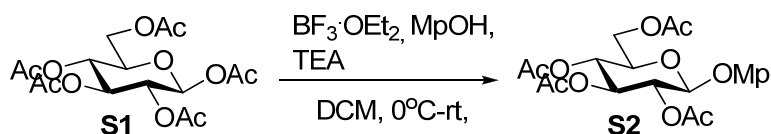


## Supporting Information

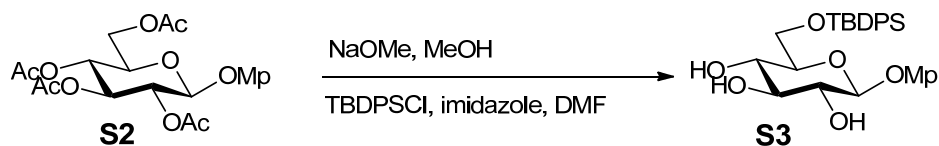
**General procedures.** Commercial reagents were used without further purification unless specialized. Solvents were dried and redistilled prior to use in the usual way. Thin layer chromatography (TLC) was performed on precoated plates of Silica Gel HF254 (0.2mm, Yantai, China). Flash column chromatography was performed on Silica Gel H (10–40 $\mu$ , Yantai, China). Optical rotations were determined with a Perkin–Elmer Model 241 MC polarimeter.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM 400 spectrometer with  $\text{Me}_4\text{Si}$  as the internal standard. Chemical shifts were recorded in  $\delta$  values and  $J$  values were given in Hz. Mass spectra were obtained on a HP5989A or a VG Quatro mass spectrometer.

### *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-glucopyranoside (**S2**)<sup>1</sup>



To a solution of *p*-methoxyphenol (16.0 g, 128.9 mmol), *per-O*-acetyl-D-glucose **S1** (35.0 g, 89.7 mmol) and triethylamine (6.5 mL, 46.6 mmol) in  $\text{CH}_2\text{Cl}_2$  (250 mL) at 0 °C was added  $\text{BF}_3\cdot\text{Et}_2\text{O}$  (28 mL, 221.9 mmol) over a period of 30 min under  $\text{N}_2$ . The reaction mixture was warmed to rt and stirred for 10 h. The mixture was washed with water, aq.  $\text{NaHCO}_3$  and brine subsequently. The organic layer was dried and concentrated to give a pale yellow residue. The residue was subjected to chromatography on silica gel (petroleum ether/ethyl acetate, 6:1–3:1) to afford glucoside **S2** (39.9 g, 98%) as a colorless crystal:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.95 (d,  $J = 9.0$  Hz, 2H), 6.82 (d,  $J = 9.0$  Hz, 2H), 5.32 – 5.20 (m, 2H), 5.16 (t,  $J = 9.3$  Hz, 1H), 4.96 (d,  $J = 7.4$  Hz, 1H), 4.29 (dd,  $J = 12.3, 5.2$  Hz, 1H), 4.17 (dd,  $J = 12.2, 2.1$  Hz, 1H), 3.83–3.79 (m, 1H), 3.77 (s, 3H), 2.08 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H).

### *p*-Methoxyphenyl 6-*O*-*tert*-butyldiphenylsilyl- $\beta$ -D-glucopyranoside (**S3**)<sup>2</sup>

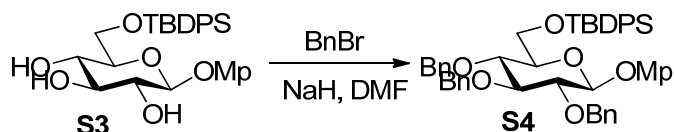


To a solution of tetraacetate **S2** (30.84 g, 67.87 mmol) in MeOH (500 mL) was added a catalytic amount of MeONa. The mixture was stirred at rt for 1 h. Amberlite IR-120 resin (H form) was added to neutralize the solution. Filtration and evaporation of the filtrate gave tetraol (19.41 g) as a white powder.

To a solution of the crude tetraol (6.29 g, 21.98 mmol) in dry DMF (110 mL) were added imidazole (4.50 g, 66.16 mmol) and TBPSCI (8.6 mL, 33.08 mmol) at rt. The mixture was stirred for 2 h. The mixture was quenched with aq.  $\text{NaHCO}_3$  and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with brine, dried over  $\text{Na}_2\text{SO}_4$ . Filtered and concentrated gave a residue, which was purified by flash column chromatography ( $\text{CH}_2\text{Cl}_2/\text{MeOH}$ , 20:1) to give triol **S3** (11.60 g, >99%) as a white solid:  $\delta_{\text{H}}$  (400 MHz,  $\text{CD}_3\text{OD}$ ) 7.65 (d,  $J = 7.5$  Hz, 4H), 7.38–7.21 (m, 6H), 7.00 (d,  $J = 9.0$  Hz, 2H), 6.68 (d,  $J = 9.0$  Hz, 2H), 5.14 (br s, 1H), 4.75 (d,  $J = 7.0$  Hz, 1H), 4.63 (br s, 1H), 4.28 (br s, 1H), 3.98 (dd,  $J = 11.6, 2.4$  Hz, 1H), 3.81 (dd,  $J = 10.9, 5.4$  Hz, 1H), 3.68 (s,

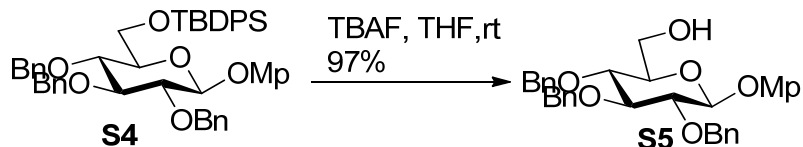
3H), 3.64–3.57 (m, 2H), 3.55–3.44 (m, 2H), 1.01 (s, 9H).

***p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-*tert*-butyldiphenylsilyl-β-D-glucopyranoside (**S4**)<sup>2</sup>**



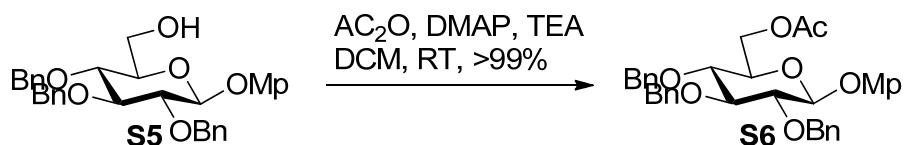
To a solution of triol **S3** (6.93 g, 13.21 mmol) in dry DMF (100 mL) were added 60% NaH (2.39 g, 59.75 mmol) and BnBr (5.5 mL, 46.30 mmol) at 0 °C. The mixture was gradually warmed to rt and stirred for 2 h. The mixture was quenched with triethylamine and brine, and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 20:1) to afford **S4** (7.38 g, 70%) as a colorless syrup:  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.70 (dd,  $J$  = 12.6, 7.3 Hz, 4H), 7.43 – 7.13 (m, 21H), 7.08 (d,  $J$  = 8.9 Hz, 2H), 6.80 (d,  $J$  = 8.9 Hz, 2H), 5.10 (d,  $J$  = 10.9 Hz, 1H), 4.96 (d,  $J$  = 10.8 Hz, 1H), 4.92 – 4.86 (m, 3H), 4.84 (d,  $J$  = 4.8 Hz, 1H), 4.66 (d,  $J$  = 10.7 Hz, 1H), 3.96 (d,  $J$  = 11.0 Hz, 1H), 3.90 (dd,  $J$  = 11.2, 4.4 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.48 (br s, 1H), 1.06 (s, 9H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 154.2, 150.6, 137.4, 137.0, 134.8, 134.5, 128.6, 127.4, 127.1, 127.0, 126.9, 126.8, 126.7, 126.6, 117.5, 113.5, 101.8, 83.7, 81.4, 76.5, 75.0, 74.9, 74.2, 74.1, 61.7, 54.6, 25.8, 18.2.

***p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-β-D-glucopyranoside (**S5**)<sup>2</sup>**



To a solution of **S4** (6.70 g, 8.43 mmol) in dry THF (80 mL) was added TBAF (1 M in THF, 17.0 mL, 17.0 mmol) at room rt. The stirring continued for another 1 h. The mixture was quenched with aq. NaHCO<sub>3</sub> and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 5:1-3:1) to give compound **S5** (4.57 g, 97%) as a white powder:  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.39 – 7.26 (m, 15H), 6.98 (d,  $J$  = 9.0 Hz, 2H), 6.84 (d,  $J$  = 9.0 Hz, 2H), 5.03 (d,  $J$  = 10.9 Hz, 1H), 4.97 (d,  $J$  = 2.4 Hz, 1H), 4.94 (s, 1H), 4.88 (d,  $J$  = 10.9 Hz, 1H), 4.86 – 4.79 (m, 2H), 4.66 (d,  $J$  = 10.9 Hz, 1H), 3.89 (d,  $J$  = 11.1 Hz, 1H), 3.78 (s, 3H), 3.75 – 3.60 (m, 4H), 3.49 – 3.44 (m, 1H).

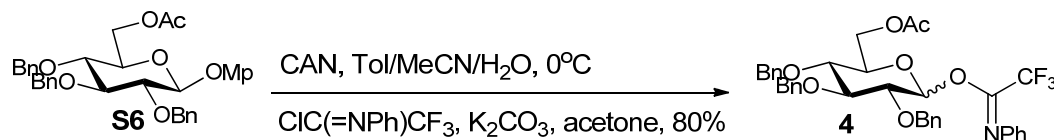
***p*-Methoxyphenyl 2,3,4-tri-*O*-benzyl-6-*O*-acetyl-β-D-glucopyranoside (**S6**)<sup>3</sup>**



To a solution of the alcohol **S5** (4.57 g, 7.63 mmol), DMAP (293 mg, 2.40 mmol) and triethylamine (4.6 mL, 32.77 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added Ac<sub>2</sub>O (1.6 mL, 16.93 mmol). The mixture was stirred for overnight and diluted with CH<sub>2</sub>Cl<sub>2</sub>. The organic layer was washed with aq. NaHCO<sub>3</sub> and brine, dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue

was applied to silica gel column chromatography (petroleum ether/EtOAc, 6:1) to gave **S6** (4.92 g, >99%) as a white solid:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.39 – 7.25 (m, 15H), 7.00 (d,  $J = 8.7$  Hz, 2H), 6.83 (d,  $J = 8.7$  Hz, 2H), 5.06 (d,  $J = 10.9$  Hz, 1H), 4.97 (d,  $J = 10.8$  Hz, 1H), 4.89 (d,  $J = 4.9$  Hz, 1H), 4.87 – 4.79 (m, 3H), 4.59 (d,  $J = 10.9$  Hz, 1H), 4.34 (d,  $J = 11.8$  Hz, 1H), 4.25 (dd,  $J = 11.6$ , 2.5 Hz, 1H), 3.78 (s, 3H), 3.74 – 3.69 (m, 2H), 3.65 – 3.55 (m, 2H), 2.03 (s, 3H).

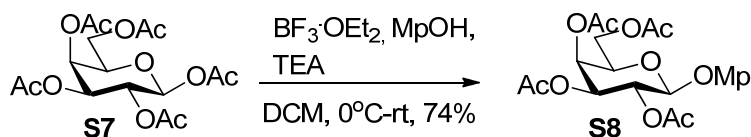
#### 2,3,4-Tri-*O*-benzyl-6-*O*-acetyl- $\beta$ -D-glucopyranosyl *N*-phenyltrifluoroacetimidate (**4**)



To a solution of **S6** (1.52 g, 2.54 mmol) in toluene/ $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (15 mL/25mL/15mL) was added CAN (3.17 g, 5.78 mmol) at  $0^\circ\text{C}$ . The stirring continued for another 1 h. The mixture was then poured into ice water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aq.  $\text{NaHCO}_3$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 3:1) to give a yellow solid (1.02 g).<sup>4,6</sup>

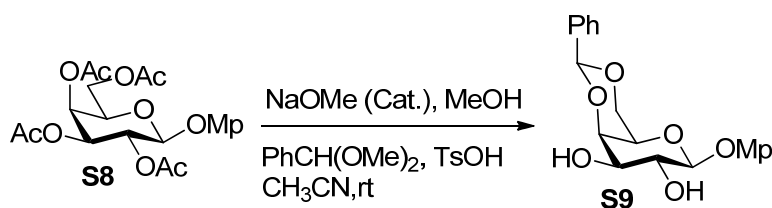
To a mixture of the yellow solid above (1.99 g, 4.04 mmol) and  $\text{K}_2\text{CO}_3$  (1.39 g, 10.06 mmol) in acetone (40 mL), was added  $\text{CIC}(=\text{NPh})\text{CF}_3$  (0.8 mL, 7.27 mmol). After stirring for 3 h, the mixture was filtered through celite and concentrated. Purification of the crude product by flash column chromatography (petroleum ether/EtOAc/TEA, 6:1:0.07) yielded the desired imidate **4** as a colorless syrup (2.63 g, 80% from **S6**). Compound **4** was not characterized due to its poor stability.

#### *p*-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl- $\beta$ -D-galactopyranoside (**S8**)<sup>7</sup>



To a solution of *p*-methoxyphenol (16.5 g, 132.91 mmol), *per*-acetyl-D-galactose **S7** (35.3 g, 90.43 mmol) and triethylamine (6.5 mL, 46.51 mmol) in  $\text{CH}_2\text{Cl}_2$  (250 mL) at  $0^\circ\text{C}$  was added  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (28.5 mL 225.90 mmol) over a period of 30 min under  $\text{N}_2$ . The mixture was warmed to rt and stirred for 10 h. The mixture was washed with water, aq.  $\text{NaHCO}_3$  and brine. The organic phase was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to give a pale yellow residue. The residue was recrystallized from MeOH to afford galactoside **S8** (30.47 g, 74%) as a colorless crystal:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 6.96 (d,  $J = 9.0$  Hz, 2H), 6.82 (d,  $J = 9.0$  Hz, 2H), 5.48 – 5.44 (m, 2H), 5.09 (dd,  $J = 10.5$ , 3.4 Hz, 1H), 4.92 (d,  $J = 8.0$  Hz, 1H), 4.23 (dd,  $J = 11.2$ , 6.9 Hz, 1H), 4.16 (dd,  $J = 11.3$ , 6.5 Hz, 1H), 4.01 (t,  $J = 6.6$  Hz, 1H), 3.78 (s, 3H), 2.18 (s, 3H), 2.09 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H).

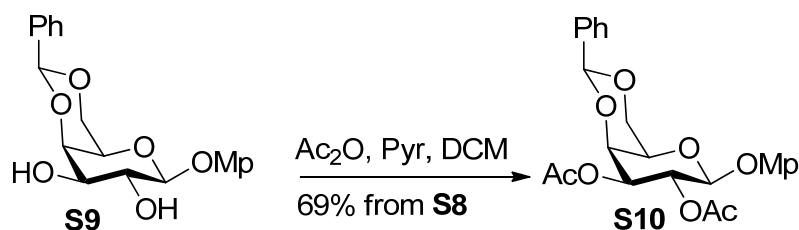
#### *p*-Methoxyphenyl 4,6-*O*-benzylidene- $\beta$ -D-galactopyranoside (**S9**)<sup>8</sup>



To a solution of the tetraacetate **S8** (28.85 g, 63.49 mmol) in MeOH (500 mL) was added a catalytic amount of sodium methoxide. The mixture was stirred at rt for 1 h. Amberlite IR-120 resin (H form) was added to neutralize the solution. Filtration and evaporation gave a tetraol (about 18 g) as a white powder.

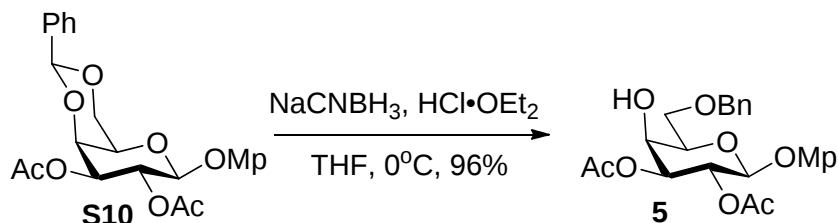
To a solution of the tetraol above and  $\alpha,\alpha$ -dimethoxytoluene (14.5 mL, 96.68 mmol) in  $\text{CH}_3\text{CN}$  (500 mL) was added *p*-toluenesulfonic acid monohydrate (0.64 g, 3.36 mmol) at rt. After stirring for 30 min, the reaction mixture was cooled and quenched with  $\text{Et}_3\text{N}$  (3 mL). Filtration and evaporation gave **S9** as a crystal:  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.52 (dd,  $J = 6.5, 2.9$  Hz, 2H), 7.41 – 7.34 (m, 3H), 7.07 (d,  $J = 9.0$  Hz, 2H), 6.83 (d,  $J = 9.0$  Hz, 2H), 5.58 (s, 1H), 4.80 (d,  $J = 7.8$  Hz, 1H), 4.37 (d,  $J = 12.5$  Hz, 1H), 4.28 (d,  $J = 3.7$  Hz, 1H), 4.11 (dd,  $J = 12.5, 1.6$  Hz, 1H), 4.01 (t,  $J = 8.6$  Hz, 1H), 3.83 – 3.72 (m, 1H), 3.78 (s, 3H), 3.59 (s, 1H), 2.67 – 2.51 (m, 2H).

#### *p*-Methoxyphenyl 2,3-*O*-acetyl-4,6-*O*-benzylidene- $\beta$ -D-galactopyranoside (**S10**)<sup>9</sup>



To a solution of diol **S9** in  $\text{CH}_2\text{Cl}_2$ /pyridine (300/100 mL) was added  $\text{Ac}_2\text{O}$  (18 mL, 190.42 mmol) at  $0^\circ\text{C}$ . The mixture was gradually warmed to rt and stirred for 10 h. The reaction was quenched by MeOH (30 mL). Concentration and recrystallization from petroleum ether/ethyl acetate afforded **S10** as a white solid (20.0 g, 69% from **S8**):  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.57 – 7.31 (m, 5H), 6.99 (d,  $J = 9.0$  Hz, 2H), 6.81 (d,  $J = 9.0$  Hz, 2H), 5.61 (dd,  $J = 10.4, 8.0$  Hz, 1H), 5.52 (s, 1H), 5.03 (dd,  $J = 10.4, 3.6$  Hz, 1H), 4.95 (d,  $J = 8.0$  Hz, 1H), 4.43 (d,  $J = 3.5$  Hz, 1H), 4.37 (d,  $J = 12.5$  Hz, 1H), 4.09 (d,  $J = 12.5$  Hz, 1H), 3.77 (s, 3H), 3.60 (s, 1H), 2.09 (s, 3H), 2.08 (s, 3H).

