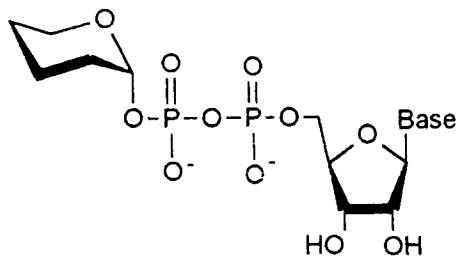


## Legends

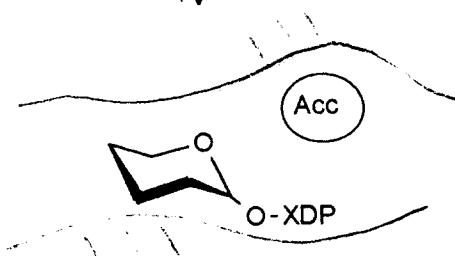
- Figure 1** Glycosylation by glycosyltransferases [21].
- Figure 2** Galactosylation with galactosyltransferase and integrated cofactor regeneration  
(Enzymes: **i** phosphoglucomutase, **ii** UDP-glucose-pyrophosphorylase, **iii** inorganic pyrophosphorylase, **iv** UDP-galactose-4-epimerase, **v** galactosyltransferase, **vi** pyruvate kinase) [31].
- Figure 3** Galactosylation with UDP-2d-Gal as donor  
(Enzymes: **i-vi** cf. Fig. 2, **vii** hexokinase) [38].
- Figure 4** Galactosylation leading to  $\beta$ 1- $\beta$ 1- and  $\beta$ 1-4-transfer products  
(Enzymes: **iv, v** cf. Fig. 2; **R<sup>1</sup>, R<sup>2</sup>** cf. Tab. 1) [43].
- Figure 5** Postulated structural map of the substrate binding site of galactosyltransferase  
(**R<sup>1</sup>, R<sup>2</sup>** cf. Tab. 1) [43].
- Figure 6** Sialylation of lactosamine derivates with  $\alpha$ 2-6-sialyltransferase [48, 55-59].
- Figure 7** Enzymatic synthesis with integrated cofactor regeneration  
(Enzymes: **iii, vi** cf. Fig. 2, **viii** sialate-cytidyl-transferase, **ix**  $\alpha$ 2-3- or  $\alpha$ 2-6-sialyltransferase, **x** adenylate kinase) [48, 65].
- Figure 8** Enzymatic fucosylation with integrated cofactor regeneration  
(Enzymes: **vi** cf. Fig. 2, **xi** GDP-fucose-pyrophosphorylase, **xii**  $\alpha$ 1-3/4-fucosyltransferase) [72].
- Figure 9** Fucosylation employing modified donors and acceptors [74].
- Figure 10** Phosphorylase catalyzed synthesis of modified maltooligosaccharides [85].
- Figure 11** Phosphorolytic formation and degradation of modified maltooligosaccharides [86].
- Table 1** Tabulation of substituent effects on acceptor ability [43].



Activated Donor  
(Gly-O-XDP)

Glycosyltransferase (GlyT)

Acceptor (Acc)



GlyT

-XDP



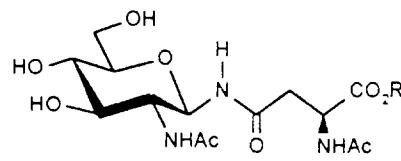
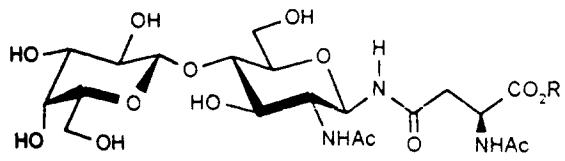
Glc

