

# SUPPLEMENTARY INFORMATION

## Experimental Details and Characterization Data

### Structure–activity relationship for calanthoside, a potential hair-growth stimulant with an indole 2-*S*-,3-*O*-bis-glucoside structure. Part 1: Role of two glucoside moieties in promoting HFDPC proliferation

Riko Suzuki<sup>a</sup>, Katsuki Takashima<sup>b</sup>, Yoshiaki Manse<sup>c</sup>, Haruto Nishikawa<sup>b</sup>, Mina Ashidate<sup>b</sup>, Shinsuke Marumoto<sup>d</sup>, Fumihiko Ishikawa<sup>b</sup>, Toshio Morikawa\*<sup>c</sup>,  
Genzoh Tanabe\*<sup>a,b,c</sup>

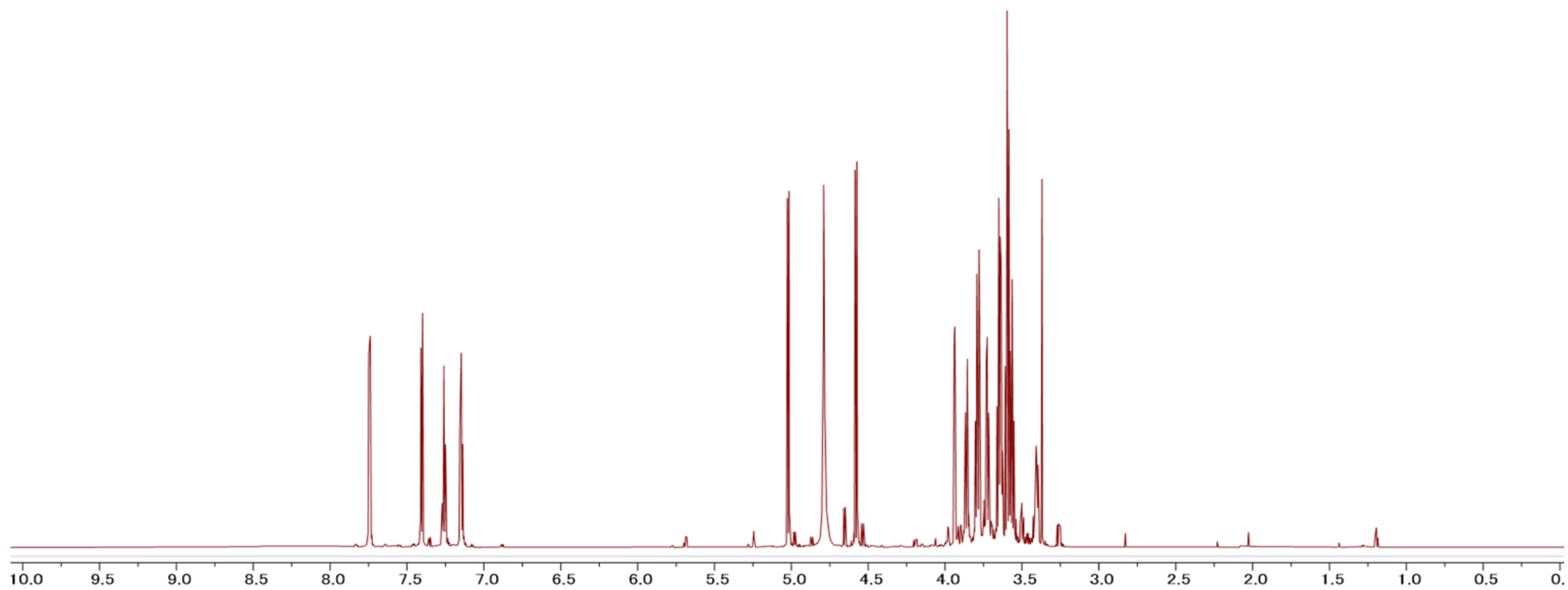
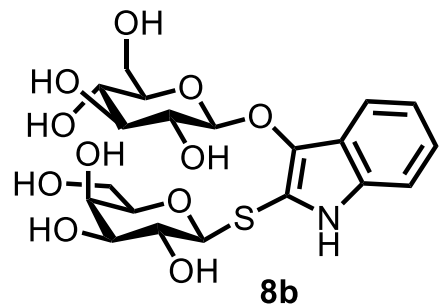
<sup>a</sup>Graduate School of Pharmacy, <sup>b</sup>Faculty of Pharmacy, <sup>c</sup>Pharmaceutical Research and Technology Institute, <sup>d</sup>Joint Research Centre, Kindai University, 3-4-1 Kowakae, Higashi-osaka, Osaka 577-8502, Japan

### Table of Contents

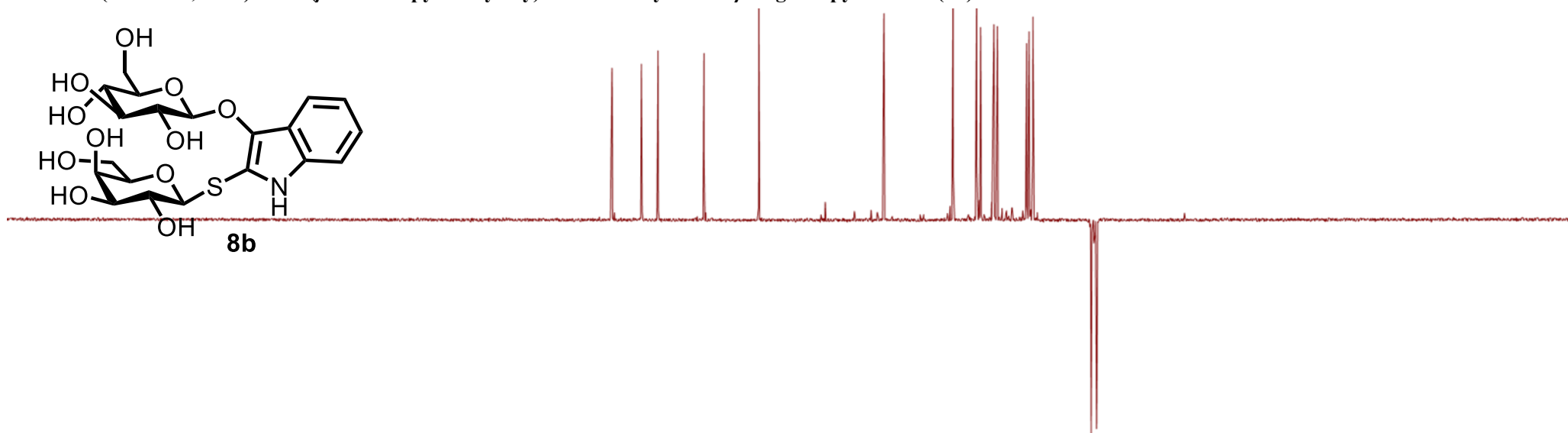
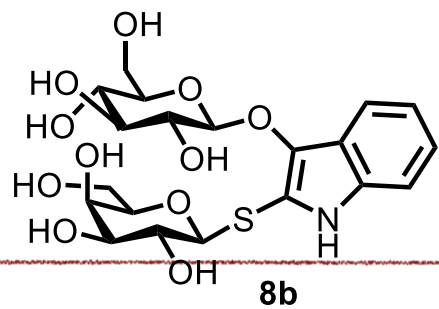
<sup>1</sup>H- AND <sup>13</sup>C-NMR SPECTROSCOPIC DATA OF SYNTHETIC COMPOUNDS

S1–S37

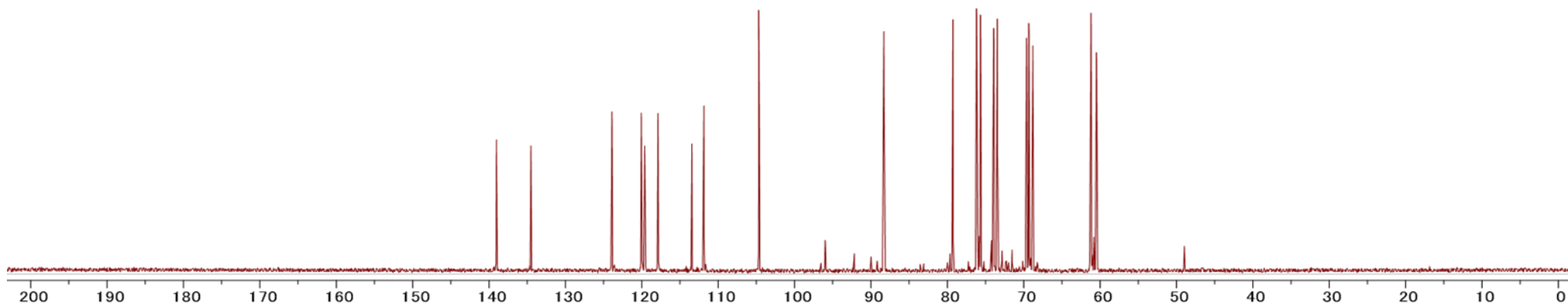
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-galactopyranoside (**8b**).



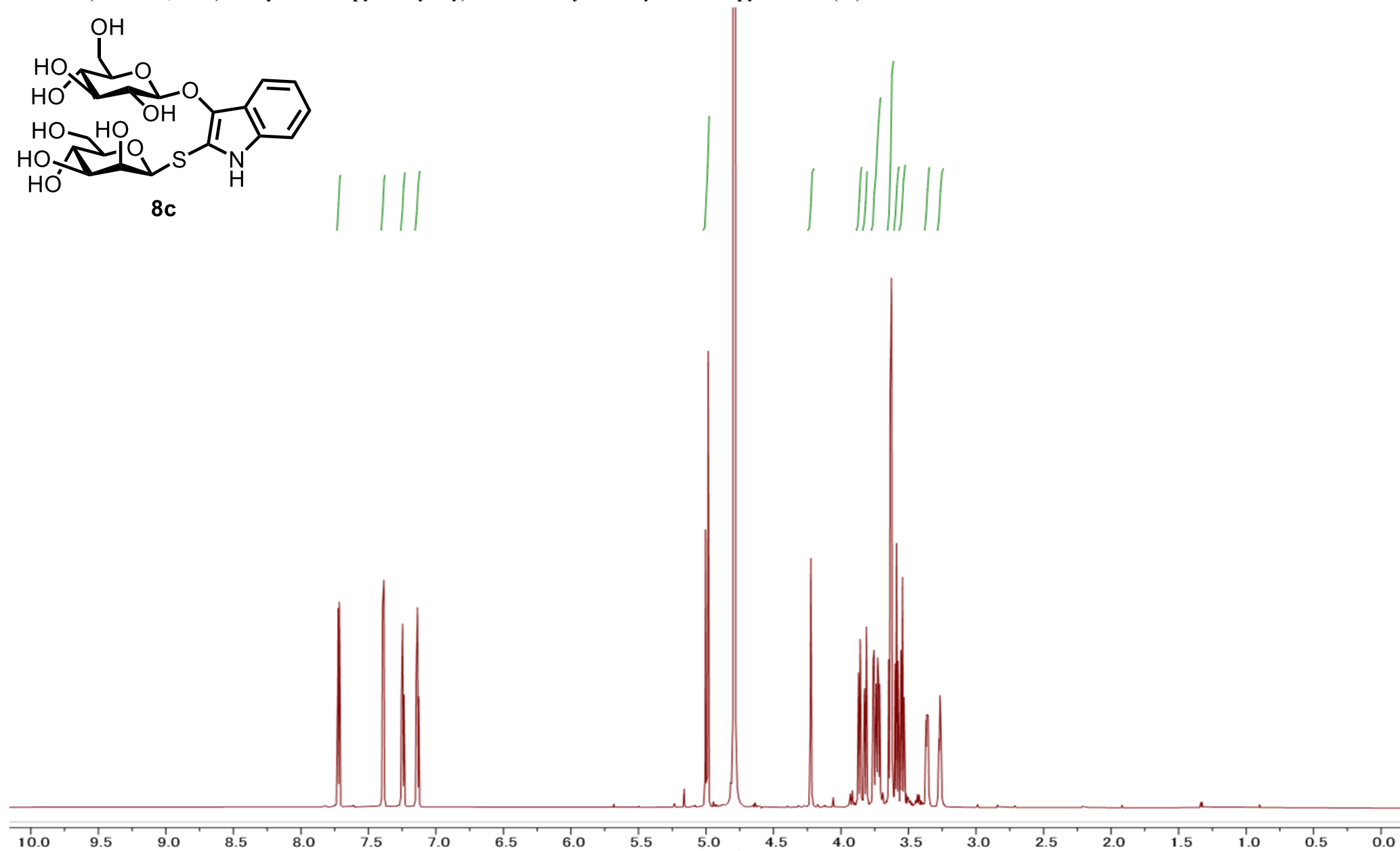
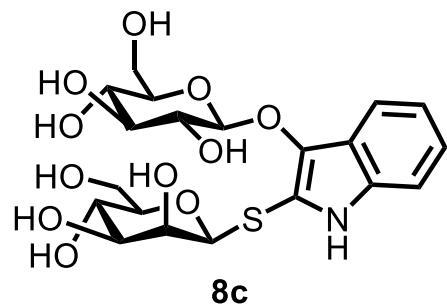
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-galactopyranoside (8b).



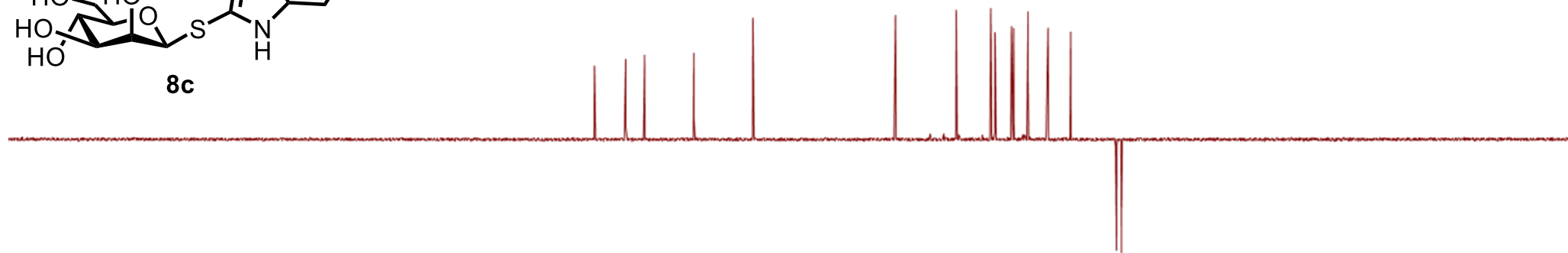
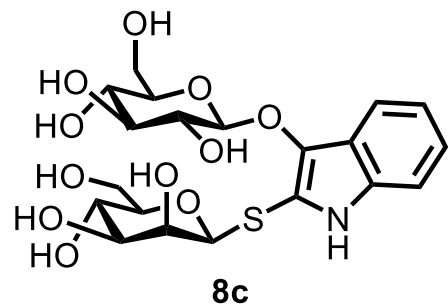
lbertone step6  
ngle pulse decoupled gated NOE



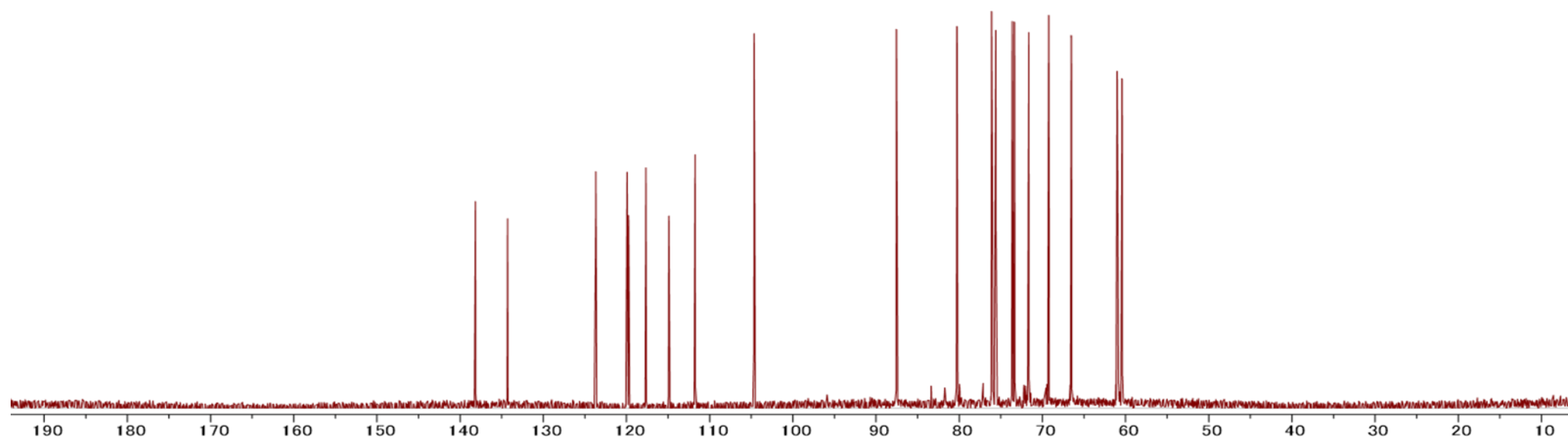
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy) -1*H*-indol-2-yl 1-thio-β-D-mannopyranoside (8c).



