1,2-*Trans*-Selective Synthesis of Glycosyl Boranophosphates and Their Utility as Building Blocks for the Synthesis of Phosphodiester-linked Disaccharides

Kazuki Sato, Natsuhisa Oka, Shoichi Fujita, Fumiko Matsumura and Takeshi Wada*

Department of Medical Genome Sciences, Graduate School of Frontier Sciences, The University of Tokyo,
Bioscience Building 702, 5-1-5 Kashiwanoha, Kashiwa, Chiba 277-8562, Japan

wada@k.u-tokyo.ac.jp

Supporting Information

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General information

All the reactions were conducted under Ar atmosphere. Dry organic solvents were prepared by appropriate procedures. ^{1}H NMR spectra were recorded at 300 MHz with tetramethylsilane (δ 0.0) as an internal standard in $CDCl_3$. ^{13}C NMR spectra were recorded at 75.5 MHz with $CDCl_3$ (δ 77.0) as an internal standard in $CDCl_3$. ^{31}P NMR spectra were recorded at 121.5 MHz with H_3PO_4 (δ 0.0) as an external standard. COSY and HMQC were used to confirm the NMR peak assignments. Silica gel column chromatography was carried out using spherical, neutral, 63–210 or 40–50 μm silica gel unless otherwise noted. Analytical TLC was performed on commercial glass plates bearing 0.25 mm layer of silica gel.

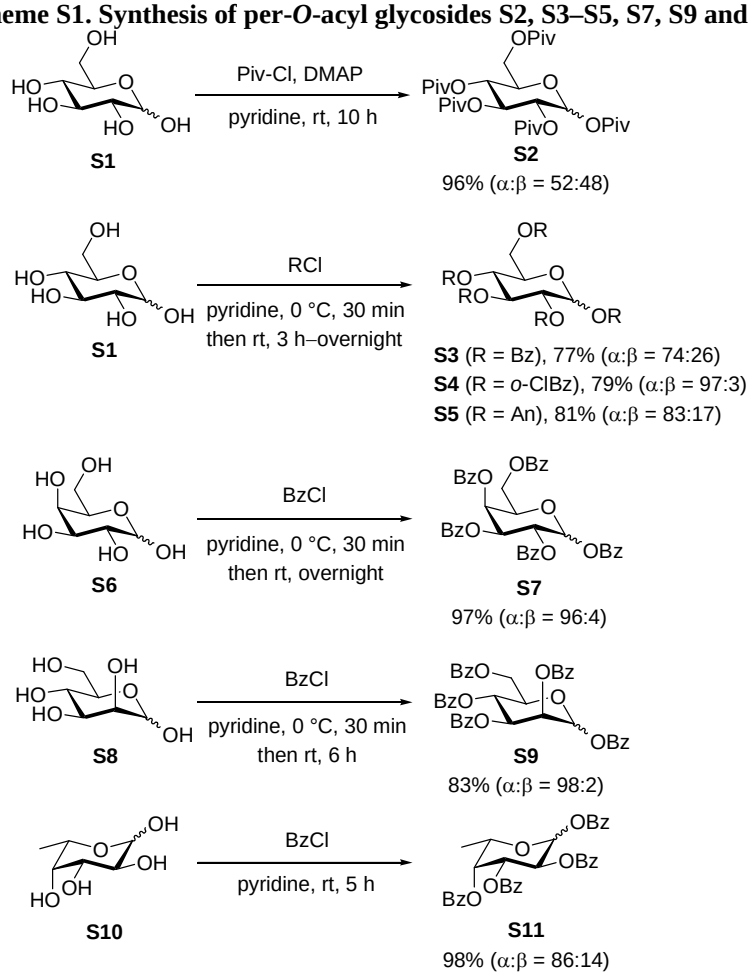
Experimental procedures

1. Preparation of per-*O*-acyl glycosides

1,2,3,4,6-Penta-*O*-pivaloyl-D-glucopyranoside (S2).

Pivaloyl chloride (12.0 mL, 99 mmol) and catalytic amount of DMAP were added to a solution of D-glucose (**S1**, 1.80 g, 10 mmol) in dry pyridine (40 mL) at rt while stirring. After 10 h, the solvent was evaporated under reduced pressure, and the residue was diluted with CH_2Cl_2 (120 mL). The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 100 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was recrystallized from methanol and purified by silica gel column chromatography using AcOEt–hexane (1:4, v/v) as an eluent to give **S2** as a colorless foam (5.73 g, 0.95 mmol, α:β = 52:48, 96%). The ^{1}H NMR spectrum was identical to the reported data.[1]

Scheme S1. Synthesis of per-*O*-acyl glycosides S2, S3–S5, S7, S9 and S11



1,2,3,4,6-Penta-*O*-benzoyl-D-glucopyranoside (S3).

Benzoyl chloride (13.9 mL, 120 mmol) was added dropwise to a solution of D-glucose (**S1**, 3.60 g, 20 mmol) in dry pyridine (24 mL) at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt and stirred for 3 h. The reaction was quenched by adding a saturated $NaHCO_3$ aqueous solution (100 mL) and methanol (10 mL), and CH_2Cl_2 (100 mL) was added to the mixture. The organic layer was separated, and washed with saturated $NaHCO_3$ aqueous solutions (3 × 150 mL). The aqueous layers were combined and back-extracted with CH_2Cl_2 (150 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was recrystallized from ethanol (75 mL) to give **S3** as a colorless solid (10.8 g, 15 mmol, α:β = 74:26, 77%). The ^{1}H NMR spectrum was identical to the reported data.[2]

1,2,3,4,6-Penta-*O*-(2-chlorobenzoyl)-D-glucopyranoside (S4).

2-Chlorobenzoyl chloride (1.52 mL, 12 mmol) was added dropwise to a solution of D-glucose (**S1**, 0.362 g, 2.0 mmol) in dry pyridine (10 mL) at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt. After being stirred for 4.5 h at rt, the reaction was quenched with methanol (1 mL), and the mixture was diluted with $CHCl_3$ (10 mL). The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 15 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (30 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was recrystallized from ethanol (50 mL) to give **S4** as a colorless solid (1.39 g, 1.6 mmol, α:β = 97:3, 79%). IR (KBr, cm^{-1}) 3071, 3033, 1750, 1592, 1571, 1474, 1437, 1253, 1107, 1020, 919, 858, 789, 744, 688, 650, 604, 515, 476. ^{1}H NMR ($CDCl_3$) δ 7.99–7.19 (m, 20H, Ar), 6.90 (d, *J* = 3.3 Hz, 1H, H-1), 6.29 (t, *J* = 9.9 Hz, 1H, H-3), 5.84 (t, *J* = 9.8 Hz, 1H, H-4), 5.68 (dd, *J* = 3.3, 10.2 Hz, 1H, H-2), 4.70–4.56 (m, 3H, H-5,6). ^{13}C NMR ($CDCl_3$) δ 165.0, 164.4, 164.2, 164.1, 163.6, 134.4, 134.1, 133.9, 133.8, 133.5, 133.3, 133.1, 132.8, 132.1, 131.8, 131.6, 131.5, 131.4, 131.2, 131.1, 131.0, 129.3, 128.7, 128.6, 128.0, 126.9,

126.8, 126.7 (C=O, Ar), 90.2 (C-1), 70.5, 70.4 (C-2,3,5), 68.8 (C-4), 62.7 (C-6). HRMS (ESI): calcd for $C_{41}H_{27}Cl_5O_{11}Na$ $[M+Na]^+$: 892.9894; found: 892.9906.

1,2,3,4,6-Penta-*O*-(4-methoxybenzoyl)-D-glucopyranoside (S5).

4-Methoxybenzoyl chloride (5.13 g, 30 mmol) was added dropwise to a solution of D-glucose (**S1**, 0.903 g, 5.0 mmol) in dry pyridine (25 mL) at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt and stirred overnight. The reaction was quenched with ethanol (3 mL) and the mixture was diluted with $CHCl_3$ (30 mL). The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (30 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was recrystallized from ethanol (80 mL) and further purified by silica gel column chromatography using AcOEt–hexane (1:1–3:2, v/v) as an eluent to give **S5** as a colorless foam (3.47 g, 4.1 mmol, α:β = 83:17, 81%). IR (KBr, cm^{-1}) 3007, 2961, 2840, 1729, 1606, 1512, 1460, 1421, 1318, 1262, 1169, 1096, 922, 846, 767, 695, 614, 509. ^{1}H NMR ($CDCl_3$) δ 8.19–7.80 (m, 10H, Ar), 7.04–6.72 (m, 11H, Ar, H-1), 6.24 (t, *J* = 10.1 Hz, 1H, H-3), 5.78 (t, *J* = 10.1 Hz, 1H, H-4), 5.61 (dd, *J* = 3.6, 10.2 Hz, 1H, H-2), 4.62–4.51 (m, 2H, H-5,6), 4.41 (dd, *J* = 4.4, 12.2 Hz, 1H, H-6), 3.91, 3.86, 3.81, 3.78, 3.78 (s, 5 × 3H, Ar-OC$\underline{H}_3$). ^{13}C NMR ($CDCl_3$) δ 165.8, 165.5, 165.0, 164.8, 164.1, 164.0, 163.7, 163.5, 163.4, 132.2, 132.0, 131.9, 131.8, 122.0, 121.3, 121.1, 121.0, 114.0, 113.6 (C=O, Ar), 89.9 (C-1), 70.4, 70.2, 70.1 (C-2,3,5), 68.6 (C-4), 62.4 (C-6), 55.5, 55.4 (Ar-O$\underline{C}H_3$). HRMS (ESI): calcd for $C_{46}H_{42}O_{16}Na$ $[M+Na]^+$: 873.2371; found: 873.2331.

1,2,3,4,6-Penta-*O*-benzoyl-D-galactopyranoside (S7).

Benzoyl chloride (3.5 mL, 30 mmol) was added dropwise to a solution of D-galactose (**S6**, 0.90 g, 5.0 mmol) in dry pyridine (25 mL) at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt and stirred overnight. Then, the reaction was quenched with methanol (3 mL), and $CHCl_3$ (18 mL) was added. The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 20 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (30 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt–hexane (1:3, v/v) as an eluent to give **S7** as a colorless foam (3.39 g, 4.8 mmol, α:β = 96:4, 97%). The ^{1}H NMR spectrum was identical to the reported data.[2]

1,2,3,4,6-Penta-*O*-benzoyl-D-mannopyranoside (S9).

Benzoyl chloride (6.3 mL, 54 mmol) was added dropwise to a solution of D-mannose (**S8**, 1.61 g, 8.9 mmol) in dry pyridine (30 mL) at 0 °C while stirring. After being kept at 0 °C for 30 min, the mixture was allowed to warm to rt and stirred for 6 h. Then, the reaction was quenched with methanol (6 mL), and $CHCl_3$ (30 mL) was added to the mixture. The mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 30 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 60 mL). The organic layers were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was recrystallized from ethanol (260 mL) to give **S9** as a colorless solid (5.17 g, 2.3 mmol, α:β = 98:2, 83%). The ^{1}H NMR spectrum was identical to the reported data.[2]

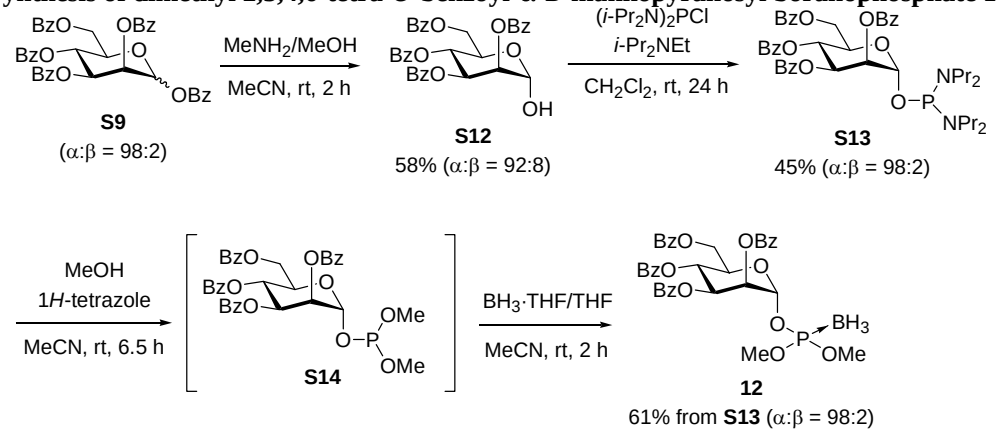
1,2,3,4-Tetra-*O*-benzoyl-L-fucopyranoside (S11).

Benzoyl chloride (3.0 mL) was added to a solution of L-fucose (**S10**, 49 mg, 3.0 mmol) in dry pyridine (10 mL) at rt while stirring. After 5 h, the mixture was diluted with CH_2Cl_2 (50 mL). The organic layer was washed with saturated $NaHCO_3$ aqueous solutions (5 × 50 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt–hexane (1:7, v/v) as an eluent to give **S11** as a colorless foam (1.71 g, 2.9 mmol, α:β = 86:14, 98%). The ^{1}H NMR spectrum was identical to the reported data.[3]

2. Synthesis of authentic sample of dimethyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl boranophosphate .

Authentic sample of **12** was prepared from 1,2,3,4,6-penta-*O*-benzoyl-D-mannopyranoside (**S9**, α:β = 98:2) in 4 steps (Scheme S2).

Scheme S2. Synthesis of dimethyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl boranophosphate 12.



2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranoside (S12).

This material was prepared according to the procedure to synthesize 2,3,4,6-tetra-*O*-benzoyl-D-glucopyranoside reported by Fukase *et al.*[4] A 40% methylamine solution in methanol (0.3 mL) was added to a solution of 1,2,3,4,6-penta-*O*-benzoyl-α-D-mannopyranoside (**S9**, 0.383 g, 0.55 mmol) in dry CH_3CN (3 mL) at rt while stirring. After 2 h, the mixture was concentrated under reduced pressure. $CHCl_3$ (10 mL) was added to the residue and the organic layer was washed with brine (10 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (2 × 10 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt–hexane (1:2, v/v) as an eluent to give **S12** as a yellow foam (0.190 g, 0.32 mmol, α:β = 92:8, 58%). The ^{1}H NMR spectrum was identical to the reported data.[5]

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite (S13).

This material was prepared according to the procedure to synthesize 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranosyl)-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite reported by Boons *et al.*[6] Chlorobis(*N*,*N*-diisopropylamino)phosphine (32 mg, 0.12 mmol) was added to a solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranoside (**S12**, 77 mg, 0.13 mmol) in dry CH_2Cl_2 (0.75 mL). The mixture was allowed to stir at rt for 10 min. Diisopropylethylamine (0.23 mL) was added dropwise to the mixture. After 24 h, the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography on NH silica gel (100–200 mesh) using AcOEt–hexane–Et_3N (12:83:15, v/v/v) as an eluent to give **S13** as a colorless oil (45 mg, 55 μmol, α:β = 98:2, 45%). IR (KBr, cm^{-1}) 3065, 2971, 1730, 1603, 1492, 1452, 1364, 1268, 1181, 1108, 1069, 1027, 958, 870, 816, 710, 646, 528. ^{1}H NMR ($CDCl_3$) δ 8.16–7.23 (m, 20H, Ar), 6.13 (t, *J* = 9.9 Hz, 1H, H-4), 6.02 (dd, *J* = 3.2, 10.1 Hz, 1H, H-3), 5.66–5.62 (m, 1H, H-2), 5.39 (dd, *J* = 2.0, 11.0 Hz, 1H, H-1), 4.68–4.56 (m, 2H, H-5,6), 4.49 (dd, *J* = 4.4, 11.6 Hz, 1H, H-6), 3.79–3.54 (m, 4H, -N-C<u>H</u>-$(CH_3)_2$), 1.35–1.21 (m, 24H, -N-CH-(C<u>H</u>$_3)_2$). ^{13}C NMR ($CDCl_3$) δ 166.3, 165.6, 165.5, 165.4 (C=O), 133.3, 133.1, 132.9, 130.0, 129.9, 129.8, 129.7, 129.5, 129.1, 129.0, 128.5, 128.4, 128.3 (Ar), 93.0 (C-1), 71.5 (C-2), 70.3 (C-3), 69.2 (C-5), 67.1 (C-4), 63.1 (C-6), 45.5, 45.3, 45.0, 44.8 (-N-<u>C</u>H-$(CH_3)_2$), 24.5, 24.4, 24.3, 24.2 (-N-CH-(<u>C</u>H$_3)_2$). ^{31}P NMR ($CDCl_3$) δ 116.2. HRMS (ESI): calcd for $C_{46}H_{55}N_2O_{10}PK$ $[M+K]^+$: 865.3231; found: 865.3257.

Authentic sample of dimethyl 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl boranophosphate (12).

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl-*N*,*N*,*N*′,*N*′-tetraisopropylphosphorodiamidite (**S13**, 45 mg, 55 μmol) was dried by repeated coevaporation with dry toluene and dry CH_3CN. The residue was treated with dry MeOH (9 μL, 0.22 mmol) and a solution of 1*H*-tetrazole (0.16 mg, 22 mmol) in dry CH_3CN (2.2 mL), which was dried over MS 3A overnight. The mixture was allowed to stir for 30 min, and dry MeOH (30 μL, 0.74 mmol) was added to the mixture. After being stirred for 6 h, the mixture was diluted with $CHCl_3$ (10 mL), and the mixture was washed with saturated $NaHCO_3$ aqueous solutions (3 × 10 mL). The aqueous layers were combined and back-extracted with $CHCl_3$ (20 mL). The organic layers were combined, and dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The

residue was dissolved in dry CH_3CN, then 0.99 M BH_3·THF/THF (0.25 mL, 0.25 mmol) was added dropwise. The mixture was allowed to stir for 2 h, washed with a saturated $NaHCO_3$ aqueous solution (7 mL), and extracted with toluene (6 mL). The organic layer was separated and washed with saturated $NaHCO_3$ aqueous solutions (2 × 7 mL). The aqueous layers were combined and back-extracted with toluene (30 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using AcOEt–hexane (1:3, v/v) as an eluent to give **12** as a colorless foam (24 mg, 34 μmol, α:β = 98:2, 61% from **S13**).

References for Supporting Information

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3) Timmons, S. C.; Mosher, R. H.; Knowles, S. A.; Jakeman, D. L. *Org. Lett*. **2007**, *9*, 857–860.
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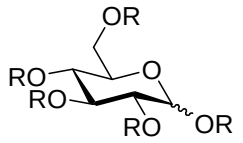
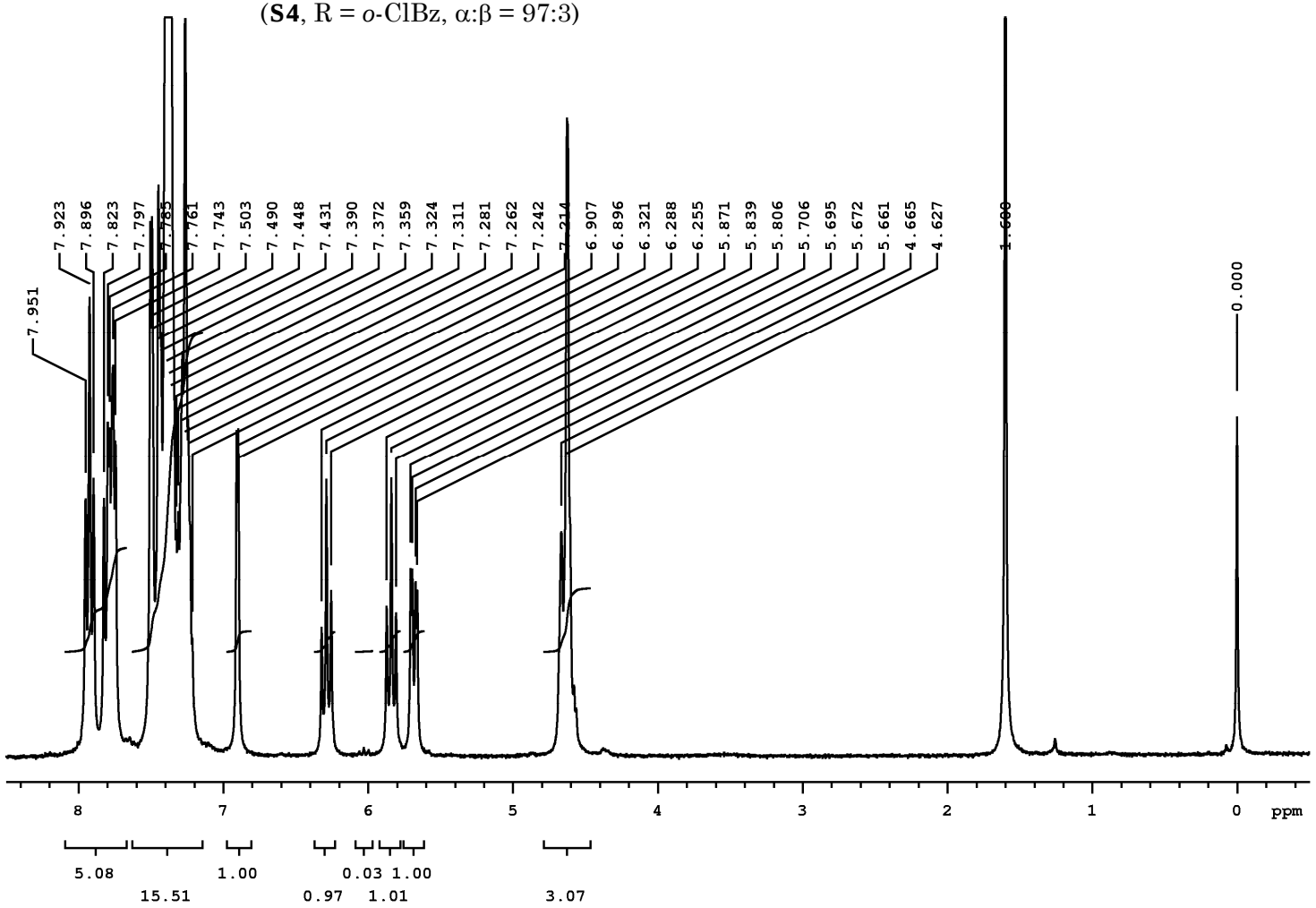
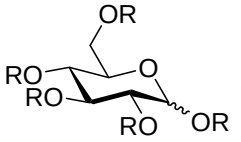
5) Mbadugha, B. N. A.; Menger, F. M. *Org. Lett*. **2003**, *5*, 4041–4044.
6) Majumdar, D.; Elsayed, G. A.; Buskas, T.; Boons, G.-J. *J. Org. Chem*. **2005**, *70*, 1691–1697.



(**S4**, R = *o*-ClBz, α:β = 97:3)

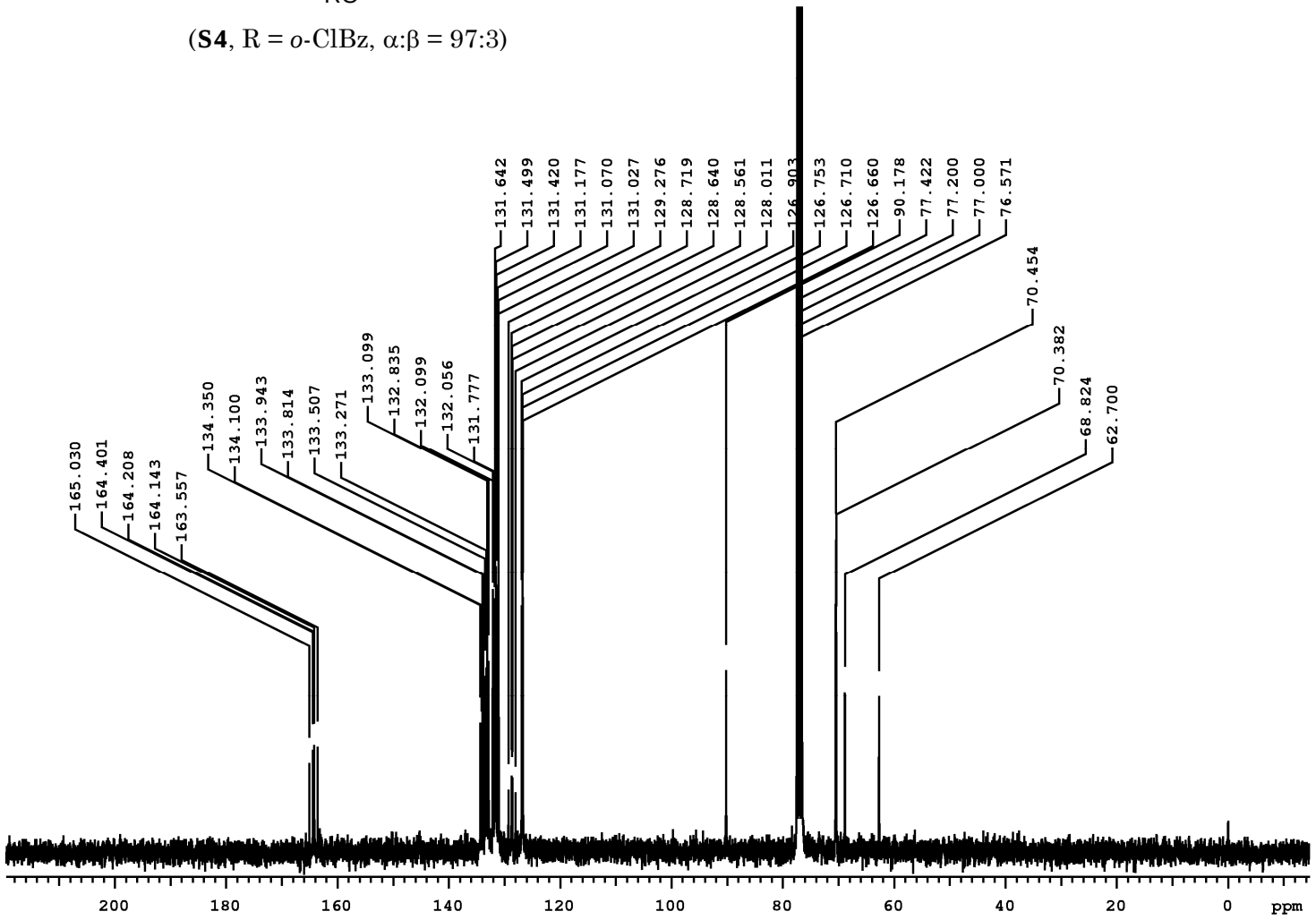
(^{1}H NMR, $CDCl_3$, 300 MHz)

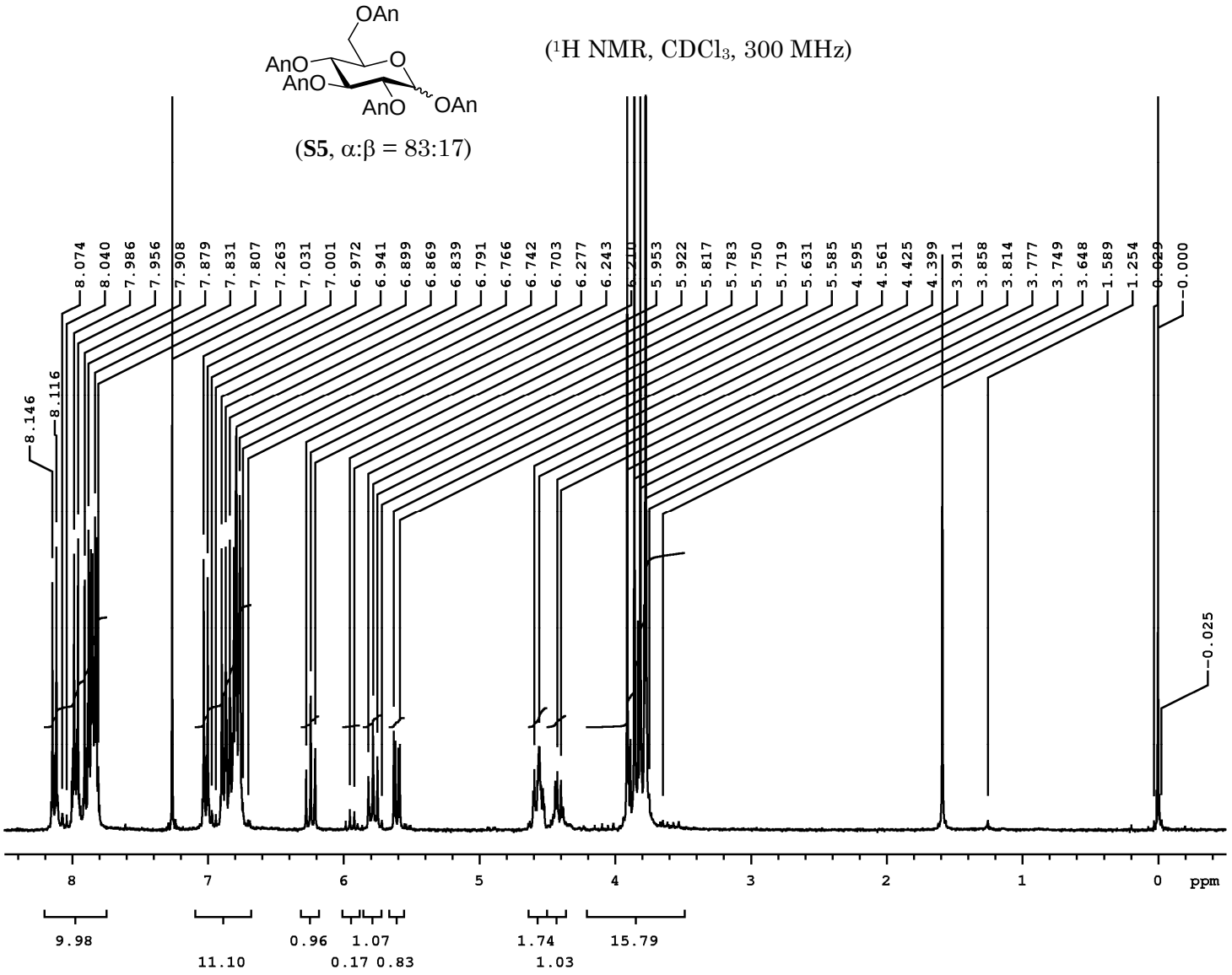




(^{13}C NMR, $CDCl_3$, 75.5 MHz)

(**S4**, R = *o*-ClBz, α:β = 97:3)

