Supporting Information: Experimental Part

Nucleophilic Substitution Reactions of Pyranose Polytosylates

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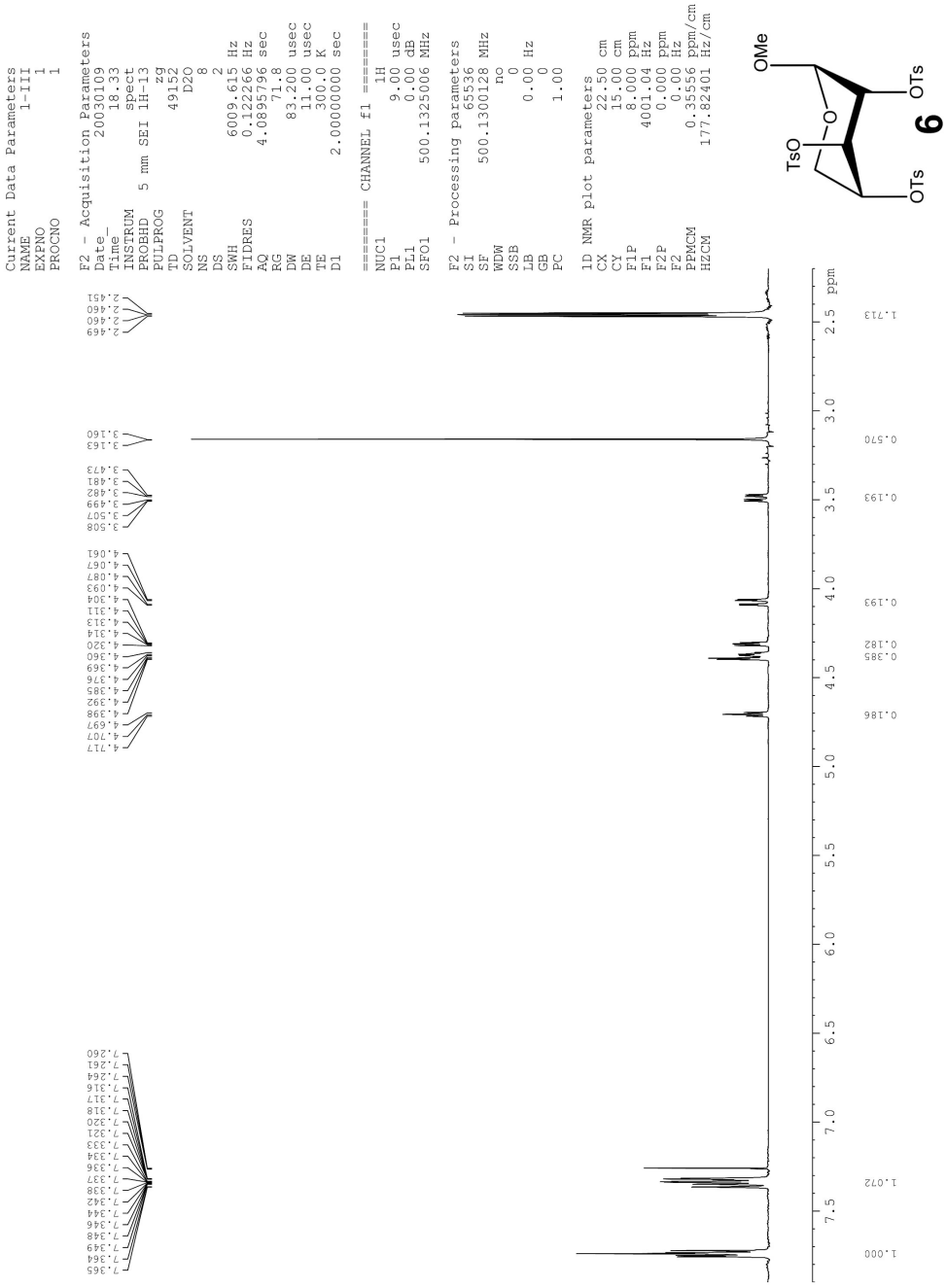
Experimental Section

Methyl b-D-Xylopyranoside (5). A mixture of D-xylose (**4**) (20.0 g, 133 mmol) and ion-exchange resin (Amberlite® IRA-120, 20.0 g) in anhydrous methanol (250 ml) was heated under reflux overnight. The cooled mixture was filtered and evaporated to a mixture of solids and oil. This was taken up in 200 ml hot ethyl acetate. Crystals formed on cooling, and the crystals were allowed to digest for three days before collecting, yielding 10.8 g. Analysis of the product by ^{1}H and ^{13}C NMR spectroscopy showed that it consisted of a 2:1 mixture of β- and α-anomers. A second recrystallization from ethanol gave the pure β-anomer (**5**), as a white powder (5.74 g, 26%), m.p. 154.5-155.5 °C (lit. m.p.[1] 156-157 °C). R_f (3:2:1 $CHCl_3$/EtOAc/MeOH): 0.23. $[\alpha]_D$ -65.6 (*c* 0.7, H_2O) (lit.[2] $[\alpha]_D$ -65.3 (*c* 1.0, H_2O)). ^{1}H NMR (500 MHz, $(CD_3)_2SO$)) 2.89-2.96 (m, 1H, H2); 3.03 (t, 1H, *J* = 10.8 Hz, H5a); 3.06-3.11 (m, 1H, H4); 3.24-3.29 (m, 1H, H3); 3.35 (s, 3H, OMe); 3.70 (dd, 1H, *J* = 5.3, 11.2 Hz, H5e); 4.00 (d, 1H, *J* = 7.6 Hz, H1); 4.89 (d, 1H, *J*

= 4.8 Hz, OH); 4.91 (d, 1H, *J* = 5.1 Hz, OH); 5.00 (d, 1H, *J* = 4.9 Hz, OH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$)) 56.5, 66.2, 70.2, 73.8, 77.1, 105.3.

Methyl 2,3,4-Tris-(*O*-4-toluenesulfonyl)-b-D-xylopyranoside (6). Methyl β-D-xylopyranoside (**5**) (500 mg, 3.05 mmol) was added to a stirred, chilled (0 °C) solution of 4-toluenesulfonyl chloride (2.32 g, 12.2 mmol) in pyridine (10 ml). After standing for 7 days, the mixture was poured onto ice water (50 ml). The product separated as a sticky mass. The mixture was extracted into CH_2Cl_2 (3x50 ml) and the combined extracts were washed with 5% HCl (3x100 ml), saturated $NaHCO_3$ (100 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to a colorless foam. The product was dissolved in a little methanol and slow evaporation of the solvent yielded the tritosylate (**6**) as colorless crystals (1.90 g, 99%), m.p. 137.5-138.5 °C (lit.[3] m.p. 140-141 °C). R_f (1:1 EtOAc/hexane): 0.34. $[\alpha]_D$ -32.2 (*c* 1.0, $CHCl_3$) (lit.[4] $[\alpha]_D$ -33.7 (*c* 1.0, $CHCl_3$). ES-MS: 627 $(MH)^+$, 644 $(M+NH_4)^+$, 649 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$) 2.44 (s, 3H, Me); 2.45 (s, 3H, Me); 2.46 (s, 3H, Me); 3.14 (s, 3H, OMe); 3.48 (ddd, 1H, *J* = 0.8, 4.6, 12.9 Hz, H5e); 4.06 (dd, 1H, *J* = 3.1, 12.9 Hz, H5a); 4.30 (ddd, 1H, *J* = 0.5, 3.4, 4.9 Hz, H2); 4.36 (dt, 1H, *J* = 3.3, 4.8, H4); 4.39 (d, 1H, *J* = 3.3 Hz, H1); 4.71 (t, 1H, *J* = 5.0, H3); 7.31-7.36 (m, 6H, Ar-H); 7.70-7.75 (m, 6H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) 21.5, 21.6, 21.7, 56.0, 58.8, 72.2, 73.0, 73.6, 99.0, 128.0, 128.1, 128.3, 129.7, 129.8., 129.9, 132.4, 132.6, 133.3, 145.0, 145.3, 145.4. HRMS (TOF) calcd for $C_{27}H_{31}O_{11}S_3$ $(M+H)^+$ 627.1029, found 627.1043.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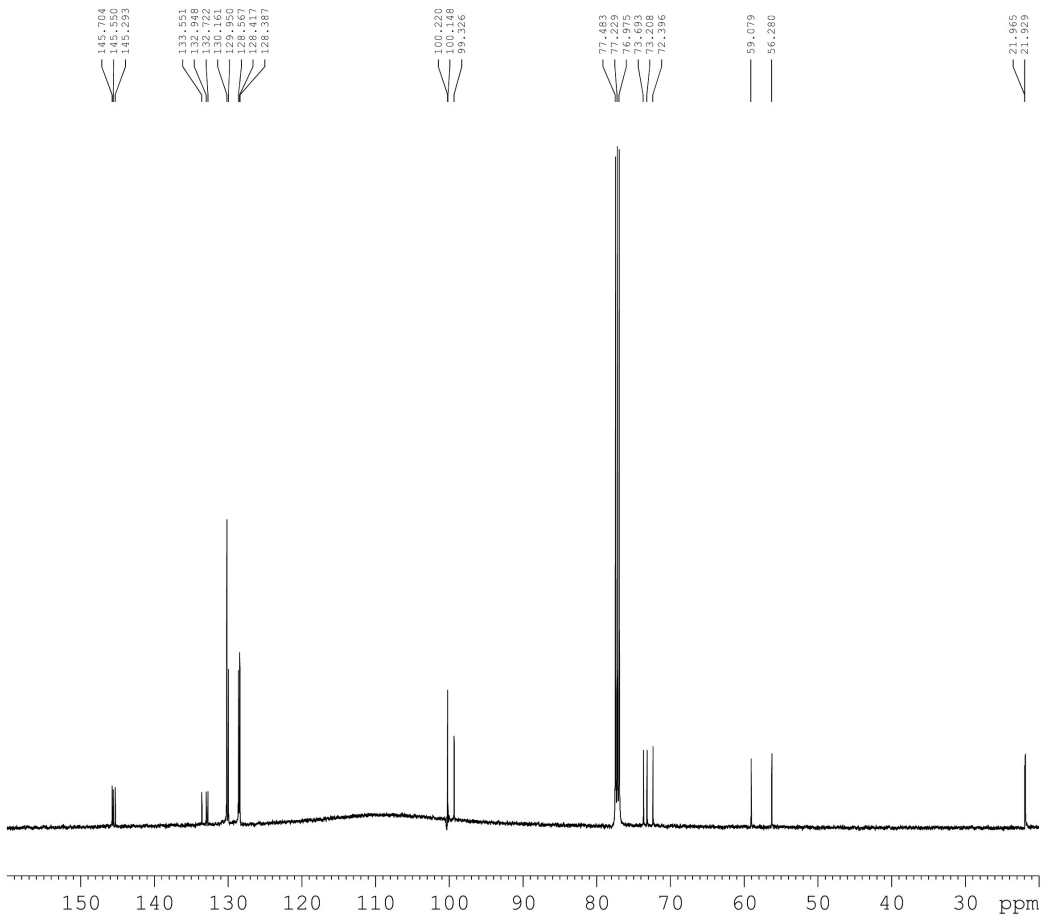


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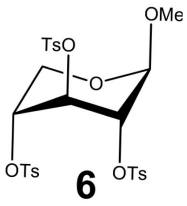


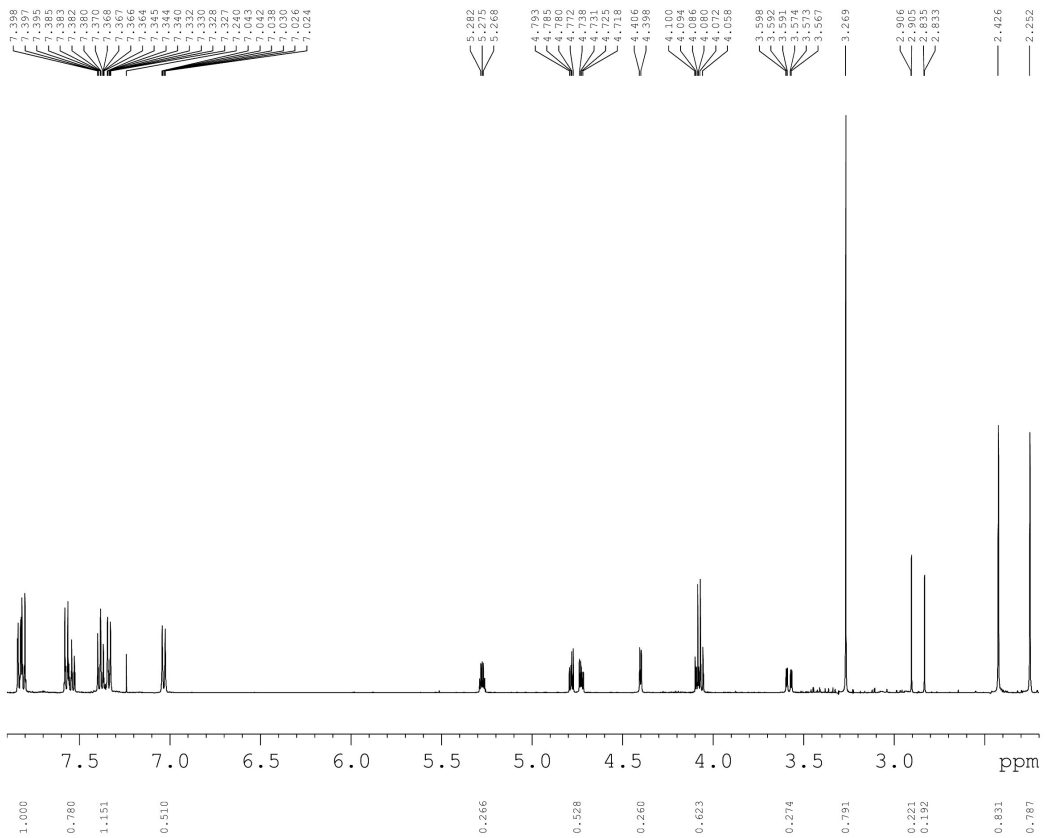
6

Methyl 4-*O*-Benzoyl-2,3-bis-(*O*-4-toluenesulfonyl)-a-L-arabino pyranoside (7).

(1) From (**6**): The tritosylate (**6**) (250 mg, 0.399 mmol) and sodium benzoate (510 mg, 3.54 mmol) were suspended in dry DMF (15 ml) and heated for 20 h at 130 °C. The cooled mixture was evaporated, and then the residue was extracted with EtOAc (50 ml). The filtered extract was washed with 5% HCl (2x50 ml), saturated $NaHCO_3$ (2x50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to a crystalline solid. This was triturated with cold hexane to give the monobenzoate (**7**) as colorless crystals (140 mg, 61%), m.p. 79-81 °C. $[\alpha]_D$ -1.4 (*c* 0.3, $CHCl_3$). ES-MS: 577 $(MH)^+$, 594 $(M+NH_4)^+$, 599 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$) 2.25 (s, 3H, Me); 2.42 (s, 3H, Me); 3.27 (s, 3H, OMe); 3.58 (ddd, 1H, *J* = 0.5, 3.1, 11.6 Hz, H5a); 4.08 (dd, 1H, *J* = 7.0, 11.2 Hz, H5b); 4.40 (d, 1H, *J* = 4.1 Hz, H1); 4.73 (dd, 1H, *J* = 3.4, 6.4 Hz, H3); 4.78 (dd, 1H, *J* = 4.1, 6.5 Hz, H2); 5.28 (dt, 1H, *J* = 3.4, 6.9 Hz, H4); 7.03 (br d, 2H, *J* = 11.2 Hz, Ar-H); 7.33 (br d, 2H, *J* = 9.3 Hz, Ar-H); 7.38 (br t, 2H, *J* = 7.9 Hz, Ar-H); 7.54 (t, 1H, *J* = 7.5 Hz, Ar-H); 7.57 (d, 2H, *J* = 8.3, Ar-H); 7.80-7.84 (m, 2H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) 21.7, 21.8, 56.5, 60.4, 66.8, 74.5, 75.4, 100.1, 128.3, 128.4, 128.5, 128.6, 129.1, 129.2, 129.9, 132.8, 133.5, 133.6, 145.1, 145.2. 165.0. HRMS (TOF) calcd for $C_{27}H_{29}O_{10}S_2$ $(M+H)^+$ 577.1202, found 577.1208.

(2) From (**9**): A solution of the ditosylate (**9**) (7.0 mg, 0.015 mmol) in pyridine (3 ml) was treated with benzoyl chloride (0.15 ml, 0.18 g, 1.3 mmol). After stirring overnight at room temperature, the solution was evaporated and the residue was dissolved in EtOAc (10 ml). This solution was washed with 5% HCl (3x10 ml), saturated $NaHCO_3$

(2x10ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to give the benzoate (**7**) (8.5 mg, 100%), identical by NMR and TLC to the sample prepared from (**6**) (above).