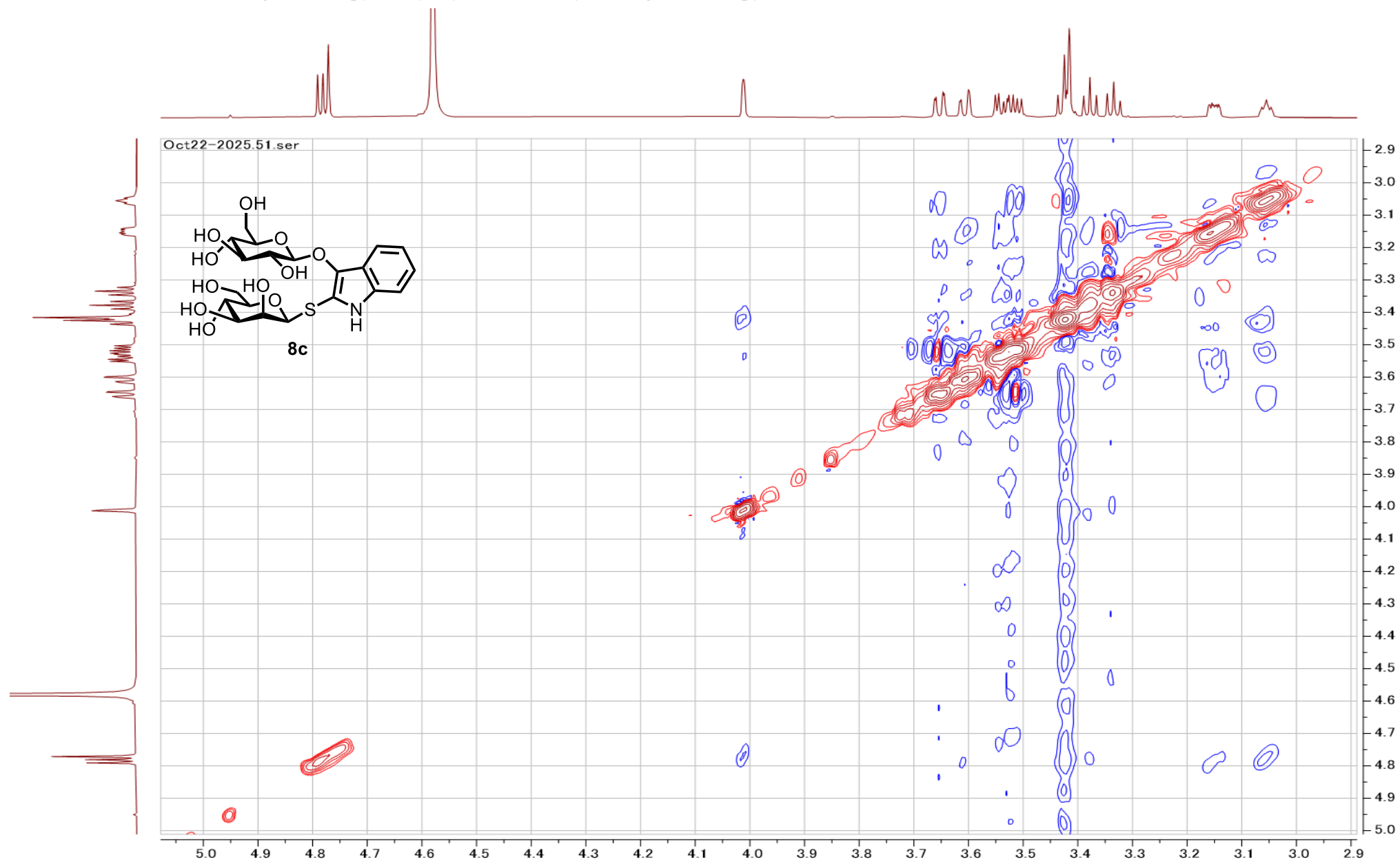
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy) -1H-indol-2-yl 1-thio-β-D-mannopyranoside (8c).



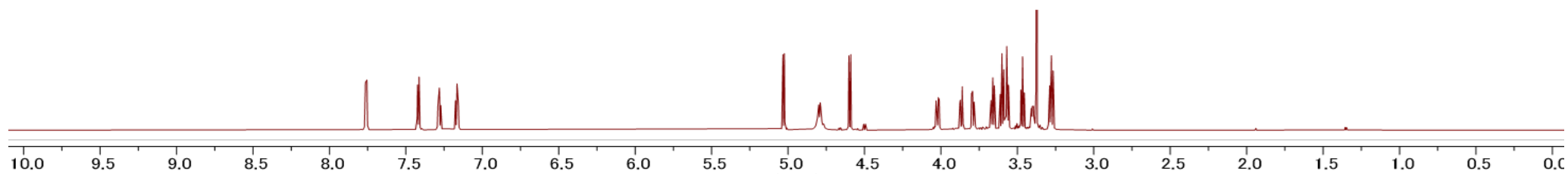
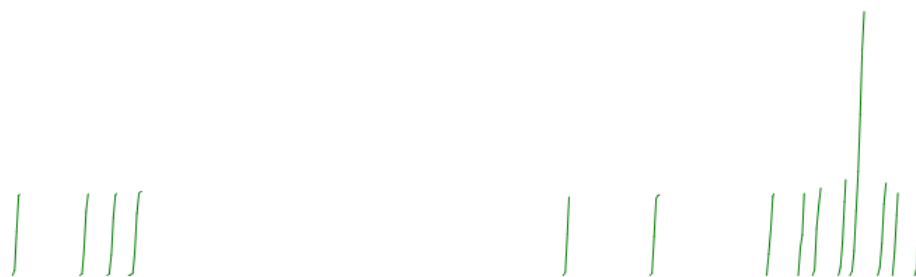
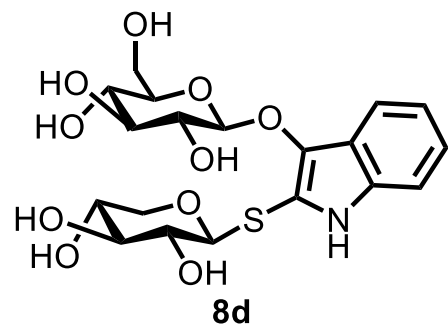
14-2025.41.fid



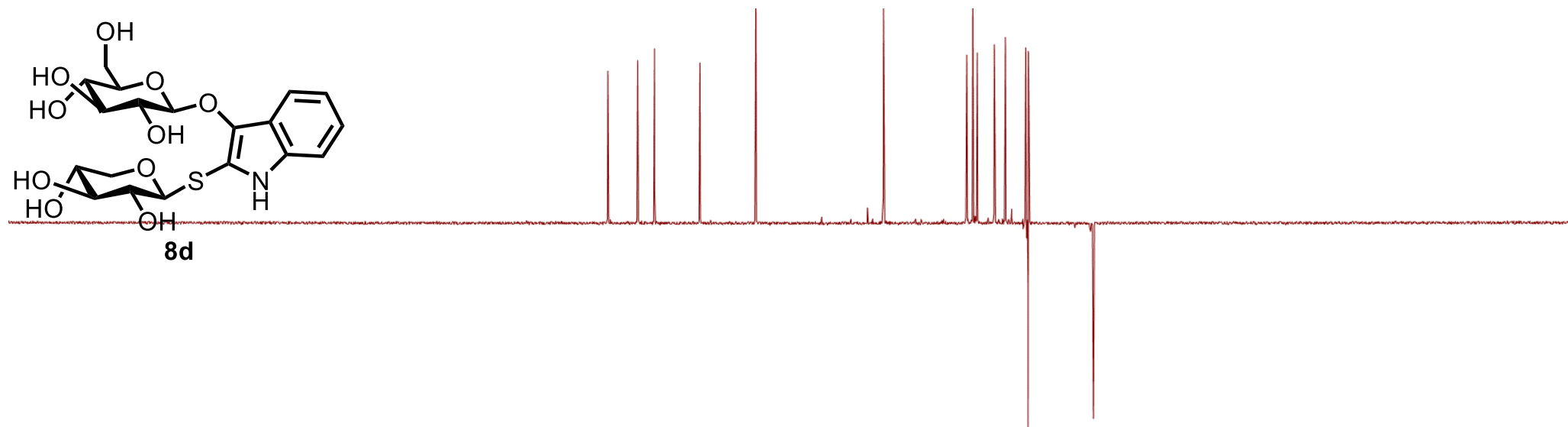
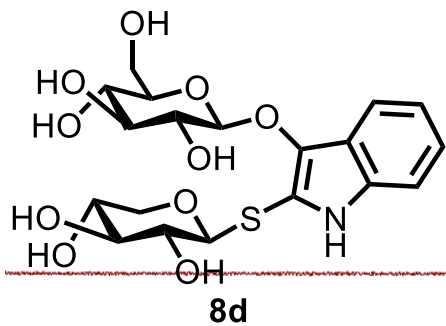
NOESY (800 MHz, D<sub>2</sub>O) of 3-( $\beta$ -D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio- $\beta$ -D-mannopyranoside (8c).



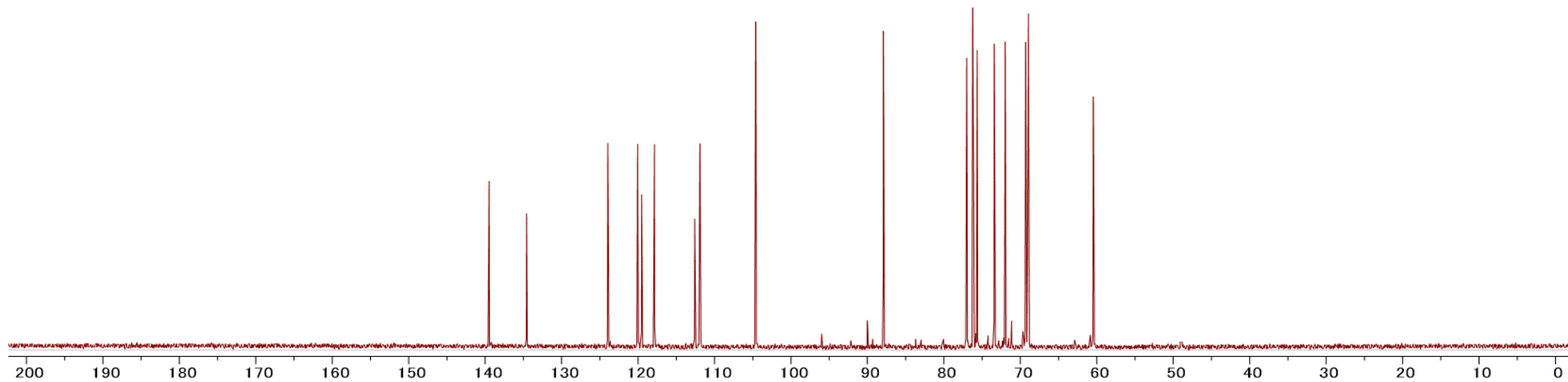
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-xylopyranoside (8d).



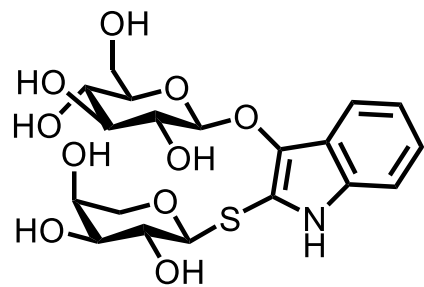
$^{13}\text{C}$ -NMR (200 MHz,  $\text{D}_2\text{O}$ ) of 3-( $\beta$ -D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio- $\beta$ -D-xylopyranoside (**8d**).



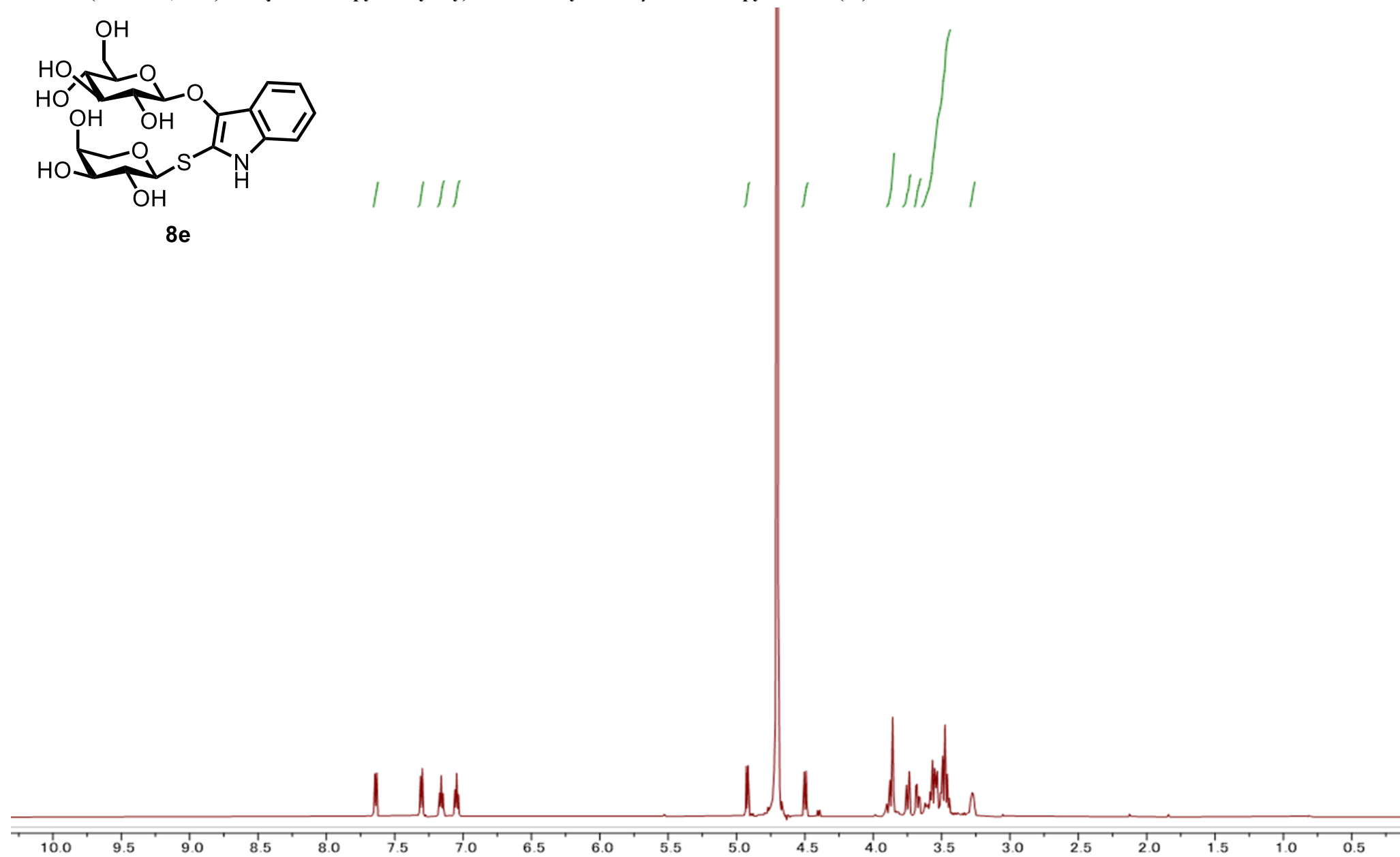
31uSXyl  
ngle pulse decoupled gated NOE



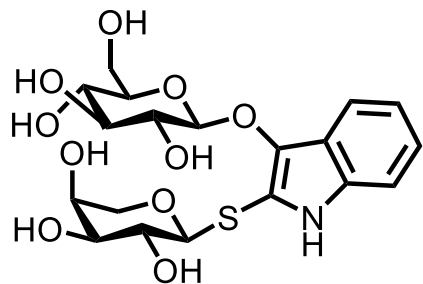
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1H-indol-2-yl 1-thio-β-D-arabinopyranoside (8e).



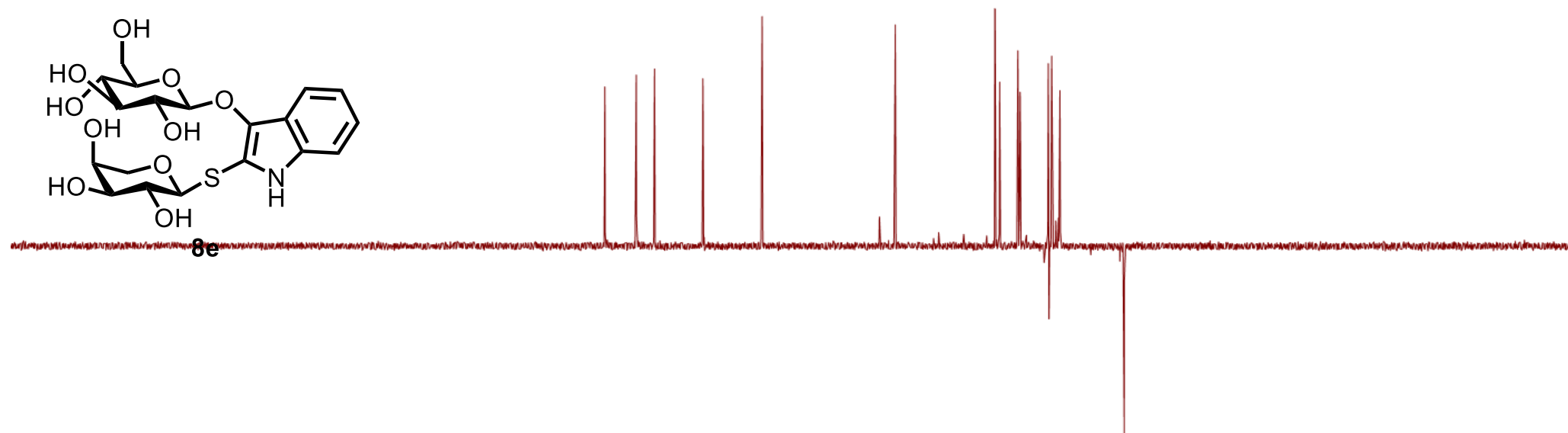
**8e**



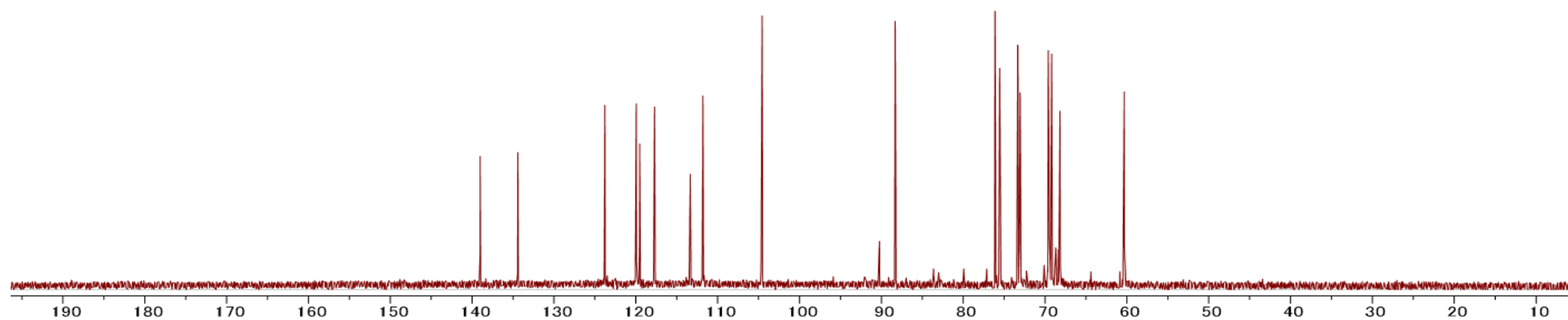
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-arabinopyranoside (8e).



