Supporting Information

Synthesis of an Analog of Amphidinol 3 Corresponding to the C31–C67 Section

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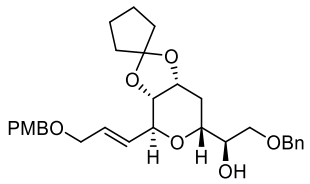
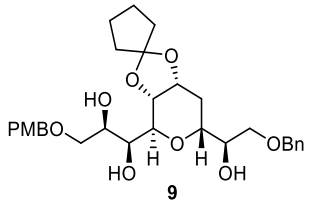
General methods. All reactions sensitive to air or moisture were performed under argon atmosphere with dry glassware unless otherwise noted in particular. The dehydrated solvents, CH_2Cl_2, tetrahydrofuran (THF), and toluene were purchased from Kanto Chemical Co. Inc. or Wako Pure Chemical Industries Ltd., and were used without further dehydration. $(COCl)_2$, dimethoxyethane, Et_3N, EtOH, Et_2O, 2,6-lutidine, THF, and thiophene were distilled before using. All other chemicals were obtained from local venders, and used as supplied unless otherwise stated. For the reaction analyses, thin-layer chromatography (TLC) was conducted using Merck pre-coated TLC plates (TLC glass plate silica gel 60 F_{254}, 0.25-mm thickness or TLC glass plate RP-18 $F_{254}S$, 0.25-mm thickness). For column chromatography, Kanto silica gel 60N (spherical, neutral, 100–210 μm) or Kanto silica gel 60N (spherical, neutral, 40–50 μm, for flash chromatography) were used. Reversed phase column chromatography was performed using Waters Sep-Pak Vac 6cc (1 g) C_{18} cartridges. IR spectra were recorded on a JASCO FT/IR-4000. ^1H and ^{13}C NMR spectra were recorded on JEOL JNM-ECA600 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane (TMS) with reference to internal residual solvent [^1H NMR: $CHCl_3$ (7.26), C_6HD_5 (7.16), CHD_2OD (3.31); ^{13}C NMR: $CDCl_3$ (77.16), C_6D_6 (128.06), CD_3OD (49.00)]. The following abbreviations are used to designate the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet. High resolution mass spectra (HRMS) were recorded on Bruker microTOFfocus. High performance liquid chromatography (HPLC) was recorded on HITACHI ELITE LaChrom HPLC system (detector: L-2455, pump: L-2130).



8

Acetal 8. 1,1-Dimethoxycyclopentane **7** (5.2 mL, 37.7 mmol) and PPTS (315 mg, 1.26 mmol) were added to a solution of triol **6** (2.79 g, 6.28 mmol) in CH_2Cl_2 (63.0 mL) at 0 °C. After the solution was stirred at room temperature for 40 min, the resultant mixture was quenched with Et_3N and diluted with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 8/1 → 2/1) afforded acetal **8** (2.81 g, 5.51 mmol, 88%) as a colorless liquid.

R_f = 0.70 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −27.1 (*c* 1.0, $CHCl_3$); IR (neat) 2953, 2894, 2856, 1612, 1463, 1362, 1249, 1103, 1038, 834 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H), 7.30–7.24 (m, 3H), 6.88 (d, *J* = 8.4 Hz, 2H), 5.90 (dtd, *J* = 14.4, 6.0, 1.2 Hz, 1H), 5.79 (ddt, *J* = 14.4, 6.0, 1.2 Hz, 1H), 4.57 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.45 (s, 2H), 4.41 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.25 (ddd, *J* = 9.0, 6.0, 6.0 Hz, 1H), 4.01 (d, *J* = 6.0 Hz, 2H), 3.87 (dd, *J* = 6.0, 6.0 Hz, 1H), 3.81–3.77 (m, 5H), 3.59 (dd, *J* = 10.2, 6.0 Hz, 1H), 3.54 (dd, *J* = 10.2, 6.0 Hz, 1H), 2.70–2.60 (brs, 1H), 1.97–1.80 (m, 4H), 1.74–1.65 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 138.1, 130.4, 130.0, 129.9, 129.6 (2C), 128.6 (2C), 127.9 (3C), 118.8, 113.9 (2C), 75.3, 73.7, 72.6, 72.4, 72.2, 71.1, 70.9, 70.0, 69.9, 55.4, 37.3, 37.2, 29.2, 23.9, 23.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{38}O_7Na$ 533.2510, found 533.2514.

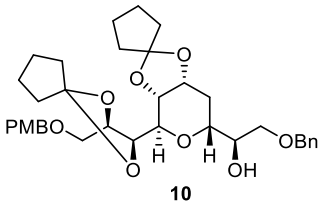


9

Triol 9. A mixture of $K_2OsO_4 \cdot 2H_2O$ (20.0 mg, 54.3 μmol), $(DHQD)_2PHAL$ (214 mg, 275 μmol), $K_3Fe(CN)_6$ (5.44 g, 16.5 mmol), K_2CO_3 (2.28 g, 16.5 mmol), and $MeSO_2NH_2$

(1.57 g, 16.5 mmol) in *t*-BuOH (14 mL) and H_2O (27 mL) was stirred at room temperature for 30 min, and then cooled to 0 °C. A solution of olefin **8** (2.81 g, 5.51 mmol) in *t*-BuOH (10 mL + 2×1.5 mL rinse) was added to the resultant suspension via cannula. After the solution was stirred at 0 °C for 11 h, the resultant mixture was quenched with solid $Na_2S_2O_3 \cdot 5H_2O$, and stirred at room temperature for 10 h. The organic layer was separated and the aqueous layer was extracted with EtOAc. Combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 2/1 → 0/1) afforded triol **9** (2.92 g, 5.36 mmol, 97%) as a colorless liquid.

R_f = 0.20 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −18.7 (*c* 1.0, $CHCl_3$); IR (neat) 2953, 2930, 2858, 1513, 1472, 1336, 1249, 1103, 1038, 834 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.35–7.31 (m, 4H), 7.30–7.25 (m, 3H), 6.88 (d, *J* = 9.0 Hz, 2H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 10.8 Hz, 1H), 4.48 (d, *J* = 10.8 Hz, 1H), 4.29 (ddd, *J* = 8.4, 6.0, 6.0 Hz, 1H), 4.11 (dd, *J* = 7.2, 6.0 Hz, 1H), 4.06–4.01 (m, 1H), 3.87–3.76 (m, 7H), 3.66–3.60 (m, 2H), 3.59–3.51 (m, 2H), 3.19–3.13 (br, 1H), 3.13–3.06 (br, 1H), 2.95–2.93 (brs, 1H), 2.07–1.95 (m, 2H), 1.89 (t, *J* = 7.2 Hz, 2H), 1.75–1.61 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 138.1, 130.0, 129.7 (2C), 128.6 (2C), 127.9 (3C), 119.3, 114.0 (2C), 73.9, 73.6 (2C), 73.4, 72.0, 71.7 (2C), 71.5, 71.1, 70.9, 69.3, 55.4, 36.9, 36.7, 28.2, 24.0, 23.3; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{30}H_{40}O_9Na$ 567.2565, found 567.2552.

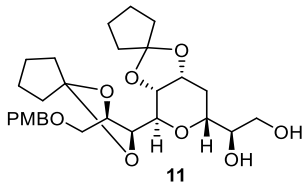


10

Acetal 10. 1,1-Dimethoxycyclopentane **7** (5.9 mL, 42.9 mmol) and PPTS (270 mg, 1.07 mmol) were added to a solution of triol **9** (2.92 g, 5.36 mmol) in CH_2Cl_2 (36.0 mL) at 0 °C. After the solution was stirred at room temperature for 2 h, the resultant mixture was quenched with Et_3N and diluted with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers

were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by silica gel column chromatography (hexane/EtOAc = 8/1 → 2/1) afforded acetal **10** (3.11 g, 5.10 mmol, 95%) as a colorless liquid.

R_f = 0.70 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −0.33 (*c* 0.86, $CHCl_3$); IR (neat) 2956, 2871, 1612, 1514, 1454, 1334, 1248, 1106, 1038, 743, 699 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.36–7.23 (m, 7H), 6.86 (d, *J* = 8.4 Hz, 2H), 4.56 (d, *J* = 12.0 Hz, 1H), 4.52 (d, *J* = 12.0 Hz, 1H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.49 (d, *J* = 11.4 Hz, 1H), 4.25 (ddd, *J* = 9.0, 6.0, 6.0 Hz, 1H), 4.18 (dd, *J* = 12.0, 6.0 Hz, 1H), 4.06 (dd, *J* = 6.0, 6.0 Hz, 1H), 4.00–3.96 (m, 2H), 3.85–3.80 (m, 1H), 3.79 (s, 3H), 3.79–3.75 (m, 1H), 3.62–3.49 (m, 4H), 1.92 (ddd, *J* = 13.2, 6.0, 4.2 Hz, 1H), 1.90–1.60 (m, 18H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 138.1, 130.0, 129.6 (2C), 128.5 (2C), 127.9 (3C), 120.0, 118.6, 113.9 (2C), 79.7, 76.7, 73.6, 73.2, 72.9, 72.2, 71.4 (2C), 71.0, 70.9, 70.4, 55.4, 37.5, 37.4, 37.33, 37.28, 29.0, 23.8, 23.7, 23.6, 23.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{35}H_{46}O_9Na$ 633.3034, found 633.3052.

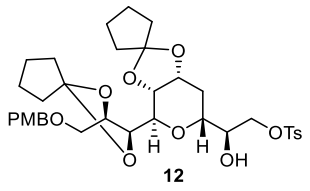


11

Diol 11. Raney Ni (excess) was added to a solution of benzyl ether **10** (1.19 g, 1.95 mmol) in EtOH (39.0 mL), and placed under H_2 atmosphere. After the solution was stirred at room temperature for 16 h, the insoluble materials were removed by filtration through a Celite pad and rinsed with EtOAc. The filtrate was concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 1/1 → 0/1) afforded diol **11** (1.02 g, 1.95 mmol, quant) as a colorless liquid.

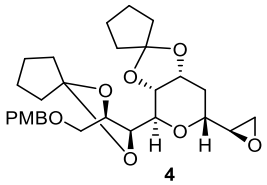
R_f = 0.20 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −3.73 (*c* 1.07, $CHCl_3$); IR (neat) 3461, 2956, 2873, 1612, 1514, 1335, 1248, 1105, 1037, 822 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.50 (d, *J* = 11.4 Hz, 1H), 4.26 (ddd, *J* = 12.6, 5.4, 5.4 Hz, 1H), 4.19 (ddd, *J* = 7.2, 5.4, 5.4 Hz, 1H), 4.06 (d, *J* = 5.4, 5.4 Hz, 1H), 4.01–3.96 (m, 2H), 3.80 (s, 3H), 3.80–3.76 (m, 1H), 3.70 (dd, *J* = 10.8, 3.0 Hz, 1H), 3.64–3.58 (m, 3H), 3.53 (dd, *J* = 10.2, 5.4 Hz, 1H), 2.37–2.02 (brs, 1H), 1.95

(ddd, J = 13.8, 6.0, 5.4 Hz, 1H), 1.90–1.73 (m, 7H), 1.72–1.64 (m, 10H). One proton is missing due to H/D exchange of hydroxy group; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 129.9, 129.7 (2C), 120.0, 118.7, 114.0 (2C), 79.5, 76.4, 73.3, 72.9, 72.8, 71.5, 71.4, 71.2, 70.5, 63.5, 55.4, 37.6, 37.3 (2C), 37.2, 28.9, 23.9, 23.7, 23.6, 23.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{28}H_{40}O_9Na$ 543.2565, found 543.2564.



12

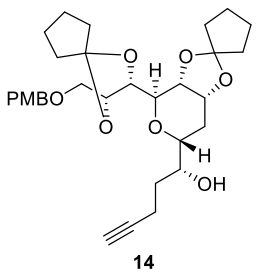
Tosylate 12. Et_3N (480 μL, 3.43 mmol), Bu_2SnO (8.5 mg, 34.3 μmol), and TsCl (360 mg, 1.89 mmol) were added to a solution of diol **11** (893 mg, 1.72 mmol) in CH_2Cl_2 (17 mL) at 0 °C. After the solution was stirred at room temperature for 13.5 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 8/1 → 0/1) afforded tosylate **12** (846 mg, 1.26 mmol, 73%) and the recovery of alcohol **11** (217.7 mg, 0.42 mmol, 24%) both as a colorless liquid.
R_f = 0.73 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −0.18 (*c* 1.04, $CHCl_3$); IR (neat) 2956, 2873, 1612, 1513, 1453, 1362, 1335, 1247, 1176, 1097, 1037, 974, 816, 666 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 4.51 (d, J = 12.0 Hz, 1H), 4.49 (d, J = 12.0 Hz, 1H), 4.25 (ddd, J = 12.6, 5.4, 5.4 Hz, 1H), 4.13–4.08 (m, 2H), 4.05–4.01 (m, 2H), 3.99–3.94 (m, 2H), 3.82–3.78 (m, 1H), 3.80 (s, 3H), 3.75 (ddd, J = 5.4, 5.4, 5.4 Hz, 1H), 3.59 (dd, J = 10.2, 5.4 Hz, 1H), 3.50 (dd, J = 10.2, 6.0 Hz, 1H), 2.43 (s, 3H), 1.90 (ddd, J = 13.8, 5.4, 4.2 Hz, 1H), 1.87–1.78 (m, 4H), 1.78–1.72 (m, 3H), 1.72–1.60 (m, 10H). One proton missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.5, 145.1, 132.9, 130.02 (2C), 129.96, 129.6 (2C), 128.1 (2C), 120.1, 118.6, 114.0 (2C), 79.9, 76.5, 73.4, 73.3, 71.11 (2C), 71.06, 70.5, 70.3, 69.7, 55.4, 37.5, 37.4, 37.3 (2C), 28.7, 23.8, 23.7, 23.5, 23.4, 21.8; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{35}H_{46}O_{11}SNa$ 697.2653, found 697.2682.



4

Epoxide 4. K_2CO_3 (605 mg, 4.37 mmol) was added to a solution of tosylate **12** (2.46 g, 3.65 mmol) in CH_2Cl_2/MeOH (10:1, v/v, 122 mL) at 0 °C. After the solution was stirred at room temperature for 1 h, the reaction mixture was quenched with pH 7 phosphate buffer. The resultant mixture was extracted with EtOAc and the combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 5/1 → 2/1) afforded epoxide **4** (1.72 g, 3.43 mmol, 94%) as a colorless liquid.

R_f = 0.67 (hexane/EtOAc = 1/1); $[\alpha]^{26}_D$ −1.4 (*c* 0.67, $CHCl_3$); IR (neat) 2956, 2873, 1612, 1514, 1334, 1303, 1037, 821 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.53 (d, *J* = 11.4 Hz, 1H), 4.50 (d, *J* = 11.4 Hz, 1H), 4.25 (ddd, *J* = 11.4, 5.4, 5.4 Hz, 1H), 4.21 (ddd, *J* = 7.8, 5.4, 5.4 Hz, 1H), 4.12 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.01 (dd, *J* = 8.4, 4.2 Hz, 1H), 3.97 (dd, *J* = 5.4, 4.2 Hz, 1H), 3.80 (s, 3H), 3.60 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.58 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.53 (ddd, *J* = 10.2, 4.2, 4.2 Hz, 1H), 3.15–3.11 (m, 1H), 2.78 (dd, *J* = 4.8, 4.8 Hz, 1H), 2.66 (dd, *J* = 6.0, 3.0 Hz, 1H), 1.99 (ddd, *J* = 13.2, 5.4, 4.8 Hz, 1H), 1.92–1.77 (m, 7H), 1.74–1.59 (m, 10H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.3, 130.2, 129.5 (2C), 120.0, 118.6, 113.9 (2C), 79.1, 76.9, 73.2, 73.1, 71.4, 71.1 (2C), 70.2, 55.4, 53.2, 44.5, 37.51, 37.47, 37.4, 37.3, 29.5, 23.8, 23.7, 23.6, 23.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{28}H_{38}O_8Na$ 525.2459, found 525.2477.

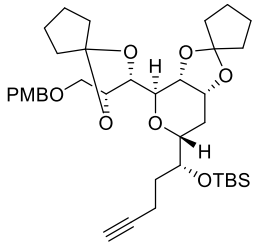


14

Alkyne 14. Two-necked flask was equipped with Liebig condenser and the exit from the condenser was connected to a trap cooled to −78 °C. A mixture of Zn powder (14.0 g, 214 mmol), EtOH (18.6 mL), and water (4.6 mL) was placed in the reaction flask. The reaction mixture was heated under reflux, and the 1,2-dichloropropene (10.0 mL, 109 mmol) was added dropwise such a rate that reflux was maintained without external heating. After the addition was complete, the reaction mixture was stirred under reflux for 1 h. The residual allene was purged from the reaction flask with a very slow stream of Ar. The crude allene was distilled at −30 °C.

Allene (1.1 mL, 17.9 mmol) and a solution of *n*-BuLi (1.55 M in hexane, 22.0 mL, 34.1 mmol) was added to the mixture of Et_2O (34.0 mL) and hexane (11.5 mL) at −78 °C. The reaction mixture was allowed to warm to −15 °C where a white precipitate was formed and stirred at this temperature for 15 min. After this time, the reaction mixture was cooled to −78 °C, epoxide **4** (900 mg, 1.79 mmol) in Et_2O/hexane (v/v = 1:1, 6.8 mL + 2 × 1.0 mL rinse) was added, and the reaction mixture was allowed to warm to room temperature over 2 h. The resultant mixture was quenched with saturated aqueous $NaHCO_3$ and diluted with Et_2O. The organic layer was separated and the aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Purification by flash column chromatography (silica gel, hexane/EtOAc = 5/1 → 0/1) afforded alkyne **14** (904 mg, 1.66 mmol, 93%) as a colorless liquid.

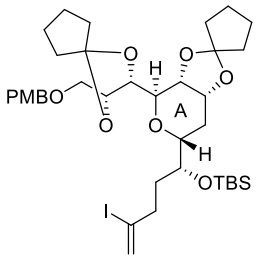
R_f = 0.30 (hexane/acetone = 3/1); $[\alpha]^{18}_D$ +8.2 (*c* 0.53, $CHCl_3$); IR (neat) 2956, 2361, 1613, 1514, 1334, 1247, 1107, 1036, 691 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.51 (d, *J* = 11.4 Hz, 1H), 4.50 (d, *J* = 11.4 Hz, 1H), 4.25 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 4.18 (ddd, *J* = 7.2, 5.4, 4.8 Hz, 1H), 4.07 (dd, *J* = 6.0, 5.4 Hz, 1H), 4.01–3.95 (m, 2H), 3.81 (s, 3H), 3.71–3.66 (m, 1H), 3.61 (dd, *J* = 10.2, 5.4 Hz, 1H), 3.58–3.52 (m, 2H), 2.67 (brs, 1H), 2.43–2.31 (m, 2H), 1.99–1.93 (m, 2H), 1.90–1.74 (m, 6H), 1.73–1.55 (m, 13H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 130.0, 129.6 (2C), 120.0, 118.7, 113.9 (2C), 84.2, 79.9, 76.5, 73.8, 73.3, 72.7, 71.7, 71.4, 71.3, 70.5, 68.7, 55.4, 37.5, 37.4, 37.33, 37.27, 31.7, 29.2, 23.8, 23.7, 23.6, 23.4, 14.9; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{31}H_{42}O_8Na$ 565.2772, found 565.2795.



15

TBS Ether 15. 2,6-Lutidine (635 μL, 5.46 mmol) and TBSOTf (538 μL, 2.34 mmol) were added to a solution of alkyne **14** (845 mg, 1.56 mmol) in CH_2Cl_2 (52.0 mL) at −20 °C and stirred at 0 °C for 1.6 h. The resultant mixture was quenched with saturated aqueous $NaHCO_3$ at −20 °C. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc = 20/1 → 10/1) to afford TBS ether **15** (1.05 g, 1.56 mmol, quant) as a colorless liquid.

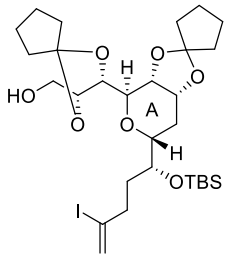
R_f = 0.60 (hexane/acetone = 3/1); $[\alpha]^{18}_D$ +34.0 (*c* 1.20, $CHCl_3$); IR (neat) 2954, 2361, 1613, 1514, 1334, 1248, 1202, 1105, 1040, 835 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.25 (ddd, *J* = 10.8, 6.0, 6.0 Hz, 1H), 4.16 (ddd, *J* = 6.6, 6.0, 6.0 Hz, 1H), 4.07 (dd, *J* = 5.4, 5.4 Hz, 1H), 3.99–3.95 (m, 2H), 3.80 (s, 3H), 3.77 (ddd, *J* = 8.4, 4.2, 4.2 Hz, 1H), 3.70 (ddd, *J* = 12.0, 4.2, 4.2 Hz, 1H), 3.59–3.52 (m, 2H), 2.30–2.16 (m, 2H), 1.93 (t, *J* = 3.0 Hz, 1H), 1.92–1.75 (m, 7H), 1.74–1.55 (m, 13H), 0.86 (s, 9H), 0.07 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 130.2, 129.4 (2C), 120.1, 118.4, 113.9 (2C), 84.3, 80.0, 76.8, 73.8, 73.2, 72.61, 72.56, 72.2, 72.0, 70.5, 68.8, 55.4, 37.5, 37.3, 37.2, 37.1, 30.8, 27.9, 26.0 (3C), 23.9, 23.7, 23.6, 23.4, 18.2, 14.9, −4.4, −4.5; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{37}H_{56}O_8SiNa$ 679.3637, found 679.3649.



