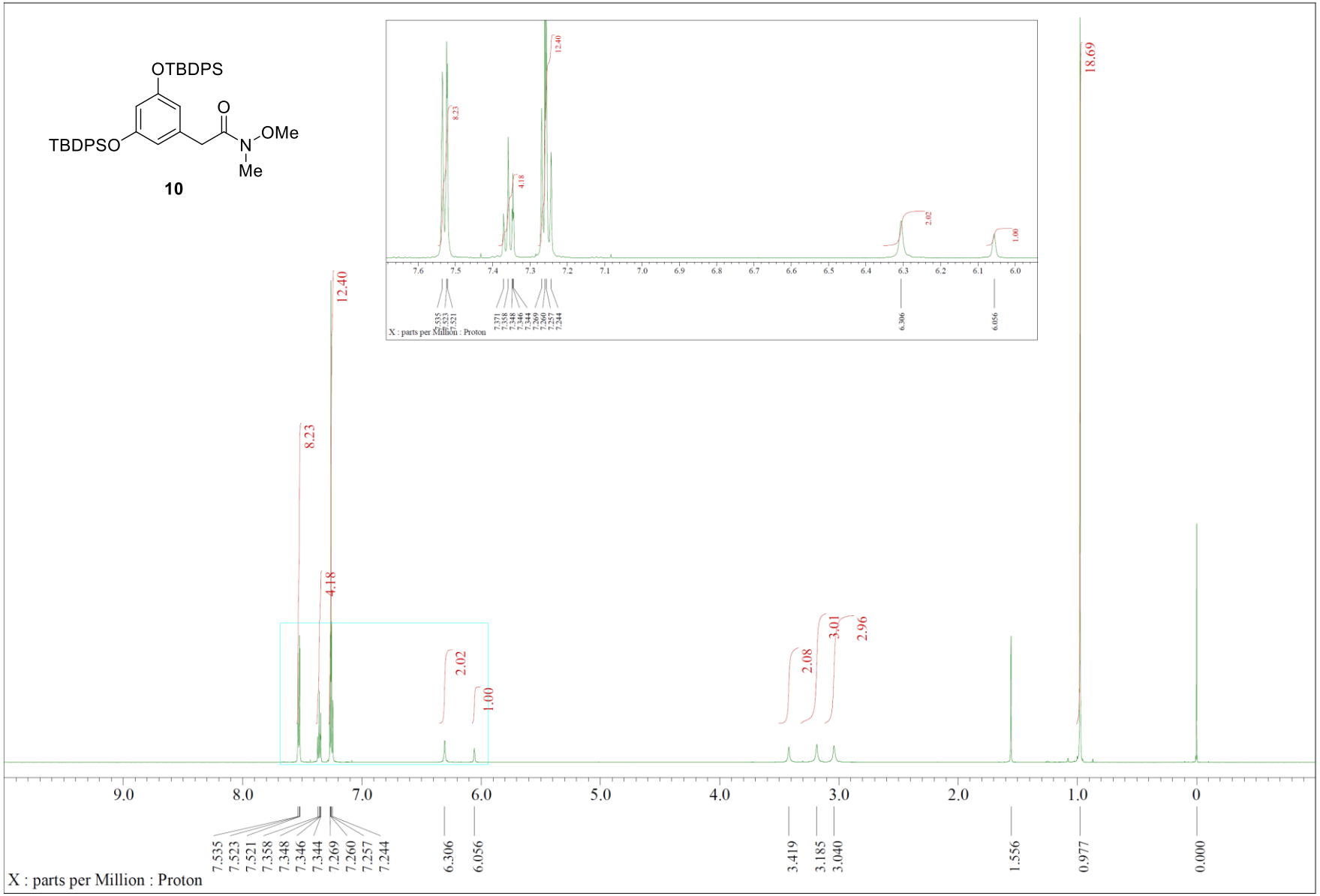


Figure S2. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 10.

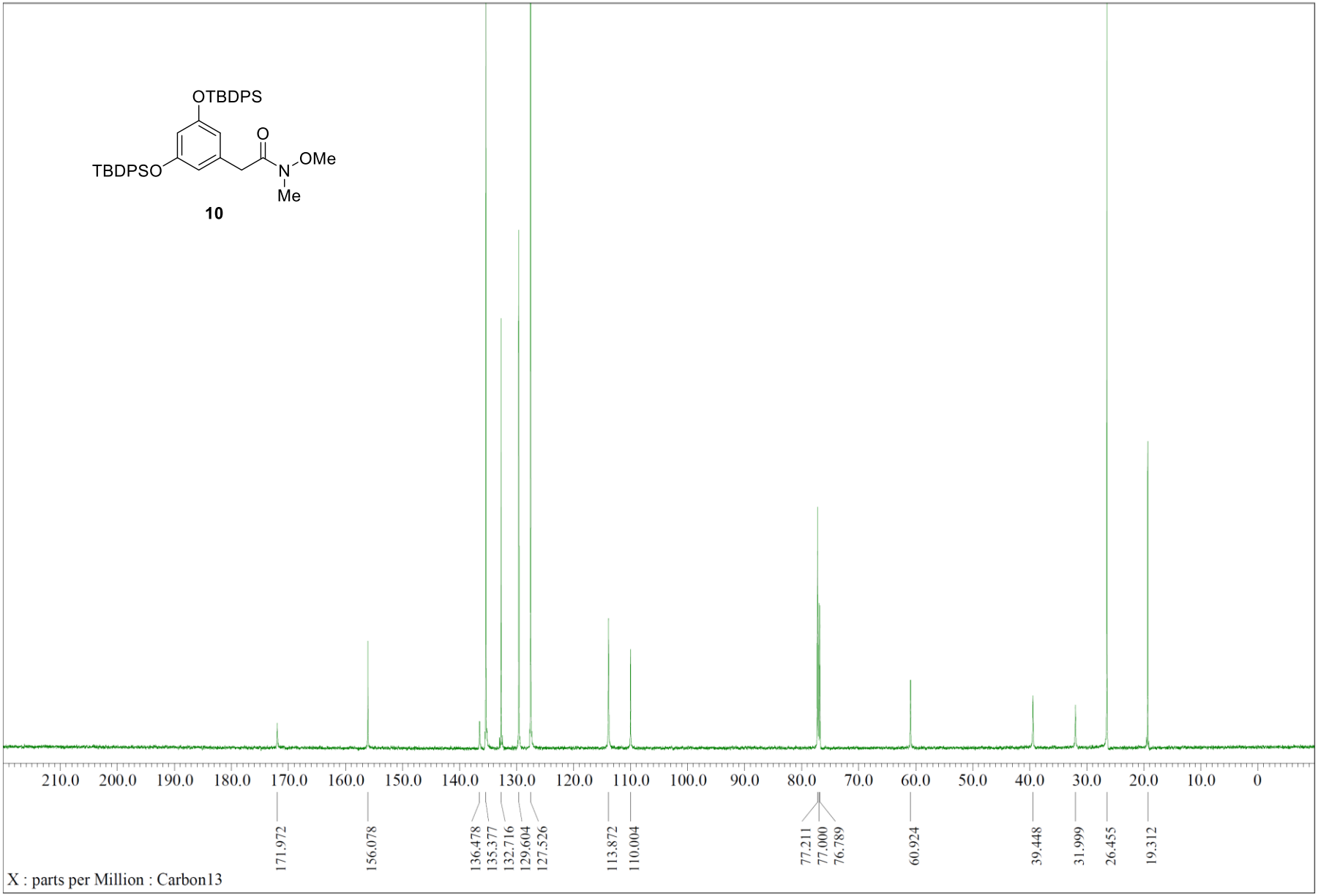


Figure S3. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 11.