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(S5, α:β = 83:17)
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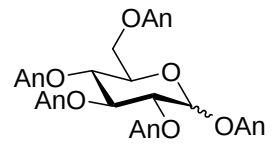
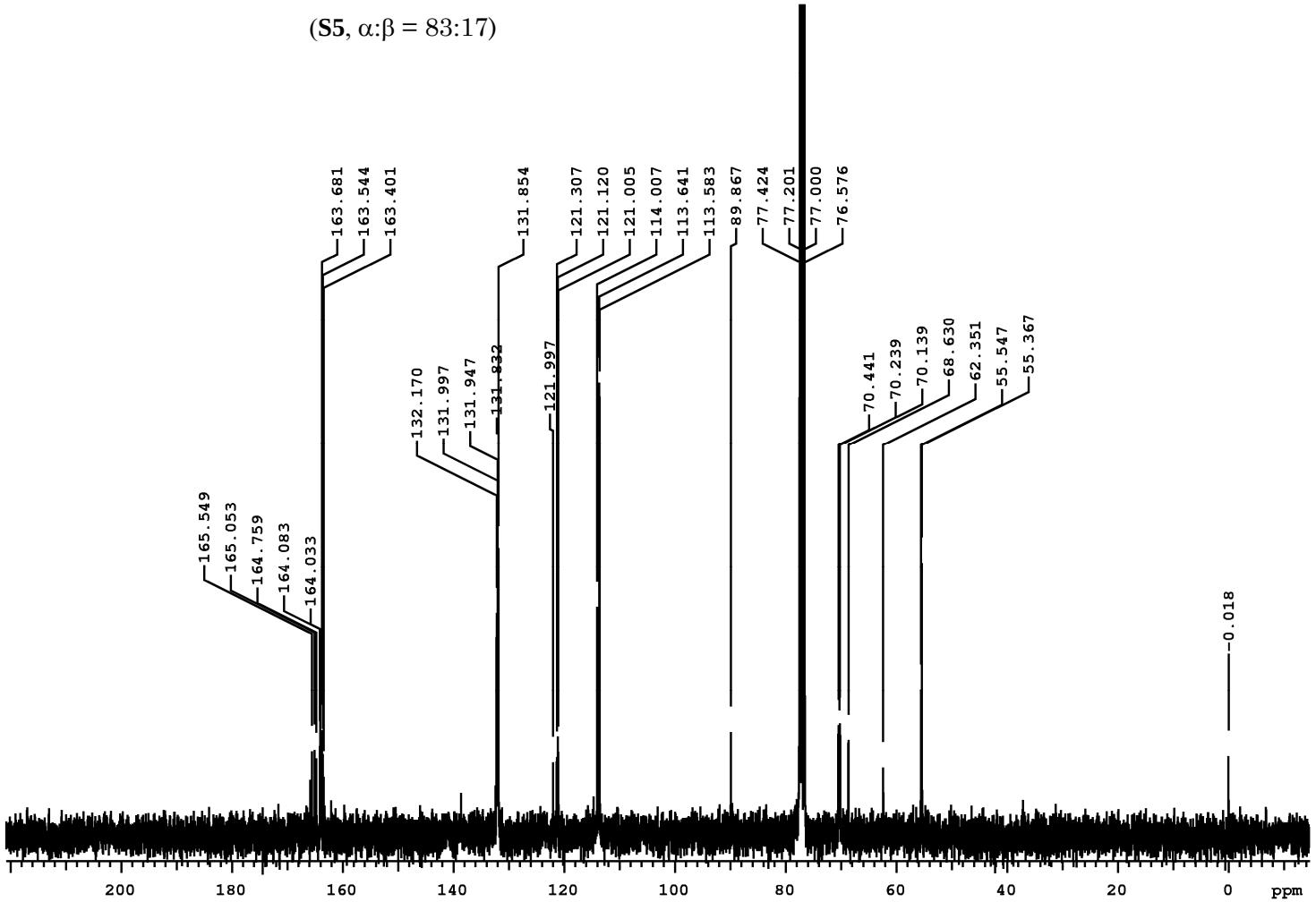
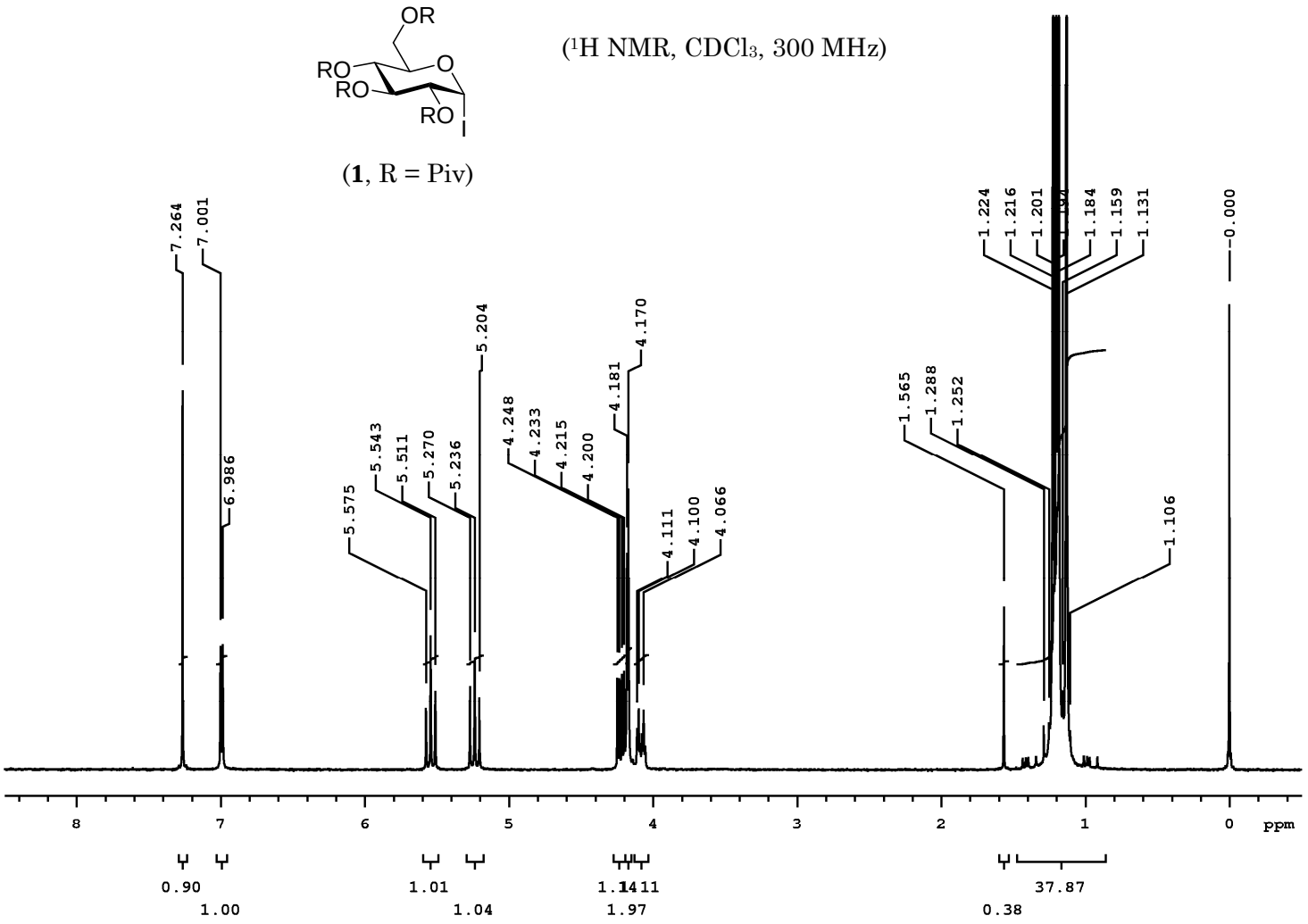


(**S5**, α:β = 83:17)

(^{13}C NMR, $CDCl_3$, 75. 5 MHz)

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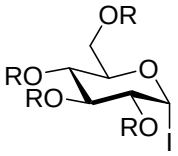
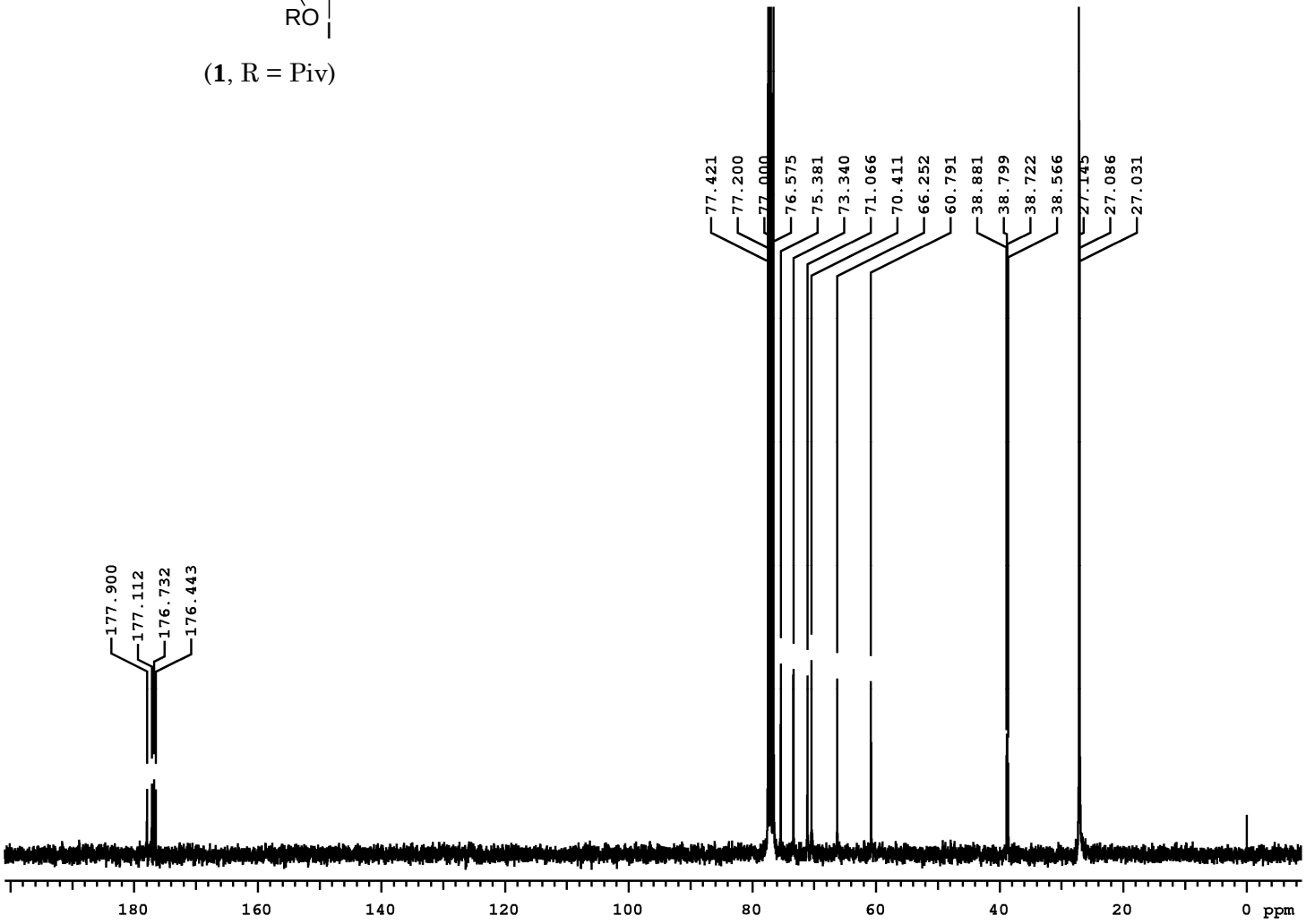
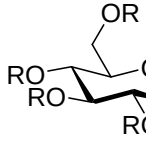


(^{13}C NMR, $CDCl_3$, 75.5 MHz)

(**1**, R = Piv)





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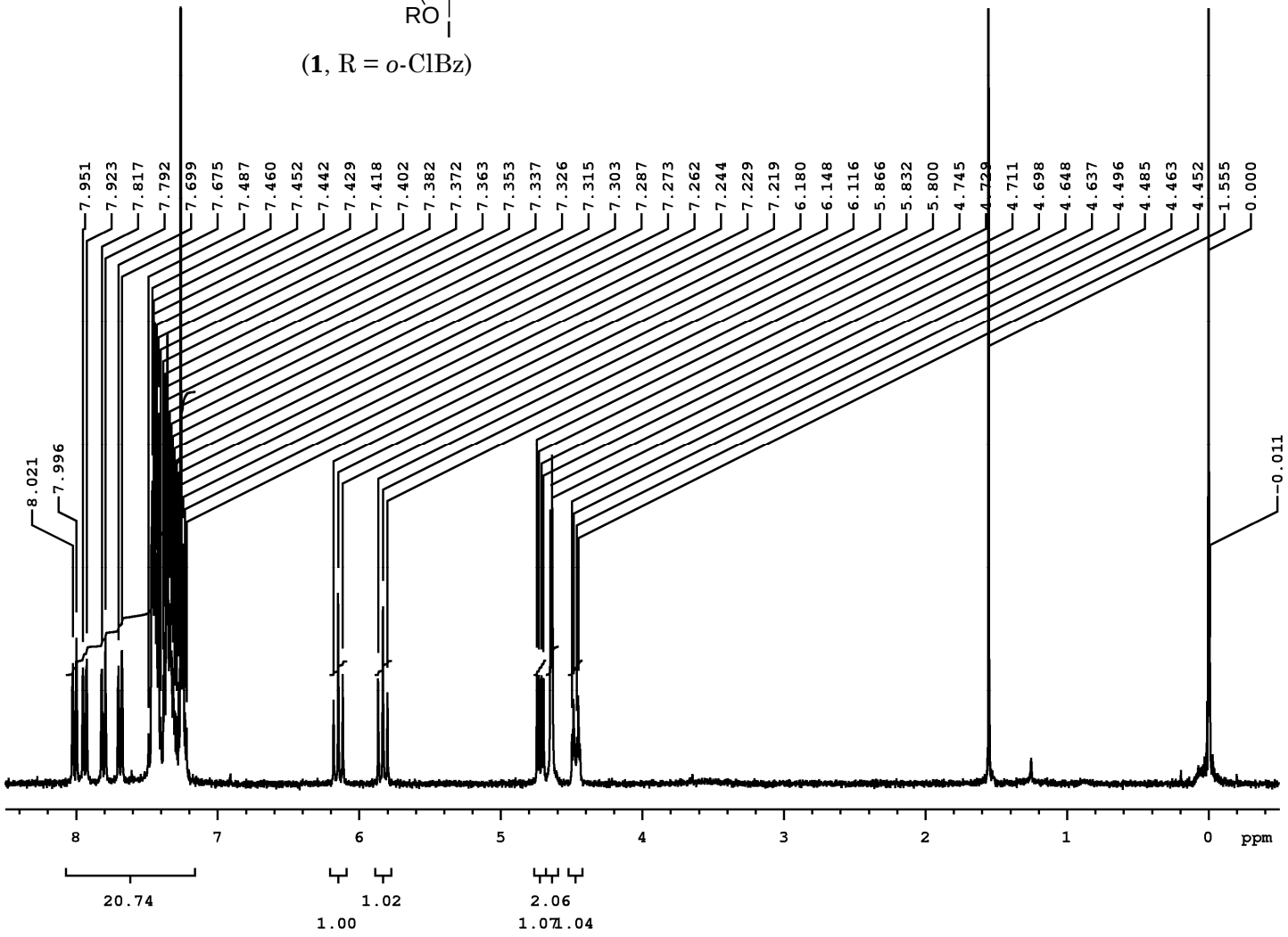
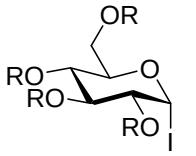
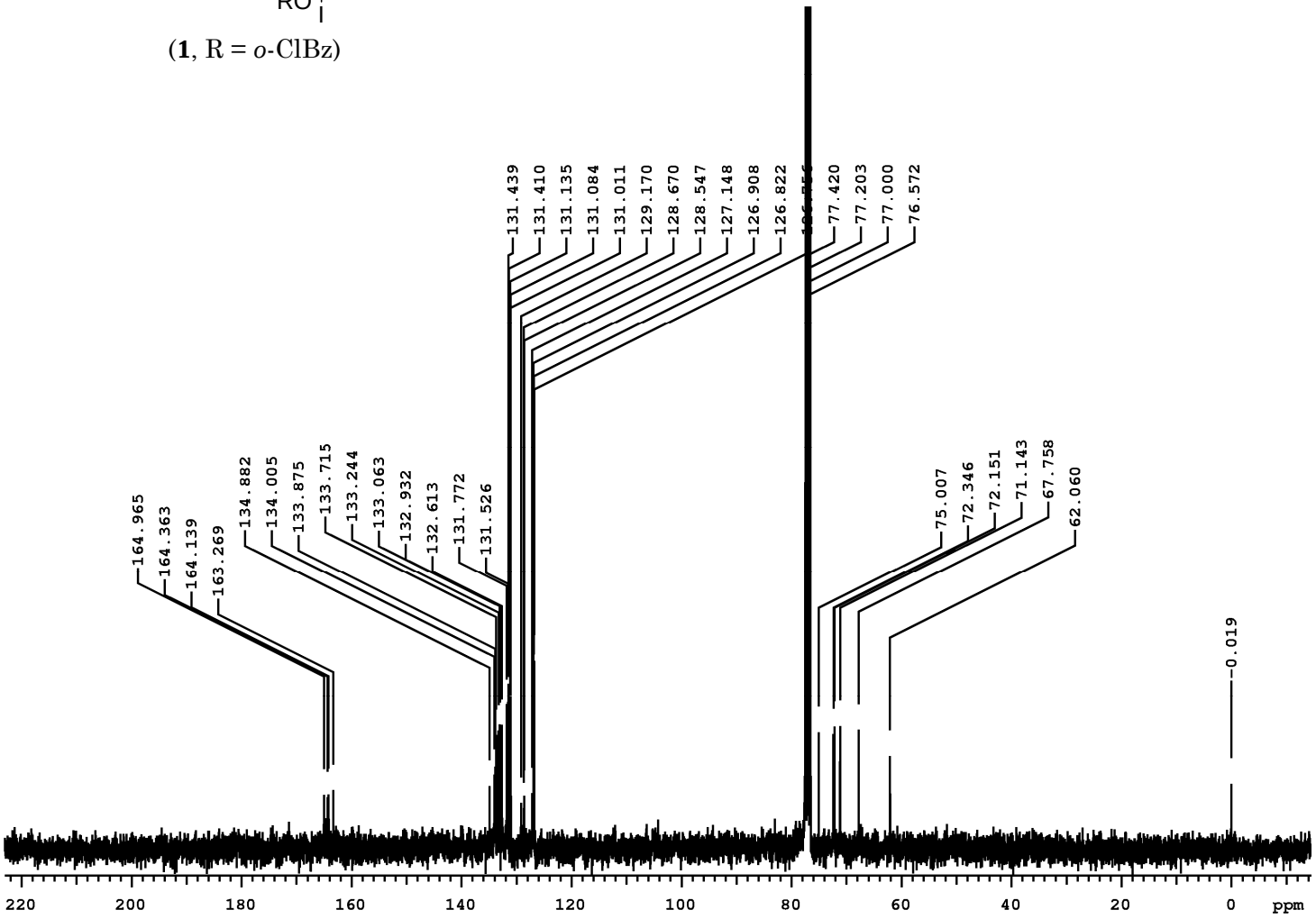
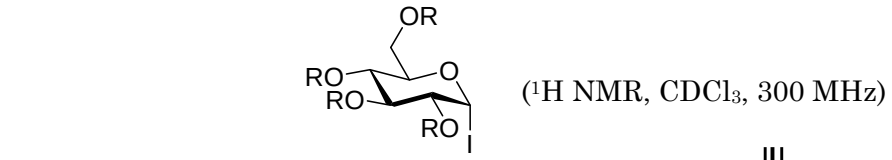




(**1**, R = *o*-ClBz)

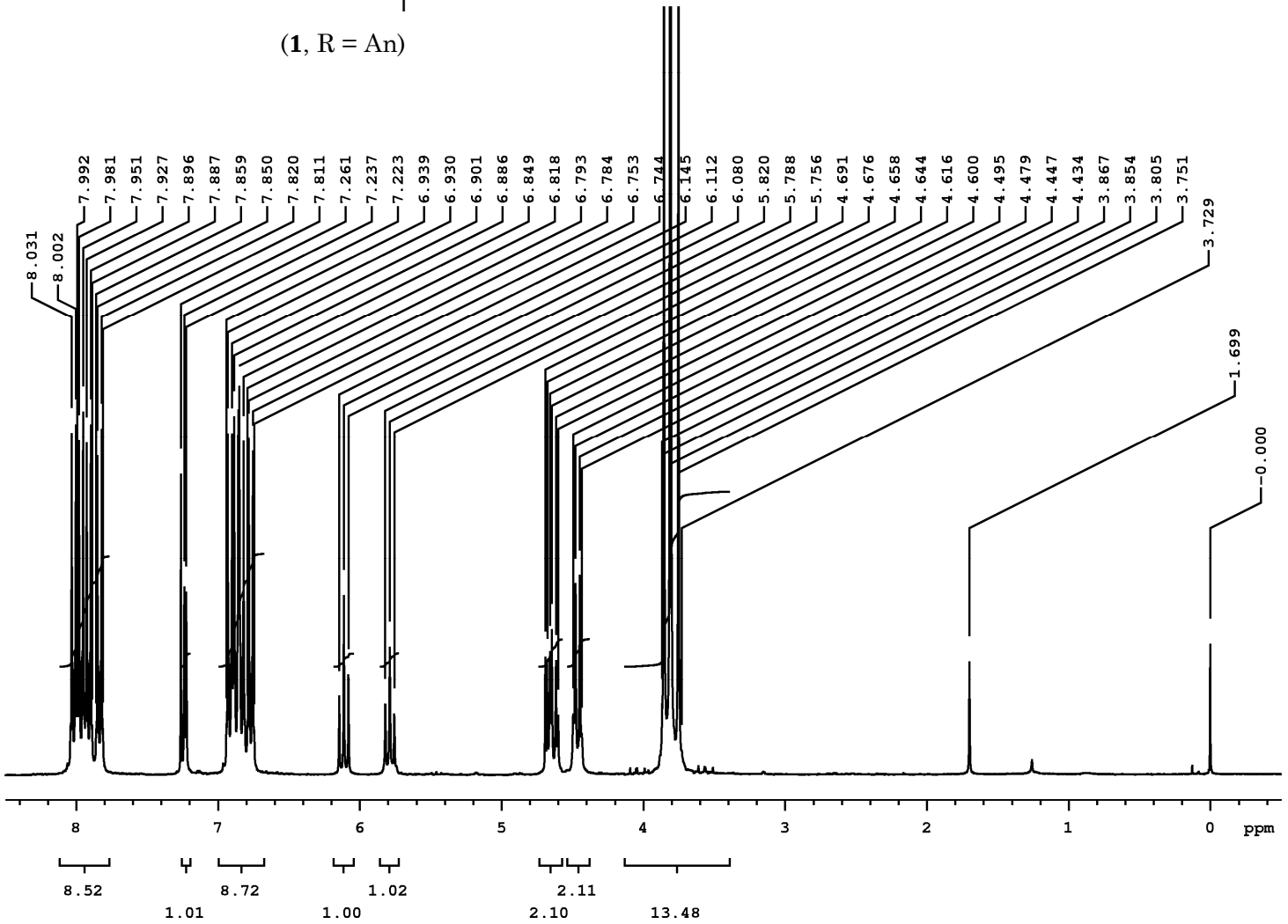
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

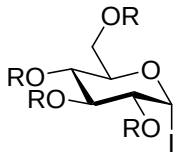




(**1**, R = An)

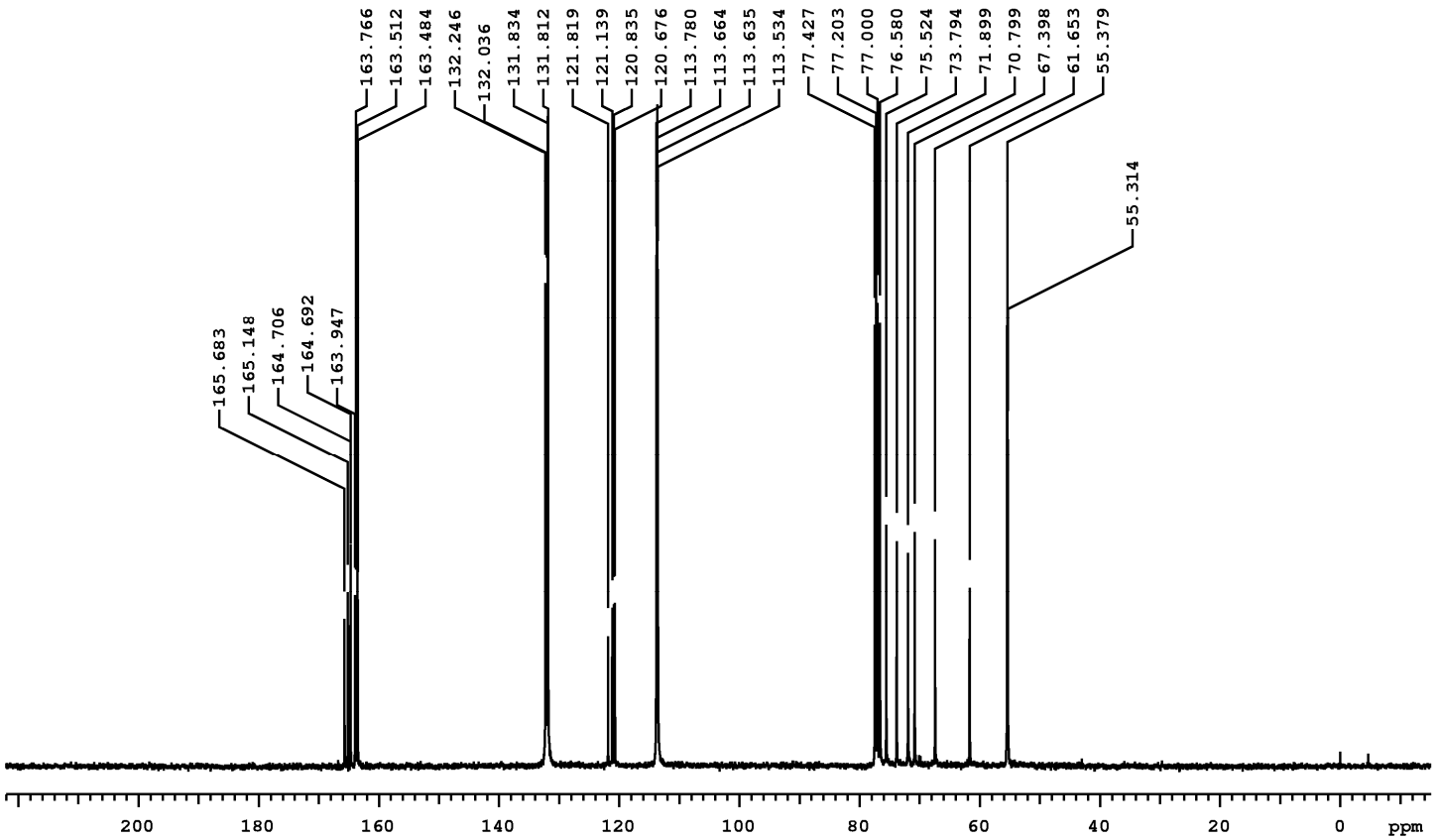
(^{1}H NMR, $CDCl_3$, 300 MHz)

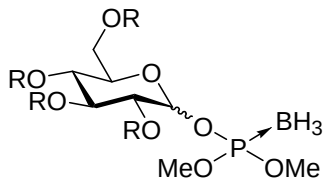




(^{13}C NMR, $CDCl_3$, 75.5 MHz)

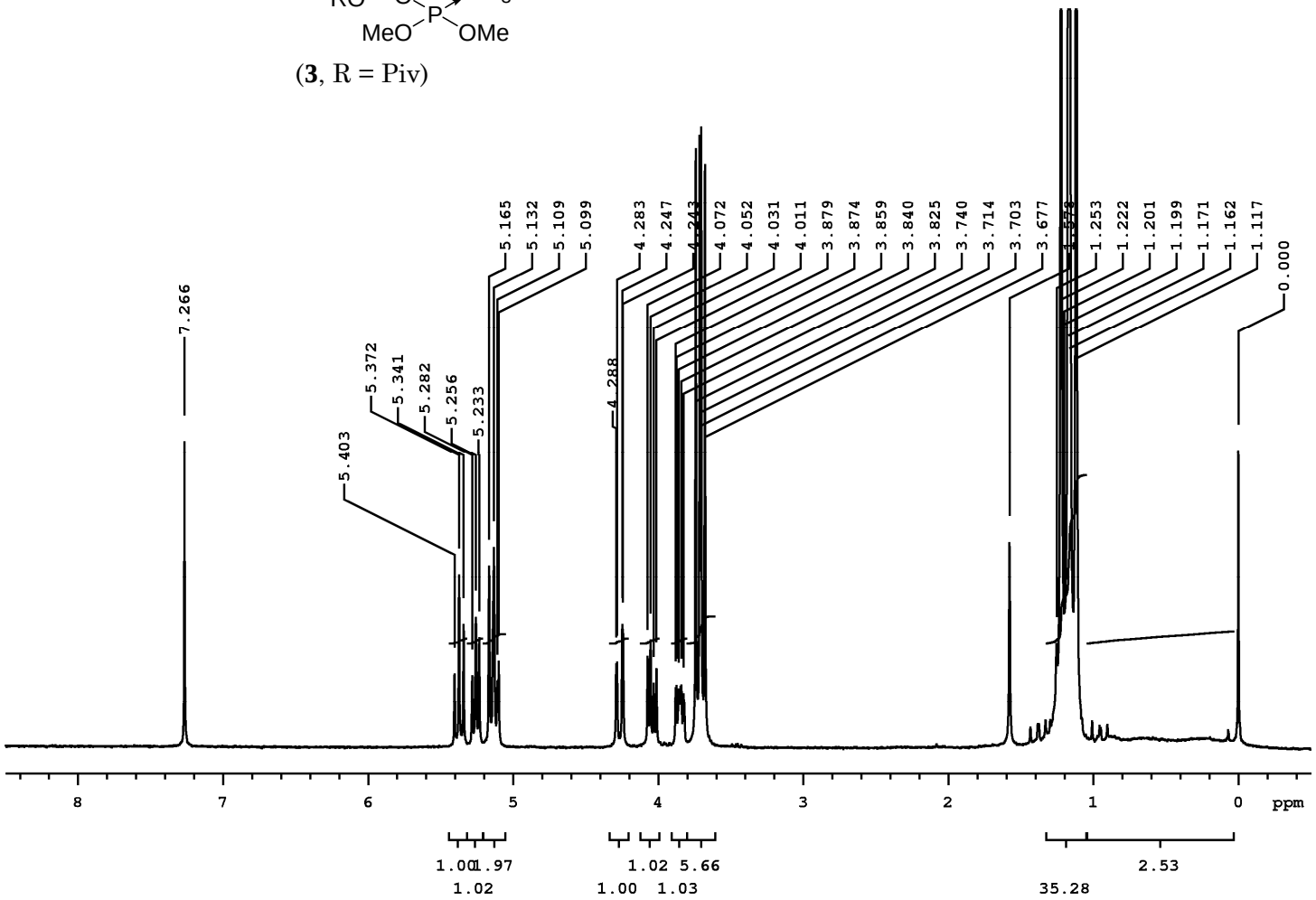
(**1**, R = An)

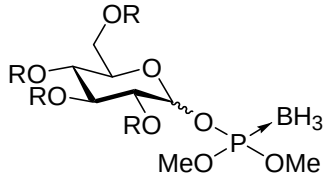




(**3**, R = Piv)

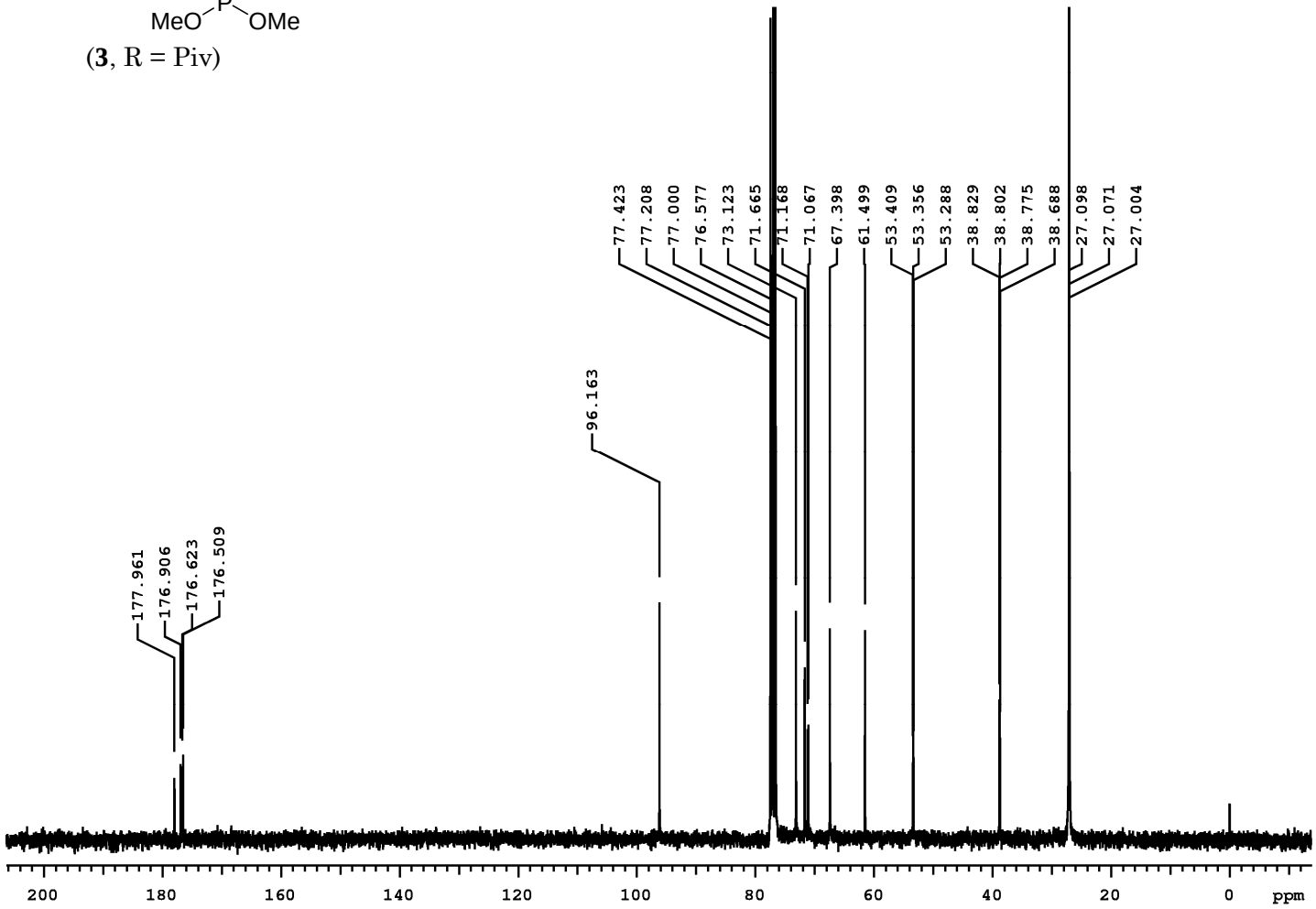
(^{1}H NMR, $CDCl_3$, 300 MHz)

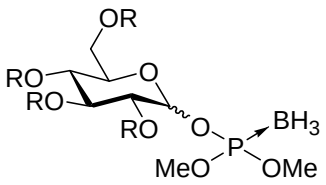




(**3**, R = Piv)

