Supporting Information for

Regioselective Benzoylation of Unprotected β-Glycopyranosides with Benzoyl Cyanide and an Amine Catalyst – Application to Saponin Synthesis

Tianlu Li,*[a,b] Tong Li,[a] Yajing Sun,[a] Yue Yang,[a] Panpan Lv,[a] Fengshan Wang,[a,b] Hongxiang Lou,[a,b] Richard R. Schmidt*[c] and Peng Peng* [a,b]

[a]*National Glycoengineering Research Center, Shandong University, Jinan, 250012, Shandong, China.*

[b]*Key Laboratory of Chemical Biology (Ministry of Education), Institute of Biochemical and Biotechnological Drugs, School of Pharmaceutical Sciences, Shandong University, Jinan, 250012, Shandong, China*

[c]*Department of Chemistry, University of Konstanz, Konstanz D-78457, Germany*

Email: richard.schmidt@uni-konstanz.de and pengpeng@sdu.edu.cn.

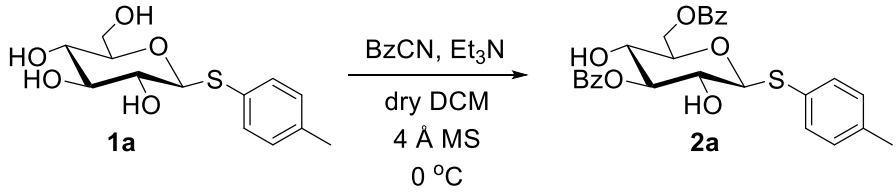
Table of Content

Experimental Section

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. ^{1}H NMR spectra were recorded on an Advance DRX Bruker-400 MHz and 600 MHz spectrometer at 25℃. High-resolution mass spectrometry was performed on a Thermo Electron LTQ-Orbitrap XL. 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 and away from light. 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.

(1) Procedures for Et_3N catalyzed cyanide-mediated regioselective benzoylation of unprotected β-D-glucopyranosides.

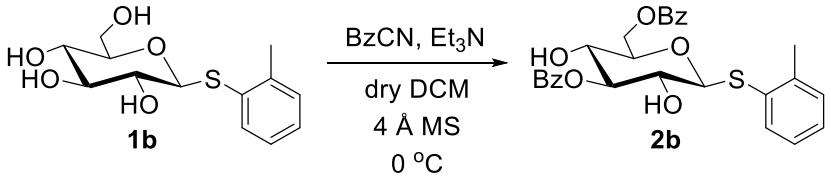


4-Methylphenyl 3,6-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (2a)[1-2]

To a solution of compound **1a** (30 mg, 104.9 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (28.2 mg, 215.0 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 10.8 μmol) was added. The reaction was further stirred for 9 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2a** (44.0 mg, 85%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 4H, Ar*H*), 7.62 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.56 (t, *J* = 7.5 Hz, 1H, Ar*H*), 7.51 – 7.39 (m, 6H, Ar*H*), 6.98 (d, *J* = 7.8 Hz, 2H, Ar*H*), 5.25 (t, *J* = 9.0 Hz, 1H,

3-H), 4.69 (d, *J* = 3.4 Hz, 2H), 4.61 (d, *J* = 9.7 Hz, 1H), 3.80 – 3.73 (m, 1H), 3.70 (td, *J* = 9.4, 4.5 Hz, 1H), 3.57 (td, *J* = 9.4, 2.6 Hz, 1H), 3.36 (d, *J* = 5.0 Hz, 1H), 2.75 (d, *J* = 3.1 Hz, 1H, OH), 2.30 (s, 3H, C*H*$_3$).

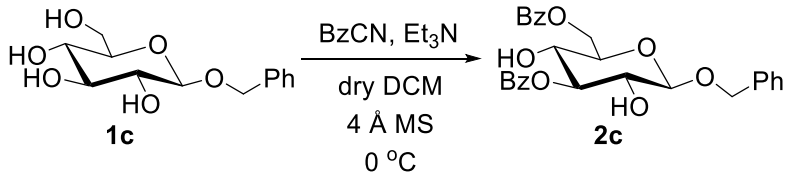
1 mmol-scale preparation: To a solution of compound **1a** (300 mg, 1.05 mmol) and 4 Å molecular sieves in 100 mL mixture of DCM was added benzoyl cyanide (275 mg, 2.1 mmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (14.6 μL, 105 μmol) was added. 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 NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2a** (435.7 mg, 84%) as semisolid.



2-Methylphenyl 3,6-di-*O*-benzoyl-1-thio-β-D-glucopyranoside (2b)

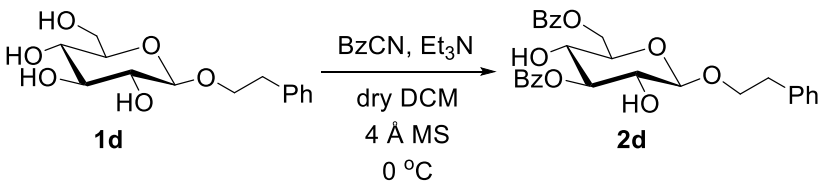
To a solution of compound **1b** (30 mg, 104.9 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (28.2 mg, 215.0 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 10.8 μmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2b** (42.0 mg, 81%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 7.98 (m, 4H, Ar*H*), 7.66 – 7.53 (m, 3H, Ar*H*), 7.44 (dt, *J* = 13.4, 7.7 Hz, 4H, Ar*H*), 7.18 (d, *J* = 4.0 Hz, 2H, Ar*H*), 7.00 (dt, *J* = 8.6, 4.3 Hz, 1H, Ar*H*), 5.26 (t, *J* = 8.8 Hz, 1H, 3-H), 4.81 – 4.53 (m, 3H, 1-H, 6-H$_a$, 6-H$_b$), 3.86 – 3.63 (m, 3H, 2-H, 4-H,

5-H), 3.33 (d, *J* = 4.6 Hz, 1H, O*H*), 2.76 (d, *J* = 3.2 Hz, 1H, O*H*), 2.44 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 166.8, 140.6, 133.6, 133.33, 133.28, 131.2, 130.4, 130.0, 129.8, 129.6, 129.2, 128.44, 128.39, 128.3, 126.6, 88.5, 79.7, 78.2, 70.7, 69.2, 63.8, 21.1. HRMS (ESI) Calcd for $C_{27}H_{27}O_7S^+$ $[M + H]^+$: 495.1472, found: 495.1471; $C_{27}H_{26}NaO_7S^+$ $[M + Na]^+$: 517.1291, found: 517.1287.



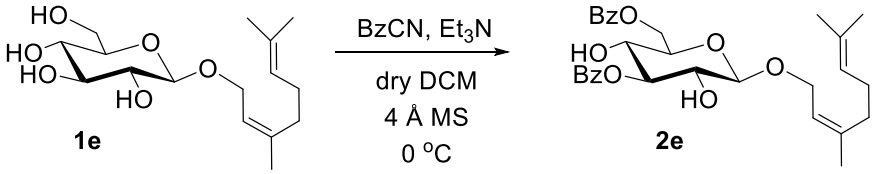
Benzyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2c)

To a solution of compound **1c** (30 mg, 111.1 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (30 mg, 229.0 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 11.1 μmol) was added. The reaction was further stirred for 7 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2c** (41.5 mg, 78%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.02 (m, 4H, Ar*H*), 7.63 – 7.53 (m, 2H, Ar*H*), 7.52 – 7.40 (m, 4H, Ar*H*), 7.38 – 7.28 (m, 5H, Ar*H*), 5.20 (t, *J* = 9.1 Hz, 1H, 3-H), 4.94 (d, *J* = 11.7 Hz, 1H, PhC*H*$_2$), 4.76 – 4.63 (m, 3H, PhC*H*$_2$, 6-H$_a$, 6-H$_b$), 4.52 (d, *J* = 7.7 Hz, 1H, 1-H), 3.84 – 3.64 (m, 3H, 2-H, 4-H, 5-H), 3.36 (d, *J* = 4.6 Hz, 1H, O*H*), 2.58 (d, *J* = 3.1 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 165.9, 135.6, 132.5, 132.3, 129.0, 128.8, 128.7, 128.3, 127.5, 127.4, 127.2, 127.1, 100.5, 77.3, 73.5, 71.2, 70.1, 68.5, 62.7. HRMS (ESI) Calcd for $C_{27}H_{27}O_8^+$ $[M + H]^+$: 479.1700, found: 479.1698; $C_{27}H_{30}NO_8^+$ $[M + NH_4]^+$: 496.1966 found: 496.1961.



2-Phenylethyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2d)

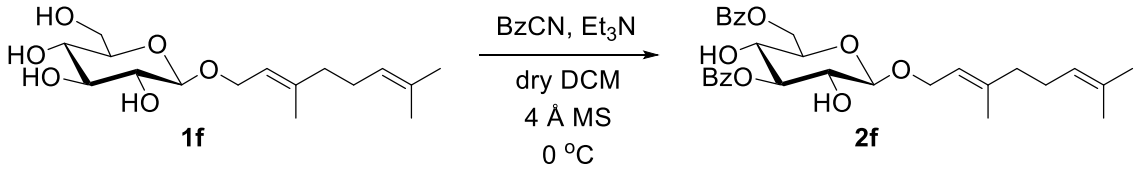
To a solution of compound **1d** (30 mg, 105.6 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (29 mg, 221.3 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 10.7 μmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2d** (43.6 mg, 84%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 7.98 (m, 4H, Ar*H*), 7.62 – 7.55 (m, 2H, Ar*H*), 7.48 – 7.38 (m, 4H, Ar*H*), 7.31 – 7.15 (m, 6H, Ar*H*), 5.20 (t, *J* = 8.9 Hz, 1H, 3-H), 4.69 (dd, *J* = 12.1, 4.4 Hz, 1H, 6-H_a), 4.63 (dd, *J* = 12.1, 2.1 Hz, 1H, 6-H_b), 4.44 (d, *J* = 7.7 Hz, 1H, 1-H), 4.18 (dt, *J* = 9.7, 6.8 Hz, 1H, OCH_2), 3.85 – 3.58 (m, 4H, 2-H, 4-H, 5-H, OCH_2), 3.40 (d, *J* = 4.0 Hz, 1H, O*H*), 3.01 – 2.88 (m, 2H, PhCH_2), 2.38 (s, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.9, 138.2, 133.5, 133.2, 130.0, 129.8, 129.6, 129.3, 128.8, 128.44, 128.40, 128.39, 126.4, 103.0, 78.2, 74.5, 72.2, 71.0, 69.4, 63.7, 36.1. HRMS (ESI) Calcd for $C_{28}H_{29}O_8^+$ $[M + H]^+$: 493.1857, found: 493.1858; $C_{27}H_{32}NO_8^+$ $[M + NH_4]^+$: 510.2122, found: 510.2123; $C_{27}H_{28}NaO_8^+$ $[M + Na]^+$: 515.1676, found: 515.1665.



(2*Z*)-3,7-dimethyl-2,6-octadien-1-yl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2e)

To a solution of compound **1e** (34 mg, 107 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (28.2 mg, 215 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 10.7 μmol) was added. The reaction was further stirred for 5 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic

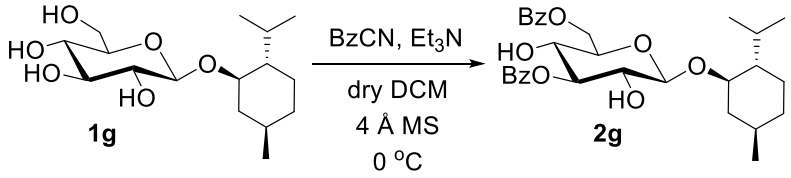
layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2e** (48 mg, 85%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.01 (m, 4H, Ar*H*), 7.62 – 7.54 (m, 2H, Ar*H*), 7.44 (td, *J* = 7.7, 3.4 Hz, 4H, Ar*H*), 5.37 (t, *J* = 7.3 Hz, 1H, C=C*H*), 5.24 (t, *J* = 8.9 Hz, 1H, 3-H), 5.09 – 4.99 (m, 1H, C=C*H*), 4.72 – 4.56 (m, 2H, 6-H_a, 6-H_b), 4.48 (d, *J* = 7.8 Hz, 1H, 1-H), 4.34 (dd, *J* = 11.9, 6.4 Hz, 1H, OCH_2), 4.23 (dd, *J* = 11.9, 7.9 Hz, 1H, OCH_2), 3.87 – 3.57 (m, 3H, 2-H, 4-H, 5-H), 3.41 (d, *J* = 4.3 Hz, 1H, O*H*), 2.60 (d, *J* = 2.7 Hz, 1H, O*H*), 2.19 – 1.96 (m, 4H, CH_2), 1.75 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.57 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.9, 142.2, 133.4, 133.2, 132.2, 130.0, 129.8, 129.7, 129.4, 128.38, 128.35, 123.5, 120.3, 101.3, 78.3, 74.4, 72.1, 69.5, 65.5, 63.8, 32.1, 26.6, 25.7, 23.5, 17.7. HRMS (ESI) Calcd for $C_{30}H_{37}O_8^+$ $[M + H]^+$: 525.2483, found: 525.2484; $C_{30}H_{40}NO_8^+$ $[M + NH_4]^+$: 542.2748, found: 542.2751; $C_{30}H_{36}NaO_8^+$ $[M + Na]^+$: 547.2302, found: 547.2297.



(2*E*)-3,7-dimethyl-2,6-octadien-1-yl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2f)

To a solution of compound **1f** (30 mg, 94.9 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (24.9 mg, 190 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.3 μL, 9.5 μmol) was added. The reaction was further stirred for 5 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2f** (43.0 mg, 86%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.02 (m, 4H, Ar*H*), 7.63 – 7.53 (m, 2H, Ar*H*), 7.50 – 7.38 (m, 4H, Ar*H*), 5.36 (t, *J* = 7.2 Hz, 1H, C=C*H*), 5.23 (t, *J* = 9.0 Hz, 1H, 3-H), 5.11 – 5.02 (m, 1H, C=C*H*), 4.72 – 4.59 (m, 2H, 6-H_a, 6-H_b), 4.48 (d, *J* = 7.8 Hz, 1H, 1-H), 4.36 (dd, *J* = 11.9, 6.4

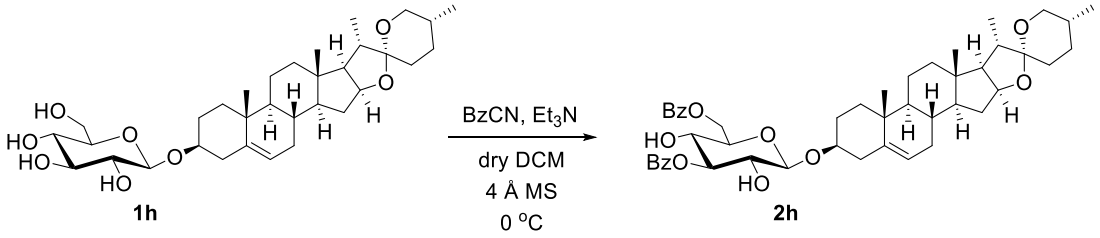
Hz, 1H, OC*H*$_2$), 4.27 (dd, *J* = 11.8, 7.9 Hz, 1H, OC*H*$_2$), 3.81 – 3.64 (m, 3H, 2-H, 4-H, 5-H), 3.39 (d, *J* = 4.3 Hz, 1H, O*H*), 2.57 (d, *J* = 2.7 Hz, 1H, O*H*), 2.14 – 2.00 (m, 4H, C*H*$_2$), 1.69 (s, 3H, C*H*$_3$), 1.65 (s, 3H, C*H*$_3$), 1.60 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.9, 142.3, 133.5, 133.2, 131.8, 130.0, 129.8, 129.7, 129.3, 128.4, 128.3, 123.7, 119.2, 100.9, 78.4, 74.5, 72.1, 69.5, 65.5, 63.8, 39.5, 26.2, 25.7, 17.7, 16.4. HRMS (ESI) Calcd for $C_{30}H_{37}O_8^+$ [M + H]$^+$: 525.2483, found: 525.2482; $C_{30}H_{40}NO_8^+$ [M + NH_4]$^+$: 542.2748, found: 542.2746.



(*1R*,*2S*,*5R*)-2-Isopropyl-5-methylcyclohexanyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2g)

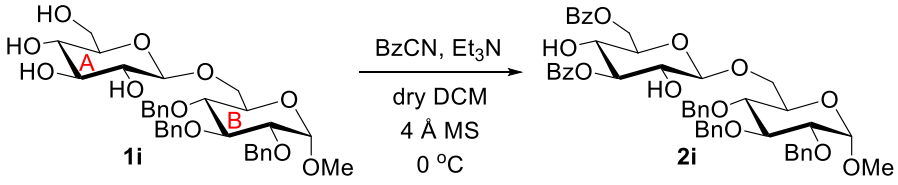
To a solution of compound **1g** (30 mg, 94.3 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (26.0 mg, 198.4 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.4 μL, 10.0 μmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2g** (35.2 mg, 71%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.95 (m, 4H, Ar*H*), 7.55 – 7.48 (m, 2H, Ar*H*), 7.41 – 7.33 (m, 4H, Ar*H*), 5.15 (t, *J* = 8.9 Hz, 1H, 3-H), 4.65 – 4.52 (m, 2H, 6-H$_a$, 6-H$_b$), 4.47 (d, *J* = 7.7 Hz, 1H, 1-H), 3.72 – 3.62 (m, 2H, 4-H, 5-H), 3.59 (ddd, *J* = 9.8, 7.8, 2.3 Hz, 1H, 2-H), 3.46 (td, *J* = 10.8, 4.2 Hz, 1H), 3.19 (d, *J* = 4.0 Hz, 1H, O*H*), 2.31 (d, *J* = 2.4 Hz, 1H, O*H*), 2.16 (td, *J* = 7.0, 2.5 Hz, 1H), 2.01 (d, *J* = 12.4 Hz, 1H), 1.65 – 1.47 (m, 2H), 1.37 – 1.08 (m, 2H), 0.96 – 0.70 (m, 3H), 0.84 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.7 Hz, 3H), 0.66 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 166.8, 133.4, 133.15, 130.0, 129.9, 129.8, 129.5, 128.4, 128.3, 99.9, 78.6, 77.7, 74.3, 72.2, 69.8, 63.8, 47.8,

40.6, 34.3, 31.5, 25.3, 23.2, 22.2, 20.8, 15.7. HRMS (ESI) Calcd for $C_{30}H_{38}O_8^+$ [M + H]$^+$: 527.2639, found: 527.2637; $C_{30}H_{42}NO_8^+$ [M + NH_4]$^+$: 544.2905, found: 544.2901.



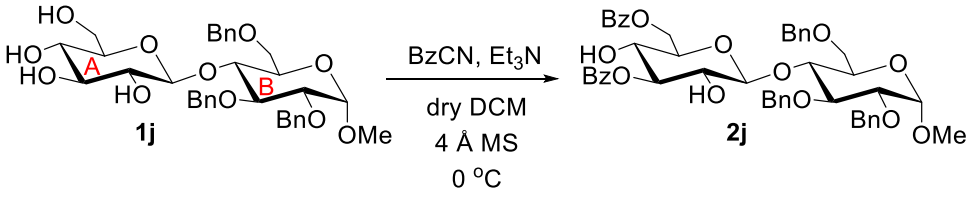
Diosgenyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2h)[3]

To a solution of compound **1h** (30 mg, 52.0 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (13.6 mg, 104 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (0.7 μL, 5.2 μmol) was added. The reaction was further stirred for 9 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2h** (34.3 mg, 84%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 4H, Ar*H*), 7.60 – 7.56 (m, 2H, Ar*H*), 7.47 – 7.42 (m, 4H, Ar*H*), 5.34 (d, *J* = 4.9 Hz, 1H), 5.21 (t, *J* = 8.5 Hz, 1H), 4.72 – 4.60 (m, 2H), 4.55 (d, *J* = 7.7 Hz, 1H), 4.41 (q, *J* = 7.4 Hz, 1H), 3.76 – 3.74 (m, 2H), 3.68 (t, *J* = 8.7 Hz, 1H), 3.57 (dp, *J* = 10.6, 4.5 Hz, 1H), 3.48 (dd, *J* = 11.1, 4.1 Hz, 1H), 3.42 – 3.30 (m, 3H), 2.38 (dd, *J* = 13.3, 4.6 Hz, 1H), 2.29 (d, *J* = 12.0 Hz, 1H), 1.99 (dt, *J* = 22.5, 13.0 Hz, 3H), 1.87 (t, *J* = 6.9 Hz, 1H), 1.82 – 1.37 (m, 14H), 1.36 – 1.04 (m, 8H), 1.04 – 0.84 (m, 8H), 0.80 – 0.79 (m, 6H).



Methyl 6-*O*-(3,6-di-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (2i)

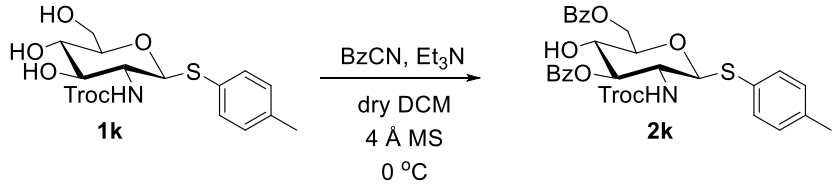
To a solution of compound **1i** (30 mg, 47.9 μmol) and 4 Å molecular sieves in 2 mL mixture of DCM was added benzoyl cyanide (12.5 mg, 95.7 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (0.7 μL, 4.8 μmol) was added. The reaction was further stirred for 0.5 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2i** (35.2 mg, 88%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 7.96 (m, 4H, Ar*H*), 7.61 – 7.53 (m, 2H, Ar*H*), 7.49 – 7.39 (m, 4H, Ar*H*), 7.37 – 7.23 (m, 15H, Ar*H*), 5.17 (t, *J* = 9.2 Hz, 1H, 3_A-H), 4.97 (d, *J* = 10.9 Hz, 1H, PhCH_2), 4.89 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.80 (d, *J* = 11.3 Hz, 1H, PhCH_2), 4.77 (d, *J* = 11.0 Hz, 1H, PhCH_2), 4.71 (dd, *J* = 12.2, 4.4 Hz, 1H, 6_A-H_a), 4.67 – 4.54 (m, 4H, PhCH_2(×2), 6_A-H_b, 1_B-H), 4.39 (d, *J* = 7.7 Hz, 1H, 1_A-H), 4.15 (dd, *J* = 11.0, 2.2 Hz, 1H, 6_B-H_a), 3.99 (t, *J* = 9.2 Hz, 1H, 3_B-H), 3.83 (ddd, *J* = 10.2, 5.1, 2.1 Hz, 1H, 5_B-H), 3.78 – 3.61 (m, 4H, 2_A-H, 6_B-H_b, 5_A-H, 4_A-H), 3.55 – 3.45 (m, 2H, 2_B-H, 4_B-H), 3.36 (s, 3H, OCH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.0, 138.6, 138.1, 138.0, 133.5, 133.3, 130.0, 129.9, 129.5, 129.3, 128.45, 128.41, 128.38, 128.1, 127.9, 127.8, 127.6, 103.7, 98.1, 81.9, 79.6, 78.3, 77.9, 75.7, 75.0, 74.5, 73.3, 72.0, 69.7, 69.2, 69.1, 63.5, 55.3. HRMS (ESI) Calcd for $C_{48}H_{54}NO_{13}^+$ [M + NH_4]$^+$: 852.3590, found: 852.3603; $C_{48}H_{50}NaO_{13}^+$ [M + Na]$^+$: 857.3144, found: 857.3139.



Methyl 4-*O*-(3,6-di-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (2j)

To a solution of compound **1j** (30 mg, 47.9 μmol) and 4 Å molecular sieves in 2 mL mixture of DCM was added benzoyl cyanide (12.5 mg, 95.7 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C,

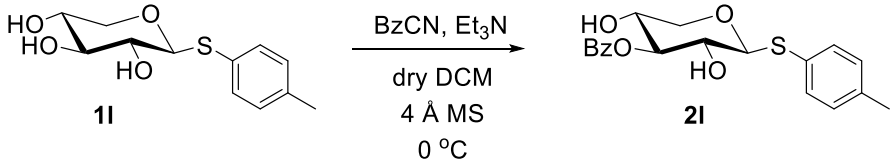
Et_3N (0.7 μL, 4.8 μmol) was added. The reaction was further stirred for 0.5 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2j** (32.0 mg, 80%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 – 8.03 (m, 2H, Ar*H*), 8.01 – 7.91 (m, 2H, Ar*H*), 7.61 – 7.50 (m, 2H, Ar*H*), 7.48 – 7.40 (m, 2H, Ar*H*), 7.39 – 7.18 (m, 18H, Ar*H*), 5.04 (d, *J* = 11.5 Hz, 1H, PhC*H*$_2$), 5.01 (t, *J* = 9.2 Hz, 1H, 3_A-H), 4.91 (d, *J* = 11.5 Hz, 1H, PhC*H*$_2$), 4.71 (d, *J* = 12.0 Hz, 1H, PhC*H*$_2$), 4.70 (d, *J* = 12.0 Hz, 1H, PhC*H*$_2$), 4.63 (d, *J* = 7.8 Hz, 1H, 1_A-H), 4.60 – 4.51 (m, 3H, 1_B-H, PhC*H*$_2$, 6_A-H$_a$), 4.49 (d, *J* = 12.0 Hz, 1H, PhC*H*$_2$), 4.27 (dd, *J* = 12.2, 2.2 Hz, 1H, 6_A-H$_b$), 4.06 – 3.92 (m, 3H, 6_B-H, 3_B-H, 4_B-H), 3.82 – 3.74 (m, 1H, 5_B-H), 3.69 – 3.57 (m, 2H, 6_B-H$_b$, 4_A-H), 3.57 – 3.47 (m, 2H, 2_B-H, 2_A-H), 3.43 (d, *J* = 3.2 Hz, 1H, O*H*), 3.35 (s, 3H, OC*H*$_3$), 3.29 – 3.23 (m, 2H, 5_A-H), 3.22 (d, *J* = 4.4 Hz, 1H, O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 167.1, 139.2, 138.0, 137.4, 133.4, 133.2, 130.0, 129.9, 129.52, 129.50, 128.5, 128.4, 128.32, 128.27, 128.18, 128.11, 127.9, 127.2, 127.0, 103.2, 98.3, 80.8, 79.3, 78.2, 75.0, 74.6, 73.7, 73.5, 73.0, 69.4, 68.9, 68.5, 63.4, 55.3. HRMS (ESI) Calcd for $C_{48}H_{54}NO_{13}^+$ $[M + NH_4]^+$: 852.3590, found: 852.3613; $C_{48}H_{50}NaO_{13}^+$ $[M + Na]^+$: 857.3144, found: 857.3145.



***p*-Tolyl 3,6-di-*O*-benzoyl- 2-deoxy-2-*N*-trichloroacetamido-1-thio-β-D-glucopyranoside (2k)**

To a solution of compound **1k** (30 mg, 65.1 μmol) and 4 Å molecular sieves in 10 mL mixture of DCM was added benzoyl cyanide (17.1 mg, 130 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (0.9 μL, 6.5 μmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction

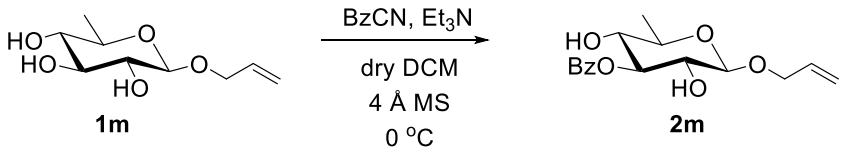
was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2k** (36.2 mg, 83%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H, Ar*H*), 7.97 – 7.89 (m, 2H, Ar*H*), 7.60 (t, *J* = 7.3 Hz, 1H, Ar*H*), 7.52 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.48 – 7.37 (m, 5H, Ar*H*), 7.33 (t, *J* = 7.6 Hz, 2H, Ar*H*), 6.93 (d, *J* = 7.8 Hz, 2H, Ar*H*), 5.66 (d, *J* = 9.7 Hz, 1H, N*H*), 5.47 (t, *J* = 9.5 Hz, 1H, 3-H), 4.89 (d, *J* = 10.4 Hz, 1H, 1-H), 4.77 – 4.67 (m, 2H, 6-H_a, OCH_2), 4.62 (dd, *J* = 12.1, 5.4 Hz, 1H, 6-H_b), 4.55 (d, *J* = 12.0 Hz, 1H, OCH_2), 3.96 – 3.88 (m, 1H, 2-H), 3.88 – 3.74 (m, 2H, 5-H, 4-H), 3.61 (d, *J* = 5.4 Hz, 1H, O*H*), 2.27 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.3, 166.9, 154.2, 138.0, 133.6, 133.3, 133.0, 130.0, 129.9, 129.6, 129.5, 128.8, 128.5, 128.40, 128.37, 95.3, 86.8, 77.9, 74.3, 69.4, 63.8, 54.8, 21.2. HRMS (ESI) Calcd for $C_{30}H_{29}Cl_3NO_8S^+$ $[M + H]^+$: 668.0674, found: 668.0677; $C_{30}H_{32}Cl_3N_2O_8S^+$ $[M + NH_4]^+$: 685.0939, found: 685.0947.



***p*-Tolyl 3-*O*-benzoyl-1-thio-β-D-xylopyranoside (2l)**

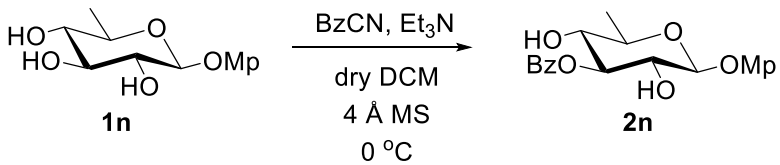
To a solution of compound **1l** (30 mg, 117 μmol) and 4 Å molecular sieves in 11 mL mixture of DCM was added benzoyl cyanide (15.3 mg, 117 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.6 μL, 11.7 μmol) was added. The reaction was further stirred for 4 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2l** (33.8 mg, 80%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 – 8.07 (m, 2H, Ar*H*), 7.62 – 7.53 (m, 1H, Ar*H*), 7.49 – 7.41 (m, 4H, Ar*H*), 7.17 – 7.11 (m, 2H, Ar*H*), 5.14 (t, *J* = 7.4 Hz, 1H, 3-H), 4.79 (d, *J* = 7.2 Hz, 1H, 1-H), 4.32

(dd, *J* = 11.9, 4.4 Hz, 1H, 5-H), 3.93 – 3.83 (m, 1H, 4-H), 3.79 – 3.70 (m, 1H, 2-H), 3.50 (dd, *J* = 11.9, 8.0 Hz, 1H, 5'-H), 3.10 – 3.08 (m, 2H, 2-O*H*, 4-O*H*), 2.35 (s, 3H, C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.2, 138.4, 133.6, 133.1, 130.0, 129.9, 129.1, 128.6, 128.5, 128.5, 89.2, 70.0, 68.2, 67.3, 21.16. HRMS (ESI) Calcd for $C_{19}H_{21}O_5S^+$ $[M + H]^+$: 361.1104, found: 361.1107; $C_{19}H_{24}NO_5S^+$ $[M + NH_4]^+$: 378.1370, found: 378.1372.



