Supramolecular Assisted *O*-Acylation of Carbohydrates

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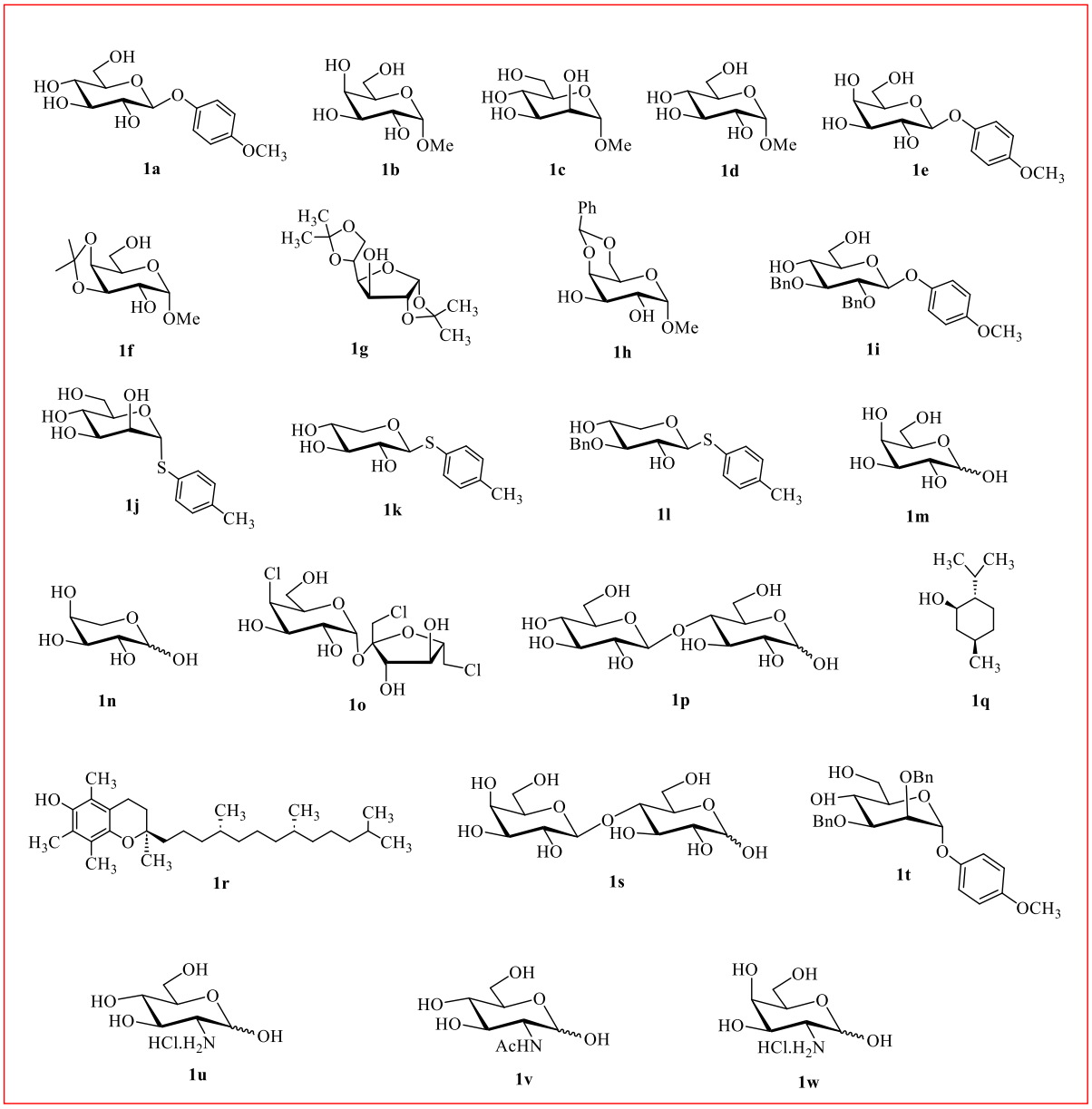
Experimental Procedures:

General:

Chemicals were purchased and used without further purification. Dry solvents were obtained by distillation using standard procedures. Reactions requiring anhydrous conditions were performed under nitrogen; glassware and needles were either flame-dried immediately prior to use or placed in an oven (100 °C) for at least 2 hours and allowed to cool either in a desiccator or under reduced pressure; liquid reagents, solutions or solvents were added *via* syringe through rubber septa; solid reagents were added *via* Schlenk type adapters. Teflon rings were used between the joints of the condensers and round bottom flasks. Reactions were monitored by TLC on Kieselgel 60 F254 (Merck). Detection was by examination under UV light (254 nm) and by charring with 10% sulfuric acid in methanol. Flash column chromatography was performed using silica gel [Merck, 230−400 mesh (40−63 μm)]. Extracts were concentrated *in vacuo* using both a Büchi rotary evaporator (bath temperatures up to 50 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature. ^{1}H NMR, and ^{13}C NMR spectra were measured in the solvent stated at 400 MHz. Chemical shifts are quoted in parts per million from a residual solvent peak ($CDCl_3$: ^{1}H - 7.26 ppm and ^{13}C - 77.16 ppm) and coupling constants (*J*) given in Hertz. Multiplicities are abbreviated as: b (broad), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) or combinations thereof. The units of the specific rotation, (deg·mL)/(g·dm), are implicit and are not included in the reported value. Concentration *c* is given in g/100 mL.

List of substrates used for this project:



Synthesis of Substrates:

Compound **1a, 1e, 1m, 1n, 1o, 1p, 1q, 1r, 1s, 1u, 1v, 1w** were purchased from TCI Chemicals and used for acylation reactions without any further purifications and other substrates were synthesised by reported literature methods (**1b**,[1] **1c**,[2] **1d**,[3] **1f**,[4] **1g**,[5] **1h**,[6] **1i**, [7] **1j**,[8] **1k**,[9] **1l**,[9] **1t**,[7]).

Precautions of using 18-crown-6:

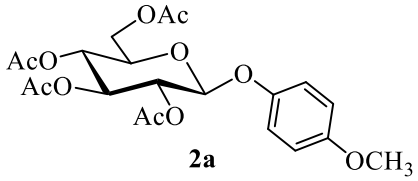
18-crown-6 can cause central nervous system (CNS) effects. It may be readily absorbed through the skin. Due to its potential toxicity and limited understanding of its toxicological properties, 18-crown-6 should be handled with care. Avoid all contact and inhalation. Wear gloves and work in a well-ventilated fume hood. [14]

General procedures for supramolecular assisted acylation:

Procedure A: Carbohydrate substrate (1.0 equiv.), KF (20 mol%), and 18-crown-6 (20 mol%) were weighed into an oven-dried round-bottom flask. Then, acetic anhydride or propionic anhydride (1.15 equiv. per -OH) was taken in the round-bottom flask. The reaction mixture was stirred in neat condition in an oil bath at 40˚C for 12h; completion of the reaction was determined by either TLC or NMR analysis of the crude material. The reaction mixture was concentrated *in vacuo* and purified by column chromatography to yield the respective per acylated product.

Procedure B: Carbohydrate substrate (1.0 equiv.), KF (20 mol%), and 18-crown-6 (20 mol%) were weighed into an oven-dried round-bottom flask. Then, 2ml acetonitrile and benzoic anhydride (1.15 equiv. per -OH) were added into the reaction mixture. The reaction solution was stirred in an oil bath at 40˚C for 12h; completion of the reaction was determined by either TLC or NMR analysis of the crude material. The reaction mixture was concentrated *in vacuo* and directly purified by column chromatography to yield the respective per benzoylated product.

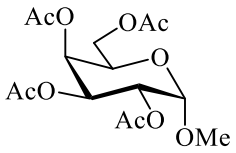
Substrates scope:



2a

4-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside (2a): Following the *general procedure (A)* glycosyl substrate **1a** (50 mg, 0.18 mmol), KF (8 mg, 0.14 mmol), 18-Crown-6 (37 mg, 0.14 mmol) and acetic anhydride (74 µL, 0.80 mmol) afford compound **2a,** a colourless semi-solid (76 mg, 94%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

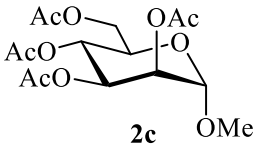
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.91 – 6.85 (m, 2H), 6.78 – 6.71 (m, 2H), 5.23 – 5.06 (m, 3H), 4.89 (d, *J* = 7.7 Hz, 1H), 4.22 (dd, *J* = 12.3, 5.3 Hz, 1H), 4.09 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.74 (ddd, *J* = 9.9, 5.1, 2.4 Hz, 1H), 3.70 (s, 3H), 2.01 (d, *J* = 2.8 Hz, 6H), 1.96 (d, *J* = 3.9 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6, 170.3, 169.4, 169.3, 155.8, 150.9, 118.8, 118.7, 114.6, 114.6, 100.3, 72.8, 71.9, 71.3, 68.3, 62.0, 55.6, 20.7, 20.6, 20.6, 20.6. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{21}H_{30}NO_{11}$: 472.1819; found: 472.1801.



2b

Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside (2b): Following the *general procedure (A)* glycosyl substrate **1b** (50 mg, 0.26 mmol), KF (12 mg, 0.21 mmol), 18-Crown-6 (54 mg, 0.21 mmol) and acetic anhydride (112 µL, 1.18 mmol) afford compound **2b,** a colourless semi-solid (84 mg, 90%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.39 (d, *J* = 4.9 Hz, 1H), 5.28 (dd, *J* = 10.9, 3.4 Hz, 1H), 5.08 (dd, *J* = 10.9, 3.7 Hz, 1H), 4.93 (d, *J* = 3.7 Hz, 1H), 4.12 (d, *J* = 5.7 Hz, 1H), 4.04 (d, *J* = 6.1 Hz, 2H), 3.35 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 170.3, 170.2, 169.9, 97.1, 68.1, 68.1, 67.5, 66.1, 61.8, 55.5, 20.8, 20.6, 20.6(2C). **HRMS (ESI-TOF)** m/z: for $[M+Na]^+$ calcd for $C_{15}H_{22}O_{10}Na$: 385.1111; found: 385.1105.

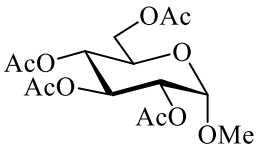


2c

Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside (2c): Following the *general procedure (A)* glycosyl substrate **1c (**50 mg, 0.26 mmol), KF (12 mg, 0.21 mmol), 18-Crown-6 (54 mg, 0.21 mmol) and acetic anhydride (112 µL, 1.18 mmol) afford compound **2c,** a colourless semi-solid (83 mg, 89%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.28 – 5.19 (m, 2H), 5.19 – 5.15 (m, 1H), 4.65 (d, *J* = 1.8 Hz, 1H), 4.22 (dd, *J* = 12.2, 5.4 Hz, 1H), 4.05 (dd, *J* = 12.2, 2.4 Hz, 1H), 3.93 – 3.86 (m, 1H), 3.34 (s, 3H), 2.09 (s, 3H), 2.04 (s, 3H), 1.98 (s, 3H), 1.92 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ

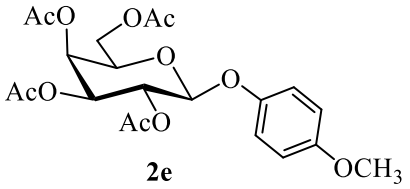
170.6, 170.0, 169.9, 169.7, 160.5, 98.5, 69.4, 69.0, 68.3, 66.1, 62.5, 55.2, 20.8, 20.7, 20.6 (2C). **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{15}H_{26}NO_{10}$: 380.1557; found: 380.1543.



2d

Methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside (2d): Following the *general procedure (A)* glycosyl substrate **1d** 50 mg, 0.26 mmol), KF (12 mg, 0.21 mmol), 18-Crown-6 (54 mg, 0.21 mmol) and acetic anhydride (112 µL, 1.18 mmol) afford compound **2d,** a colourless semi-solid (81 mg, 87%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

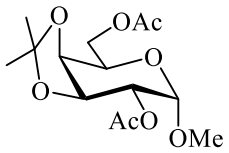
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (t, *J* = 9.7 Hz, 1H), 5.03 – 4.96 (m, 1H), 4.90 – 4.87 (m, 1H), 4.82 (dd, *J* = 10.3, 3.7 Hz, 1H), 4.20 (dd, *J* = 12.3, 4.6 Hz, 1H), 4.04 (d, *J* = 14.7 Hz, 1H), 3.96 – 3.88 (m, 1H), 3.35 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.96 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 169.9, 169.8, 169.4, 96.6, 70.6, 70.0, 68.4, 67.0, 61.8, 55.3, 20.7, 20.5, 20.5, 20.4. Spectroscopic data was in agreement with previously reported data.[11]



2e

4-Methoxyphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside (2e): Following the *general procedure (A)* glycosyl substrate **1e** (50 mg, 0.18 mmol), KF (8 mg, 0.14 mmol), 18-Crown-6 (37 mg, 0.14 mmol) and acetic anhydride (74 µL, 0.80 mmol) compound **2e,** a colourless semi-solid (74 mg, 91%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

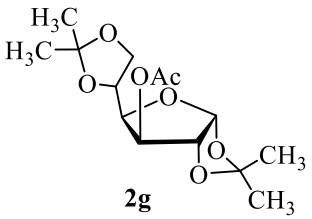
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.92 – 6.86 (m, 2H), 6.78 – 6.71 (m, 2H), 5.43 – 5.34 (m, 2H), 5.02 (dd, *J* = 10.5, 3.5 Hz, 1H), 4.85 (d, *J* = 7.9 Hz, 1H), 4.16 (dd, *J* = 11.2, 6.8 Hz, 1H), 4.09 (dd, *J* = 11.2, 6.5 Hz, 1H), 3.94 (t, *J* = 6.1 Hz, 1H), 3.71 (s, 3H), 2.11 (s, 3H), 2.02 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 170.3, 170.2, 169.4, 155.8, 151.0, 118.6, 114.6, 100.9, 70.9, 70.9, 68.8, 66.9, 61.3, 55.7, 20.8, 20.7 (2C), 20.6. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{21}H_{30}NO_{11}$: 472.1819; found: 472.1805.



2f

Methyl 2,6-di-*O*-acetyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (2f): Following the *general procedure (A)* glycosyl substrate **1f** (50 mg, 0.21 mmol), KF (5 mg, 0.09 mmol), 18-Crown-6 (23 mg, 0.09 mmol) and acetic anhydride (46 µL, 0.49 mmol) afford compound **2f,** a white solid (66 mg, 98%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 5:1).

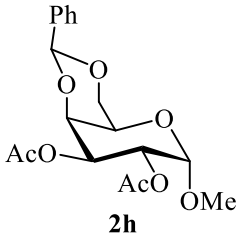
^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (dd, *J* = 8.1, 3.6 Hz, 1H), 4.79 (d, *J* = 3.6 Hz, 1H), 4.32 (dd, *J* = 11.7, 4.3 Hz, 1H), 4.29 – 4.22 (m, 2H), 4.16 (dd, *J* = 5.4, 2.6 Hz, 1H), 4.10 (ddd, *J* = 7.2, 4.3, 2.5 Hz, 1H), 3.32 (s, 3H), 2.07 (s, 3H), 2.03 (s, 3H), 1.45 (s, 3H), 1.27 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.8, 170.5, 110.0, 97.1, 73.4, 73.4, 71.7, 65.5, 63.6, 55.5, 27.8, 26.3, 21.0, 20.8. **HRMS (ESI-TOF)** m/z: for $[M+H]^+$ calcd for $C_{14}H_{23}O_8$: 319.1393; found: 319.1375.



2g

3-*O*-Acetyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2g): Following the *general procedure (A)* glycosyl substrate **1g** (100 mg, 0.38 mmol), KF (4 mg, 0.08 mmol), 18-Crown-6 (20 mg, 0.08 mmol) and acetic anhydride (42 µL, 0.44 mmol) afford compound **2g,** a colourless semi-solid (114 mg, 99%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

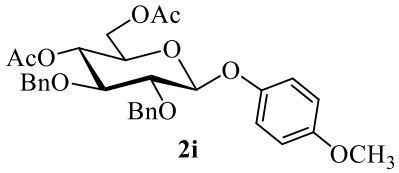
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (d, *J* = 3.7 Hz, 1H), 5.18 (d, *J* = 2.8 Hz, 1H), 4.43 (d, *J* = 3.7 Hz, 1H), 4.18 – 4.11 (m, 2H), 4.03 – 3.93 (m, 2H), 2.04 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.6, 112.3, 109.3, 105.0, 83.3, 79.7, 76.1, 72.4, 67.1, 26.8, 26.7, 26.2, 25.3, 20.9. **HRMS (ESI-TOF)** m/z: for $[M+H]^+$ calcd for $C_{14}H_{23}O_8$: 303.1444; found: 303.1428.



2h

Methyl 2,3-di-*O*-acetyl-4,6-*O*-benzylidene-α-D-galactopyranoside (2h): Following the *general procedure (A)* glycosyl substrate **1h** (50 mg, 0.18 mmol), KF (4 mg, 0.07 mmol), 18-Crown-6 (19 mg, 0.07 mmol) and acetic anhydride (39 µL, 0.41 mmol) afford compound **2h,** a white solid (60 mg, 93%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

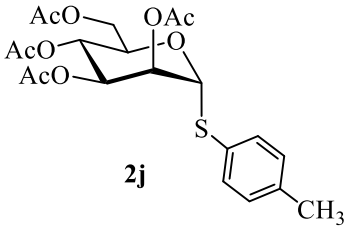
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 7.6, 2.1 Hz, 2H), 7.35 – 7.24 (m, 3H), 5.45 (s, 1H), 5.35 – 5.20 (m, 2H), 5.02 (d, *J* = 3.2 Hz, 1H), 4.40 (d, *J* = 2.0 Hz, 1H), 4.21 (dd, *J* = 12.5, 1.7 Hz, 1H), 4.00 (dd, *J* = 12.5, 1.8 Hz, 1H), 3.68 (s, 1H), 3.35 (s, 3H), 2.01 (d, *J* = 3.3 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.7, 170.3, 137.5, 130.2, 129.1, 128.5, 128.2, 126.3, 100.9, 97.8, 73.9, 69.1, 68.6, 68.1, 62.0, 55.6, 21.0, 20.9. **HRMS (ESI-TOF)** m/z: for $[M+H]^+$ calcd for $C_{18}H_{23}O_8$: 367.1393; found: 367.1370.



2i

4-Methoxyphenyl 4,6-di-*O*-acetyl-2,3-di-*O*-benzyl-β-D-glucopyranoside (2i): Following the *general procedure (A)* glycosyl substrate **1i** (50 mg, 0.11 mmol), KF (3 mg, 0.04 mmol), 18-Crown-6 (12 mg, 0.04 mmol) and acetic anhydride (27 µL, 0.25 mmol) afford compound **2i,** a white semi-solid (56 mg, 95%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 6:1).

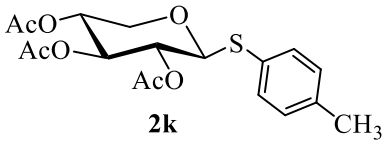
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 10H), 6.94 (d, *J* = 9.0 Hz, 2H), 6.76 (d, *J* = 9.2 Hz, 2H), 5.05 – 4.99 (m, 1H), 4.96 (d, *J* = 10.9 Hz, 1H), 4.83 – 4.72 (m, 3H), 4.57 (d, *J* = 11.6 Hz, 1H), 4.17 (dd, *J* = 12.1, 5.7 Hz, 1H), 4.03 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.71 (s, 3H), 3.68 (d, *J* = 7.7 Hz, 1H), 3.63 – 3.55 (m, 2H), 1.99 (s, 3H), 1.86 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.8, 169.6, 155.6, 151.3, 138.2, 138.0, 128.5, 128.4, 128.3, 127.9, 127.9, 127.8, 118.6, 114.6, 102.8, 81.8, 81.6, 75.3, 75.2, 72.0, 69.7, 62.5, 55.7, 20.8 (2C). **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{31}H_{38}NO_9$: 568.2547; found: 568.2531.



2j

***p*-Tolyl 2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-mannopyranoside (2j)**: Following the *general procedure (A)* glycosyl substrate **1j** (50 mg, 0.18 mmol), KF (8 mg, 0.14 mmol), 18-Crown-6 (34 mg, 0.14 mmol) and acetic anhydride (76 µL, 0.80 mmol) afford compound **2j,** a white solid (68 mg, 86%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 4:1).

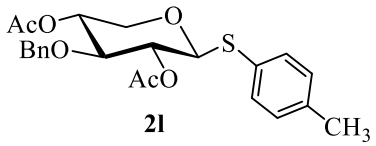
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.05 (d, *J* = 7.8 Hz, 2H), 5.46 – 5.40 (m, 1H), 5.34 (d, *J* = 1.7 Hz, 1H), 5.28 – 5.22 (m, 2H), 4.51 – 4.45 (m, 1H), 4.23 (dd, *J* = 12.2, 5.9 Hz, 1H), 4.03 (dd, *J* = 12.2, 2.4 Hz, 1H), 2.26 (s, 3H), 2.07 (s, 3H), 2.00 (d, *J* = 5.1 Hz, 6H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.6, 169.9, 169.8, 169.8, 138.5, 132.6, 130.0, 128.8, 86.0, 70.9, 69.4, 69.4, 66.4, 62.5, 21.1, 20.9, 20.7, 20.7, 20.6. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{21}H_{30}NO_9S$: 472.1641; found: 472.1607.



2k

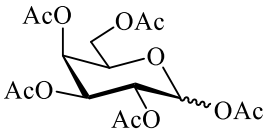
***p*-Tolyl 2,3,4-Tris-*O*-acetyl-1-thio-α-D-xylopyranoside (2k)**: Following the *general procedure (A)* glycosyl substrate **1k** (50 mg, 0.20 mmol), KF (7 mg, 0.12 mmol), 18-Crown-6 (31 mg, 0.12 mmol) and acetic anhydride (64 µL, 0.67 mmol) afford compound **2k,** a white solid (65 mg, 88%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.8 Hz, 2H), 7.05 (d, *J* = 8.3 Hz, 2H), 5.10 (t, *J* = 8.3 Hz, 1H), 4.88 – 4.78 (m, 2H), 4.64 (d, *J* = 8.8 Hz, 1H), 4.18 (dd, *J* = 11.7, 4.9 Hz, 1H), 3.32 (dd, *J* = 11.7, 9.3 Hz, 1H), 2.26 (s, 3H), 2.02 (s, 3H), 1.96 (d, *J* = 1.5 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.0, 169.8, 169.4, 138.6, 133.5, 133.2, 132.5, 132.3, 129.8, 128.1, 86.4, 72.3, 69.8, 68.5, 65.4, 21.2, 20.8, 20.7. **HRMS (ESI-TOF)** m/z: for $[M+Na]^+$ calcd for $C_{18}H_{22}O_7SNa$: 405.0984; found: 405.0959.



2l

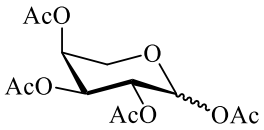
***p*-Tolyl 2,4-di-*O*-acetyl-3-*O*-benzyl-1-thio-β-D-xylopyranoside (2l)**: Following the *general procedure (A)* glycosyl substrate **1l** (50 mg, 0.14 mmol), KF (3 mg, 0.06 mmol), 18-Crown-6 (15 mg, 0.06 mmol) and acetic anhydride (31 µL, 0.33 mmol) afford compound **2l,** a white solid (57 mg, 92%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 4:1). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.40 – 7.36 (m, 2H), 7.36 – 7.26 (m, 5H), 7.14 – 7.07 (m, 2H), 5.06 (t, *J* = 6.1 Hz, 1H), 4.94 – 4.83 (m, 2H), 4.70 (q, *J* = 11.9 Hz, 2H), 4.42 (dd, *J* = 12.2, 3.9 Hz, 1H), 3.70 (t, *J* = 6.2 Hz, 1H), 3.46 (dd, *J* = 12.1, 6.3 Hz, 1H), 2.33 (s, 3H), 2.06 (s, 3H), 2.04 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.9, 169.5, 137.9, 137.6, 132.4, 130.2, 129.7, 128.5, 127.9, 127.7, 86.4, 76.4, 73.4, 70.3, 69.5, 63.0, 21.1, 21.0, 21.0. **HRMS (ESI-TOF)** m/z: for $[M+Na]^+$ calcd for $C_{23}H_{26}O_6SNa$: 453.1348; found: 453.1331.



2m

1,2,3,4,6-Penta-*O*-acetyl-D-galactopyranoside (2m): Following the *general procedure (A)* D-galactose **1m** (50 mg, 0.28 mmol), KF (16 mg, 0.28 mmol), 18-Crown-6 (73 mg, 0.28 mmol) and acetic anhydride (150 µL, 1.60 mmol) afford compound **2m,** a white solid (90 mg, 83%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.02 (d, *J* = 2.0 Hz, 1H), 5.80 (d, *J* = 1.2 Hz, 0H), 5.32 – 5.24 (m, 2H), 5.21 – 5.17 (m, 1H), 5.07 (dd, *J* = 9.9, 3.3 Hz, 0H), 4.25 – 4.19 (m, 1H), 4.18 – 4.14 (m, 1H), 4.05 (d, *J* = 2.5 Hz, 1H), 4.03 – 3.98 (m, 1H), 3.74 (ddd, *J* = 9.8, 5.3, 2.4 Hz, 0H), 3.65 – 3.60 (m, 1H), 2.15 (s, 1H), 2.11 (d, *J* = 3.2 Hz, 6H), 2.04 (s, 1H), 2.03 (s, 3H), 2.01 (s, 1H), 1.99 (s, 3H), 1.94 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 170.1, 169.9, 169.3, 168.9, 92.1, 89.6, 71.6, 70.7, 68.7, 67.8, 67.4, 67.3, 66.8, 66.4, 61.2, 61.0, 20.8, 20.7, 20.6, 20.6, 20.5. Spectroscopic data was in agreement with previously reported data.[10]

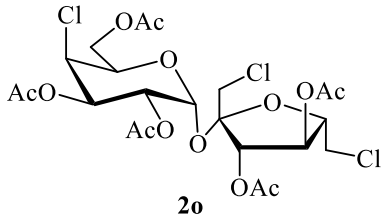


2n

1,2,3,4-Tetra-*O*-acetyl-D-arabinopyranoside (2n): Following the *general procedure (A)* D-arabinose **1n** (50 mg, 0.33 mmol), KF (15 mg, 0.27 mmol), 18-Crown-6 (70 mg, 0.27 mmol) and acetic anhydride (144 µL, 1.53 mmol) afford compound **2n,** a white solid (91 mg, 86%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.28 (d, *J* = 3.2 Hz, 1H), 6.13 (s, 0H), 5.32 (dq, *J* = 3.7, 1.2 Hz, 1H), 5.29 (q, *J* = 1.6 Hz, 1H), 5.15 (d, *J* = 2.3 Hz, 0H), 5.04 (dd, *J* = 9.0, 3.5 Hz, 0H), 4.98 (s, 0H), 4.34 – 4.25 (m, 1H), 4.16 (s, 0H), 4.04 – 3.97 (m, 1H), 3.80 – 3.70 (m, 1H), 2.09 (d, *J* = 1.1 Hz, 5H), 2.08 (s, 1H), 2.06 (d, *J* = 3.8 Hz, 3H), 2.04 (d, *J* = 1.7 Hz, 1H), 2.02 (d, *J* = 2.7 Hz, 1H), 2.00 (s, 1H), 1.98 (s, 1H), 1.96 (s, 5H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.3, 170.2, 169.9, 169.1, 107.0, 99.3, 92.1, 90.2, 80.5, 68.5, 67.0, 66.7, 62.8, 20.9, 20.9, 20.7, 20.6.

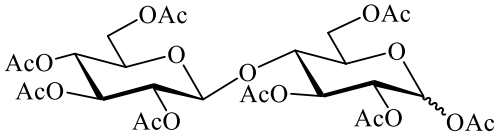
HRMS (ESI-TOF) m/z: for $[M+Na]^+$ calcd for $C_{13}H_{18}O_9Na$: 341.0849; found: 341.0824.



2o

5-*O*-(2,3,6-Ti-*O*-acetyl-4-chloro-4-deoxy-α-D-galactopyranosyl)-2,3-di-*O*-acetyl-1,6-dichloro-1,6-dideoxy-β-D-fructofuranoside (2o): Following the *general procedure (A)* Sucralose (**1o)** (50 mg, 0.13mmol), KF (7 mg, 0.13 mmol), 18-Crown-6 (33 mg, 0.13 mmol) and acetic anhydride (69 µL, 0.724 mmol) afford compound **2o,** a white semi-solid (63 mg, 85%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

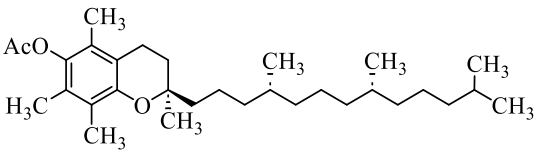
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.65 – 5.59 (m, 2H), 5.34 (t, *J* = 6.4 Hz, 1H), 5.26 – 5.19 (m, 2H), 4.54 – 4.46 (m, 2H), 4.17 (dt, *J* = 6.2, 3.2 Hz, 3H), 3.70 (d, *J* = 5.3 Hz, 2H), 3.65 (d, *J* = 12.1 Hz, 1H), 3.53 (d, *J* = 12.1 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H), 2.03 (d, *J* = 3.4 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.4, 170.2, 170.1, 169.8, 169.6, 104.4, 90.7, 80.8, 76.1, 75.9, 68.0, 67.8, 66.9, 63.6, 59.0, 44.5, 43.9, 20.8, 20.7 (2C), 20.7, 20.5. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{22}H_{33}Cl_3NO_{13}$: 624.0995; found: 624.0982.



