Supporting Information

Stereoselective Synthesis of a Fragment of Mycobacterial Arabinan

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Experimental

General procedure: All reactions sensitive to air and/or moisture were carried out under argon atmosphere with anhydrous solvents. Column chromatography was performed on silica gel 60N, 100-210 mesh (Kanto Kagaku Co., Ltd.). Preparative TLC was performed on silica gel 60 F_{254}, 0.5 mm (E. Merck). Gel filtration was performed on Bio beads SX-3 or Sephadex LH-20 (Pharmacia). Melting point was determined with Büchi 510 melting point apparatus. Optical rotations were measured with a JASCO DIP 370 polarimeter. ^{1}H NMR spectra were recorded at 400 MHz on a JEOL JNM-AL 400 spectrometer and chemical shifts are referred to internal residual solvent signals, 7.24 ppm ($CDCl_3$) or 3.30 ppm (CD_3OD). ^{13}C NMR spectra were recorded at 100 MHz on the same instrument and chemical shifts are referred to internal $CDCl_3$ (77.0 ppm) or CD_3OD (49.0 ppm). MALDI-TOF mass spectra were recorded on a SHIMADZU Kompact MALDI AXIMA-CFR spectrometer with 2,5-dihydroxybenzoic acid as the matrix. ESI-TOF mass spectra were recorded on a JEOL AccuTOF JMS-T700LCK with CF_3CO_2Na as the internal standard. Elemental analyses were performed with a Fisons EA1108 instrument. All other reagents were purchased from the Wako Pure Chemical Industries Ltd., Kanto Chemicals Co. Ink., Tokyo Kasei Kogyo Co. and Aldrich Chemical Company.

***p*-Tolyl 2,3-di-*O*-benzyl-5-*O*-*t*-butyldiphenylsilyl-1-thio-α-D-arabinofuranoside (2a).**

To a solution of **8**[1] (3.03 g, 6.13 mmol) in dry DMF (10 mL) was added NaH (736 mg, 18.4 mmol) and BnBr (1.60 mL, 13.5 mmol) at 0 °C. After stirring for 2 hrs at room temperature, the reaction was quenched by triethylamine and followed by addition of H_2O and was extracted with $CHCl_3$. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 50/1 to 20/1 to 10/1) to give the title compound (4.04 g, 98%).

$[\alpha]^{26}_D$ +79.0° (*c* 1.05, $CHCl_3$). 1H NMR ($CDCl_3$, 400 MHz): δ 1.03 (s, *t*-Bu, 9H), 2.32 (s, MePh, 3H), 3.54 (dd, *J* = 11.6, 4.8 Hz, H-5, 1H), 3.54 (dd, *J* = 11.6, 4.0 Hz, H-5, 1H), 4.08-4.14 (m, H-2, H-3, 2H), 4.31 (dt, *J* = 6.4, 4.4 Hz, H-4, 1H), 4.50 (d, *J* = 12.0 Hz, Bn, 1H), 4.51 (d, *J* = 12.0 Hz, Bn, 1H), 4.53 (d, *J* = 12.0 Hz, Bn, 1H), 4.63 (d, *J* = 12.0 Hz, Bn, 1H), 5.50 (d, *J* = 2.4 Hz, H-1, 1H), 7.08-7.67 (m, Bn x2, Tol, TBPS, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.35, 21.18, 26.95, 63.40, 72.06, 72.19, 82.01, 83.25, 88.40, 90.43, 127.53, 127.58, 127.60, 127.63, 127.76, 127.80, 128.30, 128.34, 129.55, 131.08, 131.84, 133.28, 133.33, 135.56, 135.61, 137.16, 137.43, 137.74. MALDI-TOF MS: $[M+Na]^+$ calcd for $C_{42}H_{46}O_4SiSNa$, 697.3, found 697.1.

***p*-Tolyl 5-*O*-*t*-butyldiphenylsilyl-2,3-di-*O*-acetyl-1-thio-α-D-arabinofuranoside (7).**

To the solution of 1,2,3-tri-*O*-acetyl-5-*O*-*t*-butyldiphenylsilyl-D-arabinofuranose[2] (39.55 g, 76.85 mmol) and *p*-thiocresol (11.93 g, 96.05 mmol) in CH_2Cl_2 (150 mL) was added $BF_3{\cdot}OEt_2$ (55.37 mL, 390 mmol) at 0 °C. After stirring for 30 min at 0 °C, the reaction was quenched by triethylamine (54 mL), eluted with $CHCl_3$, washed with sat $NaHCO_3$ aq. and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 25/1 to 10/1 to 5/1 to 2/1) to give the title compound (38.22 g, 86%).

$[\alpha]^{27}_D$ +110.96° (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.39 (s, TBPS, 9H), 2.02 (s, Ac, 3H), 2.07 (s, Ac, 3H), 2.32 (s, Me, 3H), 3.83-3.92 (m, H-5, 2H), 4.33 (dt, *J* = 5.2, 4.4 Hz, H-4, 1H), 5.23 (t, *J* = 2.4 Hz, H-2, 1H), 5.31 (dd, *J* = 5.2, 2.4 Hz, H-3, 1H), 5.46 (d, *J* = 2.4 Hz, H-1, 1H), 7.08-7.70 (m, TBPS, Tol, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 19.35, 20.84, 20.90, 21.20, 26.76, 63.20, 77.16, 81.75, 82.48, 90.79, 127.58, 127.62, 129.61, 129.64, 129.80, 132.59, 133.01, 133.08, 135.58, 137.74, 169.66, 169.94. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{32}H_{38}O_6SSiNa$, 601.2, found 601.4.

***p*-Tolyl 2,3-*O*-dibenzyl-1-thio-α-D-arabinofuranoside.**

To a solution of **7** (10.03 g, 17.3 mmol) in MeOH (50 mL) was added a catalytic amount of NaOMe at room temperature. After stirring for 15 min at the same temperature, the reaction was quenched by Amberlyst H^+ resin, filtered and concentrated in vacuo to give *p*-tolyl 5-*O*-*t*-butyldiphenylsilyl-1-thio-α-D-arabinofuranoside **8** (8.61 g, quant). To a solution of **8** in dry DMF (10 mL) was added NaH (2.77 g, 69.3 mmol) and BnBr (5.15 mL, 43.3 mmol) at 0 °C. After stirring for 2 hrs at room temperature, the reaction was quenched by triethylamine and worked up as usual to give crude mixture, which was used without further purification. To a solution of crude 2a in dry THF (50 mL) was added 1M solution of TBAF (34 mL, 34 mmol) at room temperature. After stirring for overnight at the same temperature, the mixture was concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 15/1 to 10/1 to 5/1 to 2/1 to 1/1) to give the title compound (7.25 g, 96% in three steps).

$[\alpha]^{26}_D$ +152.4° (*c* 1.13, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.85 (dd, *J* = 8.0, 4.8 Hz, OH, 1H), 2.27 (s, MePh, 3H), 3.63 (ddd, *J* = 12.4, 8.0, 4.0 Hz, H-5, 1H), 3.81 (ddd, *J* = 12.4, 4.8, 2.4 Hz, H-5, 1H), 4.00 (dd, *J* = 7.2, 2.8 Hz, H-3, 1H), 4.07 (t, *J* = 2.4 Hz, H-2, 1H), 4.30 (dt, *J* = 7.2, 3.6 Hz, H-4, 1H), 4.45 (d, *J* = 11.6 Hz, Bn, 1H), 4.48 (d, *J* = 11.2 Hz, Bn, 1H), 4.54 (d, *J* = 11.2 Hz, Bn, 1H), 4.57 (d, *J* = 11.6 Hz, Bn, 1H), 5.45 (d, *J* = 2.0 Hz, H-1, 1H), 7.05-7.35 (m, Bn x2, Tol, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.16, 61.76, 72.08, 72.43, 81.71, 82.68, 88.10, 90.94, 127.69, 127.82, 127.91, 127.93, 128.38, 128.41, 129.67, 130.61, 132.10, 137.06, 137.50, 137.54. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$

calcd for $C_{26}H_{28}O_4SNa$, 459.2, found 459.1.

***p*-Tolyl 2,3-di-*O*-benzyl-5-*O*-(4-methoxybenzyl)-1-thio-α-D-arabinofuranoside (2c).**
To a solution of *p*-tolyl 2,3-*O*-dibenzyl-1-thio-α-D-arabinofuranoside (3.04 g, 6.96 mmol) dry DMF (10 mL) was added NaH (418.2 mg, 14.9 μmol) and PMBCl (1.13 mL, 37.1 mmol) at 0°C. After stirring for 2 hrs at the same temperature, the reaction was quenched by triethylamine and followed by addition of brine and was extracted with $CHCl_3$. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 10/1 to 5/1 to 2/1 to 1/1) to give the title compound (3.52 g, 91%).
$[\alpha]^{27}_D$ +114.5° (*c* 1.10, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.26 (s, MePh, 3H), 3.54 (dd, *J* = 11.2, 4.8 Hz, H-5, 1H), 3.54 (dd, *J* = 11.2, 4.0 Hz, H-5, 1H), 3.72 (s, MeO, 3H), 4.00 (dd, *J* = 6.4, 4.4 Hz, H-3, 1H), 4.04 (t, *J* = 3.2 Hz, H-2, 1H), 4.30 (dt, *J* = 6.4, 4.4 Hz, H-4, 1H), 4.39 (d, *J* = 11.6 Hz, Bn, 1H), 4.43 (d, *J* = 12.0 Hz, Bn, 1H), 4.45 (d, *J* = 11.6 Hz, Bn, 1H), 4.46 (d, *J* = 11.6 Hz, Bn, 1H), 4.49 (d, *J* = 12.0 Hz, Bn, 1H), 4.57 (d, *J* = 11.6 Hz, Bn, 1H), 5.46 (d, *J* = 2.8 Hz, H-1, 1H), 6.76-7.35 (m, Bn x2, PMB, Tol, 18H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 21.17, 55.27, 68.73, 72.08, 72.24, 72.95, 80.44, 83.50, 88.39, 90.52, 113.65, 457.68, 127.72, 127.82, 127.88, 128.29, 128.35, 129.29, 129.59, 130.13, 130.89, 131.88, 137.25, 137.32, 137.69, 159.05. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{34}H_{36}O_5SNa$, 579.2, found 579.0.

***p*-Tolyl 5-*O*-*t*-butyldiphenylsilyl-2,3-*O*-(tetraisopropylsiloxane-1,3-iyl)-1-thio-α-D-arabinofuranoside (3).**
To a solution of **8** (135.2 mg, 323 μmol) in dry pyridine (1 mL) was added 1,3-dichloro-1,1,3,3-tetraisopropyldisiloxane (117 μL, 355 μmol) at room temperature. After stirring for 2 days at the same temperature, the reaction was quenched by sat. $NaHCO_3$ aq., extracted with $CHCl_3$. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 100/1 to 50/1 to 25/1 to 10/1) to give the title compound (143.0 mg, 60%).
$[\alpha]^{26}_D$ +123.0° (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.92-1.10 (m, *t*-Bu, TIPDS, 37H), 2.34 (s, MePh, 3H), 3.79 (dd, *J* = 11.6, 2.8 Hz, H-5, 1H), 3.93 (dd, *J* = 11.6, 2.0 Hz, H-5, 1H), 3.99 (dt, *J* = 8.4, 2.4 Hz, H-4, 1H), 4.42 (t, *J* = 7.6 Hz, H-2, 1H), 4.71 (dd, *J* = 8.4, 7.2 Hz, H-3, 1H), 5.32 (d, *J* = 7.6 Hz, H-1, 1H), 7.09-7.75 (m, TBPS, Tol, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.35, 12.44, 13.16, 13.25, 17.09, 17.15, 17.28, 17.51, 17.55, 19.34, 21.26, 26.77, 62.38, 77.10, 81.55, 83.36, 89.88, 127.48, 127.53, 129.42, 129.46, 129.51, 131.23, 131.28, 133.11, 133.47, 135.49, 135.65, 136.75. MALDI-TOF MS: $[M+Na]^+$ calcd for $C_{40}H_{60}O_5Si_3SNa$, 759.3, found 759.4.

***p*-Tolyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-α-D-arabinofuranoside (4g).**
Compound **4g** was synthesized from **10**,[3] which was synthesized from **7** through TBPS deprotection followed by methanolysis and TIPDS protection (quant. in three steps), according to a procedure for compound **2a**. 82%:
$[\alpha]^{26}_D$ +79.6° (*c* 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91-1.10 (m, *t*-Bu, TIPDS, 28H), 2.32 (s, MePh, 3H), 3.95-4.02 (m, C5-H, H-4, 3H), 4.03 (dd, *J* = 6.0, 4.4 Hz, H-2, 1H), 4.71 (dd, *J* = 6.8, 6.0 Hz, H-3, 1H), 5.41 (d, *J* = 4.4 Hz, H-1, 1H), 7.08-7.42 (m, Bn, Tol, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.61, 12.89, 13.20, 13.57, 17.07, 17.13, 17.16, 17.39, 17.52, 21.14, 61.25, 72.69, 76.03, 77.22, 80.09, 89.11, 89.68, 127.61, 127.68, 128.11, 128.21, 129.53, 129.59, 131.15, 131.42, 135.48, 137.12, 137.59. MALDI-TOF MS: $[M+Na]^+$ calcd for $C_{31}H_{48}O_5Si_2SNa$, 611, found 611; HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{31}H_{48}O_5Si_2SNa$, 611.2667, found 611.2659.

***p*-Tolyl 3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-1-thio-2-*O*-triisopropylsilyl-α-D-arabinofuranoside (4h).**
To a solution of diol **10** (96.3 mg, 193 μmol) and 2,6-lutidine (143 μL, 1.23 mmol) in dry DMF (1 mL) was added triisopropylsilyl trifluoromethansulfonate (138 μL, 618 μmol) at room temperature. After stirring for 4 hrs at 90 °C followed by cooling, the reaction was quenched by sat. $NaHCO_3$ aq., extracted with $CHCl_3$. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 100/1 to 50/1 to 25/1 to 10/1) to give the title compound (123.7 mg, 79%).
$[\alpha]^{27}_D$ +84.7° (*c* 1.06, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.91-1.10 (m, *t*-Bu, TIPDS, 28H), 2.32 (s, MePh, 3H), 3.95-4.02 (m, H-5, H-4, 3H), 4.03 (dd, *J* = 6.0, 4.4 Hz, H-2, 1H), 4.71 (dd, *J* = 6.8, 6.0 Hz, H-3, 1H), 5.41 (d, *J* = 4.4 Hz, H-1, 1H), 7.08-7.42 (m, Bn, Tol, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.61, 12.89, 13.20, 13.57, 17.07, 17.13, 17.16, 17.39, 17.52, 21.14, 61.25, 72.69, 76.03, 77.22, 80.09, 89.11, 89.68, 127.61, 127.68, 128.11, 128.21, 129.53, 129.59, 131.15, 131.42, 135.48, 137.12, 137.59. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{33}H_{62}O_5Si_3SNa$, 677.4, found 677.1.

***p*-Tolyl 3,5-*O*-(di-*tert*-butylsilylene)-1-thio-α-D-arabinofuranoside (11).**
To a solution of *p*-tolyl 1-thio-α-D-arabinofuranoside **9**[4] (43.5 mg, 170 μmol), which was synthesized from **7** through TBPS deprotection using TBAF followed by methanolysis (93% in two steps), in dry DMF (2 mL) were added imidazole (28.9 mg, 425 μmol) and bis(*tert*-butyl)dichlorosilane (67.0 μL, 178 μmol) at 0°C. After stirring for

overnight at room temperature, the reaction was quenched by sat. $NaHCO_3$ aq., extracted with $CHCl_3$. The combined organic phase was washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by PTLC (hexane/ethyl acetate = 8/1) to give the title compound (30.4 mg, 45%) as a white solid.
mp 137~139°C. $[\alpha]^{26}_D$ +197.9° (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94 (s, *t*-Bu, 9H), 1.05 (s, *t*-Bu, 9H), 2.31 (s, MePh, 3H), 2.87 (br s, OH, 1H), 3.83-3.95 (m, H-5, H-4, 2H), 3.98 (dd, *J* = 8.8, 7.6 Hz, H-3, 1H), 4.11 (t, *J* = 6.8 Hz, H-2, 1H), 4.31 (dd, *J* = 8.4, 4.0 Hz, H-5, 1H), 5.22 (d, *J* = 5.6 Hz, H-1, 1H), 7.10 (d, *J* = 8.0 Hz, Tol, 2H), 7.39 (d, *J* = 8.0 Hz, Tol, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.15, 21.17, 22.69, 27.12, 27.47, 67.33, 73.72, 80.73, 81.08, 91.38, 129.68, 130.14, 132.18, 137.84. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{20}H_{32}O_4SiSNa$, 419.2, found 419.2.

***p*-Tolyl 3,5-*O*-(di-*tert*-butylsilylene)-1-thio-2-*O*-triisopropylsilyl-α-D-arabinofuranoside** (**5**).
Compound **5** was synthesized from **11** according to a procedure for compound **4h**. 53%:
$[\alpha]^{25}_D$ +134.7° (*c* 0.38, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.94 (s, *t*-Bu, 9H), 1.02 (s, *t*-Bu, 9H), 1.02-1.21 (m, TIPS, 21H), 2.31 (s, MePh, 3H), 3.85-3.98 (m, H-3, H-4, H-5, 3H), 4.19 (dd, *J* = 6.4, 5.2 Hz, H-2, 1H), 4.30 (dd, *J* = 7.6, 3.6 Hz, H-5, 1H), 5.17 (d, *J* = 5.2 Hz, H-1, 1H), 7.09 (d, *J* = 8.0 Hz, Tol, 2H), 7.37 (d, *J* = 8.0 Hz, Tol, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.28, 17.99, 18.05, 20.13, 21.15, 22.71, 27.14, 27.33, 67.37, 73.31, 81.96, 82.13, 93.12, 29.60, 131.04, 131.83, 137.45. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{29}H_{52}O_4Si_2SNa$, 575.3, found 575. 5.

***p*-Tolyl 5-*O*-*t*-butyldiphenylsilyl-2,3-di-*O*-triisopropylsilyl-1-thio-α-D-arabinofuranoside (6).**
Compound **6** was synthesized from **8** according to a procedure for compound **4h**, except using two equivalent of TIPSOTf. 75%:
$[\alpha]^{27}_D$ +68.0° (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.90-1.24 (m, *t*-Bu, TIPS x2, 51H), 2.30 (s, MePh, 3H), 3.74 (dd, *J* = 10.0, 6.0 Hz, H-5, 1H), 3.80 (dd, *J* = 10.0, 8.0 Hz, H-5, 1H), 4.36 (s, H-2, 1H), 4.48 (s, H-3, 1H), 4.30 (dd, *J* = 8.0, 6.0 Hz, H-4, 1H), 5.33 (s, H-1, 1H), 7.06-7.66 (m, TBPS, Tol, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.25, 12.51, 18.03, 18.07, 18.28, 19.22, 21.12, 26.91, 64.39, 79.45, 85.13, 88.76, 96.00, 127.48, 127.50, 129.45, 129.49, 131.30, 133.42, 133.44, 135.48, 135.54, 136.45. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{46}H_{74}O_4Si_3SNa$, 829.5, found 829.3.