Allyl 3-*O*-benzoyl-β-D- quinovopyranoside (2m)

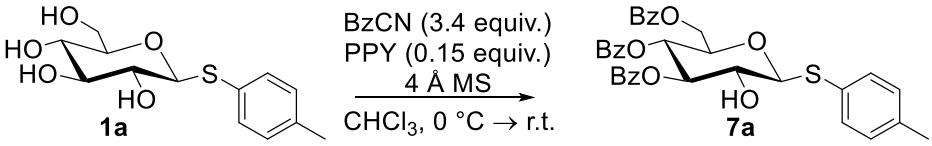
To a solution of compound **1m** (36 mg, 176 μmol) and 4 Å molecular sieves in 14 mL mixture of DCM was added benzoyl cyanide (23.1 mg, 176 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (2.5 μL, 17.6 μmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2m** (46.2 mg, 85%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.58 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.44 (t, *J* = 7.6 Hz, 2H, Ar*H*), 5.94 (m, 1H, vinylic C*H*=CH$_2$), 5.33 (m, 1H, vinylic CH=C*H*$_2$), 5.22 (d, *J* = 10.4 Hz, 1H, vinylic CH=C*H*$_2$), 5.10 (t, *J* = 8.7 Hz, 1H, 3-H), 4.40 (m, 2H, 1-H, allylic OC*H*$_2$), 4.14 (dd, *J* = 12.7, 6.4 Hz, 1H, allylic OC*H*$_2$), 3.68 (t, *J* = 8.6 Hz, 1H, 4-H), 3.50 – 3.39 (m, 2H, 2-H, 5-H), 1.37 (d, *J* = 4.8 Hz, 3H, 6-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 133.6, 133.5, 130.0, 129.4, 128.5, 118.1, 101.5, 79.0, 74.6, 72.5, 72.3, 70.4, 17.6. HRMS (ESI) Calcd for $C_{16}H_{21}O_6^+$ $[M + H]^+$: 309.1333, found: 309.1332; $C_{16}H_{20}NaO_6^+$ $[M + Na]^+$: 331.1152, found: 331.1149.



4-Methoxyphenyl 3-*O*-benzoyl-β-D- quinovopyranoside (2n)

To a solution of compound **1n** (30 mg, 111 μmol) and 4 Å molecular sieves in 10.6 mL mixture of DCM was added benzoyl cyanide (14.6 mg, 111 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, Et_3N (1.5 μL, 11.1 μmol) was added. The reaction was further stirred for 12 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2m** (34.9 mg, 85%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H, Ar*H*), 7.54 – 7.47 (m, 1H, Ar*H*), 7.36 (t, *J* = 7.7 Hz, 2H, Ar*H*), 6.96 – 6.88 (m, 2H, Ar*H*), 6.77 – 6.71 (m, 2H, Ar*H*), 5.11 (t, *J* = 8.9 Hz, 1H, 3-H), 4.78 (d, *J* = 7.8 Hz, 1H, 1-H), 3.82 (ddd, *J* = 9.7, 7.8, 2.5 Hz, 1H, 2-H), 3.69 (s, 3H, OC*H*$_3$), 3.53 – 3.36 (m, 2H, 4-H, 5-H), 2.93 (d, *J* = 4.6 Hz, 1H, 4-O*H*), 2.82 (d, *J* = 3.3 Hz, 1H, 2-O*H*), 1.30 (d, *J* = 5.4 Hz, 3H, 6-C*H*$_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.0, 155.5, 151.1, 133.6, 130.0, 129.3, 128.5, 118.5, 114.6, 101.9, 78.9, 74.4, 72.4, 72.3, 55.6, 29.7, 17.6. HRMS (ESI) Calcd for $C_{16}H_{21}O_6^+$ [M + H]$^+$: 309.1333, found: 309.1332; $C_{20}H_{22}NaO_7^+$ [M + Na]$^+$: 397.1258, found: 397.1264.

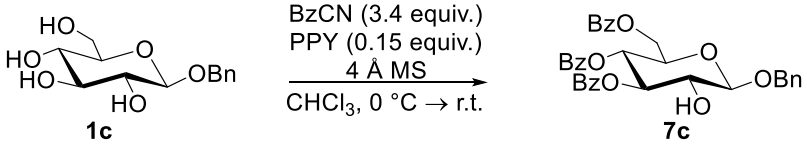
(2) Procedures for PPY catalyzed cyanide-mediated 3,4,6-tri-*O*-benzoylation of fully unprotected β-glucopyranosides.



***p*-Tolyl 3,4,6-tri-*O*-benzoyl-1-thio-β-D-glucopyranoside (7a)**

To a solution of compound **1c** (30 mg, 105 μmol) and 4 Å molecular sieves in 1.5 mL mixture of $CHCl_3$ was added benzoyl cyanide (46.7 mg, 356 μmol) at room temperature under argon atmosphere. The reaction was cooled to 0 °C and PPY (2.3 mg, 15.7 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 12 h. The reaction was quenched by addition of NH4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the

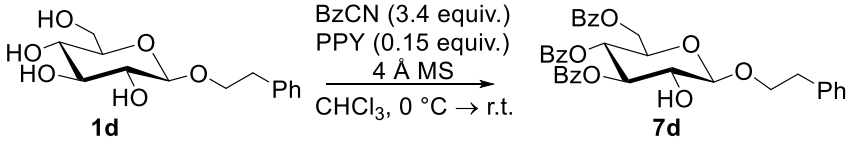
Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7a** (39.6 mg, 63%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.86 – 7.78 (m, 4H, Ar*H*), 7.49 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.40 – 7.32 (m, 6H, Ar*H*), 7.26 – 7.22 (m, 4H, Ar*H*), 6.88 (d, *J* = 7.7 Hz, 2H, Ar*H*), 5.53 (t, *J* = 9.3 Hz, 1H, 3-H), 5.42 (t, *J* = 9.7 Hz, 1H, 4-H), 4.63 (d, *J* = 9.6 Hz, 1H, 1-H), 4.56 (dd, *J* = 12.3, 2.8 Hz, 1H, 6-H_a), 4.35 (dd, *J* = 12.2, 5.5 Hz, 1H, 6-H_b), 4.02 – 3.97 (m, 1H, 5-H), 3.62 (t, *J* = 9.4 Hz, 1H, 2-H), 2.56 (br, 1H, O*H*), 2.21 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.6, 166.1, 165.4, 138.9, 134.1, 133.9, 133.5, 133.4, 133.1, 129.91, 129.86, 129.83, 129.7, 129.6, 129.1, 128.8, 128.52, 128.45, 128.39, 128.37, 126.7, 88.3, 76.5, 76.2, 70.7, 70.0, 69.0, 63.1, 21.2. HRMS (ESI) Calcd for $C_{34}H_{31}O_8S^+$ [M + H]$^+$: 599.1734, found: 599.1739; $C_{34}H_{34}NO_8S^+$ [M + NH_4]$^+$: 616.2000, found: 616.2003; $C_{34}H_{30}NaO_8S^+$ [M + Na]$^+$: 621.1554, found: 621.1547.



Benzyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (7c)

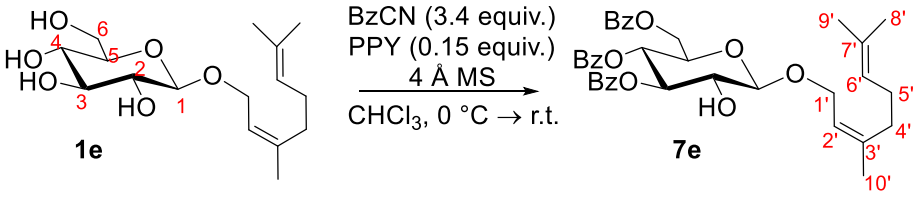
To a solution of compound **1c** (30 mg, 111 μmol) and 4 Å molecular sieves in 1.6 mL mixture of $CHCl_3$ was added benzoyl cyanide (49.5 mg, 377 μmol) at room temperature under argon atmosphere. The reaction was cooled to 0 ^{o}C and PPY (2.5 mg, 16.6 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 5 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7a** (40.9 mg, 63%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H, Ar*H*), 7.99 – 7.93 (m, 3H, Ar*H*), 7.92 – 7.87 (m, 2H, Ar*H*), 7.58 – 7.45 (m, 4H, Ar*H*), 7.43 – 7.29 (m, 11H, Ar*H*), 5.63 – 5.53 (m, 2H, 3-H, 4-H), 4.96 (d, *J* = 11.7 Hz, 1H, PhCH_2), 4.71 (d, *J* = 11.6 Hz, 1H, PhCH_2), 4.65 – 4.58 (m, 2H, 1-H, 6-H_a), 4.49 (dd, *J*

= 12.1, 5.6 Hz, 1H, 6-H_b), 4.04 (td, *J* = 5.8, 2.8 Hz, 1H, 5-H), 3.88 (td, *J* = 7.2, 3.7 Hz, 1H, 2-H), 2.63 (d, *J* = 3.0 Hz, 1H, 2-O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.5, 166.2, 165.4, 136.4, 133.5, 133.3, 133.2, 129.94, 129.91, 129.82, 129.74, 129.68, 129.2, 129.0, 128.8, 128.6, 128.43, 128.39, 128.37, 128.27, 101.4, 75.0, 72.8, 72.2, 71.2, 69.6, 63.4. HRMS (ESI) Calcd for $C_{34}H_{31}O_9^+$ [M + H]$^+$: 583.1963, found: 583.1968; $C_{34}H_{34}NO_9^+$ [M + NH_4]$^+$: 600.2228, found: 600.2232.



2-Phenylethyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (7d)

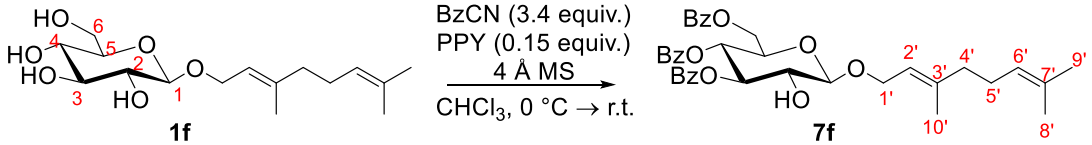
To a solution of compound **1d** (30 mg, 106 μmol) and 4 Å molecular sieves in 1.5 mL mixture of $CHCl_3$ was added benzoyl cyanide (47.0 mg, 359 μmol) at room temperature under argon atmosphere. The reaction was cooled to 0 ^{o}C and PPY (2.3 mg, 15.8 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 5 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7d** (38.5 mg, 61%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.87 (m, 4H, Ar*H*), 7.85 – 7.79 (m, 2H, Ar*H*), 7.48 – 7.37 (m, 3H, Ar*H*), 7.33 – 7.16 (m, 8H, Ar*H*), 7.13 (dt, *J* = 9.2, 3.1 Hz, 3H, Ar*H*), 5.56 – 5.44 (m, 2H, 3-H, 4-H), 4.56 – 4.46 (m, 2H, 1-H, 6-H_a), 4.39 (dd, *J* = 12.1, 5.6 Hz, 1H, 6-H_b), 4.17 – 4.07 (m, 1H, OCH_2), 3.97 (ddd, *J* = 9.1, 5.7, 3.1 Hz, 1H), 3.78 – 3.71 (m, 2H, 2-H, OCH_2), 2.94 – 2.88 (m, 2H, PhCH_2), 2.37 (d, *J* = 2.6 Hz, 1H, 2-O*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165.4, 138.2, 133.4, 133.31, 133.25, 133.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.2, 128.84, 128.82, 128.76, 128.5, 128.4, 128.3, 128.2, 126.5, 103.1, 74.9, 74.5, 72.7, 72.2, 71.1, 69.7, 69.5, 63.3, 36.1. HRMS (ESI) Calcd for $C_{35}H_{36}NO_9^+$ [M + NH_4]$^+$: 614.2385, found: 614.2401; $C_{35}H_{32}NaO_9^+$ [M + Na]$^+$: 619.1939; found: 619.1953.



1e 7e

(2*Z*)-3,7-dimethyl-2,6-octadien-1-yl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (7e)

To a solution of compound **1e** (30 mg, 94.8 μmol) and 4 Å molecular sieves in 1.35 mL mixture of $CHCl_3$ was added benzoyl cyanide (42.3 mg, 322 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, PPY (2.1 mg, 14.2 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 6.5 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7e** (37.2 mg, 62%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 4H, Ar*H*), 7.85 – 7.80 (m, 2H, Ar*H*), 7.49 – 7.37 (m, 3H, Ar*H*), 7.35 – 7.23 (m, 6H, Ar*H*), 5.58 – 5.45 (m, 2H, 3-H, 4-H), 5.32 (t, *J* = 7.2 Hz, 1H, 3'-H), 5.01 – 4.94 (m, 1H), 4.55 – 4.49 (m, 2H, 1-H, 6-H_a), 4.39 (dd, *J* = 12.1, 5.6 Hz, 1H, 6-H_b), 4.29 (dd, *J* = 11.9, 6.4 Hz, 1H, 1'-H_a), 4.20 (dd, *J* = 11.9, 7.9 Hz, 1H, 1'-H_b), 3.98 (ddd, *J* = 9.0, 5.6, 3.3 Hz, 1H, 5-H), 3.74 (t, *J* = 8.3 Hz, 1H, 2-H), 2.51 (s, 1H, 2-OH), 2.07 – 1.94 (m, 4H, 4'-H, 5'-H), 1.70 (s, 3H, 10'-H), 1.59 (s, 3H, 8'-H), 1.50 (s, 3H, 9'-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.2, 165.4, 142.5, 133.4, 133.3, 133.1, 132.2, 129.9, 129.8, 129.71, 129.68, 129.3, 128.9, 128.4, 128.3, 123.5, 120.3, 101.4, 75.0, 72.7, 72.2, 69.6, 65.6, 63.5, 32.1, 26.6, 25.7, 23.6, 17.7. HRMS (ESI) Calcd for $C_{37}H_{44}NO_9^+$ $[M + NH_4]^+$: 646.3011, found: 646.3021.

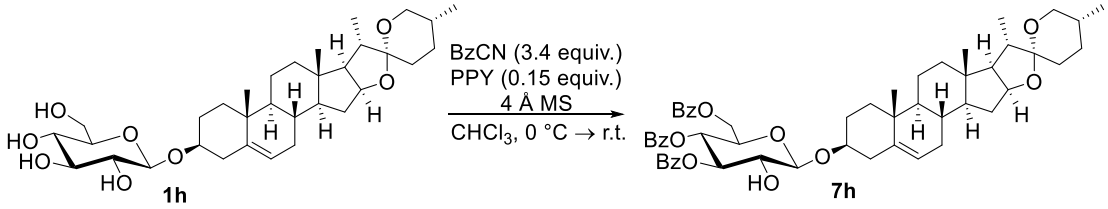


1f 7f

(2*E*)-3,7-dimethyl-2,6-octadien-1-yl 3,4,6-di-*O*-benzoyl-β-D-glucopyranoside (7f)

To a solution of compound **1f** (30 mg, 94.8 μmol) and 4 Å molecular sieves in 1.35 mL mixture of $CHCl_3$ was added benzoyl cyanide (42.3 mg, 322 μmol) at room

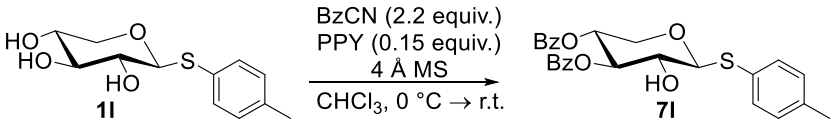
temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, PPY (2.1 mg, 14.2 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 6.5 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7f** (36.7 mg, 62%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 4H, Ar*H*), 7.85 – 7.80 (m, 2H, Ar*H*), 7.48 – 7.38 (m, 3H, Ar*H*), 7.34 – 7.22 (m, 6H, Ar*H*), 5.58 – 5.46 (m, 2H, 3-H, 4-H), 5.33 – 5.27 (m, 1H, 3'-H), 5.06 – 4.98 (m, 1H, 6'-H), 4.57 – 4.50 (m, 2H, 1-H, 6-H_a), 4.40 (dd, *J* = 12.1, 5.7 Hz, 1H, 6-H_b), 4.30 (dd, *J* = 11.9, 6.3 Hz, 1H, 1-H), 4.23 (dd, *J* = 11.8, 8.0 Hz, 1H, 1'-H), 3.97 (ddd, *J* = 9.2, 5.8, 3.2 Hz, 1H, 5-H), 3.80 – 3.71 (m, 1H, 2-H), 2.52 (d, *J* = 2.8 Hz, 1H, 2-OH), 2.07 – 1.96 (m, 4H, 4'-H, 5'-H), 1.63 (s, 3H, 8'-H), 1.58 (s, 3H, 10'-H), 1.53 (s, 3H, 9'-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165.4, 142.6, 133.4, 133.2, 133.1, 131.9, 129.9, 129.8, 129.69, 129.65, 129.2, 128.9, 128.38, 128.32, 128.29, 123.8, 119.1, 101.0, 75.0, 72.7, 72.2, 69.7, 65.6, 63.5, 39.5, 26.3, 25.7, 17.7, 16.4. HRMS (ESI) Calcd for $C_{37}H_{44}NO_9^+$ $[M + NH_4]^+$: 646.3011, found: 646.3025; $C_{37}H_{40}NaO_9^+$ $[M + Na]^+$: 651.2565; found: 651.2569.



Diosgenyl 3,4,6-tri-*O*-benzoyl-β-D-glucopyranoside (7h)

To a solution of compound **1h** (30 mg, 52.0 μmol) and 4 Å molecular sieves in 0.74 mL mixture of $CHCl_3$ was added benzoyl cyanide (23.2 mg, 177 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, PPY (1.2 mg, 7.8 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 11 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic

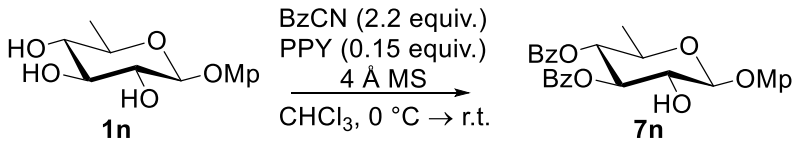
layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7h** (31.3 mg, 68%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.95 (m, 4H, Ar*H*), 7.92 – 7.87 (m, 2H, Ar*H*), 7.56 – 7.46 (m, 3H, Ar*H*), 7.40 – 7.31 (m, 7H, Ar*H*), 5.62 (t, *J* = 9.5 Hz, 1H, 3-H), 5.53 (t, *J* = 9.6 Hz, 1H, 4-H), 5.35 (d, *J* = 5.1 Hz, 1H, vinylic C*H*=CH_2), 4.66 (d, *J* = 7.7 Hz, 1H, 1-H), 4.52 (m, 2H, 6-H_a, 6-H_b), 4.42 (q, *J* = 7.4 Hz, 1H), 4.06 (ddd, *J* = 9.7, 6.1, 3.6 Hz, 1H, 5-H), 3.79 (ddd, *J* = 9.8, 7.7, 2.7 Hz, 1H, 2-H), 3.60 (tt, *J* = 10.8, 4.7 Hz, 1H), 3.48 (dt, *J* = 10.6, 3.0 Hz, 1H), 3.38 (t, *J* = 10.9 Hz, 1H), 2.59 (d, *J* = 2.7 Hz, 1H, 2-O*H*), 2.40 (ddd, *J* = 13.0, 5.1, 2.1 Hz, 1H), 2.35 – 2.25 (m, 1H), 2.06 – 1.91 (m, 3H), 1.91 – 1.84 (m, 1H), 1.83 – 1.70 (m, 3H), 1.70 – 1.55 (m, 9H), 1.47 (m, 3H), 1.36 – 1.05 (m, 4H), 0.99 (m, 5H), 0.97 – 0.95(m, 2H), 0.94 – 0.85 (m, 1H), 0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.1, 165.4, 140.2, 133.4, 133.3, 133.0, 129.9, 129.8, 129.7, 129.3, 128.9, 128.42, 128.36, 128.32, 122.0, 109.3, 101.7, 80.8, 80.1, 75.0, 72.7, 72.1, 69.8, 66.9, 63.5, 62.1, 56.5, 50.1, 41.6, 40.3, 39.8, 38.9, 37.1, 36.8, 32.1, 31.9, 31.4, 30.3, 29.7, 28.8, 20.8, 19.4, 17.2, 16.3, 14.5. HRMS (ESI) Calcd for $C_{54}H_{65}O_{11}^+$ [M + H]$^+$: 889.4521, found: 889.4530; $C_{54}H_{68}NO_{11}^+$ [M + NH_4]$^+$: 906.4787, found: 906.4795.



***p*-Tolyl 3,4-di-*O*-benzoyl-1-thio-β-D-xylopyranoside (7l)**

To a solution of compound **1l** (30 mg, 117 μmol) and 4 Å molecular sieves in 1.7 mL mixture of $CHCl_3$ was added benzoyl cyanide (33.8 mg, 257 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 ^{o}C, PPY (2.6 mg, 17.6 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 1.5 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7l** (36 mg, 67%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.00 (m, 2H, Ar*H*), 7.96 – 7.92 (m, 2H, Ar*H*), 7.57 – 7.46 (m, 4H, Ar*H*), 7.41

− 7.36 (m, 4H, Ar*H*), 7.17 (d, *J* = 7.9 Hz, 2H, Ar*H*), 5.56 (t, *J* = 8.6 Hz, 1H, 3-H), 5.27 (td, *J* = 9.0, 5.1 Hz, 1H, 4-H), 4.71 (d, *J* = 8.4 Hz, 1H, 1-H), 4.45 (dd, *J* = 11.6, 5.1 Hz, 1H, 5-H), 3.72 (td, *J* = 8.4, 4.0 Hz, 1H, 2-H), 3.58 (dd, *J* = 11.6, 9.2 Hz, 1H, 5'-H), 2.80 (d, *J* = 4.0 Hz, 1H, 2-O*H*), 2.37 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 165.5, 138.9, 133.9, 133.5, 133.4, 129.98, 129.95, 129.8, 129.3, 129.0, 128.5, 128.4, 127.3, 89.2, 74.8, 70.4, 69.3, 66.0, 21.2. HRMS (ESI) Calcd for $C_{26}H_{25}O_6S^+$ $[M + H]^+$: 465.1366, found: 465.1367; $C_{26}H_{28}NO_6S^+$ $[M + NH_4]^+$: 482.1632, found: 482.1631; $C_{26}H_{24}NaO_6S^+$ $[M + Na]^+$: 487.1186, found: 487.1180.

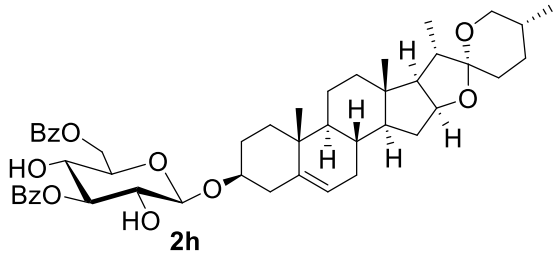


4-Methoxyphenyl 3,4-di-*O*-benzoyl-β-D-quinovopyranoside (7n)

To a solution of compound **1n** (30 mg, 111 μmol) and 4 Å molecular sieves in 0.8 mL mixture of $CHCl_3$ was added benzoyl cyanide (32.0 mg, 244 μmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 °C, PPY (2.5 mg, 16.6 μmol) was added. The reaction was further stirred and allowed to gradually warm to room temperature over 6 h. The reaction was quenched by addition of NH_4Cl (s) and MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **7n** (32.3 mg, 61%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (ddd, *J* = 14.5, 8.3, 1.4 Hz, 4H), 7.49 – 7.41 (m, 2H, Ar*H*), 7.30 (td, *J* = 7.8, 1.4 Hz, 4H, Ar*H*), 7.03 – 6.96 (m, 2H, Ar*H*), 6.82 – 6.75 (m, 2H, Ar*H*), 5.51 (t, *J* = 9.6 Hz, 1H, 3-H), 5.26 (t, *J* = 9.6 Hz, 1H, 4-H), 4.93 (d, *J* = 7.7 Hz, 1H, 1-H), 3.95 (t, *J* = 8.6 Hz, 1H, 2-H), 3.79 (dq, *J* = 9.7, 6.2 Hz, 1H, 5-H), 3.72 (s, 3H, OCH_3), 2.75 (s, 1H, 2-O*H*), 1.29 (d, *J* = 6.1 Hz, 3H, 6-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 165.6, 155.7, 151.0, 133.4, 133.3, 129.9, 129.8, 129.2, 129.1, 128.5, 128.4, 118.9, 114.6, 102.3, 75.2, 73.5, 72.9, 70.6, 55.7, 50.9, 29.7, 17.7. HRMS (ESI) Calcd for $C_{27}H_{26}NaO_8^+$ $[M + Na]^+$: 501.1520, found: 501.1529.

(3) Procedures for Et_3N catalyzed cyanide-mediated regioselective benzoylation

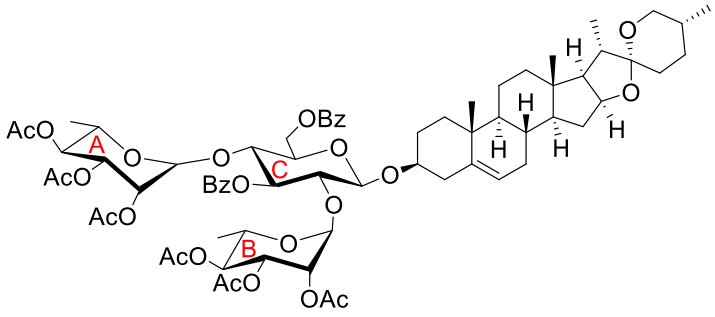
in synthesis of natural products



2h

Diosgenyl 3,6-di-*O*-benzoyl-β-D-glucopyranoside (2h)[3]

1 mmol-scale preparation: To a solution of compound **1h** (576 mg, 1 mmol) and 4 Å molecular sieves in anhydrous DCM was added benzoyl cyanide (131 mg, 2 mmol) at room temperature under argon atmosphere. After cooling down the reaction mixture to 0 ^{o}C, Et_3N (13.9 µL, 0.1 mmol) was added. The reaction was further stirred for 6 h at this temperature. After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of MeOH. Then the mixture was filtered through a pad of Celite and the Celite was further washed with DCM for 3 times. Then the organic layer was concentrated. The residue was purified by column chromatography on silica gel to afford compound **2h** (589 mg, 75%) as semisolid.



11

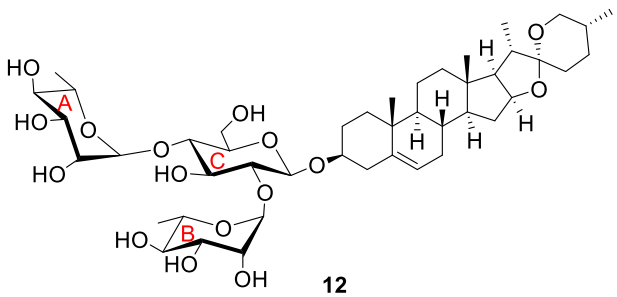
Diosgenyl 2,4-di-*O*-(2,3,4-*O*-tri-acetyl-α-L-rhamnopyranosyl)- 3,6-di-*O*-benzoyl-β-D-glucopyranoside (11)

To a solution of glycosyl donor **10** (53 mg, 115 µmol), glycosyl acceptor **2h** (30 mg, 38.2 µmol) and 4 Å molecular sieves in anhydrous DCM (2 mL) at -20 ^{o}C under argon atmosphere was added TMSOTf (4.1 µL, 22.9 µmol). The reaction was gradually allowed to -10 ^{o}C and further stirred at this temperature overnight.

After the TLC analysis showed the reaction was complete, the reaction was quenched

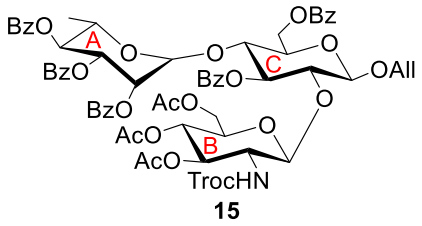
by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford compound **11** (47 mg, 92%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 4H, Ar*H*), 7.62 – 7.53 (m, 2H, Ar*H*), 7.52 – 7.37 (m, 4H, Ar*H*), 5.62 (t, *J* = 9.2 Hz, 1H, 3_C-H), 5.35 (d, *J* = 5.0 Hz, 1H, vinyl C*H*), 5.19 – 5.10 (m, 3H, 3_A-H, 3_B-H, 2_B-H), 4.98 (dd, *J* = 3.6, 1.6 Hz, 1H, 2_A-H), 4.96 – 4.83 (m, 3H, 4_A-H, 4_B-H, 1_B-H), 4.80 (dd, *J* = 12.2, 2.0 Hz, 1H, 6_C-H), 4.76 (d, *J* = 1.6 Hz, 1H, 1_A-H), 4.68 (d, *J* = 7.7 Hz, 1H, 1_C-H), 4.51 (dd, *J* = 12.2, 5.3 Hz, 1H, 6_C -H'), 4.47 – 4.31 (m, 2H, 5_B-H), 3.97 (t, *J* = 9.4 Hz, 1H, 4_C-H), 3.86 (ddd, *J* = 9.7, 5.4, 2.1 Hz, 1H, 5_C-H), 3.80 (dd, *J* = 9.3, 7.7 Hz, 1H, 2_C-H), 3.76 – 3.67 (m, 1H, 5_A-H), 3.57 (tt, *J* = 10.8, 4.6 Hz, 1H), 3.52 – 3.44 (m, 1H), 3.38 (t, *J* = 10.9 Hz, 1H), 2.40 (ddd, *J* = 13.2, 4.9, 2.2 Hz, 1H), 2.29 – 2.15 (m, 1H), 1.99 (s, 6H), 1.95 (s, 3H), 1.92 (s, 3H), 1.89 (s, 3H), 1.84 – 1.38 (m, 14H), 1.37 – 1.04 (m, 11H, 6_B-CH_3), 1.03 – 0.75 (m, 14H), 0.68 (d, *J* = 6.1 Hz, 3H, 6_A-CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.99, 169.94, 169.87, 169.84, 169.6, 168.9, 165.8, 165.0, 140.0, 133.3, 133.0, 130.0, 129.9, 129.8, 129.1, 128.4, 128.3, 122.0, 109.3, 99.4, 99.0, 98.0, 80.8, 79.5, 76.2, 75.9, 73.0, 71.0, 70.5, 70.0, 69.1, 68.7, 68.5, 67.5, 66.8, 66.5, 64.2, 62.8, 62.0, 56.4, 49.9, 41.6, 40.2, 39.7, 38.4, 36.9, 36.7, 32.0, 31.9, 31.8, 31.4, 30.3, 29.7, 29.3, 28.8, 22.7, 20.79, 20.75, 20.70, 20.68, 20.6, 20.3, 19.2, 17.1, 16.8, 16.3, 14.5, 14.1. HRMS (ESI) Calcd for $C_{71}H_{96}NO_{24}^+$ $[M + NH_4]^+$: 1346.6317, found 1346.6372.