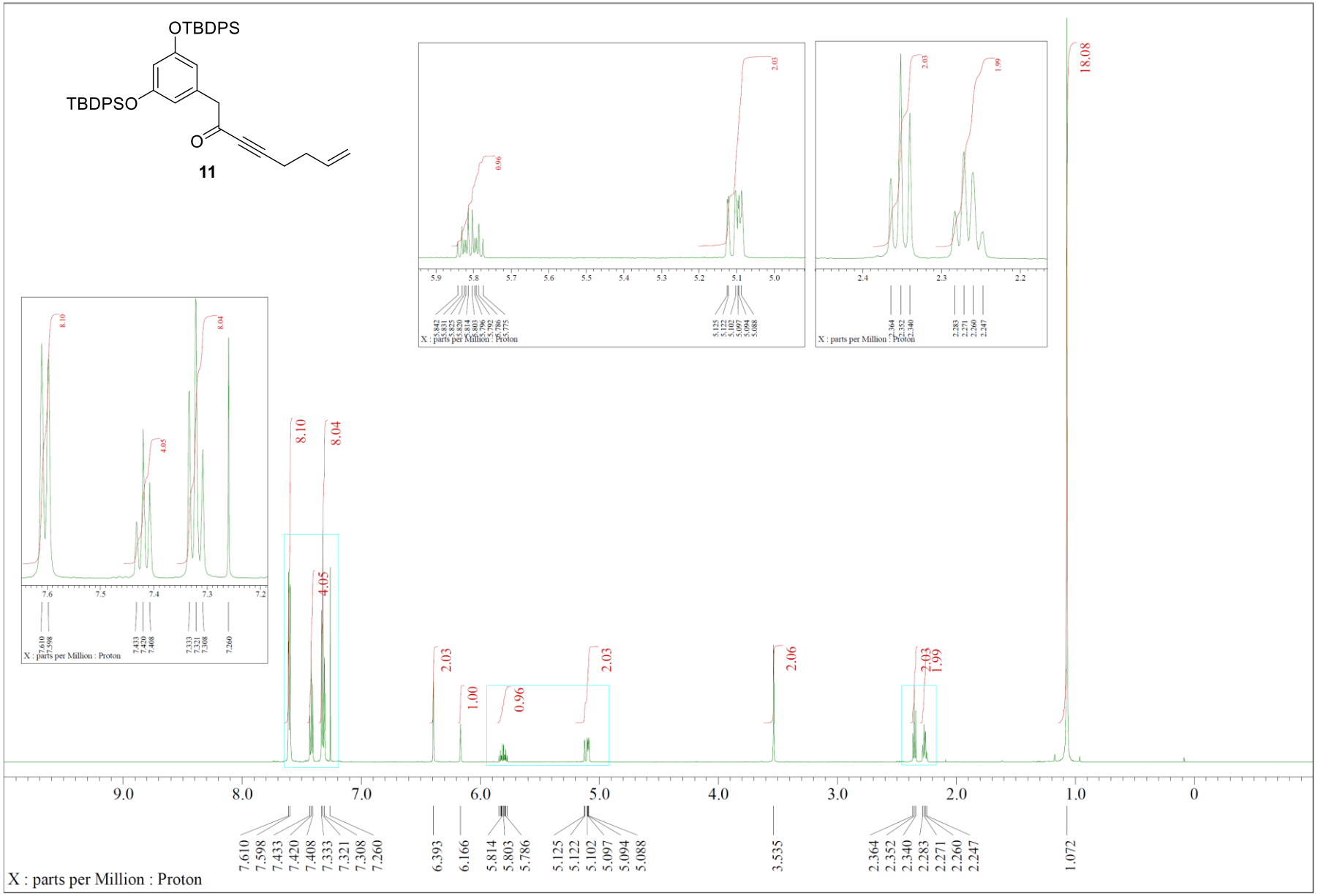


Figure S4. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 11.

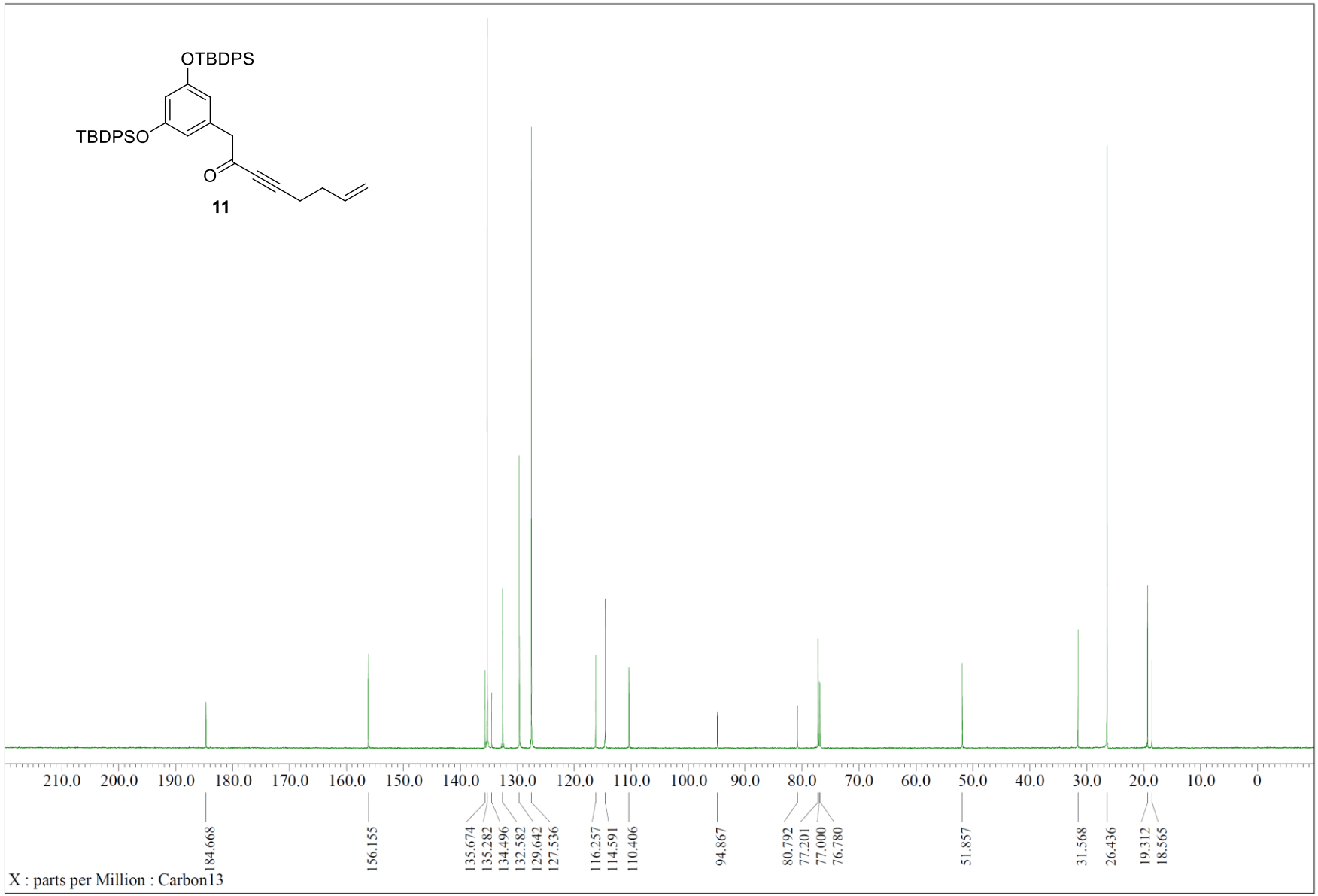


Figure S5. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 12.

