

Supporting Information

4,5-Cis Unsaturated α -GalCer Analogues Distinctly Lead to CD1d-Mediated Th1-Biased NKT Cell Responses

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The synthetic procedures of compound **5** and compound **6**

(2R, 3R, 4Z)-1, 3-O-benzylidene-4-octadecene-1, 2, 3-triol (5). A solution of *n*-BuLi (6.4 g, 56.8 mmol) in THF (20 mL) was added to the stirred solution of $\text{CH}_3(\text{CH}_2)_{12}\text{CH}_2^+\text{PPh}_3\text{Br}^-$ (17.5 g, 32.4 mmol) in THF (100 mL) at 0 °C under an argon atmosphere. After the mixture had been stirred for 30 min, **4** (5.0 g, 24.0 mmol) in THF (30 mL) was added at 0 °C. The mixture was warmed gradually to room temperature and stirred overnight, quenched by sat. NH_4Cl then extracted with CH_2Cl_2 . The organic layer was washed with brine, dried (MgSO_4). The residue was filtered and the filtrate was evaporated. The residue was purified by column chromatography (100% CH_2Cl_2) to afford **5** as a white solid (4.76 g, 51%). R_f =0.32 (100% dichloromethane). ESI/MS (m/z) 389.3 [$\text{M} + \text{H}$]⁺.

(2S,3R,4Z)-2-Azido-1,3-O-benzylidene-4-octadecene-1,3-diol (6). Anhydride Triflate (2.24 mL) was added dropwise to a solution of **5** (4.0 g, 10.43 mmol) in CH_2Cl_2 (40.0 mL) and pyridine (2.0 mL) at -15 °C under argon atmosphere. The solution was warmed gradually to room temperature and stirred for 2 h before DMF (20mL) and sodium azide (3.4 g, 52.1 mmol) was added successively. Then the mixture was stirred overnight. After the organic solvent was removed in vacuum, the residue was partitioned between ice-water and CH_2Cl_2 . The organic layer was washed with water and brine successively, dried (MgSO_4) and evaporated. The residue was purified by column chromatography (petroleum ether/ ethyl acetate 40:1) to afford **6** as a white solid (2.64 g, 62%). R_f = 0.27 (petroleum ether/ ethyl acetate 40:1). ESI/MS (m/z) 414.3 [$\text{M} + \text{H}$]⁺.

