Supporting Information

Regioselective Phosphorylation of *myo*-Inositol with BINOL-Derived Phosphoramidites, and Its Application for Protozoan Lysophosphatidylinositol

Toshihiko Aiba,[1,2] Masaki Sato,[1] Daichi Umegaki,[1] Takanori Iwasaki,[3] Nobuaki Kambe,[3] Koichi Fukase[*1] and Yukari Fujimoto[*1,2]

[1]Department of Chemistry, Graduate School of Science, Osaka University, 1-1 Machikaneyama, Toyonaka, Osaka 560-0043, Japan, [2]Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku-ku, Yokohama, Kanagawa 223-8522, Japan, and [3]Division of Applied Chemistry, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 560-0043, Japan

E-mail: fujimotoy@chem.keio.ac.jp

Table of Contents

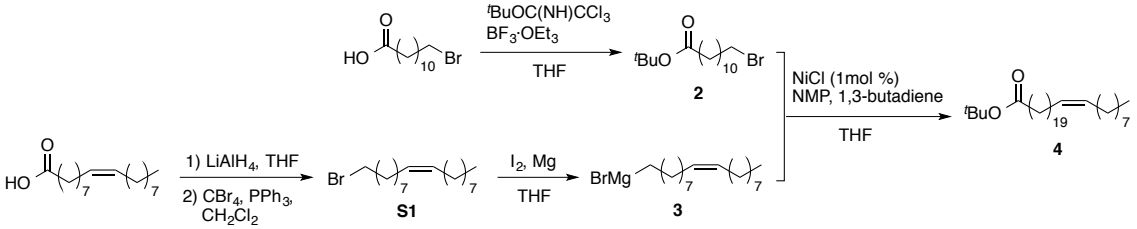
I. General information

General procedure:

Nuclear magnetic resonance (^{1}H NMR, ^{13}C NMR, ^{31}P NMR) spectra were measured at 25 $^{\circ}$C in an indicated solvent with JEOL ECA 500 or ECX 400 or Agilent INOVA 600 and analyzed Delta 5.0.4 (JEOL) or Vnmrj 32A (Agilent). The proton chemical shifts in $CDCl_3$ are reported in parts per million (δ) from trimethylsilane as an internal standard and coupling constants are in Heltz (Hz). The chemical shifts in other solvent are reported in ppm from the residual proton signal of solvent. The chemical shits for ^{13}C NMR are reported in ppm from the internal solvent signal ($CDCl_3$, δ 77.0). High-resolution mass spectra (HRMS) of synthetic compounds were obtained on an electron spray ionization quadrupole time of flight (ESI-QTOF) mass spectrometer (micrOTOF-QII-HC; BRUKER). Analytical thin layer chromatography (TLC) was performed on Silica gel 60 F_{254} Plates (Merck, 0.25 mm thickness). Preparative TLC separations were performed on PLC Silica gel 60 F_{254} Plates (Merck, 0.5 or 1.0 mm thickness). Silica gel column chromatography was performed using Silica gel 60 (Merck, 0.040 – 0.063 mm) or Silica gel 60 N [spherical neutral (Kanto Chemical Co., 40 – 50 μm)] at medium pressure (2 – 4 $kgcm^{-2}$) using indicated solvent systems. Reagents were purchased from commercial supplier (TCI, nacalai tesque, Wako pure chemical industry, Ltd., Kanto Chemical) and were used without further purification. Unless otherwise noted, Non-aqueous reactions were carried out under argon atmosphere. Anhydrous dichloromethane was prepared by distillation from calcium hydrate. Anhydrous tetrahydrofuran was prepared by distillation from Na. Anhydrous *N, N*-dimethylformamide, methanol, Toluene were purchased from Wako pure chemical industry, Ltd.

III. Experimental procedures and characterization data

Synthesis of *tert*-butyl *cis*-21-triacontenoate (4)



***tert*-butyl 12-bromododecanoate (2)**

To a stirred solution of 12-bromododecanoic acid (2.00g, 7.22 mmol) in THF (15 mL) in 0 ºC was added *tert*-butyl imidate (3.90 mL, 21.6 mmol), followed by BF_3•OEt_2 (55 μL, 1.07 mmol). After stirred for 3 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$. Ethyl acetate was added to the mixture. The organic solution was washed saturated aqueous $NaHCO_3$ (x3) and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude oil was purified with silica gel column chromatography (Hexane/EtOAc = 25/1) to afford **2** (2.3 g, 96% yield) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 3.39 (t, *J* = 6.9 Hz, 2H), 2.19 (t, *J* = 7.4 Hz, 2H), 1.84 (dt, *J* = 6.0, 14 Hz, 2H), 1.59 – 1.13 (m, 2H), 1.43 – 1.38 (m, 11H), 1.30 – 1.23 (m, 12 H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.4, 80.0, 35.7, 34.1, 32.9, 29.5, 29.5, 29.4, 29.2, 28.8, 28.3, 28.2, 25.2; **HRMS** (ESI) calculated for $C_{16}H_{31}NaO_2$ $[M+Na]^+$ 357.1400, found 357.1403

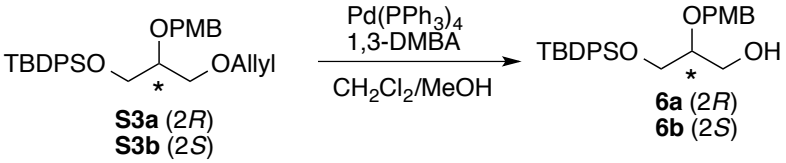
(*Z*)-1-bromooctadec-9-ene (S1)

To a stirred solution of $LiAlH_4$ (2.16 g, 57.0 mmol) in THF (50 mL) at 0 ^{o}C was added the solution of Oleic acid (12 mL, 38.0 mmol) in THF (12 mL) dropwise over a period of 15 min. The mixture was allowed to warm to room temperature, and stirred for 18 h. The reaction mixture was quenched with H_2O (2 mL), 15% aqueous NaOH (2 mL), and H_2O (6 mL). Then, it was allowed to stir for 1 h. The mixture was filtrated through a pad of celite, concentrated under reduced pressure. The crude oil was directly used for the next step. To the crude oil and CBr_4 (20.2 g, 60.8 mmol) in CH_2Cl_2 (70 mL) at room temperature was added the solution of PPh_3 (19.9 g, 76.0 mmol) in THF (30 mL). After stirred for 14 h, solvent was removed under reduced pressure. Hexane was added to the mixture, and removed triphenylphosphineoxide by filtration. The mixture was concentrated *in vacuo*. The crude material was subjected to silica gel column chromatography (Hexane only) to afford **S1** (11.2 g, 89% yield for 2 steps) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.38 – 5.31 (m, 2H), 3.40 (t, *J* = 6.9 Hz, 2H), 2.01 (dt, *J* = 6.3, 12 Hz, 4H), 1.89 – 1.82 (m, 2H) 1.44 – 1.39 (m, 2H), 1.36 – 1.27 (m, 20H), 0.88 (t, *J* = 6.9 Hz, 3H)

***tert*-butyl *cis*-21-triacontenoate (4)**

To a stirred solution of **S1** (928 mg, 2.80 mmol) were added Mg (146 mg, 6.00 mmol) and a piece of I_2 in THF (2 mL), then heated to reflux temperature. After stirred for 30 min, girignard reagent **3** from **S1** was cooled to –40 ºC. The solution of **2** (671 mg, 2.00 mmol) and NMP (193 μL) in THF (2 mL) was added to the mixture, followed by 1,3-butadiene (44.8 mL) and $NiCl_2$ (2.6 mg). The mixture was allowed to warm to 0 ºC, and stirred for 2 h. The reaction mixture was quenched with saturated aqueous NH_4Cl. AcOEt was added to the mixture, and washed with saturated aqueous NH_4Cl (x3), brine (x2). The organic solution was dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude oil was subjected to silica gel column chromatography (Hexane/EtOAc = 30/1) to afford **4** (651 mg, 64% yield) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.35 (t, J = 4.6 Hz, 2H), 2.20 (t, J = 7.5 Hz, 2H), 2.01 (dd, J = 12.5, 6.8 Hz, 4H), 1.61-1.53 (m, 2H), 1.44 (s, 9H), 1.38-1.19 (m, 44H), 0.88 (t, J = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.4, 130.0, 79.9, 35.7, 32.0, 29.9, 29.8, 29.7, 29.7, 29.7, 29.6, 29.6, 29.4, 29.2, 28.2, 27.3, 25.2 **HRMS** (ESI) calculated for $C_{34}H_{66}NaO_2$ $[M+Na]^+$ 529.4955, found 529.4965

Syntheses of 1-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (6a) and 3-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (6b)



1-allyl-3-*tert*-butyldiphenylsilyl-*sn*-glycerol (S2a)

To a stirred solution of (*S*)-(-)-2,2-dimethyl-1,3-dioxolane-4-methanol (2.5 g, 18.9 mmol) in DMF (37 mL) was added NaH (60% oil dispersion) (910 mg, 27.7 mmol). After stirring for 15 min, allyl bromide (2.5 mL, 28.3 mmol) was added to the mixture. The reaction mixture was allowed to warm to room temperature and stirred for over night. The mixture was extracted with Et_2O. The combined organic solution was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was directly used in the next step. The residue was dissolved in 90% AcOH aqueous solution (35 mL), and then stirred for over night at 70 ºC. The mixture was cooled to room temperature, and then concentrated under reduced pressure with toluene. The crude residue was used in the next step without

further purification. To a stirred solution of the crude residue and DMAP (462 mg, 4.16 mmol) in CH_2Cl_2 (95 mL) at room temperature was added Et_3N (13.2 mL, 94.5 mmol) and TBDPSCl (5.3 mL, 20.8 mmol). After stirring for over night, the reaction mixture was extracted with CH_2Cl_2. The combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude mixture was subjected to silica gel column chromatography (Hexane/EtOAc = 10/1) to afford **S2a** (5.17 g, 73% yield for 3 steps) as a color less oil. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.70-7.62 (m, 4H), 7.47-7.35 (m, 6H), 5.95-5.81 (m, 1H), 5.25 (dd, J = 17.2, 1.6 Hz, 1H), 5.18 (dd, J = 10.4, 1.0 Hz, 1H), 3.99 (dd, J = 5.7, 1.4 Hz, 2H), 3.95-3.86 (m, 1H), 3.72 (d, J = 5.3 Hz, 2H), 3.58-3.46 (m, 2H), 2.51 (d, J = 5.0 Hz, 1H), 1.06 (s, 9H) ; **^{13}C NMR** (98 MHz, $CDCl_3$) δ 135.7, 134.6, 133.3, 130.0, 127.9, 117.3, 72.4, 71.0, 70.9, 64.8, 26.9,19.4; **HRMS** (ESI) calculated for $C_{22}H_{30}NaO_3Si$ $[M+Na]^+$ 393.1864, found 393.1870

1-allyl-3-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (S3a)

To a stirred solution of **S2a** (3.0 g, 8.09 mmol) and PMBCl (1.64 mL, 12.1 mmol) in DMF (40 mL) at 0 ºC was added NaH (60% oil dispersion) (390 mg, 9.72 mmol). After stirring for over night at room temerature, the reaction was quenched with ice. The mixture was extracted with Et_2O and the combined organic phase was washed with brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The residue was purified with silica gel column chromatography (Hexane/EtOAc = 20/1) to afford **S3a** (2.11 g, 53% yield) as a color less oil. **^{1}H NMR** (390 MHz, CDl_3) δ 7.71-7.63 (m, 4H), 7.44-7.32 (m, 6H), 7.24 (d, J = 8.5 Hz, 2H), 6.83 (dd, J = 11.4, 2.7 Hz, 2H), 5.95-5.83 (m, 1H), 5.29-5.22 (m, 1H), 5.16 (dd, J = 10.4, 1.3 Hz, 1H), 4.57 (s, 2H), 3.99 (d, J = 5.5 Hz, 2H), 3.78-3.75 (m, 4H), 3.75 (s, 1H), 3.72-3.61 (m, 2H), 3.56 (dd, J = 9.9, 5.3 Hz, 1H), 1.05 (s, 9H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.2, 135.8, 135.8, 135.0, 133.7, 133.6, 131.0, 129.8, 129.5, 127.8, 116.9, 113.8, 78.5, 72.5, 72.0, 70.3, 63.7, 55.4, 27.0, 26.7, 19.4; **HRMS** (ESI) calculated for $C_{30}H_{38}NaO_4Si$ $[M+Na]^+$ 513.2432, found 513.2444

1-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (6a)

To the stirred solution of **S3a** (2.00 g, 4.08 mmol) and 1,3-dimethylbarbituric acid (1.27 g, 8.16 mmol) in CH_2Cl_2/MeOH (1/1) (20 mL) was added $Pd(PPh_3)$ (94 mg, 81.6 μmol). After the reaction mixture was stirred at 35 ºC for over night, the mixture was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (Hexane/EtOAc = 10:1) to afford **6a** (1.56 g, 85%) as a color less oil. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.71-7.63 (m, 4H), 7.46-7.33 (m, 6H), 7.20 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.56 (d, J = 11.3 Hz, 1H), 4.43 (d, J = 11.3 Hz, 1H), 3.84-3.55 (m, 8H), 2.14 (dd, J = 7.1, 5.5 Hz, 1H), 1.06 (s, 9H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.4, 135.7, 135.7, 133.4, 133.2, 130.5, 129.9, 129.5, 127.9, 114.0, 79.4, 72.0, 63.7, 62.9, 55.4, 27.0, 1

9.3; **HRMS** (ESI) calculated for $C_{27}H_{34}NaO_4Si$ $[M+Na]^+$ 473.2119, found 473.2127

3-allyl-1-*tert*-butyldiphenylsilyl-*sn*-glycerol (S2b)

In a manner similar to the synthesis of **S2a**, (*S*)-(-)-2,2-Dimethyl-1,3-dioxolane-4-methanol (10 g, 75.7 mmol) was converted into **S2b** (23.7 g, 85% yield for 3 steps) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 4H), 7.44 – 7.36 (m, 6H), 5.92 – 5.84 (m, 1H), 5.25 (ddd, *J* = 2.5, 7.0, 17 Hz, 1H), 5.17 (ddd, *J* = 1.4, 2.0, 10 Hz, 1H), 3.99 (ddd, *J* = 1.3, 1.3, 5.6 Hz, 2zH), 3.90 – 3.88 (m, 1H), 3.72 (d, *J* = 5.4 Hz, 2H), 3.35 (td, *J* = 4.7, 9.6 Hz, 2H), 2.51 (d, *J* = 5.0 Hz, 1H), 1.06 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 135.6, 134.6, 133.3, 129.9, 127.8, 117.3, 72.4, 71.1, 70.9, 64.9, 50.8, 26.9, 19.3; **HRMS** (ESI) calculated for $C_{22}H_{30}NaO_3Si$ $[M+Na]^+$ 393.1864, found 393.1870

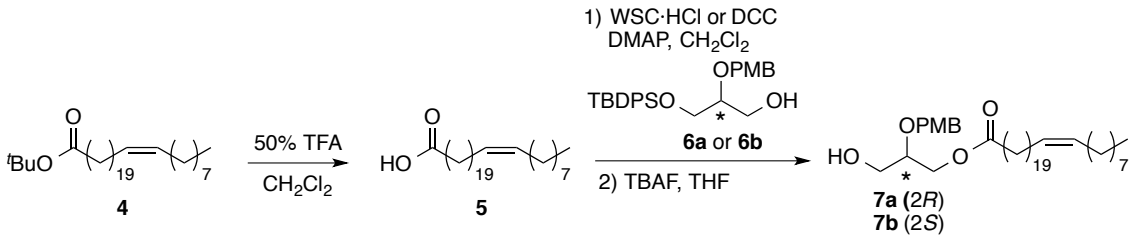
3-allyl-1-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (S3b)

In a manner similar to the synthesis of **S3a**, **S2a** (18.5 g, 50.0 mmol) was converted into **S3b** (20 g, 82% yield) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.69-7.63 (m, 4H), 7.47-7.32 (m, 6H), 7.26-7.21 (m, 2H), 6.86-6.82 (m, 2H), 5.95-5.82 (m, 1H), 5.29-5.22 (m, 1H), 5.16 (dq, J = 10.4, 1.5 Hz, 1H), 4.56 (d, J = 1.3 Hz, 2H), 4.03-3.95 (m, 2H), 3.79 (s, 3H), 3.77-3.61 (m, 4H), 3.55 (dd, J = 10.1, 5.5 Hz, 1H), 1.04 (s, 9H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.2, 135.7, 135.7, 135.6, 135.0, 129.7, 129.4, 127.9, 127.8, 116.8, 113.8, 78.5, 72.4, 72.0, 70.3, 63.6, 55.4, 26.9, 19.3; **HRMS** (ESI) calculated for $C_{30}H_{38}NaO_4Si$ $[M+Na]^+$ 513.2432, found 513.2443

3-*tert*-butyldiphenylsilyl-2-(4-methoxybenzyl)-*sn*-glycerol (6b)

In a manner similar to the synthesis of **6a**, **S3b** (1.14 g, 2.30 mmol) was converted into **6b** (0.88 g, 85% yield) as a color less oil. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.67 (dt, J = 8.0, 1.4 Hz, 4H), 7.48-7.33 (m, 6H), 7.23-7.16 (m, 2H), 6.88-6.81 (m, 2H), 4.56 (d, J = 11.3 Hz, 1H), 4.44 (d, J = 11.3 Hz, 1H), 3.83-3.74 (m, 5H), 3.74-3.56 (m, 3H), 2.03 (dd, J = 7.2, 5.5 Hz, 1H), 1.05 (s, 9H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.4, 135.7, 135.7, 135.6, 133.3, 133.2, 130.5, 129.9, 129.5, 127.8, 114.0, 79.3, 71.9, 63.6, 63.0, 55.4, 26.9, 19.3; **HRMS** (ESI) calculated for $C_{27}H_{34}NaO_4Si$ $[M+Na]^+$ 473.2119, found 473.2124

Syntheses of 2-(4-methoxybenzyl)-3-(*cis*-21-triacontenyl)-*sn*-glycerol (7a) and 2-(4-methoxybenzyl)-1-(*cis*-21-triacontenyl)-*sn*-glycerol (7b)



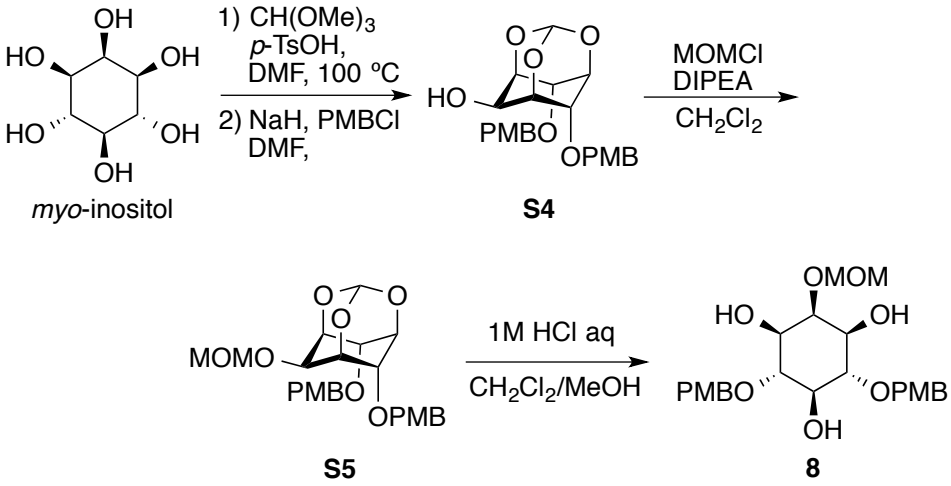
2-(4-methoxybenzyl)-3-(*cis*-21-triacontenyl)-*sn*-glycerol (7a)

4 (75 mg, 0.15 mmol) was dissolved with TFA (0.75 mL) and CH_2Cl_2 (0.75 mL) at room temperature, and stirred for 1 h. To the mixture was added toluene, and concentrated under reduce pressure. This operation was repeated 3 times. The crude acid **5** was directly used for the next step. To a stirred solution of crude material, **6a** (100 mg, 0.22 mmol) and DMAP (15 mg, 0.12 mmol) in CH_2Cl_2 (6 mL) was added WSC•HCl (71 mg, 0.37 mmol). After stirring for over night at reflux, the reaction mixture was concentrated under reduced pressure. The residue was subjected to silica gel column chromatography (Hex/EtOAc = 20/1) to afford ester (64 mg, 49%) as a color less oil. To a stirred solution of ester in THF (1.26 mL) was added TBAF (252 μL, 0.25 mmol) at room temperature. After stirred for over night, the solvent was removed under reduced pressure. The crude mixture was subjected to silica gel column chromatography (Toluene/ethyl acetate = 5/1 to 4/1) to afford **7a** (70.5 mg, 80% yield) as a white solid. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2H), 6.91-6.85 (m, 2H), 5.35 (t, J = 4.6 Hz, 2H), 4.65 (d, J = 11.4 Hz, 1H), 4.52 (d, J = 11.2 Hz, 1H), 4.21 (d, J = 4.9 Hz, 2H), 3.80 (s, 3H), 3.71-3.64 (m, 2H), 3.60 (dd, J = 12.6, 7.0 Hz, 1H), 2.32 (t, J = 7.5 Hz, 2H), 2.06-1.96 (m, 4H), 1.61 (q, J = 7.2 Hz, 2H), 1.37-1.20 (m, 44H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 173.9, 159.5, 130.5, 130.0, 129.6, 114.0, 76.9, 71.9, 62.8, 62.1, 55.4, 34.3, 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3, 27.3, 25.0, 22.8, 14.2; **HRMS** (ESI) calculated for $C_{41}H_{72}NaO_5$ $[M+Na]^+$ 667.5752, found 667.5292

2-(4-methoxybenzyl)-1-(*cis*-21-triacontenyl)-*sn*-glycerol (7b)

In a manner similar to the synthesis of **7a**, **4** (174 mg, 0.34 mmol) was converted into **7b** (177 mg, 79% yield) as a white solid.**^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 – 7.25 (m, 2H), 6.89 – 6.86 (m, 2H), 5.38 – 5.31 (m, 2H), 4.64 (d, *J* = 11 Hz, 1H), 4.52 (d, *J* = 11 Hz, 1H), 4.21 (d, *J* = 5.0 Hz, 2H), 3.80 (s, 3H), 3.70 – 3.65 (m, 2H), 3.62 – 3.59 (m, 1H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.03 – 1.98 (m, 4H), 1.65 – 1.59 (m, 2H), 1.34 – 1.25 (m, 44H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.9, 159.5, 130.0, 130.0, 129.6, 114.0, 71.9, 62.8, 62.1, 55.4, 34.3, 32.0, 29.9, 29.8, 29.8, 29.7, 29.7, 29.6, 29.6, 29.4, 29.4, 29.2, 27.3, 25.0, 22.8, 14.2; **HRMS** (ESI) calculated for $C_{41}H_{72}NaO_5$ $[M+Na]^+$ 667.5272, found 667.5286

Synthesis of 4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-*myo*-inositol (8)



myo-inositol **S4** **S5** **8**

4,6-di-*O*-p-methoxybenzyl-myo-inositol 1,3,5-*O*-orthoformate (S4)

To a suspension of *myo*-inositol (20 g, 111 mmol) in DMF (180 mL) was added *p*-TsOH (2.11 g, 11.1 mmol) and $CH(OEt)_3$ (27.7 mL, 166 mmol). The mixture was allowed to warm at 110 ºC. After stirring for 11 h, the reaction mixture was cooled to ambient temperature and then added triethylamine (1.4 mL, 11.1 mmol) and then concentrated *in vacuo*. The crude mixture was used next reaction without further purification. To the crude mixture DMF (222 mL) was added then cooled to 0 ºC. To the mixture NaH (60% oil dispersion) (8.88 g, 222 mmol) was added at 0 ºC. After stirring for 30 min, TBAI (2g, 11.1 mmol) and PMBCl (12.6 mL, 92.4 mmol) were added to the reaction mixture. The mixture was slowly warmed up to room temperature and stirred for 11 h. The reaction was quenched with 10% aqueous citric acid, and extracted with Et_2O. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (Toluene/EtOAc = 3.5/1 to 2:1) to afford **S4** (17.1 g, 35% yield for 2 steps) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (d, *J* = 8.4 Hz, 4H), 6.82 (d, *J* = 8.6 Hz, 4H), 5.44 (s, 1H), 4.58 (d, *J* = 11 Hz, 2H), 4.50 (d, *J* = 11 Hz, 2H), 4.40 - 4.39 (m, 1H), 4.33 (t, *J* = 7.3 Hz, 2H), 4.19 – 4.18 (m, 2H), 3.81 – 3.80 (m, 7H), 2.98 (d, *J* = 11 Hz, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.5, 129.7, 129.5, 113.9, 103.4, 73.5, 73.1, 71.4, 67.9, 61.5, 55.3; **HRMS** (ESI) calculated for $C_{23}H_{26}NaO_8$ $[M+Na]^+$ 453.1520, found 453.1520

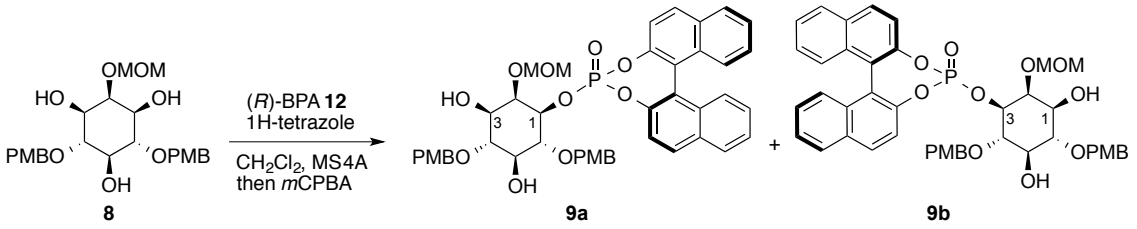
4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol 1,3,5-*O*-orthoformate (S5)

To a solution of **S4** (17.0 g, 39.5 mmol) in CH_2Cl_2 (100 mL) at room temperature was added *N,N*-diisopropylethylamine (10.5 mL, 59.2 mmol). After stirring for 10 min, MOMCl (4.5 mL, 59.2 mmol) was added to the reaction mixture. The reaction mixture was stirred for over night, and then

extracted with CH_2Cl_2. The combined organic solution was washed with water and brine and dried over anhydrous Na_2SO_4, concentrated under reduced pressure. The crude product was purified by recrystallization (EtOAc/Hexane) to afford **S5** (11.54 g). The mother liquor was concentrated under reduced pressure and then purified with silica gel chromatography (Toluene/ethyl acetate = 6/1) to afford **S5** (3.94 g, total 82% yield) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 8.3 Hz, 4H), 6.83 (d, *J* = 8.6 Hz, 4H), 5.50 (s, 1H), 4.79 (s, 2H), 4.59 (d, *J* = 11 Hz, 2H), 4.49 (d, *J* = 11 Hz, 2H), 4.38 – 4.37 (m, 1H), 4,31 (dd, *J* = 3.3, 3.4 Hz, 2H), 4.27 – 4.26 (m, 2H), 4.16 (s, 1H), 3.80 (s, 6H), 3.43 (s, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.5, 129.6, 113.9, 103.3, 96.3, 73.4, 71.6, 71.5, 68.1, 67.1, 55.8, 55.4; **HRMS** (ESI) calculated for $C_{25}H_{30}NaO_9$ $[M+Na]^+$ 497.1782, found 497.1788