Glc

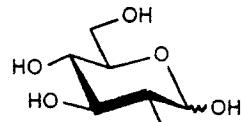
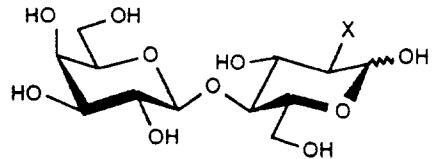
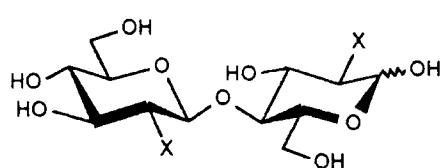
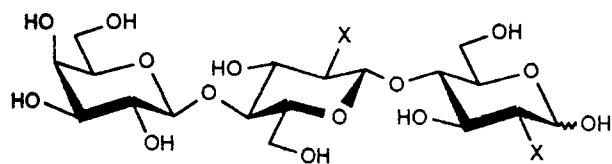
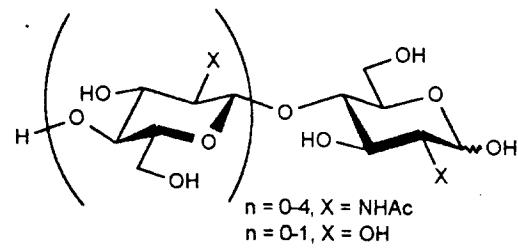
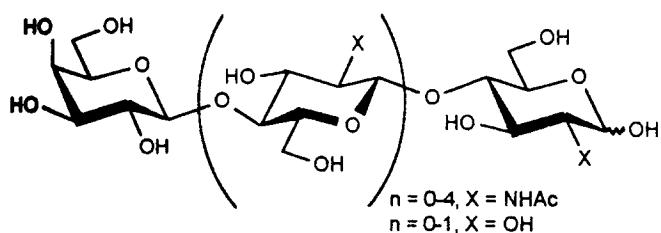
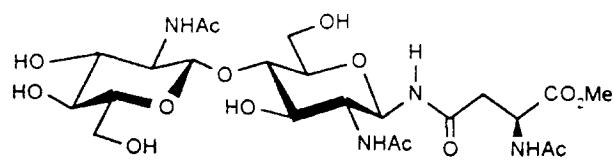
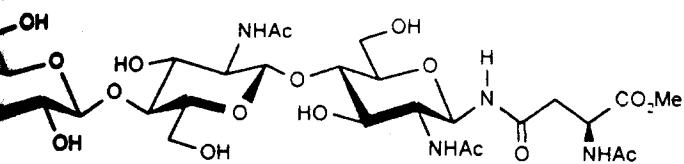
ADP

XDP

Fig. 1.

