Highly Regioselective Protection of Sugars Catalyzed by Dimethyltin Dichloride

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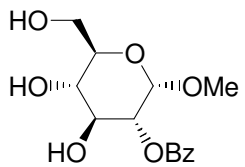
Supporting Information (*Organic Letters*)

Table of Contents

General: ^{1}H NMR spectra were measured on a Varian Gemini 300, 400 and 500 spectrometer with TMS as an internal standard. ^{13}C NMR spectra were measured on a Varian Gemini 300 and 400 spectrometer with TMS as an internal standard. IR spectra were obtained on a Shimadzu FTIR-8100A. Mass spectra were obtained on a JEOL JMS-DX 303 instrument. All reagents and solvents were used as supplied without further purification.

Experimental Procedure for Monobenzoylation of Sugar 1a

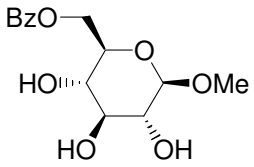
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of α-methyl glucoside (**1a**) (97 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2a** (122 mg, 82%) as a white solid.



Methyl *O*^{2}-benzoyl-α-D-glucoside (2a)[S1]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 6.9 Hz, 2H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 5.04 (d, *J* = 3.6 Hz, 1H), 4.91 (dd, *J* = 3.6, 9.9 Hz, 1H), 4.16 (t, *J* = 3.6 Hz, 1H), 3.92—3.89 (m, 2H), 3.75—3.72 (m, 2H), 3.40 (s, 3H), 2.62 (br s, 1H), 2.50 (br s, 1H), 2.00 (br s, 1H).

Experimental Procedure for Monobenzoylation of Sugar 1b

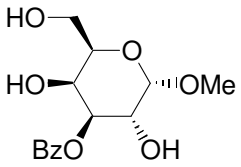
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of β-methyl glucoside (**1b**) (97 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2b** (118 mg, 79%) as a white solid.



Methyl O^6-benzoyl-β-D-glucoside (2b)[S2]**:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, J = 7.8 Hz, 2H), 7.50 (t, J = 7.3 Hz, 1H), 7.38 (t, J = 7.3 Hz, 2H), 5.06 (s, 1 H), 4.63 (d, J = 11.2 Hz, 2H), 4.55—4.38 (m, 2H), 4.21 (d, J = 7.3 Hz, 1H), 3.59 (d, J = 7.8 Hz, 2H), 3.56—3.34 (m, 4H), 2.78 (s, 1H).

Experimental Procedure for Monobenzoylation of Sugar 1c

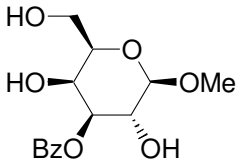
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of α-methyl galactoside (**1c**) (97 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2c** (115 mg, 84%) as a white solid.



Methyl O^3-benzoyl-α-D-galactoside (2c)[S2]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.8 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 5.27 (dd, J = 2.7, 10.5 Hz, 1H), 4.87 (d, J = 3.9 Hz, 1H), 4.25 (s, 1H), 4.21—4.18 (m, 1H), 3.85 (s, 3H), 3.42 (s, 4H), 2.97 (br s, 1H), 2.40 (d, J = 9.9 Hz, 1H).

Experimental Procedure for Monobenzoylation of Sugar 1d

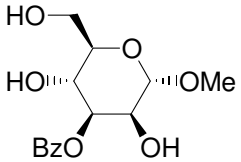
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of β-methyl galactoside (**1d**) (97 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2d** (135 mg, 91%) as a white solid.



Methyl O^3-benzoyl-β-D-galactoside (2d)[S3]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12—8.09 (m, 2H), 7.62—7.56 (m, 1H), 7.49—7.43 (m, 2H), 5.31 (dd, J = 3.0, 10.5 Hz, 1H), 4.96 (d, J = 4.2 Hz, 1H), 4.32 (s, 1H), 4.23 (dd, J = 4.2, 10.5 Hz, 1H), 4.01—3.82 (m, 3H), 3.50 (s, 3H), 2.80 (br s, 1H), 2.43 (br s, 1H), 1.62 (br s, 1H).

Experimental Procedure for Monobenzoylation of Sugar 1e

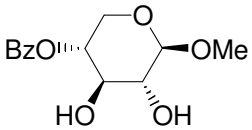
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of α-methyl mannoside (**1e**) (97 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF/H_2O = 9/1 (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2e** (144 mg, 97%) as a white solid.



Methyl O^3-benzoyl-α-D-mannoside (2e)[S4]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 8.1 Hz, 1H), 7.27 (t, J = 8.1 Hz, 2H), 5.28 (d, J = 9.9 Hz, 1H), 4.64 (s, 1H), 4.29—4.20 (m, 1H), 4.12—4.01 (m, 2H), 3.89 (br s, 1H), 3.81—3.65 (m, 3H), 3.67 (d, J = 9.6 Hz, 1H), 3.29 (s, 3H).

Experimental Procedure for Monobenzoylation of Sugar 1f

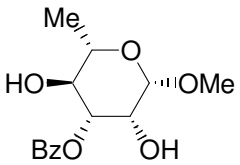
BzCl (64 μL, 0.55 mmol) was added to the stirred solution of β-methyl xyloside (**1f**) (82 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF/H_2O = 9/1 (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2f** (129 mg, 96%) as a white solid.



Methyl *O*^{4}-benzoyl-β-D-xyloside (2f): White solid; mp = 84—85 °C; IR (neat) 3584, 2800, 1720, 1451, 1320, 1271 cm^{-1}; $[\alpha]_D^{21}$ = —81.4 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 8.1 Hz, 2H), 5.12—5.05 (m, 1H), 4.41 (d, *J* = 5.7 Hz, 1H), 4.23 (dd, *J* = 4.2, 13.5 Hz, 1H), 3.61—3.50 (m, 6H), 3.05 (d, *J* = 4.8 Hz, 1H), 2.68 (d, *J* = 4.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.0, 133.4, 129.7, 129.4, 128.5, 103.4, 72.4, 71.9, 61.6, 56.8; [HR-FAB(+)]: *m/z* calcd for $C_{13}H_{17}O_6$ $[M+H]^+$ 269.1025 : found 269.1028.

Experimental Procedure for Monobenzoylation of Sugar 1g

BzCl (64 μL, 0.55 mmol) was added to the stirred solution of α-methyl rhamnoside (**1g**) (89 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF/H_2O = 9/1 (2.0 mL) and then stirred for 2.5 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to afford **2g** (135 mg, 96%) as a white solid.

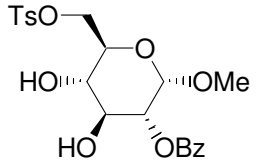


Methyl *O*^{3}-benzoyl-α-L-rhamnoside (2g): Amorphous; mp = 34—35 °C; IR (neat) 3450, 2975, 1719, 1601, 1453, 1283 cm^{-1}; $[\alpha]_D^{17}$ = —54.0 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.3 Hz, 2H), 7.52—7.48 (m, 1H), 7.47—7.30 (m, 2H), 5.22—5.10 (m, 1H), 4.61 (s, 1H), 4.09 (s, 1H), 3.77—3.70 (m, 2H), 3.33 (s, 3H), 3.00 (s, 2H), 1.33 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 133.2, 129.7, 129.5, 128.3, 100.6, 75.2, 71.0, 69.4, 68.3, 54.7, 17.4; [HR-FAB(+)]: *m/z* calcd for $C_{14}H_{19}O_6$ $[M+H]^+$ 283.1181 : found 283.1198.

Experimental Procedure for Monotosylation of Sugar 2a

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl *O*^{2}-benzoyl-α-D-glucoside (**2a**) (149 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF

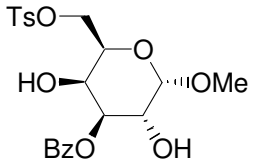
(2.0 mL) and then stirred for 22 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **3a** (199 mg, 88%) as a white solid.



Methyl *O*^{2}-benzoyl-*O*^{6}-*p*-toluenesulfonyl-α-D-glucoside (3a): White solid; mp 65—67°C; IR (neat) 3515, 2982, 2938, 1752, 1728, 1453 cm^{-1}; $[\alpha]_D^{22}$ = +109.5 (*c* 1.0, EtOH); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.2 Hz, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.96 (d, *J* = 1.6 Hz, 1H), 4.86 (dd, *J* = 1.2, 9.9 Hz, 1H), 4.41—4.26 (m, 2H), 4.14—4.07 (m, 1H), 3.85—3.80 (m, 1H), 3.62—3.58 (m, 1H), 3.34 (s, 3H), 2.75 (d, *J* = 3.6 Hz, 1H), 2.52 (d, *J* = 3.6 Hz, 1H), 2.46 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.4, 145.0, 129.9, 129.8, 128.4, 127.9, 100.6, 97.1, 73.5, 71.6, 70.1, 69.0, 55.4, 21.6; MS [HR-EI(+)] : *m/z* calcd for $C_{21}H_{24}O_9S$ $[M]^+$ 452.1141, found: 452.1157.

Experimental Procedure for Monotosylation of Sugar 2c

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl *O*^{3}-benzoyl-α-D-galactoside (**2c**) (149 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 22 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **3c** (147 mg, 65%) as a white solid.

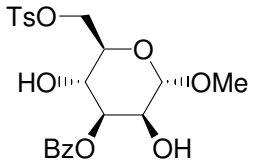


Methyl *O*^{3}-benzoyl-*O*^{6}-*p*-toluenesulfonyl-α-D-galactoside (3c): White solid; mp 66—68°C; IR (neat) 3650, 3065, 2998, 2955, 2911, 2842, 1719, 1453 cm^{-1}; $[\alpha]_D^{22}$ = +127.1 (*c* 0.76, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.07 (d, *J* = 3.5 Hz, 2H), 7.80 (d, *J* = 3.5 Hz, 2H), 7.58 (t, *J* = 3.5 Hz, 1H), 7.45 (t, *J* = 3.5 Hz, 2H), 7.35 (d, *J* = 3.5 Hz, 2H), 5.26 (dd, *J* = 1.1, 3.5 Hz, 1H), 4.82 (d, *J* = 1.3 Hz, 1H), 4.28—4.08 (m, 5H), 3.42 (s,

3H), 2.44 (s, 3H), 2.29 (s, 1H), 2.09 (d, J = 9.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 145.1, 133.5, 132.6, 129.9, 129.85, 129.4, 128.5, 127.99, 99.6, 73.4, 68.2, 67.8, 67.7, 67.1, 55.7, 21.6; MS[HR-FAB(+)]: *m/z* calcd for $C_{21}H_{25}O_9S[M+H]^+$: 453.1219, found: 453.1201.

Experimental Procedure for Monotosylation of Sugar 2e

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl O^3-benzoyl-α-D-mannoside (**2e**) (149 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol), DMAP (6.1 mg, 0.05 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 22 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **3e** (192 mg, 85%) as a white solid.

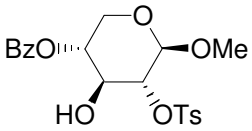


Methyl O^3-benzoyl-O^6-*p*-toluenesulfonyl-α-D-mannoside (3e): Amorphous; IR (neat) 3509, 2998, 1771, 1721, 1599, 1453, 1362 cm^{-1}; $[\alpha]_D^{19}$ = +35.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 7.8 Hz, 2H), 7.58 (t, J = 7.8 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 2H), 5.28 (dd, J = 4.8, 9.6 Hz, 1H), 4.72 (s, 1H), 4.42—4.29 (m, 2H), 4.19—4.02 (m, 2H), 3.88—3.73 (m, 1H), 3.36 (s, 3H), 2.80 (d, J = 5.4 Hz, 1H), 2.44 (s, 3H), 2.32 (d, J = 6.0 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.7, 144.9, 133.3, 132.6, 129.9, 129.8, 129.4, 128.4, 127.9, 100.7, 74.9, 70.4, 69.1, 65.0, 55.1, 21.5; [HR-EI(+)]: *m/z* calcd for $C_{21}H_{24}O_9S$ $[M]^+$ 452.1141: found 452.1124.

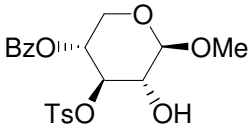
Experimental Procedure for Monotosylation of Sugar 2f

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl O^4-benzoyl-β-D-xyloside (**2f**) (134 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 22 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded

an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **3f** (55 mg, 26%) and **3f'** (80 mg, 38%) as a white solid.



Methyl *O*^{2}-*p*-toluenesulfonyl-*O*^{4}-benzoyl-β-D-xyloside (3f): White solid; mp = 71—72 °C; IR (neat) 3500, 1720, 1599, 1453, 1362, 1271 cm^{-1}; $[\alpha]_D^{19}$ = —96.6 (*c* 0.82, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.29—7.26 (m, 2H), 5.04—4.92 (m, 1H), 4.62—4.55 (m, 1H), 4.43—4.40 (m, 1H), 4.25—4.16 (m, 1H), 3.92—3.80 (m, 1H), 3.65—3.50 (m, 1H), 3.38 (s, 3H), 3.30—3.20 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 133.3, 129.9, 129.7, 128.4, 128.1, 100.0, 70.2, 69.0, 59.7, 56.4, 21.7; [HR-EI(+)]: *m/z* calcd for $C_{20}H_{22}O_8S$ $[M]^+$ 422.1035 : found 422.1057.

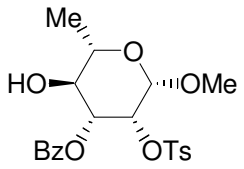


Methyl *O*^{3}-*p*-toluenesulfonyl-*O*^{4}-benzoyl-β-D-xyloside (3f'): White solid; mp = 104—105 °C; IR ($CHCl_3$) 3503, 2924, 1724, 1599, 1453, 1352, 1269 cm^{-1}; $[\alpha]_D^{19}$ = —128.2 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.8 Hz, 2H), 7.80 (d, *J* = 8.3 Hz, 2H), 7.59 (t, *J* = 7.3 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 2H), 5.30—5.15 (m, 1H), 4.95 (t, *J* = 9.3 Hz, 1H), 4.30 (d, *J* = 7.3 Hz, 1H), 4.22 (dd, *J* = 5.8, 11.7 Hz, 1H), 3.65—3.58 (m, 1H), 3.55 (s, 3H), 3.38 (t, *J* = 11.2 Hz, 1H), 2.89 (s, 1H), 2.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.2, 144.6, 133.4, 129.9, 129.5, 128.9, 128.3, 127.6, 104.0, 81.8, 71.9, 69.2, 62.4, 57.2, 21.5; [HR-EI(+)]: *m/z* calcd for $C_{20}H_{22}O_8S$ $[M]^+$ 422.1035 : found 422.0992.

Experimental Procedure for Monotosylation of Sugar 2g

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl *O*^{3}-benzoyl-α-L-rhamnoside (**2g**) (141 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 22 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded

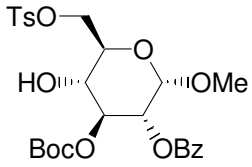
an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **3g** (109 mg, 50%) as a white solid.



Methyl *O*^{2}-*p*-toluenesulfonyl-*O*^{3}-benzoyl-α-L-rhamnoside (3g): White solid; mp = 127—129 °C; IR (neat) 3534, 2978, 1725, 1599, 1453, 1364, 1275, 1190 cm^{-1}; $[\alpha]_D^{22}$ = +3.5 (*c* 1.5, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 2H), 5.20 (dd, *J* = 7.5, 9.5 Hz, 1H), 4.85—4.83 (m, 1H), 4.79 (s, 1H), 3.81—3.72 (m, 2H), 3.39 (s, 3H), 2.38 (br s, 1H), 2.17 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.8, 144.8, 133.3, 132.7, 129.8, 129.1, 128.2, 127.8, 127.1, 98.6, 72.1, 70.4, 68.2, 55.1, 21.5, 17.4; [HR-FAB(+)]: *m/z* calcd for $C_{21}H_{25}O_8S$ $[M+H]^+$ 437.1270 : found 437.1285.

Experimental Procedure for Complete Protection of α-Methyl Glucoside and β-Methyl Xyloside

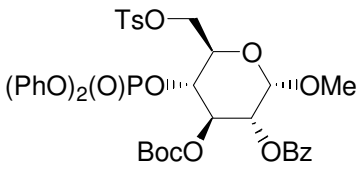
Boc_2O (120 mg, 0.55 mmol) was added to the stirred solution of methyl *O*^{2}-benzoyl-*O*^{6}-*p*-toluenesulfonyl-α-D-glucoside (**3a**) (226 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol), DMAP (67 mg, 0.55 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 30 min at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (15% EtOAc in hexane) to afford **4** (257 mg, 93%) as a white solid.



Methyl *O*^{2}-benzoyl-*O*^{3}-*t*-butoxycarbonyl-*O*^{6}-*p*-toluenesulfonyl-α-D-glucoside (4): White solid; mp 67—69°C; IR (neat) 3513, 2988, 2983, 1752, 1728, 1453 cm^{-1}; $[\alpha]_D^{22}$ = +107.1 (*c* 0.4, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (t, *J* = 6.9 Hz, 2H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.61—7.52 (m, 1 H), 7.43 (t, *J* = 8.7 Hz, 2H), 7.41—7.35 (m, 2H), 5.28 (t, *J* = 9.3 Hz, 0.5H), 5.04 (d, *J* = 3.8 Hz, 0.5H), 4.93 (d, *J* = 3.8 Hz, 0.5H), 4.92—4.84 (m, 1H), 4.64 (t, *J* = 9.3 Hz, 0.5H), 4.41—4.20 (m, 2H), 4.23—4.20 (m, 0.5H),

4.01—3.97 (m, 0.5H), 3.85—3.80 (m, 0.5H), 3.79—3.72 (m, 0.5H), 3.32 (s, 3H), 2.72 (d, J = 5.4 Hz, 0.5H), 2.55 (d, J = 5.4 Hz, 0.5H), 2.46 (s, 3H), 1.50 (s, 5H), 1.40 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.1, 165.7, 153.5, 153.1, 145.0, 144.9, 133.4, 132.8, 129.95, 129.89, 129.84, 129.8, 129.1, 128.4, 128.3, 128.0, 127.96, 96.8, 83.7, 83.1, 75.1, 73.7, 73.5, 71.7, 69.9, 69.3, 68.3, 68.0, 67.1, 55.52, 55.46, 27.7, 27.6, 27.5, 21.6; MS [HR-FAB(+)] : *m/z* calcd for $C_{26}H_{33}O_{11}S$ $[M+H]^+$: 553.1744, found: 553.1726.

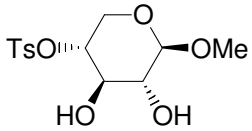
$(PhO)_2(O)PCl$ (155 μL, 0.75 mmol) was added to the stirred solution of methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^6-*p*-toluenesulfonyl-α-D-glucoside (**4**) (276 mg, 0.5 mmol), pyridine (60 μL, 0.75 mmol) and DMAP (92 mg, 0.75 mmol) in CH_2Cl_2 (2.0 mL) and then stirred for 22 h at rt. Water (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford **5** (373 mg, 95%) as a white solid.



Methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^4-diphenylphosphoryl-O^6-*p*-toluenesulfonyl-α-D-glucoside (5): White solid; mp 55—58 °C; IR (neat) 3069, 2982, 2845, 1763, 1721, 1599, 1598, 1454 cm^{-1}; $[\alpha]_D^{20}$ = +101.3 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, J = 7.2 Hz, 0.9H), 7.96 (d, J = 7.2 Hz, 1.1H), 7.83 (d, J = 8.4 Hz, 1.1H), 7.73 (d, J = 8.4 Hz, 0.9H), 7.59—6.78 (m, 15H), 5.62 (t, J = 9.6 Hz, 0.5H), 5.28 (q, J = 9.0 Hz, 0.5H), 5.06 (d, J = 3.6 Hz, 0.5H), 5.02—4.92 (m, 1.5H), 4.86 (dd, J = 3.5, 10.1 Hz, 0.5H), 4.57 (q, J = 3.5 Hz, 0.5H), 4.36—3.99 (m, 3H), 3.35 (s, 1.3H), 3.27 (s, 1.7H), 2.46 (s, 1.7H), 2.41 (s, 1.3H), 1.27 (s, 5H), 1.15 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 165.4, 157.7, 152.5, 152.0, 150.5, 150.4, 150.3, 149.9, 144.9, 144.8, 133.5, 133.1, 132.7, 130.1, 129.9, 129.8, 129.7, 129.6, 129.51, 129.50, 129.2, 128.8, 128.6, 128.3, 128.1, 127.99, 125.6, 125.5, 125.4, 125.0, 124.8, 120.6, 120.5, 120.45, 120.4, 120.2, 120.1, 119.8, 119.75, 100.5, 96.4, 96.3, 83.5, 82.8, 76.0, 75.9, 74.0, 73.9, 72.6, 72.5, 71.77, 71.74, 71.69, 71.5, 67.9, 67.8, 67.6, 67.1, 55.6, 55.5,

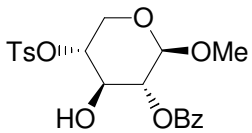
27.5, 27.2, 21.6, 21.5; MS[HR-FAB(+)]:*m/z* calcd for $C_{38}H_{42}O_{14}PS$ $[M+H]^+$: 785.2033, found: 785.2021.

TsCl (105 mg, 0.55 mmol) was added to the stirred solution of methyl β-D-xyloside (**1f**) (82 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF containing 1% H_2O (2.0 mL) and then stirred for 20 h at 50 °C. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (50% EtOAc in hexane) to give **2f'** (129 mg, 81%) as a white solid.



Methyl *O*^{4}-*p*-toluenesulfonyl-β-D-xyloside (2f')[S2]**:** ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 4.40—4.30 (m, 1H), 4.22 (d, *J* = 6.6 Hz, 1H), 4.00 (dd, *J* = 4.8, 6.0 Hz, 1H), 3.70—3.60 (m, 1H), 3.49 (s, 3H), 3.39—3.30 (m, 2H), 3.25 (s, 1H), 3.08 (s, 1H), 2.45 (s, 3H).

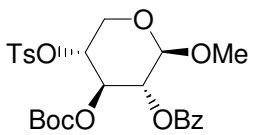
BzCl (76 μL, 0.65 mmol) was added to the stirred solution of methyl *O*^{4}-*p*-toluenesulfonyl-β-D-xyloside (**2f'**) (159 mg, 0.5 mmol), Me_2SnCl_2 (5.5 mg, 0.025 mmol) and DIPEA (174 μL, 1.0 mmol) in THF (2.0 mL) and then stirred for 24 h at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to afford **6** (129 mg, 87%) as a white solid.



Methyl *O*^{2}-benzoyl-*O*^{4}-*p*-toluenesulfonyl-β-D-xyloside (6): White solid; mp = 144—146 °C; IR (neat) 3500, 1725, 1599, 1453, 1364, 1271 cm^{-1}; $[\alpha]_D^{20}$ = —8.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.3 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.44—7.39 (m, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.98 (t, *J* = 4.4 Hz, 1H), 4.66 (s, 1H), 4.47 (s, 1H), 4.16 (d, *J* = 12.7 Hz, 1H), 3.92 (s, 1H), 3.65 (dd, *J* = 5.5, 15.9 Hz, 1H), 3.45 (s, 3H), 3.30—3.20 (m, 1H), 2.41 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 145.2, 133.3,

129.9, 129.2, 128.4, 127.9, 99.7, 70.0, 68.6, 59.6, 56.3, 21.6; [HR-EI(+)]: *m/z* calcd for $C_{20}H_{22}O_8S$ $[M]^+$ 422.1035 : found 422.1057.

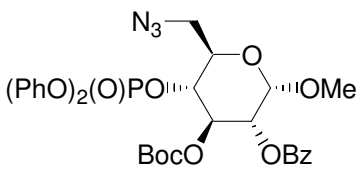
Boc_2O (66 mg, 0.33 mmol) was added to the stirred solution of methyl O^2-benzoyl-O^4-*p*-toluenesulfonyl-β-D-xyloside (**6**) (126 mg, 0.3 mmol), Me_2SnCl_2 (3.0 mg, 0.0075 mmol), DMAP (37 mg, 0.33 mmol) and DIPEA (95 μL, 0.6 mmol) in THF (1.5 mL) and then stirred for 40 min at rt. 3% aqueous HCl (20 mL) was added to the solution and extracted with EtOAc (20 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (15% EtOAc in hexane) to afford **7** (130 mg, 83%) as an amorphous.



Methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^4-*p*-toluenesulfonyl-β-D-xyloside (7): Amorphous; IR (neat) 2982, 1750, 1599, 1453, 1370, 1281, 1256 cm^{-1}; $[\alpha]_D^{21}$ = +29.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.9 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 5.08—5.06 (m, 2H), 4.57—4.48 (m, 2H), 4.28 (dd, *J* = 4.8, 6.1 Hz, 1H), 3.58 (dd, *J* = 6.0, 8.7 Hz, 1H), 3.45 (s, 3H), 2.44 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.8, 152.0, 145.1, 133.2, 132.7, 129.9, 129.8, 129.1, 128.2, 127.9, 101.5, 82.8, 74.5, 73.2, 71.0, 62.5, 56.7, 27.3, 21.6; [HR-FAB(+)]: *m/z* calcd for $C_{25}H_{31}O_{10}S$ $[M+H]^+$ 523.1638 : found 523.1627.

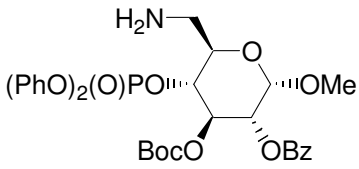
Chemical Transformation of α-Methyl Glucoside Derivative 5

Methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^4-diphenylphosphoryl-O^6-*p*-toluenesulfonyl-α-D-glucoside (**5**) (78 mg, 0.1 mmol) was added to the stirred solution of NaN_3 (10 mg, 0.15 mmol) and 15-crown-5 (2 mg, 0.01 mmol) in DMF (1.0 mL) and then stirred for 20 h at 50 °C. Water (15 mL) was added to the solution and extracted with Et_2O (15 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (10% EtOAc in hexane) to afford **8** (62 mg, 95%) as colorless oil.



Methyl *O*^{2}-benzoyl-*O*^{3}-*t*-butoxycarbonyl-*O*^{4}-diphenylphosphoryl-6-deoxy-6-azido-α-D-glucoside (8): Colorless oil; IR (neat) 2928, 2105, 1754, 1728, 1591, 1491, 1455, 1372 cm^{-1}; $[\alpha]_D^{18}$ = +116.8 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 0.9H), 7.99 (d, *J* = 8.3 Hz, 1.1H), 7.60—7.10 (m, 13H), 5.65 (t, *J* = 9.8 Hz, 0.5H), 5.33 (q, *J* = 9.2 Hz, 0.5H), 5.20—4.70 (m, 2.5H), 4.67 (q, *J* = 9.2 Hz, 0.5H), 4.01—3.97 (m, 1H), 3.42 (s, 1.4H), 3.38 (s, 1.6H), 3.49—3.38 (m, 1H), 3.28—3.26 (m, 1H), 1.28 (s, 5H), 1.17 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.6, 152.3, 133.5, 133.2, 130.2, 129.8, 129.6, 129.3, 128.7, 128.3, 128.2, 125.8, 125.6, 125.4, 125.0, 120.7, 120.6, 120.4, 119.9, 119.8, 96.6, 83.5, 82.8, 76.0, 74.9, 72.7, 72.0, 69.2, 69.1, 68.6, 55.7, 51.0, 50.4, 27.3, 27.2; [HR-FAB(+)]: *m/z* calcd for $C_{31}H_{35}N_3O_{11}P$ $[M+H]^+$ 655.1931 : found 655.1950.

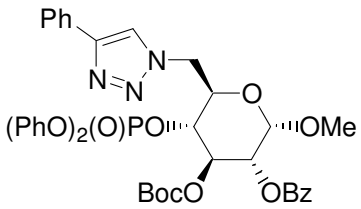
Methyl *O*^{2}-benzoyl-*O*^{3}-*t*-butoxycarbonyl-*O*^{4}-diphenylphosphoryl-6-deoxy-6-azido-α-D-glucoside (**8**) (328 mg, 0.5 mmol) was added to the stirred solution of Ph_3P (262 mg, 1.0 mmol) and H_2O (18 μl, 1.0 mmol) in THF (4.0 mL) at rt. After being stirred for 6 h, the mixture was evaporated, which was purified by column chromatography on silica gel (80% EtOAc in hexane) to afford **9** (220 mg, 70%) as colorless oil.



Methyl *O*^{2}-benzoyl-*O*^{3}-*t*-butoxycarbonyl-*O*^{4}-diphenylphosphoryl-6-deoxy-6-amino-α-D-glucoside (9): Colorless oil; IR (neat) 3200, 2980, 1752, 1748, 1593, 1491, 1281 cm^{-1}; $[\alpha]_D^{28}$ = +21.7 (*c* 1.5, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.2, 23.7 Hz, 2H), 7.58—7.10 (m, 10H), 6.91 (d, *J* = 4.2 Hz, 2H), 6.81 (d, *J* = 7.2 Hz, 1H), 5.67 (t, *J* = 8.7 Hz, 0.5H), 5.35 (q, *J* = 8.7, 17.4 Hz, 0.5H), 5.15 (d, *J* = 4.2 Hz, 0.5H), 5.10—4.90 (m, 2.5H), 4.73 (q, *J* = 8.7, 17.4 Hz, 0.5H), 3.85 (bs, 2H), 3.37 (s, 1.5H), 3.32 (s, 2H), 3.02—2.70 (m, 2H), 1.46 (s, 1H), 1.41 (s, 1H), 1.27 (s, 4H), 1.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 152.7, 130.2, 130.0, 129.9, 129.7, 129.6, 129.4, 129.2, 129.0, 128.3, 128.2, 125.7, 125.0, 120.6, 120.5, 120.3, 119.9, 119.8, 115.5, 96.7, 83.6, 82.6, 72.6,

72.0, 55.8, 55.7, 28.4, 27.3, 27.2; [HR-FAB(+)]: *m/z* calcd for $C_{31}H_{37}NO_{11}P$ $[M+H]^+$ 630.2104 : found 630.2097.

Methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^4-diphenylphosphoryl-6-deoxy-6-azido-α-D-glucoside (**8**) (328 mg, 0.5 mmol) was added to the stirred solution of phenyl acetylene (0.11 mL, 1.0 mmol), $CuSO_4$ (40 mg, 0.25 mmol) and (+)-sodium L-ascorbate (50 mg, 0.25 mmol) in *t*-BuOH/H_2O = 2/1 (1.8 mL) and then stirred for 24 h at rt. Water (15 mL) was added to the solution and extracted with EtOAc (15 mL x 3), and then dried over $MgSO_4$. Removal of the solvent afforded an oily residue, which was purified by column chromatography on silica gel (25% EtOAc in hexane) to leave **10** (283 mg, 75%) as a white solid.



Methyl O^2-benzoyl-O^3-*t*-butoxycarbonyl-O^4-diphenylphosphoryl-6-deoxy-6-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-α-D-glucoside (10): White solid; mp = 61—63 °C; IR (neat) 2988, 1752, 1727, 1591, 1489, 1281 cm^{-1}; $[\alpha]_D^{27}$ = +57.7 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 8.02 (d, *J* = 9.0 Hz, 0.5H), 7.96 (d, *J* = 9.0 Hz, 2H), 7.84 (t, *J* = 9.9 Hz, 2H), 7.60—7.12 (m, 14H), 6.91 (d, *J* = 4.5 Hz, 2H), 6.89—6.82 (m, 0.5H), 5.69 (t, *J* = 9.9 Hz, 0.5H), 5.51—5.40 (m, 0.5H), 5.12—5.10 (m, 1.5H), 4.98 (t, *J* = 9.6 Hz, 1H), 4.76 (dd, *J* = 4.5, 9.9 Hz, 0.5H), 4.67—4.63 (m, 0.5H), 4.54—4.48 (m, 0.5H), 4.38—4.20 (m, 2H), 3.06 (d, *J* = 8.1 Hz, 3H), 1.33 (s, 5.5H), 1.17 (s, 3.5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 152.5, 133.5, 133.2, 130.4, 130.2, 130.1, 130.0, 129.6, 129.3, 128.8, 128.5, 128.3, 128.2, 128.1, 126.0, 125.7, 125.5, 125.0, 120.7, 120.6, 120.5, 120.4, 119.9, 119.8, 96.5, 83.9, 82.3, 75.9, 75.5, 73.0, 72.5, 71.9, 68.4, 67.9, 55.5, 50.7, 50.3, 27.3, 27.2; [HR-FAB(+)]: *m/z* calcd for $C_{39}H_{41}N_3O_{11}P$ $[M+H]^+$ 758.2479 : found 758.2446.

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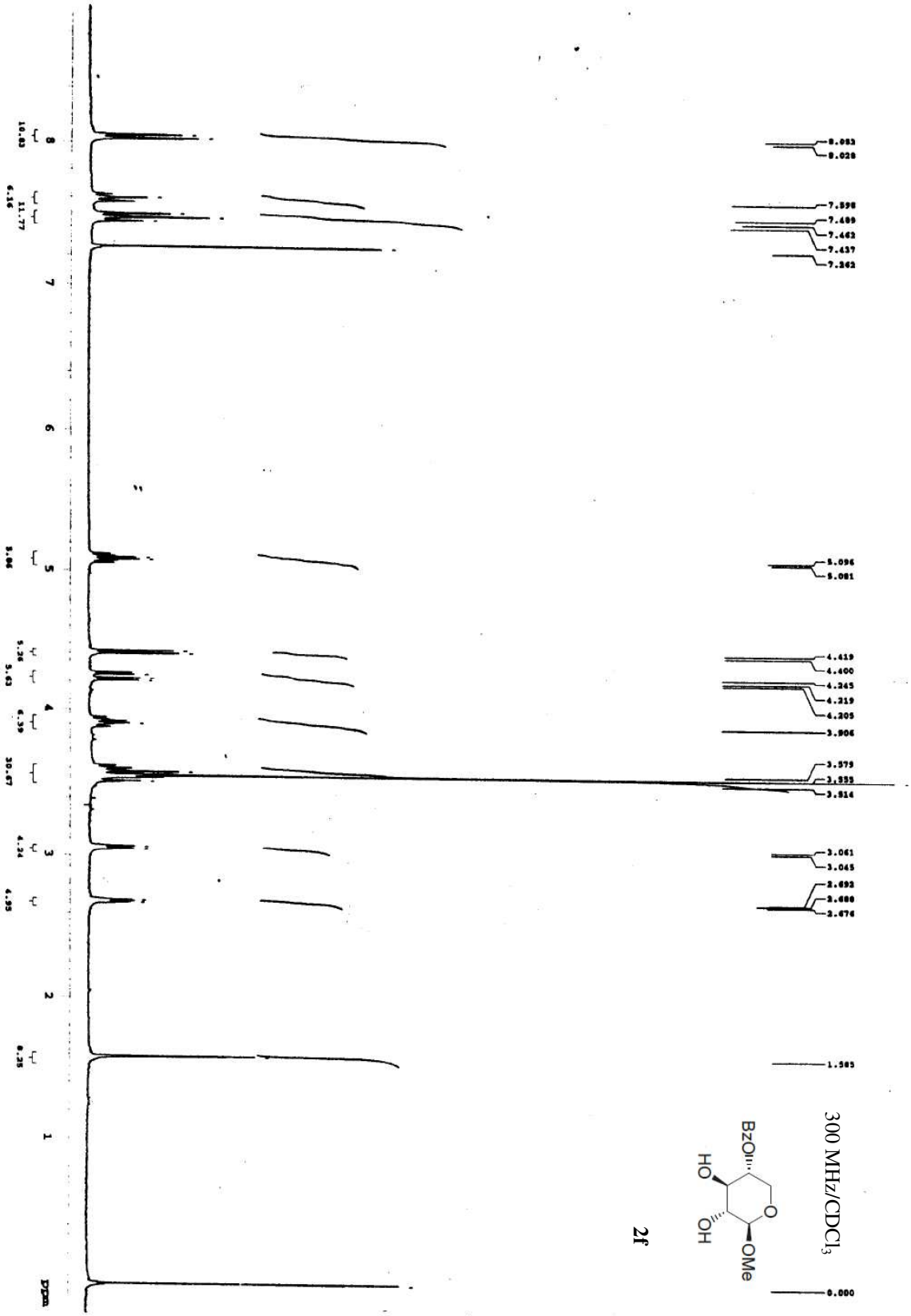
S1) Ho, W. M. ; Wong, H. N. C.; *Tetrahedron* **1995**, *51*, 7373—7388.

S2) Tsuda, Y.; Haque, Md. E. ; Yoshimoto, K. *Chem. Pharm. Bull.* **1983**, *31*, 1612—1624.

S3) Peri, F.; Cipolla, L.; Nicotra, F. *Tetrahedron Lett.* **2000**, *41*, 8587—8590.