16

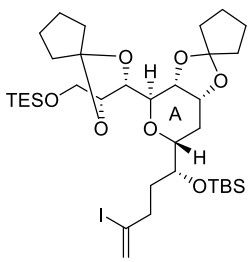
Iodoolefin 16. A solution of alkyne **15** (383 mg, 538 μmol) in THF (0.40 mL + 0.20 mL rinse) was added to a mixture of Ni(dppp)Cl_2 (9.5 mg, 17.5 μmol, stored in glove box) and DIBALH (1 M in toluene, 0.76 mL, 0.76 mmol) via cannula at 0 °C. After the solution was stirred at room temperature for 45 min, a solution of NIS (243 mg, 1.08 mmol) in THF (1.8 mL) was added to the resultant mixture via cannula at 0 °C. After the solution was stirred at 0 °C for 1 h, the reaction mixture was diluted with Et_2O and saturated aqueous Na^+/K^+ tartrate. The mixture was extracted with Et_2O. The organic layer was washed with saturated aqueous $NaHCO_3$, $Na_2S_2O_3$, and NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was roughly purified by flash column chromatography (silica gel, hexane/EtOAc = 30/1 → 5/1) to afford an inseparable mixture of iodoolefin **16** and its regioisomer (**16**: regioisomer = ca. 5:1, 370.6 mg, 472 μmol, 88%) as a colorless liquid. The ratio was determined by ^{1}H NMR analysis of the mixture.

R_f = 0.69 (hexane/EtOAc =3/1); $[\alpha]^{19}_D$ +9.6 (*c* 1.5, $CHCl_3$); IR (neat) 2954, 2856, 1512, 1332, 1249, 1200, 1104, 1038, 834 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.26 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.00 (s 1H), 5.67 (s, 1H), 4.54 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 12.0 Hz, 1H), 4.25 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 4.19–4.13 (m, 1H), 4.08 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.01–3.97 (m, 2H), 3.80 (s, 3H), 3.67 (ddd, *J* = 12.0, 4.2, 4.2 Hz, 1H), 3.62 (ddd, *J* = 7.2, 4.2, 4.2 Hz, 1H), 3.60–3.52 (m, 2H), 2.47 (ddd, *J* = 15.0, 10.2, 5.4 Hz, 1H), 2.39 (ddd, *J* = 15.0, 10.2, 5.4 Hz, 1H), 1.93–1.76 (m, 7H) 1.76–1.55 (m, 13H), 0.87 (s, 9H), 0.06 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.4, 130.2, 129.4 (2C), 125.5, 120.1, 118.5, 113.9 (2C), 112.1, 80.0, 76.9, 73.8, 73.3, 72.9, 72.6, 72.2, 72.0, 70.5, 55.4, 41.9, 37.5, 37.3, 37.2, 37.1, 32.1, 28.1, 26.0 (3C), 23.9, 23.7, 23.6, 23.4, 18.2, −4.2, −4.3; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{37}H_{57}O_8SiINa$ 807.2760, found 807.2760.



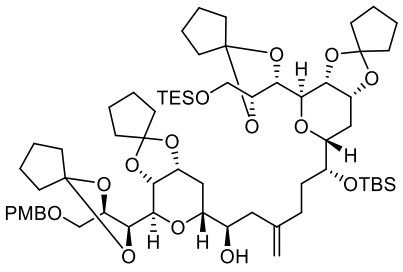
17

Primary Alcohol 17. DDQ (113 mg, 0.50 mmol) was added to a solution of the mixture of **16** and regioisomer (326 mg, 473 μmol) in CH_2Cl_2/pH 7 buffer (v/v = 10/1, 4.6 mL) at 0 °C. After the mixture was stirred at room temperature for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 15/1 → 5/1) to afford primary alcohol **17** (189 mg, 285 μmol, 68%) as a colorless liquid. R_f = 0.28 (hexane/EtOAc =3/1); $[\alpha]^{18}_D$ +8.2 (*c* 0.80, $CHCl_3$); IR (neat) 2954, 1334, 1254, 1200, 1106, 836, 775, 703 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.02 (d, *J* = 1.2 Hz, 1H), 5.68 (d, *J* = 1.2 Hz, 1H), 4.27 (ddd, *J* = 11.4, 6.0, 6.0 Hz, 1H), 4.14–4.09 (m, 2H), 4.05 (dd, *J* = 7.8, 4.2 Hz, 1H), 3.96 (dd, *J* = 5.2, 4.4 Hz, 1H), 3.81 (dd, *J* = 12.0, 3.2 Hz, 1H), 3.70–3.62 (m, 3H), 2.51–2.37 (m, 2H), 1.92–1.76 (m, 8H) 1.76–1.59 (m, 12H), 0.89 (s, 9H), 0.08 (s, 3H), 0.05 (s, 3H). One proton missing due to H/D exchange; ^{13}C NMR (150 MHz, $CDCl_3$) δ 125.7, 120.0, 118.7, 112.0, 78.6, 78.1, 74.1, 73.0, 72.5 (2C), 72.1, 62.7, 41.7, 37.5, 37.4, 37.2, 37.1, 32.3, 28.1, 26.0 (3C), 23.9, 23.7, 23.5, 23.4, 18.2, −4.27, −4.31; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{29}H_{49}O_7SiINa$ 687.2184, found 687.2189.



18

TES Ether 18. NaH (60% in oil, 26.5 mg, 662 μmol) and TESCl (55 μL, 331 μmol) were added to a solution of primary alcohol **17** (110 mg, 166 μmol) in THF (5.5 mL) at −20 °C. The reaction mixture was gradually allowed to warm to 0 °C. After the mixture was stirred at 0 °C for 1 h, the resultant mixture was quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 100/1 → 30/1) to afford TES ether **18** (123.6 mg, 159 μmol, 98%) as a colorless liquid. R_f = 0.80 (hexane/EtOAc = 3/1); $[\alpha]^{18}_D$ +10.4 (*c* 1.4, $CHCl_3$); IR (neat) 2954, 2876, 1461, 1332, 1252, 1199, 1105, 1006, 835, 777, 742 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$) δ 6.02 (d, *J* = 1.2 Hz, 1H), 5.68 (s, 1H), 4.26 (ddd, *J* = 12.0, 6.0, 6.0 Hz, 1H), 4.11 (dd, *J* = 5.4, 5.4 Hz, 1H), 4.07 (dd, *J* = 7.2, 2.4 Hz, 1H), 4.05–3.99 (m, 2H), 3.78–3.69 (m, 3H), 3.66 (ddd, *J* = 7.8, 4.8, 4.8 Hz, 1H), 2.50 (ddd, *J* = 15.0, 10.2, 5.4 Hz, 1H), 2.41 (ddd, *J* = 15.0, 10.2, 5.4 Hz, 1H), 1.92–1.76 (m, 8H), 1.74–1.57 (m, 12H), 0.96 (t, *J* = 8.4 Hz, 9H), 0.89 (s, 9H), 0.61 (q, *J* = 8.4 Hz, 6H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 125.5, 119.9, 118.4, 112.1, 80.0, 78.1, 73.9, 72.9, 72.7, 72.3, 71.8, 63.6, 41.9, 37.5, 37.24, 37.18, 37.1, 32.0, 28.1, 26.0 (3C), 23.9, 23.7, 23.5, 23.3, 18.2, 6.9 (3C), 4.5 (3C), −4.2, −4.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{35}H_{63}O_7Si_2INa$ 801.3049, found 801.3043.



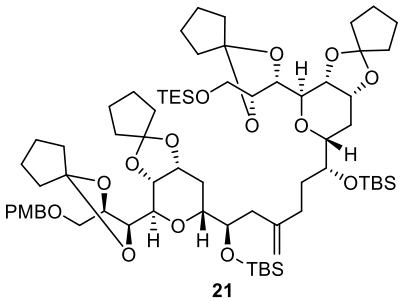
20

Alcohol 20. According to the reported procedure,[1] *n*-BuLi (1.62 M in hexane, 2.04 mL, 3.30 mmol) was added to a solution of thiophene (0.280 mL, 3.47 mmol) in THF (3.3 mL) at −78 °C. The resultant white suspension was stirred at the temperature for 15 min, and then stirred at −20 °C for 30 min to afford colorless clear solution. The solution was quickly transferred into a slurry of CuCN (300 mg, 3.30 mmol) in THF (3.3 mL) at −78 °C via cannula and rinsed with THF (2.3 + 2.2 mL). The resultant brown suspension was

warmed to −40 °C to give a brownish yellow solution of lithium 2-thienylcyanocuprate (0.3 M in THF).

In another flask, *t*-BuLi (1.58 M in pentane, 0.16 ml, 247 μmol) was added dropwise to a stirred solution of the iodoolefin **18** (96.2 mg, 124 μmol) in THF (0.35 ml) at −78 °C. The solution was stirred at −78 °C for 30 min. Then, a freshly prepared solution of lithium 2-thienylcyanocuprate (0.3 M in THF, 0.41 ml, 124 μmol) was added dropwise to the reaction mixture. The mixture was stirred at −40 °C for 1 h and then cooled to −78 °C. A solution of epoxide **4** (124.2 mg, 247 μmol) in THF (0.35 mL + 0.35 mL rinse) was added dropwise via cannula, followed by addition of $BF_3{\cdot}OEt_2$ (30 μL, 247 μmol). The solution was stirred at −78 °C for 15 min, and then it was quenched with a mixture of saturated aqueous NH_4Cl and 28% aqueous ammonium hydroxide (10:1, v/v). The mixture was poured onto water and extracted with EtOAc. The combined organic layer was washed with water, dried over Na_2SO_4 and concentrated in vacuo to leave a brown oil. Purification by flash column chromatography (silica gel, hexane/EtOAc = 30/1 → 7/1) gave alcohol **20** (45.6 mg, 39.5 μmol, 32%) as a colorless oil, and terminal olefin **19** (43.3 mg, 54%), iodohydrin **23** (61.7 mg, 40%), and recovery of epoxide **4** (30.5 mg, 25%).

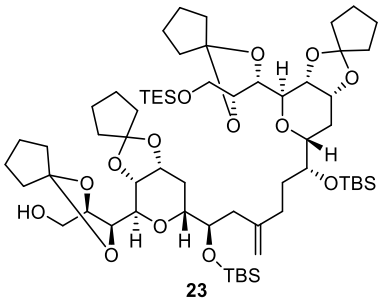
R_f = 0.35 (hexane/EtOAc = 3/1); $[\alpha]^{18}_D$ +13.3 (*c* 1.0, $CHCl_3$); IR (neat) 2955, 2357, 1513, 1333, 1248, 1106, 1037, 833, 812, 779, 723, 700, 690, 676, 662 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.23 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.01 (s, 1H), 4.98 (s, 1H), 4.42 (dd, *J* = 12.0, 5.4 Hz, 1H), 4.40–4.26 (m, 8H), 4.26–4.22 (m, 2H), 4.13 (ddd, *J* = 9.0, 6.6, 6.6 Hz, 1H), 3.87–3.77 (m, 4H), 3.74 (ddd, *J* = 4.2, 4.2, 4.2 Hz, 1H), 3.66 (dd, *J* = 10.2, 4.8 Hz, 1H), 3.59 (dd, *J* = 10.8, 5.4 Hz, 1H), 3.57–3.52 (m, 1H), 3.33 (s, 3H), 2.70 (brs, 1H), 2.41–2.32 (m, 1H), 2.32–2.24 (m, 3H), 2.10–1.85 (m, 16H), 1.85–1.70 (m, 6H), 1.64–1.51 (m, 16H), 1.03 (t, *J* = 7.8 Hz, 9H), 1.01 (s, 9H), 0.63 (q, *J* = 7.8 Hz, 6H), 0.14 (s, 6H); ^{13}C NMR (150 MHz, C_6D_6) δ 159.9, 147.0, 130.6, 129.6 (2C), 119.9, 119.8, 118.8, 118.5, 114.2 (2C), 112.3, 80.4 (2C), 79.1, 77.2, 74.9, 74.7, 73.59, 73.56, 73.4, 73.0. 72.9, 72.7, 72.6, 72.0, 71.8, 71.2, 64.0, 54.8, 40.5, 37.9, 37.83, 37.77, 37.67, 37.63, 37.60, 37.5, 37.4, 32.6, 31.0, 29.6, 29.0, 26.3 (3C), 24.1 (2C), 23.83 (2C), 23.75, 23.73, 23.6 (2C), 18.4, 7.1 (3C), 4.9 (3C), −4.0, −4.2; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{63}H_{102}O_{15}Si_2Na$ 1177.6649, found 1177.6677.



21

TBS Ether 21. 2,6-Lutidine (52 μL, 446 μmol) and TBSOTf (51 μL, 223 μmol) were added to a solution of alcohol **20** (51.5 mg, 44.6 μmol) in CH_2Cl_2 (4.5 mL) at −20 °C and stirred at 0 °C for 3 h. The resultant mixture was quenched with saturated aqueous $NaHCO_3$ at −20 °C. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography (silica gel, hexane/EtOAc = 20/1 → 10/1) to afford TBS ether **21** (55.8 mg, 44.0 μmol, 99%) as a colorless liquid.

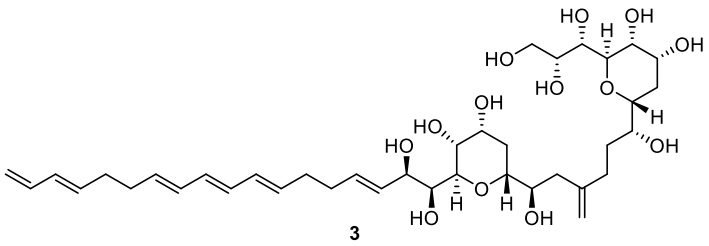
R_f = 0.54 (hexane/EtOAc = 3/1); $[\alpha]^{18}_D$ +12.3 (*c* 0.57, $CHCl_3$); IR (neat) 2955, 1250, 1106, 1044, 835, 799, 721, 709, 686, 661 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 7.25 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 5.03 (s, 1H), 5.01 (s, 1H), 4.47–4.27 (m, 11H), 4.24 (ddd, *J* = 7.8, 4.8, 4.8 Hz, 1H), 3.96–3.91 (m, 1H), 3.89–3.74 (m, 5H), 3.71–3.64 (m, 2H), 3.33 (s, 3H), 2.80 (dd, *J* = 13.2, 6.0 Hz, 1H), 2.37–2.25 (m, 2H), 2.22–2.16 (m, 1H), 2.10–1.89 (m, 18H), 1.82–1.72 (m, 4H), 1.63–1.53 (m, 16H), 1.04–1.00 (m, 27H), 0.63 (q, *J* = 7.2 Hz, 6H), 0.17–0.14 (m, 12H); ^{13}C NMR (150 MHz, C_6D_6) δ 159.8, 146.5, 130.8, 129.5 (2C), 120.0, 119.9, 118.6, 118.5, 114.1 (2C), 112.8, 80.9, 80.4, 79.1, 77.9, 75.0, 74.8, 74.7, 73.9, 73.4 (2C), 73.0, 72.8, 72.7, 72.6, 72.1, 71.1, 64.0, 54.8, 40.2, 37.94, 37.88, 37.80, 37.77, 37.69, 37.6, 37.5, 37.4, 32.9, 30.9, 29.1, 29.0, 26.2 (6C), 24.15, 24.10, 23.9, 23.84, 23.77, 23.73, 23.6 (2C), 18.46, 18.444, 7.1 (3C), 4.9 (3C), −3.97, −4.04, −4.24, −4.27; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{69}H_{116}O_{15}Si_3Na$ 1291.7514, found 1291.7517.



23

Alcohol 23. DDQ (37.5 mg, 165 μmol) was added to a solution of **21** (20.9 mg, 16.5 μmol) in CH_2Cl_2/pH 7 buffer (v/v = 2/1, 1.7 mL) at 0 °C. After the mixture was stirred at room temperature for 4 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$ and saturated aqueous $Na_2S_2O_3$. The mixture was extracted with EtOAc, and the organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc = 10/1 → 3/1) to afford primary alcohol **23** (17.3 mg, 15.1 μmol, 92%) as a colorless liquid.

R_f = 0.43 (hexane/EtOAc = 3/1); $[\alpha]^{18}_D$ +13.9 (*c* 0.35, $CHCl_3$); IR (neat) 2958, 1334, 1111, 834, 797, 743 cm^{-1}; ^1H NMR (600 MHz, C_6D_6) δ 5.02 (s, 1H), 5.01 (s, 1H), 4.42–4.30 (m, 5H), 4.29–4.21 (m, 5H), 3.93–3.88 (m, 1H), 3.87–3.70 (m, 7H), 2.75 (dd, *J* = 12.6, 6.6 Hz, 1H), 2.37–2.24 (m, 2H), 2.21 (ddd, *J* = 15.0, 11.4, 4.8 Hz, 1H), 2.10–1.72 (m, 21H), 1.65–1.53 (m, 17H), 1.06–1.00 (m, 27H), 0.65 (q, *J* = 8.4 Hz, 6H), 0.16 (s, 9H), 0.15 (s, 3H). One proton missing due to H/D exchange; ^{13}C NMR (150 MHz, C_6D_6) δ 146.5, 119.92, 119.87, 118.7, 118.5, 112.9, 80.3, 79.9, 79.3, 79.0, 75.3, 74.8, 74.7, 73.9, 73.7, 73.0, 72.7, 72.6 (2C), 72.0, 63.9, 63.2, 39.9, 37.9, 37.8 (4C), 37.6, 37.5, 37.3, 32.8, 31.0, 29.1, 28.9, 26.3 (3C), 26.2 (3C), 24.13, 24.08, 23.9, 23.8, 23.7 (2C), 23.6 (2C), 18.5, 18.4, 7.1 (3C), 4.9 (3C), −4.0, −4.1, −4.3, −4.4; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{61}H_{108}O_{14}Si_3Na$ 1171.6939, found 1171.6944.



