

## **Fragment-based development of triazole-substituted *O*-galactosyl aldoximes with fragment-induced affinity and selectivity for galectin-3**

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**Experimental procedures and <sup>1</sup>H nmr data for  
compounds 1-50**

**Supplementary <sup>1</sup>H nmr of compounds 54-77**

## Experimental procedures and $^1\text{H}$ nmr data for compounds 1-50

### ***O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 1**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (22 mg, 90  $\mu\text{mol}$ ) and 36.5% formaldehyde in water (7.4  $\mu\text{L}$ , 99  $\mu\text{mol}$ ) dissolved in  $\text{H}_2\text{O}$  (1 mL) was added 0.1 M HCl (90  $\mu\text{L}$ , 0.1 eq.) and the reaction mixture was stirred over night. Additional 36.5% formaldehyde in water was added (7  $\mu\text{L}$ , 93  $\mu\text{mol}$ ) and the reaction mixture was again stirred over night. The mixture was neutralized with 0.1 M  $\text{NaHCO}_3$  and concentrated under reduced pressure. Purification with flash chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 5:1) gave **1** (5 mg, 26%).  $^1\text{H}$  NMR (300 MHz, MeOD):  $\delta$  7.17 (d, 1H,  $J$  7.5 Hz, NCH), 6.63 (d, 1H,  $J$  6.4 Hz, NCH), 4.91 (d, 1H,  $J$  8.1 Hz, H-1), 3.87 (dd, 1H,  $J$  3.3 Hz,  $J$  0.7 Hz, H-4), 3.75-3.62 (m, 4H), 3.59 (ddd, 1H,  $J$  6.6 Hz,  $J$  5.5 Hz,  $J$  1.0 Hz, H-5), 3.53 (dd, 1H,  $J$  9.6 Hz,  $J$  3.3 Hz, H-3).

### ***N*-(2-Hydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 2**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (10 mg, 30  $\mu\text{mol}$ ) and benzaldehyde (3.4  $\mu\text{L}$ , 33  $\mu\text{mol}$ ) dissolved in  $\text{H}_2\text{O}$  (2 mL) and THF (1 mL) was added 0.1 M HCl (30  $\mu\text{L}$ , 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M  $\text{NaHCO}_3$  and concentrated under reduced pressure. The residue was dissolved in  $\text{H}_2\text{O}$  and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in  $\text{H}_2\text{O}$  and lyophilization gave **2** (6 mg, 70%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  8.27 (s, 1H, NCH), 7.66-7.63 (m, 2H, Ar-H), 7.42-7.38 (m, 3H, Ar-H), 5.01 (d, 1H,  $J$  8.2 Hz, H-1), 3.89 (dd, 1H,  $J$  3.3 Hz,  $J$  0.8 Hz, H-4), 3.82-3.70 (m, 3H), 3.65 (ddd, 1H,  $J$  6.4 Hz,  $J$  5.2 Hz,  $J$  1.2 Hz, H-5), 3.57 (dd, 1H,  $J$  9.7 Hz,  $J$  3.4 Hz, H-3).

### ***N*-(2-Hydroxy-4-methoxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 3**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (19 mg, 84  $\mu\text{mol}$ ) and 2-hydroxy-4-methoxybenzaldehyde (16 mg, 103  $\mu\text{mol}$ ) dissolved in  $\text{H}_2\text{O}$  (1 mL) and THF (0.2 mL) was added 0.1 M HCl (84  $\mu\text{L}$ , 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M  $\text{NaHCO}_3$  and concentrated under reduced pressure. The residue was dissolved in  $\text{H}_2\text{O}$  and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in  $\text{H}_2\text{O}$  and lyophilization gave **3** (8.8 mg, 32%).  $^1\text{H}$  NMR (300 MHz,  $\text{CD}_3\text{OD}$ ):  $\delta$  8.40 (s, 1H, NCH), 7.31 (d, 1H,  $J$  8.5 Hz, Ar-H), 6.48-6.43 (m, 2H, Ar-H), 4.95 (d, 1H,  $J$  8.2 Hz, H-1), 3.88 (dd, 1H,  $J$  3.3 Hz,  $J$  0.8 Hz, H-4), 3.80-3.69 (m, 6H), 3.64 (ddd, 1H,  $J$  6.4 Hz,  $J$  5.2 Hz,  $J$  0.9 Hz, H-5), 3.57 (dd, 1H,  $J$  9.7 Hz,  $J$  3.3 Hz, H-3).

### ***N*-(3-Fluorophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 4**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (18 mg, 81  $\mu\text{mol}$ ) and 3-fluorobenzaldehyde (9.4  $\mu\text{L}$ , 89  $\mu\text{mol}$ ) dissolved in  $\text{H}_2\text{O}$  (1 mL) and THF (0.2 mL) was added 0.1 M HCl (81  $\mu\text{L}$ , 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M  $\text{NaHCO}_3$  and concentrated under reduced pressure. The residue was dissolved in  $\text{H}_2\text{O}$  and applied on to C-18 silica (5 g). Elution with a

