Electronic Supplementary Information

Development of a Novel Inducer of Protein–Protein Interactions Based on Aplyronine A

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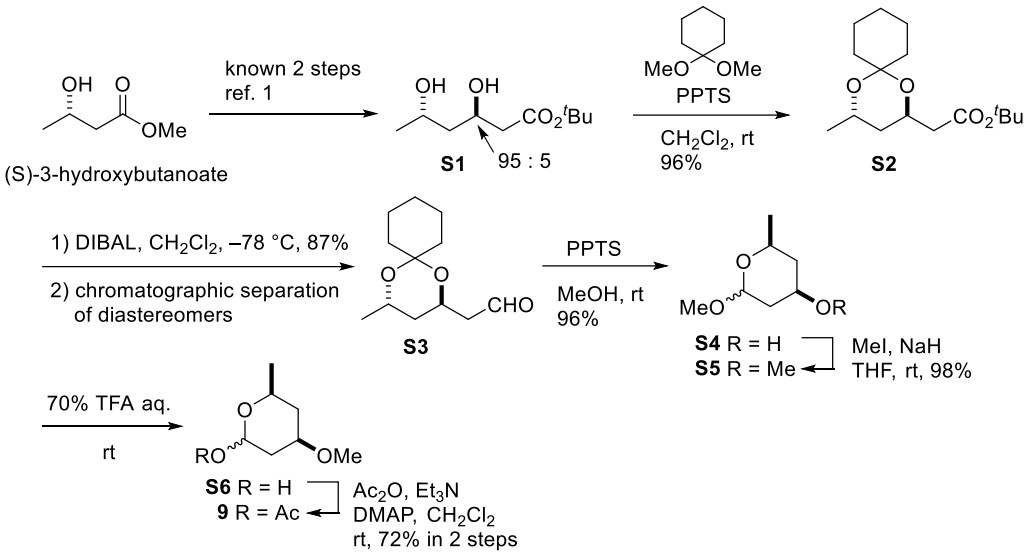
Experimental.

General: All moisture-sensitive reactions were performed under an atmosphere of argon or nitrogen, and the starting materials were azeotropically dried with benzene before use. Anhydrous MeOH, CH_2Cl_2, THF, toluene, DMSO, and pyridine were purchased from Kanto Chemical Co., Inc., or Wako Pure Chemical Industries Ltd., and used without further drying. TLC analyses were conducted on E. Merck precoated silica gel 60 F_{254} (0.25 mm layer thickness). Fuji Silysia silica gel BW-820MH (75–200 μm) and FL-60D (45–75 μm) were used for column chromatography. Optical rotations were measured with a JASCO DIP-370 polarimeter. Infrared (IR) spectra were recorded on a JASCO FT/IR-4100 instrument and only selected peaks are reported in wavenumbers (cm^{-1}). ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 600, a Bruker AVANCE 400, or a Bruker DPX 400 spectrometer. The ^1H and ^{13}C chemical shifts (δ) were referenciated with $CDCl_3$ (δ_H = 7.26 and δ_C = 77.0) respectively. *J* values are given in Hz. The following abbreviations are used for spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, and br = broad. High resolution ESI/TOF mass spectra were recorded on a JEOL AccuTOFCS JMS-T100CS spectrometer.

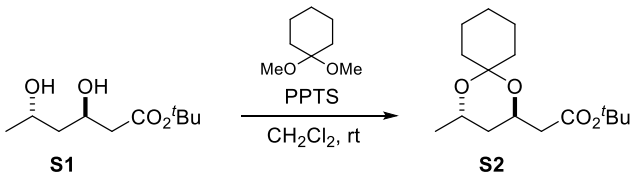
Procedures and spectroscopic data for the compounds

Synthesis of pyran segment 9

The known optically active diol **S1** was synthesized from commercially available (*S*)-3-hydroxybutanoate by Miyashita's method.[1] Diol **S1** contained the inseparable diastereomer at the newly generated secondary hydroxy group (*d.r.* = 95 : 5). For separation of the diastereomers, **S1** was transformed into cyclohexylidene acetal **S2**. Subsequent conversion of **S2** into aldehyde **S3** enabled the isolation of the desired diastereomer by silica gel chromatography. Under acidic condition, removal of cyclohexylidene acetal group and cyclization of resultant diol afforded methyl acetal **S4**, which was transformed into methyl ether **S5**. Hydrolysis of methyl acetal moiety in **S5** and acetylation of the resultant hemiacetal group in **S6** gave pyran segment **9**.

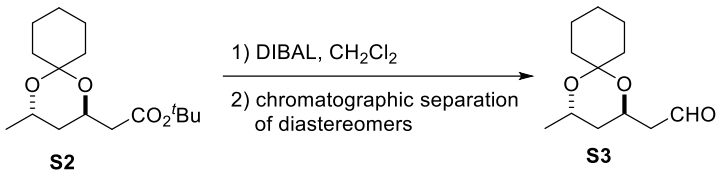


Scheme S1. Synthesis of pyran segment **9**



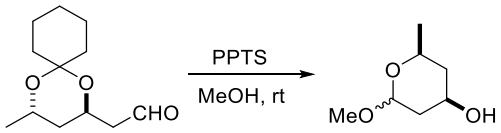
To a stirred solution of diol **S1** (95:5 diastereomeric mixture, 1.11 g, 5.43 mmol) in CH_2Cl_2 (30 mL) were added 1,1-dimethoxycyclohexane (1.34 mL, 8.92 mmol) and PPTS (300 mg, 1.19 mmol) at

room temperature. After stirring for 18 h at room temperature, the mixture was diluted with saturated aqueous $NaHCO_3$ (30 mL) and extracted with CH_2Cl_2 (3 × 30 mL). The combined extracts were washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (44 g, hexane–EtOAc 10 : 1) to give cyclohexylidene acetal **S2** (95:5 diastereomeric mixture, 1.48 g, 96%) as a colorless oil: R_f = 0.27 (hexane : EtOAc = 8 : 1); $[\alpha]_D^{28}$ +7.0 (*c* 1.11, $CHCl_3$); IR ($CHCl_3$) 2938, 1721, 1449, 1368, 1157 cm^{-1}; major isomer: ^1H NMR (400 MHz, $CDCl_3$) δ 4.25 (dddd, *J* = 13.5, 8.4, 5.2, 5.2 Hz, 1H), 3.99 (ddq, *J* = 8.1, 6.3, 6.3 Hz, 1H), 2.43 (dd, *J* = 14.9, 8.4 Hz, 1H), 2.34 (dd, *J* = 14.9, 5.2 Hz, 1H), 1.75–1.29 (m, 12H), 1.45 (s, 9H), 1.19 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6, 100.4, 80.6, 63.5, 62.3, 42.6, 39.6, 34.6, 34.0, 28.3 (3C), 25.7, 23.2, 23.2, 21.9; HRMS (ESI) *m/z* 307.1895, calcd for $C_{16}H_{28}NaO_4$ $[M+Na]^+$ 307.1885.



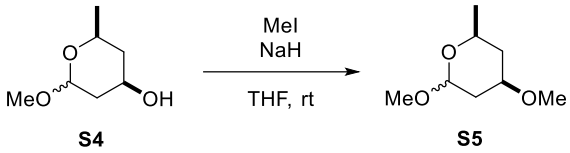
To a stirred solution of cyclohexylidene acetal **S2** (95:5 diastereomeric mixture, 1.72 g, 6.06 mmol) in CH_2Cl_2 (30 mL) was added DIBAL (1.06 M solution in hexane, 6.70 mL, 7.10 mmol) at –78 °C. After stirring for 2 h at same temperature, the mixture was diluted with saturated aqueous Na/K tartrate (10 mL) and stirred at room temperature for 2 h. The resultant mixture was extracted with CH_2Cl_2 (3 × 10 mL). The extracts were combined, washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (30 g, hexane–EtOAc 5 : 1) to give a diastereomeric mixture of aldehyde (1.24 g, 96%). Diastereomers were separated by column chromatography on silica gel (20 g, CH_2Cl_2–Et_2O 100 : 1) to give diastereomerically pure aldehyde **S3** (1.11 g, 87%) as a colorless oil: R_f = 0.23 (hexane : EtOAc = 8 : 1); $[\alpha]_D^{25}$ +18.0 (*c* 0.423, $CHCl_3$); IR ($CHCl_3$) 3026, 3003, 2939, 2858, 1725, 1448, 1364, 1129 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 9.78 (dd, *J* = 2.5, 1.8 Hz, 1H), 4.38 (dddd, *J* = 12.7,

8.8, 4.4, 4.4 Hz, 1H), 4.01 (ddq, *J* = 6.3, 6.3, 6.3 Hz, 1H), 2.61 (ddd, *J* = 16.4, 8.8, 2.5 Hz, 1H), 2.48 (ddd, *J* = 16.4, 4.4, 1.8 Hz, 1H), 1.77–1.30 (m, 12H), 1.21 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.3, 100.6, 62.3, 61.9, 49.4, 39.8, 34.4, 34.0, 25.6, 23.2, 23.1, 21.8; HRMS (ESI) *m/z* 267.1558, calcd for $C_{13}H_{24}NaO_4$ $[M+Na+MeOH]^+$ 267.1572.



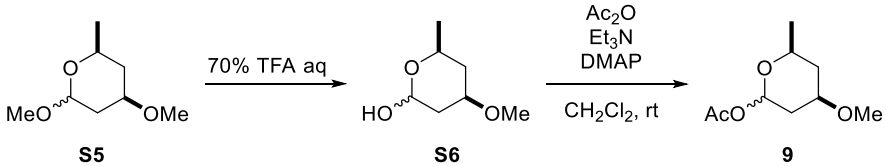
S3 **S4**

To a stirred solution of aldehyde **S3** (896 mg, 4.22 mmol) in MeOH (20 mL) was added PPTS (221 mg, 0.878 mmol) at room temperature. After stirring for 31 h at room temperature, the mixture was diluted with saturated aqueous $NaHCO_3$ (10 mL) and extracted with Et_2O (5 × 10 mL). The extracts were combined, washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (20 g, hexane–EtOAc 5 : 1) to give methyl acetal **S4** (594 mg, 96%) as a colorless oil: R_f = 0.15, 0.19 (hexane : EtOAc = 1 : 1); IR ($CHCl_3$) 3446, 3012, 1385, 1210, 1121 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 3.4 Hz, 1H) [4.29 (dd, *J* = 9.6, 2.0 Hz, 1H)], 4.09 (m, 1H) [3.81 (m, 1H)], 3.84 (ddq, *J* = 12.6, 2.0, 6.3 Hz, 1H) [3.48 (ddq, *J* = 12.5, 2.0, 6.3 Hz, 1H)], 3.33 (s, 3H) [3.50 (s, 3H)], 2.07 (dddd, *J* = 12.6, 3.7, 2.0, 2.0 Hz, 1H) [2.17 (dddd, *J* = 12.0, 4.7, 2.0, 2.0 Hz, 1H)], 1.96 (dddd, *J* = 12.3, 4.6, 2.0, 2.0 Hz, 1H) [1.92 (dddd, *J* = 12.4, 4.8, 2.0, 2.0 Hz, 1H)], 1.65 (br. s, 1H) [1.61 (br. s, 1H)], 1.49 (ddd, *J* = 12.5, 12.3, 3.4 Hz, 1H) [1.33 (ddd, *J* = 12.4, 11.5, 9.6 Hz, 1H)], 1.23 (ddd, *J* = 12.6, 12.6, 11.8 Hz, 1H) [1.18 (ddd, *J* = 12.5, 12.0, 12.0 Hz, 1H)], 1.22 (d, *J* = 6.3 Hz, 3H) [1.28 (d, *J* = 6.3 Hz, 3H)] (the minor counterparts of doubled signals in the ratio of 1:0.67 are in brackets); ^{13}C NMR (100 MHz, $CDCl_3$) δ 99.2 [101.2], 64.0 [68.2], 63.7 [67.1], 54.5 [56.5], 42.6 [42.4], 39.1 [40.8], 21.4 [21.3] (the minor counterparts of doubled signals in the ratio of 1:0.67 are in brackets); HRMS (ESI) *m/z* 169.0770, calcd for $C_7H_{14}O_3$ $[M+Na]^+$ 169.0841.



S4 **S5**

To a stirred solution of methyl acetal **S4** (595 mg, 4.07 mmol) in THF (20 mL) was added 60% NaH (267 mg, 6.66 mmol) at room temperature. After 40 min at room temperature, MeI (700 μL, 11.3 mmol) was added to the mixture, and the mixture was stirred at room temperature for 18 h. The resultant mixture was diluted with saturated aqueous NH_4Cl (20 mL) and extracted with Et_2O (3 × 20 mL). The extracts were combined, washed with brine (40 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (20 g, pentane–Et_2O 4 : 1) to give methyl ether **S5** (637 mg, 98%) as a colorless oil: R_f = 0.45, 0.48 (hexane : EtOAc = 1 : 1); IR ($CHCl_3$) 3009, 2934, 1449, 1385, 1100 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 4.84 (d, *J* = 3.5 Hz, 1H) [4.29 (dd, *J* = 9.8, 2.1 Hz, 1H)], 3.82 (ddq, *J* = 12.6, 2.0, 6.3 Hz, 1H) [3.46 (ddq, *J* = 12.3, 2.0, 6.2 Hz, 1H)], 3.62 (dddd, *J* = 11.3, 11.3, 4.6, 4.6 Hz, 1H) [3.42–3.33 (m, 1H)], 3.33 (s, 3H) [3.50 (s, 3H)], 3.32 (s, 3H) [3.35 (s, 3H)], 2.13 (dddd, *J* = 12.7, 4.6, 2.0, 1.7 Hz, 1H) [2.23 (dddd, *J* = 12.0, 4.6, 2.0, 1.9 Hz, 1H)], 2.02 (dddd, *J* = 12.4, 4.6, 1.7, 1.7 Hz, 1H) [1.98 (dddd, *J* = 12.5, 4.6, 2.1, 1.9 Hz, 1H)], 1.43 (ddd, *J* = 12.4, 11.3, 3.5 Hz, 1H) [1.29 (ddd, *J* = 12.5, 11.2, 9.8 Hz, 1H)], 1.20 (d, *J* = 6.3 Hz, 3H) [1.29 (d, *J* = 6.2 Hz, 3H)], 1.15 (ddd, *J* = 12.7, 12.6, 11.3 Hz, 1H) [1.14 (ddd, *J* = 12.3, 12.0, 11.2 Hz, 1H)] (the minor counterparts of doubled signals in the ratio of 1:0.67 are in brackets); ^{13}C NMR (100 MHz, $CDCl_3$) δ 99.4 [101.2], 72.6 [75.4], 64.0 [68.1], 55.5 [56.3], 54.7 [55.5], 39.4 [38.8], 36.0 [37.2], 21.6 [21.3] (the minor counterparts of doubled signals in the ratio of 1:0.67 are in brackets); HRMS (ESI) *m/z* 183.0987, calcd for $C_8H_{16}O_3$ $[M+Na]^+$ 183.0997.



S5 **S6** **9**

Methyl ether **S6** (941 mg, 5.87 mmol) was treated with 70% aqueous TFA (30 mL) at room temperature. After being stirred at room temperature for 2 h, the reaction mixture was diluted with

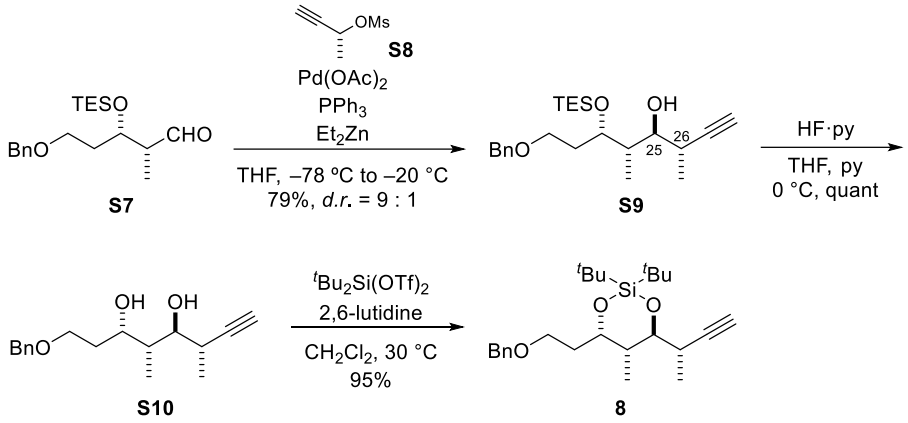
saturated aqueous $NaHCO_3$ (100 mL) at 0 °C and extracted with $CHCl_3$ (5 × 60 mL). The extracts were combined, washed with brine (50 mL), dried over Na_2SO_4, and filtered. Removal of the solvent afforded crude hemiacetal **S6** (920 mg), which was used for the next reaction without further purification.

To a stirred solution of crude hemiacetal **S6** (920 mg) in CH_2Cl_2 (38 mL) were added Et_3N (5.20 mL, 37.3 mmol), Ac_2O (1.10 mL, 11.6 mmol), and DMAP (158 mg, 1.29 mmol) at room temperature. After stirring for 1 h at room temperature, the mixture was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The extracts were combined, washed with brine (10 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (20 g, pentane–Et_2O 4 : 1) to give acetate **9** (789 mg, 72% in 2 steps) as a colorless oil: R_f = 0.39, 0.44 (hexane : EtOAc = 1 : 1); IR ($CHCl_3$) 3010, 1743, 1450, 1375, 1240, 970, 669 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.26 (d, *J* = 3.0 Hz, 1H) [5.64 (dd, *J* = 10.2, 2.3 Hz, 1H)], 3.95 (ddq, *J* = 12.5, 2.2, 6.2 Hz, 1H) [3.60 (ddq, *J* = 11.4, 2.0, 6.2 Hz, 1H)], 3.63 (dddd, *J* = 11.2, 11.2, 4.5, 4.5 Hz, 1H) [3.43 (dddd, *J* = 11.2, 11.2, 4.5, 4.5 Hz, 1H)], 3.34 (s, 3H) [3.34 (s, 3H)], 2.14 (dddd, *J* = 13.2, 4.5, 2.2, 1.9 Hz, 1H) [2.25 (dddd, *J* = 11.9, 4.5, 2.0, 2.0 Hz, 1H)], 2.07 (m, 1H) [1.99 (dddd, *J* = 12.6, 4.5, 2.3, 2.0 Hz, 1H)], 2.06 (s, 3H) [2.10 (s, 3H)], 1.54 (ddd, *J* = 11.2, 10.2, 3.0 Hz, 1H) [1.39 (ddd, *J* = 12.6, 11.2, 10.2 Hz, 1H)], 1.22 (ddd, *J* = 13.2, 12.5, 11.2 Hz, 1H) [1.17 (ddd, *J* = 11.9, 11.4, 11.2 Hz, 1H)], 1.21 (d, *J* = 6.2 Hz, 3H) [1.29 (d, *J* = 6.2 Hz, 3H)] (the minor counterparts of doubled signals in the ratio of 1:0.82 are in brackets); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5 [169.3], 93.0 [92.7], 71.9 [74.9], 66.7 [69.3], 55.3 [55.6], 38.8 [38.4], 34.7 [36.1], 21.5 [21.1], 21.2 [21.1] (the minor counterparts of doubled signals in the ratio of 1:0.82 are in brackets); HRMS (ESI) *m/z* 211.0929, calcd for $C_9H_{16}NaO_4$ $[M+Na]^+$ 211.0946.

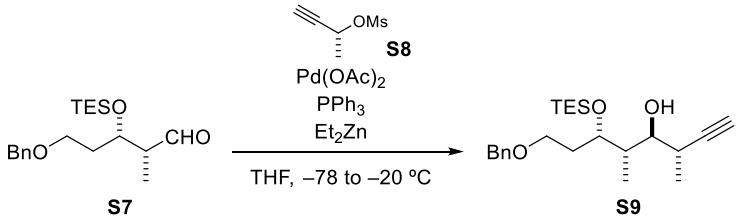
Synthesis of acetylene segment 8

We examined the synthesis of acetylene segment **8** from known aldehyde **S7,**[2] which was the

intermediate in our first-generation total synthesis of aplyronine A (Scheme S2). For the stereoselective introduction of the secondary hydroxy group at C25 and the secondary methyl group at C26, we attempted Marshall's asymmetric propargylation.[3] The addition of a chiral allenylzinc reagent, generated from **S8**, $Pd(OAc)_2$, PPh_3, and Et_2Zn, to aldehyde **S7** gave acetylene **S9**, which has the desired four contiguous stereogenic centers. Removal of the TES group gave diol **S10**, which was transformed into acetylene segment **8**.



Scheme S2. Synthesis of acetylene segment **8**

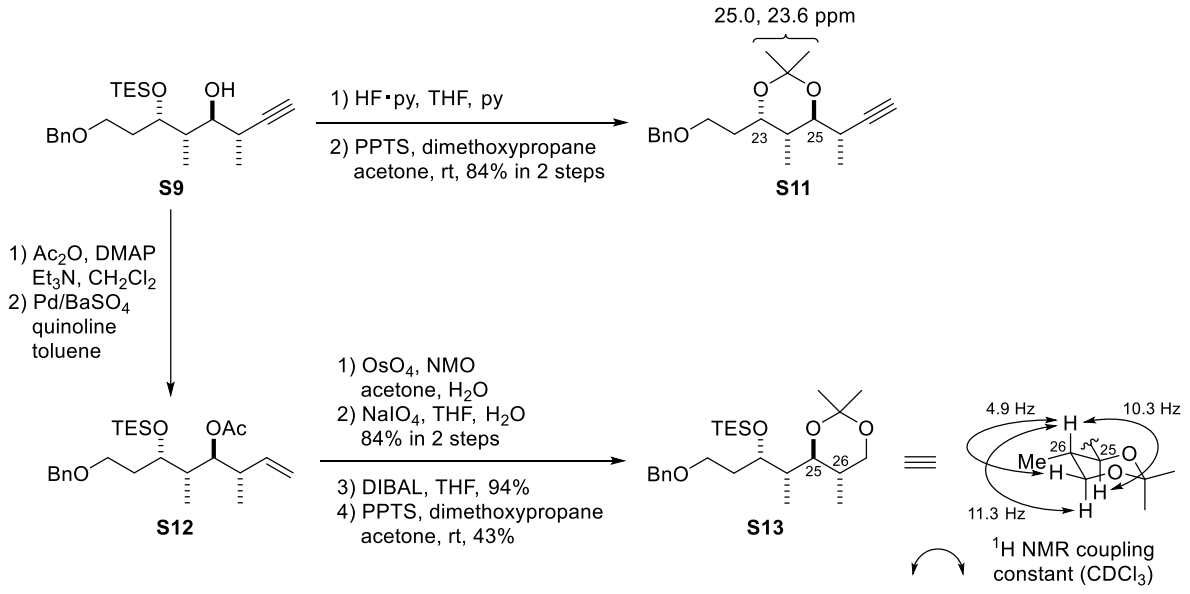


To a stirred solution of $Pd(OAc)_2$ (30.0 mg, 0.134 mmol) in THF (4.0 mL) were added solutions of PPh_3 (183 mg, 0.523 mmol) in THF (2.0 mL), aldehyde **S7** (183 mg, 0.523 mmol) in THF (2.0 mL), and mesylate **S8** (160 mg, 1.08 mmol) in THF (2.0 mL) at –78 °C. Et_2Zn (1.1 M hexane solution, 1.50 mL, 1.60 mmol) was slowly added to the mixture at –78 °C. After stirring for 5 min at –78 °C, the reaction mixture was warmed to –20 °C and stirred for 15 h. The resultant mixture was diluted with saturated aqueous NH_4Cl (6.0 mL) and extracted Et_2O (3 × 6 mL). The extracts were combined, washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (9.3 g, hexane–EtOAc 20 : 1) to afford acetylene

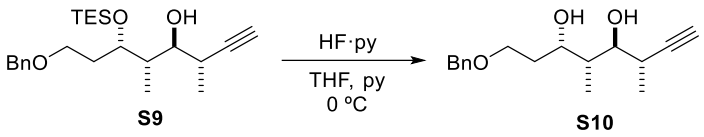
S9 (103 mg, 51%) and diastereomeric mixture of **S9** (57.3 mg, 28%, *d.r.* = 1 : 0.36) as yellow oils, respectively (total; 160 mg, 79%, *d.r.* = 91 : 1): R_f = 0.48 (hexane : EtOAc = 5 : 1); $[\alpha]_D^{26}$ –32.5 (*c* 1.00, $CHCl_3$); IR (film) 3427, 3307, 3008, 2959, 2877, 2112, 1455, 1110, 1003 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 4.52 (d, *J* = 11.8 Hz, 1H), 4.48 (d, *J* = 11.8 Hz, 1H), 4.36 (d, *J* = 2.2 Hz, 1H), 4.03 (dt, *J* = 8.9, 3.2 Hz, 1H), 3.59–3.53 (m, 2H), 3.48 (ddd, *J* = 9.9, 2.3, 2.2 Hz, 1H), 2.58 (ddq, *J* = 2.3, 2.3, 7.1 Hz, 1H), 2.11 (ddq, *J* = 9.9, 8.9, 7.0 Hz, 1H), 2.00 (d, *J* = 2.3 Hz, 1H), 1.89–1.80 (m, 2H), 1.30 (d, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.81 (d, *J* = 7.0 Hz, 3H), 0.63 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.6, 128.5 (2C), 127.8 (2C), 127.7, 85.2, 76.1, 74.3, 73.1, 70.2, 67.3, 41.6, 31.9, 30.5, 17.8, 13.5, 7.0 (3C), 5.0 (3C); HRMS (ESI) *m/z* 413.2486, calcd for $C_{23}H_{38}NaO_3Si$ $[M+Na]^+$ 413.2488.

Determination of the absolute configurations at C25 and C26 in **S9**

The stereochemistry of **S9** was determined as follows. Acetylene **S9** was converted into 1,3-acetonide **S11**. The relative stereochemistry of C23 and C25 in **S11** was determined to be anti by the ^{13}C chemical shifts of two acetonide methyl groups (δ_C 23.6, 25.0).[2] In addition, acetylene **S9** was converted into 1,3-acetonide **S13**, and the relative stereochemistry of C25 and C26 was determined to be anti by ^1H-^1H coupling constants.

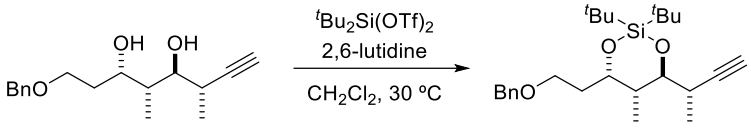


Determination of the absolute configurations at C25 and C26 in **S9**



S9 **S10**

A solution of acetylene **S9** (225 mg, 0.575 mmol) in a 1 : 3 : 5 mixture of HF·py, py, and THF (40 mL) was stirred at 0 °C for 3 h. The reaction mixture poured into saturated aqueous $NaHCO_3$ (500 mL) at 0 °C, and extracted with EtOAc (3 × 100 mL). The combined extracts were washed with brine (50 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (3.8 g, hexane–EtOAc 5 : 1 → 2 : 1) to afford diol **S10** (158 mg, quant.) as a colorless oil: R_f = 0.28 (hexane : EtOAc = 1 : 1); $[\alpha]_D^{26}$ 1.44 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3452, 3306, 3010, 2875, 2109, 1454, 1099, 984, 699, 641 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.33–7.28 (m, 5H), 4.53 (s, 2H), 4.16 (m, 1H), 3.76 (ddd, *J* = 9.2, 4.8, 4.8 Hz, 1H), 3.67 (ddd, *J* = 9.2, 9.2, 4.0 Hz, 1H), 3.53 (br. s, 1H), 3.47 (m, 1H), 3.43 (br. s, 1H), 2.63 (ddq, *J* = 2.4, 2.4, 7.1 Hz, 1H), 2.10 (d, *J* = 2.4 Hz, 1H), 2.00–1.92 (m, 2H), 1.63 (dddd, *J* = 8.9, 4.8, 4.0, 2.2 Hz, 1H), 1.28 (d, *J* = 7.1 Hz, 3H), 0.89 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.0, 128.6 (2C), 128.0, 127.8 (2C), 85.1, 76.7, 73.6 (2C), 70.7, 70.0, 40.9, 32.7, 30.6, 18.0, 12.0; HRMS (ESI) *m/z* 299.1602, calcd for $C_{17}H_{24}NaO_3$ $[M+Na]^+$ 299.1623.



S10 **8**

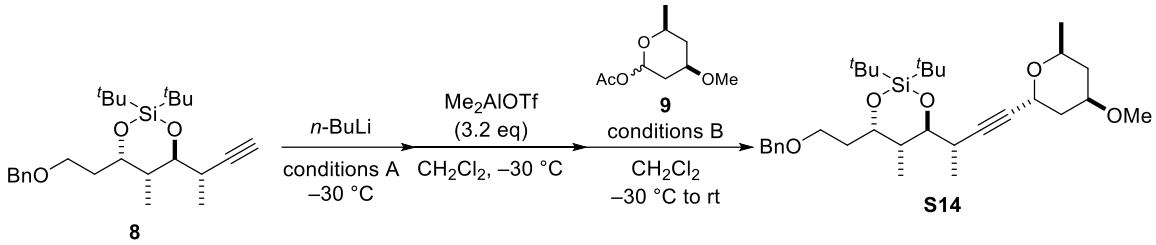
To a stirred solution of diol **S10** (21.3 mg, 77.1 μmol) in CH_2Cl_2 (0.40 mL) were added 2,6-lutidine (40.0 μL, 345 μmol) and $^tBu_2Si(OTf)_2$ (50.0 μL, 154 μmol) at room temperature. After stirring for 2 h at 30 °C, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ (1.0 mL) and extracted with EtOAc (2 × 1.0 mL). The extracts were combined, washed with brine (1.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on

silica gel (0.8 g, hexane–EtOAc 8 : 1 → 1 : 1) to afford acetylene segment **8** (30.5 mg, 95%) as a colorless oil: R_f = 0.65 (hexane : EtOAc = 5 : 1); IR ($CHCl_3$) 3306, 2964, 2934, 2859, 2109, 1474, 1363, 1149, 1065, 826, 647 cm^{-1}; $[\alpha]_D^{25}$ –62.8 (*c* 1.00, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.27 (m, 5H), 4.55 (s, 2H), 4.16 (ddd, *J* = 11.0, 5.5, 3.0 Hz, 1H), 3.76–3.68 (m, 2H), 3.67 (dd, *J* = 9.8, 2.4 Hz, 1H), 2.57 (ddq, *J* = 2.4, 2.4, 7.0 Hz, 1H), 2.49 (ddq, *J* = 9.8, 5.5, 7.1 Hz, 1H), 2.00 (d, *J* = 2.5 Hz, 1H), 1.83–1.73 (m, 2H), 1.28 (d, *J* = 7.0 Hz, 3H), 1.04 (s, 9H), 0.94 (s, 9H), 0.80 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 128.5 (2C), 127.8 (2C), 127.6, 85.4, 75.3, 73.9, 73.3, 69.8, 68.1, 39.8, 31.3, 30.5, 27.7 (3C), 27.3 (3C), 21.6, 21.0, 17.6, 13.3; HRMS (ESI) *m/z* 439.2665, calcd for $C_{25}H_{40}NaO_3Si$ $[M+Na]^+$ 439.2644.

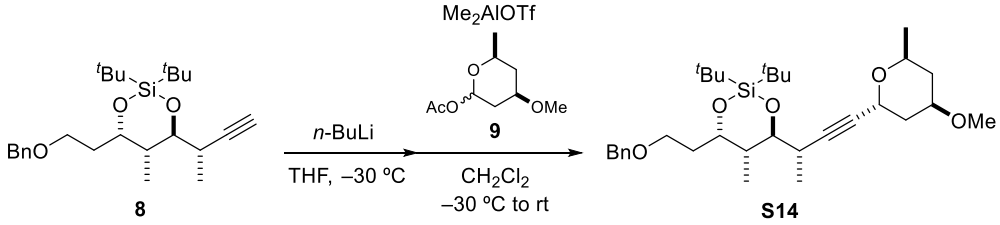
Study of coupling reaction between **8** and **9**

The coupling reaction between **8** and **9** was next examined based on the conditions reported by Miyashita[1] (Table 1). The coupling reaction using an excess of the pyran segment **9** gave the adduct **S14** in 27% yield (entry 1). Under these reaction conditions, unused acetylene segment **8** was recovered in quantitative yield but **9** was not detected. Therefore, we next examined this coupling reaction using an excess of acetylene segment **8**, resulting in an improved yield of 55% (entry 2). Next, we changed the solvent for the preparation of the Li-acetylide from **8**. The Li-acetylide was generated *in situ* from **8** in THF, and participated in the coupling reaction with Me_2AlOTf and **9** to provide the coupling compound **S14** in 66% yield (entry 3). Finally, use of the minimum amount of solvent improved the yield of **S14** (entry 4). The stereochemistry of **S14** was determined by ^1H NMR spectrum.

Table 1 Coupling reaction between acetylene segment **8** and pyran segment **9**



entry	conditions A			conditions B		yield (%)
	8 (equiv)	^{n}BuLi (equiv)	solvent	**9** (equiv)	conc (M)	
1	1.0	1.0	CH_2Cl_2	1.4	0.1	27
2	1.4	1.4	CH_2Cl_2	1.0	0.1	55
3	1.4	1.4	THF	1.0	0.1	66
4	1.4	1.4	THF	1.0	0.3	80



(Preparation of Me_2AlOTf)[2]

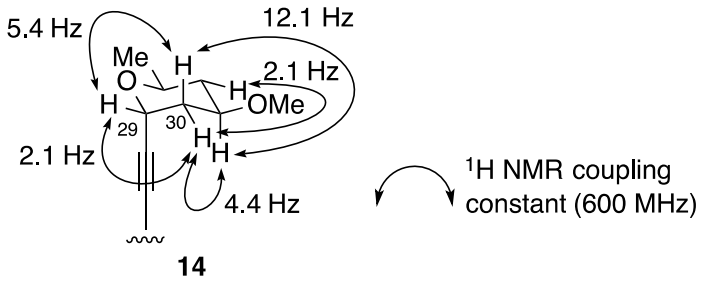
To a stirred solution of Me_3Al (1.4 M solution in hexane, 1.72 mL, 2.41 mmol) in CH_2Cl_2 (0.5 mL) was added TfOH (220 μL, 2.49 mmol) in 0 °C. The resultant mixture was stirred at 0 °C for 30 min to afford 1.0 M Me_2AlOTf solution.

To a stirred solution of acetylene segment **8** (372 mg, 0.892 mmol) in THF (0.46 mL) was added ^{n}BuLi (1.6 M hexane solution, 610 μL, 0.976 mmol) at –30 °C. After stirring for 2 h at –30 °C, the above-mentioned 1.0 M Me_2AlOTf solution (2.03 mL, 2.03 mmol) was added to the reaction mixture at –30 °C. After solution of pyran segment **9** (120 mg, 0.637 mmol) in CH_2Cl_2 (0.50 mL) was added, the reaction mixture was stirred at –30 °C for 30 min. The resultant mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was diluted with saturated aqueous Na/K

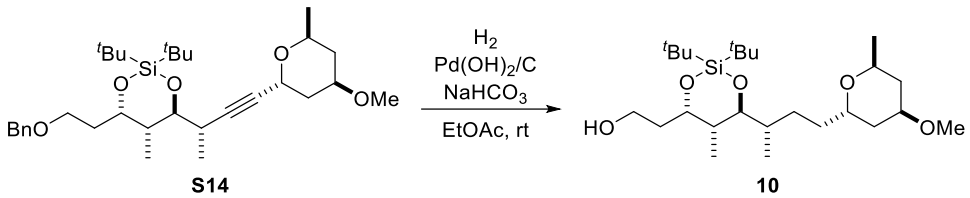
tartrate (5.0 mL) and saturated aqueous $NaHCO_3$ (5.0 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The extracts were combined, washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (10 g, hexane–EtOAc 24 : 1 → 14 : 1) to afford coupling compound **S14** (280 mg, 80%) and recovered acetylene segment **8** (126 mg, 34%) as colorless oils, respectively: R_f = 0.38 (hexane : EtOAc = 1 : 1); $[\alpha]_D^{26}$ – 66.6 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2971, 2933, 2860, 1473, 1063 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.26 (m, 5H), 4.84 (ddd, *J* = 5.4, 2.2, 2.1 Hz, 1H), 4.55 (s, 2H), 4.17 (ddd, *J* = 11.2, 5.6, 2.7 Hz, 1H), 4.00 (ddq, *J* = 12.1, 2.0, 6.2 Hz, 1H), 3.75–3.70 (m, 2H), 3.68 (dd, *J* = 9.8, 2.4 Hz, 1H), 3.64 (dddd, *J* = 12.1, 12.1, 4.4, 4.4 Hz, 1H), 3.33 (s, 3H), 2.62 (ddq, *J* = 2.4, 2.2, 7.0 Hz, 1H), 2.43 (ddq, *J* = 9.8, 5.6, 7.1 Hz, 1H), 2.06 (dddd, *J* = 12.1, 4.4, 2.1, 2.1 Hz, 1H), 2.00 (dddd, *J* = 12.4, 4.4, 2.1, 2.0 Hz, 1H), 1.82–1.72 (m, 2H), 1.56 (ddd, *J* = 12.1. 12.1, 5.4 Hz, 1H), 1.27 (d, *J* = 7.0 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.10 (ddd, *J* = 12.4, 12.1, 12.1 Hz, 1H), 1.03 (s, 9H), 0.93 (s, 9H), 0.81 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.8, 128.5 (2C), 127.8 (2C), 127.6, 87.8, 79.8, 75.1, 73.8 (2C), 73.3, 68.0, 66.8, 64.8, 55.5, 40.2, 39.8, 36.5, 31.4, 30.7, 27.6 (3C), 27.3 (3C), 21.9, 21.6, 20.9, 17.7, 13.2; HRMS (ESI) *m/z* 567.3491, calcd for $C_{32}H_{52}NaO_4Si$ $[M+Na]^+$ 567.3482.

Determination of the absolute configuration at C29 in coupling compound **S14**

Configuration at C29 in coupling compound **S14** was determined by ^1H-^1H coupling constants.

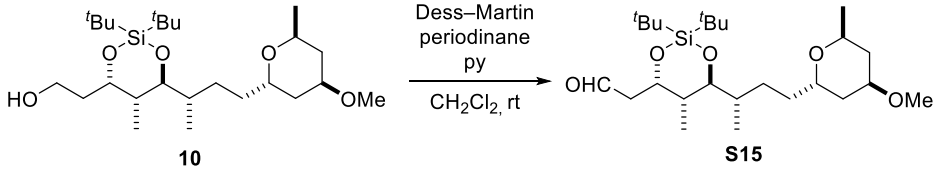


Determination of the absolute configuration at C29 in **S14**



S14 **10**

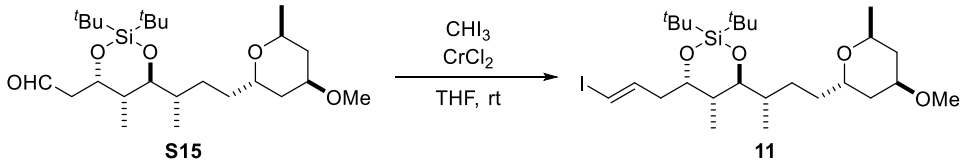
A mixture of coupling compound **S14** (179 mg, 0.329 mmol) and 20% $Pd(OH)_2/C$ (wetted with ca. 50% water, 20.5 mg) in EtOAc (4.0 mL) was stirred under hydrogen atmosphere at room temperature for 4 h. The mixture was filtered through a pad of Celite, and the residue was washed with EtOAc. The filtrate and the washings were combined and concentrated. The residual oil was purified by column chromatography on silica gel (3.5 g, hexane–EtOAc 10 : 1 → 5 : 1) to afford alcohol **10** (134 mg, 89%) as a colorless oil: R_f = 0.20 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{26}$ –78.0 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3471, 2963, 2935, 2860, 1474, 1383, 1064, 825, 648 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 4.26 (ddd, *J* = 11.4, 5.5, 1.8 Hz, 1H), 4.01 (m, 1H), 3.93–3.84 (m, 2H), 3.75 (dd, *J* = 9.2, 2.3 Hz, 1H), 3.69 (ddq, *J* = 10.2, 2.2, 6.2 Hz, 1H), 3.53 (dddd, *J* = 10.3, 10.3, 4.3, 4.3 Hz, 1H), 3.34 (s, 3H), 2.59 (br. s, 1H), 2.26 (m, 1H), 1.98 (dddd, *J* = 12.3, 4.3, 2.2, 2.2 Hz, 1H), 1.91–1.82 (m, 2H), 1.81 (dddd, *J* = 12.3, 4.3, 2.2, 2.2 Hz, 1H), 1.62–1.57 (m, 3H), 1.44–1.29 (m, 2H), 1.23 (m, 1H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.17 (ddd, *J* = 12.3, 10.3, 10.2 Hz, 1H), 1.01 (s, 9H), 1.00 (s, 9H), 1.00 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 77.9, 77.5, 73.5, 71.6, 64.7, 62.3, 55.4, 38.9, 38.9, 35.1, 34.9, 32.8, 29.2, 27.8 (3C), 27.5 (3C), 24.1, 21.9, 21.8, 21.1, 16.9, 13.5; HRMS (ESI) *m/z* 481.3348, calcd for $C_{25}H_{50}NaO_5Si$ $[M+Na]^+$ 481.3325.