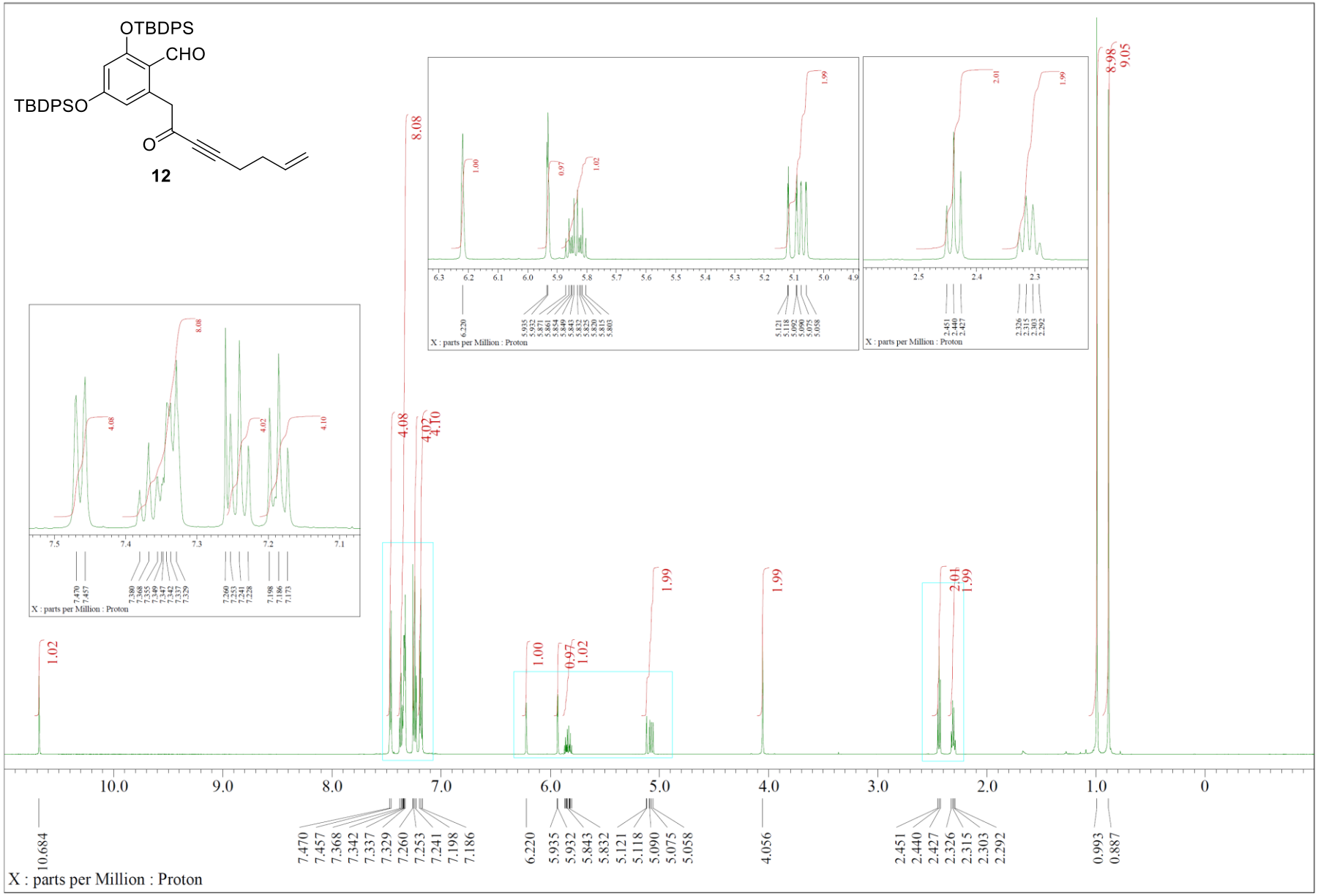


Figure S6. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 12.