2p

1,2,3,6-Tetra-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-D-glucopyranoside (2p): Following the *general procedure (A)* cellobiose (**1p)** (50 mg, 0.15mmol), KF (14 mg, 0.23 mmol), 18-Crown-6 (62 mg, 0.23 mmol) and acetic anhydride (127 µL, 1.34 mmol) afford compound **2p,** a white solid (81 mg, 82%) after purification by column chromatography (Hexane:EtOAc, 3:1 to 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.60 (d, *J* = 8.3 Hz, 1H), 5.20 – 5.13 (m, 1H), 5.08 (t, *J* = 9.4 Hz, 1H), 5.03 – 4.94 (m, 2H), 4.89 – 4.82 (m, 1H), 4.48 – 4.39 (m, 2H), 4.30 (dd, *J* = 12.5, 4.5 Hz, 1H), 4.05 (dd, *J* = 12.2, 4.7 Hz, 1H), 3.98 (dd, *J* = 12.5, 2.3 Hz, 1H), 3.80 – 3.73 (m, 1H), 3.69 (ddd, *J* = 9.9, 4.7, 2.0 Hz, 1H), 3.61 (ddd, *J* = 9.8, 4.5, 2.3 Hz, 1H), 2.06 (s, 3H), 2.03 (d, *J* = 1.3 Hz, 6H), 1.96 (d, *J* = 1.7 Hz, 9H), 1.94 (s, 3H), 1.91 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 170.5, 170.2, 170.2, 169.6, 169.5, 169.3, 169.0, 168.8, 100.6, 91.5, 75.8, 73.5, 72.8, 72.3, 71.9, 71.5, 70.4, 67.8, 61.6, 61.5, 20.8, 20.8, 20.6, 20.5 (3C), 20.4, 20.4. Spectroscopic data was in agreement with previously reported data.[11]

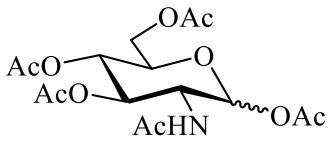


2q

(R)-2,5,7,8-Tetramethyl-2-((4R,8R)-4,8,12-trimethyltridecyl)chroman-6-yl acetate (2q): Following the *general procedure (A)* tocopherol (**1r)** (100 mg, 0.23mmol), KF (3 mg, 0.05 mmol), 18-Crown-6 (12 mg, 0.05 mmol) and acetic anhydride (25 µL, 0.27 mmol) afford compound **2q,** a colourless semi-solid (99 mg, 91%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.50 (t, *J* = 6.8 Hz, 2H), 2.23 (s, 3H), 2.01 (s, 3H), 1.93 (s, 3H), 1.89 (s, 3H), 1.75 – 1.60 (m, 2H), 1.44 (dt, *J* = 13.3, 6.6 Hz, 3H), 1.31 (tdd, *J* = 14.6, 10.7, 4.1 Hz, 4H), 1.25 – 1.10 (m, 11H), 1.09 – 0.95 (m, 6H), 0.82 – 0.73 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 169.7, 149.5, 140.6, 126.7, 124.9, 123.1, 117.4, 75.1, 39.5, 37.6, 37.5, 37.5, 37.4, 32.9, 32.8, 32.8, 31.1, 28.0, 24.9, 24.5, 22.8, 22.7, 21.1, 20.7, 20.6, 19.8, 19.8, 19.7, 19.7,

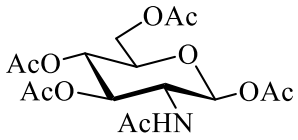
19.7, 13.0, 12.2, 11.9. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{31}H_{56}NO_3$: 490.4260; found: 490.4244.



2r

1,3,4,6-Tetra-*O*-acetyl-2-acetamido-2-deoxy-D-glucopyranoside (2r): Following the *general procedure (A)* D-glucosamine hydrochloride (**1u)** (100 mg, 0.46 mmol), KF (22 mg, 0.37 mmol), 18-Crown-6 (98 mg, 0.37 mmol) and acetic anhydride (240 µL, 2.55 mmol) afford compound **2r,** a colourless semi-solid (167 mg, 93%, α:β = 1:5) after purification by column chromatography (Hexane:EtOAc, 2:1 to 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.30 (d, *J* = 9.6 Hz, 1H), 6.10 (d, *J* = 3.7 Hz, 1H), 5.93 (d, *J* = 9.0 Hz, 1H), 5.66 (d, *J* = 8.8 Hz, 1H), 5.22 – 5.11 (m, 2H), 5.04 (d, *J* = 9.5 Hz, 2H), 4.46 – 4.38 (m, 1H), 4.26 – 4.21 (m, 1H), 4.18 (dd, *J* = 12.5, 4.0 Hz, 1H), 4.05 (dd, *J* = 12.3, 2.3 Hz, 1H), 4.02 – 3.94 (m, 2H), 3.78 (dd, *J* = 9.6, 2.3 Hz, 2H), 3.67 – 3.59 (m, 1H), 2.13 (s, 3H), 2.05 (s, 1H), 2.02 (s, 3H), 2.01 (s, 1H), 1.98 (d, *J* = 2.1 Hz, 6H), 1.97 (s, 1H), 1.87 (d, *J* = 2.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.5, 170.7, 170.3, 170.2, 169.4, 169.3, 169.1, 168.7, 92.4, 90.6, 72.6, 72.6, 70.5, 70.5, 69.6, 69.0, 67.9, 67.6, 63.6, 61.7, 61.5, 52.7, 50.9, 23.0, 22.9, 20.9, 20.9, 20.7, 20.6, 20.5. Spectroscopic data was in agreement with previously reported data.[12]

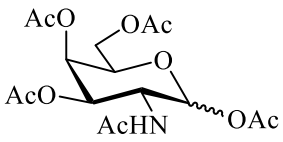


2r'

Following the *general procedure (A)* N-acetyl-D-glucosamine (**1v)** (100 mg, 0.45mmol), KF (21 mg, 0.36 mmol), 18-Crown-6 (96 mg, 0.36 mmol) and acetic anhydride (192 µL, 2.03 mmol) afford compound **2r',** a colourless semi-solid (170 mg, 97%) after purification by column chromatography (Hexane:EtOAc, 2:1 to 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.10 (d, *J* = 3.7 Hz, 1H), 5.89 (d, *J* = 9.0 Hz, 1H), 5.20 – 5.08 (m, 2H), 4.42 (ddd, *J* = 10.7, 9.1, 3.7 Hz, 1H), 4.18 (dd, *J* = 12.5, 4.1 Hz, 1H), 4.02 – 3.94 (m, 2H), 2.12 (s, 3H), 2.02 (s, 3H), 1.98 (d, *J* = 2.5 Hz, 6H), 1.87 (s, 3H). **^{13}C NMR (101 MHz,**

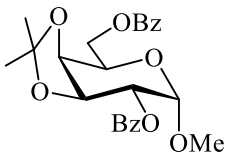
$CDCl_3$) δ 171.5, 170.6, 170.1, 169.1, 168.7, 90.6, 90.6, 90.6, 70.6, 69.6, 67.6, 61.5, 50.9, 22.9, 20.8, 20.6 (2C), 20.5. Spectroscopic data was in agreement with previously reported data.[12]



2s

1,3,4,6-Tetra-*O*-acetyl-2-acetamido-2-deoxy-D-galactopyranoside (2s): Following the *general procedure (A)* D-galactosamine hydrochloride (**1w)** (100 mg, 0.46 mmol), KF (22 mg, 0.37 mmol), 18-Crown-6 (98 mg, 0.37 mmol) and acetic anhydride (240 µL, 2.55 mmol) afford compound **2s,** a white semi-solid (177 mg, 98%, α:β = 1:5) after purification by column chromatography (Hexane:EtOAc, 2:1 to 1:2).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17 – 6.09 (m, 1H), 6.04 – 6.00 (m, 1H), 5.65 (dd, *J* = 9.0, 4.2 Hz, 1H), 5.36 (dd, *J* = 3.1, 1.4 Hz, 1H), 5.27 (dd, *J* = 9.0, 7.2 Hz, 1H), 5.18 – 5.07 (m, 1H), 4.70 – 4.64 (m, 1H), 4.18 – 4.13 (m, 2H), 4.08 – 3.95 (m, 2H), 3.65 – 3.59 (m, 1H), 2.11 (s, 3H), 2.07 (d, *J* = 0.7 Hz, 2H), 2.04 (dd, *J* = 5.3, 0.7 Hz, 4H), 2.01 (s, 3H), 1.99 (s, 3H), 1.98 – 1.95 (m, 3H), 1.92 (s, 3H), 1.89 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.1, 170.9, 170.5, 170.3, 170.2, 170.0, 169.1, 168.9, 94.0, 91.3, 78.6, 73.9, 70.6, 70.5, 70.3, 69.1, 68.5, 67.8, 66.7, 63.6, 62.1, 61.3, 56.2, 46.9, 23.1, 23.0, 21.1, 20.9, 20.8, 20.7, 20.7, 20.6. Spectroscopic data was in agreement with previously reported data.[13]

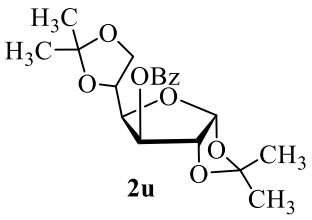


2t

Methyl 2,6-di-*O*-benzoyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (2t): Following the *general procedure (B)* glycosyl substrate **1f** (50 mg, 0.21 mmol), KF (5 mg, 0.09 mmol), 18-Crown-6 (23 mg, 0.09 mmol) and benzoic anhydride (111 mg, 0.49 mmol) afford compound **2t,** a white solid (81 mg, 86%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (ddd, *J* = 9.4, 8.4, 1.3 Hz, 4H), 7.53 – 7.47 (m, 2H), 7.38 (td, *J* = 7.6, 5.1 Hz, 4H), 5.11 (dd, *J* = 8.1, 3.6 Hz, 1H), 4.95 (d, *J* = 3.5 Hz, 1H), 4.61 – 4.52

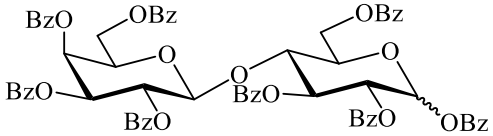
(m, 2H), 4.49 – 4.46 (m, 1H), 4.35 – 4.28 (m, 2H), 3.31 (s, 3H), 1.50 (s, 3H), 1.30 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.5, 166.1, 133.3, 133.2, 130.0, 129.7, 129.7, 128.5, 128.4, 110.2, 97.3, 73.6, 72.3, 65.7, 64.1, 55.6, 28.0, 26.4. **HRMS (ESI-TOF)** m/z: for $[M+K]^+$ calcd for $C_{24}H_{26}O_8K$: 481.1265; found: 481.1244.



2u

3-*O*-Benzoyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (2u): Following the *general procedure (B)* glycosyl substrate **1g** (100 mg, 0.38 mmol), KF (4 mg, 0.08 mmol), 18-Crown-6 (20 mg, 0.08 mmol) and benzoic anhydride (100 mg, 0.44 mmol) afford compound **2u,** a white solid (128 mg, 92%) after purification by column chromatography (Hexane:EtOAc, 6:1 to 3:1).

1H NMR (400 MHz, CDCl3) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.54 – 7.49 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 5.88 (d, *J* = 3.7 Hz, 1H), 5.43 (d, *J* = 2.8 Hz, 1H), 4.56 (d, *J* = 3.8 Hz, 1H), 4.33 – 4.24 (m, 2H), 4.07 – 3.98 (m, 2H), 1.48 (s, 3H), 1.34 (s, 3H), 1.24 (s, 3H), 1.19 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 165.2, 133.5, 129.7, 128.6, 112.4, 109.4, 105.2, 105.2, 83.4, 80.0, 76.6, 72.6, 67.3, 26.8, 26.8, 26.2, 25.2. **HRMS (ESI-TOF)** m/z: for $[M+Na]^+$ calcd for $C_{19}H_{24}O_7Na$: 387.1420; found: 387.1400.

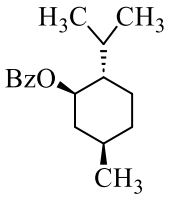


2v

1,2,3,6-Tetra-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-D-glucopyranoside (2v): Following the *general procedure (B)* disaccharide lactose (**1s)** (50 mg, 0.15mmol), KF (14 mg, 0.23 mmol), 18-Crown-6 (62 mg, 0.23 mmol) and benzoic anhydride (397 mg, 1.75 mmol) afford compound **2v,** a white semi-solid (135 mg, 79%) at 60 ˚C after purification by column chromatography (Hexane:EtOAc, 3:1 to 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.78 (m, 1H), 7.67 (dt, *J* = 8.6, 4.4 Hz, 1H), 7.58 – 7.49 (m, 1H), 7.49 – 7.23 (m, 1H), 7.19 – 7.07 (m, 1H), 6.51 (d, *J* = 3.8 Hz, 1H), 5.96 (s, 1H), 5.94

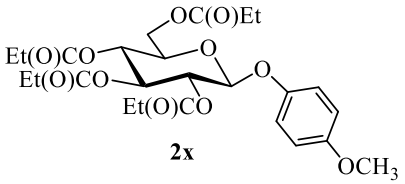
– 5.82 (m, 1H), 5.78 – 5.65 (m, 1H), 5.58 – 5.45 (m, 1H), 5.33 (ddd, *J* = 21.8, 10.1, 3.5 Hz, 1H), 5.01 (dd, *J* = 17.1, 8.0 Hz, 1H), 4.69 – 4.57 (m, 1H), 4.50 – 4.32 (m, 1H), 4.18 – 4.08 (m, 1H), 3.94 (dd, *J* = 8.7, 5.0 Hz, 1H), 3.77 (dd, *J* = 5.5, 4.2 Hz, 1H), 3.66 (s, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 171.2, 166.2, 165.6 – 165.1 (m), 164.4, 163.8, 133.9, 133.7, 133.5, 133.3, 132.9, 130.5 – 129.4 (m), 129.3 – 129.0 (m), 128.9 – 128.6 (m), 128.6 – 128.1 (m), 102.4, 82.1, 73.5, 73.0, 72.6, 71.6, 70.9, 70.4, 64.1, 62.9, 62.0, 61.7, 61.7. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{68}H_{58}NO_{19}$: 1192.3603; found: 1192.3602.



2w

(2S,5R)-2-Isopropyl-5-methylcyclohexyl benzoate (2w): Following the *general procedure (B)* l-menthol **1q** (100 mg, 0.64 mmol), KF (7 mg, 0.13 mmol), 18-Crown-6 (34 mg, 0.13 mmol) and benzoic anhydride (166 mg, 0.74 mmol) afford compound **2w,** a colourless semi-solid (96 mg, 58%) after purification by column chromatography (Hexane:EtOAc, 11:1 to 8:1).

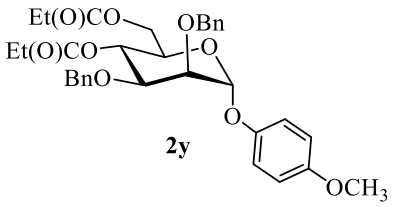
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.01 (m, 2H), 7.63 – 7.53 (m, 1H), 7.51 – 7.42 (m, 2H), 4.96 (td, *J* = 10.9, 4.4 Hz, 1H), 2.16 (dtd, *J* = 12.0, 4.2, 1.8 Hz, 1H), 1.99 (pd, *J* = 7.0, 2.7 Hz, 1H), 1.81 – 1.72 (m, 2H), 1.59 (ddt, *J* = 9.7, 6.3, 2.2 Hz, 2H), 1.22 – 1.09 (m, 2H), 0.95 (dd, *J* = 6.8, 4.3 Hz, 6H), 0.82 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 166.1, 132.7, 130.9, 129.6, 128.3, 74.8, 47.3, 41.0, 34.3, 31.5, 26.5, 23.6, 22.1, 20.8, 16.5. **HRMS (ESI-TOF)** m/z: for $[M+Na]^+$ calcd for $C_{17}H_{24}O_2Na$: 283.1674; found: 283.1661.



2x

4-Methoxyphenyl 2,3,4,6-tetra-*O*-propionyl-β-D-glucopyranoside (2x): Following the *general procedure (A)* glycosyl substrate **1a** (50 mg, 0.18 mmol), KF (8 mg, 0.14 mmol), 18-Crown-6 (37 mg, 0.14 mmol) and propionic anhydride (103 µL, 0.80 mmol) afford compound **2x,** a yellowish semi-solid (78 mg, 88%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

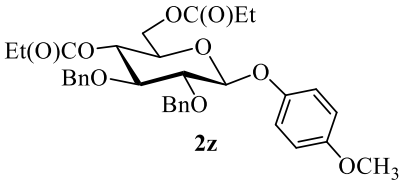
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.88 (d, *J* = 9.2 Hz, 2H), 6.74 (d, *J* = 9.2 Hz, 2H), 5.47 – 5.32 (m, 2H), 5.05 (dd, *J* = 10.4, 3.4 Hz, 1H), 4.87 (d, *J* = 8.1 Hz, 1H), 4.18 – 4.10 (m, 2H), 3.98 (t, *J* = 6.7 Hz, 1H), 3.70 (s, 3H), 2.40 (dq, *J* = 7.6, 3.9 Hz, 2H), 2.29 – 2.16 (m, 6H), 1.13 (d, *J* = 7.6 Hz, 2H), 1.10 – 1.00 (m, 10H). **^{13}C NMR (101 MHz, $CDCl_3$)** ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8 (2C), 173.4, 173.0, 155.7, 151.1, 118.6, 114.5, 100.9, 71.1, 70.8, 68.7, 66.8, 61.3, 55.7, 27.5, 27.4, 27.3, 27.3, 9.3 (2C), 9.0, 8.8. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{25}H_{38}NO_{11}$: 528.2445; found: 528.2430.



2y

4-Methoxyphenyl 4,6-di-*O*-propionyl-2,3-di-*O*-benzyl-α-D-mannopyranoside (2y): Following the *general procedure (A)* glycosyl substrate **1t** (50 mg, 0.11 mmol), KF (3 mg, 0.04 mmol), 18-Crown-6 (12 mg, 0.04 mmol) and propionic anhydride (31 µL, 0.25 mmol) afford compound **2y,** a white semi-solid (58 mg, 93%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.18 (m, 10H), 6.95 – 6.86 (m, 2H), 6.75 – 6.70 (m, 2H), 5.46 – 5.35 (m, 2H), 4.74 (d, *J* = 12.2 Hz, 1H), 4.67 – 4.55 (m, 2H), 4.51 – 4.42 (m, 1H), 4.14 – 3.99 (m, 2H), 3.98 – 3.85 (m, 3H), 3.69 (s, 3H), 2.29 – 2.13 (m, 4H), 1.02 (dt, *J* = 17.5, 7.5 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.2, 173.2, 155.1, 150.1, 138.1, 138.0, 128.4, 128.3, 127.9, 127.9, 127.8, 127.7, 127.6, 127.5, 117.8, 117.7, 114.6, 97.5, 74.2, 73.1, 72.2, 71.7, 69.9, 67.7, 62.7, 55.7, 55.6, 27.6, 27.6, 27.4, 9.1, 8.9. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{33}H_{42}NO_9$: 596.2860; found: 596.2853.

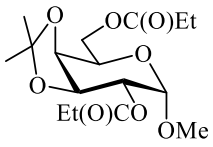


2z

4-Methoxyphenyl 4,6-di-*O*-propionyl-2,3-di-*O*-benzyl-β-D-glucopyranoside (2z): Following the *general procedure (A)* glycosyl substrate **1i** (50 mg, 0.11 mmol), KF (3 mg, 0.04 mmol), 18-Crown-6 (12 mg, 0.04 mmol) and propionic anhydride (31 µL, 0.25 mmol) afford

compound **2z,** a white semi-solid (60 mg, 96%) after purification by column chromatography (Hexane:EtOAc, 8:1 to 5:1).

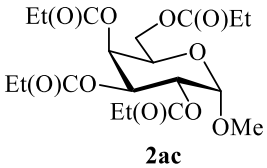
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.11 (m, 10H), 6.99 – 6.87 (m, 2H), 6.80 – 6.68 (m, 2H), 5.09 – 5.00 (m, 1H), 4.96 (d, *J* = 11.0 Hz, 1H), 4.85 – 4.70 (m, 3H), 4.56 (d, *J* = 11.5 Hz, 1H), 4.15 (dd, *J* = 12.2, 6.1 Hz, 1H), 4.05 (dd, *J* = 12.1, 2.4 Hz, 1H), 3.70 (s, 4H), 3.63 – 3.56 (m, 2H), 2.32 – 2.22 (m, 2H), 2.20 – 2.03 (m, 2H), 1.03 (dt, *J* = 22.3, 7.5 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.1, 173.0, 155.5, 151.4, 138.2, 138.1, 128.5, 128.4, 128.3, 127.9, 127.7, 127.7, 118.5, 114.6, 102.8, 81.8, 75.3, 75.2, 72.2, 69.6, 62.5, 55.7, 27.5, 27.4, 9.0 (2C). **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{33}H_{42}NO_9$: 596.2860; found: 596.2854.



2ab

Methyl 2,6-di-*O*-propionyl-3,4-*O*-isopropylidene-α-D-galactopyranoside (2ab): Following the *general procedure (A)* glycosyl substrate **1f** (50 mg, 0.21 mmol), KF (5 mg, 0.09 mmol), 18-Crown-6 (23 mg, 0.09 mmol) and propionic anhydride (63 µL, 0.49 mmol) afford compound **2ab,** a white solid (72 mg, 98%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 5:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (dd, *J* = 8.1, 3.6 Hz, 1H), 4.78 (d, *J* = 3.7 Hz, 1H), 4.33 (dd, *J* = 11.6, 4.4 Hz, 1H), 4.26 (td, *J* = 7.9, 3.0 Hz, 2H), 4.16 (dd, *J* = 5.4, 2.5 Hz, 1H), 4.10 (ddd, *J* = 7.3, 4.4, 2.5 Hz, 1H), 3.31 (s, 3H), 2.38 – 2.26 (m, 4H), 1.45 (s, 3H), 1.27 (s, 3H), 1.09 (td, *J* = 7.5, 3.5 Hz, 6H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.1, 174.0, 110.0, 97.1, 73.5, 73.4, 71.5, 65.5, 63.4, 55.4, 27.8, 27.5, 27.4, 26.3, 9.1, 8.9. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{16}H_{30}NO_8$: 364.1971; found: 364.1955.

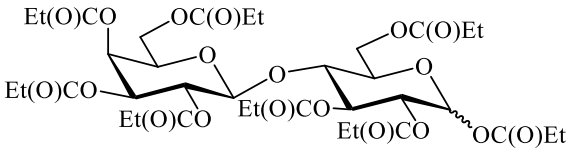


2ac

Methyl 2,3,4,6-tetra-*O*-propionyl-α-D-galactopyranoside (2ac): Following the *general procedure (A)* glycosyl substrate **1b** (50 mg, 0.26 mmol), KF (12 mg, 0.21 mmol), 18-Crown-6 (54 mg, 0.21 mmol) and propionic anhydride (151 µL, 1.18 mmol) afford compound **2ac,** a

colourless semi-solid (90 mg, 84%) after purification by column chromatography (Hexane:EtOAc, 7:1 to 4:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (dd, *J* = 3.4, 1.5 Hz, 1H), 5.31 (dd, *J* = 10.8, 3.4 Hz, 1H), 5.11 (dd, *J* = 10.9, 3.7 Hz, 1H), 4.92 (d, *J* = 3.7 Hz, 1H), 4.18 – 4.12 (m, 1H), 4.05 (d, *J* = 6.4 Hz, 2H), 3.34 (s, 3H), 2.38 – 2.24 (m, 6H), 2.15 (q, *J* = 7.3 Hz, 2H), 1.13 – 1.00 (m, 12H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 173.8 (2C), 173.6, 173.2, 97.3, 68.0, 67.9, 67.5, 66.2, 61.6, 55.4, 27.4 (2C), 27.3, 27.1, 9.2, 9.0, 8.9, 8.8. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{19}H_{34}NO_{10}$: 436.2183; found: 436.2199.

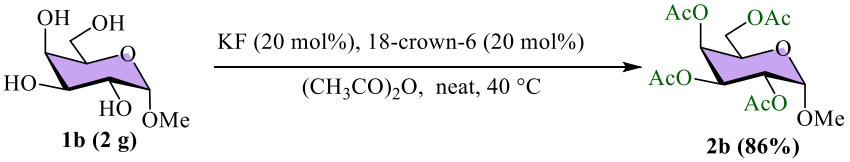


2ad

1,2,3,6-Tetra-*O*-propionyl-4-*O*-(2,3,4,6-tetra-*O*-propionyl-β-D-galactopyranosyl)-D-glucopyranoside (2ad): Following the *general procedure (A)* disaccharide lactose (**1r)** (50 mg, 0.15 mmol), KF (14 mg, 0.23 mmol), 18-Crown-6 (62 mg, 0.23 mmol) and propionic anhydride (172 µL, 1.34 mmol) afford compound **2ad,** a colourless semi-solid (95 mg, 82%) at 60 ˚C after purification by column chromatography (Hexane:EtOAc, 3:1 to 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.18 (d, *J* = 3.7 Hz, 1H), 5.58 (d, *J* = 8.5 Hz, 0H), 5.34 (ddd, *J* = 5.0, 3.4, 1.1 Hz, 1H), 5.21 (dt, *J* = 10.4, 8.1 Hz, 1H), 5.00 – 4.89 (m, 2H), 4.50 (dd, *J* = 9.2, 8.0 Hz, 1H), 4.26 – 4.20 (m, 2H), 4.17 (ddd, *J* = 5.9, 3.6, 1.0 Hz, 1H), 4.12 – 4.05 (m, 2H), 4.02 – 3.88 (m, 3H), 3.74 (dd, *J* = 9.6, 8.3 Hz, 1H), 3.68 – 3.62 (m, 1H), 3.59 (d, *J* = 3.1 Hz, 1H), 3.52 (ddd, *J* = 9.9, 8.4, 2.6 Hz, 1H), 2.45 – 2.05 (m, 16H), 1.21 – 0.95 (m, 24H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 174.0 (3C), 173.2 (3C), 172.7, 172.4, 102.0, 101.9, 91.6, 89.0, 82.1, 82.0, 73.2, 72.7, 71.6, 71.1, 70.8, 70.5, 69.6, 69.6, 68.6, 68.5, 66.7, 62.0, 61.9, 61.7, 27.5, 27.4, 27.4 (2C), 27.3, 27.2 (2C), 27.0, 9.2, 9.1, 9.1, 9.0, 9.0, 8.9, 8.8, 8.7. **HRMS (ESI-TOF)** m/z: for $[M+NH_4]^+$ calcd for $C_{36}H_{58}NO_{19}$: 808.3603; found: 808.3602.

Gram scale reaction:



1b (2 g) **2b (86%)**

For gram scale reaction, following the general procedure (A) carbohydrate substrate **1b** (2 g, 10.30 mmol), KF (0.48 g, 8.24 mmol), 18-Crown-6 (2.18 g, 8.24 mmol) and acetic anhydride (4.5 mL, 47.38 mmol) afford compound **2b,** a colourless semi-solid (3.1 g, 86%).

Catalyst recovery and reuse for acylation:

After completion of the reaction, the mixture was added to water (20 mL) and extracted with ethyl acetate (20 mL). The combined organic layers were concentrated under reduced pressure and purified by column chromatography to give the desired product. The aqueous phase was evaporated and dried under vacuum to recover the catalyst (KF and 18-Crown-6 mixture). Then, carbohydrate substrate **1b** (2 g, 10.30 mmol) and acetic anhydride (4.5 mL, 47.38 mmol) were added to the recovered catalyst and we obtained compound **2b,** a colourless semi-solid (2.9 g, 81%) after 12 hours by purifying through column chromatography (Hexane:EtOAc, 7:1 to 4:1).

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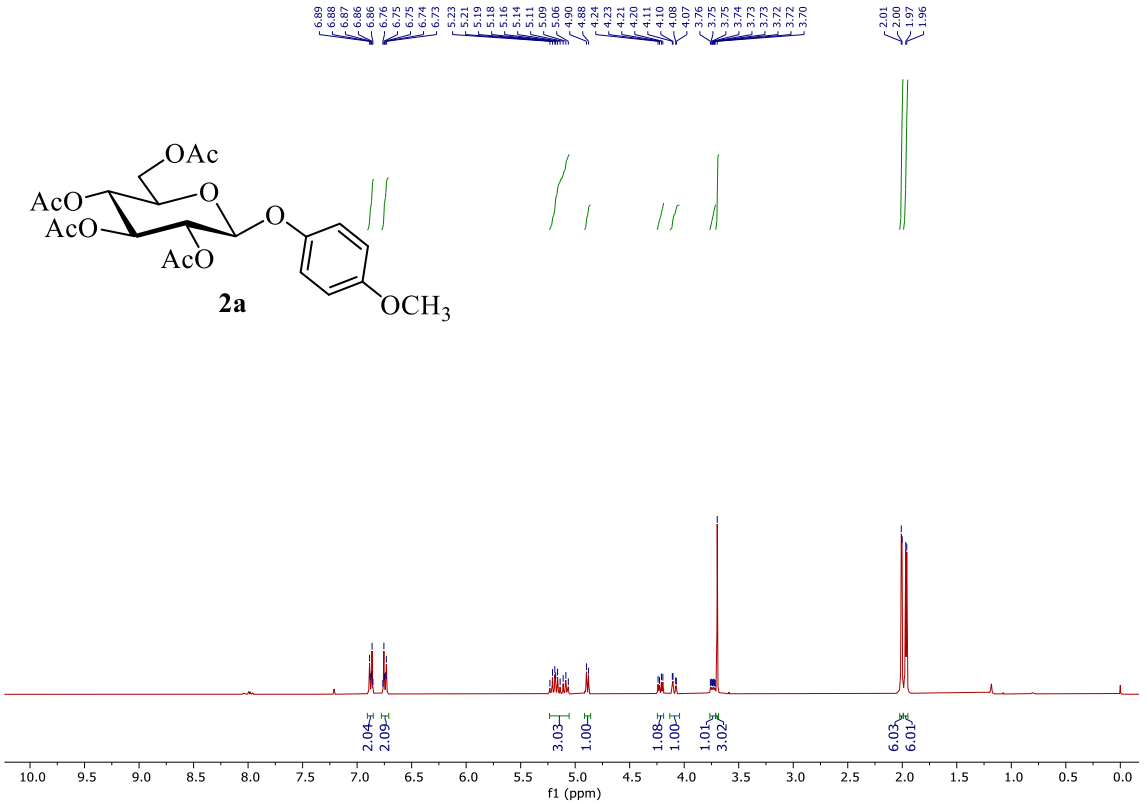
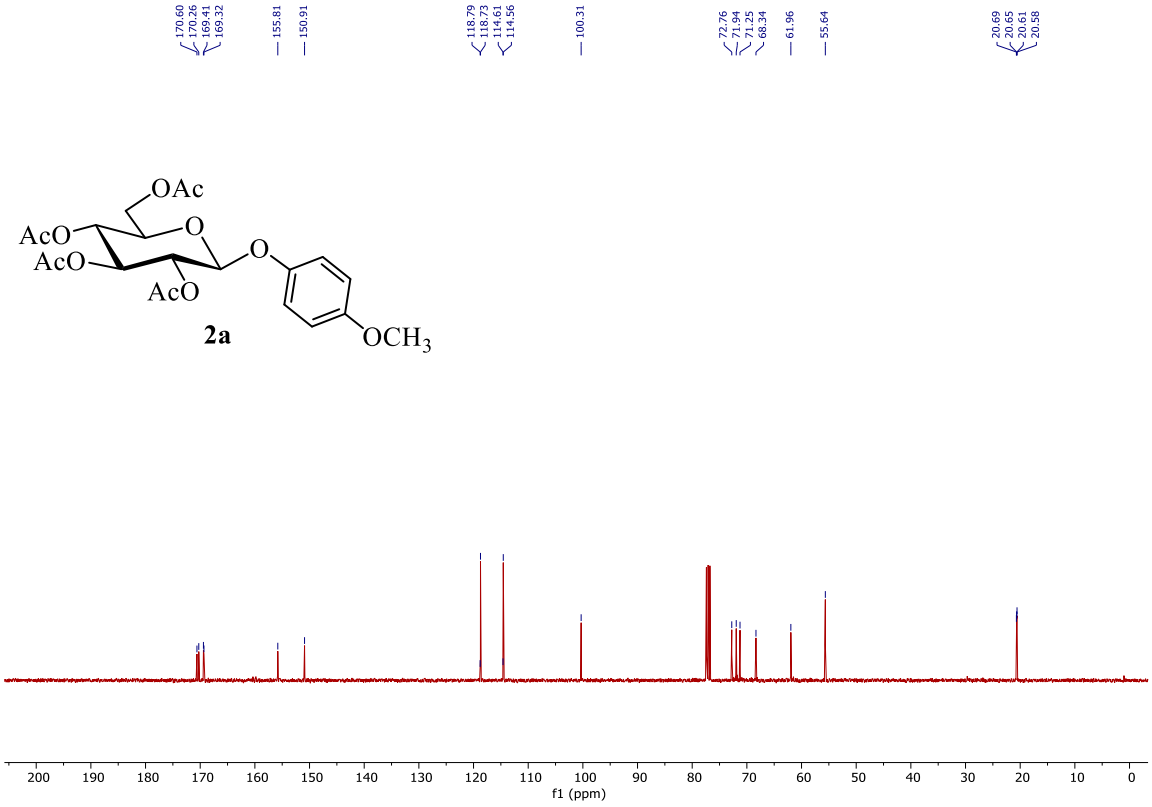
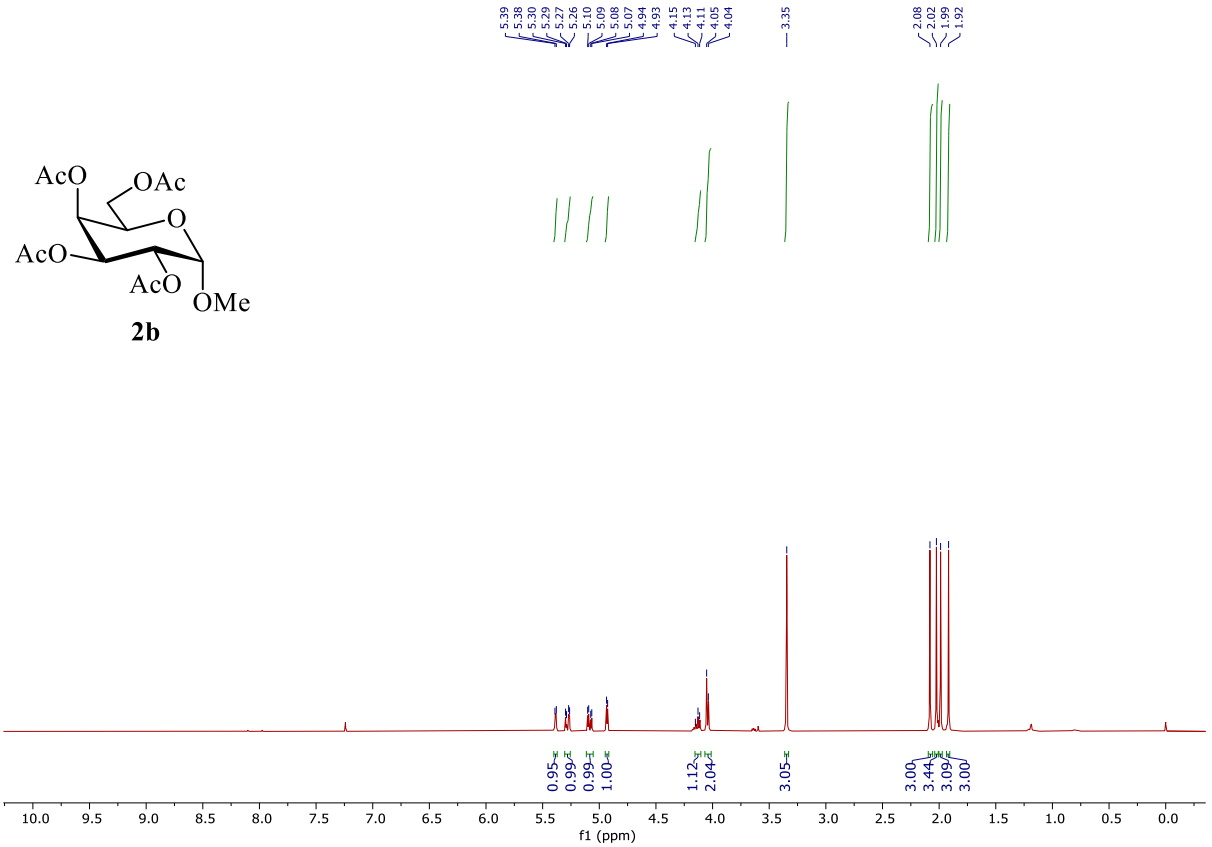
Spectra:



