Total Synthesis and Structural Revision of Sekothrixide**

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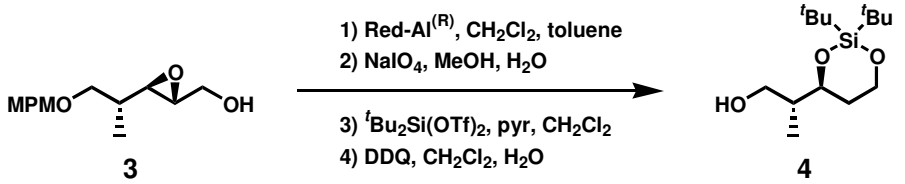
1. General methods

All reactions were monitored by thin-layer chromatography using MERCK TLC Silica gel 60 F_{254} and were visualized by UV light (254 nm) and/or stained in 12 molybdo (VI) phosphoric acid or H_2SO_4 in MeOH solutions. Column chromatography was performed using Silica Gel 60 N (spherical, neutral, 63-210 μm) or Silica Gel 60 N (spherical, neutral, 40-50 μm, for flash column chromatography) purchased from KANTO CHEMICAL.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a JEOL ECX 400 spectrometer. Chemical shifts were reported in ppm on δ scale. ^{1}H and ^{13}C chemical shifts are referenced to internal solvent resonances ($CHCl_3$ 1H, δ = 7.26 ppm; $CDCl_3$ 13C, δ = 77.0 ppm) and reported relative to Me_4Si (δ = 0.00 ppm). The multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad signal). Coupling constants, *J*, were reported in Hertz. MS spectra were measured on a JEOL JMS-GCmate II or JEOL JMS-700 MStation instruments. Infrared spectra were recorded on a SHIMADZU IRPrestige-21 spectrophotometer. Optical rotations were measured on a Jasco P-2200 polarimeter at a ϕ3.5 mm x 100 mm path-length cell at 589 nm. All concentrations are in g/100 mL.

2. Experimental procedures

Synthesis of Alcohol **4**



To a solution of epoxy alcohol **3** (21.05 g, 83.4 mmol) in dry CH_2Cl_2 (100 mL) was added Red-Al$^{(R)}$ (80.0 mL, 65 wt.% in toluene, 262 mmol) at 0 °C. The solution was warmed to ambient temperature and stirred for 22 h under Ar atmosphere. The reaction mixture was stirred at 0 °C for 5 min and quenched with MeOH (20 mL). The resultant mixture was vigorously stirred at room temperature for 2 h and filtered using Büchner funnel with MeOH. The filtrate was concentrated *in vacuo*.

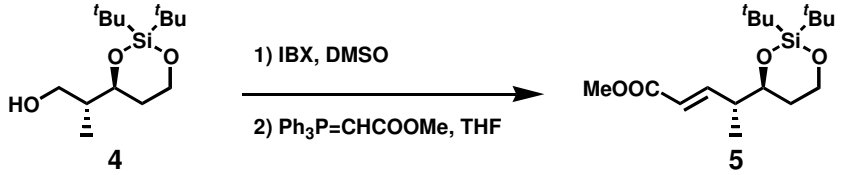
Next, to a solution of the crude diol in MeOH (40 mL) and H_2O (10 mL) was added $NaIO_4$ (9.01 g, 42.1 mmol). The reaction mixture was stirred at room temperature for 1 h and then quenched with saturated aqueous NaCl (500 mL) and H_2O (500 mL). The aqueous phase was extracted with AcOEt (5 x 200 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 1:4) to give the diol (14.42 g, 56.7 mmol, 68%, 2 steps).

To a solution of diol (13.26 g, 51.9 mmol) in dry CH_2Cl_2 (100 mL) was added pyridine (13.0 mL, 160 mmol) and $^tBu_2Si(OTf)_2$ (20.5 mL, 60.9 mmol) at 0 °C. The solution was warmed to ambient temperature and stirred for 17 h under Ar atmosphere. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (100 mL) and H_2O (100 mL). The aqueous phase was extracted with AcOEt (3 x 200 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes = 1) to give the silylene (19.40 g, 49.1 mmol, 94%).

To a solution of sylylene (108.2 mg, 0.274 mmol) in CH_2Cl_2 (3 mL) and H_2O (300 μL) was added DDQ (77.7 mg, 0.335 mmol). The solution was stirred at room temperature for 2 h. The dark reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and H_2O (5 mL). The aqueous phase was extracted with AcOEt (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (benzenes / AcOEt = 20:1) to give the alcohol **4** (67.8 mg, 0.247 mmol, 90%).

$[\alpha]_D^{28}$ = +24.1^o (c = 1.2, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.17-4.07 (m, 2H), 4.01 (ddd, *J* = 10.4, 8.0, 1.6 Hz, 1H), 3.74-3.62 (m, 2H), 3.37 (brd, *J* = 6.4 Hz, 1H), 1.94-1.78 (m, 2H), 1.74 (ddd, *J* = 14.4, 4.0, 2.0 Hz, 1H), 1.05 (s, 9H), 1.01 (s, 9H), 0.84 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 81.2, 68.4, 64.5, 41.7, 34.7, 27.4, 27.1, 22.7, 19.8, 13.4; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3441 (br), 1474, 1111; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{14}H_{31}O_3Si$ $[M+H]^+$ 275.2042, found 275.2068.

Synthesis of Conjugated Ester **5**

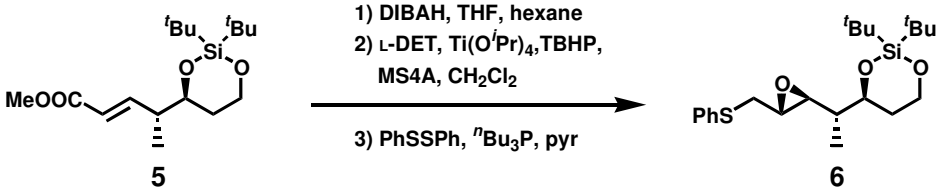


To a solution of alcohol **4** (25.1 mg, 0.0914 mmol) in DMSO (500 μL) was added IBX (54.4 mg, 0.1942 mmol). The solution was stirred at room temperature for 2 h under Ar atmosphere. The reaction mixture was filtered through a short pad of silica gel with Et_2O and solvent was removed under reduced pressure.

To a solution of filtered mixture in THF (1 mL) was added Ph_3P=CHCOOMe (83.5 mg, 0.244 mmol). The orange solution was stirred at room temperature for 1 week and solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 9:1) to give the conjugated ester **5** (25.6 mg, 0.0779 mmol, 85%, 2 steps).

$[\alpha]_D^{28}$ = +22.1° (c = 0.60, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.05 (dd, *J* = 15.6, 8.0 Hz, 1H), 5.86 (dd, *J* = 15.6, 1.2 Hz, 1H), 4.14-4.07 (m, 2H), 4.03 (ddd, *J* = 11.2, 4.4, 2.4 Hz, 1H), 3.73 (s, 3H), 2.41 (m, 1H), 1.83 (dtd, *J* = 14.0, 10.8, 6.0 Hz, 1H), 1.51 (ddd, *J* = 14.0, 4.8, 2.4 Hz, 1H), 1.12 (d, *J* = 7.2 Hz, 3H), 1.02 (s, 9H), 0.99 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 167.0, 151.0, 121.1, 77.0, 64.5, 51.4, 43.5, 33.8, 27.5, 27.1, 22.9, 20.0, 15.3; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1728, 1659; **HRMS** (EI) *m/z* calculated for $C_{17}H_{32}O_4Si$ $[M]^{+\cdot}$ 328.2070, found 328.2061.

Synthesis of Epoxy Sulfide **6**



To a solution of conjugated ester **5** (25.6 mg, 0.0779 mmol) in dry THF (2 mL) was added DIBAH (250 μL, 1.03 M in hexane, 0.257 mmol). The solution was stirred at -72 °C under Ar atmosphere for 1.5 h. The reaction mixture was quenched with MeOH (0.5 mL). The resultant mixture was vigorously stirred at room temperature for 1.5 h. The gel was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The allyl alcohol was given a 21.1 mg (0.0702 mmol, 90%).

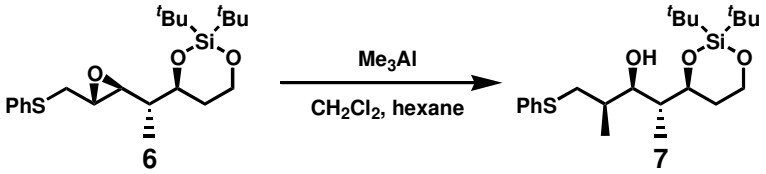
To a suspension of allyl alcohol (21.1 mg, 0.0702 mmol) and activated MS4A (700 mg) in dry CH_2Cl_2 (2 mL, dried by distillation from calcium hydride) was stirred at -30 °C under Ar atmosphere. Other two-necked flask was added dry CH_2Cl_2 (1 mL, dried by distillation from calcium hydride), $Ti(O^iPr)_4$ (20 μL, 0.065 mmol) and L-DET (15 μL, 0.087 mmol) at -30 °C under Ar atmosphere. The solution was stirred for 45 min and moved to a suspension via cannula. The suspention was added TBHP (100 μL, 1.83 M in CH_2Cl_2, 0.183 mmol) and resultant mixture was stirred for 15 h. The suspention was quenched with saturated aqueous $Na_2S_2O_3$ (200 μL) and stirred at room temperature for 15 min. The reaction mixture was filtered

through a short pad of Na_2SO_4 with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 4:1) to give the epoxy alcohol (18.4 mg, 0.0581 mmol, 83%).

To a solution of epoxy alcohol (17.1 mg, 0.0540 mmol) in pyridine (200 μL) was added $^{n}Bu_3P$ (30 μL, 0.11 mmol) and PhSSPh (25.5 mg, 0.114 mmol). The solution was stirred at room temperature under Ar atmosphere for 4 h. The reaction mixture was stirred at 50 °C for 2.5 h and solvent was removed under reduced pressure. The crude residue was purified by column chromatography on silica gel (benzenes = 1) to give the epoxy sulfide **6** (20.8 mg, 0.0508 mmol, 94%).

$[\alpha]_D^{19}$ = +38.7° (c = 1.1, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.40 (m, 2H), 7.29 (m, 2H), 7.21 (m, 1H), 4.14-4.01 (m, 3H), 3.20 (dd, *J* = 12.0, 3.2 Hz, 1H), 2.98-2.89 (m, 3H), 2.06 (dtd, *J* = 14.4, 12.0, 5.2 Hz, 1H), 1.52 (ddd, *J* = 14.4, 4.0, 2.0 Hz, 1H), 1.42 (m, 1H), 1.02 (s, 9H), 1.00 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 135.4, 129.7, 129.0, 126.5, 76.4, 64.9, 60.0, 55.0, 42.3, 36.1, 33.9, 27.5, 27.2, 22.9, 20.0, 12.5; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1582, 1474, 1381; **HRMS** (EI) *m/z* calculated for $C_{22}H_{36}O_3SSi$ $[M]^{+\cdot}$ 408.2154, found 408.2143.

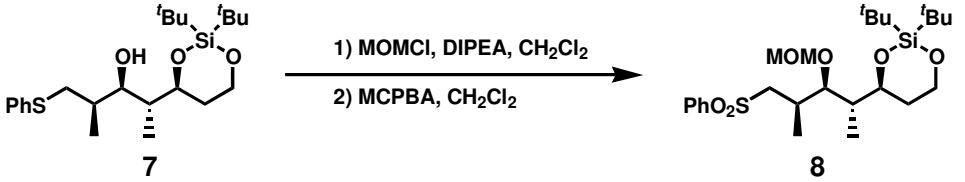
Synthesis of Sulfide **7**



To a solution of epoxy sulfide **6** (29.7 mg, 0.0726 mmol) in dry CH_2Cl_2 (1 mL, dried by distillation from calcium hydride) was added Me_3Al (200 μL, 1.08 M in hexane, 0.216 mmol). The solution was stirred at -50 °C under Ar atmosphere for 19 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (1 mL) and stirred at room temperature. The suspension was filtered through a short pad of Na_2SO_4 with CH_2Cl_2 and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1) to give the sulfide **7** (25.0 mg, 0.0588 mmol, 80%).

$[\alpha]_D^{20}$ = +54.8° (c = 1.0, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.35 (m, 2H), 7.26 (m, 2H), 7.14 (m, 1H), 4.65 (t, *J* = 1.4 Hz, 1H), 4.15-4.07 (m, 3H), 3.81 (ddd, *J* = 9.2, 4.0, 1.6 Hz, 1H), 3.15 (dd, *J* = 12.8, 7.2 Hz, 1H), 2.95 (dd, *J* = 12.8, 6.8 Hz, 1H), 1.92-1.80 (m, 3H), 1.65 (m, 1H), 1.06 (s, 9H), 1.01 (s, 9H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.68 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 137.4, 128.76, 128,74, 125.5, 81.5, 77.2, 64.4, 42.4, 38.2, 35.4, 34.6, 27.4, 27.1, 22.7, 19.8, 12.5, 11.8; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3487, 1582, 1474; **HRMS** (EI) *m/z* calculated for $C_{23}H_{40}O_3SSi$ $[M]^{+\cdot}$ 424.2467, found 424.2457.

Synthesis of Sulfone **8**



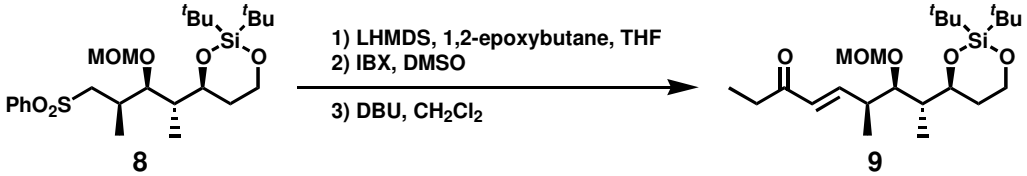
7 **8**

To a solution of sulfide **7** (17.1 mg, 0.0403 mmol) in dry CH_2Cl_2 (1 mL) was added DIPEA (50 µL, 0.28 mmol) and MOMCl (12 µL, 0.12 mmol). The solution was stirred at room temperature under Ar atmosphere for 50 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1) to give the MOM ether (18.2 mg, 0.0388 mmol, 96%).

To a solution of MOM ether (96.7 mg, 0.206 mmol) in CH_2Cl_2 (5 mL) was added MCPBA (101.6 mg, 77 wt.%, 0.453 mmol). The solution was stirred at 0 °C for 45 min. The suspension was quenched with saturated aqueous $Na_2S_2O_3$ (1 mL), 2 M aqueous NaOH (1 mL) and H_2O (10 mL). The aqueous phase was extracted with Et_2O (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 2:1) to give the sulfone **8** (95.6 mg, 0.190 mmol, 92%).

$[\alpha]_D^{26}$ = +26.5° (c = 1.1, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.92 (m, 2H), 7.65 (m, 1H), 7.56 (m, 2H), 4.59 (d, *J* = 6.8 Hz, 1H), 4.51 (d, *J* = 6.8 Hz, 1H), 4.20 (ddd, *J* = 11.0, 5.2, 1.6 Hz, 1H), 4.13 (ddd, *J* = 11.0, 4.8, 2.4 Hz, 1H), 4.05 (td, *J* = 12.0, 2.4 Hz, 1H), 3.57 (dd, *J* = 8.0, 2.4 Hz, 1H), 3.43 (dd, *J* = 14.4, 5.6 Hz, 1H), 3.34 (s, 3H), 3.00 (dd, *J* = 13.6, 6.8 Hz, 1H), 2.50 (m, 1H), 1.96 (m, 1H), 1.76 (m, 1H), 1.54 (ddd, *J* = 14.0, 4.0, 2.0 Hz, 1H), 1.10 (d, *J* = 6.8 Hz, 3H), 1.02 (s, 9H), 0.99 (s, 9H), 0.87 (d, *J* = 6.8 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 140.4, 133.6, 129.3, 127.8, 97.9, 82.8, 74.4, 64.6, 60.5, 56.0, 43.2, 31.7, 30.2, 27.5, 27.3, 22.8, 20.0 14.6, 10.9; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1474, 1389, 1304; **HRMS** (ESI) *m/z* calculated for $C_{25}H_{44}NaO_6Si$ $[M+Na]^+$ 523.2526, found 523.2542.

Synthesis of Enone **9**



8 **9**

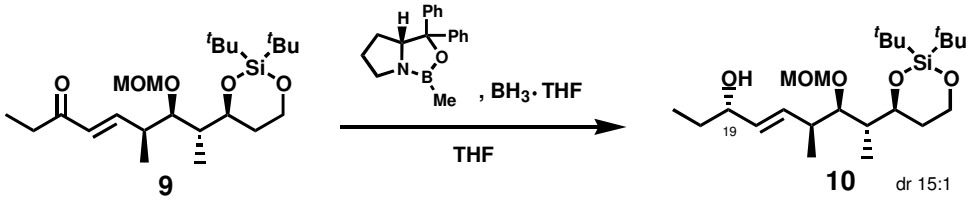
To a solution of sulfone **8** (320.6 mg, 0.6402 mmol) in dry THF (3 mL) was added 1,2-epoxybutane (280 µL, 3.22 mmol) and LHMDS (3.2 mL, 1.0 M in THF, 3.2 mmol) at 0 °C. The solution was stirred at room temperature under Ar atmosphere for 6 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and H_2O (60 mL). The aqueous phase was extracted with AcOEt (3 x 60 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude alcohol (363.5 mg) was used in the next step without purification.

To a solution of crude alcohol (363.5 mg) in DMSO (5 mL) was added IBX (536.7 mg, 1.916 mmol). The solution was stirred at room temperature for 18 h. The reaction mixture was quenched with H_2O (80 mL).The suspension was filtered using Kiriyama funnel with AcOEt, excess AcOEt was removed under reduced pressure. The aqueous phase was extracted with AcOEt (3 x 70 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude ketone (347.8 mg) was used in the next step without purification.

To a solution of crude ketone (347.8 mg) in CH_2Cl_2 (10 mL) was added DBU (150 μL, 0.982 mmol). The solution was stirred at room temperature for 2 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 9:1) to give the enone **9** (106.2 mg, 0.2477 mmol, 38%, 3 steps).

$[\alpha]_D^{25}$ = +8.0° (c = 1.5, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 6.88 (dd, *J* = 16.0, 8.0 Hz, 1H), 6.12 (dd, *J* = 16.0, 1.2 Hz, 1H), 4.61 (d, *J* = 6.8 Hz, 1H), 4.57 (d, *J* = 6.8 Hz, 1H), 4.14-4.02 (m, 3H), 3.69 (t, *J* = 5.2 Hz, 1H), 3.37 (s, 3H), 2.69 (m, 1H), 2.56 (q, *J* = 7.2 Hz, 2H), 1.99 (m, 1H), 1.80-1.66 (m, 2H), 1.13 (d, *J* = 6.8 Hz, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 1.03 (s, 9H), 1.01 (s, 9H), 0.91 (d, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 201.0, 150.1, 129.0, 97.5, 82.0, 74.8, 64.5, 56.1, 43.8, 38.9, 33.4, 33.1, 27.4, 27.2, 22.7, 19.9, 15.1, 11.1, 8.1; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1674, 1628, 1466; **HRMS** (ESI) *m/z* calculated for $C_{23}H_{44}NaO_5Si$ $[M+Na]^+$ 451.2856, found 451.2868.

Synthesis of Allyl Alcohol **10**

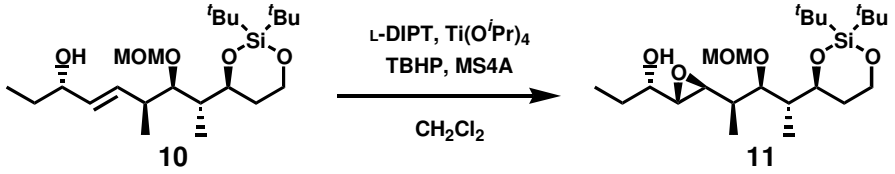


To a solution of enone **9** (176.2 mg, 0.4110 mmol) in dry THF (5 mL) was added (*R*)-Me-CBS (490 μL, 1 M in toluene, 0.490 mmol) and $BH_3 \cdot THF$ (520 μL, 0.95 M in THF, 0.494 mmol). The solution was stirred at -40 °C under Ar atmosphere for 70 min. The reaction mixture was quenched with MeOH (3 mL) and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the allyl alcohol **10** (164.8 mg, 0.3826 mmol, 93%, dr 15:1). Allyl alcohol **10** was obtained as inseparable mixture of C19 diastereomer.

$[\alpha]_D^{29}$ = +7.2° (c = 0.98, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.68 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.48 (dd, *J* =15.6, 6.8 Hz, 1H), 4.60 (s, 2H), 4.22 (ddd, *J* = 10.4, 6.8, 3.2 Hz, 1H), 4.14-4.03 (m, 2H), 3.99 (brq, *J* = 6.4 Hz, 1H), 3.57 (t, *J* = 6.0 Hz, 1H), 3.37 (s, 3H), 2.51 (m, 1H), 1.98 (m, 1H), 1.80-1.66 (m, 2H), 1.61-1.48 (m, 2H), 1.06 (d, *J* = 6.8 Hz, 3H), 1.04 (s, 9H), 1.01 (s, 9H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 135.8, 132.1, 97.7, 83.1, 74.8, 74.3, 64.7, 56.0, 43.7, 38.6, 32.9, 30.2, 27.5, 27.2, 22.8, 19.9, 16.2, 10.9, 9.7; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3449 (br), 1651, 1466,

1381; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{23}H_{47}O_5Si$ $[M+H]^+$ 431.3193, found 431.3207.

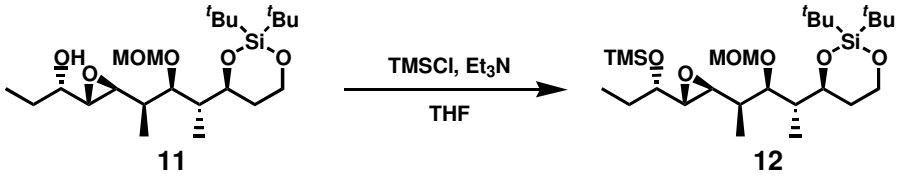
Synthesis of Epoxy Alcohol **11**



To a suspension of allyl alcohol **10** (166.7 mg, 0.3870 mmol) and activated MS4A (2 g) in dry CH_2Cl_2 (5 mL) was added TBHP (180 μL, 3.2 M in CH_2Cl_2, 0.576 mmol) at -30 °C under Ar atmosphere. Other two-necked flask was added L-DIPT (120 μL, 0.572mmol) and dry CH_2Cl_2 (3 mL) under Ar atmosphere. The solution was allowed to cool to -30 °C before the addition of $Ti(O^iPr)_4$ (137 μL, 0.462 mmol). The reaction mixture was stirred for 10 min and moved to a suspension via cannula. The suspentsion was stirred at same temperature for 18 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and then stirred at room temperature for 3 h. The suspension was filtered and added H_2O (40 mL). The aqueous phase was extracted with AcOEt (4 x 80 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (benzenes / AcOEt = 5:1) to give the epoxy alcohol **11** (144.8 mg, 0.3241 mmol, 83%).

$[\alpha]_D^{28}$ = +45.1° (c = 1.1, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.66 (d, *J* = 7.2 Hz, 1H), 4.63 (d, *J* = 7.2 Hz, 1H), 4.16-4.03 (m, 3H), 3.69 (dd, *J* = 7.2, 2.4 Hz, 1H), 3.42 (s, 3H), 3.31 (m, 1H), 2.96 (d, *J* = 1.6 Hz, 1H), 2.86 (dd, *J* = 8.0, 2.0 Hz, 1H), 2.77 (dd, *J* = 6.4, 2.4 Hz, 1H), 2.00 (m, 1H), 1.84-1.45 (m, 5H), 1.15 (d, *J* = 7.2 Hz, 3H), 1.03 (s, 9H), 1.02 (t, *J* = 8.0 Hz, 3H), 1.00 (s, 9H), 0.87 (d, *J* = 7.6 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 97.9, 82.6, 74.9, 72.9, 64.5, 61.5, 60.6, 56.1, 43.5, 38.0, 32.6, 27.5, 27.22, 27.16, 22.8, 19.9, 11.9, 11.0, 9.6; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3472 (br), 1466, 1381; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{23}H_{47}O_6Si$ $[M+H]^+$ 447.3142, found 447.3138.

Synthesis of Silyl Ether **12**

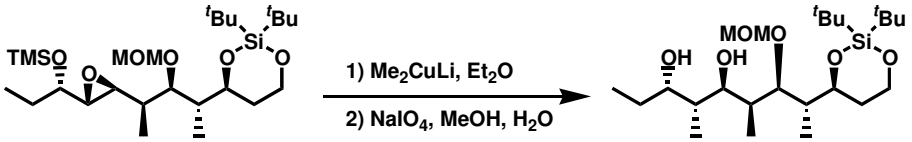


To a solution of epoxy alcohol **11** (98.8 mg, 0.221 mmol) in dry THF (2 mL) was added Et_3N (310 μL, 2.21 mmol) and TMSCl (145 μL, 1.11 mmol). The solution was stirred at room temperature under Ar atmosphere for 3 h. The reaction mixture was stirred at 0 °C, it was quenched with saturated aqueous $NaHCO_3$ (5 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude silyl ether **12** (114.6 mg) was used in the next step without purification.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.67 (d, *J* = 6.8 Hz, 1H), 4.63 (d, *J* = 6.8 Hz, 1H), 4.21-4.05 (m, 3H), 3.66

(dd, *J* = 6.0, 3.2 Hz, 1H), 3.54 (dt, *J* = 7.2, 4.8 Hz, 1H), 3.39 (s, 3H), 2.88 (dd, *J* = 6.8, 2.4 Hz, 1H), 2.79 (dd, *J* = 4.4, 2.4 Hz, 1H), 2.07 (m, 1H), 1.83-1.67 (m, 3H), 1.64-1.47 (m, 2H), 1.04 (d, *J* = 6.8 Hz, 3H), 1.03 (s, 9H), 1.00 (s, 9H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 7.2 Hz, 3H), 0.09 (s, 9H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 97.7, 81.6, 74.9, 72.4, 64.6, 60.5, 59.5, 56.2, 43.1, 37.6, 32.7, 27.9, 27.6, 27.3, 22.8, 19.9, 11.7, 11.6, 9.7, 0.3; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1466, 1381, 1250; **HRMS** (EI) *m/z* calculated for $C_{22}H_{45}O_6Si_2$ $[M-{}^tBu]^{+\cdot}$ 461.2755, found 461.2759.

Synthesis of Diol **13**



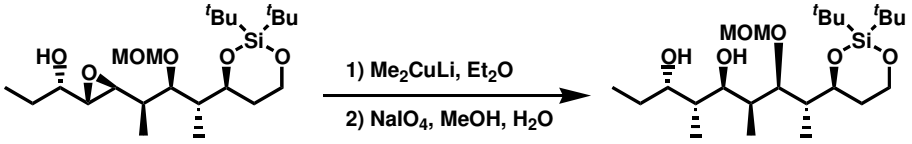
12 **13**

To a suspension of CuI (212.9 mg, 1.117 mmol) in dry Et_2O (5 mL, dried by distillation from sodium and benzophenone) was added MeLi (1.95 mL, 1.13 M in Et_2O, 2.20 mmol) at -20 °C under Ar atmosphere. The solution was added the crude silyl ether **12** (114.6 mg) in dry Et_2O (3 mL, dried by distillation from sodium and benzophenone) by gastight syringe (The silyl ether was remained 2.9 mg in a syringe). The reaction mixture was stirred for 7.5 h, it was quenched with saturated aqueous NH_4Cl (10 mL) and saturated aqueous $NaHCO_3$ (5 mL). The suspension was allowed to stir room temperature under air for 30 min and then the aqueous phase was turned to bright blue. The reaction mixture was added H_2O (30 mL) and extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*.

Next, to a solution of crude residue (119.4 mg) in MeOH (4 mL) and H_2O (2 mL) was added $NaIO_4$ (99.9 mg, 0.467 mmol). The reaction mixture was stirred at room temperature for 3.5 h (resulted in selective deprotection of TMS group and oxidative cleavage of 1,2-diol). The suspension was quenched with saturated aqueous Na_2SO_3 (10 mL), saturated aqueous $NaHCO_3$ (5 mL) and H_2O (50 mL). The aqueous phase was extracted with AcOEt (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the diol **13** (85.9 mg, 0.185 mmol, 83%).

[α]$_D^{23}$ = +27.0^o (c = 0.99, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.69 (d, *J* = 6.0 Hz, 1H), 4.67 (d, *J* = 6.0 Hz, 1H), 4.15-4.04 (m, 3H), 3.92 (m, 1H), 3.82 (dt, *J* = 9.6, 2.0 Hz, 1H), 3.74 (d, *J* = 2.0 Hz, 1H, OH), 3.62 (m, 1H), 3.41 (s, 3H), 3.08 (d, *J* = 8.0 Hz, 1H, OH), 2.04-1.86 (m, 3H), 1.82-1.70 (m, 2H), 1.56-1.39 (m, 2H), 1.04-0.98 (m, 6H), 1.02 (s, 9H), 1.00 (s, 9H), 0.89 (d, *J* = 7.6 Hz, 3H), 0.79 (d, *J* = 7.2 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 96.9, 82.5, 79.1, 76.3, 75.8, 64.1, 56.1, 44.6, 39.5, 34.7, 34.3, 27.3, 27.2, 25.4, 22.6, 19.9, 12.5, 11.3, 10.8, 7.5; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3441 (br), 1466, 1381; **HRMS** (ESI) *m/z* calculated for $C_{24}H_{50}NaO_6Si$ $[M+Na]^+$ 485.3274, found 485.3264.

Synthesis of Diol **13** from **11**

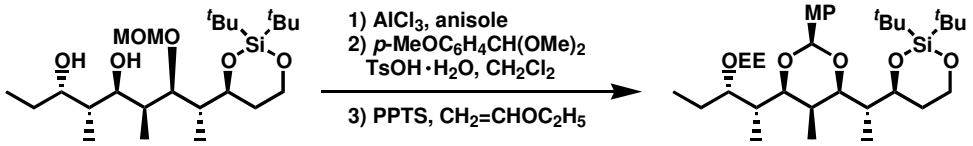


11 **13**

To a suspension of epoxy alcohol **11** (32.9 mg, 0.0703 mmol) and CuI (70.7 mg, 0.371 mmol) in dry Et_2O (1 mL, dried by distillation from sodium and benzophenone) was added MeLi (740 μL, 1.1 M in Et_2O, 0.814 mmol) -70 °C under Ar atmosphere. The raction mixture was slowly warmed to ambient temperature and stirred for 23 h. The solution was quenched with saturated aqueous NH_4Cl (1 mL) and 29 % aqueous NH_4OH (0.1 mL). The suspension was stirred under air, the aqueous phase was turned to bright blue. The reaction mixture was added H_2O (5mL) and extracted with AcOEt (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*.

Next, to a solution of crude residue (35.8 mg) in MeOH (0.5 mL) and H_2O (0.5 mL) was added $NaIO_4$ (76.0 mg, 0.355 mmol). The reaction mixture was stirred at room temperature for 4 h. The suspension was added Na_2SO_4, filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the diol **13** (12.8 mg, 0.0276 mmol, 39%).

Synthesis of Ethylvinyl Ether **15**



13 **15**

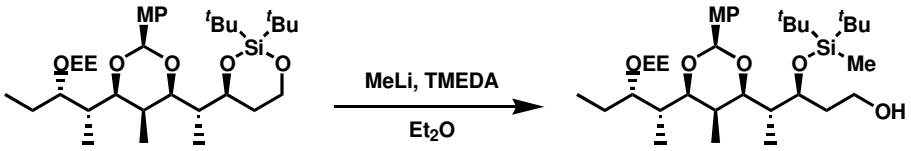
To a solution of diol **13** (25.7 mg, 0.0555 mmol) in anisole (3 mL) was added $AlCl_3$ (37.8 mg, 0.277 mmol). The solution was stirred at 0 °C under Ar atmosphere for 1 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and H_2O (10 mL). The aqueous phase was extracted with AcOEt (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 2:1) to give the triol (21.4 mg, 0.0511 mmol, 92%).