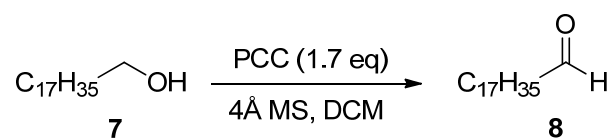
#### *p*-Methoxyphenyl 2,3-*O*-acetyl-6-*O*-benzyl- $\beta$ -D-galactopyranoside (**5**)<sup>10</sup>



To a mixture of compound **S10** (7.4g, 16.14 mmol),  $\text{NaCNBH}_3$  (8.0 g, 120.58 mmol) and 4 Å molecular sieves (7 g) in dry THF (150 mL) was added dropwise a cold saturated solution of  $\text{HCl}\cdot\text{Et}_2\text{O}$  until no more gas was bubbled. After stirring for 2 h, the reaction was quenched by adding solid  $\text{NaHCO}_3$  (12 g). The mixture was diluted with  $\text{CH}_2\text{Cl}_2$  (300 mL) and  $\text{H}_2\text{O}$  (100 mL),

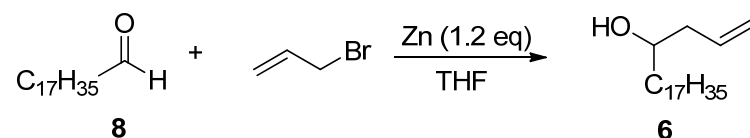
and was then filtered through celite. The organic layer was washed with aq. NaHCO<sub>3</sub> (150 mL) and brine (150 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, 3:1) to give compound **5** (7.1 g, 96%) as a white powder:  $[\alpha]_D^{27} = 4.78$  (c 1.01, CHCl<sub>3</sub>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.40 – 7.27 (m, 5H), 6.97 (d,  $J = 8.9$  Hz, 2H), 6.79 (d,  $J = 8.9$  Hz, 2H), 5.51 (dd,  $J = 10.0, 8.2$  Hz, 1H), 5.01 (dd,  $J = 10.2, 3.0$  Hz, 1H), 4.91 (d,  $J = 7.9$  Hz, 1H), 4.63 – 4.51 (m, 2H), 4.20 (s, 1H), 3.86 – 3.77 (m, 3H), 3.76 (s, 3H), 2.76 (d,  $J = 4.4$  Hz, 1H), 2.12 (s, 3H), 2.07 (s, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 170.2, 169.5, 155.3, 151.0, 137.6, 128.3, 127.7, 127.5, 118.4, 114.4, 100.6, 73.5, 73.5, 73.3, 69.2, 69.0, 67.6, 55.5, 20.7, 20.6.

### 1-Octadecanal (**8**)<sup>11</sup>



To a mixture of PCC (4.83 g, 22.39 mmol) and molecular sieves 4Å (5.4 g) in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) was added 1-octadecanol **7** (3.62 g, 13.36 mmol) under N<sub>2</sub>. The mixture was stirred at rt for 3 h, and was then concentrated. The resulting oil was applied to flash chromatography (petroleum ether/EtOAc, 20:1) to give 1-octadecanal **8** (2.23 g, 62%) as a white solid:  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 9.77 (t,  $J = 1.7$  Hz, 1H), 2.42 (td,  $J = 7.4, 1.7$  Hz, 2H), 1.67 – 1.60 (m, 2H), 1.25 (s, 34H), 0.88 (t,  $J = 6.7$  Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.1, 44.0, 32.0, 29.72, 29.69, 29.6, 29.5, 29.4, 22.7, 22.1, 14.2.

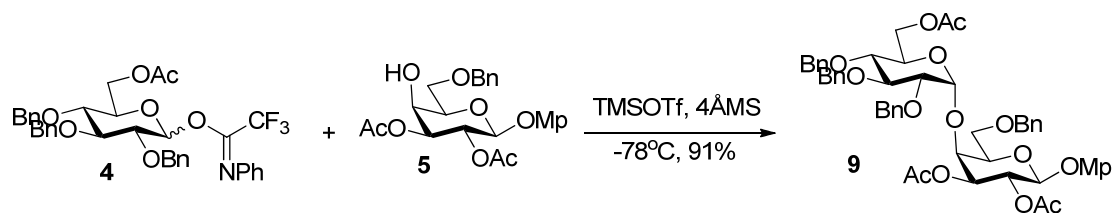
### 1-heneicosen-4-ol (**6**)<sup>12</sup>



To a solution of octadecanal **8** (2.13 g, 7.93 mmol) in anhydrous THF under Ar were added allyl bromide (0.81 mL, 9.57 mmol) and zinc powder (623 mg, 9.52 mmol). The mixture was stirred at rt for 16 hours, and then poured into saturated aq. NH<sub>4</sub>Cl and extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated. The residue was purified by chromatography on silica gel (petroleum ether/ethyl acetate, 40:1) to afford **6** (1.87 g, 6.02 mmol, 76%) as a white solid:  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 5.95 – 5.73 (m, 1H), 5.15 (d,  $J = 2.9$  Hz, 1H), 5.12 (s, 1H), 3.64 (d,  $J = 3.0$  Hz, 1H), 2.36 – 2.22 (m, 1H), 2.19 – 2.07 (m, 1H), 1.62 – 1.55 (m, 1H), 1.47 (m, 2H), 1.25 (s, 30H), 0.88 (t,  $J = 6.8$  Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 135.0, 118.1, 70.7, 42.0, 36.8, 32.0, 29.73, 29.69, 29.6, 29.4, 25.7, 22.7, 14.2.

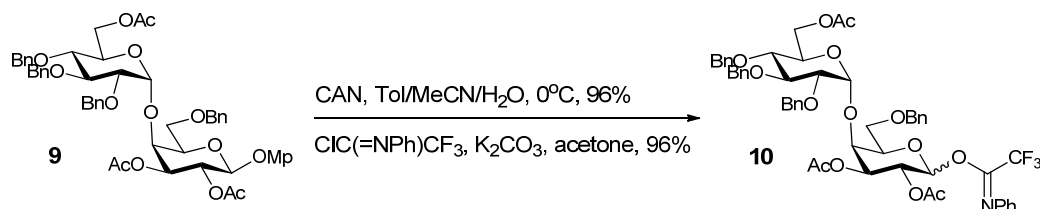
### *p*-Methoxyphenyl

**2,3-O-acetyl-6-O-benzyl-4-O-(2,3,4-tri-O-benzyl-6-O-acetyl- $\beta$ -D-glucopyranosyl)- $\beta$ -D-galactopyranoside (**9**)**



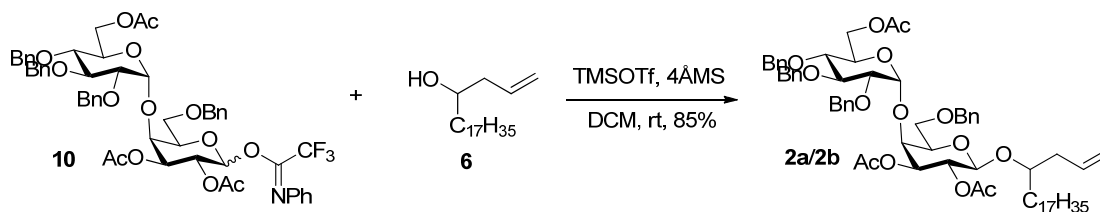
To a stirred mixture of the donor **4** (2.03 g, 3.06 mmol), acceptor **5** (1.03 g, 2.24 mmol), and freshly activated 4 Å MS (3.5 g) in dry  $\text{CH}_2\text{Cl}_2$  (55 mL) at  $-78^\circ\text{C}$ , was added TMSOTf (50  $\mu\text{L}$ , 0.27 mmol) under Ar. After stirring for 2 h, the mixture was allowed to warm up gradually to rt. The mixture was quenched with  $\text{Et}_3\text{N}$  (0.2 mL), filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/ $\text{EtOAc}$ , 4:1) to afford **9** (1.87 g, 91%) as a white solid:  $[\alpha]_D^{23} = 44.37$  (c 0.92,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.37 – 7.16 (m, 20H), 7.00 (d,  $J = 8.9$  Hz, 2H), 6.79 (d,  $J = 9.0$  Hz, 2H), 5.47 (dd,  $J = 10.5$ , 7.9 Hz, 1H), 4.98 – 4.83 (m, 5H), 4.78 (d,  $J = 3.3$  Hz, 1H), 4.76 (d,  $J = 12.1$  Hz, 1H), 4.62 (dd,  $J = 11.4$ , 3.6 Hz, 2H), 4.34 (d,  $J = 1.3$  Hz, 2H), 4.30 – 4.21 (m, 3H), 4.18 – 4.10 (m, 3H), 3.84 (t,  $J = 5.8$  Hz, 2H), 3.75 (s, 3H), 3.58 (t,  $J = 9.6$  Hz, 1H), 3.49 (dd,  $J = 9.8$ , 3.1 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 2.01 (s, 3H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 170.8, 170.6, 169.2, 155.4, 151.2, 138.5, 138.1, 1378.0, 128.42, 128.40, 128.3, 128.0, 128.0, 127.7, 127.6, 127.5, 118.4, 114.5, 100.6, 100.2, 81.7, 80.4, 75.7, 74.9, 74.5, 73.7, 73.1, 73.0, 69.7, 62.7, 55.6, 21.0, 20.8, 20.7; HRMS(MALDI) calcd for  $\text{C}_{53}\text{H}_{58}\text{O}_{15}\text{Na}$   $[\text{M}+\text{Na}]^+$  957.3668, found 957.3660.

### 2,3-O-Acetyl-6-O-benzyl-4-O-(2,3,4-tri-O-benzyl-6-O-acetyl- $\beta$ -D-galactopyranosyl)- $\beta$ -D-galactopyranosyl N-phenyltrifluoroacetimidate (**10**)



To a solution of **9** (2.09 g, 2.24 mmol) in toluene/ $\text{CH}_3\text{CN}/\text{H}_2\text{O}$  (25 mL/37mL/25mL) was added CAN (3.08 g, 5.62 mmol) at  $0^\circ\text{C}$ . After stirring for 1 h, the mixture was poured into ice water and extracted with  $\text{CH}_2\text{Cl}_2$ . The organic layer was washed with aq.  $\text{NaHCO}_3$  and brine, dried over  $\text{Na}_2\text{SO}_4$ , filtered and concentrated. The residue was purified by silica gel column chromatography (petroleum ether/ $\text{EtOAc}$ , 1.5:1) to give the corresponding lactol (1.78 g, 96%) as a yellow solid. To a solution of the crude lactol (1.73 g, 2.08 mmol) and  $\text{K}_2\text{CO}_3$  (0.71 g, 5.17 mmol) in acetone (35 mL) was added  $\text{ClC(=NPh)CF}_3$  (0.35 mL, 3.17 mmol). After stirring for 3 h, the mixture was filtered through celite and concentrated. Purification of the crude product by flash column chromatography (petroleum ether/ $\text{EtOAc}/\text{TEA}$ , 3:1:0.04) yielded **10** (2.00 g, 96% from **9**) as a colorless syrup. Compound **9** was used directly without further characterization due to its poor stability.

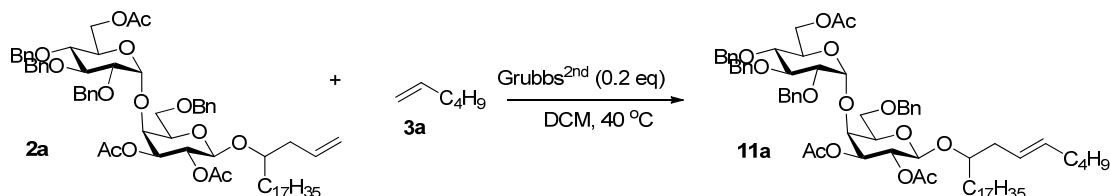
### Compounds 2a/2b



To a stirred mixture of the donor **10** (2.00 g, 2.00 mmol), acceptor **6** (0.55 g, 1.77 mmol), and freshly activated 4 Å MS (3.1 g) in dry CH<sub>2</sub>Cl<sub>2</sub> (50 mL) at 0 °C, was added TMSOTf (40 µL, 0.220 mmol) under argon. After stirring for 1 h, the reaction was allowed to warm to rt gradually and the stirring continued for another 1.5 h. The mixture was quenched with Et<sub>3</sub>N (0.2 mL), filtered, and concentrated in vacuo. The residue was purified by silica gel column chromatography (petroleum ether/EtOAc, 5:1-3:1) to afford **2a/2b** (1.68 g, d.r. = 1.1:1, 85%). **2a** was obtained as a colorless syrup:  $[\alpha]_D^{26} = 51.09$  (*c* 1.08, CHCl<sub>3</sub>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.39 – 7.06 (m, 20H), 5.91 – 5.81 (m, 1H), 5.21 (dd, *J* = 10.6, 7.9 Hz, 1H), 5.07 – 5.00 (m, 2H), 4.92 (t, *J* = 9.7 Hz, 2H), 4.88 – 4.82 (m, 2H), 4.77 (d, *J* = 3.2 Hz, 1H), 4.74 (d, *J* = 11.9 Hz, 1H), 4.60 (dd, *J* = 11.4, 2.5 Hz, 2H), 4.49 (d, *J* = 7.8 Hz, 1H), 4.36 – 4.22 (m, 4H), 4.21 – 4.03 (m, 3H), 3.83 (dd, *J* = 9.7, 5.6 Hz, 1H), 3.71 (t, *J* = 5.9 Hz, 1H), 3.65 – 3.52 (m, 3H), 3.46 (dd, *J* = 9.8, 3.3 Hz, 1H), 2.54 – 2.43 (m, 1H), 2.40 – 2.32 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.25 (s, 32H), 0.88 (t, *J* = 6.8 Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 170.7, 170.6, 169.1, 138.6, 138.2, 138.1, 138.0, 135.0, 128.4, 128.3, 128.1, 127.6, 127.4, 116.7, 101.7, 99.9, 81.5, 81.3, 80.5, 76.6, 75.6, 74.9, 73.9, 73.6, 73.1, 73.0, 69.7, 69.5, 68.7, 62.7, 34.0, 31.9, 29.8, 29.7, 29.3, 25.2, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for C<sub>67</sub>H<sub>92</sub>O<sub>14</sub>Na [M+Na]<sup>+</sup> 1143.6379, found 1143.6370.

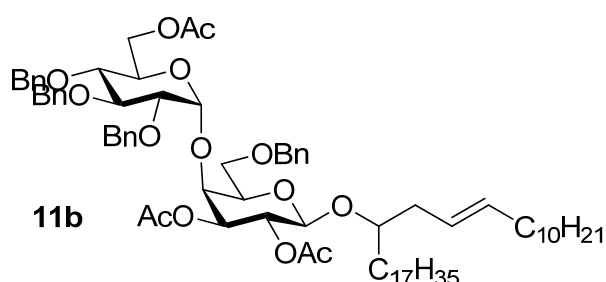
**2b** was obtained as a colorless syrup:  $[\alpha]_D^{26} = 41.34$  (*c* 0.92, CHCl<sub>3</sub>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 1H NMR (400 MHz, CDCl<sub>3</sub>) 7.43 – 7.10 (m, 20H), 5.89 – 5.69 (m, 1H), 5.19 (dd, *J* = 10.6, 7.9 Hz, 1H), 5.09 – 4.99 (m, 2H), 4.95 – 4.79 (m, 4H), 4.77 (d, *J* = 3.2 Hz, 1H), 4.73 (d, *J* = 11.9 Hz, 1H), 4.61 (s, 1H), 4.59 (s, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.36 – 4.01 (m, 7H), 3.84 (dd, *J* = 9.8, 5.7 Hz, 1H), 3.70 (t, *J* = 6.0 Hz, 1H), 3.64 – 3.60 (m, 2H), 3.54 (t, *J* = 9.5 Hz, 1H), 3.46 (dd, *J* = 9.8, 3.3 Hz, 1H), 2.24 (t, *J* = 5.8 Hz, 2H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.23 (d, *J* = 12.7 Hz, 32H), 0.88 (t, *J* = 6.8 Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 170.8, 170.6, 169.1, 138.6, 138.3, 138.1, 138.0, 134.6, 128.40, 128.39, 128.3, 127.6, 127.4, 117.0, 100.8, 99.9, 81.6, 80.5, 80.3, 75.7, 74.9, 74.0, 73.5, 73.2, 73.1, 69.6, 62.7, 38.5, 34.6, 31.9, 29.7, 29.3, 25.2, 22.7, 21.0, 20.8, 14.1; HRMS (MALDI) calcd for C<sub>67</sub>H<sub>92</sub>O<sub>14</sub>Na [M+Na]<sup>+</sup> 1143.6379, found 1143.6381.

#### Compound **11a**

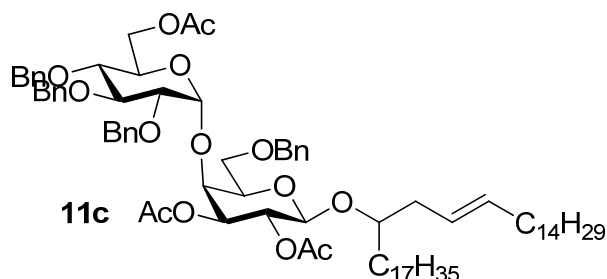


To a solution of compound **2a** (91 mg, 0.081 mmol) and 1-hexene **3a** (90 µL, 0.725 mmol, 9 equiv.) in CH<sub>2</sub>Cl<sub>2</sub> (3 mL) was added Grubbs's 2<sup>nd</sup> catalyst (7 mg, 0.0082 mmol, 0.1 equiv.). The mixture was heated to reflux. After 6 h, another 0.1 equiv. of the catalyst was added. The reaction was cooled to rt after another 6 h. Concentrated and purification by silica gel chromatography (petroleum ether/EtOAc, 6:1) afforded **11a** (82 mg, 86%) as a colorless syrup:  $[\alpha]_D^{25} = 45.78$  (*c*

2.07, CHCl<sub>3</sub>);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.44 – 7.08 (m, 20H), 5.43 (s, 2H), 5.21 (dd,  $J$  = 10.4, 7.8 Hz, 1H), 4.95 – 4.84 (m, 4H), 4.77 (d,  $J$  = 2.9 Hz, 1H), 4.74 (d,  $J$  = 12.0 Hz, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.46 (dd,  $J$  = 15.9, 7.7 Hz, 1H), 4.36 – 4.23 (m, 4H), 4.21 – 4.07 (m, 3H), 3.85 (dd,  $J$  = 9.4, 5.6 Hz, 1H), 3.75 – 3.68 (m, 1H), 3.64 (dd,  $J$  = 9.5, 6.8 Hz, 1H), 3.55 (t,  $J$  = 9.3 Hz, 2H), 3.46 (dd,  $J$  = 9.7, 2.7 Hz, 1H), 2.62 – 2.35 (m, 1H), 2.35 – 2.17 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.47 – 1.14 (m, 40H), 0.88 (t,  $J$  = 6.6 Hz, 6H);  $\delta_{\text{C}}$  NMR (100 MHz, CDCl<sub>3</sub>) 170.7, 170.6, 169.1, 138.6, 138.2, 138.1, 138.0, 138.0, 128.4, 128.3, 128.0, 128.0, 127.7, 127.6, 127.5, 127.5, 127.4, 101.8, 99.9, 81.9, 81.6, 80.4, 75.6, 74.8, 73.5, 73.0, 69.7, 69.5, 62.7, 31.9, 29.8, 29.7, 29.3, 25.2, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for C<sub>71</sub>H<sub>100</sub>O<sub>14</sub>Na [M+Na]<sup>+</sup> 1199.7005, found 1199.7031.