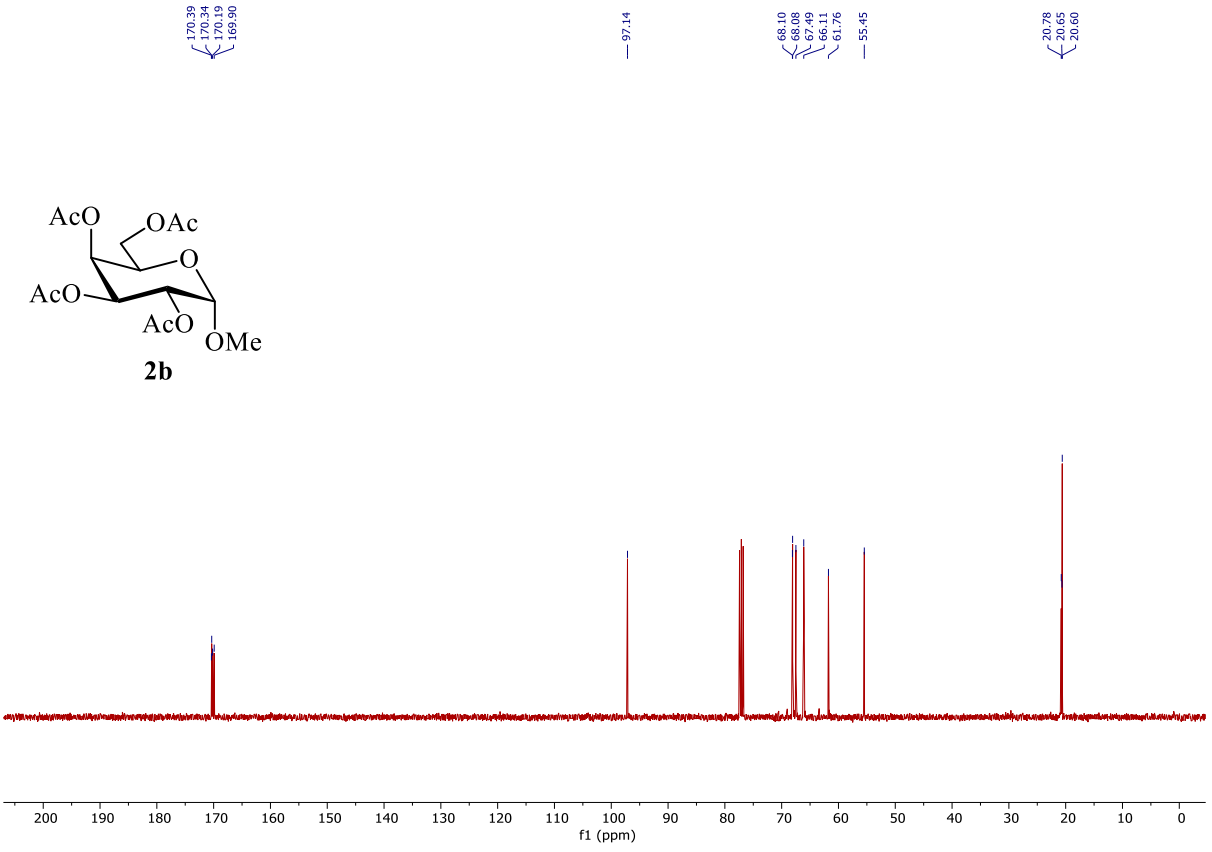
^{1}H NMR of Compound **2a (400 MHz, $CDCl_3$)**



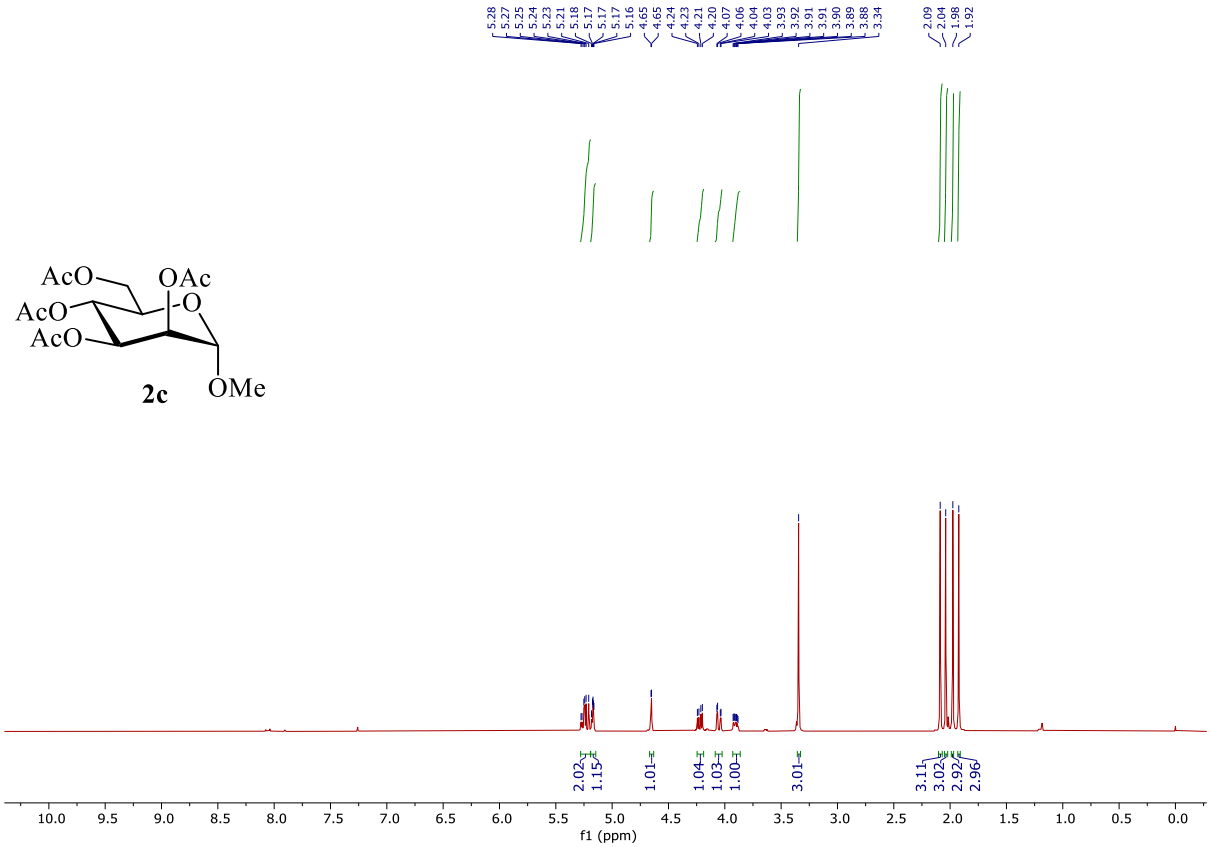
^{13}C NMR of Compound **2a (101 MHz, $CDCl_3$)**



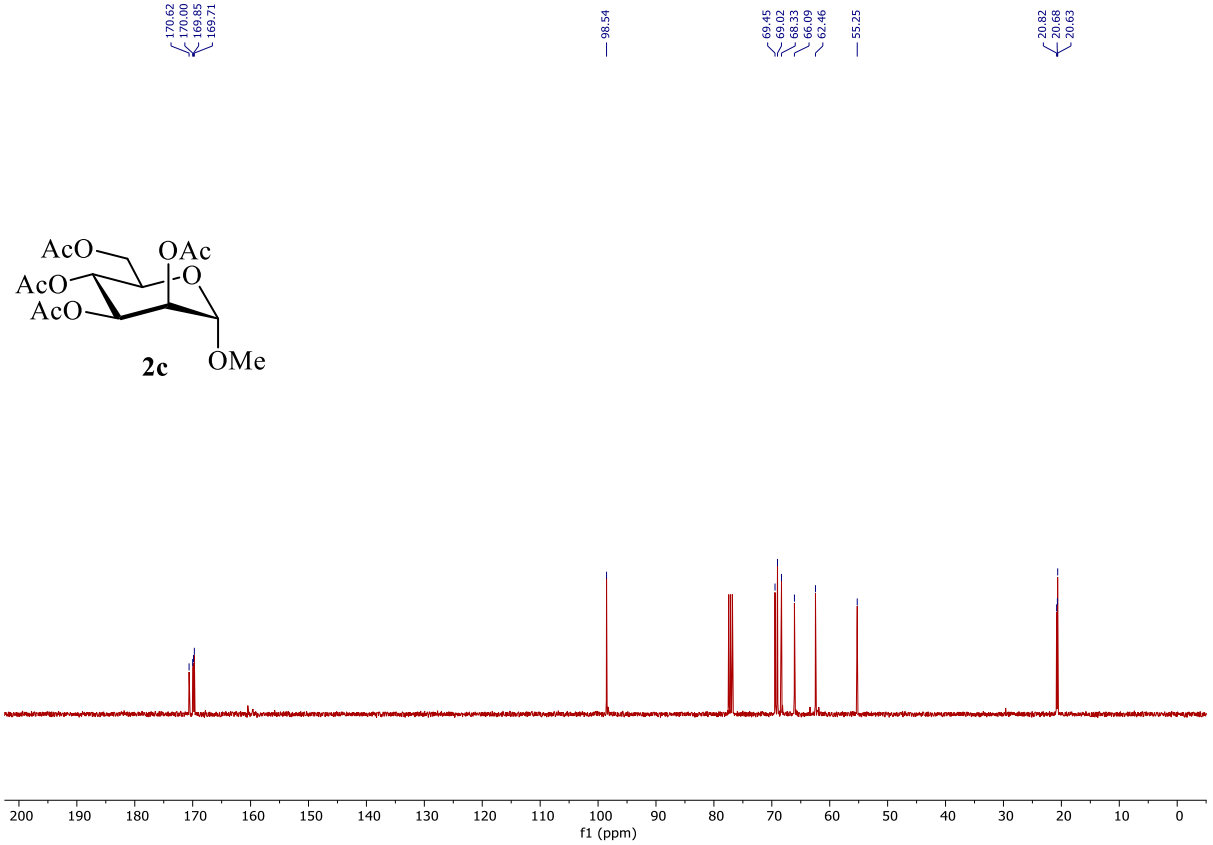
^{1}H NMR of Compound **2b (400 MHz, $CDCl_3$)**



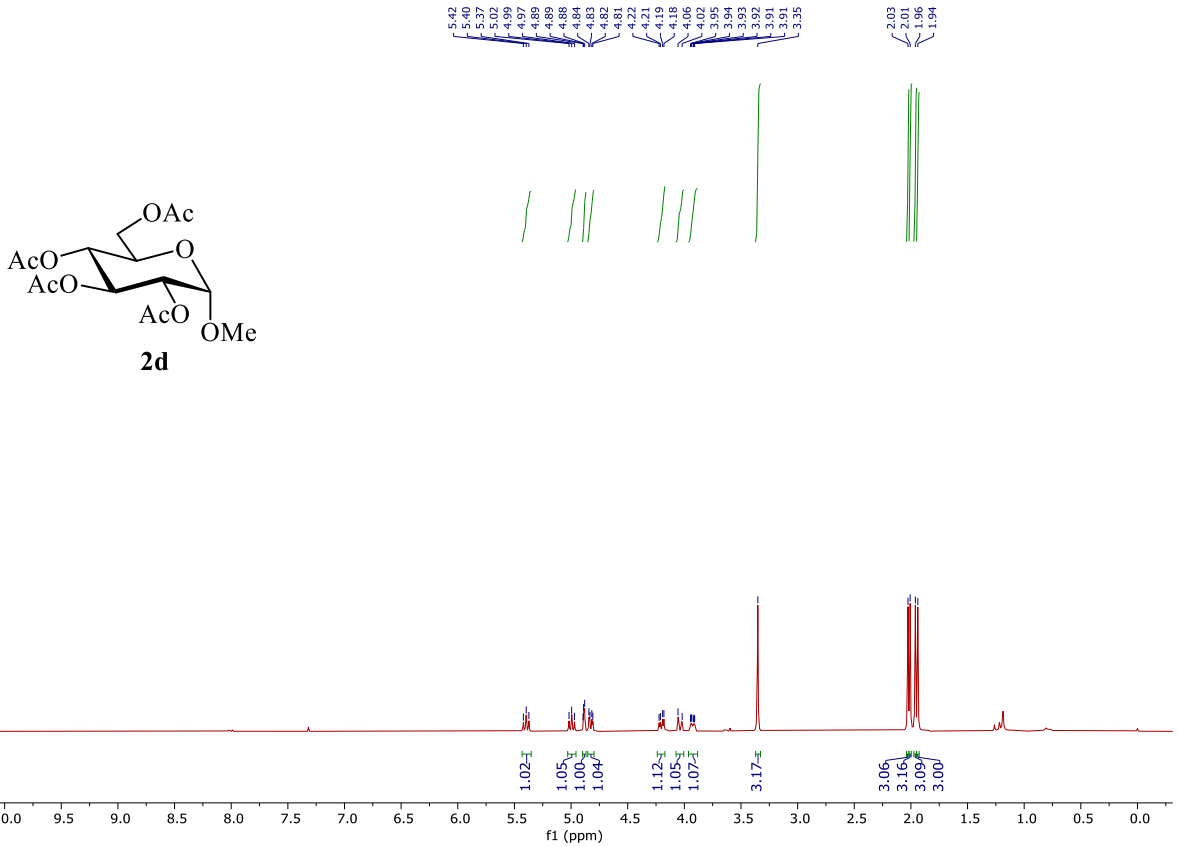
^{13}C NMR of Compound **2b (101 MHz, $CDCl_3$)**



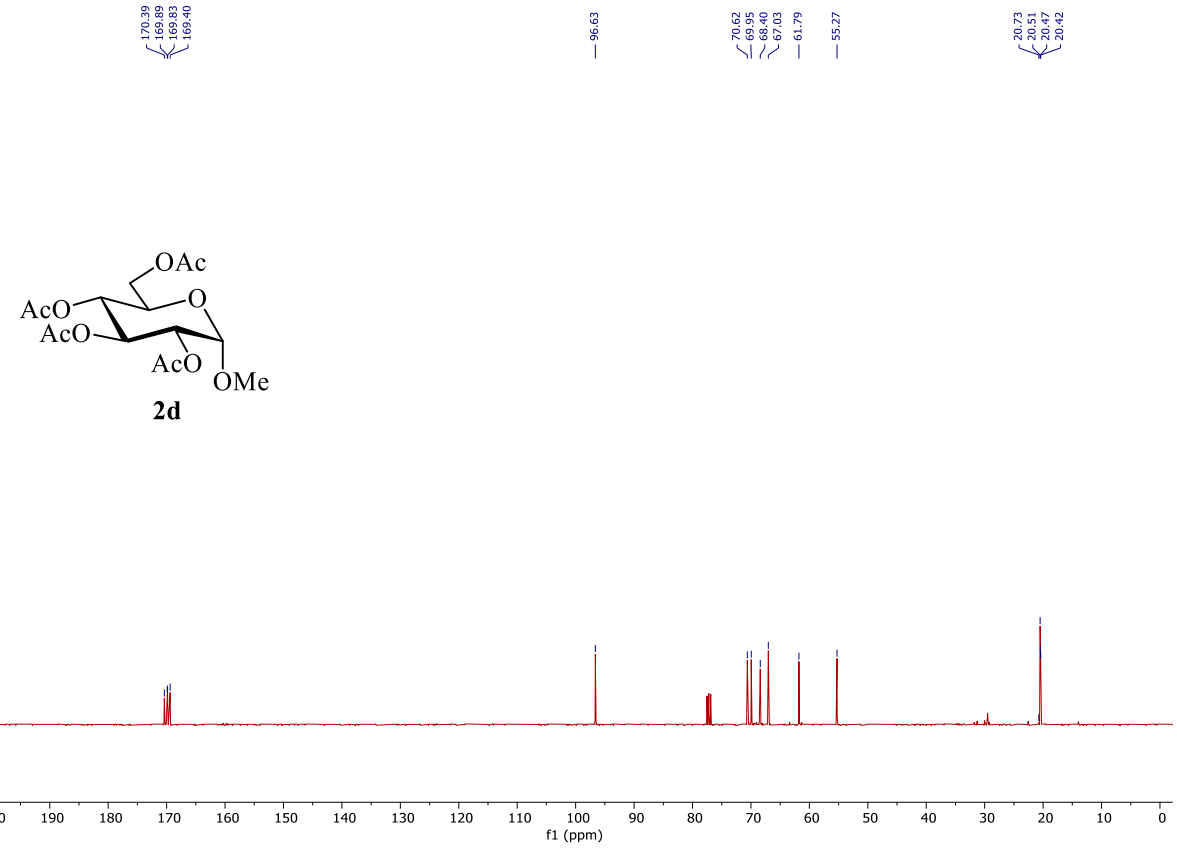
^{1}H NMR of Compound **2c (400 MHz, $CDCl_3$)**



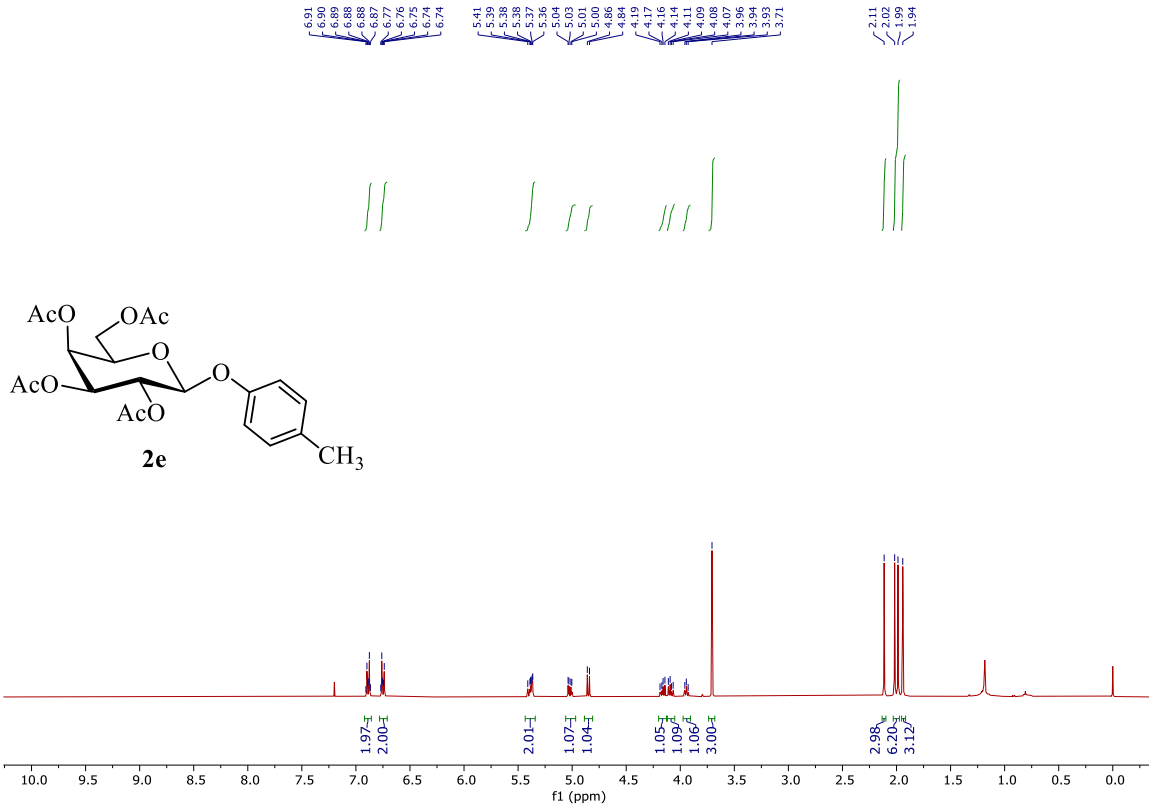
^{13}C NMR of Compound **2c (101 MHz, $CDCl_3$)**



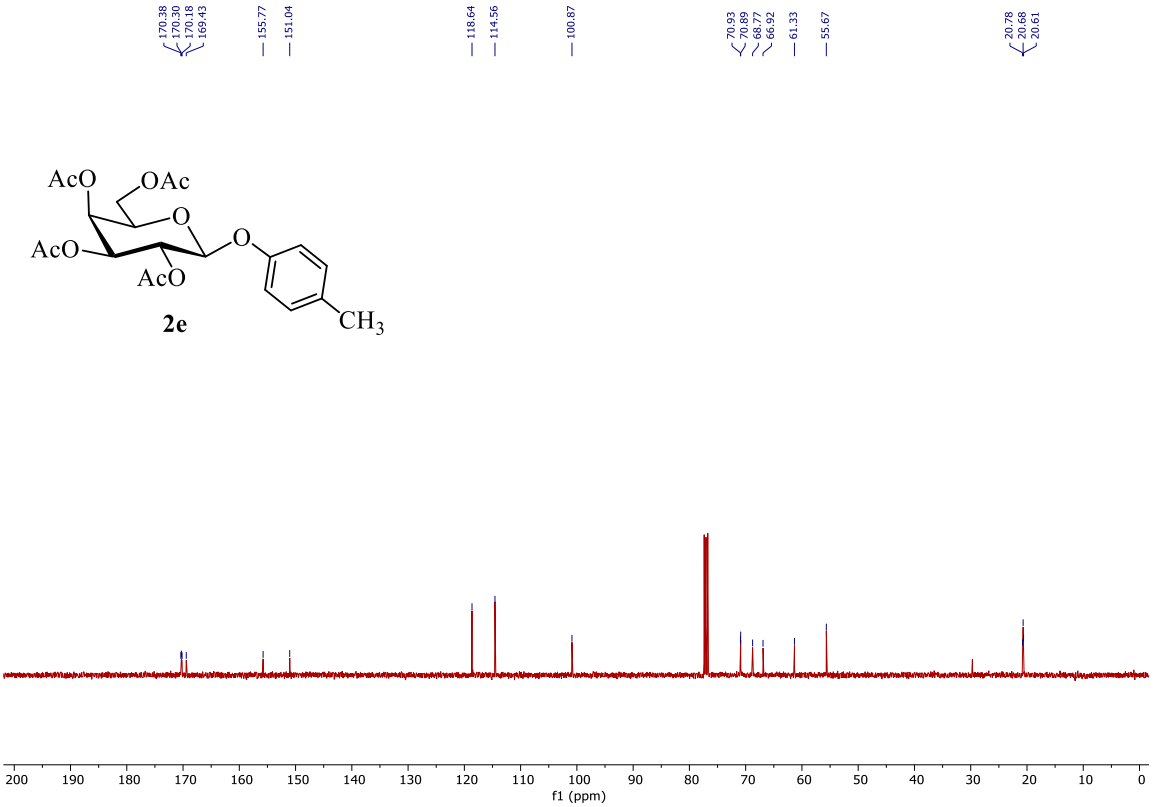
^{1}H NMR of Compound **2d (400 MHz, $CDCl_3$)**