gradient of MeOH in H<sub>2</sub>O and lyophilization gave **4** (17 mg, 69%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.27 (d, 1H, *J* 0.8 Hz, NCH), 7.45-7.41 (m, 3H, Ar-H), 7.20-7.13 (m, 1H, Ar-H), 5.02 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 1.0 Hz, H-4), 3.80-3.71 (m, 3H), 3.66 (ddd, 1H, *J* 6.9 Hz, *J* 5.2 Hz, *J* 1.0 Hz, H-5), 3.58 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(2-Nitrophenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **5****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (16 mg, 73 μmol) and 2-nitrobenzaldehyde (34 mg, 224 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (74 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **5** (18 mg, 76%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.71 (s, 1H, NCH), 8.10 (dd, 1H, *J* 8.1 Hz, *J* 1.3 Hz, Ar-H), 8.02 (dd, 1H, *J* 7.7 Hz, *J* 1.5 Hz, Ar-H), 7.75 (br dt, 1H, *J* 7.4 Hz, *J* 1.2 Hz, Ar-H), 7.75 (br dt, 1H, *J* 7.8 Hz, *J* 1.5 Hz, Ar-H), 5.05 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (dd, 1H, *J* 3.3 Hz, *J* 0.7 Hz, H-4), 3.83-3.71 (m, 3H), 3.65 (ddd, 1H, *J* 6.3 Hz, *J* 5.4 Hz, *J* 0.9 Hz, H-5), 3.58 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(2-Furfuryl) *O*-(β-D-galactopyranosyl)-carbaldoxime **6****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (21 mg, 88 μmol) and 2-furancarboxaldehyde (8 μL, 96 μmol) dissolved in H<sub>2</sub>O (3 mL) was added 0.1 M HCl (88 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **6** (23 mg, 94%) as a E/Z (8:1) mixture. <sup>1</sup>H NMR (300 MHz, D<sub>2</sub>O) for E isomer: δ 8.23 (s, 1H, NCH), 7.63 (br dd, 1H, *J* 1.1 Hz, Ar-H), 6.88 (d, 1H, *J* 3.5 Hz, Ar-H), 6.58 (dd, 1H, *J* 3.4 Hz, *J* 1.8 Hz, Ar-H), 4.99 (br d, 1H, *J* 8.2 Hz, H-1), 3.95-3.93 (m, 1H, H-4), 3.90-3.70 (m, 5H). For Z isomer δ 8.41 (s, 1H, NCH), 7.70 (br s, 1H, Ar-H), 6.37-6.36 (m, 1H, Ar-H), 6.64-6.63 (m, 1H, Ar-H), 5.08 (br d, 1H, *J* 8.5 Hz, H-1), 3.95-3.93 (m, 1H, H-4), 3.90-3.70 (m, 5H).

#### ***N*-(4-Fluorophenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **7****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (16 mg, 71 μmol) and 4-fluorobenzaldehyde (12 mg, 99 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (71 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **7** (18 mg, 86%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.26 (s, 1H, NCH), 7.69 (dd, 2H, *J* 8.9 Hz, *J* 5.4 Hz, Ar-H), 7.15 (t, 2H, *J* 8.8 Hz, Ar-H), 5.00 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.9 Hz, H-4), 3.81-3.70 (m, 3H), 3.64 (ddd, 1H, *J* 6.7 Hz, *J* 5.2 Hz, *J* 0.9 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(9-Anthryl) *O*-(β-D-galactopyranosyl)-carbaldoxime **8****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (12 mg, 61  $\mu$ mol) and 9-anthracenecarboxaldehyde (21 mg, 103  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (61  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **8** (21 mg, 87%) 18% aldehyde as impurity. HRMS (ESI) calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>6</sub>Na [M+Na]<sup>+</sup> 406.1267 found 406.1255. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  9.37 (br s, 1H, Ar-H), 8.61 (s, 1H, NCH), 8.50 (br d, 2H, *J* 8.7 Hz, Ar-H), 8.09 (br d, 2H, *J* 7.6 Hz, Ar-H), 7.61-7.50 (m, 4H, Ar-H), 5.19 (d, 1H, *J* 8.3 Hz, H-1), 3.93 (d, 1H, *J* 3.3 Hz, H-4), 3.87-3.62 (m, 5H).

#### ***N*-Methyl *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **9****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (15 mg, 79  $\mu$ mol) and acetaldehyde (4.9  $\mu$ L, 87  $\mu$ mol) dissolved in H<sub>2</sub>O (1.5 mL) was added 0.1 M HCl (79  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to size exclusion sephadex G-10 gel chromatography. Elution with degassed H<sub>2</sub>O and lyophilization gave **9** (17 mg, 98%) as a E/Z (1:1) mixture. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  7.58 (q, 1H, *J* 11.7 Hz, *J* 5.9 Hz, NCH), 5.01 (d, 1H, *J* 8.0 Hz, H-1, partly hidden in solvent residual peak), 3.88-3.85 (m, 1H, *J* 3.3 Hz, *J* 1.1 Hz, H-4), 3.77-3.49 (m, 5H). 1.85 (d, 3H, *J* 5.9 Hz, CH<sub>3</sub>). For Z isomer  $\delta$  6.93 (q, 1H, *J* 11.0 Hz, *J* 5.5 Hz, NCH), 4.81 (d, 1H, *J* 8.1 Hz, H-1), 3.88-3.85 (m, 1H, *J* 3.3 Hz, *J* 1.1 Hz), 3.77-3.49 (m, 5H). 1.91 (d, 3H, *J* 5.5 Hz, CH<sub>3</sub>).

#### ***N*-(3-Hydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **10****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (29 mg, 97  $\mu$ mol) and 2-hydroxybenzaldehyde (13 mg, 107  $\mu$ mol) dissolved in H<sub>2</sub>O (3 mL) and THF (2 mL) was added 0.1 M HCl (97  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. Purification by flash chromatography EtOAc:MeOH (4:1) gave **10** (22 mg, 77%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  8.47 (s, 1H, NCH), 7.42 (dd, 1H, *J* 7.9 Hz, *J* 1.6 Hz, Ar-H), 7.28 (ddd, 1H, *J* 8.2 Hz, *J* 8.0 Hz, *J* 1.7 Hz, Ar-H), 6.91 (m, 1H, Ar-H), 5.00 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (d, 1H, *J* 2.9 Hz, H-4), 3.81-3.72 (m, 3H), 3.66 (br t, 1H, *J* 6.0 Hz, H-5), 3.58 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(4-Dimethylaminophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **11****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (13 mg, 68  $\mu$ mol) and 4-(dimethylamino)benzaldehyde (17 mg, 116  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (68  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to size exclusion sephadex G-10 gel chromatography. Elution with degassed H<sub>2</sub>O and lyophilization gave **11** (19 mg, 83%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.14 (s, 1H, NCH), 7.47 (d, 1H, *J* 9.0 Hz, Ar-H), 6.74 (d, 1H, *J* 9.0 Hz, Ar-H), 4.94 (d, 1H, *J* 8.2 Hz, H-1), 3.88 (dd, 1H, *J* 3.4 Hz, *J* 0.8 Hz, H-4), 3.83-3.61 (m, 5H), 3.56 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3). 3.00 (s, 6H, 2CH<sub>3</sub>).