S4) Tsuda, Y.; Nishimura, M.; Kobayashi, T.; Sato, Y.; Kanemitsu, K. *Chem. Pharm. Bull.* **1991**, *39*, 2883—2887.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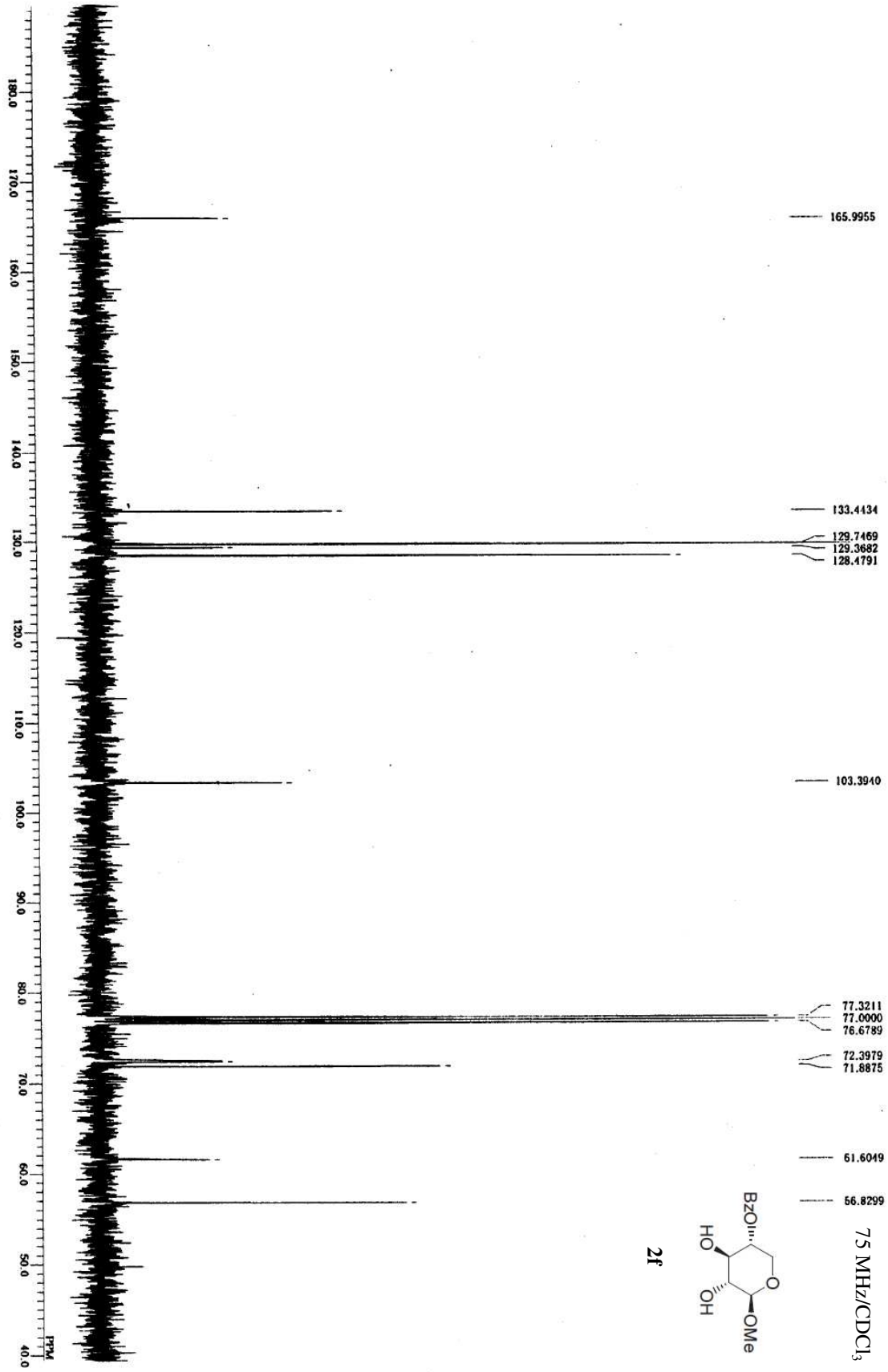
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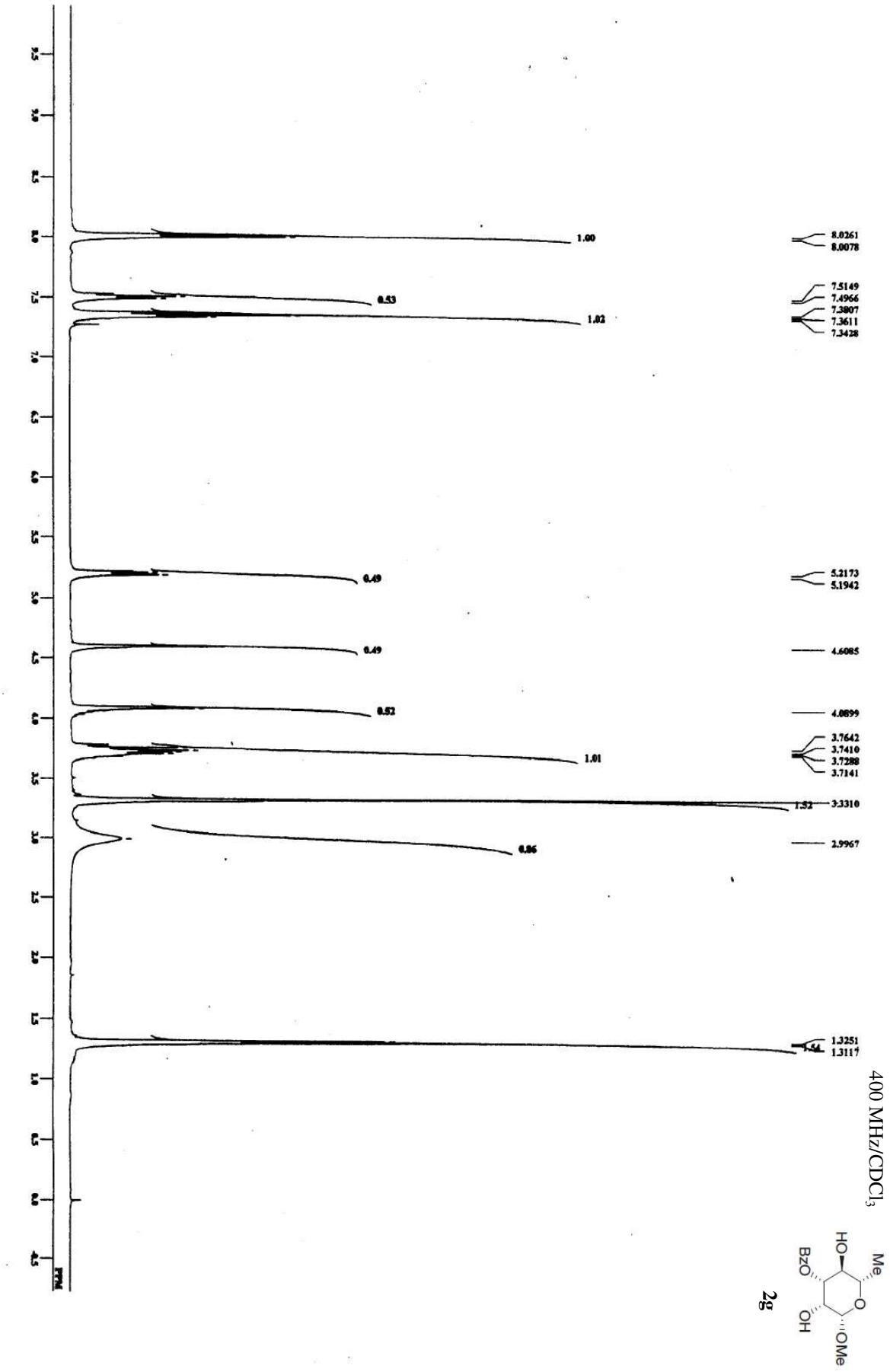
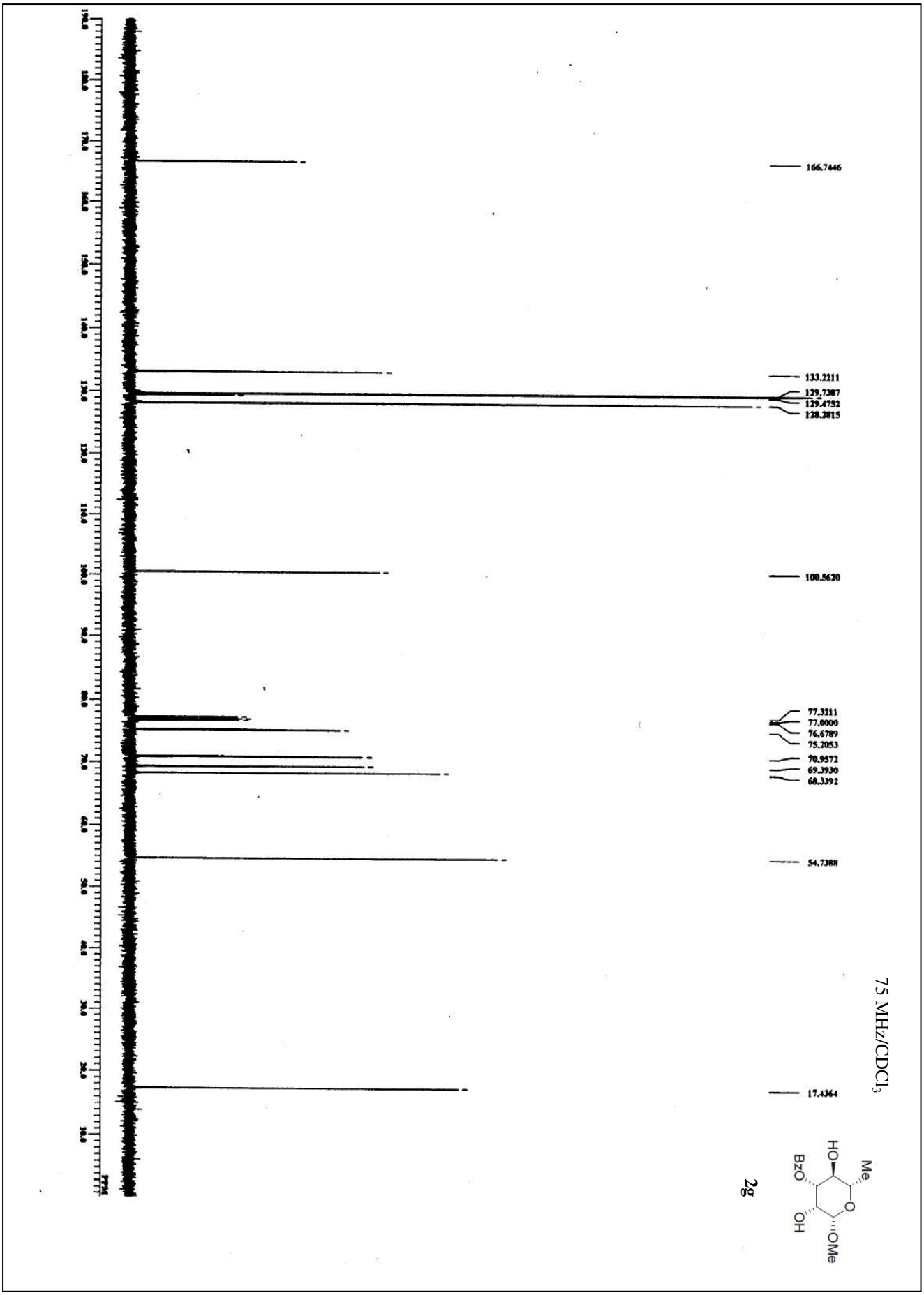
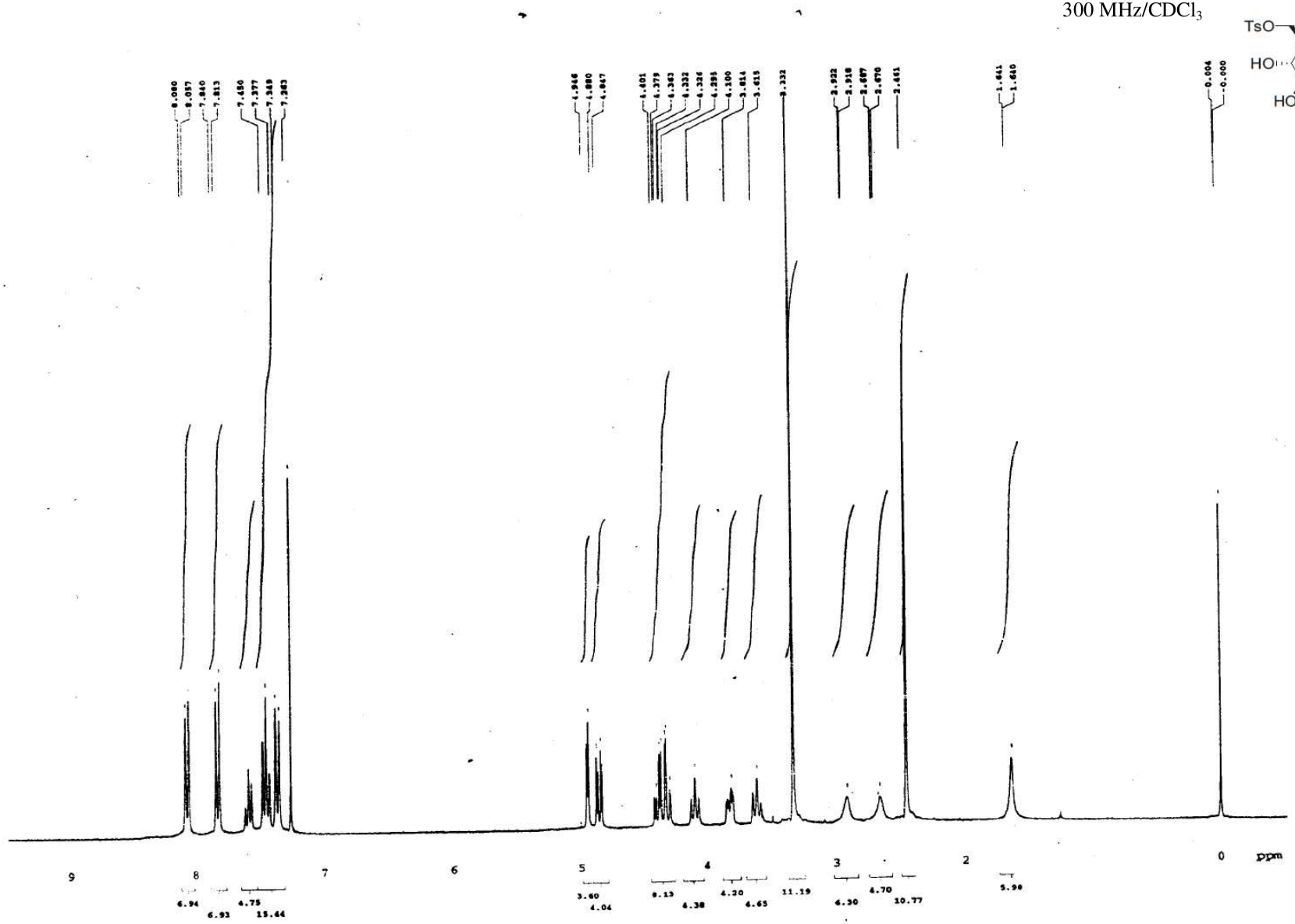
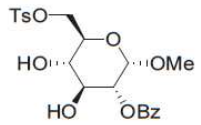
56.8299
PPM


400 MHz/CDCl3
Me
HO
BzO
OH
OMe
2g
8.0261
8.0078
7.5149
7.4966
7.3807
7.3611
7.3428
5.2173
5.1942
4.6085
4.0899
3.7642
3.7410
3.7288
3.7141
3.3310
2.9967
1.3251
1.3117
1.00
0.53
1.02
0.49
0.49
0.52
1.01
1.52
0.86
PPM

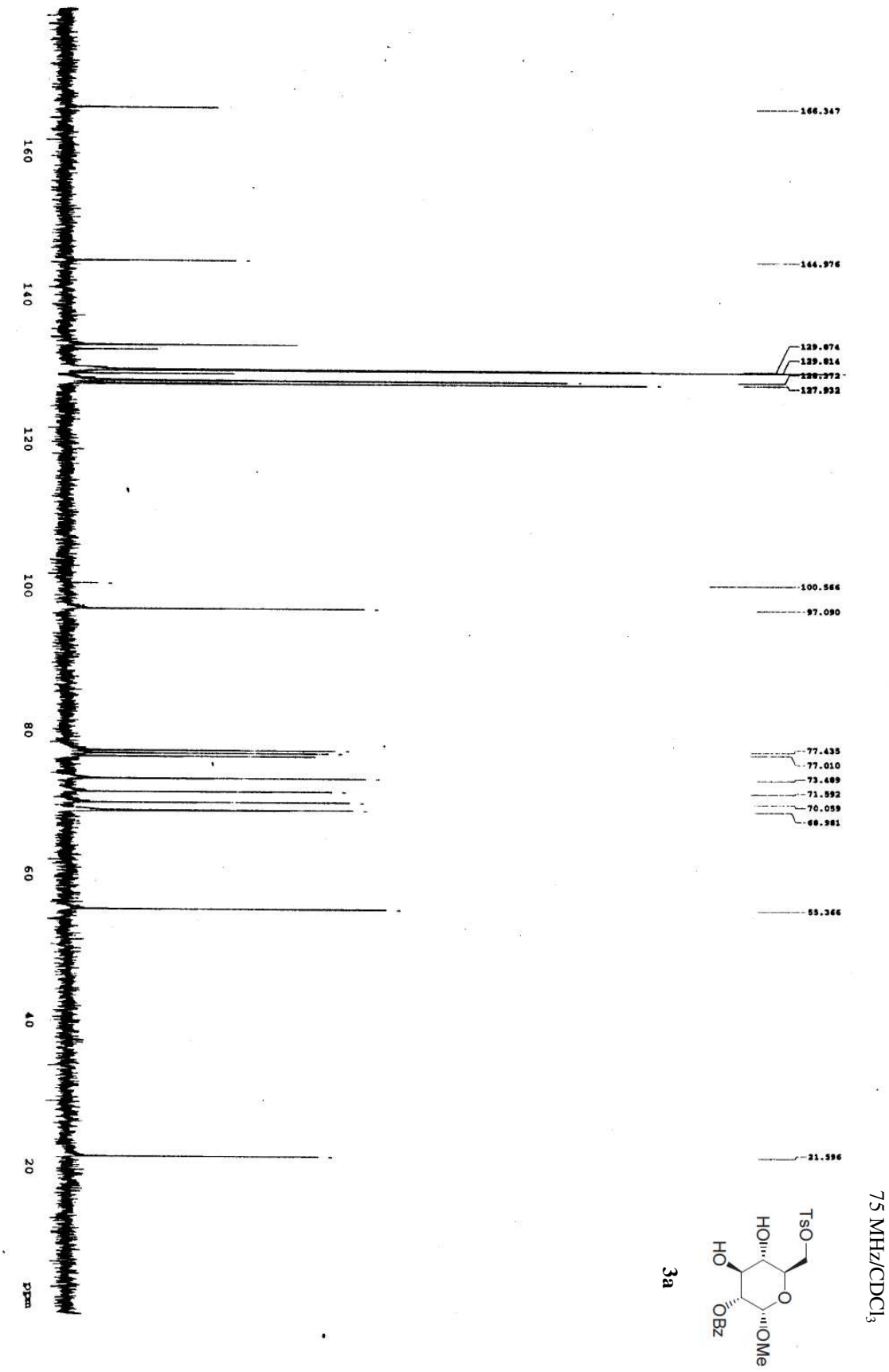

166.7446
133.2211
129.7387
129.4752
128.2815
100.5620
77.3211
77.0000
76.6789
75.2053
70.9572
69.3930
68.3392
54.7388
17.4364
2g
Me
O
OMe
HO
OH
BzO
75 MHz/CDCl3