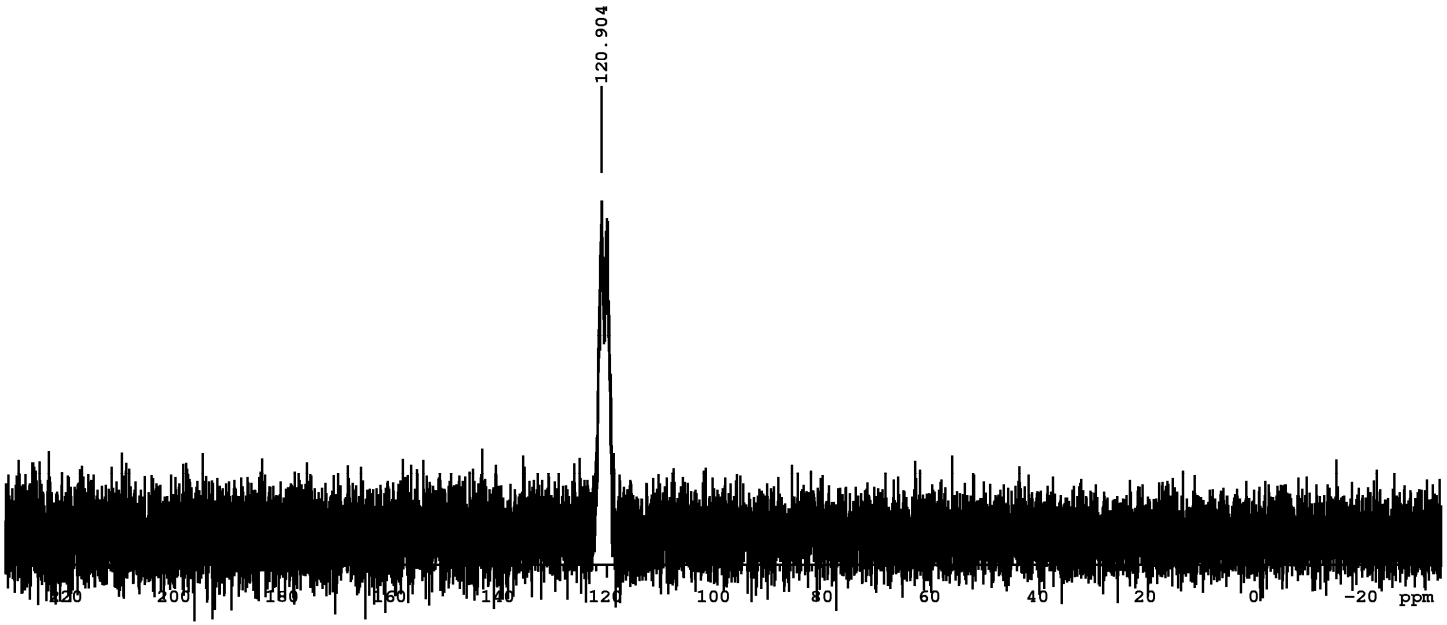
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

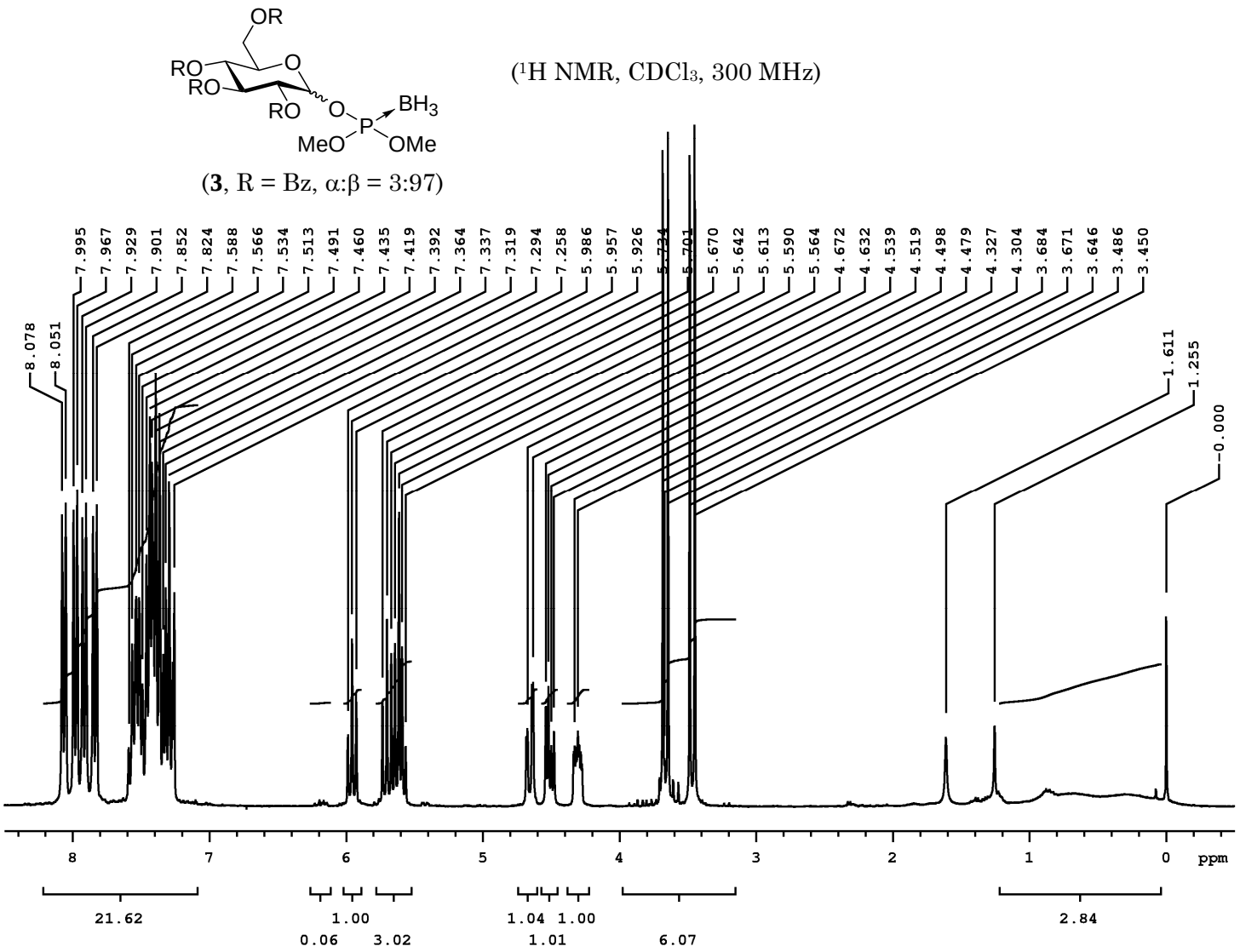




(**3**, R = Piv)

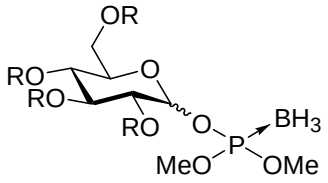
(^{31}P NMR, $CDCl_3$, 121.5 MHz)





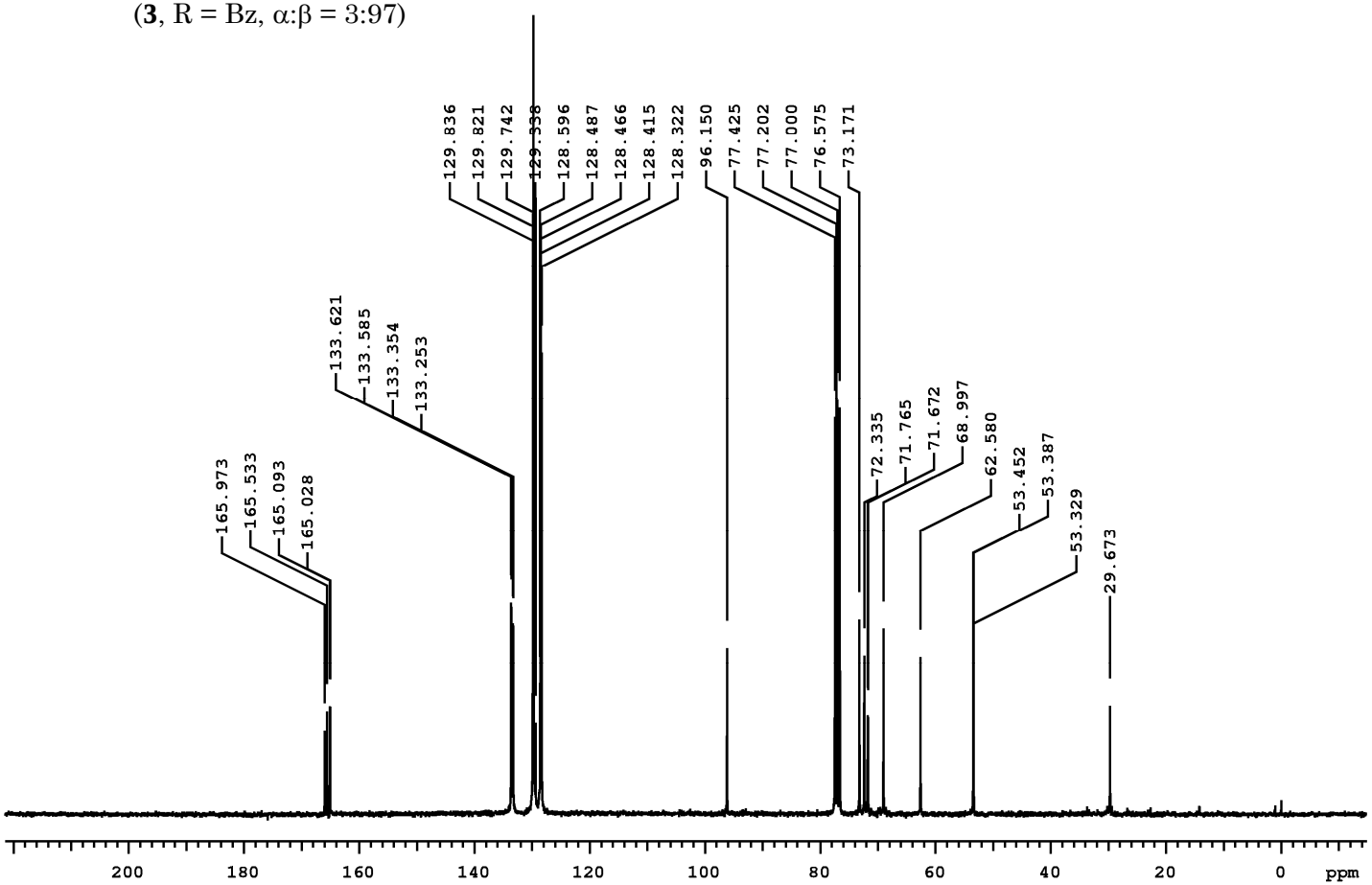
(**3**, R = Bz, α:β = 3:97)

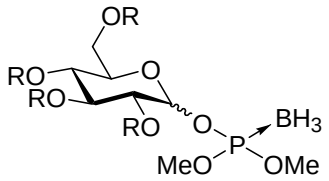
(^{1}H NMR, $CDCl_3$, 300 MHz)



(**3**, R = Bz, α:β = 3:97)

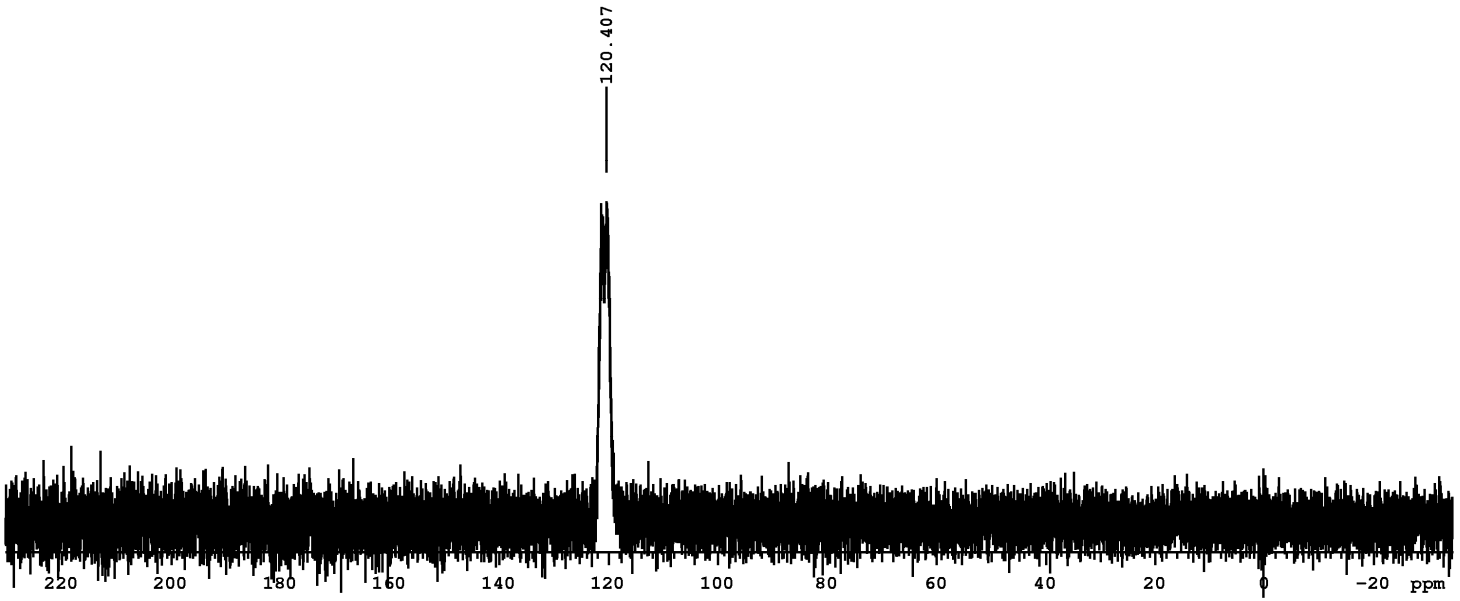
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

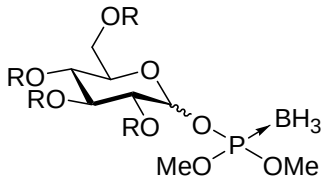




(**3**, R = Bz, α:β = 3:97)

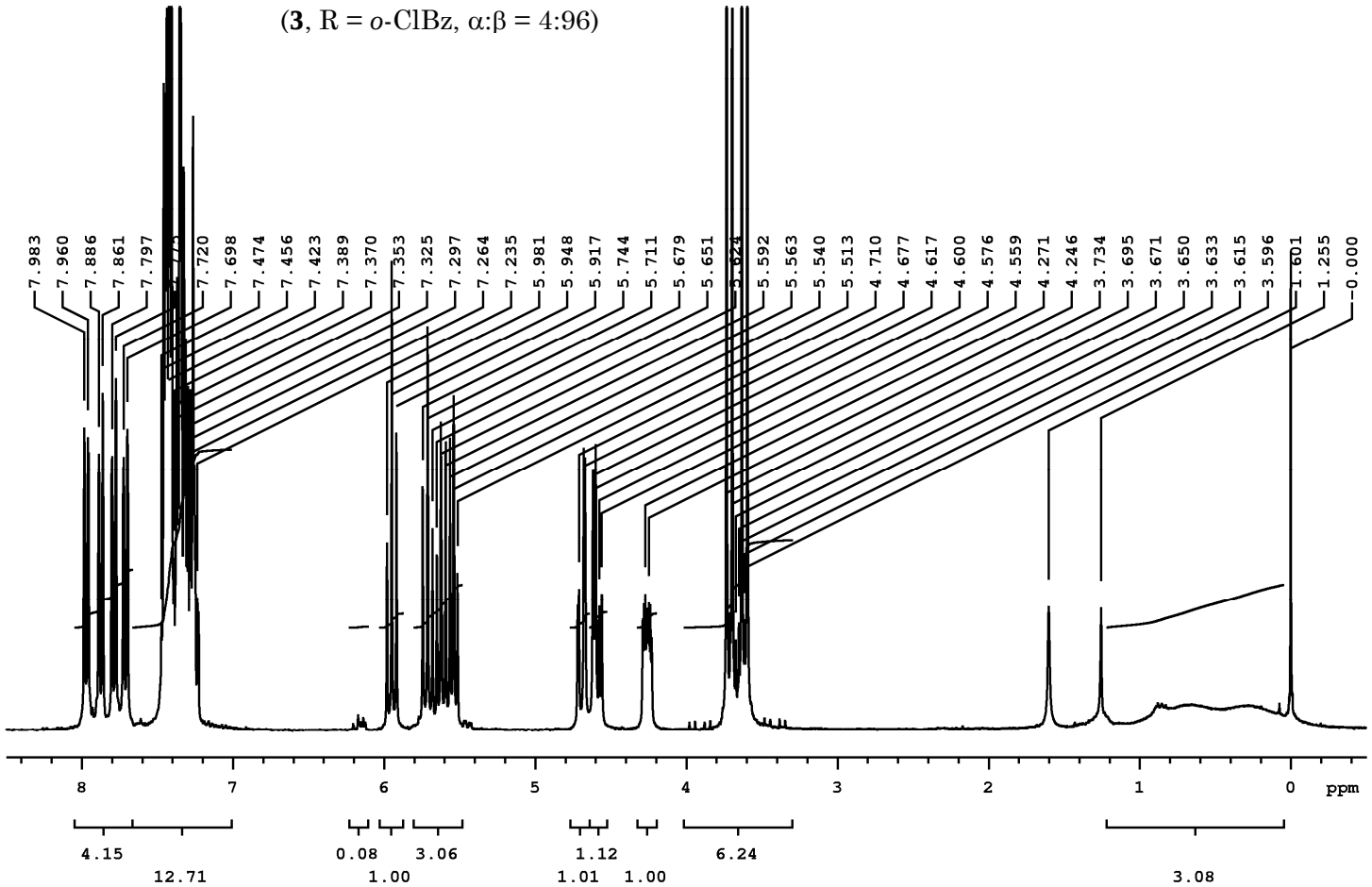
(^{31}P NMR, $CDCl_3$, 121.5 MHz)

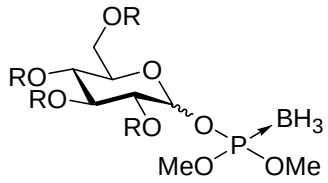




(**3**, R = *o*-ClBz, α:β = 4:96)

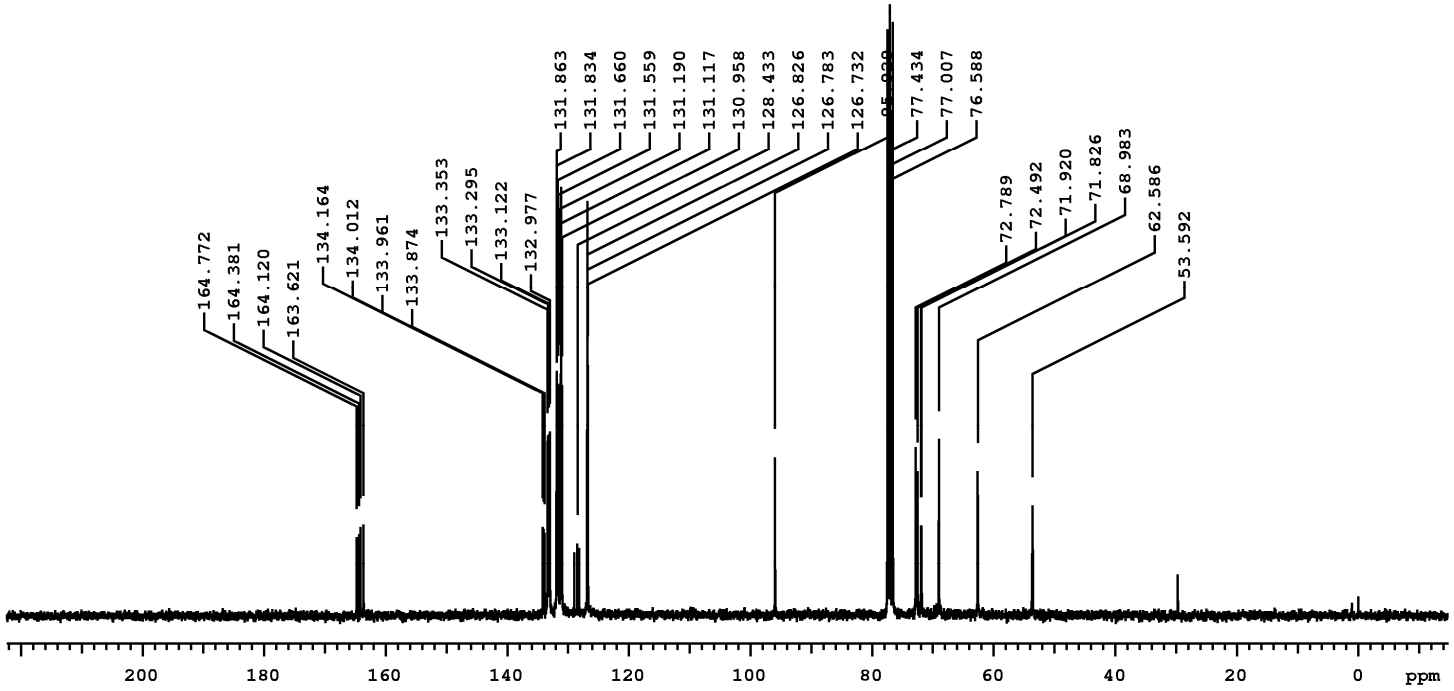
(^{1}H NMR, $CDCl_3$, 300 MHz)

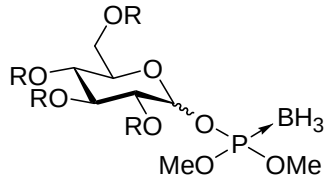




(**3**, R = *o*-ClBz, α:β = 4:96)

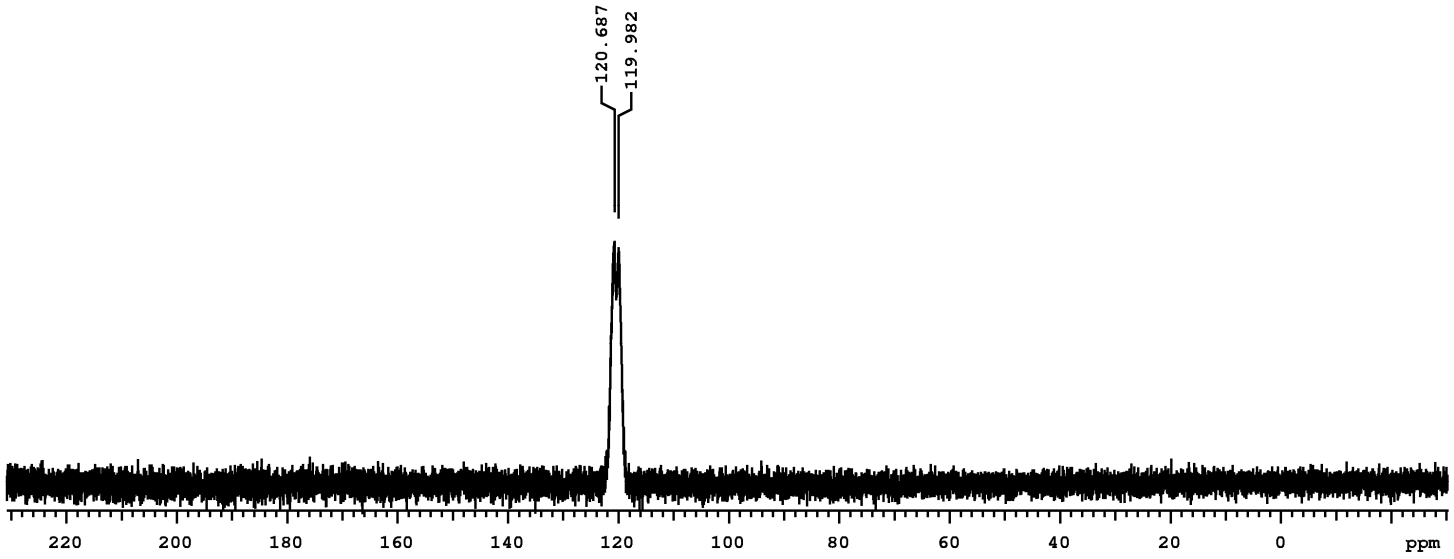
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

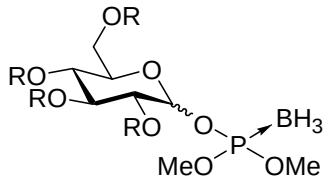




(^{31}P NMR, $CDCl_3$, 121.5 MHz)

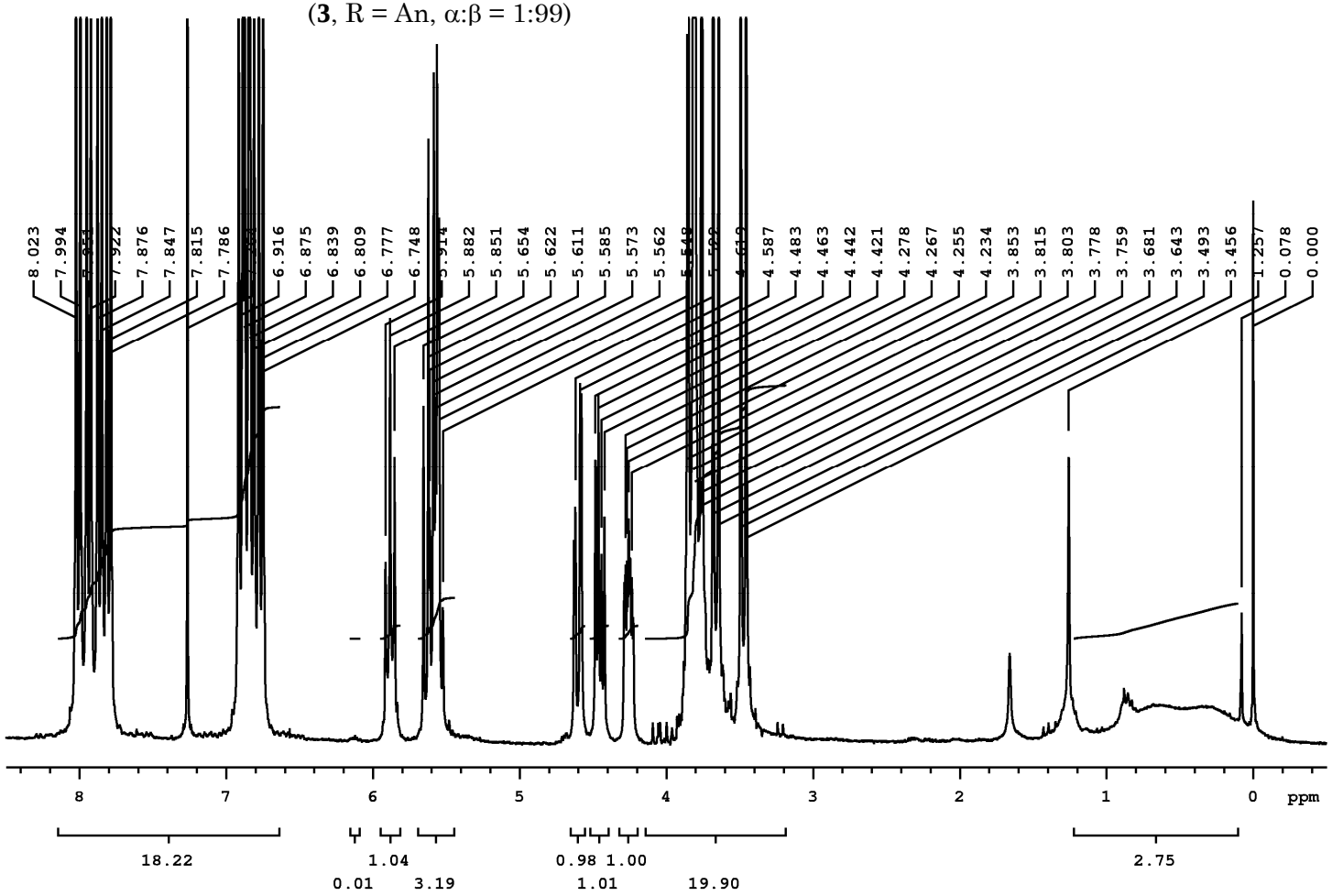
(**3**, R = *o*-ClBz, α:β = 4:96)

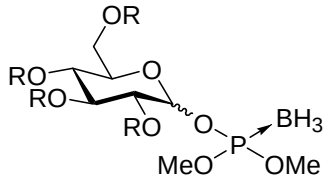




(**3**, R = An, α:β = 1:99)

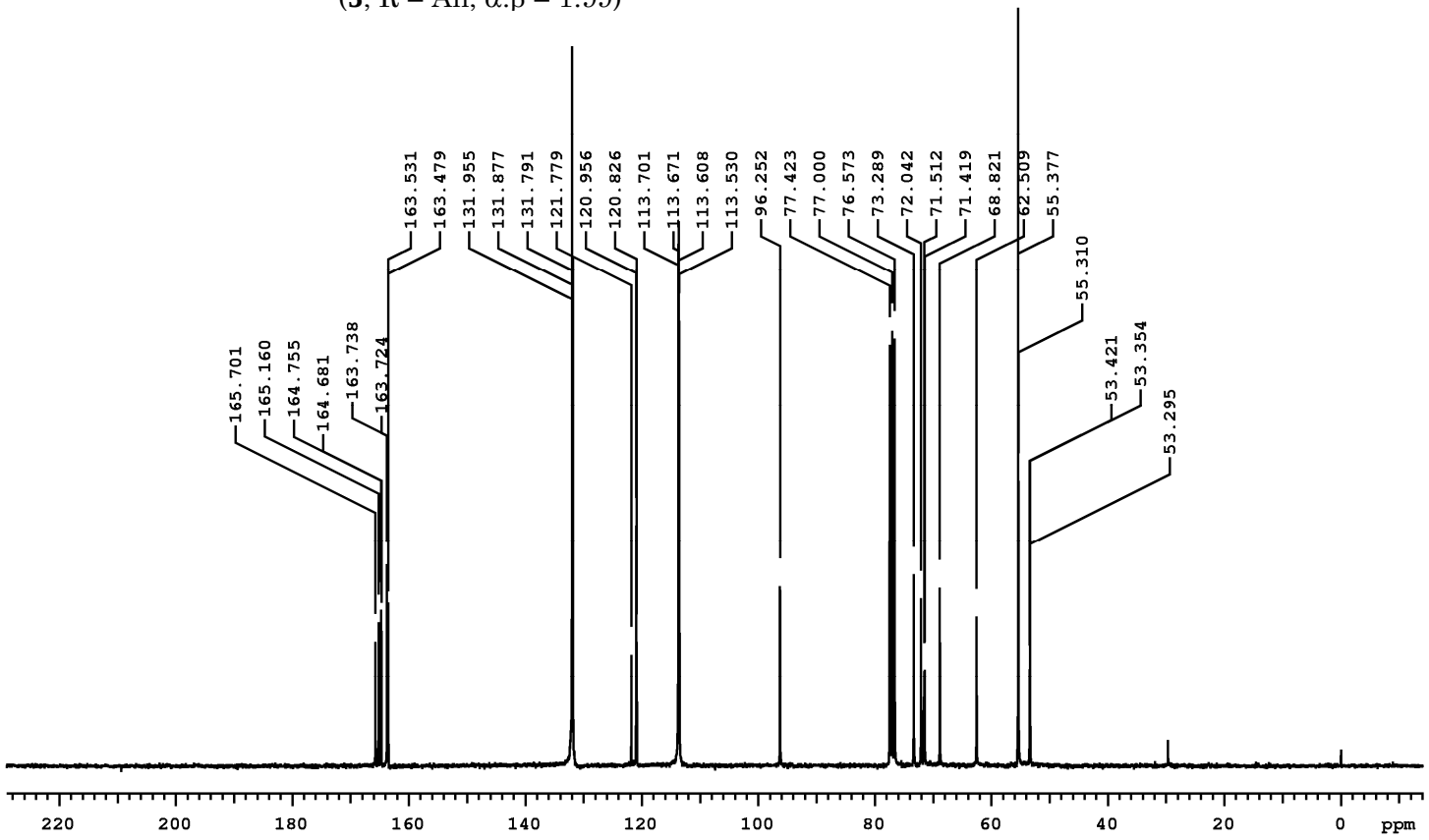
(^{1}H NMR, $CDCl_3$, 300 MHz)

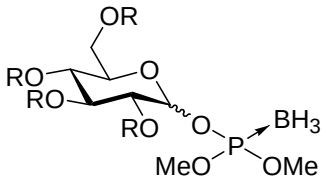




(**3**, R = An, α:β = 1:99)