To a solution of triol (72.7 mg, 0.173 mmol) in dry CH_2Cl_2 (2 mL) was added *p*-$MeOC_6H_4CH(OMe)_2$ (62 μL, 0.34 mmol) and TsOH · H_2O (3.2 mg, 0.016 mmol). The solution was stirred at room temperature under Ar atmosphere for 2 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (3 mL) and H_2O (5 mL). The aqueous phase was extracted with AcOEt (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (benzenes = 1 > hexanes / AcOEt = 5:1) to give the benzylidene acetal (86.0 mg, 0.160 mmol, 92%).

To a solution of benzylidene acetal (86.7 mg, 0.161 mmol) in CH_2=$CHOC_2H_5$ (3 mL) was added PPTS (4.0 mg, 0.016 mmol). The solution was stirred at room temperature under Ar atmosphere for 20 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and H_2O (5 mL). The aqueous phase was extracted with AcOEt (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1) to give the ethylvinyl ether **15** (86.8 mg, 0.142 mmol, 88%) as a diastereomeric mixture with a ratio of *ca*. 1:1.

$[\alpha]_D^{28}$ = +24.4° (c = 1.2, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.8 Hz, 0.5 x 2H x 2), 6.88 (d, *J* = 9.2 Hz, 0.5 x 2H), 6.87 (d, *J* = 8.8 Hz, 0.5 x 2H), 5.42 (s, 0.5H), 5.36 (s, 0.5H), 4.69 (q, *J* = 5.0 Hz, 0.5H), 4.66 (q, *J* = 5.0 Hz, 0.5H), 4.43 (brd, *J* = 12.8 Hz, 0.5H x 2), 4.17-4.02 (m, 0.5 x 2H x 2), 3.93 (ddd, *J* = 7.6, 5.2, 0.8 Hz, 0.5H), 3.89 (dd, *J* = 10.4, 2.0 Hz, 0.5H), 3.82 (m, 0.5H), 3.81 (s, 0.5 x 3H x 2), 3.74-3.58 (m, 0.5 x 2H x 2 + 0.5H), 3.50-3.39 (m, 0.5H x 2), 2.14-1.97 (m, 0.5 x 2H x 2), 1.85-1.40 (m, 0.5 x 5H x 2), 1.29 (d, *J* = 5.2 Hz, 0.5 x 3H), 1.28 (d, *J* = 4.8 Hz, 0.5 x 3H), 1.17 (t, *J* = 6.8 Hz, 0.5 x 3H), 1.11 (t, *J* = 6.8 Hz, 0.5 x 3H), 1.03-1.02 (m, 0.5 x 18H x 2), 0.96-0.91 (m, 0.5 x 6H x 2), 0.88 (d, *J* = 7.2 Hz, 0.5 x 3H), 0.86 (d, *J* = 8.0 Hz, 0.5 x 3H), 0.83 (d, *J* = 7.6 Hz, 0.5 x 3H), 0.81 (d, *J* = 6.8 Hz, 0.5 x 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 159.7, 159.6, 131.9, 131.7, 127.07 (x 2), 127.01 (x 2), 113.53 (x 2), 113.47 (x 2), 100.7, 100.47, 100.42, 99.5, 81.7, 81.5, 81.4, 80.9, 76.5, 76.0, 75.6, 75.4, 65.5, 65.4, 61.5, 60.8, 55.3 (x 2), 40.2 (x 2), 37.0, 36.5, 31.9, 31.6, 30.6 (x 2), 27.6 (x 2), 27.3 (x 2), 25.5, 25.3, 22.9 (x 2), 21.3, 20.6, 20.0 (x 2), 15.5, 15.4, 10.54, 10.52, 10.4, 10.3, 7.4, 7.1, 5.6, 5.5; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1620, 1520, 1466; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{34}H_{61}O_7Si$ $[M+H]^+$ 609.4187, found 609.4169.

Synthesis of Alcohol **16**



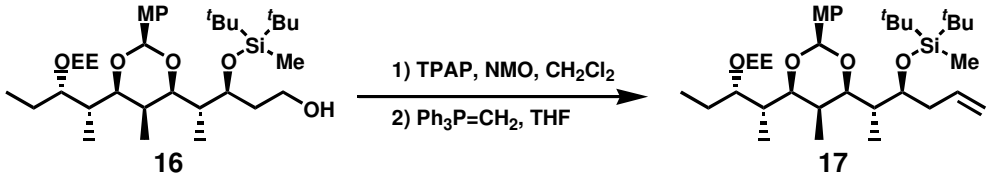
15 **16**

To a solution of ethylvinyl ether **15** (75.7 mg, 0.124 mmol) in dry Et_2O (2 mL) was added TMEDA (95 μL, 0.61 mmol) and MeLi (560 μL, 1.1 M in Et_2O, 0.61 mmol). The solution was stirred at room temperature under Ar atmosphere for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (3 mL) and H_2O (15 mL). The aqueous phase was extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the alcohol **16** (66.3 mg, 0.106 mmol, 85%) as a diastereomeric mixture with a ratio of *ca*. 1:1.

$[\alpha]_D^{28}$ = +2.3° (c = 1.0, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.360 (d, *J* = 8.8 Hz, 0.5 x 2H), 7.357 (d, *J* = 8.8 Hz, 0.5 x 2H), 6.88 (d, *J* = 9.2 Hz, 0.5 x 2H), 6.87 (d, *J* = 8.8 Hz, 0.5 x 2H), 5.40 (s, 0.5H), 5.34 (s, 0.5H), 4.71 (q, *J* = 5.2 Hz, 0.5H), 4.67 (q, *J* = 5.2 Hz, 0.5H), 4.50 (m, 0.5H x 2), 3.93 (ddd, *J* = 8.4, 6.0, 1.2 Hz, 0.5H), 3.88-3.78 (m, 0.5 x 2H x 2), 3.81 (s, 0.5 x 3H x 2), 3.75-3.59 (m, 0.5 x 3H x 2), 3.57-3.41 (m,

0.5 x 2H x 2 + 0.5H), 2.27-2.17 (m, 0.5 x 2H), 1.83-1.60 (m, 0.5 x 5H x 2), 1.55-1.39 (m, 0.5H x 2), 1.32 (d, *J* = 5.6 Hz, 0.5 x 3H), 1.30 (d, *J* = 4.8 Hz, 0.5 x 3H), 1.18 (t, *J* = 7.2 Hz, 0.5 x 3H), 1.15 (t, *J* = 6.8 Hz, 0.5 x 3H), 1.009 (s, 0.5 x 9H), 1.006 (s, 0.5 x 9H), 0.995 (s, 0.5 x 9H x 2), 0.92 (d, *J* = 6.4 Hz, 0.5 x 3H), 0.91 (d, *J* = 6.8 Hz, 0.5 x 3H), 0.89-0.78 (m, 0.5 x 9H x 2), 0.11 (s, 0.5 x 3H x 2); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 159.7, 159.6, 131.8, 131.6, 127.10, 127.01, 113.5, 113.4, 100.7, 100.53, 100.46, 99.3, 82.6, 82.4, 81.3, 80.8, 76.5, 75.7, 71.2, 71.1, 61.5, 61.3 (x 2), 60.8, 55.3 (x 2), 39.81, 39.75, 37.0, 36.5, 33.9 (x 2), 30.45, 30.41, 28.1 (x 2), 28.0 (x 2), 25.3 (x 2), 25.3 (x 2), 21.3, 21.0, 20.7, 20.6, 15.6, 15.4, 10.5, 10.4, 8.6, 8.5, 7.4, 7.1, 5.42, 5.36, -7.5 (x 2); **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3456 (br), 1620, 1520, 1466; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{35}H_{65}O_7Si$ $[M+H]^+$ 625.4500, found 625.4514.

Synthesis of Alkene **17**



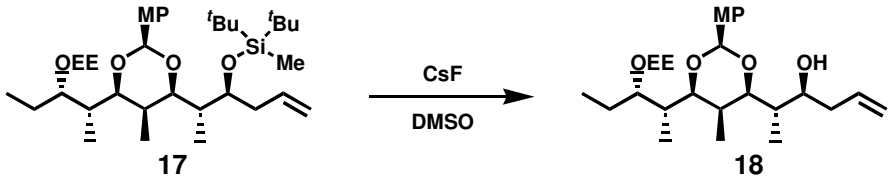
The alcohol **16** (37.0 mg, 0.0592 mmol), TPAP (11.5 mg, 0.0327 mmol) and NMO (10.7 mg, 0.885 mmol) in a flask were dried by high vacuum pump at room temperature for 20 min and purged Ar. The compounds were dissolved by dry CH_2Cl_2 (1 mL) and the solution was stirred at room temperature for 2 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The filtered aldehyde (40.1 mg) was used in the next step without purification.

The filtered aldehyde (40.1 mg) was dissolved by dry THF (2 mL) and stirred at 0 °C under Ar atmosphere. The methyltriphenylphosphonium bromide (216.6 mg, 0.594 mmol) was added dry THF (3 mL) in other two-necked flask. The suspension was added ^{n}BuLi (360 μL, 1.64 M in hexane, 0.590 mmol) and stirred at 0 °C under Ar atmosphere for 5 min. The reaction mixture was moved to aldehyde solution by gastight syringe. The solution was stirred for 10 min, quenched with saturated aqueous NH_4Cl (10 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the alkene **17** (31.3 mg, 0.0504 mmol, 85%, 2 steps) as a diastereomeric mixture with a ratio of *ca*. 1:1.

$[\alpha]_D^{28}$ = -5.0° (c = 0.92, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.8 Hz, 0.5 x 2H x 2), 6.881 (d, *J* = 8.4 Hz, 0.5 x 2H), 6.876 (d, *J* = 8.8 Hz, 0.5 x 2H), 5.94-5.82 (m, 0.5H x 2), 5.39 (s, 0.5H), 5.33 (s, 0.5H), 5.03 (dt, *J* = 16.8, 2.0 Hz, 0.5H x 2), 4.98-4.93 (m, 0.5H x 2), 4.71 (q, *J* = 5.2 Hz, 0.5H), 4.69 (q, *J* = 5.2 Hz, 0.5H), 4.39-4.33 (m, 0.5H x 2), 3.94 (t, *J* = 6.8 Hz, 0.5H), 3.88-3.77 (m, 0.5H x 2), 3.81 (s, 0.5 x 3H x 2), 3.73-3.58 (m, 0.5 x 2H x 2 + 0.5H), 3.52-3.42 (m, 0.5H x 2), 2.38-2.28 (m, 0.5H x 2), 2.24-2.13 (m, 0.5 x 2H x 2), 1.84-1.59 (m, 0.5 x 3H x 2), 1.55-1.39 (m, 0.5H x 2), 1.32 (d, *J* = 4.8 Hz, 0.5 x 3H), 1.31 (d, *J* = 5.2 Hz, 0.5 x 3H), 1.19 (t, *J* = 6.8 Hz, 0.5 x 3H), 1.16 (t, *J* = 7.6 Hz, 0.5 x 3H), 0.984 (s, 0.5 x 9H x2), 0.979 (s, 0.5 x 9H x2), 0.91-0.78 (m, 0.5 x 12H x 2), 0.071 (s, 0.5 x 3H), 0.066 (s, 0.5 x 3H);

^{13}C-NMR (100 MHz, $CDCl_3$): δ 159.6, 159.5, 137.23, 137.21, 132.1, 131.9, 127.07, 126.99, 115.9, 115.8, 113.43, 113.36, 100.5 (x 2), 100.2, 99.6, 82.4, 82.2, 81.3, 80.8, 76.5, 76.1, 72.02, 71.98, 61.5, 60.8, 55.3 (x 2), 40.3 (x 2), 37.3, 37.2, 37.1, 36.5, 30.50, 30.45, 28.1 (x 2), 28.0 (x 2), 25.5 (x 2), 25.3 (x 2), 21.3, 20.81, 20.78, 20.7, 15.5, 15.4, 10.6, 10.4, 8.6 (x 2), 7.4, 7.1, 5.3, 5.2, -7.97, -8.02; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3071, 1620, 1466; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{36}H_{65}O_6Si$ $[M+H]^+$ 621.4550, found 621.4526.

Synthesis of Left Segment **18**

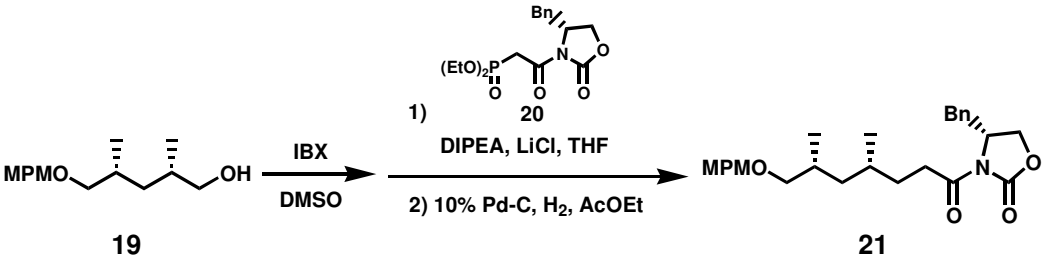


17 **18**

To a solution of alkene **17** (28.8 mg, 0.0464 mmol) in DMSO (1 mL) was added CsF (75.3 mg, 0.480 mmol). The solution was stirred at 120 °C under Ar atmosphere for 38 h. The reaction mixture was filtered through a short pad of silica gel with Et_2O and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1 > hexanes / AcOEt = 2:1) to give the left segment **18** (20.7 mg, 0.0445 mmol, 95%) as a diastereomeric mixture with a ratio of *ca*. 1:1.

$[\alpha]_D^{18}$ = +6.6° (c = 0.78, AcOEt); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 8.8 Hz, 0.5 x 2H x 2), 6.87 (d, *J* = 9.2 Hz, 0.5 x 2H), 6.86 (d, *J* = 8.8 Hz, 0.5 x 2H), 5.99-5.86 (m, 0.5H x 2), 5.51 (s, 0.5H), 5.44 (s, 0.5H), 5.15-5.06 (m, 0.5 x 2H x 2), 4.65 (q, *J* = 5.2 Hz, 0.5H), 4.61 (q, *J* = 5.2 Hz, 0.5H), 3.94-3.87 (m, 0.5H x 2), 3.85-3.71 (m, 0.5 x 4H x 2), 3.80 (s, 0.5 x 3H), 3.79 (s, 0.5 x 3H), 3.66-3.57 (m, 0.5H x 2), 3.48-3.37 (m, 0.5H x 2), 2.43-2.35 (m, 0.5H x 2), 2.17 (dt, *J* = 14.0, 8.0 Hz, 0.5H x 2), 2.01-1.88 (m, 0.5H x 2), 1.86-1.59 (m, 0.5 x 4H x 2), 1.57-1.39 (m, 0.5H x 2), 1.28 (d, *J* = 5.2 Hz, 0.5 x 3H x 2), 1.16 (t, *J* = 6.8 Hz, 0.5 x 3H), 1.11 (t, *J* = 6.8 Hz, 0.5 x 3H), 0.97 (d, *J* = 6.8 Hz, 0.5 x 3H), 0.96 (d, *J* = 6.8 Hz, 0.5 x 3H), 0.87-0.79 (m, 0.5 x 9H x 2); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 160.0, 159.9, 135.4 (x 2), 131.1, 130.9, 127.3, 127.2, 117.0, 116.9, 113.7, 113.6, 101.4, 101.1, 100.3, 99.4, 86.75, 86.70, 81.3, 80.9, 76.1, 75.8, 74.8, 74.7, 61.6, 61.0, 55.3 (x 2), 39.0 (x 2), 38.5 (x 2), 36.8, 36.4, 30.6 (x 2), 25.3, 25.1, 21.3, 20.6, 15.5, 15.3, 10.9 (x 2), 10.5, 10.3, 7.4, 7.1, 5.53, 5.46; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3495 (br), 3071, 1620, 1520; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{27}H_{45}O_6$ $[M+H]^+$ 465.3216, found 465.3207.

Synthesis of Amide **21**



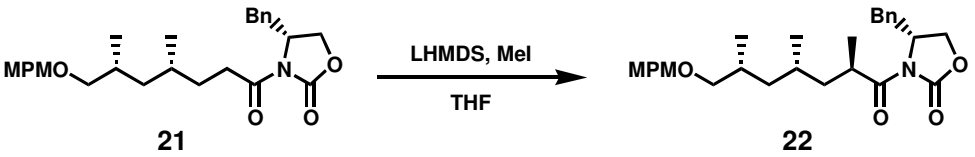
To a solution of optically active alcohol **19** (691.7 mg, 2.74 mmol) in DMSO (10 mL) was added IBX (1.158 g, 4.13 mmol). The solution was stirred at room temperature under Ar atmosphere for 3 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (50 mL) and H_2O (150 mL). The aqueous phase was extracted with AcOEt (3 x 80 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated under reduced pressur. The crude residue was filtered through a short pad of silica gel with mixed solvent (hexanes / AcOEt = 2:1) and concentrated *in vacuo*. The filtered aldehyde (667.0 mg) was used in the next step without further purification.

Next, the phosphate **20** (1.507 g, 4.24 mmol) and LiCl (578.2 mg, 13.64 mmol) in a flask were dried by high vacuum pump at room temperature for 2 h and purged Ar. The compounds were dissolved by dry THF (10 mL) and added DIPEA (770 μL, 4.42 mmol). The solution was stirred at room temperature for 20 min. The reaction mixture was add aldehyde (667.0 mg) with dry THF (total amount of used solvent was 10 mL) by Pasteur pipette. The resultant solution was stirred at room temperature for 6 days. The reaction mixture was quenched with saturated aqueous NH_4Cl (20 mL) and H_2O (150 mL). The aqueous phase was extracted with AcOEt (3 x 80 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 4:1 > hexanes / AcOEt = 1:1) to give the conjugated amide (869.1 mg, 1.924 mmol, 70%, 2 steps).

To a solution of conjugated amide (455.0 mg, 1.00 mmol) in AcOEt (20 mL) was added Pd-C (44.9 mg, 10 wt.%). The suspension was stirred at room temperature under H_2 atmosphere (balloon pressure) for 1.5 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 4:1) to give the amide **21** (412.7 mg, 0.909 mmol, 90%).

$[\alpha]_D^{27}$ = -35.2° (c = 1.1, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.30-7.24 (m, 3H), 7.23-7.19 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.65 (m, 1H), 4.45 (d, *J* = 12.0 Hz, 1H), 4.41 (d, *J* = 12.0 Hz, 1H), 4.20-4.13 (m, 2H), 3.80 (s, 3H), 3.34-3.27 (m, 2H), 3.19 (dd, *J* = 9.2, 7.6 Hz, 1H), 2.93 (t, *J* = 8.0 Hz, 2H), 2.76 (dd, *J* = 13.6, 10.0 Hz, 1H), 1.88 (m, 1H), 1.77 (m, 1H), 1.61 (m, 1H), 1.47-1.34 (m, 2H), 1.01 (m, 1H), 0.94 (d, *J* = 6.4 Hz, 3H), 0.93 (d, *J* = 6.0 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 173.6, 159.0, 153.4, 135.3, 130.9, 129.4, 129.1, 128.9, 127.3, 113.7, 75.6, 72.6, 66.1, 55.3, 55.2, 41.3, 37.9, 33.2, 30.86, 30.83, 29.7, 20.1, 17.9; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1782, 1697, 1612, 1512; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{27}H_{36}O_4N$ $[M+H]^+$ 454.2593, found 454.2584.

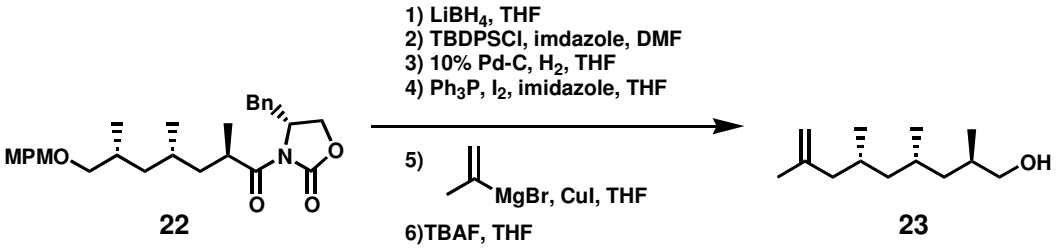
Methylation of Amide **21**



To a solution of amide **21** (407.6 mg, 0.8986 mmol) and MeI (590 μL, 9.00 mmol) in dry THF (10 mL) was added LHMDS (2.7 mL, 1.0 M in THF, 2.7 mmol). The solution was stirred at -70 °C under Ar atmosphere for 30 min. The reaction mixture was slowly warmed to -10 °C for 4 h. The solution was quenched with saturated aqueous NH_4Cl (30 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 60 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1) to give the trimethyl compound **22** (351.8 mg, 0.752 mmol, 83%).

$[\alpha]_D^{28}$ = -37.2° (c = 1.0, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.36-7.31 (m, 2H), 7.31-7.19 (m, 5H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.60 (m, 1H), 4.43 (d, *J* = 11.6 Hz, 1H), 4.39 (d, *J* = 11.2 Hz, 1H), 4.15-4.08 (m, 2H), 3.83 (m, 1H), 3.79 (s, 3H), 3.28-3.23 (m, 2H), 3.18 (dd, *J* = 8.8, 6.8 Hz, 1H), 2.75 (dd, *J* = 13.2, 9.6 Hz, 1H), 1.85 (m, 1H), 1.60 (m, 1H), 1.50-1.39 (m, 2H), 1.33 (m, 1H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.98 (m, 1H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 177.7, 159.0, 153.0, 135.4, 130.8, 129.4, 129.0, 128.9, 127.3, 113.7, 75.8, 72.6, 66.0, 55.4, 55.3, 41.9, 40.1, 37.9, 35.3, 30.7, 27.7, 19.9, 17.8, 16.8; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 1782, 1697, 1612, 1512; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{28}H_{38}NO_5$ $[M+H]^+$ 468.2750, found 468.2727.

Synthesis of Alcohol **23**



To a solution of trimetyl compound **22** (351.8 mg, 0.7523 mmol) in dry THF (10 mL) was added $LiBH_4$ (55.6 mg, 2.29 mmol). The solution was stirred at room temperature under Ar atmosphere for 6 h. The reaction mixture was quenched with saturated aqueous NH_4Cl (5 mL) and H_2O (90 mL). The aqueous phase was extracted with AcOEt (3 x 80 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1 > hexanes / AcOEt = 2:1) to give the alcohol (185.7 mg, 0.630 mmol, 83%).

To a solution of alcohol (112.5 mg, 0.3820 mmol) and imidazole (81.5 mg, 1.19 mmol) in dry DMF (2 mL) was added TBDPSCl (150 μL, 0.574 mmol). The solution was stirred at room temperature under Ar atmosphere for 6 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (10 mL) and H_2O

(20 mL). The aqueous phase was extracted with AcOEt (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1) to give the silyl ether (199.2 mg, 0.3738 mmol, 97%).

To a solution of silyl ether (187.9 mg, 0.3526 mmol) in dry THF (5 mL) was added Pd-C (20.7 mg, 10 wt.%). The suspension was stirred at room temperature under H_2 atmosphere (balloon pressure) for 56 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1) to give the alcohol (108.4 mg, 0.2626 mmol, 74%).

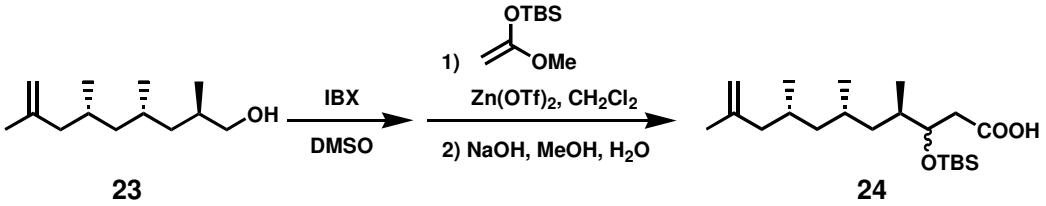
To a solution of alcohol (108.7 mg, 0.2634 mmol), imidazole (72.7 mg, 1.06 mmol) and Ph_3P (140.8 mg, 0.5260 mmol) in dry THF (5 mL) was added I_2 (141.9 mg, 0.5591 mmol). The solution was stirred at room temperature under Ar atmosphere for 20 min. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL), saturated aqueous Na_2SO_3 (2 mL) and H_2O (10 mL). The aqueous phase was extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes = 1) to give the iodide (135.0 mg, 0.2583 mmol, 98%).

To a suspension of iodide (142.2 mg, 0.2721 mmol) and CuI (77.7 mg, 0.405 mmol) in dry THF (5 mL, dried by distillation from sodium and benzophenone) was added isopropenylmagnesium bromide (2.45 mL, 0.5 M in THF, 1.22 mmol) at -20 °C under Ar atmosphere. After 20 h, the reaction mixture was quenched with saturated aqueous NH_4Cl (10 mL) and saturated aqueous $NaHCO_3$ (5 mL). The suspension was allowed to stir room temperature under air for 2 h and then the aqueous phase was turned to bright blue. The reaction mixture was added H_2O (30 mL) and extracted with AcOEt (3 x 50 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by flash column chromatography on silica gel (hexanes = 1) to give the alkene (70.6 mg, 0.1616 mmol, 59%).

To a solution of alkene (50.8 mg, 0.116 mmol) in dry THF (1 mL) was added TBAF (240 μL, 1.0 M in THF, 0.240 mmol). The solution was stirred at room temperature under Ar atmosphere for 8 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1) to give the alcohol **23** (17.7 mg, 0.0892 mmol, 77%).

$[\alpha]_D^{27}$ = +33.9° (c = 0.87, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.73 (s, 1H), 4.65 (s, 1H), 3.47 (dd, *J* = 10.8, 6.0 Hz, 1H), 3.41 (dd, *J* = 10.0, 6.4 Hz, 1H), 2.02 (dd, *J* = 12.4, 4.4 Hz, 1H), 1.79-1.56 (m, 4H), 1.69 (s, 3H), 1.34 (brs, 1H), 1.19 (ddd, *J* = 14.0, 8.0, 6.0 Hz, 1H), 1.10-1.06 (m, 2H), 1.00 (m, 1H), 0.90 (d, *J* = 6.8 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 3H), 0.82 (d, *J* = 6.4 Hz, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 144.8, 111.4, 69.2, 46.1, 45.9, 40.2, 33.2, 27.8, 27.2, 22.3, 20.1, 19.8, 16.2; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3341 (br), 3078, 1651, 1458; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{13}H_{27}O$ $[M+H]^+$ 199.2062, found 199.2091.

Synthesis of Right Segment **24**



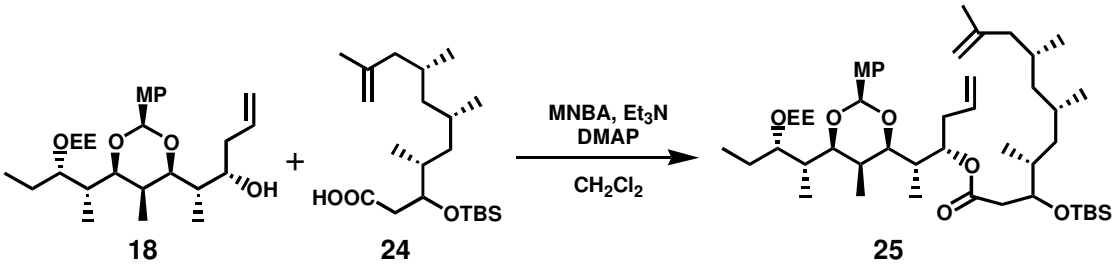
To a solution of alcohol **23** (16.6 mg, 0.0839 mmol) in DMSO (0.5 mL) was added IBX (47.7 mg, 0.170 mmol). The solution was stirred at room temperature under Ar atmosphere for 1.5 h. The reaction mixture was filtered through a short pad of silica gel with Et_2O. The solvent was removed under reduced pressure (300 mmHg, 40 °C). The aldehyde was used in the next step without further purification.

Next, to a solution of aldehyde and 1-(*tert*-Butyldimethylsilyloxy)-1-methoxyethene (38.0 μL, 0.168 mmol) in dry CH_2Cl_2 (1 mL) was added $Zn(OTf)_2$ (15.6 mg, 0.0419 mmol). The reaction mixture was stirred at room temperature under Ar atmosphere for 2 h. The suspension was quenched with saturated aqueous $NHCO_3$ (5 mL) and H_2O (10 mL). The aqueous phase was extracted with AcOEt (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 50:1) to give the aldol compound (23.2 mg, 0.0603 mmol, 72%, 2 steps) as a diastereomeric mixture with a ratio of *ca*. 2:1.

To a solution of aldol compound (21.5 mg, 0.0559 mmol) in MeOH (1 mL) was added 2 M aqueous NaOH (0.5 mL). The solution was stirred at room temperature for 28 h. The reaction mixture was quenched with saturated aqueous $NaHSO_4$ (until exhibit acidic property) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 5:1) to give the right segment **24** (16.3 mg, 0.0439 mmol, 78%) as a diastereomeric mixture with a ratio of *ca*. 2:1.

$[\alpha]_D^{27}$ = +32.2° (c = 0.84, $CHCl_3$); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 4.73 (s, 1H), 4.65 (s, 1H), 4.06-3.98 (m, 1H), 2.49-2.37 (m, 2H), 2.05-1.98 (m, 1H), 1.80-1.64 (m, 3H), 1.68 (s, 3H), 1.60-1.51 (m, 1H), 1.22-0.95 (m, 4H), 0.88 (s, 9H), 0.86-0.79 (m, 9H), 0.08 (s, 3H), 0.05 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 177.4 (C=O), 177.0 (C=O), 144.8 (major), 144.7 (minor), 111.4 (both isomers), 73.7 (minor), 73.5 (major), 46.2 (major), 46.1 (both isomers), 45.9 (minor), 39.6 (minor), 38.9 (major), 38.6 (major), 38.0 (minor), 36.3 (minor), 36.0 (major), 27.8 (both isomers), 27.3 (minor), 27.1 (major), 25.8 (3C for both isomers), 22.2 (both isomers), 20.0 (minor), 19.9 (both isomers), 19.7 (major), 18.0 (both isomers), 14.3 (major), 13.9 (minor), -4.5 (both isomers), -4.7 (major), -4.8 (minor); **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3400-2500 (br), 3071, 1713, 1651, 1458; **HRMS** (FAB matrix NBA) *m/z* calculated for $C_{21}H_{43}O_3Si$ $[M+H]^+$ 371.2981, found 371.2970.

Coupling of Both Segments

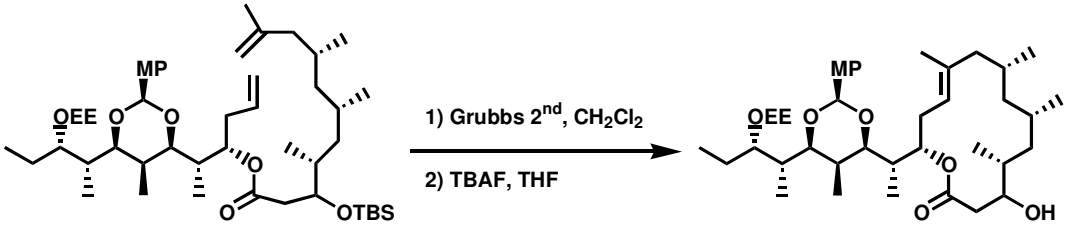


18 **24** **25**

To a solution of left segment **18** (21.41 mg, 0.04610 mmol) and right segment **24** (20.43 mg, 0.05512 mmol) in dry CH_2Cl_2 (1 mL, dried by distillation from calcium hydride) was added Et_3N (30.0 μL, 0.214 mmol), MNBA (23.78 mg, 0.06907 mmol) and DMAP (1.66 mg, 0.0135 mmol). The solution was stirred at room temperature under Ar atmosphere for 3 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (2 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 30 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1 > hexanes / AcOEt = 5:1) to give the ester **25** (27.31 mg, 0.03341 mmol, 72%, based on left segment **18**). The ester **25** was a four diastereomixture.

