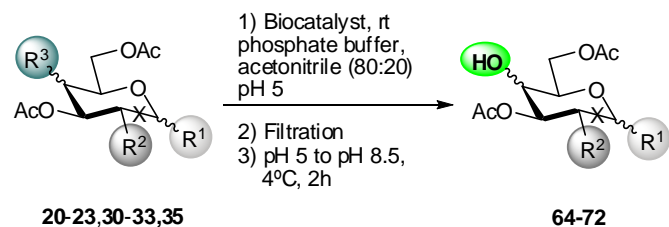


**Table 4: Synthesis of 4-hydroxy-tetraacetylated monosaccharides by acyl-chemical migration from the 6-OH monodeprotected tetraacetylated products**



Subs	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	X	pH <sup>a</sup>	DP	Prod	Yield (%)	TLC	HPLC	<sup>1</sup> H-NMR (500 MHz, CDCl <sub>3</sub> ) δ
<b>20</b>	αOAc	OAc	eq OAc	single	8.5	C-4	<b>64</b>	80	Hexane:AcOEt 5:5 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 8:2 v/v pH 4) R <sub>t</sub> = 17.5 min.	6.23 (d, <i>J</i> = 3.4 Hz, 1H, H-1), 5.28 (t, <i>J</i> = 9.8 Hz, 1H, H-3), 4.96 (dd, <i>J</i> = 10.2, 3.7 Hz, 1H, H-2), 4.21-4.41 (m, <i>J</i> = 8.6, 3.9, 12.6 Hz, 2H, H-6A, H-6B), 3.92 (m, 1H, H-5), 3.59 (t, <i>J</i> = 9.3 Hz, 1H, H-4), 1.96-2.11 (s, 12H, 4CH <sub>3</sub> ).
<b>21</b>	βOAc	OAc	eq OAc	single	8.5	C-4	<b>65</b>	70	Hexane:AcOEt 5:5 v/v	HPLC (NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 85:15 v/v pH 4) R <sub>t</sub> = 36.45 min	5.80 (d, <i>J</i> = 8.9 Hz, 1H, H-1), 5.28 (t, <i>J</i> = 9.8 Hz, 1H, H-3), 4.94 (dd, <i>J</i> = 10, 3.7 Hz, 1H, H-2), 3.90 (m, 2H, H-6A, H-6B), 3.60 (m, 1H, H-5), 3.59 (t, <i>J</i> = 9.0 Hz, 1H, H-4), 1.95–2.10 (s, 12H, 4CH <sub>3</sub> ).

<b>22</b>	$\alpha$ OAc	NHAc	eq OAc	single	8.5	C-4	<b>66</b>	79	CH <sub>2</sub> Cl <sub>2</sub> :MeOH 95:5 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 85:15 v/v pH 4) R <sub>t</sub> = 7.5 min	6.15 (d, <i>J</i> = 3.5 Hz, 1H, H-1), 5.75 (d, <i>J</i> = 8.9 Hz, 1H, NH), 5.14 (dd, 1H, H-3), 4.59 (dd, 1H, H-6B), 4.38 (m, 1H, H-2), 4.20 (dd, 1H, H-6A), 3.85 (m, 1H, H-5), 3.65 (t, 1H, H-4), 3.16 (bs, 1H, OH), 2.19 (s, 3H, CH <sub>3</sub> ), 2.13–2.15 (2s, 6H, CH <sub>3</sub> ), 1.95 (s, 3H, CH <sub>3</sub> ).
<b>23</b>	$\beta$ OAc	NHAc	eq OAc	single	8.5	C-4	<b>67</b>	78	CH <sub>2</sub> Cl <sub>2</sub> :MeOH 95:5 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 85:15 v/v pH 4) R <sub>t</sub> = 7.4 min	5.77 (d, <i>J</i> = 9.0 Hz, 1H, H-1), 5.53 (d, <i>J</i> = 7.6 Hz, 1H, NH), 5.30 (m, 1H, H-3), 5.14 (t, <i>J</i> = 9.7 Hz, 1H, H-2), 4.32 (m, 1H, H-6A), 4.20 (m, 2H, H-5, H-6B), 4.14 (m, 1H, H-4), 2.10 (s, 3H, CH <sub>3</sub> ), 2.03 (s, 3H, CH <sub>3</sub> ), 2.04 (s, 3H, CH <sub>3</sub> ), 1.96 (s, 3H, CH <sub>3</sub> ).
<b>30</b>	H	H	eq OAc	double	8.5	C-4	<b>68</b>	94	Hexane:AcOEt 4:6 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 8:2 v/v pH 4) R <sub>t</sub> = 13.5 min	6.45 (dd, <i>J</i> = 6.2, 1.5 Hz, 1H, H-1), 5.31 (ddd, <i>J</i> = 7, 2.4 Hz, 1H, H-3), 4.76 (dd, <i>J</i> = 3.6, 2.6 Hz, 1H, H-2), 4.38- 4.57 (dd, <i>J</i> = 14.7, 7 Hz, 2H, H-6A, H-6B), 4.01 (m, <i>J</i> = 2.6 Hz, 1H, H-5), 3.84 (bt, <i>J</i> = 9.6 Hz, 1H, H-4), 3.54 (bs, 1H, OH), 2.14-2.16 (s, 6H, 2CH <sub>3</sub> ).
<b>31</b>	$\alpha$ OAc	OAc	ax OAc	single	8.5	C-4	<b>69</b>	42	Hexane:AcOEt 5:5 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 8:2 v/v pH 4) R <sub>t</sub> = 16.7	6.37 (d, <i>J</i> = 3.8 Hz, 1H, H-1), 5.45 (dd, <i>J</i> = 7.1, 3.5 Hz, 1H, H-3), 5.31 (dd, <i>J</i> = 11.1, 3 Hz, 1H, H-2), 4.39 (m, 1H, H-5), 4.09-4.23 (m, 3H, H-4, H-6A, H-6B), 2.45