Diosgenyl 2,4-di-*O*-α-L-rhamnopyranosyl-β-D-glucopyranoside (12)[4-5]



To a solution of compound **11** (164 mg, 123 μmol) in DCM/MeOH (1/1, v/v) was added MeONa in MeOH dropwise until pH 10 was reached. The reaction was

monitored by TLC until completion and purified by column chromatography on silica gel to afford compound **12** (80 mg, 76%) as semisolid. ^{1}H NMR (400 MHz, Methanol-d_4) δ 5.41 (m, 1H, vinylic C*H*), 5.23 (s, 1H, 1-H), 4.88 – 4.86 (1H, 1-H, masked by water), 4.61 (s, 1H), 4.52 (d, J = 7.8 Hz, 1H, 1-H$_C$), 4.42 (d, J = 7.2 Hz, 1H), 4.20 – 4.10 (m, 1H), 3.97 – 3.94 (m, 2H), 3.88 – 3.78 (m, 2H), 3.71 – 3.50 (m, 10H), 3.45 – 3.38 (m, 7H), 2.49 – 2.45 (m, 2H), 2.34 – 2.28 (m, 1H), 2.08 – 1.87 (m, 5H), 1.83 – 1.40 (m, 16H), 1.37 – 1.11 (m, 13H), 1.07 (s, 3H), 1.05 – 0.87 (m, 5H), 0.88 – 0.77 (m, 7H).



15

Allyl 2-*O*-(2-deoxy-2-*N*-trichloroacetamido-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzoyl-β-D-glucopyranoside (15)

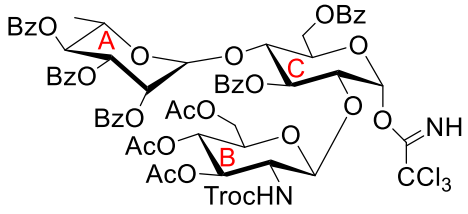
To a solution of glycosyl acceptor **2o** (220 mg, 513 μmol) and 4 Å molecular sieves in anhydrous DCM (20 mL) at -60 ^{o}C under argon atmosphere was added TfOH (5.4 μL, 61.6 μmol). The reaction stayed under stirring for 10 min, and glycosyl donor **13** (385 mg, 616 μmol) in 5 mL of anhydrous DCM was added. The reaction was further stirred for 4 h at this temperature.

After the TLC analysis showed the reaction was complete, glycosyl donor **14** (478 mg, 770 μmol) in 1.5 mL of anhydrous DCM was added, followed by addition of TfOH (6.8 μL, 77.0 μmol). The reaction was further stirred for another 3 h 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 on silica gel to afford compound **15** (579 mg, 84%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J = 7.7 Hz, 2H, Ar*H*), 8.09 –

8.05 (m, 2H, Ar*H*), 7.94 – 7.86 (m, 4H, Ar*H*), 7.83 – 7.78 (m, 2H, Ar*H*), 7.58 – 7.49 (m, 4H, Ar*H*), 7.48 – 7.35 (m, 9H, Ar*H*), 7.24 (t, *J* = 8.0 Hz, 2H, Ar*H*), 5.89 (m, 1H, vinylic C*H*=CH$_2$), 5.68 (dd, *J* = 10.2, 3.3 Hz, 1H, 3$_A$-H), 5.60 – 5.49 (m, 3H, 3$_C$-H, 2$_A$-H, 4$_A$-H), 5.35 – 5.26 (m, 2H, vinylic CH=C*H*$_2$, 3$_B$-H), 5.23 (d, *J* = 1.8 Hz, 1H, 1$_A$-H), 5.16 (dd, *J* = 10.5, 1.7 Hz, 1H, vinylic CH=C*H*$_2$), 5.11 – 4.98 (m, 4H, 1$_B$-H, 4$_B$-H, 6$_C$-H, TrocN*H*), 4.80 (d, *J* = 6.0 Hz, 1H, 1$_C$-H), 4.75 (d, *J* = 12.2 Hz, 1H, TrocC*H*$_2$CCl$_3$), 4.59 (dd, *J* = 12.4, 3.7 Hz, 1H, 6$_C$ -H'), 4.50 (d, *J* = 12.2 Hz, 1H, TrocC*H*$_2$CCl$_3$), 4.44 – 4.32 (m, 2H, allylic C*H*$_2$CH=CH$_2$, 4$_C$-H), 4.23 (dd, *J* = 12.4, 4.1 Hz, 1H, 6$_B$-H), 4.16 – 3.96 (m, 4H, 5$_A$-H, 5$_C$-H, 6 $_B$ -H', allylic C*H*$_2$CH=CH$_2$), 3.92 (t, *J* = 6.4 Hz, 1H, 2$_C$-H), 3.72 – 3.64 (m, 1H, 5$_B$-H), 3.48 (dt, *J* = 10.8, 8.4 Hz, 1H, 2$_B$-H), 2.04 (s, 3H, COC*H*$_3$), 1.99 (s, 3H, COC*H*$_3$), 1.96 (s, 3H, COC*H*$_3$), 0.82 (d, *J* = 6.2 Hz, 3H, 6$_A$-C*H*$_3$). ^{13}C NMR (100 MHz, CDCl$_3$) δ 170.7, 170.4, 169.5, 166.0, 165.7, 165.6, 165.5, 165.4, 153.8, 133.7, 133.6, 133.4, 133.3, 133.1, 133.0, 130.0, 129.9, 129.83, 129.80, 129.77, 129.7, 129.2, 129.1, 128.8, 128.5, 128.40, 128.35, 128.28, 117.0, 100.1, 99.7, 98.7, 95.6, 79.0, 76.5, 75.3, 74.2, 72.5, 71.7, 71.3, 71.2, 69.6, 69.4, 68.5, 67.8, 62.7, 61.9, 56.6, 20.7, 20.61, 20.59, 17.2. HRMS (ESI) Calcd for $C_{65}H_{68}Cl_3N_2O_{24}^+$ [M + NH$_4$]$^+$: 1365.3222, found 1365.3254.

The rhamnosyl-α-(1,4) linkage was established by high resolution coupled HSQC with an anomeric ^{13}C–^{1}H coupling constant $J_{C\text{-}1,H\text{-}1}$ = 172.2 Hz at 98.74 ppm.



17

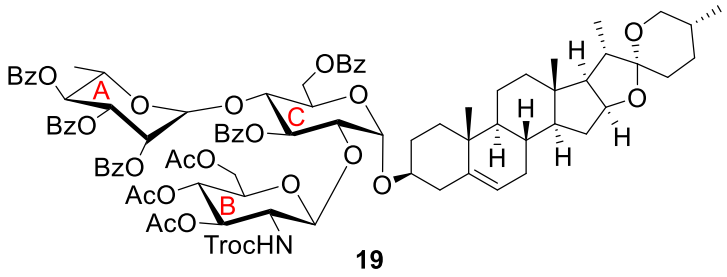
Trichloroacetimidate 2-*O*-(2-deoxy-2-*N*-trichloroacetamido-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzoyl-α-D-glucopyranoside (17)

To a solution of trisaccharide **15** (220 mg, 163 μmol) in 5 mL non anhydrous MeOH was added PdCl$_2$ (5.8 mg, 32.6 μmol). The reaction was stirred at room temperature for 8 h until the TLC analysis showed the formation of a product and consumption of

compound **15**. 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 under vacuo and the residue was purified by column chromatography on silica gel to afford compound **16** (195 mg, 91%).

Compound **16** (427 mg, 326 μmol) was dissolved in anhydrous DCM, and trichloroacetonitrile (163 μL, 1630 μmol) and DBU (4.9 μL, 68.0 μmol) were added in sequence at 0 °C. The reaction was further stirred for 5 h min at this temperature. After the TLC analysis showed the reaction was complete, the reaction was concentrated and purified by column chromatography on silica gel to afford compound **17** (400 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H, N*H*CCl_3), 8.12 (d, *J* = 7.8 Hz, 2H, Ar*H*), 8.06 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.94 – 7.87 (m, 5H, Ar*H*), 7.81 (d, *J* = 7.8 Hz, 2H, Ar*H*), 7.58 – 7.52 (m, 5H, Ar*H*), 7.46 – 7.38 (m, 11H, Ar*H*), 7.29 – 7.21 (m, 3H, Ar*H*), 6.64 (d, *J* = 3.7 Hz, 1H, 1_C-H), 5.96 (t, *J* = 9.6 Hz, 1H, 3_C-H), 5.70 (dd, *J* = 10.2, 3.3 Hz, 1H, 3_A-H), 5.56 – 5.47 (m, 2H, 2_A-H, 4_A-H), 5.31 (t, *J* = 10.0 Hz, 1H, 3_B-H), 5.22 (s, 1H, 1_A-H), 5.04 – 4.90 (m, 2H, 4_B-H, 6_C-H), 4.86 (d, *J* = 8.2 Hz, 1H, 1_B-H), 4.77 (d, *J* = 8.1 Hz, 1H, TrocN*H*), 4.64 (dd, *J* = 12.7, 3.7 Hz, 1H, 6_C-H'), 4.39 (d, *J* = 10.0 Hz, 1H, 5_C-H), 4.35 – 4.21 (m, 2H, TrocCH_2CCl_3, 4_C-H), 4.18 – 3.97 (m, 4H, 2_C-H, 5_A-H, 6_B-H (×2)), 3.87 (d, *J* = 12.2 Hz, 1H, TrocCH_2CCl_3), 3.68 (d, *J* = 9.7 Hz, 1H, 5_B-H), 3.35 (q, *J* = 9.0 Hz, 1H, 2_B-H), 2.06 (s, 3H, COCH_3), 1.97 (s, 3H, COCH_3), 1.91 (s, 3H, COCH_3), 0.73 (d, *J* = 6.1 Hz, 3H, 6_A-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 170.2, 169.5, 165.8, 165.7, 165.52, 165.47, 165.2, 160.7, 153.3, 133.5, 133.44, 133.37, 133.2, 133.0, 130.0, 129.9, 129.84, 129.80, 129.77, 129.70, 129.3, 129.1, 128.7, 128.5, 128.4, 128.33, 128.30, 100.8, 99.2, 95.4, 94.5, 91.0, 78.0, 73.6, 72.3, 71.6, 71.3, 71.2, 71.1, 70.8, 69.4, 68.7, 67.9, 62.2, 56.4, 20.8, 20.6, 20.5, 17.0. HRMS (ESI) Calcd for $C_{64}H_{60}Cl_6N_2NaO_{24}^+$ $[M + Na]^+$: 1475.1530, found 1475.1541.



19

Diosgenyl 2-*O*-(2-deoxy-2-*N*-trichloroacetamido-2,3,6-tri-*O*-acetyl-β-D-glucopyranosyl)-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzoyl-α-D-glucopyranoside (19)

To a solution of glycosyl donor **17** (20.8 mg, 14.3 μmol), glycosyl acceptor **18** (7 mg, 16.9 μmol) and 4 Å molecular sieves in anhydrous DCM (10 mL) at -78 °C under argon atmosphere was added TMSOTf (0.3 μL, 1.4 μmol). The reaction was further stirred for 5 h at this temperature.

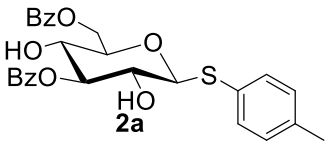
After the TLC analysis showed the reaction was complete, the reaction was quenched by addition of triethylamine and diluted with 50 mL of DCM. Then the precipitate was filtered off through a pad of Celite. The organic layer was washed with $NaHCO_3$ (aq.) and brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by column chromatography on silica gel to afford compound **19** (22 mg, 90%) as semisolid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 – 8.07 (m, 4H, Ar*H*), 7.95 – 7.89 (m, 4H, Ar*H*), 7.82 (d, *J* = 7.7 Hz, 2H, Ar*H*), 7.57 – 7.50 (m, 4H, Ar*H*), 7.43 – 7.38 (m, 9H, Ar*H*), 7.27 – 7.23 (m, 2H, Ar*H*), 5.85 (t, *J* = 9.5 Hz, 1H, 3_C-H), 5.72 (dd, *J* = 10.2, 3.2 Hz, 1H, 3_A-H), 5.56 – 5.52 (m, 1H, 2_A-H), 5.49 (d, *J* = 10.0 Hz, 1H, 4_A-H), 5.39 – 5.29 (m, 2H, 3_B-H), 5.23 (d, *J* = 3.6 Hz, 1H, 1_C-H), 5.19 (s, 1H, 1_A-H), 4.99 − 4.94 (m, 2H, 4_B-H, 6_C-H), 4.83 (d, *J* = 8.2 Hz, 1H, 1_B-H), 4.76 (d, *J* = 8.1 Hz, 1H, TrocN*H*), 4.65 (dd, *J* = 12.4, 4.6 Hz, 1H, 6_C-H'), 4.48 – 4.38 (m, 2H, 5_C-H), 4.29 (d, *J* = 12.4 Hz, 1H, TrocCH_2CCl_3), 4.22 (dd, *J* = 12.3, 4.9 Hz, 1H, 6_B-H), 4.10 – 3.94 (m, 3H, 5_A-H, 4_C-H, 6_B -H'), 3.82 – 3.74 (m, 2H, 2_C-H, TrocCH_2CCl_3), 3.66 (m, 1H, 5_B-H), 3.55 – 3.47 (m, 2H), 3.42 – 3.37 (m, 2H, 2_B-H), 2.59 – 2.37 (m, 2H), 2.05 – 1.98 (m, 8H), 1.92 (s, 4H), 1.85 – 1.73 (m, 1H), 1.73 – 1.56 (m, 7H), 1.56 – 1.40 (m, 3H), 1.37 – 1.18 (m, 8H), 1.09 (s, 3H), 0.99 – 0.85 (m, 4H), 0.84 – 0.77 (m, 6H), 0.72 (d, *J* = 6.1 Hz, 3H, 6_A-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 170.1, 169.6, 166.1, 165.7, 165.58, 165.52, 165.3,

153.3, 140.6, 133.4, 133.3, 133.1, 132.9, 130.1, 129.9, 129.8, 129.7, 129.2, 129.1, 128.6, 128.5, 128.40, 128.35, 128.3, 121.7, 109.3, 101.1, 99.0, 96.6, 95.4, 80.9, 79.2, 78.8, 78.2, 73.6, 72.5, 71.6, 71.4, 71.3, 70.9, 69.5, 68.8, 68.6, 67.8, 66.9, 62.9, 62.1, 62.0, 56.6, 50.1, 41.6, 40.3, 40.1, 39.8, 37.1, 36.9, 32.2, 31.9, 31.5, 31.4, 30.3, 29.7, 29.3, 28.8, 27.6, 27.2, 22.7, 21.1, 20.9, 20.7, 20.6, 20.5, 19.5, 17.2, 17.0, 16.3, 14.6, 14.1. HRMS (ESI) Calcd for $C_{89}H_{100}Cl_3NNaO_{26}^+$ $[M + Na]^+$: 1726.5491, found 1726.5574.

References

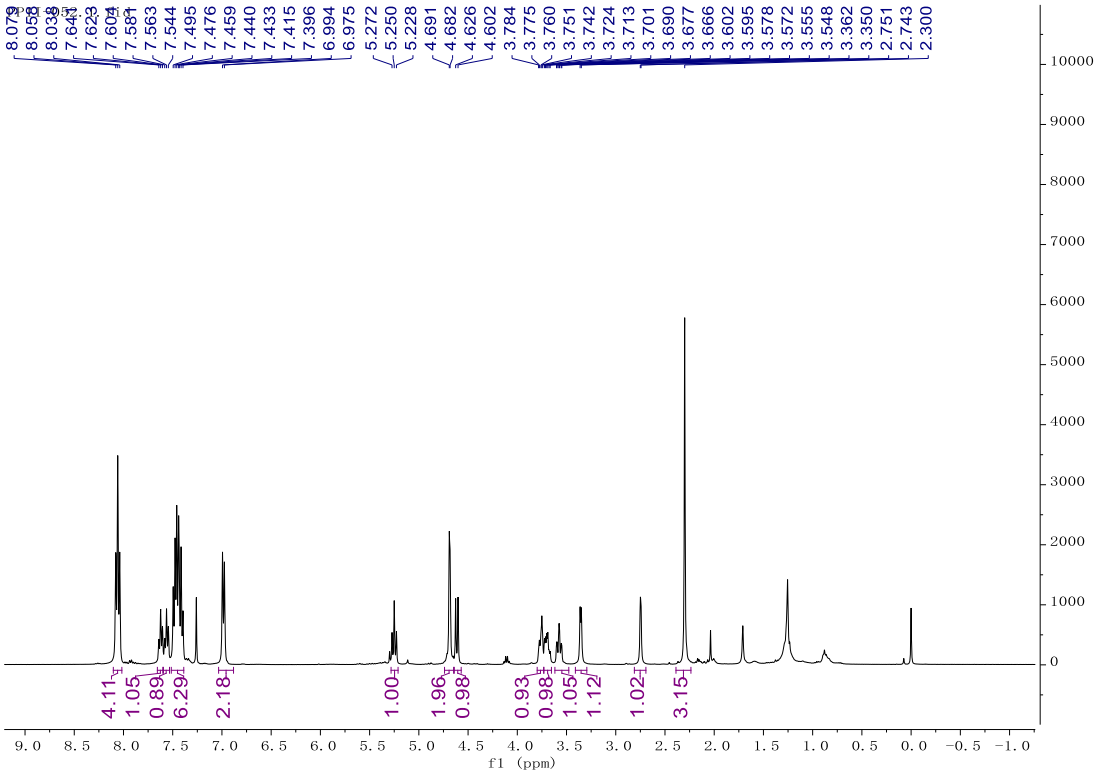
1. Chen, P.; Wang, P.; Song, N.; Li, M., *Steroids* **2013,** *78*, 959-966.
2. Song, G.; Yang, S.; Zhang, W.; Cao, Y.; Wang, P.; Ding, N.; Zhang, Z.; Guo, Y.; Li, Y., *J. Med. Chem.* **2009,** *52*, 7368-7371.
3. Du, Y.; Gu, G.; Wei, G.; Hua, Y.; Linhardt, R. J., *Org. Lett.* **2003,** *5*, 3627-3630.
4. Yu, B.; Tao, H., *Tetrahedron Lett.* **2001,** *42*, 2405-2407.
5. Nakano, K.; Murakami, K.; Takaishi, Y.; Tomimatsu, T.; Nohara, T., *Chem. Pharm. Bull.* **1989,** *37*, 116-118.

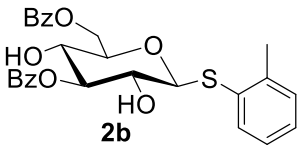
Copies of NMR Spectra



2a

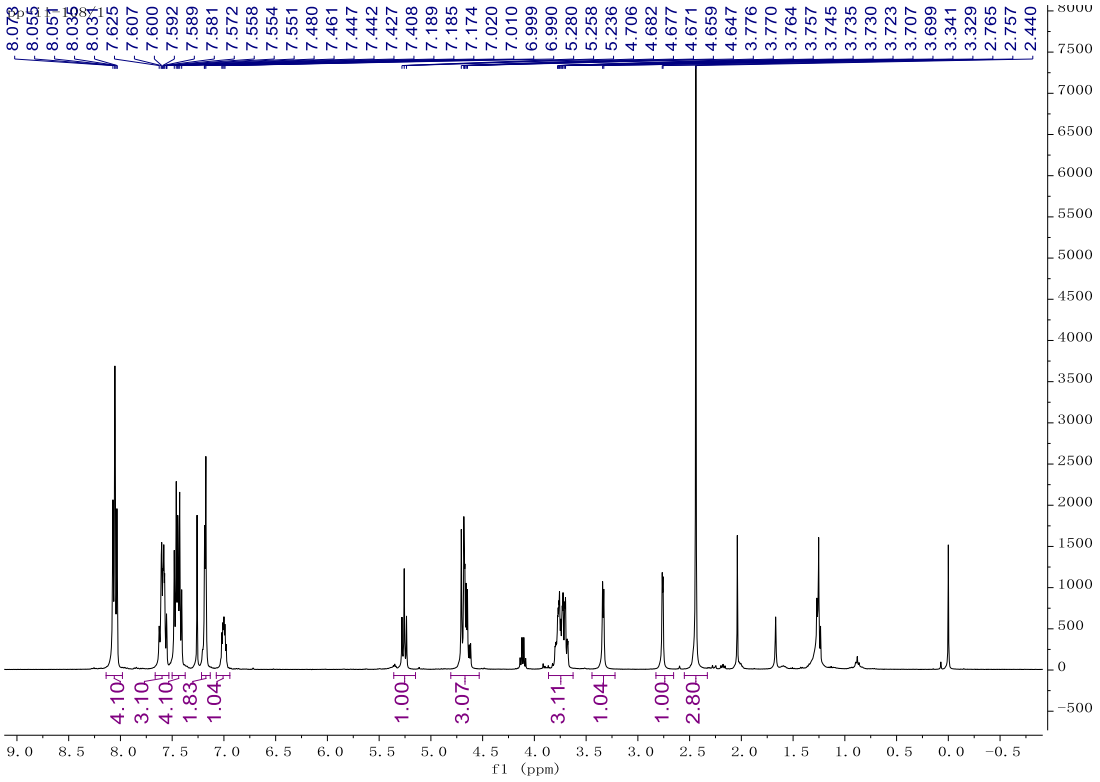
^{1}H NMR ($CDCl_3$, 400 MHz) of **2a**

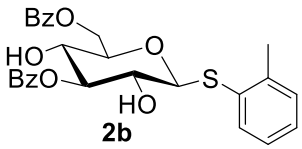




2b

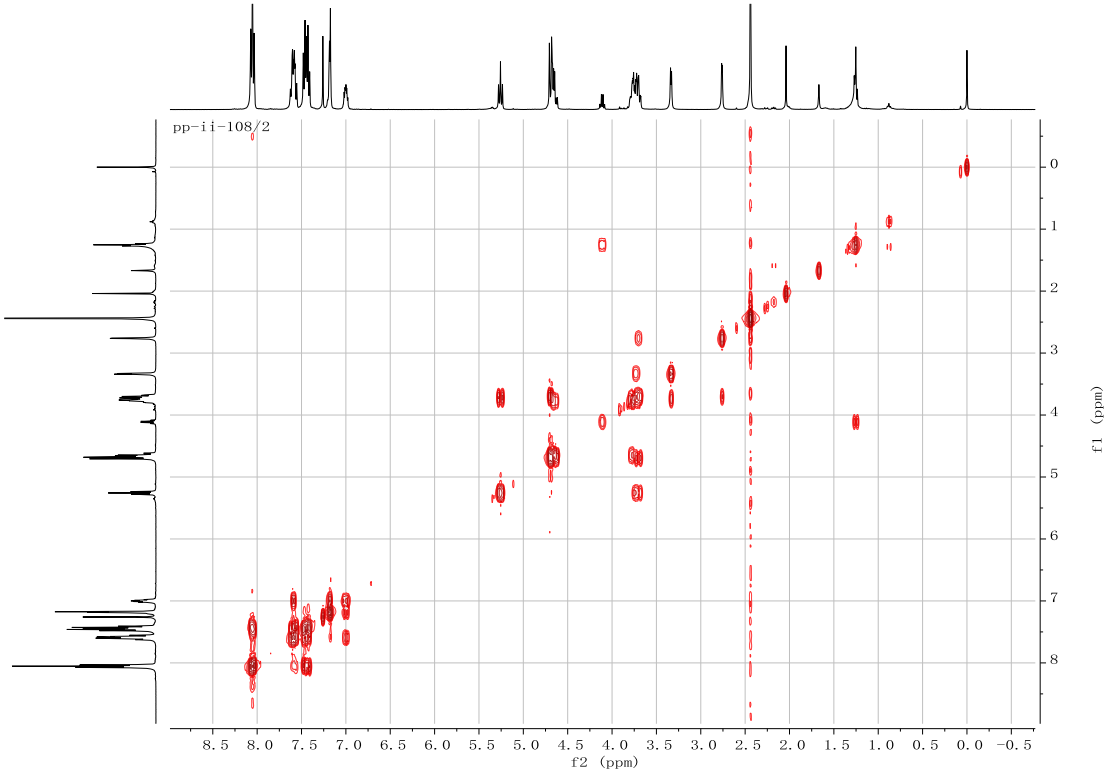
^{1}H NMR ($CDCl_3$, 400 MHz) of **2b**

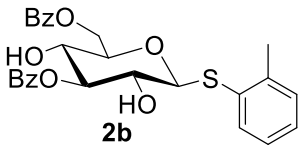




2b

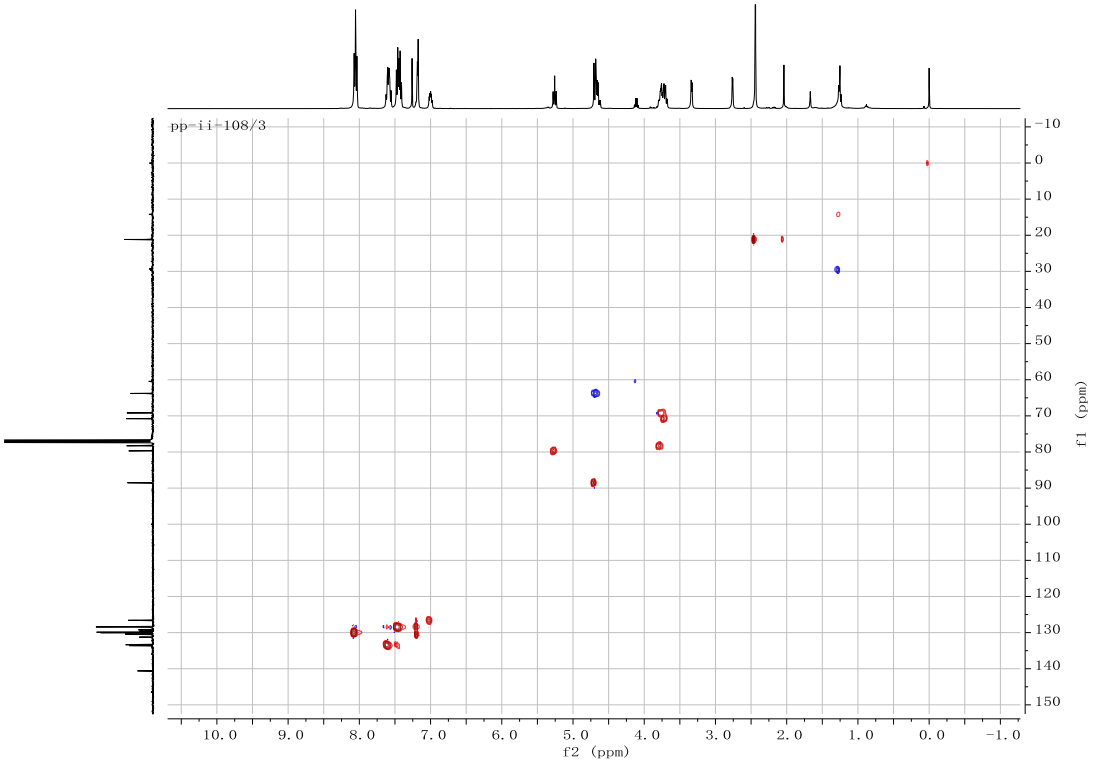
gCOSY ($CDCl_3$, 400 MHz) of **2b**

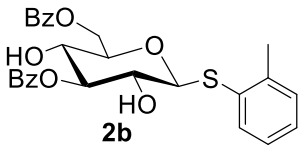




2b

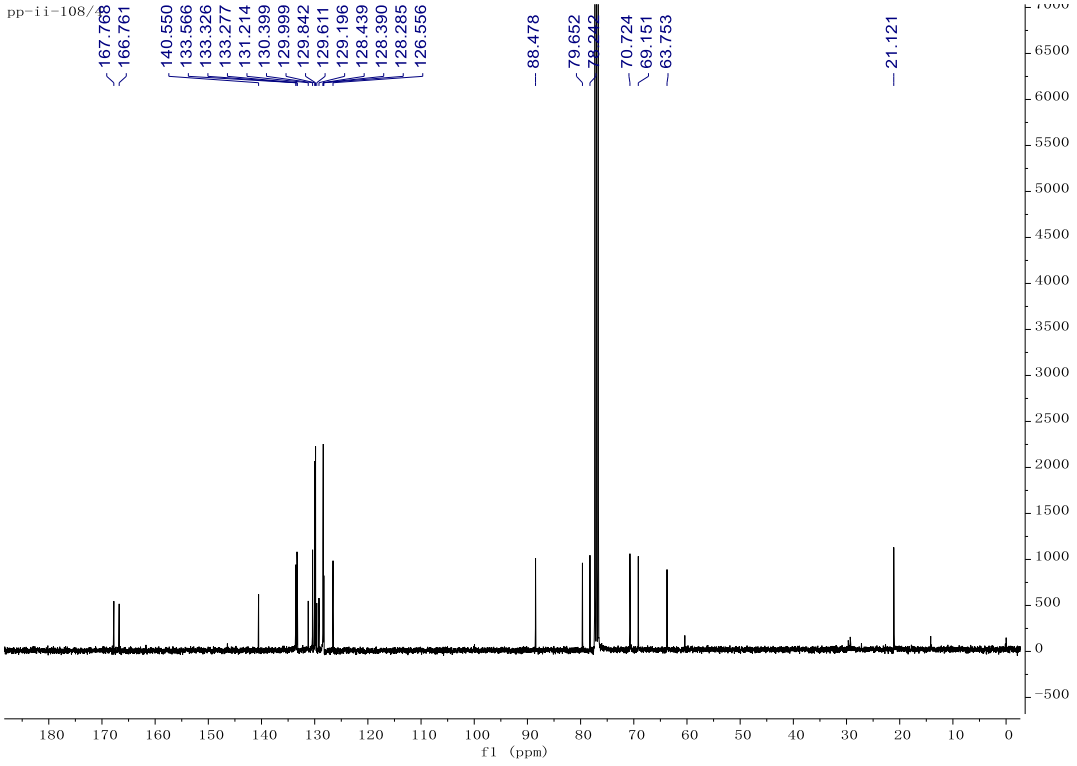
gHSQC ($CDCl_3$, 400 MHz) of **2b**

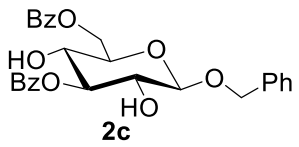




2b

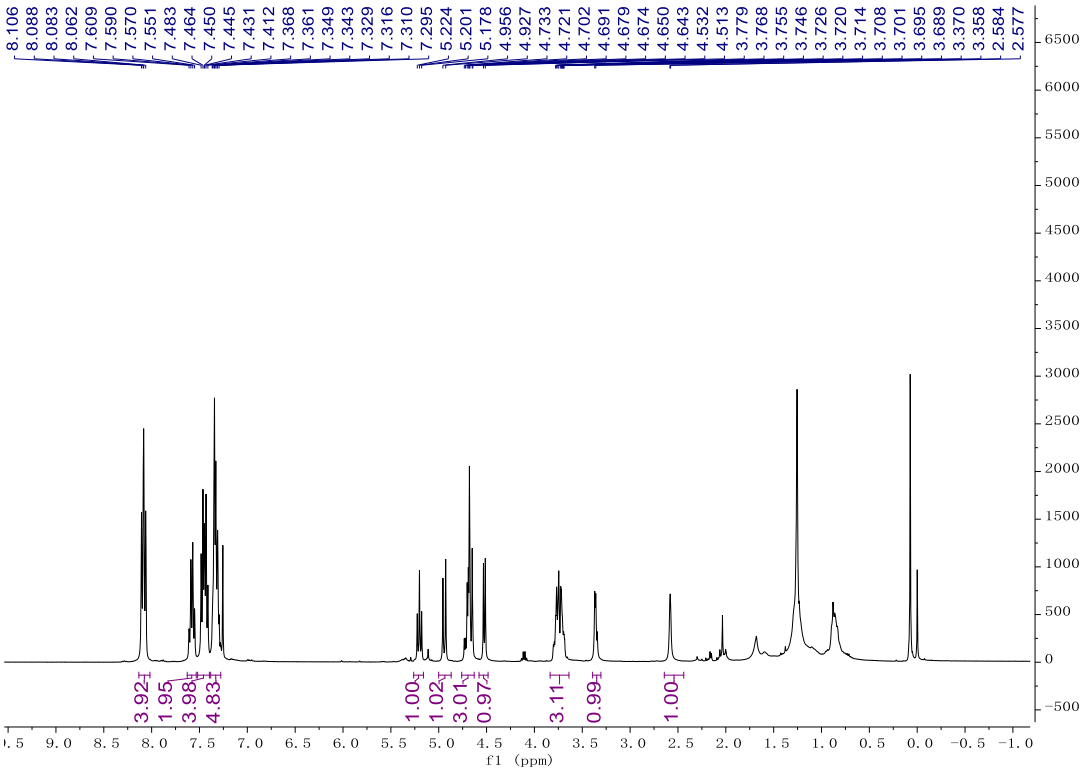
^{13}C NMR ($CDCl_3$, 101 MHz) of **2b**

