Facile glycosylation strategy with two-stage activation of allyl glycosyl donors. Application to concise synthesis of Shigella flexneri serotype Y O-antigen

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Contents

SUPPORTING INFORMATION

General Procedures. Glycosylation reactions were performed in Schlenk (Kjeldahl shape) flasks under a positive pressure of argon. The glycosylation partners were dried by azeotropic removal of water with toluene prior to initiation of the glycosylation reactions. Organic solutions were concentrated by rotary evaporation at *ca*. 12 Torr. Flash column chromatography was performed employing 230-400 mesh silica gel. Thin-layer chromatography (analytical and preparative) was performed using glass plates pre-coated to a depth of 0.25 mm with 230-400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Workup as usual (solvent) consisted of extraction with the indicated solvent, washing with brine, drying the combined organic layers over Na_2SO_4, filtration, and concentration under reduced pressure.

Materials. Tetrahydrofuran, toluene, and acetonitrile were distilled from appropriate drying reagents under a nitrogen atmosphere at 760 torr. Other chemicals were obtained from commercial vendors and used without further purification.

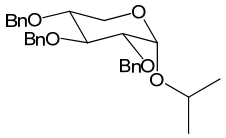
Instrumentation. Infrared (IR) data are presented as frequency of absorption (cm^{-1}). Proton and carbon-13 nuclear magnetic resonance (^1H NMR or ^{13}C NMR) spectra were recorded on a 300 MHz and a 400 MHz NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ($CHCl_3$: δ 7.26). Data are presented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiple resonances), coupling constant in Hertz (Hz), integration.

Experimental Details

entry	Donor (μmol)	Acceptor (μmol)	NIS (μmol)	TfOH (μmol)	MeCN (mL)	product	Yield (β/α)[c]
1[a]	**11** (89)	**13** (59)	89	0.9	1	**18**	44 mg, 96% (70:30)
2[a]	**11** (48)	**13** (35)	48	7.2	1	**16**	27 mg, 86% (45:55)
3[a]	**17** (85)	**13** (57)	85	4	1	**18**	49 mg, 96% (77:23)
4[a]	**17** (75)	**15** (50)	75	4	1	**19**	43 mg, 83% (74:26)
5[b]	**20** (30)	**13** (20)	30	7.5	2	**21**	12 mg, 79% (β)
6[b]	**20** (75)	**15** (50)	75	19	5	**22**	37 mg, 84% (β)
7[b]	**23** (50)	**24a** (100)	50	5	1	**25a**	25 mg, 95% (α)[d]
8[b]	**23** (50)	**24b** (100)	50	5	1	**25b**	23 mg, 95% (α)[d]
9[b]	**23** (75)	**13** (50)	75	7.5	1	**26**	35 mg, 89% (α)
10[b]	**23** (50)	**15** (75)	50	5	1	**27**	40 mg, 88% (α)[d]
11[a]	**28** (50)	**24a** (75)	50	25	1	**29a**	27 mg, 85% (α)[d]
12[a]	**28** (50)	**24b** (100)	50	25	1	**29b**	26 mg, 89% (α)[d]
13[a]	**28** (75)	**15** (50)	75	4	2	**30**	44 mg, 86% (25:75)
14[a]	**28** (45)	**15** (30)	45	11	1	**30**	25 mg, 82% (α)

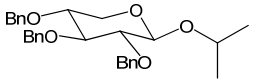
[a] isomerized with *t*BuOK. [b] isomerized with hydrogen-activated $[Ir(COD)(PMePh_2)_2]PF_6$. [c] combined yield of anomers, anomeric ratio was determined by ^1H NMR and confirmed by the isolated yield of each anomer. [d] a small quantity of β anomer (<5%) was also isolated.

Spectroscopic Data



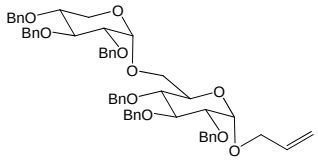
12α

Isopropyl 2,3,4 -tri-*O*-benzyl-α-D-xylopyranoside. Rf 0.50 (methylene chloride/ethyl ether 120:1); $[\alpha]_D^{24}$ = +31.3 (c = 0.15, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40-7.26 (m, 15 H, 3xPh), 4.94 (A<u>B</u>^{1}, *J* = 10.8 Hz, 1 H, Bn), 4.82 (A<u>B</u>^{1}, *J* = 10.8 Hz, 1 H, Bn), 4.78 (A<u>B</u>^{2}, *J* = 11.8 Hz, 1 H, Bn), 4.76 (d, *J* = 3.5 Hz, 1 H, H-1),4.75 (A<u>B</u>^{3}, *J* = 11.5 Hz, 1 H, Bn), 4.65 (A<u>B</u>^{2}, *J* = 12.0 Hz, 1 H, Bn), 4.63 (A<u>B</u>^{3}, *J* = 11.5 Hz, 1 H, Bn), 3.91 (dd, *J* = 9.6, 8.1 Hz, 1H, H-3), 3.82 (septet, *J* = 6.0, 1 H, CH_3<u>CH</u>CH_3), 3.62-3.52 (m, 3 H), 3.44 (dd, *J* = 9.6, 3.7 Hz, 1 H, H-2), 1.25 (d, *J* = 6.3 Hz, 3 H, <u>CH_3</u>$CHCH_3$), 1.18 (d, *J* = 6.0 Hz, 3 H, CH_3CH<u>CH_3</u>); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.1, 138.4, 128.41, 128.37, 128.31, 128.06, 1287.98, 127.82, 127.78, 127.76, 127.5, 94.8, 81.5, 79.7, 78.3, 77.2, 75.7, 73.6, 73.2, 68.9, 59.9, 23.2, 21.1. FTIR (neat film) cm^{-1} 3030, 2971, 2925, 1497, 1454, 1362, 1330, 1207, 1169, 1036; HRMS (ESI) *m/z*: Calcd for $C_{29}H_{34}O_5Na$ (M+Na) 485.2304, found 485.2299.



12β

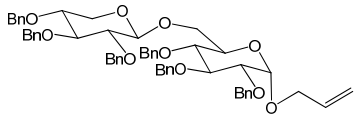
Isopropyl 2,3,4 -tri-*O*-benzyl-β-D-xylopyranoside. Rf 0.45 (methylene chloride/ethyl ether 120:1); $[\alpha]_D^{24}$ = +13.9 (c = 0.29, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37-7.26 (m, 15 H, 3xPh), 4.93 (A<u>B</u>^{1}, *J* = 10.8 Hz, 1 H, Bn), 4.87 (A<u>B</u>^{2}, *J* = 11.1 Hz, 1 H, Bn), 4.83 (A<u>B</u>^{2}, *J* = 11.1 Hz, 1 H, Bn), 4.73 (A<u>B</u>^{3}, *J* = 11.5 Hz, 1 H, Bn), 4.69 (A<u>B</u>^{1}, *J* = 9.9 Hz, 1 H, Bn), 4.61 (A<u>B</u>^{3}, *J* = 11.6 Hz, 1 H, Bn), 4.40 (d, *J* = 7.7 Hz, 1 H, H-1), 3.97 (septet, *J* = 6.2 Hz, 1 H, CH_3<u>CH</u>CH_3), 3.9 (dd, *J* = 11.5, 5.0 Hz, 1 H, H-5$_{eq}$), 3.65-3.52 (m, 2 H, H-3 and H-4), 3.34 (dd, *J* = 9.0, 7.8 Hz, 1 H, H-2), 3.18 (dd, *J* = 11.5, 9.9 Hz, 1 H, H-5$_{ax}$), 1.26 (d, *J* = 6.2 Hz, 3 H, <u>CH_3</u>$CHCH_3$), 1.23 (d, *J* = 6.2 Hz, 3 H, CH_3CH<u>CH_3</u>); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.8, 138.6, 138.3, 128.5, 128.33, 128.32, 128.13, 128.01, 127.96, 127.86, 127.83.127.61, 127.55, 102.7, 84.1, 82.1, 81.5, 79.7, 77.9, 75.6, 75.0, 73.6, 73.4, 72.1, 68.9, 63.923.7, 22.2. FTIR (neat film) cm^{-1} 3031, 2971, 2869, 1497, 1454, 1381, 1357, 1209, 1169, 1073, 1028; HRMS (ESI) *m/z*: Calcd for $C_{29}H_{34}O_5Na$ (M+Na) 485.2304, found 485.2292.



16α

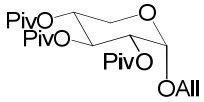
Allyl (2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16α). Rf 0.28 (petroleum ether/ethyl acetate 5 : 1). $[\alpha]_D^{25}$ = +63.8 (c = 0.19, $CHCl_3$); 1H NMR (400 MHz, $CDCl_3$) δ 7.36-7.19 (m, 30H, 6xPh), 5.91 (m, 1 H, -OCH_2<u>CH</u>=CH_2), 5.32 (dq, *J* = 17.2, 1.6 Hz, 1 H, -OCH_2CH=<u>CH_2</u>), 5.18 (ddt, *J* = 10.3, 1,6, 1.1 Hz, 1 H, -OCH_2CH=<u>CH_2</u>), 4.98 (A<u>B</u>^{1}, *J* = 10.8 Hz, 1 H, Bn), 4.91 (A<u>B</u>^{2}, *J* = 11.0 Hz, 1 H, Bn), 4.89 (A<u>B</u>^{3}, *J* = 10.9 Hz, 1 H, Bn), 4.84 (d, *J* = 3.7 Hz, 1 H, H-1), 4.82 (A<u>B</u>^{2}, *J* = 11.6 Hz, 1 H, Bn), 4.81 (A<u>B</u>^{1}, *J* = 10.8 Hz, 1 H, Bn), 4.77 (d, *J* = 3.6 Hz, 1 H, H-1), 4.73 (A<u>B</u>^{4}, *J* = 11.7 Hz, 1 H, Bn), 4.69 (A<u>B</u>^{5}, *J* = 12.2 Hz, 1 H, Bn), 4.66 (A<u>B</u>^{3}, *J* = 12.0 Hz, 1 H, Bn), 4.66 (s, 2 H, Bn), 4.60 (A<u>B</u>^{4}, *J* = 11.8 Hz, 1 H, Bn), 4.56 (A<u>B</u>^{5}, *J* = 12.0 Hz, 1 H, Bn), 4.16 (<u>A</u>BMX_2, *J* = 12.9, 5.0, 1.4 Hz, 1 H, -O<u>CH_2</u>CH=CH_2), 4.02 (t, *J* = 9.6 Hz, 1 H, H-3), 4.01 (A<u>B</u>MX_2, *J* = 12.9, 6.9, 1.2 Hz, 1 H, -O<u>CH_2</u>CH=CH_2), 3.90-3.78 (m, 3 H), 3.67 (dd, *J* = 11.2, 1.1 Hz, 1 H), 3.64 (t, *J* = 9.6 Hz, 1 H, H-3), 3.59-3.52 (m, 3 H), 3.45 (dd, *J* = 9.6, 3.6 Hz, 1 H, H-2), 3.42 (dd, *J* = 9.6, 3.5 Hz, 1 H, H-2); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.85, 138.83, 138.5, 138.44, 138.39, 138.2, 133.7, 128.39, 128.37, 128.35, 128.28, 128.07, 127.97, 127.85, 127.78, 127.66, 127.56, 127.54, 127.50, 118.4, 97.3, 95.2, 82.1, 81.0, 80.1, 79.7, 78.0, 77.8, 75.7,

75.6, 75.0, 73.4, 73.2, 72.5, 70.6, 68.0, 66.1; FTIR (neat film) 3030, 2922, 1497, 1455, 1362, 1089, 1074, 1028 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{56}H_{60}O_{10}Na$ (M+Na) 915.4084, found 915.4070.



16β

Allyl (2,3,4-tri-*O*-benzyl-α-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (16β). Rf 0.25 (petroleum ether/ethyl acetate 5 : 1). $[\alpha]_D^{24}$ = +23.7 (c = 0.14, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.26 (m, 25 H, 5xPh), 7.18-7.13 (m, 5 H, Ph), 5.88 (m, 1 H, -$OCH_2\underline{CH}$=CH_2), 5.24 (dq, *J* = 17.2, 1.6 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.17 (ddt, *J* = 10.3, 1,6, 1.2 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 4.97 ($\underline{A}B^1$, *J* = 10.9 Hz, 1 H, Bn), 4.92 ($\underline{A}B^2$, *J* = 11.1 Hz, 1 H, Bn), 4.84 (s, 2 H, Bn), 4.81 (d, *J* = 3.6 Hz, 1 H, Glu H-1), 4.77 ($A\underline{B}^1$, *J* = 10.8 Hz, 1 H, Bn), 4.75 ($A\underline{B}^2$, *J* = 11.2 Hz, 1 H, Bn), 4.75 ($\underline{A}B^3$, *J* = 11.2 Hz, 1 H, Bn), 4.71 ($\underline{A}B^4$, *J* = 11.6 Hz, 1 H, Bn), 4.71 ($\underline{A}B^5$, *J* = 10.8 Hz, 1 H, Bn), 4.63 ($A\underline{B}^5$, *J* = 13.2 Hz, 1 H, Bn), 4.60 ($A\underline{B}^4$, *J* = 11.8 Hz, 1 H, Bn), 4.50 ($A\underline{B}^3$, *J* = 11.2 Hz, 1 H, Bn), 4.28 (d, *J* = 7.6 Hz, 1 H, Xyl H-1), 4.11 ($\underline{A}BMX_2$, *J* = 12.7, 5.2, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 4.06 (dd, *J* = 10.8, 1.8 Hz, 1 H, Glu H-6), 4.00 (t, *J* = 9.8 Hz, 1 H, Glu H-3), 3.95 ($A\underline{B}MX_2$, *J* = 12.7, 5.2, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 3.90 (dd, *J* = 11.5, 4.9, 1 H, Xyl H-5_{eq}), 3.82 (m, 1 H), 3.70 (dd, *J* = 10.8, 4.1 Hz, 1 H, Glu H-6), 3.63-3.50 (m, 3 H), 3.52 (dd, *J* = 9.6, 3.4, 1 H, Glu H-2), 3.41 (dd, *J* = 8.8, 7.8 Hz, 1 H, Xyl H-2), 3.14 (dd, *J* = 11.5, 9.8 Hz, 1 H, Xyl H-5_{ax}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.9, 138.5, 138.3, 138.15, 138.10, 133.7, 128.46, 128.41, 128.32, 128.31, 128.10, 127.98, 127.94, 127.85, 127.70, 127.61, 127.56, 127.52, 127.46; FTIR (neat film) 3064, 3030, 2924, 2855, 1497, 1453, 1398, 1358, 1324, 1260, 1212, 1087, 1073, 1028 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{56}H_{60}O_{10}Na$ (M+Na) 915.4084, found 915.4050.



