Supporting Information

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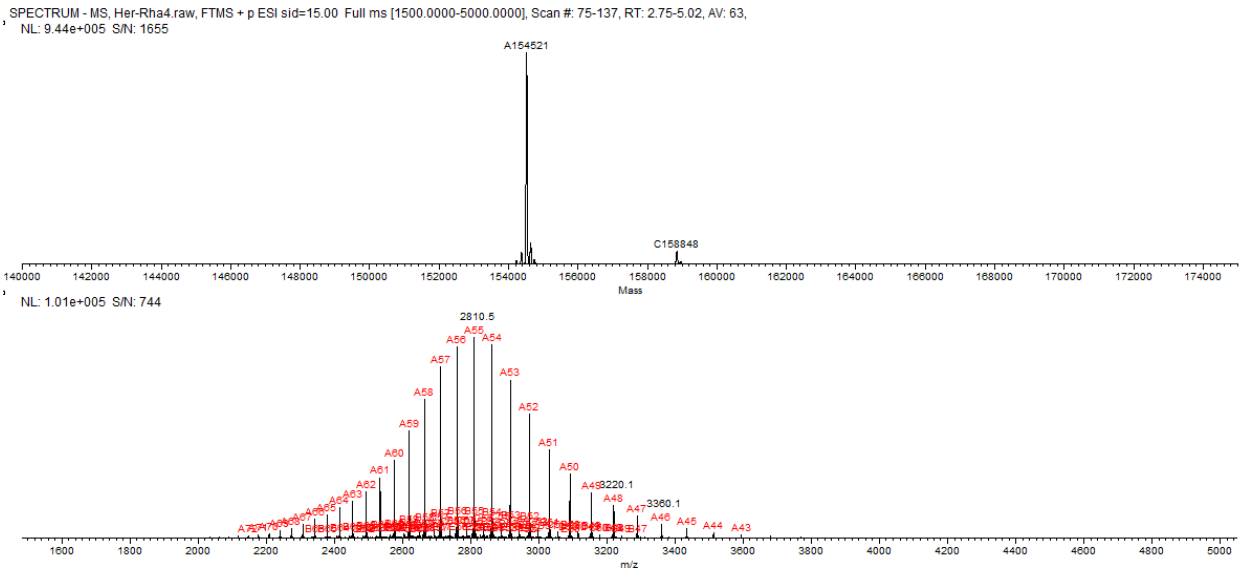


Figure S1. LC-ESI-MS analysis of the intact rhamnose functionalized antibody (**21**)

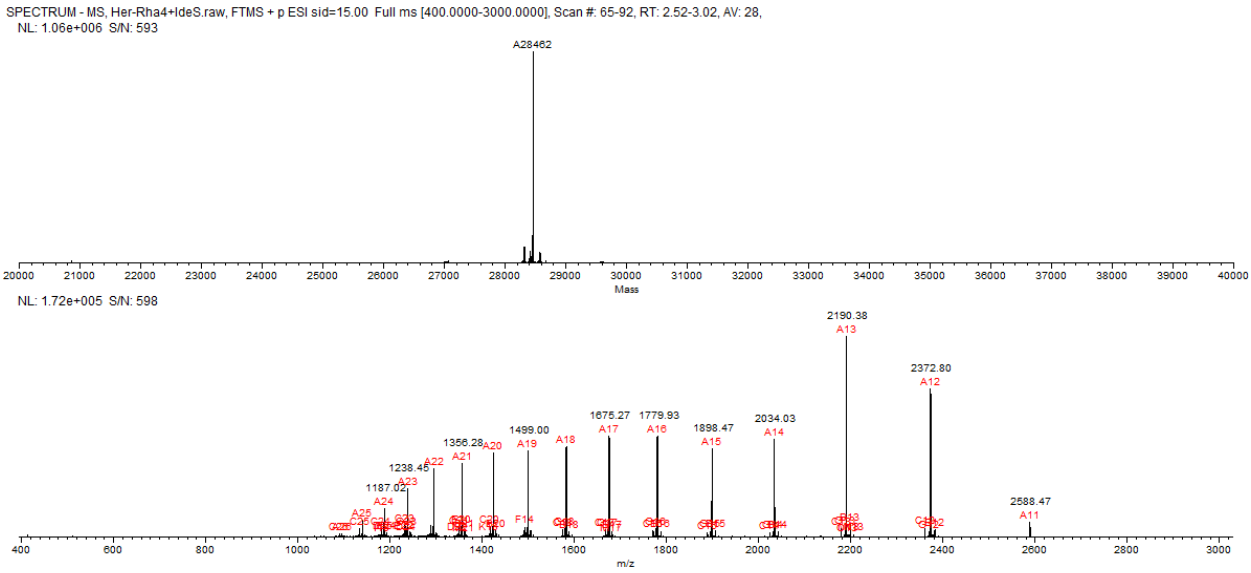


Figure S2. LC-ESI-MS analysis of the Fc domains released by IdeS treatment of the rhamnose functionalized antibody (**21**)

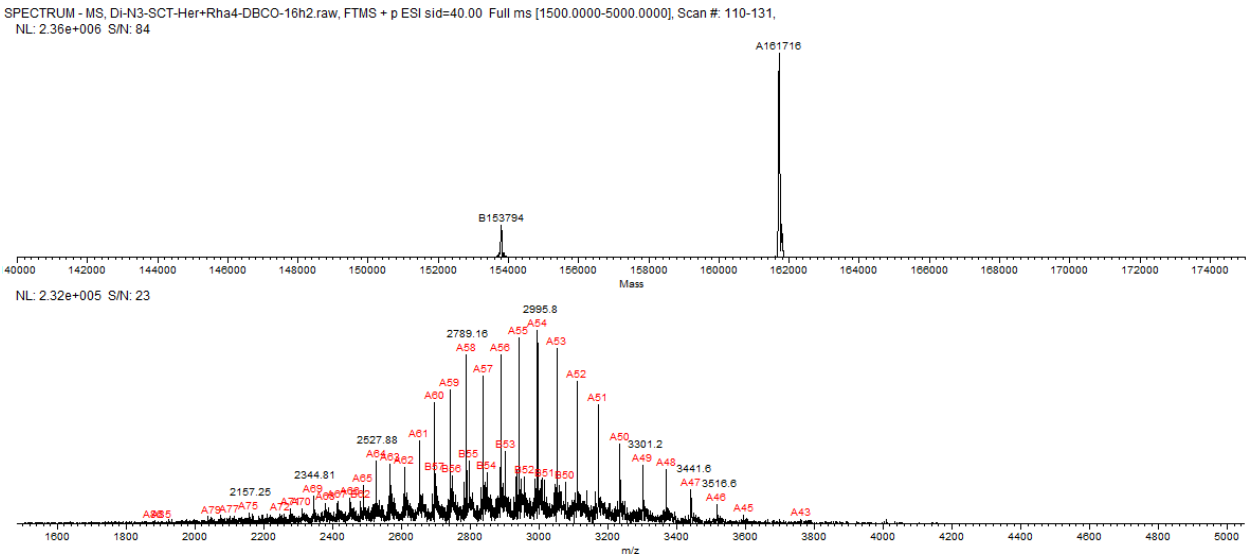


Figure S3. LC-ESI-MS analysis of the intact rhamnose cluster functionalized antibody (**22**)