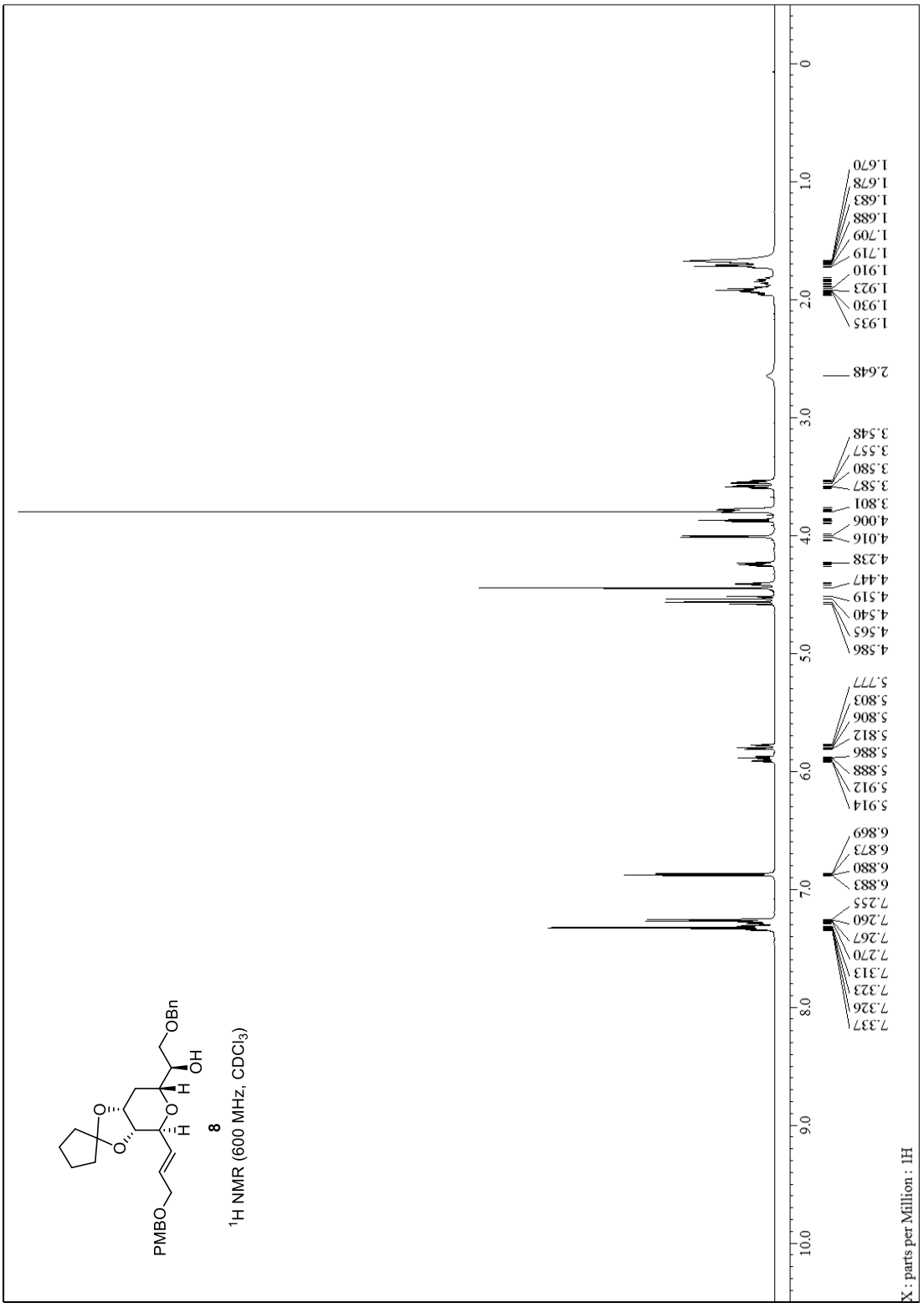
3

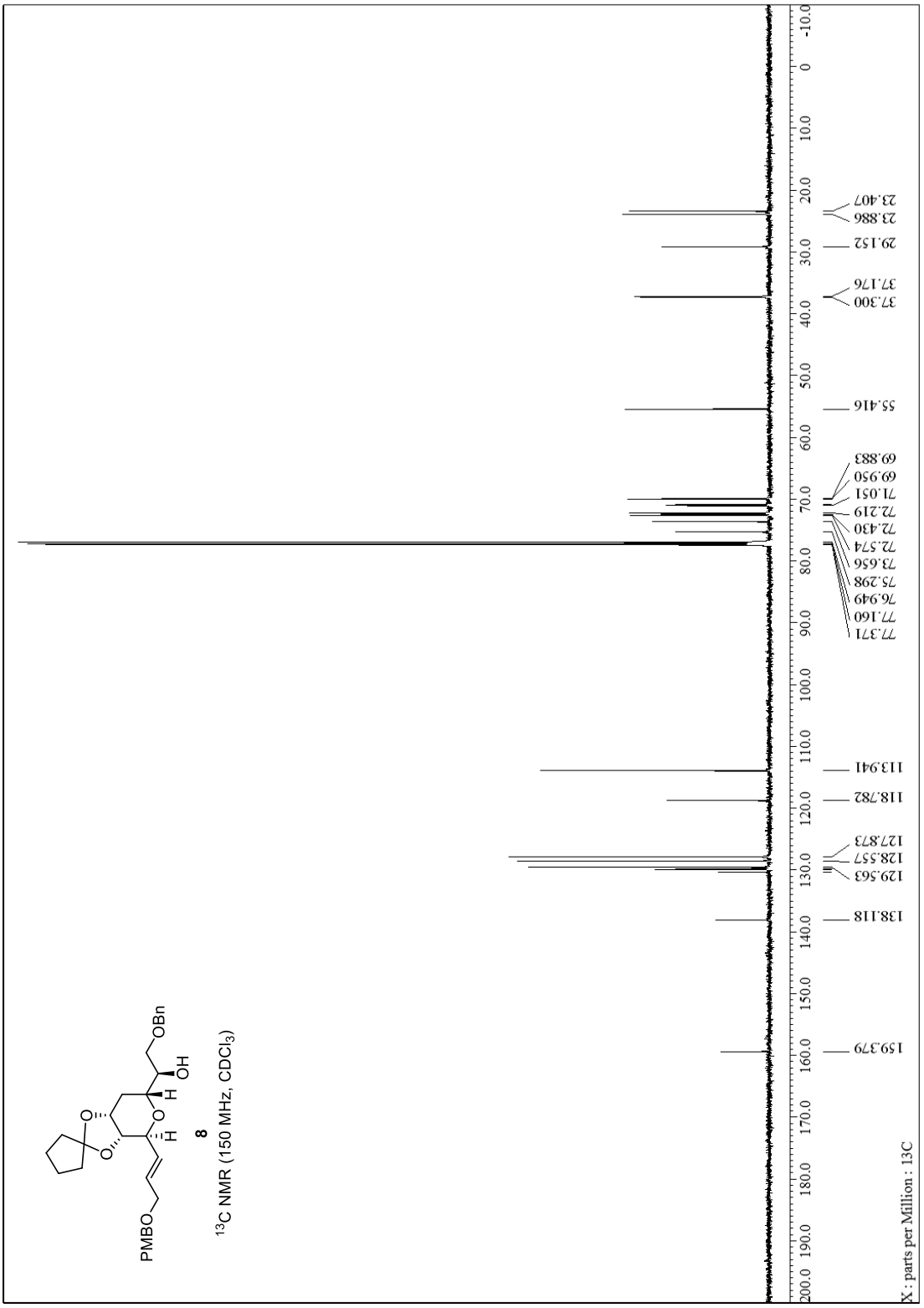
Analog 3. DMSO (30 μL, 422 μmol) was added dropwise to a solution of $(COCl)_2$ (20 μL, 230 μmol) in CH_2Cl_2 (1.1 mL) at –78 °C, and the mixture was stirred for 15 min. A solution of alcohol **23** (25.6 mg, 22.3 μmol) was added dropwise to the resultant activated DMSO complex solution, and the reaction mixture was stirred for 5 min. Et_3N (120 μL, 937 μmol) was added to the solution, and the reaction mixture was allowed to warm to room tempureture over 1 h. The reaction was quenched with saturated aqueous NH_4Cl at −78 °C. The organic layer was separated, and the aqueous layer was extracted with EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The solvent was removed in vacuo to leave the crude aldehyde **24** (26.1 mg), which was used in the next reaction without further purification.

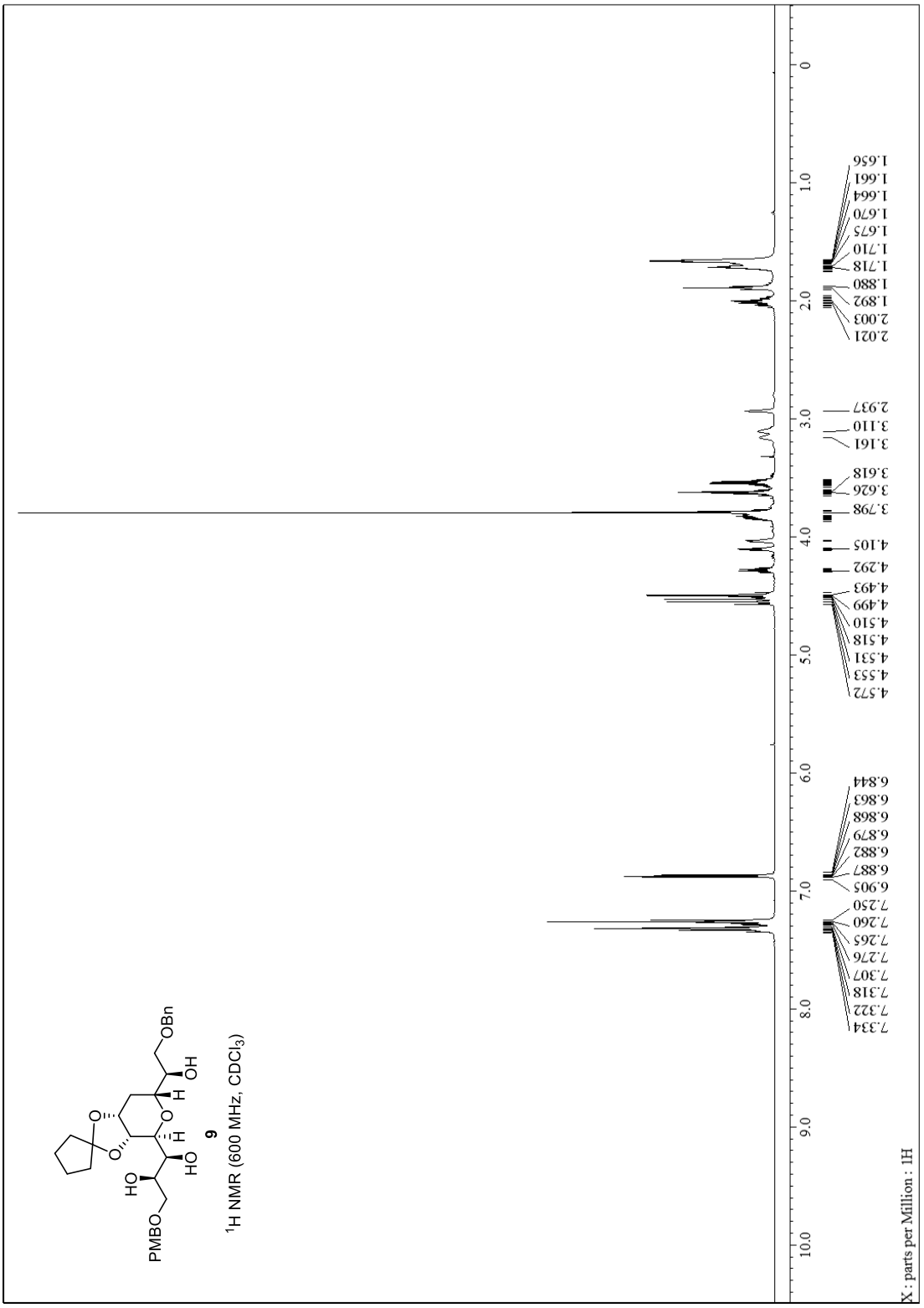
KHMDS (0.5 M in toluene, 64 μL, 32.0 μmol) was added dropwise to a solution of sulfone **25** (18.3 mg, 44.6 μmol) in THF (0.82 mL) at −78 °C, and the solution was stirred for 15 min. After a solution of crude aldehyde **24** in THF (1.1 mL) was added to the resulting solution, the reaction mixture was allowed to warm to room temperature and stirred for 18 h at the temperature. The resultant mixture was quenched with saturated aqueous NH_4Cl at 0 °C and extracted with EtOAc. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was roughly purified by flash silica gel column chromatography (hexane/EtOAc = 100/1 → 5/1) to afford **26** as a mixture of *E* and *Z* isomers in a 2 :1 ratio (11.2 mg), which was used in the next reaction without further purification.

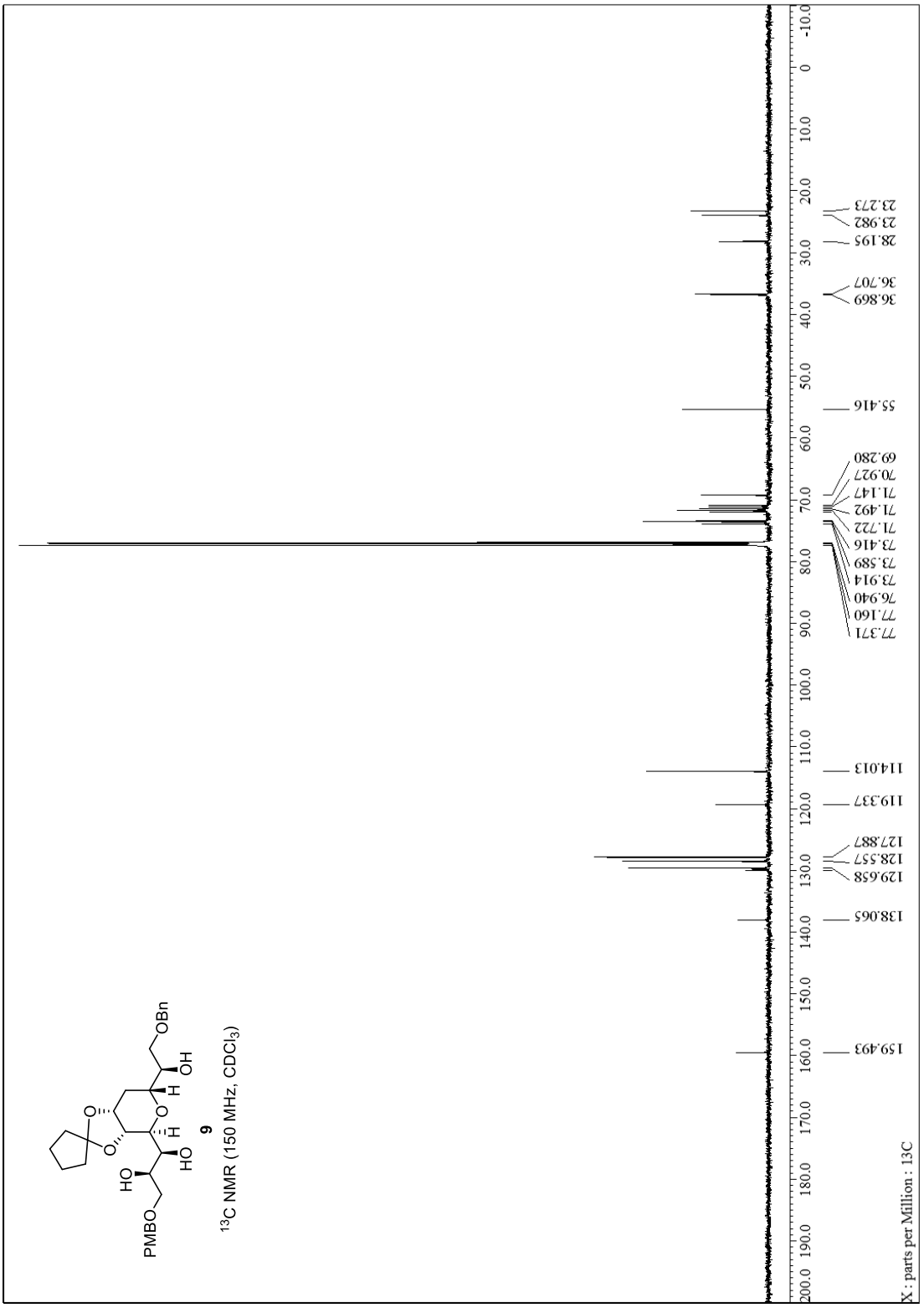
18% HF·Py (ca. 9.6 M in Py, 180 μL, 1.7 mmol) was added to a solution of above crude **26** in THF (1.7 mL) at 0 °C and stirred at 50 °C for 2 days. 18% HF·Py (90 μL, 0.9 mmol) and MeOH (0.3 mL) were added to the reaction mixture and stirred at 50 °C for 1 day. While stirring at 50 °C, the reaction mixture was treated with 70% HF·Py (90 μL, 3.5 mmol) for three times after 1day, 2 days, and 5 days. After 1 day from the final addition of HF·Py, the reaction mixture was quenched with Et_3N. The resultant mixture was concentrated by blowing argon stream. Purification by reversed phase column chromatography (ODS, H_2O/MeOH = 1/1 → 1/3) afforded a crude mixture (4.5 mg). Further purification by HPLC (ODS, C18-MS-II Waters 10 × 250 mm column, eluted with 65% MeOH in water, 4.5 mL/min, detected at 260 nm) afforded the designed analog **3** (1.2 mg, 1.6 μmol, 7% for three steps) as a colorless solid.

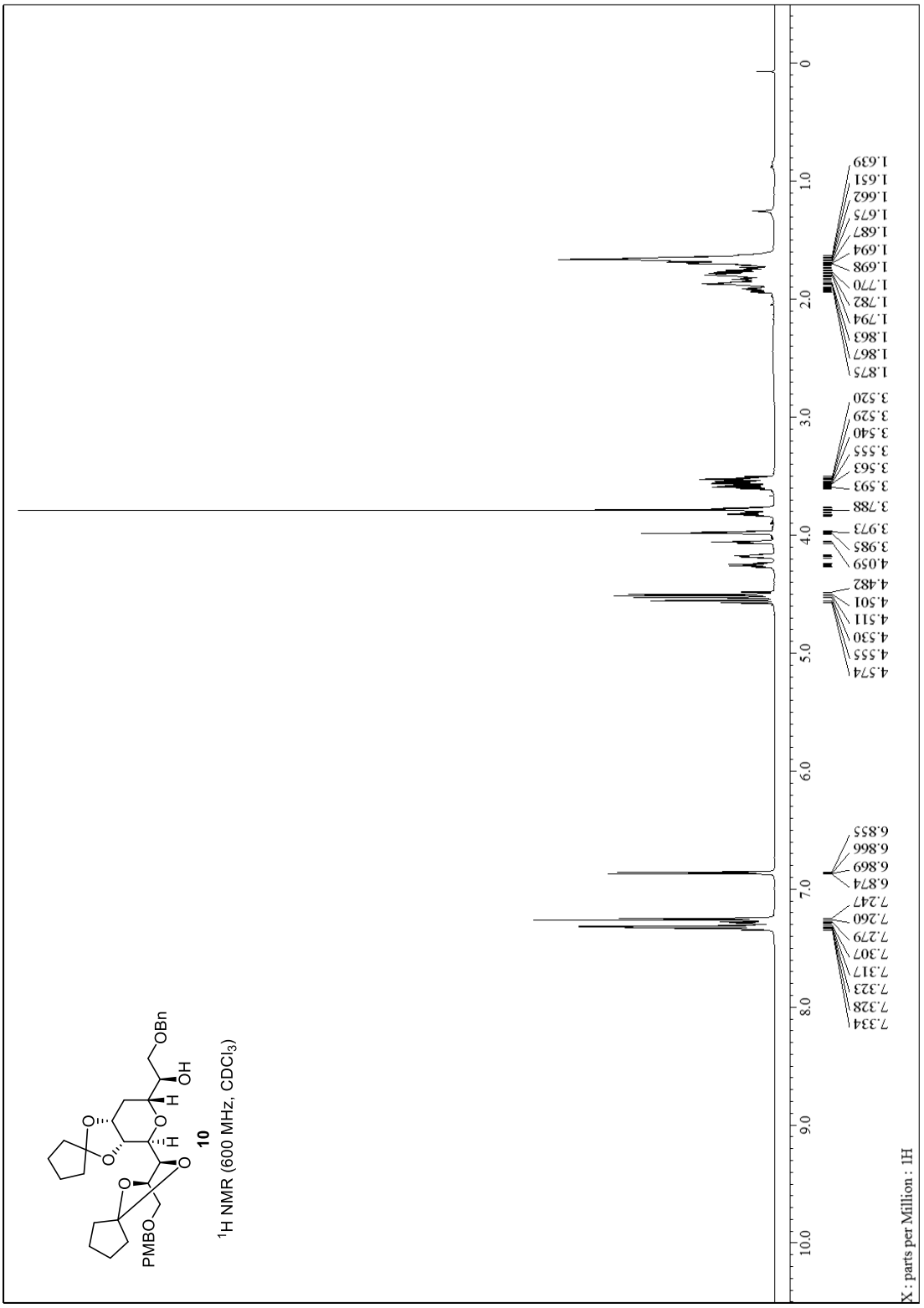
R_f = 0.50 (ODS, MeOH/H_2O = 4/1); $[\alpha]^{18}_D$ +3.8 (*c* 0.12, MeOH); IR (neat) 3337, 995, 726, 687, 669 cm^{-1}; ^1H NMR (600 MHz, CD_3OD/C_5D_5N = 2:1, micro-bottomed tube SP-504, residual CHD_2OD was adjusted to 3.31 ppm) δ 6.26 (ddd, *J* = 17.4, 10.2, 10.2 Hz, 1H), 6.08–5.97 (m, 5H), 5.79–5.75 (m, 2H), 5.66–5.56 (m, 3H), 5.04 (d, *J* = 17.4 Hz, 1H), 4.90 (d, *J* = 10.2 Hz, 1H), 4.85 (s, 1H), 4.84 (s, 1H), 4.42 (brs, 1H), 4.30 (brs, 1H), 4.27–4.20 (m, 3H), 4.14–4.09 (m, 3H), 4.06 (dd, *J* = 5.4, 5.4 Hz, 1H), 3.90–3.84 (m, 2H), 3.82–3.79 (m, 2H), 3.64–3.55 (m, 3H), 2.37–2.29 (m, 2H), 2.26 (dd, *J* = 12.0, 9.6 Hz, 1H), 2.23–2.15 (m, 1H), 2.14–1.98 (m, 10H), 1.78–1.60 (m, 4H). 11 protons are missing due to H/D exchange; ^{13}C NMR (150 MHz, CD_3OD/C_5D_5N = 2:1, micro-bottomed tube SP-504, residual CD_3OD was adjusted to 49.00 ppm) δ 147.8, 138.5, 135.3, 134.5, 134.2, 132.7, 132.5, 132.33, 132.26, 132.2 (3C), 115.5, 112.3, 78.4, 78.3, 75.2, 75.1, 73.9, 72.6, 72.4, 72.3, 71.0, 69.2, 69.1, 68.2 67.34, 67.25, 64.2, 40.9, 33.53, 33.45, 33.35, 33.31, 33.1, 32.0, 31.60, 31.56; HRMS (ESI-TOF) *m/z* $[M + Na]^+$ calcd for $C_{38}H_{60}O_{13}Na$ 747.3926, found 747.3927.