$[\alpha]_D^{25}$ = +30.8° (c = 0.97, AcOEt); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.90-6.86 (m, 2H), 5.84-5.70 (m, 1H), 5.44-5.28 (m, 2H), 5.05 (d, *J* = 16.8 Hz, 1H), 4.99 (d, *J* = 10.0 Hz, 1H), 4.75-4.60 (m, 3H), 4.09-3.58 (m, 5H), 3.81 and 3.80 (s for each peak, 3H), 3.50-3.40 (m, 1H), 2.47-2.26 (m, 4H), 2.26-2.16 (m, 1H), 2.05-1.97 (m, 1H), 1.86-1.40 (m, 8H), 1.68 (s, 3H), 1.33-1.29 (m, 3H), 1.27-1.11 (m, 5H), 1.07-0.94 (m, 2H), 0.92-0.78 (m, 20H), 0.87 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 171.4, 171.3, 159.7, 159.6, 144.86, 144.83, 135.25, 135.20, 135.15, 135.11, 131.7, 131.5, 127.2, 127.1, 116.9, 116.8, 113.53, 113.45, 111.3, 100.7, 100.48, 100.42, 99.4, 82.20, 82.17, 82.0, 81.2, 80.7, 76.36, 76.31, 76.01, 75.96, 73.8, 73.6, 73.46, 73.40, 61.6, 60.93, 60.87, 55.3, 46.21, 46.16, 46.05, 46.00, 39.9, 39.4, 39.17, 39.13, 38.7, 37.25, 37.20, 36.9, 36.5, 36.0, 35.5, 34.27, 34.25, 34.06, 34.04, 30.4, 27.79, 27.74, 27.2, 27.1, 25.9, 25.4, 25.2, 22.2, 21.3, 20.7, 20.0, 19.9, 19.8, 19.6, 18.1, 15.5, 15.4, 14.81, 14.75, 13.3, 10.5, 10.4, 10.0, 9.87, 9.80, 7.3, 7.1, 5.37, 5.29, -4.5, -4.62, -4.68; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3071, 1736, 1520; **HRMS** (EI) *m/z* calculated for $C_{44}H_{75}O_8Si$ $[M-{}^tBu]^{+\cdot}$ 759.5231, found 759.5235.

Synthesis of Alcohol **26**



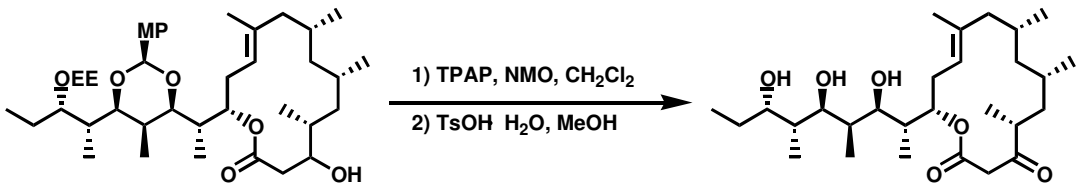
25 **26**

To a solution of ester **25** (19.44 mg, 0.02378 mmol) and Grubbs 2nd (6.09 mg, 7.17 μmol) in ultrasonic degassed dry CH_2Cl_2 (48 mL, 0.5 mM) was stirred under Ar atmosphere and heated reflux for 47 h. The reaction mixture was filtered through a short pad of silica gel with mixed solvent (hexanes / AcOEt = 10 / 1) and concentrated *in vacuo*. The filtered macrolactone (16.05 mg) was used in the next step without purification.

To a solution of macrolactone (16.05 mg) in dry THF (300 μL) was added TBAF (55 μL, 1.0 M in THF, 0.055 mmol).The solution was stirred at room temperature under Ar atmosphere for 50 h. The reaction mixture was concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1) to give the secondary alcohol **26** (9.74 mg, 0.0144 mmol, 60%, 2 steps). The secondary alcohol **26** was a four diastereomixture.

$[\alpha]_D^{26}$ = +24.2^o (c = 0.49, AcOEt); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 2H), 6.91-6.86 (m, 2H), 5.55-5.32 (m, 2H), 5.17 and 5.05 (m for each peak, 1H), 4.72-4.60 (m, 1H), 3.98-3.58 (m, 5H), 3.803 and 3.801 (s for each peak, 3H), 3.51-3.39 (m, 1H), 2.59-2.48 (m, 1H), 2.46-2.01 (m, 5H), 1.82-1.34 (m, 9H), 1.58 (s, 3H), 1.32-1.28 (m, 3H), 1.20-1.10 (m, 4H), 1.08-0.71 (m, 24H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 172.3, 171.78, 171.75, 159.7, 159.6, 137.2, 137.1, 136.2, 136.1, 131.7, 131.6, 131.5, 131.4, 127.3, 127.2, 121.34, 121.27, 120.5, 113.5, 113.4, 100.9, 100.6, 100.4, 99.4, 82.7, 82.5, 81.1, 80.7, 76.3, 75.9, 75.40, 75.35, 74.7, 73.3, 72.02, 71.99, 62.3, 61.7, 60.9, 60.4, 55.3, 46.71, 46.68, 45.56, 43.3, 43.1, 42.5, 39.33, 39.26, 38.8, 38.3, 38.12, 38.09, 37.7, 36.9, 36.43, 36.37, 36.34, 35.2, 30.5, 30.1, 30.0, 28.9, 28.20, 28.16, 28.0, 25.3, 25.2, 22.8, 21.8, 21.3, 21.22, 21.19, 20.7, 19.68, 19.62, 18.8, 16.51, 16.47, 15.5, 15.4, 15.1, 10.5, 10.4, 10.0, 9.9, 7.3, 7.1, 5.44, 5.37; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3456 (br), 1721, 1612, 1520; **HRMS** (EI) *m/z* calculated for $C_{38}H_{60}O_7$ $[M\text{-}EtOH]^{+\cdot}$ 628.4339, found 628.4363.

Synthesis of Proposed Structure (**2**)



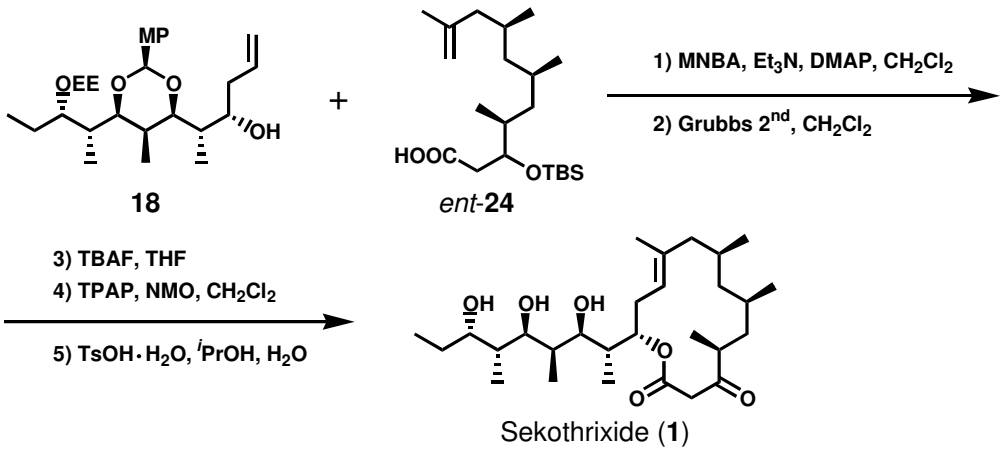
26 **2**

The secondary alcohol **26** (9.74 mg, 0.0144 mmol) and NMO (2.8 mg, 0.020 mmol) in a flask were dried by high vacuum pump at room temperature for 5 min and purged Ar. The compounds were dissolved by dry CH_2Cl_2 (0.5 mL). The reaction mixture was added TPAP (5.5 mg, 0.015 mmol). The solution was stirred at room temperature for 1.5 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The ketolide was given a 6.59 mg (9.79 μmol, 67%) as a diastereomeric mixture with a ratio of *ca*. 1:1.

To a solution of ketolide (2.23 mg, 3.31 μmol) in MeOH (100 μL) was added TsOH · H_2O (trace). The solution was stirred at room temperature for 10 h. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (100 μL). The suspension was filtered through a short pad of Na_2SO_4 with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 4:1 > hexanes / AcOEt = 3:2) to give the proposed structure of sekothrixide (**2**) (0.65 mg, 1.34 μmol, 40%).

$[\alpha]_D^{20}$ = +9.3° (c = 0.035, MeOH); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.19 (m, 1H), 5.08 (t, *J* = 6.0 Hz, 1H), 4.03 (brs, 1H), 3.84 (d, *J* = 9.6 Hz, 1H), 3.75-3.69 (m, 1H), 3.67-3.63 (m, 1H), 3.49 (d, *J* = 12.4 Hz, 1H), 3.40 (d, *J* = 12.4 Hz, 1H), 3.33 (brs, 1H), 2.72 (m, 1H), 2.46 (d, *J* = 5.6 Hz, 1H), 2.39 (m, 1H), 2.26 (m, 1H), 2.15-2.04 (m, 2H), 1.93-1.77 (m, 2H), 1.75-1.65 (m, 3H), 1.63 (s, 3H), 1.60-1.30 (m, 4H), 1.09 (d, *J* = 7.6 Hz, 3H), 1.06-0.95 (m, 1H), 1.01 (t, *J* = 7.2 Hz, 3H), 0.908 (d, *J* = 7.6 Hz, 3H), 0.900 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 6H), 0.78 (d, *J* = 6.8 Hz, 3H), 0.72 (m, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 205.1, 166.0, 137.5, 120.4, 79.6, 79.4, 77.3, 76.4, 47.6, 47.2, 45.3, 43.4, 40.1, 39.8, 39.6, 35.2, 29.3, 28.7, 26.8, 25.1, 23.5, 21.0, 18.0, 17.6, 12.1, 11.2, 11.1, 4.0; **IR** ν_{max} (thin film/NaCl) cm^{-1}:3410 (br), 1736, 1713, 1458; **HRMS** (EI) *m/z* calculated for $C_{28}H_{50}O_6$ $[M]^{+\cdot}$ 482.3607, found 482.3617.

Synthesis of Sekothrixide (**1**)



To a solution of left segment **18** (28.83 mg, 0.06208 mmol) and right segment *ent*-**24** (28.88 mg, 0.07791 mmol) in dry CH_2Cl_2 (2 mL) was added Et_3N (44.0 μL, 0.314 mmol), MNBA (43.2 mg, 0.125 mmol) and DMAP (1.01 mg, 8.2 μmol). The solution was stirred at room temperature under Ar atmosphere for 5.5 h. Additionally, the reaction mixture was added Et_3N (22.0 μL, 0.157 mmol) and MNBA (21.02 mg, 0.0610 mmol). After 13 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ (5 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt (3 x 40 mL). The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1) to give the ester (47.13 mg, 0.05766 mmol, 92%, based on left segment **18**). The ester was a four diastereomixture.

To a solution of ester (9.81 mg, 0.0120 mmol) and Grubbs 2nd (3.12 mg, 3.67 μmol) in ultrasonic degassed dry CH_2Cl_2 (24 mL, 0.5 mM) was stirred under Ar atmosphere and heated reflux for 56 h. The solvent was removed under reduced pressure. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The macrolactone (15.3 mg) was used in the next step without further purification.

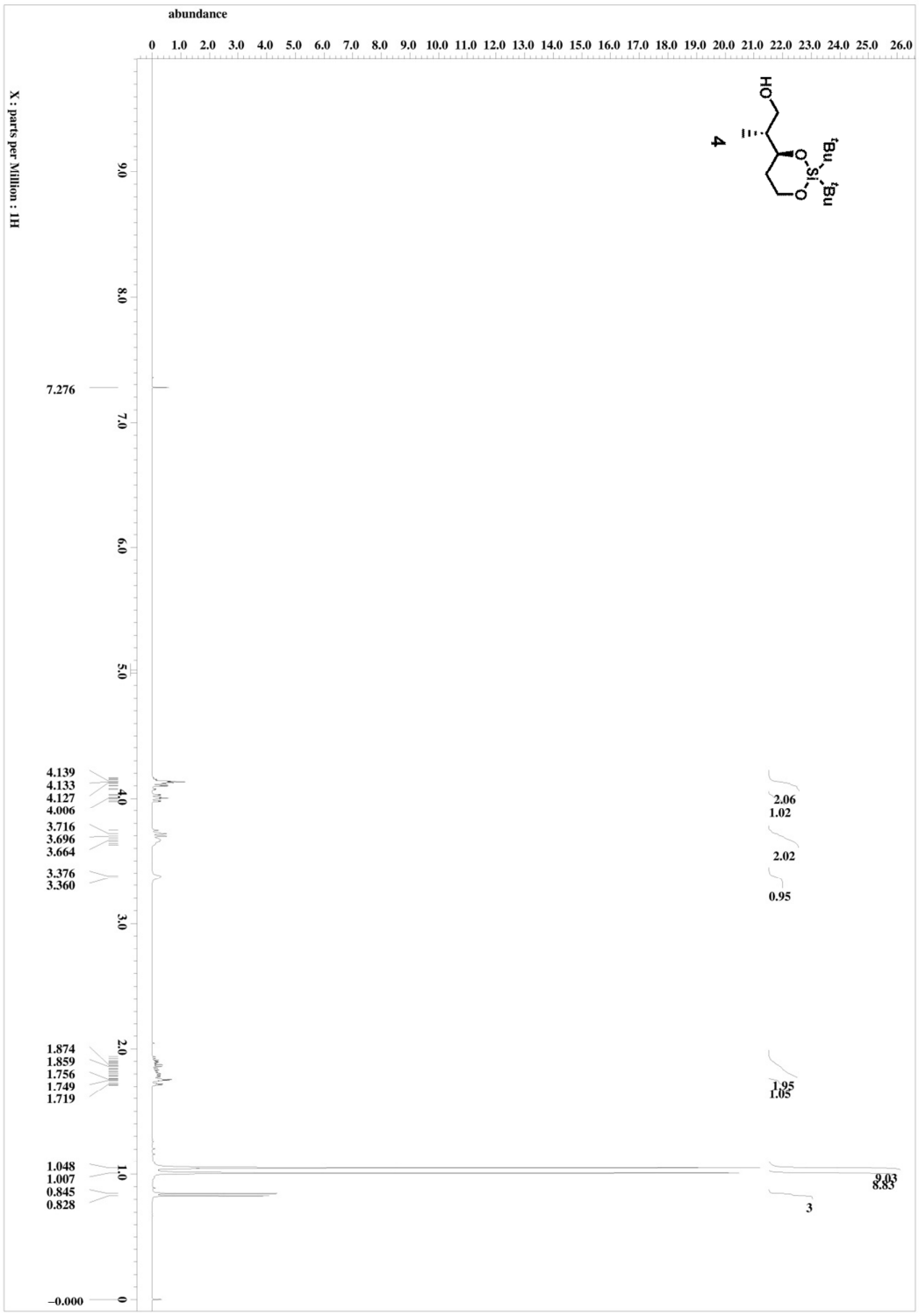
To a solution of macrolactone (15.3 mg) in dry THF (300 μL) was added TBAF (120 μL, 1.0 M in THF, 0.120 mmol).The solution was stirred at room temperature under Ar atmosphere for 27 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 10:1 > hexanes / AcOEt = 4:1 > hexanes / AcOEt = 1:1) to give the secondary alcohol (4.97 mg, 7.38 μmol, 61%, 2 steps). The ester was a four diastereomixture.

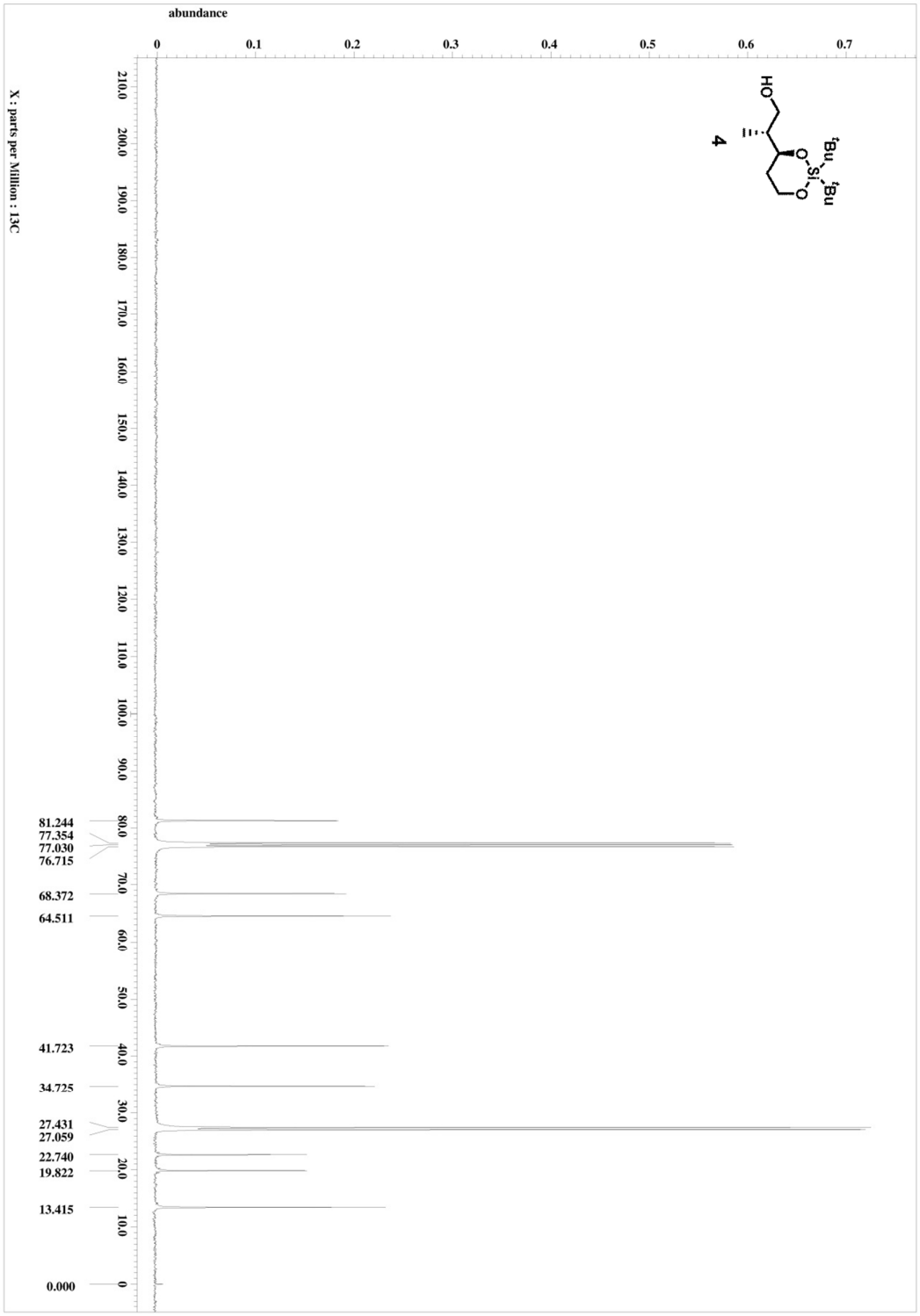
The secondary alcohol (13.78 mg, 0.02041 mmol) and NMO (4.7 mg, 0.039 mmol) in a flask were dried by high vacuum pump at room temperature for 5 min and purged Ar. The compounds were dissolved by dry CH_2Cl_2 (1 mL). The reaction mixture was added TPAP (7.9 mg, 0.022 mmol). The solution was stirred at room temperature for 2 h. The reaction mixture was filtered through a short pad of silica gel with AcOEt and concentrated *in vacuo*. The ketolide was given a 12.60 mg (0.01872 μmol, 91%) as a diastereomeric mixture with a ratio of *ca*. 1:1.

To a solution of ketolide (12.60 mg, 0.01872 mmol) in ^{i}PrOH (3 mL) and H_2O (0.3 mL) was added TsOH · H_2O (11.1 mg, 0.0585 mmol). The solution was stirred at room temperature for 51 h at 40 °C. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ (1 mL) and H_2O (20 mL). The aqueous phase was extracted with AcOEt. The combined organic phases were dried over Na_2SO_4, filtered and concentrated *in vacuo*. The crude residue was purified by column chromatography on silica gel (hexanes / AcOEt = 3:1 > hexanes / AcOEt = 1:1) to give the sekothrixide **1** (3.50 mg, 7.25 μmol, 38%).

$[\alpha]_D^{27}$ = -46.4° (c = 0.18, MeOH); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ 5.27 (m, 1H), 5.05 (m, 1H), 4.04 (brs, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.73 (m, 1H), 3.63 (d, *J* = 9.6 Hz, 1H), 3.54 (d, *J* = 13.6 Hz, 1H), 3.45 (brs, 1H), 3.30 (d, *J* = 13.6 Hz, 1H), 2.92 (m, 1H), 2.43 (d, *J* = 5.6 Hz, 1H), 2.36 (ddd, *J* = 14.4, 10.8, 9.2 Hz, 1H), 2.16 (m, 1H), 2.11-1.98 (m, 2H), 1.95-1.85 (m, 2H), 1.74-1.45 (m, 5H), 1.59 (s, 3H), 1.31 (ddd, *J* = 11.2, 6.4, 4.8 Hz, 1H), 1.12 (d, *J* = 8.4 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.96 (m, 1H), 0.91 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.0 Hz, 3H), 0.89 (d, *J* = 6.4 Hz, 3H), 0.85 (d, *J* = 7.6 Hz, 3H), 0.78 (d, *J* = 7.2 Hz, 3H), 0.52 (ddd, *J* = 14.8, 8.0, 6.8 Hz, 1H); **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 205.7, 167.0, 137.3, 121.6, 79.6, 79.1, 77.1, 76.5, 49.03, 49.01, 41.6, 41.4, 39.83, 39.78, 39.34, 35.2, 29.8, 28.1, 27.1, 25.1, 23.3, 21.1, 19.3, 16.7, 12.1, 11.1, 10.8, 3.9; **IR** ν_{max} (thin film/NaCl) cm^{-1}: 3418 (br), 1728, 1705, 1458; **HRMS** (EI) *m/z* calculated for $C_{28}H_{50}O_6$ $[M]^{+\cdot}$ 482.3607, found 482.3612.