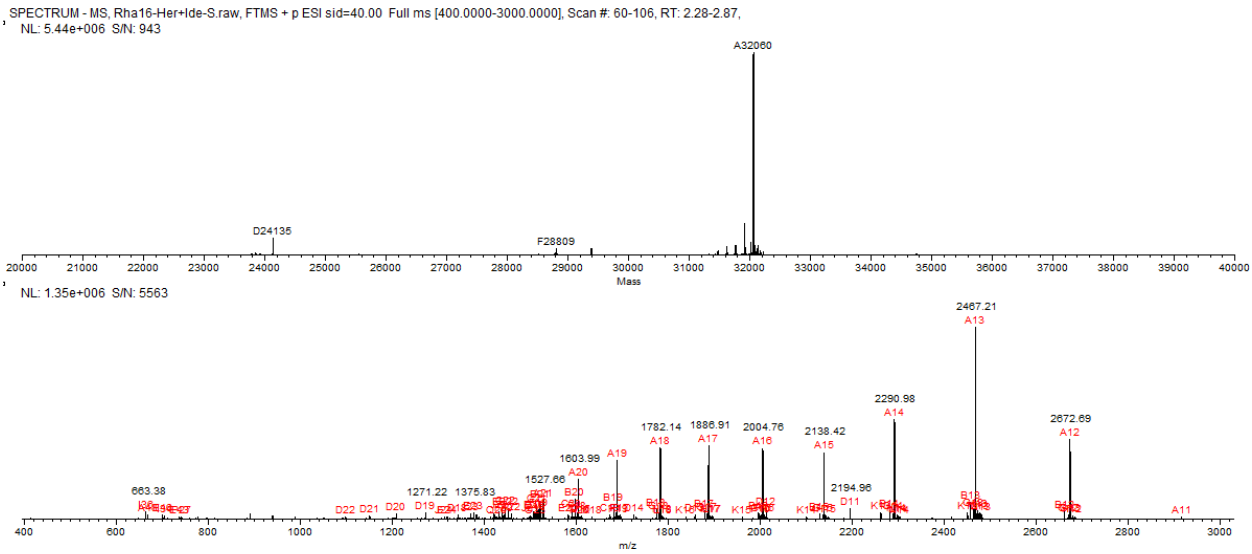


Figure S4. LC-ESI-MS analysis of the Fc domains released by IdeS treatment of the rhamnose cluster functionalized antibody (**22**)

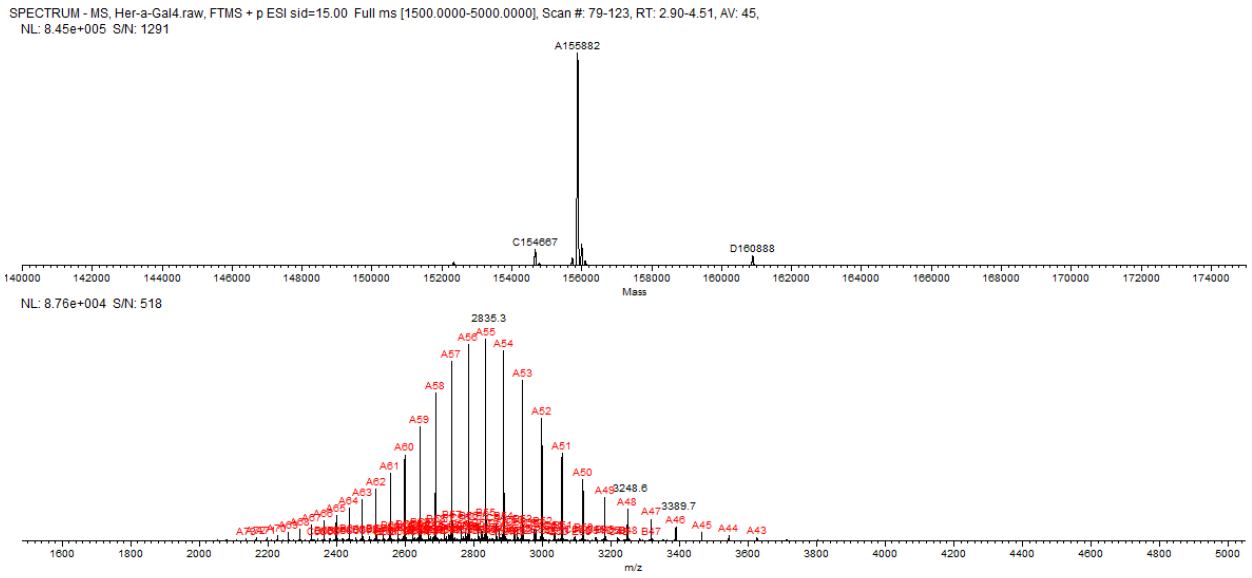


Figure S5. LC-ESI-MS analysis of the intact α-Gal functionalized antibody (**23**)

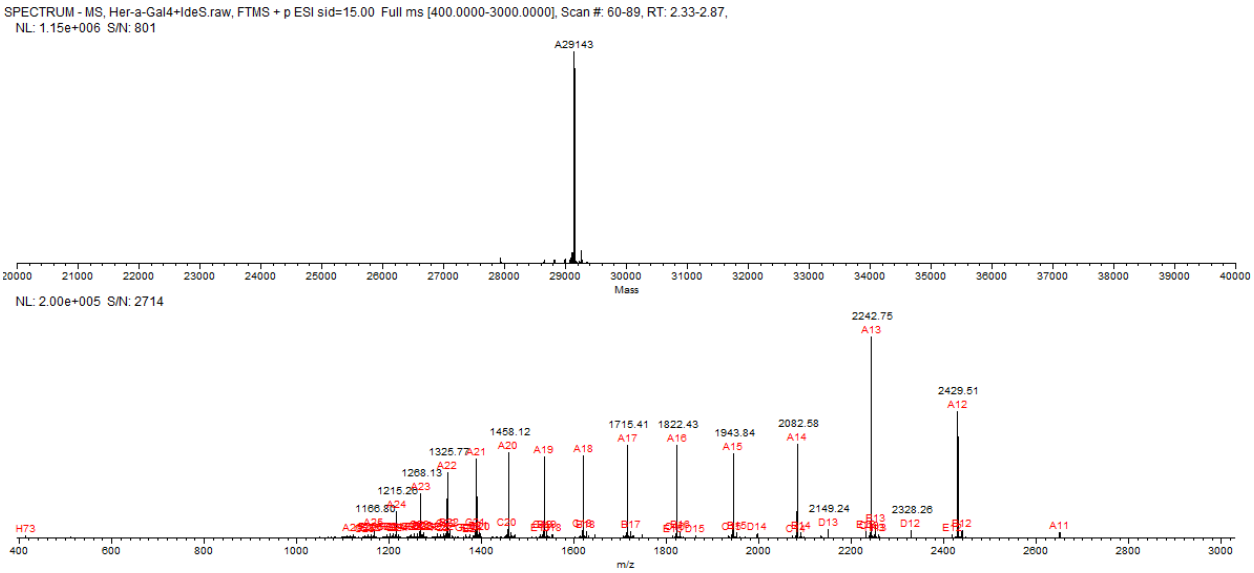


Figure S6. LC-ESI-MS analysis of the Fc domains released by IdeS treatment of the α-Gal functionalized antibody (**23**)