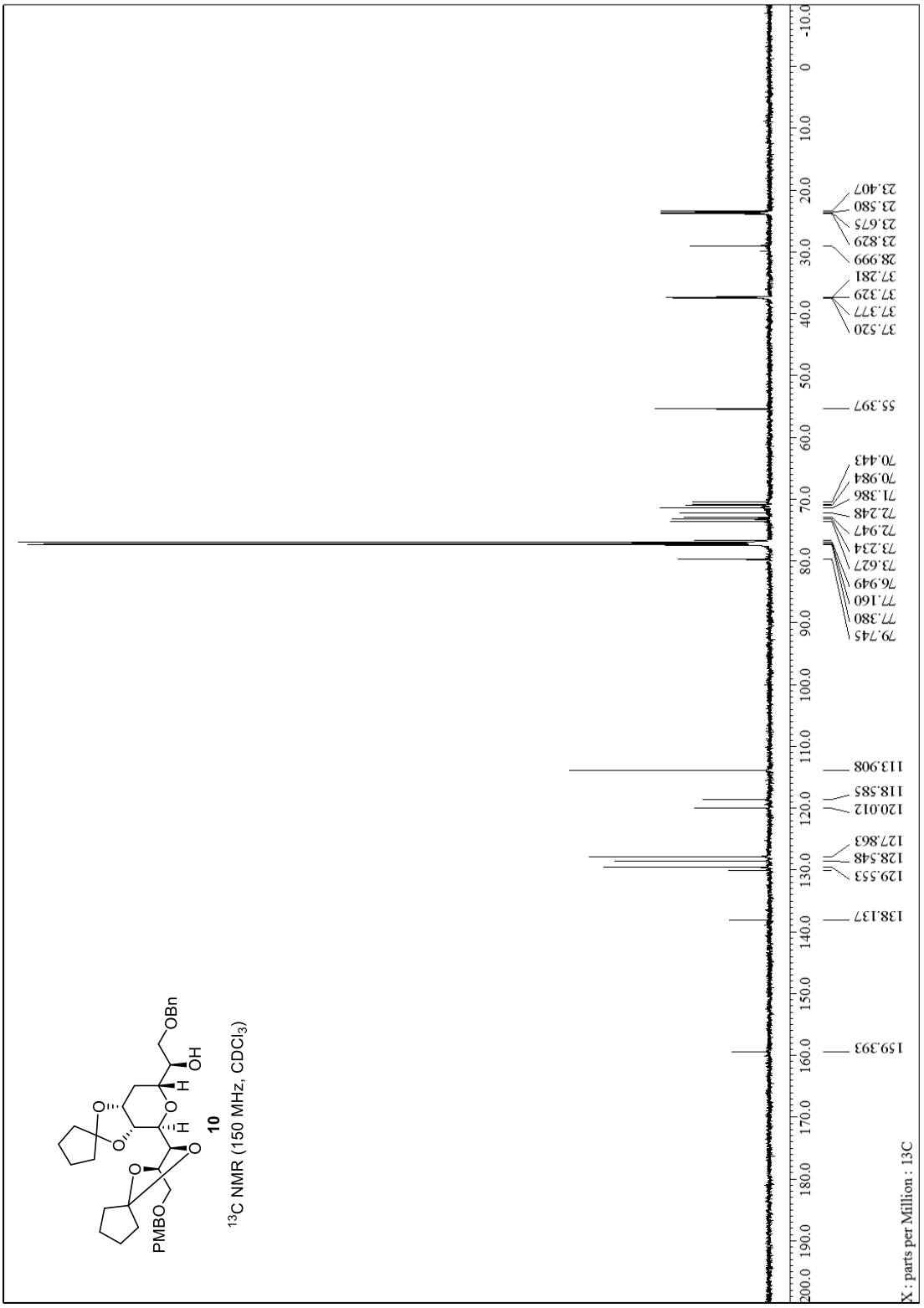

PMBO
OBn
OH
H
H
O
O
O
O
8
^{1}H NMR (600 MHz, CDCl$_3$)
X : parts per Million : 1H
7.337
7.326
7.323
7.313
7.270
7.267
7.260
7.255
6.883
6.880
6.873
6.869
5.914
5.912
5.888
5.886
5.812
5.806
5.803
5.777
4.586
4.565
4.540
4.519
4.447
4.238
4.016
4.006
3.801
3.587
3.580
3.557
3.548
2.648
1.935
1.930
1.923
1.910
1.719
1.709
1.688
1.683
1.678
1.670

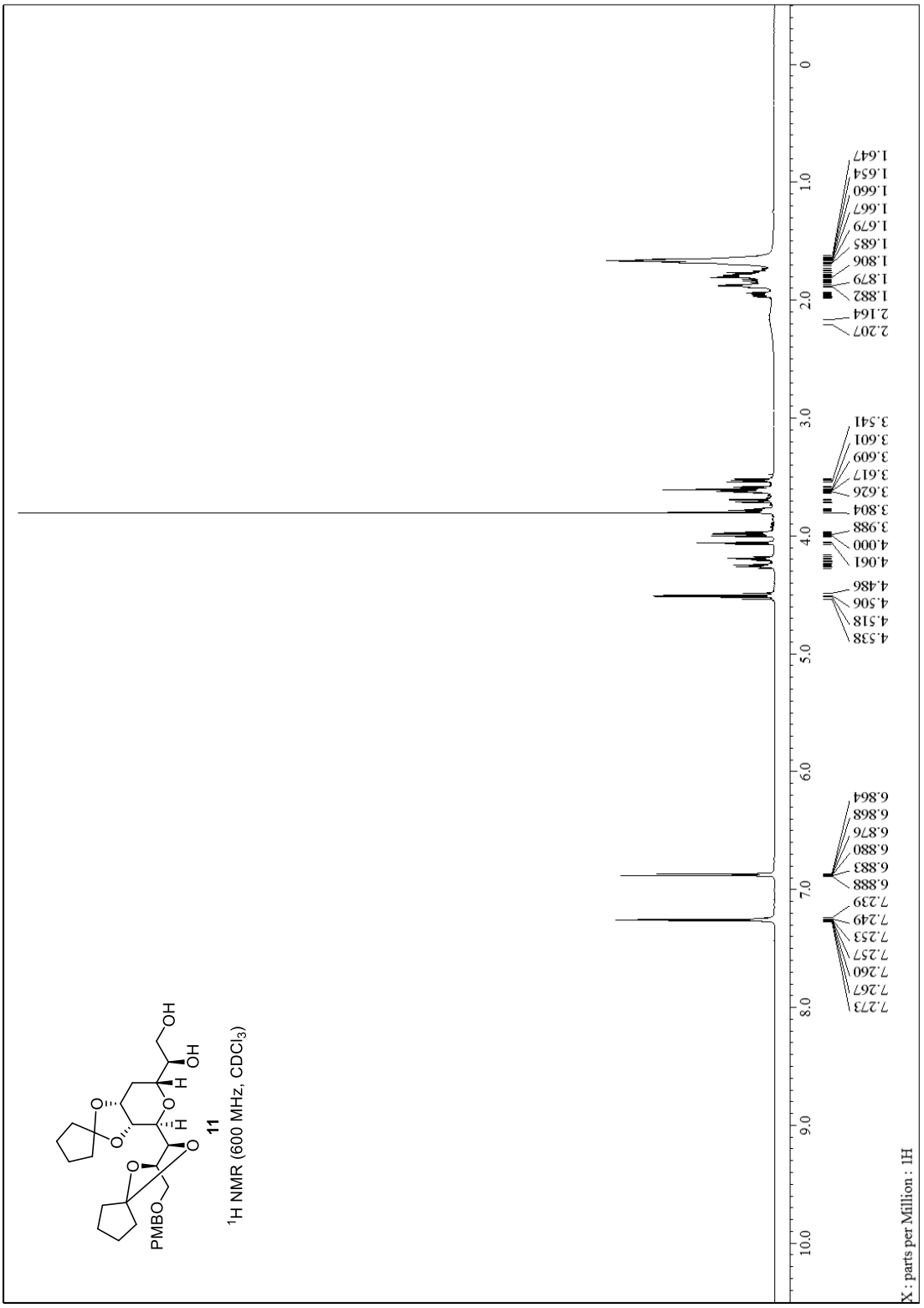

PMBO
OBn
OH
H
H
O
O
O
O
8
^{13}C NMR (150 MHz, $CDCl_3$)
159.379
138.118
129.563
128.557
127.873
118.782
113.941
77.371
77.160
76.949
75.298
73.656
72.574
72.430
72.219
71.051
69.950
69.883
55.416
37.300
37.176
29.152
23.886
23.407
X : parts per Million : 13C

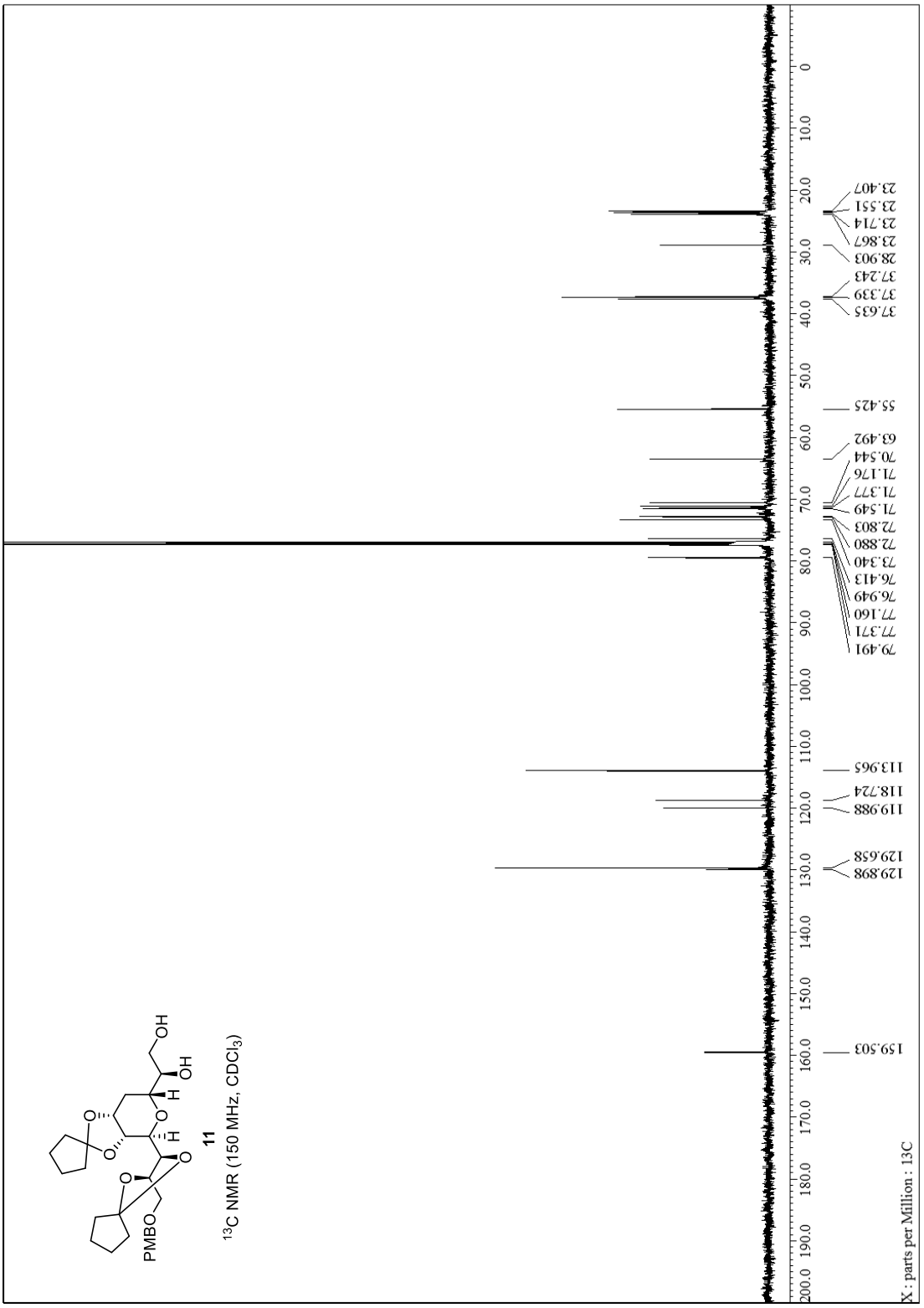

OBn
OH
H
O
O
O
H
HO
HO
PMBO
9
^{1}H NMR (600 MHz, $CDCl_3$)
7.334
7.322
7.318
7.307
7.276
7.265
7.260
7.250
6.905
6.887
6.882
6.879
6.868
6.863
6.844
4.572
4.553
4.531
4.518
4.510
4.499
4.493
4.292
4.105
3.798
3.626
3.618
3.161
3.110
2.937
2.021
2.003
1.892
1.880
1.718
1.710
1.675
1.670
1.664
1.661
1.656
X : parts per Million : 1H

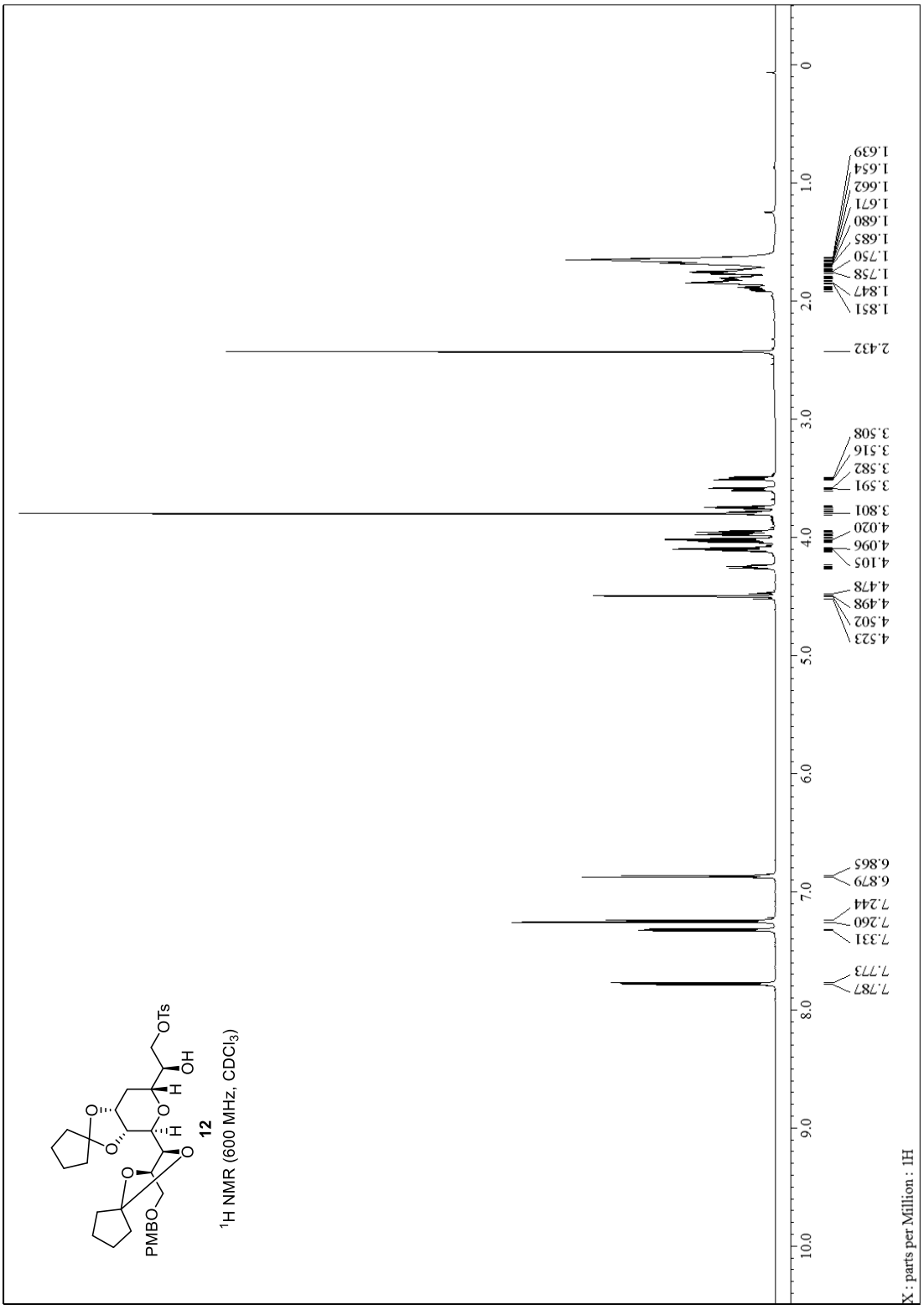

PMBO
HO
HO
H
O
O
O
O
H
OH
OBn
9
^{13}C NMR (150 MHz, CDCl$_3$)
159.493
138.065
129.658
128.557
127.887
119.337
114.013
77.371
77.160
76.940
73.914
73.589
73.416
71.722
71.492
71.147
70.927
69.280
55.416
36.869
36.707
28.195
23.982
23.273
X : parts per Million : 13C

