Supporting Information

Integrating ReSET with Glycosyl Iodide Glycosylation in Step-Economy
Syntheses of Tumor Associated Carbohydrate Antigens and Immunogenic Glycolipids

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**General Information**

All reactions were conducted under a dried argon atmosphere. The anhydrous solvents (dichloromethane (DCM) 99.8%, benzene (PhH) 99.8%, Methanol (MeOH) 99.8%, $N,N$-dimethylformamide (DMF) 99.8% and pyridine (pyr.) 99.8%) were purchased from commercial sources without further purification. In order to maintain water content of the solvents under 15 ppm, the solvents were dried and stored under 4 Å molecular sieves according to literature procedure.\(^1\) Trimethylsilyl iodide (TMSI, stabilized with copper) was stored at -20 °C under a desiccated Ar atmosphere. TMSI in good condition should be a colorless transparent liquid. All other solvents and reagents were purchased from commercial sources and used without further purification. All glassware utilized was oven-dried or flame-dried before use. Glass-backed TLC plates (Silica Gel 60 with a 254 nm fluorescent indicator) were used without further manipulation and stored with desiccant. TLC plates were visualized using a short-wave UV lamp, stained with an I$_2$-SiO$_2$ mixture, and/or by heating TLC plates that were dipped in a solution of ammonium molybdate/cerium (IV) sulfate or anisaldehyde/H$_2$SO$_4$/AcOH/EtOH. Flash column
chromatography (FCC) was performed using a silica gel (32-63 µm) stationary phase with a variable mobile phase correlated with TLC mobility. NMR experiments were conducted on either 800 or 600 MHz instruments using C₆D₆ (99.5% D), CDCl₃ (99.9% D), methanol-d₄ (99.8% D) or pyridine-d₅ (99.5% D) as the solvent. Chemical shifts were referenced to the appropriate deuterated solvent peak (7.16 ppm for C₆D₆; 7.26 ppm for CDCl₃; 3.31 ppm for methanol-d₄; 8.74 ppm for pyridine-d₅) and were reported in parts per million (ppm). Coupling constants of the coupled protons were averaged to match with each other. High resolution mass spectra were recorded using ESI-Orbitrap LC-MS with internal calibration. The microwave-assisted regioselective silyl exchange technology (ReSET) reactions were conducted in sealed 10 mL microwave vessels in a commercial microwave reactor (CEM Discover™) which was operated by the Synergy™ software. The reaction temperatures were monitor by the reactor’s built-in infrared (IR) detector.

Reference

$^1$H NMR spectrum of compound 3 (CDCl$_3$, 800 MHz)
$^{13}$C and DEPT135 NMR spectrum of compound 3 (CDCl$_3$, 200 MHz)
$^1$H-$^1$H COSY spectrum of compound 3 (CDCl$_3$, 800 MHz)
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