

Supporting Information

Regioselective One-Pot Benzoylation of Triol and Tetraol Arrays in Carbohydrates

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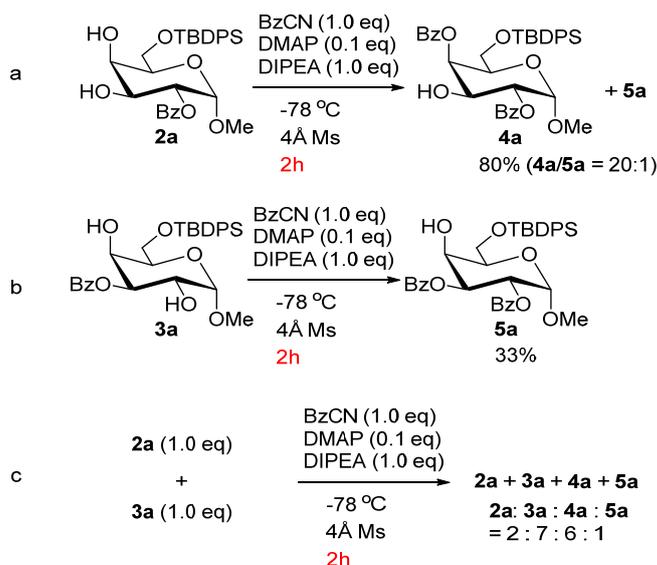
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Experimental Section

1. General Procedures

All reagents and solvents were dried prior to use according to standard methods. Commercial reagents were used without further purification, unless otherwise stated. ^1H NMR spectra were recorded on an Advance DRX Bruker-400 MHz spectrometer at 25°C. High-resolution mass spectrometry was performed on a Bruker APEX IV. All reactions were performed in flame-dried modified Schlenk (Kjeldahl shape) flasks fitted with a glass stopper or rubber septa under a positive pressure of argon. Analytical TLC was performed on silica gel 60-F254 precoated on aluminum plates (E. Merck), with detection by fluorescence and/or by staining with acidic ceric ammonium molybdate. Column chromatography was performed employing Silica Gel 230-400 mesh.

2. Competitive reactions for the investigation of the benzylation rate.

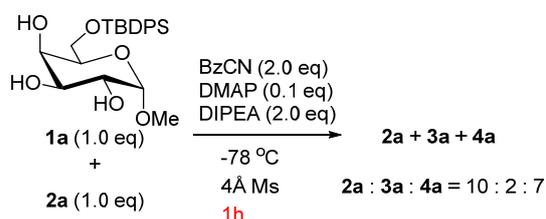


(a) **2a** (1.0 eq) and BzCN (1.0 eq) reacted at -78 °C with DMAP (0.1 eq) and DIPEA (1.0 eq) as base. After 2 h, the reaction was quenched with 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford mono benzylation product in 80% yield (4a : 5a = 20 : 1, analyzed by NMR) with 15% **2a** recovered.

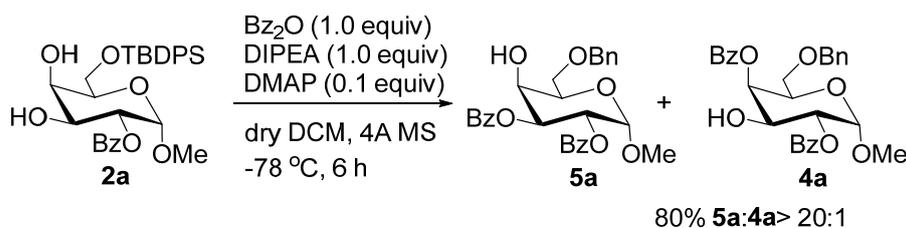
(b) **3a** (1.0 eq) and BzCN (1.0 eq) reacted at -78 °C with DMAP (0.1 eq) and DIPEA (1.0 eq) as base. After 2 h, the reaction was quenched with 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through

a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford mono benzylation product **5a** in 33% yield with 60% **3a** recovered and no **4a** was detected.

(c) **2a** (1.0 eq), **3a** (1.0 eq) and BzCN (1.0 eq) reacted at -78 °C with DMAP (0.1 eq) and DIPEA (1.0 eq) as base. After 2 h, the reaction was quenched with 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was analyzed by proton NMR directly. **2a** : **3a** : **4a** : **5a** = 2 : 7 : 6 : 1



1a (1.0 eq), **2a** (1.0 eq) and BzCN (2.0 eq) reacted at -78 °C with DMAP (0.1 eq) and DIPEA (2.0 eq) as base. After 1 h, the reaction was quenched with 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was analyzed by proton NMR directly. **2a** : **3a** : **4a** = 10 : 2 : 7. However, **1a** and **5a** was rarely found in the mixture.



1a (1.0 eq) and Bz₂O (1.0 eq) reacted at -78 °C with DMAP (0.1 eq) and DIPEA (1.0 eq) as base. After 6 h, the reaction was quenched with 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 5 : 1) on silica gel to afford compound monobenylation product in 80% yield (**5a** : **4a** >20:1, NMR analysis).

3. Procedures for DMAP catalyzed cyanide-mediated regioselective benzylation of Triols and Tetraols:



Methyl 6-*O*-*tert*-butyl-diphenylsilyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**4a**)

To a solution of compound **1a** (30 mg, 69.4 μ mol) and 4 Å molecular sieves in 4 mL mixture of CHCl₃ and DCM (V:V = 3:1) was added benzoyl cyanide (19.1 mg, 145.8 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to -78 °C, DIPEA (25 μ L, 145 μ mol) and 4-dimethylaminopyridine (DMAP) (1 mg, 7.1 μ mol) was added. The reaction was further stirred for 10 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 5 : 1) on silica gel to afford compound **4a**¹ (33.6 mg, 76%) as foam.

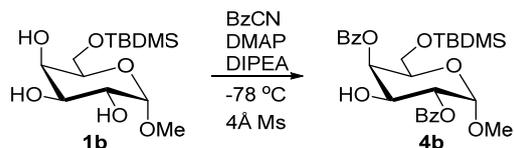
1 mmol scale experiment:

To a solution of compound **1a** (432 mg, 1 mmol) and 4 Å molecular sieves was added the 88 mL mixture of CHCl₃ and DCM (V:V = 3:1). After cooling down the reaction mixture to -78 °C, benzoyl cyanide (268 mg, 2.05 mmol) was added under nitrogen atmosphere. After stirring 10 min at this temperature, DIPEA (350 μ L, 2.0 mmol) and 4-dimethylaminopyridine (DMAP) (12 mg, 0.1 mmol) was added. The reaction was further stirred for 12 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction mixture was poured into 50 mL 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite to remove the molecular sieves. The organic layer was washed with 1N HCl (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 8 : 1) on silica gel to afford compound **4a** (459 mg, 72%) as white foam.

1 mmol scale experiment with the investigation of addition rate:

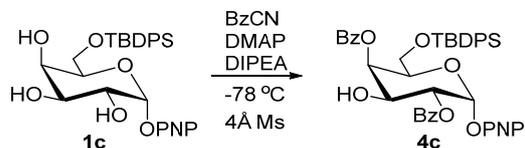
To a solution of compound **1a** (432 mg, 1 mmol) and 4 Å molecular sieves was added the 88 mL mixture of CHCl₃ and DCM (V:V = 3:1). After cooling down the reaction mixture to -78 °C, DIPEA (350 μ L, 2.0 mmol) and 4-dimethylaminopyridine (DMAP) (12 mg, 0.1 mmol) was added. Then benzoyl cyanide (268 mg, 2.05 mmol) solved in 10 mL DCM was added dropwise to the reaction over 30 min. The reaction was further stirred for 12 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction mixture was poured into 50 mL 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite to remove the molecular sieves. The organic layer was washed with 1N HCl (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified

by column chromatography (hexane/ethyl acetate = 8 : 1) on silica gel to afford compound **4a** (440 mg, 69%) as white foam.



Methyl 6-*O*-*tert*-butyl-dimethylsilyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**4b**)

To a solution of compound **1b** (30 mg, 97.4 μ mol) and 4 Å molecular sieves in 4 mL mixture of CHCl₃ and DCM (V:V = 3:1) was added benzoyl cyanide (26.2 mg, 199.6 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to -78 °C, DIPEA (35 μ L, 199.6 μ mol) and 4-dimethylaminopyridine (DMAP) (1.2 mg, 10.0 μ mol) was added. The reaction was further stirred for 10 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 4 : 1) on silica gel to afford compound **4b** (36.3 mg, 72%) as foam. ¹H NMR (400 MHz, CDCl₃) δ = 8.16 – 8.06 (m, 4H, ArH), 7.64 – 7.53 (m, 2H, ArH), 7.46 (m, 4H, ArH), 5.73 (d, *J* = 3.4 Hz, 1H, 4-H), 5.32 (dd, *J* = 10.3, 3.7 Hz, 1H, 2-H), 5.16 (d, *J* = 3.6 Hz, 1H, 1-H), 4.50 (m, 1H, 3-H), 4.13 (t, *J* = 6.6 Hz, 1H, 5-H), 3.80 – 3.67 (m, 2H, 6-H, 6'-H), 3.44 (s, 3H, OMe), 2.41 (d, *J* = 5.0 Hz, 1H, OH), 0.85 (s, 9H, *tert*-Butyl), -0.00 (s, 3H, SiMe), -0.04 (s, 3H SiMe). ¹³C NMR (100 MHz, CDCl₃) δ = 166.71, 166.65, 133.36, 133.32, 129.92, 129.89, 129.55, 129.48, 128.51, 128.39, 97.50, 72.41, 71.44, 69.65, 67.66, 61.54, 55.50, 25.74, 18.13, -5.58, -5.62. HRMS (ESI) Calcd for C₂₇H₃₇O₈Si [M+H]⁺: 517.2252, found: 517.2252; Calcd for 27₃H₃₆NaO₈Si[M+Na]⁺: 539.2070, found: 539.2072.

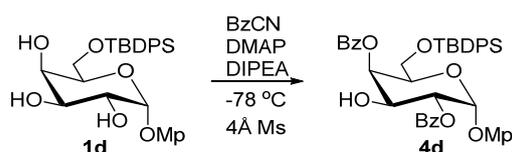


4-Nitrophenyl

6-*O*-*tert*-butyl-diphenylsilyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**4c**)

To a solution of compound **1c** (30 mg, 55.6 μ mol) and 4 Å molecular sieves in 4 mL mixture of CHCl₃ and DCM (V:V = 3:1) was added benzoyl cyanide (15.0 mg, 114.5 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to -78 °C, DIPEA (20 μ L, 114.8 μ mol) and 4-dimethylaminopyridine (DMAP) (1 mg, 7.1 μ mol) was added. The reaction was further stirred for 10 h at this

temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 5 : 1) on silica gel to afford compound **4c** (29.0 mg, 70%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.18 – 8.10 (m, 2H, ArH), 8.09 – 8.03 (m, 4H, ArH), 7.65 – 7.23 (m, 16H, ArH), 7.20 – 7.11 (m, 4H, ArH), 6.00 (d, *J* = 3.6 Hz, 1H, 1-H), 5.86 (d, *J* = 3.4 Hz, 1H, 4-H), 5.48 (dd, *J* = 10.4, 3.6 Hz, 1H, 2-H), 4.78 – 4.63 (m, 1H, 3-H), 4.20 (t, *J* = 6.6 Hz, 1H, 5-H), 3.77 (qd, *J* = 10.4, 6.6 Hz, 2H, 6-H, 6'-H), 2.68 (d, *J* = 4.5 Hz, 1H, OH), 0.94 (s, 9H, *tert*-Butyl). ¹³C NMR (100 MHz, CDCl₃) δ = 166.56, 166.48, 161.39, 142.85, 135.37, 135.34, 133.61, 133.54, 132.72, 132.51, 129.97, 129.81, 129.76, 129.16, 129.04, 128.57, 128.50, 127.67, 127.60, 125.83, 116.74, 95.53, 71.38, 71.01, 70.85, 67.49, 61.77, 26.60, 18.99. HRMS (ESI) Calcd for C₄₂H₄₃NO₁₀Si [M+H]⁺: 748.2581, found: 748.2572; Calcd for C₄₂H₄₂NNaO₁₀Si [M+Na]⁺: 770.2393, found: 770.2392.

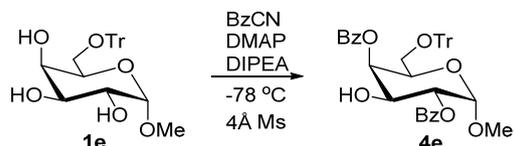


4-Methoxyphenyl

6-*O*-*tert*-butyl-diphenylsilyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (4d)

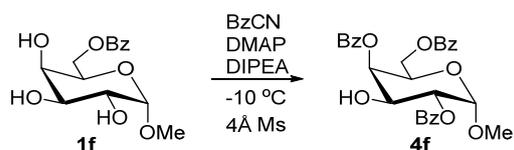
To a solution of compound **1d** (30 mg, 57.3 μ mol) and 4 Å molecular sieves in 4 mL mixture of CHCl₃ and DCM (V:V = 3:1) was added benzoyl cyanide (15.0 mg, 114.5 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to -78 °C, DIPEA (20 μ L, 114.8 μ mol) and 4-dimethylaminopyridine (DMAP) (1 mg, 7.1 μ mol) was added. The reaction was further stirred for 10 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 5 : 1) on silica gel to afford compound **4d** (29.2 mg, 70%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.14 – 8.05 (m, 4H, ArH), 7.64 – 7.52 (m, 4H, ArH), 7.53 – 7.27 (m, 10H, ArH), 7.16 (t, *J* = 7.5 Hz, 2H, ArH), 7.03 – 6.94 (m, 2H, ArH), 6.79 – 6.72 (m, 2H, ArH), 5.88 (dd, *J* = 3.4, 1.3 Hz, 1H, 4-H), 5.72 (d, *J* = 3.7 Hz, 1H, 1-H), 5.43 (dd, *J* = 10.4, 3.7 Hz, 1H, 2-H), 4.72 (dt, *J* = 10.4, 4.0 Hz, 1H, 3-H), 4.46 – 4.38 (m, 1H, 5-H), 3.84 – 3.75 (m, 2H, 6-H, 6'-H), 3.73 (s, 3H, PhOMe), 2.57 (d, *J* =

4.7 Hz, 1H, *OH*), 0.99 (s, 9H, *tert*-Butyl). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.64, 155.39, 151.00, 135.48, 135.42, 133.38, 133.36, 132.92, 132.74, 129.99, 129.85, 129.69, 129.64, 129.44, 129.41, 128.50, 128.44, 127.69, 127.59, 118.72, 114.63, 97.00, 71.98, 71.28, 70.17, 67.71, 61.91, 55.61, 26.66, 19.04. HRMS (ESI) Calcd for $\text{C}_{43}\text{H}_{45}\text{O}_9\text{Si}$ $[\text{M}+\text{H}]^+$: 733.2834, found: 733.2827; Calcd for $\text{C}_{43}\text{H}_{44}\text{NaO}_9\text{Si}$ $[\text{M}+\text{Na}]^+$: 755.2646, found: 755.2647.



Methyl 6-*O*-triphenylmethyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**4e**)

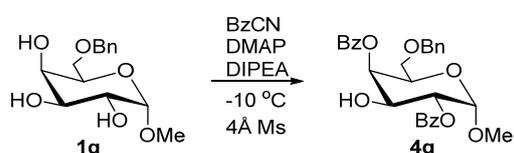
To a solution of compound **1e** (30 mg, 68.8 μmol) and 4 Å molecular sieves in 4 mL mixture of CHCl_3 and DCM (V:V = 3:1) was added benzoyl cyanide (19.0 mg, 144.5 μmol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-78\text{ }^\circ\text{C}$, DIPEA (25 μL , 145 μmol) and 4-dimethylaminopyridine (DMAP) (1 mg, 7.1 μmol) was added. The reaction was further stirred for 10 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 5 : 1) on silica gel to afford compound **4e** (31.7 mg, 72%) as foam. ^1H NMR (400 MHz, CDCl_3) δ = 8.10 – 8.02 (m, 2H, *ArH*), 8.00 – 7.90 (m, 2H, *ArH*), 7.57 (td, J = 7.3, 1.9 Hz, 2H, *ArH*), 7.49 – 7.34 (m, 11H, *ArH*), 7.23 – 7.09 (m, 9H, *ArH*), 5.79 (d, J = 3.4 Hz, 1H, 4-H), 5.25 (dd, J = 10.4, 3.7 Hz, 1H, 2-H), 5.12 (d, J = 3.7 Hz, 1H, 1-H), 4.57 – 4.40 (m, 1H, 3-H), 4.12 (t, J = 6.7 Hz, 1H, 5-H), 3.41 (s, 3H, *OMe*), 3.39 (dd, J = 9.6, 6.4 Hz, 1H, 6-H), 3.23 (dd, J = 9.4, 7.2 Hz, 1H, 6'-H), 2.36 (d, J = 4.8 Hz, 1H, *OH*). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.65, 166.57, 143.51, 133.31, 133.21, 129.94, 129.88, 129.48, 129.34, 128.49, 128.38, 128.36, 127.76, 127.00, 97.44, 86.90, 72.28, 71.63, 67.93, 67.55, 61.71, 55.55. HRMS (ESI) Calcd for $\text{C}_{40}\text{H}_{37}\text{O}_8$ $[\text{M}+\text{H}]^+$: 645.2483 found: 645.2483; Calcd for $\text{C}_{40}\text{H}_{36}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$: 667.2305, found: 667.2302.



Methyl 2,4,6-tri-*O*-benzoyl- α -D-galactopyranoside (**4f**)

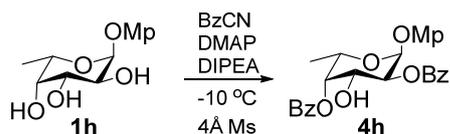
To a solution of compound **1f** (30 mg, 100.6 μmol) and 4 Å molecular sieves in 30

mL of dry CHCl_3 was added benzoyl cyanide (27.0 mg, 206.1 μmol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-10\text{ }^\circ\text{C}$, DIPEA (36 μL , 206 μmol) and 4-dimethylaminopyridine (DMAP) (2.2 mg, 18.0 μmol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound **4f**² (37.3 mg, 73%) as semisolid.



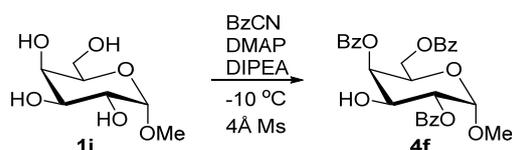
Methyl 6-*O*-benzyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**4g**)

To a solution of compound **1g** (30 mg, 105.6 μmol) and 4 Å molecular sieves in 30 mL of dry CHCl_3 was added benzoyl cyanide (29.1 mg, 222.1 μmol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-10\text{ }^\circ\text{C}$, DIPEA (38 μL , 222 μmol) and 4-dimethylaminopyridine (DMAP) (2.4 mg, 19.6 μmol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound **4g** (36.7 mg, 71%) as semisolid. ^1H NMR (400 MHz, CDCl_3) δ = 8.14 – 8.05 (m, 4H, ArH), 7.60 – 7.54 (m, 2H, ArH), 7.48 – 7.41 (m, 4H, ArH), 7.31 – 7.17 (m, 5H, ArH), 5.74 (d, J = 3.5 Hz, 1H, 4-H), 5.34 (dd, J = 10.3, 3.7 Hz, 1H, 2-H), 5.17 (d, J = 3.7 Hz, 1H, 1-H), 4.53 (d, J = 11.8 Hz, 1H, PhCH_2), 4.51 – 4.46 (m, 1H, 3-H), 4.44 (d, J = 11.7 Hz, 1H, PhCH_2), 4.27 (t, J = 6.2 Hz, 1H, 5-H), 3.62 (d, J = 6.2 Hz, 2H, 6-H, 6'-H), 3.44 (s, 3H, OMe), 2.47 (d, J = 5.4 Hz, 1H, OH). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.71, 166.53, 137.64, 133.37, 133.32, 129.95, 129.86, 129.48, 129.34, 128.49, 128.37, 128.30, 127.63, 97.53, 73.58, 72.28, 71.82, 68.63, 68.10, 67.41, 55.57. HRMS (ESI) Calcd for $\text{C}_{28}\text{H}_{29}\text{O}_8$ $[\text{M}+\text{H}]^+$: 493.1849, found: 493.1857; Calcd for $\text{C}_{28}\text{H}_{28}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$: 515.1662, found: 515.1676.



4-Methoxyphenyl 2,4-di-*O*-benzoyl- α -L-fucopyranoside (**4h**)

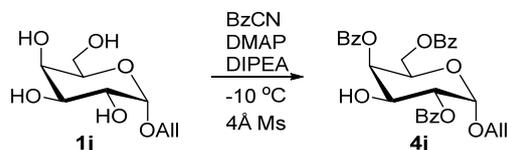
To a solution of compound **1h** (30 mg, 111.1 μ mol) and 4 Å molecular sieves in 30 mL of dry CHCl_3 was added benzoyl cyanide (29.4 mg, 228.0 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-10\text{ }^\circ\text{C}$, DIPEA (40 μ L, 228 μ mol) and 4-dimethylaminopyridine (DMAP) (2.7 mg, 22.0 μ mol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl(aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (DCM/ethyl acetate = 20 : 1) on silica gel to afford compound **4h** (40.1 mg, 75%) as semisolid. ^1H NMR (400 MHz, CDCl_3) δ = 8.17 (dd, J = 8.0, 1.4 Hz, 2H, ArH), 8.08 (d, J = 8.1, 1.4 Hz, 2H, ArH), 7.65 – 7.55 (m, 2H, ArH), 7.47 (m, 4H, ArH), 7.06 – 6.98 (m, 2H, ArH), 6.84 – 6.75 (m, 2H, ArH), 5.74 (d, J = 3.7 Hz, 1H, 1-H), 5.64 (d, J = 3.5 Hz, 1H, 4-H), 5.49 (dd, J = 10.4, 3.7 Hz, 1H, 2-H), 4.76 – 4.64 (m, 1H, 3-H), 4.44 (q, J = 6.6 Hz, 1H, 5-H), 3.76 (s, 3H, OMe), 2.49 (d, J = 6.1 Hz, 1H, OH), 1.24 (d, J = 6.7 Hz, 3H, CH_3). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.78, 166.69, 155.25, 150.99, 133.45, 133.42, 129.97, 129.85, 129.40, 129.34, 128.57, 128.44, 118.15, 114.67, 96.66, 74.17, 71.84, 67.55, 66.00, 55.64, 16.30. Calcd for $\text{C}_{27}\text{H}_{27}\text{O}_8$ $[\text{M}+\text{H}]^+$: 479.1700, found: 479.1706; Calcd for $\text{C}_{27}\text{H}_{26}\text{NaO}_8$ $[\text{M}+\text{Na}]^+$: 501.1520, found: 501.1524.



Methyl 2,4,6-tri-*O*-benzoyl- α -D-galactopyranoside (**4f**)

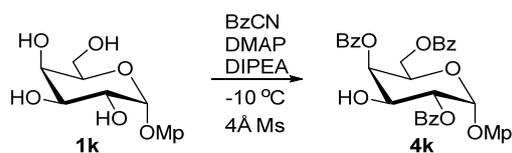
To a solution of compound **1i** (30 mg, 154.6 μ mol) and 4 Å molecular sieves in 30 mL of dry CHCl_3 was added benzoyl cyanide (62.7 mg, 479.3 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-10\text{ }^\circ\text{C}$, DIPEA (90 μ L, 510 μ mol) and 4-dimethylaminopyridine (DMAP) (3.0 mg, 24.4 μ mol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl(aq). Then the mixture was diluted with 100 mL of

DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound **4f**² (48.3 mg, 62%) as semisolid.



Allyl 2,4,6,-tri-*O*-benzoyl- α -D-galactopyranoside (**4j**)

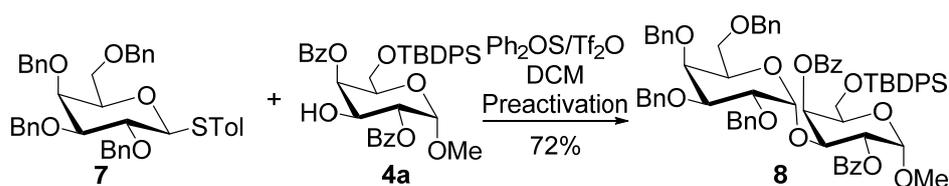
To a solution of compound **1j** (20 mg, 90.9 μ mol) and 4 Å molecular sieves in 30 mL of dry CHCl₃ was added benzoyl cyanide (36.9 mg, 281.8 μ mol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to -10 °C, DIPEA (55 μ L, 315.7 μ mol) and 4-dimethylaminopyridine (DMAP) (3.0 mg, 24.4 μ mol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl(aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and Na₂S₂O₃ (aq), dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound **4j** (32.3 mg, 62%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.16 – 8.11 (m, 2H, ArH), 8.10 – 8.06 (m, 2H, ArH), 8.04 – 8.00 (m, 2H, ArH), 7.64 – 7.53 (m, 3H, ArH), 7.51 – 7.40 (m, 6H, ArH), 5.93 – 5.78 (m, 1H, -CH₂-CH=CH₂), 5.84 (d, *J* = 4.0 Hz, 1H, 4-H), 5.42 (dd, *J* = 10.3, 3.7 Hz, 1H, 2-H), 5.35 (d, *J* = 3.7 Hz, 1H, 1-H), 5.32 – 5.21 (m, 1H, -CH₂-CH=CH₂), 5.14 (dd, *J* = 10.4, 1.6 Hz, 1H, -CH₂-CH=CH₂), 4.64 – 4.46 (m, 3H, H-3, H-5, H-6), 4.41 (dd, *J* = 9.5, 3.8 Hz, 1H, H-6'), 4.23 (ddd, *J* = 13.1, 5.2, 1.5 Hz, 1H, -CH₂-CH=CH₂), 4.07 (ddd, *J* = 13.2, 6.0, 1.4 Hz, 1H, -CH₂-CH=CH₂), 2.44 (d, *J* = 5.7 Hz, 1H, OH). ¹³C NMR (100 MHz, CDCl₃) δ = 166.74, 166.37, 166.03, 133.54, 133.41, 133.36, 133.17, 130.01, 129.85, 129.79, 129.66, 129.59, 129.43, 129.14, 128.58, 128.44, 128.39, 117.78, 95.80, 72.03, 71.48, 68.87, 67.43, 67.33, 62.91. HRMS (ESI) Calcd for C₃₀H₂₉O₉ [M+H]⁺: 533.1806, found: 533.1802; Calcd for C₃₀H₂₈NaO₉ [M+Na]⁺: 555.1626, found: 555.1622.



4-Methoxyphenyl 2,4,6,-tri-*O*-benzoyl- α -D-galactopyranoside (**4k**)

To a solution of compound **1k** (30 mg, 104.8 μmol) and 4 Å molecular sieves in 30 mL of dry CHCl_3 was added benzoyl cyanide (42.6 mg, 325.1 μmol) at room temperature under nitrogen atmosphere. After cooling down the reaction mixture to $-10\text{ }^\circ\text{C}$, DIPEA (60 μL , 346 μmol) and 4-dimethylaminopyridine (DMAP) (3.0 mg, 24.4 μmol) was added. The reaction was allowed to raise the temperature to room temperature over 8 h. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of 1N HCl (aq). Then the mixture was diluted with 100 mL of DCM and the precipitate was filtered off through a pad of Celite. The organic layer was washed with 1N HCl (aq) and $\text{Na}_2\text{S}_2\text{O}_3$ (aq), dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound **4k** (38.3 mg, 61%) as semisolid. ^1H NMR (400 MHz, CDCl_3) δ = 8.19 – 8.13 (m, 2H, ArH), 8.11 – 8.06 (m, 2H, ArH), 7.96 – 7.87 (m, 2H, ArH), 7.68 – 7.36 (m, 9H, ArH), 7.07 – 6.97 (m, 2H, ArH), 6.76 – 6.66 (m, 2H, ArH), 5.88 (dd, J = 3.6, 1.2 Hz, 1H, 4-H), 5.82 (d, J = 3.7 Hz, 1H, 1-H), 5.54 (dd, J = 10.4, 3.7 Hz, 1H, 2-H), 4.74 (ddd, J = 9.9, 5.8, 3.5 Hz, 1H, 3-H), 4.70 – 4.64 (m, 1H, 5-H), 4.52 (dd, J = 11.6, 7.9 Hz, 1H, 6-H), 4.44 (dd, J = 11.5, 4.5 Hz, 1H, 6'-H), 3.70 (s, 3H, PhOMe), 2.61 (d, J = 5.8 Hz, 1H, OH). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.71, 166.37, 165.98, 155.38, 150.47, 133.65, 133.52, 133.11, 130.03, 129.87, 129.73, 129.49, 129.25, 129.00, 128.62, 128.48, 128.28, 118.51, 114.55, 96.50, 71.72, 71.38, 68.05, 67.46, 63.11, 55.52. HRMS (ESI) Calcd for $\text{C}_{34}\text{H}_{31}\text{O}_{10}$ $[\text{M}+\text{H}]^+$: 599.1912, found : 599.1912; Calcd for $\text{C}_{34}\text{H}_{30}\text{NaO}_{10}$ $[\text{M}+\text{Na}]^+$: 621.1713, found: 621.1713.