3. NMR spectra

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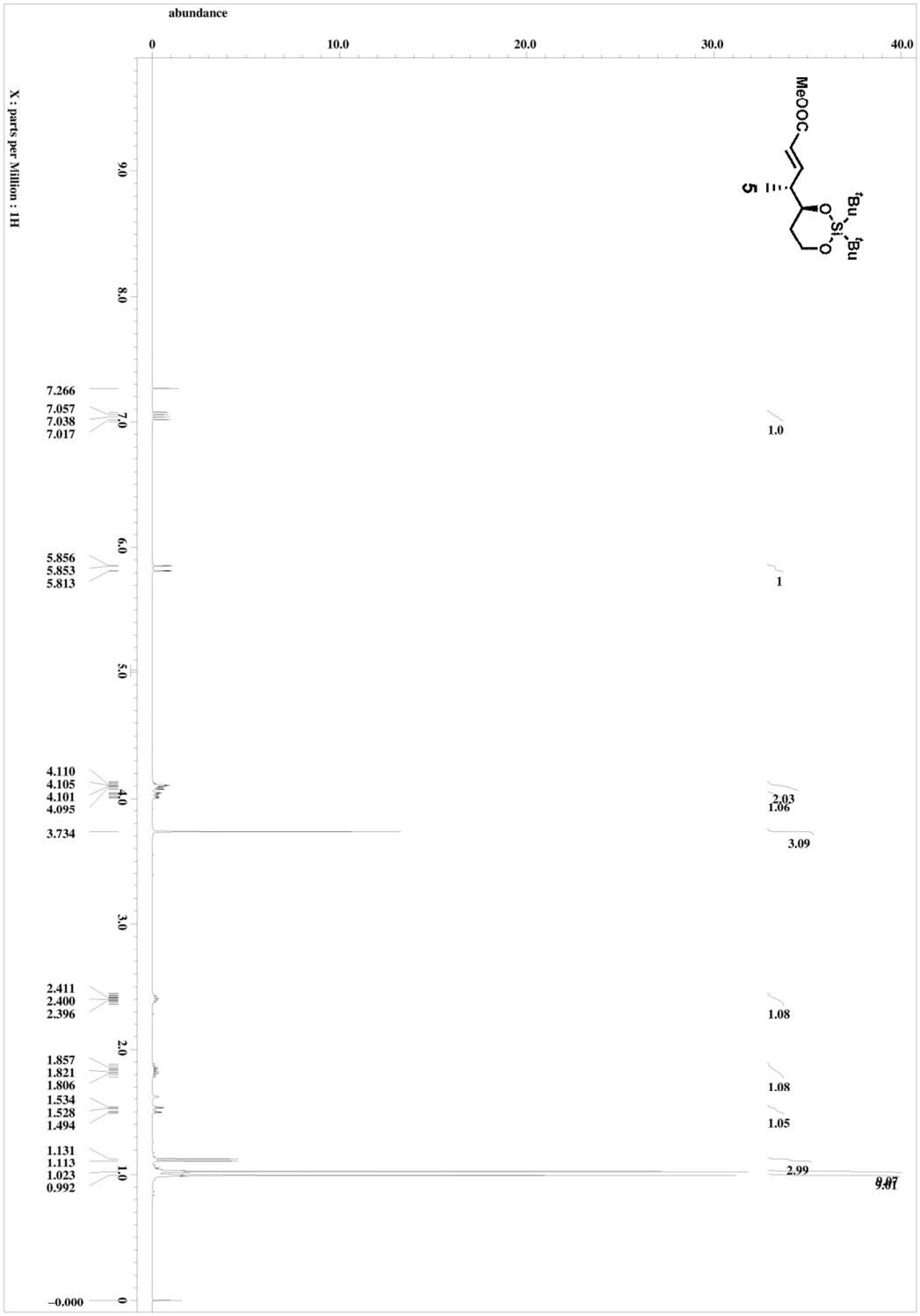
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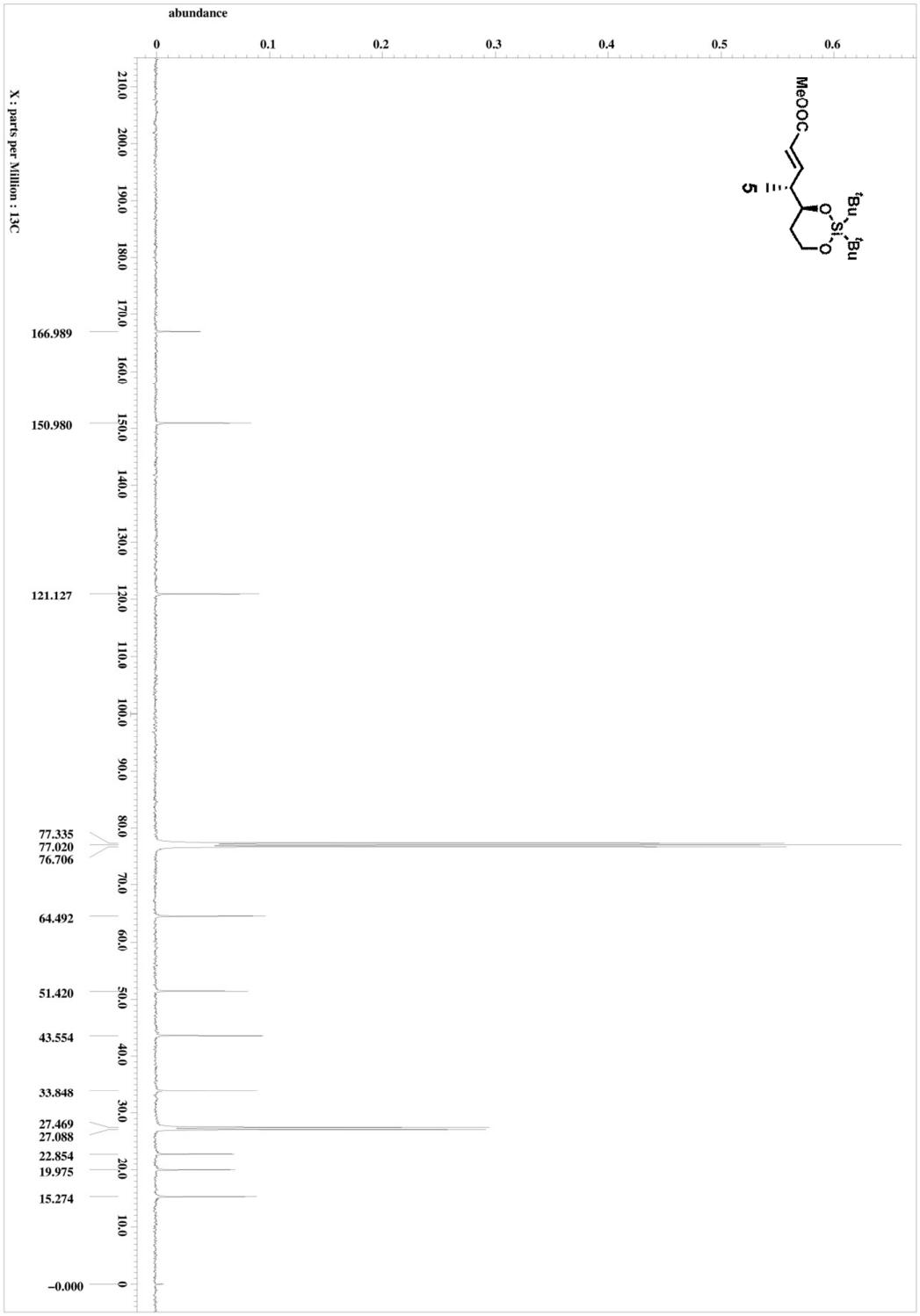
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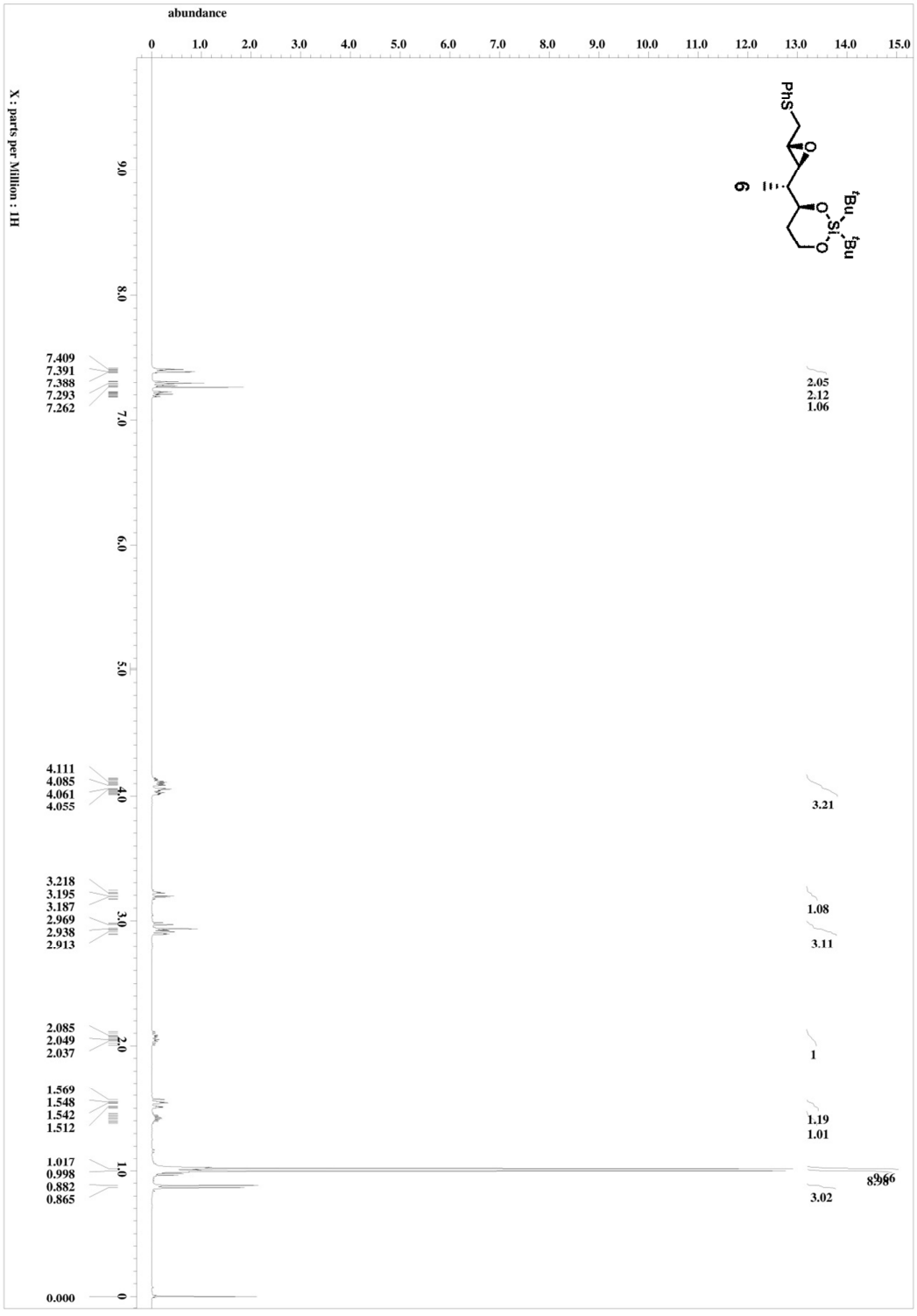
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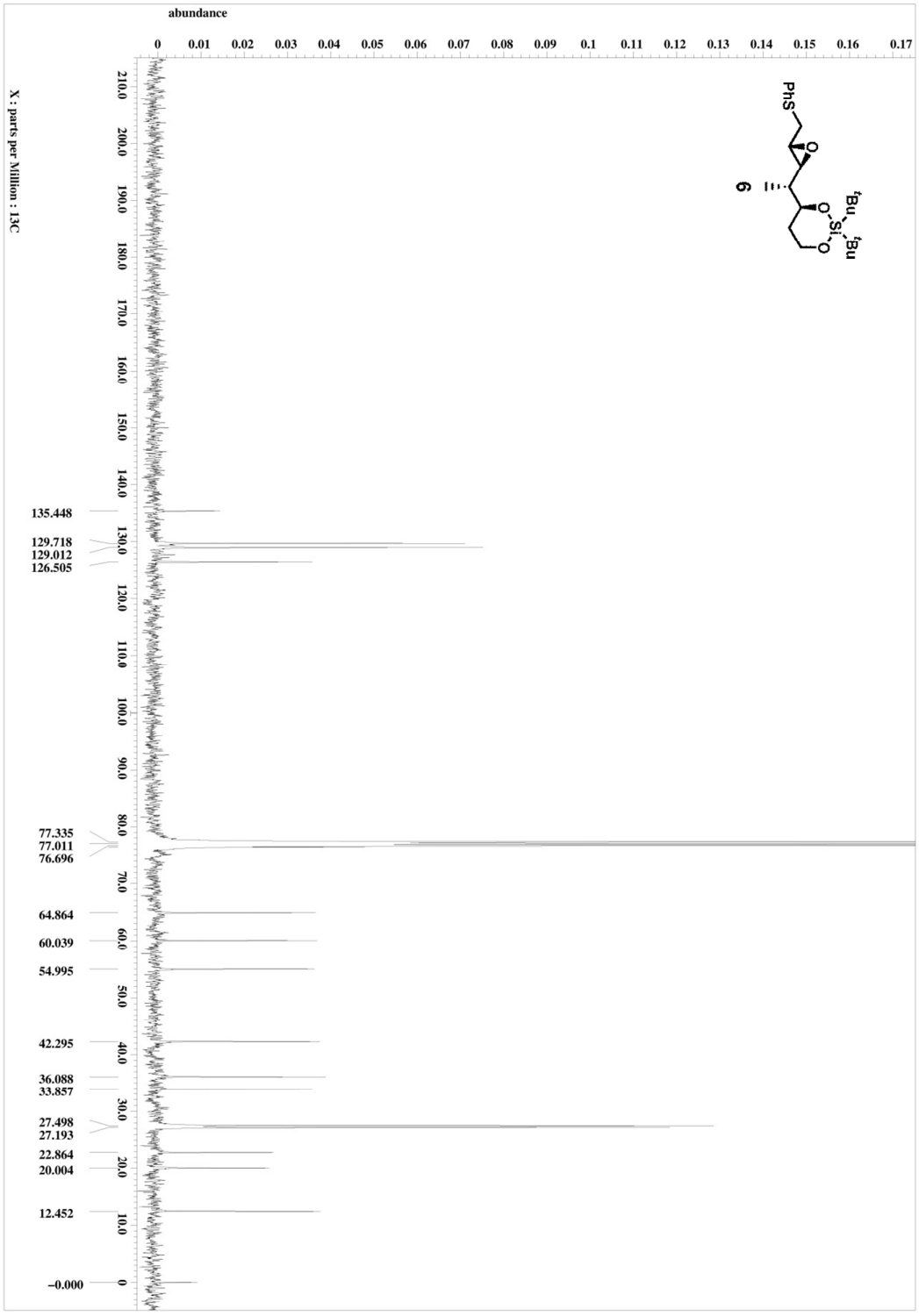
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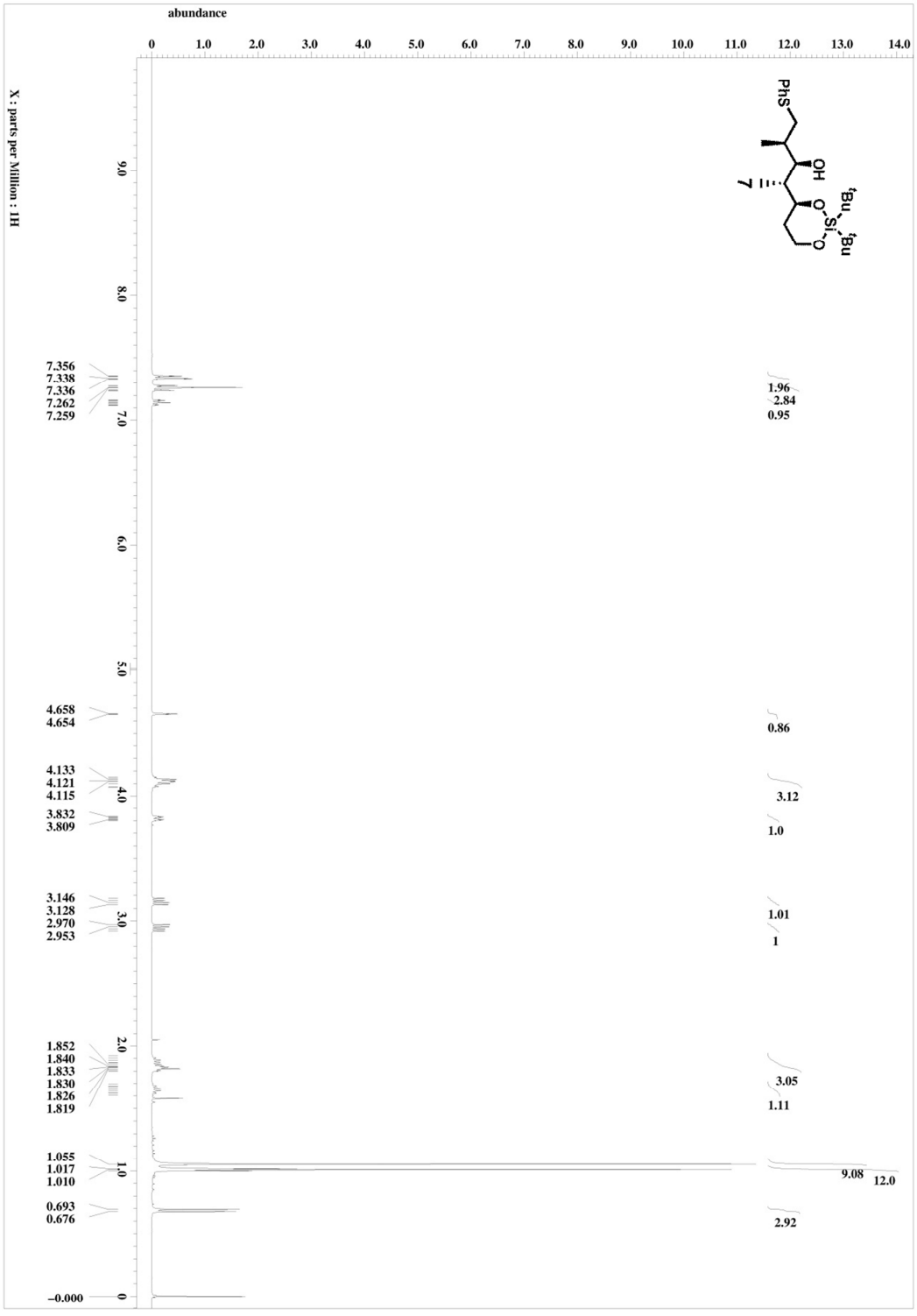
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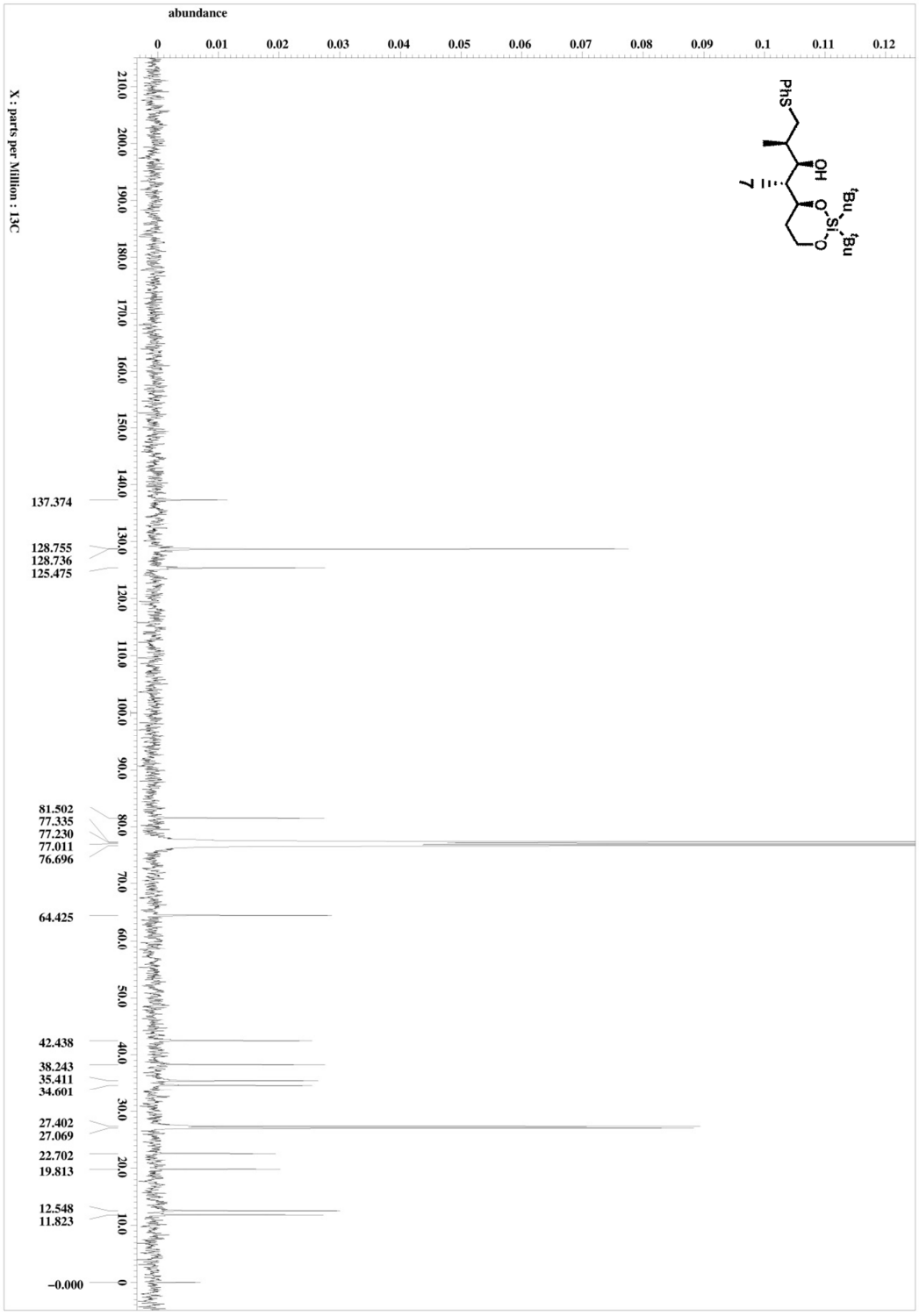
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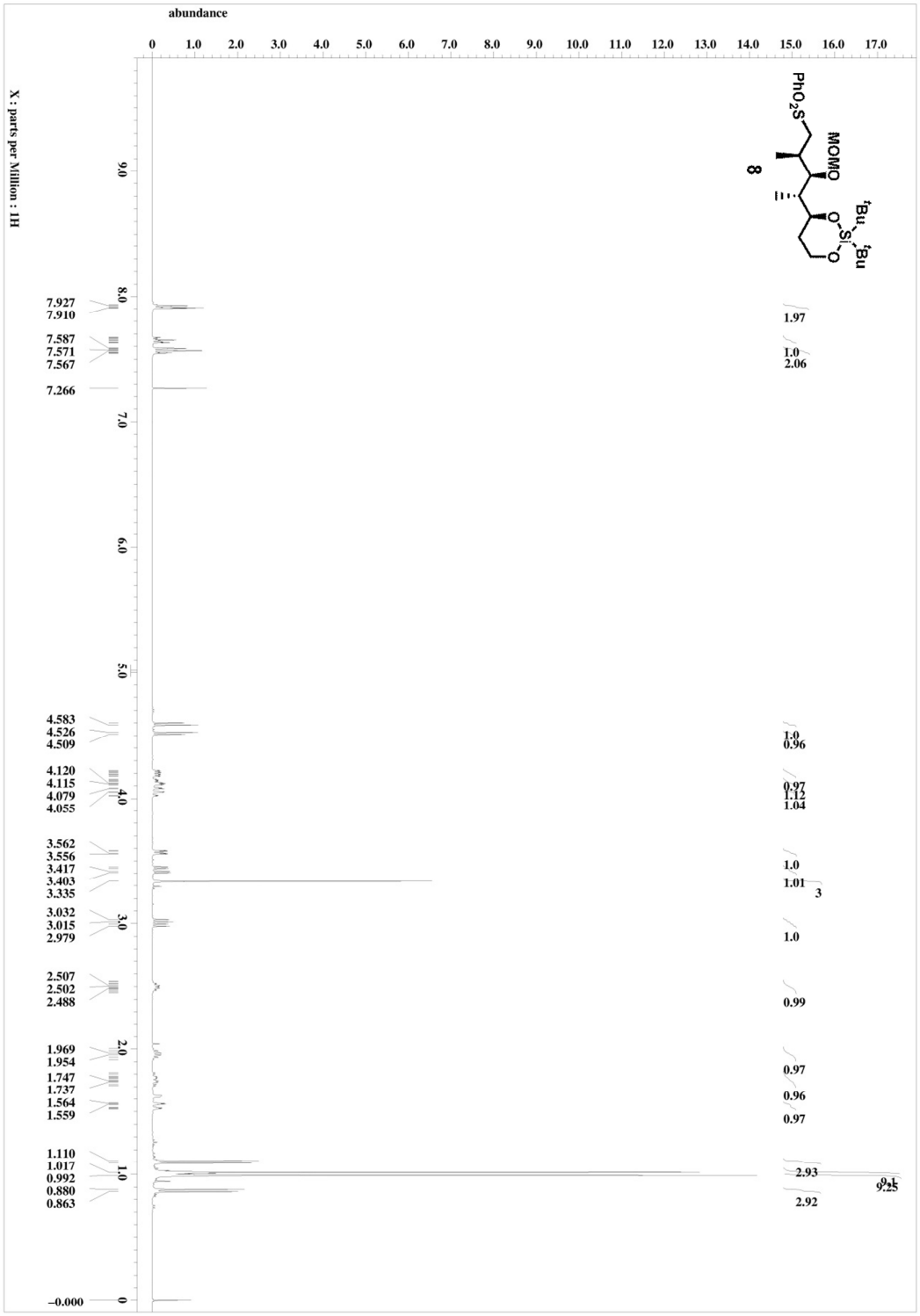
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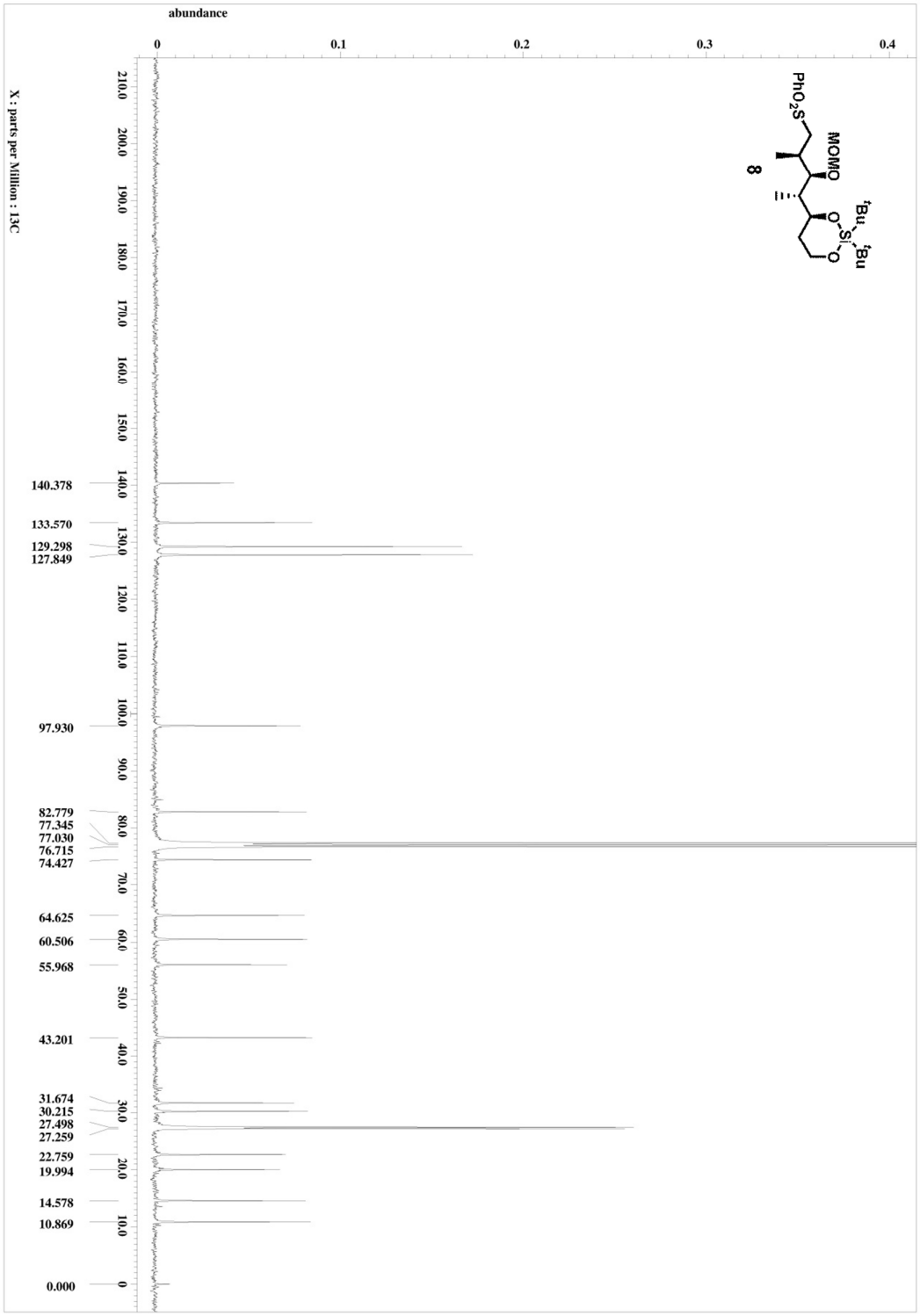
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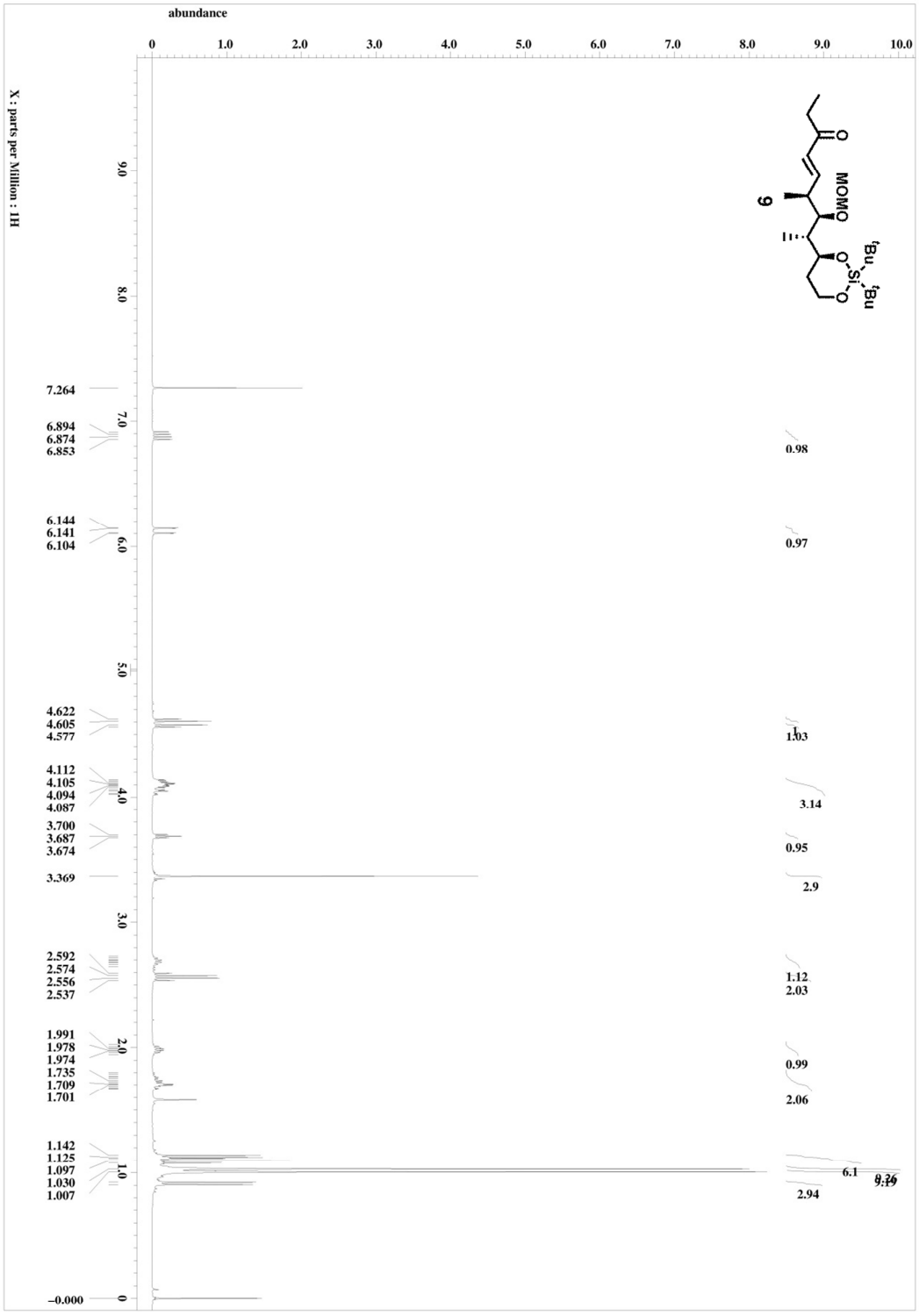
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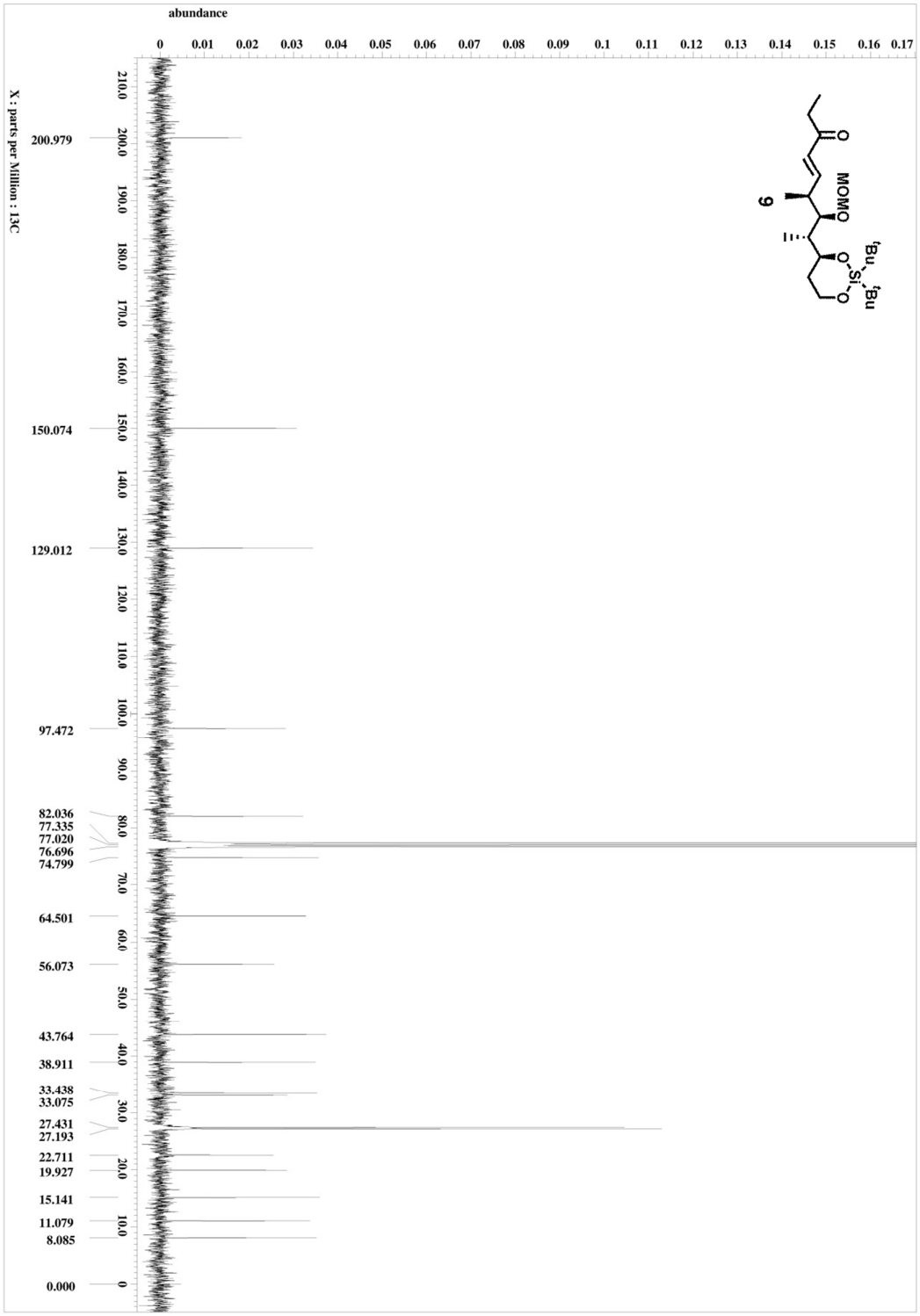
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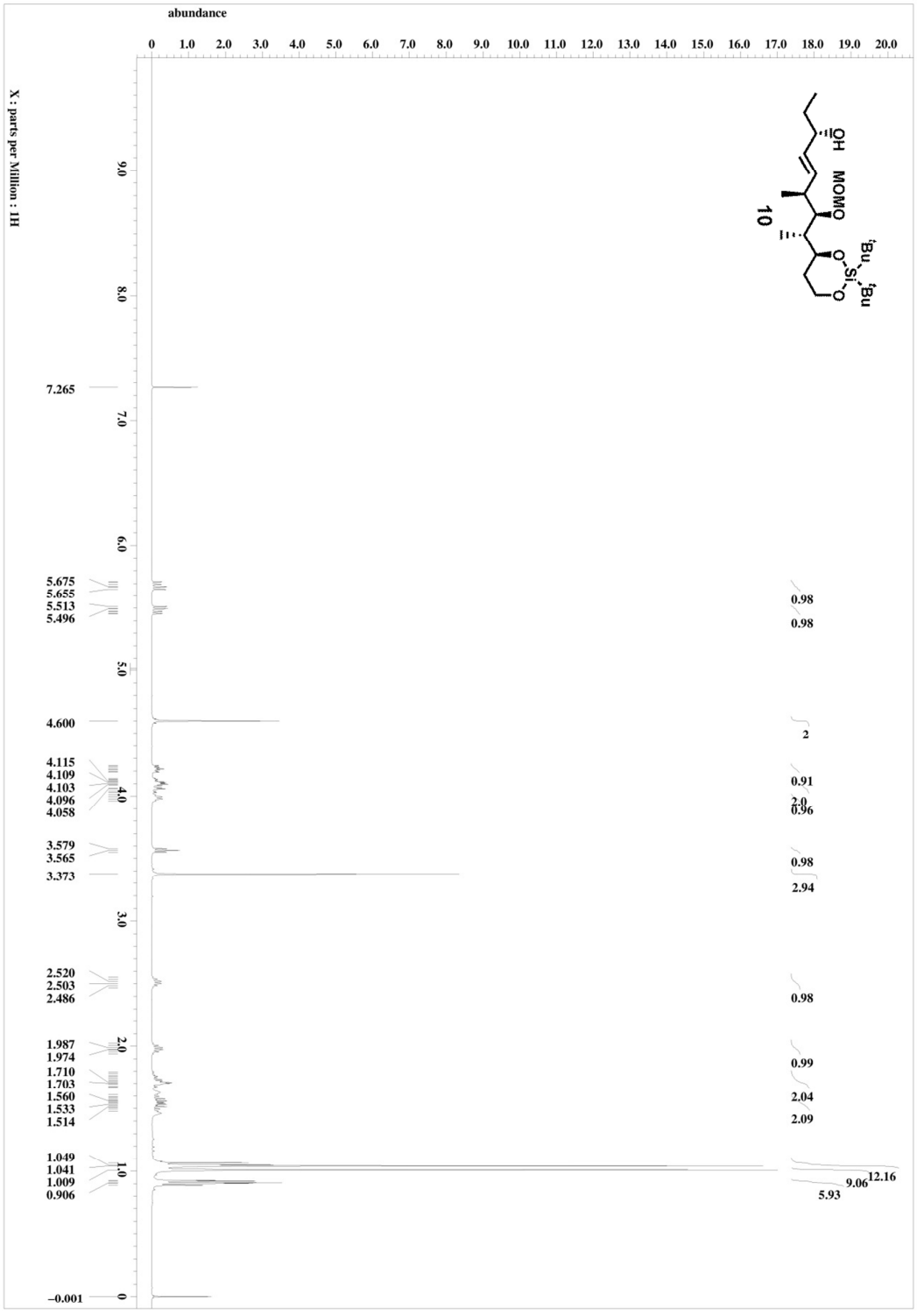
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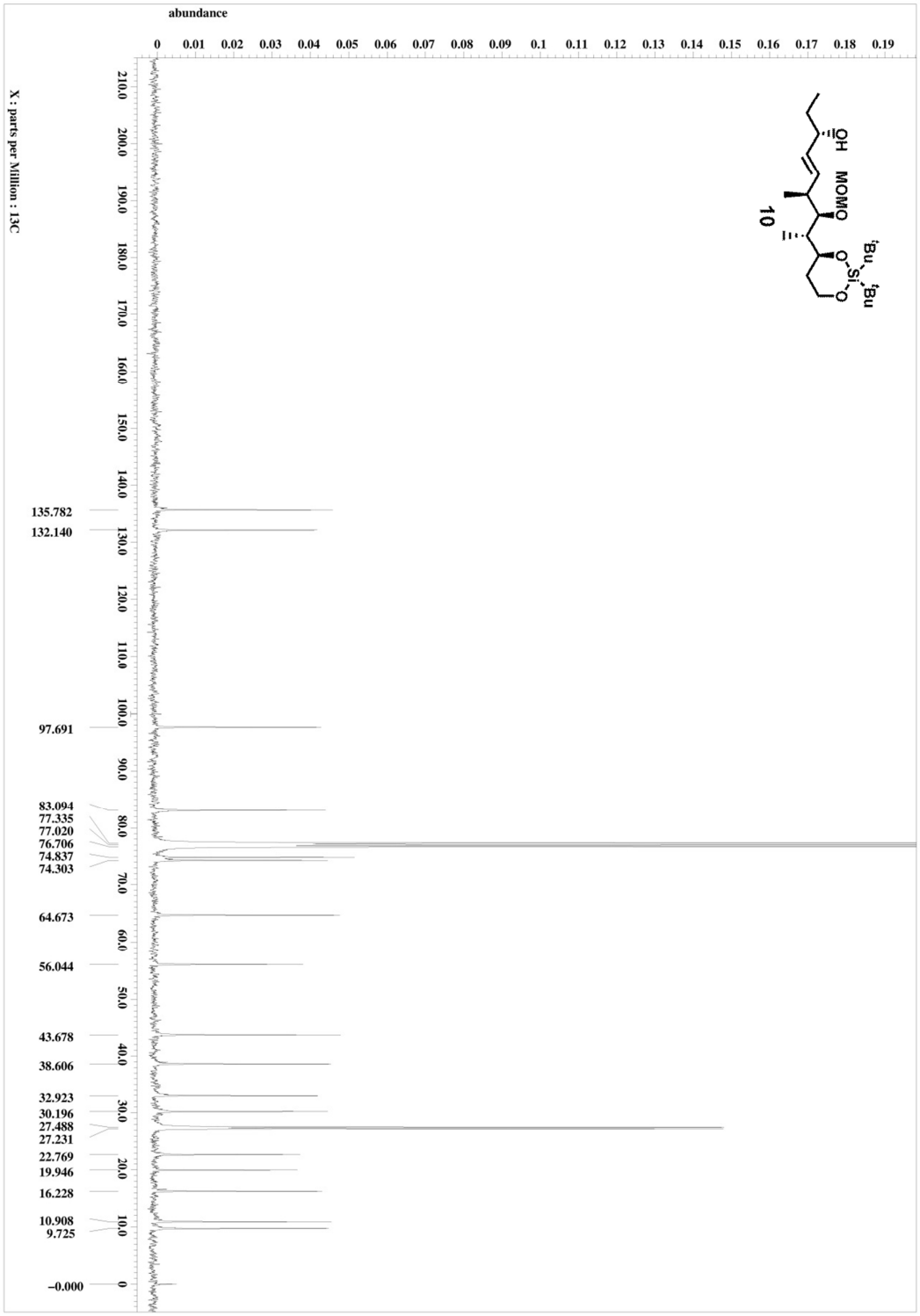
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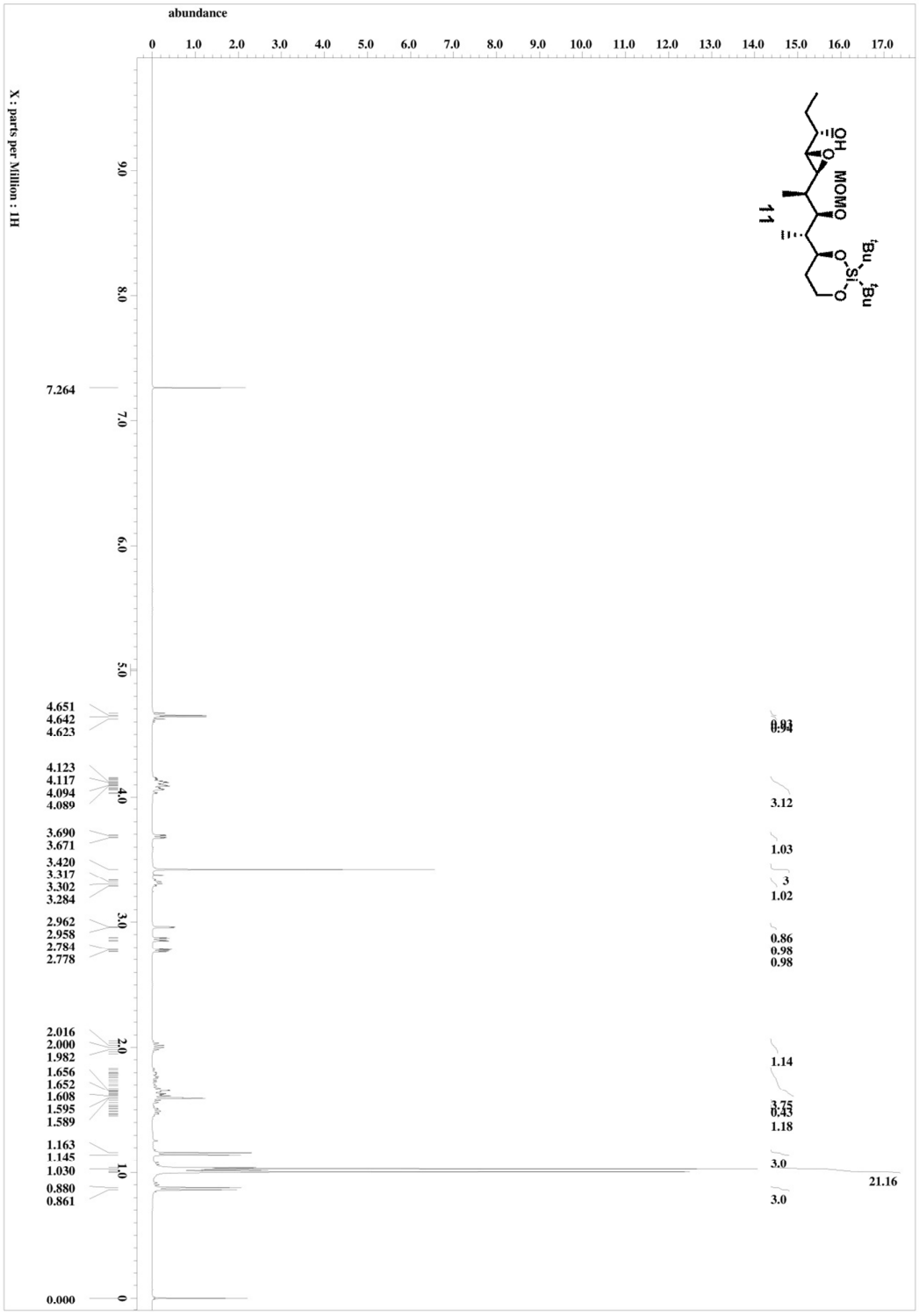
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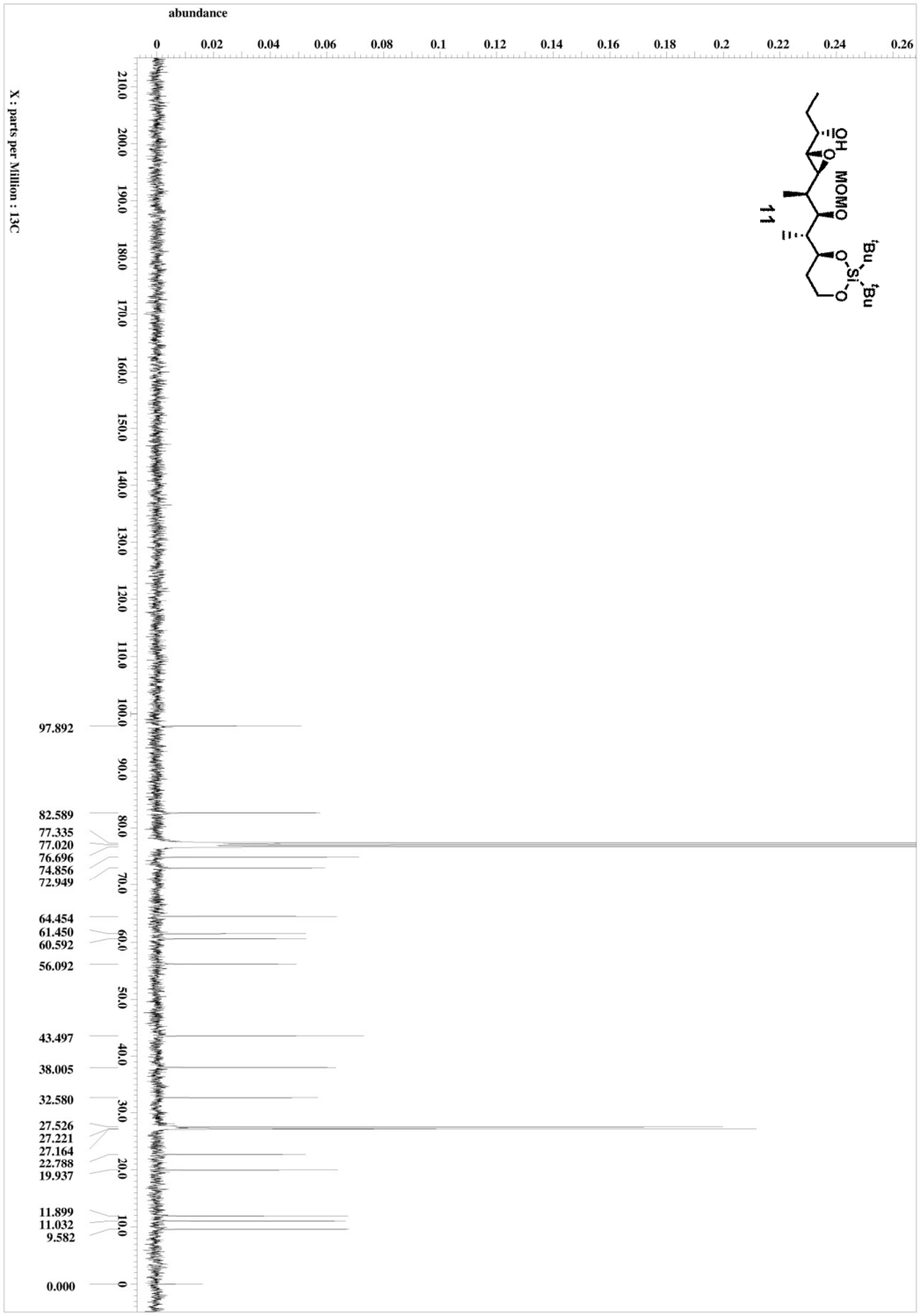
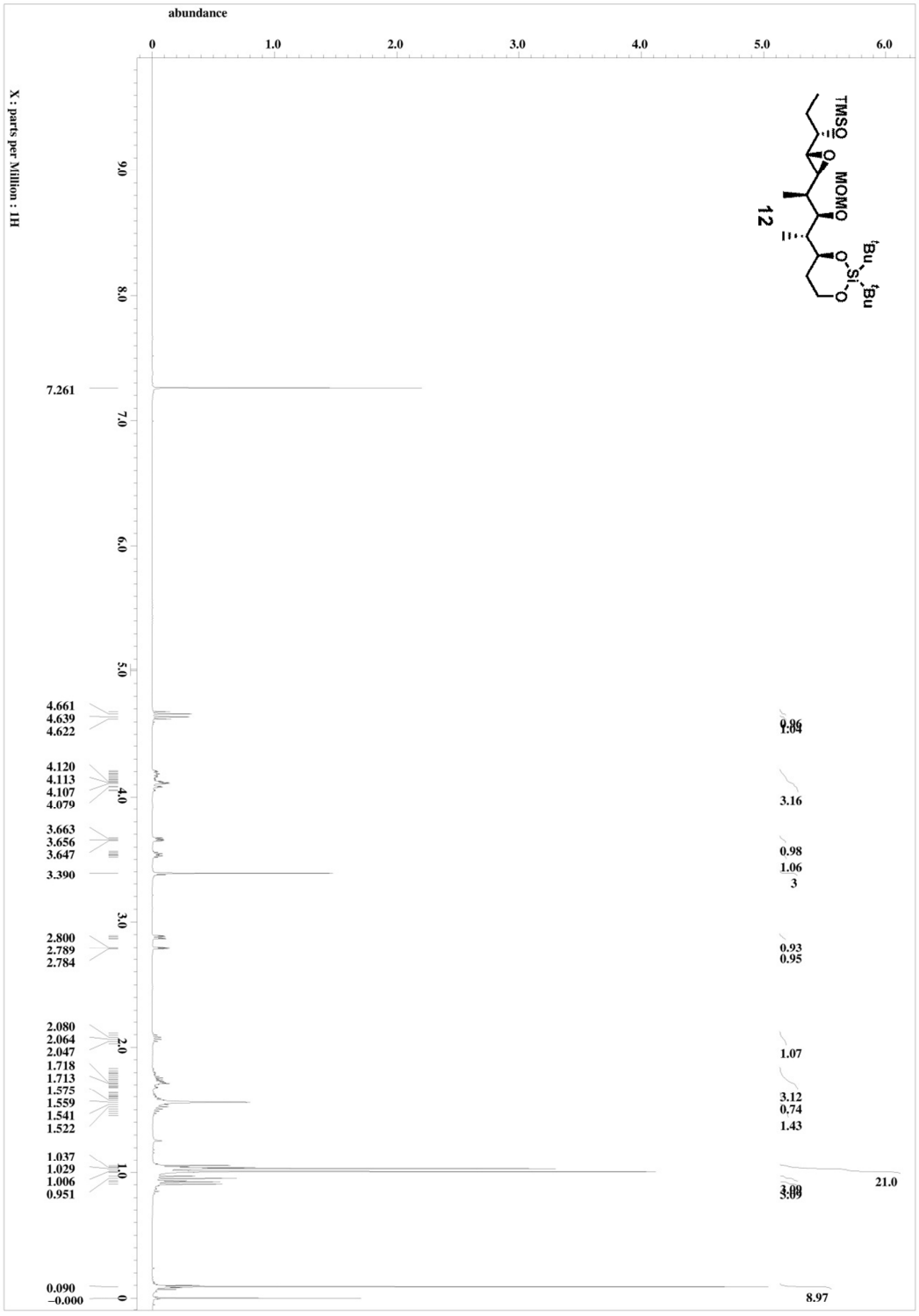
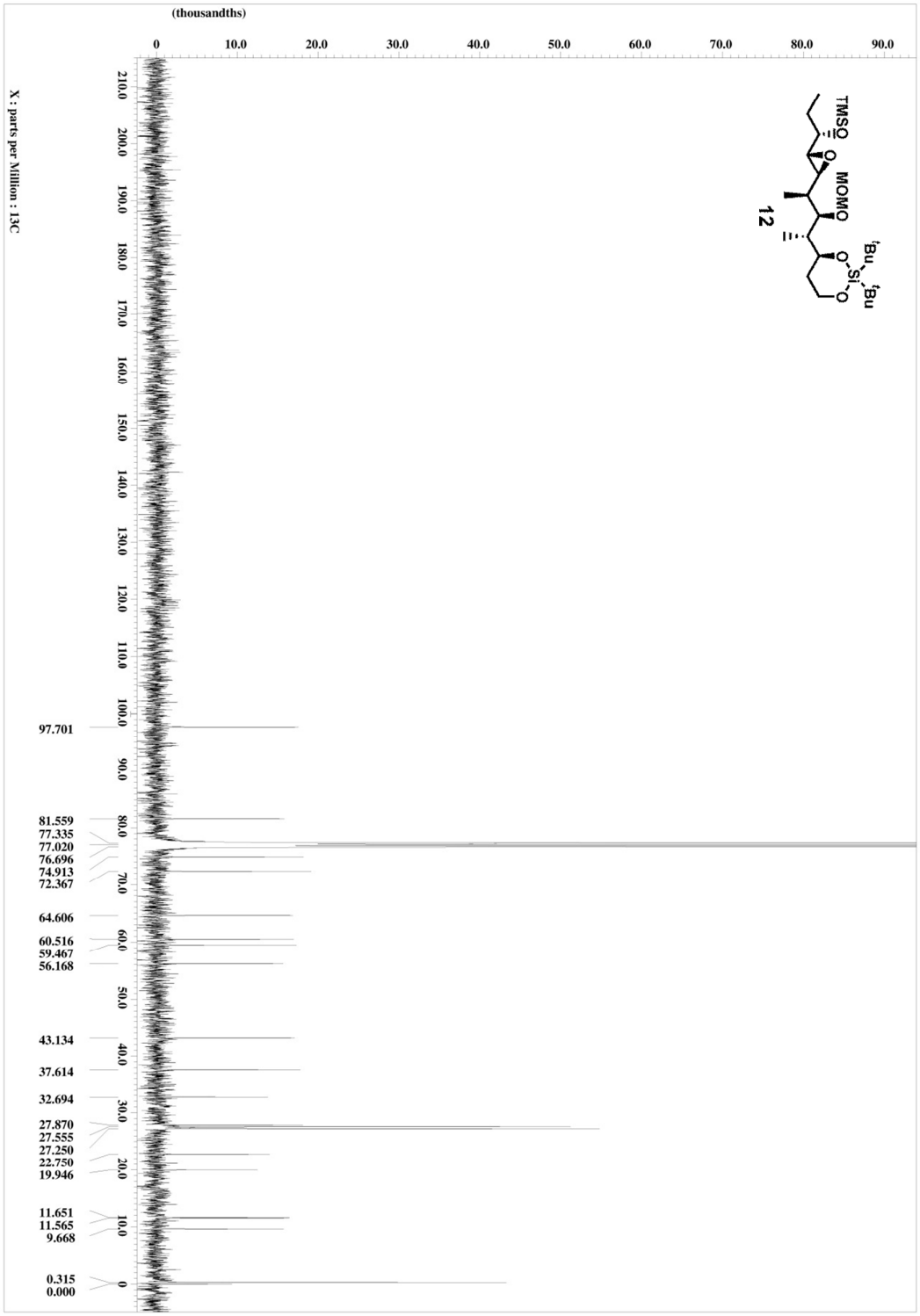
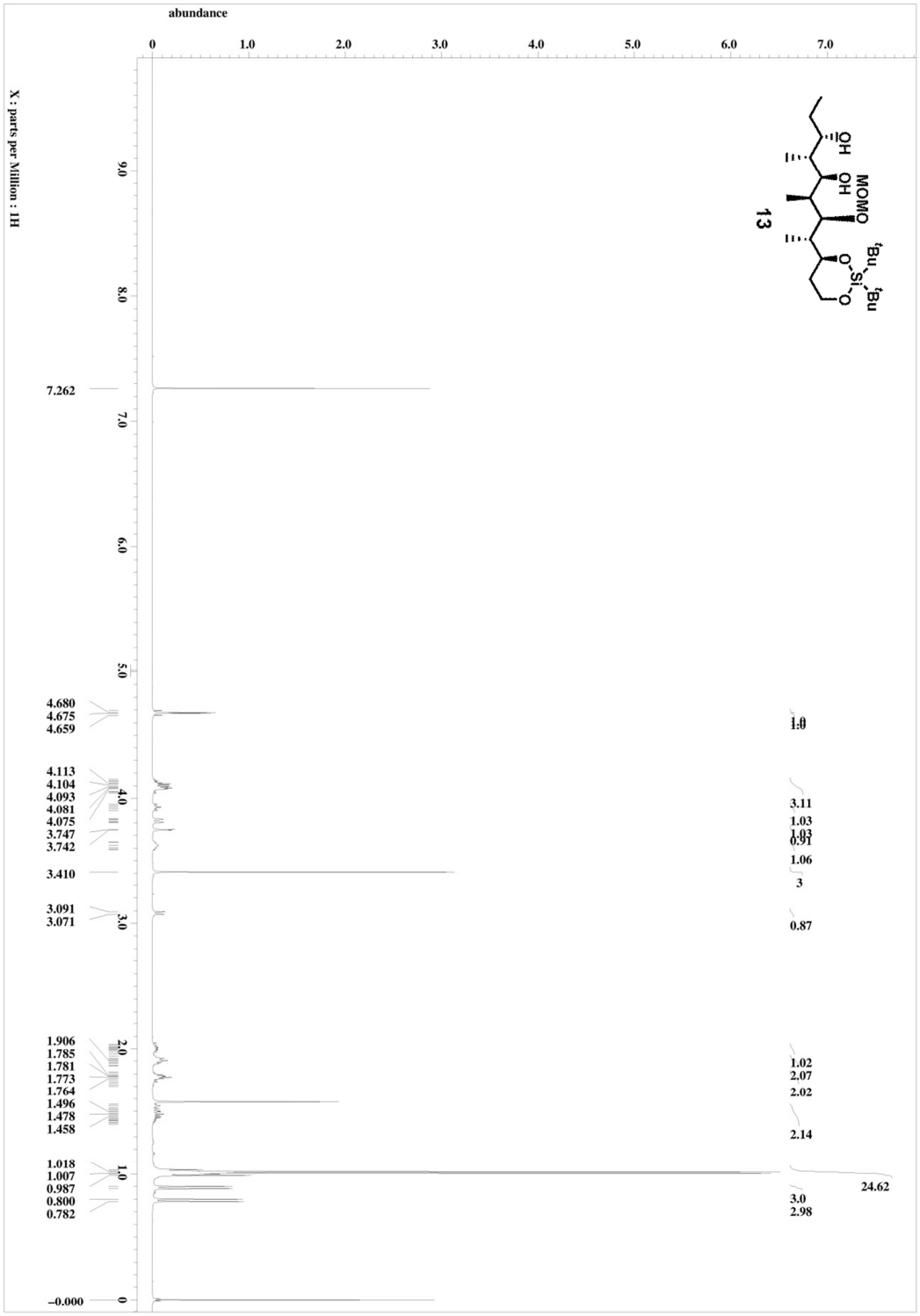
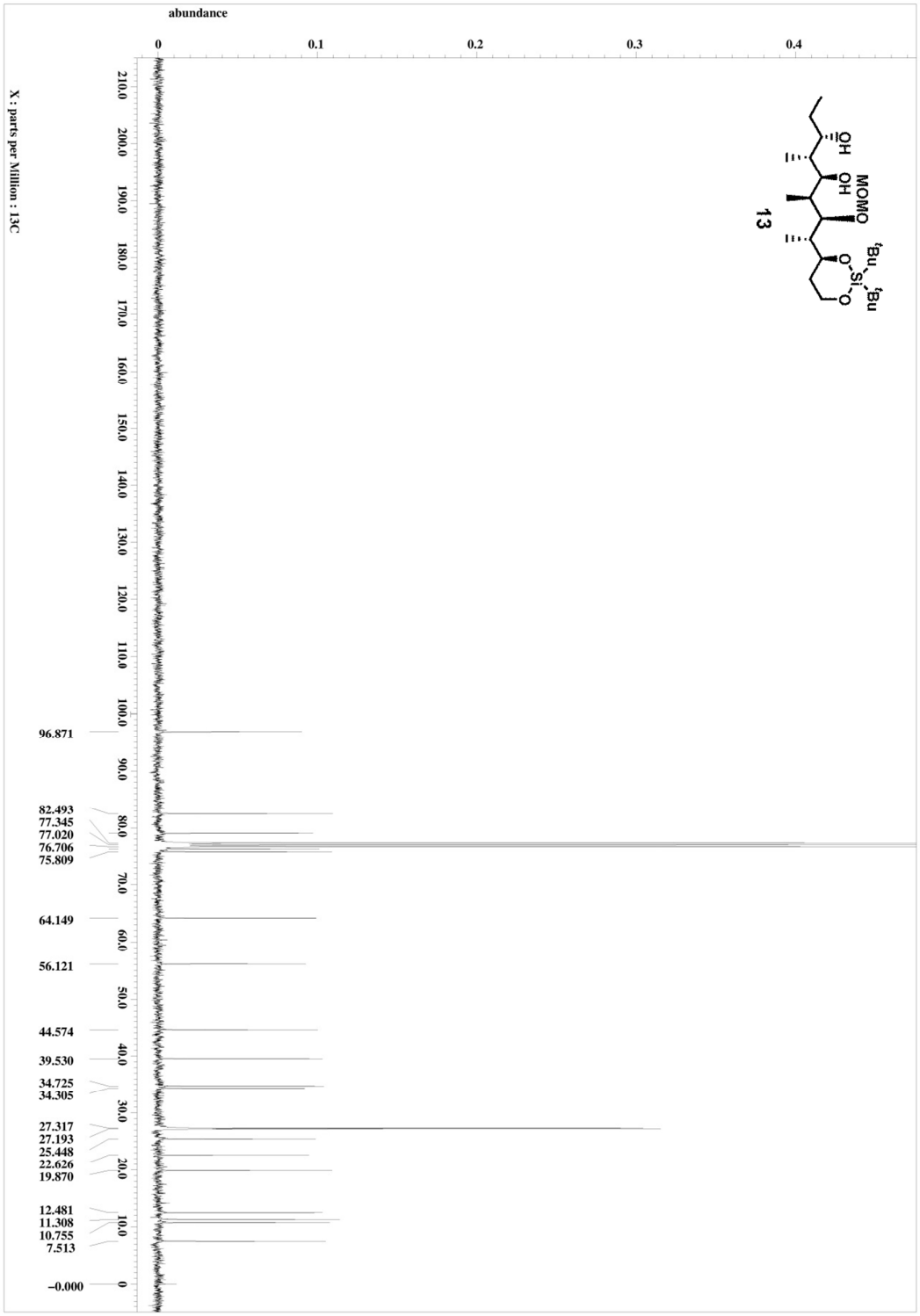
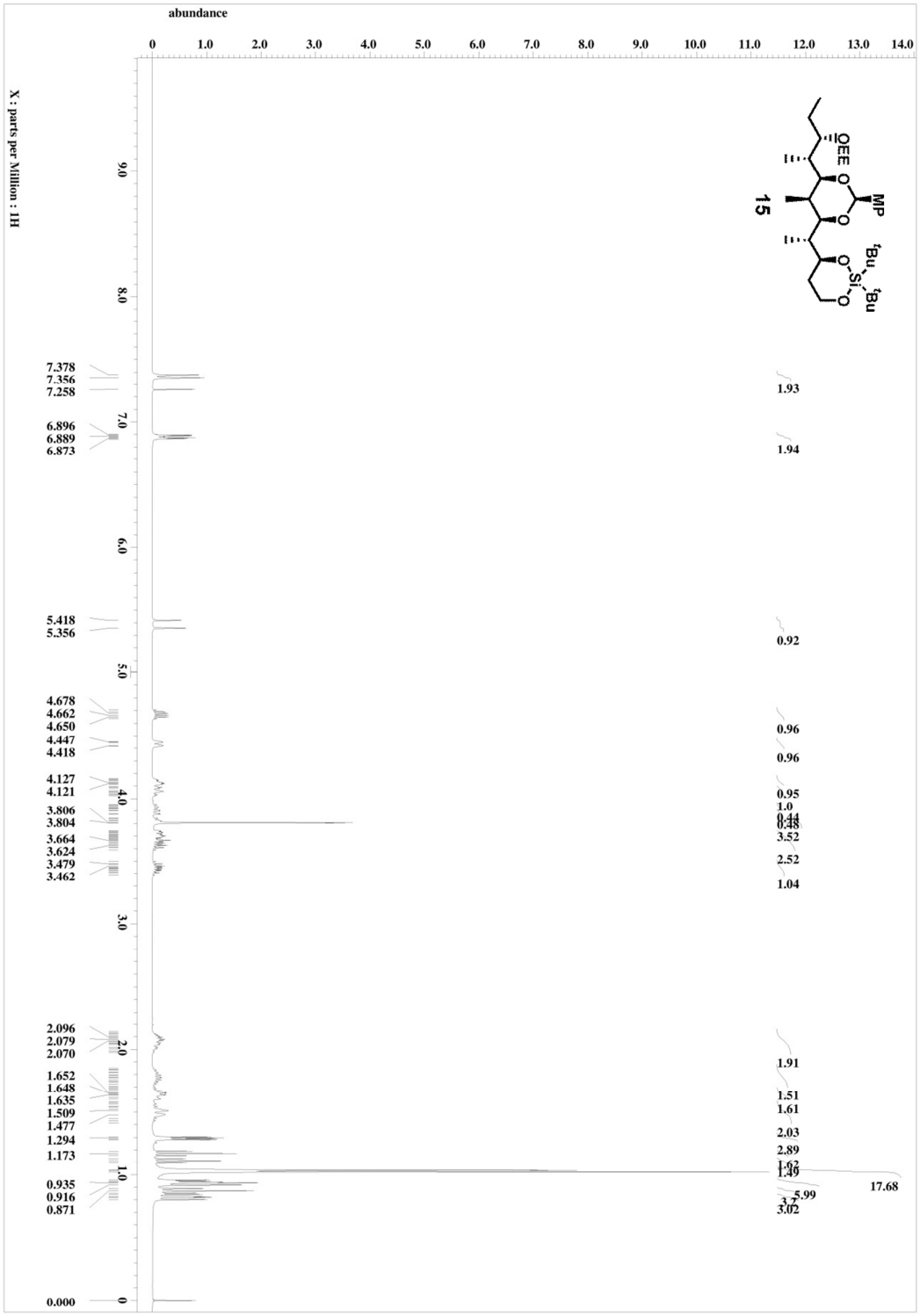