### ***N*-(4-*tert*-Butylphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **12****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 78  $\mu$ mol) and 4-*tert*-butylbenzaldehyde (18  $\mu$ L, 110  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (78  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **12** (20 mg, 76%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.24 (s, 1H, NCH), 7.57 (br d, 2H, *J* 8.6 Hz, Ar-H), 7.45 (br d, 2H, *J* 8.5 Hz, Ar-H), 4.99 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.8 Hz, H-4), 3.82-3.69 (m, 3H), 3.64 (br ddd, 1H, *J* 6.4 Hz, *J* 5.5 Hz, *J* 1.2 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3), 1.33 (s, 9H, CH<sub>3</sub>).

### ***N*-(3-Nitrophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **13****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (17 mg, 77  $\mu$ mol) and 3-nitrobenzaldehyde (20 mg, 134  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (77  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **13** (22 mg, 86%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  8.53 (d, 1H, *J* 1.5 Hz, NCH), 8.40 (s, 1H, Ar-H), 8.29-8.27 (m, 1H, Ar-H), 8.16 (br d, 1H, *J* 7.4 Hz, Ar-H), 7.68 (br t, 1H, *J* 8.0 Hz, Ar-H), 5.07 (d, 1H, *J* 8.3 Hz, H-1), 3.90 (d, 1H, *J* 3.3 Hz, H-4), 3.79-3.73 (m, 3H), 3.69 (br t, 1H, *J* 5.9 Hz, H-5), 3.59 (dd, 1H, *J* 9.6 Hz, *J* 3.4 Hz, H-3).

### ***N*-(3-Furfuryl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **14****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (18 mg, 90  $\mu$ mol) and 3-furancarboxaldehyde (10  $\mu$ L, 126  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (90  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to size exclusion sephadex G-10 gel chromatography. Elution with degassed H<sub>2</sub>O and lyophilization gave **14** (24 mg, 46%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  8.23 (s, 1H, NCH), 7.85-7.84 (m, 1H), 7.56-7.55 (m, 1H), 6.74-6.73 (m, 1H), 4.94 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.4 Hz, *J* 0.9 Hz, H-4), 3.79-3.62 (m, 4H), 3.56 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3). For Z isomer  $\delta$  8.29 (br s, 1H, NCH), 7.48 (s, 1H), 6.81 (dd, 1H, *J* 1.9 Hz, *J* 0.7 Hz), 5.00 (d, 1H, *J* 8.2 Hz, H-1).

### ***N*-(3-Biphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **15****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (17 mg, 85  $\mu$ mol) and 3-biphenylcarboxaldehyde (19  $\mu$ L, 119  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (85  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **15** (19 mg, 61%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  8.36 (s, 1H, NCH), 7.91 (t, 1H, *J* 1.7 Hz, Ar-H), 7.70-7.67 (m, 1H, Ar-H), 7.66-7.61 (m, 3H, Ar-H), 7.52-7.43 (m, 3H, Ar-H), 7.39-7.36 (m, 1H, Ar-

H), 5.04 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (dd, 1H, *J* 3.4 Hz, *J* 0.8 Hz, H-4), 3.81-3.72 (m, 3H), 3.67 (ddd, 1H, *J* 6.9 Hz, *J* 5.1 Hz, *J* 1.0 Hz, H-5), 3.59 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(9-Ethylcarbazol-3-yl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 16**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 82  $\mu$ mol) and 9-ethyl-3-carbazolecarboxaldehyde (27  $\mu$ L, 121  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (82  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **16** (15 mg, 46%) 27% aldehyde as impurity. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.43 (s, 1H, NCH), 8.32 (d, 1H, *J* 1.5 Hz, Ar-H), 8.09 (br dd, 1H, *J* 7.0 Hz, *J* 0.8 Hz, Ar-H), 7.77 (dd, 1H, *J* 8.6 Hz, *J* 1.6 Hz, Ar-H), 7.51-7.43 (m, 3H, Ar-H), 7.21 (ddd, 1H, *J* 7.8 Hz, *J* 6.5 Hz, *J* 1.6 Hz, Ar-H), 5.05 (d, 1H, *J* 8.2 Hz, H-1), 4.41 (q, 2H, *J* 14.3 Hz, *J* 7.1 Hz, CH<sub>2</sub>), 3.91 (d, 1H, *J* 2.7 Hz, H-4), 3.85-3.73 (m, 3H), 3.71-3.67 (m, 1H, H-5), 3.61 (dd, 1H, *J* 9.6 Hz, *J* 3.4 Hz, H-3), 1.38 (t, 3H, *J* 7.2 Hz, CH<sub>3</sub>).

#### ***N*-Chloromethyl *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 17**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (18 mg, 94  $\mu$ mol) and 50% 2-chloroacetaldehyde in H<sub>2</sub>O (100  $\mu$ L) dissolved in H<sub>2</sub>O (1 mL) was added 0.1 M HCl (94  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. Purification with flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH, 9:1) gave **17** (20 mg, 82%) as a E/Z (3:1) mixture. HRMS (ESI) calcd. for C<sub>8</sub>H<sub>14</sub>ClNO<sub>6</sub>Na [M+Na]<sup>+</sup> 278.0407 found 278.0395. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  7.62 (t, 1H, *J* 6.4 Hz, NCH), 4.89 (1H, H-1, partly hidden in solvent residual peak), 4.19 (d, 2H, *J* 6.4 Hz, CH<sub>2</sub>), 3.87 (d, 1H, *J* 3.2 Hz, H-4), 3.77-3.59 (m, 4H), 3.53 (dd, 1H, *J* 9.7 Hz, *J* 3.3 Hz, H-3). For Z isomer  $\delta$  7.02 (t, 1H, *J* 4.9 Hz, NCH), 4.40 (d, 2H, *J* 4.9 Hz, CH<sub>2</sub>).

#### ***N*-(4-Hydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 18**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (20 mg, 82  $\mu$ mol) and 4-hydroxybenzaldehyde (14 mg, 115  $\mu$ mol) dissolved in H<sub>2</sub>O (3 mL) was added 0.1 M HCl (82  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **18** (24 mg, 99%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.28 (s, 1H, NCH), 7.52 (br d, 2H, *J* 8.6 Hz, Ar-H), 6.87 (br d, 2H, *J* 8.6 Hz, Ar-H), 5.01 (br d, 1H, *J* 8.1 Hz, H-1), 3.95 (br d, 1H, H-4), 3.79-3.70 (m, 5H).