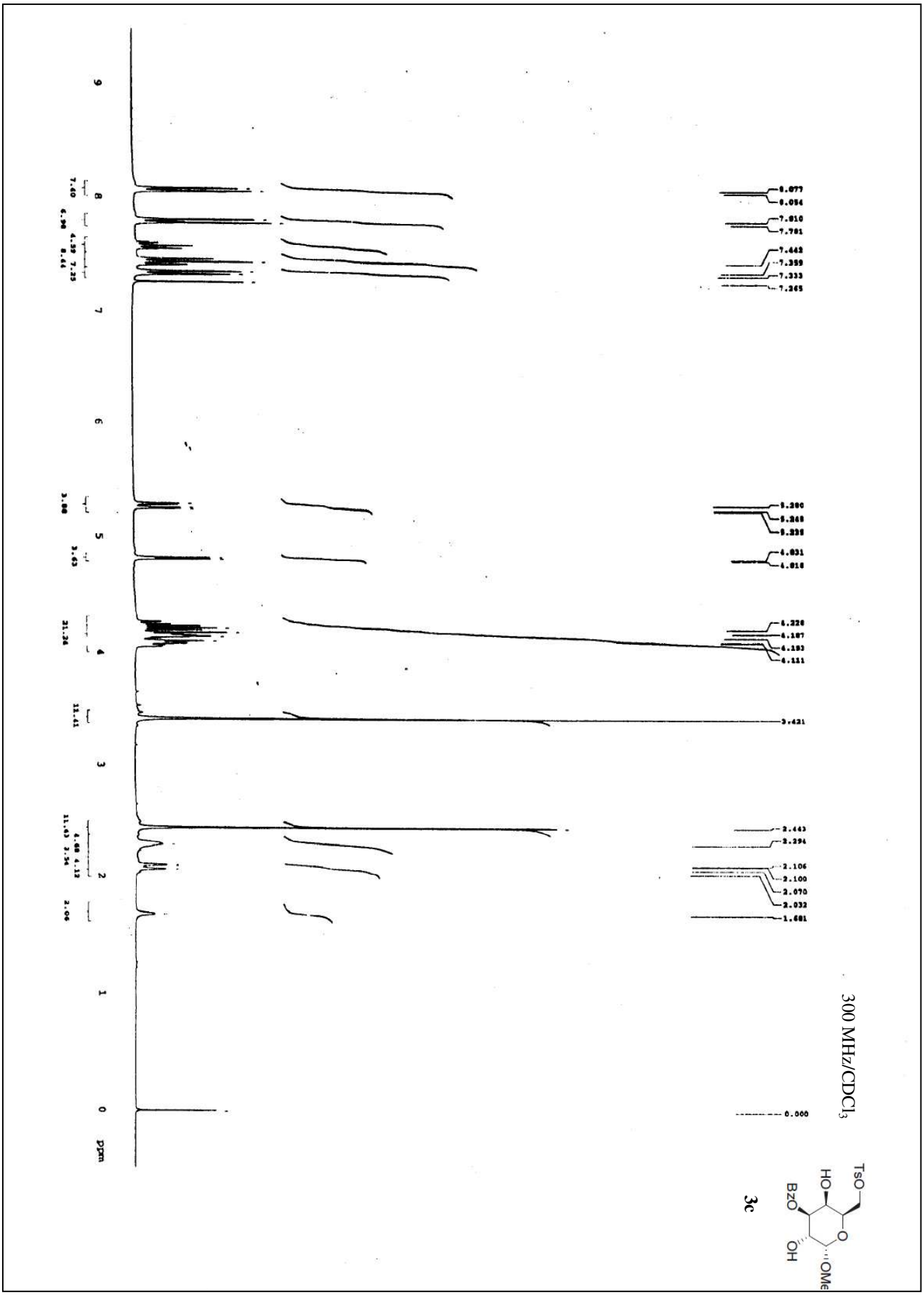
300 MHz/$CDCl_3$

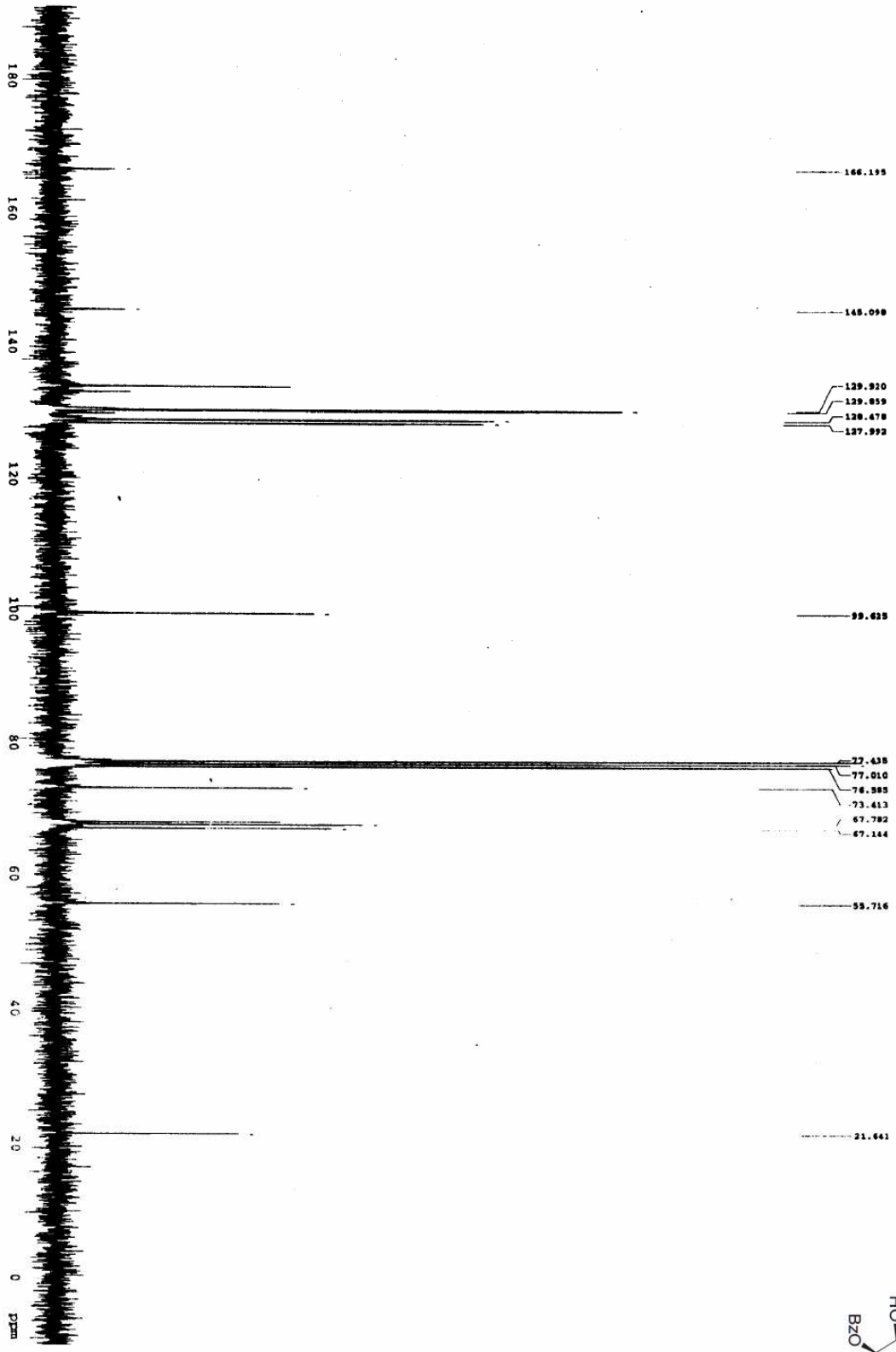


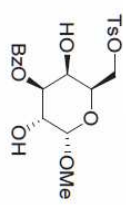


3a


166.347
144.976
129.674
129.014
128.372
127.932
100.566
97.090
77.435
77.010
73.489
71.592
70.059
68.981
55.366
21.596
TsO
HO
HO
O
OMe
OBz
3a
75 MHz/CDCl3
160
140
120
100
80
60
40
20
ppm

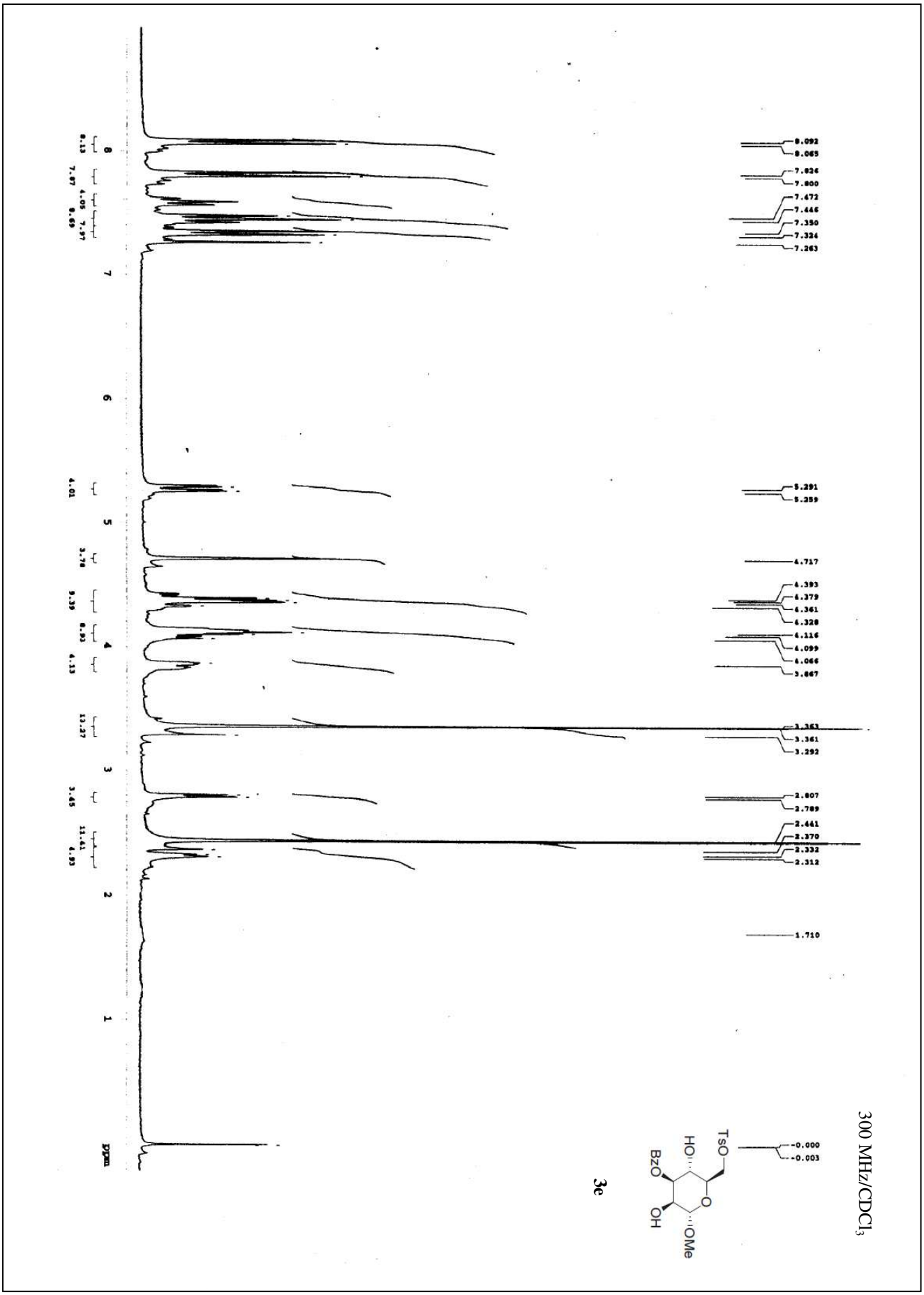

300 MHz/CDCl3
3c
TsO
HO
BzO
OH
OMe
8.077
8.054
7.810
7.781
7.442
7.359
7.333
7.265
5.280
5.268
5.238
4.831
4.818
4.220
4.187
4.153
4.111
3.421
2.443
2.294
2.106
2.100
2.070
2.032
1.681
0.000
ppm

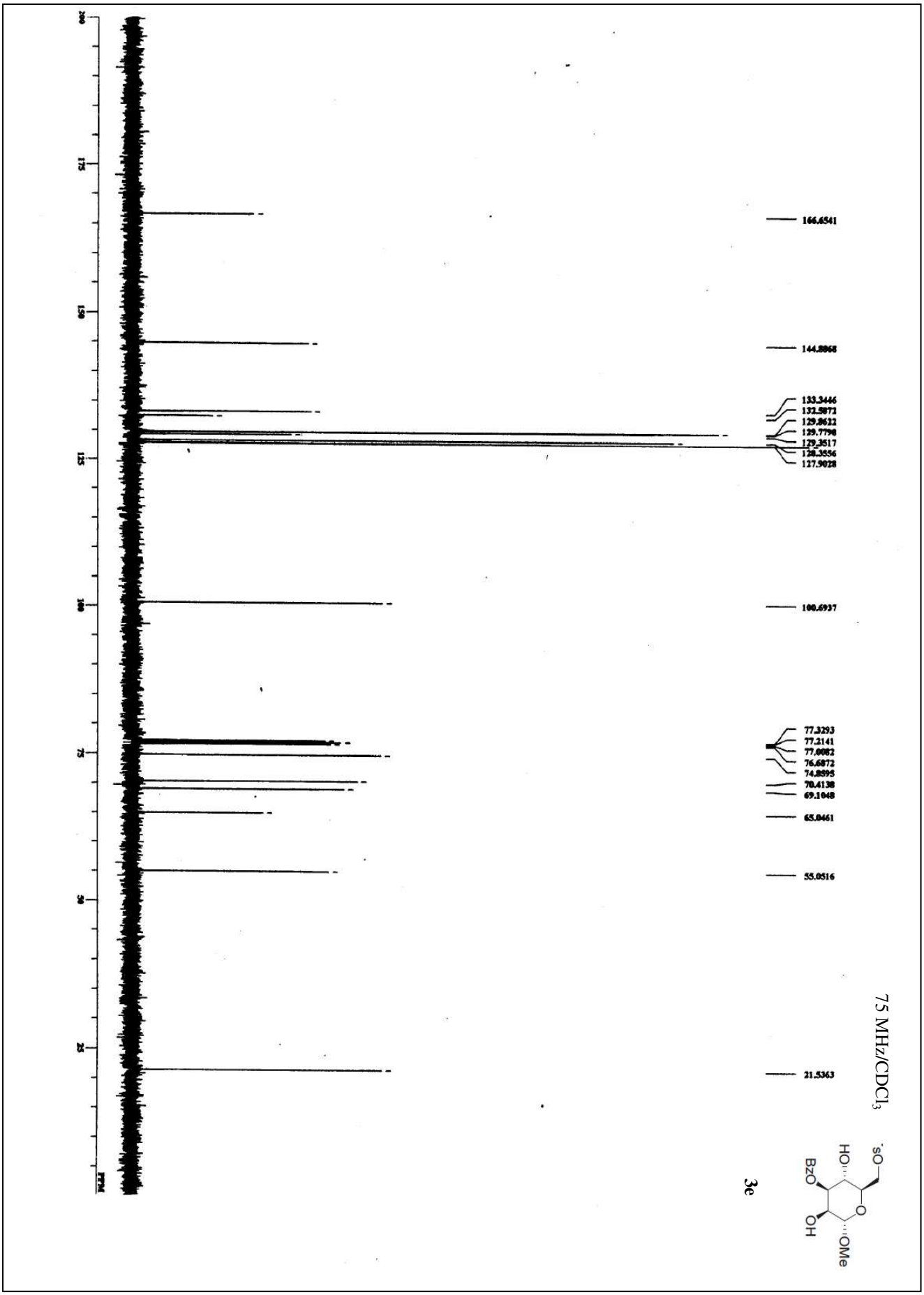


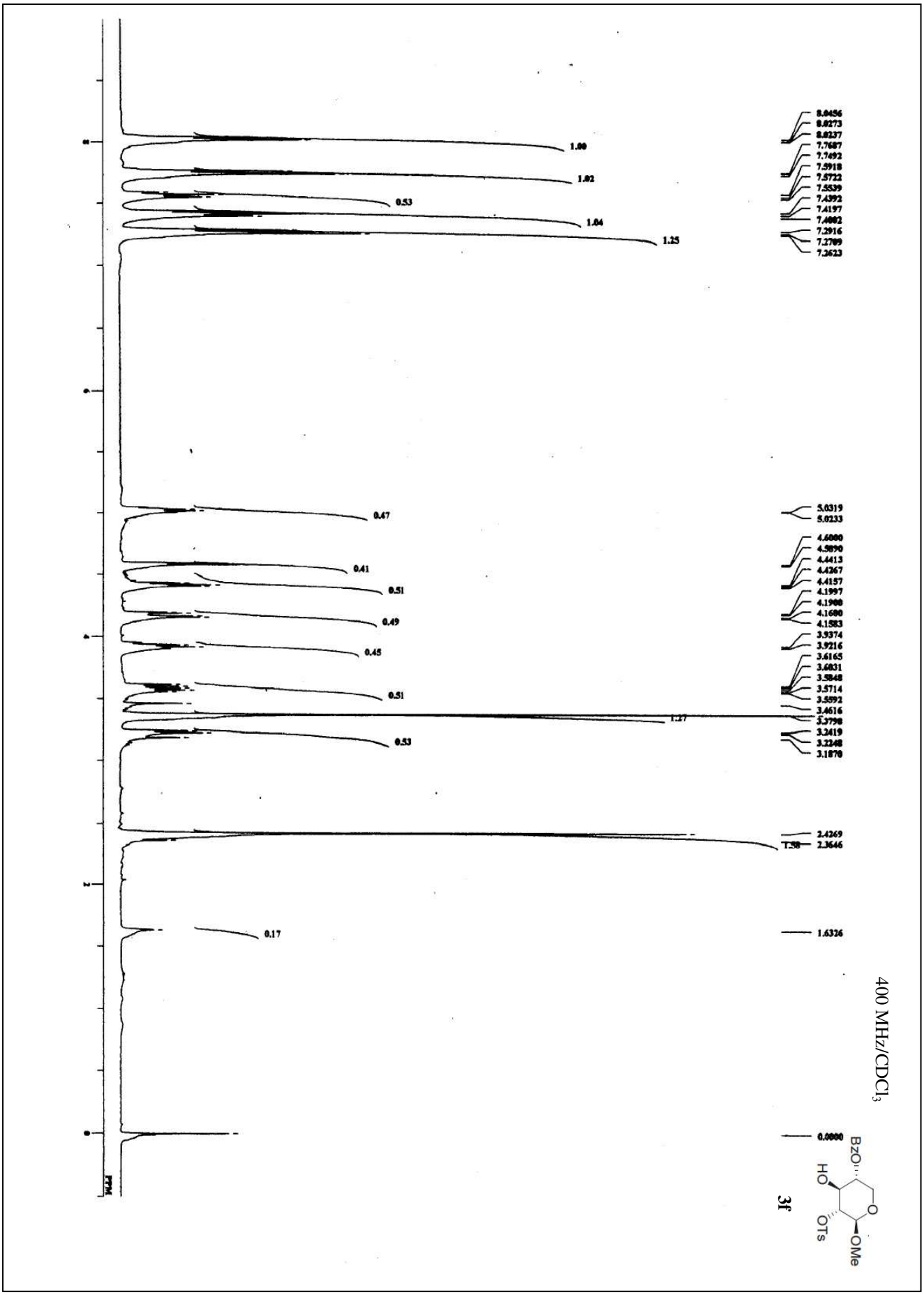


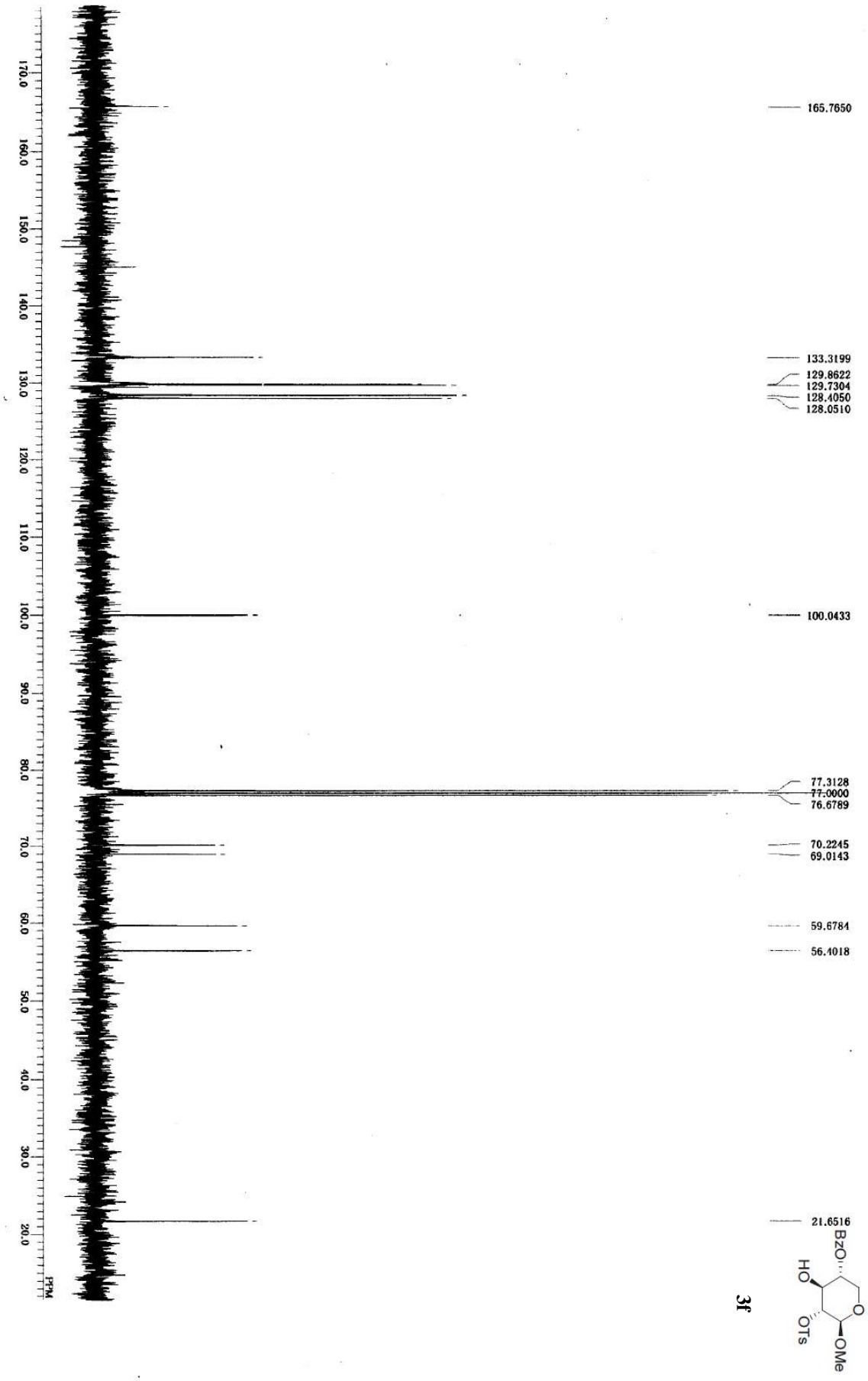
75 MHz/$CDCl_3$

3c


300 MHz/CDCl3
3e
TsO
HO
BzO
OH
O
OMe
8.092
8.065
7.826
7.800
7.472
7.446
7.350
7.324
7.263
5.291
5.259
4.717
4.393
4.379
4.361
4.328
4.116
4.099
4.066
3.867
3.363
3.361
3.292
2.807
2.789
2.441
2.370
2.332
2.312
1.710
-0.000
-0.003
ppm