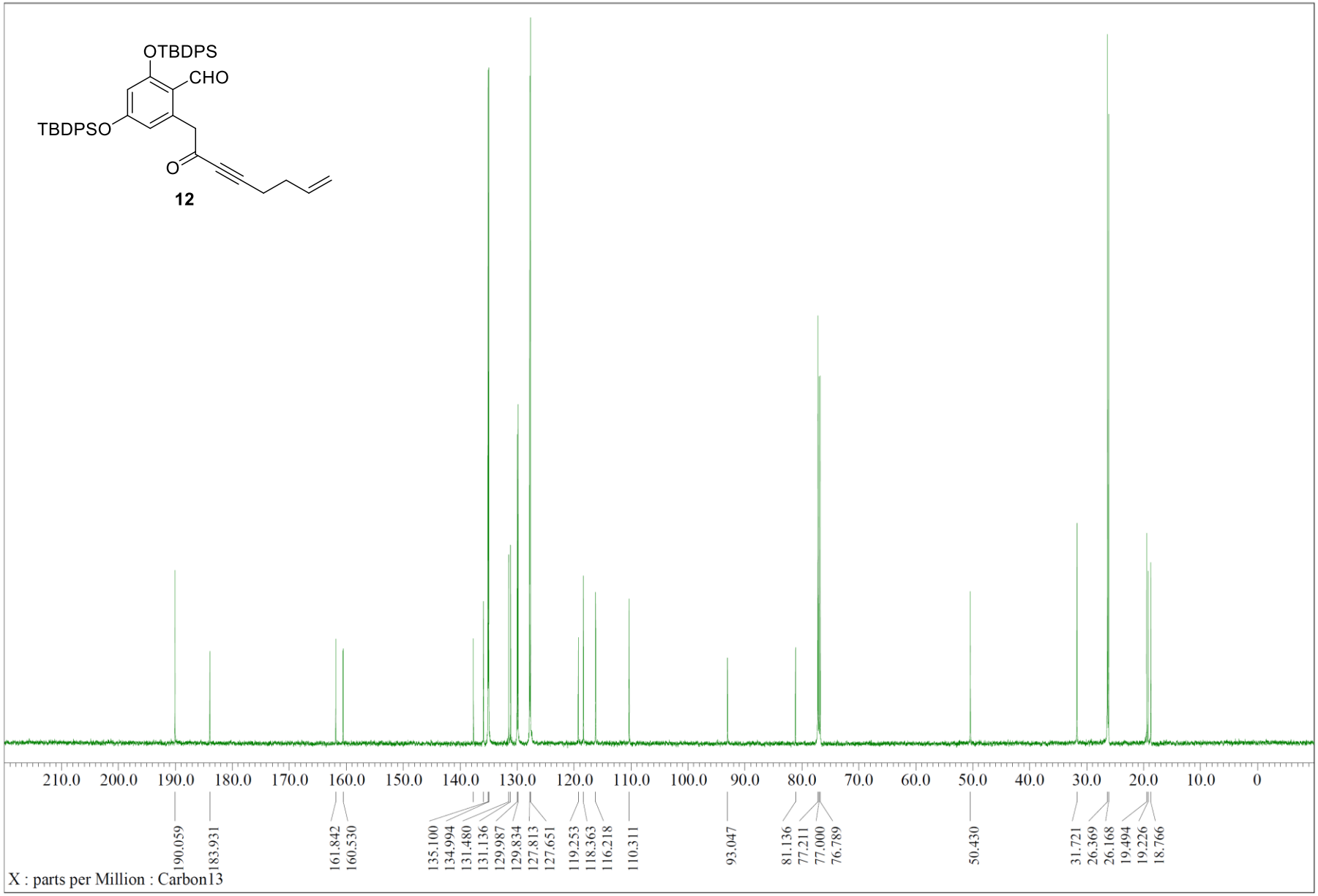


Figure S7. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 13.

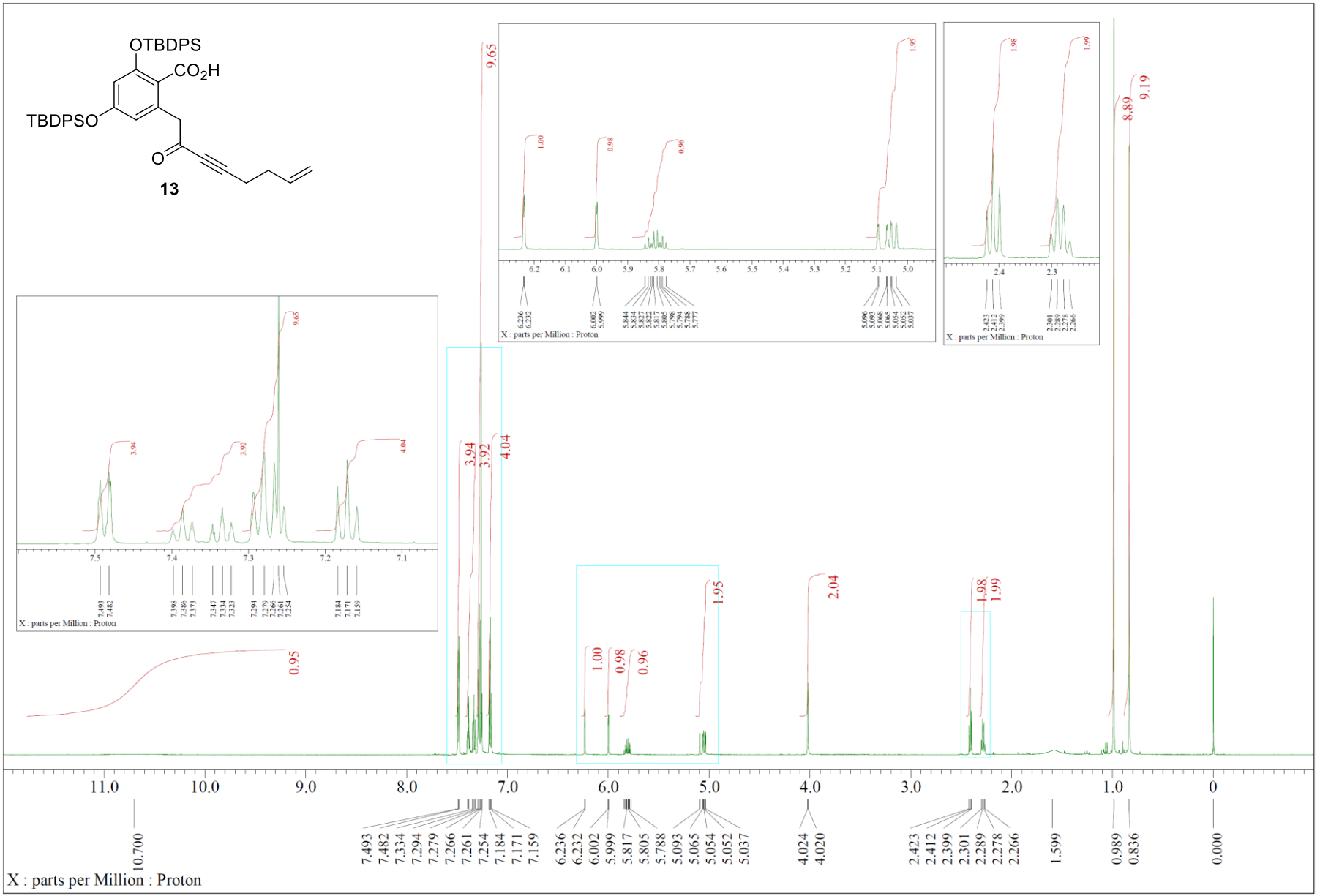


Figure S8. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 13.