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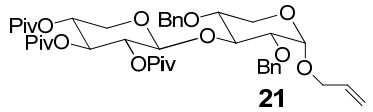
Allyl 2,3,4-tri-*O*-pivaloyl-α-D-xylopyranoside. Rf 0.2 (petroleum ether/ethyl acetate 19:1); $[\alpha]_D^{23}$ = +62.9 (c = 0.4 , $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (m, 1H, -$OCH_2\underline{CH}$=CH_2), 5.61 (t, *J* = 9.8 Hz, 1 H, H-3), 5.31 (dq, *J* = 17.2, 1.6 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.21 (ddt, *J* = 10.4, 1.6, 1.2 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.06 (d, *J* = 3.7 Hz, 1 H, H-1), 4.98 (ddd, *J* = 10.7, 9.6, 6.0 Hz, 1 H, H-4), 4.79 (dd, *J* = 10.1, 3.7 Hz, 1 H, H-2), 4.22 ($\underline{A}BMX_2$, *J* = 12.9, 5.1, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 3.92 ($A\underline{B}MX_2$, *J* = 13.0, 6.2, 1.3 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 3.76 (dd, *J* = 10.7, 6.0 Hz, 1 H, H-5_{eq}), 3.60 (t, *J* = 10.7 Hz, 1 H, H-5_{ax}), 1.17 (s, 9 H, 3xCH_3), 1.15 (s, 9 H, 3xCH_3), 1.14 (s, 9 H, 3xCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.14, 177.86, 177.31, 133.7, 118.3, 95.1, 71.5, 69.6, 69.4, 69.1, 58.7, 39.16, 39.13, 39.11, 27.57, 27.48, 27.44; FTIR (neat film) 2974, 1740, 1639, 1481, 1398, 1280, 1147, 1049, 943 cm^{-1} ; HRMS (ESI) *m/z*: Calcd for $C_{23}H_{38}O_8$ $(M+Na)^+$ 465.2459, found 465.2463.



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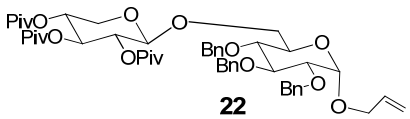
Allyl (2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-(1→3)-2,4-di-*O*-benzyl-α-D-xylopyranoside (21). Rf 0.25 (benzene/ethyl acetate 19:1); $[\alpha]_D^{24}$ = +13.2 (c = 0.11, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32-7.19 (m, 10 H, 2xPh), 5.79 (m, 1 H, -$OCH_2\underline{CH}$=CH_2), 5.21 (dq, *J* = 17.2, 1.6 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.19 (t, *J* = 9.0 Hz, 1 H, H-3‘), 5.12 (ddt, *J* = 10.4, 1.6, 1.3 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.06 (d, *J* = 7.4 Hz, 1 H, H-1‘), 5.00 (dd, *J* = 9.1, 7.4 Hz, 1 H, H-2‘), 4.92 (td, *J* = 9.3, 5.5 Hz, 1 H, H-4‘), 4.75 ($\underline{A}B^1$, *J* = 11.8 Hz, 1 H, Bn), 4.60 (d, *J* = 4.6 Hz, 1 H, H-1), 4.59 ($\underline{A}B^2$, *J* = 8.4 Hz, 1 H, Bn), 4.56 ($A\underline{B}^2$, *J* = 9.7 Hz, 1 H, Bn), 4.44 ($A\underline{B}^1$, *J* = 11.7 Hz, 1 H, Bn), 4.19 (t, *J* = 8.9 Hz, 1 H, H-3), 4.04-3.97 (m, 2 H, -$O\underline{CH_2}CH$=CH_2, H-5_{eq}‘), 3.78 ($A\underline{B}MX_2$, *J* = 12.8, 6.5, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 3.45 (m, 2 H, H-5_{eq} and H-5_{ax}), 3.37 (dd, *J* = 8.7, 7.3 Hz, 1H, H-4), 3.33 (dd, *J* = 9.4, 3.5 Hz, 1 H,

H-2), 3.07 (dd, *J* = 11.6, 9.8 Hz, 1 H, H-5_{ax}'), 1.12 (s, 9 H, 3xCH_3), 1.08 (s, 9 H, 3xCH_3), 1.07 (s, 9 H, 3xCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 177.1, 176.7, 138.4, 138.0, 133.6, 128.5, 128.4, 128.1, 128.03, 128.0, 127.7, 118.1, 100.4, 95.0, 80.7, 75.6, 73.6, 72.8, 71.7, 71.6, 69.2, 68.0, 62.4, 59.9, 38.8, 38.7, 27.20, 27.16, 27.0; FTIR (neat film) 2969, 2935, 2873, 1742, 1480, 1456, 1398, 1364, 1278, 1178, 1143, 1113, 1090, 1076, 1037 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{42}H_{58}O_{12}$ (M) 754.3928, found 754.3921.



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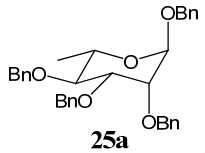
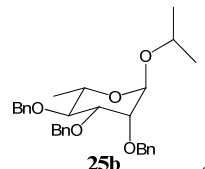
Allyl (2,3,4-tri-*O*-pivaloyl-β-D-xylopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (22). Rf 0.30 (benzene/ethyl acetate 19:1); $[\alpha]_D^{23}$ = +1.72 (c = 0.46, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.3-7.1 (m, 15 H, 3xPh), 5.85 (m, 1 H, -$OCH_2\underline{CH}{=}CH_2$), 5.26 (dq, *J* = 17.2, 1.6 Hz, 1 H, -$OCH_2CH{=}\underline{CH_2}$), 5.17 (t, *J* = 8.9 Hz, 1 H, Xyl H-3), 5.14 (ddt, *J* = 10.3, 1.7, 1.2 Hz, 1 H, -$OCH_2CH{=}\underline{CH_2}$), 4.92 ($\underline{A}B^1$, *J* = 10.7 Hz, 1 H, Bn), 4.9 (dd, *J* = 9.1, 7.1 Hz, 1 H, Xyl H-2), 4.86 (td, *J* = 9.1, 5.4 Hz, 1 H, Xyl H-4), 4.79 ($\underline{A}B^2$, *J* = 11.1 Hz, 1 H, Bn), 4.73 ($A\underline{B}^1$, *J* = 10.7 Hz, 1 H, Bn), 4.67 (d, *J* = 3.5 Hz, 1 H, Glu H-1), 4.66 ($\underline{A}B^3$, *J* = 12.1 Hz, 1 H, Bn), 4.58 ($A\underline{B}^3$, *J* = 12.1 Hz, 1 H, Bn), 4.5 ($A\underline{B}^2$, *J* = 11.1 Hz, 1 H, Bn), 4.38 (d, *J* = 7.1 Hz, 1 H, Xyl H-1), 4.06 ($\underline{AB}MX_2$, *J* = 12.9, 5.1, 1.4 Hz, 1 H, -$O\underline{CH_2}CH{=}CH_2$), 3.98 (dd, *J* = 11.4, 5.1 Hz, 1H, Xyl H-5_{eq}), 3.96 (t, *J* = 9.1 Hz, 1H, Glu H-3), 3.90 ($\underline{AB}MX_2$, *J* = 12.9, 5.1, 1.4 Hz, 1 H, -$O\underline{CH_2}CH{=}CH_2$), 3.83 (dd, *J* = 10.7, 1.8 Hz, 1 H, Glu H-6), 3.73 (m, 1 H, H-5, Glu), 3.54 (dd, *J* = 10.8, 5.4 Hz, 1 H, Glu H-6), 3.41 (dd, *J* = 9.6, 3.6 Hz, 1 H, Glu H-2), 3.36 (dd, *J* = 10.1, 9.0 Hz, 1 H, Glu H-4), 3.17 (dd, *J* = 11.7, 9.2 Hz, 1 H, Xyl H-5_{ax}), 1.08 (s, 9 H, 3xCH_3), 1.06 (s, 9 H, 3xCH_3), 1.05 (s, 9 H, 3xCH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.3, 177.11, 177.10, 176.4, 138.9, 138.2, 138.1, 133.7, 128.42, 128.39, 128.32, 128.06, 127.85, 127.82, 127.77, 127.73, 127.48, 118.1, 101.1, 95.3, 81.9, 79.7, 77.8, 75.6, 74.9, 73.0, 71.3, 70.6, 69.9, 68.9, 68.0, 62.2, 38.7, 38.68,38.65, 27.10, 27.09, 27.04; FTIR (neat film) 3066, 3032, 2971, 2934, 2873, 1742, 1497, 1480, 1456, 1398, 1366, 1278, 1208, 1144, 1090, 1038 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{50}H_{66}O_{13}Na$ (M+Na) 897.4401, found 897.4379.



25a (known compound)

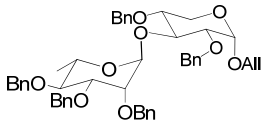
Benzyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (25a). Rf 0.25 (petroleum ether/ethyl acetate 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 20 H), 4.95 ($\underline{A}B^1$, *J* = 10.8 Hz, 1 H), 4.85 (d, *J* = 1.8 Hz, 1 H), 4.74 ($\underline{A}B^2$, *J* = 12.6 Hz, 1 H), 4.70 ($A\underline{B}^2$, *J* = 12.4 Hz, 1 H), 4.67 ($\underline{A}B^3$, *J* = 11.8 Hz, 1 H), 4.64 ($A\underline{B}^1$, *J* = 10.8 Hz, 1 H), 4.63 ($\underline{A}B^4$, *J* = 11.8 Hz, 1 H), 4.60 ($A\underline{B}^4$, *J* = 11.8 Hz, 1 H), 4.22 ($A\underline{B}^3$, *J* = 12.0 Hz, 1 H), 3.91 (dd, *J* = 9.3, 3.2 Hz, 1 H), 3.81 (dd, *J* = 3.1, 1.9 Hz, 1 H), 3.80-3.73 (m, 1 H), 3.64 (t, *J* = 9.4 Hz, 1 H), 1.35 (d, *J* = 6.2 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.0, 138.7, 137.8, 128.37, 128.34, 128.31, 128.0, 127.9, 127.72, 127.70, 127.62, 127.60, 127.5, 97.7, 80.5, 80.1, 75.4, 74.8, 72.7, 72.2, 68.8, 68.2, 18.4; HRMS (ESI) *m/z*: Calcd for $C_{34}H_{36}O_5$ (M) 524.2563, found 524.2543.



25b (known compound)

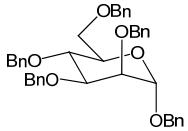
Isopropyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (25b). Rf 0.30 (petroleum ether/ethyl acetate 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.25 (m, 15 H), 4.94 ($\underline{A}B^1$, *J* = 10.7 Hz, 1 H), 4.83 (d, *J* = 1.8 Hz, 1 H), 4.79 ($\underline{A}B^2$, *J* = 12.5 Hz, 1 H), 4.71 ($A\underline{B}^2$, *J* = 12.5 Hz, 1 H), 4.64 ($A\underline{B}^1$, *J* = 10.7 Hz, 1 H), 4.63 (s, 2 H), 3.88 (dd, *J* = 9.4, 3.1 Hz, 1 H), 3.84 (pentalet, *J* = 6.1 Hz, 1 H), 3.81-3.71 (m, 2 H), 3.61 (t, *J* = 9.4 Hz, 1 H), 1.32 (d, *J* = 6.2 Hz, 3 H), 1.13

(d, *J* = 6.3 Hz, 3 H); 1.04 (d, *J* = 6.1 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.6, 138.4, 128.36, 128.31, 128.1, 127.9, 127.63, 127.61, 127.5, 127.4, 95.8, 80.7, 80.3, 75.5, 75.4, 72.8, 72.1, 68.6, 67.9, 23.2, 21.1, 18.0; HRMS (ESI) *m/z*: Calcd for $C_{30}H_{36}O_5$ (M) 476.2563, found 476.2545.