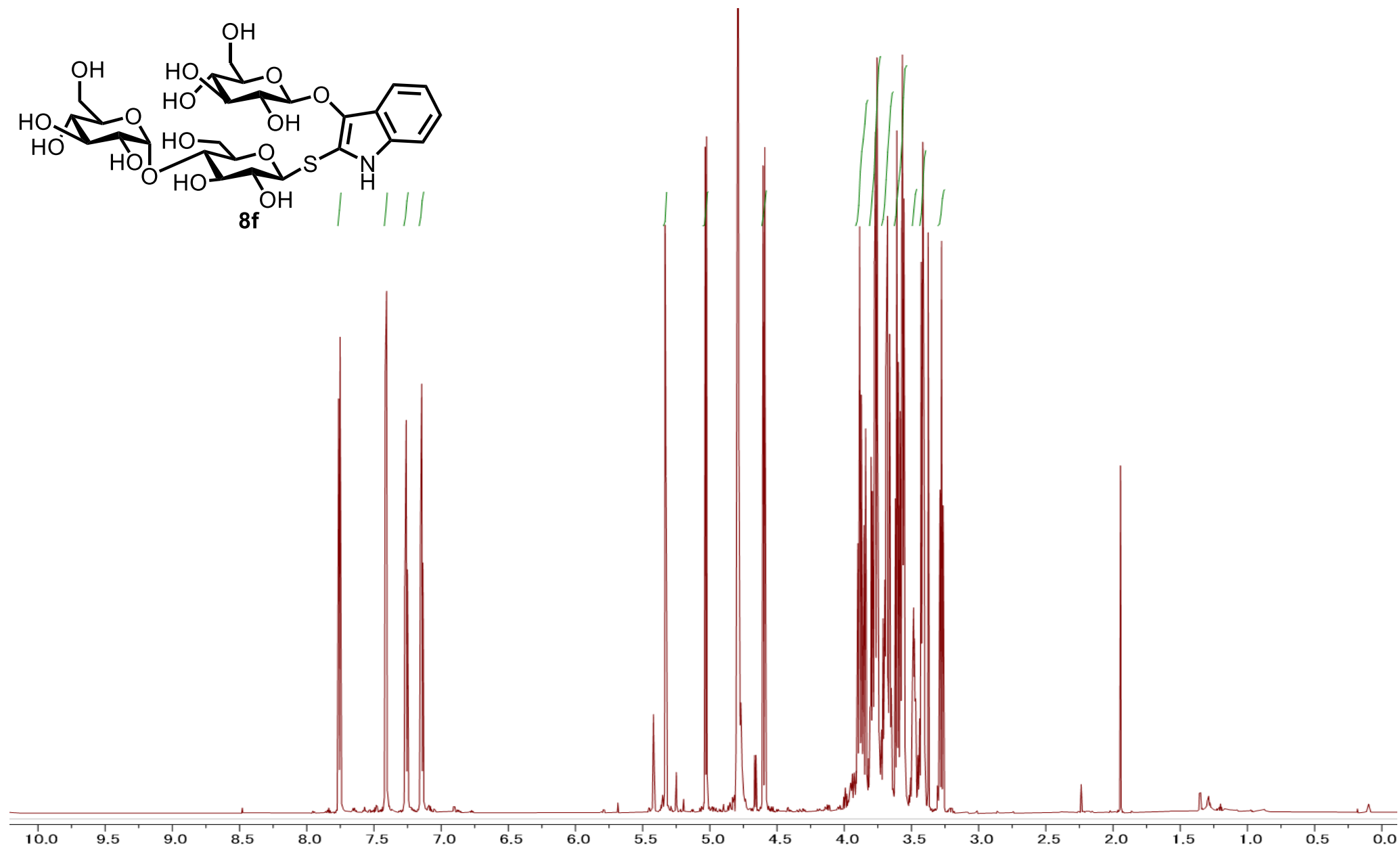
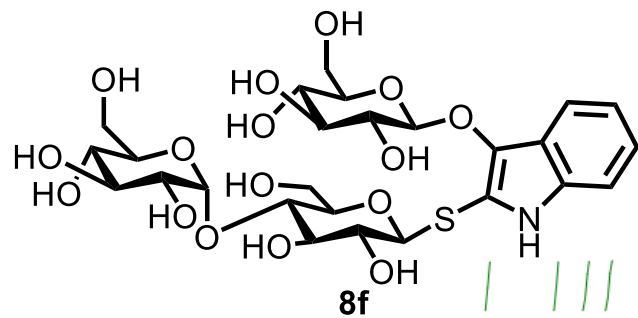
8e



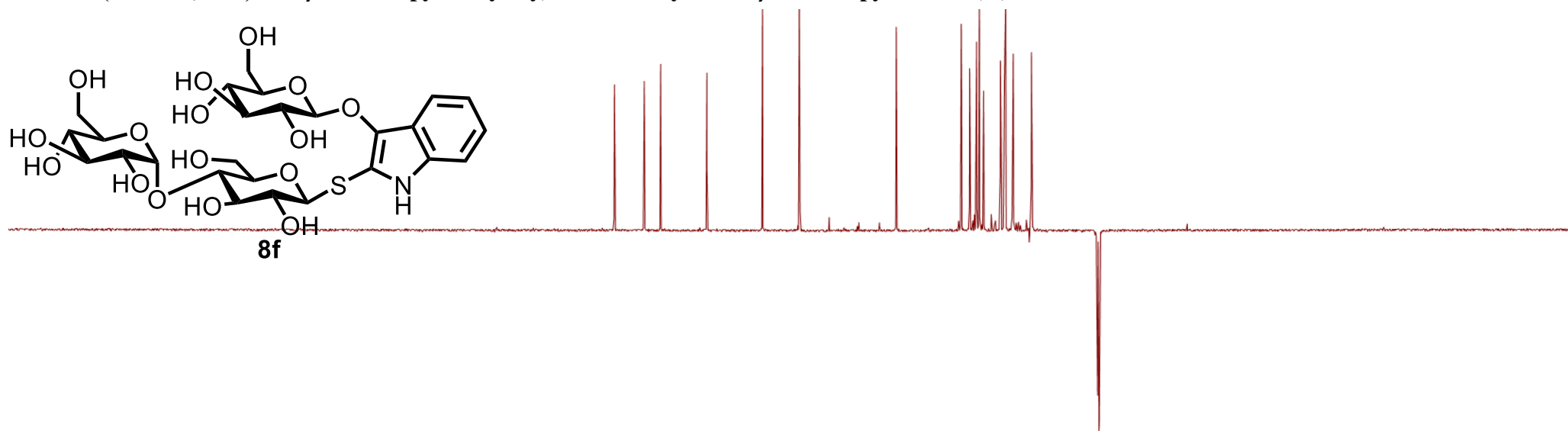
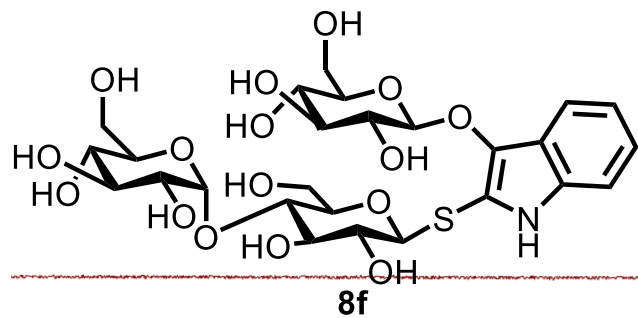
st27-2022.2.fid



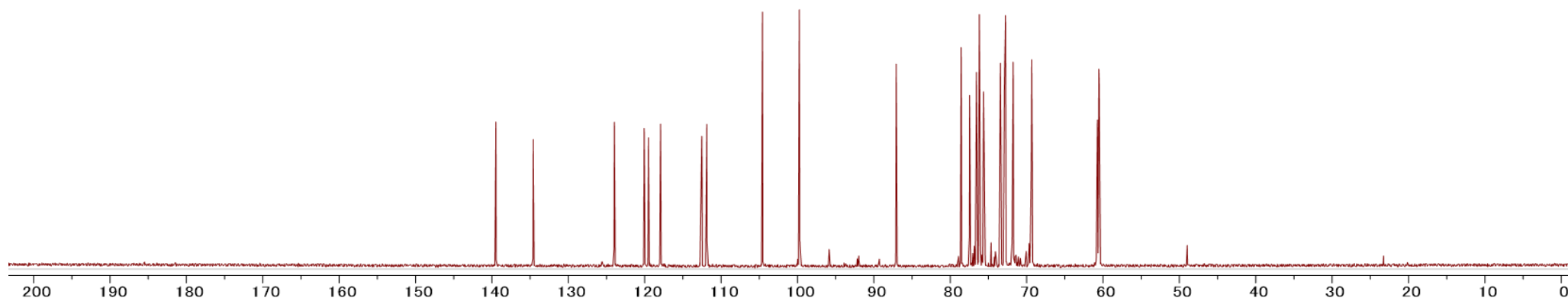
**<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-maltopyranoside (8f).**



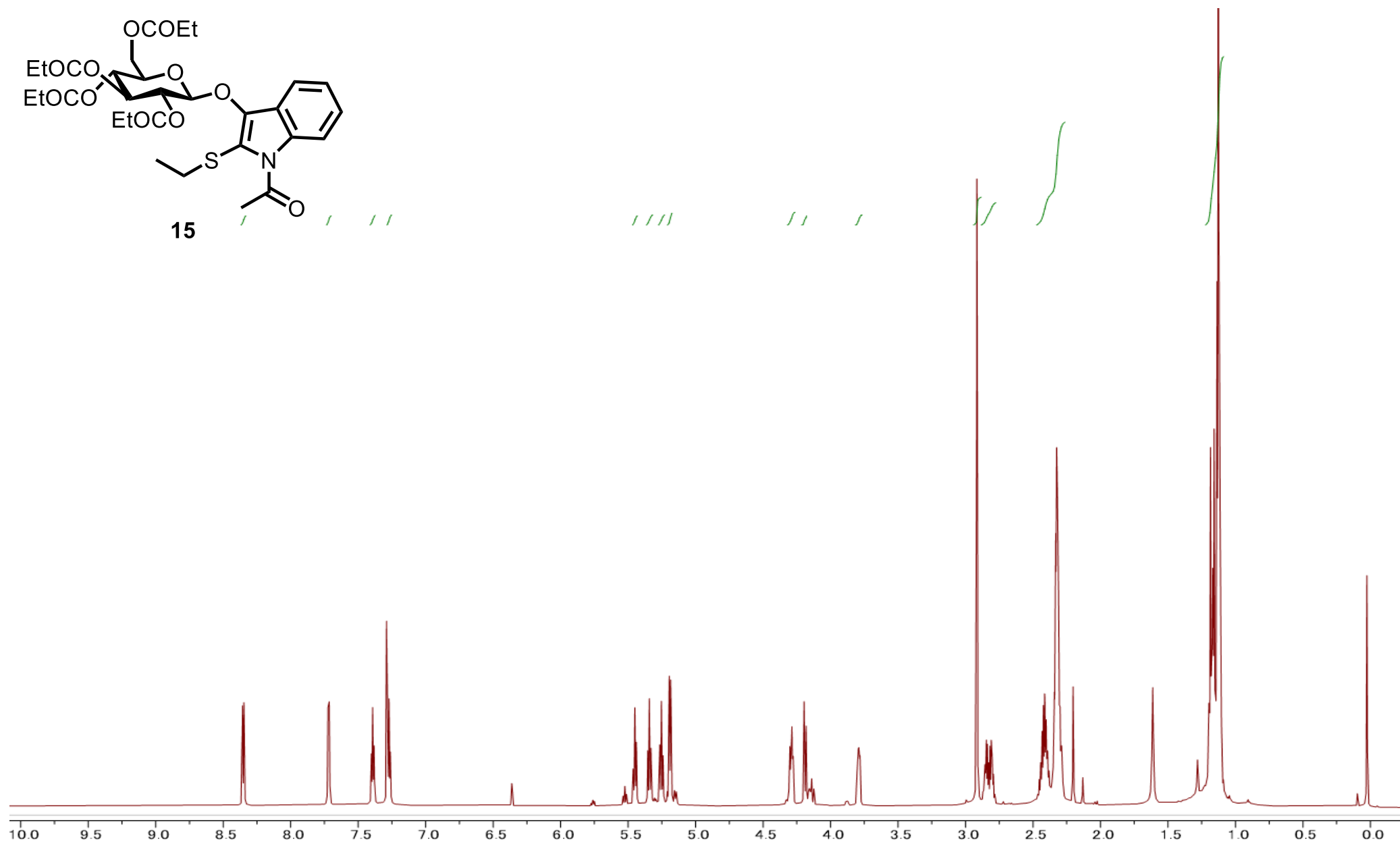
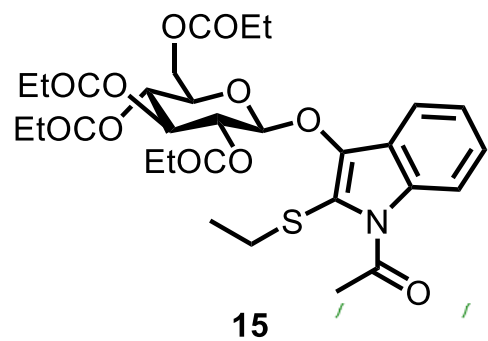
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Glucopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-maltopyranoside (8f).



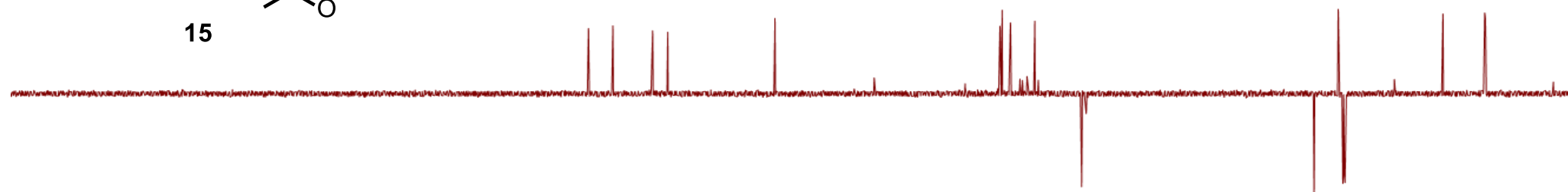
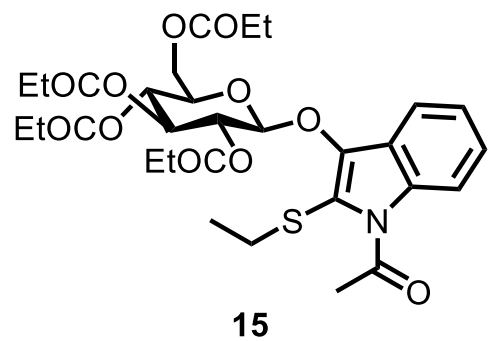
<sup>1</sup>GluSMal  
single pulse decoupled gated NOE



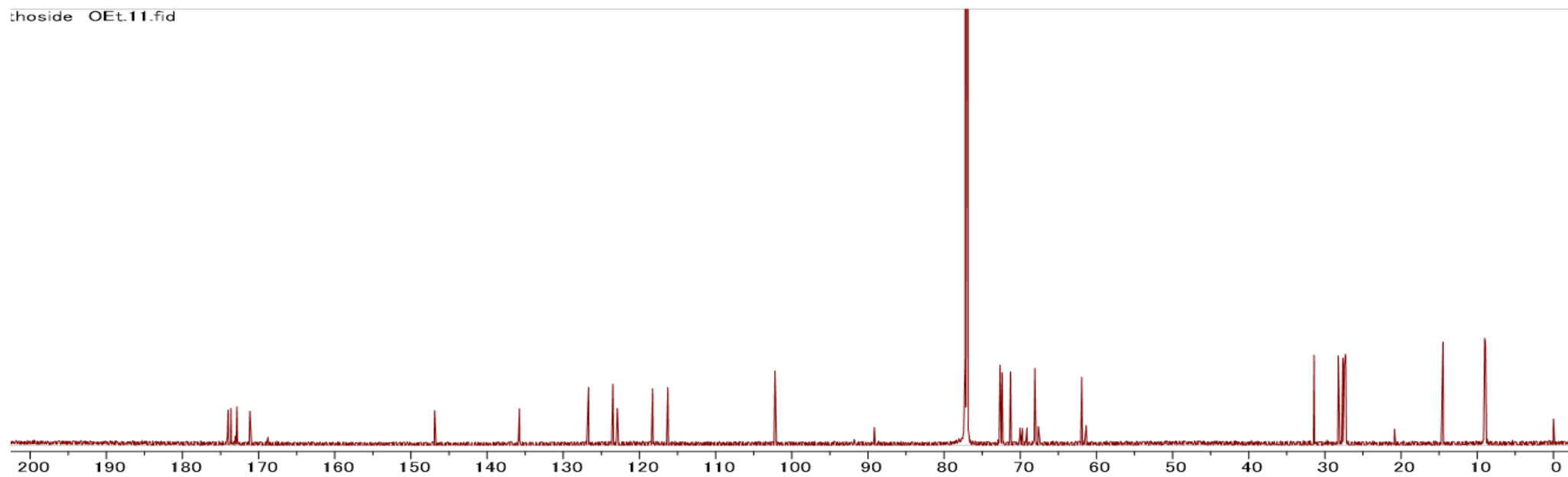
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of *N*-Acetyl-2-(ethylthio)-1*H*-indol-3-yl 2,3,4,6-tetra-*O*-propionyl-1-thio-β-*D*-glucopyranoside (15).



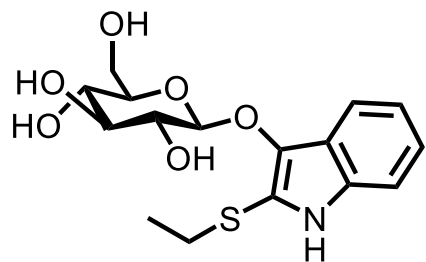
<sup>13</sup>C-NMR (200 MHz, CDCl<sub>3</sub>) of *N*-Acetyl-2-(ethylthio)-1*H*-indol-3-yl 2,3,4,6-tetra-*O*-propionyl-1-thio-β-*D*-glucopyranoside (15).