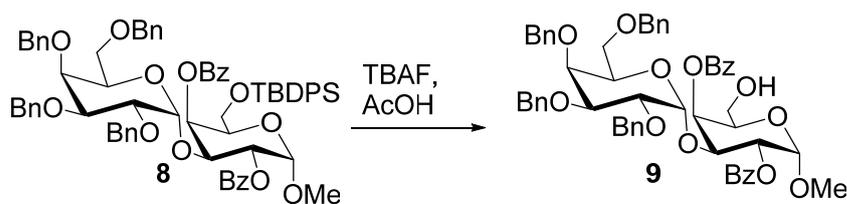
3. Branched and liner oligosaccharide synthesis



Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl)-6-*O*-benzyl-*tert*-butyl-diphenylsilyl-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**8**)

A mixture of thioglycoside donor **7** (101 mg, 156.0 μmol), Ph_2SO (34.6 mg, 171.2 μmol) and activated 4 Å molecular sieves in dry dichloromethane (5 mL) was stirred at room temperature under a nitrogen atmosphere for 10 min. Then the mixture was cooled to $-78\text{ }^\circ\text{C}$ and Tf_2O (26 μL , 160.0 μmol , 1.2 eq) was added. After the donor was completely consumed (detected by TLC analysis), acceptor **4a** (90 mg, 140.6 μmol) was added. The reaction was further stirred for 5h at this temperature. After the

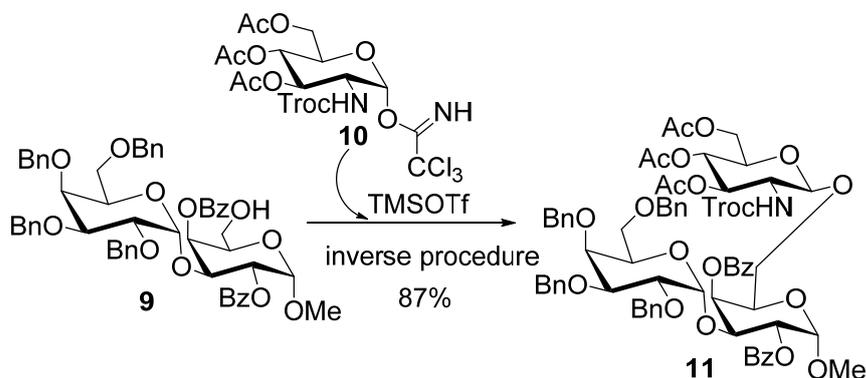
TLC analysis showed the reaction was complete, the reaction was quenched by addition of NaHCO₃ (aq.) and diluted with 50 mL DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO₃ (aq.) and brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford the α disaccharide **8** (117.8 mg, 72%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.06 – 7.97 (m, 4H, ArH), 7.68 – 7.62 (m, 2H, ArH), 7.56 – 7.45 (m, 4H, ArH), 7.41 – 7.04 (m, 33H, ArH), 5.97 (d, *J* = 3.2 Hz, 1H, 4a-H), 5.54 (dd, *J* = 10.6, 3.7 Hz, 1H, 2a-H), 5.44 (d, *J* = 3.3 Hz, 1H, 1b-H), 5.19 (d, *J* = 3.7 Hz, 1H, 1a-H), 4.80 (d, *J* = 11.3 Hz, 1H, PhCH₂), 4.62 – 4.57 (m, 2H, 3a-H, PhCH₂), 4.51 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.49 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.46 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.39 (d, *J* = 11.6 Hz, 1H, PhCH₂), 4.38 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.28 (d, *J* = 11.7 Hz, 1H, PhCH₂), 4.15 – 4.09 (m, 2H, 5a-H, 5b-H), 3.96 (dd, *J* = 10.1, 3.3 Hz, 1H, 2b-H), 3.76 – 3.68 (m, 2H, 6a-H, 6a'-H), 3.65 (dd, *J* = 10.1, 2.8 Hz, 1H, 3b-H), 3.59 (d, *J* = 2.8 Hz, 1H, 4b-H), 3.54 (dd, *J* = 9.4, 6.1 Hz, 1H, 6b-H), 3.45 (dd, *J* = 9.4, 6.8 Hz, 1H, 6b'-H), 3.35 (s, 3H, OMe), 1.01 (s, 9H, *tert*-Butyl). ¹³C NMR (100 MHz, CDCl₃) δ = 165.99, 165.55, 138.77, 138.59, 138.54, 138.29, 135.54, 135.44, 133.07, 132.91, 132.88, 129.98, 129.76, 129.73, 129.63, 129.59, 128.36, 128.30, 128.27, 128.17, 128.10, 128.07, 127.99, 127.93, 127.79, 127.71, 127.64, 127.59, 127.57, 127.50, 127.43, 127.26, 127.13, 127.00, 97.33, 94.06, 78.66, 75.64, 75.04, 74.63, 73.25, 73.00, 72.55, 70.89, 69.64, 69.51, 68.87, 67.24, 62.20, 55.32, 26.65, 19.05. HRMS (ESI) Calcd for C₇₁H₇₄SiNaO₁₃ [M+Na]⁺: 1185.4791, found: 1185.4784.



Methyl 3-*O*-(2, 3, 4, 6-tetra-*O*-benzyl- α -D-galactopyranosyl)-2,4-di-*O*-benzoyl- α -D-galactopyranoside (**9**)

To a solution of TBAF (7 mL, 1M in THF) was added the acetic acid to adjust the PH to 6. Then transfer the TBAF solution to a solution of compound **8** (117.8 mg, 101.4 μ mol) in 2 mL of THF via a plastic syringe. The reaction was further stirred for 3h at room temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of NH₄Cl(aq.) and diluted with 50 mL DCM. The organic layer was washed with NH₄Cl(aq.) and brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl

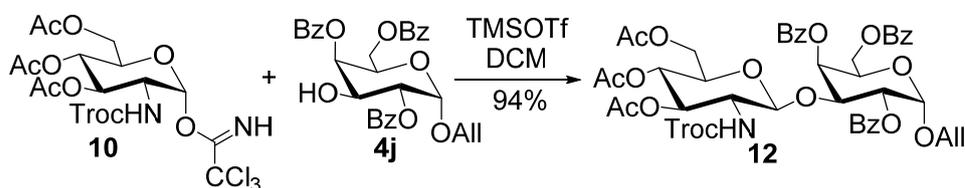
acetate = 1 : 1) on silica gel to afford the disaccharide **9** (80.0 mg, 85%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.13 (d, *J* = 7.7 Hz, 2H, Ar*H*), 8.09 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.57 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.51 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.45 (t, *J* = 7.7 Hz, 2H, Ar*H*), 7.37 – 7.10 (m, 22H, Ar*H*), 7.09 – 7.05 (m, 2H, Ar*H*), 5.73 (d, *J* = 3.3 Hz, 1H, 4a-H), 5.63 (dd, *J* = 10.5, 3.7 Hz, 1H, 2a-H), 5.15 (d, *J* = 3.7 Hz, 1H, 1a-H), 4.98 (d, *J* = 3.4 Hz, 1H, 1b-H), 4.76 (d, *J* = 11.2 Hz, 1H, PhCH₂), 4.47 (dd, *J* = 10.4, 3.3 Hz, 1H, 3a-H), 4.42 (s, 2H, PhCH₂ x 2), 4.36 (d, *J* = 11.3 Hz, 1H, PhCH₂), 4.31 – 4.20 (m, 3H, PhCH₂ x 3), 4.17 (d, *J* = 11.7 Hz, 1H, PhCH₂), 4.09 (t, *J* = 7.1 Hz, 1H, 5a-H), 3.98 (t, *J* = 6.8 Hz, 1H, 5b-H), 3.88 (dd, *J* = 9.9, 3.4 Hz, 1H, 2a-H), 3.72 – 3.51 (m, 4H, 6a-H, 4b-H, 3b-H, 6a'-H), 3.43 – 3.34 (m, 1H, 6b-H), 3.39 (s, 3H, OMe), 3.22 (dd, *J* = 8.9, 5.5 Hz, 1H, 6b'-H), 3.02 (t, *J* = 7.2 Hz, 1H, OH). ¹³C NMR (100 MHz, CDCl₃) δ = 167.79, 166.06, 138.62, 138.59, 138.24, 138.05, 133.48, 133.21, 130.21, 129.90, 129.58, 129.33, 128.51, 128.39, 128.23, 128.13, 128.10, 128.06, 128.04, 127.59, 127.52, 127.39, 127.35, 127.17, 97.46, 96.77, 79.08, 74.94, 74.69, 74.66, 73.16, 72.86, 72.67, 71.61, 70.46, 69.73, 69.18, 68.95, 68.32, 60.47, 55.52. HRMS (ESI) Calcd for C₅₅H₅₇O₁₃ [M+H]⁺: 925.3794, found: 925.3789; Calcd for C₅₅H₅₆NaO₁₃ [M+Na]⁺: 947.3613, found: 947.3611.



Methyl 3-O-(2, 3, 4, 6- tetra-O-benzyl-α-D-galactopyranosyl)-3-O-(3, 4, 6-tri-O-acetyl-2deoxy-2-N-Troc-β-D-glucopyranosyl)-2,4-di-O-benzoyl-α-D-galactopyranoside (11)

To a solution of disaccharide acceptor **9** (50.0 mg, 54.1 μmol) and 4 Å molecular sieves in 3 mL of dry DCM was added TMSOTf (1 μL, 5 μmol) at – 60 °C. Then donor **10** (40.0 mg, 64.4 μmol), dissolved in 1 mL of dry DCM, was slowly added into the reaction. The reaction was further stirred for 2h min at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO₃ (aq.)

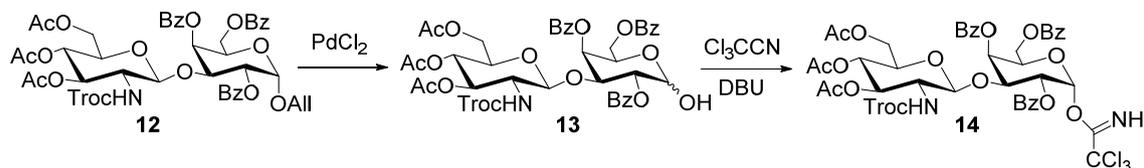
and brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) on silica gel to afford compound **11** (65.2 mg, 87%) as semisolid. ¹H NMR (400 MHz, CDCl₃) δ = 8.10 – 8.00 (m, 4H, ArH), 7.58 – 7.46 (m, 2H, ArH), 7.44 – 7.37 (m, 2H, ArH), 7.36 – 7.06 (m, 23H, ArH), 5.81 (d, *J* = 3.3 Hz, 1H, 4a-H), 5.56 (dd, *J* = 10.5, 3.6 Hz, 1H, 2a-H), 5.28 (dd, *J* = 11.1, 8.7 Hz, 1H, 3c-H), 5.22 (d, *J* = 3.2 Hz, 1H, 1b-H), 5.20 (m, 1H, NH), 5.17 (d, *J* = 3.7 Hz, 1H, 1a-H), 5.03 (t, *J* = 9.6 Hz, 1H, 4c-H), 4.82 – 4.72 (m, 2H, Cl₃CCH₂, PhCH₂), 4.64 (d, *J* = 8.2 Hz, 1H, 1c-H), 4.58 – 4.48 (m, 3H, 3a-H, Cl₃CCH₂, PhCH₂), 4.44 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.43 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.40 (d, *J* = 12.0 Hz, 1H, PhCH₂), 4.36 (d, *J* = 11.2 Hz, 1H, PhCH₂), 4.31 (d, *J* = 11.6 Hz, 1H, PhCH₂), 4.26 (d, *J* = 11.6 Hz, 1H, PhCH₂), 4.22 (dd, *J* = 8.3, 3.8 Hz, 1H), 4.17 (dd, *J* = 12.2, 4.8 Hz, 1H, 6c-H), 4.07 – 3.95 (m, 3H, 5b-H, 6c'-H, 6a-H), 3.91 (dd, *J* = 9.7, 3.3 Hz, 1H, 2b-H), 3.68 – 3.55 (m, 5H, 2c-H, 3b-H, 5c-H, 6a'-H), 3.41 (d, *J* = 6.6 Hz, 2H, 6b-H, 6b'-H), 3.37 (s, 3H, OMe), 2.00 (bs, 9H, OAc x 3). ¹³C NMR (100 MHz, CDCl₃) δ = 170.58, 170.50, 169.41, 165.96, 165.81, 153.87, 138.63, 138.52, 138.39, 138.13, 133.20, 133.14, 129.95, 129.82, 129.78, 129.55, 129.41, 128.43, 128.36, 128.24, 128.05, 128.03, 127.97, 127.66, 127.56, 127.51, 127.38, 127.19, 127.13, 127.10, 100.67, 97.24, 95.32, 94.79, 78.68, 75.19, 74.89, 74.60, 74.32, 73.18, 72.86, 72.49, 71.76, 71.64, 70.48, 69.56, 69.40, 68.80, 68.60, 68.47, 68.40, 68.04, 61.85, 56.26, 55.35, 20.59, 20.57. HRMS (ESI) Calcd for C₇₀H₇₅Cl₃NO₂₂ [M+H]⁺: 1386.3841, found: 1386.3875; Calcd for C₇₀H₇₄Cl₃NNaO₂₂ [M+Na]⁺: 1408.3660, found: 1408.3683.



Allyl 3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-N-Troc-β-D-glucopyranosyl)-2,4,6-tri-O-benzoyl-α-D-galactopyranoside (12)

To a solution of glycosyl donor **10** (127 mg, 203.2 μmol) and glycosyl acceptor **4j** (90 mg, 169.2 μmol) and 4 Å molecular sieves in 3 mL of dry DCM was added TMSOTf (4 μL, 20 μmol) at – 60 °C. The reaction was further stirred for 2h at this temperature.

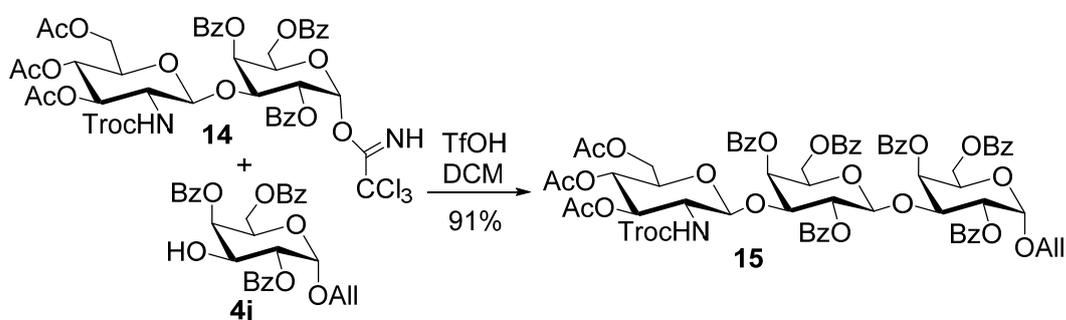
After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO₃ (aq.) and brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) on silica gel to afford compound **11** (157.0 mg, 94%) as foam. ¹H NMR (400 MHz, CDCl₃) δ = 8.14 – 8.08 (m, 4H, ArH), 8.06 – 7.99 (m, 2H, ArH), 7.67 – 7.37 (m, 9H, ArH), 5.88 (d, *J* = 3.5 Hz, 1H, 4a-H), 5.86 – 5.78 (m, 1H, -CH₂-CH=CH₂), 5.59 (dd, *J* = 10.5, 3.8 Hz, 1H, 2a-H), 5.39 (t, *J* = 10.0 Hz, 1H, 3b-H), 5.32 (d, *J* = 3.7 Hz, 1H, 1a-H), 5.23 – 5.16 (m, 1H, -CH₂-CH=CH₂), 5.11 – 5.08 (m, 1H, -CH₂-CH=CH₂), 5.06 (d, *J* = 8.0 Hz, 1H, 1b-H), 4.98 (t, *J* = 9.6 Hz, 1H, 4b-H), 4.89 – 4.79 (m, 1H, NH), 4.57 – 4.35 (m, 4H, 3a-H, 5a-H, Cl₃CCH₂ x 2), 4.28 (dd, *J* = 12.2, 2.4 Hz, 1H, 6b-H), 4.22 – 4.12 (m, 2H, 6b'-H, 6a-H), 4.10 – 3.98 (m, 2H, 6a'-H, -CH₂-CH=CH₂), 3.97 – 3.87 (m, 1H, -CH₂-CH=CH₂), 3.75 – 3.67 (m, 1H, 5b-H), 3.30 – 3.18 (m, 1H, 2b-H), 2.02 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.90 (s, 3H, OAc). ¹³C NMR (100 MHz, CDCl₃) δ = 170.73, 169.39, 166.06, 165.59, 153.14, 133.50, 133.22, 133.15, 133.08, 129.99, 129.87, 129.82, 129.68, 129.64, 129.59, 129.30, 128.64, 128.42, 128.37, 128.31, 118.04, 100.11, 95.48, 95.17, 73.81, 73.51, 71.56, 70.99, 70.82, 70.36, 68.79, 68.49, 67.59, 63.34, 61.42, 56.54, 20.63, 20.55, 20.42. HRMS (ESI) Calcd for C₄₅H₄₆Cl₃NNaO₁₈ [M+Na]⁺: 1016.1673, found:1016.1646.



3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-*N*-Troc-β-*D*-glucopyranosyl)-2,4,6-tri-*O*-benzoyl-α-*D*-galactopyranosyl trichloroacetimidate (14**)**

To a solution of disaccharide **12** (80 mg, 80.5 μmol) in 5 mL DCM and MeOH (V:V = 10:1) was added PdCl₂ (20 mg). The reaction was stirred at room temperature for 3 h until the TLC analysis showed the formation of a product and consumption of compound **12**. The reaction was diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was concentrated and the residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) on silica gel to afford compound 1-OH compound **13** (65 mg, 85%). Then compound **13** (65 mg, 68.2 μmol) was dissolved in dry DCM (2 mL), and trichloroacetonitrile (68 μL, 682 μmol) and DBU (2 μL, 13.6 μmol) were added in sequence at 0 °C. The

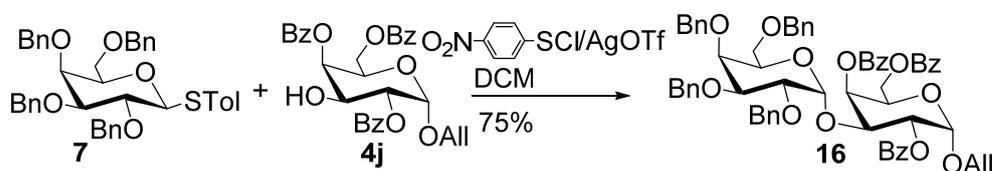
reaction was further stirred for 2h min at this temperature. After the TLC analysis showed the reaction was complete, the reaction was concentrated and purified by column chromatography (hexane/ethyl acetate = 2 : 1) on silica gel to afford compound **14** (52.5 mg, 70%) as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ = 8.55 (s, 1H, C=NH), 8.11 (d, *J* = 7.6 Hz, 2H, Ar*H*), 8.04 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.97 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.66 – 7.57 (m, 2H, Ar*H*), 7.57 – 7.44 (m, 5H, Ar*H*), 7.42 – 7.34 (m, 2H, Ar*H*), 6.76 (d, *J* = 3.8 Hz, 1H, 1a-H), 5.99 (d, *J* = 3.3 Hz, 1H, 4a-H), 5.82 (dd, *J* = 10.4, 3.8 Hz, 1H, 2a-H), 5.37 (t, *J* = 10.0 Hz, 1H, 3b-H), 5.06 (d, *J* = 8.2 Hz, 1H, 1b-H), 4.98 (t, *J* = 9.6 Hz, 1H, 4b-H) 4.93 (d, *J* = 7.9 Hz, 1H, NH), 4.71 – 4.66 (m, 1H, 5a-H), 4.60 – 4.51 (m, 2H, 3a-H, 6a-H), 4.38 (dd, *J* = 11.8, 7.6 Hz, 1H, 6a'-H), 4.25 (d, *J* = 12.1 Hz, 1H, 6b-H), 4.16 (dd, *J* = 12.2, 4.4 Hz, 1H, 6b'-H), 3.93 (d, *J* = 12.3 Hz, 1H, Cl₃CCH₂), 3.84 (d, *J* = 12.2 Hz, 1H, Cl₃CCH₂), 3.80 – 3.71 (m, 1H, 5b-H), 3.37 – 3.24 (m, 1H, 2b-H), 2.01 (s, 3H, OAc), 1.99 (s, 3H, OAc), 1.90 (s, 3H, OAc). ¹³C NMR (100 MHz, CDCl₃) δ = 170.70, 170.18, 169.38, 166.03, 165.33, 165.20, 160.22, 153.18, 133.67, 133.35, 133.09, 130.01, 129.86, 129.82, 129.64, 129.50, 129.33, 128.86, 128.60, 128.52, 128.31, 128.26, 100.36, 95.13, 93.65, 90.78, 74.14, 73.46, 71.71, 70.77, 70.32, 68.96, 68.38, 63.11, 61.52, 56.46, 20.63, 20.55, 20.41. HRMS (ESI) Calcd for C₄₄H₄₂Cl₆N₂NaO₁₈ [M+Na]⁺: 1121.0426, found: 1121.0423.



Allyl [3-O-[3-O-(3,4,6-tri-O-acetyl-2-deoxy-2-N-Troc-β-D-glucopyranosyl)-2,4,6-tri-O-benzoyl-α-D-galactopyranosyl]-2,4,6-tri-O-benzoyl-α-D-galactopyranoside (15)

To a solution of glycosyl donor **14** (50 mg, 45.6 μmol) and glycosyl acceptor **4j** (30 mg, 56.3 μmol) and 4 Å molecular sieves in 3 mL of dry DCM was added TfOH (1 μL, 11.3 μmol) at -30 °C. The reaction was further stirred for 2h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO₃ (aq.) and brine, dried over Na₂SO₄, filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) on silica gel to

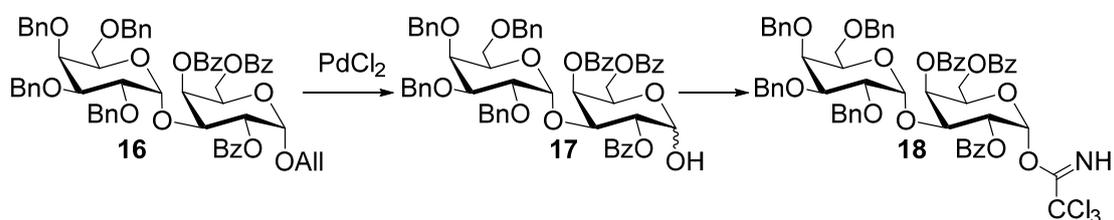
afford compound **15** (60.8 mg, 91%) as foam. ^1H NMR (400 MHz, CDCl_3) δ = 8.15 – 8.08 (m, 4H, ArH), 8.09 – 8.01 (m, 4H, ArH), 7.85 (d, J = 7.7 Hz, 2H, ArH), 7.65 – 7.50 (m, 8H, ArH), 7.50 – 7.34 (m, 12H, ArH), 7.09 (t, J = 7.7 Hz, 2H, ArH), 5.99 (d, J = 3.5 Hz, 1H, 4a-H), 5.81 (d, J = 3.4 Hz, 1H, 4b-H), 5.79 – 5.64 (m, 1H, - $\text{CH}_2\text{-CH=CH}_2$), 5.44 (dd, J = 10.4, 3.7 Hz, 1H, 2a-H), 5.38 (dd, J = 10.1, 7.8 Hz, 1H, 2b-H), 5.30 (t, J = 10.0 Hz, 3c-H), 5.26 (d, J = 4.0 Hz, 1a-H), 5.13 (dd, J = 17.1, 1.7 Hz, 1H, - $\text{CH}_2\text{-CH=CH}_2$), 5.03 (dd, J = 10.3, 1.5 Hz, 1H, - $\text{CH}_2\text{-CH=CH}_2$), 5.00 (d, J = 7.8 Hz, 1H, 1b-H), 4.91 (t, J = 9.6 Hz, 1H, 4c-H), 4.86 (d, J = 8.1 Hz, 1H, 1c-H), 4.68 (d, J = 8.0 Hz, 1H, NH), 4.61 – 4.31 (m, 6H, 3a-H, 6b-H, 6b'-H, 6a-H, 6a'-H, 5a-H), 4.26 – 4.14 (m, 2H, 6c-H, 5b-H), 4.15 – 3.91 (m, 5H, 3b-H, - $\text{CH}_2\text{-CH=CH}_2 \times 2$, 6c'-H, CH_2CCl_3), 3.62 – 3.48 (m, 2H, 5c-H, CH_2CCl_3), 3.15 – 2.98 (m, 1H, 2c-H), 2.00 (s, 3H, OAc), 1.96 (s, 3H, OAc), 1.86 (s, 3H, OAc). ^{13}C NMR (100 MHz, CDCl_3) δ = 170.70, 169.97, 169.39, 166.14, 165.97, 165.70, 165.27, 164.20, 153.02, 133.24, 133.14, 133.08, 133.03, 132.95, 132.78, 130.13, 130.01, 129.87, 129.71, 129.59, 129.57, 129.40, 129.29, 129.24, 128.43, 128.36, 128.31, 128.17, 117.83, 101.35, 99.84, 95.25, 95.17, 73.30, 72.85, 71.66, 71.51, 71.46, 70.77, 70.48, 69.60, 68.63, 68.53, 67.50, 63.34, 62.67, 61.41, 56.38, 20.63, 20.54, 20.38. HRMS (ESI) Calcd for $\text{C}_{72}\text{H}_{68}\text{Cl}_3\text{NNaO}_{26}[\text{M}+\text{Na}]^+$: 1490.2987, found: 1490.2983.



Allyl 3-O-(2,3,4,6-tetra-O-benzyl- α -D-galactopyranosyl)-2,4,6-tri-O-benzoyl- α -D-galactopyranoside (16)

A mixture of thioglycoside donor (35mg, 54.1 μmol), acceptor (23 mg, 43.0 μmol), AgOTf (40 mg, 157 μmol) and activated 4 Å molecular sieves in dry dichloromethane (3 mL) was stirred at room temperature under a nitrogen atmosphere for 10 min. Then the mixture was cooled to -60°C and a solution of *p*-nitrobenzenesulfonyl chloride (12 mg, 64.0 μmol) in dry CH_2Cl_2 (0.5 mL) was added. The reaction was further stirred for 5h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of NaHCO_3 (aq.) and diluted with 50 mL DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO_3 (aq.) and brine, dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford the α

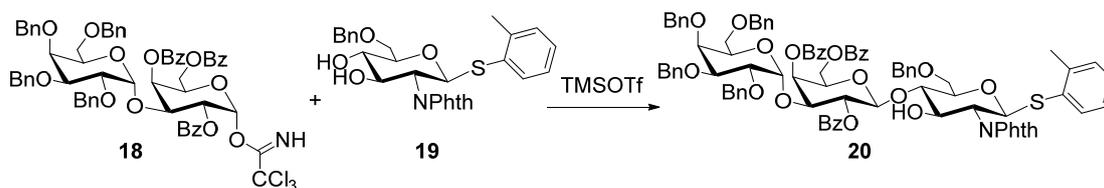
disaccharide **16** (42.8mg, 75%). ^1H NMR (400 MHz, CDCl_3) δ = 8.06 (dd, J = 19.9, 7.8 Hz, 6H, *ArH*), 7.59 – 7.05 (m, 30H, *ArH*), 5.99 (d, J = 3.2 Hz, 1H, 4a-H), 5.88 – 5.73 (m, J = 16.2, 10.6, 5.4 Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 5.64 (dd, J = 10.5, 3.7 Hz, 1H, 2a-H), 5.40 (d, J = 3.7 Hz, 1H, 1a-H), 5.30 (d, J = 3.3 Hz, 1H, 2a-H), 5.25 (d, J = 17.2 Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 5.08 (d, J = 10.4 Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 4.77 (d, J = 11.4 Hz, 1H, PhCH_2), 4.63 (dd, J = 10.6, 3.3 Hz, 1H, 3a-H), 4.57 – 4.34 (m, 8H, 6a-H, 6a'-H, 5a-H, $\text{PhCH}_2 \times 5$), 4.30 (d, J = 11.1 Hz, 1H, PhCH_2), 4.27 (d, J = 11.1 Hz, 1H, PhCH_2), 4.19 (dd, J = 13.4, 5.0 Hz, 1H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 4.11 – 3.99 (m, 2H, 5b-H, $-\text{CH}_2-\text{CH}=\text{CH}_2$), 3.94 (dd, J = 10.0, 3.3 Hz, 1H, 2b-H), 3.63 (dd, J = 10.0, 2.8 Hz, 1H, 3b-H), 3.56 (d, J = 2.7 Hz, 1H, 4b-H), 3.47 – 3.34 (m, 2H, 6b-H, 6b'-H). ^{13}C NMR (100 MHz, CDCl_3) δ = 166.01, 165.89, 165.85, 138.70, 138.54, 138.42, 138.13, 133.45, 133.18, 133.12, 133.09, 130.04, 129.74, 129.66, 129.65, 129.40, 128.42, 128.39, 128.35, 128.26, 128.13, 128.08, 127.97, 127.70, 127.54, 127.43, 127.25, 127.16, 127.08, 117.35, 95.65, 94.70, 78.71, 75.45, 74.92, 74.62, 73.25, 72.98, 72.57, 70.40, 69.62, 69.27, 68.62, 68.56, 67.72, 67.41, 63.00. HRMS (ESI) Calcd for $\text{C}_{64}\text{H}_{62}\text{NaO}_{14} [\text{M}+\text{Na}]^+$: 1077.4032, found: 1077.4047.