10 **S15**

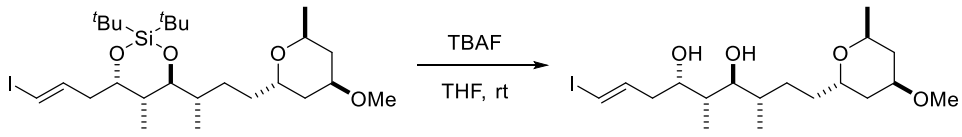
To a stirred solution of alcohol **10** (198 mg, 0.434 mmol) in CH_2Cl_2 (2.2 mL) were added pyridine (120 μL, 1.49 mmol) and Dess–Martin periodinane (200 mg, 0.472 mmol) at 0 °C. After stirring for 20 min at room temperature, the mixture was diluted with saturated aqueous $Na_2S_2O_3$ (5.0 mL), saturated aqueous $NaHCO_3$ (5.0 mL), and H_2O (5.0 mL). The resultant mixture was extracted with

Et_2O (3 × 5.0 mL). The extracts were combined, washed with brine (1.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (24.7 g, hexane–EtOAc 20 : 1 → 19 : 1 → 5 : 1) to afford aldehyde **S15** (167 mg, 85%) as a colorless oil: R_f = 0.53 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{24}$ –71.9 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2963, 2934, 2860, 1726, 1473, 1384, 1128, 1021, 825, 669 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 9.84 (dd, *J* = 4.0, 1.4 Hz, 1H), 4.69 (ddd, *J* = 11.2, 5.6, 3.2 Hz, 1H), 4.03–3.99 (m, 1H), 3.73 (dd, *J* = 9.7, 1.9 Hz, 1H), 3.69 (ddq, *J* = 10.1, 2.0, 6.3 Hz, 1H), 3.54 (dddd, *J* = 10.1, 10.1, 4.2, 4.2 Hz, 1H), 3.34 (s, 3H), 2.65 (ddd, *J* = 15.2, 11.2, 4.0 Hz, 1H), 2.39 (ddd, *J* = 15.2, 3.2, 1.4 Hz, 1H), 2.36 (ddq, *J* = 9.7, 5.6, 7.1 Hz, 1H), 1.98 (dddd, *J* = 12.5, 4.2, 2.0, 2.0 Hz, 1H), 1.90 (m, 1H), 1.81 (dddd, *J* = 12.9, 4.2, 2.0, 2.0 Hz, 1H), 1.67–1.58 (m, 2H), 1.43–1.32 (m, 2H), 1.23 (m, 1H), 1.20 (d, *J* = 6.3 Hz, 3H), 1.18 (ddd, *J* = 12.5, 10.1, 10.1 Hz, 1H), 1.01 (d, *J* = 6.8 Hz, 3H), 1.00 (s, 9H), 0.97 (s, 9H), 0.74 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.6, 77.2, 73.5, 73.1, 71.4, 64.8, 55.4, 45.8, 38.8, 38.3, 35.2, 34.4, 29.1, 27.6 (3C), 27.3 (3C), 23.7, 21.9, 21.8, 20.9, 16.9, 13.2; HRMS (ESI) *m/z* 479.3172, calcd for $C_{25}H_{48}NaO_5Si$ $[M+Na]^+$ 479.3169.



THF was degassed by freeze-thawing. To a stirred solution of aldehyde **S15** (167 mg, 0.366 mmol) in THF (6.8 mL) were added $CrCl_2$ (460 mg, 3.74 mmol) and CHI_3 (288 mg, 0.731 mmol) at room temperature in a glove box. After stirring for 2 h at room temperature in a glove box, the resultant mixture was diluted with saturated aqueous $NaHCO_3$ (5.0 mL) and extracted with Et_2O (3 × 5.0 mL). The extracts were combined, washed with brine (1.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (42.0 g, hexane–EtOAc 50 : 1 → 0 : 1) to afford iodoolefin **11** (179 mg, 85%, *E* / *Z* = 5.5 : 1) as a colorless solid: R_f = 0.18 (hexane : EtOAc = 2 : 1); m.p. 104–106 °C; $[\alpha]_D^{25}$ –97.5 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$)

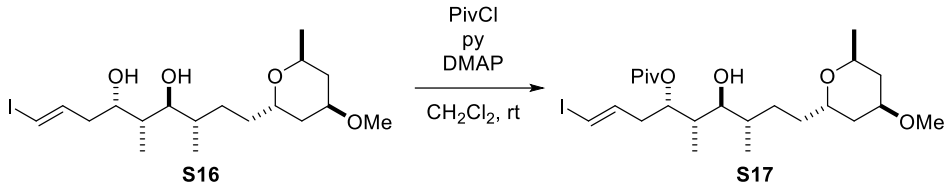
2934, 2859, 2736, 1474, 1384, 1125, 1065, 825, 669 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.70 (ddd, *J* = 14.5, 7.6, 6.5 Hz, 1H), 6.08 (ddd, *J* = 14.5, 1.2, 1.2 Hz, 1H), 4.05 (ddd, *J* = 11.0, 5.3, 2.8 Hz, 1H), 4.01 (m, 1H), 3.72 (dd, *J* = 9.6, 2.1 Hz, 1H), 3.68 (ddq, *J* = 10.2, 2.1, 6.3 Hz, 1H), 3.54 (dddd, *J* = 10.2, 10.2, 4.2, 4.2 Hz, 1H), 3.34 (s, 3H), 2.31 (dddd, *J* = 14.5, 11.0, 6.5, 1.2 Hz, 1H), 2.26 (ddq, *J* = 9.6, 5.3, 7.1 Hz, 1H), 2.17 (dddd, *J* = 14.5, 7.6, 2.8, 1.2 Hz, 1H), 1.98 (dddd, *J* = 12.5, 4.2, 2.1, 2.1 Hz, 1H), 1.89 (m, 1H), 1.81 (dddd, *J* = 12.8, 4.2, 2.1, 2.1 Hz, 1H), 1.62–1.57 (m, 2H), 1.42–1.30 (m, 2H), 1.24 (m, 1H), 1.19 (d, *J* = 6.3 Hz, 3H), 1.17 (ddd, *J* = 12.5, 10.2, 10.2 Hz, 1H), 1.00 (s, 9H), 0.99 (d, *J* = 6.5 Hz, 3H), 0.99 (s, 9H), 0.75 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.6, 77.5, 76.0, 75.8, 73.5, 71.5, 64.7, 55.4, 38.9, 38.7, 38.0, 35.1, 34.6, 29.1, 27.7 (3C), 27.4 (3C), 23.9, 21.9, 21.8, 21.0, 16.9, 13.3; HRMS (ESI) *m/z* 603.2345, calcd for $C_{26}H_{49}INaO_4Si$ $[M+Na]^+$ 603.2342.



11 **S16**

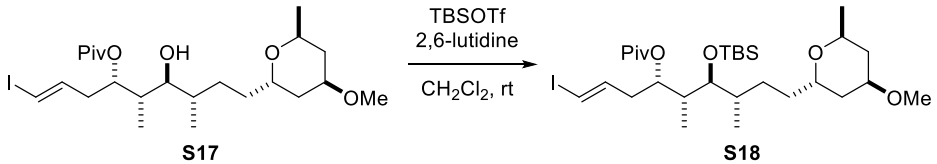
To a stirred solution of iodoolefin **11** (166 mg, 0.286 mmol) in THF (1.7 mL) was added TBAF (1.0 M solution in THF, 170 μL, 1.70 mmol) at room temperature. After stirring for 1.5 d at room temperature, the reaction mixture was diluted with water and extracted with EtOAc (4 × 3.0 mL). The extracts were combined, washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (5.0 g, hexane–EtOAc 4 : 1 → 3 : 1 → 1 : 1) to afford diol **S16** (125 mg, 99%) as a colorless oil: R_f = 0.22 (hexane : EtOAc = 1 : 1); $[\alpha]_D^{22}$ –14.9 (*c* 1.08, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$) δ 6.55 (ddd, *J* = 14.4, 7.4, 7.0 Hz, 1H), 6.13 (d, *J* = 14.4 Hz, 1H), 4.05–3.96 (m, 2H), 3.72 (dddd, *J* = 12.5, 9.3, 6.2, 3.0 Hz, 1H), 3.53 (ddq, *J* = 8.8, 3.9, 6.3 Hz, 1H), 3.33 (s, 3H), 3.35 (m, 1H), 2.97 (br. s, 1H), 2.31 (ddd, *J* = 14.2, 7.5, 7.4 Hz, 1H), 2.13 (ddd, *J* = 14.2, 7.0, 6.7 Hz, 1H), 1.96 (m, 1H), 1.89–1.74 (m, 3H), 1.70 (m, 1H), 1.66–1.56 (m, 2H), 1.21 (d, *J* = 6.3 Hz, 3H), 1.34–1.18 (m, 2H), 0.97 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.98–0.85 (m, 1H) A signal due to a proton (OH) was not obserbed.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.2, 80.4, 76.9, 73.2, 71.3, 70.6, 65.0, 55.3, 40.9, 38.1, 37.3, 35.3, 34.9, 29.0, 27.7, 21.6,

16.5, 11.4; HRMS (ESI) *m/z* 463.1326, calcd for $C_{18}H_{33}NaIO_4$ $[M+Na]^+$ 463.1321.



S16 **S17**

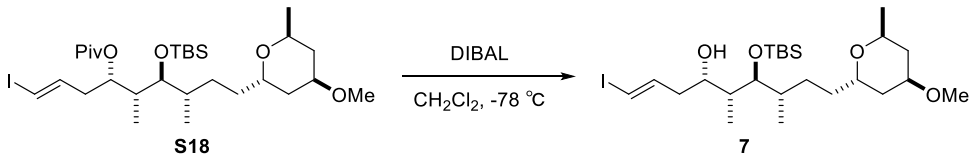
To a stirred solution of diol **S16** (22.7 mg, 51.5 μmol) in CH_2Cl_2 (0.50 mL) and pyridine (0.25 mL) were added PivCl (12.7 μL, 103 μmol) and DMAP (3.1 mg, 25.8 μmol) at room temperature. After stirring for 5 h at room temperature, the reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 2.0 mL). The extracts were combined, washed with brine (3.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (0.7 g, hexane–EtOAc 6 : 1 → 4 : 1) to afford pivalate **S17** (27.0 mg, quant.) as a colorless oil: R_f = 0.78 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{25}$ –8.5 (*c* 0.95, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (ddd, *J* = 14.4, 7.7, 6.4 Hz, 1H), 6.12 (d, *J* = 14.4 Hz, 1H), 5.30 (ddd, *J* = 7.4, 4.2, 1.5 Hz, 1H), 3.99 (m, 1H), 3.68 (dddd, *J* = 12.8, 9.4, 6.3, 3.0 Hz, 1H), 3.53 (ddq, *J* = 9.8, 4.7, 6.2 Hz, 1H), 3.33 (s, 3H), 3.04 (br. s, 1H), 2.95 (dd, *J* = 9.5, 2.3 Hz, 1H), 2.48 (ddd, *J* = 15.2, 7.7, 7.4 Hz, 1H), 2.21 (dddd, *J* = 15.2, 6.4, 4.4, 1.5 Hz, 1H), 1.97 (m, 1H), 1.88 (m, 1H), 1.80 (dddd, *J* = 12.8, 4.0, 2.0, 1.8 Hz, 1H), 1.75 (dddd, *J* = 16.2, 7.1, 6.7, 1.8 Hz, 1H), 1.66 (m, 1H), 1.59 (ddd, *J* = 12.8, 10.4, 5.4 Hz, 1H), 1.39 (ddd, *J* = 12.8, 6.7, 3.1 Hz, 1H), 1.22 (d, *J* = 6.2 Hz, 3H), 1.20 (s, 9H), 1.32-1.13 (m, 3H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.85 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.6, 141.7, 77.6, 76.5, 73.3, 71.6, 71.4, 64.6, 55.3, 40.0, 39.4, 39.1, 38.6, 34.9, 33.3, 29.2, 27.3 (3C), 24.2, 21.8, 17.7, 9.7; HRMS (ESI) *m/z* 547.1868, calcd for $C_{23}H_{41}NaIO_5$ $[M+Na]^+$ 547.1896.



S17 **S18**

To a stirred solution of pivalate **S17** (145 mg, 0.276 mmol) in CH_2Cl_2 (2.5 mL) were added 2,6-lutidine (130 μL, 1.11 mmol) and TBSOTf (0.13 mL, 0.55 mmol) at room temperature. After stirring

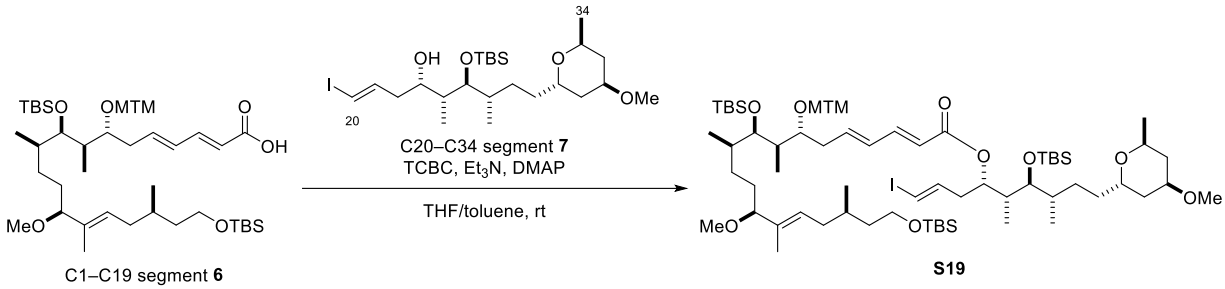
for 2 h at room temperature, the reaction mixture was diluted with water and extracted with CH_2Cl_2 (3 × 3.0 mL). The extracts were combined, washed with brine (5.0 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (4.4 g, hexane–EtOAc 12 : 1 → 9 : 1) to afford TBS ether **S18** (172 mg, 97%) as a colorless oil: R_f = 0.67 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{29}$ –20.7 (*c* 2.11, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$) δ 6.41 (ddd, *J* = 14.5, 7.4, 7.4 Hz, 1H), 6.06 (ddd, *J* = 14.5, 1.0, 1.0 Hz, 1H), 5.02 (ddd, *J* = 6.4, 6.4, 4.2 Hz, 1H), 3.96 (dddd, *J* = 9.6, 4.8, 4.8, 2.6 Hz, 1H), 3.66 (dddd, *J* =13.0, 9.6, 6.4, 3.0 Hz, 1H), 3.51 (ddq, *J* = 9.8, 4.7, 6.1 Hz, 1H), 3.39 (dd, *J* = 6.7, 2.4 Hz, 1H), 3.33 (s, 3H), 2.33 (ddd, *J* = 7.4, 6.4, 1.0 Hz, 2H), 1.97 (m, 1H), 1.86–1.76 (m, 3H), 1.65–1.53 (m, 2H), 1.42 (m, 1H), 1.27–1.13 (m, 3H), 1.19 (d, *J* = 6.1 Hz, 3H), 1.17 (s, 9H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.90 (d, *J* = 6.7 Hz, 3H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 177.7, 141.8, 78.3, 73.3, 72.3, 71.9, 64.6, 55.2, 41.1, 39.8, 39.0, 38.7, 36.2, 34.8, 29.8, 27.5, 27.3, 27.2 (3C), 26.2 (3C), 25.9, 21.7, 18.4, 17.3, 11.4, –3.9, –4.1; HRMS (ESI) *m/z* 661.2742, calcd for $C_{29}H_{55}NaIO_5Si$ $[M+Na]^+$ 661.2761.



S18 **7**

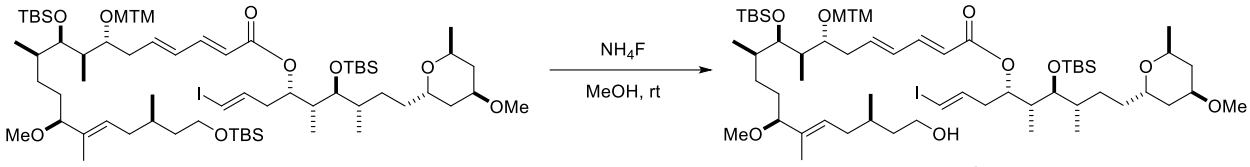
To a stirred solution of TBS ether **S18** (35.0 mg, 54.8 μmol) in CH_2Cl_2 (1.0 mL) was added solution of DIBAL (1.06 M solution in CH_2Cl_2, 160 μL, 170 μmol) at –78 °C. After stirring for 2 h at –78 °C, the reaction mixture was diluted with saturated aqueous Na/K tartrate (10 mL) and stirred at room temperature for 2 h. The resultant mixture was extracted with CH_2Cl_2 (3 × 2 mL). The extracts were combined, washed with brine (3 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography on silica gel (1.1 g, hexane–EtOAc 9 : 1 → 7 : 1 → 5 : 1) to afford alcohol **7** (25.6 mg, 84%) as a colorless oil: R_f = 0.51 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{29}$ –25.5 (*c* 2.13, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (ddd, *J* = 14.5, 7.9, 6.8 Hz, 1H), 6.10 (ddd, *J* = 14.5, 1.3, 1.3 Hz, 1H), 4.12 (dd, *J* = 6.9, 6.8 Hz, 1H), 3.96 (m, 1H), 3.70 (dddd, *J* = 12.8, 9.5, 6.4,

3.0 Hz, 1H), 3.57–3.46 (m, 3H), 3.33 (s, 3H), 2.28 (dddd, *J* = 14.2, 7.9, 6.8, 1.3 Hz, 1H), 2.05 (ddd, *J* = 14.2, 6.9, 6.8 Hz, 1H), 1.97 (ddq, *J* = 12.4, 8.5, 2.1 Hz, 1H), 1.87–1.76 (m, 2H), 1.76–1.65 (m, 2H), 1.60 (ddd, *J* = 12.9, 10.0, 5.4 Hz, 1H), 1.52 (m, 1H), 1.29–1.16 (m, 2H), 1.21 (d, *J* = 7.5 Hz, 3H), 1.08 (ddd, *J* = 10.7, 4.1, 2.4 Hz, 1H), 0.98 (d, *J* = 8.5 Hz, 3H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.91 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 83.1, 76.5, 73.2, 71.6, 70.0, 64.9, 55.3, 41.3, 38.3, 38.1, 36.8, 34.8, 30.2, 29.7, 26.1 (3C), 21.7, 18.2, 15.7, 12.3, –3.9, –4.0; HRMS (ESI) *m/z* 577.2175, calcd for $C_{24}H_{47}NaIO_4Si$ $[M+Na]^+$ 577.2186.



To a stirred solution of the C1–C19 segment **6** (86.0 mg, 0.120 mmol) in THF (5.0 mL) were added Et_3N (100 μL, 0.720 mmol) and TCBC (94.0 μL, 0.601 mmol) at 0 °C. After stirring at 0 °C for 5 min, the mixture was allowed to warm to room temperature and stirred for 2 h. Then, a solution of the C20–C34 segment **7** (92.5 mg, 0.170 mmol) and DMAP (147 mg, 1.20 mmol) in toluene (5.0 mL) was added. The resulting mixture was stirred for 1 h, poured into saturated aqueous $NaHCO_3$ (10 mL), and extracted with EtOAc (10 mL × 3). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (5.4 g, hexane–EtOAc 15 : 1) to afford ester **S19** (124.9 mg, 83%) as a pale yellow oil: R_f = 0.64 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{24}$ –18.8 (*c* 1.38, $CHCl_3$); IR ($CHCl_3$) 3000, 2955, 2929, 2857, 1704, 1640, 1463, 1382, 1363, 1256, 1177, 1089, 1038, 1004, 940, 908, 836; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 15.4, 10.4 Hz, 1H), 6.46 (ddd, *J* = 14.4, 7.3, 7.2 Hz, 1H), 6.24 (dd, *J* = 14.8, 10.3 Hz, 1H), 6.19 (ddd, *J* = 14.8, 7.1, 7.1 Hz, 1H), 6.09 (d, *J* = 14.4 Hz, 1H), 5.78 (d, *J* = 15.4 Hz, 1H), 5.34 (ddd, *J* = 7.2, 7.2, 1.0 Hz, 1H), 5.11 (dd, *J* = 10.1, 6.3 Hz, 1H), 4.61 (d, *J* = 11.6 Hz, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 3.96 (m, 1H), 3.75–3.46 (m, 6H), 3.44 (dd, *J* = 6.3, 3.1 Hz, 1H), 3.38 (dd,

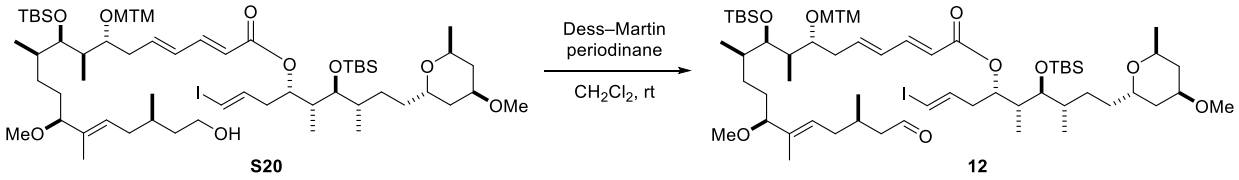
J = 6.9, 6.9 Hz, 1H), 3.33 (s, 3H), 3.15 (s, 3H), 2.49–2.23 (m, 4H), 2.14 (s, 3H), 2.09 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.98 (m, 1H), 1.91–1.76 (m, 4H), 1.72–1.39 (m, 11H), 1.49 (s, 3H), 1.30–1.15 (m, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 0.96–0.81 (m, 4H), 0.94 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 5.8 Hz, 3H), 0.889 (s, 9H), 0.888 (s, 9H), 0.885 (s, 9H), 0.84 (d, *J* = 7.1 Hz, 3H), 0.05 (s, 3H), 0.044 (s, 3H), 0.039 (s, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 144.7, 141.7, 140.8, 134.9, 130.4, 128.0, 119.8, 88.2, 79.0, 78.5, 77.3, 75.8, 73.3, 73.2, 72.5, 72.0, 64.6, 61.4, 55.6, 55.3, 40.2, 39.6, 39.52, 39.50, 38.7, 37.5, 36.4, 35.0, 34.8, 33.5, 31.7, 30.2, 29.8, 29.7, 28.6, 27.5, 26.2 (3C), 26.1 (3C), 26.0 (3C), 21.8, 19.7, 18.4, 18.3, 17.2, 15.6, 14.4, 11.5, 11.0, 10.4, –3.7, –3.8, –3.9 (2C), –5.3 (2C); HRMS (ESI) *m/z* 1273.6816, calcd for $C_{62}H_{119}NaIO_9SSi_3$ $[M+Na]^+$ 1273.6815.



S19 **S20**

To a stirred solution of ester **S19** (124 mg, 99.8 μmol) in MeOH (6.0 mL) was added NH_4F (370 mg, 9.98 mmol) at room temperature. The mixture was stirred at room temperature for 3.5 d, poured into a mixture of saturated aqueous NH_4Cl (8 mL) and H_2O (8 mL), and extracted with EtOAc (10 mL × 3). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (3.7 g, hexane–EtOAc 4 : 1 → 3 : 1) to afford alcohol **S20** (106 mg, 93%) as a colorless oil: R_f = 0.30 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{26}$ –38.3 (*c* 1.17, $CHCl_3$); IR ($CHCl_3$) 3477, 3004, 2955, 2930, 2857, 1702, 1644, 1616, 1463, 1382, 1362, 1301, 1256, 1176, 1089, 1042, 1003, 955, 941, 854, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 15.4, 10.8 Hz, 1H), 6.45 (ddd, *J* = 14.4, 7.2, 7.1 Hz, 1H), 6.24 (dd, *J* = 14.9, 10.8 Hz, 1H), 6.18 (ddd, *J* = 14.9, 7.2, 7.2 Hz, 1H), 6.10 (d, *J* = 14.4 Hz, 1H), 5.78 (d, *J* = 15.4 Hz, 1H), 5.34 (dd, *J* = 7.1, 6.9 Hz, 1H), 5.11 (dd, *J* = 10.1, 6.2 Hz, 1H), 4.61 (d, *J* = 11.4 Hz, 1H), 4.59 (d, *J* = 11.4 Hz, 1H), 3.96 (m, 1H), 3.74–3.63 (m, 3H), 3.61 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.57 (ddd, *J* = 6.4, 6.4, 3.5 Hz, 1H), 3.51 (ddq, *J* = 9.9, 4.8, 6.2 Hz, 1H), 3.43 (dd, *J* = 6.2, 3.0 Hz, 1H), 3.38 (dd, *J* = 6.9, 6.9 Hz, 1H), 3.33 (s, 3H), 3.15 (s, 3H), 2.49–2.26 (m, 4H), 2.14 (s, 3H), 2.10 (ddd, *J* = 14.2, 7.1, 6.9 Hz, 1H),

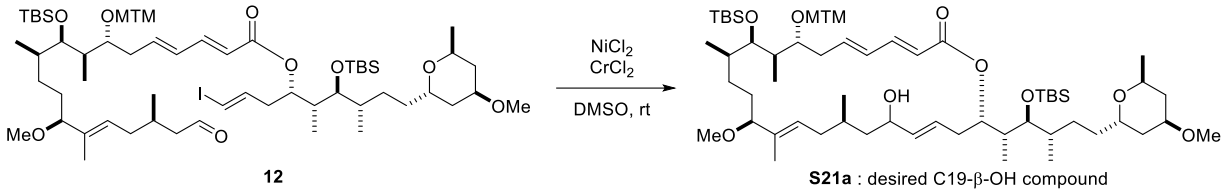
1.98 (m, 1H), 1.91 (ddd, *J* = 14.2, 7.2, 7.1 Hz, 1H), 1.87–1.76 (m, 4H), 1.74–1.34 (m, 11H), 1.50 (s, 3H), 1.32–1.13 (m, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.00–0.86 (m, 1H), 0.94 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.5 Hz, 3H), 0.89 (s, 18H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.05 (s, 6H), 0.043 (s, 3H), 0.038 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 144.8, 141.7, 140.7, 135.1, 130.4, 127.6, 119.8, 88.1, 79.0, 78.5, 77.4, 75.8, 73.30, 73.27, 72.6, 72.0, 64.6, 61.1, 55.7, 55.3, 40.2, 39.7, 39.58, 39.55, 38.7, 37.5, 36.4, 34.9, 34.8, 33.5, 31.7, 30.2, 29.9, 28.6, 27.6, 26.2 (3C), 26.1 (3C), 21.8, 19.7, 18.44, 18.42, 17.2, 15.5, 14.4, 11.5, 11.0, 10.4, –3.7, –3.9, –3.96, –3.98; HRMS (ESI) *m/z* 1159.5940, calcd for $C_{56}H_{105}NaIO_9SSi_2$ $[M+Na]^+$ 1159.5960.



S20 **12**

To a stirred solution of alcohol **S20** (12.1 mg, 0.107 mmol) in CH_2Cl_2 (3.0 mL) was added Dess–Martin periodinane (6.7 mg, 0.158 mmol) at room temperature. The mixture was stirred at room temperature for 1 h, poured into a mixture of saturated aqueous $Na_2S_2O_3$ (2.0 mL), saturated aqueous $NaHCO_3$ (2.0 mL), and H_2O (2.0 mL), and extracted with CH_2Cl_2 (5 mL × 3). The combined extracts were washed with brine (10 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (0.24 g, hexane–EtOAc 7 : 1) to afford aldehyde **12** (11.2 mg, 93%) as a colorless oil: R_f = 0.64 (hexane : EtOAc = 3 : 1); $[\alpha]_D^{23}$ –22.3 (*c* 1.27, $CHCl_3$); IR ($CHCl_3$) 3004, 2955, 2930, 2857, 1718, 1704, 1644, 1463, 1382, 1362, 1301, 1255, 1176, 1136, 1090, 1039, 1003, 954, 940, 854, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.76 (br. t, 1H), 7.23 (dd, *J* = 15.4, 10.7 Hz, 1H), 6.46 (ddd, *J* = 14.3, 7.3, 7.3 Hz, 1H), 6.24 (dd, *J* = 14.9, 10.7 Hz, 1H), 6.18 (ddd, *J* = 14.9, 7.2, 7.2 Hz, 1H), 6.10 (d, *J* = 14.3 Hz, 1H), 5.78 (d, *J* = 15.4 Hz, 1H), 5.33 (dd, *J* = 6.8, 6.8 Hz, 1H), 5.11 (dd, *J* = 10.1, 6.1 Hz, 1H), 4.61 (d, *J* = 11.7 Hz, 1H), 4.59 (d, *J* = 11.7 Hz, 1H), 3.96 (m, 1H), 3.68 (ddd, *J* = 9.5, 6.5, 2.8 Hz, 1H), 3.61 (dd, *J* = 3.4, 3.4 Hz, 1H), 3.57 (ddd, *J* = 6.5, 6.5, 3.3 Hz, 1H), 3.52 (ddq, *J* = 9.9, 4.8, 6.2 Hz, 1H), 3.44 (dd, *J* = 6.1, 3.0 Hz, 1H), 3.38 (dd, *J* = 6.8, 6.8 Hz, 1H), 3.33 (s, 3H), 3.15 (s, 3H), 2.47–2.29 (m, 5H), 2.26 (ddd, *J* = 16.3, 7.8, 2.3 Hz, 1H), 2.13 (m,

1H), 2.14 (s, 3H), 2.02–1.94 (m, 2H), 1.89–1.77 (m, 3H), 1.67–1.37 (m, 9H), 1.50 (s, 3H), 1.26–1.13 (m, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.01–0.80 (m, 1H), 0.98 (d, *J* = 6.5 Hz, 3H), 0.94 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.89 (s, 18H), 0.87 (d, *J* = 7.3 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.05 (s, 6H), 0.043 (s, 3H), 0.039 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 202.5, 166.6, 144.7, 141.7, 140.7, 136.4, 130.4, 126.3, 119.9, 88.0, 78.9, 78.5, 75.8, 73.30, 73.25, 72.5, 72.0, 64.6, 55.8, 55.3, 50.6, 40.2, 39.6 (2C), 38.7, 37.5, 36.4, 34.8, 34.7, 33.5, 31.8, 29.9, 29.7, 28.7, 28.6, 27.6, 25.2 (3C), 26.1 (3C), 21.8, 20.0, 18.44, 18.43, 17.2, 15.6, 14.4, 11.6, 11.0, 10.5, –3.7, –3.8, –3.96, –3.98; HRMS (ESI) *m/z* 1157.5798, calcd for $C_{56}H_{103}NaIO_9SSi_2$ $[M+Na]^+$ 1157.5804.



12

S21a : desired C19-β-OH compound
S21b : undesired C19-α-OH compound

DMSO was degassed by freeze-thawing. To a stirred solution of aldehyde **12** (71.6 mg, 63.1 μmol) in DMSO (5.0 mL) were added $CrCl_2$ (77.5 mg, 631 μmol) and $NiCl_2$ (1.6 mg, 12.6 μmol) at room temperature in a glove box. The mixture was stirred at room temperature for 6 h in a glove box, poured into H_2O (15 mL), and extracted with Et_2O (15 mL × 3). The combined extracts were washed with brine (10 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (5.0 g, hexane–EtOAc 7 : 1 → 5 : 1 → 2 : 1) to afford **S21a** (30.6 mg, 46%) and **S21b** (22.6 mg, 35%) as colorless oils, respectively: **S21a**: R_f = 0.20 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{27}$ –8.0 (*c* 1.86, $CHCl_3$); IR ($CHCl_3$) 3622, 3453, 3006, 2956, 2930, 2858, 1704, 1642, 1463, 1382, 1362, 1302, 1254, 1177, 1138, 1082, 1046, 1003, 970, 909, 875, 857, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 15.4, 10.1 Hz, 1H), 6.24–6.26 (m, 2H), 5.82 (d, *J* = 15.3 Hz, 1H), 5.57 (ddd, *J* = 15.0, 10.5, 4.3 Hz, 1H), 5.30–5.20 (m, 2H), 5.05 (m, 1H), 4.59 (d, *J* = 11.6 Hz, 1H), 4.53 (d, *J* = 11.6 Hz, 1H), 4.09 (ddd, *J* = 9.2, 9.2, 4.7 Hz, 1H), 3.96 (m, 1H), 3.67 (dddd, *J* = 13.5, 10.2, 7.0, 3.7 Hz, 1H), 3.60 (m, 1H), 3.52 (m, 2H), 3.43 (dd, *J* = 5.0, 4.1 Hz, 1H), 3.38 (dd, *J* = 10.6, 4.4 Hz, 1H), 3.33 (s, 3H), 3.18 (s, 3H), 2.39 (ddd, *J* = 13.9, 1.9, 1.9 Hz, 1H), 2.33 (m, 1H), 2.25 (ddd, *J* = 13.9,

10.9, 10.9 Hz, 1H), 2.17 (s, 3H), 2.03–1.94 (m, 2H), 1.86–1.76 (m, 3H), 1.75–1.36 (m, 10H), 1.45 (s, 3H), 1.35–1.06 (m, 6H), 1.20 (d, *J* = 6.24 Hz, 3H), 0.98–0.77 (m, 1H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.922 (d, *J* = 6.8 Hz, 3H), 0.916 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.81 (d, *J* = 6.1 Hz, 3H), 0.12 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H) A signal due to a proton (OH) was not obserbed.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 144.4, 140.7, 135.1, 134.2, 130.0, 129.8, 129.5, 120.4, 87.5, 79.1, 77.5, 76.8, 73.3, 72.7, 72.2, 72.1, 64.6, 55.6 (2C), 55.3, 42.7, 38.7, 38.5, 37.5, 36.6, 36.3, 34.8, 32.9, 30.7, 29.9, 29.7, 29.6, 27.9, 26.2 (3C), 26.0 (3C), 22.7, 21.8, 21.0, 20.1, 18.5, 18.3, 17.2, 14.5, 14.2, 12.5, 12.0, 9.8, –3.8, –4.0, –4.3 (2C); HRMS (ESI) *m/z* 1031.6837, calcd for $C_{56}H_{104}NaO_9SSi_2$ $[M+Na]^+$ 1031.6837; **S21b**: R_f = 0.49 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{27}$ – 2.5 (*c* 1.89, $CHCl_3$); IR ($CHCl_3$) 3453, 2999, 2954, 2930, 2857, 1703, 1641, 1463, 1382, 1362, 1301, 1256, 1178, 1136, 1088, 1038, 1003, 973, 909, 857, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 15.5, 10.7 Hz, 1H), 6.22 (dd, *J* = 15.0, 10.7 Hz, 1H), 6.14 (ddd, *J* = 15.0, 7.3, 7.3 Hz, 1H), 5.78 (d, *J* = 15.5 Hz, 1H), 5.62 (ddd, *J* = 15.2, 8.7, 4.9 Hz, 1H), 5.50 (dd, *J* = 15.2, 5.0 Hz, 1H), 5.30–5.17 (m, 2H), 4.61–4.55 (m, 2H), 4.16–4.02 (m, 1H), 3.96 (m, 1H), 3.71–3.62 (m, 2H), 3.58–3.47 (m, 2H), 3.46 (dd, *J* = 6.4, 4.8 Hz, 1H), 3.36 (dd, *J* = 9.6, 5.0 Hz, 1H), 3.33 (s, 3H), 3.15 (s, 3H), 2.52–2.23 (m, 3H), 2.17 (s, 3H), 2.15 (m, 1H), 1.97 (m, 1H), 1.87–1.74 (m, 3H), 1.48 (s, 3H), 1.72–1.36 (m, 10H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.31–1.07 (m, 6H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.6 Hz, 3H), 1.01–0.79 (m, 4H), 0.11 (s, 3H), 0.06 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H) A signal due to a proton (OH) was not obserbed.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.7, 144.7, 140.0, 135.9, 134.5, 130.3, 128.2, 125.8, 120.1, 87.9, 78.9, 73.4, 73.3 (2C), 73.1, 72.0, 69.8, 64.6, 55.5, 55.2 (2C), 44.5, 42.3, 38.7, 37.4, 36.5, 34.8, 31.6, 30.9, 29.9, 29.7, 29.5, 27.9, 26.2 (3C), 26.01, 25.96 (3C), 22.6, 21.7, 19.8, 18.4, 18.3, 17.3, 14.5, 14.4, 14.1, 12.4, 12.0, 10.1, –3.8. –4.0, –4.2 (2C); HRMS (ESI) *m/z* 1031.6809, calcd for $C_{56}H_{104}NaO_9SSi_2$ $[M+Na]^+$ 1031.6837.

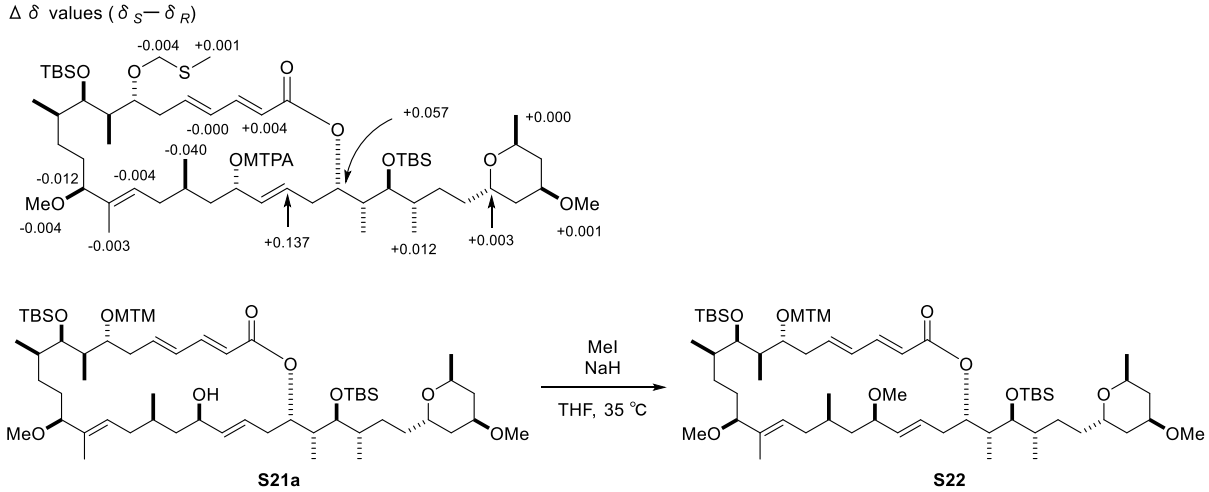
Determination of the absolute configuration at C19 of **S21b**

(*S*)-MTPA ester of S21b

To a stirred solution of alcohol **S21b** (2.5 mg, 2.5 μmol) in CH_2Cl_2 (1.0 mL) were added (*R*)-(+)-MTPACl (9.4 μL, 50 μmol) and DMAP (9.1 mg, 75 μmol). The reaction mixture was stirred at room temperature for 2 h, poured into saturated aqueous $NaHCO_3$ (2.0 mL), and extracted with CH_2Cl_2 (3.0 mL × 3). The combined extracts were washed with brine (5 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by preparative TLC (hexane–EtOAc 9 : 1) to afford (*S*)-MTPA ester of **S21b** (2.6 mg, 87%) as a colorless oil.

