**Aggregation of a Tetrasaccharide Acceptor Observed by NMR:
Synthesis of Pentasaccharide Fragments of the Le^aLe^x
Tumor-Associated Hexasaccharide Antigen**

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Supplementary Material

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General Experimental Procedures

^1H NMR (400 and 600 MHz) and ^{13}C NMR (100.6 or 150.9) spectra were recorded with Bruker Avance spectrometers in CDCl_3 (internal standard, for ^1H residual CHCl_3 δ_{H} 7.24; for ^{13}C CDCl_3 , δ_{C} 77.0), CD_3COD (internal standard, for ^1H residual CD_2HOD δ_{H} 3.30; for ^{13}C δ_{C} 49.0) or D_2O [external standard (3-(trimethylsilyl)-propionic acid- d_4 , sodium salt (TSP) for δ_{H} 0.00; for ^{13}C δ_{C} 0.0). ^1H NMR and ^{13}C NMR chemical shifts are reported in part per million (ppm). Coupling constants (J) were obtained from a first-order analysis of one-dimensional spectra and are reported in Hertz (Hz). Assignments of proton and carbon resonances were based on two dimensional ^1H - ^1H COSY and ^{13}C - ^1H HSQC correlation experiments. ^1H NMR data are reported using standard abbreviations: singlet (s) doublet (d), triplet (t), doublet of doublet (dd), double of doublet of doublet (ddd), triplet of doublet (td), broad signal (br, s) and multiplet (m). Analytical thin-layer chromatography (TLC) was performed on aluminium plates pre-coated with Silica Gel 60 F234 (250 μm) containing a fluorescent indicator. The plates were visualized under UV and/or charred with 20% solution of H_2SO_4 in EtOH. Compounds were purified by flash chromatography with Silica Gel 60 (230-400 mesh) unless otherwise stated. Solvents were distilled and dried according to standard procedures and organic solutions were dried over Na_2SO_4 and concentrated under reduced pressure. All reagents were purchased from commercial suppliers and used without further purification. Molecular sieves were activated by heating at 300 $^\circ\text{C}$ overnight under reduced pressure. Zinc powder (2 g) was activated by successive washings with 1 N HCl (25 mL), H_2O (50 mL), MeOH (50 mL), and Et_2O (50 mL) on a fritted glass. Sonication reactions were carried out in a thermo-controlled (50 ± 4 $^\circ\text{C}$) ultrasonic cleaning water bath at 40 kHz. RP-HPLC purifications were carried out on Prep Nova Pak® HR C18, 6 μm 60 Å columns using a mixture of HPLC grade acetonitrile and milli-Q water. Optical rotations were measured at 22 $^\circ\text{C}$ and are reported as follows: $[\alpha]_{\text{D}}$ [c in g per 100 mL of solvent]. Purifications with gel permeation chromatography were carried out on a Biogel P2 column (95 cm $\times$ 1.5 cm) eluted with Milli-Q water or with a 0.05 M aqueous ammonium acetate solution.

Compound **11**, 400 MHz, 296 K, CDCl₃

Compound **11**, 101 MHz, 296 K, CDCl₃

Compound **5**, 400 MHz, 295 K, CDCl₃

Compound **5**, 101 MHz, 297 K, CDCl₃

Compound **13**, 400 MHz, 295 K, CDCl₃

Compound **13**, 101 MHz, 297 K, CDCl₃

Compound **15**, 400 MHz, 295 K, CDCl₃

Compound **15**, 101 MHz, 297 K, CDCl₃

Compound **16**, 600 MHz, 296 K, CDCl₃

Compound **16**, 151 MHz, 296 K, CDCl₃

Compound **17**, 600 MHz, 296 K, CDCl₃

Compound **17**, 151 MHz, 296 K, CDCl₃

Compound **18**, 400 MHz, 296 K, CDCl₃

Compound **18**, 101 MHz, 296 K, CDCl₃

Compound **6**, 400 MHz, 296 K, CDCl₃

Compound **6**, 101 MHz, 296 K, CDCl₃

Compound **19**, 400 MHz, 296 K, CDCl₃

Compound **19**, 101 MHz, 296 K, CDCl₃

Compound **20**, 400 MHz, 296 K, CDCl₃

Compound **20**, 101 MHz, 297 K, CDCl₃

Compound **21**, 400 MHz, 296 K, CDCl₃

Compound **21**, 101 MHz, 296 K, CDCl₃

Compound **22**, 400 MHz, 295 K, CDCl₃

Compound **22**, 101 MHz, 297 K, CDCl₃

Compound **23**, 600 MHz, 295 K, CDCl₃

Compound **23**, 151 MHz, 295 K, CDCl₃

Compound **24**, 400 MHz, 296 K, CD₃OD

Compound **24**, 101 MHz, 296 K, CD₃OD

Compound **25**, 600 MHz, 297 K, CDCl₃

Compound **25**, 151 MHz, 297 K, CDCl₃

Compound **26**, 400 MHz, 296 K, CDCl₃

Compound **26**, 101 MHz, 296 K, CDCl₃

Compound **2**, 600 MHz, 296 K, D₂O

Compound **2**, 151 MHz, 296 K, D₂O

Compound **3**, 600 MHz, 295 K, D₂O

Compound **3**, 151 MHz, 295 K, D₂O

Compound **4**, 600 MHz, 295 K, D₂O

Compound **4**, 151 MHz, 295 K, D₂O