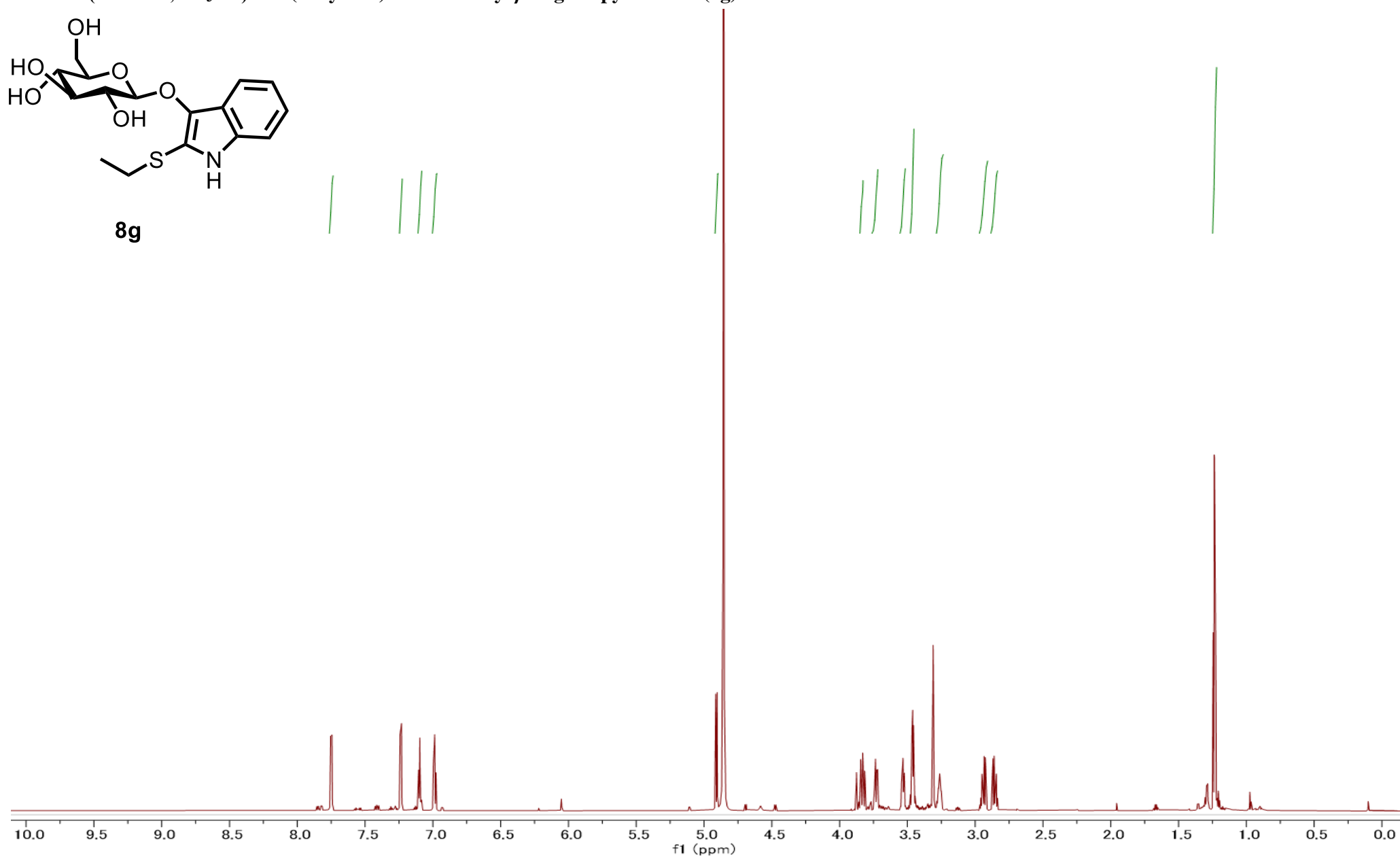
thoside OEt.11.fid



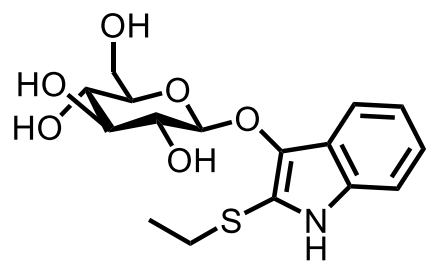
<sup>1</sup>H-NMR (800 MHz, CD<sub>3</sub>OD) of 2-(Ethylthio)-1*H*-indol-3-yl β-D-glucopyranoside (**8g**).



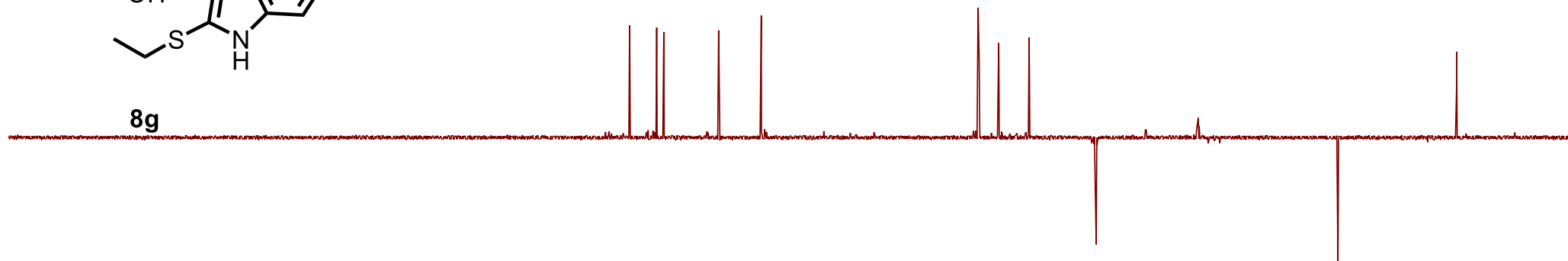
**8g**



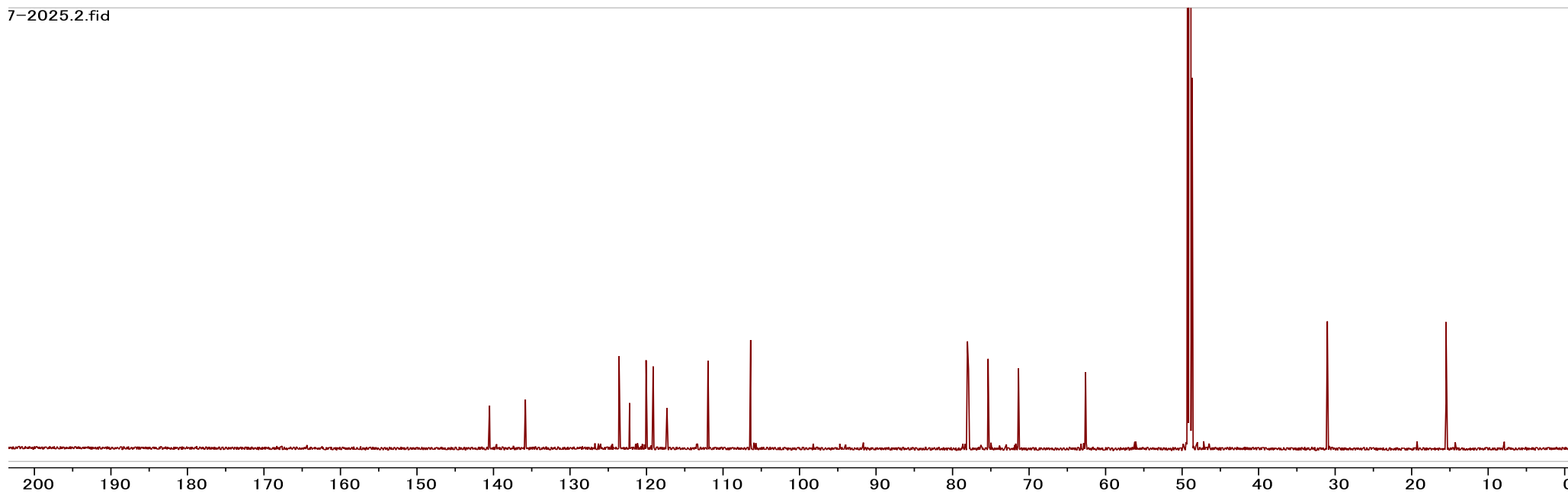
<sup>13</sup>C-NMR (200 MHz, CD<sub>3</sub>OD) of 2-(Ethylthio)-1*H*-indol-3-yl β-D-glucopyranoside (8g).



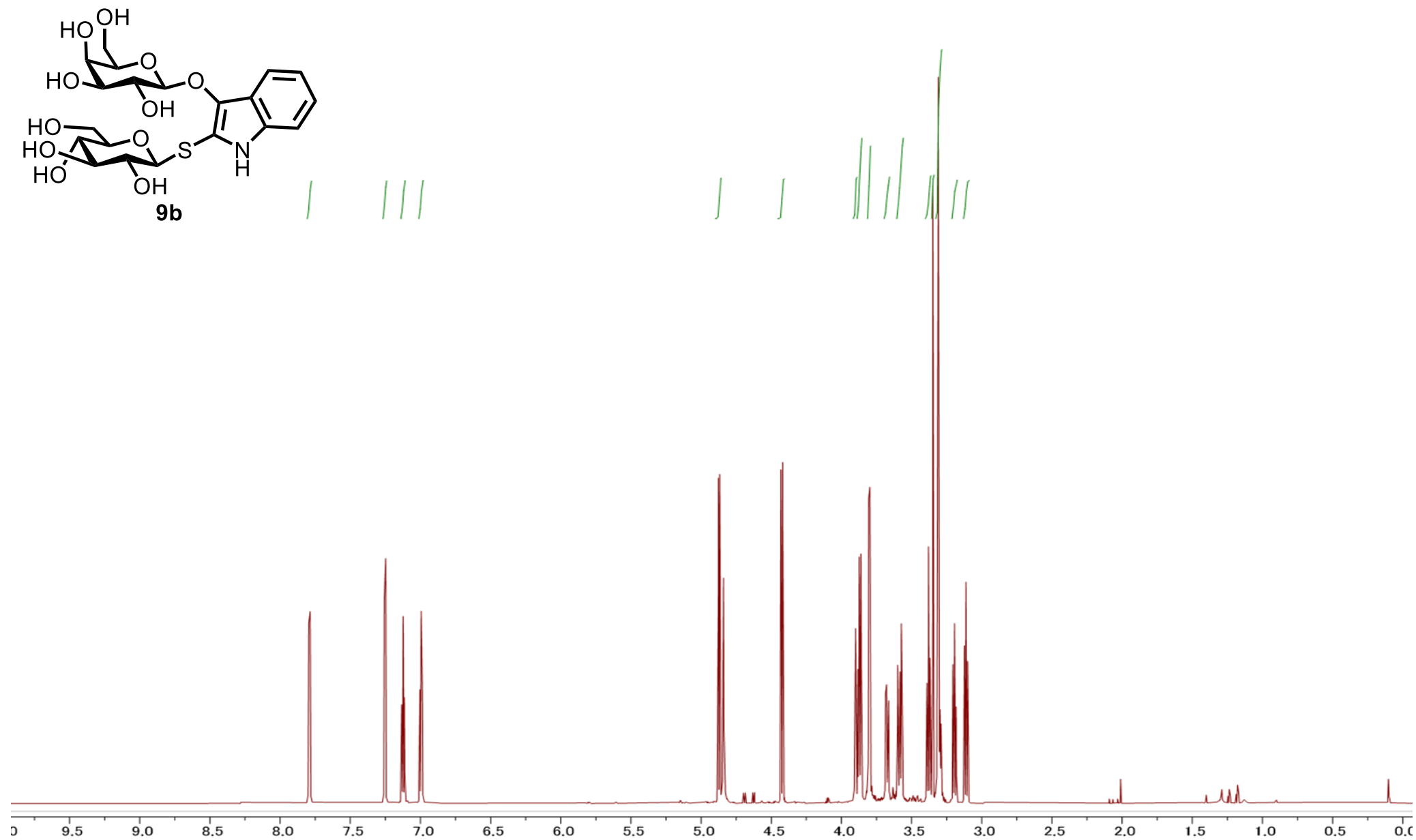
8g



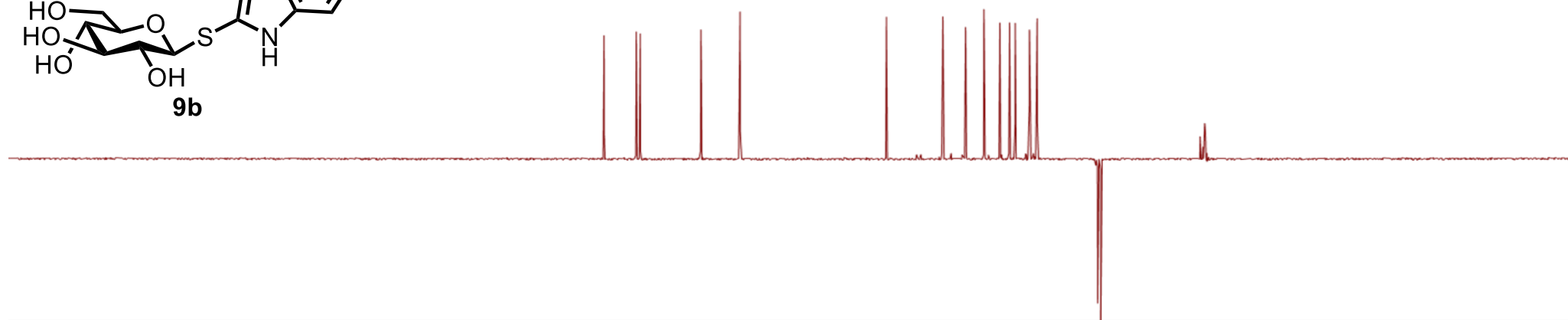
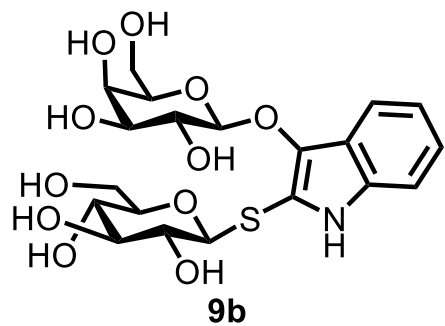
7-2025.2.fid



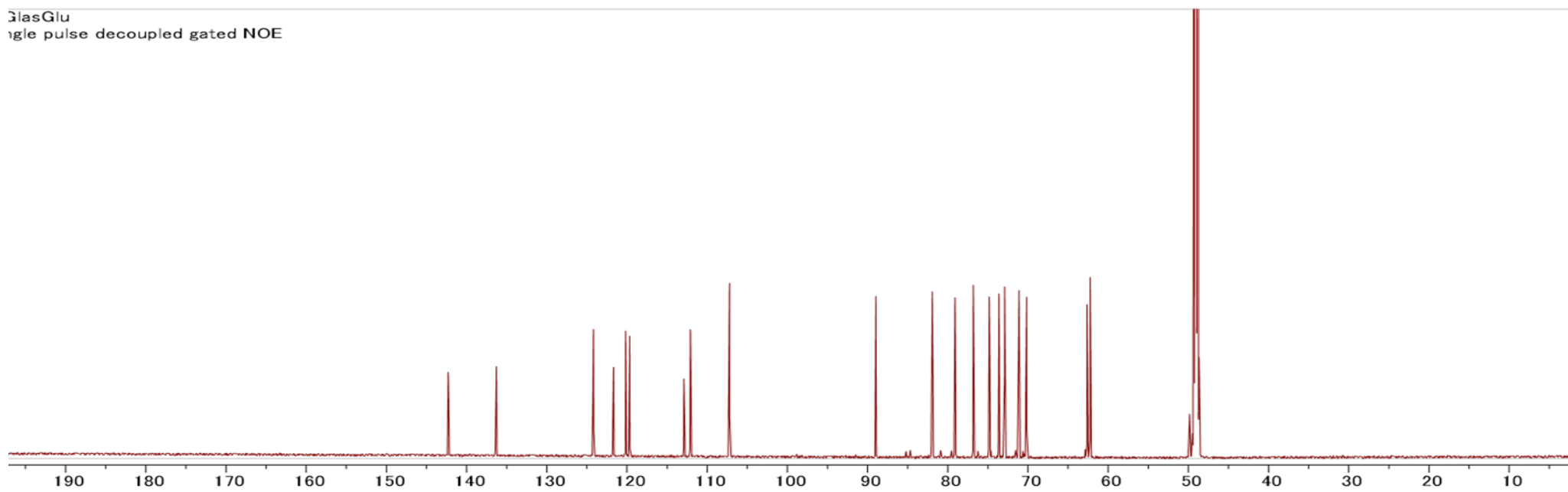
<sup>1</sup>H-NMR (800 MHz, CD<sub>3</sub>OD) of 3-(β-D-Glactopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-glucopyranoside (**9b**).



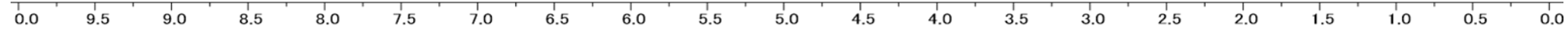
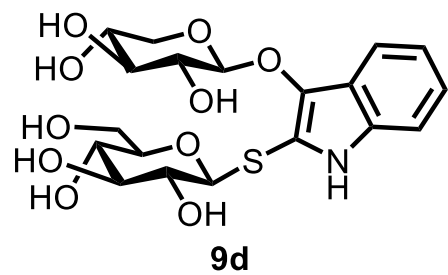
$^{13}\text{C}$ -NMR (200 MHz,  $\text{CD}_3\text{OD}$ ) of 3-( $\beta$ -D-Glactopyranosyloxy)-1*H*-indol-2-yl 1-thio- $\beta$ -D-glucopyranoside (**9b**).



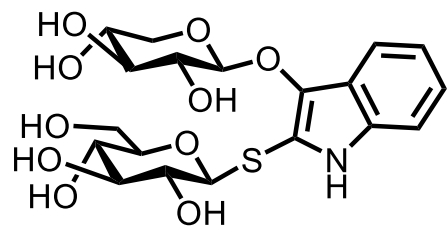
aliasGlu  
single pulse decoupled gated NOE



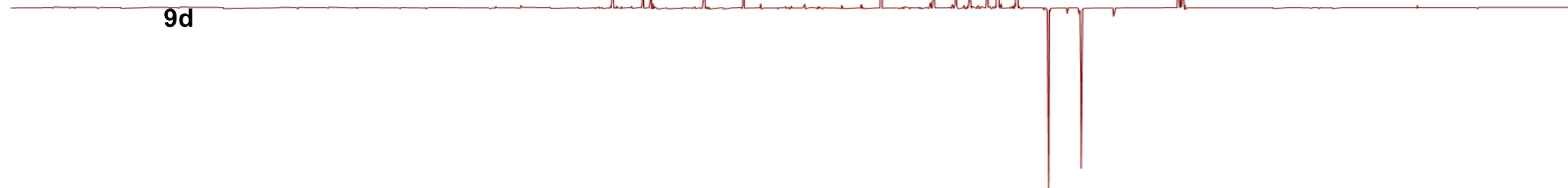
<sup>1</sup>H-NMR (800 MHz, CD<sub>3</sub>OD) of 3-(β-D-Xylopyranosyloxy)-1H-indol-2-yl 1-thio-β-D-gluco-*pyranoside* (9d).