									min	(bs, 1H, OH), 2.02–2.18 (s, 12H, 4CH <sub>3</sub> ).	
<b>32</b>	βOAc	OAc	ax OAc	single	8.5	C-4	<b>70</b>	45	Hexane:AcOEt 4:6 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 8:2 v/v pH 4) R <sub>t</sub> =17.2 min	5.93 (d, J= 9 Hz, 1H, H-1), 5.38 (dd, J= 7.0, 3.5 Hz, 1H, H-3), 5.30 (dd, J= 10.8, 3.2 Hz, 1H, H-2), 4.20 (m, 3H, H-4, H-6A, H-6B), 3.98 (m, 1H, H-5), 2.45 (bs, 1H, OH), 1.98-2.16 (s, 12H, 4CH <sub>3</sub> ).
<b>33</b>	αOAc	NHAc	ax OAc	single	8.5	C-4	<b>71</b>	42	CH <sub>2</sub> Cl <sub>2</sub> :MeOH 95:5 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 8:2 v/v pH 4) R <sub>t</sub> = 13.7min	6.20 (d, J= 3.7 Hz, 1H, H-1), 5.52 (d, J= 9 Hz, 1H, NH), 5.19 (dd, J= 9.2, 11 Hz, 1H, H-3), 4.83 (ddd, J= 11, 3.6 Hz, 1H, H-2), 4.27-4.36 (dd, J= 6.3, 11.3 Hz, 2H, H-6A, H-6B), 4.1 (m, 1H, H-5), 4.07 (m, 1H, H-4), 1.96-2.18 (s, 12H, 4CH <sub>3</sub> ).
<b>35</b>	H	H	ax OAc	double	8.5	C-4	<b>72</b>	80	Hexane:AcOEt 4:6 v/v	(NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> 10mM buffer:ACN 7:3 v/v pH 4) R <sub>t</sub> = 8.6 min	6.43 (dd, J= 6.3, 1.8 Hz, 1H, H-1), 5.37 (dt, J= 4.7, 3.8Hz, 1H, H-3), 4.76 (dd, J= 3.8, 1.7Hz, 1H, H-2), 4.38-4.57 (dd, J= 12.2, 7.7Hz, 2H, H-6A, H-6B), 4.01 (m, J= 7.7, 1.6 Hz, 1H, H-5), 3.84 (bt, 1H, H-4), 3.54 (bs, 1H, OH), 2.14-2.16 (s, 6H, 2CH <sub>3</sub> ).

Subs: Substrate

DP: deprotected position

Prod: Product

Eq: equatorial, ax: axial

<sup>a</sup> 6-OH alcohol solution was incubated at 4°C