

Supplementary Information

Expedient Synthesis of α -S-(1 \rightarrow 6)-Linked Pentaglucoyl Thiol

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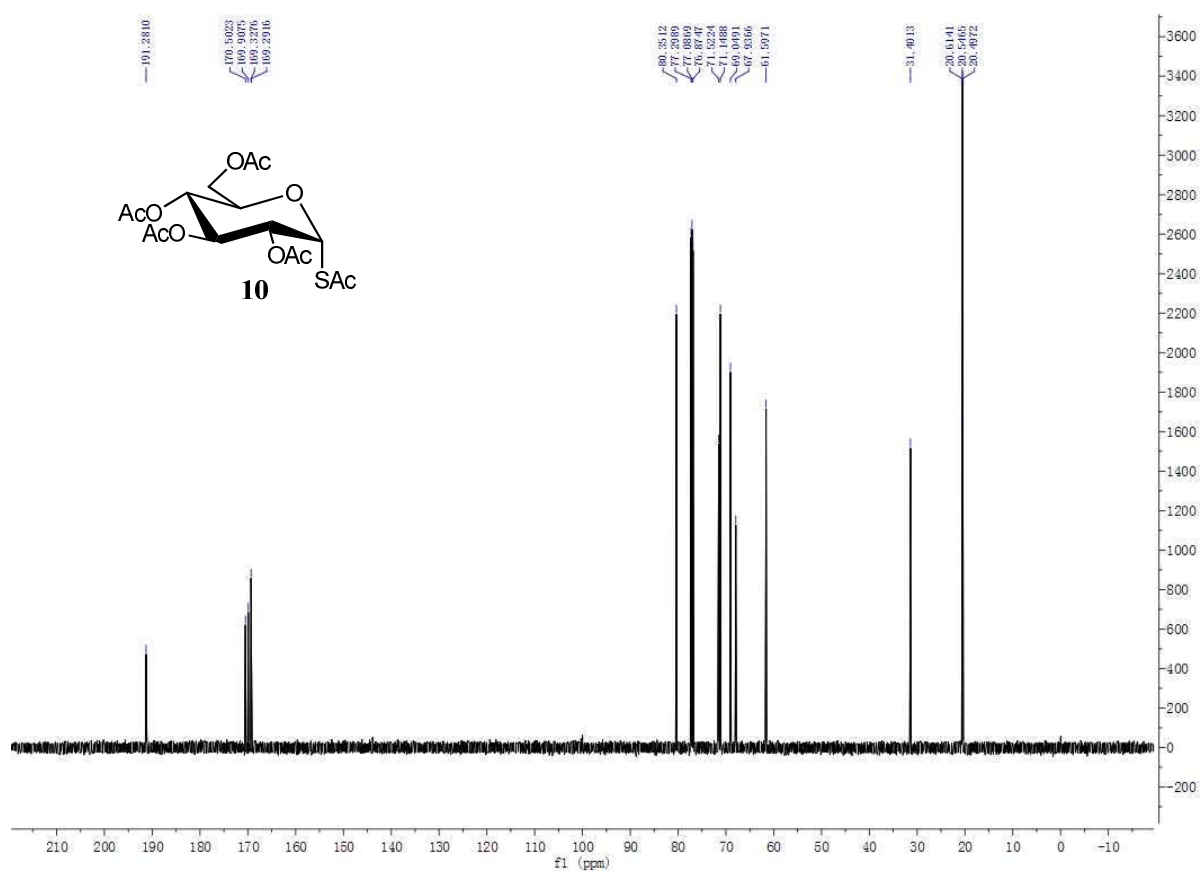
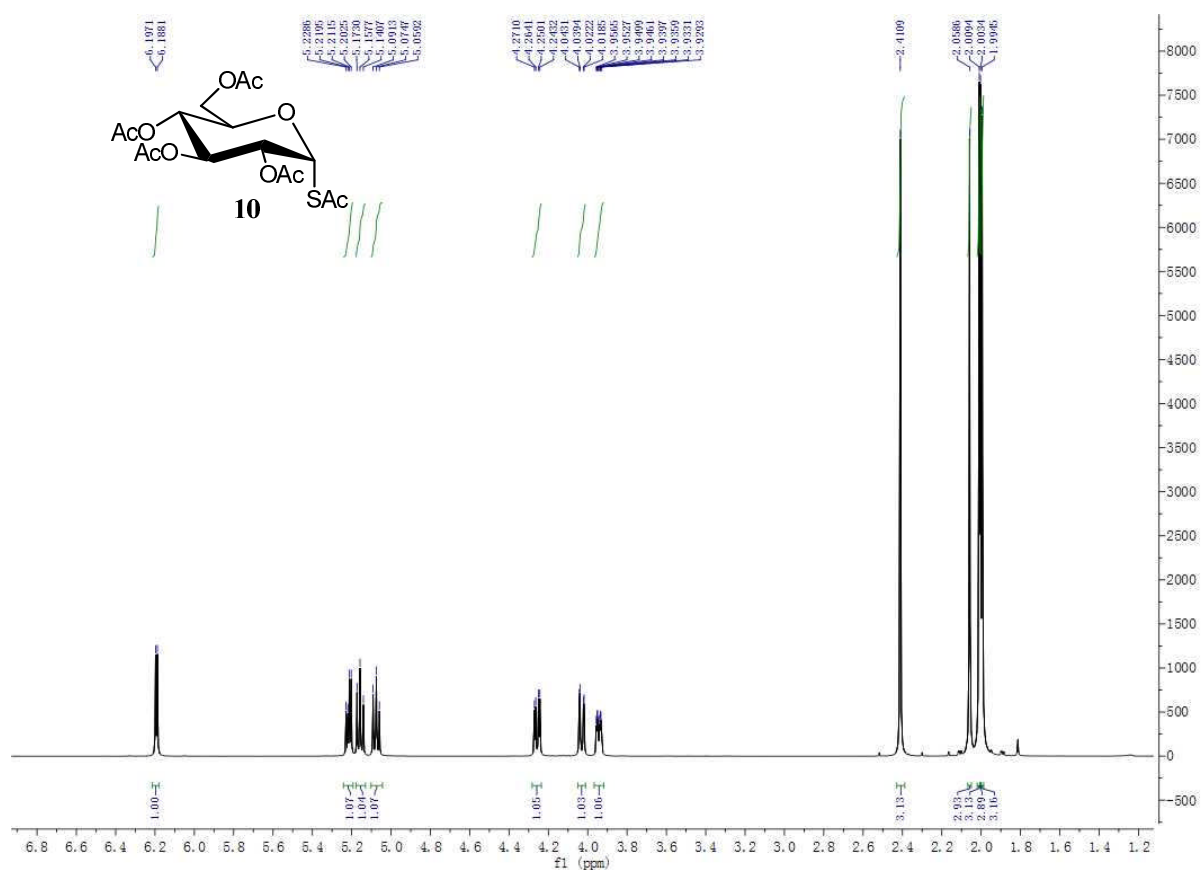
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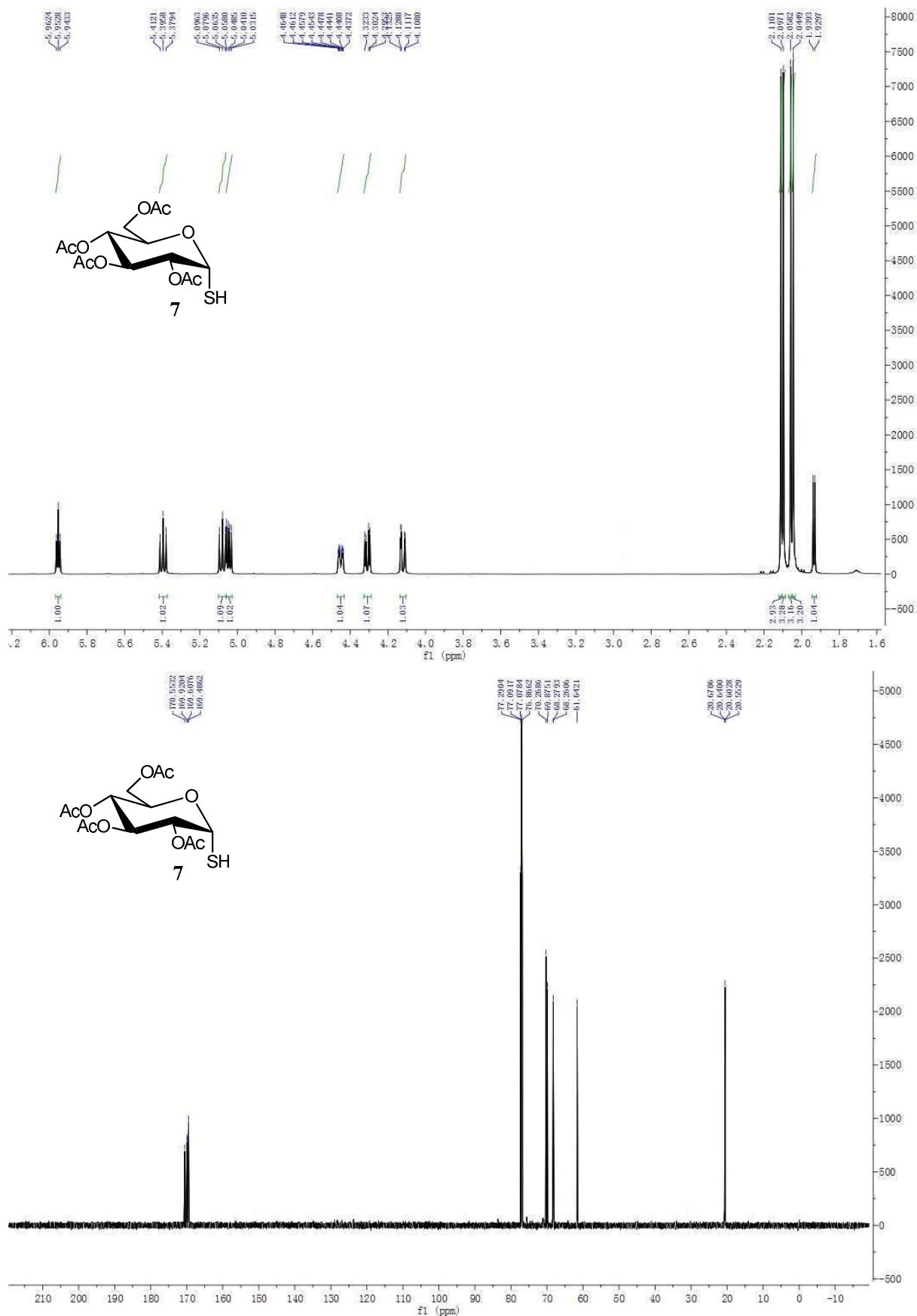
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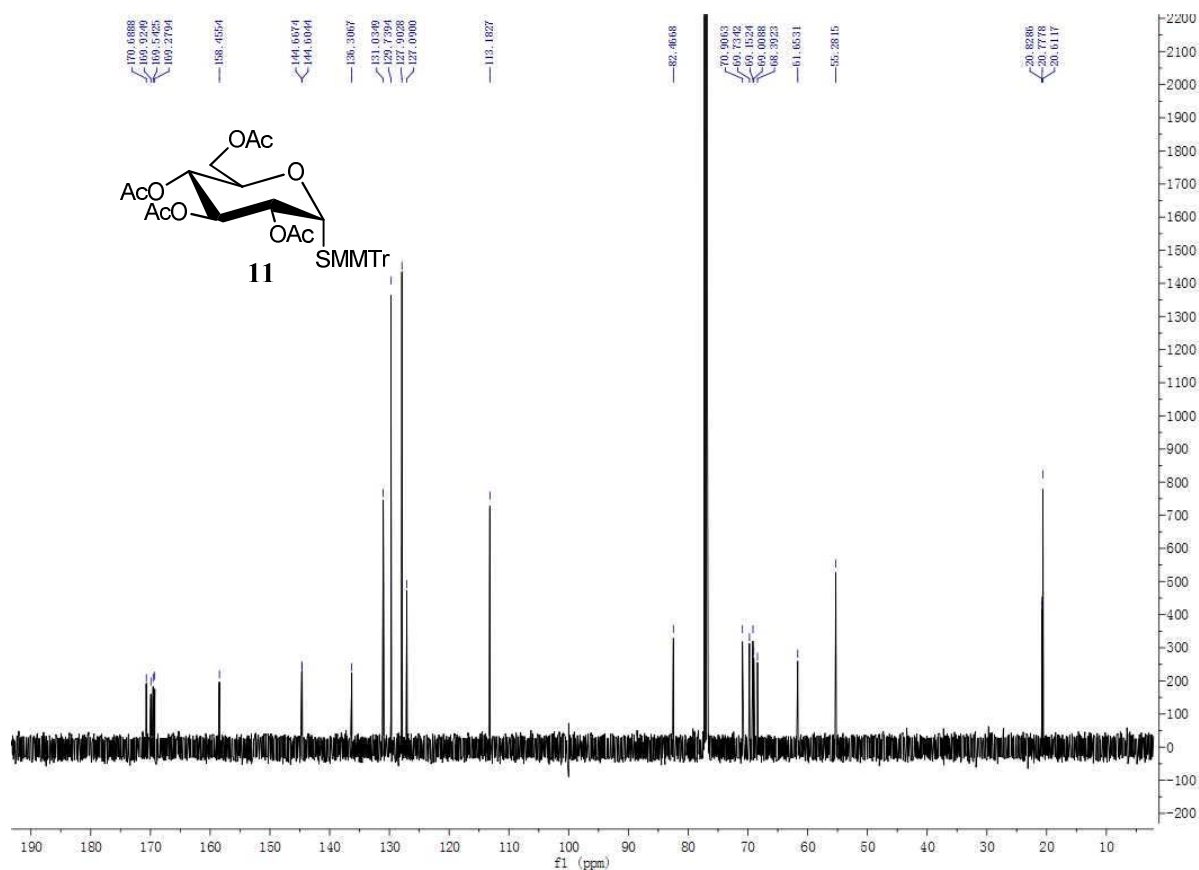
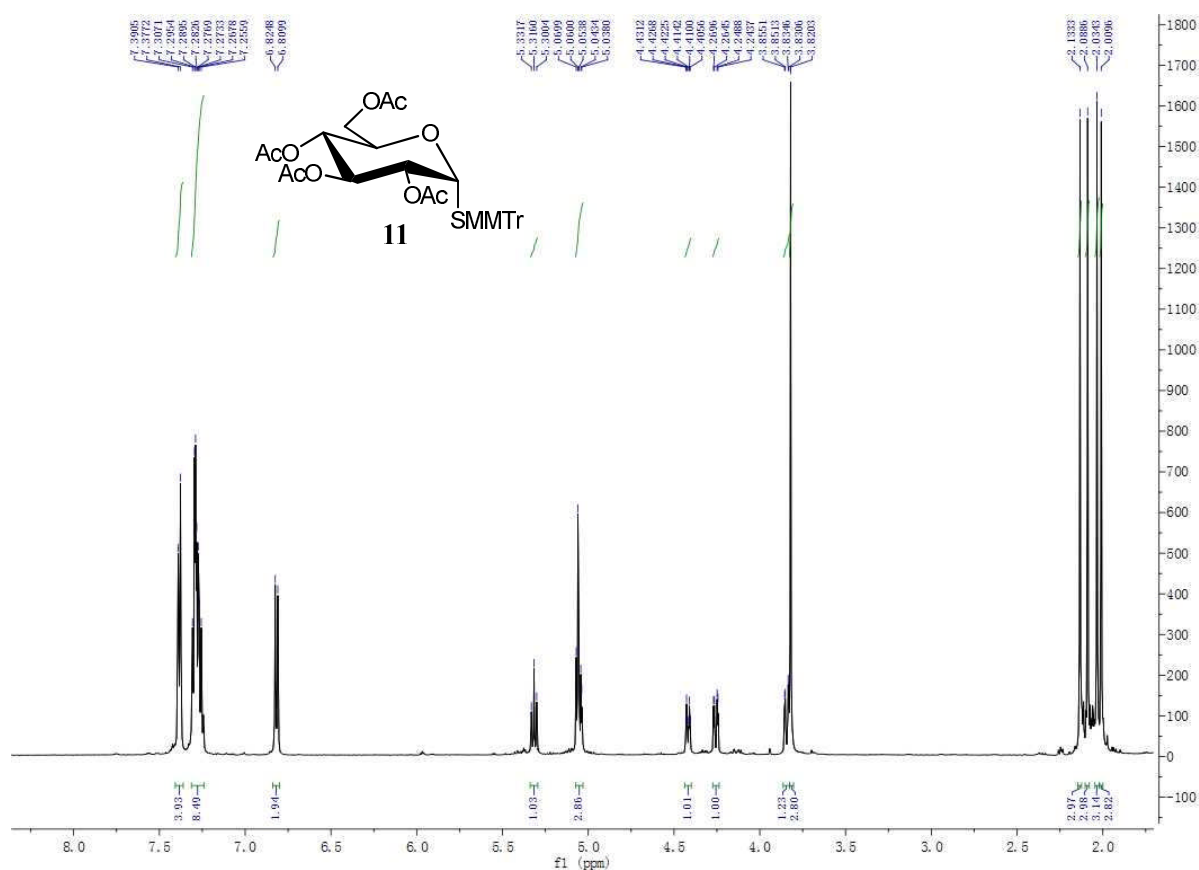
¹H NMR and ¹³C NMR spectra of compound 10