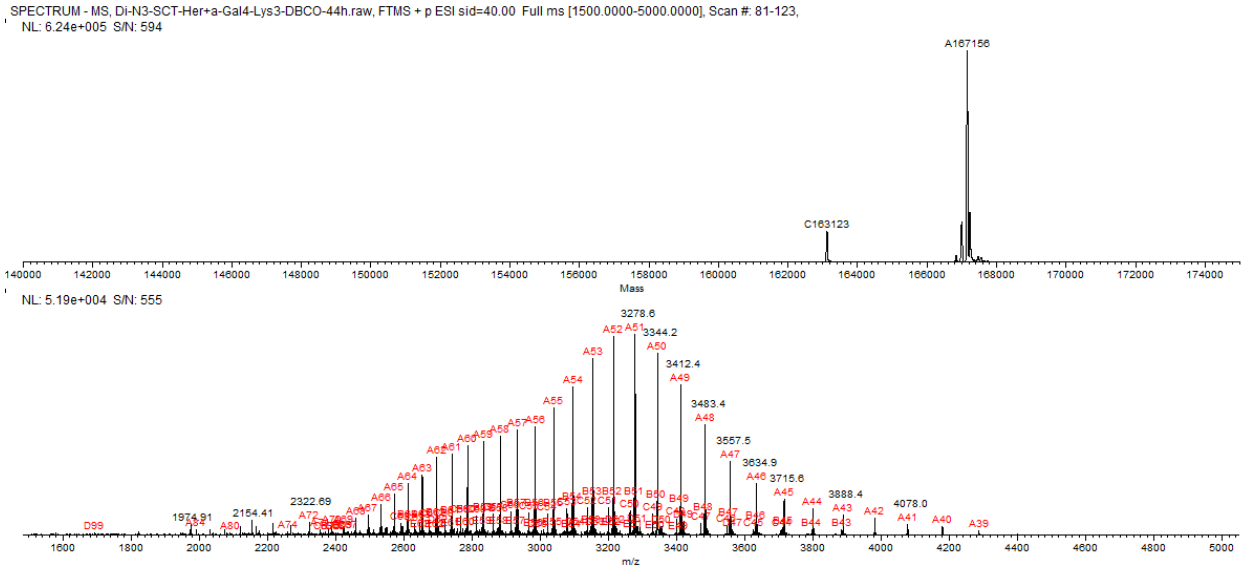


Figure S7. LC-ESI-MS analysis of the intact α-Gal cluster functionalized antibody (**24**)

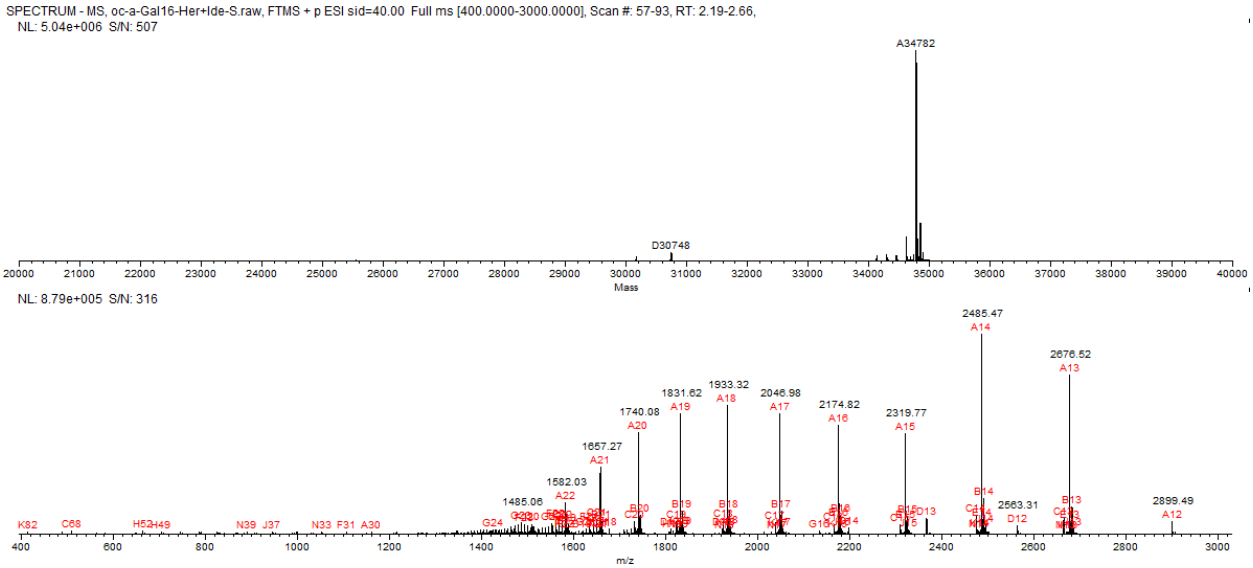


Figure S8. LC-ESI-MS analysis of the Fc domains released by IdeS treatment of the α-Gal functionalized antibody (**24**)

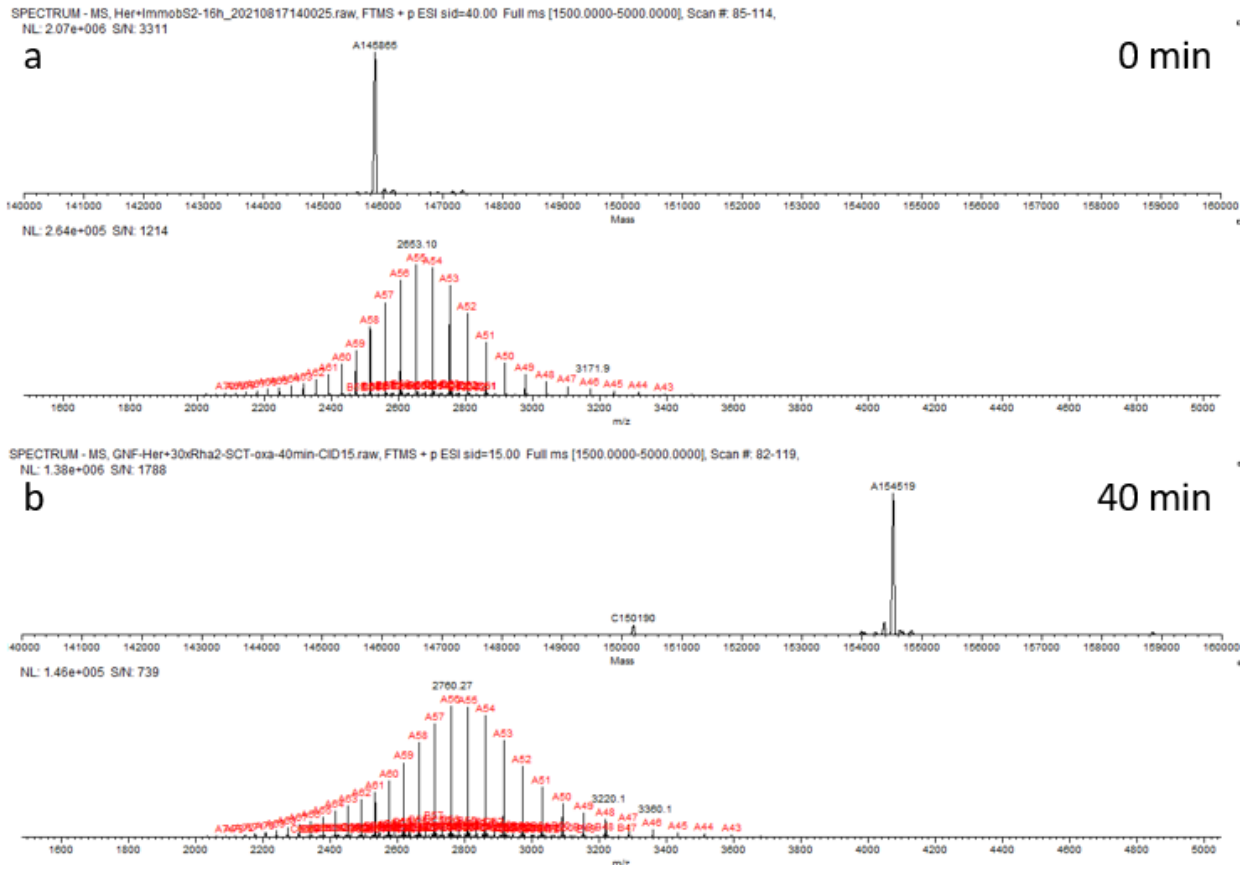


Figure S9. The LC-ESI-MS monitoring of the glycosylation reactions between azide-glycan oxazoline **27a** and antibody **28** catalyzed by Endo-S2 D184M. A mixture of the deglycosylated antibody **28** (0.5 mg, 3.3 nmol, 25 mg/mL), glycan oxazoline **27a** (0.44 mg, 100 nmol, 30 *mol. equiv.* of the antibody), and the mutant enzyme (0.1 mg/mL) in a Tris buffer (100 mM, pH 7.2) was incubated at 30 ^{o}C and the reaction was monitored by LC-ESI-MS analysis of the intact antibodies at 20 min intervals. a) the deconvoluted mass of **28**; b) the deconvoluted mass of the reaction mixture catalyzed by Endo-S2 D184M at 40 min.