#### ***N*-(4-Acetamidophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 19**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (17 mg, 74  $\mu$ mol) and 4-acetamidobenzaldehyde (17 mg, 105  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (74  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution

with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **19** (15 mg, 61%). HRMS (ESI) calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>Na [M+Na]<sup>+</sup> 363.1168 found 363.1157. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.26 (s, 1H, NCH), 7.61 (br s, 4H, Ar-H), 5.00 (d, 1H, *J* 8.1 Hz, H-1), 3.91 (dd, 1H, *J* 3.4 Hz, *J* 0.7 Hz, H-4), 3.83-3.66 (m, 4H), 3.61 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3), 2.15 (s, 3H, CH<sub>3</sub>). TOF HRMS (ES+) calcd. for C<sub>15</sub>H<sub>20</sub>N<sub>2</sub>O<sub>7</sub>Na [M+Na] 363.1169, found 363.1179.

#### ***N*-(2-Biphenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **20****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (15 mg, 76 μmol) and 2-biphenylcarboxaldehyde (18 μL, 106 μmol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (76 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **20** (16 mg, 58%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.14 (s, 1H, NCH), 7.97 (dd, 1H, *J* 7.8 Hz, *J* 1.5 Hz, Ar-H), 7.49-7.29 (m, 8H, Ar-H), 5.00 (d, 1H, *J* 8.1 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.9 Hz, H-4), 3.83-3.62 (m, 4H), 3.56 (dd, 1H, *J* 9.7 Hz, *J* 3.3 Hz, H-3).

#### ***N*-(4-Nitrophenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **21****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (14 mg, 70 μmol) and 4-nitrobenzaldehyde (14 mg, 90 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (70 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **21** (19 mg, 82%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.39 (s, 1H, NCH), 8.28 (d, 2H, *J* 8.9 Hz, Ar-H), 7.90 (d, 2H, *J* 8.9 Hz, Ar-H), 5.06 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (dd, 1H, *J* 3.3 Hz, *J* 0.8 Hz, H-4), 3.80-3.74 (m, 3H), 3.66 (ddd, 1H, *J* 6.4 Hz, *J* 5.2 Hz, *J* 1.2 Hz, H-5), 3.56 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(5-Nitro-furfur-2-yl) *O*-(β-D-galactopyranosyl)-carbaldoxime **22****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (15 mg, 90 μmol) and 5-nitro-2-furancarboxaldehyde (10.3 μL, 99 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (76 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to size exclusion sephadex G-10 gel chromatography. Elution with degassed H<sub>2</sub>O and lyophilization gave **22** (20 mg, 82%) as a E/Z (9:2) mixture. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) for E isomer: δ 8.27 (s, 1H, NCH), 7.52 (d, 1H, *J* 3.9 Hz, 2CH), 7.06 (d, 1H, *J* 3.9 Hz, 2CH), 5.04 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (br d, 1H, *J* 3.3, H-4), 3.83-3.71 (m, 3H), 3.68-3.64 (m, 1H, H-5), 3.58 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3). For Z isomer: δ 7.74 (s, 1H, NCH), 7.56 (d, 2H, *J* 1.6 Hz, 2CH), 5.07 (d, 1H, *J* 8.2 Hz, H-1).

#### ***N*-(4-Biphenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **23****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (18 mg, 79 μmol) and 4-biphenylcarboxaldehyde (15 mg, 95 μmol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.5 mL)

was added 0.1 M HCl (76  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **23** (17 mg, 66%). HRMS (ESI) calcd. for C<sub>17</sub>H<sub>20</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 334.1291 found 334.1300. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  8.94 (s, 1H, NCH), 8.61 (br d, 1H, *J* 8.4 Hz, Ar-H), 7.97-7.92 (m, 2H, Ar-H), 7.82 (br d, 1H, Ar-H), 7.61-7.50 (m, 3H, Ar-H), 5.13 (d, 1H, *J* 8.2 Hz, H-1), 3.92 (d, 1H, *J* 3.4 Hz, H-4), 3.82-3.74 (m, 3H), 3.69 (br t, 1H, *J* 6.0 Hz, H-5), 3.62 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(1-Ethylpropyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **24****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 72  $\mu$ mol) and 2-ethylbutyraldehyde (12  $\mu$ L, 93  $\mu$ mol) dissolved in H<sub>2</sub>O (1 mL) and THF (05 mL) was added 0.1 M HCl (73  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **24** (14 mg, 72%) as a E/Z (9:1) mixture. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  7.34 (d, 1H, *J* 8.4 Hz, NCH), 4.84 (d, 1H, *J* 8.1 Hz, H-1, partly hidden in solvent residual peak), 3.87 (d, 1H, *J* 3.3 Hz, H-4), 3.76-3.72 (m, 2H), 3.64-3.57 (m, 1H), 3.53 (dd, 1H, *J* 9.7 Hz, *J* 3.3 Hz, H-3), 2.11-2.03 (m, 1H, CH), 1.58-1.40 (m, 4H, 2CH<sub>2</sub>), 0.91 (br t, 6H, *J* 7.4 Hz, 2CH<sub>3</sub>). For Z isomer  $\delta$  6.62 (d, 1H, *J* 8.2 Hz, NCH), 4.83 (d, 1H, *J* 8.1 Hz, H-1, partly hidden in solvent residual peak).

#### ***N*-(2,5-Dihydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **25****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (11 mg, 32  $\mu$ mol) and 2,5-dihydroxybenzaldehyde (5.5 mg, 40  $\mu$ mol) dissolved in H<sub>2</sub>O (2 mL) and THF (1 mL) was added 0.1 M HCl (32  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred for three days. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **25** (8.5 mg, 84%). HRMS (ESI) calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>8</sub>Na [M+Na]<sup>+</sup> 338.0852 found 338.0854. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.40 (s, 1H, NCH), 6.87 (dd, 1H, *J* 2.5 Hz, *J* 0.7 Hz, Ar-H), 6.74-6.73 (m, 2H, Ar-H), 4.98 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.9 Hz, H-4), 3.78-3.65 (m, 3H), 3.65 (ddd, 1H, *J* 6.7 Hz, *J* 5.1 Hz, *J* 0.9 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.5 Hz, H-3).