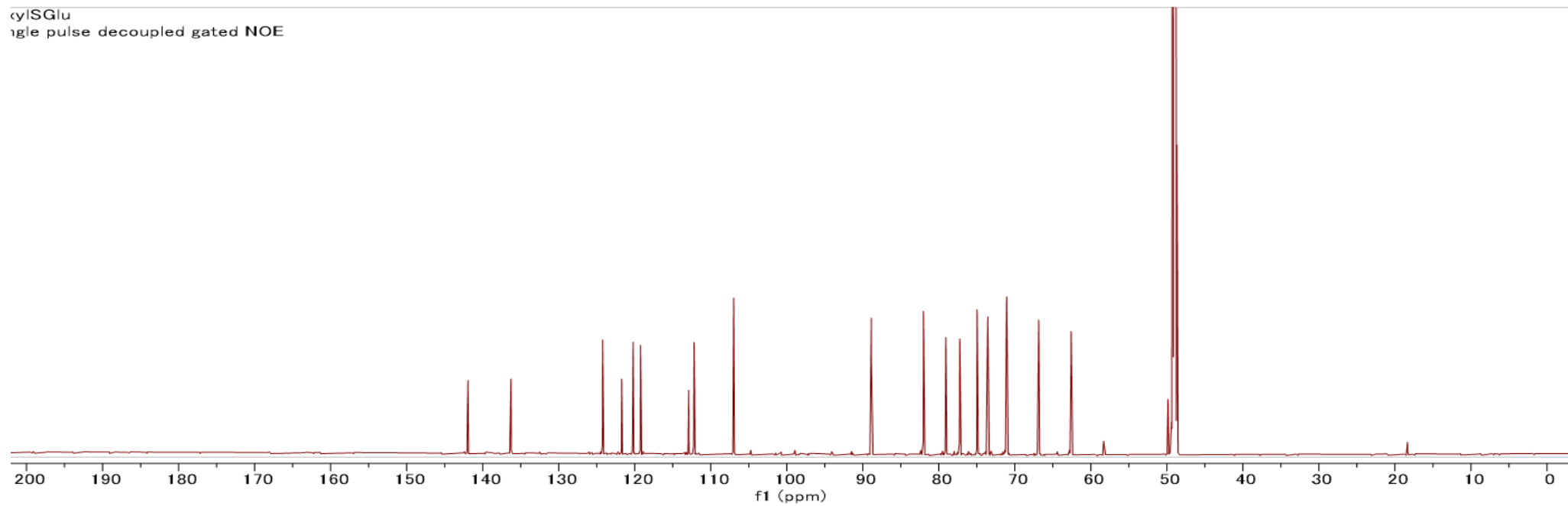
<sup>13</sup>C-NMR (200 MHz, CD<sub>3</sub>OD) of 3-(β-D-Xylopyranosyloxy)-1H-indol-2-yl 1-thio-β-D-glucopyranoside (9d).



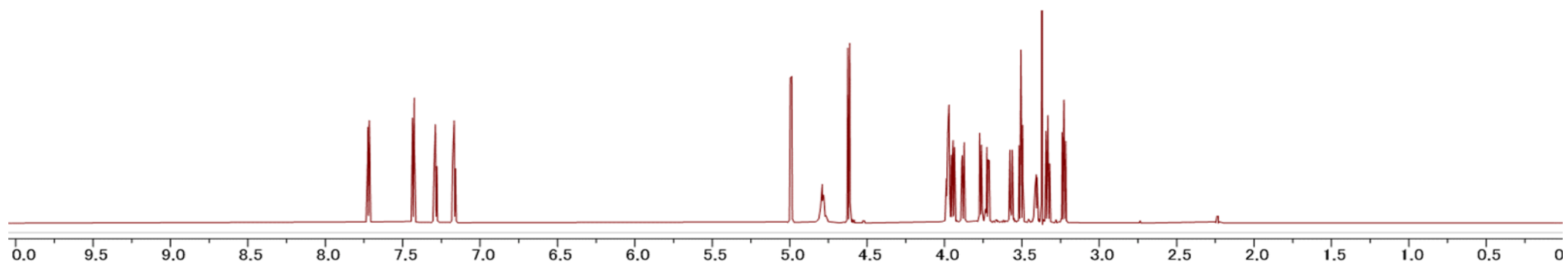
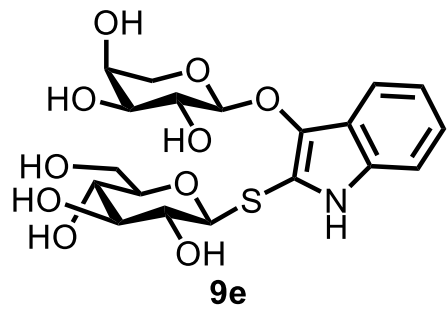
9d



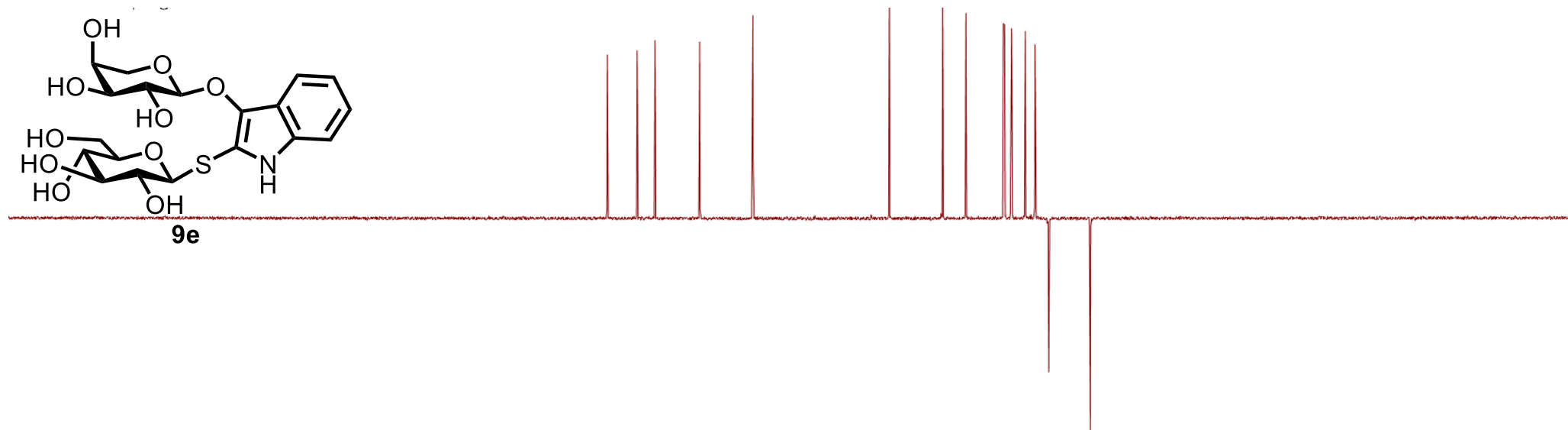
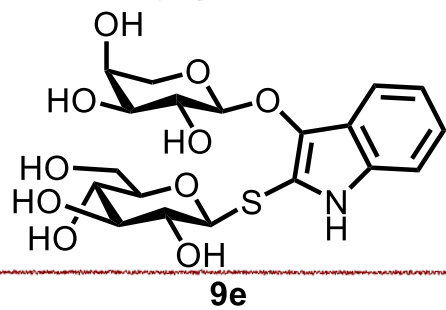
γ|S|Glu  
ngle pulse decoupled gated NOE



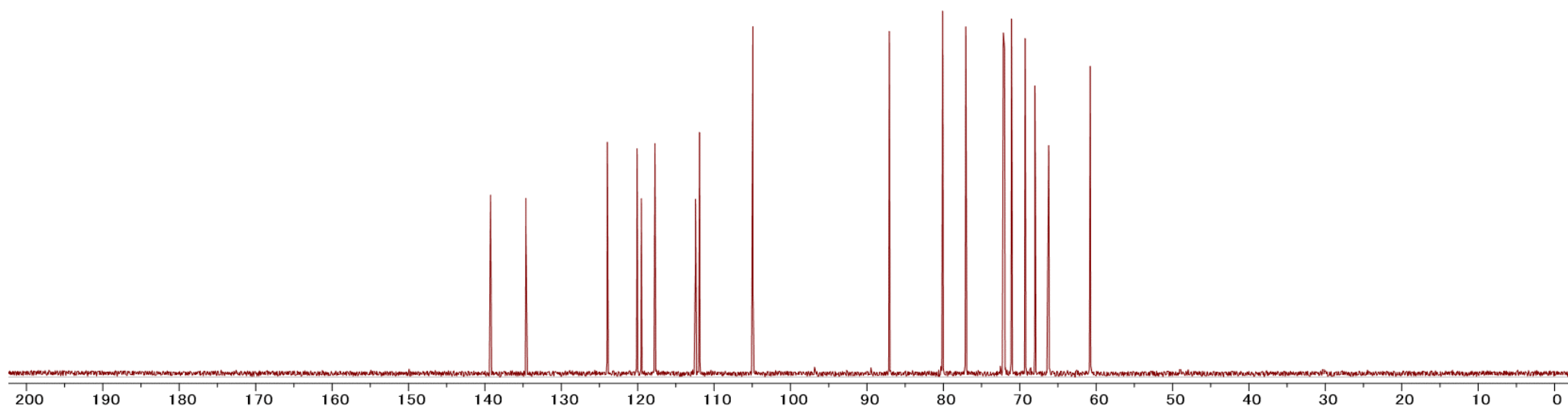
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Arabinopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-glucopyranoside (9e).



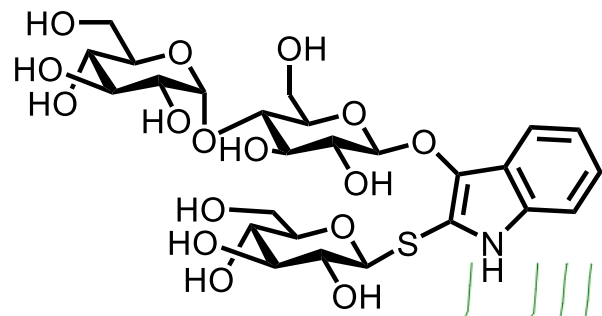
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Arabinopyranosyloxy)-1H-indol-2-yl 1-thio-β-D-gluco-*pyranoside* (**9e**).



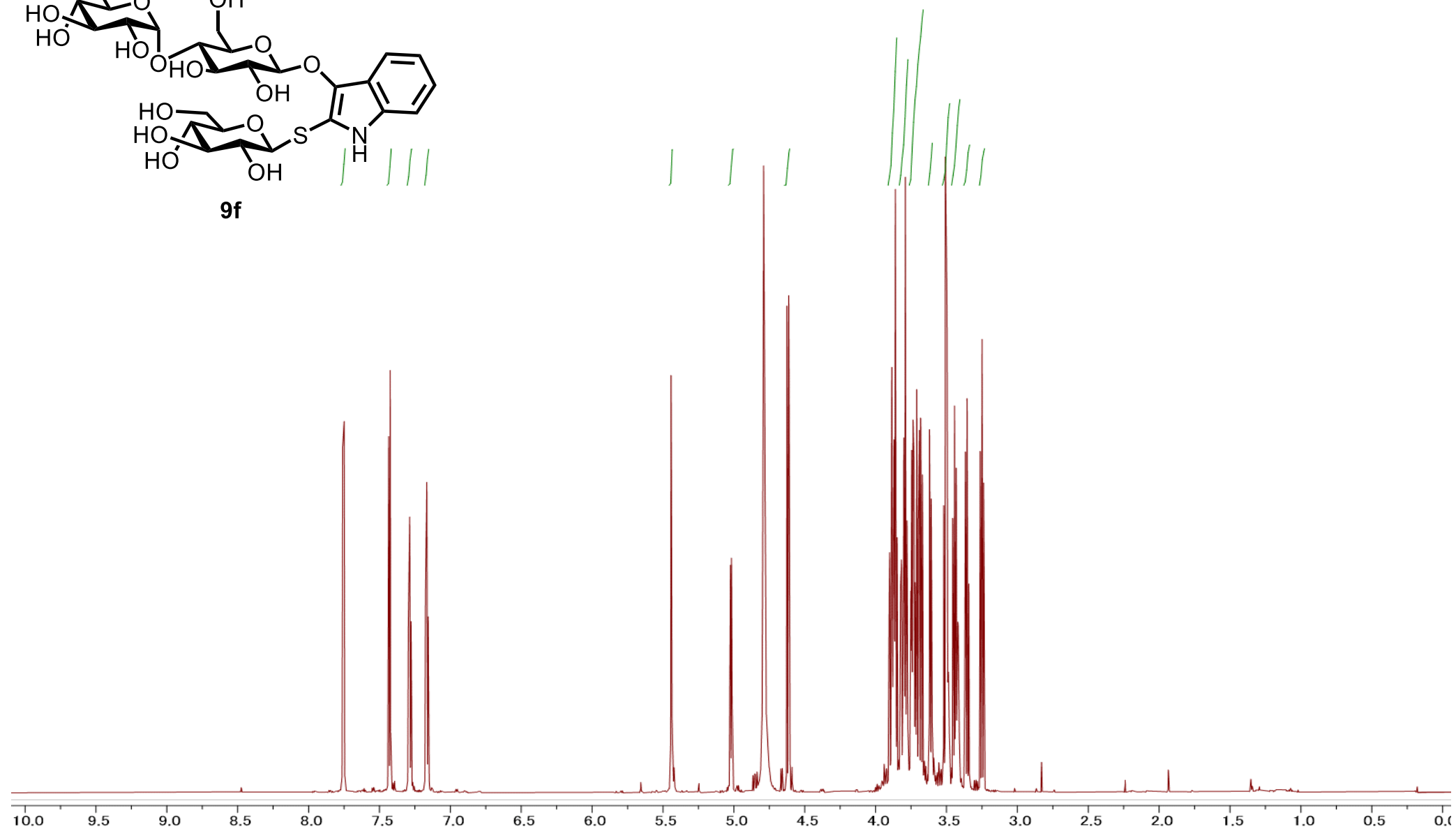
ArabSGlu  
1g pulse decoupled gated NOE



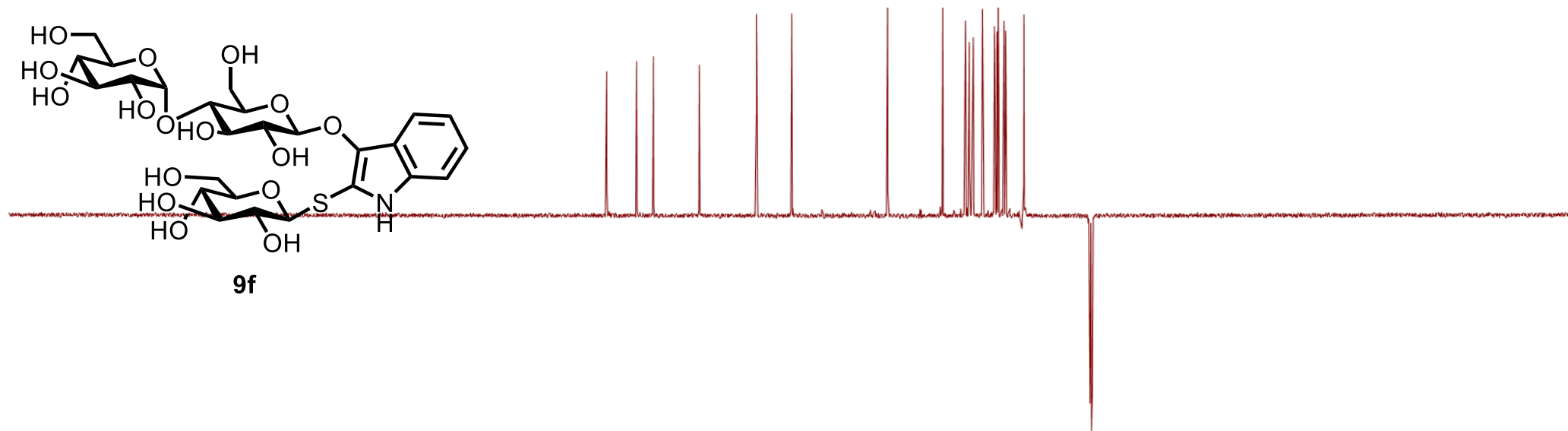
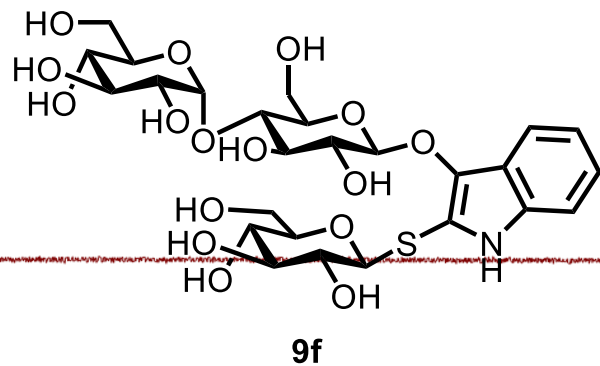
<sup>1</sup>H-NMR (800 MHz, D<sub>2</sub>O) of 3-(β-D-Maltopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-glucopyranoside (9f).