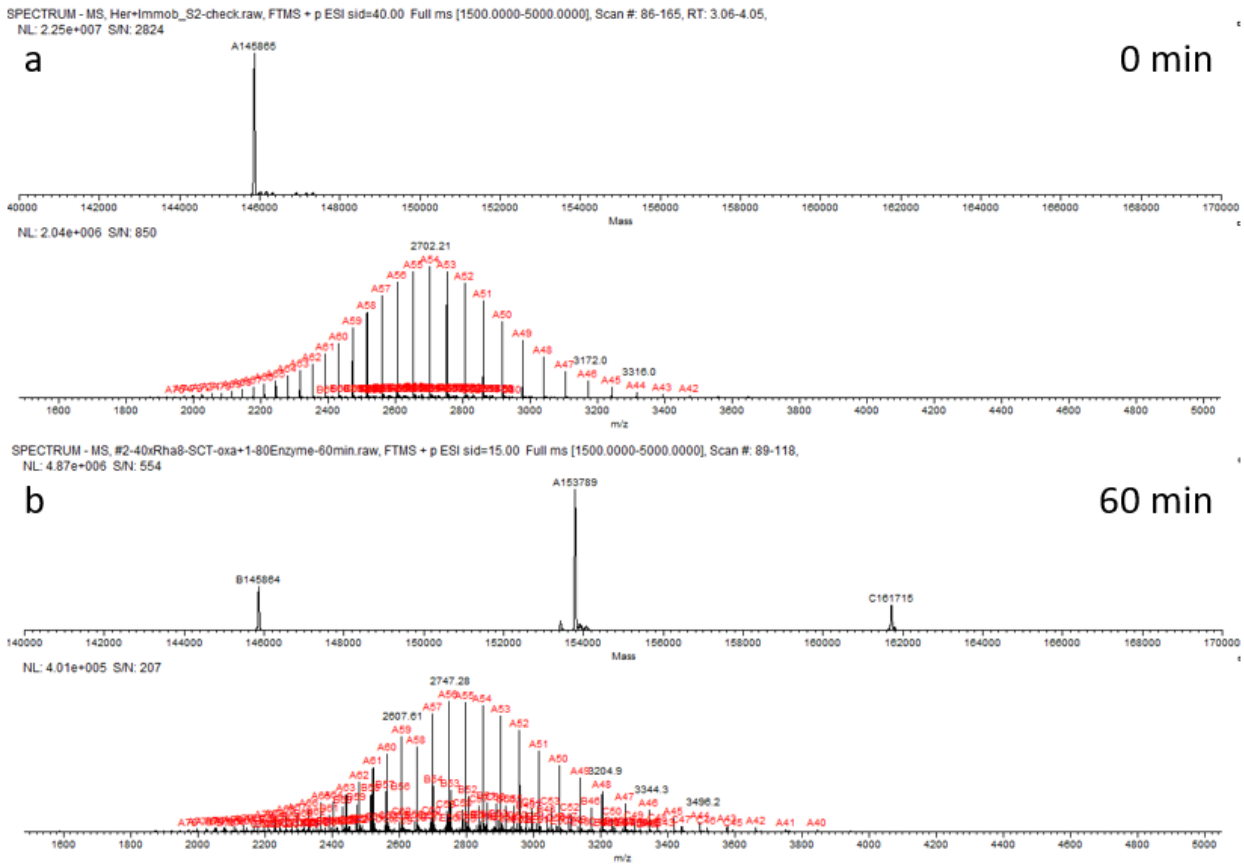


Figure S10. The LC-ESI-MS monitoring of the glycosylation reactions between azide-glycan oxazoline **27b** and antibody **28** catalyzed by Endo-S2 D184M. A mixture of the deglycosylated antibody **28** (0.1 mg, 3.3 nmol, 25 mg/mL), glycan oxazoline **27b** (0.44 mg, 100 nmol, 40 *mol. equiv.* of the antibody), and the mutant enzyme (0.4 mg/mL) in a Tris buffer (100 mM, pH 7.2) was incubated at 30 ºC and the reaction was monitored by LC-ESI-MS analysis of the intact antibodies at 20 min intervals. a) the deconvoluted mass of **28**; b) the deconvoluted mass of the reaction mixture catalyzed by Endo-S2 D184M at 60 min.

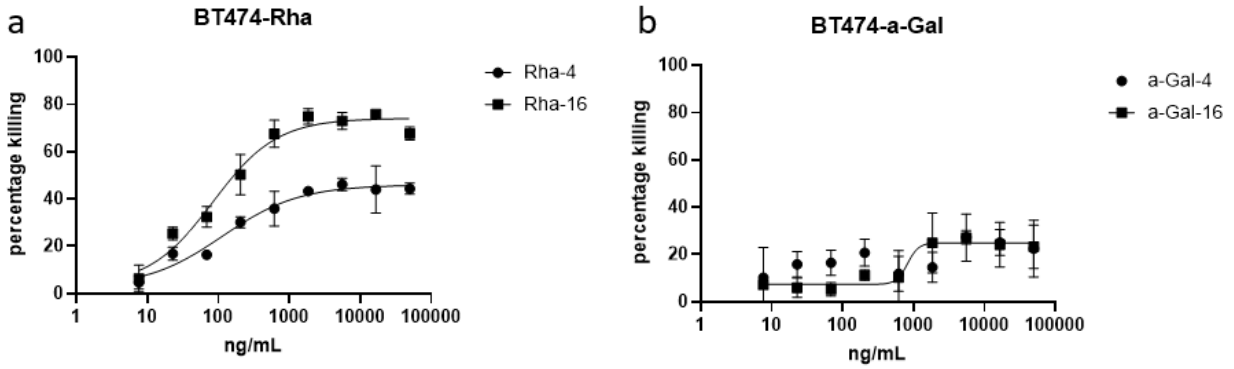


Figure S11. Cell killing assays for breast cancer cell lines a) Rhamnose conjugates with BT-474 (HER2 overexpression); b) α-Gal conjugates with BT-474 (HER2 overexpression). The human serum was purchesed from Cosmo Bio USA. All assays were performed in triplicate.

