

Supporting Information

Synthesis of Thioglycoside Analogues of Maradolipid

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Crystal structure analysis of 7

The compound **7** was crystallized from methanol at -15 °C. A clear prism of $C_{36}H_{86}O_{10}SSi_8$ having approximate dimensions of 0.781 mm×0.320mm×0.272mm was chosen. Data were collected at ambient temperature. A semi-empirical absorption correction based on redundant reflections was performed by the program SADABS [X-1]. The structure was solved by direct methods using SHELXS-97 [X-2] and refined by full matrix least-squares on F² for all data using SHELXL-97 [X-2]. Hydrogen atoms were added at calculated positions and refined using a riding model. Their isotropic thermal displacement parameters were fixed to 1.2 times (1.5 times for methyl groups) the equivalent one of the parent atom. Anisotropic thermal displacement parameters were used for all non-hydrogen atoms. Further refinement details are compiled in the Table below.

[X-1] Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.

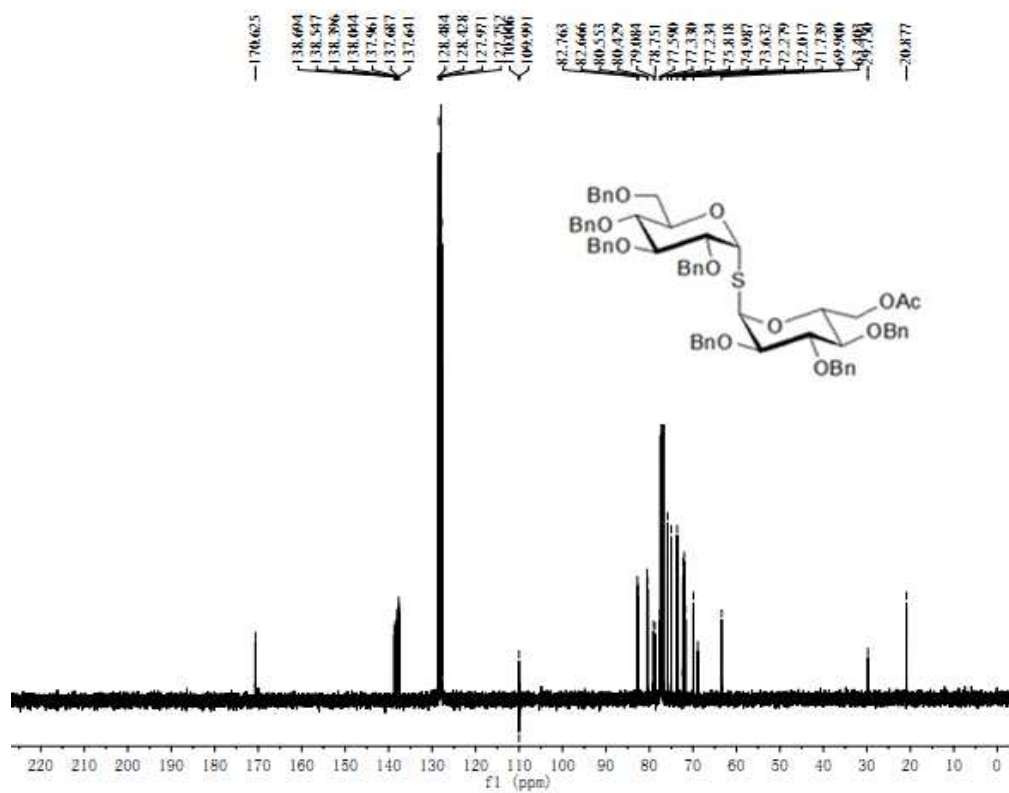
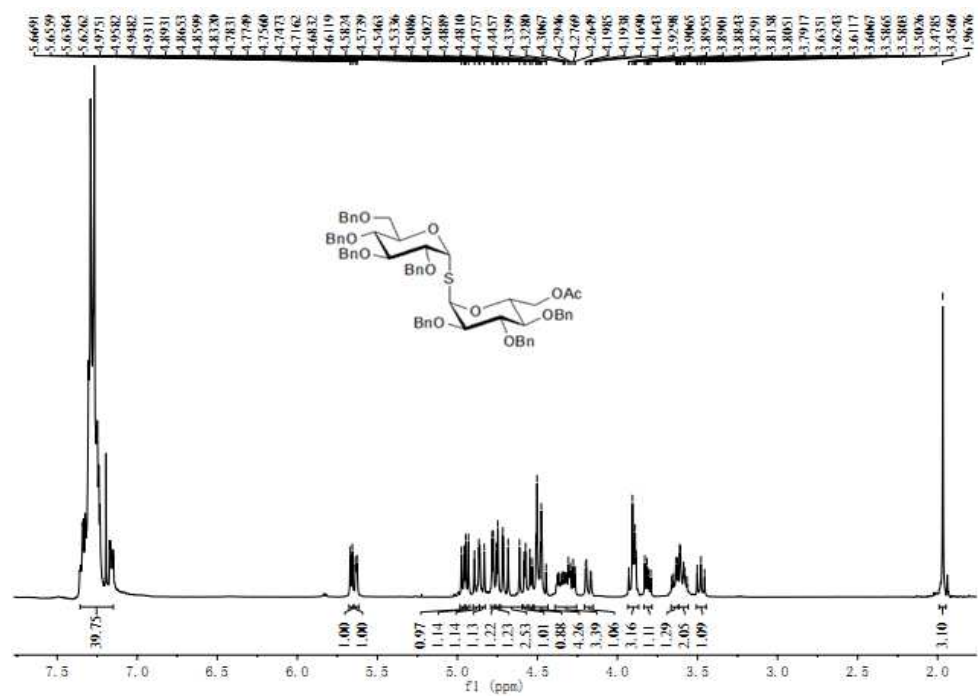
[X-2] Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112-122.

Crystal data and structure refinement for 1-thiotrehalose **7**:

Identification code	a	
Empirical formula	$C_{36} H_{86} O_{10} S Si_8$	
Formula weight	933.81	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 13.0314(3) Å	$\alpha = 90^\circ$.
	b = 19.7442(6) Å	$\beta = 116.922(1)^\circ$.
	c = 13.2272(3) Å	$\gamma = 90^\circ$.

Volume	3034.45(13) Å ³
Z	2
Density (calculated)	1.022 Mg/m ³
Absorption coefficient	0.251 mm ⁻¹
F(000)	1016
Crystal size	.781 x .320 x .272 mm ³
Theta range for data collection	2.01 to 25.00°.
Index ranges	-15<=h<=15, -23<=k<=23, -15<=l<=15
Reflections collected	22245
Independent reflections	10394 [R(int) = 0.0630]
Completeness to theta = 25.00°	99.7 %
Absorption correction	Empirical
Max. and min. transmission	.934 and .908
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	10394 / 1 / 479
Goodness-of-fit on F ²	1.682
Final R indices [I>2sigma(I)]	R1 = 0.0990, wR2 = 0.2428
R indices (all data)	R1 = 0.1575, wR2 = 0.2589
Absolute structure parameter	0.00(18)
Largest diff. peak and hole	0.565 and -1.535 e.Å ⁻³