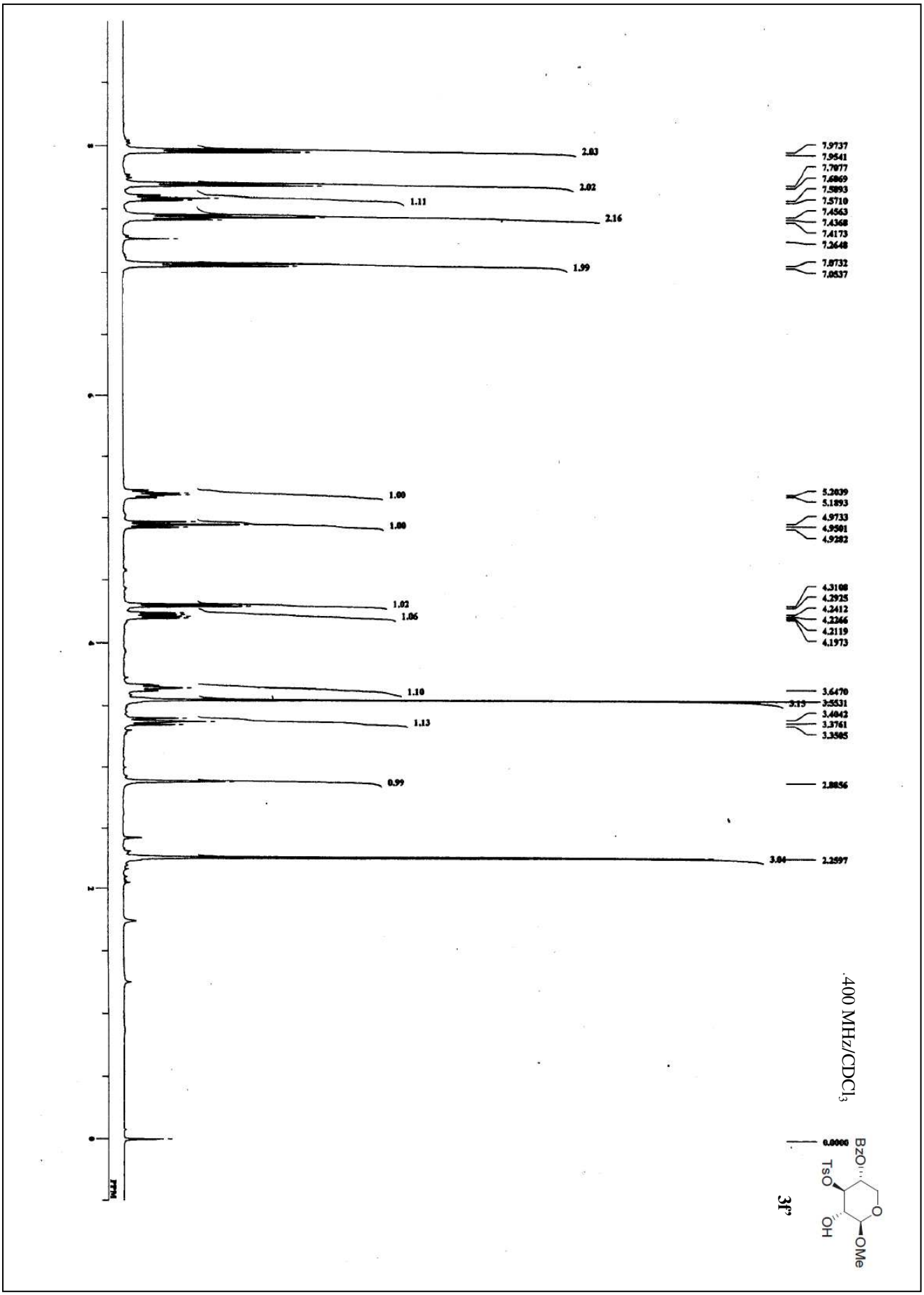

166.6541
144.8068
133.3446
132.5872
129.8622
129.7798
129.3517
128.3556
127.9028
100.6937
77.3293
77.2141
77.0082
76.6872
74.8595
70.4138
69.1048
65.0461
55.0516
21.5363
75 MHz/CDCl3
3e
HO
BzO
OH
O
OMe
O
PPM

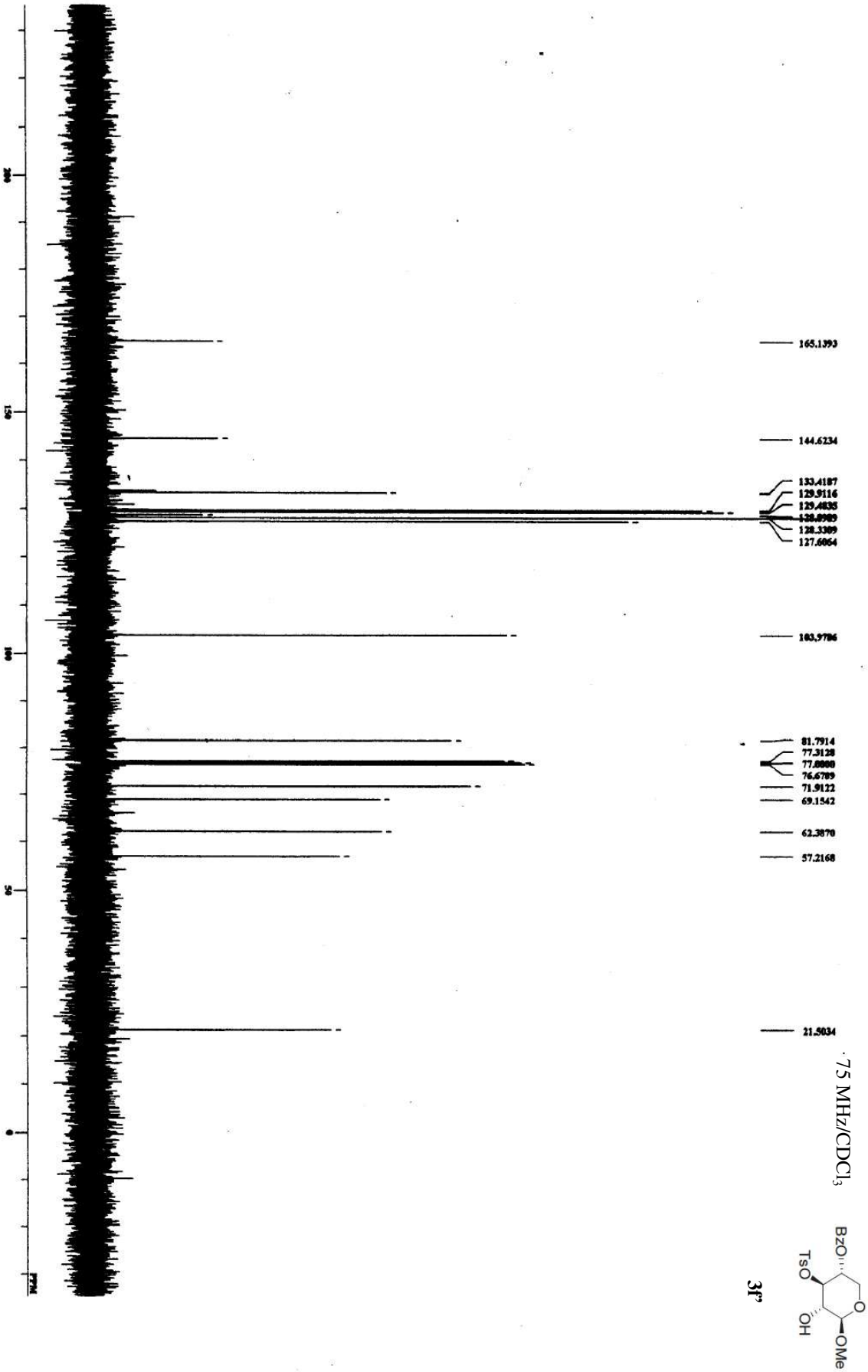

400 MHz/CDCl3
3f
BzO
HO
OTs
OMe
8.0456
8.0273
8.0237
7.7687
7.7492
7.5918
7.5722
7.5539
7.4392
7.4197
7.4002
7.2916
7.2709
7.2623
5.0319
5.0233
4.6000
4.5890
4.4413
4.4267
4.4157
4.1997
4.1900
4.1680
4.1583
3.9374
3.9216
3.6165
3.6031
3.5848
3.5714
3.5592
3.4616
3.3798
3.2419
3.2248
3.1870
2.4269
2.3646
1.6326
0.0000
1.00
1.02
0.53
1.04
1.25
0.47
0.41
0.51
0.49
0.45
0.51
1.27
0.53
0.17
PPM

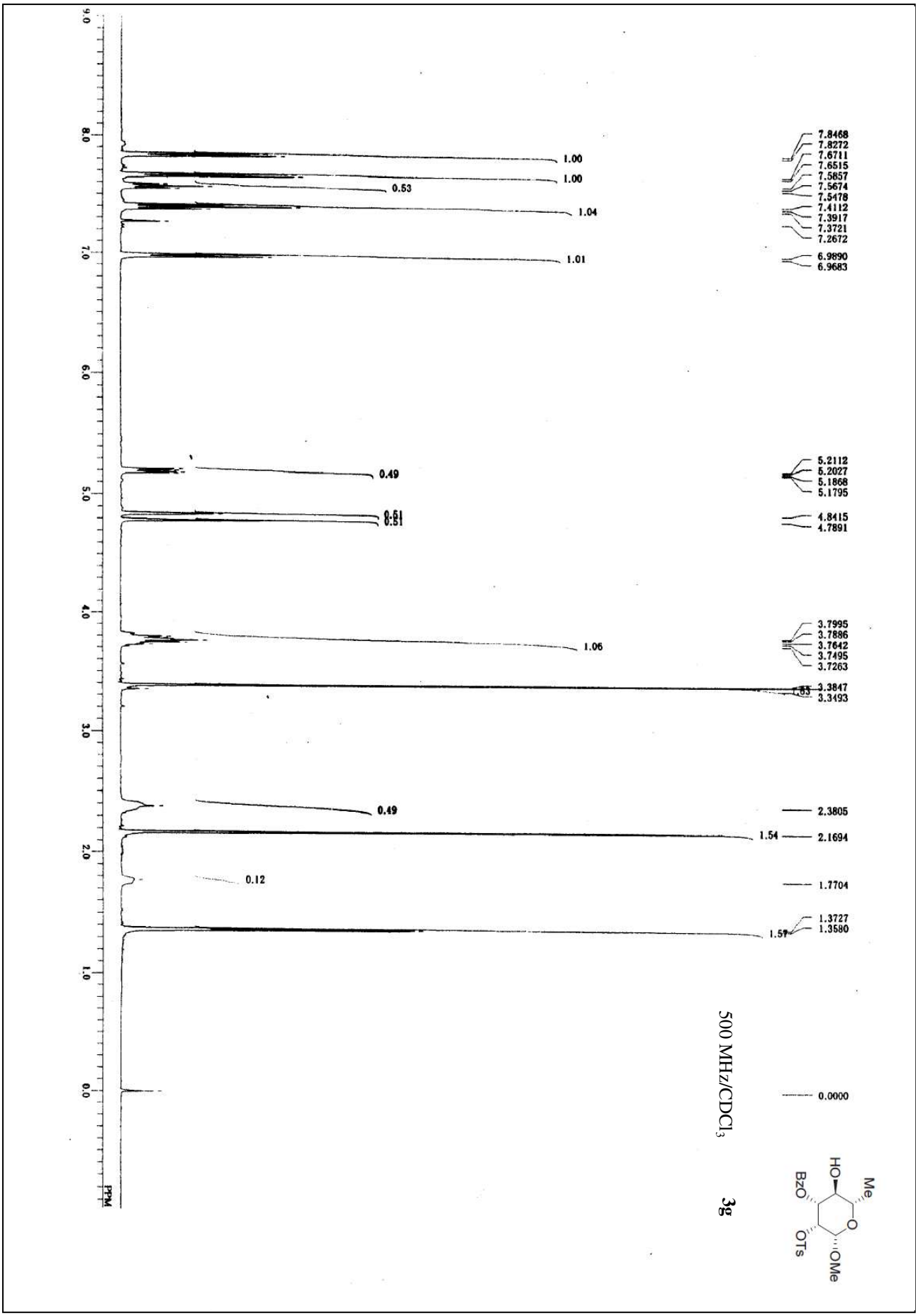


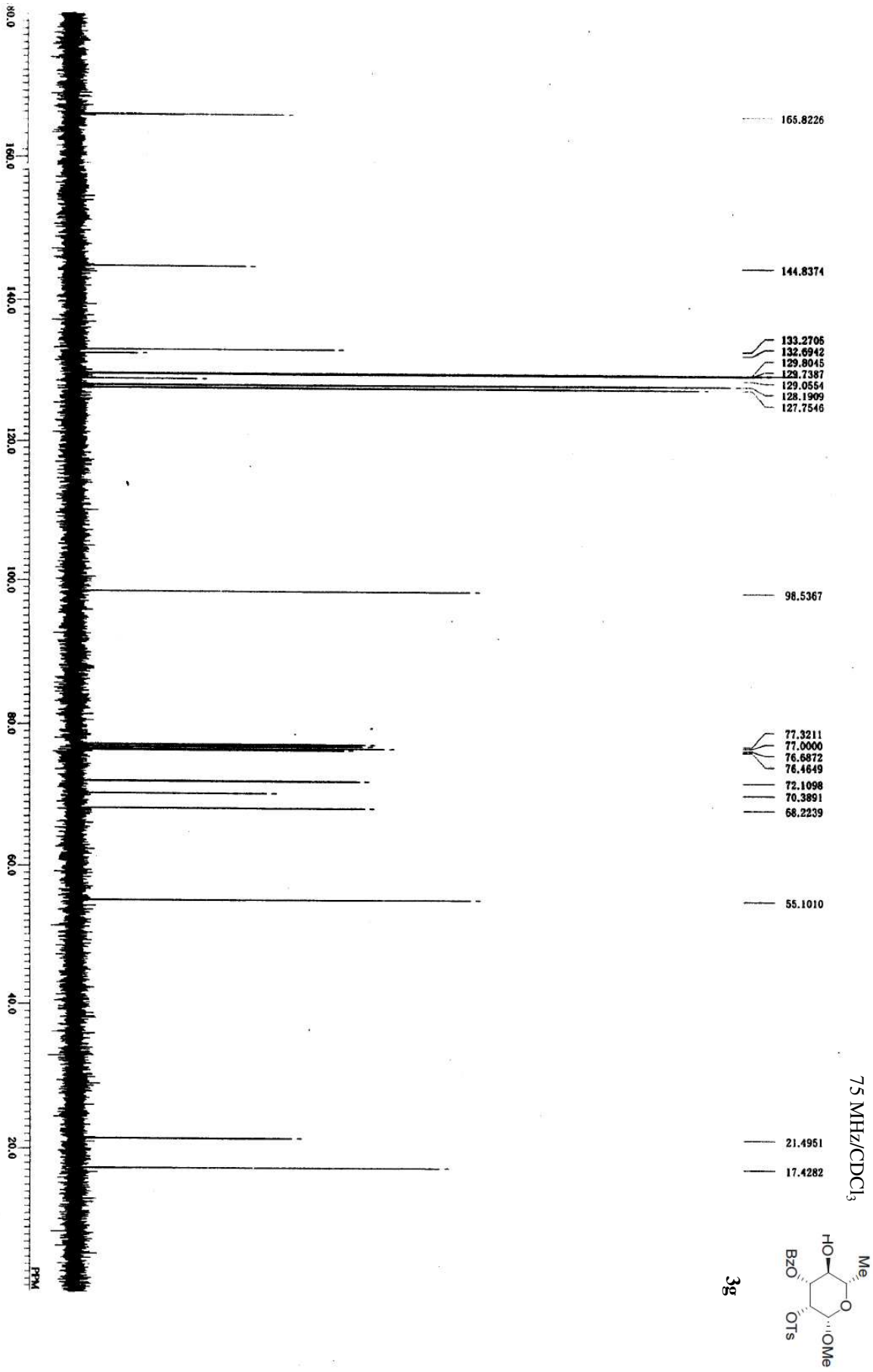
3f

75 MHz/$CDCl_3$

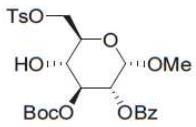

400 MHz/CDCl3
BzO
TsO
OH
OMe
O
3f'
7.9737
7.9541
7.7077
7.6869
7.5893
7.5710
7.4563
7.4368
7.4173
7.2648
7.0732
7.0537
5.2039
5.1893
4.9733
4.9501
4.9282
4.3108
4.2925
4.2412
4.2266
4.2119
4.1973
3.6470
3.5531
3.4042
3.3761
3.3505
2.8856
2.2597
0.0000
2.03
2.02
1.11
2.16
1.99
1.00
1.00
1.02
1.06
1.10
1.13
0.99
3.04
PPM


165.1393
144.6234
133.4187
129.9116
129.4835
128.8989
128.3389
127.6064
103.9786
81.7914
77.3128
77.0000
76.6789
71.9122
69.1542
62.3870
57.2168
21.5034
PPM
200
150
100
50
0
75 MHz/CDCl3
BzO
TsO
OH
O
OMe
3f'

