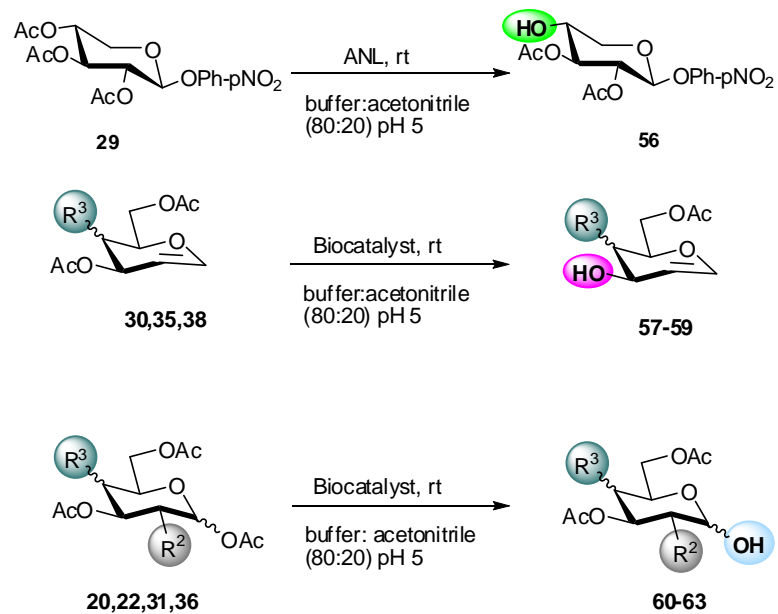


Table 3: Regioselective enzymatic monodeprotection of per-*O*-acetylated glycopyranosides



Subs	R ¹	R ²	R ³	X	Biocat	DP	Prod	Yield (%)	TLC	HPLC	¹ H-NMR (500 MHz, CDCl ₃) δ
29	βPhNO ₂	OAc	eq OH	single	ANL ^a	C-4	56	96	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v	8.10 (d, <i>J</i> =8.4 Hz, 2H, H-3', H-5'), 6.88 (d, <i>J</i> =8.3 Hz, 2H, H-2', H-6'), 5.21 (d, <i>J</i> =5.3 Hz, 1H, H-1), 5.16 (m,

										pH 4) R_t = 8.3 min	1H, H-2), 4.78 (m, 1H, H-3), 4.12 (m, 1H, H-5), 3.92 (m, 1H, H-4), 3.55 (m, 1H, H-5), 2.10 (s, 3H, CH ₃), 2.05 (s, 3H, CH ₃).
30	H	H	eq OAc	double	CAL-B ^a	C-3	57	99	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	6.42 (dd, J =6.1 Hz, 1H, H-1), 4.95 (dd, J =6.2, 2. Hz, 1H, H-4), 4.84 (dd, J =6.2, 3.2, 2.7 Hz, 1H, H-2), 4.43 (ddd, J =6.7, 5.3 Hz, 1H, H-5), 4.22-4.38 (m, 2H, H-6A, H-6B), 4.20-4.11 (dd, J =6.2, 2.2 Hz, 1H, H-3), 2.55 (bs, 1H, OH), 2.16 (s, 3H, CH ₃), 2.11 (s, 3H, CH ₃).
35	H	H	ax OAc	double	PFL ^a	C-3	58	90 ^c	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 7:3 v/v pH 4) R_t = 4.7 min	6.40 (dd, J =6.2, 1.6 Hz, 1H, H-1), 5.48 (m, 1H, H-4), 4.75 (m, 1H, H-2), 4.30-4.15 (m, 1H, H-6A, H-6B), 4.14-4.10 (m, 1H, H-3), 2.11(s, 3H, CH ₃), 2.03(s, 3H, CH ₃)
38	H	H	eq Gal	double	RML ^a	C-3	59	95	AcOEt:CH ₂ Cl ₂ 3:7 v/v)	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) R_t = 11.10 min	6.33 (d, J =5.9 Hz, 1H, H-1), 5.38 (d, J =3.3 Hz, 1H, H-4'), 5.25 (t, J =8.3 Hz, 1H, H-2'), 5.00 (dd, 1H, H-3'), 4.76 (dd, 1H, H-2), 4.59 (d, J = 8.0 Hz, 1H, H-1'), 4.43 (m, 1H, H-3), 4.20-4.10 (m, 2H, H-6A, H-6B), 4.13-4.07 (m, 2H, H-6A', 6B'), 4.08 (m, 1H, H-5'), 3.98 (m, 1H, H-5), 3.63 (m, 1H, H-4), 2.15-2.09 (5s, 15 H, 5

CH₃).