4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-*myo*-inositol (8)

To a solution of **S5 (**11.54 g, 9.53 mmol) in methanol (432 mL) at room temperature was added 1M HCl aq (48 mL). Precipitate immediately formed upon addition, and dichloromethane was added until the precipitate completely dissolved. The reaction mixture was stirred for 18 h at room temperature. The solution was neutralized with saturated aqueous $NaHCO_3$, and then concentrated under reduced pressure to provide the oil containing NaCl salt. The oil was dissolved with ethyl acetate, and then NaCl was removed by filtration. The solvent was removed *in vacuo* to afford the crude mixture. The crude material was purified with column chromatography (Toluene/EtOAc = 5/6 to 2/3) to afford **8** (6.41 g, 56% yield) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.4 Hz, 4H), 6.88 (d, *J* = 8.2 Hz, 4H), 4.83 – 4.77 (m, 6H), 3.96 (s, 1H), 3.80 (s, 6H), 3.58 – 3.49 (m, 5H), 3.45 (s, 3H), 2.96 (d, *J* = 5.7 Hz, 2H), 2.49 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.4, 130.8, 129.9, 129.8, 114.1, 99.1, 81.7, 75.0, 74.7, 71.5, 56.2, 55.4; **HRMS** (ESI) calculated for $C_{24}H_{32}NaO_9$ $[M+Na]^+$ 487.1939, found 487.1944

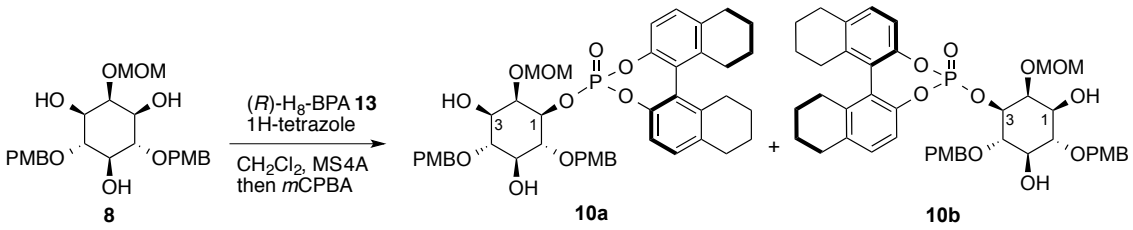


8 **9a** **9b**

General procedure for regioselective phosphorylation: synthesis of 4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-((*R*)-1,1'-bi-2-naphtyl) Phosphate (9a) and synthesis of 4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-((*R*)-1,1'-bi-2-naphtyl) Phosphate (9b)

The solution of **8** (500 mg, 1.08 mmol), 1H-tetrazole (377 mg, 5.38 mmol) and MS4A powder in CH_2Cl_2

(15 mL) and the solution of (*R*)-BPA **12** (2.24 g, 5.38 mmol) and MS4A powder in CH_2Cl_2 (15 mL) were stirred for 30 min. Then, the solution of (*R*)-BPA **12** was added to the solution of **8** and 1H-tetrazole via cannula. After stirred for 1 day, the reaction mixture was cooled to 0 °C, and then added *m*CPBA (928 mg, 5.38 mmol). The mixture was stirred for 1 hour, and then filtrated through a pad of Celite®. The mixture was washed with aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and brine. The organic solution was dtied over anhydrous Na_2SO and concentrated under reduced presser. The crude product was purified with column chromatography (toluene/ethyl acetate = 2/1) to afford a mixture of **9a** and **9b** (629 mg, 74% yield, **9a** : **9b** = 3.8 : 1) as white foam. **9a** (major isomer): **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01-7.96 (m, 2H), 7.94 (d, J = 8.2 Hz, 1H), 7.90 (d, J = 8.2 Hz, 1H), 7.52-7.45 (m, 3H), 7.43-7.37 (m, 2H), 7.35-7.28 (m, 5H), 6.89-6.85 (m, 4H), 6.59-6.54 (m, 2H), 4.89 (dd, J = 9.6, 6.6 Hz, 2H), 4.83 (d, J = 11.0 Hz, 1H), 4.76 (d, J = 11.0 Hz, 1H), 4.58-4.52 (m, 1H), 4.45-4.39 (m, 2H), 4.35 (d, J = 10.5 Hz, 1H), 3.80-3.73 (m, 4H), 3.71-3.66 (m, 3H), 3.60-3.54 (m, 1H), 3.53-3.45 (m, 5H), 3.37-3.30 (m, 1H), 2.54 (s, 1H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 159.5, 159.1, 132.3, 132.3, 131.7, 131.7, 131.1, 130.8, 130.3, 129.9, 129.4, 128.6, 128.6, 127.4, 127.1, 126.9, 126.0, 121.5, 121.3, 120.7, 120.3, 114.0, 113.7, 98.9, 81.0, 80.5, 79.8, 79.8, 79.7, 79.6, 75.1, 74.7, 74.5, 71.0, 56.3, 55.4, 55.3; **HRMS** (ESI) calculated for $C_{44}H_{43}NaO_{12}P$ $[M+Na]^+$ 817.2384, found 817.2391. **9b** (minor isomer): **^{1}H NMR** (390 MHz, $CDCl_3$) δ 8.04 (d, J = 9.0 Hz, 1H), 7.95 (d, J = 8.3 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.82 (d, J = 9.0 Hz, 1H), 7.57 (d, J = 8.9 Hz, 1H), 7.52-7.44 (m, 2H), 7.39-7.26 (m, 8H), 7.20-7.15 (m, 1H), 6.92-6.84 (m, 4H), 4.85-4.66 (m, 4H), 4.65-4.57 (m, 2H), 4.50 (d, J = 6.5 Hz, 1H), 4.33 (s, 1H), 3.87-3.72 (m, 8H), 3.59-3.46 (m, 3H), 3.28 (d, J = 6.1 Hz, 1H), 3.11 (d, J = 7.0 Hz, 3H), 2.56 (s, 1H), 2.35 (s, 1H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.4, 159.3, 147.5, 146.2, 132.3, 132.0, 131.7, 131.6, 131.1, 130.7, 130.7, 129.9, 129.4, 129.1, 128.7, 128.5, 128.3, 127.3, 127.1, 127.0, 126.0, 125.4, 121.5, 121.2, 120.6, 120.5, 114.0, 98.7, 81.0, 80.3, 79.6, 79.5, 79.2, 77.4, 74.7, 74.5, 74.4, 71.0, 55.8, 55.4; **HRMS** (ESI) calculated for $C_{44}H_{43}NaO_{12}P$ $[M+Na]^+$ 817.2384, found 817.2407.



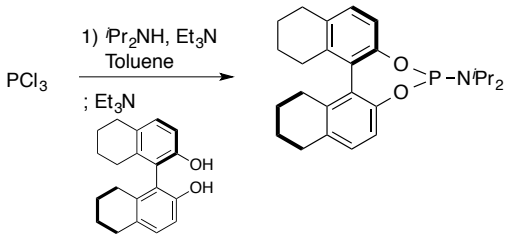
8 **10a** **10b**

4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-myo-inositol-1-((*R*)-5,5',6,6',7,7',8,8'-octahydro-1,1'-bi-2-naphtyl) Phosphate (10a) and 4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-myo-inositol-3-((*R*)-5,5',6,6',7,7',8,8'-octahydro-

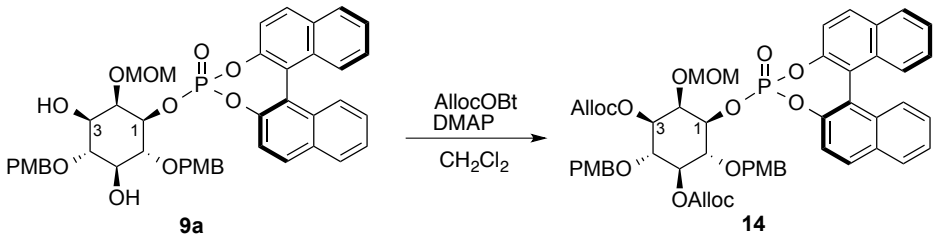
1,1'-bi-2-naphtyl) Phosphate (10b)

In a manner similar to the synthesis of **9a** and **9b**, triol **8** (50 mg, 0.11 mmol) was reacted with (*R*)-H_8-BPA **13** (226 mg, 0.54 mmol) to affoad **10a** and **10b** (41.9 mg, 49% yield) (**10a**:**10b**:diphosphate = 9:1:9)

(*R*)-5,5',6,6',7,7',8,8'-octahydro-1,1-binaphtylphosphinite diisopropylamidite (13)



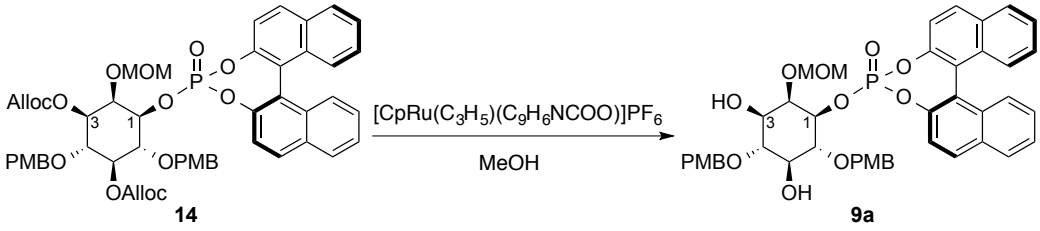
A solution of diisopropylamine (332 μL, 2.36 mmol) and triethylamine (362 μL, 2.36 mmol) in Toluene (1.2 mL) was added to a solution of PCl_3 (210 μL, 2.36 mmol) in Toluene (17 mL). The reaction mixture was warmed up to 70 ºC and stirred for over night. The reaction mixture was cooled to room temperature and then Et_3N (724 μL, 4.72 mmol) and (*R*)-2,2'-dihydroxy-5,5',6,6',7,7',8,8'-octahydro-1,1-binaphtyl (695 mg, 2.36 mmol) were added. The mixture was stirred for 8 h and then evaporated to remove the solvent. The crude mixture was subjected to silica gel column chromatogramphy (eluting with toluene) to afford **13** (807 mg, 80%) as a white solid. **^{1}H NMR** (392 MHz, $CDCl_3$) δ 7.04 (d, 1H, J = 8.2 Hz), 6.98 (d, 2H, J = 7.9 Hz), 6.89 (d, 1H, J = 8.2 Hz), 3.22-3.33 (m, 2H), 2.71-2.86 (m, 4H), 2.57-2.70 (m, 2H), 2.16-2.32 (m, 2H), 1.70-1.82 (m, 6H), 1.47-1.63 (m, 2H), 1.17 (s, 3H), 1.16 (s, 3H), 1.15 (s, 3H), 1.14 (s, 3H); **^{13}C NMR** (99 MHz, $CDCl_3$) δ 149.70, 148.83, 137.95, 137.29, 133.85, 132.51, 129.54, 129.33, 129.15, 128.67, 128.34, 127.66, 119.04, 118.77, 44.64, 44.50, 29.31, 29.19, 27.93, 27.77, 24.68, 24.63, 24.59, 22.98, 22.86, 22.67; **^{31}P NMR** (159 MHz, $CDCl_3$) δ 146.75; HRMS (ESI) calculated for $C_{26}H_{34}NNaO_2P$ $[M+Na]^+$ 446.2219, found 446.2220.



3,5-di-*O*-allyloxycarbonyl-4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-myo-inositol-1-((*R*)-1,1' -bi-2-naphtyl) Phosphate (14)

To a solution of AllocOBt (26 g, 119 mmol) and DMAP (7.27 g, 59.5 mmol) in CH_2Cl_2 (120 mL) was

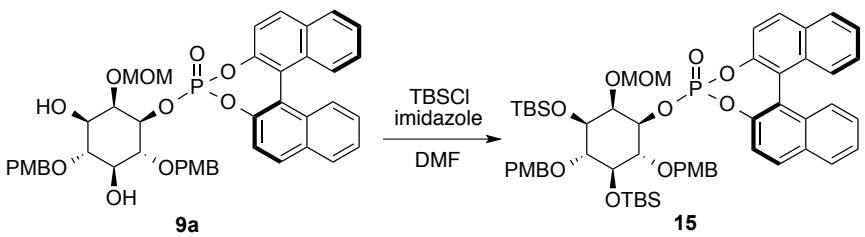
added **9a** and **9b** (8.82 g (**9a**:**9b** = 3.8:1), 11.1 mmol). The reaction mixture was stirred for over night, and then 10% aqueous citric acid and then extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The crude product was purified with column chromatography elution with toluene/ethyl acetate (6/1) to afford **14** (6.27 g, 74% yield (from **9a**)) as white foam. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 8.03-7.88 (m, 4H), 7.54-7.43 (m, 3H), 7.40 (d, J = 8.4 Hz, 1H), 7.36-7.27 (m, 3H), 7.23-7.13 (m, 3H), 6.87 (d, J = 8.6 Hz, 2H), 6.82 (dd, J = 11.4, 2.8 Hz, 2H), 6.62 (dd, J = 11.4, 2.7 Hz, 2H), 6.02-5.89 (m, 1H), 5.89-5.75 (m, 1H), 5.39 (dd, J = 17.2, 1.3 Hz, 1H), 5.32 (dd, J = 4.8, 1.2 Hz, 1H), 5.28 (t, J = 1.5 Hz, 1H), 5.20 (dd, J = 10.4, 1.2 Hz, 1H), 4.95-4.85 (m, 2H), 4.75-4.59 (m, 7H), 4.58-4.49 (m, 3H), 4.37 (s, 2H), 4.04-3.90 (m, 2H), 3.78 (s, 3H), 3.73 (s, 3H), 3.46 (s, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.3, 159.0, 154.1, 147.6, 147.5, 146.4, 132.4, 132.2, 132.0, 131.7, 131.6, 131.5, 131.1, 130.1, 129.6, 129.1, 128.6, 127.4, 127.0, 126.9, 126.0, 121.3, 120.8, 120.3, 119.3, 119.2, 113.7, 113.5, 98.1, 79.0, 78.3, 76.0, 75.1, 74.7, 69.0, 68.9, 56.3, 55.3; **HRMS** (ESI) calculated for $C_{52}H_{51}NaO_{16}P$ $[M+Na]^+$ 985.2807, found 985.2812.



14 **9a**

4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-((*R*)-1,1'-bi-2-naphtyl) Phosphate (9a)

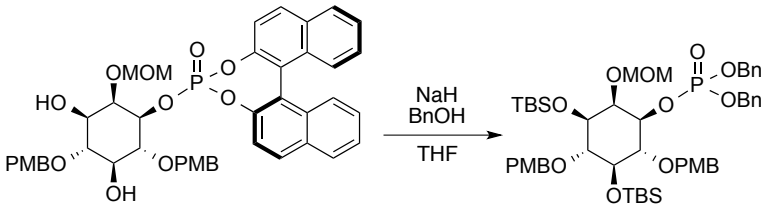
The solution of **14** (1.00 g, 1.04 mmol), and $[CpRu(C_3H_5)(C_9H_7NCOO^-)]PF_6$ (11 mg, 0.021 mmol) in MeOH (10.4 mL) was stirred at 35 ºC. After stirring for 3 hour, the reaction mixture was concentrated under reduced pressure. The crude residue was purified with silica gel column chromatography (toluene/ethyl acetate = 1/1) to afford **9a** (1.1461 g, quant) as white foam.



9a **15**

3,5-di-*O*-*tert*-butyldimethylsilyl-4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-((*R*)-1,1'-bi-2-naphtyl) Phosphate (15)

To a solution of **9a** (1.20 g, 1.50 mmol) in DMF (7.5 mL) at room temperature were added *tert*-butyldimethylsilyl chloride (2.27 g, 15.0 mmol) and imidazole (1.23 g, 18.0 mmol). The mixture was allowed to warm to 60 ºC. After stirring for 1 day, methanol was added to the reaction, and then extracted with Et_2O and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude material was purified with column chromatography (toluene/ethyl acetate =15/1) to afford **15** (1.46 g, 95% yield) as white foam. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.97-7.84 (m, 4H), 7.53-7.40 (m, 3H), 7.32-7.17 (m, 7H), 6.97 (d, J = 8.5 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 8.6 Hz, 2H), 4.93 (s, 2H), 4.87 (d, J = 11.9 Hz, 1H), 4.71 (d, J = 11.7 Hz, 1H), 4.58-4.48 (m, 2H), 4.40 (d, J = 10.5 Hz, 1H), 4.33 (s, 1H), 3.80-3.74 (m, 4H), 3.71-3.63 (m, 4H), 3.59-3.53 (m, 1H), 3.53-3.45 (m, 4H), 0.83 (s, 9H), 0.79 (s, 9H), 0.10 (s, 3H), -0.03 (s, 3H), -0.12 (s, 3H), -0.14 (s, 3H); 158.4, 158.3, 147.6, 147.5, 146.4, 146.4, 132.3, 132.2, 131.9, 131.6, 131.4, 131.3, 131.0, 130.7, 129.7, 129.2, 128.6, 128.5, 128.3, 127.5, 127.3, 127.1, 126.8, 125.9, 125.8, 125.4, 121.4, 121.2, 120.8, 120.6, 113.9, 113.2, 113.2, 98.0, 81.8, 80.4, 80.3, 80.2, 80.2, 78.1, 77.4, 75.1, 74.8, 73.3, 56.2, 55.2, 26.1, 25.2, 18.1, 18.1, –3.8, –4.2, –4.7; **HRMS** (ESI) calculated for $C_{56}H_{71}NaO_{12}PSi_2$ $[M+Na]^+$ 1045.4114, found 1045.4130



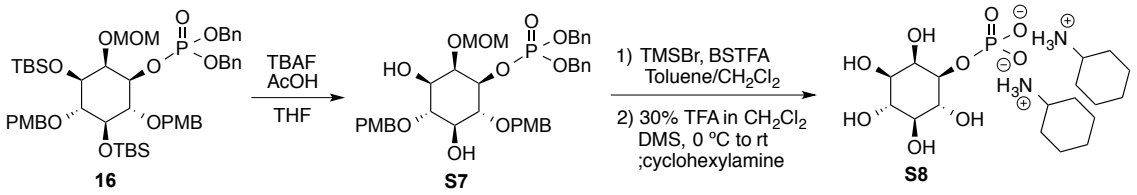
15 **16**

3,5-di-*O*-*tert*-butyldimethylsilyl-4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-dibenzyl Phosphate (16)

To a suspension of NaH (60% oil dispersion) (35 mg, 0.87 mmol) in THF (2.8 mL) at 0 ºC was added benzyl alcohol (100 μL, 0.96 mmol). After stirring for 30 min, the solution of **15** (297 mg, 0.29 mmol) in THF (3 mL) was added to the reaction at 0 ºC. The reaction mixture was warmed up to room temperature, and stirred for 4 h. The reaction was cooled to 0 ºC, and then quenched with 10% aqueous citric acid. The mixture was diluted with ethyl acetate. The organic solution was washed with saturated aqueous $NaHCO_3$ and brine, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude mixture was purified with column chromatography (toluene/ethyl acetate = 18/1) to afford **16** (175 mg, 63% yield) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 10H), 7.19 – 7.17 (m, 4H), 6.83 – 6.80 (m, 2H), 6.77 – 6.74 (m, 2H), 4.97 – 4.84 (m, 6H), 4.80 (d, *J* = 6.2 Hz, 1H), 4.76 – 4.69 (m, 3H), 4.22 – 4.18 (m, 1H), 4.13 (t, *J* = 2.3 Hz, 1H), 3.83 – 3.79 (m, 4H), 3.73 (s, 3H), 3.64 (t, *J* = 9.4 Hz, 1H),

3.51 (dd, *J* = 2.1, 9.6 Hz, 1H), 3.46 (t, *J* = 8.9 Hz, 1H), 3.40 (s, 3H), 0.81 (s, 9H), 0.78 (s, 9H), –0.03 (s, 3H), –0.05 (s, 3H), –0.07 (s, 3H), –0.13 (s, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 158.8, 158.3, 131.4, 130.9, 129.0, 128.6, 128.5, 128.5, 128.4, 128.0, 127.8, 127.5, 113.4, 113.2, 97.9, 8 1.8, 80.3, 80.3, 78.2, 78.1, 77.9, 75.1, 75.1, 74.7 73.5, 69.4, 69.3, 69.1, 69.0, 55.9, 55.2, 26.1, 25.9, 18.1, 18.0, 0.1, –3.8, –3.8, –4.4, –4.8; **HRMS** (ESI) calculated for $C_{50}H_{73}NaO_{12}PSi_2$ $[M+Na]^+$ 975.4270, found 975.4269

Synthesis of D-*myo*-inositol 1-phosphate Dicyclohexylammonium salt (S8)



4,6-di-*O*-*p*-methoxybenzyl-2-*O*-methoxymethyl-D-*myo*-inositol-1-dibenzyl Phosphate (S7)

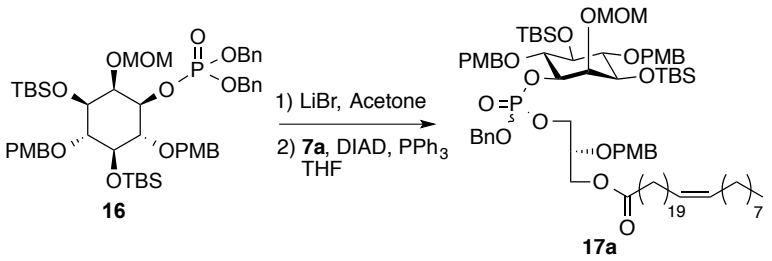
To a stirred solution of **16** (55 mg, 57.7 μmol) in THF (577 μL) at 40 ºC was added TBAF (577 μL, 0.577 mmol) and AcOH (33 μL, 0.577 mmol). After the reaction mixture was stirred for 2 h, the reaction was diluted with $CHCl_3$. Organic phase was washed with H_2O and brine and them filtrated and concentrated under reduced pressure. The residue was purified with silica gel column chromatography eluting with toluene/ethyl acetate (2/1 to 1/1) to afford **S7** (33.5 mg, 80%) as a white solid. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.37-7.22 (m, 14H), 6.90-6.84 (m, 2H), 6.81-6.75 (m, 2H), 5.05-4.96 (m, 4H), 4.83 (d, J = 11.0 Hz, 1H), 4.74 (dd, J = 10.3, 3.4 Hz, 3H), 4.68 (d, J = 11.0 Hz, 1H), 4.61 (d, J = 6.5 Hz, 1H), 4.21 (td, J = 8.1, 2.7 Hz, 1H), 4.12 (t, J = 2.5 Hz, 1H), 3.83-3.75 (m, 4H), 3.73 (s, 3H), 3.53 (t, J = 9.4 Hz, 1H), 3.49-3.38 (m, 2H), 3.36 (s, 3H), 3.30 (d, J = 7.2 Hz, 1H), 2.52 (s, 1H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 159.4, 159.3, 135.7, 130.8, 130.6, 129.9, 129.7, 128.7, 128.7, 128.0, 128.0, 114.0, 113.9, 98.8, 81.1, 80.7, 79.8, 79.8, 77.6, 77.5, 77.1, 76.8, 75.0, 74.6, 71.0, 69.6, 69.6, 69.5, 69.4, 56.0, 55.4, 55.3

D-*myo*-inositol 1-phosphate Dicyclohexylammonium salt (S8)

To a stirred solution of **S7** (10 mg, 13.8 μmol) in Toluene (300 μL) and CH_2Cl_2 (100 μL) were added BSTFA (36 μL), followed by TMSBr (18 μL). The reaction mixture was stirred for 1 h, and then concentrated under reduced pressure. The residue was dried under highly reduced pressure. To the residue was added CH_2Cl_2 (350 μL) and Me_2S (15 μL) and then cooled to 0 ºC. TFA (150 μL) was added to the mixture at 0 ºC and stirred 1 h at room temperature. The reaction mixture was concentrated under reduced pressure. The product was purified with Dowex-1X8 (HCO_3^-) anion exchange resin column (eluting with H_2O to 0.1 M NH_4HCO_3 aq to 0.5 M NH_4HCO_3 aq) to afford D-*myo*-inositol 1-phosphate diammonium

salt and then acidified with Dowex-50WX8 (H^+). Phosphoric acid was neutlized with cyclohexylammonium (10 μL) and then lyophylized to afford D-*myo*-inositol 1-phosphate dicyclohexylammonium salt (containing cyclohexylammonium salt) **S8** (7.78 mg, quant.) as a white solid. 1H-NMR (390 MHz, D_2O) δ 4.07 (t, J = 2.8 Hz, 1H), 3.74 (dt, J = 8.4, 2.8 Hz, 1H), 3.59 (t, J = 9.6 Hz, 1H), 3.48 (t, J = 9.6 Hz, 1H), 3.42 (dd, J = 10.0, 2.8 Hz, 1H), 3.18 (t, J = 9.3 Hz, 1H), 3.04-2.94 (m, 3H), 1.88-1.77 (m, 6H), 1.70-1.59 (m, 6H), 1.54-1.45 (m, 3H), 1.25-1.10 (m, 14H), 1.08-0.95 (m, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 74.4, 74.3, 72.3, 72.3, 71.7, 70.8, 50.4, 30.3, 24.3, 23.8; $[\alpha]_D^{24}$ +2.0º (*c* 0.389, H_2O), (lit, $[\alpha]_D^{28}$ +3.9º (*c* 3.0, H_2O))[1)]

1) Akiyama, T.; Takechi, N.; Ozaki, S.; Shiota, K.*Bull. Chem. Soc. Jpn.*, **1992**, *65*, 366-372

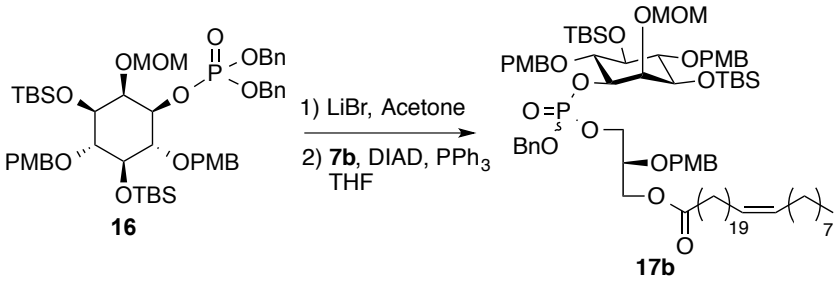


16 **17a**

3,5-di-*O*-*tert*-butyldimethylsilyl-4,6-di-*O*-4-methoxybenzyl-2-(4-methoxybenzyl)-3-*O*-((*cis*-21-triaco ntenyl)-*sn*-glycerol-3-benzylphosphate)-2-*O*-methoxymethyl-D-*myo*-inositol (17a)