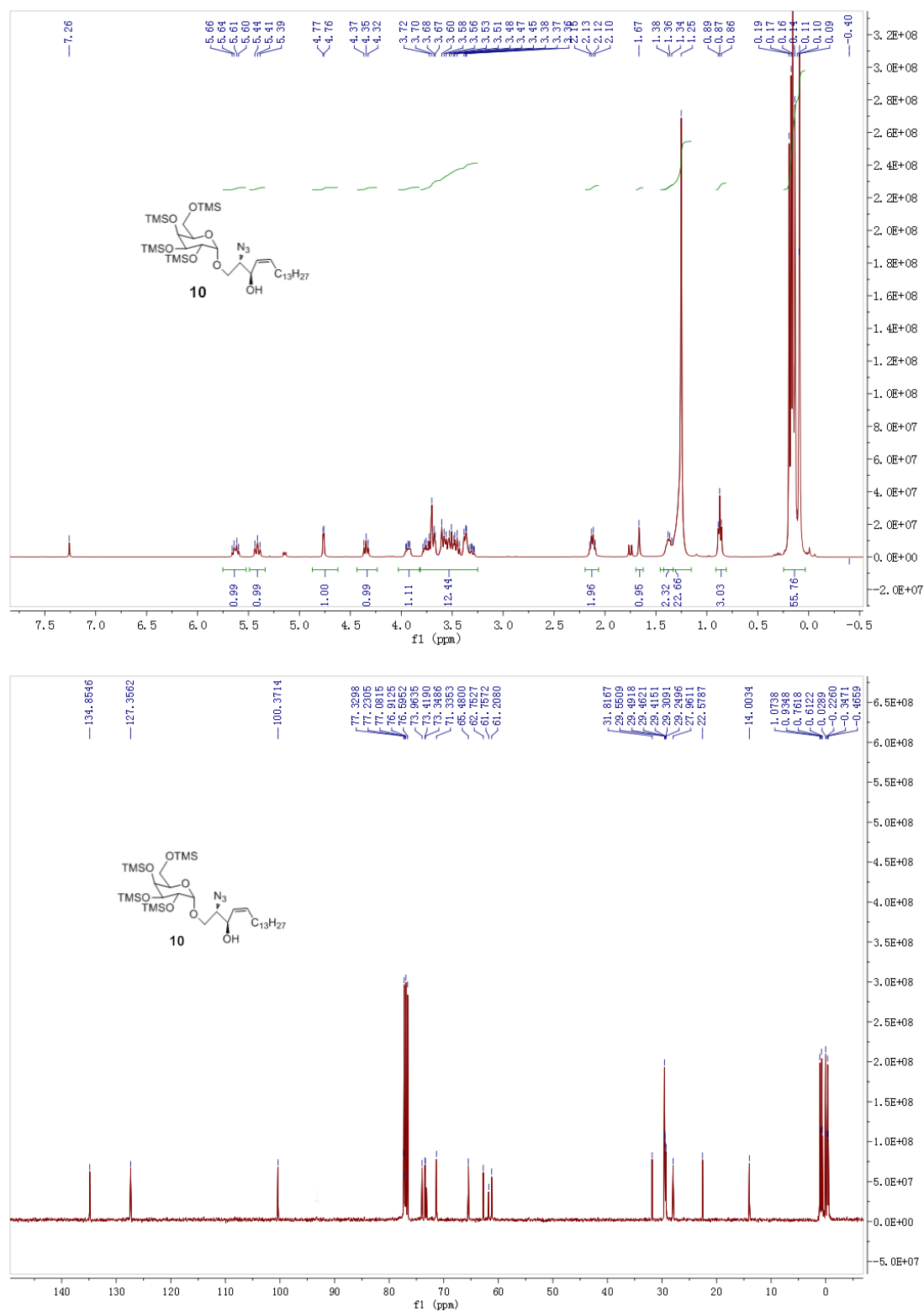


Figure S1. NMR Spectra of compound **10**

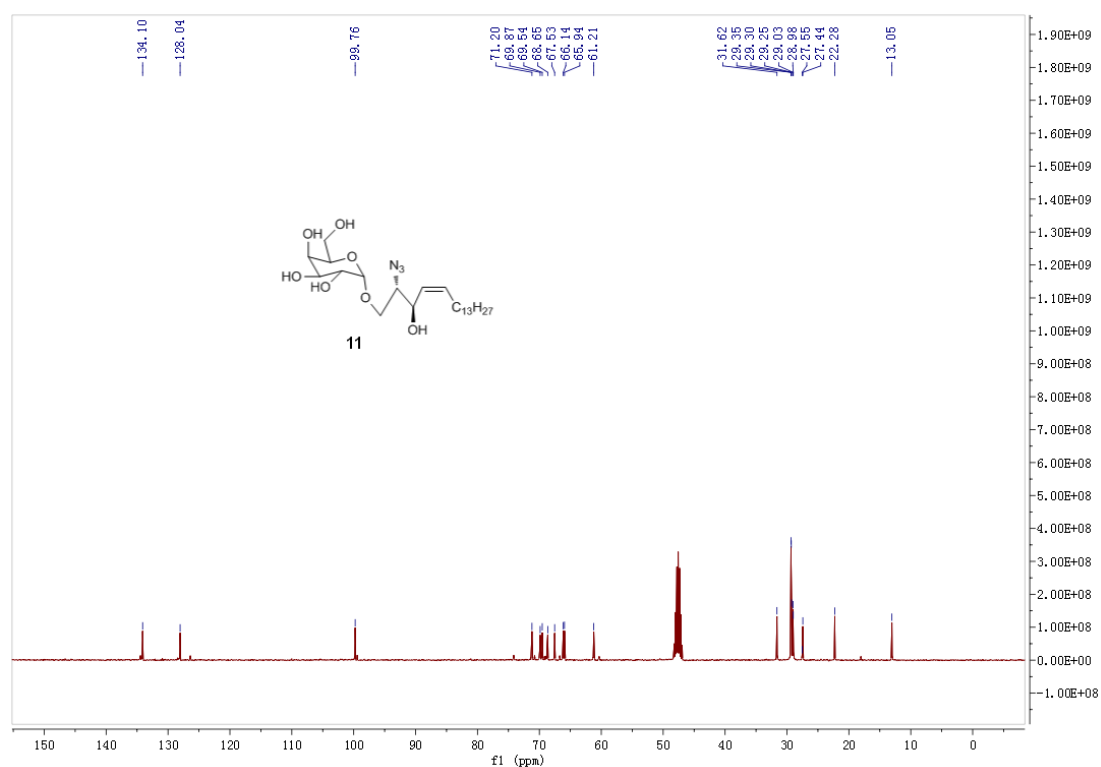
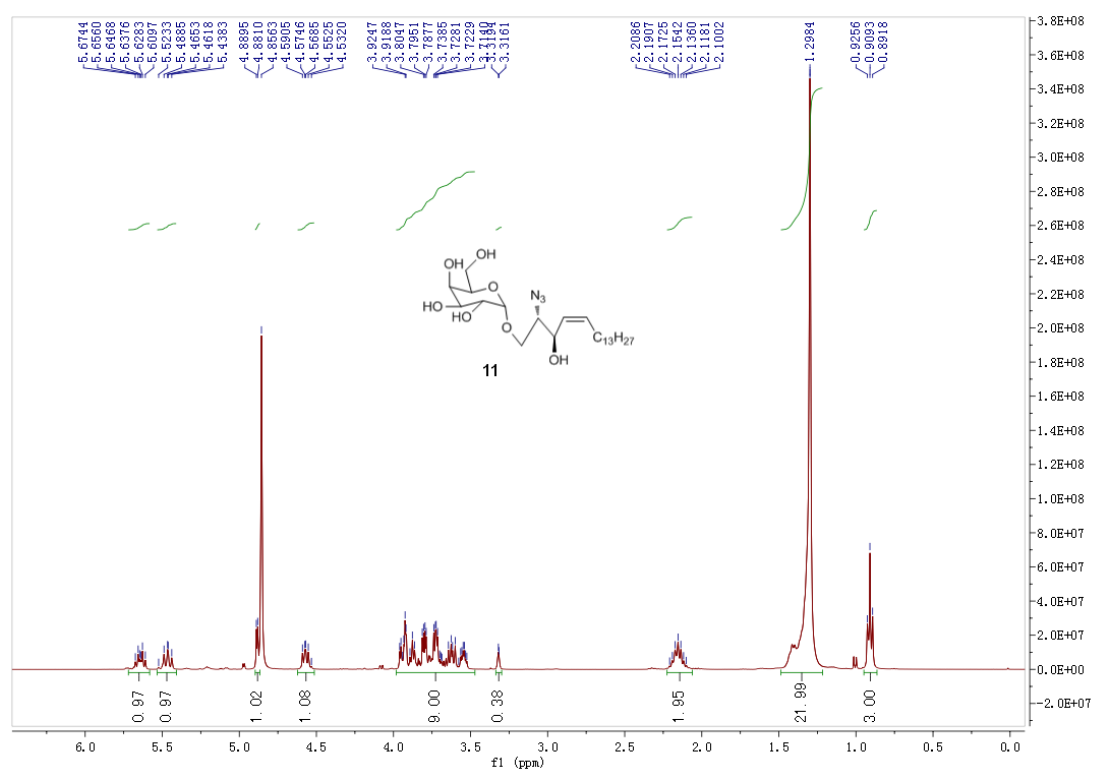