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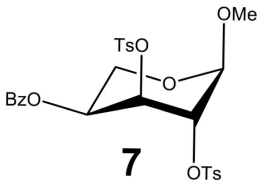

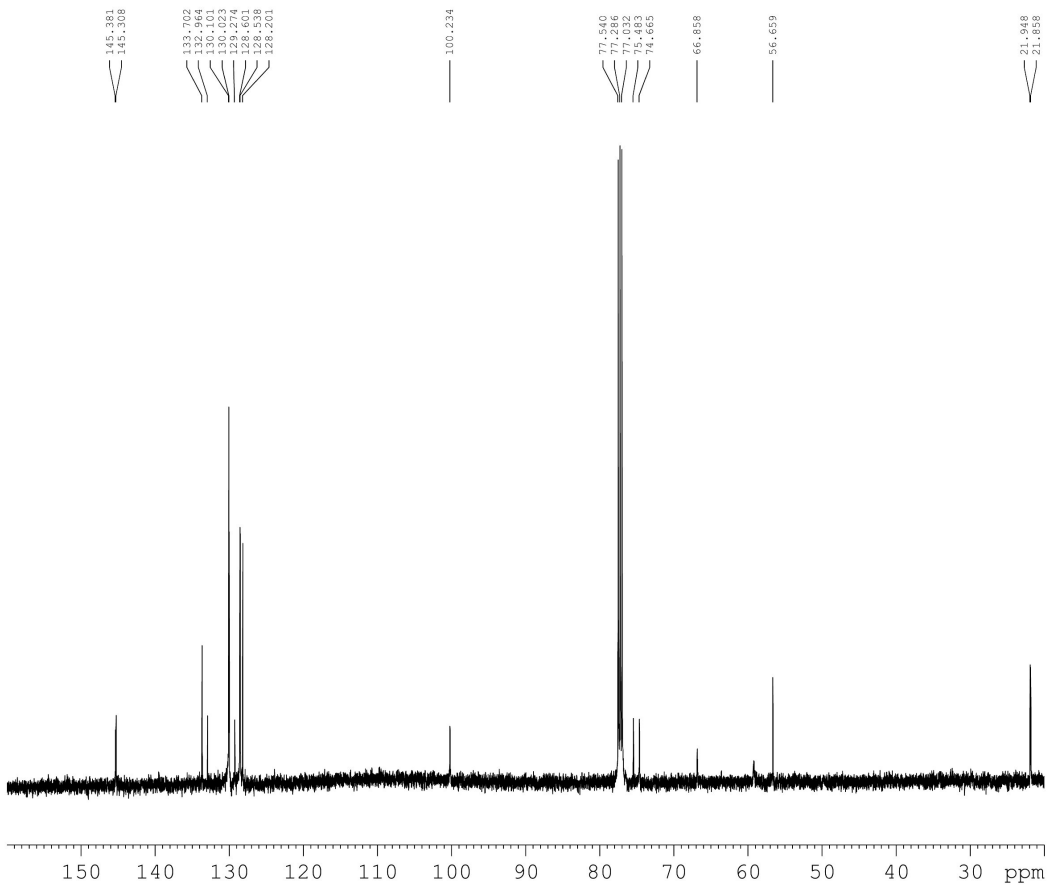


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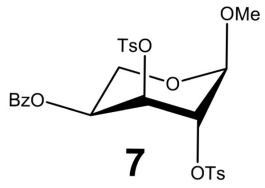
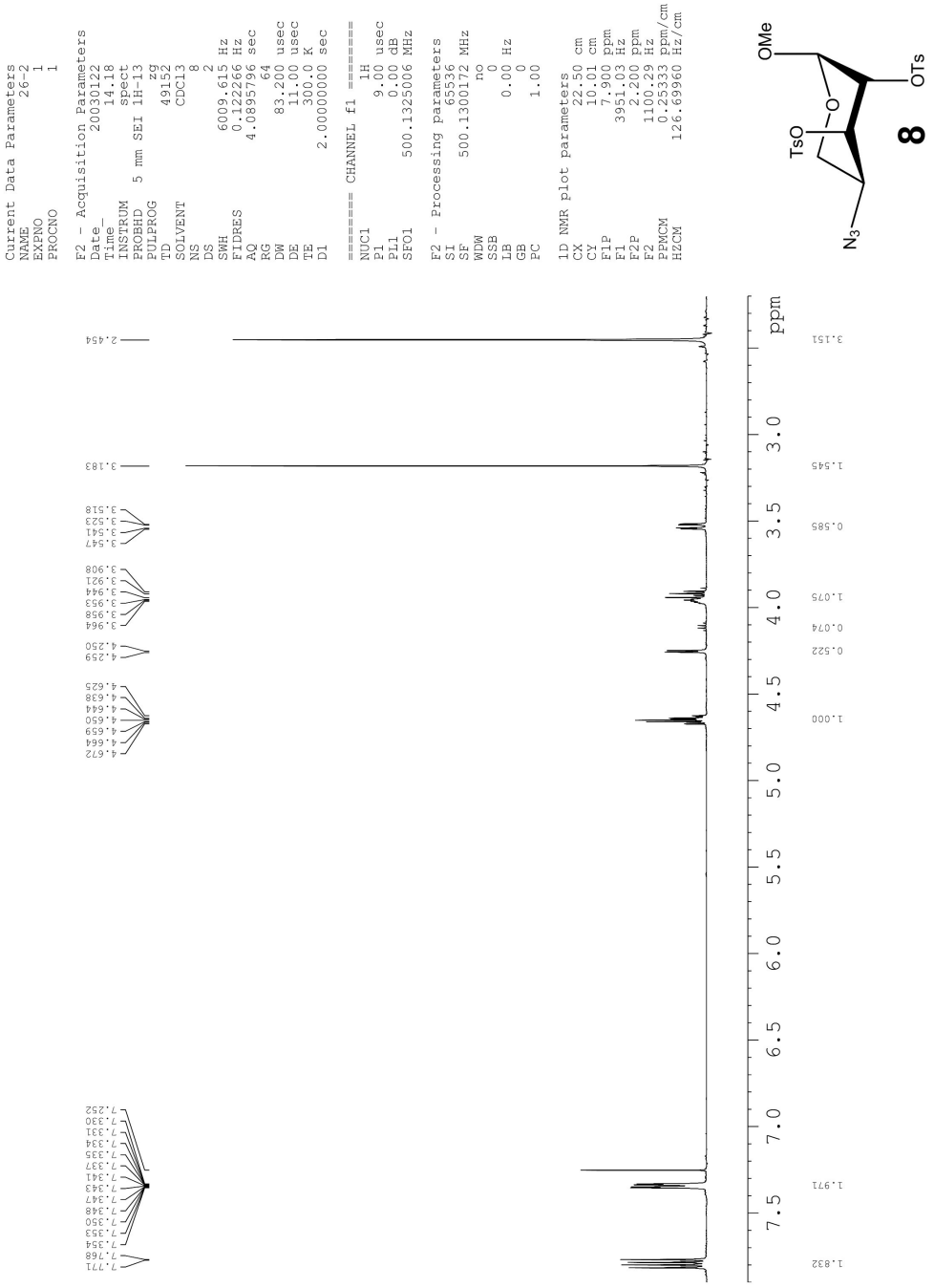


7

Methyl 4-Azido-2,3-Bis-(*O*-4-toluenesulfonyl)-4-deoxy-a-L-arabino pyranoside (8).

The tritosylate (**6**) (50 mg, 80 μmol) and sodium azide (27 mg, 0.41 mmol) were suspended in dry DMF (5 ml) and heated for 20 h at 130 °C. The cooled mixture was evaporated, and then the residue was extracted with EtOAc (50 ml). The filtered extract was washed with 5% HCl (2x50 ml), saturated $NaHCO_3$ (2x50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to a yellow crystalline solid. This was recrystallized from EtOAc/hexane to give the azido derivative (**8**) as colorless crystals (45 mg, 98%), m.p. 176-178 °C (softening at 165 °C). $[\alpha]_D$ -11.8 (*c* 0.2, $CHCl_3$). ES-MS: 498 $(MH)^+$, 515 $(M+NH_4)^+$, 520 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$) 2.42 (s, 3H, Me); 2.45 (s, 3H, Me); 3.17 (s, 3H, OMe); 3.53 (dd, 1H, *J* = 2.7, 11.7 Hz, H5e); 3.93 (dd, 1H, *J* = 6.3, 11.6 Hz, H5a); 3.96-3.99 (m, 1H, H4); 4.26 (d, 1H, *J* = 4.4 Hz, H1); 4.64 (dd, 1H, *J* = 3.1, 6.7 Hz, H3); 4.66 (dd, 1H, *J* = 4.3, 6.8 Hz, H2); 7.32-7.36 (m, 4H, Ar-H); 7.78 (br d, 2H, *J* 8.6 Hz, Ar-H); 7.81 (br d, 2H, *J* = 8.5 Hz, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$) 22.1, 22.2, 56.8, 57.1, 60.3, 75.5, 75.7, 100.1, 128.7, 128.9, 130.2, 130.4, 132.7, 133.9, 145.6, 146.1. HRMS (TOF) calcd for $C_{20}H_{24}N_3O_8S_2$ $(M+H)^+$ 498.1005, found 498.1002.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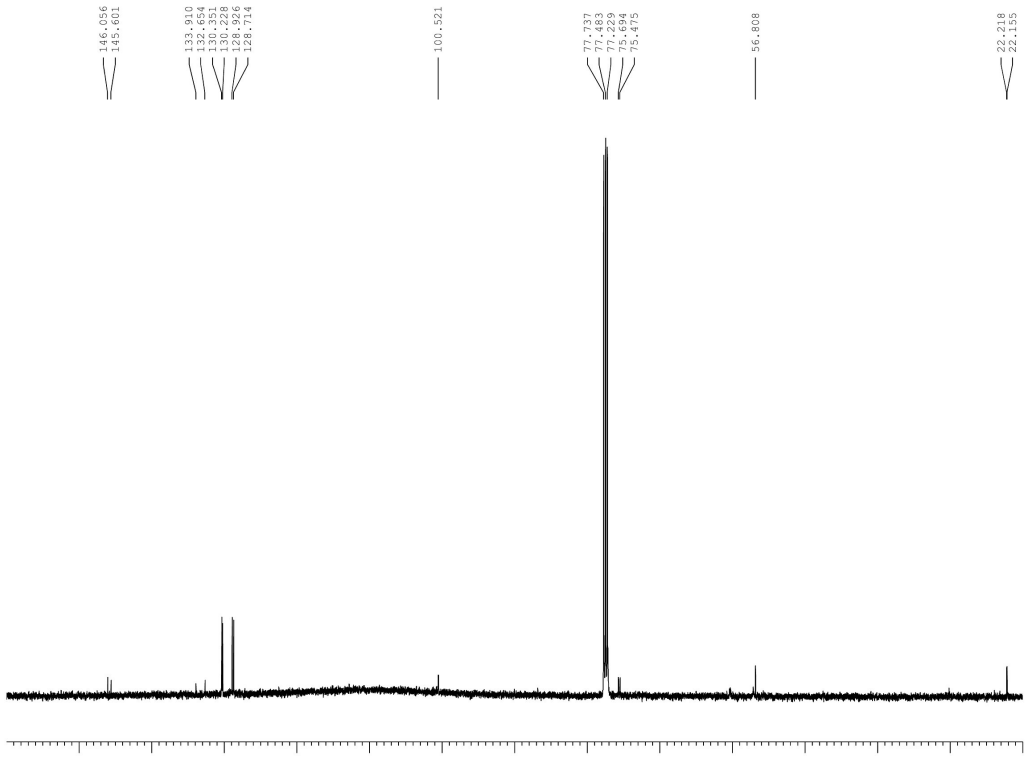


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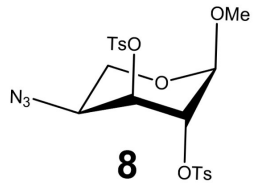
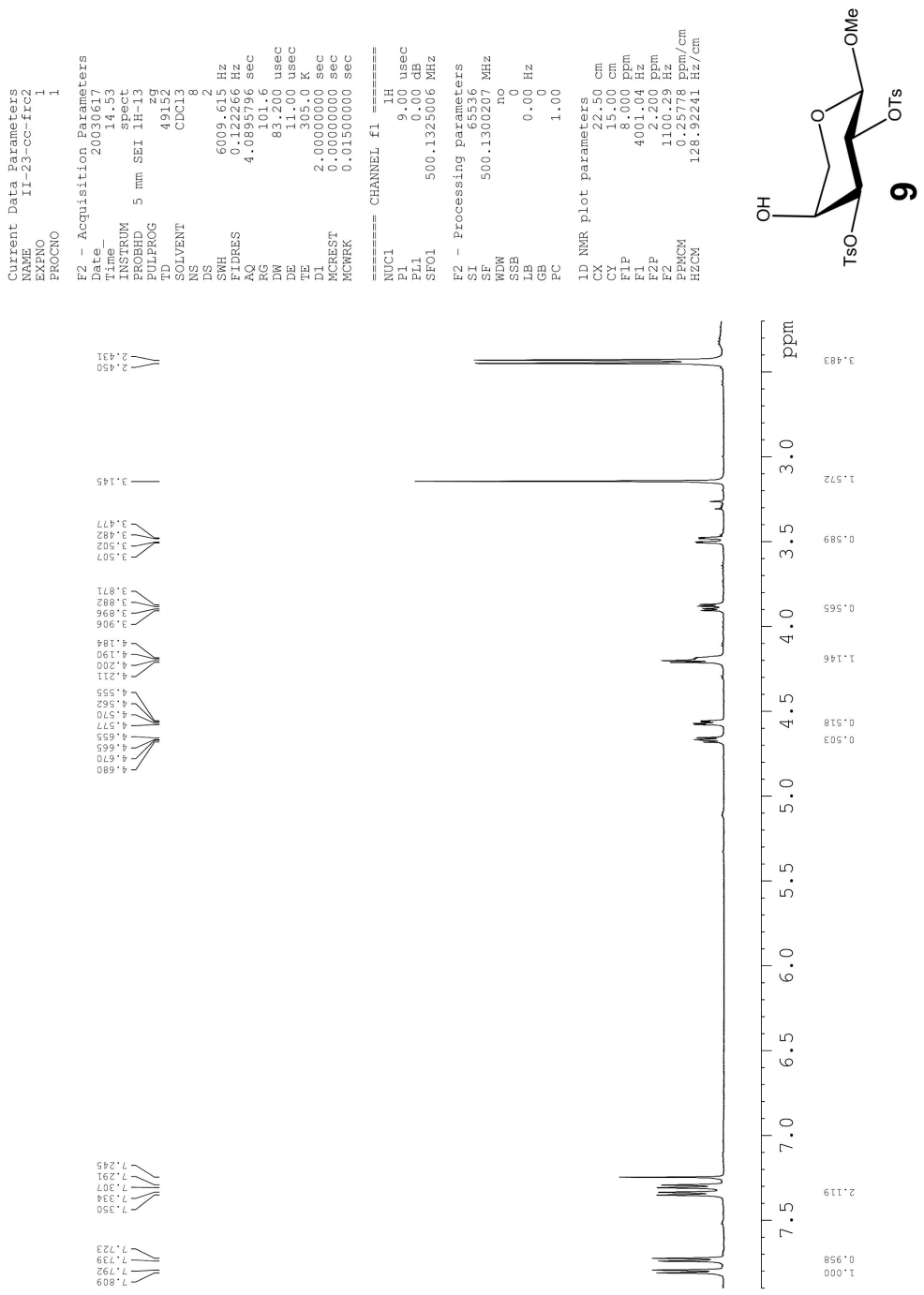


