Supporting Information

Synthesis and Toll-Like Receptor 4 (TLR4) Activity of Phosphatidylinositol Dimannoside Analogues

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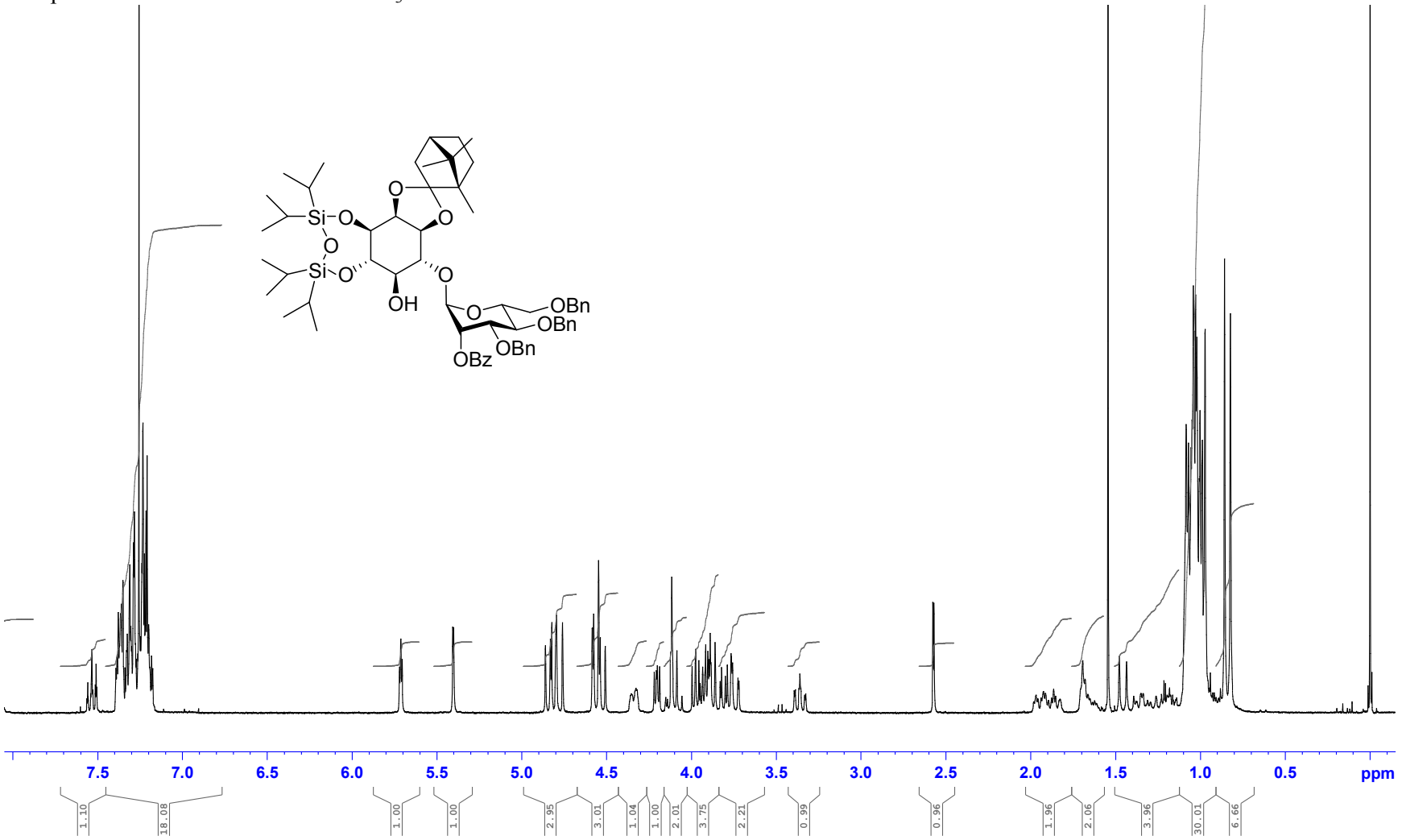
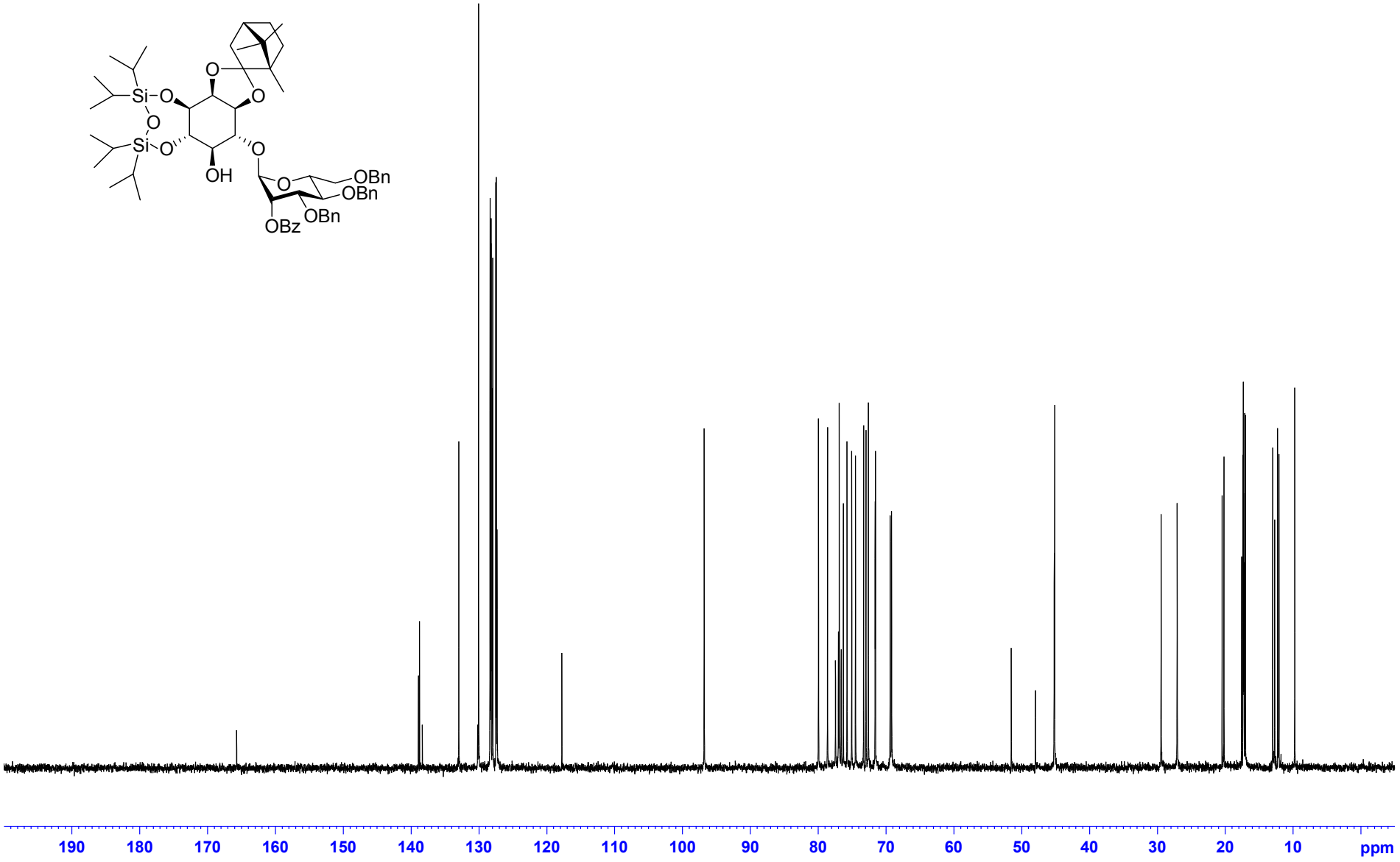
NMR Data

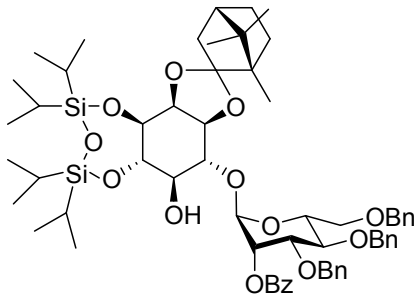
Compound **11** 300 MHz ^{1}H NMR $CDCl_3$

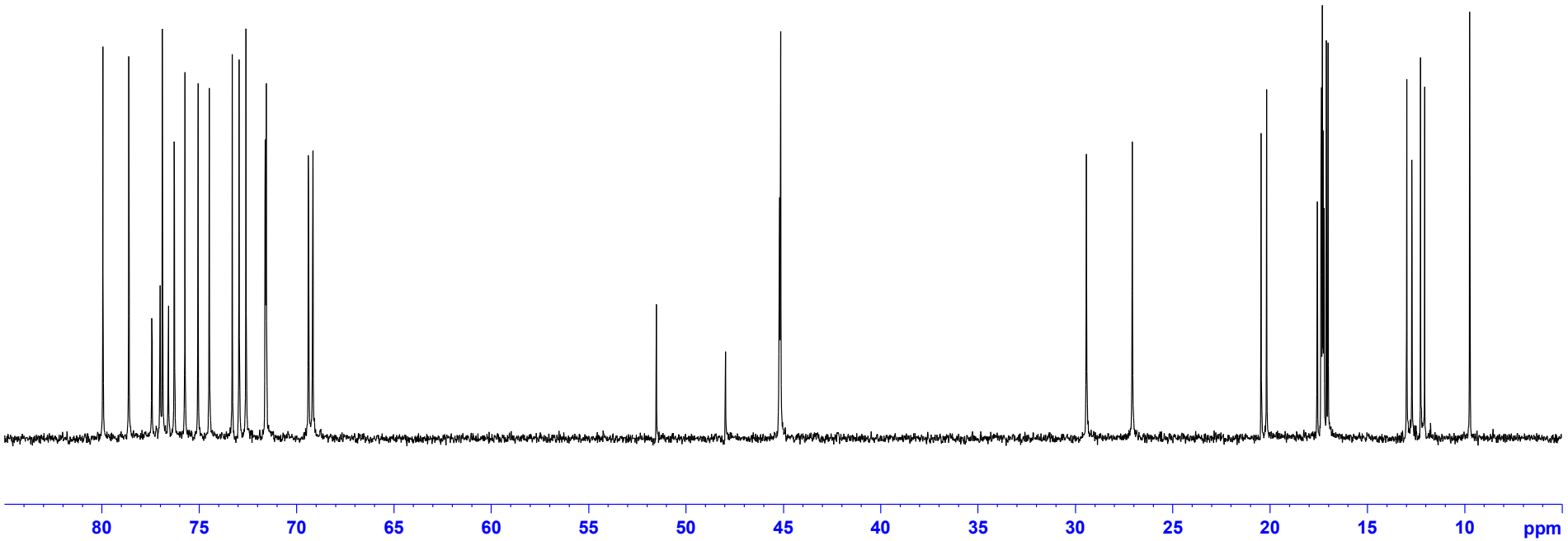


Compound **11** MHz ^{13}C NMR $CDCl_3$

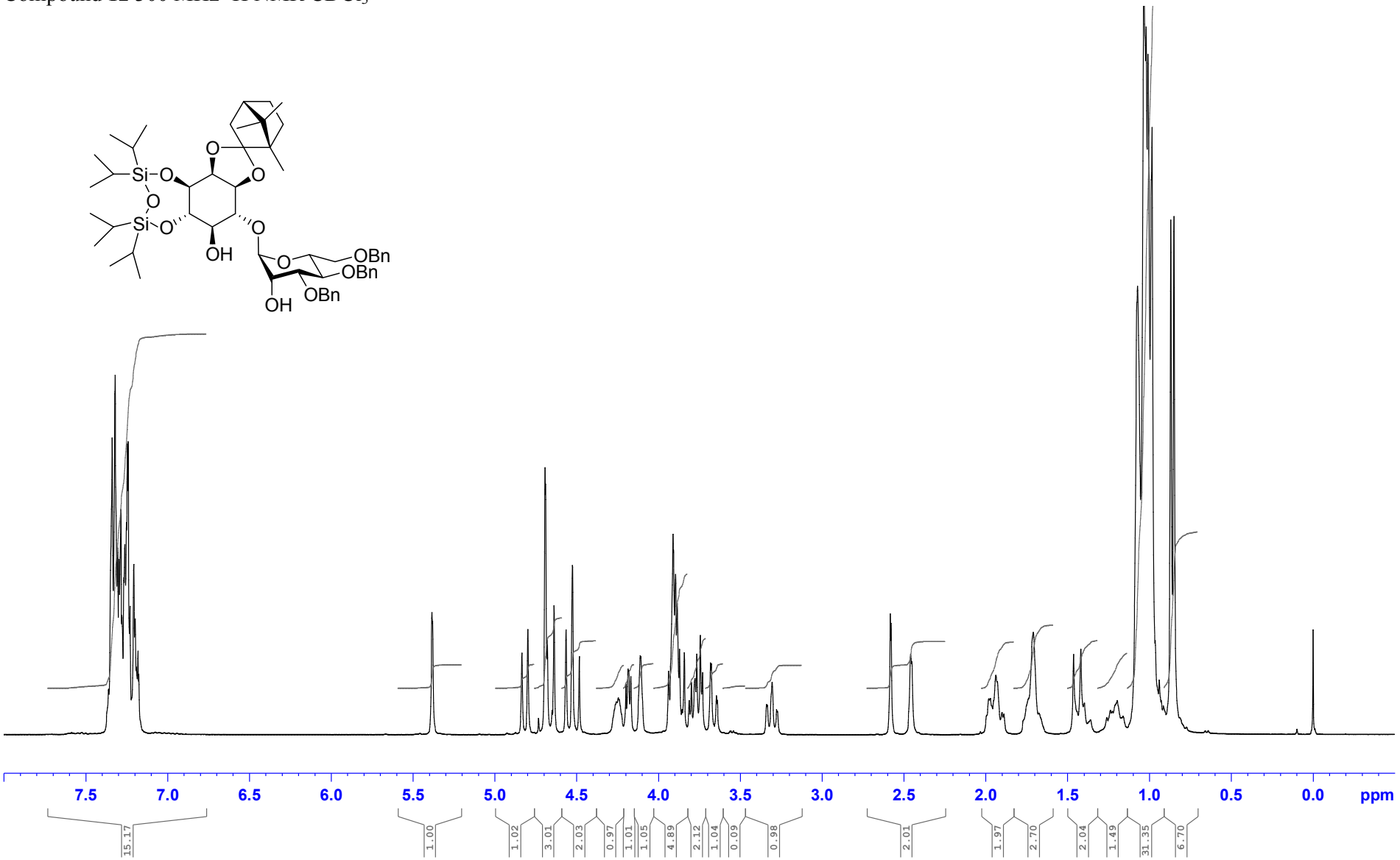


Compound **11** 75 MHz ^{13}C NMR $CDCl_3$

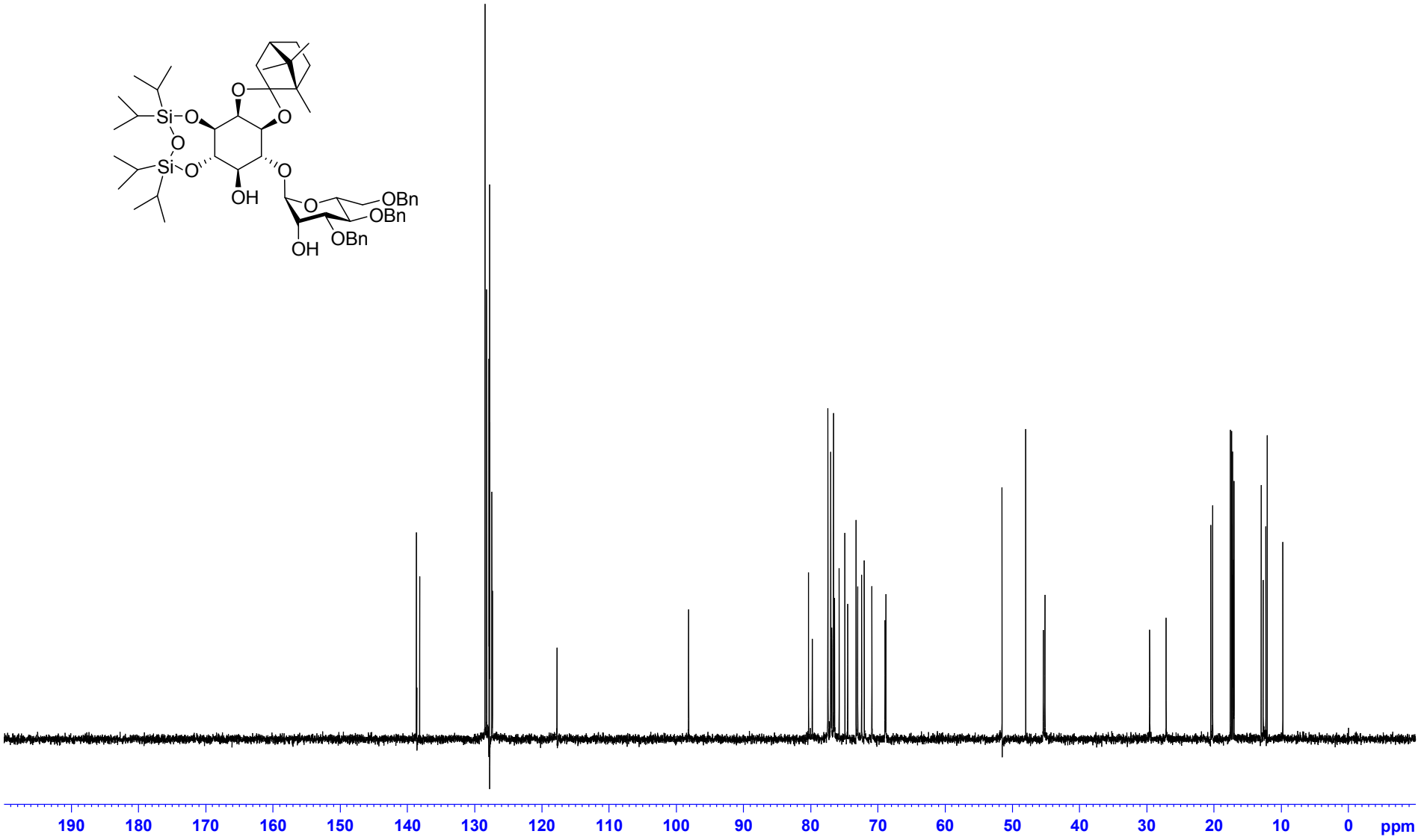




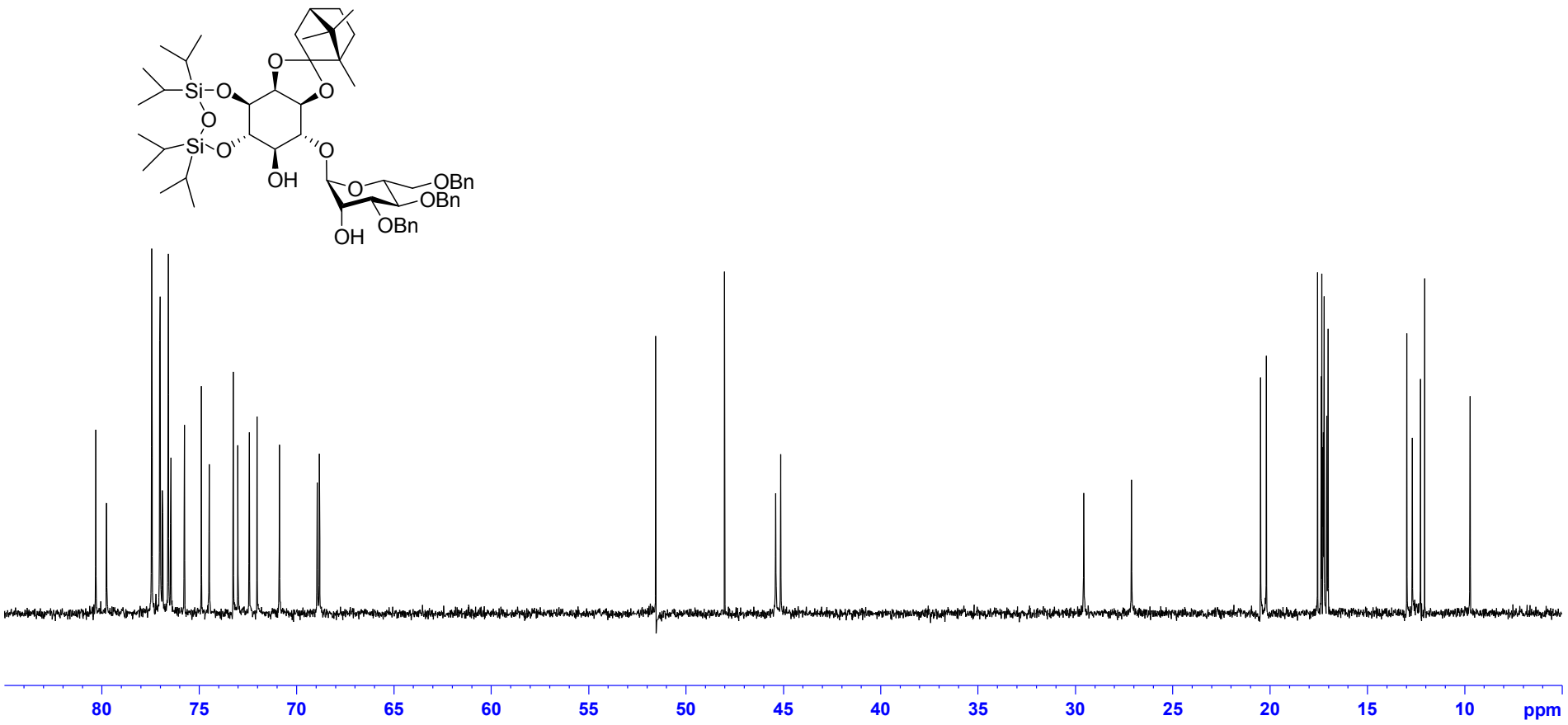
Compound **12** 300 MHz ^{1}H NMR $CDCl_3$



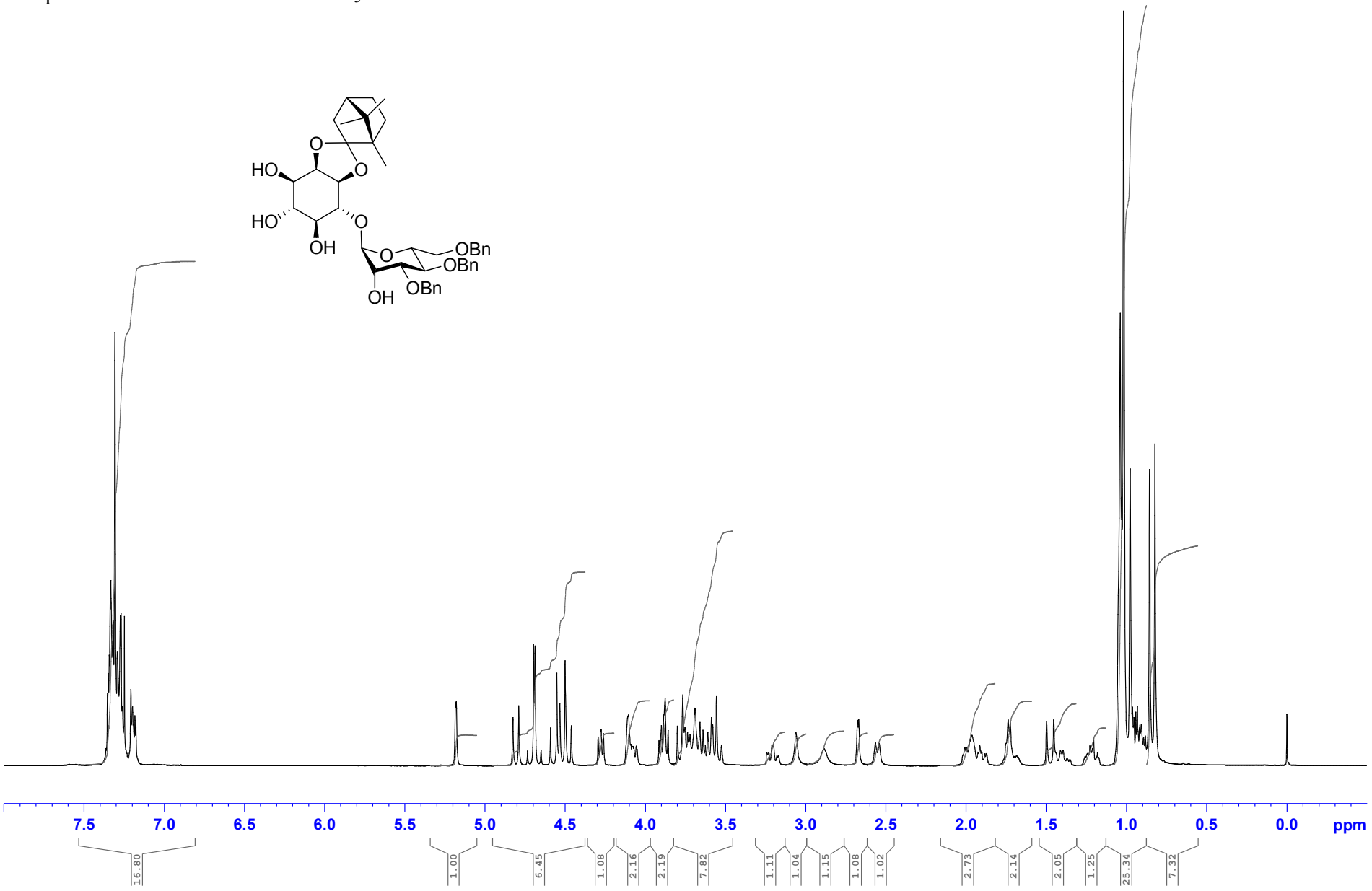
Compound **12** 75 MHz ^{13}C NMR $CDCl_3$



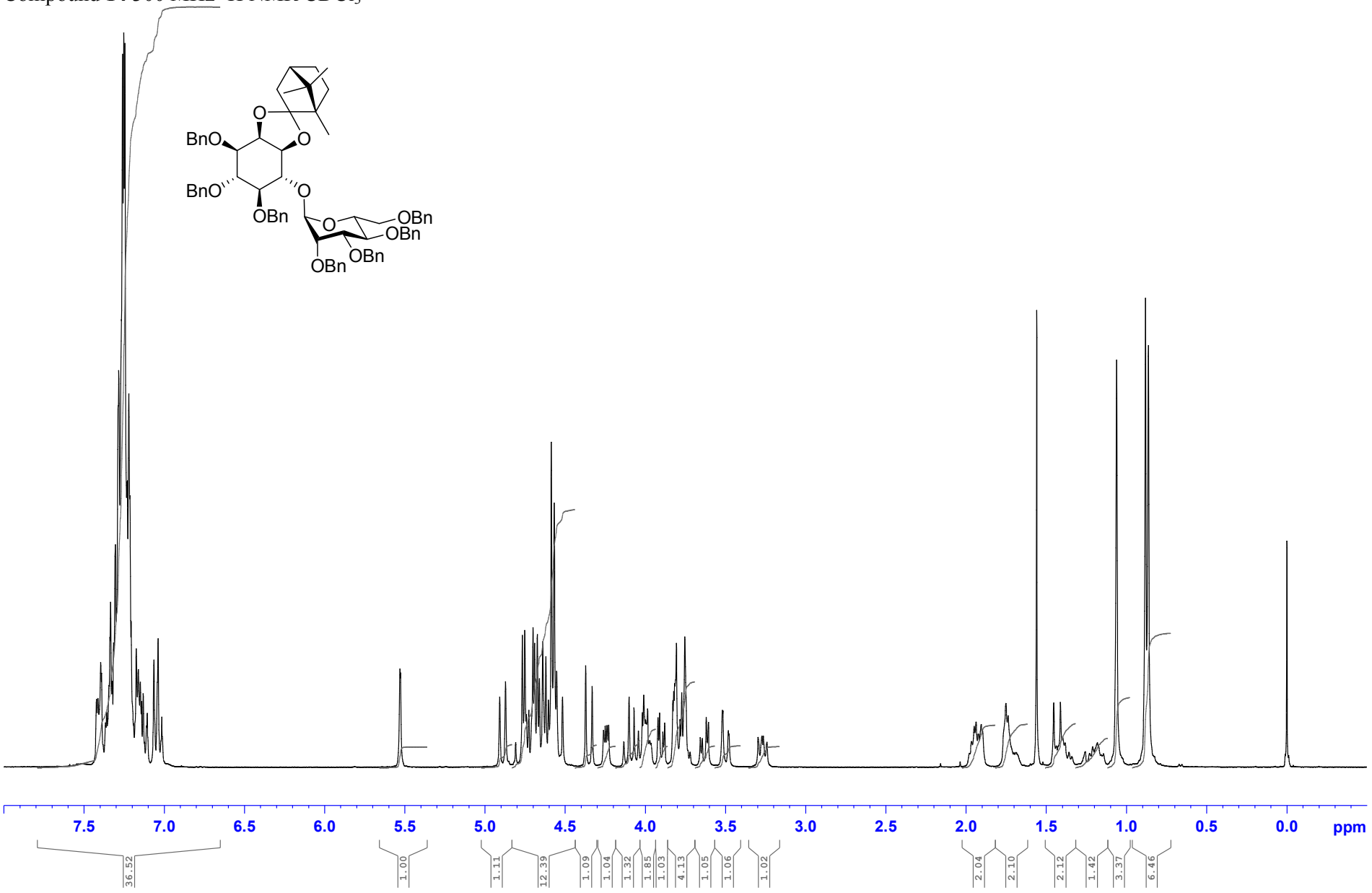
Compound **12** 75 MHz ^{13}C NMR $CDCl_3$