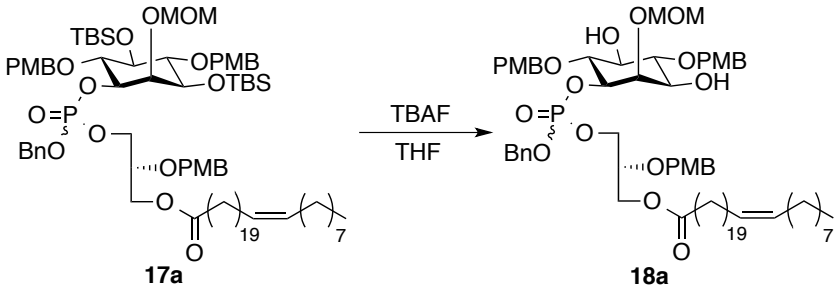
To a stirred solution of **16** (120 mg, 0.13 mmol) in Acetone (4 mL) was added LiBr (33 mg, 0.38 mmol). The reaction mixture was refluxed for over night. The mixture was cooled to ambient temperature, and then concentrated under reduced pressure. The residue was purified with silica gel column chromatography eluting with toluene/EtOAc (1:1) to CH_2Cl_2/MeOH (6:1) to afford lithium salt. The salt was passed through the cation exchange resin column (Dowex 50WX8 50-100) to obtain acid form. Fractions containing the desire product was collected and concentrated under reduced pressure. The residue was dissolved with THF (1.0 mL). **7a** (60 mg, 93.0 μmol), PPh_3 (73 mg, 0.28 mmol) was added to the solution. To the mixture was added DIAD (55 μL, 0.28 mmol). After stirred for over night, the reaction mixture was concentrated under reduced pressure. The residue was purified with silica gel column eluted with toluene/EtOAc (5:1) to afford **17a** (43.6 mg, 31%) as a color less oil. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.35-7.26 (m, 6H), 7.23-7.11 (m, 5H), 6.85-6.71 (m, 6H), 5.34 (t, J = 4.6 Hz, 2H), 5.03-4.67 (m, 8H), 4.53-4.36 (m, 2H), 4.33-3.84 (m, 6H), 3.84-3.75 (m, 7H), 3.75-3.69 (m, 3H), 3.67-3.58 (m, 2H), 3.57-3.44 (m, 2H), 3.44-3.35 (m, 3H), 2.28-2.16 (m, 2H), 2.01 (dd, J = 12.0, 6.4 Hz, 4H), 1.60-1.52 (m, 2H), 1.37-1.19 (m, 44H), 0.87 (t, J = 6.8 Hz, 3H), 0.81 (s, 9H), 0.79 (s, 9H), 0.00--0.04 (m, 3H), -0.06 (d, J = 3.3 Hz, 6H), -0.11--0.18 (m, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 173.5, 159.4, 158.8, 158.2, 131.4, 130.9, 130.0, 129.9, 129.5, 129.4, 129.2, 129.1, 129.0, 128.8, 128.7, 128.6,

128.5, 128.3, 128.0, 127.8, 127.4, 125.4, 113.9, 113.5, 113.2, 97.8, 81.9, 80.3, 80.3, 78.2, 77.9, 77.8, 77.7, 75.1, 74.8, 74.8, 74.7, 73.4, 71.7, 55.9, 55.3, 34.2, 32.0, 29.9, 29.8, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3, 29.2, 27.3, 26.1, 26.0, 25.0, 22.8, 21.6, 18.1, 14.2, –3.8, –4.3, –4.8; **HRMS** (ESI) calculated for $C_{84}H_{137}NaO_{16}PSi_2$ $[M+Na]^+$ 1511.9075, found 1511.9075



3,5-di-*O*-*tert*-butyldimethylsilyl-4,6-di-*O*-4-methoxybenzyl-2-(4-methoxybenzyl)-3-*O*-((*cis*-21-triacontenyl)-*sn*-glycerol-1-benzylphosphate)-2-*O*-methoxymethyl-D-*myo*-inositol (17b)

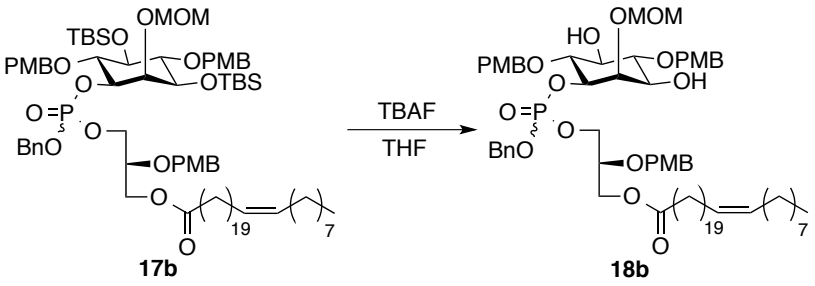
In a manner similar to the synthesis of **17a**, **16** (250 mg, 0.26 mmol) was converted into **17b** (299 mg, 81%) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 6H), 7.23-7.10 (m, 5H), 6.85-6.73 (m, 6H), 5.40-5.28 (m, 2H), 5.04-4.65 (m, 8H), 4.53-4.34 (m, 2H), 4.32-3.85 (m, 6H), 3.84-3.75 (m, 7H), 3.75-3.70 (m, 3H), 3.67-3.57 (m, 2H), 3.58-3.44 (m, 2H), 3.43-3.35 (m, 3H), 2.28-2.17 (m, 2H), 2.07-1.92 (m, 4H), 1.57-1.50 (m, 2H), 1.37-1.18 (m, 44H), 0.87 (t, J = 6.9 Hz, 3H), 0.81 (s, 9H), 0.79 (s, 9H), 0.03--0.01 (m, 3H), -0.03--0.10 (m, 6H), -0.10--0.17 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.4, 159.4, 158.8, 158.3, 131.4, 130.9, 130.5, 130.0, 129.9, 129.5, 129.3, 129.0, 128.9, 128.8, 128.8, 128.6, 128.6, 127.9, 127.8, 127.5, 113.8, 113.5, 113.2, 97.8, 81.9, 75.1, 75.0, 74.7, 73.5, 55.9, 55.3, 55.2, 34.2, 32.0, 29.9, 29.8, 29.8, 29.7, 29.6, 29.4, 27.3, 26.1, 25.9, 25.0, 22.8, 18.1, 14.2, –3.8, –4.3, –4.8; **HRMS** (ESI) calculated for $C_{84}H_{137}NaO_{16}PSi_2$ $[M+Na]^+$ 1511.9075, found 1511.9075



4,6-di-*O*-4-methoxybenzyl-2-(4-methoxybenzyl-3-*O*-((*cis*-21-triacontenyl)-*sn*-glycerol-3-benzylphosphate)-2-methoxymethyl-D-*myo*-inositol (18a)

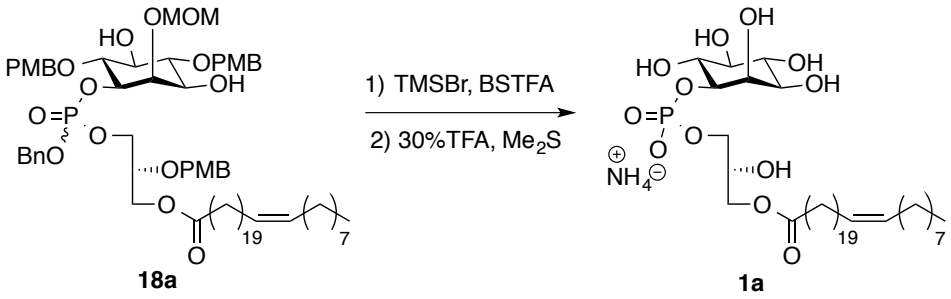
To a stirred solution of **17a** (43.6 mg, 29.2 μmol) in THF (600 μL) at 35 ºC was added TBAF (293 μL, 29.3 μmol) and AcOH (17 μL, 29.2 μmol). After the reaction mixture was stirred for 4.5 h, TBAF (293

μL, 29.3 μmol) was added and then stirred at 40 ºC for 5 h. To the mixture was added another TBAF (586 μL, 58.6 μmol) and stirred for 5h. The reaction was concentrated under reduced pressure. The residue was purified with silica gel column chromatography eluting with toluene/ethyl acetate (2/1) to afford **18a** (32.6 mg, 88%) as a color less oil. **^{1}H NMR** (390 MHz, $CDCl_3$) δ 7.37-7.23 (m, 9H), 7.23-7.14 (m, 2H), 6.91-6.85 (m, 2H), 6.84-6.76 (m, 4H), 5.40-5.27 (m, 2H), 5.07-4.96 (m, 2H), 4.87-4.79 (m, 1H), 4.79-4.60 (m, 5H), 4.51-4.43 (m, 2H), 4.29-3.95 (m, 6H), 3.81-3.62 (m, 11H), 3.58-3.48 (m, 1H), 3.48-3.30 (m, 5H), 2.30-2.19 (m, 2H), 2.06-1.93 (m, 4H), 1.63-1.49 (m, 2H), 1.38-1.20 (m, 44H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$) δ 173.6, 159.4, 159.3, 135.8, 135.8, 130.8, 130.6, 130.0, 129.8, 129.6, 129.6, 129.5, 128.7, 128.7, 128.0, 114.0, 113.9, 98.8, 81.0, 80.6, 80.6, 80.5, 80.5, 79.8, 79.7, 77.5, 77.1, 76.8, 75.0, 75.0, 74.9, 74.8, 74.8, 74.6, 71.8, 71.0, 71.0, 69.7, 69.9, 69.5, 66.5, 66.4, 66.4, 66.3, 62.4, 56.0, 55.3, 34.2, 32.0, 29.9, 29.8, 29.7, 29.6, 29.4, 29.3, 27.3, 25.0, 22.8, 14.2; **HRMS** (ESI) calculated for $C_{72}H_{109}NaO_{16}P$ $[M+Na]^+$ 1283.7345, found 1283.7374



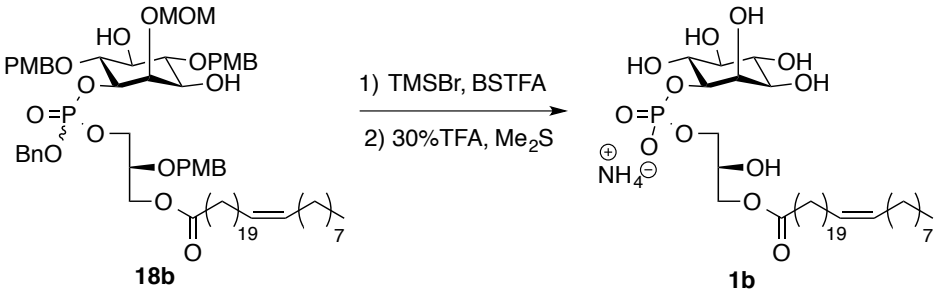
4,6-di-*O*-4-methoxybenzyl-2-(4-methoxybenzyl-3-*O*-((*cis*-21-triacontenyl)-*sn*-glycerol-1-benzylphosphate)-2-methoxymethyl-D-*myo*-inositol (18b)

In a manner similar to the synthesis of **18a**, **17b** (289 mg, 0.19 μmol) was converted into **18b** (205.4 mg, 84%) as a color less oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 6H), 7.23-7.10 (m, 5H), 6.85-6.73 (m, 6H), 5.40-5.28 (m, 2H), 5.04-4.65 (m, 8H), 4.53-4.34 (m, 2H), 4.32-3.85 (m, 6H), 3.84-3.75 (m, 7H), 3.75-3.70 (m, 3H), 3.67-3.57 (m, 2H), 3.58-3.44 (m, 2H), 3.43-3.35 (m, 3H), 2.28-2.17 (m, 2H), 2.07-1.92 (m, 4H), 1.57-1.50 (m, 2H), 1.37-1.18 (m, 44H), 0.87 (t, J = 6.9 Hz, 3H), 0.81 (s, 9H), 0.79 (s, 9H), 0.03--0.01 (m, 3H), -0.03--0.10 (m, 6H), -0.10--0.17 (m, 3H); **^{13}C NMR** (125 MHz, $CDCl_3$) δ 173.5, 159.4, 159.3, 135.8, 130.8, 130.7, 130.5, 130.0, 129.8, 129.6, 129.6, 129.6, 129.5, 129.1, 128.7, 128.7, 128.3, 128.0, 128.0, 125.4, 114.0, 113.9, 98.7, 81.1, 80.6, 80.5, 79.8, 79.7, 79.2, 77.6, 74.9, 74.9, 74.9, 74.8, 74.8, 74.6, 74.5, 71.8, 71.8, 71.1, 71.0, 69.7, 65.5, 62.4, 62.4, 56.0, 55.4, 55.3, 34.2, 32.7, 32.0, 29.9, 29.8, 29.8, 29.7, 29.6, 29.4, 29.3, 27.3, 24.9, 22.8, 14.2; **HRMS** (ESI) calculated for $C_{72}H_{109}NaO_{16}P$ $[M+Na]^+$ 1283.7345, found 1283.7345



EhPIa-C30:1 (1a)

To a stirred solution of **18a** (5 mg, 3.90 μmol) in Toluene (200 μL) was added BSTFA (31 μL), followed by TMSBr (120 μL). The reaction mixture was stirred for 3.5h, and then concentrated under reduced pressure. To the residue was added MeOH and stirred for 30 min. The mixture was concentrated under reduced pressure. The residue was dried under highly reduced pressure. To the residue was added CH_2Cl_2 (350 μL) and Me_2S (14 μL) and then cooled to 0 ºC. TFA (150 μL) was added to the mixture at 0 ºC and stirred for 5 min and then stirred for 30 min at room temperature. The reaction mixture was concentrated under reduced pressure. The product was purified with silica gel column chromatography eluting with $CHCl_3$/MeOH/2.2M NH_4OH (25 : 10 : 2) to afford **EhPIa-C30:1** (**1a**) (1.32 mg, 43% for 2 steps) as a white solid (ammonium salt). **^{1}H NMR** (390 MHz, $CDCl_3$:CD_3OD:D_2O = 25:10:2) δ 5.30-5.19 (m, 2H), 4.11 (s, 1H), 4.00 (d, *J* = 15.3 Hz, 2H), 3.90 (s, 4H), 3.63 (t, *J* = 9.6 Hz, 1H), 3.50 (d, J = 9.4 Hz, 1H), 3.34 (d, J = 9.4 Hz, 1H), 3.16 (d, J = 8.8 Hz, 1H), 2.27-2.20 (m, 2H), 1.91 (d, J = 6.3 Hz, 4H), 1.49 (s, 2H), 1.27-1.11 (m, 44H), 0.79-0.74 (m, 3H); **^{13}C NMR** (98 MHz, $CDCl_3$:CD_3OD:D_2O = 25:10:2) δ 174.7, 129.8, 76.2, 74.1, 72.3, 71.5, 71.2, 68.5, 66.6, 64.9, 49.0, 48.8, 48.6, 48.4, 48.2, 47.9, 47.7, 33.8, 31.8, 29.7, 29.6, 29.4, 29.4, 29.3, 29.2, 29.2, 29.1, 29.1, 27.0, 24.7, 22.5, 13.8; **^{31}P NMR** (158 MHz, $CDCl_3$: CD_3OD:D_2O = 25:10:2) δ 0.027; **HRMS** (ESI) calculated for $C_{39}H_{74}O_{12}P$ $[M-H]^-$ 765.4923, found 765.4941



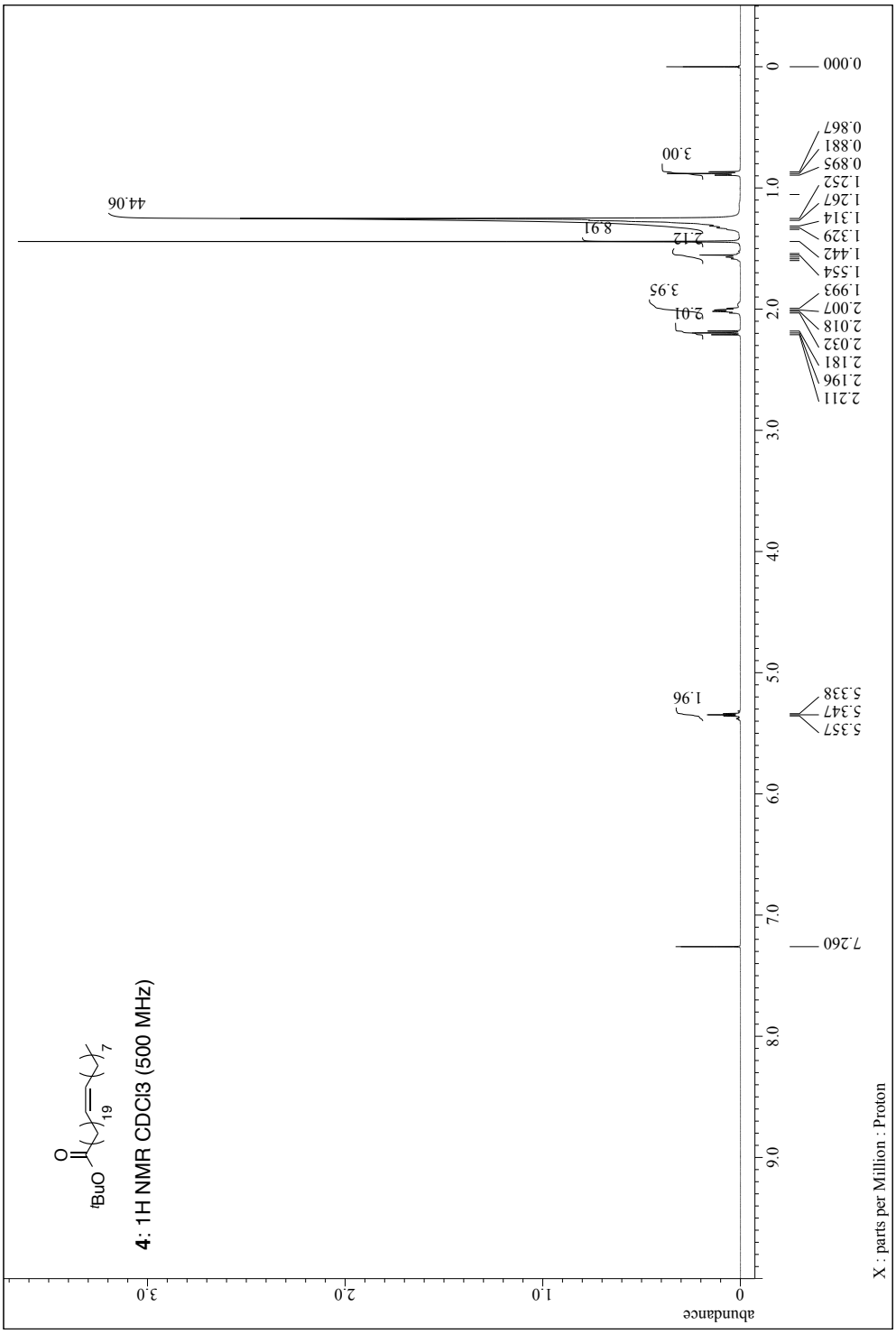
2'-*epi*-EhPIa-C30:1 (1b)

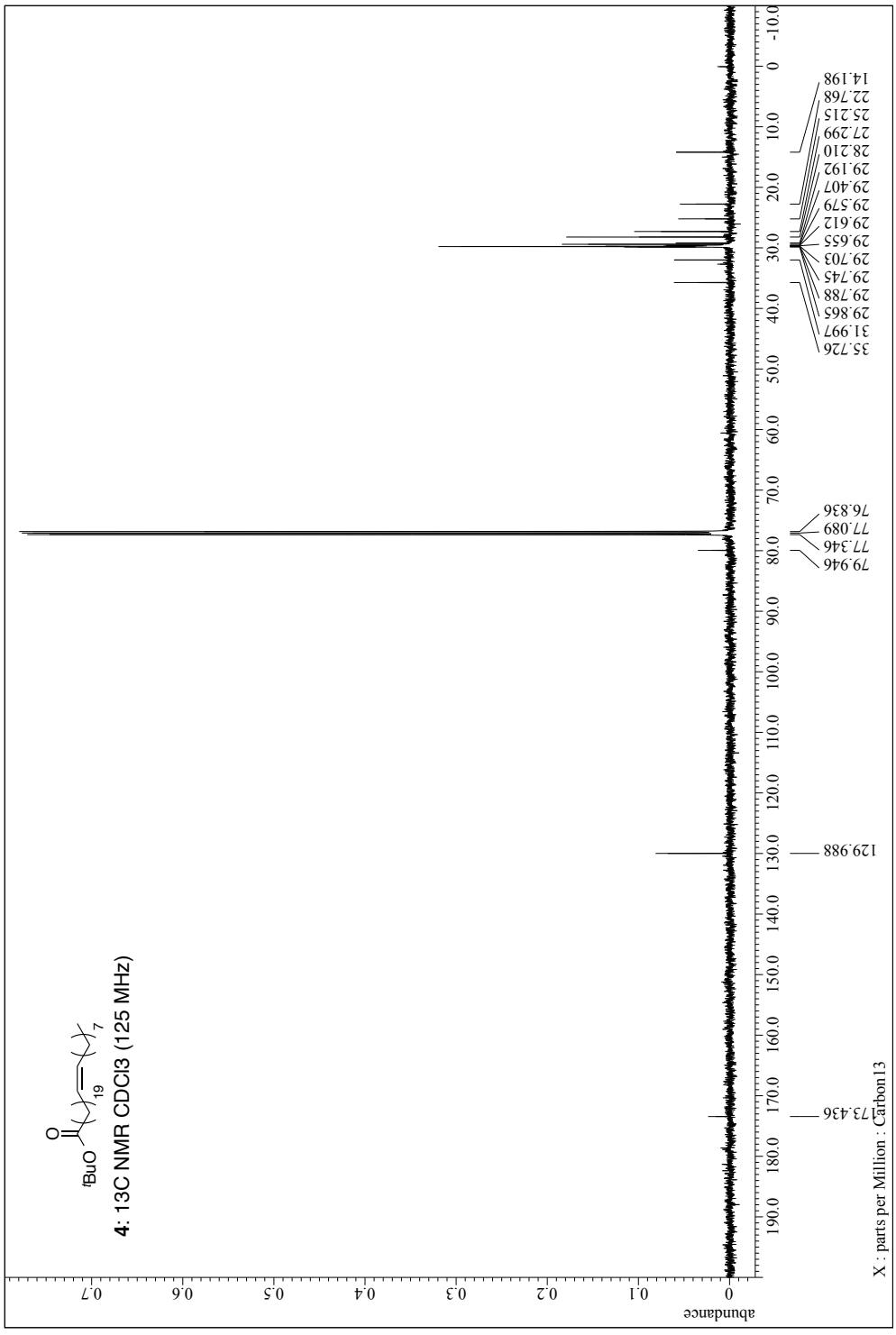
In a manner similar to the synthesis of **1a, 18b** (103 mg, 81.6 μmol) was converted into **2'-*epi*-EhPIa-C30:1 (1b)** (19.7 mg, 31% for 2 steps) as a white solid (ammonium salt). **^{1}H NMR** (600 MHz, $CDCl_3$:CD_3OD:D_2O = 5:5:1) δ 5.40 – 5.35 (m, 2H), 4.24 (s, 1H), 4.18 – 4.15 (m, 1H), 4.13 – 4.10 (m, 1H), 4.03 – 3.98 (m, 2H), 3.95 – 3.92 (m, 2H), 3.76 (t, *J* = 9.6 Hz, 1H), 3.64 (t, *J* = 9.6 Hz, 1H), 3.46 (dd, *J* = 2.4, 9.6 Hz, 1H), 3.27 (t, *J* = 9.6 Hz, 1H), 2.36 (t, *J* = 7.2 Hz, 2H), 2.05 – 1.96 (m, 4H), 1.61 (dd, *J* = 7.2 Hz, 2H)1.38 – 1.28 (m, 44H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (150 MHz, $CDCl_3$:CD_3OD: D_2O = 5:5:1) δ 174.0, 129.6, 129.0, 75.8, 73.7, 71.8, 71.0, 70.7, 70.4, 67.9, 65.9, 64.3, 48.9, 48.0, 33.1, 31.6, 31.0, 29.7, 28.8, 28.8, 28.6, 28.5, 28.4, 28.4, 28.3, 28.3, 26.2, 24.3, 23.9, 21.7, 12.9; **^{31}P NMR** (242 MHz, $CDCl_3$:CD_3OD:D_2O = 5:5:1) δ 1.57; **HRMS** (ESI) calculated for $C_{39}H_{74}O_{12}P$ $[M-H]^-$ 765.4923, found 765.4941