^{13}C NMR of Compound **2d (101 MHz, $CDCl_3$)**



^{1}H NMR of Compound **2e (400 MHz, $CDCl_3$)**



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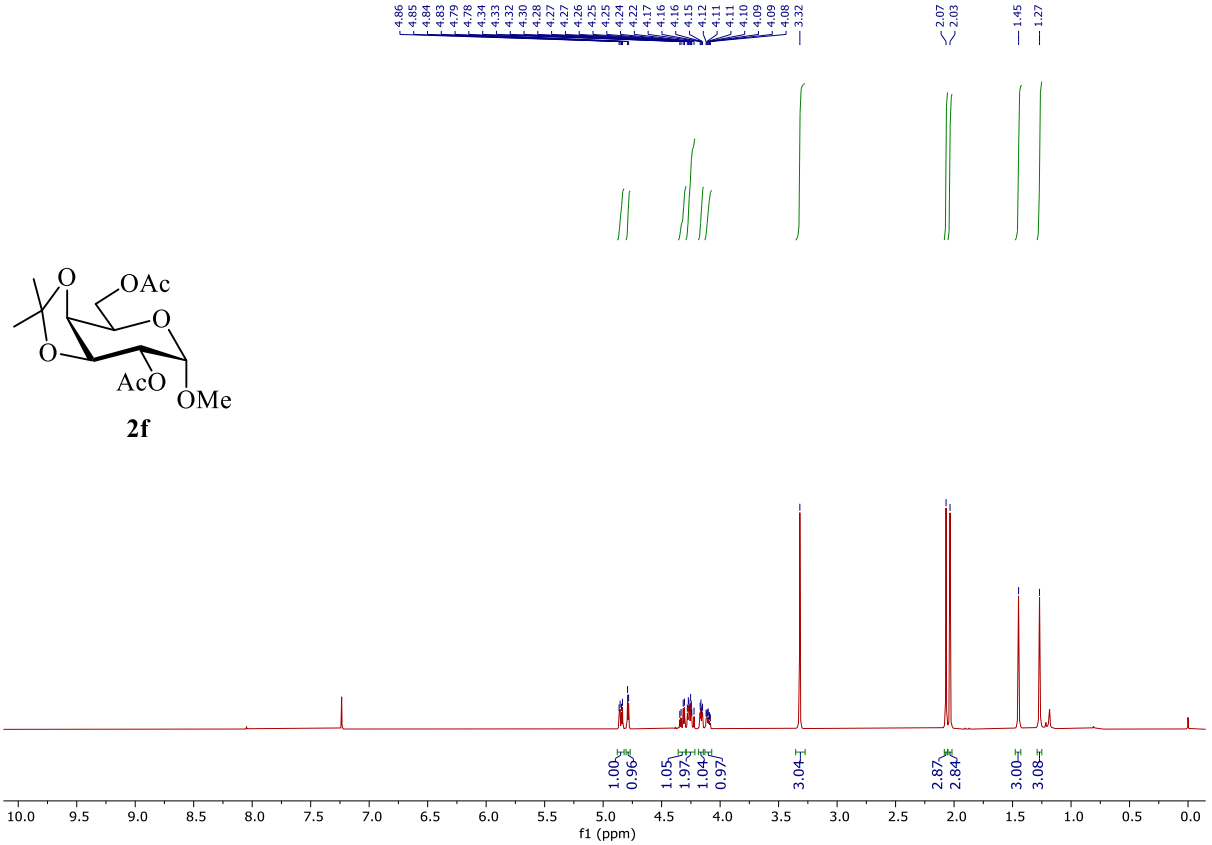
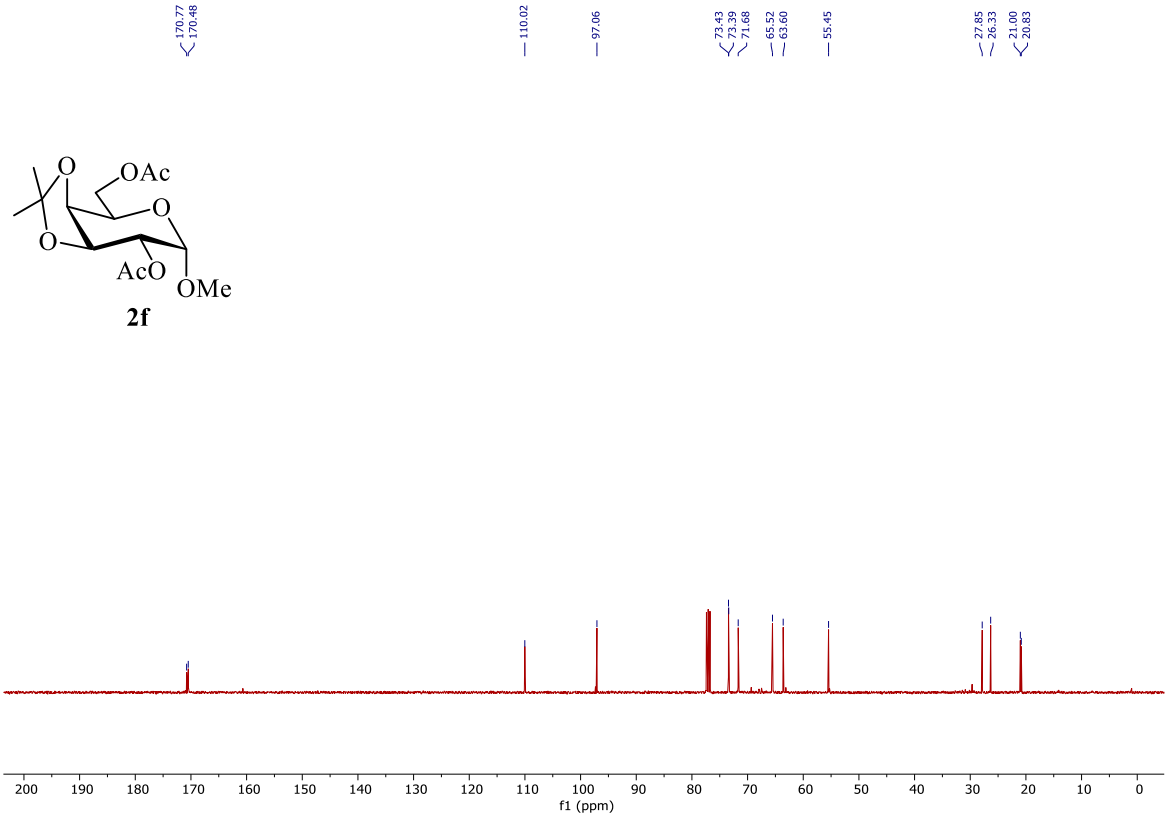
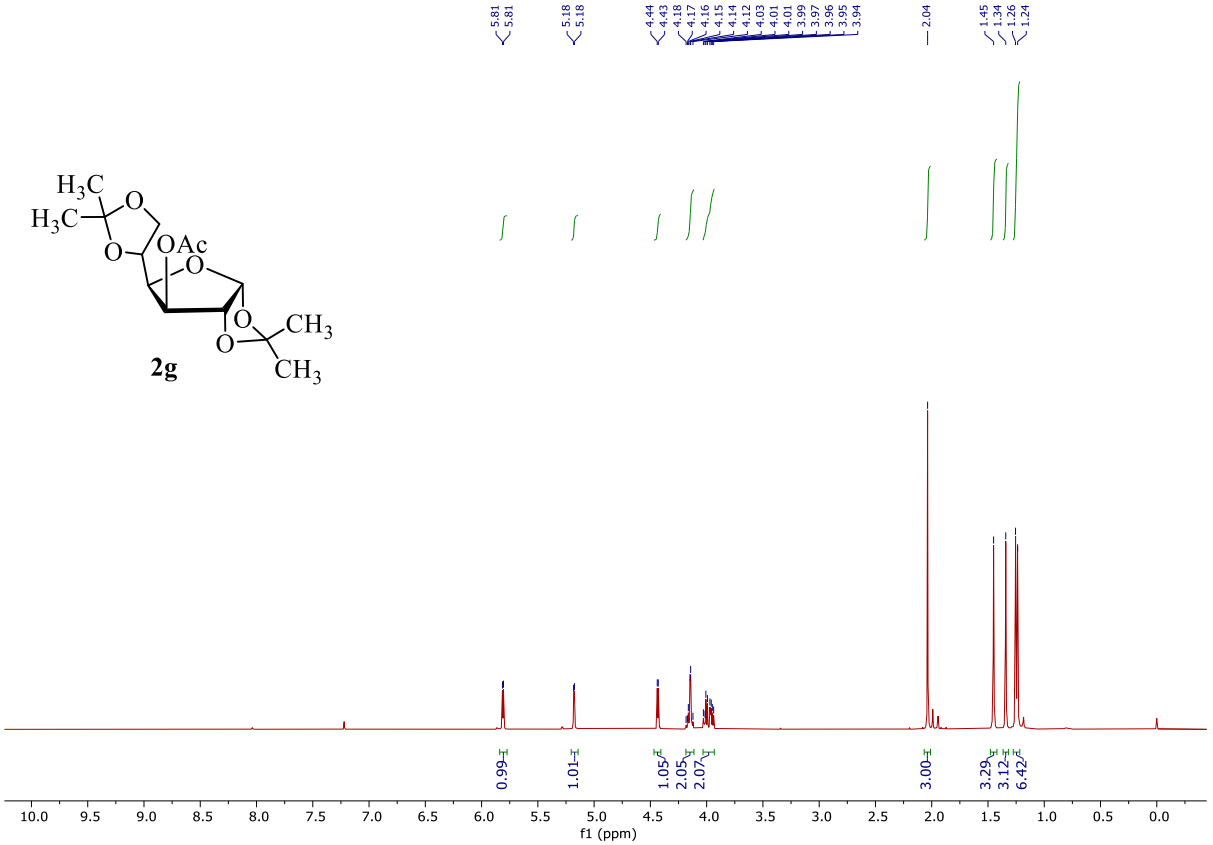


^{1}H NMR of Compound **2f (400 MHz, $CDCl_3$)**

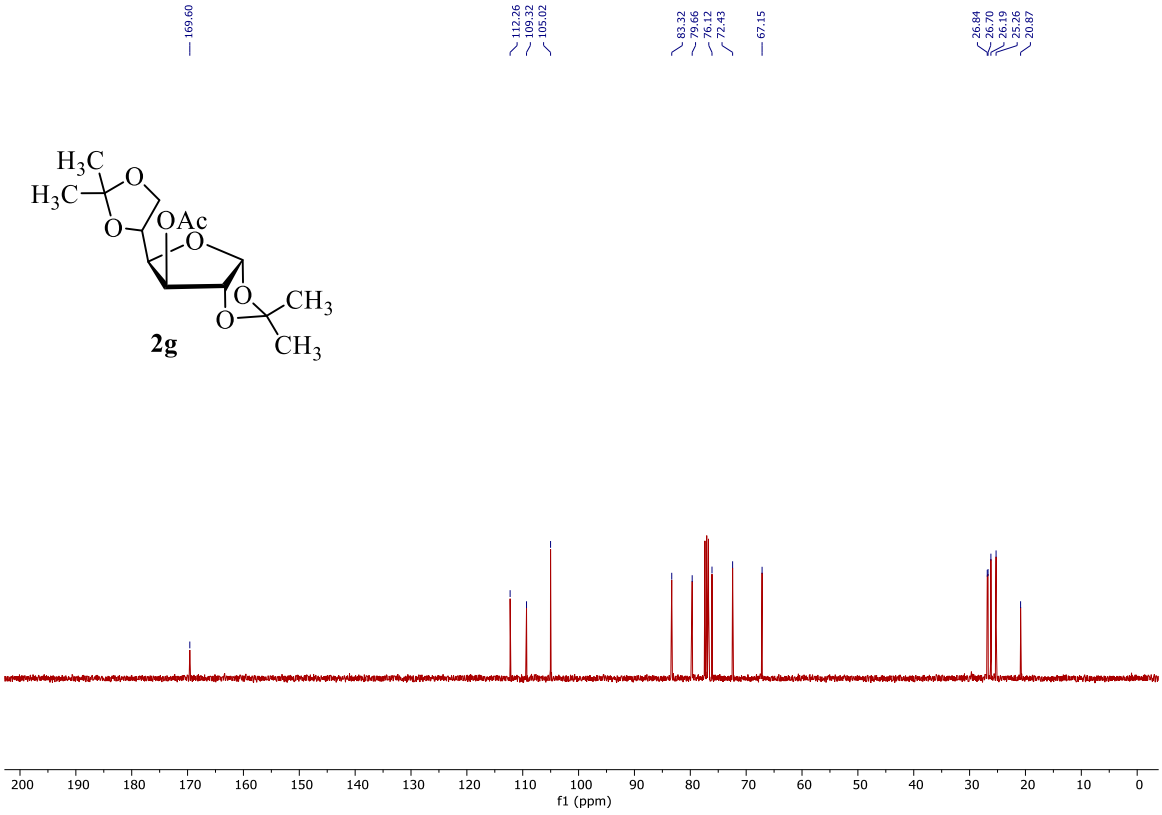


^{13}C NMR of Compound **2f (101 MHz, $CDCl_3$)**



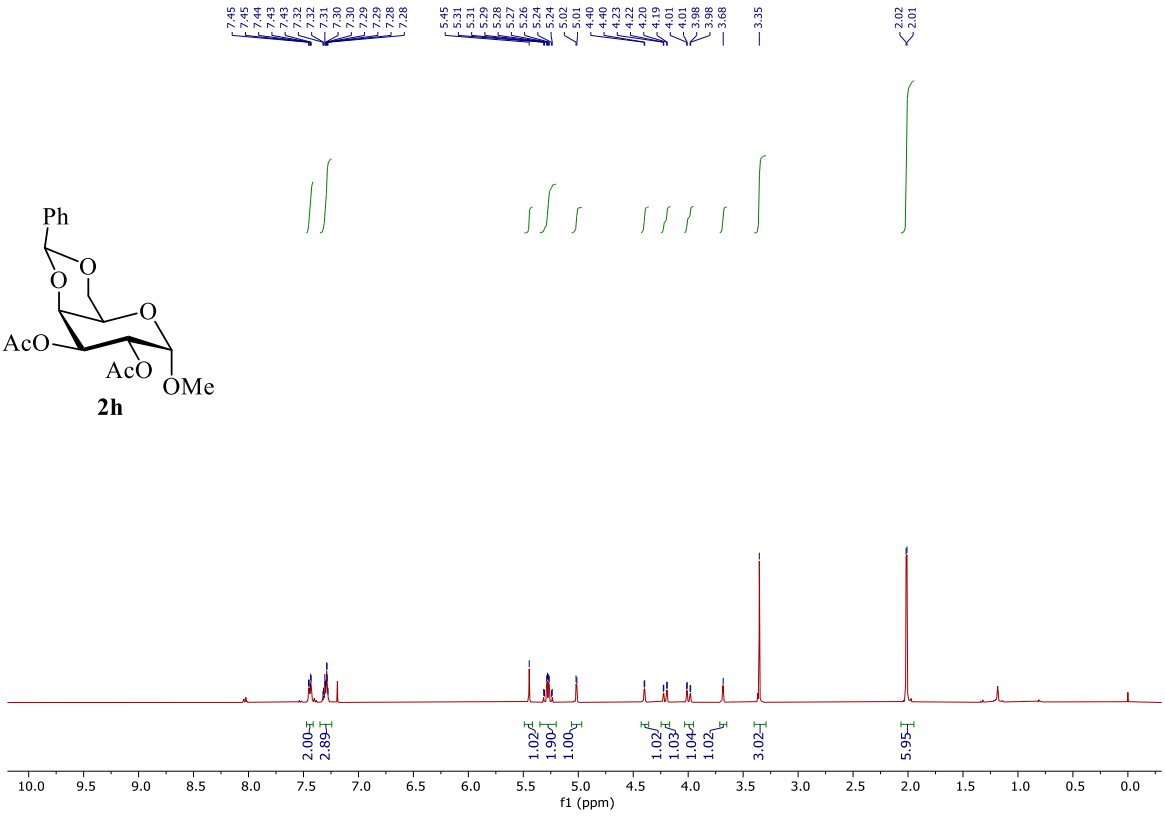
2g

^{1}H NMR of Compound **2g (400 MHz, $CDCl_3$)**

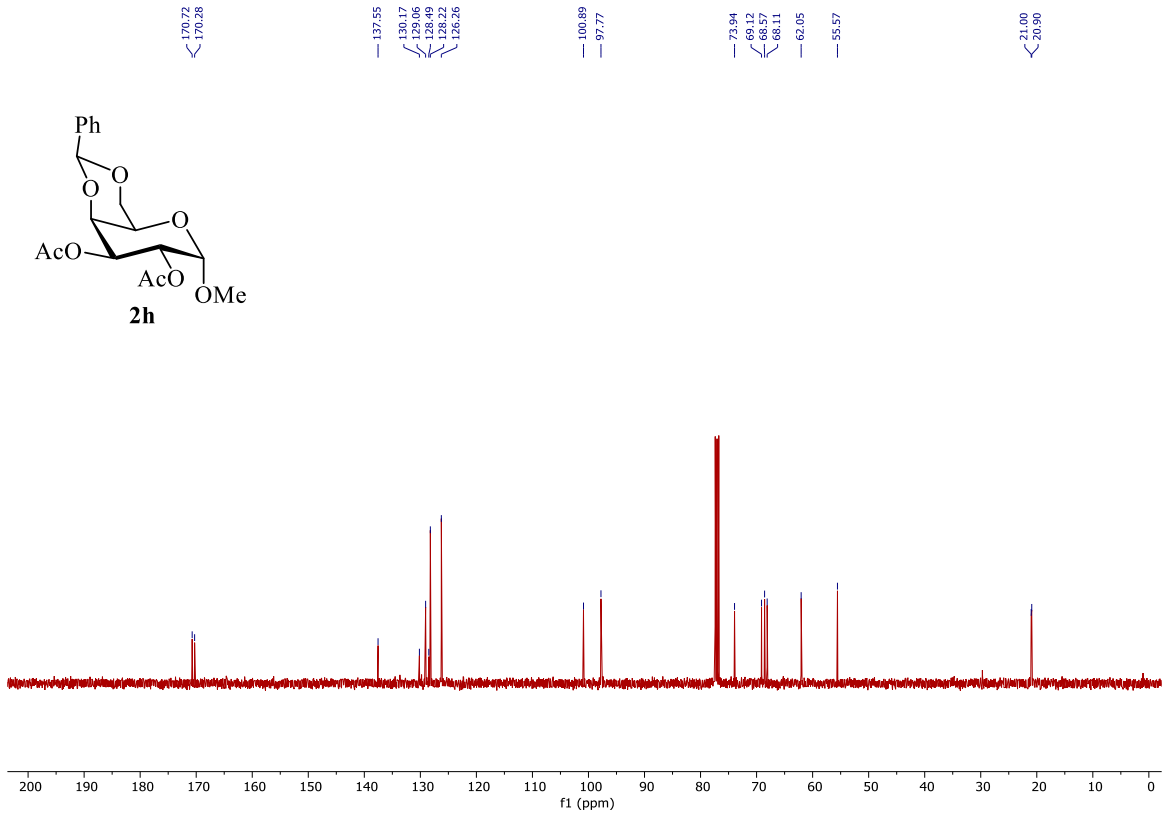


2g

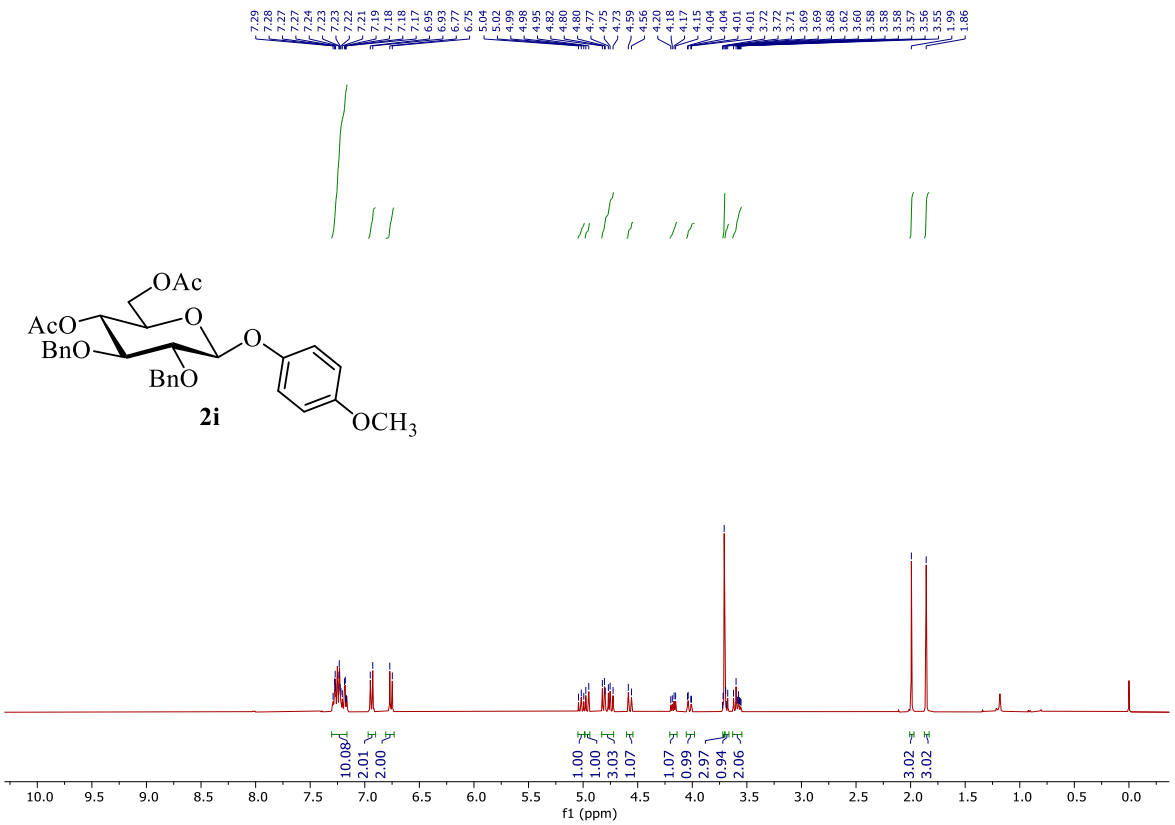
^{13}C NMR of Compound **2g (101 MHz, $CDCl_3$)**



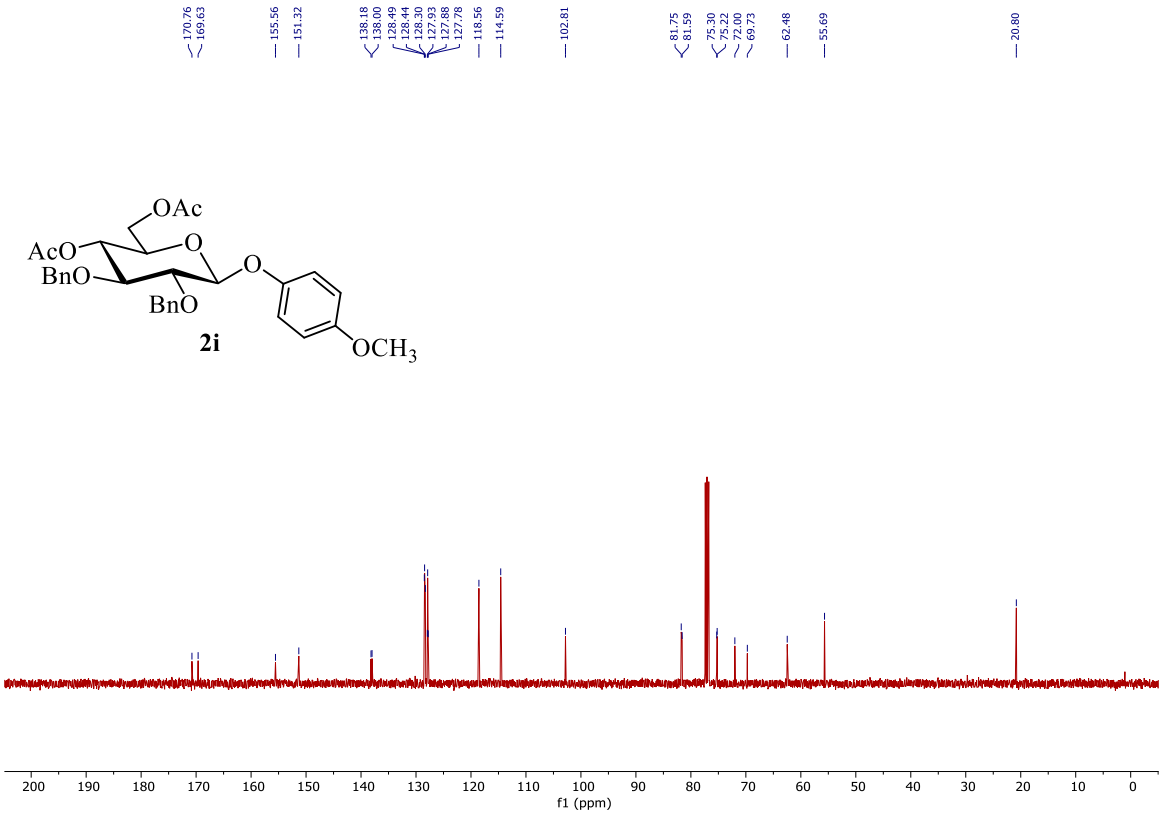
^{1}H NMR of Compound **2h (400 MHz, $CDCl_3$)**



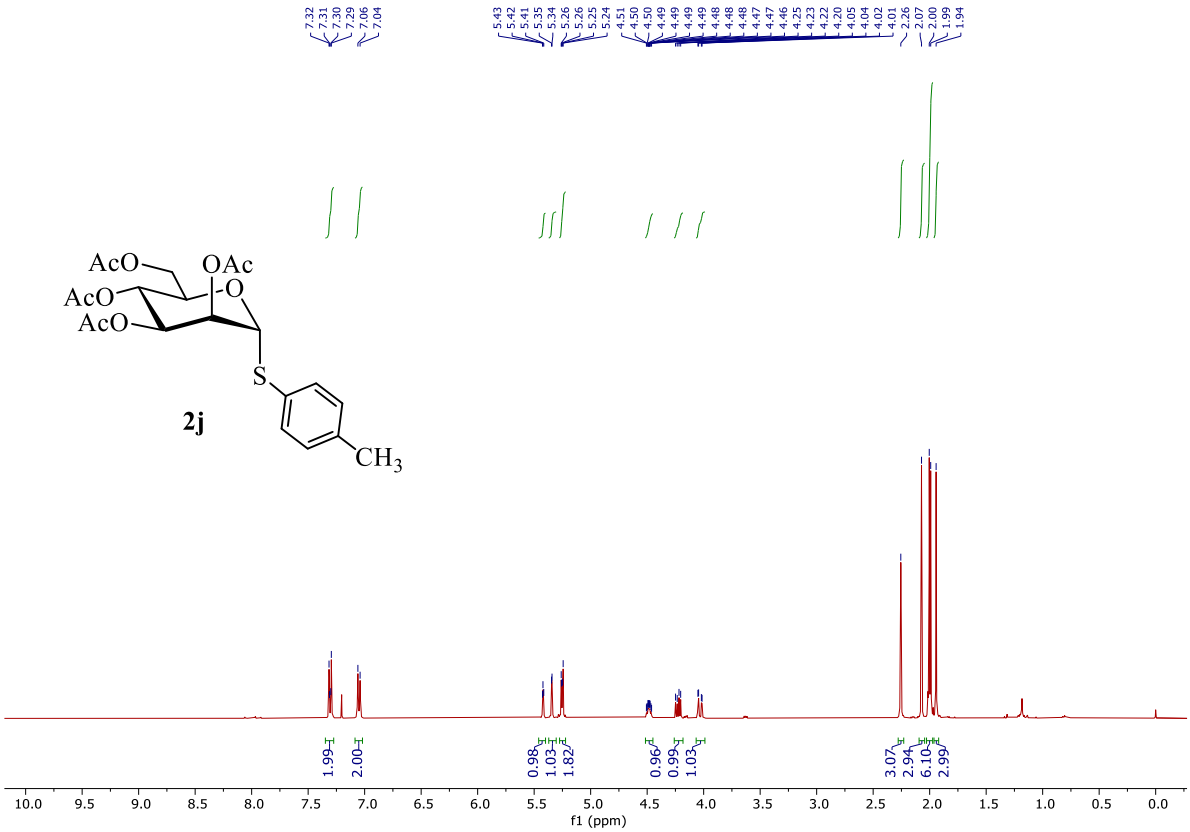
^{13}C NMR of Compound **2h (101 MHz, $CDCl_3$)**



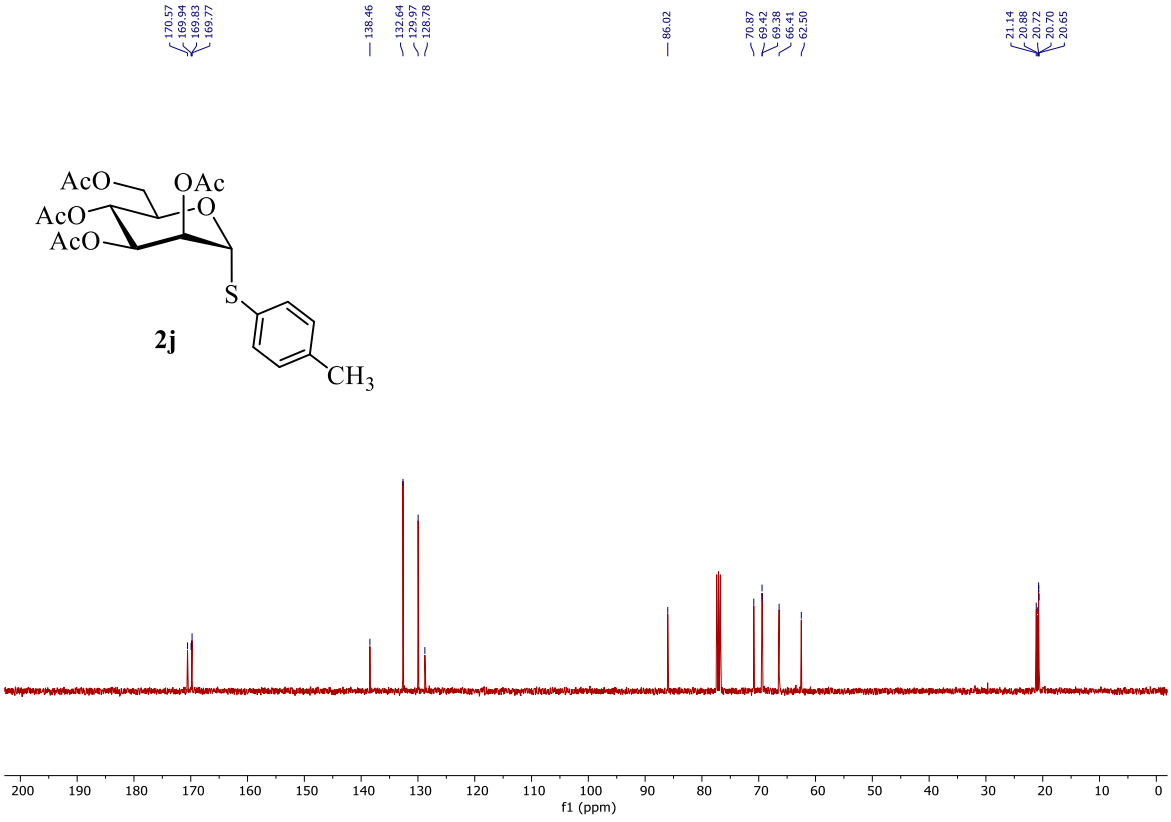
^{1}H NMR of Compound **2i (400 MHz, $CDCl_3$)**



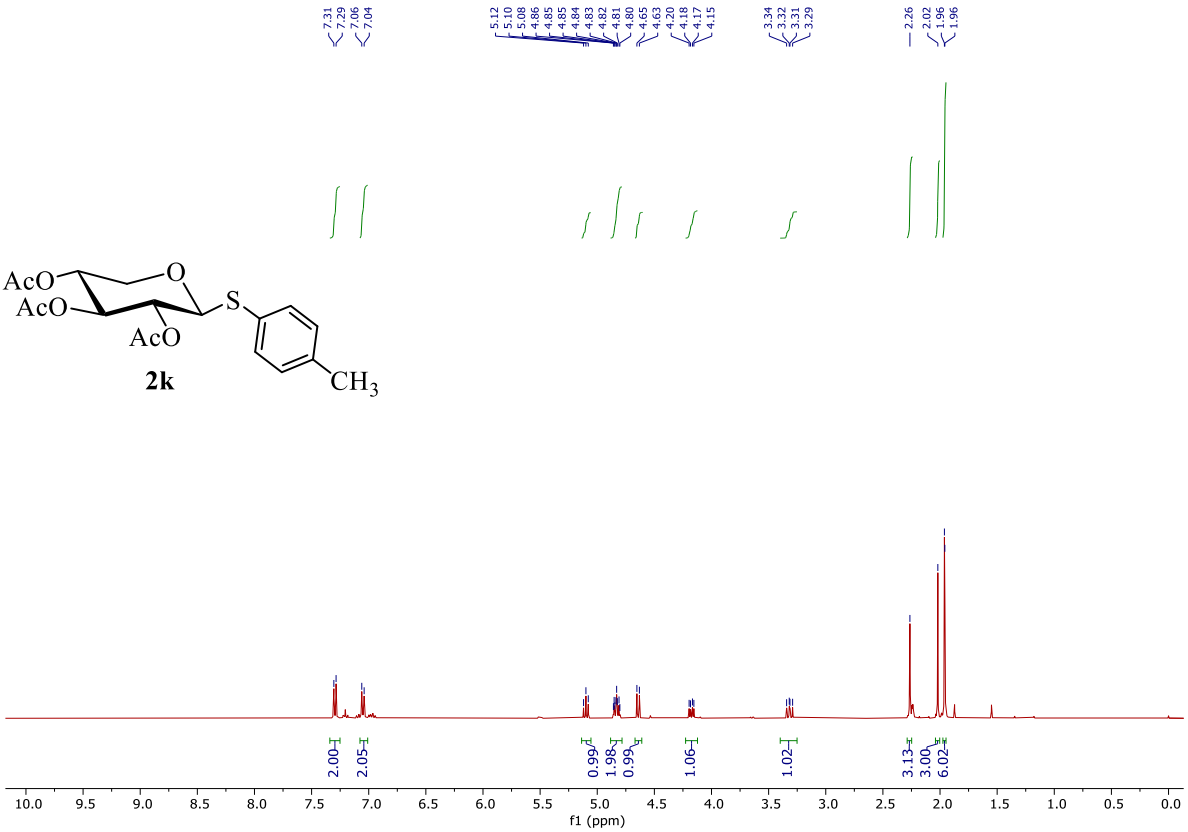
^{13}C NMR of Compound **2i (101 MHz, $CDCl_3$)**