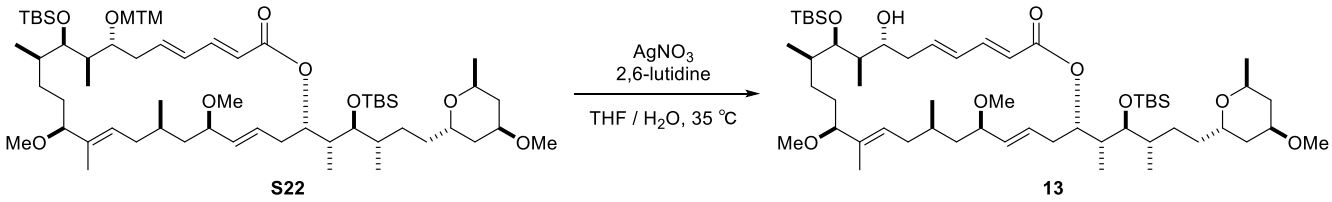
(*R*)-MTPA ester of S21b

A solution of alcohol **S21b** (2.9 mg, 2.9 μmol) in CH_2Cl_2 (1.0 mL) was similarly treated with (*S*)-MTPACl and DMAP to afford (*R*)-MTPA ester of **S21b** (2.8 mg, 80%) as a colorless oil. The Δδ values (δ_S–δ_R) for these MTPA esters are described below:



To a stirred solution of **S21a** (6.7 mg, 6.64 μmol) in THF (2.0 mL) were added MeI (33.0 μL, 530 μmol) and NaH (60% in mineral oil, 13.3 mg, 332 μmol) at room temperature. The mixture was allowed to warm to 35 °C, and stirring was continued for 9 h. The reaction mixture was poured into saturated aqueous NH_4Cl (2.0 mL) and extracted with EtOAc (2.0 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel (0.2 g, hexane–EtOAc 9 : 1 → 6 : 1) to afford methyl ether **S22** (5.6

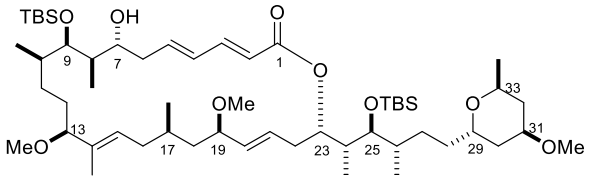
mg, 82%) as a colorless oil: R_f = 0.63 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{26}$ +38.9 (*c* 1.81, $CHCl_3$); IR ($CHCl_3$) 3003, 2954, 2930, 2857, 2824, 1703, 1645, 1617, 1462, 1379, 1362, 1302, 1257, 1177, 1137, 1081, 1045, 1003, 972, 909, 858, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.22 (dd, *J* = 15.3, 10.2 Hz, 1H), 6.27–6.14 (m, 2H), 5.82 (d, *J* = 15.3 Hz, 1H), 5.55 (ddd, *J* = 15.0, 10.6, 4.2 Hz, 1H), 5.28 (ddd, *J* = 11.1, 4.8, 1.9 Hz, 1H), 5.05 (m, 2H), 4.59 (d, *J* = 11.5 Hz, 1H), 4.53 (d, *J* = 11.5 Hz, 1H), 3.96 (m, 1H), 3.68 (dddd, *J* = 12.9, 9.5, 6.4, 3.0 Hz, 1H), 3.60 (m, 1H), 3.56–3.46 (m, 3H), 3.44 (dd, *J* = 5.3, 4.0 Hz, 1H), 3.38 (dd, *J* = 10.7, 4.4 Hz, 1H), 3.33 (s, 3H), 3.19 (s, 3H), 3.16 (s, 3H), 2.44 (ddd, *J* = 14.0, 1.9, 1.9 Hz, 1H), 2.33 (m, 1H), 2.28 (ddd, *J* = 14.0, 10.8, 10.8 Hz, 1H), 2.16 (s, 3H), 2.02–1.94 (m, 2H), 1.88–1.77 (m, 3H), 1.74–1.38 (m, 10H), 1.44 (s, 3H), 1.35–1.05 (m, 6H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.03–0.71 (m, 1H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.924 (d, *J* = 6.8 Hz, 3H), 0.918 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 9H), 0.88 (s, 9H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.79 (d, *J* = 6.3 Hz, 3H), 0.12 (s, 3H), 0.06 (s, 3H), 0.044 (s, 3H), 0.039 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 144.4, 140.6, 134.1, 132.9, 131.3, 130.0, 129.6, 120.4, 87.5, 81.4, 79.0, 77.5, 76.8, 73.3, 72.7, 72.1 (2C), 64.6, 55.6 (2C), 55.3, 42.9, 38.7, 38.5, 37.5, 36.5, 36.3, 34.8, 32.9, 30.6, 29.9, 29.7, 29.5, 27.9, 26.2 (3C), 26.0 (3C), 22.7, 21.8 (2C), 20.1, 18.5, 18.3, 17.2, 14.5, 14.1, 12.4, 12.1, 9.8, –3.8, –4.0, –4.3 (2C); HRMS (ESI) *m/z* 1045.6997, calcd for $C_{57}H_{106}NaO_9SSi_2$ $[M+Na]^+$ 1045.6994.



To a stirred solution of methyl ether **S22** (17.8 mg, 17.4 μmol) in THF (2.0 mL) and H_2O (0.4 mL) were added 2,6-lutidine (0.40 mL, 3.45 mmol) and $AgNO_3$ (640 mg, 3.77 mmol) at room temperature. After stirring at 30 °C for 19 h in the dark, the reaction mixture was filtered through a pad of Celite, and the residue was washed with EtOAc (20 mL). The filtrate and the washings were combined, washed and brine (10 mL), dried over $MgSO_4$, and concentrated. The crude product was purified by column chromatography on silica gel (0.53 g, hexane–EtOAc 8 : 1 → 6 : 1) to afford alcohol **13** (15.1

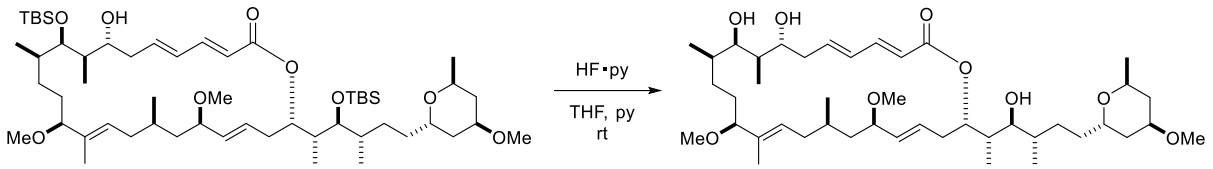
mg, 90%) as a colorless oil: R_f = 0.54 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{27}$ +32.8 (*c* 0.71, $CHCl_3$); IR ($CHCl_3$) 3449, 3003, 2954, 2930, 2857, 2825, 1704, 1643, 1616, 1463, 1380, 1362, 1302, 1257, 1139, 1083, 1024, 1003, 973, 908, 853, 837; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.23 (dd, *J* = 15.4, 10.4 Hz, 1H), 6.23 (dd, *J* = 15.2, 10.4 Hz, 1H), 6.18 (m, 1H), 5.80 (d, *J* = 15.4 Hz, 1H), 5.52 (ddd, *J* = 14.9, 10.4, 4.3 Hz, 1H), 5.26 (m, 1H), 5.19–5.08 (m, 2H), 3.95 (m, 1H), 3.78 (m, 1H), 3.67 (m, 1H), 3.60 (m, 1H), 3.55–3.47 (m, 2H), 3.45 (dd, *J* = 4.3, 4.3 Hz, 1H), 3.39 (dd, *J* = 9.7, 4.8 Hz, 1H), 3.33 (s, 3H), 3.19 (s, 3H), 3.15 (s, 3H), 2.68 (br. s, 1H), 2.45 (m, 1H), 2.36 (ddd, *J* = 14.3, 5.3, 5.3 Hz, 1H), 2.33–2.23 (m, 2H), 2.05 (ddd, *J* = 6.3, 6.2, 6.2 Hz, 1H), 1.97 (m, 1H), 1.87–1.76 (m, 3H), 1.72–1.36 (m, 9H), 1.45 (s, 3H), 1.36–1.10 (m, 6H), 1.19 (d, *J* = 6.2 Hz, 3H), 0.95 (d, *J* = 7.1 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.91–0.88 (m, 4H), 0.90 (s, 9H), 0.89 (s, 9H), 0.88 (d, *J* = 7.4 Hz, 3H), 0.79 (d, *J* = 6.5 Hz, 3H), 0.12 (s, 3H), 0.08 (s, 3H), 0.062 (s, 3H), 0.059 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.5, 144.6, 140.2, 134.0, 133.5, 130.6, 130.5, 129.1, 120.3, 87.7, 82.0, 79.0, 76.8, 74.1, 73.3, 73.0, 72.1, 64.6, 55.7, 55.6, 55.2, 42.9, 42.2, 40.4, 38.7, 38.3, 38.1, 36.6, 35.5, 34.8, 31.6, 30.4, 29.9, 29.7, 27.9, 26.2 (3C), 25.9 (3C), 21.8, 20.2, 18.5, 18.2, 17.3, 16.4, 14.1, 13.3, 12.4, 10.1, –3.8, –4.1, –4.3, –4.4 ; HRMS (ESI) *m/z* 985.6936, calcd for $C_{55}H_{102}NaO_9Si_2$ $[M+Na]^+$ 985.6960.

Assignment of ^{1}H NMR spectra of alcohol **13**



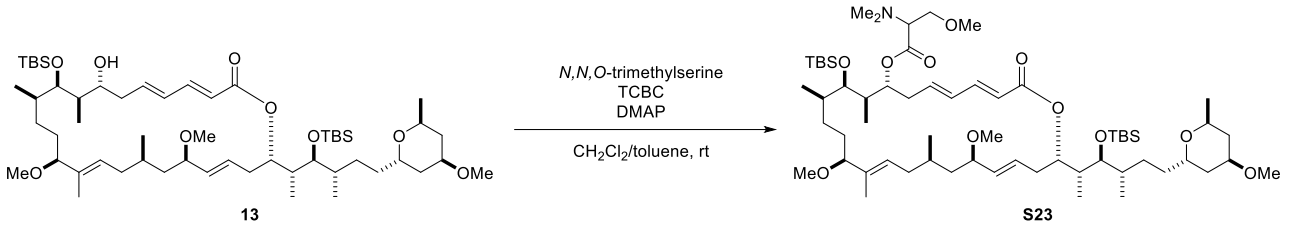
2 : 5.80 (d)	10 : 1.72–1.36	19 : 3.55–3.47 (m)	27 : 1.72–1.36, 1.36–1.10
3 : 7.23 (dd)	11 : 1.72–1.36 1.36–1.10	20 : 5.19–5.08 (m)	28 : 1.87–1.76, 1.72–1.36
4 : 6.23 (dd)	12 : 1.72–1.36, 1.36–1.10	21 : 5.52 (ddd)	29 : 3.95 (m)
5 : 6.18 (m)	13 : 3.45 (dd)	22 : 2.36 (ddd), 1.72–1.36	30 : 1.87–1.76, 1.72–1.36
6 : 2.33–2.23 (m)	15 : 5.19–5.08 (m)	23 : 5.26 (m)	31 : 3.55–3.47 (m)
7 : 3.60 (m)	16 : 2.05 (dd), 1.72–1.36	24 : 1.87–1.76	32 : 1.36–1.10
8 : 1.72–1.36	17 : 0.91–0.88	25 : 3.78 (m)	33 : 3.67 (m)
9 : 3.39 (dd)	18 : 1.36–1.10	26 : 1.72–1.36	34 : 1.19 (d)

^{1}H NMR data for alcohol **13** in $CDCl_3$ [carbon number : chemical shift (coupling pattern)]



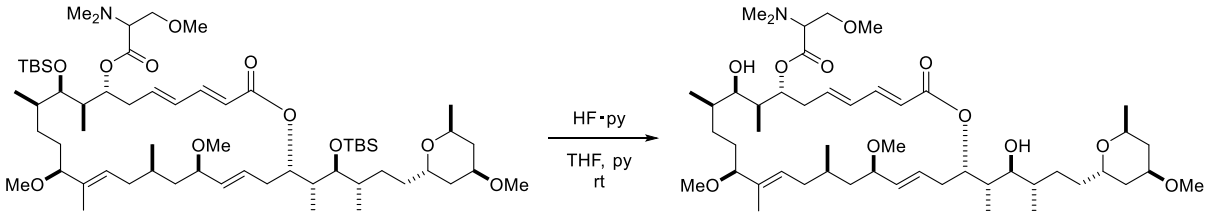
13 aplyronine C–swinholide A hybrid **14**

A solution of alcohol **13** (7.8 mg, 8.1 μmol) in a 5 : 3 : 7 mixture of HF·py, py, and THF (2.0 mL) was stirred at room temperature for 12 h. The mixture was poured into saturated aqueous $NaHCO_3$ (15 mL) and stirred at 0 °C for 30 min. The resultant mixture was extracted with EtOAc (8.0 mL × 3). The combined extracts were washed with brine (15 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (0.25 g, hexane–acetone 2 : 1 → 1 : 1) to give ApC–SwA hybrid **14** (5.0 mg, 83%) as a colorless oil: R_f = 0.21 (hexane : acetone = 2 : 1); $[\alpha]_D^{27}$ +16.5 (*c* 0.44, $CHCl_3$); IR ($CHCl_3$) 3445, 3005, 2931, 2875, 2825, 1704, 1685, 1637, 1617, 1457, 1378, 1362, 1261, 1244, 1145, 1099, 1081, 1002, 972, 869; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 15.3, 10.6 Hz, 1H), 6.23 (dd, *J* = 15.1, 10.6 Hz, 1H), 6.16 (ddd, *J* = 15.1, 9.8, 5.5 Hz, 1H), 5.85 (d, *J* = 15.3 Hz, 1H), 5.55 (ddd, *J* = 14.9, 10.5, 4.6 Hz, 1H), 5.41 (d, *J* = 10.5 Hz, 1H), 5.15 (dd, *J* = 15.3, 9.0 Hz, 1H), 5.11 (dd, *J* = 7.3, 7.3 Hz, 1H), 4.00 (m, 1H), 3.73 (m, 1H), 3.69 (ddd, *J* = 9.6, 6.5, 2.9 Hz, 1H), 3.64 (dd, *J* = 7.6, 3.7 Hz, 1H), 3.57–3.46 (m, 2H), 3.42 (dd, *J* = 8.5, 6.5 Hz, 1H), 3.33 (s, 3H), 3.23 (d, *J* = 4.8 Hz, 1H), 3.20 (s, 3H), 3.18 (s, 3H), 3.01 (ddd, *J* = 9.6, 6.4, 2.4 Hz, 1H), 2.53 (ddd, *J* = 14.4, 9.8, 7.6 Hz, 1H), 2.50–2.42 (m, 2H), 2.37 (dq, *J* = 9.6, 6.8 Hz, 1H), 2.25 (ddd, *J* = 14.4, 5.5, 3.7 Hz, 1H), 2.20 (m, 1H), 2.03–1.94 (m, 2H), 1.88 (dddd, *J* = 13.5, 9.3, 9.3, 3.8 Hz, 1H), 1.85–1.72 (m, 3H), 1.72–1.55 (m, 5H), 1.52–1.43 (m, 1H), 1.46 (s, 3H), 1.40 (dddd, *J* = 12.7, 7.1, 6.4, 3.4 Hz, 1H), 1.34–1.17 (m, 5H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.08 (m, 1H), 1.04 (d, *J* = 7.0 Hz, 3H), 0.99 (d, *J* = 6.8 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.76 (d, *J* = 5.7 Hz, 3H). A signal due to two protons (OH) were not obserbed.; ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.0, 145.1, 140.7, 134.7, 133.1, 131.1, 130.4, 128.9, 119.6, 87.2, 81.3, 76.4, 75.4, 74.8, 73.3, 73.1, 71.5, 64.7, 55.7, 55.6, 55.2, 41.4, 40.1, 38.6, 38.14, 38.09, 36.6, 36.2, 35.7, 35.0, 33.2, 29.7, 29.5, 29.3, 26.3, 24.2, 21.8, 19.6, 17.6, 15.5, 11.9, 10.04, 10.02; HRMS (ESI) *m/z* 757.5216, calcd for $C_{43}H_{74}NaO_9$ $[M+Na]^+$ 757.5231.



To a stirred solution of alcohol **13** (8.3 mg, 8.6 μmol), L-*N*,*N*,*O*-trimethylserine (21.1 mg, 14.3 μmol), and D-*N*,*N*,*O*-trimethylserine (10.6 mg, 71.8 μmol) in CH_2Cl_2 (2.0 mL) and toluene (2.0 mL) were added Et_3N (66.0 μL, 474 μmol), TCBC (53.8 μL, 345 μmol), and DMAP (26.3 mg, 215 μmol) at room temperature. After stirring at room temperature for 1 h, the reaction mixture was diluted with saturated aqueous $NaHCO_3$ (3.0 mL) and extracted with CH_2Cl_2 (5.0 mL × 2). The combined extracts were washed with brine (5.0 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (0.50 g, hexane–EtOAc 1 : 1 → 2 : 3) to afford trimethylserine ester **S23** (*S*/*R* = 1/1 as to the trimethylserine part) (9.1 mg, 97%) as a colorless oil: R_f = 0.11 (hexane : EtOAc = 2 : 1); $[\alpha]_D^{27}$ +13.9 (*c* 0.83, $CHCl_3$); IR ($CHCl_3$) 3000, 2930, 2857, 2827, 1705, 1646, 1617, 1463, 1382, 1361, 1303, 1256, 1175, 1100, 1086, 1036, 1002, 971, 858, 838; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 15.3, 11.0 Hz, 1H), 6.21 (dd, *J* = 14.7, 11.0 Hz, 1H), 6.08 (ddd, *J* = 14.7, 7.4, 7.4 Hz, 1H), 5.822 [5.818] (d, *J* = 15.3 Hz, 1H), 5.54 (ddd, *J* = 15.0, 10.5, 4.3 Hz, 1H), 5.27 (ddd, *J* = 11.0, 2.4, 2.4 Hz, 1H), 5.16–4.98 (m, 2H), 4.83 (m, 1H), 3.95 (m, 1H), 3.68 (dddd, *J* = 12.8, 9.5, 6.4, 3.0 Hz, 1H), 3.64–3.60 (m, 2H), 3.56–3.46 (m, 2H), 3.46–3.41 (m, 2H), 3.41–3.34 (m, 2H), 3.36 [3.35] (s, 3H), 3.33 (s, 3H), 3.187 [3.188] (s, 3H), 3.163 [3.162] (s, 3H), 2.55–2.34 (m, 3H), 2.40 (s, 6H), 2.28 (m, 1H), 2.08–1.88 (m, 3H), 1.88–1.77 (m, 3H), 1.77–1.37 (m, 8H), 1.47 (s, 3H), 1.37–1.11 (m, 6H), 1.19 (d, *J* = 6.2 Hz, 3H), 1.09–0.85 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.773 (d, *J* = 6.2 Hz, 3H), 0.769 (d, *J* = 6.1 Hz, 3H), 0.12 (s, 3H), 0.06 (s, 3H), 0.03 (s, 3H), 0.02 (s, 3H) (the counterparts of doubled signals in the ratio of about 1:1 are in brackets); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.2, 166.16 [166.14], 144.0 [143.9], 138.9, 134.5, 133.1, 131.0, 130.9, 129.3 [129.2], 121.0 [120.9], 87.62 [87.57], 81.3, 79.07 [79.04], 75.3, 73.3, 72.9, 72.0, 71.4 [71.3], 67.4, 67.2, 64.7, 59.13 [59.08], 55.61 [55.60],

55.3 (2C), 42.81 [42.77], 42.3, 42.2 (2C), 41.1, 38.7, 38.5 [38.4], 36.6, 36.1, 34.8, 32.8, 29.9, 29.7, 29.6, 28.0, 26.2 (3C), 26.0 (3C), 21.8, 20.1, 18.5, 18.3, 17.21, 17.19, 14.8, 12.4, 11.84, 11.76, 9.8, –3.8, –4.1, –4.2, –4.3 (the counterparts of doubled signals in the ratio of about 1:1 are in brackets); HRMS (ESI) *m/z* 1114.7725, calcd for $C_{61}H_{113}NO_{11}Si_2$ $[M+H]^+$ 1114.7750.



S23 aplyronine A–swinholide A hybrid **4**

A solution of trimethylserine ester **S23** (8.6 mg, 7.9 μmol) in a 5 : 3 : 7 mixture of HF·py, py, and THF (2.0 mL) was stirred at room temperature for 12 h. The mixture was poured into saturated aqueous $NaHCO_3$ (15 mL) and stirred at 0 °C for 30 min. The resultant mixture was extracted with EtOAc (8.0 mL × 3). The combined extracts were washed with brine (15 mL), dried over Na_2SO_4, and concentrated. The crude product was purified by column chromatography on silica gel (0.25 g, $CHCl_3$–MeOH 20 : 1) to give ApA–SwA hybrid **4** (6.0 mg, 88%) as a colorless oil: R_f = 0.45 ($CHCl_3$: MeOH = 9 : 1); $[\alpha]_D^{27}$ +40.3 (*c* 0.55, $CHCl_3$); IR ($CHCl_3$) 3502, 3003, 2930, 2874, 2829, 1717, 1644, 1618, 1457, 1382, 1299, 1271, 1245, 1174, 1146, 1100, 1039, 1001, 972, 867, 841; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 15.3, 10.8 Hz, 1H), 6.22 (dd, *J* = 15.0, 10.8 Hz, 1H), 6.12 (ddd, *J* = 15.0, 9.5, 5.2 Hz, 1H), 5.90 (d, *J* = 15.3 Hz, 1H), 5.56 (ddd, *J* = 14.9, 10.4, 4.3 Hz, 1H), 5.42 (d, *J* = 11.0 Hz, 1H), 5.11–5.00 (m, 2H), 4.77 (m, 1H), 4.00 (m, 1H), 3.69 (dddd, *J* = 12.9, 9.5, 6.4, 3.0 Hz, 1H), 3.65–3.59 (m, 2H), 3.56–3.45 (m, 3H), 3.43 (ddd, *J* = 10.5, 3.9, 3.9 Hz, 1H), 3.37–3.32 (m, 1H), 3.35 [3.36] (s, 3H), 3.34 (s, 3H), 3.19 (s, 3H), 3.18 (s, 3H), 3.08 (d, *J* = 4.7 Hz, 1H), 3.03 (m, 1H), 2.54–2.44 (m, 2H), 2.38 (s, 6H), 2.23 (ddd, *J* = 14.2, 5.2, 1.8 Hz, 1H), 2.22 (br. s, 1H), 2.02–1.84 (m, 4H), 1.84–1.76 (m, 2H), 1.73–1.53 (m, 6H), 1.49 (d, *J* = 2.8 Hz, 3H), 1.44–1.32 (m, 2H), 1.32–1.05 (m, 7H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.10 (m, 1H), 1.00 (d, *J* = 7.4 Hz, 3H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.98 (d, *J* = 4.6 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.718 [0.724] (d, *J* = 6.0 Hz, 3H) (the counterparts of doubled signals in the ratio of about 1:1 are in brackets); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0

[170.2], 167.6, 144.49 [145.53], 139.48 [139.51], 135.03 [134.99], 132.9, 131.43 [131.41], 130.87 [130.84], 129.15 [129.21], 120.43 [120.38], 86.8 [86.7], 81.6, 77.2, 76.4, 73.3, 72.9, 71.52 [71.46], 70.6, 67.49 [67.46], 64.7, 59.12 [59.14], 55.712, 55.714, 55.6, 55.3, 42.43 [42.40] (2C), 41.3, 40.11, 40.09, 38.6, 37.1, 36.8, 35.0, 33.5, 33.2, 29.8, 29.3, 28.9, 24.2, 21.8, 19.7, 17.6, 15.70, 15.66, 12.1, 12.0, 10.00, 9.98 (the counterparts of doubled signals in the ratio of about 1:1 are in brackets); HRMS (ESI) *m/z* 886.6003, calcd for $C_{49}H_{85}NO_{11}$ $[M+H]^+$ 886.6020.

References

1) Nakamura, R.; Tanino, K.; Miyashita, M. *Org. Lett*. **2005**, *7*, 2929.

2) Kigoshi, H.; Ojika, M.; Ishigaki, T.; Suenaga, K.; Mutou, T.; Sakakura, A.; Ogawa, T.; Yamada, K. *J. Am. Chem. Soc.* **1994**, *116*, 7443; (b) Kigoshi, H.; Suenaga, K.; Mutou, T.; Ishigaki, T.; Atsumi, T.; Ishikawa, H.; Sakakura, A.; Ogawa, T.; Ojika, M.; Yamada, K. *J. Org. Chem*. **1996**, *61*, 5326.

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Cytotoxic activity

Stock cultures of HeLa S3 cells were maintained in Eagle's Minimum Essential Medium containing Earle's Balanced Salts and 10% fetal bovine serum and 1% antibiotic-antimycotic mixed stock solution at 37 °C under 5% CO_2. For the purpose of the experiment, 2×10^4 cells suspended in 100 uL of medium per well were plated in 96-well plate. After 12 h incubation at 37 °C under 5% CO_2 to allow cell attachment, compounds in 100 uL of medium were added to the well at different concentrations and incubated for 96 h under the same conditions. After 3 h of the MTT addition to each well, the medium/MTT mixtures were removed, and the formazan crystals formed were dissolved in 150 uL of DMSO per well. After 30 min, optical absorbance at 540 nm were measured with a microplate reader. The cytotoxic effects of each compound were abtained as IC_{50} values.

Actin depolymerizing activity

To a solution of actin (3 μM, from rabbit skeletal muscle, Cytoskeleton) in G-buffer (200 μL) was added a 0.12 M solution of $MgCl_2$ (1.6 μL), and the mixture was stirred at 25 °C for 30 min to give F-actin solution. To the solutions of F-actin were added samples in DMSO, and the resulting mixtures were stirred at 25 °C for 30 min and then ultracentrifuged (60000 rpm, 22 °C, 1 h). The supernatants and the precipitates were dissolved in 1 × SDS buffer (30 μL, Sigma) and boiled at 95 °C for 5 min. SDS-PAGE was performed by using a precast 10% polyacrylamide gel (ATTO), and the gels were stained with a Quick-CBB kit (Wako).

Tubulin depolymerizing assay

To a solution of actin (6 μM, from rabbit skeletal muscle, Cytoskeleton) in BRB80 (50 μL) were added samples (1 mM or 10 mM in DMSO, 1.0 μL), tubulin in BRB80 (50 μL), H_2O (0.5 μL), and taxol (2 mM in DMSO, 0.3 μL). The resulting mixtures were standed at 37 °C for 30 min and then ultracentrifuged (60000 rpm, 37 °C, 1 h). The supernatants and the precipitates were dissolved in 1 × SDS buffer (20 μL, Sigma) and boiled at 95 °C for 5 min. SDS-PAGE was performed by using a precast 10% polyacrylamide gel (ATTO), and the gels were stained with a Quick-CBB kit (Wako).

*When the samples were not added, the same amount of the corresponding solution was added.

lane	1	2	3	4	5	6	7	8	9
tubulin (6 μM)	+	+	+	+	–	+	+	+	–
actin (6 μM)	–	–	–	+	+	+	–	+	+
$CaCl_2$ (5 mM)	+	–	–	–	–	–	–	–	–
taxol (2 μM)	–	+	+	+	–	+	+	+	–
1 (10 μM)	–	–	+	+	+	–	–	–	–
4 (100 μM)	–	–	–	–	–	–	+	+	+

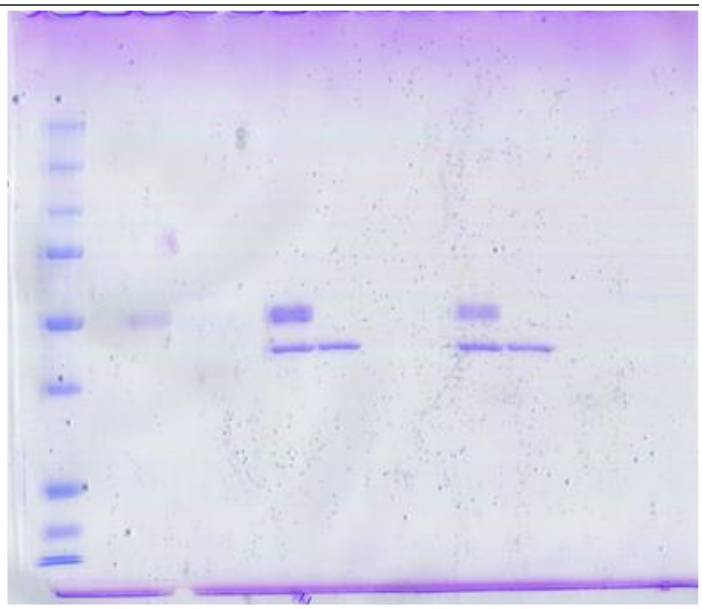

Figure S1. SDS-PAGE of the supernatants
Tubulin was polymerized with taxol in the presence of actin and/or **1** or **4**, and then precipitated by ultracentrifugation. Proteins in the supernatant and the precipitate were analyzed by SDS-PAGE, and detected with CBB stain. Depolymerized protein was detected in the supernatant fraction.

lane	1	2	3	4	5	6	7	8	9
tubulin (6 μM)	+	+	+	+	–	+	+	+	–
actin (6 μM)	–	–	–	+	+	+	–	+	+
$CaCl_2$ (5 mM)	+	–	–	–	–	–	–	–	–
taxol (2 μM)	–	+	+	+	–	+	+	+	–
1 (10 μM)	–	–	+	+	+	–	–	–	–
4 (100 μM)	–	–	–	–	–	–	+	+	+

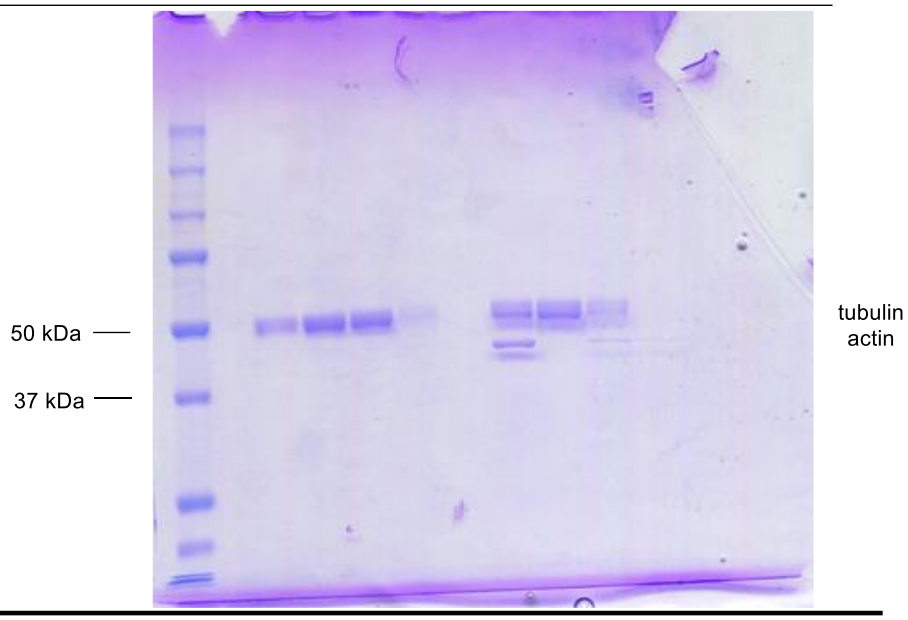

Figure S2. SDS-PAGE of the preipitates
Tubulin was polymerized with taxol in the presence of actin and/or **1** or **4**, and then precipitated by ultracentrifugation. Proteins in the supernatant and the precipitate were analyzed by SDS-PAGE, and detected with CBB stain. Polymerized protein was detected in the precipitate fraction.

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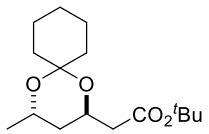

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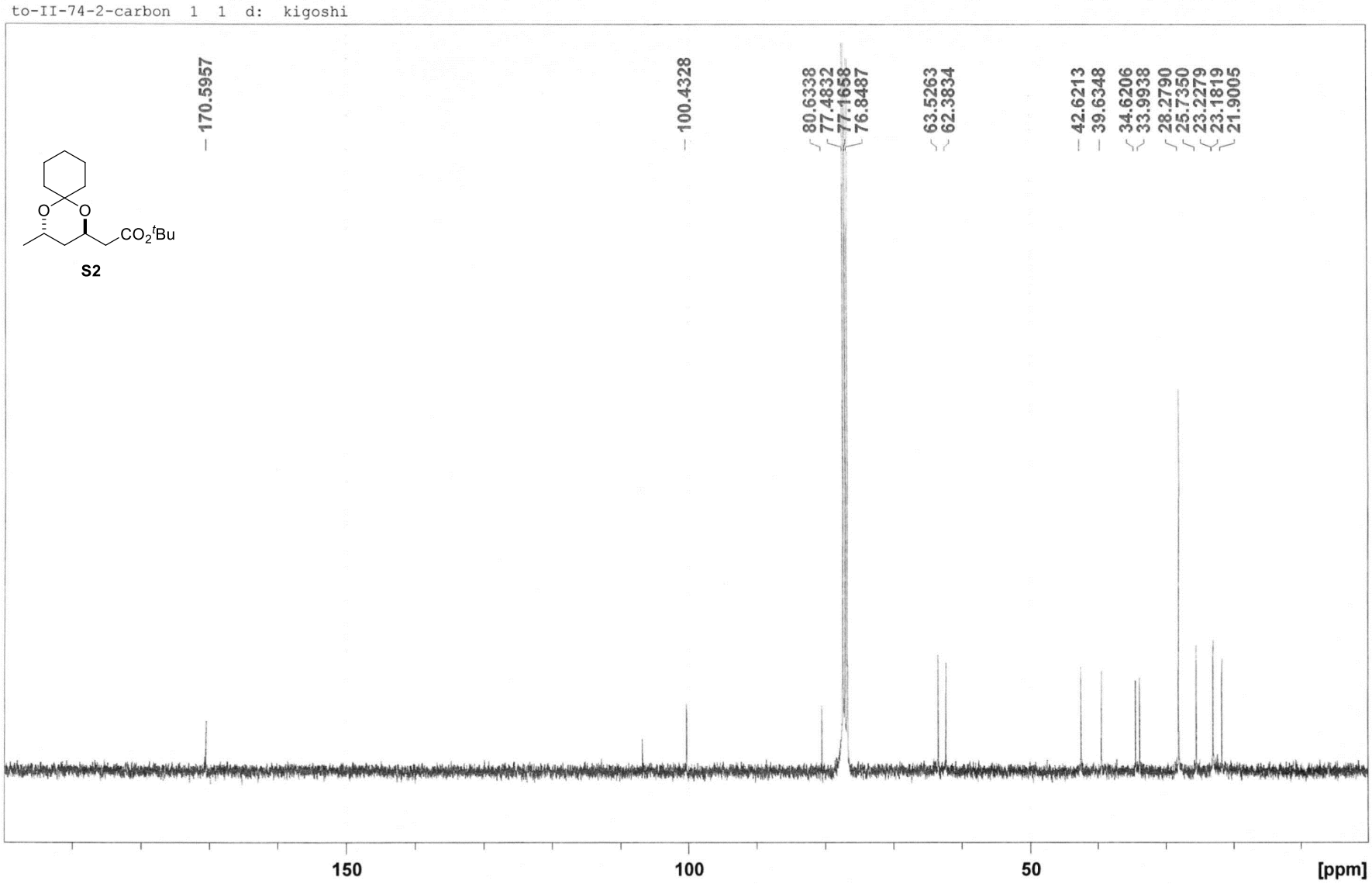
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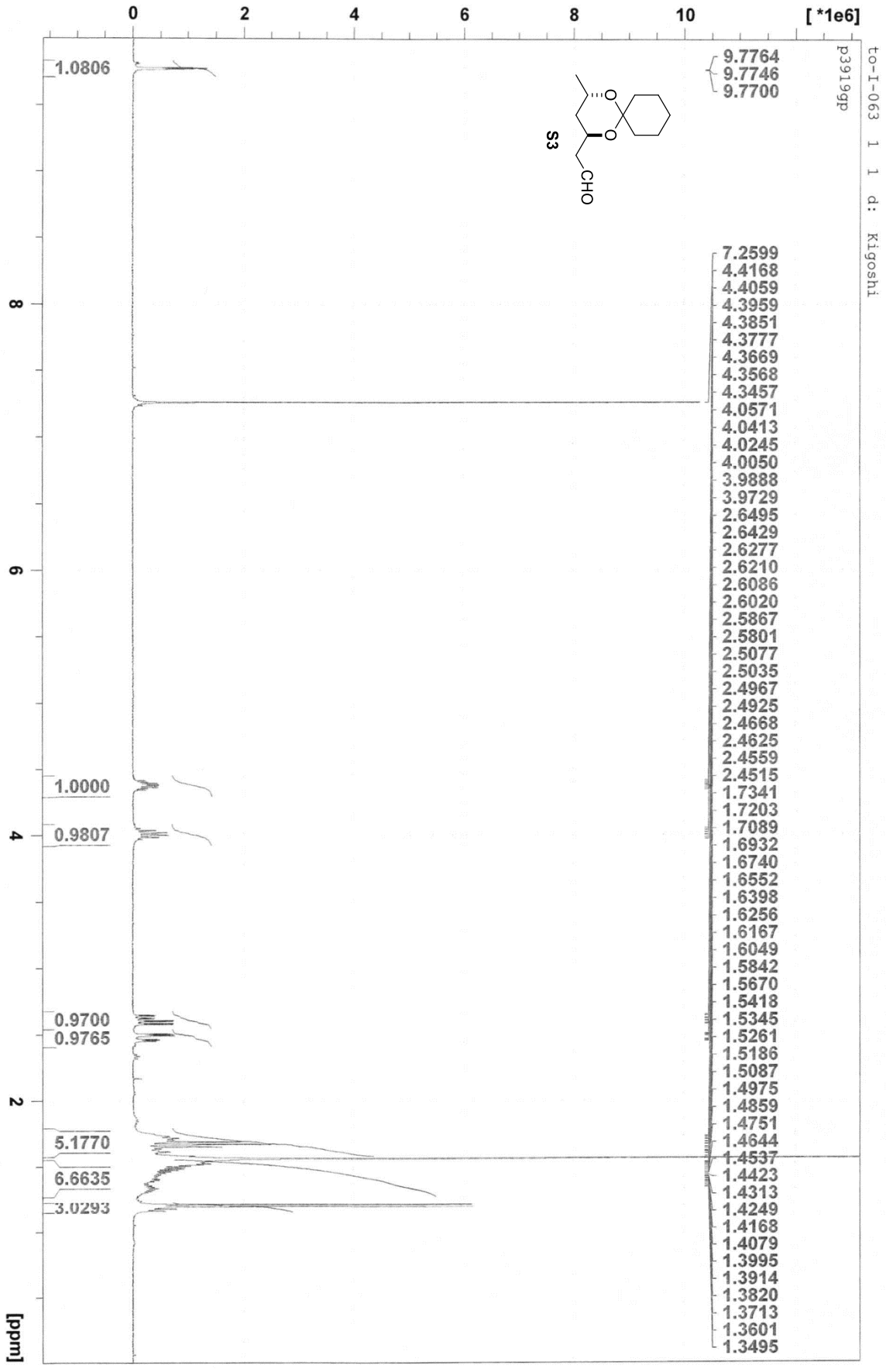
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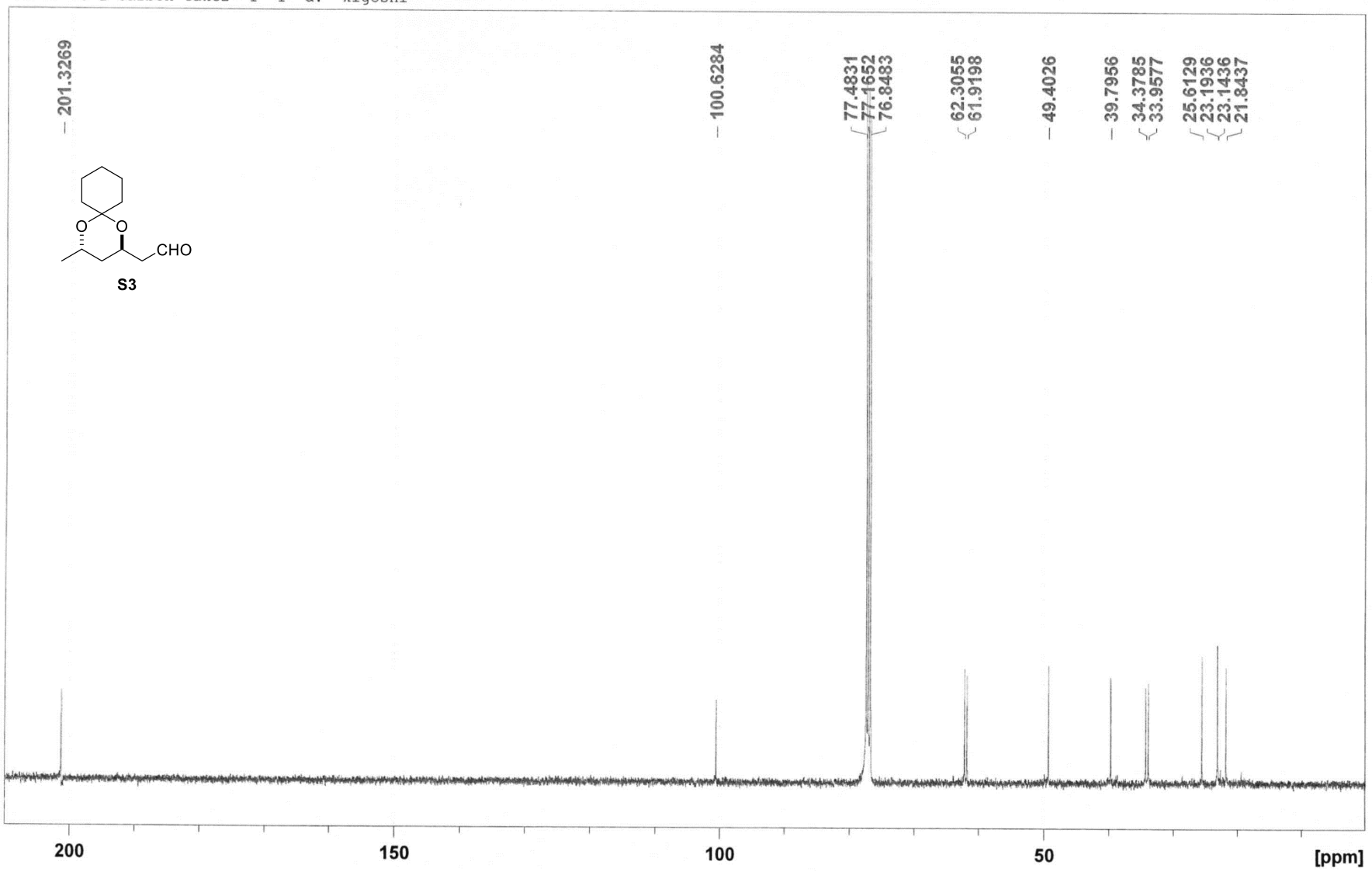