For the synthesis of 13

Benzyl 2-*O*-acetyl-3,5-di-*O*-benzyl-α-D-arabinofuranoide.
To the solution of 1,2-di-*O*-acetyl-3,5-di-*O*-benzyl-D-arabinofuranose[3] (547.5 mg, 1.32 mmol), BnOH (273 μL, 2.64 mmol) and MS 4A (0.5 g) in $(CH_2Cl)_2$ (5.0 mL) were added $BF_3{\cdot}OEt_2$ (25 μL, 197 μmol) at 0°C. After stirring for 2 hrs, $BF_3{\cdot}OEt_2$ (350 μL, 2.76 mmol) was added to the mixture and further more $BF_3{\cdot}OEt_2$ (400 μL, 3.16 mmol) was added after another 2 hrs. The mixture was stirred for total 6 hrs at the same temperature. Then the reaction was quenched by triethylamine and followed by filtration through Celite pad and washing of pad with $CHCl_3$. The combined solutions were washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 10/1 to 5/1) to give the title compound (566.2 mg, 92%).
$[\alpha]^{27}_D$ +87.4° (*c* 1.00, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.88 (s, Ac, 3H), 3.58 (dd, *J* = 10.8, 5.2 Hz, H-5, 1H), 3.64 (dd, *J* = 10.8, 4.0 Hz, H-5, 1H), 3.90 (br d, *J* = 4.2 Hz, H-3, 1H), 4.34 (td, *J* = 5.2, 4.0 Hz, H-4, 1H), 4.50 (d, *J* = 12.4 Hz, Bn, 1H), 4.56 (d, *J* = 12.0 Hz, Bn, 1H), 4.57 (d, *J* = 12.0 Hz, Bn, 1H), 4.58 (d, *J* = 12.4 Hz, Bn, 1H), 4.75 (d, *J* = 12.4 Hz, Bn, 1H), 4.81 (d, *J* = 12.4 Hz, Bn, 1H), 5.11 (s, H-1, 1H), 5.21 (d, *J* = 1.6 Hz, H-2, 1H), 7.25-7.38 (m, Bn x3, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 20.71, 68.26, 69.14, 71.92, 73.19, 81.39, 81.97, 83.14, 104.64, 127.36, 127.39, 127.45, 127.47, 127.59, 127.63, 127.96, 128.07, 128.76, 137.17, 137.49, 137.74, 169.50. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{28}H_{30}O_6Na$, 485.2, found 485.0.

Benzyl 3,5-di-*O*-benzyl-α-D-arabinofuranoside (13).
To a solution of from benzyl 2-*O*-acetyl-3,5-di-*O*-benzyl-α-D-arabinofuranoide (521.3 g, 1.12 mmol) in MeOH (5 mL) was added a catalytic amount of NaOMe at room temperature. After stirring for 1 h at the same temperature, the reaction was quenched by Amberlyst H^+ resin, filtered, concentrated in vacuo and purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 10/1 to 5/1, 2/1, 1/1) to give the title compound **13** (399.7 mg, 85%).
$[\alpha]^{29}_D$ +116.9° (*c* 1.04, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.51-3.57 (m, H-5, OH, 2H), 3.21 (dd, *J* = 10.4, 2.4 Hz, H-5, 1H), 3.94 (d, *J* = 2.4 Hz, H-3, 1H), 4.27 (br d, *J* = 10,0 Hz, H-2, 1H), 4.37 (quintet, *J* = 2.4 Hz, H-4, 1H), 4.52 (d, *J* = 12.0 Hz, Bn, 1H), 4.55 (d, *J* = 12.4 Hz, Bn, 1H), 4.58 (d, *J* = 12.4 Hz, Bn, 1H), 4.64 (d, *J* = 12.0 Hz, Bn, 1H), 4.73 (d, *J* = 12.0 Hz, Bn, 1H), 4.86 (d, *J* = 12.0 Hz, Bn, 1H), 5.14 (s, H-1, 1H), 7.29-7.42 (m, Bn x3, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 68.50, 69.58, 71.80, 73.54, 83.24, 85.13, 107.72, 127.26, 127.54, 127.58, 127.65, 127.83, 128.07, 128.16, 128.34, 136.83, 137.59, 137.69. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{26}H_{28}O_5Na$, 443.2, found 443.8.

General procedure of glycosylation

To the mixture of acceptor **13** (22.6 mg, 14.9 μmol) and donor **4g** (21.9 mg, 37.1 μmol) in dry CH_2Cl_2 (2 mL) was added MS3A (250 mg, freshly dried) at room temperaure. After cooling to –40 °C, NIS (13.2 mg, 55.8 μmol) and AgOTf (1.5 mg, 5.84 μmol) were added to the mixture. After stirring for 3 hrs at the same temperature, the reaction was quenched by triethylamine and followed by filtration through Celite pad and washing of pad with $CHCl_3$. The combined solutions were washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by gel filtration (Bio beads SX-3, toluene/ethyl acetate = 1/1) to give the mixture of the isomers **15g**.

Benzyl 2,3-*O*-dibenzyl-5-*O*-4-methoxybenzyl-β-D-arabinofuranosyl-(1→2)-3,5-dibenzyl-α-D-arabinofuranoside (15c). 13+**2c** = **15c** (94%, 1 : 4.25).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15cβ)**: δ 3.47-3.63 (m, H_2-5^{Araf1}, H_2-5^{Araf2}, 4H), 3.73 (s, OMe, 3H), 3.95-4.03 (m, H-3^{Araf1}, H-2^{Araf2}, 2H), 4.02-4.09 (m, H-3^{Araf2}, H-4^{Araf2}, 2H), 4.24-4.29 (m, H-4^{Araf1}, Bn/PMB, 2H), 4.33 (d, *J* = 12.0 Hz, Bn/PMB, 1H), 4.35 (dd, *J* = 3.2, 1.2 Hz, H-2^{Araf1}, 1H), 4.38-4.52 (m, Bn/PMB x3, 6H), 4.55 (d, *J* = 12.4 Hz, Bn/PMB, 1H), 4.63 (d, *J* = 12.0 Hz, Bn/PMB, 1H), 4.64 (d, *J* = 12.0 Hz, Bn/PMB, 1H), 4.78 (d, *J* = 12.4 Hz, Bn/PMB, 1H), 4.97 (d, *J* = 4.4 Hz, H-1^{Araf2}, 1H), 5.05 (br s, H-1^{Araf1}, 1H), 7.19-7.36 (m, Bn x6, 30H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.22, 68.71, 70.10, 71.84, 72.17, 72.32, 72.36, 72.74, 73.30, 80.04, 81.36, 82.92, 83.82, 84.12, 86.03, 100.20 ($J_{C\text{-}H}$ = 170.8 Hz), 104.87 ($J_{C\text{-}H}$ = 170.7 Hz), 113.75, 127.47, 127.50, 127.54, 127.61, 127.66, 127.78, 127.88, 128.25, 128.27, 128.35, 128.53, 129.10, 129.21, 129.27, 130.03, 137.48, 138.02, 138.07, 159.01. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{53}H_{56}O_{10}Na$, 875.4, found 875.8.

Benzyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-α-D-arabinofuranoside (15f). 13+**3** = **15f** (96%, 1 : 2.45).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15fβ)**: δ 0.91-1.02 (m, TIPDS, TBPS, 37H), 3.47-3.55 (m, H_2-5^{Araf1}, 2H), 3.70-3.78 (m, H_2-5^{Araf2}, 2H), 3.80-3.89 (m, H-3^{Araf1}, H-4^{Araf2}, 2H), 4.10-4.25 (m, H-4^{Araf1}, H-^{2}Ara^{f2}, H-3Araf2, $^{3H)}$, 4.28-4.57 (m, H-2Araf1, Bn, 6H), 4.74 (d, J $^{=1}$2.4 Hz, Bn, 1H), 4.9^{1} (d, $_{J}$ = 4.0 Hz, H-1Araf2, 1H), 5.08 (br s, H-1Araf1, 1H), 7.12-7.62 (m, Bn x3, TBPS, 25H); 13C NMR (CDCl3, 100 MHz): δ 12.44, 12.54, 12.70, 13.00, 13.20, 17.01, 17.08, 17012, 17.18, 17.27, 17.30, 17.48, 17.52, 19.30, 26.90, 66.63, 68.73, 70.28, 72.09, 73.23, 77.41, 79.60, 81.31, 82.75, 84.39, 86.96, 101.52 ($J_{C\text{-}H}$ = 173.3 Hz), 105.81 ($J_{C\text{-}H}$ = 170.0 Hz), 127.39, 127.43, 127.48, 127.55, 127.58, 127.59, 127.64, 127.71, 128.10, 128.19, 128.21, 128.24, 129.51, 129.55, 133.35, 133.39, 135.46, 135.62, 137.85, 137.89, 138.11. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{59}H_{80}O_{10}Si_3Na$, 1055.5, found 1055.8.

Benzyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-α-D-arabinofuranoside (15g). 13+**4g** = **15g** (94%, 1 : 12.5).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15gβ)**: δ 0.91-1.02 (m, TIPDS, TIPS, 49H), 3.54-3.62 (m, H_2-5^{Araf1}, 2H), 3.75-3.81 (m, H-4^{Araf2}, H-5^{Araf2}, 2H), 3.85-3.89 (m, H-2^{Araf2}, H-5^{Araf2}, 2H), 3.94 (dd, *J* = 6.4, 3.2 Hz, H-3^{Araf1}, 1H), 4.22-4.30 (m, H-2^{Araf1}, H-4^{Araf1}, 2H), 4.42-4.50 (m, H-3^{Araf2}, Bn, 6H), 4.77 (d, *J* = 12.4 Hz, Bn, 1H), 4.81 (d, *J* = 4.4 Hz, H-1^{Araf2}, 1H), 5.01 (br s, H-1^{Araf1}, 1H), 7.18-7.28 (m, Bn x3, 15H); DIF NOE ($CDCl_3$, 400 MHz): irr. δ 4.81 (H-1^{Araf2}), enhanced 3.86 (7.0%, H-2^{Araf2}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.57, 12.86, 13.32, 13.52, 17.09, 17.13, 17.18, 17.43, 17.48, 17.52, 17.59, 66.24, 68.75, 70.04, 72.22, 72.50, 73.31,77.21, 81.16, 81.73, 84.05, 84.19, 86.18, 99.13 ($J_{C\text{-}H}$ = 168.3 Hz), 105.05 ($J_{C\text{-}H}$ = 174.1 Hz), 127.52, 127.56, 127.66, 127.73, 127.77, 127.83, 128.26, 128.29, 137.68, 137.70, 137.86, 138.03. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{50}H_{68}O_{10}Si_2Na$, 907.4, found 907.2.

Benzyl 3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-2-*O*-triisopropylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-α-D-arabinofuranoside (15h). 13+**4h** = **15h** (93%, 1 : 20.0).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15hβ)**: δ 0.91-1.02 (m, TIPDS, TIPS, 49H), 3.46-3.54 (m, H_2-5^{Araf1}, 2H), 3.73 (br d, *J* = 9.6 Hz, H-5^{Araf2}, 1H), 3.75-3.80 (m, H-4^{Araf2}, 1H), 3.82 (br d, *J* = 9.6 Hz, H-5^{Araf2}, 1H), 3.87 (dd, *J* = 6.0, 2.4 Hz, H-3^{Araf1}, 1H), 4.13 (dd, *J* = 7.2, 4.8 Hz, H-2^{Araf2}, 1H), 4.19-4.24 (m, H-2^{Araf1}, H-4^{Araf1}, 2H), 4.30 (dd, *J* = 7.2, 5.6 Hz, H-3^{Araf2}, 1H), 4.42-4.50 (m, Bn x2, 4H), 4.61 (d, *J* = 11.6 Hz, Bn, 1H), 4.70 (d, *J* = 12.0 Hz, Bn, 1H), 4.70 (d, *J* = 4.4 Hz, H-1^{Araf2}, 1H), 4.99 (br s, H-1^{Araf1}, 1H), 7.18-7.28 (m, Bn x3, 15H); DIF NOE ($CDCl_3$, 400 MHz): irr. δ 4.70 (H-1^{Araf2}), enhanced 4.13 (6.2 %, H-2^{Araf2}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.44, 12.76, 13.03, 13.49, 17.01, 17.16, 17.31, 17.41, 17.51, 17.64, 17.99, 18.03, 66.55, 68.54, 70.22, 72.09, 73.27, 79.06, 79.33, 81.61, 81.98, 84.24, 86.08, 100.68 ($J_{C\text{-}H}$ = 169.9 Hz), 104.59 ($J_{C\text{-}H}$ = 169.1 Hz), 127.49, 127.53, 127.60, 127.66, 127.88, 128.20, 128.25, 137.57, 137.88, 138.07. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{52}H_{82}O_{10}Si_3Na$, 973.5, found 973.0.

Benzyl 3,5-*O*-(di-*tert*-butylsilylene)-2-*O*-triisopropylsilyl-β-D-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-α-D-arabinofuranoside (15i). 13+**5** = **15i** (70%, 1 : 5.36).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15iβ)**: δ 0.87-1.06 (m, TIPS, DTBS, 39H), 3.49 (dd, *J* = 10.8, 6.0 Hz, H-

5^{Araf1}, 1H), 3.52 (dd, *J* = 10.8, 4.0 Hz, H-5^{Araf1}, 1H), 3.56-3.61 (m, H-4^{Araf2}, 1H), 3.70 (dd, *J* = 10.8, 8.8 Hz, H-5^{Araf2}, 1H), 3.91 (dd, *J* = 6.4, 3.2 Hz, H-3^{Araf1}, 1H), 4.05-4.12 (m, H-2^{Araf2}, H-3^{Araf2}, 2H), 4.13-4.22 (m, H-4^{Araf1}, H-5^{Araf2}, 2H), 4.25 (dd, *J* = 3.2, 1.2 Hz, H-2^{Araf1}, 1H), 4.41-4.50 (m, Bn, 4H), 4.62 (d, *J* = 12.0 Hz, Bn, 1H), 4.62 (d, *J* = 12.0 Hz, Bn, 1H), 4.87 (d, *J* = 4.4 Hz, H-1^{Araf2}, 1H), 5.01 (br s, H-1^{Araf1}, 1H), 7.18-7.27 (m, Bn x3, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.11, 17.79, 17.87, 20.12, 22.68, 27.17, 27.47, 68.65, 68.76, 70.02, 71.79, 73.30, 73.68, 76.02, 78.92, 81.11, 83.33, 86.88, 100.91(J_{C-H} = 171.6 Hz), 105.34 (J_{C-H} = 174.1 Hz), 127.42, 127.47, 127.55, 127.60, 127.67, 127.75, 127.83, 128.18, 128.23, 137.63, 137.84, 138.07. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{48}H_{72}O_9Si_2Na$, 871.46, found 871.93.

Benzyl 5-*O*-*tert*-butyldiphenylsilyl-2,3-*O*-di(tri-*iso*-propylsilyl)-β-D-arabinofuranosyl-(1→2)-3,5-*O*-dibenzyl-α-D-arabinofuranoside (15j). 13+6 = 15j (99%, 5.26 : 1).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (15jα)**: δ 0.97-1.09 (m, TIPS x2, TBPS, 51H), 3.52-3.61 (m, H_2-5^{Araf2}, 2H), 3.68 (dd, *J* = 10.4, 6.0 Hz, H-5^{Araf1}, 1H), 3.71 (dd, *J* = 10.4, 6.4 Hz, H-5^{Araf1}, 1H), 3.77 (dd, *J* = 6.4, 2.4 Hz, H-3^{Araf2}, 1H), 4.14 (td, *J* = 6.4, 2.0 Hz, H-4^{Araf1}, 1H), 4.16 (br s, H-2^{Araf2}, 1H), 4.22 (br s, H-3^{Araf1}, 1H), 4.25 (d, *J* = 1.6 Hz, H-2^{Araf2}, 1H), 4.26-4.29 (m, H-4^{Araf2}, 1H), 4.44-4.59 (m, Bn, 4H), 4.64 (d, *J* = 12.0 Hz, Bn, 1H), 4.76 (d, *J* = 12.4 Hz, Bn, 1H), 5.01 (br s, H-1^{Araf2}, 1H), 5.20 (br s, H-1^{Araf1}, 1H), 7.18-7.67 (m, Bn x3, TBPS, 25H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.31, 12.44, 18.03, 18.07, 18.18, 18.20, 19.25, 26.61, 64.81, 68.89, 70.32, 71.34, 73.26, 79.42, 80.64, 83.81, 83.95, 85.98, 88.89, 106.39 (J_{C-H} = 174.9 Hz), 108.66 (J_{C-H} = 173.3 Hz), 127.28, 127.40, 127.44, 127.50, 127.53, 127.62, 127.73, 127.83, 128.01, 128.10, 128.21, 129.48, 133.41, 133.47, 135.37, 135.49, 135.54, 135.73, 137.85, 137.93, 138.17. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{65}H_{94}O_9Si_3Na$, 1125.6, found 1126.4.

***p*-Methoxyphenyl 3,4,6-tri-*O*-benzyl-α-D-mannopyranoside (22).**

Compound **22** was synthesized from 1,2-di-*O*-acetyl-3,4,6-tri-*O*-benzyl-D-mannose[4] according to a two step procedure for compound **13** except using p-methoxyphenol as an acceptor instead of BnOH. 48% in two steps:

$[\alpha]^{26}_D$ +102.3° (*c* 1.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.58 (br s, OH, 1H), 3.62 (br d, *J* = 11.2 Hz, H-6, 1H), 3.70 (s, OMe, 3H), 3.71 (dd, *J* = 11.2, 4.0 Hz, H-6, 1H), 3.85-3.95 (m, H-4, H-5, 2H), 4.03 (dd, *J* = 8.4, 3.2 Hz, H-3, 1H), 4.17 (br d, *J* = 3.2 Hz, H-2, 1H), 4.41 (d, *J* = 12.0 Hz, Bn, 1H), 4.49 (d, *J* = 10.8 Hz, Bn, 1H), 4.57 (d, *J* = 12.0 Hz, Bn, 1H), 4.69 (d, *J* = 12.0 Hz, Bn, 1H), 4.73 (d, *J* = 12.0 Hz, Bn, 1H), 4.80 (d, *J* = 10.8 Hz, Bn, 1H), 5.14 (br s, H-1, 1H), 6.73-7.36 (m, MP, Bn x3, 19H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 55.60, 68.32, 68.74, 71.55, 72.13, 73.33, 74.11, 75.15, 79.97, 98.12 (J_{C1-H1} = 170.8 Hz), 114.49, 117.72, 127.43, 127.60, 127.75, 127.77, 127.80, 127.90, 128.17, 128.26, 128.48, 137.76, 138.08, 138.15, 149.96, 154.83. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{34}H_{36}O_7Na$, 579.2, found 578.5.

For Table 3

Methyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside. 20+4g (97%, 1 : 1.15).

