

Supporting Information for Manuscript:

Carbohydrate-Bearing 3-Hydroxy-4-pyridinonato

Complexes of Gallium(III) and Indium(III)

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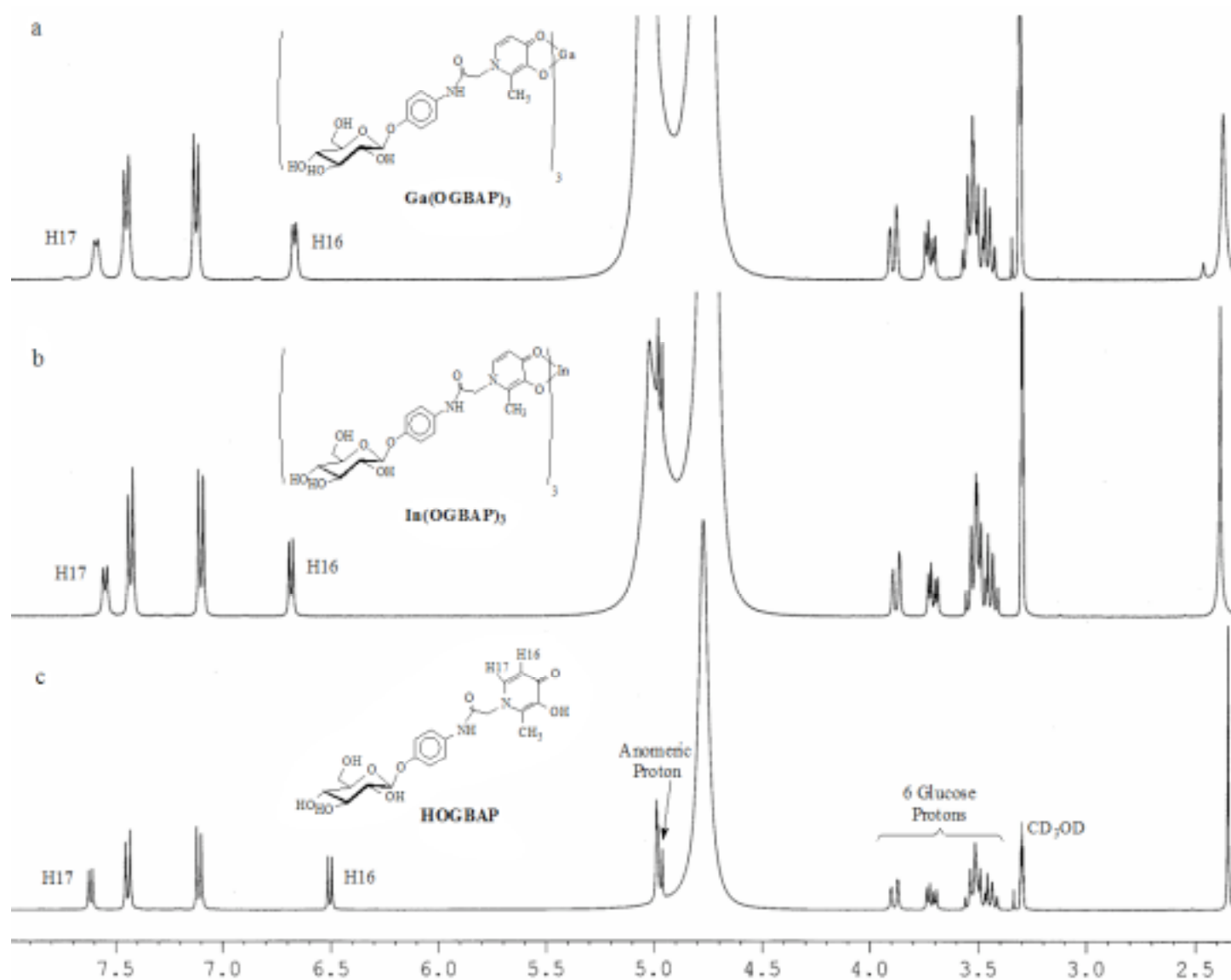


Figure S1: ^1H NMR spectra (400 MHz) in 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$ for (a) $\text{Ga}(\text{OGBAP})_3$ (b) $\text{In}(\text{OGBAP})_3$ (c) HOGBAP .

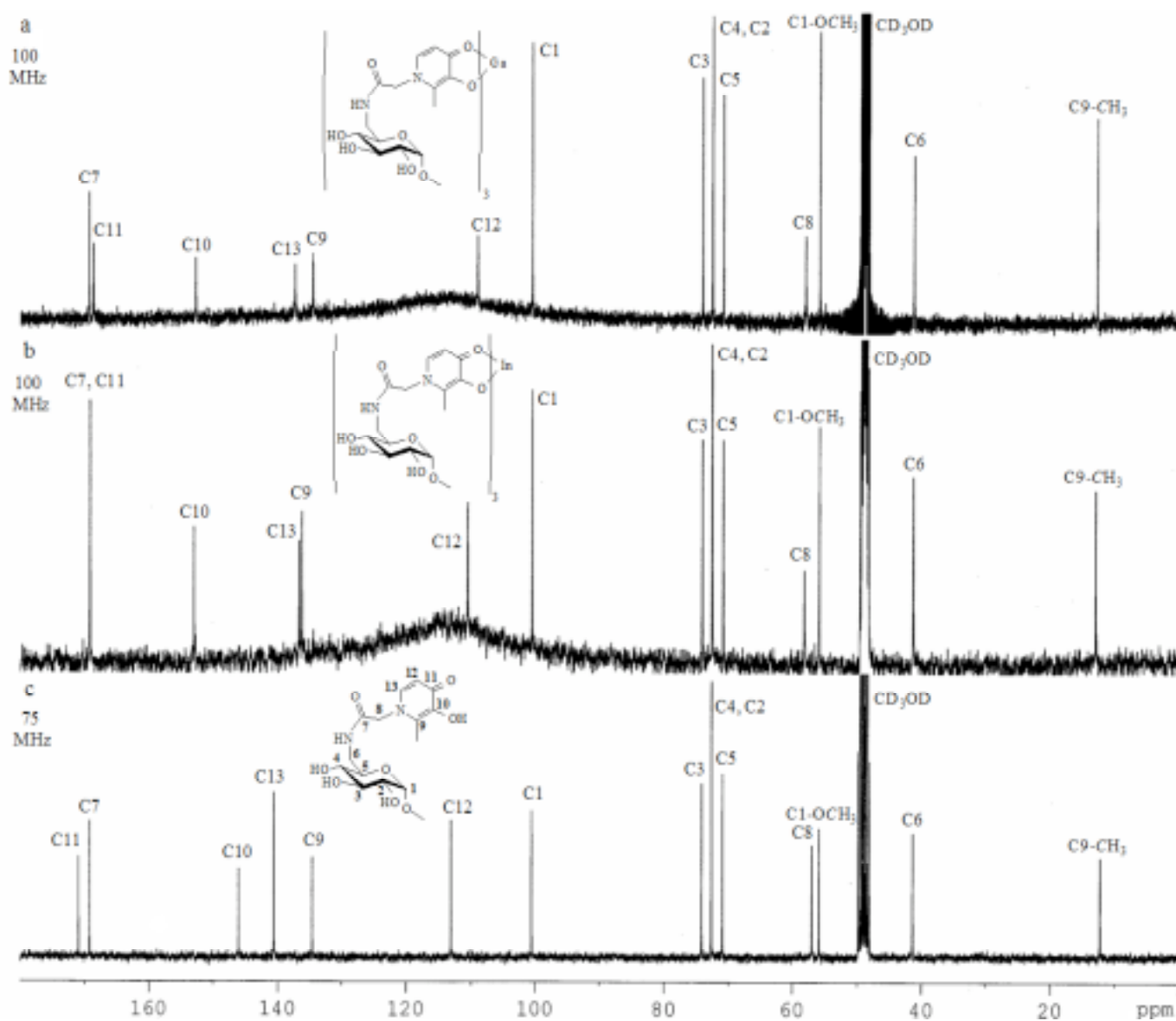


Figure S2: ^{13}C NMR spectra in 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$ for (a) $\text{Ga}(\text{OG6GP})_3$ (b) $\text{In}(\text{OG6GP})_3$ (c) HOG6GP.

¹H and ¹³C NMR assignments for all compounds.