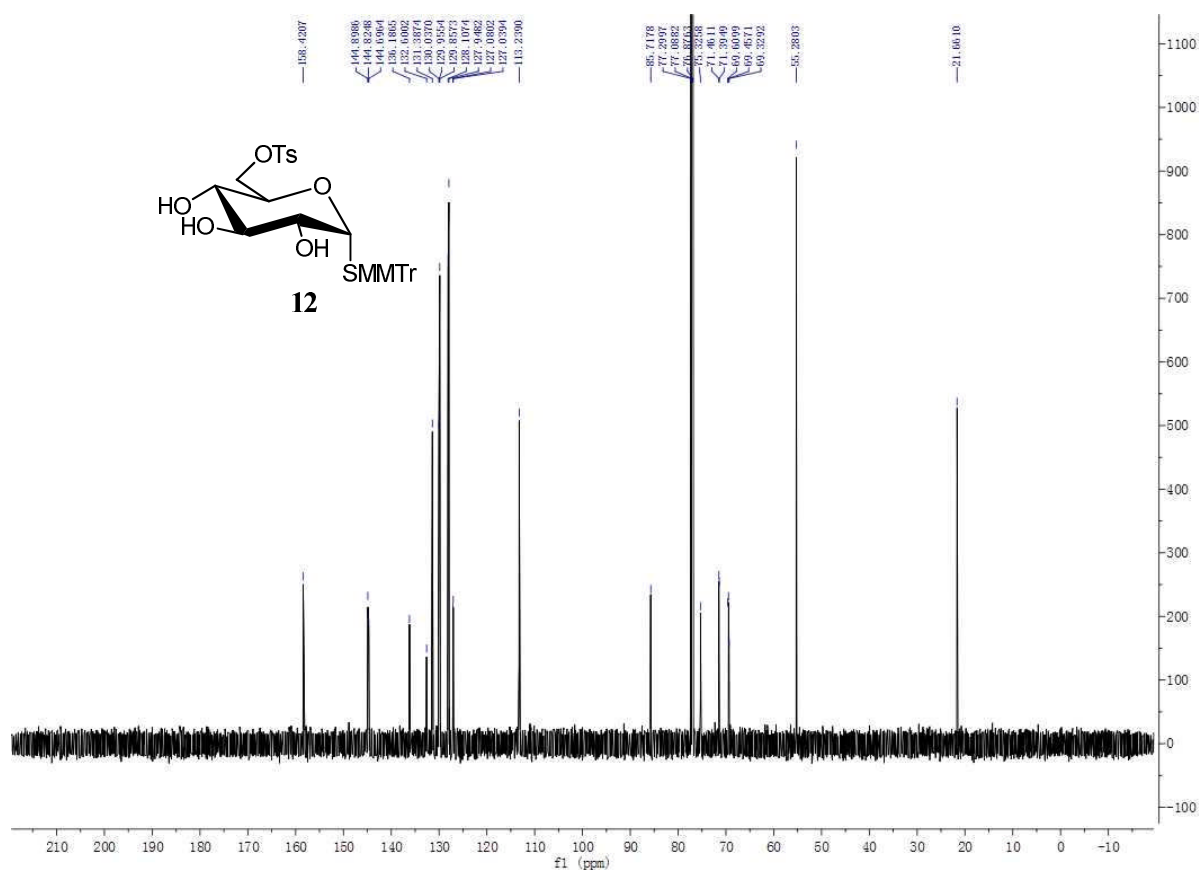
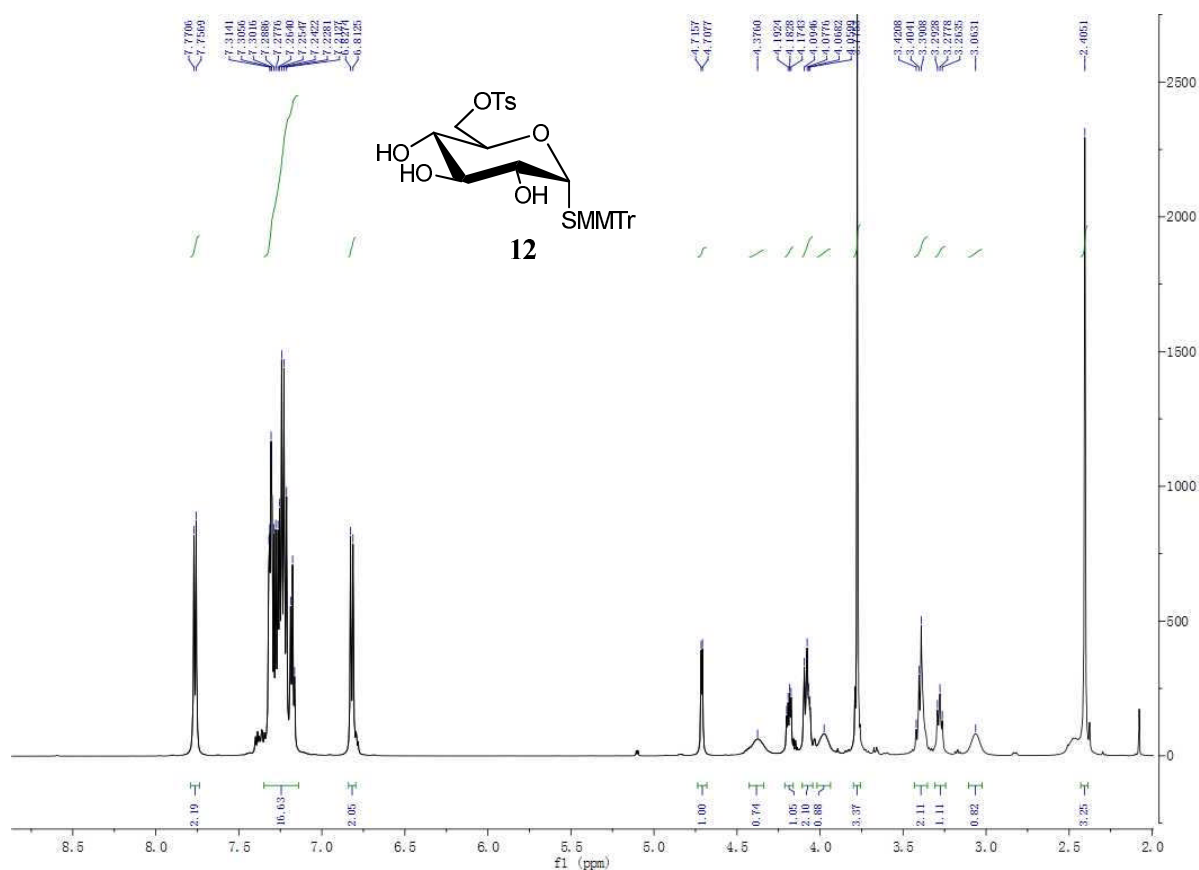
¹H NMR and ¹³C NMR spectra of compound 7