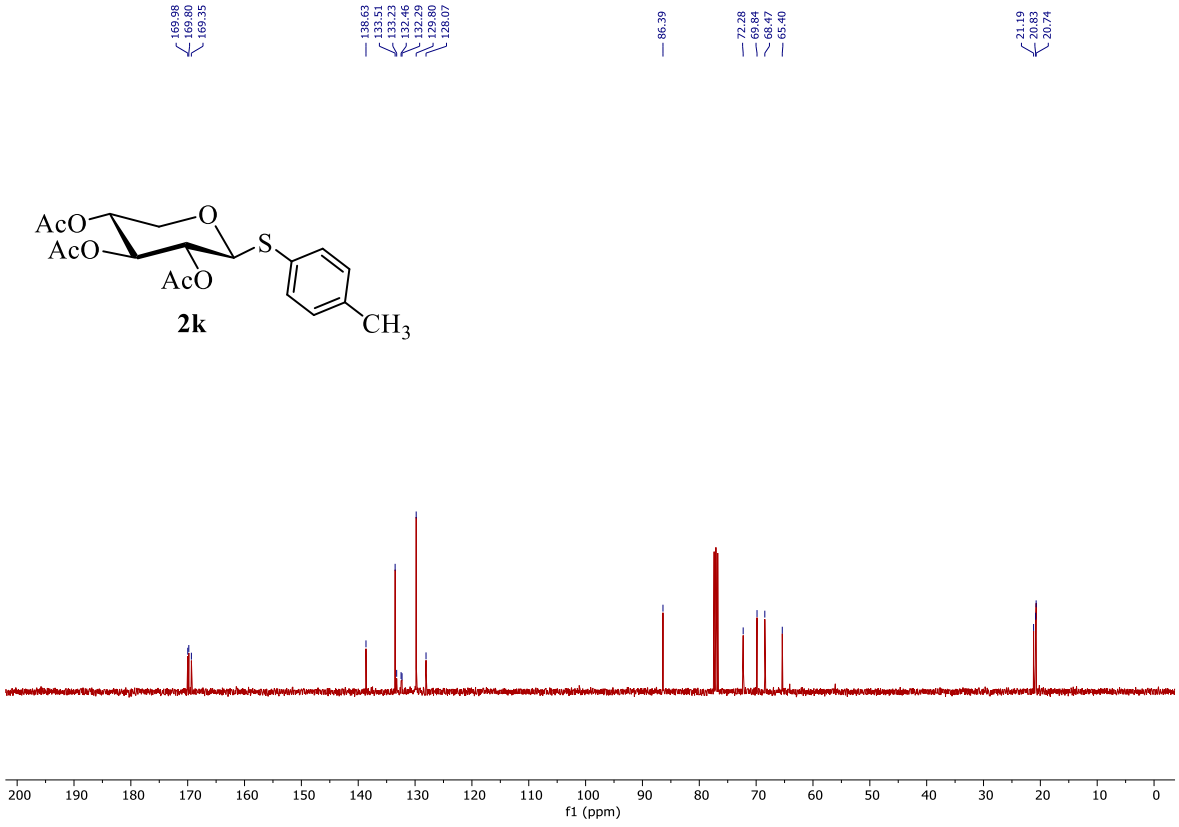
^{1}H NMR of Compound **2j (400 MHz, $CDCl_3$)**



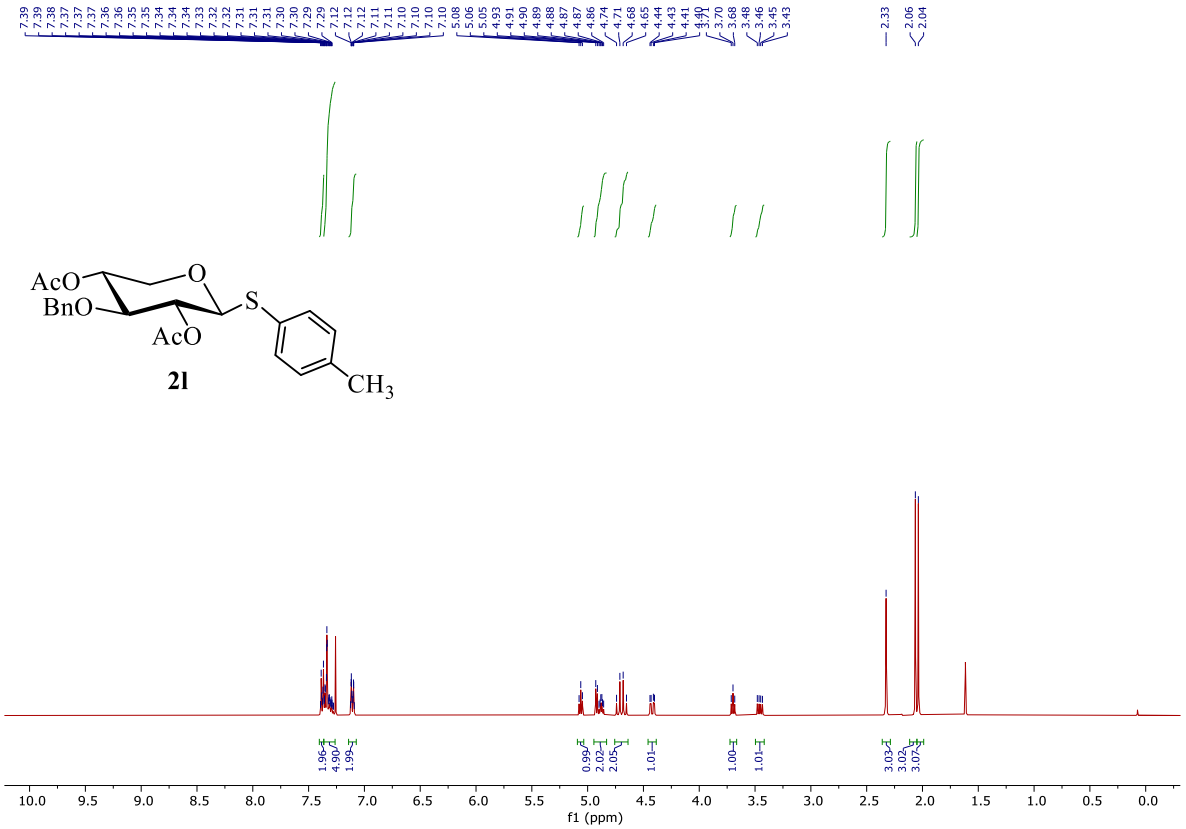
^{13}C NMR of Compound **2j (101 MHz, $CDCl_3$)**



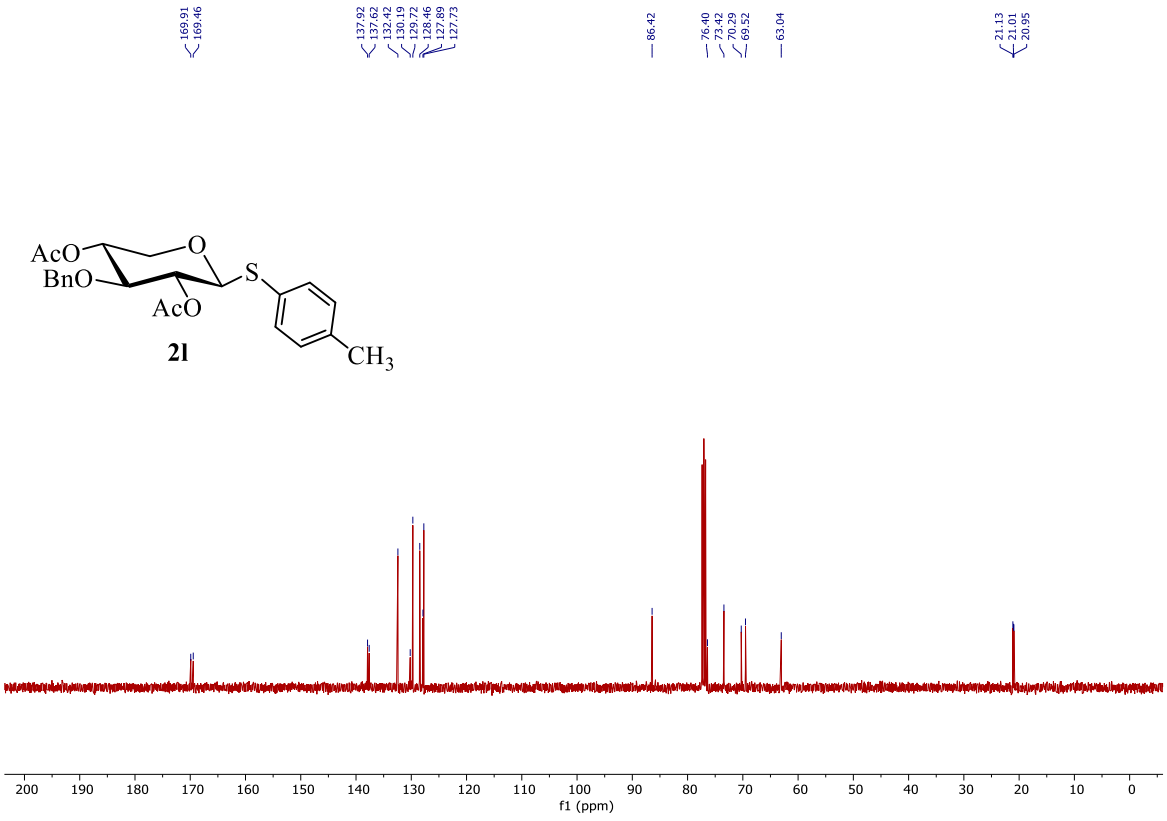
^{1}H NMR of Compound **2k (400 MHz, $CDCl_3$)**



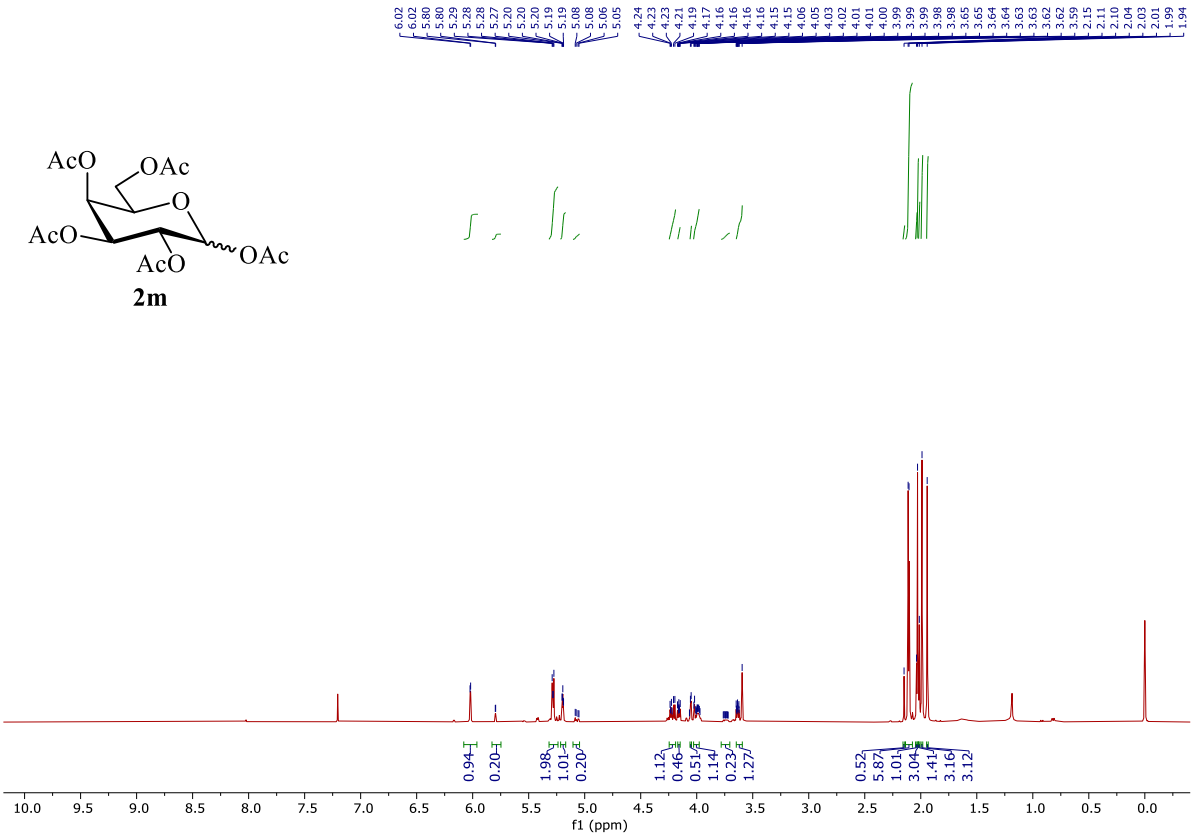
^{13}C NMR of Compound **2k (101 MHz, $CDCl_3$)**



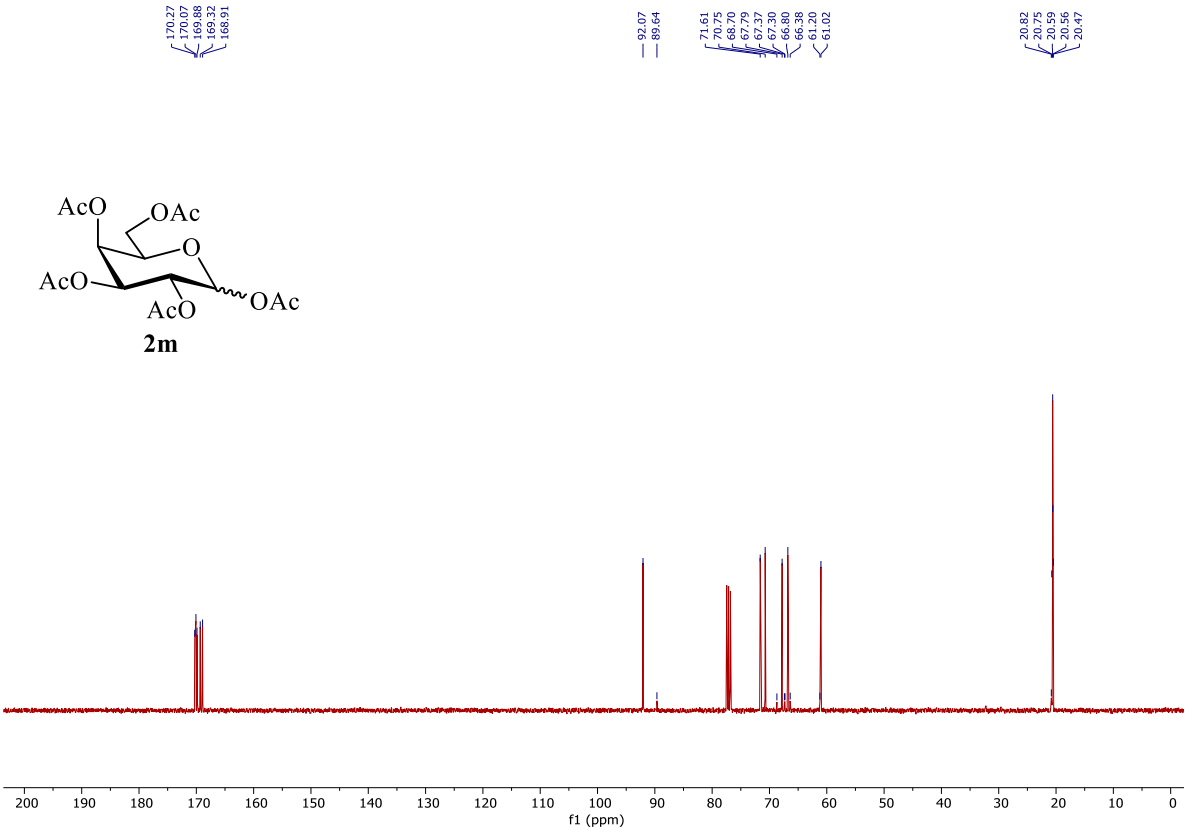
^{1}H NMR of Compound **2l (400 MHz, $CDCl_3$)**



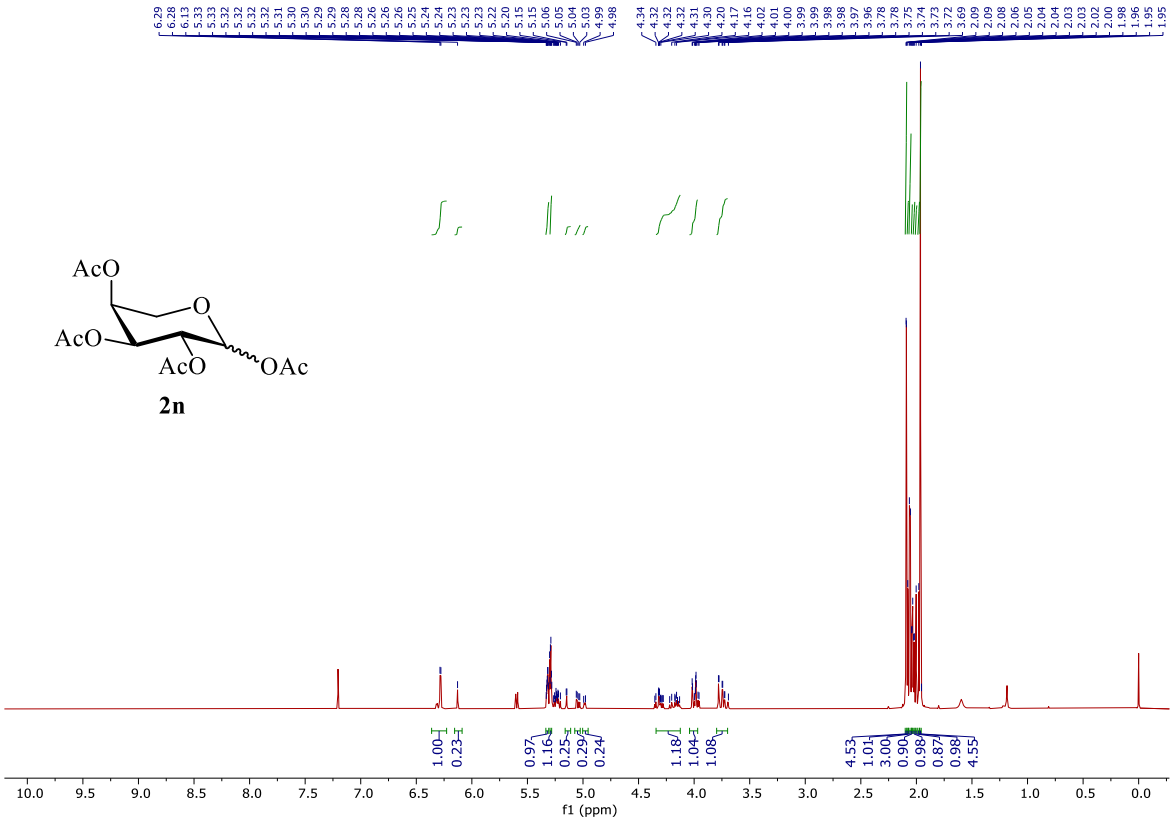
^{13}C NMR of Compound **2l (101 MHz, $CDCl_3$)**



^{1}H NMR of Compound **2m (400 MHz, $CDCl_3$)**



^{13}C NMR of Compound **2m (101 MHz, $CDCl_3$)**



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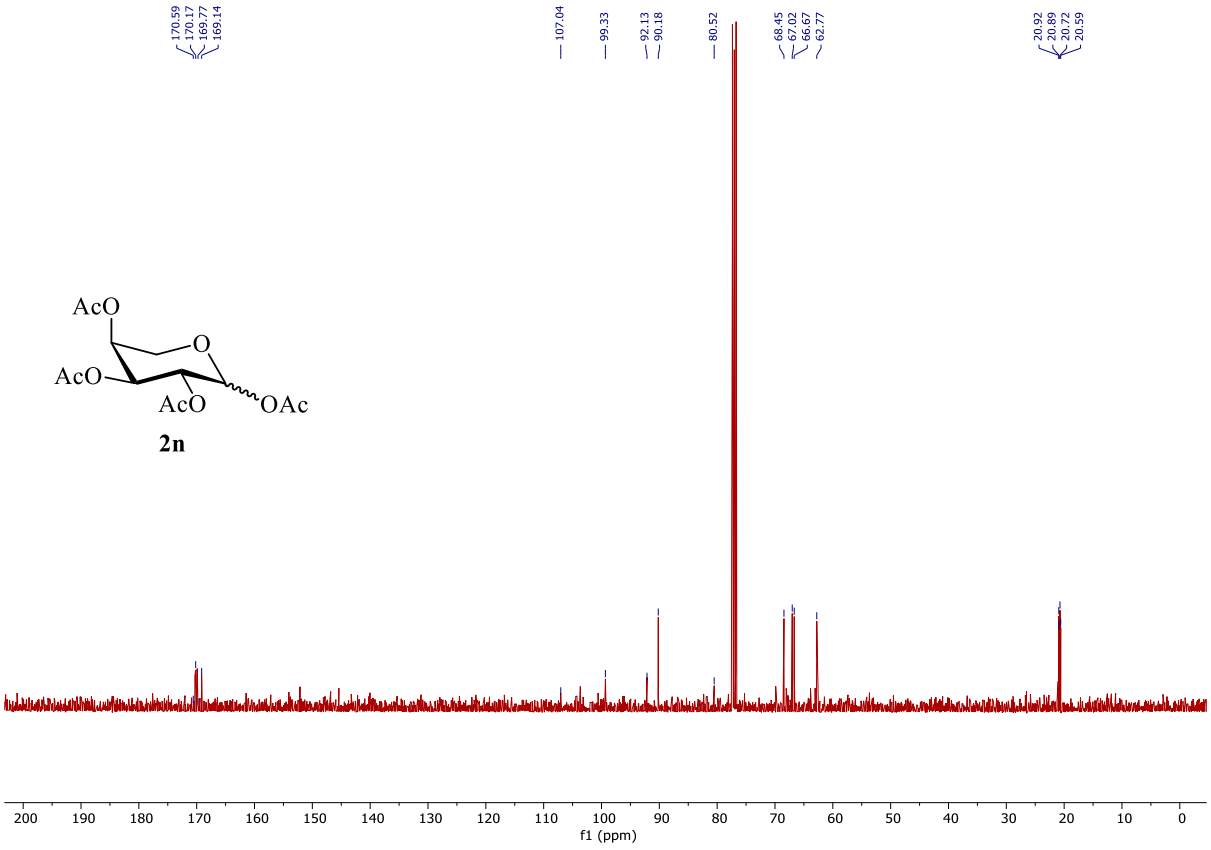
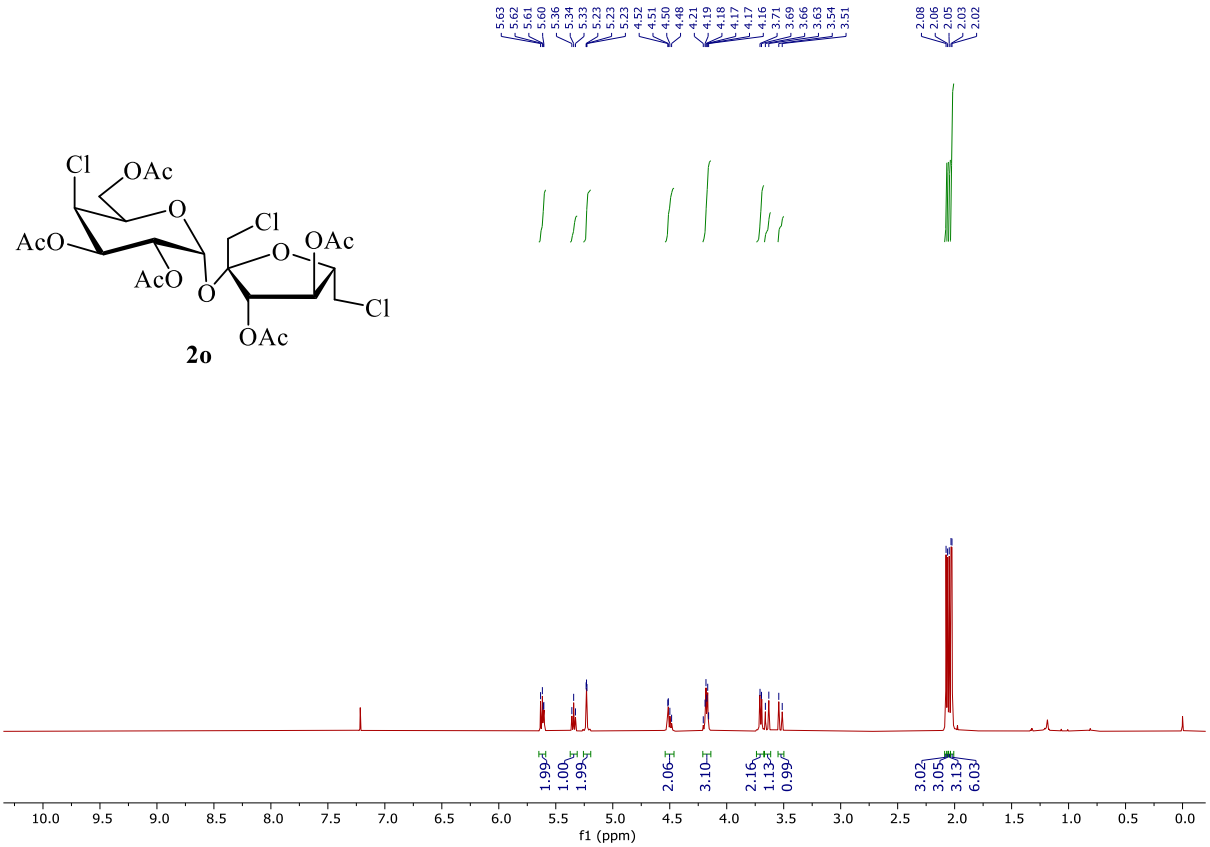
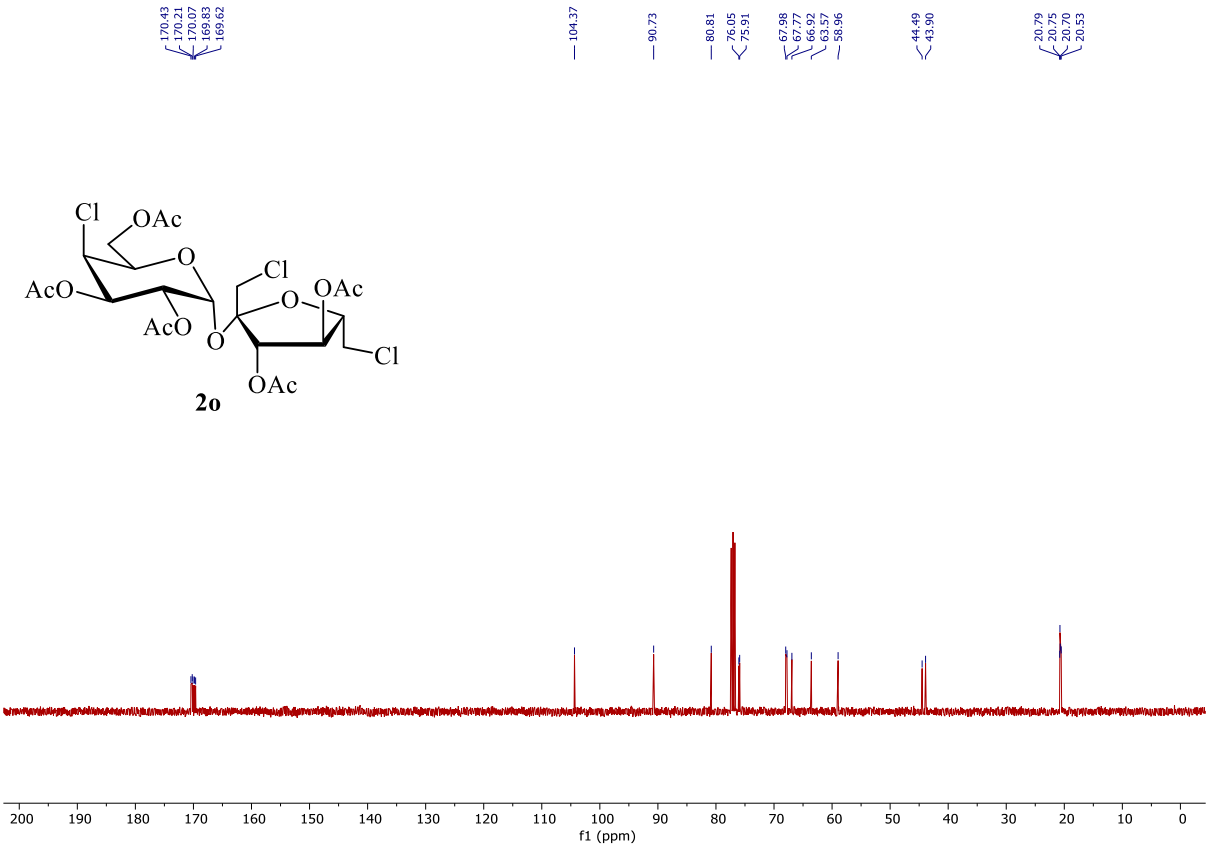


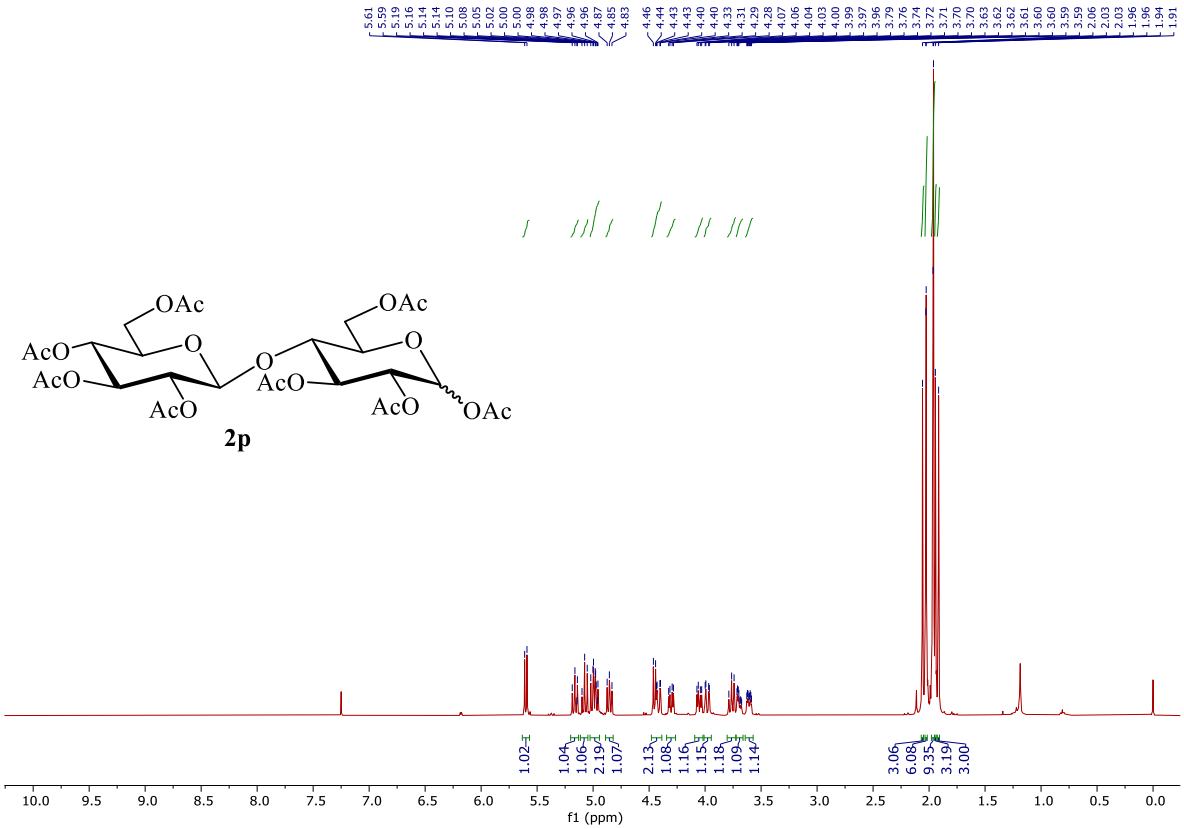
^{13}C NMR of Compound **2n (101 MHz, $CDCl_3$)**