8

Methyl 2,3-Bis-(*O*-4-toluenesulfonyl)-α-L-arabinopyranoside (9). The tritosylate (**6**) (100 mg, 0.16 mmol) and sodium nitrite (100 mg, 1.45 mmol) were suspended in dry DMF (5 ml) and heated at 130 °C for 72 h. The cooled mixture was evaporated, and the residue was extracted with EtOAc (20 ml). The organic extract was washed with 5% HCl (2x20 ml), then saturated $NaHCO_3$ (2x20 ml) and brine (15 ml), then dried ($MgSO_4$) and evaporated to a colorless foam. This was purified by column chromatography (eluent: EtOAc/$CHCl_3$/hexane 3:2:1) to give the ditosylate (**9**) as colorless crystals (42 mg, 56%), m.p. 122-123 °C. $[\alpha]_D$ -2.9 (*c* 0.5, $CHCl_3$). ES-MS: 473 $(MH)^+$, 490 $(M+NH_4)^+$, 495 $(M+Na)^+$. R_f (3:2:1 EtOAc/$CHCl_3$/hexane): 0.18. ^{1}H NMR (500 MHz, $CDCl_3$) 2.43 (s, 3H, Me); 2.44 (s, 3H, Me); 3.14 (s, 3H, OMe); 3.49 (dd, 1H, *J* = 2.6, 12.5 Hz, H5a); 3.89 (dd, 1H, *J* = 5.1, 12.4 Hz, H5b); 4.13-4.18 (m, 1H, H4); 4.19 (d, 1H, *J* = 5.3 Hz, H1); 4.57 (dd, 1H, *J* = 3.3, 7.5 Hz, H3); 4.67 (dd, 1H, *J* = 5.3, 7.4 Hz, H2); 7.30 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.34 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.72 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.80 (br d, 2H, *J* = 8.2, Ar-H); OH not observed. ^{13}C NMR (125 MHz, $CDCl_3$) 22.1, 22.2, 56.8, 63.2, 66.5, 76.4, 78.3, 101.0, 128.7, 128.8, 130.1, 130.4, 133.0, 134.7, 145.3, 146.0. HRMS (TOF) calcd for $C_{20}H_{25}O_9S_2$ $(M+H)^+$ 473.0940, found 473.0950.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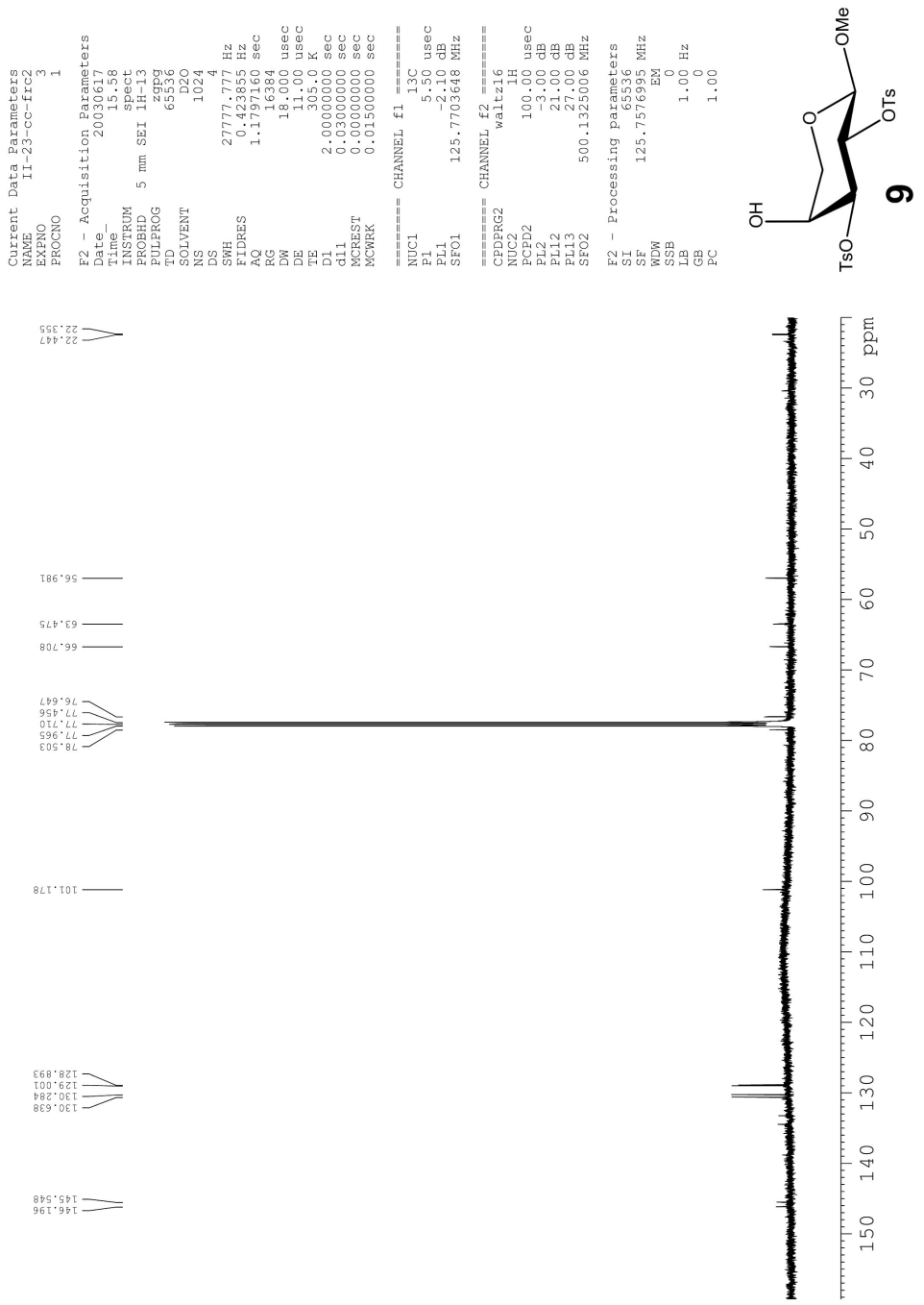
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OMe
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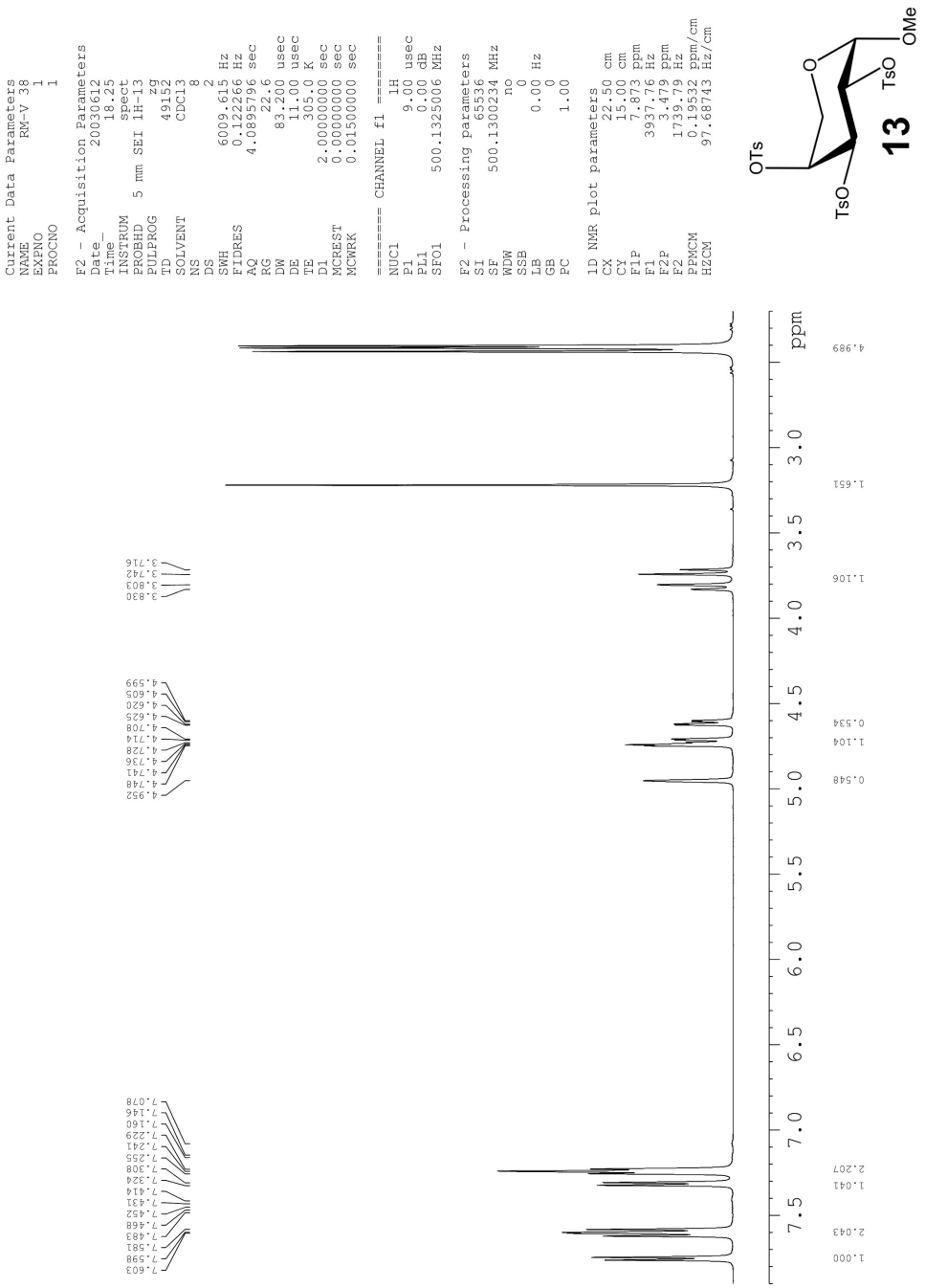
101.178
128.893
129.001
130.284
130.638
145.548
146.196
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

Methyl 2,3,4-Tris-(*O*-methanesulfonyl)-β-D-xylopyranoside (10). Methyl β-D-xylopyranoside (**5**) (500 mg, 3.05 mmol) was added to a stirred, chilled (0 °C) solution of methanesulfonyl chloride (0.95 ml, 1.40 g, 12.2 mmol) in pyridine (10 ml). After standing for 7 d, the dark crystalline mass was poured onto ice (50 ml). After the ice had melted, the dark mixture was shaken with CH_2Cl_2 (3x50 ml) and filtered through a layer of Celite. The organic phase was washed with 5% HCl (3x50 ml), saturated $NaHCO_3$ (100 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to a yellow foam. The product was dissolved in a little methanol and slow evaporation of the solvent yielded tan crystals of the trimesylate (**10**) (1.19 g, 98%), m.p. 137.5-138.5 °C (lit.[5] m.p. 147.5-148.5). $[\alpha]_D$ -33.0 (*c* 0.3, $CHCl_3$) (lit.[5] $[\alpha]_D$ -33.6 (*c* 1.4, $CHCl_3$). R_f (EtOAc): 0.57. ^{1}H NMR (500 MHz, $CDCl_3$) 3.15 (s, 3H, Me); 3.16 (s, 3H, Me); 3.22 (s, 3H, Me); 3.49 (dd, 1H, *J* = 10.1, 12.0 Hz, H5a); 3.55 (s, 3H, OMe); 4.32 (dd, 1H, *J* = 5.7, 12.0 Hz, H5b); 4.40 (d, 1H, *J* = 7.6 Hz, H1); 4.49 (dd, 1H, *J* = 7.6, 9.4 Hz, H2); 4.65 (ddd, 1H, *J* = 5.7, 9.1, 10.1 Hz, H4); 4.85 (t, 1H, *J* = 9.3, H3). ^{13}C NMR (125 MHz, $CDCl_3$) 38.4, 39.3, 39.6, 57.1, 63.3, 74.0, 77.6, 78.3, 101.4.

Methyl β-L-Arabinopyranoside (12). A mixture of L-arabinose (**11**) (11.0 g, 73.3 mmol) and ion-exchange resin (Amberlite® IRA-120, 20.0 g) in anhydrous methanol (150 ml) was heated under reflux overnight. The cooled mixture was filtered and evaporated to a cream solid. This was recrystallized from ethanol to give the pure β-anomer (**12**) as colorless crystals (4.40 g, 37%), m.p. 166.5-168.5 °C (lit.[6] m.p. 167-169 °C). $[\alpha]_D$ 240 (*c* 0.6, H_2O) (lit.[7] $[\alpha]_D$ 243 (*c* 0.6, H_2O)). ^{1}H NMR (500 MHz, $(CD_3)_2SO$)) 3.30 (s, 3H, OMe); 3.44 (dd, 1H, *J* = 2.9, 11.9 Hz, H5); 3.52-3.62 (m, 3H, H2,3,5); 3.69

(m, 1H, H4); 4.45 (d, 1H, *J* = 3.5 Hz, H1); 4.49-4.54 (m, 3H, 3xOH). ^{13}C NMR (125 MHz, $(CD_3)_2SO$)) 54.8, 62.9, 68.2, 68.6, 69.1, 100.6.

Methyl 2,3,4-Tris-(*O*-4-toluenesulfonyl)-b-L-arabinopyranoside (13). Methyl β-L-arabinopyranoside (**12**) (1.33 g, 8.10 mmol) was added portionwise to a chilled (0 °C) solution of 4-toluenesulfonyl chloride (6.18 g, 32.4 mmol) in pyridine (20 ml). After standing for 7 days at room temperature, the solution was poured into 100 ml of ice water, and the product separated as a sticky mass. The mixture was extracted with $CHCl_3$, (3x100 ml) and the combined extracts were washed with 5% HCl (2x50 ml), water (50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to a colorless foam (4.95 g). This was recrystallized twice from ethanol to give the tritosylate (**13**) as colorless crystals (3.46 g, 68%), m.p. 112-113 °C (lit.[3] m.p. 116-117 °C). $[\alpha]_D$ 97.7 (*c* 0.9, $CHCl_3$) (lit.[8] $[\alpha]_D$ 101 (*c* 0.9, $CHCl_3$)). ES-MS: 627 $(MH)^+$, 644 $(M+NH_4)^+$, 649 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.43 (s, 3H, Me); 2.44 (s, 3H, Me); 2.46 (s, 3H, Me); 3.25 (s, 3H, OMe); 3.75 (dd, 1H, *J* = 0.7, 13.3 Hz, H5a); 3.85 (dd, 1H, *J* = 2.3, 13.3 Hz, H5b); 4.64 (dd, 1H, *J* = 3.4, 10.2 Hz, H2); 4.75 (dd, 1H, *J* = 3.3, 10.1 Hz, H3); 4.77 (d, 1H, *J* = 3.4 Hz, H1); 4.98 (m, 1H, H4); 7.26 (br d, 2H, *J* = 8.2 Hz, Ar-H); 7.28 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.34 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.62 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.64 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.78 (br d, 2H, *J* = 8.2 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 21.7, 21.8, 21.8, 56.0, 60.3, 72.1, 73.3, 97.9, 128.1, 128.2, 128.3, 129.8, 129.9, 130.1, 132.5, 133.2, 133.3, 145.1, 145.2, 145.3.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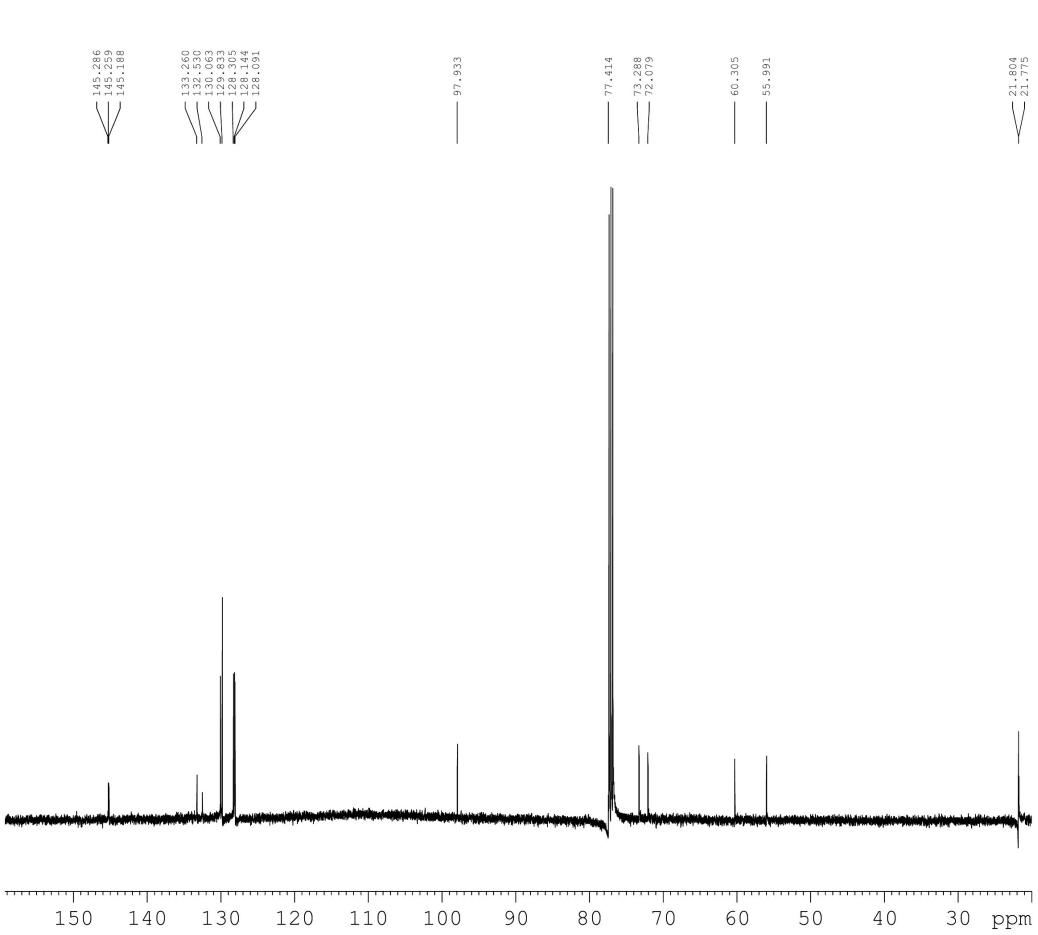


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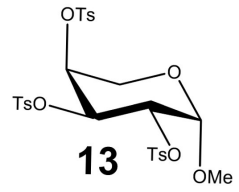
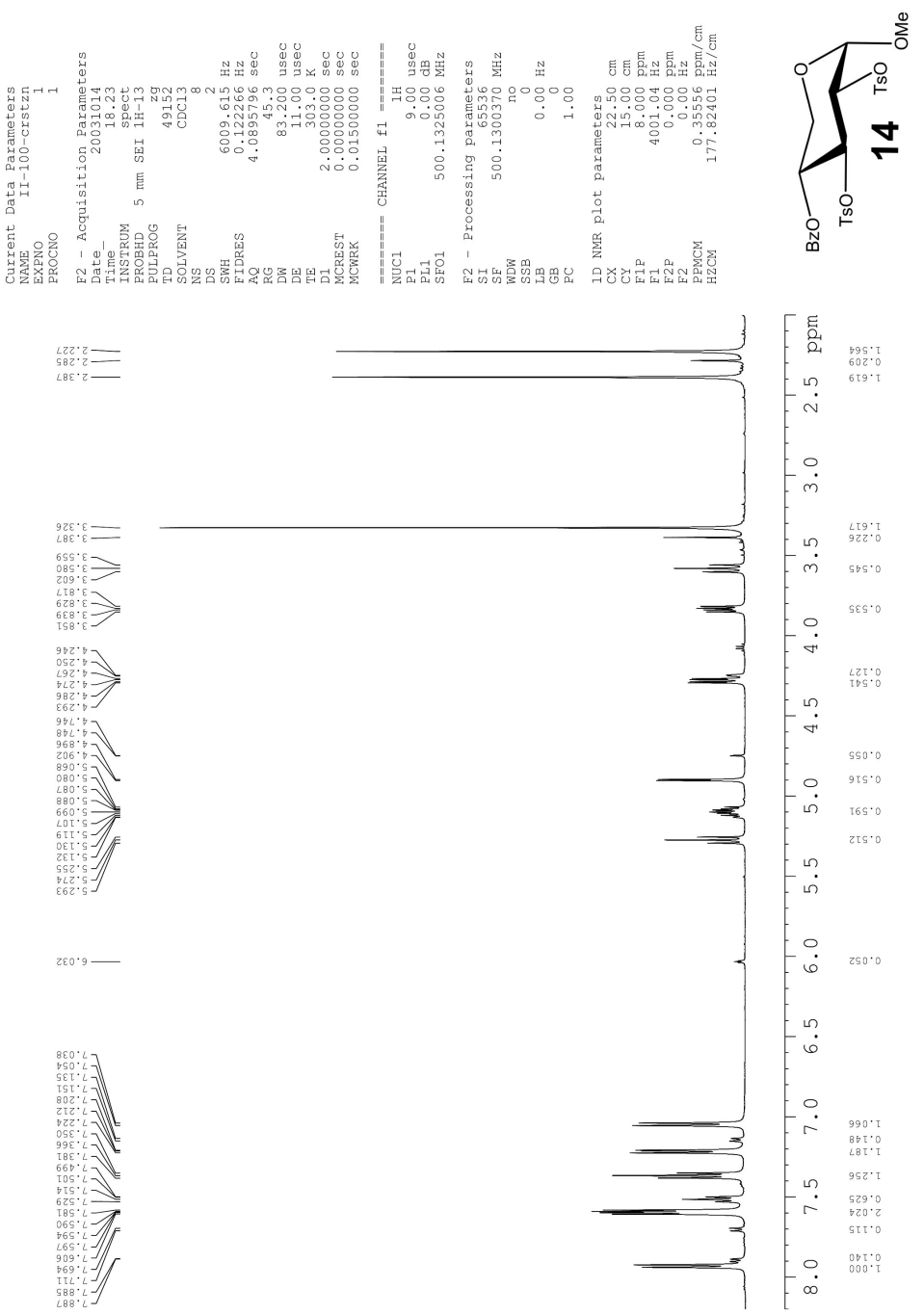


Methyl 4-*O*-Benzoyl-2,3-bis-(*O*-4-toluenesulfonyl)-a-D-xylopyranoside (14).