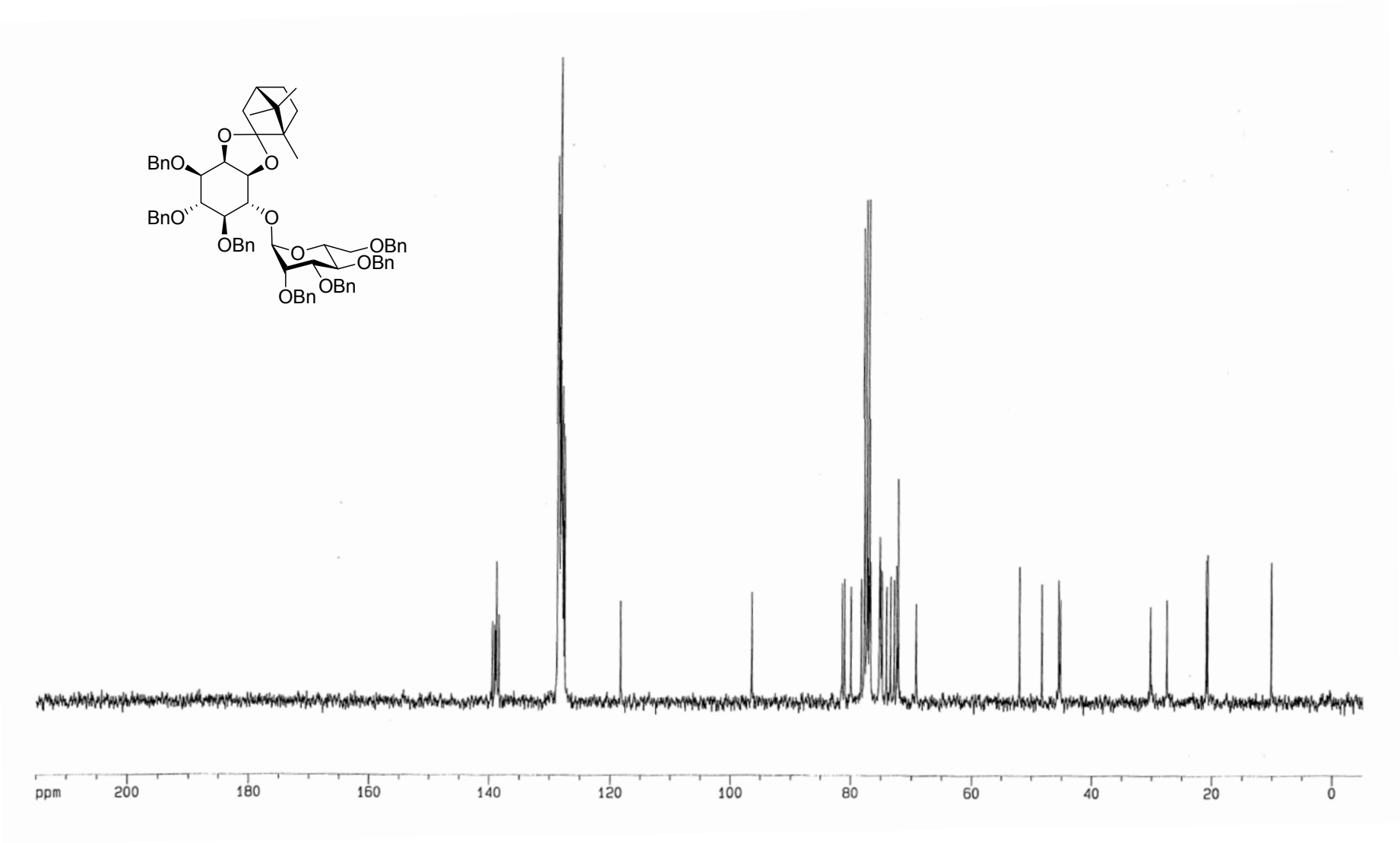
Compound **13** 300 MHz ^{1}H NMR $CDCl_3$



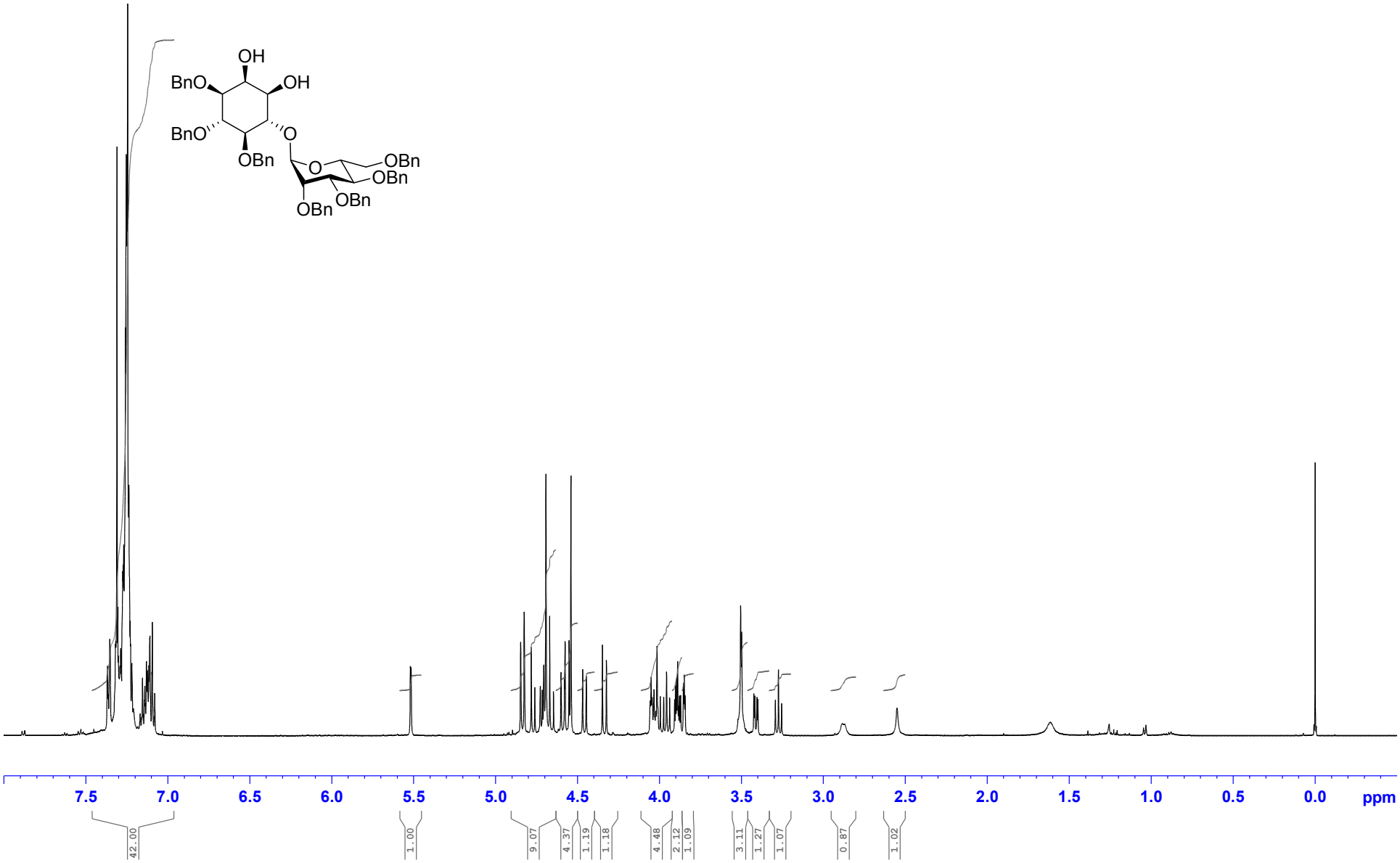
Compound **14** 300 MHz ^{1}H NMR $CDCl_3$



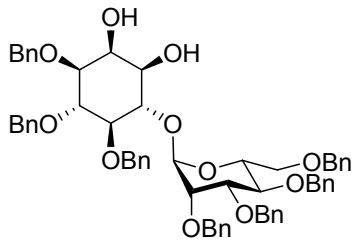
Compound **14** 75 MHz ^{13}C NMR $CDCl_3$



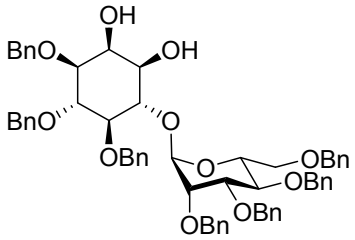
Compound **15** 500 MHz ^{1}H NMR $CDCl_3$



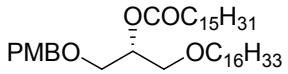
Compound **15** 125 MHz ^{13}C NMR $CDCl_3$



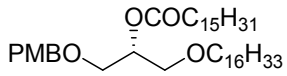
Compound **15** 125 MHz ^{13}C NMR $CDCl_3$



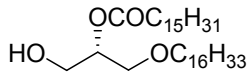
Compound **20** 300 MHz ^{1}H NMR $CDCl_3$



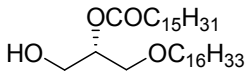
Compound **20** 75 MHz ^{13}C NMR $CDCl_3$



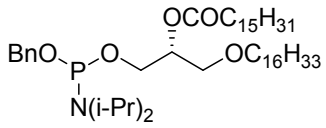
Compound **21** 300 MHz ^{1}H NMR $CDCl_3$



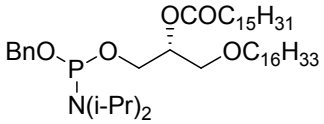
Compound **21** 75 MHz ^{13}C NMR $CDCl_3$



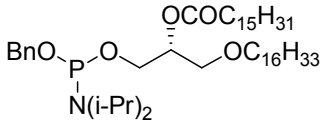
Compound **17** 300 MHz ^{1}H NMR $CDCl_3$



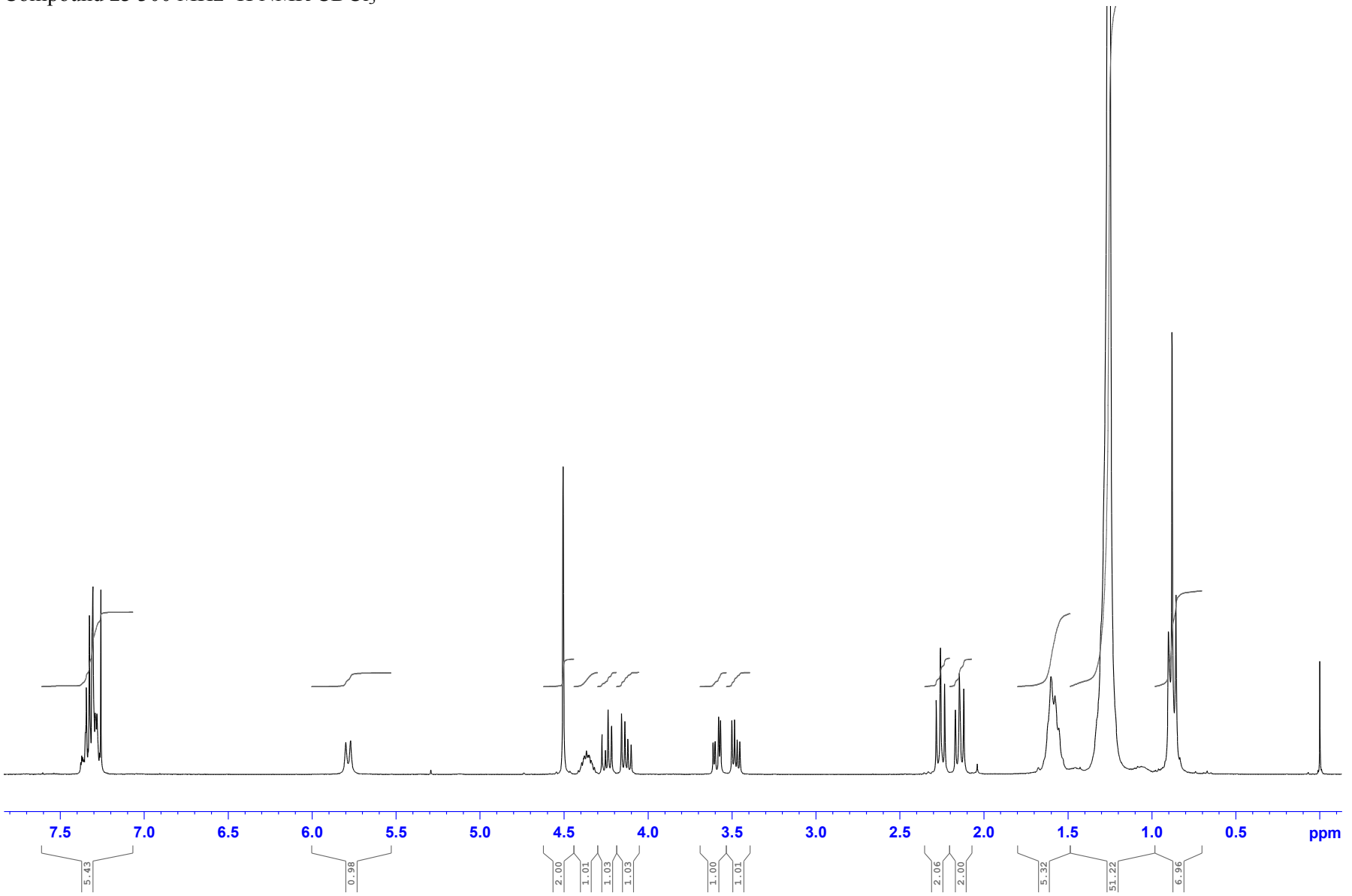
Compound **17** 75 MHz ^{13}C NMR $CDCl_3$

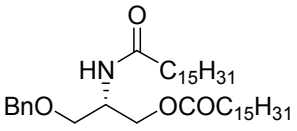


Compound **17** 121 MHz ^{31}P NMR $CDCl_3$

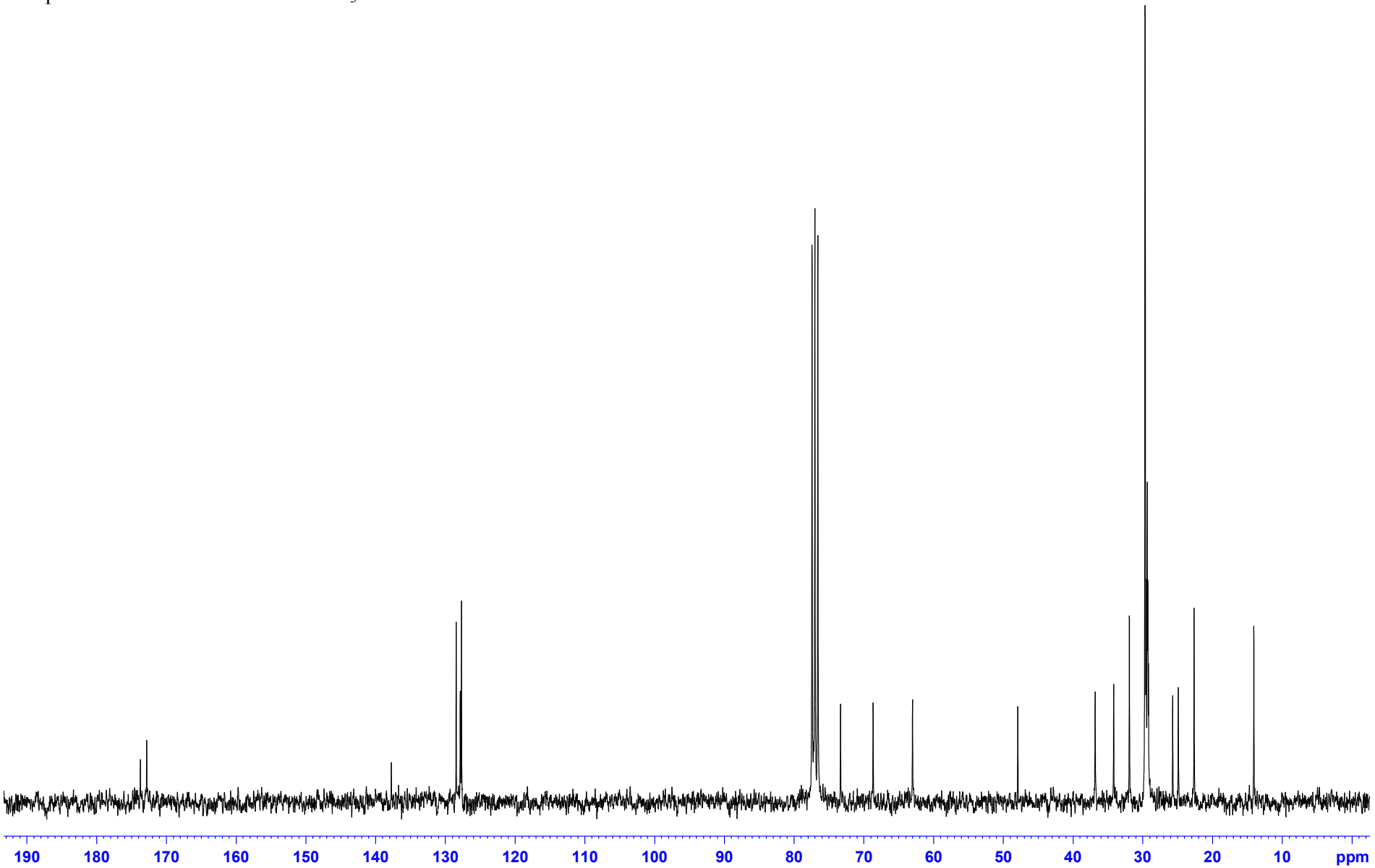


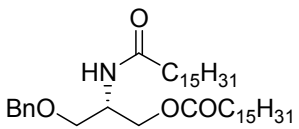
Compound **23** 300 MHz ^{1}H NMR $CDCl_3$



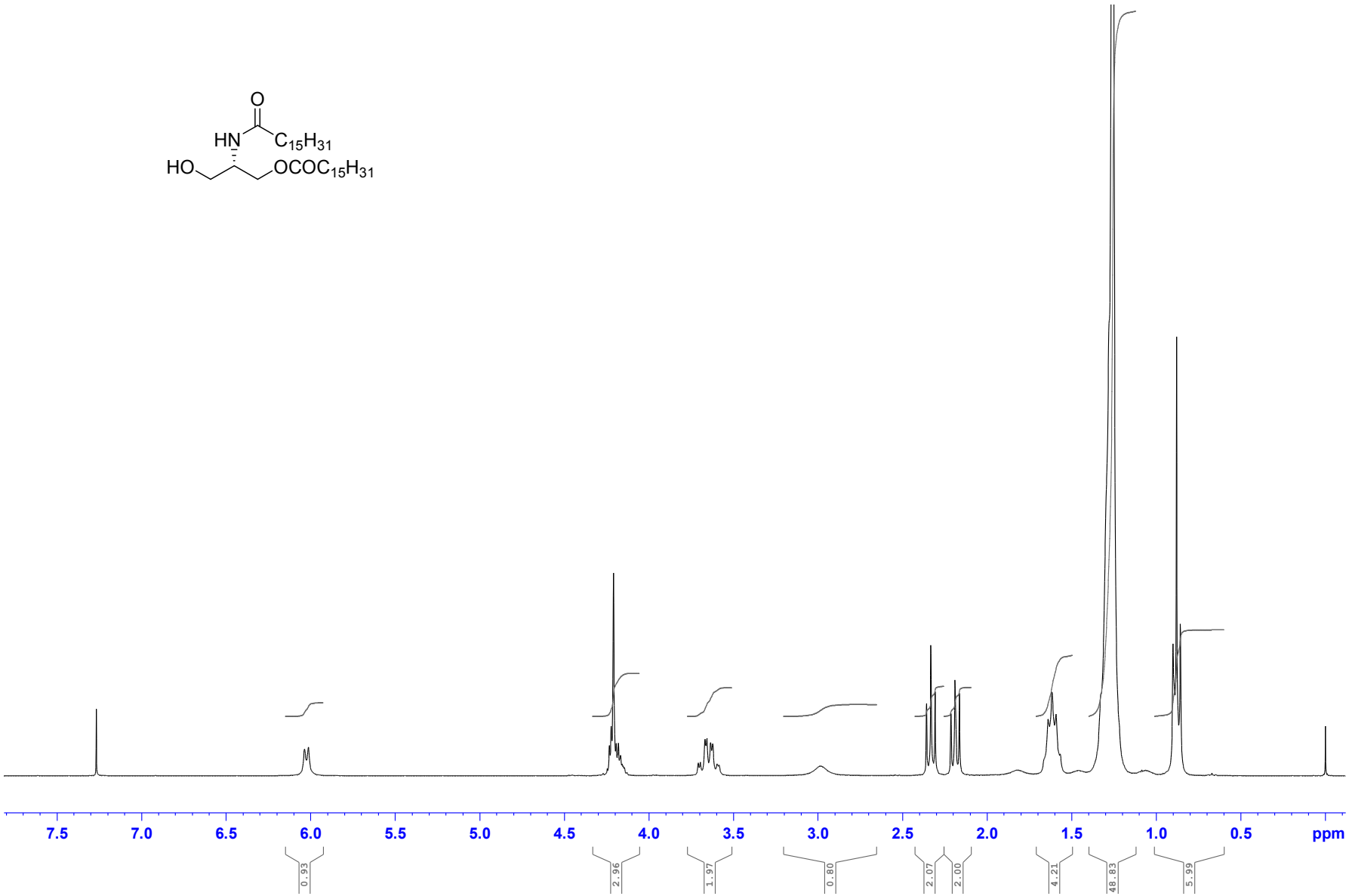


Compound **23** 75 MHz ^{13}C NMR $CDCl_3$

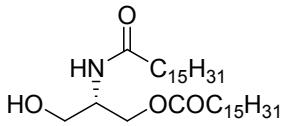




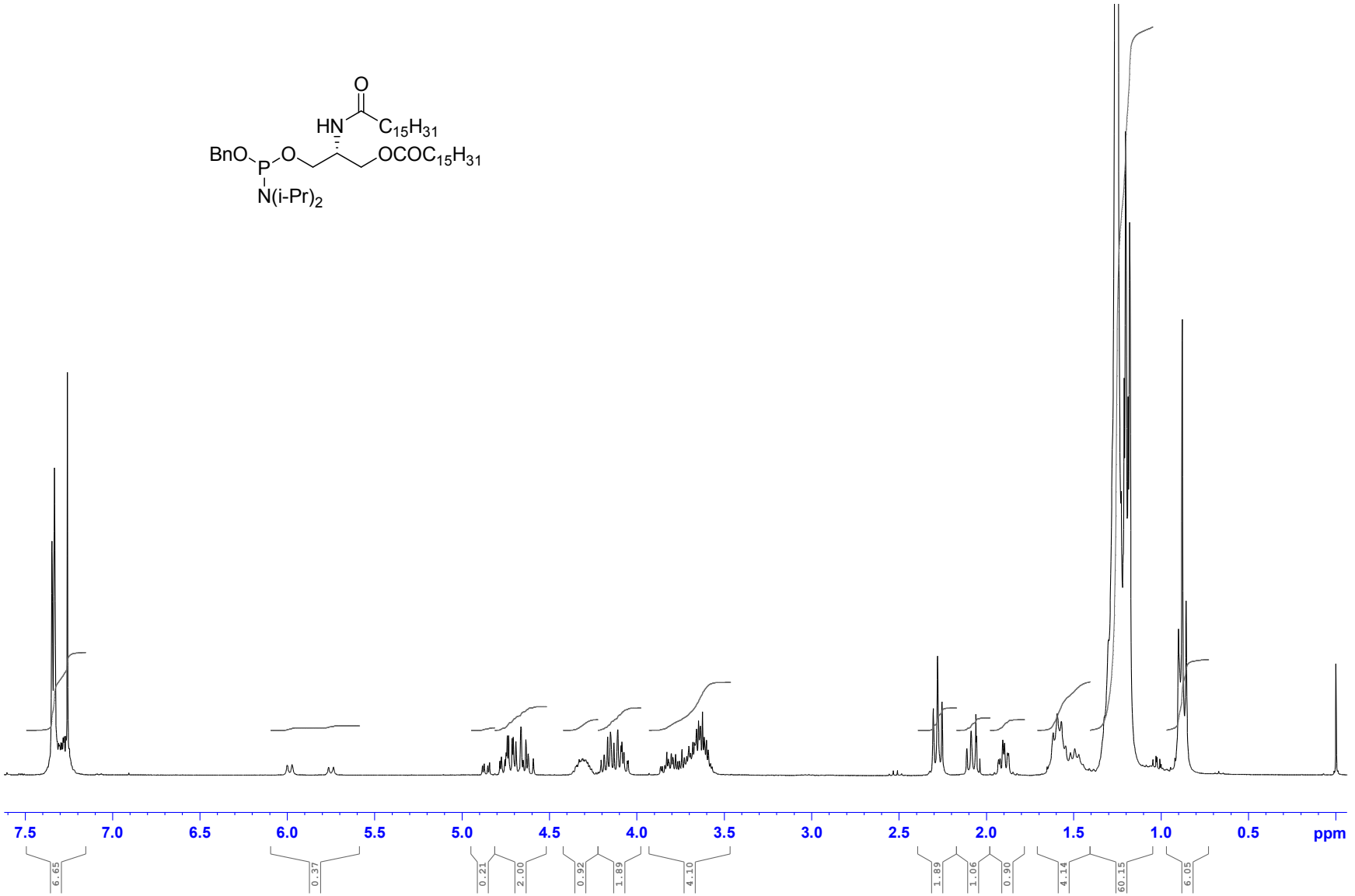
Compound **24** 300 MHz ^{1}H NMR $CDCl_3$