^1H NMR and ^{13}C NMR spectra of compound 5



^1H NMR and ^{13}C NMR spectra of compound 6

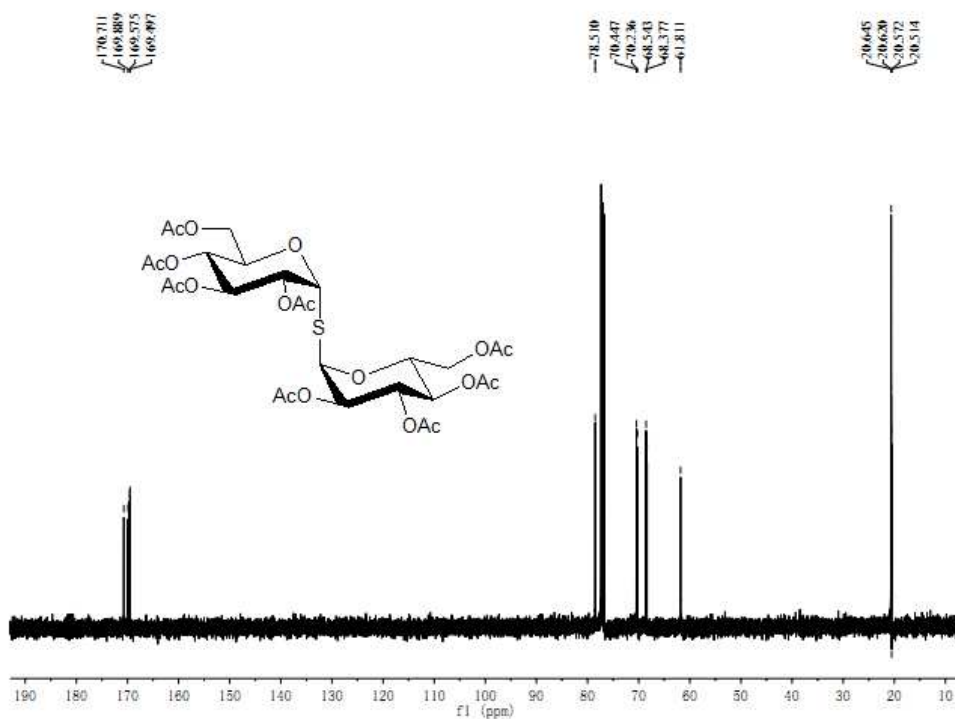
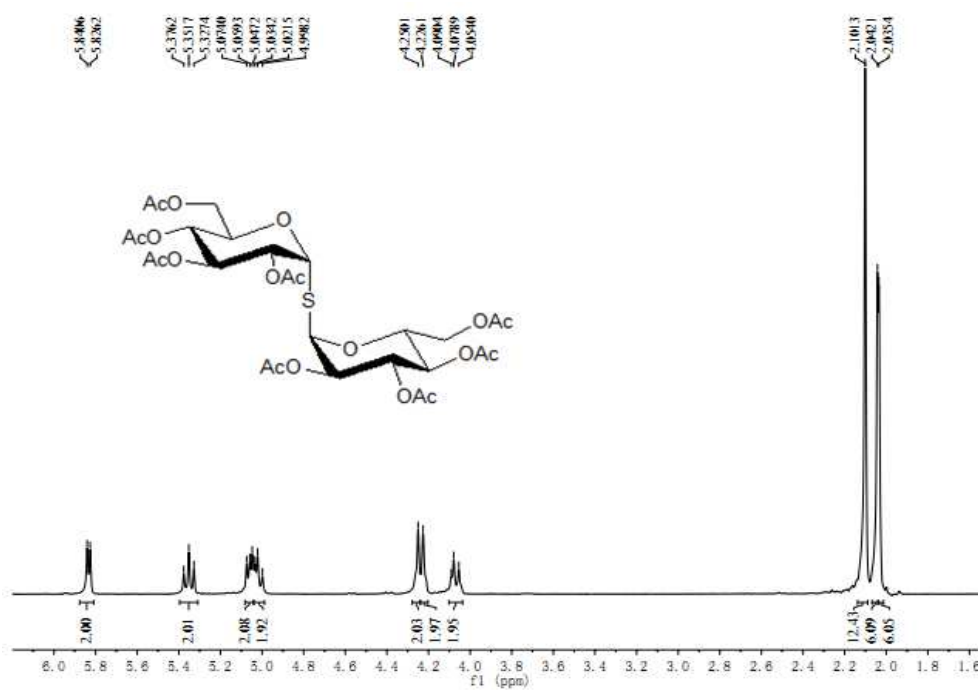
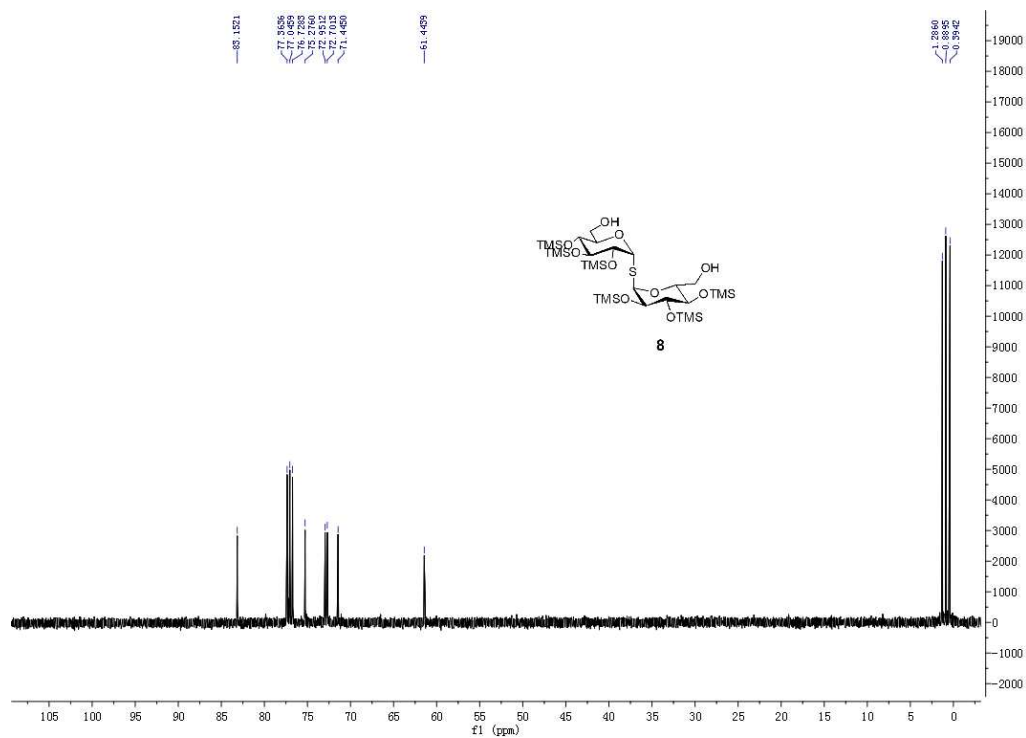


Figure 1 displays the ^1H and ^{13}C NMR spectra of compound **7**, along with its chemical structure.