^{1}H NMR ($CDCl_3$, 400 MHz) **(αβ)**: δ 0.91-1.08 (m, TIPDS, 28H), 3.34 (s, MeO, 3H), 3.36 (s, MeO, 3H), 3.56 (dd, *J* = 11.2, 6.4 Hz, H-5^{Araf3}, 1H), 3.61 (dd, *J* = 11.2, 4.0 Hz, H-5^{Araf4}, 1H), 3.72 (dd, *J* = 11.2, 3.2 Hz, H-5^{Araf3}, 1H), 3.80 (dd, *J* = 6.4, 3.6 Hz, H-3^{Araf3}, 1H), 3.80-3.87 (m, H-4^{Araf2}, H_2-5^{Araf1}, H-5^{Araf3}, H-5^{Araf2}, 5H), 3.89-4.01 (m, H-2^{Araf1}, H-2^{Araf2}, H-2^{Araf3}, H-2^{Araf4}, H-3^{Araf1}, H-3^{Araf4}, H-5^{Araf2}, 7H), 4.15 (dd, *J* = 6.8, 4.8 Hz, H-4^{Araf4}, 1H), 4.20-4.26 (m, H-4^{Araf1}, H-4^{Araf3}, 2H), 4.44-4.67 (m, H-3^{Araf2}, Bn x3, 7H), 4.90 (br s, H-1^{Araf3}, H-1^{Araf4}, 2H), 4.92 (d, *J* = 4.0 Hz, H-1^{Araf2}, 1H), 4.98 (d, *J* = 2.0 Hz, H-1^{Araf1}, 1H), 7.22-7.35 (m, Bn x3, 15H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.57, 12.64, 12.89, 12.93, 13.22, 13.41, 13.52, 13.58, 17.10, 17.16, 17.41, 17.50, 17.55, 17.66, 54.93, 61.54, 66.78, 66.96, 67.63, 71.91, 72.00, 72.17, 72.24, 72.36, 76.18, 78.28, 80.42, 80.54, 81.22, 82.19, 83.41, 83.87, 84.73, 88.01, 88.32, 89.38, 99.69 (J_{C-H} = 170.8 Hz), 105.94 (J_{C-H} = 172.4 Hz), 107.20 (J_{C-H} = 171.6 Hz), 107.29 (J_{C-H} = 172.4 Hz), 127.43, 127.50, 127.62, 127.68, 127.74, 127.76, 127.81, 128.16, 128.27, 128.30, 128.35, 137.79. MALDI-TOF MS (*m*/*z*): [M + Na]$^+$ calcd for $C_{44}H_{64}O_{10}Si_2Na$, 831.4, found 831.8.

***p*-Methoxyphenyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside. 21+4g** (100%, 1 : 7.35).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (β)**: δ 0.91-2.30 (m, TIPDS, cHex, 38H), 3.30-3.38 (m, H-5^{Glc}, 1H), 3.69-3.72 (m, H-2^{Glc}, 1H), 3.78 (s, OMe, 3H), 3.75-4.10 (m, H-2^{Araf}, H-4^{Araf}, H_2-5^{Araf}, H-3^{Glc}, H-4^{Glc}, H_2-6^{Glc}, 8H), 4.57 (d, *J* = 12.4 Hz, Bn, 1H), 4.60 (dd, *J* = 7.6, 5.6 Hz, H-3^{Araf}, 1H), 4.70 (d, *J* = 12.4 Hz, Bn, 1H), 4.84 (d, *J* = 11.2 Hz, Bn, 1H), 4.20 (d, *J* = 7.6 Hz, H-1^{Glc}, 1H), 5.02 (d, *J* = 11.2 Hz, Bn, 1H), 5.41 (d, *J* = 4.4 Hz, H-1^{Araf}, 1H), 6.81-7.35 (m, MP, Bn x2, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.75, 13.08, 13.41, 13.55, 17.13, 17.14, 17.28, 17.35, 17.41, 17.44, 17.61, 17.66, 17.85, 22.42, 22.73, 25.61, 27.87, 39.93, 55.65, 61.43, 67.55, 71.04, 72.13, 74.66, 77.20, 78.53, 78.91, 82.52, 82.68, 84.39, 99.78, 100.11 (J_{C-H} = 178.2 Hz), 102.92 (J_{C-H} = 166.6 Hz), 114.51, 118.31, 127.20, 127.35, 127.45, 127.79,

128.13, 128.25, 137.74, 138.25, 150.98, 155.33. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{50}H_{72}O_{12}Si_2Na$, 943.4, found 943.5.

***p*-Methoxyphenyl 3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-2-*O*-triisopropylsilyl-β-D-arabinofuranosyl-(1→3)-2-*O*-benzyl-4,6-*O*-cyclohexylidene-α-D-glucopyranoside. 21+4h** (61%, 1.80 : 1).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (α)**: δ 0.87-2.15 (m, TIPDS, TIPS, cHex, 59H), 3.27 (td, *J* = 10.0, 5.6 Hz, H-5^{Glc}, 1H), 3.52 (dd, *J* = 9.2, 8.0 Hz, H-2^{Glc}, 1H), 3.68-3.83 (m, H_2-5^{Araf}, H_2-6^{Glc}, 4H), 3.86-4.10 (m, H-4^{Araf}, H-3^{Glc}, H-4^{Glc}, 3H), 4.15 (dd, *J* = 8.0, 4.8 Hz, H-3^{Araf}, 1H), 4.29 (dd, *J* = 4.8, 1.6 Hz, H-2^{Araf}, 1H), 4.75 (d, *J* = 11.2 Hz, Bn, 1H), 4.81 (d, *J* = 11.2 Hz, Bn, 1H), 4.92 (d, *J* = 11.2 Hz, Bn, 1H), 4.94 (d, *J* = 8.0 Hz, H-1^{Glc}, 1H), 5.02 (d, *J* = 11.2 Hz, Bn, 1H), 5.22 (d, *J* = 1.6 Hz, H-1^{Araf}, 1H), 6.81-7.35 (m, MP, Bn x2, 14H); ^{13}C NMR ($CDCl_3$, 100 MHz) (αβ): δ 12.42, 12.51, 12.59, 12.67, 12.71, 12.90, 13.16, 13.22, 13.35, 13.55, 13.59, 13.61, 13.78, 17.00, 17.12, 17.17, 17.21, 17.26, 17.29, 17.37, 17.41, 17.53, 17.58, 17.61, 17.69, 18.11, 18.15, 18.17, 18.40, 19.38, 22.30, 22.71, 22.86, 22.94, 25.77, 27.54, 27.71, 37.83, 37.97, 55.66 (x2), 61.18, 61.66, 61.73, 66.68, 67.08, 67.32, 71.14, 73.21, 74.03, 74.72, 74.89, 75.14, 79.69, 80.23, 80.63, 82.35, 82.82, 84.98, 98.56 (J_{C-H} = 169.9 Hz), 99.36, 99.79, 102.67 (J_{C-H} = 165.0 Hz), 103.24 (J_{C-H} = 163.4 Hz), 106.62 (J_{C-H} = 175.7 Hz), 114.50, 118.36, 127.21, 127.34, 127.43, 127.97, 128.12, 128.20, 138.14, 150.86, 151.06, 155.30, 155.34. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{52}H_{86}O_{12}Si_3Na$, 1009.6, found 1010.4.

***p*-Methoxyphenyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. 22+4g** (77%, 1 : 2.66).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (β)**: δ 0.91-1.24 (m, TIPDS, TIPS, 49H), 3.66 (br d, *J* = 11.6 Hz, H-6^{Man}, 1H), 3.74 (s, OMe, 3H), 3.71 (dd, *J* = 11.2, 6.4 Hz, H-6^{Man}, 1H), 3.80-3.90 (m, H_2-5^{Araf}, H-4^{Man}, H-5^{Man}, 3H), 3.90-4.08 (m, H-3^{Araf}, H-4^{Araf}, H-2^{Man}, 3H), 4.12-4.19 (m, H-2^{Araf}, H-3^{Man}, 2H), 4.30-4.85 (m, Bn x4, 8H), 5.20 (d, *J* = 3.2 Hz, H-1^{Man}, 1H), 5.39 (d, *J* = 2.0 Hz, H-1^{Araf}, 1H), 6.69-7.28 (m, MP, Bn x4, 24H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.55, 12.92, 13.17, 13.54, 17.06, 17.17, 17.40, 17.51, 55.63, 60.79, 69.04, 71.59, 72.22, 72.79, 72.82, 73.27, 74.21, 74.35, 75.04, 75.17, 77.21, 79.76, 79.83, 88.27, 99.06 (J_{C-H} = 174.0 Hz), 107.43 (J_{C-H} = 170.8 Hz), 114.45, 117.98, 127.33, 127.61, 127.64, 127.74, 127.81, 127.88, 128.04, 128.16, 128.20, 128.28, 128.38, 137.85, 137.93, 138.20, 138.29, 150.24, 154.82. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{58}H_{76}O_{12}Si_2Na$, 1043.5, found 1043.8.

***p*-Methoxyphenyl 3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-2-*O*-triisopropylsilyl-β-D-arabinofuranosyl-(1→2)-3,4,6-tri-*O*-benzyl-α-D-mannopyranoside. 22+4h** (47%, 1 : 2.80).

^{1}H NMR ($CDCl_3$, 400 MHz) **major isomer (β)**: δ 0.91-1.24 (m, TIPDS, TIPS, 49H), 3.66 (br d, *J* = 11.2 Hz, H-6^{Man}, 1H), 3.74 (s, OMe, 3H), 3.71 (dd, *J* = 11.2, 4.4 Hz, H-6^{Man}, 1H), 3.84-3.94 (m, H-5^{Araf}, H-4^{Man}, H-5^{Man}, 3H), 3.96-4.08 (m, H-3^{Araf}, H-4^{Araf}, H-5^{Araf}, 3H), 4.20 (dd, *J* = 7.2, 4.8 Hz, H-3^{Man}, 1H), 4.29 (t, *J* = 2.4 Hz, H-2^{Araf}, 1H), 4.41 (dd, *J* = 4.8, 1.2 Hz, H-2^{Man}, 1H), 4.43-4.88 (m, Bn x3, 6H), 5.23 (br s, H-1^{Man}, 1H), 5.37 (d, *J* = 1.6 Hz, H-1^{Araf}, 1H), 6.74-7.35 (m, MP, Bn x3, 19H); DIF NOE ($CDCl_3$, 400 MHz): irr. δ 5.37 (H-1^{Araf}), enhanced 4.29 (5.5%, H-2^{Araf}); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.59, 12.98, 13.07, 13.39, 13.83, 17.23, 17.35, 17.45, 17.49, 17.61, 18.14, 18.21, 18.23, 18.26, 55.67, 62.38, 69.00, 71.63, 72.43, 72.50, 73.32, 74.86, 75.18, 77.20, 79.73, 80.08, 81.71, 84.27, 99.02 (J_{C-H} = 171.6 Hz), 107.98 (J_{C-H} = 174.8 Hz), 114.38, 117.69, 127.23, 127.41, 127.46, 127.49, 127.51, 127.55, 127.61, 127.68, 127.74, 127.83, 128.11, 128.18, 138.11, 138.30, 138.33, 150.12, 154.59. MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{60}H_{90}O_{12}Si_3Na$, 1109.6, found 1110.5.

For Scheme 3

Methyl 2-*O*-benzoyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (25a).

To the mixture of disaccharide acceptor **23** (239.4 mg, 397 μmol) and donor **24** (236.1 mg, 361 μmol) in dry CH_2Cl_2 (4 mL) was added MS3A (500 mg, freshly dried) at room temperaure. After cooling to –40 °C, NIS (141.1 mg, 596 μmol) and AgOTf (18.5 mg, 72.0 μmol) were added to the mixture. After stirring for 1 hrs at the same temperature, and for 18 hrs at –20 °C, the reaction was quenched by triethylamine and followed by filtration through celite pad and washing of pad with $CHCl_3$. The combined solutions were washed with 20% aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 15/1 to 10/1 to 5/1 to 2/1) to give the title trisaccharide **25a** (349.4 mg, 85%).

$[\alpha]^{27}_D$ +43.2° (*c* 1.20, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.85-1.20 (m, TIPDS, 28H), 3.36 (s, MeO, 3H), 3.63 (dd, *J* = 10.8, 4.8 Hz, H-5$^{Araf1\text{ or }Araf2}$, 1H), 3.68 (dd, *J* = 12.0, 3.6 Hz, H-5$^{Araf1\text{ or }Araf2}$, 1H), 3.85-3.90 (m, H-5^{Araf1}, H-5^{Araf2}, 2H), 3.92-4.25 (m, H-2^{Araf1}, H-3^{Araf1}, H-4^{Araf1}, H-2^{Araf2}, H-3^{Araf2}, H-4^{Araf2}, H-4^{Araf3}, H-5^{Araf3}, 9H), 4.41-4.60 (m. H-4^{Araf3}, Bn x4, 9H), 4.91 (br s, H-1$^{Araf1\text{ or }Araf2}$, 1H), 5.08 (br s, H-1^{Araf3}, 1H), 5.13 (br s, H-1$^{Araf1\text{ or }Araf2}$, 1H), 3.68 (br d, *J* = 4.0 Hz, H-2^{Araf3}, 1H), 7.21-8.02 (m, Bn x4, Bz, 25H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.18, 12.81, 13.16, 13.43, 16.87, 16.92, 16.99, 17.32, 17.45, 54.80, 61.55, 65.98, 67.23, 71.68, 71.80, 72.06, 72.25, 76.04, 80.52, 81.00, 83.08, 83.60, 84.07,

87.90, 88.30, 105.44, 106.26, 107.08, 127.50, 127.59, 127.65, 127.69, 128.13, 128.17, 128.20, 129.45, 129.50, 132.99, 137.42, 137.53, 137.80, 137.91, 165.12. HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{63}H_{82}O_{15}Si_2Na$, 1157.5090, found 1157.5143.

Methyl 2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (25b).

The trisaccharide **25a** (155.4 mg, 137 μmol) was dissolved in dry THF, and to the mixture was added 1 M solution of tetrabutylammonium fluoride (411 μL, 411 mmol) at room temperature. The mixture was stirred for 12 hrs at room temperature, then quenched with sat. $KHSO_4$ aq. After concentration, the residue was eluted with $CHCl_3$, and water. After extraction, combined organic phase were washed with brine and dried over Na_2SO_4. After concentration, the residuewas purified by flash column chromatography using gradient solvent system (hexane/ethyl acetate = 20/1 to 15/1 to 10/1 to 5/1 to 2/1) to give the title compound **25b** (115.9 mg, 95%).

$[\alpha]^{27}_D$ +92.9° (*c* 0.51, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.35 (s, MeO, 3H), 3.66-3.73 (m, H-5^{Araf1}, H-5^{Araf2}, H-5^{Araf3}, 3H), 3.79-3.87 (m, H-5^{Araf1}, H-5^{Araf2}, H-5^{Araf3}, 3H), 3.91 (dd, *J* = 6.4, 2.8 Hz, H-3^{Araf2}, 1H), 3.98 (br d, *J* = 2.4 Hz, H-2^{Araf1}, 1H), 4.00-4.07 (m, H-3^{Araf1}, H-2^{Araf2}, H-4^{Araf3}, 3H), 4.10-4.20 (m, H-4^{Araf1}, H-4^{Araf2}, H-3^{Araf3}, 9H), 4.40-4.56 (m. Bn x4, 8H), 4.90 (br s, H-1 ^{Araf1}, 1H), 5.10 (br d, *J* = 2.0 Hz, H-2 ^{Araf3}, 1H), 5.14 (br s, H-1^{Araf2}, 1H), 5.25 (br s, H-1^{Araf3}, 1H), 7.24-7.98 (m, Bn x4, Bz, 25H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 54.86, 61.98, 66.02, 66.22, 71.87, 71.89, 71.98, 72.25, 76.25, 76.69, 80.45, 83.17, 83.41, 84.72, 85.18, 87.40, 88.27, 105.02, 106.27, 107.09, 127.57, 127.61, 127.64, 127.66, 127.69, 127.73, 127.74, 127.89, 128.22, 128.24, 128.25, 128.29, 128.36, 128.97, 129.62, 133.39, 137.25, 137.39, 137.58, 137.77, 166.15. HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{51}H_{56}O_{14}Na$, 915.3568, found 915.3547.

Methyl 3,5-di-*O*-benzyl-2-*O*-chloroacetyl-α-D-arabinofuranosyl-(1→3)-[2-*O*-chloroacetyl-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (27).

To the mixture of acceptor **25b** (54.5 mg, 62.5 μmol) and donor **26** (70.5 mg, 137.4 μmol) in dry CH_2Cl_2 (2 mL) was added MS4A (250 mg, freshly dried) at room temperaure. After cooling to –40 °C, NIS (48.8 mg, 206.1 μmol) and AgOTf (6.4 mg, 24.9 μmol) were added to the mixture. After stirring for 12 hrs at the same temperature, the reaction was quenched by triethylamine and followed by filtration through celite pad and washing of pad with $CHCl_3$. The combined solutions were washed with 20% aqueous $Na_2S_2O_3$, saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by gel filtration (Bio beads SX-3, toluene/ethyl acetate = 1/1) to give the title pentasaccharide **27** (103.4 mg, 99%).

$[\alpha]^{26}_D$ +99.2° (*c* 1.01, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.32 (s, MeO, 3H), 3.36-3.43 (m, H-5^{Araf2}, H-5^{Araf3}, 2H), 3.47-3.52 (m, H-5^{Araf2}, H-5^{Araf3}, 2H), 3.61-3.91 (m, H-5^{Araf1}, H-3^{Araf2}, H-3^{Araf3}, H-5^{Araf4}, H-5^{Araf5}, ClAc x2, 12H), 3.94-3.95 (m, H-2^{Araf5}, 1H), 3.98 (dd, *J* = 6.0, 3.2 Hz, H-3^{Araf5}, 1H), 3.94-3.95 (m, H-2^{Araf5}, 1H), 4.05 (dd, *J* = 6.4, 3.6 Hz, H-3^{Araf4}, 1H), 4.11-4.20 (m, H-4^{Araf1}, H-4^{Araf2}, H-4^{Araf3}, H-4^{Araf4}, H-4^{Araf5}, 5H), 4.28-4.66 (m, H-3^{Araf1}, Bn x8, 17H), 4.87 (br s, H-1 ^{Araf5}, 1H), 5.10 (br s, H-1^{Araf4}, 1H), 5.11 (br s, H-2^{Araf3}, 1H), 5.13 (br s, H-1^{Araf3}, 1H), 5.20 (br s, H-2^{Araf2}, 1H), 5.25 (br s, H-1^{Araf2}, 1H), 5.34 (br s, H-2^{Araf1}, 1H), 5.43 (br s, H-1^{Araf1}, 1H), 7.12-7.98 (m, Bn x8, Bz, 45H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 40.52, 40.56, 54.88, 68.81, 71.73, 71.85, 71.98, 72.21, 72.25, 73.34, 73.39, 79.84, 80.23, 80.56, 81.60, 82.21, 82.30, 82.49, 82.58, 82.71, 82.81, 83.05, 83.14, 88.00, 88.32, 104.63, 105.44, 105.83, 106.31, 107.11, 127.44, 127.52, 127.55, 127.56, 127.58, 127.662, 127.64, 127.67, 127.69, 127.75, 127.77, 127.82, 128.14, 128.18, 128.20, 128.24, 128.26, 128.32, 129.31, 129.68, 133.15, 137.46, 137.49, 137.54, 137.58, 137.76, 137.82, 137.83, 138.01, 165.19, 165.96 (x2). HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{93}H_{98Cl2}O_{24}Na$, 1691.5723, found 1691.5709.

Methyl 3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (28).

Pentasaccharide **27** (2.1 mg, 1.26 μmol) was dissolved in dry CH_2Cl_2–MeOH–DMF (3.5 mL, 2:0.5:1), and to the mixture was added $AcOH{\cdot}H_2NNH_2$ (13.2 mg, 14.6 mmol). The mixture was stirred for 1.5 hrs at 40 °C and for 2 hrs at 50 °C. After cooling to room temperature, the mixture was diluted with CH_2Cl_2 and washed with H_2O and dried over Na_2SO_4. After concentration, the residue was purified by PTLC (SiO_2, toluene/ethyl acetate = 2/1) to give the title compound **28** (1.8 mg, 94%).