#### ***N*-(2-Trifluoromethoxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **26****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (13 mg, 67  $\mu$ mol) and 2-(trifluoromethoxy)benzaldehyde (15  $\mu$ L, 87  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (63  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **26** (18 mg, 74%). HRMS (ESI) calcd. for C<sub>14</sub>H<sub>16</sub>F<sub>3</sub>NO<sub>7</sub>Na [M+Na]<sup>+</sup> 390.0777 found 390.0770. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  8.48 (s, 1H, NCH), 7.99 (dd, 1H, *J* 7.9 Hz, *J* 1.6 Hz, Ar-H), 7.54 (dt, 1H, *J* 7.9 Hz, *J* 1.7 Hz, Ar-H), 7.43-7.36 (m, 2H, Ar-H), 5.05 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (br d,

1H, *J* 2.9 Hz, H-4), 3.81-3.73 (m, 3H), 3.66 (br t, 1H, *J* 6.0 Hz, H-5), 3.59 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

***N*-(4-Bromophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **27****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (24 mg, 109  $\mu$ mol) and 4-bromobenzaldehyde (23 mg, 122  $\mu$ mol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.2 mL) was added 0.1 M HCl (109  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **27** (25 mg, 62%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.25 (s, 1H, NCH), 7.57 (s, 4H, Ar-H), 5.00 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.4 Hz, *J* 0.9 Hz, H-4), 3.79-3.71 (m, 3H), 3.64 (ddd, 1H, *J* 6.9 Hz, *J* 5.3 Hz, *J* 0.9 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

***N*-(2,4-Dinitrophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **28****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (15 mg, 75  $\mu$ mol) and 2,4-dinitrobenzaldehyde (20 mg, 105  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (75  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **28** (17 mg, 59%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) impurity might be  $\alpha$  product:  $\delta$  8.91 (d, 1H, *J* 2.3 Hz, Ar-H), 8.78 (s, 1H, NCH), 8.56 (br dd, 1H, *J* 8.7 Hz, *J* 2.0 Hz, Ar-H), 8.31 (d, 1H, *J* 8.77 Hz, Ar-H), 5.09 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (br d, 1H, *J* 3.2 Hz, H-4), 3.82-3.66 (m, 4H), 3.59 (dd, 1H, *J* 9.6 Hz, *J* 3.4 Hz, H-3).

***N*-(3-Pyridyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **29****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (17 mg, 85  $\mu$ mol) and 3-pyridinecarboxaldehyde (10  $\mu$ L, 106  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (85  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **29** (18 mg, 72%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.78 (d, 1H, *J* 1.7 Hz, Ar-H), 8.57 (dd, 1H, *J* 4.9 Hz, *J* 1.6 Hz, Ar-H), 8.35 (s, 1H, NCH), 8.14 (br dt, 1H, *J* 8.1 Hz, *J* 1.9 Hz, Ar-H), 7.49 (br dd, 1H, Ar-H), 5.04 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (br d, 1H, *J* 2.7 Hz, H-4), 3.79-3.73 (m, 3H), 3.66 (br t, 1H, *J* 5.7 Hz, H-5), 3.58 (dd, 1H, *J* 9.6 Hz, *J* 3.3 Hz, H-3).

***N*-Diphenylmethyl *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **30****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (14 mg, 70  $\mu$ mol) and diphenylacetaldehyde (17  $\mu$ L, 98  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (70  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **30** (21 mg, 79%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.04 (d, 1H, *J* 8.6 Hz, NCH), 7.35-7.30 (m, 4H, Ar-H), 7.27-7.21 (m,

6H, Ar-H), 4.93-4.88 (m, 2H, H-1 and Ar-CH), 3.86 (dd, 1H,  $J$  3.3 Hz,  $J$  1.0 Hz, H-4), 3.79-3.64 (m, 3H), 3.61-3.57 (m, 1H), 3.53 (dd, 1H,  $J$  9.7 Hz,  $J$  3.3 Hz, H-3).

### ***N*-(Cyclohexyl *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 31**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (18 mg, 90  $\mu$ mol) and cyclohexanecarboxaldehyde (15  $\mu$ L, 126  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (90  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **31** (18 mg, 69%) as a E/Z (8:1) mixture. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  7.43 (d, 1H,  $J$  6.6 Hz, NCH), 4.82 (d, 1H,  $J$  8.1 Hz, H-1), 3.86 (dd, 1H,  $J$  3.3 Hz,  $J$  1.0 Hz, H-4), 3.77-3.71 (m, 2H), 3.64-3.49 (m, 3H), 2.27-2.22 (m, 1H, CH), 1.80-1.67 (m, 5H), 1.37-1.18 (m, 5H). For Z isomer  $\delta$  6.65 (d, 1H,  $J$  7.5 Hz, NCH), 4.83 (d, 1H,  $J$  7.3 Hz, H-1).

### ***N*-(3,4-Dihydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 32**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (10 mg, 30  $\mu$ mol) and 3,4-dihydroxybenzaldehyde (4.6 mg, 33  $\mu$ mol) dissolved in H<sub>2</sub>O (2 mL) and THF (1 mL) was added 0.1 M HCl (30  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. Purification with flash chromatography (CH<sub>2</sub>Cl<sub>2</sub>/MeOH (4:1)) gave **32** (4.5 mg, 48%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.10 (s, 1H, NCH), 7.12 (d, 1H,  $J$  2.0 Hz, Ar-H), 6.92 (dd, 1H,  $J$  8.4 Hz,  $J$  2.0 Hz, Ar-H), 6.77 (d, 1H,  $J$  8.2 Hz, Ar-H), 4.95 (d, 1H,  $J$  8.2 Hz, H-1, partly hidden in solvent residual peak), 3.88 (dd, 1H,  $J$  3.3 Hz,  $J$  0.8 Hz, H-4), 3.82-3.61 (m, 4H), 3.56 (dd, 1H,  $J$  9.7 Hz,  $J$  3.4 Hz, H-3).

### ***N*-(3-Trifluoromethoxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 33**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 80  $\mu$ mol) and 3-(trifluoromethoxy)benzaldehyde (16  $\mu$ L, 113  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (80  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **33** (17 mg, 59%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.31 (s, 1H, NCH), 7.64-7.58 (m, 2H, Ar-H), 7.52 (t, 1H,  $J$  8.0 Hz, Ar-H), 7.35-7.32 (m, 1H, Ar-H), 5.03 (d, 1H,  $J$  8.2 Hz, H-1), 3.89 (dd, 1H,  $J$  3.3 Hz,  $J$  0.9 Hz, H-4), 3.82-3.71 (m, 3H), 3.66 (ddd, 1H,  $J$  6.3 Hz,  $J$  5.1 Hz,  $J$  1.0 Hz, H-5), 3.58 (dd, 1H,  $J$  9.6 Hz,  $J$  3.4 Hz, H-3).