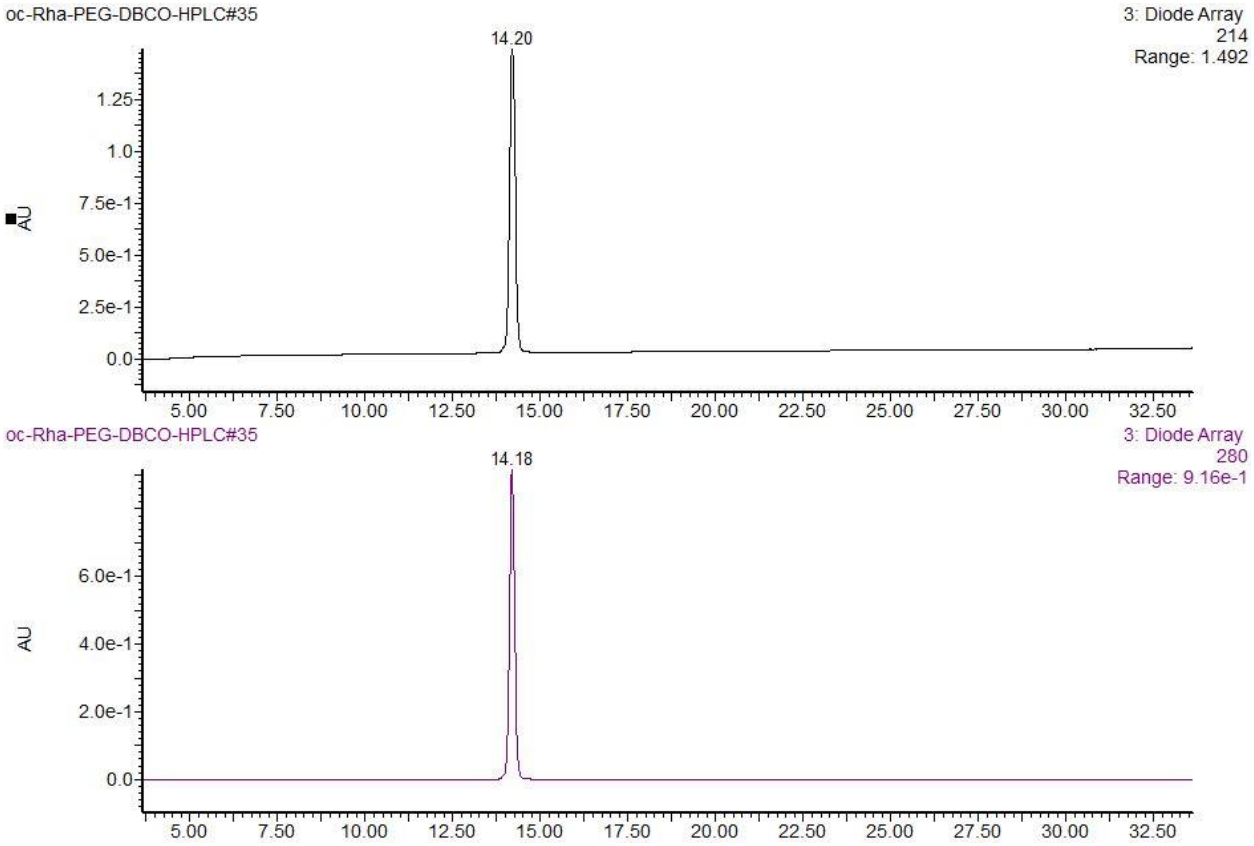


Figure S12. HPLC profile for **3**, 0.4 mL/min, 25-60%B, 30 min

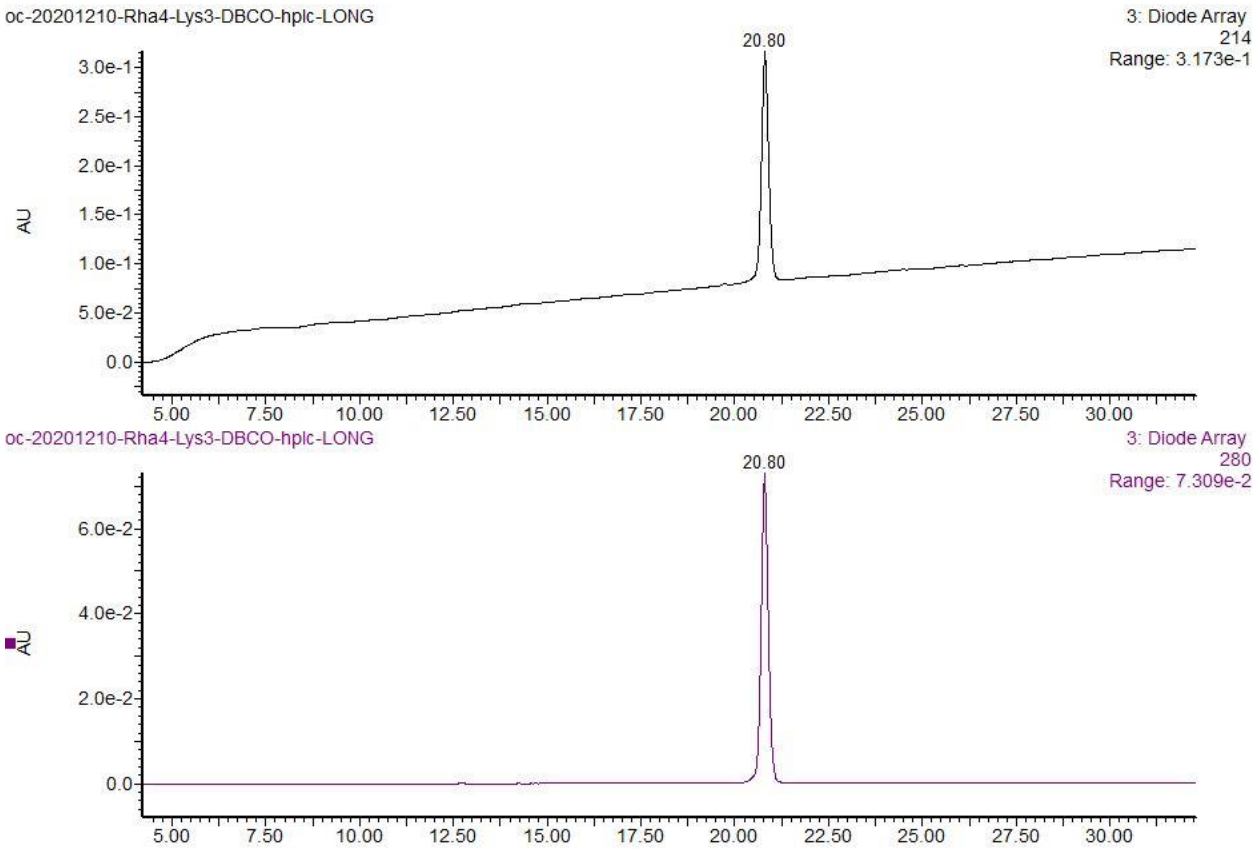


Figure S13. HPLC profile for **13**, 0.4 mL/min, 10-50%B, 30 min