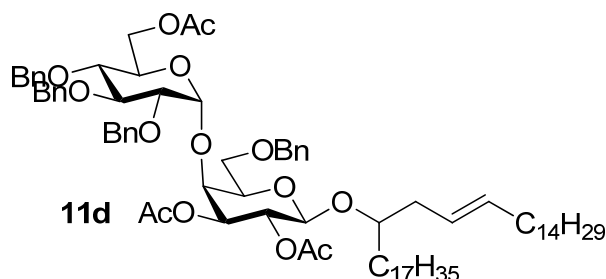


A similar procedure as used for the preparation of **11a** was employed. Thus, **11b** (73 mg, 78%) was obtained as a colorless syrup:  $[\alpha]_{\text{D}}^{25}$  = 43.48 ( $c$  2.22, CHCl<sub>3</sub>);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.37 – 7.15 (m, 20H), 5.42 (d,  $J$  = 3.0 Hz, 2H), 5.21 (dd,  $J$  = 10.4, 8.0 Hz, 1H), 4.97 – 4.81 (m, 4H), 4.77 (d,  $J$  = 2.9 Hz, 1H), 4.74 (d,  $J$  = 12.0 Hz, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.48 (d,  $J$  = 7.8 Hz, 1H), 4.38 – 4.21 (m, 4H), 4.20 – 4.05 (m, 3H), 3.84 (dd,  $J$  = 9.5, 5.5 Hz, 1H), 3.71 (t,  $J$  = 2.0 Hz, 1H), 3.64 (dd,  $J$  = 9.6, 6.6 Hz, 1H), 3.59 – 3.49 (m, 2H), 3.46 (dd,  $J$  = 9.7, 2.9 Hz, 1H), 2.52 – 2.41 (m, 1H), 2.31 – 2.24 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.25 (s, 54H), 0.86 (t,  $J$  = 6.8 Hz, 6H);  $\delta_{\text{C}}$  (100 MHz, CDCl<sub>3</sub>) 170.8, 170.6, 169.1, 138.6, 138.3, 138.1, 138.0, 133.2, 128.4, 128.3, 128.1, 128.0, 127.7, 127.6, 127.5, 127.4, 125.9, 101.9, 99.9, 82.0, 81.6, 80.5, 75.6, 74.9, 73.5, 73.1, 73.1, 69.7, 69.5, 62.7, 38.8, 31.9, 29.8, 29.7, 29.64, 29.55, 29.3, 29.2, 22.7, 21.0, 20.8, 20.7, 14.1; MALDI-MS:  $m/z$  1283.8 [M + Na]<sup>+</sup>; HRMS (MALDI) calcd for C<sub>77</sub>H<sub>112</sub>O<sub>14</sub>Na [M+Na]<sup>+</sup> 1283.7944, found 1283.7967.

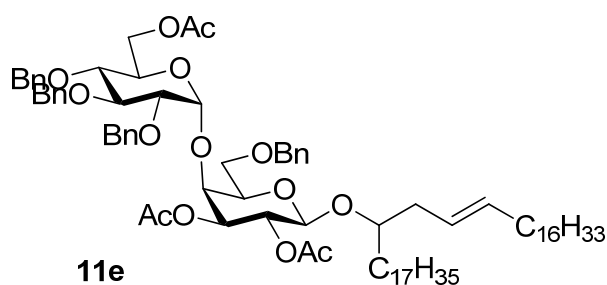


A similar procedure as used for the preparation of **11a** was employed. Thus, **11c** (69 mg, 80%) was obtained as a colorless syrup:  $[\alpha]_{\text{D}}^{26}$  = 44.15 ( $c$  2.23, CHCl<sub>3</sub>);  $\delta_{\text{H}}$  (400 MHz, CDCl<sub>3</sub>) 7.38 – 7.15 (m, 20H), 5.48 – 5.34 (m, 2H), 5.21 (dd,  $J$  = 10.6, 7.9 Hz, 1H), 4.97 – 4.81 (m, 4H), 4.77 (d,  $J$  = 3.2 Hz, 1H), 4.74 (d,  $J$  = 11.9 Hz, 1H), 4.60 (d,  $J$  = 11.1 Hz, 2H), 4.49 (dd,  $J$  = 7.7, 3.5 Hz, 1H), 4.36 – 4.23 (m, 4H), 4.18 (d,  $J$  = 10.0 Hz, 1H), 4.15 – 4.05 (m, 2H), 3.84 (dd,  $J$  = 9.7, 5.6 Hz, 1H), 3.71 (t,  $J$  = 5.9 Hz, 1H), 3.64 (dd,  $J$  = 9.7, 6.6 Hz, 1H), 3.58 – 3.50 (m, 2H), 3.46 (dd,  $J$  = 9.8, 3.2 Hz, 1H), 2.52 – 2.41 (m, 1H), 2.34 – 2.22 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.98 (s, 3H), 1.50 –

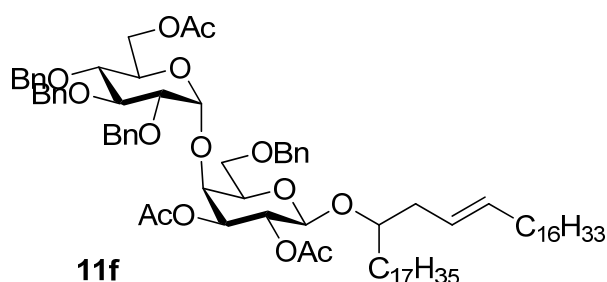
1.15 (m, 61H), 0.88 (t,  $J = 6.7$  Hz, 6H);  $\delta_{\text{C}}$  NMR (100 MHz,  $\text{CDCl}_3$ ) 170.7, 170.6, 169.1, 138.6, 138.3, 138.1, 138.0, 133.1, 128.4, 128.3, 128.04, 128.01, 127.7, 127.59, 127.56, 127.5, 127.4, 125.9, 101.8, 99.9, 82.0, 81.6, 80.4, 75.6, 74.8, 73.9, 73.5, 73.0, 69.7, 62.7, 38.8, 31.9, 29.8, 29.7, 29.6, 29.6, 29.3, 29.2, 22.7, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for  $\text{C}_{81}\text{H}_{120}\text{O}_{14}\text{Na}$   $[\text{M}+\text{Na}]^+$  1339.8570, found 1339.8531.



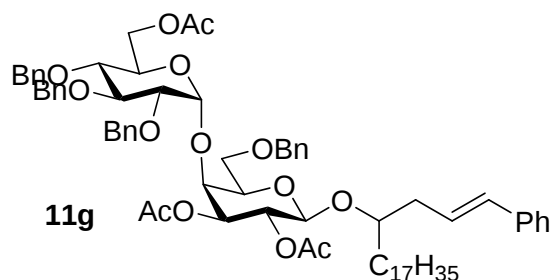
A similar procedure as used for the preparation of **11a** was employed. Thus, **11d** (106 mg, 75%) was obtained from **2b** as a colorless syrup:  $[\alpha]_{\text{D}}^{26} = 39.27$  ( $c$  1.12,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.38 – 7.14 (m, 20H), 5.51 – 5.40 (m, 1H), 5.39 – 5.29 (m, 1H), 5.19 (dd,  $J = 10.5, 8.0$  Hz, 1H), 4.96 – 4.80 (m, 4H), 4.77 (d,  $J = 3.1$  Hz, 1H), 4.73 (d,  $J = 11.9$  Hz, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.48 (d,  $J = 7.8$  Hz, 1H), 4.38 – 4.23 (m, 4H), 4.18 (d,  $J = 10.0$  Hz, 1H), 4.13 – 4.09 (m, 2H), 3.85 (dd,  $J = 9.7, 5.7$  Hz, 1H), 3.70 (t,  $J = 5.8$  Hz, 1H), 3.64 – 3.52 (m, 3H), 3.46 (dd,  $J = 9.8, 3.2$  Hz, 1H), 2.17 (t,  $J = 5.6$  Hz, 2H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 1.35 – 1.20 (br s, 56H), 0.88 (t,  $J = 6.7$  Hz, 6H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 170.7, 170.6, 169.1, 138.6, 138.2, 138.1, 138.0, 133.3, 128.4, 128.3, 128.1, 128.0, 127.7, 127.59, 127.57, 127.5, 127.4, 125.4, 100.6, 99.9, 81.6, 80.44, 80.38, 76.6, 75.6, 74.9, 73.9, 73.5, 73.2, 73.0, 69.6, 69.5, 68.6, 62.7, 37.2, 34.2, 32.7, 31.9, 29.8, 29.6, 29.6, 29.5, 29.3, 29.2, 25.2, 22.7, 21.0, 20.80, 20.76, 14.1; HRMS (MALDI) calcd for  $\text{C}_{81}\text{H}_{120}\text{O}_{14}\text{Na}$   $[\text{M}+\text{Na}]^+$  1339.8570, found 1339.8561.



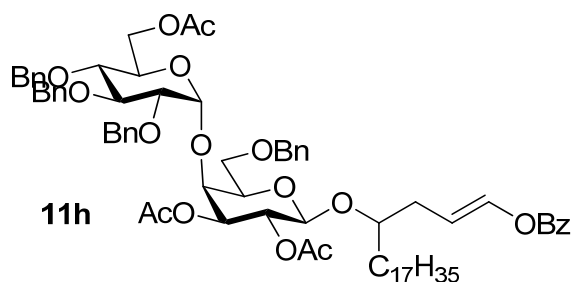
A similar procedure as used for the preparation of **11a** was employed. Thus, **11e** (50 mg, 76%) was obtained as a colorless syrup:  $[\alpha]_{\text{D}}^{25} = 41.53$  ( $c$  2.01,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.31 – 7.03 (m, 21H), 5.42 (d,  $J = 3.0$  Hz, 2H), 5.21 (dd,  $J = 10.3, 8.0$  Hz, 1H), 5.01 – 4.80 (m, 4H), 4.77 (d,  $J = 2.7$  Hz, 1H), 4.74 (d,  $J = 12.0$  Hz, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.48 (d,  $J = 7.8$  Hz, 1H), 4.38 – 4.21 (m, 4H), 4.20 – 4.01 (m, 3H), 3.84 (dd,  $J = 9.3, 5.4$  Hz, 1H), 3.71 (t,  $J = 5.7$  Hz, 1H), 3.64 (dd,  $J = 9.4, 6.7$  Hz, 1H), 3.60 – 3.48 (m, 2H), 3.46 (dd,  $J = 9.7, 2.8$  Hz, 1H), 2.56 – 2.36 (m, 1H), 2.36 – 2.21 (m, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.48 – 1.15 (m, 63H), 0.88 (t,  $J = 6.5$  Hz, 6H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 170.8, 170.6, 169.1, 138.6, 138.3, 138.0, 133.2, 128.4, 128.3, 128.1, 128.0, 127.7, 127.61, 127.58, 127.5, 127.4, 125.9, 101.9, 100.0, 82.0, 81.6, 80.5, 75.7, 74.9, 73.5, 73.15, 73.07, 69.7, 68.7, 62.7, 38.9, 31.9, 29.7, 29.7, 29.6, 29.3, 25.2, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for  $\text{C}_{83}\text{H}_{124}\text{O}_{14}\text{Na}$   $[\text{M}+\text{Na}]^+$  1367.8883, found 1367.8875.



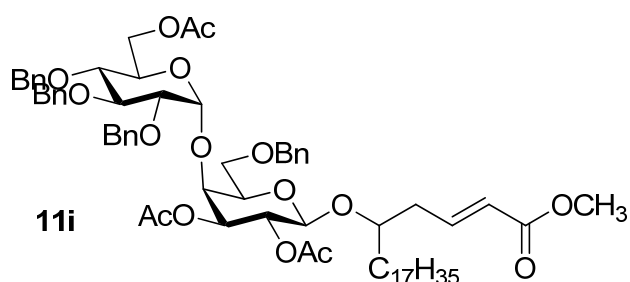
A similar procedure as used for the preparation of **11a** was employed. Thus, **11f** (87 mg, 79%) was obtained from **2b** as a colorless syrup:  $[\alpha]_D^{27} = 36.66$  ( $c$  1.43,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.32 – 7.18 (m, 21H), 5.46 – 5.33 (m, 2H), 5.23 – 5.14 (m, 1H), 4.95 – 4.83 (m, 4H), 4.77 (d,  $J = 3.1$  Hz, 1H), 4.73 (d,  $J = 11.9$  Hz, 1H), 4.62 (s, 1H), 4.59 (s, 1H), 4.47 (dd,  $J = 10.2, 8.1$  Hz, 1H), 4.34 – 4.25 (m, 4H), 4.18 (d,  $J = 10.0$  Hz, 1H), 4.13 – 4.09 (m, 2H), 3.85 (dd,  $J = 9.7, 5.8$  Hz, 1H), 3.70 (t,  $J = 5.8$  Hz, 1H), 3.64 – 3.52 (m, 3H), 3.46 (dd,  $J = 9.8, 3.2$  Hz, 1H), 2.17 (t,  $J = 5.7$  Hz, 1H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H), 2.00 – 1.92 (m, 1H), 1.24 (d,  $J = 13.7$  Hz, 67H), 0.88 (t,  $J = 6.7$  Hz, 6H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ ) 170.7, 170.6, 169.1, 138.6, 138.2, 138.1, 138.0, 133.3, 130.9, 128.4, 128.3, 128.1, 128.0, 127.7, 127.63, 127.58, 127.6, 127.5, 127.4, 125.4, 100.6, 99.9, 81.6, 80.4, 75.6, 74.9, 73.9, 73.5, 73.2, 73.0, 69.5, 62.7, 32.7, 32.6, 31.9, 29.7, 29.6, 29.5, 29.3, 29.2, 25.3, 25.2, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for  $\text{C}_{83}\text{H}_{124}\text{O}_{14}\text{Na}$   $[\text{M}+\text{Na}]^+$  1367.8883, found 1367.8854.



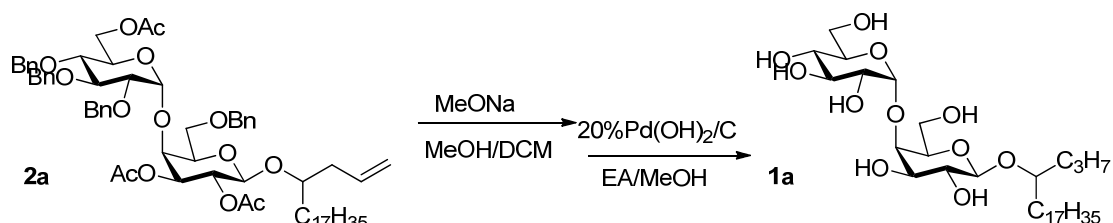
A similar procedure as used for the preparation of **11a** was employed. Thus, **11g** (54 mg, >99%) was obtained as a colorless syrup:  $[\alpha]_D^{26} = 39.94$  ( $c$  1.92,  $\text{CHCl}_3$ );  $\delta_{\text{H}}$  (400 MHz,  $\text{CDCl}_3$ ) 7.34 – 7.14 (m, 25H), 6.45 (dd,  $J = 44.2, 15.9$  Hz, 1H), 6.27 (dt,  $J = 24.8, 8.0$  Hz, 1H), 5.24 (dd,  $J = 10.6, 8.0$  Hz, 1H), 4.95 – 4.84 (m, 4H), 4.77 (d,  $J = 3.3$  Hz, 1H), 4.73 (d,  $J = 11.9$  Hz, 1H), 4.63 (d,  $J = 2.0$  Hz, 1H), 4.60 (s, 1H), 4.52 (d,  $J = 7.8$  Hz, 1H), 4.33 (s, 2H), 4.28 – 4.07 (m, 5H), 3.85 (dd,  $J = 9.8, 5.5$  Hz, 1H), 3.73 (t,  $J = 5.9$  Hz, 1H), 3.67 – 3.63 (m, 2H), 3.56 (t,  $J = 9.5$  Hz, 1H), 3.47 (dd,  $J = 9.9, 3.2$  Hz, 1H), 2.64 (dt,  $J = 11.3, 5.5$  Hz, 1H), 2.51 (dt,  $J = 14.0, 7.0$  Hz, 1H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.49 (br s, 2H), 1.25 (d,  $J = 3.8$  Hz, 31H), 0.88 (t,  $J = 6.8$  Hz, 3H);  $\delta_{\text{C}}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 170.6, 169.1, 138.6, 138.2, 138.1, 138.0, 137.7, 131.9, 128.4, 128.3, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 126.9, 126.0, 101.9, 100.0, 81.7, 81.6, 80.4, 76.8, 75.6, 74.9, 74.0, 73.5, 73.2, 73.1, 69.7, 69.5, 68.8, 62.7, 39.3, 34.2, 31.9, 29.7, 29.7, 29.3, 25.3, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for  $\text{C}_{73}\text{H}_{96}\text{O}_{14}\text{Na}$   $[\text{M}+\text{Na}]^+$  1219.6692, found 1219.6653.



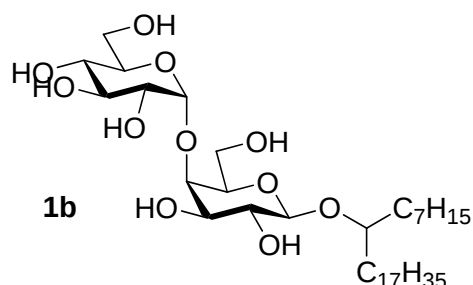
A similar procedure as used for the preparation of **11a** was employed. Thus, **11h** (38 mg, 63%) was obtained as a colorless syrup:  $[\alpha]_D^{26} = 48.36$  (*c* 1.05, CHCl<sub>3</sub>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 8.02 (d, *J* = 7.3 Hz, 2H), 7.55 – 7.16 (m, 25H), 5.95 – 5.79 (m, 1H), 5.77 – 5.68 (m, 1H), 5.21 (dd, *J* = 10.5, 8.0 Hz, 1H), 4.97 – 4.72 (m, 8H), 4.60 (d, *J* = 10.7 Hz, 2H), 4.48 (d, *J* = 7.9 Hz, 1H), 4.35 – 4.22 (m, 4H), 4.18 – 4.08 (m, 3H), 3.82 (dd, *J* = 9.6, 5.3 Hz, 1H), 3.72 (t, *J* = 5.6 Hz, 1H), 3.67 – 3.53 (m, 3H), 3.46 (dd, *J* = 9.8, 3.2 Hz, 1H), 2.54 – 2.36 (m, 2H), 2.05 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.26 (t, *J* = 9.0 Hz, 32H), 0.88 (t, *J* = 6.7 Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 170.8, 170.7, 169.1, 166.3, 138.6, 138.2, 138.0, 132.8, 132.5, 130.3, 129.6, 128.4, 128.32, 128.28, 128.1, 128.0, 127.8, 127.62, 127.58, 127.4, 126.3, 101.9, 99.9, 81.6, 81.3, 80.5, 75.6, 74.9, 73.9, 73.6, 73.1, 69.6, 69.5, 68.8, 65.6, 62.7, 38.5, 34.0, 31.9, 29.7, 29.3, 25.2, 22.7, 21.0, 20.8, 20.7, 14.1; HRMS (MALDI) calcd for C<sub>75</sub>H<sub>98</sub>O<sub>16</sub>Na [M+Na]<sup>+</sup> 1277.6747, found 1277.6733.