(1) From (**13**): A suspension of the arabinose tritosylate (**13**) (200 mg, 0.32 mmol) and sodium benzoate (460 mg, 3.19 mmol) in dry DMF (25 ml) was heated at 130 °C for 4 days. The cooled reaction mixture was evaporated and the residue was extracted with EtOAc (45 ml). The organic extract was washed with 5% HCl (2x25 ml), saturated $NaHCO_3$ (2x25 ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to a foam. This was triturated with hexane to give the monobenzoate (**14**) as a gum (120 mg, 65%). Crystallization from EtOAc/hexane gave colorless crystals (73 mg, 40%), m.p. 58-60 °C. R_f (1:2:3 EtOAc/$CHCl_3$/ hexane): 0.55. $[\alpha]_D$ -26.0 (*c* 0.4, $CHCl_3$) (lit.[4] $[\alpha]_D$ -24.1 (*c* 4.6, $CHCl_3$). ES-MS: 577 $(MH)^+$, 594 $(M+NH_4)^+$, 599 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.26 (s, 3H, Me); 2.43 (s, 3H, Me); 3.37 (s, 3H, OMe); 3.63 (t, 1H, *J* = 10.8 Hz, H5a); 3.88 (dd, 1H, *J* = 6.1, 11.0 Hz, H5e); 4.34 (dd, 1H, *J* = 3.5, 9.7 Hz, H2); 4.94 (d, 1H, *J* = 3.5 Hz, H1); 5.07-5.19 (m, 1H, H4); 5.33 (t, 1H, *J* = 9.5 Hz, H3); 7.09 (br d, 2H, *J* 8.6 Hz, Ar-H); 7.27 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.41 (br t, 2H, *J* = 8.5 Hz, Ar-H); 7.56 (br t, 1H, *J* = 8.7 Hz, Ar-H); 7.64 (br d, 4H, *J* = 8.3 Hz, Ar-H); 7.97 (br d, 2H, *J* = 8.4 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 21.7, 21.8, 56.0, 58.4, 69.5, 75.8, 76.6, 97.6, 127.8, 128.4, 128.9, 129.7, 129.8, 130.1, 130.2, 132.6, 133.5, 134.2, 144.6, 145.4. HRMS (TOF) calcd for $C_{27}H_{29}O_{10}S_2$ $(M+H)^+$ 577.1202, found 577.1242.

(2) From (**16**): A solution of the alcohol (**16**) (10.9 mg, 0.023 mmol) in pyridine (3 ml) was treated with benzoyl chloride (0.15 ml, 0.18 g, 1.3 mmol). After stirring overnight at room temperature, the solution was evaporated and the residue was dissolved in EtOAc (15 ml). This solution was washed with 5% HCl (2x10 ml), saturated $NaHCO_3$

(2x10ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to give the benzoate (**14**) (13 mg, 100%), identical by NMR and TLC to the sample prepared from (**13**) (above).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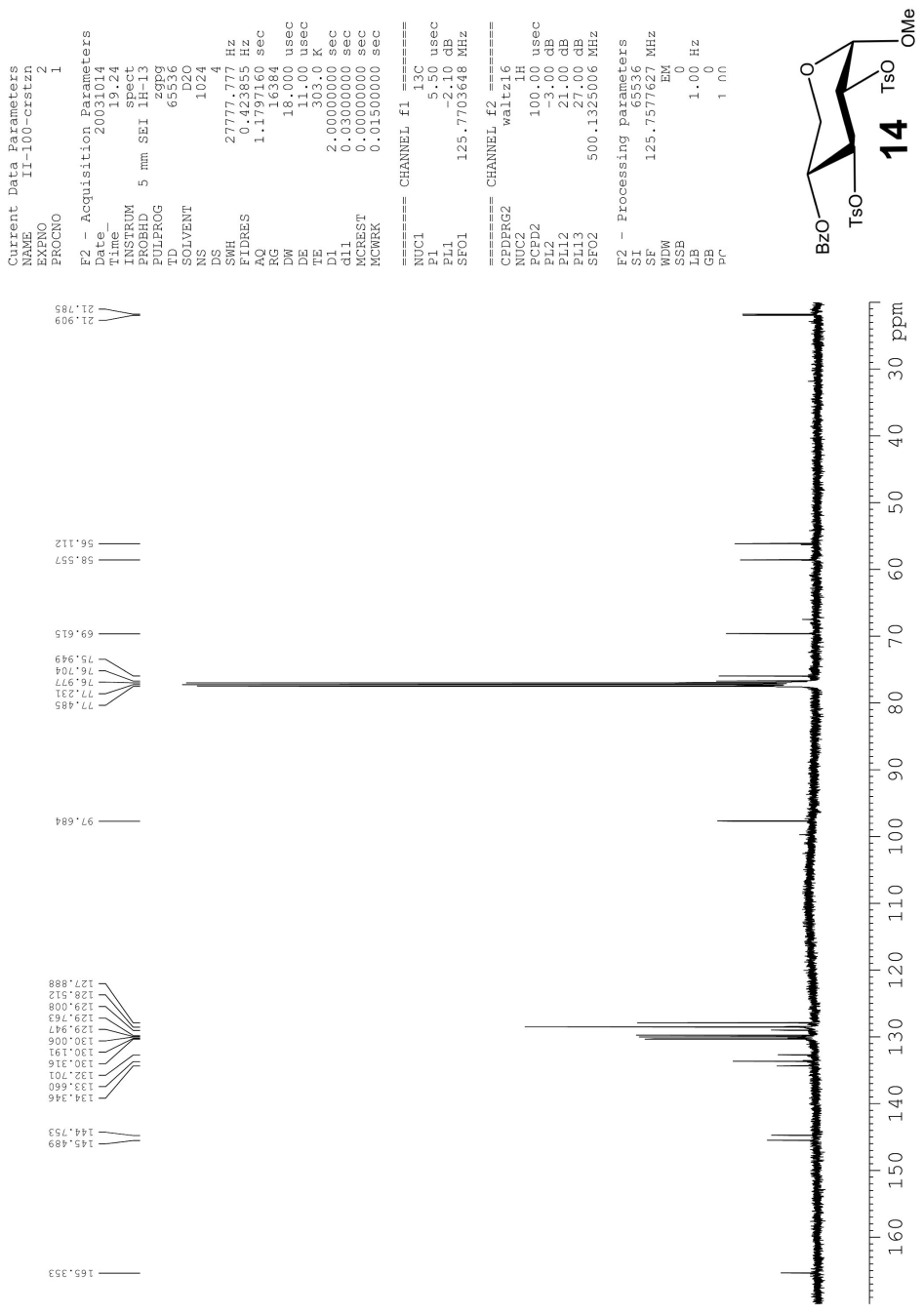
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70
60
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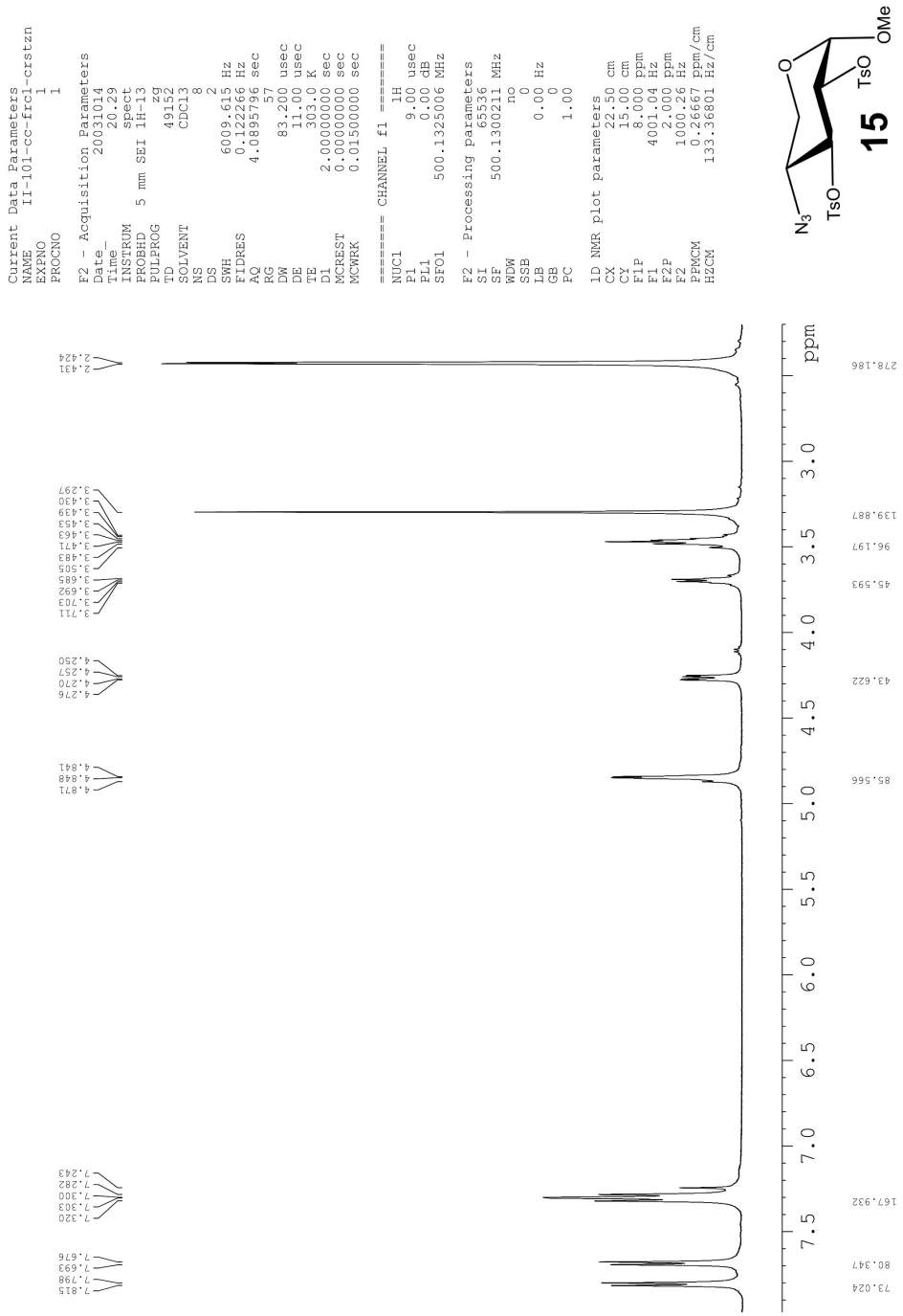
40
30
ppm

Methyl 4-Azido-2,3-bis-(*O*-4-toluenesulfonyl)-4-deoxy-a-D-xylopyranoside (15). A suspension of the tritosylate (**13**) (200 mg, 0.32 mmol) and sodium azide (22 mg, 3.06 mmol) in dry DMF (30 ml) was heated at 130 °C for 45 days. The cooled reaction mixture was evaporated and the residue was extracted with EtOAc (45 ml). The organic extract was washed with 5% HCl (2x25 ml), saturated $NaHCO_3$ (2x25 ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to a gum. This was purified by column chromatography (eluent: EtOAc/$CHCl_3$/hexane 1:2:3) to give the title azido derivative (**15**) as a colorless gum (75 mg, 47%). Recrystallization from EtOAc/hexane gave colorless crystals (25 mg, 13%), m.p. 55-57 °C. $[\alpha]_D$ 81.0 (*c* 0.5, $CHCl_3$). ES-MS: 498 $(MH)^+$, 515 $(M+NH_4)^+$, 520 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.41 (s, 3H, Me); 2.42 (s, 3H, Me); 3.29 (s, 3H, OMe); 3.44-3.50 (m, 2H, H4,5e); 3.68 (dd, 1H, *J* = 4.1, 9.7 Hz, H5a); 4.27 (dd, 1H, *J* = 4.5, 9.7 Hz, H2); 4.83-4.88 (m, 2H, H1,3); 7.29 (br d, 2H, *J* = 8.4 Hz, Ar-H); 7.30 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.69 (br d, 2H, *J* = 8.4 Hz, Ar-H); 7.79 (br d, 2H, *J* = 8.3 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$): 22.1, 22.2, 56.3, 59.8, 63.3, 61.2, 76.0, 98.0, 128.6, 128.7, 130.2, 130.3, 133.2, 134.4, 145.4, 145.8. HRMS (TOF) calcd for $C_{20}H_{24}O_8S_2$ $(M+H)^+$ 498.1005, found 498.0971.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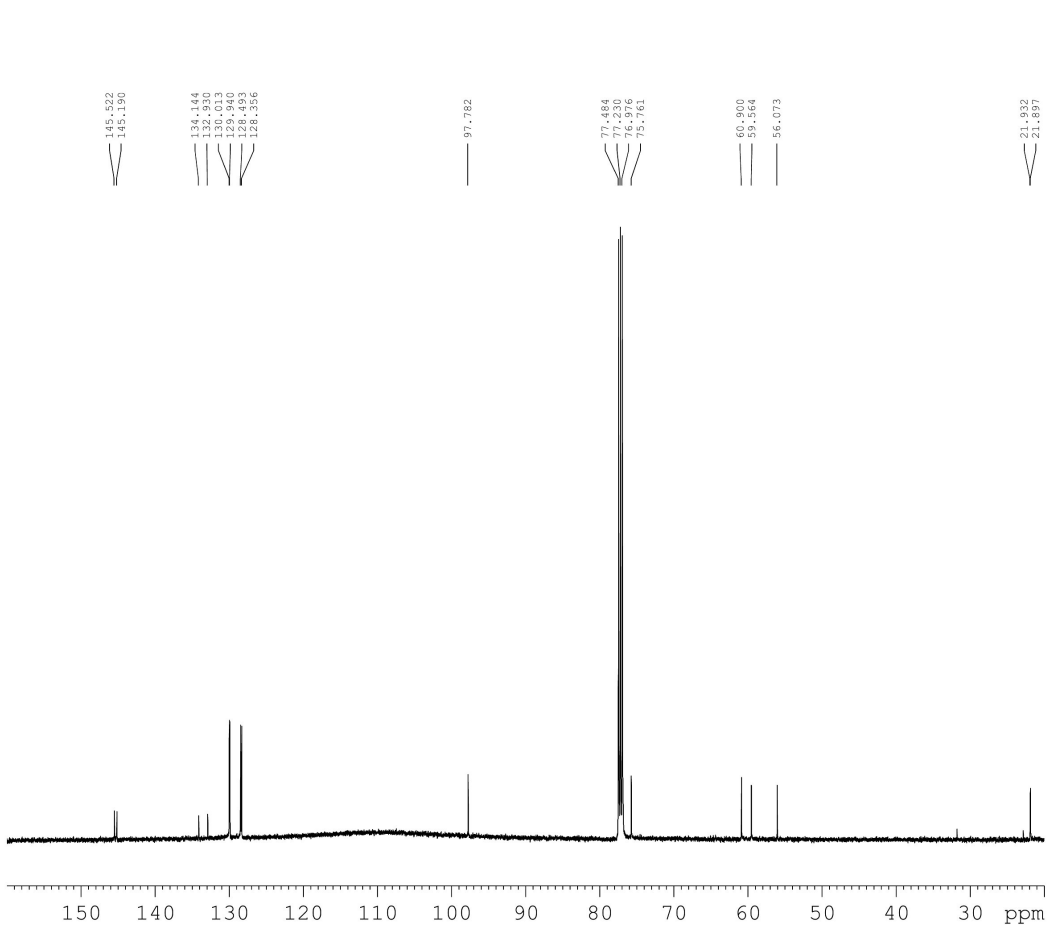