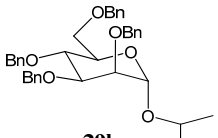
26

Allyl (2,3,4-tri-*O*-benzyl-α-L-rhamnopyranosyl)-(1→3)-2, 4-di-*O*-benzyl-α-D-xylopyranoside (26). Rf 0.45 (methylene chloride/ethyl ether 60 : 1). $[\alpha]_D^{24}$ = +10.3 (c = 0.21, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 25 H, 5xPh), 5.88 (m, 1 H, -$OCH_2\underline{CH}$=CH_2), 5.31 (d, *J* = 1.3 Hz, 1 H, Rha H-1), 5.29 (dq, *J* = 17.2, 1.6 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.19 (ddt, *J* = 10.3, 1,6, 1.2 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 4.95 ($\underline{A}B^1$, *J* = 11.1 Hz, 1 H, Bn), 4.67 (d, *J* = 3.4 Hz, 1 H, Xyl H-1), 4.64 ($\underline{A}B^2$, *J* = 11.9 Hz, 1 H, Bn), 4.64-4.62 (m, 2 H, Bn), 4.62 ($A\underline{B}^1$, *J* = 11.1 Hz, 1 H, Bn), 4.55 ($\underline{A}B^5$, *J* = 12.6 Hz, 1 H, Bn), 4.48-4.46(m, 2 H, Bn), 4.46 ($A\underline{B}^5$, *J* = 12.5 Hz, 1 H, Bn), 4.43 ($A\underline{B}^2$, *J* = 12.0 Hz, 1 H, Bn), 4.11 ($\underline{A}BMX_2$, *J* = 12.9, 5.0, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 4.08-4.02 (m, 1 H, Rha H-5), 4.05 (t, *J* = 9.3 Hz, 1 H, Rha H-4), 3.91-3.85 (m, 2 H, -$O\underline{CH_2}CH$=CH_2 and Xyl H-2), 3.80 (dd, *J* = 3.0, 1.9 Hz, 1 H, Rha H-2), 3.60 (t, *J* = 9.4 Hz, 1 H, Xyl H-3), 3.56 (dd, *J* = 10.6, 4.4 Hz,1 H, Xyl H-5), 3.51 (t, *J* = 10.7 Hz, 1 H, Xyl H-5), 3.40-3.35 (m, 1 H, Xyl H-4), 3.33 (dd, *J* = 9.5, 3.5 Hz, 1 H, Rha H-3), 1.12 (d, *J* = 6.2 Hz, 3 H, CH_3); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.1, 138.9, 138.6, 138.0, 137.8, 133.7, 128.8, 128.4, 128.34, 128.26, 128.18, 128.13, 127.88, 127.80, 127.78, 127.58, 127.51, 127.35, 127.29, 117.9, 98.6 ($^1J_{CH}$ = 170 Hz), 95.2 ($^1J_{CH}$ = 173 Hz), 80.8, 80.6, 80.1, 76.8, 76.4, 75.3, 75.2, 73.4, 72.4, 72.0, 71.9, 68.12, 68.05, 59.9, 17.8; FTIR (neat film) 3063, 3030, 2870, 1497, 1454, 1364, 1260, 1208, 1088, 1074, 1029 cm^{-1}; HRMS (ESI) *m/z*: Calcd for $C_{49}H_{54}O_9Na$ (M+Na) 809.3666, found 809.3647.



29a (known compound)

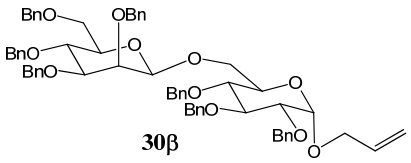
Benzyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (29a). Rf 0.30 (petroleum ether/ethyl acetate 7:1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38-7.23 (m, 23 H), 7.17-7.14 (m, 2H), 4.98 (d, *J* = 1.8 Hz, 1 H), 4.88 ($\underline{A}B^1$, *J* = 10.7 Hz, 1 H), 4.71 ($\underline{A}B^2$, *J* = 11.9 Hz, 1 H), 4.71 (s, 2 H), 4.68 ($\underline{A}B^3$, *J* = 11.9 Hz, 1 H), 4.61 (s, 2 H), 4.56 ($A\underline{B}^2$, *J* = 12.1 Hz, 1 H), 4.50 ($A\underline{B}^1$, *J* = 10.7 Hz, 1 H), 4.45 ($A\underline{B}^3$, *J* = 11.9 Hz, 1 H), 4.05-3.90 (m, 2 H), 3.86-3.72 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.52, 138.45, 138.42, 138.3, 137.3, 128.36, 128.29, 128.27, 128.0, 127.8, 127.7, 127.6, 127.54, 127.49, 127.42, 97.2, 80.2, 75.1, 75.0, 74.7, 73.4, 72.5, 72.2, 72.1, 69.3, 68.9; HRMS (ESI) *m/z*: Calcd for $C_{41}H_{42}O_6$ (M) 630.2981, found 630.2981.



29b (known compound)

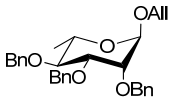
Isopropyl 2,3,4,6-tetra-*O*-benzyl-α-D-mannopyranoside (29b). Rf 0.20 (petroleum ether/ethyl acetate 9:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.24 (m, 18 H), 7.16-7.13 (m, 2H), 4.96 (d, *J* = 1.8 Hz, 1 H), 4.87 ($\underline{A}B^1$, *J* = 10.6 Hz, 1 H), 4.78 ($\underline{A}B^2$, *J* = 12.5 Hz, 1 H), 4.71 ($A\underline{B}^2$, *J* = 12.6 Hz, 1 H), 4.68 ($\underline{A}B^3$, *J* = 12.2 Hz, 1 H), 4.63 (s, 2 H), 4.54 ($A\underline{B}^3$, *J* = 12.1 Hz, 1 H), 4.49 ($A\underline{B}^1$, *J* = 10.6 Hz, 1 H), 4.0 (t, *J* = 9.4 Hz, 1 H), 3.94-3.70 (m, 6 H), 1.19 (d, *J* = 6.3 Hz, 3 H); 1.09 (d, *J* = 6.1 Hz, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.7, 138.5, 128.3, 128.2, 128.1, 127.8,

127.7, 127.56, 127.52, 127.45, 127.39, 95.8, 80.4, 75.3, 75.19, 75.17, 73.3, 72.6, 72.1, 71.8, 69.4, 68.9, 23.2, 21.2; HRMS (ESI) *m/z*: Calcd for $C_{37}H_{42}O_6$ (M) 582.2981, found 582.2977.



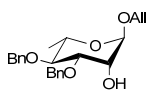
30β

Allyl (2,3,4,6-tetra-*O*-benzyl-β-D-mannopyranosyl)-(1→6)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (30β). Rf 0.2 (petroleum ether/diethyl ether 2:1); $[\alpha]_D^{25}$ = +3.49 (c = 0.17 in $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.19 (m, 35 H, 7xPh), 5.90 (m, 1 H, -$OCH_2\underline{CH}$=CH_2), 5.26 (dq, *J* = 17.2, 1.5 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.18 (ddt, *J* = 10.3, 1.5, 1.1 Hz, 1 H, -OCH_2CH=$\underline{CH_2}$), 5.03 ($\underline{A}B^1$, *J* = 10.9 Hz, 1 H, Bn), 4.94 ($\underline{A}B^2$, *J* = 12.6 Hz, 1 H, Bn), 4.88 ($\underline{A}B^3$, *J* = 10.7 Hz, 1H, Bn), 4.83 ($A\underline{B}^1$, *J* = 10.9 Hz, 1H, Bn), 4.81 ($\underline{A}B^4$, *J* = 11.5 Hz, 1 H, Bn), 4.77 (d, *J* = 3.4 Hz, 1 H, Glu H-1), 4.78 ($A\underline{B}^2$, *J* = 12.5 Hz, 1 H, Bn), 4.76 ($\underline{A}B^5$, *J* = 12.1 Hz, 1 H, Bn), 4.65 ($A\underline{B}^5$, *J* = 12.1 Hz, 1 H, Bn), 4.58 (s, 2 H, Bn), 4.52 ($\underline{A}B^6$, *J* = 11.8 Hz, 1 H, Bn), 4.52 ($A\underline{B}^3$, *J* = 10.7 Hz, 1 H, Bn), 4.51 ($A\underline{B}^4$, *J* = 11.5 Hz, 1 H, Bn), 4.46 ($A\underline{B}^6$, *J* = 11.9 Hz, 1 H, Bn), 4.16 (dd, *J* = 10.5, 2.0 Hz, 1 H, Glu H-6), 4.14 (m, 1 H, -$O\underline{CH_2}CH$=CH_2), 4.08 (s, 1 H, Man H-1), 4.05 (dd, *J* = 9.3, 9.2 Hz, 1 H, Man H-4), 3.96 ($AB\underline{M}X_2$, *J* = 12.9, 5.3, 1.4 Hz, 1 H, -$O\underline{CH_2}CH$=CH_2), 3.86-3.84 (m, 1 H), 3.83 (t, *J* = 9.6 Hz, 1 H, Glu H-3), 3.77 (d, *J* = 2.0 Hz, 1 H, Man H-2), 3.72 ($A\underline{B}^6$, *J* = 7.1 Hz, 1 H, Man H-6), 3.69 ($A\underline{B}^6$, *J* = 6.2 Hz, 1 H, Man H-6), 3.52 (dd, *J* = 9.7, 3.6 Hz, 1 H, Glu H-2), 3.47 (t, *J* = 9.5 Hz, 1 H, Glu H-4), 3.45 (dd, *J* = 10.4, 5.2 Hz, 1 H, Glu H-6), 3.41 (dd, *J* = 9.4, 3.0 Hz, 1 H, Man H-3), 3.40-3.36 (m, 1 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 139.1, 138.8, 138.7, 138.6, 138.55, 138.49, 138.85, 128.83, 138.81, 133.8, 128.79, 128.77, 128.76, 128.71, 128.6, 128.56, 128.53, 128.52, 128.4, 128.3, 128.24, 128.22, 128.16, 128.10, 128.08, 128.05, 128.0, 127.95, 127.89, 127.84, 118.7, 101.8 ($^1J_{CH}$ = 153.5 Hz), 95.5 ($^1J_{CH}$ = 167 Hz), 82.7, 82.5, 80.2, 78.0, 76.4, 76.1, 75.6, 75.4, 75.2, 74.1, 73.9, 73.6, 71.9, 70.3, 70.1, 68.6, 68.3; FTIR (neat film) 3088, 3063, 3031, 2922, 2866, 1497, 1454, 1361, 1107, 1059, 1072, 1028; HRMS (ESI) *m/z*: Calcd for $C_{64}H_{68}O_{11}Na$ (M+Na) 1035.4659, found 1035.4690.

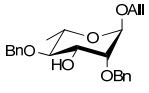


23 (known compound)

Allyl 2,3,4-tri-*O*-benzyl-α-L-rhamnopyranoside (**23**). To a solution of **35** (1.26 g, 6.2 mmol) in DMF (15 mL) at 0 °C was added sodium hydride (1.1 g, 28 mmol) and the reaction mixture was stirred for 1 hour. Benzyl bromide (4.5 mL, 37 mmol) was added and the reaction continued at room temperature for 20 hours before quenched with ice-water (15 mL). Workup as usual (ethyl acetate) afforded the crude material which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate 9:1, Rf 0.3) to provide **23** (2.48 g, 84% yield) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.25 (m, 15 H), 5.84 (m, 1 H), 5.20 (dq, *J* = 17.2, 1.7 Hz, 1 H), 5.14 (ddt, *J* = 10.4, 1.7, 1.3 Hz, 1 H),4.95 ($\underline{A}B^1$, *J* = 10.8 Hz, 1 H), 4.80 (d, *J* = 1.8 Hz, 1 H), 4.77 ($\underline{A}B^2$, *J* = 12.5 Hz, 1 H), 4.72 ($A\underline{B}^2$, *J* = 12.5 Hz, 1 H), 4.64 ($A\underline{B}^1$, *J* = 10.8 Hz, 1 H), 4.62 (s, 2 H), 4.11 ($\underline{A}BMX_2$, *J* = 13.0, 5.0, 1.6 Hz, 1 H), 3.93-3.87 (m, 2 H), 3.80 (dd, *J* = 3.1, 1.8 Hz, 1 H), 3.75-3.68 (m, 1 H), 3.63 (t, *J* = 9.3 Hz, 1 H), 1.34 (d, *J* = 6.1 Hz, 3 H); HRMS (ESI) *m/z*: Calcd for $C_{30}H_{34}O_5$ (M) 474.2406, found 474.2394.



32



33 (known compound)

Allyl 2,3-*O*-benzylidene-4-*O*-benzyl-α-L-rhamnopyranosi-de (**36**). To allyl rhamnoside **35** (213 mg, 1.05 mmol) stirred in benzaldehyde dimethyl acetal (0.8 mL, 5.3mmol) was added *p*-toluenesulfonic acid (4.0 mg, 0.02mmol). The reaction mixture was heated in a microwave oven at 190 °C for 10 minutes and then cooled

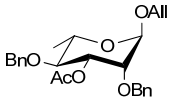
down to room temperature. The reaction mixture was diluted with water and underwent usual workup (ethyl acetate). Flash column chromatography on silica gel (hexane/ethyl acetate 3:1, Rf 0.25) of the crude residue gave O-Allyl 2,3-O-benzylidene-L-rhamnoside (233 mg,76 % yield) as a colorless syrup.