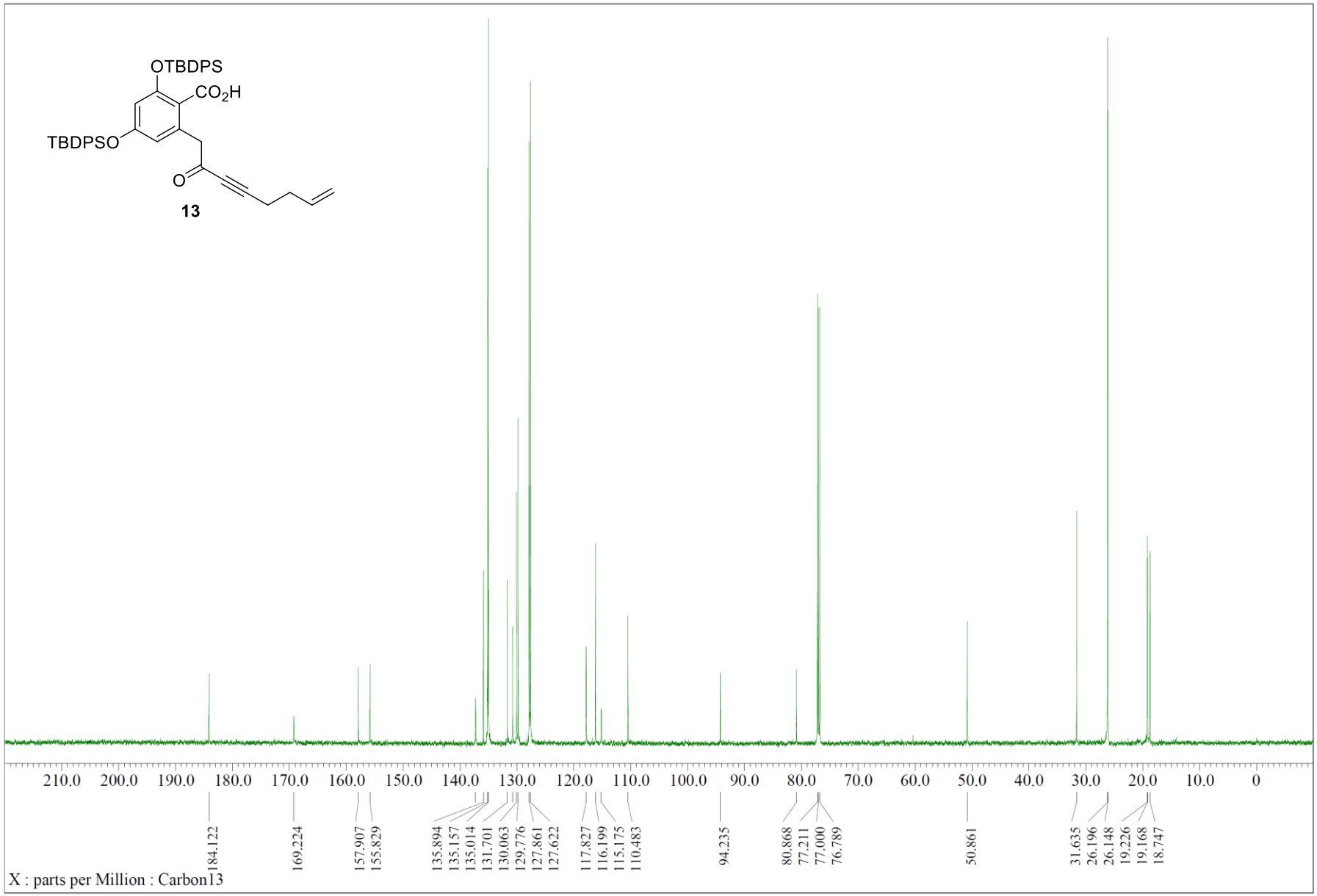


Figure S9. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound 15.

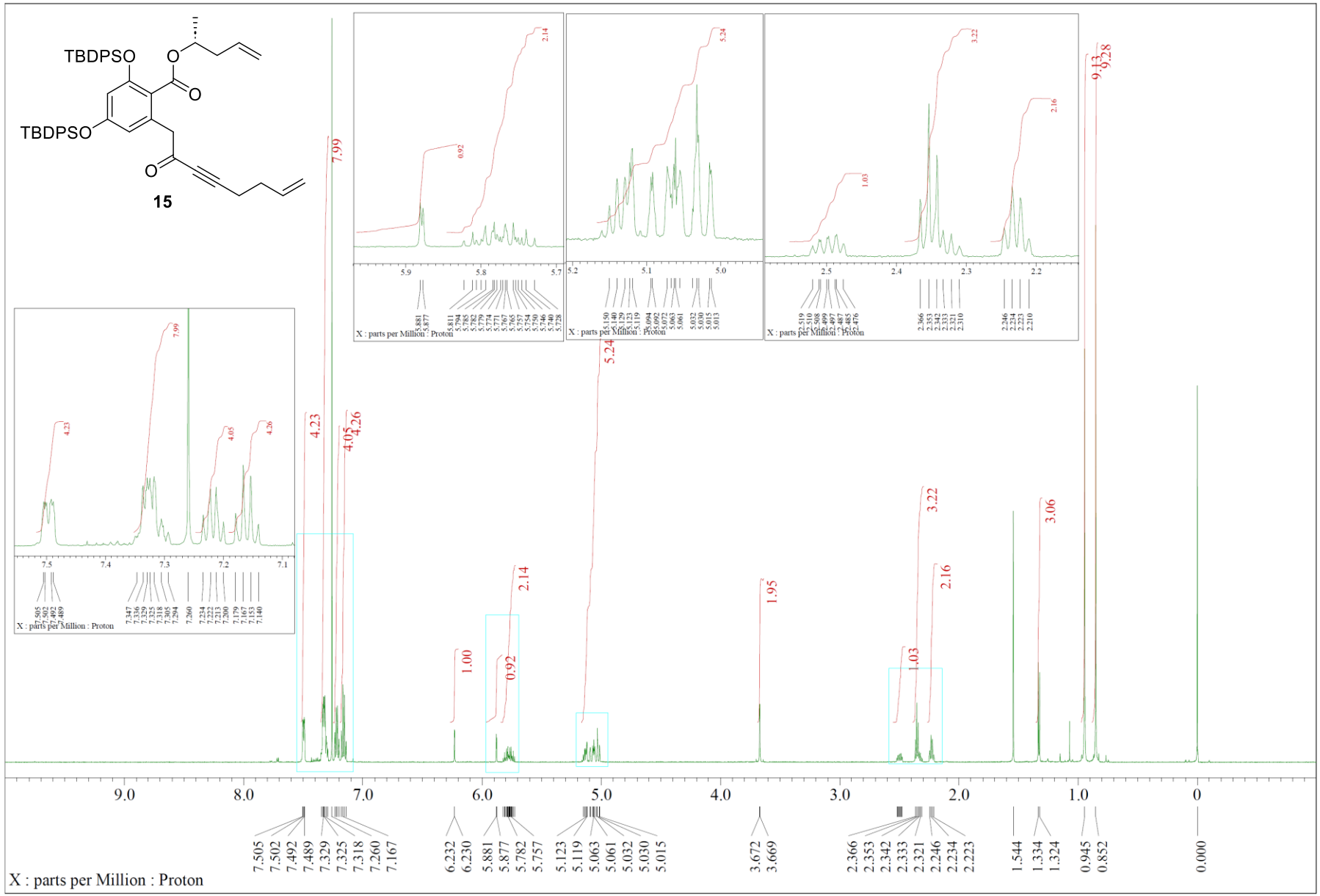


Figure S10. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of compound 15.