Figure S2. NMR Spectra of compound **11**

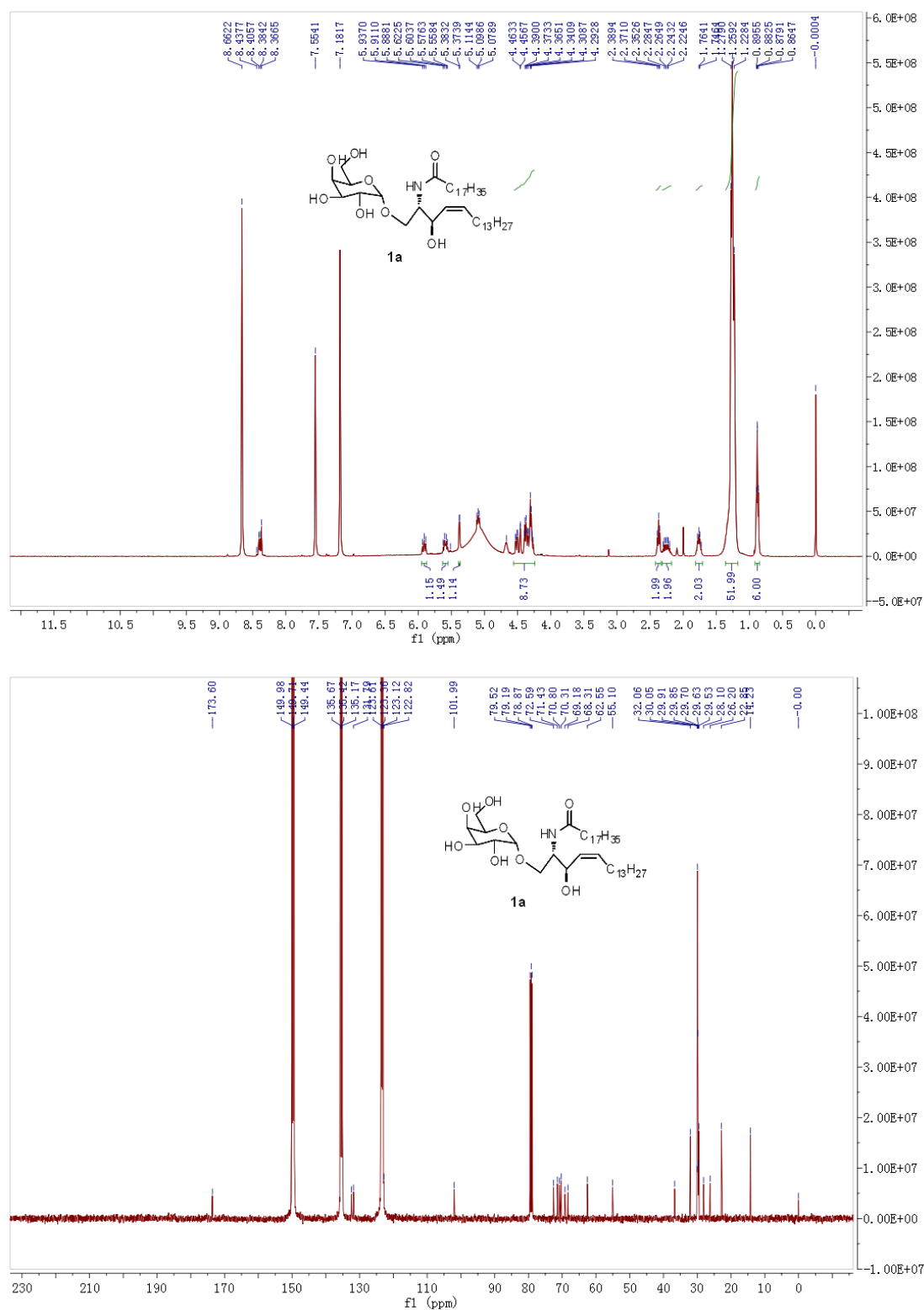


Figure S3. NMR Spectra of compound **1a**