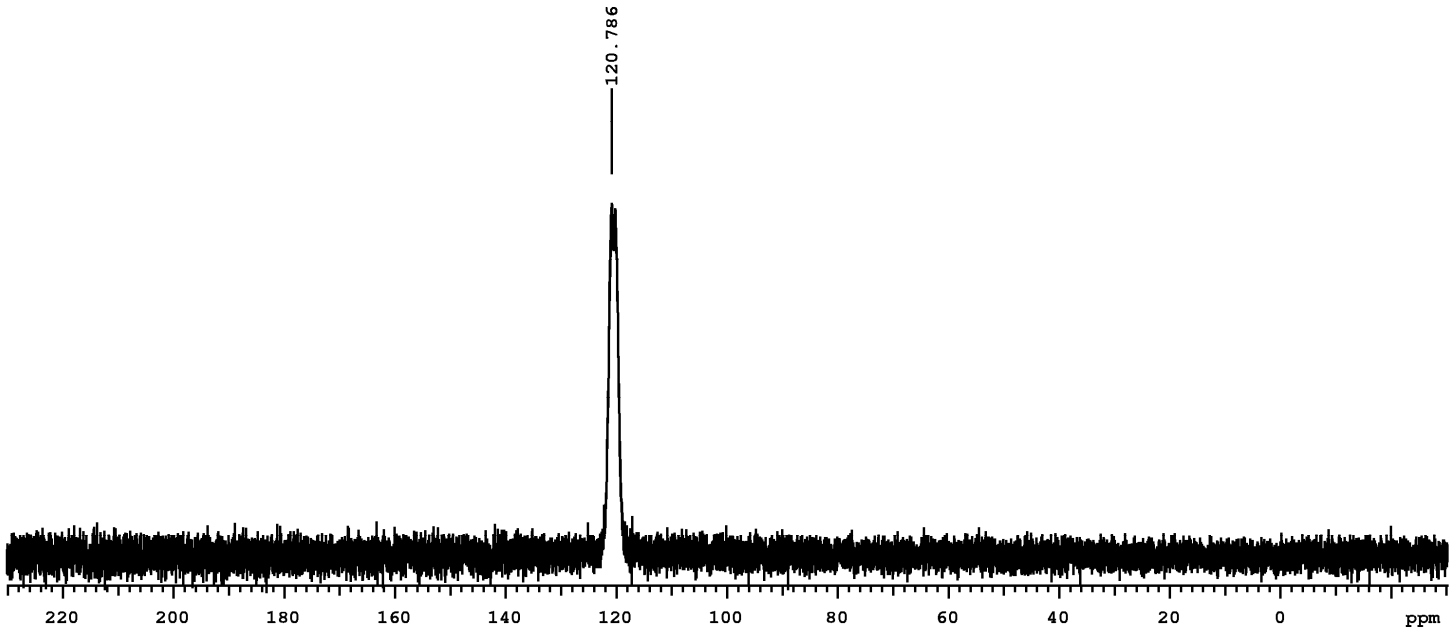
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

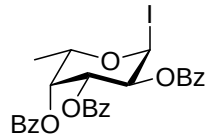




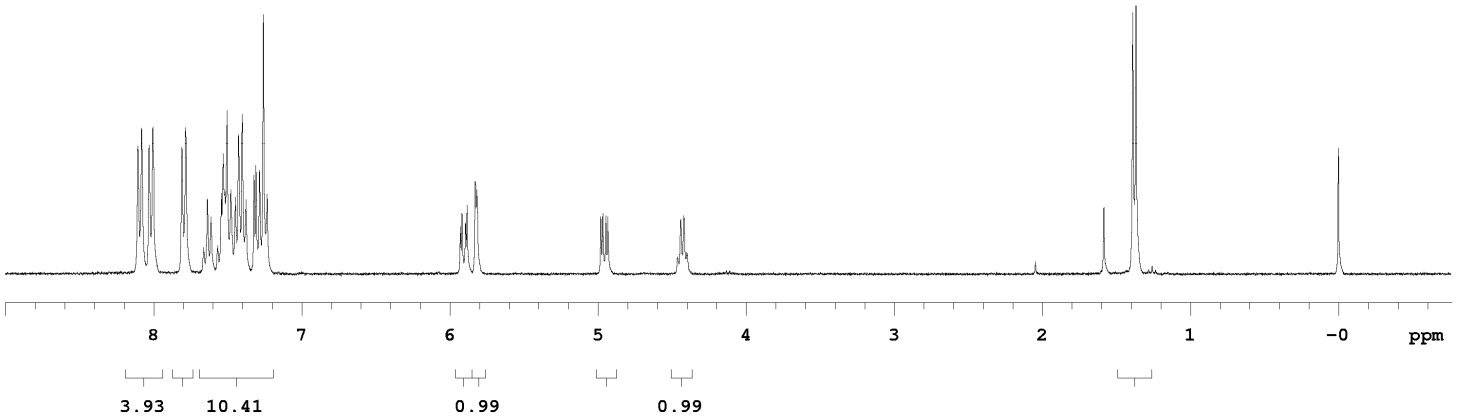
(**3**, R = An, α:β = 1:99)

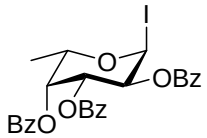
(^{31}P NMR, $CDCl_3$, 121.5 MHz)





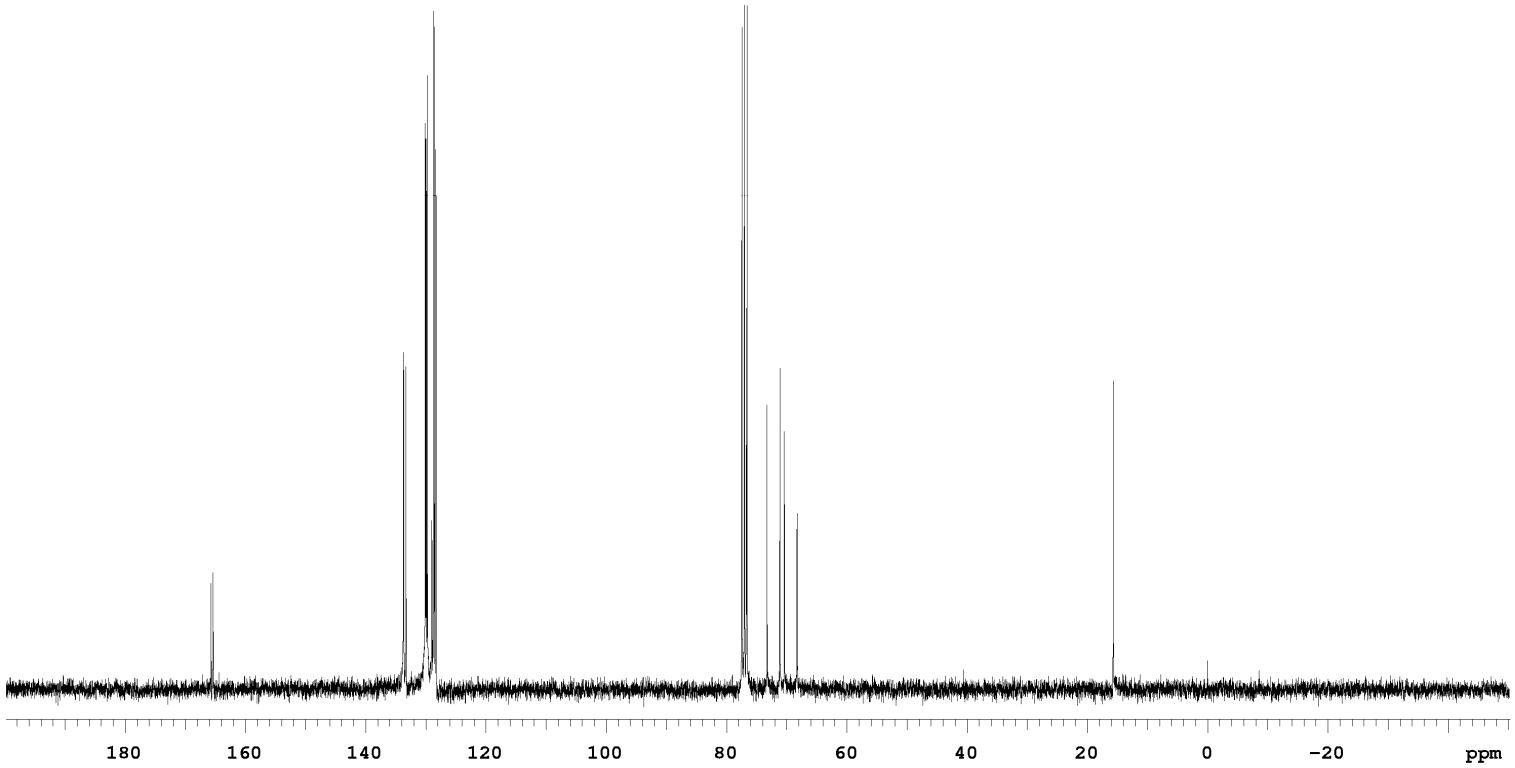
(**10**) (^{1}H NMR, $CDCl_3$, 300 MHz)

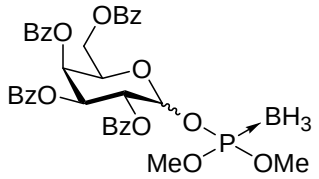




(^{13}C NMR, $CDCl_3$, 75.5 MHz)

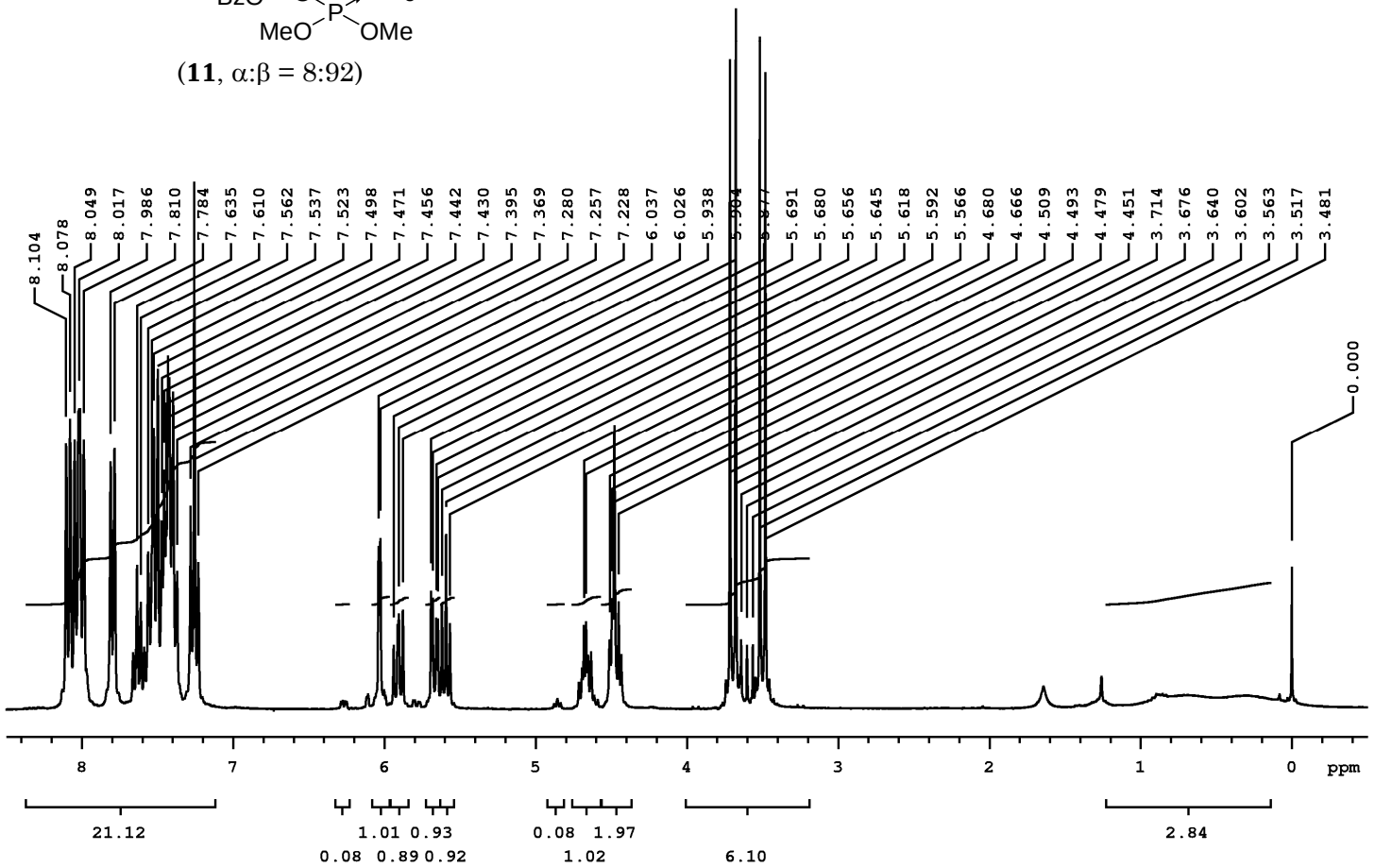
(**10**)

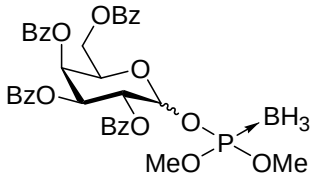




(**11**, α:β = 8:92)

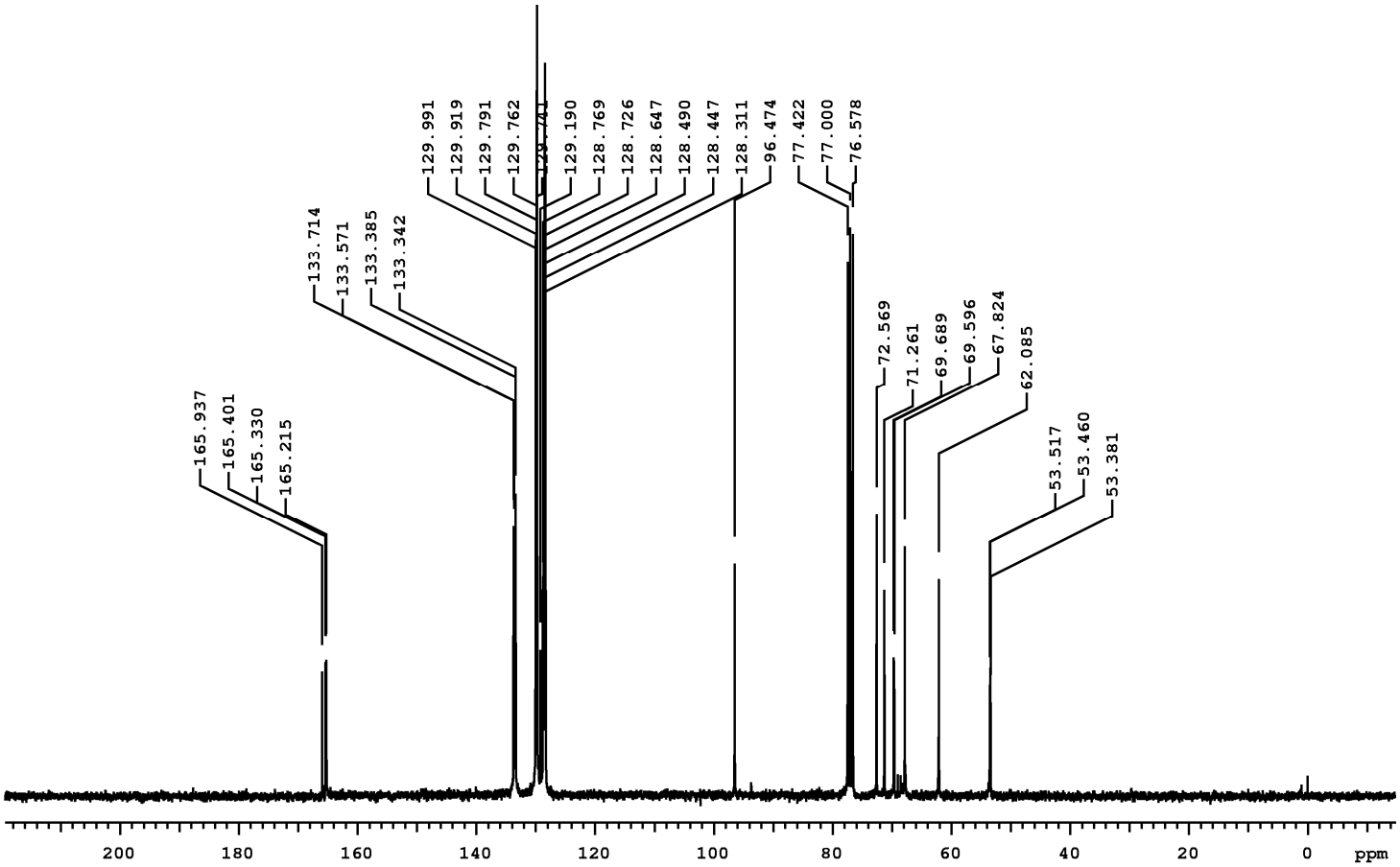
(^{1}H NMR, $CDCl_3$, 300 MHz)

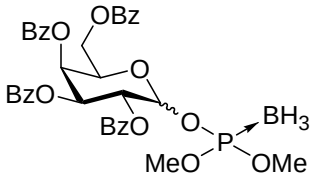




(**11**, α:β = 8:92)

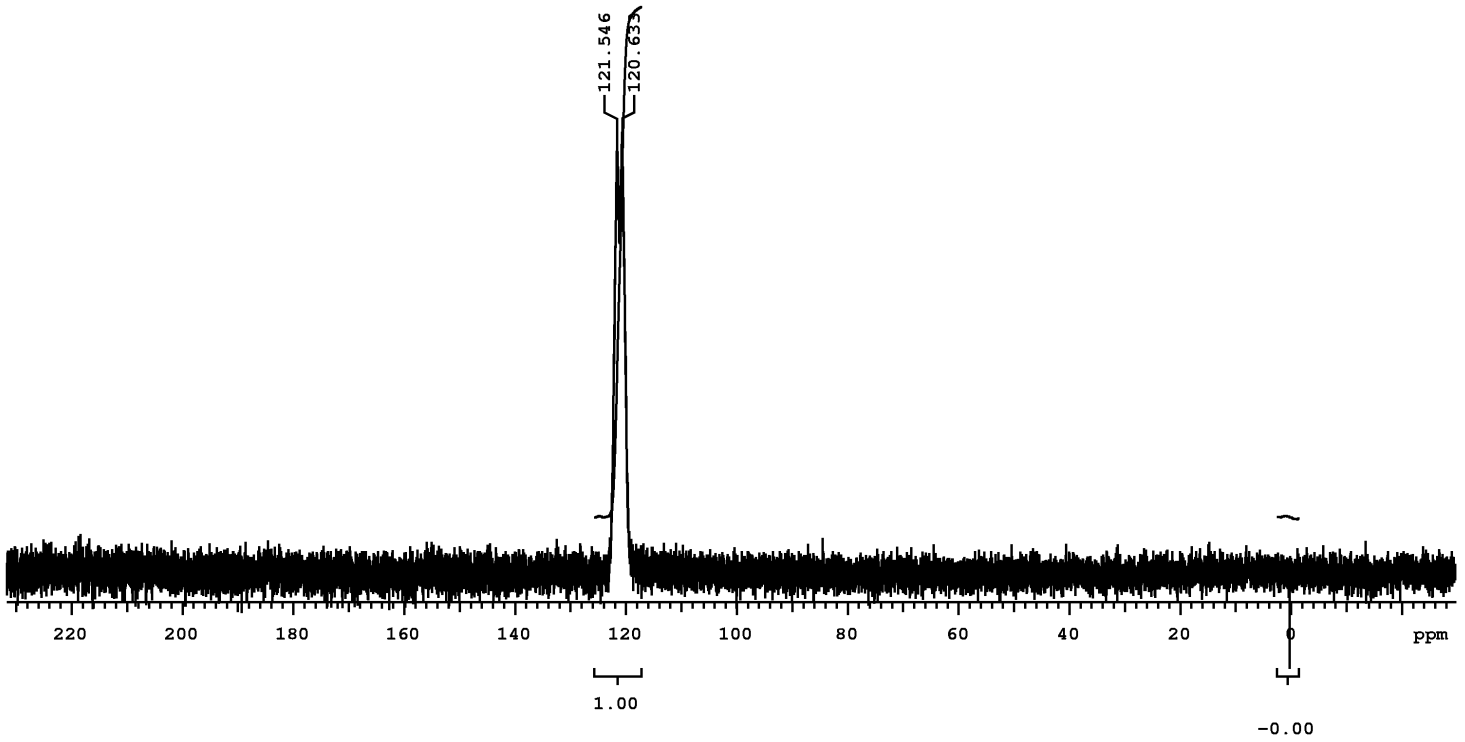
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

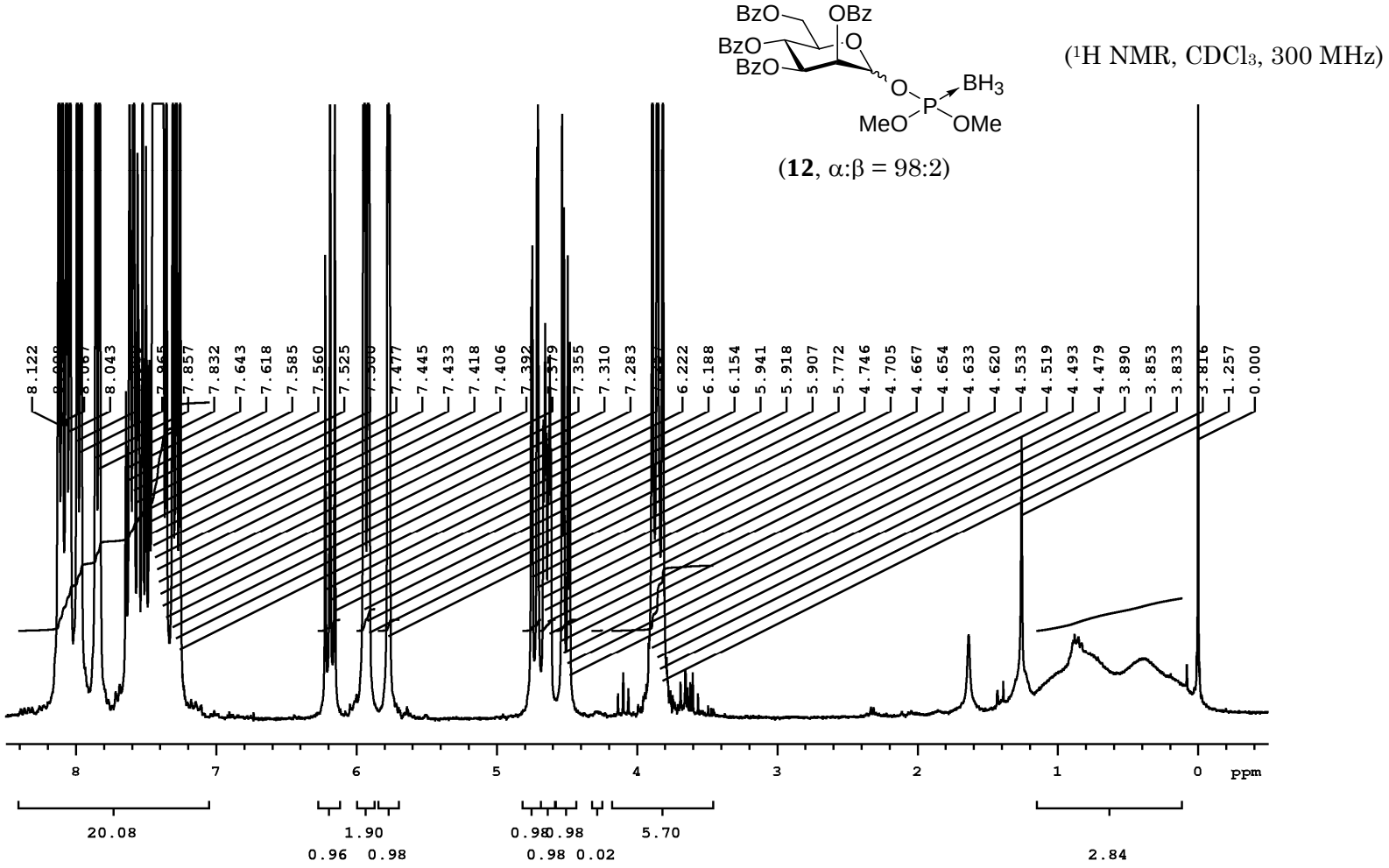




(**11**, α:β = 8:92)

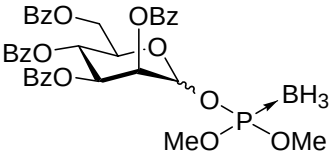
(^{31}P NMR, $CDCl_3$, 121.5 MHz)





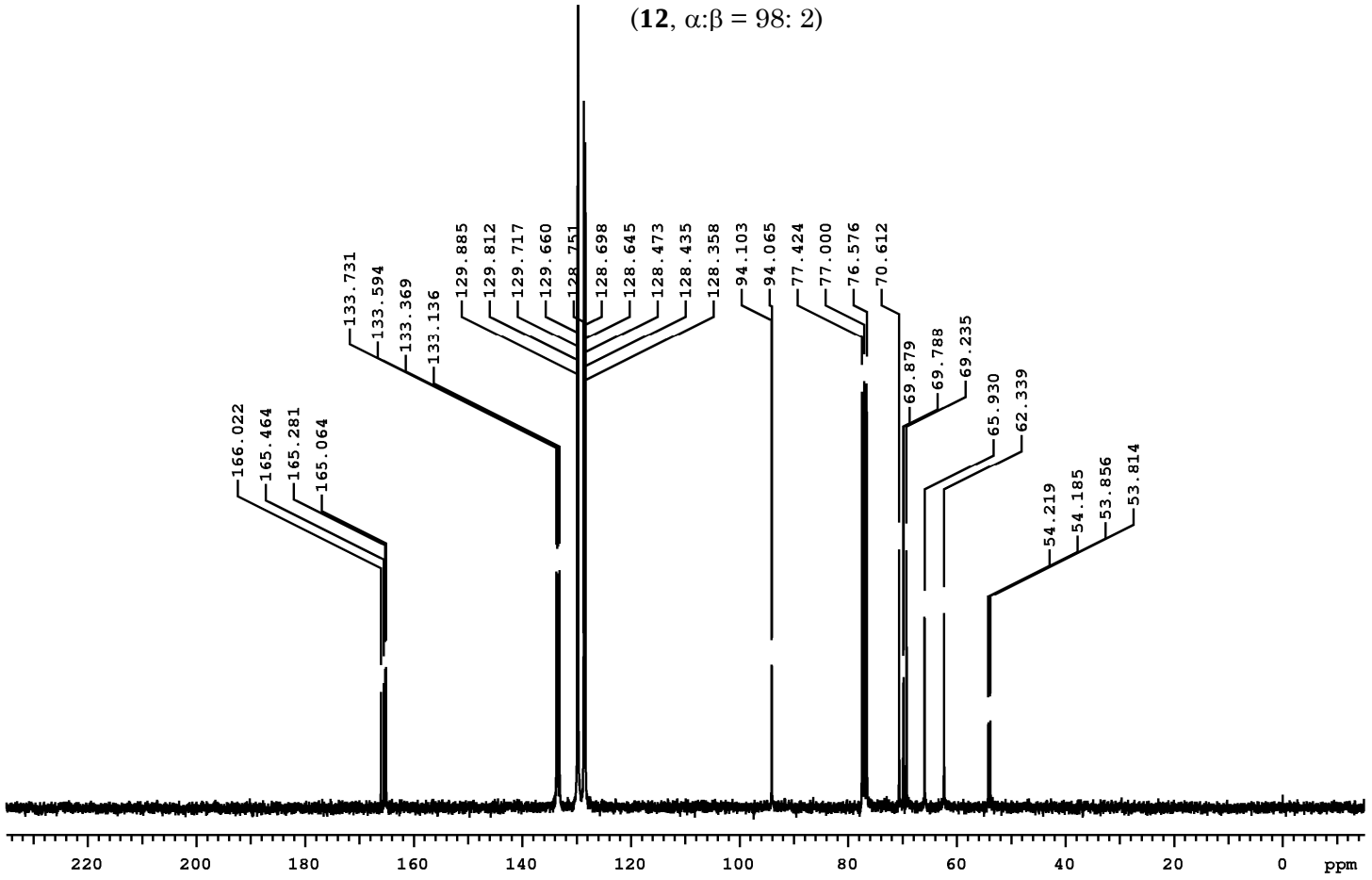
(**12**, α:β = 98:2)

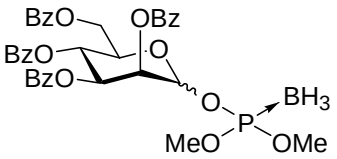
(^{1}H NMR, $CDCl_3$, 300 MHz)



(^{13}C NMR, $CDCl_3$, 75.5 MHz)

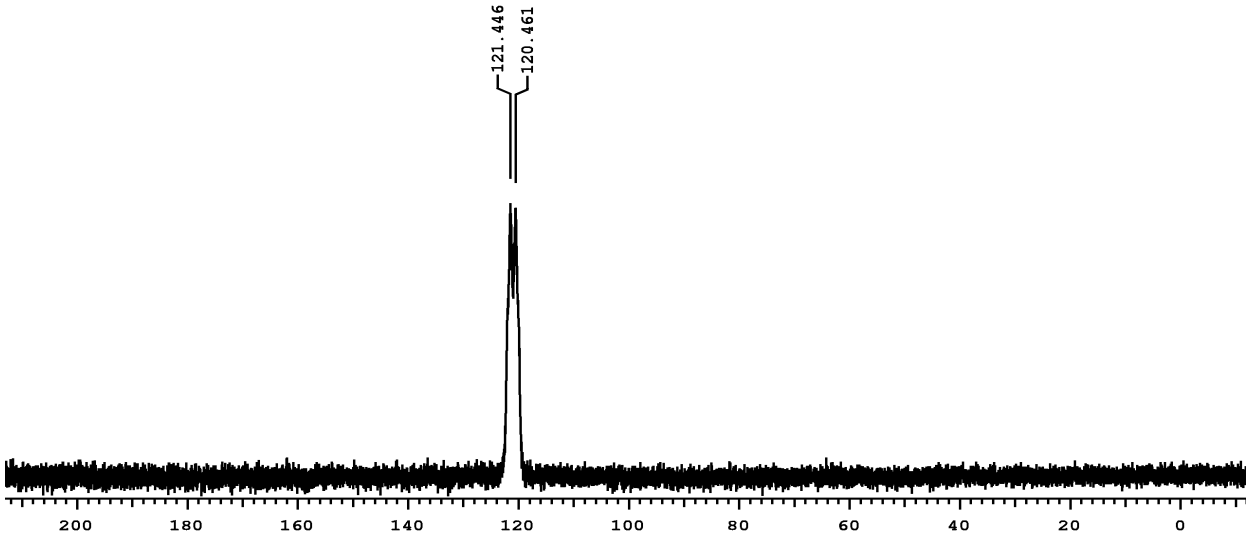
(**12**, α:β = 98: 2)

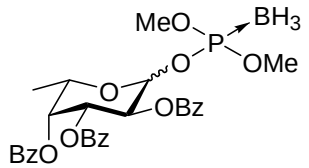




(^{31}P NMR, $CDCl_3$, 121.5 MHz)

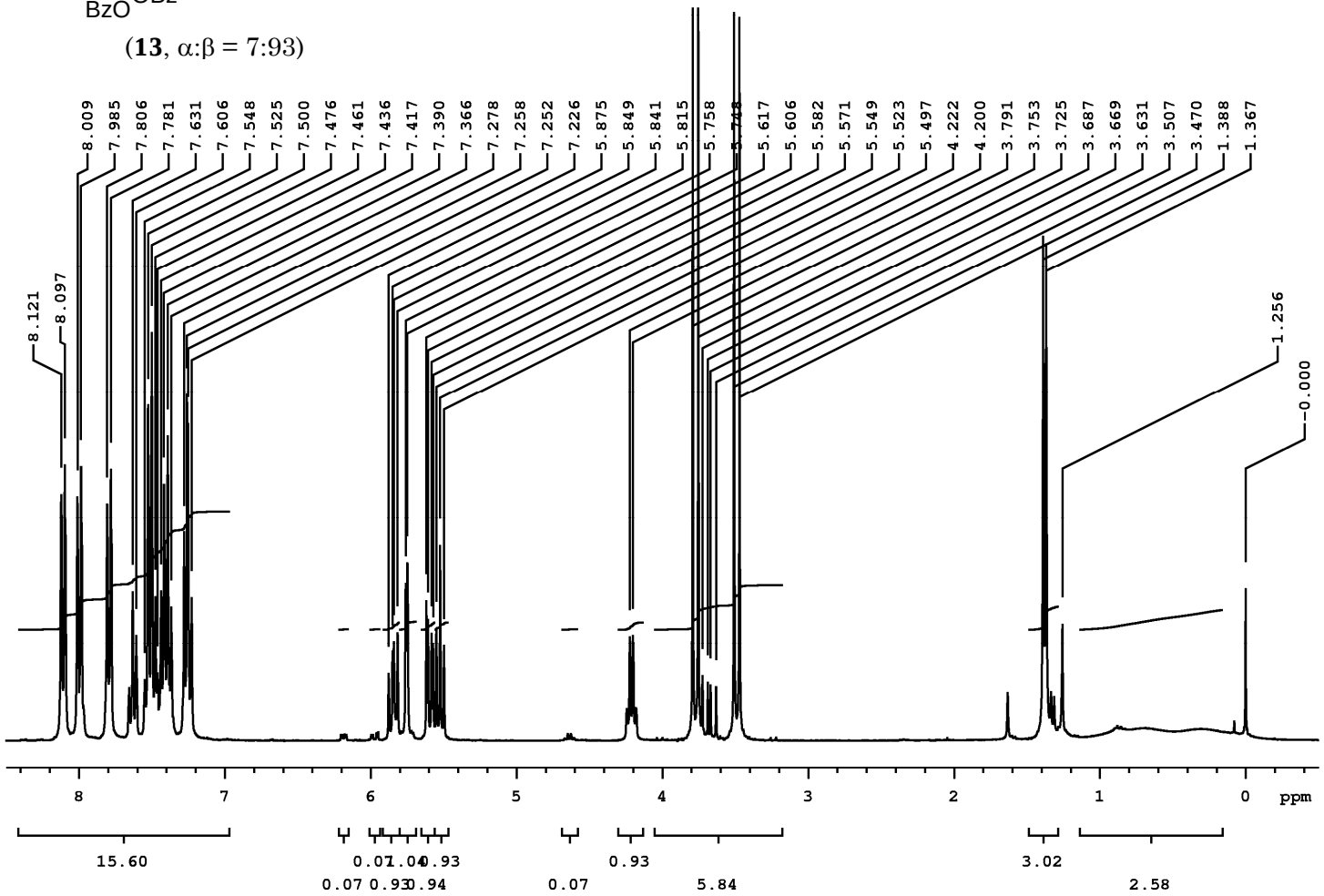
(**12**, α:β = 98: 2)

