Supporting Information

SYNTHESES OF TWO NEW FLUOROUS CROWN ETHERS CARRYING SUGAR MOLECULES WITH A MULTIVALENT BFP MODIFICATION: INVESTIGATIONS OF THEIR PARTITION RATIOS IN FLUOROUS BIPHASIC SYSTEMS AND RECYCLABILITY DURING ACETOXYLATION REACTION

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Contents of Supporting Information

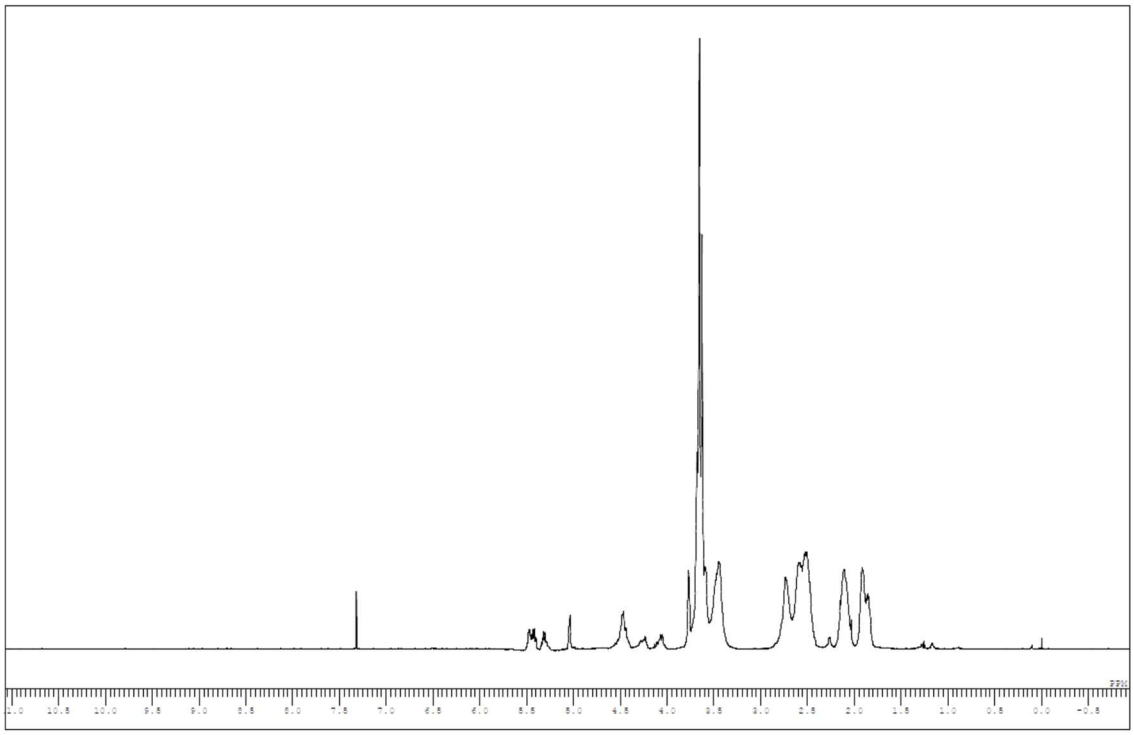
1. General procedure to determine the partition ratios of 1 and 2 between the fluorous and organic solvents in a biphasic system

To a mixed solution of FC 72 (2.5 mL) and organic solvent (2.5 mL) was added **1** or **2** (20 mg). The mixture was stirred at room temperature for 1 h. After 2 ml of each solvent was separated and taken, each of the separated solvent was evaporated. Each residue was measured by ^{19}F- NMR with benzotrifluoriden (standard) in $CDCl_3$. The partition ratio of **1** or **2** between the fluorous and organic solvent was determined by the comparison of both CF_3 groups of Bfp and benzotrifluoride.