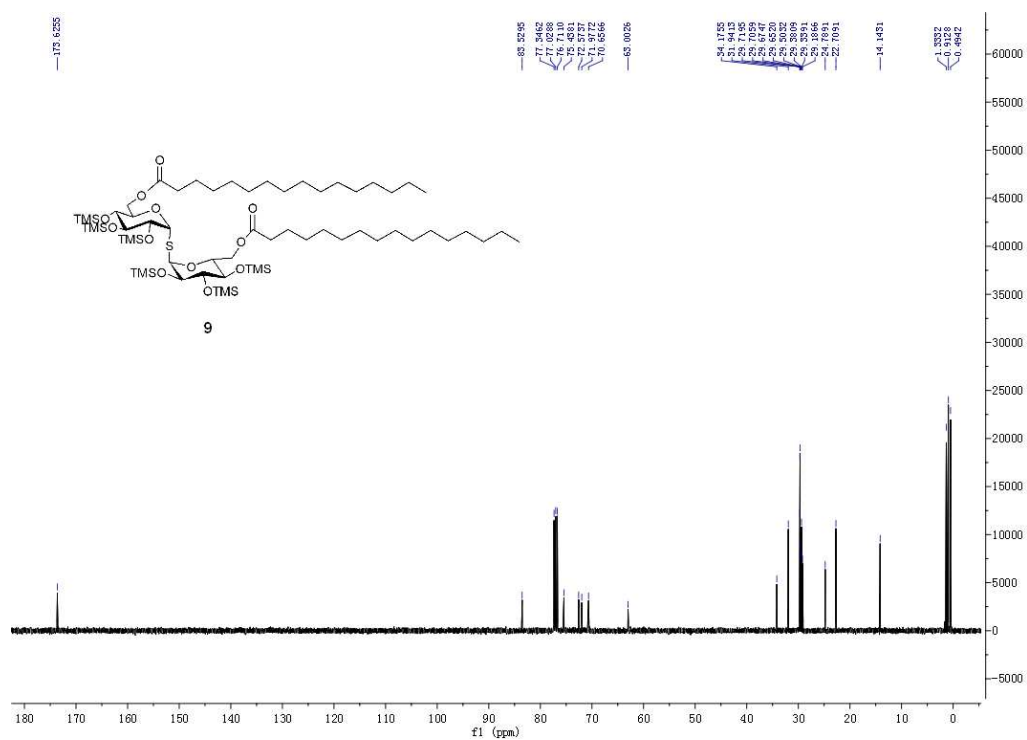
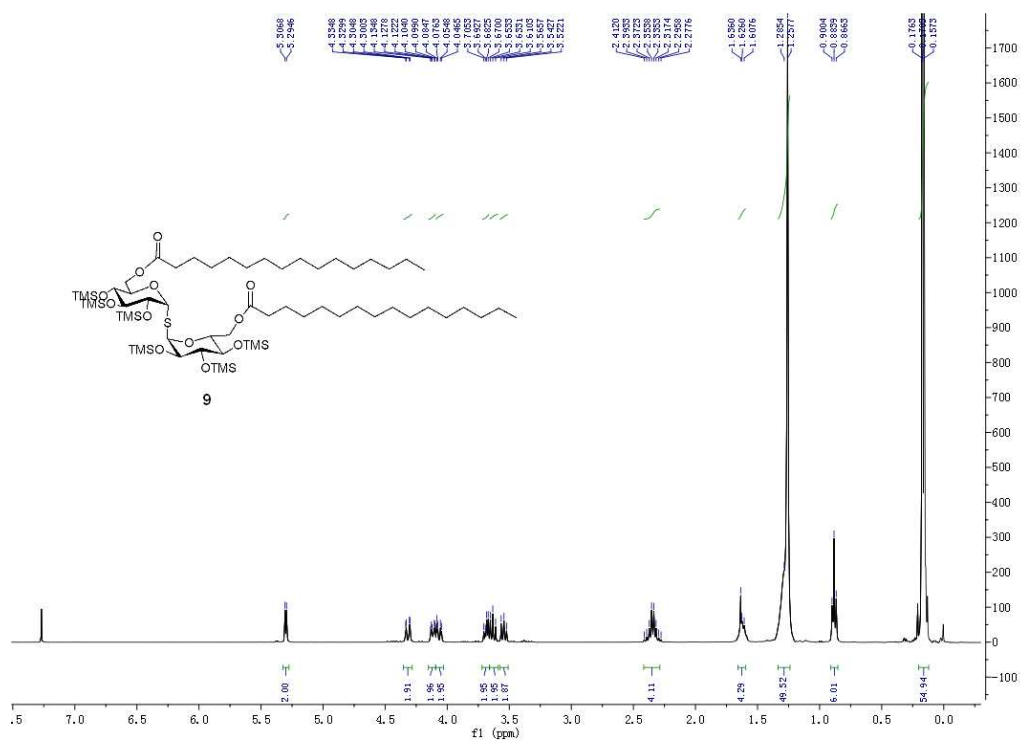
Chemical Structure of 7: The structure shows a dimeric molecule consisting of two pyranose rings linked by a sulfur atom. Each ring is substituted with two trimethylsilyl (TMS) groups and one hydroxyl (OH) group.

^1H NMR Spectrum (400 MHz, CDCl_3): The spectrum shows peaks in the aromatic region (7.0–7.5 ppm), a broad peak around 5.2 ppm, a multiplet between 3.5–4.0 ppm, and a sharp peak near 0.1 ppm. Integration values are provided below the baseline.

^{13}C NMR Spectrum (100 MHz, CDCl_3): The spectrum shows peaks in the 61.6–85.9 ppm range, corresponding to the carbon atoms in the molecule. Integration values are provided below the baseline.

[illegible]

¹H NMR and ¹³C NMR spectra of compound 9



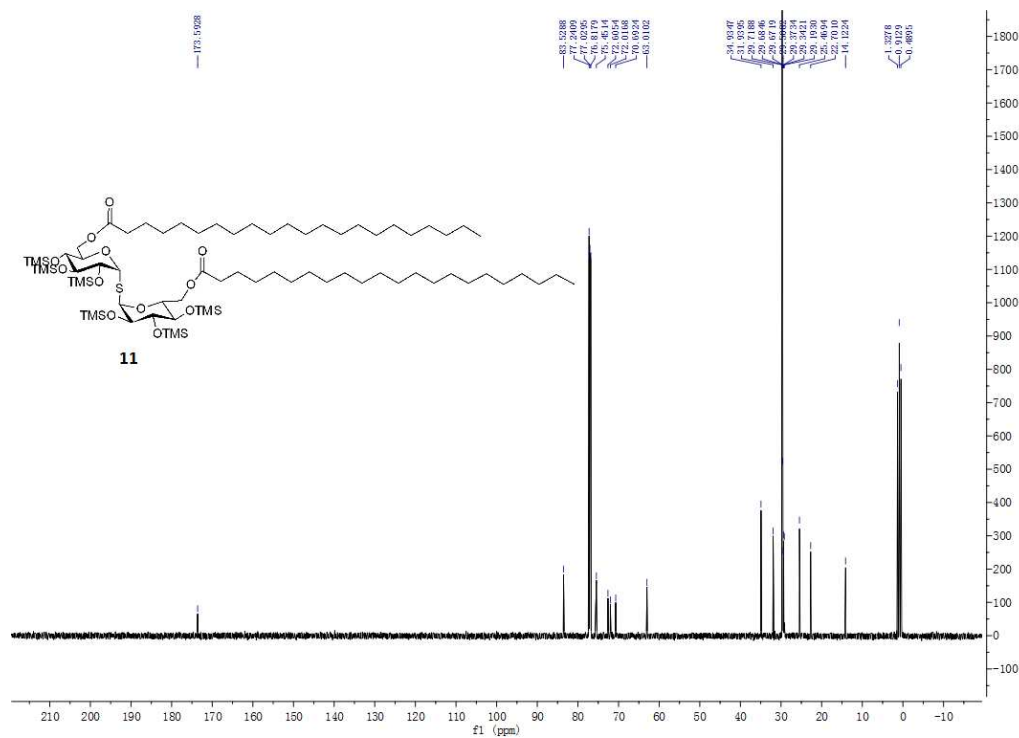
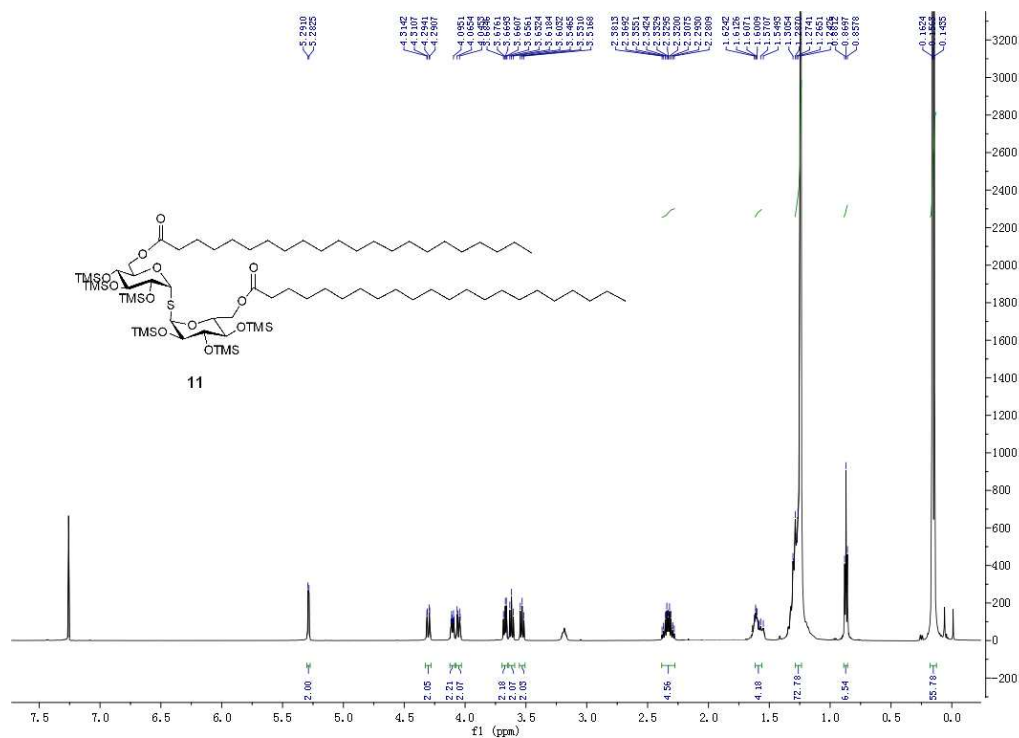
Chemical structure of compound **10** is shown above the spectrum. The structure is a complex molecule featuring a central carbon atom bonded to a TMS group, a TMSO group, a TMSO group, and a TMSO group. The molecule also contains a long alkyl chain and a TMSO group.