$[\alpha]^{27}_D$ +93.6° (*c* 0.31, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.85-0.99 (m, TIPDS, 28H), 3.27 (s, MeO, 3H), 3.39-3.50 (m, H_2-5^{Araf1}, H_2-5^{Araf5}, 4H), 3.54-3.58 (m, H-5^{Araf4}, H-5^{Araf7}, 2H), 3.62-3.84 (m, H-5^{Araf2}, H-4^{Araf3}, H_2-5^{Araf3}, H-5^{Araf4}, H-3^{Araf5}, H-2^{Araf6}, H-4^{Araf6}, H_2-5^{Araf6}, H-5^{Araf7}, 11H), 3.87-3.97 (m, H-3^{Araf1}, H-5^{Araf2}, H-2^{Araf3}, H-2^{Araf4}, H-3^{Araf4}, H-2^{Araf7}, H-3^{Araf7}, 7H), 4.03-4.18 (m, H-4^{Araf1}, H-4^{Araf2}, H-4^{Araf4}, H-2^{Araf5}, H-4^{Araf5}, H-4^{Araf7}, 6H), 4.23-4.53 (m, H-2^{Araf1}, H-3^{Araf2}, H-3^{Araf3}, H-3^{Araf6}, Bn x10, 24H), 4.81 (br s, H-1^{Araf7}, 1H), 4.87 (d, *J* = 4.4 Hz, H-1^{Araf6}, 1H), 4.97 (br s, H-1^{Araf5}, 1H), 5.02 (br s, H-1^{Araf4}, 1H), 5.13 (d, *J* = 4.4 Hz, H-1^{Araf3}, 1H), 5.18 (br s, H-1^{Araf2}, 1H), 5.24 (br s, H-2^{Araf2}, 1H), 5.28 (br s, H-1^{Araf1}, 1H), 7.03-7.86 (m, Bn x10, Bz, 55H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 54.91, 65.20, 65.64, 66.19, 69.65, 69.69, 71.61, 71.77, 71.88, 71.90, 72.23, 72.30, 73.54, 73.62, 78.19, 78.68, 79.95, 80.19, 80.58, 81.89, 82.49, 82.73, 82.89, 83.15, 83.20,

84.68, 84.82, 88.15, 88.36, 105.78, 106.33, 107.14, 107.76, 108.89, 127.36, 127.45, 127.51, 127.59, 127.62, 127.69, 127.73, 127.78, 127.85, 127.95, 128.20, 128.24, 128.28, 128.30, 128.37, 128.41, 129.43, 129.76, 133.11, 137.09, 137.22, 137.48, 137.74, 137.82, 137.95, 138.01, 165.19. HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{89}H_{96}O_{22}Na$, 1539.6201, found 1539.6195.

Methyl 2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→3)-[2-*O*-benzyl-3,5-*O*-(tetraisopropylsiloxane-1,3-diyl)-β-D-arabinofuranosyl-(1→2)-3,5-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)]-2-*O*-benzoyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranosyl-(1→5)-2,3-di-*O*-benzyl-α-D-arabinofuranoside (29).

To the mixture of pentasaccharide diol acceptor **28** (22.6 mg, 14.9 μmol) and donor 4g (21.9 mg, 37.1 μmol) in dry CH_2Cl_2 (2 mL) was added MS3A (250 mg, freshly dried) at room temperaure. After cooling to –40 °C, NIS (13.2 mg, 55.8 μmol) and AgOTf (1.5 mg, 5.84 μmol) were added to the mixture. After stirring for 3 hrs at the same temperature, the reaction was quenched by triethylamine and followed by filtration through celite pad and washing of pad with $CHCl_3$. The combined solutions were washed with saturated aqueous $NaHCO_3$ and brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by gel filtration (Bio beads SX-3, toluene/ethyl acetate = 1/1) to give the mixture of the isomers (34.1 mg, 94%: ββ : other isomers = 10.8 : 1). The desired isomers were separated by PTLC (SiO_2, toluene/ethyl acetate = 5/1).

$[\alpha]^{29}_D$ +14.5° (*c* 0.11, $CHCl_3$). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.32 (s, MeO, 3H), 3.36-3.43 (m, H-5^{Araf2}, H-5^{Araf3}, 2H), 3.47-3.52 (m, H-5^{Araf2}, H-5^{Araf3}, 2H), 3.61-3.91 (m, H-5^{Araf1}, H-3^{Araf2}, H-3^{Araf3}, H-5^{Araf4}, H-5^{Araf5}, ClAc x2, 12H), 3.94-3.95 (m, H-2^{Araf5}, 1H), 3.98 (dd, *J* = 6.0, 3.2 Hz, H-3^{Araf5}, 1H), 3.94-3.95 (m, H-2^{Araf5}, 1H), 4.05 (dd, *J* = 6.4, 3.6 Hz, H-3^{Araf4}, 1H), 4.11-4.20 (m, H-4^{Araf1}, H-4^{Araf2}, H-4^{Araf3}, H-4^{Araf4}, H-4^{Araf5}, 5H), 4.28-4.66 (m, H-3^{Araf1}, Bn x8, 17H), 4.87 (br s, H-1^{Araf5}, 1H), 5.10 (br s, H-1^{Araf4}, 1H), 5.11 (br s, H-2^{Araf3}, 1H), 5.13 (br s, H-1^{Araf3}, 1H), 5.20 (br s, H-2^{Araf2}, 1H), 5.25 (br s, H-1^{Araf2}, 1H), 5.34 (br s, H-2^{Araf1}, 1H), 5.43 (br s, H-1^{Araf1}, 1H), 7.12-7.98 (m, Bn x8, Bz, 45H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 12.59, 12.61, 12.84, 12.85, 13.31, 13.34, 13.50 (x2), 17.13, 17.15, 17.19, 17.22, 17.45, 17.47, 17.51, 17.60, 54.91, 65.11, 65.75, 66.14, 66.38, 66.42, 69.60, 69.86, 71.72, 71.77, 71.89, 72.08, 72.16, 72.21, 72.28, 72.32, 73.22, 73.25, 77.73, 78.78, 80.41, 80.61, 80.97, 81.02, 81.16, 81.69, 81.74, 82.00, 82.99, 83.15, 83.61, 83.84, 84.10, 84.12, 84.27, 85.27, 85.65, 87.82, 88.38, 98.55, 98.84, 105.77, 106.01, 106.43, 106.50, 107.14, 127.31, 127.36, 127.38, 127.41, 127.46, 127.50, 127.54, 127.60, 127.64, 127.72, 127.79, 127.90, 128.09, 128.15, 128.16, 128.19, 128.24, 128.27, 128.30, 128.43, 128.54, 129.39, 129.73, 133.06, 137.51, 137.57, 137.75, 137.86, 137.89, 137.96, 137.97, 138.09, 138.13, 165.19. MALDI-TOF MS: $[M+H]^+$ calcd for $C_{137}H_{176}O_{32}Si_4Na$, 2468 found 2469; HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{137}H_{176}O_{32}Si_4Na$, 2468.1119, found 2468.1075.

Methyl β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→3)-[β-D-arabinofuranosyl-(1→2)-α-D-arabinofuranosyl-(1→5)]-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranosyl-(1→5)-α-D-arabinofuranoside (32).

Heptasaccharide **29** (13.0 mg, 5.31 μmol) was dissolved in dry THF (1.0 mL), and to the mixture was added 1M solution of tetrabutylammonium fluoride (32.0 μL, 32 μmol) at room temperature. The mixture was stirred for 30 min at room temperature. After concentration, the residue was used for next reaction without further purification.

30: MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{113}H_{124}O_{30}Na$, 1983.8, found 1983.0.

To the solution of crude heptasaccharide 30 in methanol (5 mL) was added NaOMe to justify to alkaline, indicated by phenolphthalein, at room temperature, and the mixture was stirred for 1.5 hrs at the same temperature. Amberlist 15 H^+ was added to the mixture to quench excess NaOMe. Resin was filtered off and concentrated. Crude residue was used for next reaction without further purification.

31: MALDI-TOF MS (*m*/*z*): $[M + Na]^+$ calcd for $C_{113}H_{124}O_{30}Na$, 1879.8, found 1879.3.

To the solution of heptasaccharide **31** in 4:1 mixture of methanol and H_2O (5 mL) under argon atmosphere was added $Pd(OH)_2$ (3.0 mg), and the mixture was stirred for 24 hrs under H_2 atmosphere at the same temperature. After filtration and concentration, the residue was purified by gel filtration (LH-20, MeOH/H_2O = 1/1) to give **32** (5.2 mg, quant. in three steps from **29**).

$[\alpha]^{26}_D$ +127.1° (*c* 0.14, MeOH). ^{1}H NMR (CD_3OD, 400 MHz, 50°C): δ 3.36 (s, 3H), 3.60-4.21 (m, 31H), 4.75 (s, 1H), 4.93-4.97 (m, 2H), 5.02-5.05 (m, 2H), 5.07 (d, *J* = 1.5 Hz, 1H), 5.15 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (CD_3OD, 100 MHz): δ 55.34, 62.34, 62.41, 64.33, 64.36, 67.73, 67.82, 68.19 x2, 75.64, 75.72, 76.19, 76.36, 78.69 x2, 79.02, 81.52, 82.82, 82.90, 83.15, 83.32, 83.72, 83.79, 83.78, 83.88, 84.21, 84.34, 84.41, 89.10, 89.35, 102.28, 102.38, 106.90, 107.25, 109.46 x2, 110.46; ESI-TOF MS calcd. for $C_{36}H_{60}O_{29}Na$ ($[M+H]^+$) 979, found 979; HRMS ESI-TOF (*m*/*z*): $[M + Na]^+$ calcd for $C_{36}H_{60}O_{29}Na$, 979.3118, found 979.3114.

Molecular modeling experiment.

The modeling was performed on MacroModel ver8.1 through conformational search program. Conformational profiles were generated by 2000 or 3000 step Monte Carlo (MCMM)[5] searches with the MM3*,[6] AMBER*,[7] or MMFF94s*[8] force fields in the gas phase or in $CHCl_3$ and then reminimize by multiple minimization program with their force fields in order to give a sufficient global minimum when the structure did not reach a gradient to <0.05 kJ/Å·mol by C-search. From this examination, we observed that global minimum structure of all β-isomer shows axially oriented glycosidic bond as we expected, and results of MMFF[9] were selected for an explanation on of influence the outcome of a reaction (Figure SI-1 and Table SI-1).

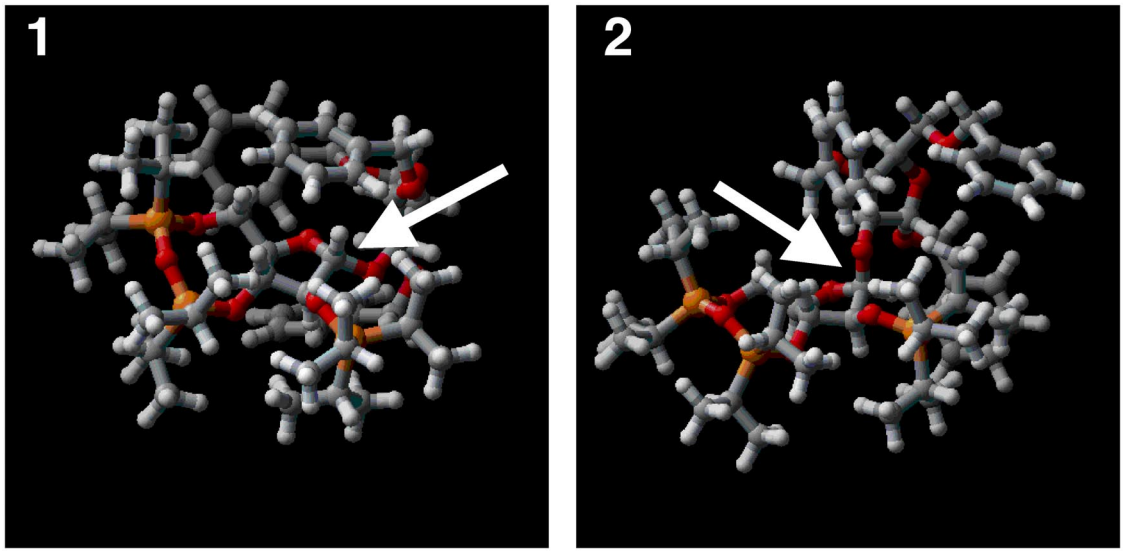

Figure SI-1. Result of molecular modeling of glycosylated products from the most selective entry (Table 2, entry 3), calculated by MacroModel, version 8.1, in the gas phase. (1) α-Isomer (total energy = 662.8322 kJ/mol). (2) β-Isomer (656.5997 kJ/mol). White arrows indicate newly formed anomeric linkages.

Table SI-1. Result of molecular modeling by MacroModel ver8.1 with MMFFs

	MMFFs		MMFFs in $CHCl_3$	
kJ/mol	α	β	α	β
Total	662.8321	**656.5998**	557.2175	**555.3101**
Streach	139.3347	127.6295	125.4379	127.5446
Bend	168.1776	153.9762	152.7223	157.4457
Torsion	69.9728	72.4018	71.4031	63.2765
Improper torsion	0.0629	0.0390	0.0803	0.0674
VDW	336.9513	330.1970	350.3180	334.2250
Electrostatic	57.1309	67.8642	60.4323	68.8281
Cross term	–108.7378	–95.5110	–90.1467	–94.0522
Solvation	-	-	–113.0329	–102.0282
Dihedral angle /°				
C5-O_{endo}-C1-C2	18.4	23.5	7.8	23.6
O_{endo}-C1-C2-C3	–35.7	–40.1	–30.3	–40.8
O_{exo}-C1-C2-C3	–156.2	78.7	–148.9	78.1

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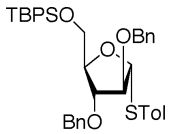
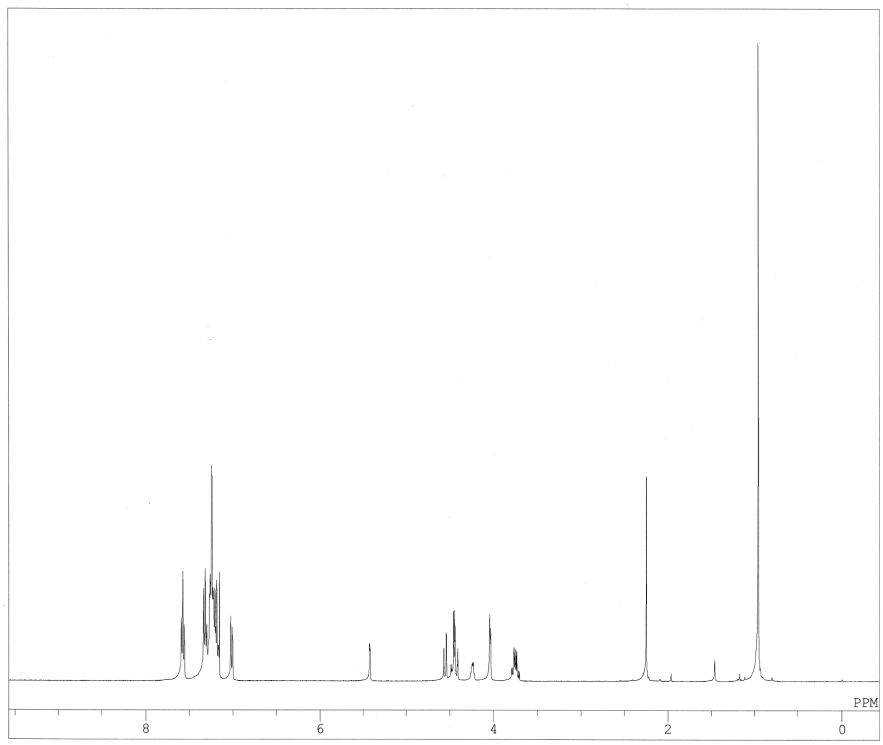
9) MMFF have been used for small polar cyclic molecule mainly due to its representation of molecular electrostatics with uniformly applied electrostatic potential atomic charges similar to AMBER, See; Nevin, N.; Cicero, D.; Snyder, J. P. *J. Org. Chem.* **1999**, *64*, 3979–3986.



2a

^{1}H NMR



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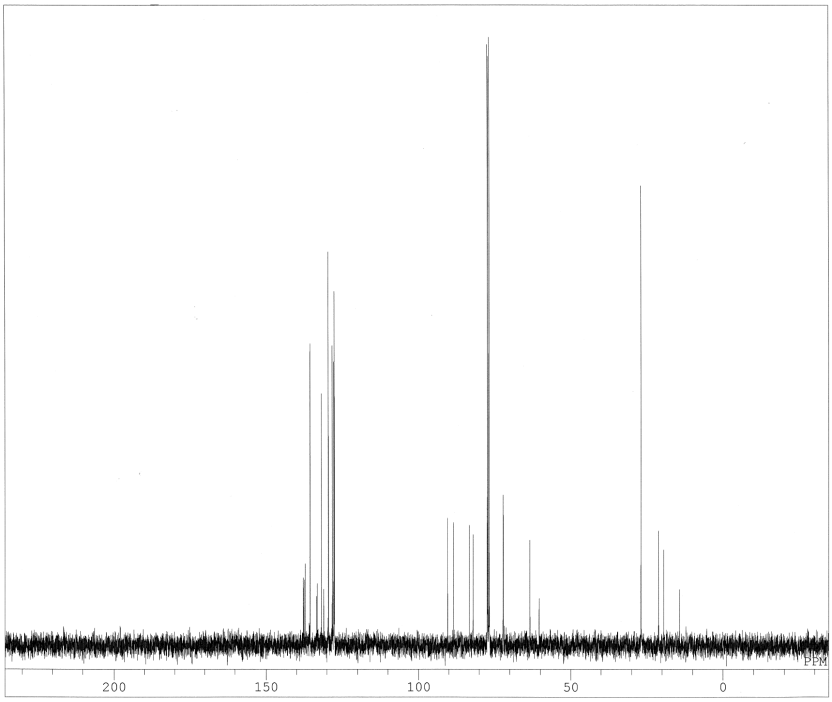

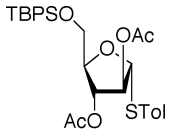

7

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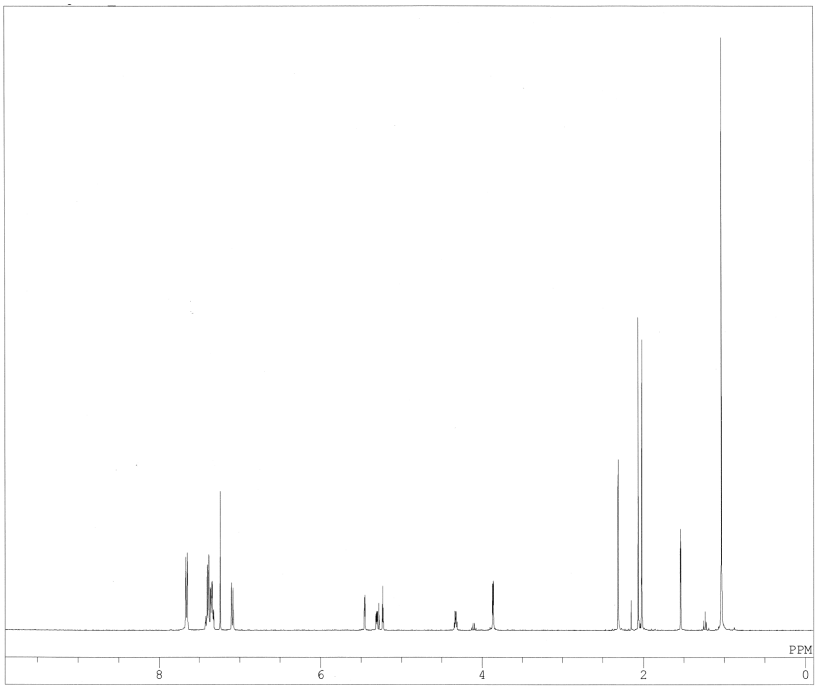

