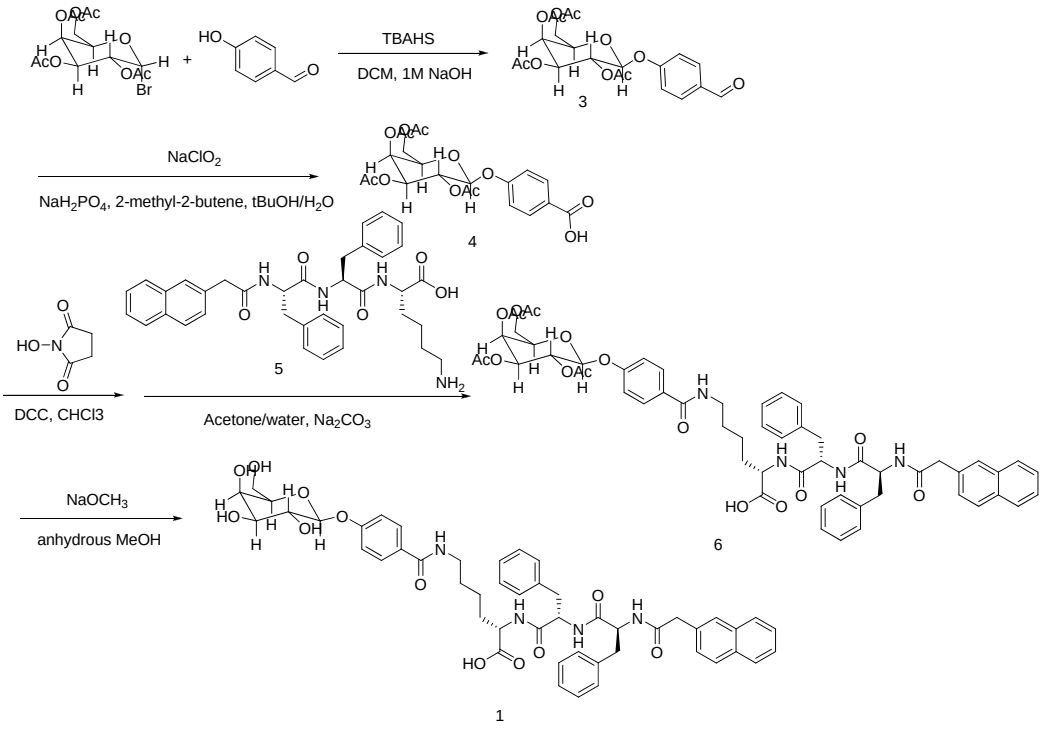
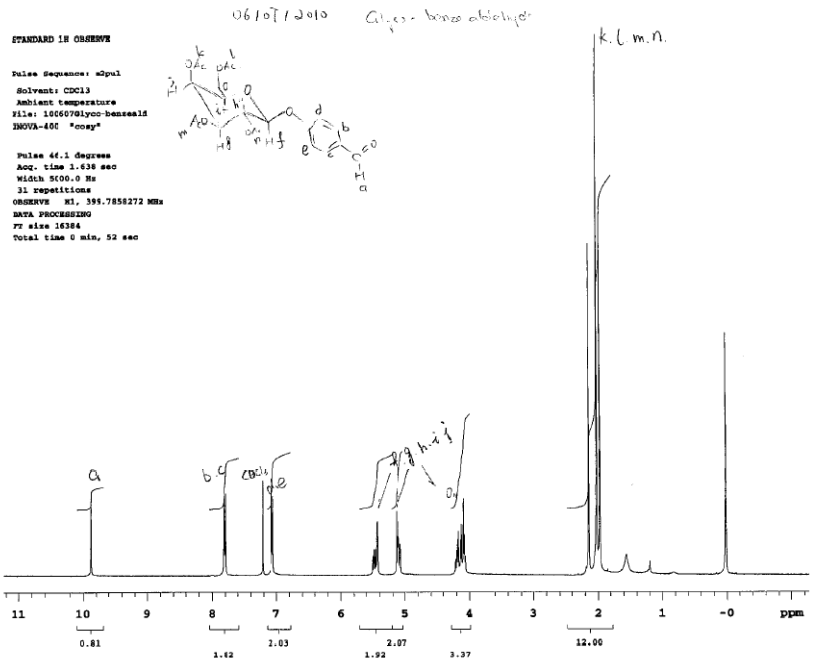