3-*O*-(2,3,4,6-tetra-*O*-benzyl- α -D-galactopyranosyl)-2,4,6-tri-*O*-benzoyl- α -D-galactopyranosyl trichloroacetimidate (**18**)

To a solution of disaccharide **16** (200 mg, 189.7 μmol) in 5 mL DCM and MeOH (V:V = 10:1) was added PdCl_2 (50 mg). The reaction was stirred at room temperature for 1 h until the TLC analysis showed the formation of a product and consumption of compound **16**. The reaction was diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was concentrated and the residue was purified by column chromatography (hexane/ethyl acetate = 3 : 1) on silica gel to afford compound 1-OH compound **17** (140.0 mg, 71%). Then compound **17** (140 mg, 138.0 μmol) was dissolved in dry DCM (3 mL), and trichloroacetimidate (100 μL , 1000 μmol) and DBU (10 μL , 68.0 μmol) were added in sequence at 0 $^\circ\text{C}$. The reaction was further stirred for 2h min at this temperature. After the TLC analysis

showed the reaction was complete, the reaction was concentrated and purified by column chromatography (hexane/ethyl acetate = 2 : 1) on silica gel to afford compound **18** (120.5 mg, 75%) as colorless oil. ^1H NMR (400 MHz, CDCl_3) δ = 8.56 (s, 1H, C=NH), 8.08 (d, J = 7.7 Hz, 2H, ArH), 8.00 (dd, J = 7.9, 3.7 Hz, 4H, ArH), 7.60 – 7.05 (m, 31H, ArH), 6.85 (d, J = 3.7 Hz, 1H, 1a-H), 6.09 (d, J = 3.1 Hz, 1H, 4a-H), 5.86 (dd, J = 10.6, 3.7 Hz, 1H, 2a-H), 5.38 (d, J = 3.4 Hz, 1H, 2b-H), 4.77 (d, J = 11.3 Hz, 1H, PhCH_2), 4.71 (dd, J = 10.6, 3.1 Hz, 1H, 3a-H), 4.66 (t, J = 6.4 Hz, 1H, 5a-H), 4.57 – 4.34 (m, 7H, 6a-H, 6a'-H, $\text{PhCH}_2 \times 5$), 4.31 (d, J = 11.6 Hz, 1H,), 4.24 (d, J = 11.7 Hz, 1H, PhCH_2), 4.10 (dd, J = 8.1, 5.4 Hz, 1H, 5b-H), 3.96 (dd, J = 9.7, 3.4 Hz, 1H, 2b-H), 3.66 – 3.57 (m, 2H, 3b-H, 4b-H), 3.53 (t, J = 8.4 Hz, 1H, 6b-H), 3.43 (dd, J = 8.6, 5.3 Hz, 1H, 6b'-H). ^{13}C NMR (100 MHz, CDCl_3) δ = 165.96, 165.70, 165.51, 160.45, 138.58, 138.33, 137.92, 133.41, 133.35, 133.16, 130.06, 129.74, 129.72, 129.02, 128.52, 128.45, 128.36, 128.34, 128.10, 128.07, 127.99, 127.97, 127.88, 127.74, 127.60, 127.43, 127.23, 127.18, 127.09, 94.05, 93.80, 90.86, 78.49, 75.35, 74.76, 74.72, 73.56, 72.87, 72.55, 70.11, 69.44, 69.02, 68.45, 68.23, 66.63, 62.59. HRMS (ESI) Calcd for $\text{C}_{63}\text{H}_{58}\text{Cl}_3\text{NNaO}_{14} [\text{M}+\text{Na}]^+$: 1180.2815, found: 1180.2755; Calcd for $\text{C}_{63}\text{H}_{58}\text{Cl}_3\text{KNO}_{14} [\text{M}+\text{K}]^+$: 1196.2554, found: 1196.2543.



2-Methylphenyl

4-O

[3-O-(2,3,4,6-tetra-O-benzyl- α -D-galactopyranosyl)-2,4,6-tri-O-benzoyl- α -D-galactopyranosyl]-2-deoxy-2-N-phthalimido- β -D-glucopyranoside (**20**)

To a solution of glycosyl donor **18** (65 mg, 56.2 μmol) and glycosyl acceptor **19** (35 mg, 69.3 μmol) and 4 Å molecular sieves in 3 mL of dry DCM was added TfOH (1 μL , 11.3 μmol) at -60 °C. The reaction was further stirred for 2h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with NaHCO_3 (aq.) and brine, dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by column chromatography (hexane/ethyl acetate = 1 : 1) on silica gel to afford compound **11** (76.0 mg, 90%) as semisolid. ^1H NMR (400 MHz, CDCl_3) δ = 8.11 – 7.96 (m, 6H, ArH), 7.92 – 7.83 (m, 1H, ArH), 7.81 – 7.75 (m, 1H, ArH), 7.74 – 7.62 (m, 2H, ArH), 7.57 – 7.36 (m, 9H, ArH), 7.36 – 7.18 (m, 17H, ArH), 7.18 – 7.02 (m, 14H, ArH), 7.01 – 6.90 (m, 1H, ArH), 5.80 (d, J = 3.2 Hz, 1H, 4b-H), 5.70 (dd, J = 10.2, 8.0 Hz, 1H, 2b-H), 5.52 (d, J = 10.5 Hz, 1H, 1a-H), 5.14 (d, J = 3.3 Hz, 1H,

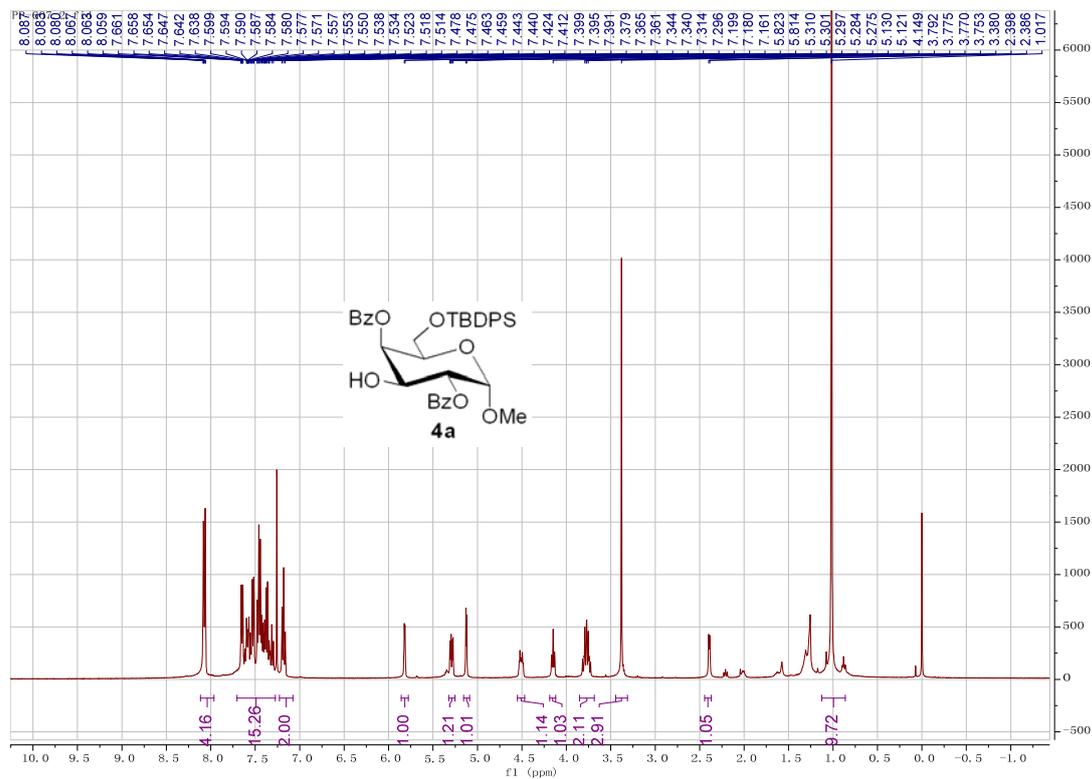
1c-H), 4.70 (d, $J = 11.8$ Hz, 2H, PhCH₂, 6b-H), 4.65 (d, $J = 8.1$ Hz, 1H, 1b-H), 4.61 – 4.53 (m, 2H, 3a-H, OH), 4.51 – 4.34 (m, 5H, 2a-H, PhCH₂ x 4), 4.28 (d, $J = 11.6$ Hz, 1H, PhCH₂), 4.26 (d, $J = 11.6$ Hz, 1H, PhCH₂), 4.21 (d, $J = 11.6$ Hz, 1H, PhCH₂), 4.18 – 4.07 (m, 4H, 3b-H, 6b'-H, PhCH₂ x 2), 3.95 (dd, $J = 9.1, 3.1$ Hz, 1H, 5b-H), 3.87 (dd, $J = 10.1, 3.3$ Hz, 1H, 2c-H), 3.83 (t, $J = 6.4$ Hz, 5c-H), 3.74 – 3.59 (m, 2H, 4a-H, 5a-H), 3.51 – 3.40 (m, 3H, 3c-H, 6c-H, 6c'-H), 3.30 – 3.26 (m, 2H, 4c-H, 6a-H), 3.20 (dd, $J = 9.4, 6.0$ Hz, 1H, 6a'-H), 2.18 (s, 3H, *o*-MePh). ¹³C NMR (100 MHz, CDCl₃) $\delta = 168.01, 167.45, 166.14, 165.72, 164.52, 139.84, 138.62, 138.35, 138.26, 138.11, 134.00, 133.92, 133.45, 133.40, 133.17, 132.78, 132.05, 131.76, 131.61, 130.07, 130.04, 129.89, 129.84, 129.18, 129.02, 128.85, 128.55, 128.50, 128.43, 128.39, 128.14, 128.12, 128.07, 128.00, 127.79, 127.76, 127.68, 127.65, 127.47, 127.35, 127.22, 127.20, 127.14, 126.49, 123.52, 123.19, 102.16, 95.06, 83.64, 82.84, 78.75, 77.72, 74.99, 74.64, 74.42, 73.32, 73.09, 73.06, 72.77, 72.59, 72.39, 70.88, 70.66, 70.03, 68.97, 68.33, 66.38, 63.04, 55.10, 20.82. HRMS (ESI) Calcd for C₈₉H₈₃NNaO₁₉S [M+Na]⁺: 1524.5172, found: 1524.5184.$

Reference:

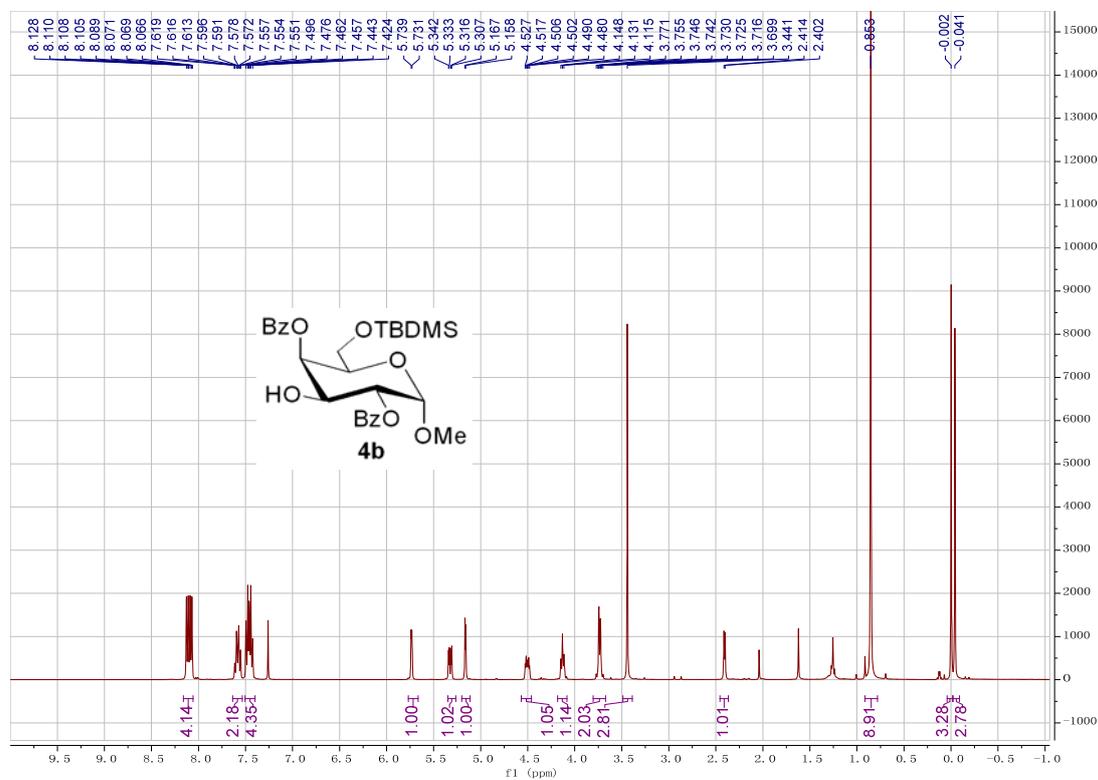
1. Ashmus, R. A.; Lowary, T. L., *Org. Lett.* **2014**, *16*, 2518.
2. Sherman, A. A.; Yudina, O. N.; Mironov, Y. V.; Sukhova, E. V.; Shashkov, A. S.; Menshov, V. M.; Nifantiev, N. E., *Carbohydr. Res.* **2001**, *336*, 13.

Copies of NMR Spectra for the new compounds

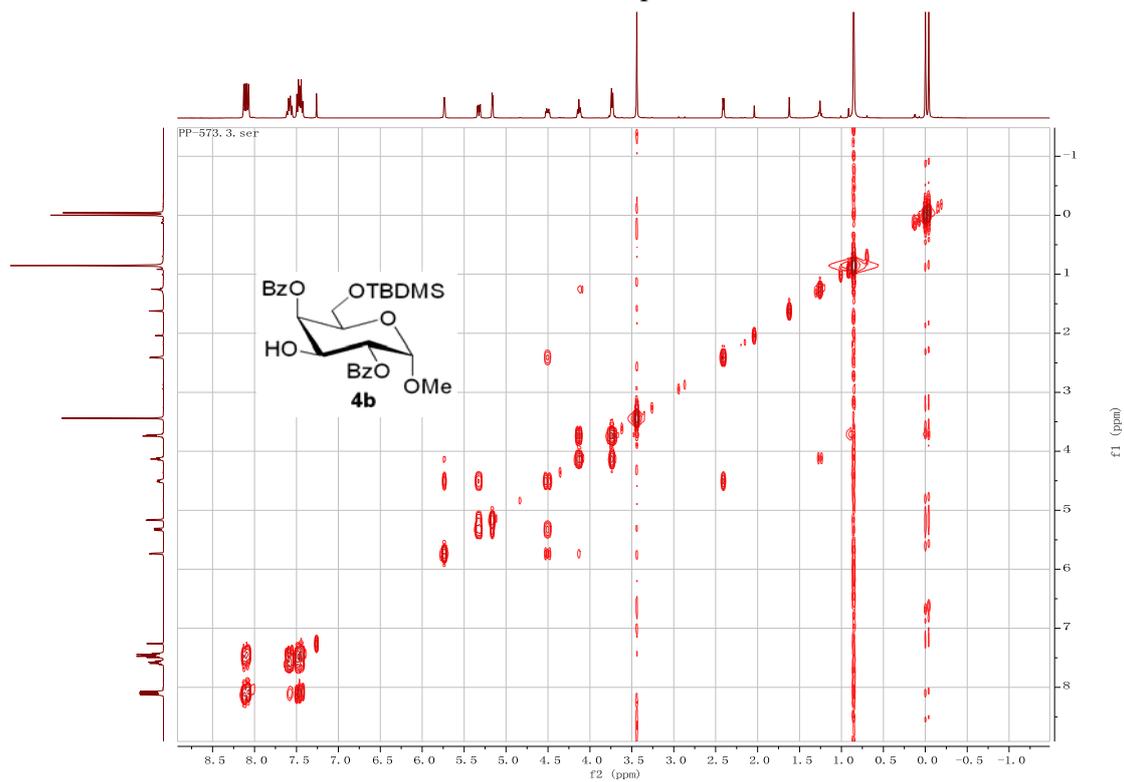
¹H spectrum of compound 4a (400 MHz, CDCl₃)



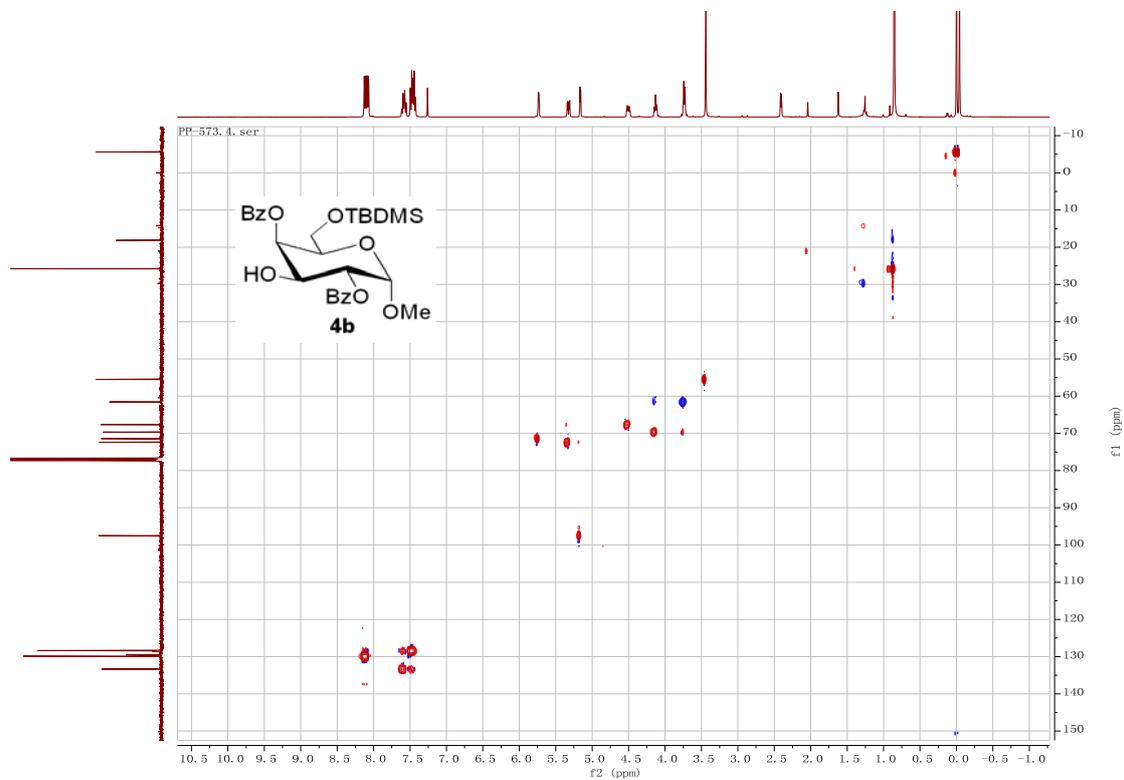
¹H spectrum of compound 4b (400 MHz, CDCl₃)



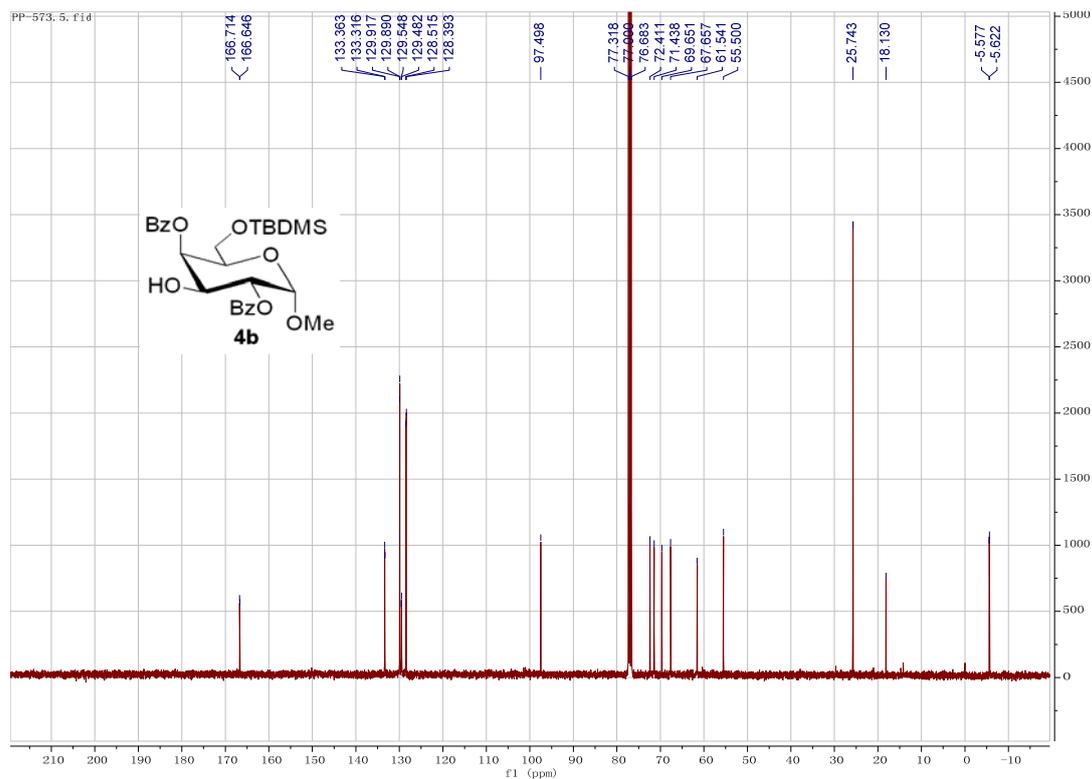
^1H - ^1H COSY of compound **4b**



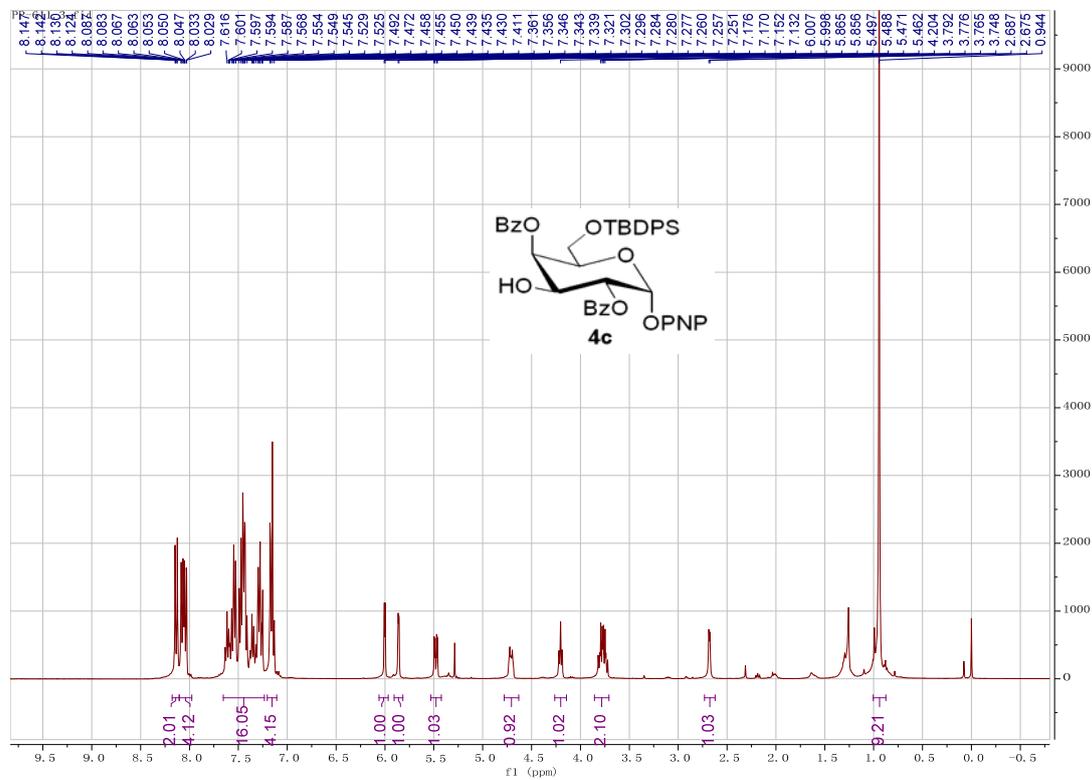
HSQC of compound **4b**



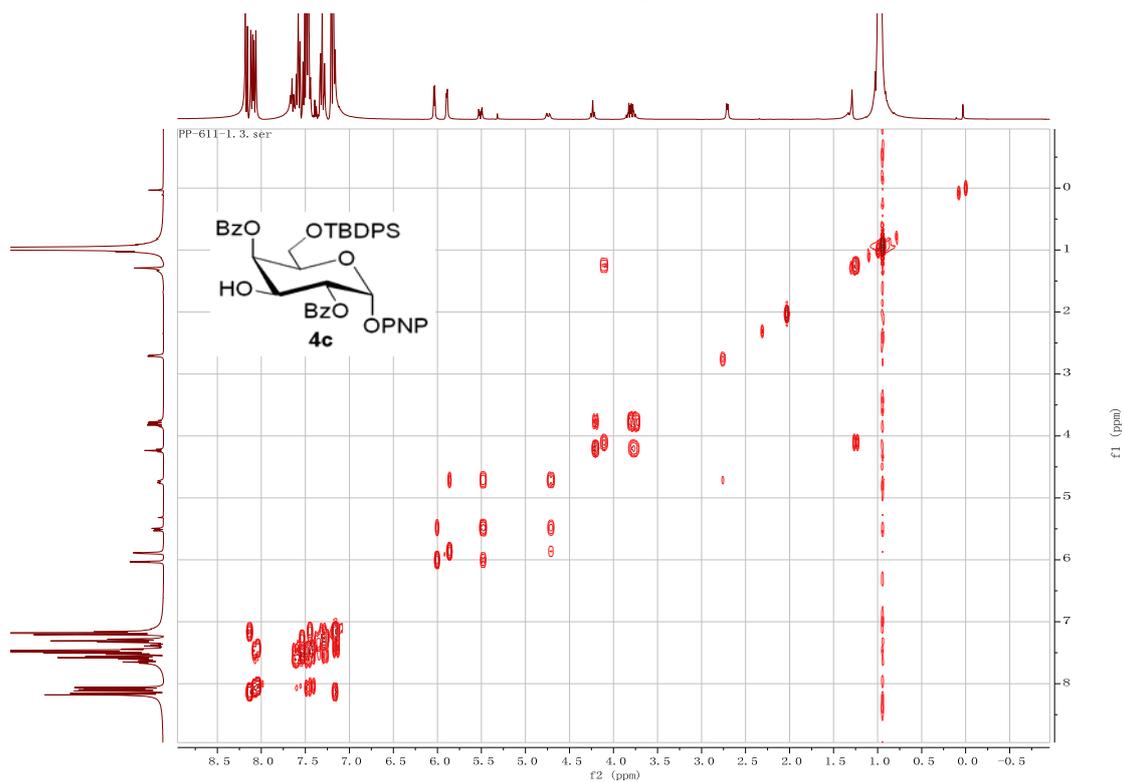
^{13}C spectrum of compound **4b** (100 MHz, CDCl_3)



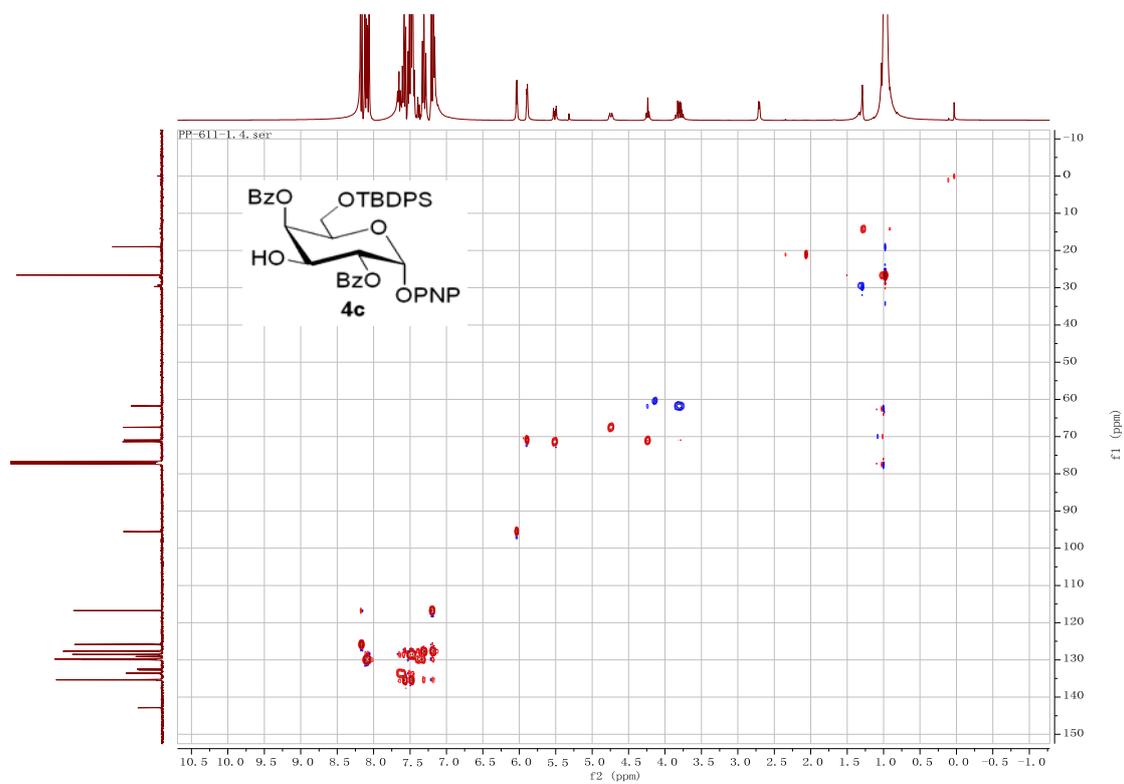
^1H spectrum of compound **4c** (400 MHz, CDCl_3)