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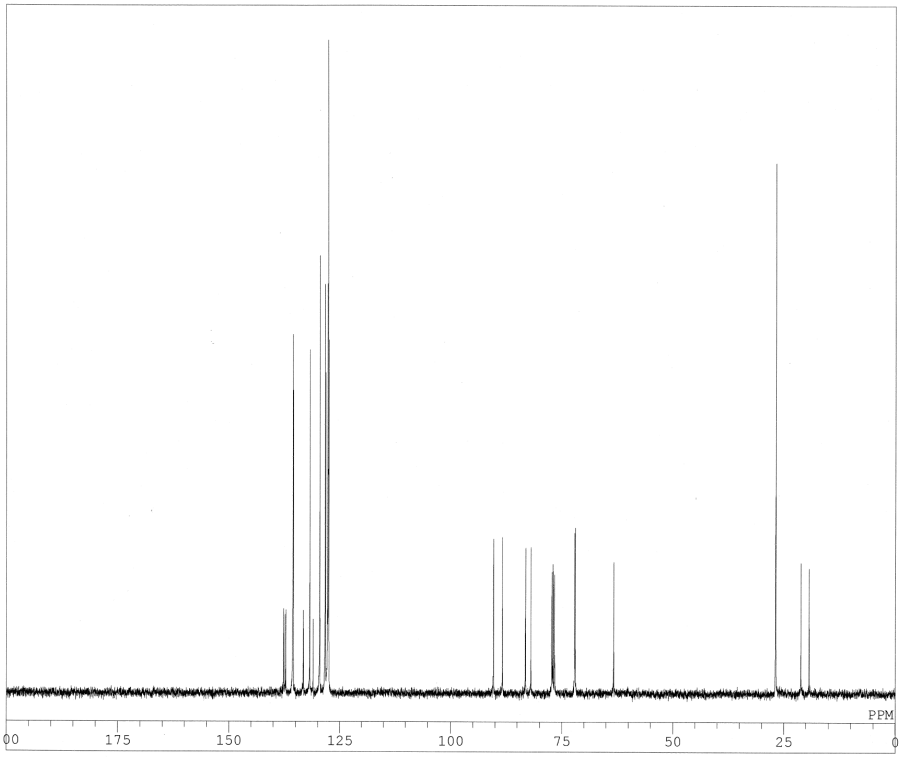

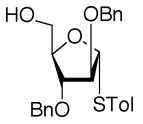

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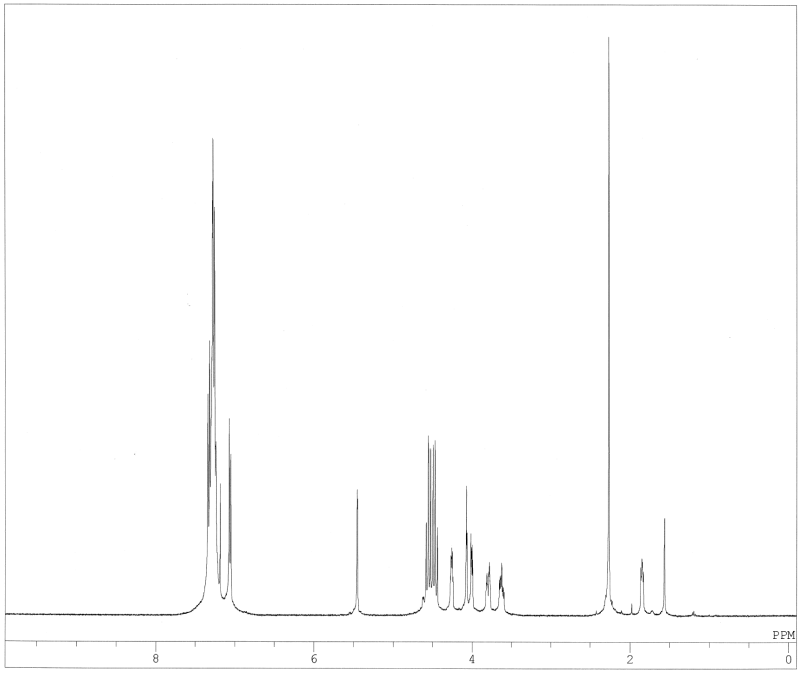

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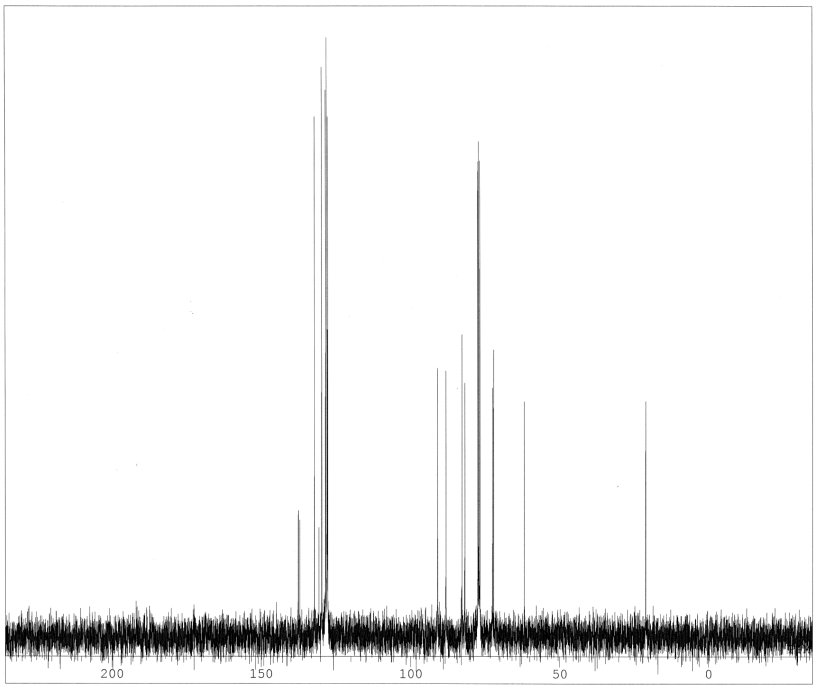

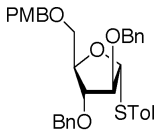

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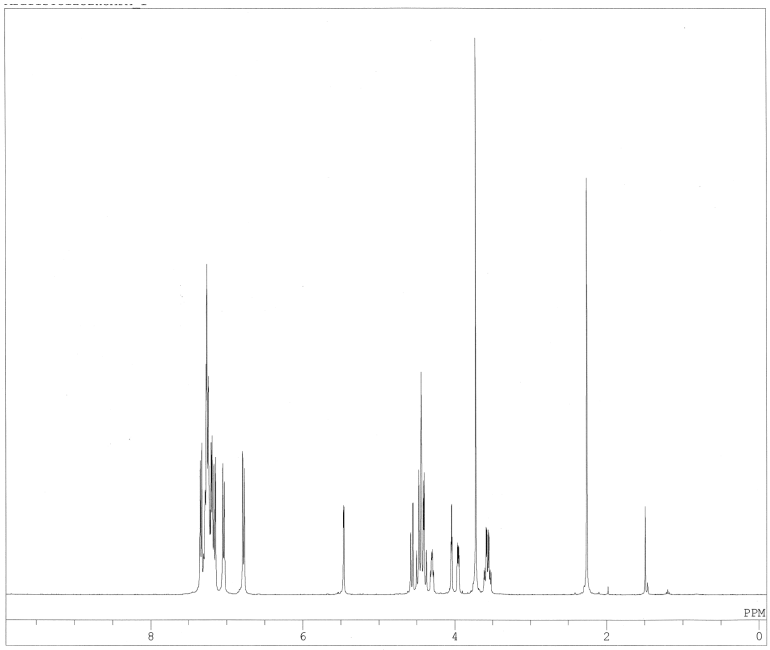

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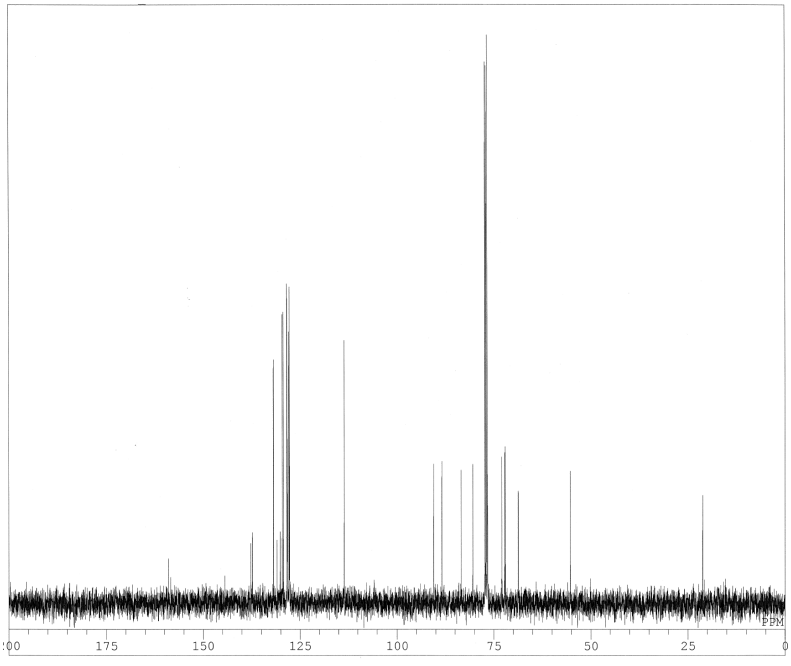

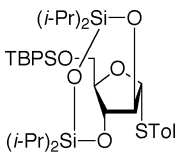

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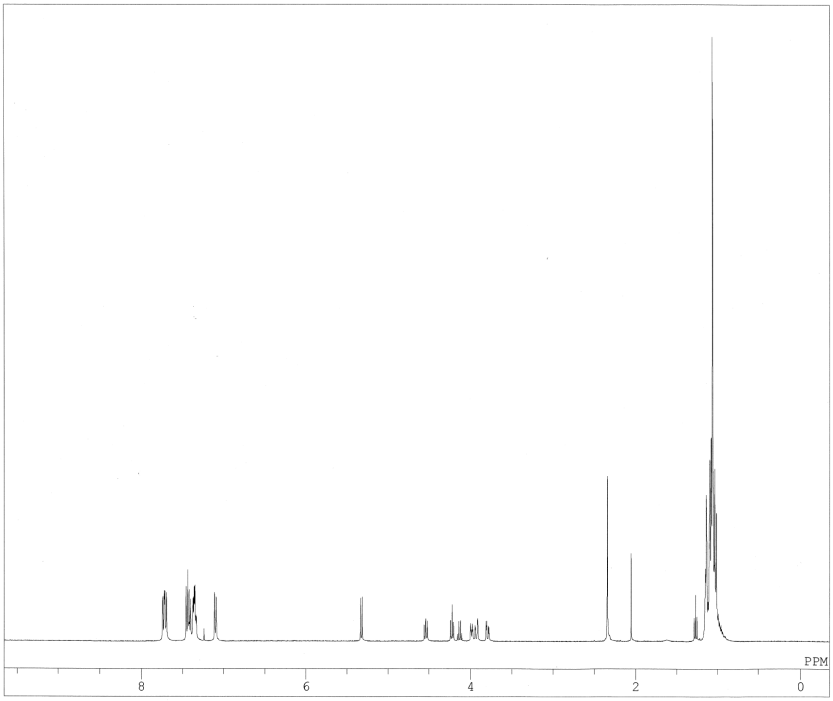

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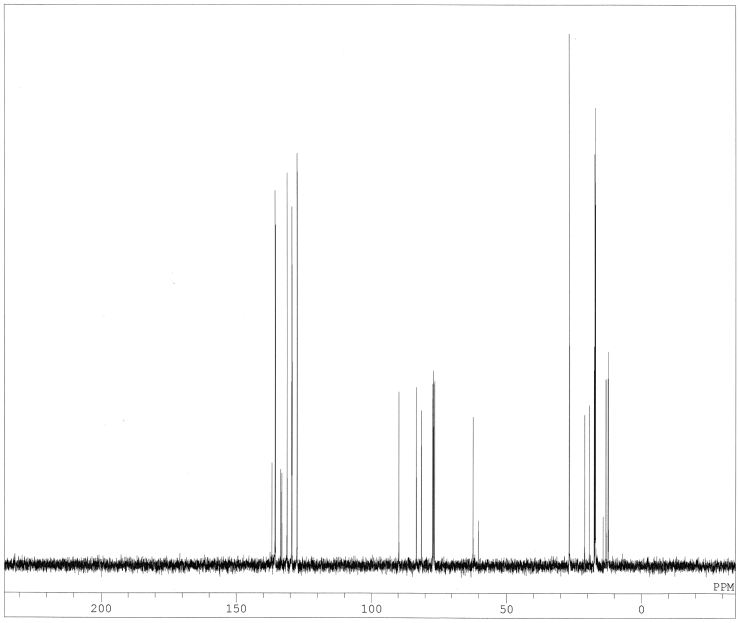

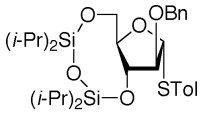

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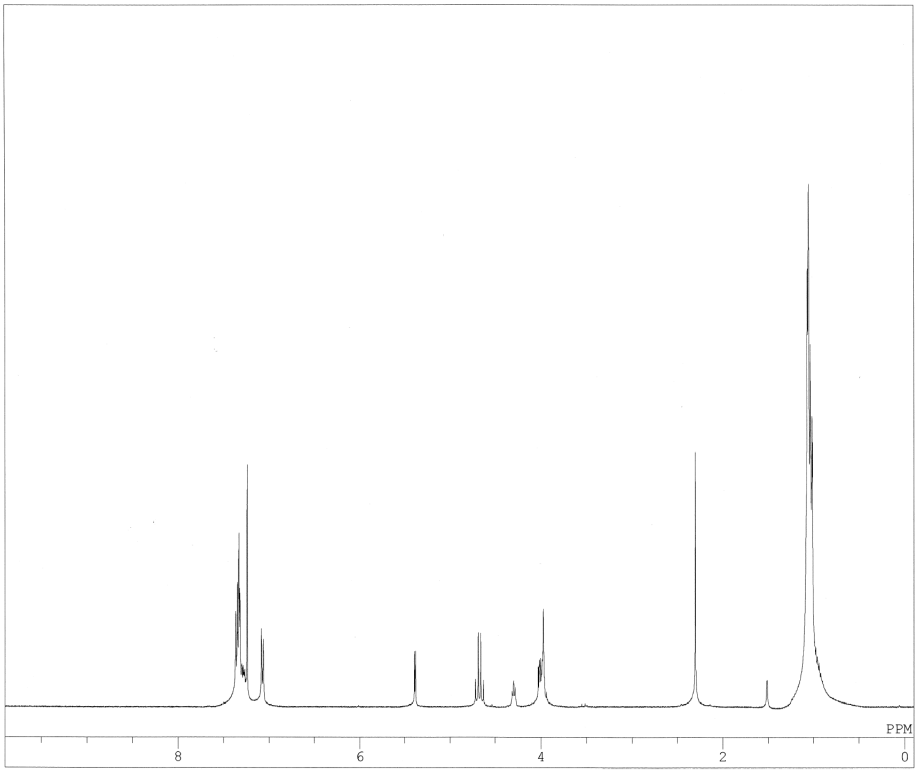

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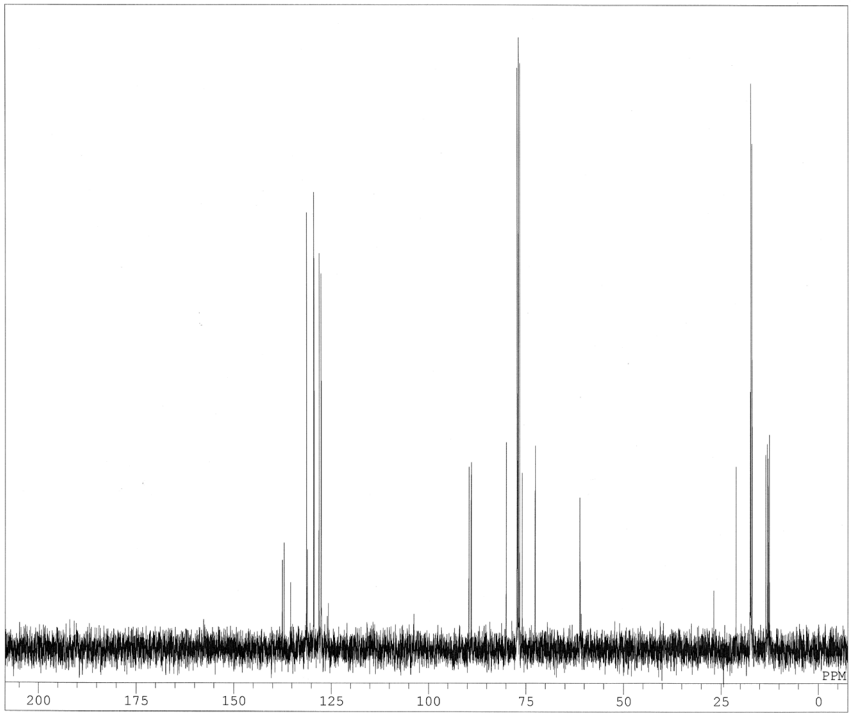

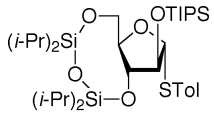

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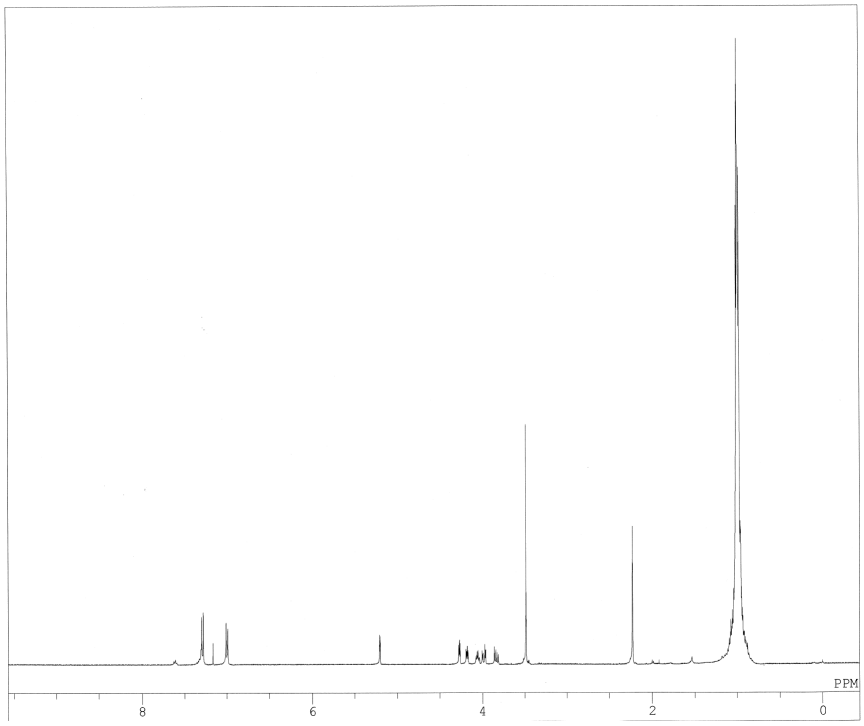