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
97.892
82.589
77.335
77.020
76.696
74.856
72.949
64.454
61.450
60.592
56.092
43.497
38.005
32.580
27.526
27.221
27.164
22.788
19.937
11.899
11.032
9.582
0.000
OH
O
MOMO
11
tBu
tBu
Si
O
O

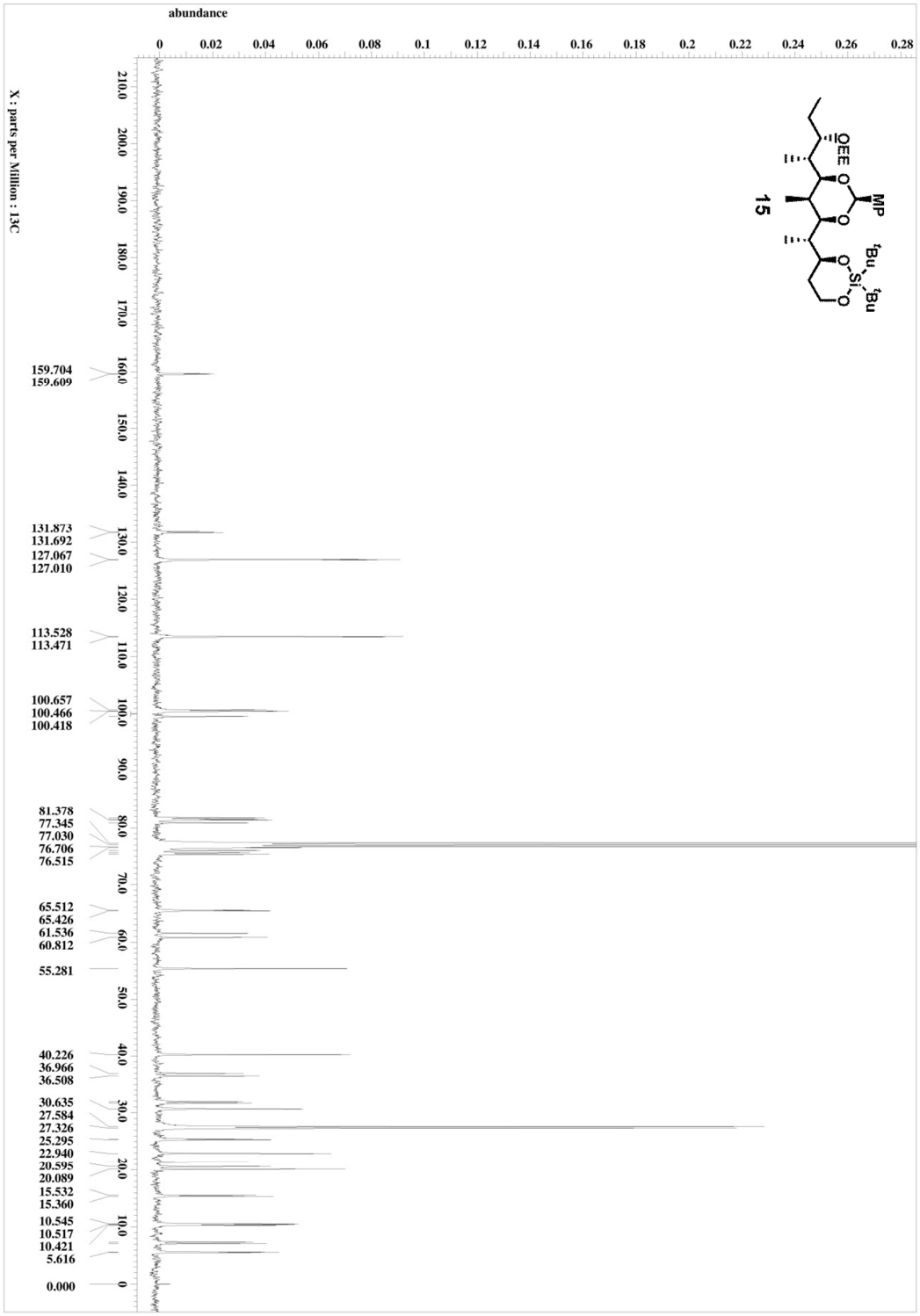

abundance
X : parts per Million : 1H
12
TMSO
MOMO
tBu
tBu
tBu
Si
O
7.261
4.661
4.639
4.622
4.120
4.113
4.107
4.079
3.663
3.656
3.647
3.390
2.800
2.789
2.784
2.080
2.064
2.047
1.718
1.713
1.575
1.559
1.541
1.522
1.037
1.029
1.006
0.951
0.090
−0.000
3.16
0.98
1.06
3
0.93
0.95
1.07
3.12
0.74
1.43
21.0
8.97