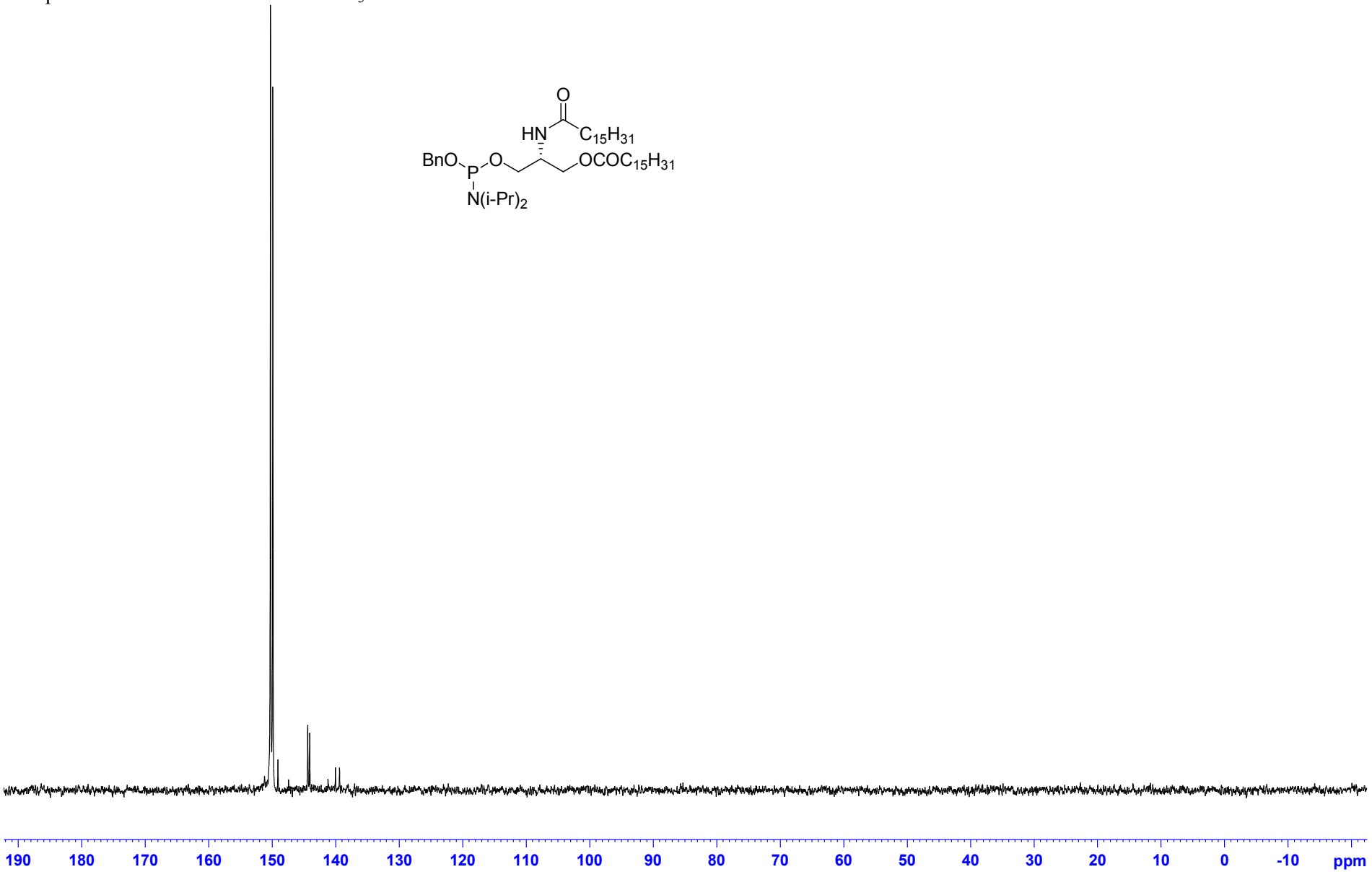
Compound **24** 75 MHz ^{13}C NMR $CDCl_3$



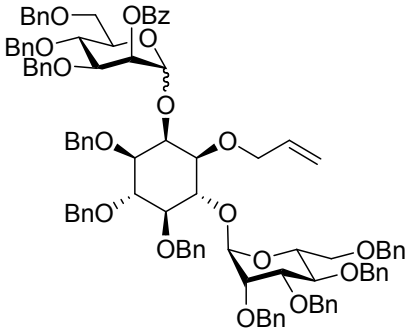
Compound **18** 300 MHz ^{1}H NMR $CDCl_3$



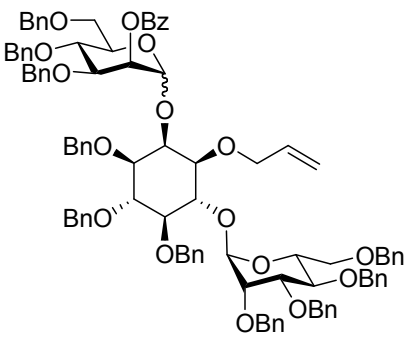
Compound **18** 121 MHz ^{31}P NMR $CDCl_3$



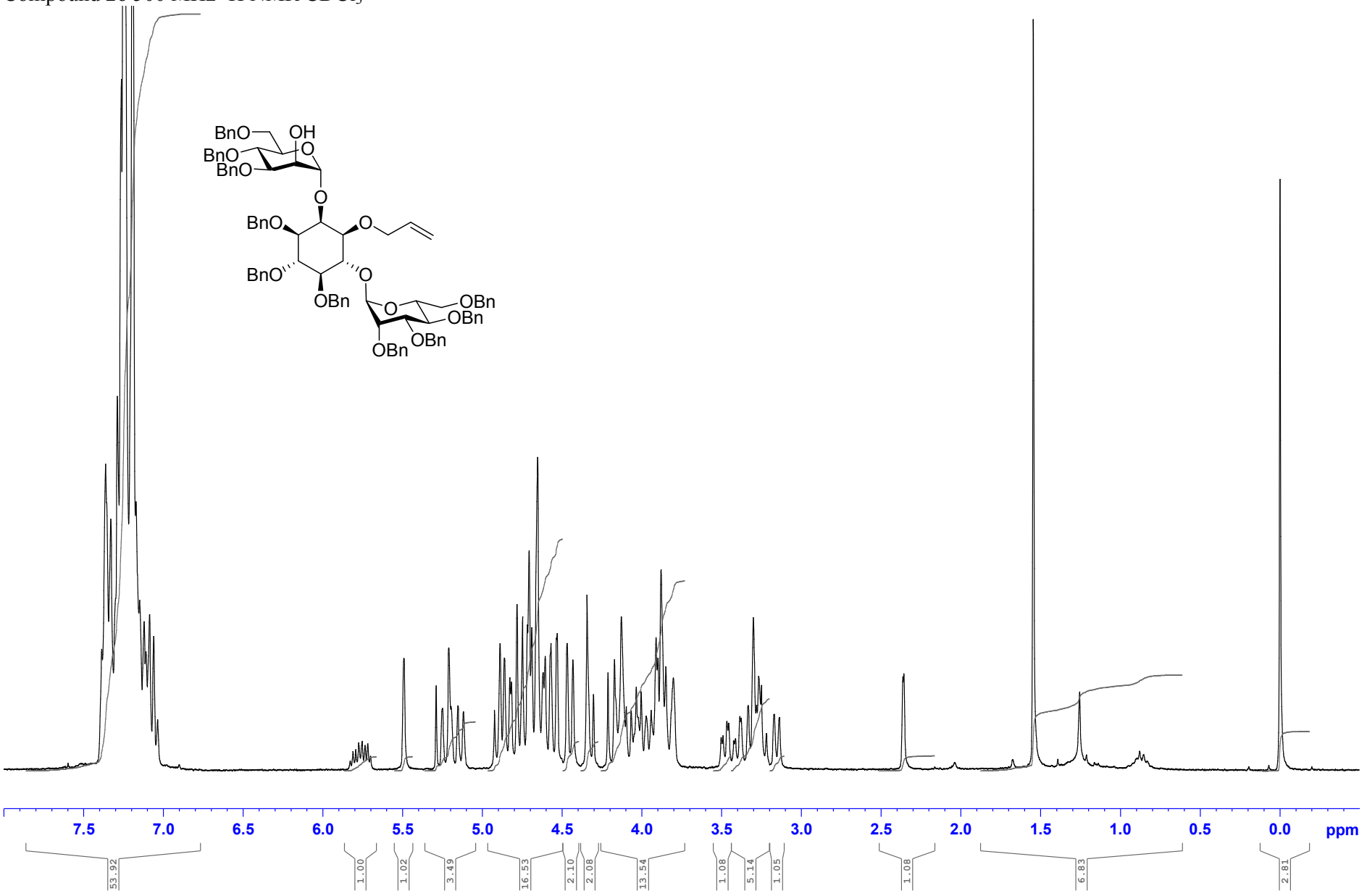
Compound **25** 300 MHz ^{1}H NMR $CDCl_3$



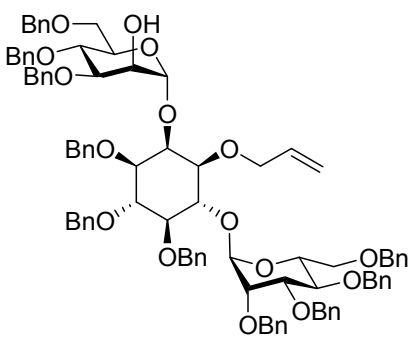
Compound **25** 75 MHz ^{13}C NMR $CDCl_3$



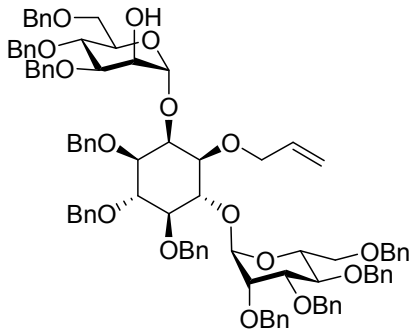
Compound **26** 500 MHz ^{1}H NMR $CDCl_3$



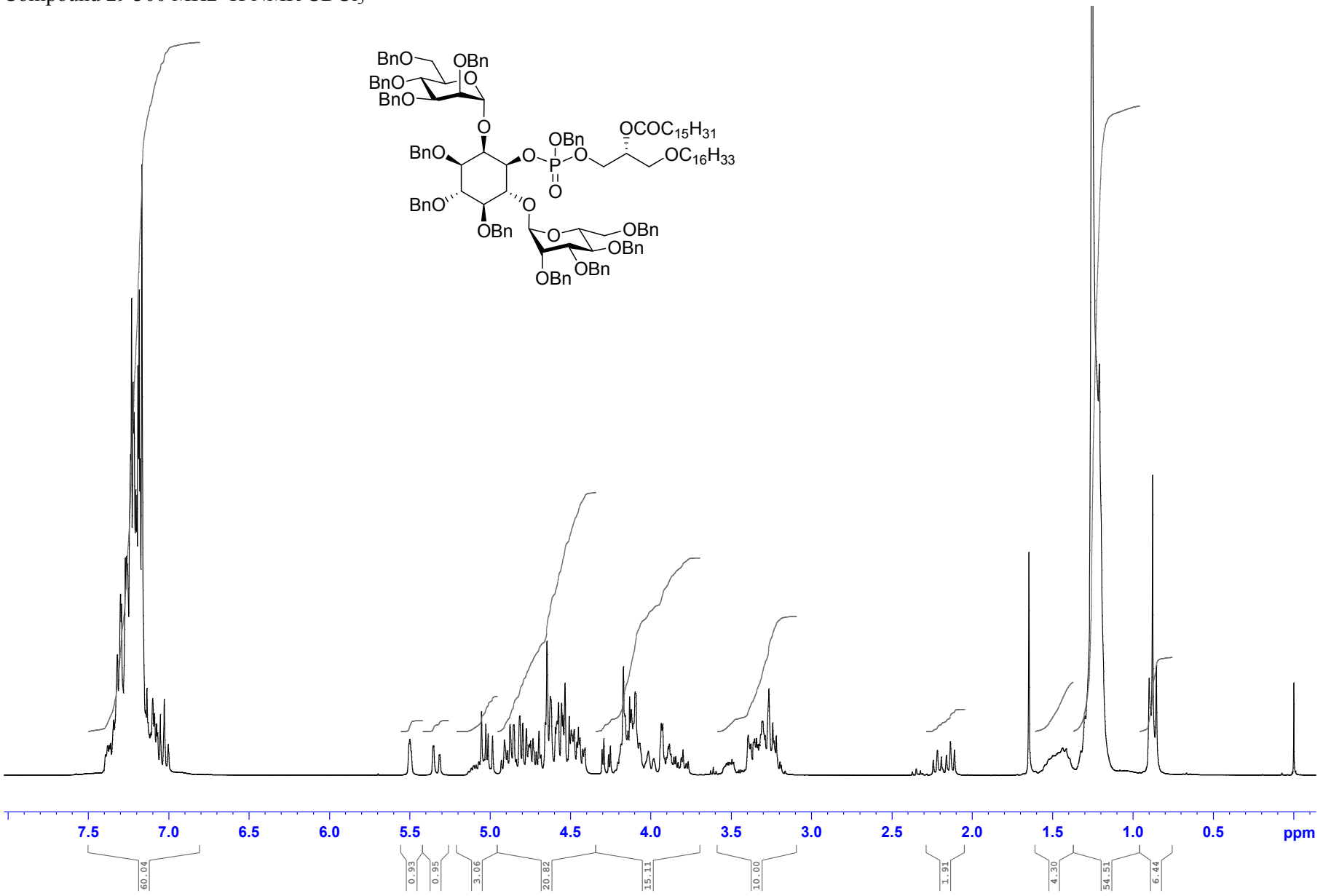
Compound **26** 125 MHz ^{13}C NMR $CDCl_3$



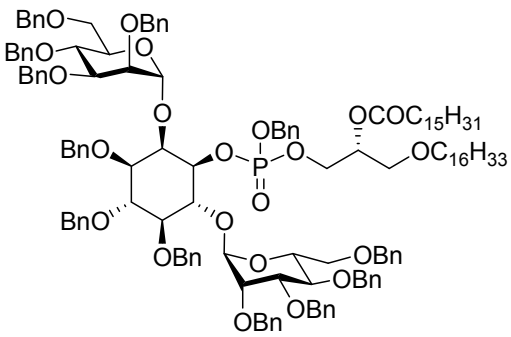
Compound **26** 125 MHz ^{13}C NMR $CDCl_3$



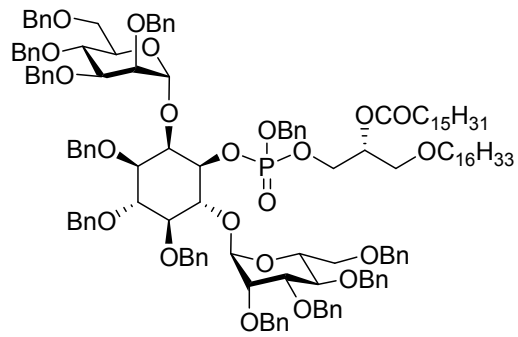
Compound **29** 300 MHz ^{1}H NMR $CDCl_3$



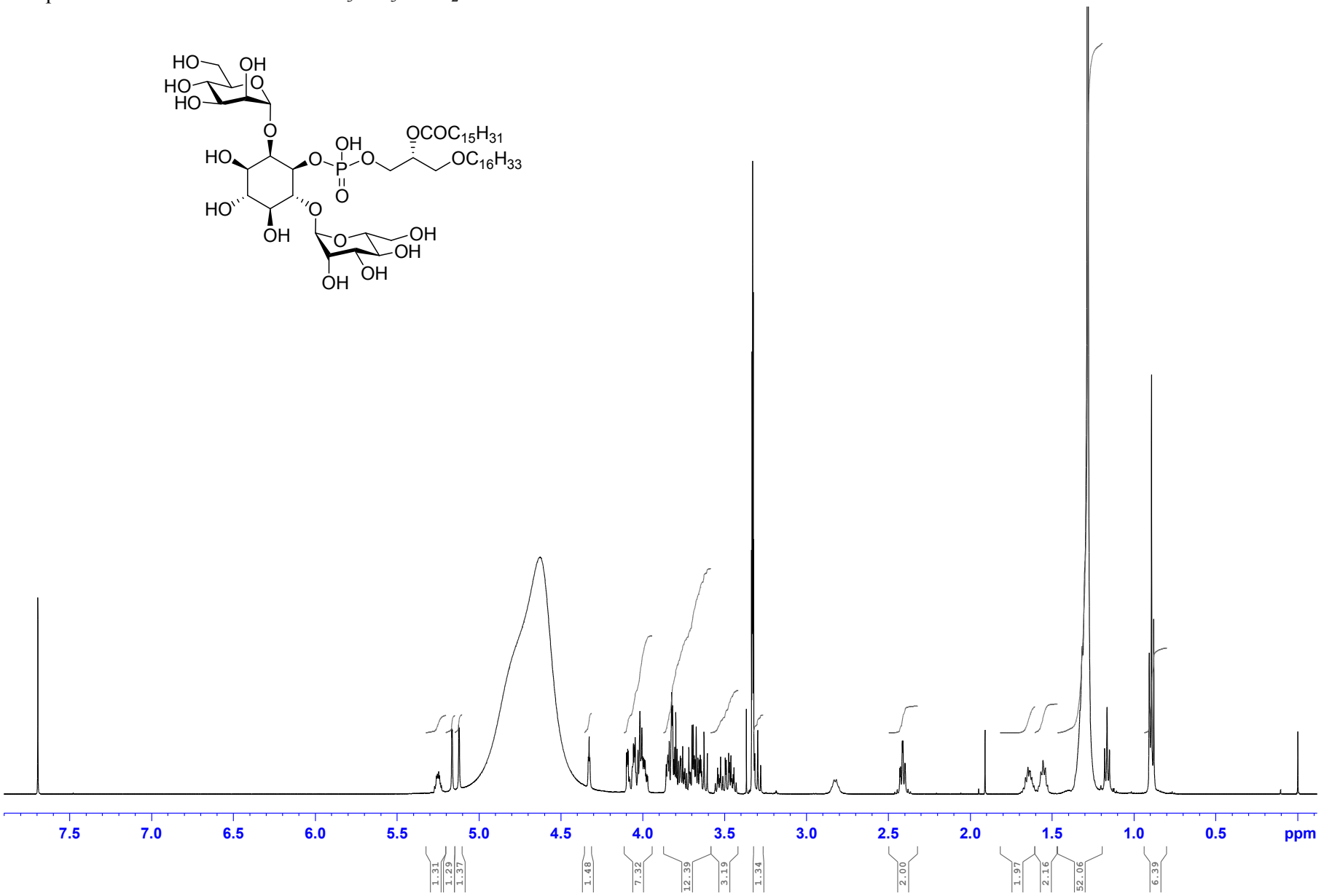
Compound **29** 75 MHz ^{13}C NMR $CDCl_3$



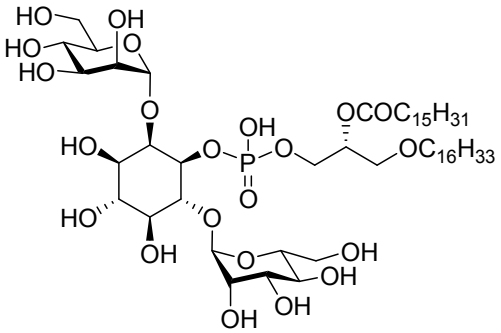
Compound **29** 125 MHz ^{31}P NMR $CDCl_3$



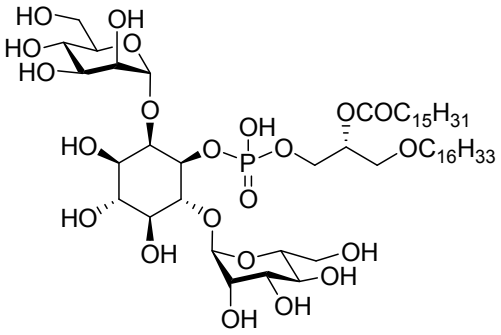
Compound **4** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



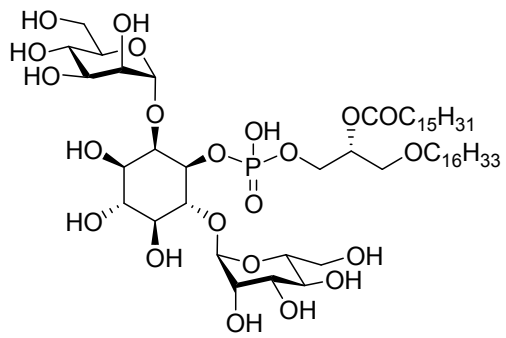
Compound **4** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



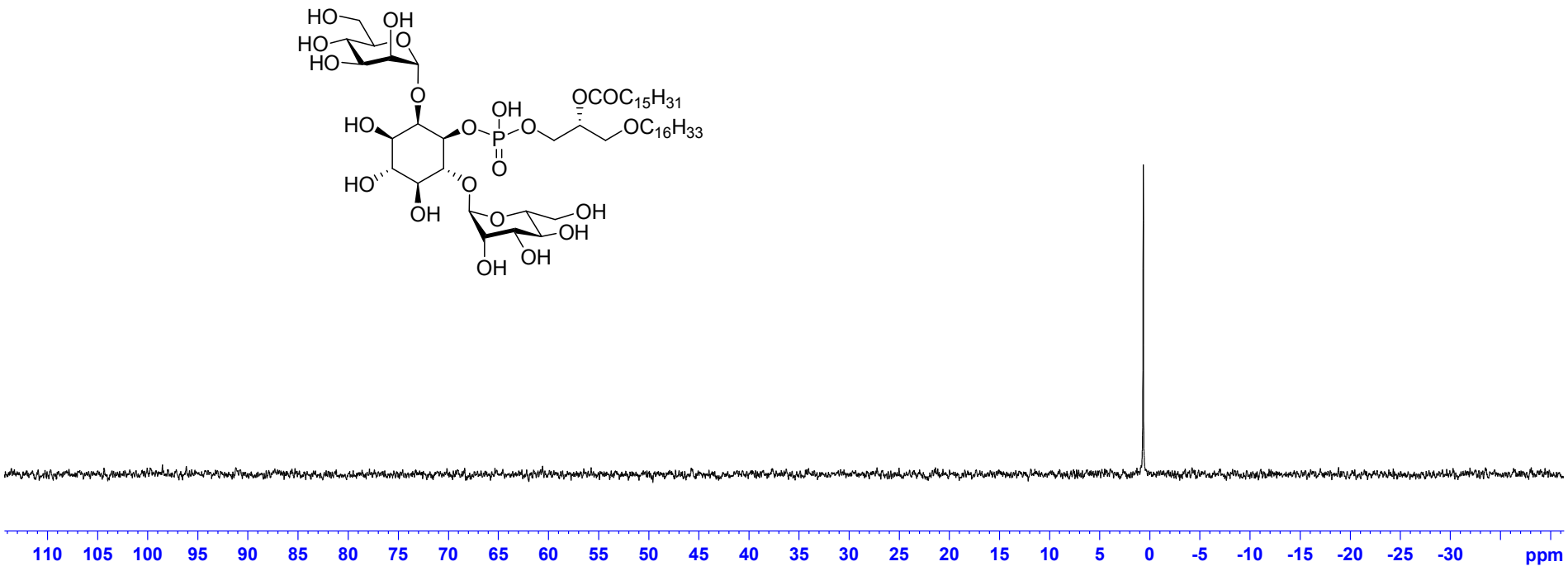
Compound **4** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



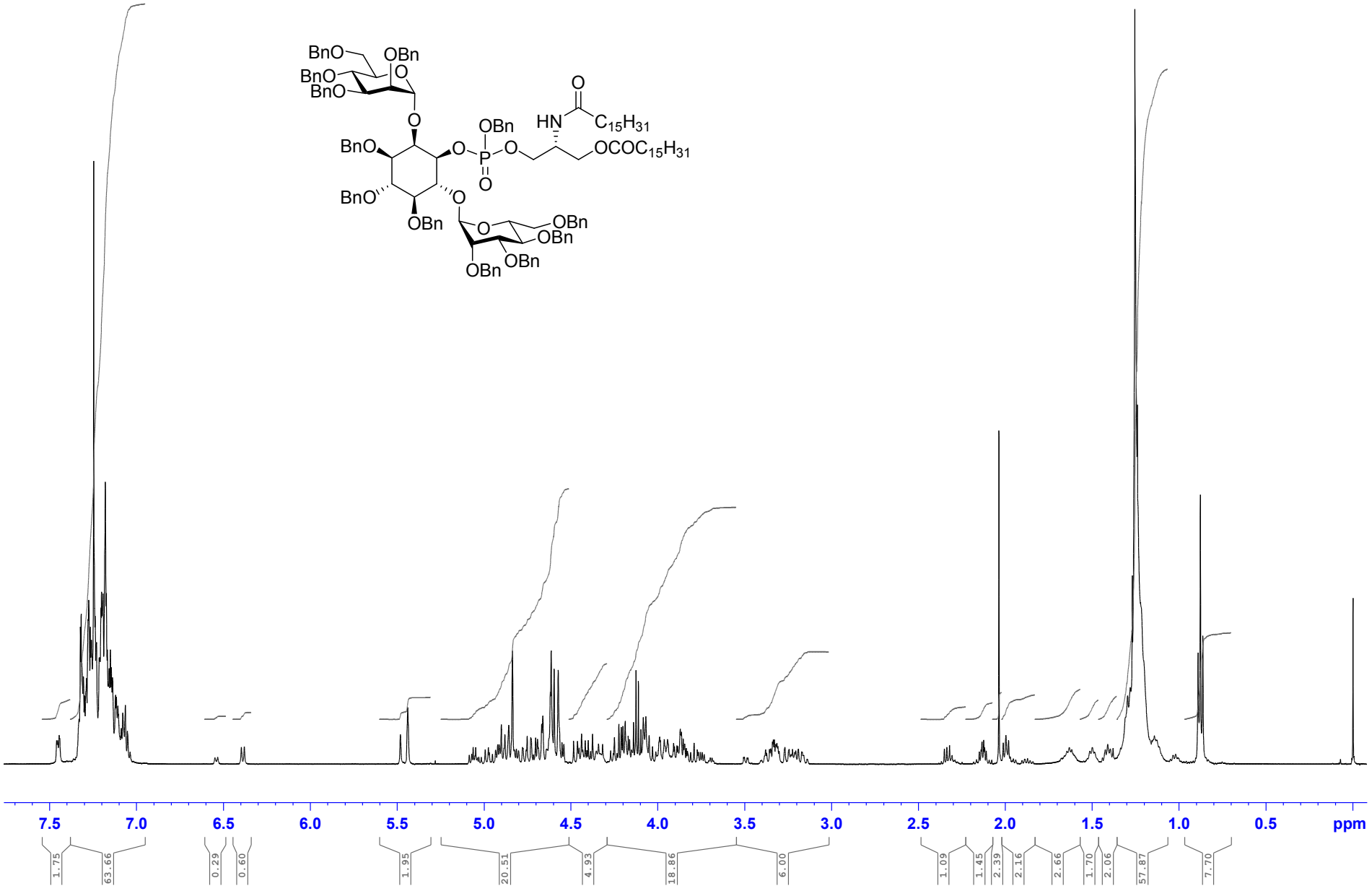
Compound **4** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



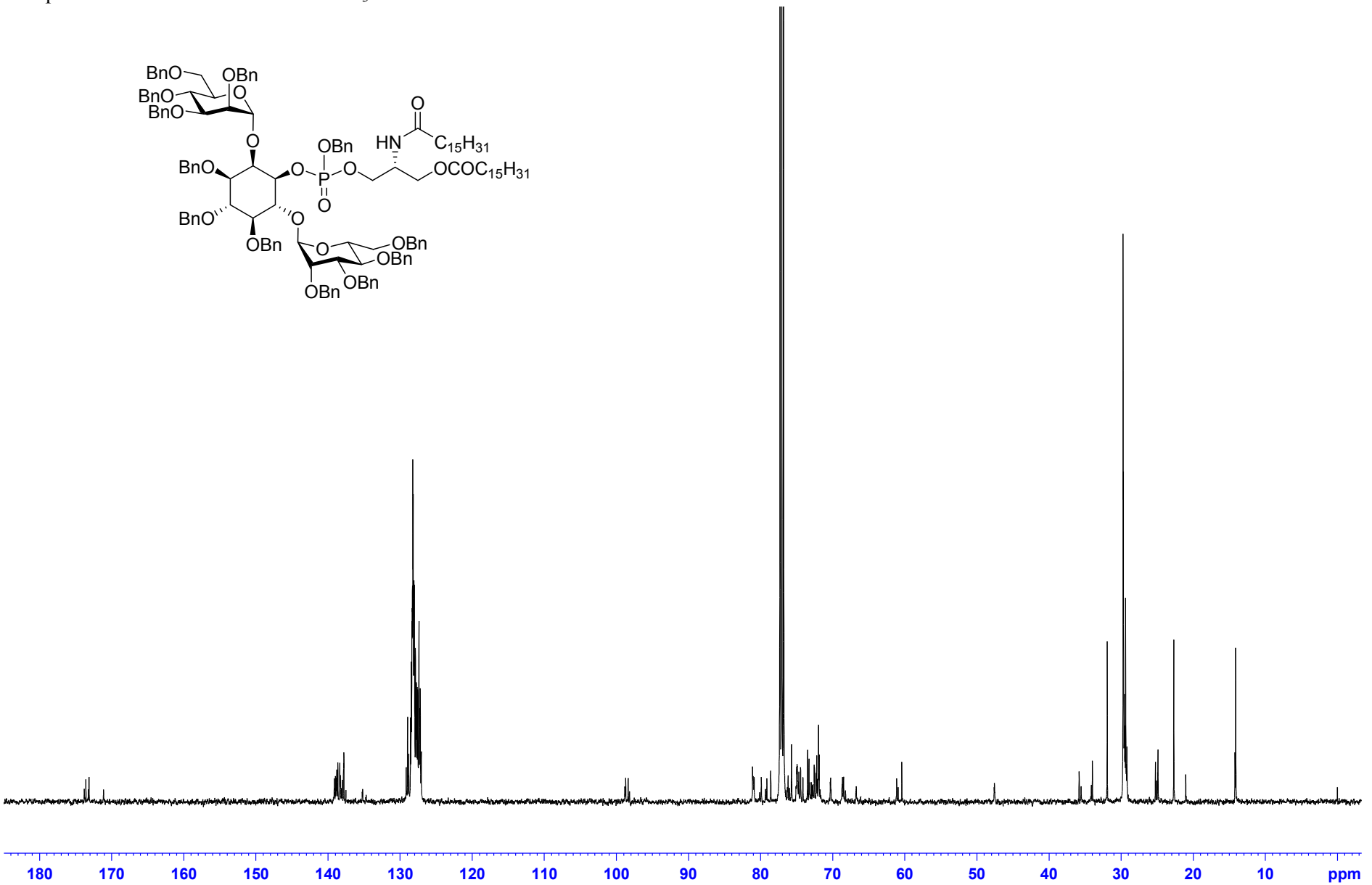
Compound **4** 121 MHz ^{31}P NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