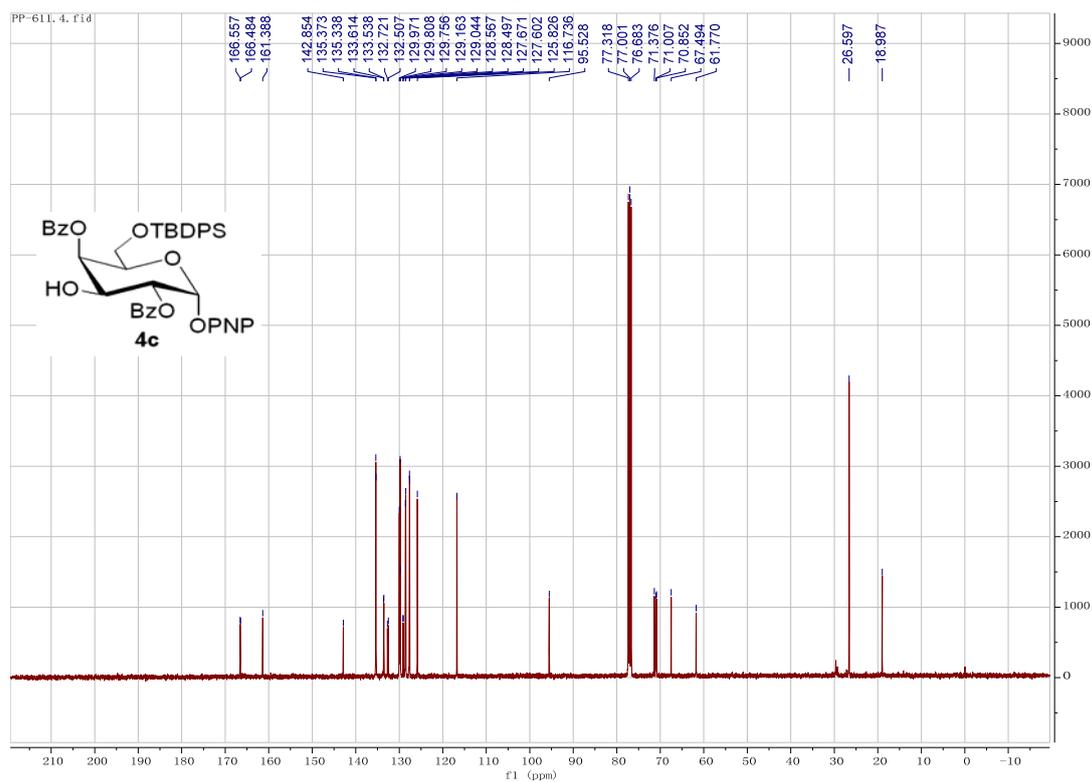
^1H - ^1H COSY of compound **4c**



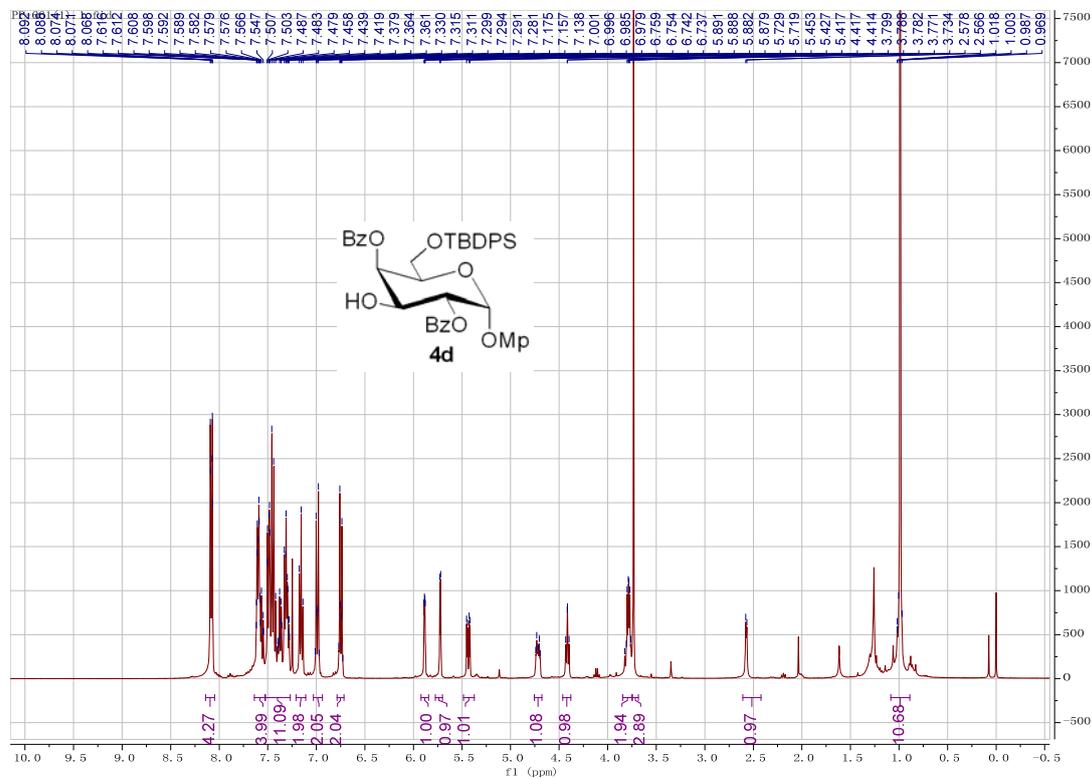
HSQC of compound **4c**



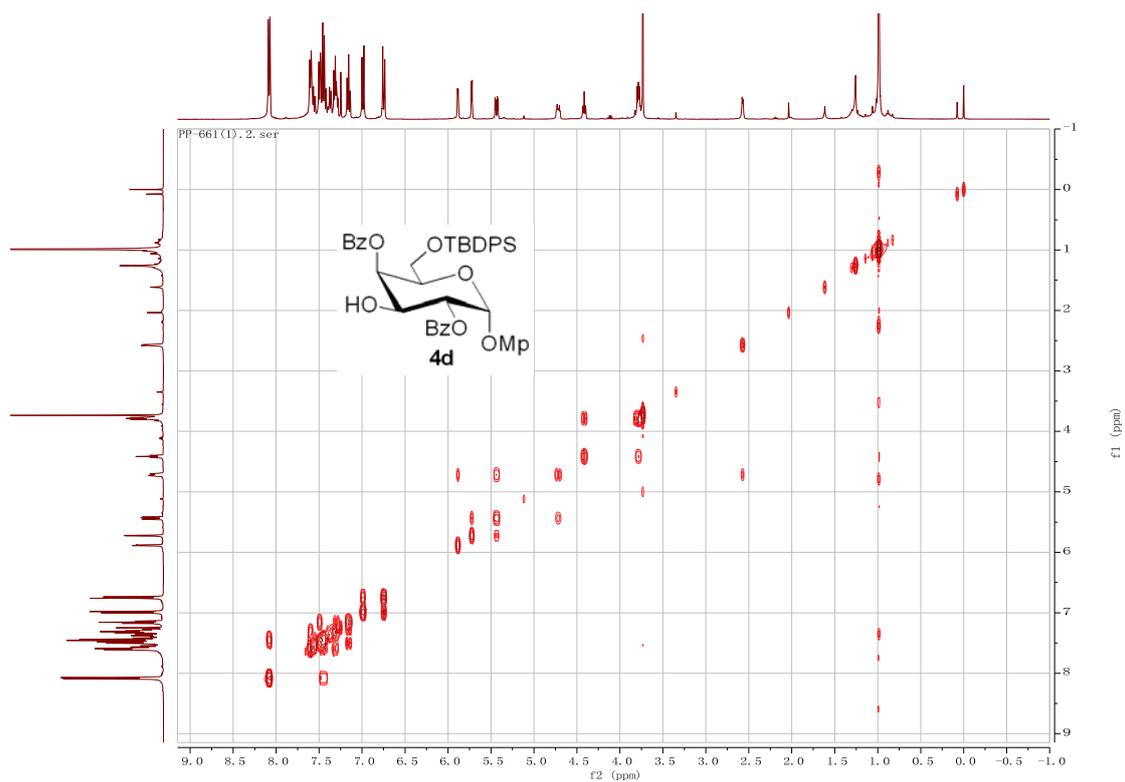
¹³C spectrum of compound **4c** (100 MHz, CDCl₃)



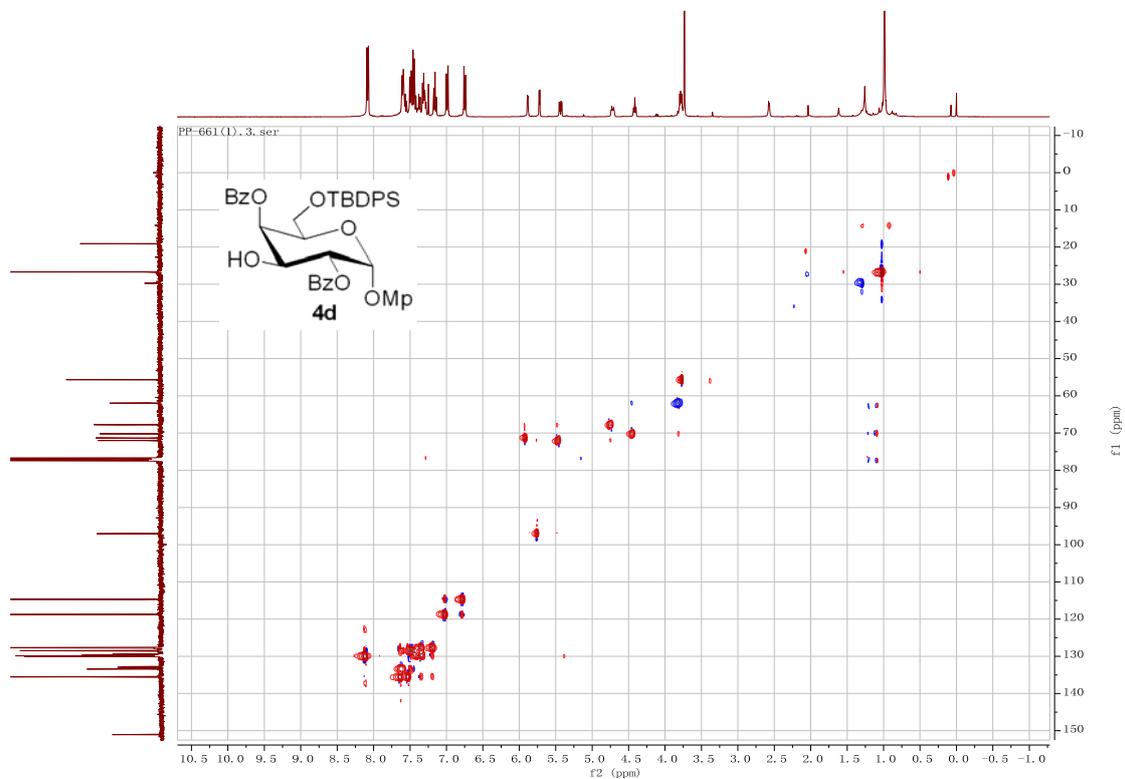
¹H spectrum of compound **4d** (400 MHz, CDCl₃)



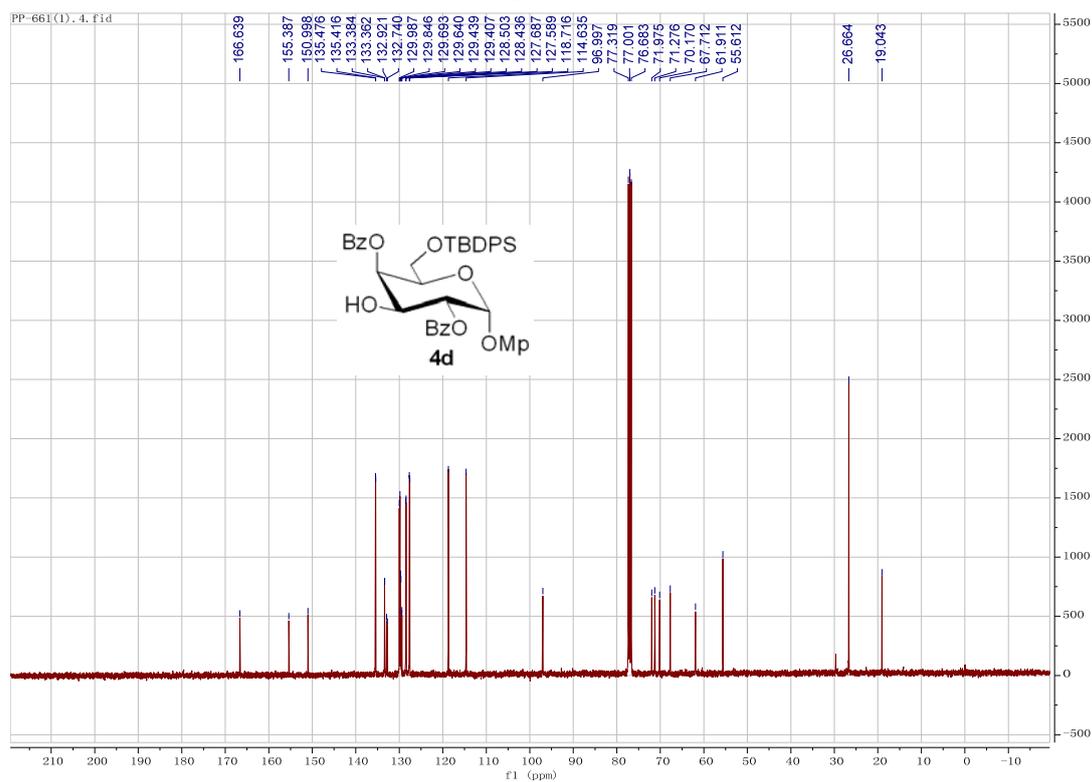
^1H - ^1H COSY of compound **4d**



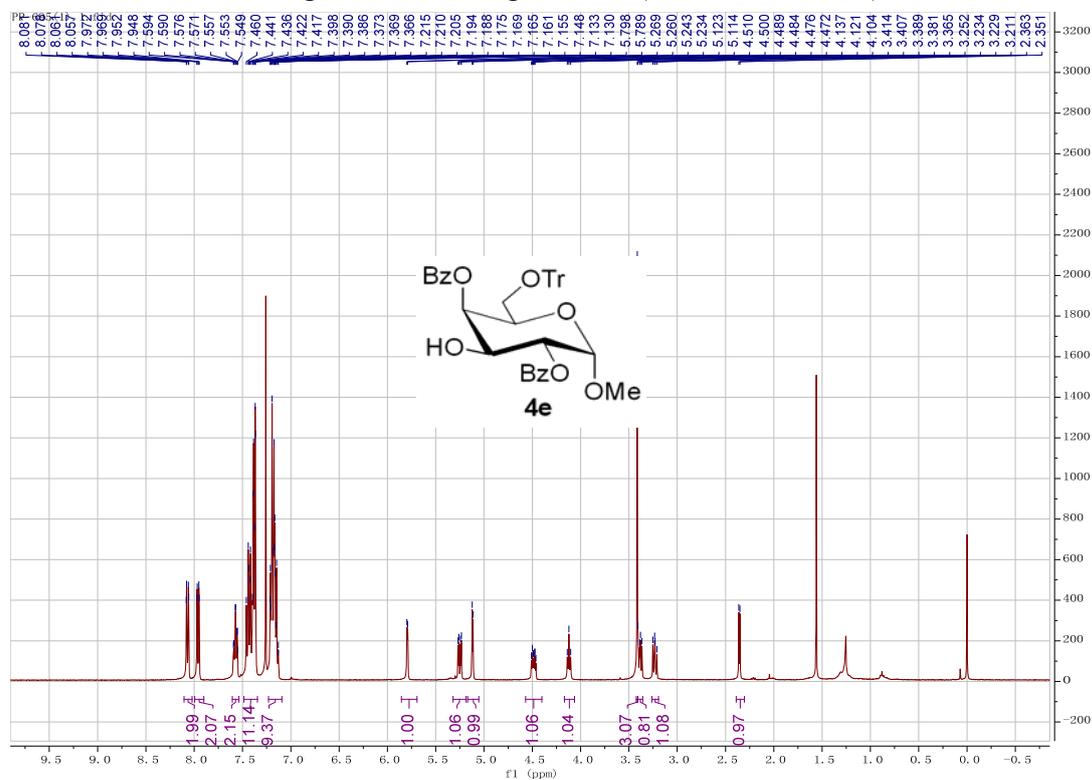
HSQC of compound **4d**



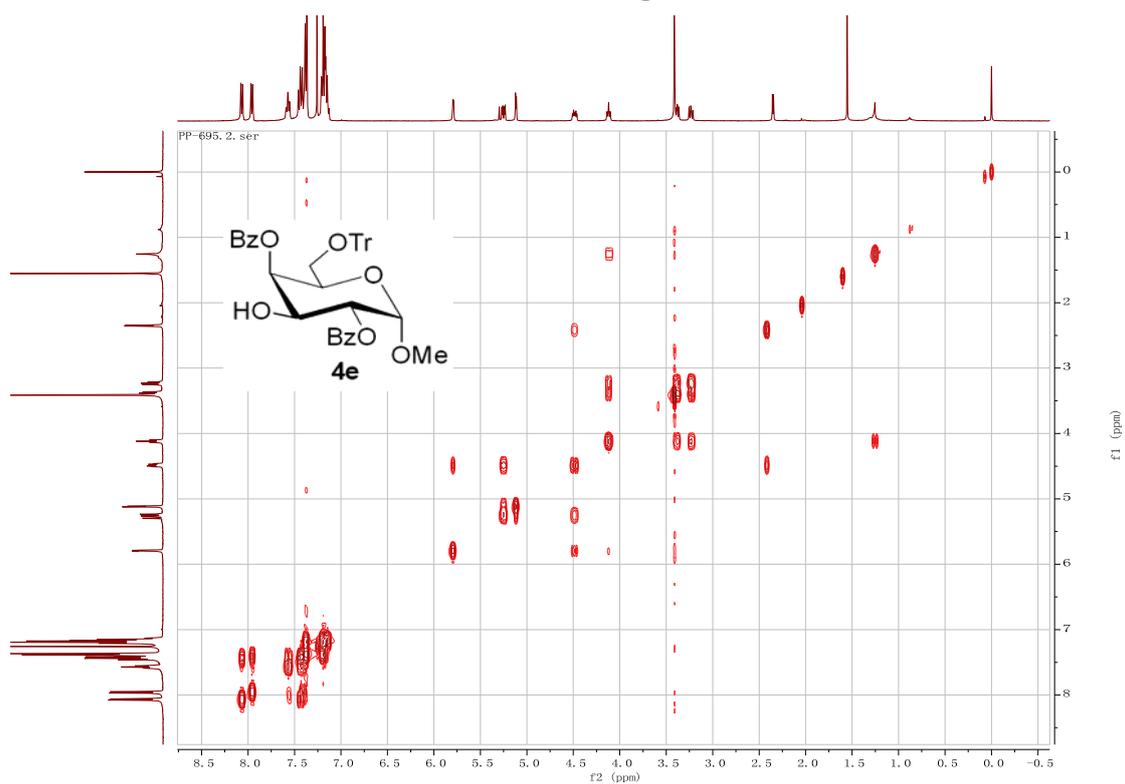
^{13}C spectrum of compound **4d** (100 MHz, CDCl_3)



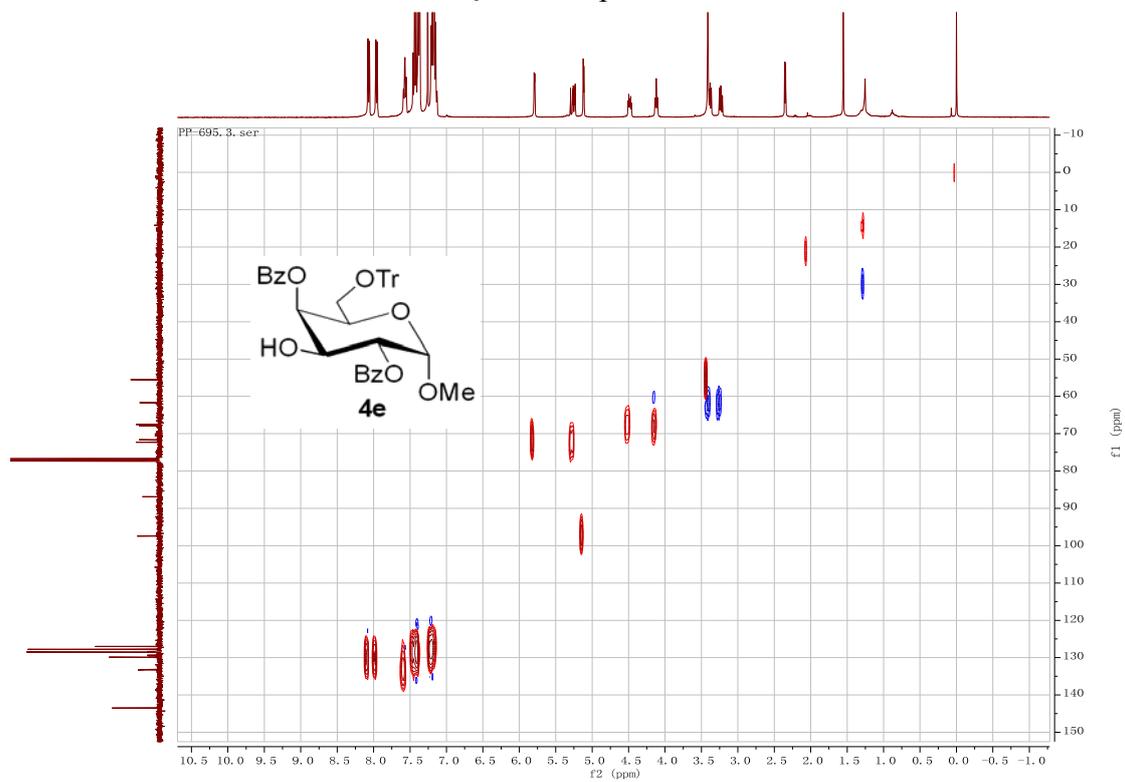
^1H spectrum of compound **4e** (400 MHz, CDCl_3)



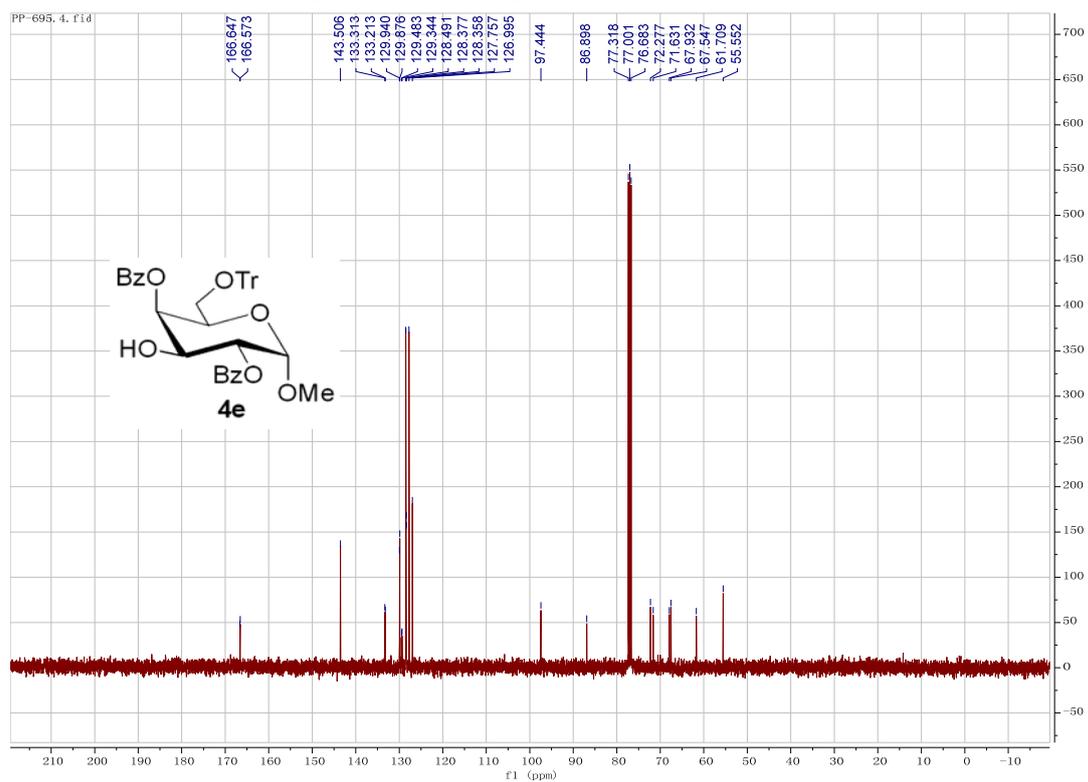
^1H - ^1H COSY of compound **4e**



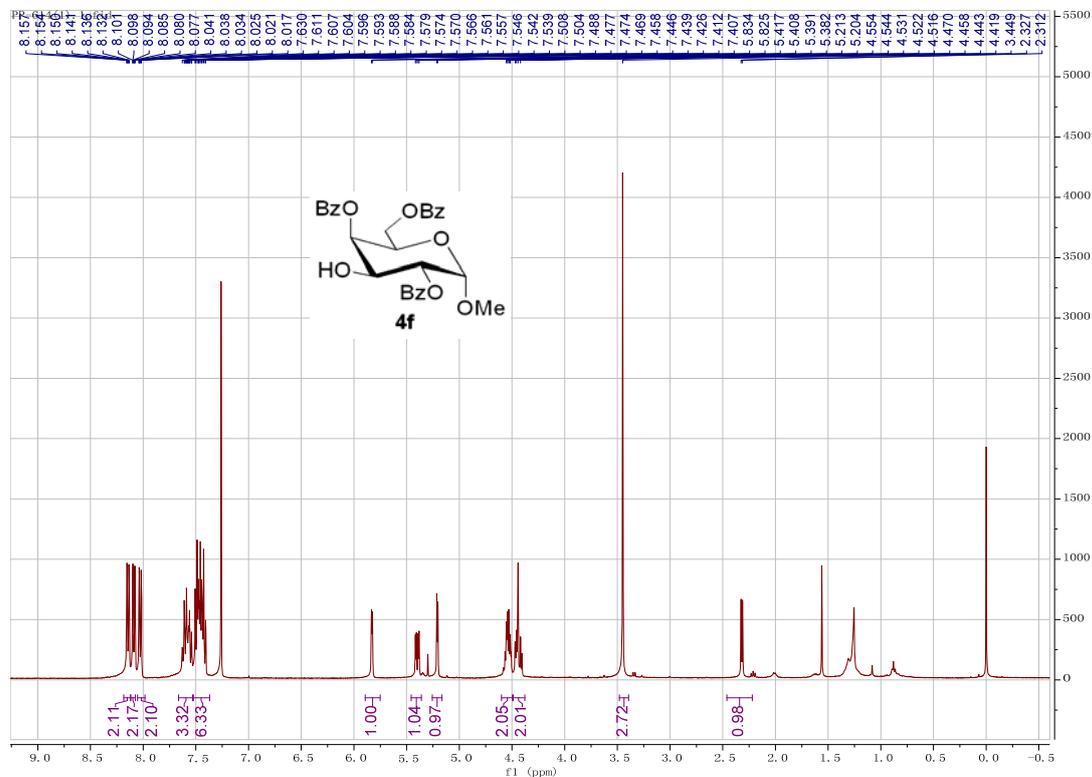
HSQC of compound **4e**



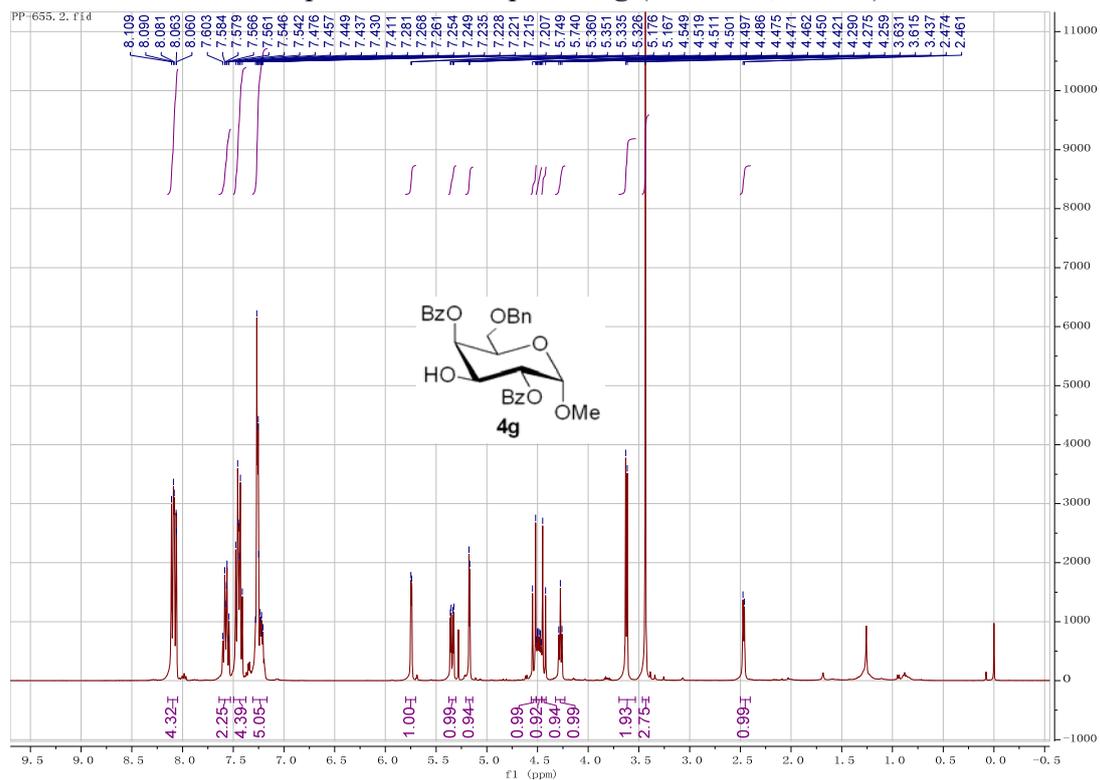
¹³C spectrum of compound **4e** (100 MHz, CDCl₃)



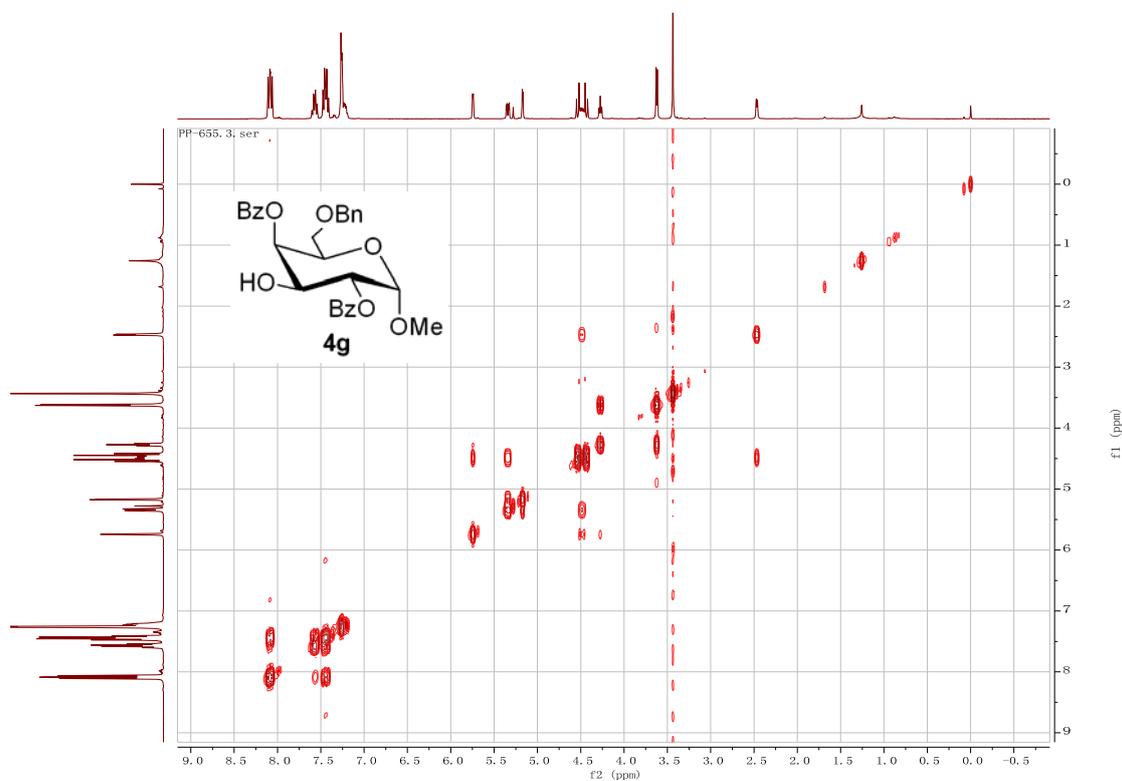
¹H NMR spectrum of compound **4f** (400 MHz, CDCl₃)