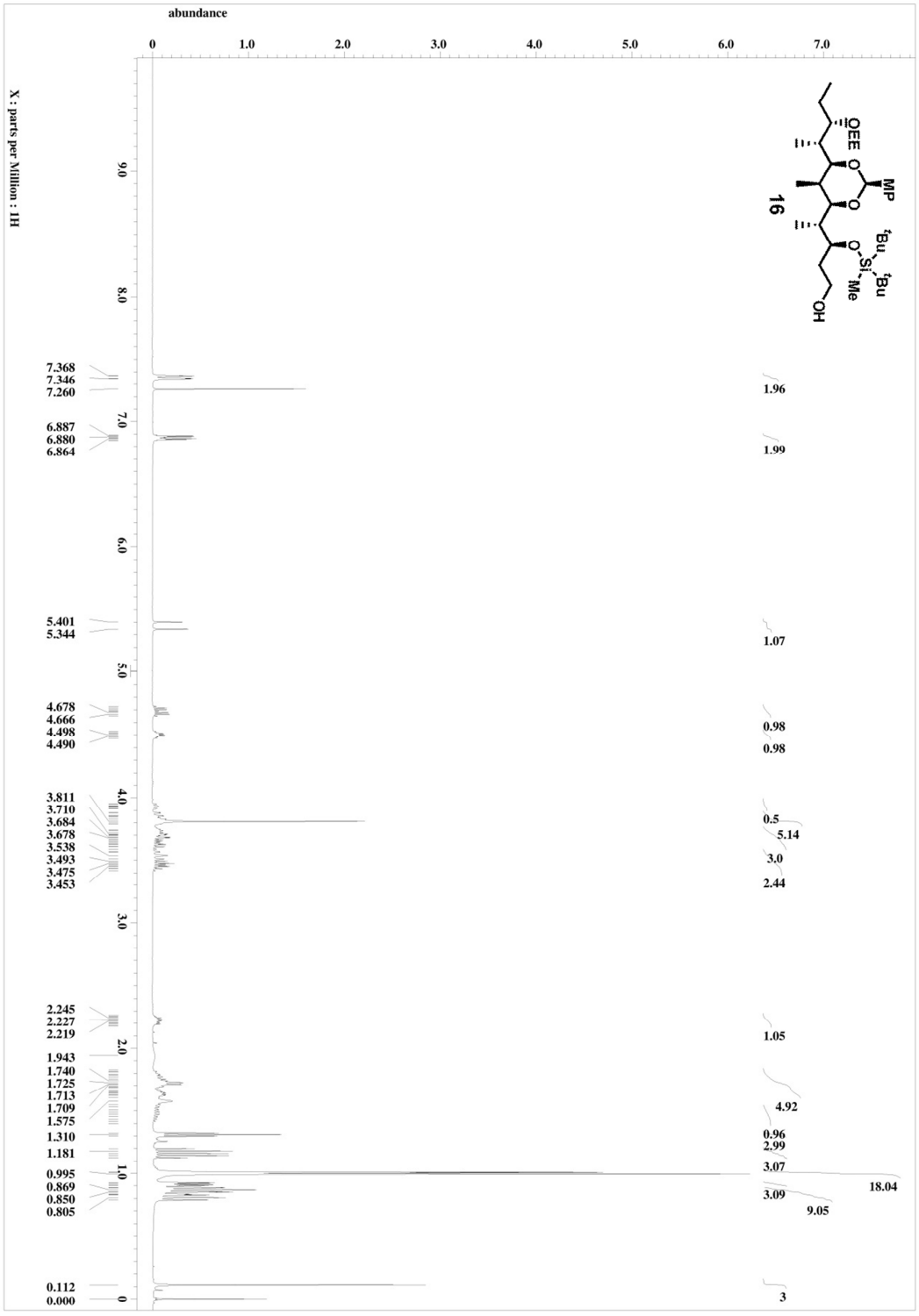

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
97.701
81.559
77.335
77.020
76.696
74.913
72.367
64.606
60.516
59.467
56.168
43.134
37.614
32.694
27.870
27.555
27.250
22.750
19.946
11.651
11.565
9.668
0.315
0.000
TMSO
MOMO
12
tBu
tBu
Si
O

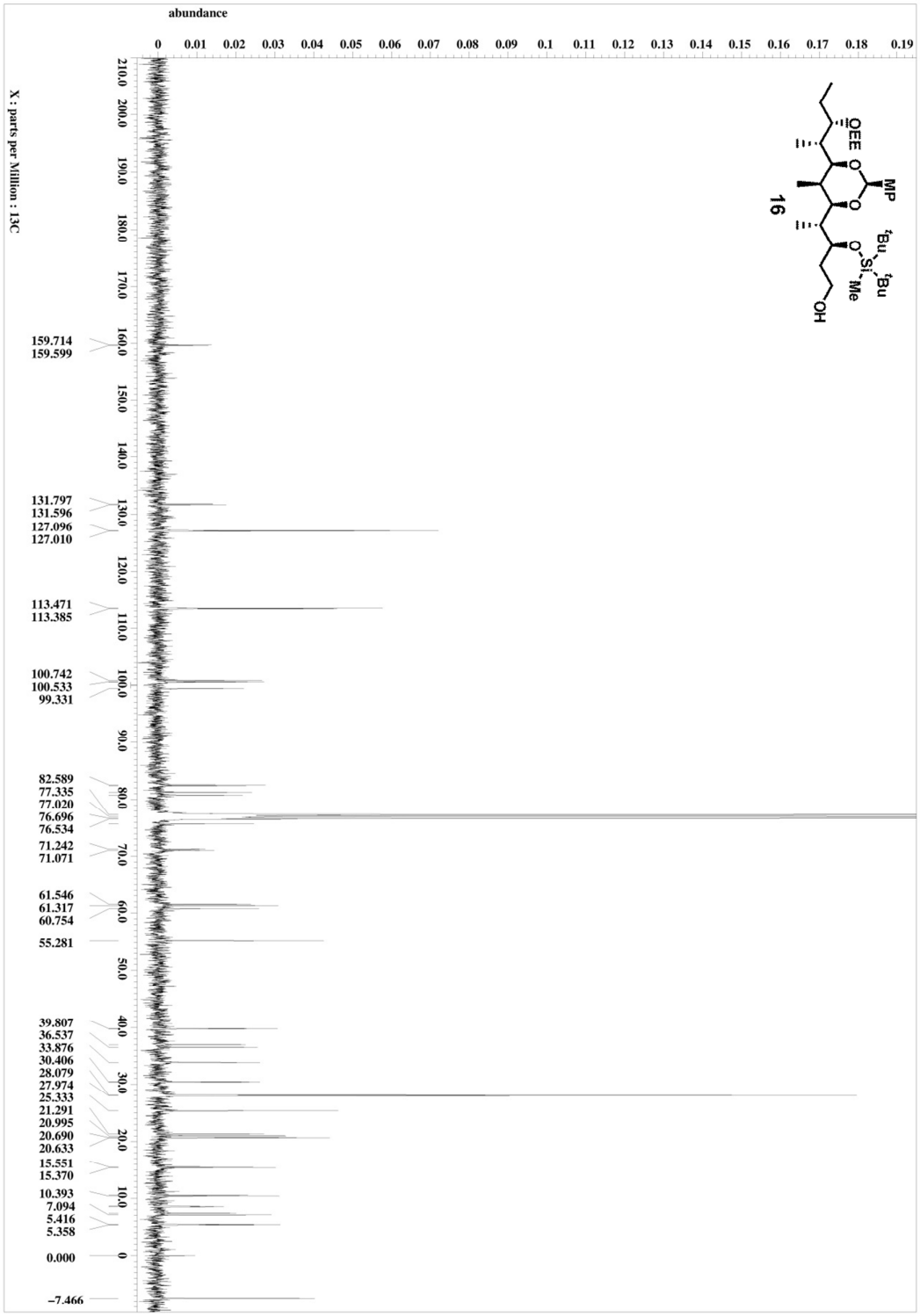

abundance
X : parts per Million : 1H
13
MOMO
OH
OH
tBu
tBu
Si
O
7.262
4.680
4.675
4.659
4.113
4.104
4.093
4.081
4.075
3.747
3.742
3.410
3.091
3.071
1.906
1.785
1.781
1.773
1.764
1.496
1.478
1.458
1.018
1.007
0.987
0.800
0.782
−0.000
1.0
1.0
3.11
1.03
1.03
0.91
1.06
3
0.87
1.02
2.07
2.02
2.14
24.62
3.0
2.98

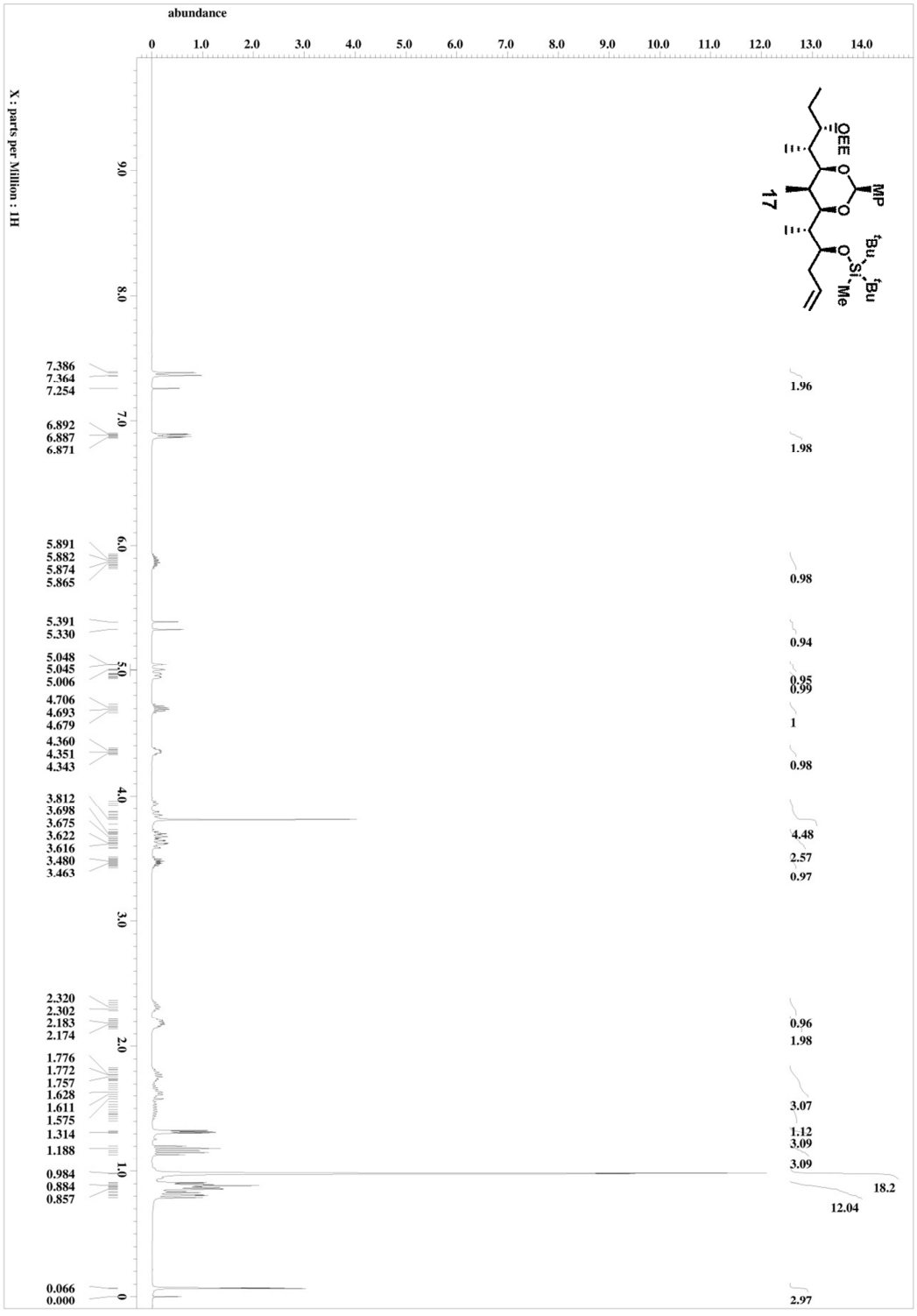

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
96.871
82.493
77.345
77.020
76.706
75.809
64.149
56.121
44.574
39.530
34.725
34.305
27.317
27.193
25.448
22.626
19.870
12.481
11.308
10.755
7.513
−0.000
MOMO
OH
OH
tBu
tBu
Si
O
O
13

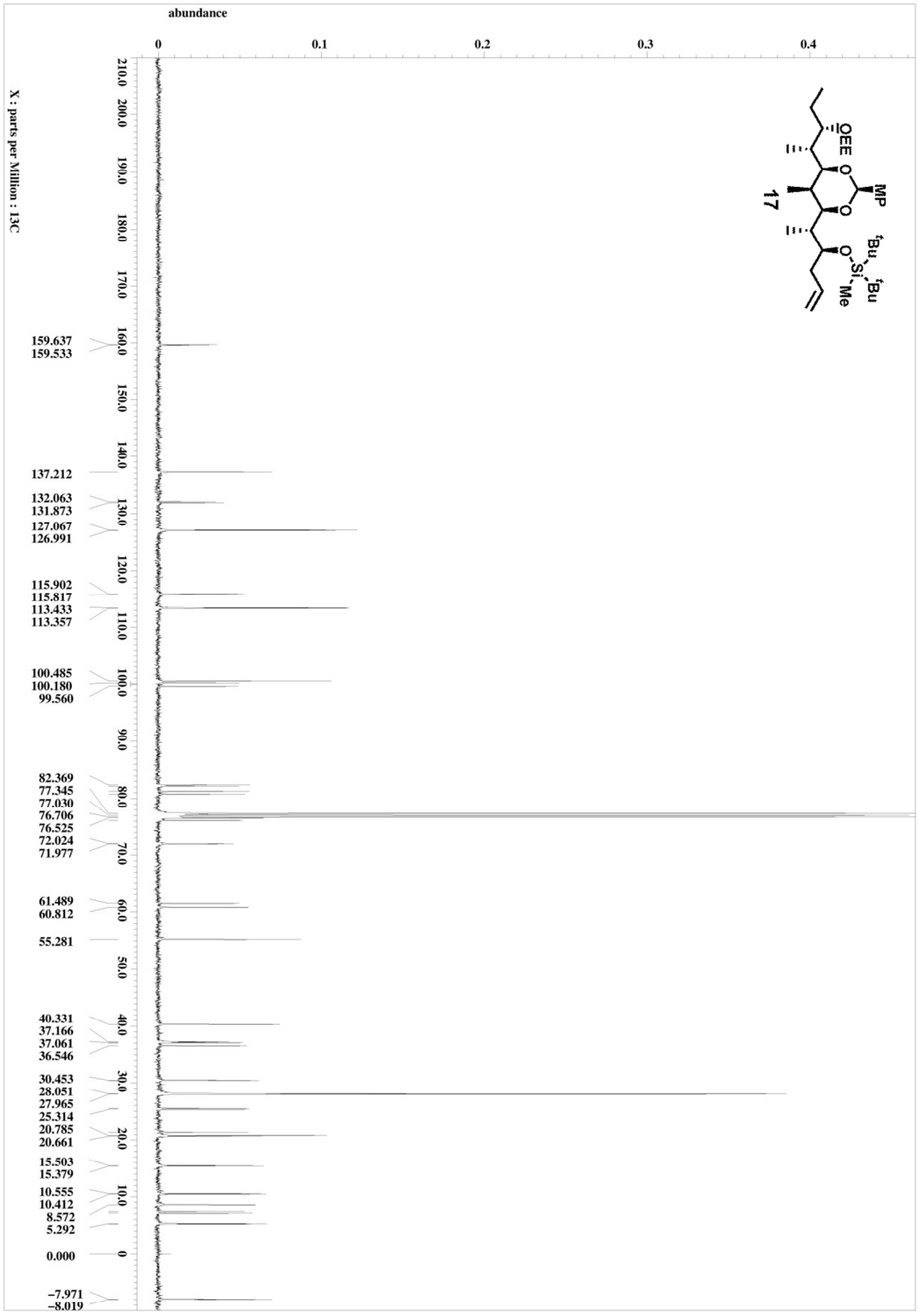

abundance
X : parts per Million : 1H
15
OEE
MP
tBu
tBu
Si
7.378
7.356
7.258
6.896
6.889
6.873
5.418
5.356
4.678
4.662
4.650
4.447
4.418
4.127
4.121
3.806
3.804
3.664
3.624
3.479
3.462
2.096
2.079
2.070
1.652
1.648
1.635
1.509
1.477
1.294
1.173
0.935
0.916
0.871
0.000
1.93
1.94
0.92
0.96
0.96
0.95
1.0
0.44
0.48
3.52
2.52
1.04
1.91
1.51
1.61
2.03
2.89
1.62
1.49
17.68
5.99
3.02

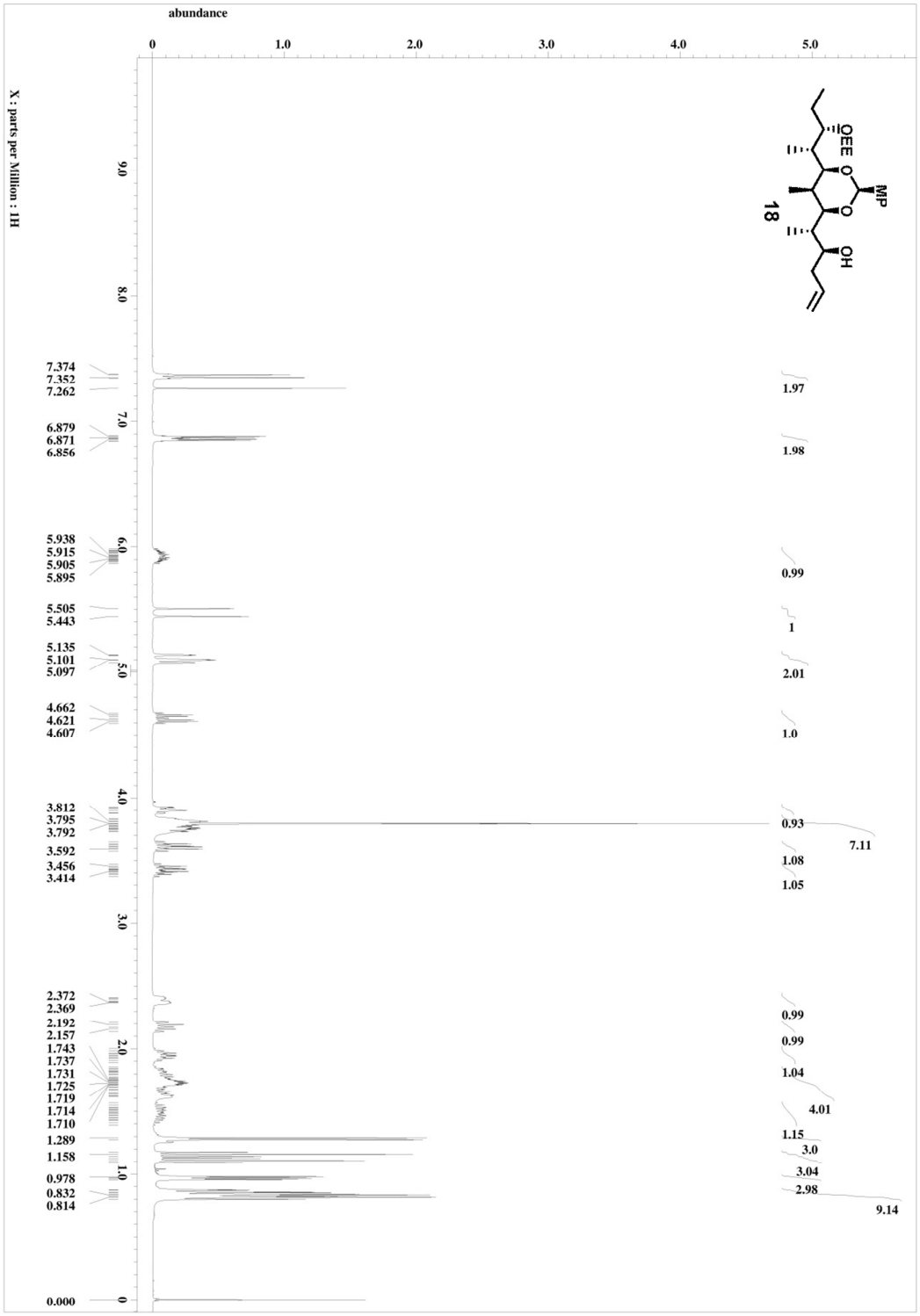

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
0.26
0.28
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.704
159.609
131.873
131.692
127.067
127.010
113.528
113.471
100.657
100.466
100.418
81.378
77.345
77.030
76.706
76.515
65.512
65.426
61.536
60.812
55.281
40.226
36.966
36.508
30.635
27.584
27.326
25.295
22.940
20.595
20.089
15.532
15.360
10.545
10.517
10.421
5.616
0.000
OEE
MP
tBu
tBu
Si
O
O
O
O
O
15

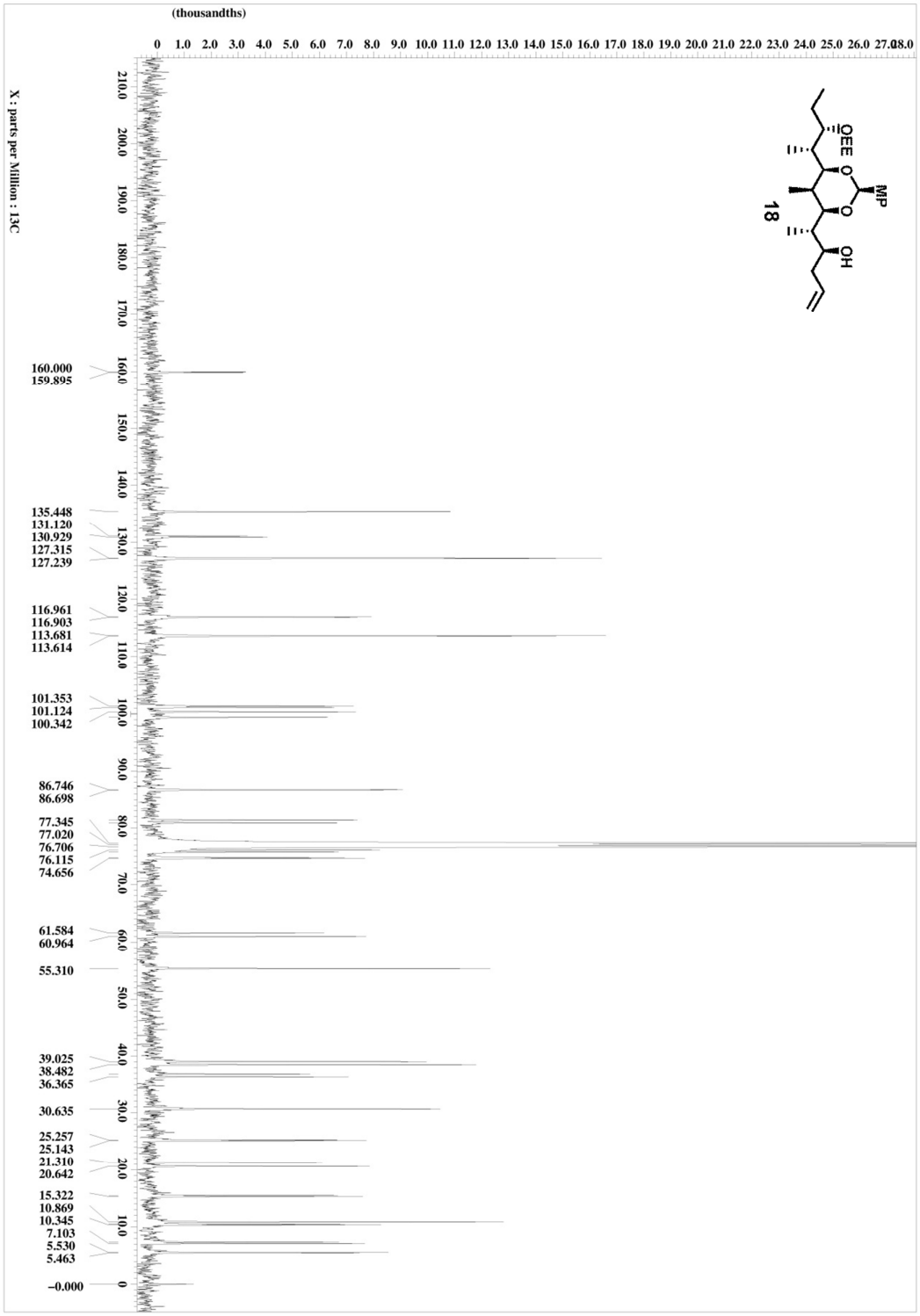

abundance
X : parts per Million : 1H
16
MP
OEE
tBu
tBu
Si
Me
OH
7.368
7.346
7.260
6.887
6.880
6.864
5.401
5.344
4.678
4.666
4.498
4.490
3.811
3.710
3.684
3.678
3.538
3.493
3.475
3.453
2.245
2.227
2.219
1.943
1.740
1.725
1.713
1.709
1.575
1.310
1.181
0.995
0.869
0.850
0.805
0.112
0.000
1.96
1.99
1.07
0.98
0.98
0.5
5.14
3.0
2.44
1.05
4.92
0.96
2.99
3.07
18.04
3.09
9.05
3

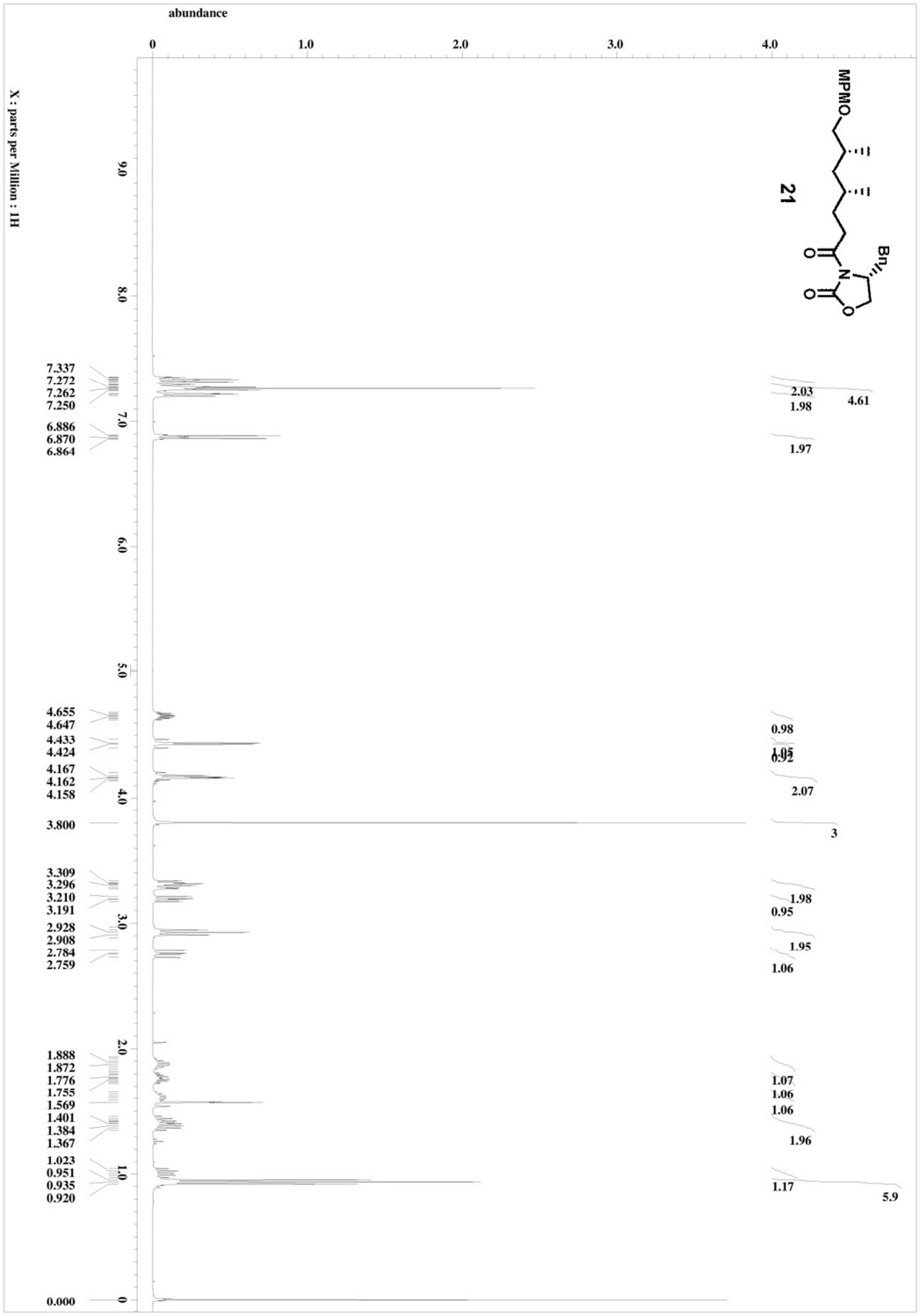

abundance
0 0.01 0.02 0.03 0.04 0.05 0.06 0.07 0.08 0.09 0.1 0.11 0.12 0.13 0.14 0.15 0.16 0.17 0.18 0.19
X : parts per Million : 13C
210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0
159.714
159.599
131.797
131.596
127.096
127.010
113.471
113.385
100.742
100.533
99.331
82.589
77.335
77.020
76.696
76.534
71.242
71.071
61.546
61.317
60.754
55.281
39.807
36.537
33.876
30.406
28.079
27.974
25.333
21.291
20.995
20.690
20.633
15.551
15.370
10.393
7.094
5.416
5.358
0.000
−7.466
16
OEE
MP
tBu
tBu
Si
Me
OH