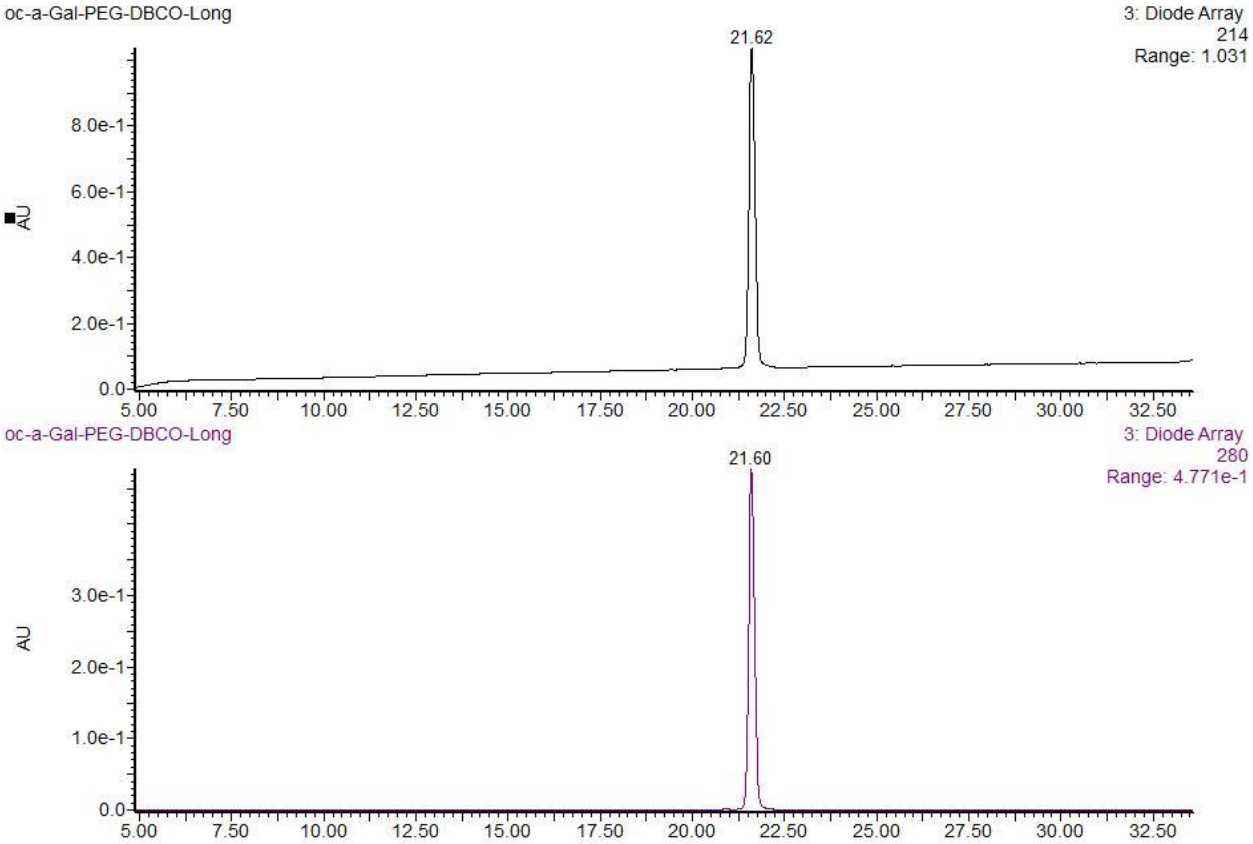


Figure S14. HPLC profile for **15**, 0.4 mL/min, 10-50%B, 30 min

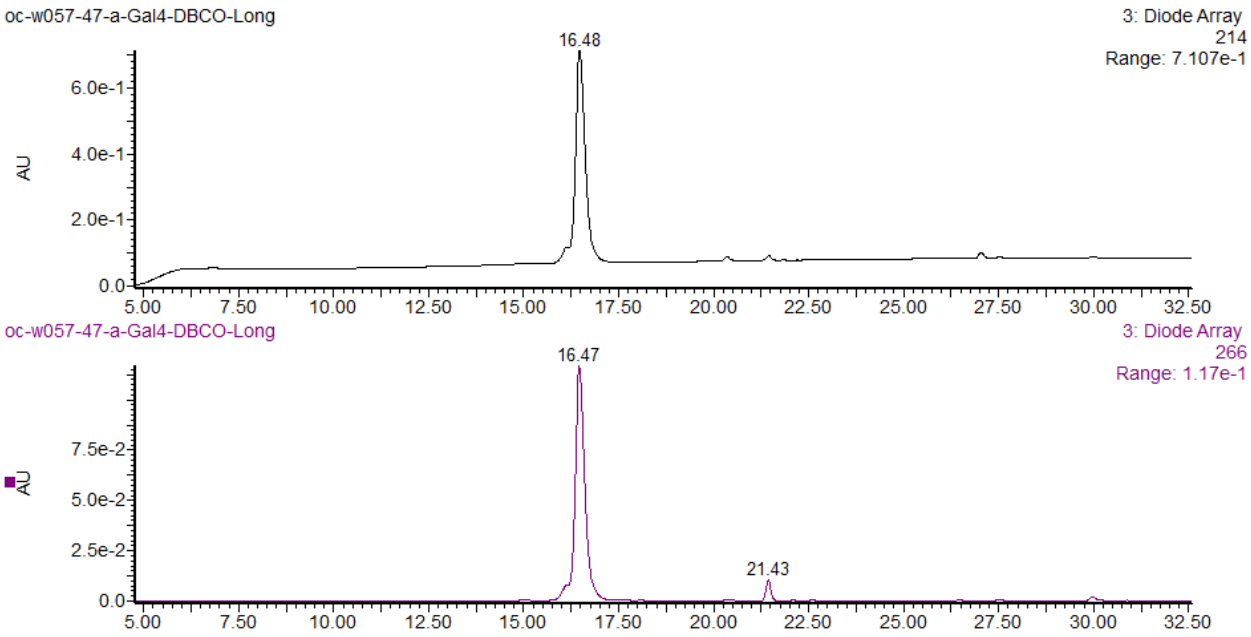
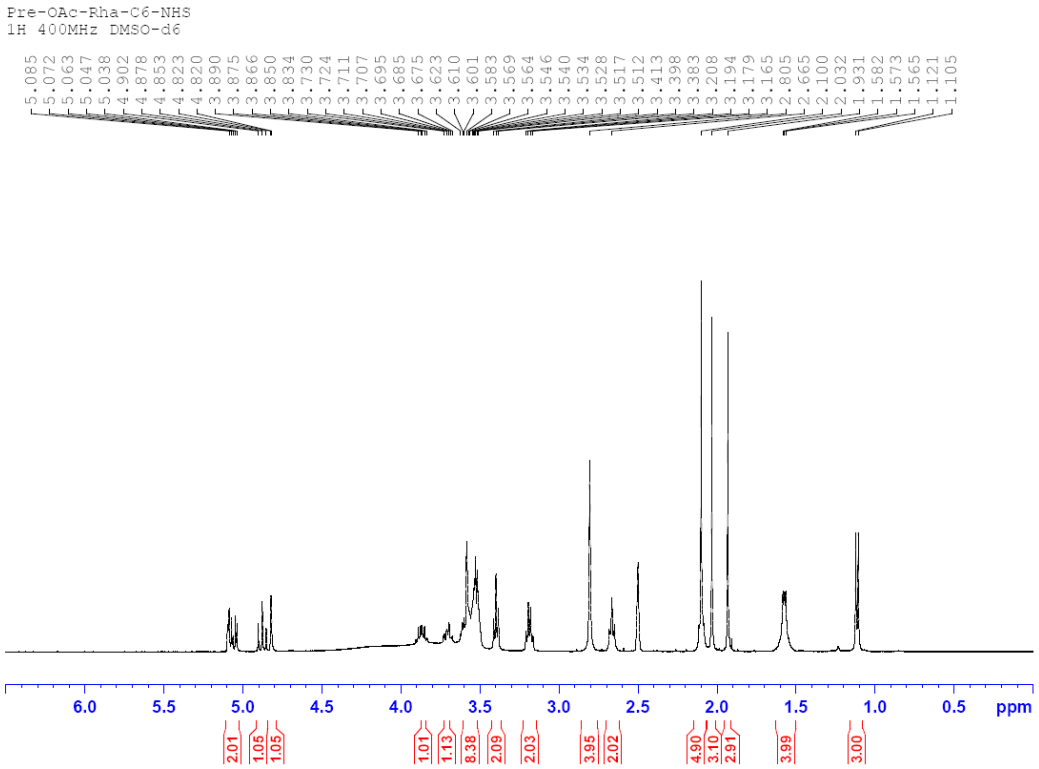
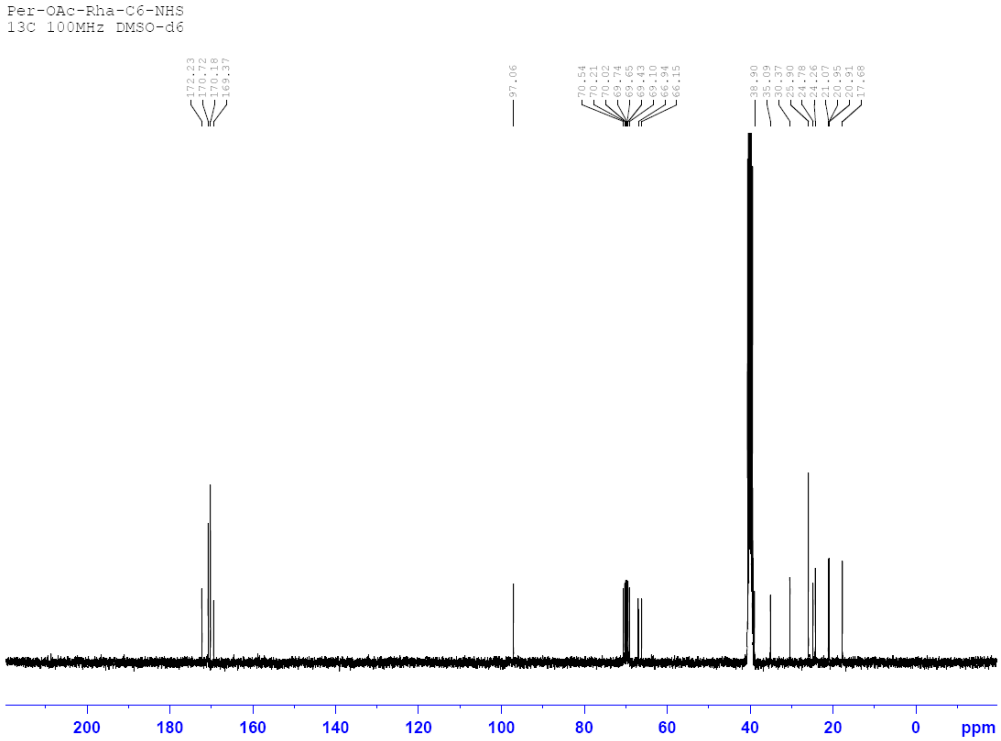