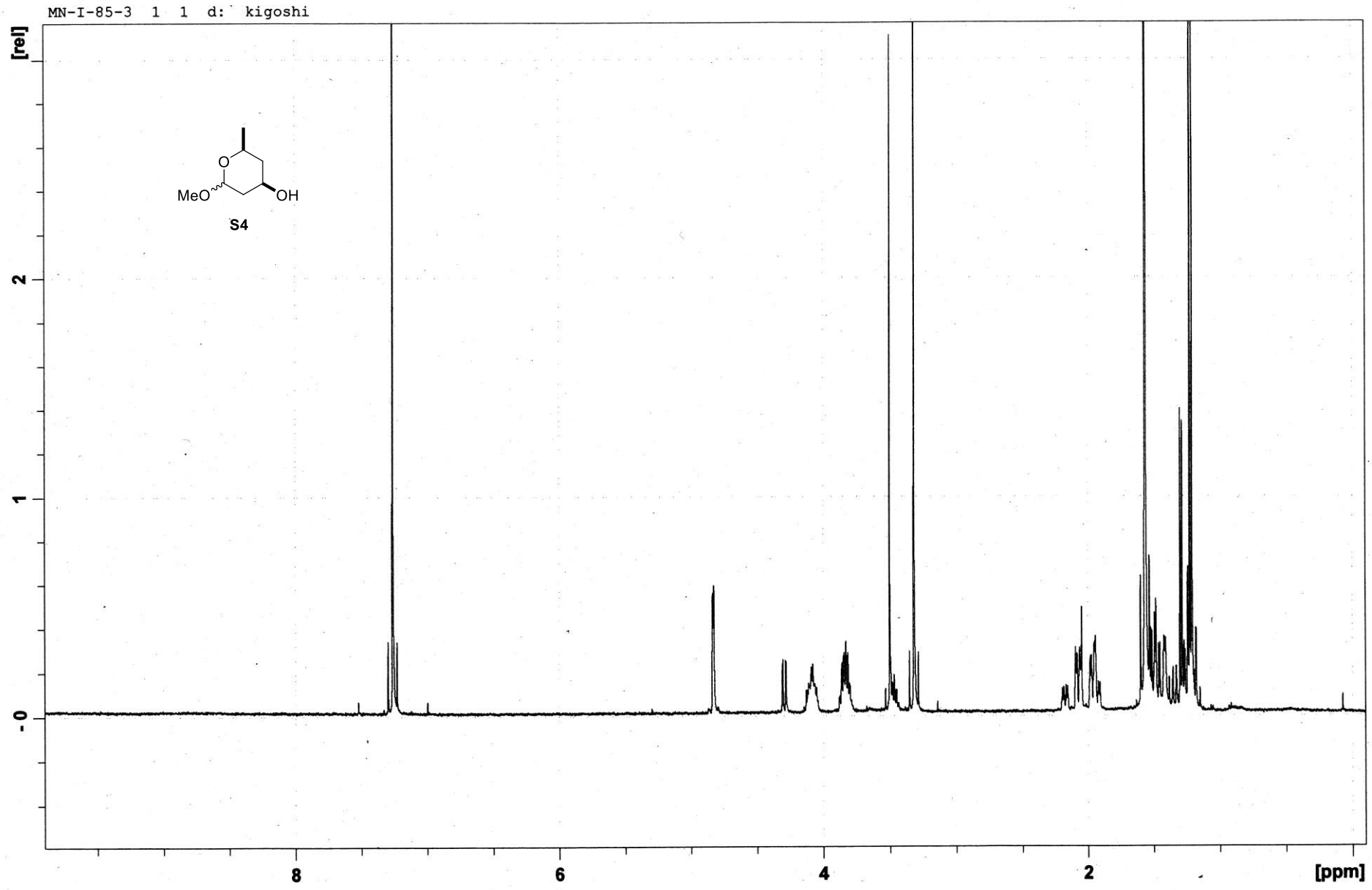
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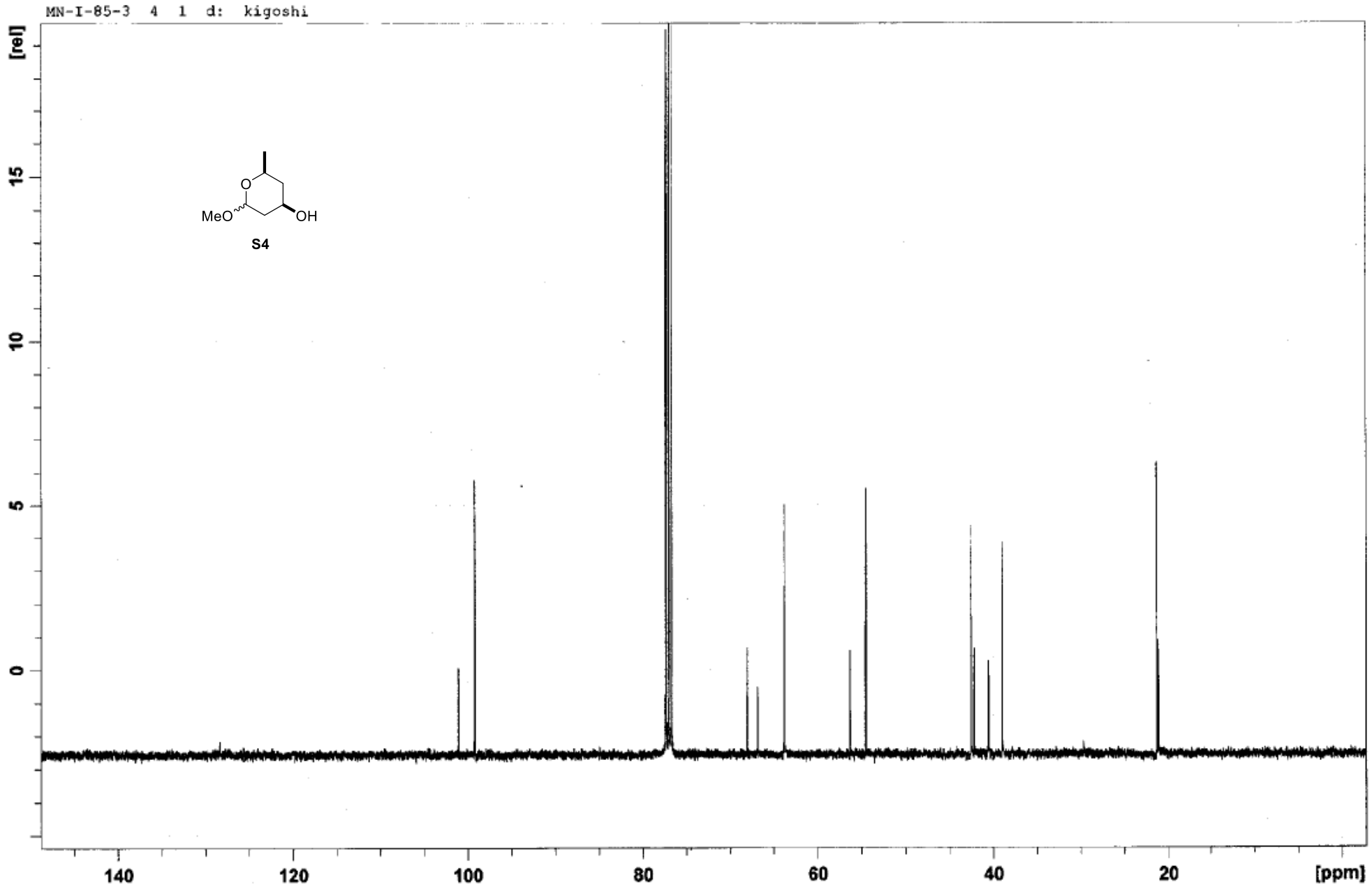
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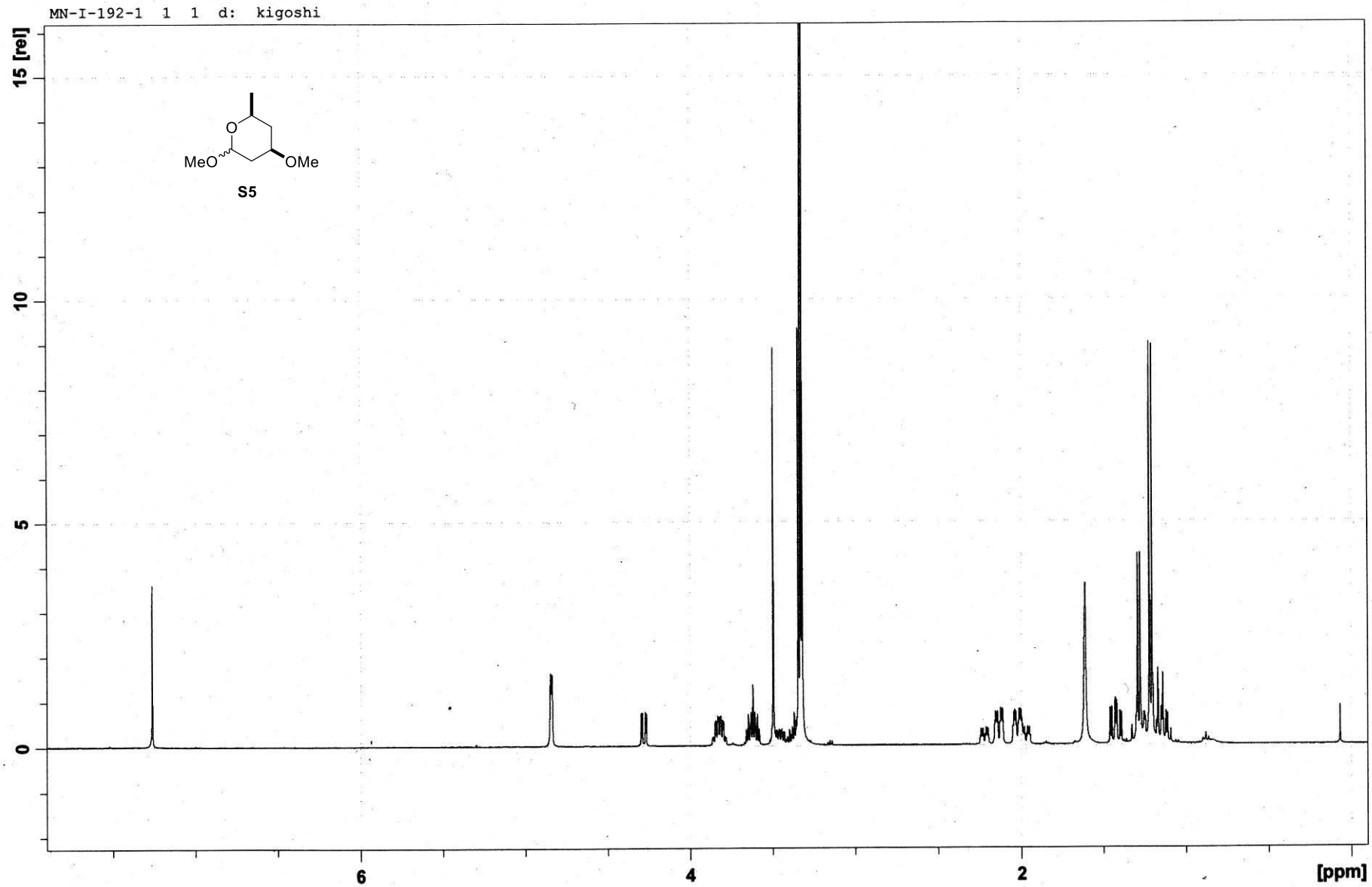
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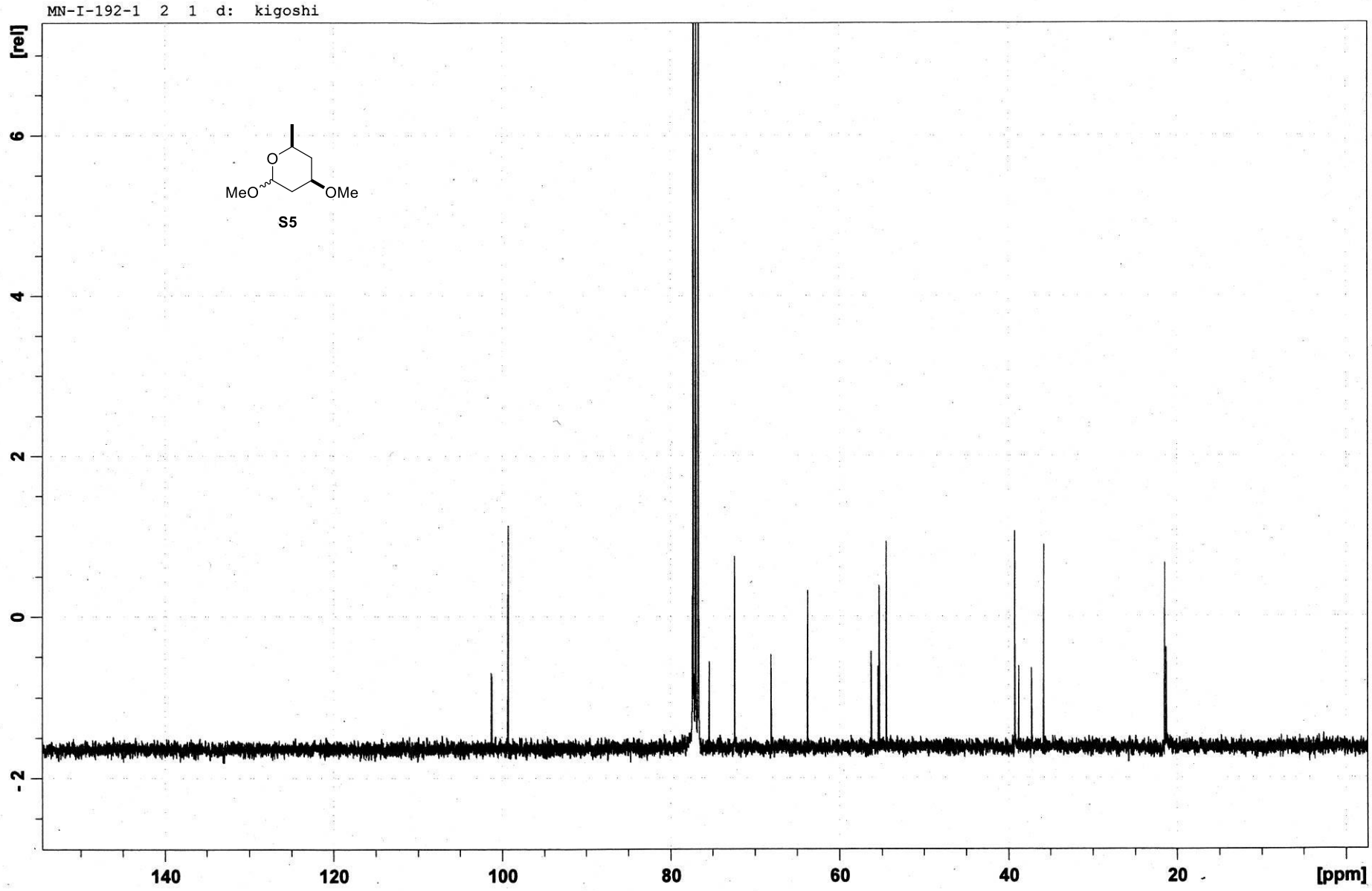
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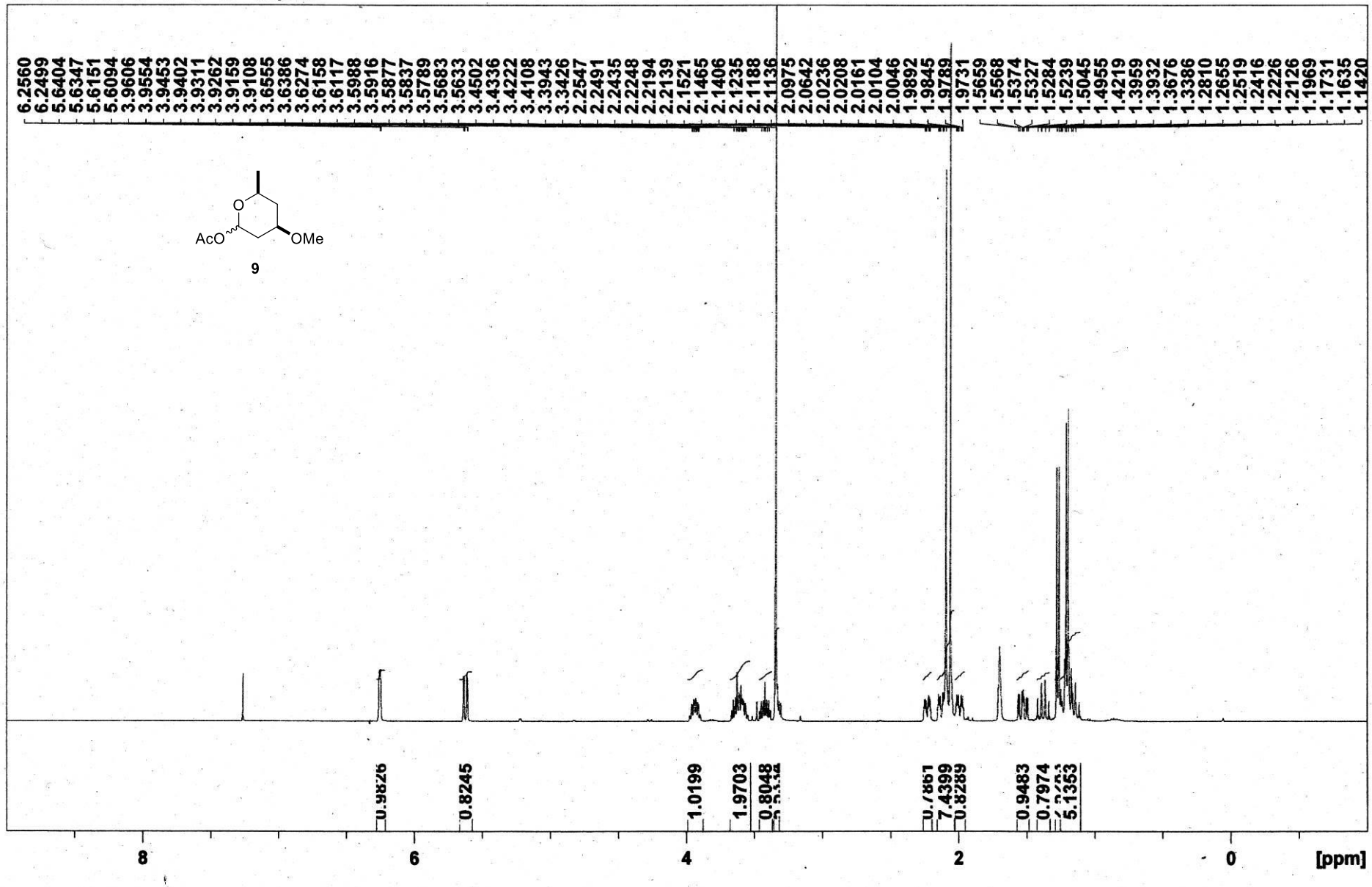
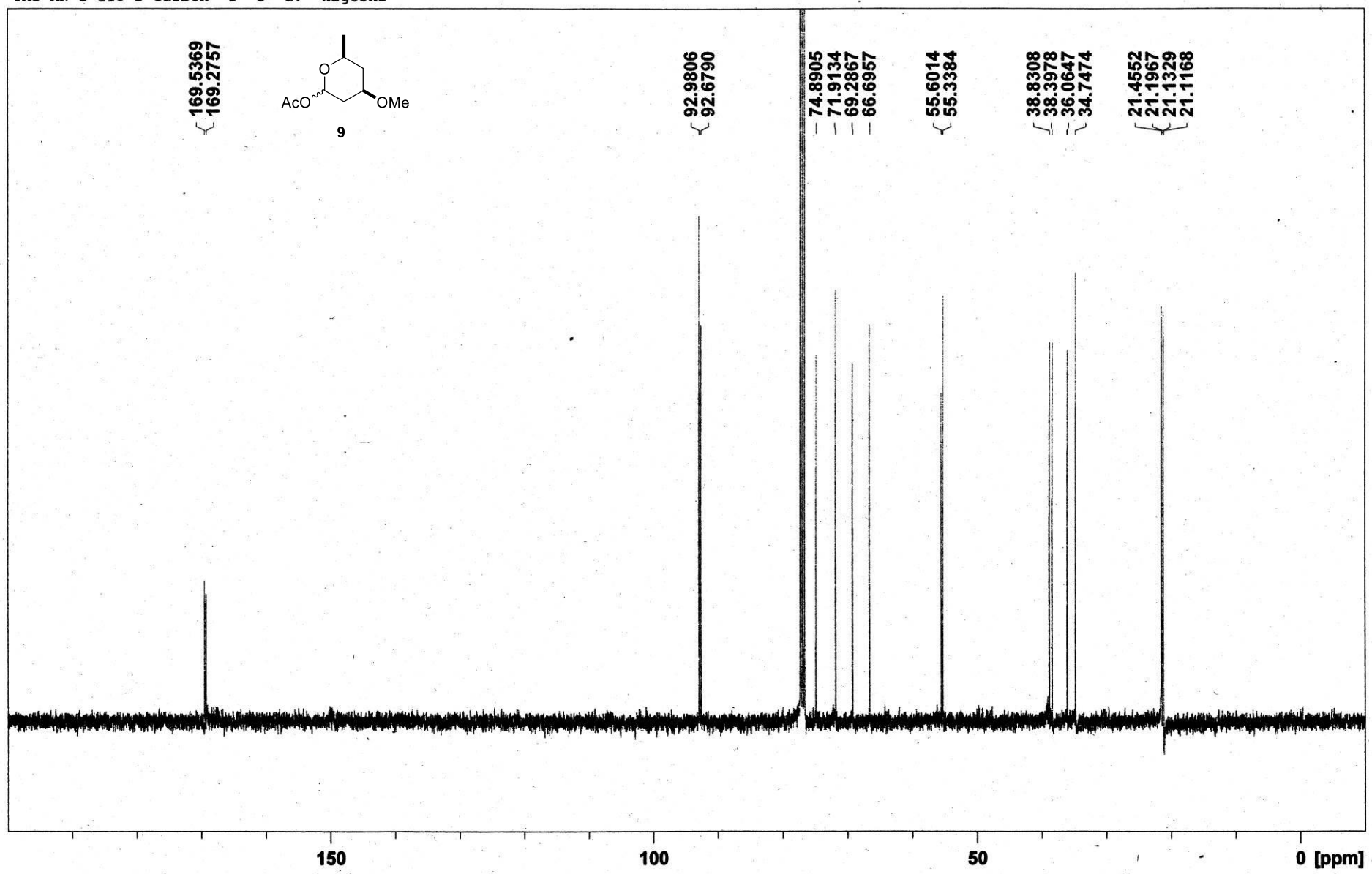
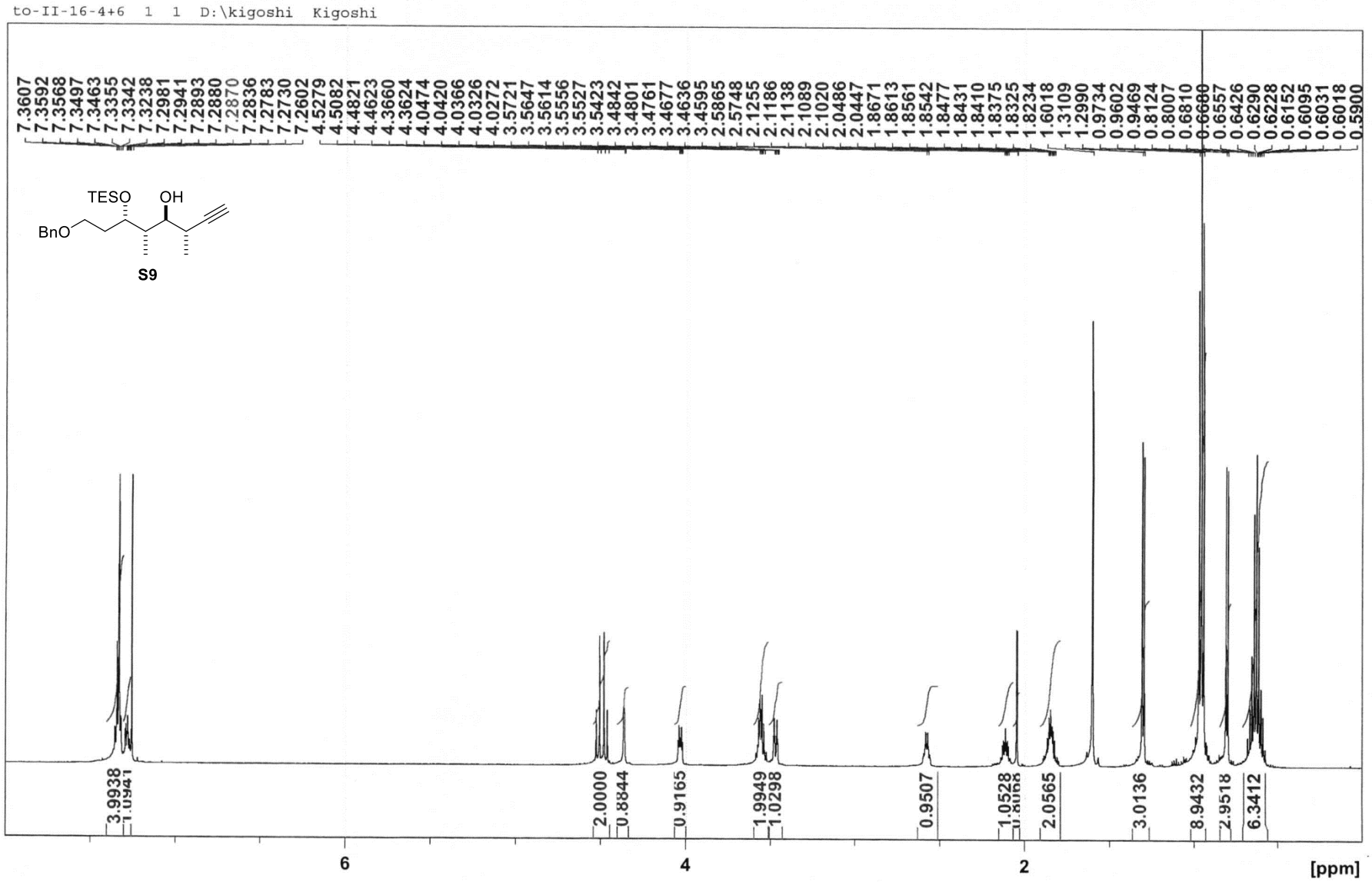
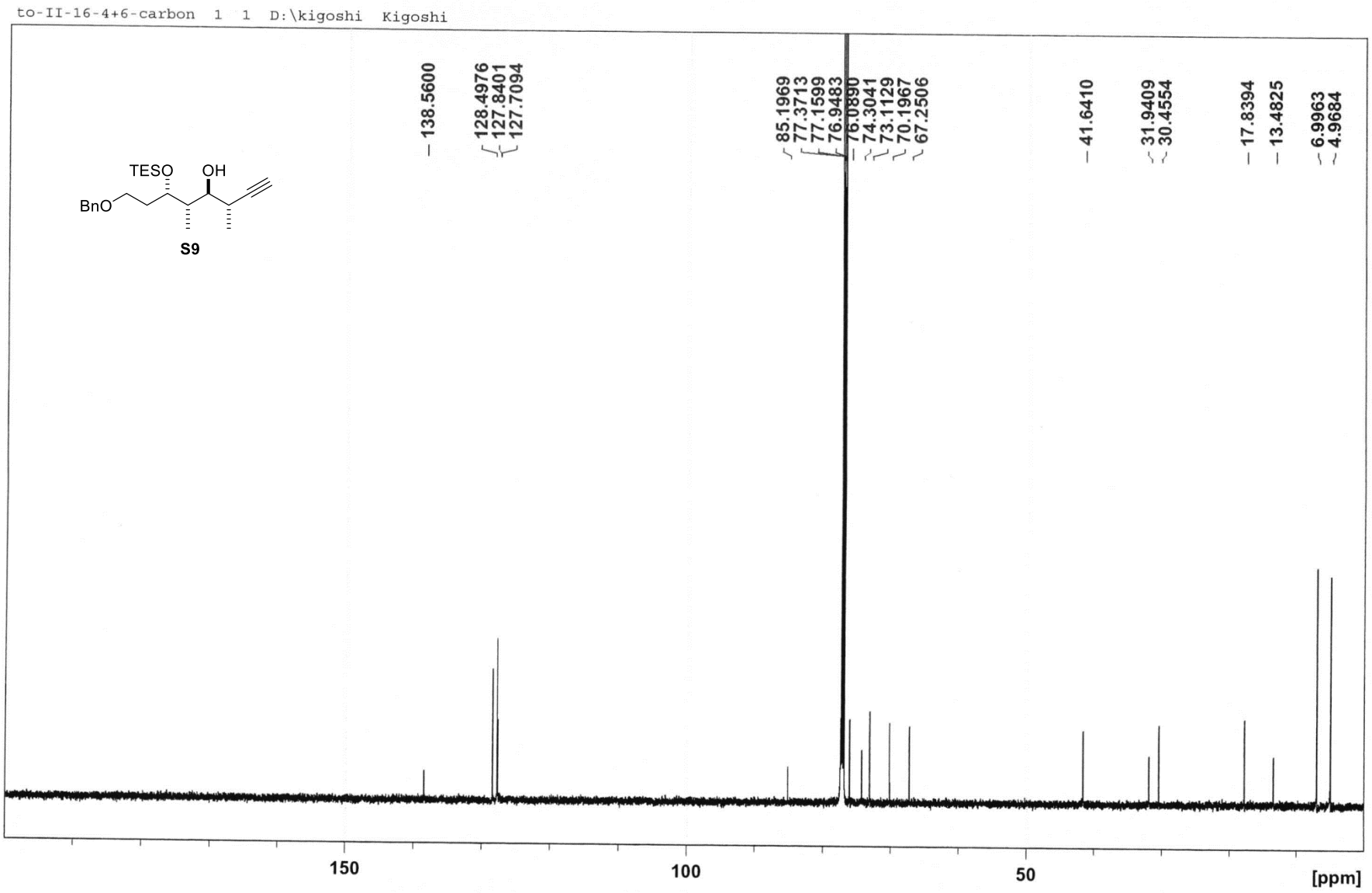
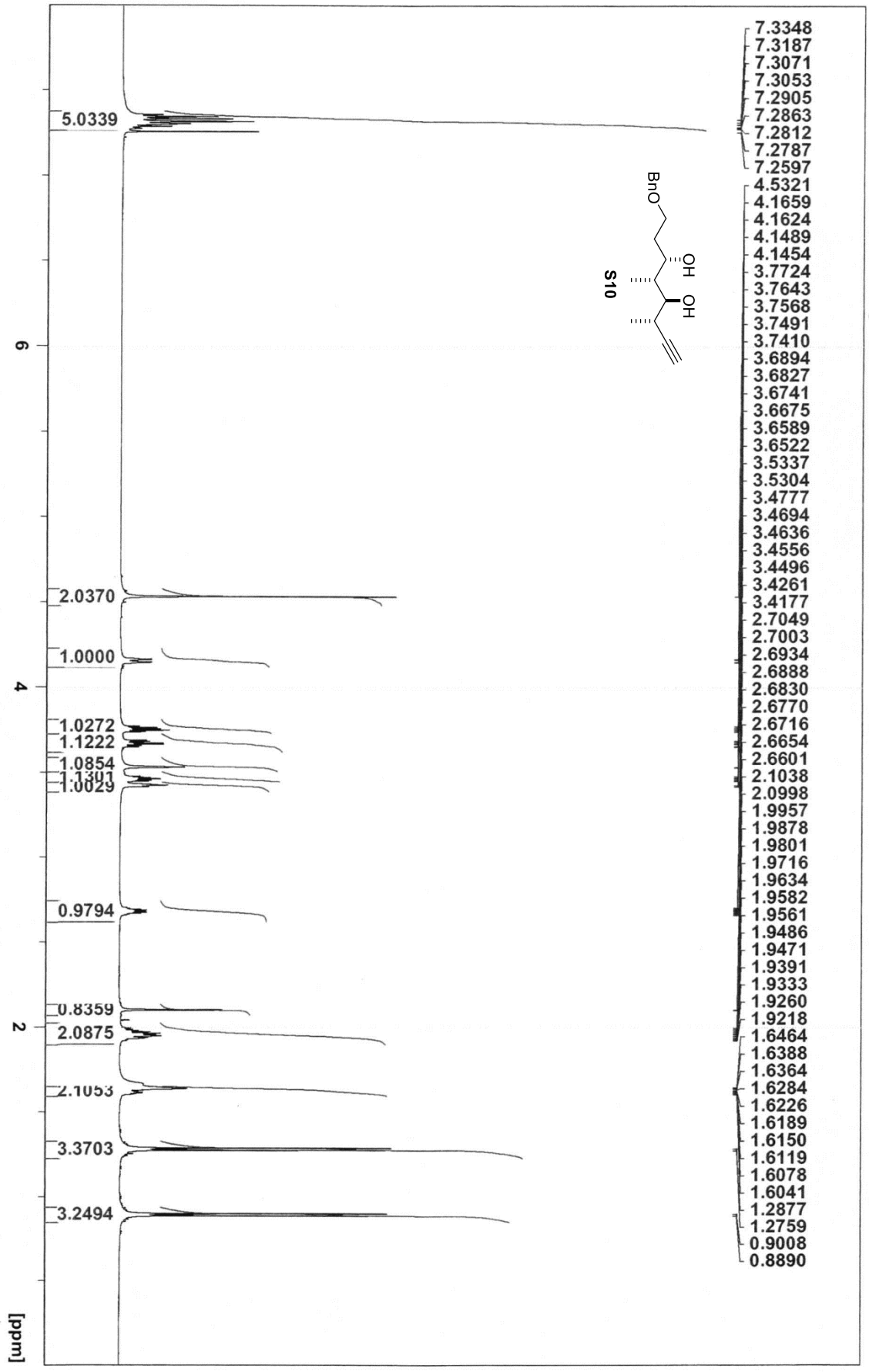


YMI-MN-I-118-2-carbon 1 1 d: kigoshi

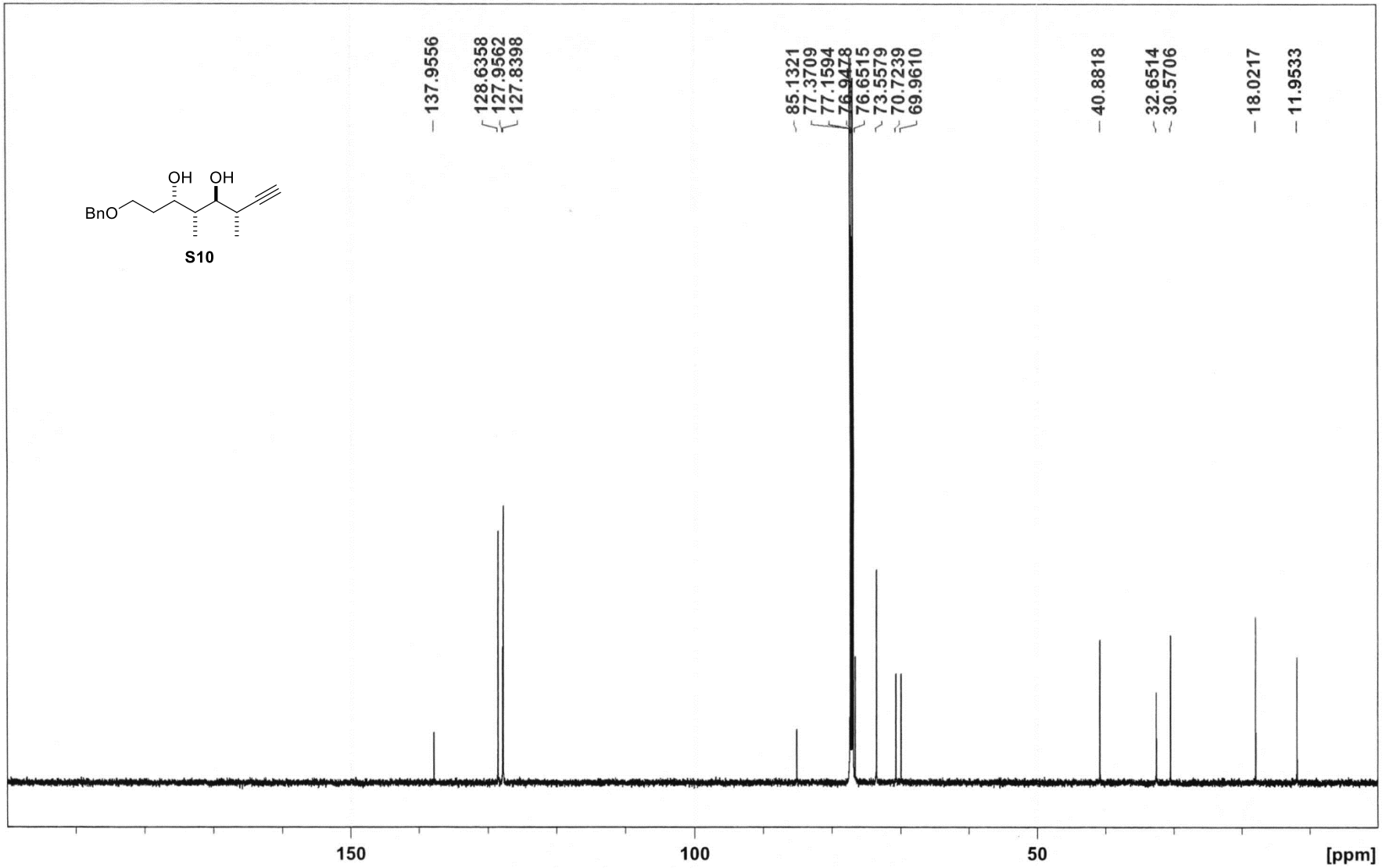



to-II-16-4+6 1 1 D:\kigoshi Kigoshi
TESO
OH
BnO
S9
[ppm]