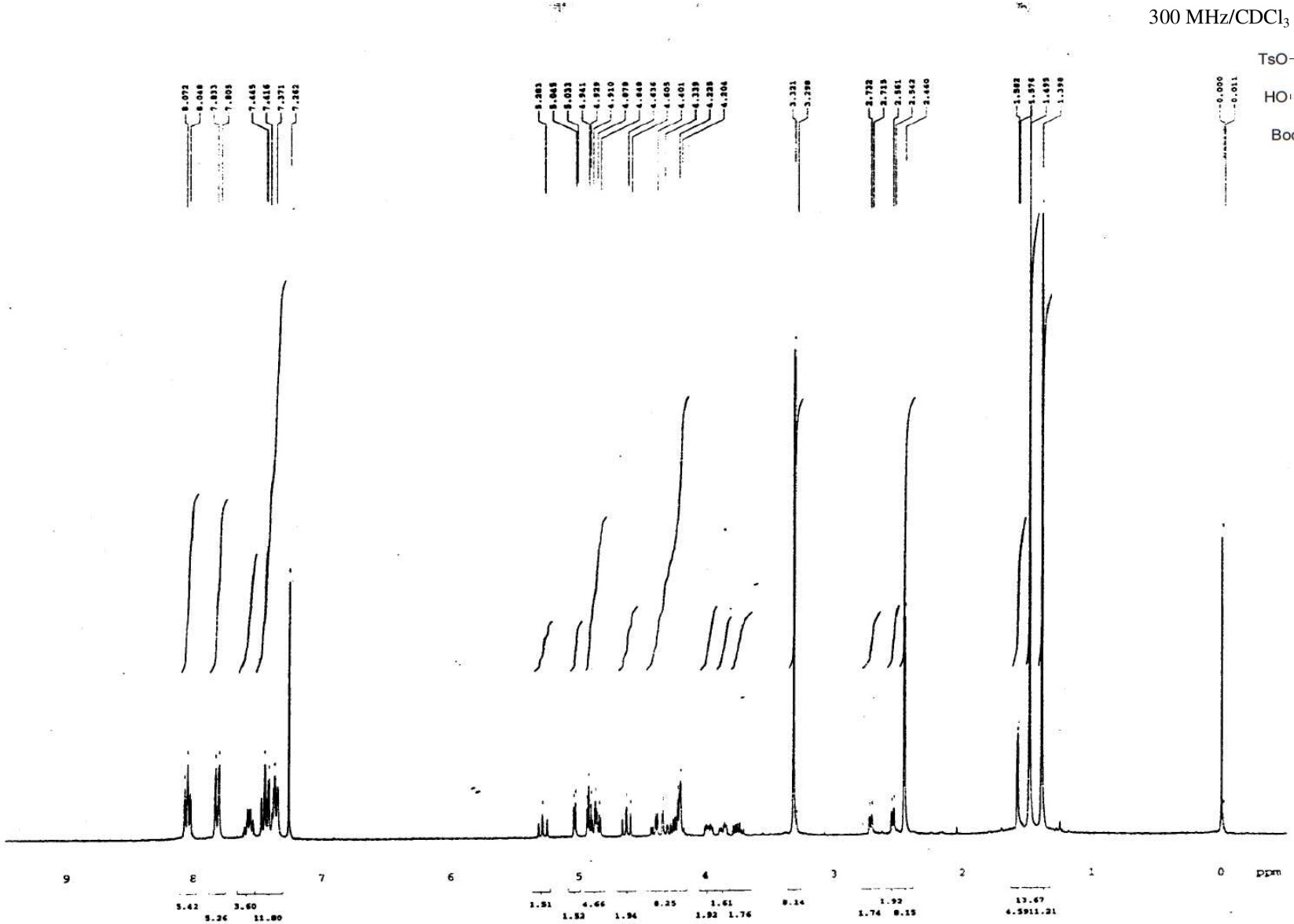

7.8468
7.8272
7.6711
7.6515
7.5857
7.5674
7.5478
7.4112
7.3917
7.3721
7.2672
6.9890
6.9683
5.2112
5.2027
5.1868
5.1795
4.8415
4.7891
3.7995
3.7886
3.7642
3.7495
3.7263
3.3847
3.3493
2.3805
2.1694
1.7704
1.3727
1.3580
0.0000
1.00
1.00
0.53
1.04
1.01
0.49
1.06
0.49
1.54
0.12
1.57
500 MHz/CDCl3
3g
Me
HO
BzO
OTs
OMe
O
PPM

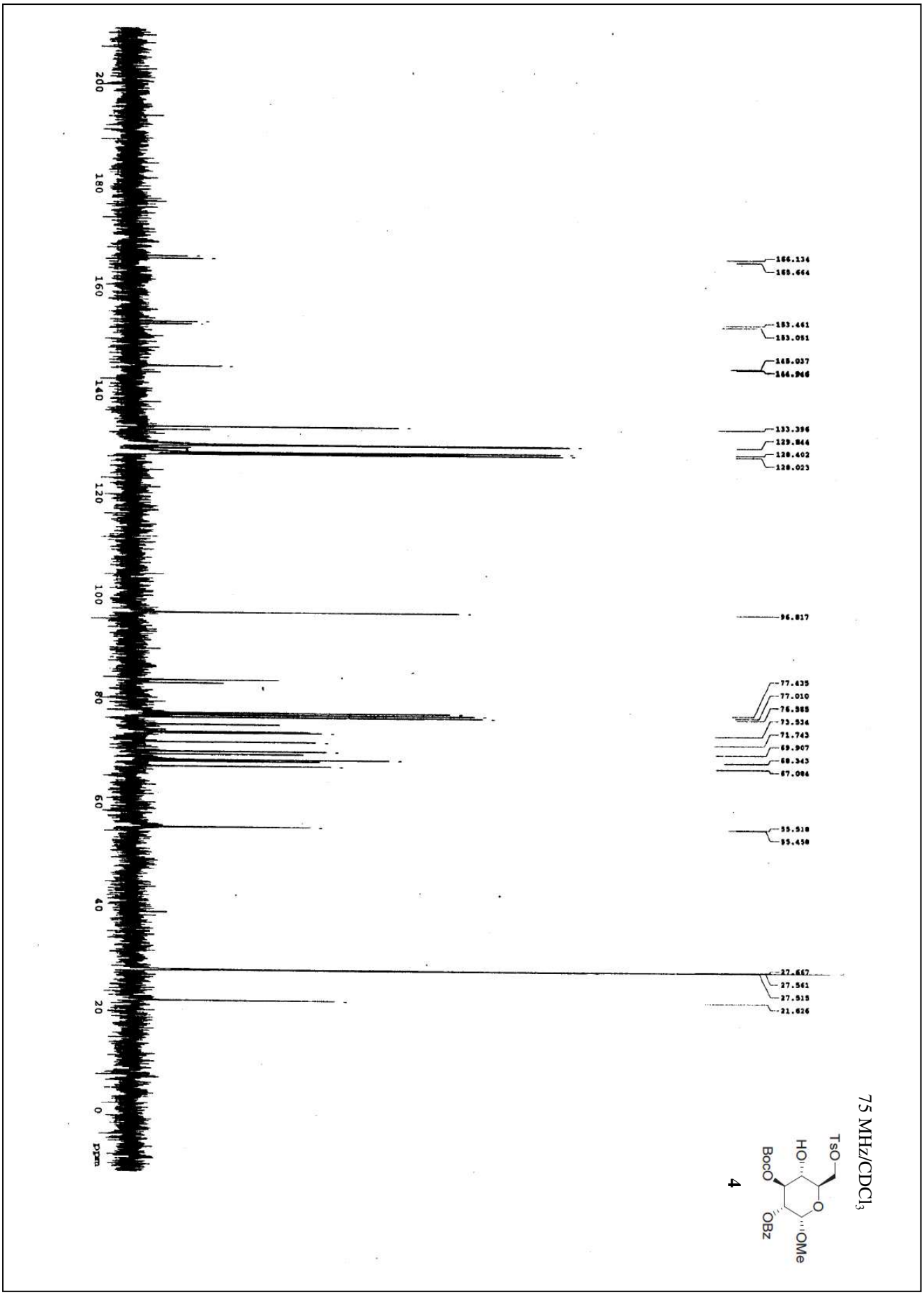

75 MHz/CDCl3
Me
HO
BzO
O
OTs
OMe
3g
165.8226
144.8374
133.2705
132.6942
129.8045
129.7387
129.0554
128.1909
127.7546
98.5367
77.3211
77.0000
76.6872
76.4649
72.1098
70.3891
68.2239
55.1010
21.4951
17.4282
PPM
160.0
140.0
120.0
100.0
80.0
60.0
40.0
20.0