3-Benzoyloxy-2-methyl-4-pyranone (2) (benzyl maltol). ¹H NMR (300 MHz, CDCl₃): δ = 2.078 (s, 3H, C2-CH₃), 5.146 (s, 2H, Bn CH₂), 6.397 (d, 1H, H5, ³J_{5,6} = 5.6 Hz), 7.34 (m, 5H, Bn C₆H₅), 7.595 (d, 1H, H6, ³J_{6,5} = 5.6 Hz).

3-Benzoyloxy-1-(carboxymethyl)-2-methyl-4(1H)-pyridinone (3). ¹H NMR (300 MHz, CD₃OD): δ = 2.130 (s, 3H, C2-CH₃), 4.819 (s, 2H, CH₂CO₂H), 5.097 (s, 2H, Bn CH₂), 6.604 (d, 1H, H5, ³J_{5,6} = 7.4 Hz), 7.39 (m, 5H, Bn C₆H₅), 7.786 (d, 1H, H6, ³J_{6,5} = 7.4 Hz). MS (+LSIMS): m/z 274 [M+H]⁺.

Methyl 6-deoxy-6-tosyl- α -D-glucopyranoside (5). ¹H NMR (500 MHz, CD₃OD): δ = 2.403 (s, 3H, Ts-CH₃), 3.305 (s, 3H, C1-OCH₃), 3.430 (dd, 1H, H4, ³J_{4,3} = 9.7 Hz, ³J_{4,5} = 9.7 Hz), 3.458 (dd, 1H, H2, ³J_{2,1} = 3.8 Hz, ³J_{2,3} = 9.7 Hz), 3.685 (dd, 1H, H3, ³J_{3,2} = 9.7 Hz, ³J_{3,4} = 9.7 Hz), 3.704 (ddd, 1H, H5, ³J_{5,4} = 9.7 Hz, ³J_{5,6a} = 2.0 Hz, ³J_{5,6b} = 4.9 Hz), 4.215 (dd, 1H, H6b, ³J_{6b,5} = 2.0 Hz, ²J_{6b,6a} = 11.9 Hz), 4.293 (dd, 1H, H6a, ³J_{6a,5} = 4.9 Hz, ²J_{6a,6b} = 11.9 Hz), 4.656 (d, 1H, H1, ³J_{1,2} = 3.8 Hz), 7.307 (d, 2H, arom H, J = 8.2 Hz), 7.766 (d, 2H, arom H, J = 8.2 Hz). ¹³C{¹H} NMR (125 MHz, CD₃OD): δ = 21.61 (Ts-CH₃), 55.35 (C1-OCH₃), 69.20 (C6), 69.39 (C5), 69.56 (C4), 71.74 (C2), 74.08 (C3), 99.35 (C1), 127.97 (arom C), 129.86 (arom C), 132.76 (arom C), 144.92 (arom C).

Methyl 6-azido-6-deoxy- α -D-glucopyranoside (6). ¹H NMR (500 MHz, CD₃OD): δ = 3.246 (dd, 1H, H4, ³J_{4,3} = 9.8 Hz, ³J_{4,5} = 9.8 Hz), 3.385 (dd, 1H, H6b, ³J_{6b,5} = 6.6 Hz, ²J_{6b,6a} = 13.1 Hz), 3.407 (dd, 1H, H2, ³J_{2,1} = 3.8 Hz, ³J_{2,3} = 9.8 Hz), 3.424 (s, 3H, C1-OCH₃), 3.491 (dd, 1H, H6a, ³J_{6a,5} = 2.3 Hz, ²J_{6a,6b} = 13.1 Hz), 3.587 (dd, 1H, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 3.665 (ddd, 1H, H5, ³J_{5,4} = 9.8 Hz, ³J_{5,6a} = 2.3 Hz, ³J_{5,6b} = 6.6 Hz), 4.685 (d, 1H, H1, ³J_{1,2} = 3.8 Hz). ¹³C{¹H}

NMR (125 MHz, CD₃OD): δ = 52.70 (C6), 55.71 (C1-OCH₃), 72.51 (C4), 72.58 (C5), 73.37 (C2), 74.82 (C3), 101.25 (C1).

Methyl 6-amino-6-deoxy- α -D-glucopyranoside (7). ¹H NMR (500 MHz, CD₃OD): δ = 3.014 (dd, 1H, H6b, ³J_{6b,5} = 6.8 Hz, ²J_{6b,6a} = 13.1 Hz), 3.166 (dd, 1H, H4, ³J_{4,3} = 9.6 Hz, ³J_{4,5} = 9.6 Hz), 3.343 (dd, 1H, H6a, ³J_{6a,5} = 3.0 Hz, ²J_{6a,6b} = 13.1 Hz), 3.414 (dd, 1H, H2, ³J_{2,1} = 3.7 Hz, ³J_{2,3} = 9.6 Hz), 3.439 (s, 3H, C1-OCH₃), 3.608 (dd, 1H, H3, ³J_{3,2} = 9.6 Hz, ³J_{3,4} = 9.6 Hz), 3.732 (ddd, 1H, H5, ³J_{5,4} = 9.6 Hz, ³J_{5,6a} = 3.0 Hz, ³J_{5,6b} = 6.8 Hz), 4.730 (d, 1H, H1, ³J_{1,2} = 3.7 Hz). ¹³C{¹H} NMR (125 MHz, CD₃OD): δ = 42.26 (C6), 56.26 (C1-OCH₃), 69.30 (C5), 73.20 (C2), 73.43 (C4), 74.54 (C3), 101.53 (C1).

3-Benzoyloxy-1- $\{[[(2R,3S,4S,5R,6S)-3,4,5$ -trihydroxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl-2-methyl-4(1H)-pyridinone (8). ¹H NMR (500 MHz, CD₃OD): δ = 2.079 (s, 3H, C9-CH₃), 3.105 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.359 (s, 3H, C1-OCH₃), 3.371 (dd, partially overlapped with C1-OCH₃, H2, ³J_{2,1} = 3.7 Hz, ³J_{2,3} = 9.8 Hz), 3.390 (dd, partially overlapped with C1-OCH₃, H6b, ²J_{6b,6a} = 13.2 Hz, ³J_{6b,5} = 6.7 Hz), 3.56 (ddd, overlapped with H3, H5), 3.597 (dd, partially overlapped with H5, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 3.651 (dd, 1H, H6a, ²J_{6a,6b} = 13.2 Hz, ³J_{6a,5} = 2.6 Hz), 4.637 (d, 1H, H1, ³J_{1,2} = 3.7 Hz), 4.723 (s, 2H, H8), 5.042 (s, 2H, Bn CH₂), 6.466 (d, 1H, H12, ³J_{12,13} = 7.4 Hz), 7.37 (m, 5H, Bn C₆H₅), 7.606 (d, 1H, H13, ³J_{13,12} = 7.4 Hz).

1- $\{[[(2R,3S,4S,5R,6S)-3,4,5$ -Triacetoxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl-3-benzoyloxy-2-methyl-4(1H)-pyridinone hemihydrate (9·0.5H₂O). ¹H NMR (400 MHz, CD₃OD): δ = 1.956 (s, 3H, COCH₃), 1.977 (s, 3H, COCH₃), 2.031 (s, 3H, COCH₃), 2.100 (s, 3H, C9-CH₃), 3.32 (dd, partially overlapped with CD₃OD, H6b), 3.388 (s, 3H, C1-OCH₃), 3.609 (dd, 1H, H6a, ²J_{6a,6b} = 14.4 Hz, ³J_{6a,5} = 5.1 Hz), 3.895 (ddd, 1H, H5, ³J_{5,4} = 9.9 Hz, ³J_{5,6a} = 5.1 Hz, ³J_{5,6b} = 2.5 Hz), 4.714 (s, 2H, H8), 4.87 (overlapped with CD₃OH, H2), 4.919

(dd, partially overlapped with H1, $H4$, $^3J_{4,3} = 9.8$ Hz, $^3J_{4,5} = 9.8$ Hz), 4.936 (d, partially overlapped with $H4$, $H1$, $^3J_{1,2} = 3.7$ Hz), 5.045 (s, 2H, Bn CH_2), 5.380 (dd, 1H, $H3$, $^3J_{3,2} = 9.8$ Hz, $^3J_{3,4} = 9.8$ Hz), 6.460 (d, 1H, $H12$, $^3J_{12,13} = 7.4$ Hz), 7.38 (m, 5H, Bn C_6H_5), 7.588 (d, 1H, $H13$, $^3J_{13,12} = 7.4$ Hz).

