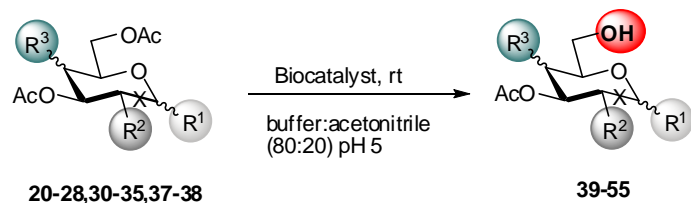


Table 2: Regioselective enzymatic C-6 monodeprotection of per-O-acetylated glycopyranosides.



Subs	R ¹	R ²	R ³	X	Biocat	DP	Prod	Yield (%)	TLC	HPLC	¹ H-NMR (500 MHz, CDCl ₃) δ
20	αOAc	OAc	eq OAc	single	CRL ^a	C-6	39	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH4) R _t =7.7 min	6.38 (d, <i>J</i> =3.7 Hz, 1H, H-1), 5.56 (t, <i>J</i> =9.9 Hz, 1H, H-3), 5.14 (t, <i>J</i> =9.9 Hz, 1H, H-4), 5.10 (dd, <i>J</i> =3.7, 9.9Hz, 1H, H-2), 3.96 (m, 1H, H-5), 3.61-3.75 (dd, <i>J</i> =4.2, 2.4, 12.9 Hz, 2H, H-6A, H-6B), 2.00-2.25(4s, 12H, CH ₃).
21	βOAc	OAc	eq OAc	single	ANL ^a	C-6	40	60 ^d	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH4) R _t =10 min	5.70 (d, 1H, <i>J</i> =8.4 Hz, 1H, H-1), 5.27 (t, <i>J</i> =9.7 Hz, 1H, H-3), 5.07 (m, <i>J</i> = 8.4, 9.7 Hz, 2H, H-2, H-4), 3.73 (dd, <i>J</i> = 2.3, 12.5 Hz, 1H, H-6A), 3.62 (ddd, <i>J</i> = 2.3, 4.2, 9.7 Hz, 1H, H-5), 3.55 (dd, <i>J</i> = 4.2, 12.5 Hz, 1H, H-6B), 2.08 (s, 3H, CH ₃), 2.03 (s, 3H, CH ₃), 2.00 (s,

											3H, CH ₃), 1.99 (s, 3H, CH ₃).
22	αOAc	NHAc	eq OAc	single	CRL ^a	C-6	41	95	CH ₂ Cl ₂ :MeOH 95:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 8:2 v/v pH4) R _t =5.70 min	6.19 (d, <i>J</i> =3.3 Hz, 1H, H-1), 5.61 (d, <i>J</i> =9 Hz, 1H, NH), 5.30 (t, <i>J</i> =9.9 Hz, 1H, H-3), 5.16 (t, <i>J</i> =9.7 Hz, 1H, H-4), 4.46 (m, <i>J</i> =10.4, 8.4, 3.7 Hz, 1H, H-2), 3.81 (m, 1H, H-5), 3.59-3.71 (2dd, <i>J</i> =8.5, 3.9, 12.4 Hz, 2H, H-6A, H-6B), 2.20 (s, 3H, CH ₃), 2.05-2.11 (2s, 6H, 2CH ₃), 1.96 (s, 3H, CH ₃).
23	βOAc	NHAc	eq OAc	single	ANL ^a	C-6	42	70 ^d	CH ₂ Cl ₂ :MeOH 95:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 85:15 v/v pH4) R _t =8.4 min	5.80 (d, <i>J</i> =3.5 Hz, 1H, H-1), 5.50 (d, <i>J</i> =9 Hz, 1H, NH), 5.30 (t, <i>J</i> =9.9 Hz, 1H, H-3), 5.10 (t, <i>J</i> =9.6 Hz, 1H, H-4), 4.35 (dd, <i>J</i> = 9.8, 6.7 Hz, 1H, H-2), 4.28-4.20 (m, 2H, H-6A, H-6B), 4.19-4.10 (m, 1H, H-5), 2.21 (s, 9H, 3CH ₃), 1.96 (s, 3H, CH ₃).
24	βOMe	OAc	eq OAc	single	CRL ^a	C-6	43	95	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R _t = 6.7 min	5.04 (t, <i>J</i> = 9.5 Hz, 1H, H-3), 5.00 (t, <i>J</i> = 9.8 Hz, 1H-4), 4.94 (dd, <i>J</i> = 9.7, 8 Hz, 1H, H-2), 4.46 (d, <i>J</i> =7.9 Hz, 1H, H-1), 3.6-3.8 (m, <i>J</i> =7.9, 2, 12.5 Hz, 2H, H-6A, H-6B), 3.53 (m, 1H-5), 3.52 (s, 3H, CH ₃), 1.92-2.01 (s, 9H, 3CH ₃).