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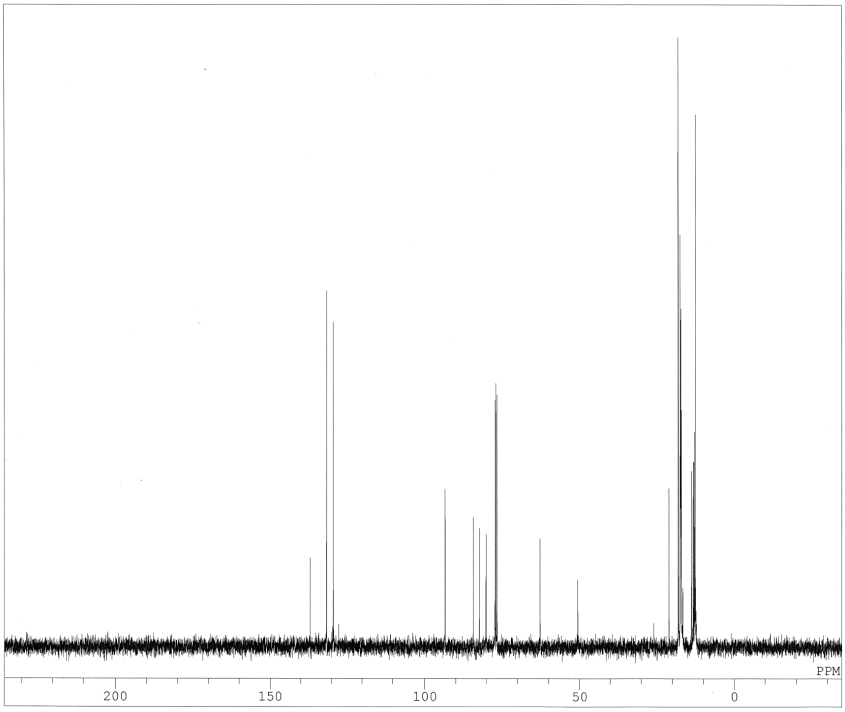

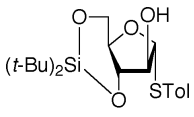

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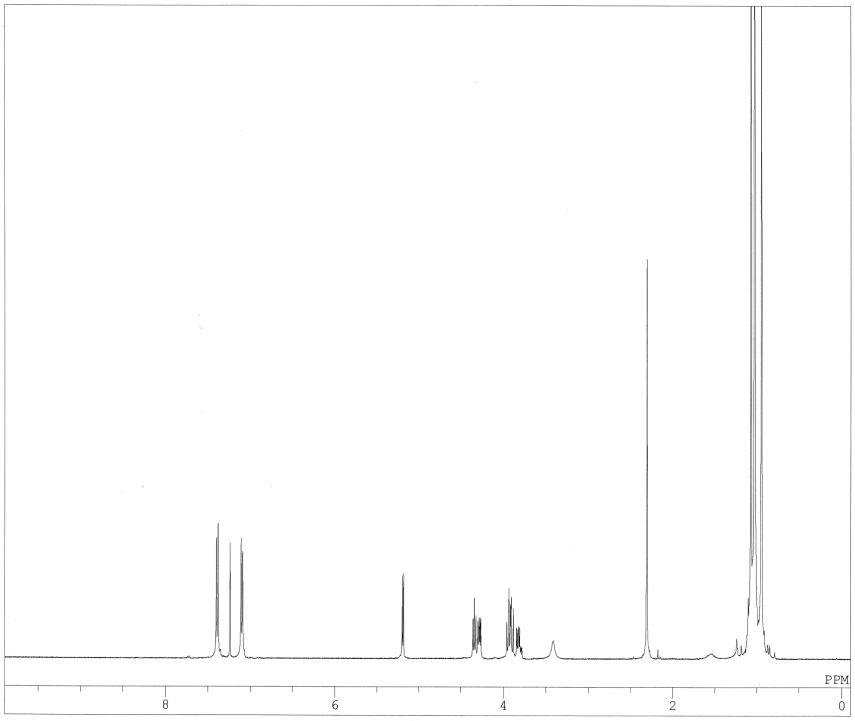

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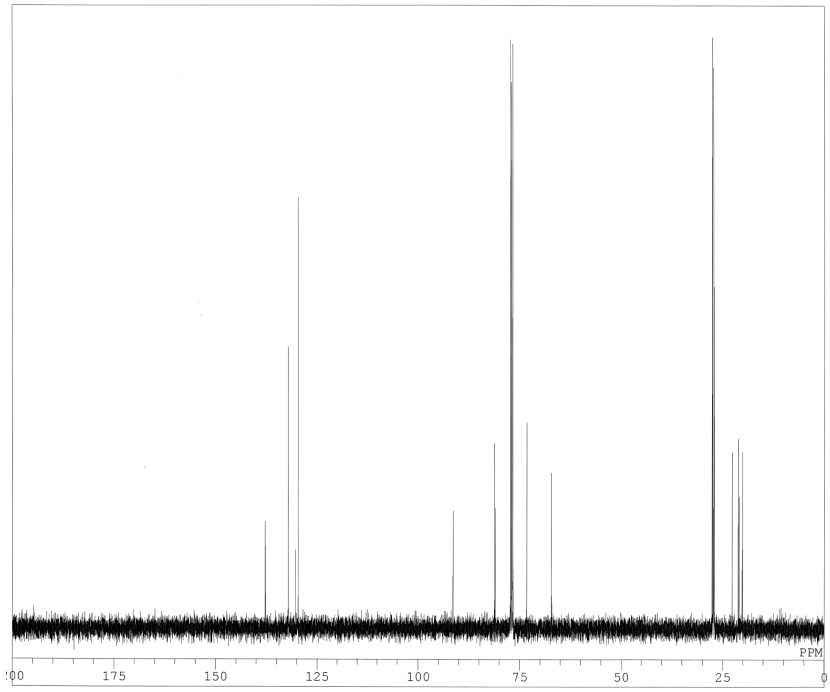

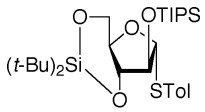

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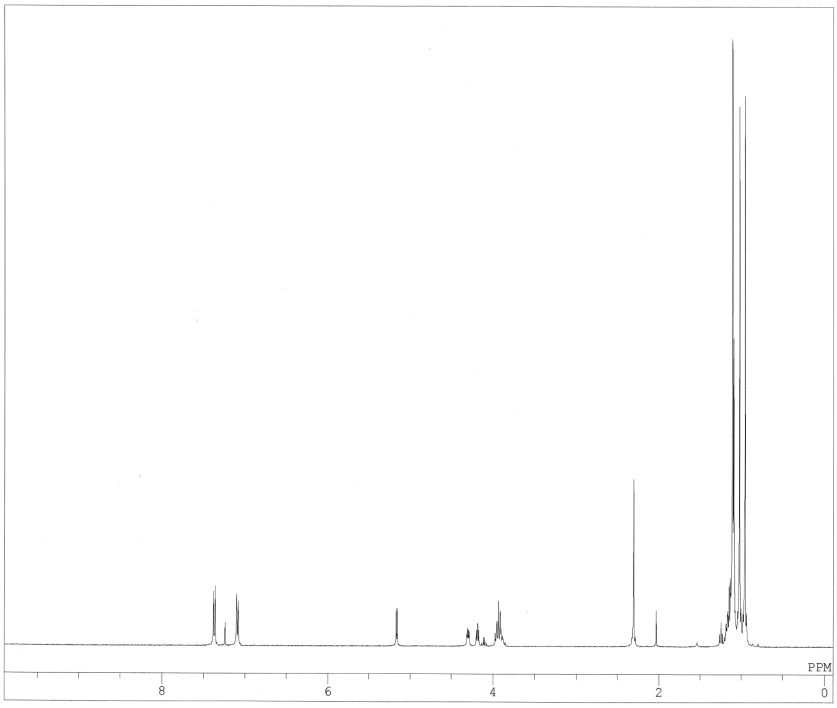

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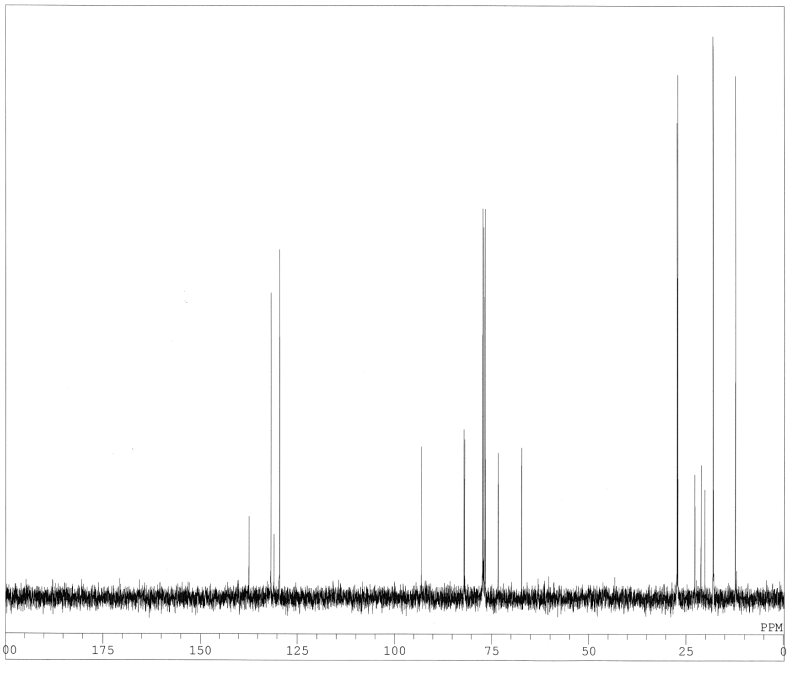

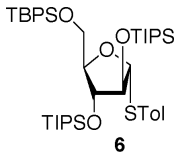

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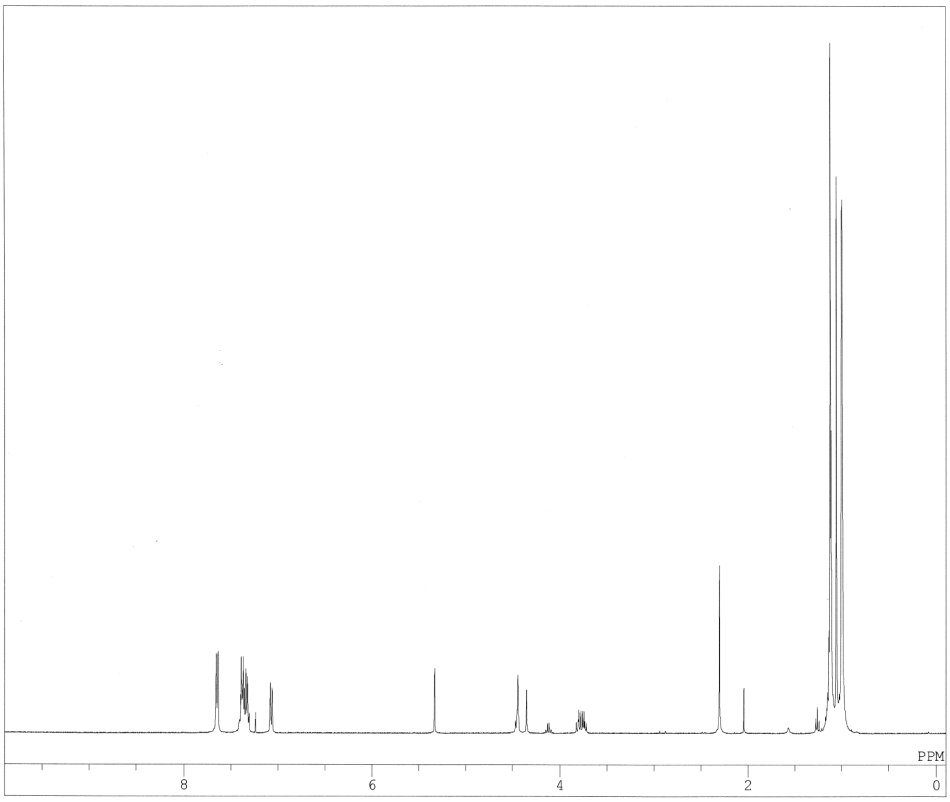

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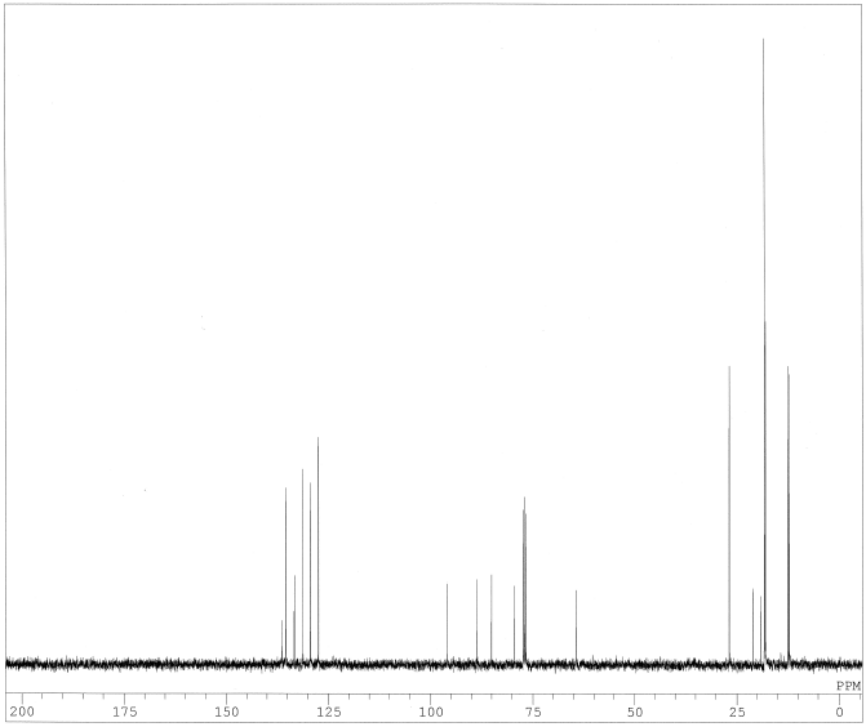

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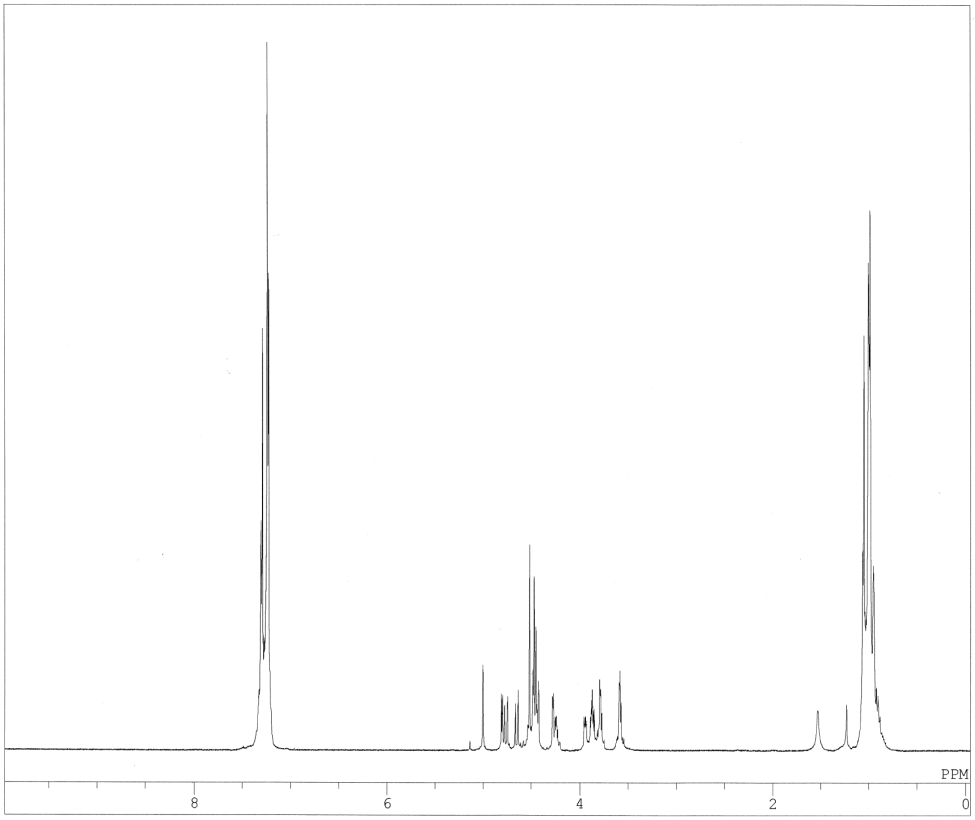

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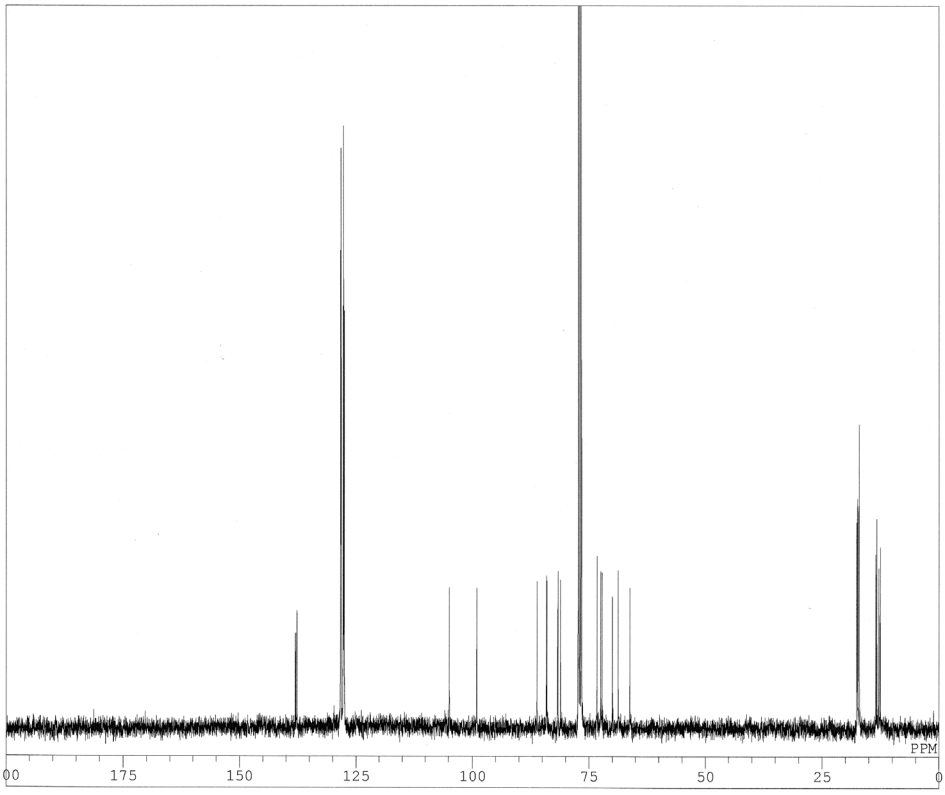