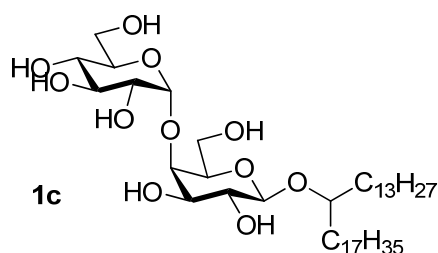
A similar procedure as used for the preparation of **11a** was employed. Thus, **11i** (56 mg, 92%) was obtained as a colorless syrup:  $[\alpha]_D^{26} = 47.29$  (*c* 1.02, CHCl<sub>3</sub>);  $\delta_H$  (400 MHz, CDCl<sub>3</sub>) 7.35 – 7.17 (m, 21H), 6.98 – 6.85 (dt, *J* = 15.7, 7.6 Hz 1H), 5.86 (d, *J* = 15.7 Hz, 1H), 5.20 (dd, *J* = 10.6, 7.9 Hz, 1H), 4.93 – 4.82 (m, 4H), 4.76 (d, *J* = 3.3 Hz, 1H), 4.72 (d, *J* = 11.9 Hz, 1H), 4.61 (s, 1H), 4.59 (d, *J* = 1.9 Hz, 1H), 4.48 (d, *J* = 7.8 Hz, 1H), 4.36 – 4.25 (m, 4H), 4.17 (d, *J* = 10.0 Hz, 1H), 4.09 (t, *J* = 9.4 Hz, 2H), 3.83 (dd, *J* = 9.8, 5.6 Hz, 1H), 3.74 – 3.69 (m, 2H), 3.71 (s, 3H) 3.63 (dd, *J* = 9.8, 6.4 Hz, 1H), 3.55 (t, *J* = 9.5 Hz, 1H), 3.46 (dd, *J* = 9.8, 3.3 Hz, 1H), 2.47 – 2.29 (m, 2H), 2.05 (s, 3H), 2.04 (s, 3H), 1.99 (s, 3H), 1.67 (br s, 1H), 1.51 (br s, 1H), 1.23 (d, 32H), 0.88 (t, *J* = 6.7 Hz, 3H);  $\delta_C$  (100 MHz, CDCl<sub>3</sub>) 170.7, 170.6, 169.2, 166.6, 145.1, 138.5, 138.2, 138.0, 137.9, 128.38, 128.36, 128.3, 128.1, 128.0, 127.8, 127.6, 127.6, 127.5, 127.4, 123.2, 100.5, 99.9, 81.6, 80.4, 78.9, 77.2, 75.6, 74.9, 73.9, 73.5, 73.1, 73.0, 69.5, 69.4, 68.6, 62.6, 51.4, 36.7, 34.8, 31.9, 29.7, 29.6, 29.3, 25.2, 22.6, 21.0, 20.8, 20.6, 14.1; HRMS (MALDI) calcd for C<sub>69</sub>H<sub>94</sub>O<sub>16</sub>Na [M+Na]<sup>+</sup> 1201.6434, found 1201.6447.



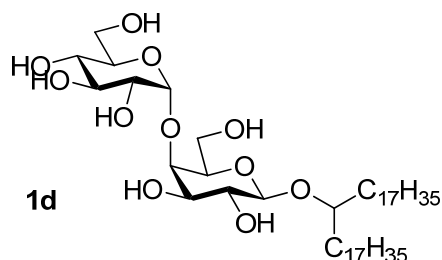
To a solution of triacetate **2a** (27 mg, 0.024 mmol) in  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  (2 mL/2 mL) was added a catalytic amount of MeONa. The mixture was stirred at rt for 3 h. Amberlite IR-120 resin (H form) was added to neutralize the solution. Filtration and evaporation gave a residue. To a solution of the above residue in ethyl acetate/MeOH (3 mL/2 mL) was added 20%  $\text{Pd}(\text{OH})_2/\text{C}$  (35 mg) at rt. After stirring under  $\text{H}_2$  (1 atm) for 5 h, the mixture was filtered and concentrated. The residue was purified by thin layer chromatography on silica gel ( $\text{CHCl}_3/\text{MeOH}$ , 11:1) to afford **1a** (11 mg, 66%) as a white powder:  $[\alpha]_D^{25} = 18.86$  ( $c$  0.38,  $\text{CHCl}_3/\text{MeOH}$ , 3:1);  $\delta_{\text{H}}$  (400 MHz, pyridine- $d_5$ ) 5.78 (d,  $J = 3.6$  Hz, 1H), 4.92 – 4.88 (m, 1H), 4.79 (d,  $J = 7.5$  Hz, 1H), 4.71 (d,  $J = 2.1$  Hz, 1H), 4.56 (t,  $J = 9.8$  Hz, 1H), 4.56 (t,  $J = 9.2$  Hz, 1H), 4.46 (dd,  $J = 11.2$ , 1.6 Hz, 1H), 4.35 – 4.26 (m, 3H), 4.19 – 4.14 (m, 3H), 4.10 (t,  $J = 7.2$  Hz, 1H), 3.92 – 3.87 (m, 1H), 1.75 – 1.42 (m, 9H), 1.28 (s, 38H), 0.86 (t,  $J = 6.0$  Hz, 6H);  $\delta_{\text{C}}$  (100 MHz, pyridine- $d_5$ ) 104.6, 102.6, 79.7, 79.5, 75.4, 75.1, 74.9, 74.7, 74.2, 72.9, 72.1, 62.4, 60.5, 37.6, 34.6, 32.0, 30.2, 29.9, 29.8, 29.5, 25.3, 22.8, 18.8, 14.3, 14.2; HRMS (MALDI) calcd for  $\text{C}_{33}\text{H}_{64}\text{O}_{11}\text{Na}$   $[\text{M}+\text{Na}]^+$  659.4341, found 659.4345.



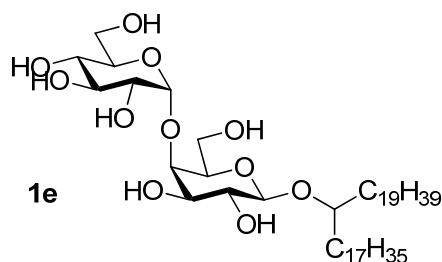
A similar procedure as used for the preparation of **1a** was employed. Thus, **1b** (22 mg, 61%) was obtained as a white powder:  $[\alpha]_D^{27} = 30.06$  ( $c$  0.26,  $\text{CHCl}_3/\text{MeOH}$ , 3:1);  $\delta_{\text{H}}$  (400 MHz, pyridine- $d_5$ ) 5.79 (d,  $J = 3.5$  Hz, 1H), 4.91 – 4.88 (m, 1H), 4.82 (d,  $J = 6.1$  Hz, 1H), 4.73 (s, 1H), 4.68 (t,  $J = 9.3$  Hz, 1H), 4.56 (t,  $J = 9.2$  Hz, 1H), 4.46 (dd,  $J = 11.3$ , 1.8 Hz, 1H), 4.37 – 4.28 (m, 3H), 4.19 – 4.13 (m, 4H), 3.93 (br s, 1H), 1.80 – 1.60 (m, 6H), 1.28 (s, 29H), 0.86 (t,  $J = 6.6$  Hz, 6H);  $\delta_{\text{C}}$  (100 MHz, pyridine- $d_5$ ) 104.6, 102.6, 79.9, 79.7, 75.5, 75.1, 74.9, 74.7, 74.2, 72.9, 72.1, 62.4, 60.4, 35.4, 34.6, 32.0, 30.2, 29.9, 29.8, 29.5, 25.3, 22.8, 14.2; HRMS (MALDI) calcd for  $\text{C}_{37}\text{H}_{72}\text{O}_{11}\text{Na}$   $[\text{M}+\text{Na}]^+$  715.4967, found 715.4974.



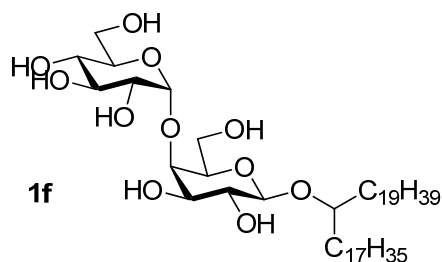
A similar procedure as used for the preparation of **1a** was employed. Thus, **1c** (26 mg, 83%) was obtained as a white powder:  $[\alpha]_D^{25} = 15.26$  (*c* 0.15, CHCl<sub>3</sub>/MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 5.79 (d, *J* = 3.1 Hz, 1H), 4.89 (s, 1H), 4.83 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H), 4.66 (t, *J* = 9.6 Hz, 1H), 4.55 (t, *J* = 9.2 Hz, 1H), 4.46 (d, *J* = 10.2 Hz, 1H), 4.41 – 4.35 (m, 1H), 4.30 – 4.26 (m, 2H), 4.18 – 4.12 (m, 4H), 3.95 (t, *J* = 5.2 Hz, 1H), 1.87 – 1.45 (m, 12H), 1.26 (d, *J* = 14.1 Hz, 6H), 0.86 (t, *J* = 6.1 Hz, 8H);  $\delta_C$  (100 MHz, pyridine-*d*<sub>5</sub>) 104.6, 102.6, 80.0, 79.7, 75.5, 75.1, 74.9, 74.7, 74.1, 72.9, 72.1, 62.4, 60.5, 35.5, 34.5, 32.0, 30.3, 30.1, 29.92, 29.89, 29.8, 29.5, 25.6, 25.3, 22.8, 14.2; HRMS (MALDI) calcd for C<sub>43</sub>H<sub>84</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup> 799.5906, found 799.5928.



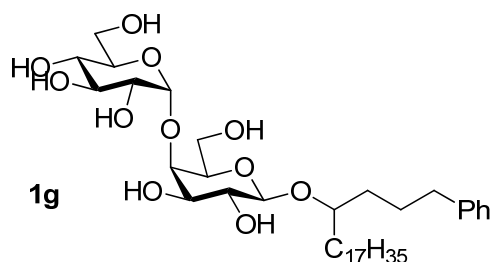
A similar procedure as used for the preparation of **1a** was employed. Thus, **1d** (26 mg, 91%) was obtained as a white powder:  $[\alpha]_D^{26} = 6.38$  (*c* 0.11, CHCl<sub>3</sub>/MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 5.80 (d, *J* = 3.7 Hz, 1H), 4.92 – 4.89 (m, 1H), 4.84 (d, *J* = 7.5 Hz, 1H), 4.74 (d, *J* = 2.1 Hz, 1H), 4.69 (t, *J* = 9.8 Hz, 1H), 4.56 (t, *J* = 9.2 Hz, 1H), 4.46 (dd, *J* = 11.3, 2.0 Hz, 1H), 4.36 (dd, *J* = 9.6, 7.6 Hz, 1H), 4.34 – 4.28 (m, 2H), 4.19 – 4.12 (m, 4H), 3.98 – 3.93 (m, 1H), 1.84 – 1.60 (m, 10H), 1.27 (d, 6H), 0.87 (t, *J* = 6.6 Hz, 6H);  $\delta_C$  (100 MHz, pyridine-*d*<sub>5</sub>) 104.6, 102.6, 79.9, 79.7, 75.5, 75.1, 74.9, 74.7, 74.1, 72.9, 72.1, 62.4, 60.5, 35.5, 34.5, 32.0, 30.3, 30.1, 29.9, 29.8, 29.5, 25.6, 25.3, 22.8, 14.2; HRMS (MALDI) calcd for C<sub>47</sub>H<sub>92</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup> 855.6532, found 855.6536.



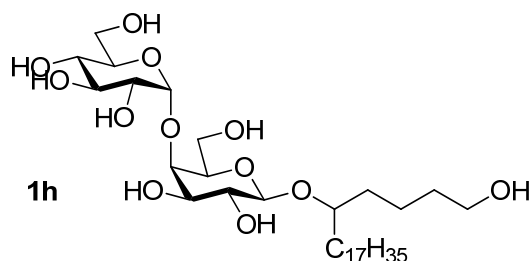
A similar procedure as used for the preparation of **1a** was employed. Thus, **1e** (25 mg, 85%) was obtained as a white powder:  $[\alpha]_D^{26} = 8.13$  (*c* 0.15, MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 5.79 (d, *J* = 3.0 Hz, 1H), 4.91 – 4.88 (br s, 1H), 4.83 (d, *J* = 7.5 Hz, 1H), 4.73 (s, 1H), 4.68 (t, *J* = 9.6 Hz, 1H), 4.56 (t, *J* = 9.1 Hz, 1H), 4.46 (d, *J* = 10.3 Hz, 1H), 4.38 – 4.28 (m, 3H), 4.19 – 4.12 (m, 4H), 3.96 (t, *J* = 4.2 Hz, 1H), 1.82 – 1.66 (m, 8H), 1.30 (s, 86H), 0.88 (t, *J* = 6.3 Hz, 6H);  $\delta_C$  (100 MHz, pyridine-*d*<sub>5</sub>) 104.5, 102.6, 79.9, 79.6, 75.4, 75.0, 74.8, 74.6, 74.0, 72.8, 72.0, 62.3, 60.4, 35.4, 34.4, 32.0, 30.2, 29.8, 29.8, 29.4, 25.5, 25.2, 22.8, 14.1; HRMS (MALDI) calcd for C<sub>49</sub>H<sub>96</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup> 883.6845, found 883.6856.



A similar procedure as used for the preparation of **1a** was employed. Thus, **1f** (21 mg, 90%) was obtained as a white powder:  $[\alpha]_D^{26} = 17.78$  (*c* 0.13, CHCl<sub>3</sub>/MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 5.79 (d, *J* = 2.8 Hz, 1H), 4.91 (br, 1H), 4.84 (d, *J* = 7.4 Hz, 1H), 4.73 (br s, 1H), 4.68 (t, *J* = 9.6 Hz, 1H), 4.56 (t, *J* = 9.2 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.36 (t, *J* = 9.2 Hz, 1H), 4.34 – 4.29 (m, 2H), 4.19 – 4.10 (m, 4H), 3.97 (t, *J* = 4.2 Hz, 1H), 1.83 – 1.60 (m, 8H), 1.29 (s, 76H), 0.88 (t, *J* = 6.3 Hz, 6H);  $\delta_C$  (100 MHz, pyridine-*d*<sub>5</sub>) 104.6, 102.6, 79.9, 79.7, 75.5, 75.1, 74.9, 74.7, 74.1, 72.9, 72.1, 62.4, 60.5, 35.5, 34.5, 32.0, 29.9, 29.8, 29.5, 25.6, 25.3, 22.8, 14.2; HRMS (MALDI) calcd for C<sub>49</sub>H<sub>96</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup> 883.6845, found 883.6849.

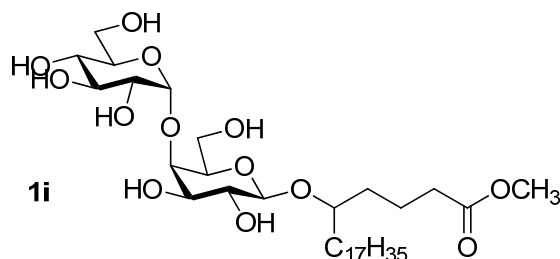


A similar procedure as used for the preparation of **1a** was employed. Thus, **1g** (21 mg, 67%) was obtained as a white powder:  $[\alpha]_D^{24} = 29.71$  (*c* 0.36, CHCl<sub>3</sub>/MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 7.39 – 7.21 (m, 5H), 5.79 (d, *J* = 3.1 Hz, 1H), 4.90 (br s, 1H), 4.80 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H), 4.66 (t, *J* = 9.2 Hz, 1H), 4.57 (t, *J* = 9.2 Hz, 1H), 4.46 (d, *J* = 10.0 Hz, 1H), 4.37 – 4.27 (m, 3H), 4.19 – 4.09 (m, 4H), 3.94 (br, 1H), 2.63 – 2.53 (m, 2H), 1.80 – 1.53 (m, 9H), 1.27 (d, *J* = 4.7 Hz, 37H), 0.85 (t, *J* = 6.7 Hz, 6H);  $\delta_C$  (100 MHz, pyridine-*d*<sub>5</sub>) 143.1, 128.8, 128.6, 125.9, 104.4, 102.6, 79.7, 79.4, 75.5, 75.1, 74.9, 74.7, 74.2, 72.9, 72.1, 62.4, 60.5, 36.0, 34.8, 34.6, 32.0, 29.9, 29.8, 29.5, 27.3, 25.3, 22.8, 14.2; HRMS (MALDI) calcd for C<sub>39</sub>H<sub>68</sub>O<sub>11</sub>Na [M+Na]<sup>+</sup> 735.4654, found 735.4648.