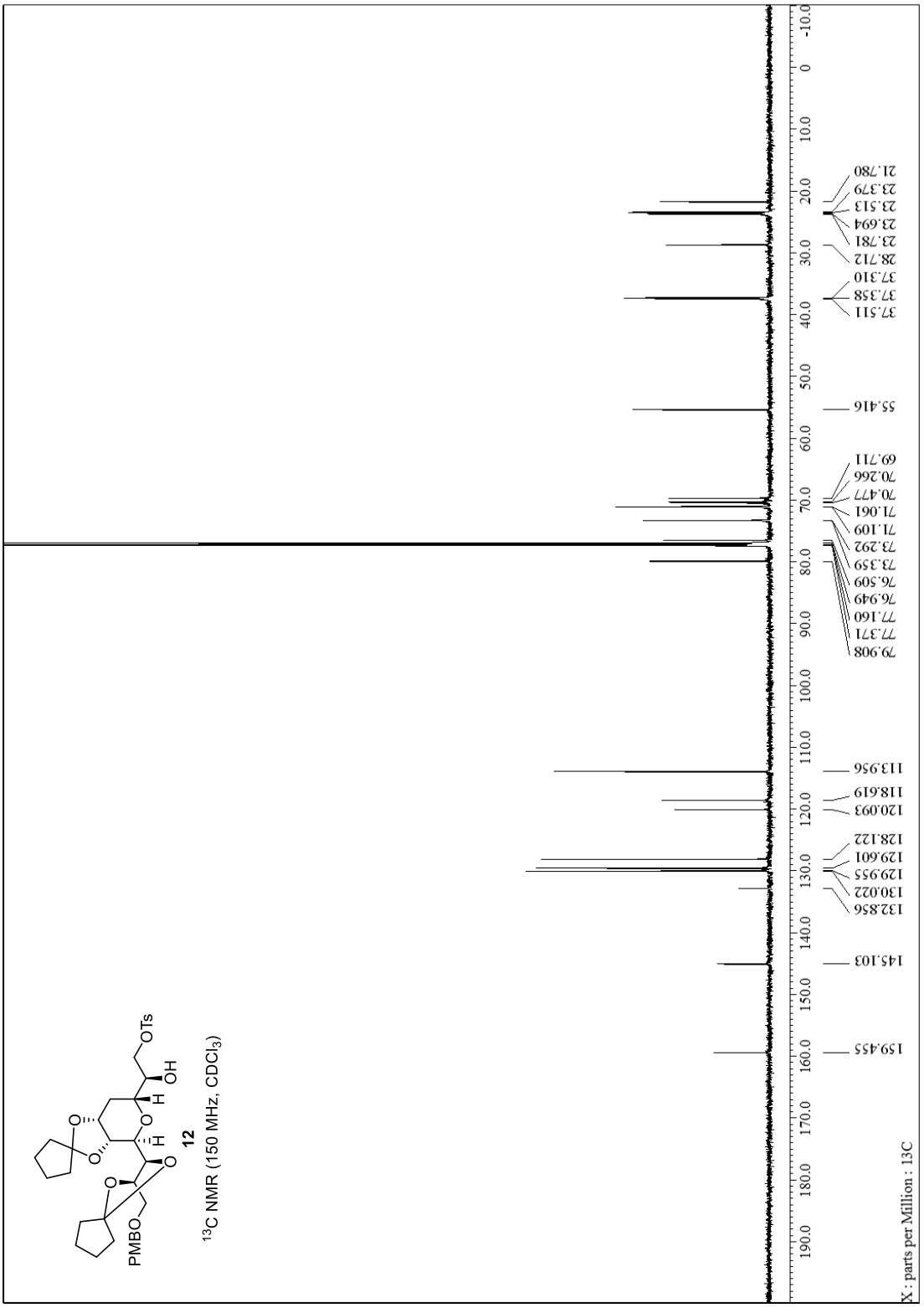

OBn
OH
PMBO
10
^{1}H NMR (600 MHz, CDCl$_3$)
X : parts per Million : 1H

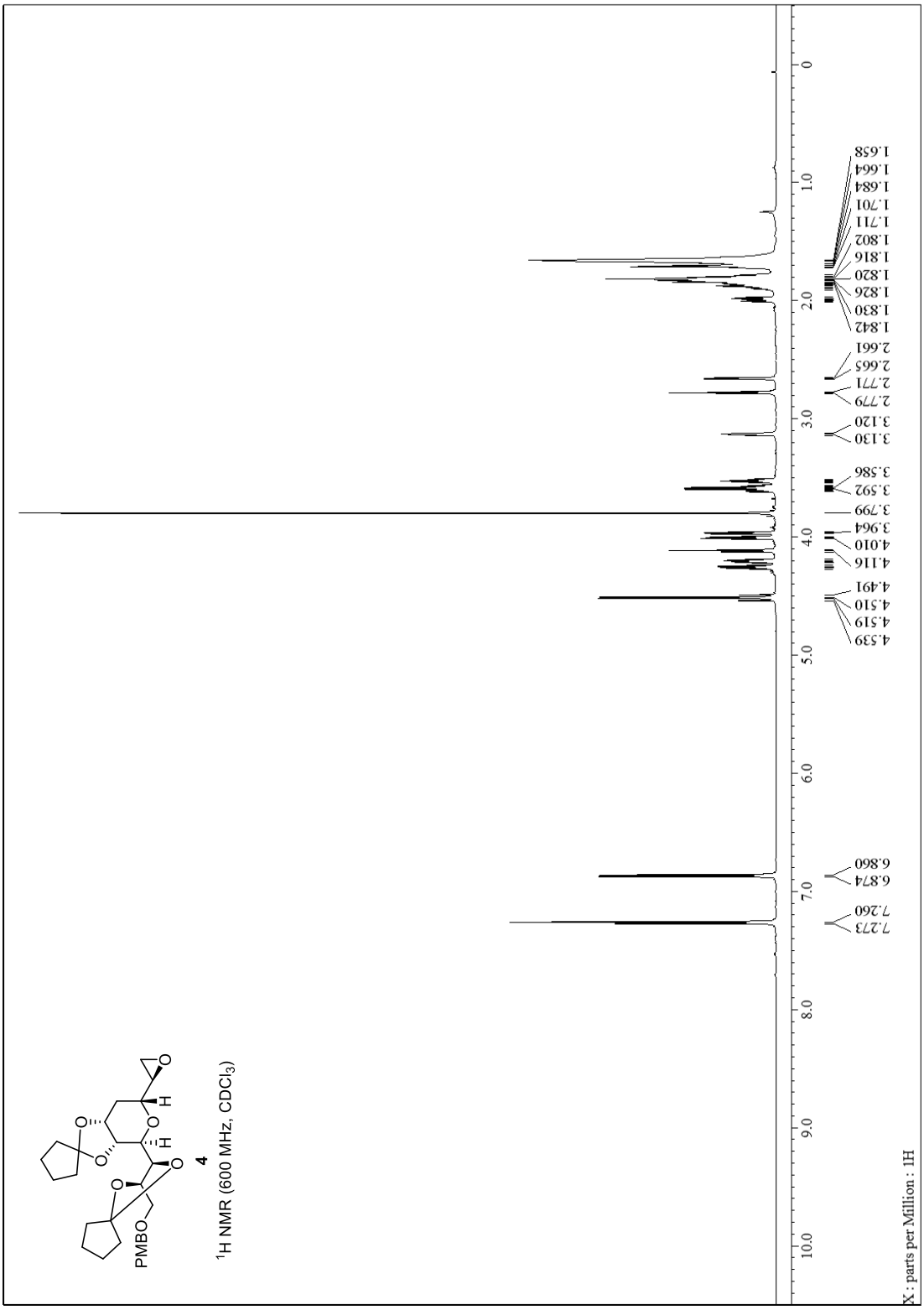

PMBO
OBn
OH
10
^{13}C NMR (150 MHz, $CDCl_3$)
159.393
138.137
129.553
128.548
127.863
120.012
118.585
113.908
79.745
77.380
77.160
76.949
73.627
73.234
72.947
72.248
71.386
70.984
70.443
55.397
37.520
37.377
37.329
37.281
28.999
23.829
23.675
23.580
23.407
X : parts per Million : 13C

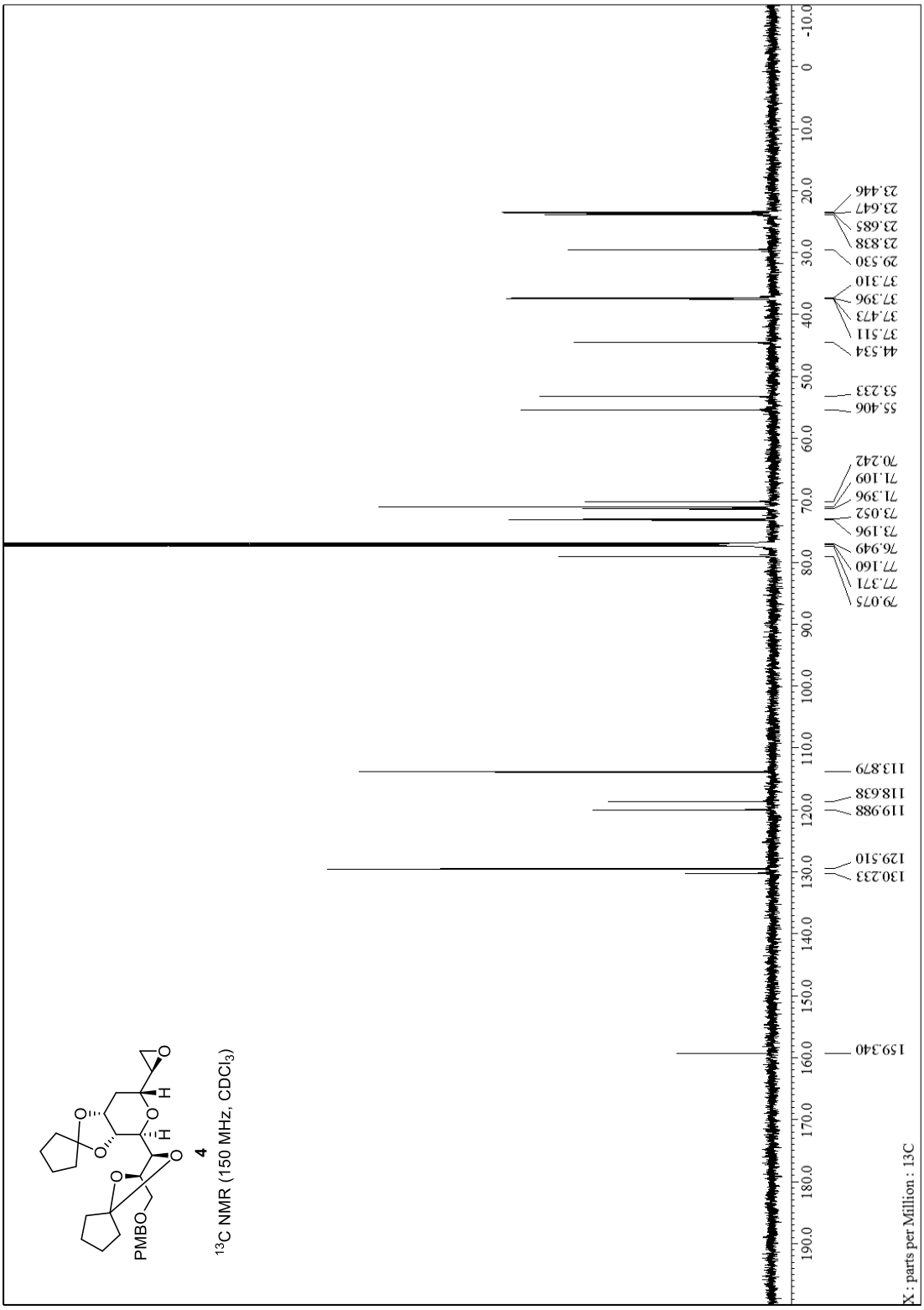

PMBO
OH
OH
H
H
O
O
O
O
O
O
11
^{1}H NMR (600 MHz, $CDCl_3$)
7.273
7.267
7.260
7.257
7.253
7.249
7.239
6.888
6.883
6.880
6.876
6.868
6.864
4.538
4.518
4.506
4.486
4.061
4.000
3.988
3.804
3.626
3.617
3.609
3.601
3.541
2.207
2.164
1.882
1.879
1.806
1.685
1.679
1.667
1.660
1.654
1.647
X : parts per Million : 1H

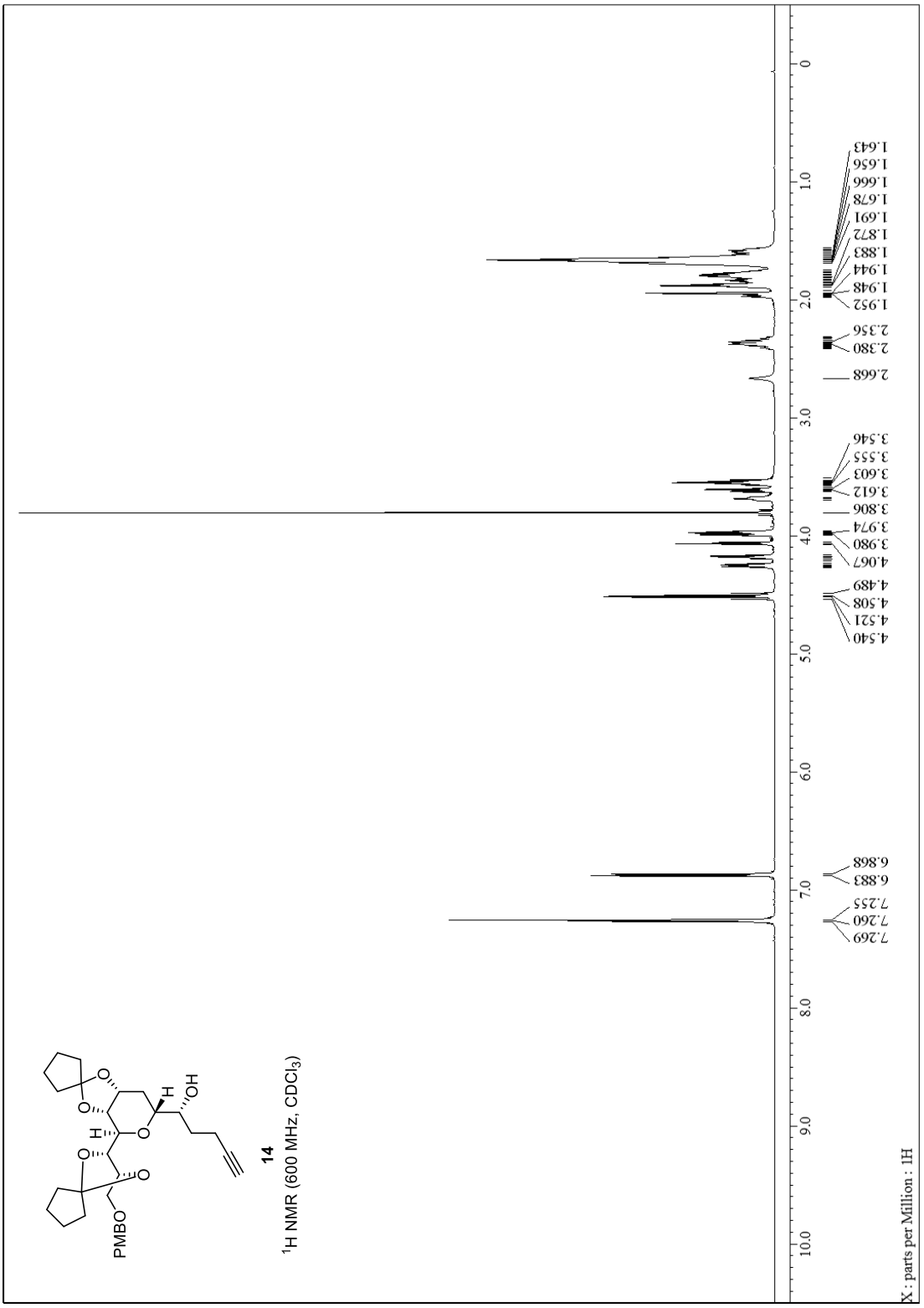

PMBO
OH
OH
H
H
O
O
O
O
O
O
11
^{13}C NMR (150 MHz, $CDCl_3$)
159.503
129.898
129.658
119.988
118.724
113.965
79.491
77.371
77.160
76.949
76.413
73.340
72.880
72.803
71.549
71.377
71.176
70.544
63.492
55.425
37.635
37.339
37.243
28.903
23.867
23.714
23.551
23.407
X : parts per Million : 13C

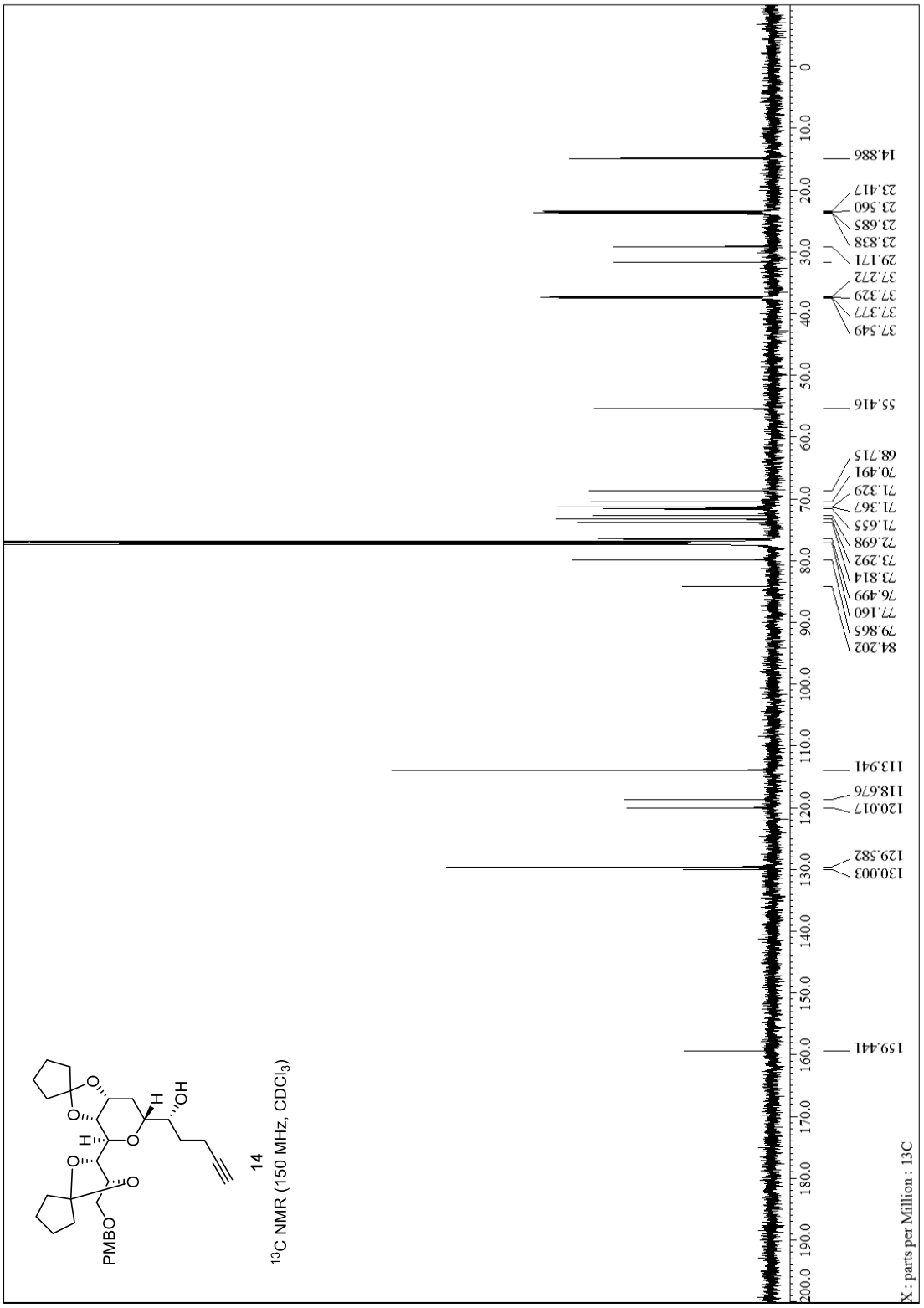

PMBO
OTs
OH
H
H
O
O
O
O
O
O
12
^{1}H NMR (600 MHz, CDCl$_3$)
X : parts per Million : 1H
7.787
7.773
7.331
7.260
7.244
6.879
6.865
4.523
4.502
4.498
4.478
4.105
4.096
4.020
3.801
3.591
3.582
3.516
3.508
2.432
1.851
1.847
1.758
1.750
1.685
1.680
1.671
1.662
1.654
1.639

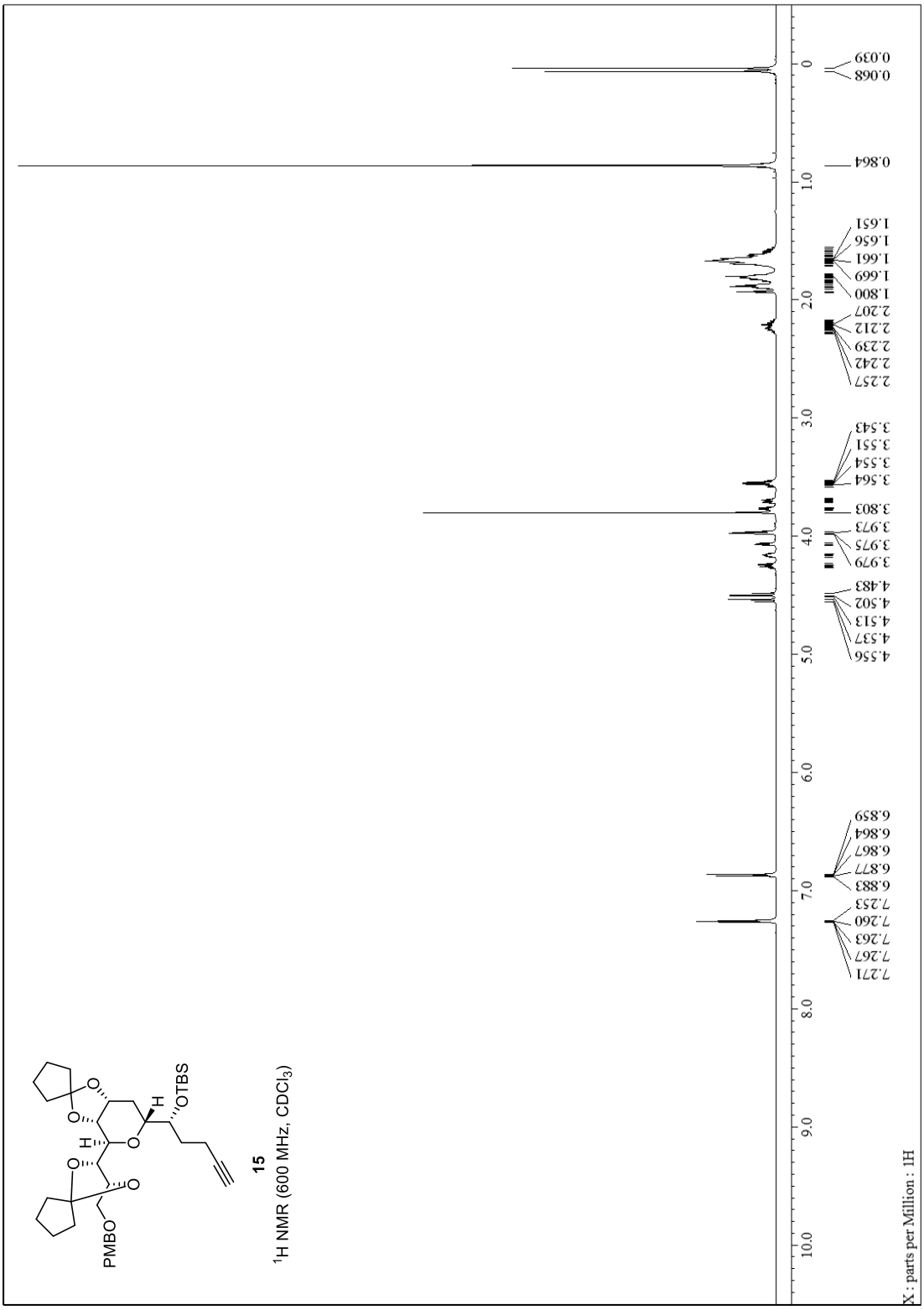

PMBO
OTs
OH
H
H
12
^{13}C NMR (150 MHz, $CDCl_3$)
159.455
145.103
132.856
130.022
129.955
129.601
128.122
120.093
118.619
113.956
79.908
77.371
77.160
76.949
76.509
73.359
73.292
71.109
71.061
70.477
70.266
69.711
55.416
37.511
37.358
37.310
28.712
23.781
23.694
23.513
23.379
21.780
X : parts per Million : 13C