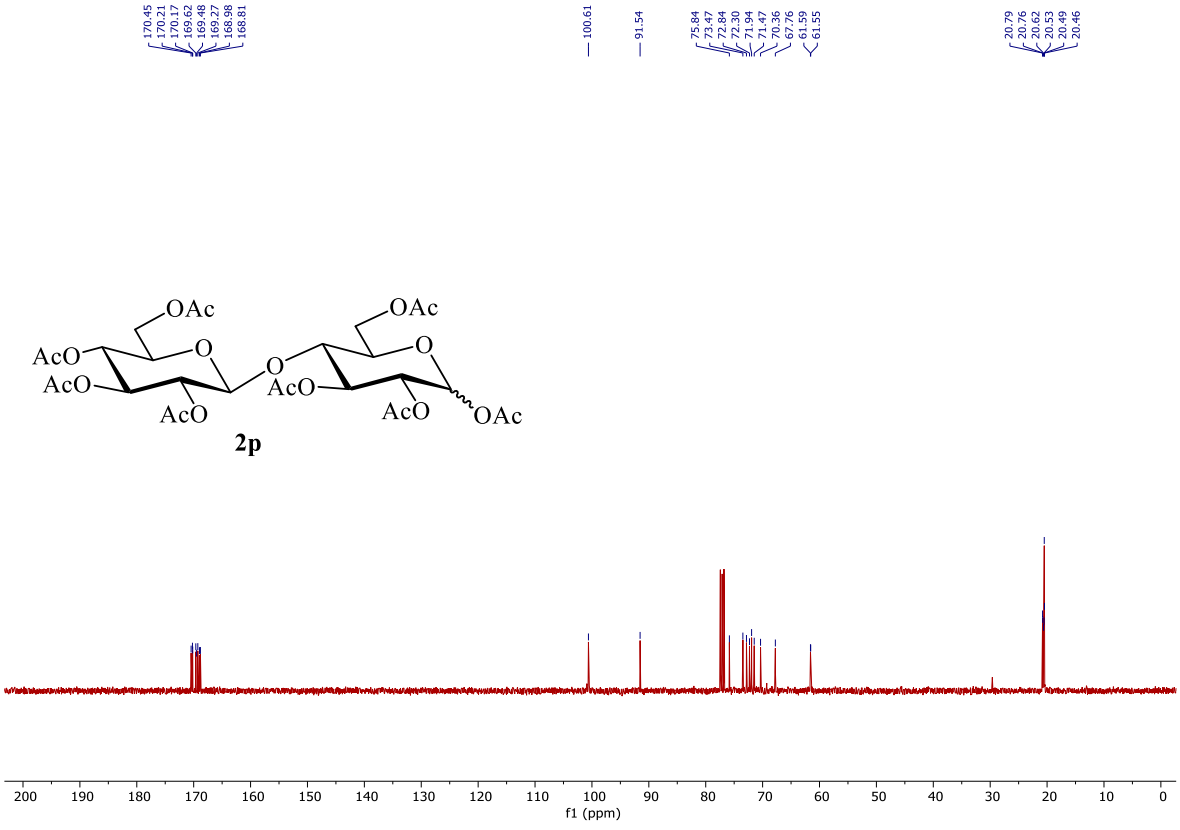
^{1}H NMR of Compound **2o (400 MHz, $CDCl_3$)**



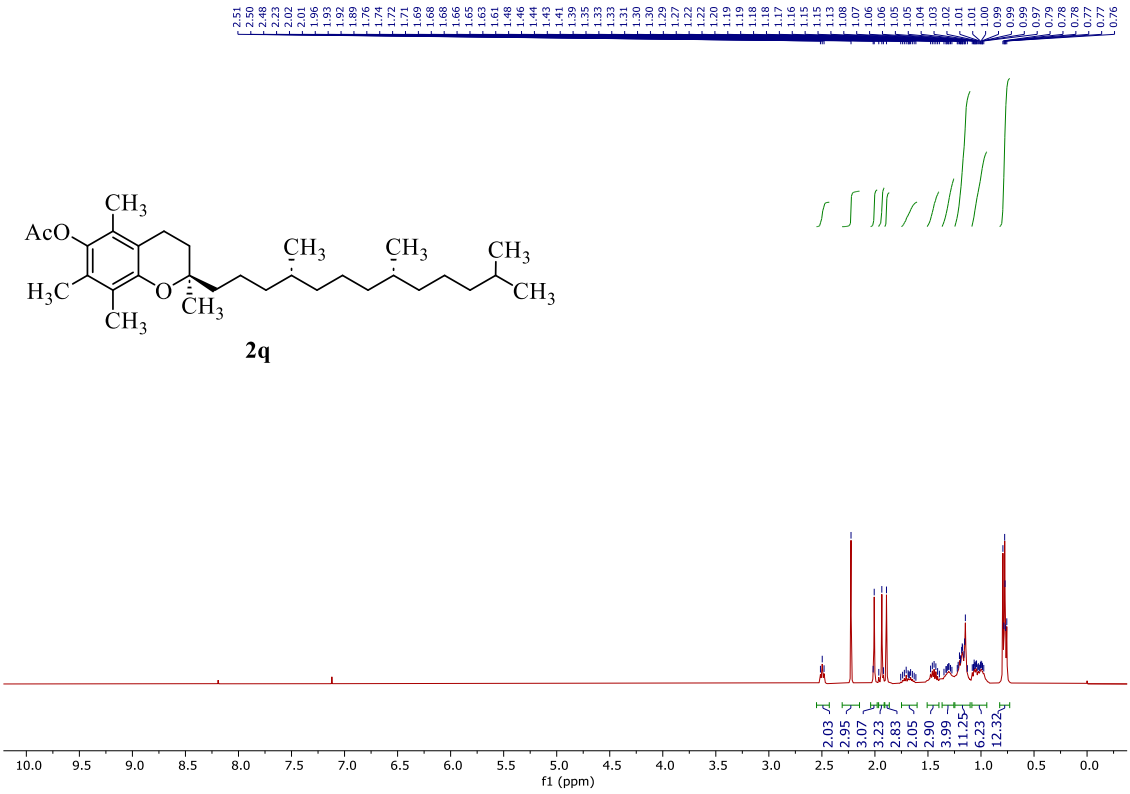
^{13}C NMR of Compound **2o (101 MHz, $CDCl_3$)**



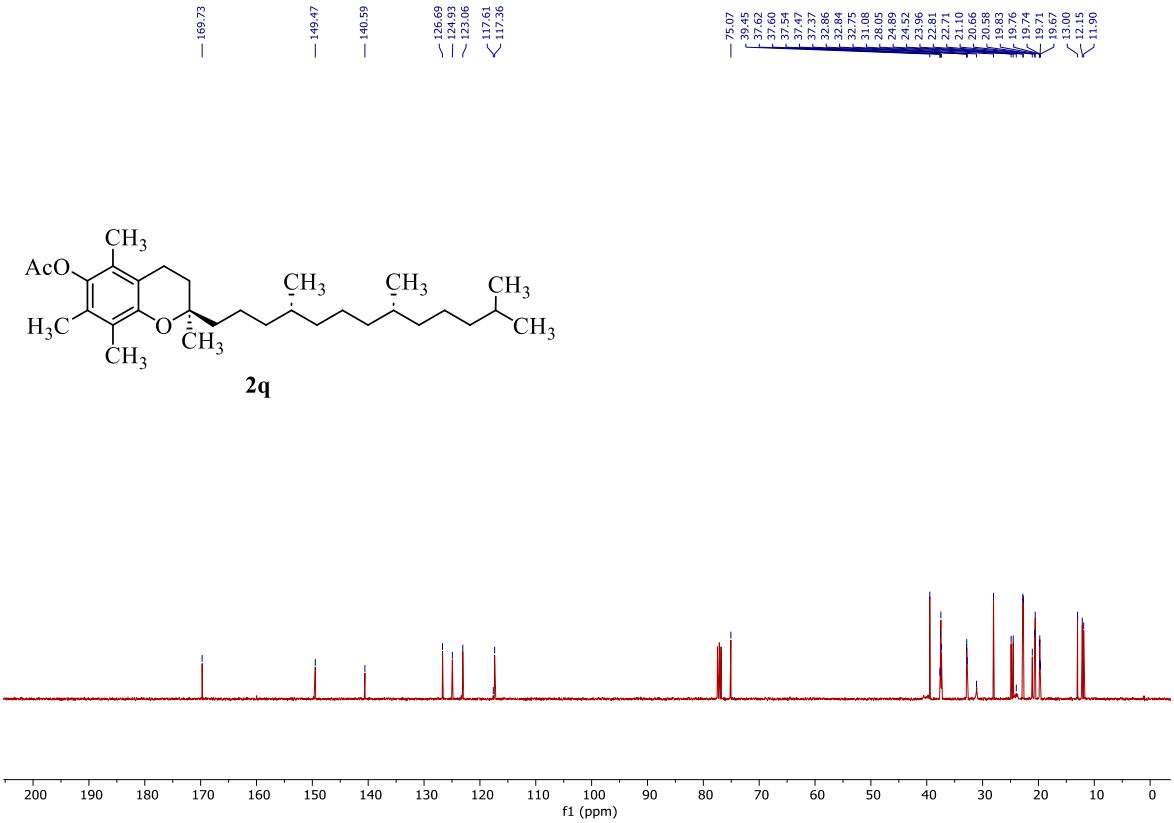
^{1}H NMR of Compound **2p (400 MHz, $CDCl_3$)**



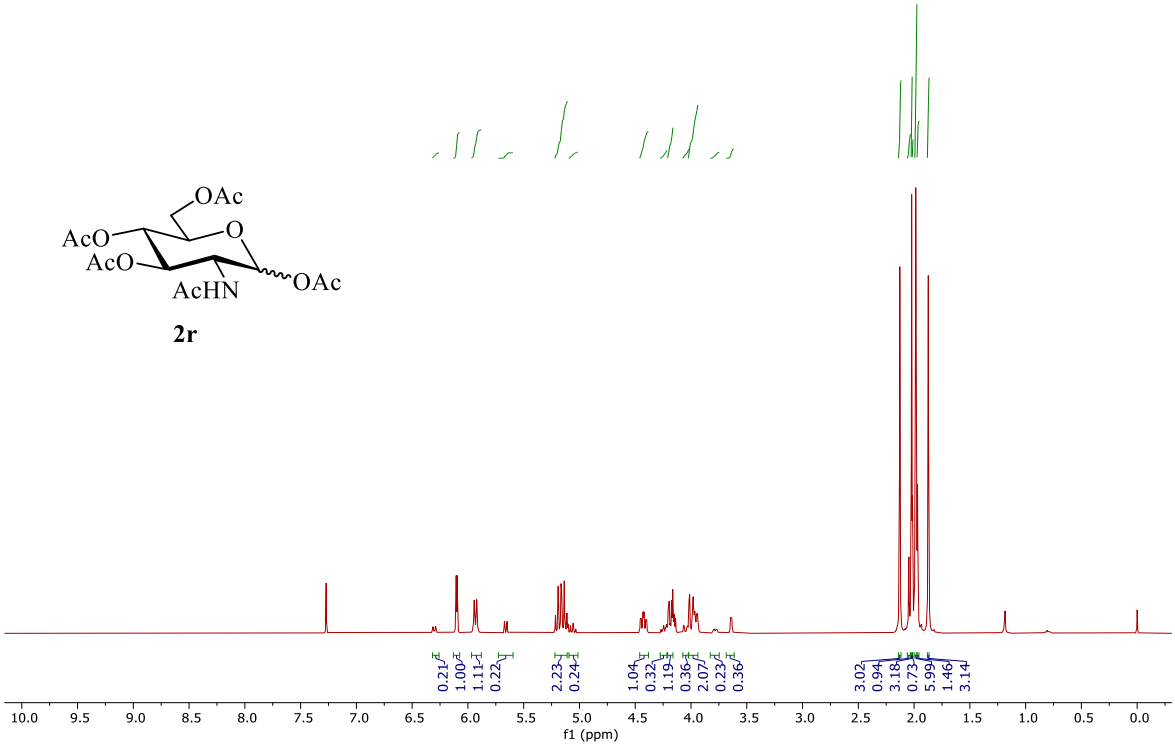
^{13}C NMR of Compound **2p (101 MHz, $CDCl_3$)**



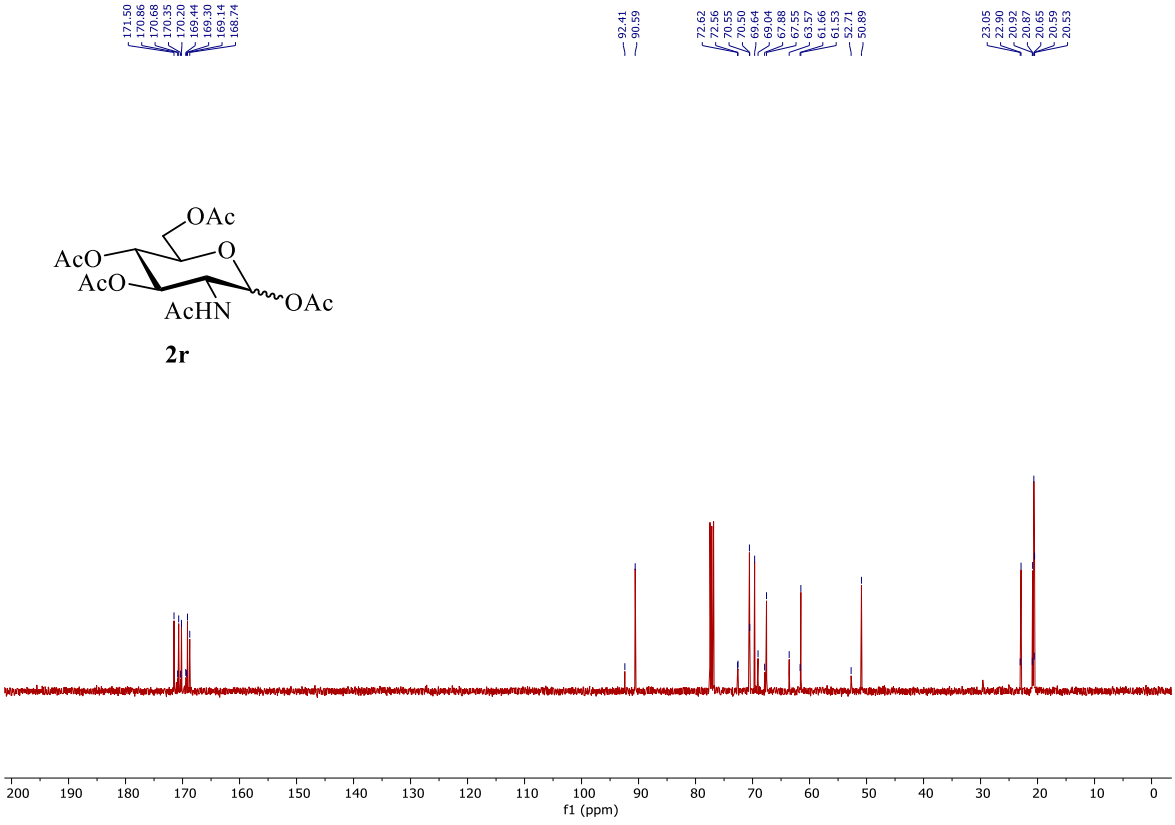
^{1}H NMR of Compound **2q (400 MHz, $CDCl_3$**



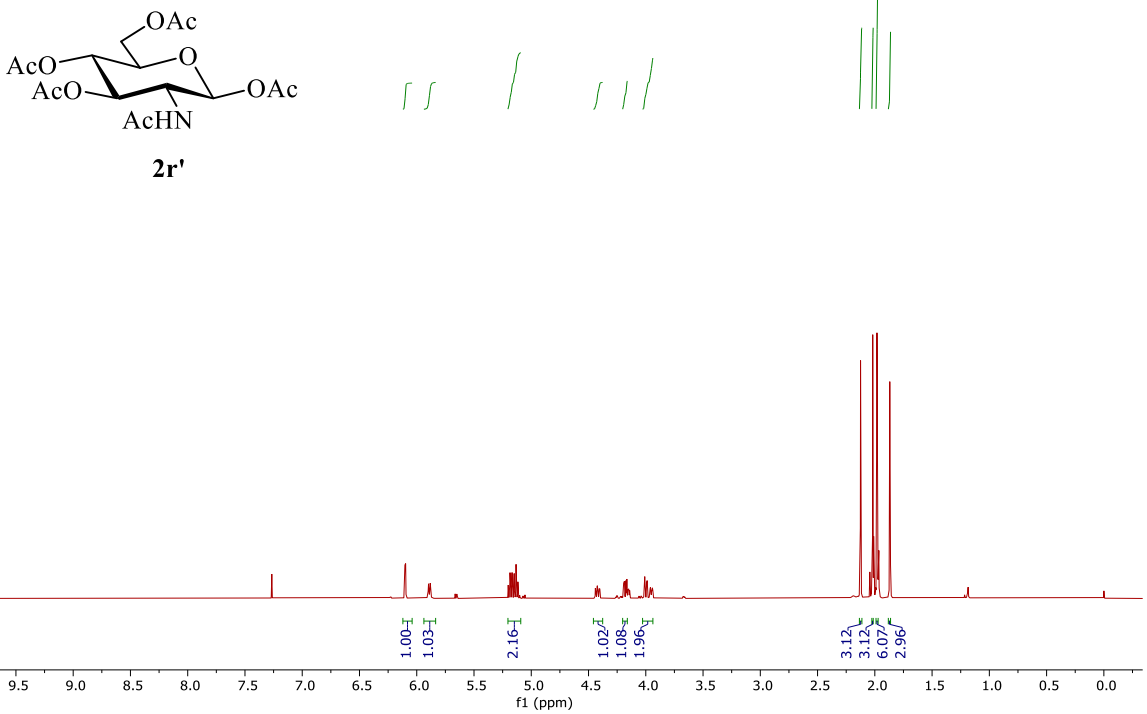
^{13}C NMR of Compound **2q (101 MHz, $CDCl_3$)**



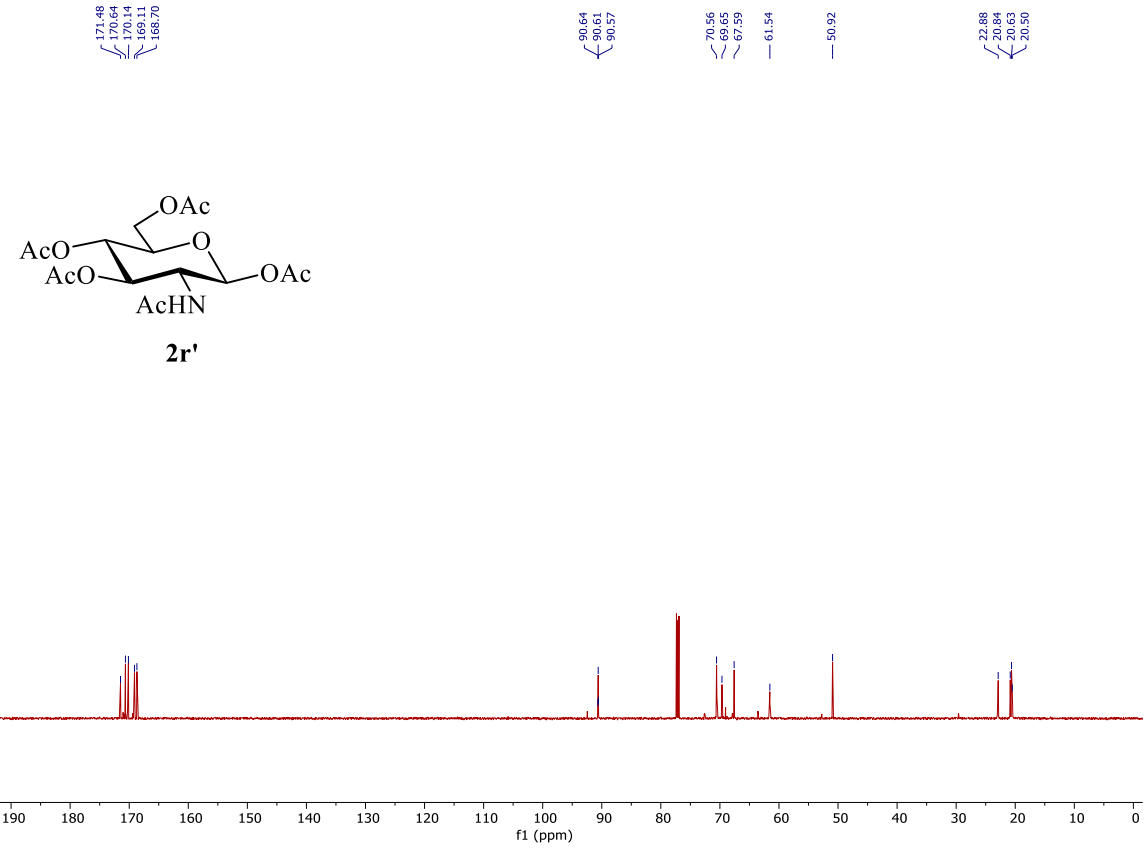
^{1}H NMR of Compound **2r (400 MHz, $CDCl_3$)**



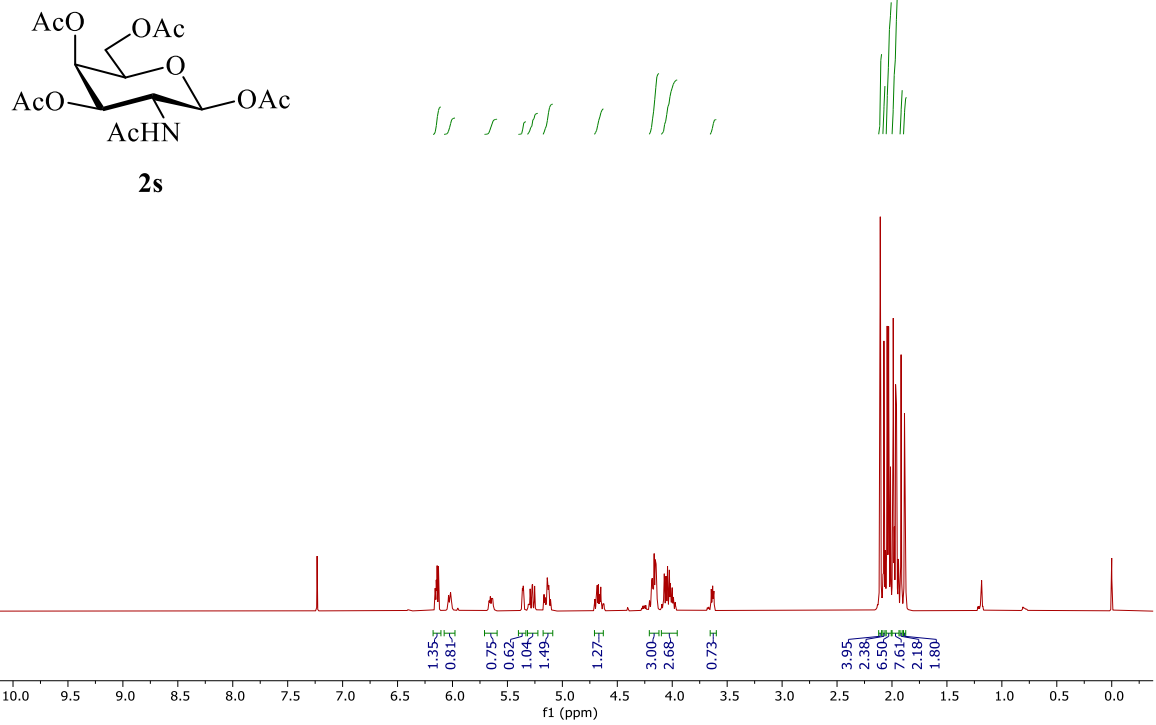
^{13}C NMR of Compound **2r (101 MHz, $CDCl_3$)**



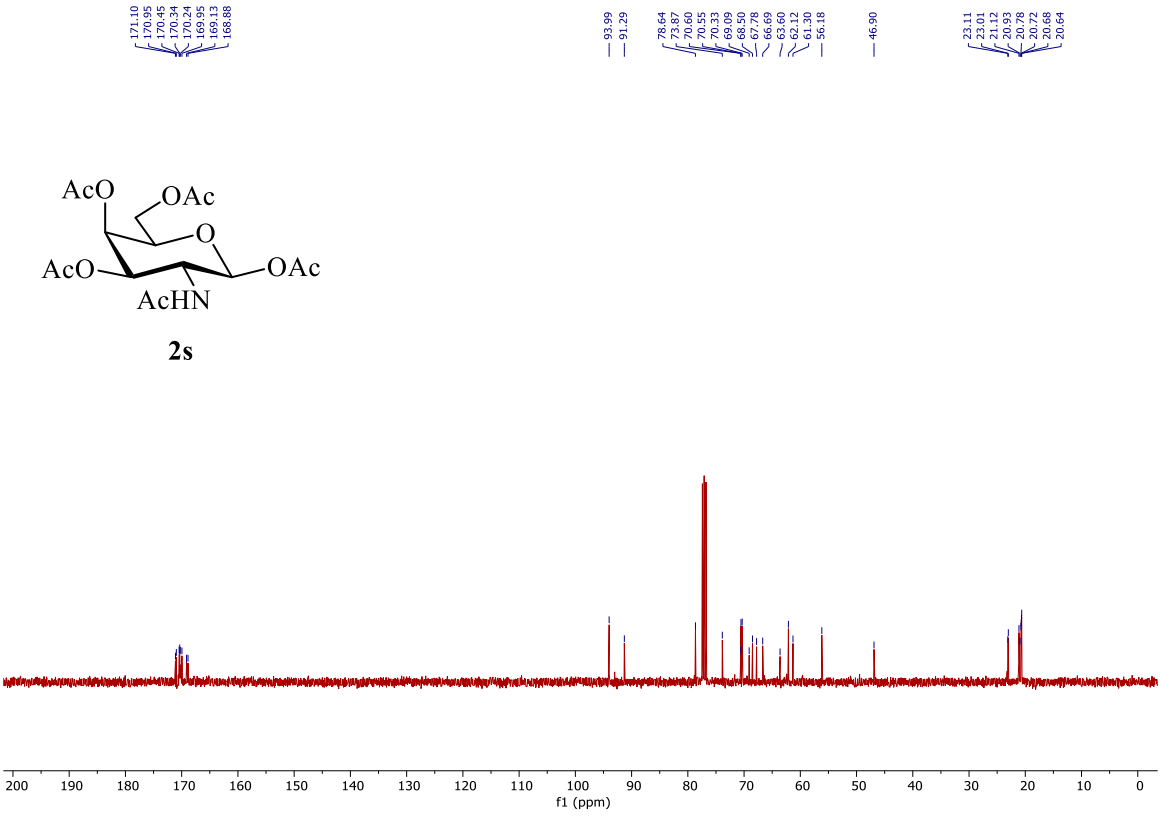
^{1}H NMR of Compound **2r' (400 MHz, $CDCl_3$)**



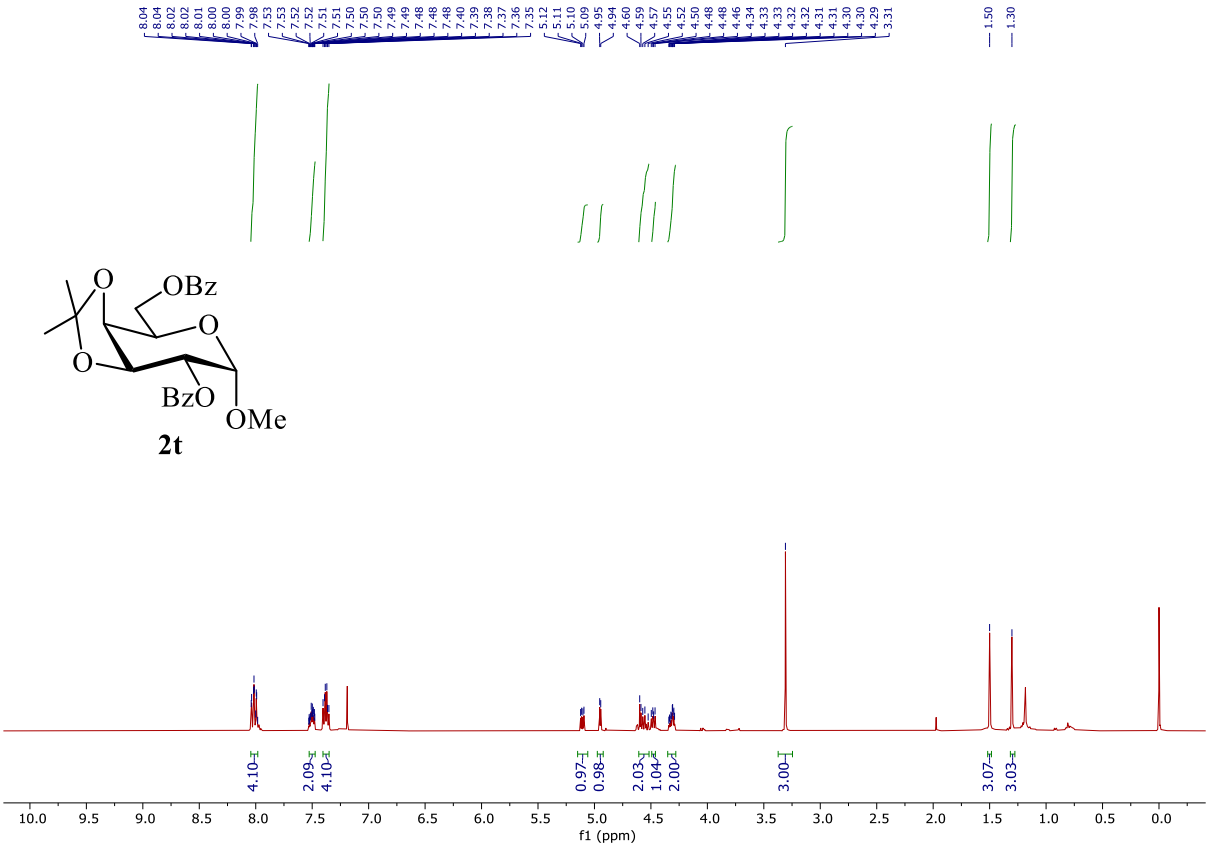
^{13}C NMR of Compound **2r' (101 MHz, $CDCl_3$)**