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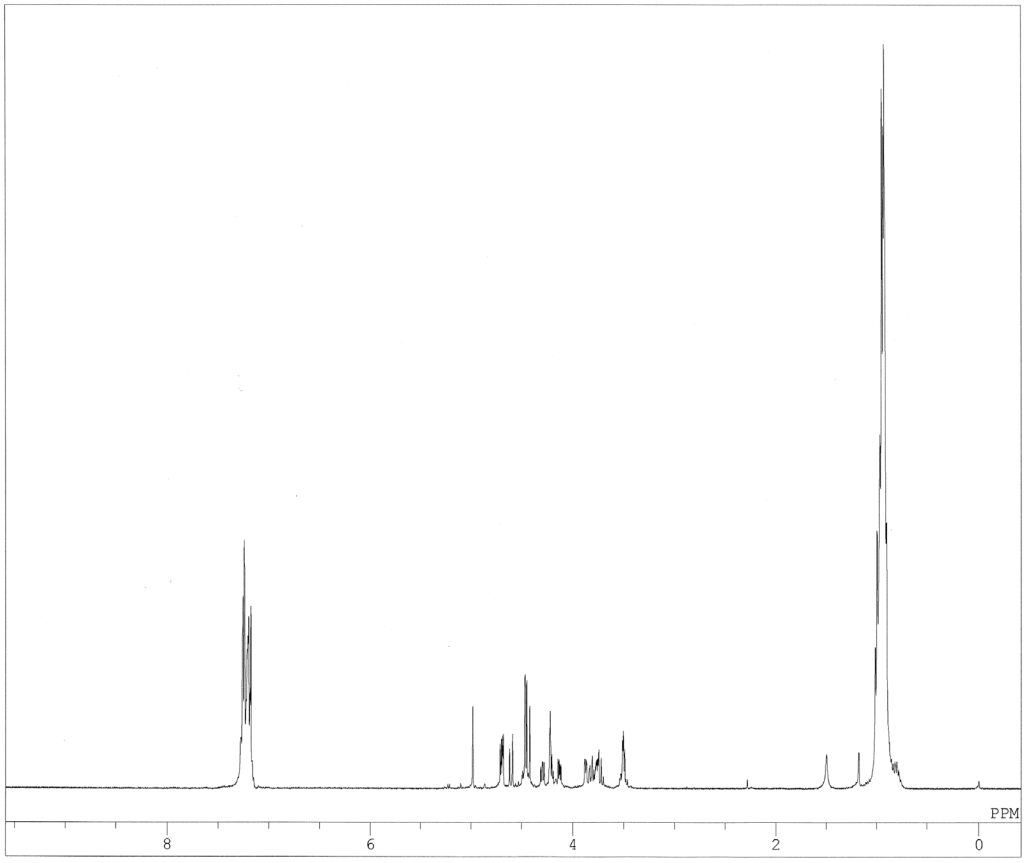

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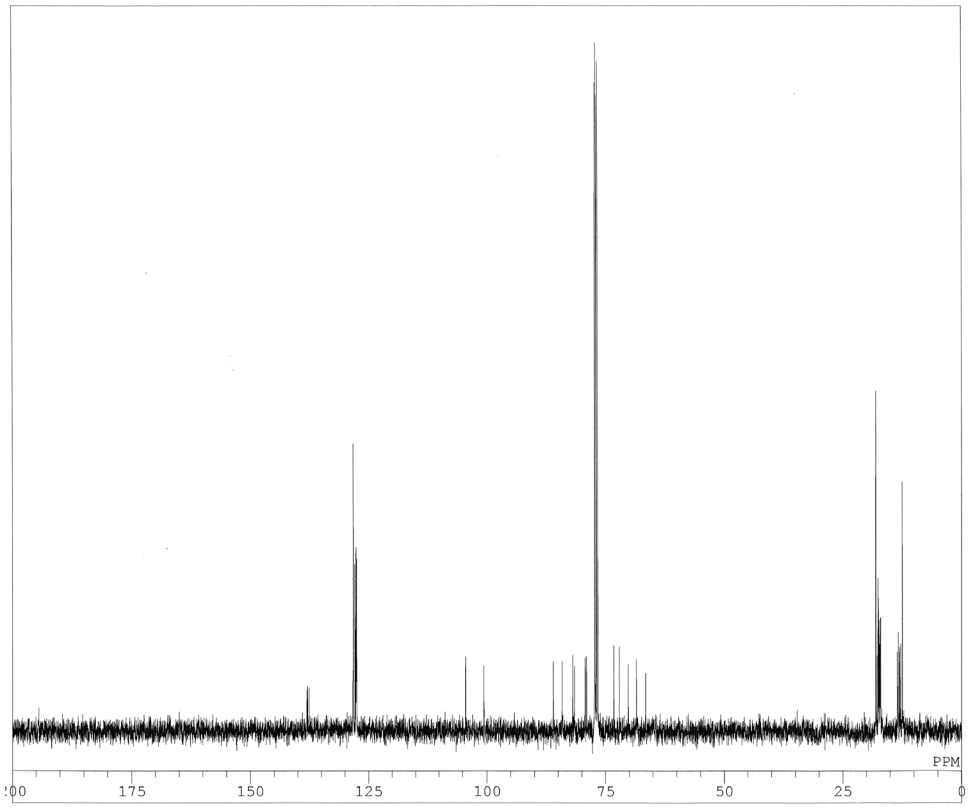

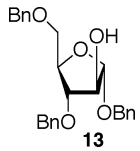

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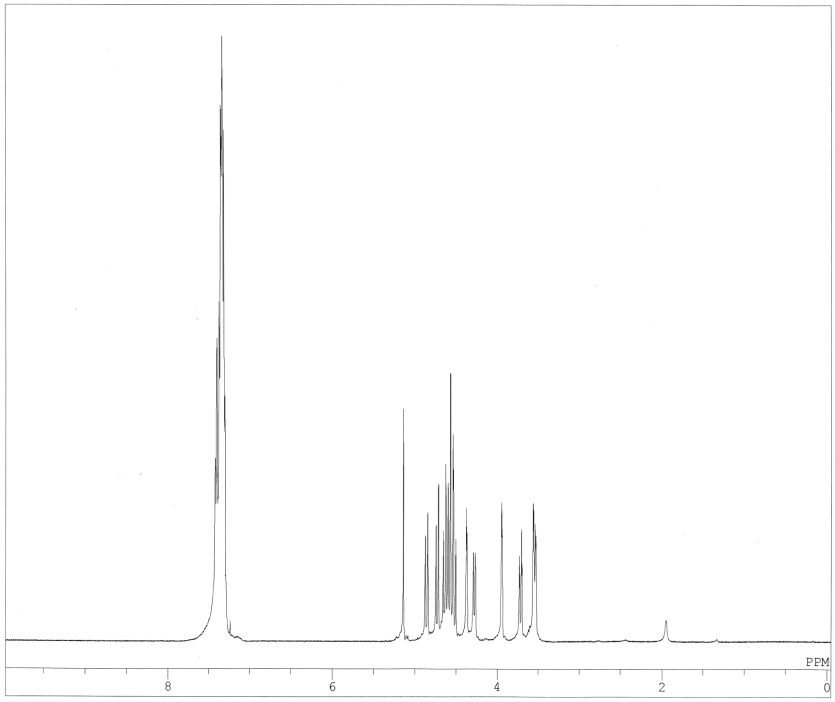

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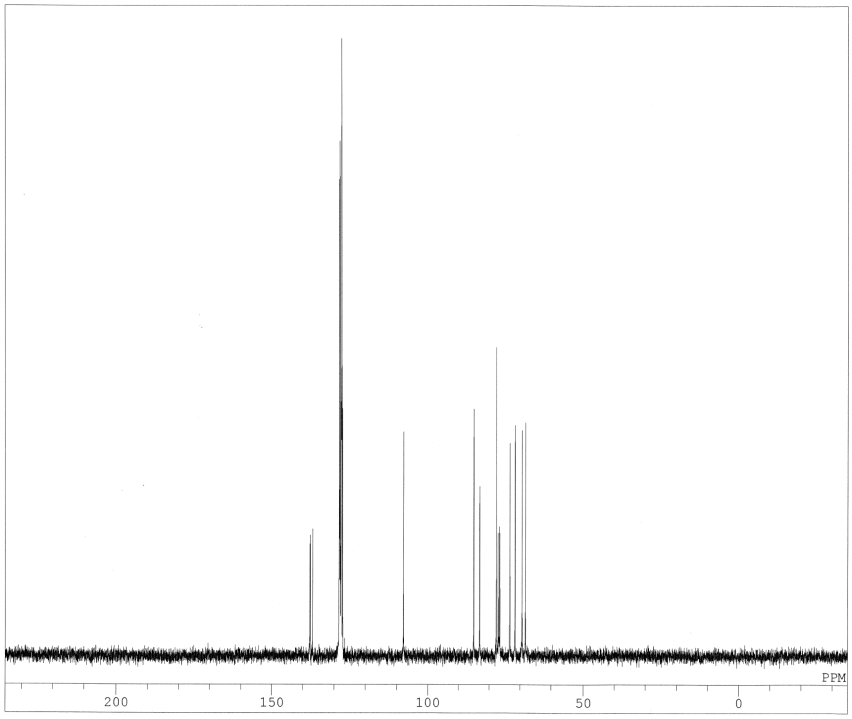

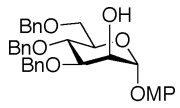

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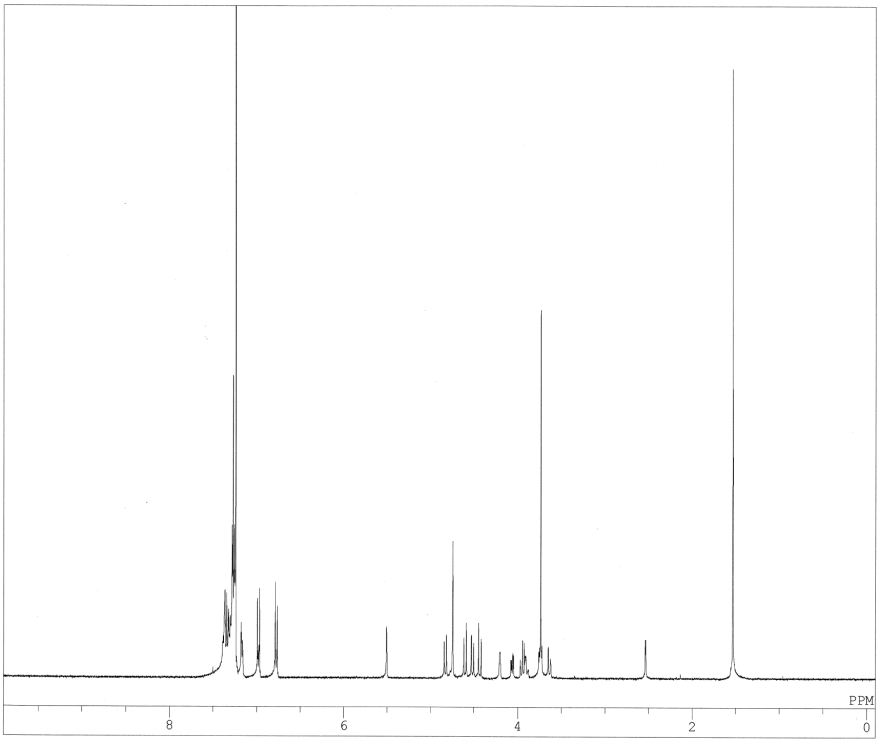

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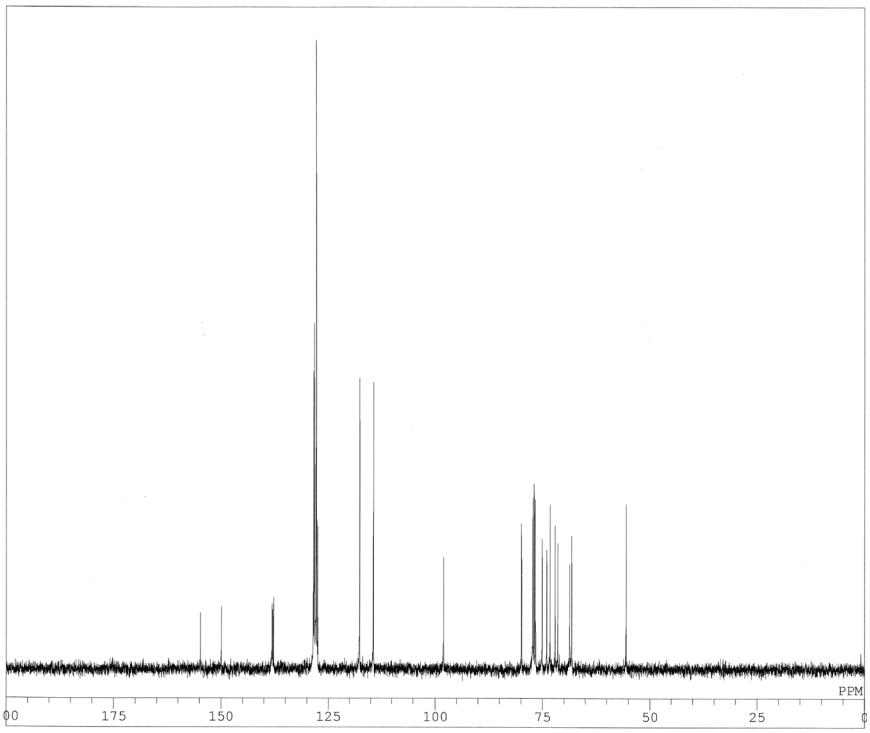

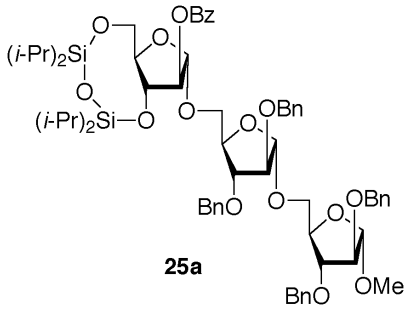

25a

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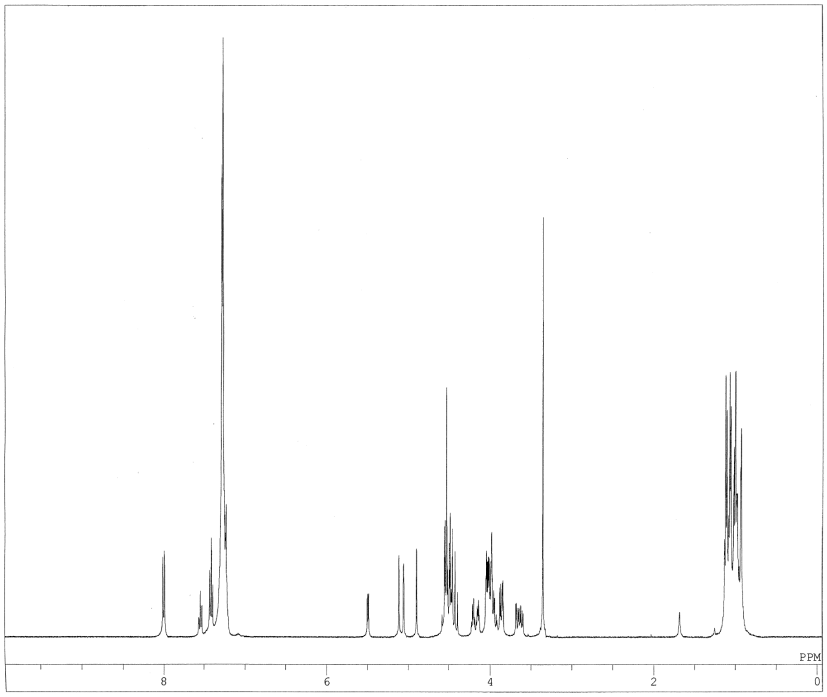
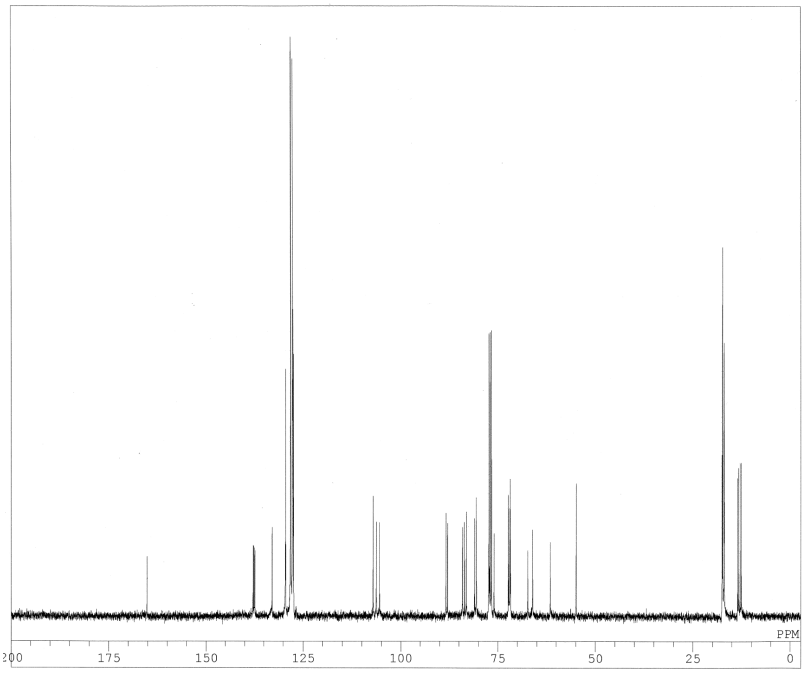
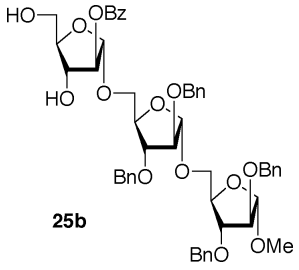