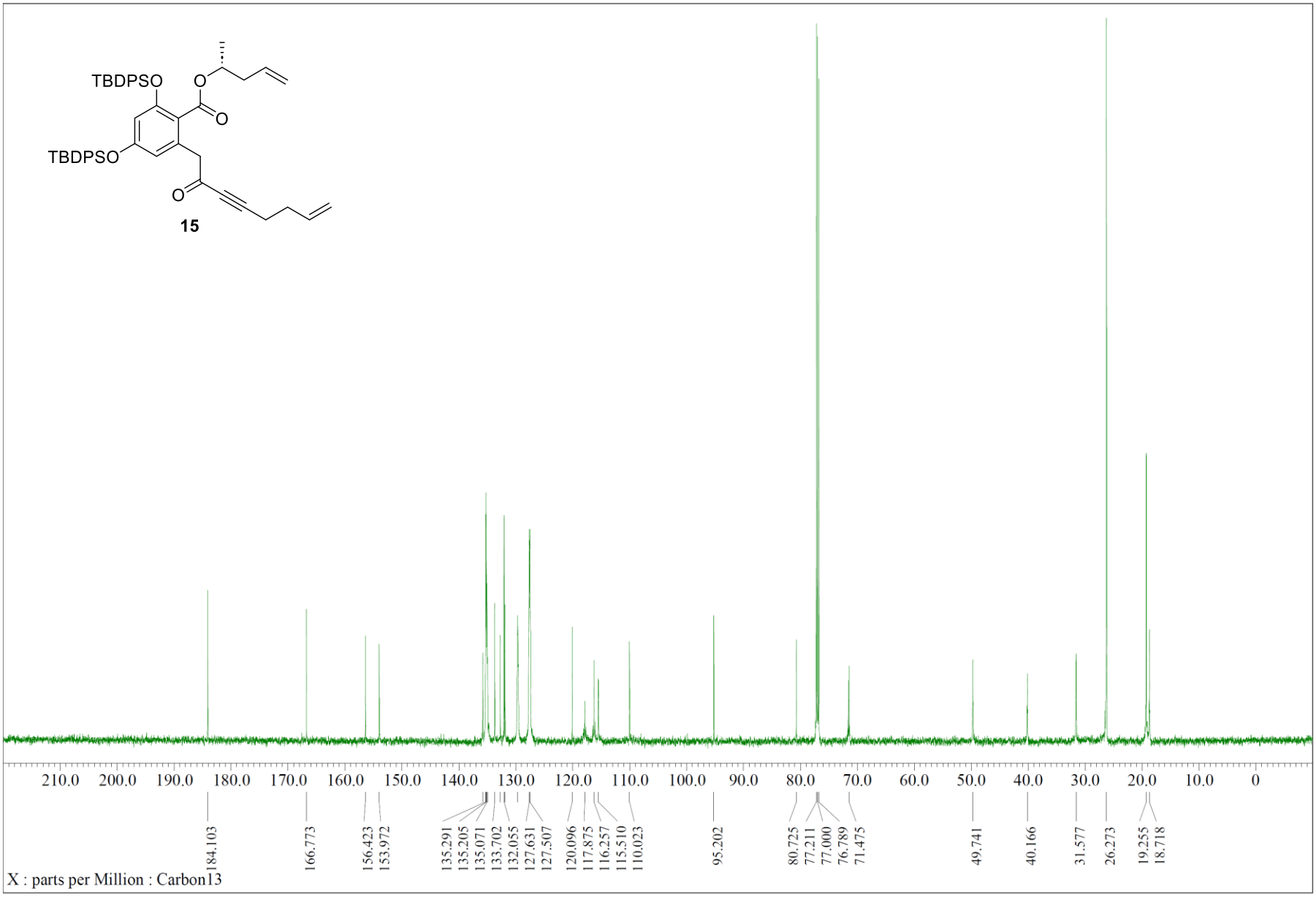


Figure S11. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of compound (*Z*)-16.

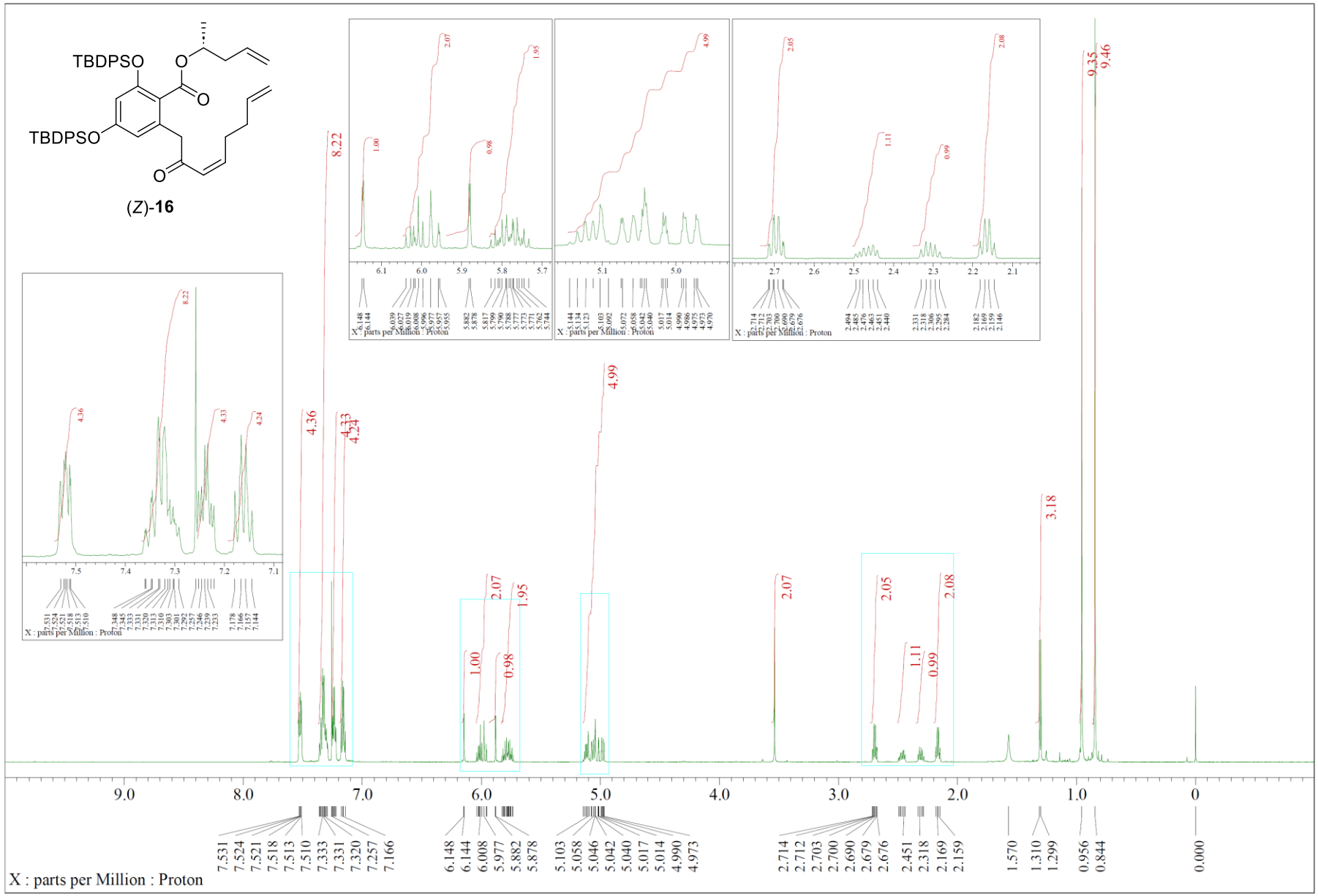


Figure S12. ^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 17.