To allyl 2,3-*O*-benzylidene-α-L-rhamnoside (146 mg, 0.5 mmol) in DMF (0.3 mL) at 0 °C was added sodium hydride (40 mg, 1 mmol). After 1 hour, benzyl bromide (0.18 mL, 1.5mmol) was added. The reaction mixture was stirred at room temperature for 4 hours before quenched by ice-water (15 mL). Workup as usual (ethyl acetate) afforded crude reaction residue which was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 9:1, Rf 0.4) to gave **32** (178 mg, 93 % yield) as a colorless syrup.

Allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**32**) **and allyl 2,4-di-*O*-benzyl-α-L-rhamnopyran-oside (33).** To a stirred solution of **36** (440 mg, 1.1 mmol) and lithium aluminum hydride (86 mg, 2.3 mmol) in 6 mL of CH_2Cl_2 at reflux was added dropwise $AlCl_3$ (452 mg, 3.4 mmol) in 2.5 mL ethyl ether. The reaction mixture was stirred for 1 hour, cooled down to room temperature and quenched by ice-water (15ml). Workup as usual (ethyl acetate) furnished a colorless syrup which was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate gradient (5:1 to 1:1) to give **32** (210 mg, 46% yield) and **33** (240 mg, 53% yield) as a colorless syrup.

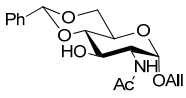
Allyl 3,4-di-*O*-benzyl-α-L-rhamnopyranoside (**32**) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 10 H), 5.87 (m, 1 H), 5.26 (dq, *J* = 17.2, 1.7 Hz, 1 H), 5.18 (ddt, *J* = 10.4, 1.7, 1.3 Hz, 1 H), 4.89 (AB, *J* = 10.9 Hz, 1 H), 4.85 (d, *J* = 1.8 Hz, 1 H), 4.69 (s, 2 H), 4.64 (AB, *J* = 10.9 Hz, 1 H), 4.15 (ABMX$_2$, *J* = 12.9, 6.1, 1.3 Hz, 1 H), 3.04 (m, 1 H), 3.96 (ABMX$_2$, *J* = 12.9, 6.1, 1.3 Hz, 1 H), 3.87 (dd, *J* = 9.1, 3.3 Hz, 1 H), 3.79-3.72 (m, 1 H), 3.46 (t, *J* = 9.3 Hz, 1 H),), 2.54 (d, *J* = 1.3 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.3, 137.9, 133.7, 128.5, 128.4, 127.97, 127.93, 127.8, 127.7, 117.4, 98.0, 80.0, 79.9, 75.4, 72.0, 68.5, 67.8, 67.3, 17.8; HRMS (ESI) *m/z*: Calcd for $C_{23}H_{28}O_5$ (M) 384.1937, found 384.1929.

Allyl 2,4-di-*O*-benzyl-α-L-rhamnopyranoside (33) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.28 (m, 10 H), 5.85 (m, 1 H), 5.25 (dq, *J* = 17.2, 1.7 Hz, 1 H), 5.16 (ddt, *J* = 10.4, 1.5, 1.3 Hz, 1 H), 4.90 (AB^1, *J* = 11.0 Hz, 1 H), 4.86 (d, *J* = 1.3 Hz, 1 H), 4.73 (AB^2, *J* = 11.8 Hz, 1 H), 4.65 (AB^1, *J* = 11.0 Hz, 1 H), 4.58 (AB^2, *J* = 11.8 Hz, 1 H), 4.14 (ABMX$_2$, *J* = 13.0, 5.0, 1.5 Hz, 1 H), 4.00-3.90 (m, 2 H), 3.75 (dd, *J* = 3.8, 1.6 Hz, 1 H), 3.73-3.66 (m, 1 H), 3.32 (t, *J* = 9.3 Hz, 1 H), 2.33 (d, *J* = 9.3 Hz, 1H), 1.33 (d, *J* = 6.3 Hz, 3 H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 137.7, 133.7, 128.6, 128.4, 128.03, 127.97, 127.95, 127.7, 117.2, 96.1, 82.3, 78.7, 75.1, 73.1, 71.7, 67.8, 67.2, 18.0; HRMS (ESI) *m/z*: Calcd for $C_{23}H_{28}O_5$ (M) 384.1937, found 384.1928.



37 (known compound)

Allyl 3-*O*-acetyl-2,4-di-*O*-benzyl-α-L-rhamnopyranoside (**37**). Triethyl amine (0.25 ml, 1.8 mmol) was added to a stirred solution of **33** (275 mg, 0.72 mmol) and 4-(N,N-dimethylamino)pyridine (2 mg) in 10 mL of CH_2Cl_2, followed by acetic anhydride (0.17 mL, 1.8 mmol). The reaction mixture was stirred at room temperature for 20 hours and then concentrated. The residue was purified by flash column chromatography on silica gel (methylene chloride/diethyl ether 60:1, Rf 0.33) to afford **37** (295 mg, 97% yield) as a colorless syrup. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.26 (m, 10 H), 5.85 (m, 1 H), 5.25 (dq, *J* = 17.2, 1.6 Hz, 1 H), 5.22 (dd, *J* = 9.6, 3.4 Hz, 1 H), 5.16 (ddt, *J* = 10.4, 1.6, 1.3 Hz, 1 H), 4.79 (d, *J* = 1.8 Hz, 1 H), 4.71 (AB^1, *J* = 11.2 Hz, 1 H), 4.66 (AB^2, *J* = 12.2 Hz, 1 H), 4.64 (AB^1, *J* = 11.2 Hz, 1 H), 4.57 (AB^2, *J* = 12.2 Hz, 1 H), 4.14 (ABMX$_2$, *J* = 13.0, 5.0, 1.5 Hz, 1 H), 3.95 (ABMX$_2$, *J* = 13.0, 6.1, 1.4 Hz, 1 H), 3.87 (dd, *J* = 3.4, 1.9 Hz, 1 H), 3.81-3.76 (m, 1 H), 3.63 (t, *J* = 9.3 Hz, 1 H), 1.97 (s, 3H), 1.33 (d, *J* = 6.2 Hz, 3 H).

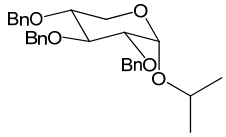


(known compound)

Allyl 2-acetamido-4,6-O-benzylidene-2-deoxy-α-D-glucopyranoside (34). To *N*-acetyl-D-glucos-amine (442 mg, 2 mmol) in 8 mL of allyl alcohol at 0 °C was added boron trifluoride diethyl etherate (0.24 mL, 2 mmol). The reaction mixture was then stirred at 70 °C for 3 hours, cooled down and concentrated. The residue was recrystalized in EtOH-Et_2O (3:1) to afford allyl 2-acetamido-2-deoxy-D-glucopyranoside (344 mg, 66% yield) as white powder.

Allyl 2-acetamido-2-deoxy-α-D-glucopyranoside (260 mg, 1 mmol), benzaldehyde dimethyl acetal (0.35

mL, 2.3 mmol) and *p*TsOH (19 mg, 0.1 mmol) were stirred in DMSO (2.5 mL) at 60 ^{o}C for 10 hours. The reaction mixture was then quenched with saturated aqueous solution of $NaHCO_3$ (0.2 ml) and extracted with CH_2Cl_2/MeOH (8:1) (3 × 20 mL). The combined organic layers was concentrated and the residue was recrystalized in EtOH-Et_2O (3:1) to afford the desired product (248 mg, 71% yield) as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51-7.49 (m, 2 H), 7.39-7.36 (m, 3 H), 6.00 (d, *J* = 8.8 Hz, 1 H), 5.91 (m, 1 H), 5.58 (s, 1H), 5.32 (dq, *J* = 17.2, 1.5 Hz, 1 H), 5.26 (ddt, *J* = 10.4, 1.3, 1.0 Hz, 1 H), 4.91 (d, *J* = 3.8 Hz, 1 H), 4.28 (dd, *J* = 9.9, 4.5 Hz, 1 H), 4.25-4.19 (m, 2 H), 4.01 (A<u>B</u>MX_2, *J* = 12.8, 6.3, 1.2 Hz, 1 H), 3.95 (t, *J* = 9.6 Hz, 1 H), 3.86 (td, *J* = 9.7, 4.7 Hz, 1 H), 3.77 (t, *J* = 10.1 Hz, 1 H), 3.61 (t, *J* = 9.2 Hz, 1 H), 2.07 (s, 3H); HRMS (ESI) *m/z*: Calcd for $C_{18}H_{23}NO_6$ (M) 349.1525, found 349.1523.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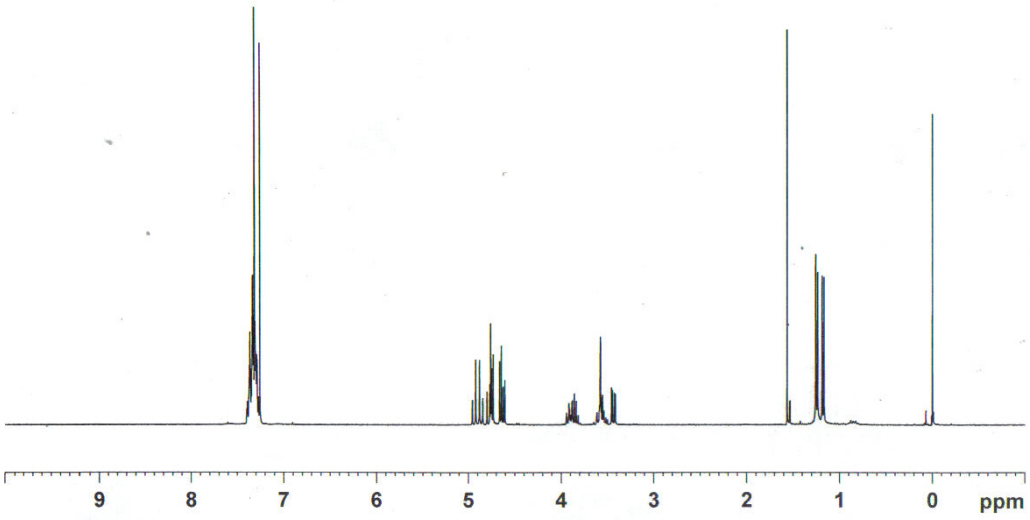
O
O