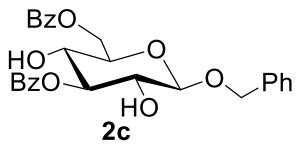




2c

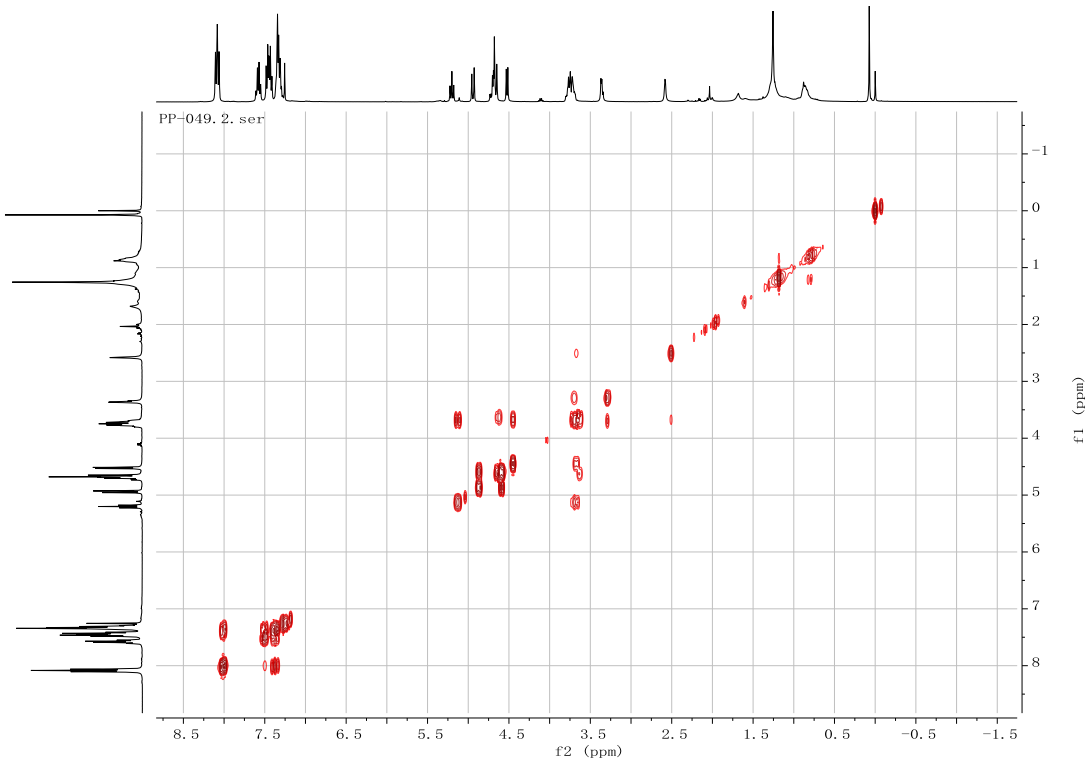
^{1}H NMR ($CDCl_3$, 400 MHz) of **2c**

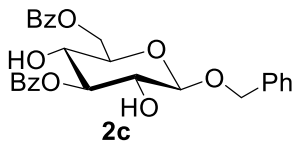




2c

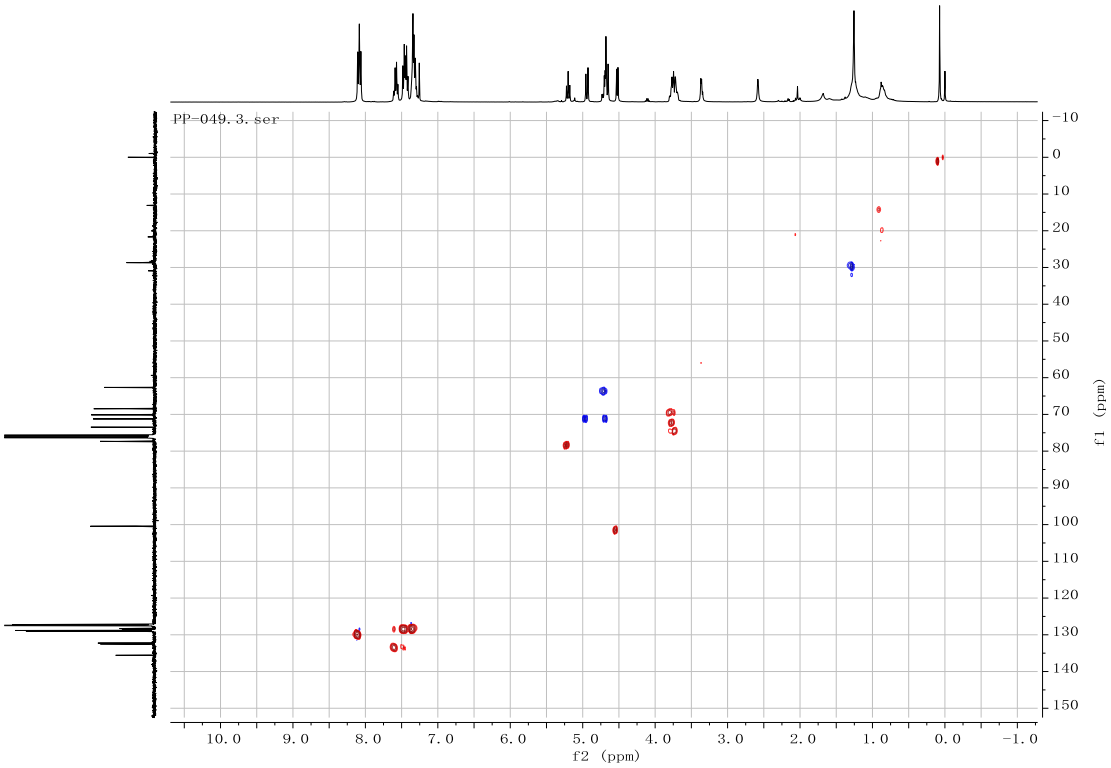
gCOSY ($CDCl_3$, 400 MHz) of **2c**

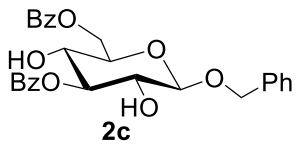




2c

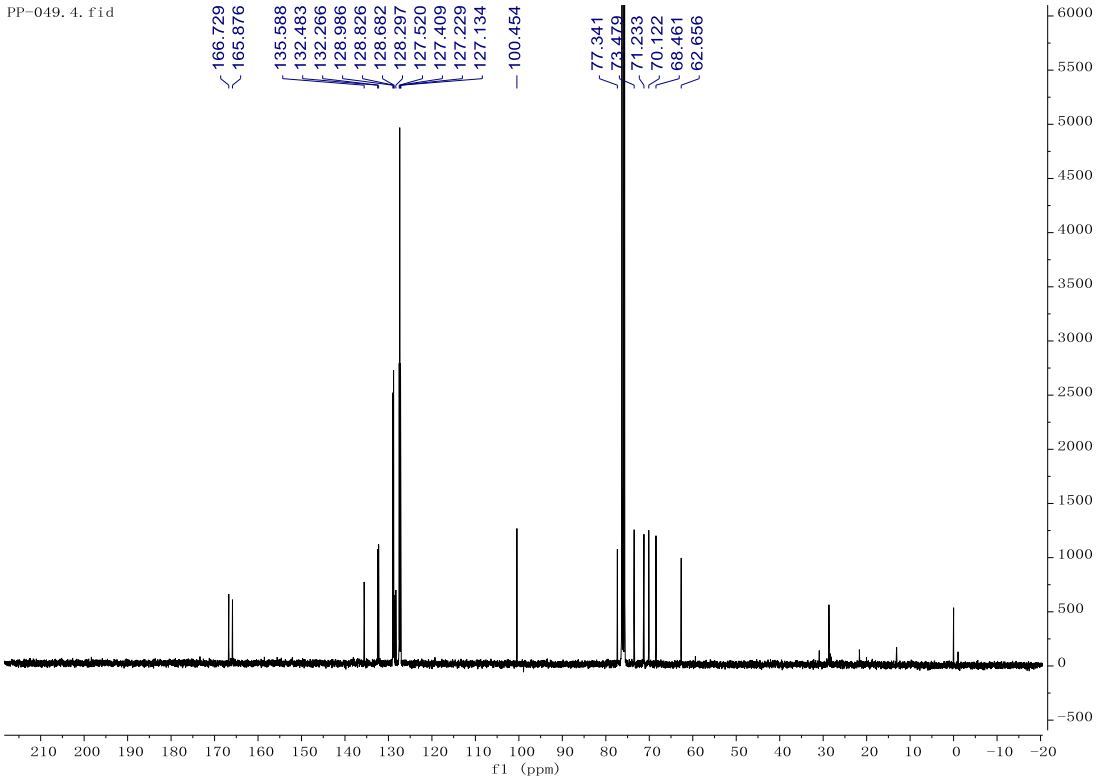
gHSQC ($CDCl_3$, 400 MHz) of **2c**

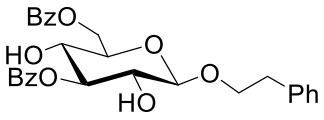




2c

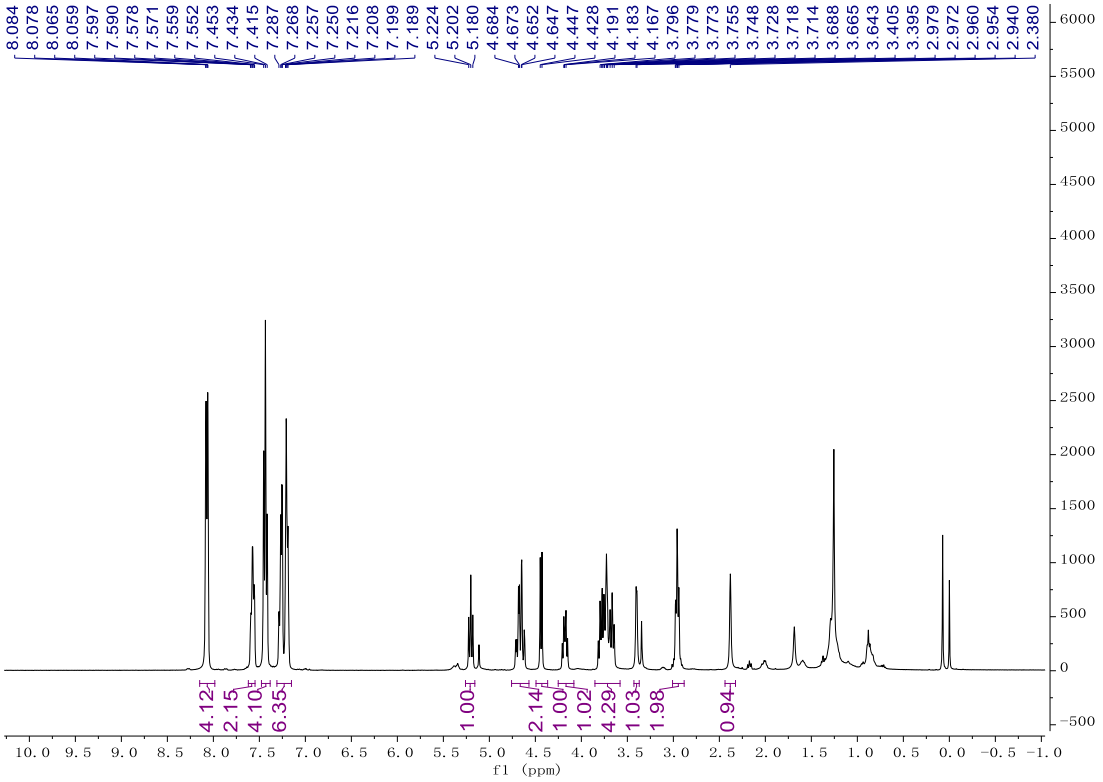
^{13}C NMR ($CDCl_3$, 101 MHz) of **2c**

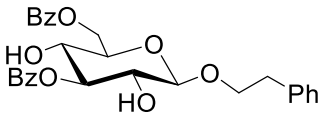




2d

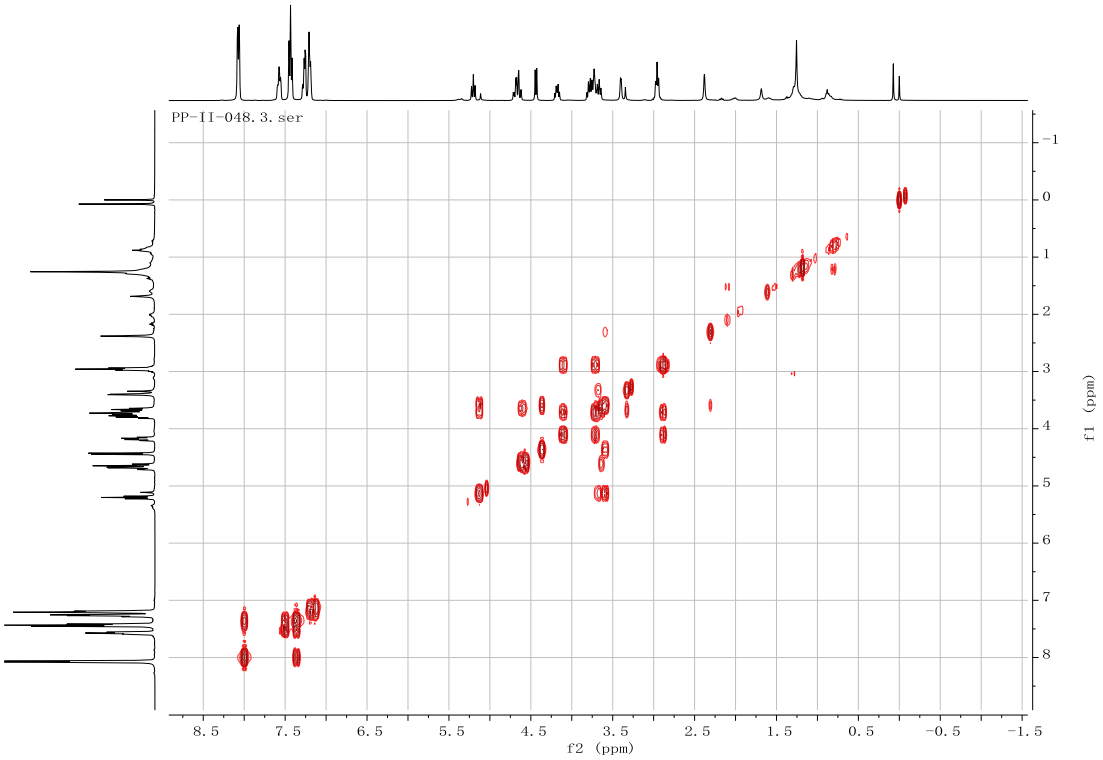
^{1}H NMR ($CDCl_3$, 400 MHz) of **2d**

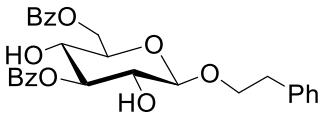




2d

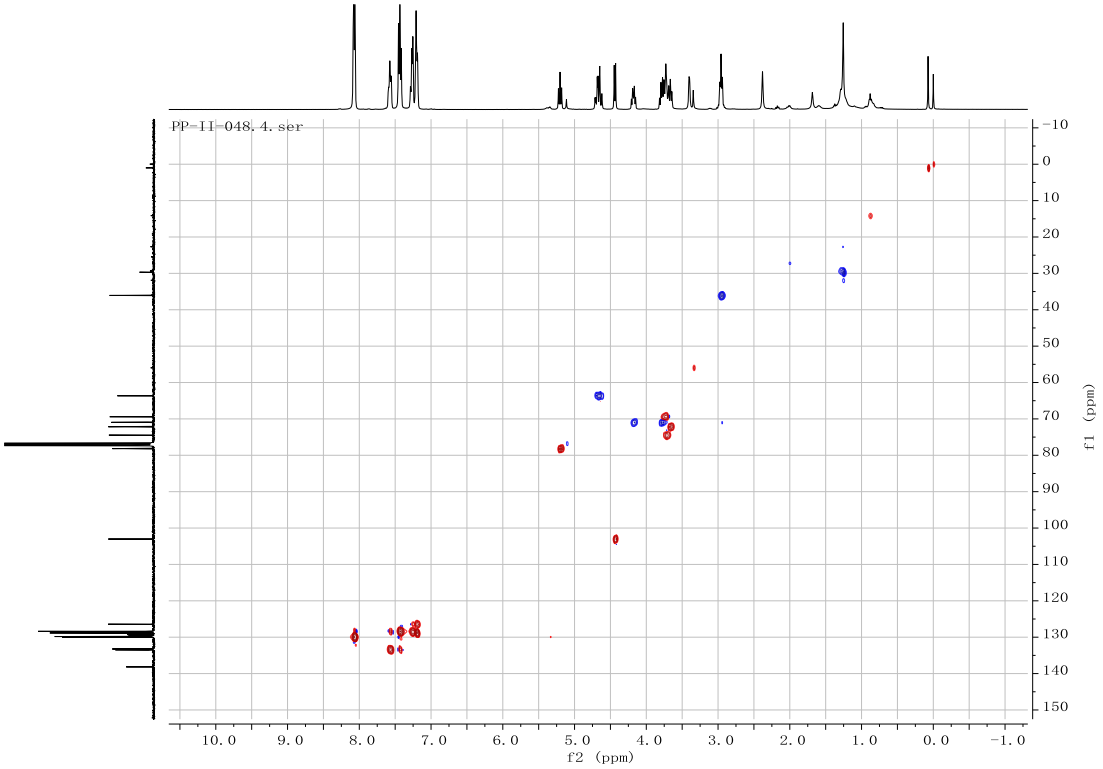
gCOSY ($CDCl_3$, 400 MHz) of **2d**

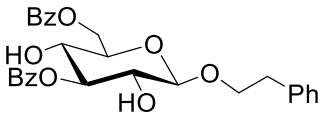




2d

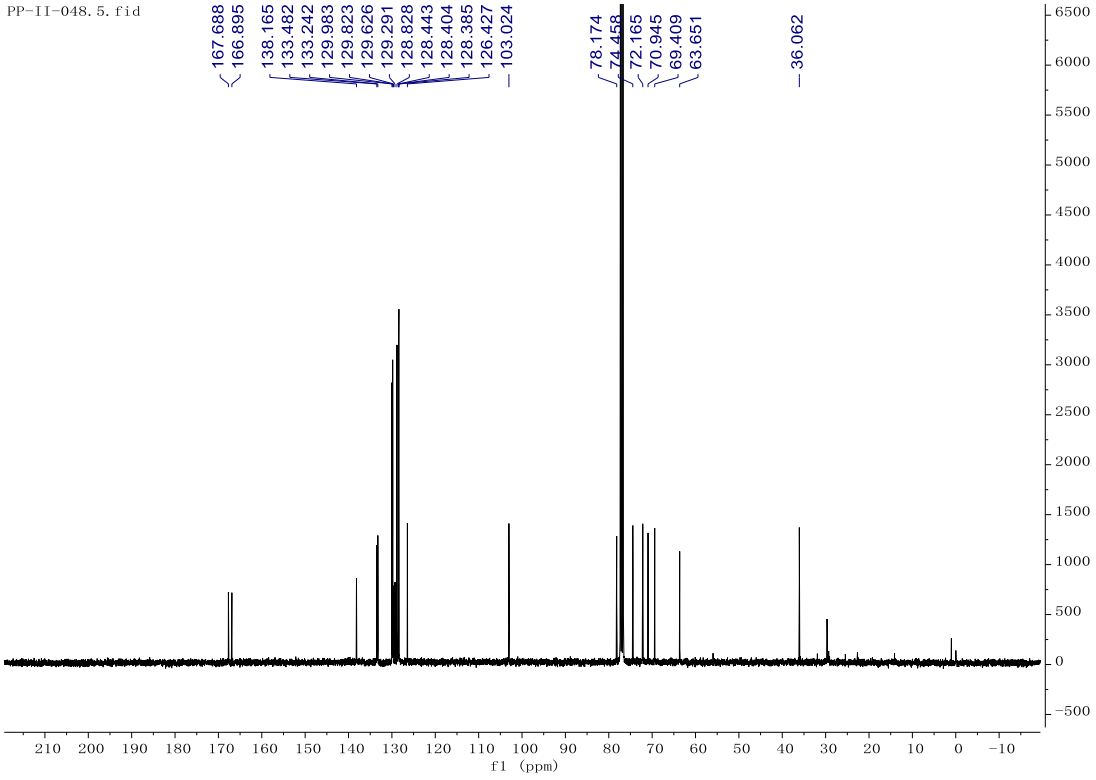
gHSQC ($CDCl_3$, 400 MHz) of **2d**

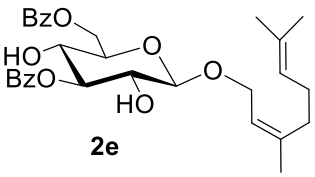




2d

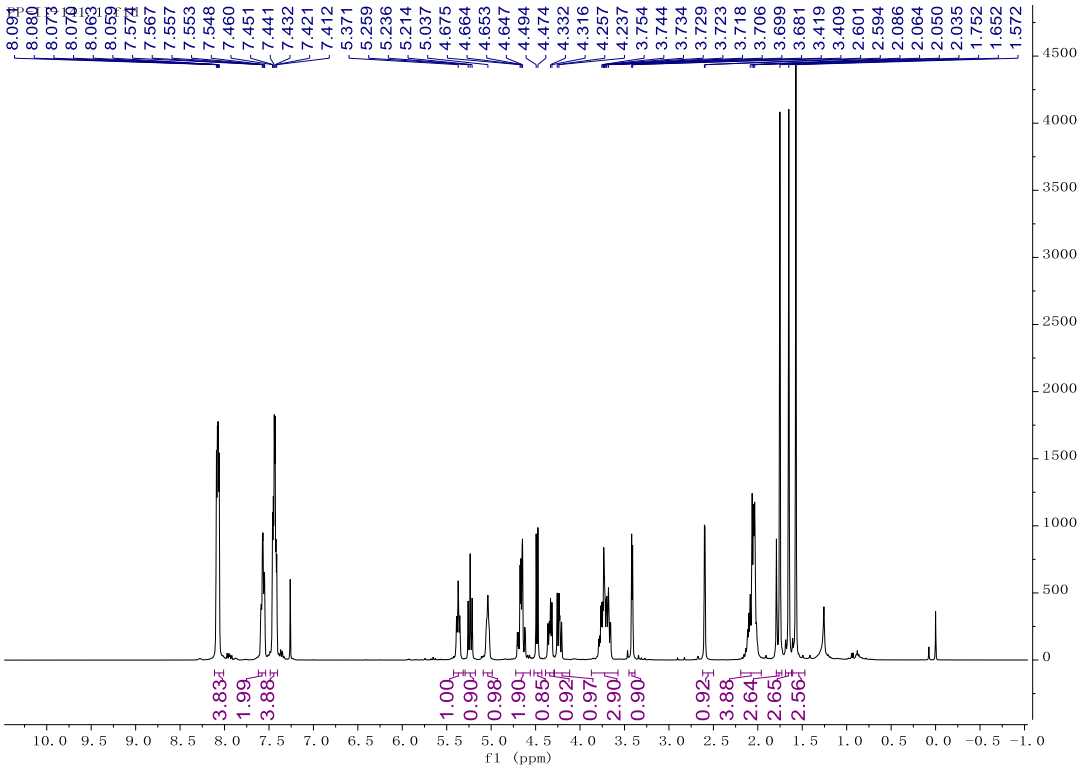
^{13}C NMR ($CDCl_3$, 101 MHz) of **2d**