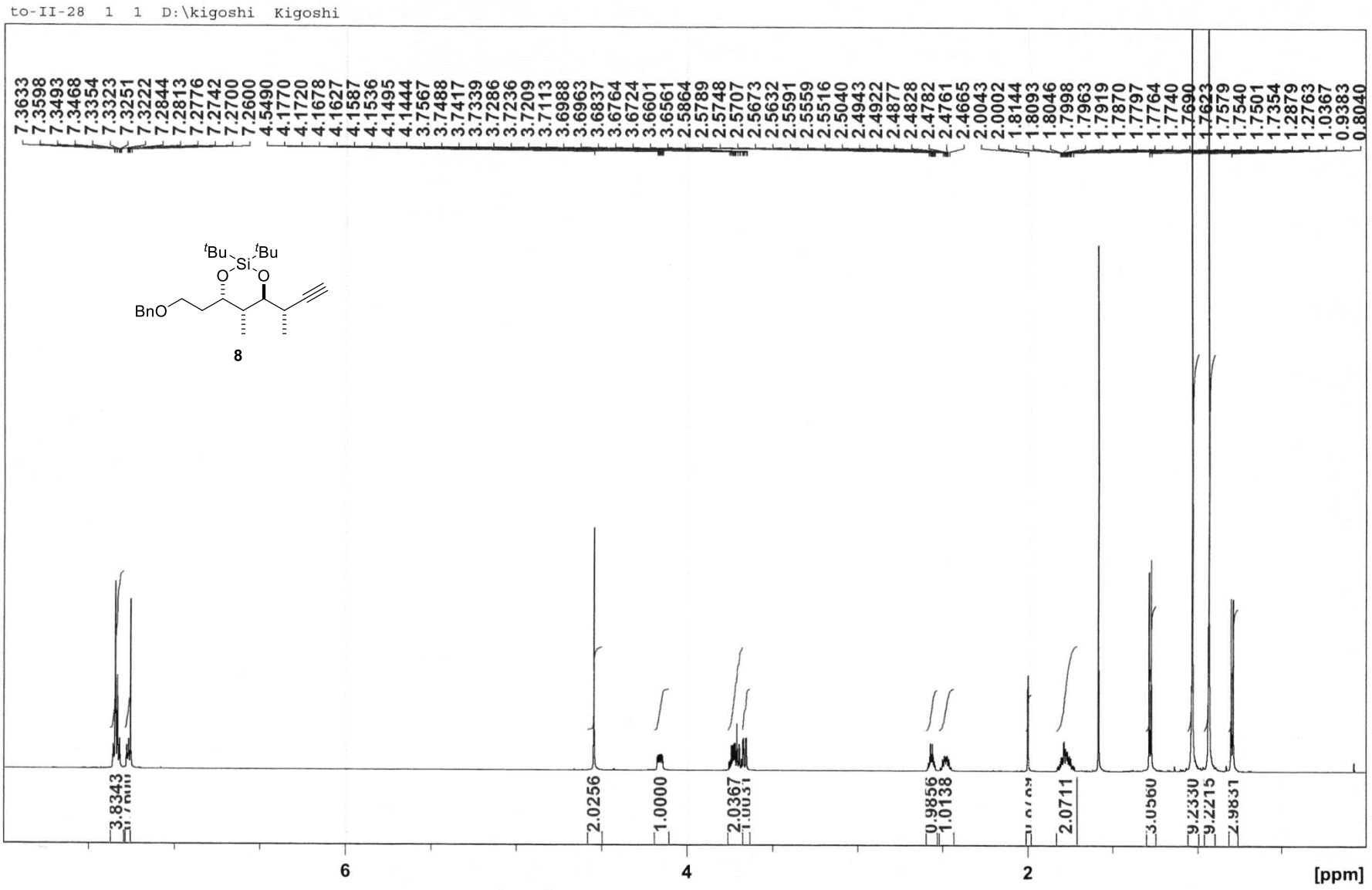

to-II-16-4+6-carbon 1 1 D:\kigoshi Kigoshi
138.5600
128.4976
127.8401
127.7094
85.1969
77.3713
77.1599
76.9483
76.0890
74.3041
73.1129
70.1967
67.2506
41.6410
31.9409
30.4554
17.8394
13.4825
6.9963
4.9684
TESO
OH
BnO
S9
150
100
50
[ppm]

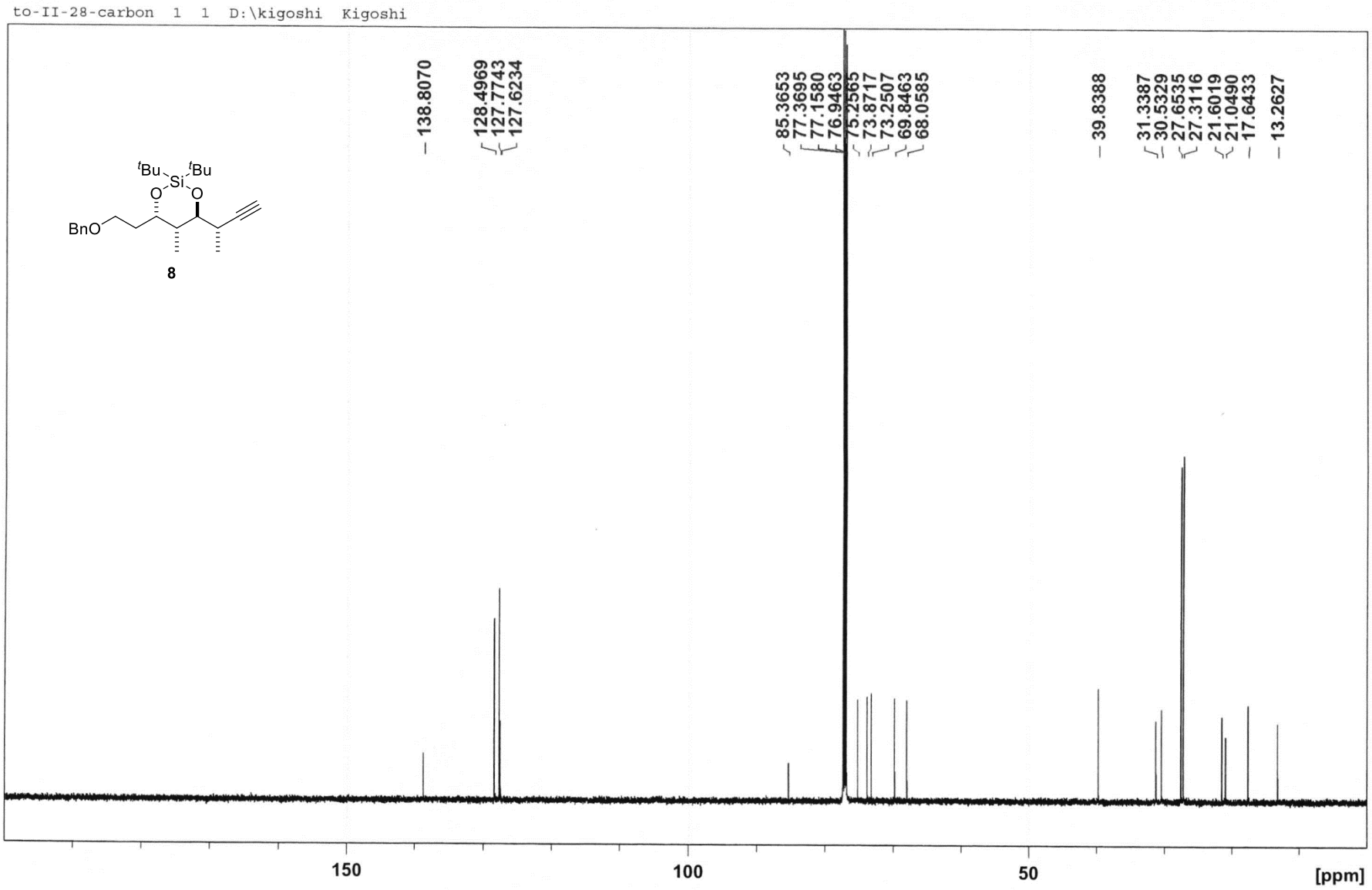

to-II-20-2 1 1 D:\kigoshi Kigoshi
7.3348
7.3187
7.3071
7.3053
7.2905
7.2863
7.2812
7.2812
7.2787
7.2597
4.5321
4.1659
4.1624
4.1489
4.1454
3.7724
3.7643
3.7568
3.7491
3.7410
3.6894
3.6827
3.6741
3.6675
3.6589
3.6522
3.5337
3.5304
3.4777
3.4694
3.4636
3.4556
3.4496
3.4261
3.4177
2.7049
2.7003
2.6934
2.6888
2.6830
2.6770
2.6716
2.6654
2.6601
2.1038
2.0998
1.9957
1.9878
1.9801
1.9716
1.9634
1.9582
1.9561
1.9486
1.9471
1.9391
1.9333
1.9260
1.9218
1.6464
1.6388
1.6364
1.6284
1.6226
1.6189
1.6150
1.6119
1.6078
1.6041
1.2877
1.2759
0.9008
0.8890
BnO
OH
OH
S10
5.0339
2.0370
1.0000
1.0272
1.1222
1.0854
1.1301
1.0029
0.9794
0.8359
2.0875
2.1053
3.3703
3.2494
6
4
2
[ppm]

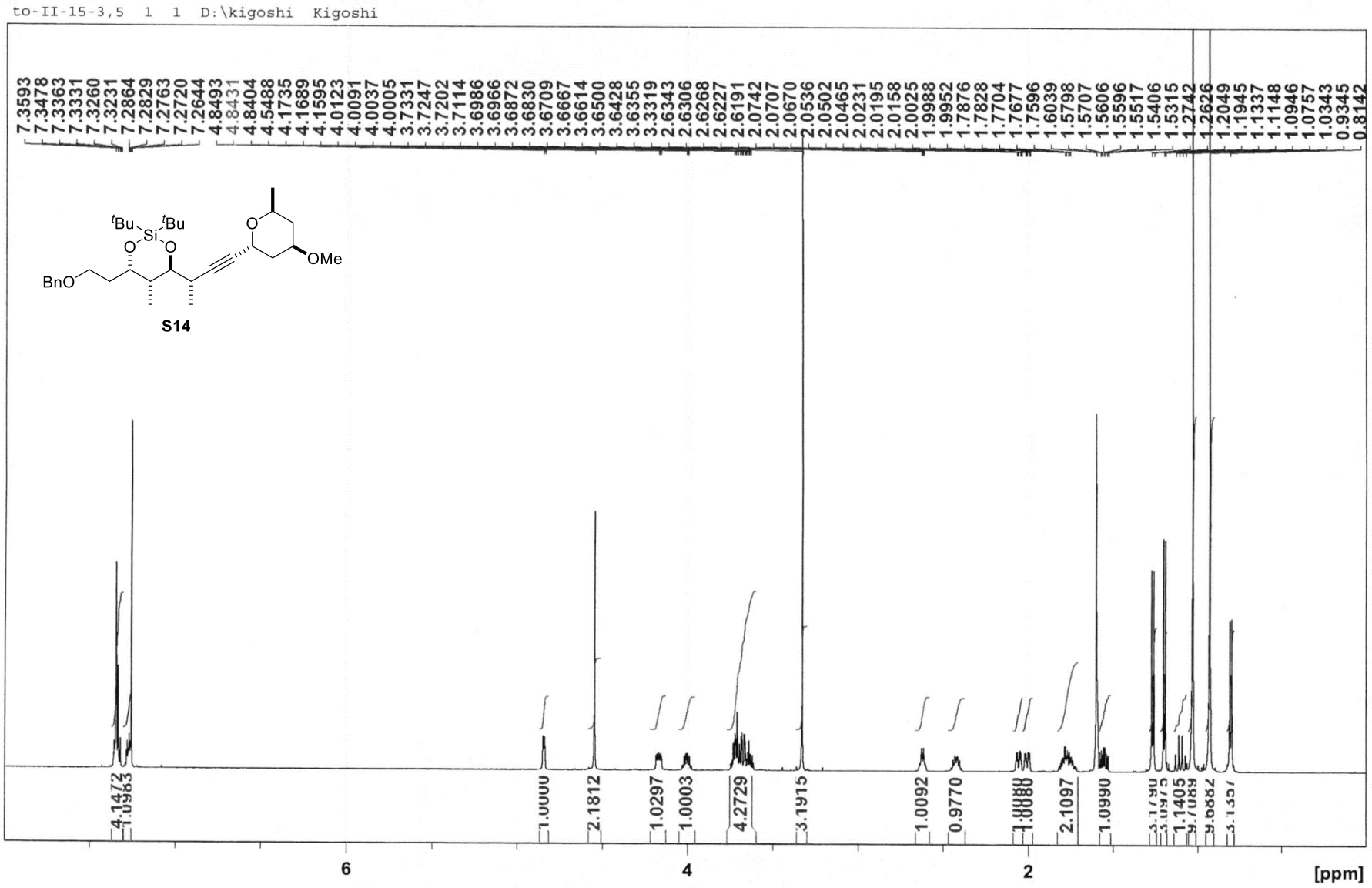
to-II-20-2-carbon 1 1 D:\kigoshi Kigoshi



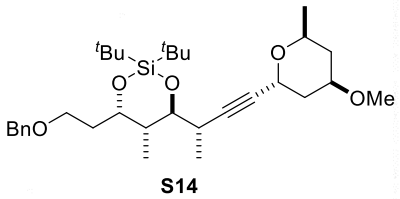
S10


to-II-28 1 1 D:\kigoshi Kigoshi
7.3633
7.3598
7.3493
7.3468
7.3354
7.3323
7.3251
7.3222
7.2844
7.2813
7.2776
7.2742
7.2700
7.2600
4.5490
4.1770
4.1720
4.1678
4.1627
4.1587
4.1536
4.1495
4.1444
3.7567
3.7488
3.7417
3.7339
3.7286
3.7236
3.7209
3.7113
3.6988
3.6963
3.6837
3.6764
3.6724
3.6601
3.6561
2.5864
2.5789
2.5748
2.5707
2.5673
2.5632
2.5591
2.5559
2.5516
2.5040
2.4943
2.4922
2.4877
2.4828
2.4782
2.4761
2.4665
2.0043
2.0002
1.8144
1.8093
1.8046
1.7998
1.7963
1.7919
1.7870
1.7797
1.7764
1.7740
1.7690
1.7623
1.7579
1.7540
1.7501
1.7354
1.2879
1.2763
1.0367
0.9383
0.8040
tBu
Si
tBu
O
O
BnO
8
3.8343
2.0256
1.0000
2.0367
1.0031
0.9856
1.0138
2.0711
3.0560
9.2330
9.2215
2.9831
6
4
2
[ppm]


to-II-28-carbon 1 1 D:\kigoshi Kigoshi
138.8070
128.4969
127.7743
127.6234
85.3653
77.3695
77.1580
76.9463
75.2565
73.8717
73.2507
69.8463
68.0585
39.8388
31.3387
30.5329
27.6535
27.3116
21.6019
21.0490
17.6433
13.2627
tBu
tBu
Si
O
O
BnO
8
150
100
50
[ppm]


to-II-15-3,5 1 1 D:\kigoshi Kigoshi
7.3593
7.3478
7.3363
7.3331
7.3260
7.3231
7.2864
7.2829
7.2763
7.2720
7.2644
4.8493
4.8431
4.8404
4.5488
4.1735
4.1689
4.1595
4.0123
4.0091
4.0037
4.0005
3.7331
3.7247
3.7202
3.7114
3.6986
3.6966
3.6872
3.6830
3.6709
3.6667
3.6614
3.6500
3.6428
3.6355
3.3319
2.6343
2.6306
2.6268
2.6227
2.6191
2.0742
2.0707
2.0670
2.0536
2.0502
2.0465
2.0231
2.0195
2.0158
2.0025
1.9988
1.9952
1.7876
1.7828
1.7704
1.7677
1.7596
1.6039
1.5798
1.5707
1.5606
1.5596
1.5517
1.5406
1.5315
1.2742
1.2626
1.2049
1.1945
1.1337
1.1148
1.0946
1.0757
1.0343
0.9345
0.8142
tBu
tBu
Si
O
O
O
O
OMe
BnO
S14
4.1472
1.0983
1.0000
2.1812
1.0297
1.0003
4.2729
3.1915
1.0092
0.9770
2.1097
1.0990
6
4
2
[ppm]

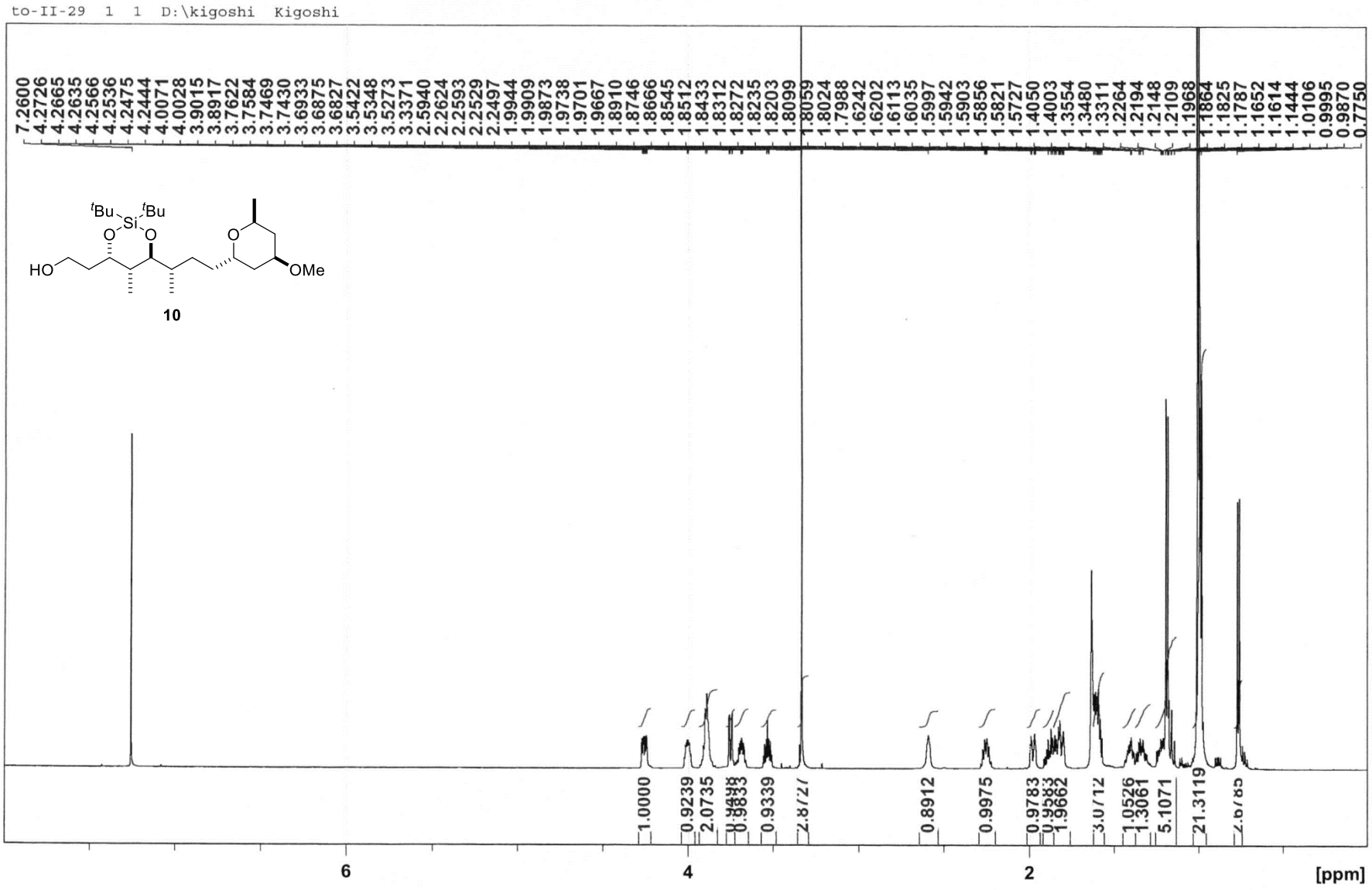
to-II-15-3,5-carbon 1 1 D:\kigoshi Kigoshi



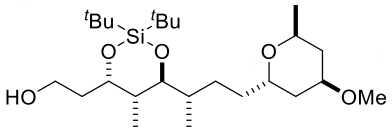
S14

138.7631
128.5088
127.7748
127.6452
87.7763
79.7585
77.3721
77.1607
76.9491
75.0770
73.8424
73.7953
73.2599
67.9671
66.7904
64.7644
55.4508
40.2489
39.8449
36.5447
31.4057
30.7478
27.6044
27.3022
21.9455
21.6445
20.9039
17.6991
13.2300

150 100 50 [ppm]


to-II-29 1 1 D:\kigoshi Kigoshi
7.2600
4.2726
4.2665
4.2635
4.2566
4.2536
4.2475
4.2444
4.0071
4.0028
3.9015
3.8917
3.7622
3.7584
3.7469
3.7430
3.6933
3.6875
3.6827
3.5422
3.5348
3.5273
3.3371
2.5940
2.2624
2.2593
2.2529
2.2497
1.9944
1.9909
1.9873
1.9738
1.9701
1.9667
1.8910
1.8746
1.8666
1.8545
1.8512
1.8433
1.8312
1.8272
1.8235
1.8203
1.8099
1.8059
1.8024
1.7988
1.6242
1.6202
1.6113
1.6035
1.5997
1.5942
1.5903
1.5856
1.5821
1.5727
1.4050
1.4003
1.3554
1.3480
1.3311
1.2264
1.2194
1.2148
1.2109
1.1968
1.1864
1.1825
1.1787
1.1652
1.1614
1.1444
1.0106
0.9995
0.9870
0.7750
tBu
Si
tBu
O
O
O
HO
OMe
10
1.0000
0.9239
2.0735
0.9339
0.8912
0.9975
0.9783
1.9662
1.0526
1.3061
5.1071
21.3119
6
4
2
[ppm]

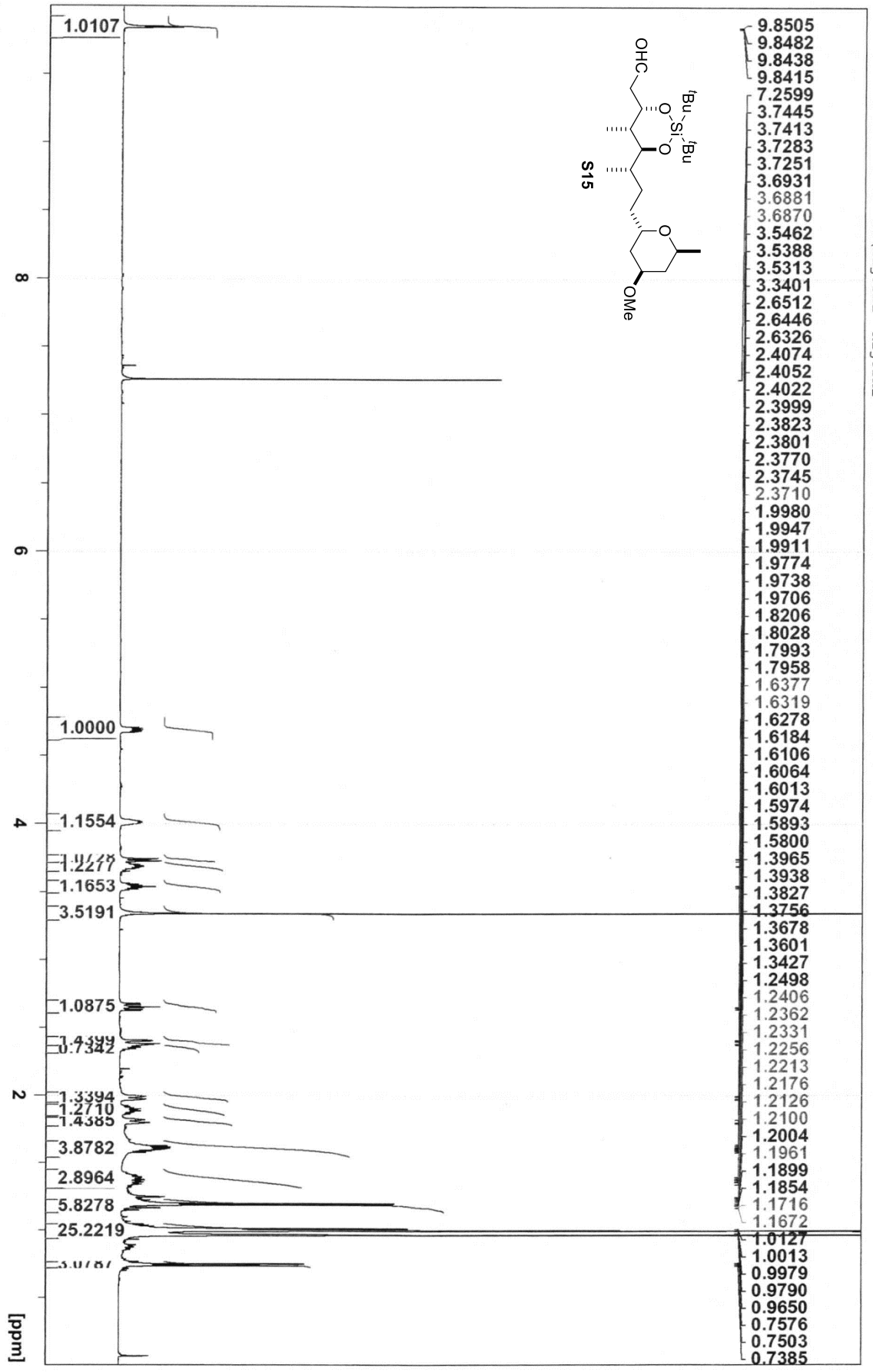
to-II-17-1-1-carbon 1 1 D:\kigoshi Kigoshi

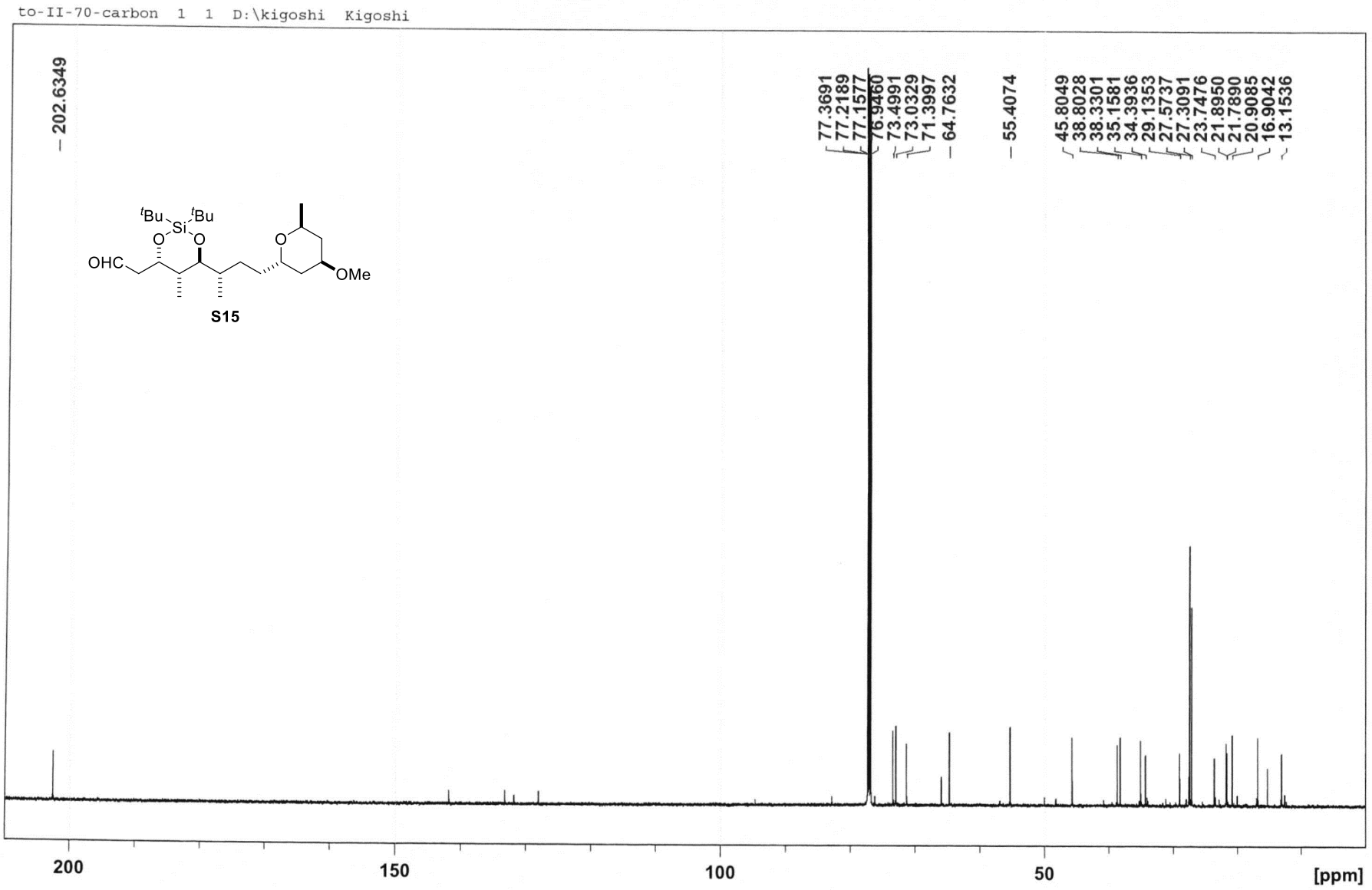


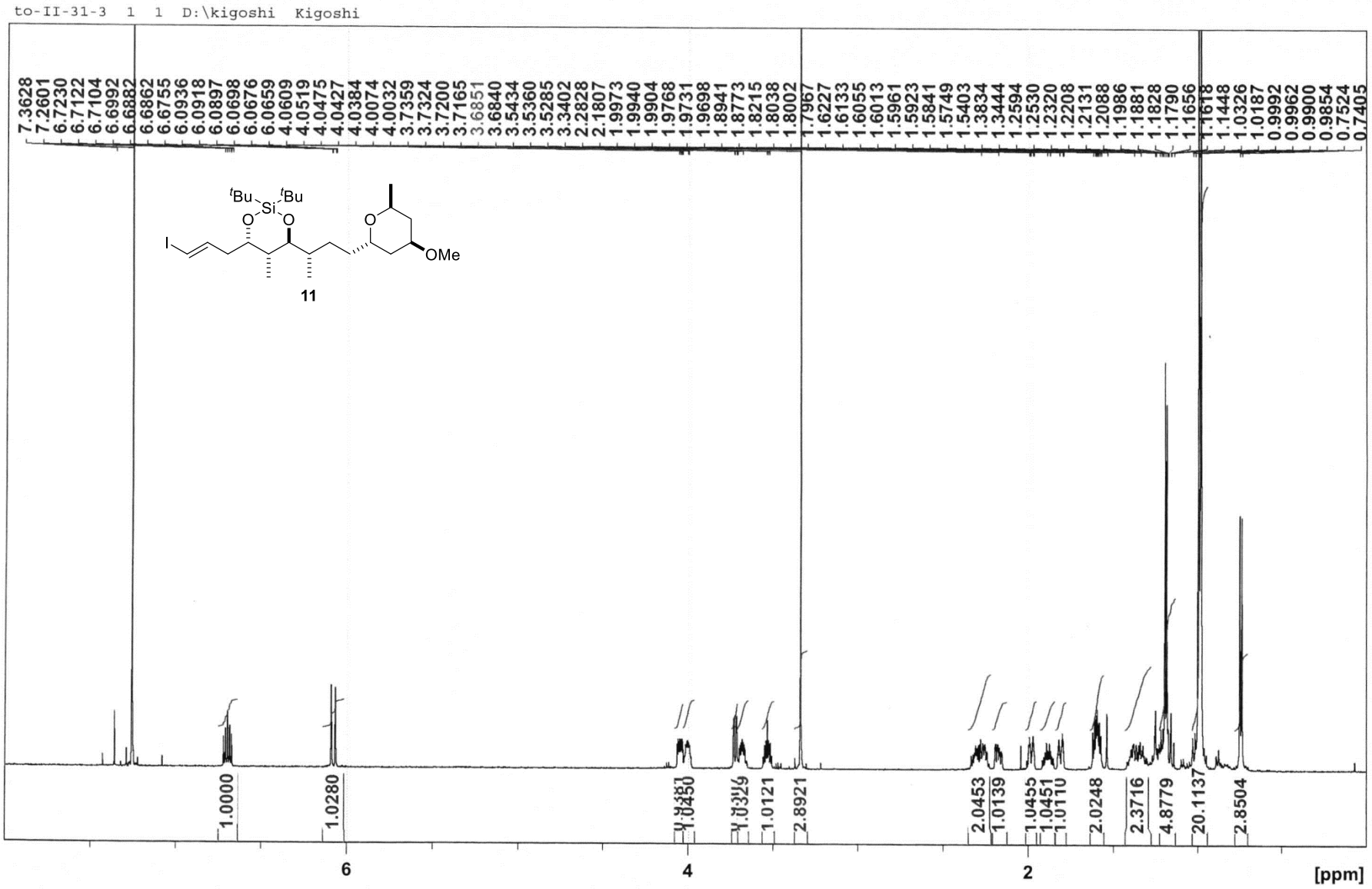
10

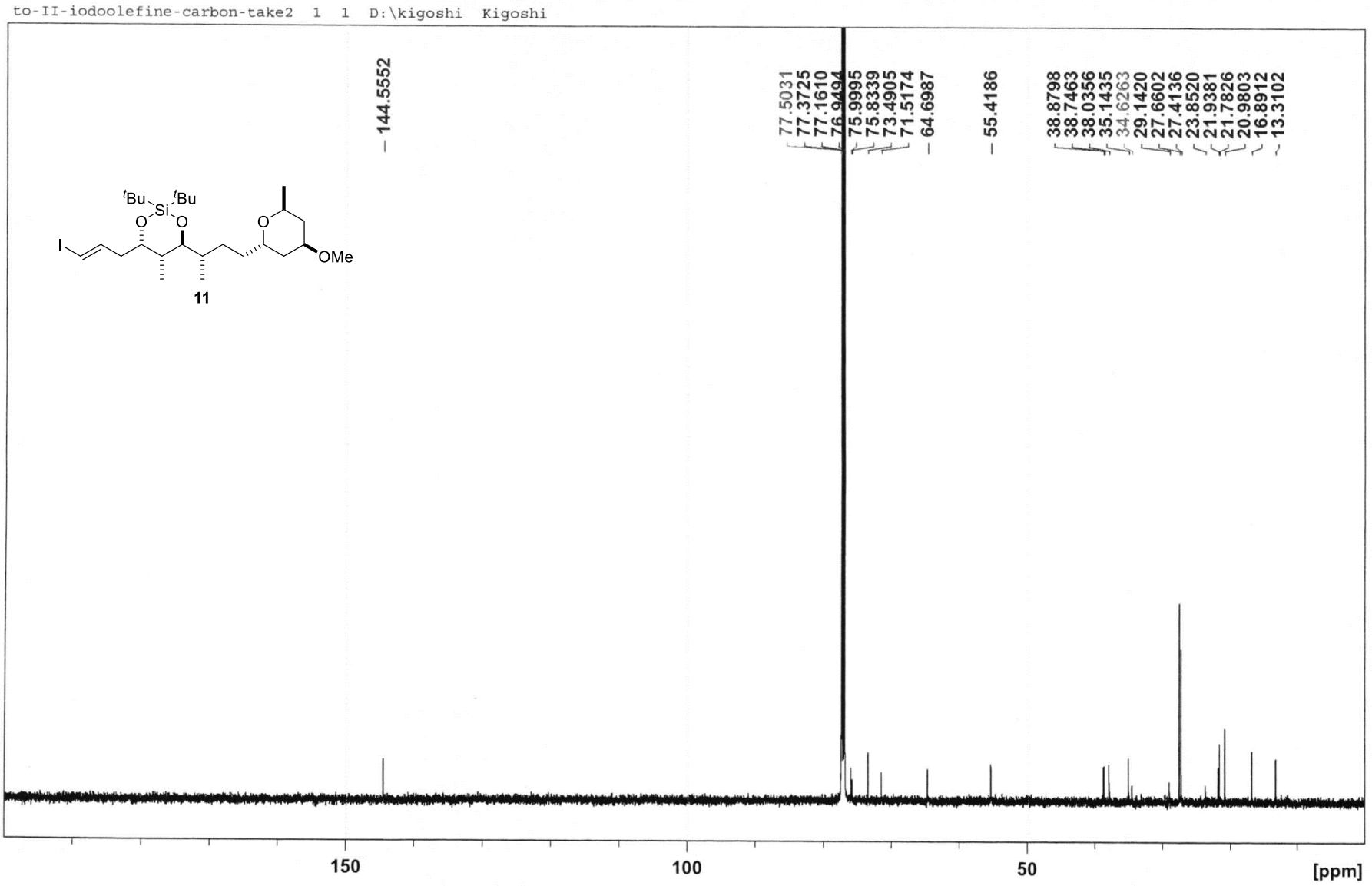
77.8758
77.4994
77.3720
77.1005
76.9491
73.5067
71.5973
64.7345
62.2663
55.4119
38.8971
38.8747
35.1411
34.9247
32.8241
29.2019
27.7711
27.4646
24.1265
21.9298
21.8275
21.1293
16.8697
13.4571

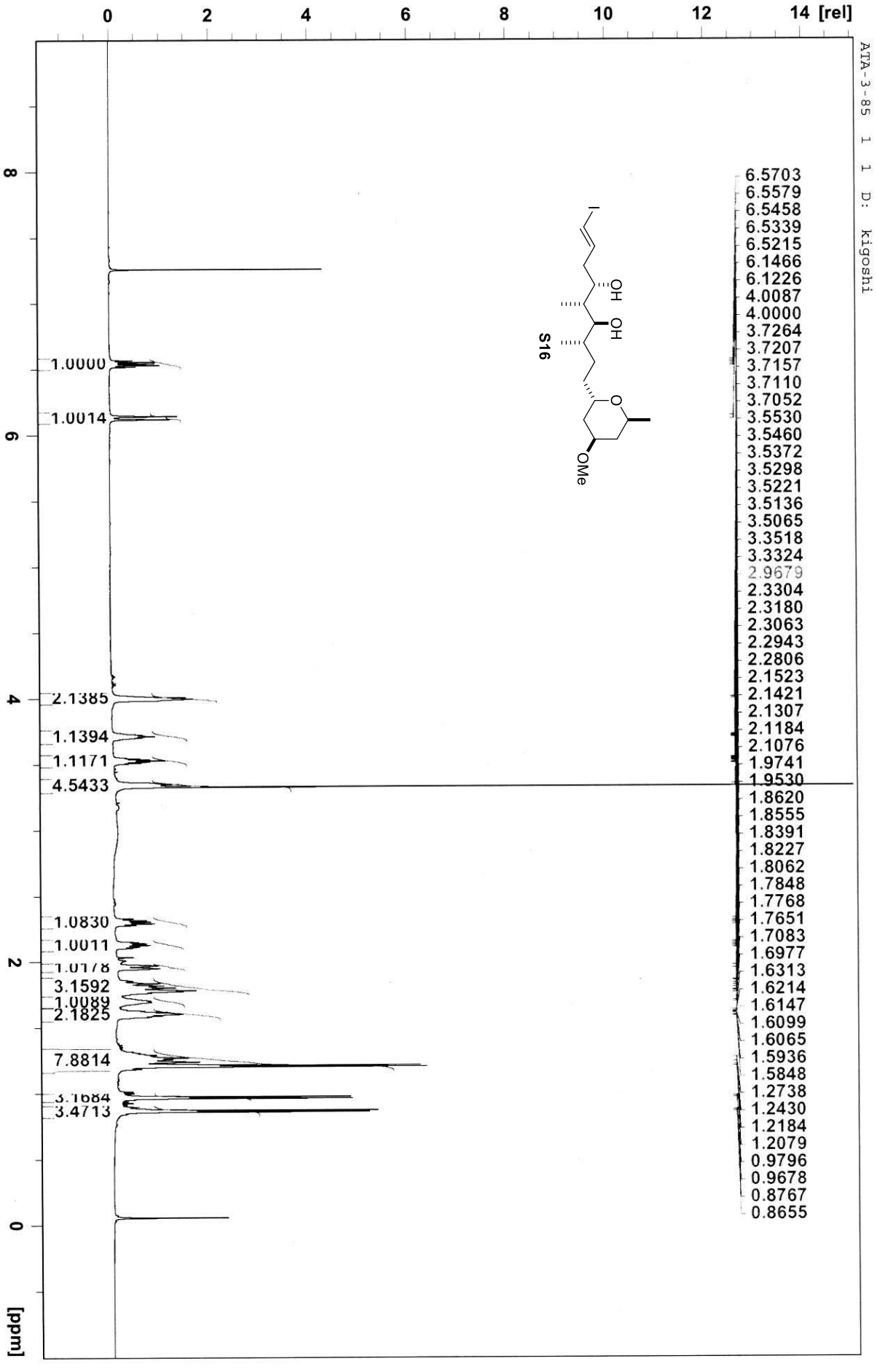
150 100 50 [ppm]