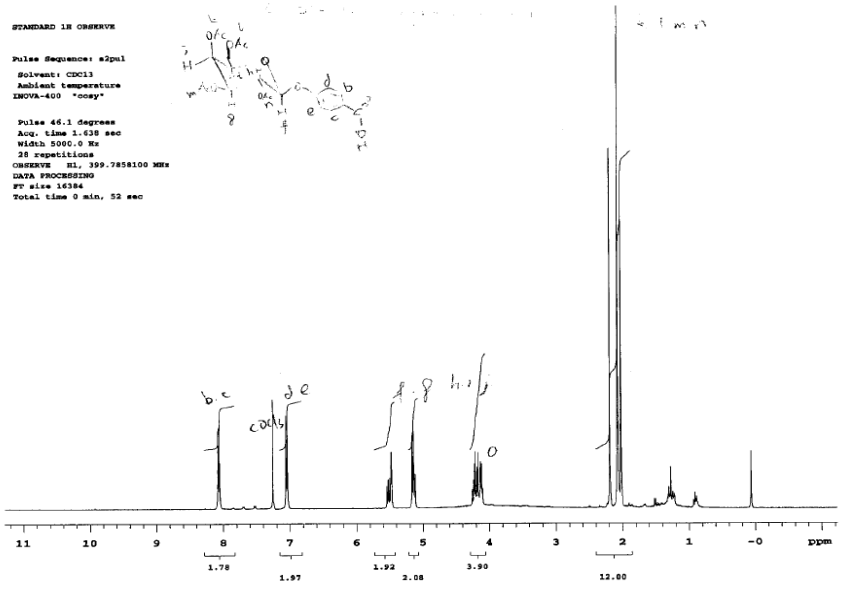
Synthetic Route