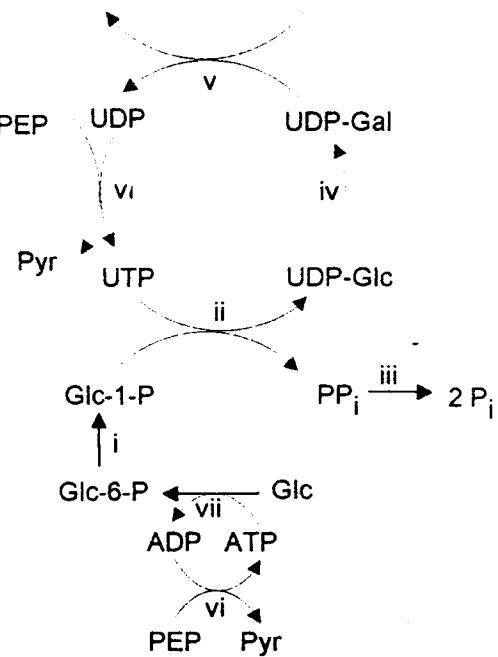


R = H, Me



Products

X = OH, NHAc



OISAE

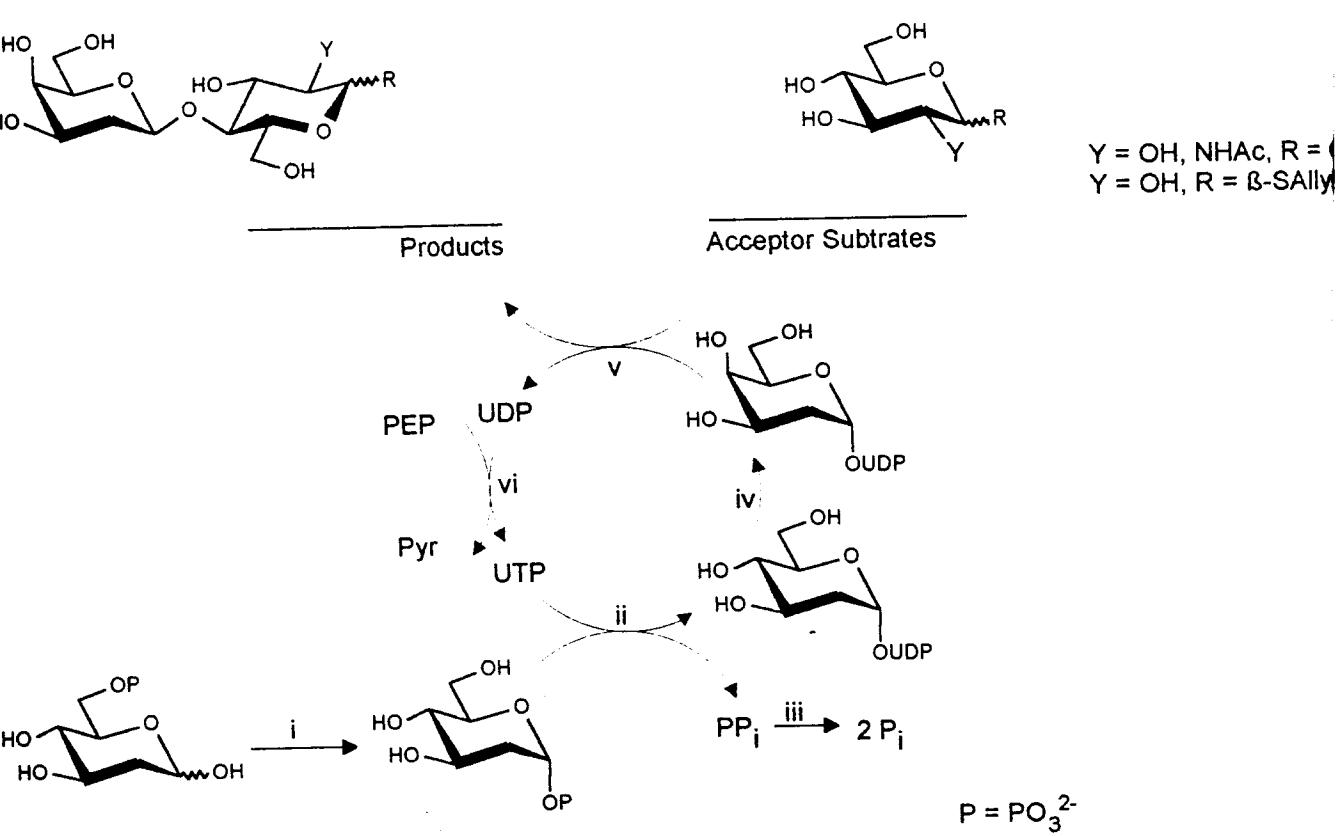
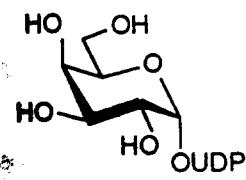
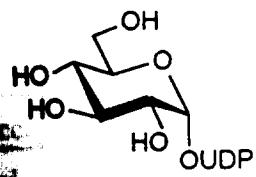
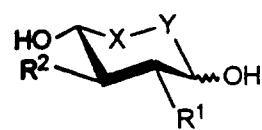


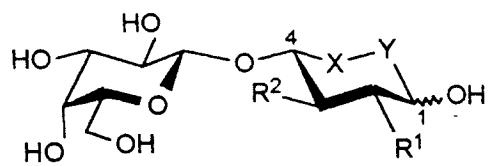
Fig. 3.