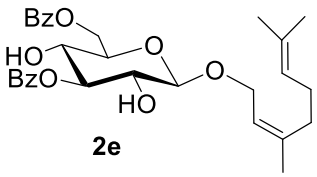




2e

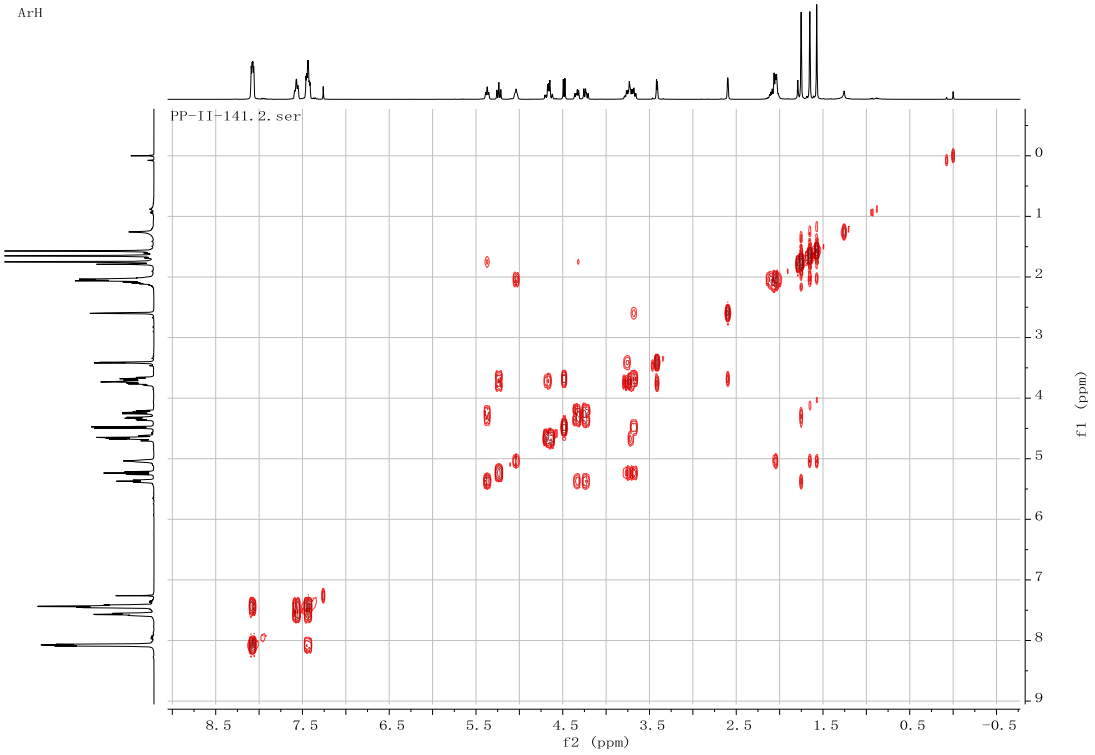
^{1}H NMR ($CDCl_3$, 400 MHz) of **2e**

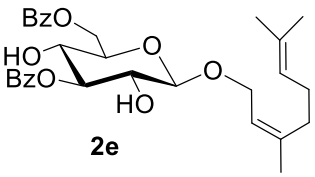




2e

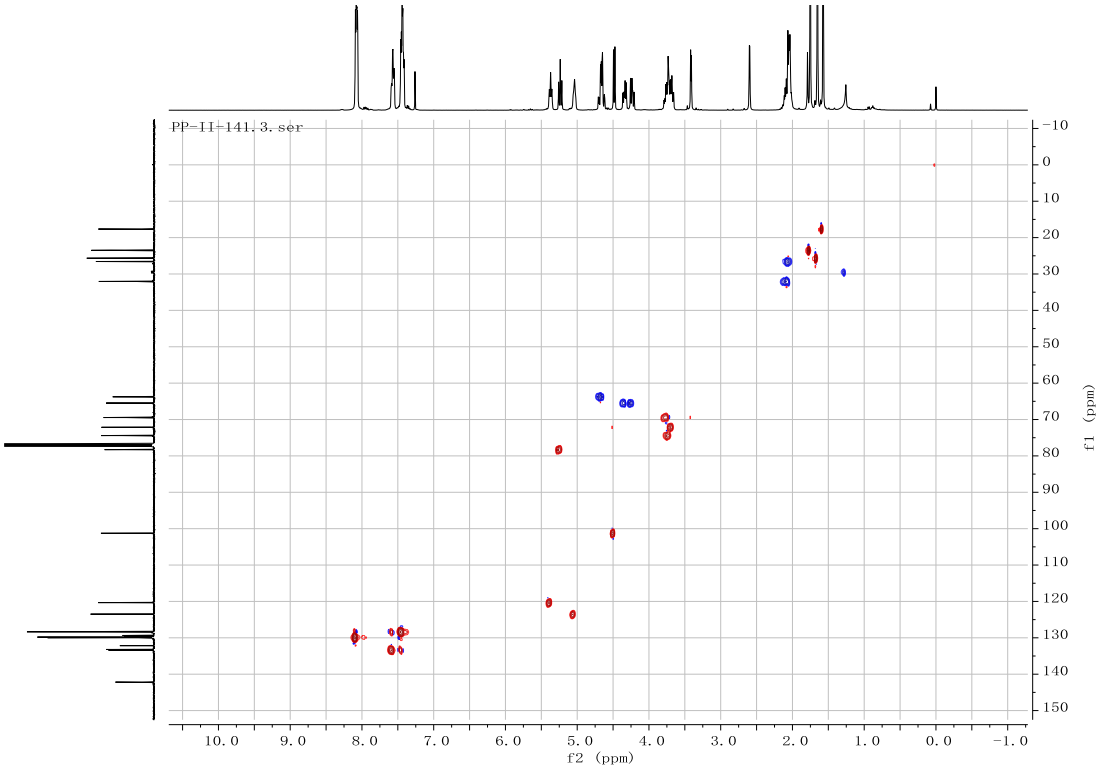
gCOSY ($CDCl_3$, 400 MHz) of **2e**

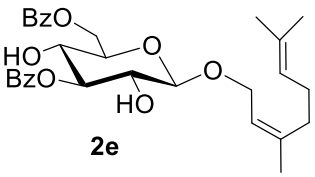




2e

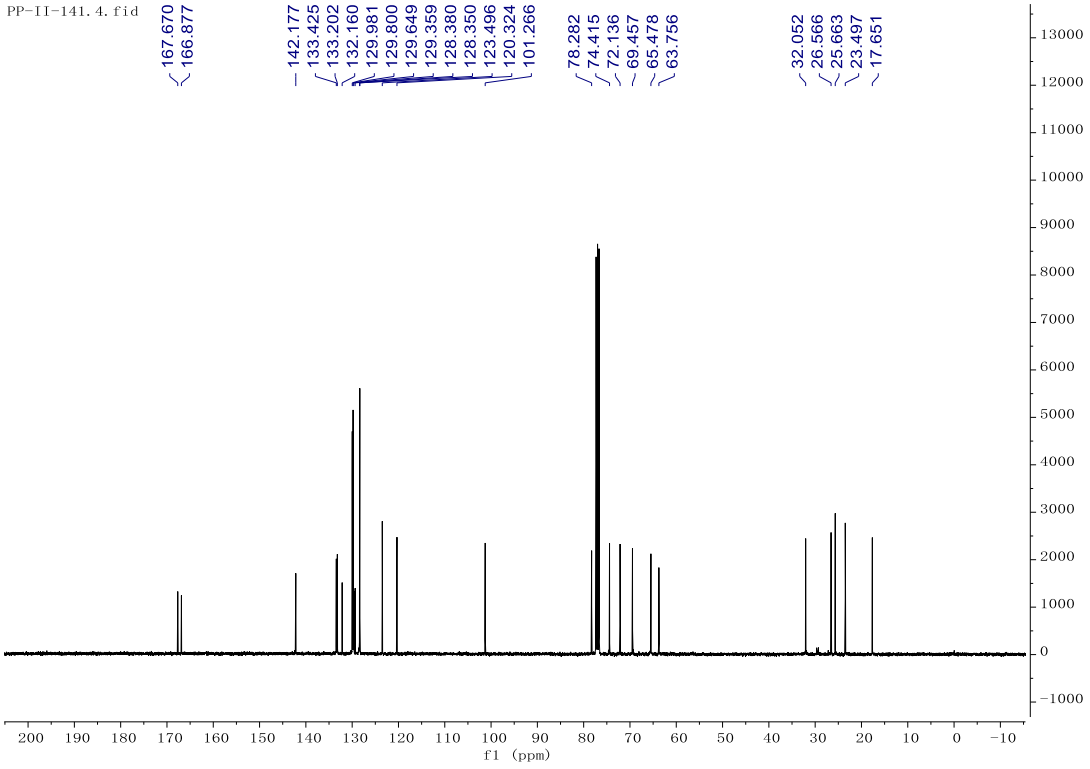
gHSQC ($CDCl_3$, 400 MHz) of **2e**

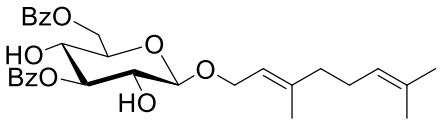




2e

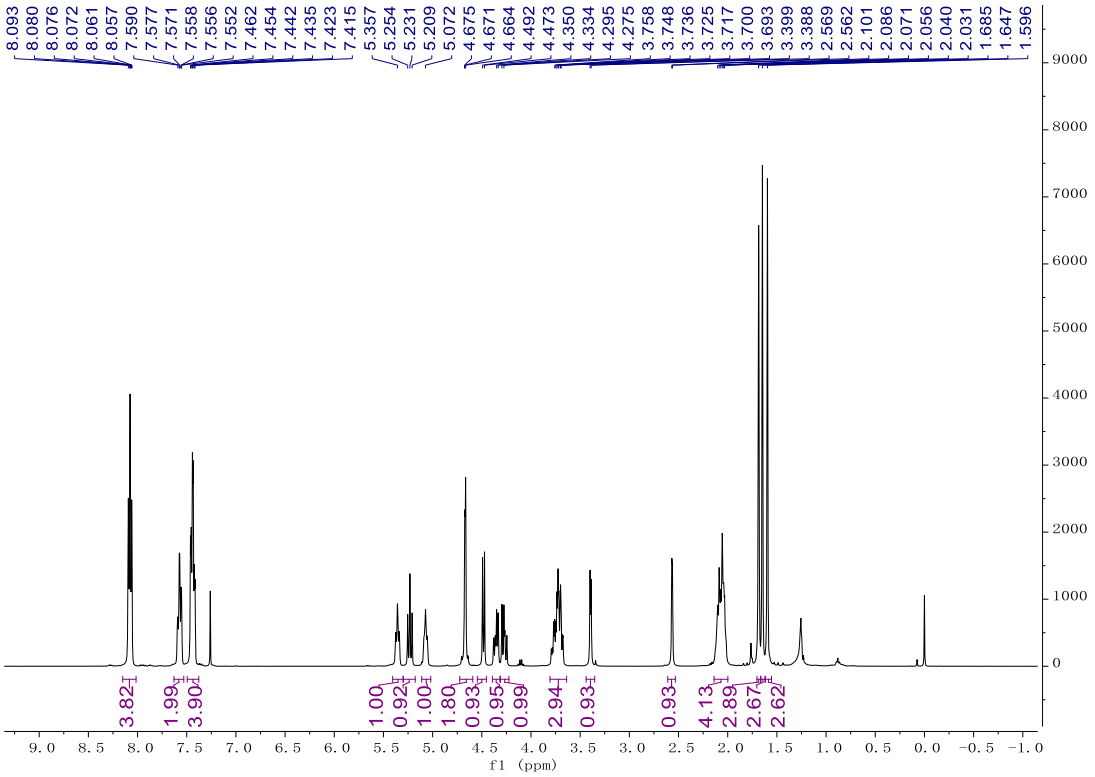
^{13}C NMR ($CDCl_3$, 101 MHz) of **2e**

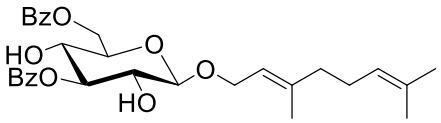




2f

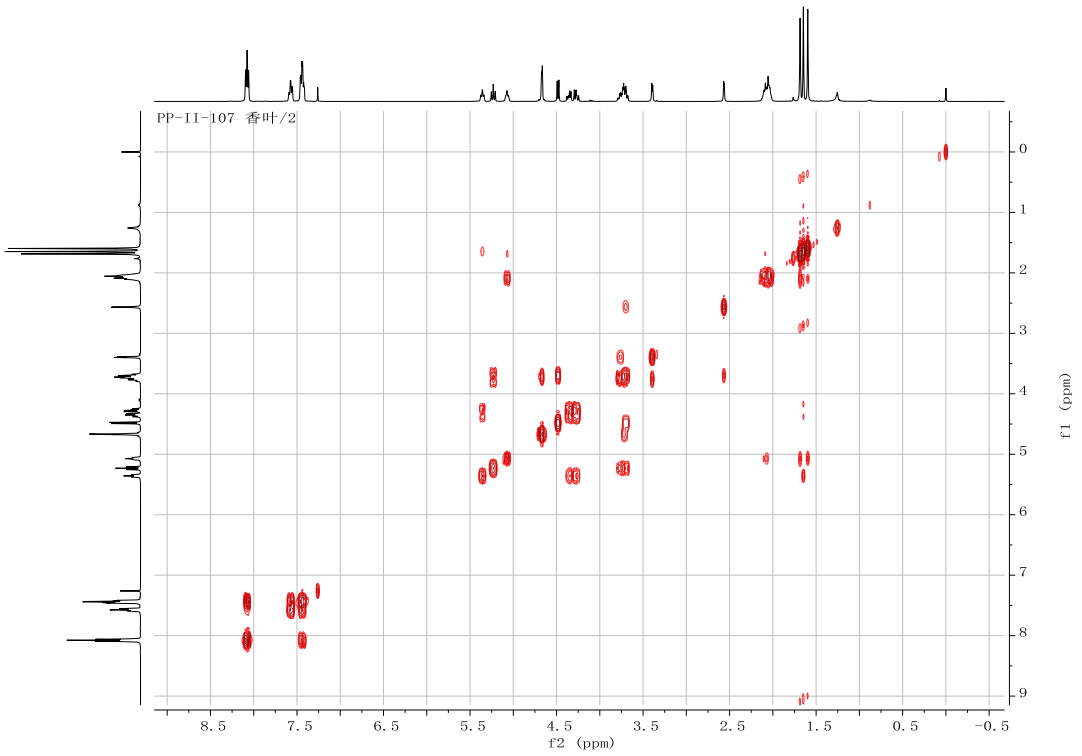
^{1}H NMR ($CDCl_3$, 400 MHz) of **2f**

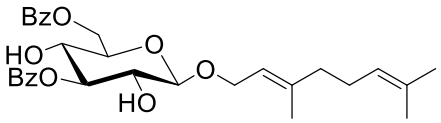




2f

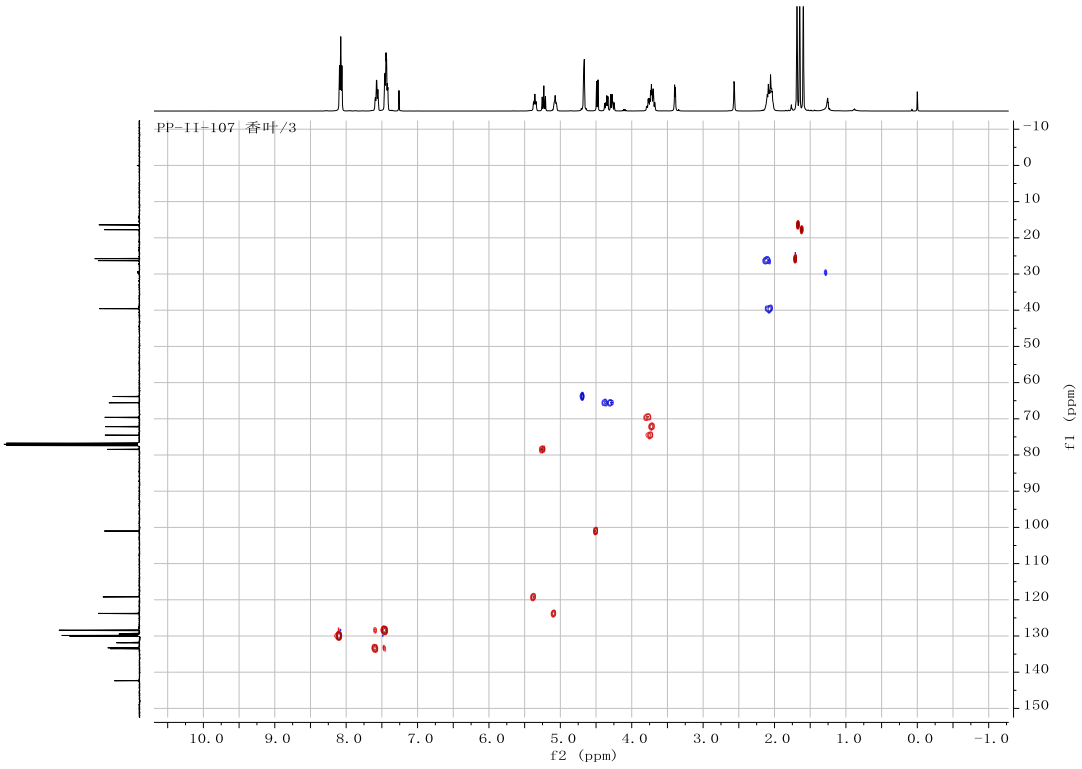
gCOSY ($CDCl_3$, 400 MHz) of **2f**

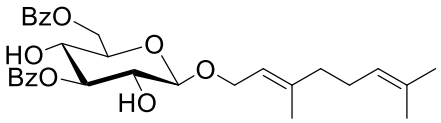




2f

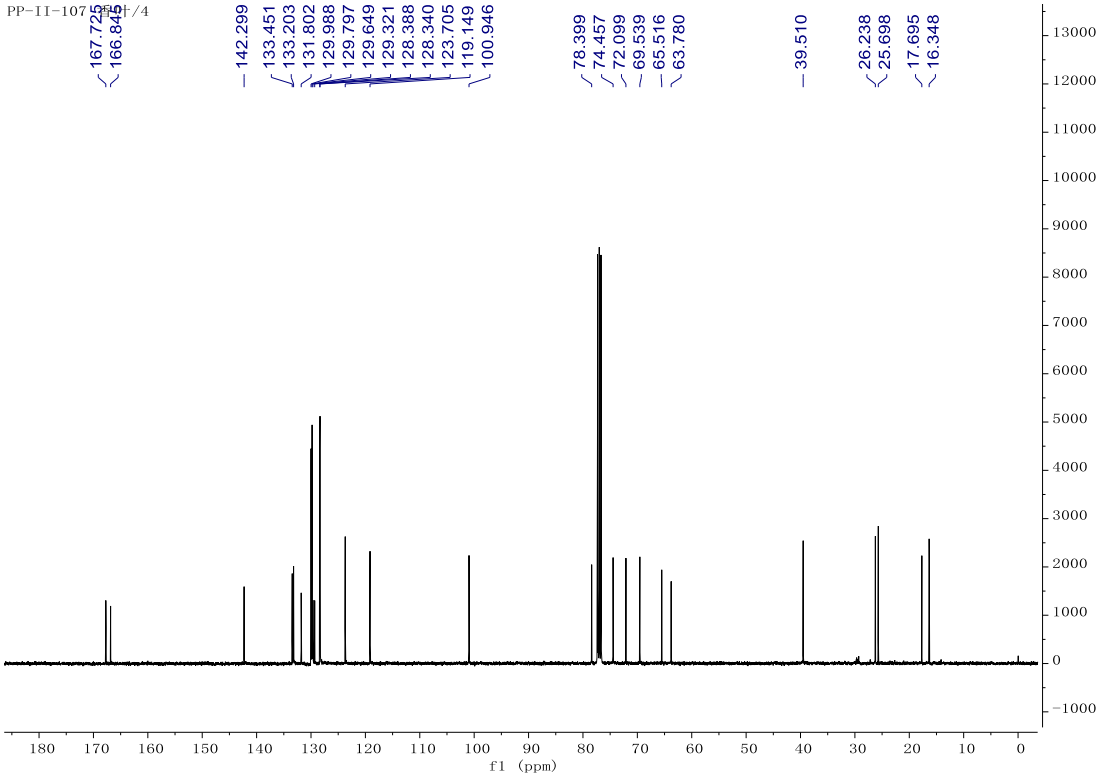
gHSQC ($CDCl_3$, 400 MHz) of **2f**

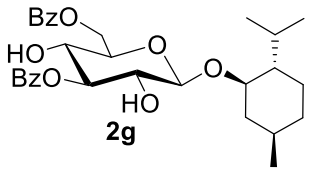




2f

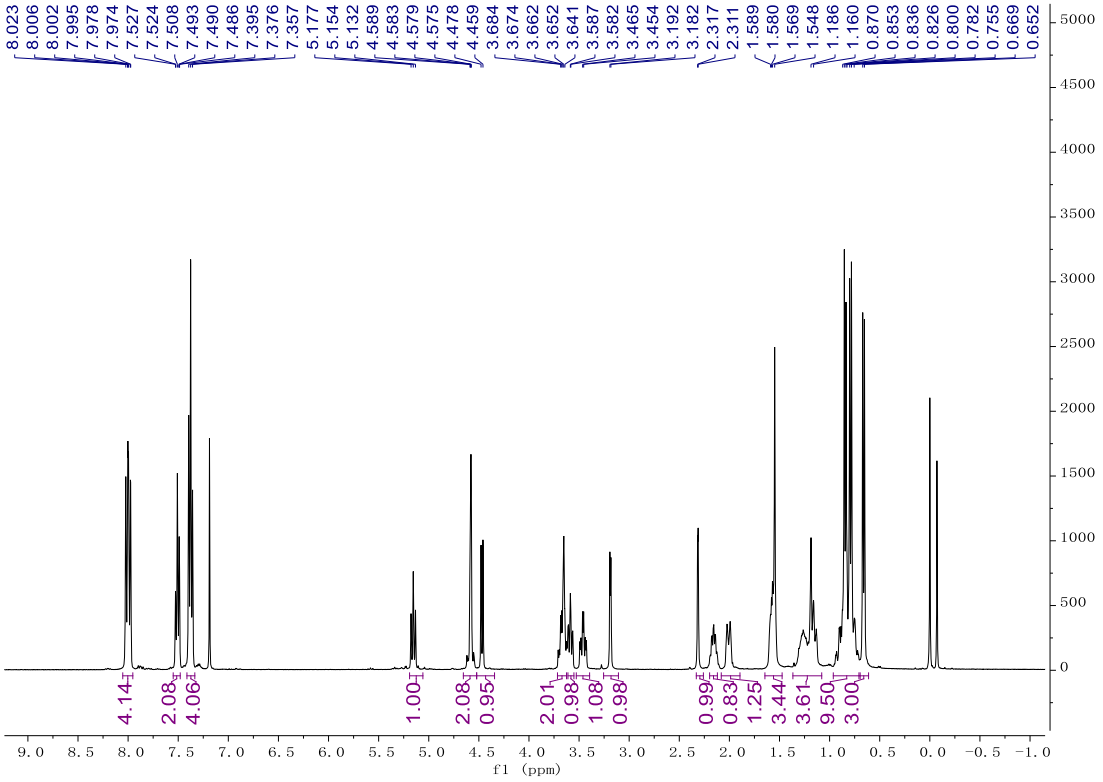
^{13}C NMR ($CDCl_3$, 101 MHz) of **2f**

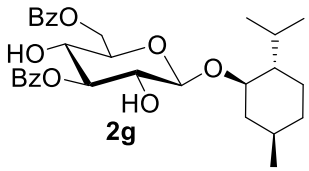




2g

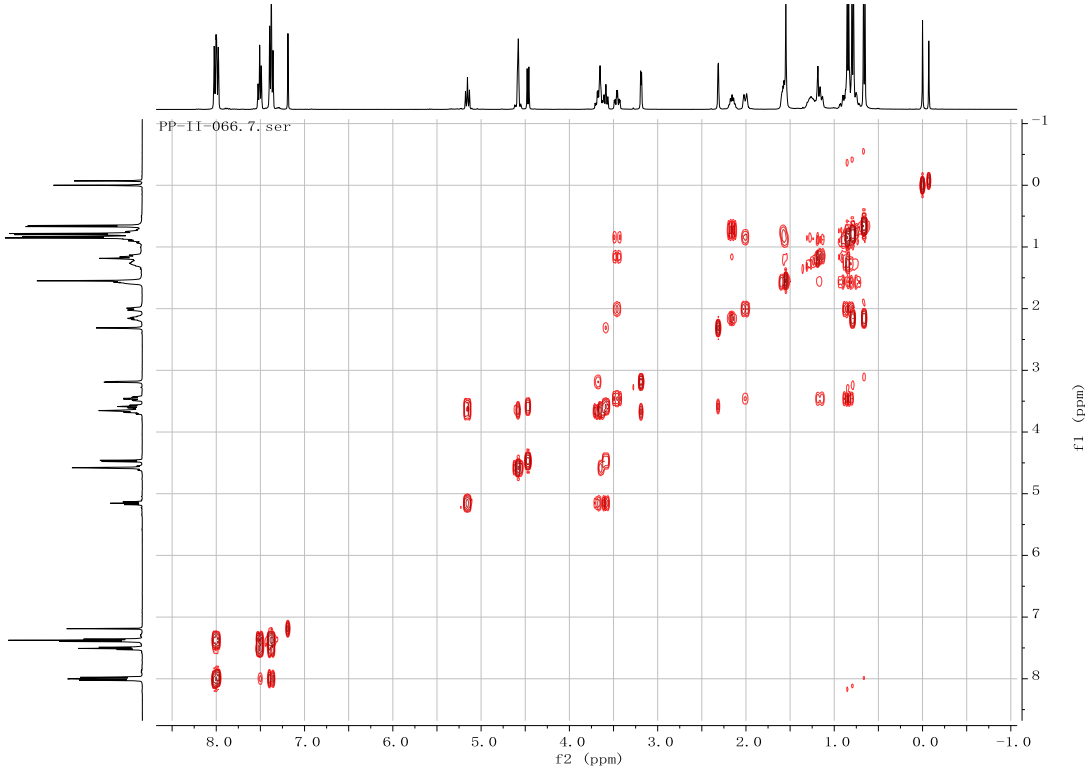
^{1}H NMR ($CDCl_3$, 400 MHz) of **2g**

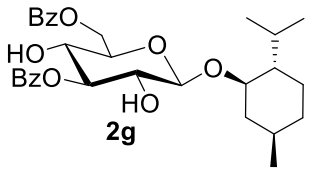




2g

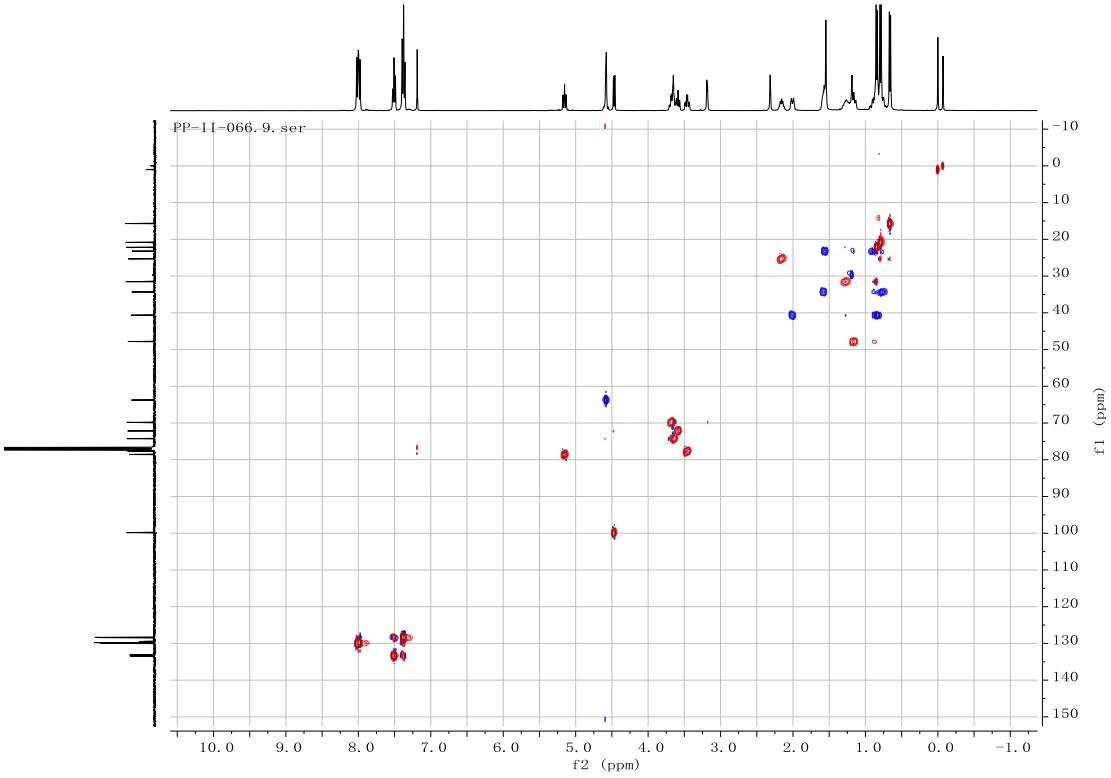
gCOSY ($CDCl_3$, 400 MHz) of **2g**

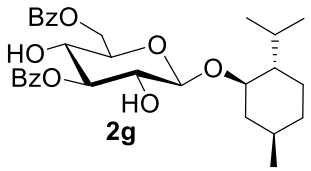




2g

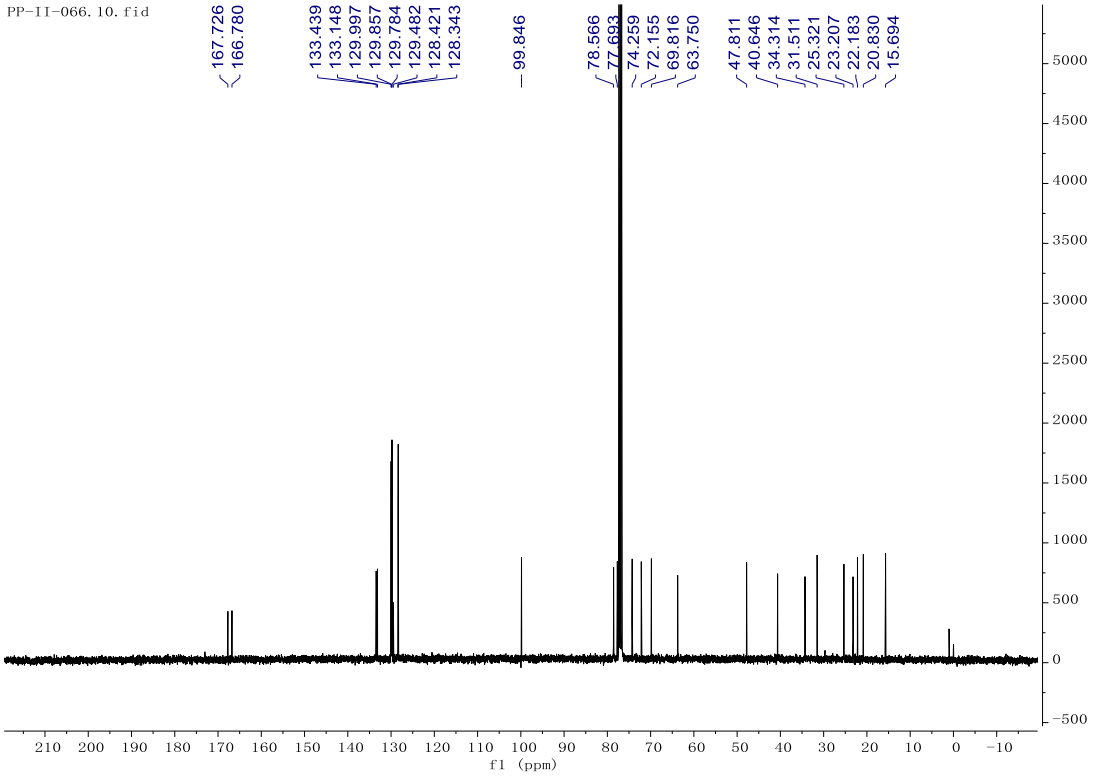
gHSQC ($CDCl_3$, 400 MHz) of **2g**

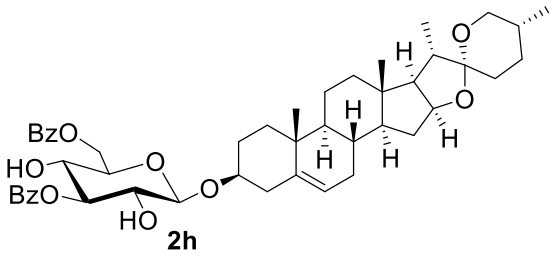




2g

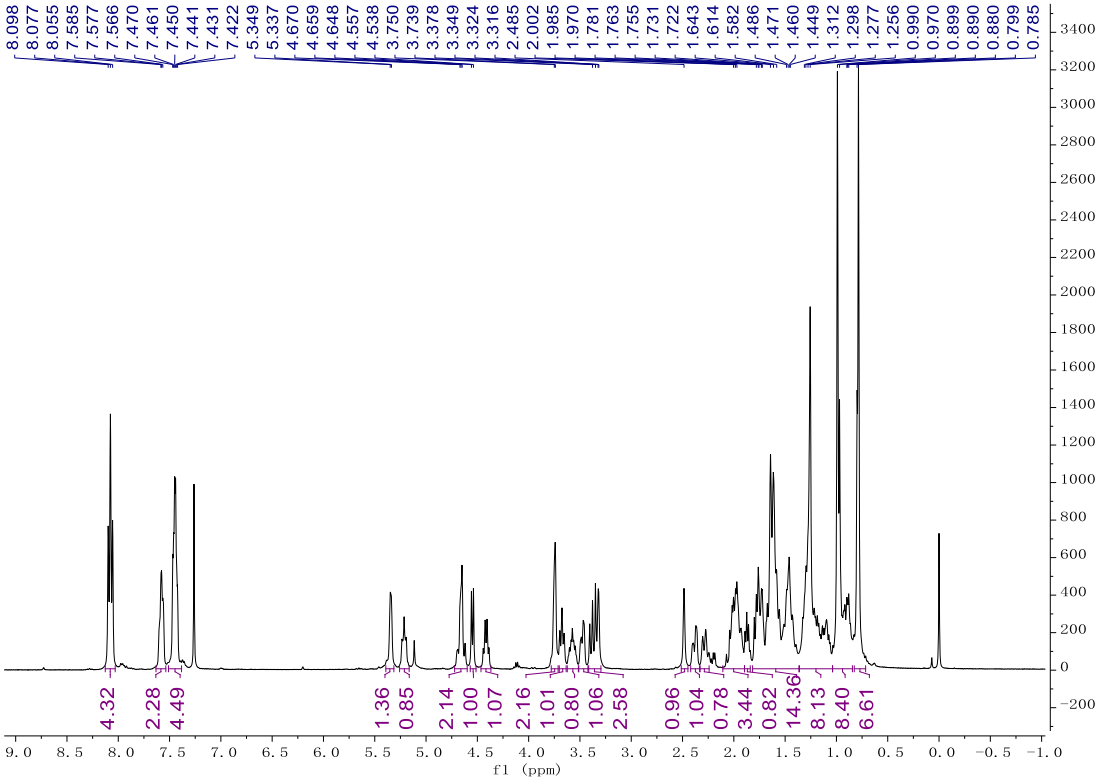
^{13}C NMR ($CDCl_3$, 101 MHz) of **2g**