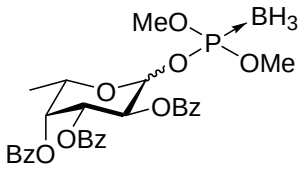




(**13**, α:β = 7:93)

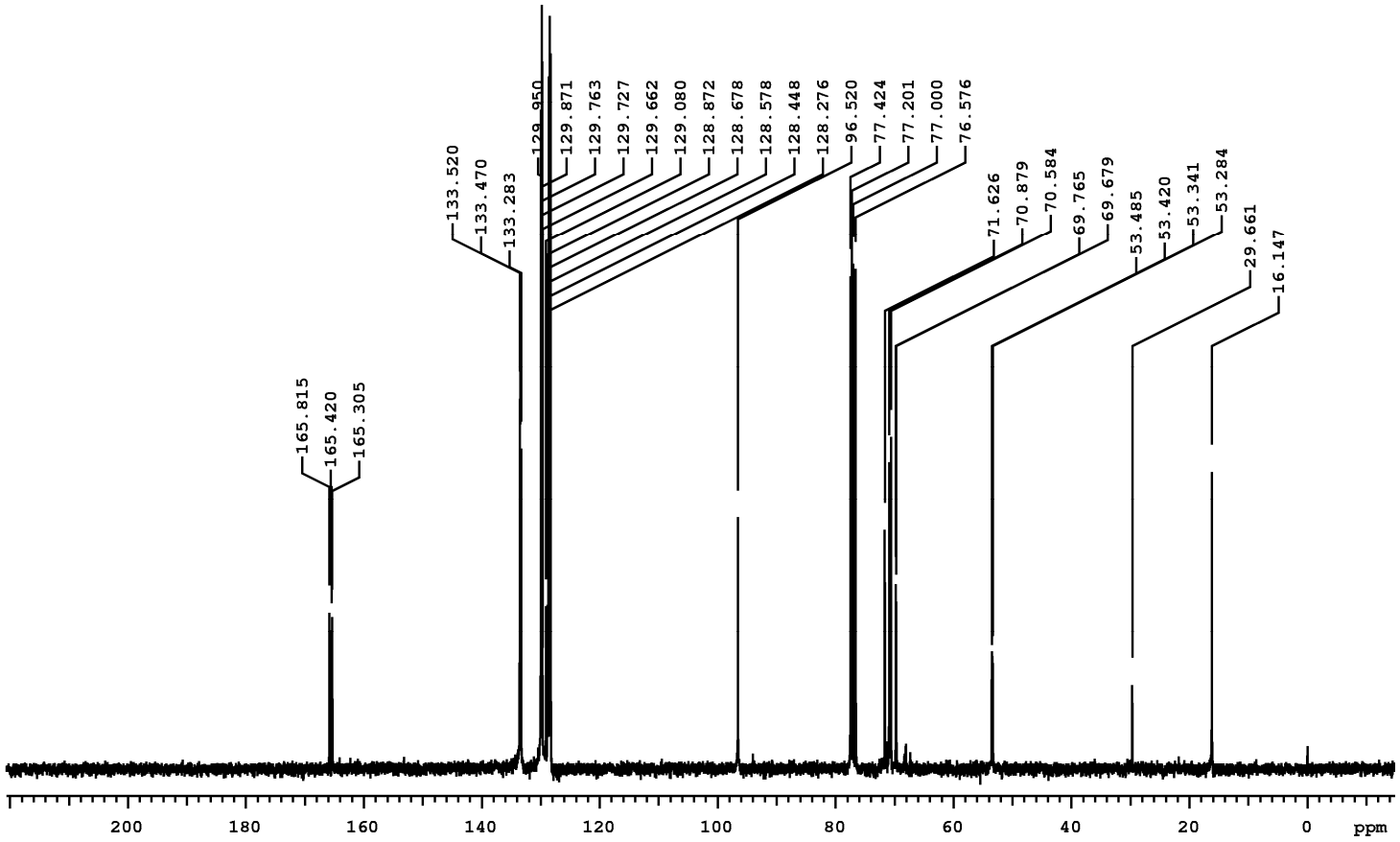
(¹H NMR, $CDCl_3$, 300 MHz)

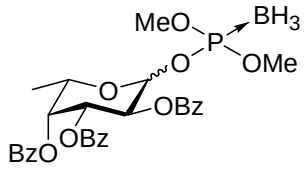




(^{13}C NMR, $CDCl_3$, 75. 5 MHz)

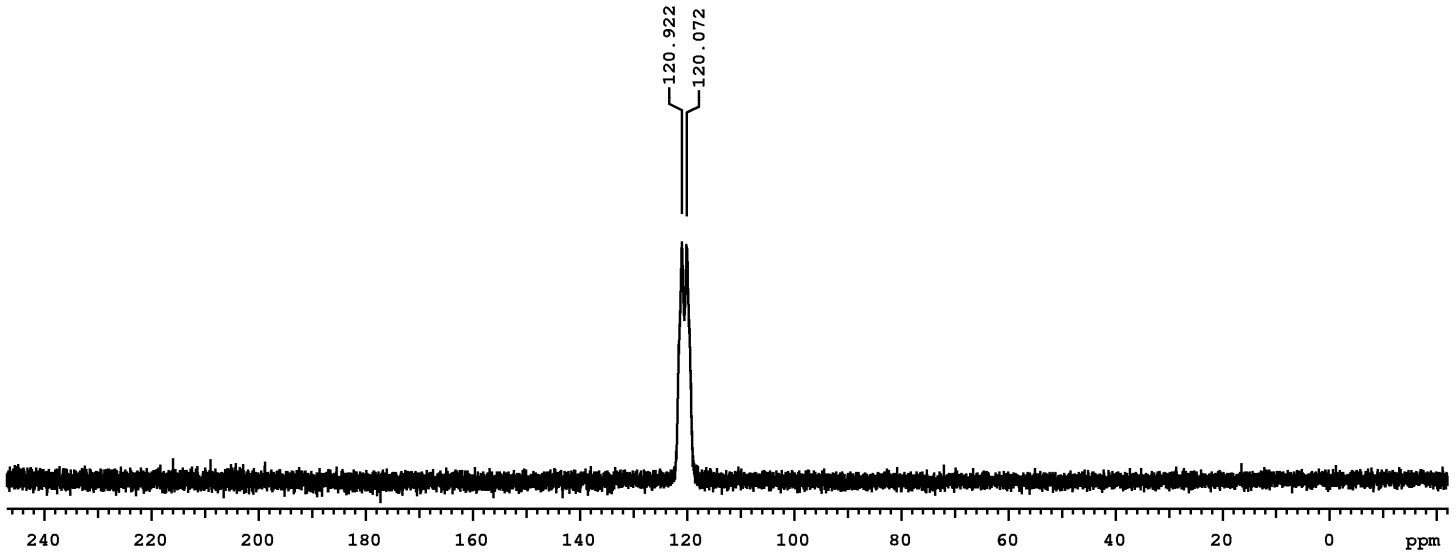
(**13**, α:β = 7:93)

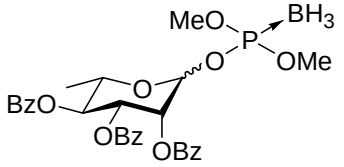




(**13**, α:β = 7:93)

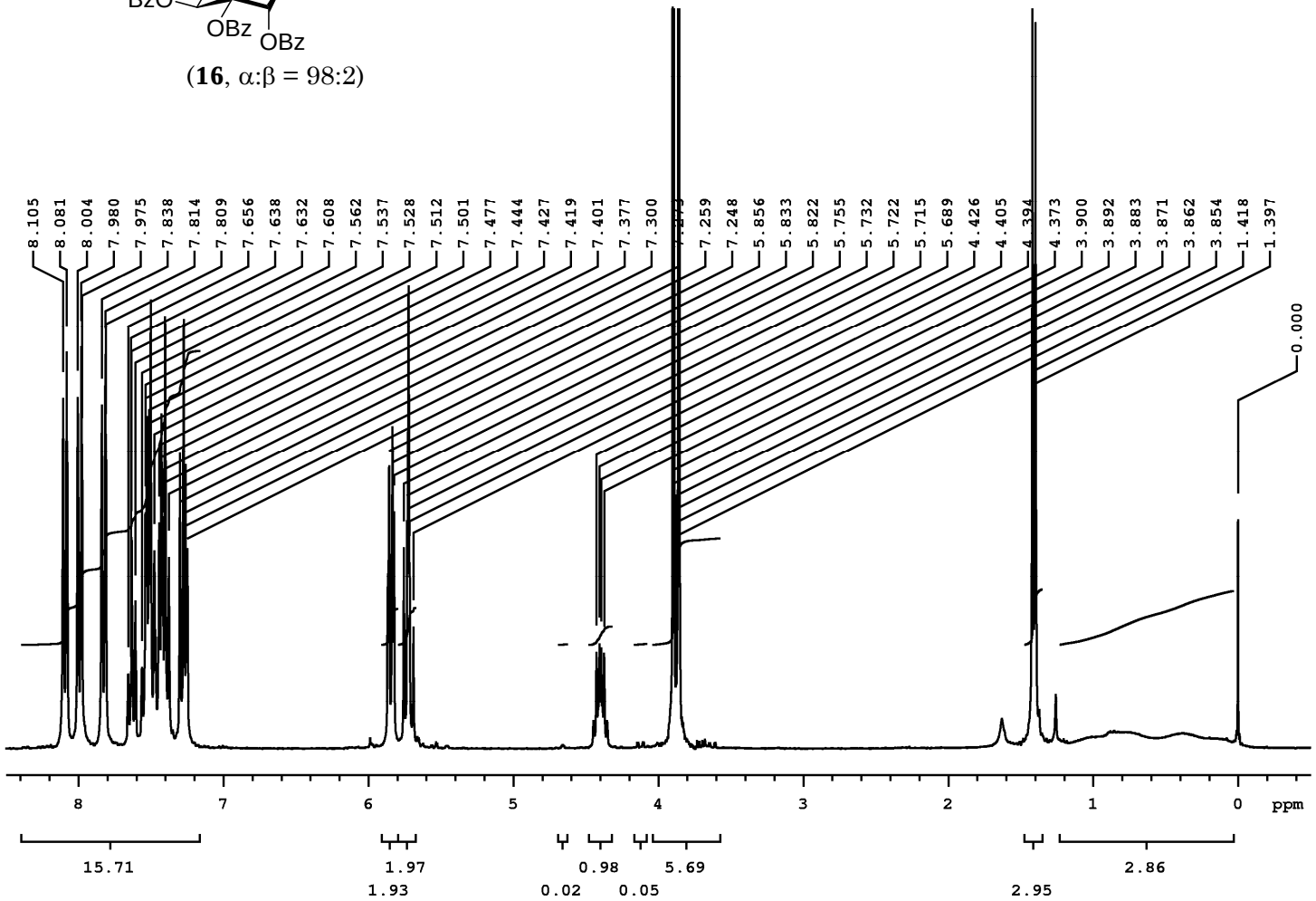
(^{31}P NMR, $CDCl_3$, 121.5 MHz)

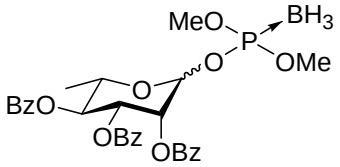




(**16**, α:β = 98:2)

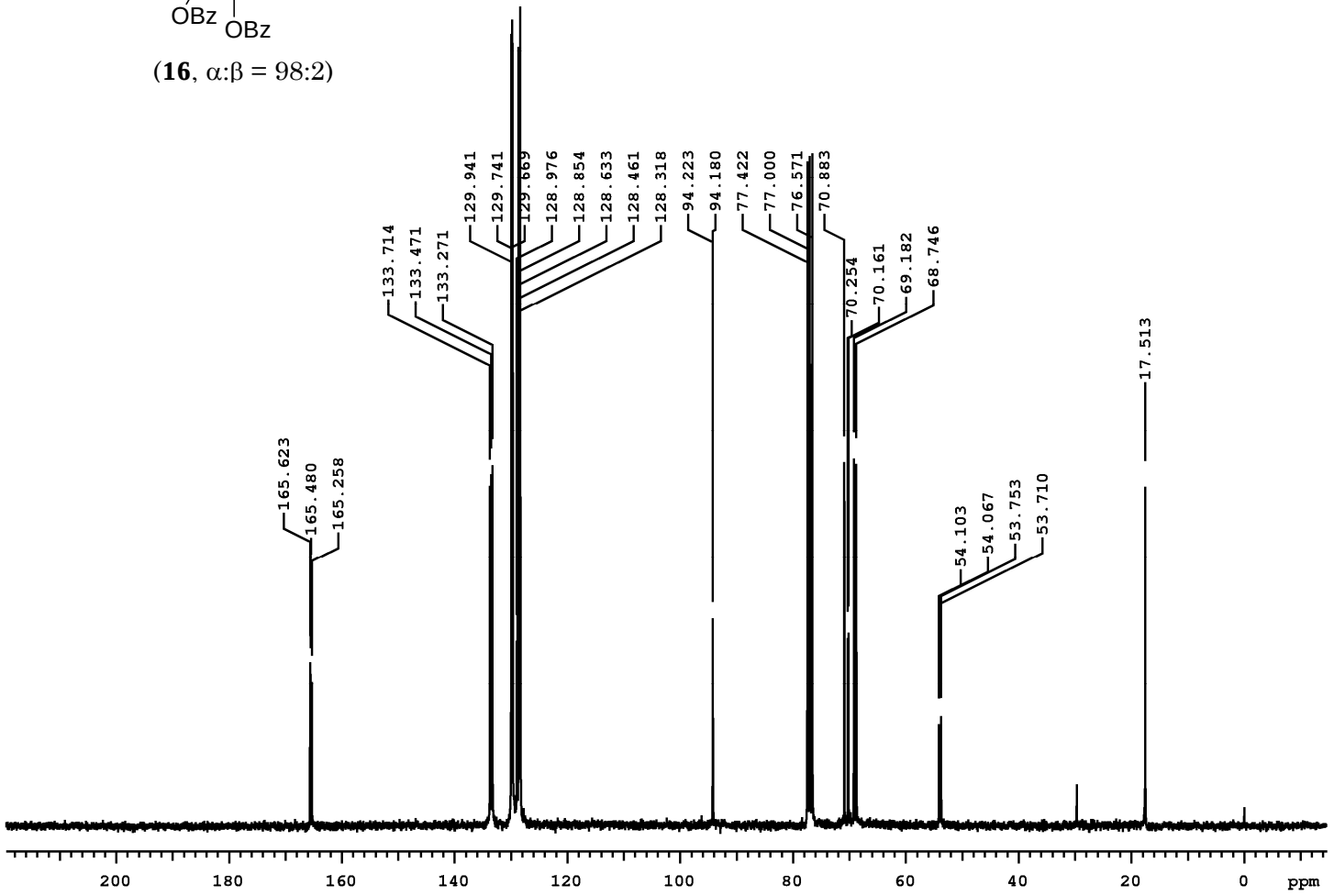
(^{1}H NMR, $CDCl_3$, 300 MHz)

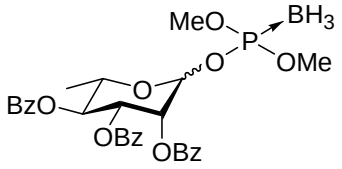




(**16**, α:β = 98:2)

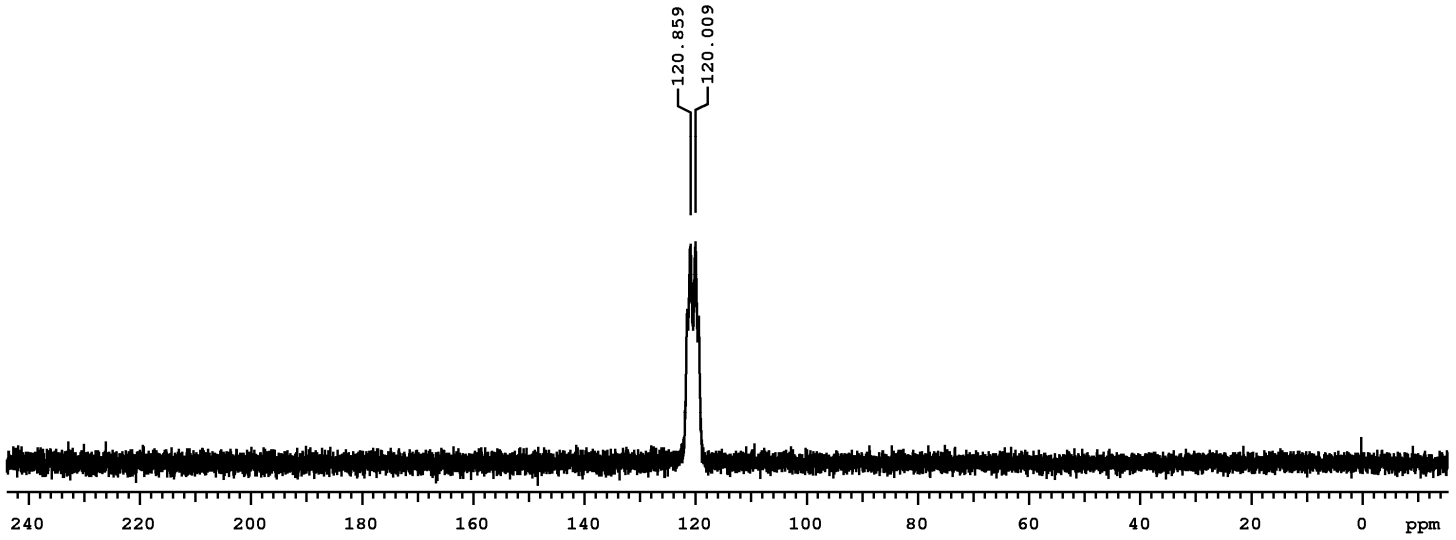
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

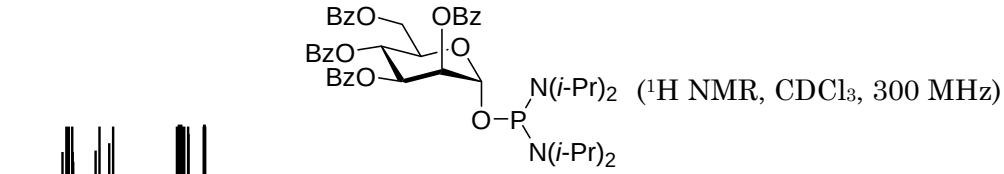




(**16**, α:β = 98:2)

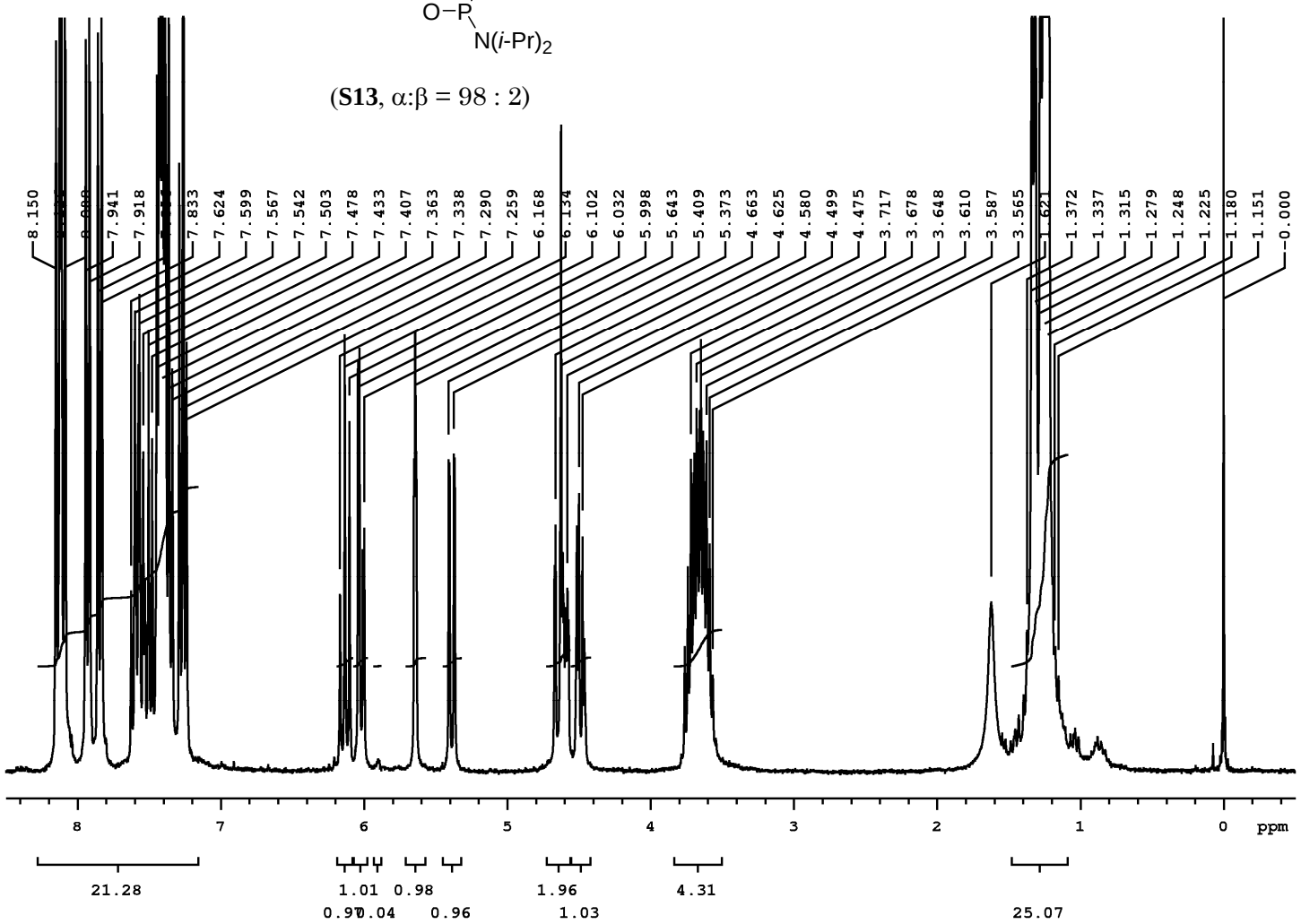
(^{31}P NMR, $CDCl_3$, 121.5 MHz)

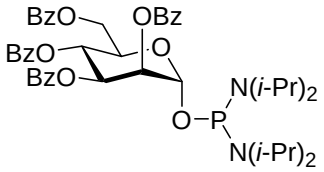




(^{1}H NMR, $CDCl_3$, 300 MHz)

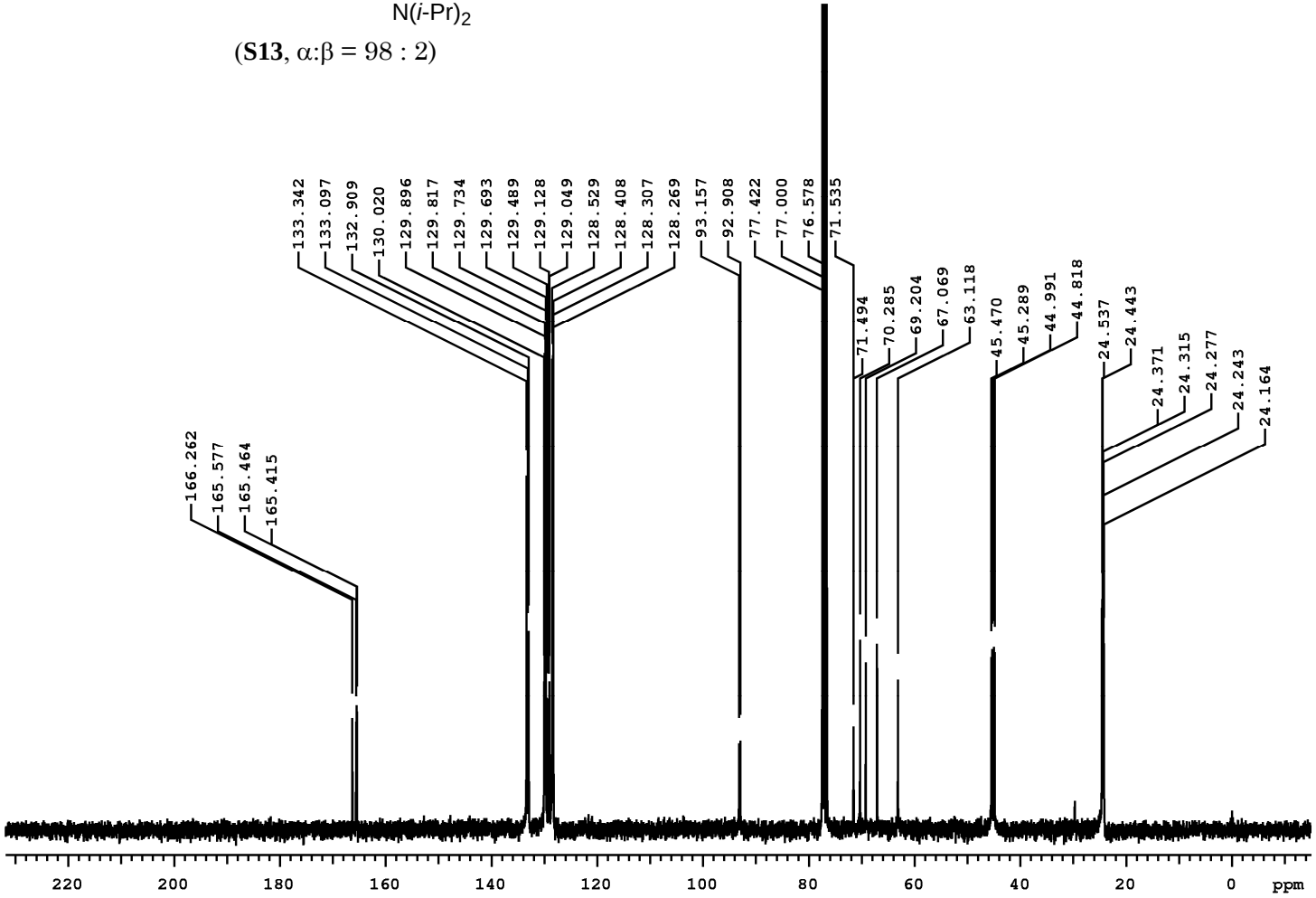
(**S13**, α:β = 98 : 2)

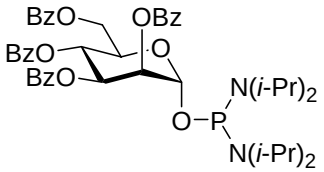




(^{13}C NMR, $CDCl_3$, 75.5 MHz)

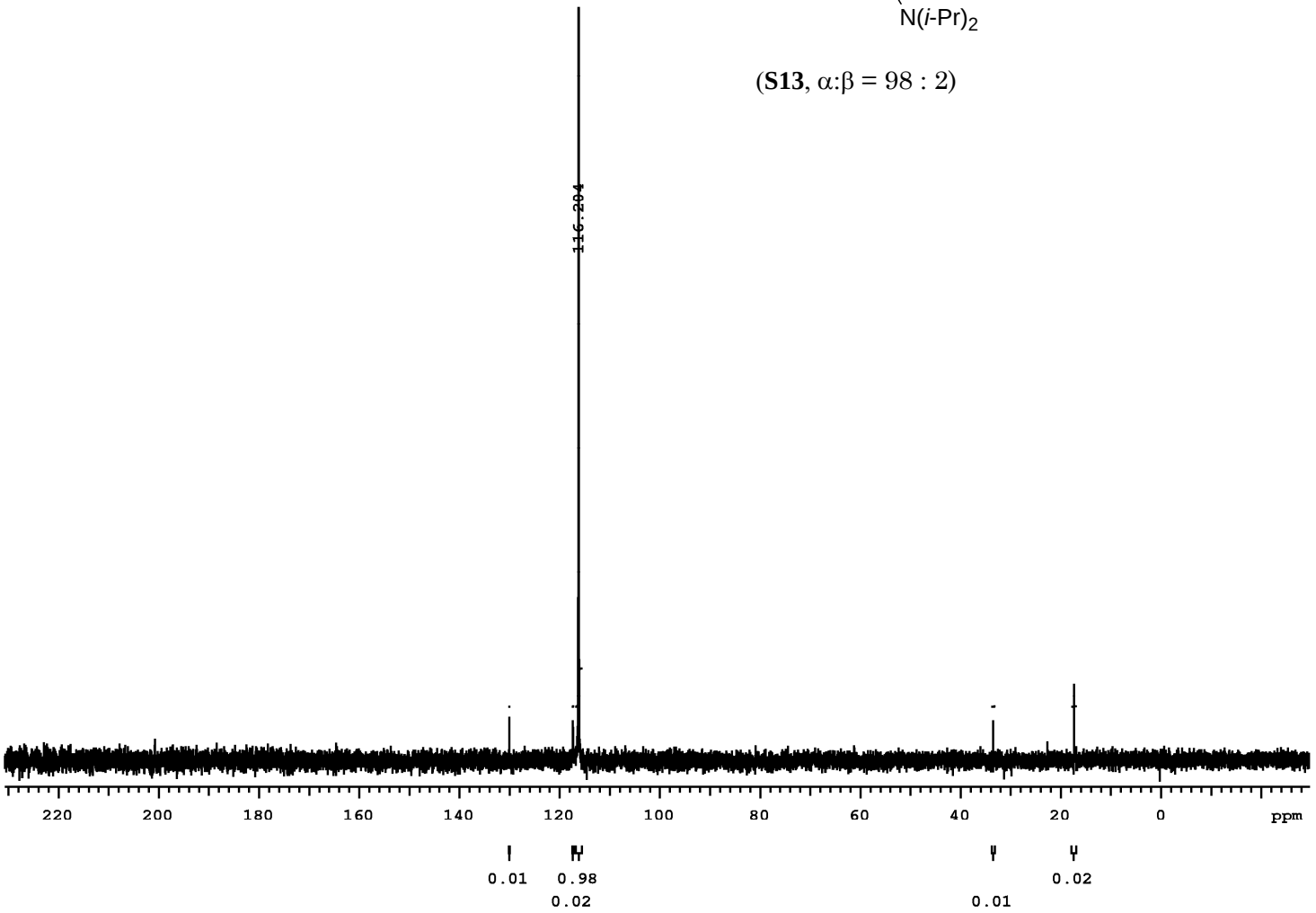
(**S13**, α:β = 98 : 2)

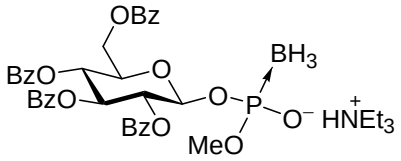




(^{31}P NMR, $CDCl_3$, 121.5 MHz)