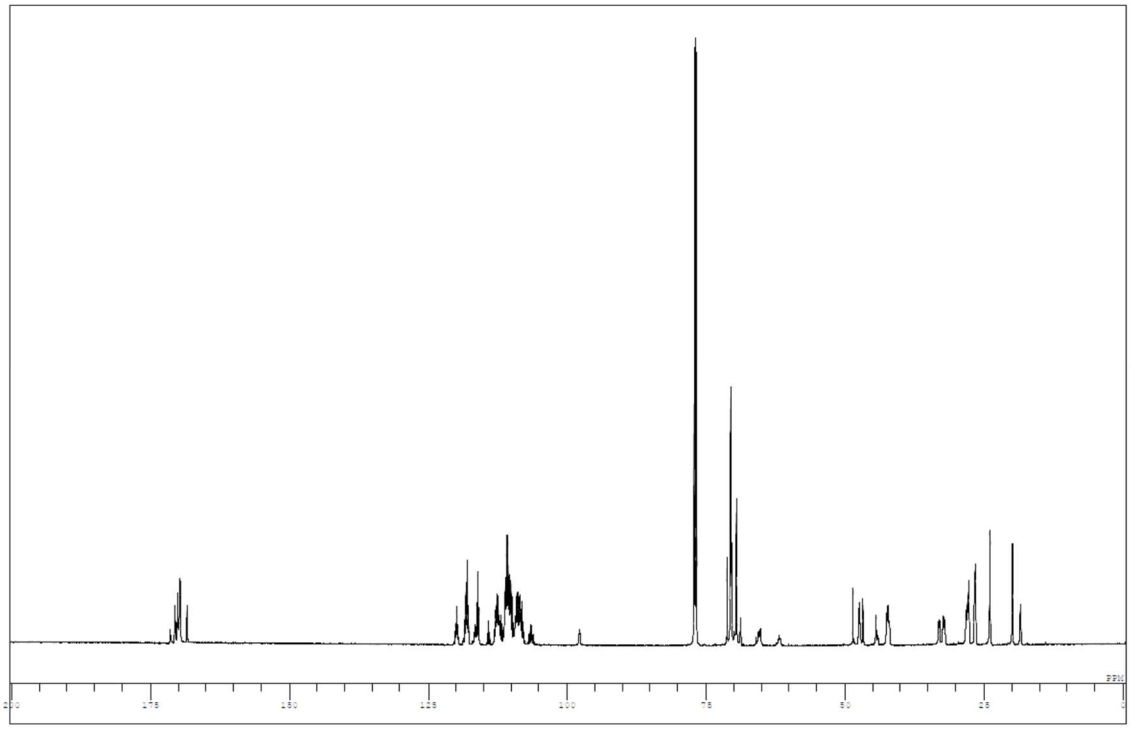
2. Experimental procedure of acetoxylation reactions in a fluorous biphasic system

To a solution of acetonitrile/FC 72 (1 mL/1 mL) was added **13** (33.2 mg, 0.15 mmol), potassium acetate (22.6 mg, 0.23 mmol), and **1** (127.8 mg, 0.03 mmol). After the reaction mixture was refluxed at 85 ℃ for 1.5 h, the reaction mixture was filtered to remove the precipitation. A few mL of acetonitrile solvent was added into the reaction mixture, and the acetonitrile layer was decantated, and this process was repeated several times. The acetonitrile solvent was evaporated under reduced pressure. The residue was purified by thin layer chromatography (hexane: AcOEt= 9: 1) to yield **14** (29.5 mg, 98%) as a yellow oil. The separated FC 72 layer was used the second reaction without further purification.