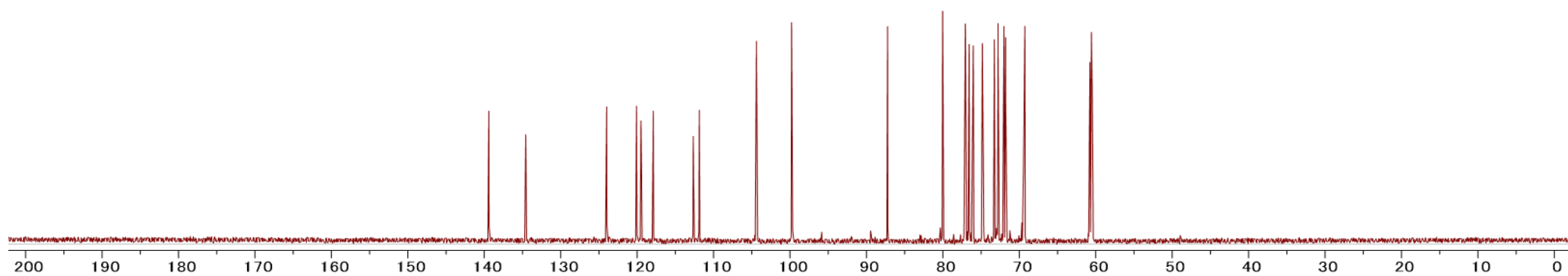
9f



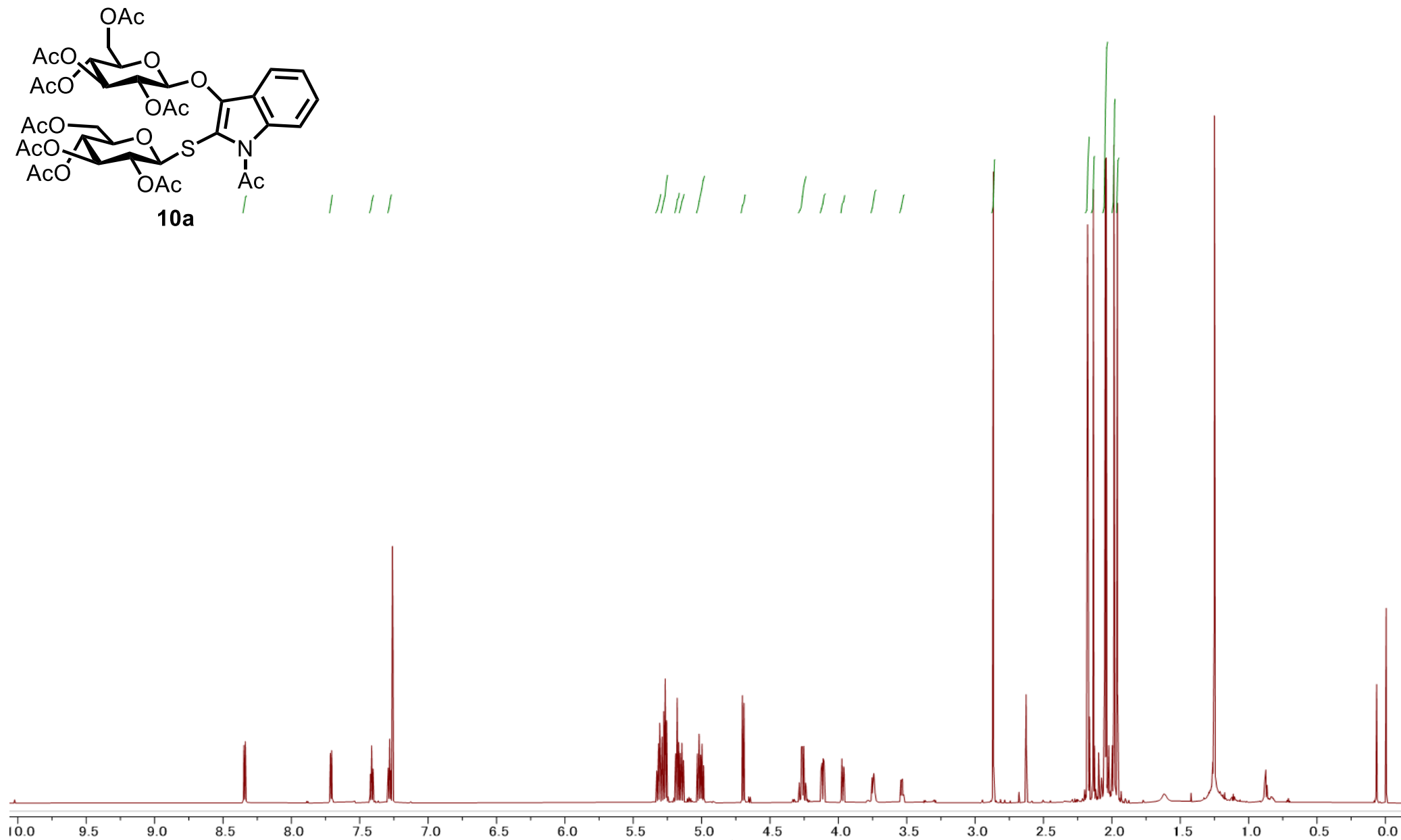
<sup>13</sup>C-NMR (200 MHz, D<sub>2</sub>O) of 3-(β-D-Maltopyranosyloxy)-1*H*-indol-2-yl 1-thio-β-D-glucopyranoside (9f).



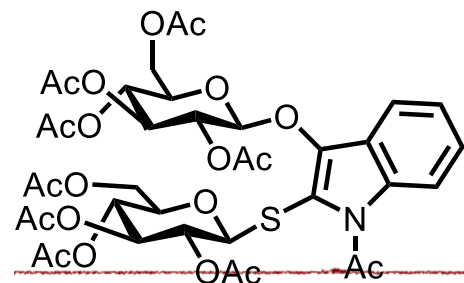
Glu  
pulse decoupled gated NOE



<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 3-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyloxy)-1*H*-indol-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (10a).

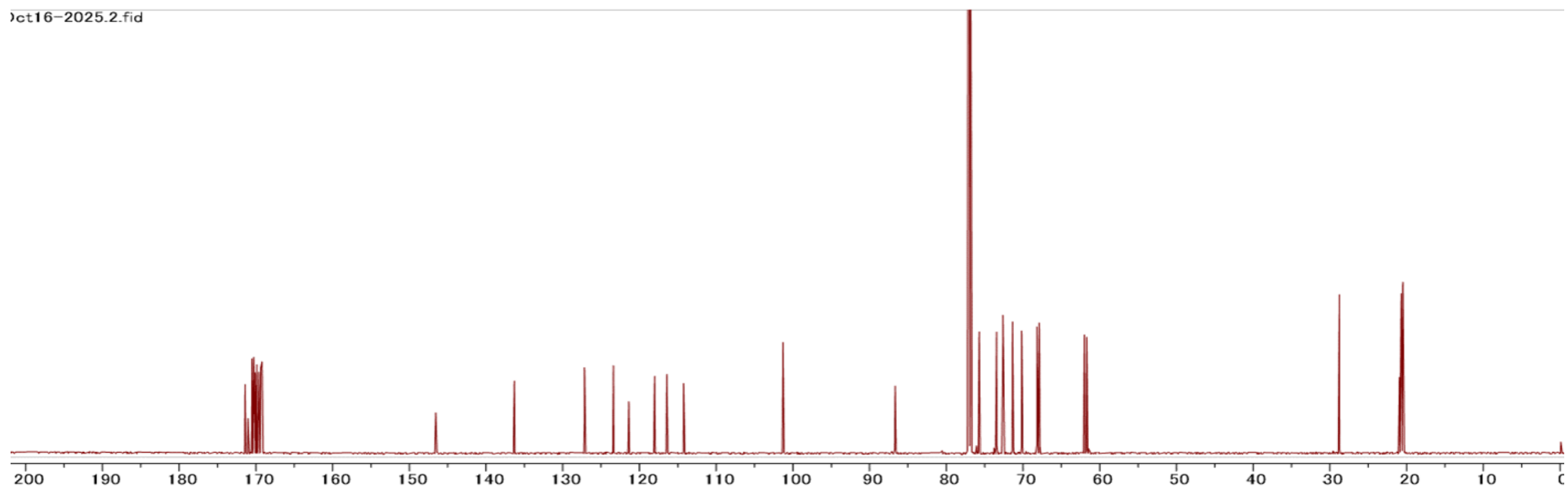


$^{13}\text{C}$ -NMR (200 MHz,  $\text{CDCl}_3$ ) of 3-(2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranosyloxy)-1*H*-indol-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside (10a).

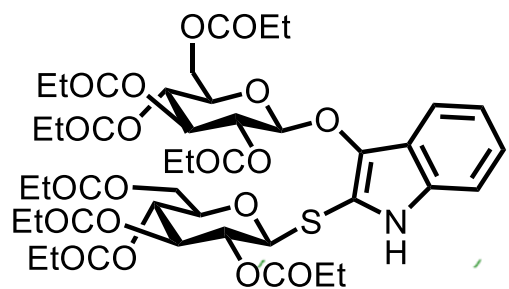


10a

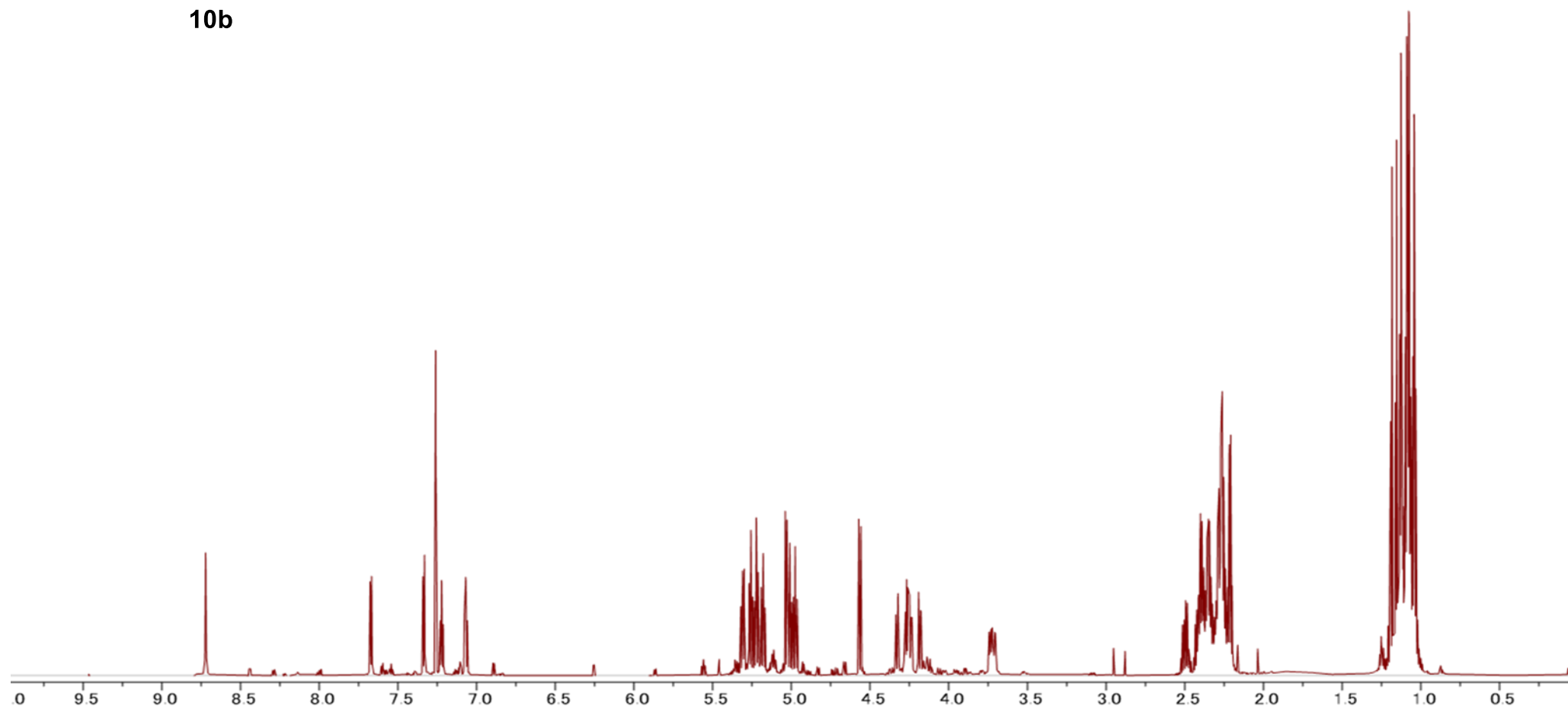
oct16-2025.2.fid



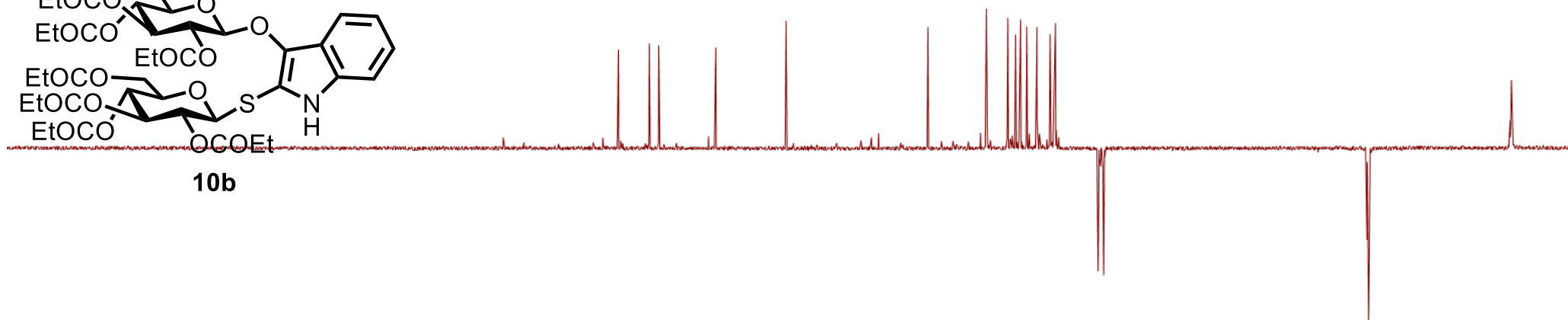
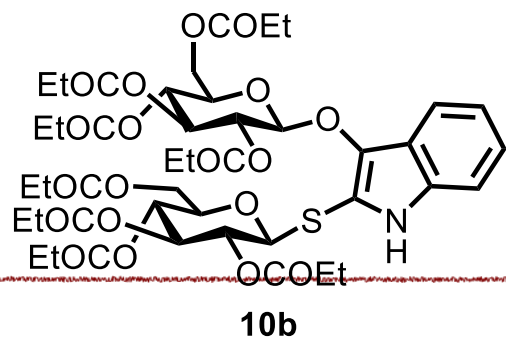
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 3-(2,3,4,6-Tetra-*O*-propionyl-β-D-glucopyranosyloxy)-1*H*-5-indol-2-yl 2,3,4,6-tetra-*O*-propionyl-1-thio-β-D-glucopyranoside (10b).



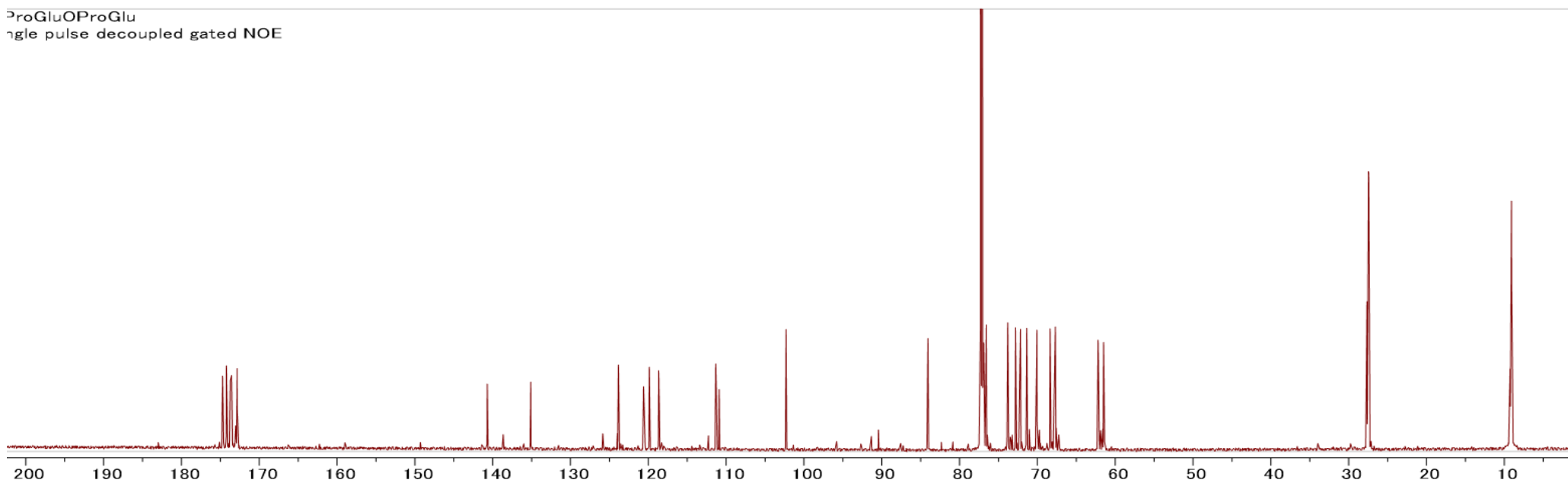
**10b**



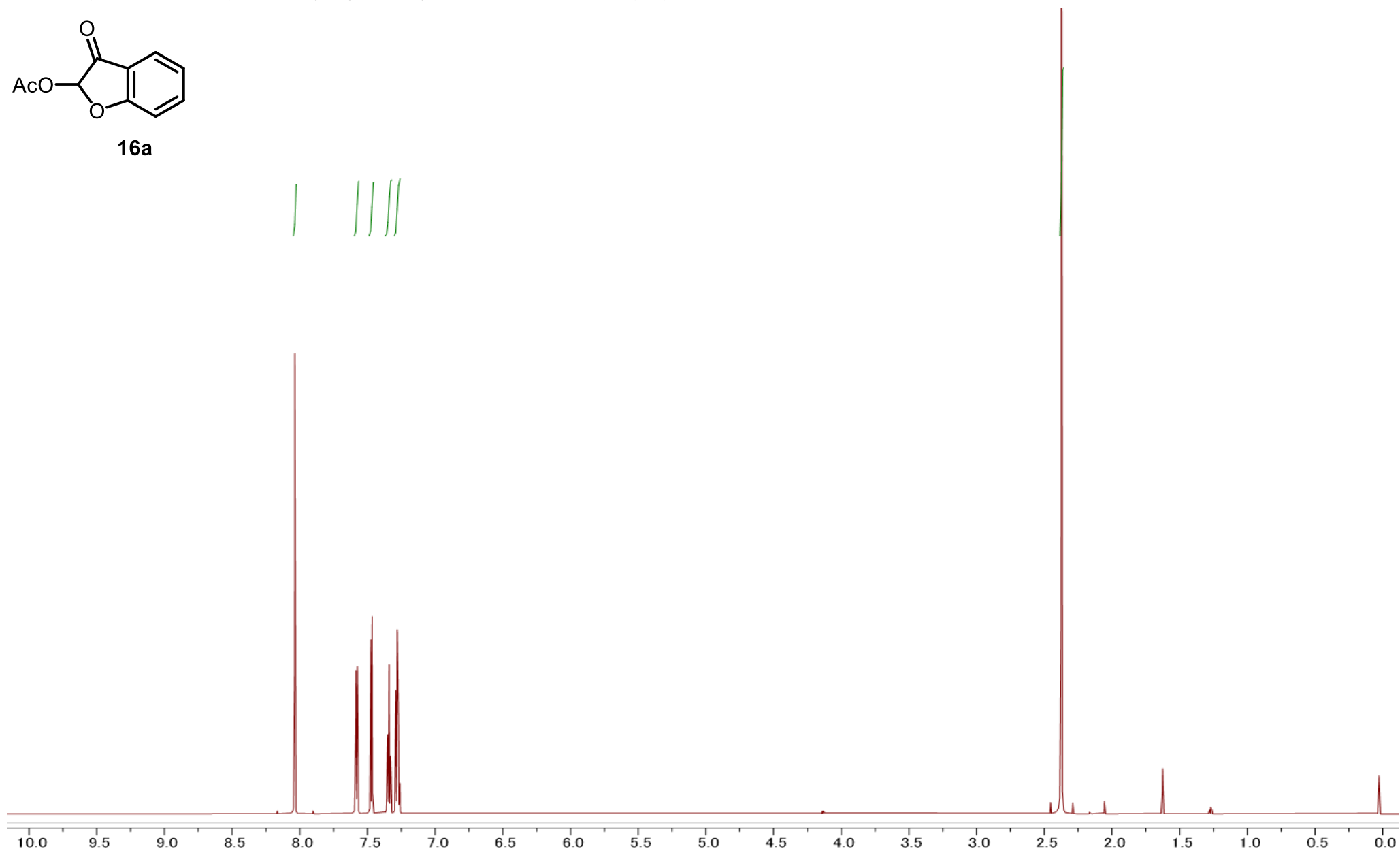
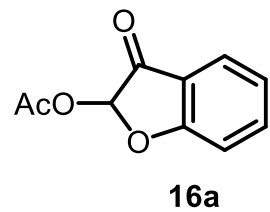
$^{13}\text{C}$ -NMR (200 MHz,  $\text{CDCl}_3$ ) of 3-(2,3,4,6-Tetra-*O*-propionyl- $\beta$ -D-glucopyranosyloxy)-1*H*-5-indol-2-yl 2,3,4,6-tetra-*O*-propionyl-1-thio- $\beta$ -D-glucopyranoside (10b).