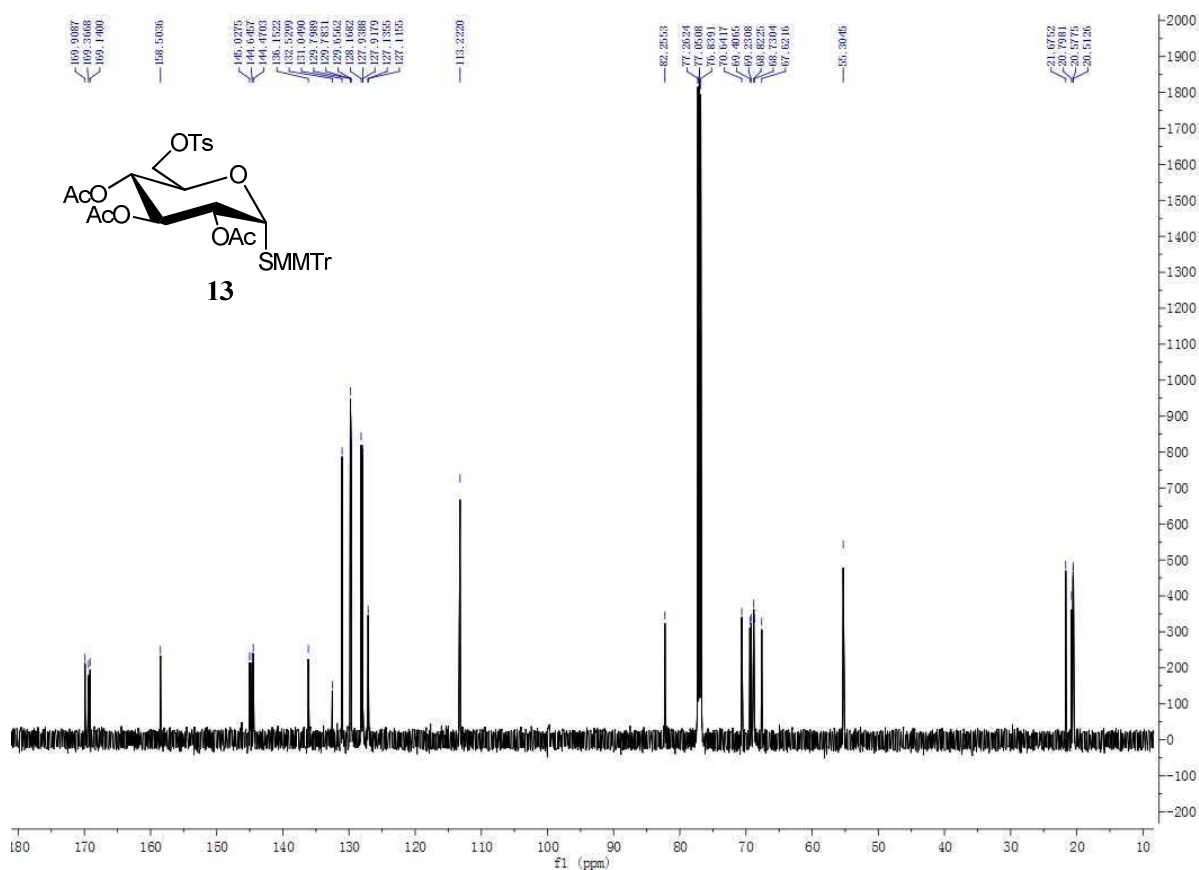
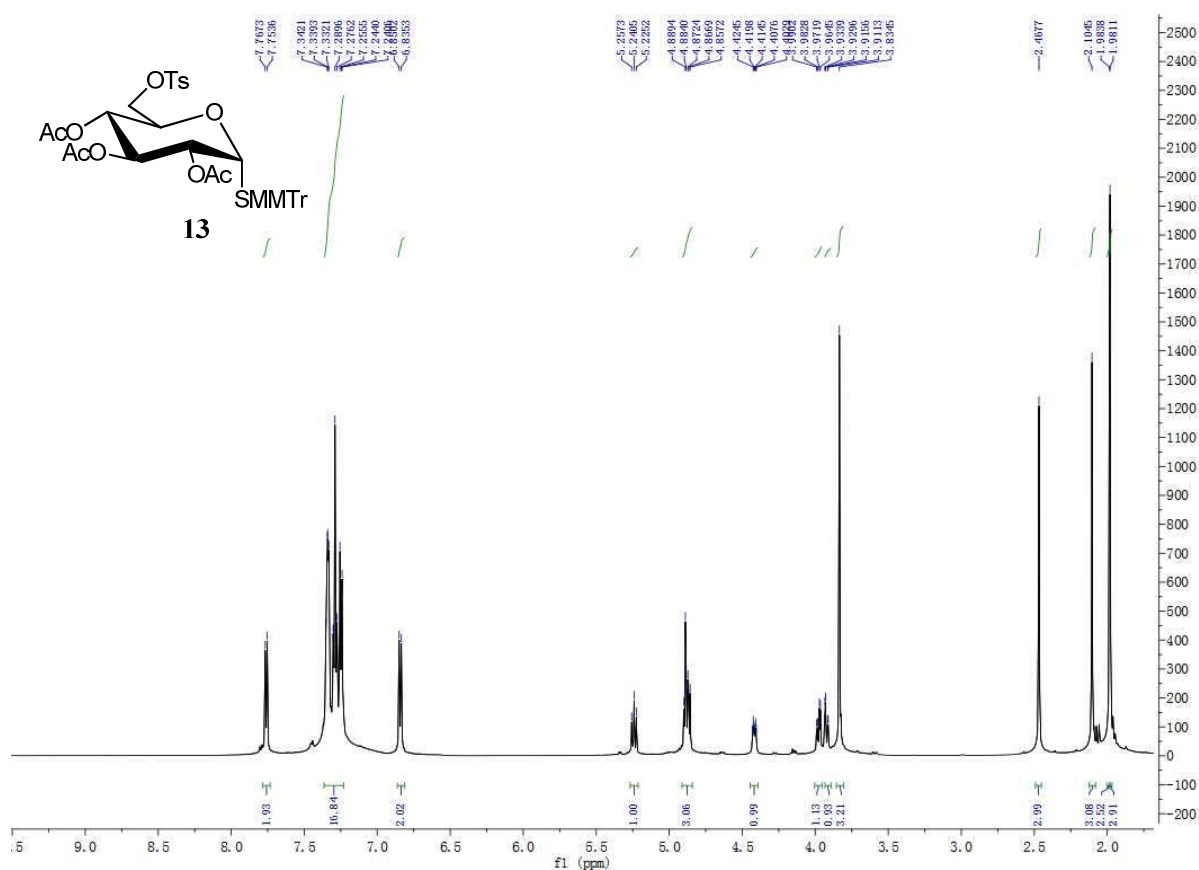
¹H NMR and ¹³C NMR spectra of compound 11