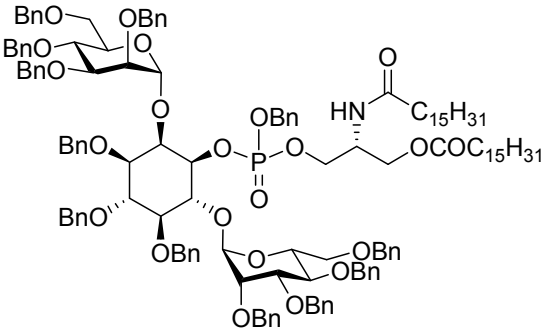
Compound **30** 500 MHz ^{1}H NMR $CDCl_3$



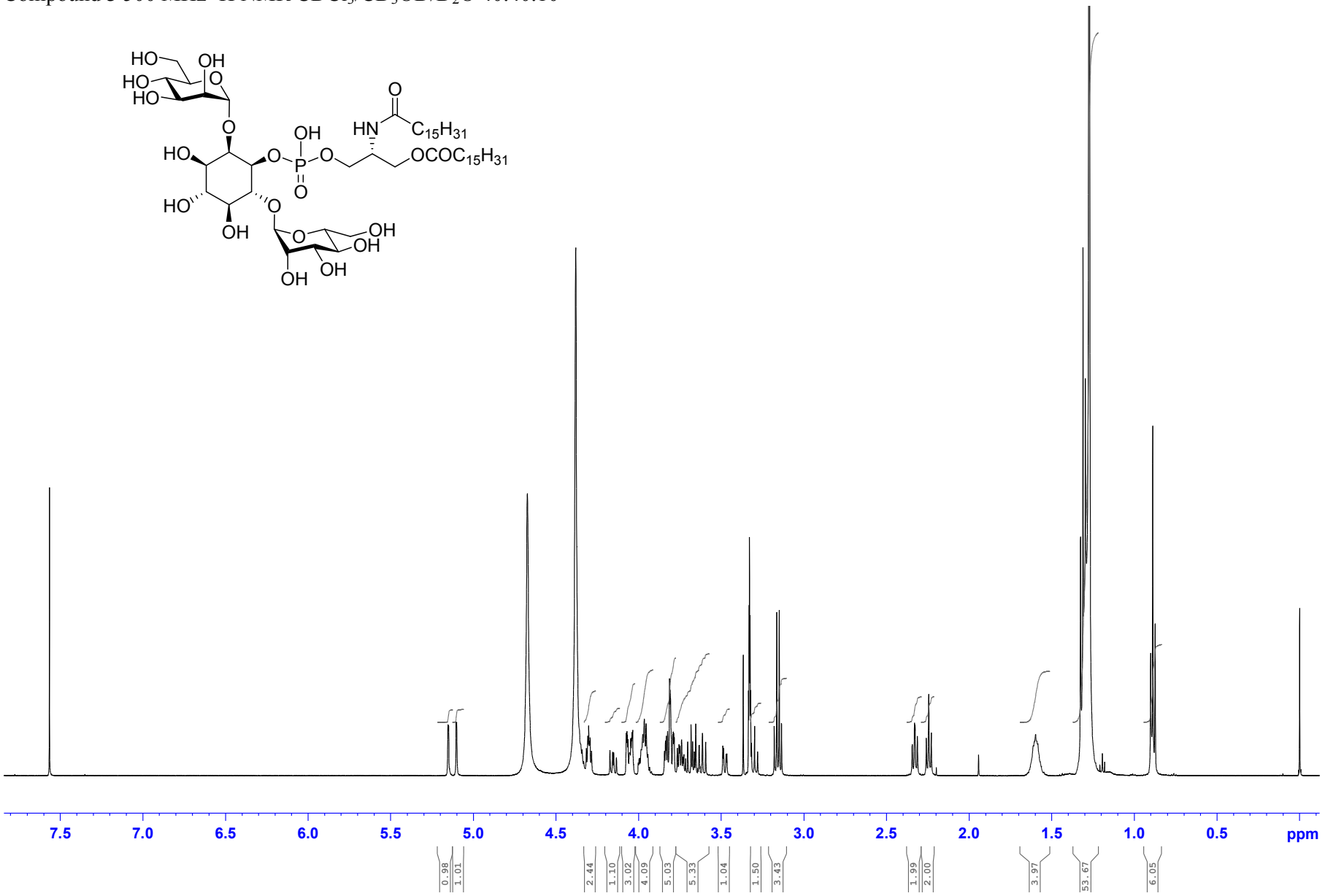
Compound **30** 126 MHz ^{13}C NMR $CDCl_3$



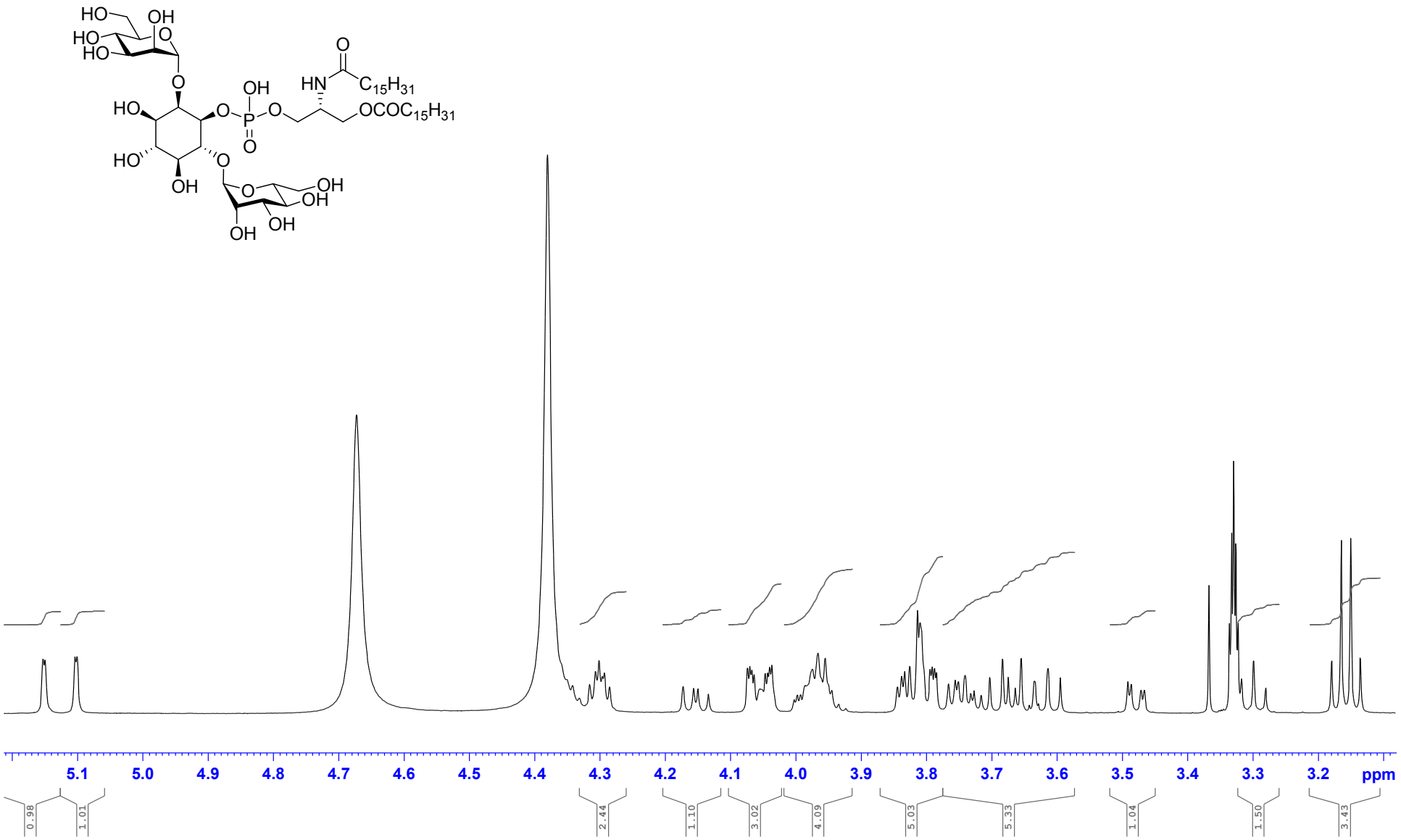
Compound **30** 121 MHz ^{31}P NMR $CDCl_3$



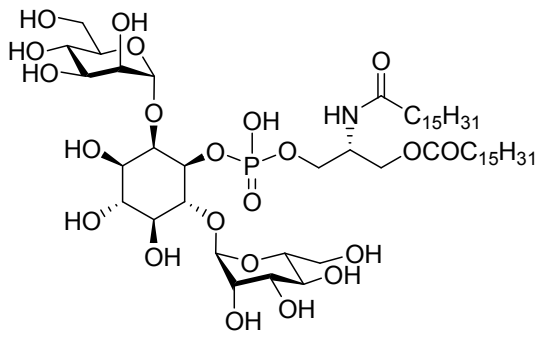
Compound **3** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 40:40:10



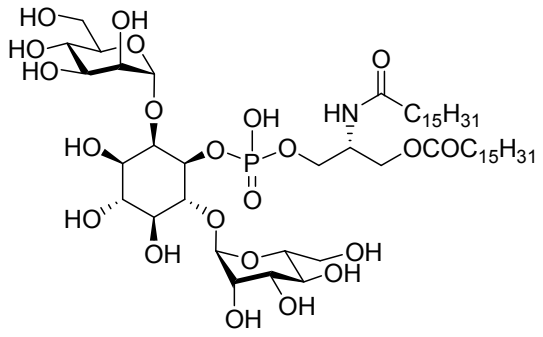
Compound **3** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 40:40:10



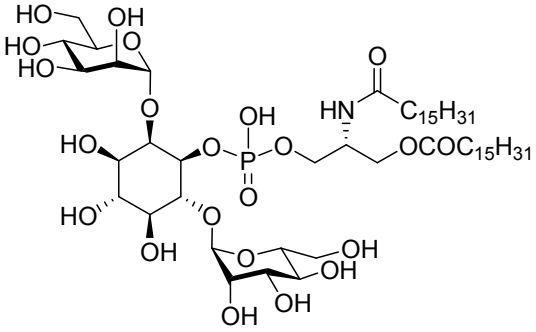
Compound **3** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 40:40:10

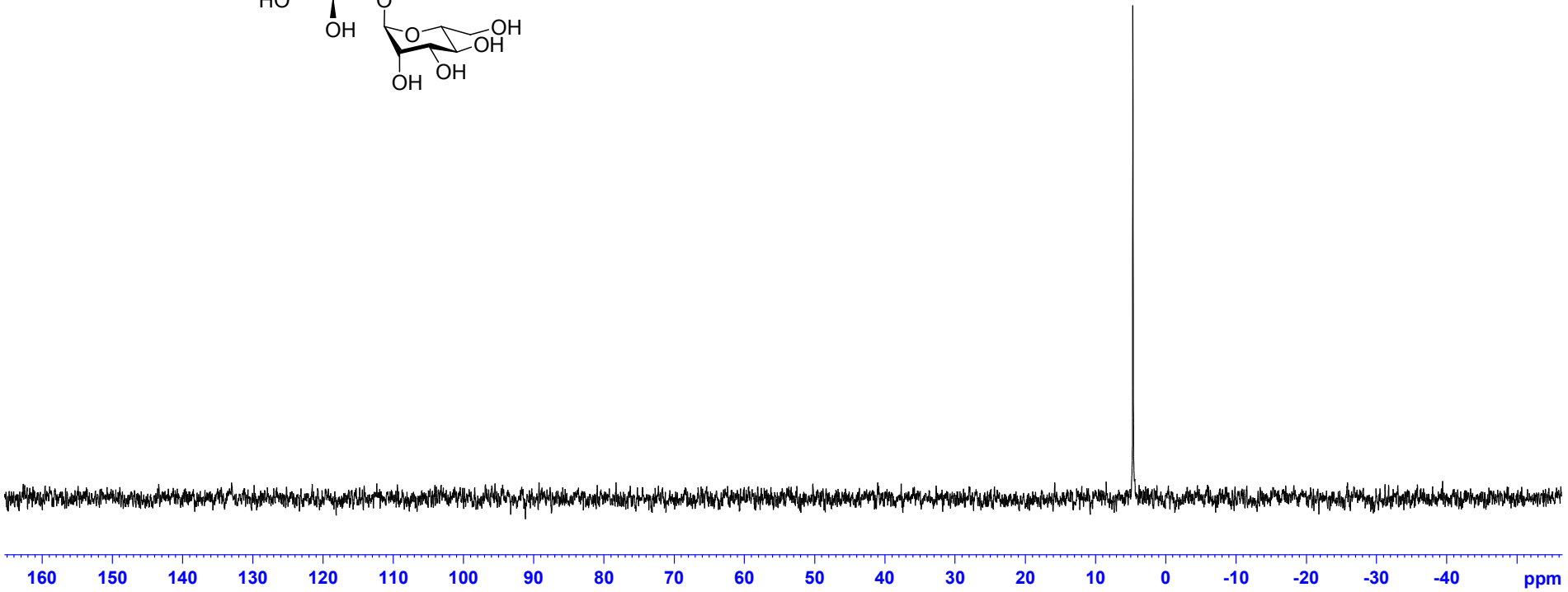


Compound **3** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 40:40:10

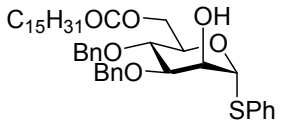


Compound **3** 121 MHz ^{31}P NMR $CDCl_3/CD_3OD/D_2O$ 40:40:10

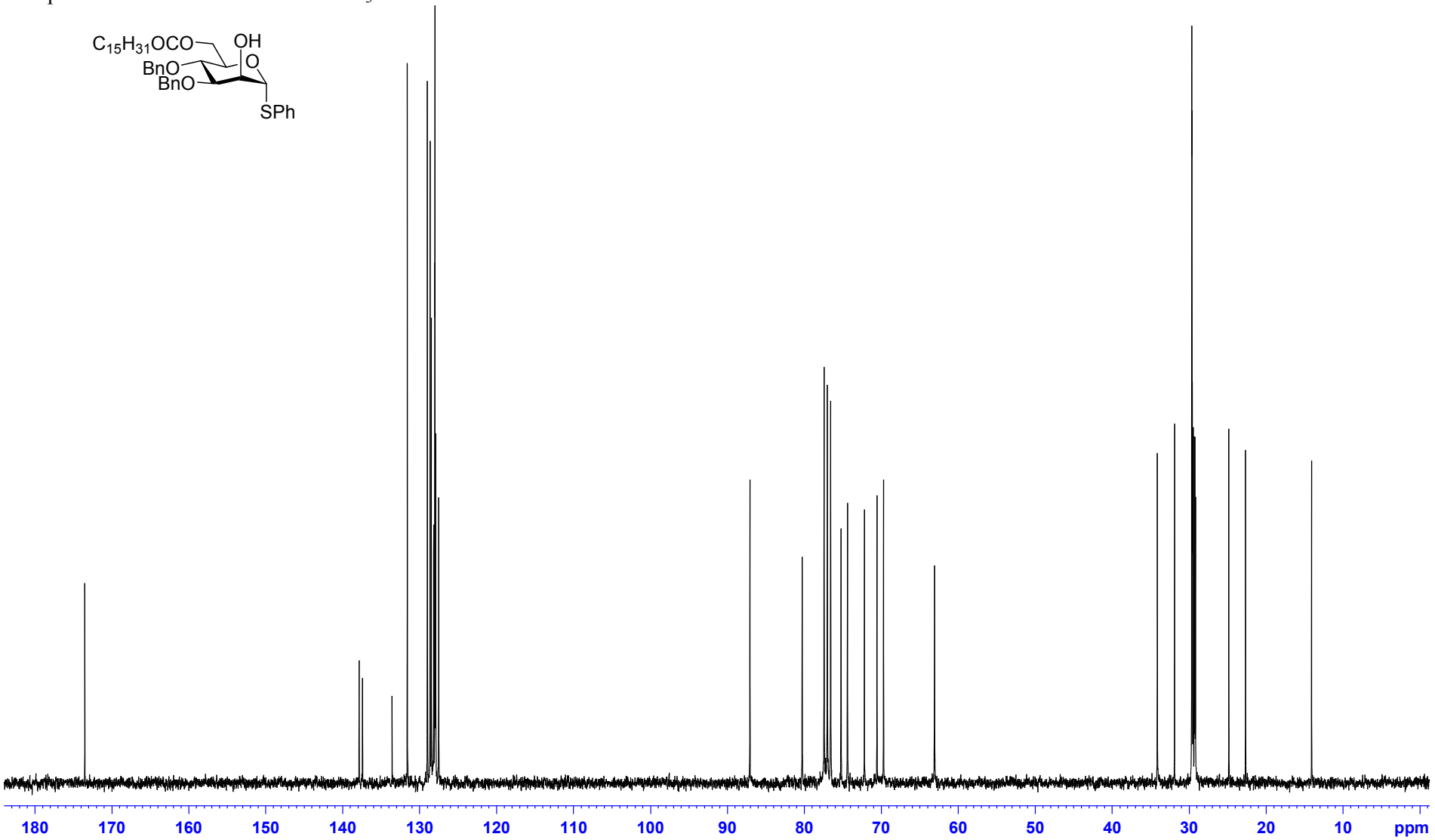




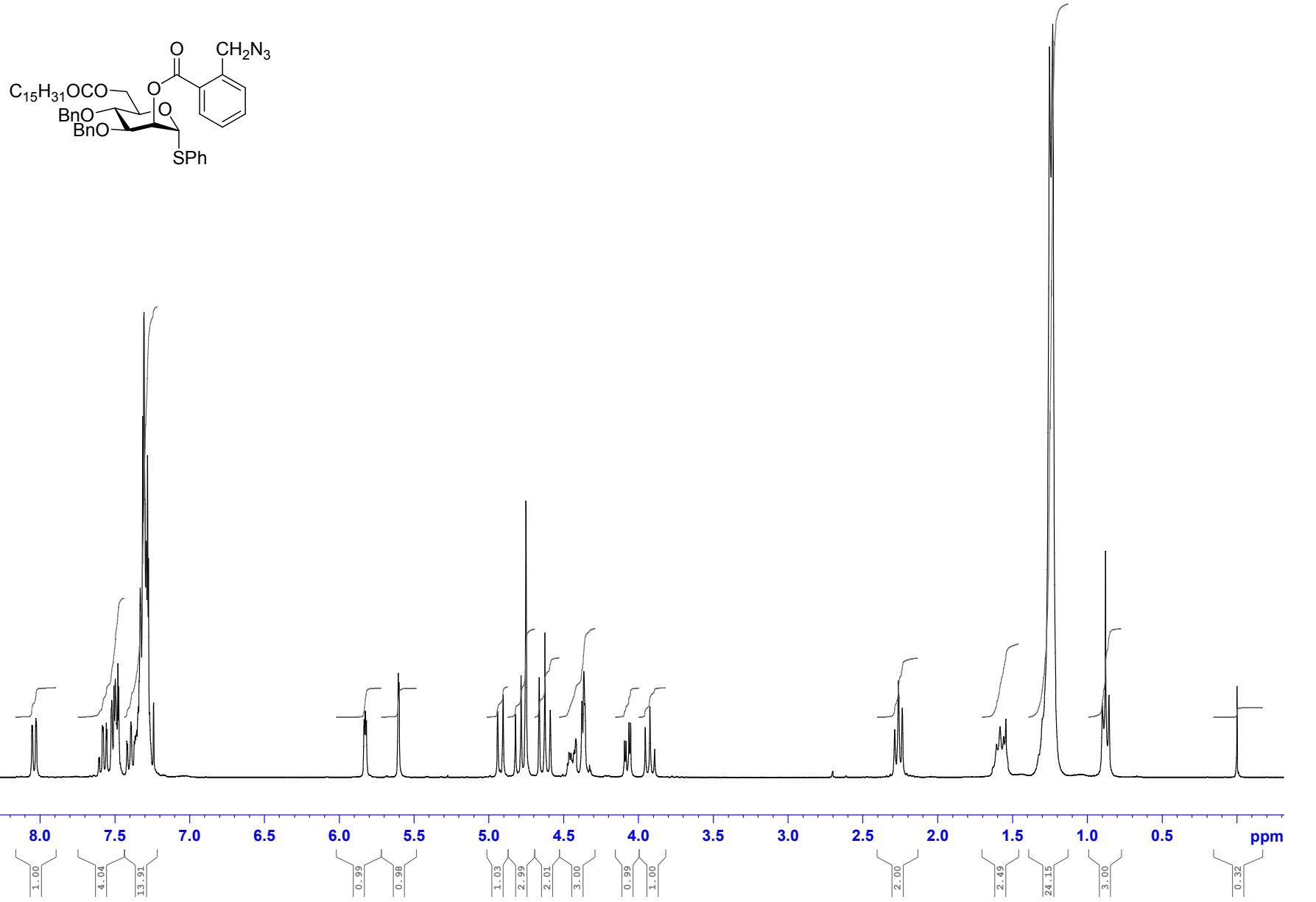
Compound **33** 300 MHz ^{1}H NMR $CDCl_3$



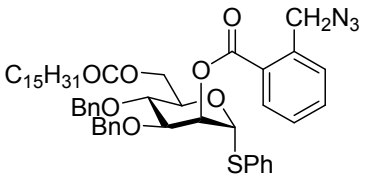
Compound **33** 75 MHz ^{13}C NMR $CDCl_3$



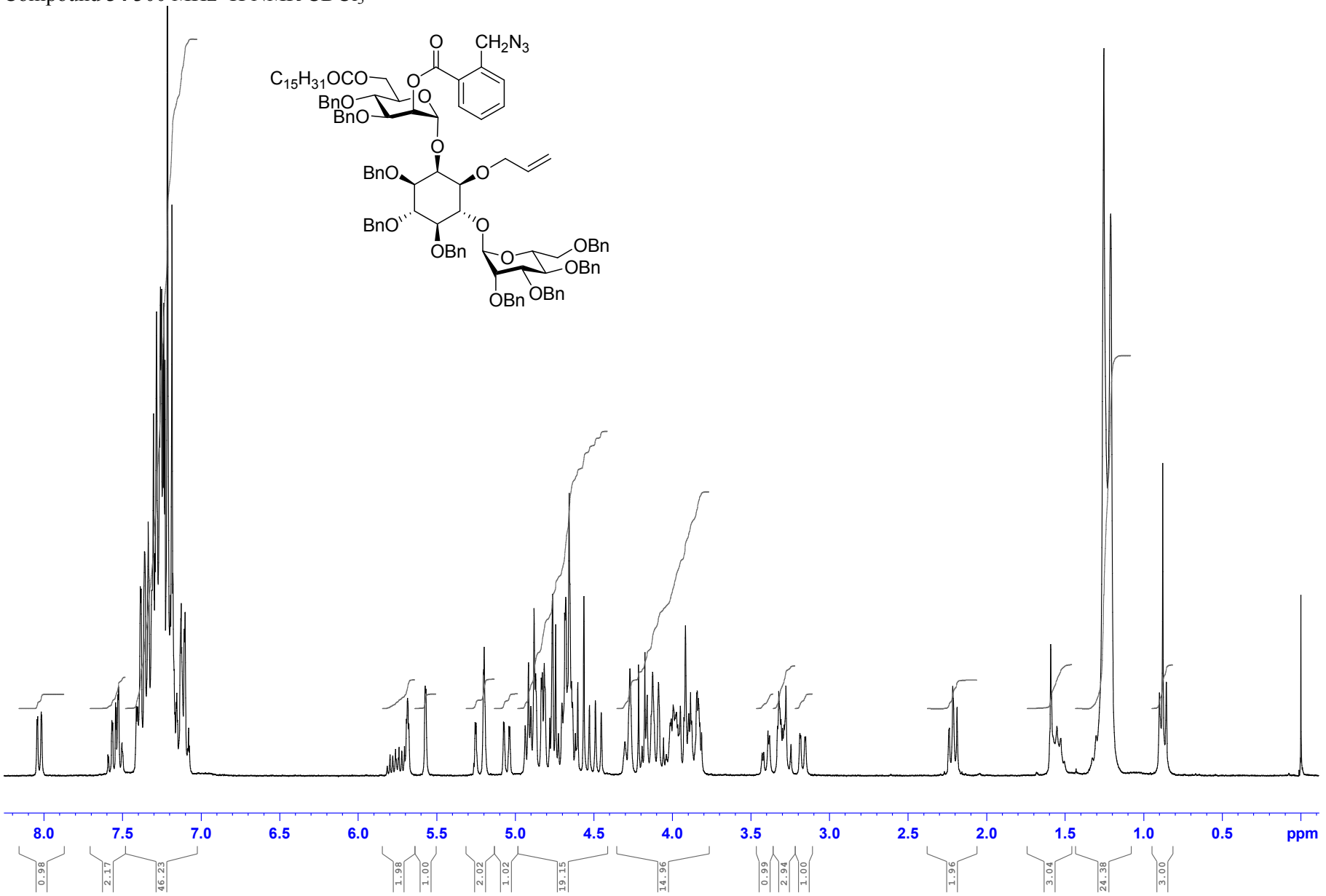
Compound **31** 300 MHz ^{1}H NMR $CDCl_3$



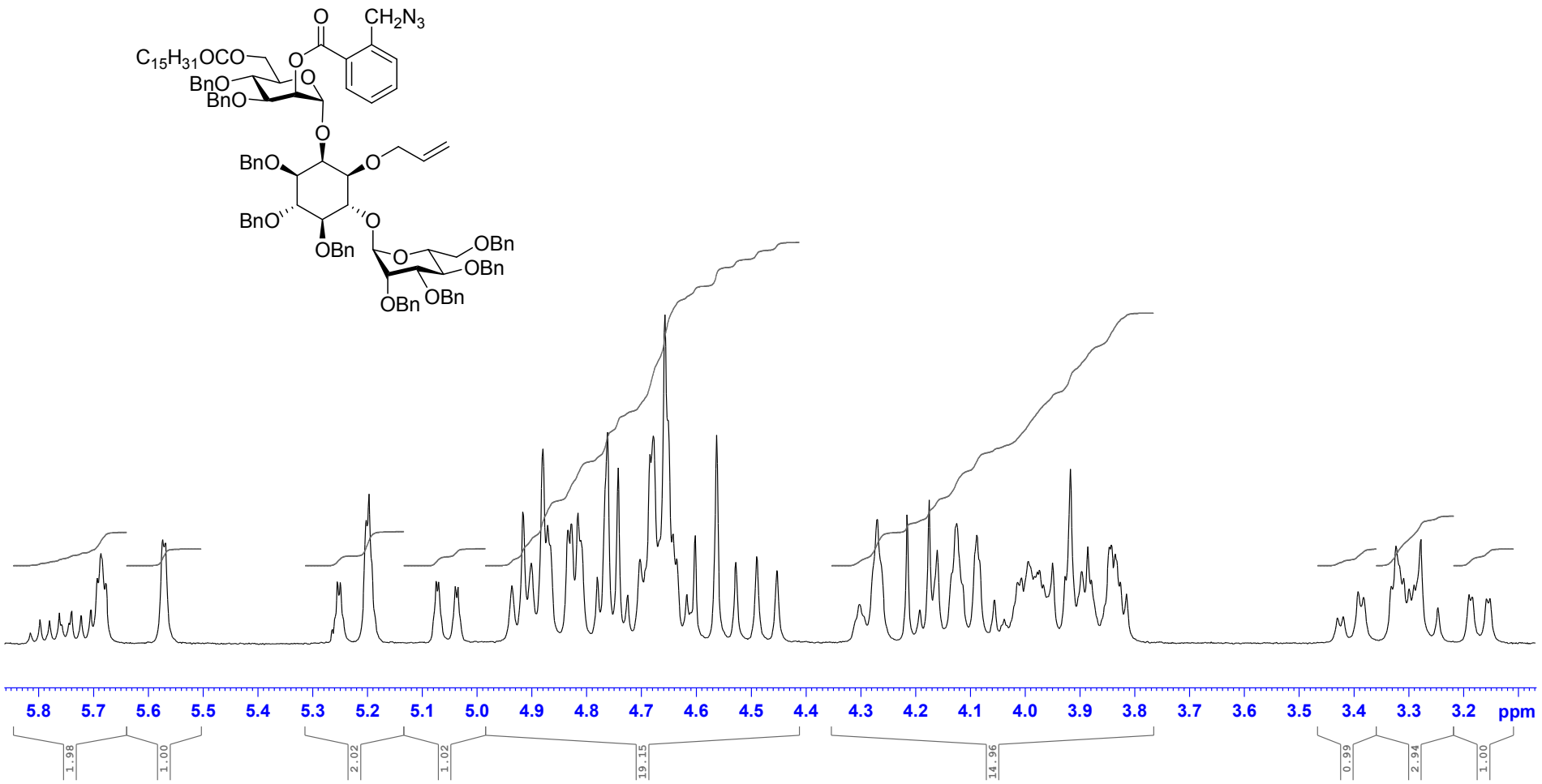
Compound **31 cmh653.1** 75 MHz ^{13}C NMR $CDCl_3$