### ***N*-(5-Bromo-2-hydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 34**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (20 mg, 89  $\mu$ mol) and 5-bromo-2-hydroxybenzaldehyde (20 mg, 99  $\mu$ mol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.2 mL) was added 0.1 M HCl (86  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **34** (20 mg, 61%). HRMS (ESI) calcd. for C<sub>13</sub>H<sub>17</sub>BrNO<sub>7</sub> [M+H]<sup>+</sup> 378.0188 found 378.0172. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$

8.45 (s, 1H, NCH), 7.65 (d, 1H,  $J$  2.5 Hz, Ar-H), 7.36 (dd, 1H,  $J$  8.8 Hz,  $J$  2.5 Hz, Ar-H), 6.81 (d, 1H,  $J$  6.8 Hz, Ar-H), 5.00 (d, 1H,  $J$  8.2 Hz, H-1), 3.89 (dd, 1H,  $J$  3.3 Hz,  $J$  0.8 Hz, H-4), 3.82-3.74 (m, 3H). 3.66 (ddd, 1H,  $J$  6.9 Hz,  $J$  5.4 Hz,  $J$  0.9 Hz, H-5), 3.58 (dd, 1H,  $J$  9.7 Hz,  $J$  3.4 Hz, H-3).

#### ***N*-(2-Hydroxy-5-nitrophenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 35**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 79  $\mu$ mol) and 2-hydroxy-5-nitrobenzaldehyde (17 mg, 103  $\mu$ mol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.3 mL) was added 0.1 M HCl (79  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **35** (15 mg, 54%) HRMS (ESI) calcd. for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O<sub>9</sub>Na [M+Na]<sup>+</sup> 367.0754 found 367.0745. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.60 (s, 1H, NCH), 8.50 (d, 1H,  $J$  3.1 Hz, Ar-H), 7.96 (dd, 1H,  $J$  9.4 Hz,  $J$  3.1 Hz, Ar-H), 6.52 (d, 1H,  $J$  9.4 Hz, Ar-H), 4.98 (d, 1H,  $J$  8.1 Hz, H-1), 3.88 (dd, 1H,  $J$  3.4 Hz,  $J$  0.8 Hz, H-4), 3.85-3.64 (m, 5H). 3.57 (dd, 1H,  $J$  9.7 Hz,  $J$  3.4 Hz, H-3).

#### ***N*-(3-Pyridyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 36**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (13 mg, 67  $\mu$ mol) and 4-pyridinecarboxaldehyde (8.4  $\mu$ L, 88  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (67  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **36** (17 mg, 88%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.61-8.59 (m, 2H, Ar-H), 8.35 (s, 1H, NCH), 7.69-7.66 (m, 2H, Ar-H), 5.07 (d, 1H,  $J$  8.2 Hz, H-1), 3.93 (br dd, 1H,  $J$  2.7 Hz,  $J$  1.0 Hz, H-4), 3.80-3.68 (m, 4H), 3.63 (dd, 1H,  $J$  9.7 Hz,  $J$  3.3 Hz, H-3).

#### ***N*-(2-Quinolyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 37**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (11 mg, 57  $\mu$ mol) and 2-quinolinecarboxaldehyde (12 mg, 74  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (57  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **37** (17 mg, 92%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.43 (s, 1H, NCH), 8.36 (br d, 2H,  $J$  8.6 Hz, Ar-H), 8.08-8.04 (m, 2H, Ar-H), 7.97-7.95 (m, 1H, Ar-H), 7.80 (ddd, 1H,  $J$  8.4 Hz,  $J$  7.0,  $J$  1.4 Hz, Ar-H), 7.65 (ddd, 1H,  $J$  8.2 Hz,  $J$  7.0,  $J$  1.2 Hz, Ar-H), 5.12 (d, 1H,  $J$  8.2 Hz, H-1), 3.92 (dd, 1H,  $J$  3.2 Hz,  $J$  0.8 Hz, H-4), 3.84-3.77 (m, 3H), 3.71-3.67 (m, 1H, H-5), 3.61 (dd, 1H,  $J$  9.7 Hz,  $J$  3.3 Hz, H-3).

#### ***N*-(2,4-Dihydroxyphenyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime 38**

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (11 mg, 32  $\mu$ mol) and 2,4-dihydroxybenzaldehyde (4.8 mg, 35  $\mu$ mol) dissolved in H<sub>2</sub>O (2 mL) and THF (1 mL) was added 0.1 M HCl (32  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred for two days. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure.

The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **38** (9.3 mg, 93%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.34 (s, 1H, NCH), 7.19 (d, 1H, *J* 8.4 Hz, Ar-H), 6.35 (dd, 2H, *J* 8.4 Hz, *J* 2.3 Hz, Ar-H), 6.31 (d, 1H, *J* 2.3 Hz, Ar-H), 4.94 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.8 Hz, H-4), 3.79-3.62 (m, 4H), 3.56 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(4-Benzoylphenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime 39**

To *O*-(β-D-galactopyranosyl)-hydroxylamine (21 mg, 90 μmol) and 4-(4-formylphenyl)benzoate (30 mg, 133 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (90 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **39** (22 mg, 61%). HRMS (ESI) calcd. for C<sub>20</sub>H<sub>21</sub>NO<sub>8</sub> [M+H]<sup>+</sup> 404.1345 found 404.1351. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.32 (s, 1H, NCH), 8.20-8.17 (m, 2H, Ar-H), 7.77-7.68 (m, 3H, Ar-H), 7.60-7.55 (m, 2H, Ar-H), 7.32-7.29 (m, 2H, Ar-H), 5.03 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.3 Hz, *J* 0.9 Hz, H-4), 3.81-3.72 (m, 3H), 3.66 (br t, 1H, *J* 6.5 Hz, H-5), 3.58 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(Benzyl) *O*-(β-D-galactopyranosyl)-carbaldoxime 40**

To *O*-(β-D-galactopyranosyl)-hydroxylamine (14 mg, 70 μmol) and phenylacetaldehyde (11 μL, 90 μmol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (70 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **40** (16 mg, 78%) as a E/Z (2:1) mixture. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer: δ 7.64 (t, 1H, *J* 6.6 Hz, NCH), 7.34-7.23 (m, 5H, Ar-H), 4.94 (d, 1H, *J* 8.2 Hz, H-1), 3.90-3.87 (m, 1H, H-4), 3.80-3.74 (m, 3H), 3.64-3.52 (m, 4H), for Z isomer δ 6.96 (t, 1H, *J* 5.4 Hz, NCH), 4.88 (d, 1H, H-1, partly hidden behind solvent residual peak).