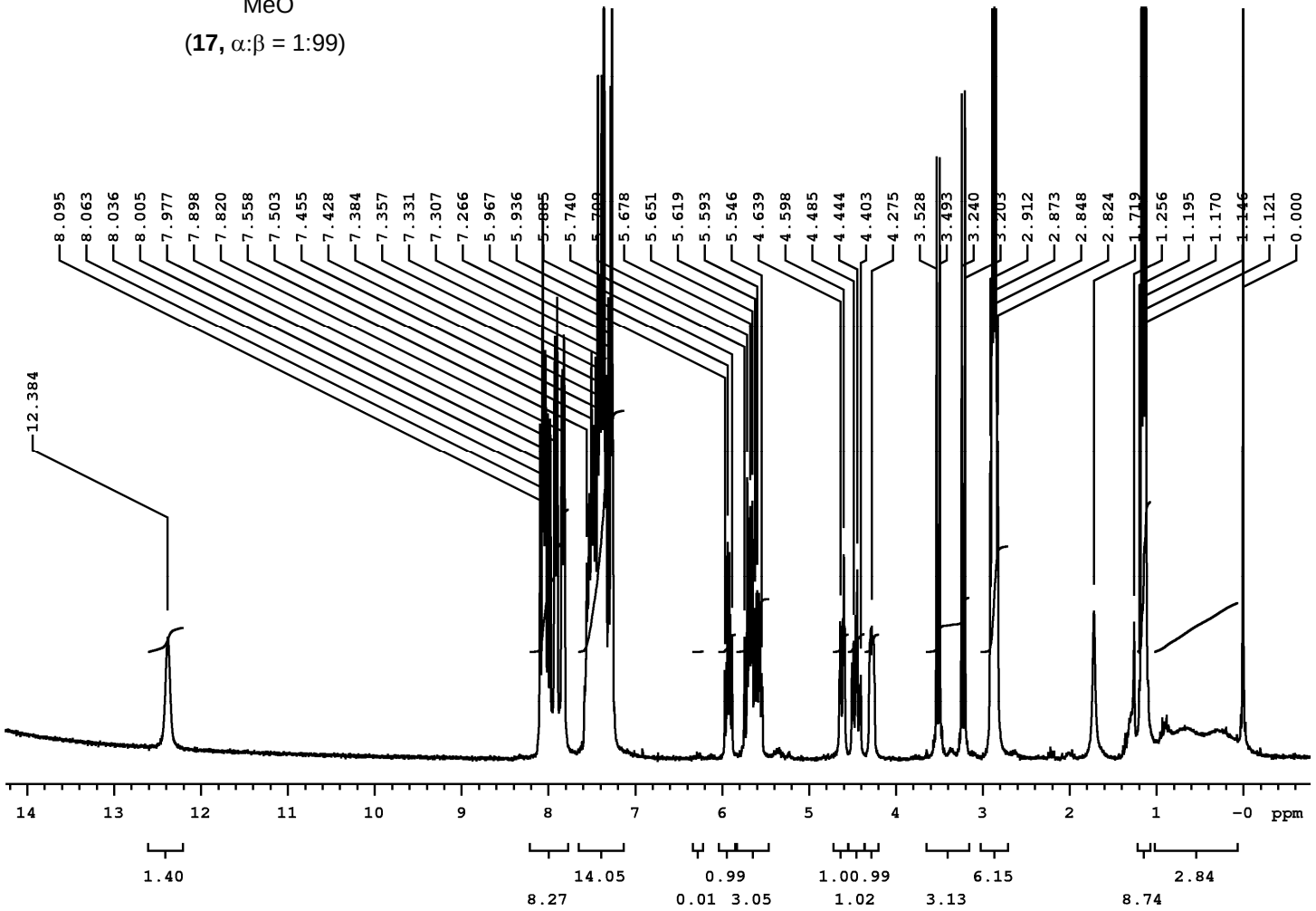
(**S13**, α:β = 98 : 2)

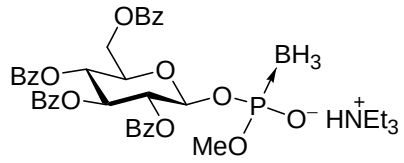




(**17,** α:β = 1:99)

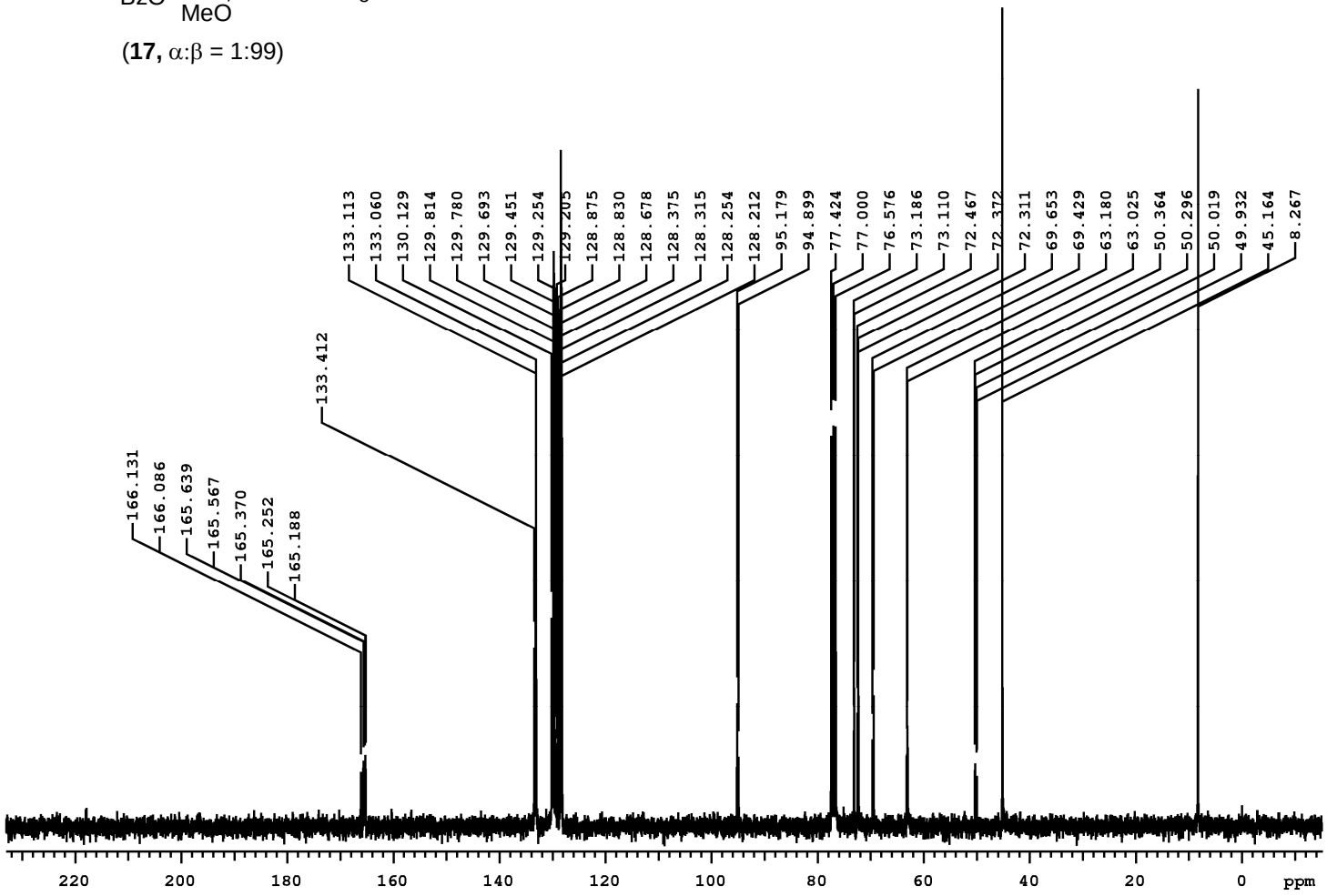
(^{1}H NMR, $CDCl_3$, 300 MHz)

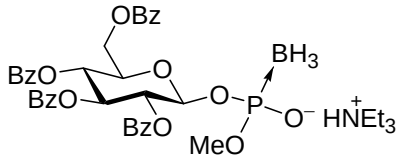




(**17,** α:β = 1:99)

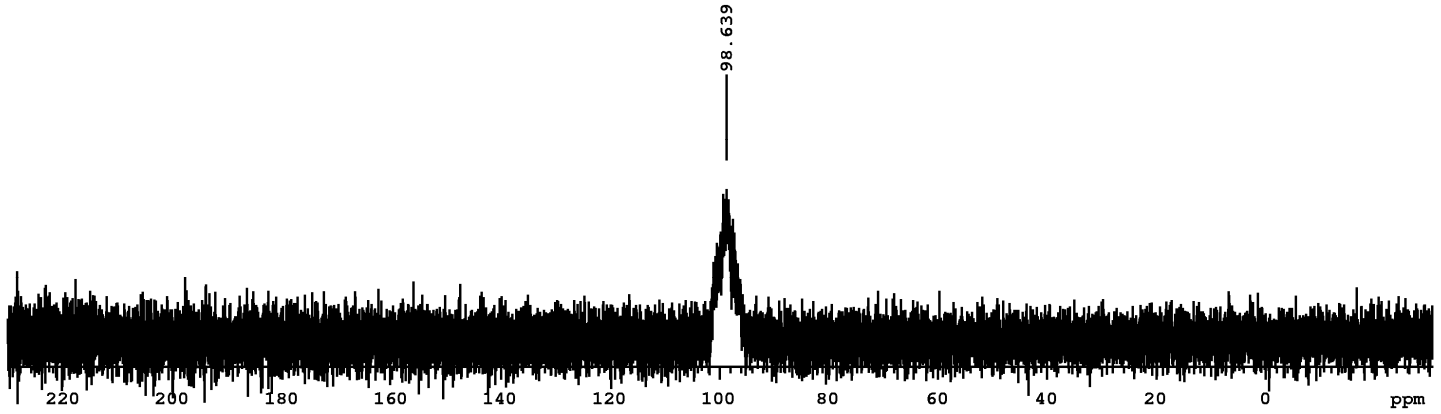
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

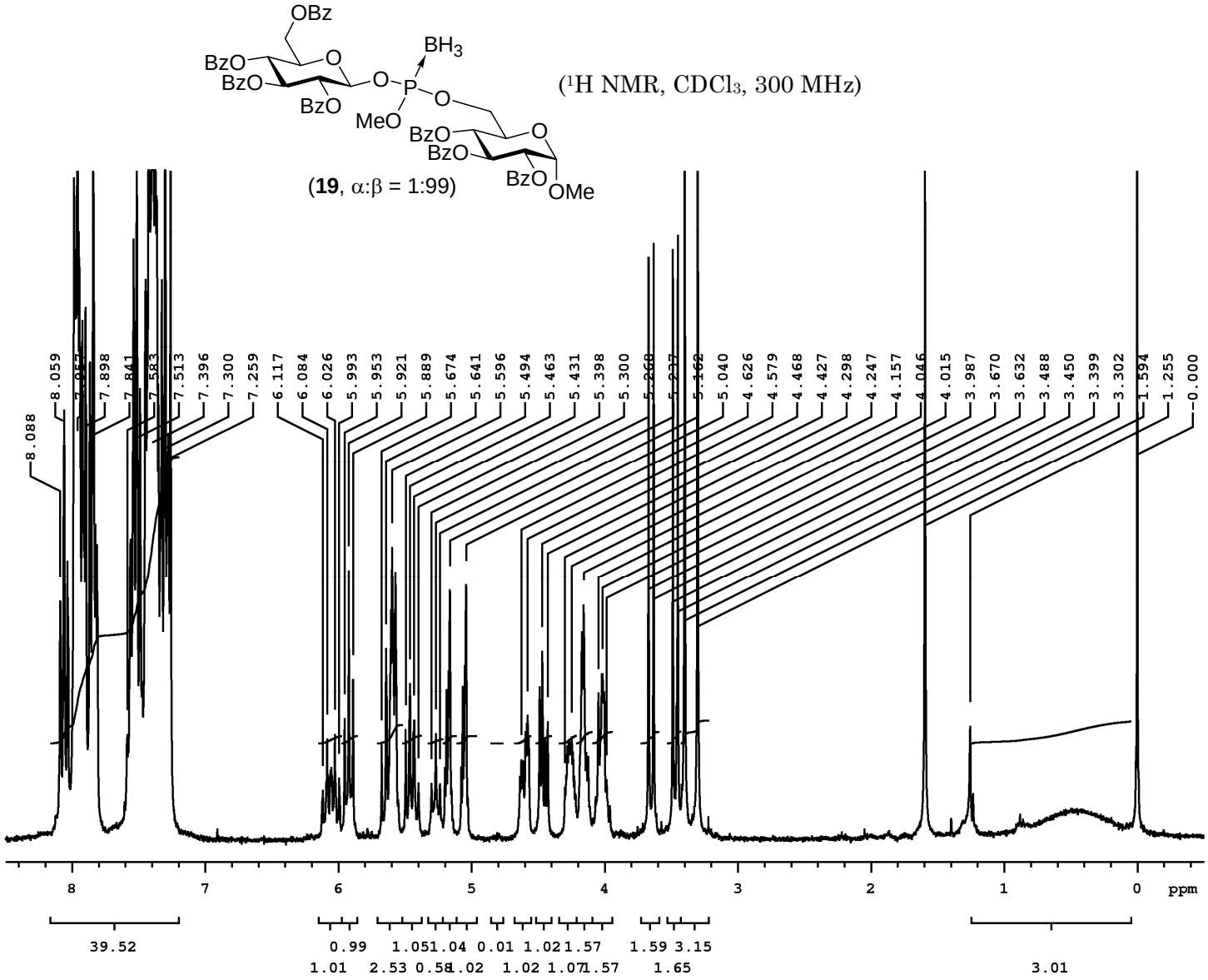




(**17,** α:β = 1:99)

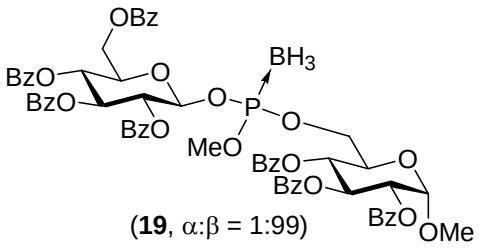
(^{31}P NMR, $CDCl_3$, 121.5 MHz)





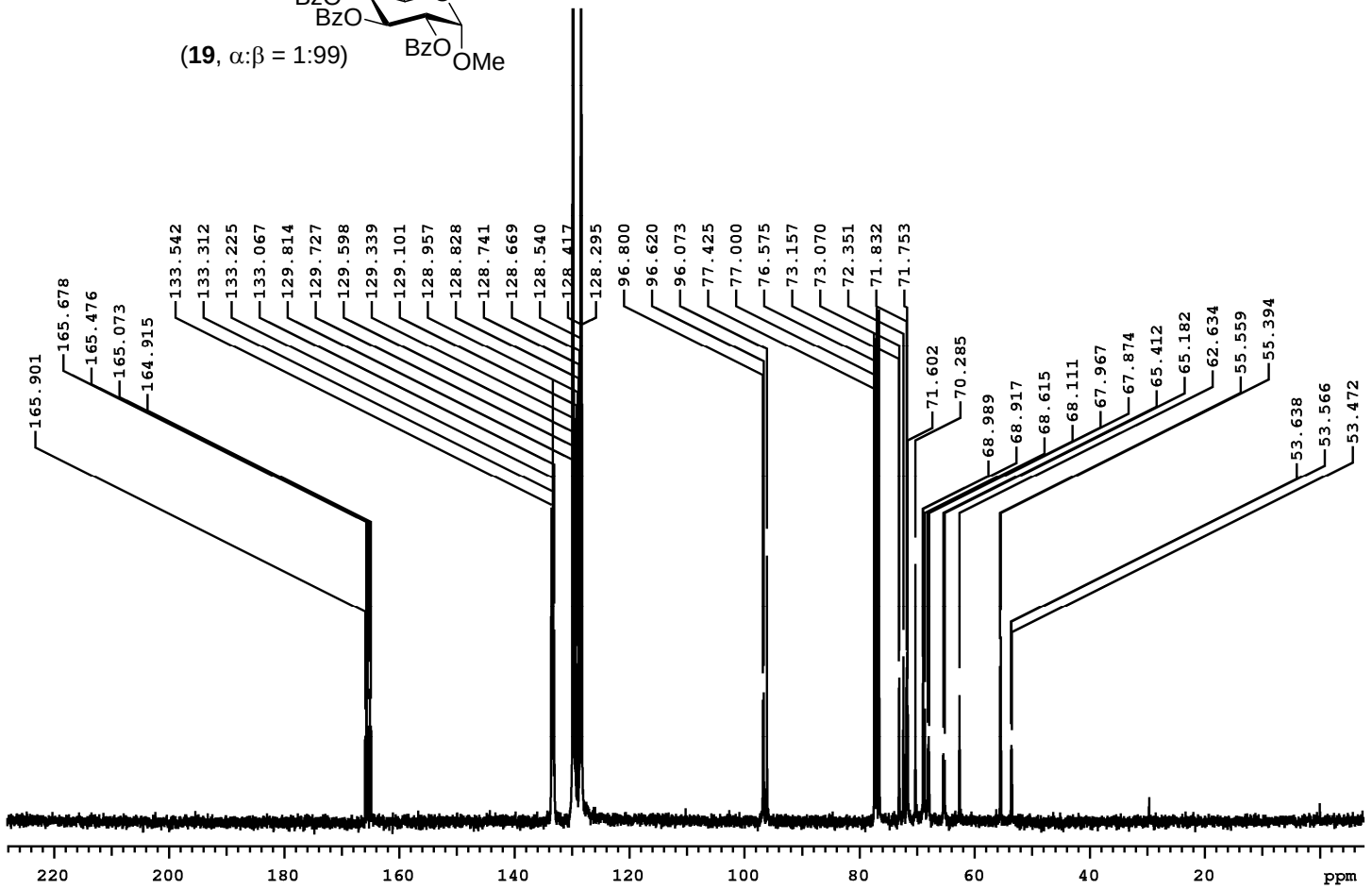
(**19**, α:β = 1:99)

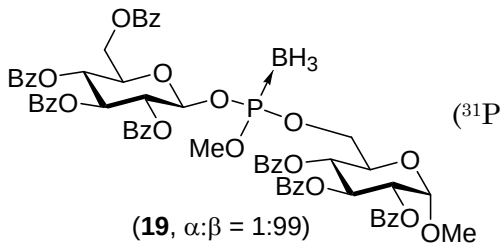
(^{1}H NMR, $CDCl_3$, 300 MHz)



(**19**, α:β = 1:99)

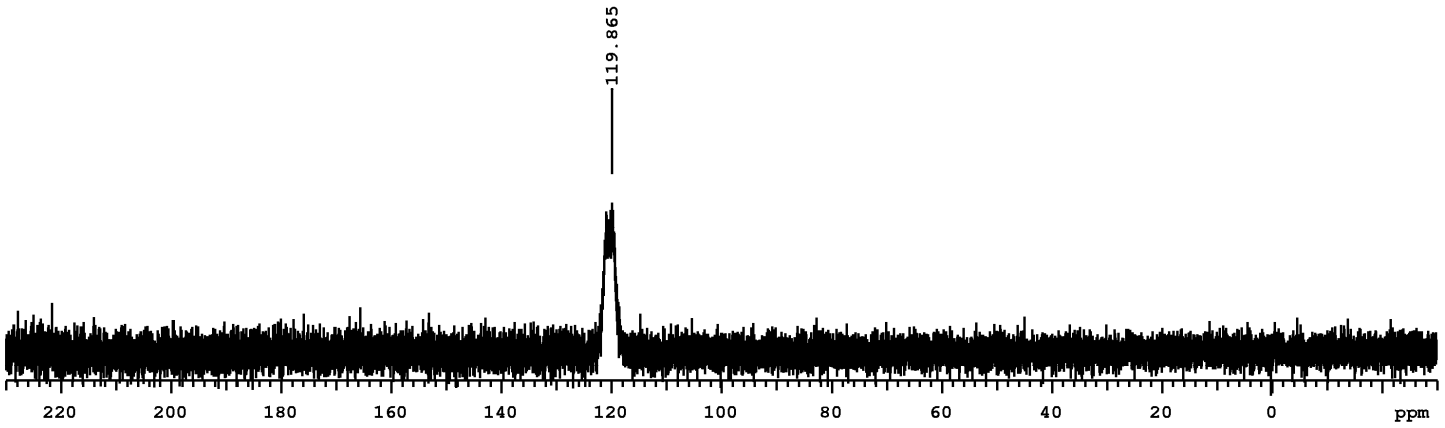
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

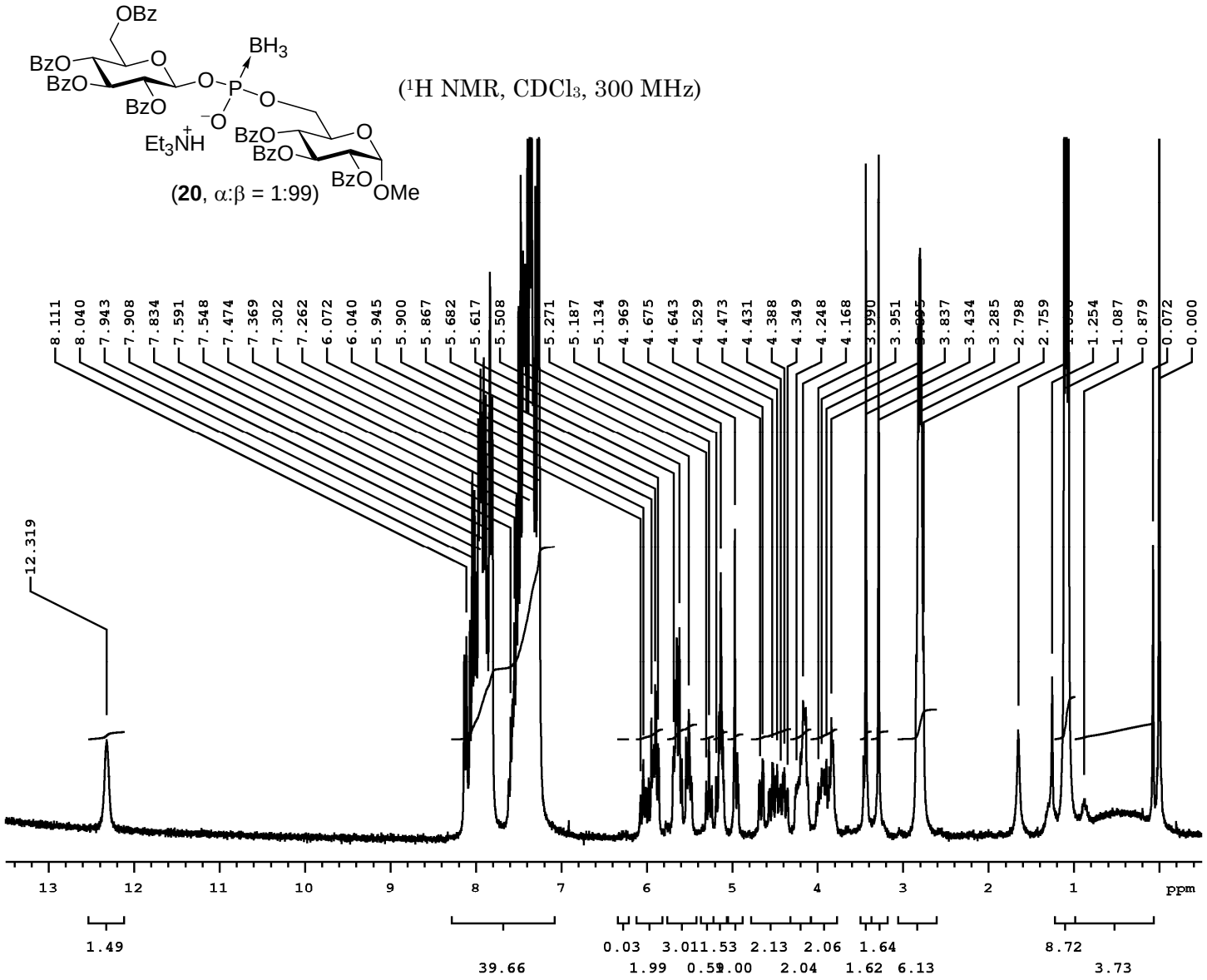


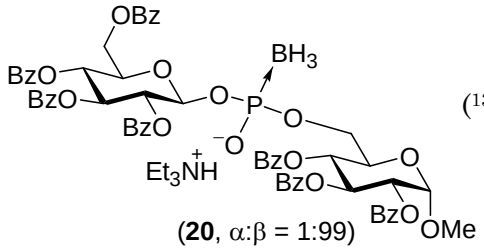


(**19**, α:β = 1:99)

(^{31}P NMR, $CDCl_3$, 121.5 MHz)

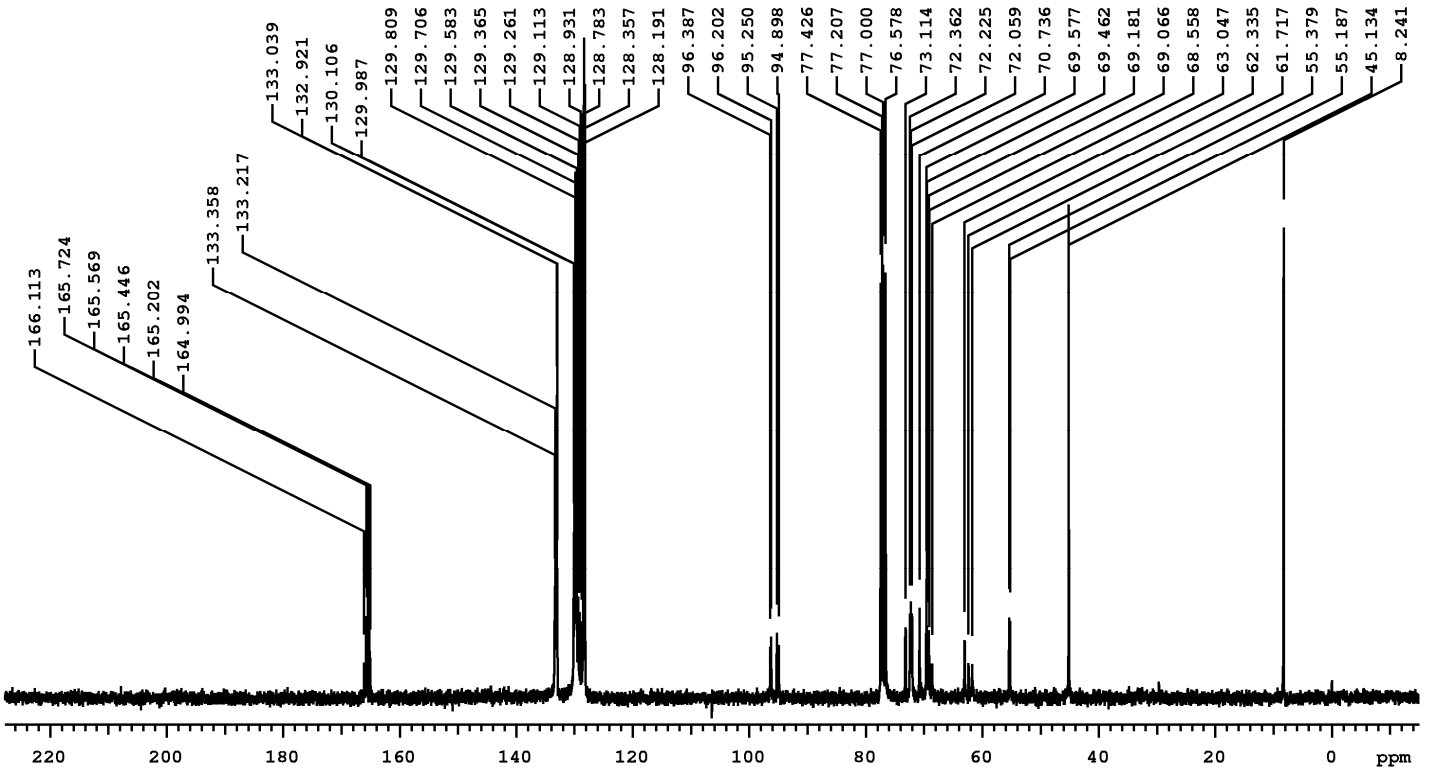


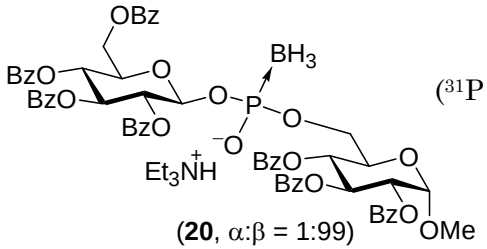

OBz
BzO
BzO
BzO
O
O
P
BH3
O
−O
Et3NH+
BzO
BzO
BzO
O
OMe
(20, α:β = 1:99)
(1H NMR, CDCl3, 300 MHz)
8.111
8.040
7.943
7.908
7.834
7.591
7.548
7.474
7.369
7.302
7.262
6.072
6.040
5.945
5.900
5.867
5.682
5.617
5.508
5.271
5.187
5.134
4.969
4.675
4.643
4.529
4.473
4.431
4.388
4.349
4.248
4.168
3.990
3.951
3.837
3.434
3.285
2.798
2.759
1.254
1.087
0.879
0.072
0.000
12.319
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
1.49
39.66
0.03
1.99
3.01
0.59
1.53
1.00
2.13
2.04
2.06
1.62
1.64
6.13
8.72
3.73



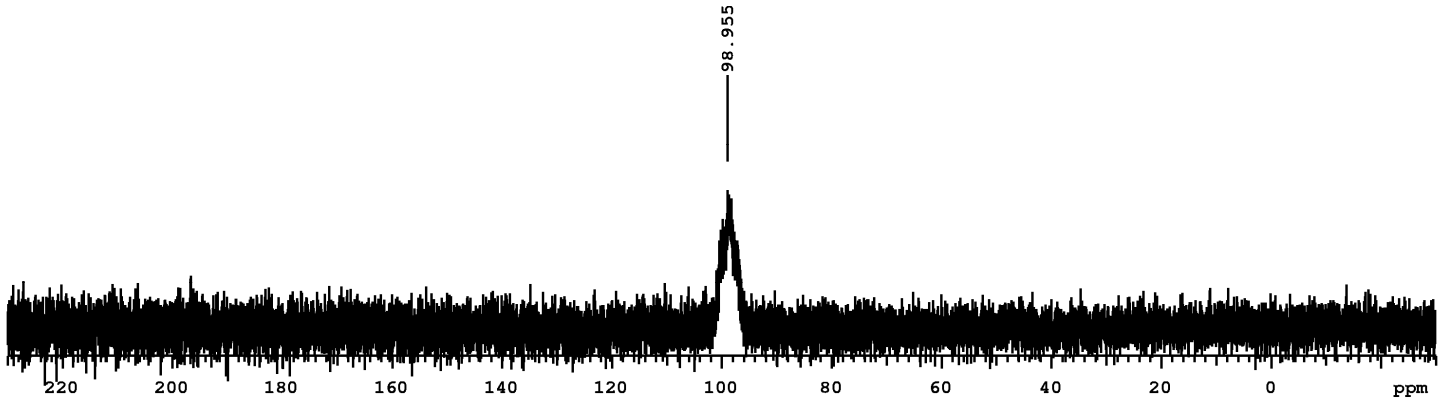
(**20**, α:β = 1:99)

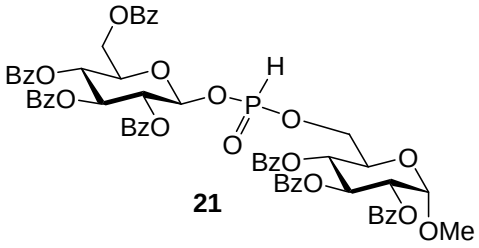
(^{13}C NMR, $CDCl_3$, 75.5 MHz)





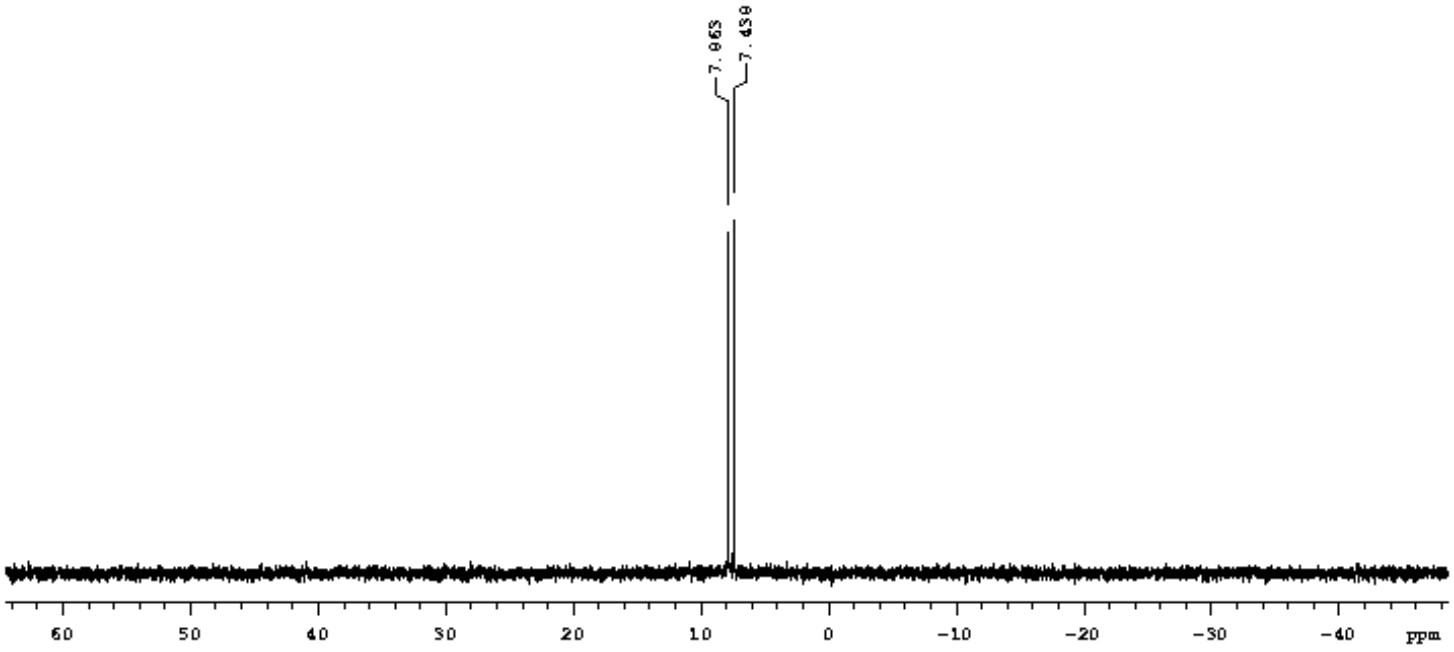
(**20**, α:β = 1:99) (^{31}P NMR, $CDCl_3$, 121.5 MHz)