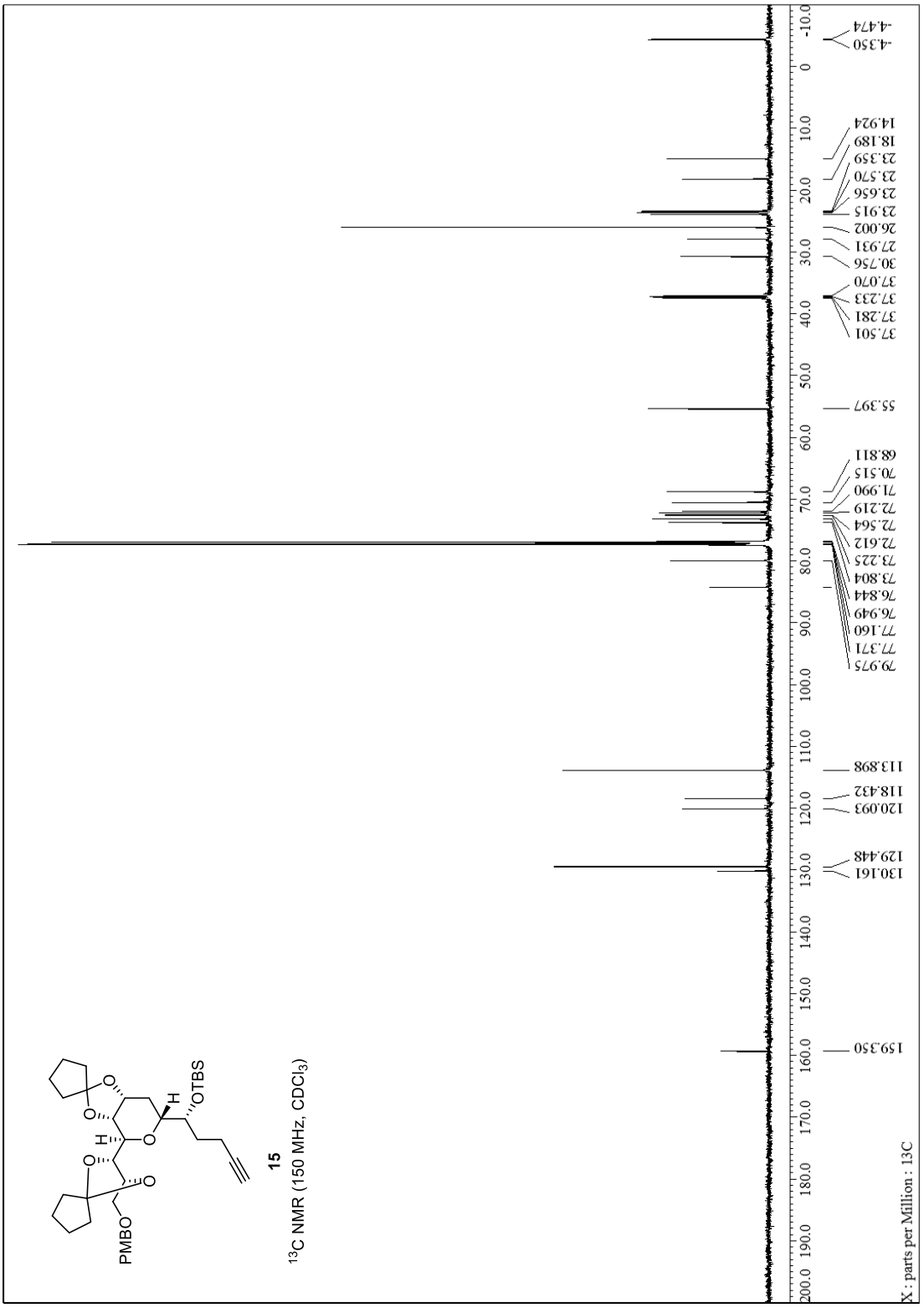

PMBO
4
^{1}H NMR (600 MHz, $CDCl_3$)
7.273
7.260
6.874
6.860
4.539
4.519
4.510
4.491
4.116
4.010
3.964
3.799
3.592
3.586
3.130
3.120
2.779
2.771
2.665
2.661
1.842
1.830
1.826
1.820
1.816
1.802
1.711
1.701
1.684
1.664
1.658
X : parts per Million : 1H

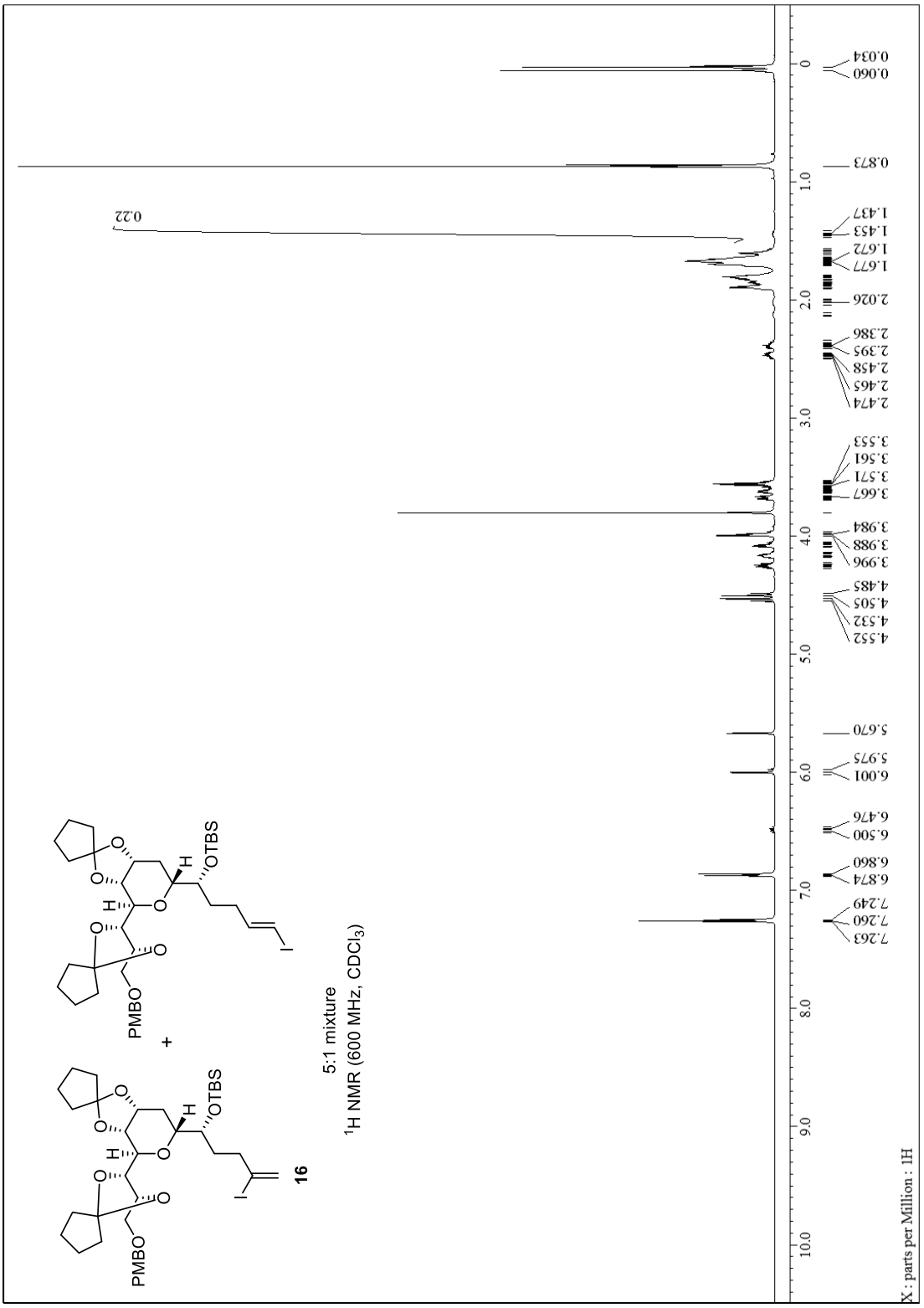

PMBO
4
^{13}C NMR (150 MHz, $CDCl_3$)
159.340
130.233
129.510
119.988
118.638
113.879
79.075
77.371
77.160
76.949
73.196
73.052
71.396
71.109
70.242
55.406
53.233
44.534
37.511
37.473
37.396
37.310
29.530
23.838
23.685
23.647
23.446
X : parts per Million : 13C

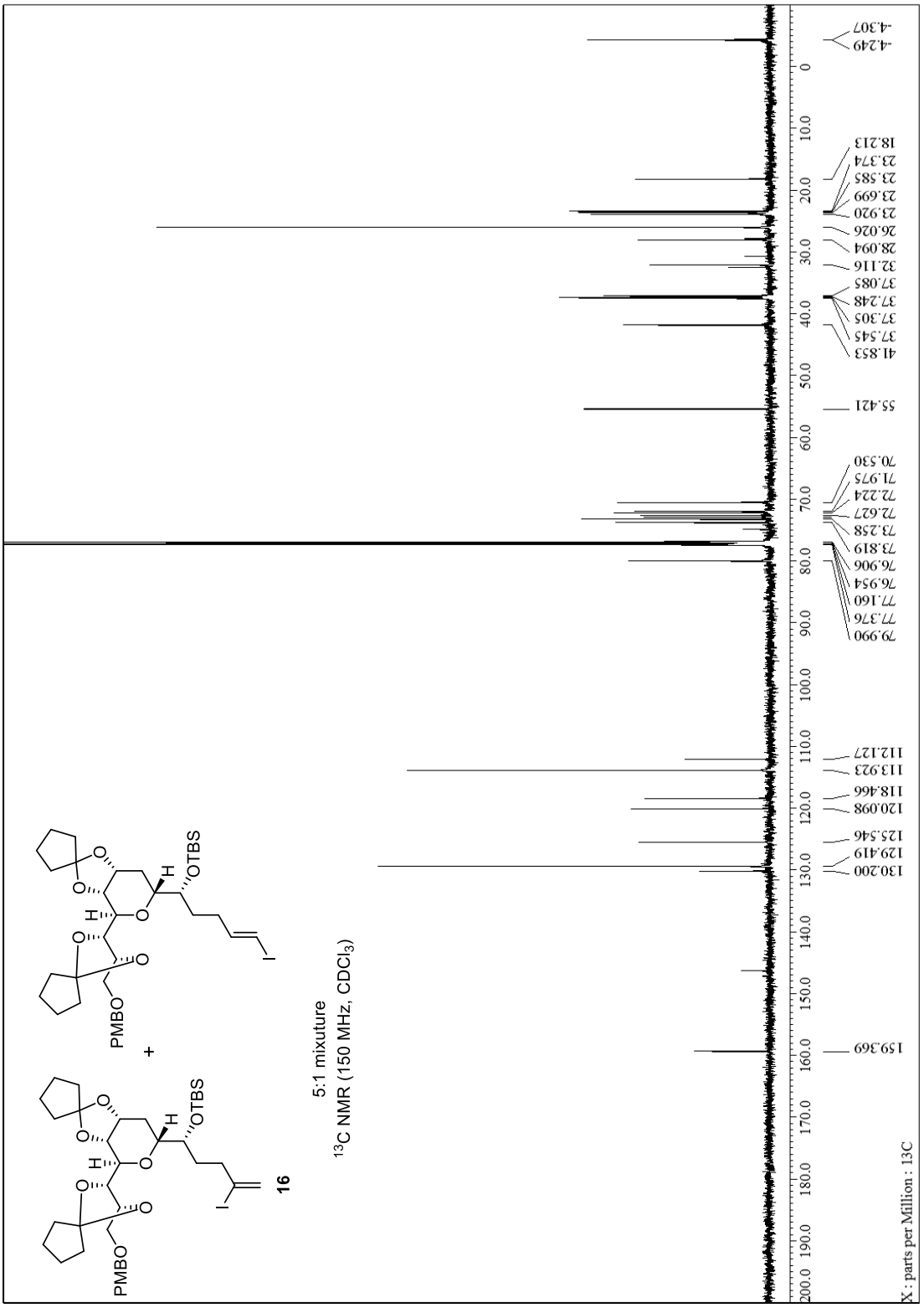

PMBO
OH
14
^{1}H NMR (600 MHz, $CDCl_3$)
X : parts per Million : 1H

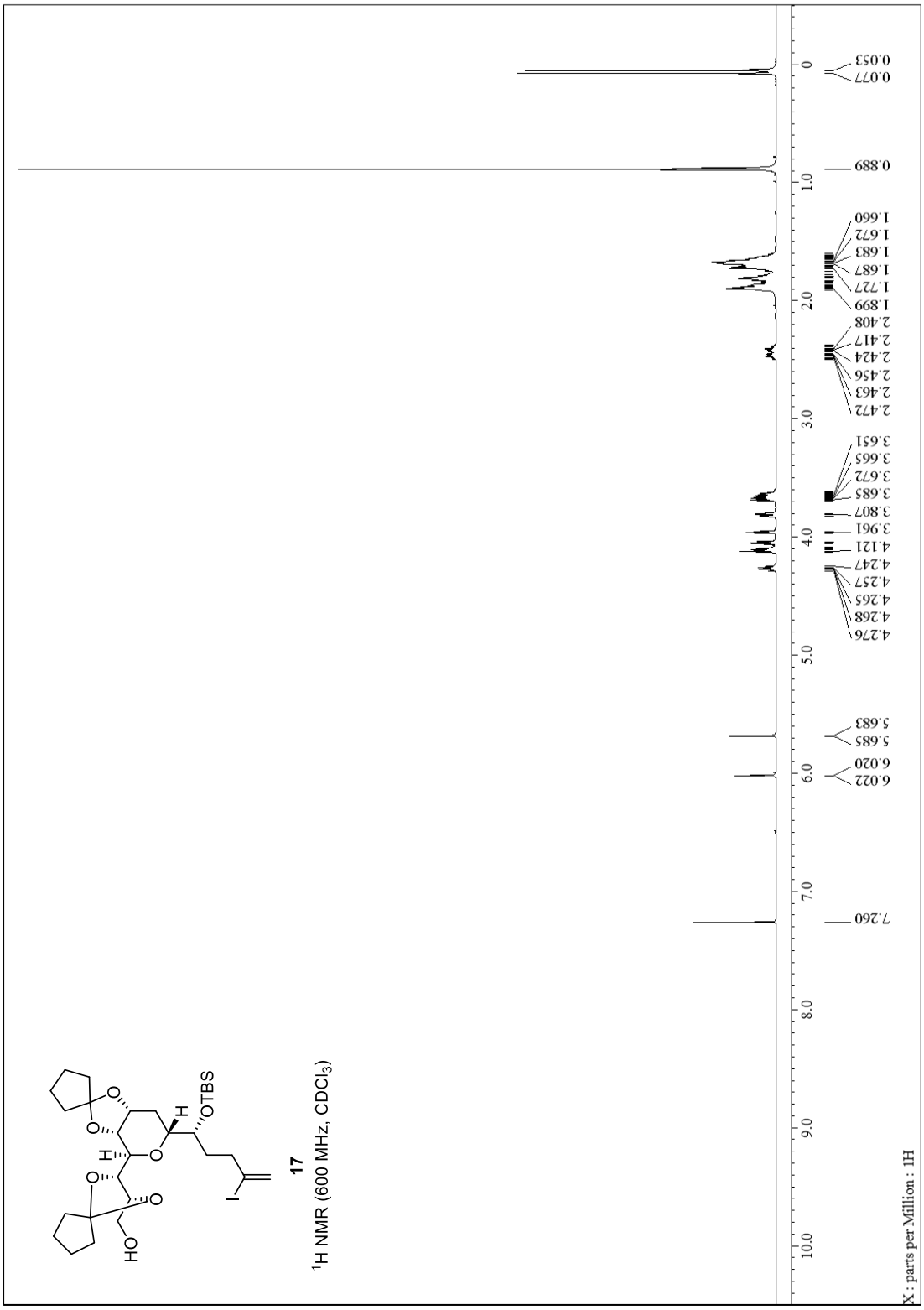

14
^{13}C NMR (150 MHz, $CDCl_3$)
PMBO
OH
H
H
O
14.886
23.417
23.560
23.685
23.838
29.171
37.272
37.329
37.377
37.549
55.416
68.715
70.491
71.329
71.367
71.655
72.698
73.292
73.814
76.499
77.160
79.865
84.202
113.941
118.676
120.017
129.582
130.003
159.441
X : parts per Million : 13C

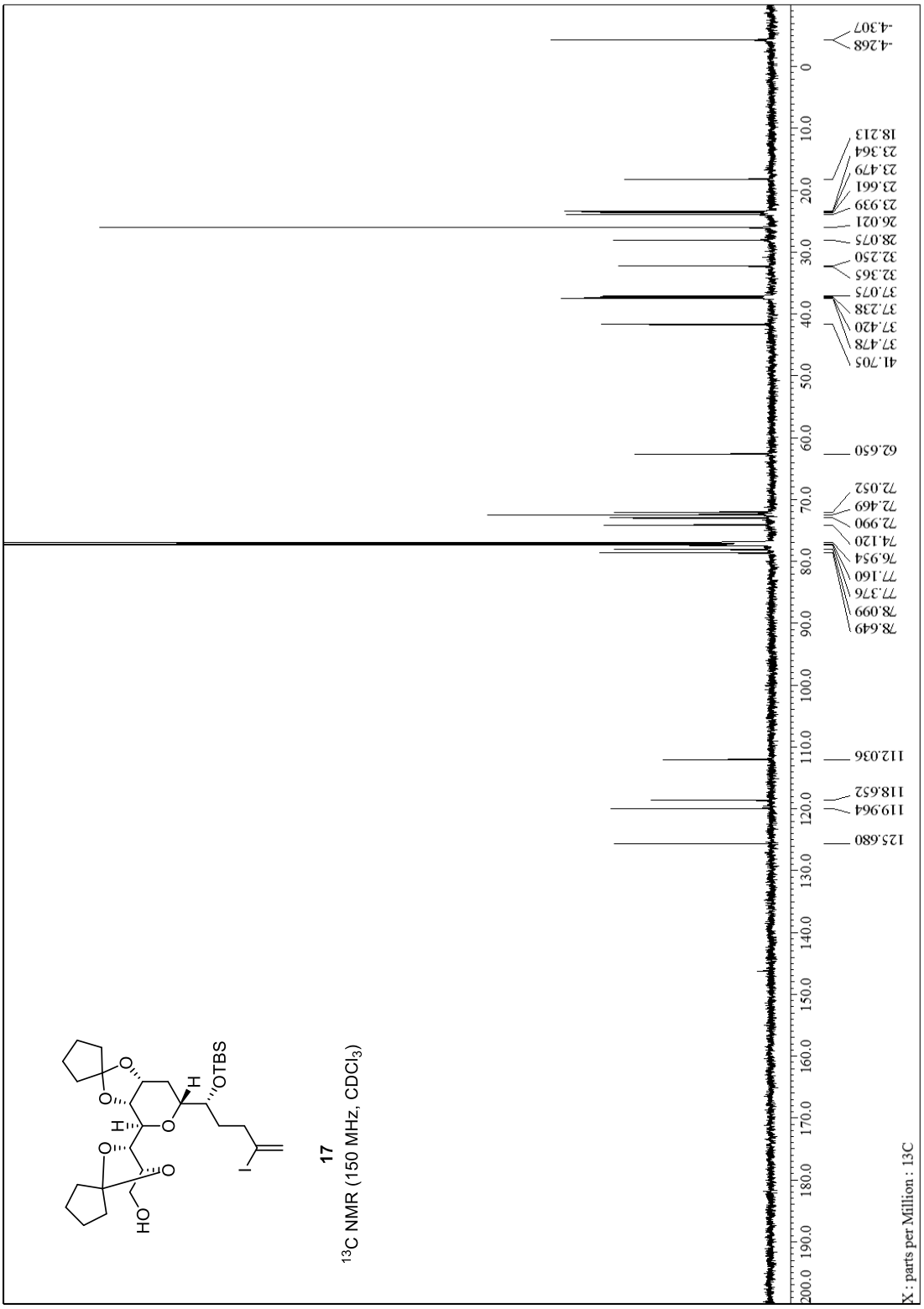

PMBO
OTBS
H
H
O
O
O
O
O
O
15
^{1}H NMR (600 MHz, $CDCl_3$)
0.039
0.068
0.864
1.651
1.656
1.661
1.669
1.800
2.207
2.212
2.239
2.242
2.257
3.543
3.551
3.554
3.564
3.803
3.973
3.975
3.979
4.483
4.502
4.513
4.537
4.556
6.859
6.864
6.867
6.877
6.883
7.253
7.260
7.263
7.267
7.271
X : parts per Million : 1H