#### ***N*-(1-Naphthyl) *O*-(β-D-galactopyranosyl)-carbaldoxime 41**

To *O*-(β-D-galactopyranosyl)-hydroxylamine (17 mg, 76 μmol) and 1-naphthaldehyde (14 mg, 91 μmol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.5 mL) was added 0.1 M HCl (79 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **41** (16 mg, 55%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.32 (s, 1H, NCH), 7.75-7.64 (m, 6H, Ar-H), 7.48-7.43 (m, 2H, Ar-H), 7.39-7.35 (m, 1H, Ar-H), 5.03 (d, 1H, *J* 8.2 Hz, H-1), 3.90 (dd, 1H, *J* 3.4 Hz, *J* 0.8 Hz, H-4), 3.83-3.72 (m, 3H), 3.66 (ddd, 1H, *J* 6.4 Hz, *J* 5.2 Hz, *J* 1.2 Hz, H-5), 3.59 (dd, 1H, *J* 9.6 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(4-Quinolyl) *O*-(β-D-galactopyranosyl)-carbaldoxime 42**

To *O*-(β-D-galactopyranosyl)-hydroxylamine (22 mg, 112 μmol) and 4-quinolinecarboxaldehyde (26 mg, 167 μmol) dissolved in H<sub>2</sub>O (1 mL) and THF (1 mL) was added 0.1 M HCl (112 μL, 0.1 eq.) and the reaction mixture was stirred over night.



The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **42** (18 mg, 47%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.99 (s, 1H, NCH), 8.90 (d, 1H, *J* 4.6 Hz, Ar-H), 8.61 (br d, 1H, *J* 8.7 Hz, Ar-H), 8.10 (br d, 1H, *J* 8.4 Hz, Ar-H), 7.87-7.81 (m, 2H, Ar-H), 7.71 (ddd, 1H, *J* 8.5 Hz, *J* 6.99 Hz, *J* 1.4 Hz, Ar-H), 4.94 (d, 1H, *J* 8.2 Hz, H-1), 3.92 (br d, 1H, *J* 2.5 Hz, H-4), 3.86-3.77 (m, 3H), 3.72-3.68 (m, 1H, H-5), 3.62 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(5-norbornen-2-yl) *O*-(β-D-galactopyranosyl)-carbaldoxime **43****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (18 mg, 81 μmol) and 5-norbornene-2-carboxaldehyde (9.9 mg, 97 μmol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.5 mL) was added 0.1 M HCl (81 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **43** (19 mg, 77%) as a E/Z (1:1) mixture. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for the mixture of E and Z isomers: δ 7.16 (d, 1H, *J* 7.9 Hz, NCH), 6.25-6.97 (m, 4H), 4.83-4.79 (m, 2H, H-1, partly hidden behind solvent residual peak), 3.87-3.85 (m, 2H), 3.77-3.71 (m, 4H), 3.62-3.50 (m, 6H), 2.95-2.88 (m, 4H), 2.06-1.95 (m, 2H), 1.53-1.30 (m, 6H), 1.08-0.98 (m, 2H). For Z isomer δ 7.12 (d, 1H, *J* 8.3 Hz, NCH),

#### ***N*-Phenyl *O*-(β-D-galactopyranosyl)-carbaldoxime **44****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (30 mg, 97 μmol) and 3-hydroxybenzaldehyde (13 mg, 107 μmol) dissolved in H<sub>2</sub>O (3 mL) and THF (2 mL) was added 0.1 M HCl (97 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. Purification by flash chromatography EtOAc:MeOH (4:1) gave **44** (27 mg, 91%). HRMS (ESI) calcd. for C<sub>13</sub>H<sub>17</sub>NO<sub>7</sub>Na [M+Na]<sup>+</sup> 322.0903 found 322.0890. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD): δ 8.19 (s, 1H, NCH), 7.21 (t, 1H, *J* 7.8 Hz, Ar-H), 7.09-7.05 (m, 2H, Ar-H), 6.84 (ddd, 1H, *J* 8.1 Hz, *J* 2.5 Hz, *J* 0.95 Hz, Ar-H), 4.99 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (d, 1H, *J* 3.3 Hz, H-4), 3.81-3.70 (m, 3H), 3.66-3.63 (ddd, 1H, *J* 6.9 Hz, *J* 5.3 Hz, *J* 1.2 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(2-Hydroxy-3-methoxyphenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **45****

To *O*-(β-D-galactopyranosyl)-hydroxylamine (25 mg, 111 μmol) and 2-hydroxy-3-methoxybenzaldehyde (23 mg, 152 μmol) dissolved in H<sub>2</sub>O (1 mL) and THF (0.2 mL) was added 0.1 M HCl (111 μL, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **45** (17 mg, 47%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD): δ 8.55 (s, 1H, NCH), 7.15 (dd, 1H, *J* 7.9 Hz, *J* 1.3 Hz, Ar-H), 6.98 (dd, 1H, *J* 8.5 Hz, *J* 1.4 Hz, Ar-H), 6.81 (t, 1H, *J* 8.0 Hz, Ar-H), 4.99 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (d, 1H, *J* 3.4 Hz, H-4), 3.86 (s, 3H, CH<sub>3</sub>), 3.82-3.70 (m, 3H), 3.65 (ddd, 1H, *J* 5.6 Hz, *J* 4.3 Hz, *J* 1.2 Hz, H-5), 3.57 (dd, 1H, *J* 9.7 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(2-Fluorophenyl) *O*-(β-D-galactopyranosyl)-carbaldoxime **46****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (17 mg, 74  $\mu$ mol) and 2-fluorobenzaldehyde (11  $\mu$ L, 104  $\mu$ mol) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (74  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **46** (18 mg, 79%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  8.47 (s, 1H, NCH), 7.86 (dt, 1H, *J* 7.6 Hz, *J* 1.7 Hz, Ar-H), 7.50-7.42 (m, 1H, Ar-H), 7.24-7.14 (m, 2H, Ar-H), 5.03 (d, 1H, *J* 8.2 Hz, H-1), 3.89 (dd, 1H, *J* 3.4 Hz, *J* 0.9 Hz, H-4), 3.80-3.71 (m, 3H), 3.65 (ddd, 1H, *J* 6.8 Hz, *J* 5.2 Hz, *J* 1.0 Hz, H-5), 3.58 (dd, 1H, *J* 9.6 Hz, *J* 3.4 Hz, H-3).