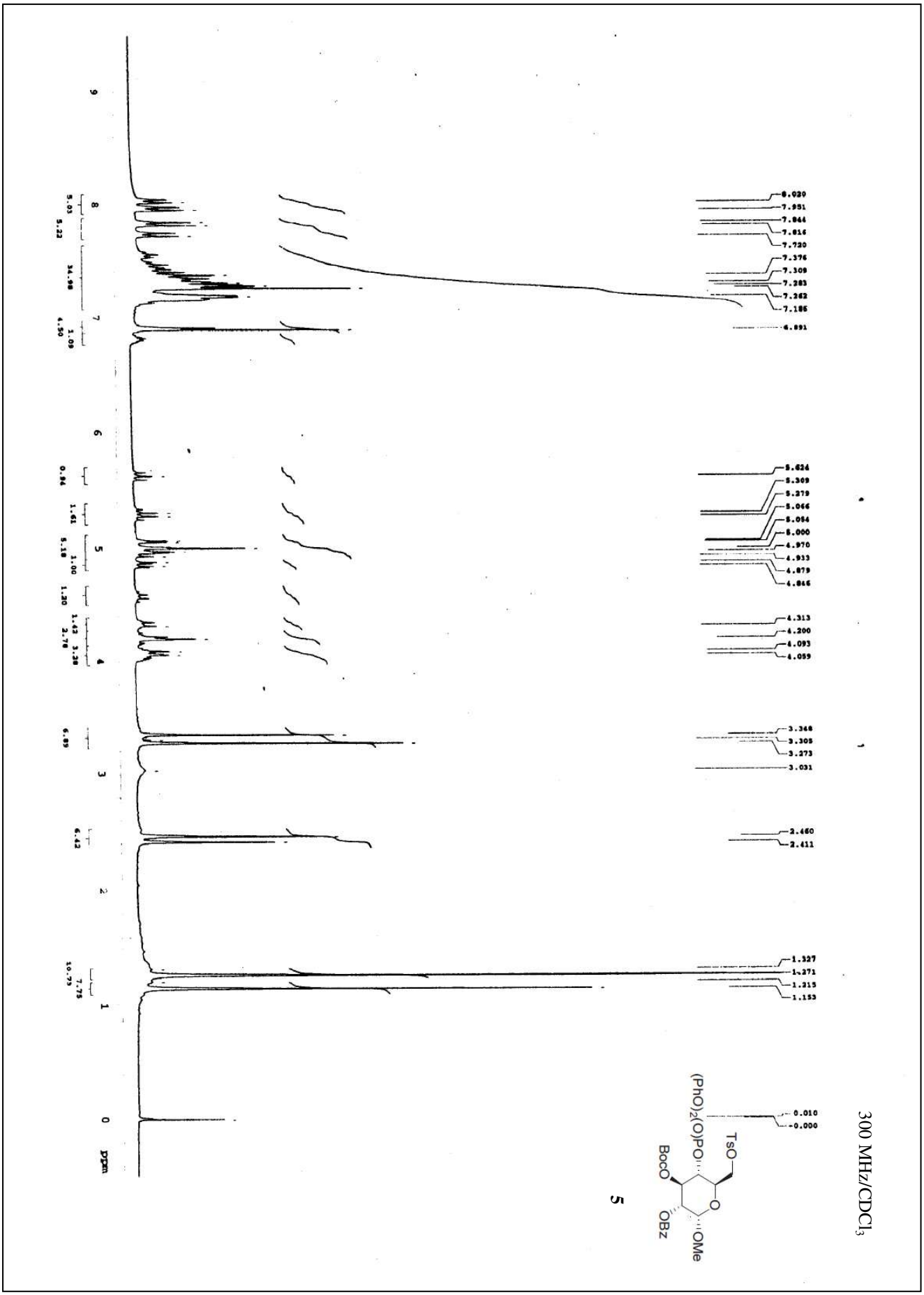
300 MHz/$CDCl_3$

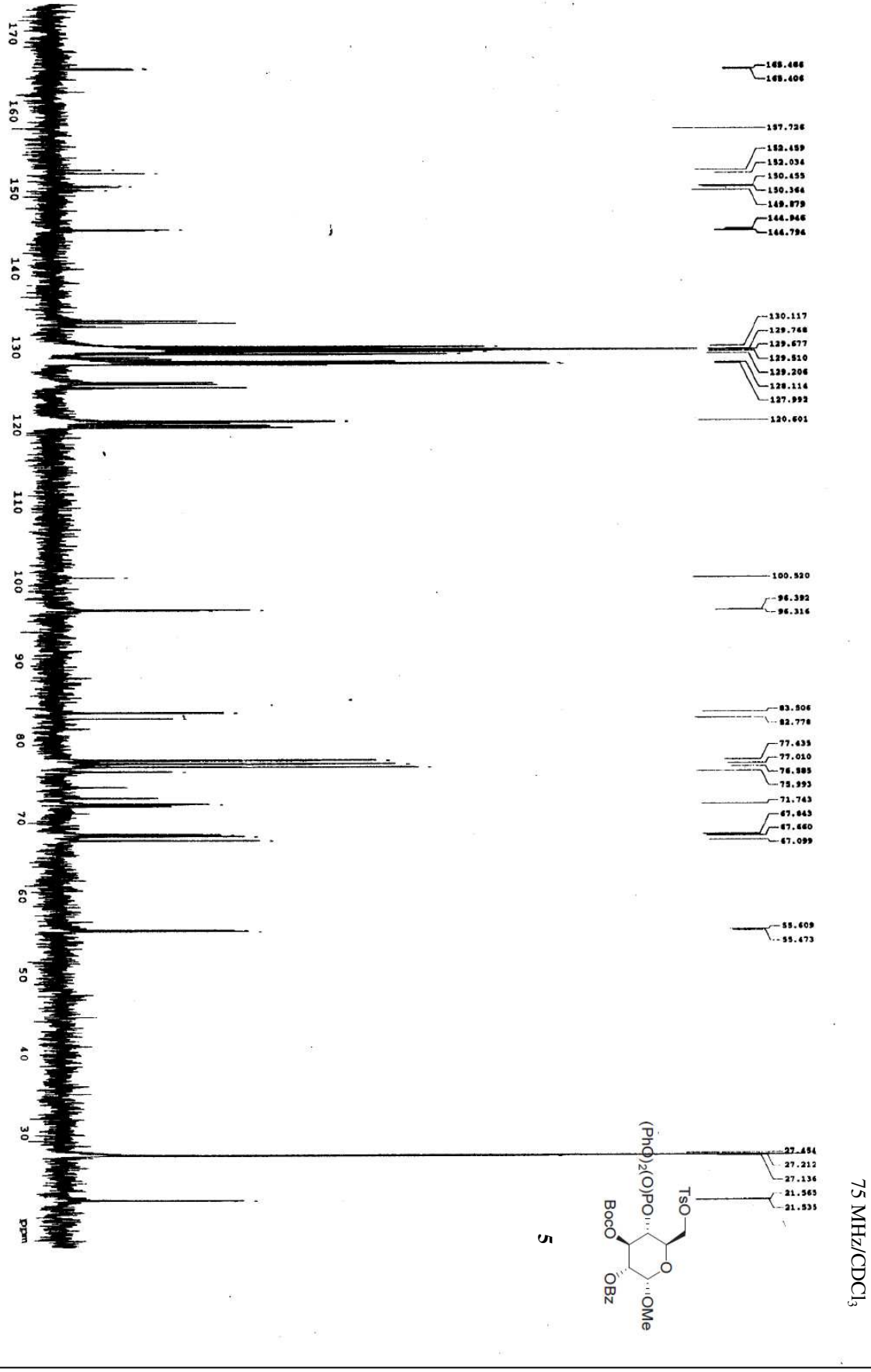


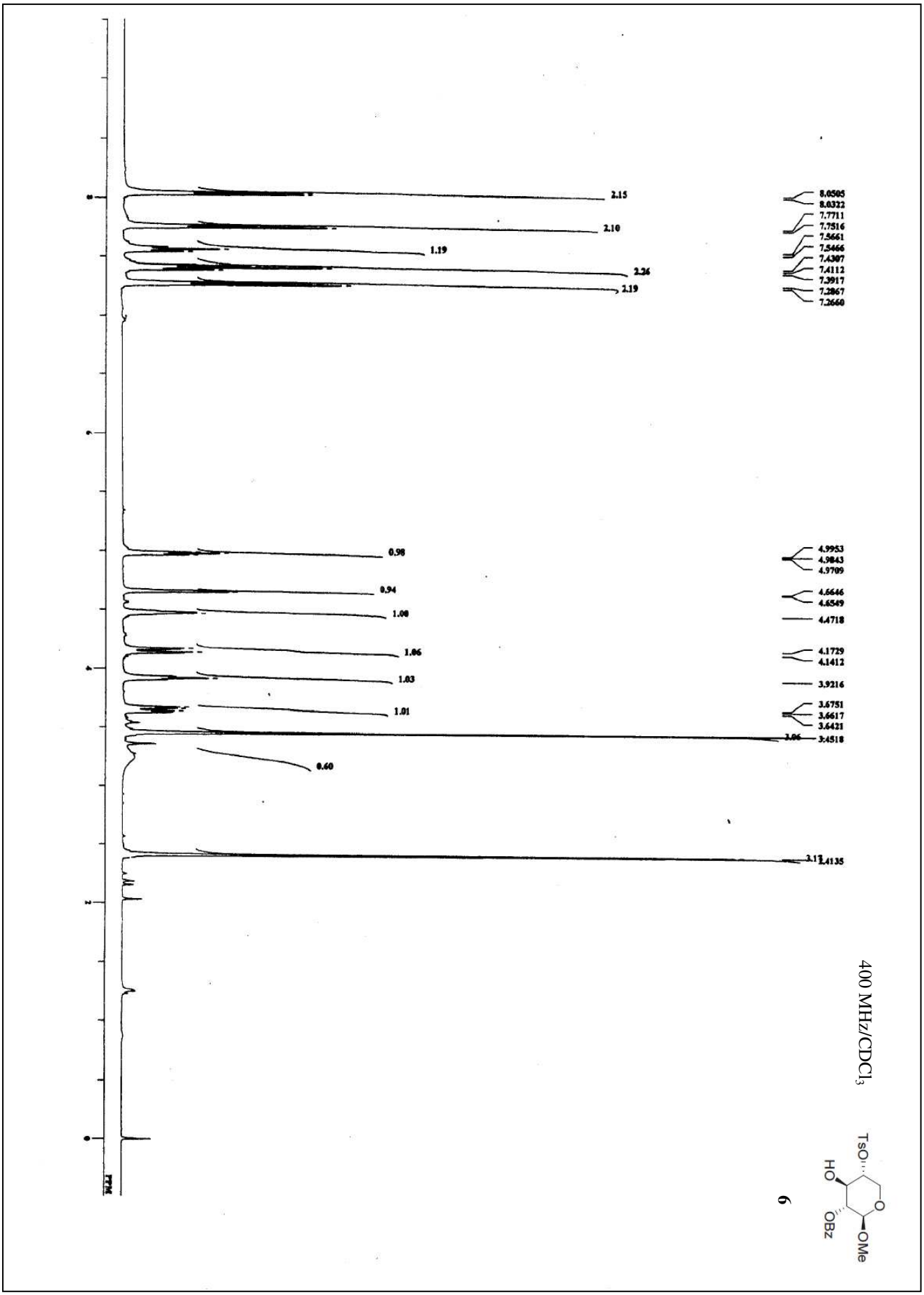
4

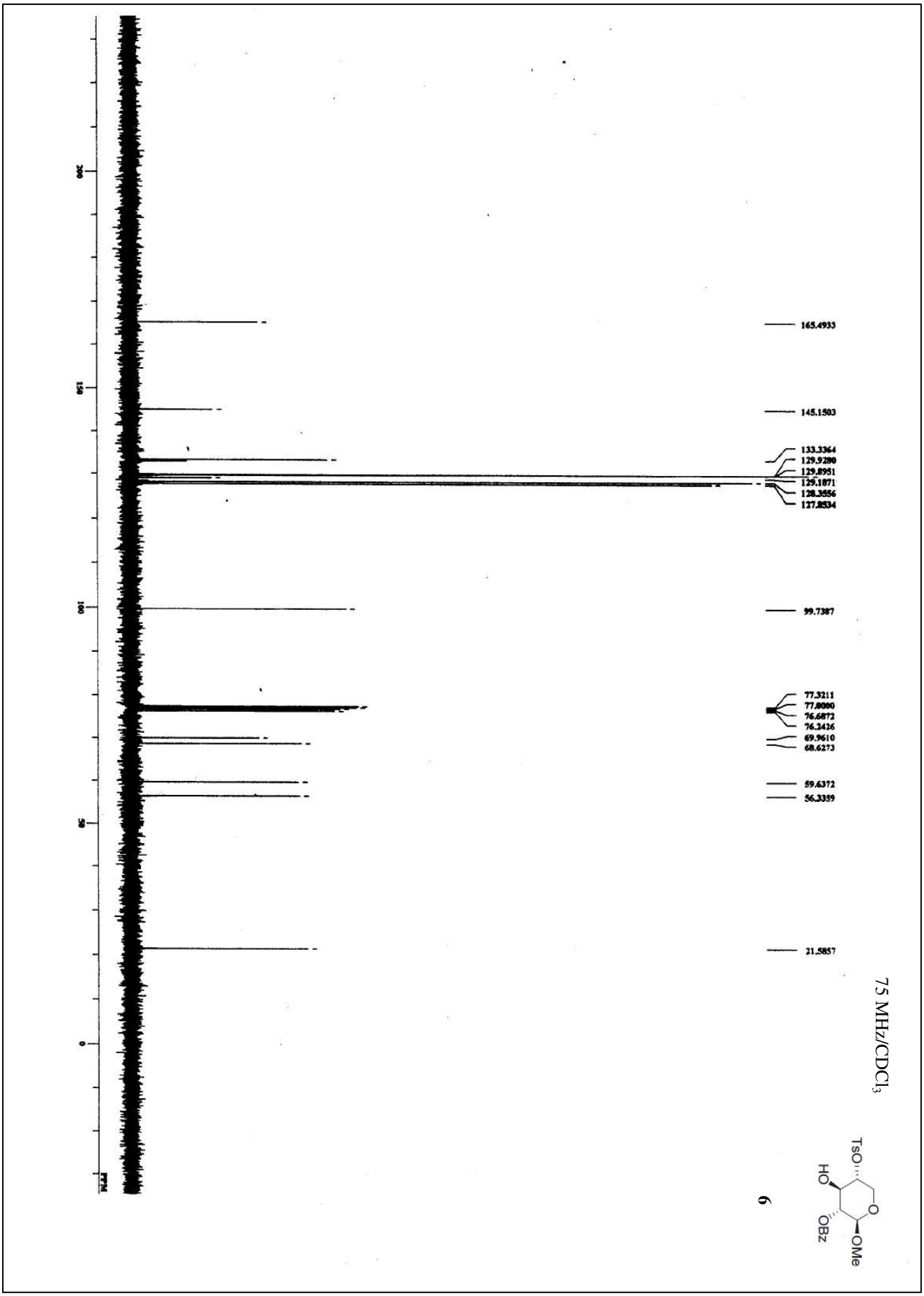



75 MHz/CDCl3
TsO
HO
O
OMe
BocO
OBz
4
166.134
165.664
153.461
153.051
145.037
144.946
133.396
129.844
128.402
128.023
96.817
77.435
77.010
76.585
73.534
71.743
69.907
68.343
67.084
55.518
55.450
27.667
27.561
27.515
21.626
200
180
160
140
120
100
80
60
40
20
0
ppm

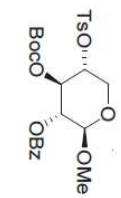

300 MHz/CDCl3
5
TsO
(PhO)2(O)PO
BocO
OBz
OMe
0.010
-0.000
8.020
7.951
7.844
7.816
7.720
7.376
7.309
7.283
7.262
7.186
6.891
5.624
5.309
5.279
5.066
5.054
5.000
4.970
4.933
4.879
4.846
4.313
4.200
4.093
4.059
3.348
3.305
3.273
3.031
2.460
2.411
1.327
1.271
1.215
1.153
ppm


75 MHz/CDCl3
5
TsO
(PhO)2(O)PO
BocO
OBz
O
OMe
27.454
27.212
27.136
21.565
21.535
55.609
55.473
67.643
67.660
67.099
71.743
77.435
77.010
76.585
75.993
83.506
82.778
96.392
96.316
100.520
120.601
130.117
129.768
129.677
129.510
129.206
128.114
127.992
144.946
144.794
150.455
150.364
149.879
152.459
152.034
157.726
169.486
169.406
ppm

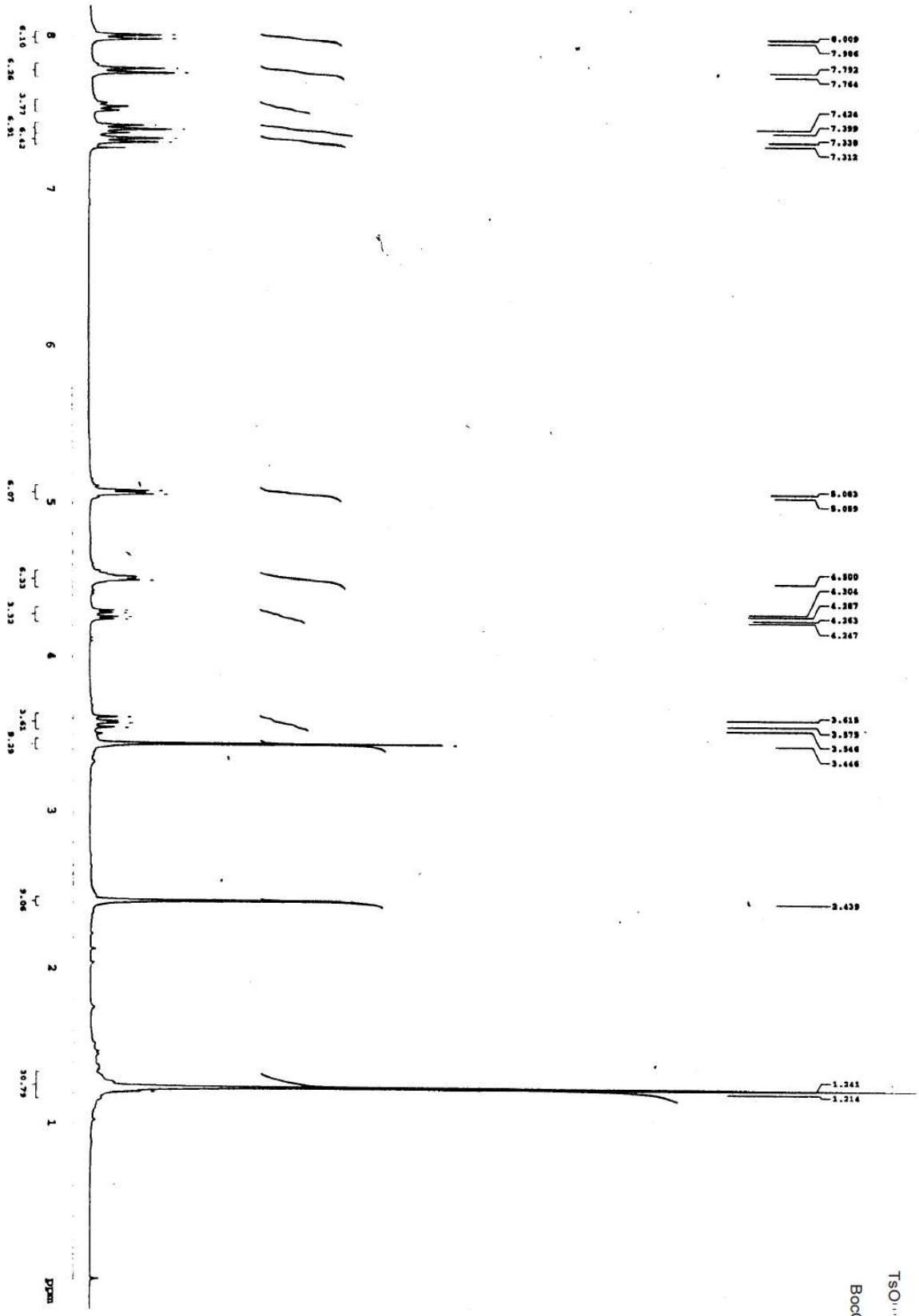

400 MHz/CDCl3
TsO
HO
OBz
O
OMe
6
8.0505
8.0322
7.7711
7.7516
7.5661
7.5466
7.4307
7.4112
7.3917
7.2867
7.2660
4.9953
4.9843
4.9709
4.6646
4.6549
4.4718
4.1729
4.1412
3.9216
3.6751
3.6617
3.6421
3.4518
2.4135
2.15
2.10
1.19
2.26
2.19
0.98
0.94
1.00
1.06
1.03
1.01
0.60
PPM

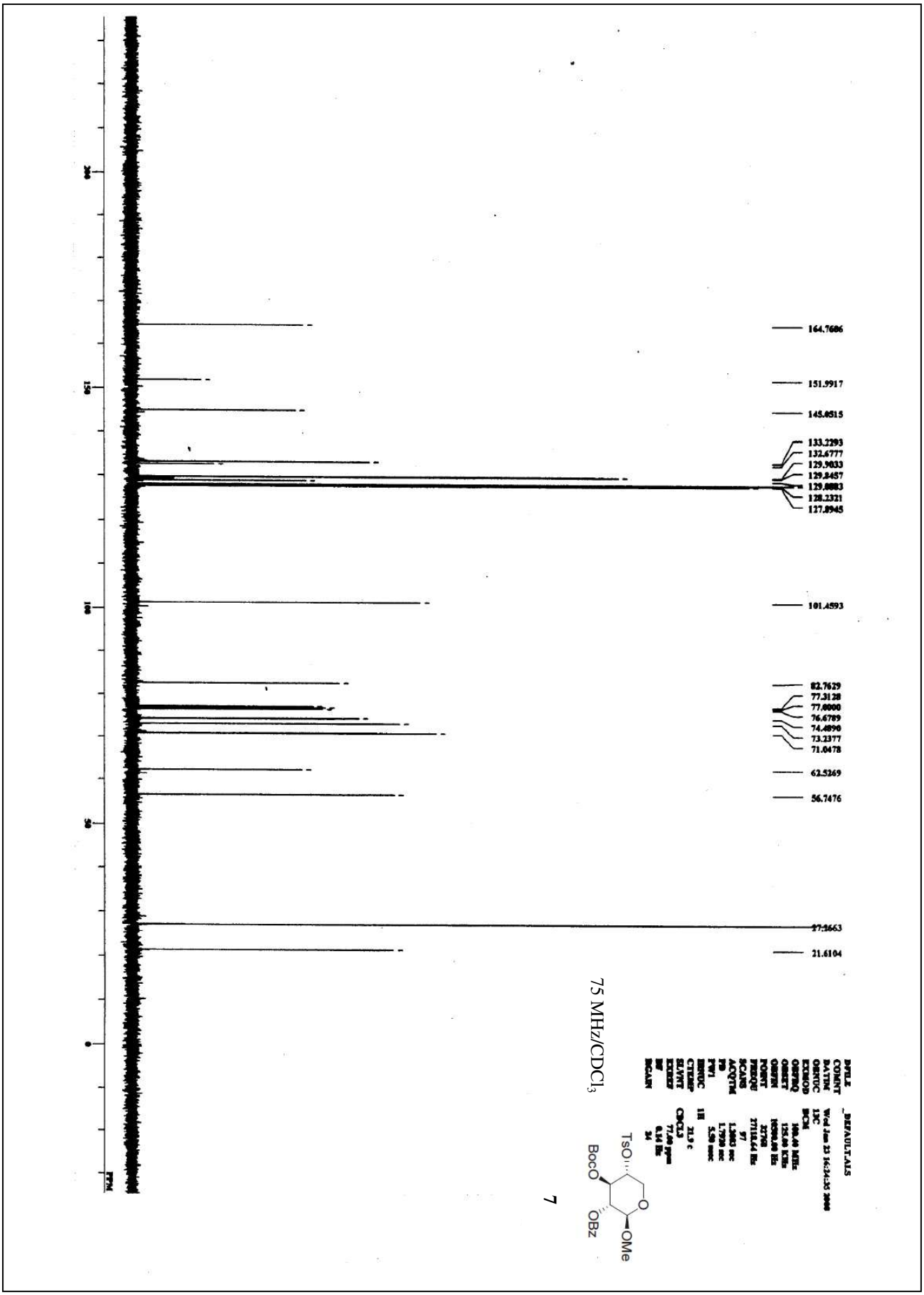

75 MHz/CDCl3
TsO
HO
OBz
O
OMe
6
165.4933
145.1503
133.3364
129.9280
129.8951
129.1871
128.3556
127.8534
99.7387
77.3211
77.0000
76.6872
76.2426
69.9610
68.6273
59.6372
56.3359
21.5857
200
150
100
50
0
PPM

