Supporting Information

for

**The 4,6-*O*-[α -(2-(2-Iodophenyl)ethylthiocarbonyl)benzylidene]
Protecting Group: Stereoselective Glycosylation, Reductive Radical
Fragmentation, and the Synthesis of β -D-Rhamnopyranosides and
Other Deoxy Sugars**

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***S*-Phenyl 4,6-*O*- α -(methoxycarbonyl)benzylidene-2,3-di-*O*-benzyl-1-thio- α -D-mannopyranoside (3 and 4).**

To a stirred mixture of **1** (1.41 g, 3.12 mmol) and CSA (0.380 g, 1.64 mmol) in acetonitrile (50 mL) was added **2** (6.00 g, 28.5 mmol). The reaction mixture was refluxed for 13 h and concentrated. The residue was taken up with CH₂Cl₂ (50 mL), washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate 8:1) afforded a mixture in the ratio 3:1 (**3/4**) (1.58 g, 85%).

***S*-Phenyl 4,6-*O*- α -[2-(2-iodophenyl)ethylthiocarbonyl]benzylidene-2,3-di-*O*-benzyl-1-thio- α -D-mannopyranoside (5 and 6).**

To a stirred solution of 2-(2-iodophenyl)ethanethiol (589 mg, 2.23 mmol) in toluene (30 mL) was added AlMe₃ (1.68 mL, 2M in hexane, 3.35 mmol) at 0 °C. After stirring for a further 30 min at 0 °C, the solution was warmed to rt and a mixture of **3** and **4** (667 mg, 1.11 mmol) was added. The solution was then heated to reflux for 4 h, cooled to rt, diluted with ethyl acetate (30 mL), washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Concentration and purification by column chromatography on silica gel (eluent: hexane/ethyl acetate 10:1) afforded **5** and **6** (833 mg, 90%).

General procedure for the glycosylation.

A mixture of **5** or **6** (331 mg, 0.40 mmol), BSP (100 mg, 0.48 mmol), TTBP (224 mg, 0.80 mmol) and molecular sieves in CH₂Cl₂ (25 mL) was stirred for 30 min at –60 °C and Tf₂O (87 μ L, 0.52 mmol) was added at this temperature. After 10 min, acceptor (1.20 mmol in 2 mL CH₂Cl₂) was added. The solution was further stirred for 1 h at –60 °C, and slowly warmed to rt over a period of 3 h and filtered. The filtrate was washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate 6:1) afforded β -D-mannopyranoside only.

For **8**, first separation gave an inseparable mixture of acceptor and **8**. The mixture was treated with pyridine (4 mL), Ac₂O (4 mL) and DMAP (20 mg), stirred overnight and concentrated. The residue was taken with ethyl acetate (15 mL), washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate 6:1) afforded **8** in 71% yield.

Preparation of methyl 2,3-diacetyl-4,6-O-[α -2-(2-iodophenyl)ethylthiocarbonyl]benzylidene- α -D-glucopyranoside (19**).**

To a stirred mixture of **26** (0.60 g, 3.09 mmol) and CSA (0.358 g, 1.54 mmol) in acetonitrile (25 mL) was added **2** (3.25 g, 30.9 mmol). The reaction mixture was refluxed overnight and concentrated. The residue was taken up with CH₂Cl₂ (30 mL), washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate = 1:1) afforded an isomeric mixture of **27** (0.799 g, 76%).

TMSOTf (0.496 mL, 2.74 mmol) was added to a mixture of **27** (0.311 g, 0.914 mmol) and NEt₃ (0.382 mL, 0.914 mmol) in CH₂Cl₂ (10 mL) at 0°C. Then the reaction solution was stirred at rt for 1 h, washed with saturated aq. Na₂CO₃, brine and dried over anhydrous Na₂SO₄. Removal of solvent afforded crude **28** (452mg) which was used for next step without purification. To a stirred solution of 2-(2-iodophenyl)ethanethiol (0.483

