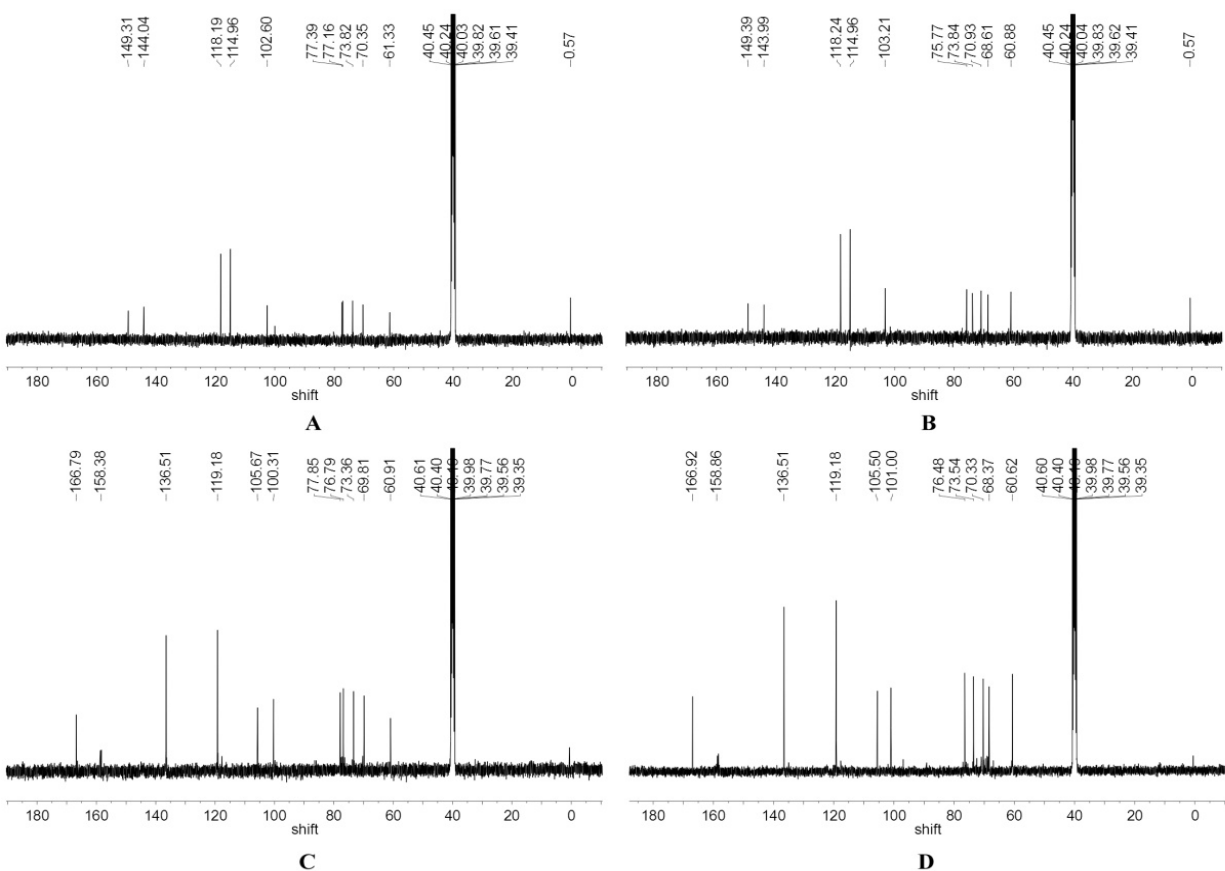


## Primary Arylamine-Based Tyrosine-Targeted Protein Modification

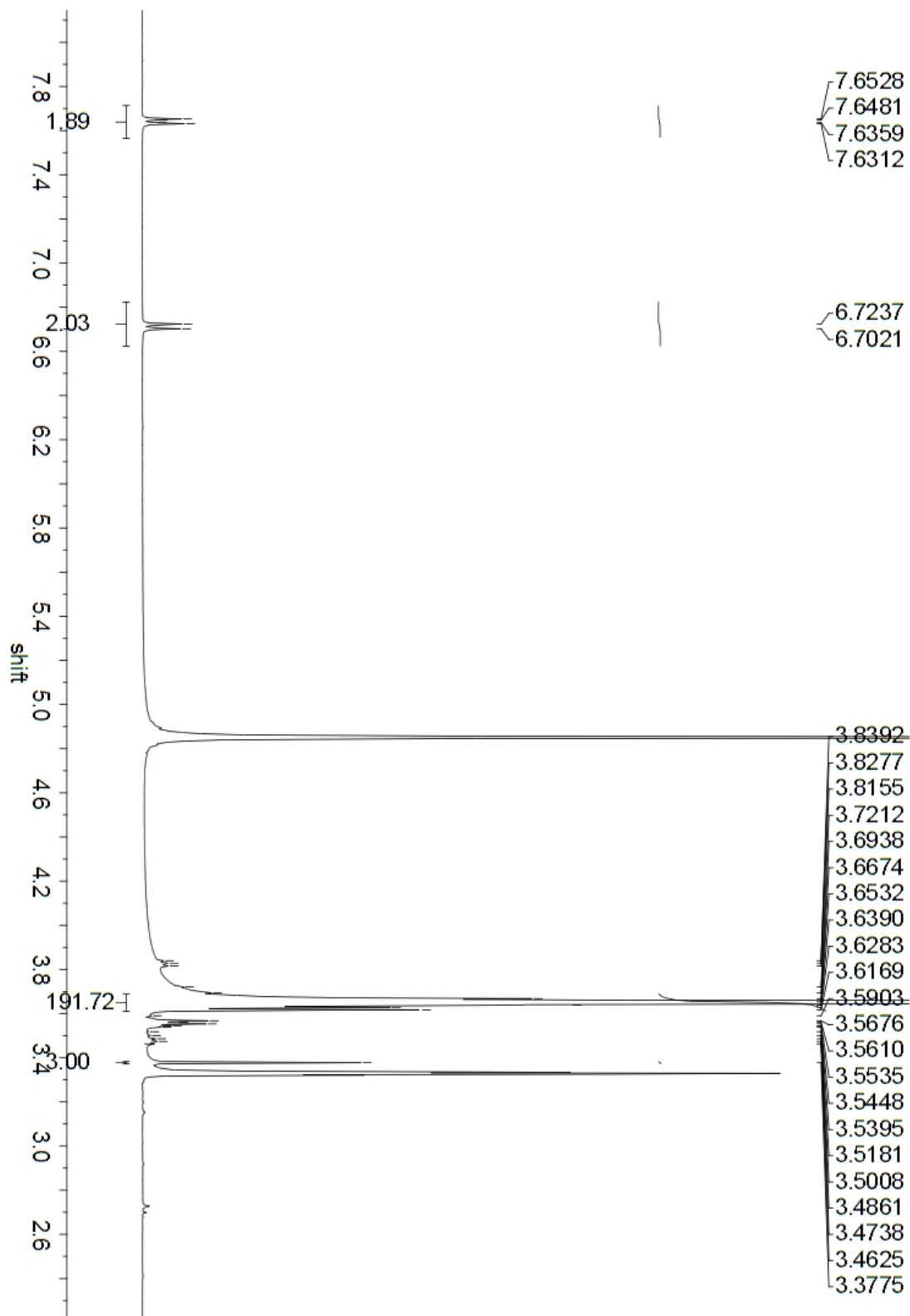
Lin Wang<sup>a</sup>, Valentinas Gruzdis<sup>b</sup>, Nan Pang<sup>b</sup>, Fanhao Meng<sup>\*a</sup>, and Xue-Long Sun<sup>\*b</sup>

### Supporting Information

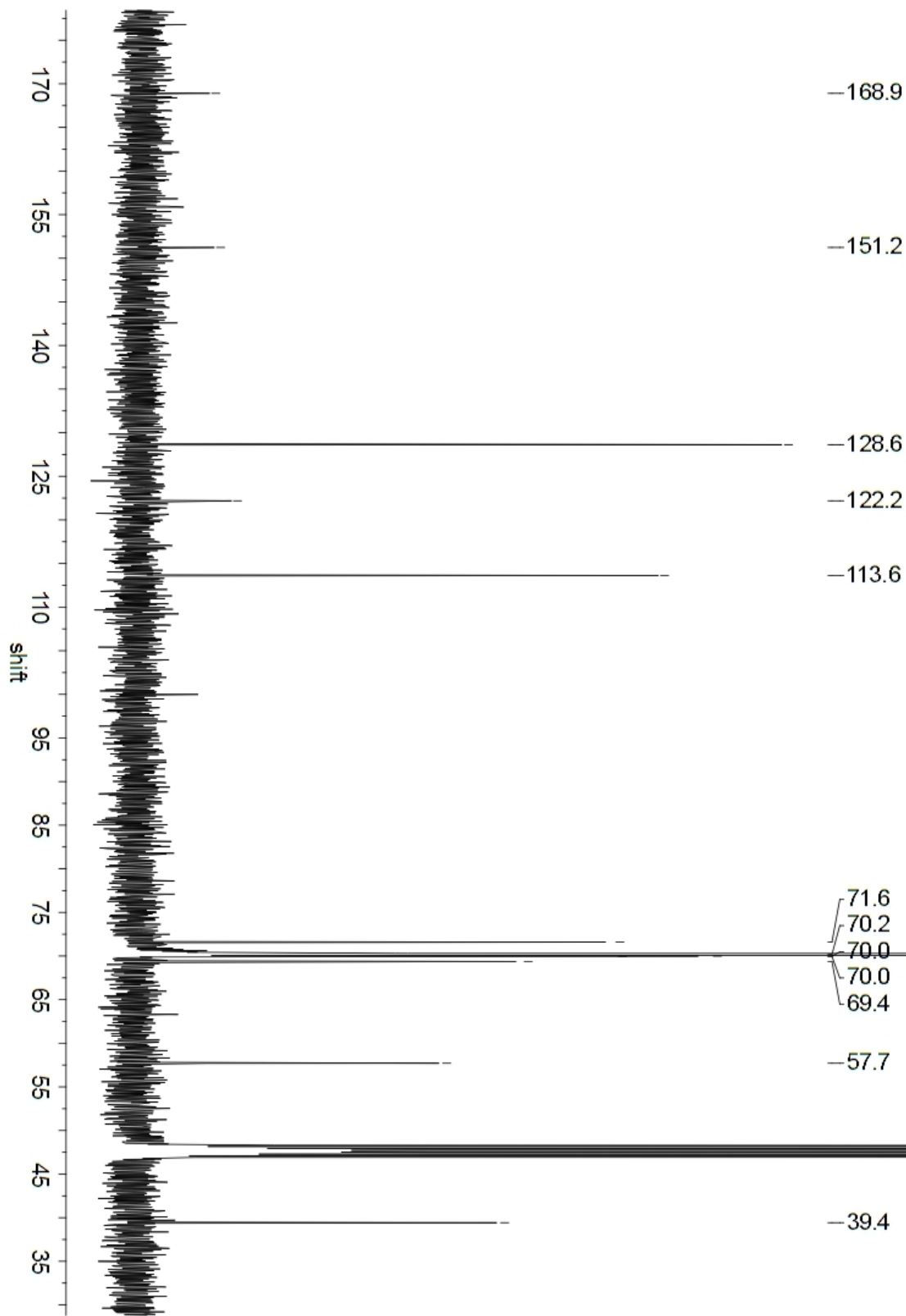
**S1. <sup>13</sup>C NMR analysis of stability of *O*-glycoside under Method *a* reaction condition.** 4-aminophenyl β-D-glucopyranoside and 4-aminophenyl β-D-galactopyranoside were subjected to the same reaction under Method *a* condition without BSA and then lyophilized and their <sup>13</sup>C NMR spectra were taken in DMSO-D<sub>6</sub>, respectively.