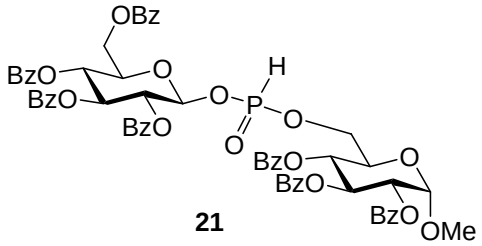




21

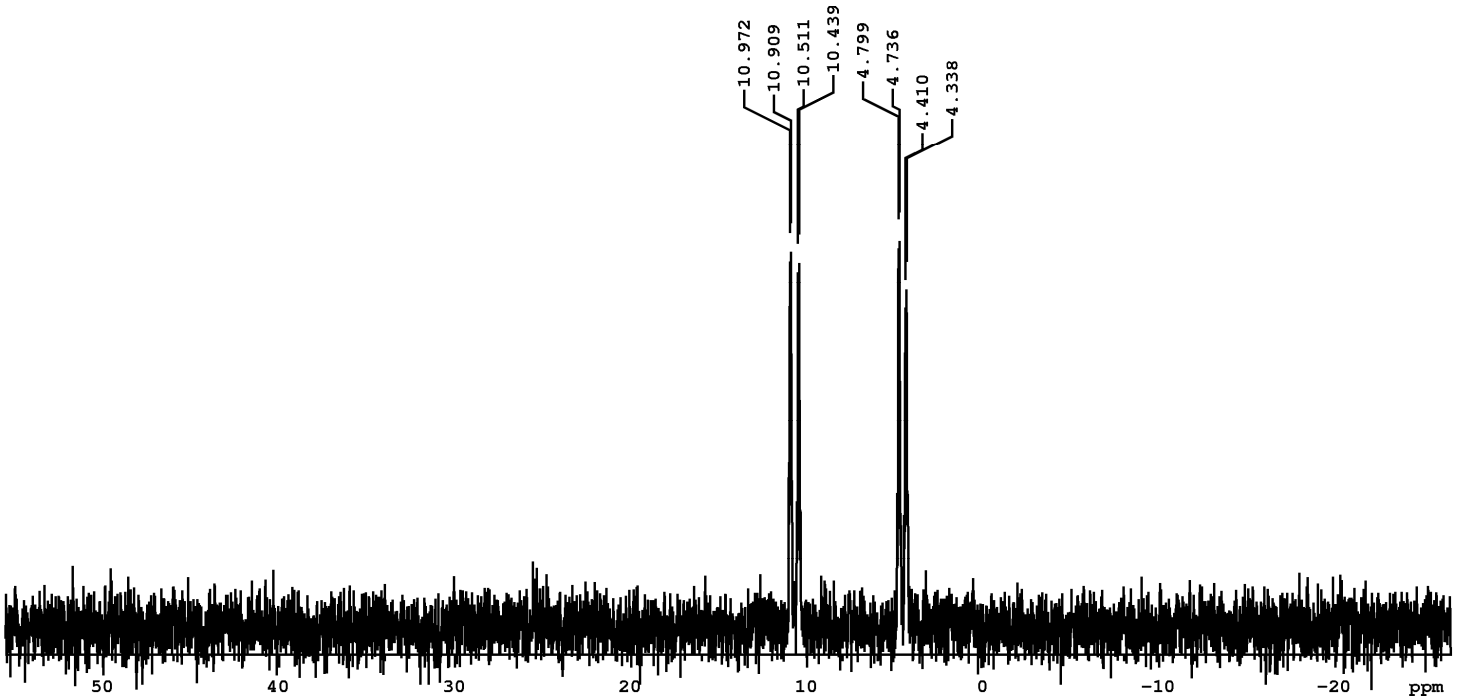
(^{31}P NMR, $CDCl_3$, 121.5 MHz, P–H decoupling)

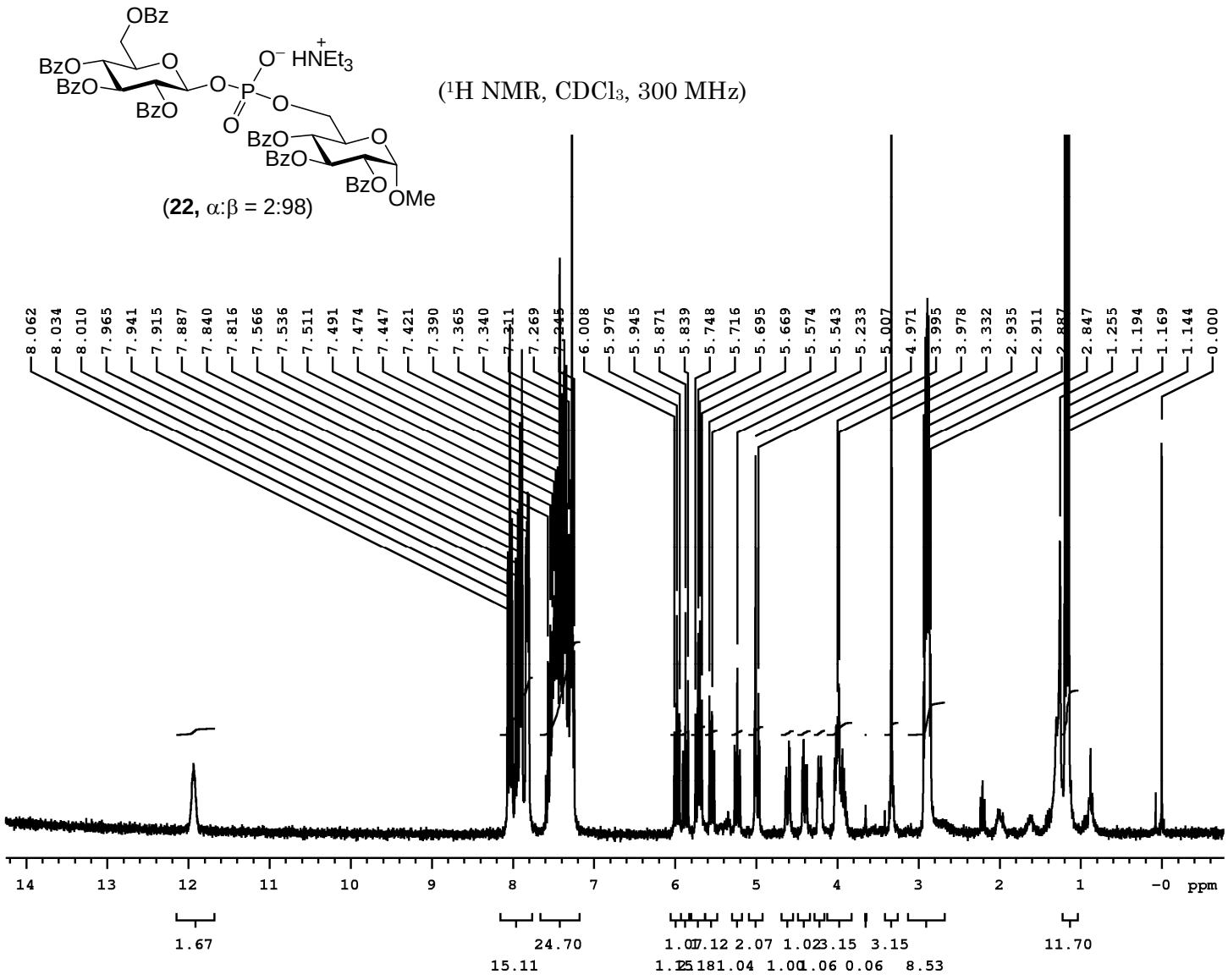


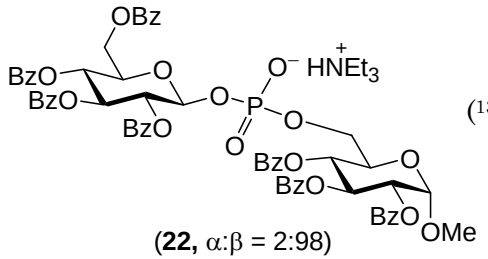


21

(^{31}P NMR, $CDCl_3$, 121.5 MHz, P–H coupling)

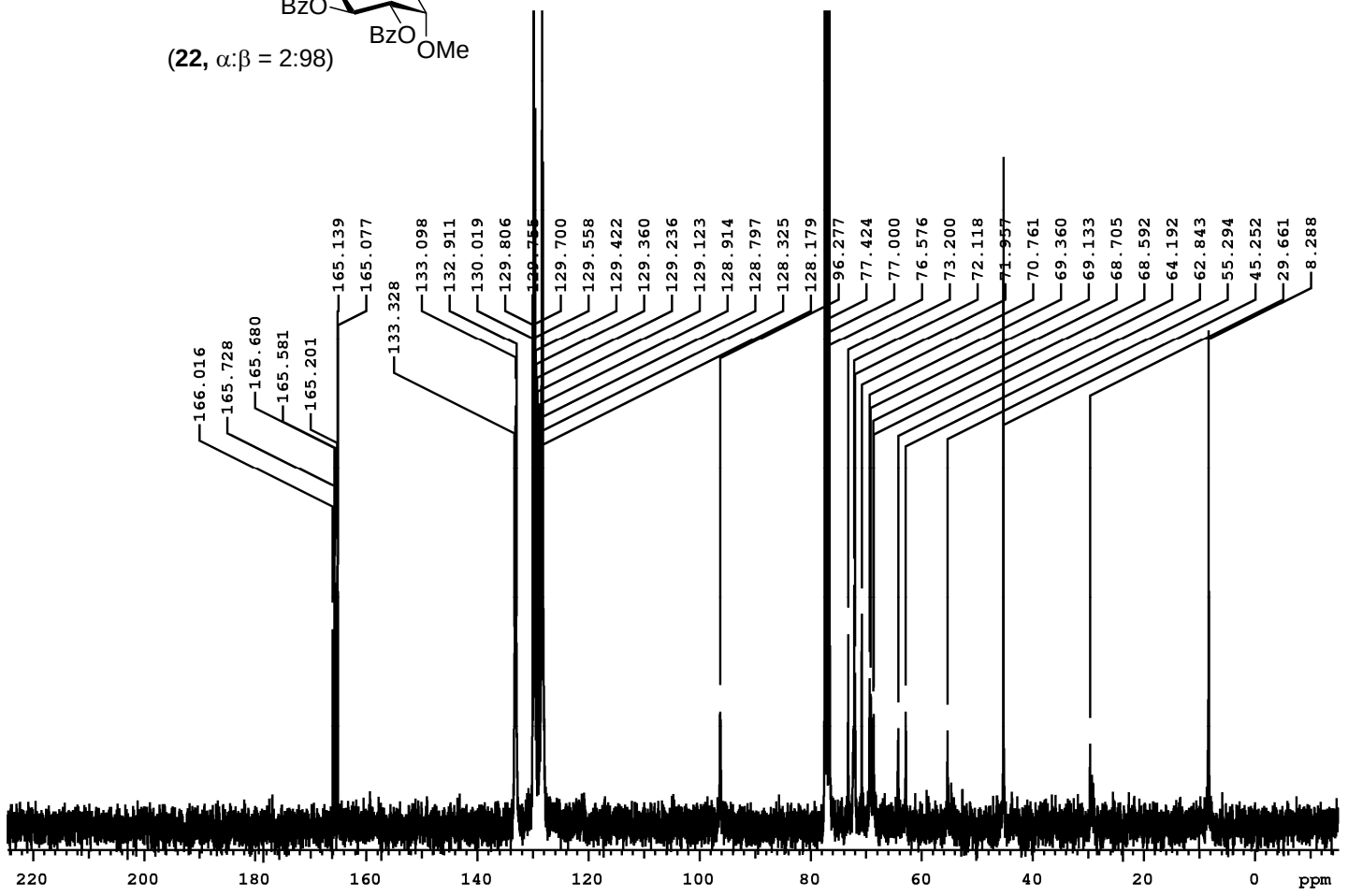


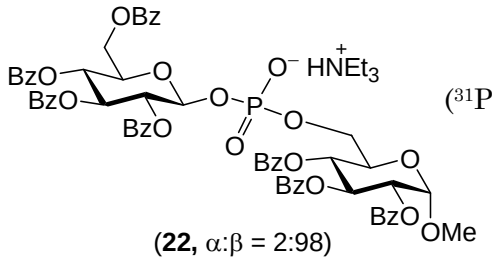

OBz
BzO
BzO
BzO
O
O
O⁻ HNEt3+
P
O
O
BzO
BzO
BzO
O
OMe
(22, α:β = 2:98)
(1H NMR, CDCl3, 300 MHz)
8.062
8.034
8.010
7.965
7.941
7.915
7.887
7.840
7.816
7.566
7.536
7.511
7.491
7.474
7.447
7.421
7.390
7.365
7.340
7.311
7.269
7.245
6.008
5.976
5.945
5.871
5.839
5.748
5.716
5.695
5.669
5.574
5.543
5.233
5.007
4.971
3.995
3.978
3.332
2.935
2.911
2.887
2.847
1.255
1.194
1.169
1.144
0.000
14
13
12
11
10
9
8
7
6
5
4
3
2
1
−0
ppm
1.67
15.11
24.70
1.07
7.12
2.07
1.02
3.15
3.15
11.70
1.25
18
1.04
1.00
1.06
0.06
8.53



(**22,** α:β = 2:98)

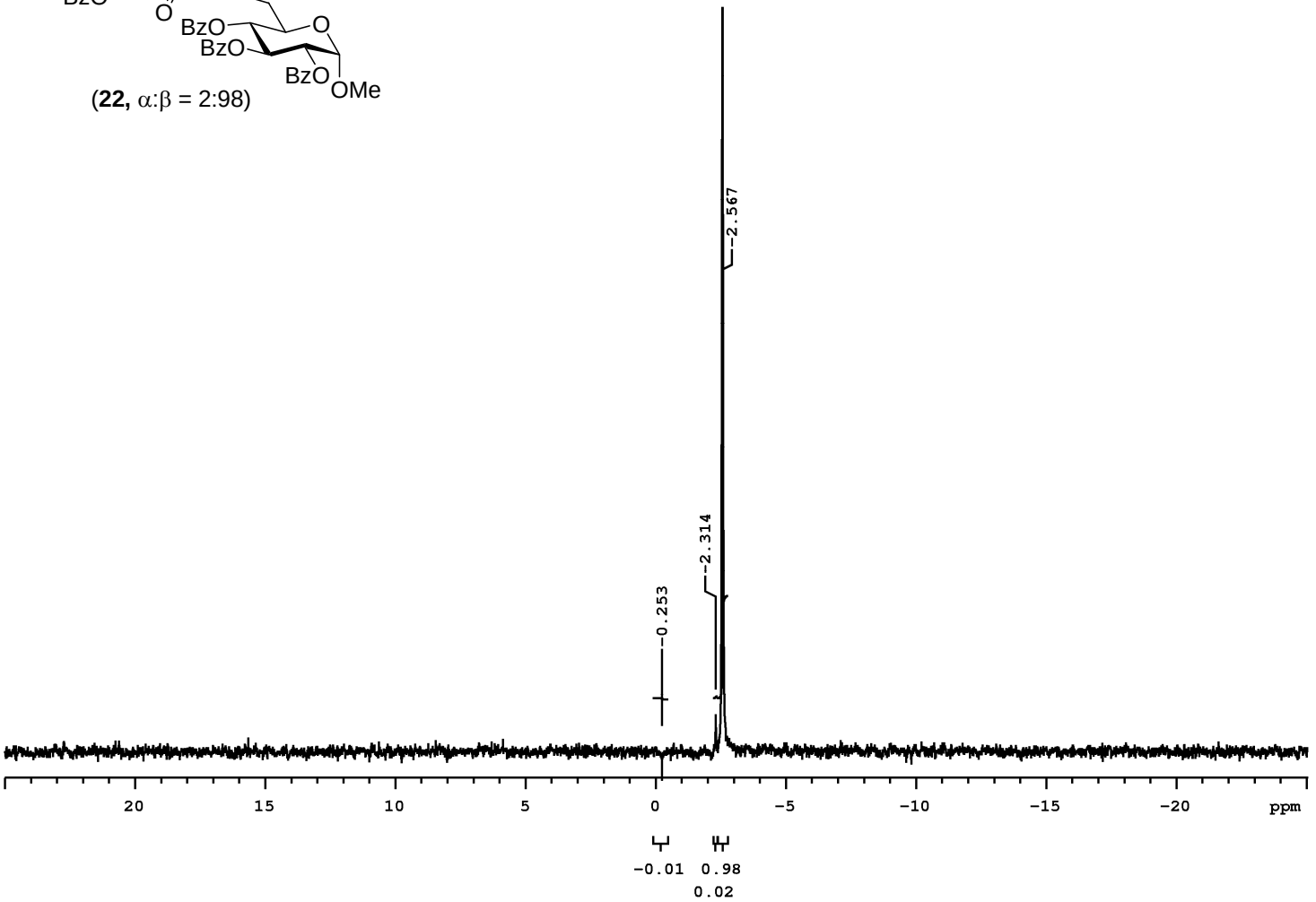
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

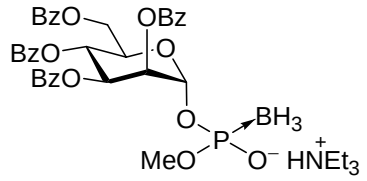




(**22,** α:β = 2:98)

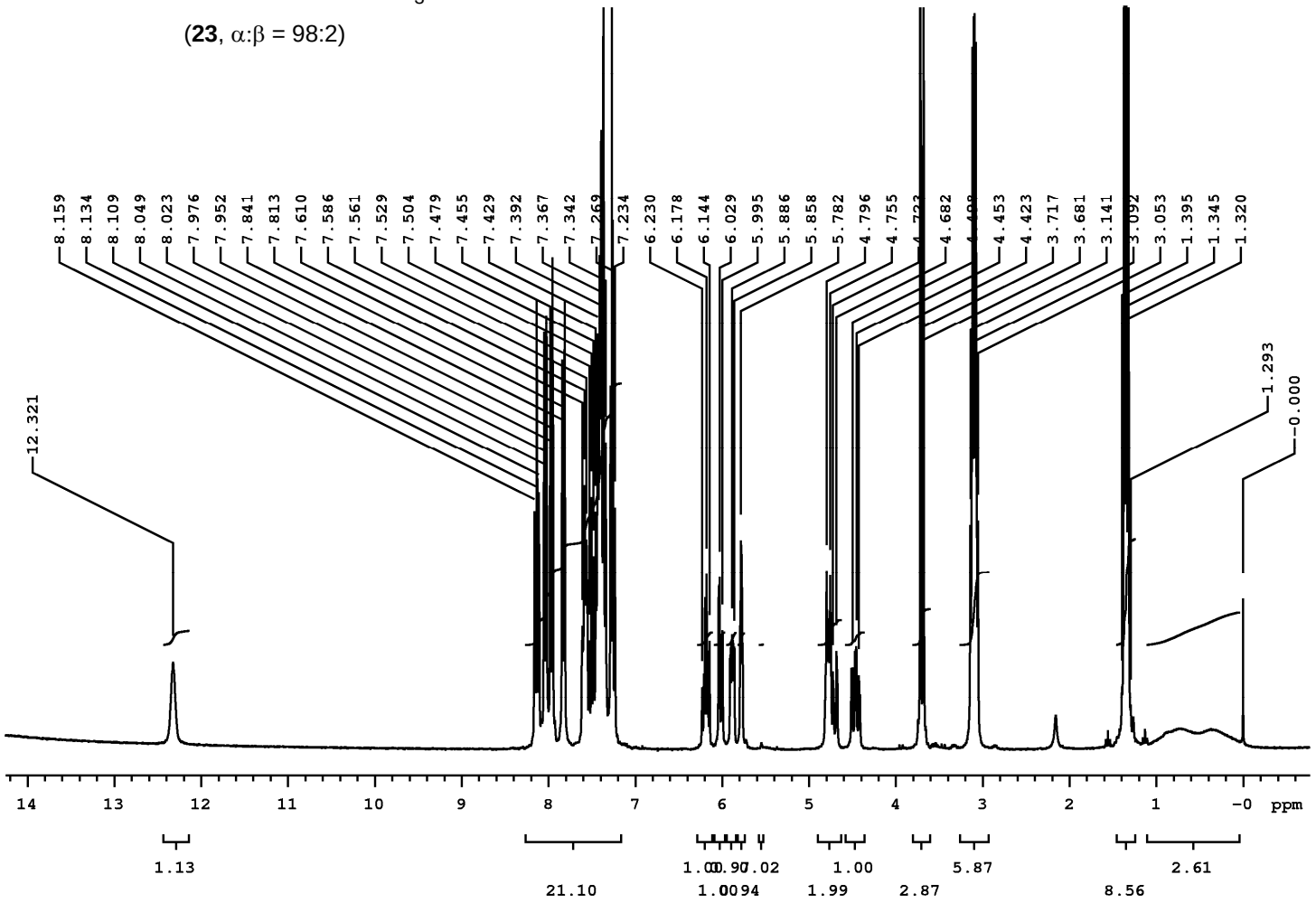
(^{31}P NMR, $CDCl_3$, 121.5 MHz)

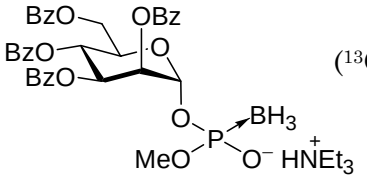




(**23**, α:β = 98:2)

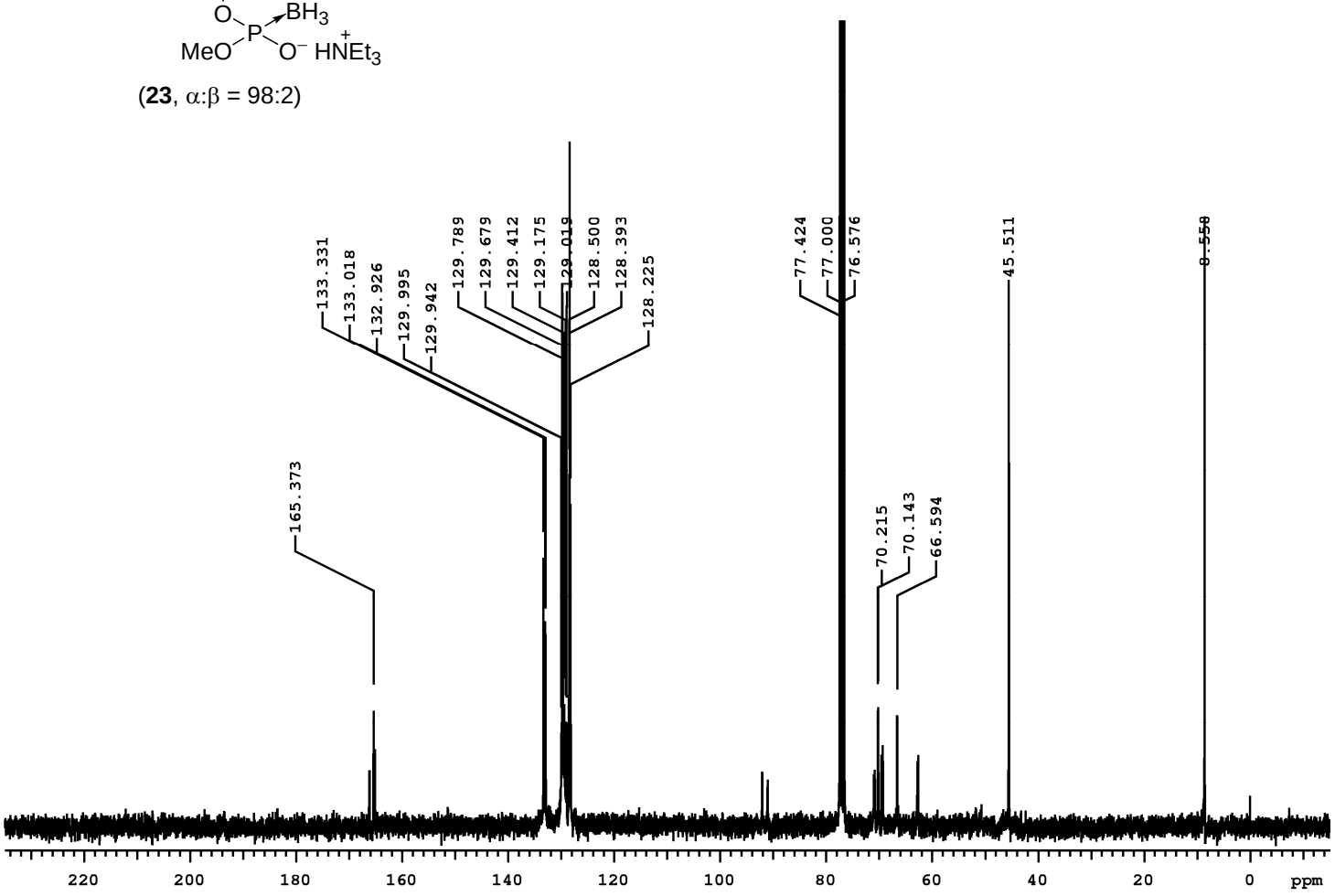
(^{1}H NMR, $CDCl_3$, 300 MHz)

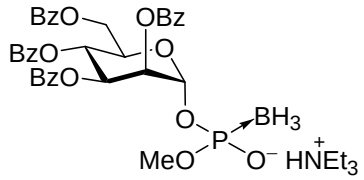




(**23**, α:β = 98:2)

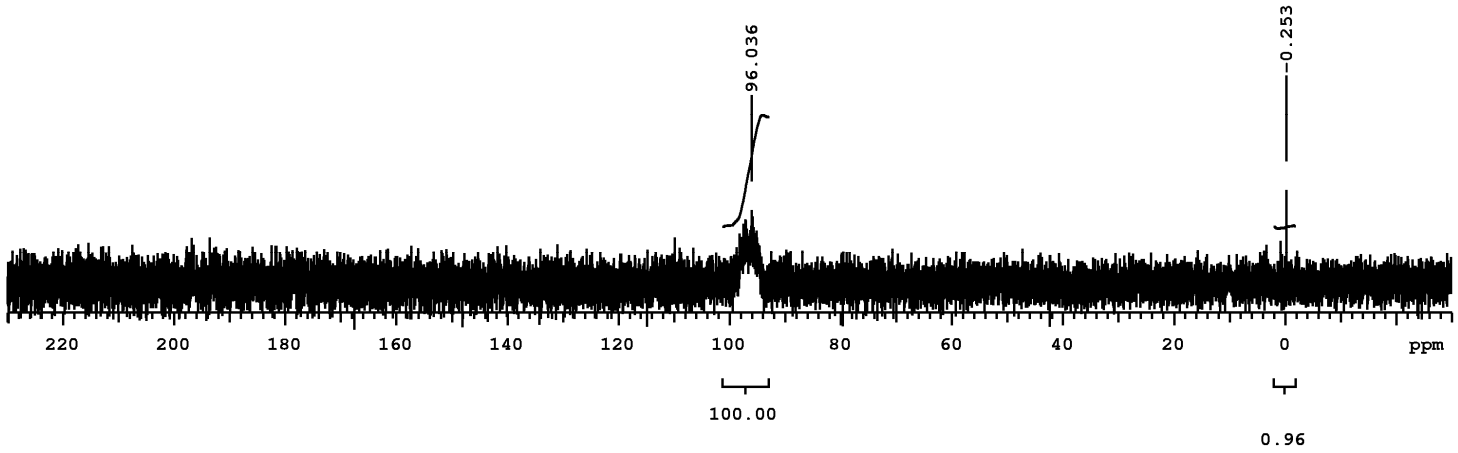
(^{13}C NMR, $CDCl_3$, 75.5 MHz)

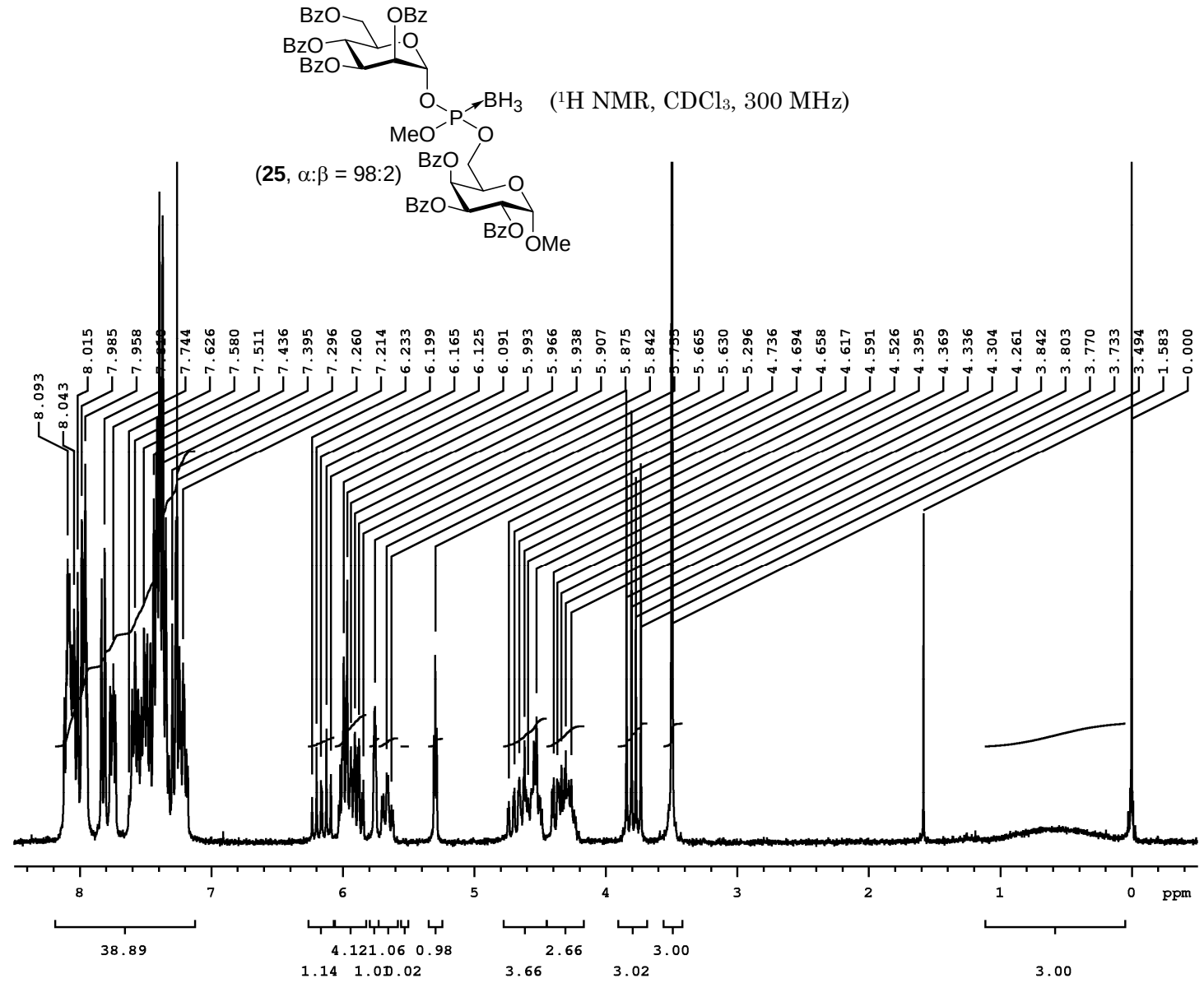




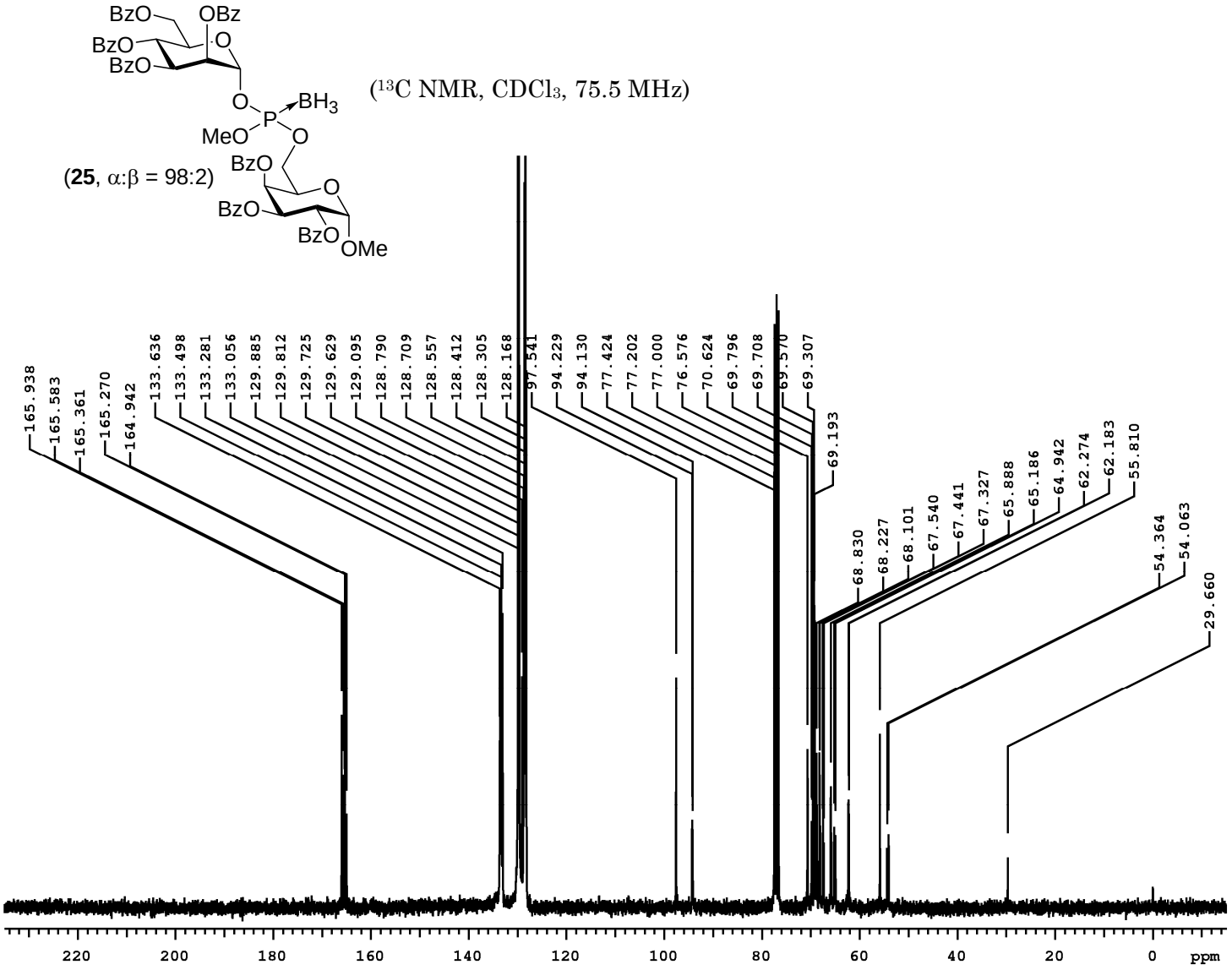
(**23**, α:β = 98:2)