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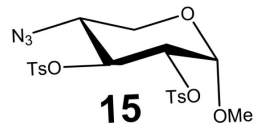
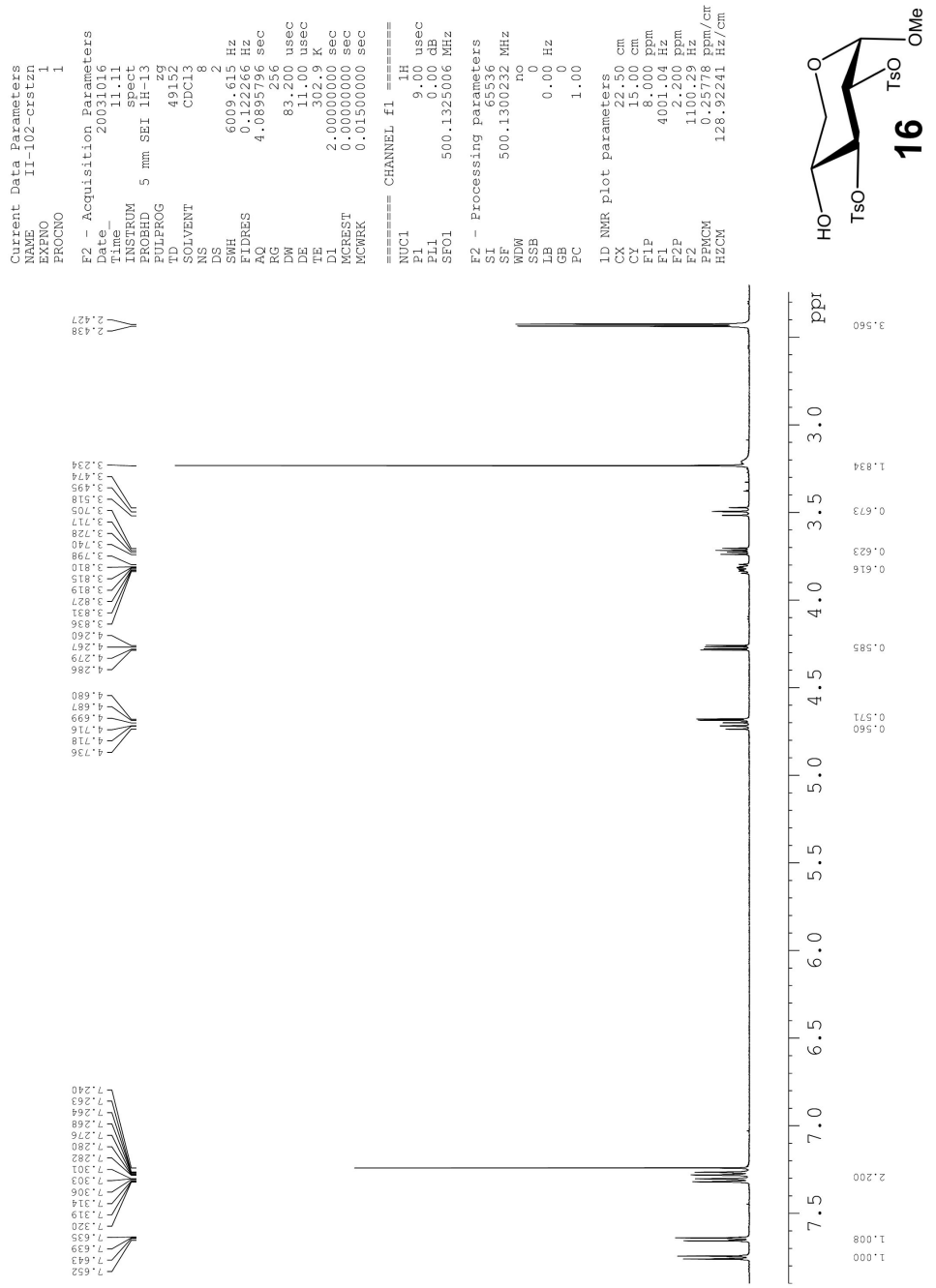


Methyl 2,3-Bis-(*O*-4-toluenesulfonyl)-a**-D-xylopyranoside (16).** A suspension of the tritosylate (**13**) (200 mg, 319 mmol) and sodium nitrite (220 mg, 3.19 mmol) in dry DMF (5 ml) was heated at 130 °C for 7 days. The cooled mixture was evaporated and the residue was taken up in EtOAc (15 ml). The organic phase was washed with 5% HCl (2x15 ml), saturated $NaHCO_3$ (2x15 ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to give the ditosylate as colorless crystals (48 mg, 32%), m.p. 152-154 °C. Recrystallization from EtOAc/hexane raised the m.p. to 164-166 °C (lit.[4] m.p. 168-169 °C). $[\alpha]_D$ 59.5 (*c* 0.1, $CHCl_3$) (lit.[4] $[\alpha]_D$ 60.3 (*c* 1.7, $CHCl_3$). ES-MS: 473 $(MH)^+$, 490 $(M+NH_4)^+$, 495 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.42 (s, 3H, Me); 2.44 (s, 3H, Me); 3.23 (s, 3H, OMe); 3.50 (br t, 1H, *J* = 11.0 Hz, H5a); 3.72 (dd, 1H, *J* = 6.1, 11.4 Hz, H5b); 3.80-3.85 (m, 1H, H4); 4.28 (dd, 1H, *J* = 3.6, 9.6 Hz, H2); 4.69 (d, 1H, *J* = 3.5 Hz, H1); 4.72 (dd, 1H, *J* = 8.6, 9.6 Hz, H3); 7.27 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.31 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.64 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.75 (br d, 2H, *J* = 8.3 Hz, Ar-H); OH not observed. ^{13}C NMR (125 Hz, $CDCl_3$): 21.9, 22.0, 55.7, 60.9, 69.3, 75.8, 80.9, 97.3, 128.2, 128.6, 130.0, 130.1, 132.5, 133.3, 145.4, 145.7.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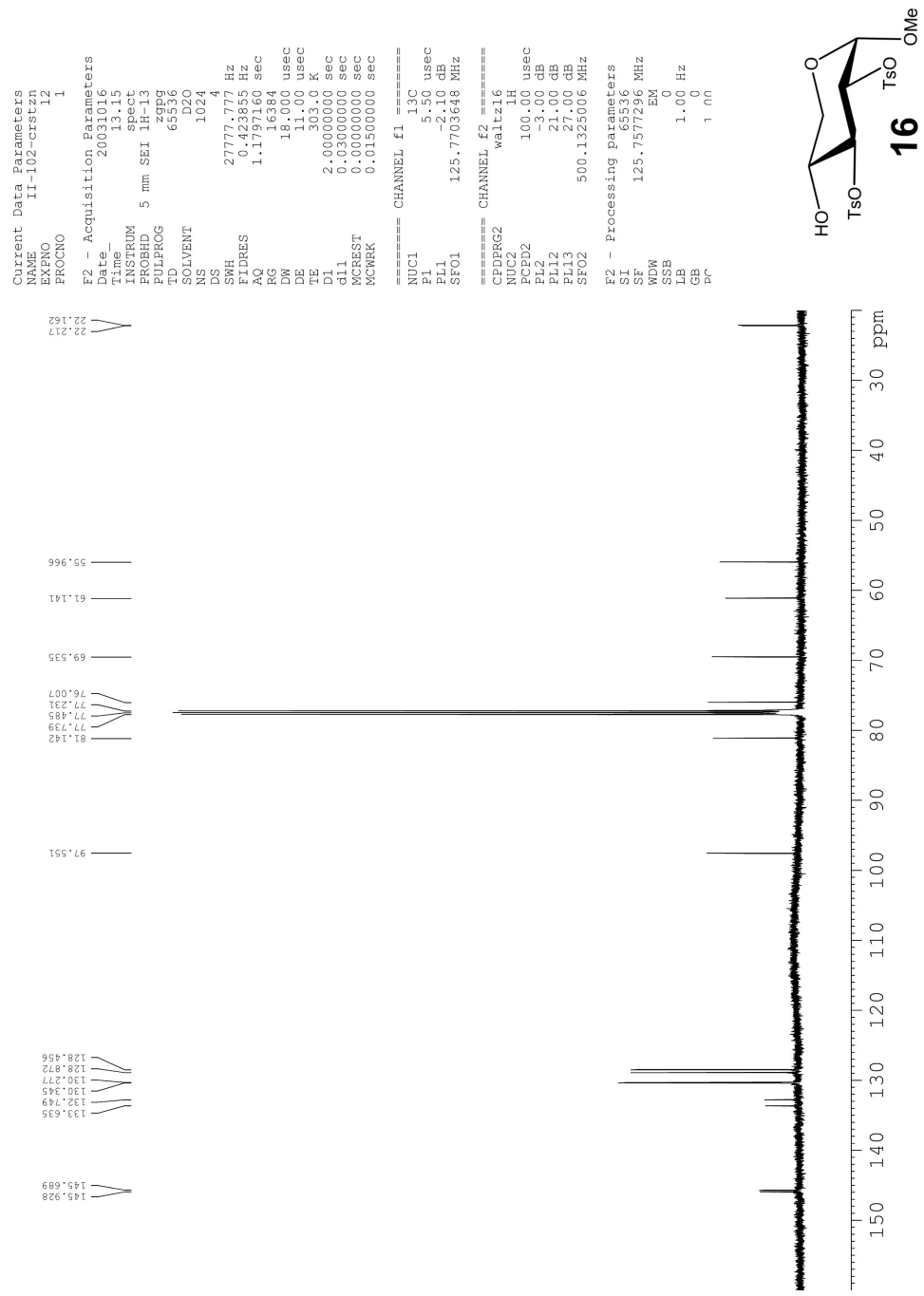
ppm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77.485
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81.142
97.551
128.456
128.872
130.277
130.345
132.749
133.635
145.928
145.689
150 140 130 120 110 100 90 80 70 60 50 40 30 ppm

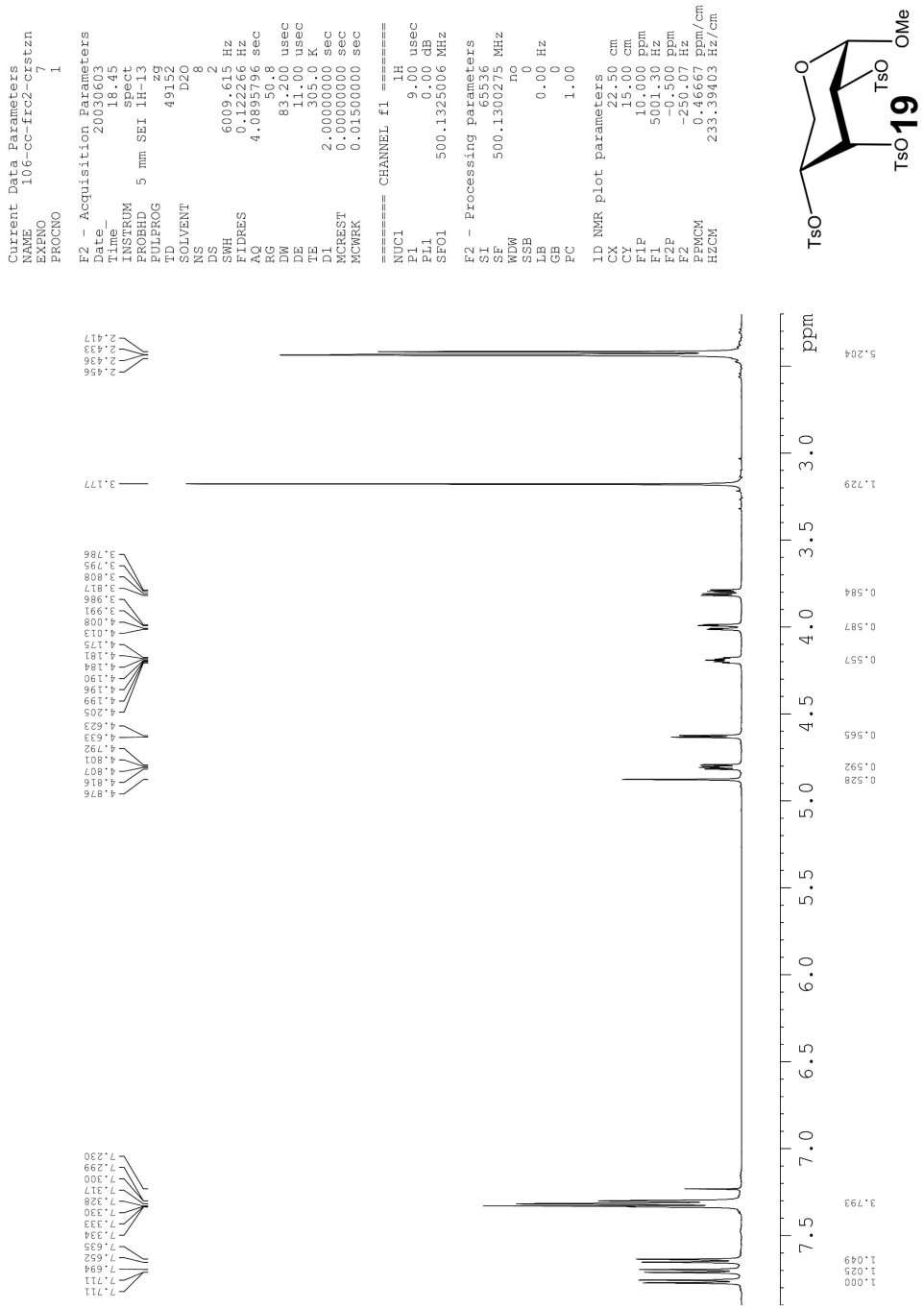
Methyl a **-D-Ribopyranoside (18).** A solution of D-ribose (**17**) (2.00 g, 13.3 mmol) in MeOH (100 ml) was treated dropwise with acetyl chloride (2.0 ml). The solution was then heated at 50 °C overnight. The cooled solution was neutralized by the addition of sodium methoxide solution, and then the mixture was filtered through Celite® and evaporated to a syrup (2.60 g) R_f (3:2:1 $CHCl_3$/EtOAc/MeOH): 0.23.

A small sample of this was converted to its triacetate by treatment with acetic anhydride in pyridine. The ^{1}H NMR spectrum of the triacetate showed that mixture contained the α- and β-anomers in a ratio of 85:15. The crude mixture of anomers (**18**) was used directly for the next step.

Triacetate derivative (α-anomer): ^{1}H NMR (500 MHz, $CDCl_3$): 2.00 (s, 3H, OAc); 2.07 (s, 3H, OAc); 2.09 (s, 3H, OAc); 3.39 (s, 3H, OMe); 3.76 (dd, 1H, *J* = 4.1, 12.6 Hz, H5a); 3.96 (dd, 1H, *J* = 2.7, 12.6 Hz, H5e); 4.68 (d, 1H, *J* = 3.3 Hz, H1); 5.00 (dt, 1H, *J* = 0.9, 3.5 Hz, H4); 5.10-5.12 (m, 1H, H2); 5.34 (t, 1H, *J* = 3.6 Hz, H3).