12α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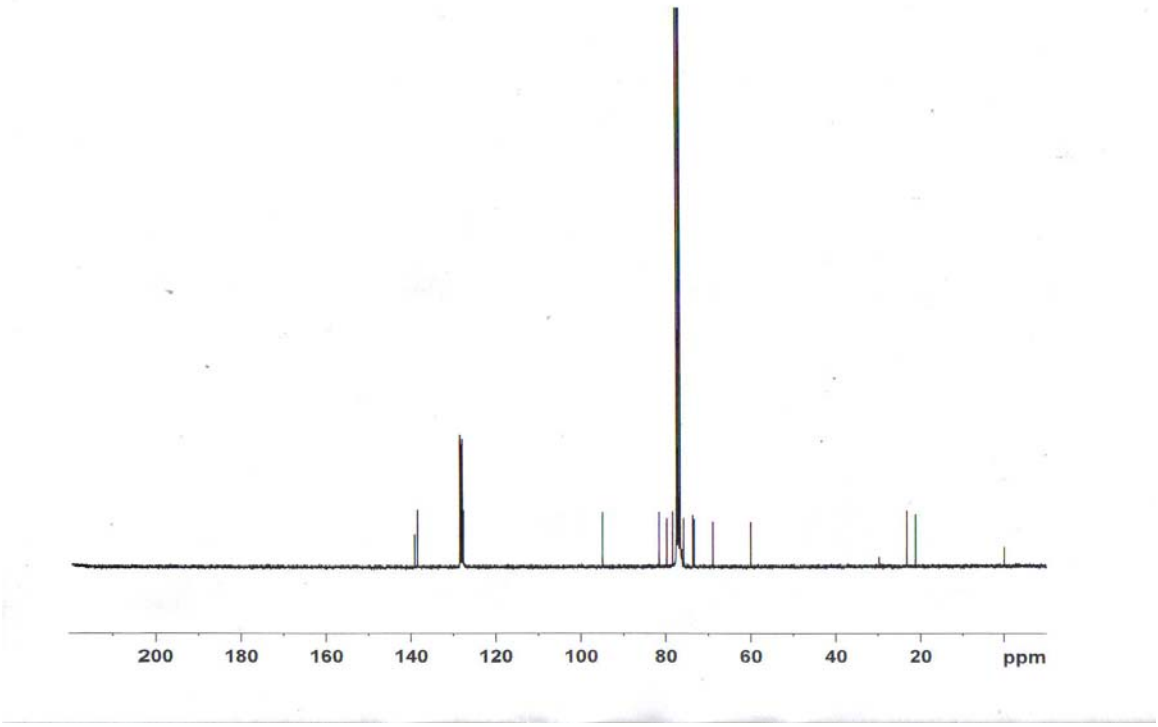
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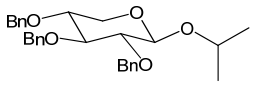
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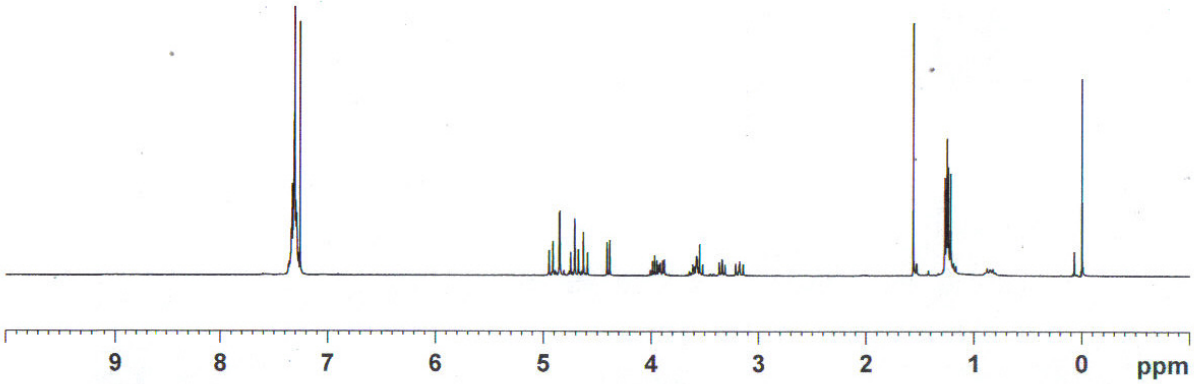
12β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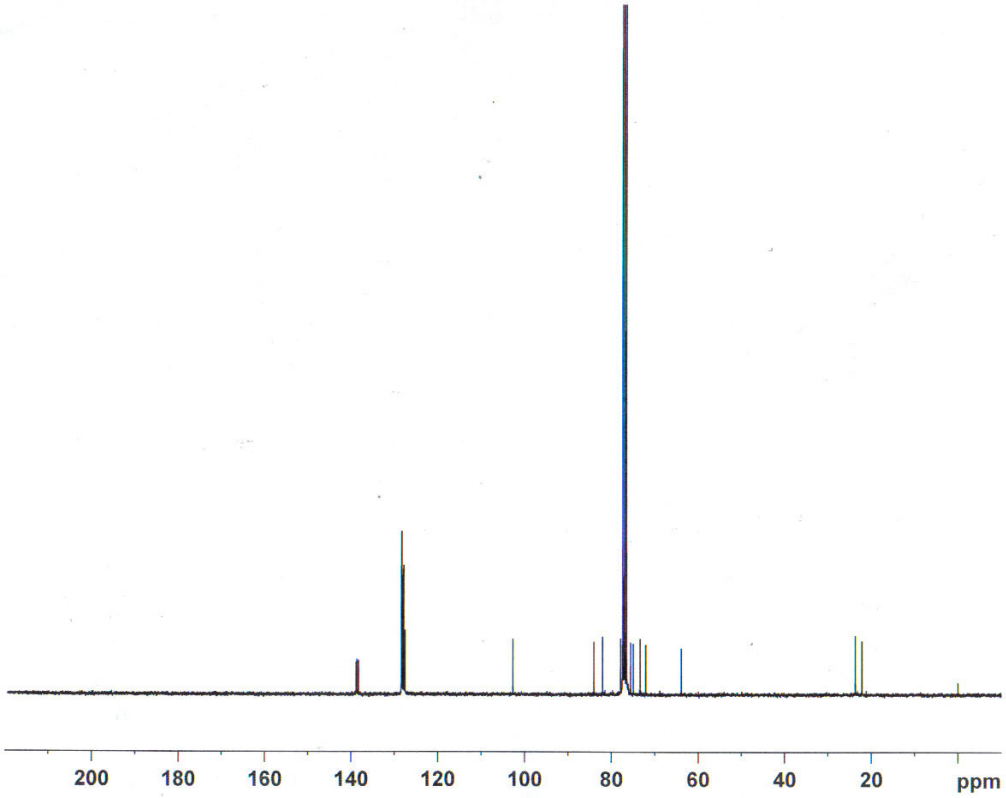
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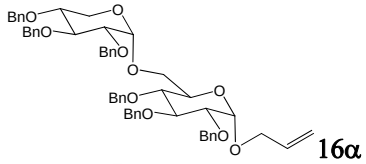
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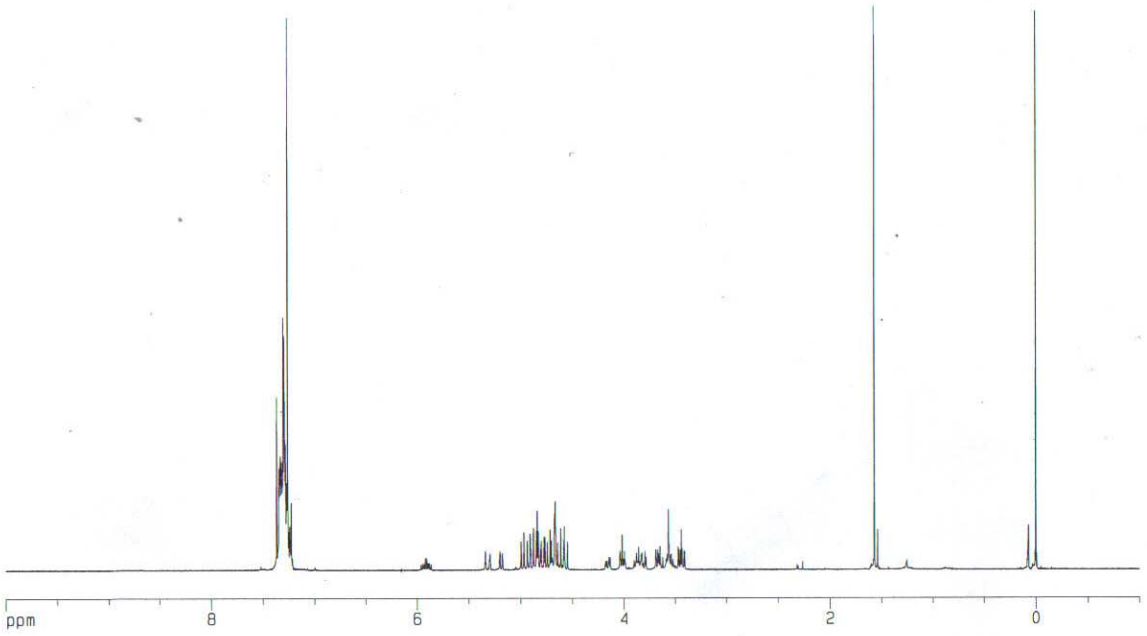
O
O

16α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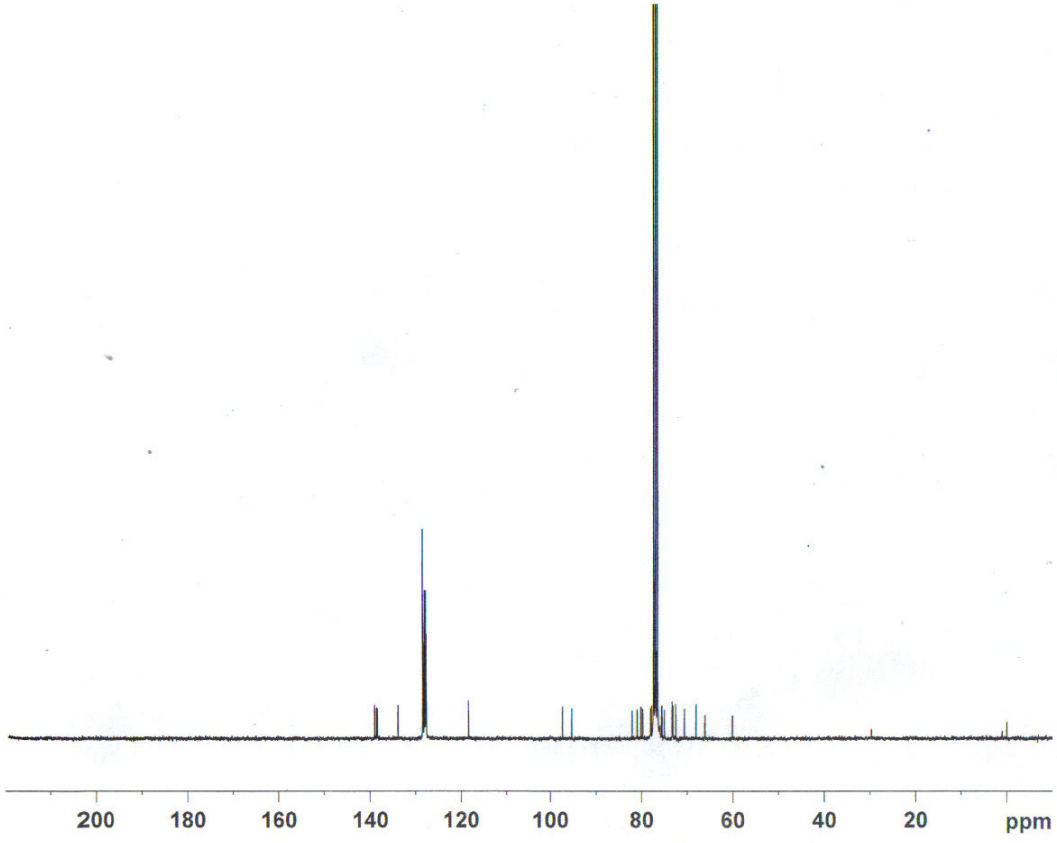
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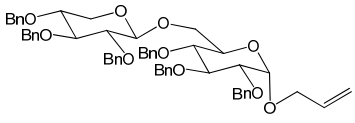
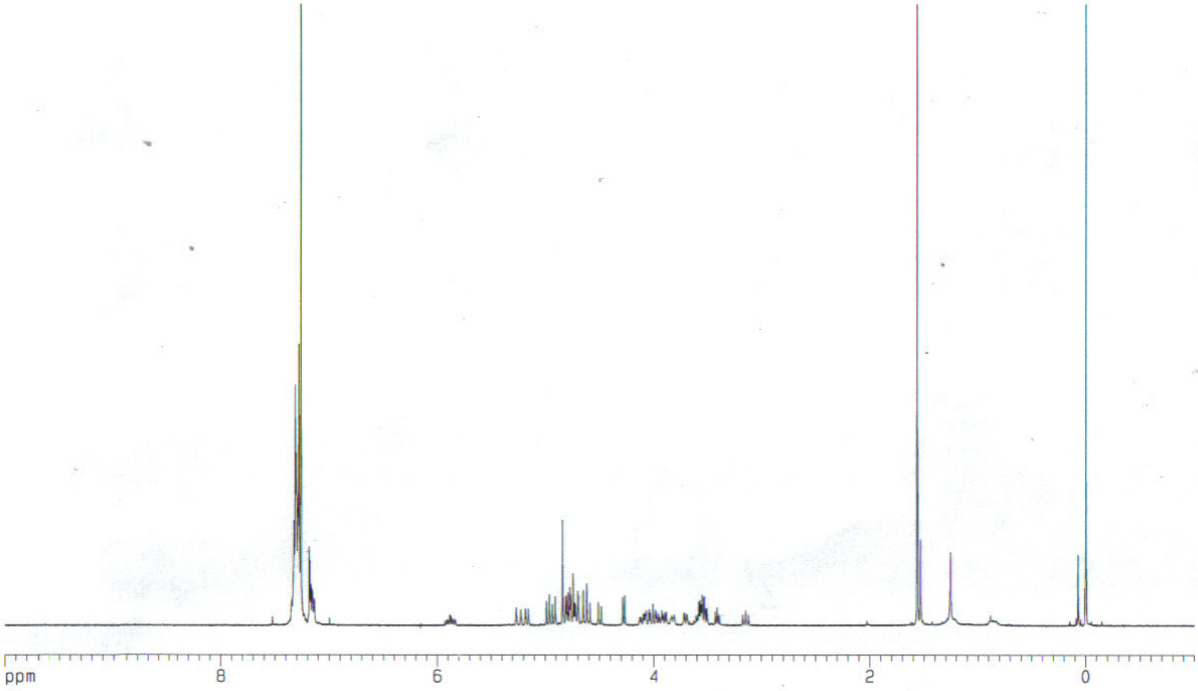
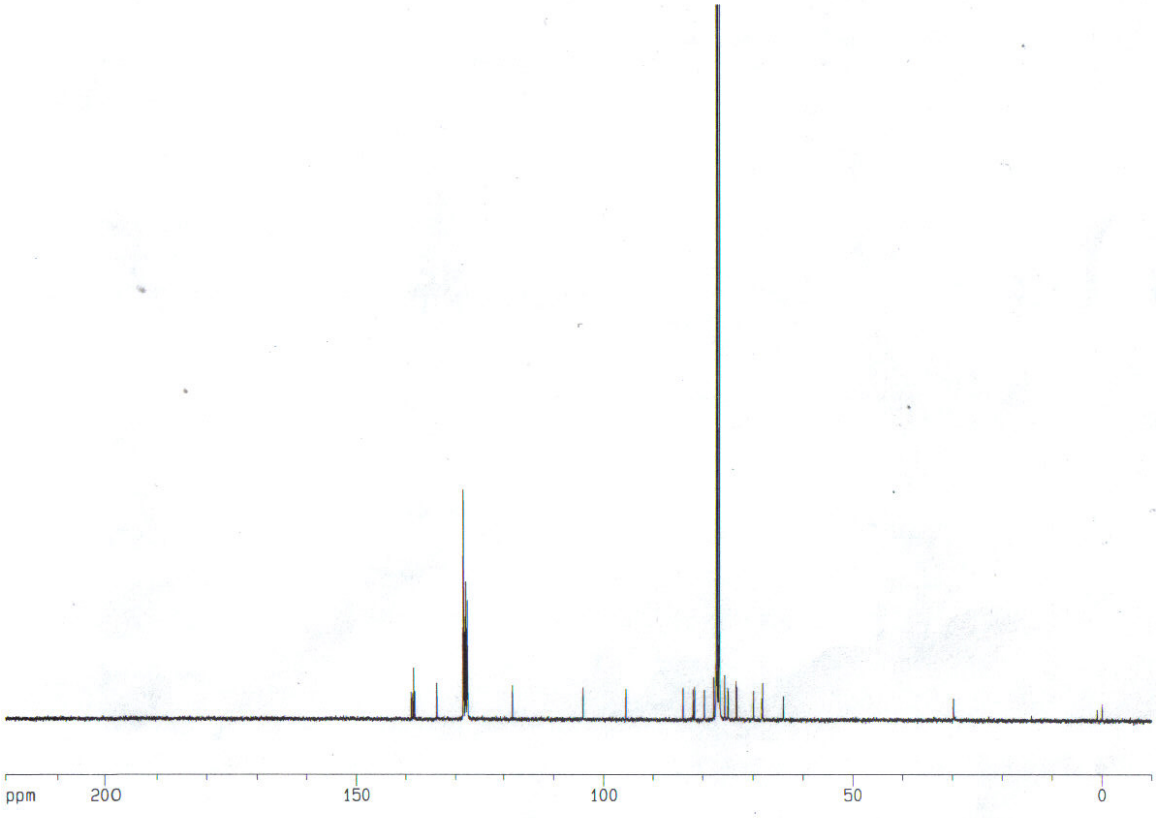
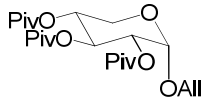