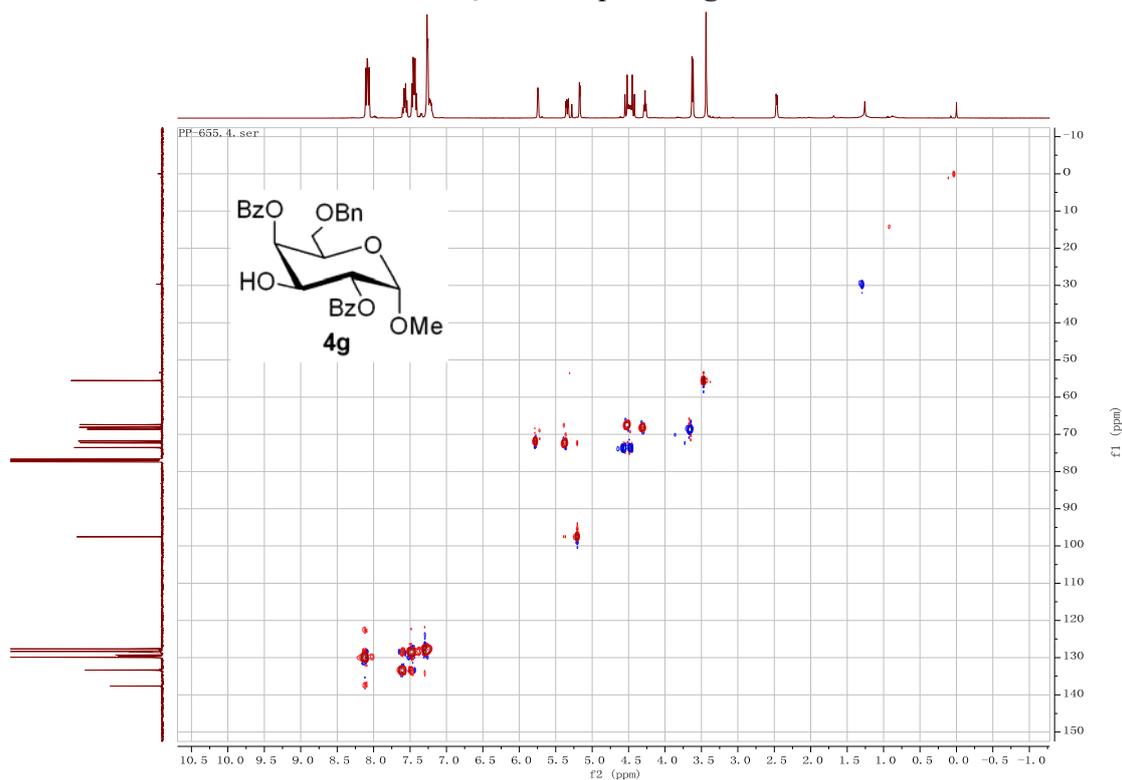
^1H spectrum of compound **4g** (400 MHz, CDCl_3)



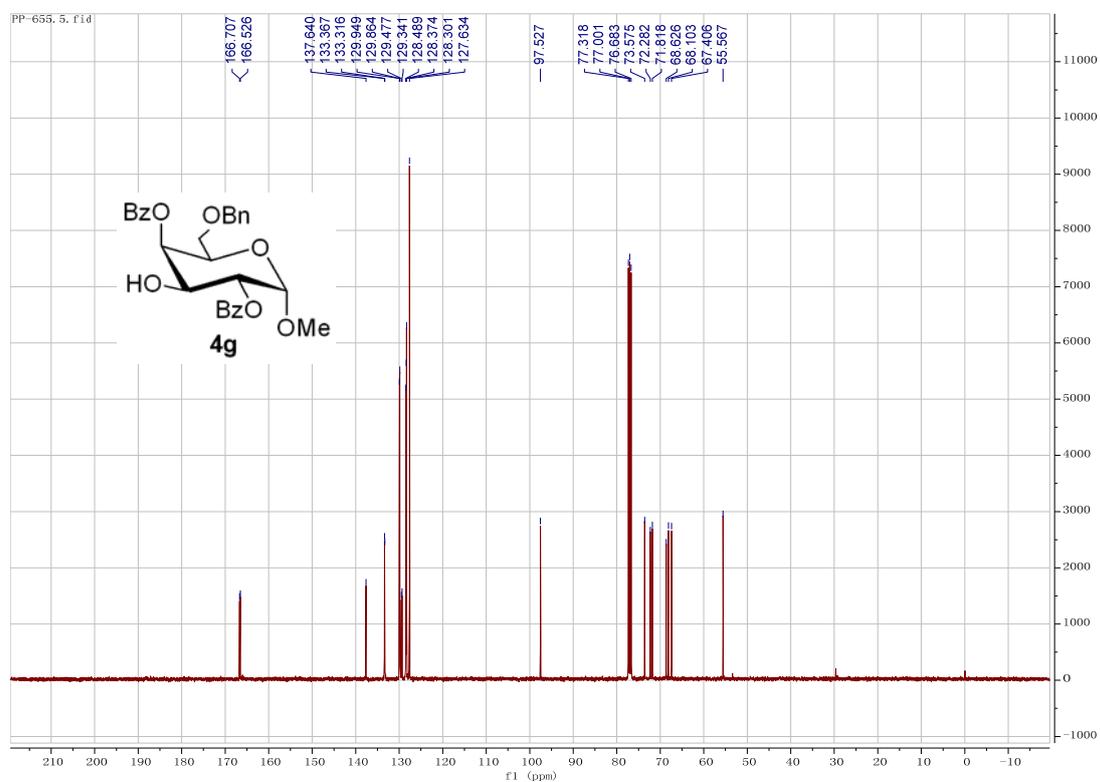
^1H - ^1H COSY of compound **4g**



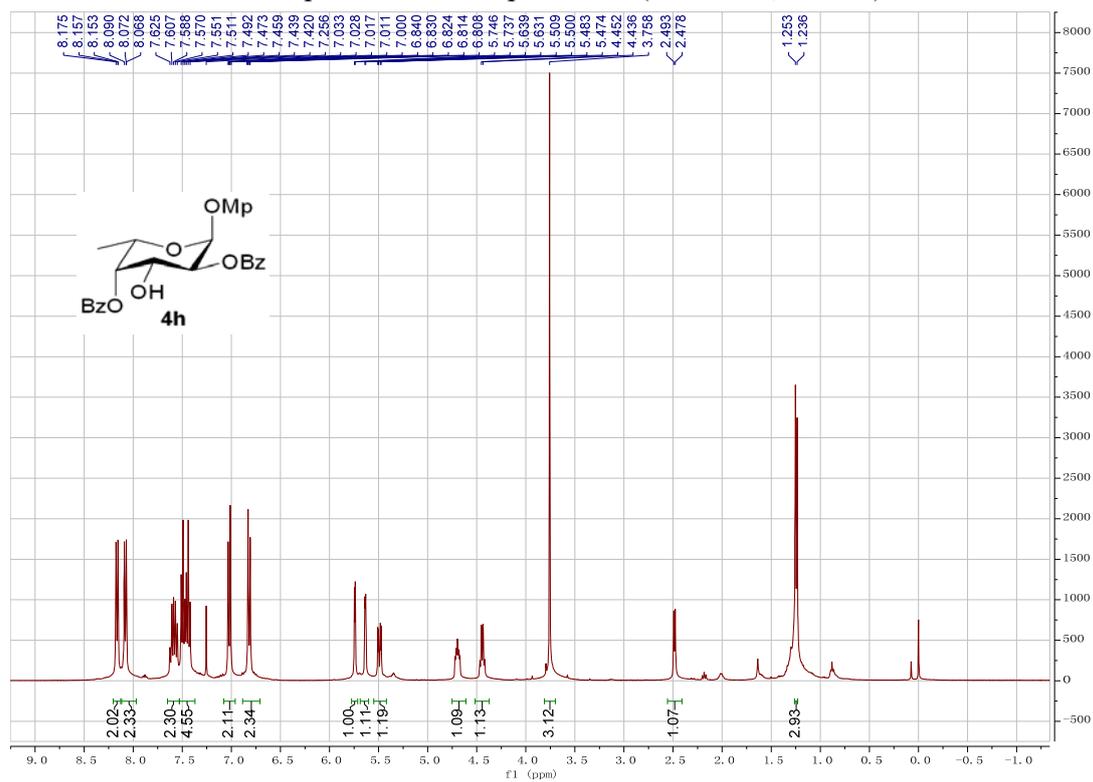
HSQC of compound 4g



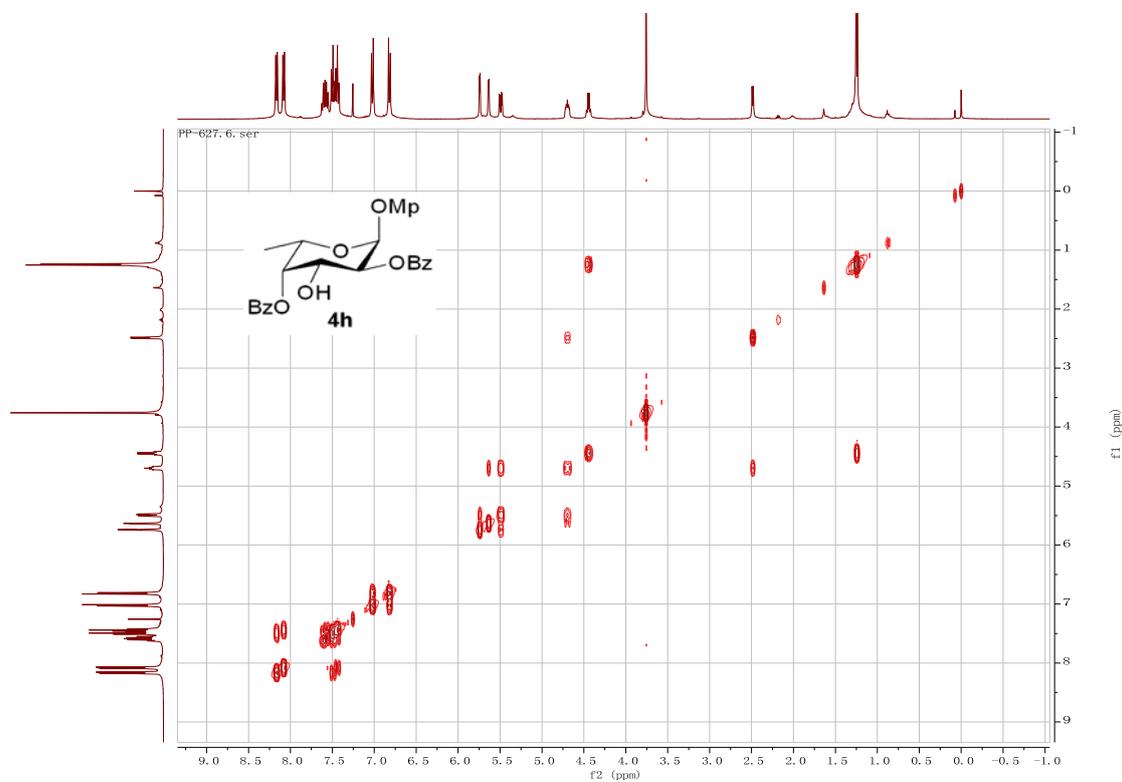
¹³C spectrum of compound 4g (100 MHz, CDCl₃)



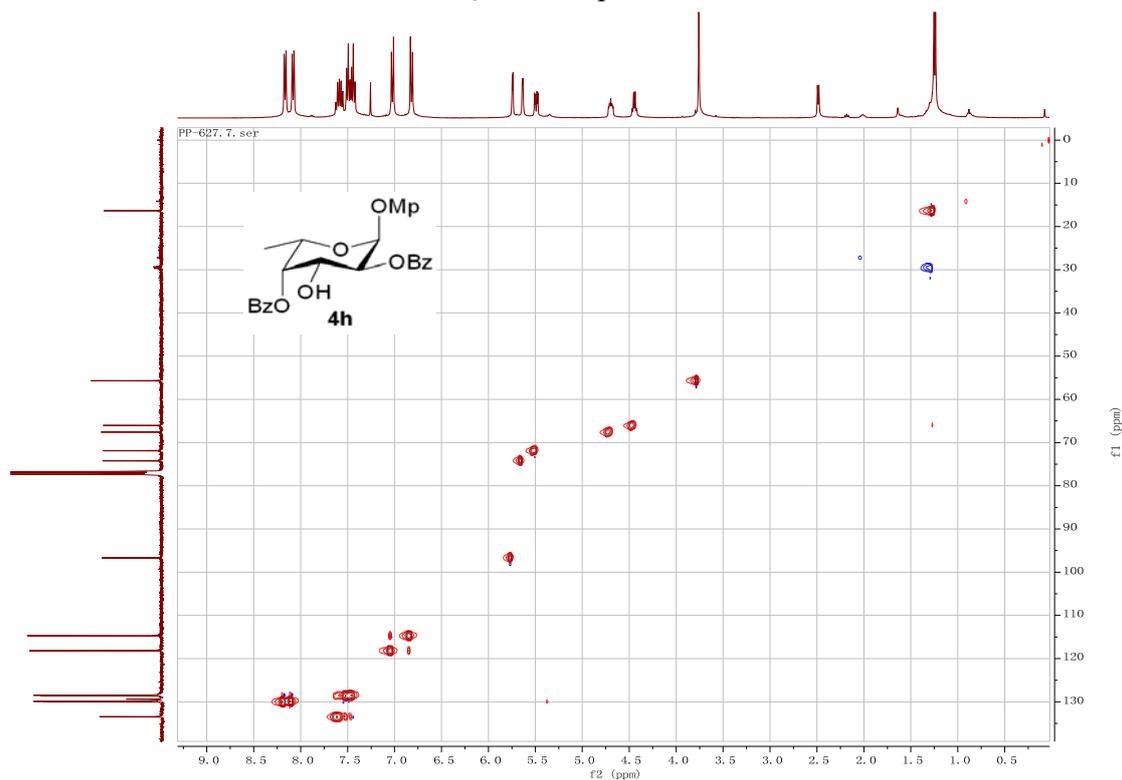
^1H spectrum of compound **4h** (400 MHz, CDCl_3)



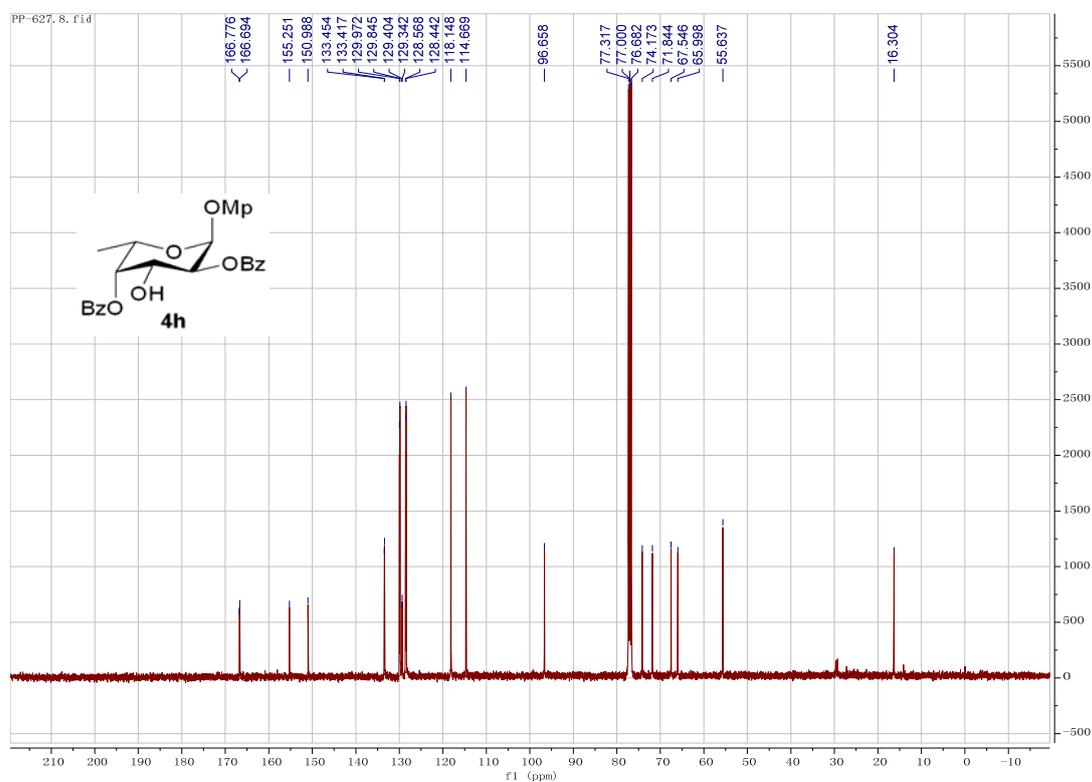
^1H - ^1H COSY of compound **4h**



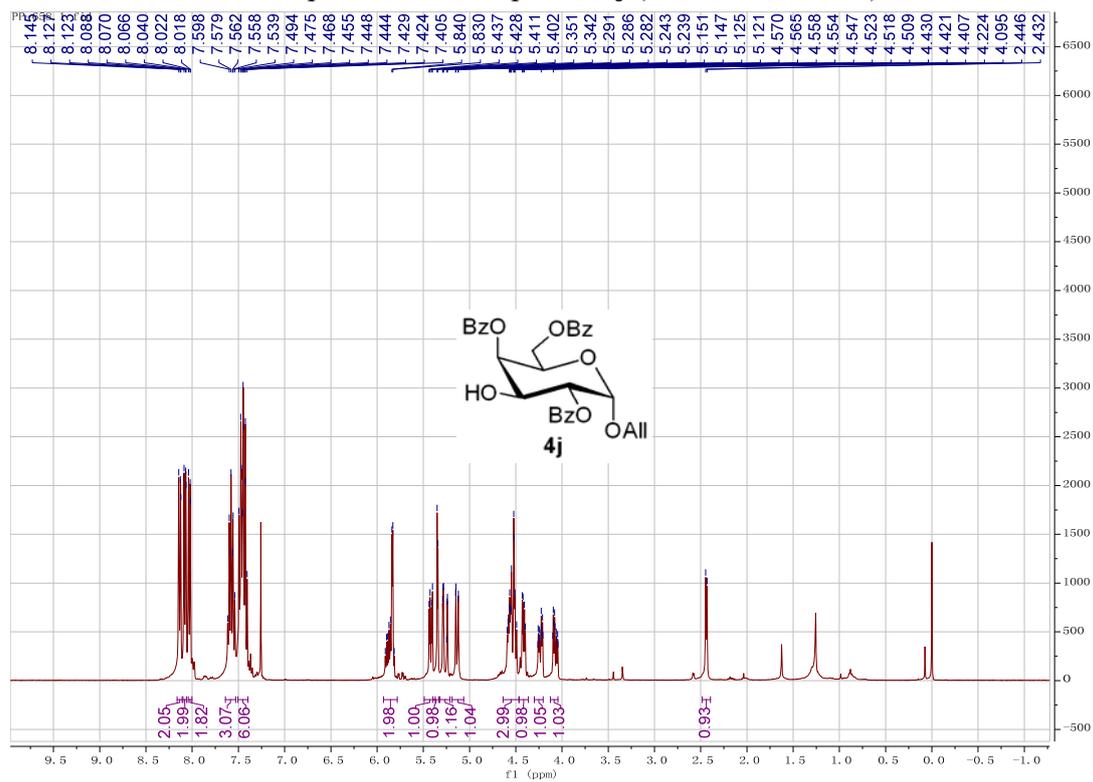
HSQC of compound 4h



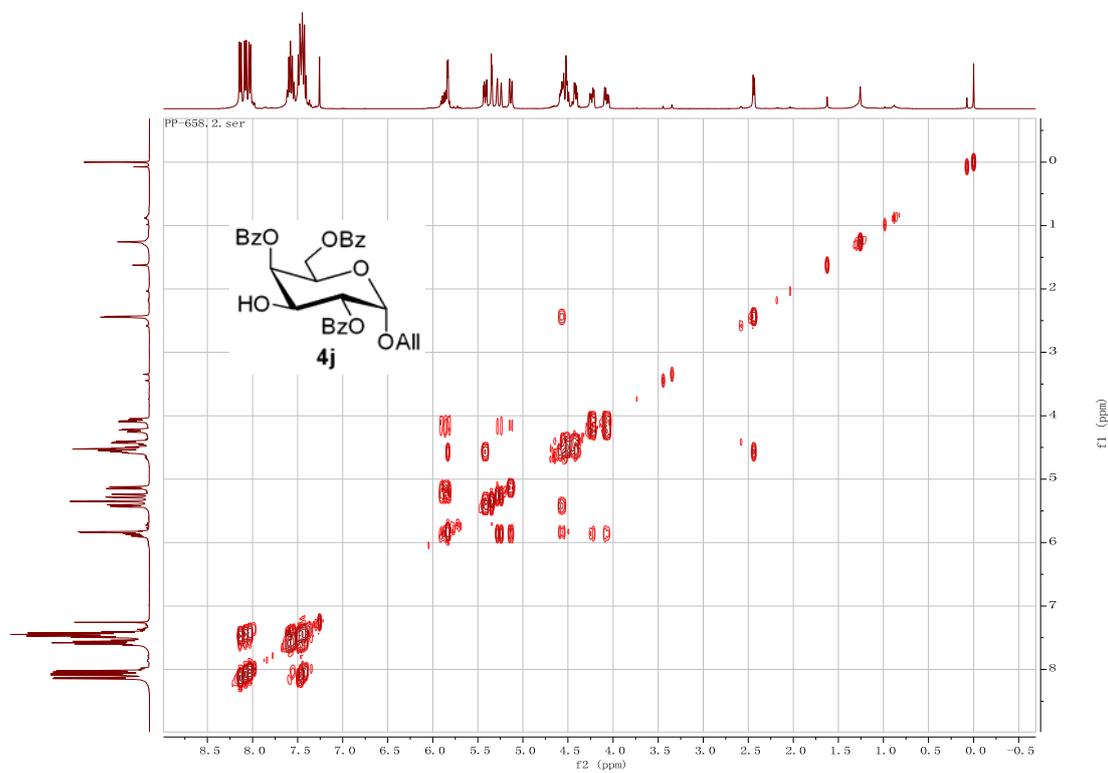
^{13}C spectrum of compound 4h (100 MHz, CDCl_3)



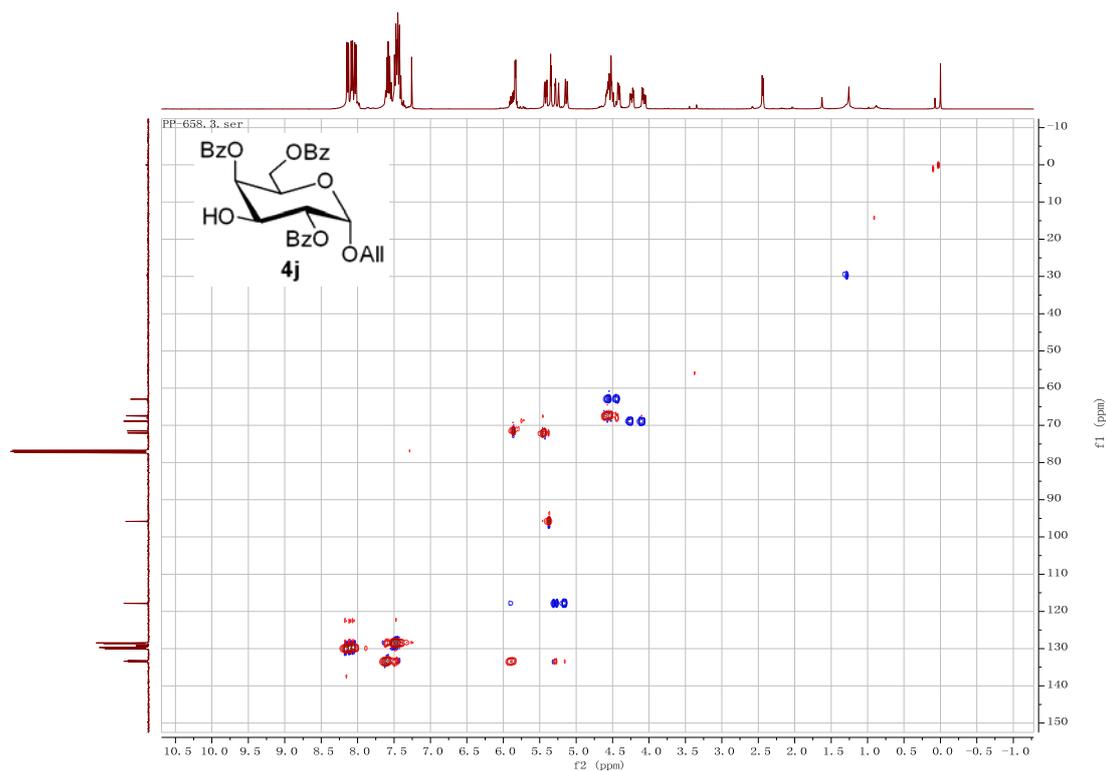
¹H spectrum of compound **4j** (400 MHz, CDCl₃)



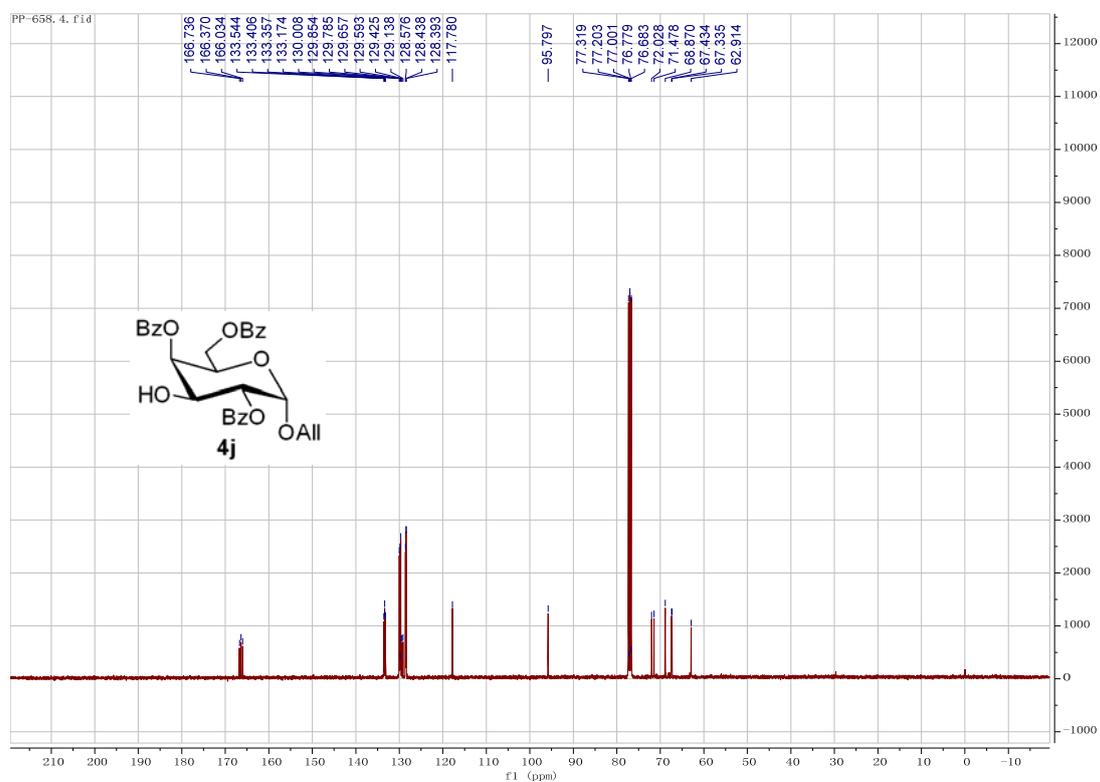
¹H-¹H COSY of compound **4j**



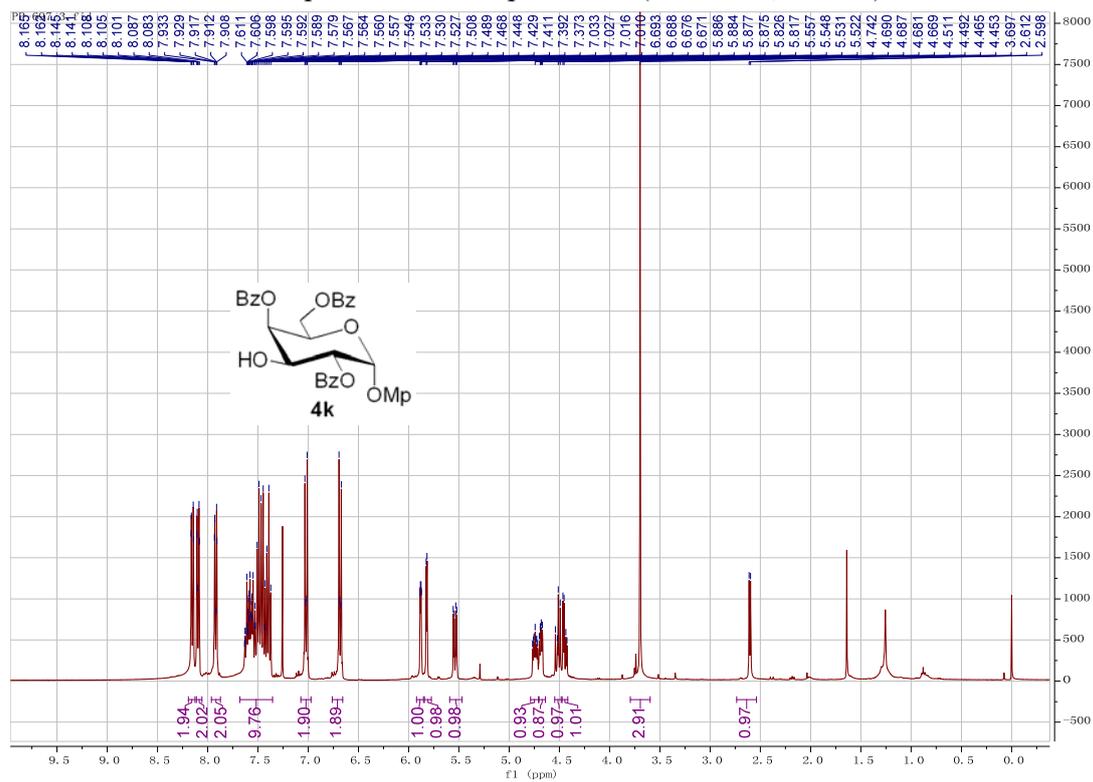
HSQC of compound 4j



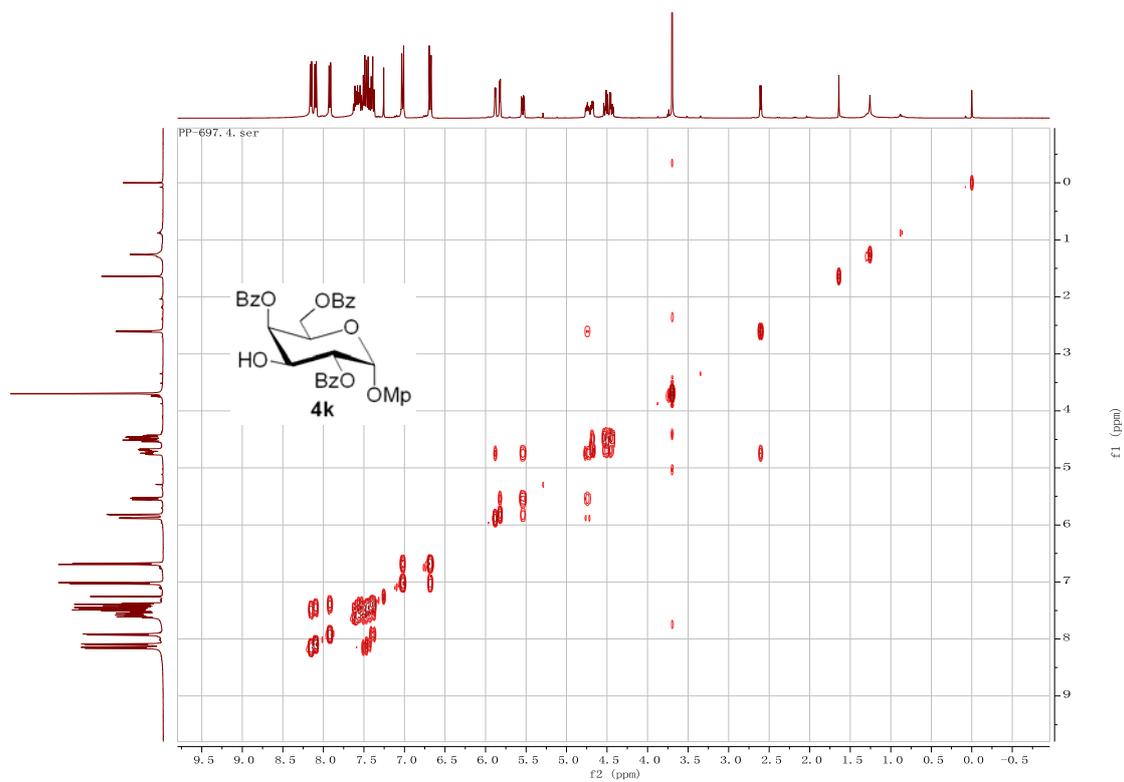
¹³C spectrum of compound 4j (100 MHz, CDCl₃)