A similar procedure as used for the preparation of **1a** was employed. Thus, **1h** (5 mg, 32%) was obtained as a white solid:  $[\alpha]_D^{26} = 19.70$  (*c* 0.18, CHCl<sub>3</sub>/MeOH, 3:1);  $\delta_H$  (400 MHz, pyridine-*d*<sub>5</sub>) 5.79 (d, *J* = 3.5 Hz, 1H), 4.93 (d, *J* = 6.2 Hz, 1H), 4.83 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H), 4.65 (t, *J* = 9.6 Hz, 1H), 4.59 (t, *J* = 9.2 Hz, 1H), 4.49 (d, *J* = 9.6 Hz, 1H), 4.38 – 4.30 (m, 3H), 4.21 – 4.17

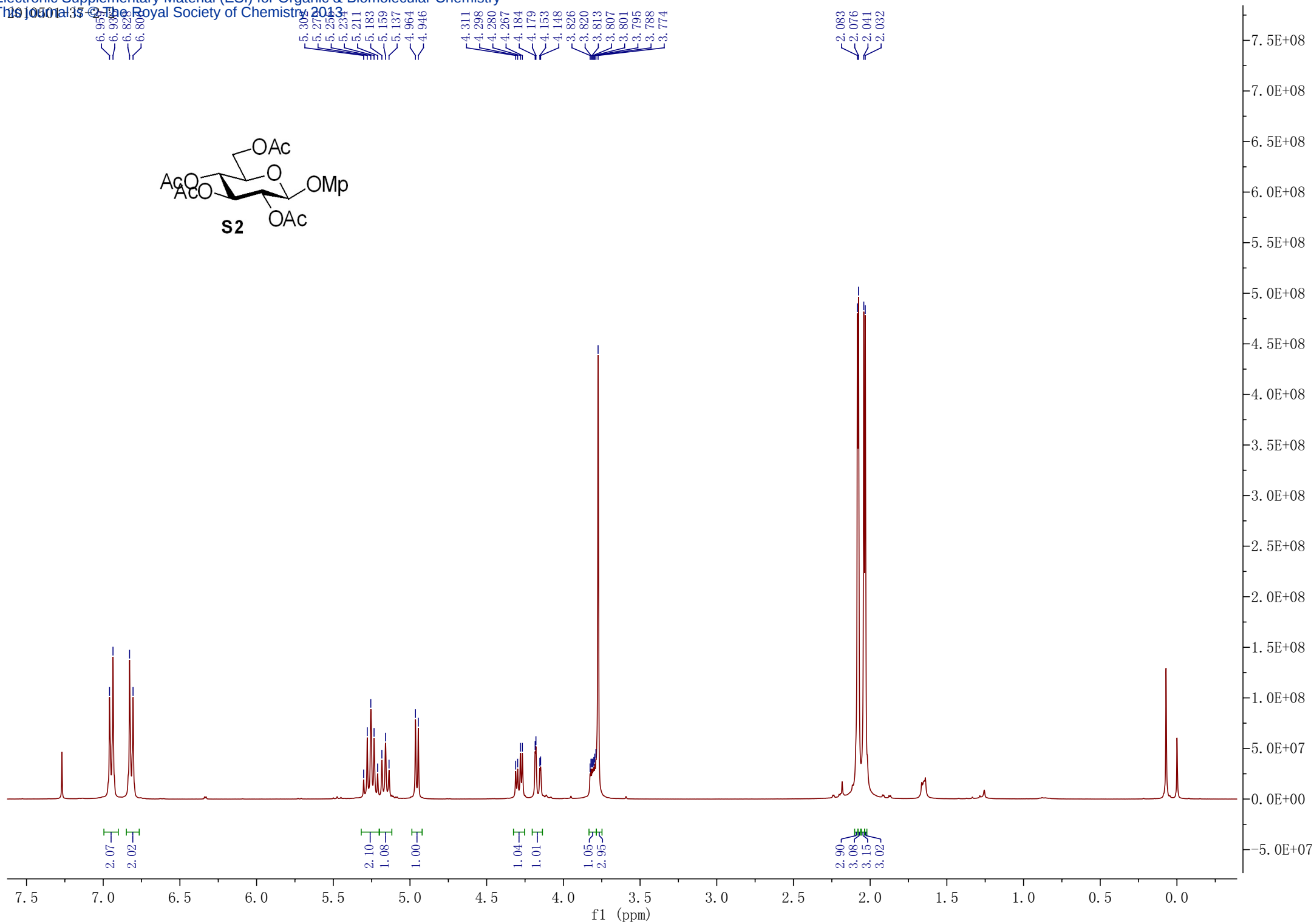
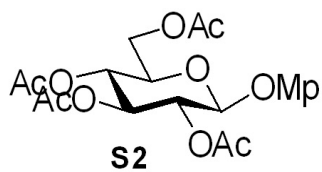
(m, 3H), 4.12 (t,  $J = 6.8$  Hz, 1H), 3.96 (br s, 1H), 3.84 (t,  $J = 5.7$  Hz, 2H), 1.70 (m, 9H), 1.29 (s, 33H), 0.88 (t,  $J = 6.4$  Hz, 3H);  $\delta_{\text{C}}$  (100 MHz, pyridine- $d_5$ ) 104.5, 102.6, 79.8, 79.7, 75.6, 75.1, 74.9, 74.7, 74.2, 72.9, 72.1, 62.4, 62.0, 60.5, 35.2, 34.6, 33.7, 32.0, 30.3, 29.9, 29.8, 29.5, 25.4, 22.8, 22.1, 14.2; HRMS (MALDI) calcd for  $\text{C}_{34}\text{H}_{66}\text{O}_{12}\text{Na}$   $[\text{M}+\text{Na}]^+$  689.4446, found 689.4459.

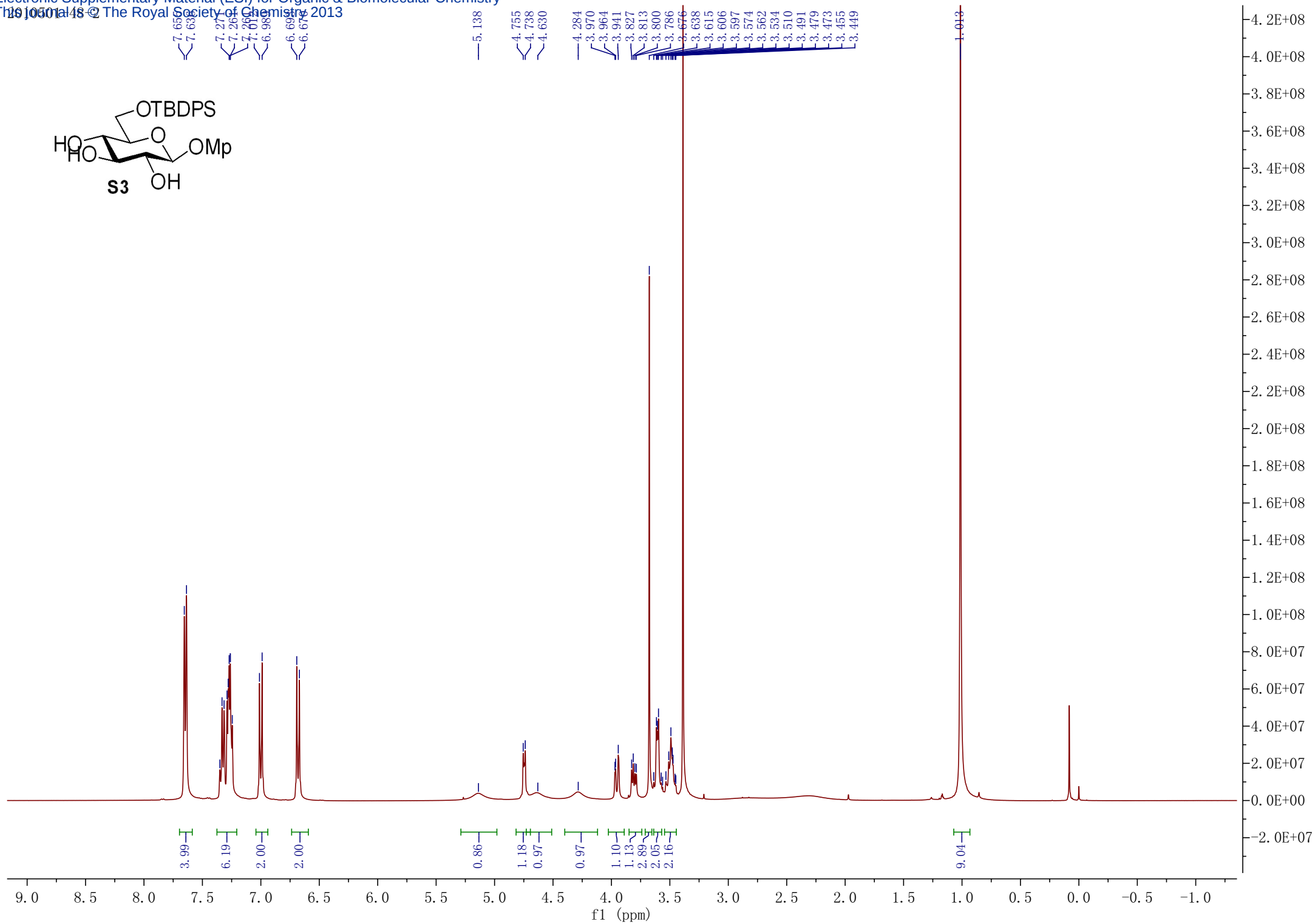
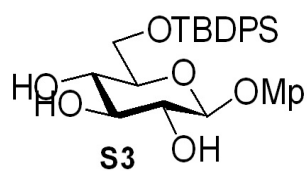


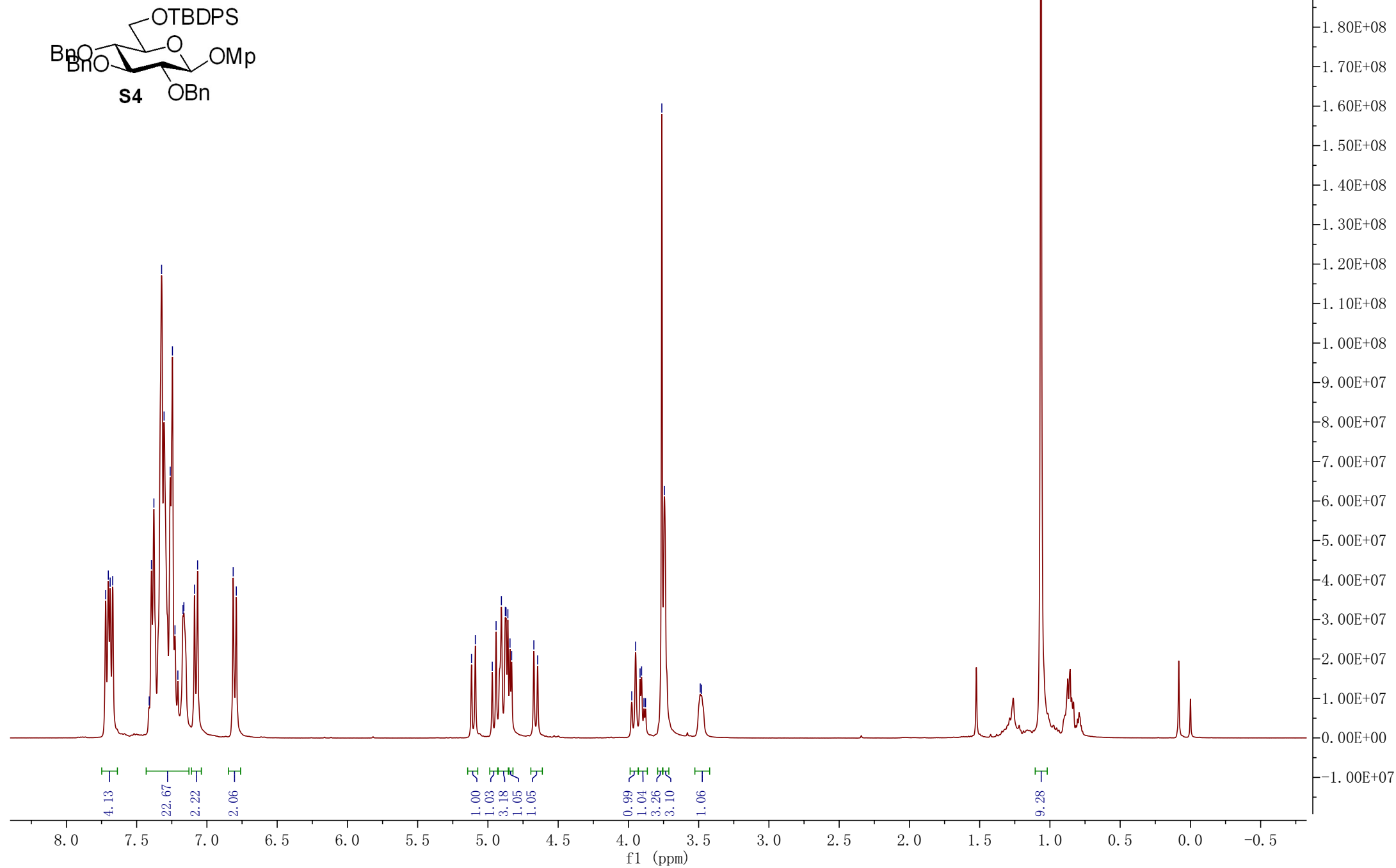
A similar procedure as used for the preparation of **1a** was employed. Thus, **1i** (18 mg, 99%) was obtained as a white solid:  $[\alpha]_{\text{D}}^{26} = 27.95$  ( $c$  0.42,  $\text{CHCl}_3/\text{MeOH}$ , 3:1);  $\delta_{\text{H}}$  (400 MHz, pyridine- $d_5$ ) 5.80 (d,  $J = 3.6$  Hz, 1H), 4.94 – 4.90 (m, 1H), 4.79 (d,  $J = 7.5$  Hz, 1H), 4.73 (d,  $J = 2.2$  Hz, 1H), 4.68 (t,  $J = 9.6$  Hz, 1H), 4.58 (t,  $J = 9.2$  Hz, 1H), 4.48 (dd,  $J = 11.3, 1.9$  Hz, 1H), 4.40 – 4.29 (m, 3H), 4.20 – 4.10 (m, 4H), 3.93 (t,  $J = 4.2$  Hz, 1H), 3.61 (s, 3H), 2.41 (t,  $J = 7.3$  Hz, 2H), 2.02 – 1.60 (m, 6H), 1.29 (s, 29H), 0.87 (t,  $J = 6.6$  Hz, 3H).  $\delta_{\text{C}}$  (100 MHz, pyridine- $d_5$ ) 173.8, 104.6, 102.6, 98.9, 79.7, 79.6, 75.5, 75.1, 74.9, 74.7, 74.1, 72.8, 72.1, 62.4, 60.4, 51.1, 34.2, 32.0, 29.9, 29.8, 29.5, 25.6, 22.8, 20.7, 14.2; HRMS (MALDI) calcd for  $\text{C}_{35}\text{H}_{66}\text{O}_{13}\text{Na}$   $[\text{M}+\text{Na}]^+$  717.4396, found 717.4392.

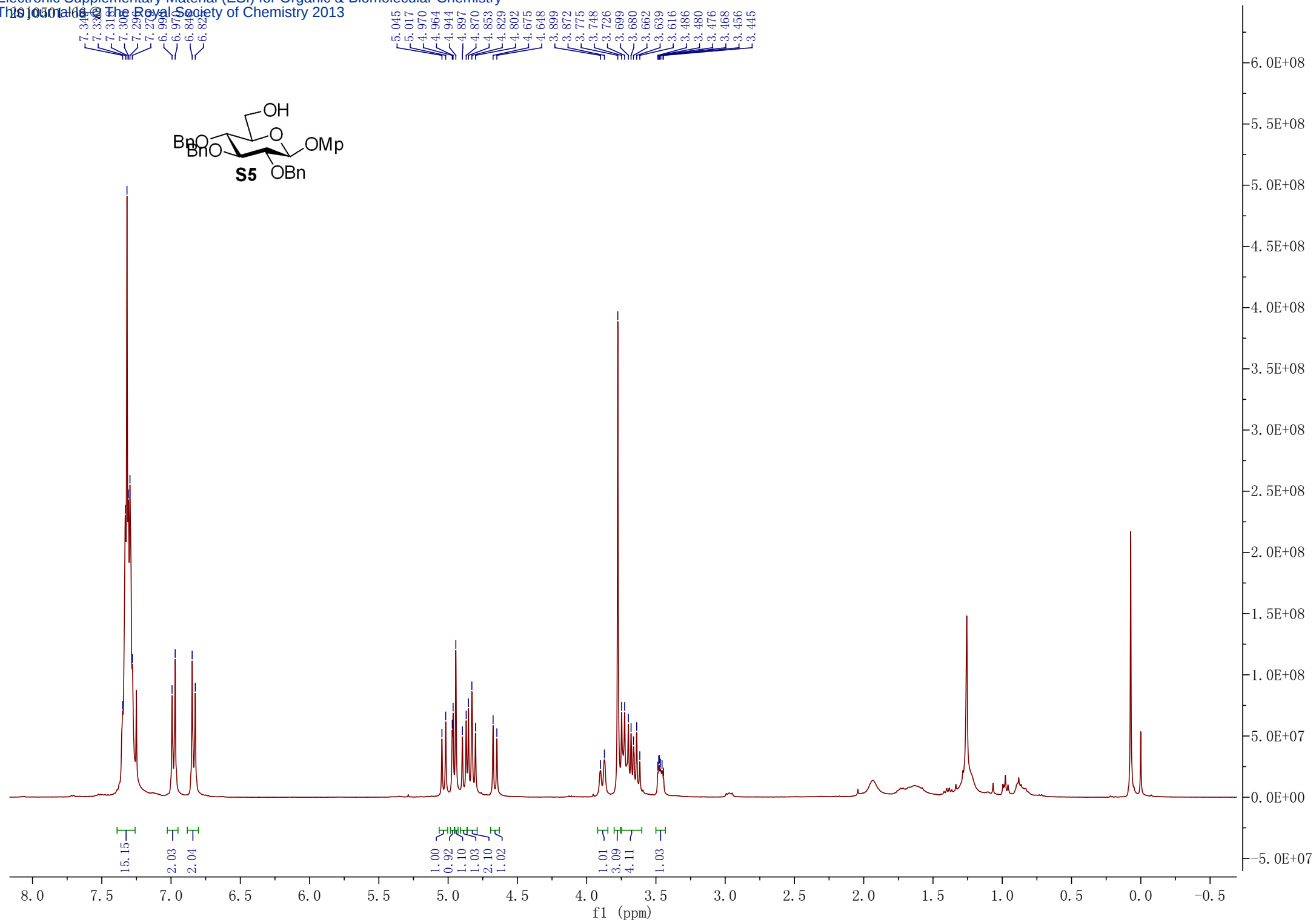
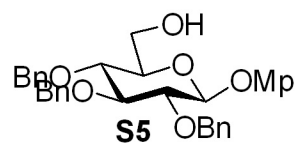
## References