UDP



v



+

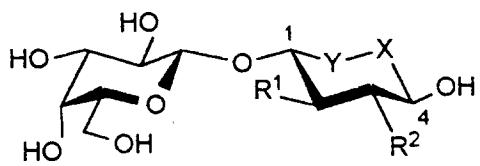


Fig. 4,

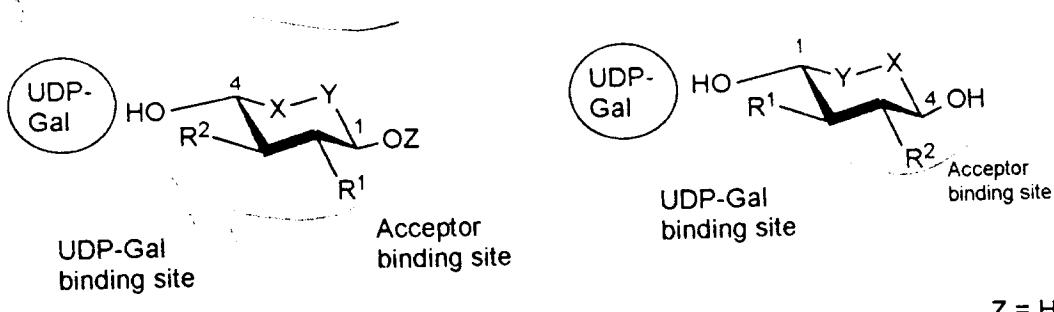
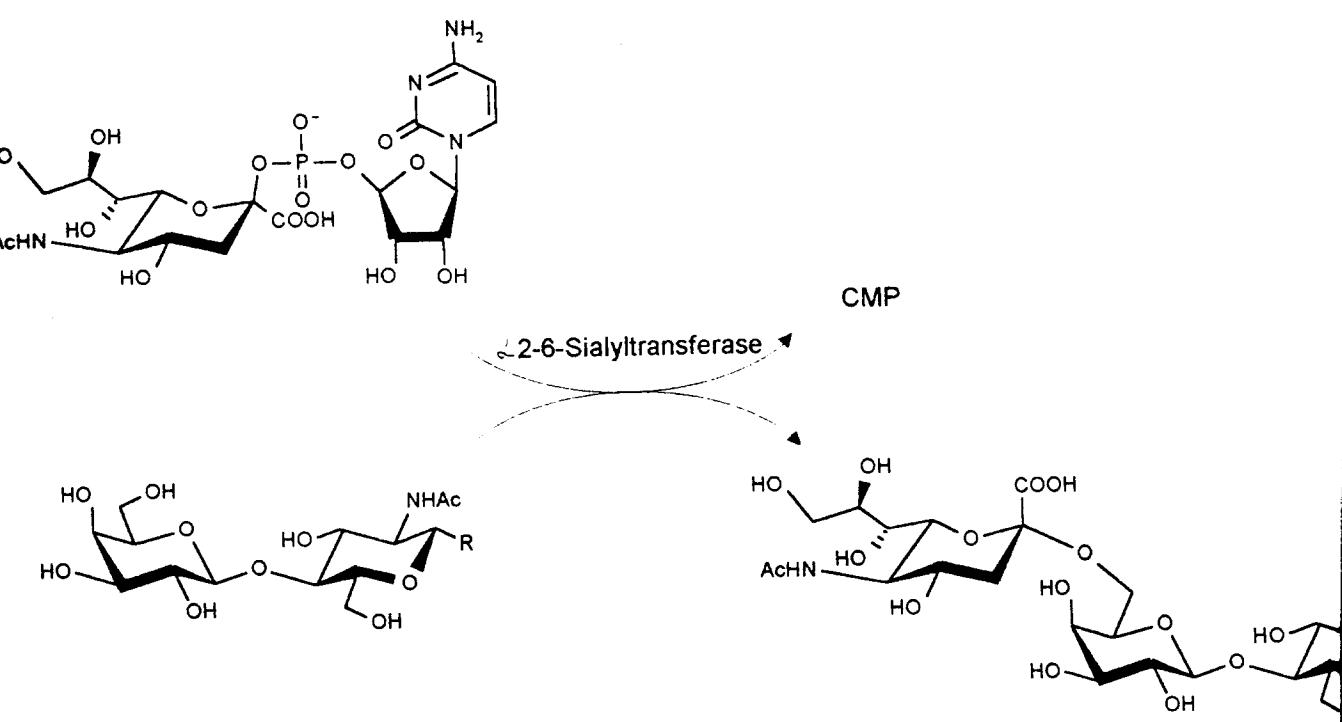


Fig. 5.