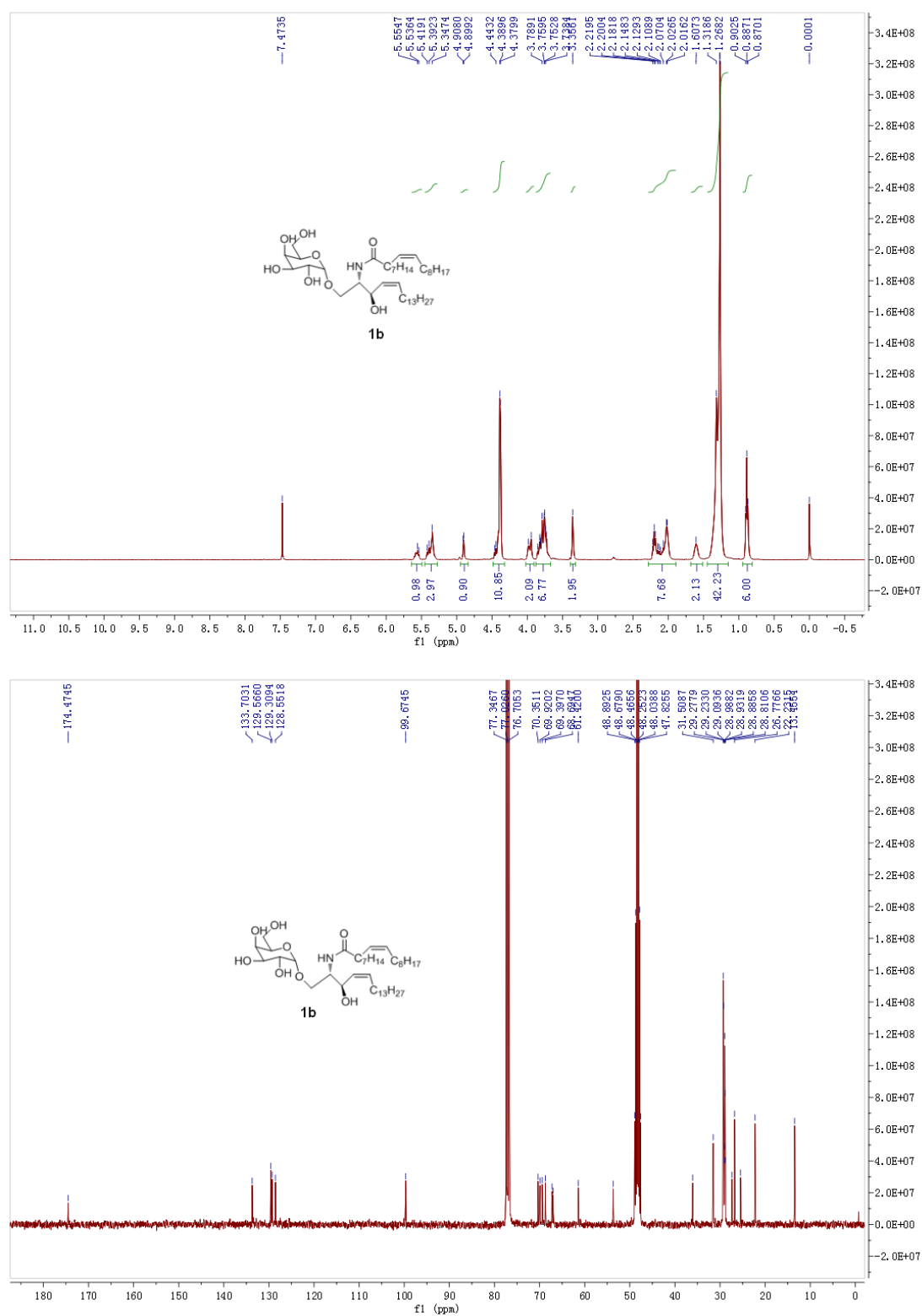


Figure S4. NMR Spectra of compound **1b**

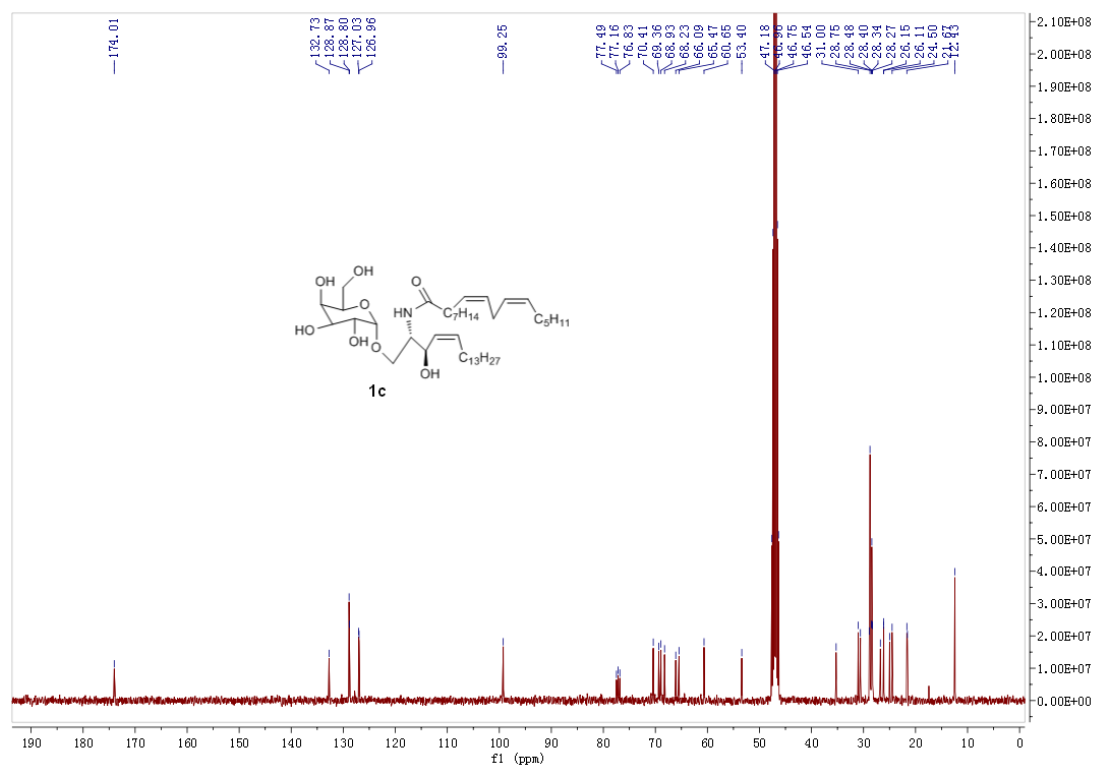
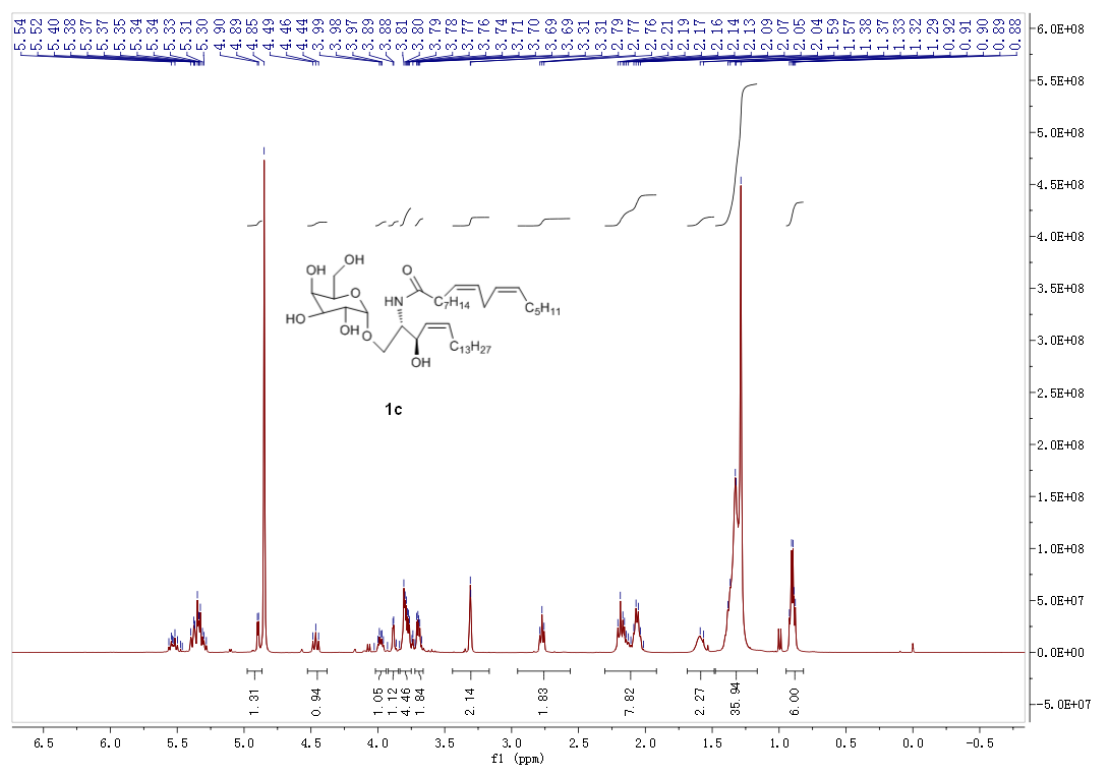