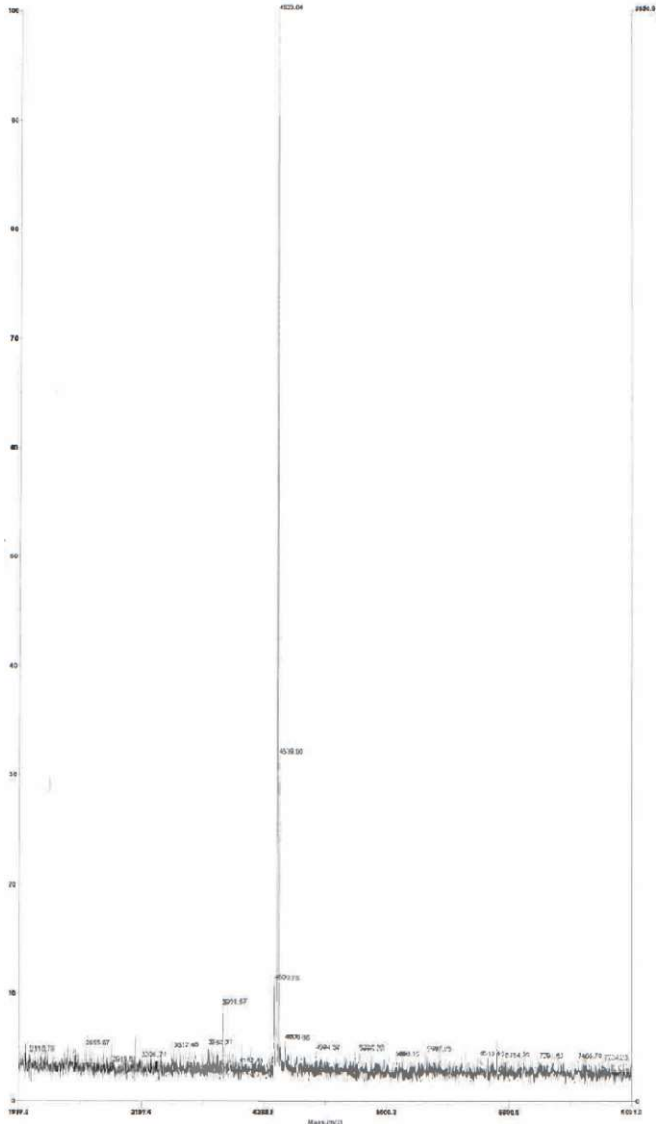
3. ^{1}H-NMR spectrum of compound 1



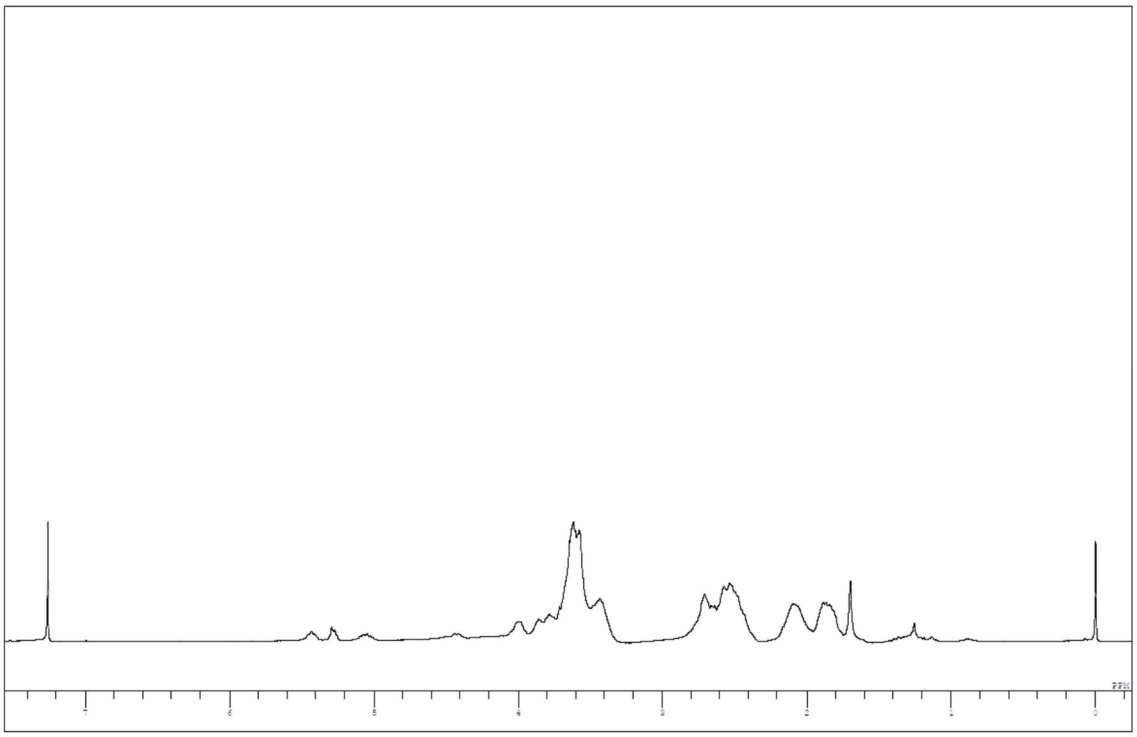
4. ^{13}C-NMR spectrum of compound 1



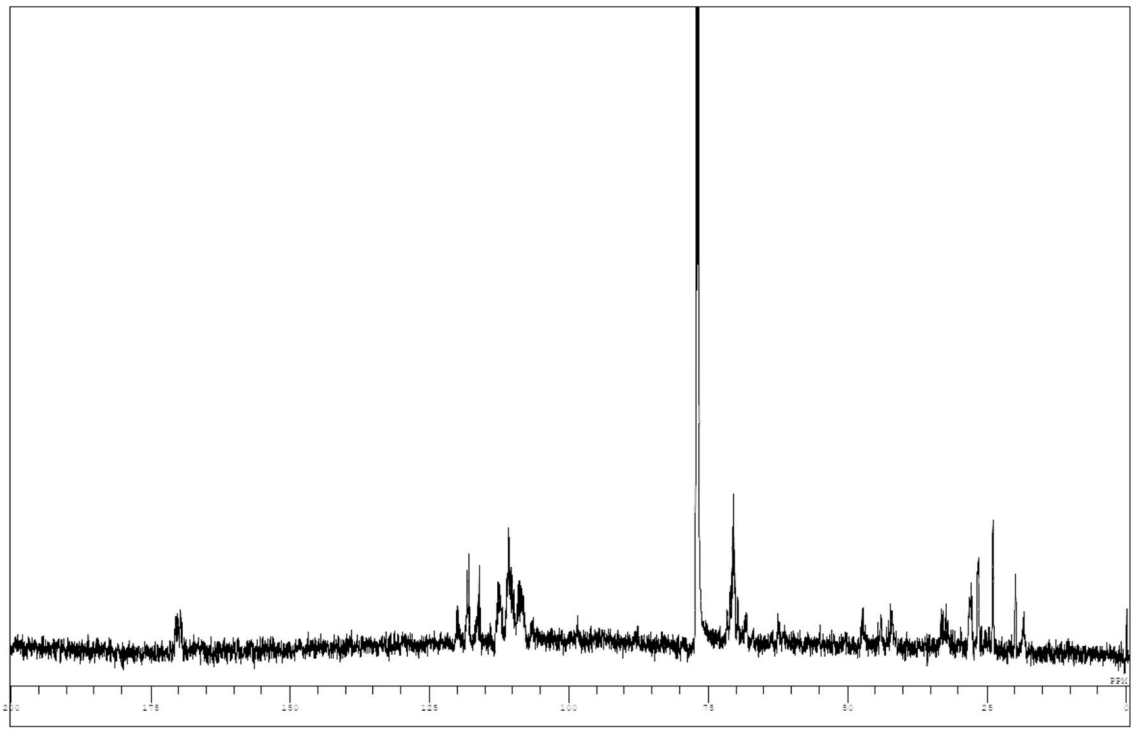
5. MALDI-TOF MASS spectrum of compound 1



6. ^{1}H-NMR spectrum of compound 2



7. ^{13}C-NMR spectrum of compound 2



8. MALDI-TOF MASS spectrum of compound 2