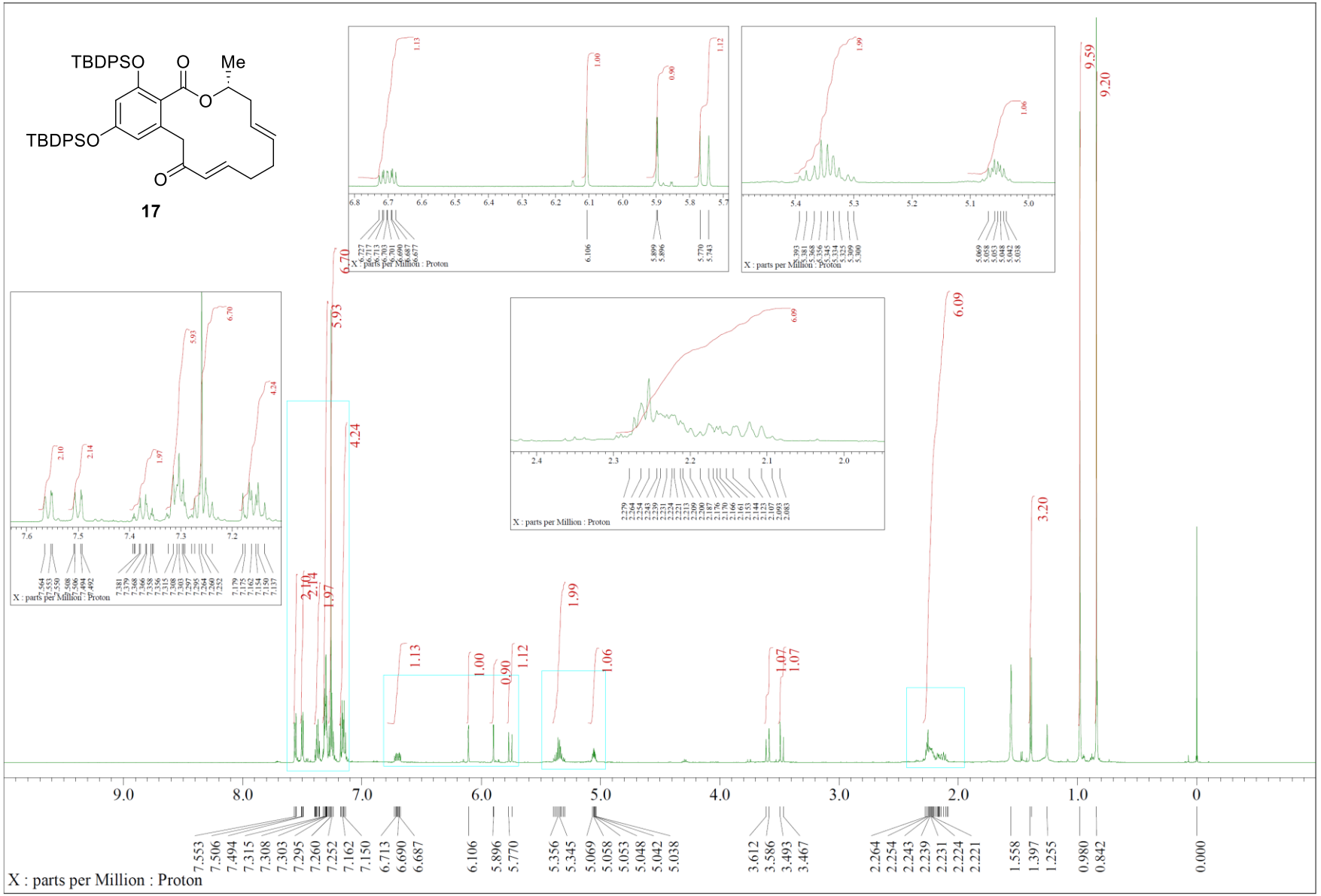


Figure S13. ^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 17.

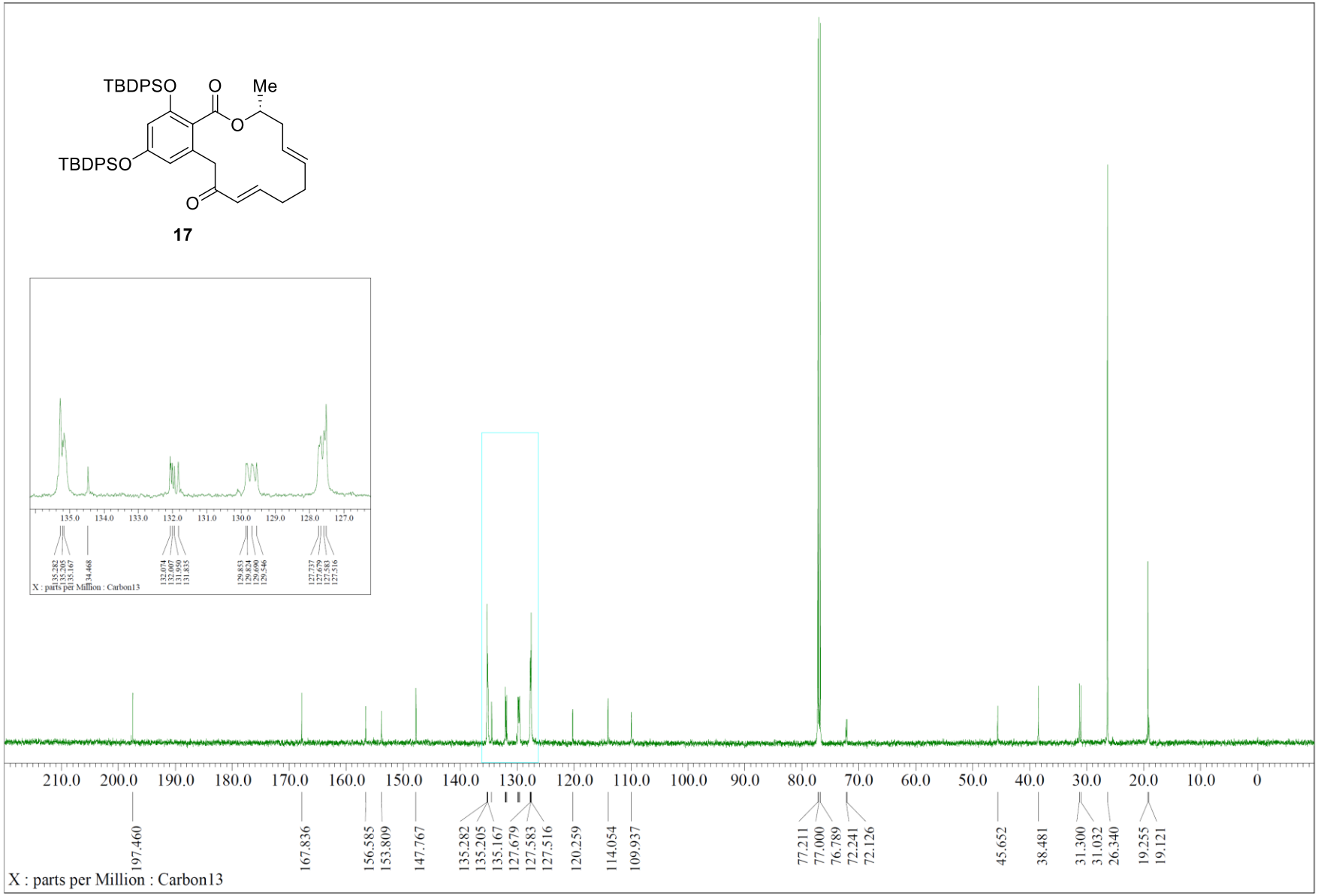


Figure S14. ^{1}H NMR spectrum (600 MHz, CD_3OD) of compound 1.