Figure S5. NMR Spectra of compound 1c

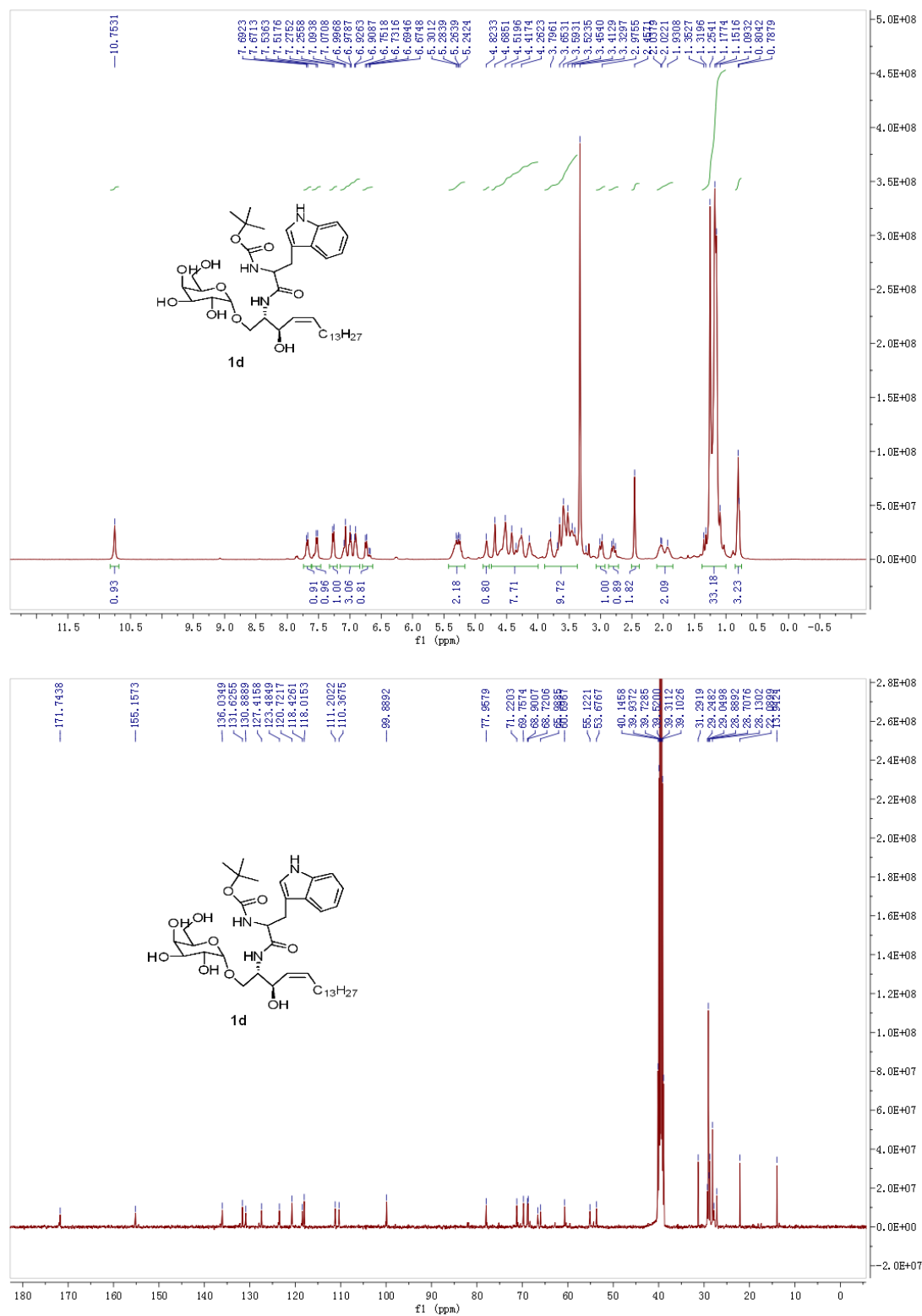


Figure S6. NMR Spectra of compound **1d**

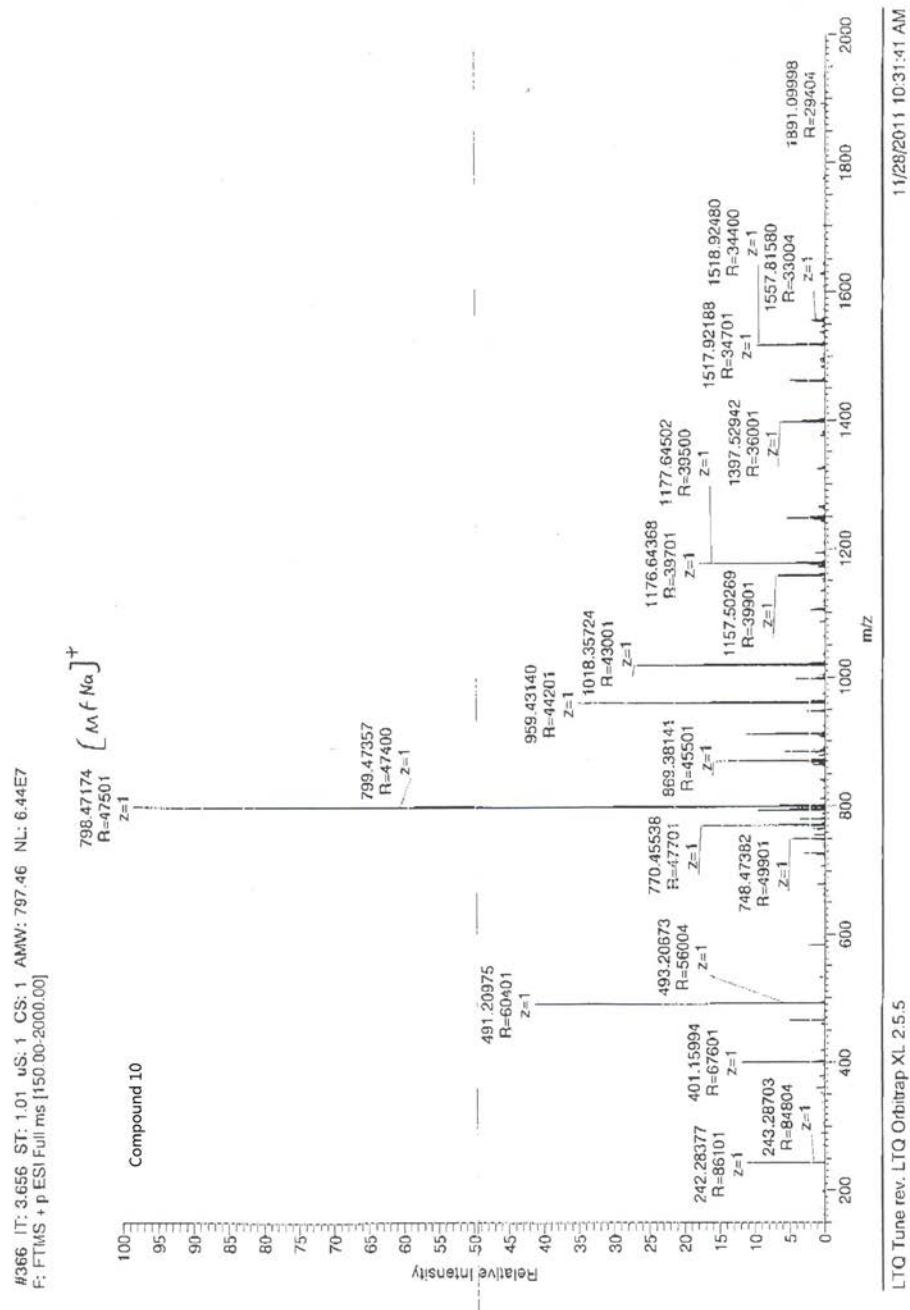