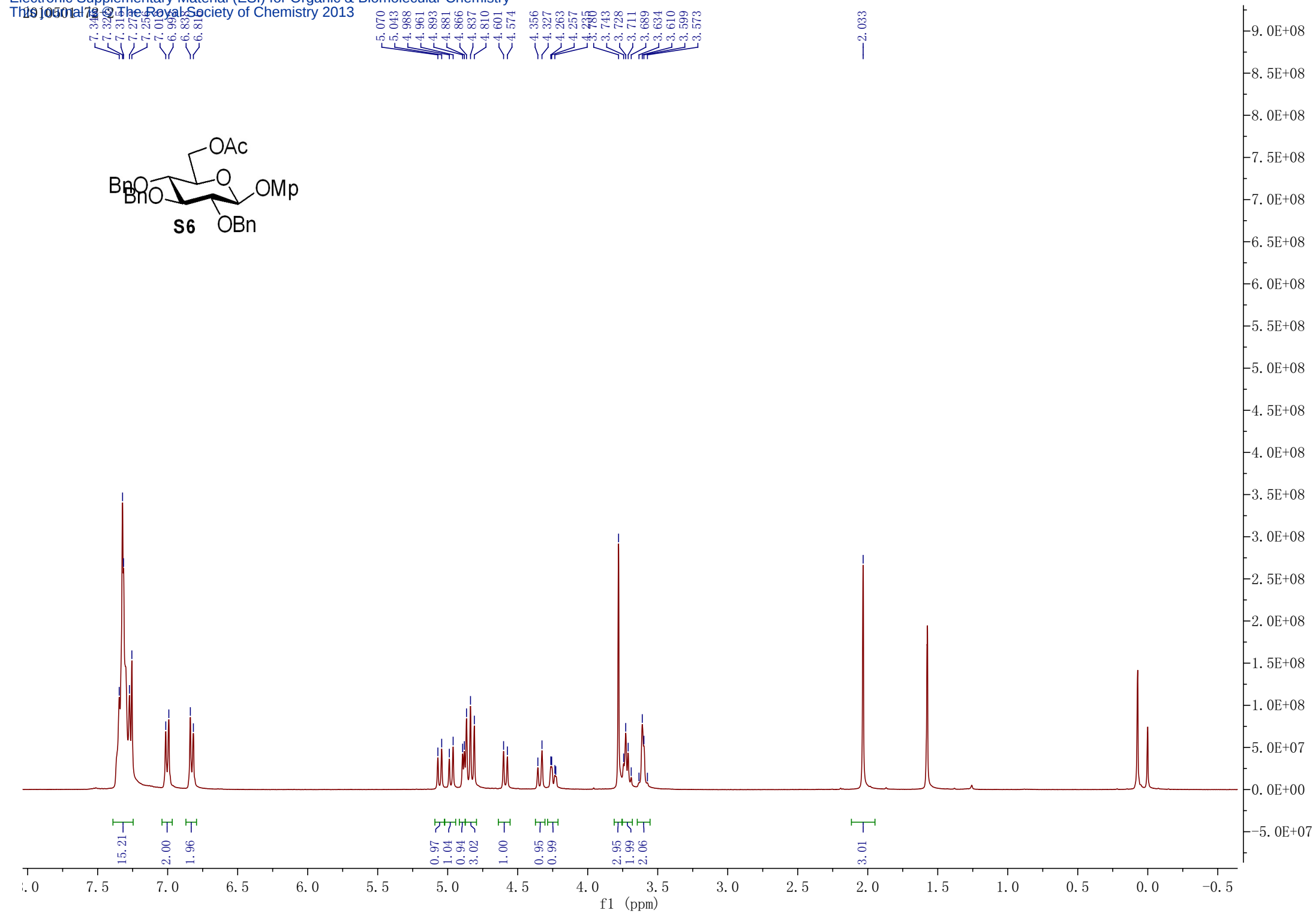
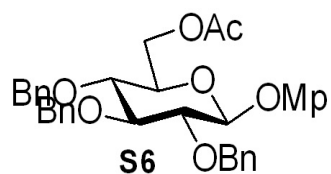
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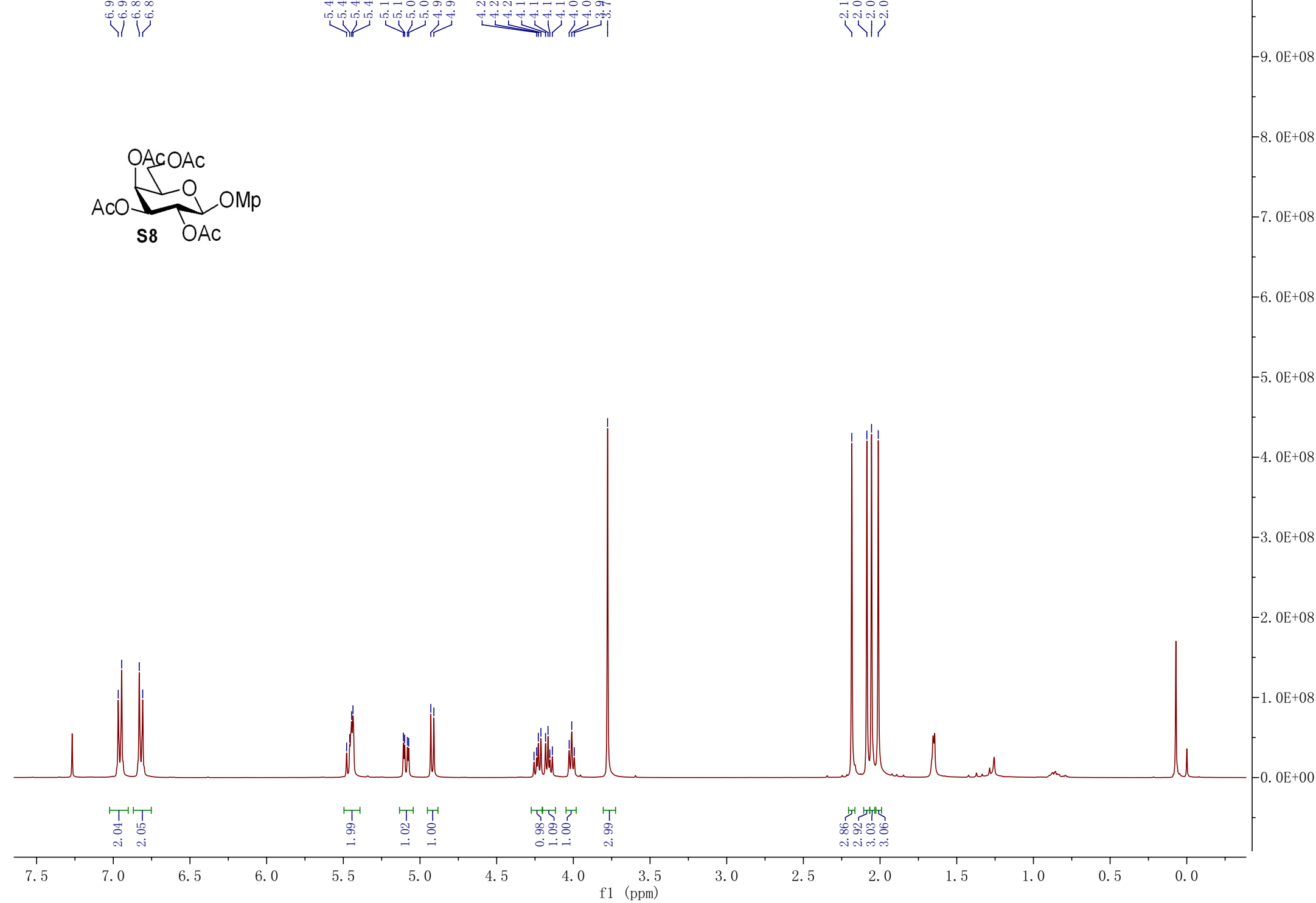


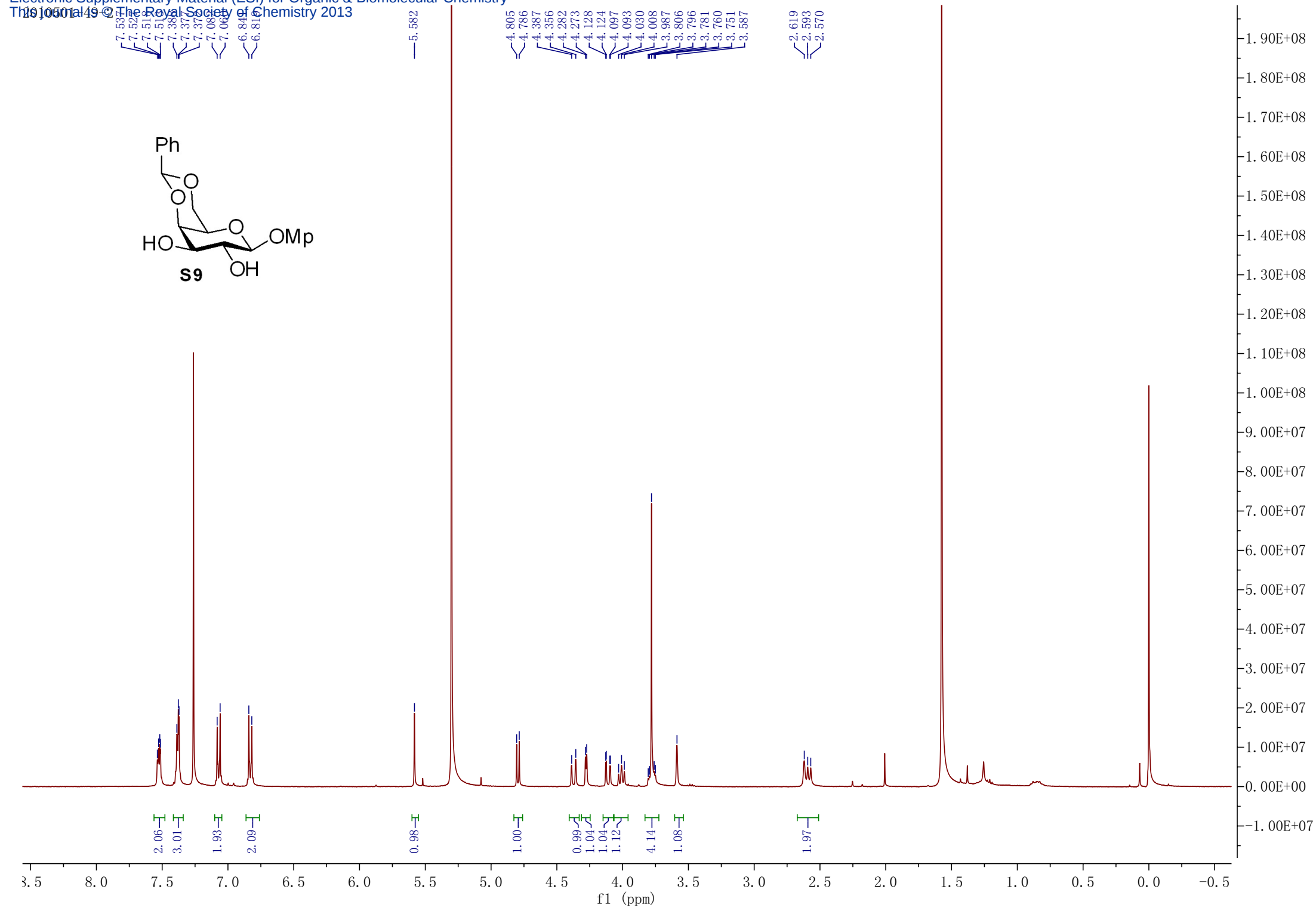
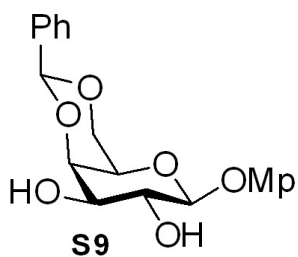


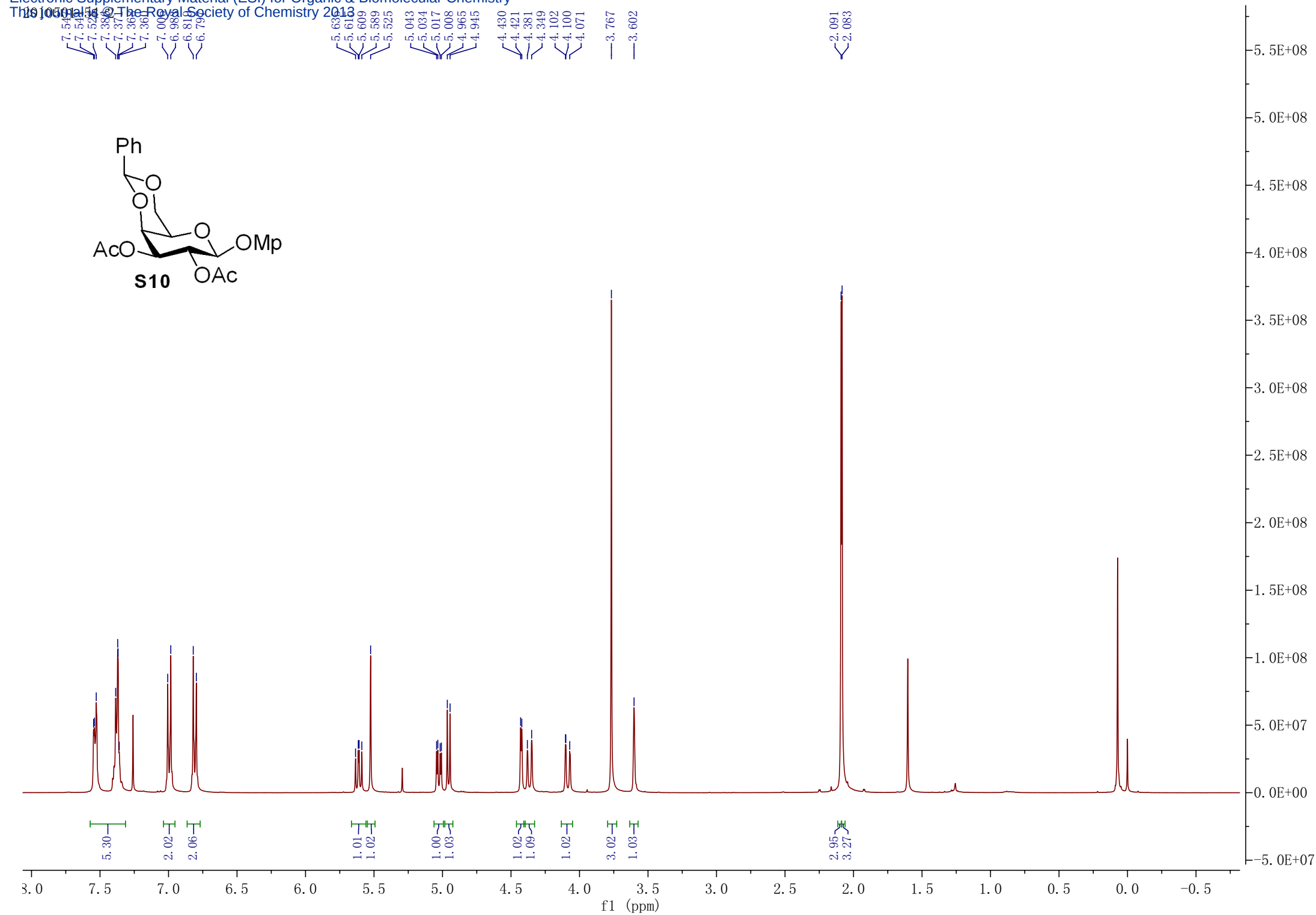
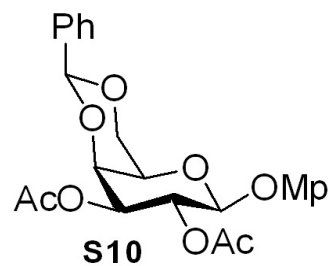


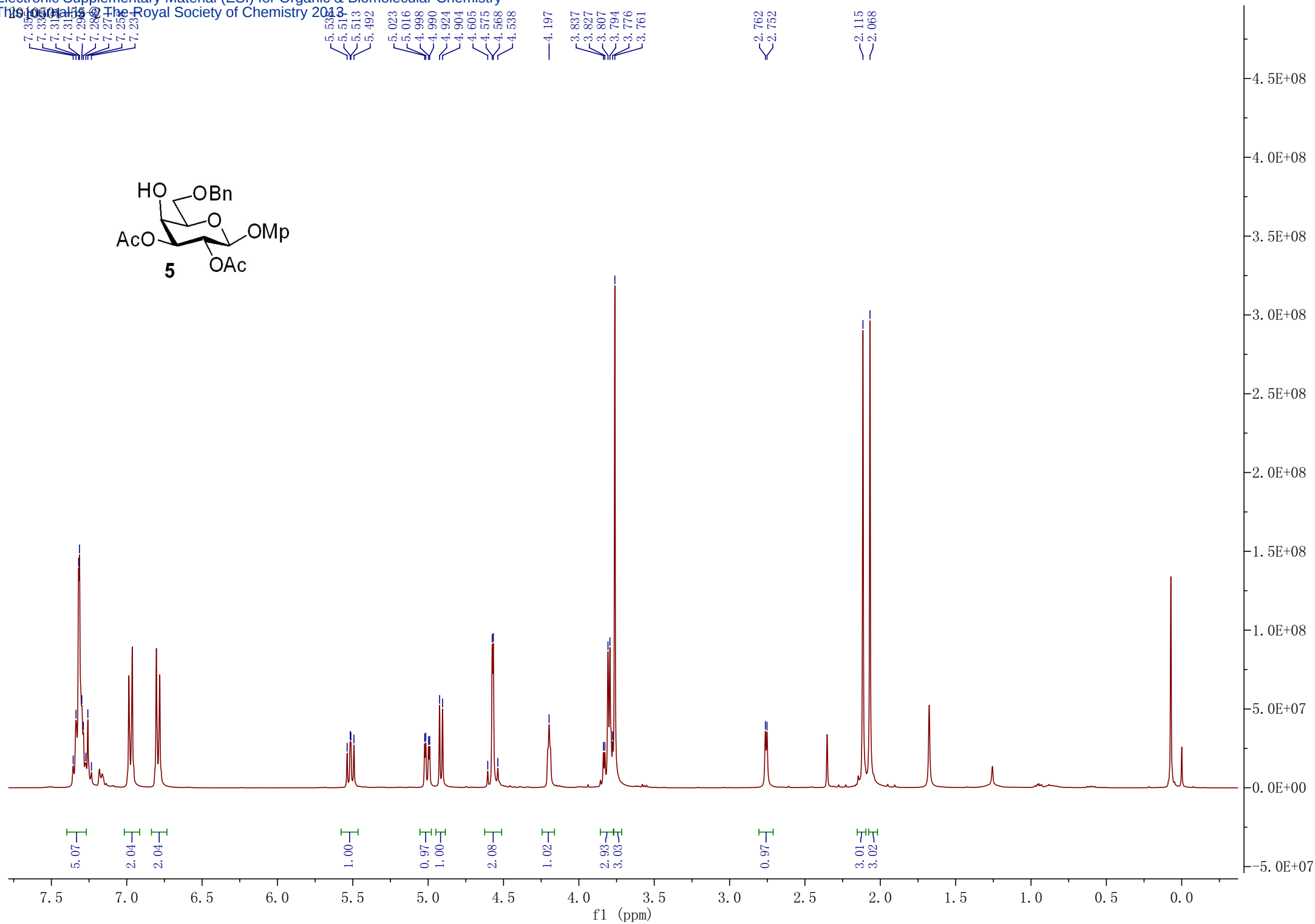
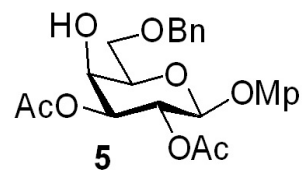


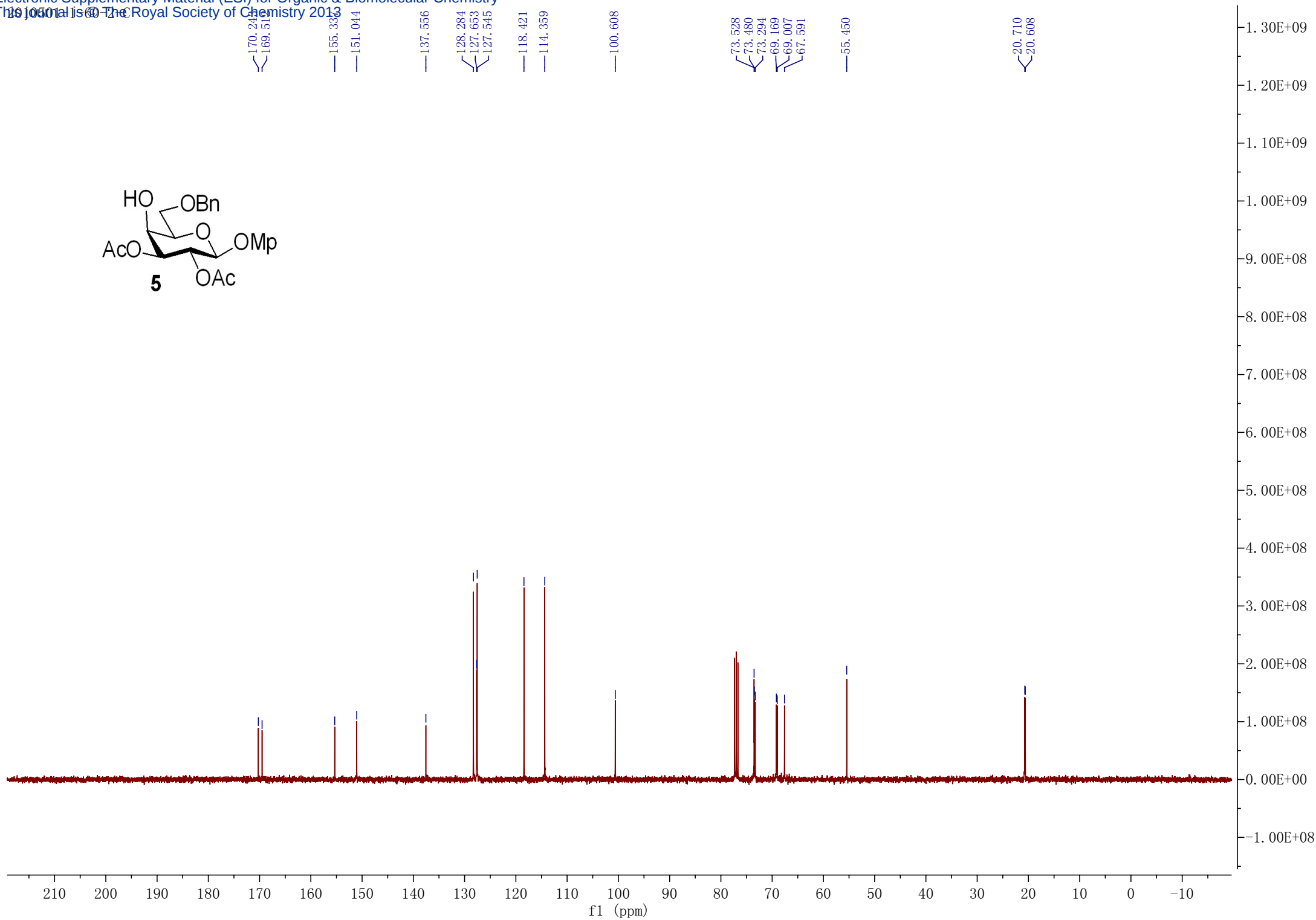
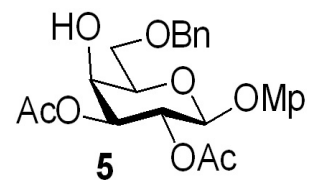