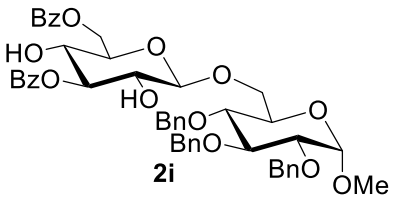




2h

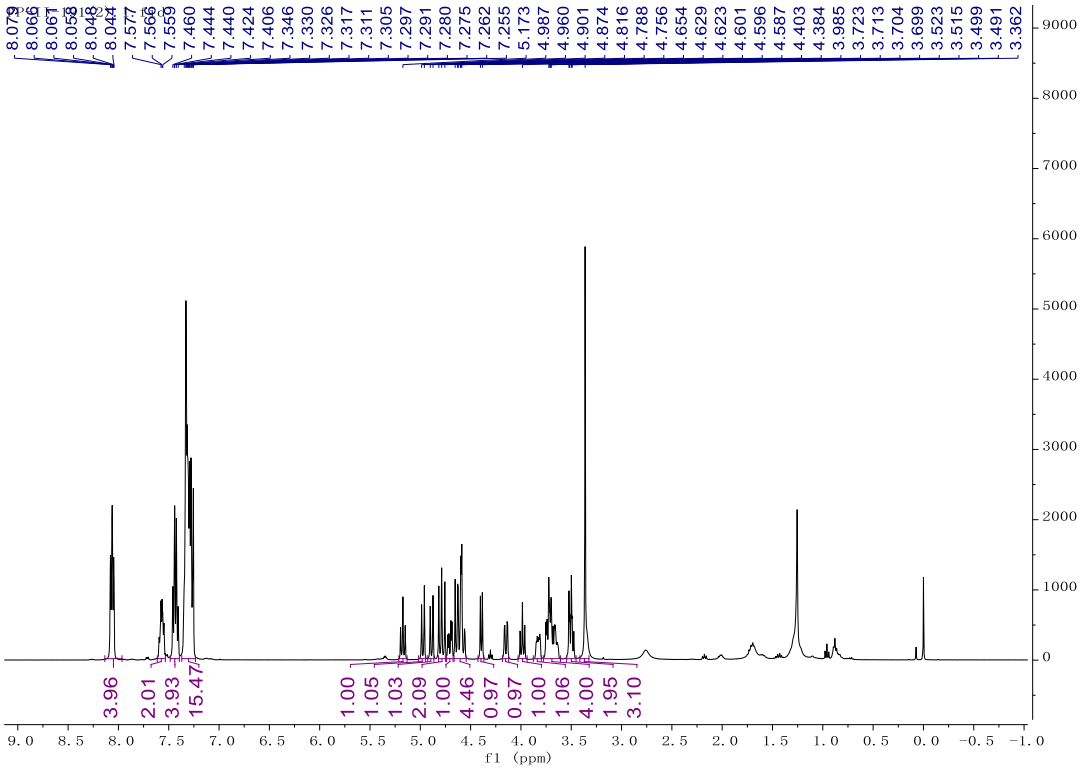
^{1}H NMR ($CDCl_3$, 400 MHz) of **2h**

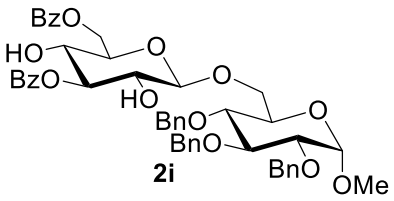




2i

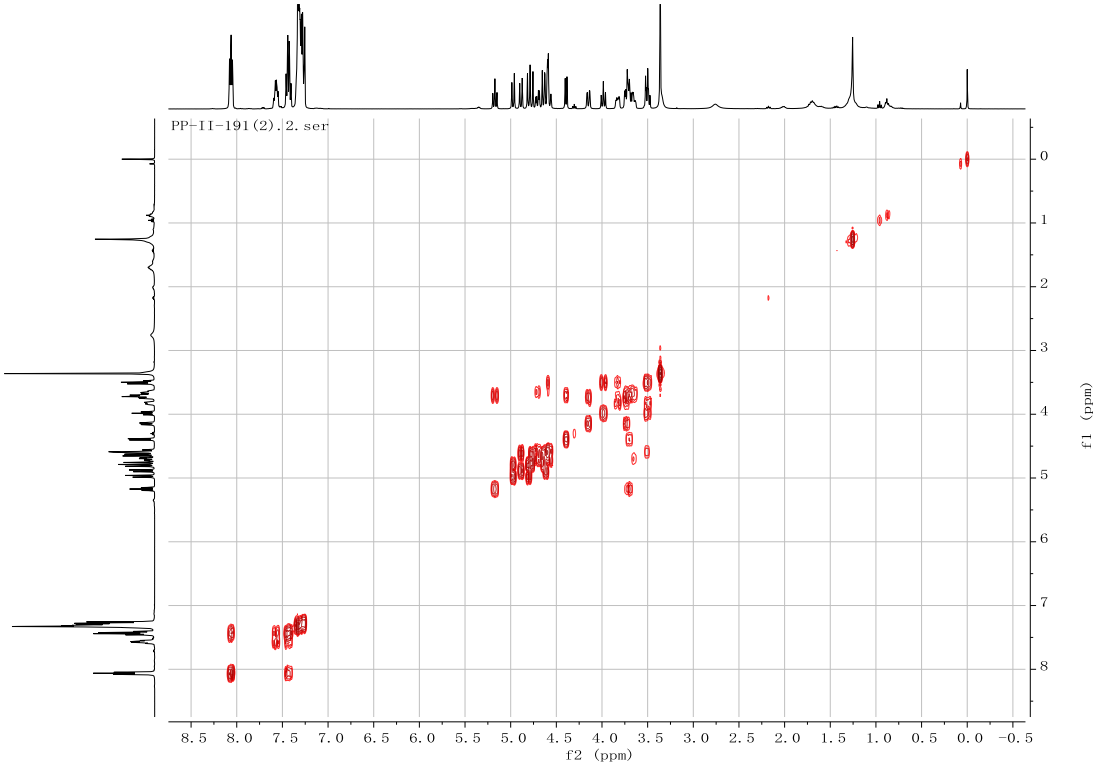
^{1}H NMR ($CDCl_3$, 400 MHz) of **2i**

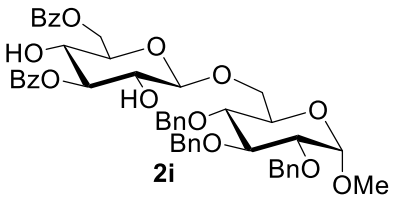




2i

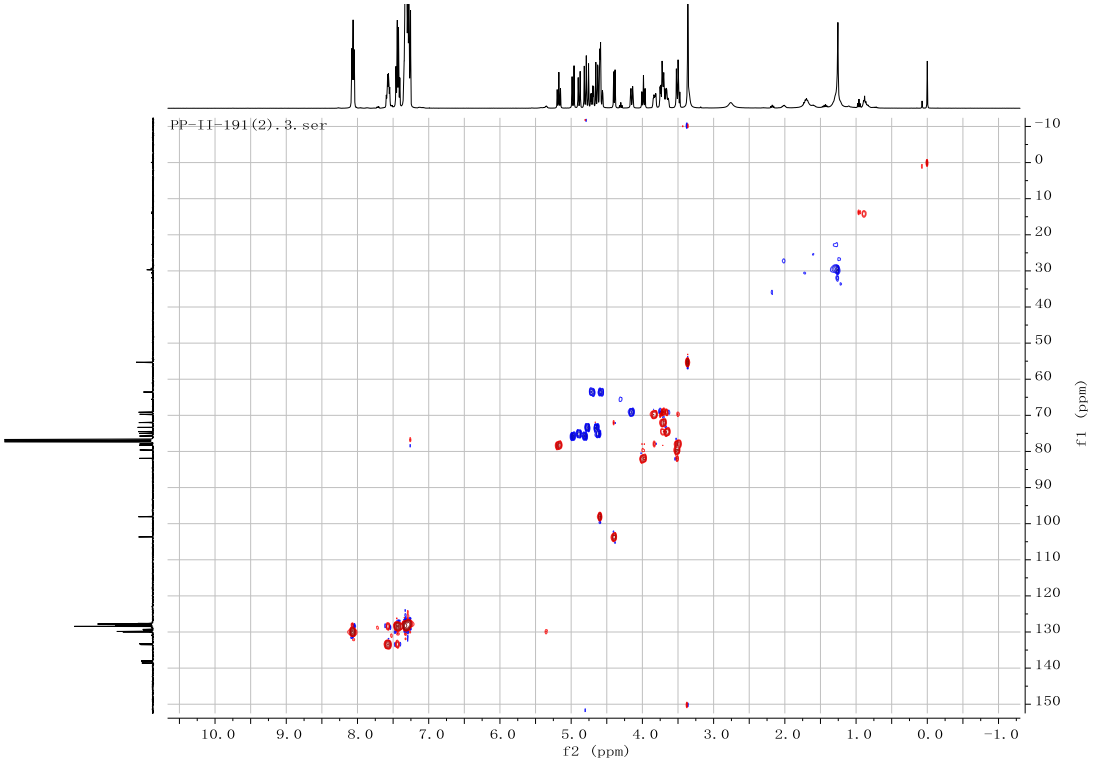
gCOSY ($CDCl_3$, 400 MHz) of **2i**

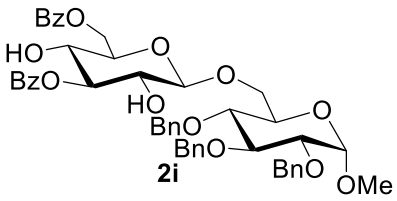




2i

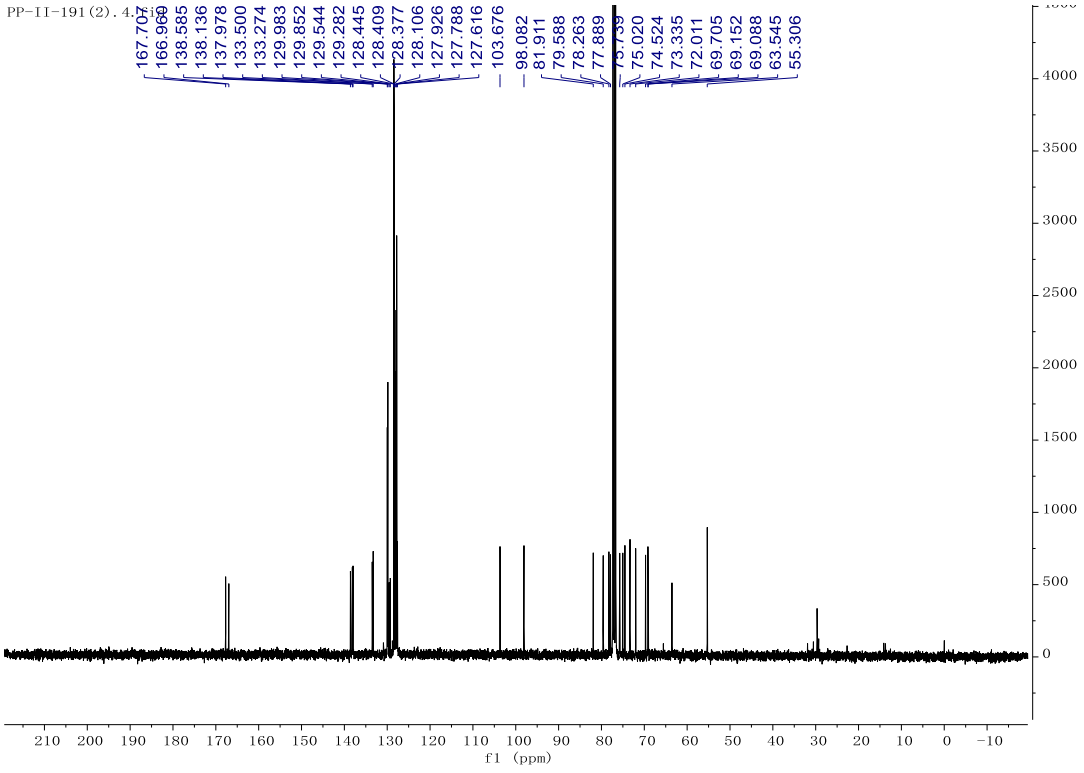
gHSQC ($CDCl_3$, 400 MHz) of **2i**

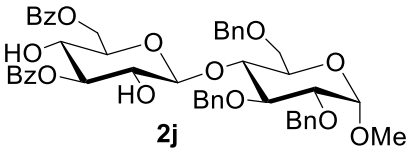




2i

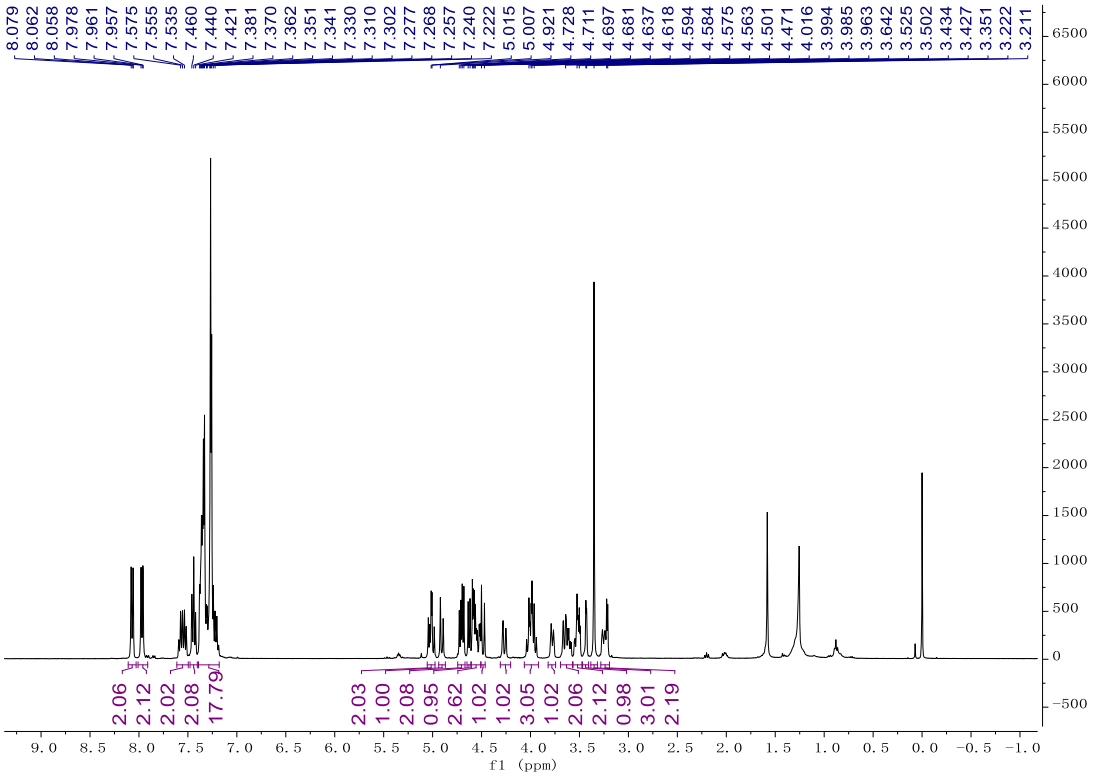
^{13}C NMR ($CDCl_3$, 101 MHz) of **2i**

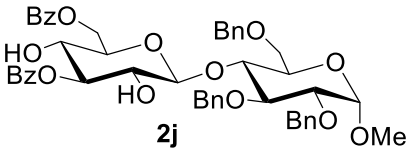




2j

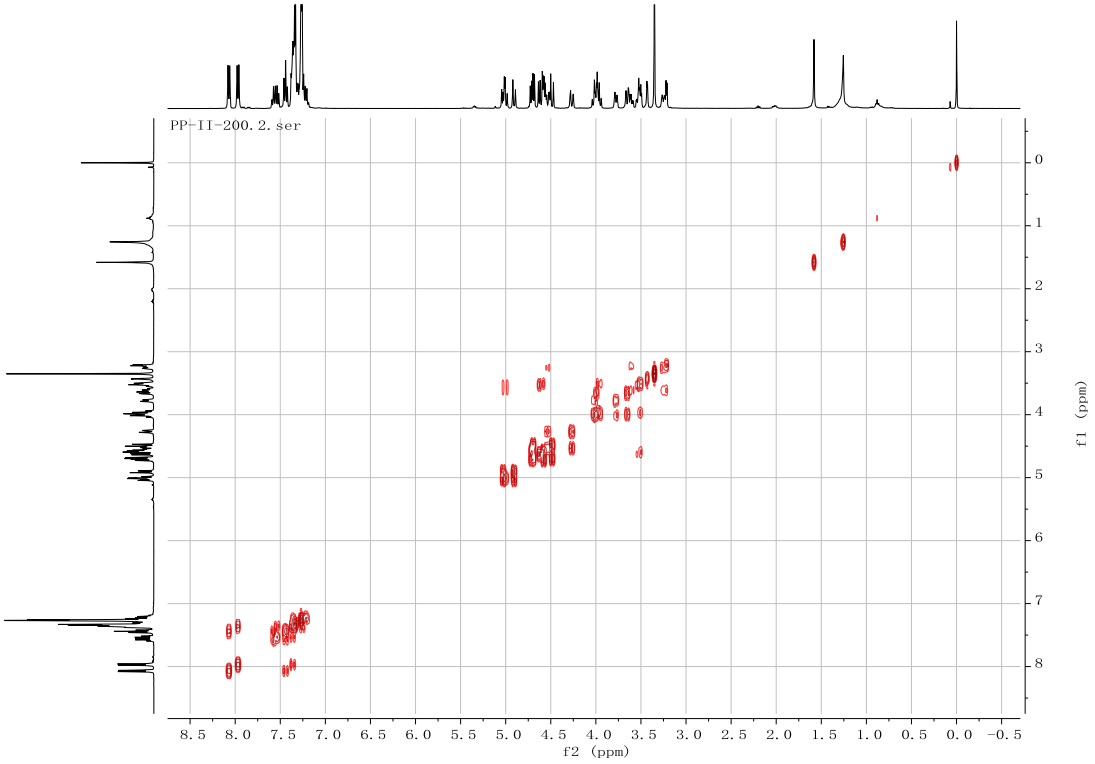
^{1}H NMR ($CDCl_3$, 400 MHz) of **2j**

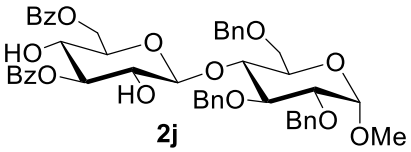




2j

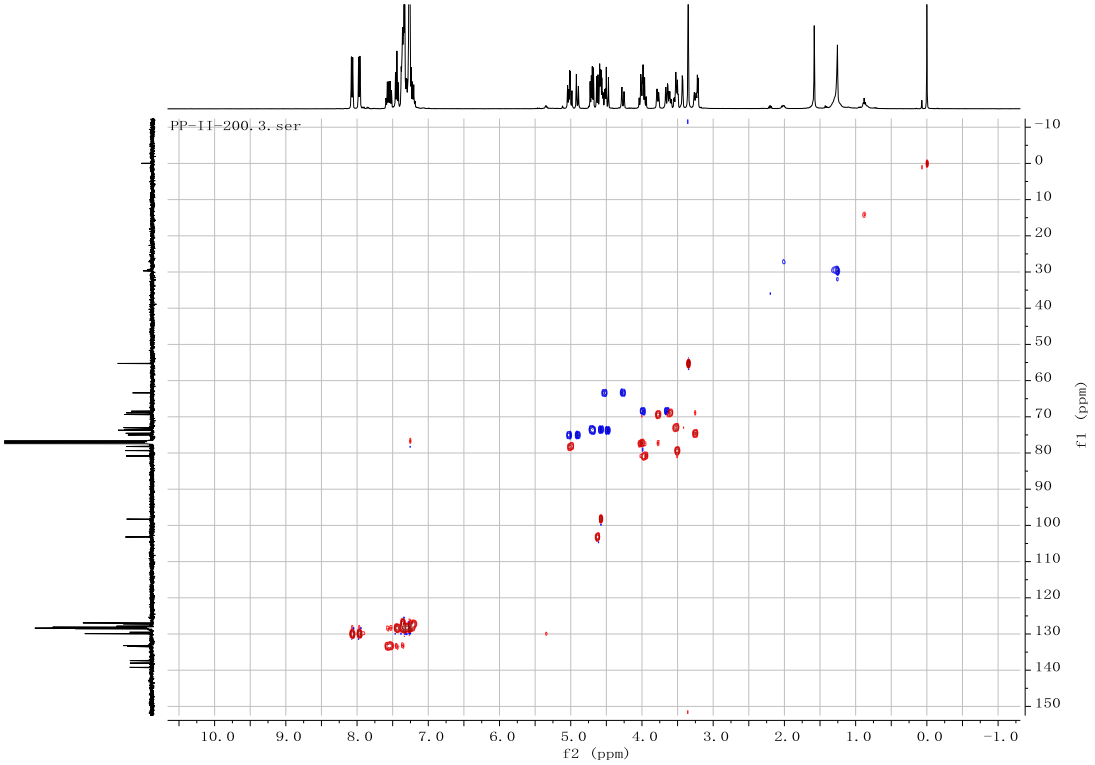
gCOSY ($CDCl_3$, 400 MHz) of **2j**

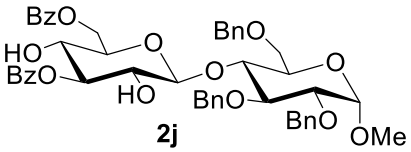




2j

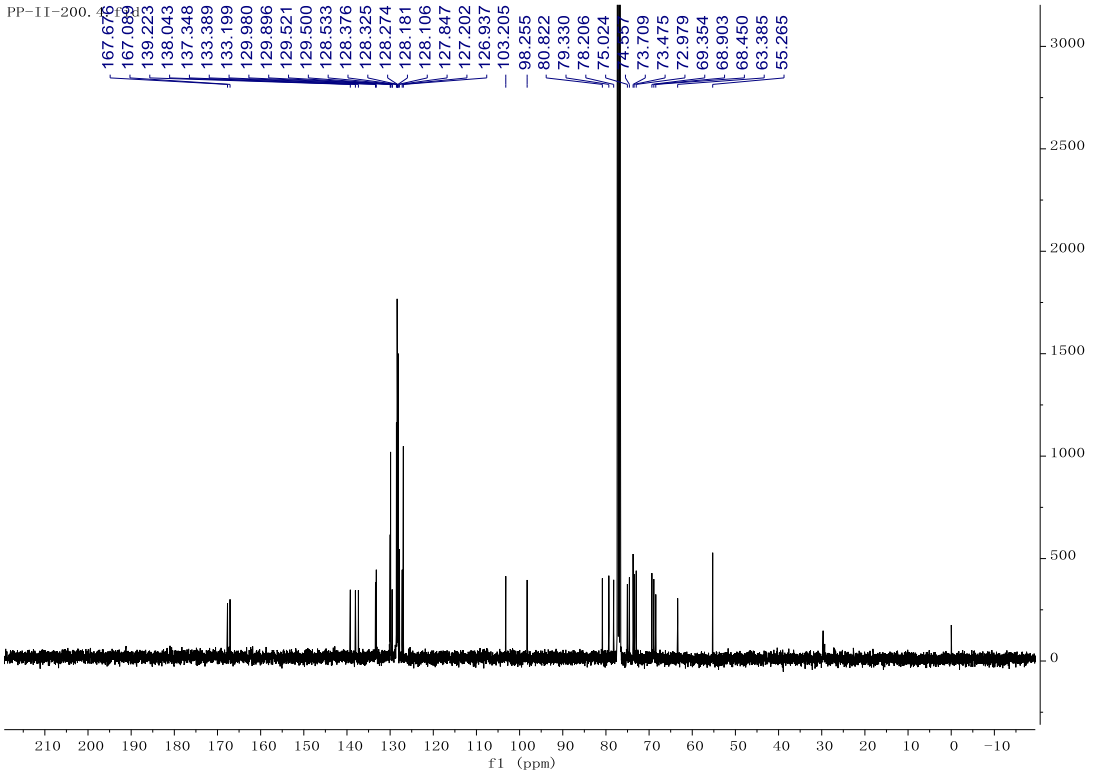
gHSQC ($CDCl_3$, 400 MHz) of **2j**

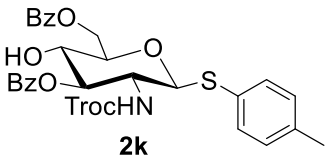




2j

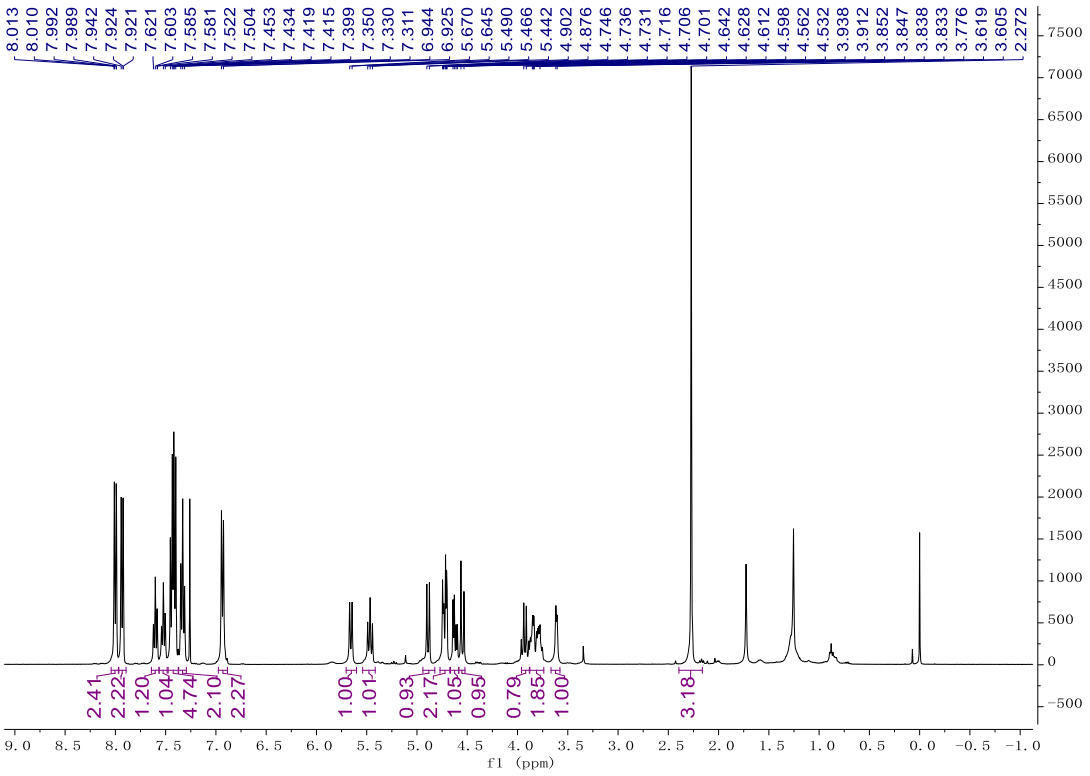
^{13}C NMR ($CDCl_3$, 101 MHz) of **2j**