16β



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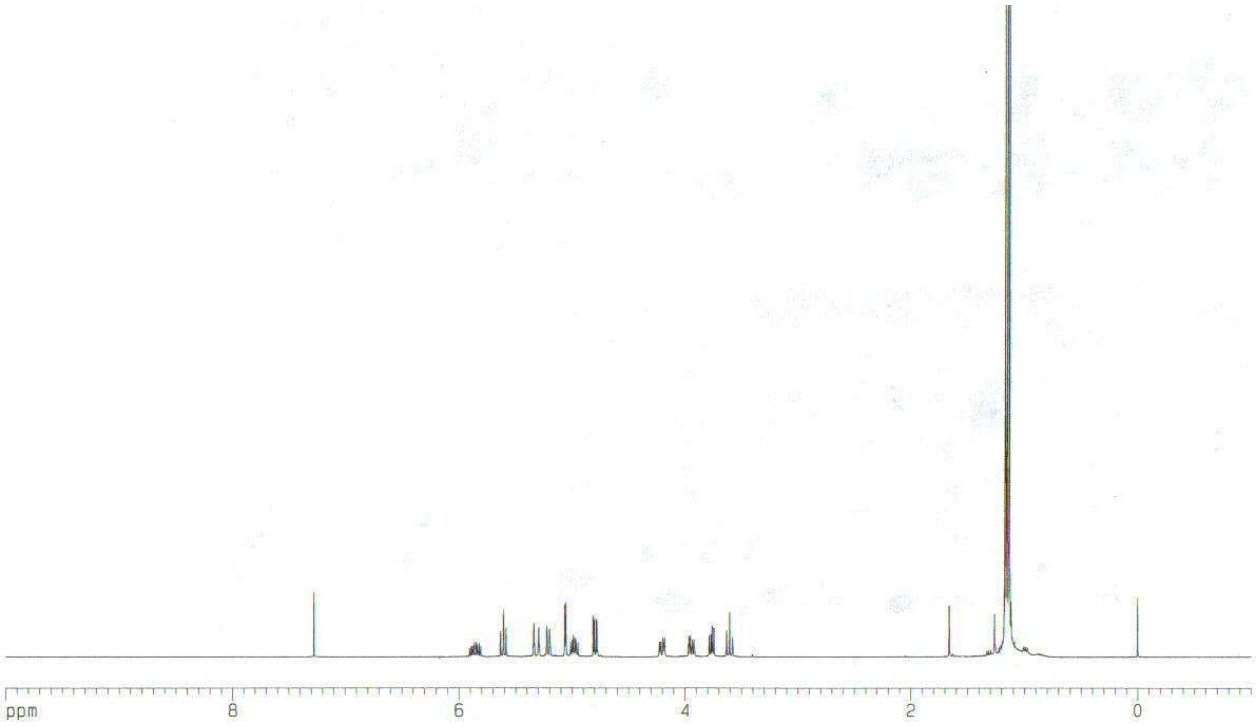
PivO
OAll

20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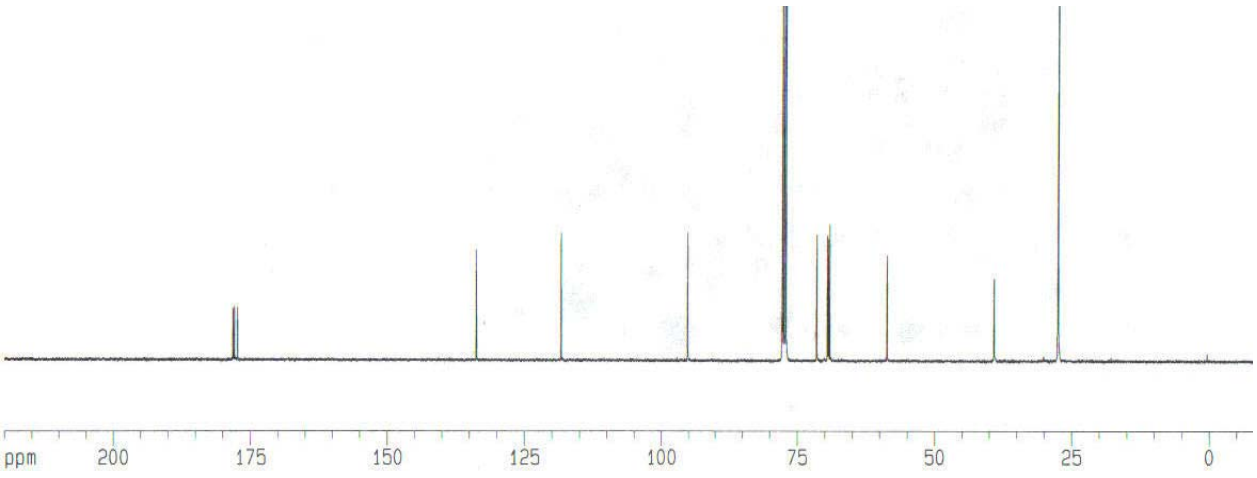
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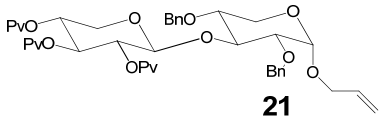

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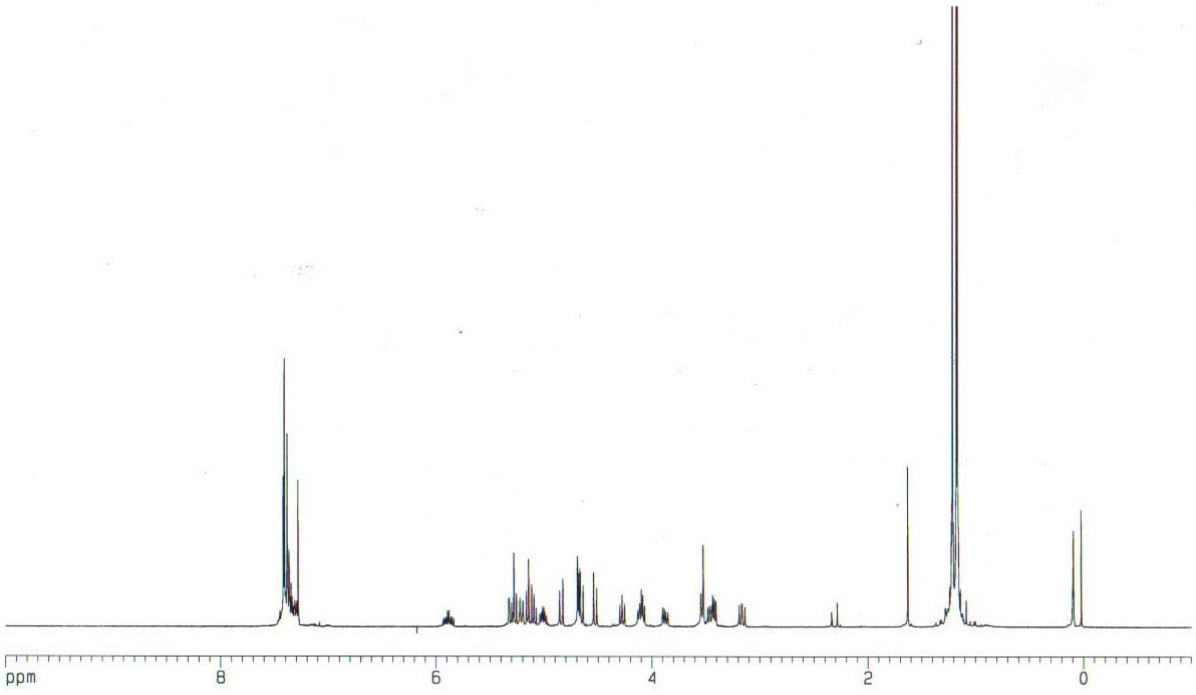