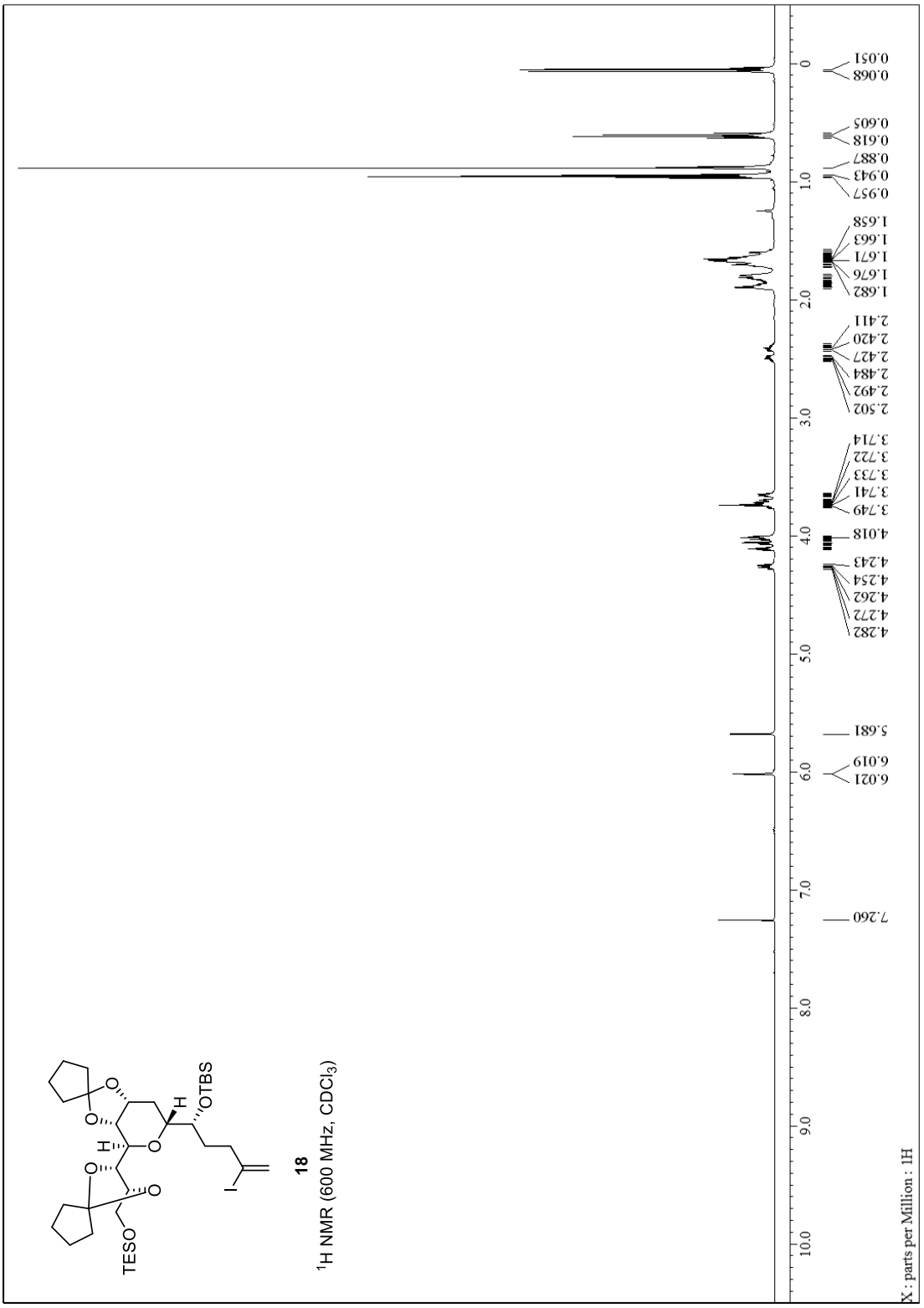

PMBO
OTBS
H
H
15
^{13}C NMR (150 MHz, $CDCl_3$)
-4.474
-4.350
14.924
18.189
23.359
23.570
23.656
23.915
26.002
27.931
30.756
37.070
37.233
37.281
37.501
55.397
68.811
70.515
71.990
72.219
72.564
72.612
73.225
73.804
76.844
76.949
77.160
77.371
79.975
113.898
118.432
120.093
129.448
130.161
159.350
X : parts per Million : 13C

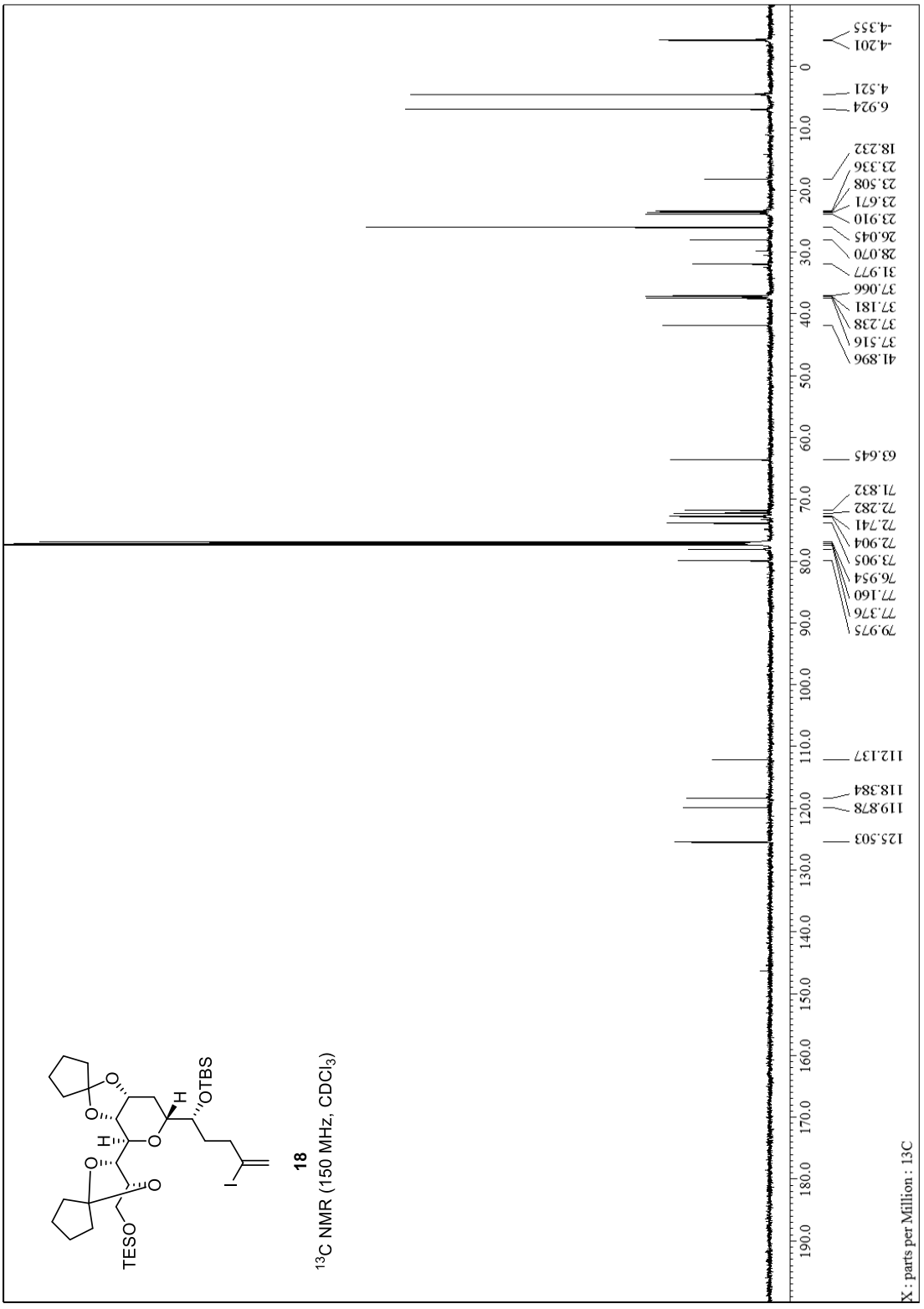

PMBO
OTBS
+
PMBO
OTBS
16
5:1 mixture
^{1}H NMR (600 MHz, $CDCl_3$)
0.22
0.873
0.060
0.034
1.437
1.453
1.672
1.677
2.026
2.386
2.395
2.458
2.465
2.474
3.553
3.561
3.571
3.667
3.984
3.988
3.996
4.485
4.505
4.532
4.552
5.670
5.975
6.001
6.476
6.500
6.860
6.874
7.249
7.260
7.263
X : parts per Million : 1H

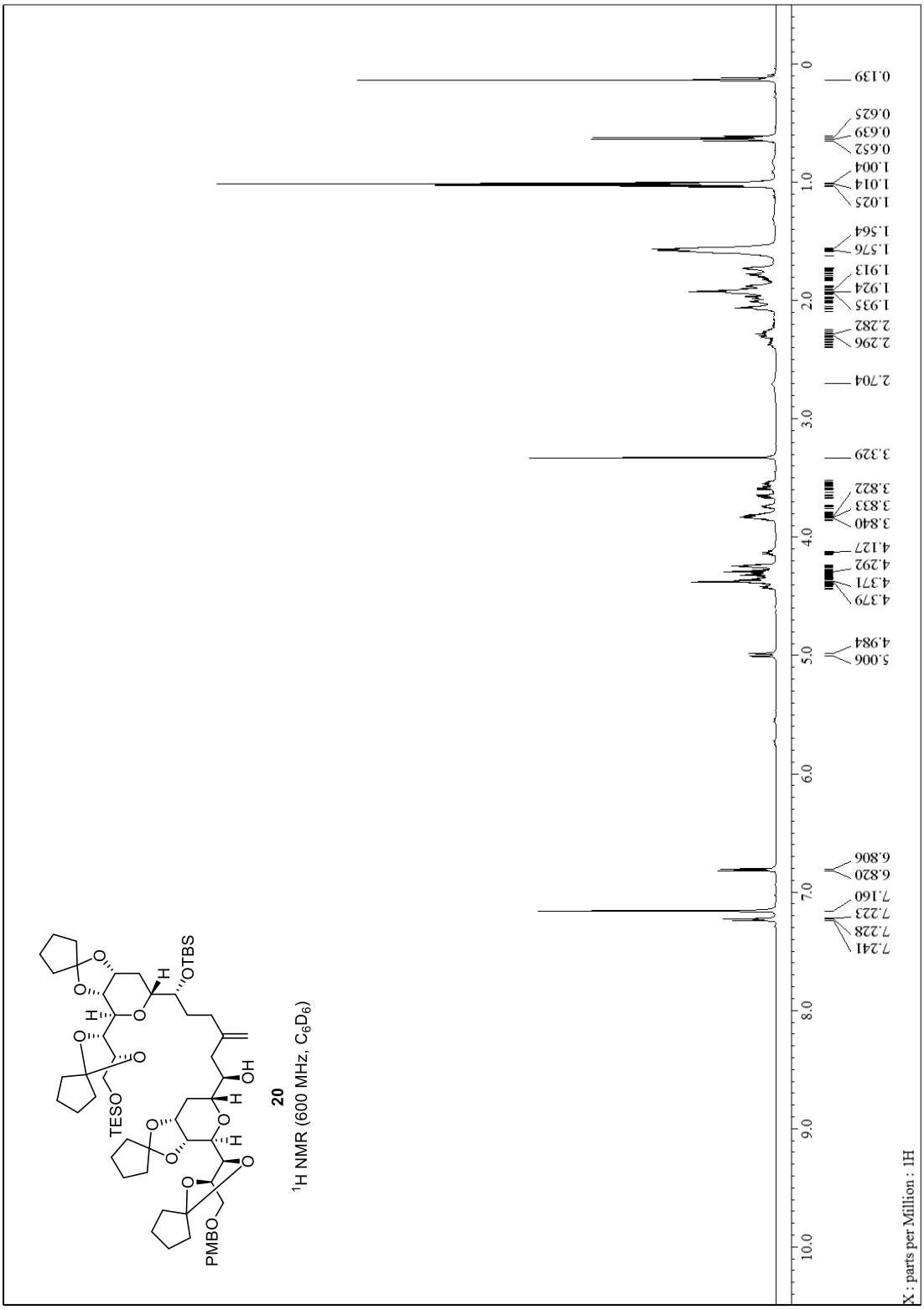

PMBO
OTBS
+
PMBO
OTBS
16
5:1 mixuture
13C NMR (150 MHz, CDCl3)
-4.307
-4.249
18.213
23.374
23.585
23.699
23.920
26.026
28.094
32.116
37.085
37.248
37.305
37.545
41.853
55.421
70.530
71.975
72.224
72.627
73.258
73.819
76.906
76.954
77.160
77.376
79.990
112.127
113.923
118.466
120.098
125.546
129.419
130.200
159.369
X : parts per Million : 13C

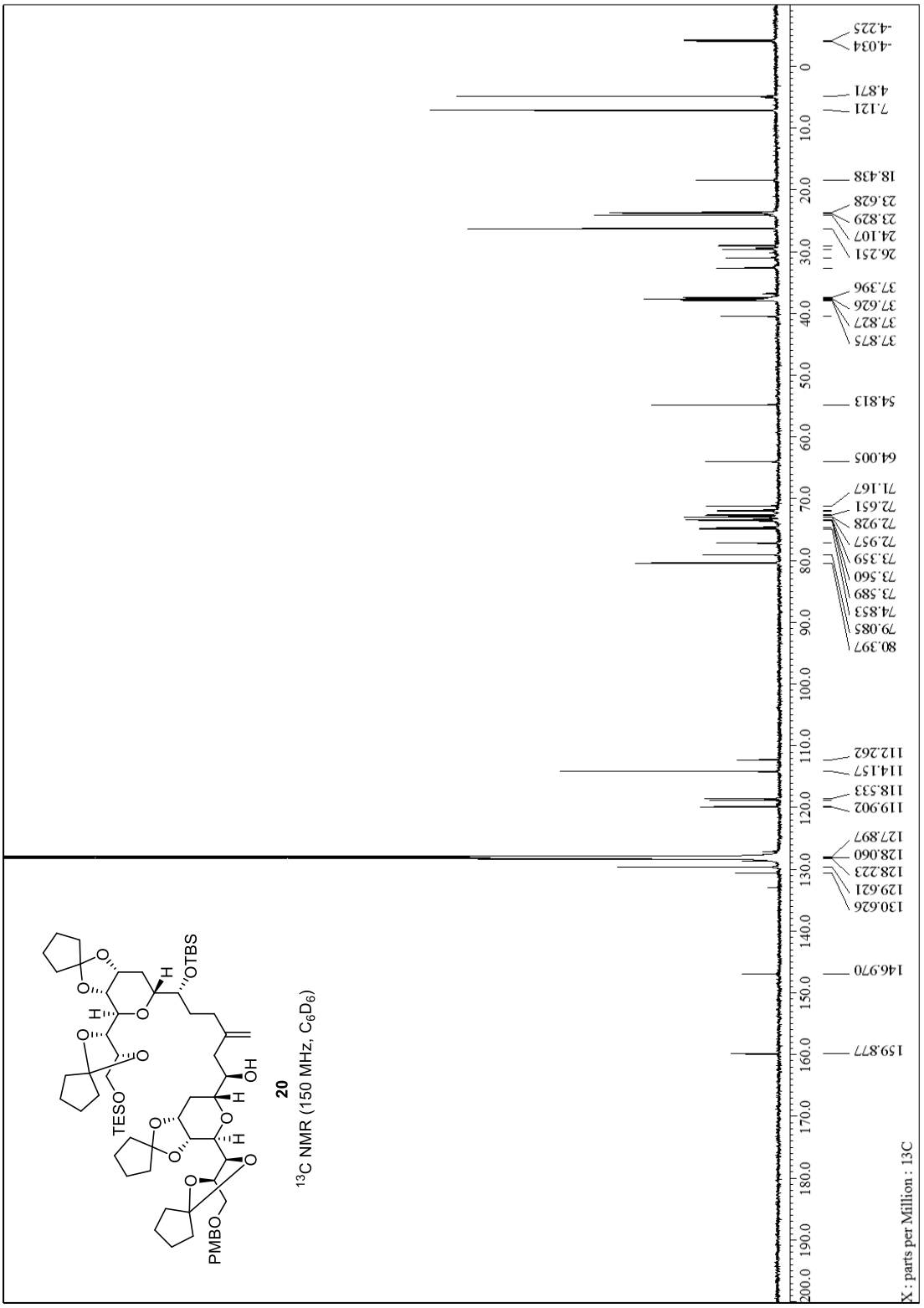

OTBS
HO
17
^{1}H NMR (600 MHz, CDCl$_3$)
0.053
0.077
0.889
1.660
1.672
1.683
1.687
1.727
1.899
2.408
2.417
2.424
2.456
2.463
2.472
3.651
3.665
3.672
3.685
3.807
3.961
4.121
4.247
4.257
4.265
4.268
4.276
5.683
5.685
6.020
6.022
7.260
X : parts per Million : 1H

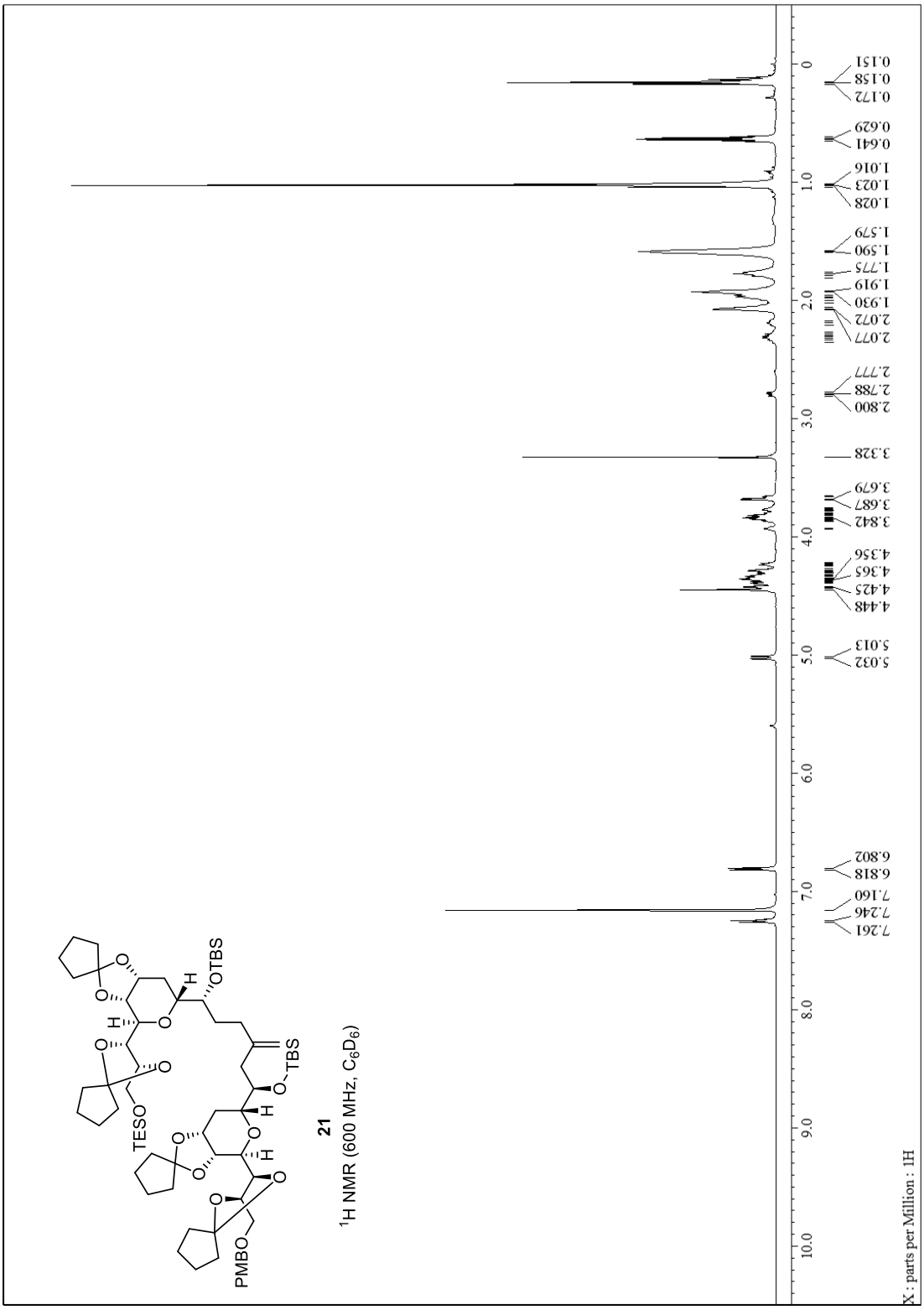

-4.307
-4.268
18.213
23.364
23.479
23.661
23.939
26.021
28.075
32.250
32.365
37.075
37.238
37.420
37.478
41.705
62.650
72.052
72.469
72.990
74.120
76.954
77.160
77.376
78.099
78.649
112.036
118.652
119.964
125.680
0
10.0
20.0
30.0
40.0
50.0
60.0
70.0
80.0
90.0
100.0
110.0
120.0
130.0
140.0
150.0
160.0
170.0
180.0
190.0
200.0
X : parts per Million : 13C
17
13C NMR (150 MHz, CDCl3)
OTBS
HO