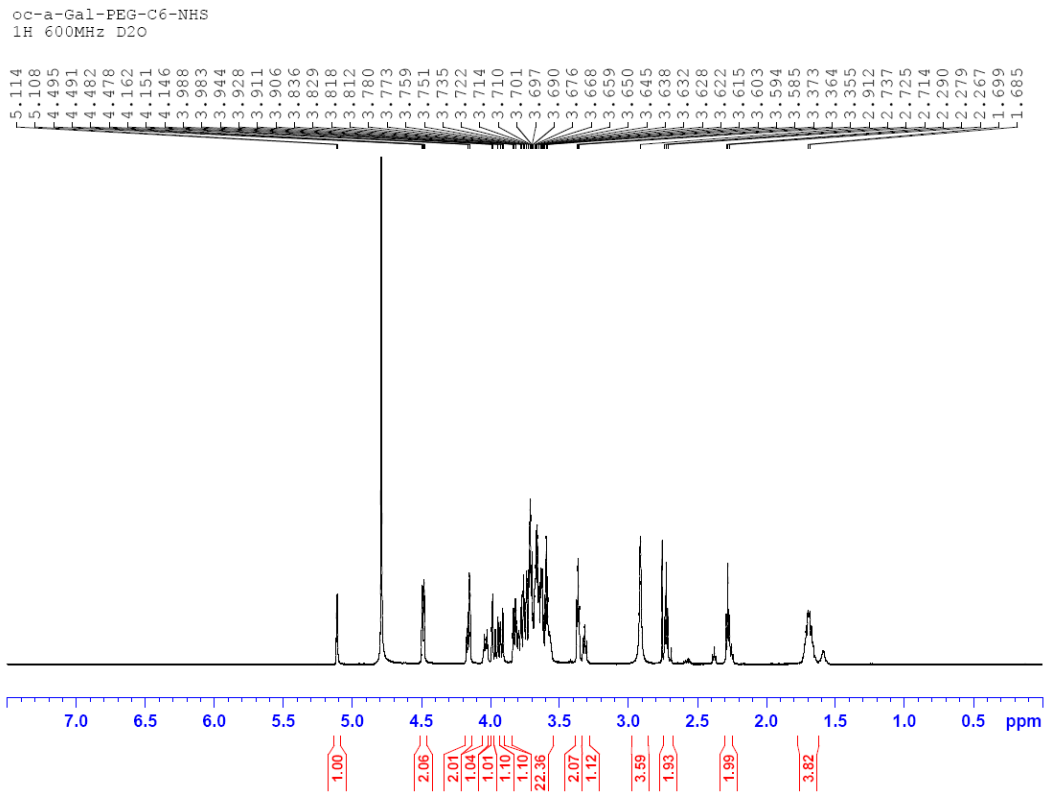
Figure S15. HPLC profile for **18**, 0.4 mL/min, 10-50%B, 30 min



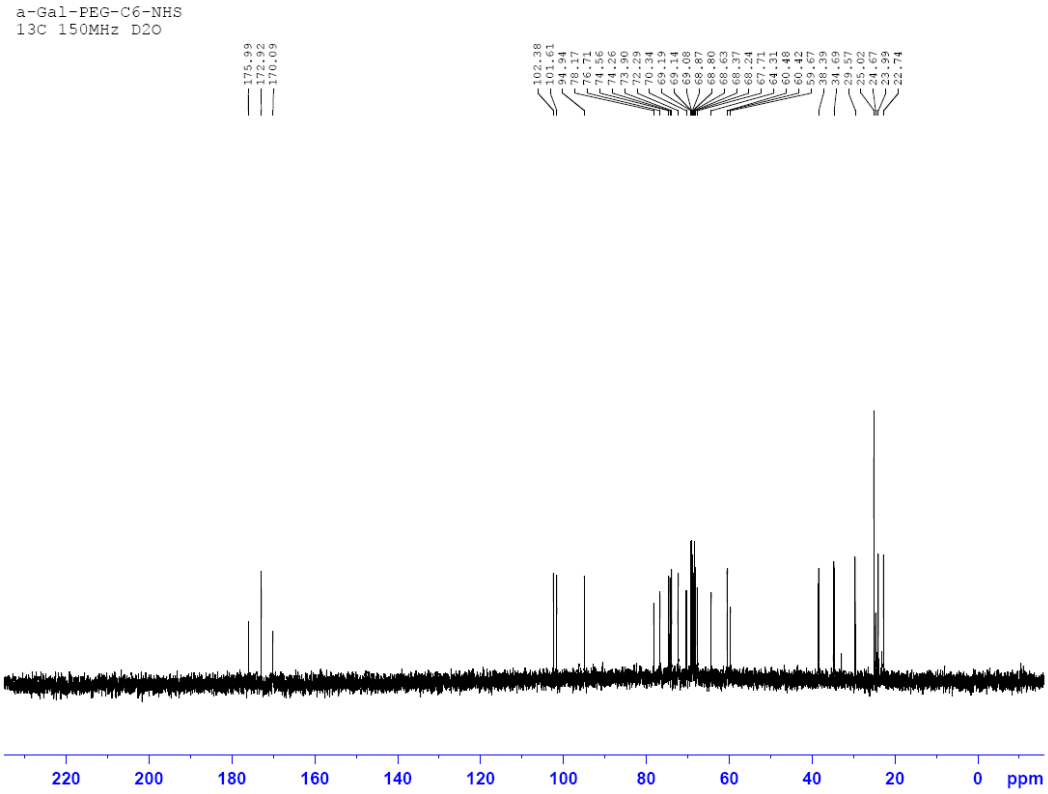
^{1}H NMR spectrum (400 MHz, DMSO-*d*6): compound **10**