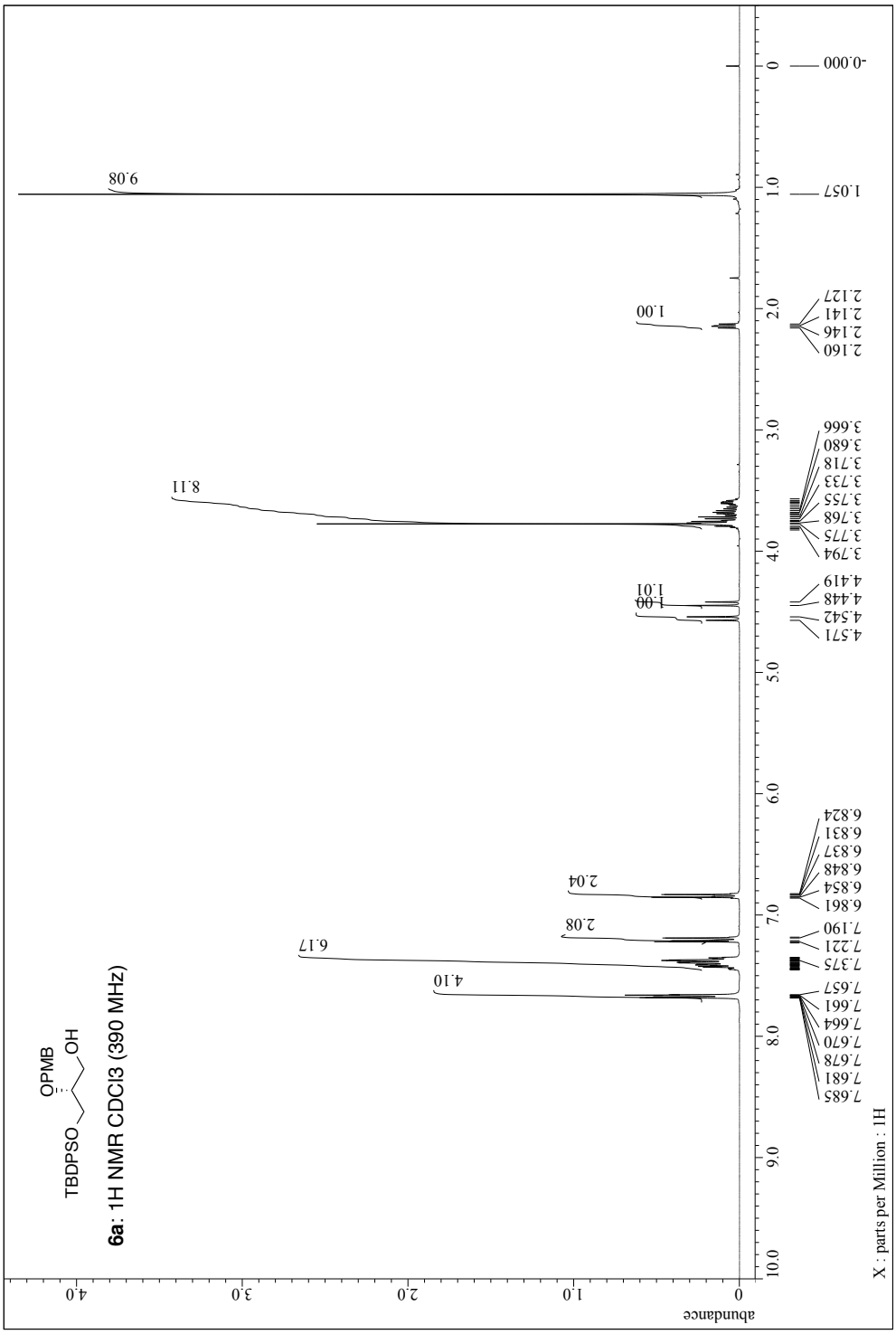
III. Abbreviation

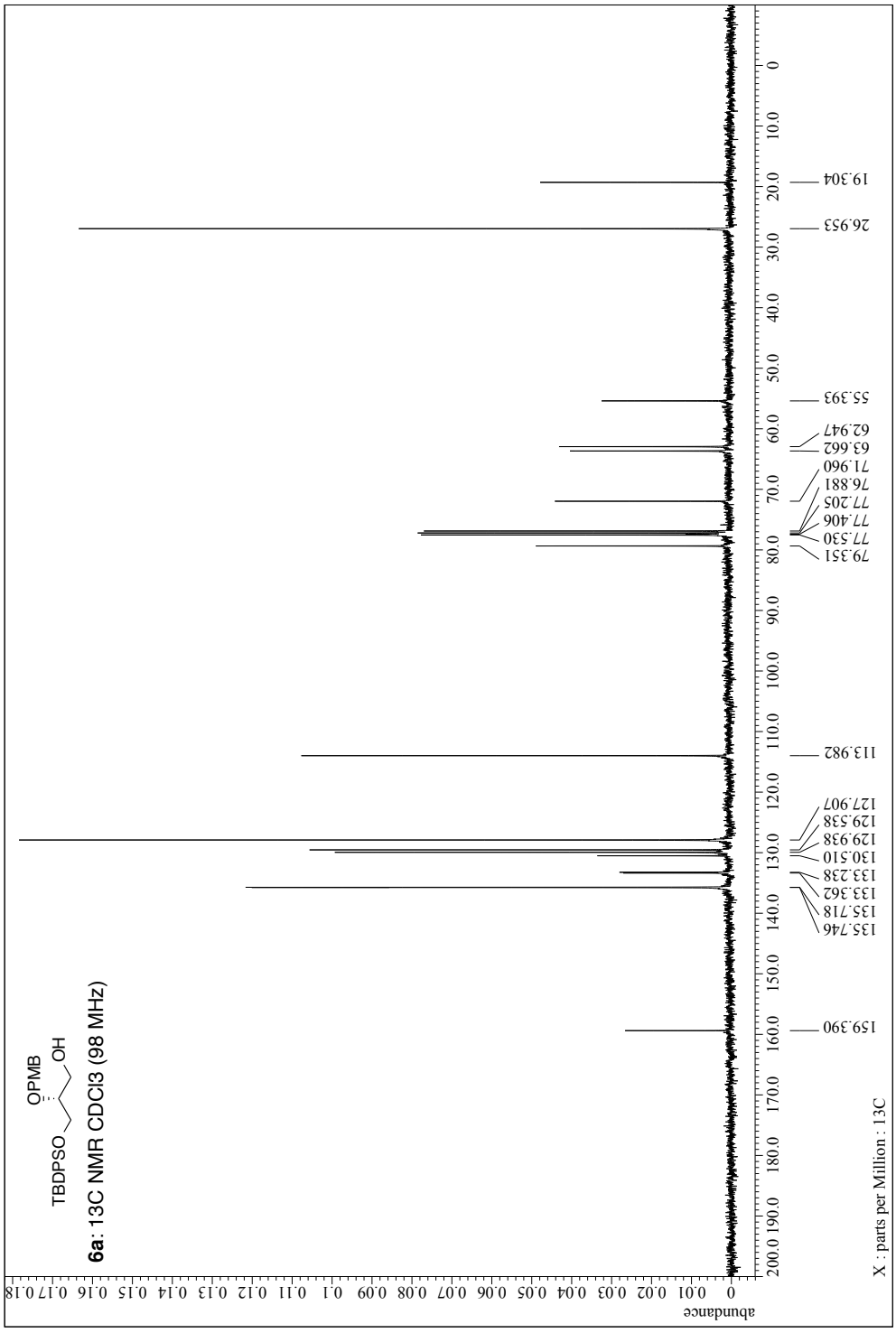
NMP: *N*-methylpyrrolidone, THF: tetrahydrofurane, TFA: trifluoroacetic acid, TBDPS: *tert*-butyldiphenylsilyl, PMB: *p*-methoxybenzyl, WSC: water soluble carbodiimide, DMAP: 4-dimethylamino pyridine, TBAF: tetrabutylanmmonium fluoride, DCC: dicyclohexylcarbodiimide, *m*CPBA: *m*-chloroperbenzoic acid, MOM: methoxymethyl, Bt: benzotriazole, Alloc: allyloxycarbonyl, TBS: *tert*-butyldimethylsilyl, DMF: dimethylformamide, DIAD: diisopropyl azodicarboxylate, TMSBr: trimethylsilyl bromide, BSTFA: *N*,*O*-Bis(trimethylsilyl)trifluoroacetamide, 1,3-DMBA: 1,3-dimethylbarbituric acid, DIPEA: diisopropylethylamine, DMS: dimethylsulfide

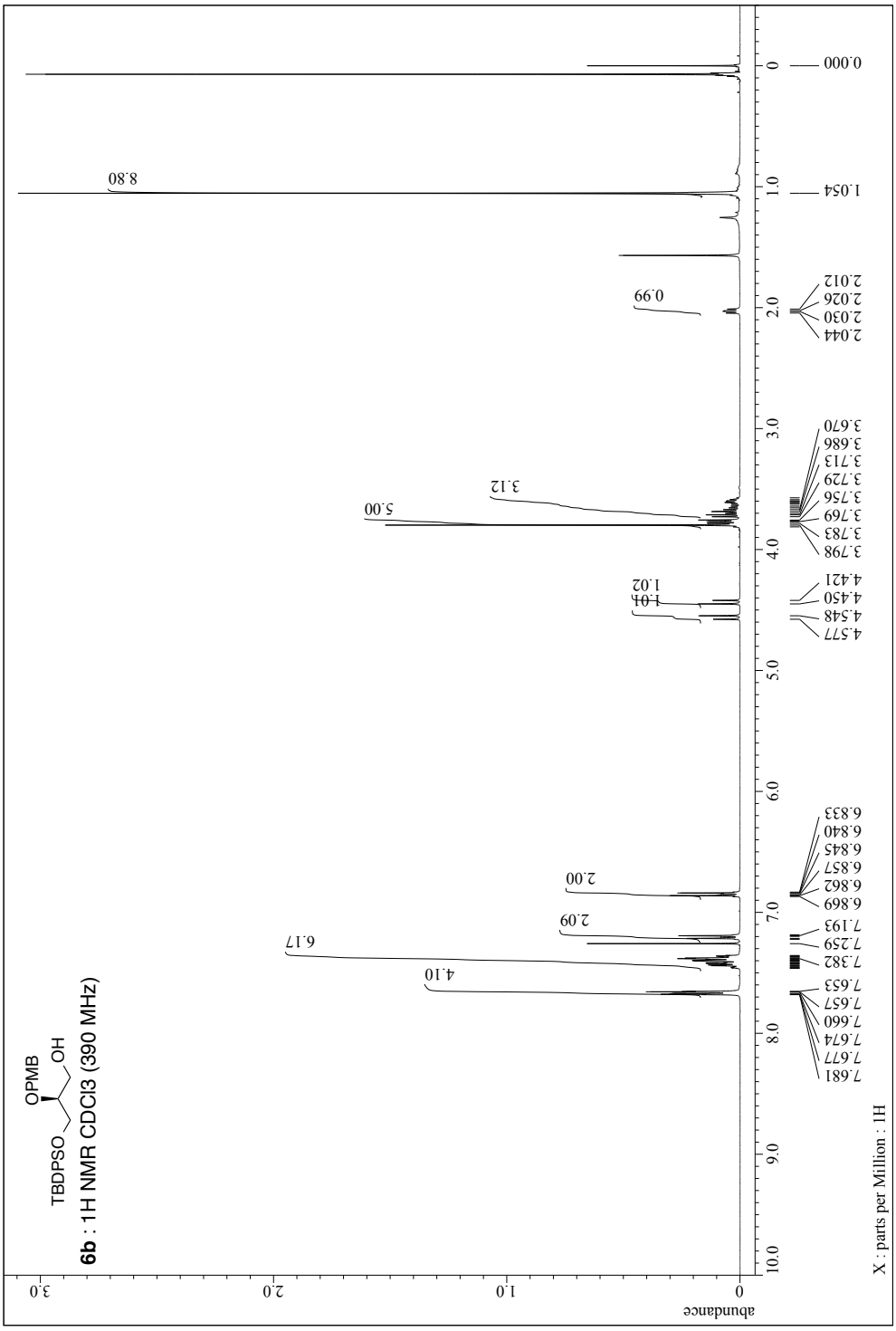
IV. 1H and 13C NMR spectra of compounds

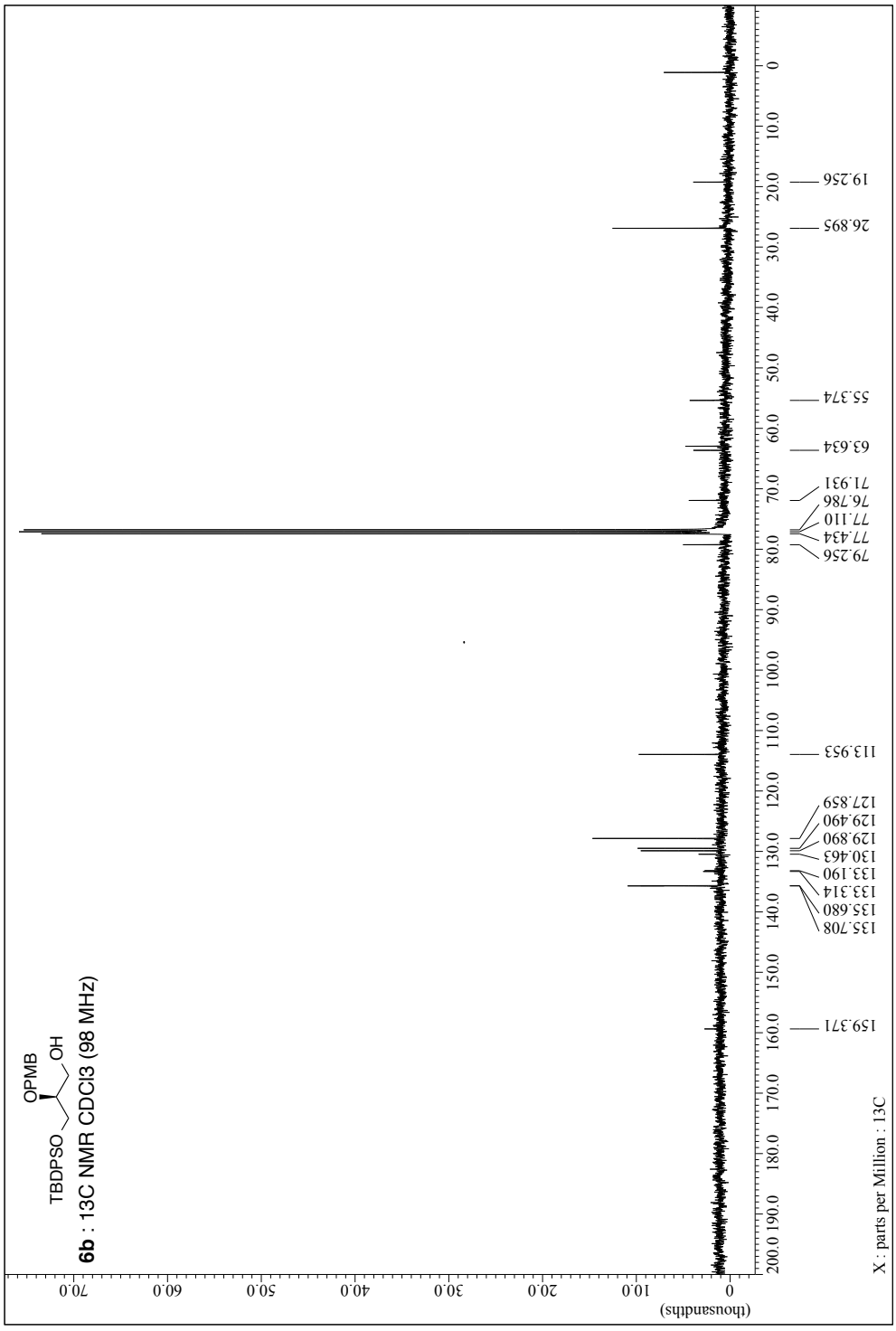


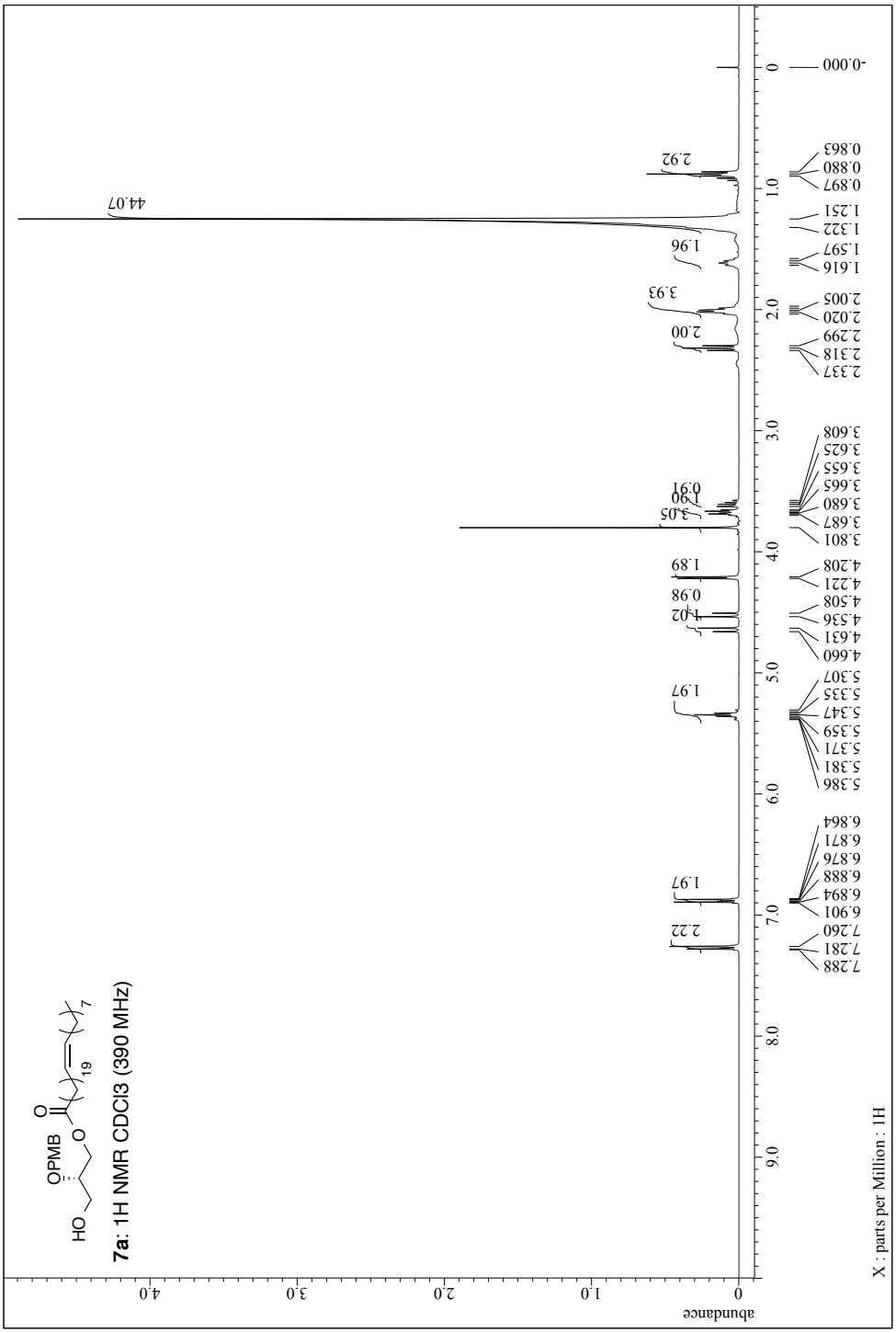

4: 13C NMR CDCl3 (125 MHz)
tBuO
O
19
7
abundance
X : parts per Million : Carbon13
73.436
129.988
79.946
77.346
77.089
76.836
35.726
31.997
29.865
29.788
29.745
29.703
29.655
29.612
29.579
29.407
29.192
28.210
27.299
25.215
22.768
14.198

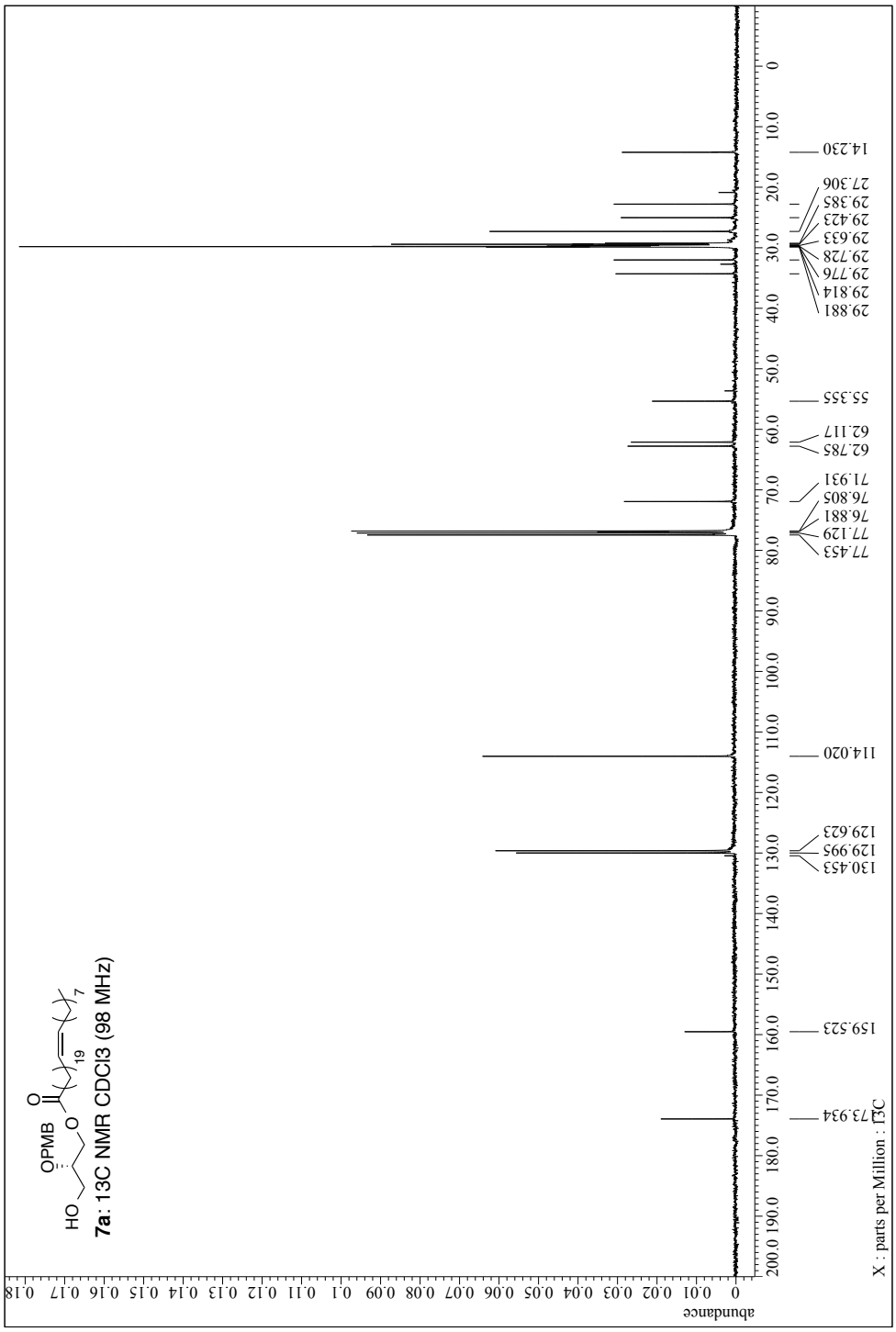

6a: 1H NMR CDCl3 (390 MHz)
TBDPSO
OPMB
OH
abundance
X : parts per Million : 1H
9.08
8.11
6.17
4.10
2.04
2.08
1.00
1.01
1.00
1.057
-0.000

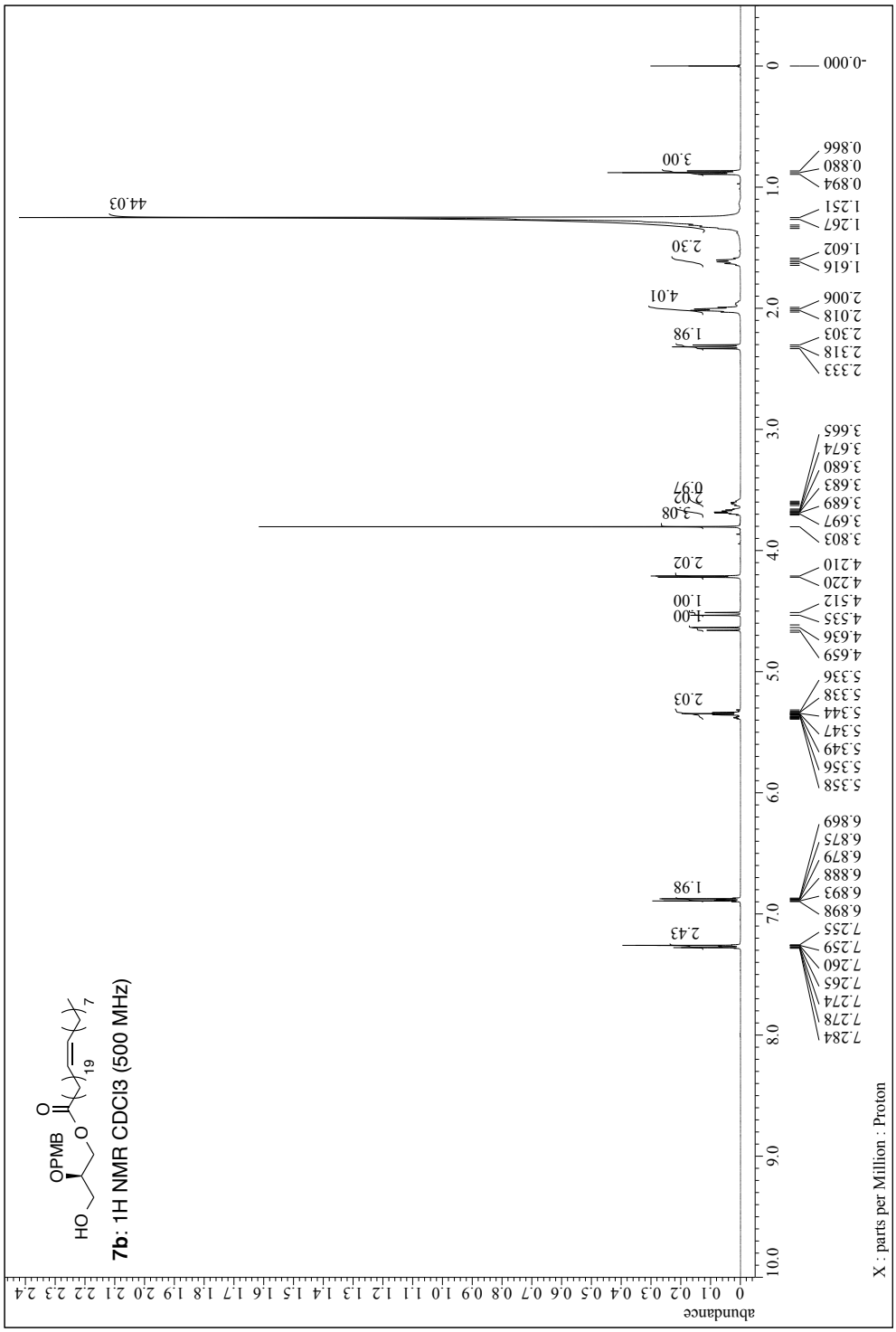

6a: 13C NMR CDCl3 (98 MHz)
TBDPSO
OPMB
OH
abundance
X : parts per Million : 13C
159.390
135.746
135.718
133.362
133.238
130.510
129.938
129.538
127.907
113.982
79.351
77.530
77.406
77.205
76.881
71.960
63.662
62.947
55.393
26.953
19.304