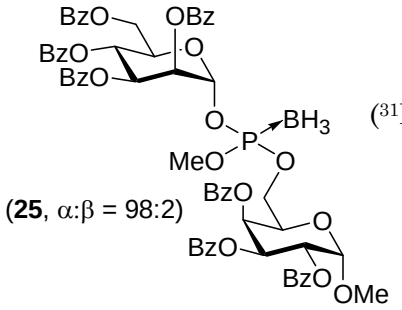
(^{31}P NMR, $CDCl_3$, 121.5 MHz)





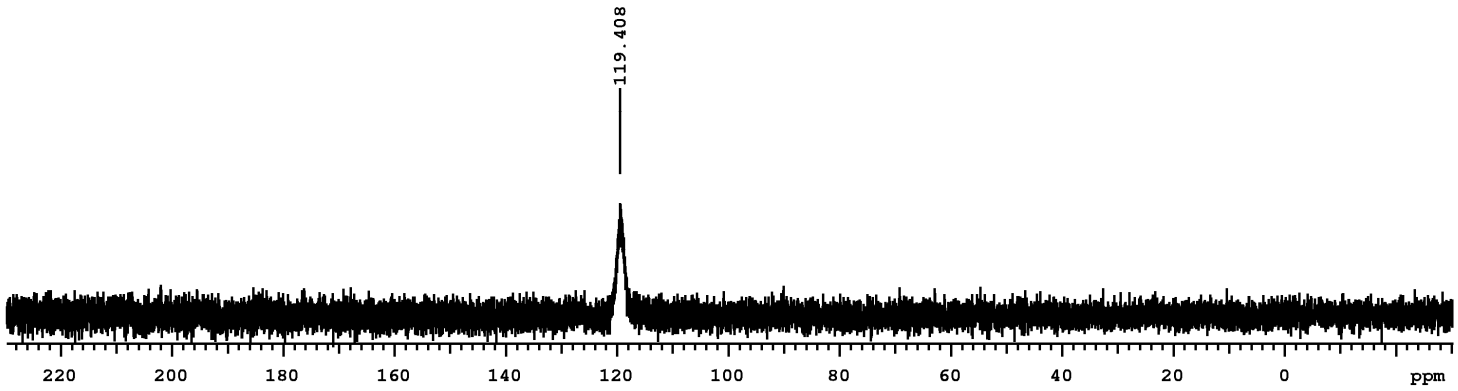
(**25**, α:β = 98:2) (^{1}H NMR, $CDCl_3$, 300 MHz)

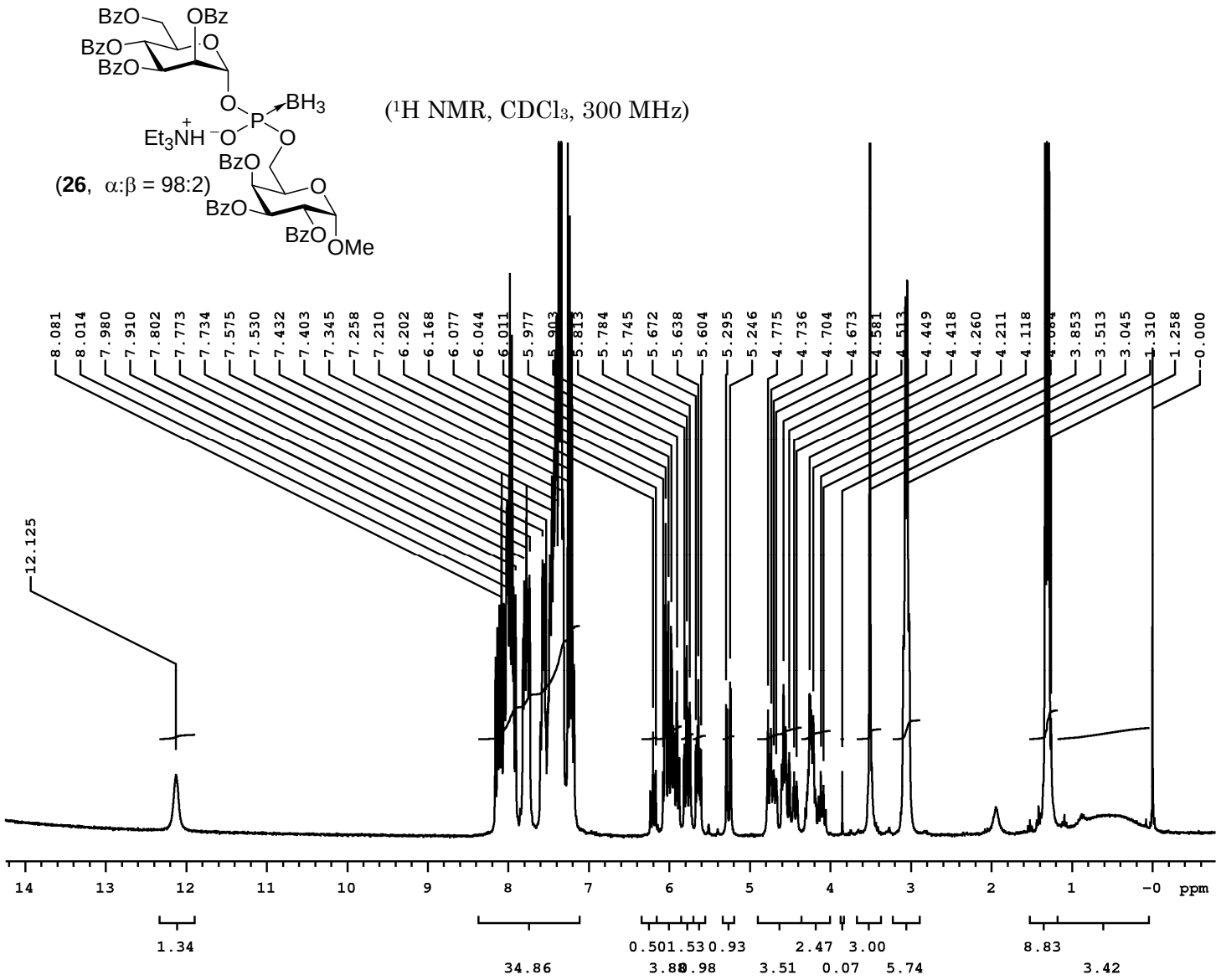

BzO
OBz
BzO
BzO
O
O
P
BH3
MeO
O
BzO
O
BzO
BzO
OMe
(25, α:β = 98:2)
(13C NMR, CDCl3, 75.5 MHz)
165.938
165.583
165.361
165.270
164.942
133.636
133.498
133.281
133.056
129.885
129.812
129.725
129.629
129.095
128.790
128.709
128.557
128.412
128.305
128.168
97.541
94.229
94.130
77.424
77.202
77.000
76.576
70.624
69.796
69.708
69.570
69.307
69.193
68.830
68.227
68.101
67.540
67.441
67.327
65.888
65.186
64.942
62.274
62.183
55.810
54.364
54.063
29.660
220
200
180
160
140
120
100
80
60
40
20
0
ppm

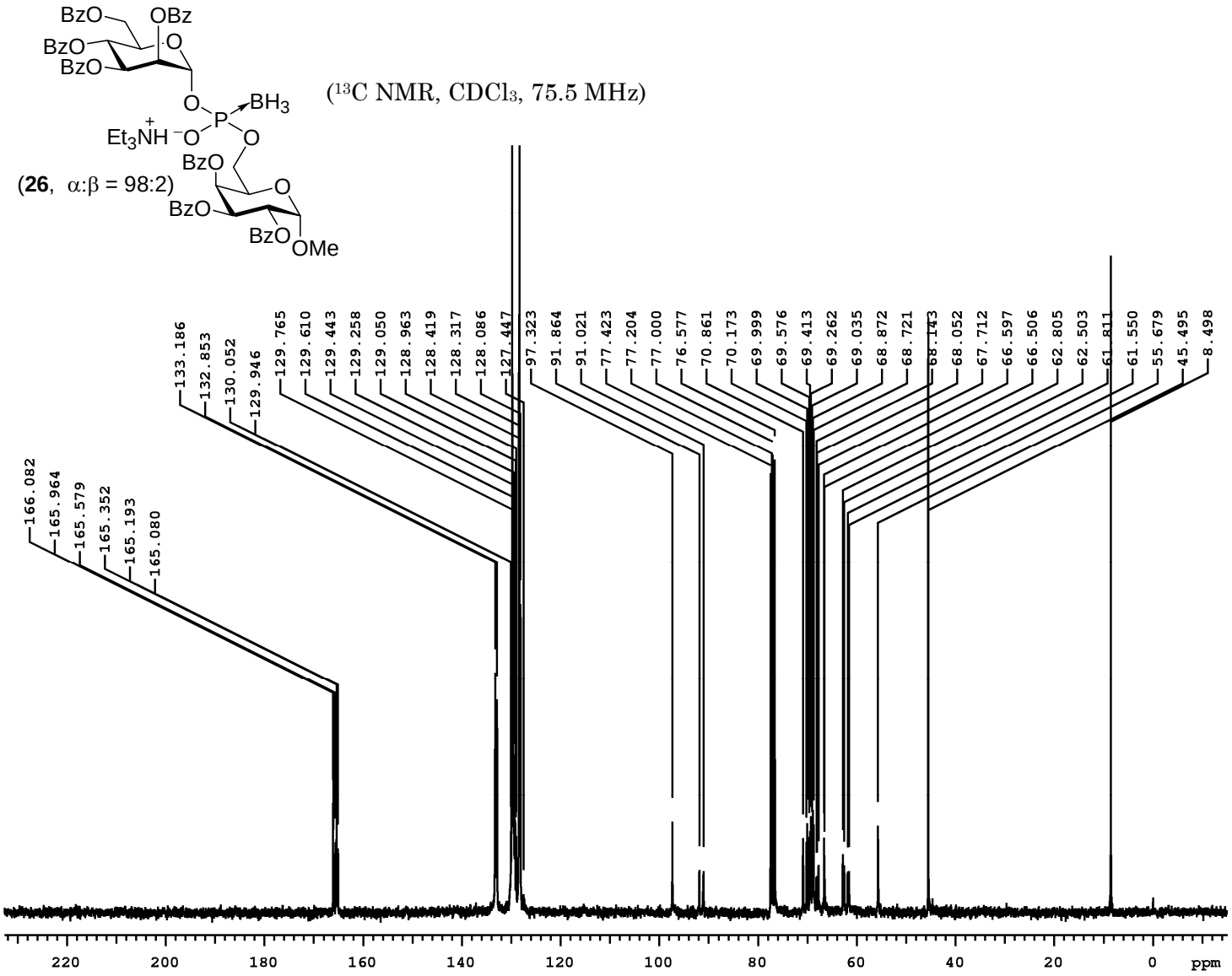


(**25**, α:β = 98:2)

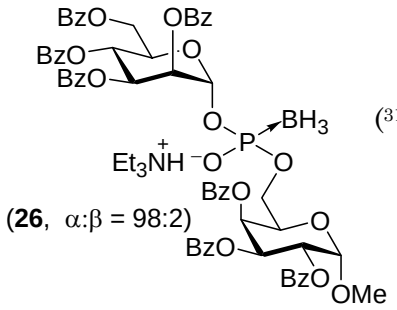
(^{31}P NMR, $CDCl_3$, 121.5 MHz)




BzO
OBz
BzO
BzO
O
O
P
BH3
Et3NH
O
O
BzO
O
BzO
BzO
OMe
(26, α:β = 98:2)
(1H NMR, CDCl3, 300 MHz)
8.081
8.014
7.980
7.910
7.802
7.773
7.734
7.575
7.530
7.432
7.403
7.345
7.258
7.210
6.202
6.168
6.077
6.044
6.011
5.977
5.903
5.813
5.784
5.745
5.672
5.638
5.604
5.295
5.246
4.775
4.736
4.704
4.673
4.581
4.513
4.449
4.418
4.260
4.211
4.118
4.084
3.853
3.513
3.045
1.310
1.258
0.000
12.125
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.34
34.86
0.50
1.53
0.93
2.47
3.00
8.83
3.42
3.88
0.98
3.51
0.07
5.74

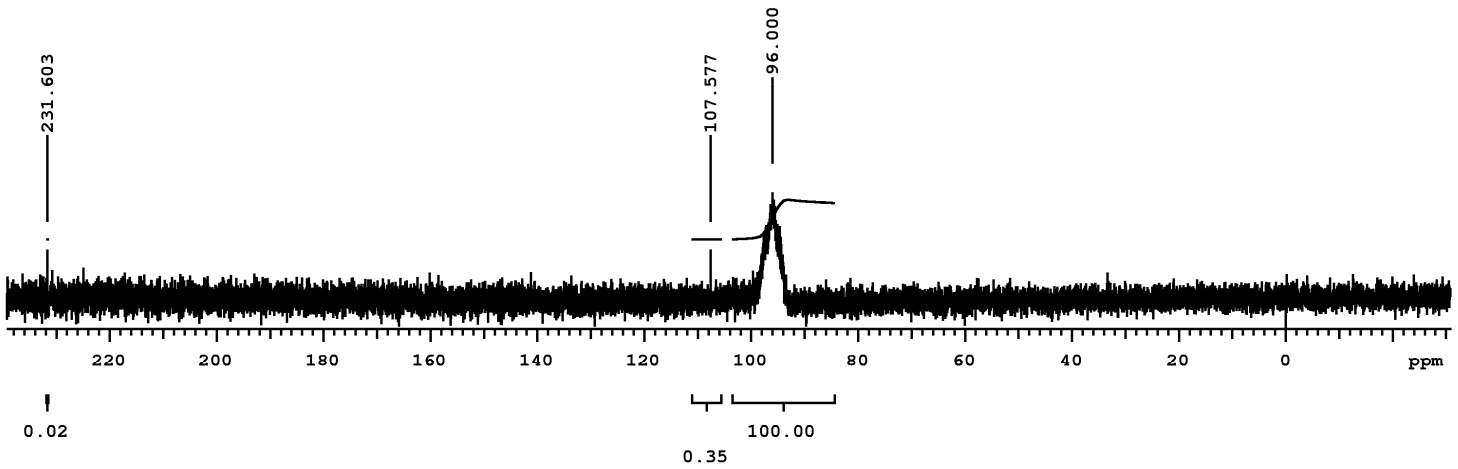


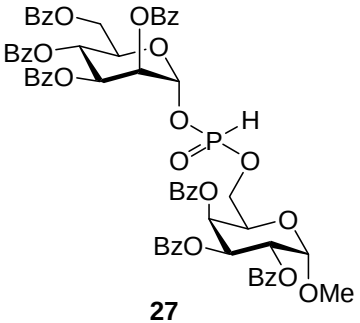
(**26**, α:β = 98:2) (^{13}C NMR, $CDCl_3$, 75.5 MHz)



(**26**, α:β = 98:2)

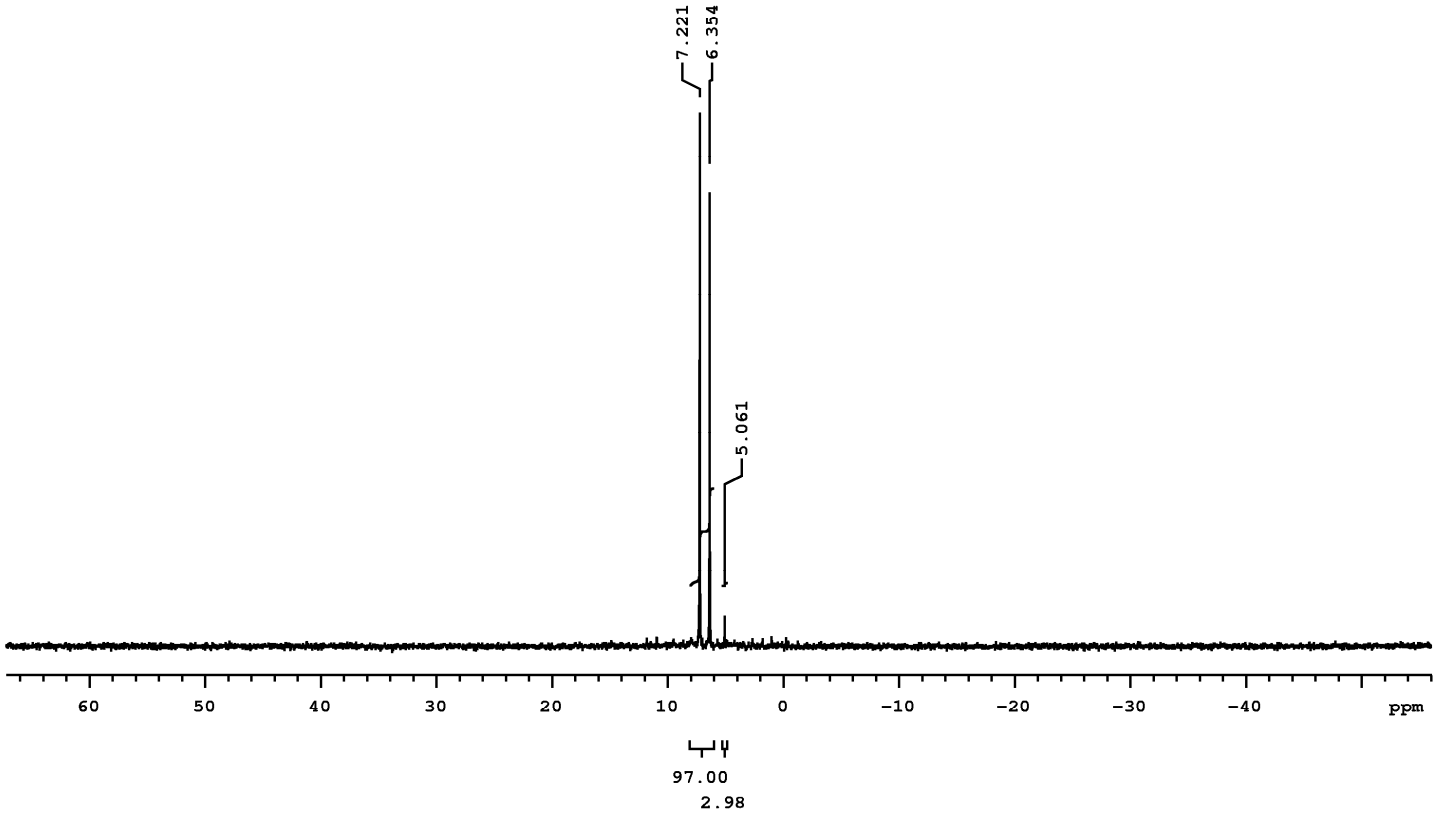
(^{31}P NMR, $CDCl_3$, 121.5 MHz)

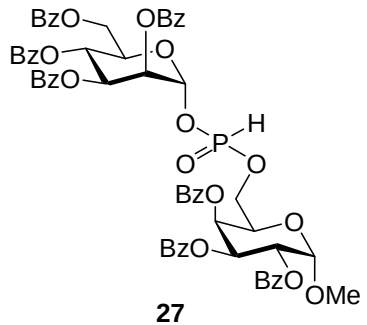




27

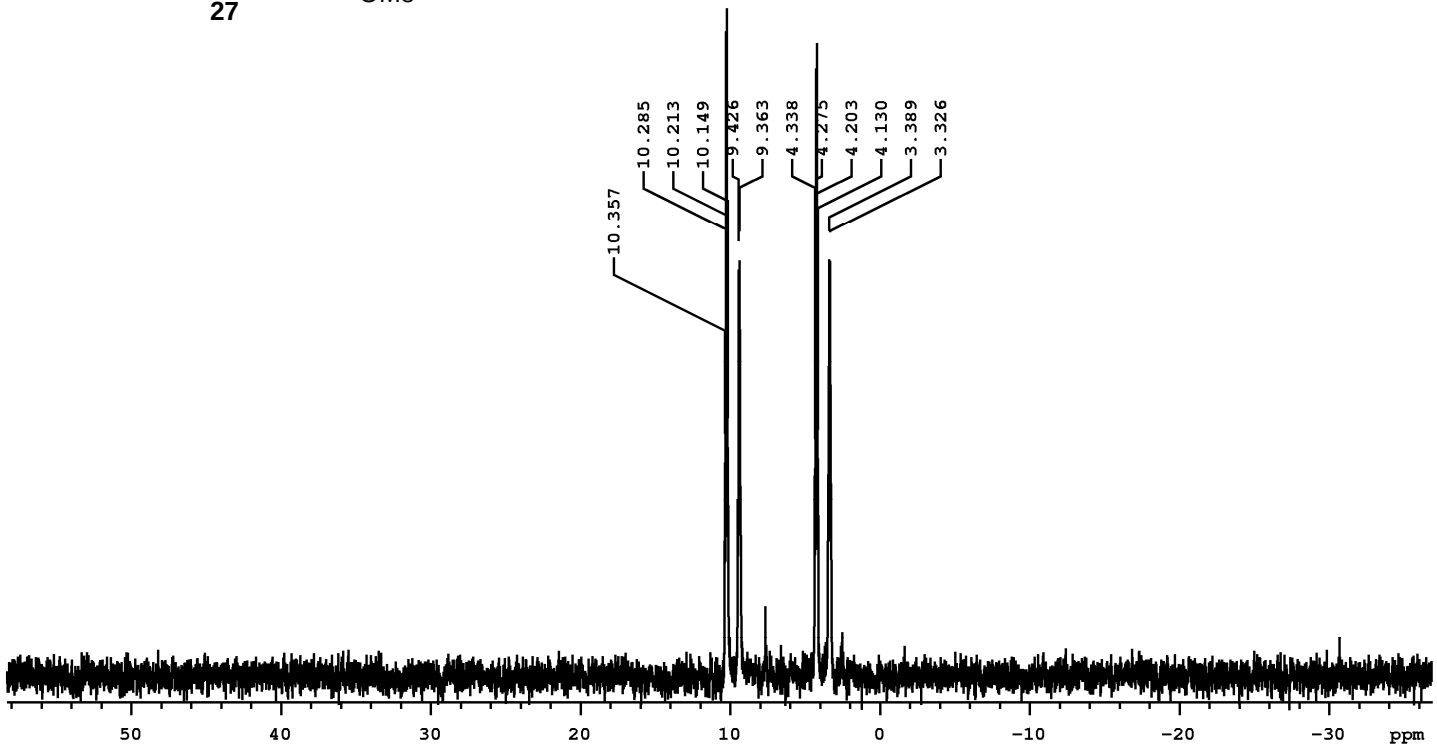
(^{31}P NMR, $CDCl_3$, 121.5 MHz, P–H decoupling)

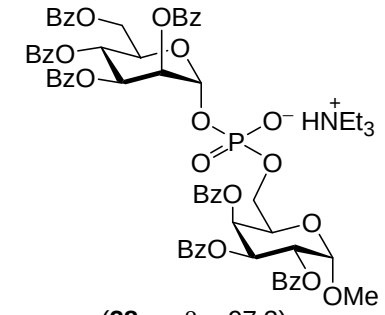




27

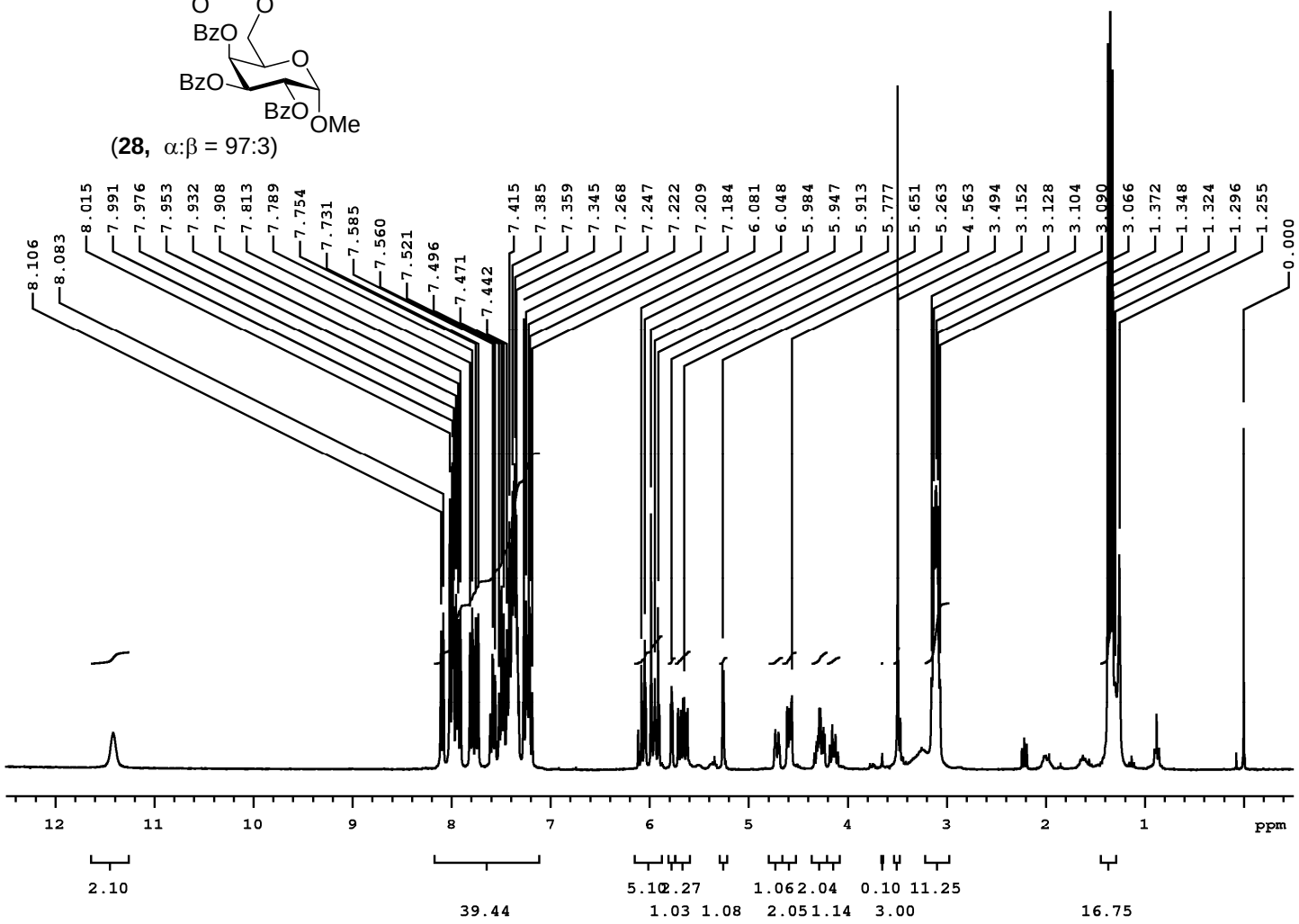
(^{31}P NMR, $CDCl_3$, 121.5 MHz, P–H coupling)

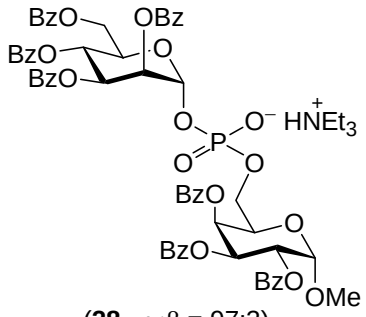




(**28,** α:β = 97:3)

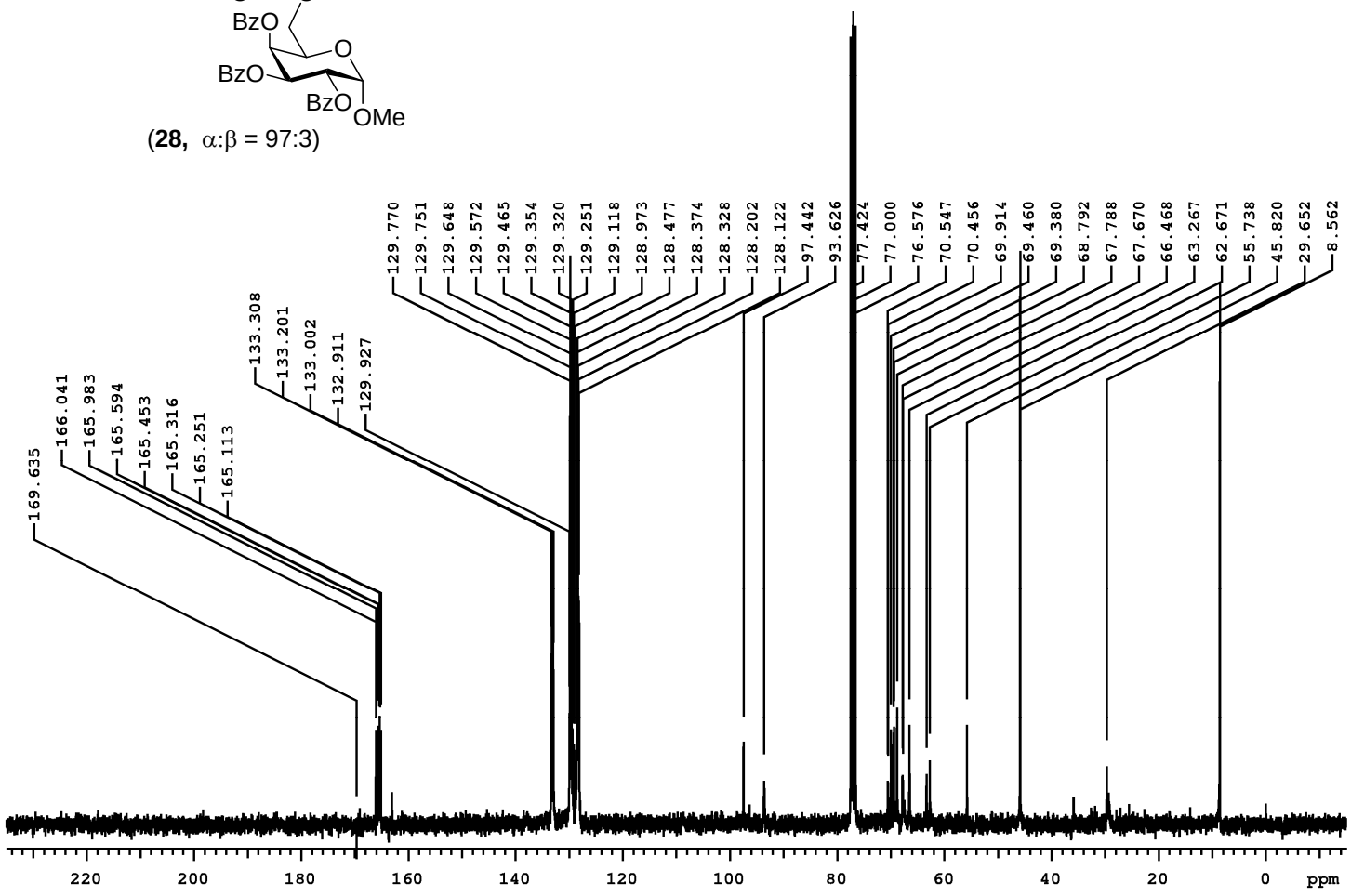
(^{1}H NMR, $CDCl_3$, 300 MHz)

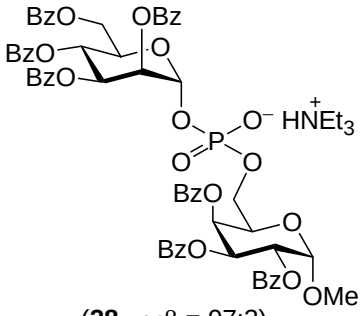




(**28,** α:β = 97:3)

(^{13}C NMR, $CDCl_3$, 75.5 MHz)





(**28,** α:β = 97:3)

(^{31}P NMR, $CDCl_3$, 121.5 MHz)