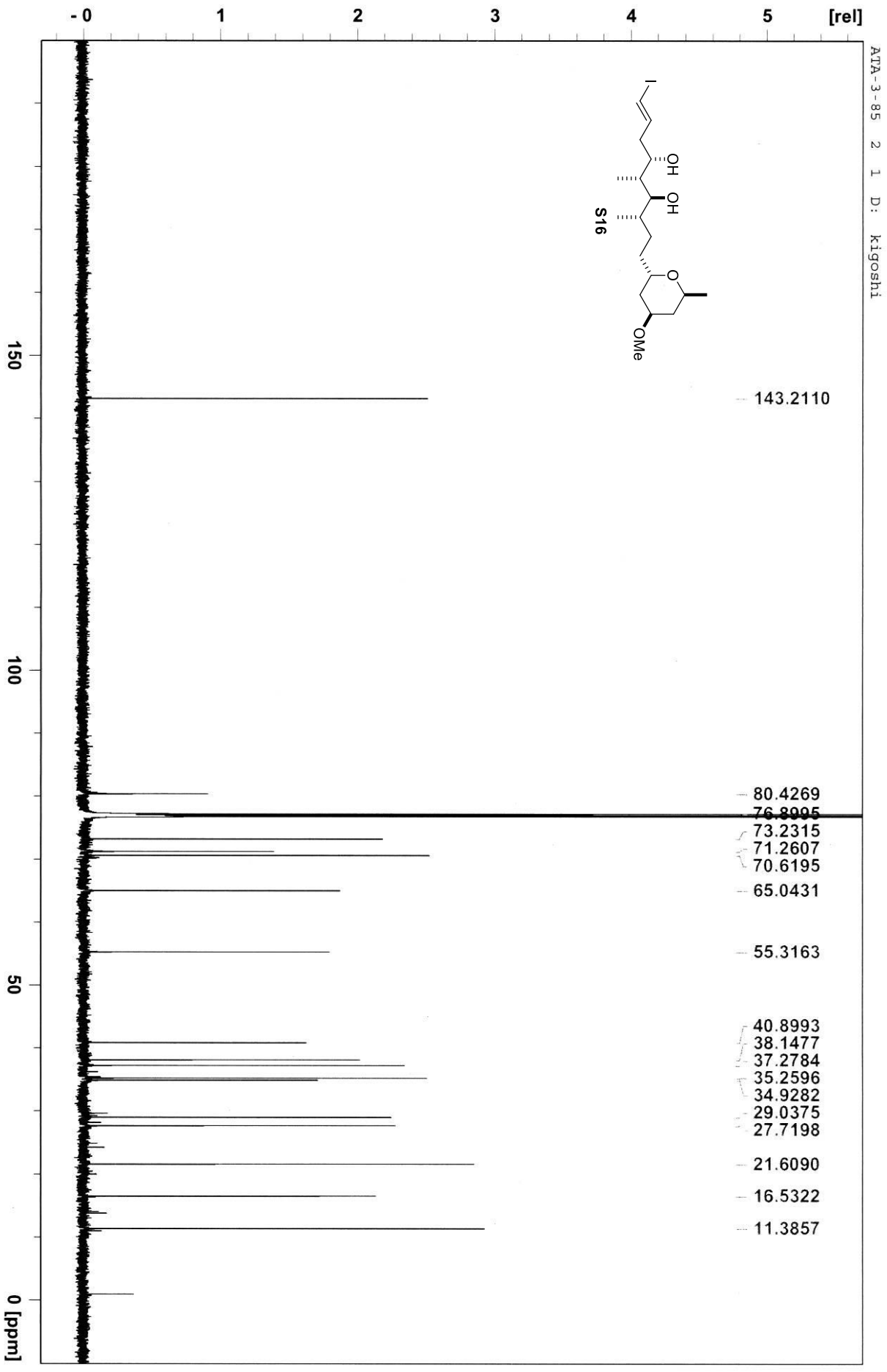

to-II-18-take2 1 1 D:\kigoshi Kigoshi
S15
OHC
tBu
tBu
Si
O
O
OMe
9.8505
9.8482
9.8438
9.8415
7.2599
3.7445
3.7413
3.7283
3.7251
3.6931
3.6881
3.6870
3.5462
3.5388
3.5313
3.3401
2.6512
2.6446
2.6326
2.4074
2.4052
2.4022
2.3999
2.3823
2.3801
2.3770
2.3745
2.3710
1.9980
1.9947
1.9911
1.9774
1.9738
1.9706
1.8206
1.8028
1.7993
1.7958
1.6377
1.6319
1.6278
1.6184
1.6106
1.6064
1.6013
1.5974
1.5893
1.5800
1.3965
1.3938
1.3827
1.3756
1.3678
1.3601
1.3427
1.2498
1.2406
1.2362
1.2331
1.2256
1.2213
1.2176
1.2126
1.2100
1.2004
1.1961
1.1899
1.1854
1.1716
1.1672
1.0127
1.0013
0.9979
0.9790
0.9650
0.7576
0.7503
0.7385
1.0107
1.0000
1.1554
1.2277
1.1653
3.5191
1.0875
0.7342
1.3394
1.2710
1.4385
3.8782
2.8964
5.8278
25.2219
8
6
4
2
[ppm]

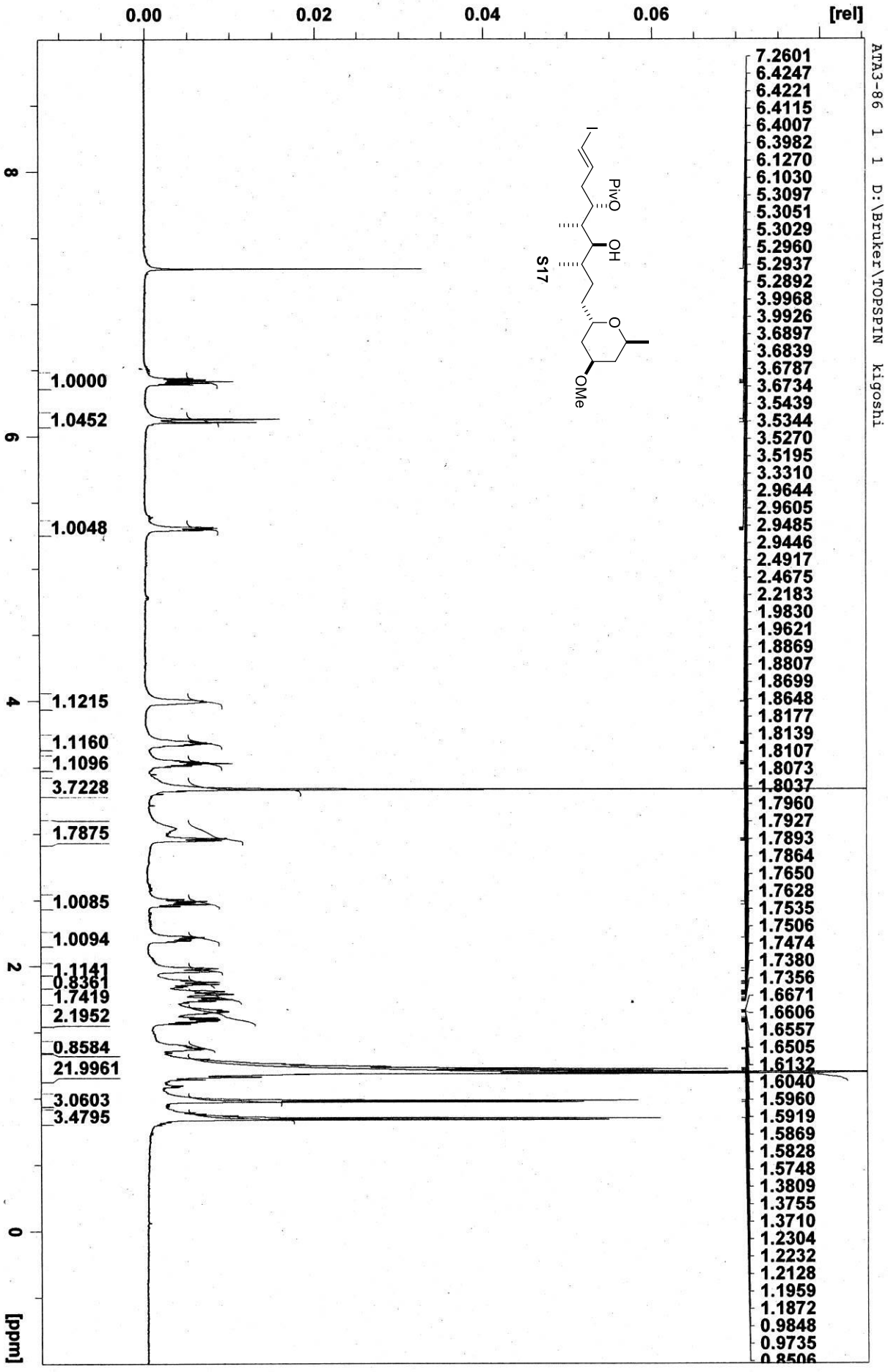

to-II-70-carbon 1 1 D:\kigoshi Kigoshi
202.6349
77.3691
77.2189
77.1577
76.9460
73.4991
73.0329
71.3997
64.7632
55.4074
45.8049
38.8028
38.3301
35.1581
34.3936
29.1353
27.5737
27.3091
23.7476
21.8950
21.7890
20.9085
16.9042
13.1536
tBu
Si
tBu
O
O
O
OHC
OMe
S15
200
150
100
50
[ppm]

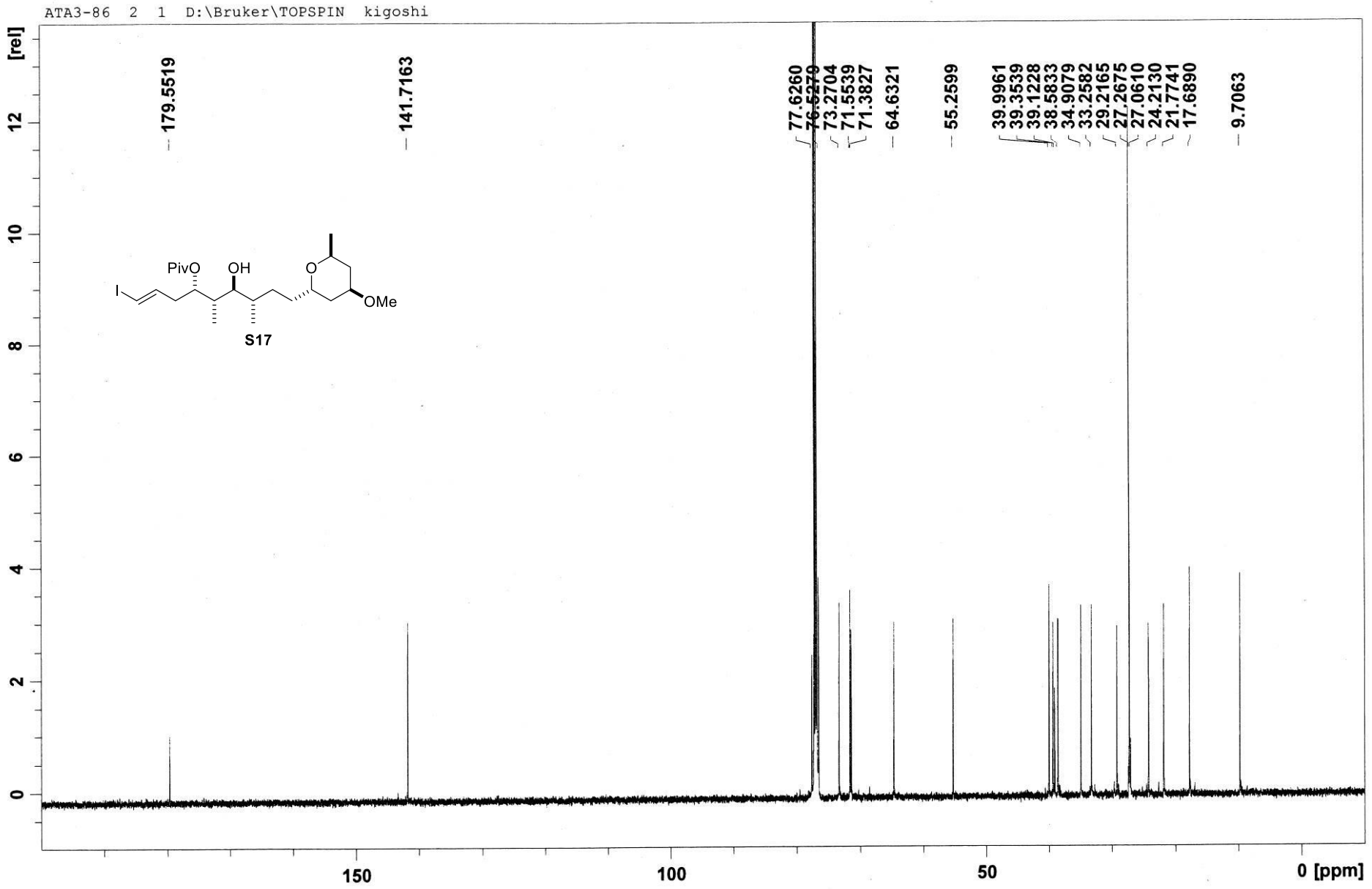

to-II-31-3 1 1 D:\kigoshi Kigoshi
7.3628
7.2601
6.7230
6.7122
6.7104
6.6992
6.6882
6.6862
6.6755
6.0936
6.0918
6.0897
6.0698
6.0676
6.0659
4.0609
4.0519
4.0475
4.0427
4.0384
4.0074
4.0032
3.7359
3.7324
3.7200
3.7165
3.6851
3.6840
3.5434
3.5360
3.5285
3.3402
2.2828
2.1807
1.9973
1.9940
1.9904
1.9768
1.9731
1.9698
1.8941
1.8773
1.8215
1.8038
1.8002
1.7967
1.6227
1.6133
1.6055
1.6013
1.5961
1.5923
1.5841
1.5749
1.5403
1.3834
1.3444
1.2594
1.2530
1.2320
1.2208
1.2131
1.2088
1.1986
1.1881
1.1828
1.1790
1.1656
1.1618
1.1448
1.0326
1.0187
0.9992
0.9962
0.9900
0.9854
0.7524
0.7405
tBu
tBu
Si
O
O
O
I
OMe
11
1.0000
1.0280
1.0121
2.8921
2.0453
1.0139
2.0248
2.3716
4.8779
20.1137
2.8504
6
4
2
[ppm]

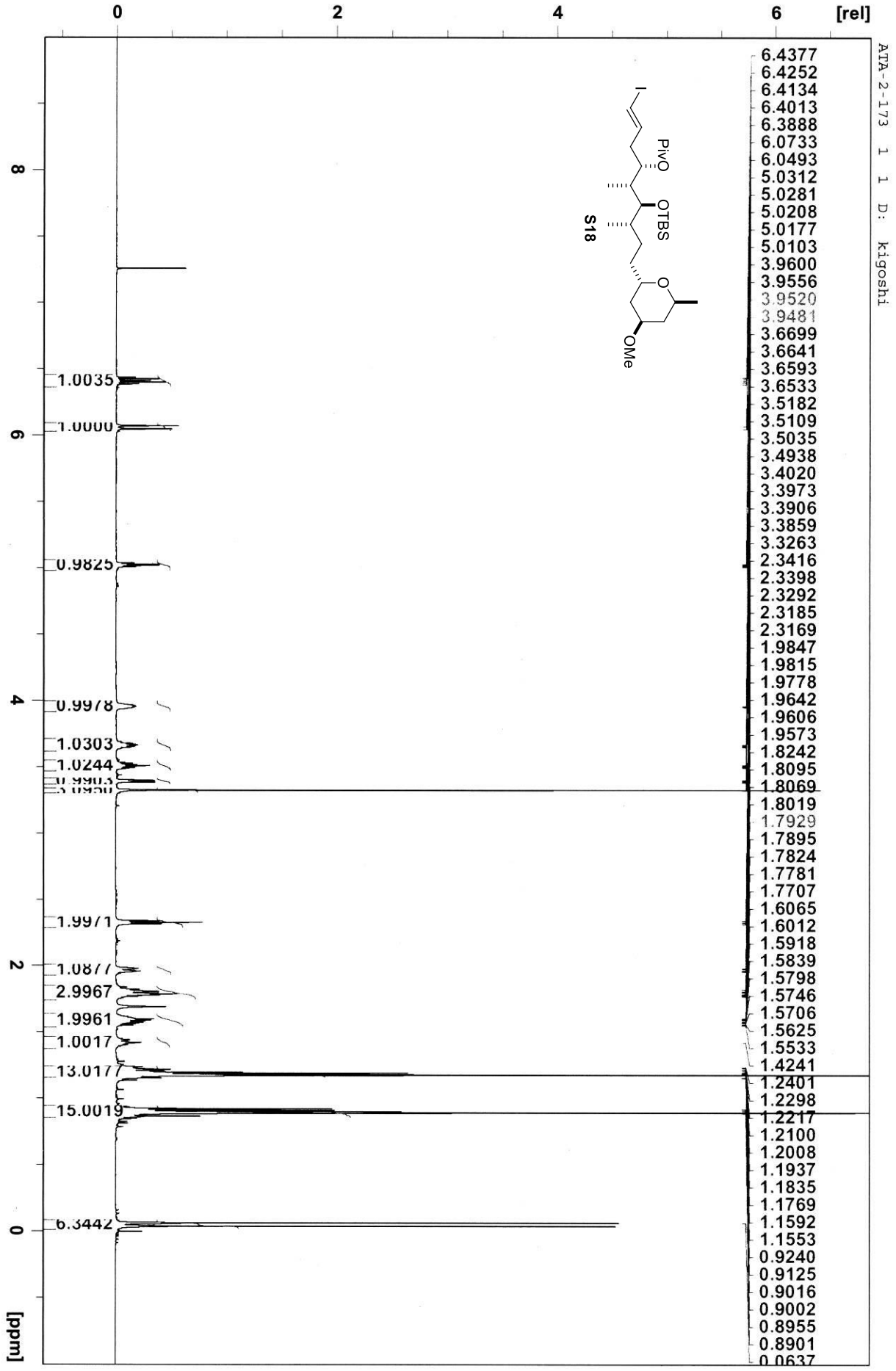

to-II-iodoolefine-carbon-take2 1 1 D:\kigoshi Kigoshi
144.5552
77.5031
77.3725
77.1610
76.9494
75.9995
75.8339
73.4905
71.5174
64.6987
55.4186
38.8798
38.7463
38.0356
35.1435
34.6263
29.1420
27.6602
27.4136
23.8520
21.9381
21.7826
20.9803
16.8912
13.3102
tBu
tBu
Si
O
O
O
I
OMe
11
150
100
50
[ppm]

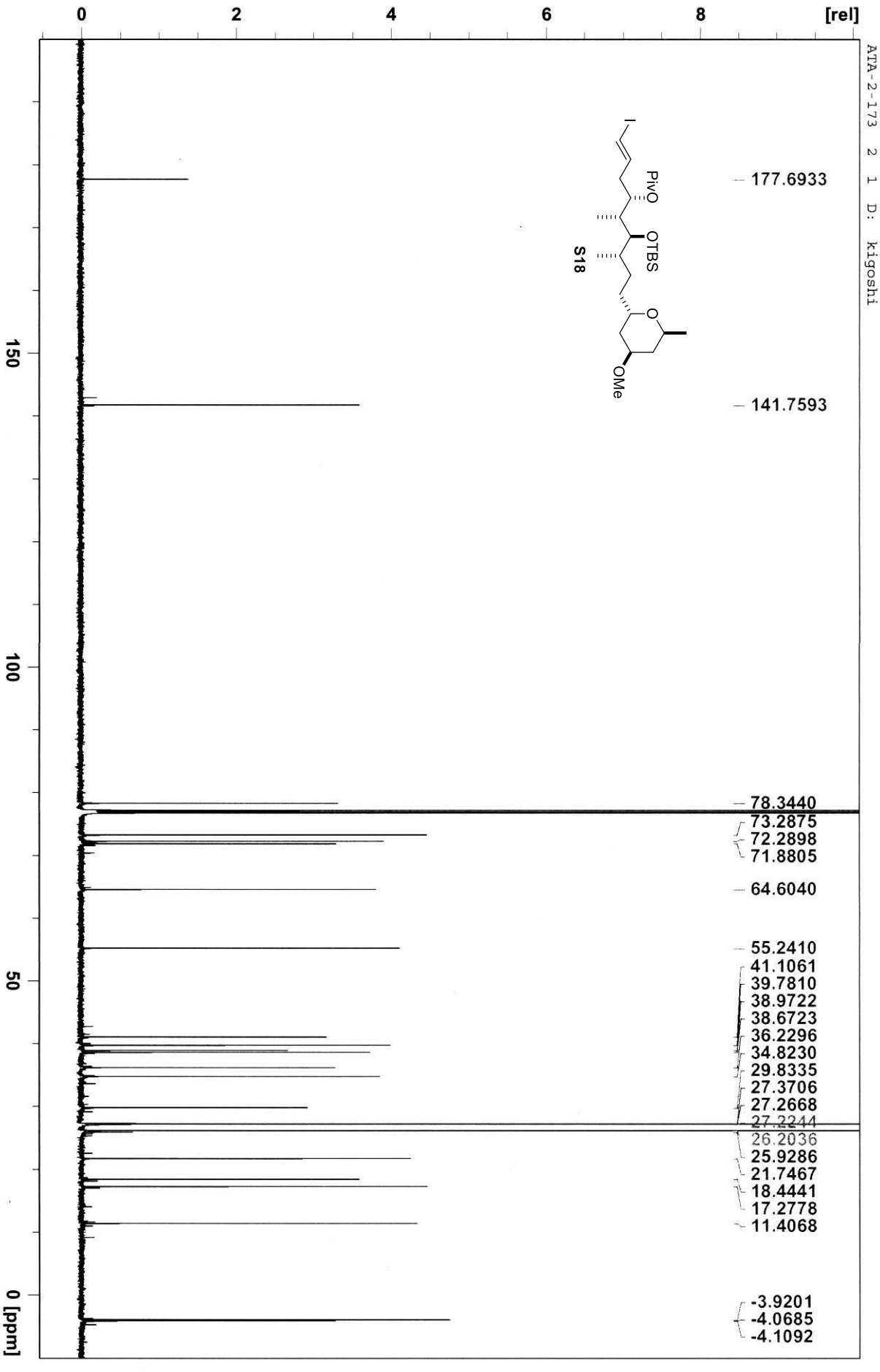

ATA-3-85 1 1 D: kigoshi
0 2 4 6 8 10 12 14 [rel]
8 6 4 2 0 [ppm]
S16
OH
OH
O
OMe
I
1.0000
1.0014
2.1385
1.1394
1.1171
4.5433
1.0830
1.0011
1.0178
3.1592
1.0089
2.1825
7.8814
3.1684
3.4713
6.5703
6.5579
6.5458
6.5339
6.5215
6.1466
6.1226
4.0087
4.0000
3.7264
3.7207
3.7157
3.7110
3.7052
3.5530
3.5460
3.5372
3.5298
3.5221
3.5136
3.5065
3.3518
3.3324
2.9679
2.3304
2.3180
2.3063
2.2943
2.2806
2.1523
2.1421
2.1307
2.1184
2.1076
1.9741
1.9530
1.8620
1.8555
1.8391
1.8227
1.8062
1.7848
1.7768
1.7651
1.7083
1.6977
1.6313
1.6214
1.6147
1.6099
1.6065
1.5936
1.5848
1.2738
1.2430
1.2184
1.2079
0.9796
0.9678
0.8767
0.8655

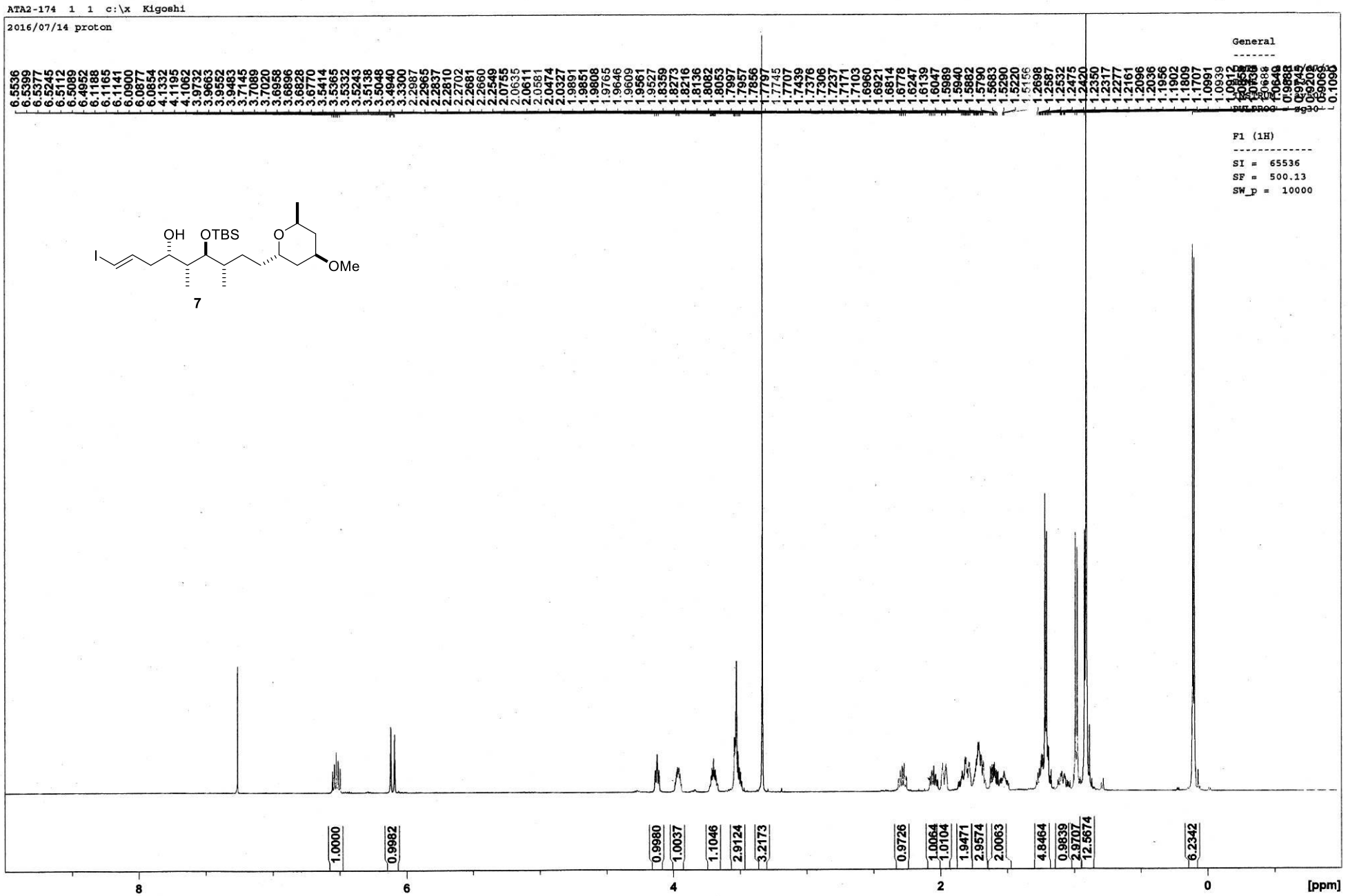

- 0
1
2
3
4
5
[rel]
150
100
50
0 [ppm]
OH
OH
O
OMe
I
S16
143.2110
80.4269
76.8995
73.2315
71.2607
70.6195
65.0431
55.3163
40.8993
38.1477
37.2784
35.2596
34.9282
29.0375
27.7198
21.6090
16.5322
11.3857
ATA-3-85 2 1 D: kigoshi

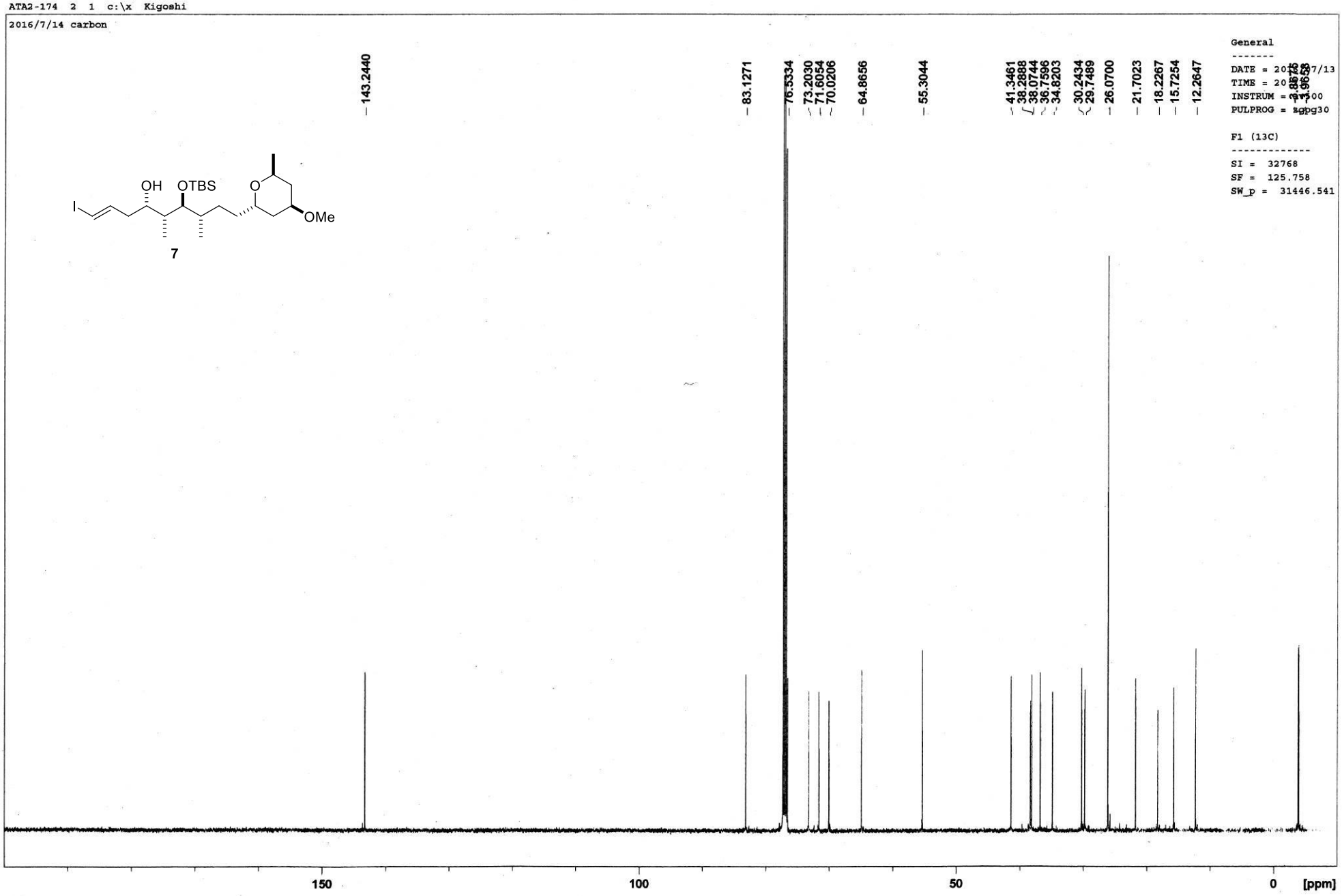

ATA3-86 1 1 D:\Bruker\TOPSPIN kigoshi
[rel]
0.00
0.02
0.04
0.06
[ppm]
8
6
4
2
0
PivO
OH
OMe
O
I
S17
1.0000
1.0452
1.0048
1.1215
1.1160
1.1096
3.7228
1.7875
1.0085
1.0094
1.1141
0.8361
1.7419
2.1952
0.8584
21.9961
3.0603
3.4795
7.2601
6.4247
6.4221
6.4115
6.4007
6.3982
6.1270
6.1030
5.3097
5.3051
5.3029
5.2960
5.2937
5.2892
3.9968
3.9926
3.6897
3.6839
3.6787
3.6734
3.5439
3.5344
3.5270
3.5195
3.3310
2.9644
2.9605
2.9485
2.9446
2.4917
2.4675
2.2183
1.9830
1.9621
1.8869
1.8807
1.8699
1.8648
1.8177
1.8139
1.8107
1.8073
1.8037
1.7960
1.7927
1.7893
1.7864
1.7650
1.7628
1.7535
1.7506
1.7474
1.7380
1.7356
1.6671
1.6606
1.6557
1.6505
1.6132
1.6040
1.5960
1.5919
1.5869
1.5828
1.5748
1.3809
1.3755
1.3710
1.2304
1.2232
1.2128
1.1959
1.1872
0.9848
0.9735
0.8506

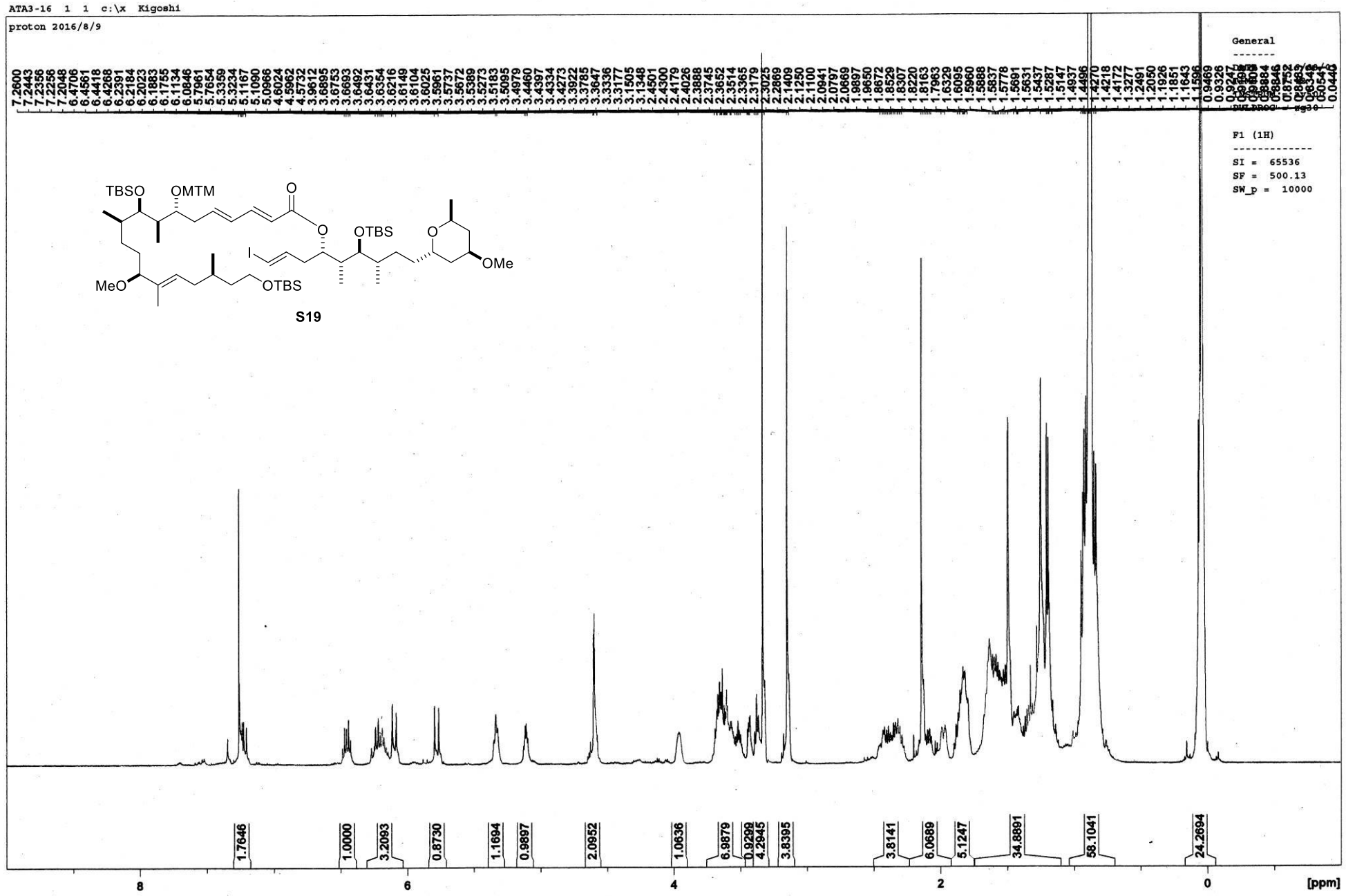

ATA3-86 2 1 D:\Bruker\TOPSPIN kigoshi
[rel]
179.5519
141.7163
77.6260
76.5279
73.2704
71.5539
71.3827
64.6321
55.2599
39.9961
39.3539
39.1228
38.5833
34.9079
33.2582
29.2165
27.2675
27.0610
24.2130
21.7741
17.6890
9.7063
PivO
OH
O
I
OMe
S17
0
2
4
6
8
10
12
150
100
50
0 [ppm]

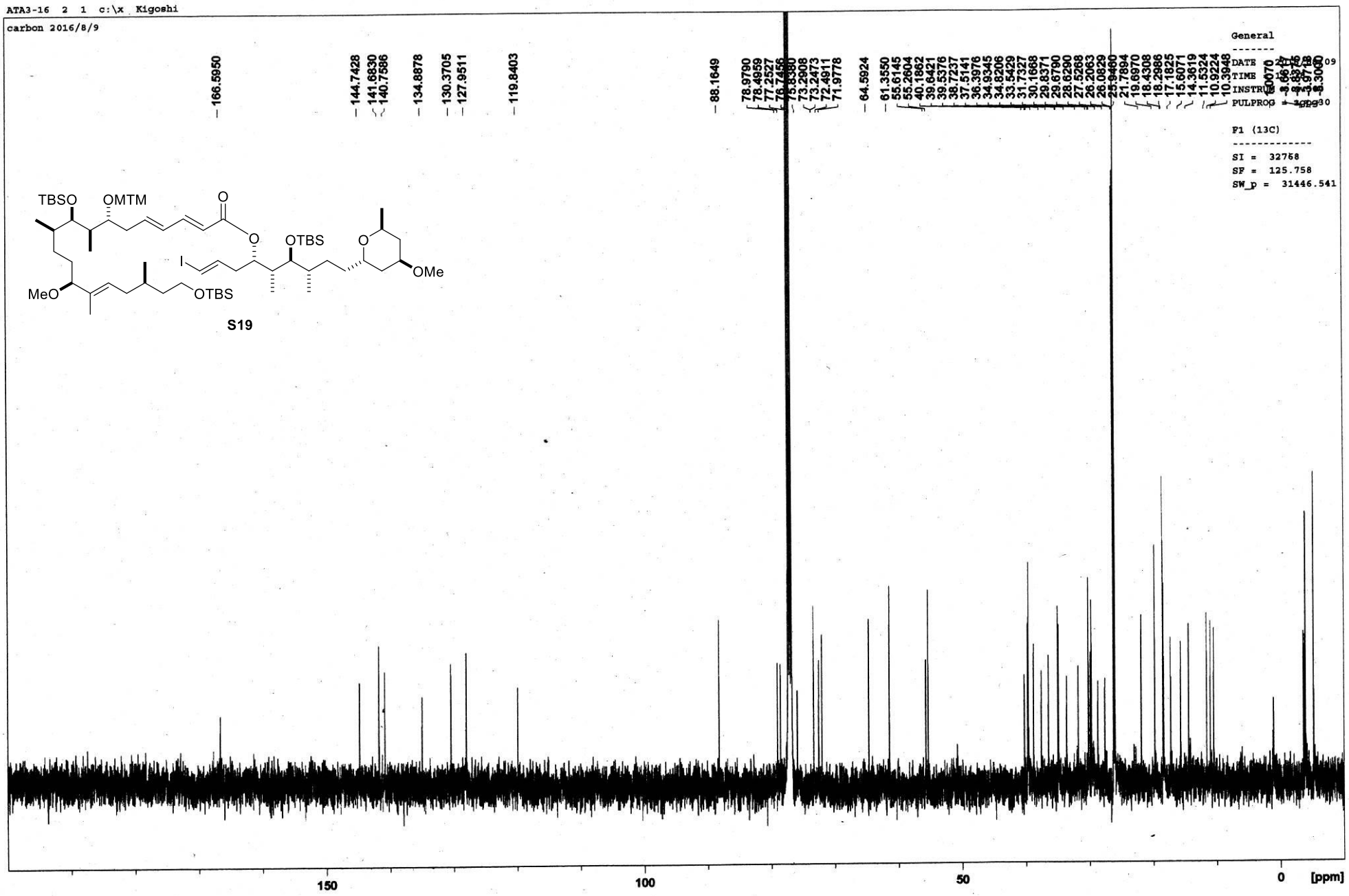

ATA-2-173 1 1 D: kigoshi
[rel]
[ppm]
PivO
OTBS
OMe
S18
1.0035
0.9825
0.9978
1.0303
1.0244
1.9971
1.0877
2.9967
1.9961
1.0017
13.0177
15.0019
6.3442