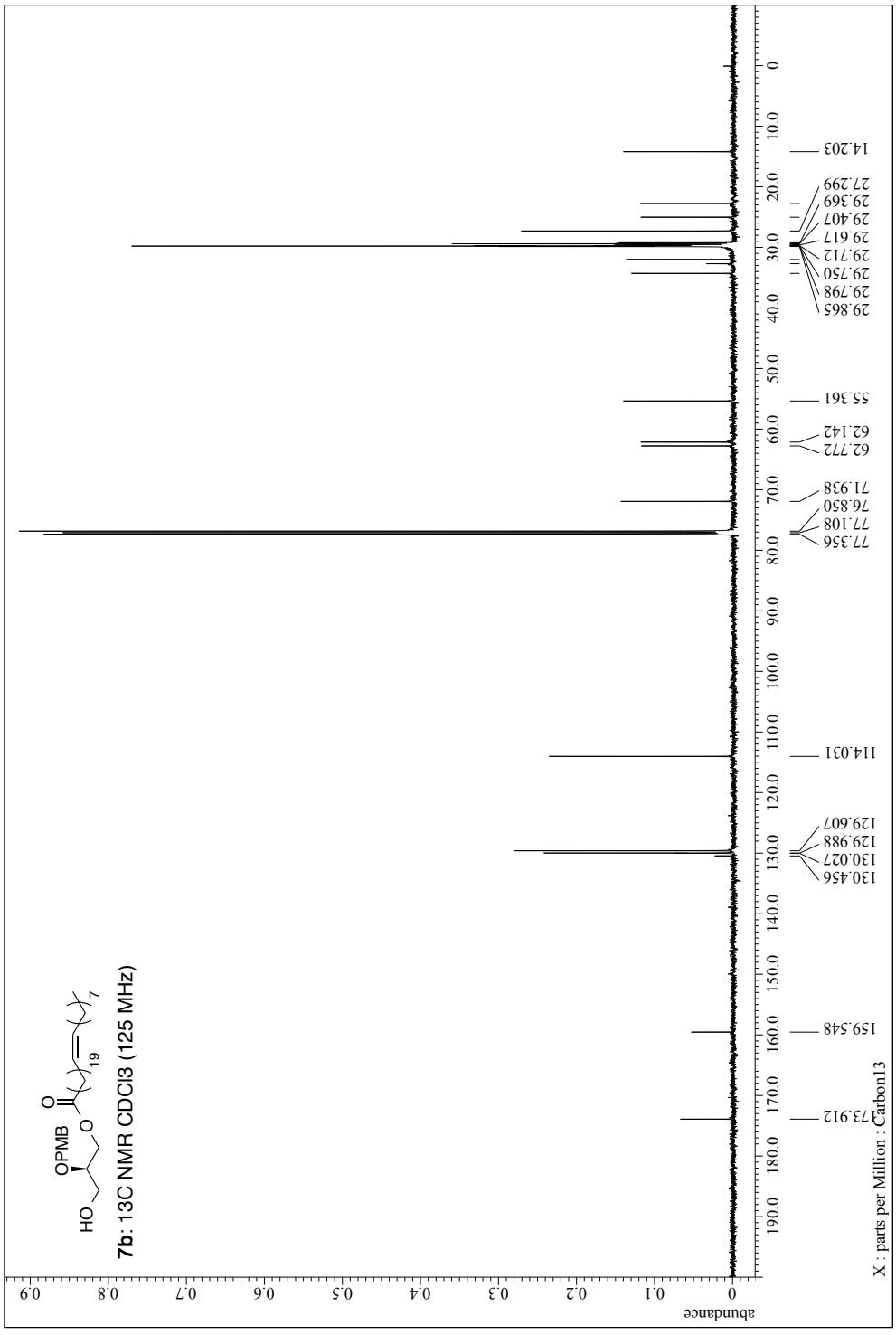

6b : 1H NMR CDCl3 (390 MHz)
TBDPSO
OPMB
OH
abundance
X : parts per Million : 1H
0.000
1.054
8.80
0.99
2.044
2.030
2.026
2.012
3.798
3.783
3.769
3.756
3.729
3.713
3.686
3.670
3.12
5.00
1.01
1.02
4.577
4.548
4.450
4.421
2.00
2.09
6.17
4.10
7.681
7.677
7.674
7.660
7.657
7.653
7.382
7.259
7.193
6.869
6.862
6.857
6.845
6.840
6.833

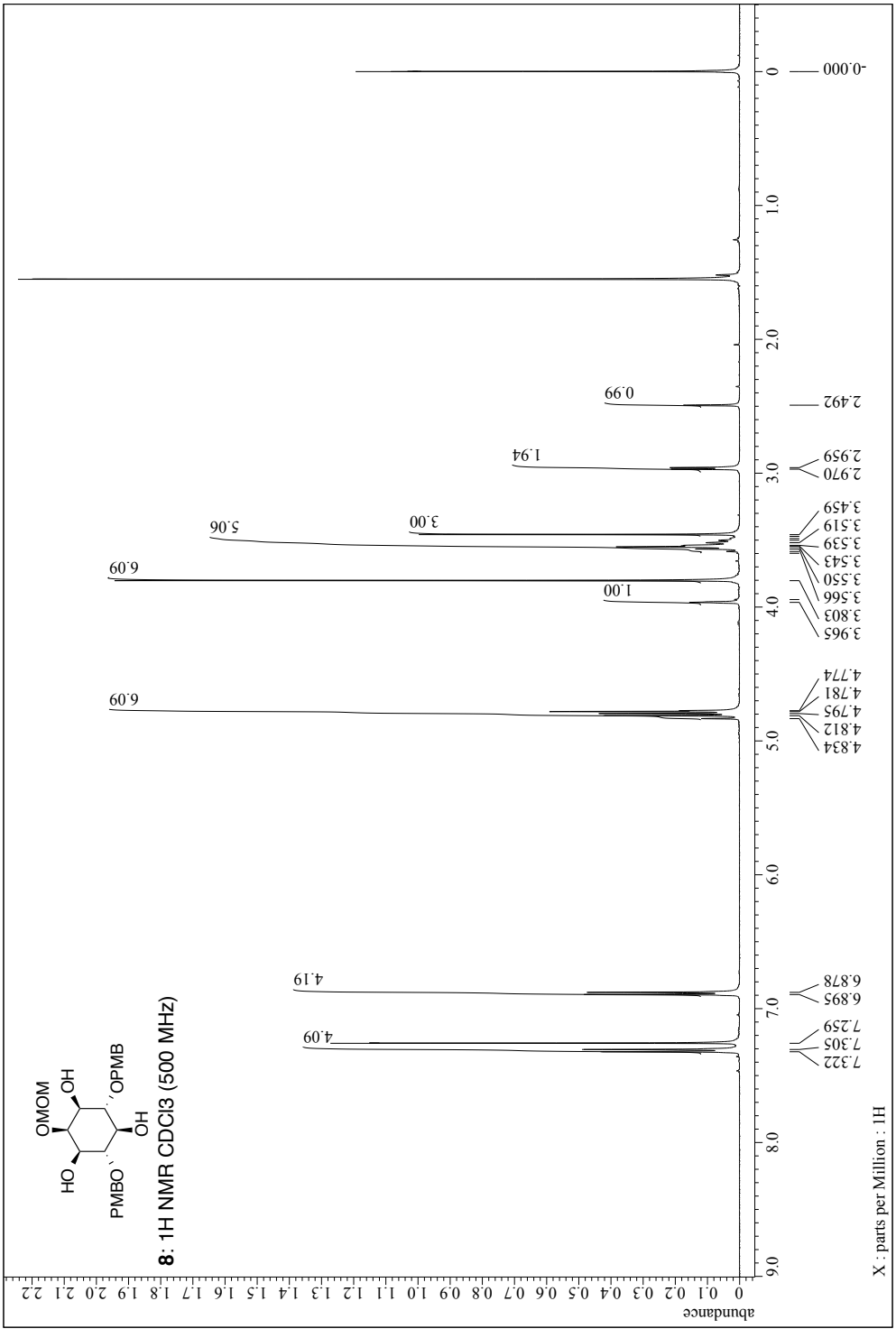

6b : 13C NMR CDCl3 (98 MHz)
TBDPSO
OPMB
OH
(thousandths)
X : parts per Million : 13C
159.371
135.708
135.680
133.314
133.190
130.463
129.890
129.490
127.859
113.953
79.256
77.434
77.110
76.786
71.931
63.634
55.374
26.895
19.256

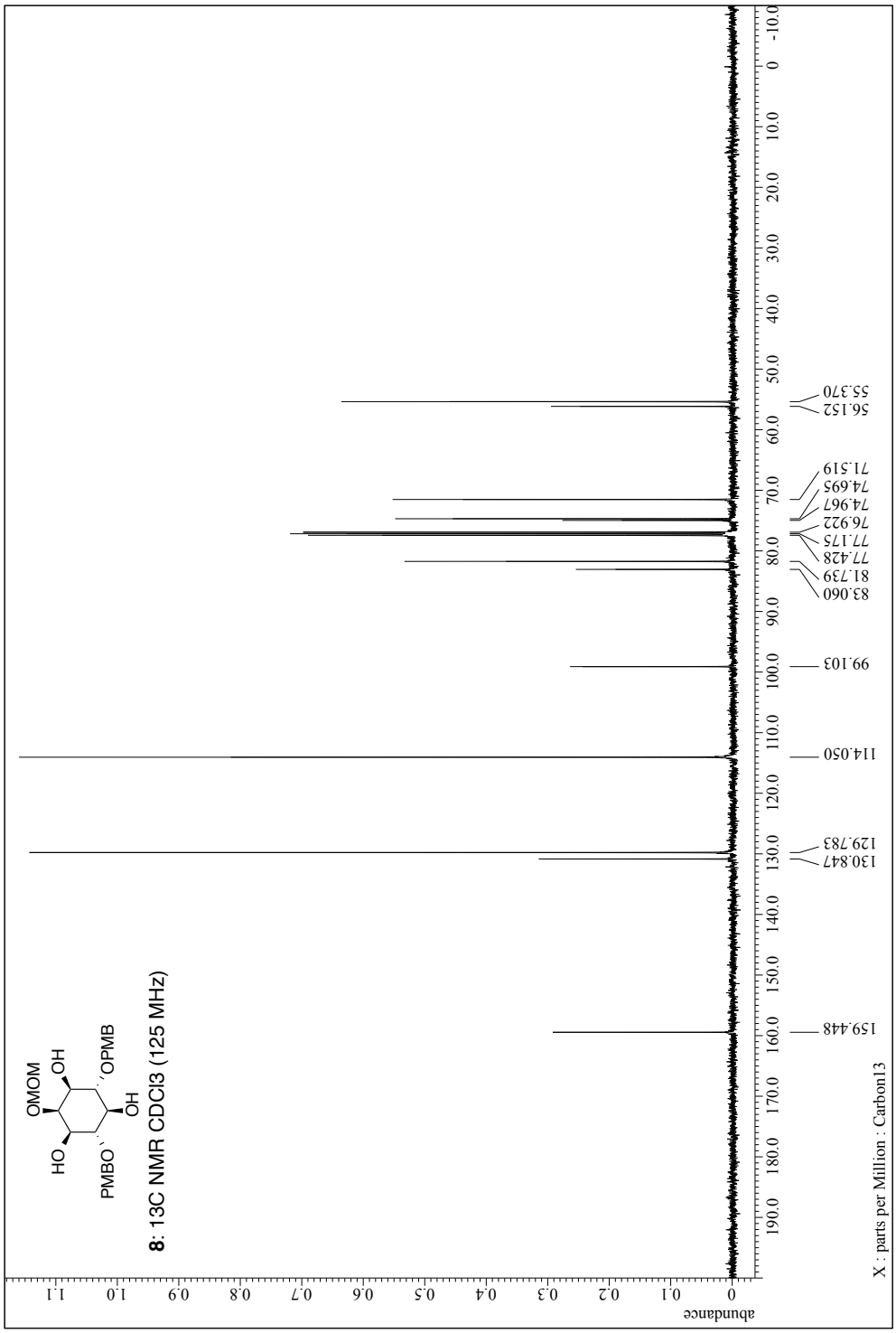

7a: 1H NMR CDCl3 (390 MHz)
OPMB
HO
abundance
X : parts per Million : 1H

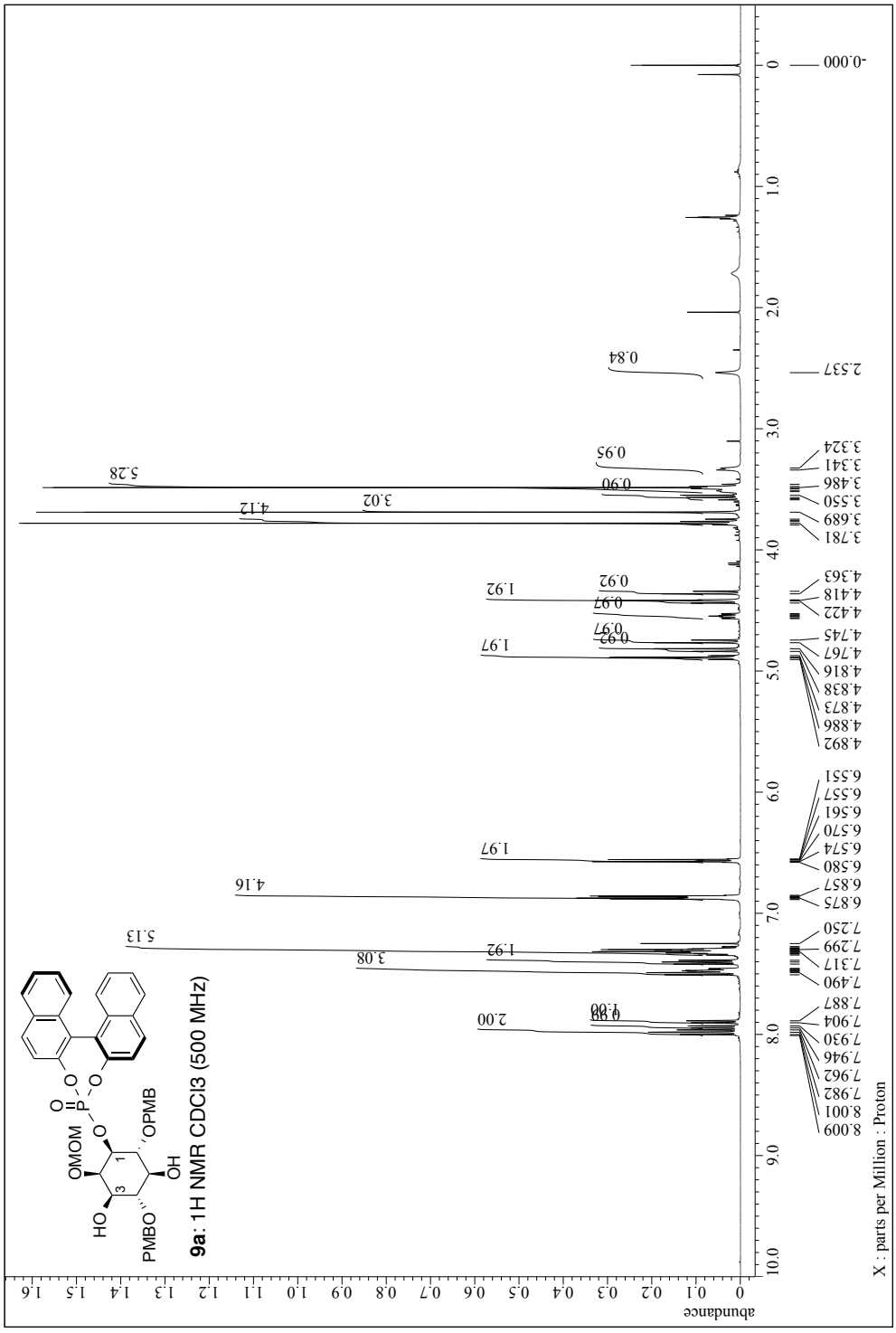

7a: 13C NMR CDCl3 (98 MHz)
HO
OPMB
O
O
19
7
abundance
X : parts per Million : 13C
14.230
27.306
29.385
29.423
29.633
29.728
29.776
29.814
29.881
55.355
62.117
62.785
71.931
76.805
76.881
77.129
77.453
114.020
129.623
129.995
130.453
159.523
173.934

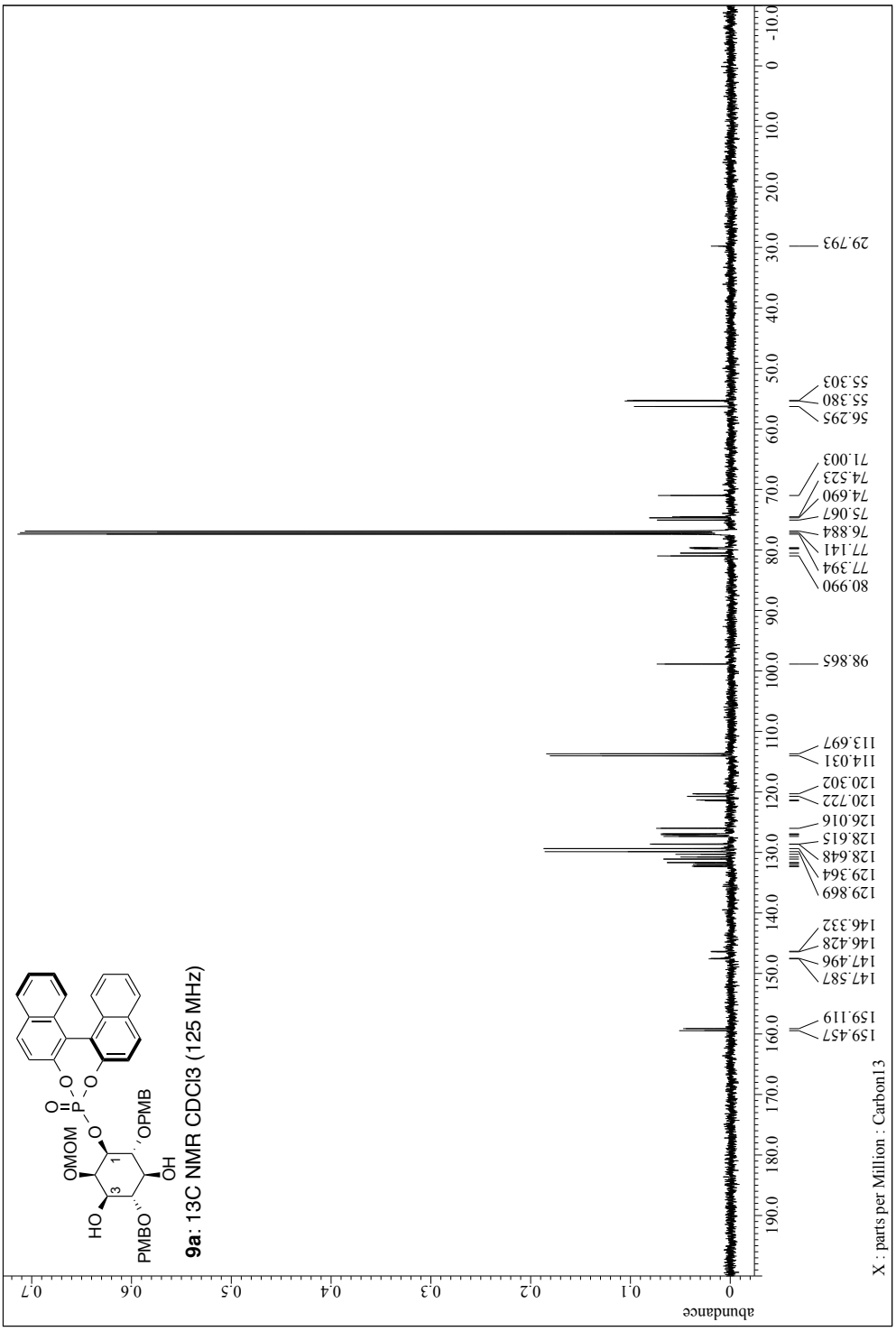

7b: 1H NMR CDCl3 (500 MHz)
HO
OPMB
O
O
19
7
abundance
X : parts per Million : Proton
-0.000
0.866
0.880
0.894
1.251
1.267
1.602
1.616
2.006
2.018
2.303
2.318
2.333
3.665
3.674
3.680
3.683
3.689
3.697
3.803
4.210
4.220
4.512
4.535
4.636
4.659
5.336
5.338
5.344
5.347
5.349
5.356
5.358
6.869
6.875
6.879
6.888
6.893
6.898
7.255
7.259
7.260
7.265
7.274
7.278
7.284
2.43
1.98
2.03
1.00
1.00
2.02
3.08
2.02
0.97
1.98
4.01
2.30
44.03
3.00

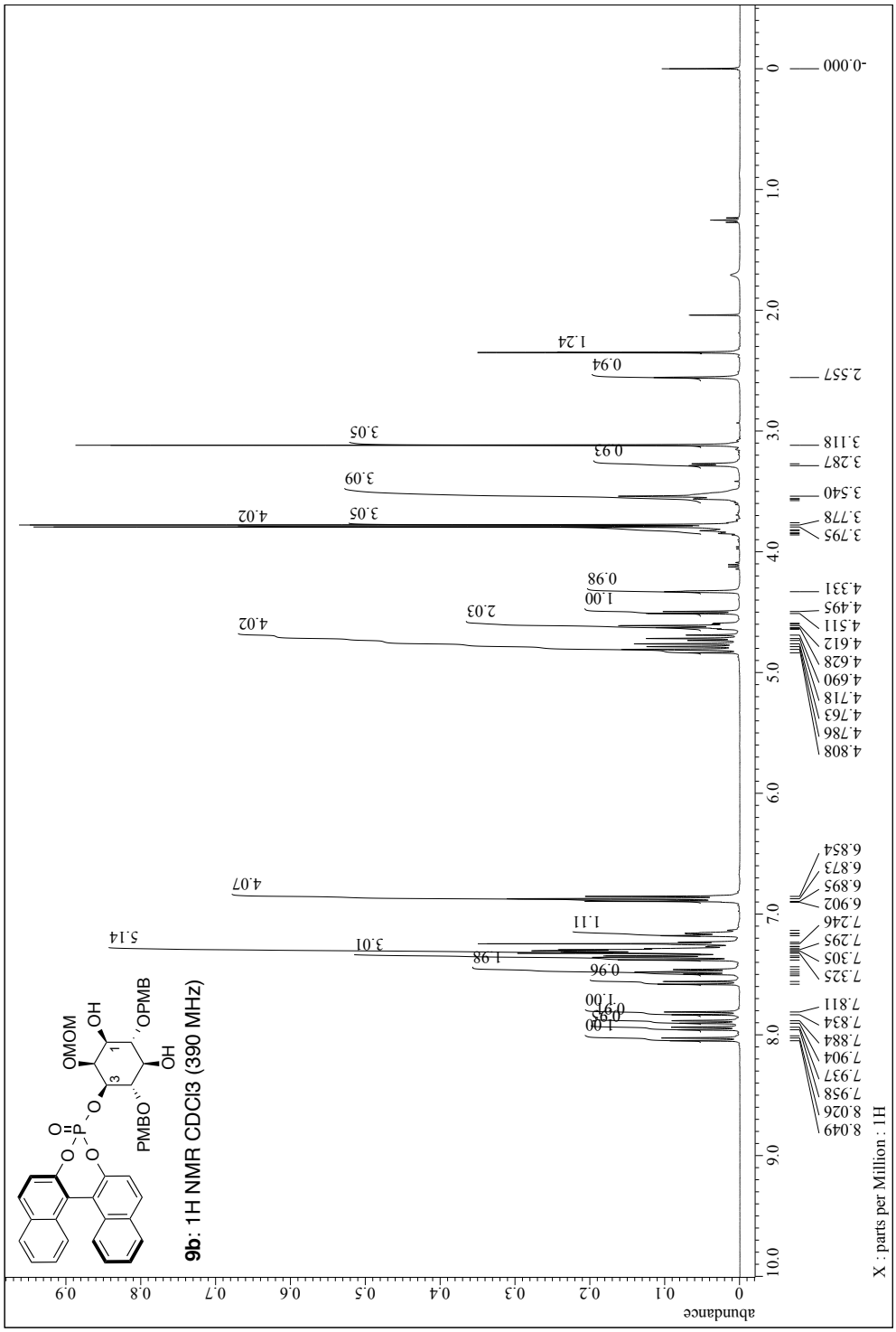

7b: 13C NMR CDCl3 (125 MHz)
HO
OPMB
O
O
19
7
abundance
X : parts per Million : Carbon13
173.912
159.548
130.456
130.027
129.988
129.607
114.031
77.356
77.108
76.850
71.938
62.772
62.142
55.361
29.865
29.798
29.750
29.712
29.617
29.407
29.369
27.299
14.203

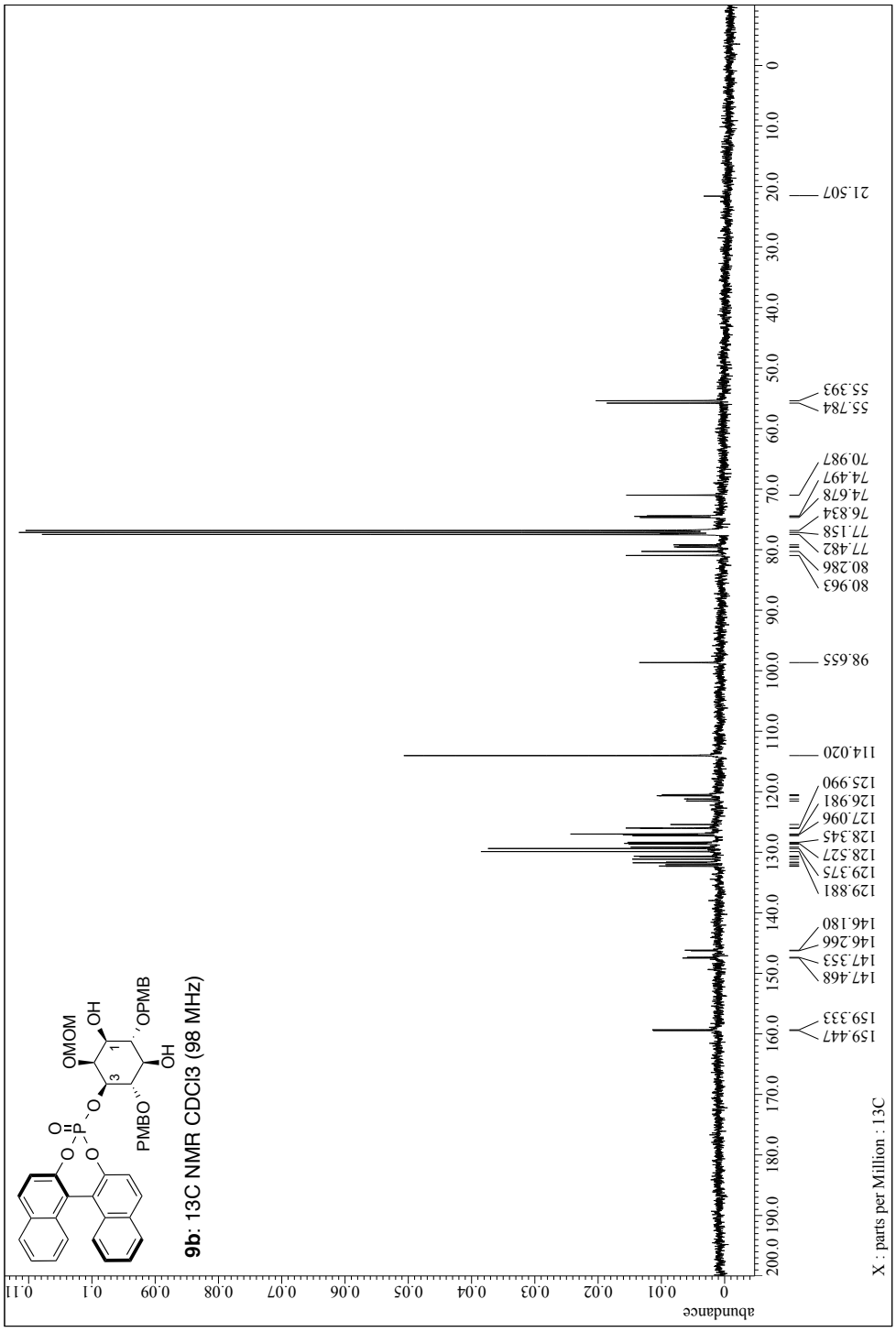

8: 1H NMR CDCl3 (500 MHz)
OMOM
OH
OPMB
HO
PMBO
OH
abundance
X : parts per Million : 1H
7.322
7.305
7.259
6.895
6.878
4.834
4.812
4.795
4.781
4.774
3.965
3.803
3.566
3.550
3.543
3.539
3.519
3.459
2.970
2.959
2.492
-0.000
4.09
4.19
6.09
6.09
1.00
6.09
5.06
3.00
1.94
0.99