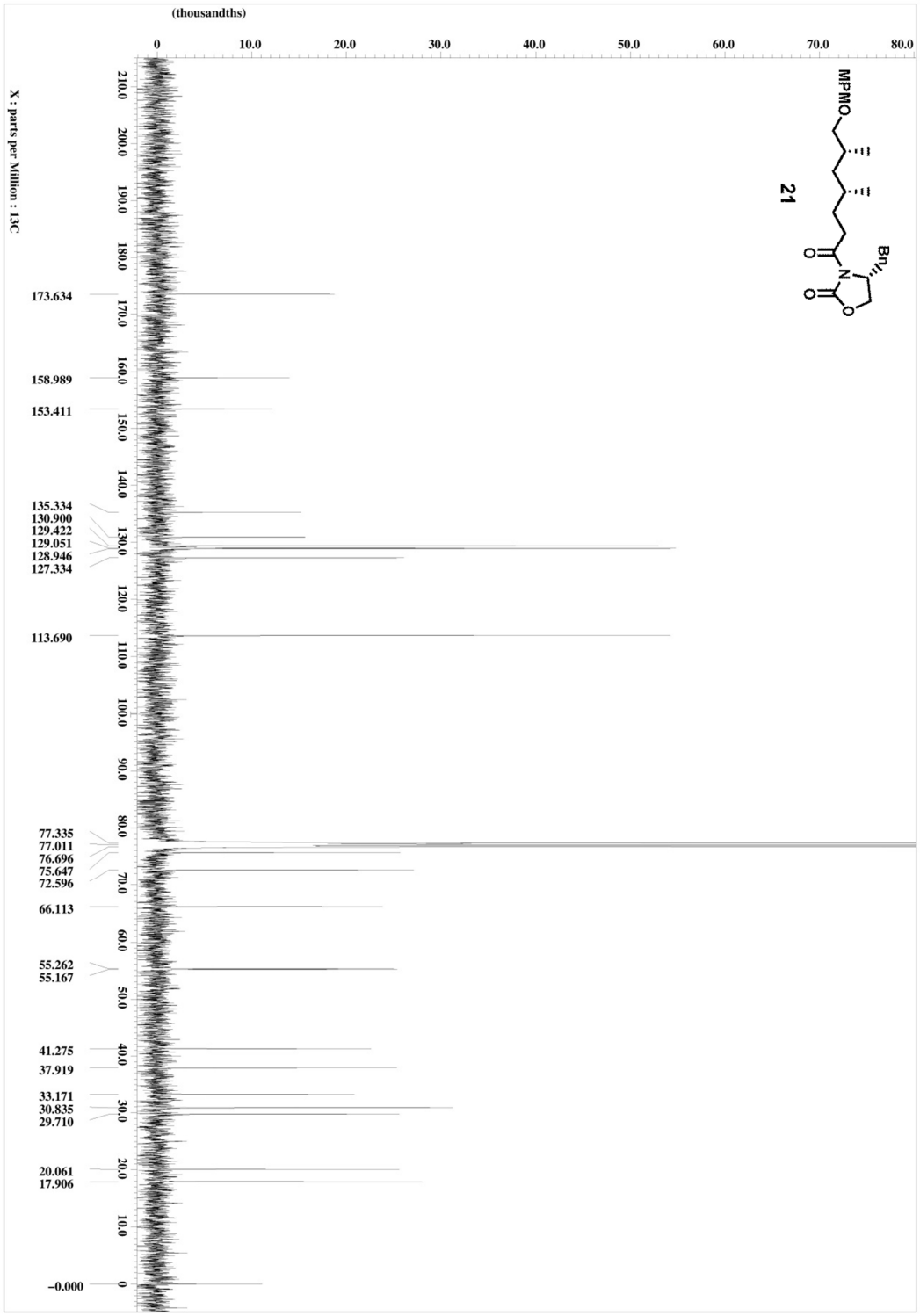

abundance
X : parts per Million : 1H
17
MP
OEE
tBu
tBu
Si
Me
7.386
7.364
7.254
6.892
6.887
6.871
5.891
5.882
5.874
5.865
5.391
5.330
5.048
5.045
5.006
4.706
4.693
4.679
4.360
4.351
4.343
3.812
3.698
3.675
3.622
3.616
3.480
3.463
2.320
2.302
2.183
2.174
1.776
1.772
1.757
1.628
1.611
1.575
1.314
1.188
0.984
0.884
0.857
0.066
0.000
1.96
1.98
0.98
0.94
0.95
0.99
1
0.98
4.48
2.57
0.97
0.96
1.98
3.07
1.12
3.09
3.09
18.2
12.04
2.97

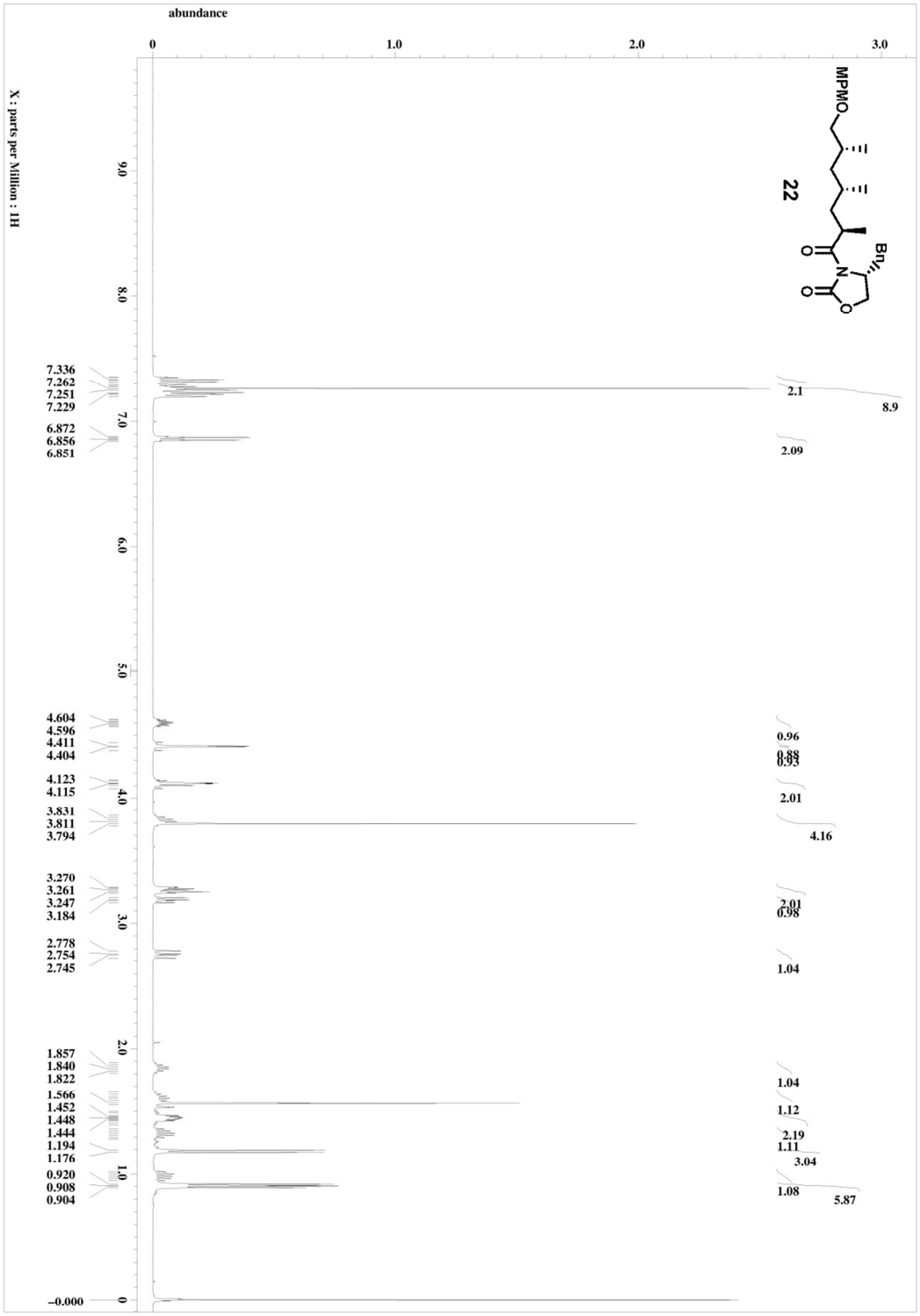

abundance
0
0.1
0.2
0.3
0.4
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
159.637
159.533
137.212
132.063
131.873
127.067
126.991
115.902
115.817
113.433
113.357
100.485
100.180
99.560
82.369
77.345
77.030
76.706
76.525
72.024
71.977
61.489
60.812
55.281
40.331
37.166
37.061
36.546
30.453
28.051
27.965
25.314
20.785
20.661
15.503
15.379
10.555
10.412
8.572
5.292
0.000
−7.971
−8.019
17
MP
OEE
tBu
tBu
Si
Me

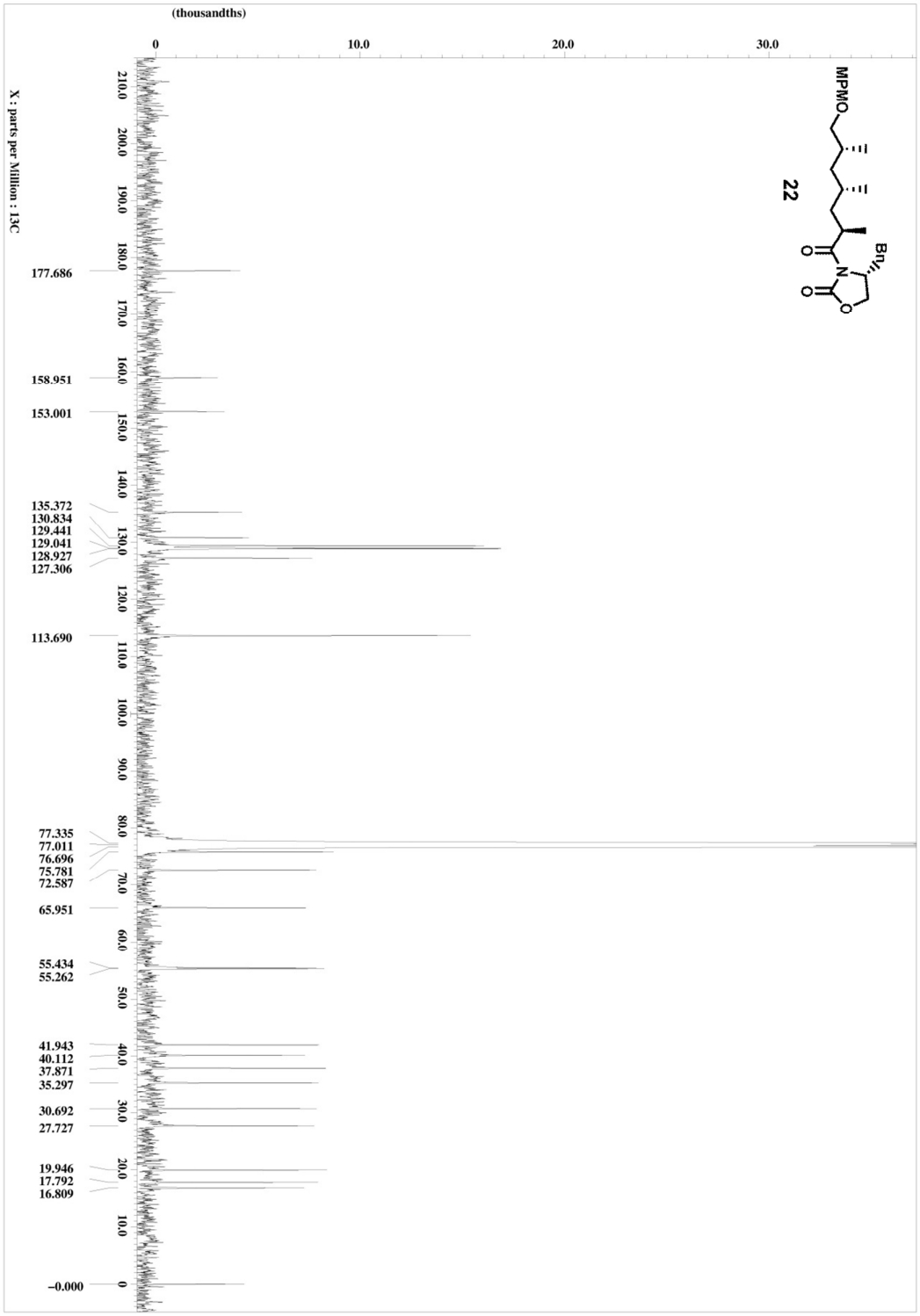

abundance
X : parts per Million : 1H
18
OEE
MP
OH
7.374
7.352
7.262
6.879
6.871
6.856
5.938
5.915
5.905
5.895
5.505
5.443
5.135
5.101
5.097
4.662
4.621
4.607
3.812
3.795
3.792
3.592
3.456
3.414
2.372
2.369
2.192
2.157
1.743
1.737
1.731
1.725
1.719
1.714
1.710
1.289
1.158
0.978
0.832
0.814
0.000
1.97
1.98
0.99
1
2.01
1.0
0.93
7.11
1.08
1.05
0.99
0.99
1.04
4.01
1.15
3.0
3.04
2.98
9.14

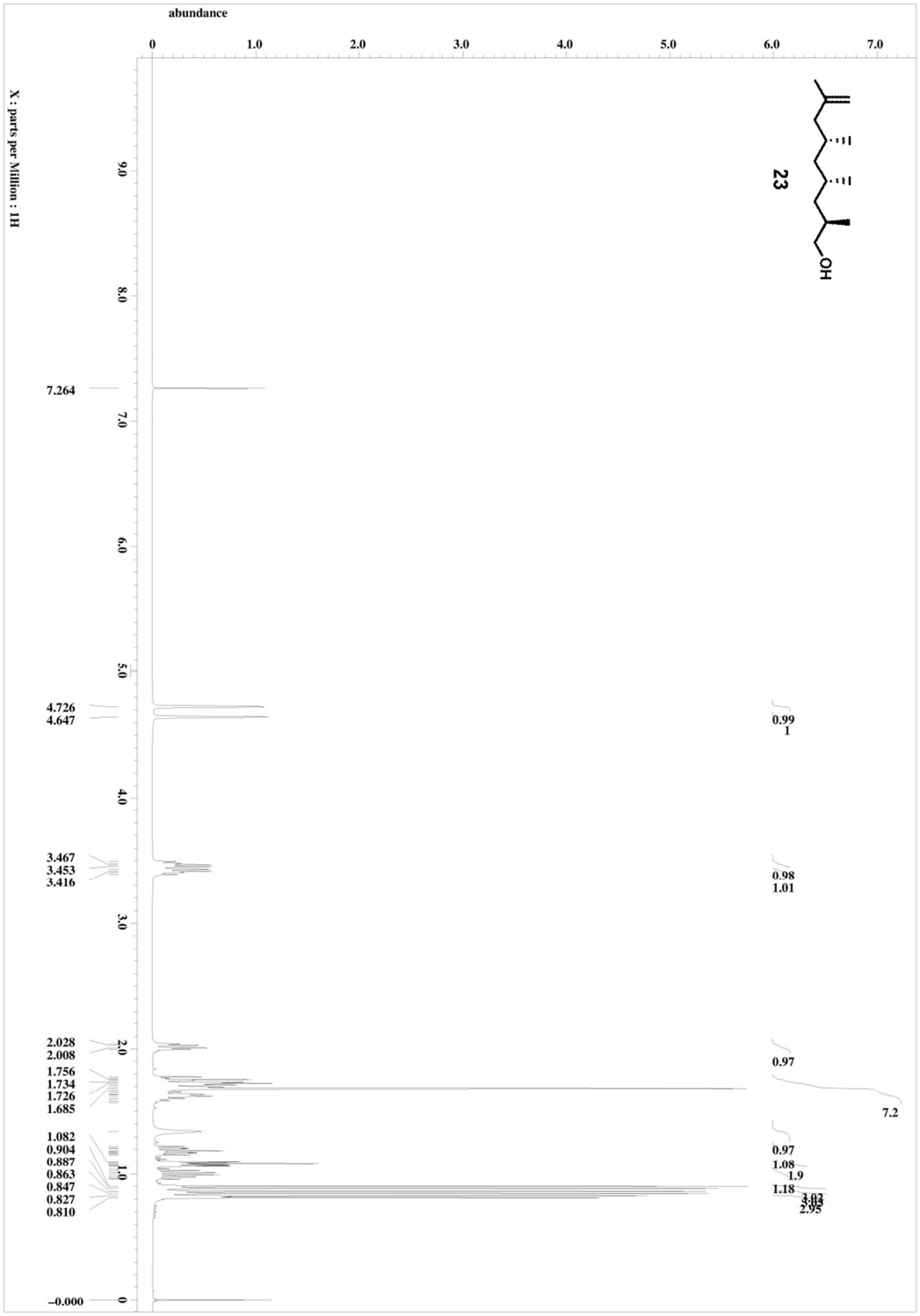

(thousandths)
X : parts per Million : 13C
160.000
159.895
135.448
131.120
130.929
127.315
127.239
116.961
116.903
113.681
113.614
101.353
101.124
100.342
86.746
86.698
77.345
77.020
76.706
76.115
74.656
61.584
60.964
55.310
39.025
38.482
36.365
30.635
25.257
25.143
21.310
20.642
15.322
10.869
10.345
7.103
5.530
5.463
-0.000
OEE
MP
OH
18

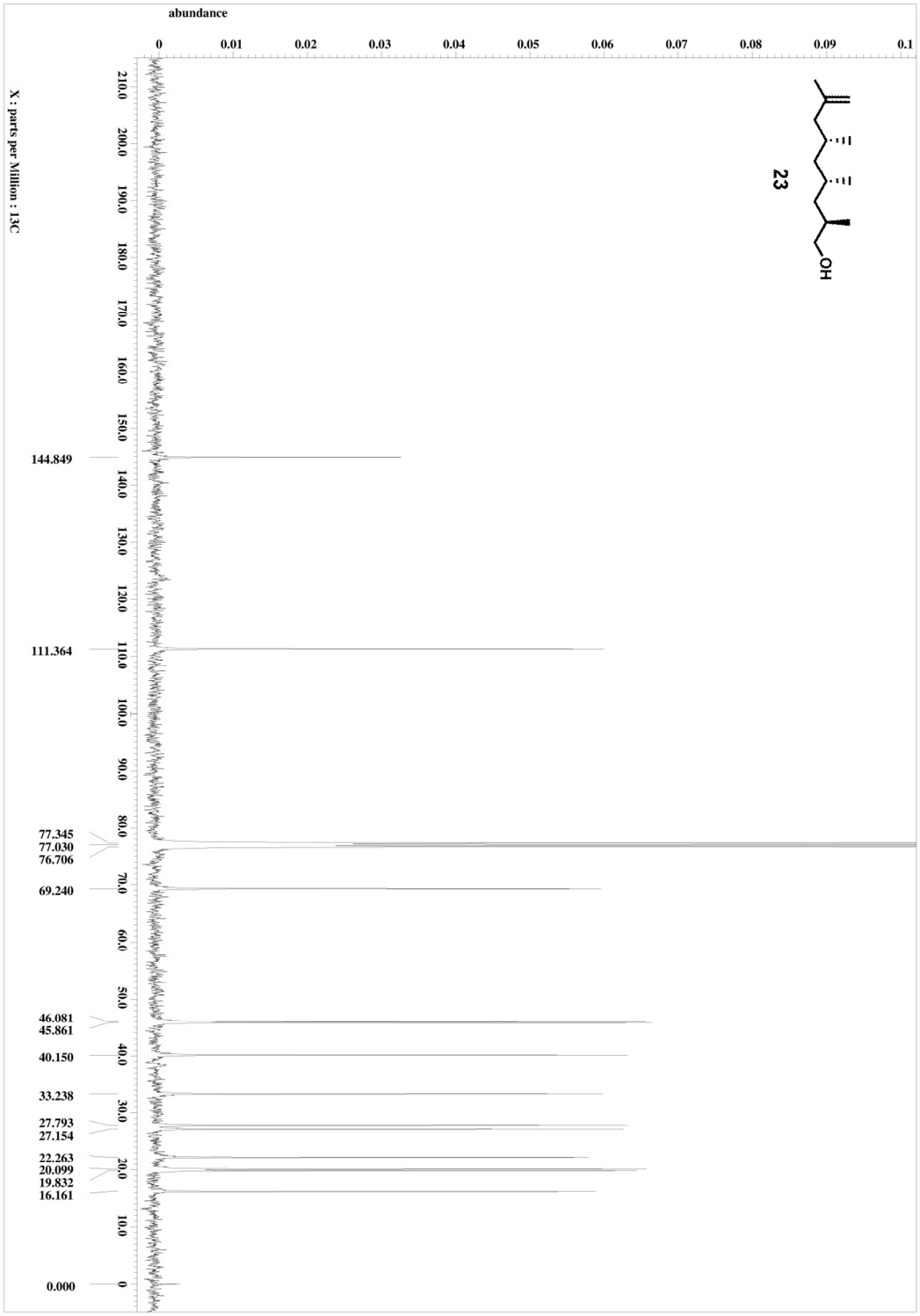

abundance
X : parts per Million : 1H
MPMO
21
Bn
7.337
7.272
7.262
7.250
6.886
6.870
6.864
4.655
4.647
4.433
4.424
4.167
4.162
4.158
3.800
3.309
3.296
3.210
3.191
2.928
2.908
2.784
2.759
1.888
1.872
1.776
1.755
1.569
1.401
1.384
1.367
1.023
0.951
0.935
0.920
0.000
2.03
1.98
4.61
1.97
0.98
0.92
2.07
3
1.98
0.95
1.95
1.06
1.07
1.06
1.06
1.96
1.17
5.9

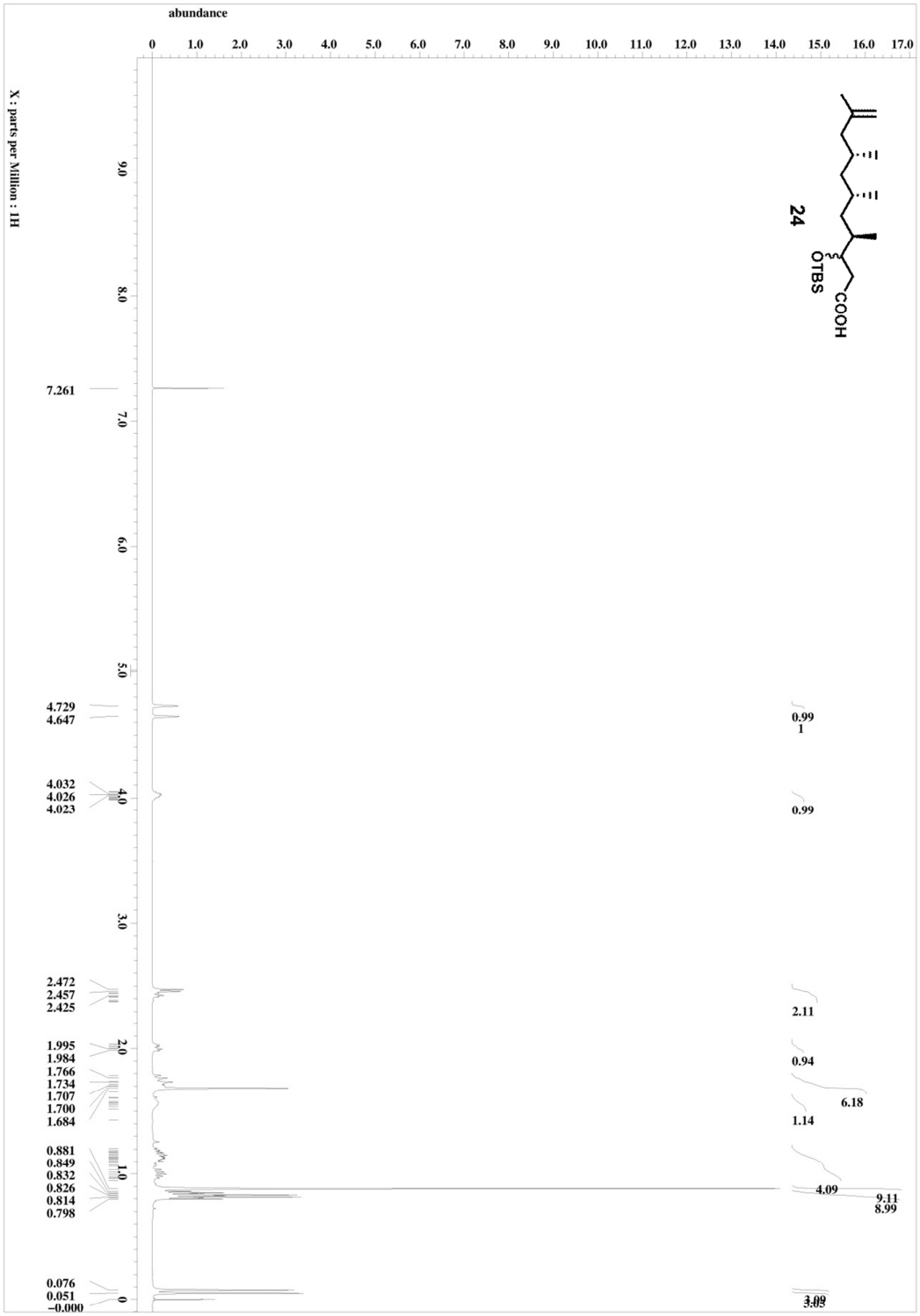

(thousandths)
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
173.634
158.989
153.411
135.334
130.900
129.422
129.051
128.946
127.334
113.690
77.335
77.011
76.696
75.647
72.596
66.113
55.262
55.167
41.275
37.919
33.171
30.835
29.710
20.061
17.906
−0.000
MPMO
Bn
N
O
O
O
21

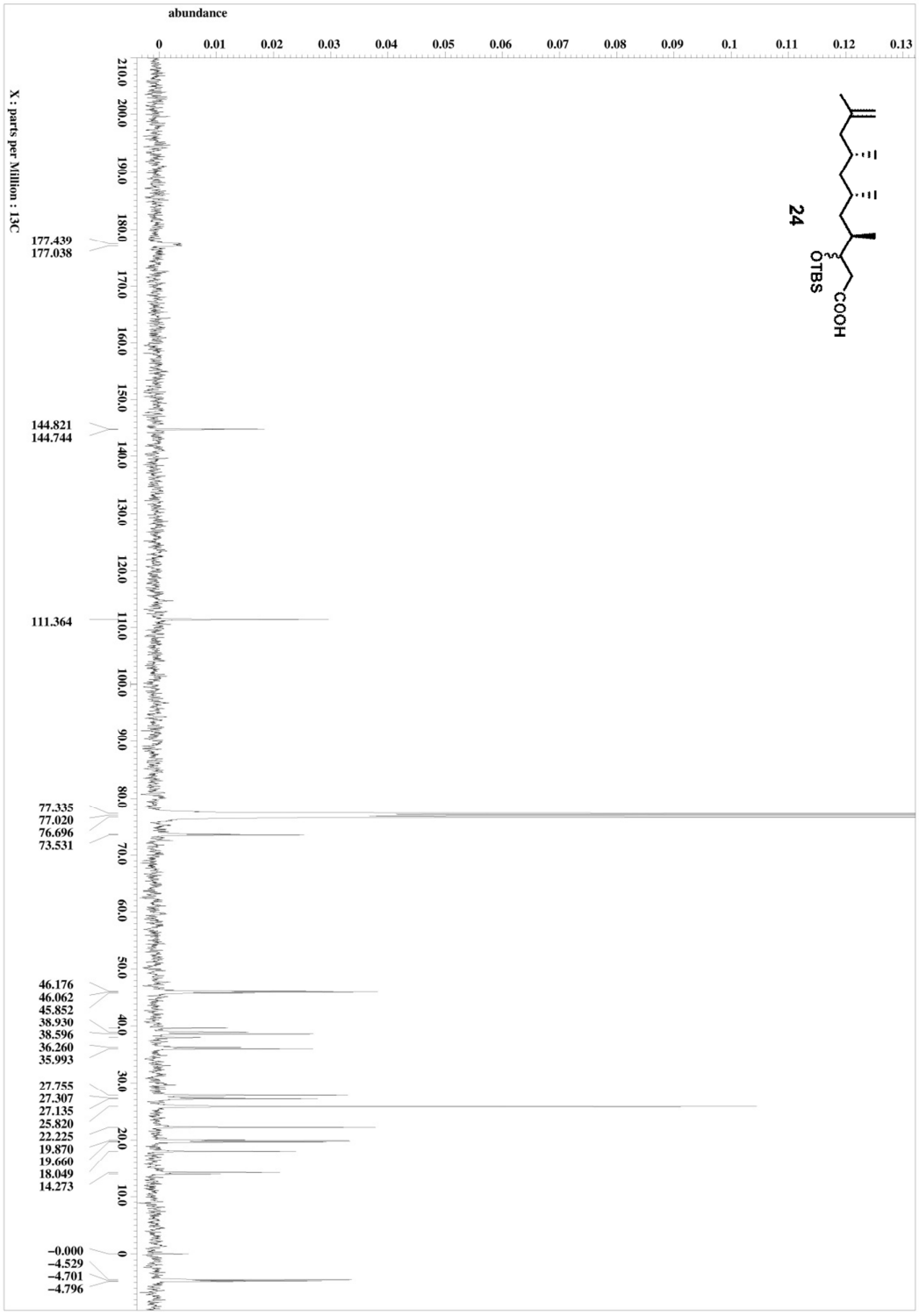

abundance
X : parts per Million : 1H
MPMO
22
Bn
7.336
7.262
7.251
7.229
6.872
6.856
6.851
4.604
4.596
4.411
4.404
4.123
4.115
3.831
3.811
3.794
3.270
3.261
3.247
3.184
2.778
2.754
2.745
1.857
1.840
1.822
1.566
1.452
1.448
1.444
1.194
1.176
0.920
0.908
0.904
−0.000
2.1
8.9
2.09
0.96
0.88
0.93
2.01
4.16
2.01
0.98
1.04
1.04
1.12
2.19
1.11
3.04
1.08
5.87

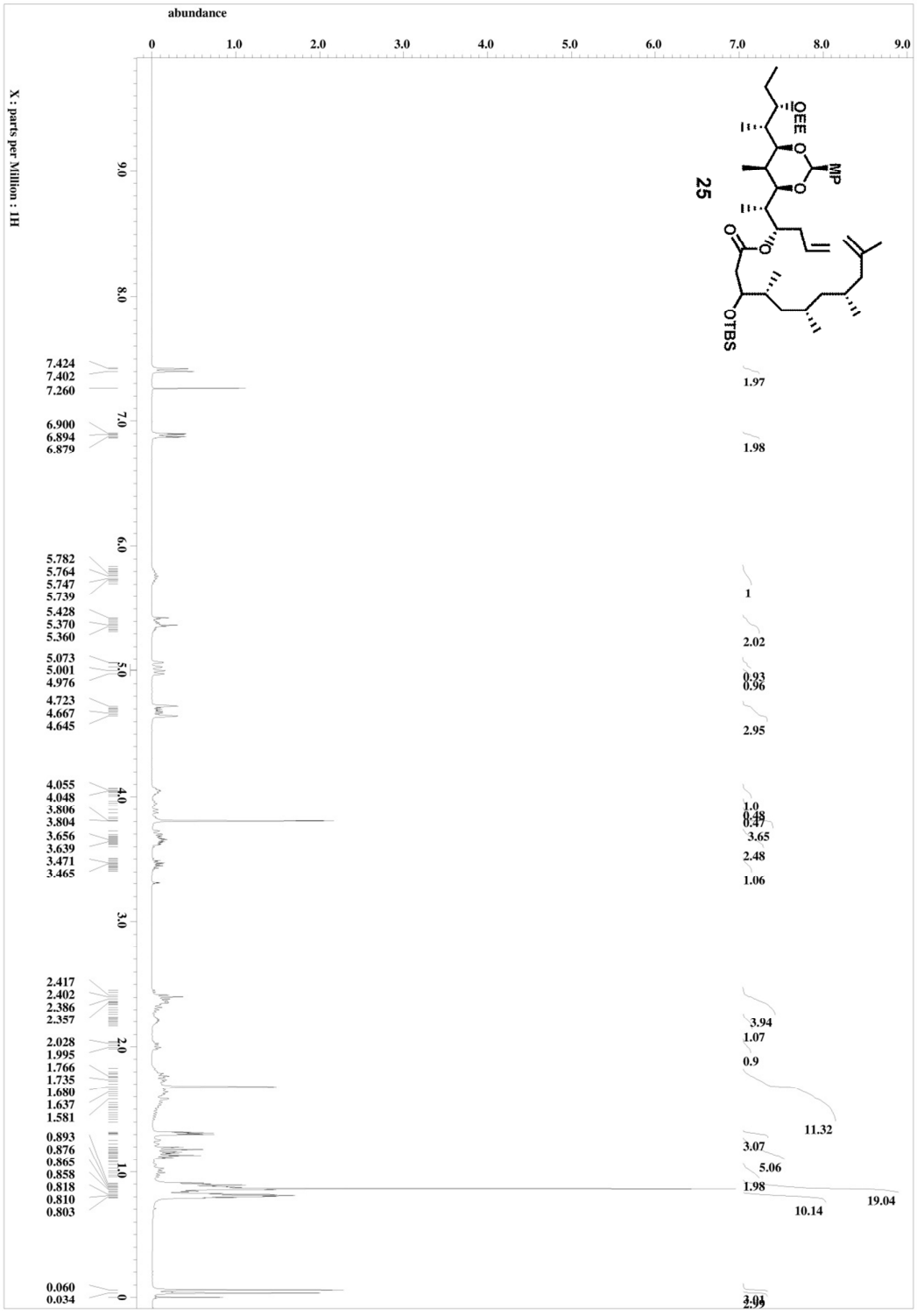

(thousandths)
0
10.0
20.0
30.0
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
177.686
158.951
153.001
135.372
130.834
129.441
129.041
128.927
127.306
113.690
77.335
77.011
76.696
75.781
72.587
65.951
55.434
55.262
41.943
40.112
37.871
35.297
30.692
27.727
19.946
17.792
16.809
−0.000
MPMO
22
Bn
N
O
O
O