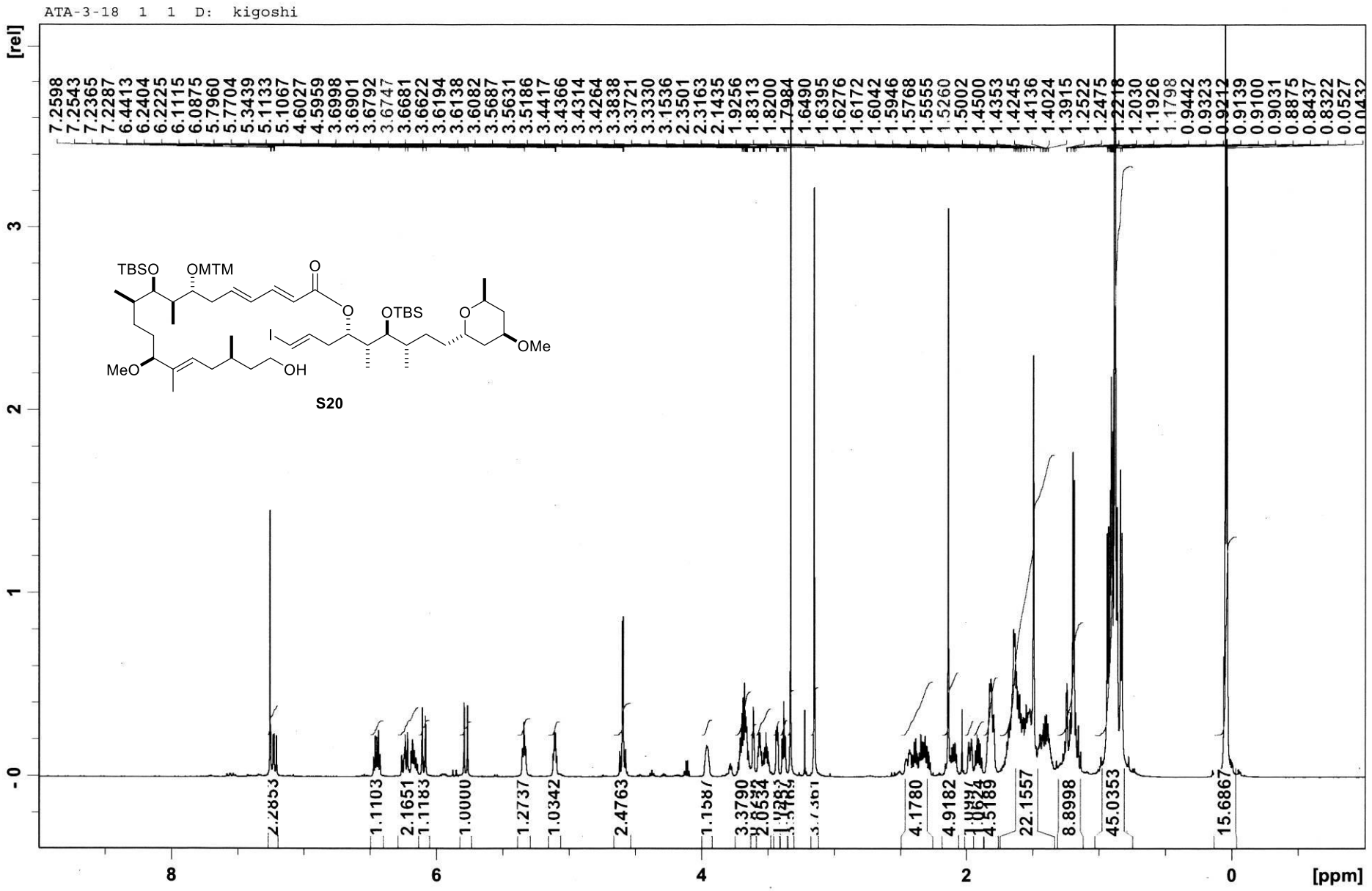

ATA-2-173 2 1 D: kigoshi
0
2
4
6
8
[rel]
150
100
50
0 [ppm]
PivO
OTBS
OMe
O
I
S18
177.6933
141.7593
78.3440
73.2875
72.2898
71.8805
64.6040
55.2410
41.1061
39.7810
38.9722
38.6723
36.2296
34.8230
29.8335
27.3706
27.2668
27.2244
26.2036
25.9286
21.7467
18.4441
17.2778
11.4068
-3.9201
-4.0685
-4.1092

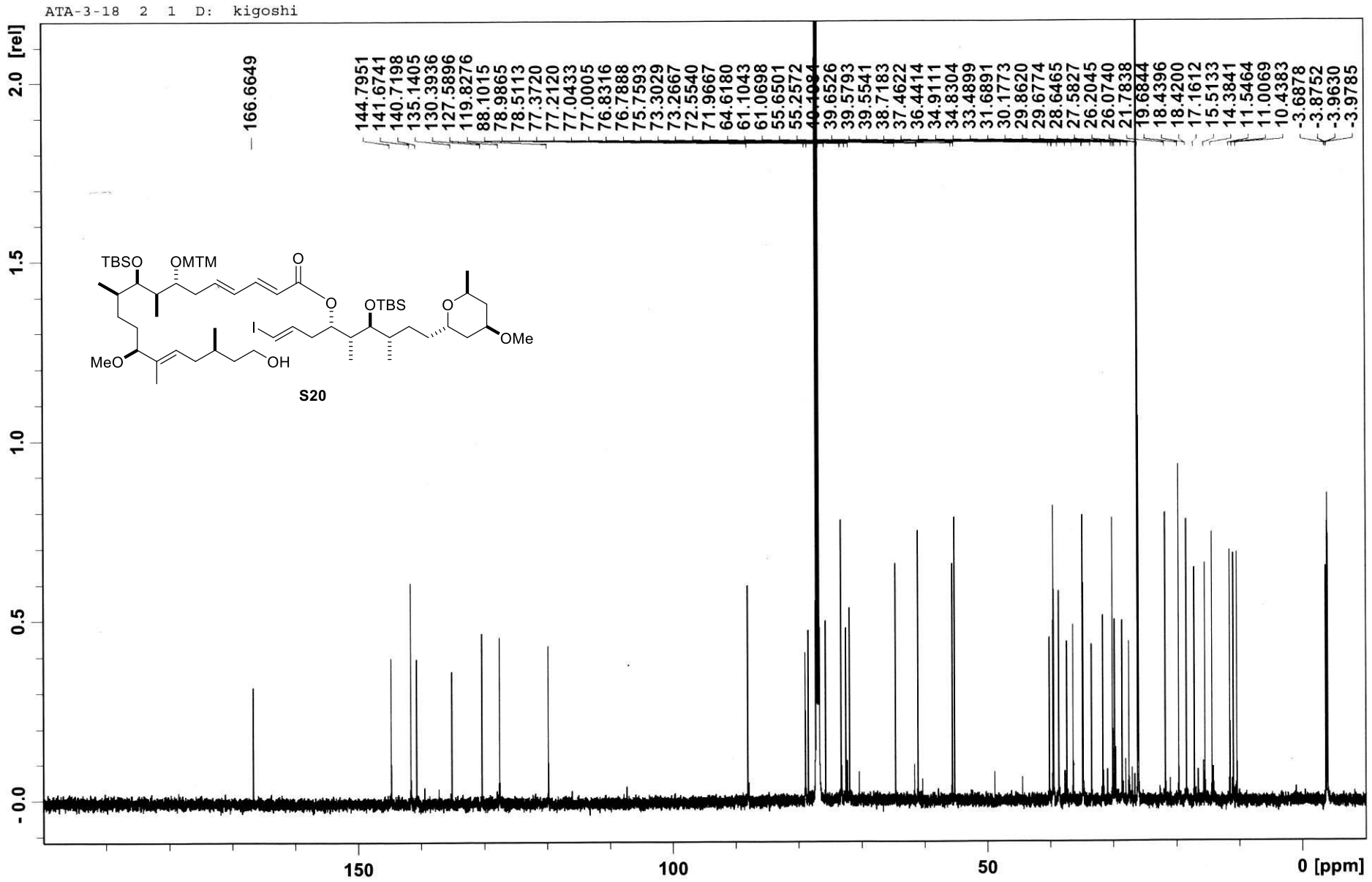

ATA2-174 1 1 c:\x Kigoshi
2016/07/14 proton
General
F1 (1H)
SI = 65536
SF = 500.13
SW_p = 10000
OH
OTBS
O
I
OMe
7
1.0000
0.9982
0.9980
1.0037
1.1046
2.9124
3.2173
0.9726
1.0064
1.0104
1.9471
2.9574
2.0063
4.8464
0.9839
2.9707
12.5674
6.2342
8
6
4
2
0
[ppm]

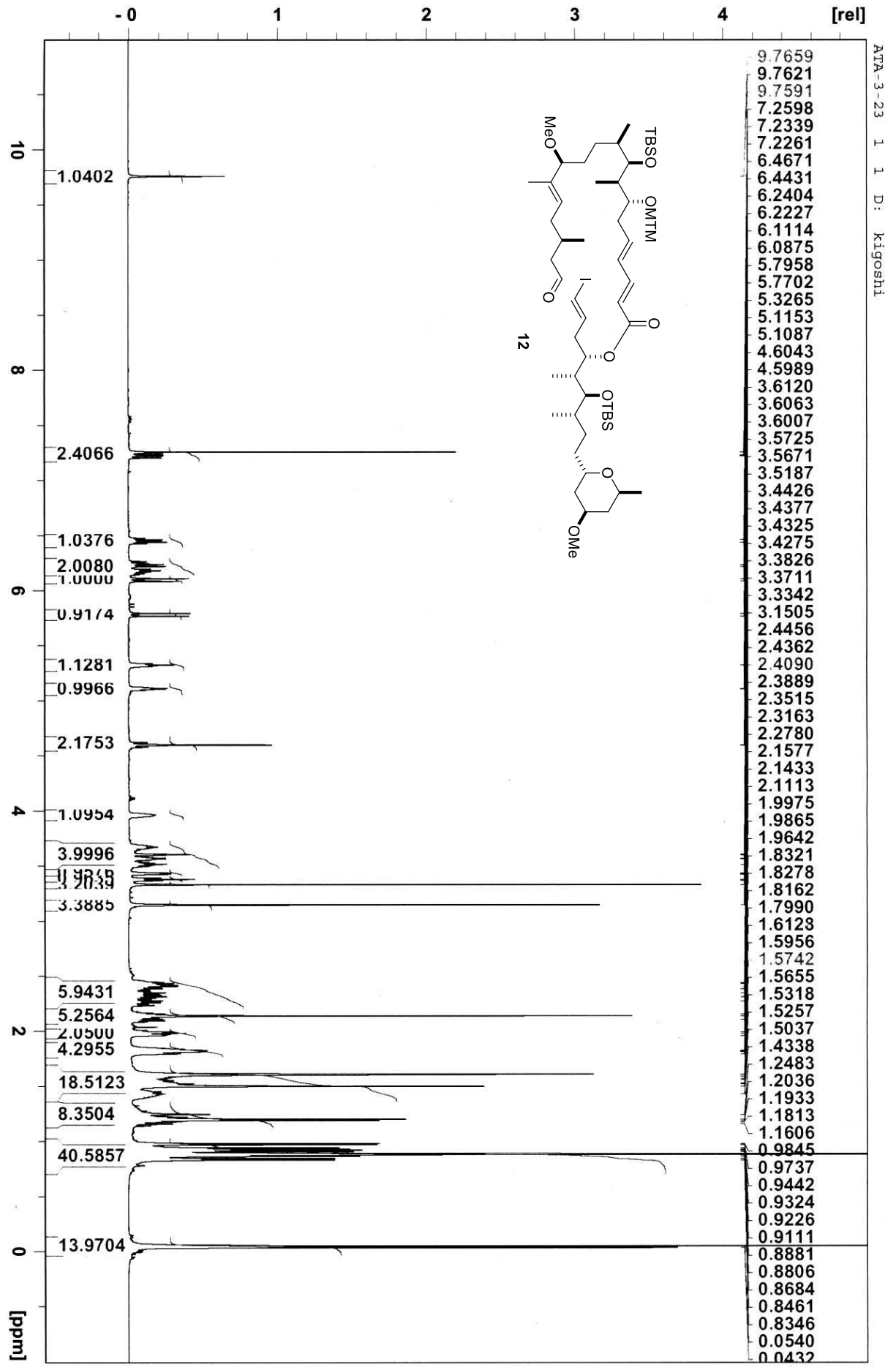

ATA2-174 2 1 c:\x Kigoshi
2016/7/14 carbon
143.2440
83.1271
76.5334
73.2030
71.6054
70.0206
64.8656
55.3044
41.3461
38.2888
38.0744
36.7596
34.8203
30.2434
29.7489
26.0700
21.7023
18.2267
15.7254
12.2647
General
DATE = 2016/7/13
TIME = 20
INSTRUM = 400
PULPROG = zgpg30
F1 (13C)
SI = 32768
SF = 125.758
SW_p = 31446.541
OH
OTBS
O
I
OMe
7
150
100
50
0
[ppm]

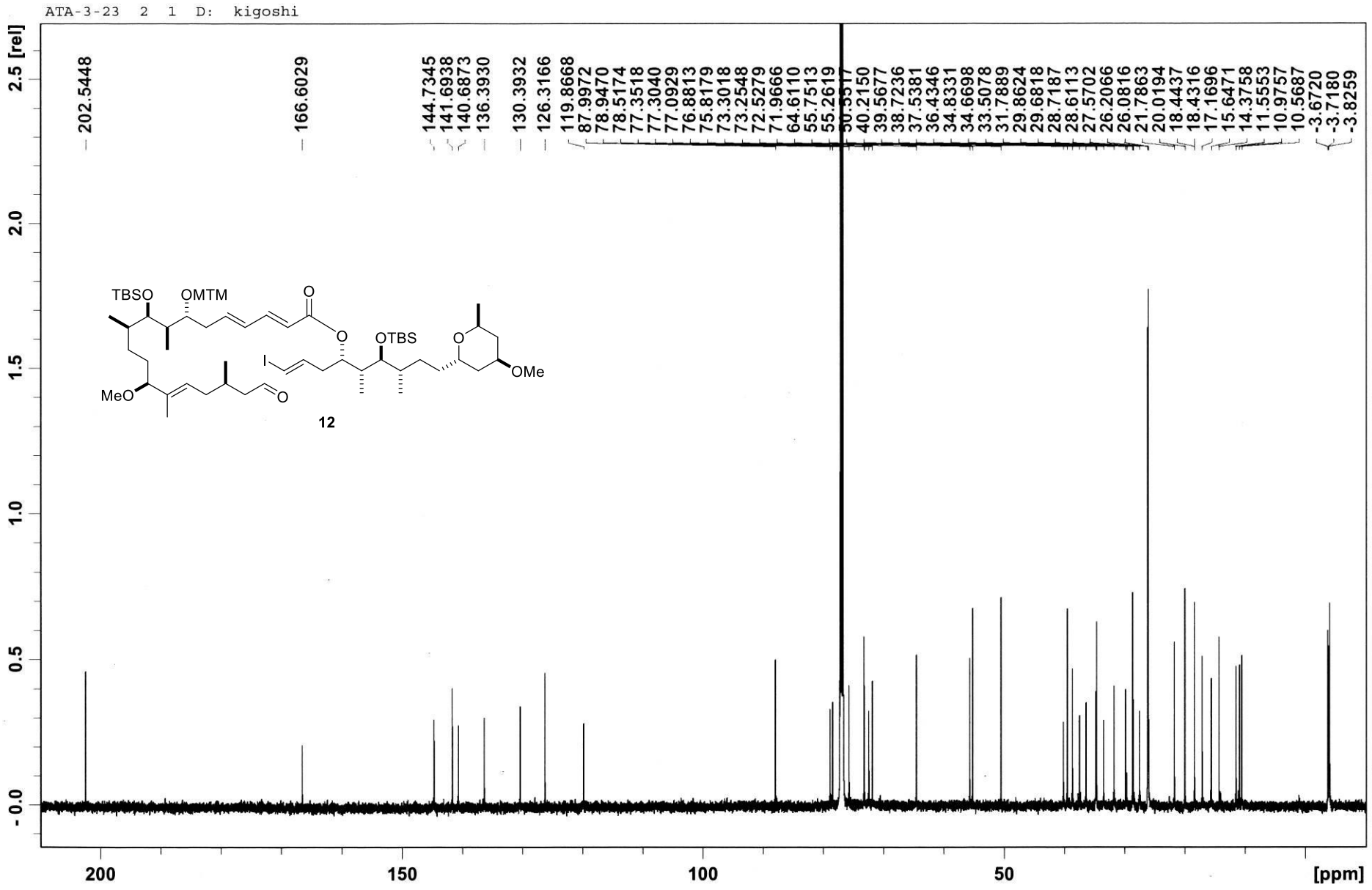

ATA3-16 1 1 c:\x Kigoshi
proton 2016/8/9
General
F1 (1H)
SI = 65536
SF = 500.13
SW_p = 10000
TBSO
OMTM
O
O
OTBS
O
I
OMe
MeO
OTBS
S19
1.7646
1.0000
3.2093
0.8730
1.1694
0.9897
2.0952
1.0636
6.9879
0.9299
4.2945
3.8395
3.8141
6.0689
5.1247
34.8891
58.1041
24.2694
8
6
4
2
0
[ppm]

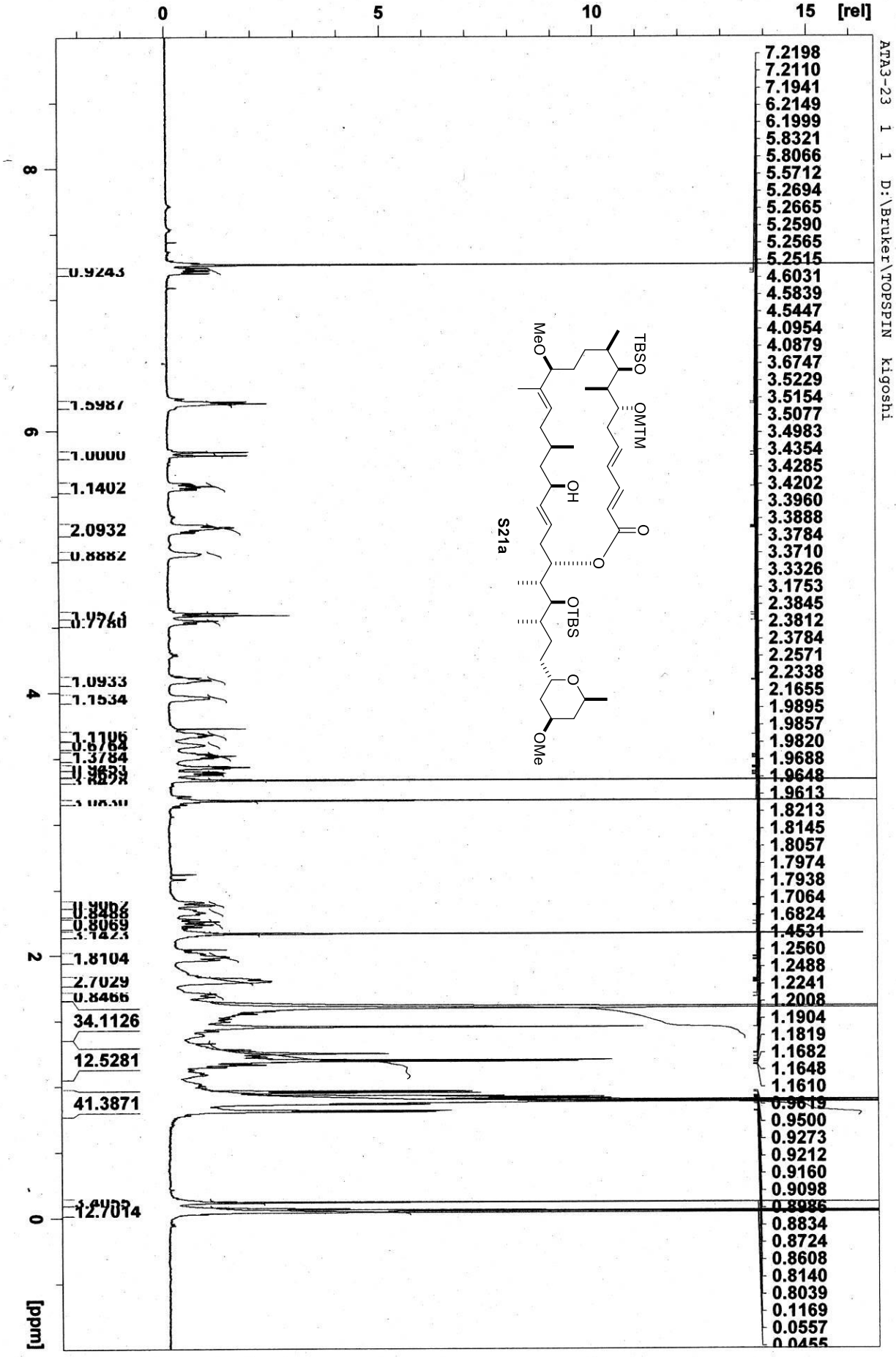

ATA3-16 2 1 c:\x Kigoshi
carbon 2016/8/9
166.5950
144.7428
141.6830
140.7586
134.8878
130.3705
127.9511
119.8403
88.1649
78.9790
78.4959
77.2527
76.7456
75.8380
73.2908
73.2473
72.4911
71.9778
64.5924
61.3550
55.6145
55.2604
40.1862
39.6421
39.5376
38.7237
37.5141
36.3976
34.9345
34.8206
33.5429
31.7327
30.1668
29.8371
29.6790
28.6290
27.5268
26.2063
26.0829
25.9460
21.7894
19.6970
18.4308
18.2986
17.1825
15.6071
14.3619
11.5324
10.9224
10.3948
TBSO
OMTM
O
O
OTBS
O
I
OMe
MeO
OTBS
S19
General
DATE
TIME
INSTRUM
PULPROG
F1 (13C)
SI = 32758
SF = 125.758
SW_p = 31446.541
150
100
50
0
[ppm]

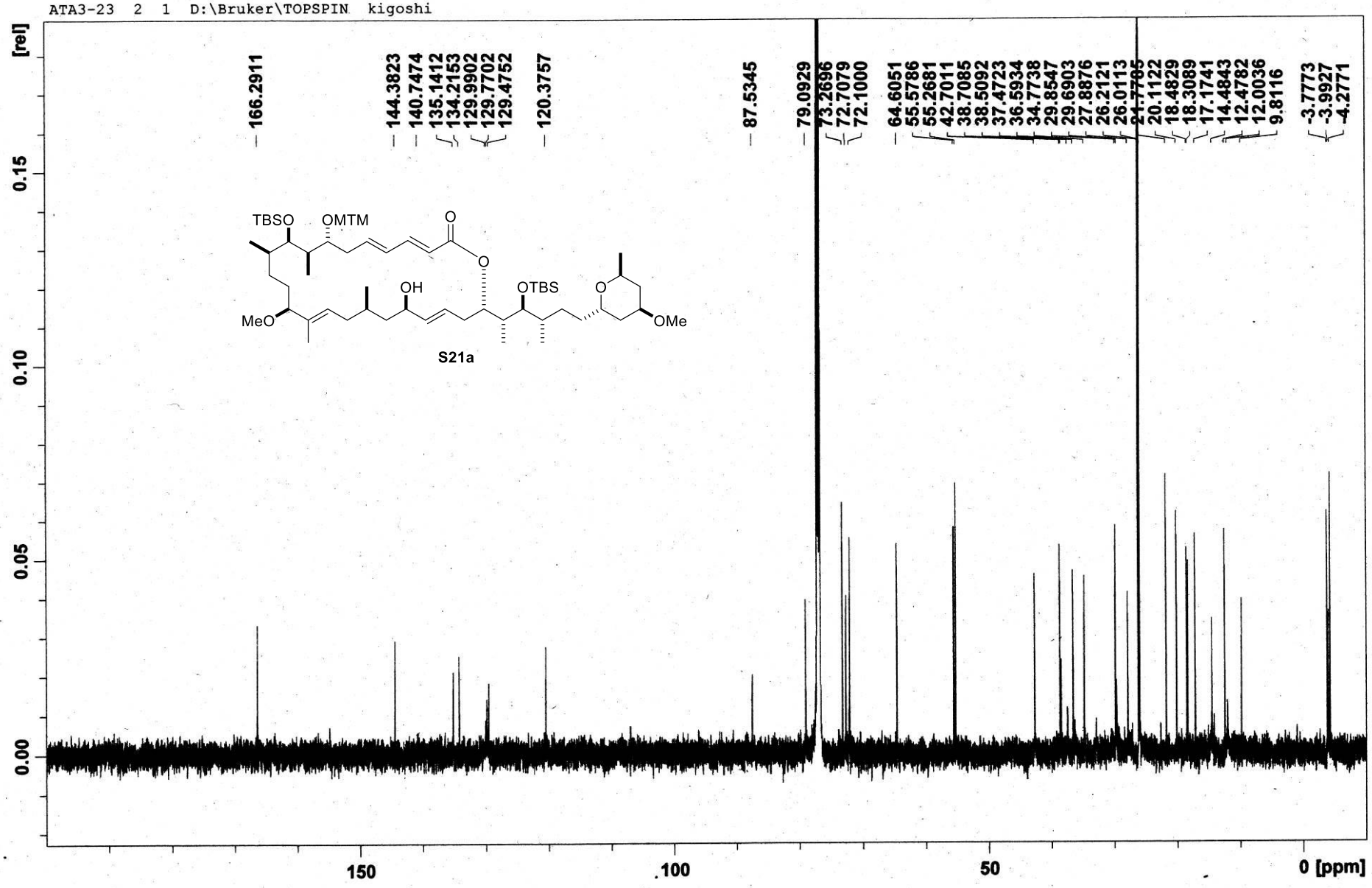

ATA-3-18 1 1 D: kigoshi
[rel]
[ppm]
TBSO
OMTM
OTBS
OMe
MeO
OH
S20

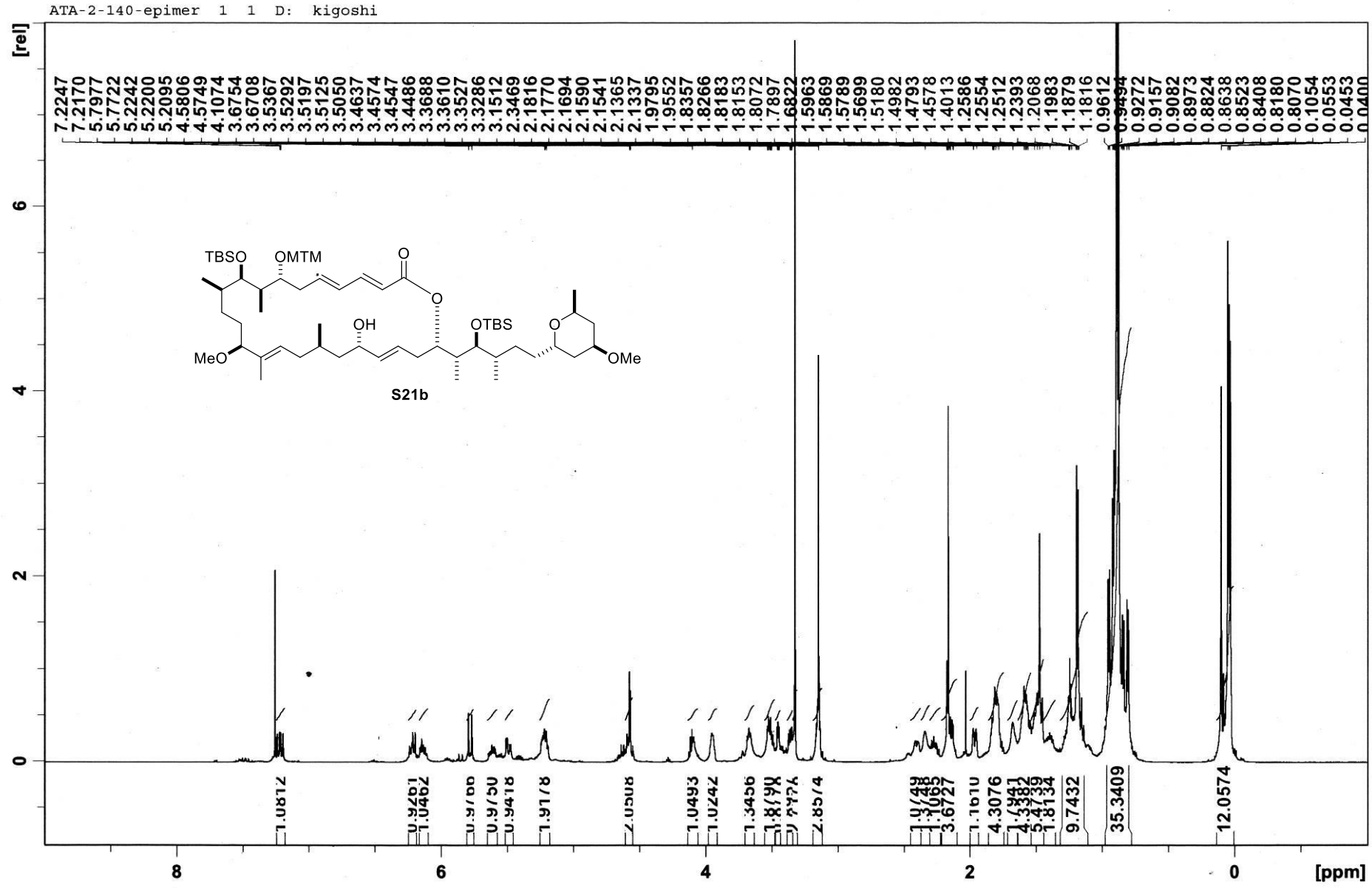

ATA-3-18 2 1 D: kigoshi
166.6649
144.7951
141.6741
140.7198
135.1405
130.3936
127.5896
119.8276
88.1015
78.9865
78.5113
77.3720
77.2120
77.0433
77.0005
76.8316
76.7888
75.7593
73.3029
73.2667
72.5540
71.9667
64.6180
61.1043
61.0698
55.6501
55.2572
39.6526
39.5793
39.5541
38.7183
37.4622
36.4414
34.9111
34.8304
33.4899
31.6891
30.1773
29.8620
29.6774
28.6465
27.5827
26.2045
26.0740
21.7838
19.6844
18.4396
18.4200
17.1612
15.5133
14.3841
11.5464
11.0069
10.4383
-3.6878
-3.8752
-3.9630
-3.9785
TBSO
OMTM
O
O
OTBS
O
I
OMe
MeO
OH
S20
2.0 [rel]
1.5
1.0
0.5
- 0.0
150
100
50
0 [ppm]

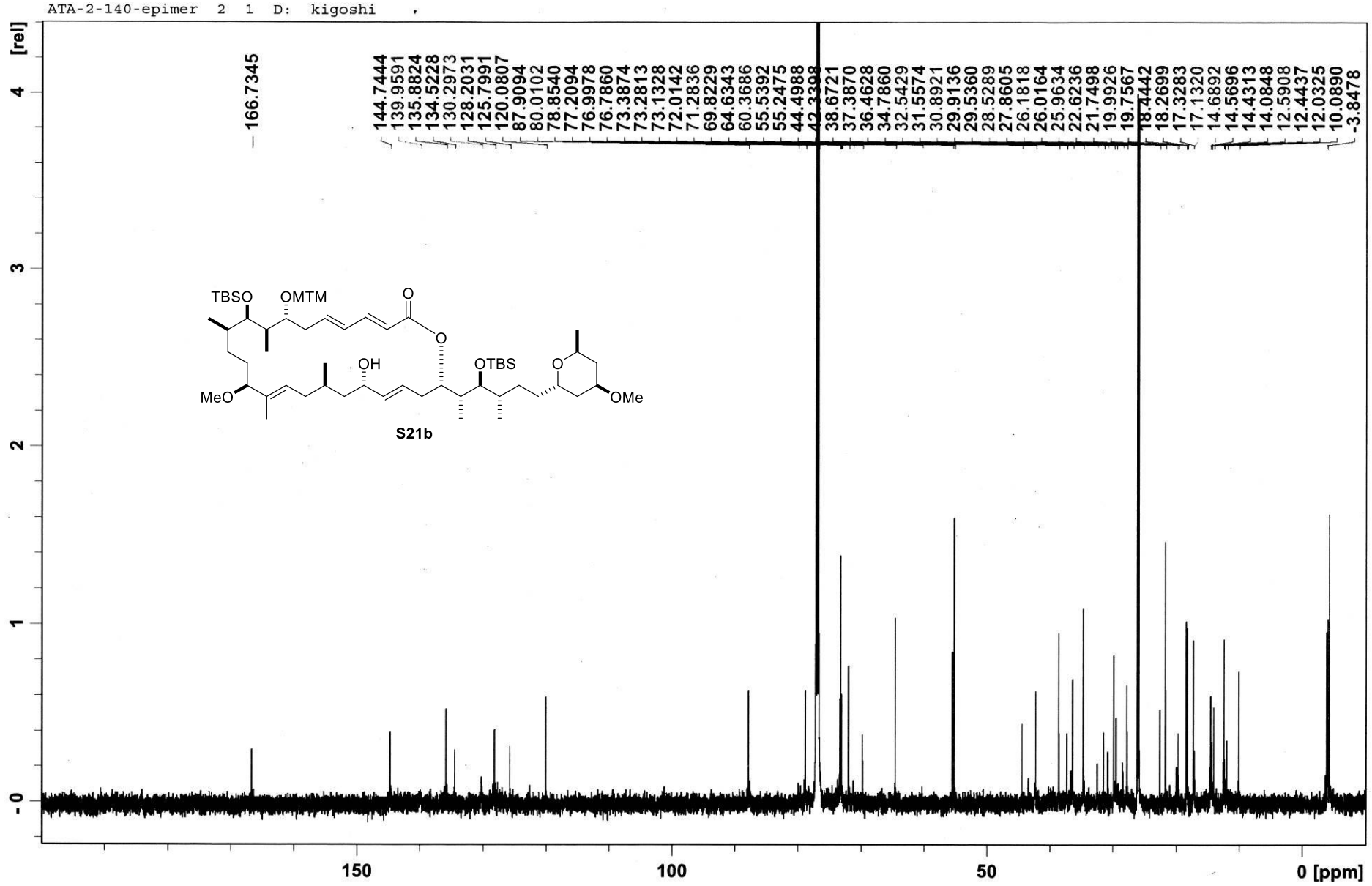

ATA-3-23 1 1 D: kigoshi
- 0
1
2
3
4
[rel]
10
8
6
4
2
0
[ppm]
1.0402
2.4066
1.0376
2.0080
0.9174
1.1281
0.9966
2.1753
1.0954
3.9996
3.3885
5.9431
5.2564
4.2955
18.5123
8.3504
40.5857
13.9704
MeO
TBSO
OMTM
OTBS
OMe
12
9.7659
9.7621
9.7591
7.2598
7.2339
7.2261
6.4671
6.4431
6.2404
6.2227
6.1114
6.0875
5.7958
5.7702
5.3265
5.1153
5.1087
4.6043
4.5989
3.6120
3.6063
3.6007
3.5725
3.5671
3.5187
3.4426
3.4377
3.4325
3.4275
3.3826
3.3711
3.3342
3.1505
2.4456
2.4362
2.4090
2.3889
2.3515
2.3163
2.2780
2.1577
2.1433
2.1113
1.9975
1.9865
1.9642
1.8321
1.8278
1.8162
1.7990
1.6123
1.5956
1.5742
1.5655
1.5318
1.5257
1.5037
1.4338
1.2483
1.2036
1.1933
1.1813
1.1606
0.9845
0.9737
0.9442
0.9324
0.9226
0.9111
0.8881
0.8806
0.8684
0.8461
0.8346
0.0540
0.0432

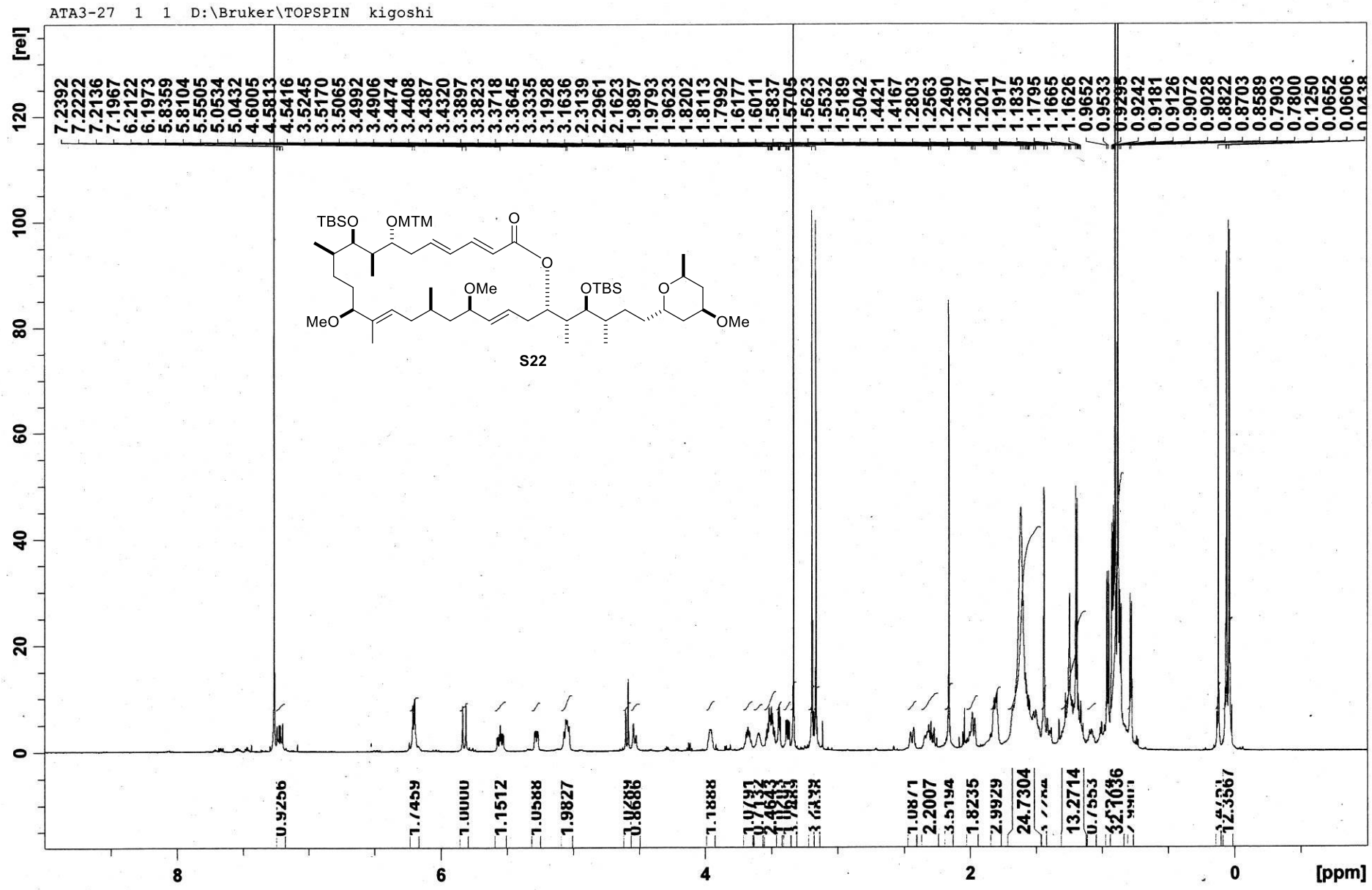

ATA-3-23 2 1 D: kigoshi
202.5448
166.6029
144.7345
141.6938
140.6873
136.3930
130.3932
126.3166
119.8668
87.9972
78.9470
78.5174
77.3518
77.3040
77.0929
76.8813
75.8179
73.3018
73.2548
72.5279
71.9666
64.6110
55.7513
55.2619
50.3517
40.2150
39.5677
38.7236
37.5381
36.4346
34.8331
34.6698
33.5078
31.7889
29.8624
29.6818
28.7187
28.6113
27.5702
26.2066
26.0816
21.7863
20.0194
18.4437
18.4316
17.1696
15.6471
14.3758
11.5553
10.9757
10.5687
-3.6720
-3.7180
-3.8259
2.5 [rel]
2.0
1.5
1.0
0.5
- 0.0
200
150
100
50
[ppm]
TBSO
OMTM
O
O
OTBS
O
I
OMe
MeO
O
12