4-Nitrophenyl 2,3,4,6-tetra-O-acetyl- α -D-glucopyranoside (11). 1H NMR (300 MHz, CD_3OD): $\delta = 1.994$ (s, 3H, $COCH_3$), 2.028 (s, 3H, $COCH_3$), 2.030 (s, 3H, $COCH_3$), 2.036 (s, 3H, $COCH_3$), 4.15 (ddd, partially overlapped with H6b, $H5$), 4.161 (dd, partially overlapped with H5, H6b, $^2J_{6b,6a} = 12.7$ Hz, $^3J_{6b,5} = 2.2$ Hz), 4.309 (dd, 1H, $H6a$, $^2J_{6a,6b} = 12.7$ Hz, $^3J_{6a,5} = 5.4$ Hz), 5.126 (dd, 1H, $H4$, $^3J_{4,5} = 9.6$ Hz, $^3J_{4,3} = 9.6$ Hz), 5.209 (dd, 1H, $H2$, $^3J_{2,1} = 7.8$ Hz, $^3J_{2,3} = 9.6$ Hz), 5.405 (dd, 1H, $H3$, $^3J_{3,2} = 9.6$ Hz, $^3J_{3,4} = 9.6$ Hz), 5.546 (d, 1H, $H1$, $^3J_{1,2} = 7.8$ Hz), 7.190 (d, 2H, arom H , $J = 9.4$ Hz), 7.524 (d, 2H, arom H , $J = 9.4$ Hz).

4-Nitrophenyl α -D-glucopyranoside (12). 1H NMR (300 MHz, CD_3OD): $\delta = 3.34$ (dd, partially overlapped with CD_3OD , $H4$), 3.45 (m, 3H, $H2$, $H3$, and $H5$ overlapped), 3.693 (dd, 1H, H6b, $^2J_{6b,6a} = 12.1$ Hz, $^3J_{6b,5} = 5.5$ Hz), 3.901 (dd, 1H, $H6a$, $^2J_{6a,6b} = 12.1$ Hz, $^3J_{6a,5} = 2.0$ Hz), 4.914 (d, 1H, $H1$, $^3J_{1,2} = 7.2$ Hz), 7.231 (d, 2H, arom H , $J = 9.1$ Hz), 8.208 (d, 2H, arom H , $J = 9.1$ Hz).

4-Aminophenyl α -D-glucopyranoside, hydrochloride salt (13). 1H NMR (300 MHz, $(CD_3)_2SO$): $\delta = 3.17$ (m, 4H), 3.447 (m, 1H, H6b), 3.697 (m, 1H, H6b), 4.529 (dd, 1H, $J = 5.2$ Hz, $J = 5.2$ Hz), 4.566 (d, 1H, $H1$, $^3J_{1,2} = 7.4$ Hz), 4.952 (d, 1H, $J = 5.0$ Hz), 5.014 (d, 1H, $J = 4.4$ Hz), 5.198 (d, 1H, $J = 5.0$ Hz), 6.475 (d, 2H, arom H , $J = 8.7$ Hz), 6.756 (d, 2H, arom H , $J = 8.7$ Hz).

3-Benzoyloxy-1- $\{[4-(\alpha$ -D-glucopyranosyloxy)phenylcarbamoyl]methyl $\}$ -2-methyl-4(1H)-pyridinone (14). 1H NMR (400 MHz, 9:1 $CD_3OD:D_2O$): $\delta = 2.038$ (s, 3H, $C13-CH_3$), 3.410 (dd, 1H, $H4$, $^3J_{4,5} = 9.8$ Hz, $^3J_{4,3} = 9.8$ Hz), 3.47 (m, partially overlapped with H5 and H3, $H2$), 3.47 (m, partially overlapped with H2 and H3, $H5$), 3.48 (m, partially overlapped with H2 and H5, $H3$),

3.705 (dd, 1H, *H*6b, $^2J_{6b,6a} = 12.3$ Hz, $^3J_{6b,5} = 5.4$ Hz), 3.886 (dd, 1H, *H*6a, $^2J_{6a,6b} = 12.3$ Hz, $^3J_{6a,5} = 2.0$ Hz), 4.855 (s, partially overlapped with water, *H*12), 4.907 (d, partially overlapped with water peak, *H*1, $^3J_{1,2} = 7.2$ Hz), 5.042 (s, partially overlapped with water peak, *H*12), 6.532 (d, 1H, *H*16, $^3J_{16,17} = 7.4$ Hz), 7.090 (d, 2H, *H*8, $^3J_{8,9} = 9.0$ Hz), 7.30 (m, 5H, Bn C₆H₅), 7.441 (d, 2H, *H*9, $^3J_{9,8} = 9.0$ Hz), 7.655 (d, 1H, *H*17, $^3J_{17,16} = 7.4$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CD₃OD): $\delta = 13.05, 57.31, 63.21, 71.09, 74.62, 74.89, 77.51, 77.80, 102.31, 117.13, 118.23, 122.85, 129.43, 129.52, 130.36, 133.45, 137.95, 142.82, 145.93, 146.56, 155.75, 166.39, 175.27$.

1-[[4-(2,3,4,6-Tetra-O-acetyl- β -D-glucopyranosyloxy)phenylcarbamoyl]methyl]-3-benzyloxy-2-methyl-4(1H)-pyridinone hemihydrate (15·0.5 H₂O). ^1H NMR (400 MHz, CD₃OD): $\delta = 1.983$ (s, 3H, COCH₃), 2.016 (s, 3H, COCH₃), 2.031 (s, 6H, 2-COCH₃), 2.342 (s, 3H, C13-CH₃), 4.055 (ddd, 1H, *H*5, $^3J_{5,4} = 9.9$ Hz, $^3J_{5,6a} = 5.1$ Hz, $^3J_{5,6b} = 2.3$ Hz), 4.136 (dd, 1H, *H*6b, $^2J_{6b,6a} = 12.3$ Hz, $^3J_{6b,5} = 2.3$ Hz), 4.296 (dd, 1H, *H*6a, $^2J_{6a,6b} = 12.3$ Hz, $^3J_{6a,5} = 5.1$ Hz), 4.845 (s, partially overlapped with CD₃OD, *H*12), 5.059 (s, 2H, Bn CH₂), 5.089 (dd, 1H, *H*4, $^3J_{4,5} = 9.9$ Hz, $^3J_{4,3} = 9.6$ Hz), 5.135 (dd, 1H, *H*2, $^3J_{2,1} = 7.9$ Hz, $^3J_{2,3} = 9.6$ Hz), 5.282 (d, 1H, *H*1, $^3J_{1,2} = 7.9$ Hz), 5.362 (dd, 1H, *H*3, $^3J_{3,2} = 9.6$ Hz, $^3J_{3,4} = 9.6$ Hz), 6.481 (d, 1H, *H*16, $^3J_{16,17} = 7.4$ Hz), 6.995 (d, 2H, *H*9, $^3J_{9,8} = 9.0$ Hz), 7.163 (m, 3H, Bn C₆H₅), 7.396 (m, 2H, Bn C₆H₅), 7.480 (d, 2H, *H*8, $^3J_{9,8} = 9.0$ Hz), 7.653 (d, 1H, *H*17, $^3J_{17,16} = 7.4$ Hz).

3-Benzyloxy-1-(4-hydroxyphenyl)-2-methyl-4(1H)-pyridinone (17). ^1H NMR (300 MHz, CD₃OD): $\delta = 1.855$ (s, 3H, C2-CH₃), 5.112 (s, 2H, Bn CH₂), 6.010 (d, 1H, *H*5, $^3J_{5,6} = 7.3$ Hz), 6.883 (d, 2H, phenol arom H, $J = 8.8$ Hz), 7.091 (d, 2H, phenol arom H, $J = 8.8$ Hz), 7.38 (m, 5H, Bn C₆H₅), 7.622 (d, 1H, *H*6, $^3J_{6,5} = 7.3$ Hz).