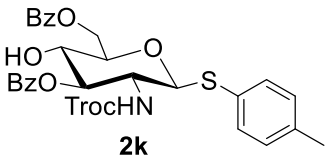




2k

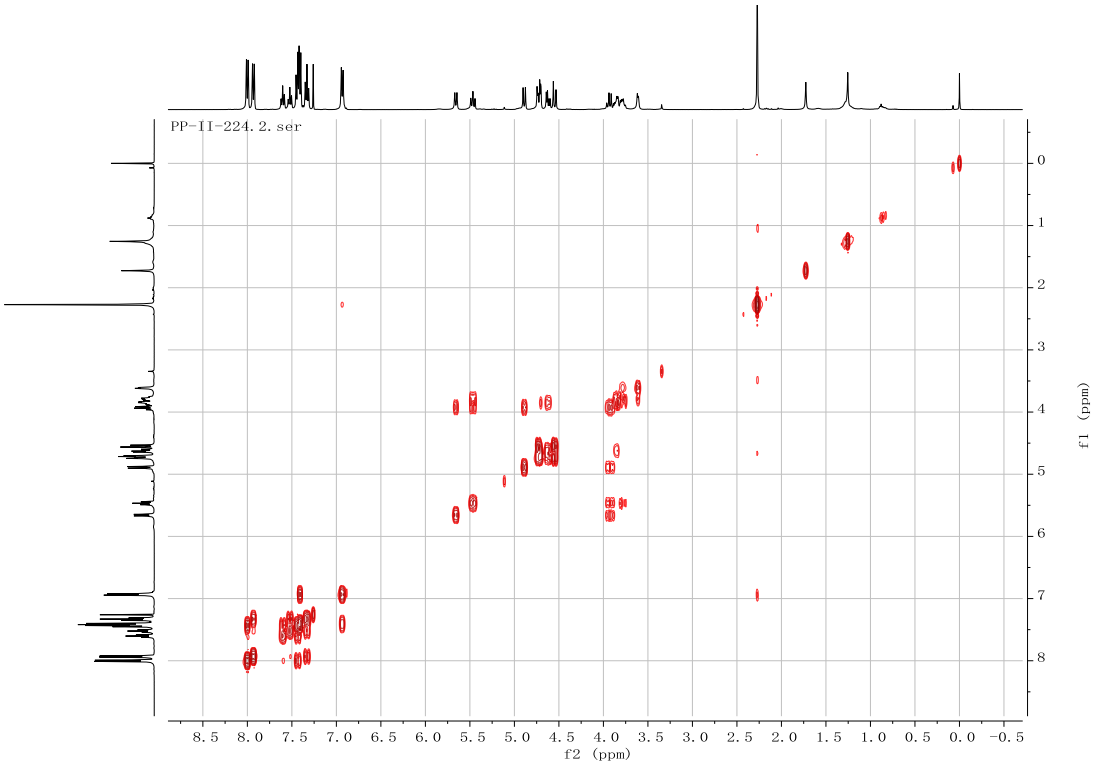
^{1}H NMR ($CDCl_3$, 400 MHz) of **2k**

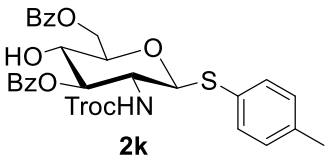




2k

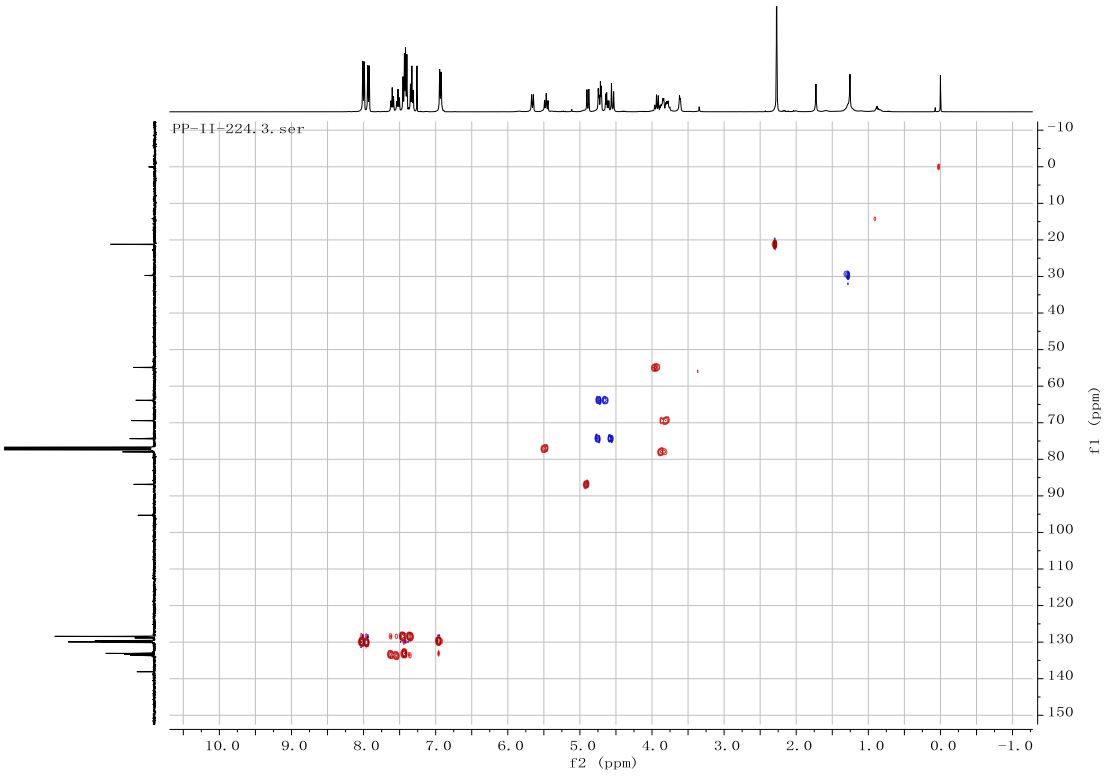
gCOSY ($CDCl_3$, 400 MHz) of **2k**

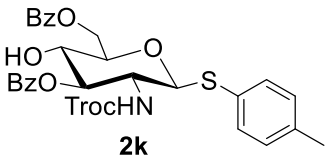




2k

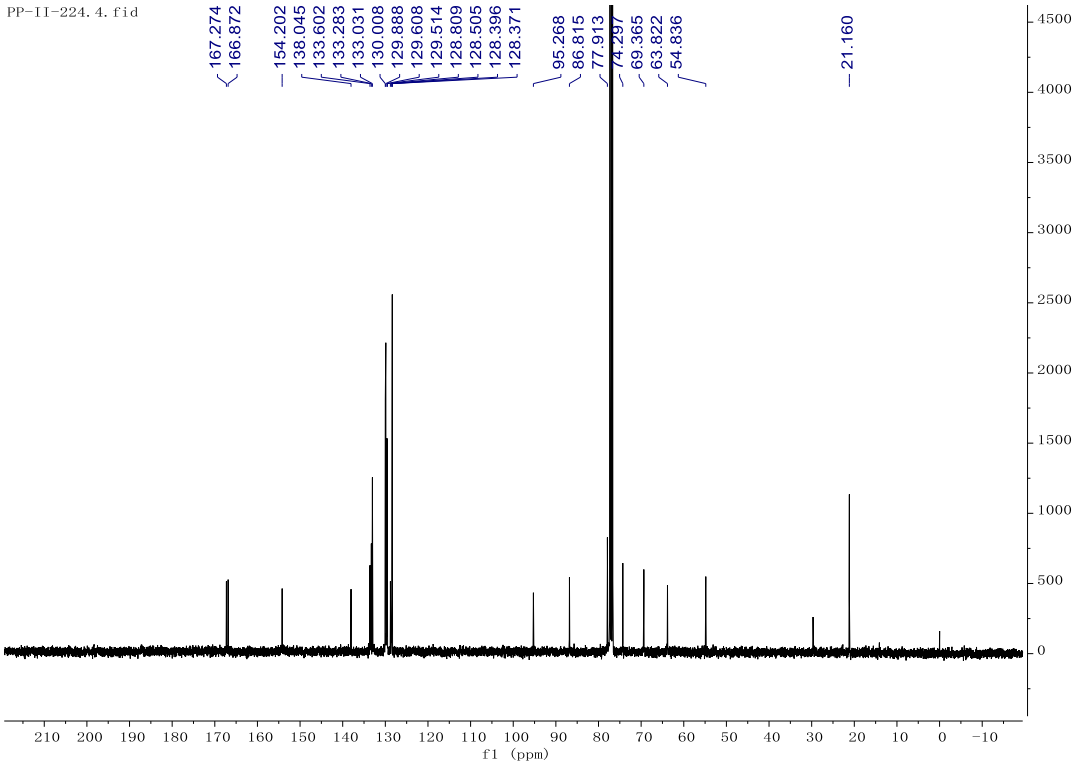
gHSQC ($CDCl_3$, 400 MHz) of **2k**

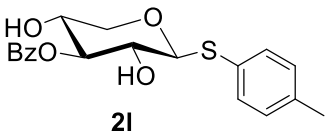




2k

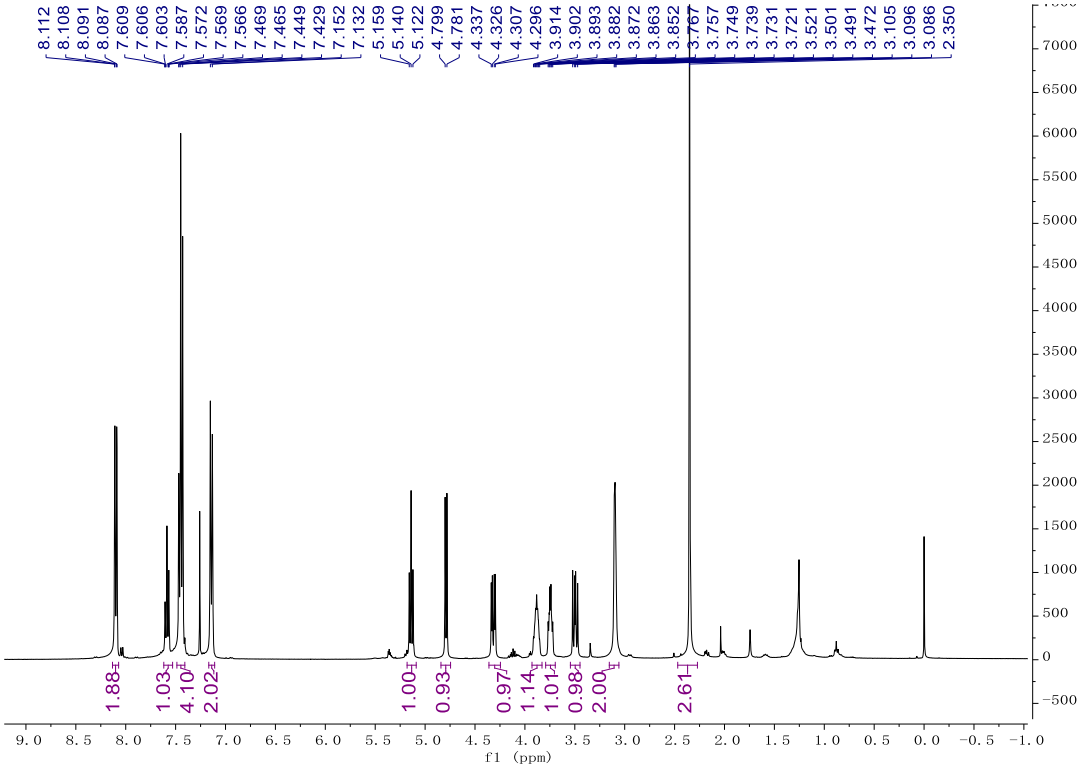
^{13}C NMR ($CDCl_3$, 101 MHz) of **2k**

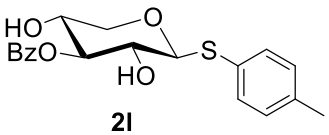




2l

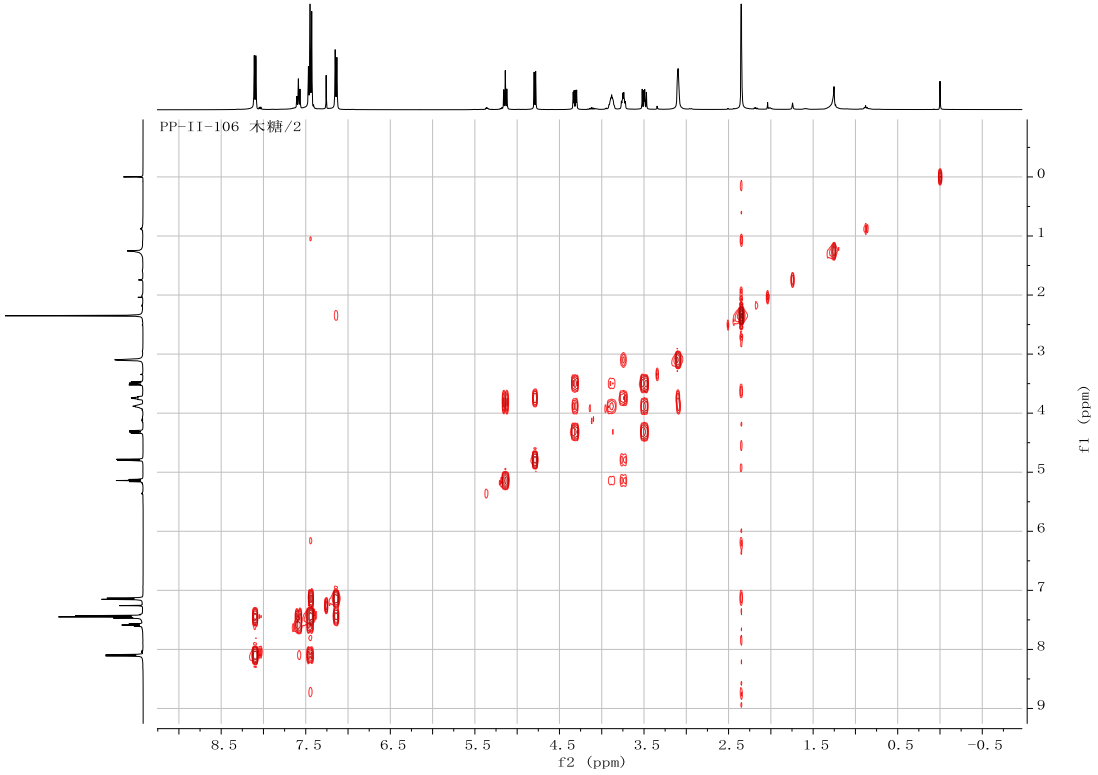
^{1}H NMR ($CDCl_3$, 400 MHz) of **2l**

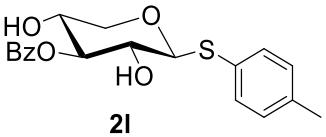




2l

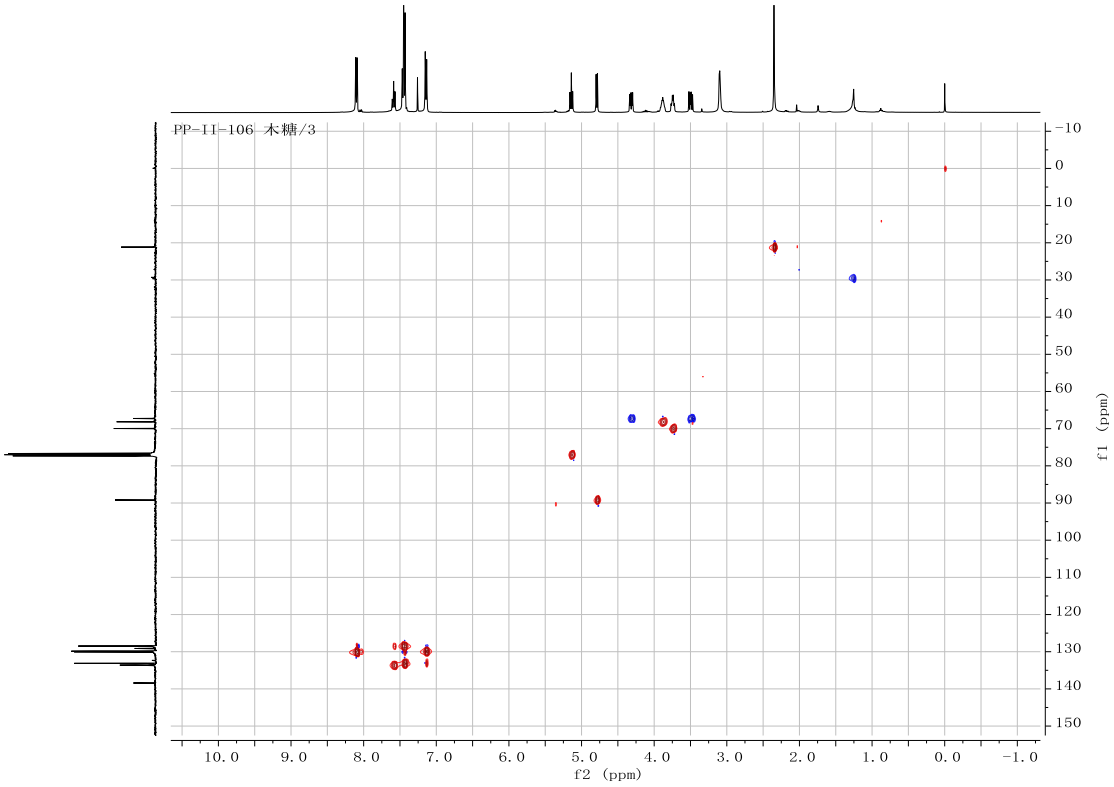
gCOSY ($CDCl_3$, 400 MHz) of **2l**

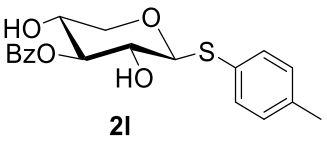




2l

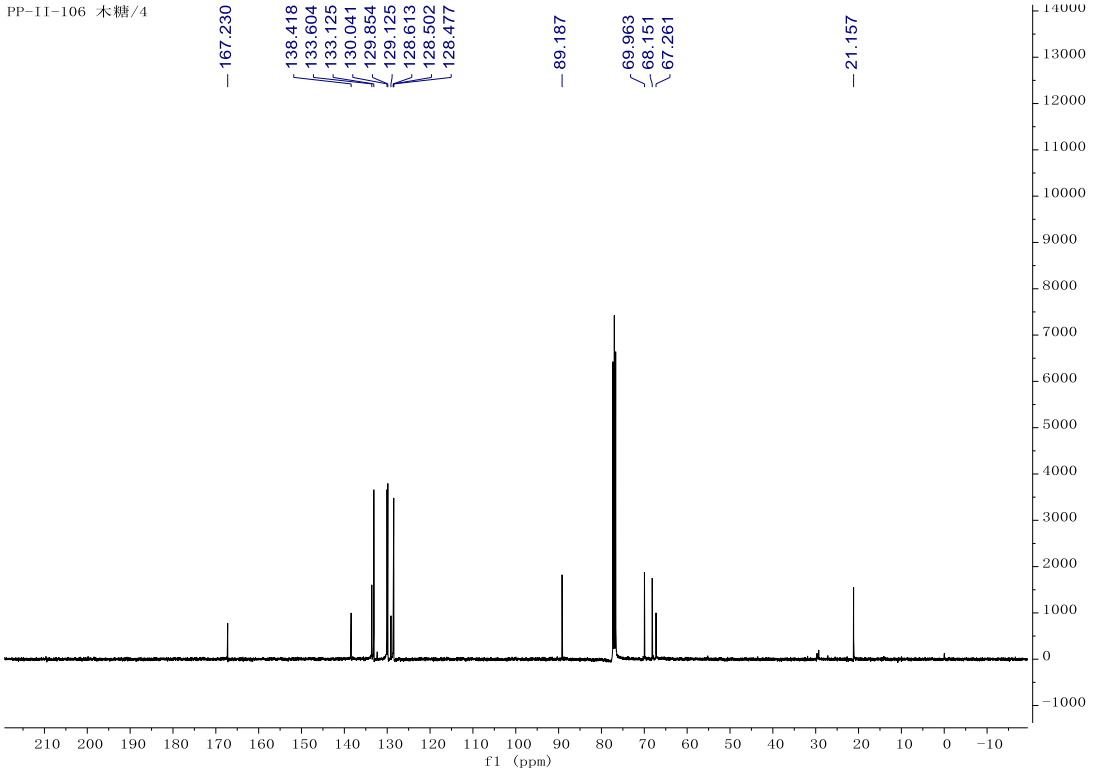
gHSQC ($CDCl_3$, 400 MHz) of **2l**

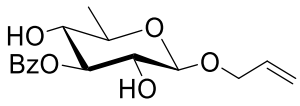




2l

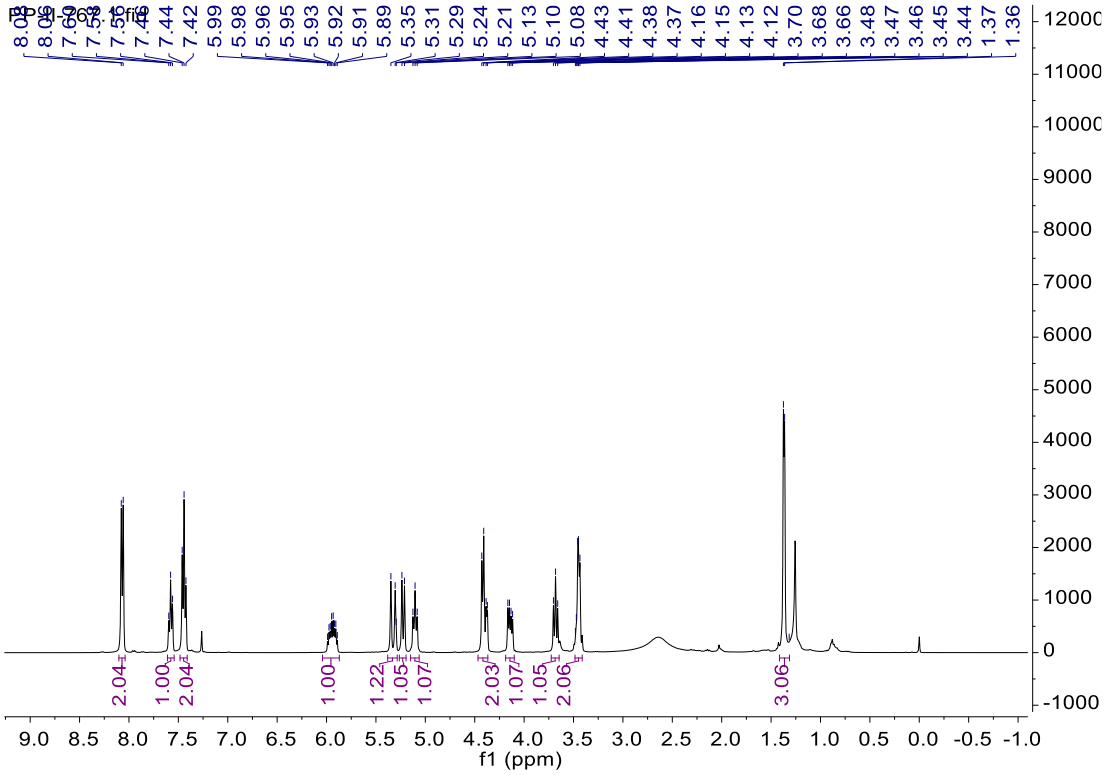
^{13}C NMR ($CDCl_3$, 101 MHz) of **2l**

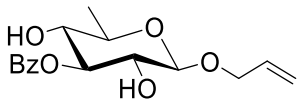




2m

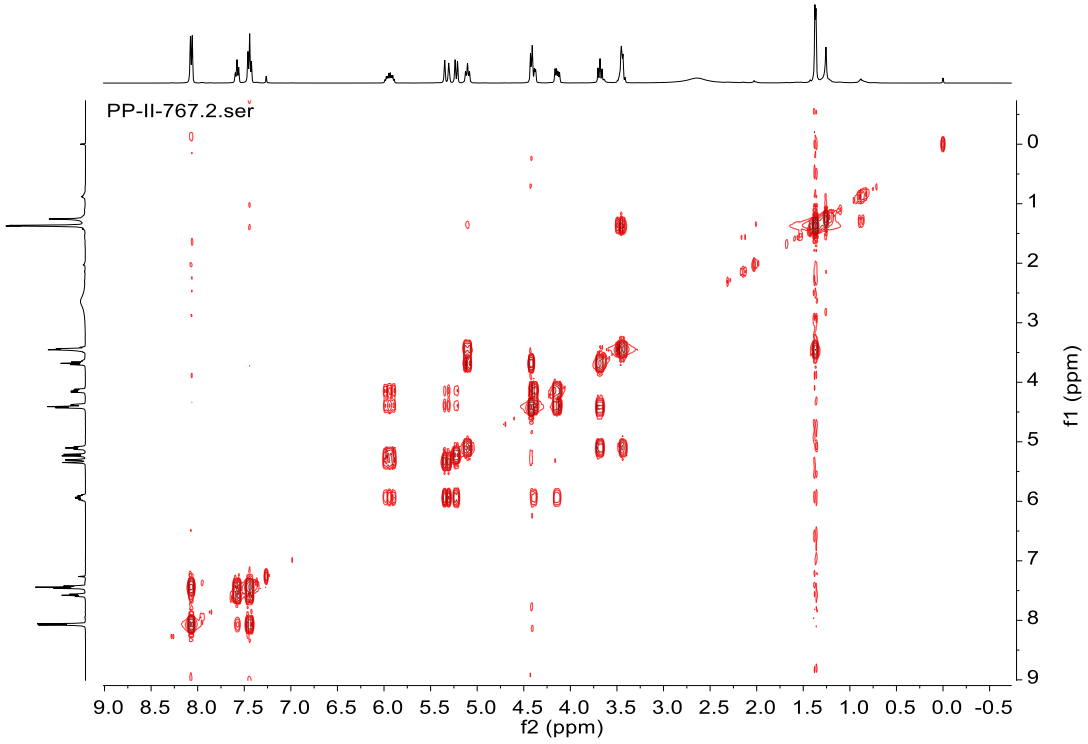
^{1}H NMR ($CDCl_3$, 400 MHz) of **2m**

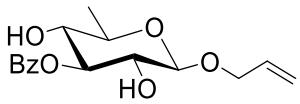




2m

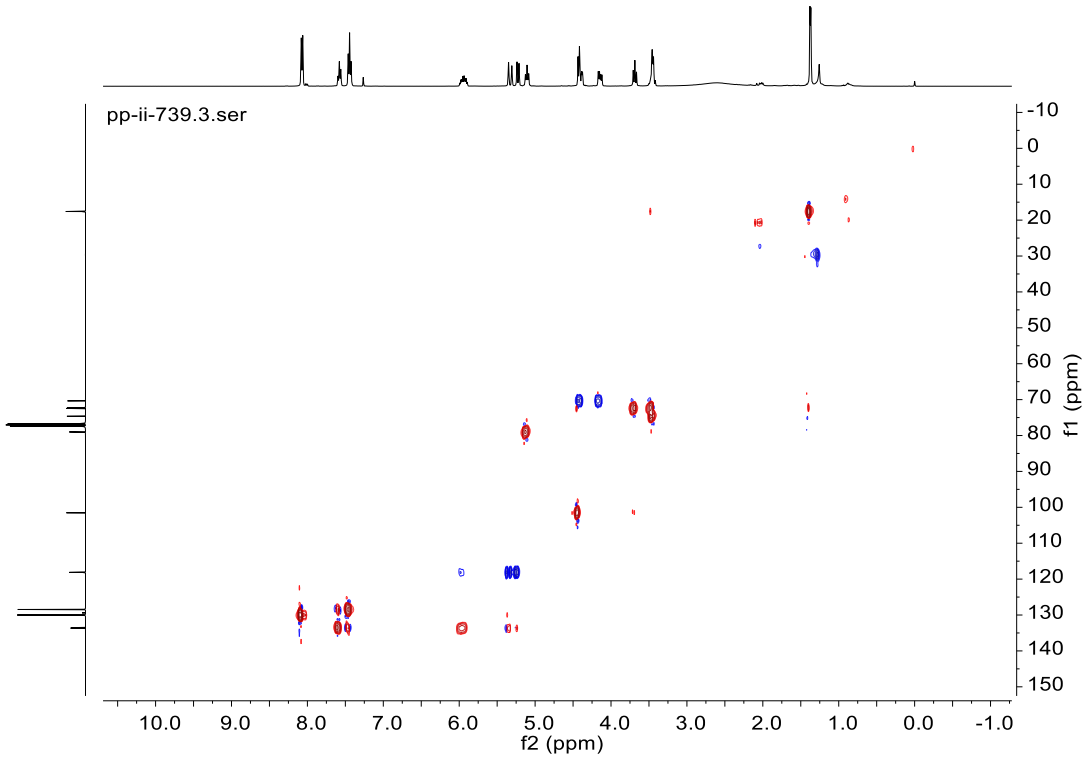
gCOSY ($CDCl_3$, 400 MHz) of **2m**

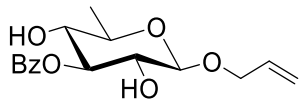




2m

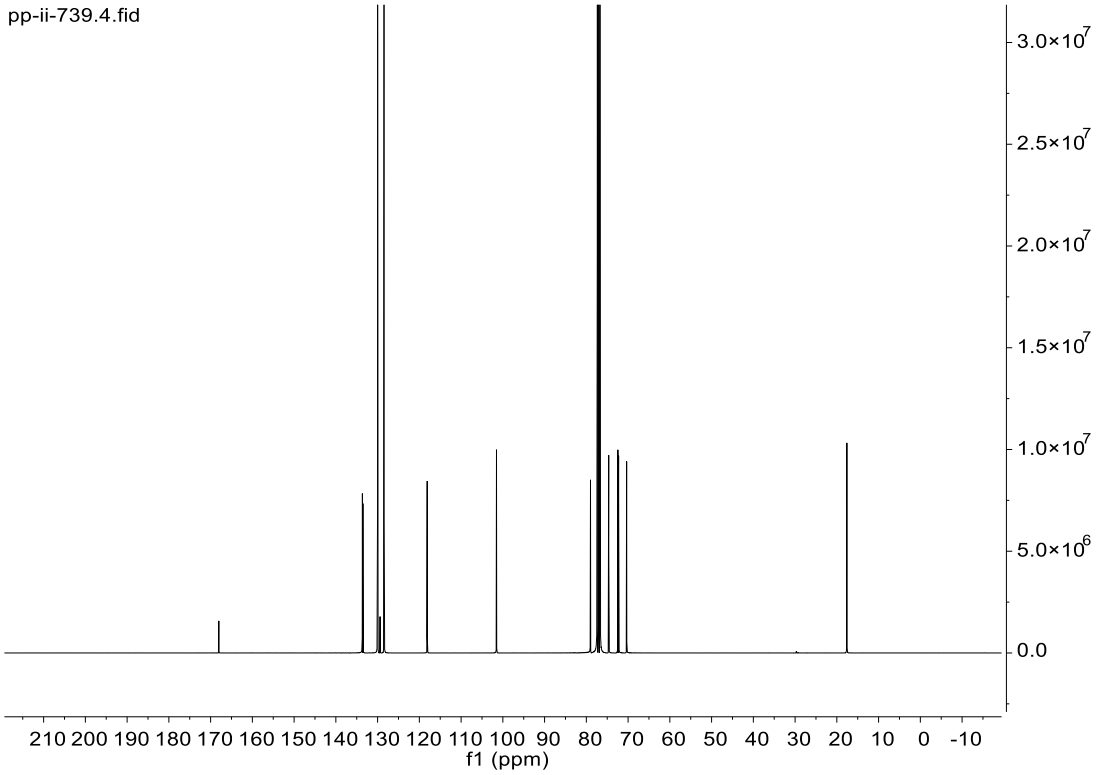
gHSQC ($CDCl_3$, 400 MHz) of **2m**

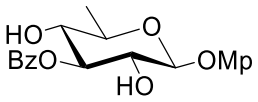




2m

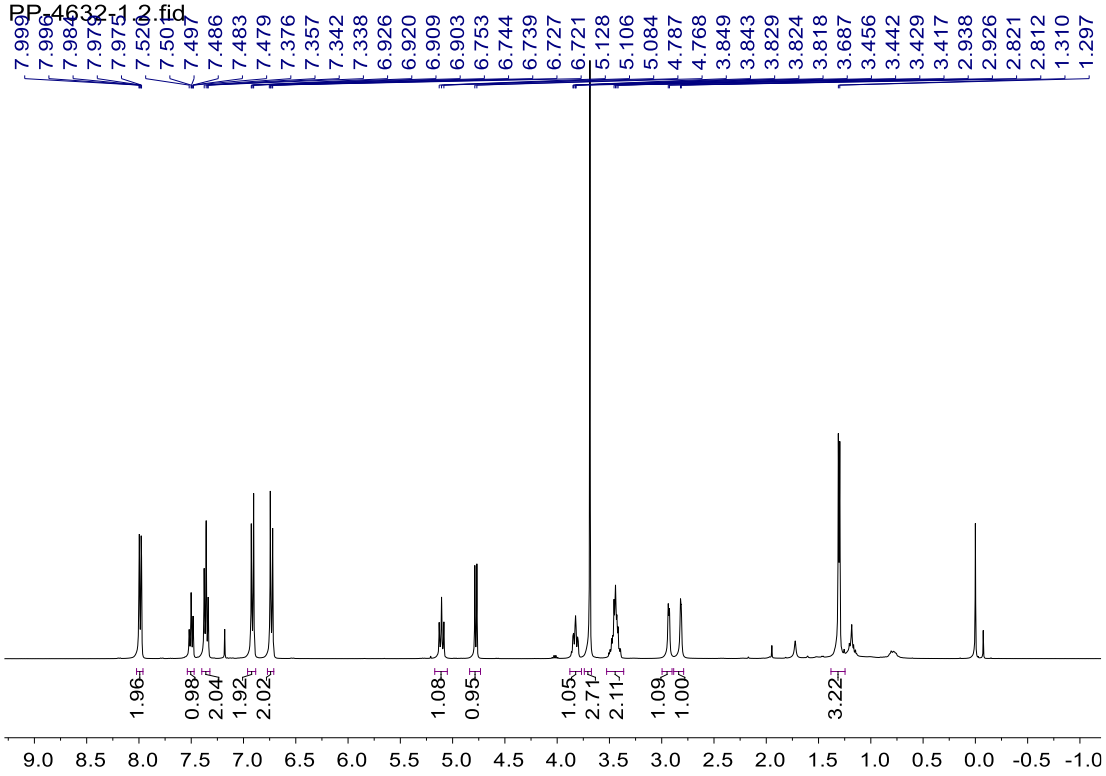
^{13}C NMR ($CDCl_3$, 101 MHz) of **2m**