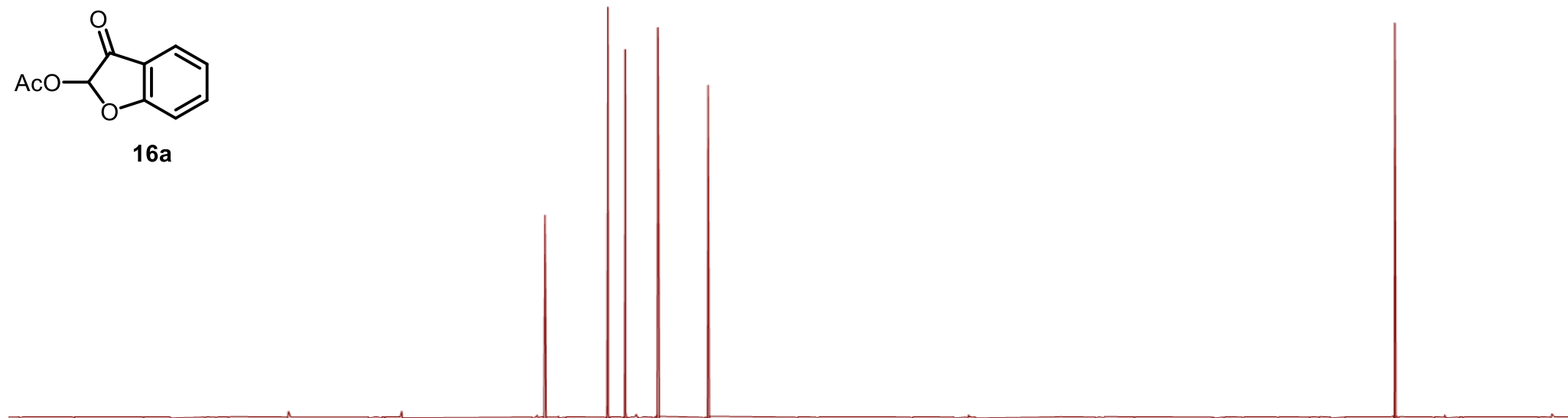
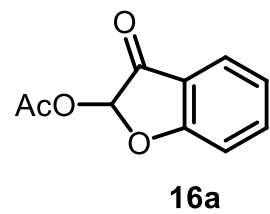
ProGluOProGlu  
angle pulse decoupled gated NOE



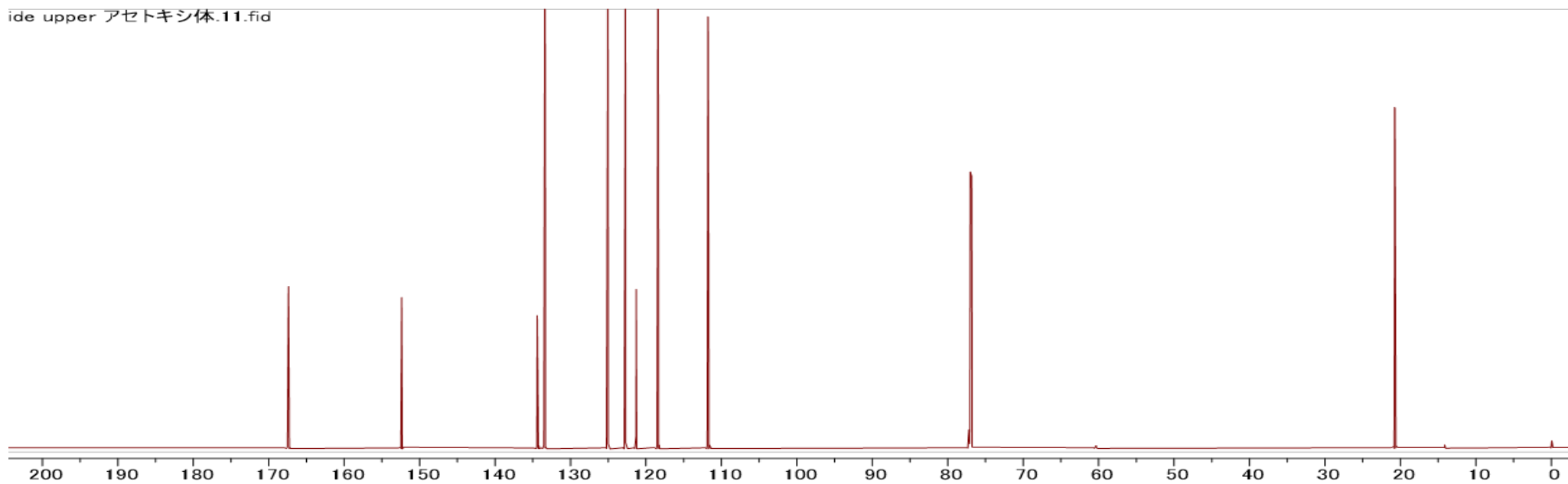
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 2-Acetyloxy-2,3-dihydro-1-benzofuran-3-one (16a).



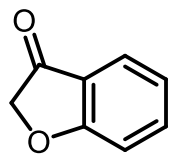
<sup>13</sup>C-NMR (200 MHz, CDCl<sub>3</sub>) of 2-Acetyloxy-2,3-dihydro-1-benzofuran-3-one (16a).



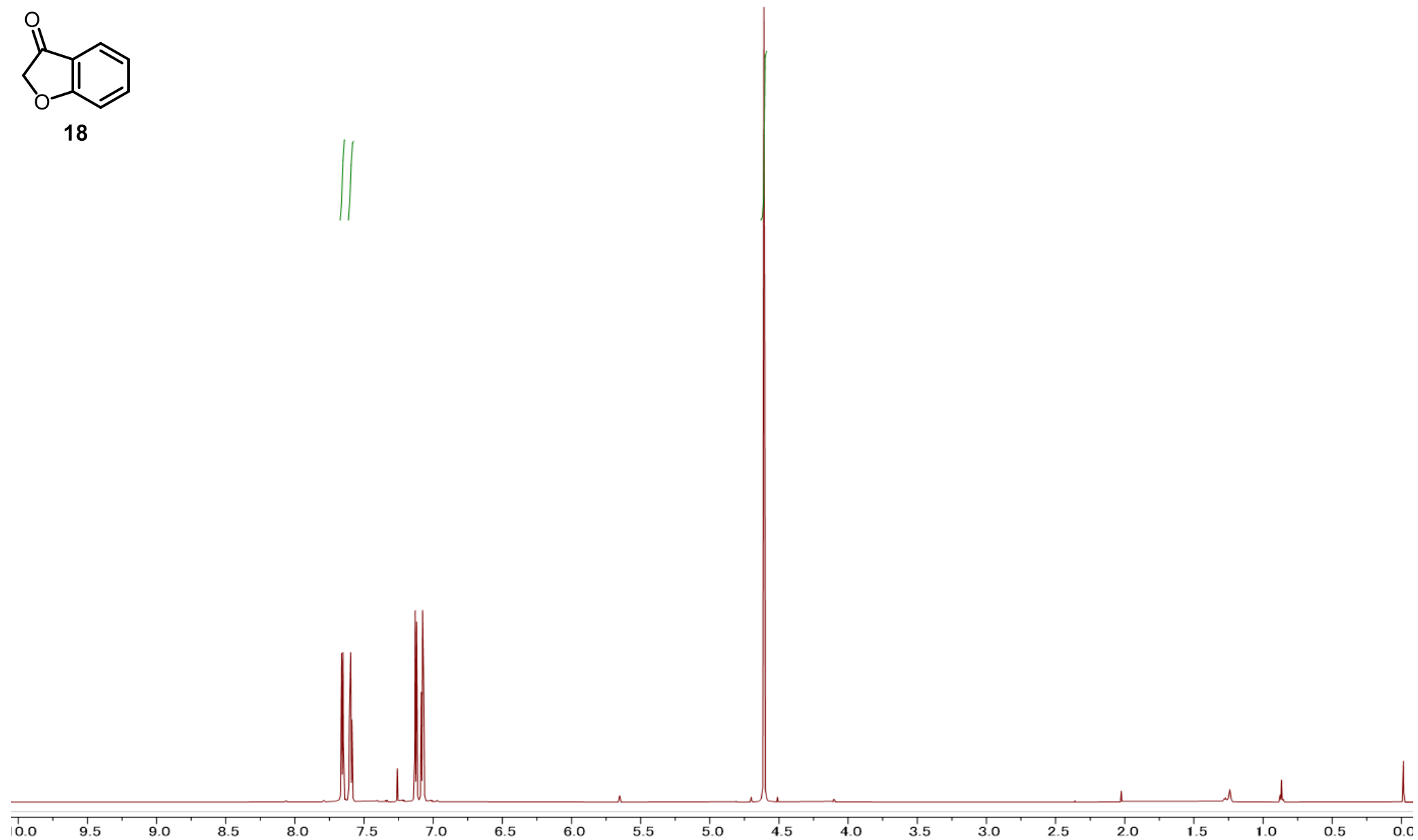
ide upper アセトキシ体.11.fid



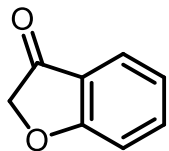
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 2,3-Dihydro-1-benzofuran-3-one (18).



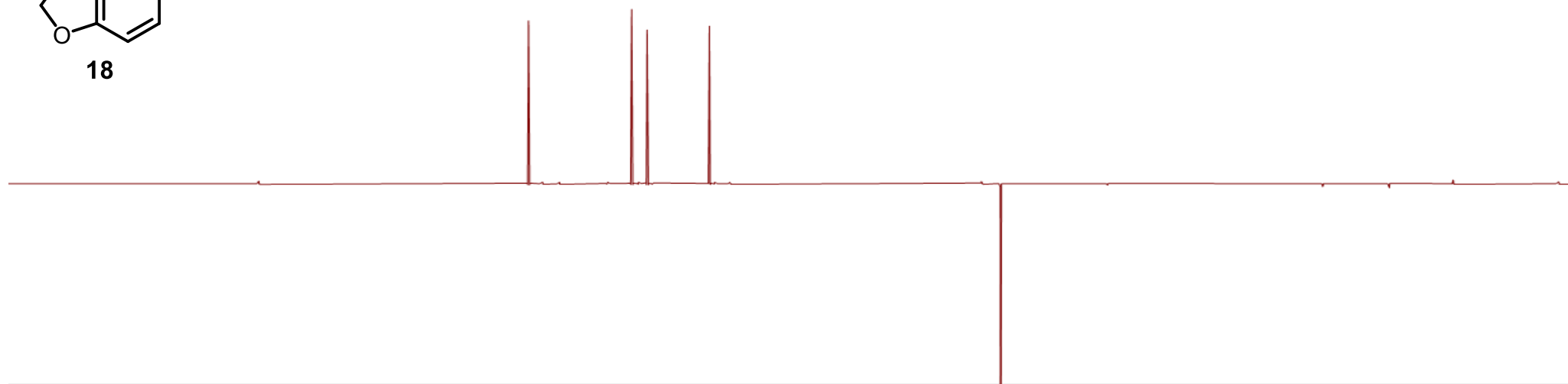
18



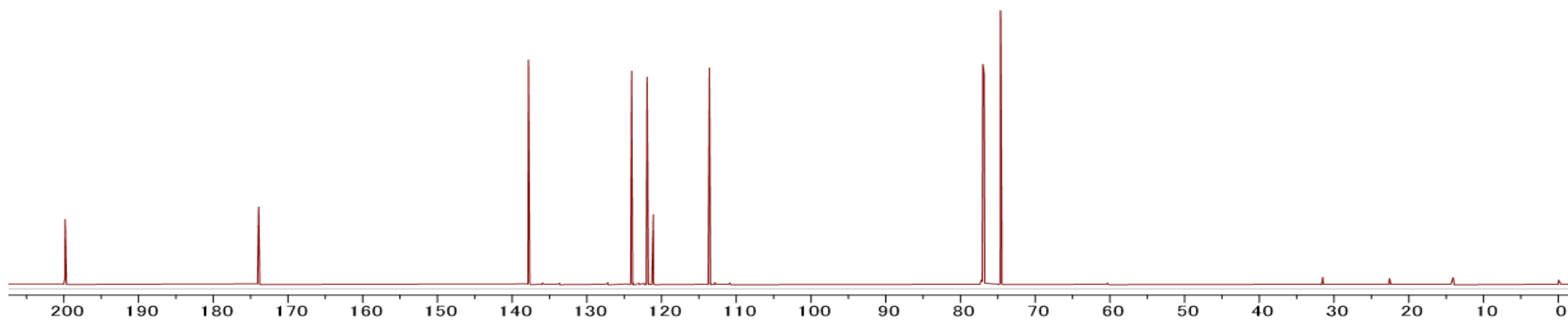
<sup>13</sup>C-NMR (200 MHz, CDCl<sub>3</sub>) of 2,3-Dihydro-1-benzofuran-3-one (18).



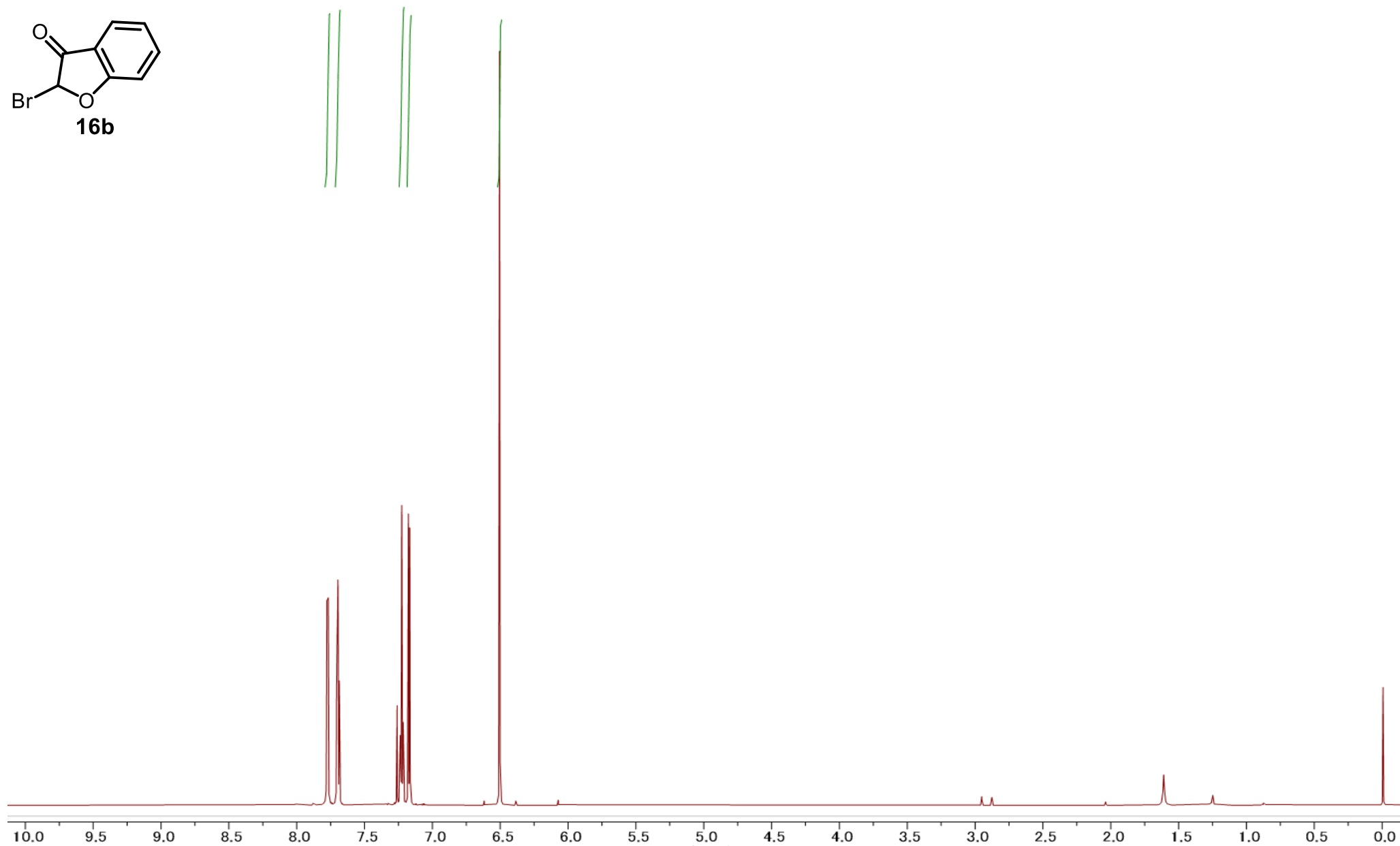
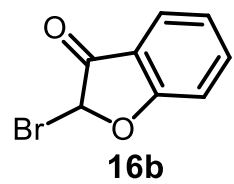
18