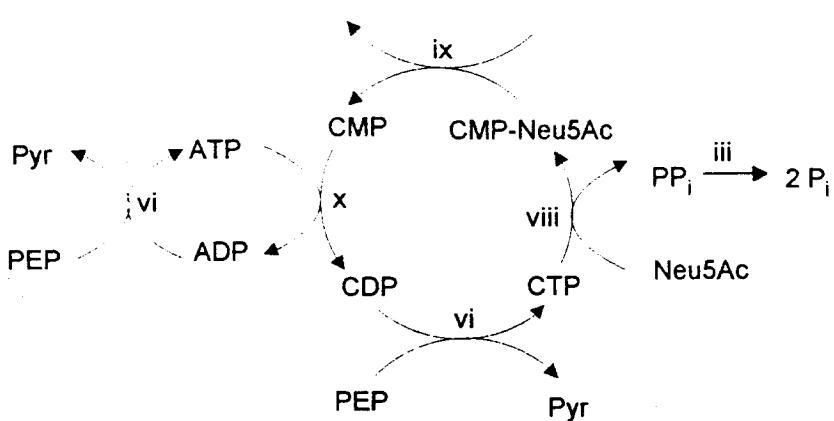
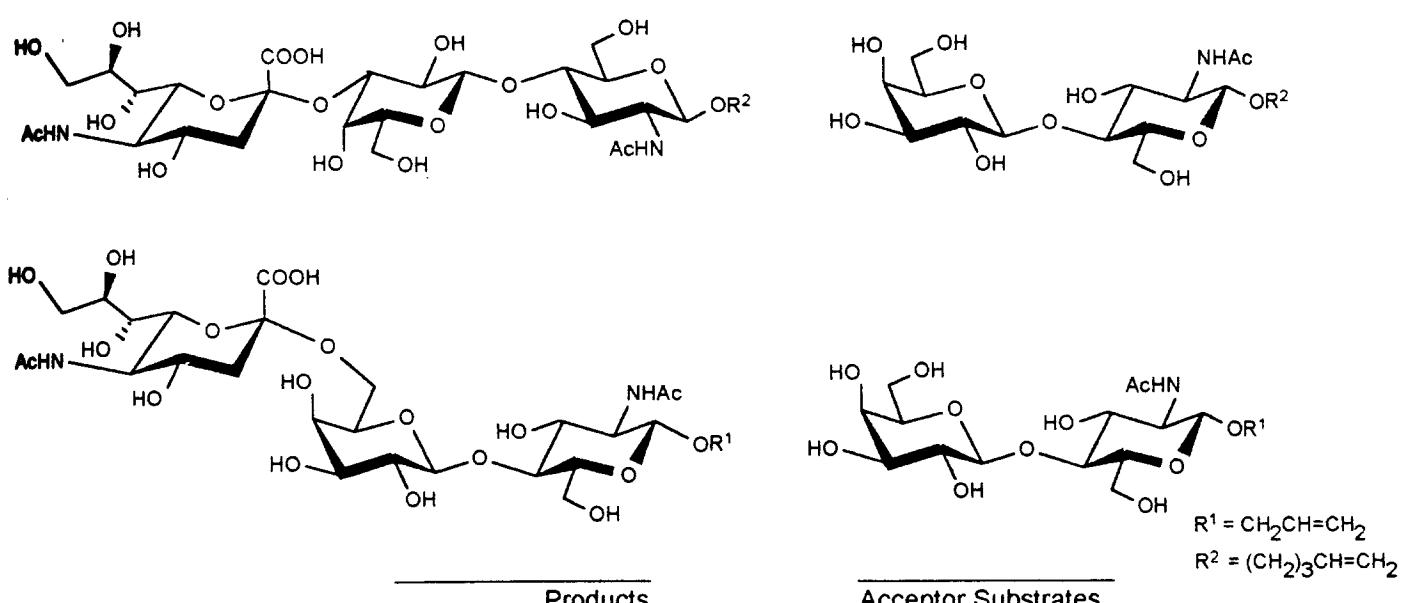
Acceptors	R <sup>1</sup>	R <sup>2</sup>	X	Y	Substrate	Orientation	Product
<b>Xyl</b>	OH	OH	CH <sub>2</sub>	O	+	n	$\beta 1-4$
	OH	OH	O	CH <sub>2</sub>	+	r	$\beta 1-\beta 1$
<b>Glc</b>	OH	OH	e-CH(CH <sub>2</sub> OH)	O	+	n	$\beta 1-4$
	OH	OH	O	CHe-(CH <sub>2</sub> OH)	-	r	
<b>GlcNAc</b>	OH	NHAc	e-CH(CH <sub>2</sub> OH)	O	-	n	
	NHAc	OH	O	CHe-(CH <sub>2</sub> OH)	+	r	$\beta 1-\beta 1$
<b>Xyl3NAc</b>	OH	NHAc	CH <sub>2</sub>	O	-	n	
	NHAc	OH	O	CH <sub>2</sub>	+	r	$\beta 1-\beta 1$
<b>GlcNAc</b>	NHAc	OH	e-CH(CH <sub>2</sub> OH)	O	+	n	$\beta 1-4$
	OH	NHAc	O	CHe-CH <sub>2</sub> OH)	-	r	
<b>SSXyl3NAc</b>	OH	NHAc	CH <sub>2</sub>	S	-	n	
	OH	NHAc	CH <sub>2</sub>	S	+	r	$\beta 1-\beta 1$