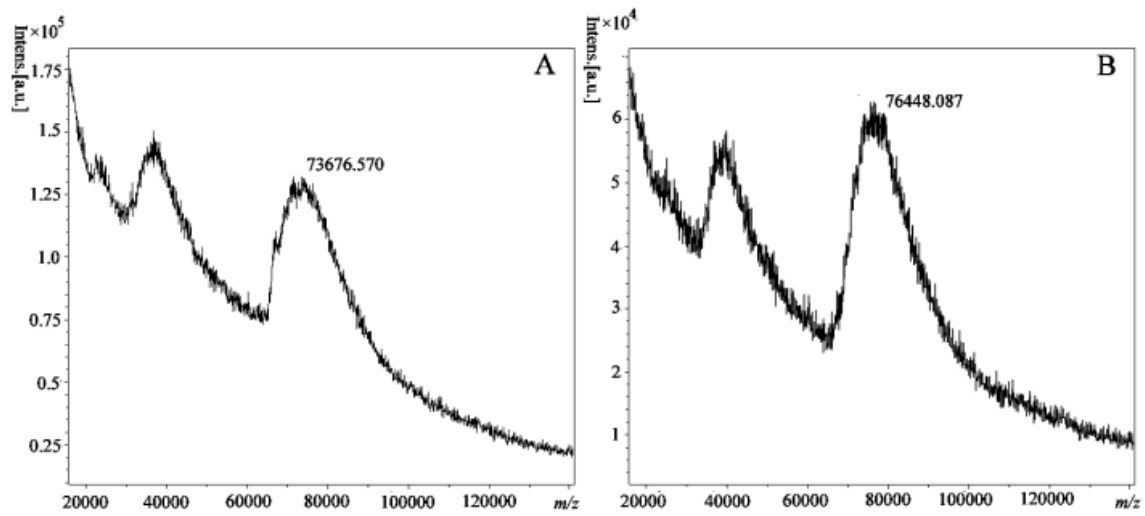
**Figure S1.** <sup>13</sup>C NMR spectra of standard 4-aminophenyl β-D-glucopyranoside (**A**) and 4-aminophenyl β-D-galactopyranoside (**B**), 4-aminophenyl β-D-glucopyranoside in acidic reaction condition without BSA (**C**) and 4-aminophenyl β-D-galactopyranoside in acidic reaction condition without BSA (**D**).



**Figure S2.**  $^1\text{H}$  NMR spectrum of 4-aminobenzoyl-*N*-PEG<sub>2000</sub>-OMe in CD<sub>3</sub>OD



**Figure S3.**  $^{13}\text{C}$  NMR spectrum of 4-aminobenzoyl-*N*-PEG<sub>2000</sub>-OMe in CD<sub>3</sub>OD



**Figure S4.** MALDI-TOF-MS spectra of tyrosine-specific PEGylation of BSA *via* Method *a* (A) and *b* (B). Matrix: saturated solution of sinapinic acid in 0.1% TFA/ACN (1:1, v/v).