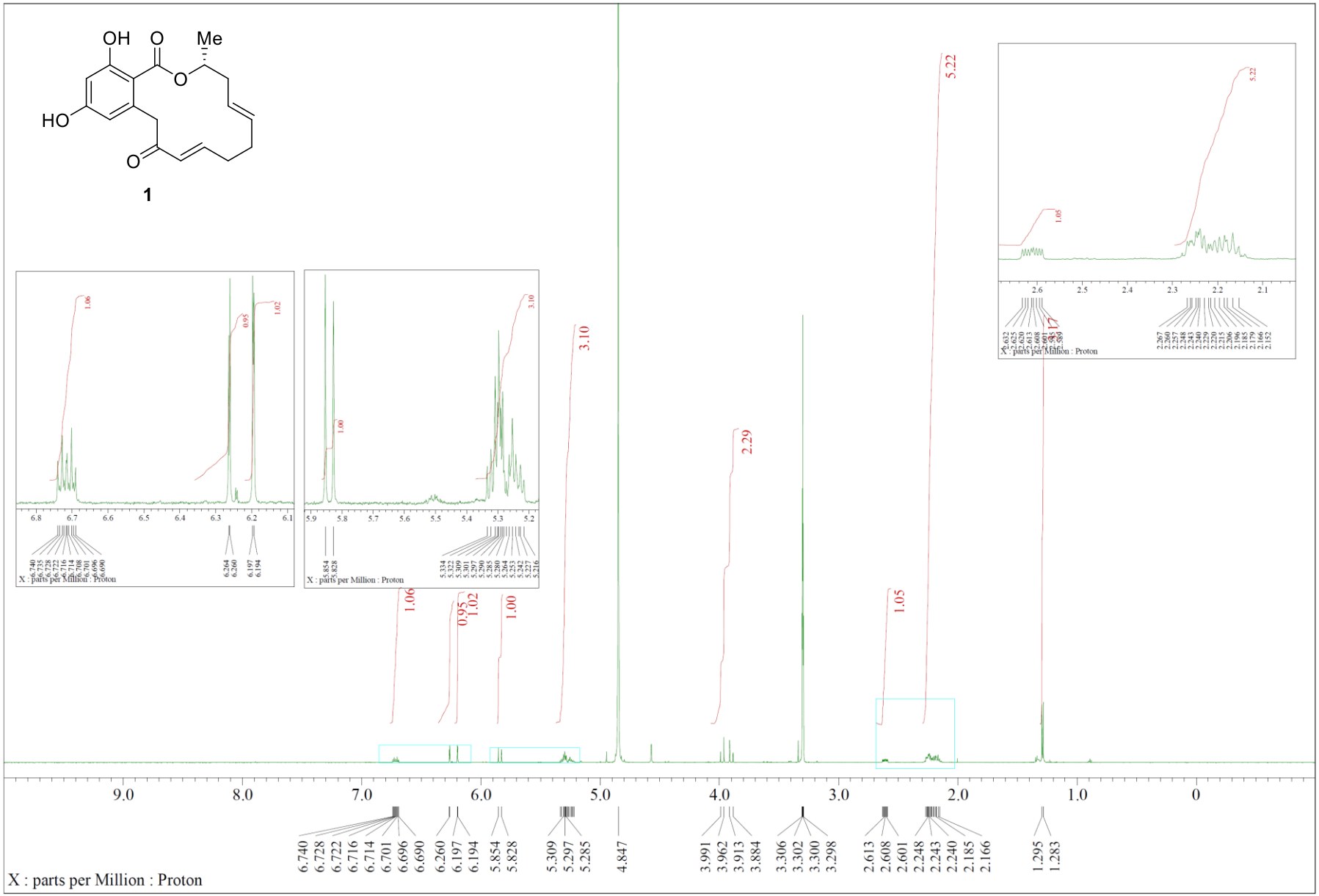
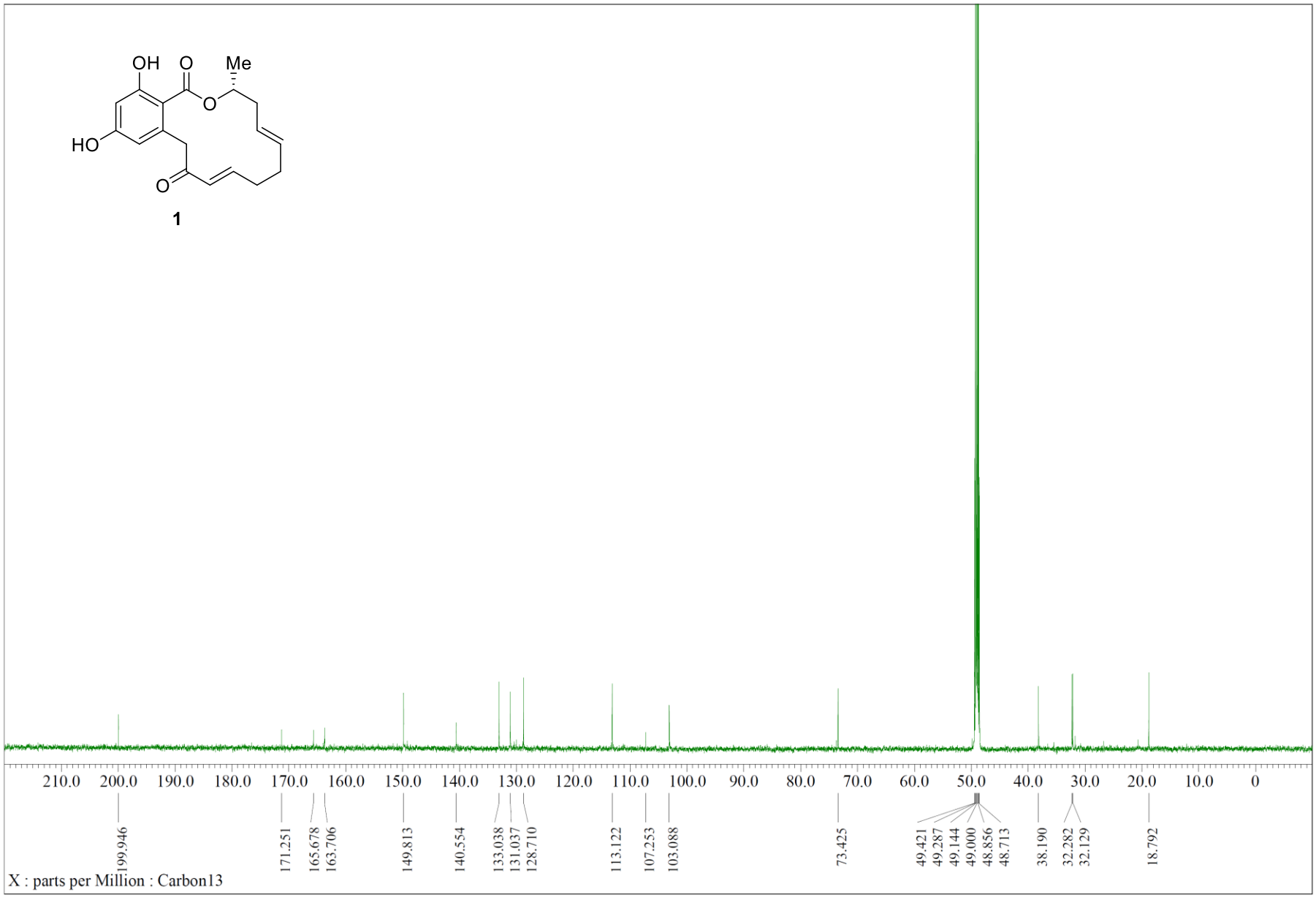


Figure S15. ^{13}C NMR spectrum (150 MHz, CD_3OD) of compound 1.



4. References

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S2) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 16*, Revision C.02, Gaussian, Inc., Wallingford CT, 2019.