¹H NMR and ¹³C NMR spectra of compound 12



¹H NMR and ¹³C NMR spectra of compound 13



Chemical structure of compound 5:

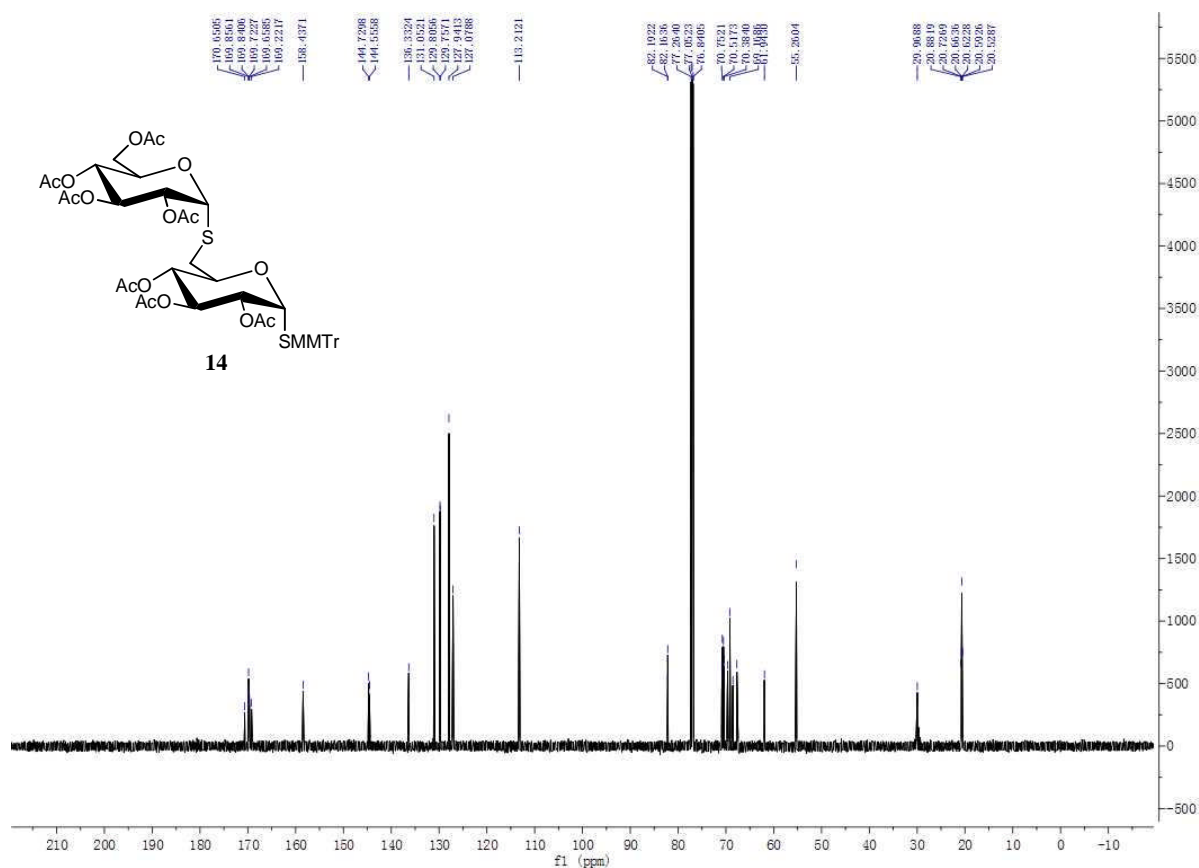
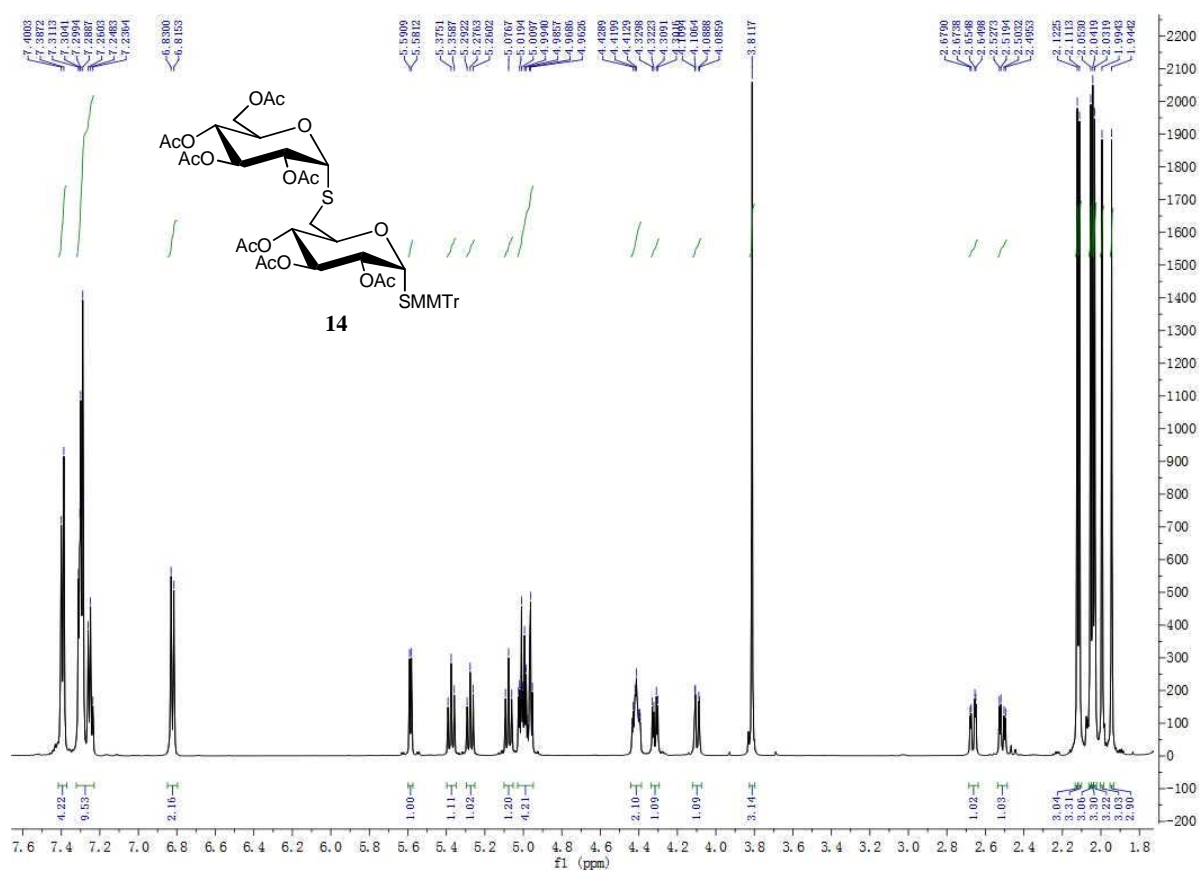
CCOC(=O)[C@H]1[C@@H](OC(=O)C)[C@H](I)[C@@H](OC(=O)C)[C@H]1OC(=O)C