Methyl 2,3,4-Tris-(*O*-4-toluenesulfonyl)-a **-D-ribopyranoside (19).** 4-Toluenesulfonyl chloride (35.0 g, 184 mmol) was added portionwise to a stirred, chilled (0 °C) solution of the crude mixture of anomers of (**18**) (2.60 g, 13.3 mmol) in pyridine (50 ml). After stirring for 5 days, the mixture was subjected to ultrasonication in a cleaning bath for 3 h. The mixture was poured onto 100 g ice. After the ice had melted, the mixture was extracted with EtOAc (2x100 ml). The organic phase was washed with 5% HCl (2x100 ml), saturated $NaHCO_3$ (2x100 ml) and brine (100 ml), then dried ($MgSO_4$) and evaporated to give a syrup. This was chromatographed on silica (eluent: EtOAc/$CHCl_3$/hexane 1:2:3) to give the α-tritosylate (**19**) as colorless syrup,

contamininated with a little of the β-anomer (2.04 g, 21%). A sample recrystallized twice from EtOAc/hexane gave the pure α-isomer, m.p. 147-149 °C. $[\alpha]_D$ 31.0 (*c* 0.5, $CHCl_3$). ES-MS: 627 $(MH)^+$, 644 $(M+NH_4)^+$, 649 $(M+Na)^+$. ^1H NMR (500 MHz, $CDCl_3$): 2.41 (s, 3H, Me); 2.43 (s, 6H, 2xMe); 3.18 (s, 3H, OMe); 3.80 (dd, 1H, *J* = 4.5, 11.0 Hz, H5a); 4.00 (dd, 1H, *J* = 2.9, 10.9 Hz, H5b); 4.21 (ddd, 1H, *J* = 2.9, 4.4, 7.4 Hz, H4); 4.63 (d, 1H, *J* = 4.7 Hz, H2); 4.81 (dd, 1H, *J* = 4.7, 7.6 Hz, H3); 4.89 (s, 1H, H1); 7.22-7.25 (m, 6H, Ar-H); 7.54 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.70 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.77 (br d, 2H, *J* = 8.3 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 22.1, 22.2, 22.3, 55.7, 68.0, 74.8, 77.3, 79.5, 105.6, 128.4, 128.5, 128.7, 130.4, 130.5, 130.7, 132.1, 132.9, 133.0, 145.6, 146.0, 146.5. HRMS (TOF) calcd for $C_{27}H_{30}O_{11}S_3Na$ $(M+Na)^+$ 649.0848, found 649.1091. HRMS (TOF) calcd for $C_{26}H_{27}O_{10}S_3$ $(M+H-MeOH)^+$ 595.0766, found 595.1001.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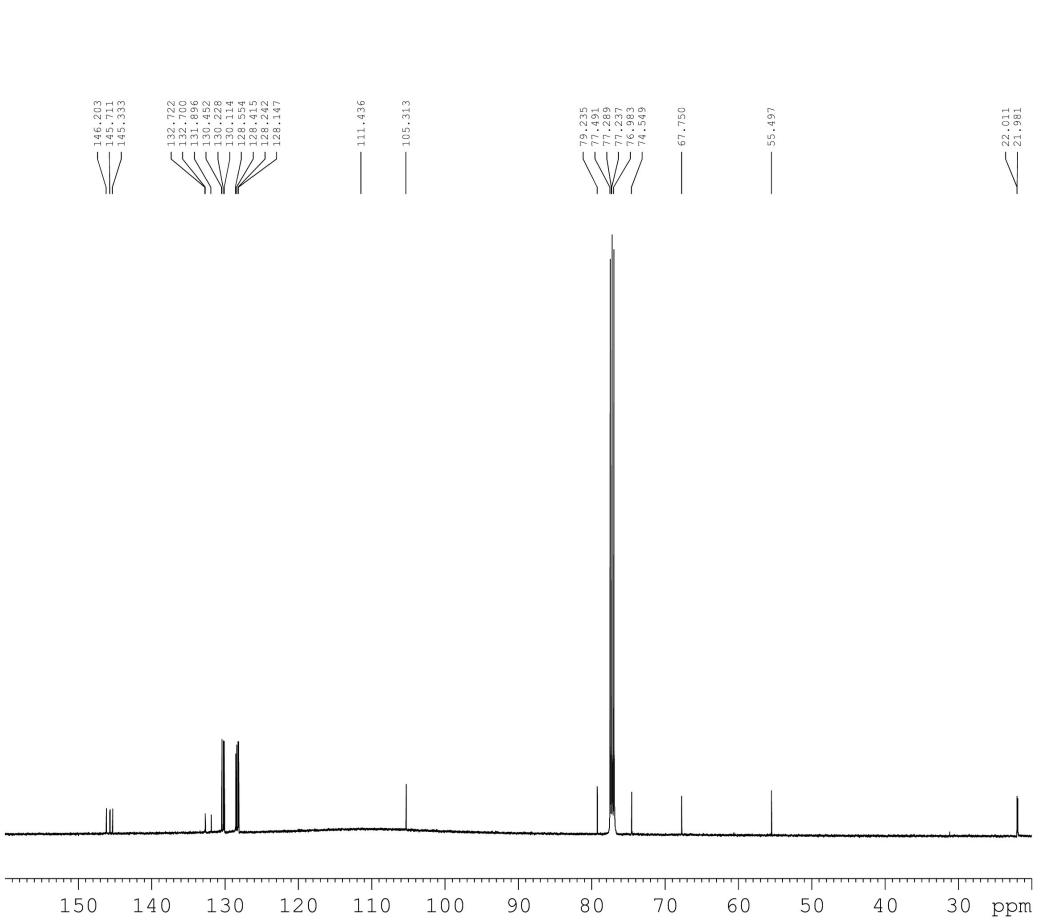
ppm

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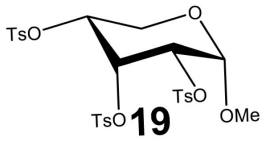
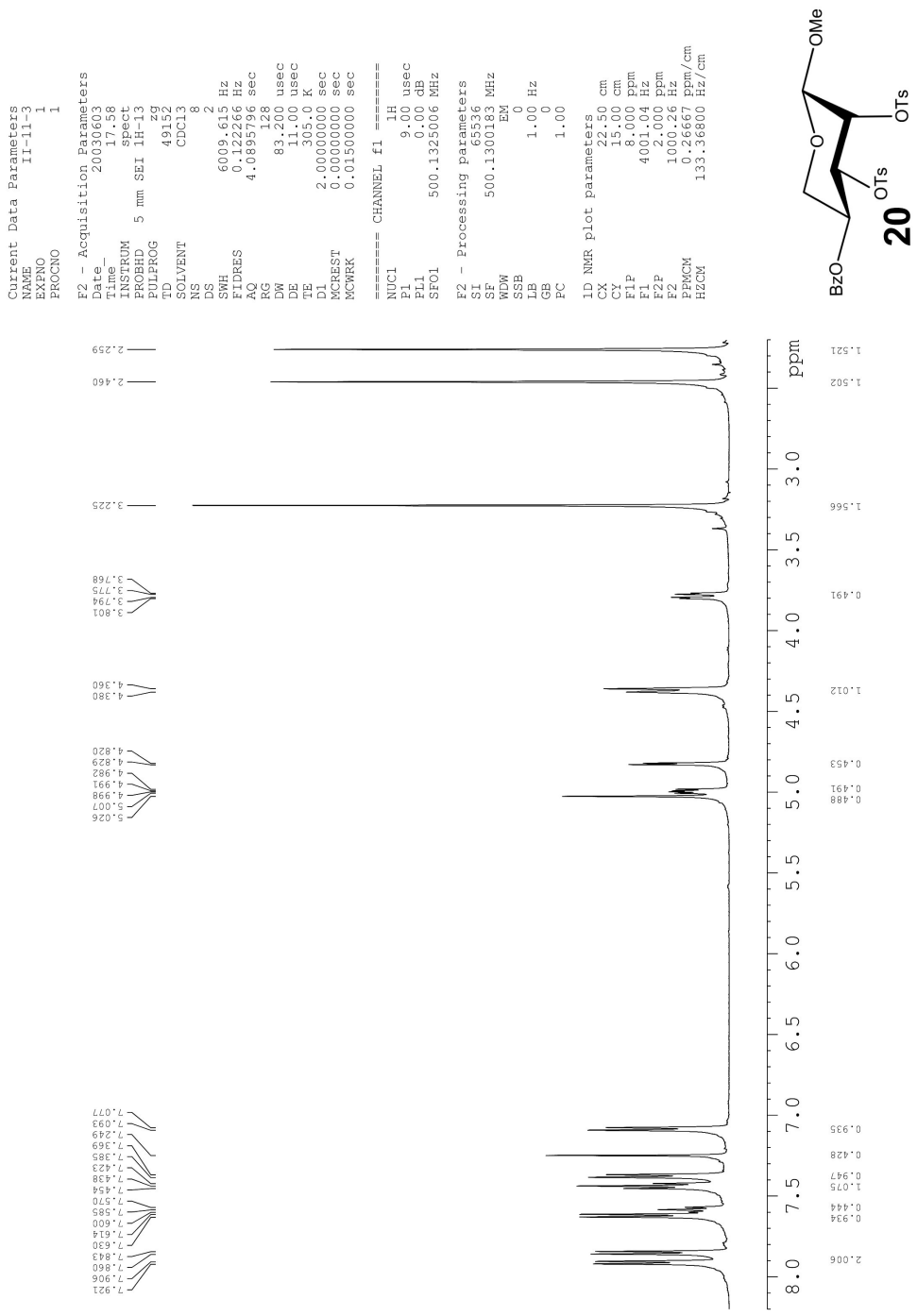


19

Methyl 4-Benzoyl-2,3-bis-(*O*-4-toluenesulfonyl)-b-L-lyxopyranoside (20).

(1) From (**19**): A suspension of the tritosylate (**19**) (30 mg, 0.048 mmol) and sodium benzoate (48 mg, 0.34 mmol) in 2.5 ml of dry DMF was heated at 130 °C for 20 h. The cooled reaction mixture was evaporated, and the residue was taken up into 50 ml EtOAc and washed with 5% HCl (2x50 ml), saturated $NaHCO_3$ (2x50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to give the benzoate (**20**) as a solid (21 mg, 76%), m.p. 85-87 °C. Recrystallization from EtOAc/hexane raised the m.p. to 90-92 °C. $[\alpha]_D$ 21.2 (*c* 0.2, $CHCl_3$). ES-MS: 577 $(MH)^+$, 594 $(M+NH_4)^+$, 599 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.27 (s, 3H, Me); 2.47 (s, 3H, Me); 3.22 (s, 3H, OMe); 3.79 (dd, 1H, *J* = 3.8, 13.1 Hz, H5a); 4.34-4.39 (m, 2H, H4,5b); 4.83 (d, 1H, *J* = 4.4 Hz, H2); 5.00 (dd, 1H, *J* = 4.5, 7.7 Hz, H3); 5.02 (br s, 1H, H1); 7.09 (br d, 2H, *J* = 8.5 Hz, Ar-H); 7.41 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.45 (br t, 2H, *J* = 6.5 Hz, Ar-H); 7.60 (br t, 1H, *J* = 7.5 Hz, Ar-H); 7.85 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.92 (br d, 2H, *J* = 8.3 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 21.7, 21.8, 55.4, 62.0, 74.4, 77.4, 79.6, 105.4, 128.1, 128.4, 128.6, 129.7, 130.1, 131.9, 132.8, 133.3, 133.4, 145.5, 145.9, 165.6. HRMS (TOF) calcd for $C_{27}H_{29}O_{10}S_2$ $(M+H)^+$ 577.1202, found 577.1201.

(2) From (**22**): A solution of the ditosylate (**22**) (13 mg, 0.028 mmol) in pyridine (3 ml) was treated with benzoyl chloride (0.15 ml, 0.18 g, 1.3 mmol). After stirring overnight the solution was evaporated, then taken up in EtOAc (10 ml). This was washed with 5% HCl (3x10 ml), saturated $NaHCO_3$ (2x10 ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to give the benzoate (**20**) (10 mg, 63%), identical by NMR and TLC to that prepared from (**19**) (above).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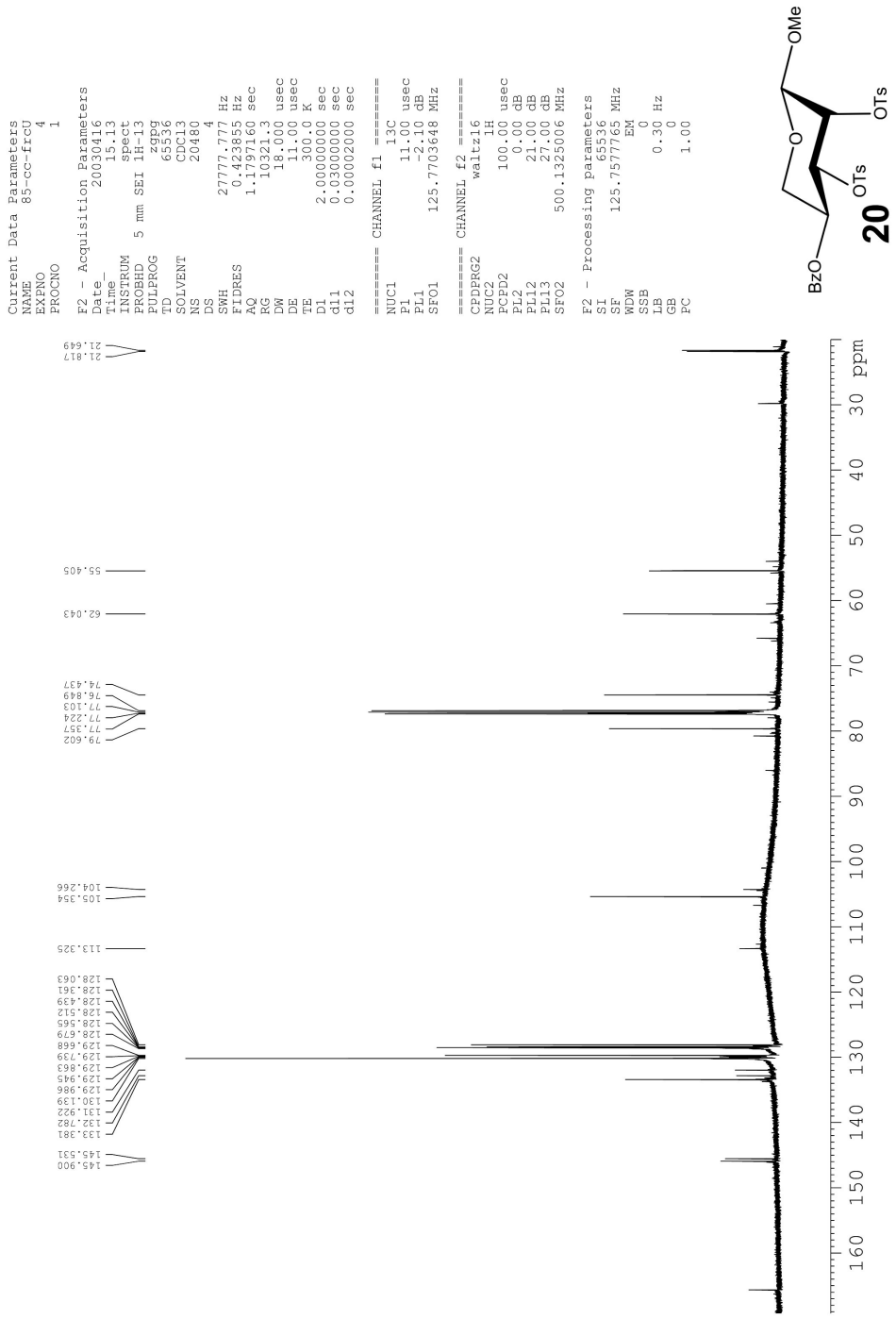
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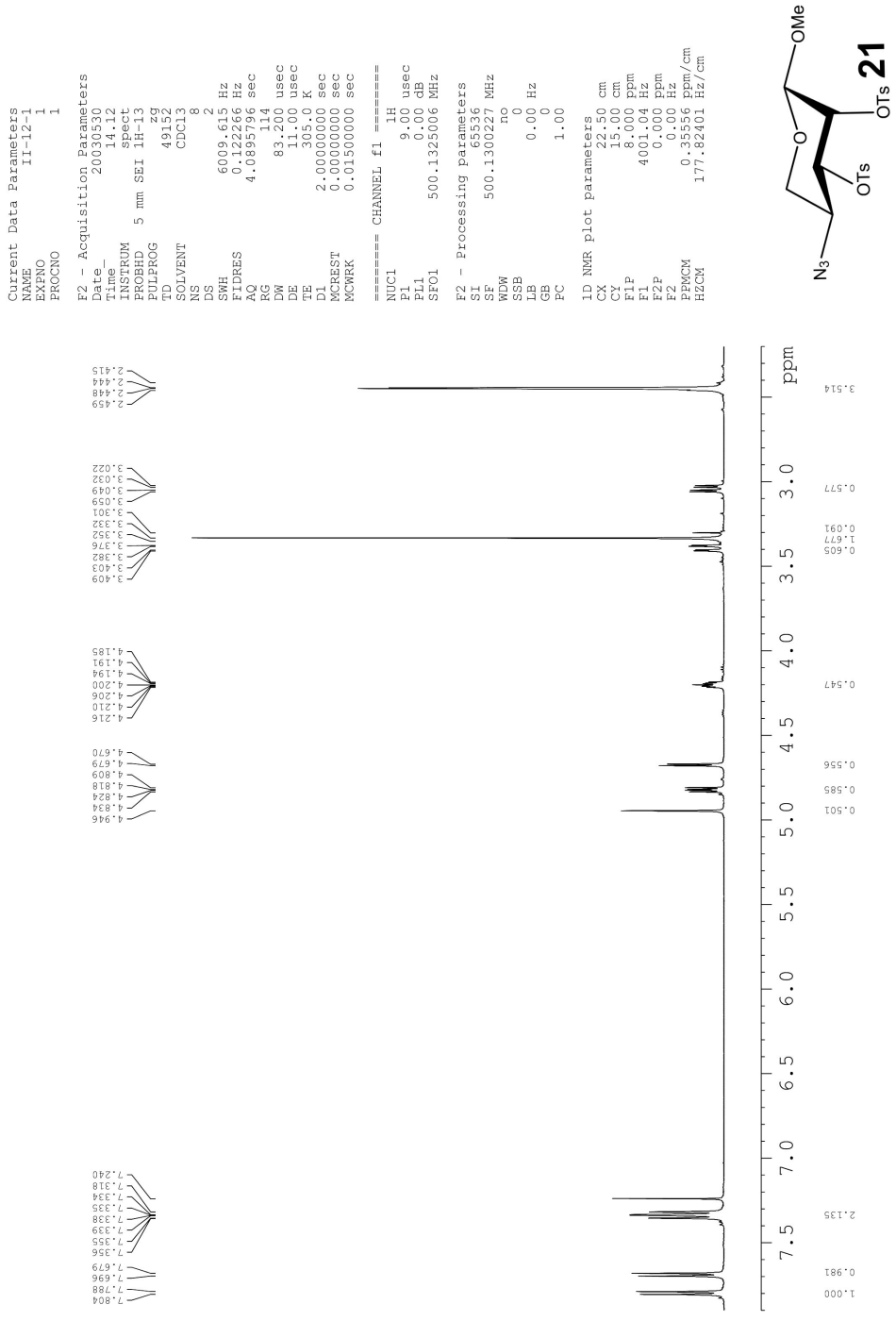
ppm
OMe
OTs
OTs
BzO
20