g, 1.83 mmol) in toluene (10 mL) was added a solution of AlMe_3 (2M in hexane, 0.68 mL, 1.36 mmol) at 0 °C. The stirring was continued for 30 min at 0 °C. The solution was then warmed to RT and a solution of crude product **28** (452 mg) in toluene (5 mL) was added. The solution was then heated to reflux for 5 h, cooled to rt, diluted with ethyl acetate (20 mL), washed with saturated aq. Na_2CO_3 , brine and dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was dissolved in CH_2Cl_2 (10 mL) and treated with TBAF (3 mL, 1M in hexane). The reaction mixture was stirred at rt for 1 h, washed with saturated aq. NH_4Cl , dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was dissolved in Ac_2O (3 mL) and pyridine (3 mL) and treated with catalytic DMAP (20 mg). After the solution was stirred for 3 h, it was diluted with ethyl acetate (20 mL), washed with saturated aq. Na_2CO_3 , brine and dried over anhydrous Na_2SO_4 . Concentration and purification by column chromatography over silica gel (eluent: hexane/ethyl acetate = 4:1) afforded **19** (347 mg, 58%) and **29** (82.6 mg, 14%).

Preparation of methyl 2,3-diacetyl-4, 6-O-[α -2-(2-iodophenyl)ethylthiocarbonyl]benzylidene- β -D-galactopyranoside (21**).**

To a solution of **30** (250 mg, 1.29 mmol) in DMF (10 mL) was added NaH (309 mg, 60% in mineral oil, 7.23 mmol) at rt. After 30 min, the solution was cooled to 0°C, TMSOTf (1.49 mL, 7.23 mmol) was added and stirred for 1 h. The reaction mixture was diluted

with ethyl acetate (30 mL), washed with saturated aq. Na_2CO_3 , brine, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was dissolved in CH_2Cl_2 (10 mL), followed by addition of **2** (600 mg, 2.85 mmol) and TMSOTf (0.116 mL, 0.645 mmol). The reaction mixture was stirred overnight, washed with saturated aq. Na_2CO_3 , brine and dried over anhydrous Na_2SO_4 . Removal of the solvent afforded crude **31** (1.02g) which was used in the next step without purification. To a stirred solution of 2-(2-iodophenyl)ethanethiol (823 mg, 3.12 mmol) in toluene (10 mL) was added a solution of AlMe_3 (2M in hexane, 1.60 mL, 3.20 mmol) at 0 °C. The stirring was continued for 30 min at 0 °C. Then the solution was warmed to RT and a solution of **31** (1.02g) in toluene (5 mL) was added. The solution was then heated to reflux for 5h, diluted with ethyl acetate (20 mL), washed with saturated aq. Na_2CO_3 , brine, dried over anhydrous Na_2SO_4 and concentrated. The crude reaction mixture was dissolved in CH_2Cl_2 (10 mL), treated with TBAF (4 mL, 1M in hexane) and stirred at rt for 1 h, washed with NH_4Cl , dried over anhydrous Na_2SO_4 . Concentration and purification by column chromatography on silica gel (eluent: hexane/ethyl acetate = 1:1) afforded an isomeric mixture of **32** (450 mg, 61%).

32 (79.2 mg, 0.138 mmol) was dissolved in Ac_2O (1 mL) and pyridine (1 mL) and treated with catalytic DMAP (19.5 mg). After the reaction was stirred for 3 h, it was diluted with ethyl acetate (15 mL), washed with saturated aq. Na_2CO_3 , brine and dried over anhydrous Na_2SO_4 . Concentration and purification by column chromatography on silica gel (eluent: hexane/ethyl acetate = 5:1) afforded an isomeric mixture of **21** (80.8 mg, 89%)

Methyl 4,6-*O*- α -(methoxycarbonyl)benzylidene-2,3-di-*O*-*p*-methoxybenzyl- β -D-galactopyranoside (24**).**

CSA (17.2 mg, 0.074 mmol) was added to a mixture of **32** (144 mg, 0.252 mmol) and **33** (400 mg, 1.42 mmol) in CH₂Cl₂ (10 mL). After 30 h, the solution was washed with saturated aq. Na₂CO₃, brine, dried over anhydrous Na₂SO₄ and concentrated. Purification by column chromatography on silica gel (eluent: hexane/ethyl acetate = 8:1) afforded an isomeric mixtures of **24** (146mg, 71%).