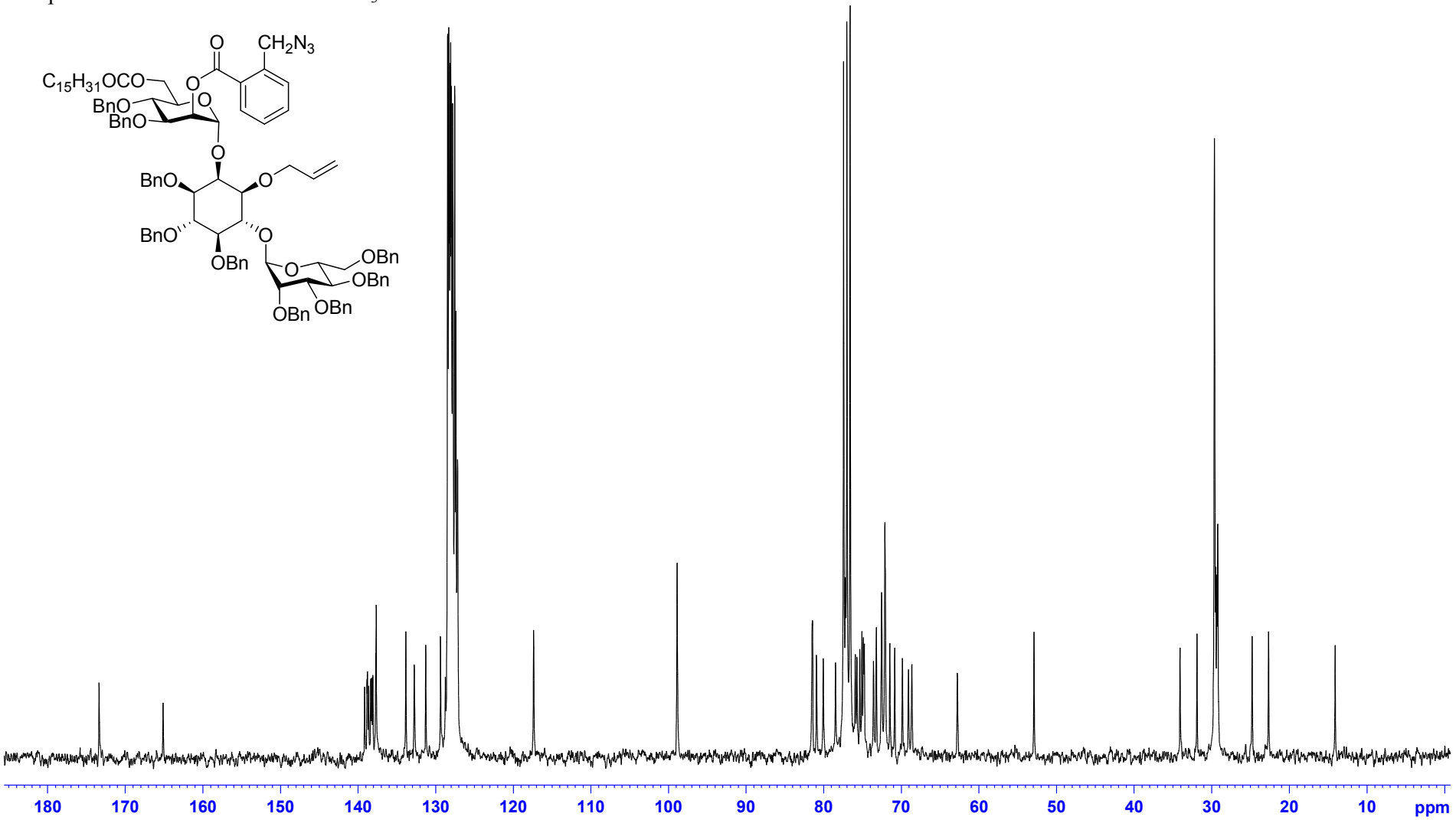
Compound **34** 300 MHz ^{1}H NMR $CDCl_3$



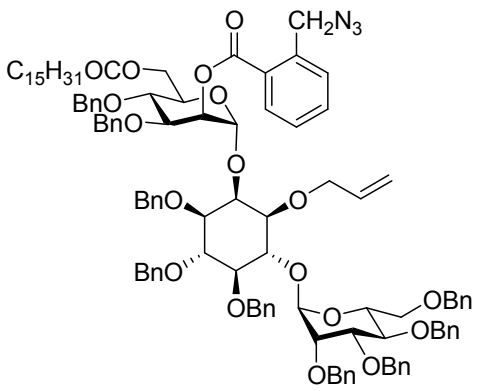
Compound **34** 300 MHz ^{1}H NMR $CDCl_3$



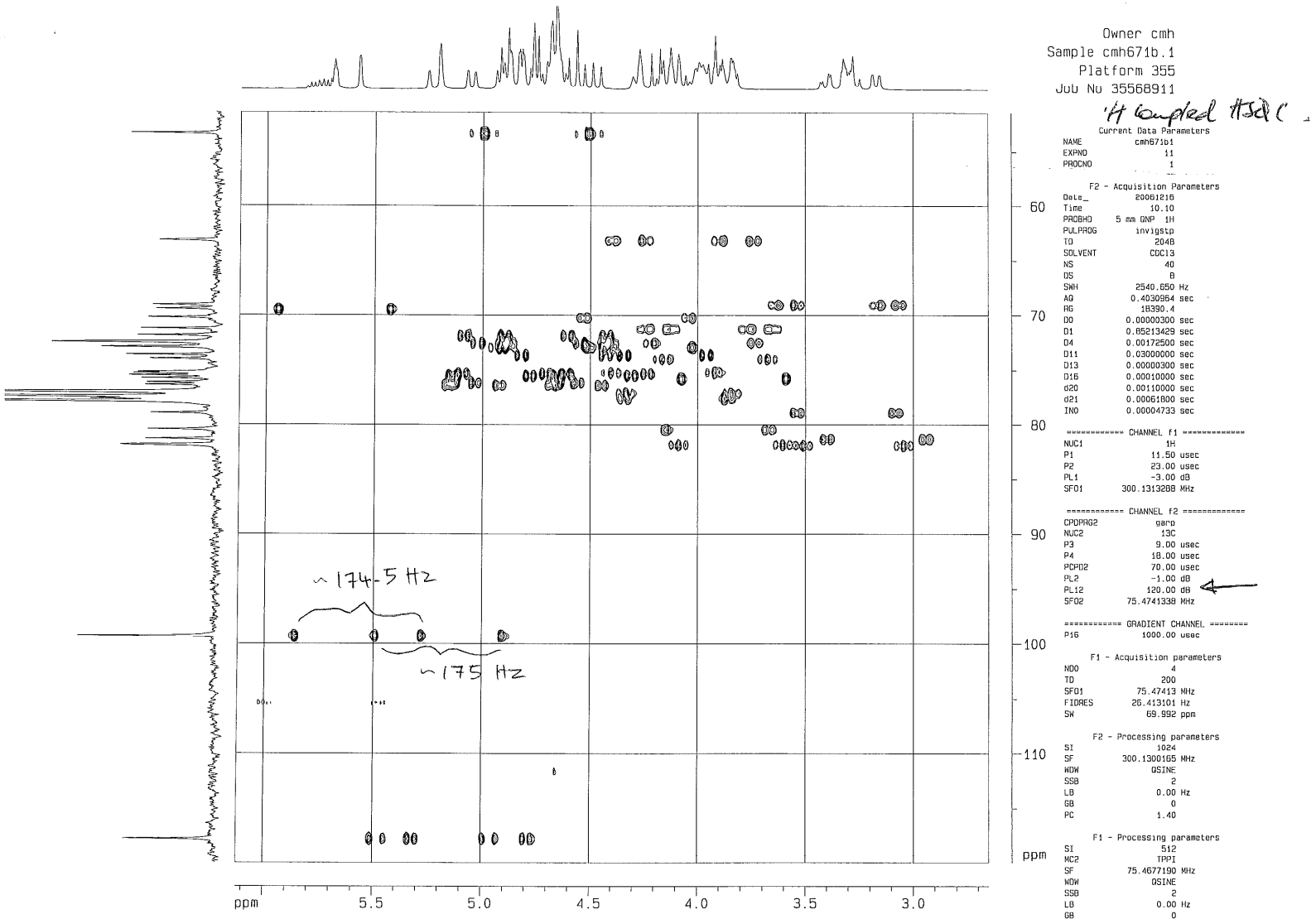
Compound **34** 75 MHz ^{13}C NMR $CDCl_3$



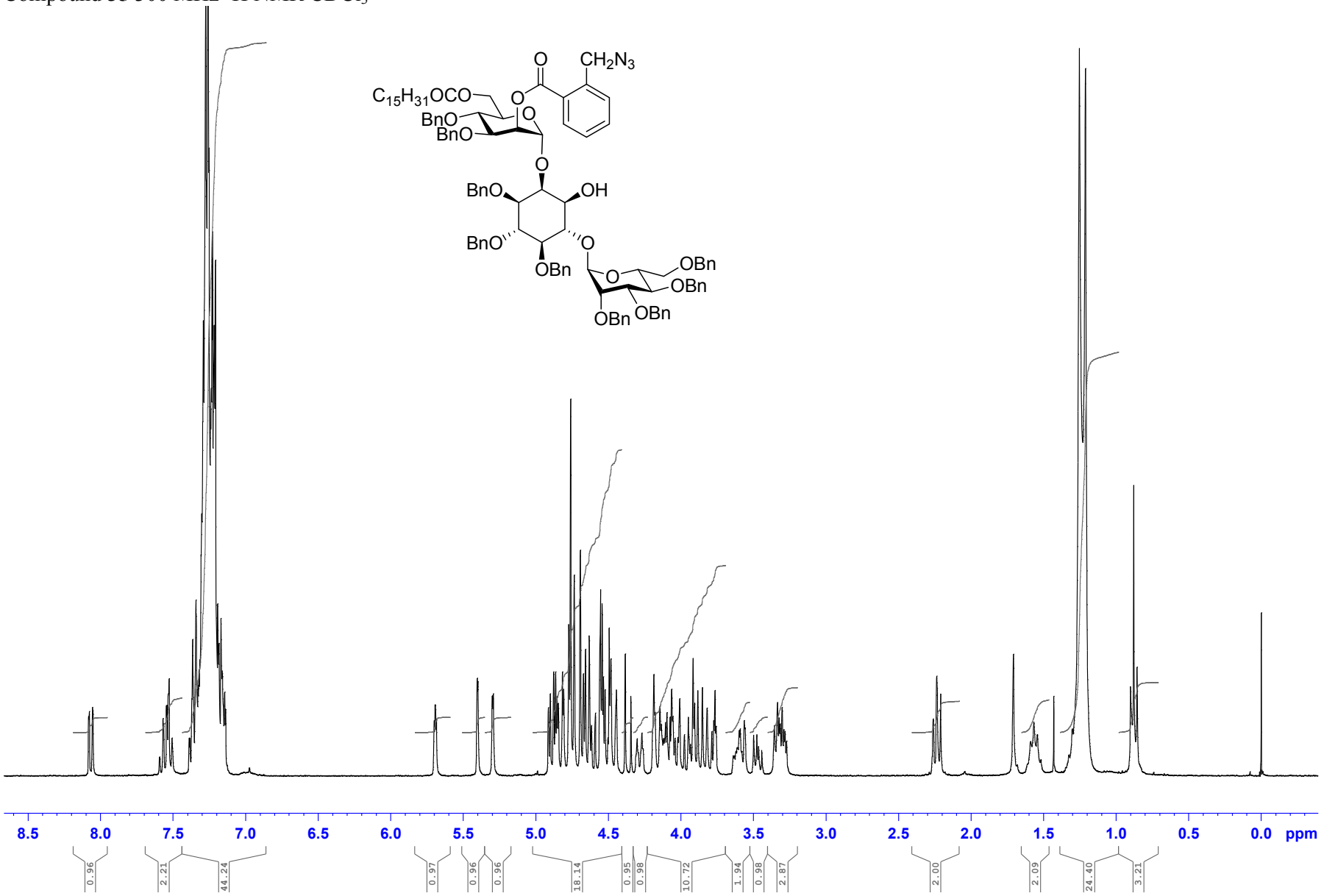
Compound **34** 75 MHz ^{13}C NMR $CDCl_3$



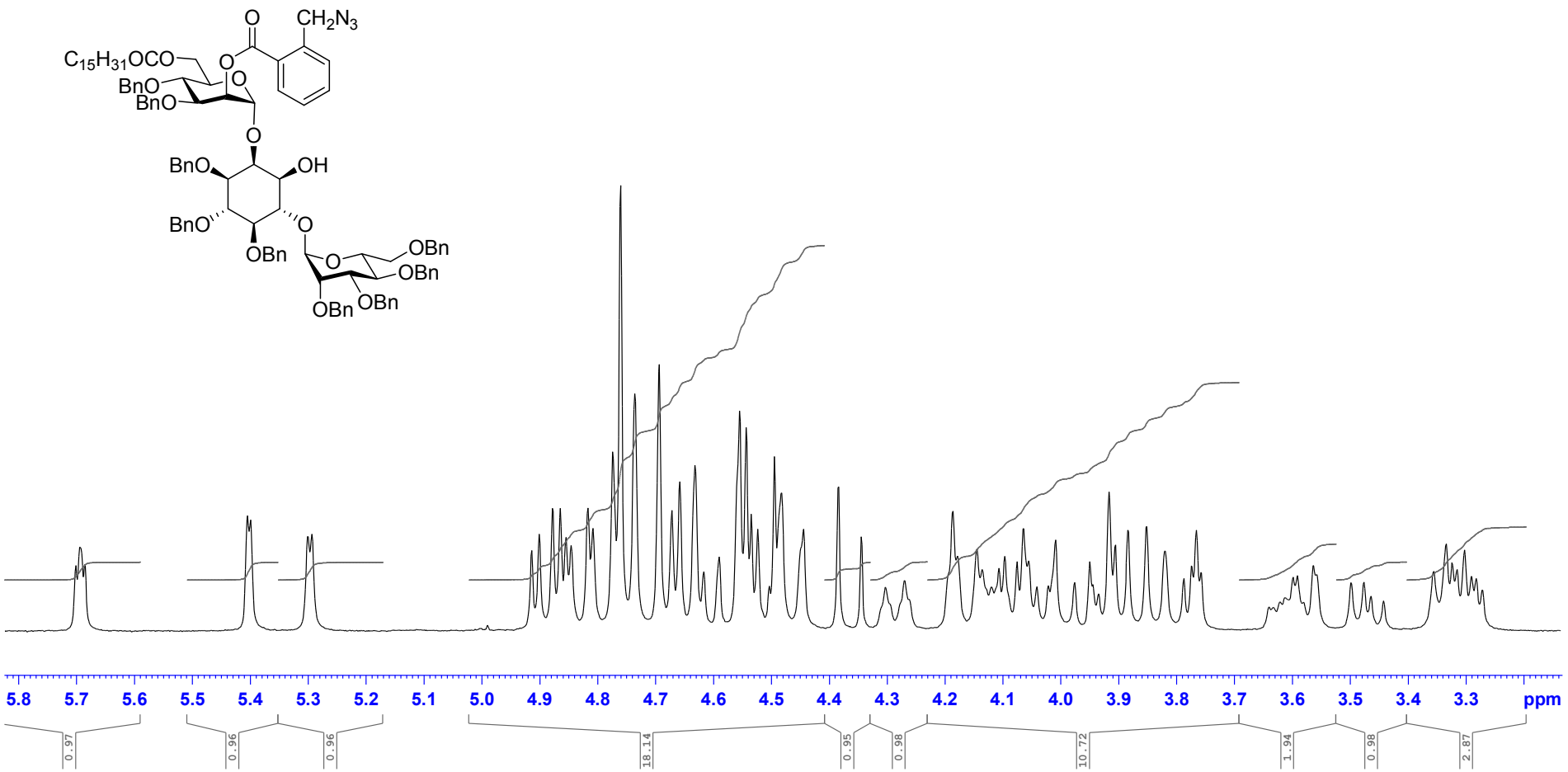
Compound **34** 300 MHz HSQC NMR without ^{13}C decoupling during acquisition



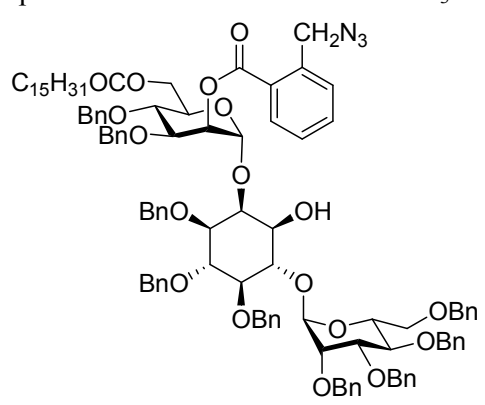
Compound **35** 300 MHz ^{1}H NMR $CDCl_3$



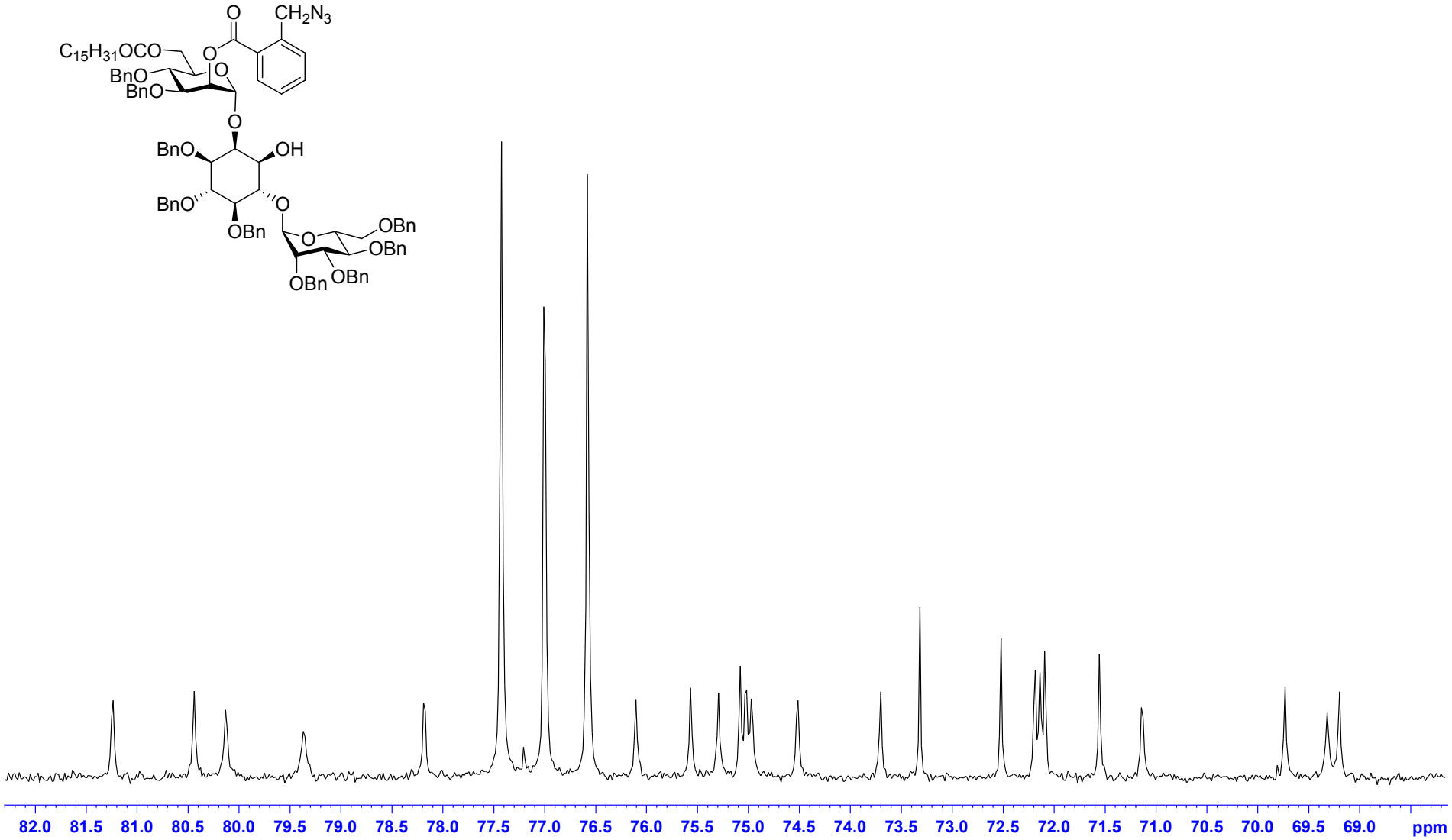
Compound **35** 300 MHz ^{1}H NMR $CDCl_3$



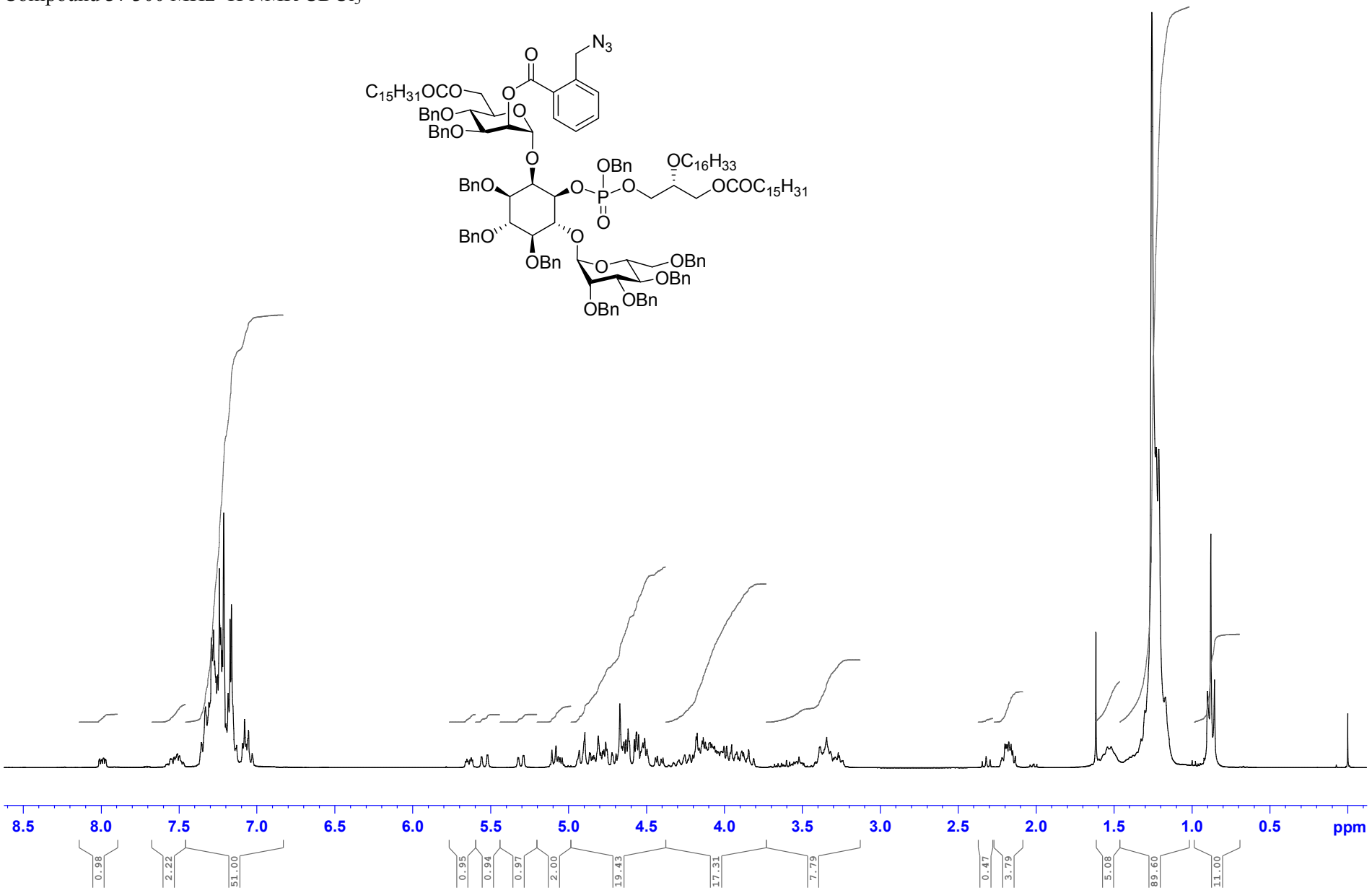
Compound **35** 75 MHz ^{13}C NMR $CDCl_3$



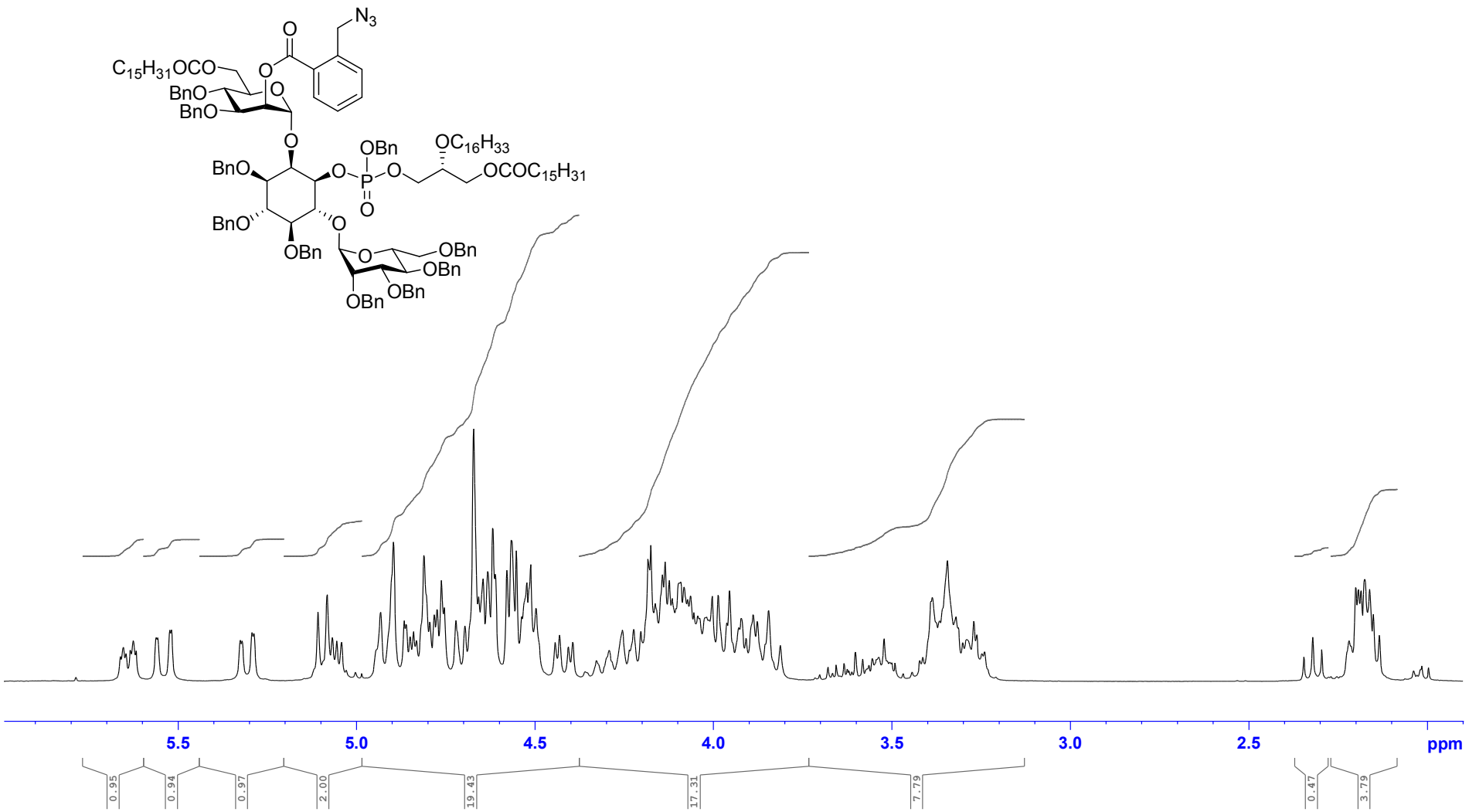
Compound **35** 5 MHz ^{13}C NMR $CDCl_3$