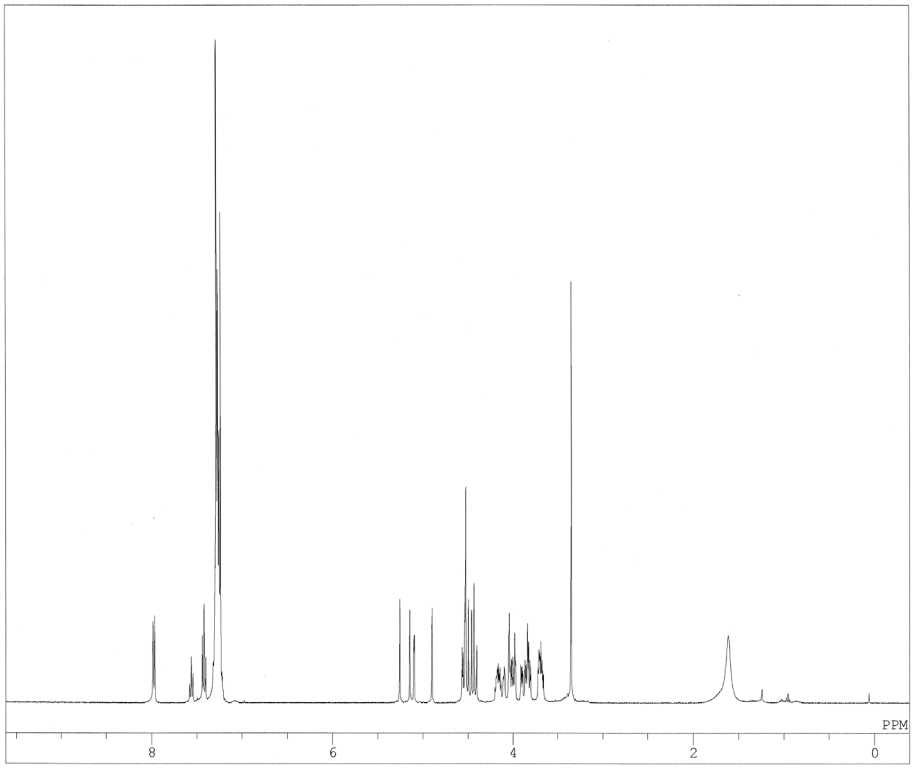
^{13}C NMR



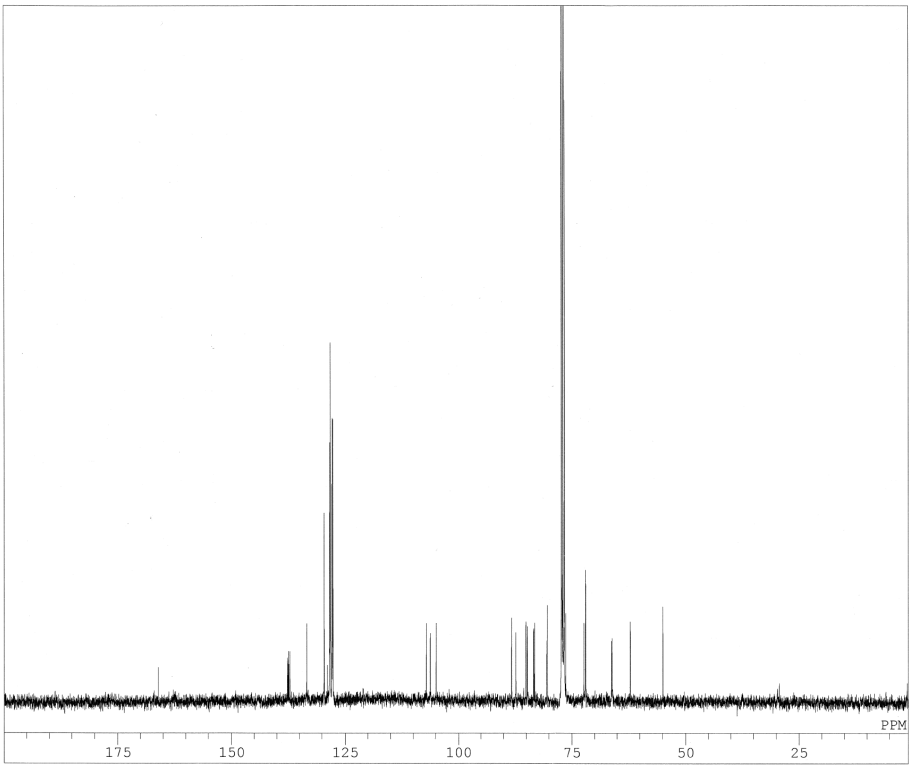


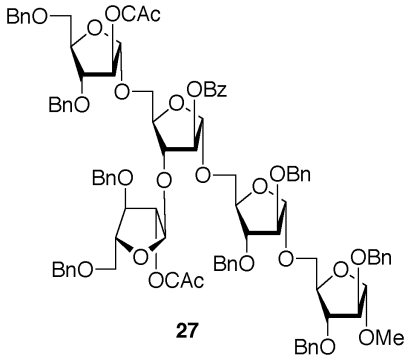
25b

^{1}H NMR



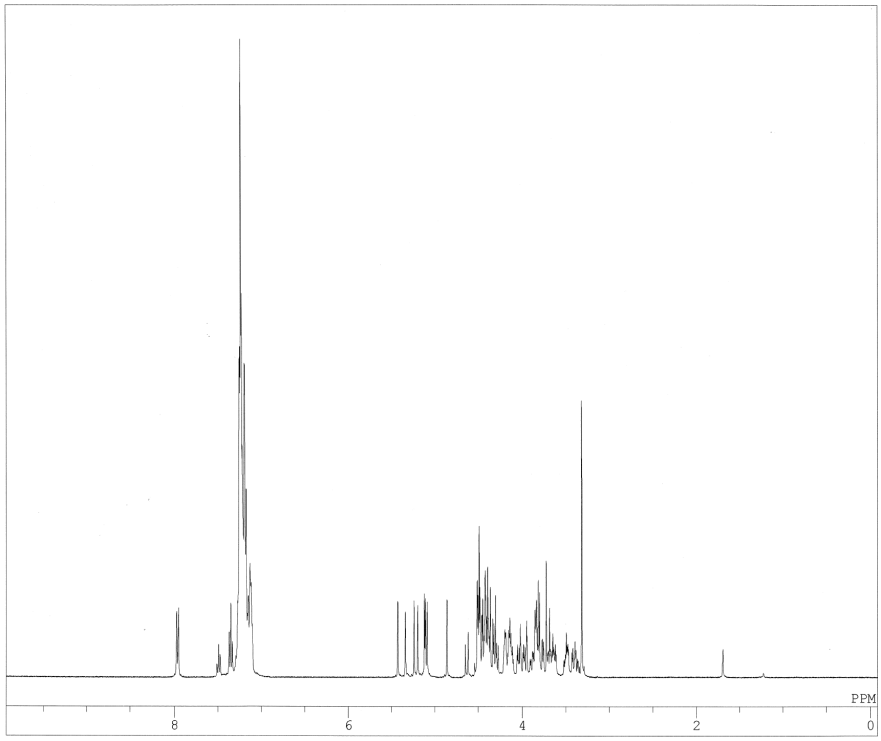
^{13}C NMR



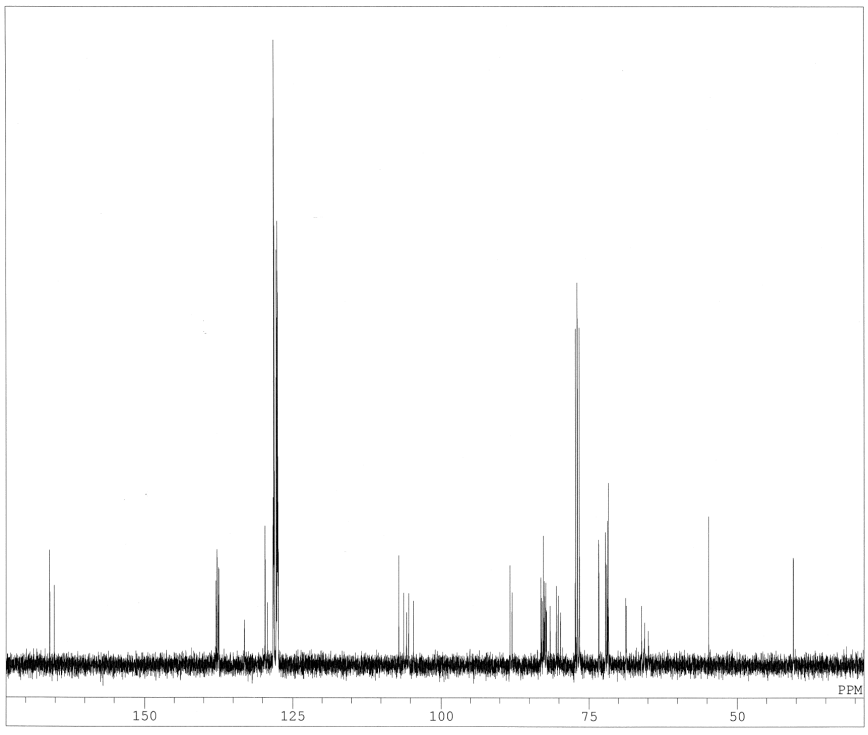


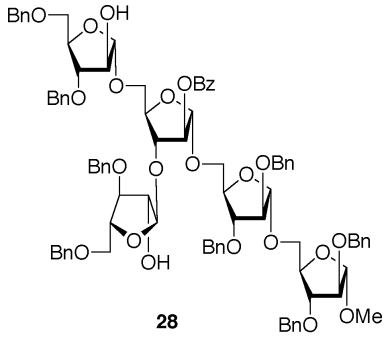
27

^{1}H NMR



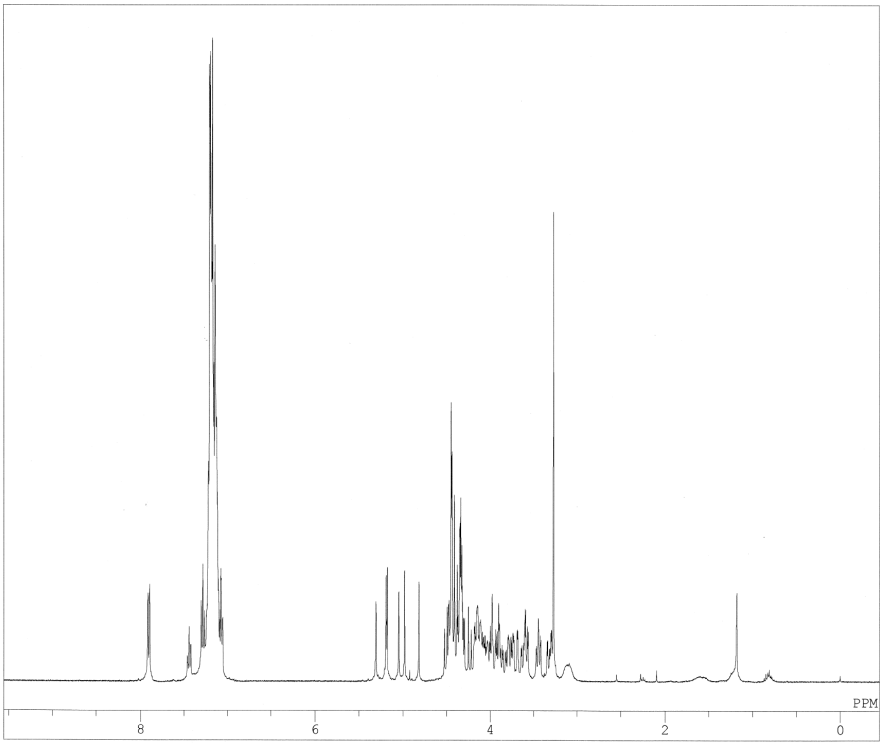
^{13}C NMR



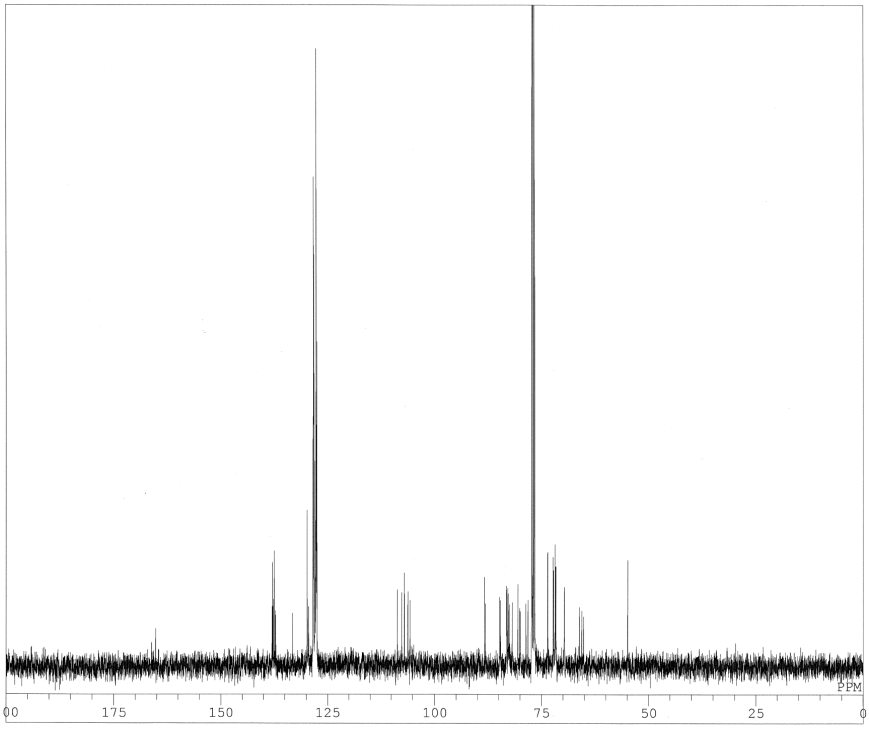


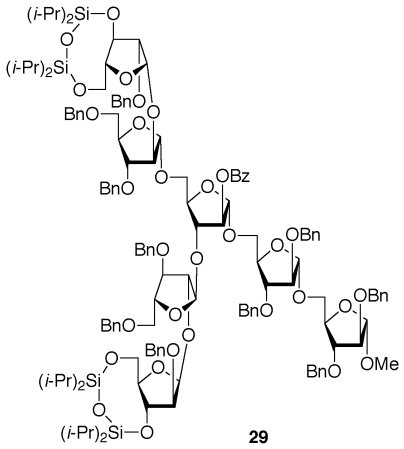
28

^{1}H NMR



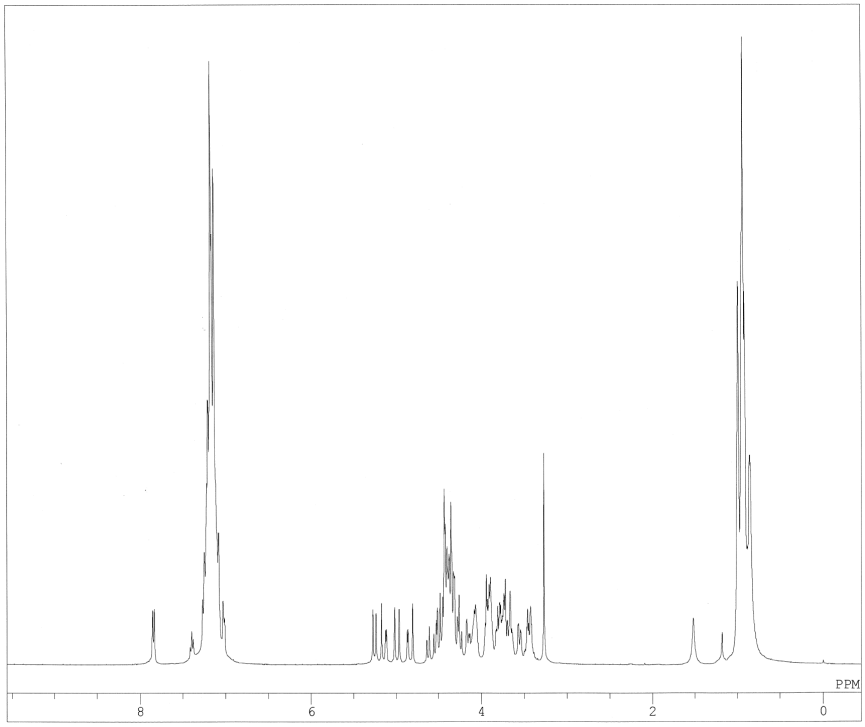
^{13}C NMR



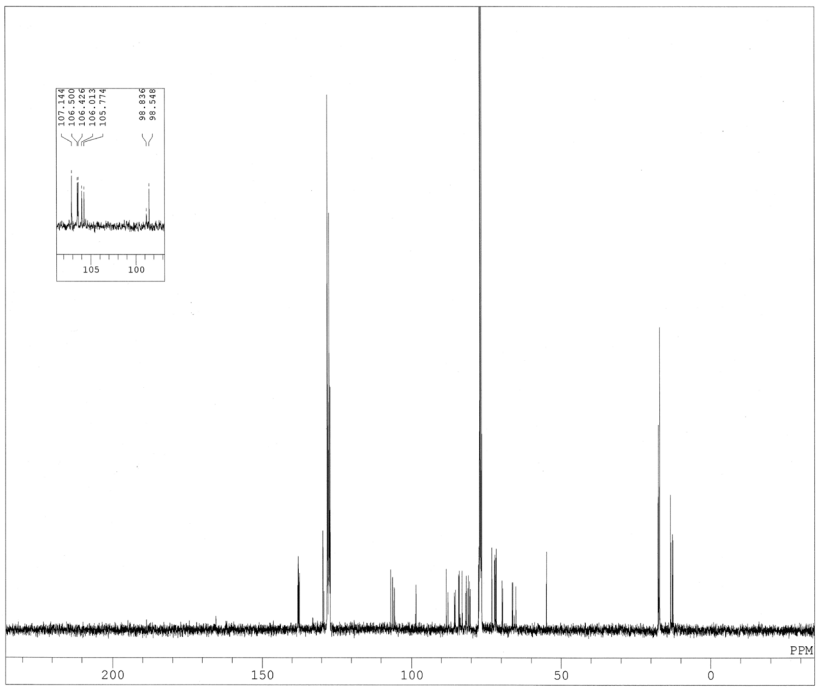


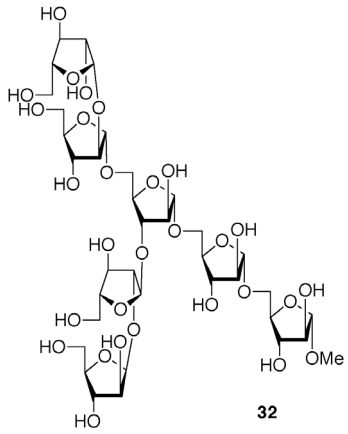
29

^{1}H NMR



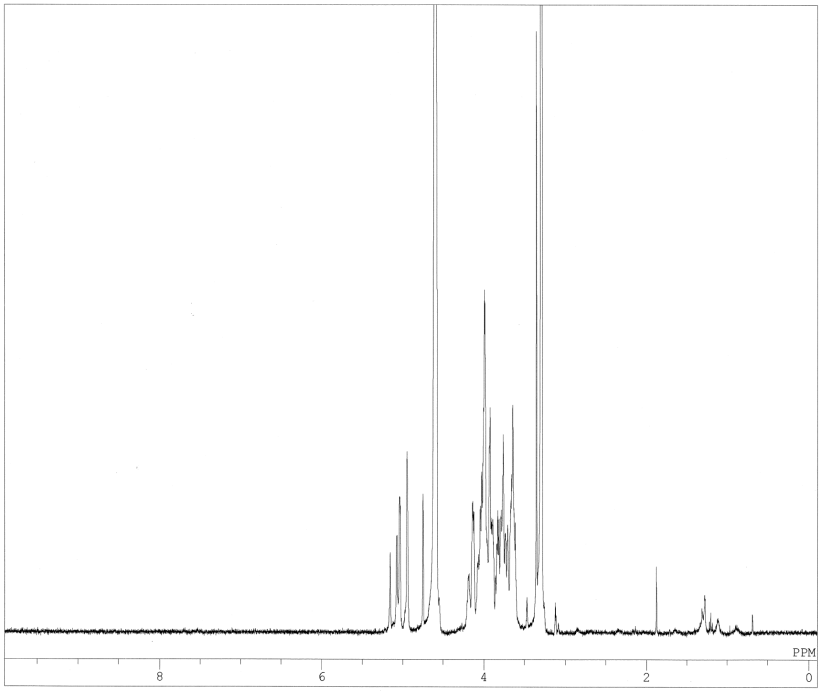
^{13}C NMR





32

^{1}H NMR



^{13}C NMR