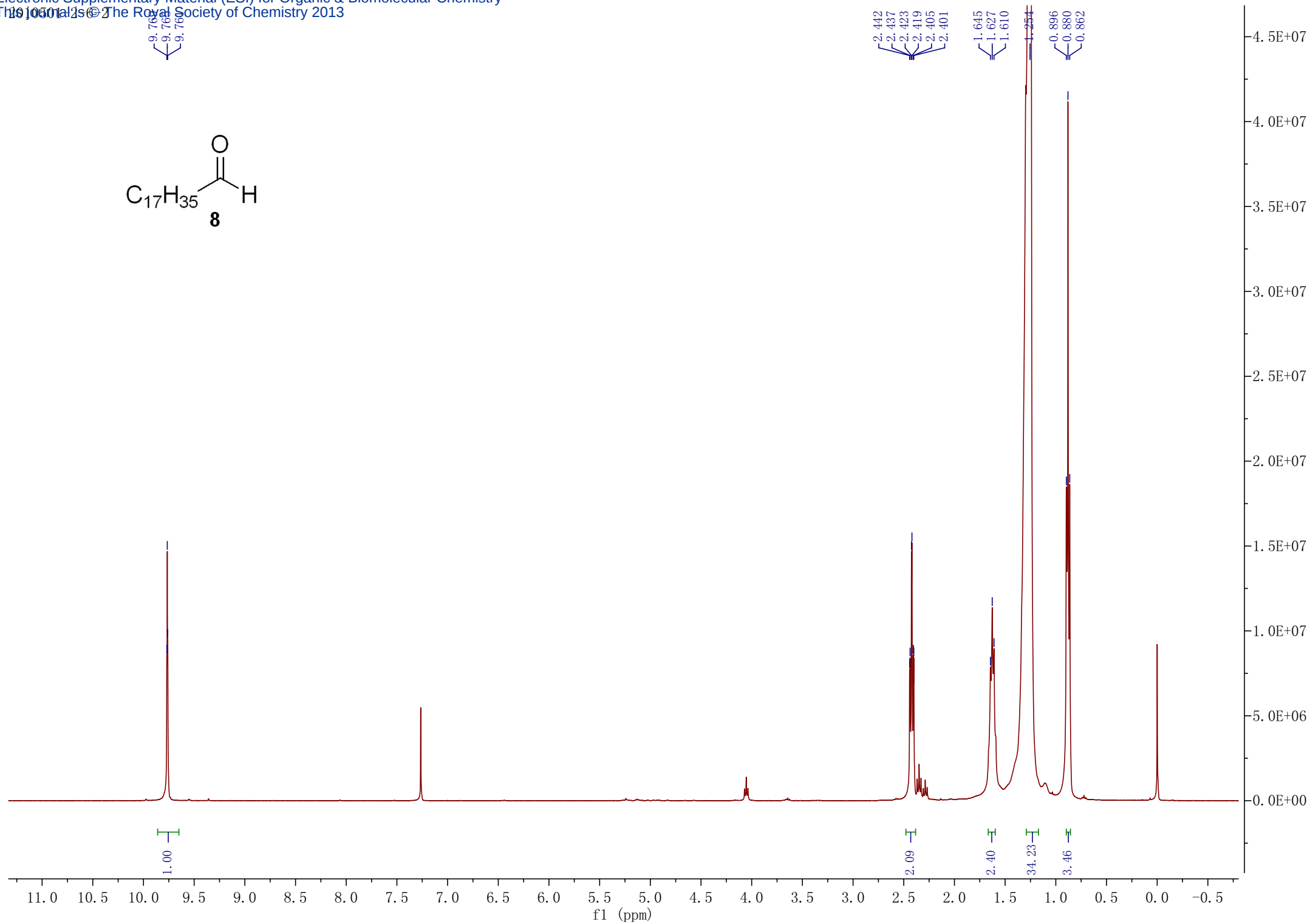
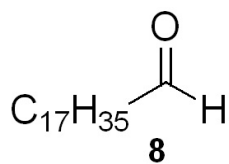


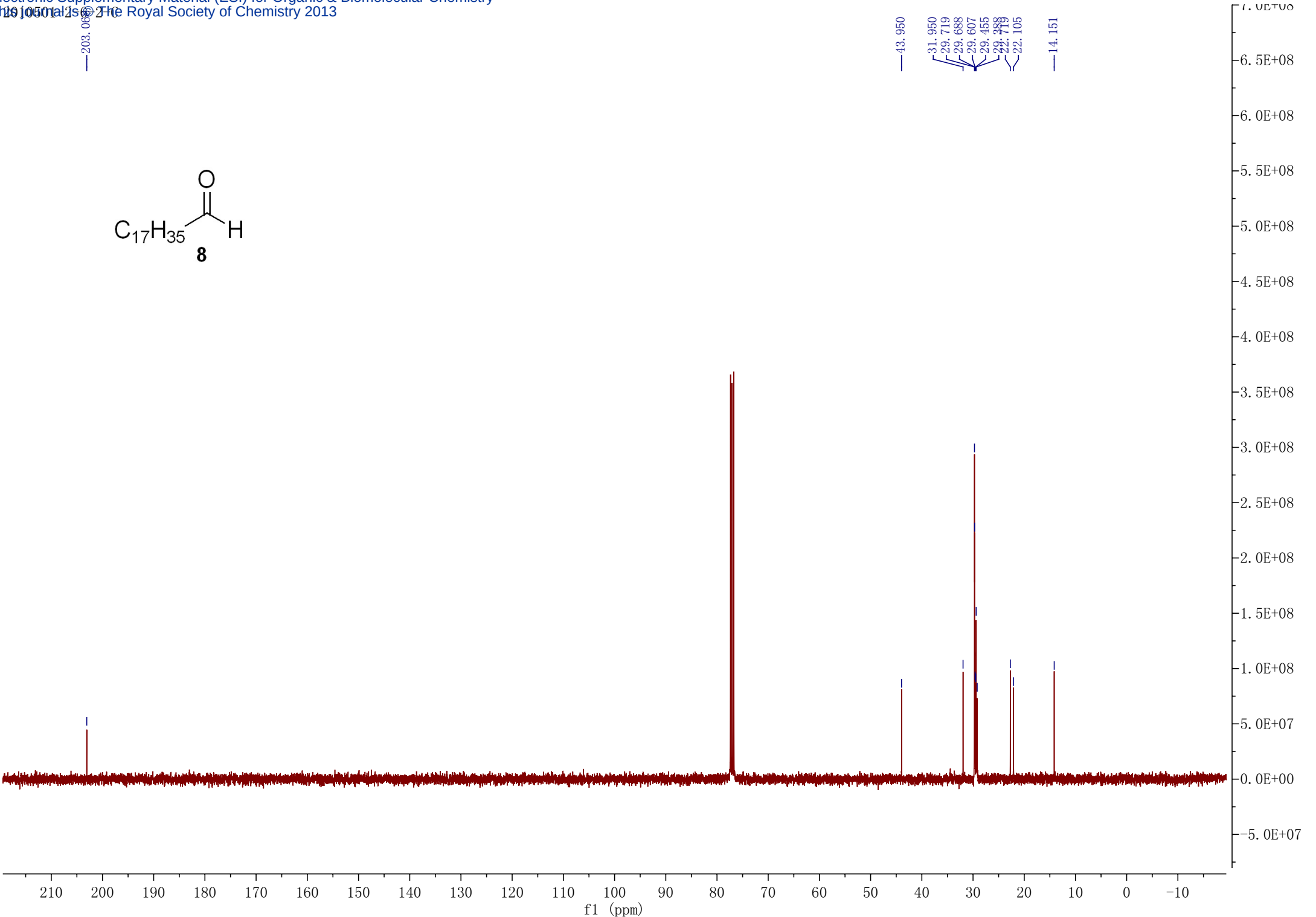
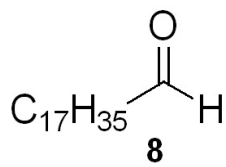


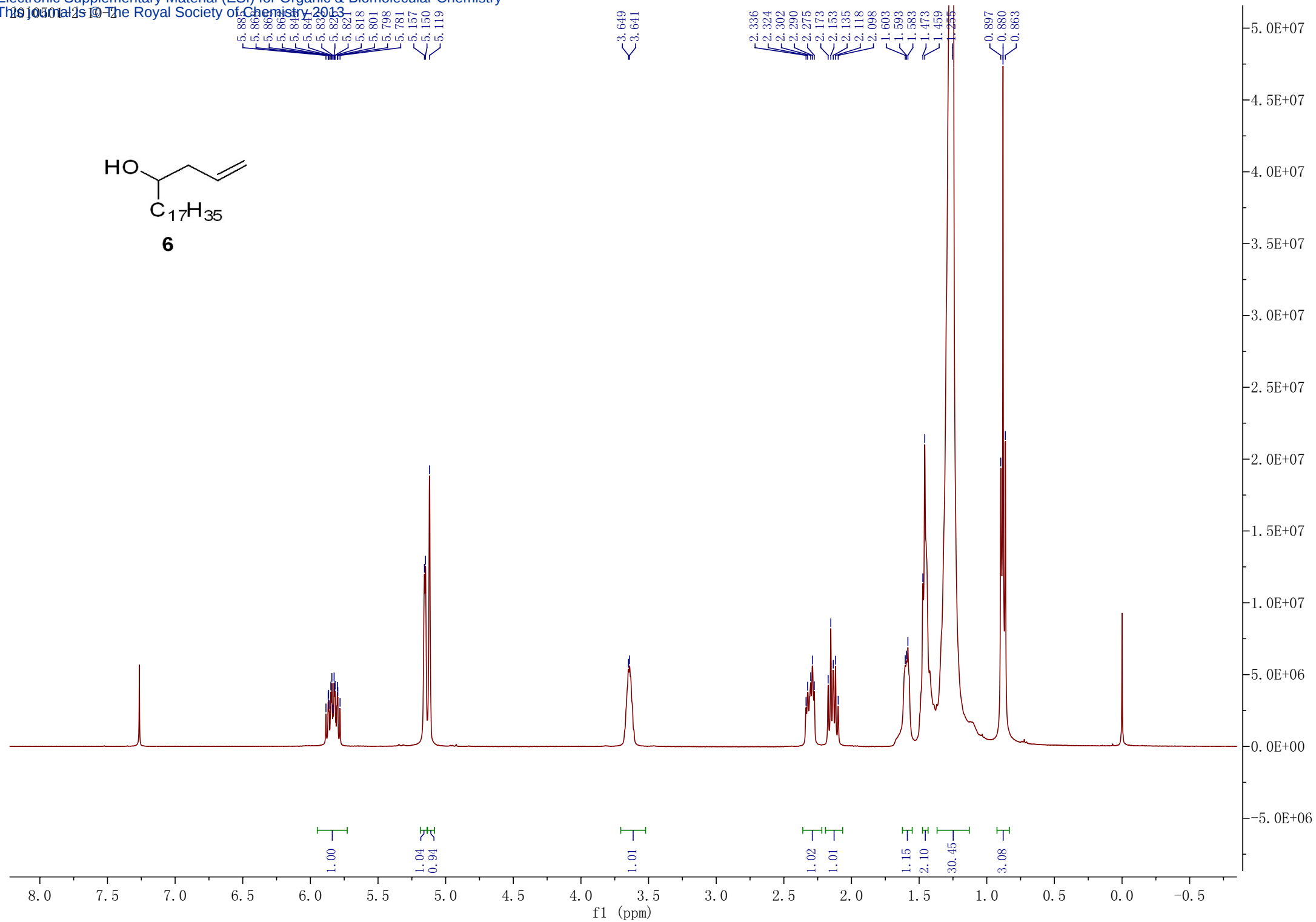
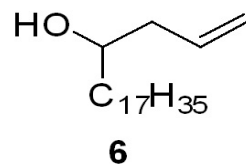


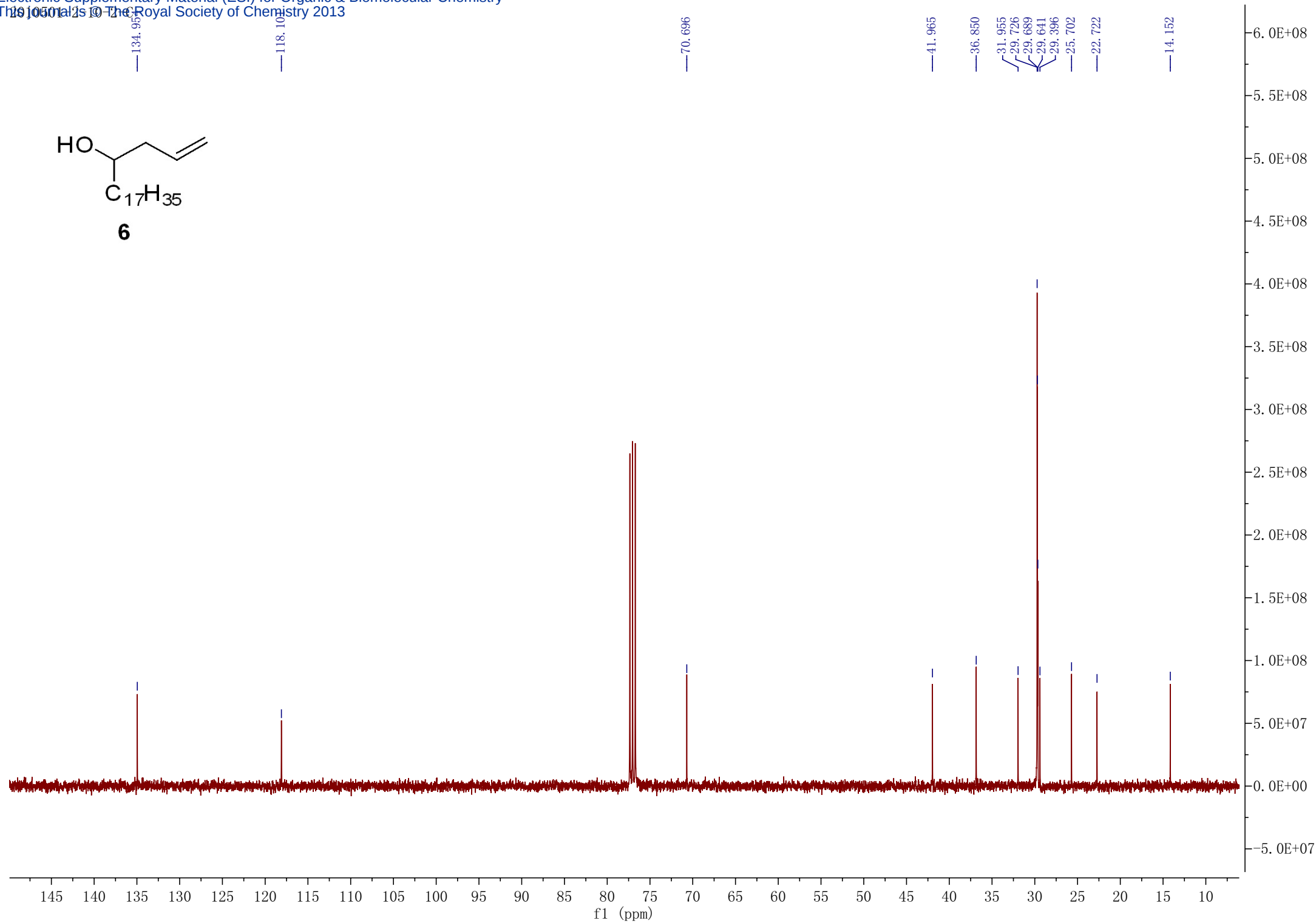
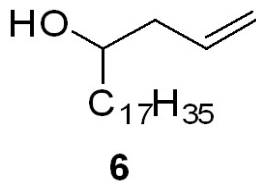


