## **Supporting Information**

## Fluorescently labeled xylosides offer insight into the biosynthetic pathways of glycosaminoglycans.

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1.	Chromatographic analysis	S2-S3
2.	<sup>1</sup> H-NMR and <sup>13</sup> C-NMR spectra	S4-S23



**Supplementary Figure 1.** Size-exclusion chromatography analysis of conditioned medium from A549 cells treated with 0.1 mM **XylNap**, **5**, **7** or **9**. Fluorescence was monitored at 229/372 (Ex./Em.) for XylNap and 410/455 (Ex./Em.) for PacBlue compounds.



**Supplementary Figure 2.** Reversed-phase chromatography analysis of products secreted by A549 cells after stimulation with 0.1 mM non-acetylated (top, 7) or fully acetylated (bottom, **19**) compound.



**Supplementary Figure 3.** Reversed-phase chromatography analysis of conditioned medium and cell lysate from A549 cells treated with 0.1 mM **5.** 



Figure S5 –  $^{1}$ H and  $^{13}$ C spectrum for compound 5







Figure S7 –  $^{1}$ H and  $^{13}$ C spectrum for compound 7



Figure S8 –  $^{1}$ H and  $^{13}$ C spectrum for compound 8



Figure S9 –  $^{1}$ H and  $^{13}$ C spectrum for compound 9



Figure S10 –  $^{1}$ H and  $^{13}$ C spectrum for compound 11



Figure S11 –  $^{1}H$  and  $^{13}C$  spectrum for compound 12



Figure S12 –  $^{1}$ H and  $^{13}$ C spectrum for compound 13



Figure S13 – <sup>1</sup>H and <sup>13</sup>C spectrum for compound 14



Figure S14 –  $^{1}$ H and  $^{13}$ C spectrum for compound 15



Figure S15 –  $^{1}$ H and  $^{13}$ C spectrum for compound 16



Figure S16 – <sup>1</sup>H and <sup>13</sup>C spectrum for compound 17



Figure S17–<sup>1</sup>H and <sup>13</sup>C spectrum for compound 18



Figure S18–<sup>1</sup>H and <sup>13</sup>C spectrum for compound 19



Figure S19 –  $^{1}$ H and  $^{13}$ C spectrum for compound 20



Figure S20 – <sup>1</sup>H and <sup>13</sup>C spectrum for compound 21



Figure S21 –  $^{1}H$  and  $^{13}C$  spectrum for compound 22



Figure S22 –  $^{1}H$  and  $^{13}C$  spectrum for compound 24



Figure S23 –  $^{1}$ H and  $^{13}$ C spectrum for compound 25



Figure S24 – <sup>1</sup>H and <sup>13</sup>C spectrum for compound 26