1-[4-(2,3,4,6-Tetra-O-benzyl- β -D-glucopyranosyloxy)phenyl]-3-benzyloxy-2-methyl-4(1H)-pyridinone (18). ^1H NMR (300 MHz, CDCl₃): $\delta = 2.342$ (s, 3H, C13-CH₃), 3.73 (m, 6H), 4.56 (m, 3H), 4.86 (m, 3H), 4.99 (m, 3H), 5.238 (s, 2H, Bn CH₂), 6.467 (d, 1H, *H*14, $^3J_{14,15} = 7.6$ Hz),

7.043 (d, 2H, *H*8, $^3J_{8,9} = 8.9$ Hz), 7.119 (d, 2H, *H*9, $^3J_{9,8} = 8.9$ Hz), 7.201 (m, 3H, Bn C_6H_5), 7.31 (m, 21H, Bn C_6H_5), 7.45 (m, 1H, Bn C_6H_5), 7.460 (d, 1H, *H*15, $^3J_{15,14} = 7.6$ Hz). MS (+LSIMS): m/z 830 $[M+H]^+$.

3-Benzoyloxy-1-[[[(1R,2R,3S,4R,5R/S)-4-hydroxymethyl-2,3,5-trihydroxy-tetrahydropyran-1-yl]carbamoyl]methyl]-2-methyl-4(1H)-pyridinone (19). 1H NMR (400 MHz, $CD_3OD:D_2O$) α anomer: $\delta = 2.00$ (s, 3H, $COCH_3$), 3.45 (m, 1H *H*3) 3.72-3.86 (m, 4H, *H*4, *H*5, *H*6) 3.89 (d, 1H, *H*14, $^3J_{14,15} = 7.6$ Hz) (dd, 1H, *H*2, $^2J = 11.27$ Hz, $^2J = 1.52$ Hz) 4.81 (s, 2H, *H*8), 5.02 (s, 2H, *H*15), 5.16 (d, 1H, *H*1, $^2J_{1,2} = 3.96$ Hz) 6.56 (d, 1H, *H*12, $^2J_{13,12} = 7.30$ Hz) 7.4 (m, 5H, Aryl) 7.65 (d, 1H, *H*13, $^2J_{12,13} = 7.31$ Hz); β anomer: $\delta = 2.06$ (s, 3H, $COCH_3$), 3.42 (m, 2H, *H*3, *H*4) 3.55 (m, 1H, *H*5) 3.68 (dd, 1H, *H*2, $^2J = 8.22$ Hz) 3.72-3.87 (m, 2H, *H*6) 4.70 (d, 1H, *H*1, $^2J_{1,2} = 8.22$ Hz) 4.81 (s, 2H, *H*8) 5.02 (s, 2H, *H*15) 6.56 (d, 2H, *H*12, $^2J_{12,13} = 7.30$ Hz) 7.4 (m, 5H, Aryl) 7.65 (d, 1H, *H*13, $^2J_{13,12} = 7.31$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz, $CD_3OD:D_2O$) for the α anomer $\delta = 13.15$ (*C*14), 55.40 (*C*2), 56.92 (*C*8), 61.73 (*C*6), 71.30 (*C*3), 71.80 (*C*4), 72.62 (*C*5), 75.13 (*C*15), 91.8 (*C*1), 116.98 (*C*12), 129.59, 129.70, 129.73, 130.40, 130.53 (*C*17-*C*21), 137.07 (*C*9) 143.01 (*C*13), 145.81 (*C*16), 146.70 (*C*10), 169.09 (*C*7), 174.90 (*C*11); β anomer: $\delta = 13.10$ (*C*14), 57.17 (*C*8), 58.11 (*C*2), 61.84 (*C*6), 71.09 (*C*3), 74.80 (*C*5), 77.11 (*C*4), 75.10 (*C*15), 95.8 (*C*1), 116.98 (*C*12), 129.59, 129.70, 129.73, 130.40, 130.53 (*C*17-*C*21), 137.14 (*C*9) 142.98 (*C*13), 145.81 (*C*16), 146.70 (*C*10), 169.43 (*C*7), 174.87 (*C*11).

3-Hydroxy-1-[[[(2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl]-2-methyl-4(1H)-pyridinone (HOG6GP). 1H NMR (400 MHz, 1:1 $CD_3OD:D_2O$): $\delta = 2.314$ (s, 3H, *C*9- CH_3), 3.216 (dd, 1H, *H*4, $^3J_{4,5} = 9.8$ Hz, $^3J_{4,3} = 9.8$ Hz), 3.370 (s, 3H, *C*1- OCH_3), 3.429 (dd, 1H, *H*6b, $^2J_{6b,6a} = 13.9$ Hz, $^3J_{6b,5} = 6.8$ Hz), 3.481 (dd, 1H, *H*2, $^3J_{2,1} = 3.7$ Hz, $^3J_{2,3} = 9.8$ Hz), 3.61 (dd, overlapped with *H*5, *H*3, $^3J_{3,2} = 9.8$ Hz, $^3J_{3,4} = 9.8$ Hz), 3.62 (ddd, overlapped with *H*3, *H*5), 3.671 (dd, 1H, *H*6a, $^2J_{6a,6b} = 13.9$ Hz, $^3J_{6a,5} = 2.7$ Hz), 4.727 (d, partially overlapped with water peak, *H*1, $^3J_{1,2} = 3.7$ Hz), 4.86 (s, partially overlapped with water peak, *H*8),

6.486 (d, 1H, *H*12, $^3J_{12,13} = 7.2$ Hz), 7.579 (d, 1H, *H*13, $^3J_{13,12} = 7.2$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$): $\delta = 12.30$ (C9- CH_3), 41.39 (C6), 55.89 (C1- OCH_3), 57.00 (C8), 70.92 (C5), 72.63 (C2), 72.63 (C4), 74.16 (C3), 100.55 (C1), 113.13 (C12), 134.59 (C9), 140.62 (C13), 146.10 (C10), 169.26 (C7), 170.95 (C11).

Tris(1-{\{[(2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) tetrahydrate (Ga(OG6GP)₃·4H₂O). ^1H NMR (500 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$): $\delta = 2.343$ (s, 3H, C9- CH_3), 3.207 (dd, 1H, *H*4, $^3J_{4,5} = 9.8$ Hz, $^3J_{4,3} = 9.8$ Hz), 3.354 (s, 3H, C1- OCH_3), 3.441 (dd, 1H, *H*6b, $^2J_{6b,6a} = 13.9$ Hz, $^3J_{6b,5} = 6.9$ Hz), 3.471 (dd, 1H, *H*2, $^3J_{2,1} = 3.7$ Hz, $^3J_{2,3} = 9.8$ Hz), 3.60 (dd, overlapped with *H*5, *H*3, $^3J_{3,2} = 9.8$ Hz, $^3J_{3,4} = 9.8$ Hz), 3.61 (ddd, overlapped with *H*3, *H*5), 4.711 (d, 1H-partially overlapped with water peak, *H*1, $^3J_{1,2} = 3.7$ Hz), 3.658 (dd, 1H, *H*6a, $^2J_{6a,6b} = 13.9$ Hz, $^3J_{6a,5} = 2.3$ Hz), 4.924 (s, 2H-partially overlapped with water peak, *H*8), 6.649 (d, 1H, *H*12, $^3J_{12,13} = 6.7$ Hz), 7.521 (d, 1H, *H*13, $^3J_{13,12} = 6.7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$): $\delta = 13.00$ (C9- CH_3), 41.36 (C6), 55.94 (C1- OCH_3), 58.11 (C8), 70.90 (C5), 72.57 (C2), 72.59 (C4), 74.12 (C3), 100.48 (C1), 109.04 (C12), 134.43 (C9), 137.24 (C13), 152.57 (C10), 168.61 (C11), 169.24 (C7).

Tris(1-{\{[(2R,3S,4S,5R,6S)-3,4,5-trihydroxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)indium(III) monohydrate (In(OG6GP)₃·H₂O). ^1H NMR (400 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$): $\delta = 2.367$ (s, 3H, C9- CH_3), 3.202 (dd, 1H, *H*4, $^3J_{4,5} = 9.8$ Hz, $^3J_{4,3} = 9.8$ Hz), 3.346 (s, 3H, C1- OCH_3), 3.429 (dd, 1H, *H*6b, $^2J_{6b,6a} = 13.8$ Hz, $^3J_{6b,5} = 5.9$ Hz), 3.465 (dd, 1H, *H*2, $^3J_{2,1} = 3.7$ Hz, $^3J_{2,3} = 9.8$ Hz), 3.60 (dd, overlapped with *H*5, *H*3, $^3J_{3,2} = 9.8$ Hz, $^3J_{3,4} = 9.8$ Hz), 3.61 (ddd, overlapped with *H*3, *H*5), 3.657 (dd, 1H, *H*6a, $^2J_{6a,6b} = 13.6$ Hz, $^3J_{6a,5} = 2.7$ Hz), 4.701 (d, partially overlapped with water peak, *H*1, $^3J_{1,2} = 3.7$ Hz), 4.919 (s, 2H-partially overlapped with water peak, *H*8), 6.618 (d, 1H, *H*12, $^3J_{12,13} = 6.7$ Hz), 7.537 (d, 1H, *H*13, $^3J_{13,12} = 6.7$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$): $\delta = 13.18$

(C9-CH₃), 41.38 (C6), 55.94 (C1-OCH₃), 58.24 (C8), 70.91 (C5), 72.59 (C2), 72.62 (C4), 74.13 (C3), 100.51 (C1), 110.59 (C12), 136.19 (C9), 136.65 (C13), 152.88 (C10), 169.13 (C7), 169.13 (C11).