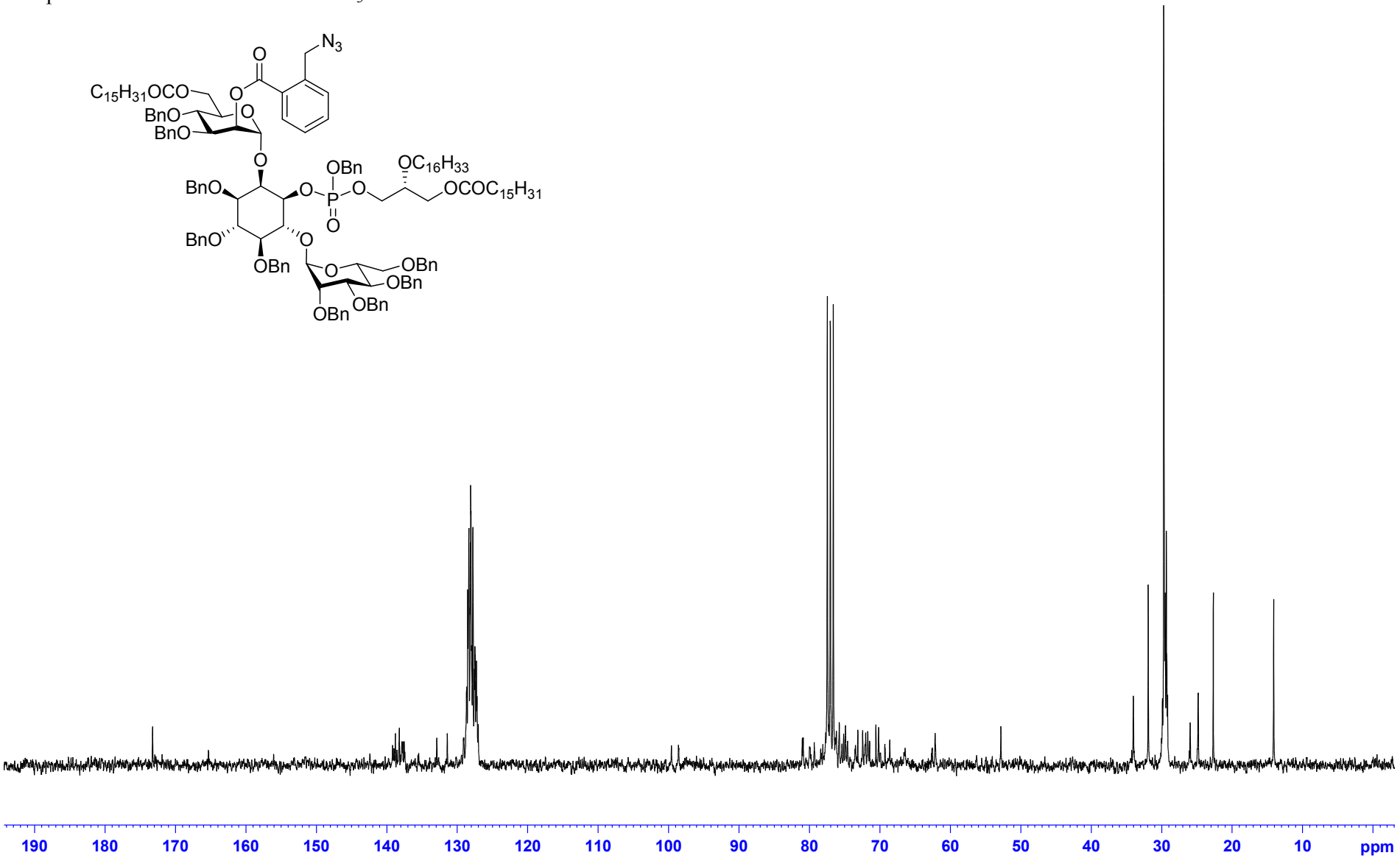
Compound **37** 300 MHz ^{1}H NMR $CDCl_3$



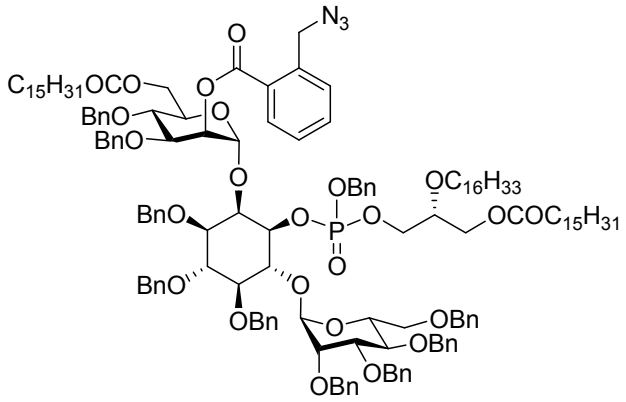
Compound **37** 300 MHz ^{1}H NMR $CDCl_3$



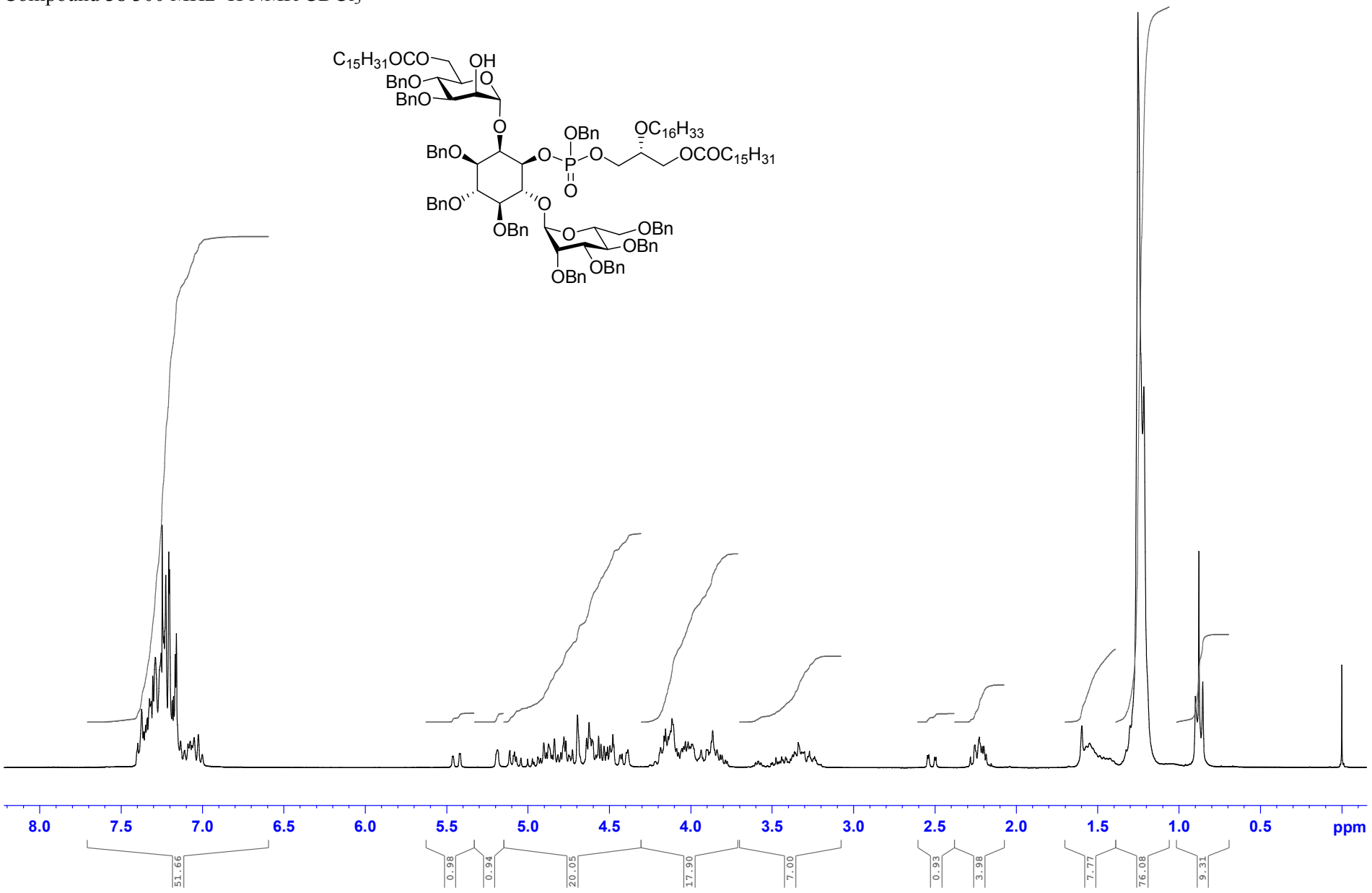
Compound **37** 75 MHz ^{13}C NMR $CDCl_3$



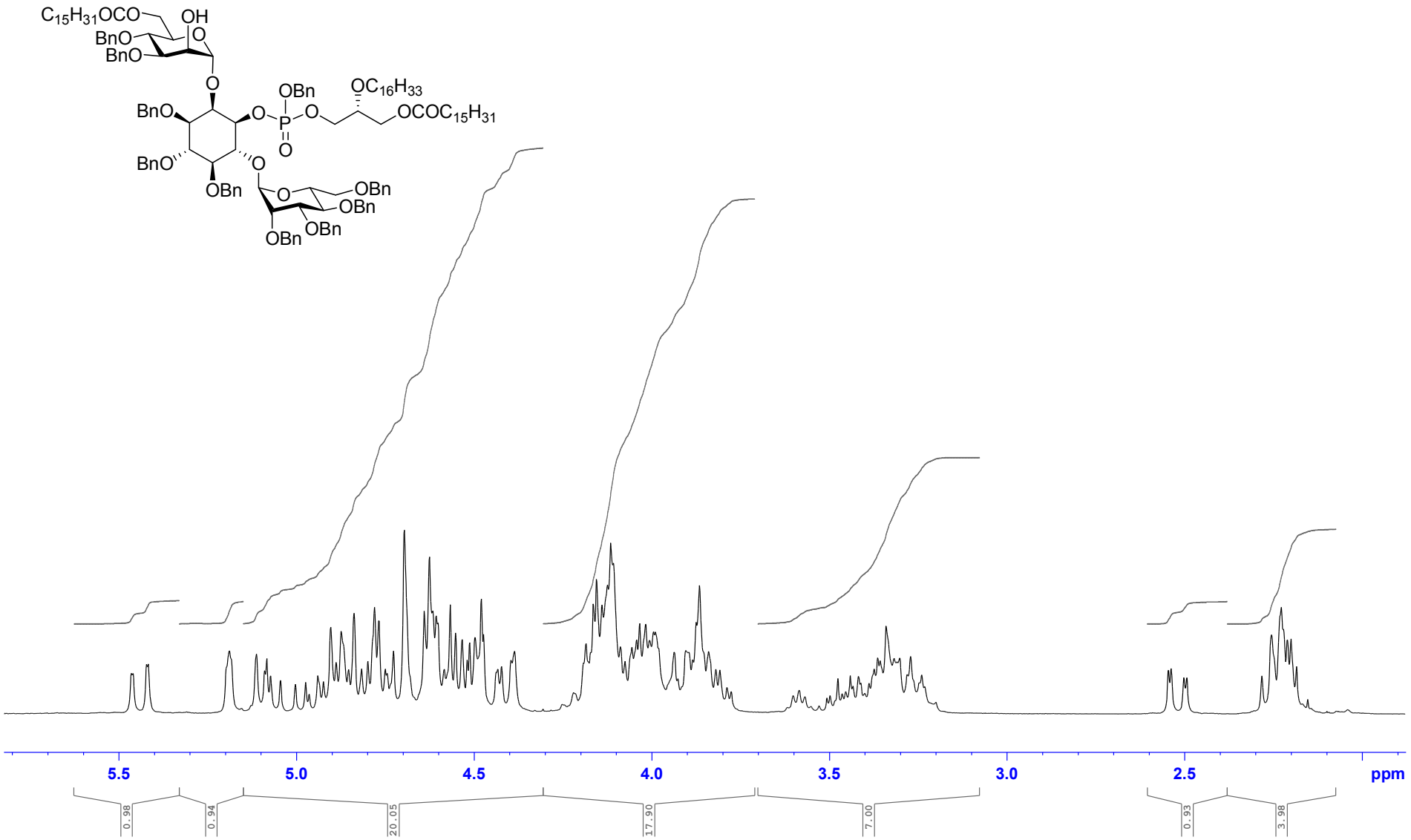
Compound **37** 121 MHz ^{31}P NMR $CDCl_3$



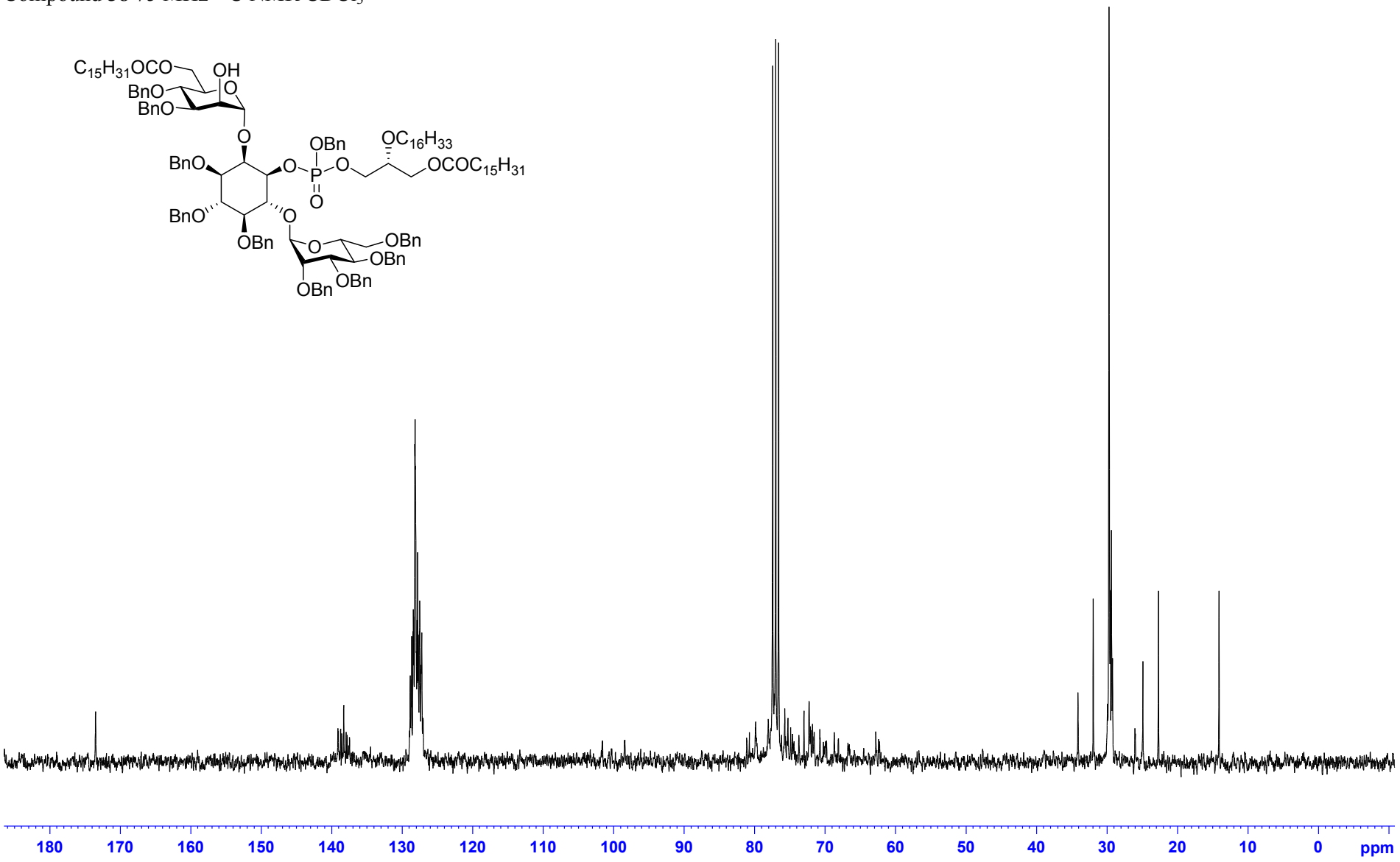
Compound **38** 300 MHz ^{1}H NMR $CDCl_3$



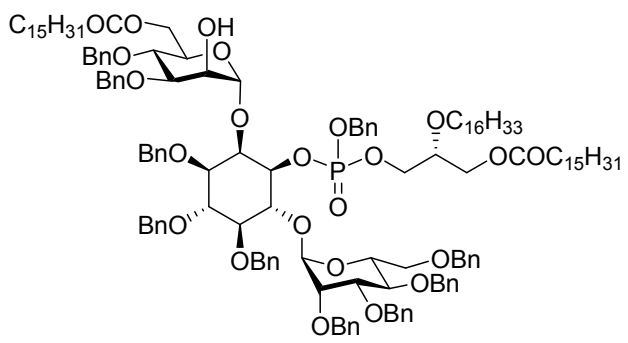
Compound **38** 300 MHz ^{1}H NMR $CDCl_3$



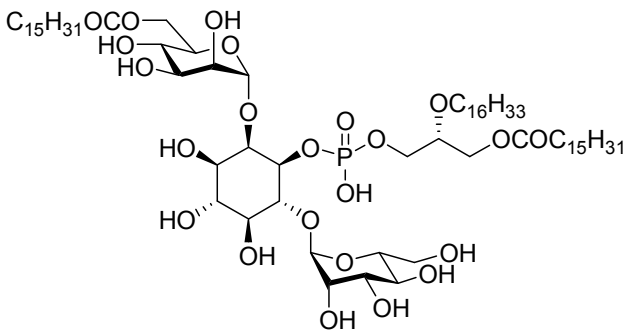
Compound **38** 75 MHz ^{13}C NMR $CDCl_3$



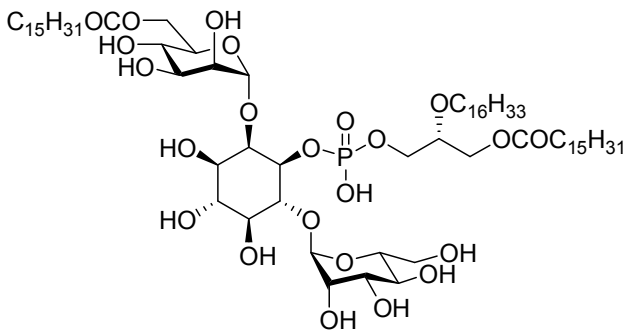
Compound **38** 121 MHz ^{31}P NMR $CDCl_3$



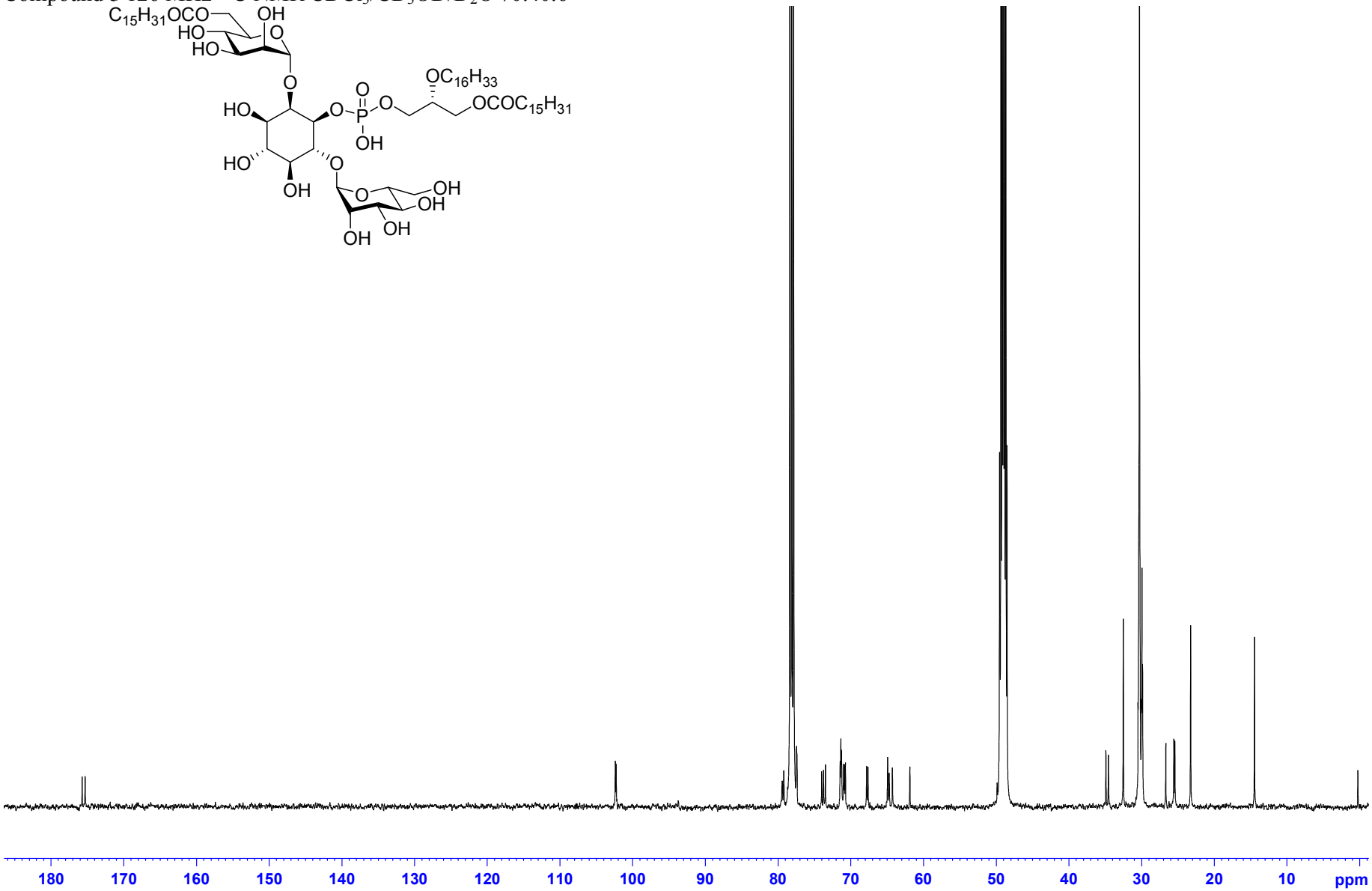
Compound **5** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



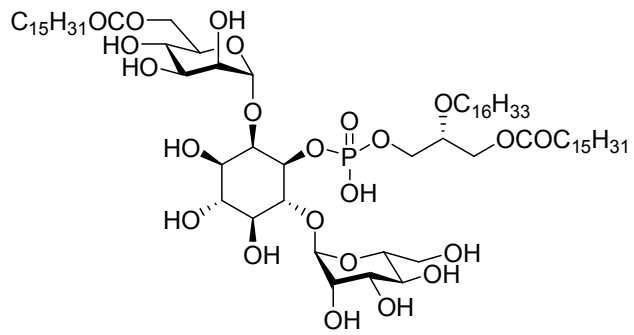
Compound **5** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6



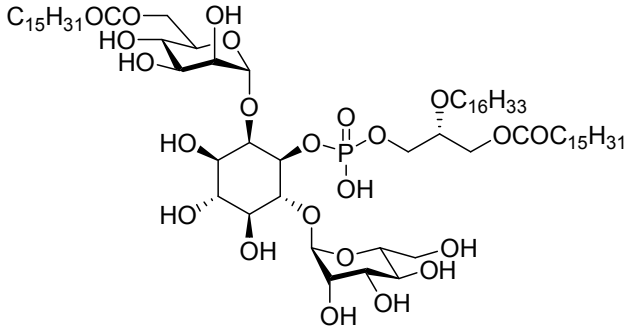
Compound **5** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6