¹H NMR spectrum (CDCl₃):

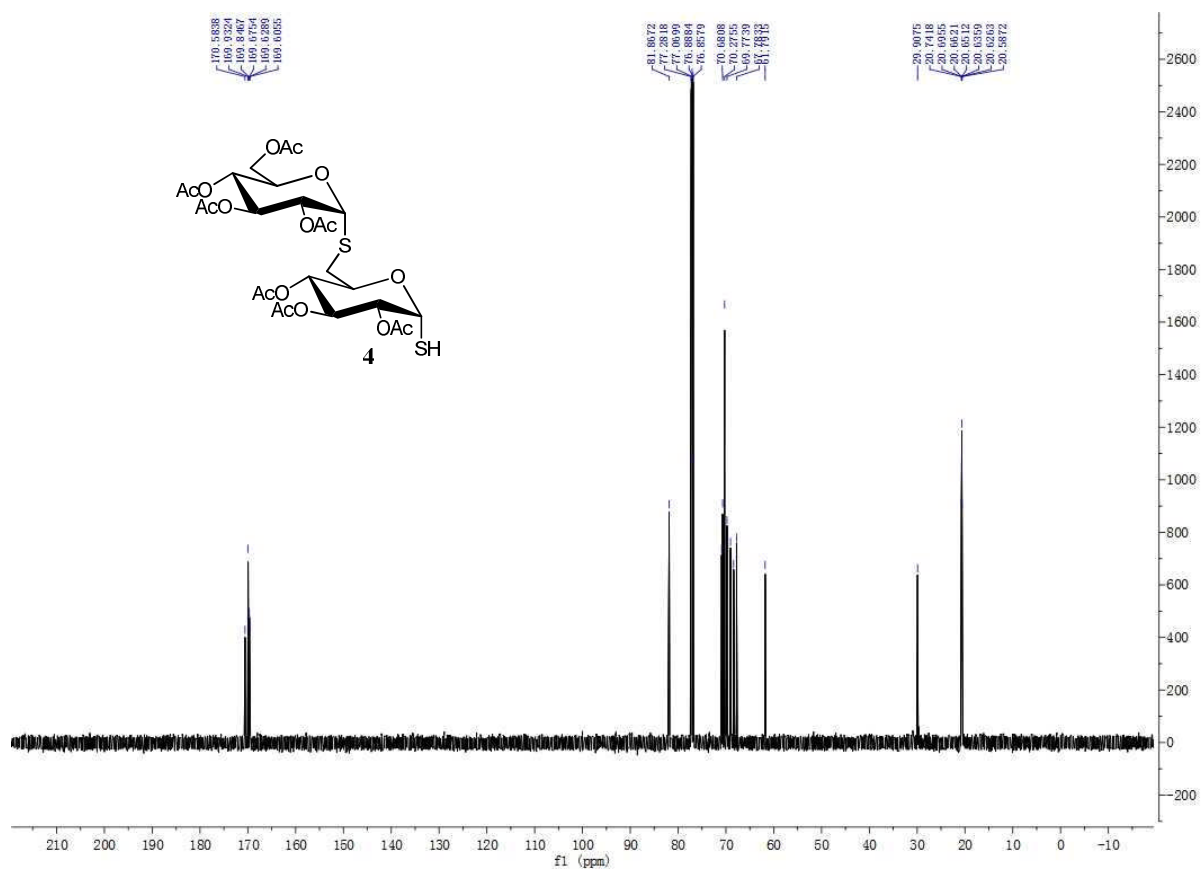
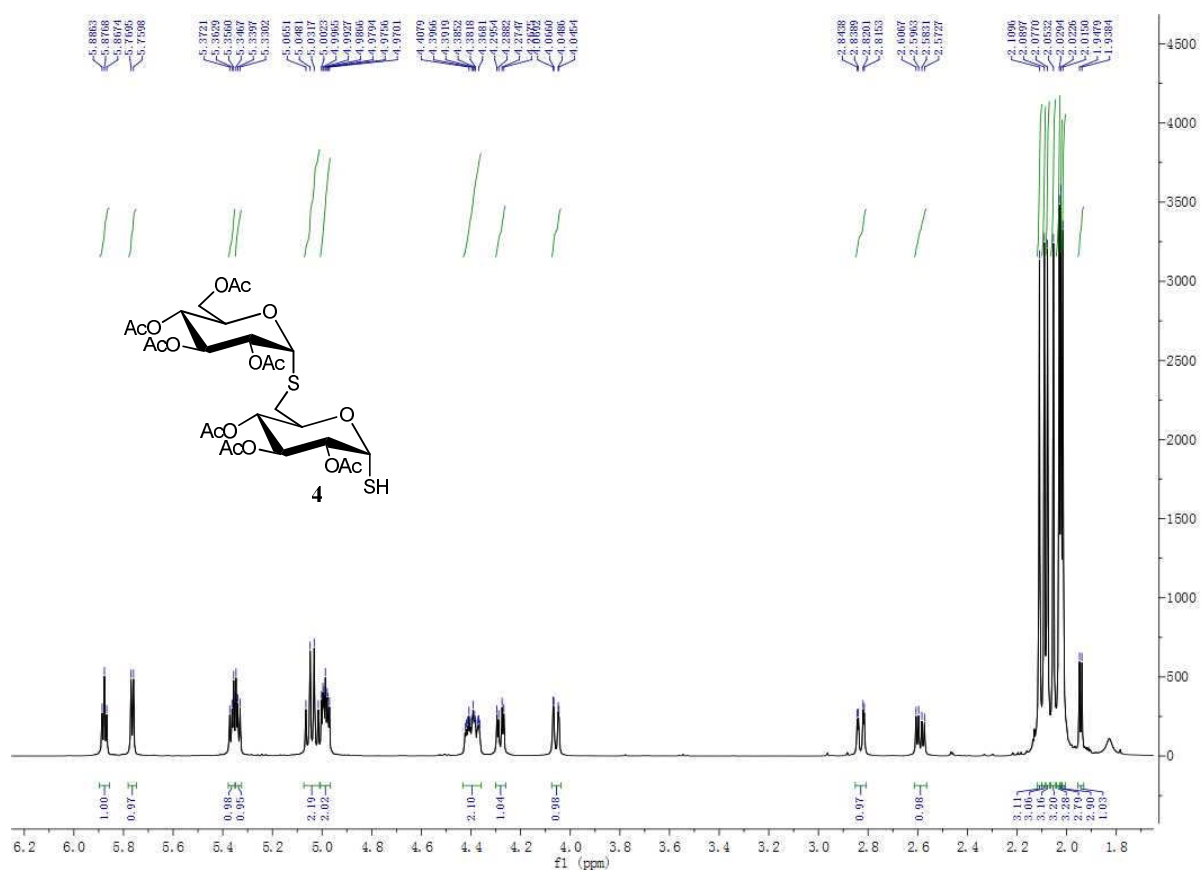
Chemical Shift (ppm)	Integration
7.4380, 7.4128, 7.3160, 7.3027, 7.2858, 7.2684, 7.2561	4.47, 9.18
6.8325, 6.8187	2.06
5.3520, 5.3271, 5.3244, 5.3196, 5.1154, 5.1059, 5.0531, 5.0222, 5.0255, 4.9259, 4.9245, 4.9070	1.00, 0.98, 1.02, 1.01
3.9187, 3.9131, 3.9074, 3.8971, 3.8914, 3.8220	1.11, 3.01
3.1159, 3.1105, 3.0972, 3.0919, 3.0865, 3.0787, 3.0722, 3.0661	1.64, 3.39
2.1540, 2.0537, 2.0411	3.01, 3.07, 3.05