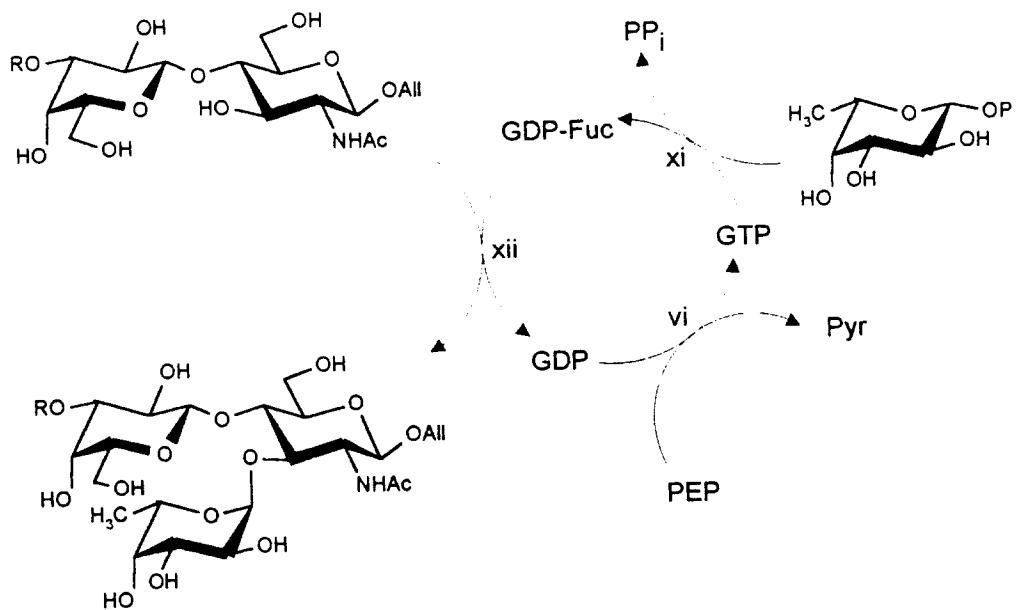


a: R = OH, b: R = OCH<sub>3</sub>, c: R = NH-CO-CH<sub>2</sub>-CH(NH<sub>2</sub>)COOH, d: R = Aloc-Phe-Asn-Thr-Ile-OH,

e: R = , f: R =

Fig. 6.

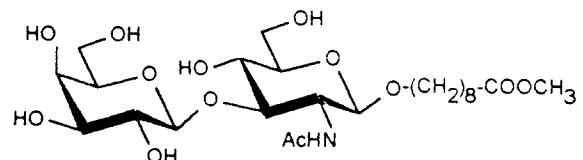




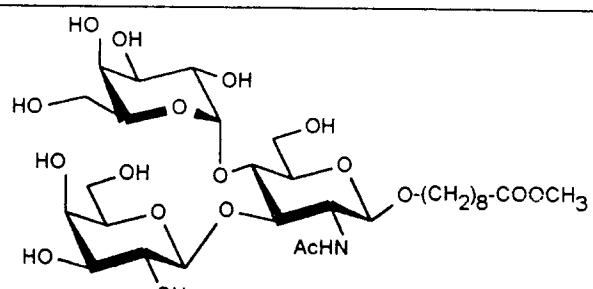
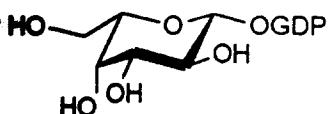
$R = H, Neu5Ac$

Fig. 8.

Acceptor Substrate



Donor Substrates



Acceptor Substrate