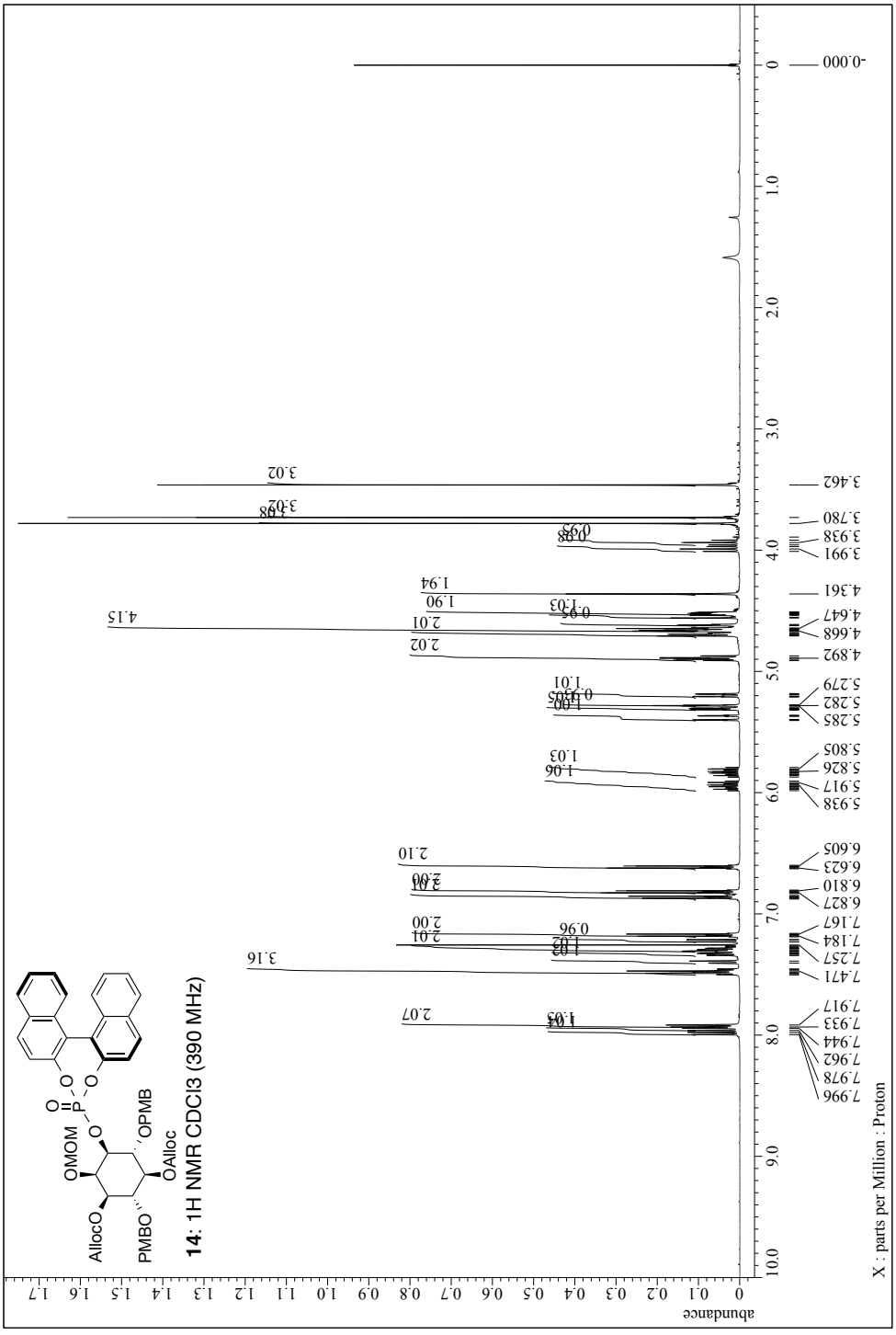

8: 13C NMR CDCl3 (125 MHz)
OMOM
OH
HO
OPMB
OH
PMBO
159.448
130.847
129.783
114.050
99.103
83.060
81.739
77.428
77.175
76.922
74.967
74.695
71.519
56.152
55.370
abundance
X : parts per Million : Carbon13

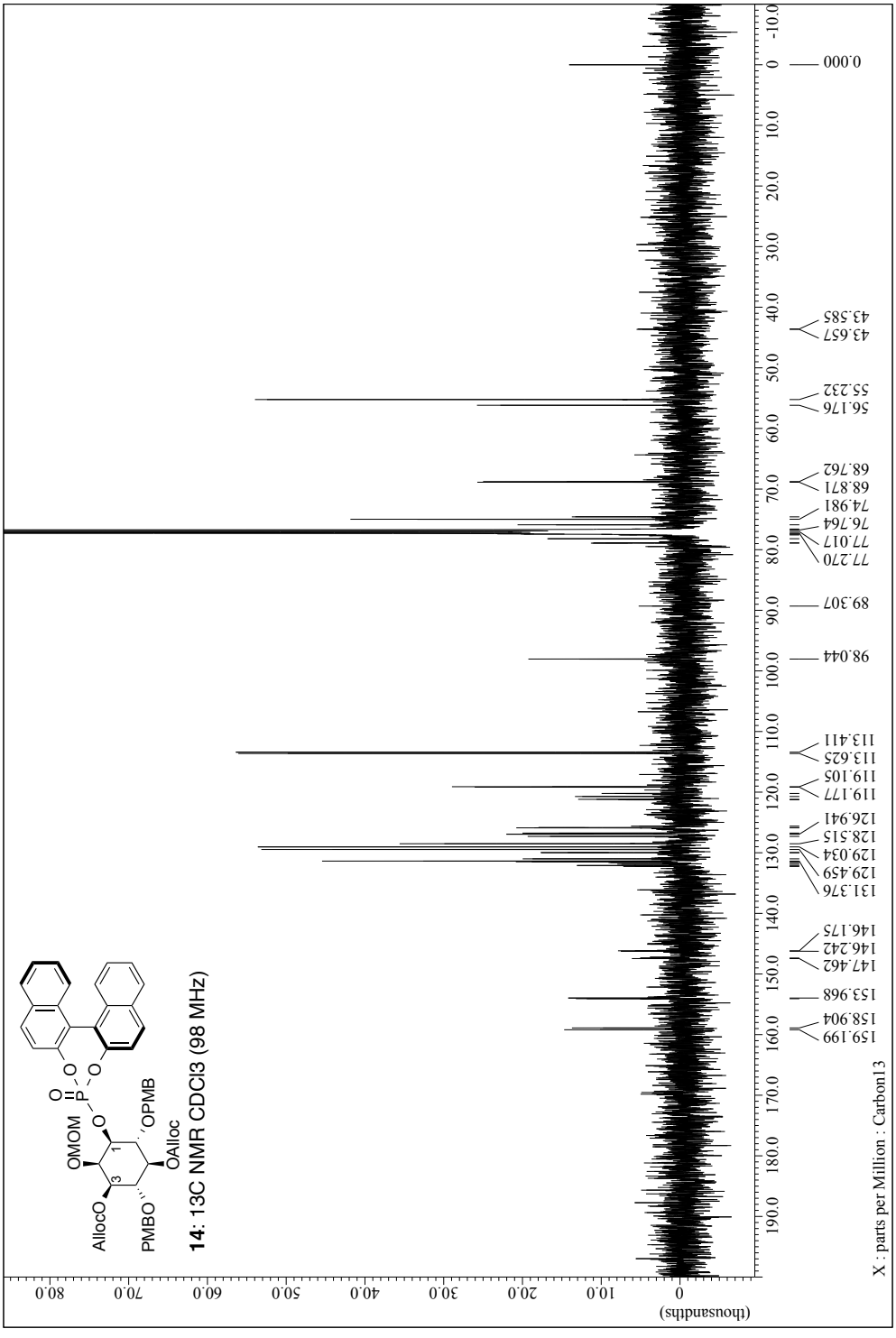

9a: 1H NMR CDCl3 (500 MHz)
X : parts per Million : Proton
abundance

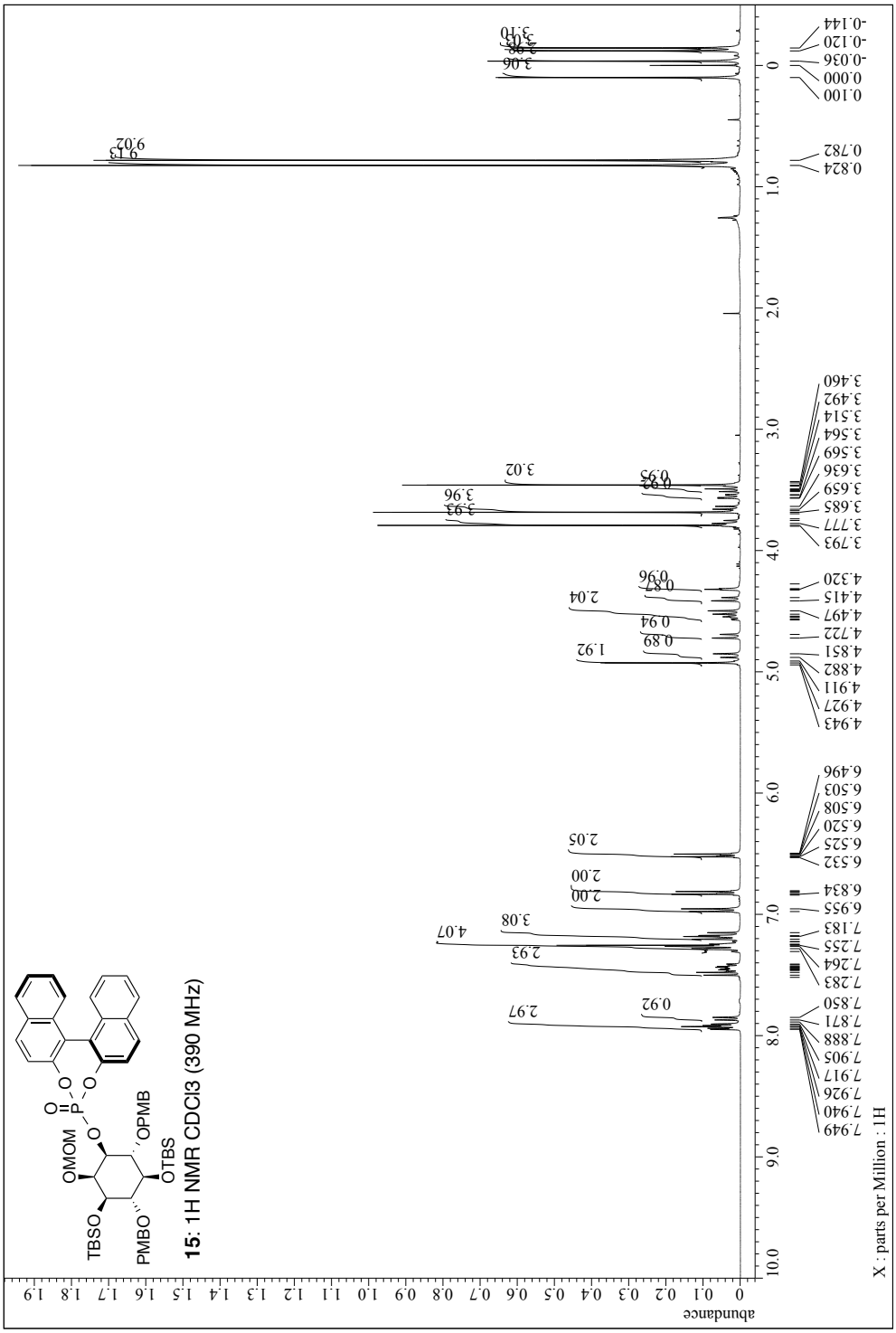

9a: 13C NMR CDCl3 (125 MHz)
PMBO
HO
OMOM
OPMB
OH
abundance
X : parts per Million : Carbon13
159.457
159.119
147.587
147.496
146.428
146.332
129.869
129.364
128.648
128.615
126.016
120.722
120.302
114.031
113.697
98.865
80.990
77.394
77.141
76.884
75.067
74.690
74.523
71.003
56.295
55.380
55.303
29.793

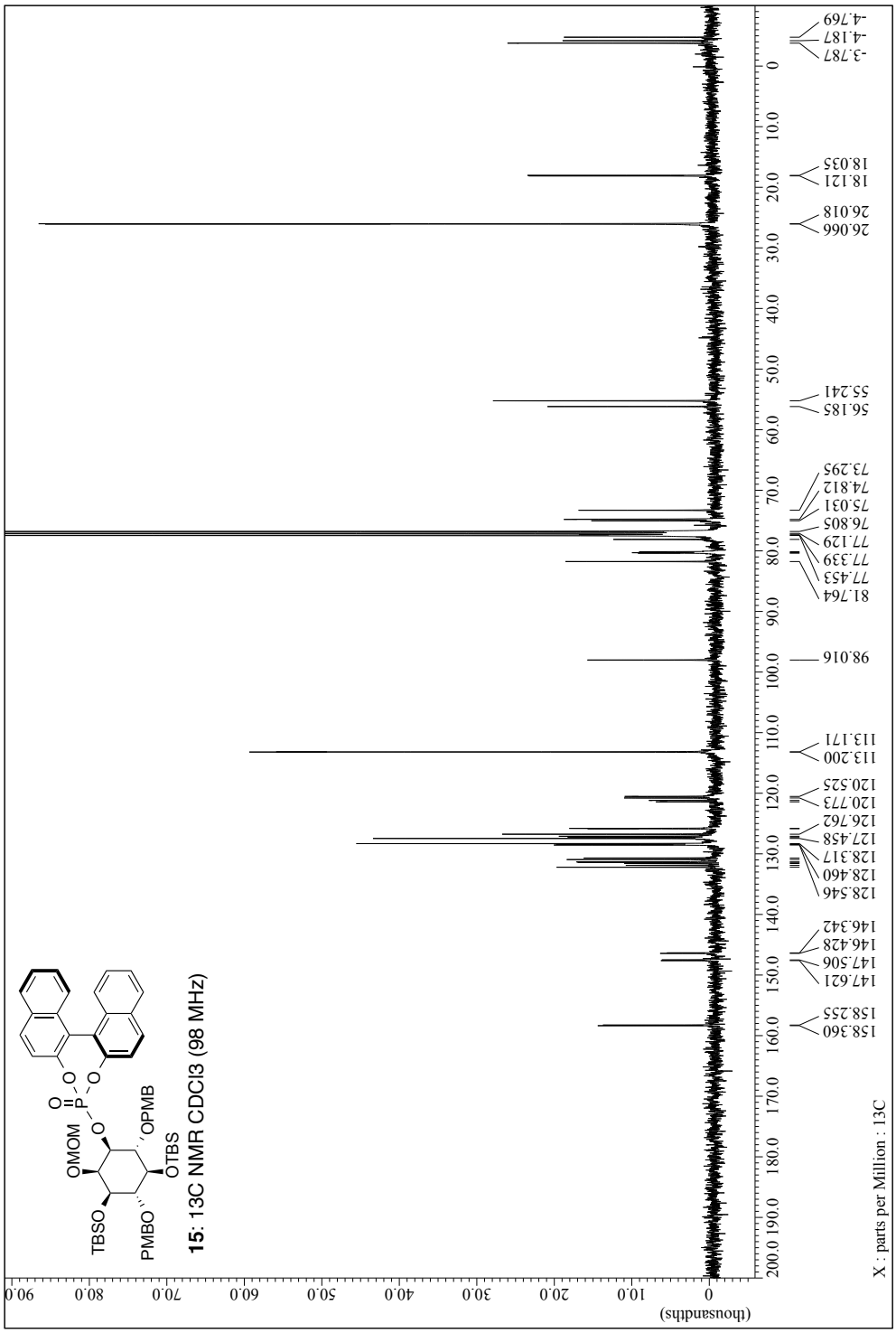

9b: 1H NMR CDCl3 (390 MHz)
OMOM
OH
OPMB
PMBO
OH
X : parts per Million : 1H
abundance

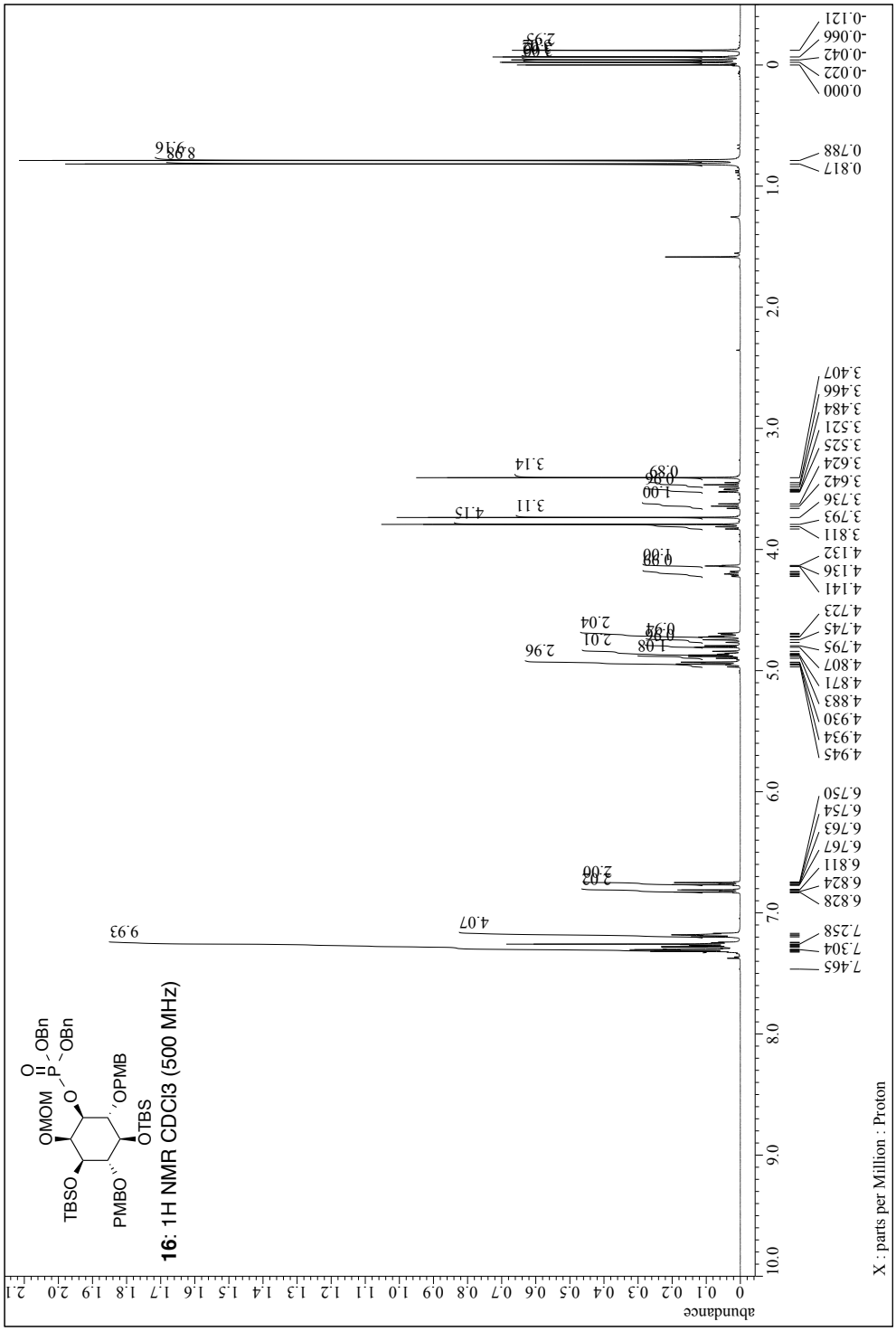

9b: 13C NMR CDCl3 (98 MHz)
OMOM
OH
OPMB
PMBO
OH
abundance
X : parts per Million : 13C
159.447
159.333
147.468
147.353
146.266
146.180
129.881
129.375
128.527
128.345
127.096
126.981
125.990
114.020
98.655
80.963
80.286
77.482
77.158
76.834
74.678
74.497
70.987
55.784
55.393
21.507

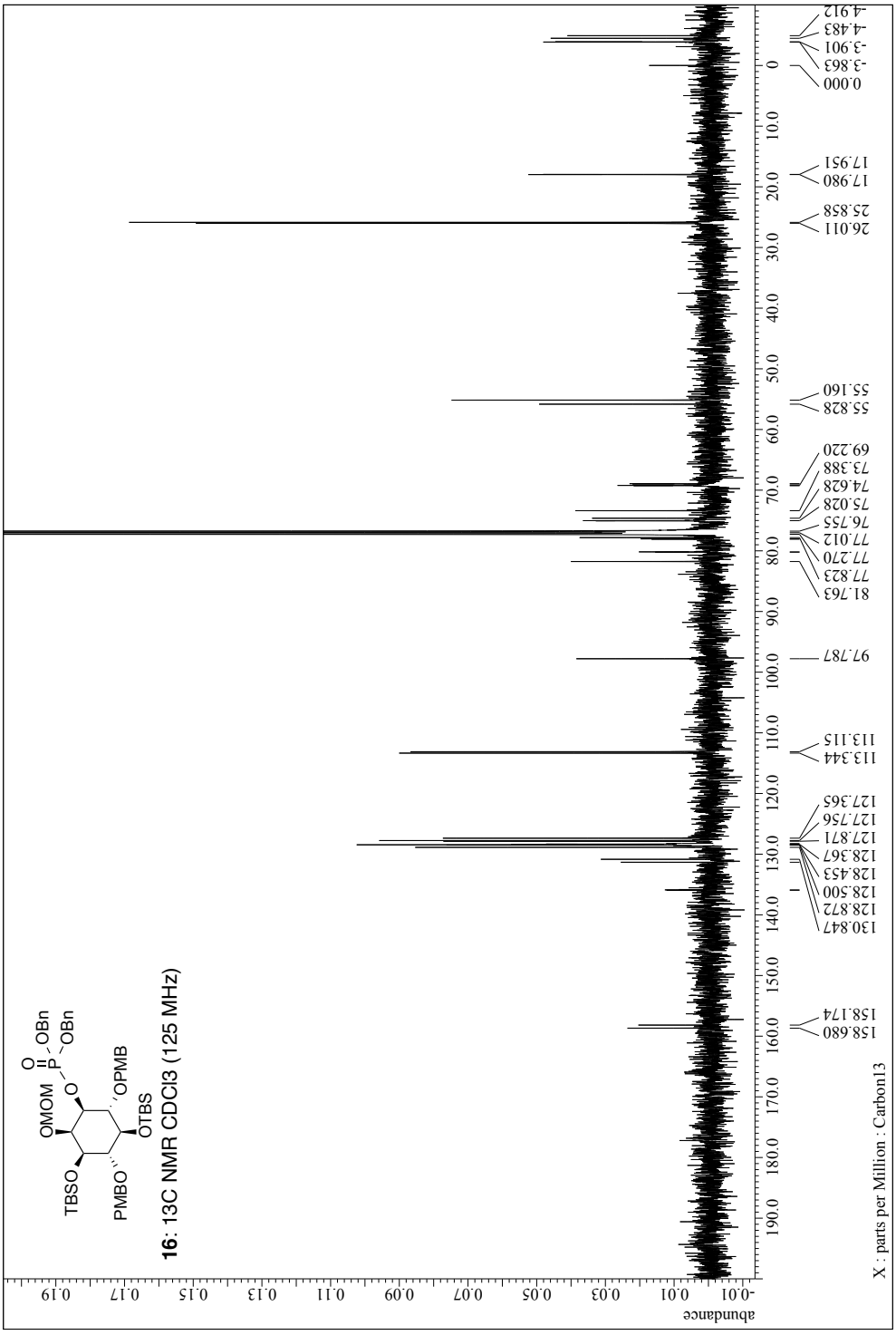

14: 1H NMR CDCl3 (390 MHz)
OMOM
OPMB
OAlloc
AllocO
PMBO
X : parts per Million : Proton
abundance

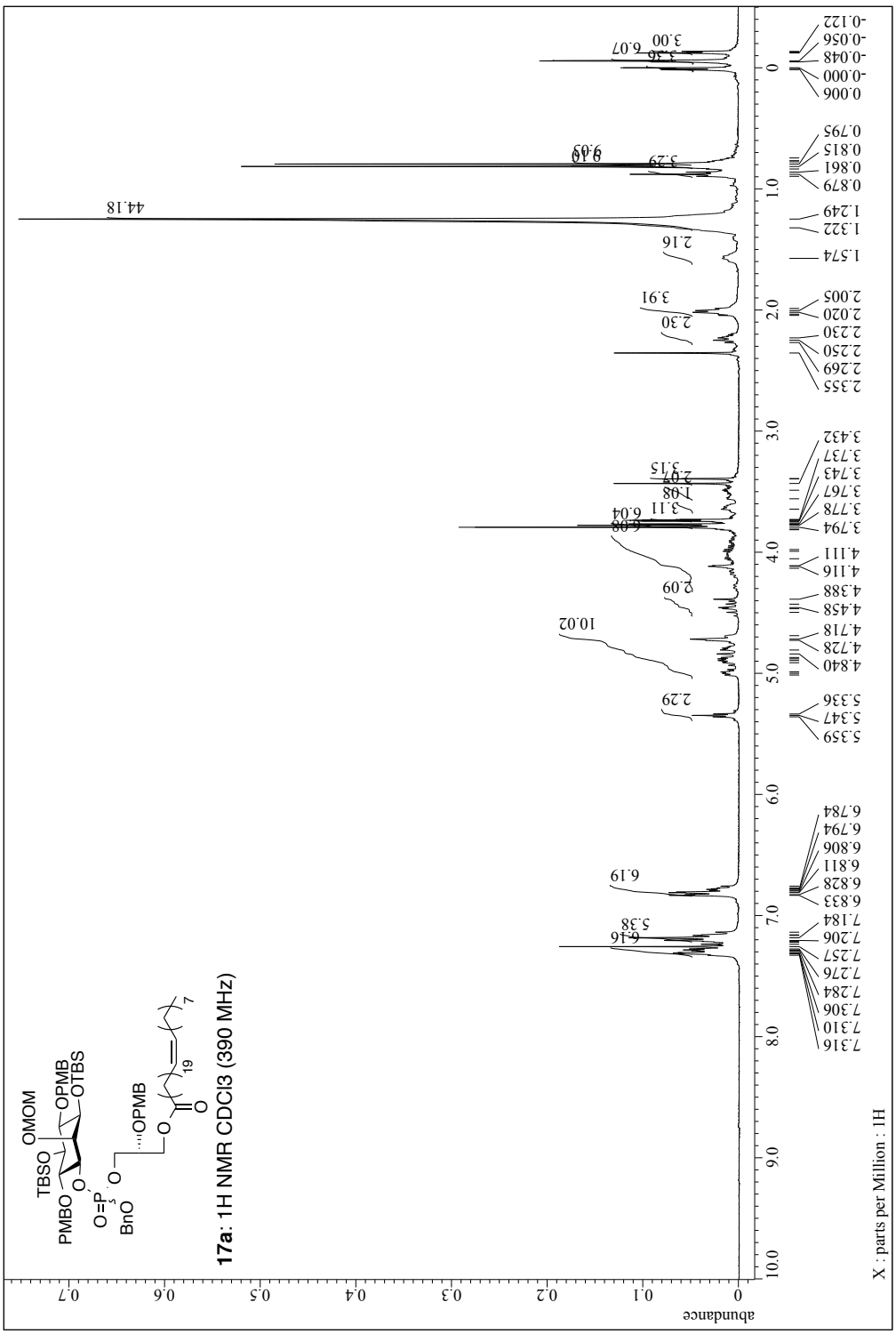

14: 13C NMR CDCl3 (98 MHz)
AllocO
PMBO
OMOM
OAlloc
OPMB
(thousandths)
X : parts per Million : Carbon13
159.199
158.904
153.968
147.462
146.242
146.175
131.376
129.459
129.034
128.515
126.941
119.177
119.105
113.625
113.411
98.044
89.307
77.270
77.017
76.764
74.981
68.871
68.762
56.176
55.232
43.657
43.585
0.000