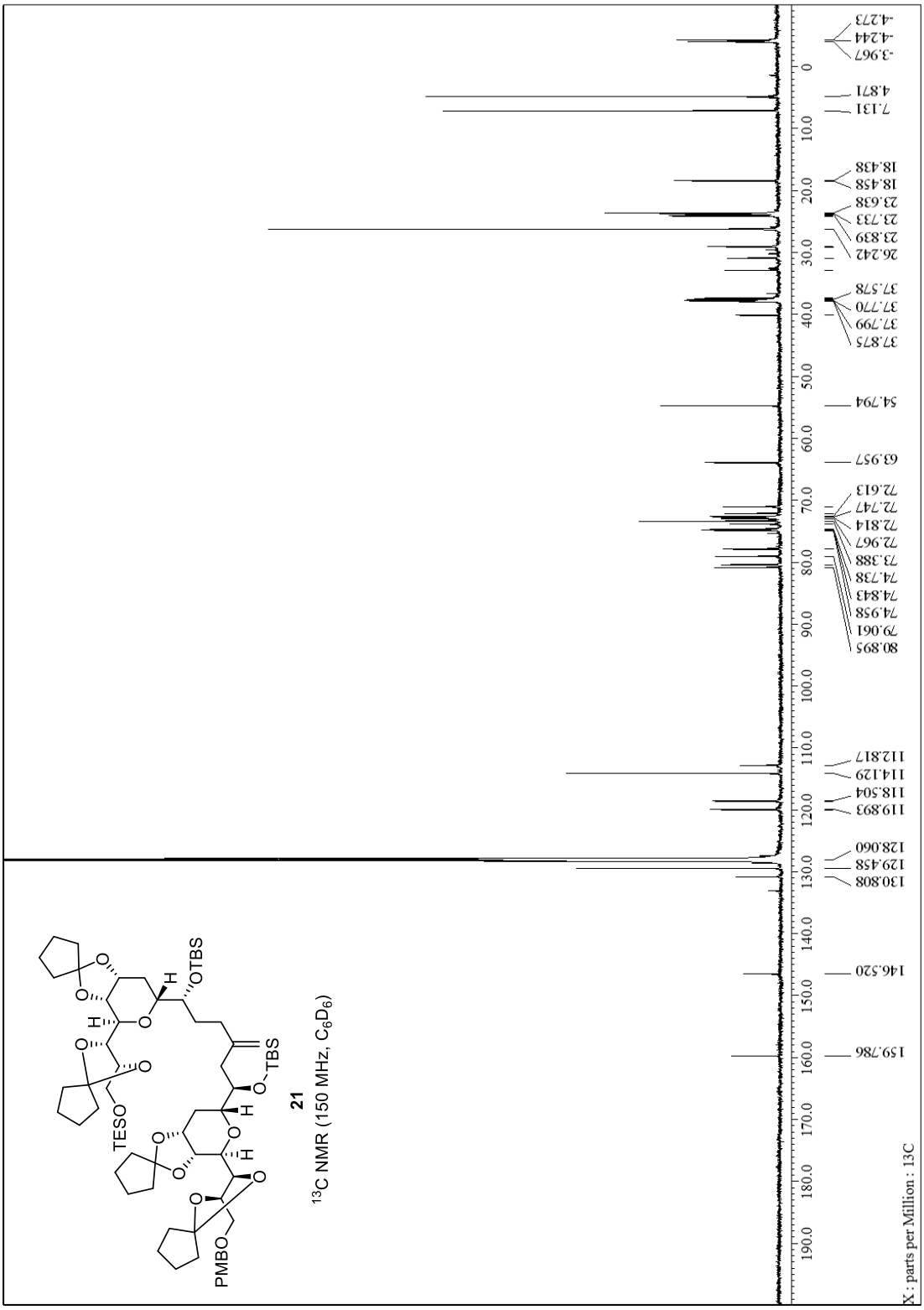

TESO
OTBS
18
^{1}H NMR (600 MHz, $CDCl_3$)
0.051
0.068
0.605
0.618
0.887
0.943
0.957
1.658
1.663
1.671
1.676
1.682
2.411
2.420
2.427
2.484
2.492
2.502
3.714
3.722
3.733
3.741
3.749
4.018
4.243
4.254
4.262
4.272
4.282
5.681
6.019
6.021
7.260
X : parts per Million : 1H

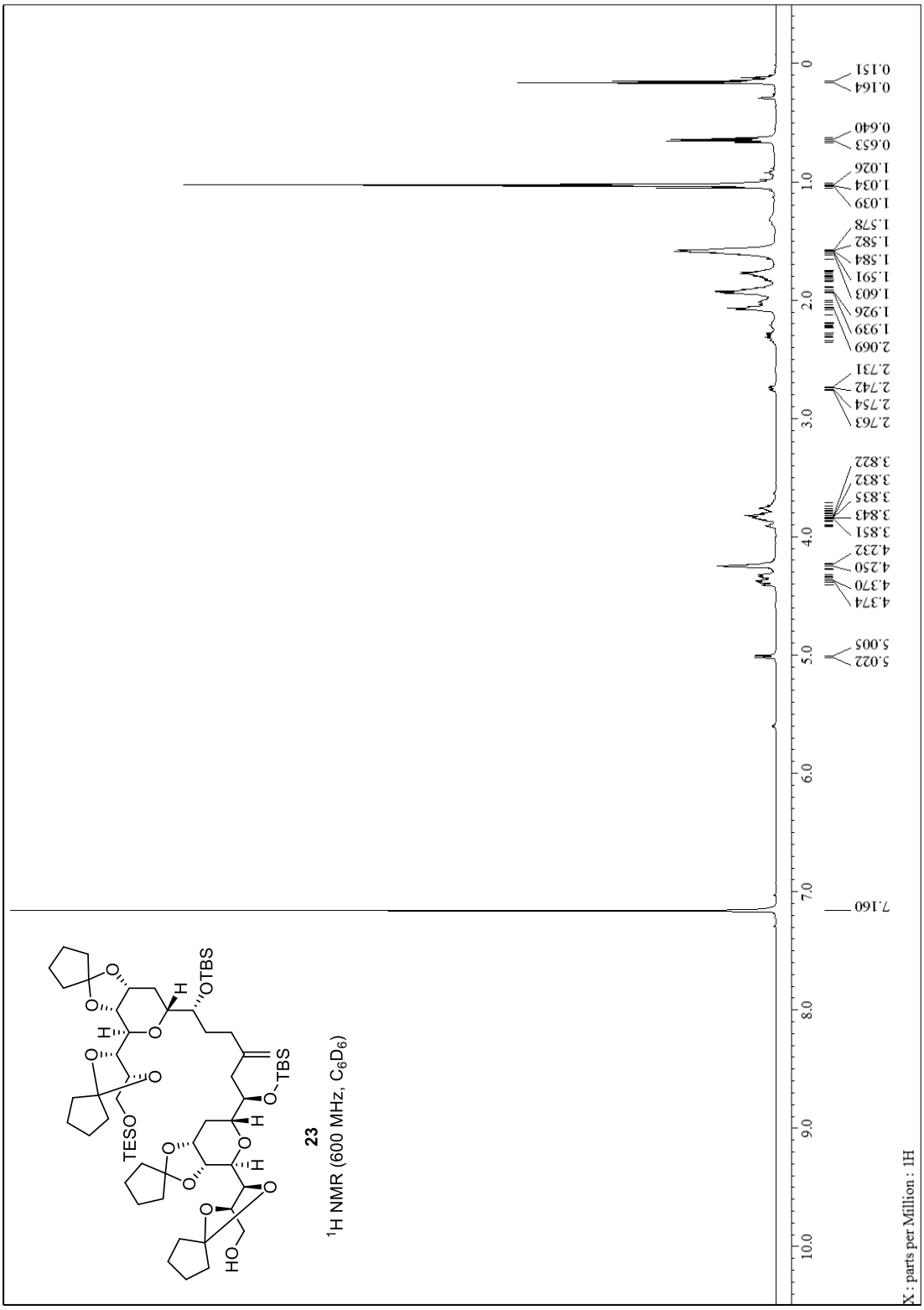

TESO
OTBS
18
13C NMR (150 MHz, CDCl3)
X : parts per Million : 13C

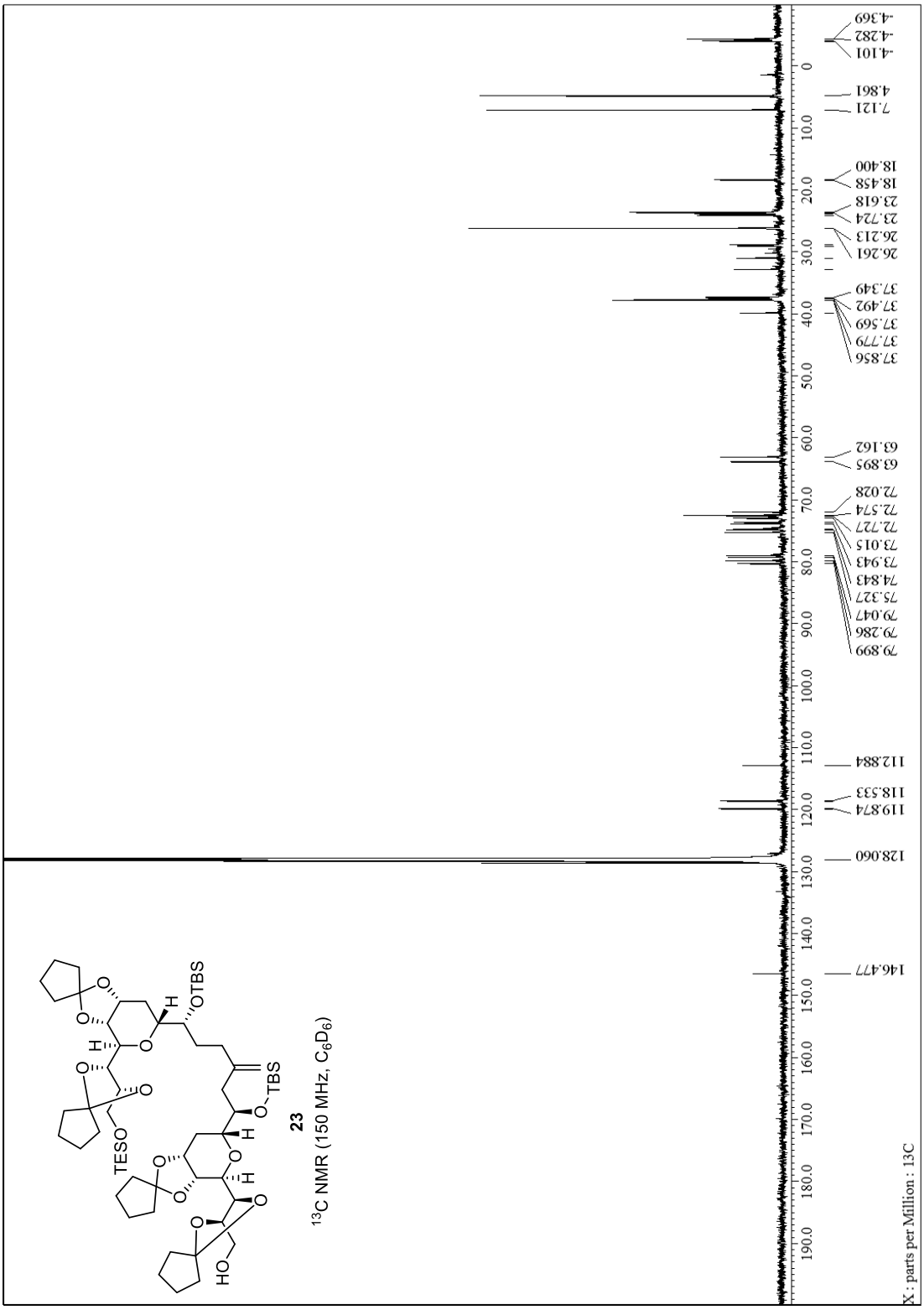

OTBS
H
O
TESO
OH
PMBO
20
1H NMR (600 MHz, C6D6)
0.139
0.625
0.639
0.652
1.004
1.014
1.025
1.564
1.576
1.913
1.924
1.935
2.282
2.296
2.704
3.329
3.822
3.833
3.840
4.127
4.292
4.371
4.379
4.984
5.006
6.806
6.820
7.160
7.223
7.228
7.241
X : parts per Million : 1H


-4.225
-4.034
4.871
7.121
18.438
23.628
23.829
24.107
26.251
37.396
37.626
37.827
37.875
54.813
64.005
71.167
72.651
72.928
72.957
73.359
73.560
73.589
74.853
79.085
80.397
112.262
114.157
118.533
119.902
127.897
128.060
128.223
129.621
130.626
146.970
159.877
X : parts per Million : 13C
TESO
PMBO
OTBS
OH
20
13C NMR (150 MHz, C6D6)


21
^{1}H NMR (600 MHz, C_6D_6)
OTBS
TBS
TESO
PMBO
0.151
0.158
0.172
0.629
0.641
1.016
1.023
1.028
1.579
1.590
1.775
1.919
1.930
2.072
2.077
2.777
2.788
2.800
3.328
3.679
3.687
3.842
4.356
4.365
4.425
4.448
5.013
5.032
6.802
6.818
7.160
7.246
7.261
X : parts per Million : 1H

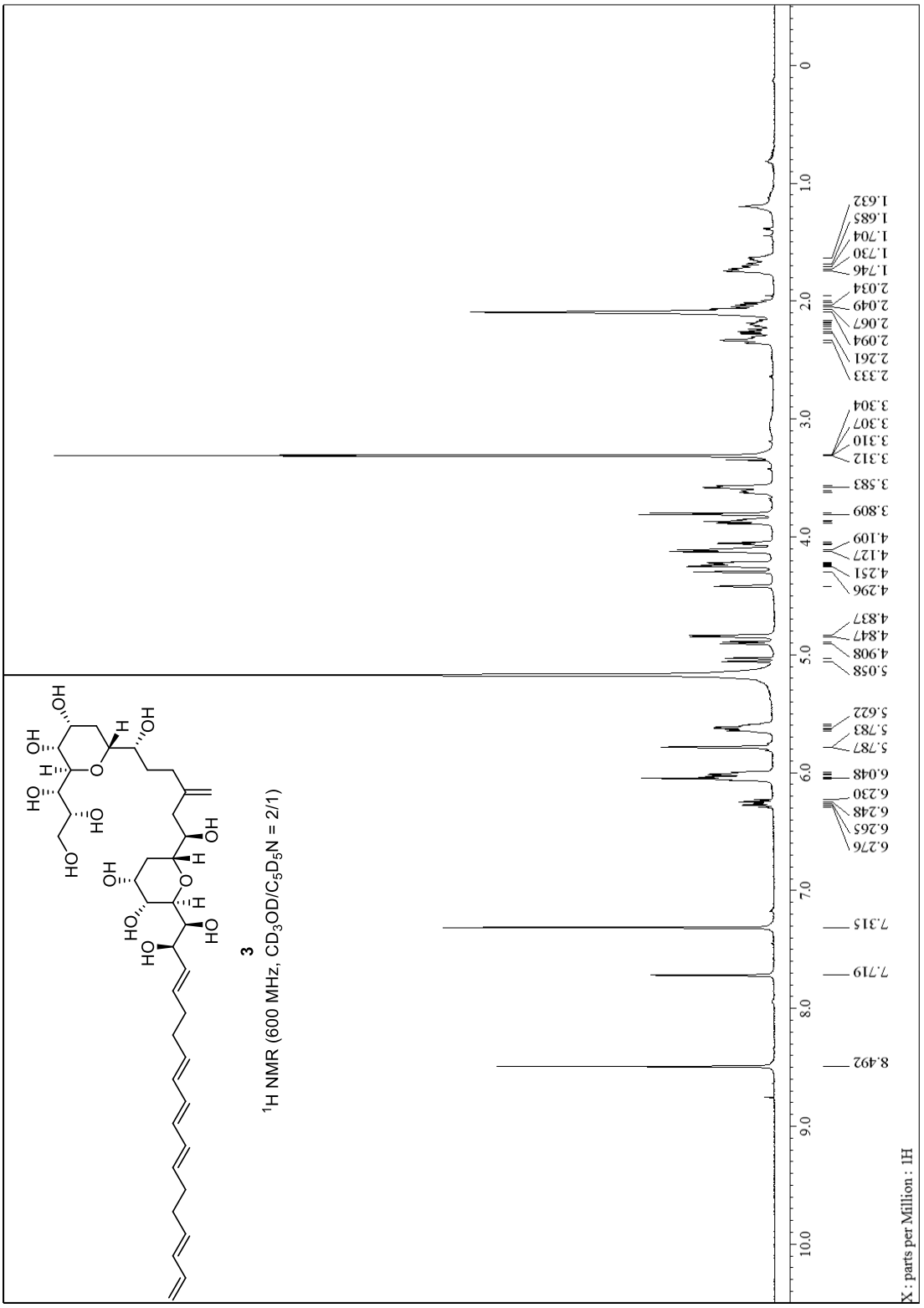

TESO
OTBS
TBS
PMBO
21
^{13}C NMR (150 MHz, C_6D_6)
X : parts per Million : 13C

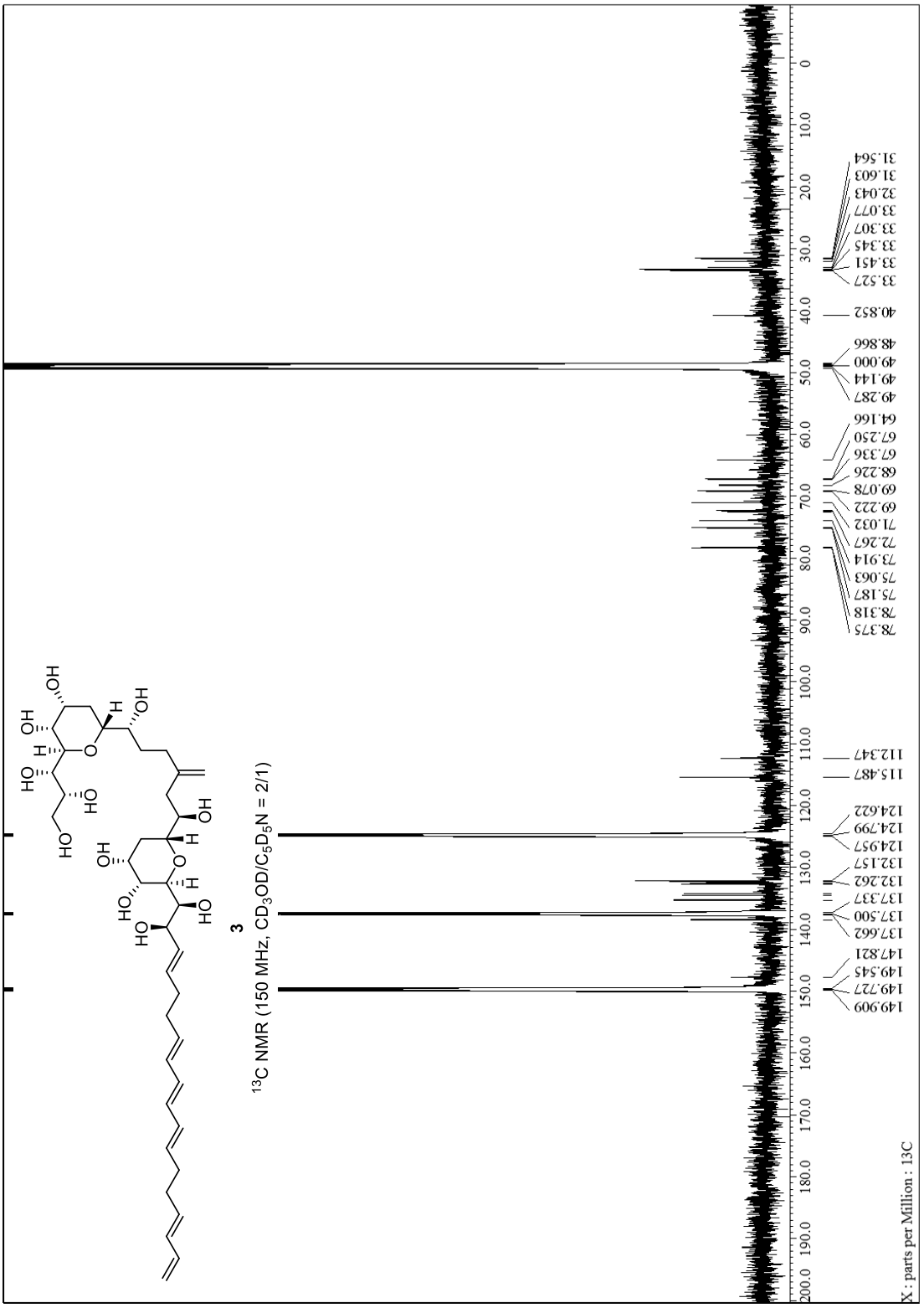

TESO
OTBS
TBS
HO
23
^{1}H NMR (600 MHz, C_6D_6)
X : parts per Million : 1H



23

^{13}C NMR (150 MHz, C_6D_6)


3
^{1}H NMR (600 MHz, CD_3OD/C_5D_5N = 2/1)
X : parts per Million : 1H


3
^{13}C NMR (150 MHz, CD_3OD/C_5D_5N = 2/1)
149.909
149.727
149.545
147.821
137.662
137.500
137.337
132.262
132.157
124.957
124.799
124.622
115.487
112.347
78.375
78.318
75.187
75.063
73.914
72.267
71.032
69.222
69.078
68.226
67.336
67.250
64.166
49.287
49.144
49.000
48.866
40.852
33.527
33.451
33.345
33.307
33.077
32.043
31.603
31.564
X : parts per Million : 13C