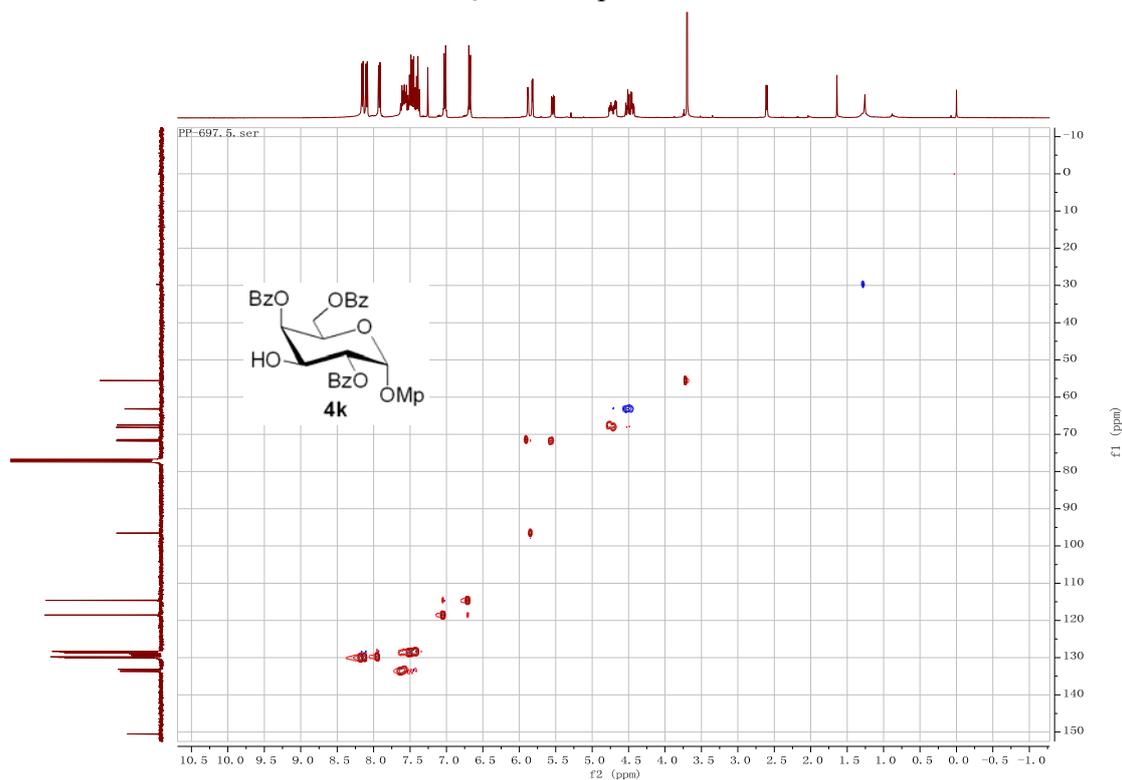
^1H spectrum of compound **4k** (400 MHz, CDCl_3)



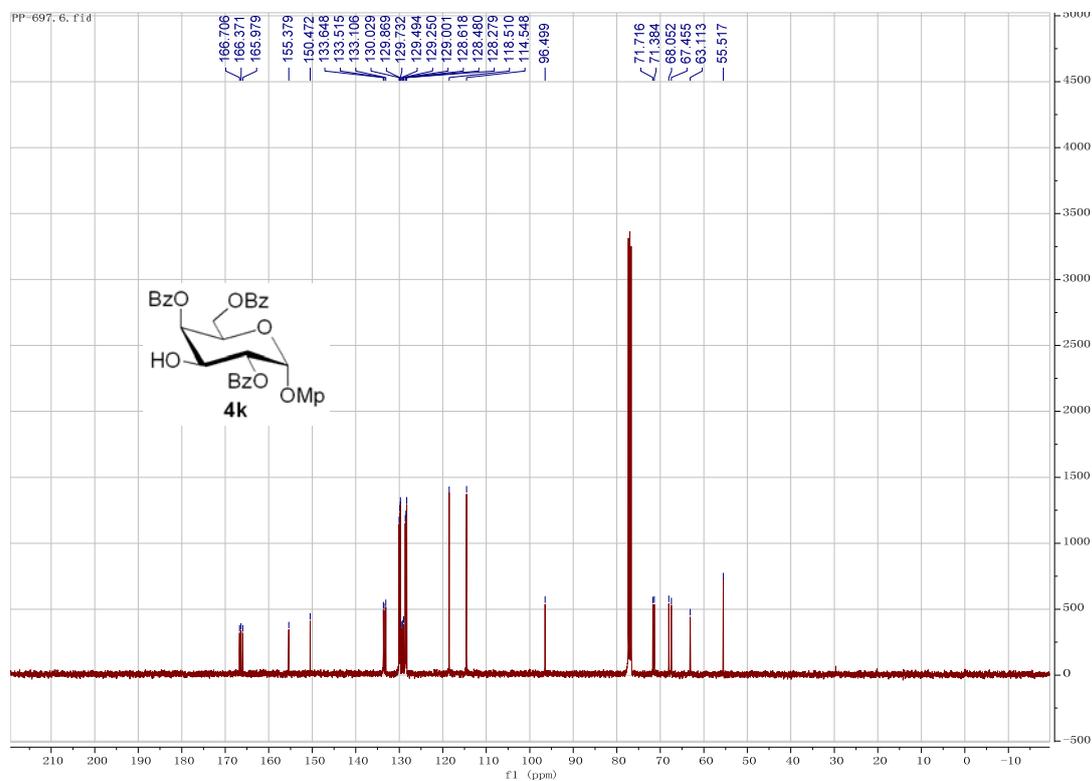
^1H - ^1H COSY of compound **4k**



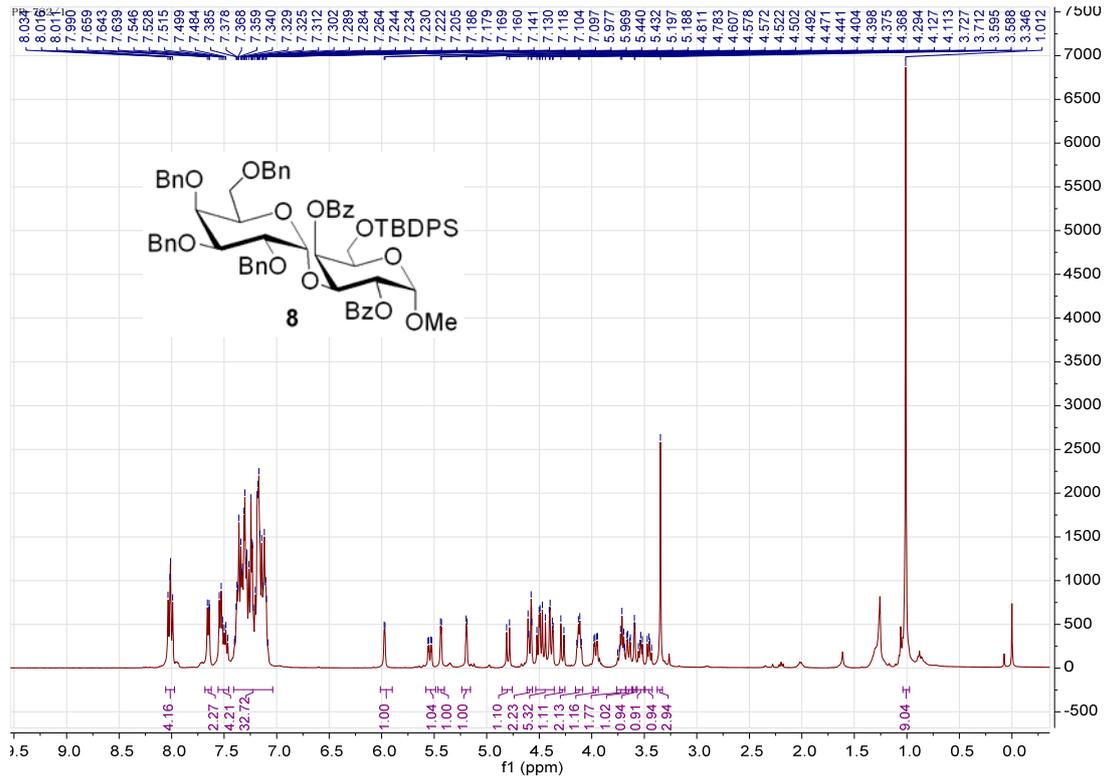
HSQC of compound 4k



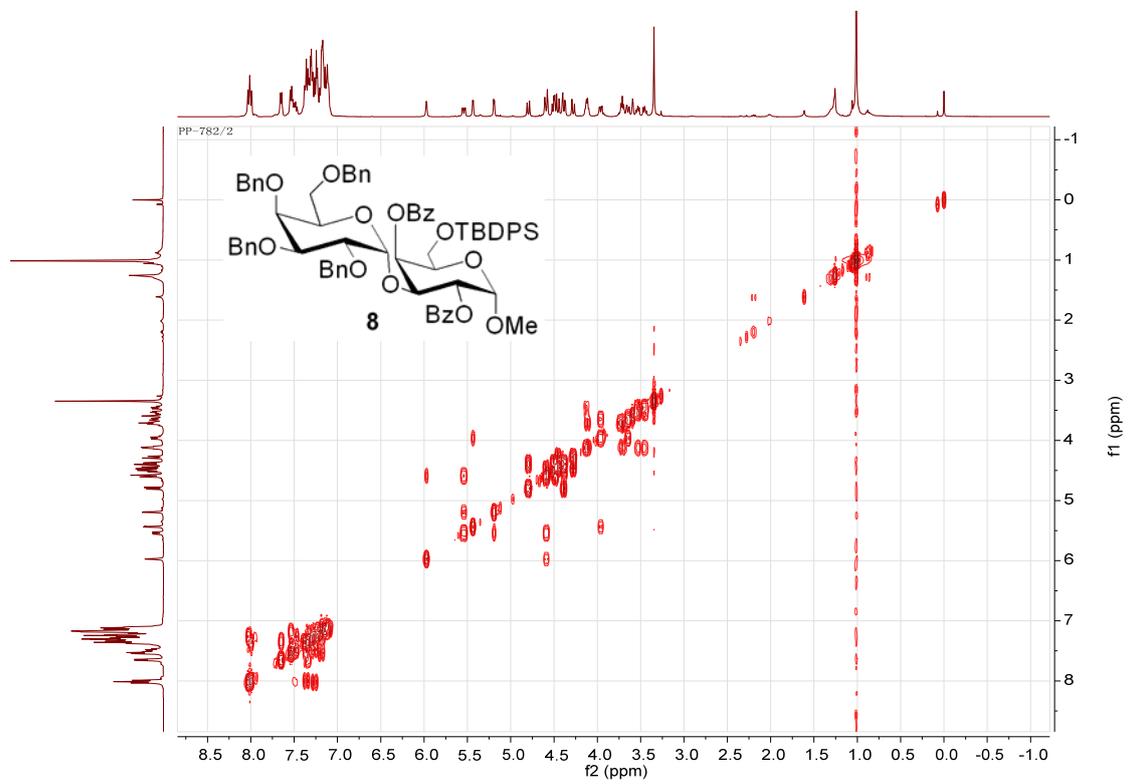
¹³C spectrum of compound 4k (100 MHz, CDCl₃)



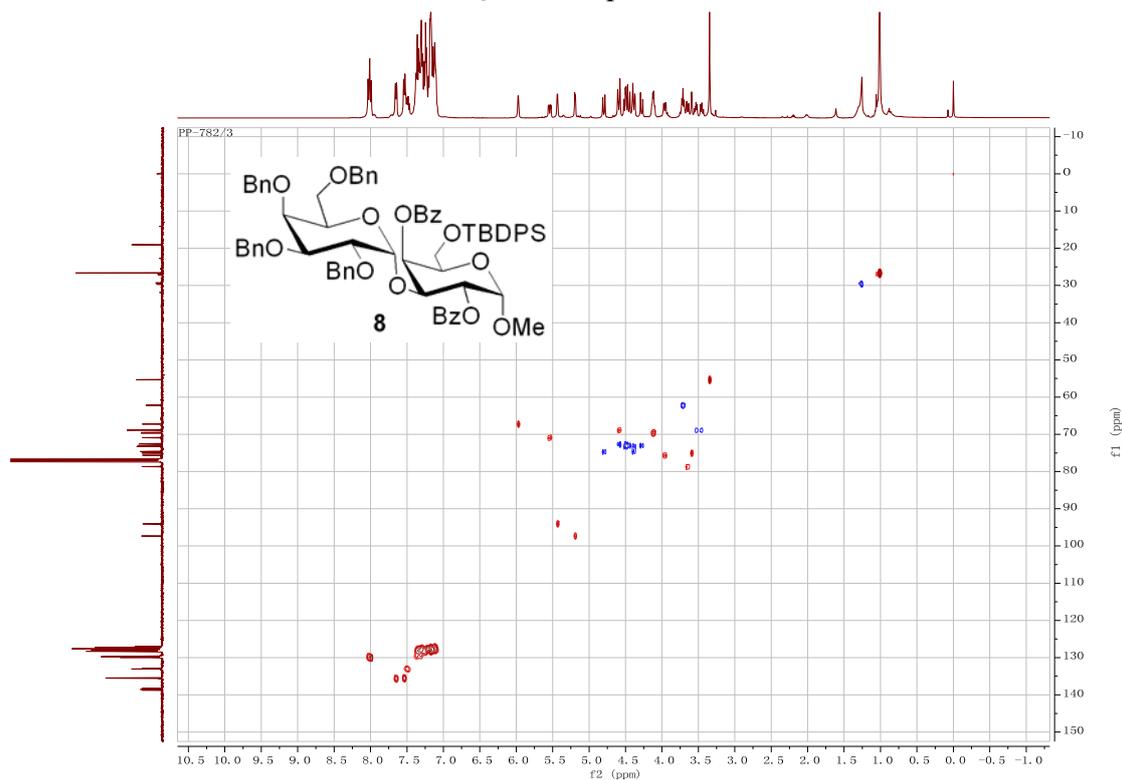
¹H spectrum of compound **8** (400 MHz, CDCl₃)



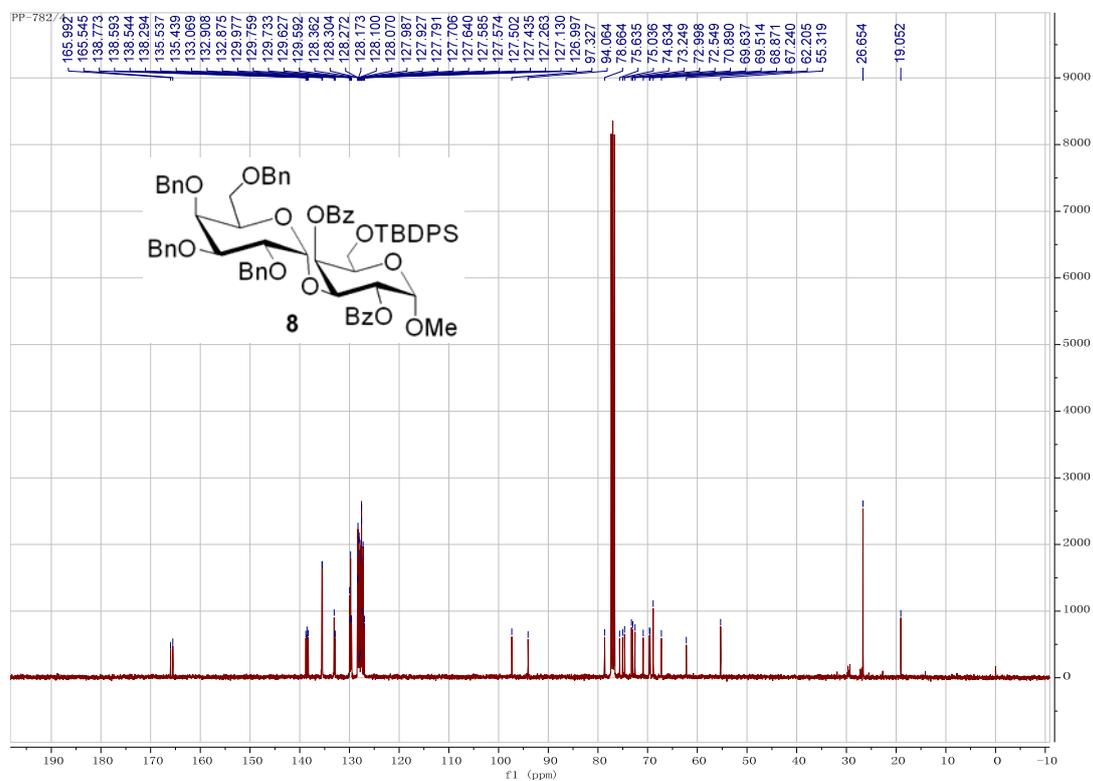
¹H-¹H COSY of compound **8**



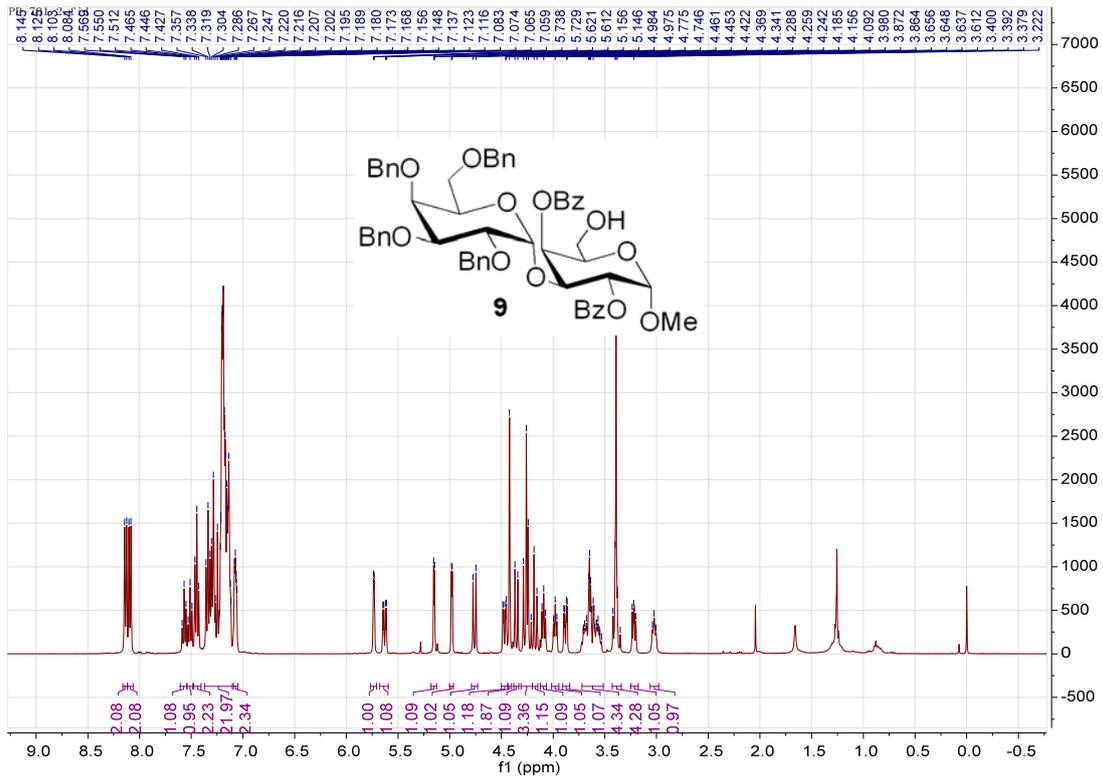
HSQC of compound 8



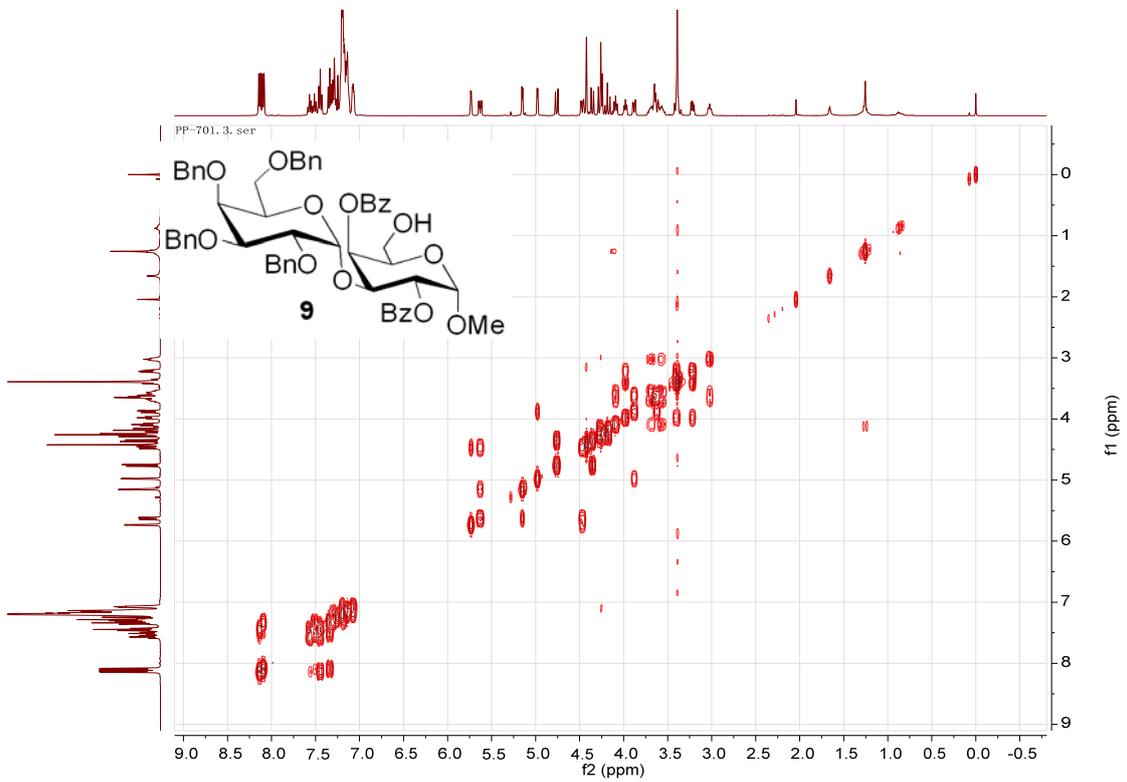
¹³C spectrum of compound 8 (100 MHz, CDCl₃)



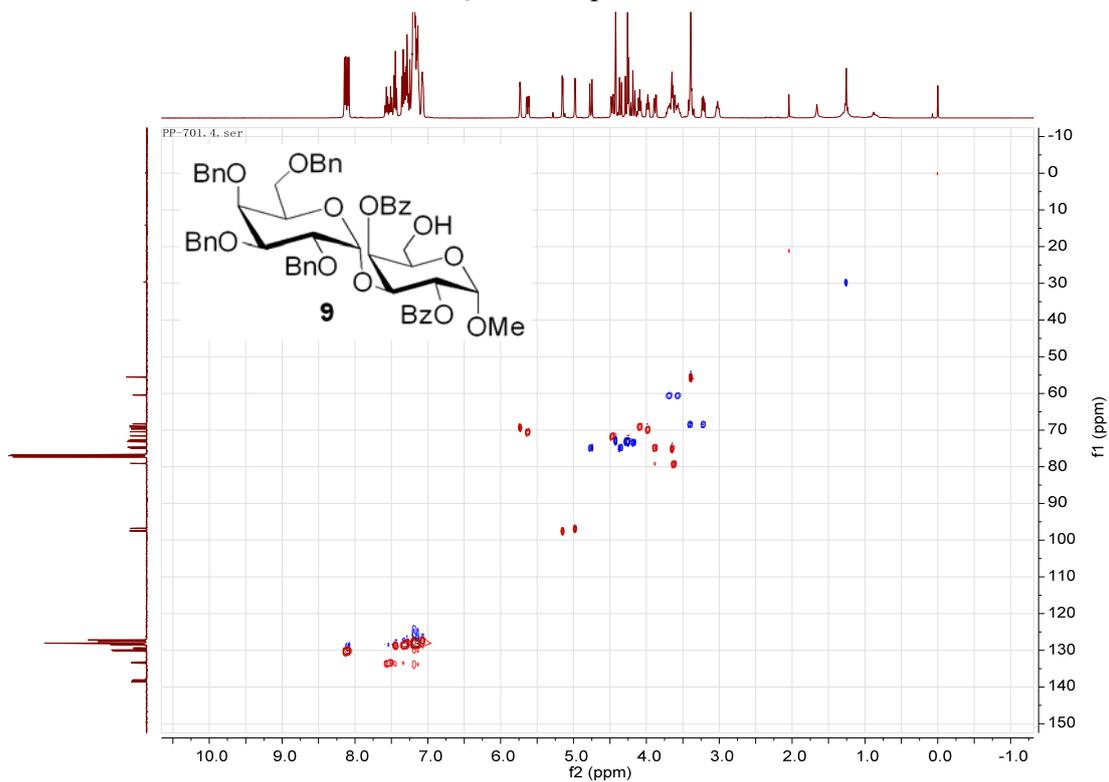
¹H spectrum of compound **9** (400 MHz, CDCl₃)