1H NMR spectrum (CDCl₃) data:

Chemical Shift (ppm)	Integration
0.0	1.00
0.1	1.00
0.9	1.00
1.3	1.00
2.3	1.00
3.5	1.00
4.0	1.00
4.3	1.00



¹H NMR and ¹³C NMR spectra of compound 11



Chemical structure of compound **12** is shown above the spectrum. The structure is a complex molecule featuring a central sulfur atom bonded to two 2,3,4,6-tetra-O-TMS-β-D-glucopyranosyl groups and two long-chain fatty acid chains (C₁₇H₃₃O₂).

The ¹H NMR spectrum (CDCl₃) shows the following peaks (ppm) and integrations:

Chemical Shift (ppm)	Integration
~7.5	0.05
5.5 - 6.5	1.00
3.5 - 4.5	1.00
~2.8	0.05
2.0 - 2.5	1.00
~1.2	1.00
~0.1	1.00



Chemical structure of compound **13** is shown above the spectrum. The structure is a bis-silyl ether derivative of a disulfide-linked tetrahydropyran system, featuring long alkyl chains and TMSO/OTMS protecting groups.

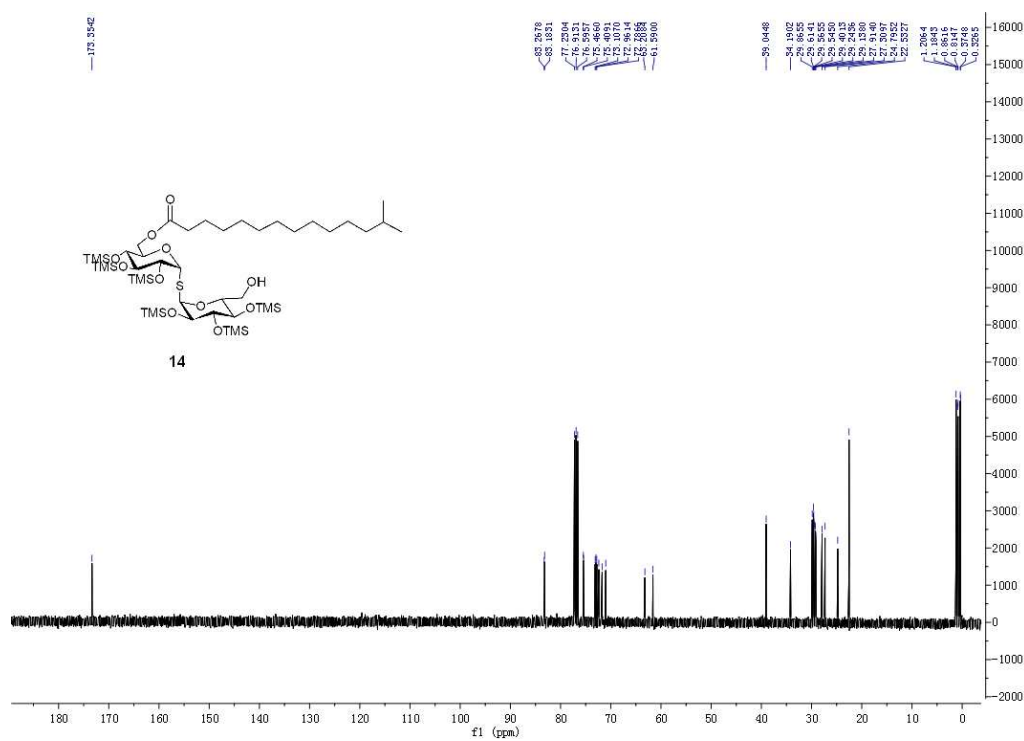
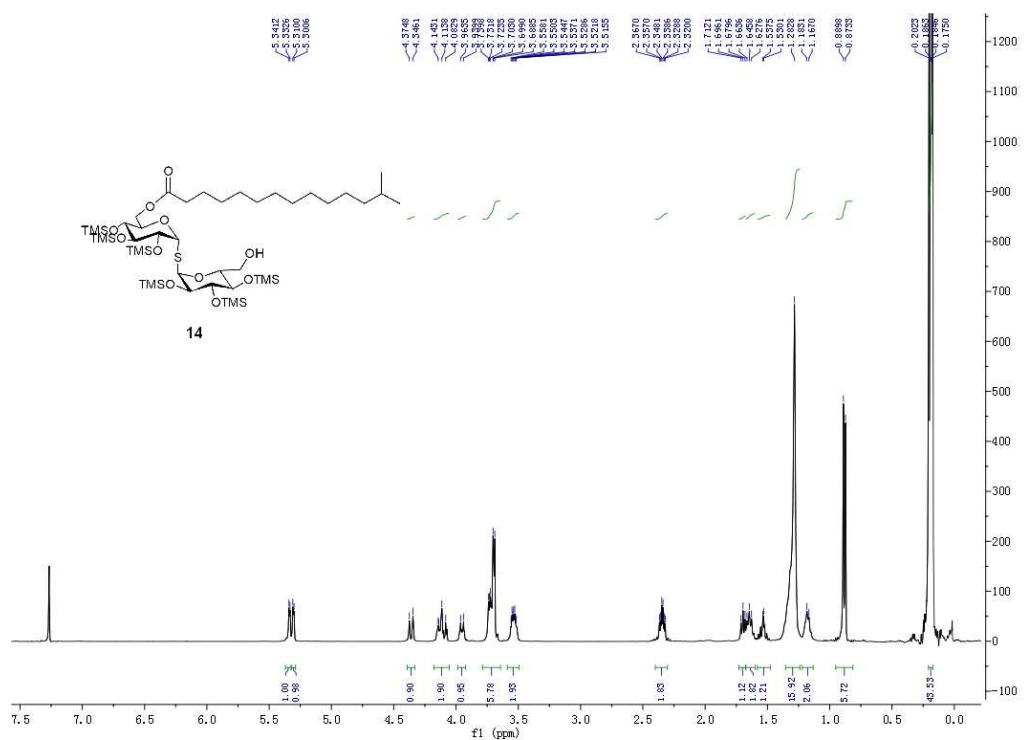
¹H NMR spectrum (CDCl₃) of compound **13**. The x-axis represents the chemical shift in ppm (f1), ranging from 0.0 to 7.5. The y-axis represents the intensity, ranging from 0 to 4000. The spectrum shows several distinct signals, including a sharp peak at ~7.2 ppm (TMSO), a multiplet at ~4.0-4.5 ppm (sugar protons), a multiplet at ~1.5-2.0 ppm (alkyl chain protons), and a large peak at ~0.1 ppm (TMS). Integration values are shown below the baseline, and chemical shifts are listed at the top.