25	β OBu	OAc	eq OAc	single	ANL ^b	C-6	44	77 ^d	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) $R_t = 8.3$ min	5.25 (t, $J = 9.5$ Hz, 1H, H-3), 5.00 (t, $J = 9.8$ Hz, 1H, H-4), 4.98 (dd $J = 7.9, 9.6$ Hz, 1H, H-2), 4.43 (d, $J = 7.8$ Hz, 1H, H-1), 3.90-3.79 (m, 2H, H-6A, H-6B), 3.64 (m, $J = 9.5$ Hz, 1H, H-5), 3.46-3.41 (m, 2H, CH _{2α}), 2.01-1.93 (s, 12H, 4CH ₃), 1.55-1.46 (m, 2H, CH ₂), 1.32-1.22 (m, 2H, CH ₂), 0.90 (t, $J = 7.4$ Hz, 3H, CH ₃).
26	β OPh	OAc	eq OAc	single	ANL ^b	C-6	45	61 ^d	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) $R_t = 7.5$ min	7.35-7.11 (m, 5 H, Ar-H), 5.26 (t, $J = 9.5$ Hz, 1H, H-3), 5.16 (dd $J = 7.9, 9.6$ Hz, 1H, H-2), 4.80 (d, $J = 7.8$ Hz, 1H, H-1), 4.65 (t, $J = 9.8$ Hz, 1H, H-4), 3.90-3.82 (m, 2H, H-6A, H-6B), 3.64 (m, $J = 9.5$ Hz, 1H, H-5), 2.11-1.98 (s, 9H, 3CH ₃).
27	β OPhNO ₂	OAc	eq OAc	single	ANL ^b	C-6	46	50 ^d	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) $R_t = 6$ min	8.10 (d, $J = 8.5$ Hz, 2H, H-3', H-5'), 6.88 (d, $J = 8.3$ Hz, 2H, H-2', H-6'), 5.25 (t, $J = 9.4$ Hz, 1H, H-3), 5.14 (dd $J = 7.8, 9.5$ Hz, 1H, H-2), 4.81 (d, $J = 7.7$ Hz, 1H, H-1), 4.66 (t, $J = 9.7$ Hz, 1H, H-4), 3.92-3.84 (m, 2H, H-6A, H-6B), 3.65 (m, $J = 9.4$ Hz, 1H, H-5), 2.19 (s, 3H, CH ₃), 2.11-2.09 (s, 6H, 2CH ₃).