Methyl 4-Azido-2,3-bis-(*O*-4-toluenesulfonyl)-4-deoxy-β-L-lyxopyranoside (21). A suspension of the tritosylate (**19**) (30 mg, 0.048 mmol) and sodium azide (28 mg, 0.43 mmol) in 2.5 ml of dry DMF was heated at 130 °C for 40 h. The cooled reaction mixture was evaporated, and the residue was taken up into 50 ml EtOAc and washed with 5% HCl (2x50 ml), saturated $NaHCO_3$ (2x50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated to give the azide (**21**) as a solid (16 mg, 67%), m.p. 110-115 °C. $[\alpha]_D$ 70.8 (*c* 0.6, $CHCl_3$). ES-MS: 498 $(MH)^+$, 515 $(M+NH_4)^+$, 520 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.44 (s, 3H, Me); 2.45 (s, 3H, Me); 3.04 (dd, 1H, *J* = 4.7, 13.4 Hz, H5a); 3.33 (s, 3H, OMe); 3.39 (dd, 1H, *J* = 3.0, 13.4 Hz, H5b); 4.20 (ddd, 1H, *J* = 3.1, 4.7, 7.8 Hz, H4); 4.67 (d, 1H, *J* = 4.7, H2); 4.82 (dd, 1H, *J* = 4.7, 7.8 Hz, H3); 4.95 (br s, 1H, H1); 7.32 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.34 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.69 (br d, 2H, *J* = 8.3 Hz, Ar-H); 7.79 (br d, 2H, *J* = 8.3 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 21.9, 22.0, 51.6, 56.2, 75.1, 78.5, 79.6, 106.3, 128.3, 128.4, 130.2, 130.3, 132.4, 133.0, 145.7, 146.0. HRMS (TOF) calcd for $C_{20}H_{24}N_3O_8S_2$ $(M+H)^+$ 498.1005, found 498.1182.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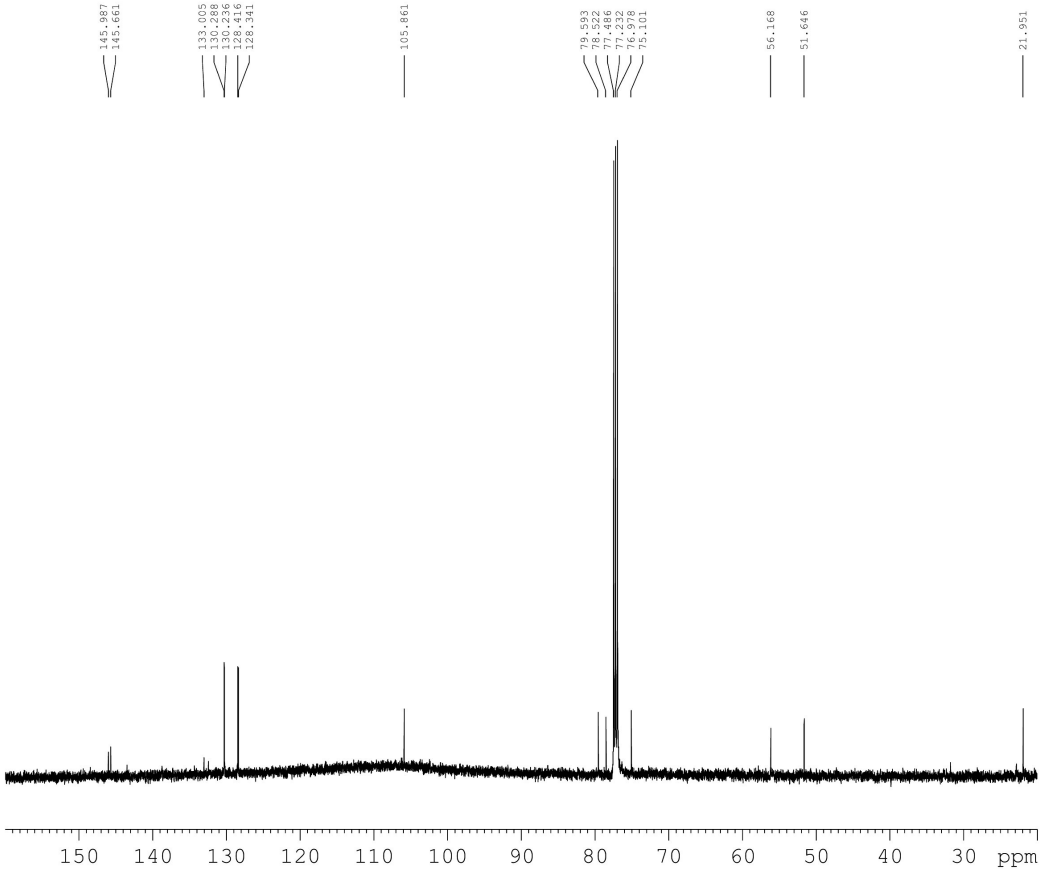


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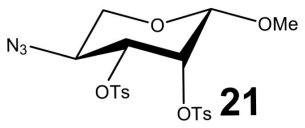
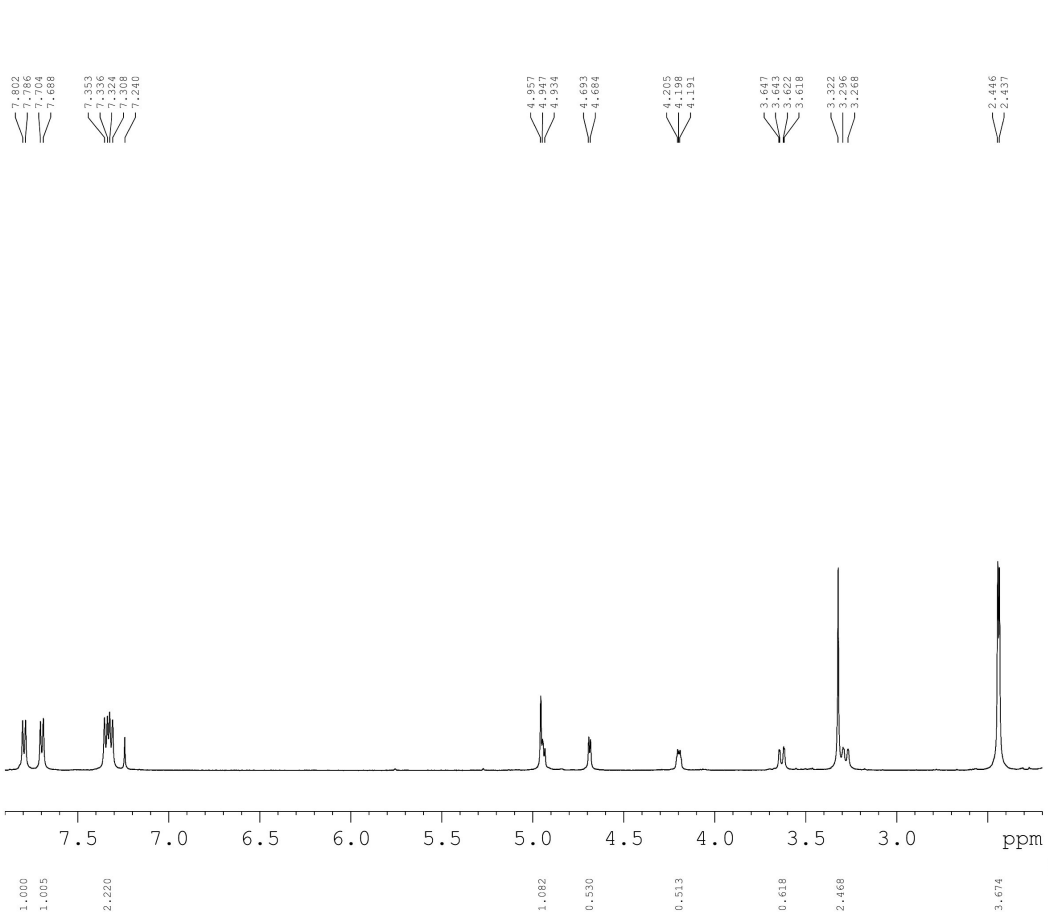


21

Methyl 2,3-Bis-(*O*-4-toluenesulfonyl)-b-L-lyxopyranoside (22). A suspension of the tritosylate (**21**) (50 mg, 0.080 mmol) and sodium nitrite (55 mg, 0.80 mmol) in dry DMF (5 ml) was heated at 130 °C for 48 h. The cooled mixture was evaporated and the residue was extracted with EtOAc (25 ml). The organic extract was washed with 5% HCl (2x10 ml), saturated $NaHCO_3$ (2x10 ml) and brine (10 ml), then dried ($MgSO_4$) and evaporated to a gum. This was triturated with hexane to give the ditosylate (**22**) as a colorless oil (30 mg, 81%). $[\alpha]_D$ 15.3 (*c* 0.2, $CHCl_3$). R_f (1:2:3 EtOAc/$CHCl_3$/hexane): 0.15. ES-MS: 473 $(MH)^+$, 490 $(M+NH_4)^+$, 495 $(M+Na)^+$. ^1H NMR (500 MHz, $CDCl_3$): 2.43 (s, 3H, Me); 2.45 (s, 3H, Me); 3.28 (br d, 1H, *J* = 12.2 Hz, H5a); 3.32 (s, 3H, OMe); 3.64 (dd, 1H, *J* = 2.3, 12.4 Hz, H5b); 4.19-4.21 (m, 1H, H4); 4.69 (d, 1H, *J* = 4.7 Hz, H1); 4.93-4.96 (m, 2H, H2,3); 7.31 (br d, 2H, *J* = 8.1 Hz, Ar-H); 7.35 (br d, 2H, *J* = 8.2 Hz, Ar-H); 7.70 (br d, 2H, *J* = 8.1 Hz, Ar-H); 7.80 (br d, 2H, *J* = 8.1 Hz, Ar-H); OH not observed. ^{13}C NMR (125 Hz, $CDCl_3$) 21.8, 21.8, 56.1, 61.1, 74.5, 79.8, 81.0, 106.0, 128.2, 128.2, 130.1, 130.2, 132.5, 132.8, 145.5, 145.7. HRMS (TOF) calcd for $C_{20}H_{25}O_9S_2$ $(M+H)^+$ 473.0940, found 473.0900.

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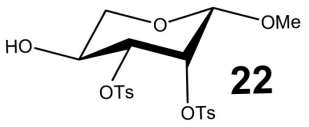

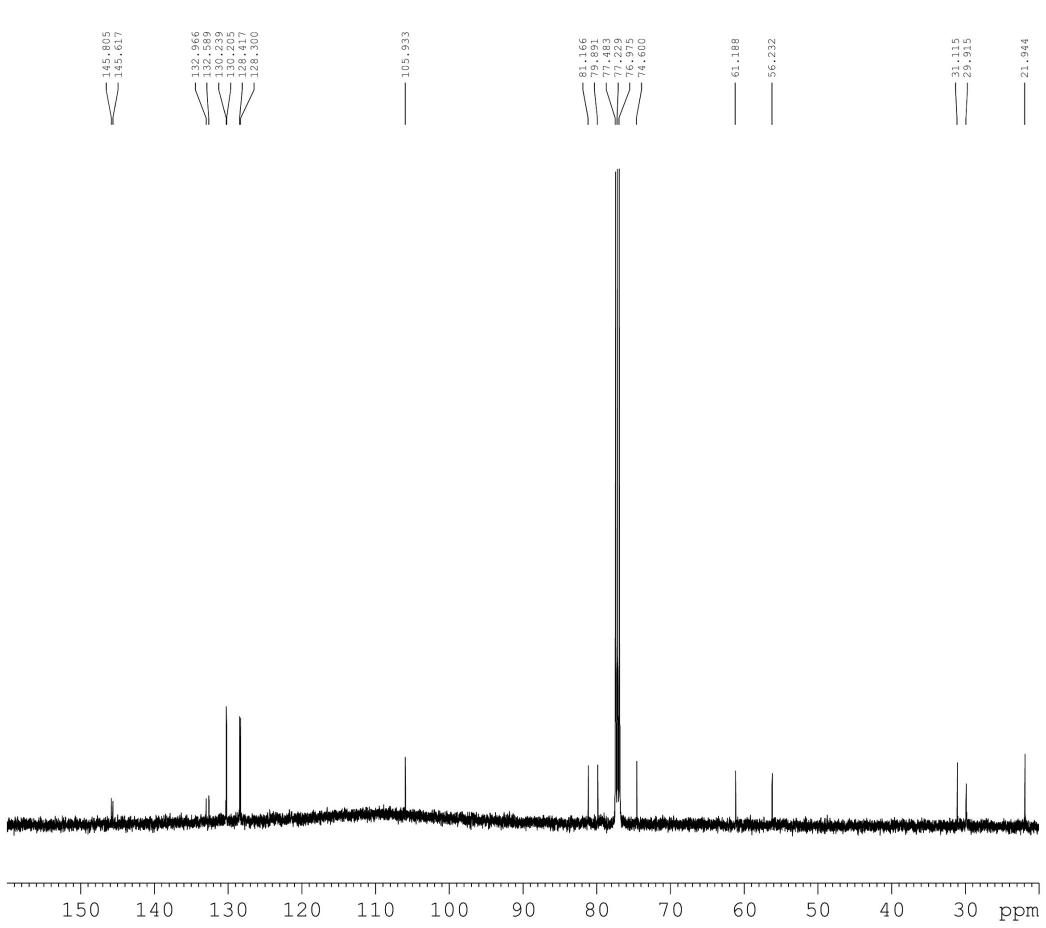


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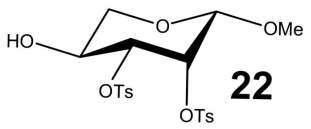


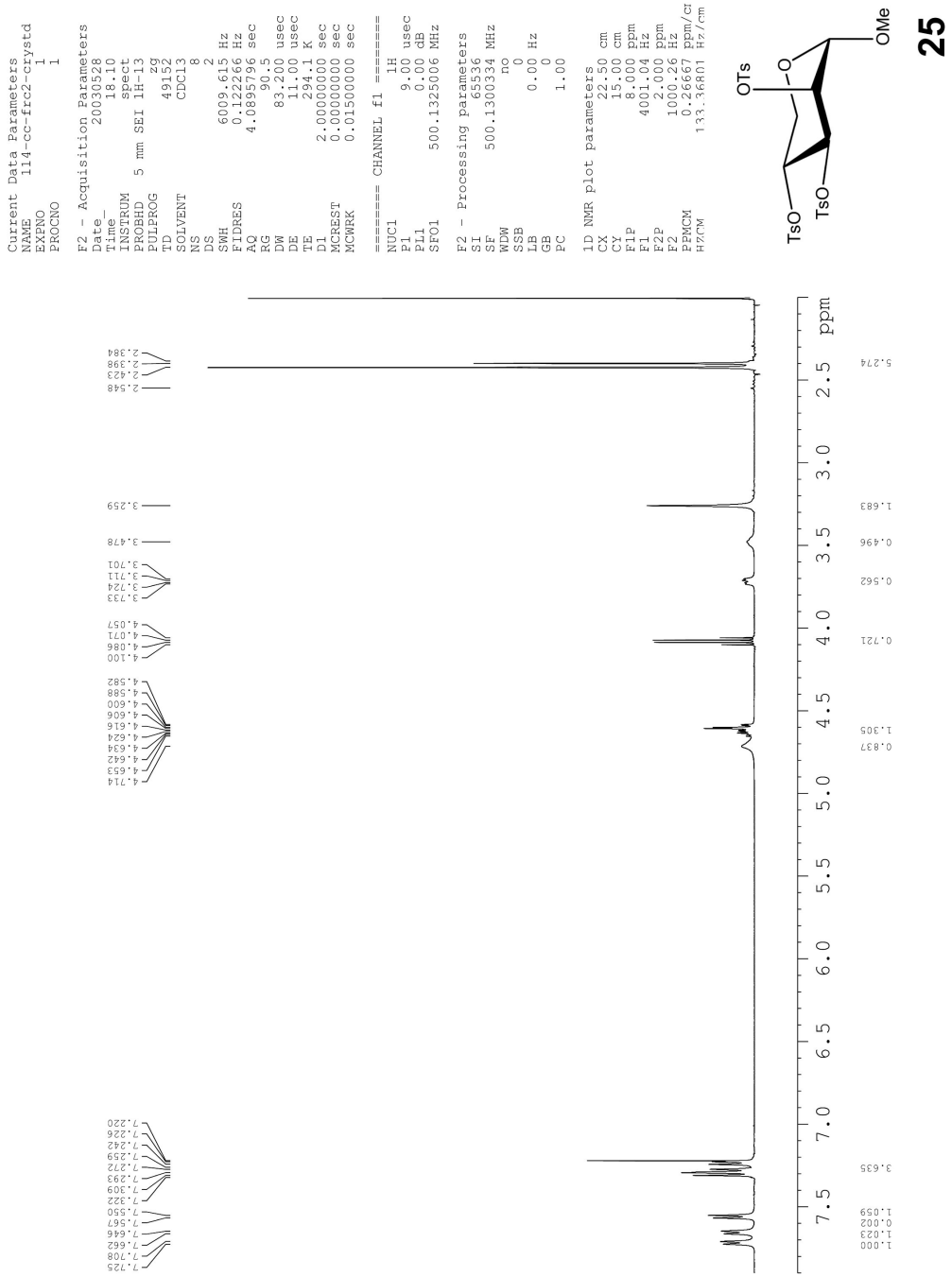
22

Methyl a **-D-Lyxopyranoside (24).** Acetyl chloride (1.0 ml, 14 mmol) was added dropwise to a stirred solution of D-lyxose (**23**) (1.00 g, 6.6 mmol) in dry MeOH (50 ml). The solution was heated overnight at 50 °C, and then cooled in ice. The solution was then neutralized by the addition of solid Ag_2CO_3. Stirring was continued for 2 h at this temperature, then the mixture was filtered through Celite® and the filtrate evaporated to give the methyl pyranoside (**24**) as a syrup, in quantitative yield. The crude product was used directly for subsequent steps. Crystals slowly formed on standing, m.p. 91-93 °C (lit. m.p.[6] 102-103 °C; lit. m.p.[9] 108-109 °C). R_f (3:2:1 $CHCl_3$/EtOAc/MeOH): 0.23.