Chemical shifts (ppm) listed at the top of the spectrum:

- 7.329, 7.325, 7.321, 7.316, 7.312, 7.308, 7.304, 7.300, 7.296, 7.292, 7.288, 7.284, 7.280, 7.276, 7.272, 7.268, 7.264, 7.260, 7.256, 7.252, 7.248, 7.244, 7.240, 7.236, 7.232, 7.228, 7.224, 7.220, 7.216, 7.212, 7.208, 7.204, 7.200, 7.196, 7.192, 7.188, 7.184, 7.180, 7.176, 7.172, 7.168, 7.164, 7.160, 7.156, 7.152, 7.148, 7.144, 7.140, 7.136, 7.132, 7.128, 7.124, 7.120, 7.116, 7.112, 7.108, 7.104, 7.100, 7.096, 7.092, 7.088, 7.084, 7.080, 7.076, 7.072, 7.068, 7.064, 7.060, 7.056, 7.052, 7.048, 7.044, 7.040, 7.036, 7.032, 7.028, 7.024, 7.020, 7.016, 7.012, 7.008, 7.004, 7.000, 6.996, 6.992, 6.988, 6.984, 6.980, 6.976, 6.972, 6.968, 6.964, 6.960, 6.956, 6.952, 6.948, 6.944, 6.940, 6.936, 6.932, 6.928, 6.924, 6.920, 6.916, 6.912, 6.908, 6.904, 6.900, 6.896, 6.892, 6.888, 6.884, 6.880, 6.876, 6.872, 6.868, 6.864, 6.860, 6.856, 6.852, 6.848, 6.844, 6.840, 6.836, 6.832, 6.828, 6.824, 6.820, 6.816, 6.812, 6.808, 6.804, 6.800, 6.796, 6.792, 6.788, 6.784, 6.780, 6.776, 6.772, 6.768, 6.764, 6.760, 6.756, 6.752, 6.748, 6.744, 6.740, 6.736, 6.732, 6.728, 6.724, 6.720, 6.716, 6.712, 6.708, 6.704, 6.700, 6.696, 6.692, 6.688, 6.684, 6.680, 6.676, 6.672, 6.668, 6.664, 6.660, 6.656, 6.652, 6.648, 6.644, 6.640, 6.636, 6.632, 6.628, 6.624, 6.620, 6.616, 6.612, 6.608, 6.604, 6.600, 6.596, 6.592, 6.588, 6.584, 6.580, 6.576, 6.572, 6.568, 6.564, 6.560, 6.556, 6.552, 6.548, 6.544, 6.540, 6.536, 6.532, 6.528, 6.524, 6.520, 6.516, 6.512, 6.508, 6.504, 6.500, 6.496, 6.492, 6.488, 6.484, 6.480, 6.476, 6.472, 6.468, 6.464, 6.460, 6.456, 6.452, 6.448, 6.444, 6.440, 6.436, 6.432, 6.428, 6.424, 6.420, 6.416, 6.412, 6.408, 6.404, 6.400, 6.396, 6.392, 6.388, 6.384, 6.380, 6.376, 6.372, 6.368, 6.364, 6.360, 6.356, 6.352, 6.348, 6.344, 6.340, 6.336, 6.332, 6.328, 6.324, 6.320, 6.316, 6.312, 6.308, 6.304, 6.300, 6.296, 6.292, 6.288, 6.284, 6.280, 6.276, 6.272, 6.268, 6.264, 6.260, 6.256, 6.252, 6.248, 6.244, 6.240, 6.236, 6.232, 6.228, 6.224, 6.220, 6.216, 6.212, 6.208, 6.204, 6.200, 6.196, 6.192, 6.188, 6.184, 6.180, 6.176, 6.172, 6.168, 6.164, 6.160, 6.156, 6.152, 6.148, 6.144, 6.140, 6.136, 6.132, 6.128, 6.124, 6.120, 6.116, 6.112, 6.108, 6.104, 6.100, 6.096, 6.092, 6.088, 6.084, 6.080, 6.076, 6.072, 6.068, 6.064, 6.060, 6.056, 6.052, 6.048, 6.044, 6.040, 6.036, 6.032, 6.028, 6.024, 6.020, 6.016, 6.012, 6.008, 6.004, 6.000, 5.996, 5.992, 5.988, 5.984, 5.980, 5.976, 5.972, 5.968, 5.964, 5.960, 5.956, 5.952, 5.948, 5.944, 5.940, 5.936, 5.932, 5.928, 5.924, 5.920, 5.916, 5.912, 5.908, 5.904, 5.900, 5.896, 5.892, 5.888, 5.884, 5.880, 5.876, 5.872, 5.868, 5.864, 5.860, 5.856, 5.852, 5.848, 5.844, 5.840, 5.836, 5.832, 5.828, 5.824, 5.820, 5.816, 5.812, 5.808, 5.804, 5.800, 5.796, 5.792, 5.788, 5.784, 5.780, 5.776, 5.772, 5.768, 5.764, 5.760, 5.756, 5.752, 5.748, 5.744, 5.740, 5.736, 5.732, 5.728, 5.724, 5.720, 5.716, 5.712, 5.708, 5.704, 5.700, 5.696, 5.692, 5.688, 5.684, 5.680, 5.676, 5.672, 5.668, 5.664, 5.660, 5.656, 5.652, 5.648, 5.644, 5.640, 5.636, 5.632, 5.628, 5.624, 5.620, 5.616, 5.612, 5.608, 5.604, 5.600, 5.596, 5.592, 5.588, 5.584, 5.580, 5.576, 5.572, 5.568, 5.564, 5.560, 5.556, 5.552, 5.548, 5.544, 5.540, 5.536, 5.532, 5.528, 5.524, 5.520, 5.516, 5.512, 5.508, 5.504, 5.500, 5.496, 5.492, 5.488, 5.484, 5.480, 5.476, 5.472, 5.468, 5.464, 5.460, 5.456, 5.452, 5.448, 5.444, 5.440, 5.436, 5.432, 5.428, 5.424, 5.420, 5.416, 5.412, 5.408, 5.404, 5.400, 5.396, 5.392, 5.388, 5.384, 5.380, 5.376, 5.372, 5.368, 5.364, 5.360, 5.356, 5.352, 5.348, 5.344, 5.340, 5.336, 5.332, 5.328, 5.324, 5.320, 5.316, 5.312, 5.308, 5.304, 5.300, 5.296, 5.292, 5.288, 5.284, 5.280, 5.276, 5.272, 5.268, 5.264, 5.260, 5.256, 5.252, 5.248, 5