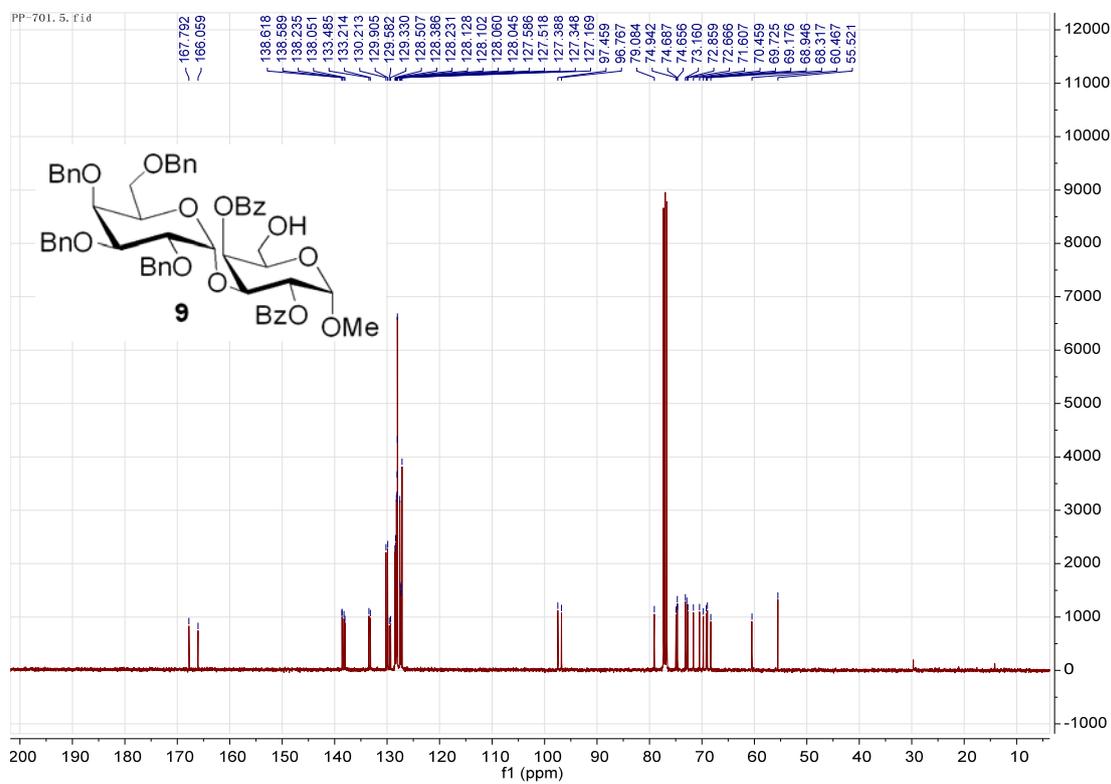
¹H-¹H COSY of compound **9**



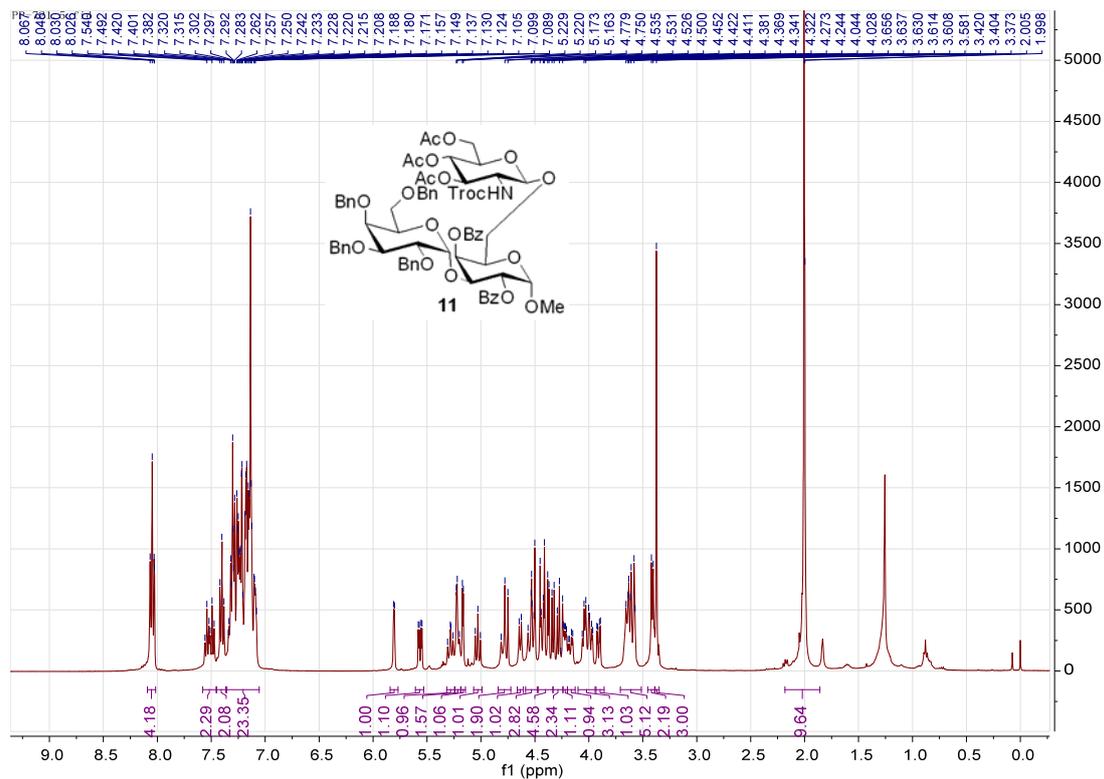
HSQC of compound 9



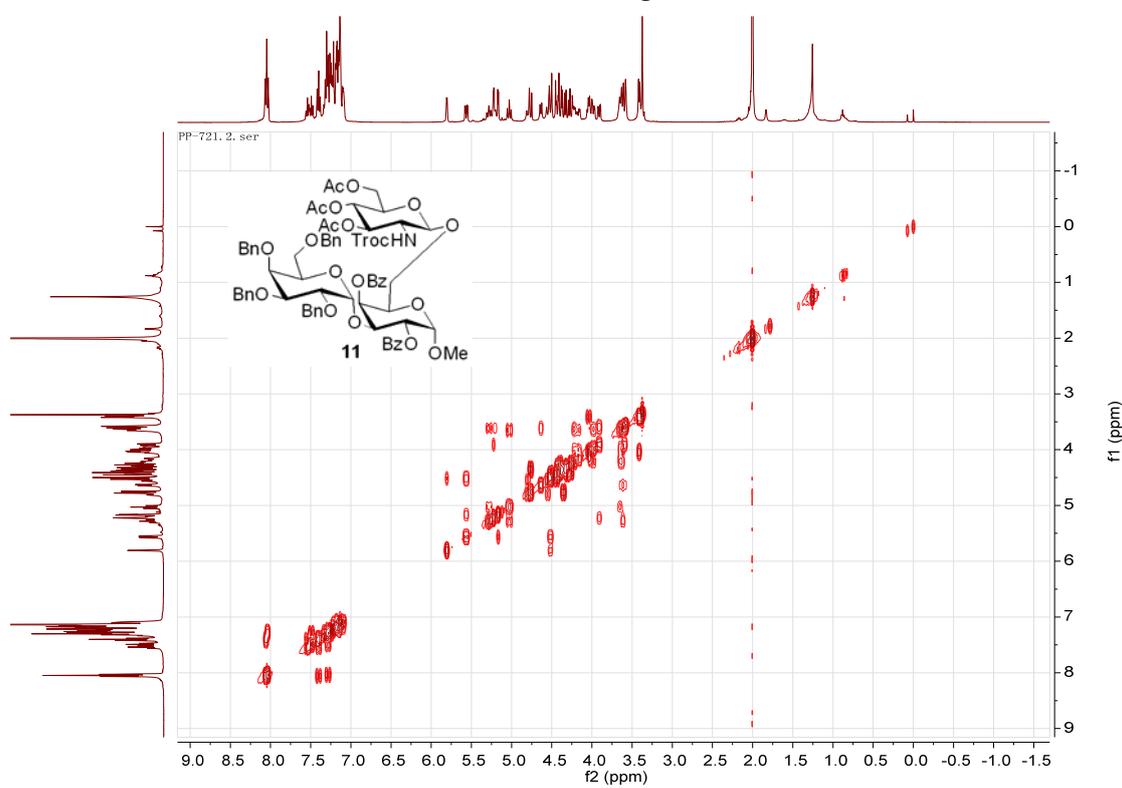
^{13}C spectrum of compound 9 (100 MHz, CDCl_3)



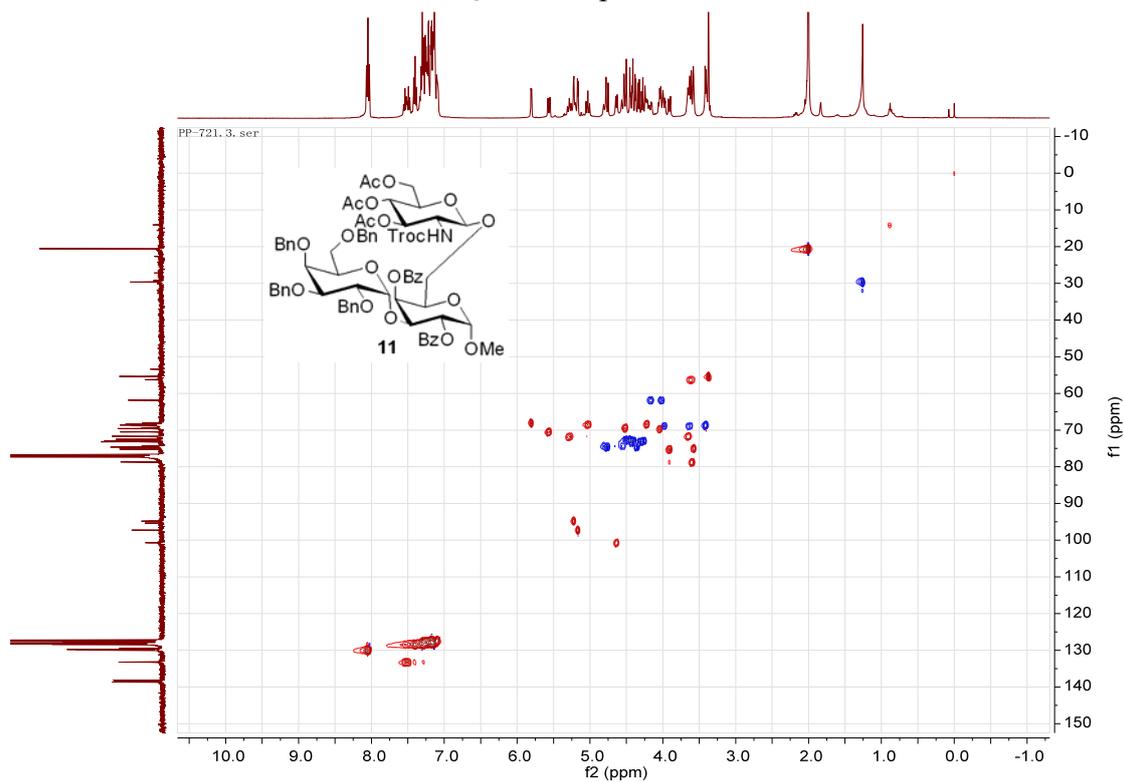
¹H spectrum of compound **11** (400 MHz, CDCl₃)



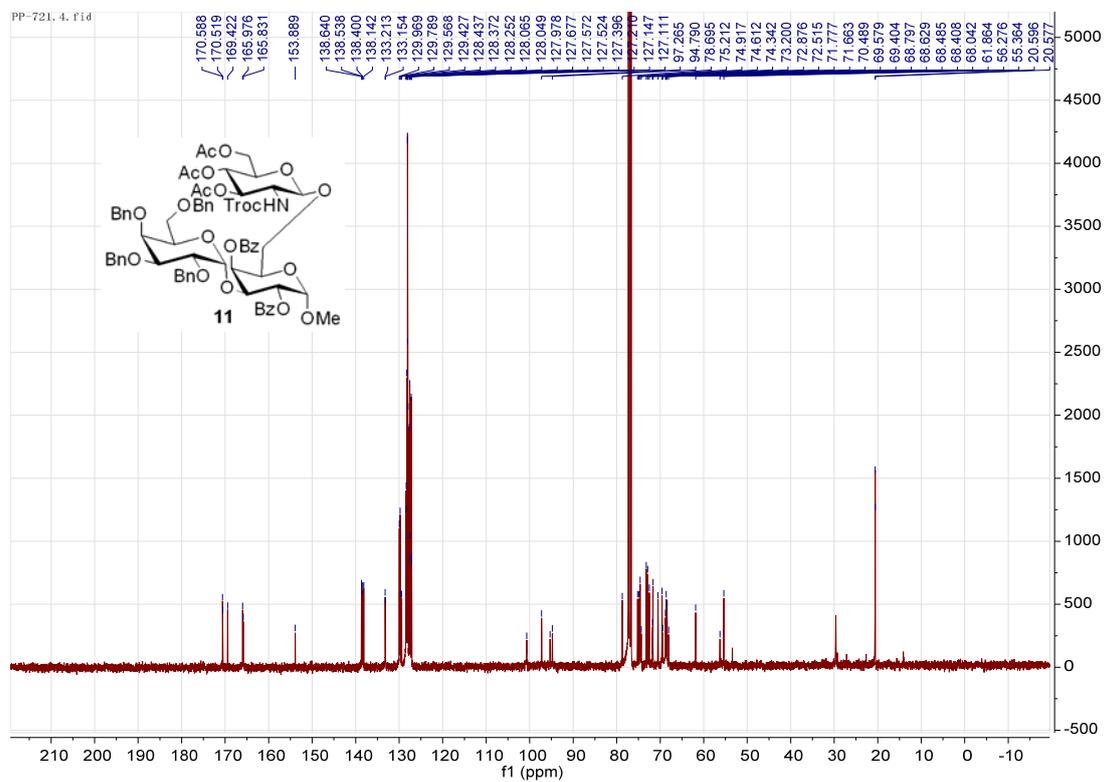
¹H-¹H COSY of compound **11**



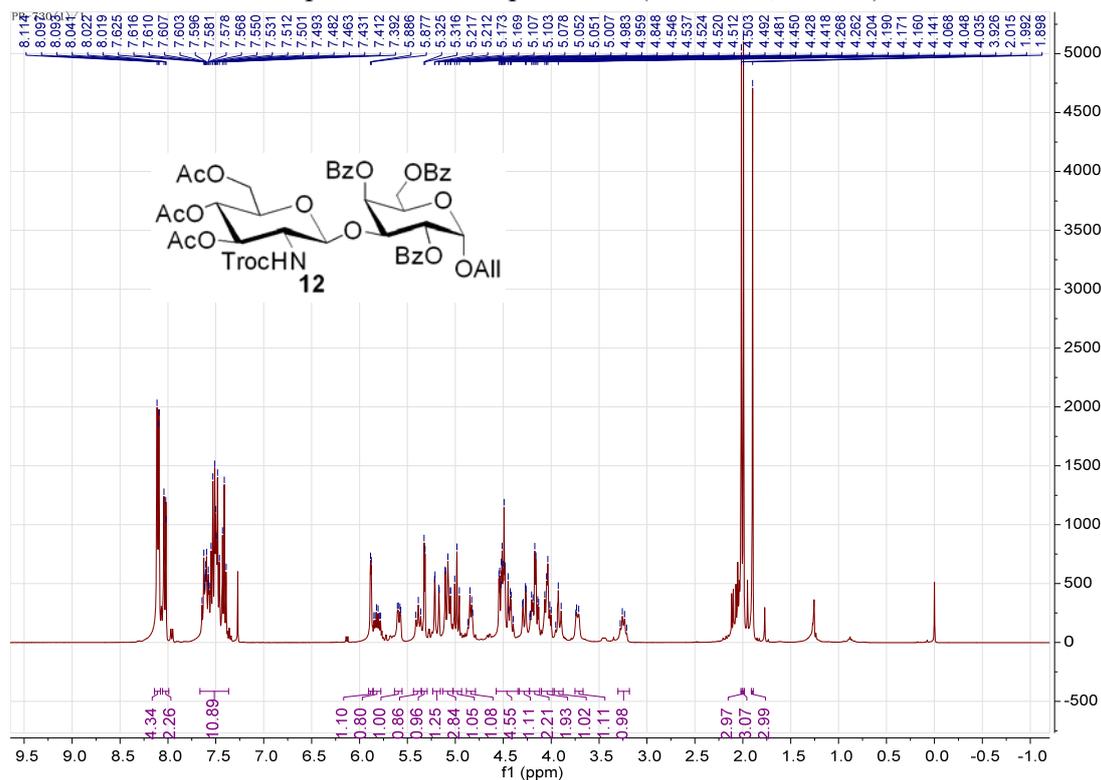
HSQC of compound 11



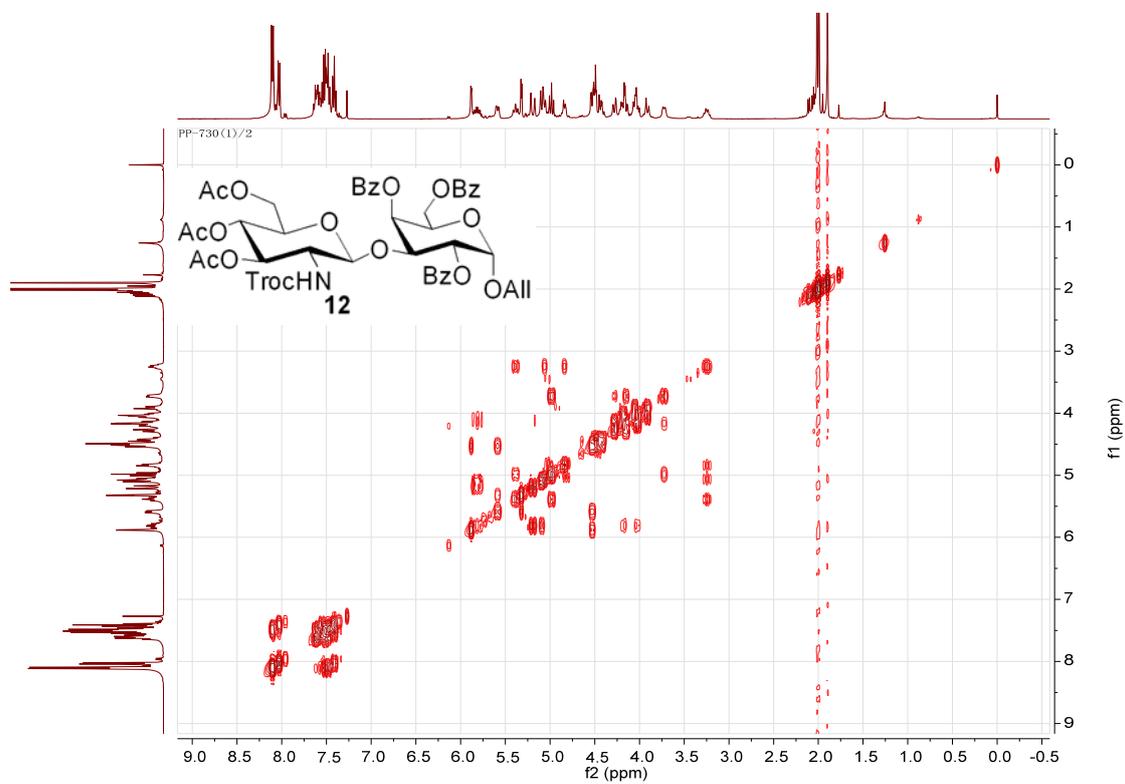
¹³C spectrum of compound 11 (100 MHz, CDCl₃)



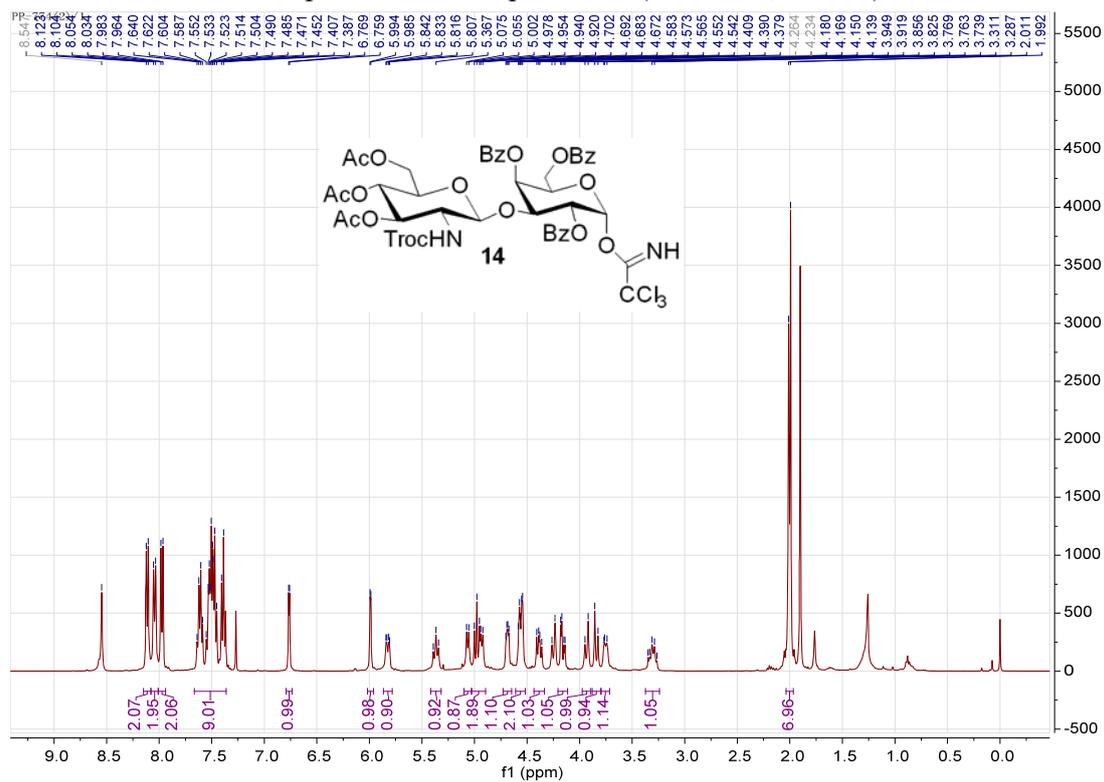
¹H spectrum of compound **12** (400 MHz, CDCl₃)



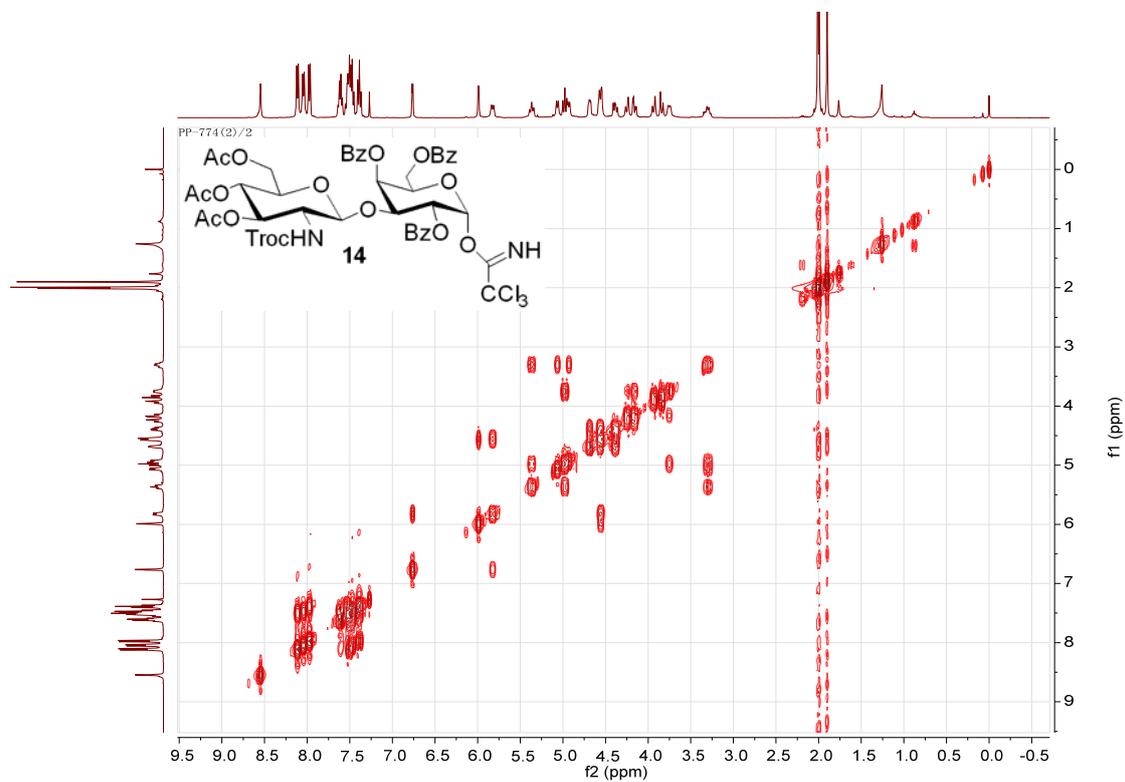
¹H-¹H COSY of compound **12**



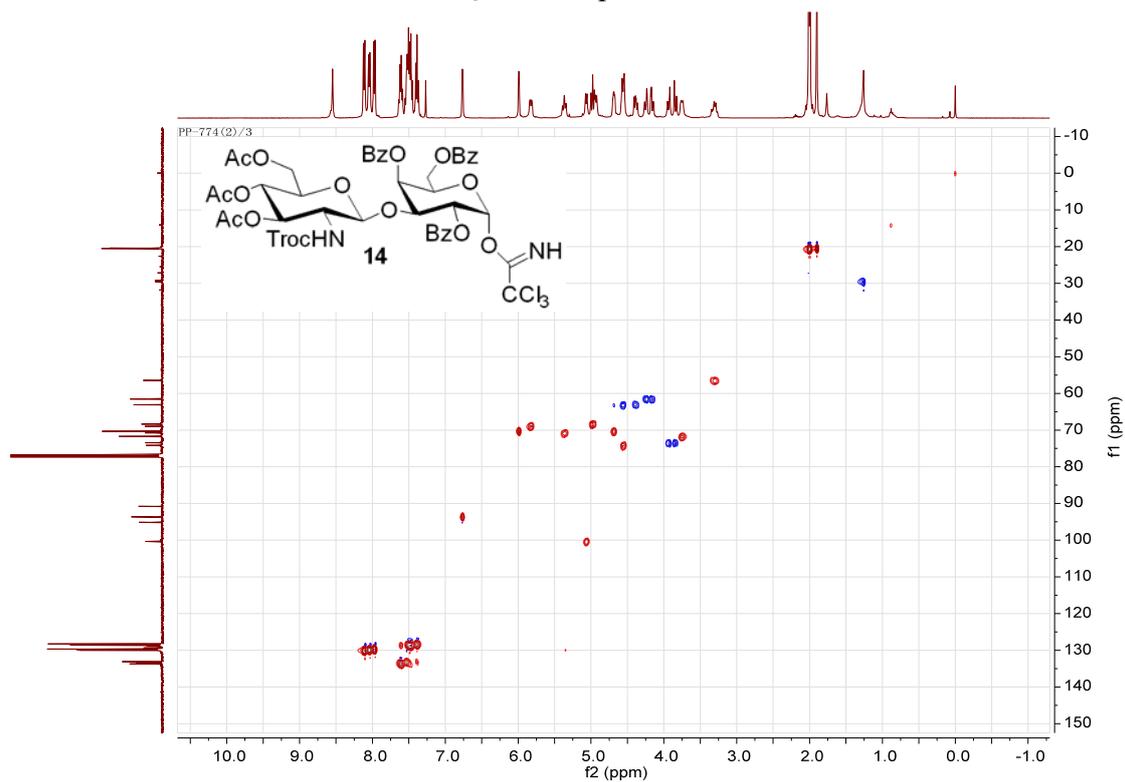
¹H spectrum of compound 14 (400 MHz, CDCl₃)