¹H NMR and ¹³C NMR spectra of compound 14



¹H NMR and ¹³C NMR spectra of compound 4



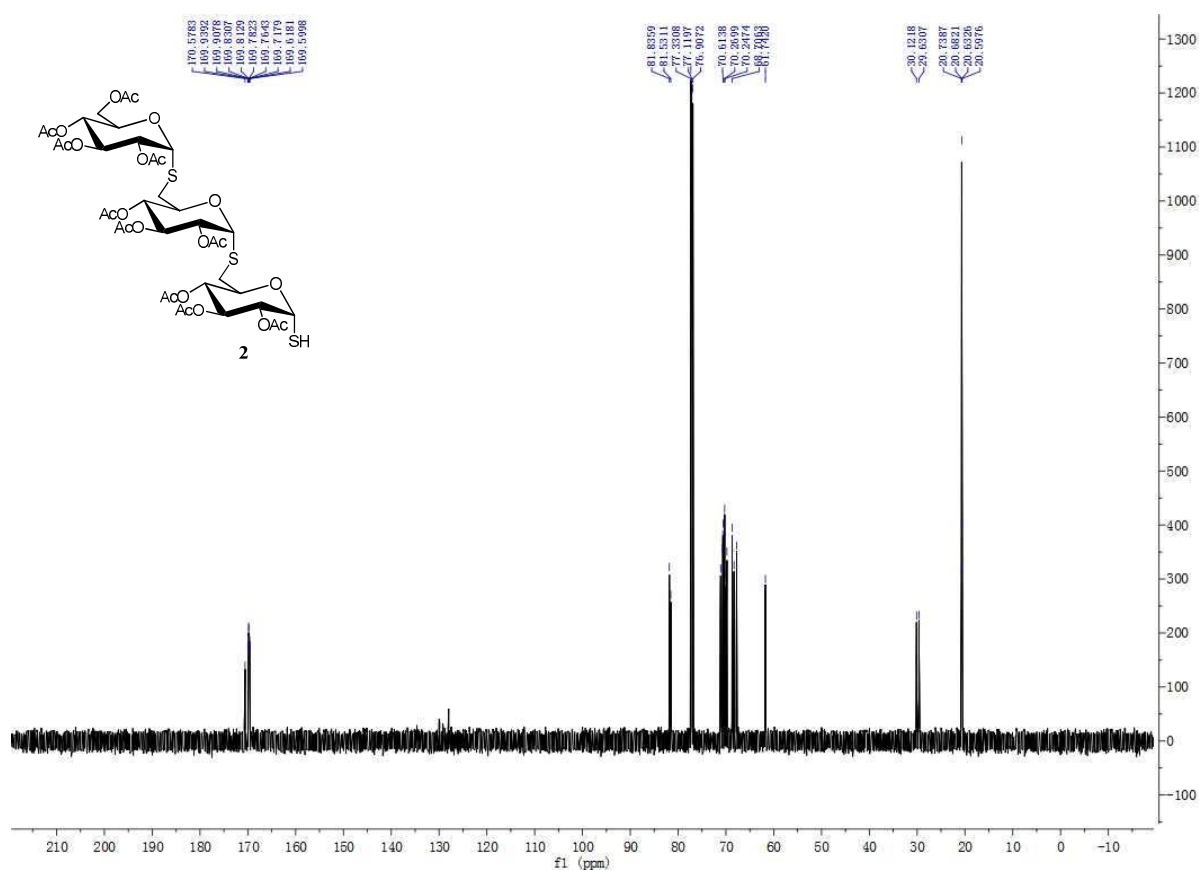
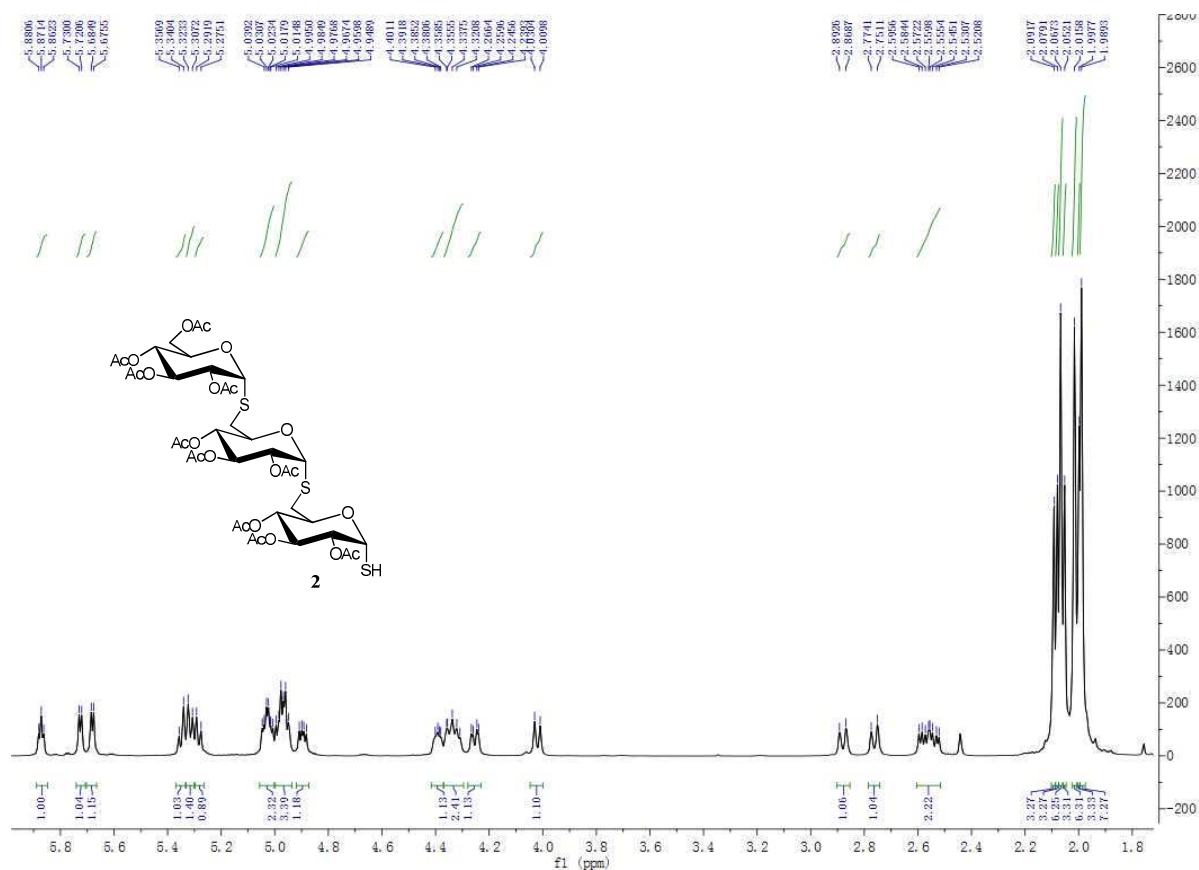
Chemical structure of compound **15** is shown above the spectrum. The structure is a branched trisaccharide consisting of three glucose units linked by (1->3) glycosidic bonds. All hydroxyl groups are protected as acetate (OAc) esters. The anomeric carbons are linked to an SMMTr group.

¹H NMR spectrum (CDCl₃) of compound **15**. The x-axis represents the chemical shift in ppm (f1), ranging from 0 to 8. The y-axis represents intensity. The spectrum shows several characteristic peaks for the structure, including anomeric protons (7.3 ppm), acetoxy methyl protons (2.3 ppm), and various sugar protons (3.0-5.5 ppm). Integration values are provided below the baseline, and a list of chemical shifts is shown at the top.