#### ***N*-(2-Phenylethyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **47****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (21 mg, 109  $\mu$ mol) and hydrocinnamaldehyde (20  $\mu$ L, 152  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (109  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **47** (30 mg, 88%) as a E/Z (3:1) mixture. <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  7.57 (t, 1H, *J* 6.0 Hz, NCH), 7.31-7.17 (m, 5H, *J* 9.0 Hz, Ar-H), 4.82 (d, 1H, *J* 8.1 Hz, H-1), 3.86 (dd, 1H, *J* 3.2 Hz, *J* 1.0 Hz, H-4), 3.75-3.50 (m, 5H), 2.85-2.80 (m, 2H, CH<sub>2</sub>), 2.55-2.48 (m, 2H, CH<sub>2</sub>). For Z isomer  $\delta$  6.86 (t, 1H, *J* 5.1 Hz, NCH), 4.86 (d, 1H Hz, H-1, partly hidden in solvent residual peak), 2.77-2.72 (m, 2H, CH<sub>2</sub>).

#### ***N*-(2-Naphthyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **48****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (16 mg, 81  $\mu$ mol) and 2-naphtaldehyde (18 mg, 113  $\mu$ mol) dissolved in H<sub>2</sub>O (0.7 mL) and THF (0.5 mL) was added 0.1 M HCl (81  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **48** (15 mg, 55%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD):  $\delta$  8.43 (s, 1H, NCH), 7.80 (s, 1H, Ar-H), 7.91-7.86 (m, 4H, Ar-H), 7.55-7.50 (m, 2H, Ar-H), 5.06 (s, 1H, *J* 8.2 Hz, H-1), 3.91 (d, 1H, *J* 3.0 Hz, H-4), 3.83-3.71 (m, 3H), 3.68 (br t, 1H, *J* 6.0 Hz, H-5), 3.60 (dd, 1H, *J* 9.7 Hz, *J* 3.4, H-3).

#### ***N*-(3-Indolyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **49****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (15 mg, 77  $\mu$ mol) and indole-3-carboxaldehyde (13 mg, 88  $\mu$ M) dissolved in H<sub>2</sub>O (0.6 mL) and THF (0.6 mL) was added 0.1 M HCl (76  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **49** (21.5 mg, 87 %). HRMS (FAB+) calcd. for C<sub>15</sub>H<sub>18</sub>N<sub>2</sub>O<sub>6</sub>Na [M+Na]<sup>+</sup> 345.1063 found 345.1071. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) for E isomer:  $\delta$  3.61-3.78 (m, 5H, H-2, H-3, H-5, H-6, H-6'), 3.91 (dd, 1H, H-4), 5.04 (d, 1H, *J*=8.9 Hz, H-1), 7.26-7.31 (m, 2H, Ar-H), 7.49 (d, 1H, *J*=7.6 Hz, Ar-H), 7.61 (s, 1H, Ar-H), 7.98 (bd, 1H, *J*=6.9 Hz, Ar-H), 8.51 (s, 1H, NCH). For Z isomer  $\delta$  3.74-3.83 (m, 4H,

H-3, H-5, H-6, H-6'), 3.90, (dd, 1H,  $J=8.2, 1.7$  Hz, H-2), 3.99 (dd, 1H,  $J=3.3$  Hz, H-4), 5.11 (d, 1H,  $J=8.2$  Hz, H-1), 7.24-7.34 (m, 2H, Ar-H), 7.55 (bd, 1H,  $J=7.3$  Hz, Ar-H), 7.84 (bd, 1H,  $J=7.2$  Hz, Ar-H), 7.98 (s, 1H, Ar-H), 8.30 (s, 1H, NCH).

***N*-(2-Hydroxy-1-naphthyl) *O*-( $\beta$ -D-galactopyranosyl)-carbaldoxime **50****

To *O*-( $\beta$ -D-galactopyranosyl)-hydroxylamine (19 mg, 97  $\mu$ mol) and 2-hydroxy-1-naphthaldehyde (22 mg, 127  $\mu$ mol) dissolved in H<sub>2</sub>O (1.5 mL) and THF (1.0 mL) was added 0.1 M HCl (97  $\mu$ L, 0.1 eq.) and the reaction mixture was stirred over night. The mixture was neutralized with 0.1 M NaHCO<sub>3</sub> and concentrated under reduced pressure. The residue was dissolved in H<sub>2</sub>O and applied on to C-18 silica (5 g). Elution with a gradient of MeOH in H<sub>2</sub>O and lyophilization gave **50** (25 mg, 72%). <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD):  $\delta$  9.27 (s, 1H, NCH), 8.33 (br d, 1H,  $J$  8.3 Hz, Ar-H), 7.78 (br t, 2H,  $J$  9.4 Hz, Ar-H), 7.49 (ddd, 1H,  $J$  8.2 Hz,  $J$  6.96 Hz,  $J$  1.3 Hz, Ar-H), 7.31 (br t, 1H,  $J$  7.5 Hz, Ar-H), 7.12 (d, 1H,  $J$  9.1 Hz, Ar-H), 5.08 (d, 1H,  $J$  8.2 Hz, H-1), 3.91 (br d, 1H,  $J$  3.5 Hz, H-4), 3.82-3.68 (m, 4H), 3.61 (dd, 1H,  $J$  9.6 Hz,  $J$  3.4 Hz, H-3).

# Supplementary <sup>1</sup>H nmr of compounds 54-77