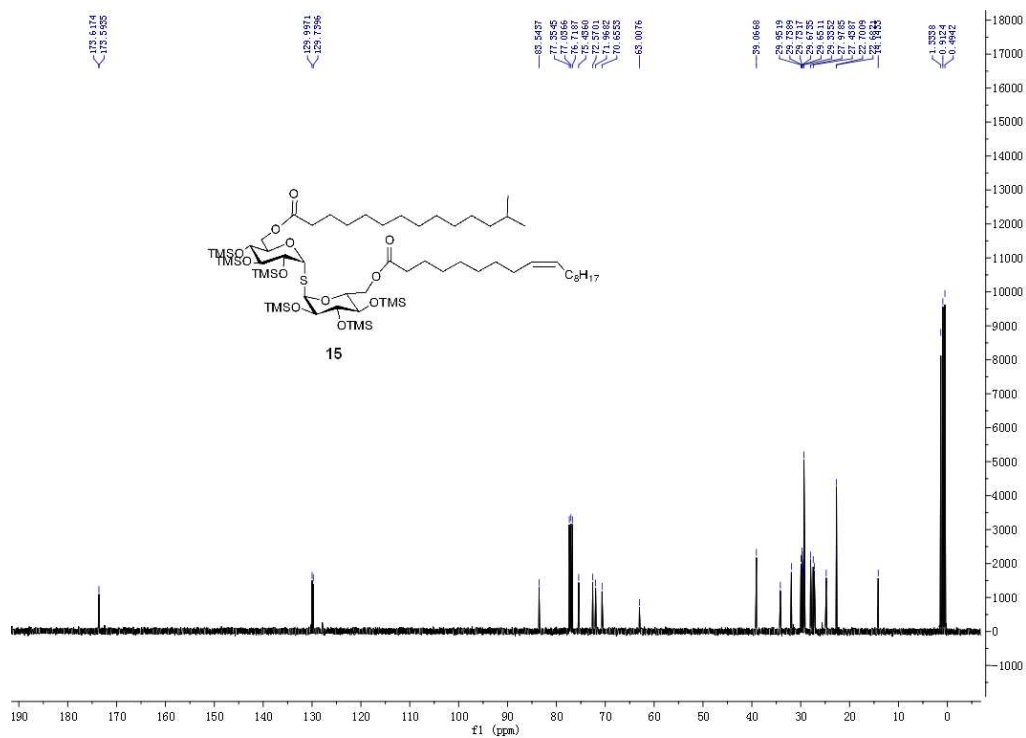
¹H NMR and ¹³C NMR spectra of compound 14



Chemical structure of compound **15** is shown above the spectrum. The structure is a complex molecule featuring a central core with multiple TMSO (trimethylsilyloxy) groups and long alkyl chains, including a terminal C_8H_{17} group.

The 1H NMR spectrum (CDCl₃) shows the following chemical shifts (ppm) and integrations:

- 7.200, 7.178, 7.167, 7.144, 7.124, 7.115, 7.111, 7.103, 7.088, 7.073, 7.054, 7.032, 7.020, 7.004, 6.989, 6.973, 6.951 (Aromatic region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 5.500, 5.478, 5.467, 5.444, 5.424, 5.415, 5.411, 5.403, 5.388, 5.373, 5.354, 5.332, 5.320, 5.304, 5.289, 5.273, 5.251 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 4.500, 4.478, 4.467, 4.444, 4.424, 4.415, 4.411, 4.403, 4.388, 4.373, 4.354, 4.332, 4.320, 4.304, 4.289, 4.273, 4.251 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 3.500, 3.478, 3.467, 3.444, 3.424, 3.415, 3.411, 3.403, 3.388, 3.373, 3.354, 3.332, 3.320, 3.304, 3.289, 3.273, 3.251 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 2.500, 2.478, 2.467, 2.444, 2.424, 2.415, 2.411, 2.403, 2.388, 2.373, 2.354, 2.332, 2.320, 2.304, 2.289, 2.273, 2.251 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 1.500, 1.478, 1.467, 1.444, 1.424, 1.415, 1.411, 1.403, 1.388, 1.373, 1.354, 1.332, 1.320, 1.304, 1.289, 1.273, 1.251 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 1.200, 1.178, 1.167, 1.144, 1.124, 1.115, 1.111, 1.103, 1.088, 1.073, 1.054, 1.032, 1.020, 1.004, 0.989, 0.973, 0.951 (Alkene region, integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00)
- 0.000 (TMS, integration: 3.00)



Chemical structure of compound **16** is shown above the spectrum. The spectrum displays peaks corresponding to the structure, with integration values and chemical shift values (ppm) indicated.

Chemical shift values (ppm) listed above the spectrum:

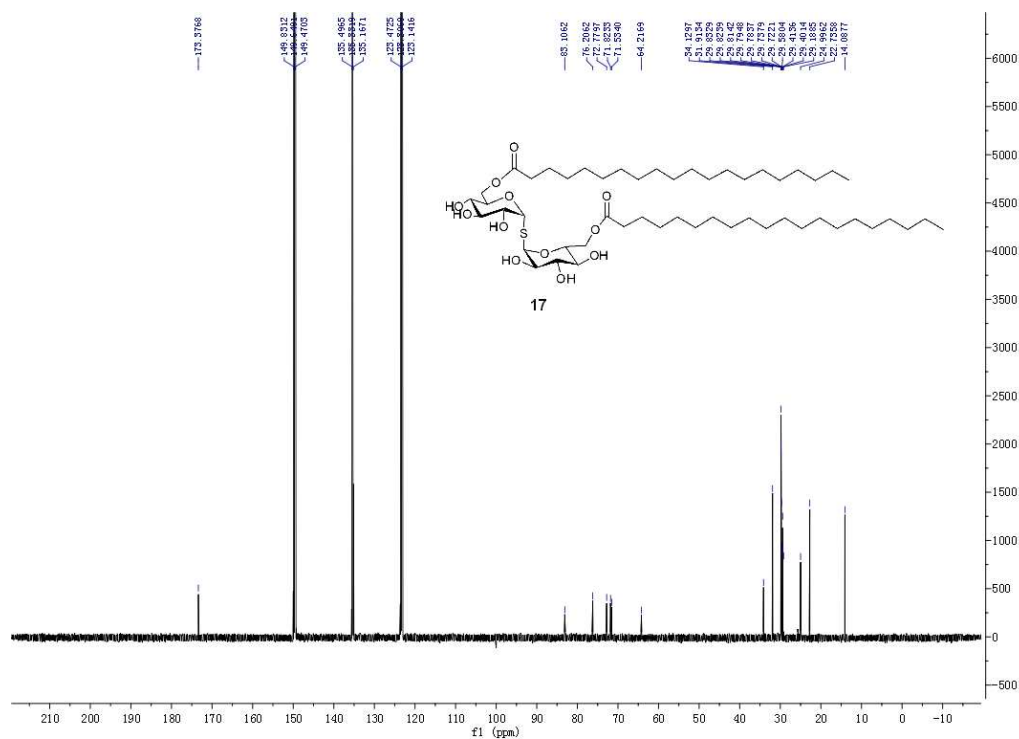
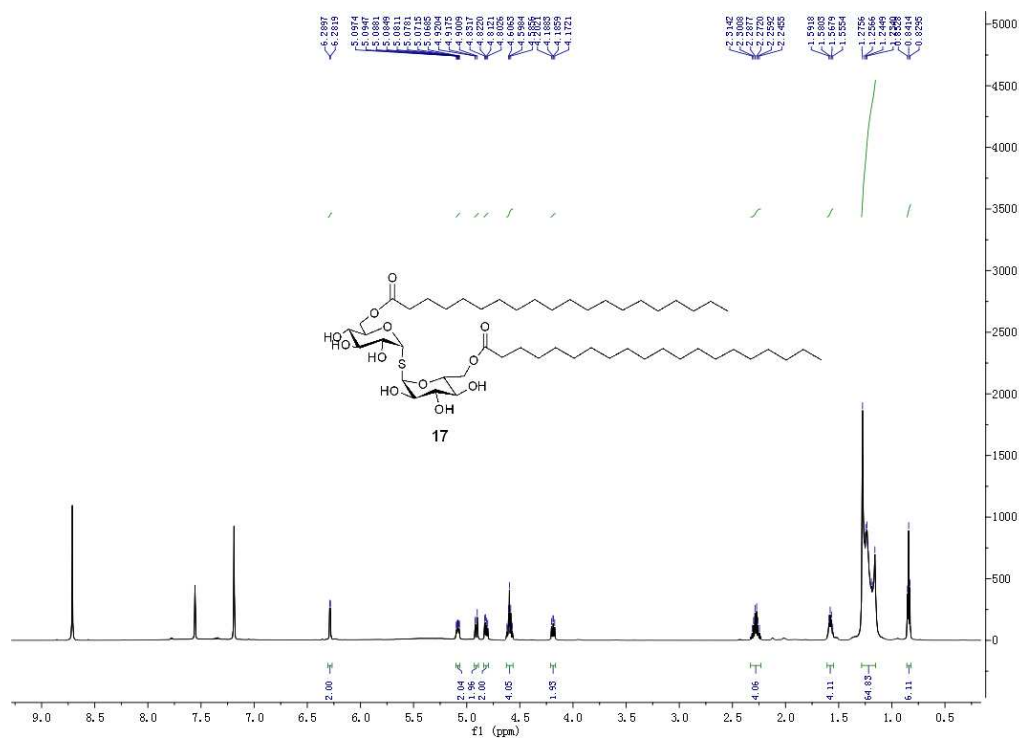
- 8.2109, 8.2021
- 5.0787, 5.0625, 5.0525, 4.9102, 4.8925, 4.8825, 4.8187, 4.8102, 4.8002, 4.7900
- 5.5928, 5.5830, 5.5800, 5.5750, 5.5700, 4.1720, 4.1585
- 2.3196, 2.3171, 2.2781, 2.2650
- 1.5566, 1.5154, 1.5050, 1.4974, 1.2441, 0.8561, 0.8482, 0.8354