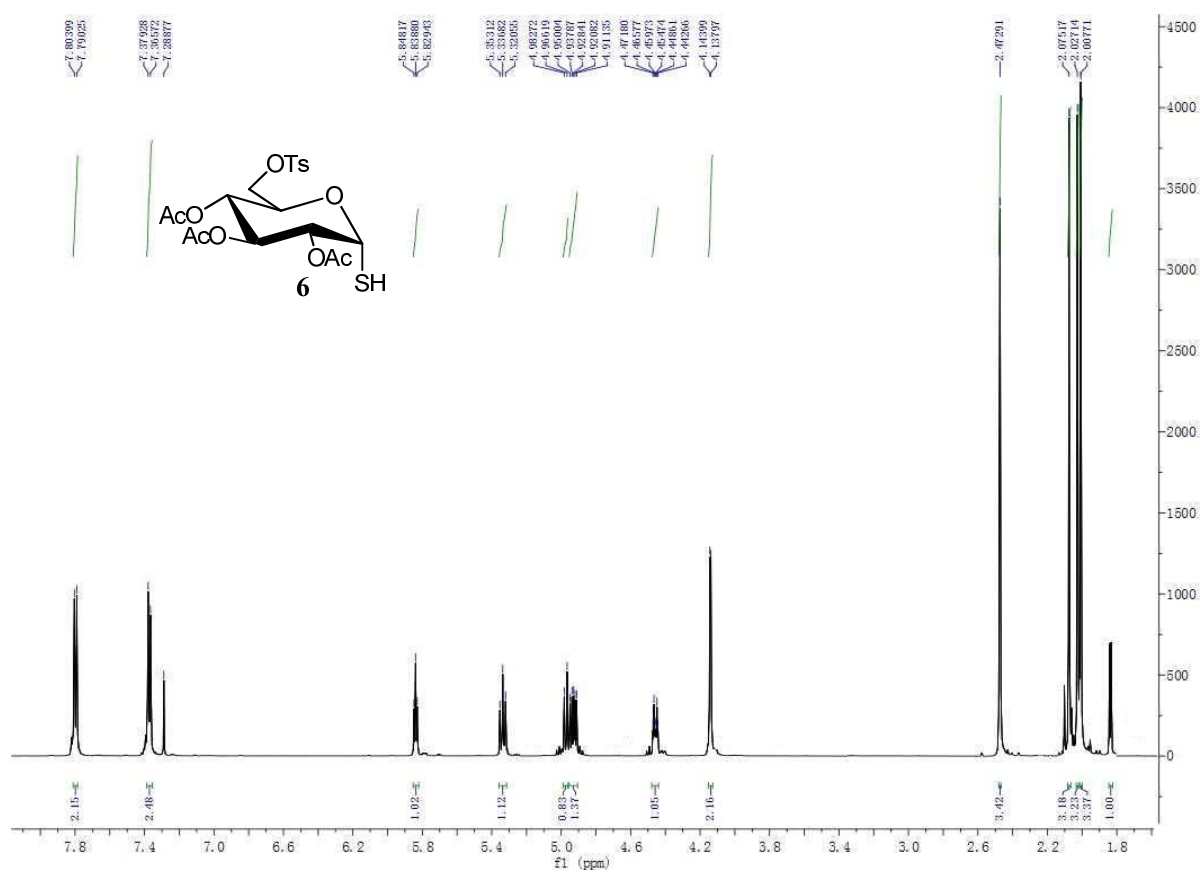
Chemical shifts (ppm): 7.3970, 7.3896, 7.3783, 7.3074, 7.3060, 7.2921, 7.2878, 7.2782, 7.2768, 6.8046, 5.7492, 5.7395, 5.4541, 5.4446, 5.4140, 5.3978, 5.3814, 5.3706, 5.3599, 5.3496, 5.0789, 5.0362, 5.0252, 5.0287, 5.0185, 5.0134, 5.0102, 4.9628, 3.9995, 3.9888, 3.9854, 3.9788, 3.9747, 3.9643, 3.9547, 3.9500, 3.9450, 3.9395, 3.9345, 3.9295, 3.9245, 3.9195, 3.9145, 3.9095, 3.9045, 3.8995, 3.8945, 3.8895, 3.8845, 3.8795, 3.8745, 3.8695, 3.8645, 3.8595, 3.8545, 3.8495, 3.8445, 3.8395, 3.8345, 3.8295, 3.8245, 3.8195, 3.8145, 3.8095, 3.8045, 3.7995, 3.7945, 3.7895, 3.7845, 3.7795, 3.7745, 3.7695, 3.7645, 3.7595, 3.7545, 3.7495, 3.7445, 3.7395, 3.7345, 3.7295, 3.7245, 3.7195, 3.7145, 3.7095, 3.7045, 3.6995, 3.6945, 3.6895, 3.6845, 3.6795, 3.6745, 3.6695, 3.6645, 3.6595, 3.6545, 3.6495, 3.6445, 3.6395, 3.6345, 3.6295, 3.6245, 3.6195, 3.6145, 3.6095, 3.6045, 3.5995, 3.5945, 3.5895, 3.5845, 3.5795, 3.5745, 3.5695, 3.5645, 3.5595, 3.5545, 3.5495, 3.5445, 3.5395, 3.5345, 3.5295, 3.5245, 3.5195, 3.5145, 3.5095, 3.5045, 3.4995, 3.4945, 3.4895, 3.4845, 3.4795, 3.4745, 3.4695, 3.4645, 3.4595, 3.4545, 3.4495, 3.4445, 3.4395, 3.4345, 3.4295, 3.4245, 3.4195, 3.4145, 3.4095, 3.4045, 3.3995, 3.3945, 3.3895, 3.3845, 3.3795, 3.3745, 3.3695, 3.3645, 3.3595, 3.3545, 3.3495, 3.3445, 3.3395, 3.3345, 3.3295, 3.3245, 3.3195, 3.3145, 3.3095, 3.3045, 3.2995, 3.2945, 3.2895, 3.2845, 3.2795, 3.2745, 3.2695, 3.2645, 3.2595, 3.2545, 3.2495, 3.2445, 3.2395, 3.2345, 3.2295, 3.2245, 3.2195, 3.2145, 3.2095, 3.2045, 3.1995, 3.1945, 3.1895, 3.1845, 3.1795, 3.1745, 3.1695, 3.1645, 3.1595, 3.1545, 3.1495, 3.1445, 3.1395, 3.1345, 3.1295, 3.1245, 3.1195, 3.1145, 3.1095, 3.1045, 3.0995, 3.0945, 3.0895, 3.0845, 3.0795, 3.0745, 3.0695, 3.0645, 3.0595, 3.0545, 3.0495, 3.0445, 3.0395, 3.0345, 3.0295, 3.0245, 3.0195, 3.0145, 3.0095, 3.0045, 2.9995, 2.9945, 2.9895, 2.9845, 2.9795, 2.9745, 2.9695, 2.9645, 2.9595, 2.9545, 2.9495, 2.9445, 2.9395, 2.9345, 2.9295, 2.9245, 2.9195, 2.9145, 2.9095, 2.9045, 2.8995, 2.8945, 2.8895, 2.8845, 2.8795, 2.8745, 2.8695, 2.8645, 2.8595, 2.8545, 2.8495, 2.8445, 2.8395, 2.8345, 2.8295, 2.8245, 2.8195, 2.8145, 2.8095, 2.8045, 2.7995, 2.7945, 2.7895, 2.7845, 2.7795, 2.7745, 2.7695, 2.7645, 2.7595, 2.7545, 2.7495, 2.7445, 2.7395, 2.7345, 2.7295, 2.7245, 2.7195, 2.7145, 2.7095, 2.7045, 2.6995, 2.6945, 2.6895, 2.6845, 2.6795, 2.6745, 2.6695, 2.6645, 2.6595, 2.6545, 2.6495, 2.6445, 2.6395, 2.6345, 2.6295, 2.6245, 2.6195, 2.6145, 2.6095, 2.6045, 2.5995, 2.5945, 2.5895, 2.5845, 2.5795, 2.5745, 2.5695, 2.5645, 2.5595, 2.5545, 2.5495, 2.5445, 2.5395, 2.5345, 2.5295, 2.5245, 2.5195, 2.5145, 2.5095, 2.5045, 2.4995, 2.4945, 2.4895, 2.4845, 2.4795, 2.4745, 2.4695, 2.4645, 2.4595, 2.4545, 2.4495, 2.4445, 2.4395, 2.4345, 2.4295, 2.4245, 2.4195, 2.4145, 2.4095, 2.4045, 2.3995, 2.3945, 2.3895, 2.3845, 2.3795, 2.3745, 2.3695, 2.3645, 2.3595, 2.3545, 2.3495, 2.3445, 2.3395, 2.3345, 2.3295, 2.3245, 2.3195, 2.3145, 2.3095, 2.3045, 2.2995, 2.2945, 2.2895, 2.2845, 2.2795, 2.2745, 2.2695, 2.2645, 2.2595, 2.2545, 2.2495, 2.2445, 2.2395, 2.2345, 2.2295, 2.2245, 2.2195, 2.2145, 2.2095, 2.2045, 2.1995, 2.1945, 2.1895, 2.1845, 2.1795, 2.1745, 2.1695, 2.1645, 2.1595, 2.1545, 2.1495, 2.1445, 2.1395, 2.1345, 2.1295, 2.1245, 2.1195, 2.1145, 2.1095, 2.1045, 2.0995, 2.0945, 2.0895, 2.0845, 2.0795, 2.0745, 2.0695, 2.0645, 2.0595, 2.0545, 2.0495, 2.0445, 2.0395, 2.0345, 2.0295, 2.0245, 2.0195, 2.0145, 2.0095, 2.0045, 1.9995, 1.9945, 1.9895, 1.9845, 1.9795, 1.9745, 1.9695, 1.9645, 1.9595, 1.9545, 1.9495, 1.9445, 1.9395, 1.9345, 1.9295, 1.9245, 1.9195, 1.9145, 1.9095, 1.9045, 1.8995, 1.8945, 1.8895, 1.8845, 1.8795, 1.8745, 1.8695, 1.8645, 1.8595, 1.8545, 1.8495, 1.8445, 1.8395, 1.8345, 1.8295, 1.8245, 1.8195, 1.8145, 1.8095,