1-{[4-(-D-Glucopyranosyloxy)phenylcarbamoyl]methyl}-3-hydroxy-2-methyl-4(1H)-pyridinone hemihydrate (HOGBAP·0.5H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.187 (s, 3H, C13-CH₃), 3.438 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.49 (dd, partially overlapped with H5, H2, ³J_{2,1} = 7.4 Hz, ³J_{2,3} = 9.8 Hz), 3.52 (m, partially overlapped with H3 and H2, H5), 3.539 (dd, partially overlapped with H5, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 3.716 (dd, 1H, H6b, ²J_{6b,6a} = 12.4 Hz, ³J_{6b,5} = 5.6 Hz), 3.887 (dd, 1H, H6a, ²J_{6a,6b} = 12.4 Hz, ³J_{6a,5} = 2.2 Hz), 4.97 (d, partially overlapped with H12 and water peak, H1, ³J_{1,2} = 7.4 Hz), 4.99 (s, partially overlapped with H1 and water peak, H12), 6.505 (d, 1H, H16, ³J_{16,17} = 7.3 Hz), 7.108 (d, 2H, H8, ³J_{8,9} = 9.1 Hz), 7.443 (d, 2H, H9, ³J_{9,8} = 9.1 Hz), 7.617 (d, 1H, H17, ³J_{17,16} = 7.3 Hz). ¹³C{¹H} NMR (125 MHz, (CD₃)₂SO): δ = 11.59 (C13-CH₃), 55.52 (C12), 60.75 (C6), 69.76 (C4), 73.26 (C2), 76.63 (C3), 77.01 (C5), 100.76 (C1), 110.41 (C16), 116.63 (C8), 120.58 (C9), 129.38 (C13), 132.64 (C10), 139.22 (C17), 145.05 (C14), 153.68 (C7), 165.04 (C11), 169.41 (C15).

Tris(1-{[4-(-D-glucopyranosyloxy)phenylcarbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) dihydrate (Ga(OGBAP)₃·2H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.371 (s, 3H, C13-CH₃), 3.437 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.49 (dd, partially overlapped with H5, H2, ³J_{2,1} = 7.4 Hz, ³J_{2,3} = 9.8 Hz), 3.52 (m, partially overlapped with H3 and H2, H5), 3.537 (dd, partially overlapped with H5, H3, ³J_{3,2} = 9.3 Hz, ³J_{3,4} = 9.8 Hz), 3.712 (dd, 1H, H6b, ²J_{6b,6a} = 12.4 Hz, ³J_{6b,5} = 5.6 Hz), 3.881 (dd, 1H, H6a, ²J_{6a,6b} = 12.4 Hz, ³J_{6a,5} = 2.2 Hz), 4.97 (d, partially overlapped with H12 and water peak, H1, ³J_{1,2} = 7.4 Hz), 5.01 (s, partially overlapped with H1 and water peak, H12), 6.643 (d, 1H, H16, ³J_{16,17} = 6.8 Hz), 7.098 (d, 2H, H8, ³J_{8,9} = 9.0 Hz), 7.429 (d, 2H, H9, ³J_{9,8} = 9.0 Hz), 7.567 (d, 1H, H17, ³J_{17,16} = 6.8 Hz). ¹³C{¹H} NMR (100 MHz, (CD₃)₂SO): δ = 12.35 (C13-CH₃), 56.90 (C12), 60.68 (C6), 69.71 (C4), 73.25

(C2), 76.60 (C3), 76.96 (C5), 100.73 (C1), 106.14 (C16), 116.56 (C8), 120.48 (C9), 129.134 (C13), 132.71 (C10), 134.78 (C17), 152.82 (C14), 153.62 (C7), 164.61 (C11), 168.29 (C15).

*Tris(1-{[4-(-D-glucopyranosyloxy)phenylcarbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)indium(III) pentahydrate (**In(OGBAP)**₃·5H₂O)*. ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.407 (s, 3H, C13-CH₃), 3.437 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.49 (dd, partially overlapped with H5, H2, ³J_{2,1} = 7.4 Hz, ³J_{2,3} = 9.8 Hz), 3.52 (m, partially overlapped with H3 and H2, H5), 3.537 (dd, partially overlapped with H5, H3, ³J_{3,2} = 9.3 Hz, ³J_{3,4} = 9.8 Hz), 3.713 (dd, 1H, H6b, ²J_{6b,6a} = 12.4 Hz, ³J_{6b,5} = 5.6 Hz), 3.882 (dd, 1H, H6a, ²J_{6a,6b} = 12.4 Hz, ³J_{6a,5} = 2.2 Hz), 4.97 (d, partially overlapped with H12 and water peak, H1, ³J_{1,2} = 7.4 Hz), 5.03 (s, partially overlapped with H1 and water peak, H12), 6.691 (d, 1H, H16, ³J_{16,17} = 6.9 Hz), 7.101 (d, 2H, H8, ³J_{8,9} = 9.1 Hz), 7.434 (d, 2H, H9, ³J_{9,8} = 9.1 Hz), 7.562 (d, 1H, H17, ³J_{17,16} = 6.9 Hz). ¹³C{¹H} NMR (100 MHz, (CD₃)₂SO): δ = 12.42 (C13-CH₃), 57 (C12), 60.79 (C6), 69.81 (C4), 73.31 (C2), 76.65 (C3), 77.01 (C5), 100.80 (C1), 107.94 (C16), 116.70 (C8), 120.68 (C9), 131.72 (C13), 132.64 (C10), 134.30 (C17), 153.31 (C14), 153.76 (C7), 164.61 (C11), 168.96 (C15).

*1-[4-(-D-glucopyranosyloxy)phenyl]-3-hydroxy-2-methyl-4(1H)-pyridinone monohydrate (**HOGBPP**·H₂O)*. ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.097 (s, 3H, C11-CH₃), 3.470 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.57 (dd, partially overlapped with H5, H2), 3.60 (m, partially overlapped with H3 and H2, H5), 3.61 (dd, partially overlapped with H5, H3), 3.735 (dd, 1H, H6b, ²J_{6b,6a} = 12.3 Hz, ³J_{6b,5} = 5.7 Hz), 3.915 (dd, 1H, H6a, ²J_{6a,6b} = 12.3 Hz, ³J_{6a,5} = 2.0 Hz), 5.101 (d, partially overlapped with water peak, H1, ³J_{1,2} = 7.3 Hz), 6.543 (d, 1H, H14, ³J_{14,15} = 7.2 Hz), 7.264 (d, 2H, H8, ³J_{8,9} = 9.0 Hz), 7.328 (d, 2H, H9, ³J_{9,8} = 9.0 Hz), 7.613 (d, 1H, H15, ³J_{15,14} = 7.2 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:D₂O): δ = 14.04 (C11-CH₃), 61.75 (C6), 70.63 (C4), 74.12 (C2), 76.88 (C3), 77.43 (C5), 101.28 (C1), 113.00 (C14), 118.44 (C8), 128.94 (C9), 135.03 (C11), 137.13 (C10), 139.84 (C15), 145.73 (C12), 158.67 (C7), 170.99 (C13).