Benzaldehyde acetyl-galactoside 3. acetobromo-α-D-galactose (3 mmol), p-hydroxylbenzaldehyde (2 eq.) and tetrabutylammonium hydrogen sulfate (1 eq.) was added into DCM (10 ml) and 1M aq. NaOH solution (10 ml). The solution was stirred vigorously at room temperature and the reaction was complete after 45 mins. Flash chromatography using hexane/EA gave **3** in 70% yield. The procedure for working up is exactly following Ref. (*Can. J. Chem.* **1991**, *69*, 817-821.)



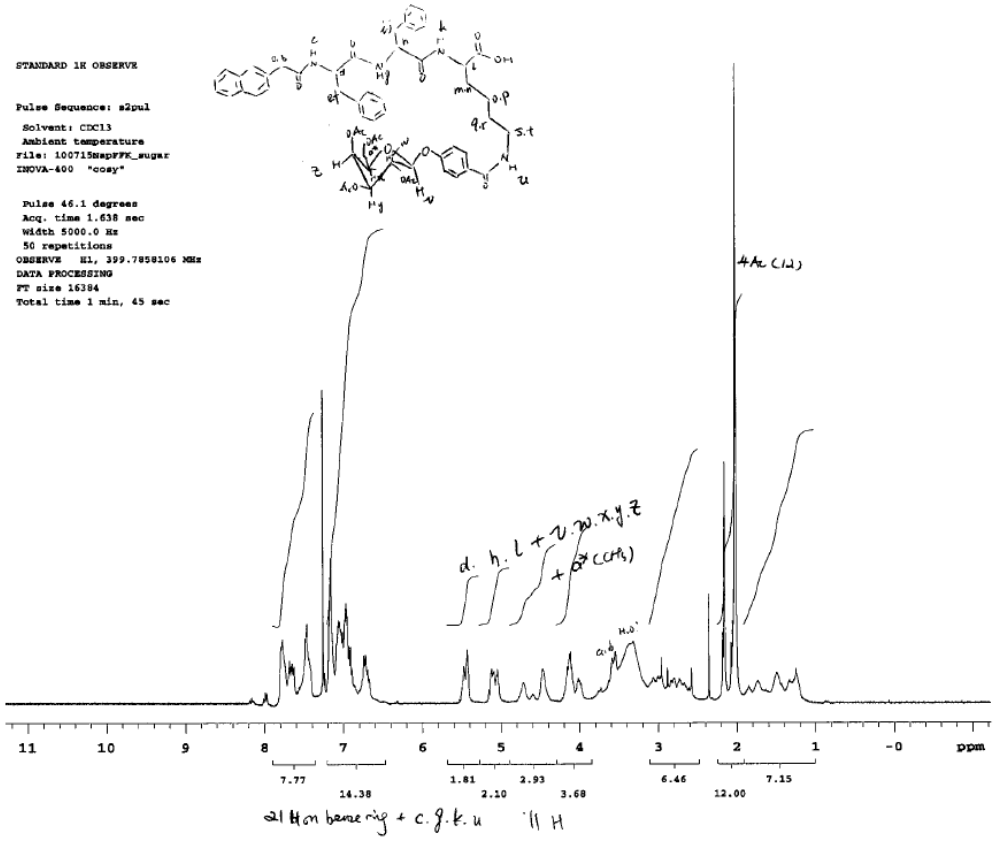
Benzoic acid acetyl-galactoside 4. Sequentially add 2-methyl-2-butene (10 eq.) in THF, aq. NaH_2PO_4 solution (5 eq., 690 mg in 5mL H_2O) and aq. $NaClO_2$ solution (3 eq., 271.5 mg in 5mL H_2O) to a stirred soltuon of the compound **3** (1mmol) in tBuOH (10ml). The solution was stirred vigorously at room temperature and the reaction was complete in 4 hours with 98% yield. The procedure for working up is exactly following Ref. (*Angew. Chem. Int. Ed.* **2008**, *47*, 6579-6582)



NapFFK 5. The peptide 5 was synthesized using 2-chlorotrityl chloride resin by standard Fmoc solid phase peptide synthesis procedure. Ref. *Fmoc solid phase*

peptide synthesis-A Practical Approach. Chan, W. C., White, P. D, Eds; Oxford University Press: New York, 2000.

NapFFK-benozic amide acetyl-galactoase 6. To a solution of compound **4** (0.5 mmol) and N-hydrozysuccinimide (1 eq.) in $CHCl_3$ (10mL) was added N,N'-Dicyclohexylcarbodiimide (1.2 eq.) in $CHCl_3$ (5mL). After being stirred for 3 hours at room temperature, the solvent was evaporated. Add 20 mL acetone into the reaction mixture and filter the solution. To the stirred acetone solution was added compound **5** (1 eq., 0.5 mmol) in aq. Na2CO3 solution (0.9 eq., 48 mg in 5mL H_2O). The reaction was complete after overnight. The reaction mixture was rotary evaporated and the pH of the aqueous solution was change to 3 to allow the product to precipitate. The precipitates were filtered and dried. Flash chromatography using hexane/EA gave **4** in 60% yield.



NapFFK-benozic amide galactoase 1. The standard Zemplen de-O-acetylation was used. Under positive nitrogen pressure, **6** (0.18 mmol) was dissolved in anhydrous MeOH (5 mL), and then NaOMe (0.3 eq.) was added. The reaction was complete in 3 hours according to LC-MS. The pH of the solution was changed to 7 by adding dry ice. The compound is purified by HPLC with a yield (90%).