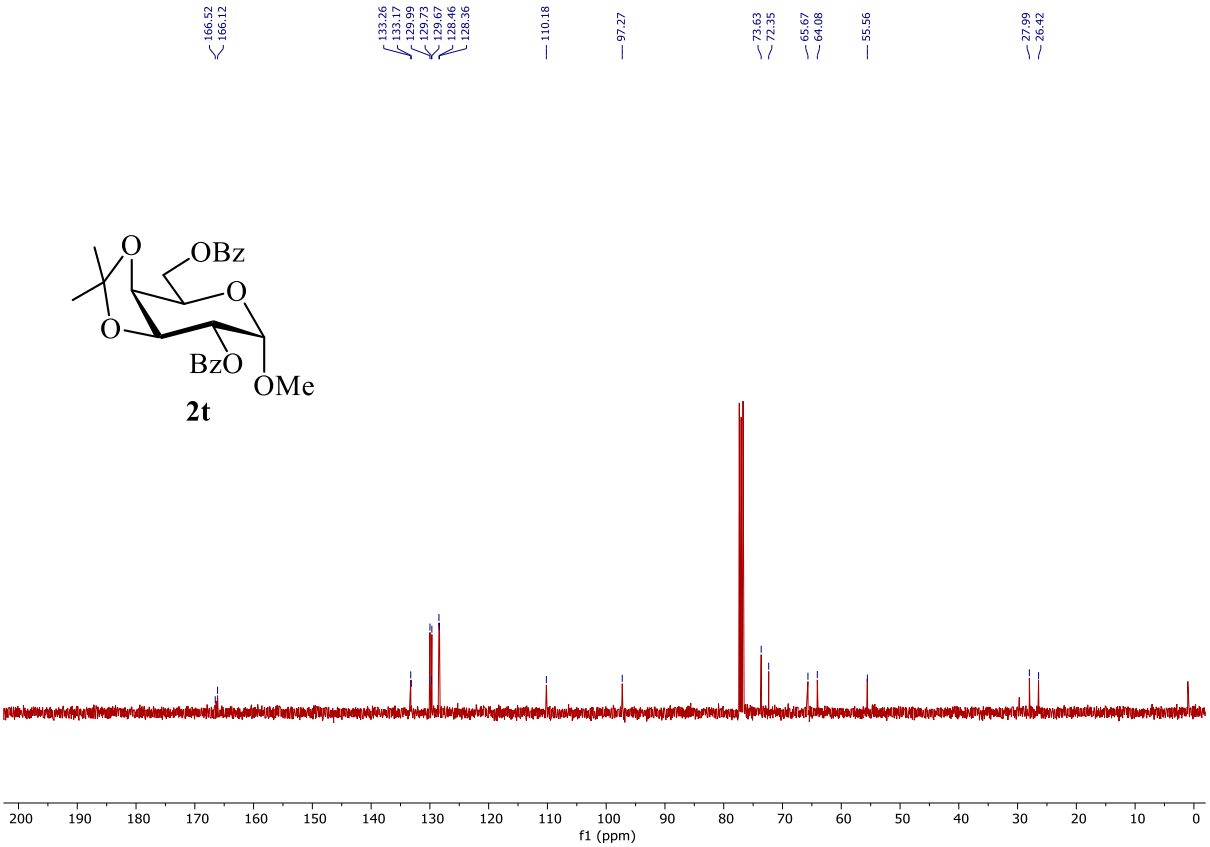
^{1}H NMR of Compound **2s (400 MHz, $CDCl_3$)**



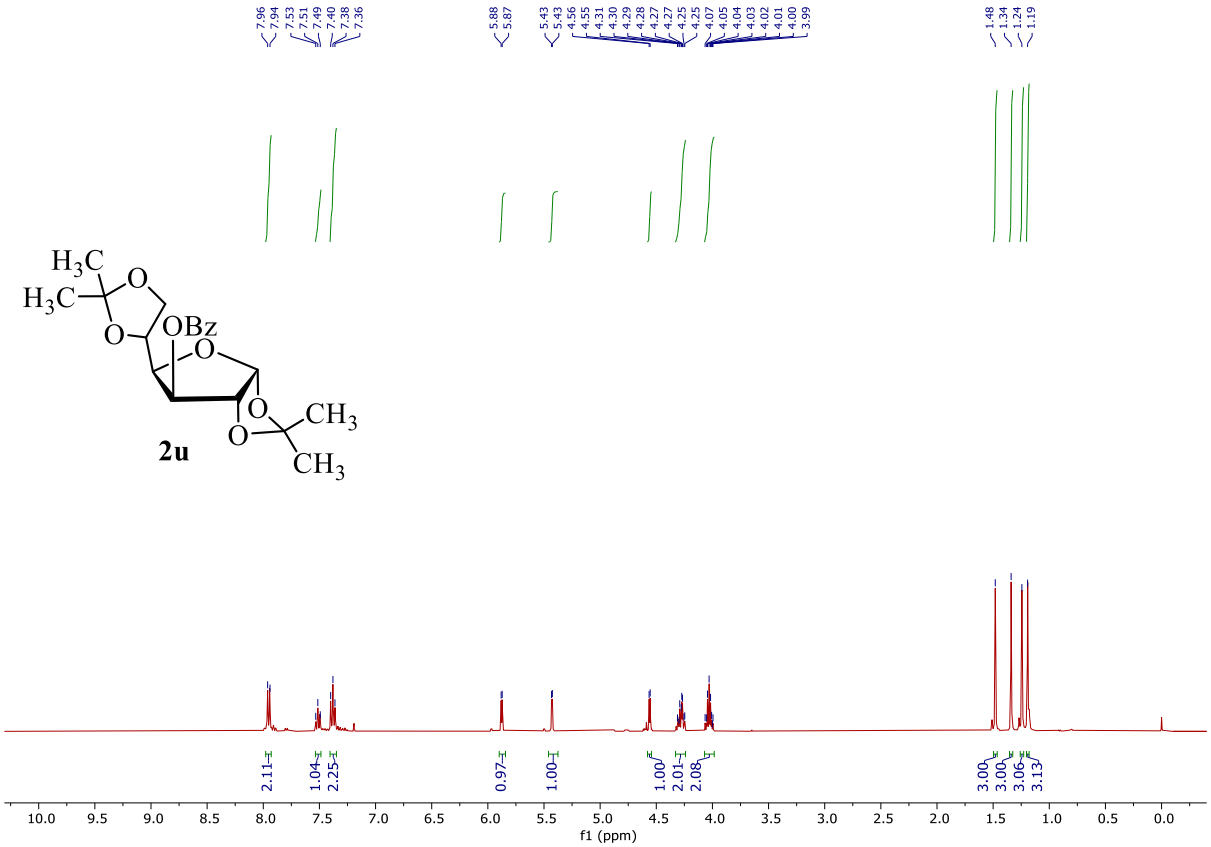
^{13}C NMR of Compound **2s (101 MHz, $CDCl_3$)**



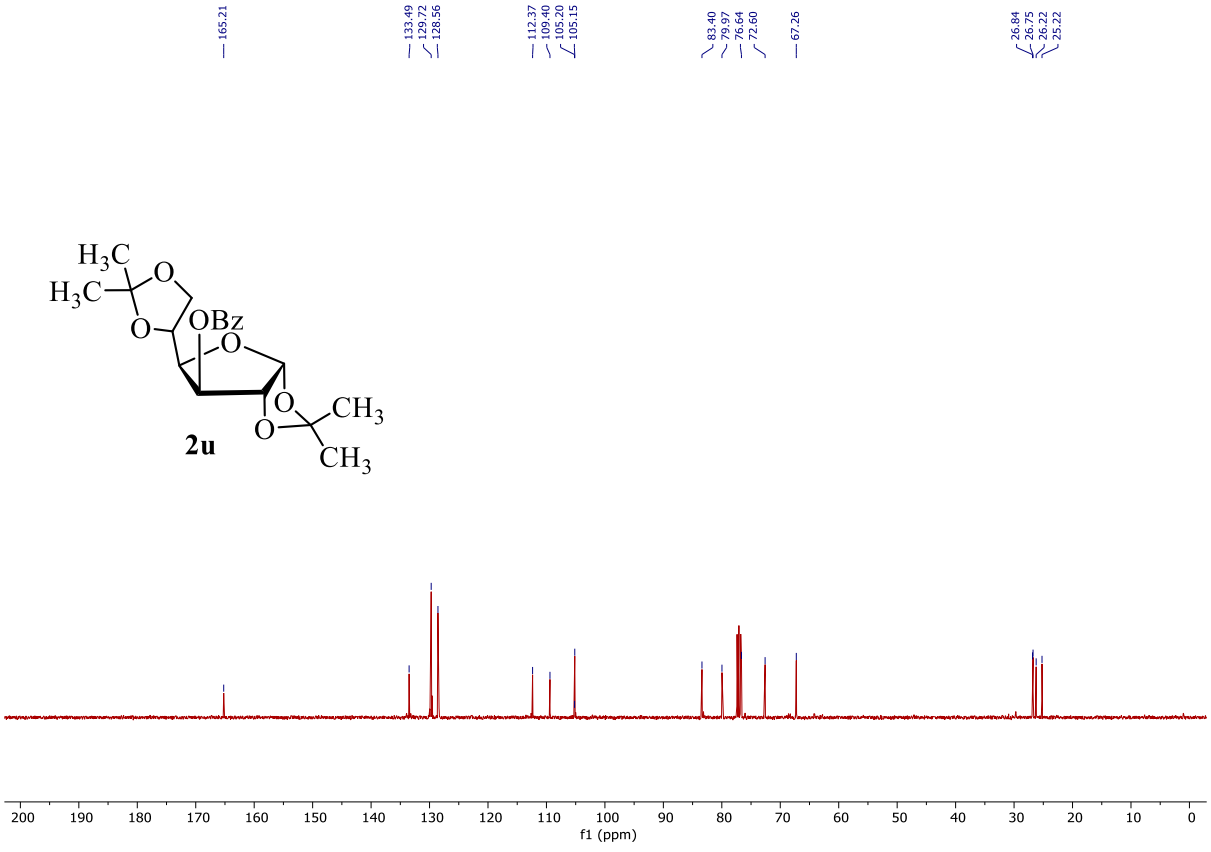
^{1}H NMR of Compound **2t (400 MHz, $CDCl_3$)**



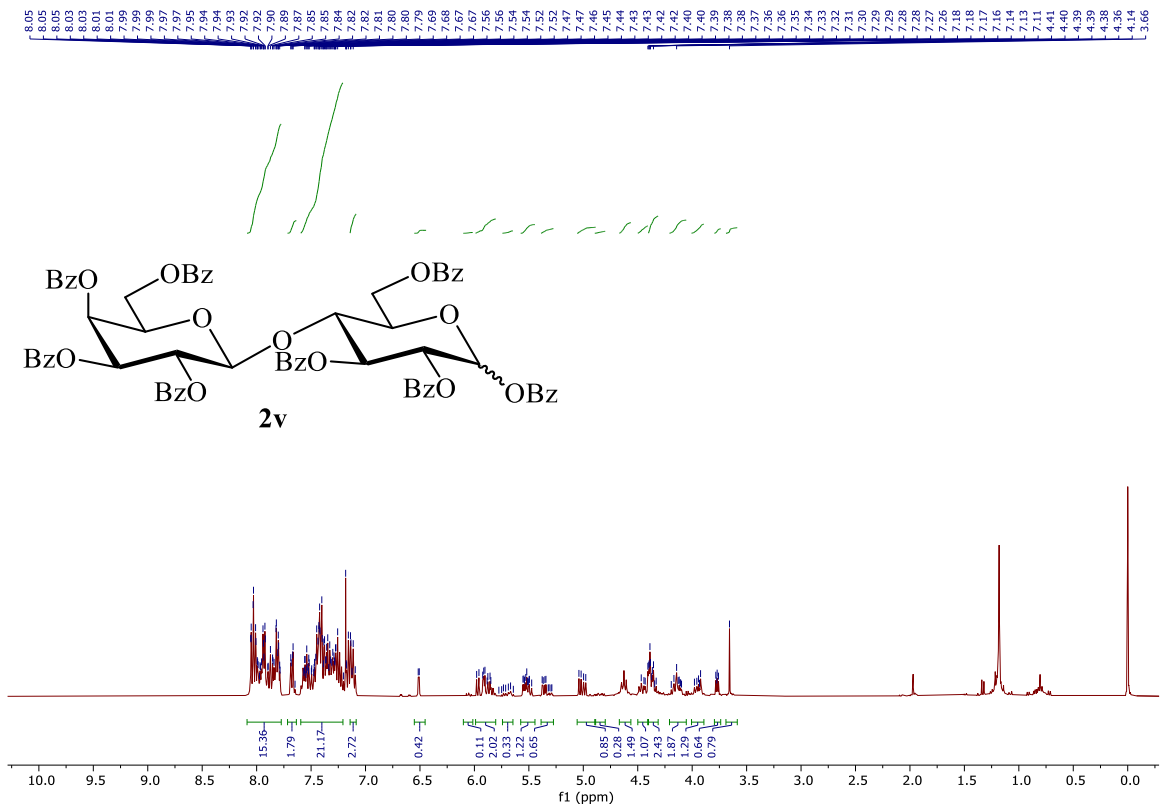
^{13}C NMR of Compound **2t (101 MHz, $CDCl_3$)**



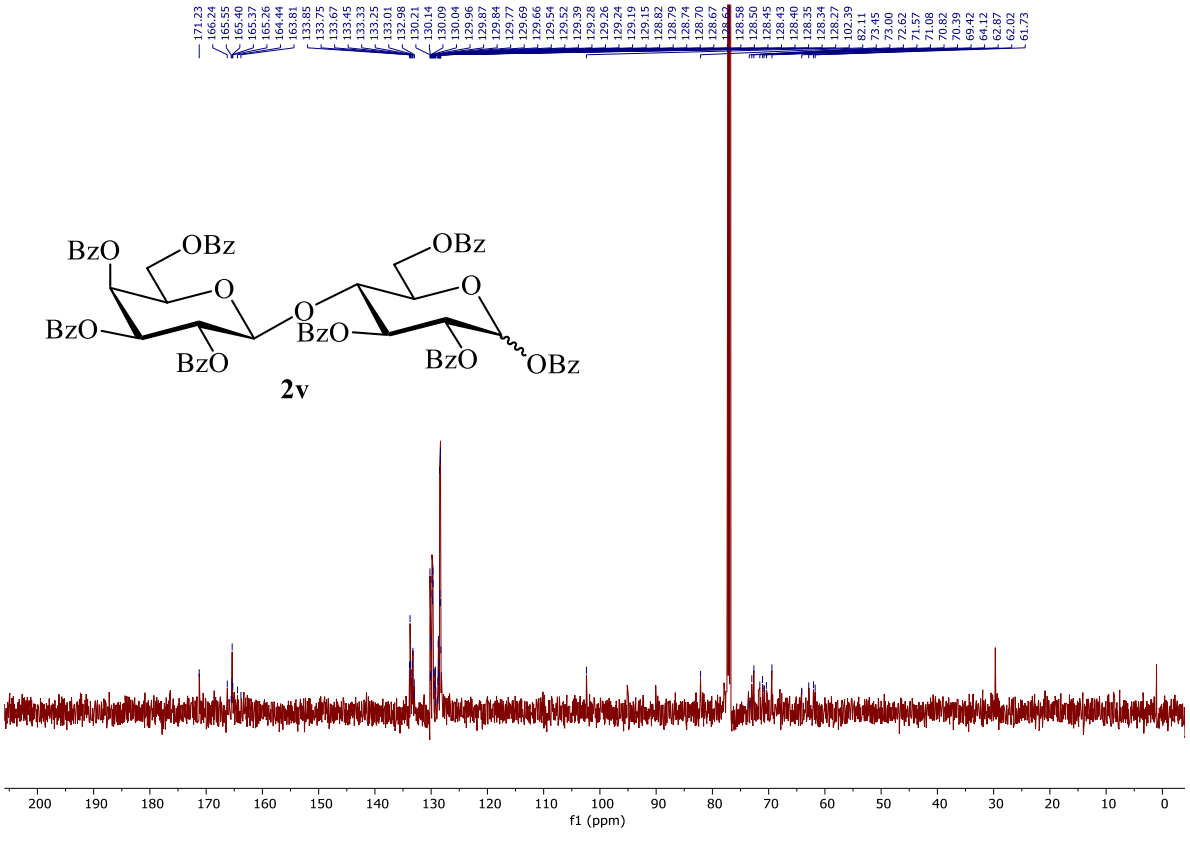
^{1}H NMR of Compound **2u (400 MHz, $CDCl_3$)**



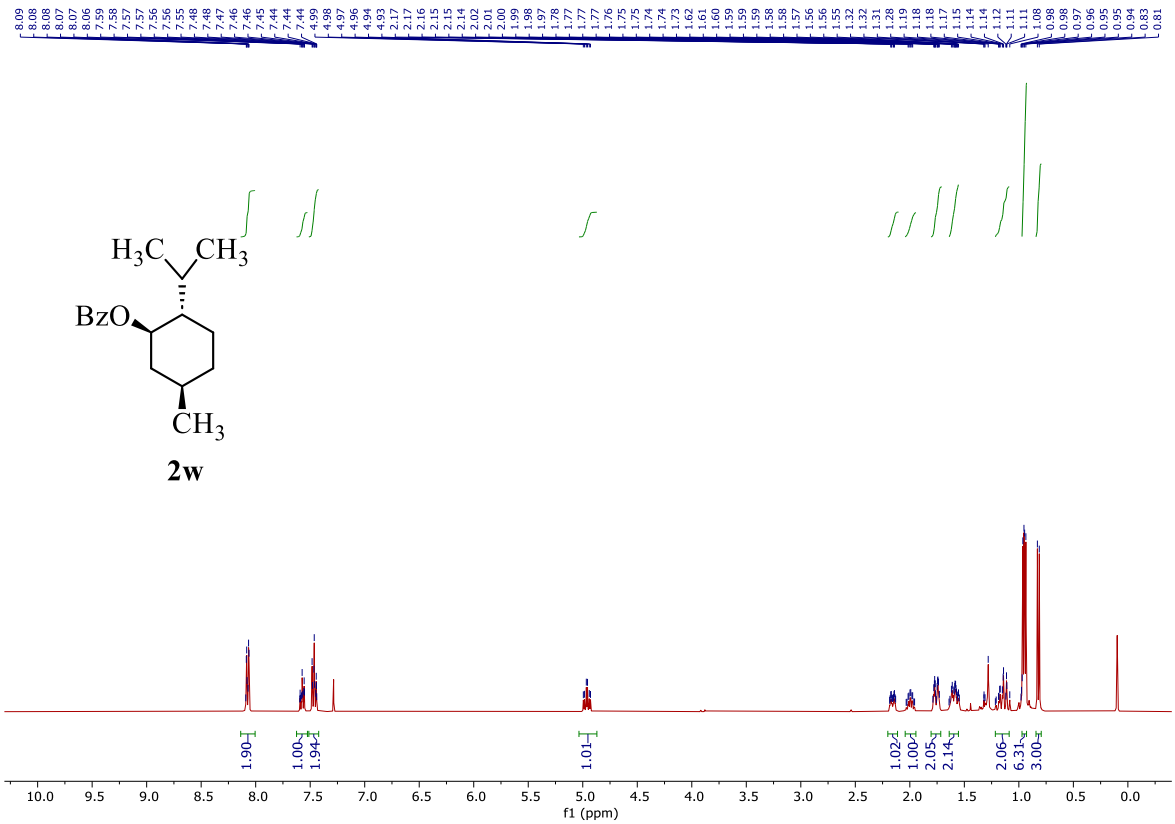
^{13}C NMR of Compound **2u (101 MHz, $CDCl_3$)**



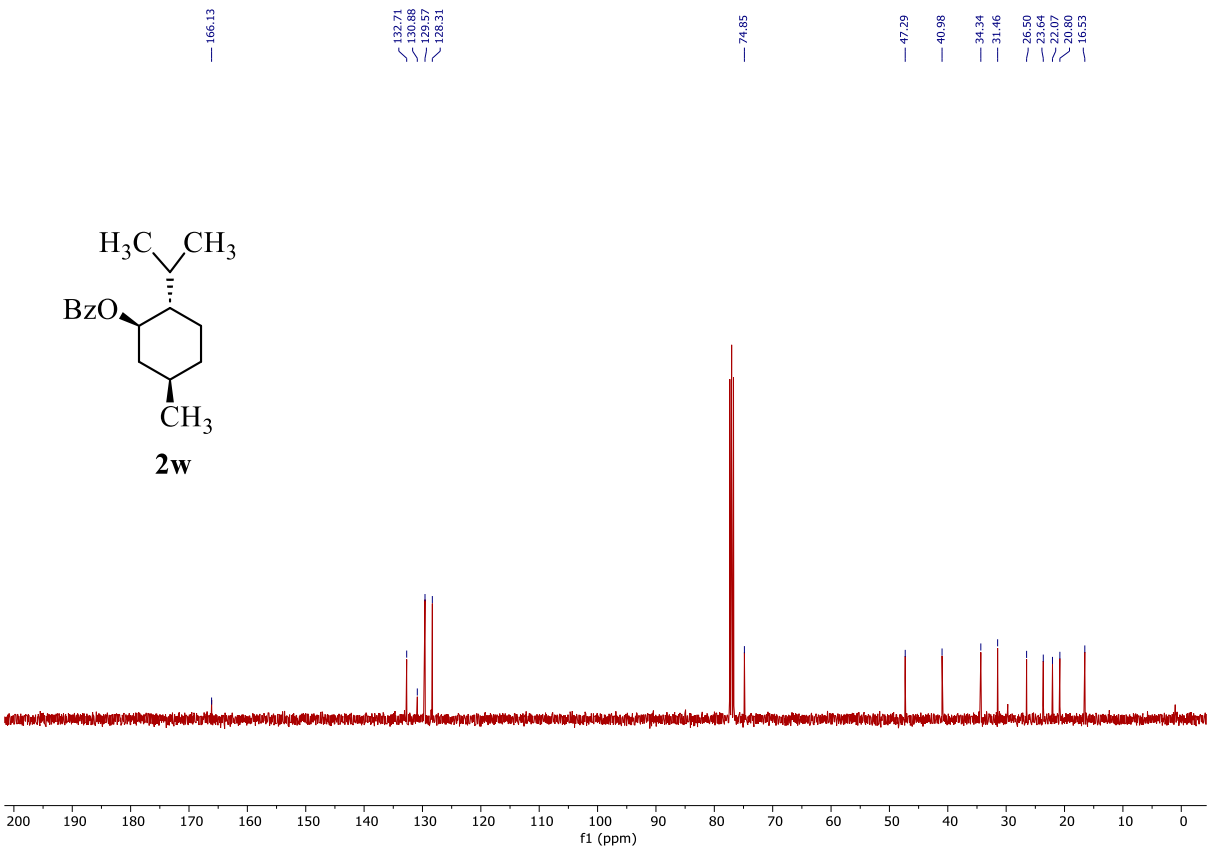
^{1}H NMR of Compound **2v (400 MHz, $CDCl_3$)**



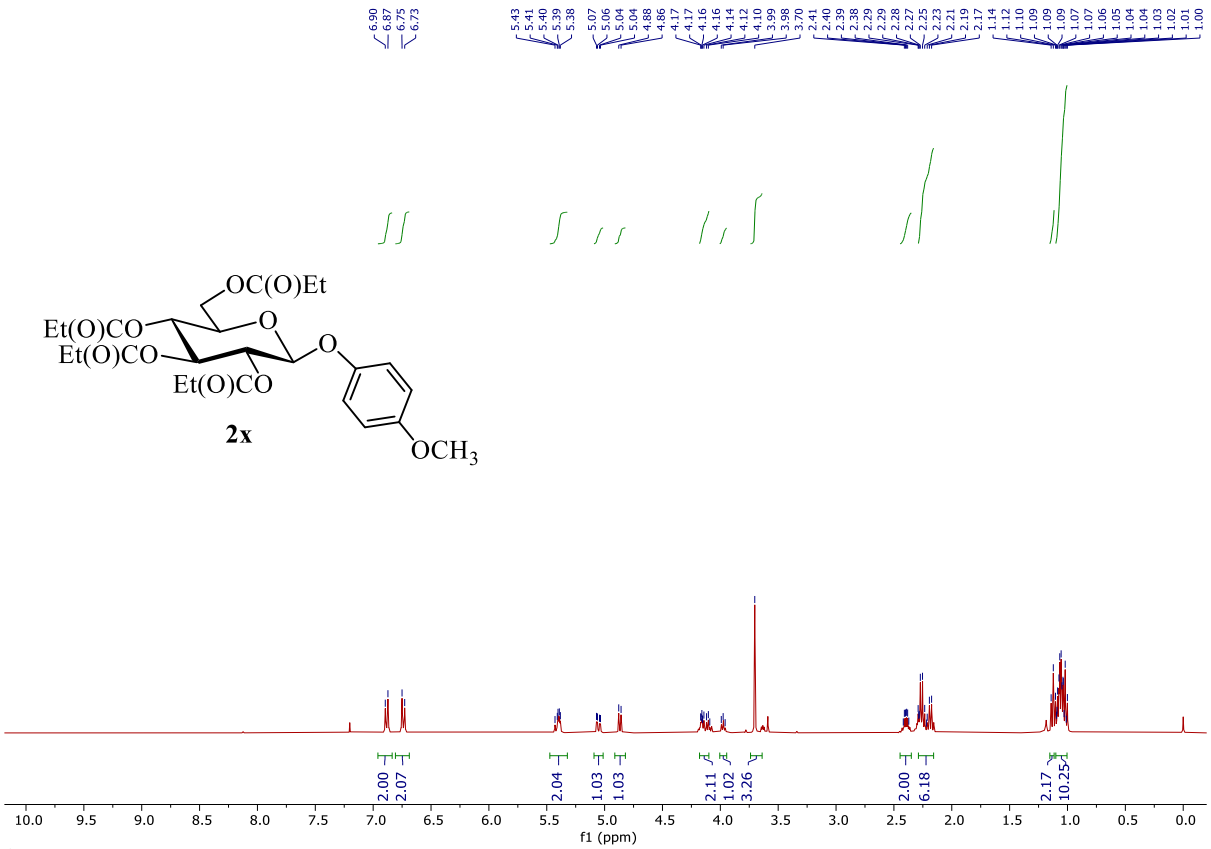
^{13}C NMR of Compound **2v (101 MHz, $CDCl_3$)**



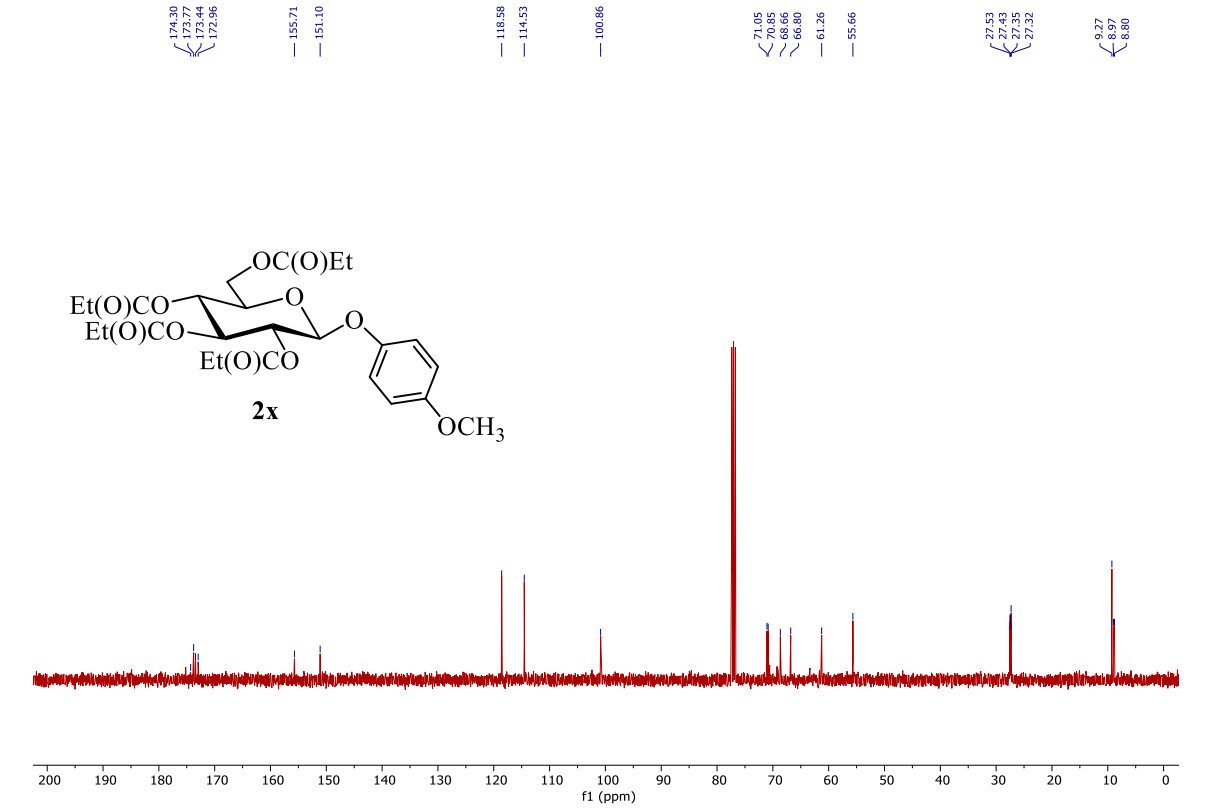
^{1}H NMR of Compound **2w (400 MHz, $CDCl_3$)**



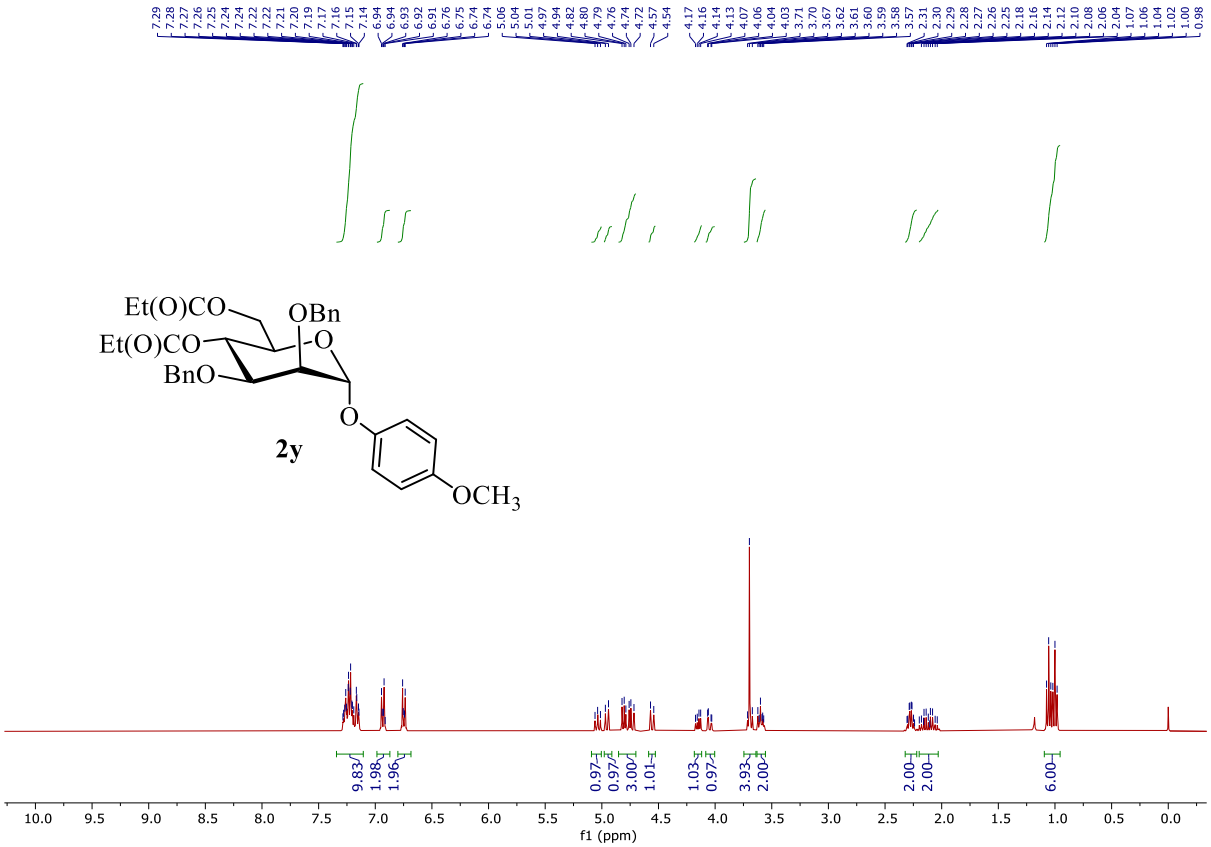
^{13}C NMR of Compound **2w (101 MHz, $CDCl_3$)**