Tris{1-[4-(-D-glucopyranosyloxy)phenyl]-2-methyl-3-oxy-4(1H)-pyridinonato}gallium(III) dihydrate (Ga(OGBPP)₃·2H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.114 (s, 3H, C11-CH₃), 3.459 (dd, 1H, H4, ³J_{4,5} = 9.7 Hz, ³J_{4,3} = 9.7 Hz), 3.56 (dd, partially overlapped with H5, H2), 3.59 (m, partially overlapped with H3 and H2, H5), 3.60 (dd, partially overlapped with H5, H3), 3.722 (dd, 1H, H6b, ²J_{6b,6a} = 12.1 Hz, ³J_{6b,5} = 5.5 Hz), 3.908 (dd, 1H, H6a, ²J_{6a,6b} = 12.1 Hz, ³J_{6a,5} = 2.0 Hz), 5.090 (d, partially overlapped with water peak, H1, ³J_{1,2} = 7.1 Hz), 6.683 (d, 1H, H14, ³J_{14,15} = 6.8 Hz), 7.256 (d, 2H, H8, ³J_{8,9} = 9.0 Hz), 7.337 (d, 2H, H9, ³J_{9,8} = 9.0 Hz), 7.556 (d, 1H, H15, ³J_{15,14} = 6.8 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:D₂O): δ = 14.80 (C11-CH₃), 61.76 (C6), 70.64 (C4), 74.12 (C2), 76.87 (C3), 77.41 (C5), 101.29 (C1), 108.80 (C14), 118.32 (C8), 128.73 (C9), 134.74 (C11), 136.43 (C15), 137.85 (C10), 152.24 (C12), 158.61 (C7), 168.66 (C13).

Tris{1-[4-(-D-glucopyranosyloxy)phenyl]-2-methyl-3-oxy-4(1H)-pyridinonato}indium(III) tetrahydrate (In(OGBPP)₃·4H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:D₂O): δ = 2.106 (s, 3H, C11-CH₃), 3.456 (dd, 1H, H4, ³J_{4,5} = 9.8 Hz, ³J_{4,3} = 9.8 Hz), 3.56 (dd, partially overlapped with H5, H2), 3.59 (m, partially overlapped with H3 and H2, H5), 3.60 (dd, partially overlapped with H5, H3), 3.719 (dd, 1H, H6b, ²J_{6b,6a} = 12.1 Hz, ³J_{6b,5} = 5.6 Hz), 3.906 (dd, 1H, H6a, ²J_{6a,6b} = 12.2 Hz, ³J_{6a,5} = 2.1 Hz), 5.086 (d, partially overlapped with water peak, H1, ³J_{1,2} = 7.2 Hz), 6.709 (d, 1H, H14, ³J_{14,15} = 6.8 Hz), 7.246 (d, 2H, H8, ³J_{8,9} = 9.0 Hz), 7.338 (d, 2H, H9, ³J_{9,8} = 9.0 Hz), 7.547 (d, 1H, H15, ³J_{15,14} = 6.8 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:D₂O): δ = 14.96 (C11-CH₃), 61.78 (C6), 70.67 (C4), 74.14 (C2), 76.91 (C3), 77.44 (C5), 101.34 (C1), 110.38 (C14), 118.34 (C8), 128.68 (C9), 135.87 (C15), 136.34 (C11), 137.86 (C10), 152.49 (C12), 158.65 (C7), 169.17 (C13).

1-{[[(2R,3S,4S,5R,6S)-3,4,5-Triacetoxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl}-3-hydroxy-2-methyl-4(1H)-pyridinone monohydrate (HAG6GP·H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:CD₃CN): δ = 1.992 (s, 3H, COCH₃), 2.000 (s, 3H, COCH₃),

2.048 (s, 3H, COCH₃), 2.314 (s, 3H, C9-CH₃), 3.382 (dd, 1H, H6b, ²J_{6b,6a} = 14.5 Hz, ³J_{6b,5} = 5.5 Hz), 3.422 (s, 3H, C1-OCH₃), 3.555 (dd, 1H, H6a, ²J_{6a,6b} = 14.5 Hz, ³J_{6a,5} = 5.5 Hz), 3.924 (ddd, 1H, H5, ³J_{5,4} = 9.9 Hz, ³J_{5,6a} = 5.5 Hz, ³J_{5,6b} = 2.6 Hz), 4.720 (s, 2H, H8), 4.918 (dd, partially overlapped with H1, H2, ³J_{2,1} = 3.6 Hz, ³J_{2,3} = 9.9 Hz), 4.944 (d, partially overlapped with H2 and H3, H1, ³J_{1,2} = 3.6 Hz), 4.962 (dd, partially overlapped with H1, H4, ³J_{4,3} = 9.9 Hz, ³J_{4,5} = 9.9 Hz), 5.387 (dd, 1H, H3, ³J_{3,2} = 9.9 Hz, ³J_{3,4} = 9.9 Hz), 6.379 (d, 1H, H12, ³J_{12,13} = 7.3 Hz), 7.476 (d, 1H, H13, ³J_{13,12} = 7.3 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:D₂O): δ = 12.17 (C9-CH₃), 20.71 (COCH₃), 20.78 (2_COCH₃), 40.10 (C6), 55.92 (C1-OCH₃), 56.60 (C8), 68.93 (C5), 70.13 (C4), 70.97 (C3), 71.72 (C2), 97.92 (C1), 112.01 (C12), 132.78 (C9), 140.40 (C13), 146.40 (C10), 168.25 (C7), 170.89 (C11), 171.23 (C4-COCH₃), 171.50 (C2-COCH₃), 171.53 (C3-COCH₃).

Tris(1-[[[(2R,3S,4S,5R,6S)-3,4,5-triacetoxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) monohydrate (Ga(AG6GP)₃·H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:CD₃CN): δ = 1.988 (s, 3H, COCH₃), 1.998 (s, 3H, COCH₃), 2.044 (s, 3H, COCH₃), 2.328 (s, 3H, C9-CH₃), 3.357 (dd, 1H, H6b, ²J_{6b,6a} = 14.5 Hz, ³J_{6b,5} = 5.5 Hz), 3.407 (s, 3H, C1-OCH₃), 3.520 (dd, 1H, H6a, ²J_{6a,6b} = 14.5 Hz, ³J_{6a,5} = 5.5 Hz), 3.918 (ddd, 1H, H5, ³J_{5,4} = 9.8 Hz, ³J_{5,6a} = 5.5 Hz, ³J_{5,6b} = 2.6 Hz), 4.782 (s, 2H, H8), 4.909 (dd, partially overlapped with H1, H2, ³J_{2,1} = 3.6 Hz, ³J_{2,3} = 9.8 Hz), 4.929 (d, partially overlapped with H2 and H3, H1, ³J_{1,2} = 3.6 Hz), 4.958 (dd, partially overlapped with H1, H4, ³J_{4,3} = 9.8 Hz, ³J_{4,5} = 9.8 Hz), 5.379 (dd, 1H, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 6.498 (d, 1H, H12, ³J_{12,13} = 6.9 Hz), 7.395 (d, 1H, H13, ³J_{13,12} = 6.9 Hz). ¹³C{¹H} NMR (75 MHz, 1:1 CD₃OD:D₂O): δ = 12.72 (C9-CH₃), 20.70 (COCH₃), 20.79 (2_COCH₃), 40.27 (C6), 55.98 (C1-OCH₃), 57.81 (C8), 68.98 (C5), 70.33 (C4), 71.02 (C3), 71.76 (C2), 97.91 (C1), 108.08 (C12), 132.79 (C9), 136.21 (C13), 153.88 (C10), 168.02 (C7), 169.57 (C11), 171.17 (C4-COCH₃), 171.44 (C2-COCH₃), 171.50 (C3-COCH₃).