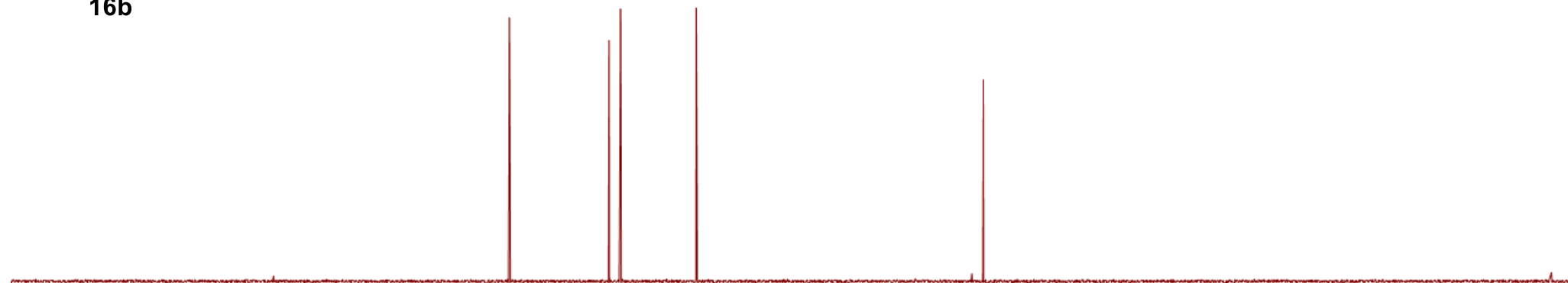
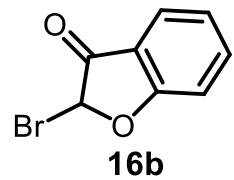
凡体.21.fid



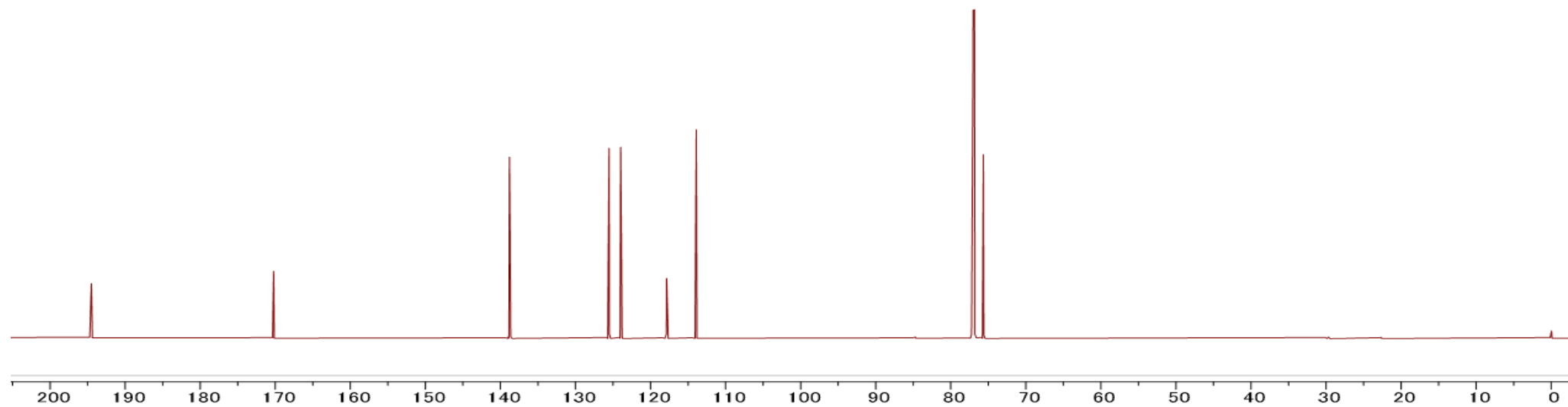
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 2-Bromo-2,3-dihydro-1-benzofuran-3-one (16b).



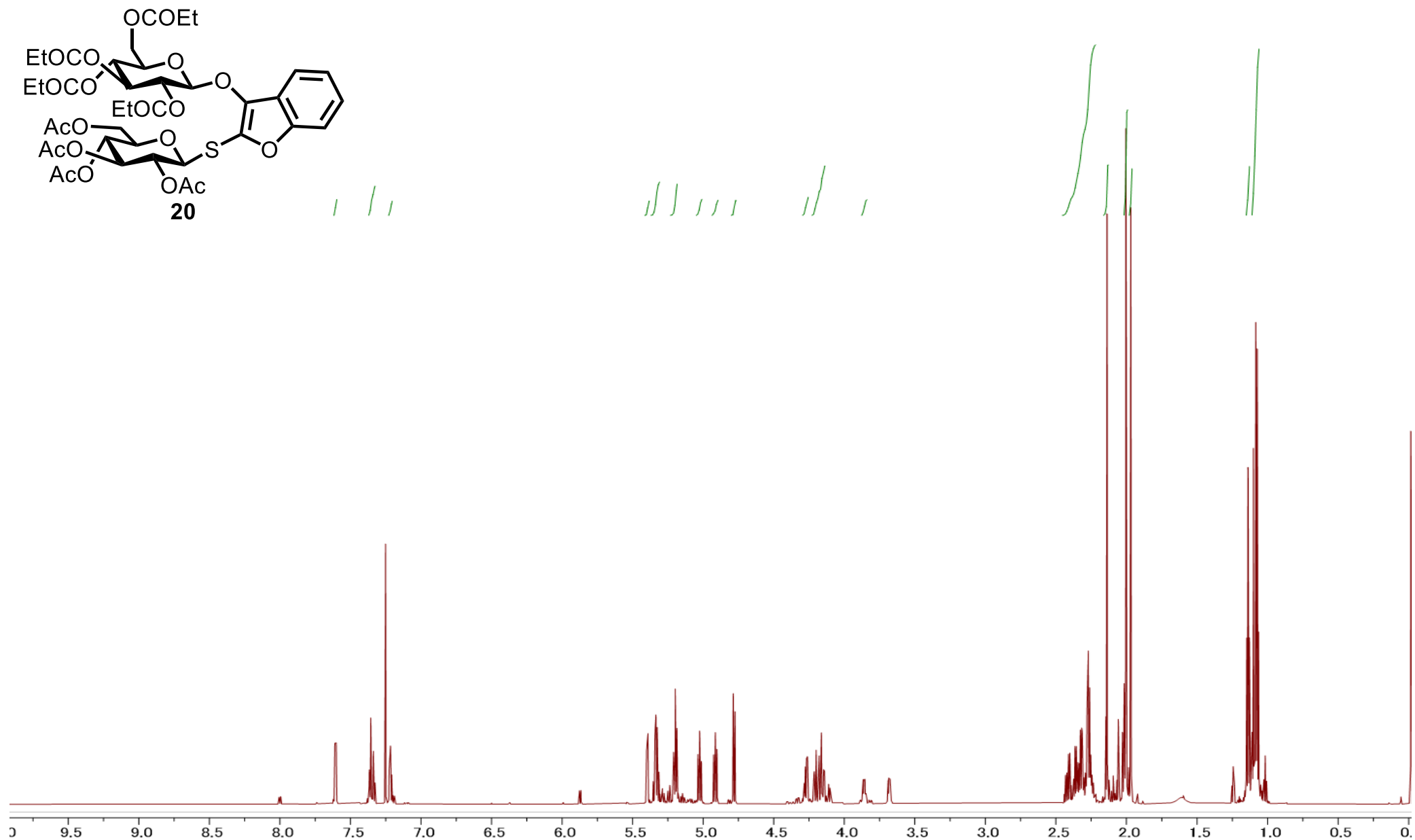
<sup>13</sup>C-NMR (200 MHz, CDCl<sub>3</sub>) of 2-Bromo-2,3-dihydro-1-benzofuran-3-one (16b).



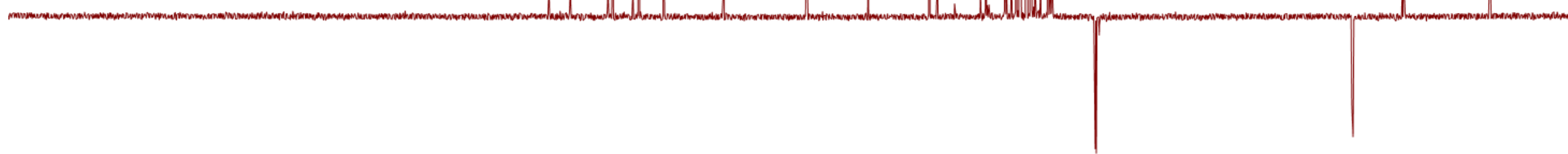
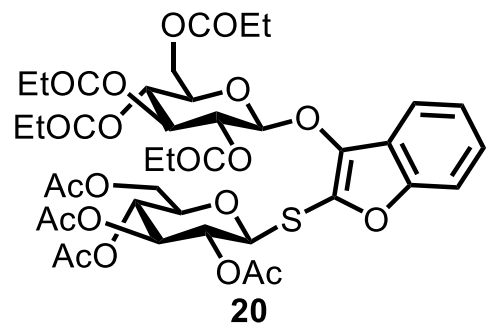
side Br体.41.fid



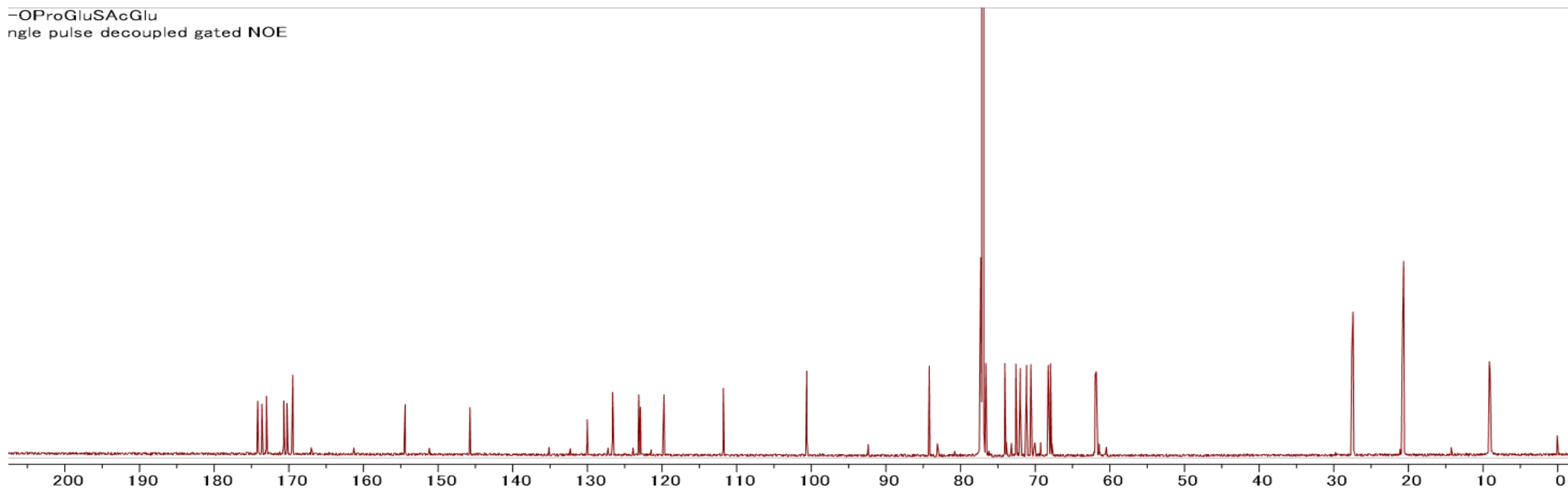
<sup>1</sup>H-NMR (800 MHz, CDCl<sub>3</sub>) of 3-(2,3,4,6-Tetra-*O*-propionyl-β-D-glucopyranosyloxy)-benzofura-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-glucopyranoside (**20**).



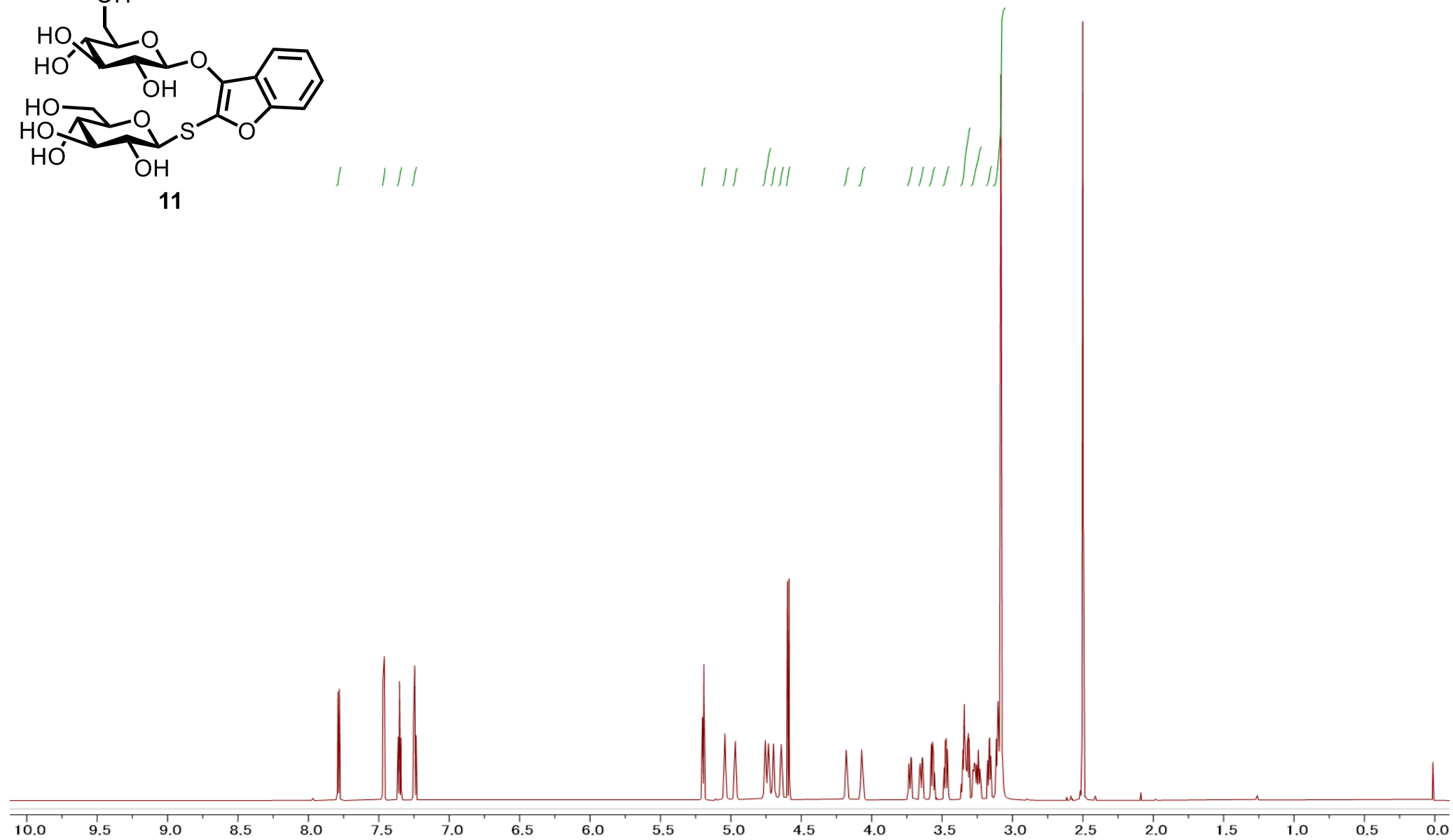
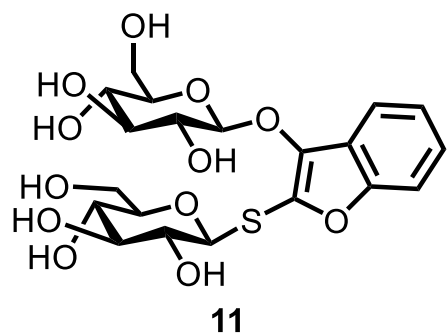
$^{13}\text{C}$ -NMR (200 MHz,  $\text{CDCl}_3$ ) of 3-(2,3,4,6-Tetra-*O*-propionyl- $\beta$ -D-glucopyranosyloxy)-benzofura-2-yl 2,3,4,6-tetra-*O*-acetyl-1-thio- $\beta$ -D-glucopyranoside (20).



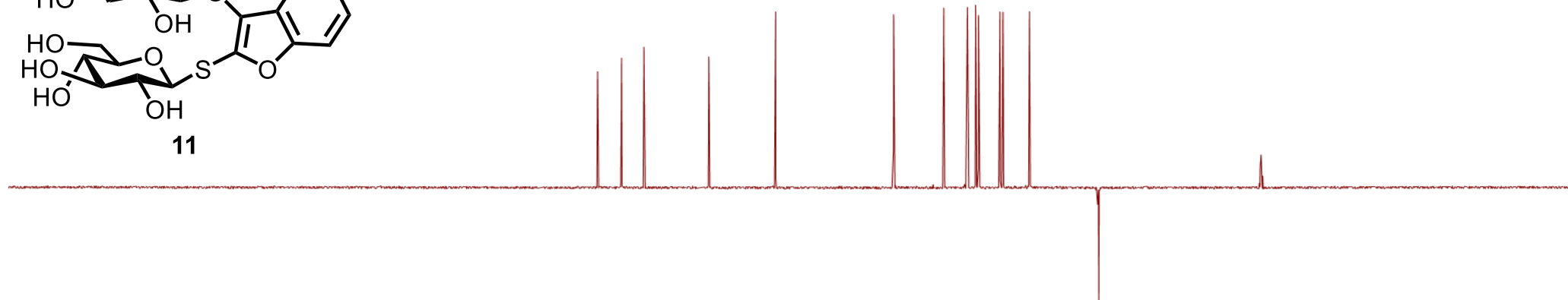
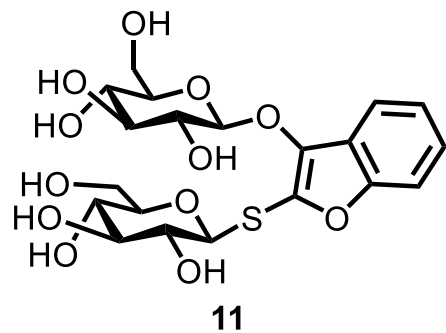
-OProGluSAcGlu  
ngle pulse decoupled gated NOE



<sup>1</sup>H-NMR (800 MHz, DMSO-*d*<sub>6</sub>) of 3-(β-D-Glucopyranosyloxy)benzofuran-2-yl 1-thio-β-D-glucopyranoside (11).



<sup>13</sup>C-NMR (200 MHz, DMSO-*d*<sub>6</sub>) of 3-(β-D-Glucopyranosyloxy)benzofuran-2-yl 1-thio-β-D-glucopyranoside (11).



-GluSGlu  
ngle pulse decoupled gated NOE