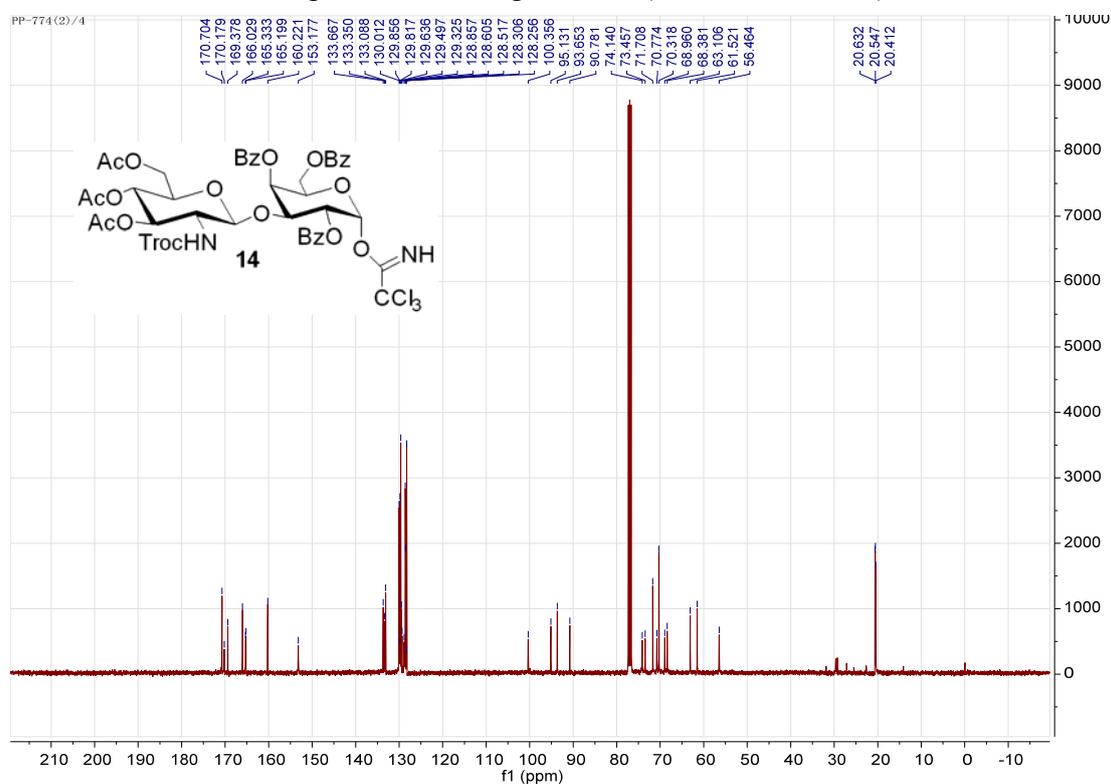
¹H-¹H COSY of compound 14



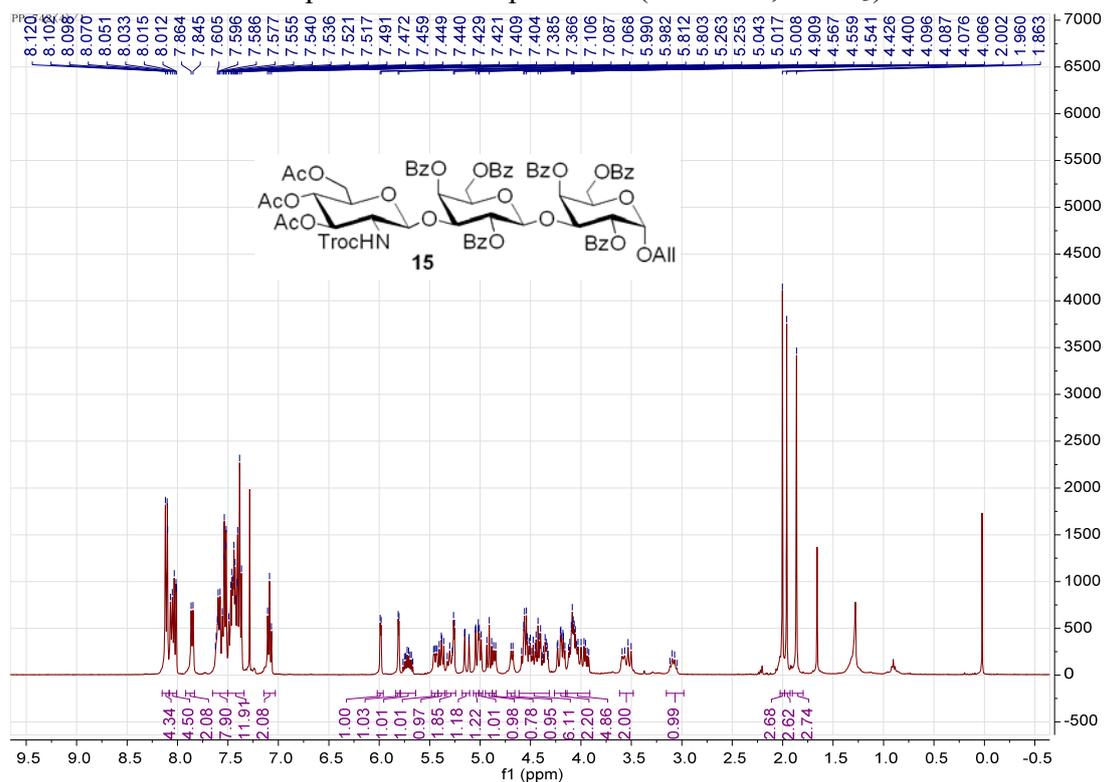
HSQC of compound 14



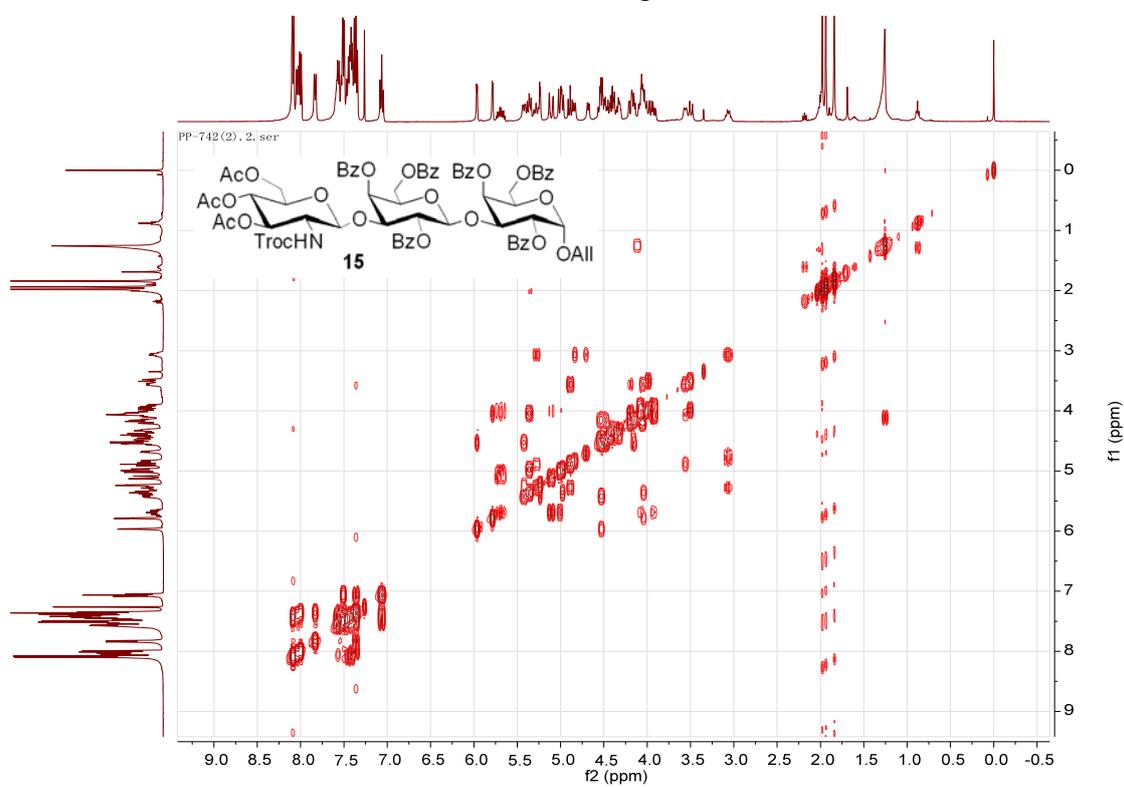
^{13}C spectrum of compound 14 (100 MHz, CDCl_3)



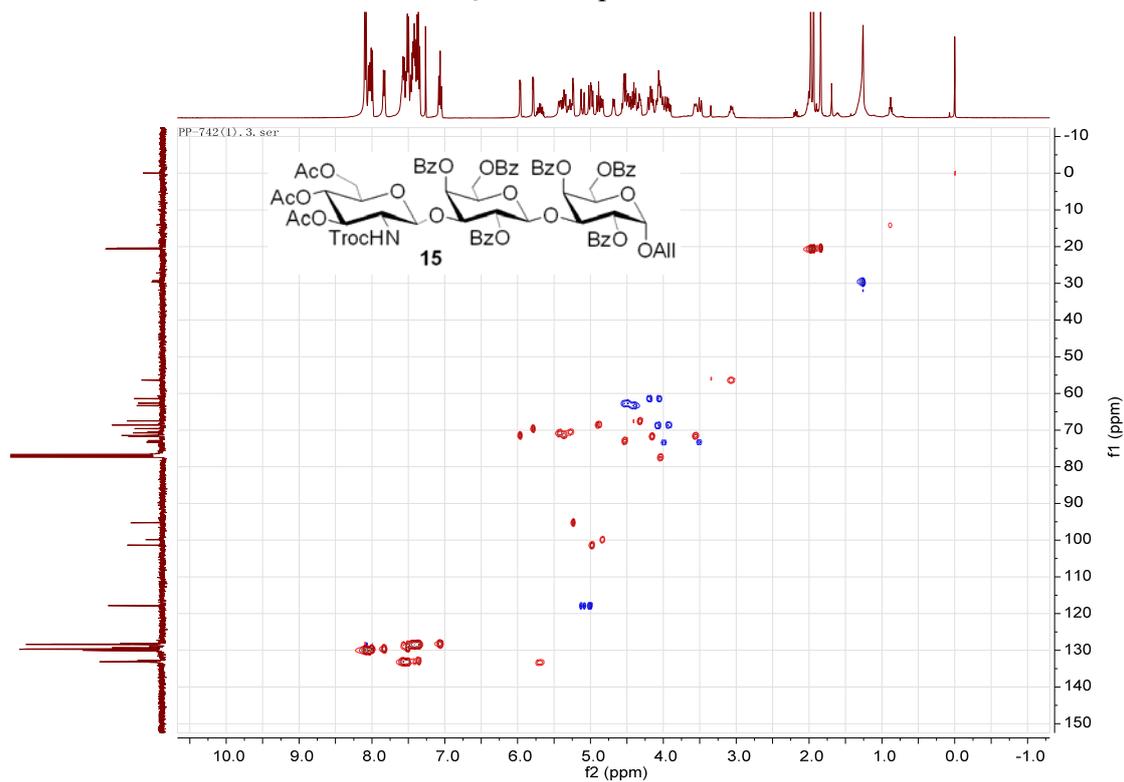
¹H spectrum of compound 15 (400 MHz, CDCl₃)



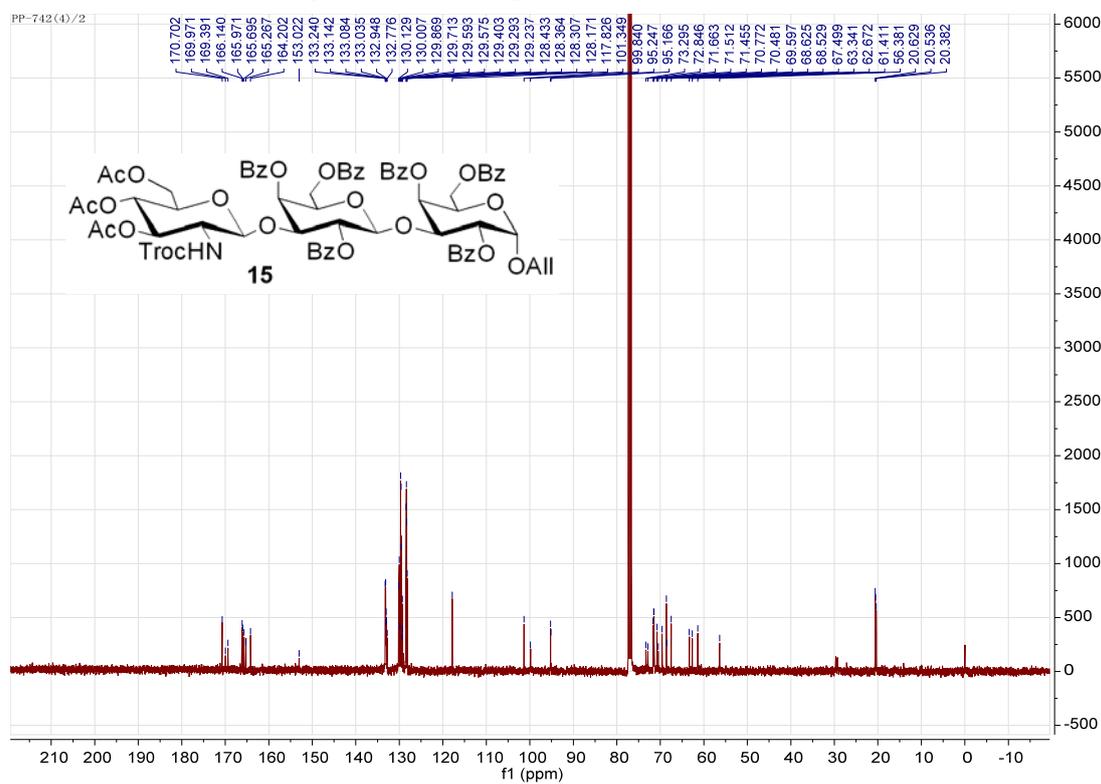
¹H-¹H COSY of compound 15



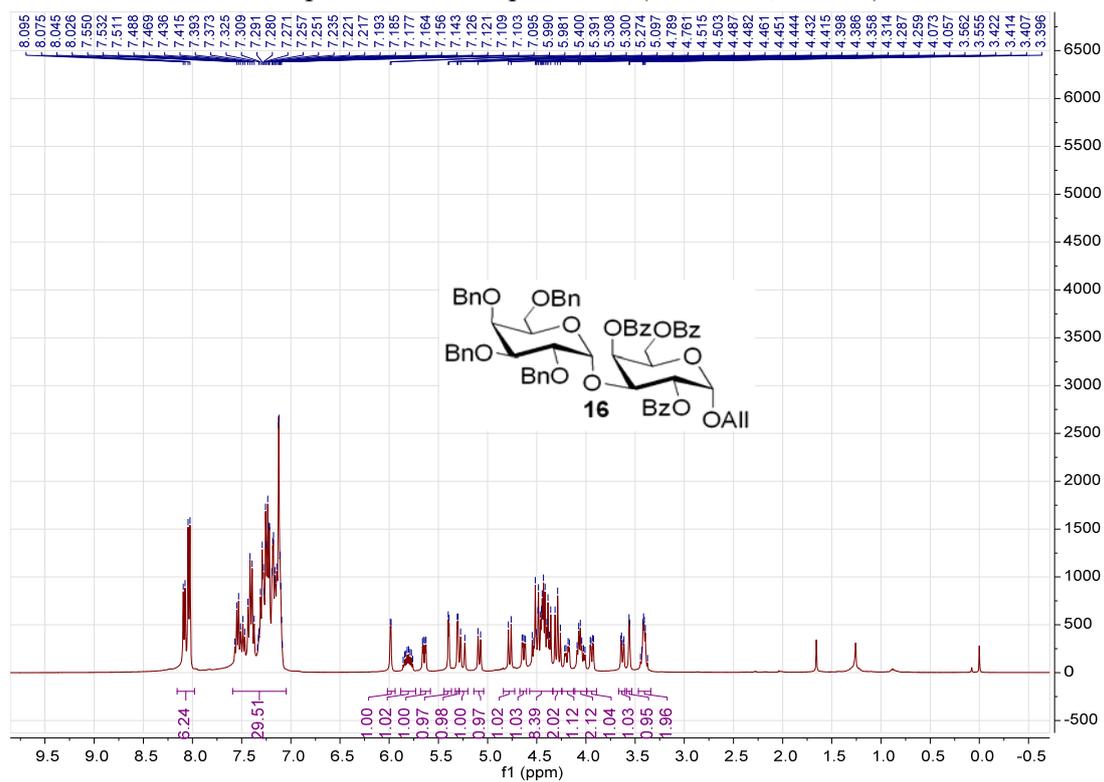
HSQC of compound 15



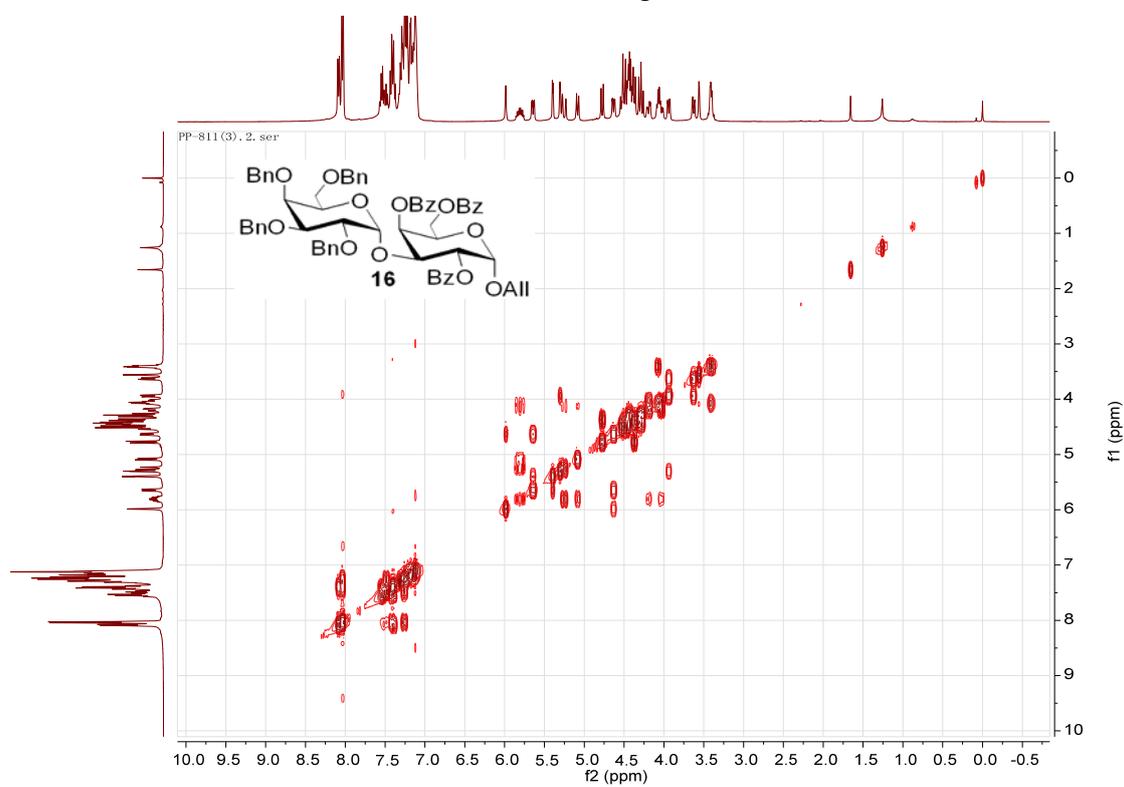
¹³C spectrum of compound 15 (100 MHz, CDCl₃)



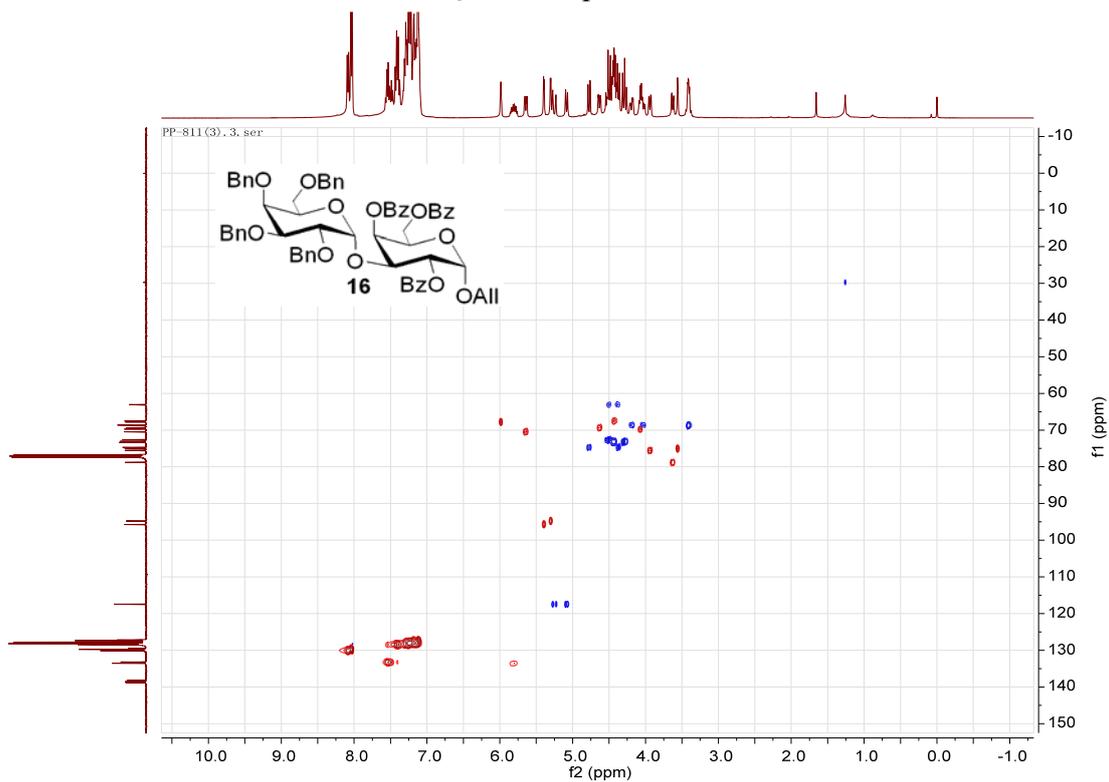
¹H spectrum of compound 16 (400 MHz, CDCl₃)



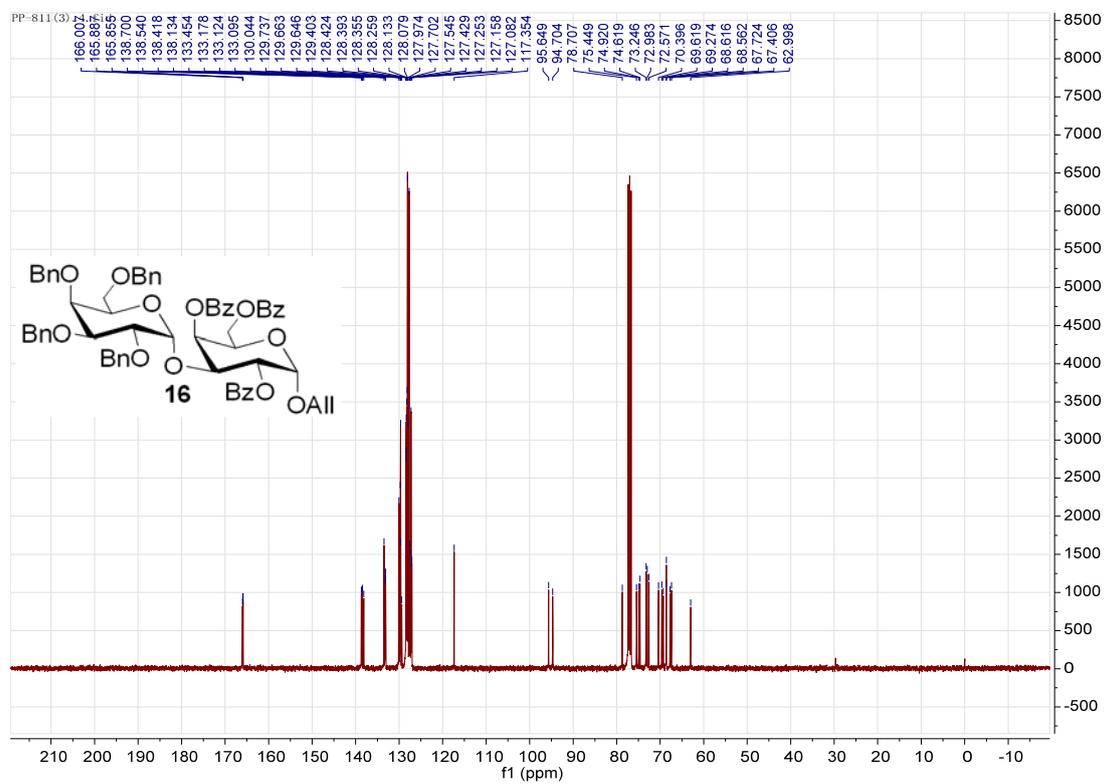
¹H-¹H COSY of compound 16



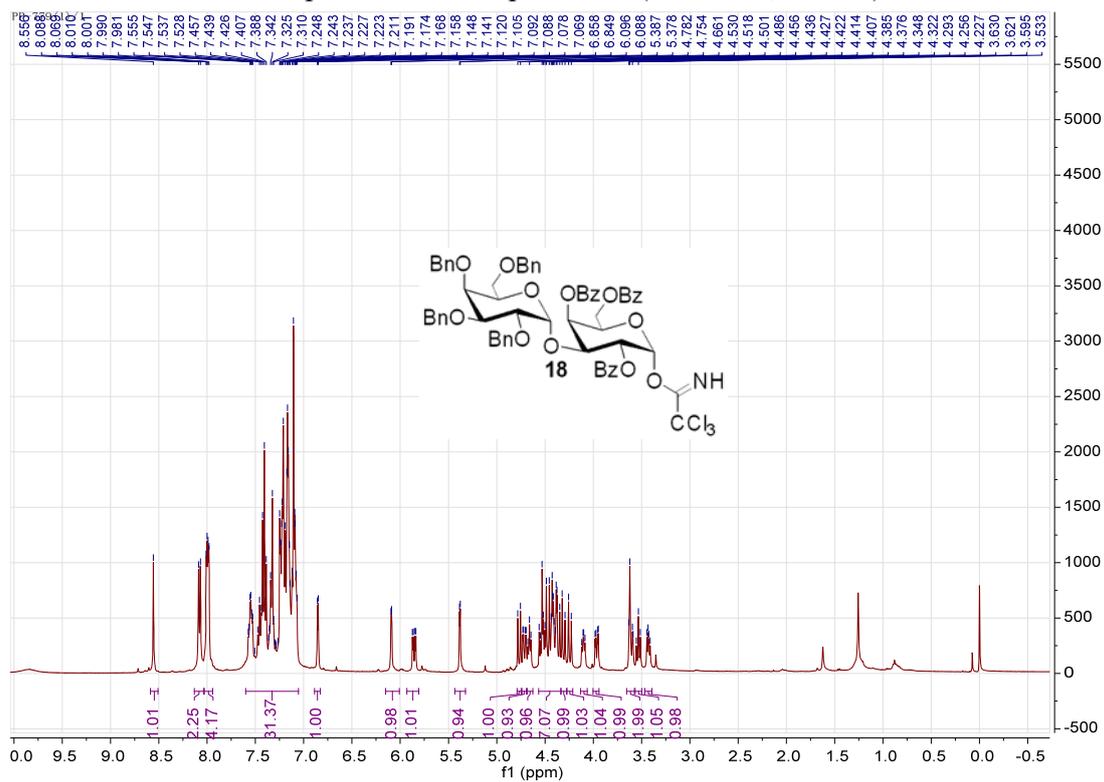
HSQC of compound 16



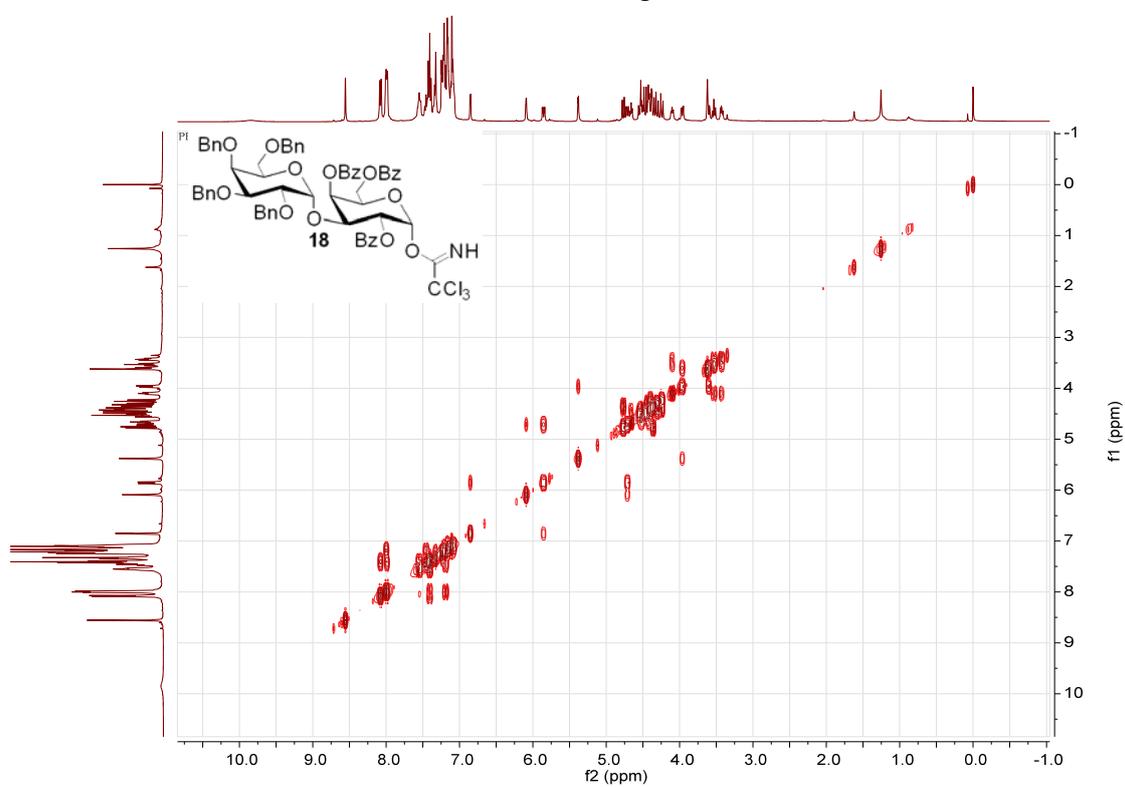
¹³C spectrum of compound 16 (100 MHz, CDCl₃)



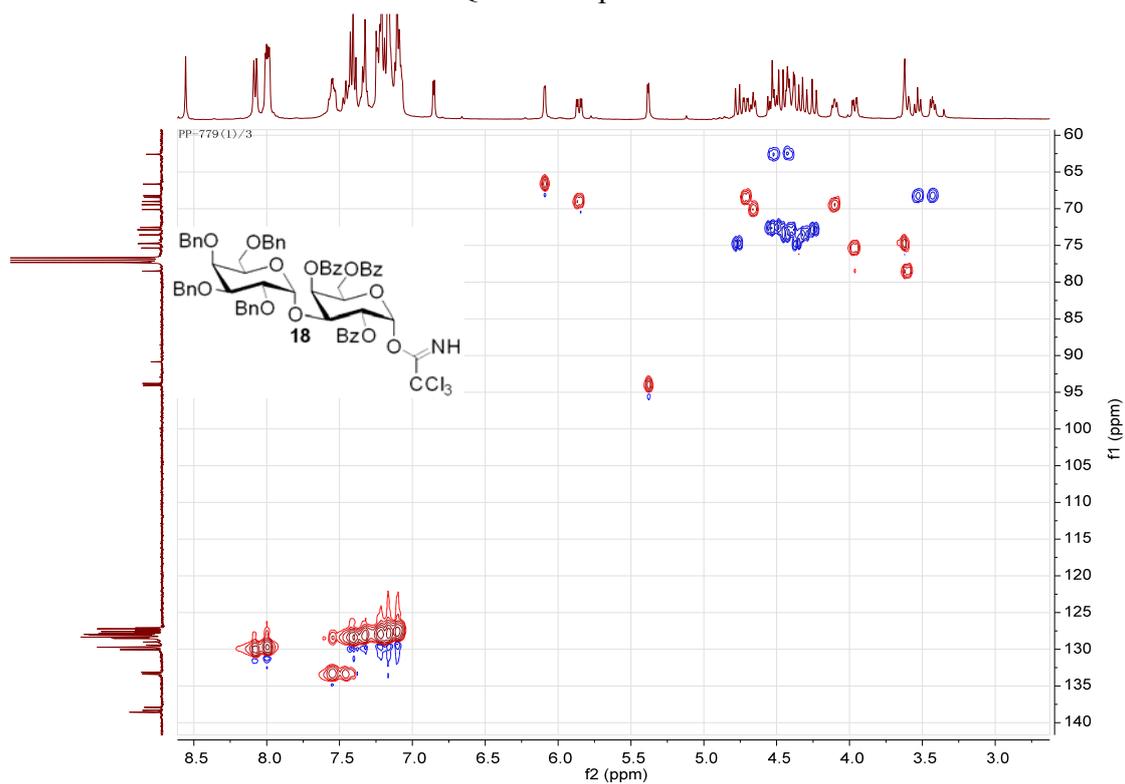
^1H spectrum of compound **18** (400 MHz, CDCl_3)



^1H - ^1H COSY of compound **18**



HSQC of compound 18



¹³C spectrum of compound 18 (100 MHz, CDCl₃)