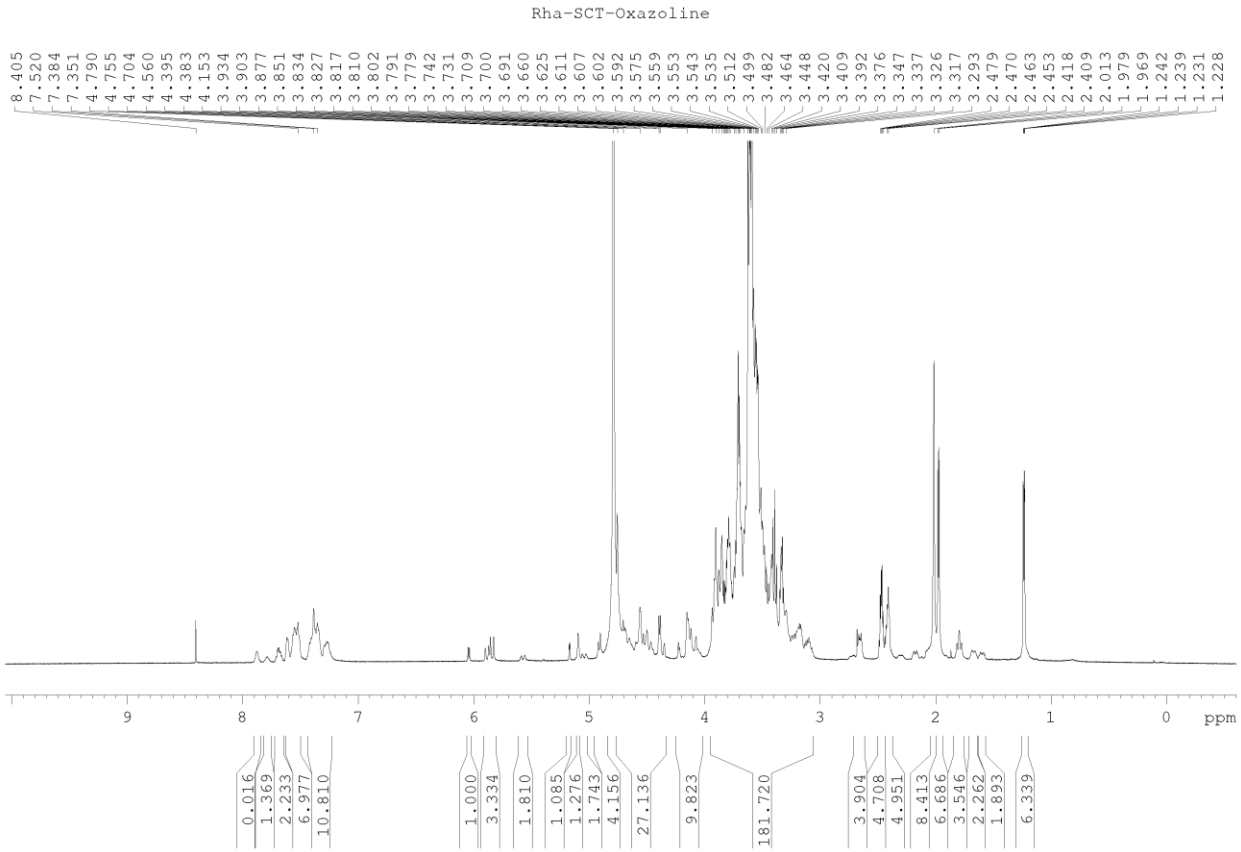
^{13}C NMR spectrum (100 MHz, DMSO-*d*6): compound **10**



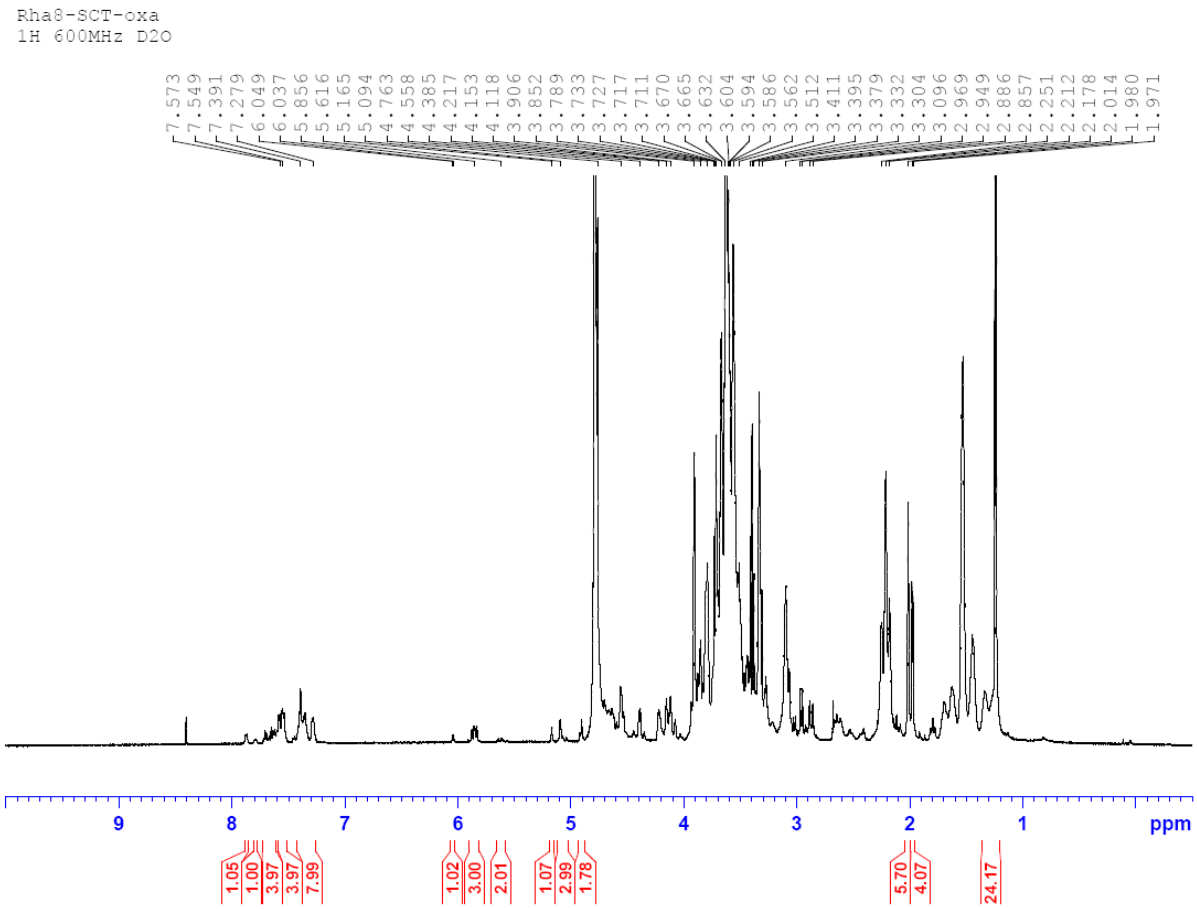
^{1}H NMR spectrum (600 MHz, D_2O): compound **16**



^{13}C NMR spectrum (150 MHz, D_2O): compound **16**



^{1}H NMR spectrum (600 MHz, D_2O): compound **26a**



^{1}H NMR spectrum (600 MHz, D_2O): compound **26b**