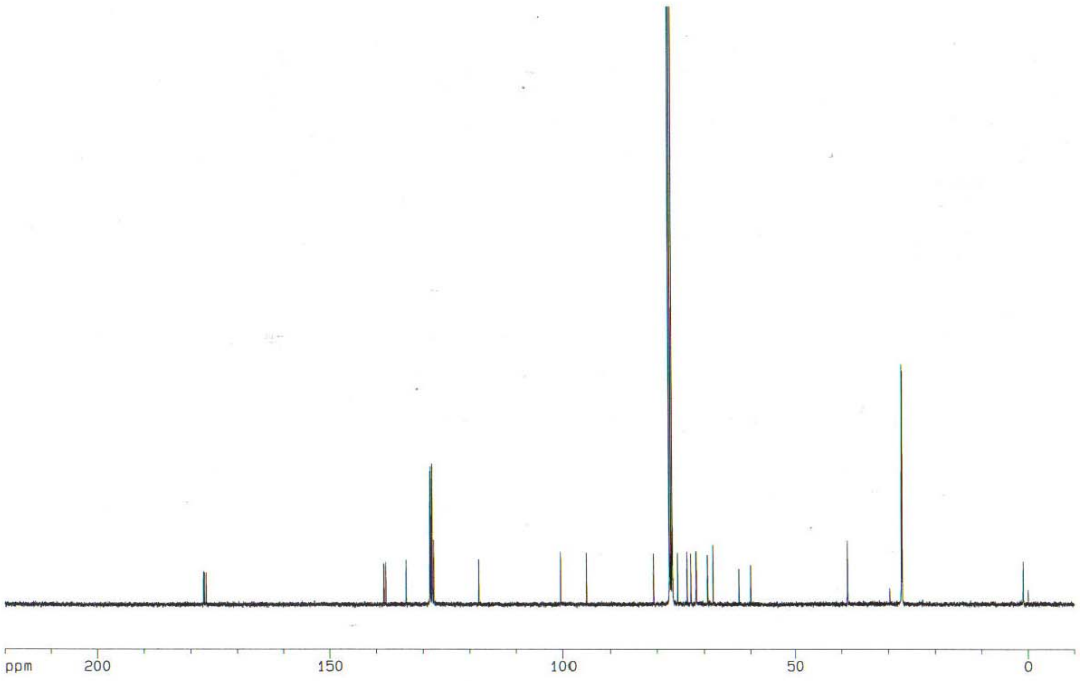

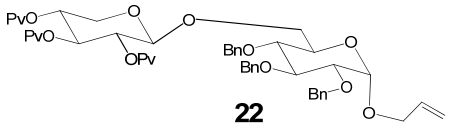

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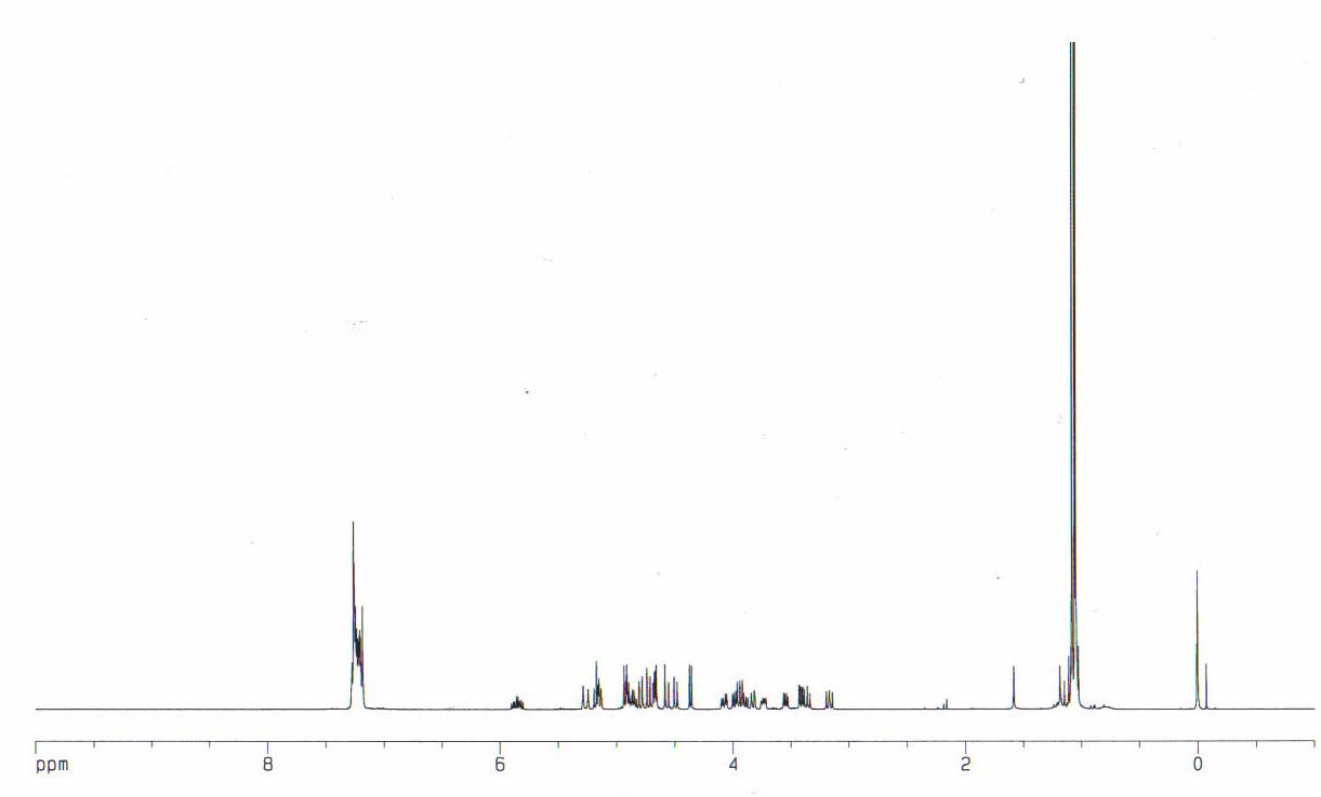

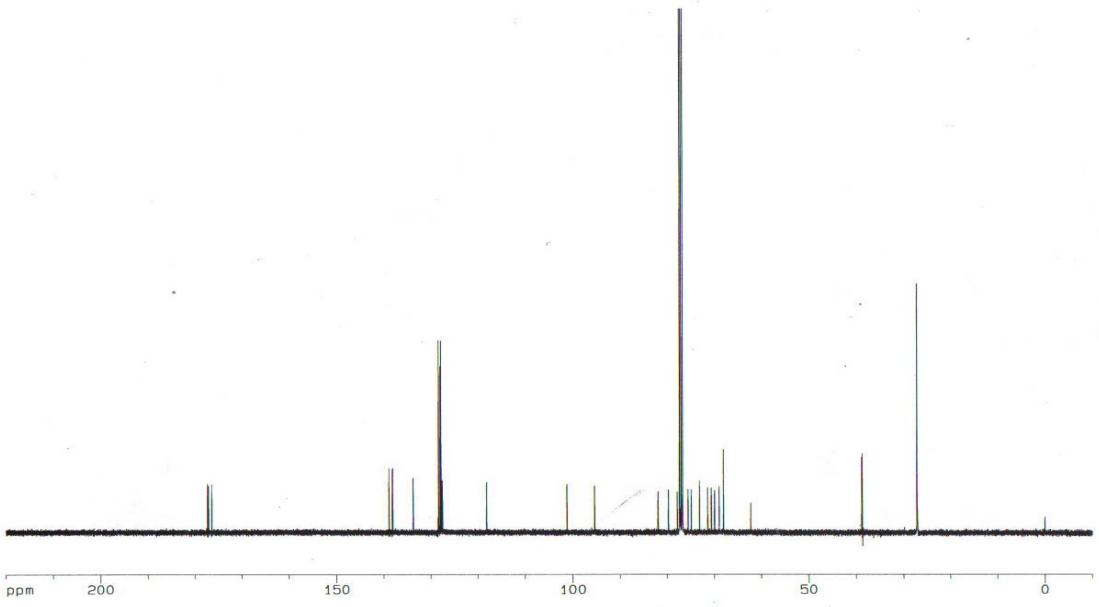

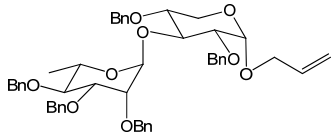
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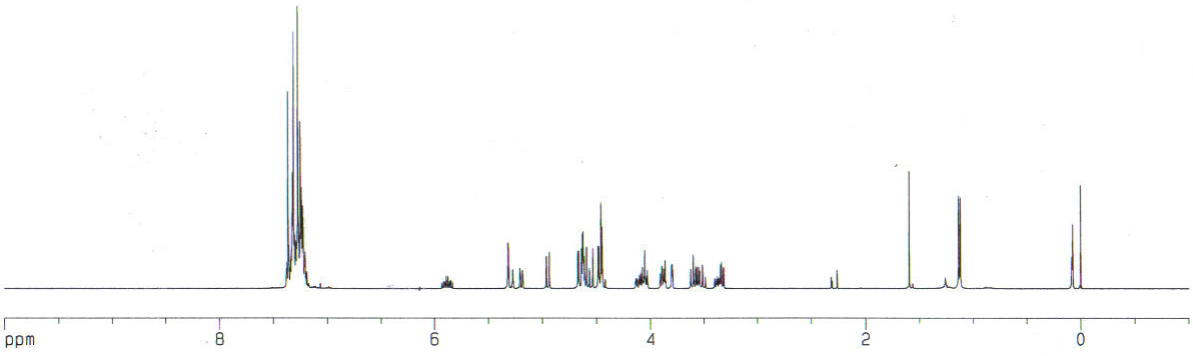
26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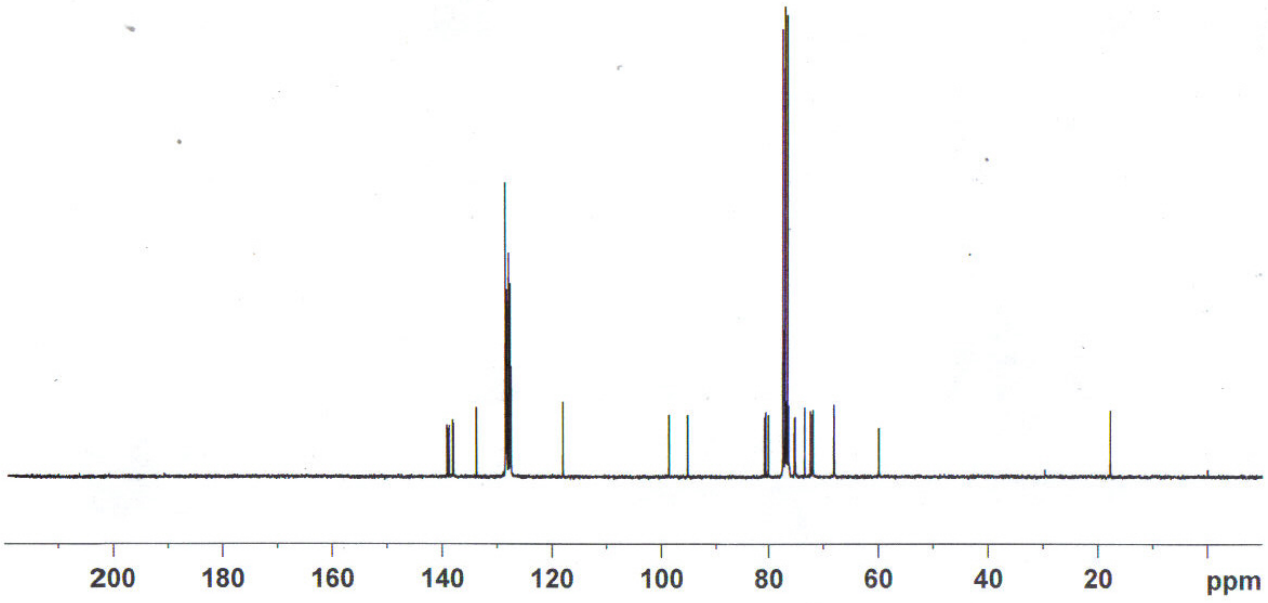
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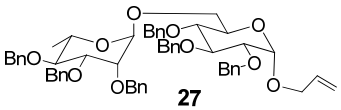

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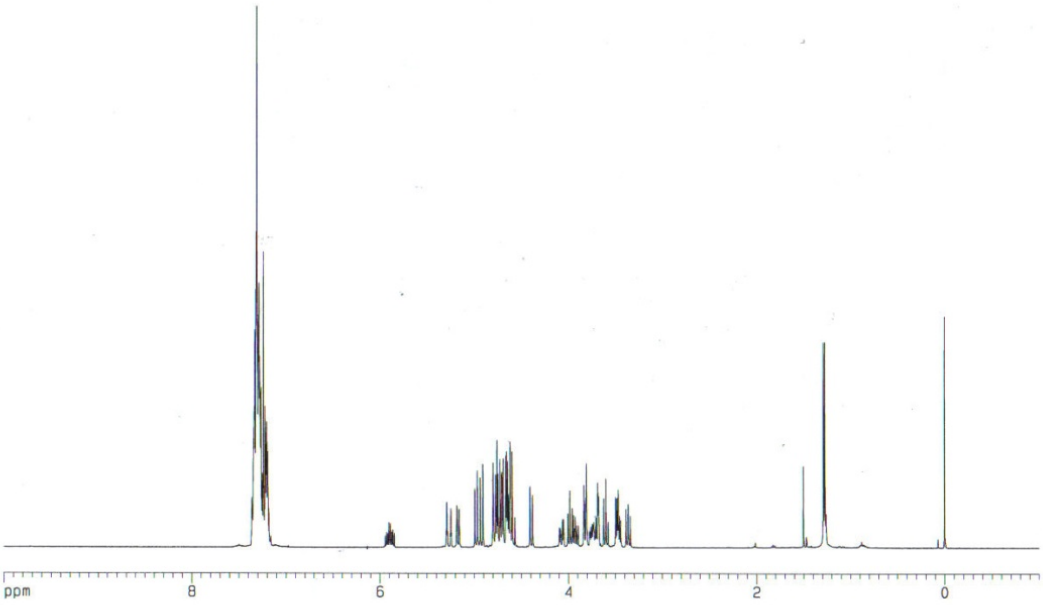
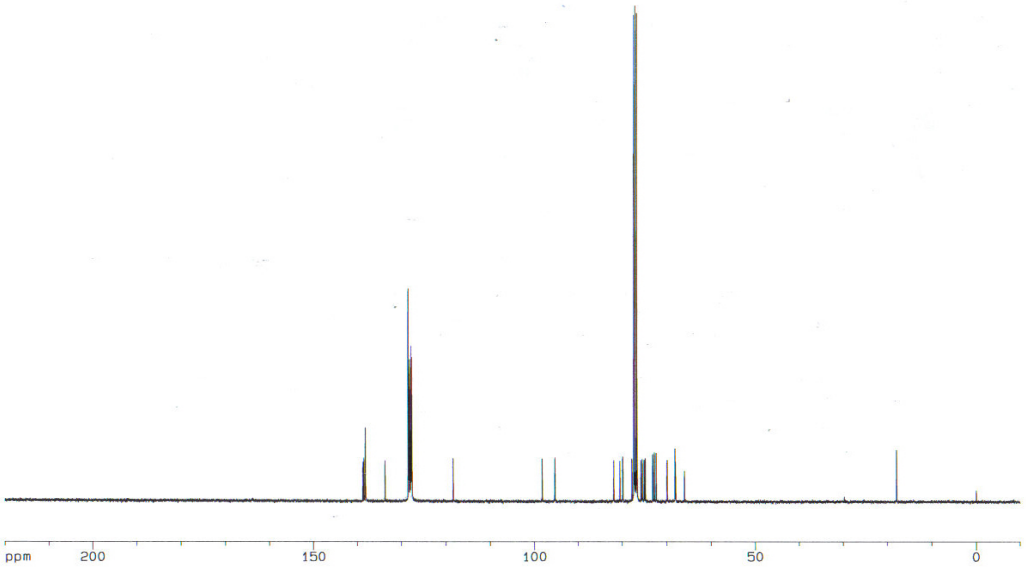
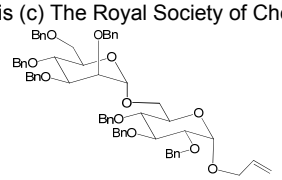
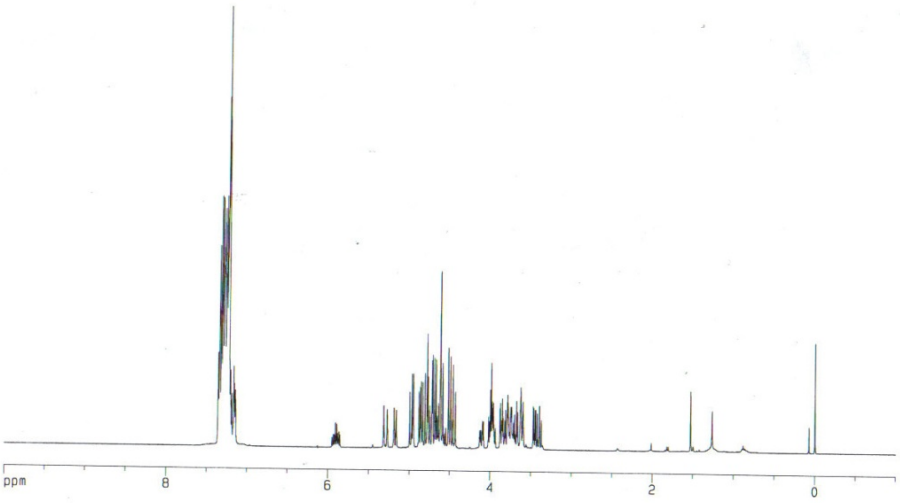
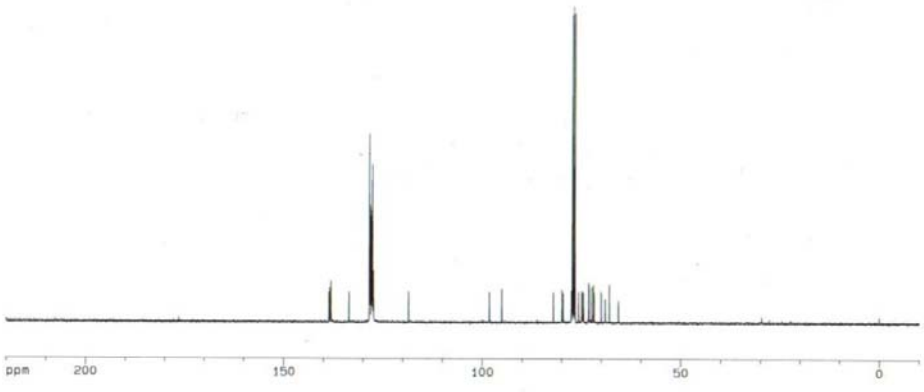