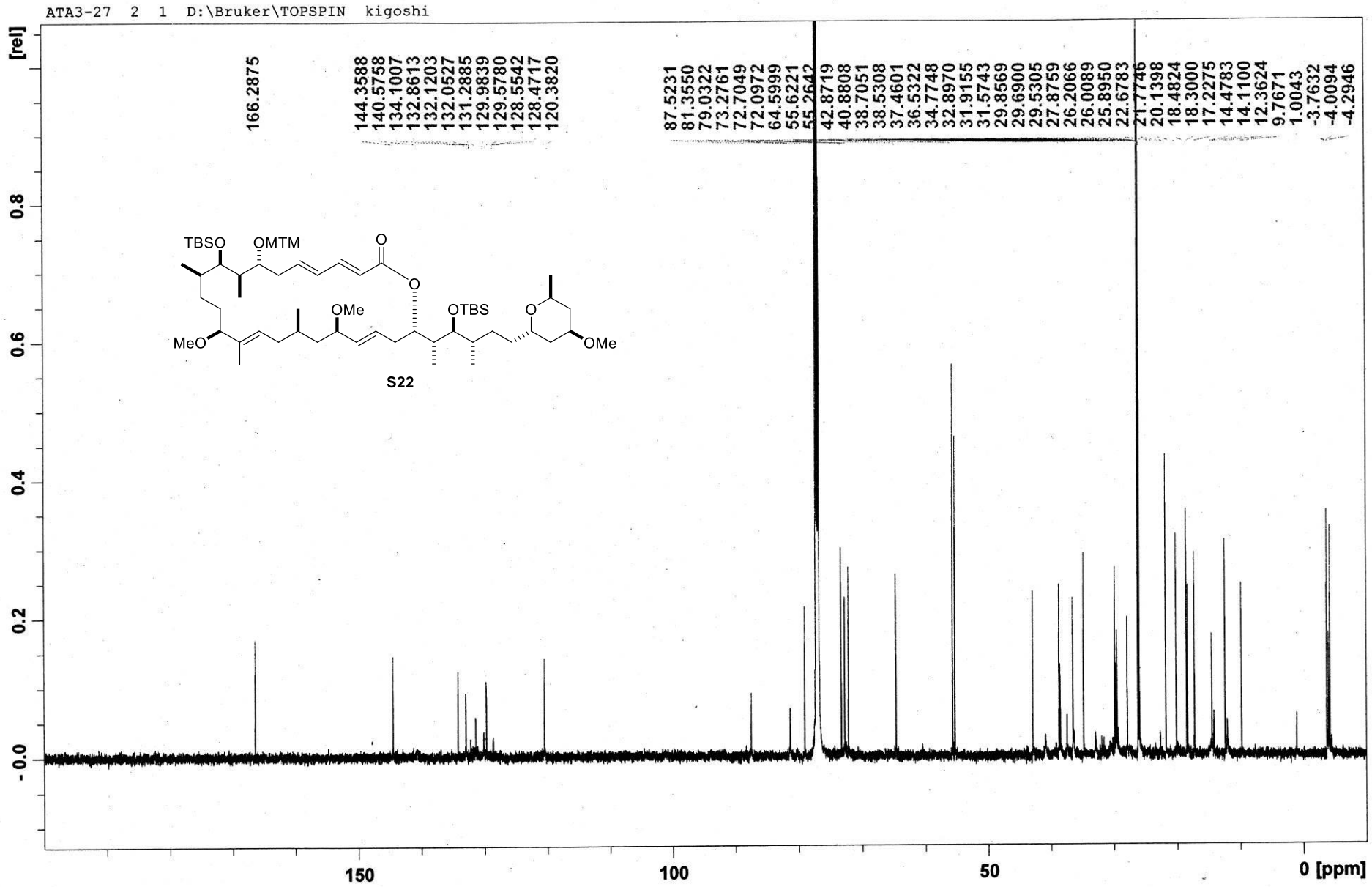

ATA3-23 1 1 D:\Bruker\TOPSPIN kigoshi
[rel]
[ppm]
S21a
MeO
TBSO
OMTM
OH
OTBS
OMe
O
7.2198
7.2110
7.1941
6.2149
6.1999
5.8321
5.8066
5.5712
5.2694
5.2665
5.2590
5.2565
5.2515
4.6031
4.5839
4.5447
4.0954
4.0879
3.6747
3.5229
3.5154
3.5077
3.4983
3.4354
3.4285
3.4202
3.3960
3.3888
3.3784
3.3710
3.3326
3.1753
2.3845
2.3812
2.3784
2.2571
2.2338
2.1655
1.9895
1.9857
1.9820
1.9688
1.9648
1.9613
1.8213
1.8145
1.8057
1.7974
1.7938
1.7064
1.6824
1.4531
1.2560
1.2488
1.2241
1.2008
1.1904
1.1819
1.1682
1.1648
1.1610
0.9619
0.9500
0.9273
0.9212
0.9160
0.9098
0.8834
0.8724
0.8608
0.8140
0.8039
0.1169
0.0557
0.9243
1.5987
1.0000
1.1402
2.0932
0.8882
1.0933
1.1534
1.3784
1.8104
2.7029
0.8466
34.1126
12.5281
41.3871
12.7014


ATA3-23 2 1 D:\Bruker\TOPSPIN kigoshi
[rel]
0.15
0.10
0.05
0.00
166.2911
144.3823
140.7474
135.1412
134.2153
129.9902
129.7702
129.4752
120.3757
87.5345
79.0929
73.2696
72.7079
72.1000
64.6051
55.5786
55.2681
42.7011
38.7085
38.5092
37.4723
36.5934
34.7738
29.8547
29.6903
27.8876
26.2121
26.0113
21.7785
20.1122
18.4829
18.3089
17.1741
14.4843
12.4782
12.0036
9.8116
-3.7773
-3.9927
-4.2771
TBSO
OMTM
O
O
OH
OTBS
O
MeO
OMe
S21a
150
100
50
0 [ppm]


ATA-2-140-epimer 1 1 D: kigoshi
[rel]
[ppm]
TBSO
OMTM
OH
OTBS
MeO
OMe
S21b


ATA-2-140-epimer 2 1 D: kigoshi ,
[rel]
4
3
2
1
- 0
166.7345
144.7444
139.9591
135.8824
134.5228
130.2973
128.2031
125.7991
120.0807
87.9094
80.0102
78.8540
77.2094
76.9978
76.7860
73.3874
73.2813
73.1328
72.0142
71.2836
69.8229
64.6343
60.3686
55.5392
55.2475
44.4988
42.3398
38.6721
37.3870
36.4628
34.7860
32.5429
31.5574
30.8921
29.9136
29.5360
28.5289
27.8605
26.1818
26.0164
25.9634
22.6236
21.7498
19.9926
19.7567
18.4442
18.2699
17.3283
17.1320
14.6892
14.5696
14.4313
14.0848
12.5908
12.4437
12.0325
10.0890
-3.8478
TBSO
OMTM
O
O
OH
OTBS
O
MeO
OMe
S21b
150
100
50
0 [ppm]


ATA3-27 1 1 D:\Bruker\TOPSPIN kigoshi
[rel]
[ppm]
TBSO
OMTM
OMe
OTBS
MeO
OMe
S22


ATA3-27 2 1 D:\Bruker\TOPSPIN kigoshi
[rel]
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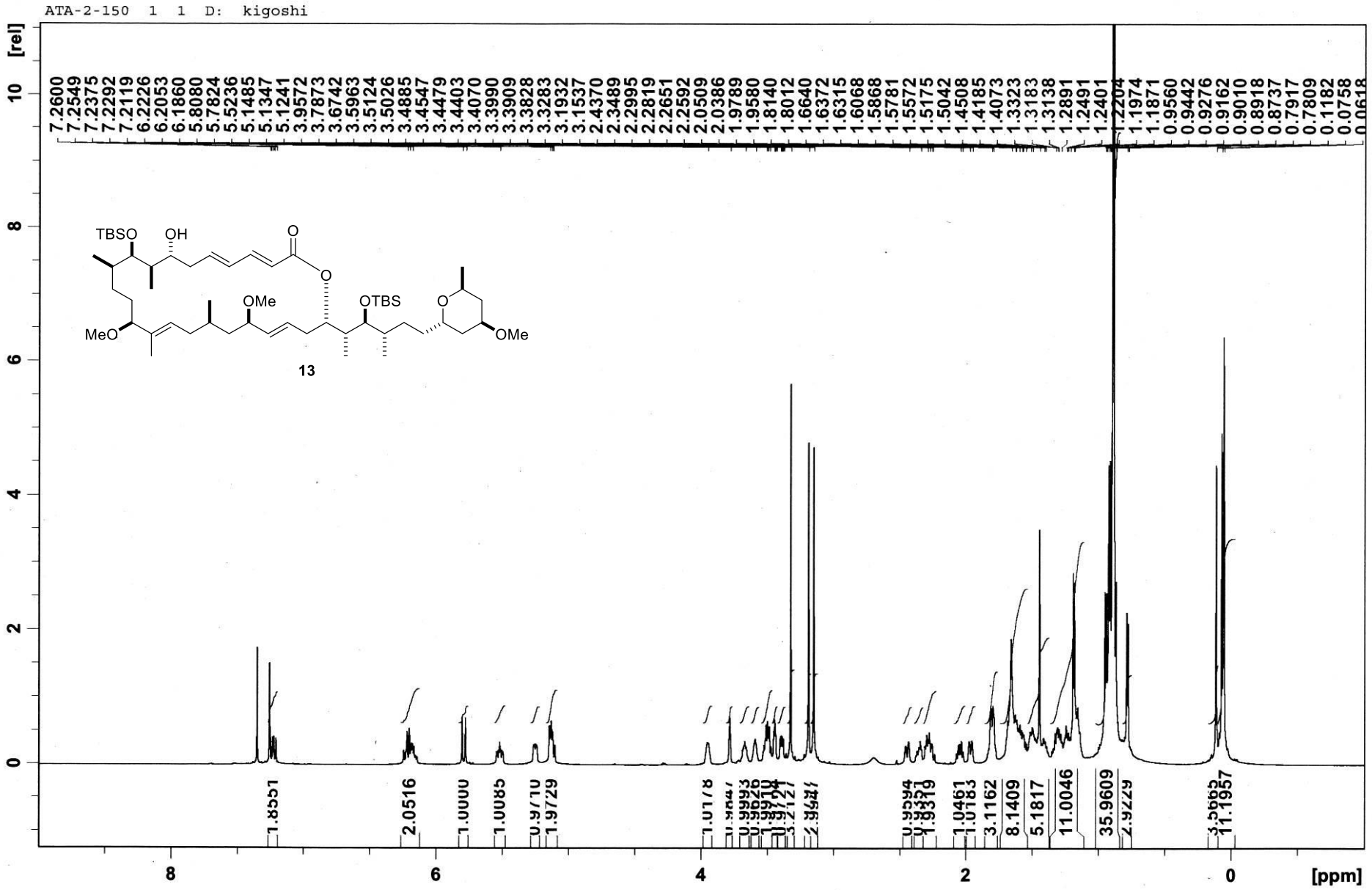
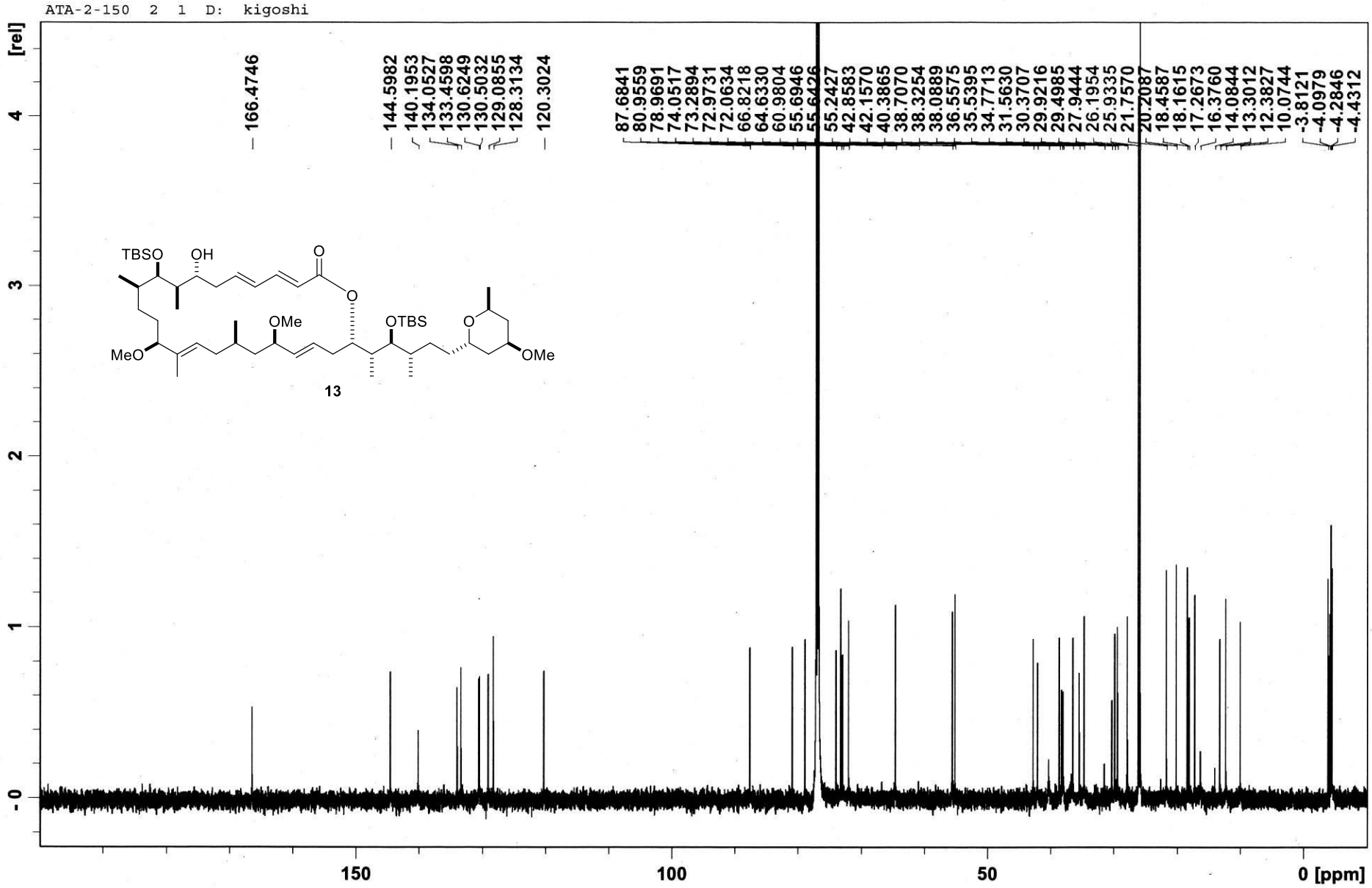
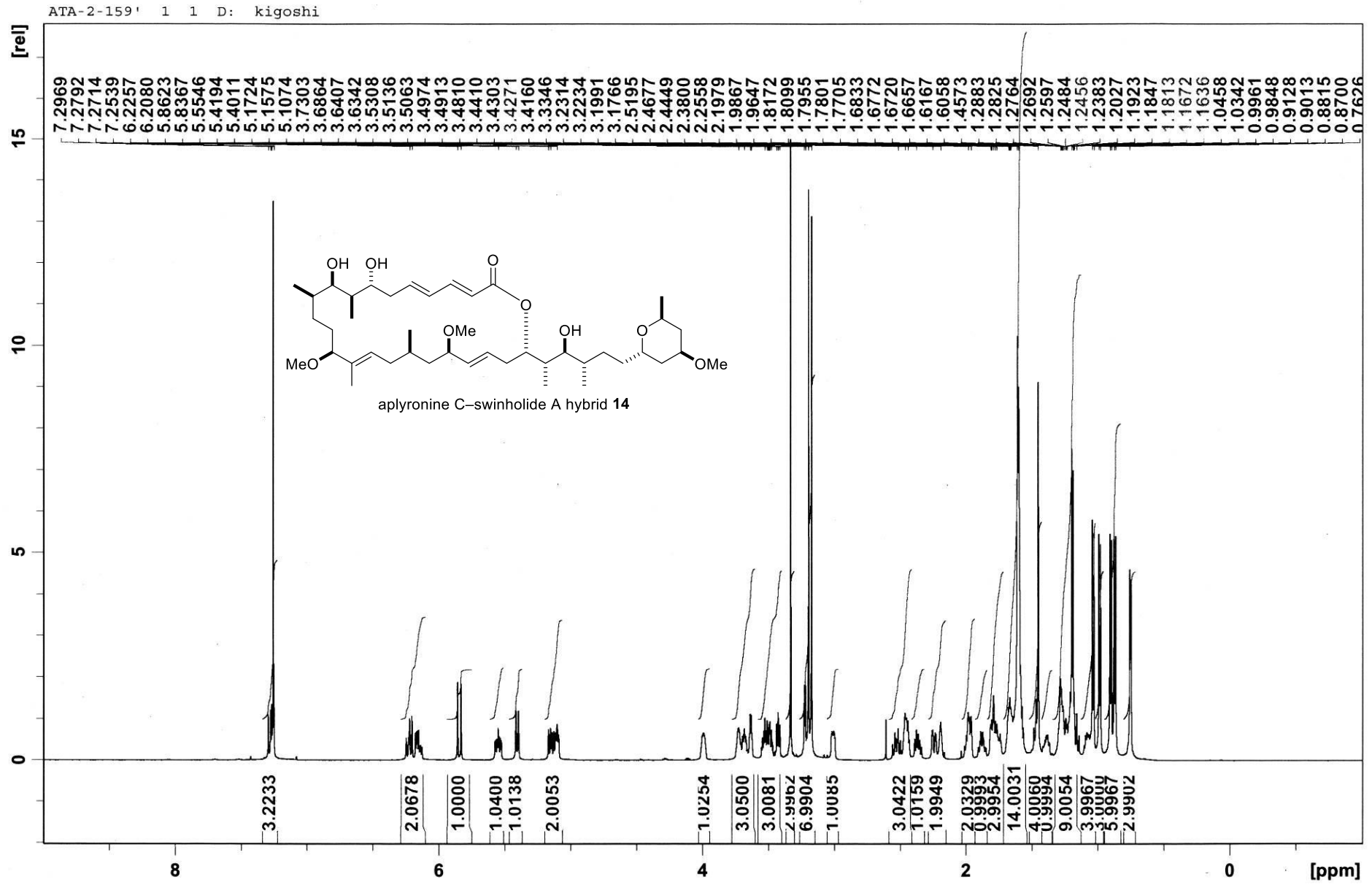
0.6
0.4
0.2
-0.0
166.2875
144.3588
140.5758
134.1007
132.8613
132.1203
132.0527
131.2885
129.9839
129.5780
128.5542
128.4717
120.3820
87.5231
81.3550
79.0322
73.2761
72.7049
72.0972
64.5999
55.6221
55.2642
42.8719
40.8808
38.7051
38.5308
37.4601
36.5322
34.7748
32.8970
31.9155
31.5743
29.8569
29.6900
29.5305
27.8759
26.2066
26.0089
25.8950
22.6783
21.7746
20.1398
18.4824
18.3000
17.2275
14.4783
14.1100
12.3624
9.7671
1.0043
-3.7632
-4.0094
-4.2946
TBSO
OMTM
O
O
OMe
OTBS
O
MeO
OMe
S22
150
100
50
0 [ppm]


ATA-2-150 1 1 D: kigoshi
[rel]
[ppm]
TBSO
OH
O
OMe
OTBS
MeO
OMe
13


ATA-2-150 2 1 D: kigoshi
[rel]
4
3
2
1
-0
166.4746
144.5982
140.1953
134.0527
133.4598
130.6249
130.5032
129.0855
128.3134
120.3024
87.6841
80.9559
78.9691
74.0517
73.2894
72.9731
72.0634
66.8218
64.6330
60.9804
55.6946
55.6426
55.2427
42.8583
42.1570
40.3865
38.7070
38.3254
38.0889
36.5575
35.5395
34.7713
31.5630
30.3707
29.9216
29.4985
27.9444
26.1954
25.9335
21.7570
20.2087
18.4587
18.1615
17.2673
16.3760
14.0844
13.3012
12.3827
10.0744
-3.8121
-4.0979
-4.2846
-4.4312
TBSO
OH
O
O
OMe
OTBS
O
MeO
OMe
13
150
100
50
0 [ppm]


ATA-2-159' 1 1 D: kigoshi
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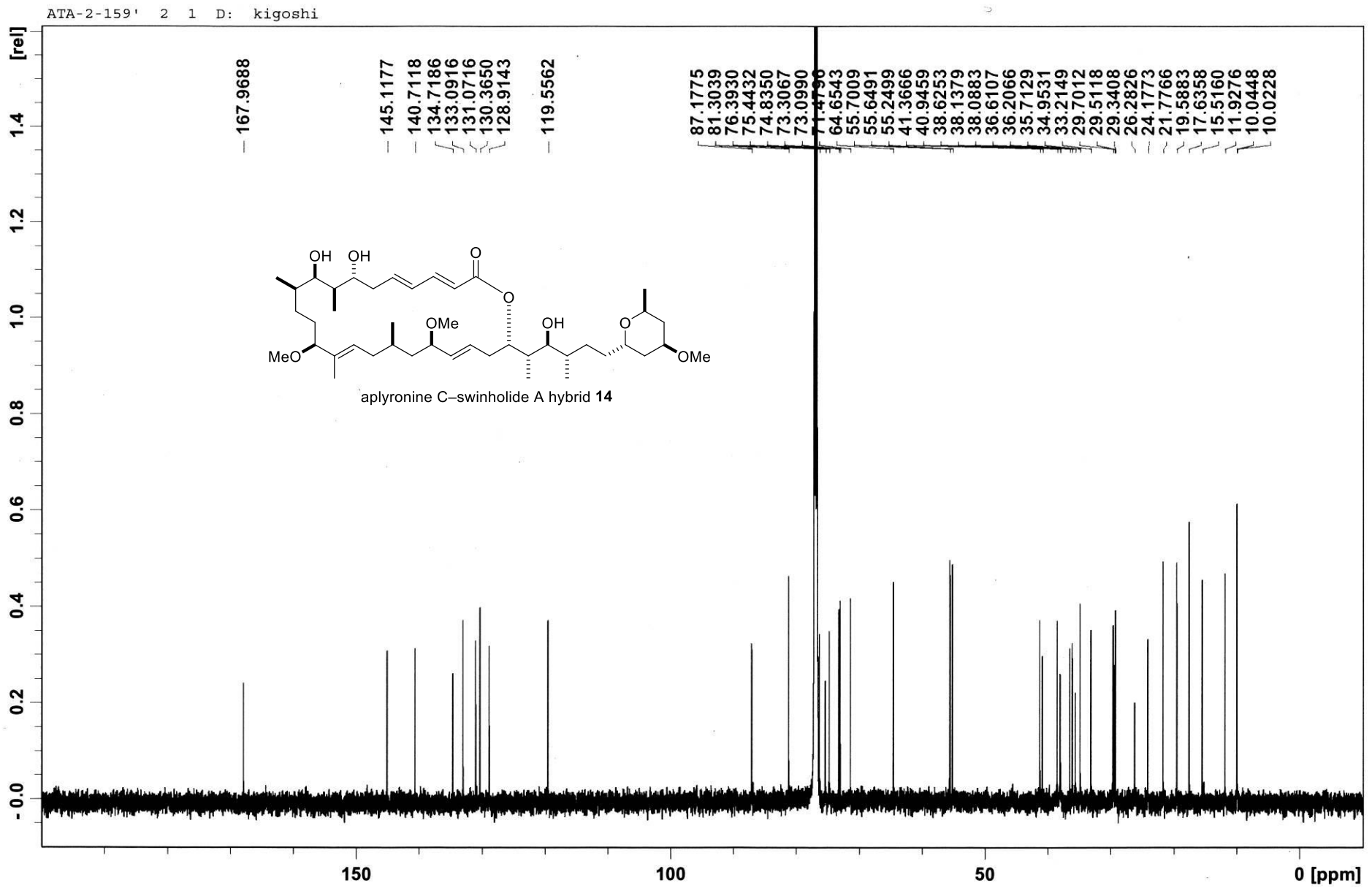
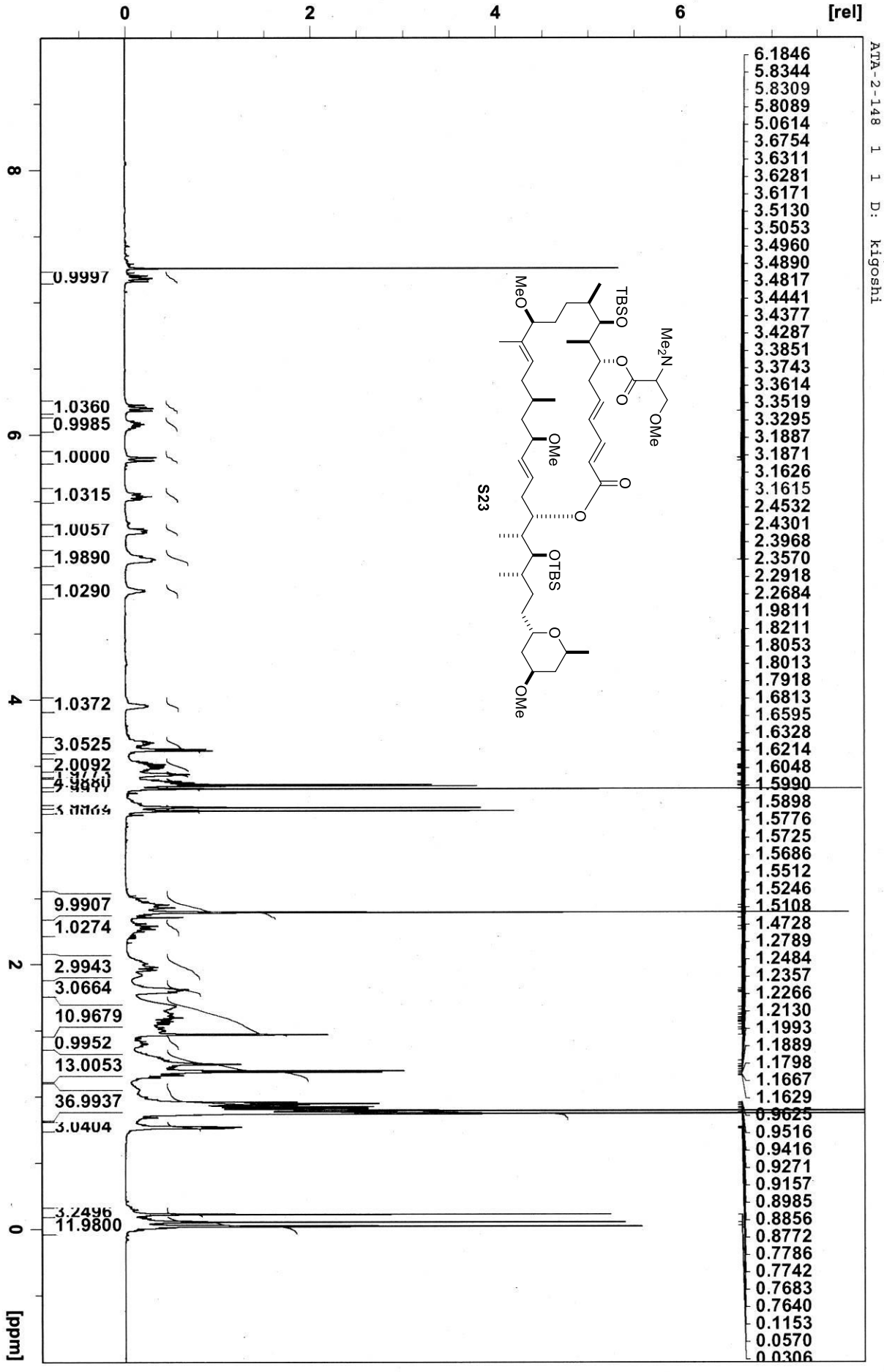
[ppm]
aplyronine C–swinholide A hybrid **14**



aplyronine C–swinholide A hybrid **14**


ATA-2-148 1 1 D: kigoshi
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[ppm]
S23
TBSO
MeO
OMe
OTBS
OMe
Me2N
OMe
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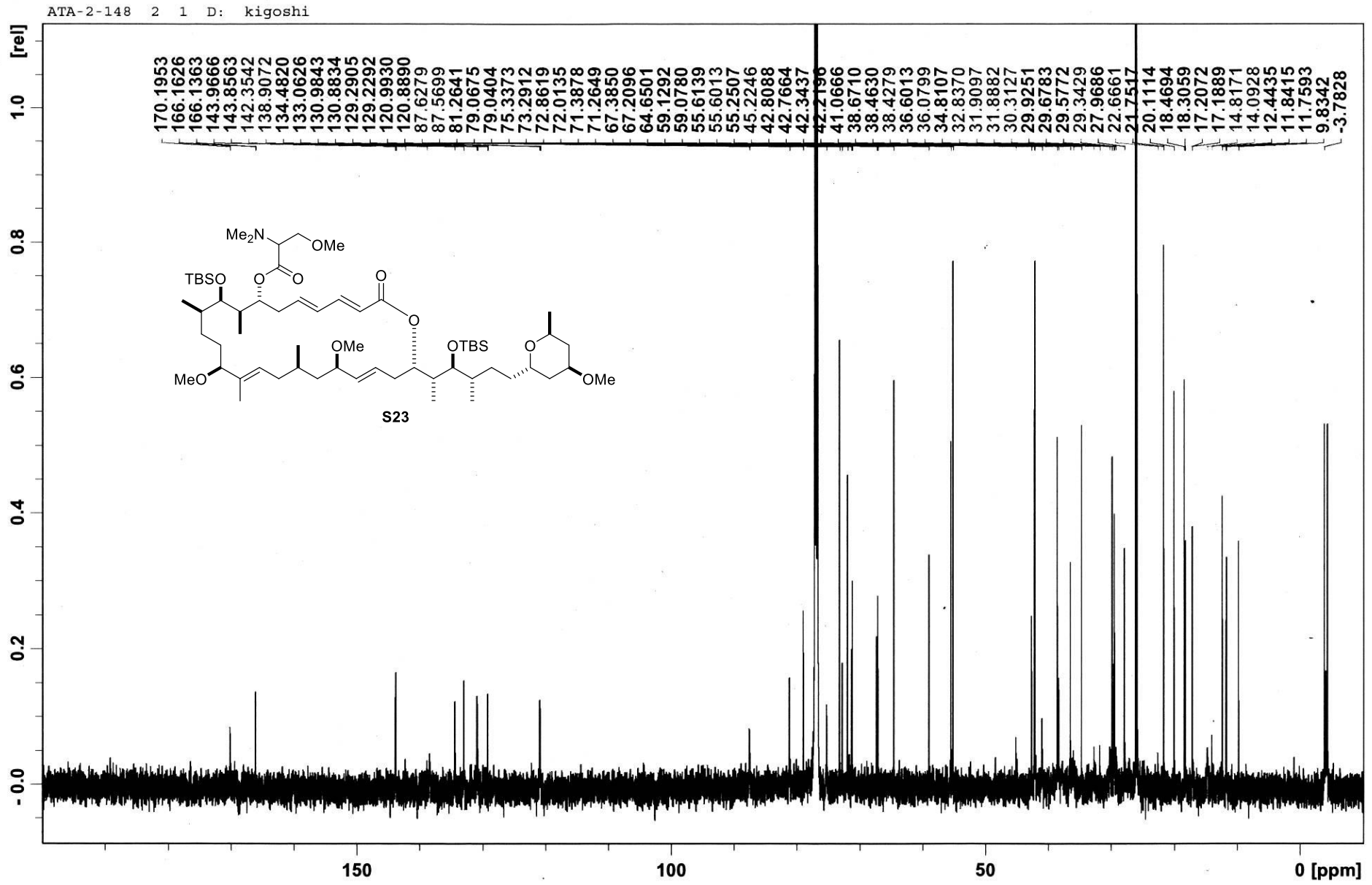
1.0360
0.9985
1.0000
1.0315
1.0057
1.9890
1.0290
1.0372
3.0525
2.0092
9.9907
1.0274
2.9943
3.0664
10.9679
0.9952
13.0053
36.9937
11.9800


ATA-2-148 2 1 D: kigoshi
[rel]
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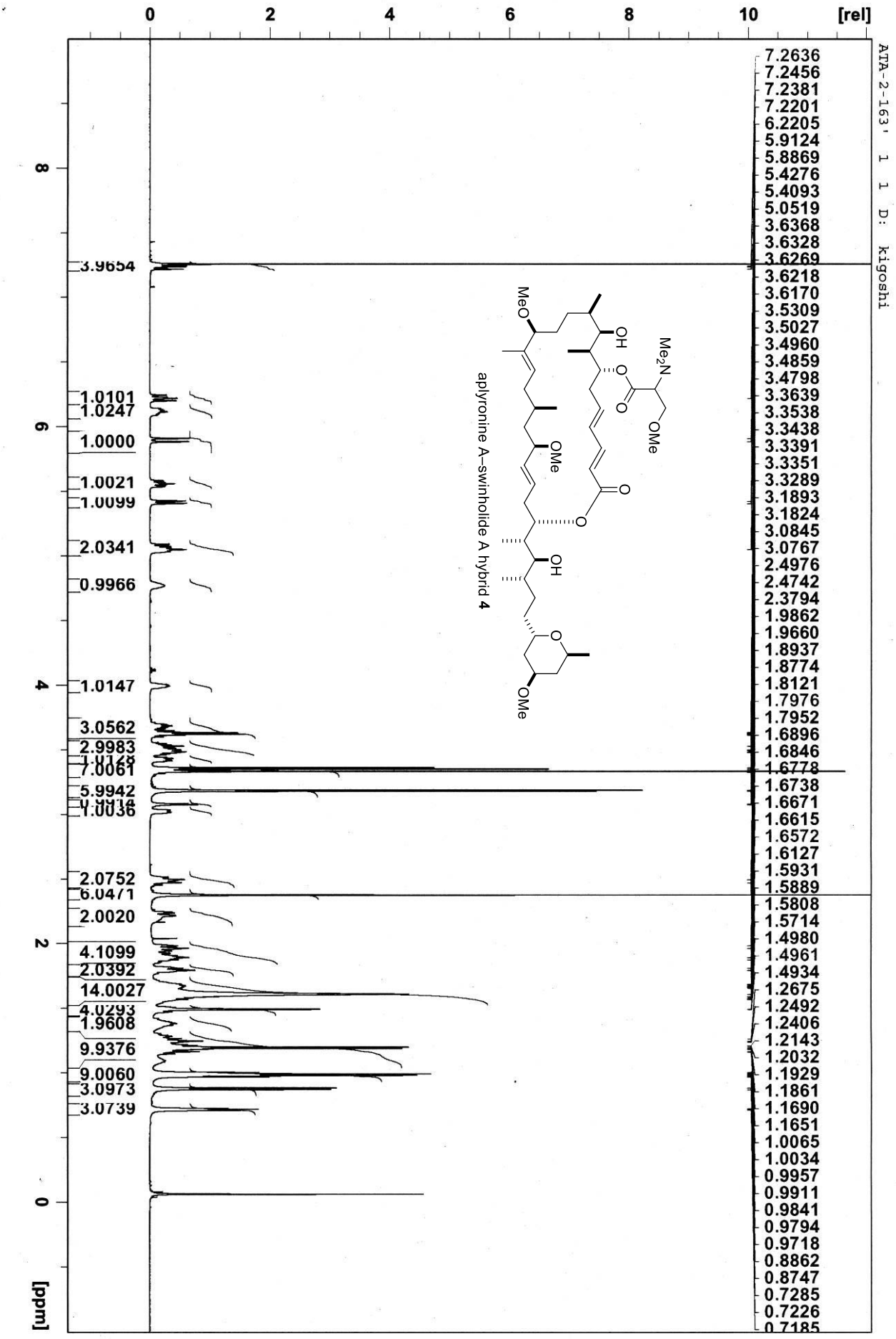
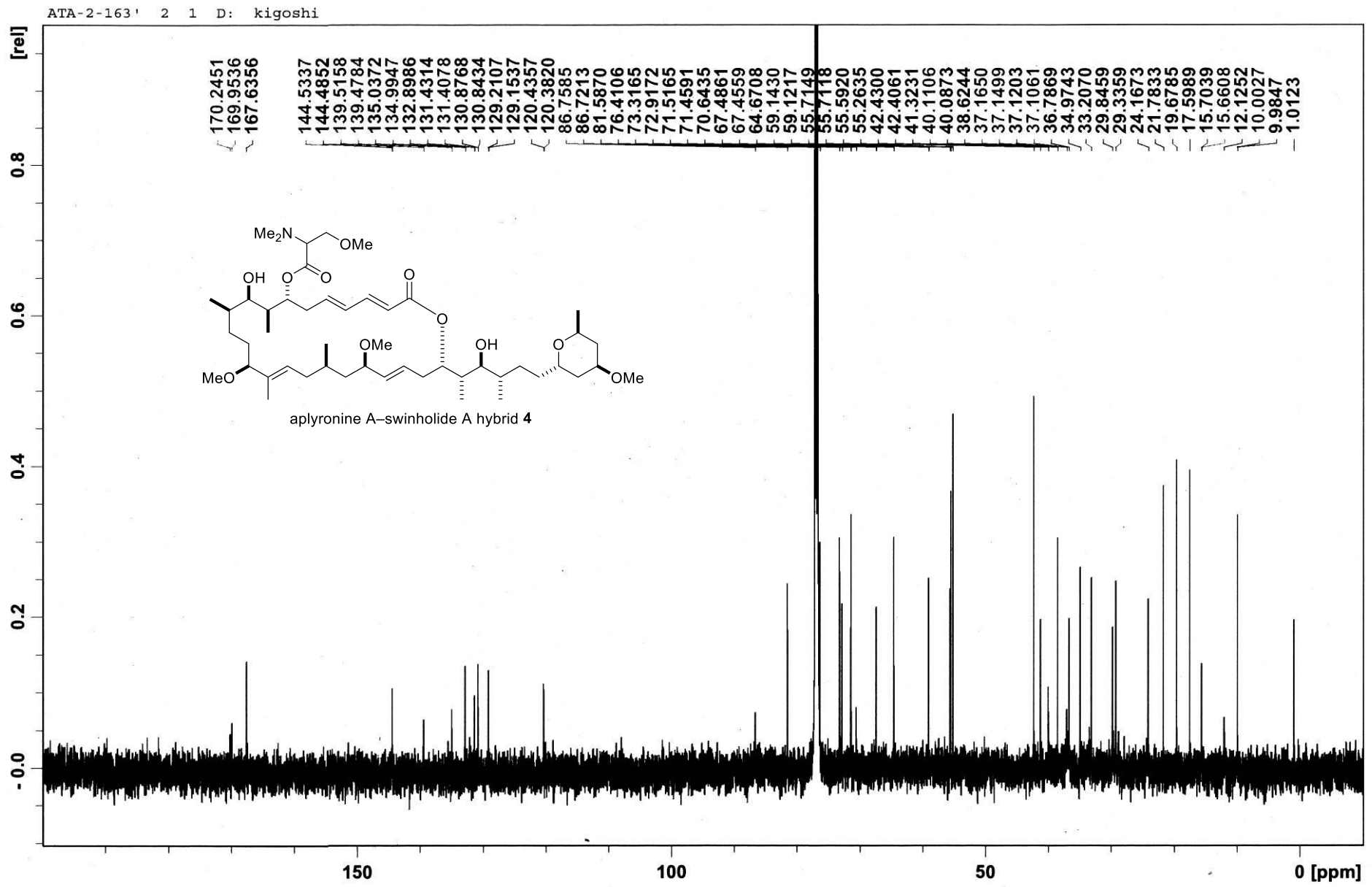
0.8
0.6
0.4
0.2
-0.0
170.1953
166.1626
166.1363
143.9666
143.8563
142.3542
138.9072
134.4820
133.0626
130.9843
130.8834
129.2905
129.2292
120.9930
120.8890
87.6279
87.5699
81.2641
79.0675
79.0404
75.3373
73.2912
72.8619
72.0135
71.3878
71.2649
67.3850
67.2096
64.6501
59.1292
59.0780
55.6139
55.6013
55.2507
45.2246
42.8088
42.7664
42.3437
41.0666
38.6710
38.4630
38.4279
36.6013
36.0799
34.8107
32.8370
31.9097
31.8882
30.3127
29.9251
29.6783
29.5772
29.3429
27.9686
22.6661
21.7517
20.1114
18.4694
18.3059
17.2072
17.1889
14.8171
14.0928
12.4435
11.8415
11.7593
9.8342
-3.7828
Me2N
OMe
TBSO
O
O
O
O
OMe
OTBS
O
MeO
OMe
S23
150
100
50
0 [ppm]


ATA-2-163' 1 1 D: kigoshi
[rel]
[ppm]
aplyronine A–swinholide A hybrid 4
MeO
OH
Me2N
OMe
OMe
OH
OMe
O
7.2636
7.2456
7.2381
7.2201
6.2205
5.9124
5.8869
5.4276
5.4093
5.0519
3.6368
3.6328
3.6269
3.6218
3.6170
3.5309
3.5027
3.4960
3.4859
3.4798
3.3639
3.3538
3.3438
3.3391
3.3351
3.3289
3.1893
3.1824
3.0845
3.0767
2.4976
2.4742
2.3794
1.9862
1.9660
1.8937
1.8774
1.8121
1.7976
1.7952
1.6896
1.6846
1.6778
1.6738
1.6671
1.6615
1.6572
1.6127
1.5931
1.5889
1.5808
1.5714
1.4980
1.4961
1.4934
1.2675
1.2492
1.2406
1.2143
1.2032
1.1929
1.1861
1.1690
1.1651
1.0065
1.0034
0.9957
0.9911
0.9841
0.9794
0.9718
0.8862
0.8747
0.7285
0.7226
0.7185
3.9654
1.0101
1.0247
1.0000
1.0021
1.0099
2.0341
0.9966
1.0147
3.0562
2.9983
7.0061
5.9942
1.0036
2.0752
2.0020
4.1099
2.0392
14.0027
1.9608
9.9376
9.0060
3.0973
3.0739



aplyronine A–swinholide A hybrid **4**