Tris(1-{[[(2R,3S,4S,5R,6S)-3,4,5-triacetoxy-6-methoxy-tetrahydropyran-2-yl-methyl]carbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)indium(III) tetrahydrate (In(AG6GP)₃·4H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:CD₃CN): δ = 1.988 (s, 3H, COCH₃), 1.997 (s, 3H, COCH₃), 2.043 (s, 3H, COCH₃), 2.356 (s, 3H, C9-CH₃), 3.360 (dd, 1H, H6b, ²J_{6b,6a} = 14.5 Hz, ³J_{6b,5} = 5.7 Hz), 3.404 (s, 3H, C1-OCH₃), 3.522 (dd, 1H, H6a, ²J_{6a,6b} = 14.4 Hz, ³J_{6a,5} = 5.7 Hz), 3.907 (ddd, 1H, H5, ³J_{5,4} = 9.8 Hz, ³J_{5,6a} = 5.7 Hz, ³J_{5,6b} = 2.5 Hz), 4.786 (s, 2H, H8), 4.910 (dd, partially overlapped with H1, H2, ³J_{2,1} = 3.6 Hz, ³J_{2,3} = 9.8 Hz), 4.927 (d, partially overlapped with H2 and H3, H1, ³J_{1,2} = 3.6 Hz), 4.956 (dd, partially overlapped with H1, H4, ³J_{4,3} = 9.8 Hz, ³J_{4,5} = 9.8 Hz), 5.378 (dd, 1H, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 6.531 (d, 1H, H12, ³J_{12,13} = 7.0 Hz), 7.386 (d, 1H, H13, ³J_{13,12} = 7.0 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD: CD₃CN): δ = 12.90 (C9-CH₃), 20.70 (COCH₃), 20.79 (2-COCH₃), 40.23 (C6), 55.96 (C1-OCH₃), 57.93 (C8), 68.95 (C5), 70.28 (C4), 71.00 (C3), 71.74 (C2), 97.88 (C1), 109.76 (C12), 134.79 (C9), 135.61 (C13), 154.15 (C10), 168.00 (C7), 170.05 (C11), 171.17 (C4-COCH₃), 171.45 (C2-COCH₃), 171.51 (C3-COCH₃).

1-{[4-(2,3,4,6-Tetra-O-acetyl-D-glucopyranosyloxy)phenylcarbamoyl]methyl}-3-hydroxy-2-methyl-4(1H)-pyridinone monohydrate (HAGBAP·H₂O) . ¹H NMR (400 MHz, 1:1 CD₃OD:CD₃CN): δ = 2.011 (s, 3H, COCH₃), 2.038 (s, 3H, COCH₃), 2.054 (s, 3H, COCH₃), 2.055 (s, 3H, COCH₃), 2.342 (s, 3H, C13-CH₃), 4.123 (ddd, partially overlapped with CD₃OH/H₂O peak, H5, ³J_{5,4} = 9.7 Hz, ³J_{5,6a} = 5.3 Hz, ³J_{5,6b} = 2.3 Hz), 4.167 (dd, 1H, H6b, ²J_{6b,6a} = 12.3 Hz, ³J_{6b,5} = 5.3 Hz), 4.291 (dd, 1H, H6a, ²J_{6a,6b} = 12.3 Hz, ³J_{6a,5} = 2.3 Hz), 4.857 (s, 2H, H12), 5.136 (dd, 1H, H4, ³J_{4,5} = 9.7 Hz, ³J_{4,3} = 9.7 Hz), 5.184 (dd, 1H, H2, ³J_{2,1} = 8.0 Hz, ³J_{2,3} = 9.7 Hz), 5.287 (d, 1H, H1, ³J_{1,2} = 8.0 Hz), 5.382 (dd, 1H, H3, ³J_{3,2} = 9.8 Hz, ³J_{3,4} = 9.8 Hz), 6.402 (d, 1H, H16, ³J_{16,17} = 7.2 Hz), 7.031 (d, 2H, H8, ³J_{8,9} = 9.0 Hz), 7.524 (d, 2H, H9, ³J_{9,8} = 9.0 Hz), 7.535 (d, 1H, H17, ³J_{17,16} = 7.2 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:CD₃CN): δ = 12.24 (C13-CH₃), 20.75 (4-COCH₃), 57.08 (C12), 62.87 (C6), 69.40 (C4), 72.21 (C2), 72.82 (C5), 73.54 (C3), 99.82 (C1), 112.02 (C16), 118.26 (C8), 122.49 (C9), 132.74 (C13), 134.48 (C10), 140.53 (C17), 146.42 (C14),

154.65 (C7), 166.15 (C11), 170.94 (C15), 170.94 (C2-COCH₃), 171.07 (C4-COCH₃), 171.41 (C3-COCH₃), 171.93 (C6-COCH₃).

*Tris(1-{[4-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyloxy)phenylcarbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) tetrahydrate (**Ga(AGBAP)**₃·4H₂O). ¹H NMR (400 MHz, 1:1 CD₃OD:CD₃CN): δ = 2.010 (s, 3H, COCH₃), 2.037 (s, 3H, COCH₃), 2.044 (s, 3H, COCH₃), 2.051 (s, 3H, COCH₃), 2.340 (s, 3H, C13-CH₃), 4.049 (ddd, partially overlapped with CD₃OH/H₂O peak, H5, ³J_{5,4} = 9.6 Hz, ³J_{5,6a} = 5.2 Hz, ³J_{5,6b} = 2.2 Hz), 4.163 (dd, 1H, H6b, ²J_{6b,6a} = 12.3 Hz, ³J_{6b,5} = 5.2 Hz), 4.288 (dd, 1H, H6a, ²J_{6a,6b} = 12.3 Hz, ³J_{6a,5} = 2.2 Hz), 4.895 (s, 2H, H12), 5.130 (dd, 1H, H4, ³J_{4,5} = 9.6 Hz, ³J_{4,3} = 9.6 Hz), 5.167 (dd, 1H, H2, ³J_{2,1} = 8.0 Hz, ³J_{2,3} = 9.6 Hz), 5.282 (d, 1H, H1, ³J_{1,2} = 8.0 Hz), 5.376 (dd, 1H, H3, ³J_{3,2} = 9.6 Hz, ³J_{3,4} = 9.6 Hz), 6.509 (d, 1H, H16, ³J_{16,17} = 6.3 Hz), 7.014 (d, 2H, H8, ³J_{8,9} = 8.7 Hz), 7.450 (d, 1H, H17, ³J_{17,16} = 6.3 Hz), 7.505 (d, 2H, H9, ³J_{9,8} = 8.7 Hz). ¹³C{¹H} NMR (100 MHz, 1:1 CD₃OD:CD₃CN): δ = 12.87 (C13-CH₃), 20.78 (COCH₃), 20.81 (2-COCH₃), 20.87 (COCH₃), 58.13 (C12), 62.85 (C6), 69.39 (C4), 72.23 (C2), 72.81 (C5), 73.57 (C3), 99.78 (C1), 108.22 (C16), 118.20 (C8), 122.37 (C9), 133.08 (C13), 134.58 (C10), 136.59 (C17), 153.73 (C14), 154.50 (C7), 165.88 (C11), 169.45 (C15), 170.94 (C2-COCH₃), 171.05 (C4-COCH₃), 171.39 (C3-COCH₃), 171.92 (C6-COCH₃).*

*Tris(1-{[4-(2,3,4,6-tetra-O-acetyl- β -D-glucopyranosyloxy)phenylcarbamoyl]methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)indium(III) dihydrate (**In(AGBAP)**₃·2H₂O). ¹H NMR (300 MHz, 1:1 CD₃OD:CD₃CN): δ = 2.010 (s, 3H, COCH₃), 2.007 (s, 3H, COCH₃), 2.033 (s, 6H, 2-COCH₃), 2.044 (s, 3H, COCH₃), 2.341 (s, 3H, C13-CH₃), 4.046 (ddd, partially overlapped with CD₃OH/H₂O peak, H5, ³J_{5,4} = 9.6 Hz, ³J_{5,6a} = 5.2 Hz, ³J_{5,6b} = 2.3 Hz), 4.158 (dd, 1H, H6b, ²J_{6b,6a} = 12.3 Hz, ³J_{6b,5} = 2.3 Hz), 4.287 (dd, 1H, H6a, ²J_{6a,6b} = 12.3 Hz, ³J_{6a,5} = 5.2 Hz), 4.885 (s, 2H, H12), 5.128 (dd, 1H, H4, ³J_{4,5} = 9.6 Hz, ³J_{4,3} = 9.6 Hz), 5.177 (dd, 1H, H2, ³J_{2,1} = 7.98.0 Hz, ³J_{2,3} = 9.6 Hz), 5.280 (d, 1H, H1, ³J_{1,2} = 7.9 Hz), 5.376 (dd, 1H, H3, ³J_{3,2} = 9.6 Hz, ³J_{3,4} = 9.6 Hz), 6.532 (d, 1H, H16, ³J_{16,17} = 6.3 Hz), 7.001 (d, 2H, H8, ³J_{8,9} = 8.6 Hz), 7.424 (d, 1H, H17, ³J_{17,16} = 6.3 Hz), 7.488 (d, 2H, H9,*

$^3J_{9,8} = 8.6$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, 1:1 $\text{CD}_3\text{OD}:\text{CD}_3\text{CN}$): $\delta = 13.01$ (C13- CH_3), 20.78 (3- COCH_3), 20.83 (COCH_3), 58.43 (C12), 62.87 (C6), 69.42 (C4), 72.25 (C2), 72.83 (C5), 73.59 (C3), 99.82 (C1), 109.85 (C16), 118.22 (C8), 122.45 (C9), 134.54 (C10), 134.92 (C13), 135.87 (C17), 154.10 (C14), 154.58 (C7), 165.85 (C11), 170.08 (C15), 170.93 (C2- COCH_3), 171.05 (C4- COCH_3), 171.38 (C3- COCH_3), 171.91 (C6- COCH_3).