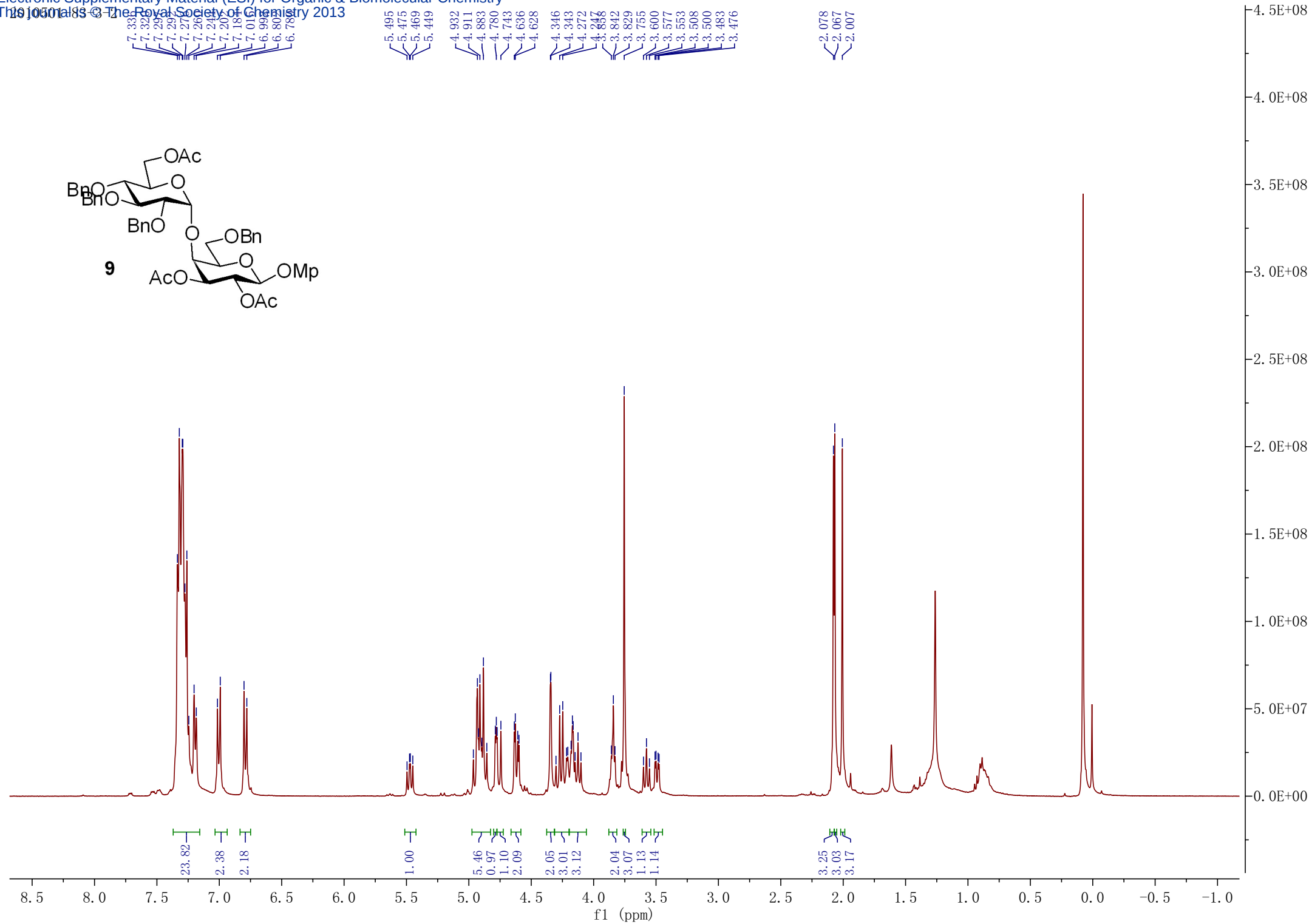
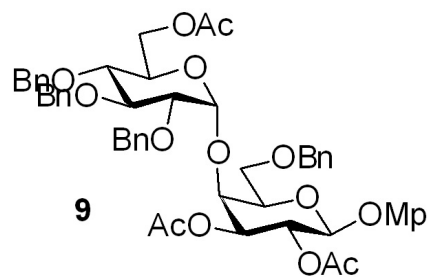


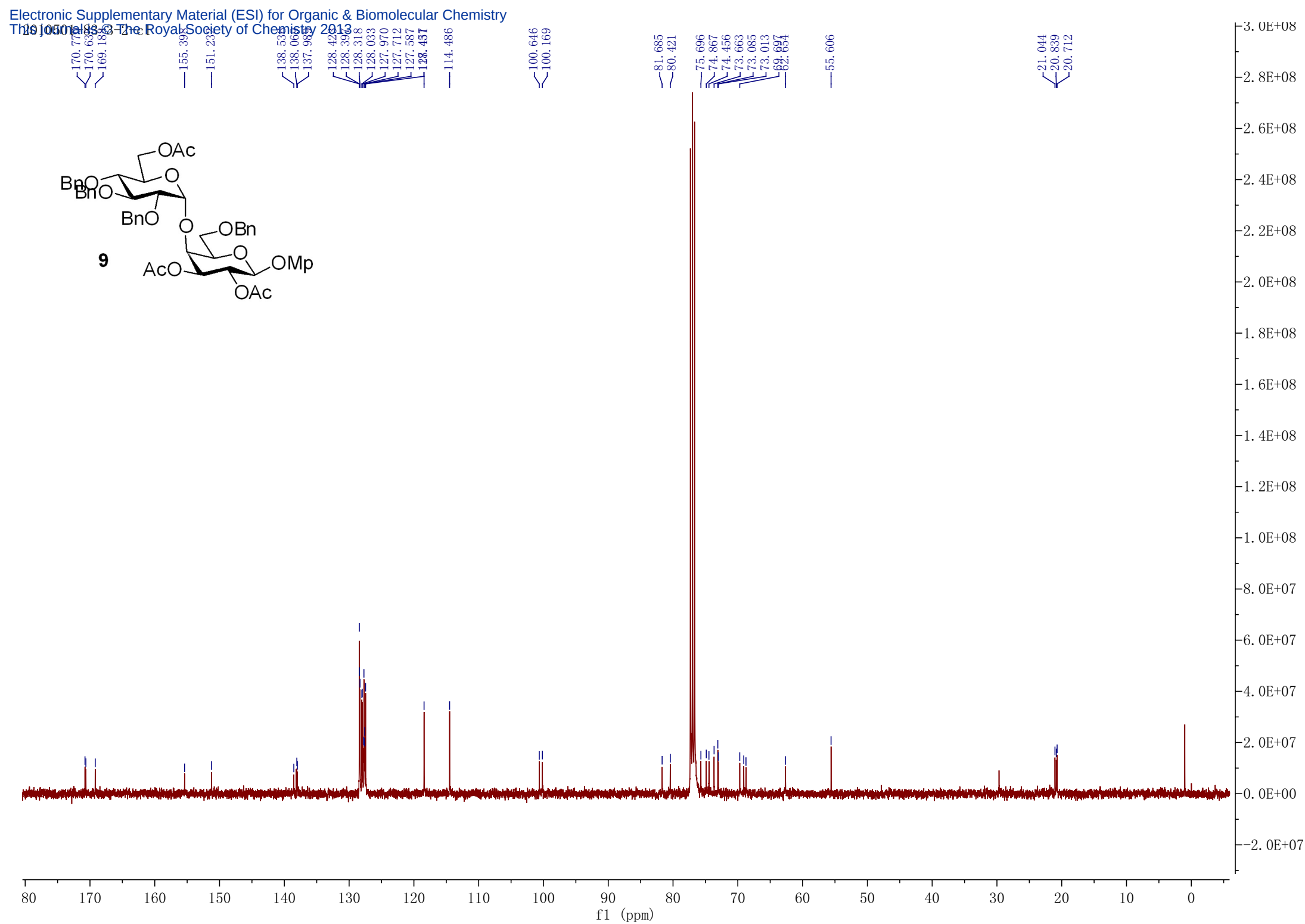


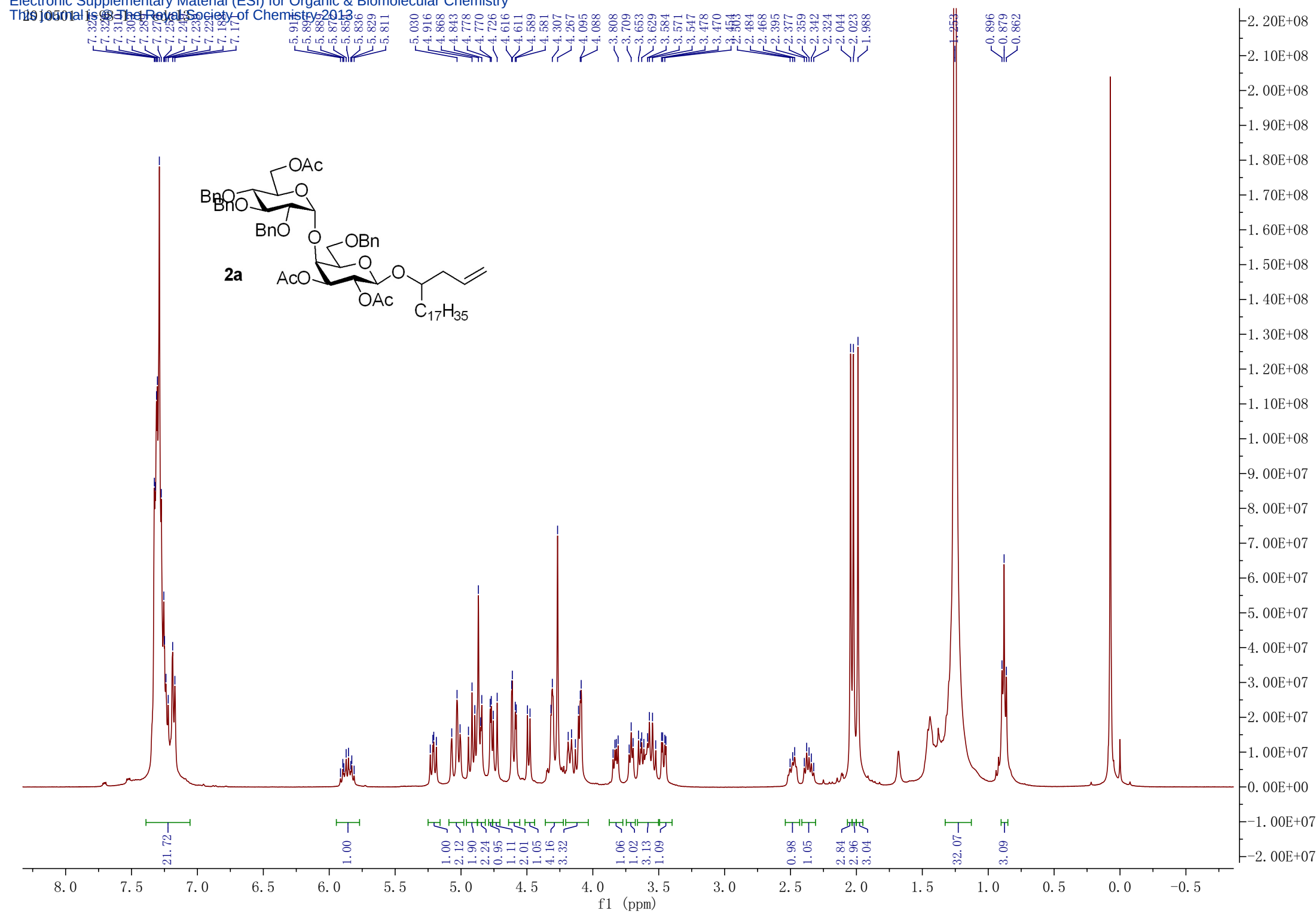


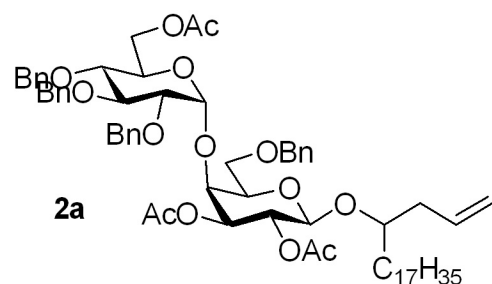












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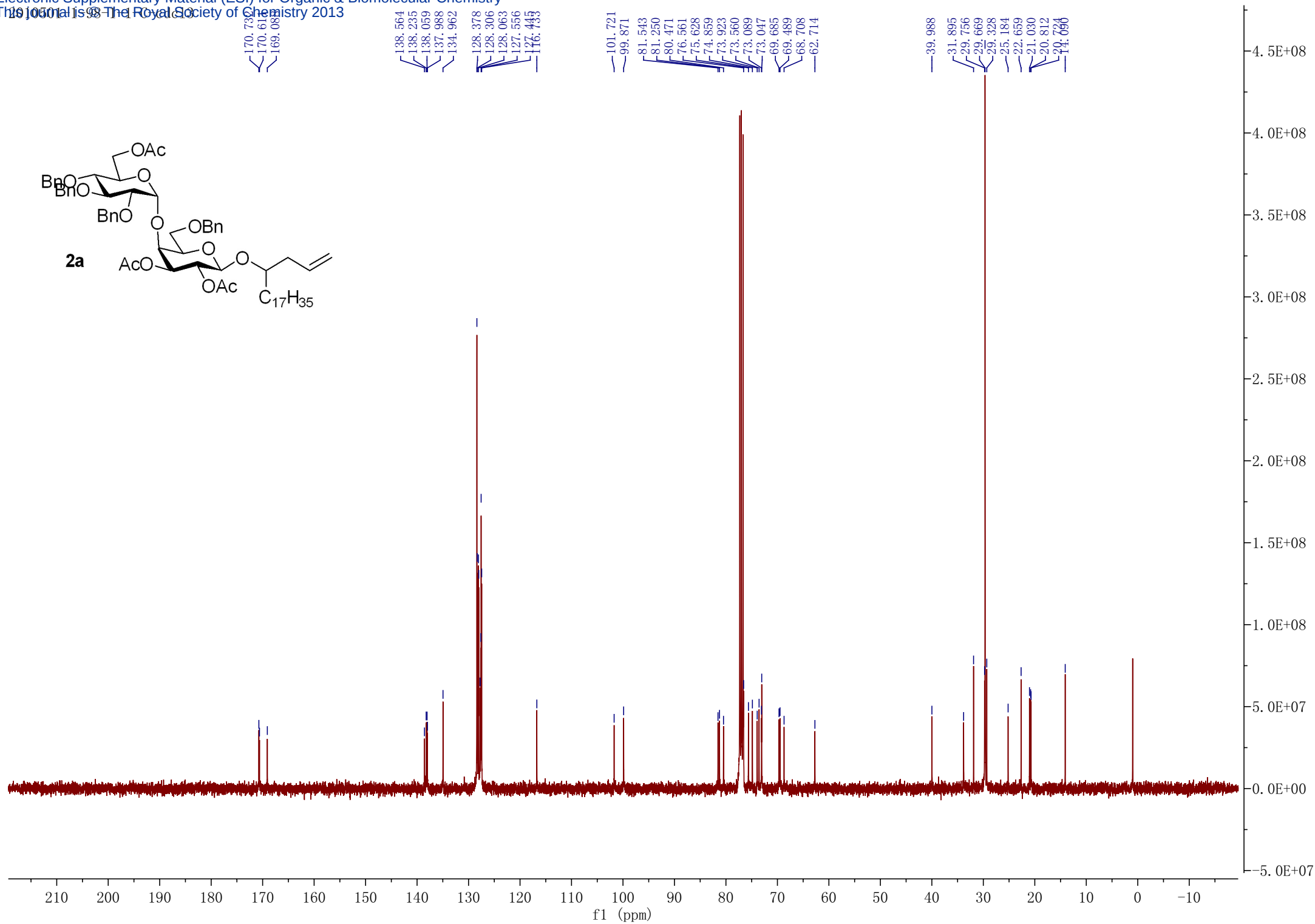
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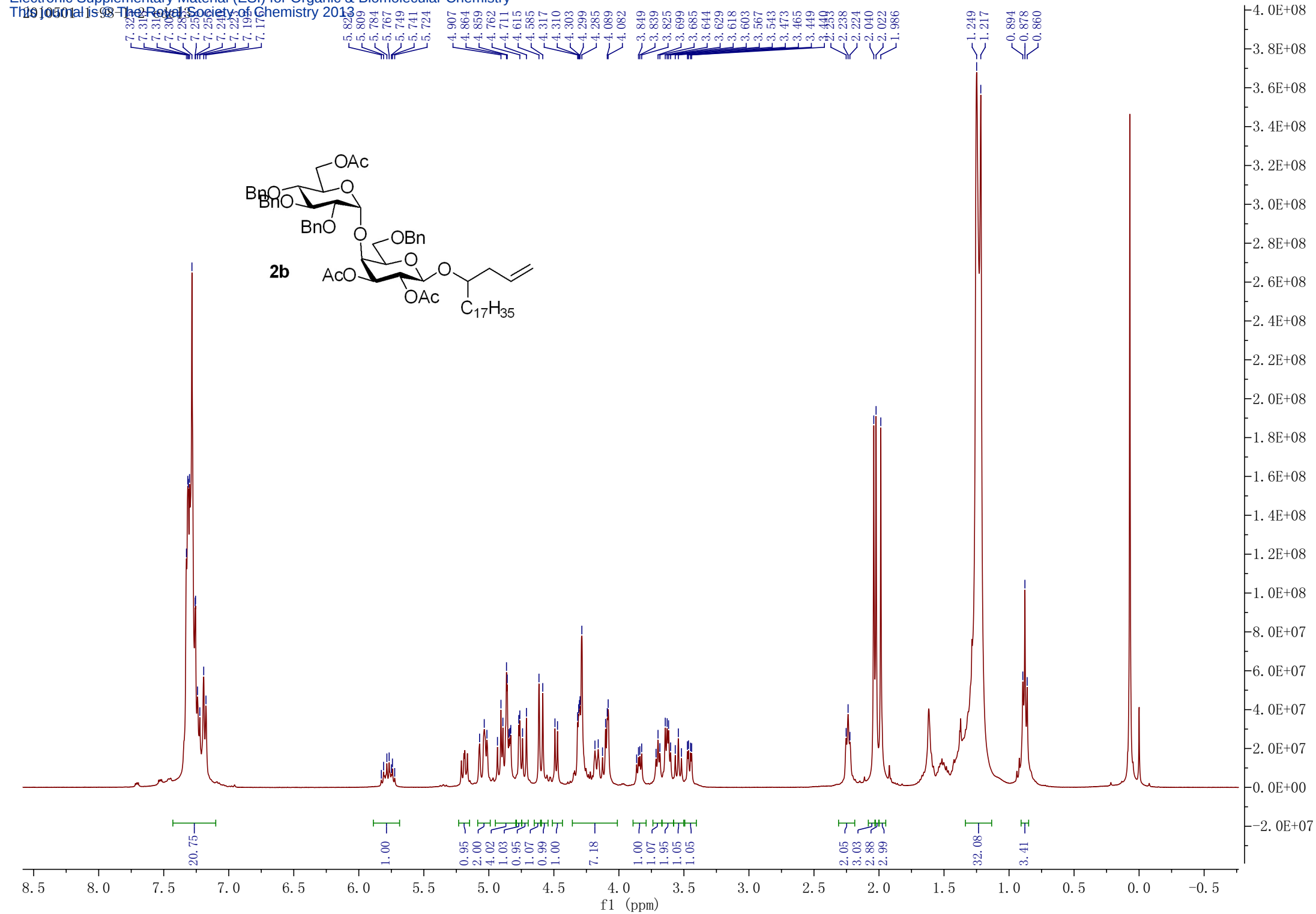
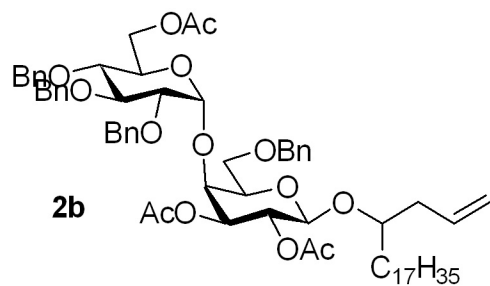
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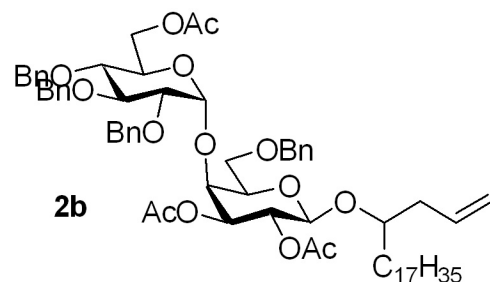
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