Integration values listed below the spectrum:

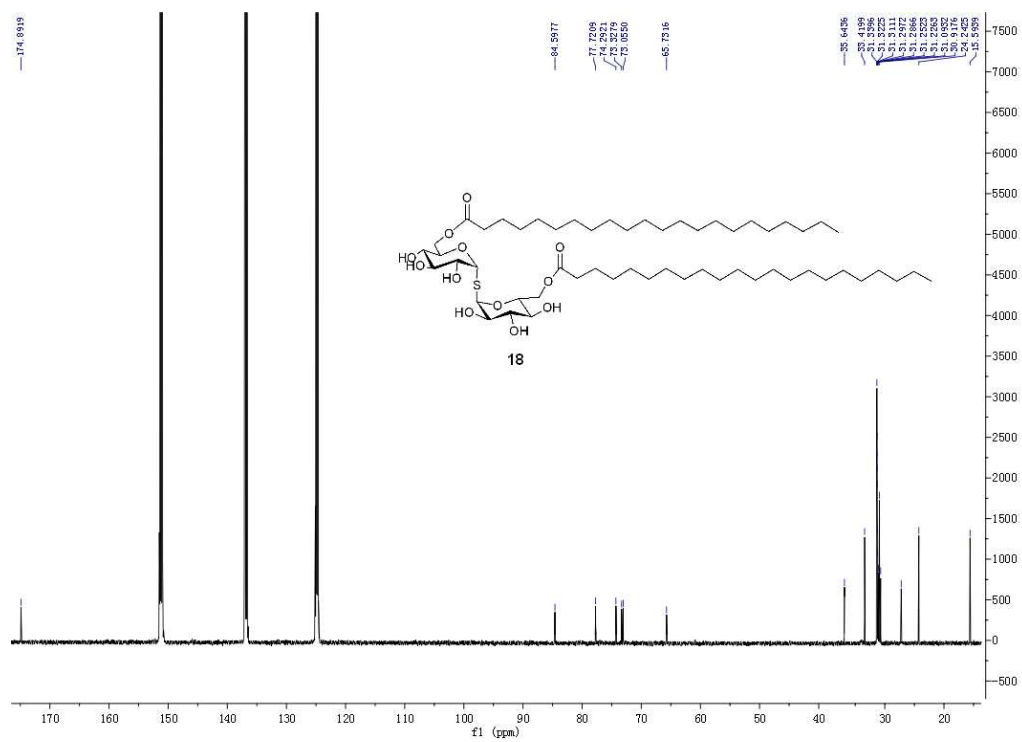
- 2.00
- 2.00, 2.00, 2.00, 2.00, 2.00, 2.00
- 2.00
- 2.00
- 4.13, 4.13, 4.08, 50.27, 6.75



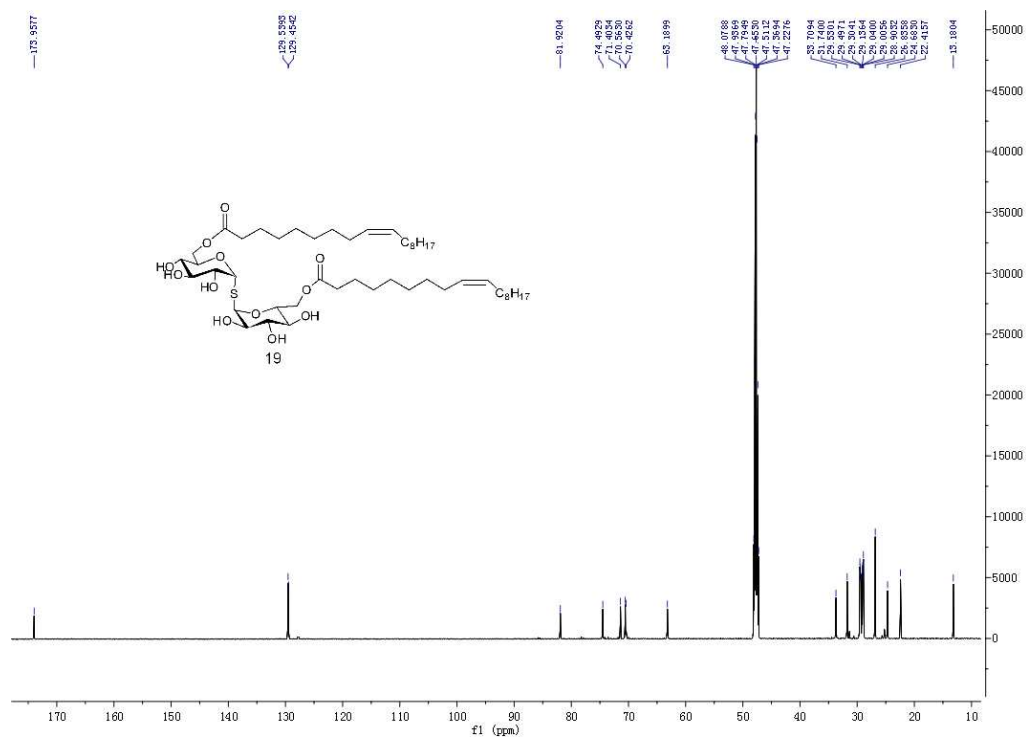
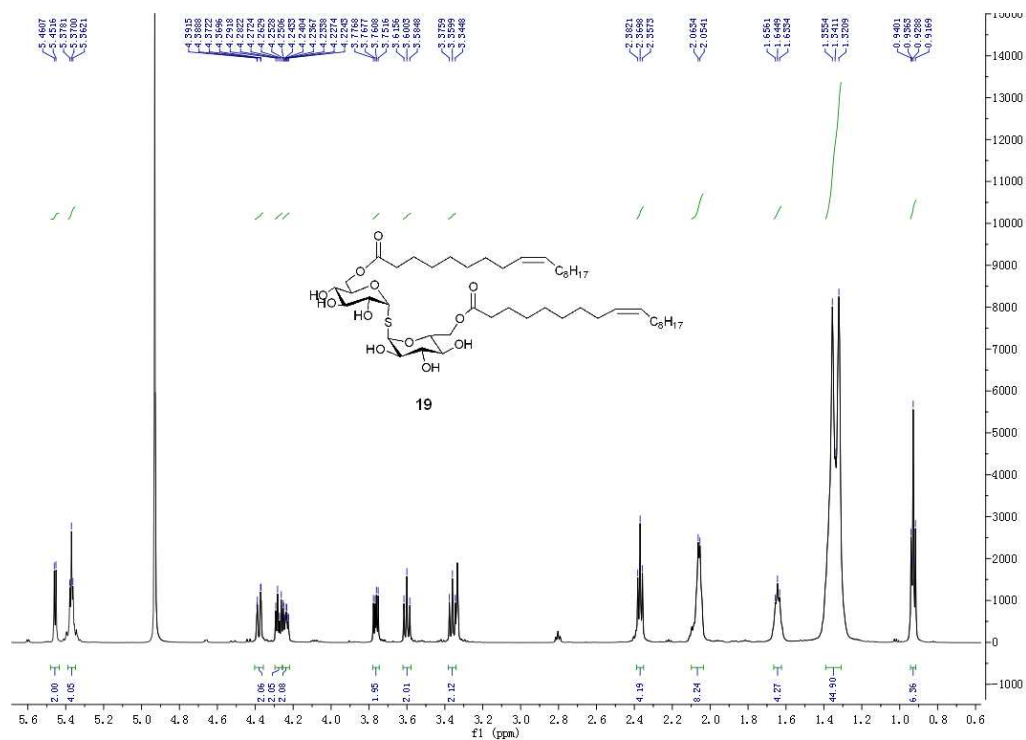
¹H NMR and ¹³C NMR spectra of compound 17