A small sample of the crude syrup was acetylated with Ac_2O/pyridine gave the triacetate derivative, which was shown by ^{1}H NMR spectroscopy to be an 87:13 mixture of the α/β anomers. ^{1}H NMR (500 MHz, $CDCl_3$): (α-anomer) 1.98 (s, 3H, OAc); 2.01 (s, 3H, OAc); 2.09 (s, 3H, OAc); 3.37 (s 3H, OMe); 3.58 (dd, 1H, J = 9.3, 11.0 Hz, H5); 3.85 (dd, 1H, J = 5.4, 11.0 Hz, H5); 4.61 (d, 1H, J = 2.4 Hz, H1); 5.17 (dd, 1H, J = 5.4, 9.7 Hz, H4); 5.19 (dd, 1H, J = 2.5, 3.4 Hz, H2); 5.31 (dd, 1H, J = 3.5, 10.3 Hz, H3).

Methyl 2,3,4-Tris-(*O*-4-toluenesulfonyl)-a **-D-lyxopyranoside (25).** A stirred, chilled (0 °C) solution of the crude methyl α-D-lyxopyranoside (**24**) (5.00 g, 30.5 mmol) in pyridine (50 ml) was treated portionwise during 30 min with 4-toluenesulfonyl chloride (40.0 g, 210 mmol). After stirring for 5 days at room temperature, the mixture was sonicated in a cleaning bath for 3 h, and then poured onto 100 g ice. After the ice had melted, the mixture was extracted into EtOAc (200 ml) and washed with 5% HCl (2x100 ml), saturated $NaHCO_3$ (2x100 ml) and brine (100 ml), then dried ($MgSO_4$) and

evaporated to a syrup. This was triturated with hexane, and then the residue was purified by column chromatography (eluent: EtOAc/$CHCl_3$/hexane 1:2:3) to give the tritosylated lyxose (**25**) (10.9 g, 57%), which was shown by ^{1}H NMR spectroscopy to be contaminated with 7% of the β-anomer. Two recrystallizations from EtOAc/hexane gave the pure tritosylate (**25**) as colorless crystals, m.p. 66-68 °C. $[\alpha]_D$ 7.2 (*c* 1.0, $CHCl_3$). ES-MS: 627 $(MH)^+$, 644 $(M+NH_4)^+$, 649 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): 2.41 (s, 3H, Me); 2.42 (s, 3H, Me); 2.44 (s, 3H, Me); 3.28 (s, 3H, OMe); 3.45-3.54 (m, 1H, H5a); 3.74 (dd, 1H, *J* = 4.6, 11.3 Hz, H5b); 4.62 (dd, 1H, *J* = 3.1, 9.0 Hz, H3); 4.63-4.74 (m, 3H, H1,2,4); 7.26 (br d, 2H, *J* = 8.1 Hz, Ar-H); 7.31 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.34 (br d, 2H, *J* = 8.2 Hz, Ar-H); 7.58 (br d, 2H, *J* = 8.2 Hz, Ar-H); 7.68 (br d, 2H, *J* = 8.0 Hz, Ar-H); 7.75 (br d, 2H, *J* = 8.0 Hz, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 22.4, 56.4, 61.1, 72.9, 74.2, 76.9, 99.0, 128.8, 128.9, 129.0, 130.5, 130.6, 130.7, 132.8, 133.3, 133.6, 146.0, 146.5. HRMS (TOF) calcd for $C_{27}H_{31}O_{11}S_3$ $(M+H)^+$ 627.1029, found 627.1073.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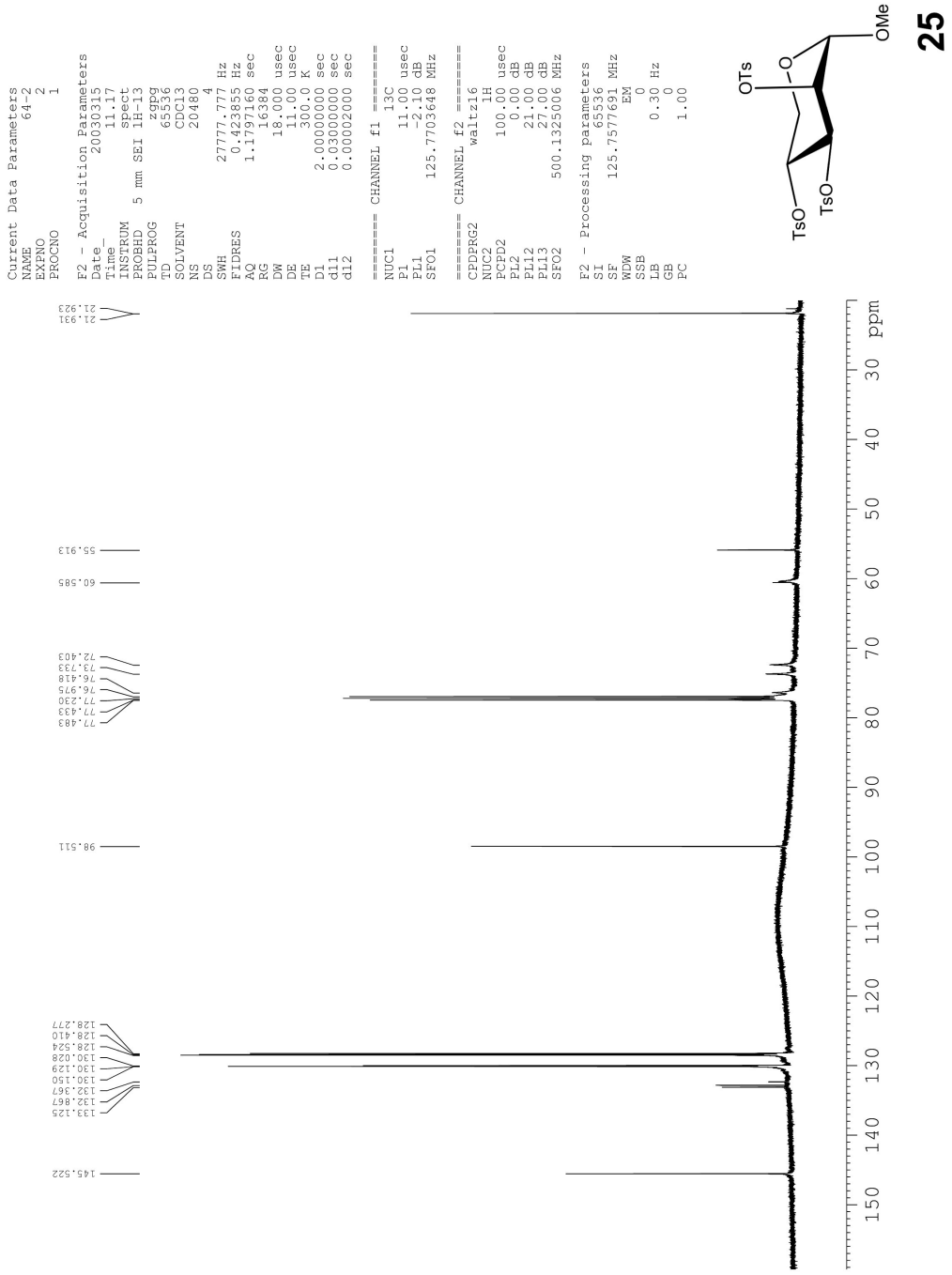
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TsO
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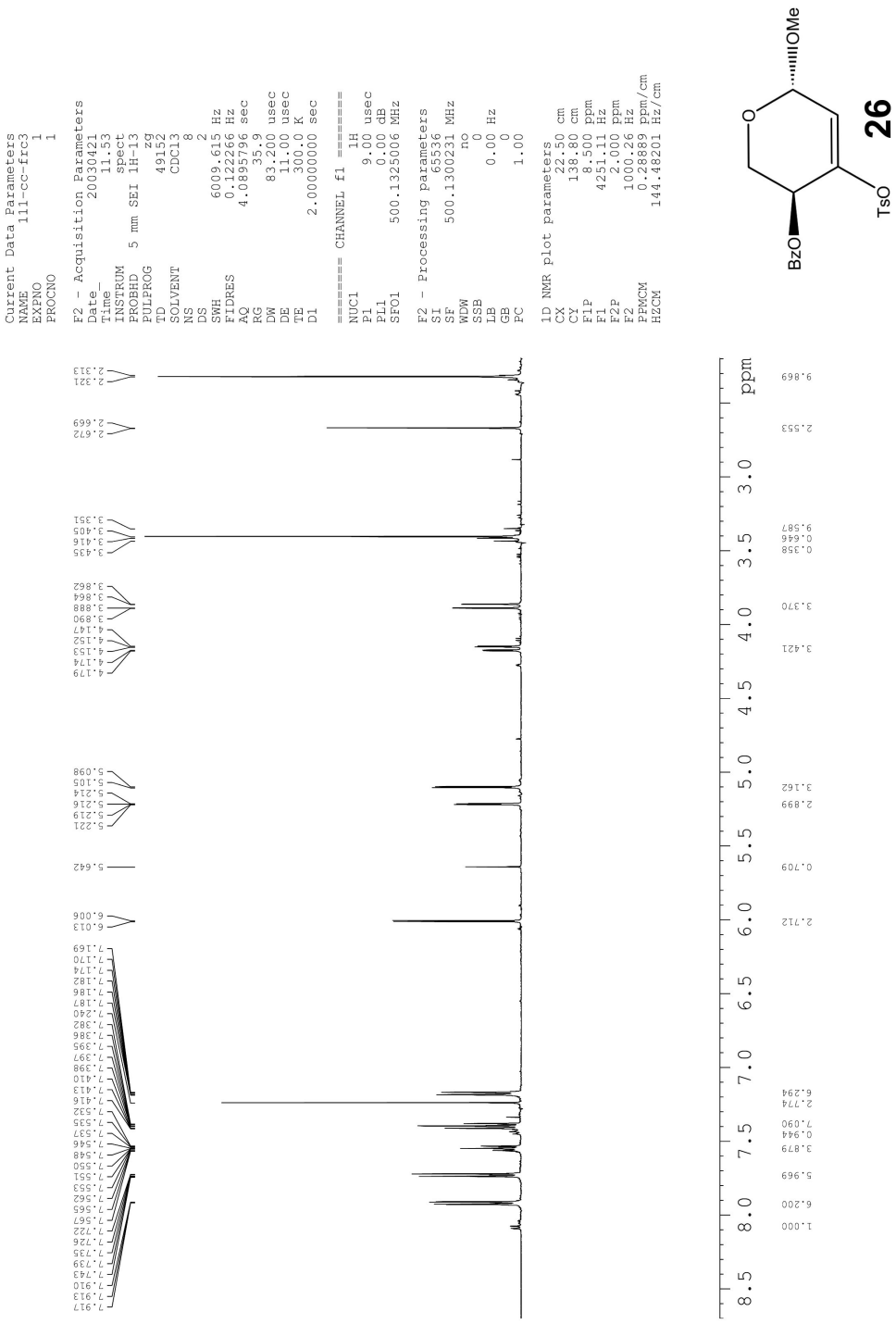
3*R*,6*S*-3-Benzoyloxy-6-methoxy-4-(4-toluene sulfonyloxy)-3,6-dihydro-2*H*-pyran (26). A mixture of the pure tritosylated lyxose (**25**) (80 mg, 0.13 mmol) and sodium benzoate (250 mg, 1.74 mmol) in DMF (20 ml) was heated at 130 °C for 5 days. The cooled mixture was evaporated then the residue was extracted into EtOAc (50 ml) and filtered. The filtrate was washed with 5% HCl (2x50 ml), saturated $NaHCO_3$ (2x50 ml) and brine (50 ml), then dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography to give the dihydropyran (**26**) as a colorless oil (15 mg, 29%). $[\alpha]_D$ 10.3 (*c* 1.2, $CHCl_3$). ES-MS: 405 $(MH)^+$, 422 $(M+NH_4)^+$, 427 $(M+Na)^+$. ^{1}H NMR (500 MHz, $CDCl_3$): (carbohydrate numbering) 2.32 (s, 3H, Me); 3.40 (s, 3H, OMe); 3;87 (dd, 1H, *J* = 1.1, 13.2 Hz, H5a); 4.16 (dd, 1H, *J* = 2.7, 13.2 Hz, H5b); 5.10 (d, 1H, *J* = 3.5 Hz, H1); 5.22 (dd, 1H, *J* = 1.0, 2.7 Hz, H4); 6.01 (d, 1H, *J* = 3.5 Hz, H2); 7.19 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.41 (br t, 2H, *J* = 7.8 Hz, Ar-H); 7.55 (br t, 1H, *J* = 7.1 Hz, Ar-H); 7.71 (br d, 2H, *J* = 8.6 Hz, Ar-H); 7.92 (br d, 2H, *J* = 8.4, Ar-H). ^{13}C NMR (125 Hz, $CDCl_3$) 22.7, 57.0, 63.3, 66.3, 96.2, 129.3, 129.4, 130.4, 130.8, 131.0, 134.0, 134.4, 138.0, 146.3, 146.5, 166.7. HRMS (TOF) calcd for $C_{20}H_{20}O_7SNa$ $(M+Na)^+$ 427.0827, found 427.0813.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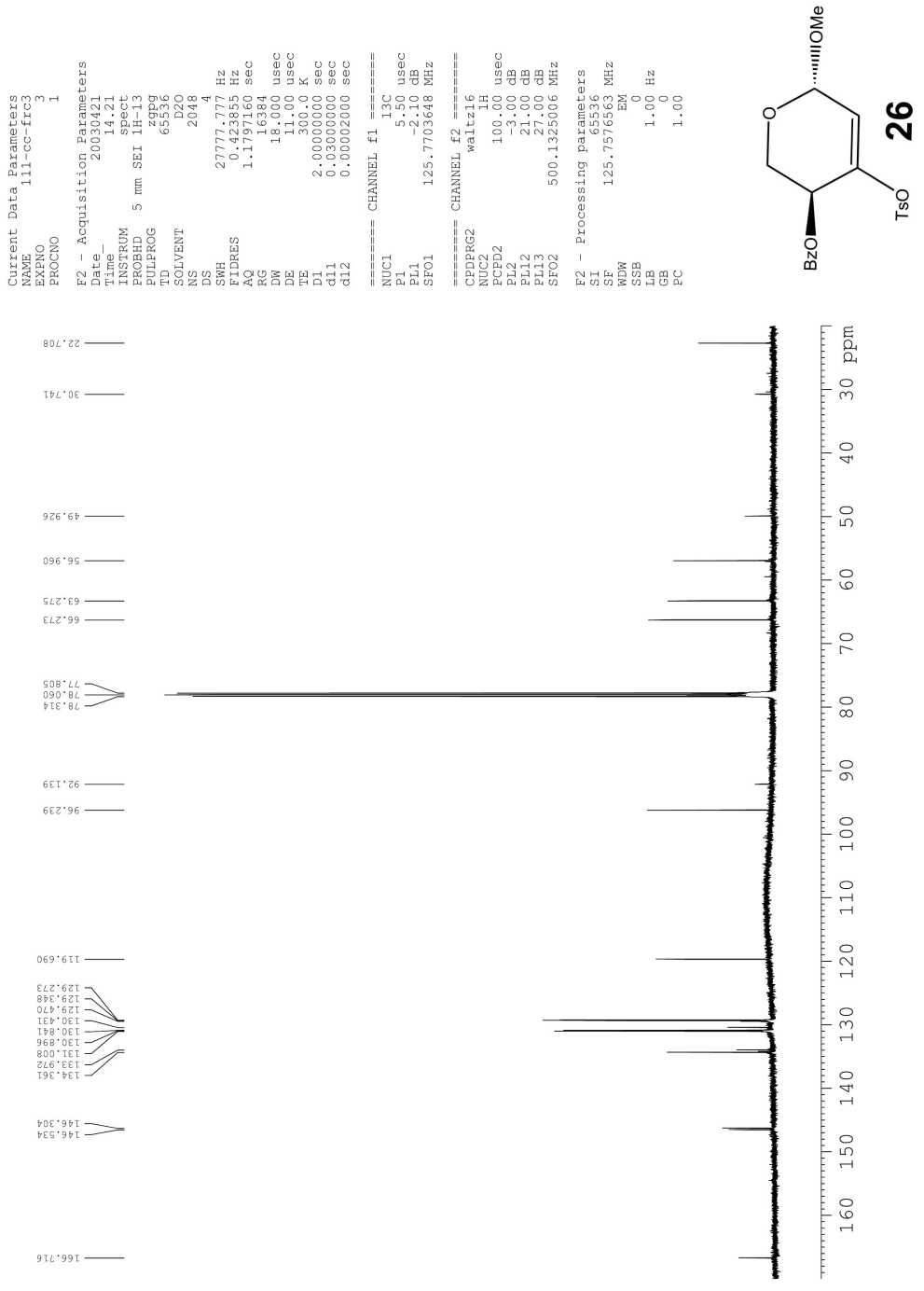
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BzO
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26

References:

(1) Indurugalla, D.; Bennet, A. J. *Journal of the American Chemical Society* **2001**, *123*, 10889-10898.
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