Figure S7. HRMS Spectra of compound 10

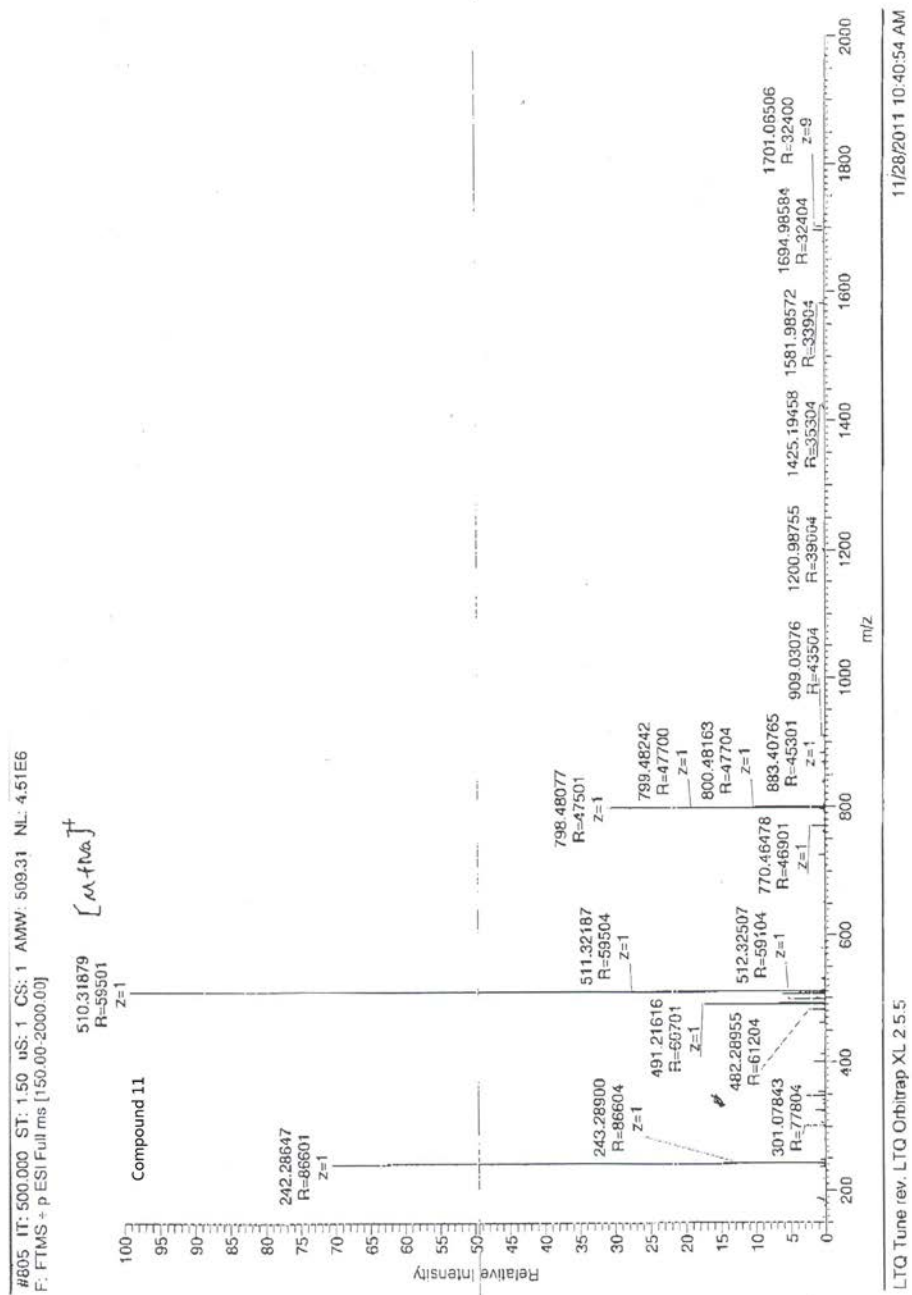


Figure S8. HRMS Spectra of compound **11**

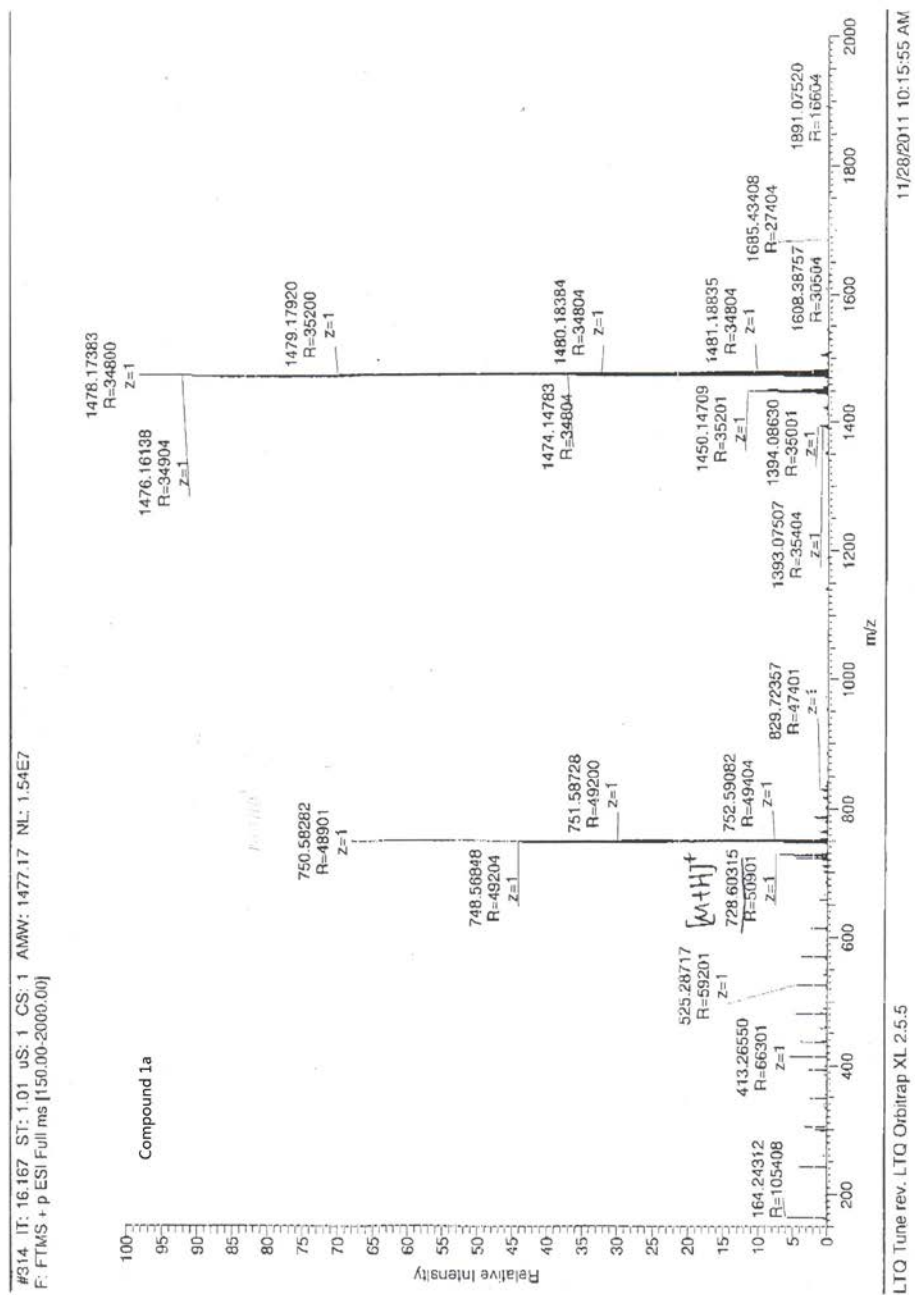