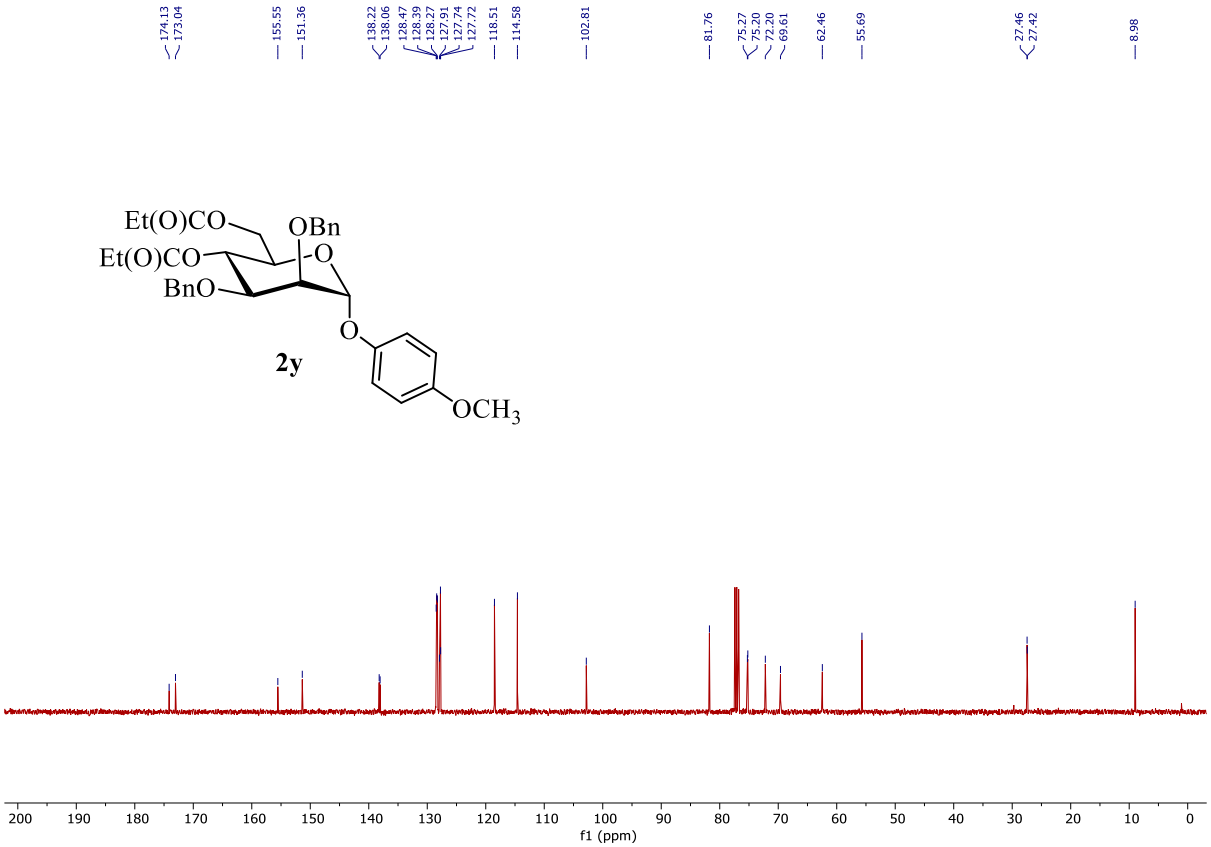
^{1}H NMR of Compound **2x (400 MHz, $CDCl_3$)**



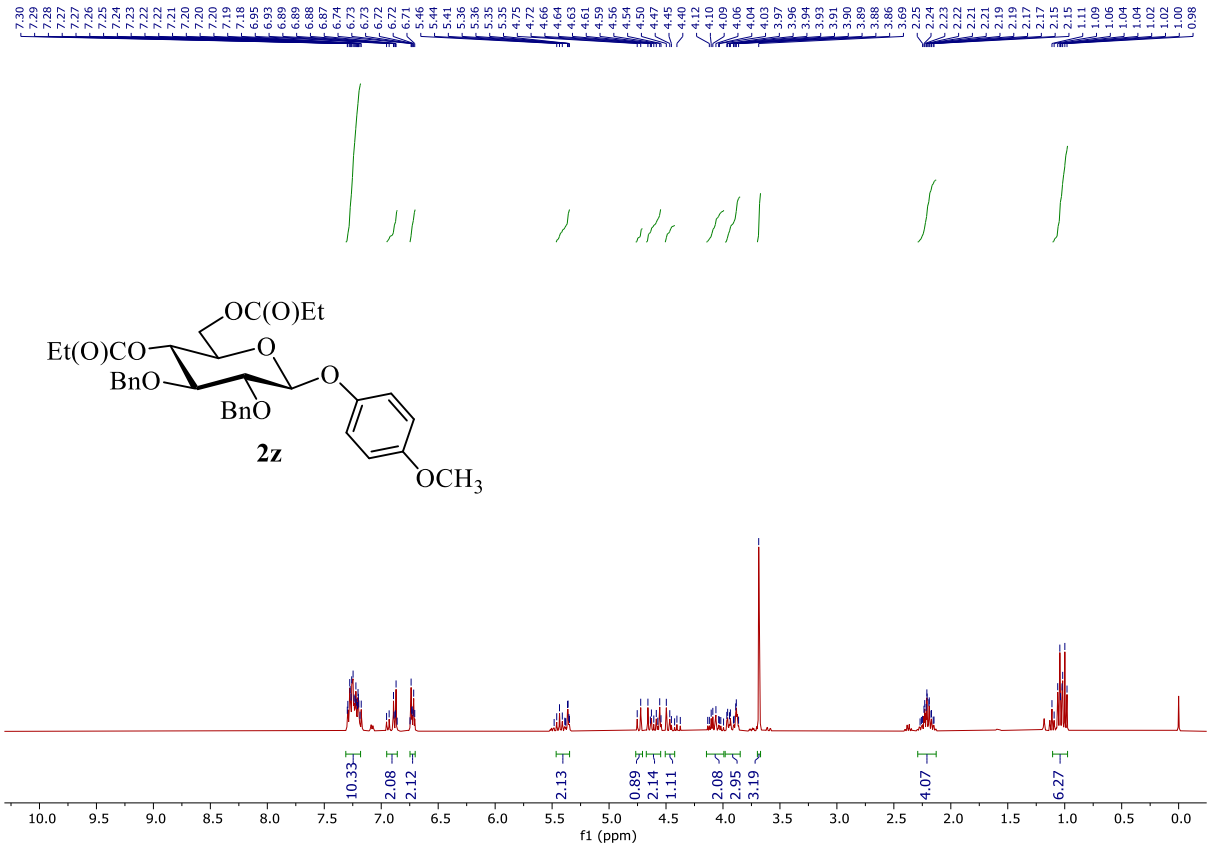
^{13}C NMR of Compound **2x (101 MHz, $CDCl_3$)**



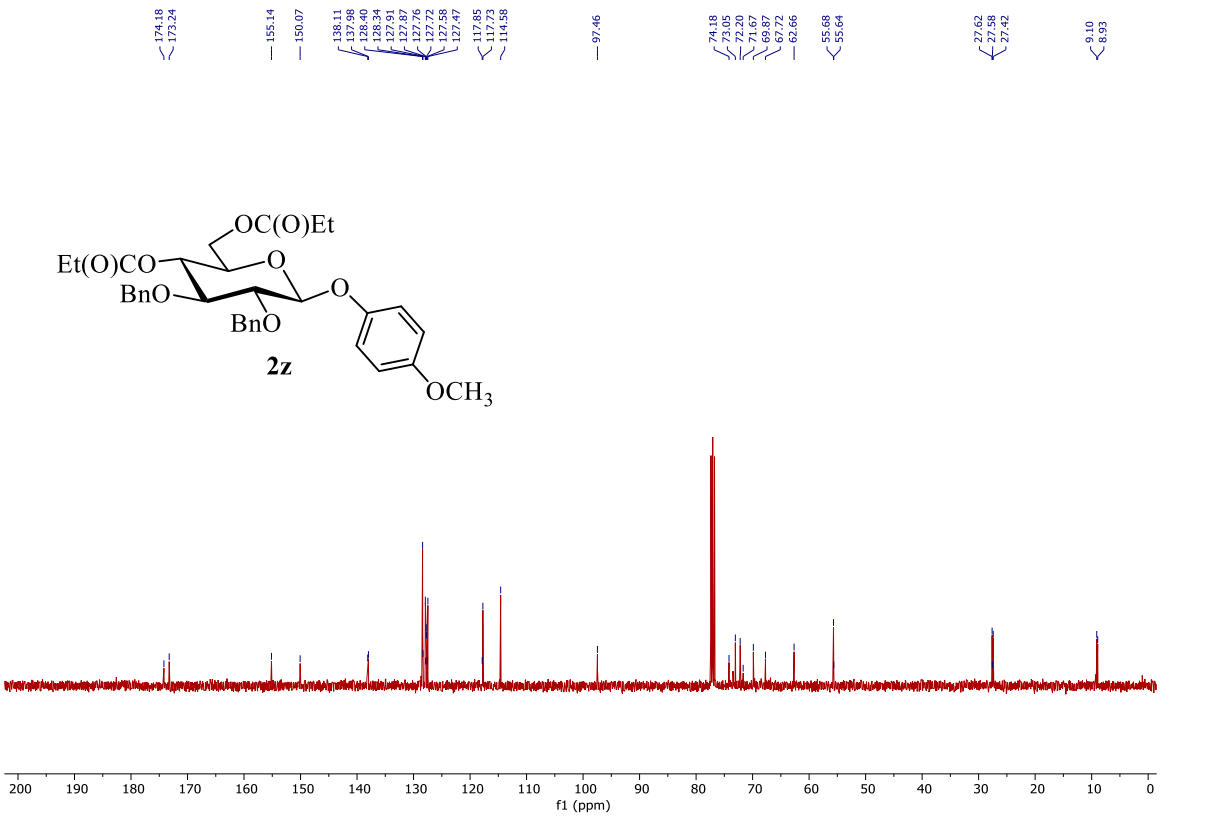
^{1}H NMR of Compound **2y (400 MHz, $CDCl_3$)**



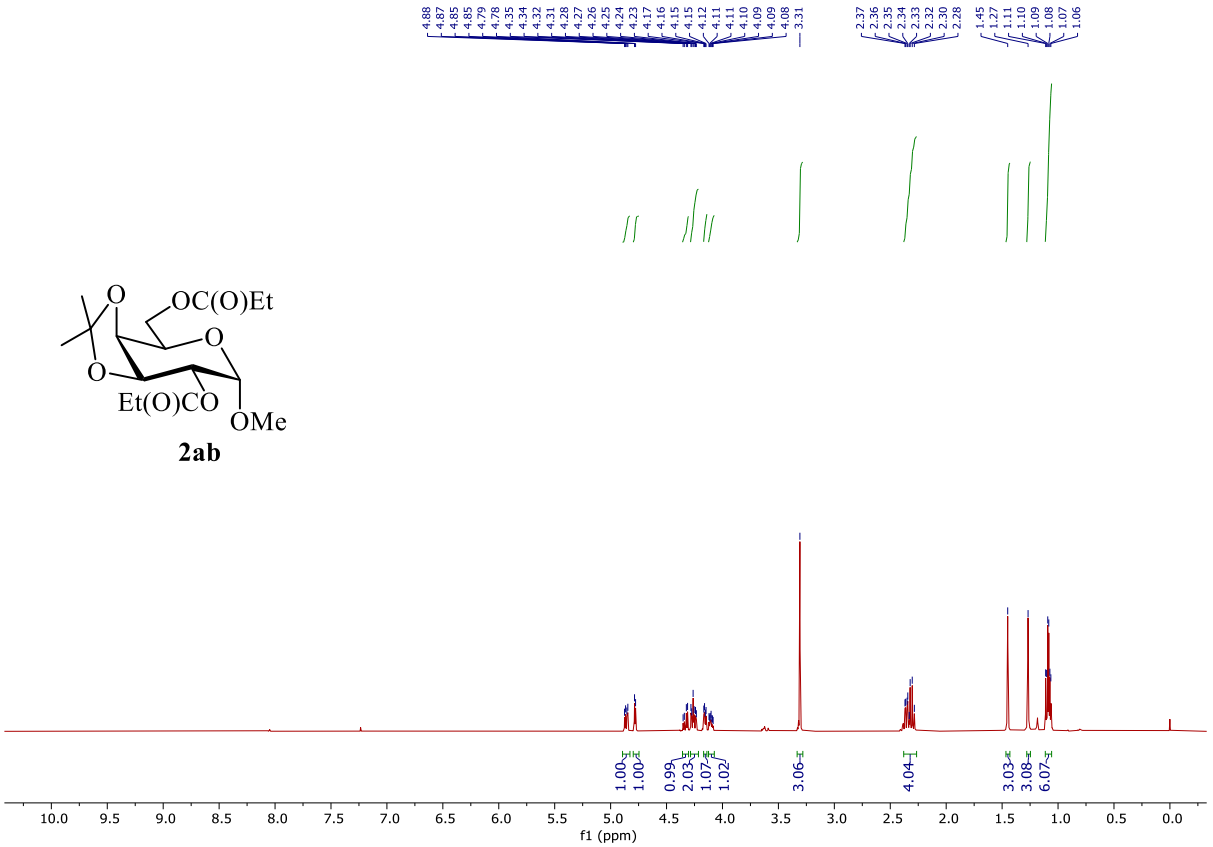
^{13}C NMR of Compound **2y (101 MHz, $CDCl_3$)**



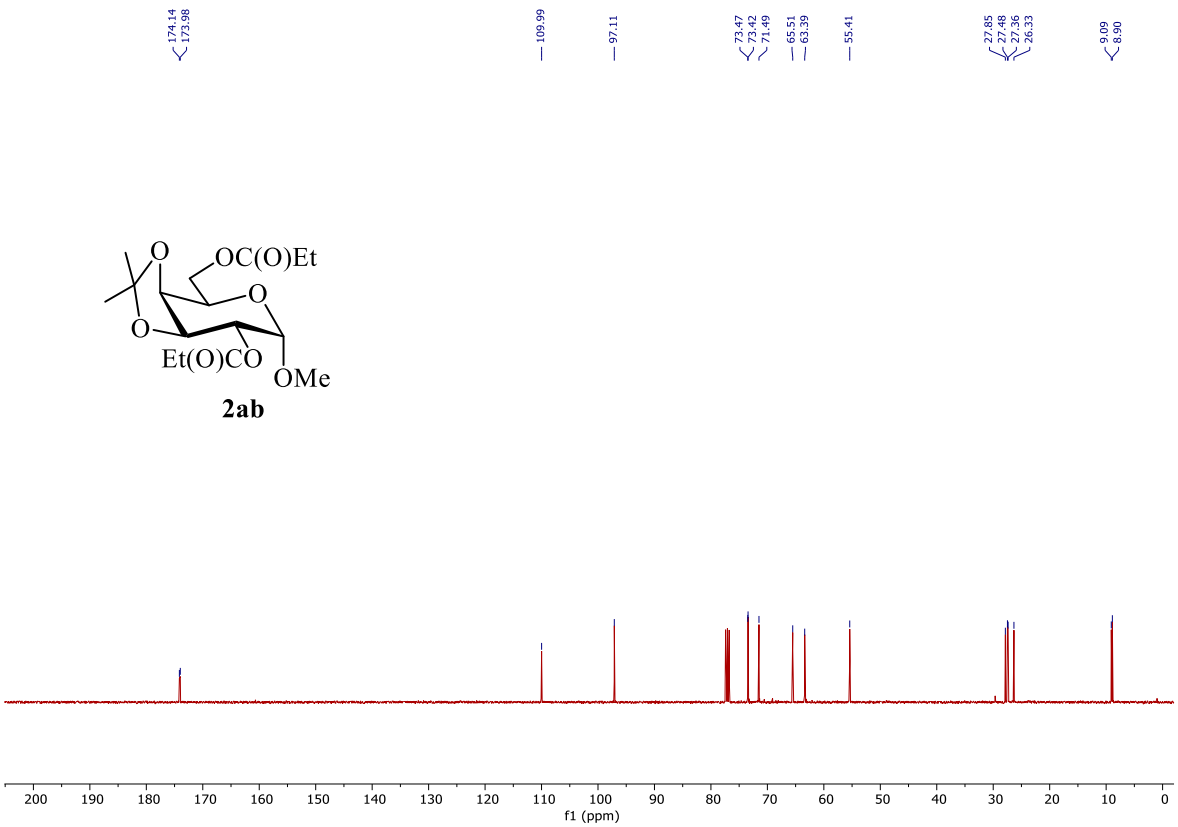
^{1}H NMR of Compound **2z (400 MHz, $CDCl_3$)**



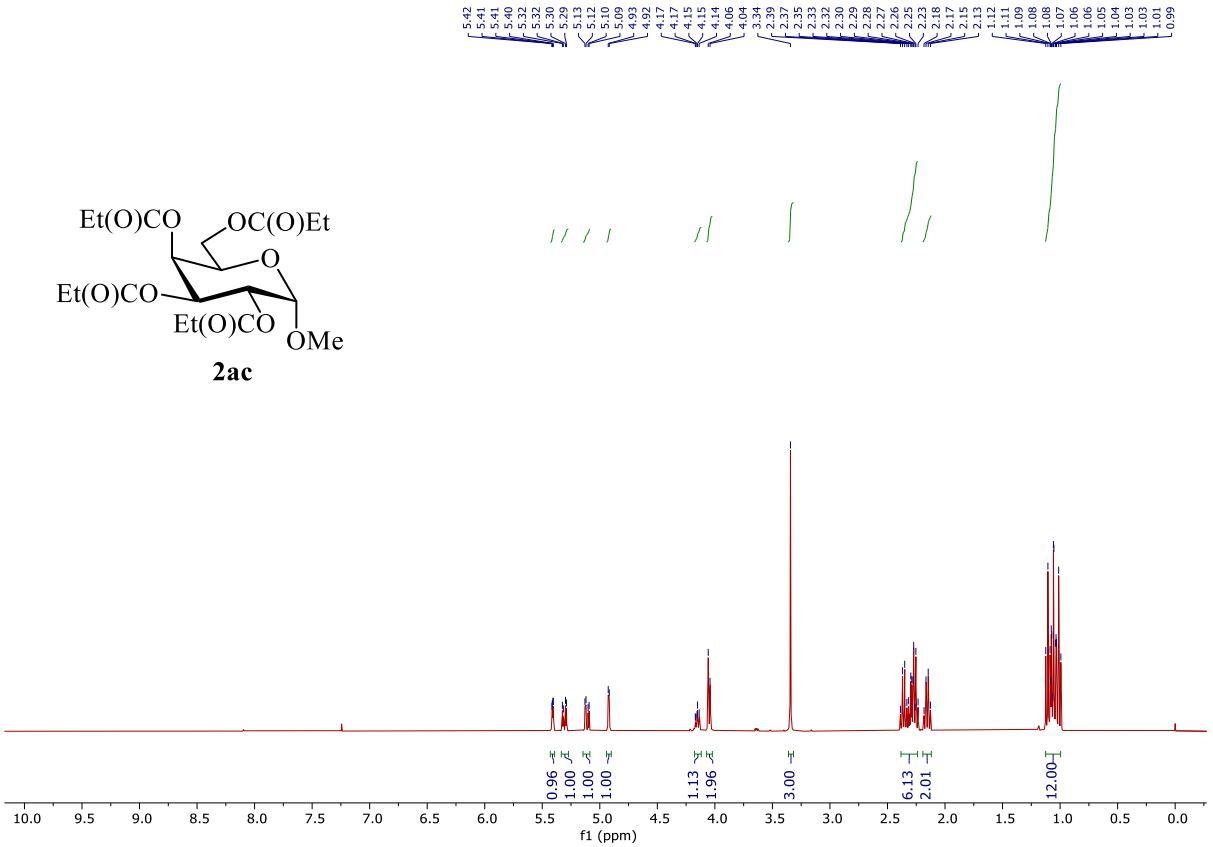
^{13}C NMR of Compound **2z (101 MHz, $CDCl_3$)**



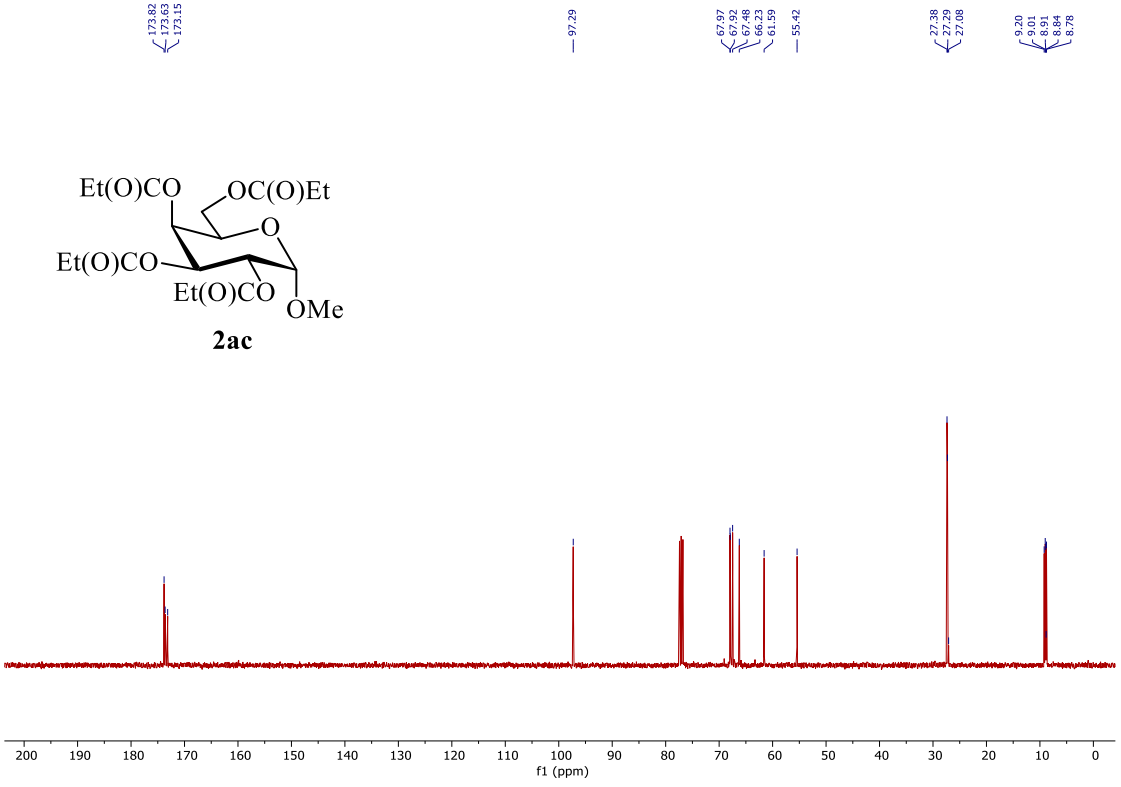
^{1}H NMR of Compound **2ab (400 MHz, $CDCl_3$)**



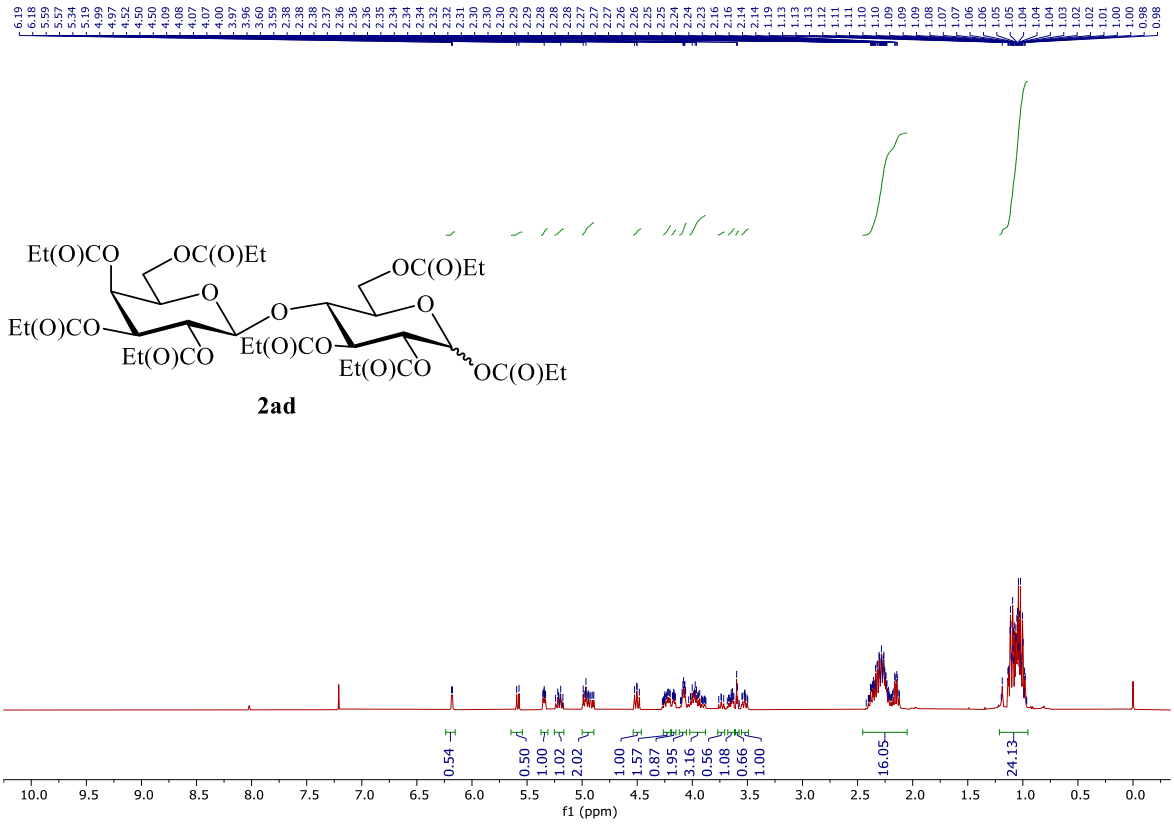
^{13}C NMR of compound **2ab (101 MHz, $CDCl_3$)**



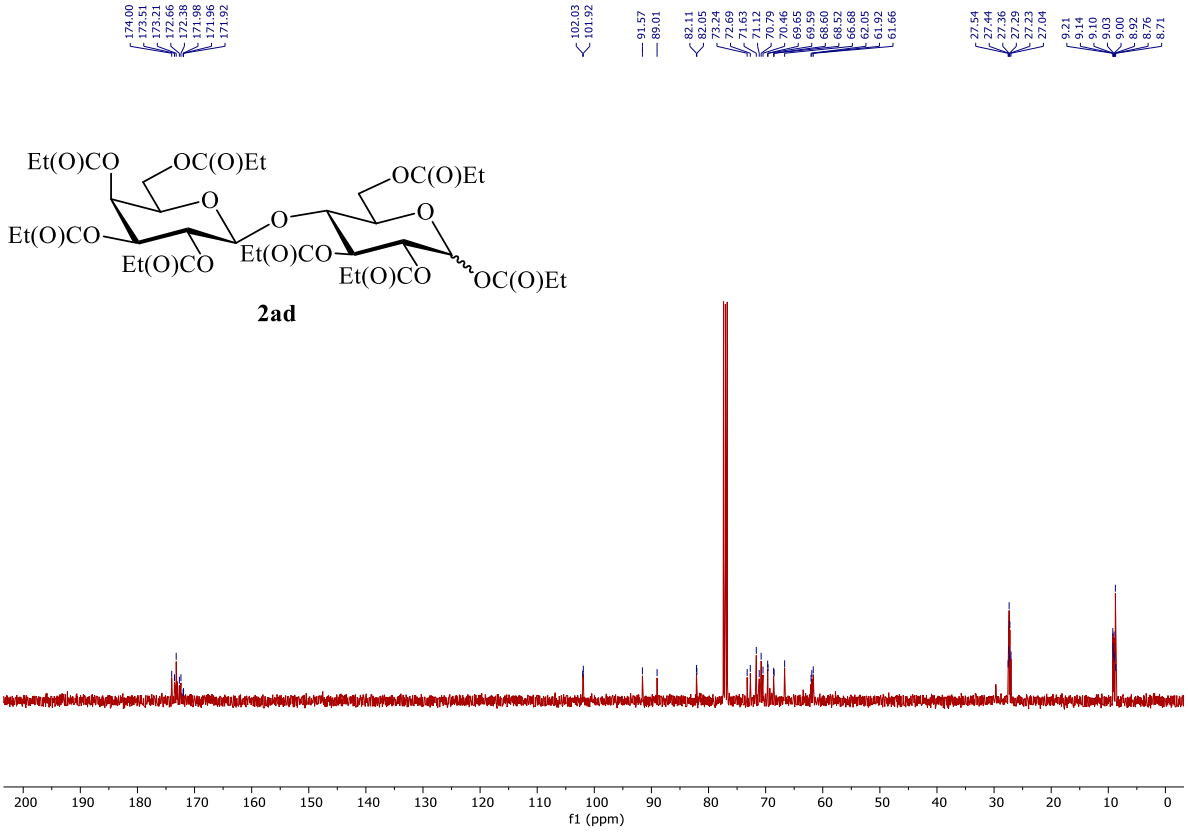
^{1}H NMR of Compound **2ac (400 MHz, $CDCl_3$)**



^{13}C NMR of Compound **2ac (101 MHz, $CDCl_3$)**



^{1}H NMR of Compound **2ad (400 MHz, $CDCl_3$)**



^{13}C NMR of Compound **2ad (101 MHz, $CDCl_3$)**