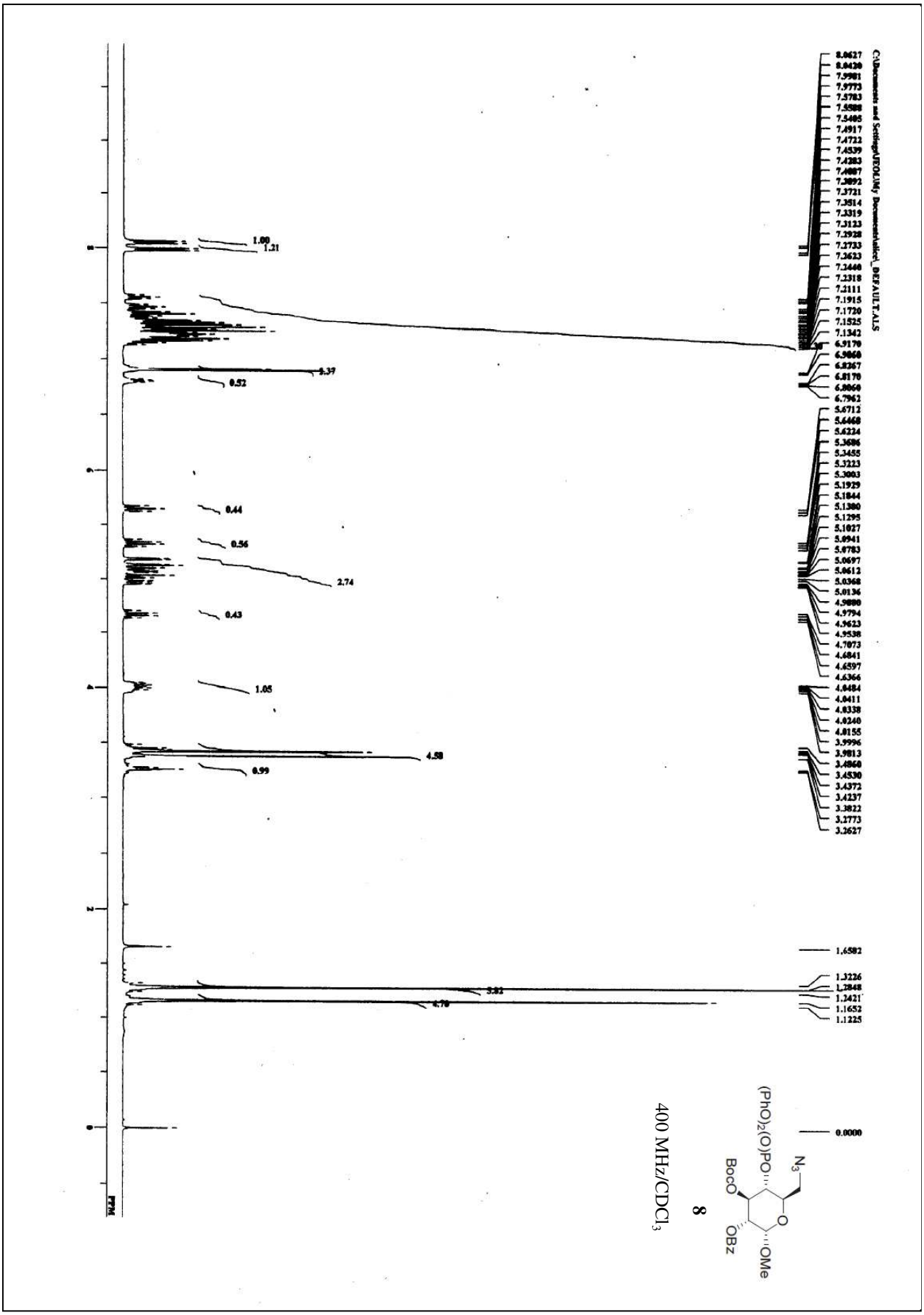
300 MHz/$CDCl_3$

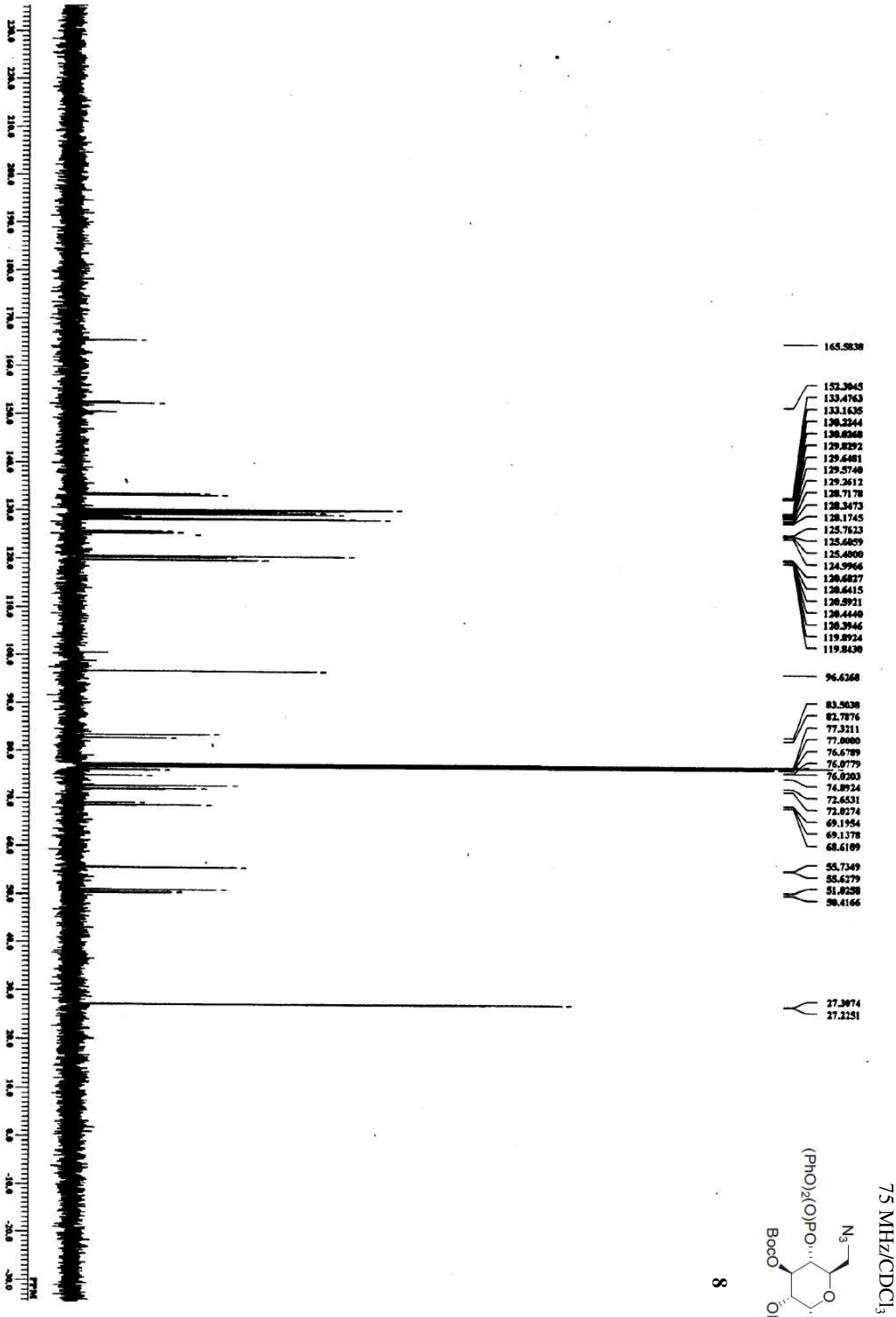


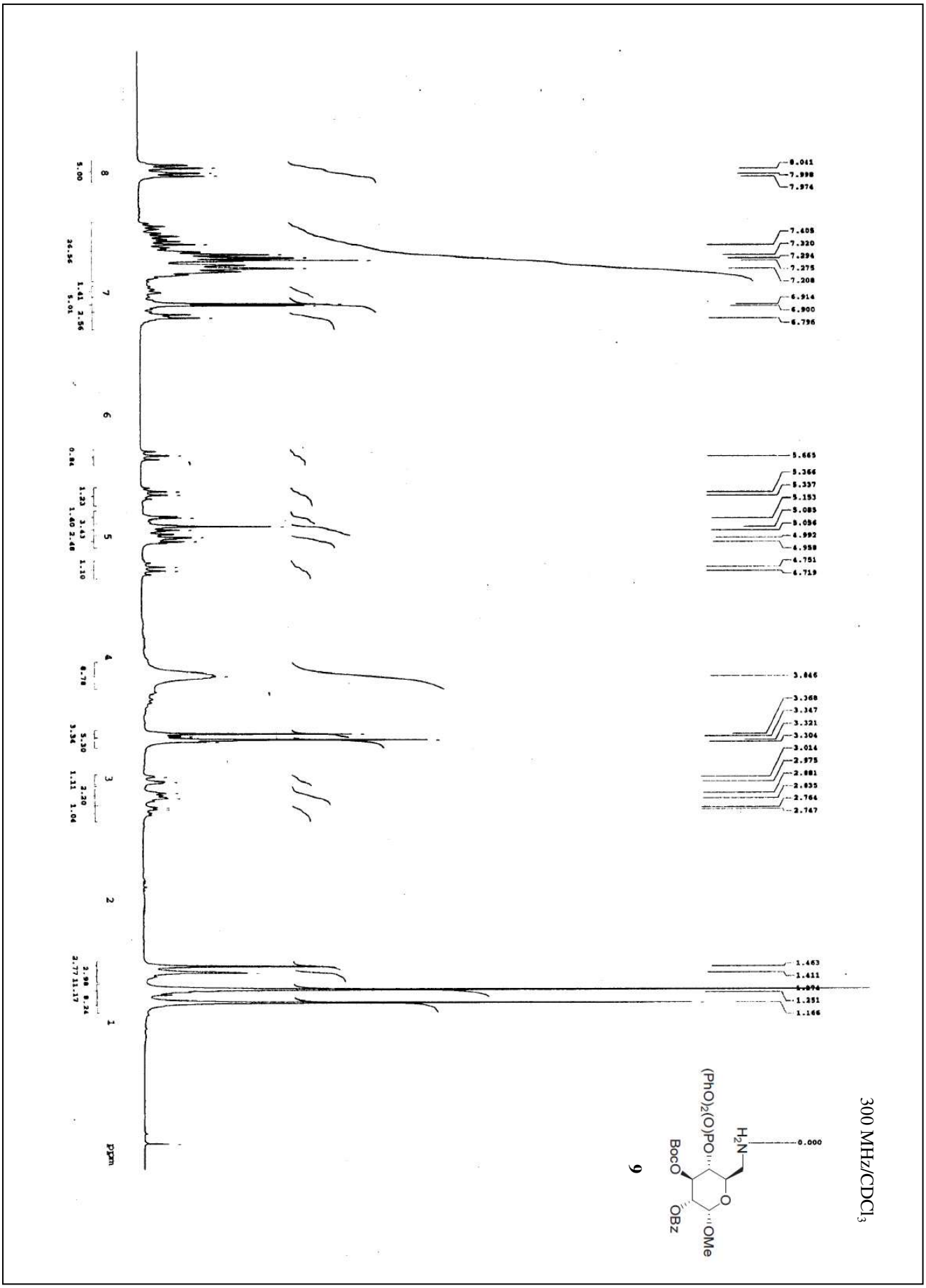
7

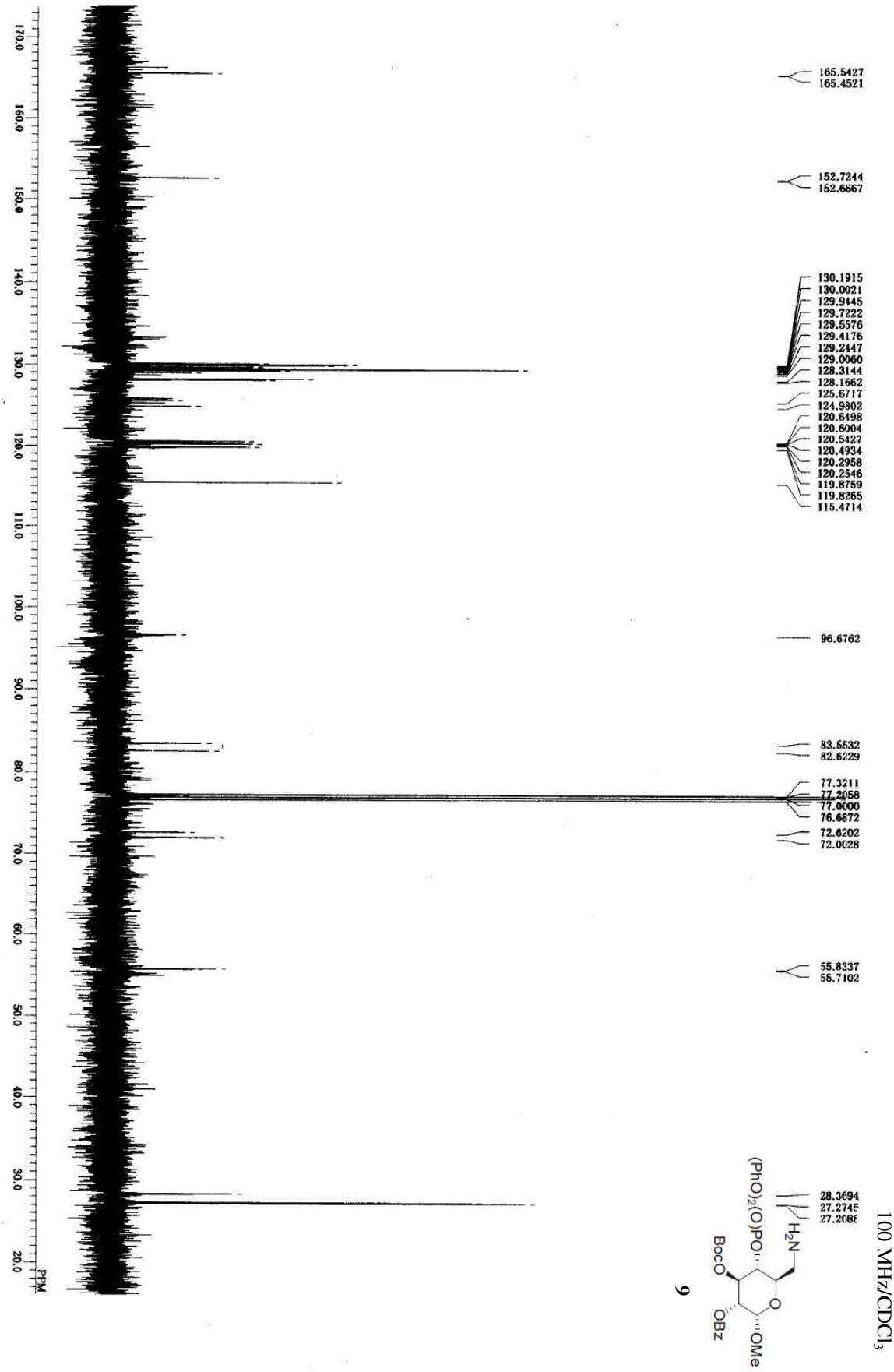



164.7686
151.5917
145.0515
133.2293
132.6777
129.9033
129.8457
129.8083
128.2321
127.8945
101.4593
82.7629
77.3128
77.0000
76.6789
74.4890
73.2377
71.0478
62.5269
56.7476
27.5663
21.6104
75 MHz/CDCl3
7
TsO
OMe
BocO
OBz
O
PPM

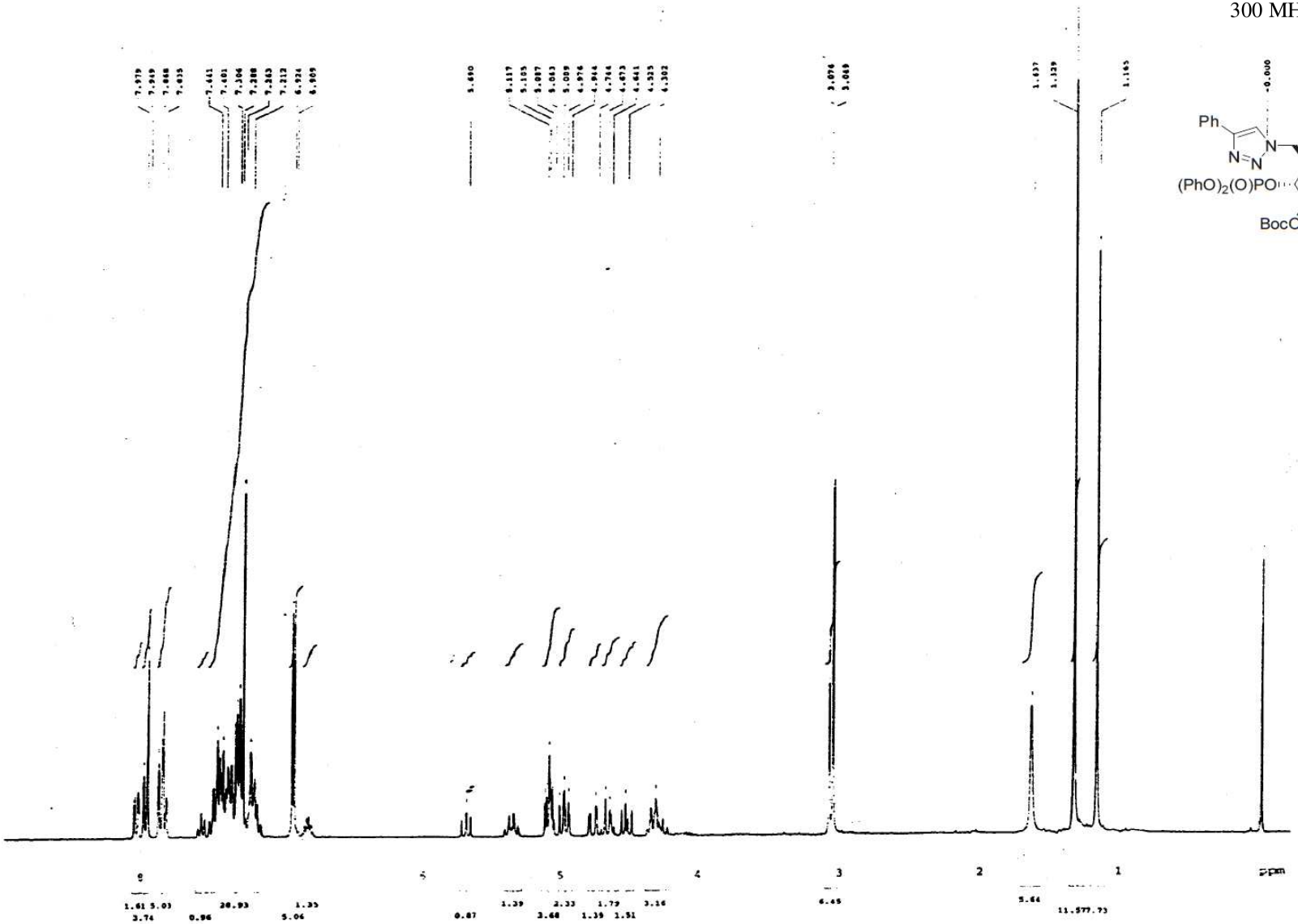

8
400 MHz/CDCl3
(PhO)2(O)PO
N3
BocO
OBz
OMe
0.0000
1.6582
1.3226
1.2848
1.2421
1.1652
1.1225
3.2627
3.2773
3.3822
3.4237
3.4372
3.4530
3.4860
3.9813
3.9996
4.0155
4.0240
4.0338
4.0411
4.0484
4.6366
4.6597
4.6841
4.7073
4.9538
4.9623
4.9794
4.9880
5.0136
5.0368
5.0612
5.0697
5.0783
5.0941
5.1027
5.1295
5.1380
5.1844
5.1929
5.3003
5.3223
5.3455
5.3686
5.6224
5.6468
5.6712
6.7962
6.8060
6.8170
6.8267
6.9060
6.9170
7.1342
7.1525
7.1720
7.1915
7.2111
7.2318
7.2440
7.2623
7.2733
7.2928
7.3123
7.3319
7.3514
7.3721
7.3892
7.4087
7.4283
7.4539
7.4722
7.4917
7.5405
7.5588
7.5783
7.5973
7.5981
8.0420
8.0627
1.00
1.21
5.37
0.52
0.44
0.56
2.74
0.43
1.05
4.58
0.99
5.82
4.79
PPM

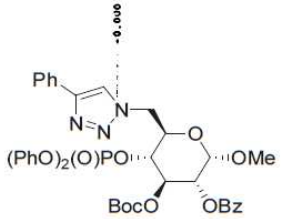

75 MHz/CDCl3
8
(PhO)2(O)PO
N3
BocO
OBz
OMe
O
165.5838
152.3045
133.4763
133.1635
130.2244
130.0368
129.8292
129.6481
129.5740
129.2612
128.7178
128.3473
128.1745
125.7623
125.6059
125.4000
124.9966
120.6827
120.6415
120.5921
120.4440
120.3946
119.8924
119.8430
96.6268
83.5038
82.7876
77.3211
77.0000
76.6789
76.0779
76.0203
74.8924
72.6531
72.0274
69.1954
69.1378
68.6189
55.7349
55.6279
51.0258
50.4166
27.3074
27.2251
PPM


300 MHz/CDCl3
9
H2N
(PhO)2(O)PO
BocO
OBz
OMe
0.000
8.041
7.998
7.974
7.405
7.320
7.294
7.275
7.208
6.914
6.900
6.796
5.665
5.366
5.337
5.153
5.085
5.056
4.992
4.958
4.751
4.719
3.846
3.368
3.347
3.321
3.304
3.014
2.975
2.881
2.835
2.764
2.747
1.463
1.411
1.351
1.166
ppm

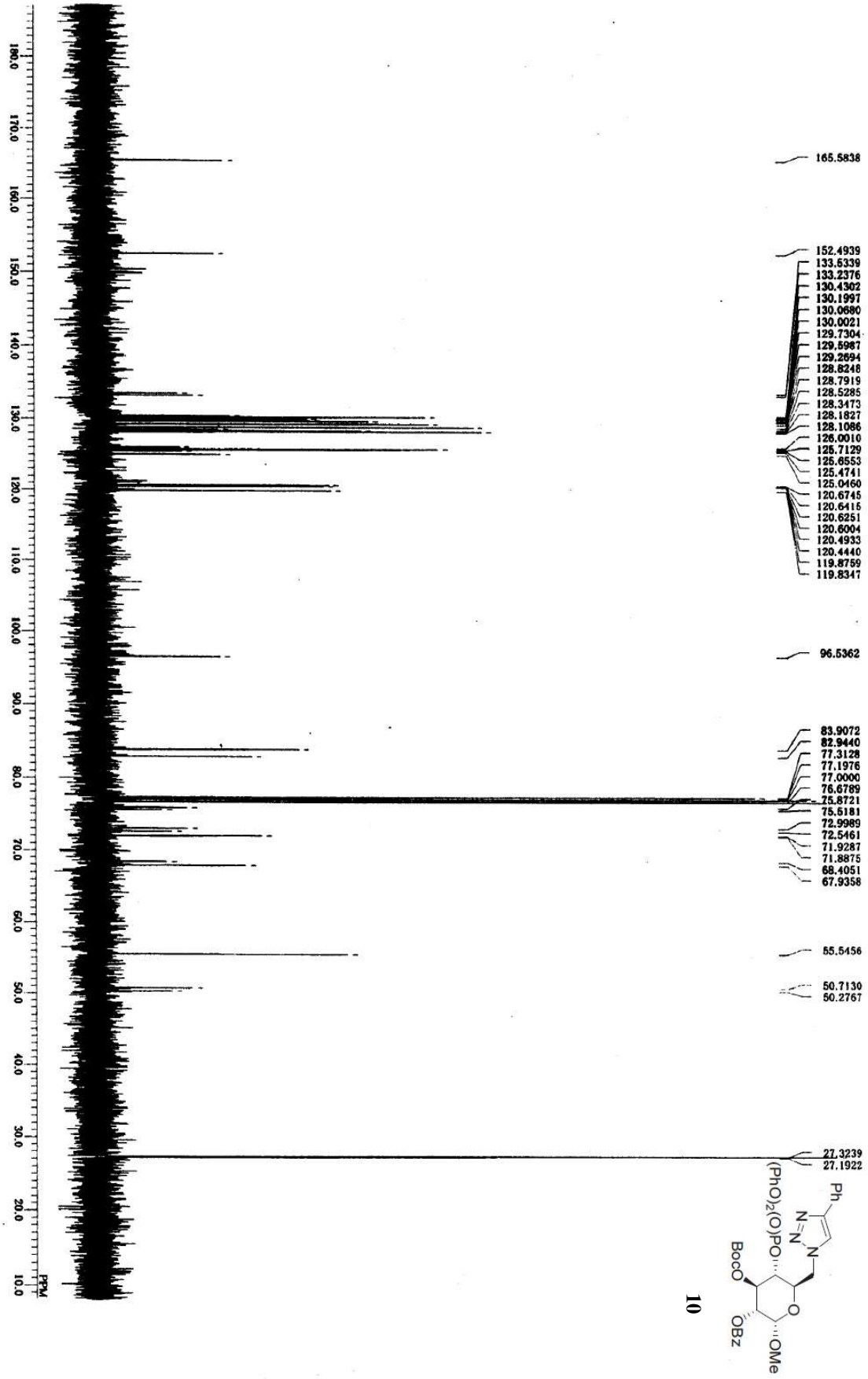

100 MHz/CDCl3
9
(PhO)2(O)PO
H2N
BocO
OBz
OMe
O
165.5427
165.4521
152.7244
152.6667
130.1915
130.0021
129.9445
129.7222
129.5576
129.4176
129.2447
129.0060
128.3144
128.1662
125.6717
124.9802
120.6498
120.6004
120.5427
120.4934
120.2958
120.2546
119.8759
119.8265
115.4714
96.6762
83.5532
82.6229
77.3211
77.2058
77.0000
76.6872
72.6202
72.0028
55.8337
55.7102
28.3694
27.2745
27.2086
PPM

300 MHz/$CDCl_3$





10


100 MHz/CDCl3
10
Ph
N
N
N
(PhO)2(O)PO
BocO
OBz
O
OMe
165.5838
152.4939
133.5339
133.2376
130.4302
130.1997
130.0680
130.0021
129.7304
129.5987
129.2694
128.8248
128.7919
128.5285
128.3473
128.1827
128.1086
126.0010
125.7129
125.6553
125.4741
125.0460
120.6745
120.6415
120.6251
120.6004
120.4933
120.4440
119.8759
119.8347
96.5362
83.9072
82.9440
77.3128
77.1976
77.0000
76.6789
75.8721
75.5181
72.9989
72.5461
71.9287
71.8875
68.4051
67.9358
55.5456
50.7130
50.2767
27.3239
27.1922
PPM