Figure S9. HRMS Spectra of compound **1a**

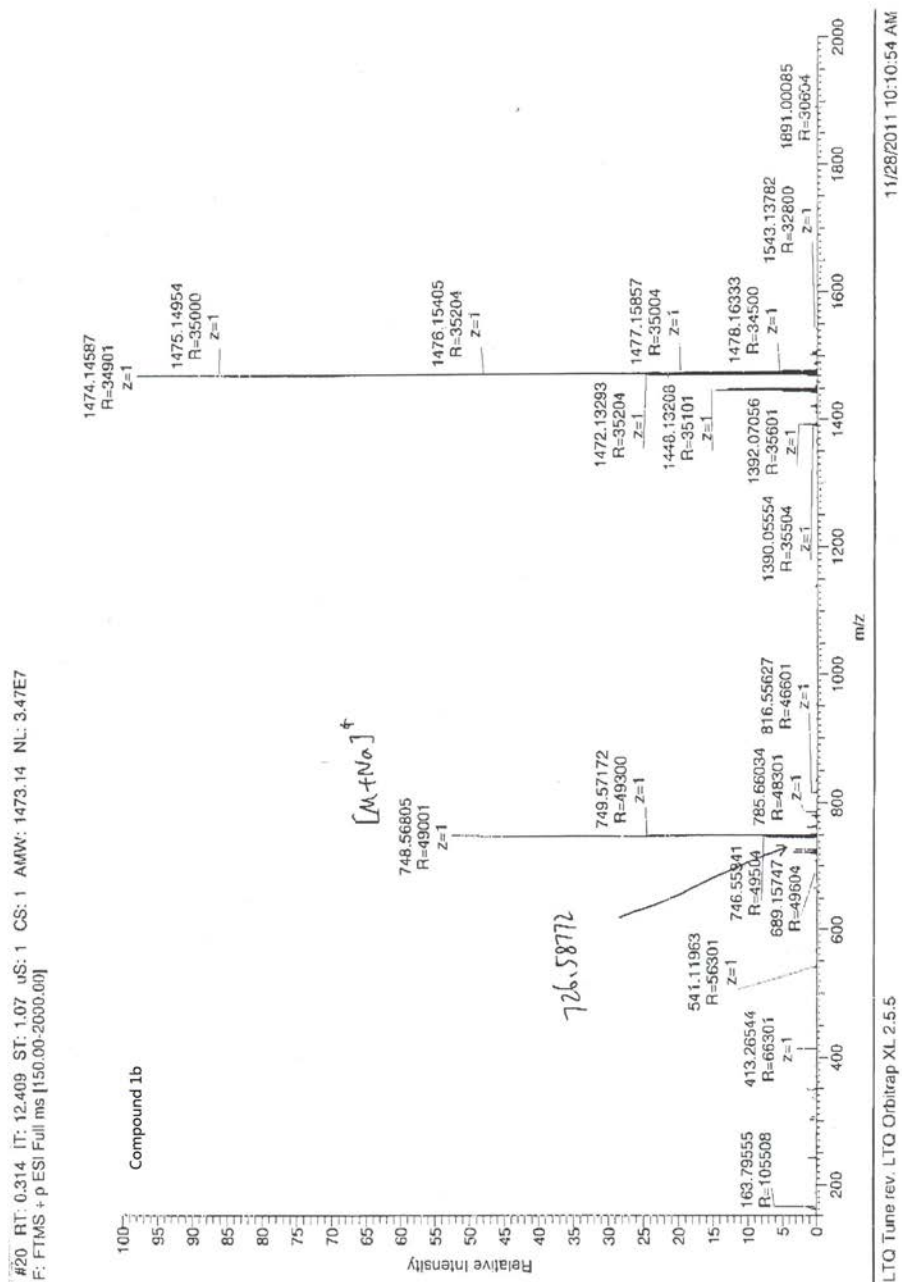


Figure S10. HRMS Spectra of compound **1b**

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