General procedure for Radical Cleavage.

Method A for **7**, **9**, **10**, **19**, **21**, and **24**

A solution of **7** (**9**, **10**, **19**, **21**, and **24**) (0.18 mmol) in degassed toluene (30 mL) was heated to reflux and a solution of AIBN (4.41 mg, 15%) and Bu₃SnH (72 μ L, 1.5 equiv) in degassed toluene (10 mL) was added over a period of 4 h. Removal of solvent and purification by column chromatography of the crude mixture on silica gel provided the corresponding deoxy pyranosides.

Method B for **8**

A solution of **8** (200 mg, 0.17 mmol) in degassed toluene (30 mL) was heated to reflux and a solution of AIBN (5.5 mg, 20%) and Bu₃SnH (90.8 μ L, 2.0 equiv.) in degassed toluene (4 mL) was added over a period of 5.3 h. Removal of solvent and purification by

column chromatography of the crude mixture on silica gel (eluent: hexane/chloroform/methanol 100:100:1) provided **12**.

Compounds **20**² and **23**³ were known compounds.

1 Portnoy, M.; Dahan, A. *J. Org. Chem.* **2001**, 66, 6480.

2 Roberts, B. P.; Smits, T. M. *Tetrahedron Lett.* **2001**, 42, 3663.

3. Groneberg, R. D. ; Miyazaki, T.; Stylianides, N. A.; Schulze, T. J.; Stahl, W.; Schreiner, E. P.; Suzuki, T.; Iwabuchi, Y.; Smith, A. L, Nicolaou, K. C. *J. Am. Chem. Soc.* **1993**, 115, 7593.

Table-1: Analytical/HRMS data for new compounds

	3	4	5	6
$[\alpha]_D^{28}$	+117.0° (c = 1.2)	+135.2° (c = 1.0)	+92.3° (c = 1.5)	+98.8° (c = 1.2)
Anal.				
Calc	C, 70.21; H, 5.72	C, 70.21;H,5.72	C,60.72;H,4.73	C,60.72;H,4.73
Found	C, 70.44; H, 5.88	C, 70.01;H,5.80	C,60.35;H,4.78	C,61.03;H,4.81

	7	8	9	10
$[\alpha]_D^{28}$	-41.8° (c = 1.2)	-4.6° (c = 1.3)	+29.6°(c = 1.7)	-13.6° (c = 1.6)
Anal.				
Calc	C, 58.85; H, 5.48	C, 64.86;H,5.53	C,64.86;H,5.53	C,63.30;H5.56
Found	C, 58.71; H, 5.51	C, 64.88;H,5.64	C,64.77;H,5.67	C,63.27;H,5.81

	11	12	13	14
$[\alpha]_D^{28}$	-81.3° (c = 0.7)	-40.4°(c = 0.9)	-29.4°(c = 1.4)	-77.3 (c= 1.0)
Anal.				
Calc	C, 68.23; H, 6.52	C,73.81; H,6.53	C,73.81;H,6.53	C,76.26;H,7.26
Found	C, 68.63; H, 6.81	C, 73.93;H,6.59	C,73.58;H,6.63	C,76.27;H,7.27

	19	21	22	24
$[\alpha]_D^{28}$	+26.4° (c=1.6)	-24.7° (c=1.9)	-51.5° (c=1.1)	-12.6° (c=1.8)
ESIHRMS	$[M+K]^+$	$[M+Na]^+$	$[M+Na]^+$	$M+Na]^+$
Calc	695.0214	679.0297	389.1212/	835.1444
Found	695.0221	679.0321	389.1212	835.1414

	25	27	29	32
$[\alpha]_D^{28}$	-30.4° (c=0.25)	+62.1°(c=0.81)	+69.8° (c=1.0)	-113° (c=4.1)
ESIHRMS	$[M+Na]^+$	FAB $[M+H]^+$	$[M+Na]^+$	$[M+Na]^+$
Calc	545.2151	341.1236	679.0297	595.0263
Found	545.2172	341.1208	679.0285	595.0273

9

21

22

24

S-24

25

S-25

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