28	β OPhNO ₂	NHAc	eq OAc	single	ANL ^b	C-6	47	51 ^d	CH ₂ Cl ₂ :MeOH 95:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) <i>R</i> _t =5.2 min	8.14 (d, <i>J</i> =8.6 Hz, 2H, H-3', H-5'), 7.10 (d, <i>J</i> =8.5 Hz, 2H, H-2', H-6'), 5.89 (d, <i>J</i> = 10 Hz, 1H, NH), 5.28 (t, <i>J</i> = 9.5 Hz, 1H, H-3), 4.85 (d, <i>J</i> =7.7 Hz, 1H, H-1), 4.79 (m, 1H, H-2), 4.66 (t, <i>J</i> =9.5 Hz, 1H, H-4), 3.85-3.70 (m, 2H, H-6A, H-6B), 3.65 (m, 1H, H-5), 2.20 (s, 6H, 2CH ₃), 1.84 (s, 3H, CH ₃).
30	H	H	eq OAc	double	CRL ^a	C-6	48	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) <i>R</i> _t = 5.5 min	6.49 (dd, <i>J</i> =6.1 Hz, 1H, H-1), 5.41-5.50 (m, 1H, H-3), 5.22 (dd, <i>J</i> =9.0, 6.5 Hz, 1H, H-4), 4.81 (dd, <i>J</i> =5.9, 2.8 Hz, 1H, H-2), 3.98-4.09 (m, 1H, H-5), 3.66-3.86 (m, 2H, H-6A, H-6B), 2.07-2.13 (2s, 6H, 2CH ₃).
31	α OAc	OAc	ax OAc	single	CRL ^a	C-6	49	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) <i>R</i> _t = 8.6 min	.37 (d, <i>J</i> =2.1 Hz, 1H, H-1), 5.49 (d, <i>J</i> =2.2Hz, 1H, H-4), 5.32 (m, 2H, H-2, H-3), 4.10 (t, <i>J</i> =6.5, 1H, H-5), 3.70-3.50 (dd, <i>J</i> =2.2, 6.6, 11.9 Hz, 2H, H-6A, H-6B), 1.98-2.20 (4s, 12H, CH ₃).
32	β OAc	OAc	ax OAc	single	LECI/ TLL ^a	C-6	50	95	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) <i>R</i> _t =10.6 min	5.73 (d, <i>J</i> = 8.2 Hz, 1H, H-1), 5.44 (d, <i>J</i> =3.3 Hz, 1H, H-4), 5.32 (t, <i>J</i> =8.3 Hz, 1H, H-3), 5.13 (dd, <i>J</i> =3.4, 10.4 Hz, 1H, H-2), 3.91 (dt, <i>J</i> =6.4 Hz, 1H, H-5), 3.8-3.51 (m, 2H, H-6A, H-6B), 2.14-1.97 (s, 12H, 4CH ₃).

33	α OAc	NHAc	ax OAc	single	CRL ^a	C-6	51	80 ^d	CH ₂ Cl ₂ :MeOH 95:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R_t = 5.9 min	6.22 (d, J = 3.4 Hz, 1H, H-1), 5.56 (bd, J =9.1 Hz, 1H, NH), 5.41 (bdd, 1H, H-4), 5.27 (dd, J =8.7, 3.1 Hz, 1H, H-3), 4.76 (ddd, J = 11, 9.9, 3.6 Hz, 1H, H-2), 4.08 (bt, J = 6.6 Hz, 1H, H-5), 3.48-3.62 (dd, J = 2.2, 4.4, 12.4 Hz, 2H, H-6A, H-6B), 1.96-2.23 (4s, 12H, CH ₃).
34	β S-Prop _{iso}	OAc	ax OAc	single	CRL ^a	C-6	52	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R_t = 8.6 min	5.40 (d, J =2.9 Hz, 1H, H-4), 5.20 (t, J = 9.9 Hz, 1H, H- 2), 5.08 (dd, J =6.6, 3.1 Hz, 1H, H-3), 4.58 (d, J =10.0 Hz, 1H, H-1), 3.78-3.68 (m, 2H, H-5, H-6A), 3.52-3.46 (m, 1H, H-6B), 3.23-3.14 (m, J =6.6 Hz, 1H, CH), 2.16 (s, 3H, CH ₃), 2.10 (s, 3H, CH ₃), 1.99 (s, 3H, CH ₃), 1.30 (m, 6H, 2CH ₃).
35	H	H	ax OAc	doble	CRL ^a	C-6	53	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R_t = 5.2 min	6.50 (dd, J = 6.2, 1.8 Hz, 1H, H-1), 5.60-5.55 (m, 1H, H-3), 5.50-5.44 (dt, J = 7.4, 3.6 Hz, 1H, H-4), 4.73 (dt, J = 5.9, 2.8Hz, 1H, H-2), 4.22-4.16 (m, J = 7 Hz, 1H, H- 5), 3.83-3.61 (dd, J = 11.6, 5.8 Hz, 2H, H-6A, H-6B), 2.31 (bs, 1H, OH), 2.16 (s, 3H, CH ₃), 2.05 (s, 3H, CH ₃).