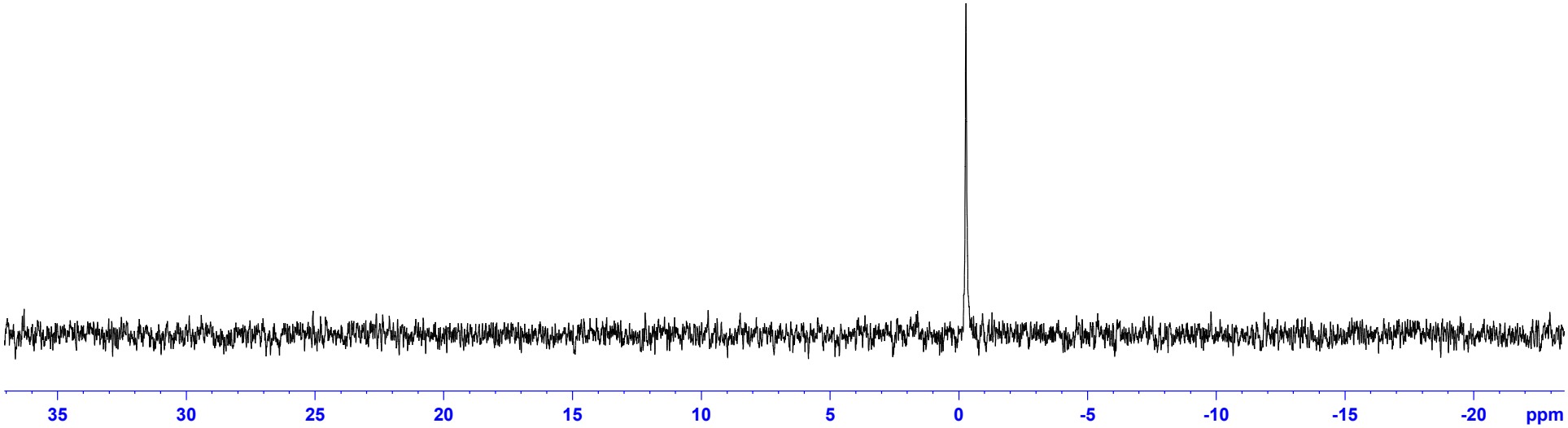


Compound **5** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6

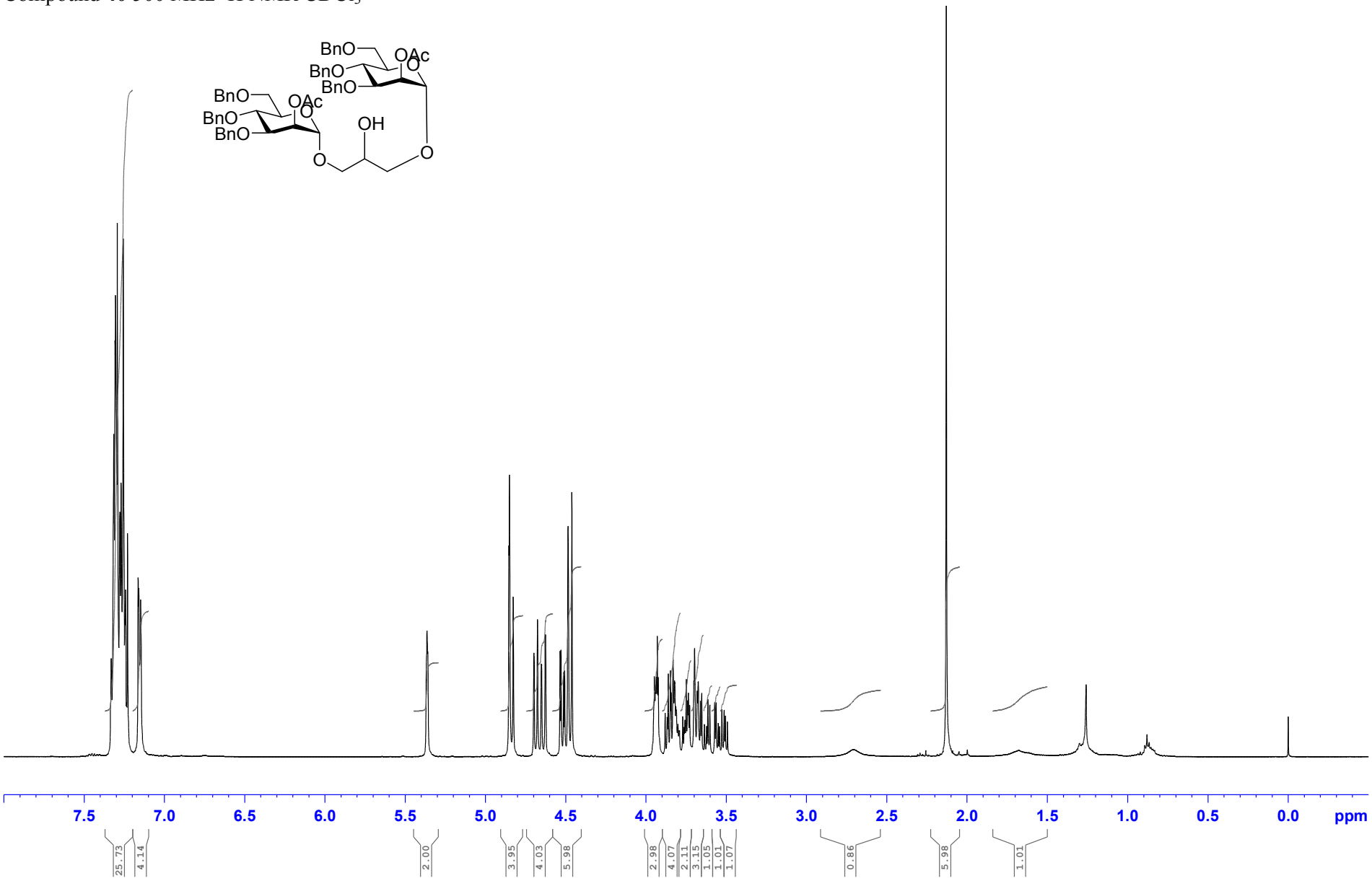


Compound **5** 202 MHz ^{31}P NMR $CDCl_3/CD_3OD/D_2O$ 70:40:6

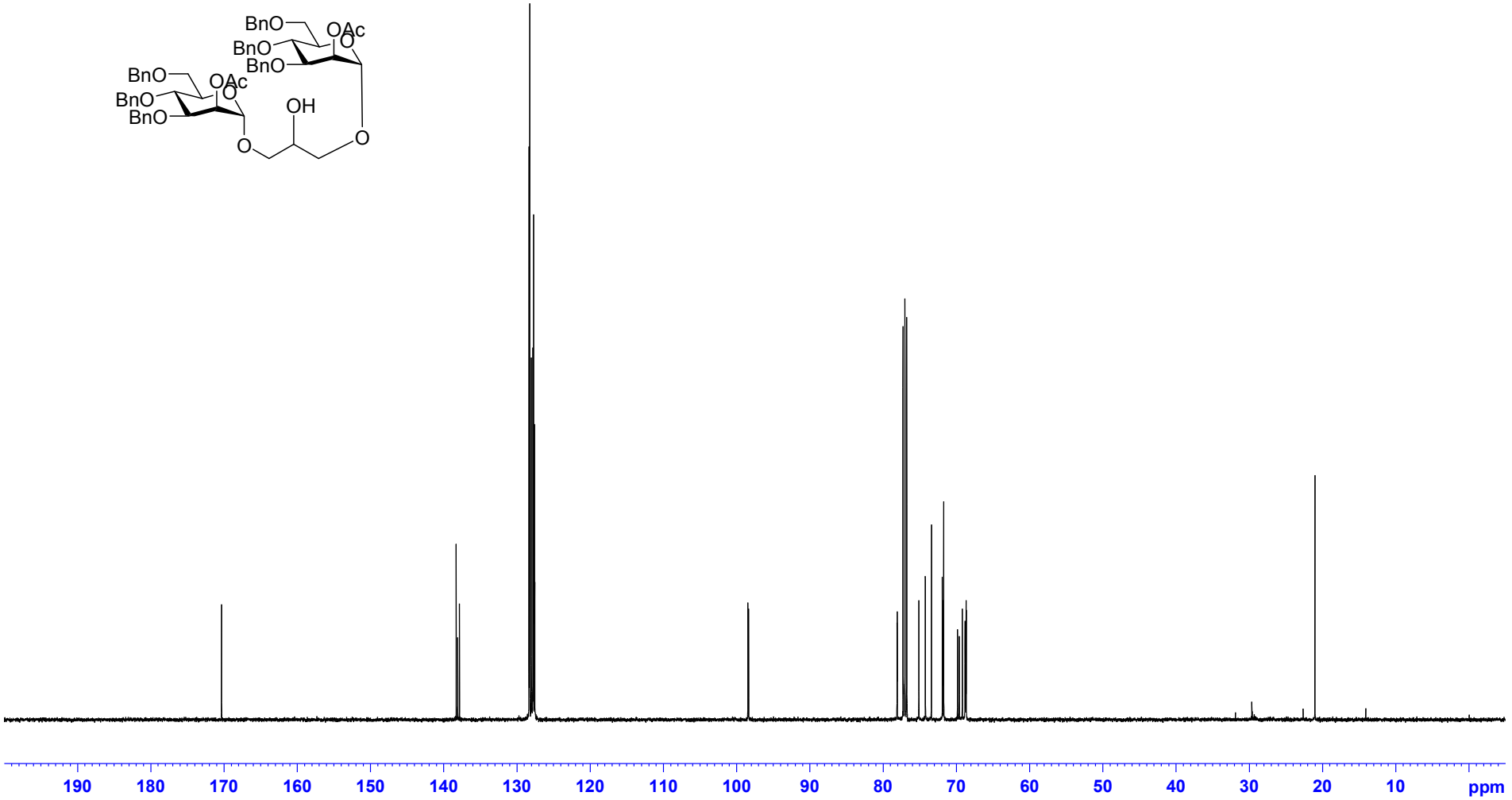




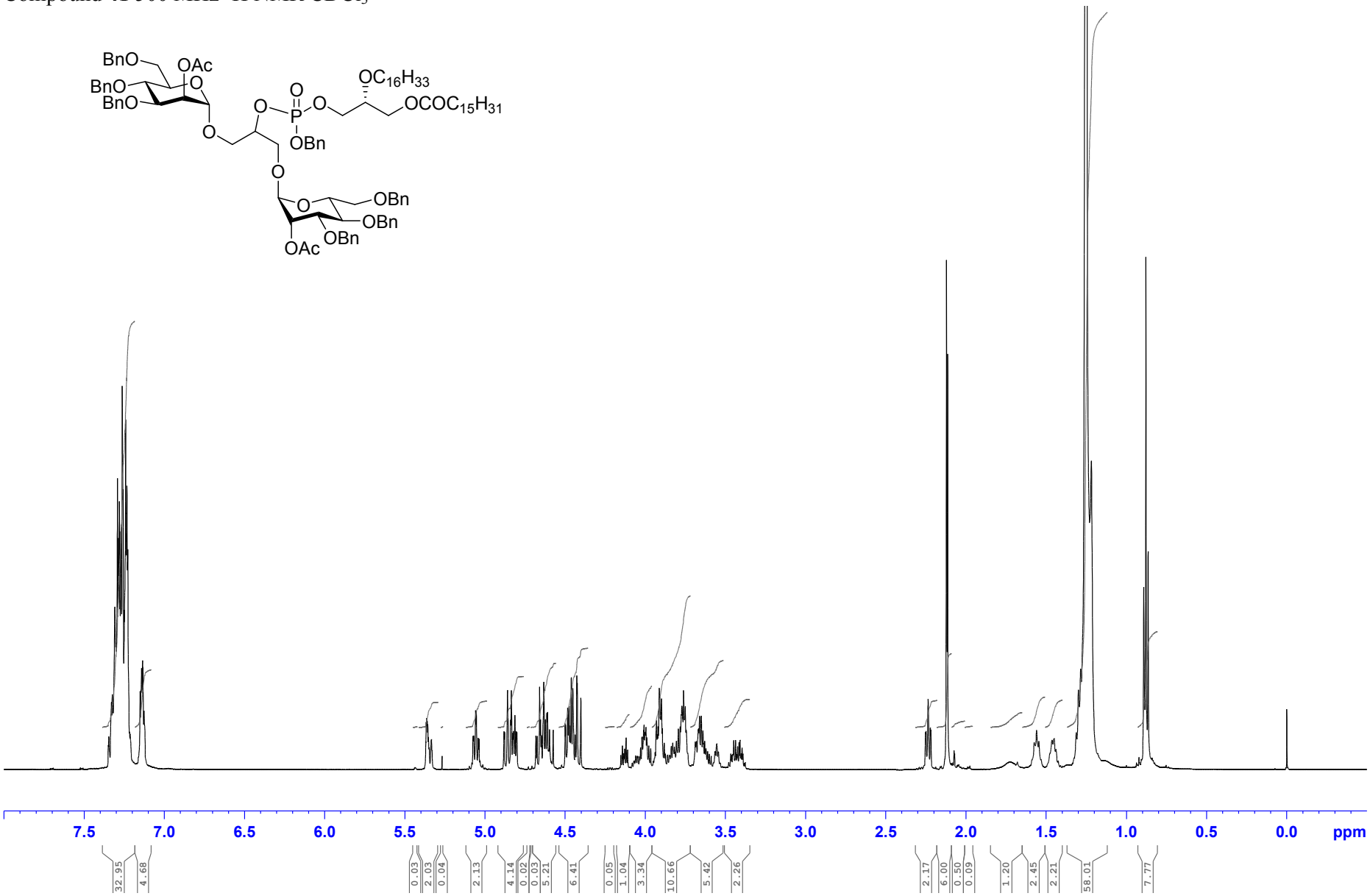
Compound **40** 500 MHz ^{1}H NMR $CDCl_3$



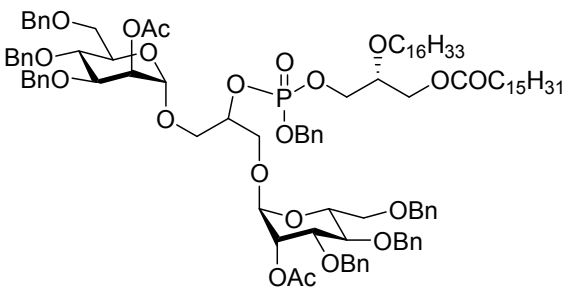
Compound **40** 125 MHz ^{13}C NMR $CDCl_3$



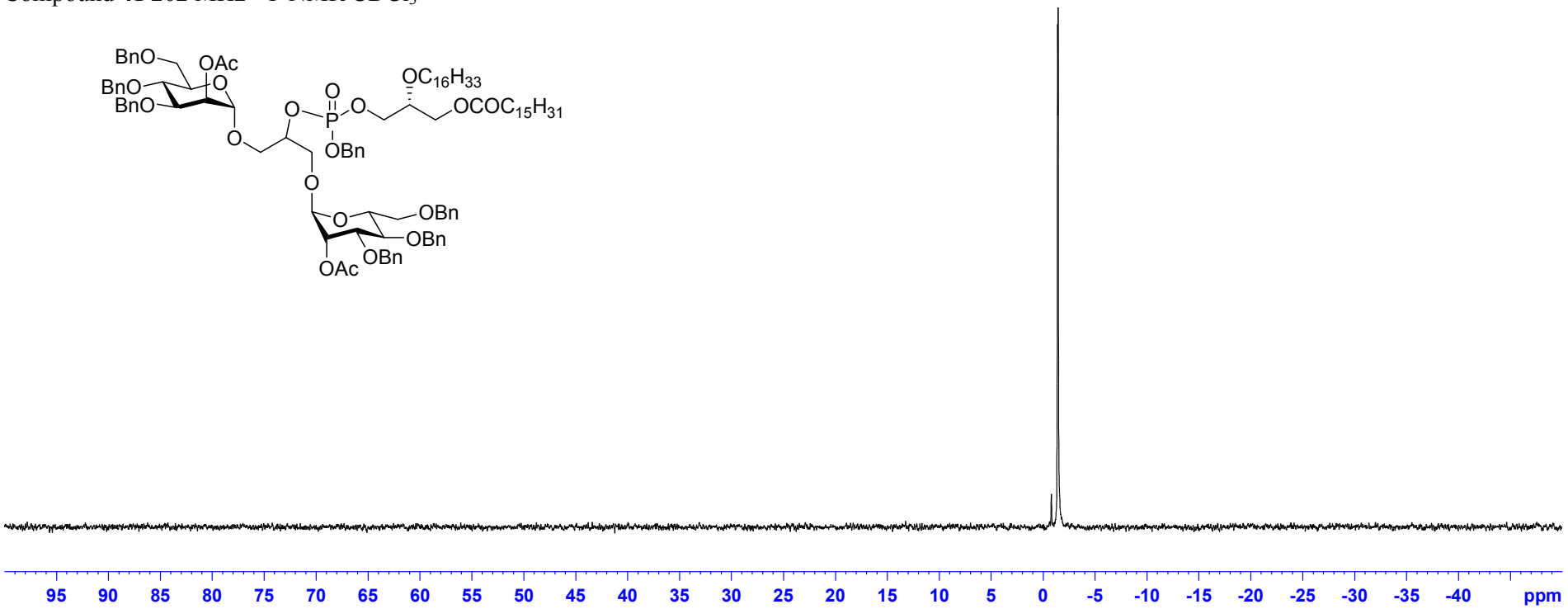
Compound **41** 500 MHz ^{1}H NMR $CDCl_3$



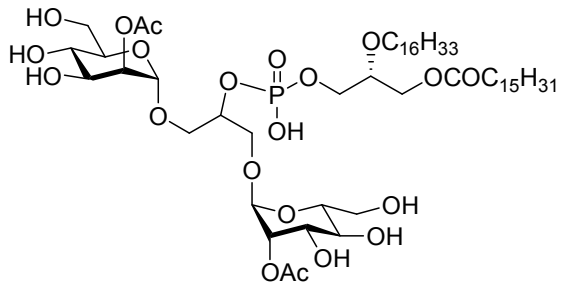
Compound **41** 125 MHz ^{13}C NMR $CDCl_3$



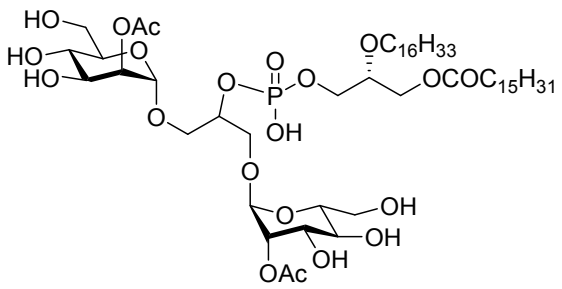
Compound **41** 202 MHz ^{31}P NMR $CDCl_3$



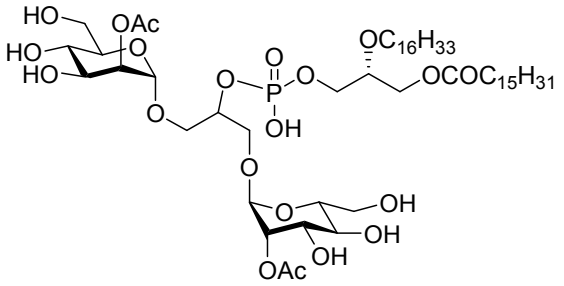
Compound **42** 500 MHz ^{1}H NMR 2:1 $CDCl_3/CD_3OD$

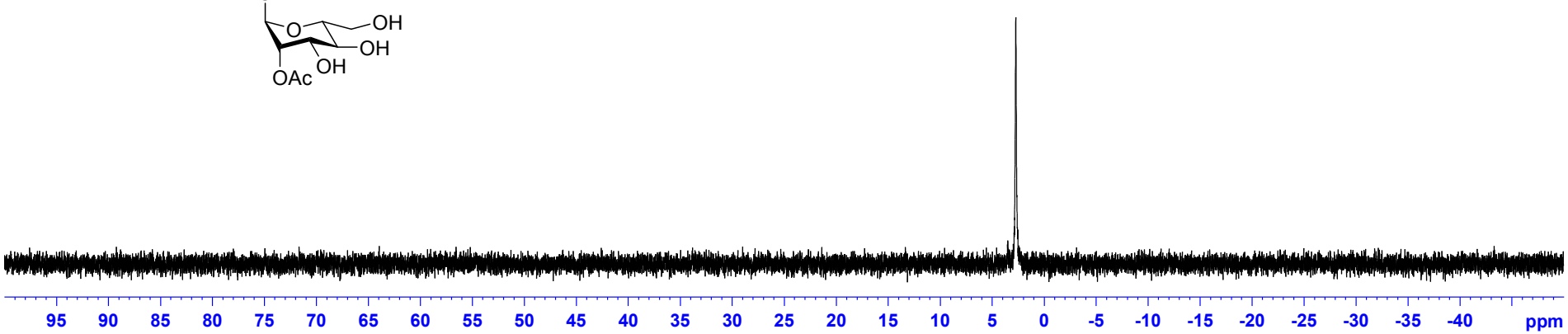


Compound **42** 125 MHz ^{13}C NMR 2:1 $CDCl_3/CD_3OD$

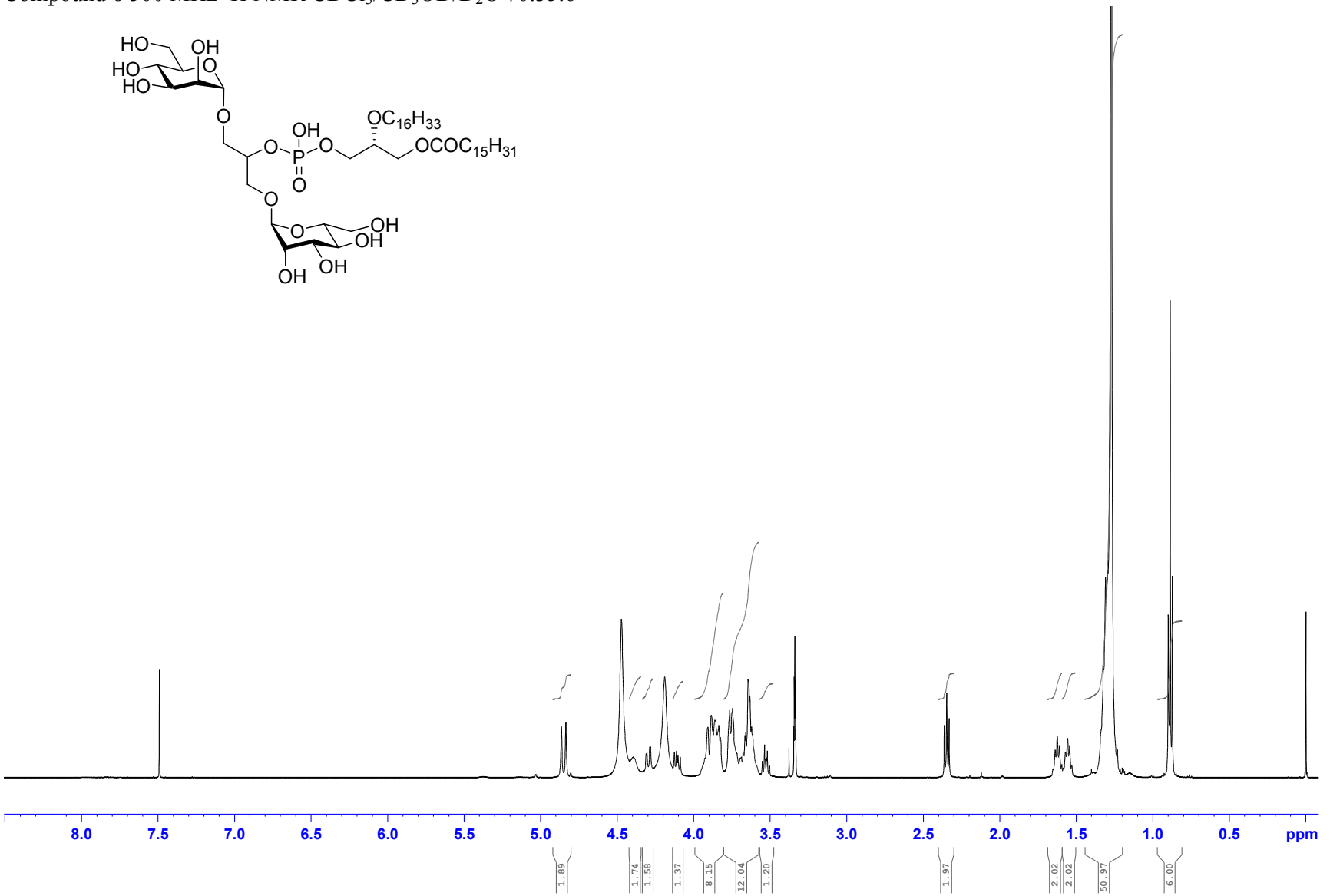


Compound **42** 202 MHz ^{31}P NMR 2:1 $CDCl_3/CD_3OD$

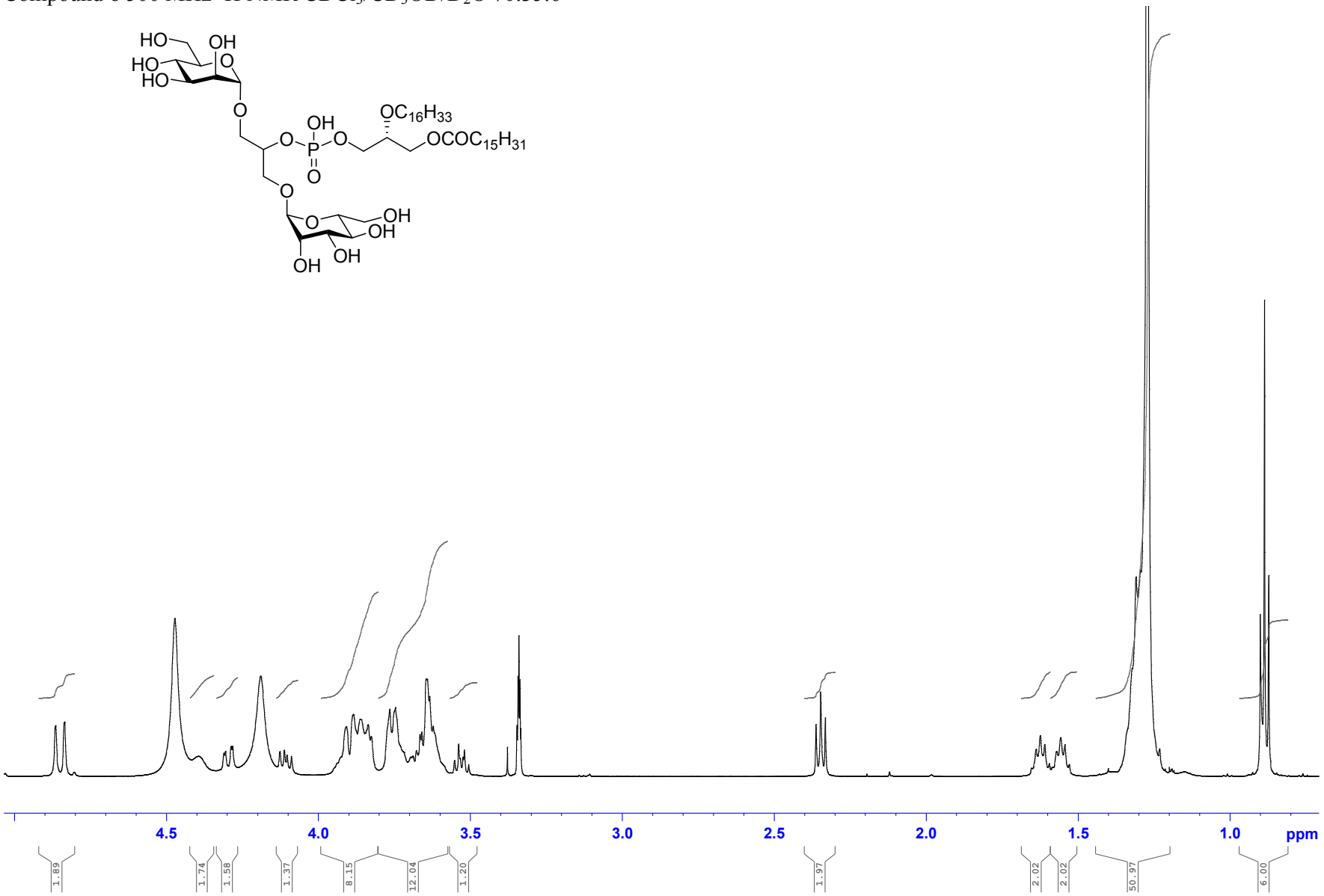




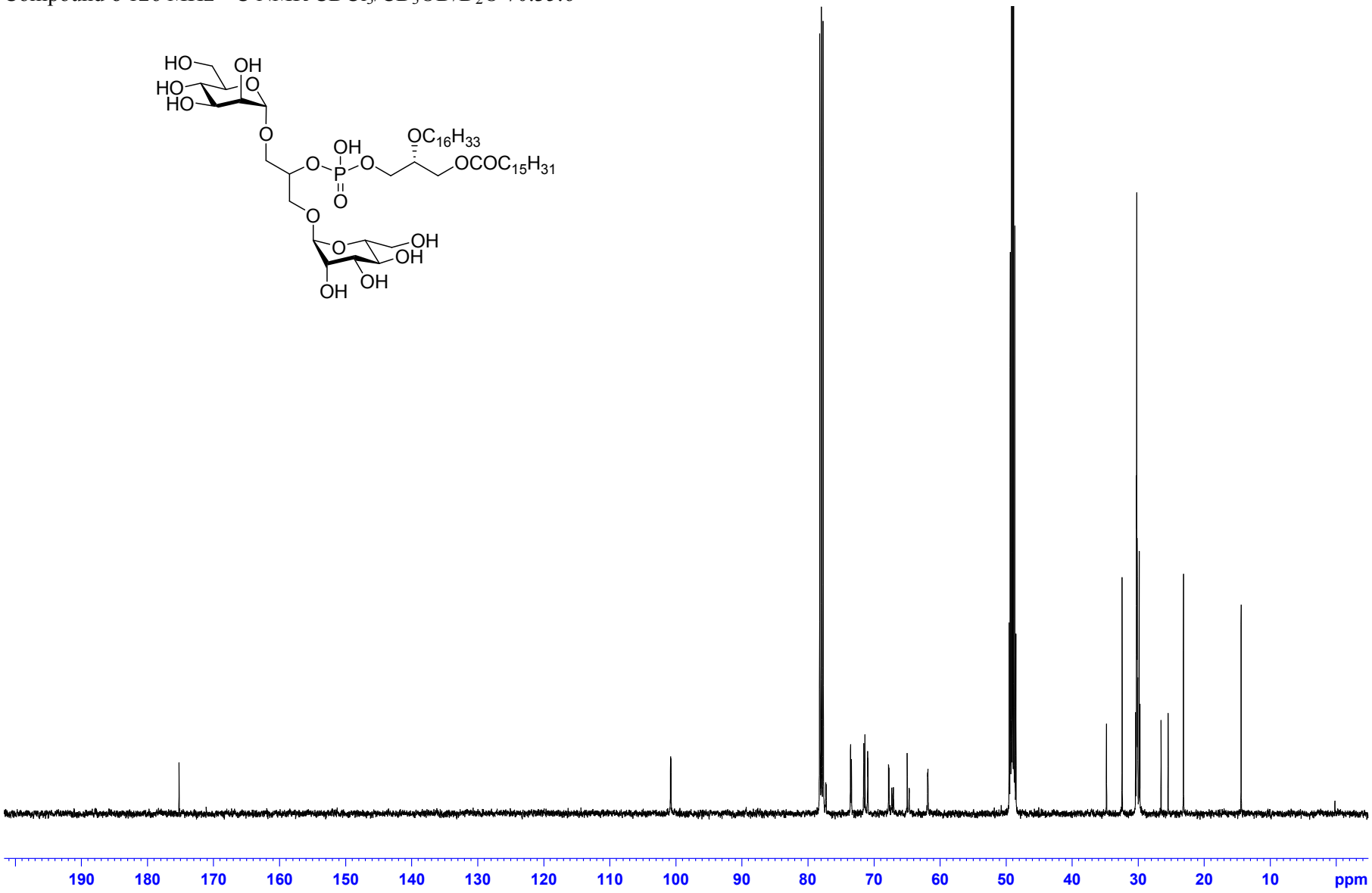
Compound **6** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:35:6