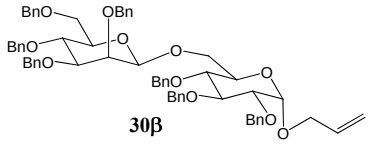




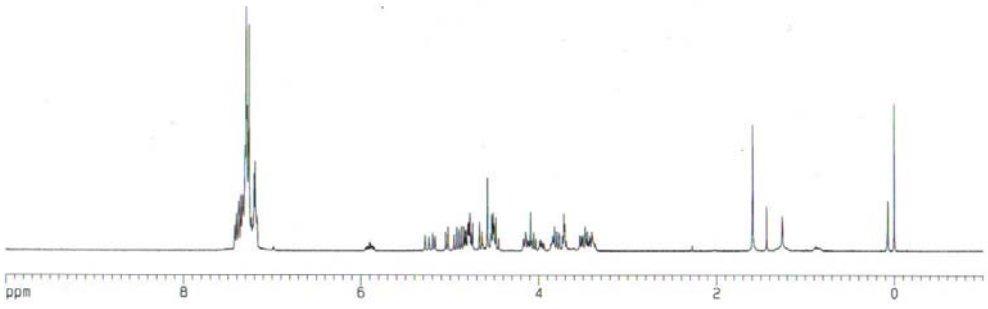
30α

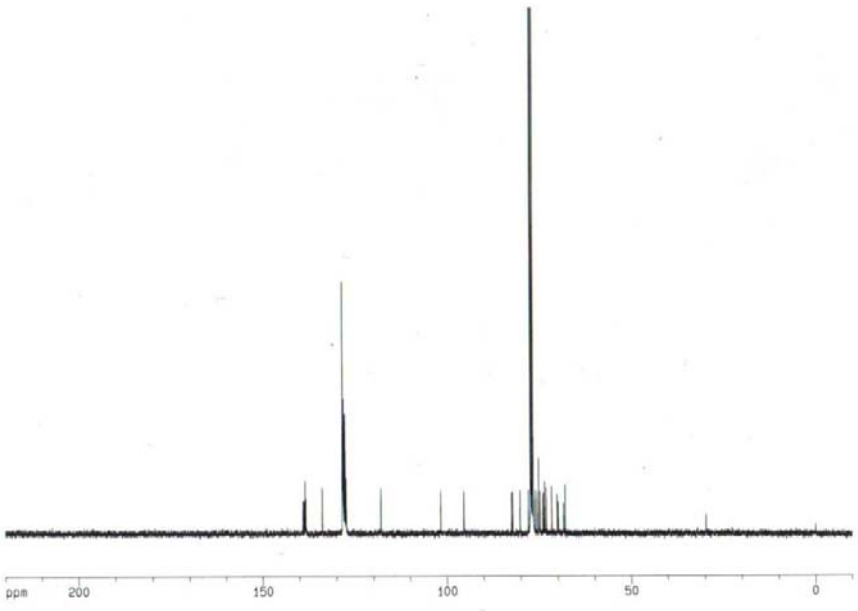


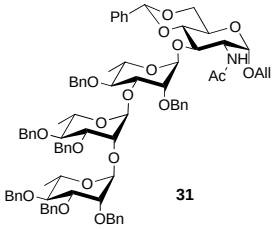




30β



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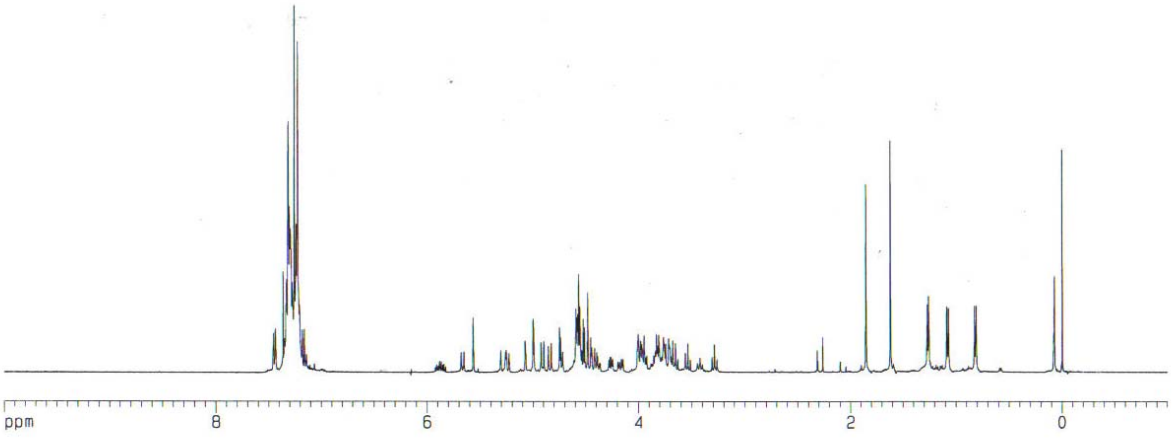
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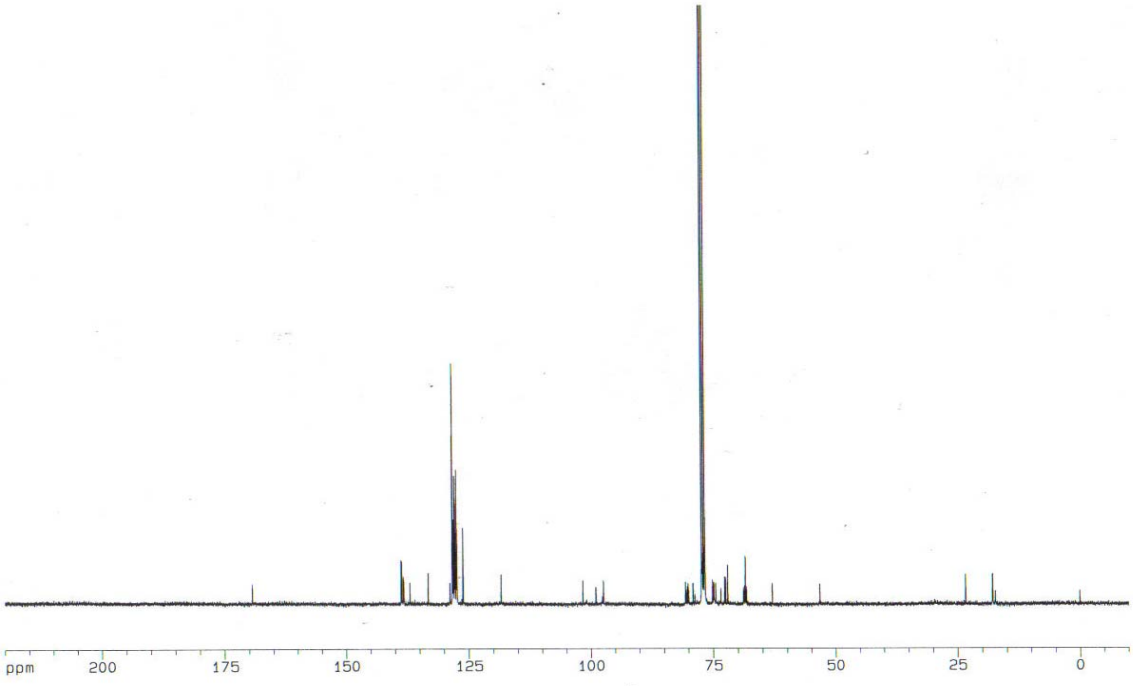
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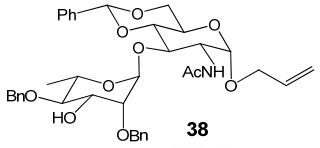
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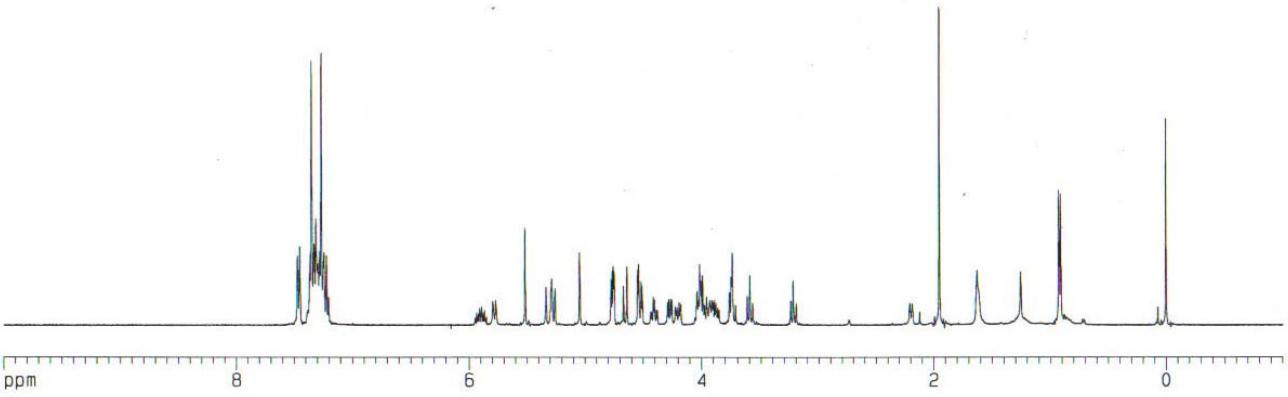
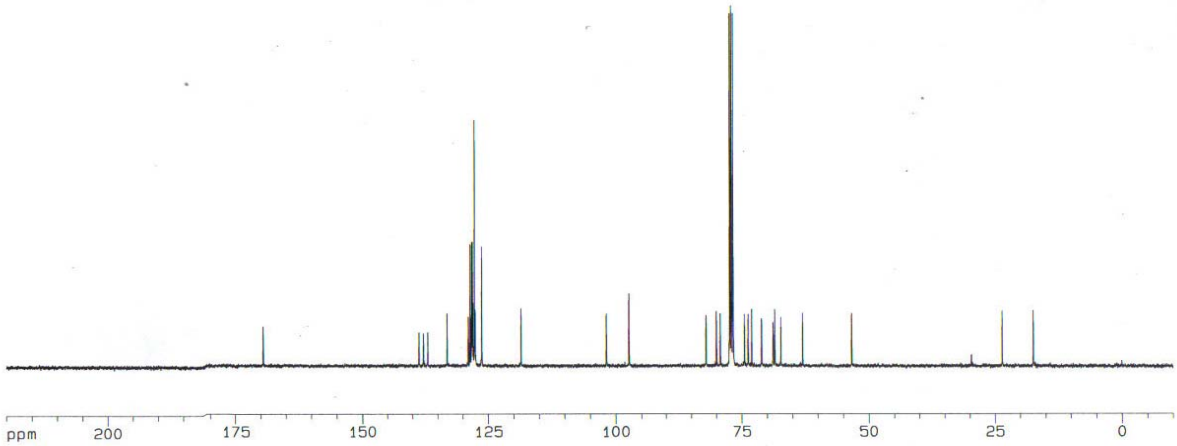
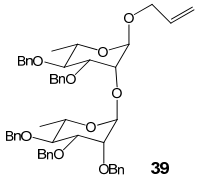
OBn

38


ppm
8
6
4
2
0


ppm
200
175
150
125
100
75
50
25
0



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