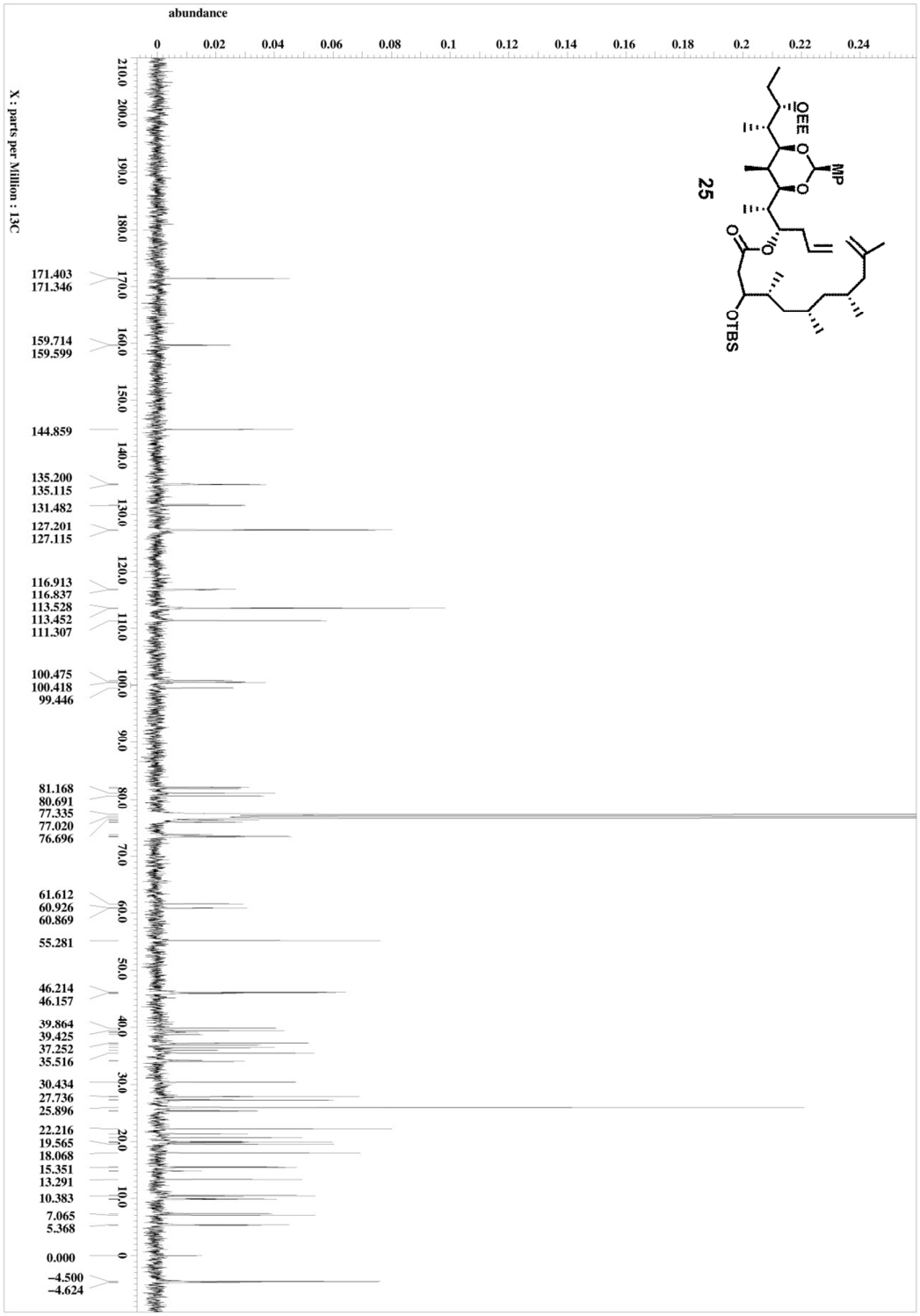

abundance
X : parts per Million : 1H
23
OH
7.264
4.726
4.647
3.467
3.453
3.416
2.028
2.008
1.756
1.734
1.726
1.685
1.082
0.904
0.887
0.863
0.847
0.827
0.810
−0.000
0.99
1
0.98
1.01
0.97
7.2
0.97
1.08
1.9
1.18
3.03
2.95

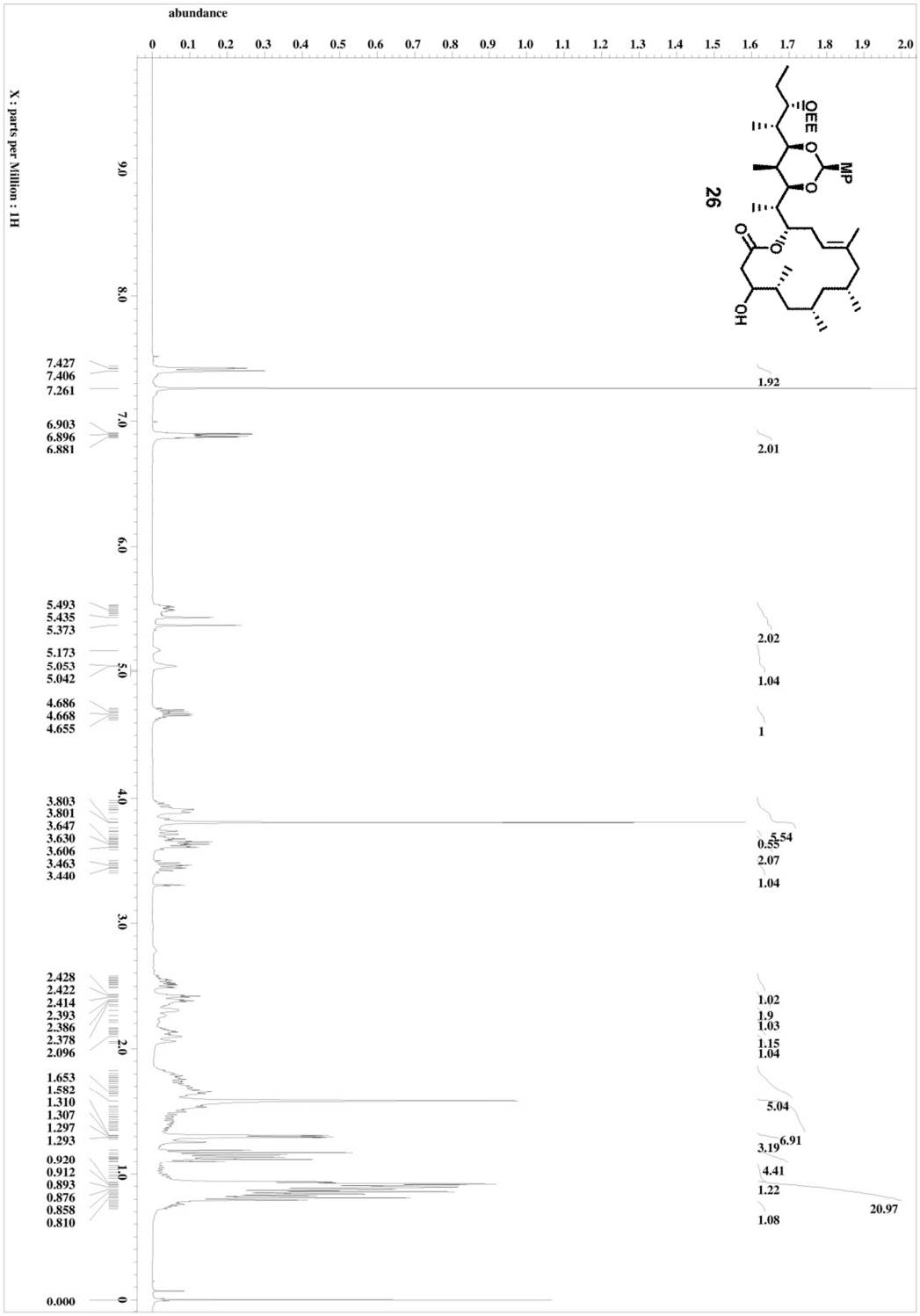

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
144.849
111.364
77.345
77.030
76.706
69.240
46.081
45.861
40.150
33.238
27.793
27.154
22.263
20.099
19.832
16.161
0.000
23
OH

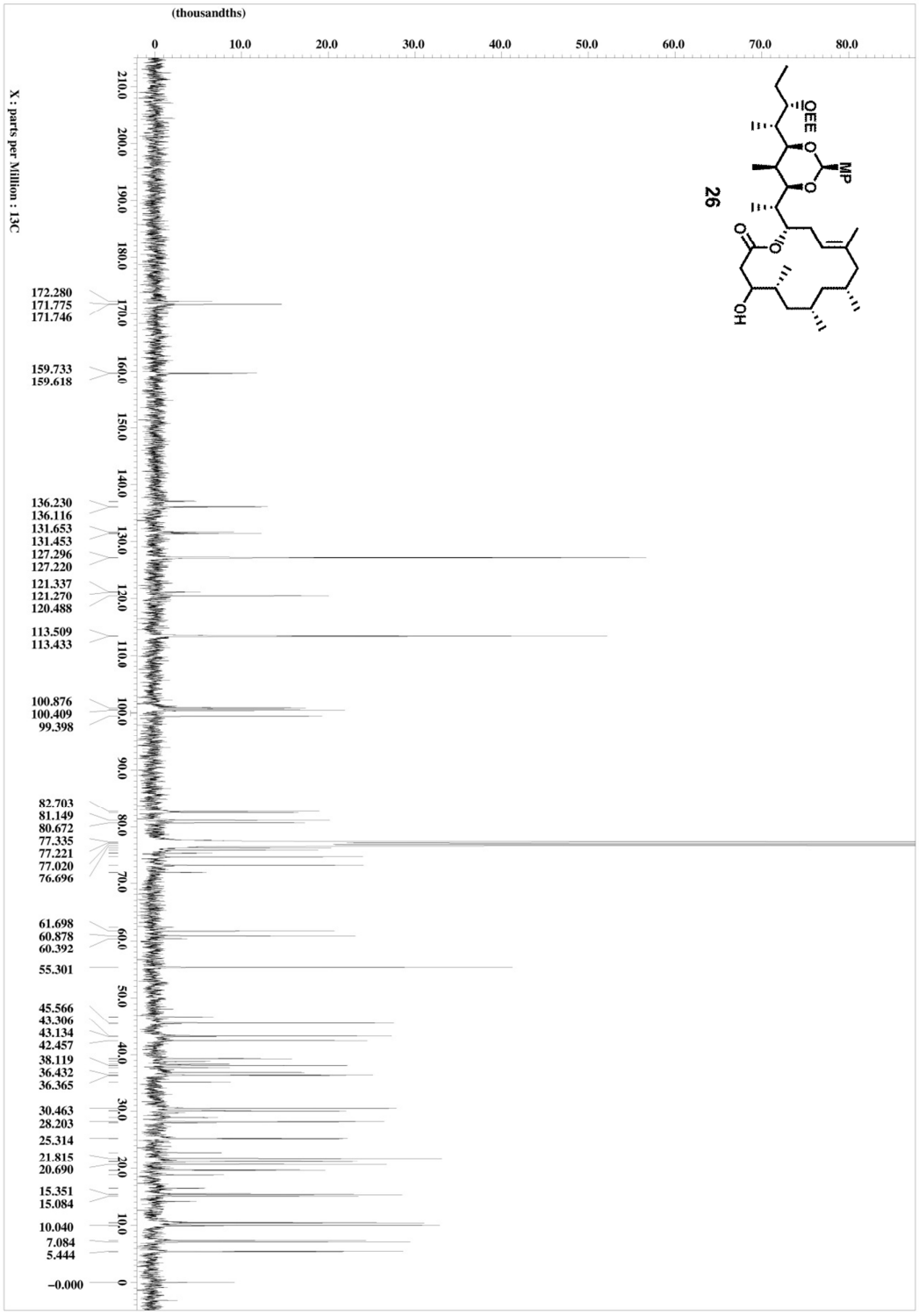

abundance
X : parts per Million : 1H
24
OTBS
COOH
7.261
4.729
4.647
4.032
4.026
4.023
2.472
2.457
2.425
1.995
1.984
1.766
1.734
1.707
1.700
1.684
0.881
0.849
0.832
0.826
0.814
0.798
0.076
0.051
−0.000
0.99
1
0.99
2.11
0.94
6.18
1.14
4.09
9.11
8.99
3.09
3.05

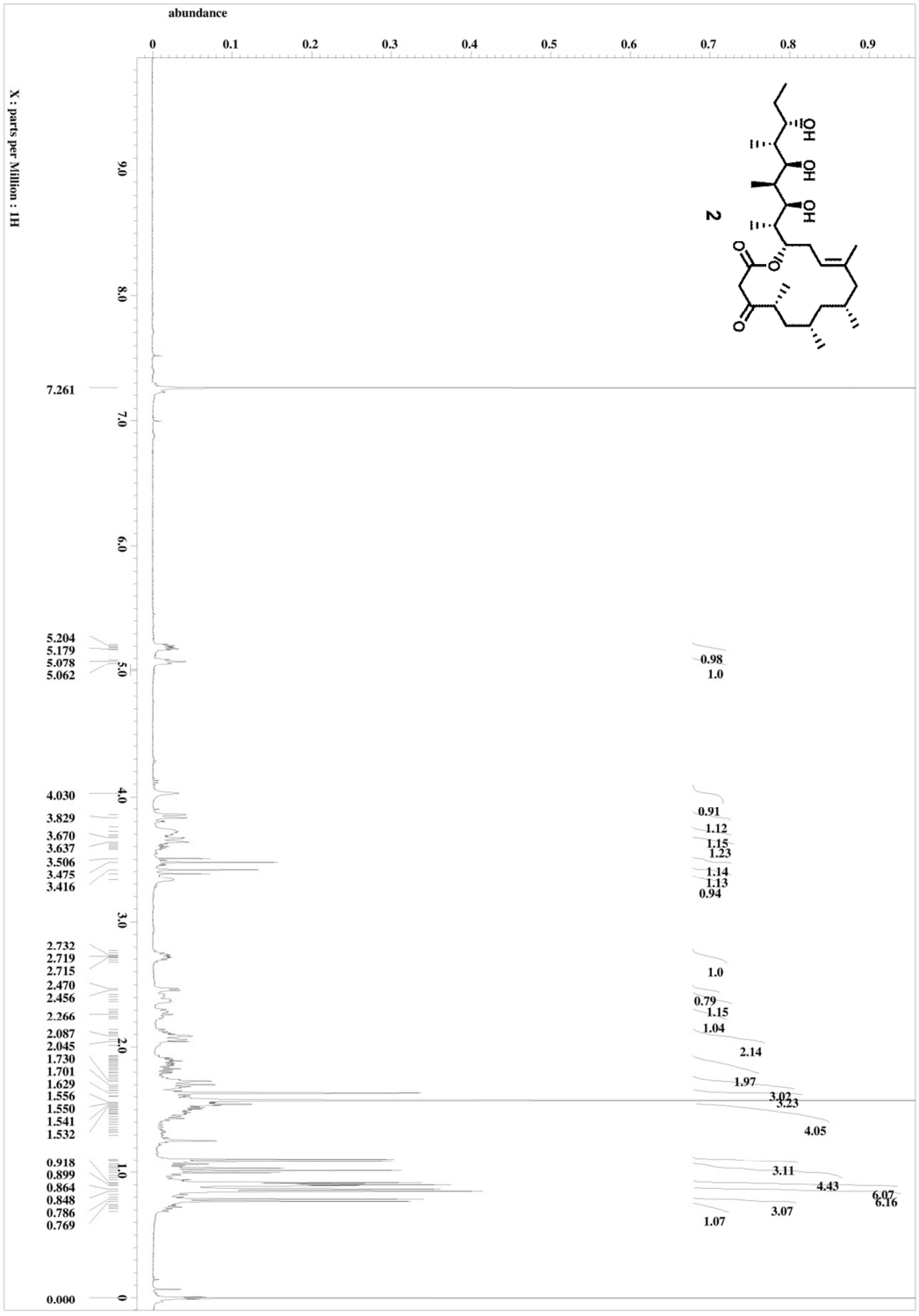

abundance
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
0.08
0.09
0.1
0.11
0.12
0.13
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
177.439
177.038
144.821
144.744
111.364
77.335
77.020
76.696
73.531
46.176
46.062
45.852
38.930
38.596
36.260
35.993
27.755
27.307
27.135
25.820
22.225
19.870
19.660
18.049
14.273
−0.000
−4.529
−4.701
−4.796
24
OTBS
COOH

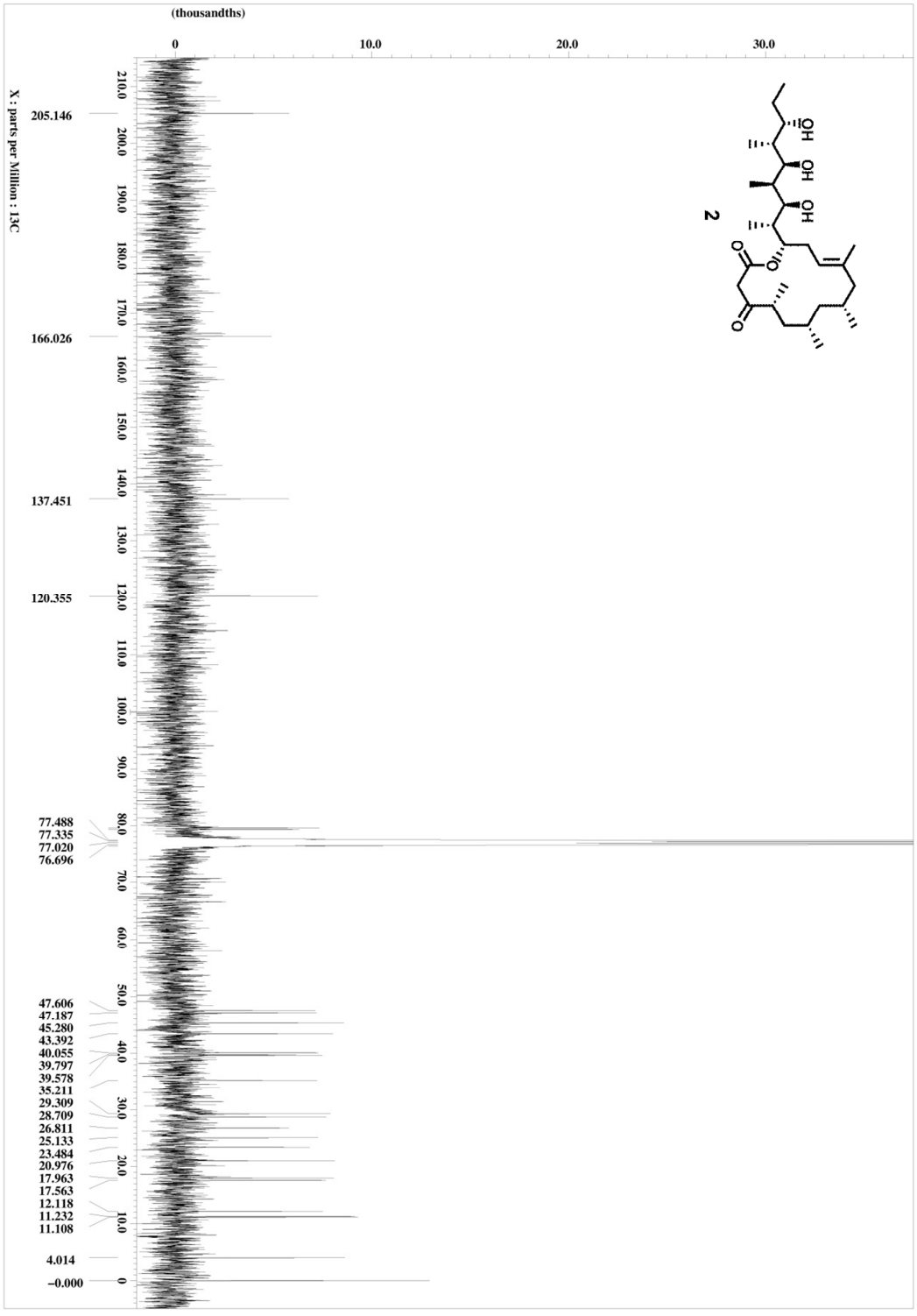

abundance
X : parts per Million : 1H
25
OEE
MP
OTBS
7.424
7.402
7.260
6.900
6.894
6.879
5.782
5.764
5.747
5.739
5.428
5.370
5.360
5.073
5.001
4.976
4.723
4.667
4.645
4.055
4.048
3.806
3.804
3.656
3.639
3.471
3.465
2.417
2.402
2.386
2.357
2.028
1.995
1.766
1.735
1.680
1.637
1.581
0.893
0.876
0.865
0.858
0.818
0.810
0.803
0.060
0.034
1.97
1.98
1
2.02
0.93
0.96
2.95
1.0
0.48
0.47
3.65
2.48
1.06
3.94
1.07
0.9
11.32
3.07
5.06
1.98
19.04
10.14

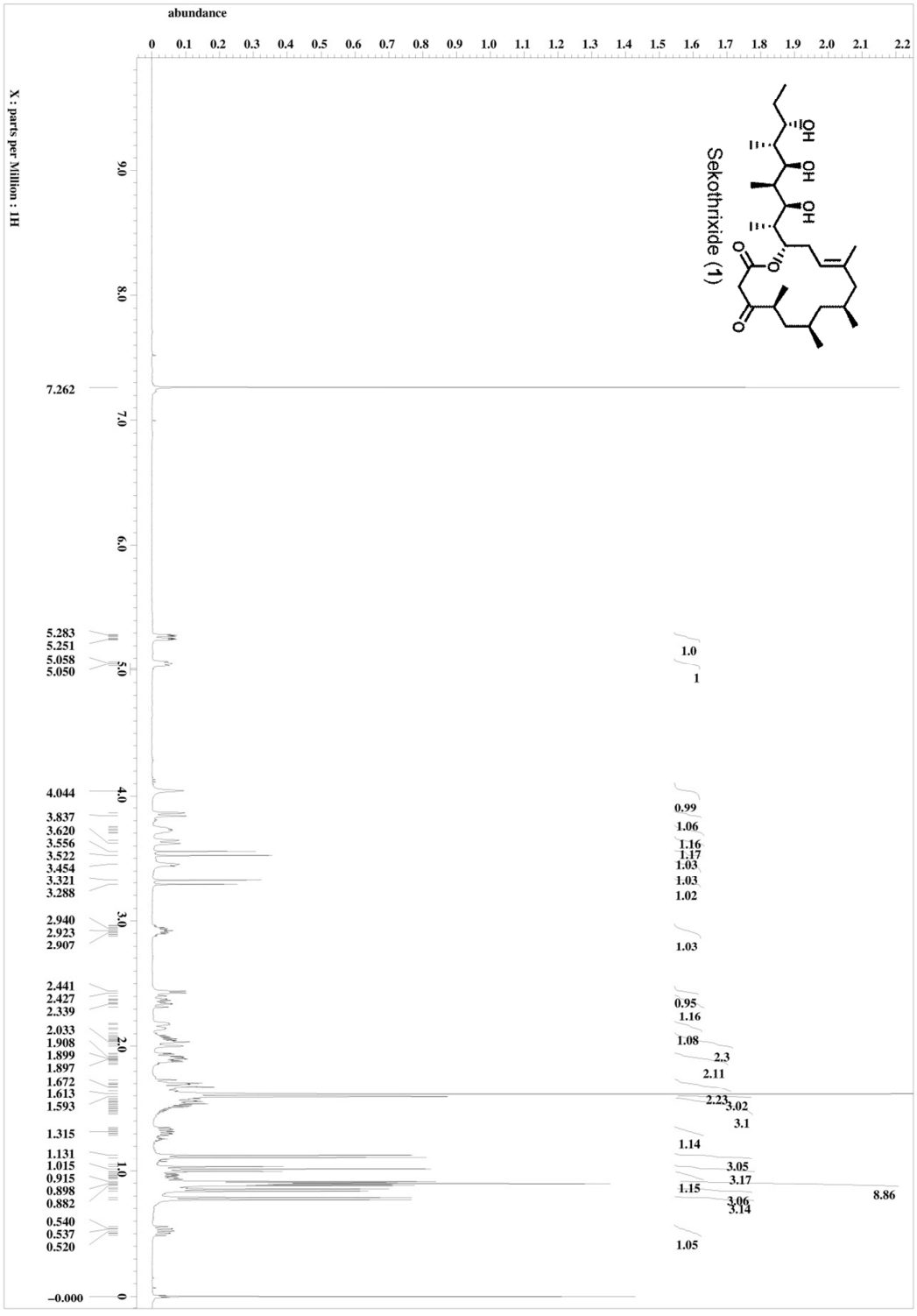

abundance
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
0.16
0.18
0.2
0.22
0.24
X : parts per Million : 13C
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
171.403
171.346
159.714
159.599
144.859
135.200
135.115
131.482
127.201
127.115
116.913
116.837
113.528
113.452
111.307
100.475
100.418
99.446
81.168
80.691
77.335
77.020
76.696
61.612
60.926
60.869
55.281
46.214
46.157
39.864
39.425
37.252
35.516
30.434
27.736
25.896
22.216
19.565
18.068
15.351
13.291
10.383
7.065
5.368
0.000
−4.500
−4.624
25
OEE
MP
OTBS

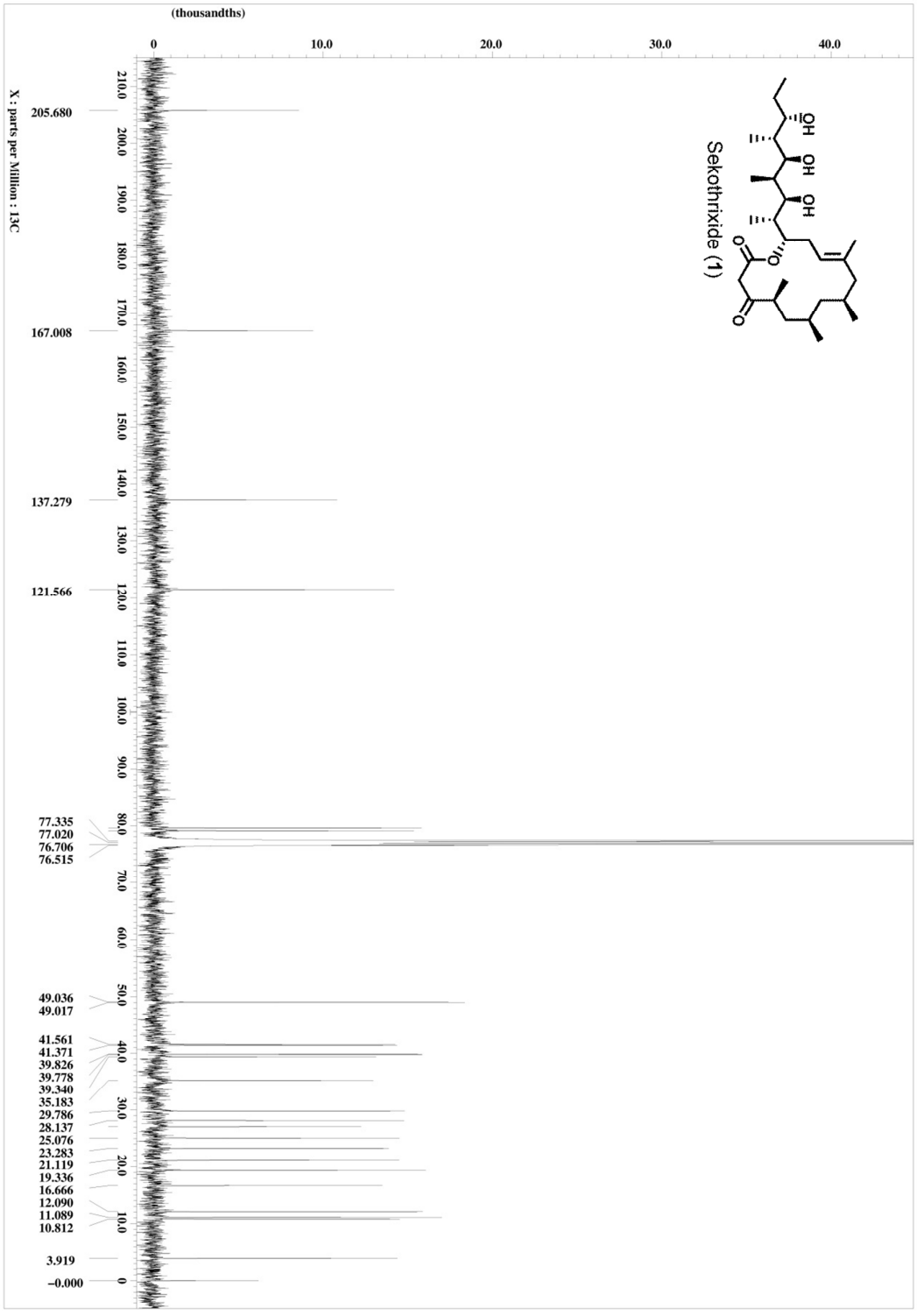

abundance
X : parts per Million : 1H
26
OEE
MP
OH
7.427
7.406
7.261
6.903
6.896
6.881
5.493
5.435
5.373
5.173
5.053
5.042
4.686
4.668
4.655
3.803
3.801
3.647
3.630
3.606
3.463
3.440
2.428
2.422
2.414
2.393
2.386
2.378
2.096
1.653
1.582
1.310
1.307
1.297
1.293
0.920
0.912
0.893
0.876
0.858
0.810
0.000
1.92
2.01
2.02
1.04
1
5.54
0.55
2.07
1.04
1.02
1.9
1.03
1.15
1.04
5.04
6.91
3.19
4.41
1.22
20.97
1.08


(thousandths)
X : parts per Million : 13C
172.280
171.775
171.746
159.733
159.618
136.230
136.116
131.653
131.453
127.296
127.220
121.337
121.270
120.488
113.509
113.433
100.876
100.409
99.398
82.703
81.149
80.672
77.335
77.221
77.020
76.696
61.698
60.878
60.392
55.301
45.566
43.306
43.134
42.457
38.119
36.432
36.365
30.463
28.203
25.314
21.815
20.690
15.351
15.084
10.040
7.084
5.444
-0.000
OEE
MP
OH
26


abundance
X : parts per Million : 1H
2
HO
HO
HO
O
O
O
7.261
5.204
5.179
5.078
5.062
4.030
3.829
3.670
3.637
3.506
3.475
3.416
2.732
2.719
2.715
2.470
2.456
2.266
2.087
2.045
1.730
1.701
1.629
1.556
1.550
1.541
1.532
0.918
0.899
0.864
0.848
0.786
0.769
0.000
0.98
1.0
0.91
1.12
1.15
1.23
1.14
1.13
0.94
1.0
0.79
1.15
1.04
2.14
1.97
3.02
3.23
4.05
3.11
4.43
6.07
6.16
3.07
1.07


(thousandths)
0
10.0
20.0
30.0
X : parts per Million : 13C
205.146
166.026
137.451
120.355
77.488
77.335
77.020
76.696
47.606
47.187
45.280
43.392
40.055
39.797
39.578
35.211
29.309
28.709
26.811
25.133
23.484
20.976
17.963
17.563
12.118
11.232
11.108
4.014
−0.000
HO
HO
HO
O
O
O
2


abundance
X : parts per Million : 1H
Sekothrixide (1)
OH
OH
OH
O
O
O
7.262
5.283
5.251
5.058
5.050
4.044
3.837
3.620
3.556
3.522
3.454
3.321
3.288
2.940
2.923
2.907
2.441
2.427
2.339
2.033
1.908
1.899
1.897
1.672
1.613
1.593
1.315
1.131
1.015
0.915
0.898
0.882
0.540
0.537
0.520
−0.000
1.0
1
0.99
1.06
1.16
1.17
1.03
1.03
1.02
1.03
0.95
1.16
1.08
2.3
2.11
2.23
3.02
3.1
1.14
3.05
3.17
1.15
3.06
3.14
8.86
1.05


(thousandths)
0
10.0
20.0
30.0
40.0
X : parts per Million : 13C
205.680
167.008
137.279
121.566
77.335
77.020
76.706
76.515
49.036
49.017
41.561
41.371
39.826
39.778
39.340
35.183
29.786
28.137
25.076
23.283
21.119
19.336
16.666
12.090
11.089
10.812
3.919
−0.000
Sekothrixide (1)
OH
OH
OH
O
O
O