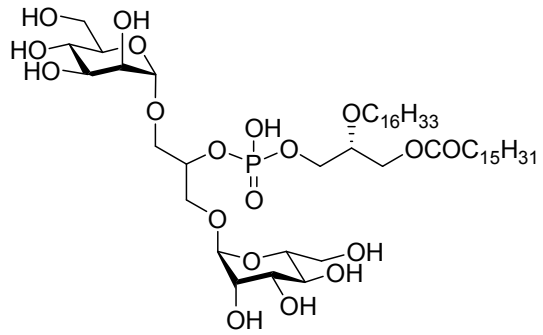
Compound **6** 500 MHz ^{1}H NMR $CDCl_3/CD_3OD/D_2O$ 70:35:6



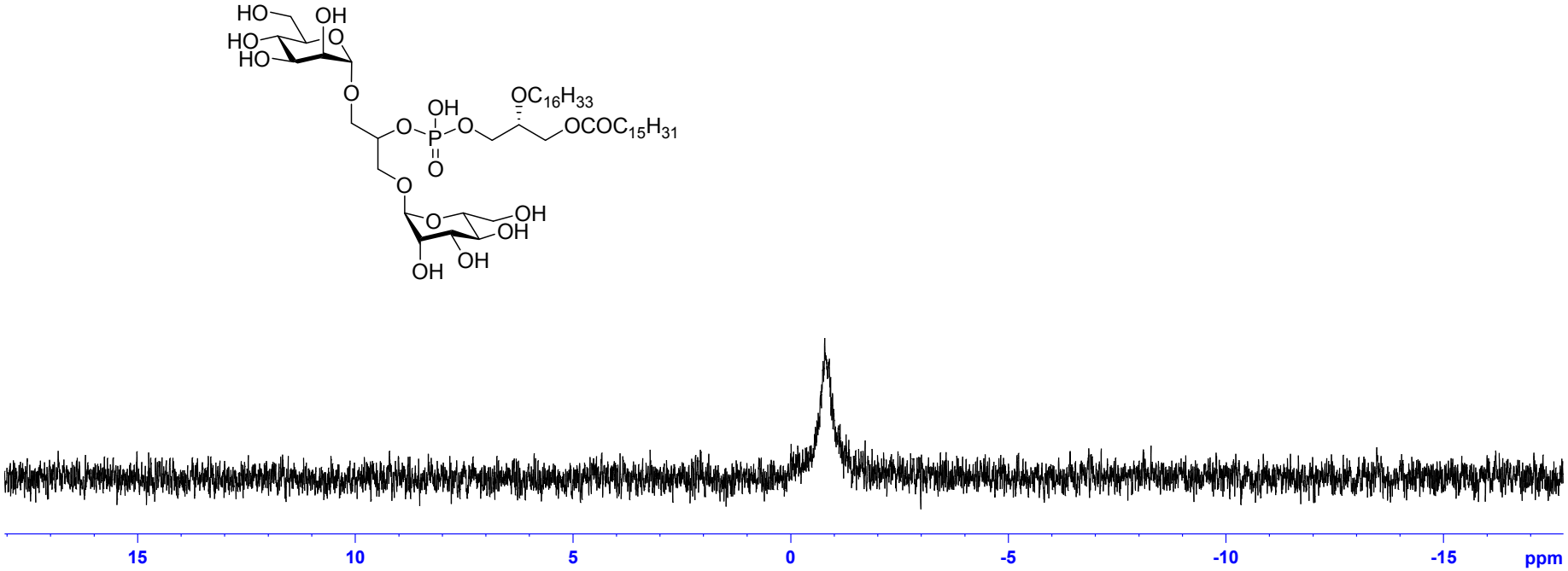
Compound **6** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:35:6



Compound **6** 126 MHz ^{13}C NMR $CDCl_3/CD_3OD/D_2O$ 70:35:6



Compound **6** 202 MHz ^{31}P NMR $CDCl_3/CD_3OD/D_2O$ 70:35:6

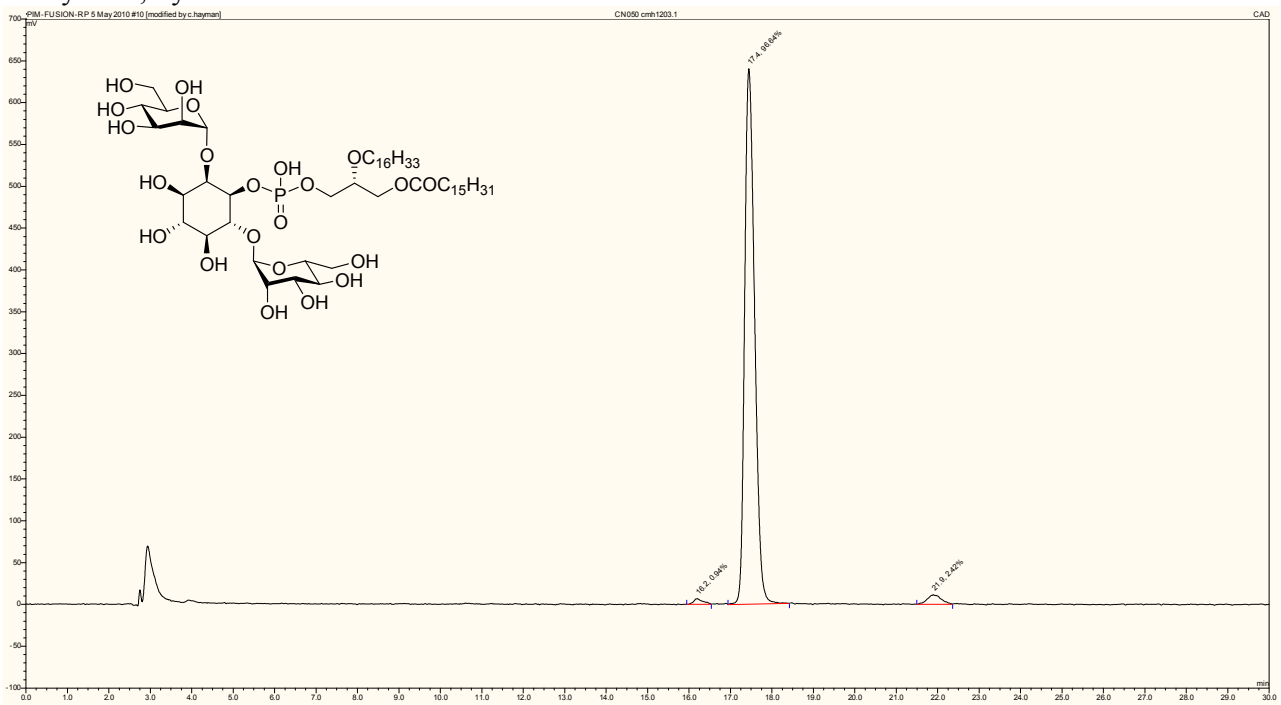


HPLC Conditions

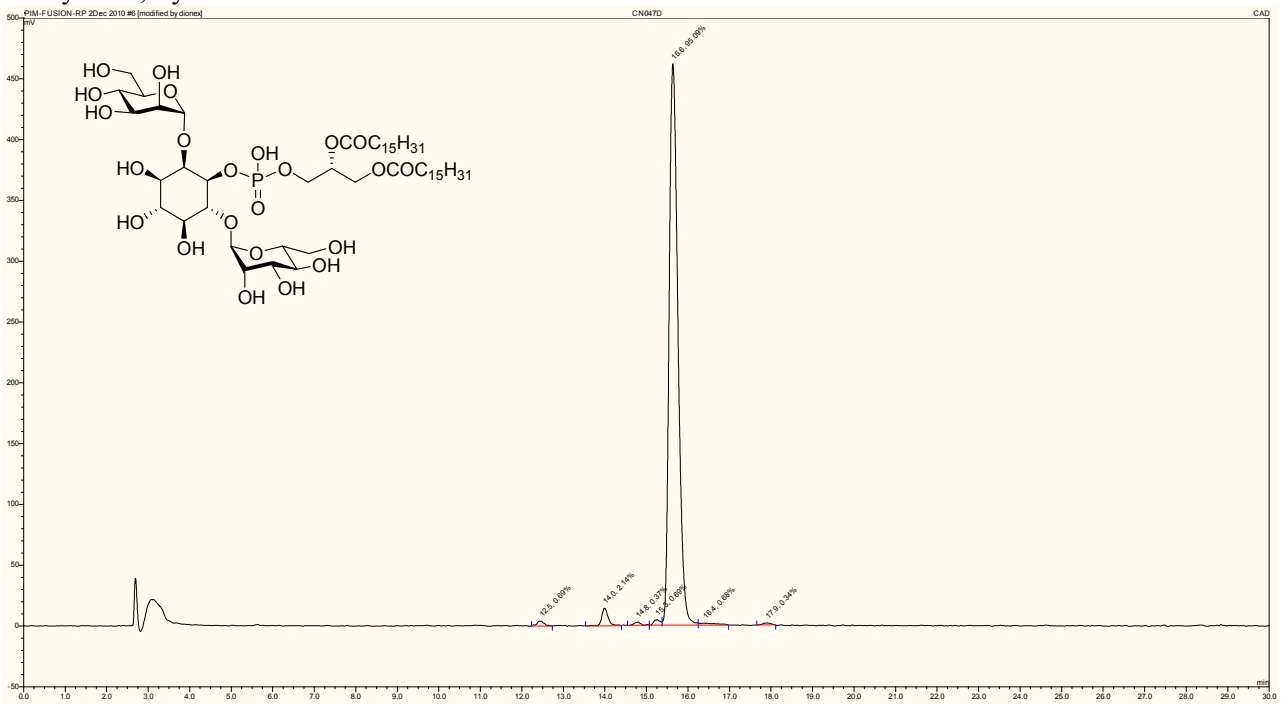
The HPLC analyses of **1-4** and **6-8** used System 1; HPLC: Column: Phenomenex Synergi 4 μm Fusion-RP (80 Å, 3.0 × 250 mm). Detection: ESA Corona charged aerosol detector (Filter = none). Flow rate; 1 mL/min. Column temperature; 40 °C. Solvents; A H_2O; B Water containing 50 mM NH_4OAc adjusted to pH 5.0; C Methanol. Gradient Program; 0–10 min 10–0% A, 10% B, 80–90%C, 10-28 min hold (0% A, 10% B, 90% C), 28-30 min return to starting conditions then equilibrate for 10 min prior to next injection. The HPLC analysis of **5** used System 2; Column, detector and column temperature were as for System 1. Flow rate 0.8 ml/Min. Solvents; A 1:1 water/MeOH + 50 mM NH_4OAc adjusted to pH 5.0 prior to dilution; B MeOH; C Isopropanol. Gradient Program; 0 min 10% A, 90% C; 15min 10%A, 65% B, 25% C; 15-35 min hold 10%A, 65% B, 25% C; 35-40 min return to starting conditions then equilibrate for 10 min prior to next injection. All chromatograms were corrected by subtraction of a blank injection prior to integrating signals after a four min cut-off. Integration values are not corrected for detector non-linearity

HPLC Data

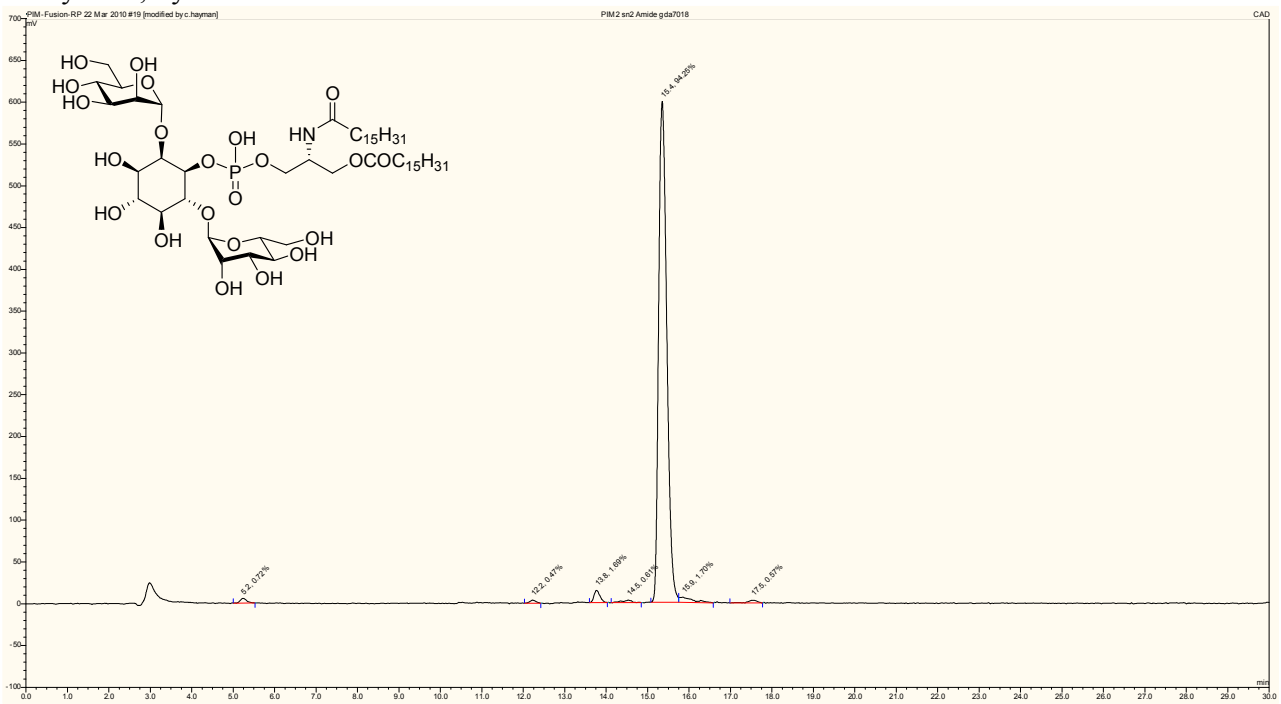
HPLC Compound **1**
Purity 97%; System 1



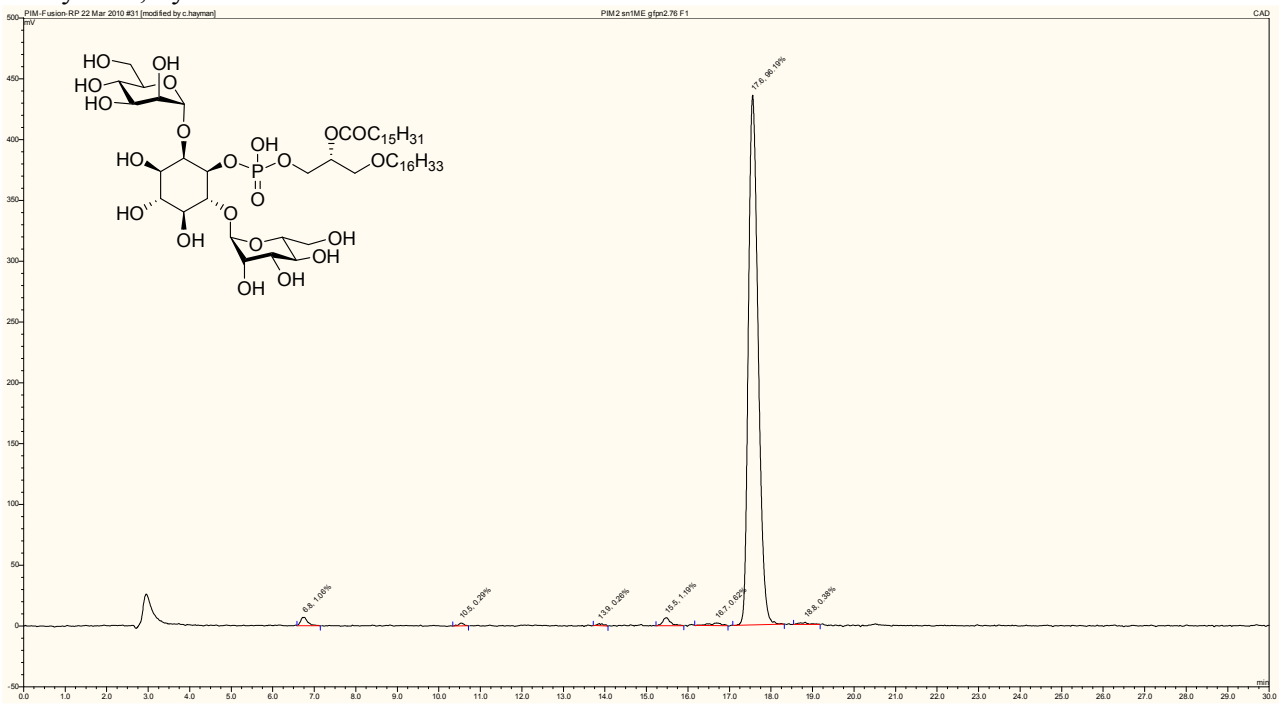
HPLC Compound **2**
Purity 95%; System 1



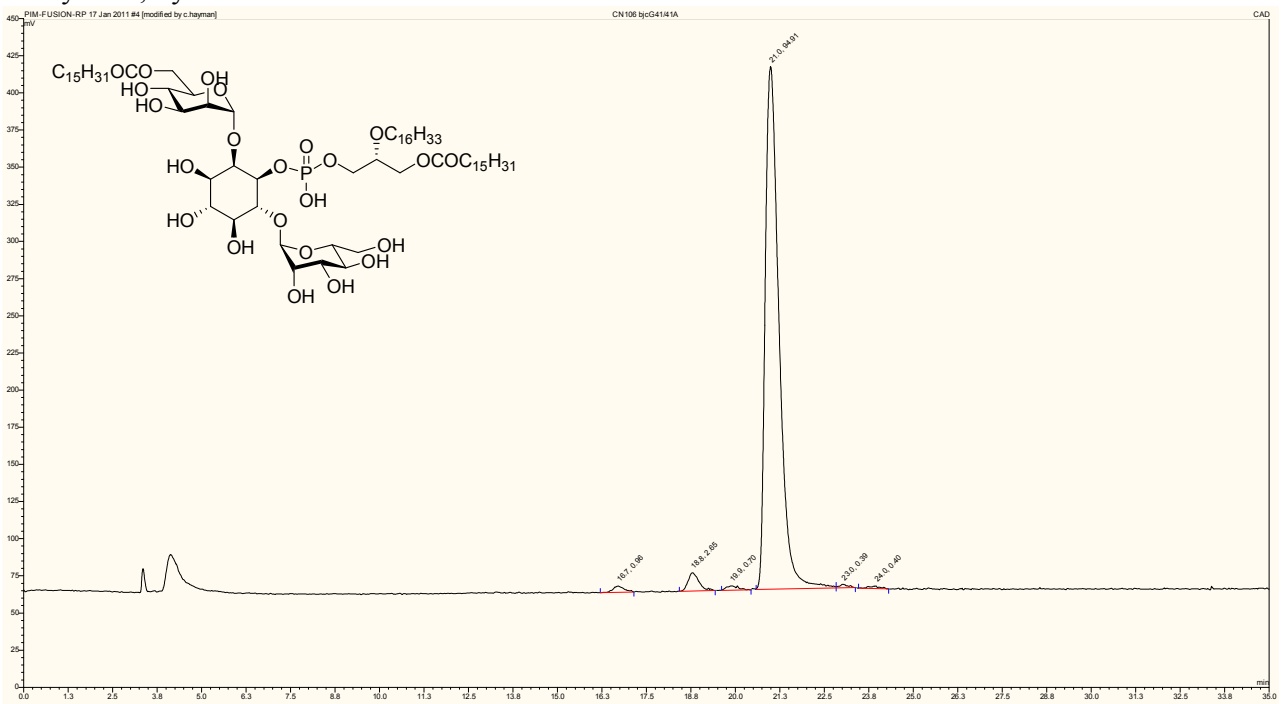
HPLC Compound **3**
Purity 94%; System 1



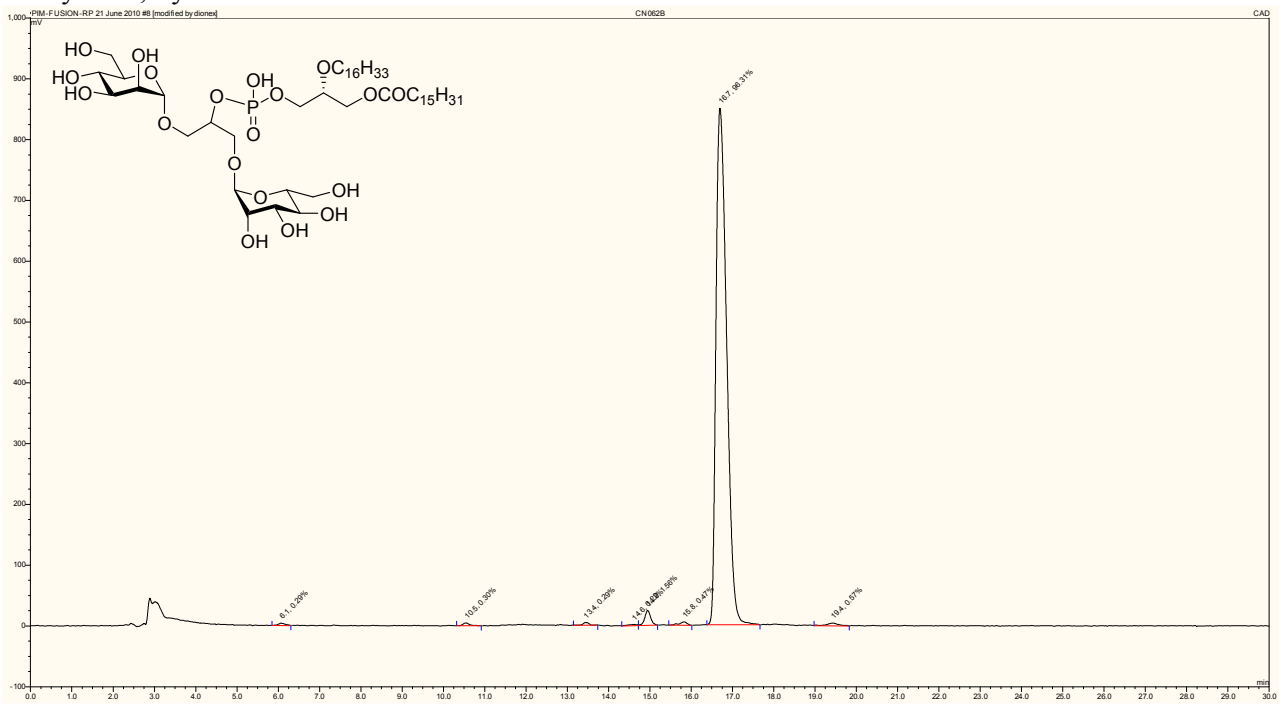
HPLC Compound **4**
Purity 96%; System 1



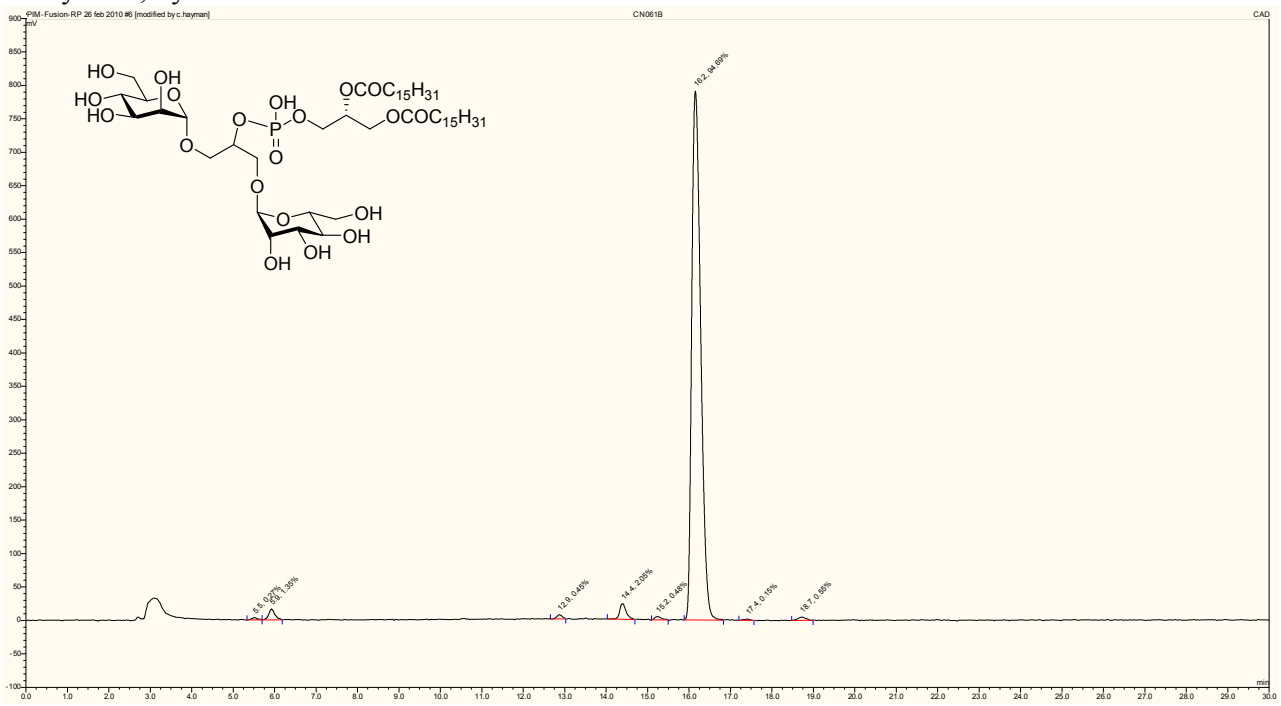
HPLC Compound **5**
Purity 95%; System 2



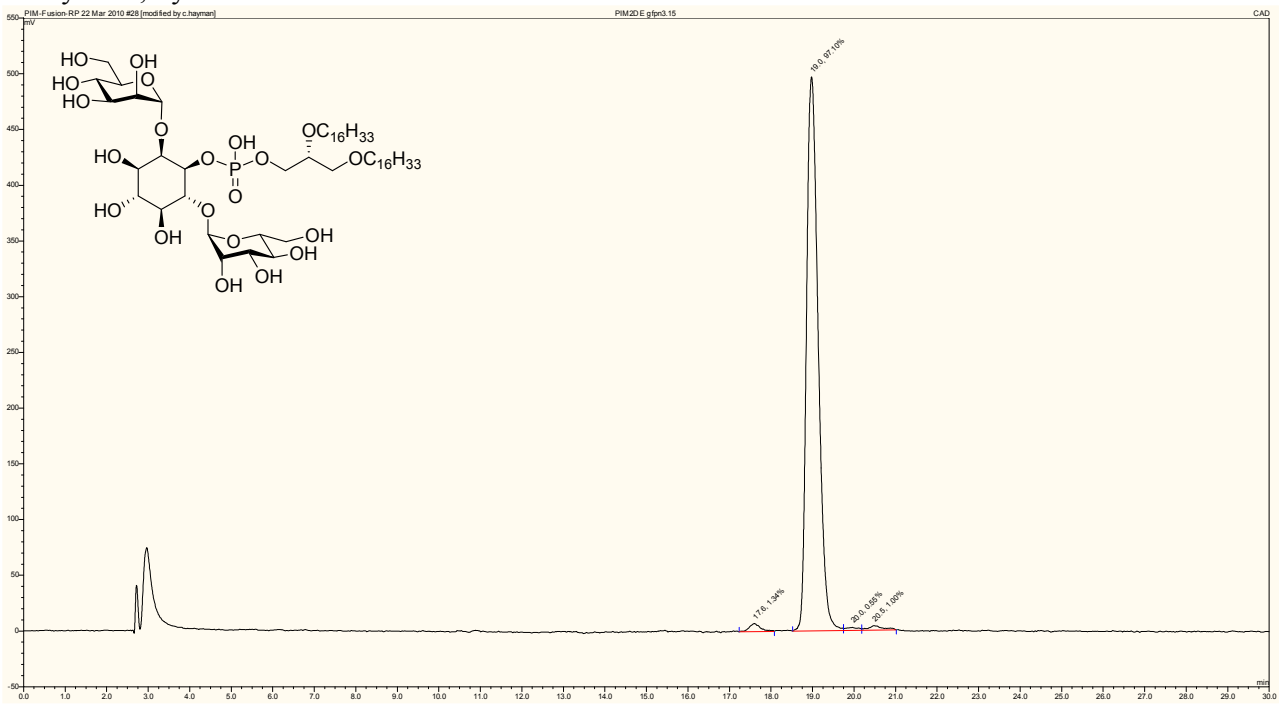
HPLC Compound **6**
Purity 96%; System 1



HPLC Compound **7**
Purity 95%; System 1



HPLC Compound **8**
Purity 97%; System 1



Cell, thioglycollate-induced peritoneal macrophages, viability data, compounds **1 - 8**