*3-Hydroxy-1-{\{[(1R,2R,3S,4R,5R/S)-4-hydroxymethyl-2,3,5-trihydroxy-tetrahydropyran-1-yl]carbamoyl\}methyl}-2-methyl-4(1H)-pyridinone hydrate (**HOG2GP**· H_2O or **Feralex-G**· H_2O).*
 ^1H NMR (400 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$) α anomer: $\delta = 2.33$ (s, 3H, COCH_3), 3.44 (m, 1H H_3) 3.74-3.86 (m, 4H, H_4 , H_5 , H_6) 3.91 (dd, 1H, H_2 , $^2J = 12.35$ Hz) 4.90 (s, 2H, H_8), 5.19 (d, 1H, H_1 , $^2J_{1,2} = 3.50$ Hz) 6.49 (d, 1H, H_{12} , $^2J_{12,13} = 7.16$ Hz) 7.59 (d, 1H, H_{13} , $^2J_{13,12} = 7.14$ Hz); β anomer: $\delta = 2.34$ (s, 3H, COCH_3), 3.41 (m, 2H, H_3 , H_4) 3.55 (m, 1H, H_5) 3.67 (dd, 1H, H_2 , $^2J = 8.40$ Hz) 3.72-3.87 (m, 2H, H_6) 4.71 (d, 1H, H_1 , $^2J_{1,2} = 8.38$ Hz) 4.88 (s, 2H, H_8) 6.49 (d, 2H, H_{12} , $^2J_{12,13} = 7.16$ Hz) 7.61 (d, 1H, H_{13} , $^2J_{13,12} = 7.16$ Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$) α anomer: $\delta = 12.04$ (C14), 55.21 (C2), 56.66 (C8), 61.53 (C6), 71.13 (C3), 71.63 (C4), 72.39 (C5), 91.54 (C1), 112.81 (C12), 134.72 (C9) 140.48 (C13), 145.63 (C10), 169.33 (C7), 170.57 (C11); β anomer: $\delta = 11.98$ (C14), 56.96 (C8), 57.96 (C2), 61.64 (C6), 70.92 (C3), 74.62 (C5), 76.93 (C4), 95.64 (C1), 112.81 (C12), 134.78 (C9) 140.42 (C13), 145.63 (C10), 169.04 (C7), 170.54 (C11).

*Tris(\{[(1R,2R,3S,4R,5R/S)-4-hydroxymethyl-2,3,5-trihydroxy-tetrahydropyran-1-yl]carbamoyl\}methyl)-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) pentahydrate (**Ga(OG2GP)** $_3$ · $5\text{H}_2\text{O}$).* ^1H NMR (400 MHz, 1:1 $\text{CD}_3\text{OD}:\text{D}_2\text{O}$) α anomer: $\delta = 2.36$ (s, 3H, COCH_3), 3.43 (m, 1H, H_3) 3.72-3.86 (m, 4H, H_4 - H_6) 3.91 (dd, 1H, H_2) 4.96 (s, 2H, H_8), 5.18 (d, 1H, H_1 , $^2J_{1,2} = 2.81$ Hz) 6.62 (d, 1H, H_{12} , $^2J_{12,13} = 5.80$ Hz) 7.55 (d, 1H, H_{13}); β anomer $\delta = 2.38$ (s, 3H, COCH_3), 3.40 (m, 2H, H_3 , H_4) 3.54 (m, 1H, H_5) 3.68 (dd, 1H, H_2) 3.8 (m, 2H, H_6) 4.71 (d, 1H, H_1) 4.95 (s, 2H, H_8) 6.62 (d, 2H, H_{12} , $^2J_{12,13} = 5.80$ Hz) 7.55 (d, 1H, H_{13}). $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, D_2O) α anomer: $\delta = 13.04$ (C14), 55.28 (C2), 58.13 (C8), 61.55 (C6), 71.09

(C3), 71.67 (C4), 72.52 (C5), 91.62 (C1), 109.2 (C12), 135.26 (C9) 137.77 (C13), 151.85 (C10), 168.14 (C7), 169.69 (C11); β anomer: δ = 12.98 (C14), 58.44 (C8), 57.90 (C2), 61.69 (C6), 70.94 (C3), 74.54 (C5), 76.90 (C4), 96.0 (C1), 109.2 (C12), 135.26 (C9) 137.77 (C13), 151.85 (C10), 168.09 (C7), 170.00 (C11).

Tris({[(((1R,2R,3S,4R,5R/S)-4-hydroxymethyl-2,3,5-trihydroxy-tetrahydropyran-1-yl)carbamoyl)methyl}-2-methyl-3-oxy-4(1H)-pyridinonato)indium(III) tetrahydrate (In(OG2GP)₃·4H₂O). ¹H NMR (400 M Hz, 1:1 CD₃OD:D₂O) α anomer: δ = 2.38 (s, 3H, COCH₃), 3.46 (m, 1H *H*3) 3.72-3.84 (m, 4H, *H*4, *H*5, *H*6) 3.93 (dd, 1H, *H*2) 5.03 (s, 2H, *H*8), 5.24 (d, 1H, *H*1, ²*J*_{1,2} = 3.27 Hz) 6.73 (d, 1H, *H*12) 7.60 (d, 1H, *H*13); β anomer: δ = 2.38 (s, 3H, COCH₃), 3.43 (m, 2H, *H*3, *H*4) 3.55 (m, 1H, *H*5) 3.63 (dd, 1H, *H*2) 3.8 (m, 2H, *H*6) 4.72 (d, 1H, *H*1) 5.03 (s, 2H, *H*8) 6.73 (d, 2H, *H*12, ²*J*_{12,13} = 5.80 Hz) 7.60 (d, 1H, *H*13). ¹³C{¹H} NMR (100 MHz, D₂O) α anomer: δ = 13.23 (C14), 55.29 (C2), 58.20 (C8), 61.55 (C6), 71.09 (C3), 71.69 (C4), 72.52 (C5), 91.64 (C1), 110.86 (C12), 137 (C9) 137 (C13), 151.82 (C10), 168.34 (C7), 169.61 (C11); β anomer δ = 13.18 (C14), 57.91 (C2), 58.25 (C8), 61.69 (C6), 70.93 (C3), 74.57 (C5), 76.91 (C4), 95.64 (C1), 110.86 (C12), 137 (C9) 137 (C13), 151.82 (C10), 168.34 (C7), 169.90 (C11).

3-Hydroxy-1-(4-hydroxyphenyl)-2-methyl-4(1H)-pyridinone (Hhpp). ¹H NMR (400 MHz, (CD₃)₂SO): δ = 1.931 (s, 3H, C2-CH₃), 6.164 (d, 1H, *H*5, ³*J*_{5,6} = 7.3 Hz), 6.859 (d, 2H, arom *H*, *J* = 8.7 Hz), 7.204 (d, 2H, arom *H*, *J* = 8.7 Hz), 7.473 (d, 1H, *H*6, ³*J*_{6,5} = 7.3 Hz). MS (+ESI): *m/z* 218 [M+H]⁺. Anal. Calcd (found) for C₁₂H₁₁NO₃: C, 66.35 (65.89); H, 5.10 (4.98); N, 6.45 (6.33).

Tris(1-(4-hydroxyphenyl)-2-methyl-3-oxy-4(1H)-pyridinonato)gallium(III) sesquihydrate (Ga(hpp)₃·1.5H₂O). (from **Method A**): ¹H NMR (400 MHz, (CD₃)₂SO): δ = 1.832 (s, 3H, C2-

CH_3), 6.415 (d, 1H, $H5$, $^3J_{5,6} = 6.7$ Hz), 6.887 (d, 2H, arom H , $J = 8.5$ Hz), 7.233 (d, 2H, arom H , $J = 8.5$ Hz), 7.474 (d, 1H, $H6$, $^3J_{6,5} = 6.7$ Hz).