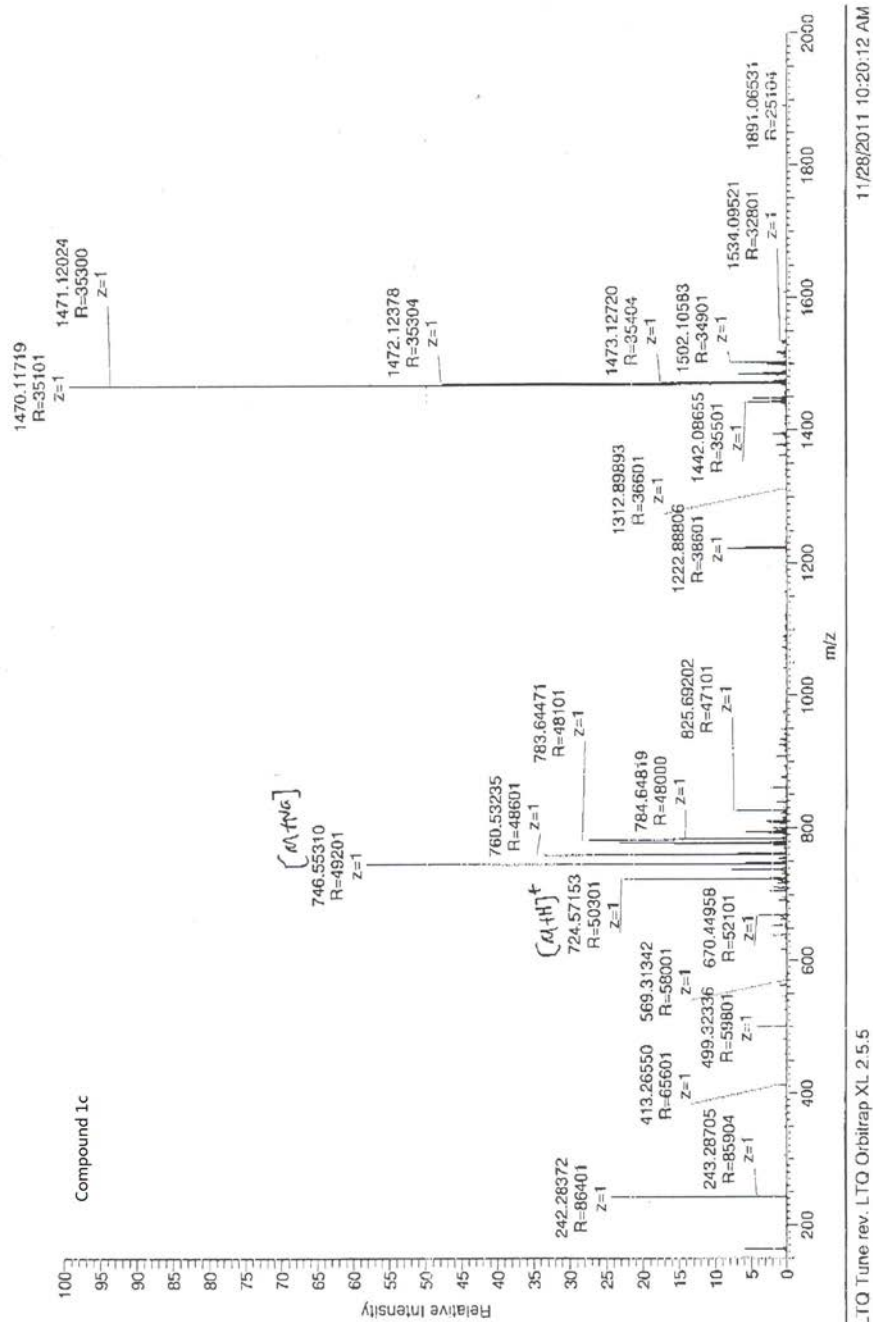


Figure S11. HRMS Spectra of compound 1c

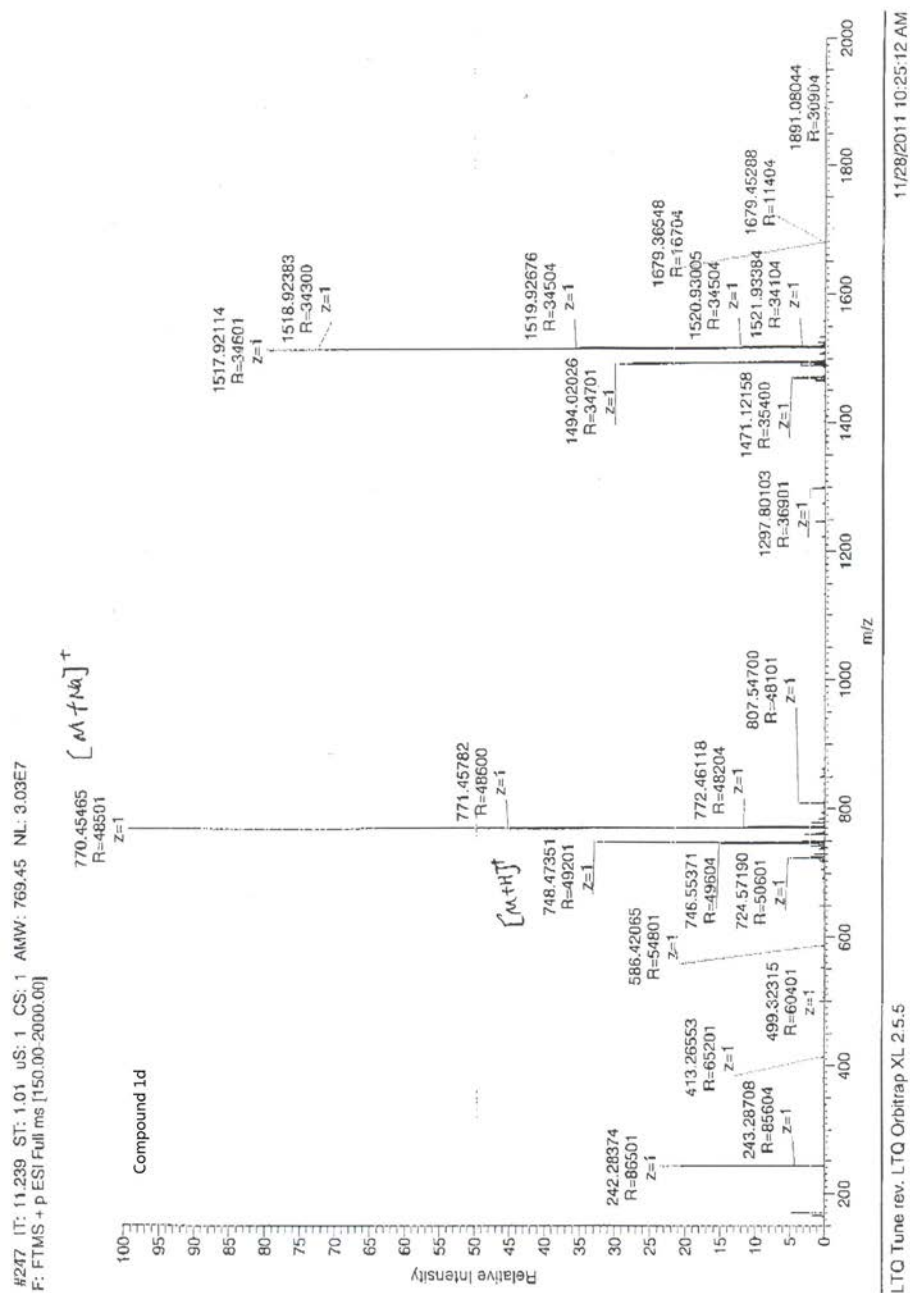


Figure S12. HRMS Spectra of compound 1d