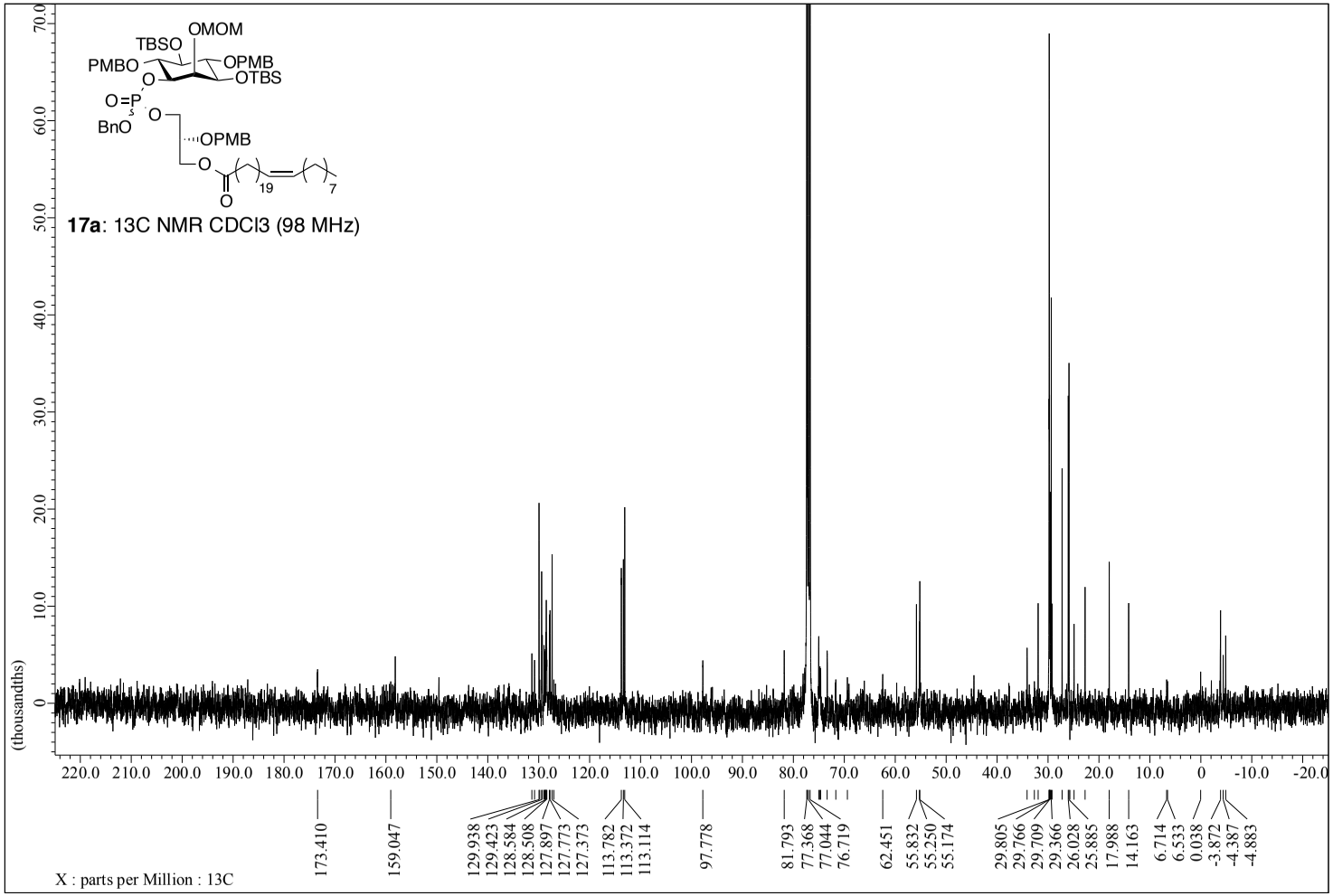

15: 1H NMR CDCl3 (390 MHz)
TBSO
PMBO
OMOM
OPMB
OTBS
abundance
X : parts per Million : 1H

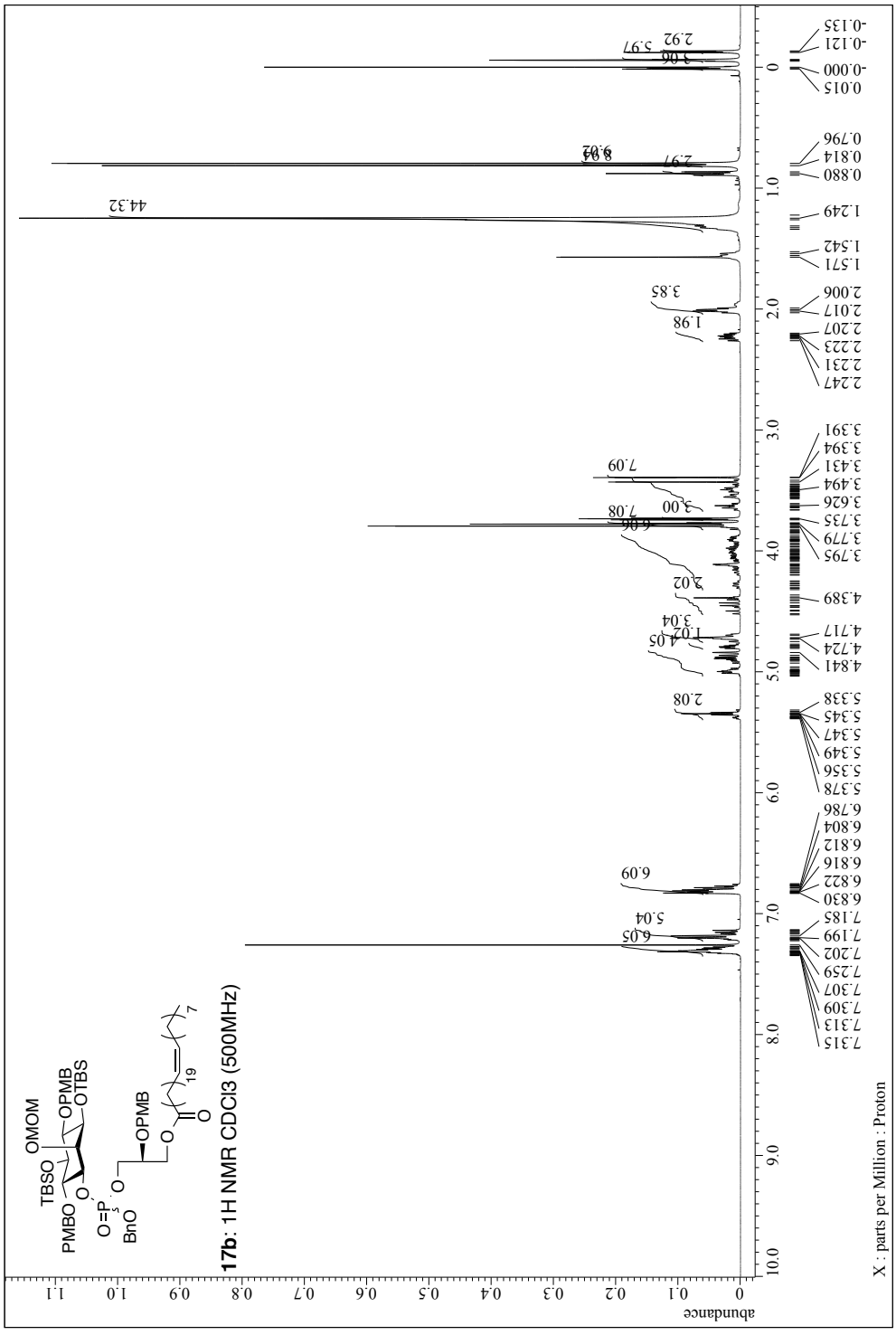

15: 13C NMR CDCl3 (98 MHz)
TBSO
PMBO
OMOM
OTBS
OPMB
O
P
(thousandths)
X : parts per Million : 13C
158.360
158.255
147.621
147.506
146.428
146.342
128.546
128.460
128.317
127.458
126.762
120.773
120.525
113.200
113.171
98.016
81.764
77.453
77.339
77.129
76.805
75.031
74.812
73.295
56.185
55.241
26.066
26.018
18.121
18.035
-3.787
-4.187
-4.769

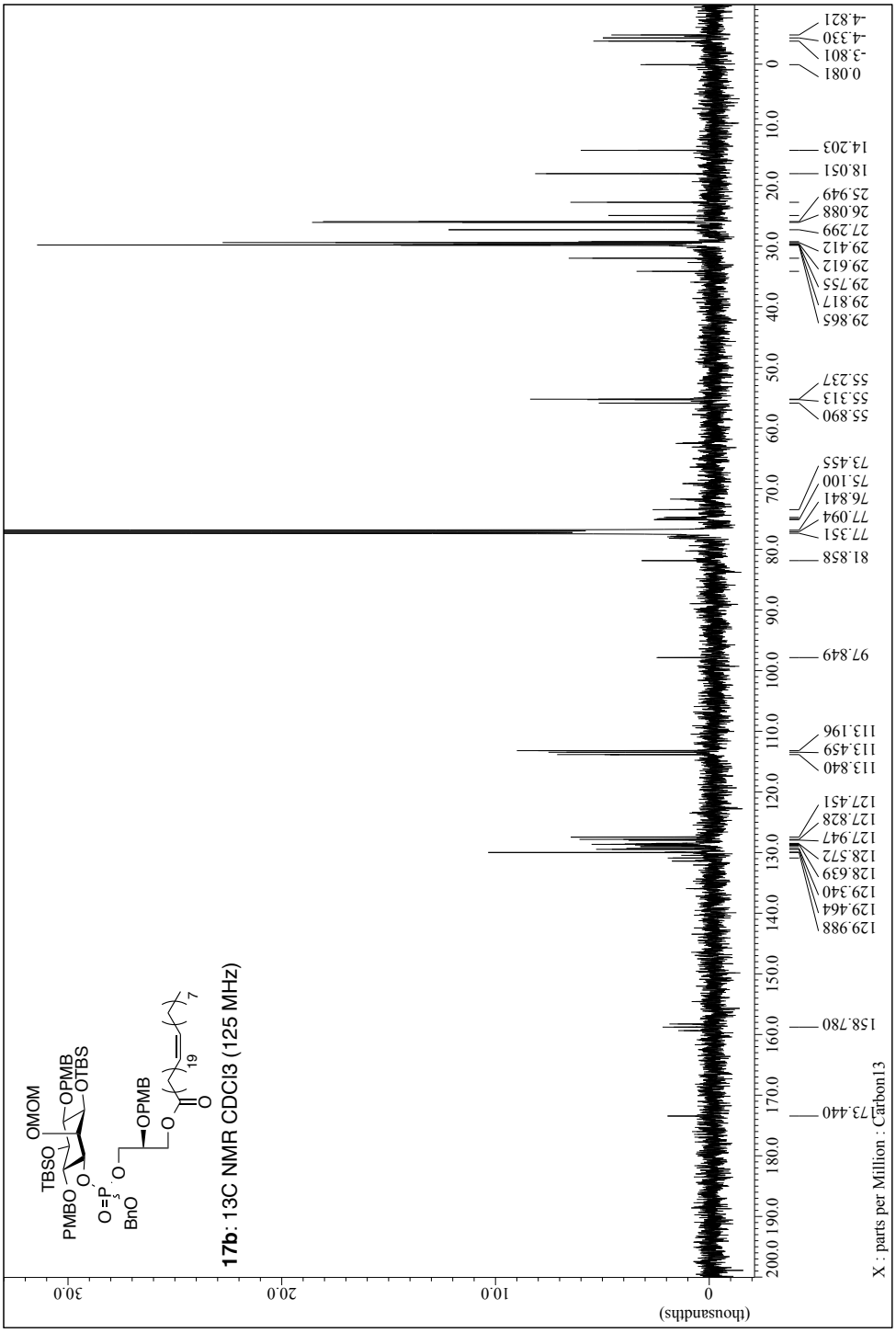

16: 1H NMR CDCl3 (500 MHz)
OMOM
TBSO
PMBO
OTBS
OPMB
OBn
OBn
abundance
X : parts per Million : Proton

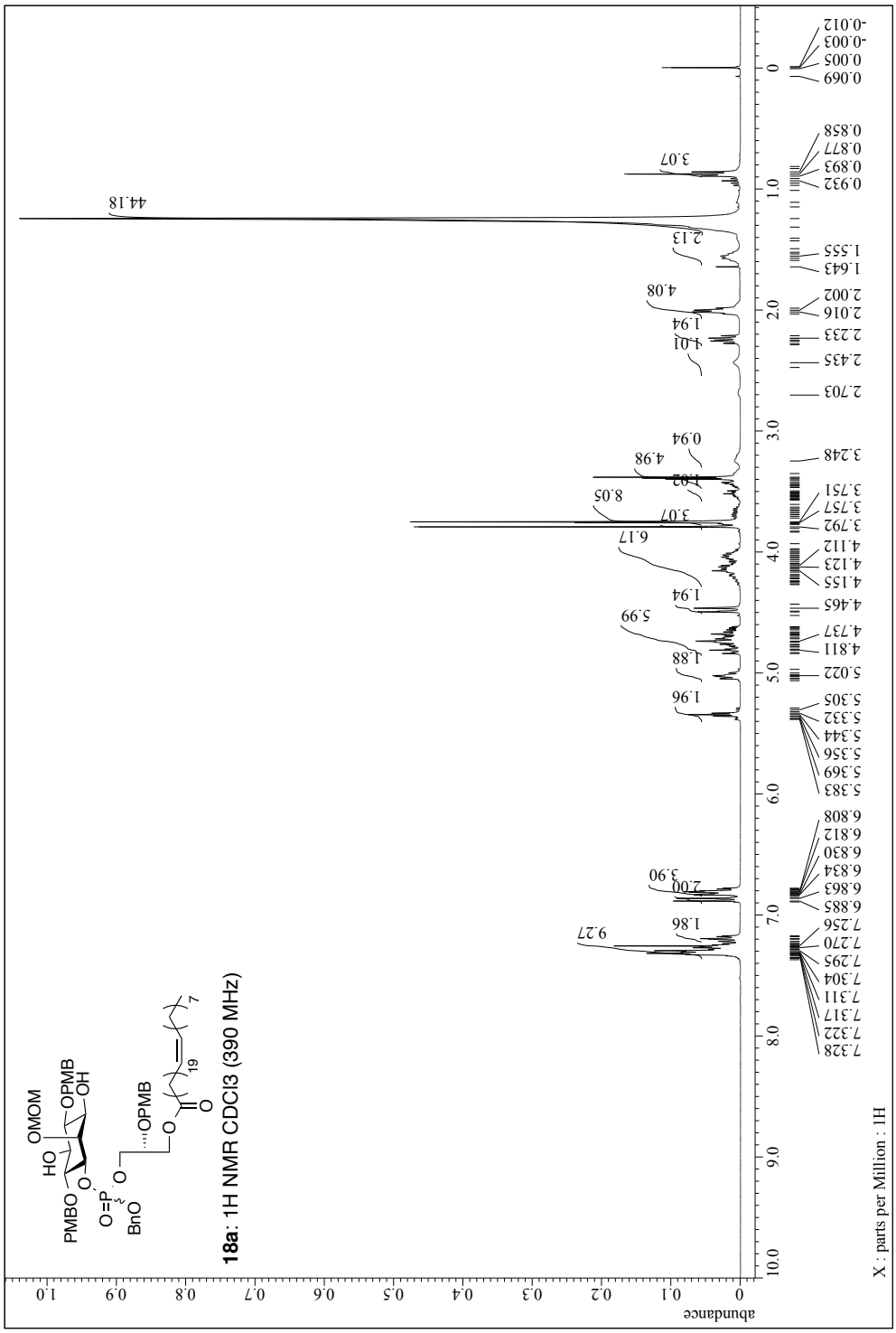

16: 13C NMR CDCl3 (125 MHz)
TBSO
PMBO
OMOM
OTBS
OPMB
OBn
OBn
abundance
X : parts per Million : Carbon13
158.680
158.174
130.847
128.872
128.500
128.453
128.367
127.871
127.756
127.365
113.344
113.115
97.787
81.763
77.823
77.270
77.012
76.755
75.028
74.628
73.388
69.220
55.828
55.160
26.011
25.858
17.980
17.951
0.000
-3.863
-3.901
-4.483
-4.912

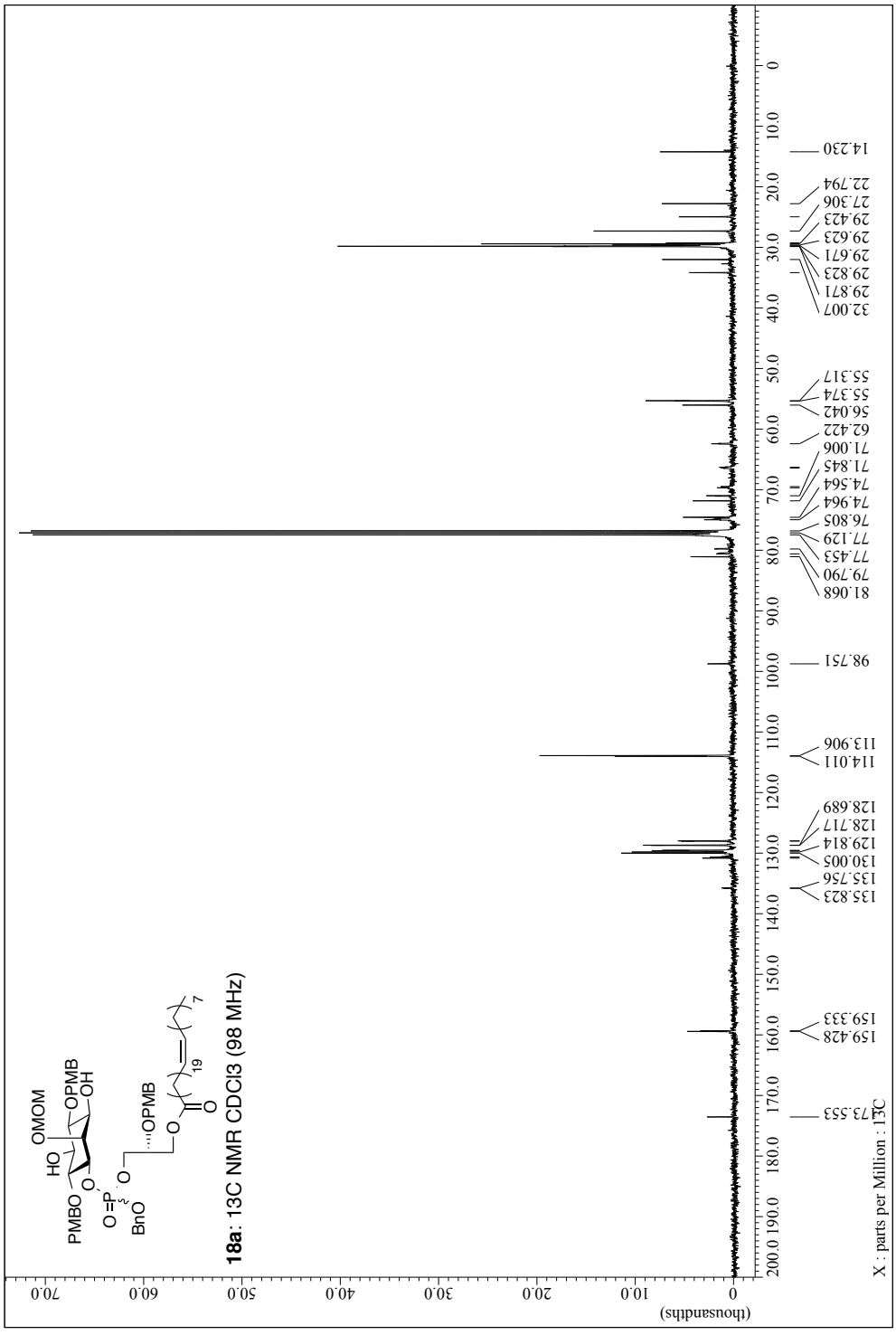

17a: 1H NMR CDCl3 (390 MHz)
OMOM
TBSO
PMBO
OPMB
OTBS
O=P
BnO
OPMB
abundance
X : parts per Million : 1H

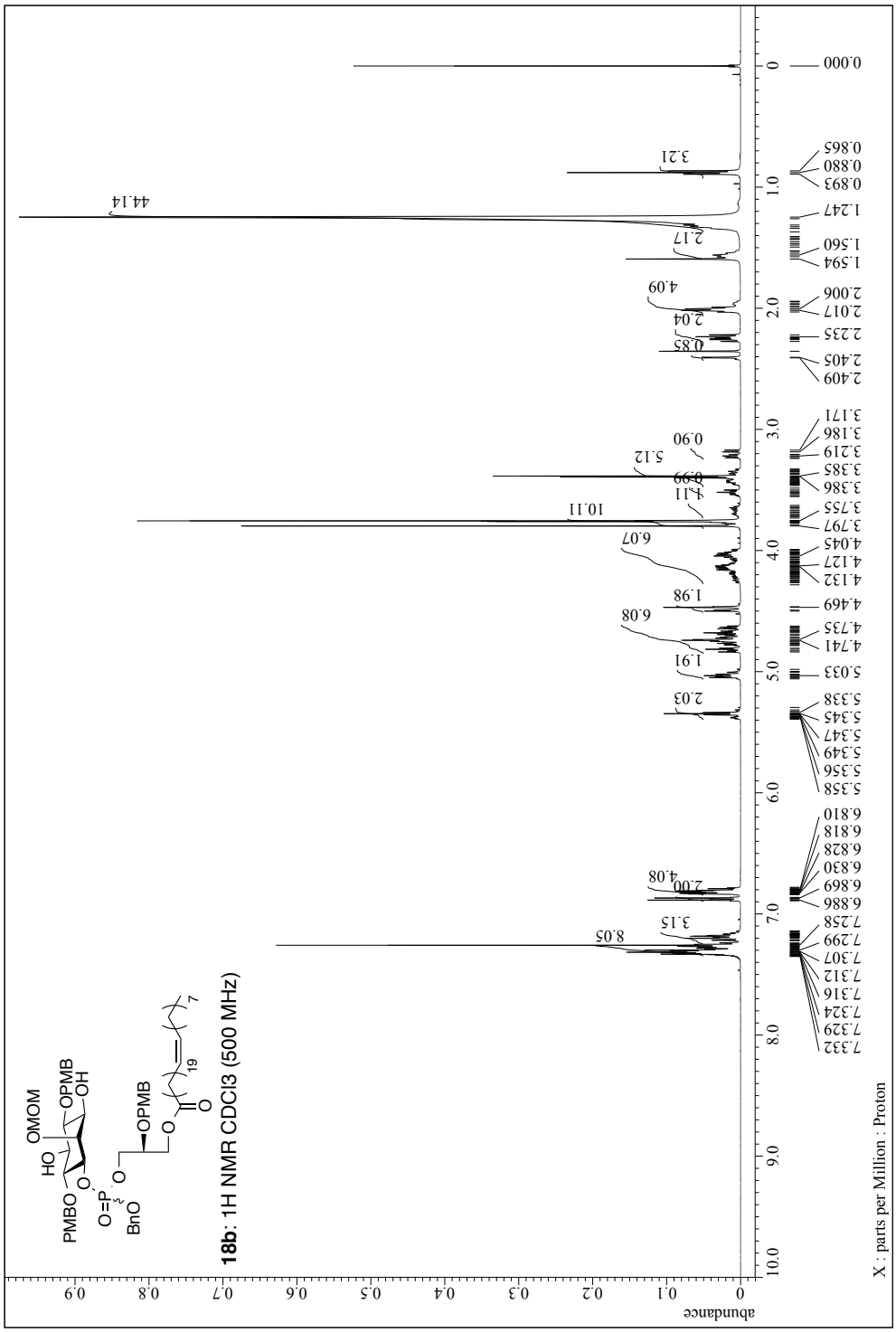

OMOM
TBSO
PMBO
OPMB
OTBS
O
O=P
S
O
BnO
OPMB
O
19
7
O
17a: 13C NMR CDCl3 (98 MHz)
(thousandths)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
173.410
159.047
129.938
129.423
128.584
128.508
127.897
127.773
127.373
113.782
113.372
113.114
97.778
81.793
77.368
77.044
76.719
62.451
55.832
55.250
55.174
29.805
29.766
29.709
29.366
26.028
25.885
17.988
14.163
6.714
6.533
0.038
-3.872
-4.387
-4.883
X : parts per Million : 13C