37	β OMe	NHAc	eq Gal	single	AXE ^c	C-6	54	60 ^d	Acetone:CH ₂ Cl ₂ 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) R _t = 6.8 min	5.89 (d, <i>J</i> =10 Hz, 1H, NH), 5.38 (bd, <i>J</i> =3.2 Hz, 1H, H-4'), 5.11-5.18 (m, 2H, H-2', H-3), 5.04 (dd, <i>J</i> =3.4, 10.2 Hz, 1H, H-3'), 4.56 (d, <i>J</i> =8.0Hz, 1H, H-1'), 4.53 (dd, <i>J</i> = 4.0, 11.7 Hz, 1H, H-6B), 4.41 (d, <i>J</i> = 6.4 Hz, 1H, H-1), 4.16 (dd, <i>J</i> = 5.4, 11.7 Hz, 1H, H-6A), 4.06-4.15 (m, 1H, H-2), 3.85 (br. t, <i>J</i> = 7.4 Hz, 1H, H-4), 3.69-3.77 (m, 3H, H-5, H-5', H-6B'), 3.49-3.55 (m, 1H, H-6A'), 3.47 (s, 3H, OCH ₃), 2.01, 2.09, 2.10, 2.13, 2.18, 2.19 (s, 18H, 6COCH ₃).
38	H	H	eq Gal	double	AXE ^c	C-6	55	70 ^d	AcOEt:CH ₂ Cl ₂ 3:7 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R _t =6.4 min	6.47 (dd, <i>J</i> = 0.9, 6.2 Hz, 1H, H-1), 5.46 (br. t, <i>J</i> = 4.2 Hz, 1H, H-3), 5.37 (d, <i>J</i> = 3.2 Hz, 1H, H-4'), 5.23 (dd, <i>J</i> = 7.9, 10.5 Hz, 1H, H-2'), 5.05 (dd, <i>J</i> = 3.5, 10.5 Hz, 1H, H-3'), 4.83 (dd, <i>J</i> = 4.2, 6.2 Hz, 1H, H-2), 4.68 (d, <i>J</i> = 7.9 Hz, 1H, H-1'), 4.40 (dd, <i>J</i> = 2.8, 11.2 Hz, 1H, H-6A), 4.19-4.28 (m, 2H, H-5, H-6B), 3.98 (br. t, <i>J</i> = 5.2 Hz, 1H, H-4), 3.71-3.79 (m, 2H, H-5', H-6B'), 3.53 (dd, <i>J</i> = 3.8, 10.4 Hz, 1H, H-6A'), 2.01, 2.09, 2.10, 2.14, 2.18 (5s, 15H, COCH ₃).

Subs: Substrate

Biocat: Biocatalyst

DP: deprotected position

Prod: Product

Eq: equatorial, ax: axial

^a Lipase was immobilized on octyl-Sepharose

^b Lipase was immobilized on CNBr-Sepharose

^c Commercial immobilized preparation of Acetyl Xylan esterase from *B. pumilus*

^d Purified by column chromatography

Methyl 2,3,4-tri-*O*-acetyl- β -D-galactopyranosyl-(1 \rightarrow 4)-2-deoxy-2-acetamido-3,6-di-*O*-acetyl- β -D-glucopyranoside (54).

¹³C-NMR (400 MHz, CDCl₃) δ : 170.3, 170.6, 171.0, 171.2, 171.5 (COCH₃), 102.2 (CH), 101.6 (CH), 75.4 (CH), 74.9 (CH), 73.3 (CH), 72.9 (CH), 71.4 (CH), 70.1 (CH), 68.3 (CH), 63.3 (CH₂), 61.5 (CH₂), 57.3 (OCH₃), 52.9 (CH), 24.0 (CH₃CON), 21.2, 21.3, 21.6, 21.6 (COCH₃).

MS (FAB): Calcd. for C₂₅H₃₇NO₁₆ + Na⁺: 630.55; found [M+Na]: 630.26.

3,6,2',3',4'-Penta-*O*-acetyl-D-lactal (55).

¹³C-NMR (100 MHz, CDCl₃) δ : 170.0, 170.7, 171.2, 171.4, 171.5 (COCH₃), 146.4 (CH), 102.2 (CH), 98.9 (CH), 75.1 (2CH), 74.8 (CH), 71.5 (CH), 69.8 (CH), 68.8 (CH), 68.5 (CH), 62.3 (CH₂), 61.9 (CH₂), 21.3, 21.5, 21.9 (COCH₃).

HRMS (FAB): Calcd. for C₂₂H₃₀O₁₄ + Na⁺: 541.00; found [M+Na]: 541.1541.