21	βOAc	OAc	eq OAc	single	PFL ^a	C-1	60	96	Hexane:AcOEt 5:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) R _t =8.5 min	5.47 (t, <i>J</i> = 9.7 Hz, 1H, H-3α), 5.38 (d, <i>J</i> = 3.5 Hz, 1H, H-1α), 5.18 (t, <i>J</i> = 9.6 Hz, 1H, H-3β), 5.03 (t, <i>J</i> = 9.7 Hz, 2H, H-4α, H-4β), 4.86 (dd, <i>J</i> = 8.1, 9.7 Hz, 1H, H-2β), 4.83 (dd, <i>J</i> = 3.6, 10.1 Hz, 1H, H-2α), 4.70 (d, <i>J</i> = 8.0 Hz, H-1β), 3.95–4.25 (m, 3H, H-5α, 2H-6α/β), 3.71 (m, 1H, H-5β), 1.90–2.20 (s, 12H, 4CH ₃).
23	βOAc	NHAc	eq OAc	single	ANL ^b	C-1	61	25 ^c	CH ₂ Cl ₂ :MeOH 95:5 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 8:2 v/v pH 4) R _t =6.5 min	6.04 (d, <i>J</i> = 9.5 Hz, NH), 5.25 (dd, <i>J</i> = 10.0, 9.5 Hz, 1H, H-3), 5.15 (d, <i>J</i> = 3.5 Hz, 1H, H-1), 5.07 (t, <i>J</i> = 9.5 Hz, 1H, H-4), 4.73 (d, <i>J</i> = 8.5 Hz, 1H, H-1β), 4.22 (m, 1H, H-5), 4.16 (m, 2H, H-2, H-6A), 4.02 (m, 1H, H-6B), 2.03 (s, 3H, CH ₃), 1.97 (s, 3H, CH ₃), 1.96 (s, 3H, CH ₃), 1.90 (s, 3H, NH-COCH ₃).
32	βOAc	OAc	ax OAc	single	ANL ^b	C-1	62	95	Hexane:AcOEt 4:6 v/v	(NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) R _t =8.3 (β anomer), 9.8 min	5.52 (bd, <i>J</i> = 3.4 Hz, 1H, H-1), 5.48 (dd, <i>J</i> = 1.2 Hz, 1H, H-4), 5.41 (dd, <i>J</i> = 3.4 Hz, 1H, H-3), 5.19 (dd, <i>J</i> = 7.3, 3.4 Hz, 1H, H-2), 4.72 (dt, <i>J</i> = 6.5 Hz, 1H, H-5), 4.12–4.08 (dd, <i>J</i> = 11.5 Hz, 2H, H-6A, H-6B), 2.15–1.99 (s, 12H,

36	β OAc	OAc	eq Gal4Ac	single	LECI ^b	C-1	63	96	MeOH:Toluene 1:9 v/v	(α -anomer) (NH ₄ H ₂ PO ₄ 10mM buffer:ACN 6:4 v/v pH 4) <i>R</i> _t =8.82 min (α -anomer), 9.33 (β anomer)	5.51 (t, <i>J</i> = 9.7 Hz, 1H, H-3 α), 5.36 (d, <i>J</i> = 3.4 Hz, 1H, H-1 α), 5.34 (dd, <i>J</i> = 0.5, 1H, H-4'), 5.22 (t, <i>J</i> = 9.3Hz, 1H, H-3 β), 5.11 (dd, <i>J</i> = 10.5 Hz, 1H, H-2' α), 5.09 (dd, <i>J</i> = 10.6 Hz, 1H, H-2' β), 4.94 (dd, <i>J</i> = 3.2 Hz, 1H, H-3'), 4.81 (dd, 1H, H-2 α), 4.76 (m, 2H, H-1 β , H-2 β), 4.49 (d, <i>J</i> = 7.9 Hz, 1H, H-1' α), 4.48 (dd, <i>J</i> = 3.4, 11.2 Hz, 1H, H-6B), 4.47 (d, <i>J</i> =7.7 Hz, H-1' β), 4.22-4.00 (m, 4H, H-5, H-6A, H-6'A, H-6'B), 3.86 (dt, <i>J</i> = 6.3, 1H, 5'-H), 3.75 (dd, <i>J</i> = 9.3 Hz, H-4 α), 2.15-1.96 (s, 21H, 7CH ₃).
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Subs: Substrate

Biocat: Biocatalyst

Prod: Product

DP: deprotected position

Eq: equatorial, ax: axial

^a Lipase was immobilized on octyl-Sepharose

^b Lipase was immobilized on CNBr-Sepharose

^c Purified by column chromatography

6,2',3',4',6'-Penta-*O*-acetyl-D-lactal (59).

¹³C-NMR (100 MHz, CDCl₃) δ: 170.58, 170.03, 169.60 (COCH₃), 143.75 (CH), 102.66 (CH), 102.19 (CH), 81.96 (CH), 73.77 (CH), 71.51 (CH), 70.82 (CH), 68.70 (CH), 68.26 (CH), 66.98 (CH), 62.58 (CH₂), 62.10 (CH₂), 20.79, 20.59, 20.55, 20.45 (COCH₃).

HRMS (FAB): Calcd. for C₂₂H₃₀O₁₄: 518.1636; found [M+Na]: 541.1541.

2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α/β-D-glucopyranose (63).

¹³C-NMR (100 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).