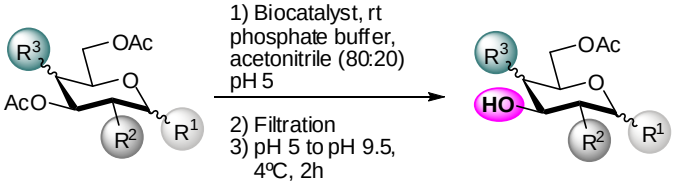
Table 5: Synthesis of 3-hydroxy-tetraacetylated monosaccharides by acyl-chemical migration from the 6-OH monodeprotected tetraacetylated products.



20-23,31-33 **73-79**

Subs	R^1	R^2	R^3	X	pH[a]	DP	Prod	Yield (%)	TLC	HPLC	^{1}H-NMR (500 MHz, $CDCl_3$) δ
20	αOAc	OAc	eq OAc	single	9.5	*C*-3	**73**	30	Hexane:AcOEt 5:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 8:2 v/v pH 4) R_t 15.5 min	6.33 (d, *J*= 3.5 Hz, 1H, H-1), 5.45 (t, *J*= 9.8 Hz, 1H, H-4), 5.18 (dd, *J*= 10.2, 3.7 Hz, 1H, H-2), 4.31 (t, *J*= 9.3 Hz, 1H, H-3), 4.05-4.27 (dd, *J*= 4.0, 2.1, 12.6 Hz, 2H, H-6A, H-6B), 4.15 (m, 1H, H-5), 2.00-2.20 (s, 12H, $4CH_3$).
21	βOAc	OAc	eq OAc	single	9.5	*C*-3	**74**	20	Hexane:AcOEt 5:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 85:15 v/v pH 4) R_t = 24.8	5.88 (d, *J*= 9.1 Hz, 1H, H-1), 5.38 (t, *J*= 9.8 Hz, 1H, H-4), 5.10 (dd, *J*= 10, 3.6 Hz, 1H, H-2), 4.11 (t, *J*= 9.5 Hz, 1H, H-3), 3.80 (m, 2H, H-6A, H-6B), 3.75 (m, 1H,

										min	H-5), 2.00-2.20 (s, 12H, $4CH_3$).
22	αOAc	NHAc	eq OAc	single	9.5	*C*-3	**75**	30	CH_2Cl_2:MeOH 95:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 85:15 v/v pH 4) R_t =9.3 min	6.19 (d, *J*= 3.2 Hz, 1H, H-1), 5.96 (d, *J*= 6.9 Hz 1H, NH), 5.02 (t, *J*= 9.5 Hz 1H, H-4), 4.35 (ddd, *J*= 12.4, 4.1Hz, 1H, H-2), 4.09-4.30 (dd, *J*= 12.4, 1.6 Hz, 2H, H-6A, H-6B), 3.99 (m, 1H, H-5), 3.80 (t, *J*= 9.9 Hz, 1H, H-3), 2.00-2.30 (s, 12H, $4CH_3$).
23	βOAc	NHAc	eq OAc	single	9.5	*C*-3	**76**	20	CH_2Cl_2:MeOH 95:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 85:15 v/v pH 4) R_t =9.4 min	5.78 (d, *J*= 9.2 Hz, 1H, H-1), 5.50 (d, *J*= 7.50 Hz, 1H, NH), 5.29 (m, 2H, H-4, H-2), 5.15 (m, 1H, H-3), 4.30 (m, 1H, H-6A), 4.20 (m, 1H, H-6B), 4.18 (m, 1H, H-5), 2.10 (s, 3H, CH_3), 2.03 (s, 6H, $2CH_3$), 1.96 (s, 3H, CH_3).
31	αOAc	OAc	ax OAc	single	9.5	*C*-3	**77**	50	Hexane:AcOEt 5:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 8:2 v/v pH 4) R_t = 18.8 min	6.33 (d, *J*= 3.6 Hz, 1H, H-1), 5.45 (d, *J*=2.5, 1 Hz, 1H, H-4), 5.18 (dd, *J*= 6.7, 3.7 Hz, 1H, H-2), 4.30 (t, *J*= 0.9, 6.1 Hz, 1H, H-5), 4.05-4.27 (dd, 2H, H-6A, H-6B), 4.22 (dd, *J*= 7, 3.4 Hz 1H, H-3), 2.41 (bs, 1H, OH), 2.00-2.20 (s, 12H, $4CH_3$).
32	βOAc	OAc	ax OAc	single	9.5	*C*-3	**78**	50	Hexane:AcOEt	($NH_4H_2PO_4$ 10mM	5.89 (d, *J*= 7 Hz, 1H, H-1), 5.30 (m, 1H, H-4), 5.15

										4:6 v/v	buffer:ACN 8:2 v/v pH 4) R_t=23.4 min	(dd, 1H, H-2), 4.30 (t, 1H, H-3), 4.10-4.15 (m, 2H, H-6A, H-6B), 3.68 (m, 1H, H-5), 1.96-2.10 (s, 12H, $4CH_3$).
33	αOAc	NHAc	ax OAc	single	9.5	*C*-3	**79**	48	CH_2Cl_2:MeOH 95:5 v/v	($NH_4H_2PO_4$ 10mM buffer:ACN 8:2 v/v pH 4) R_t = 17.06 min	6.22 (d, *J*= 3.4 Hz, 1H, H-1), 5.67 (d, *J*= 8.1 Hz, 1H, NH), 5.41 (bd, *J*= 2.5 Hz, 1H, H-4), 4.52 (ddd, *J*= 11.3, 8.1, 3.6 Hz, 1H, H-2), 4.07-4.15 (dd, *J*= 6.7, 11.5 Hz, 2H, H-6A, H-6B), 4.22 (bt, *J*= 6.7 Hz, 1H, H-5), 4.01 (dd, *J*= 2.9, 7.9 Hz, 1H, H-3), 2.05-2.21(s, 12H, $4CH_3$).

Subs: Substrate
DP: deprotected position
Prod: Product
Eq: equatorial, ax: axial
[a] 6-OH alcohol solution was incubated at 4ºC