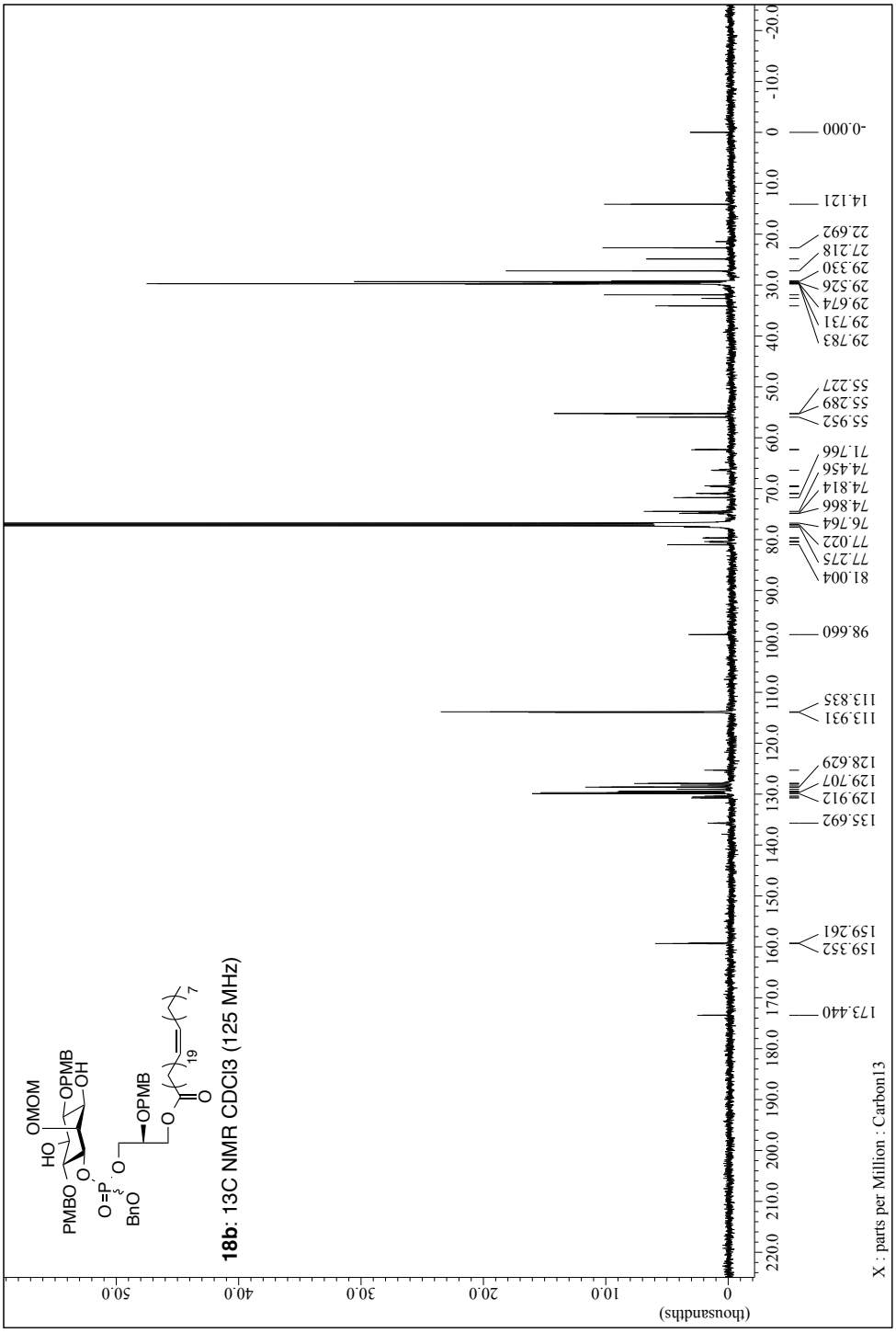

17b: 1H NMR CDCl3 (500MHz)
X : parts per Million : Proton
abundance

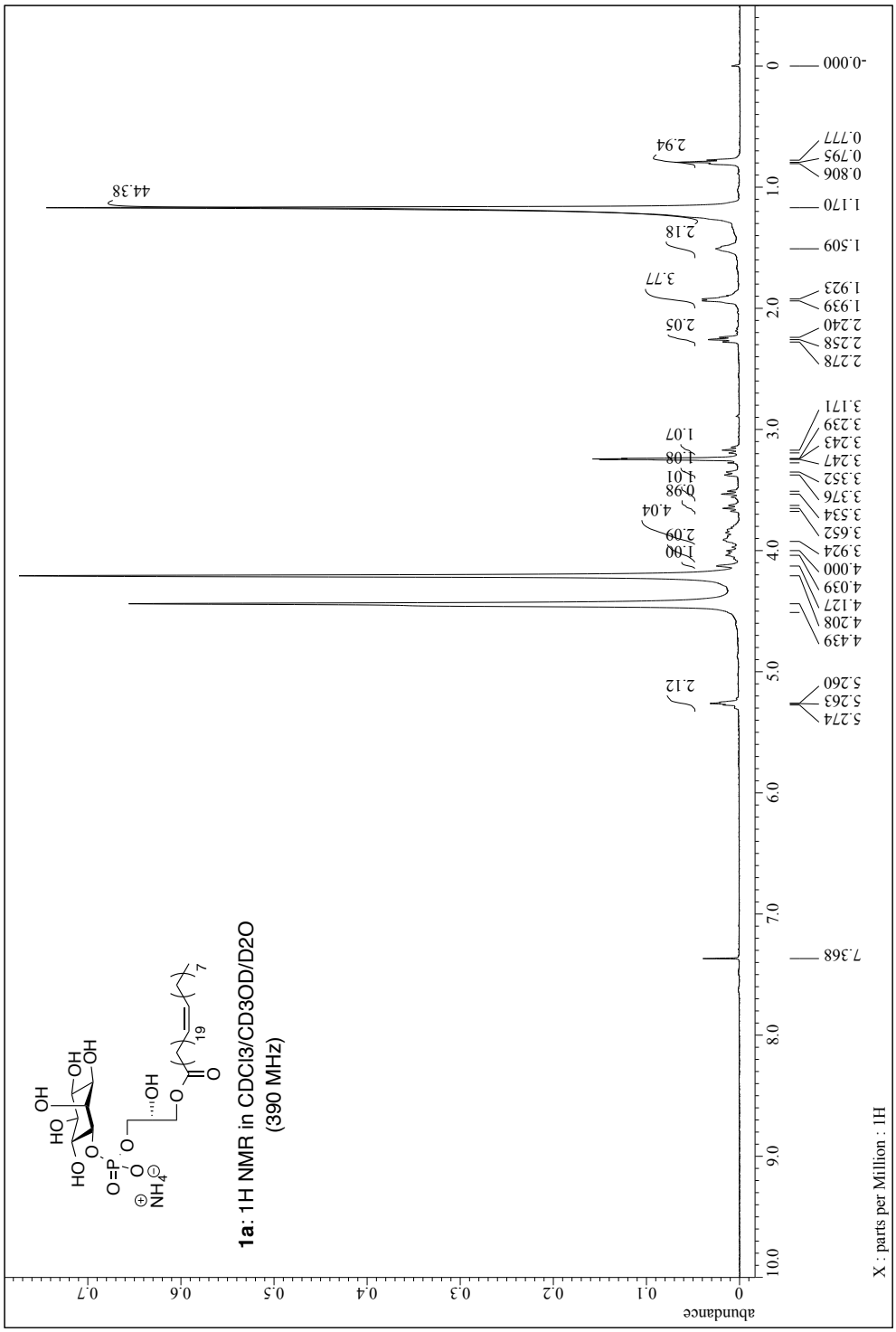

17b: 13C NMR CDCl3 (125 MHz)
X : parts per Million : Carbon13
(thousandths)
173.440
158.780
129.988
129.464
129.340
128.639
128.572
127.947
127.828
127.451
113.840
113.459
113.196
97.849
81.858
77.351
77.094
76.841
75.100
73.455
55.890
55.313
55.237
29.865
29.817
29.755
29.612
29.412
27.299
26.088
25.949
18.051
14.203
0.081
-3.801
-4.330
-4.821

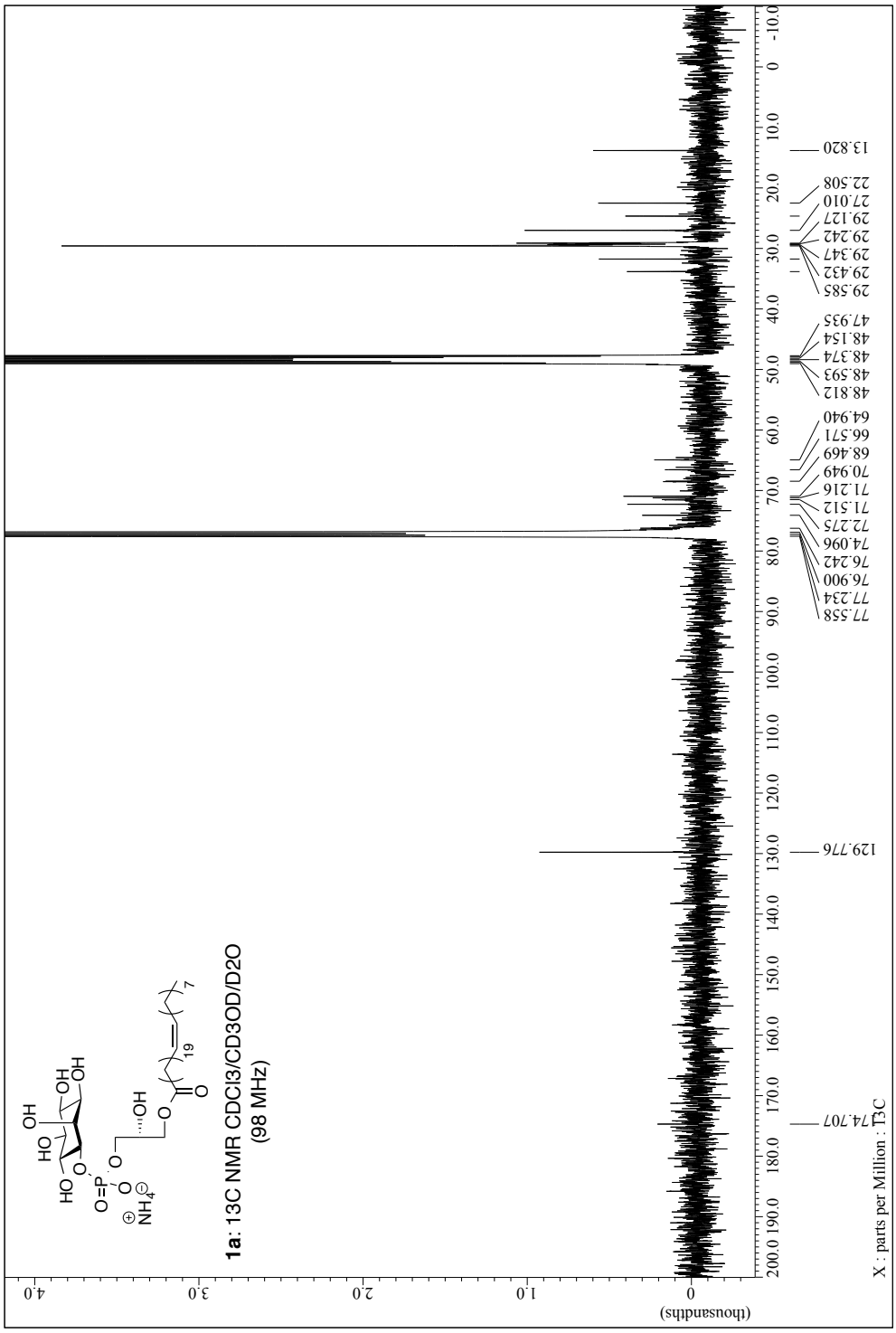

18a: 1H NMR CDCl3 (390 MHz)
X : parts per Million : 1H
abundance

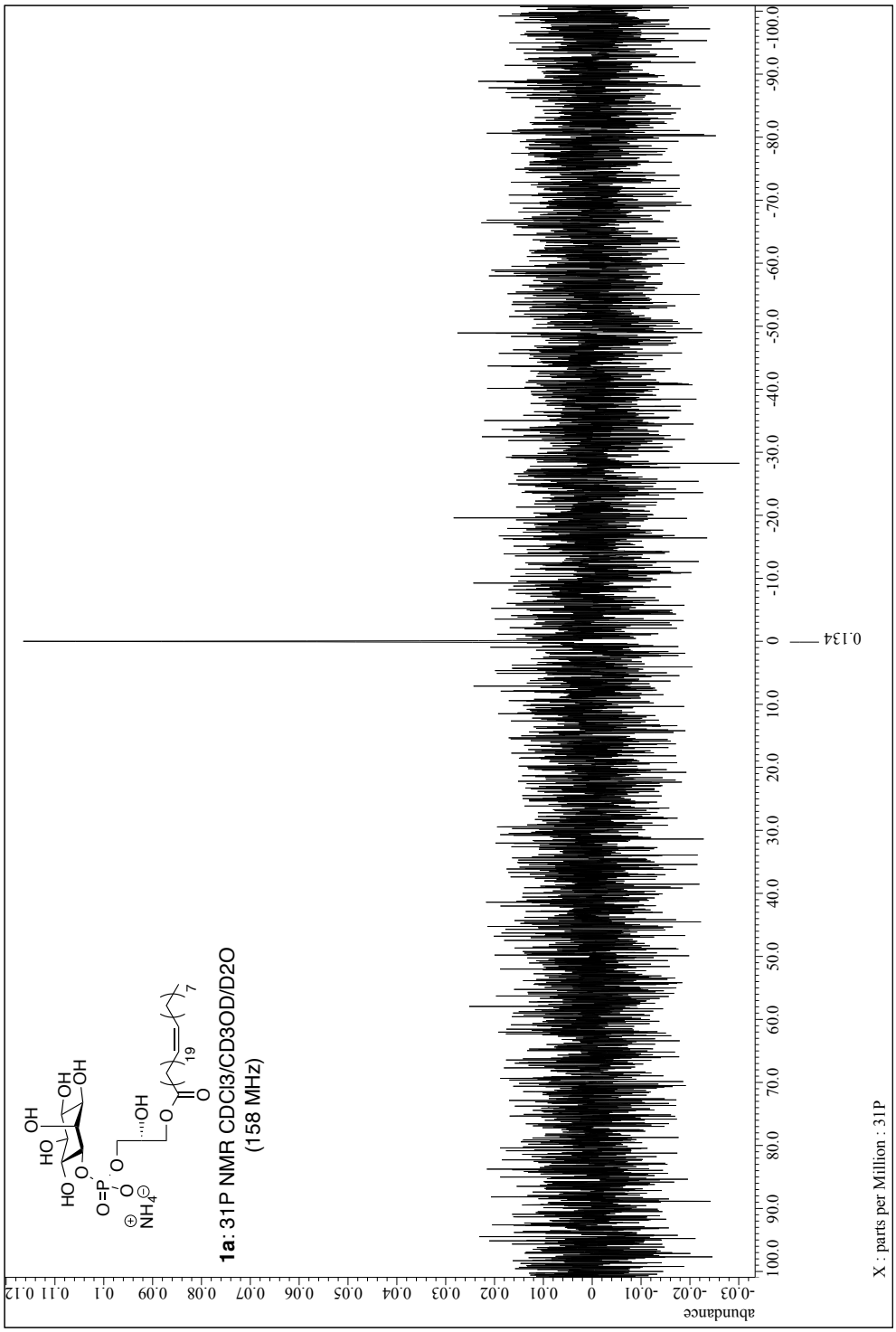

18a: 13C NMR CDCl3 (98 MHz)
X : parts per Million : 13C
(thousandths)
14.230
22.794
27.306
29.423
29.623
29.671
29.823
29.871
32.007
55.317
55.374
56.042
62.422
71.006
71.845
74.564
74.964
76.805
77.129
77.453
79.790
81.068
98.751
113.906
114.011
128.689
128.717
129.814
130.005
135.756
135.823
159.333
159.428
173.553

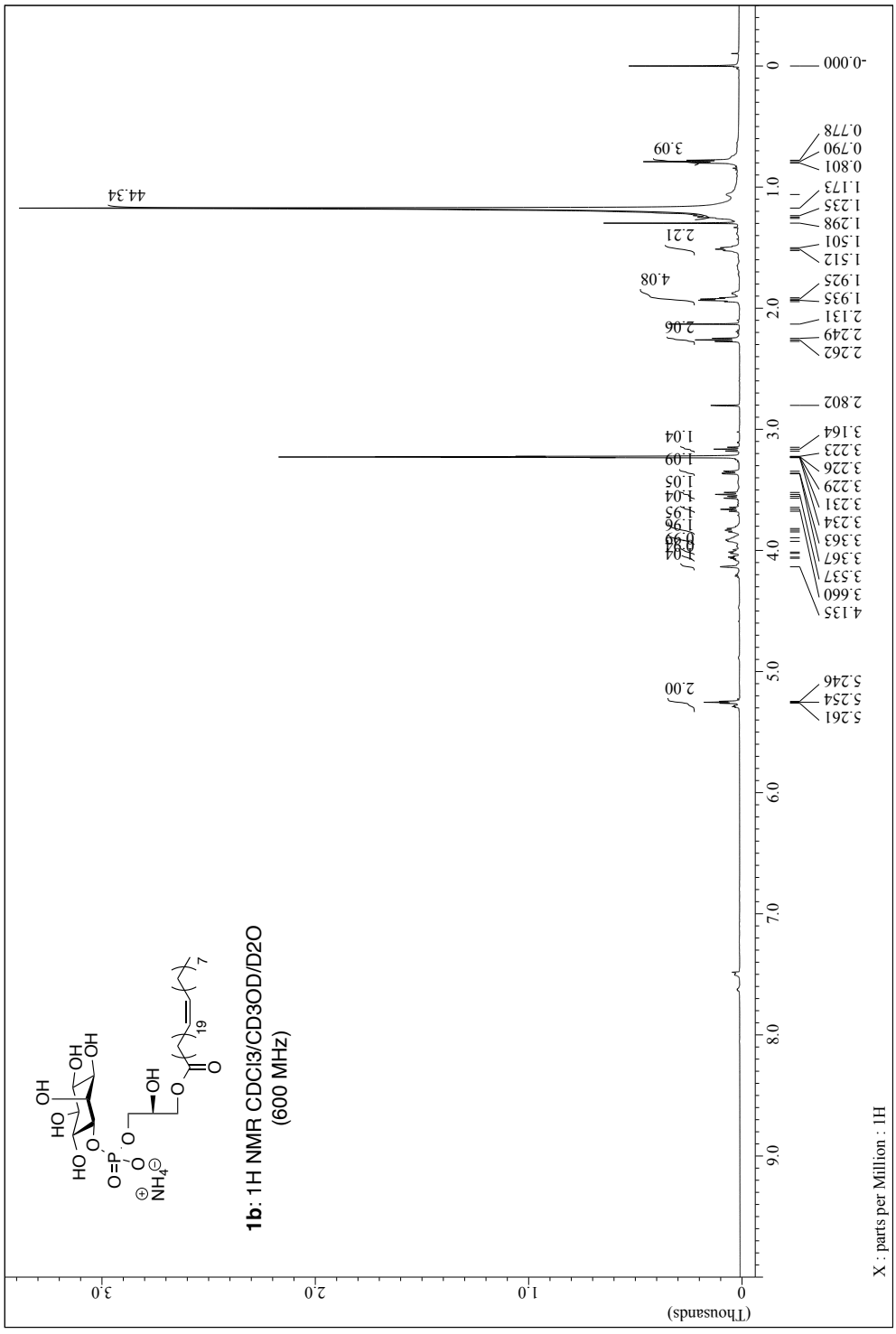

18b: 1H NMR CDCl3 (500 MHz)
X : parts per Million : Proton
abundance

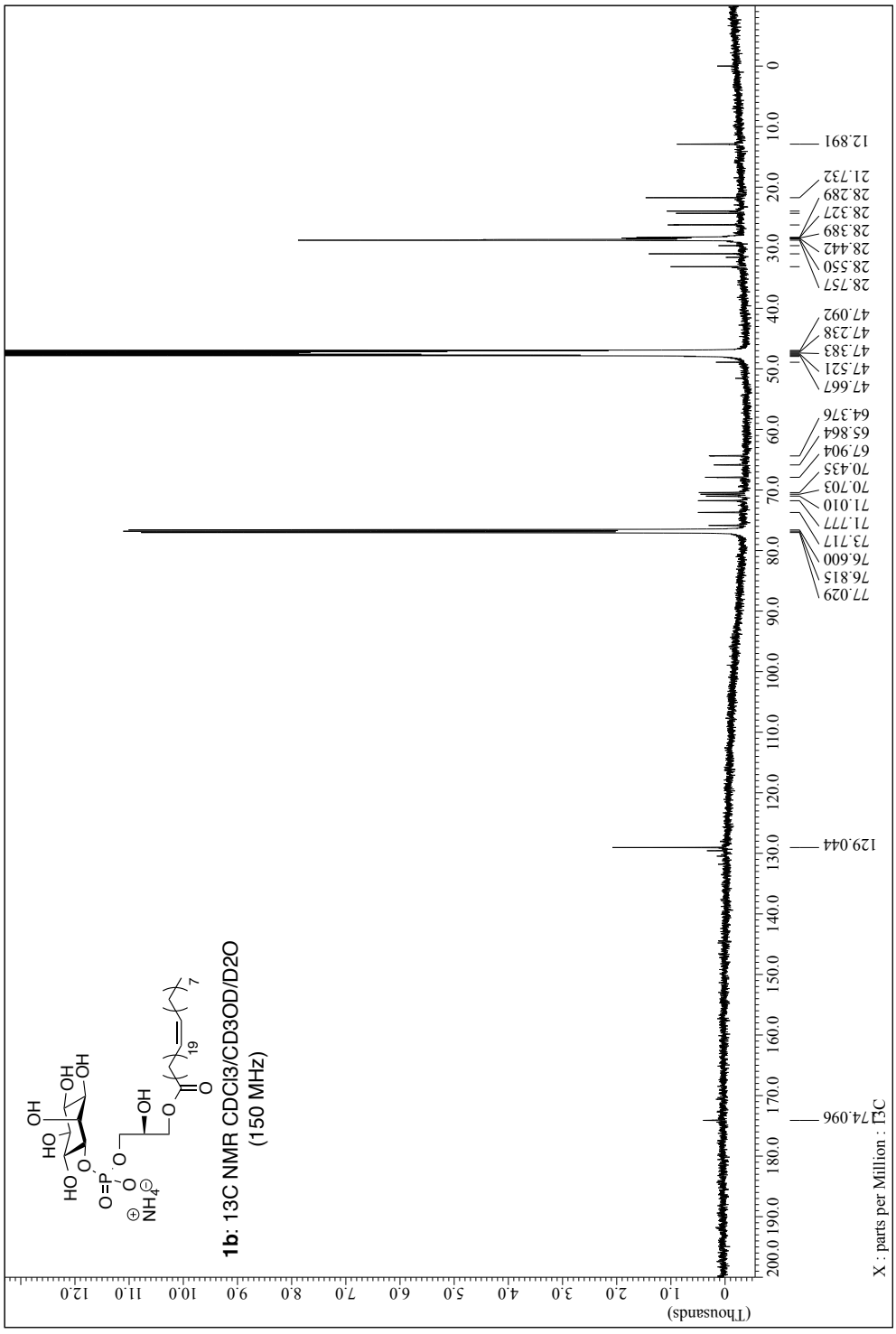

18b: 13C NMR CDCl3 (125 MHz)
X : parts per Million : Carbon13
(thousandths)
173.440
159.352
159.261
135.692
129.912
129.707
128.629
113.931
113.835
98.660
81.004
77.275
77.022
76.764
74.866
74.814
74.456
71.766
55.952
55.289
55.227
29.783
29.731
29.674
29.526
29.330
27.218
22.692
14.121
-0.000

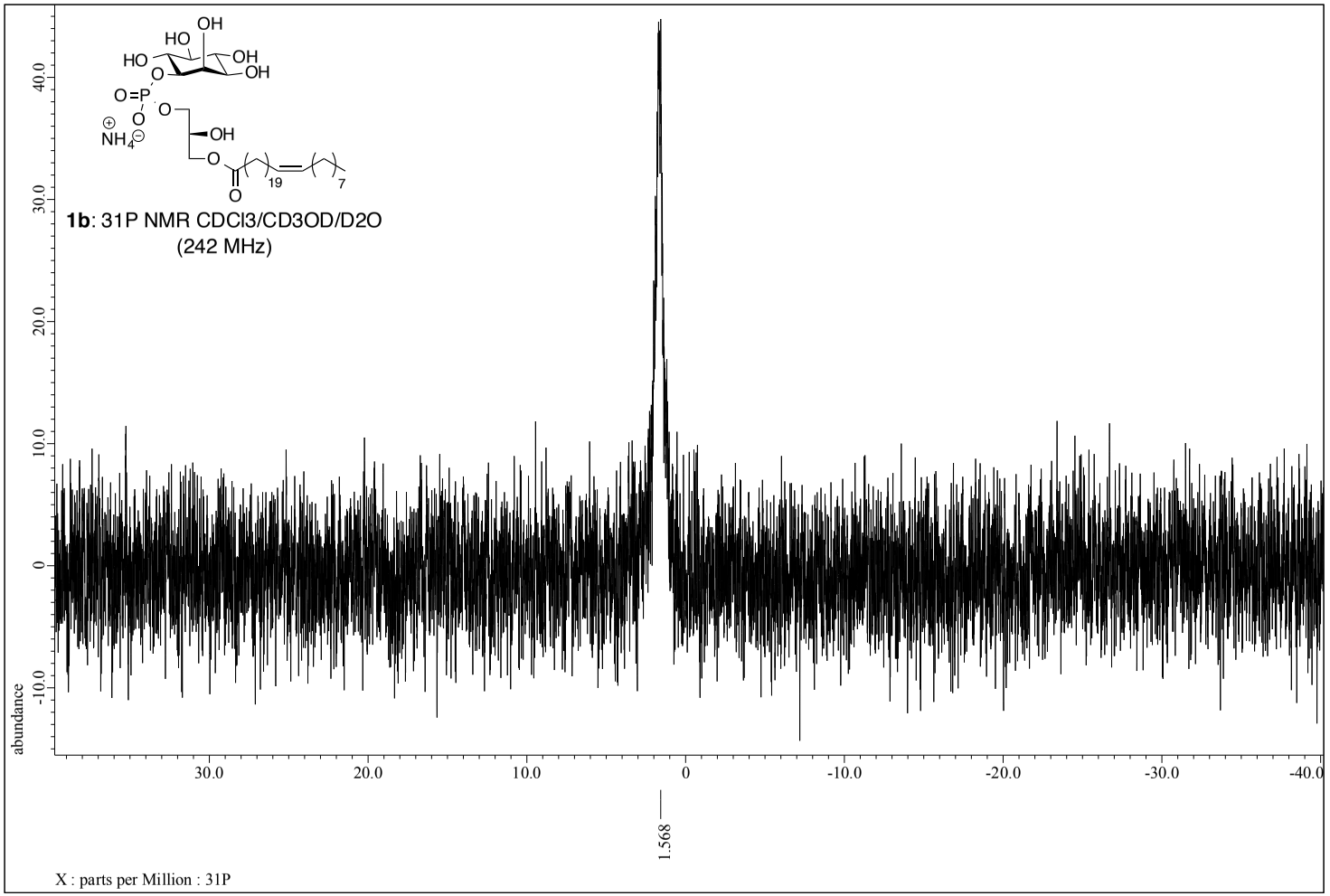

1a: 1H NMR in CDCl3/CD3OD/D2O
(390 MHz)
X : parts per Million : 1H
abundance


1a: 13C NMR CDCl3/CD3OD/D2O
(98 MHz)
X : parts per Million : 13C
(thousandths)
174.707
129.776
77.558
77.234
76.900
76.242
74.096
72.275
71.512
71.216
70.949
68.469
66.571
64.940
48.812
48.593
48.374
48.154
47.935
29.585
29.432
29.347
29.242
29.127
27.010
22.508
13.820


1a: 31P NMR CDCl3/CD3OD/D2O
(158 MHz)
0.134
X : parts per Million : 31P
abundance


1b: 1H NMR CDCl3/CD3OD/D2O
(600 MHz)
(Thousands)
X : parts per Million : 1H
-0.000
0.778
0.790
0.801
1.173
1.235
1.298
1.501
1.512
1.925
1.935
2.131
2.249
2.262
2.802
3.164
3.223
3.226
3.229
3.231
3.234
3.363
3.367
3.537
3.660
4.135
5.246
5.254
5.261
44.34
3.09
2.21
4.08
2.06
2.00
1.04
1.09
1.05
1.04
O=P
NH4
OH
HO
O
7
19


1b: 13C NMR CDCl3/CD3OD/D2O
(150 MHz)
X : parts per Million : 13C
(Thousands)
12.891
21.732
28.289
28.327
28.389
28.442
28.550
28.757
47.092
47.238
47.383
47.521
47.667
64.376
65.864
67.904
70.435
70.703
71.010
71.777
73.717
76.600
76.815
77.029
129.044
174.096


1b: 31P NMR CDCl3/CD3OD/D2O
(242 MHz)
abundance
40.0
30.0
20.0
10.0
0
-10.0
30.0
20.0
10.0
0
-10.0
-20.0
-30.0
-40.0
1.568
X : parts per Million : 31P