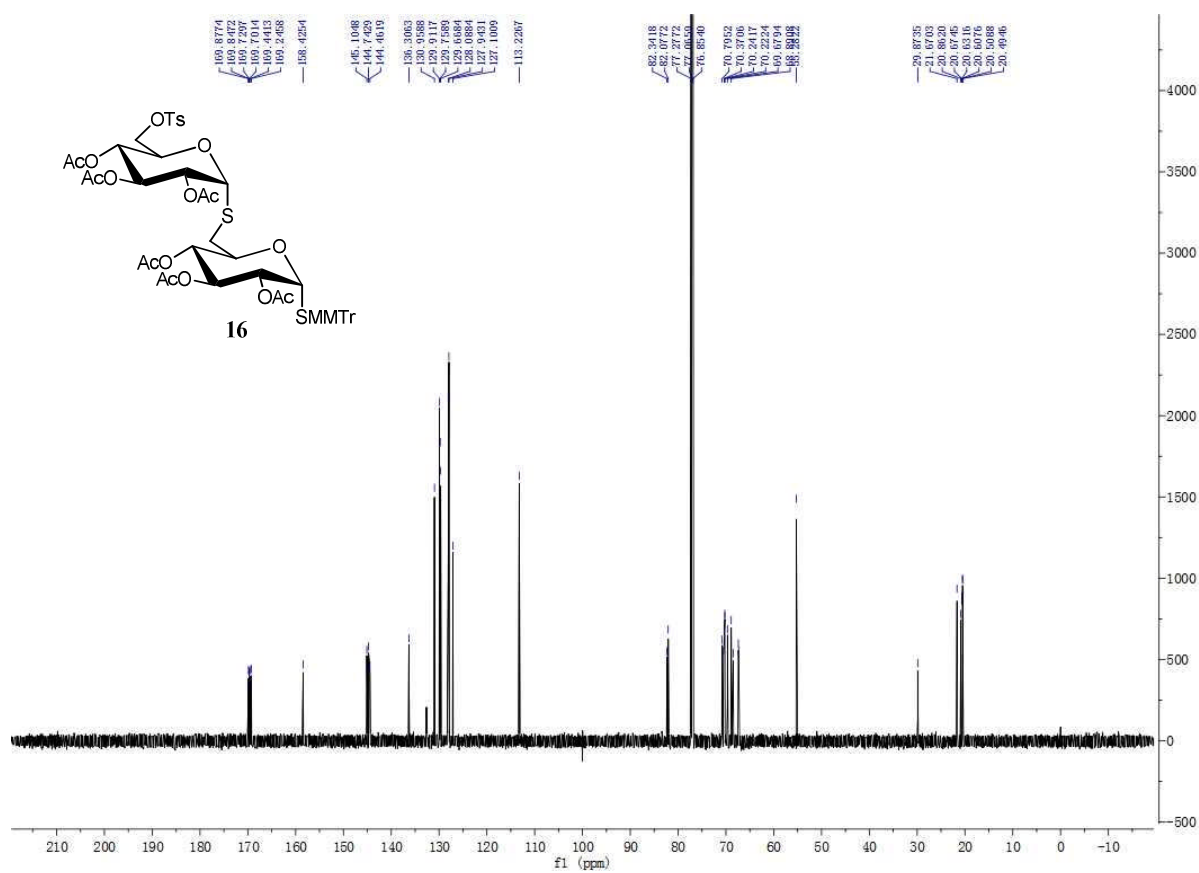
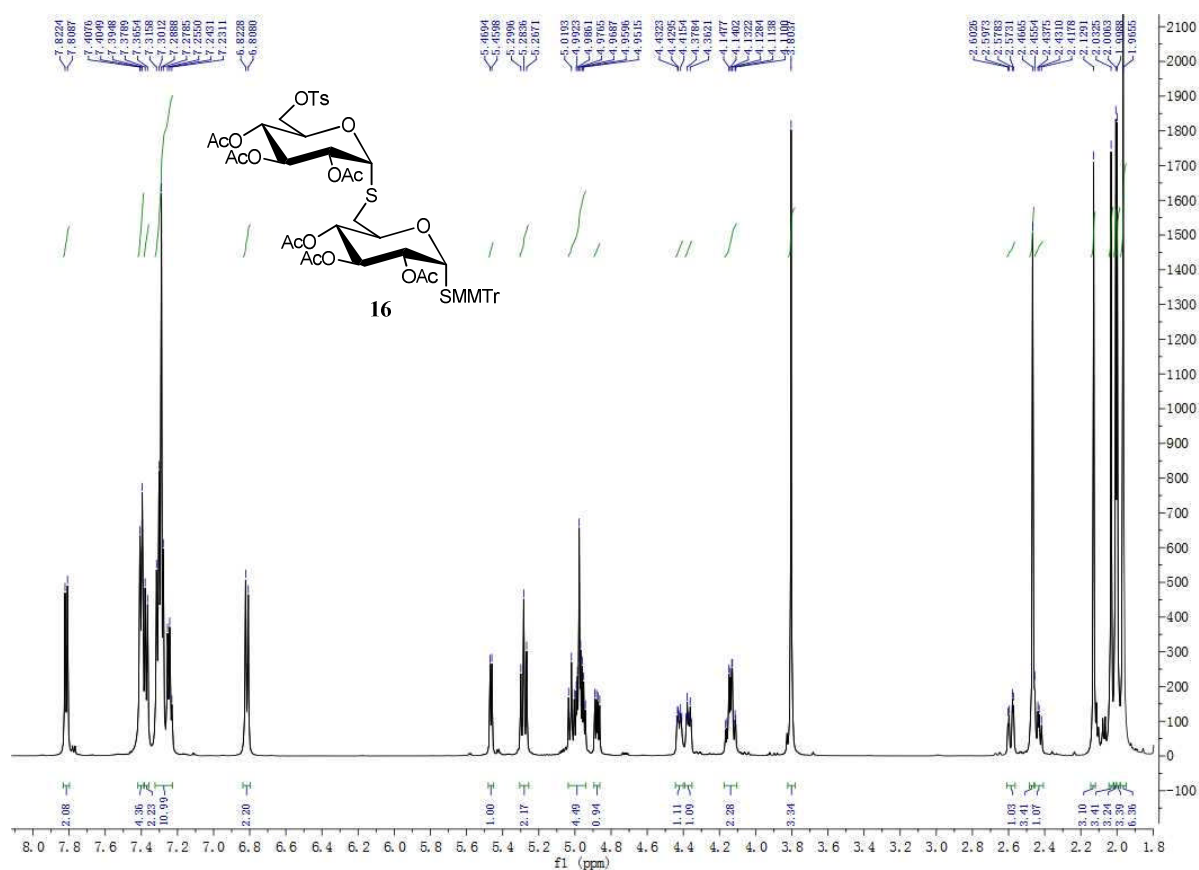
¹H NMR and ¹³C NMR spectra of compound 2



¹H NMR and ¹³C NMR spectra of compound 6



¹H NMR and ¹³C NMR spectra of compound 16



Chemical structure of compound 3:

CC(=O)OC1C(OC(=O)C)OC(OC(=O)C)C1S[C@@H]2C(OC(=O)C)OC(OC(=O)C)C2

¹H NMR spectrum (CDCl₃):

Peak list (ppm): 7.4238, 7.4134, 7.4012, 7.3770, 7.3575, 7.3221, 7.3157, 7.3035, 7.2890, 7.2804, 6.8269, 5.5260, 5.5255, 5.3037, 5.3475, 5.3310, 5.2652, 4.9152, 4.9062, 4.8553, 4.9067, 4.8987, 4.8952, 4.4241, 4.4178, 4.4135, 4.4079, 4.4018, 4.2275, 4.2184, 4.2148, 4.2148, 4.2148, 4.2023, 4.1981, 3.8186, 3.3404, 3.3362, 3.3220, 3.3179, 3.3137, 3.2995, 3.2919, 3.1966, 3.1836, 2.8160, 2.8107, 2.7911, 2.7859, 2.5663, 2.5611, 2.5414, 2.5342, 2.1219, 2.0781, 2.0597, 2.0211, 2.0211, 1.9316.

Integration values: 4.36, 11.22, 2.19, 1.00, 1.10, 1.10, 1.13, 1.02, 1.02, 3.07, 1.02, 1.04, 1.00, 1.02, 3.01, 3.42, 3.41, 3.04, 2.99.



Chemical structure of compound 17 is shown above the spectrum. The structure is a branched oligosaccharide with four pyranose rings and one furanose ring, all with acetoxy (OAc) protecting groups. The label "17" and "SMMTr" are present below the structure.

¹H NMR spectrum (CDCl₃) of compound 17. The x-axis represents the chemical shift in ppm (f1), ranging from 2.0 to 7.5. The y-axis represents the intensity. The spectrum shows several peaks, with the most prominent ones in the anomeric region (4.5-5.5 ppm) and the acetoxy methyl region (2.0-2.5 ppm). Integration values are provided below the baseline.

Integration values (from left to right): 4.40, 10.37, 2.11, 2.00, 1.00, 0.94, 1.10, 1.10, 1.14, 1.46, 2.13, 2.09, 1.07, 1.47, 4.07, 1.13, 1.08, 3.05, 0.65, 0.90, 1.15, 1.06, 3.25, 1.11, 5.78, 2.38, 3.16, 2.90, 5.90, 3.31, 3.08, 3.15, 3.05, 2.78.



[illegible]