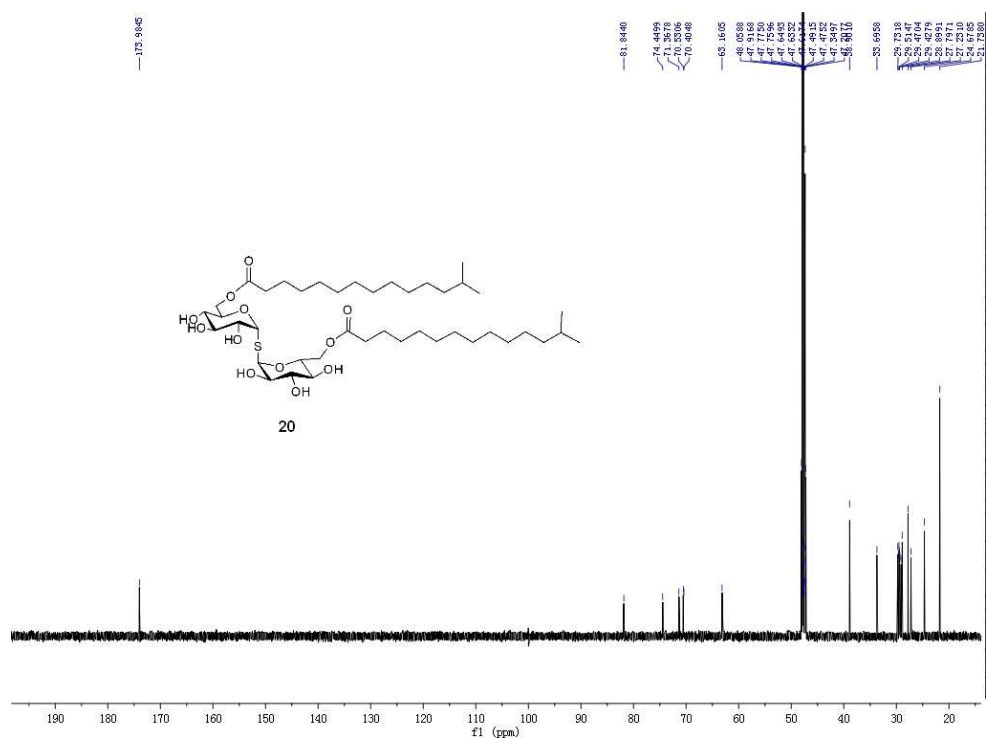
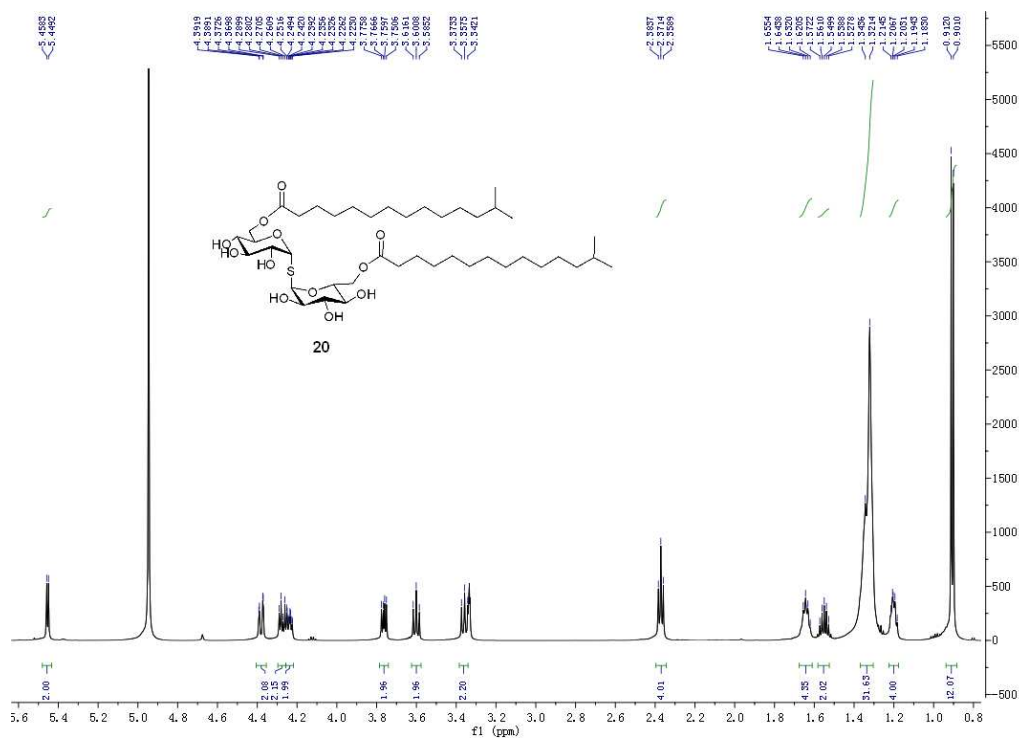
Chemical structure of compound 18 is shown above the spectrum. The structure is a disaccharide derivative with two long alkyl chains. The spectrum shows peaks from 0 to 9 ppm. Key peaks are labeled with their chemical shifts: 8.281, 8.275, 5.088, 5.084, 5.081, 5.071, 5.063, 4.920, 4.911, 4.903, 4.820, 4.814, 4.809, 4.634, 4.626, 4.623, 4.596, 4.588, 4.195, 4.190, 4.166, 2.179, 2.165, 2.152, 2.142, 2.132, 2.123, 2.105, 2.095, 1.585, 1.581, 1.574, 1.559, 1.555, 1.551, 1.547, 1.542, 1.532, 1.523, 1.513, 1.505, 1.496, 1.486, 1.476, 1.466, 1.456, 1.446, 1.436, 1.426, 1.416, 1.406, 1.396, 1.386, 1.376, 1.366, 1.356, 1.346, 1.336, 1.326, 1.316, 1.306, 1.296, 1.286, 1.276, 1.266, 1.256, 1.246, 1.236, 1.226, 1.216, 1.206, 1.196, 1.186, 1.176, 1.166, 1.156, 1.146, 1.136, 1.126, 1.116, 1.106, 1.096, 1.086, 1.076, 1.066, 1.056, 1.046, 1.036, 1.026, 1.016, 1.006, 0.996, 0.986, 0.976, 0.966, 0.956, 0.946, 0.936, 0.926, 0.916, 0.906.



¹H NMR and ¹³C NMR spectra of compound 19



¹H NMR and ¹³C NMR spectra of compound 20



¹H NMR and ¹³C NMR spectra of compound 2