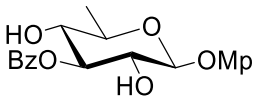




2n

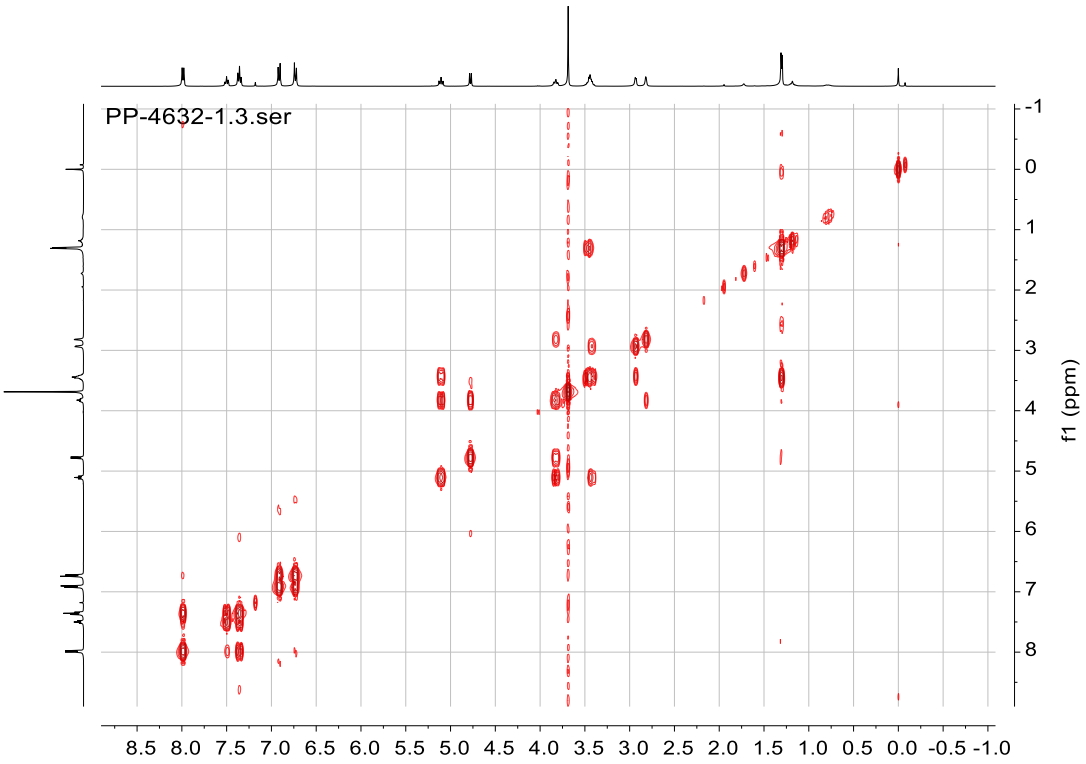
^{1}H NMR ($CDCl_3$, 400 MHz) of **2n**

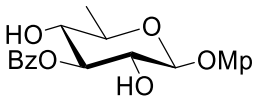




2n

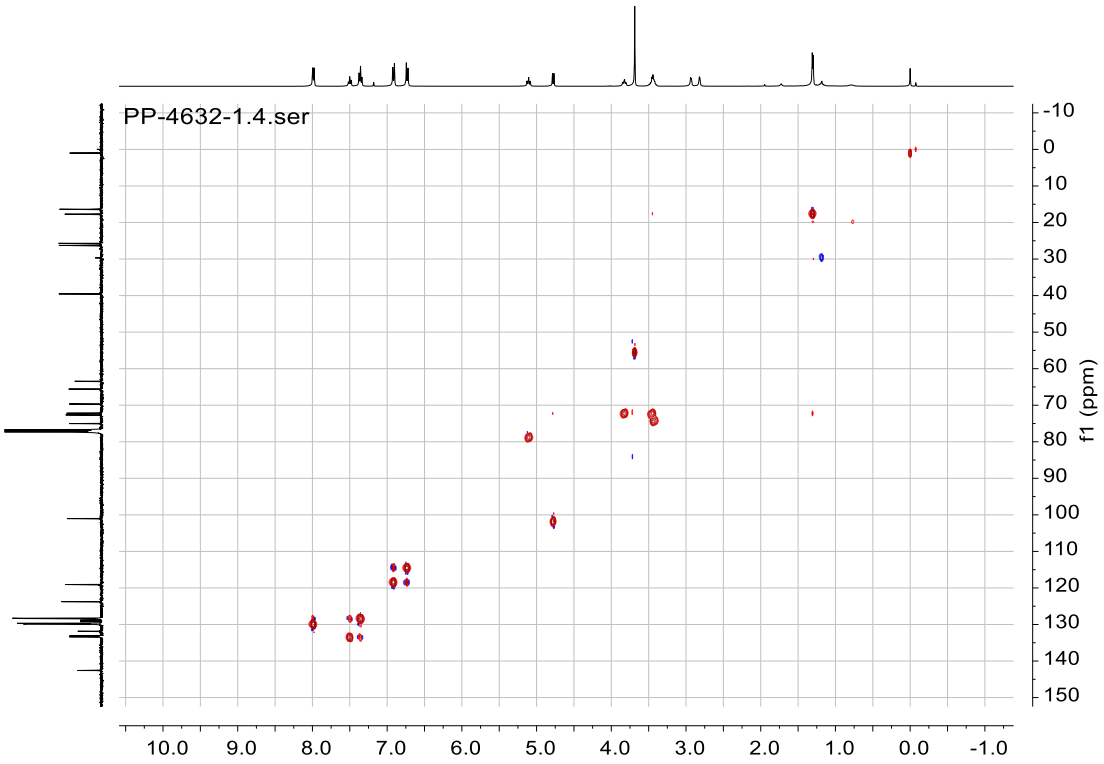
gCOSY ($CDCl_3$, 400 MHz) of **2n**

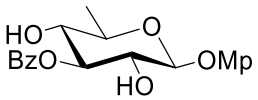




2n

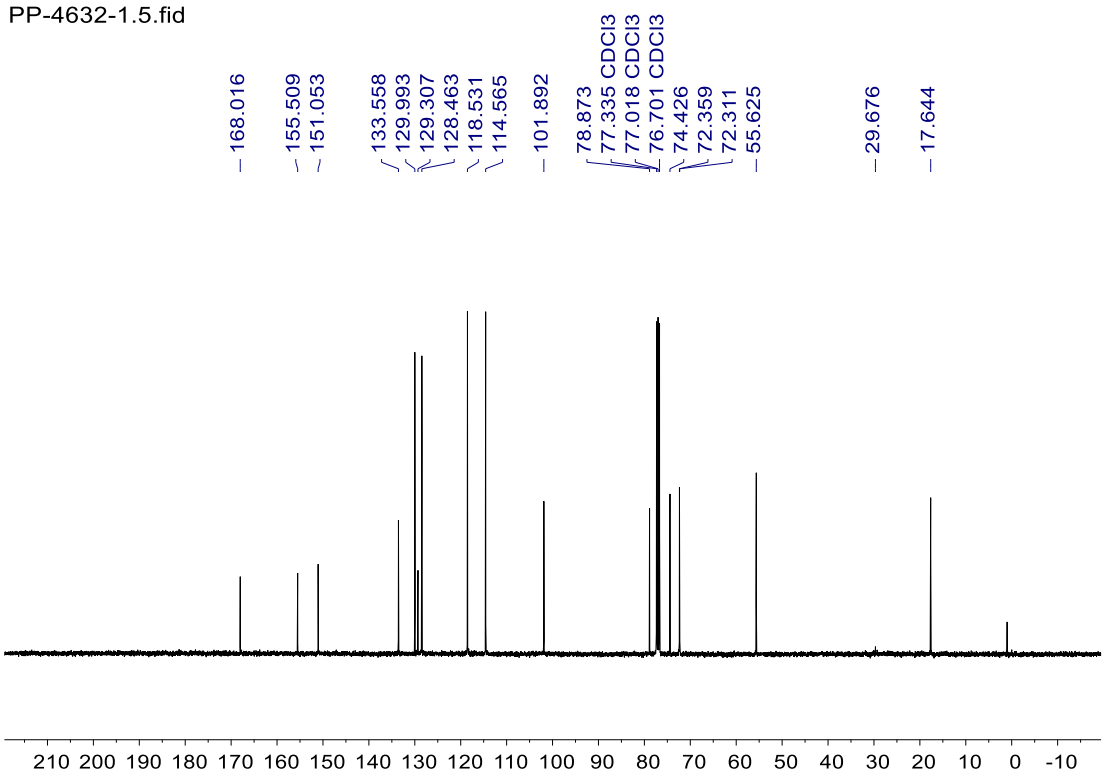
gHSQC ($CDCl_3$, 400 MHz) of **2n**

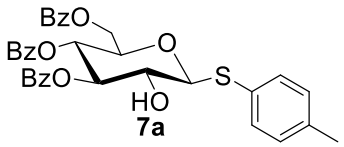




2n

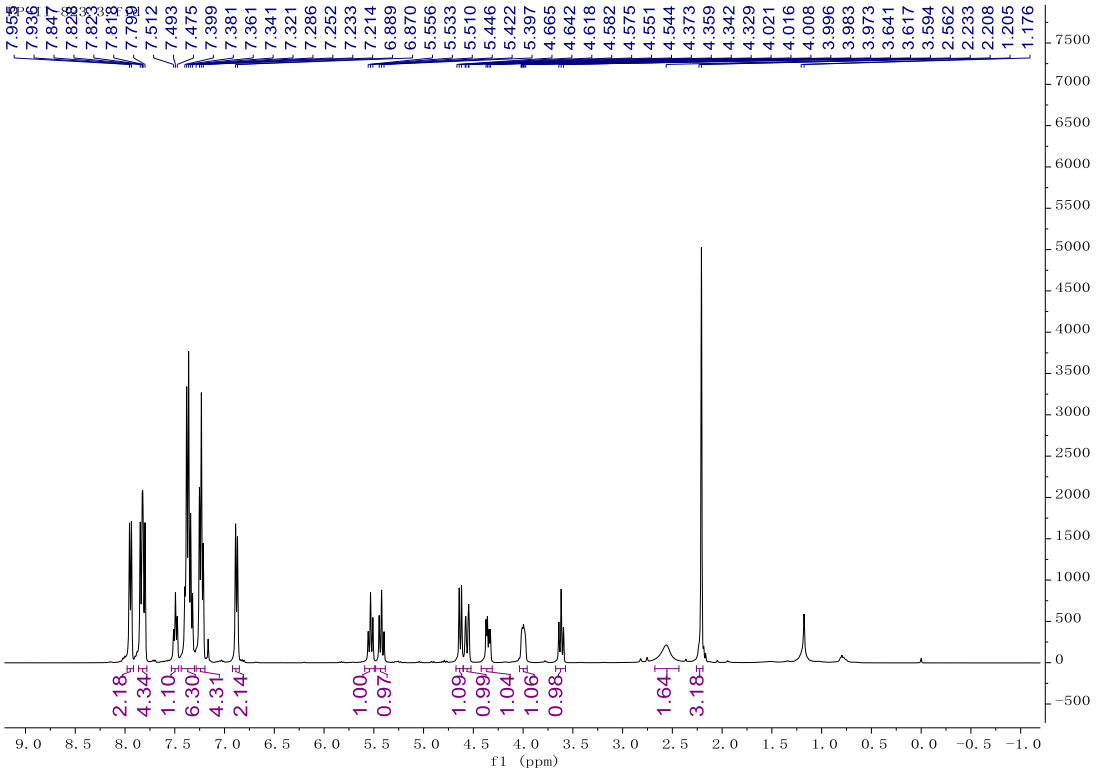
^{13}C NMR ($CDCl_3$, 101 MHz) of **2n**

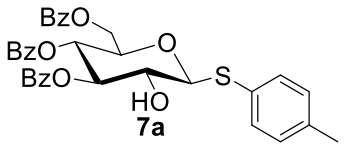




7a

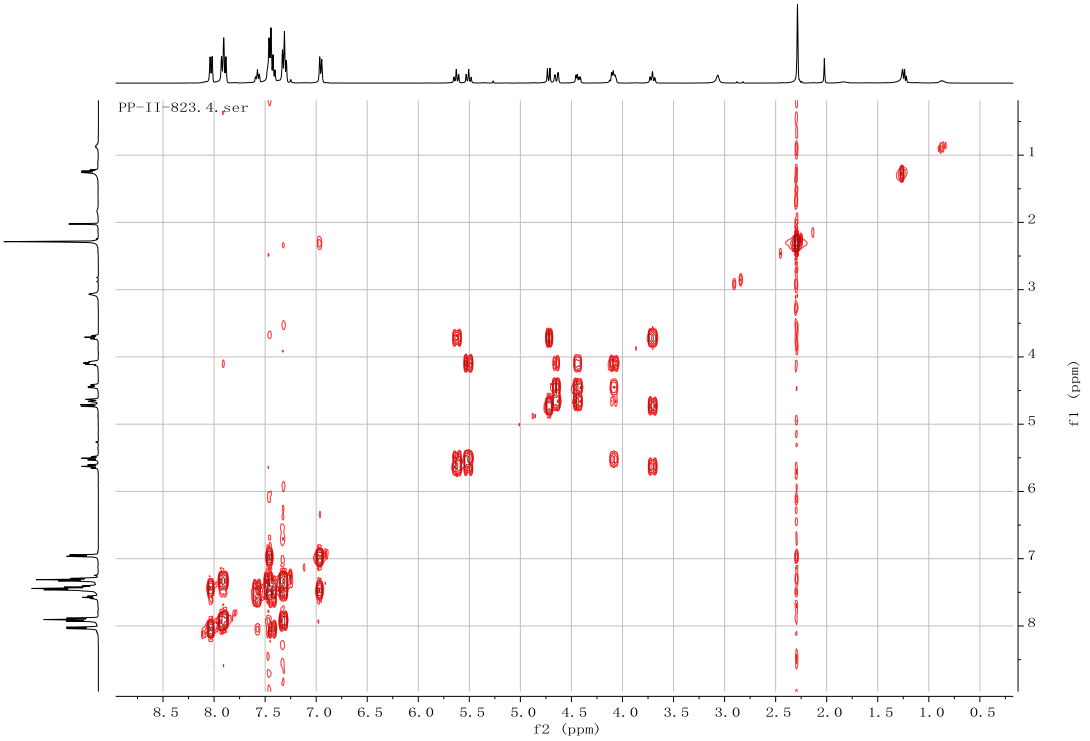
^{1}H NMR ($CDCl_3$, 400 MHz) of **7a**

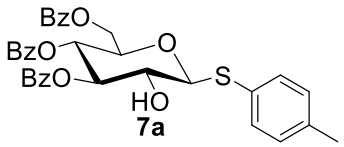




7a

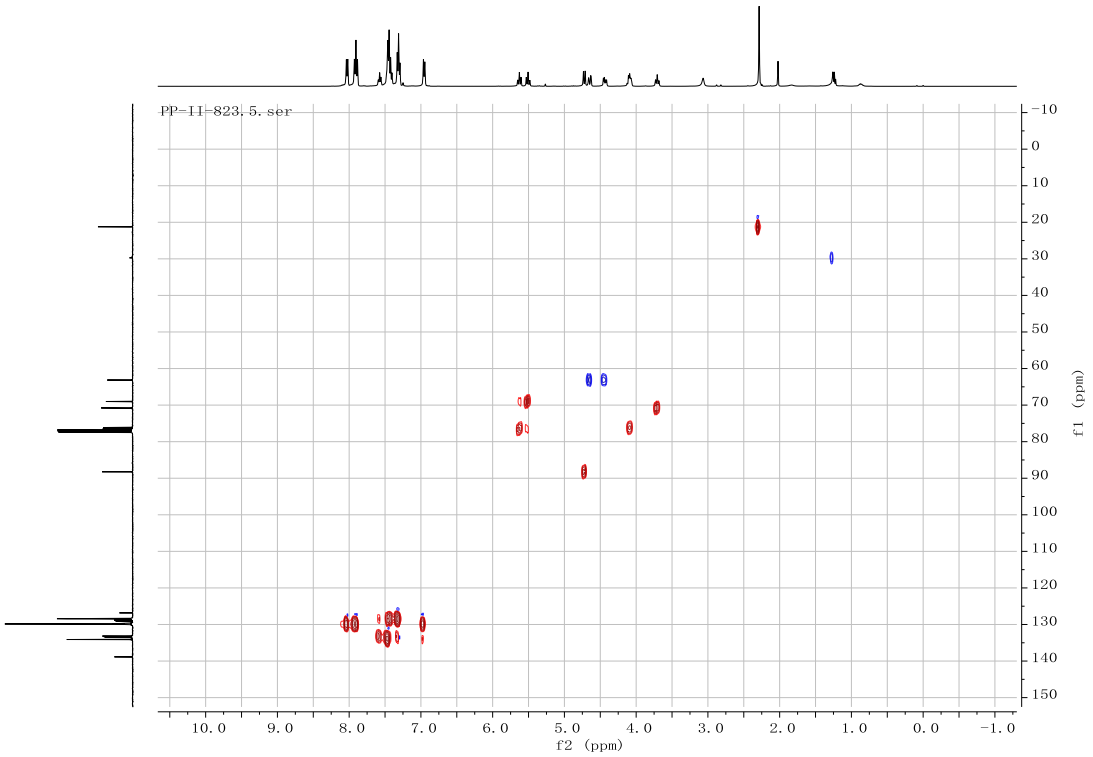
gCOSY ($CDCl_3$, 400 MHz) of **7a**

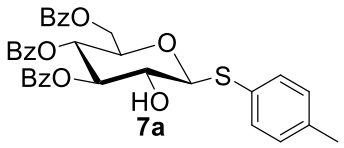




7a

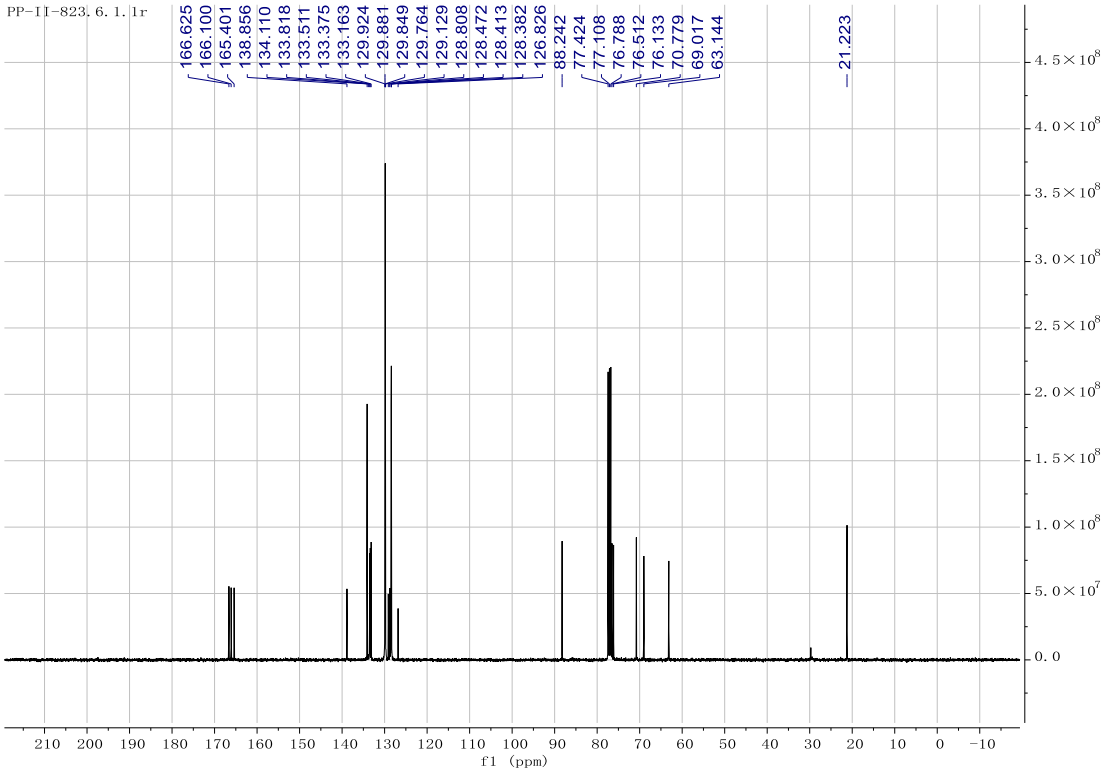
gHSQC ($CDCl_3$, 400 MHz) of **7a**

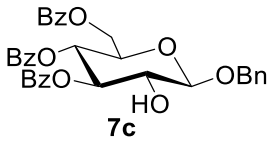




7a

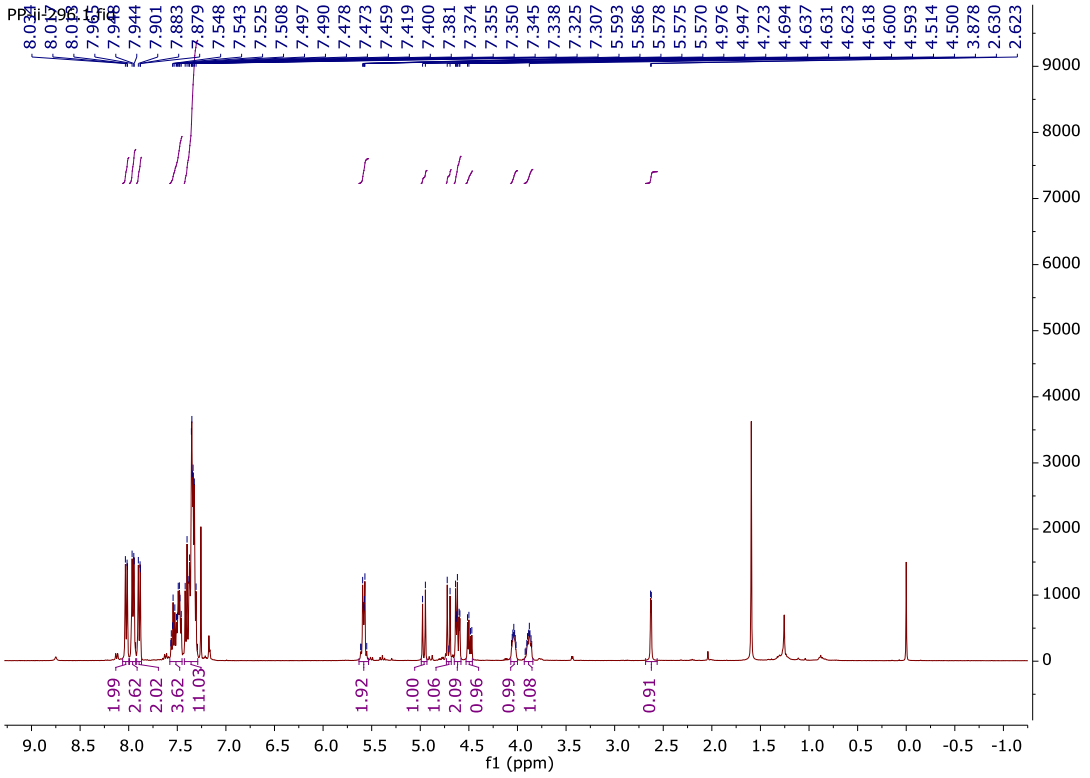
^{13}C NMR ($CDCl_3$, 101 MHz) of **7a**

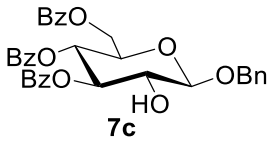




7c

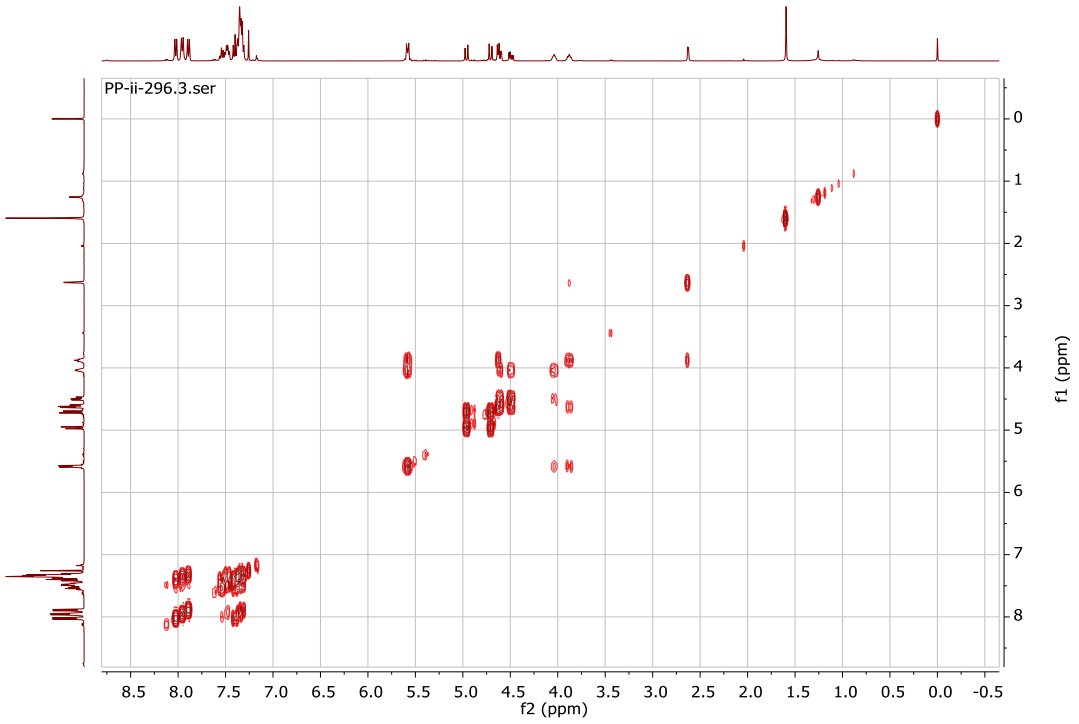
^{1}H NMR ($CDCl_3$, 400 MHz) of **7c**

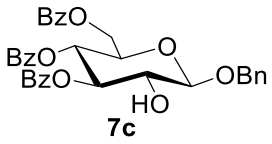




7c

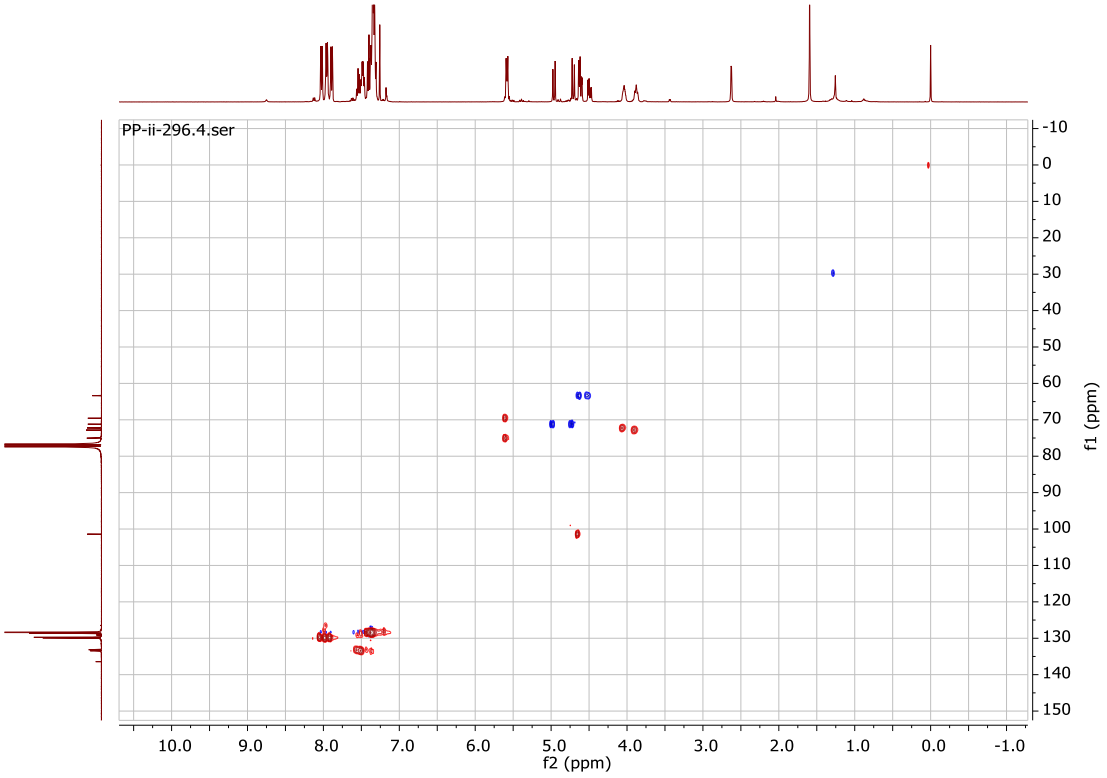
gCOSY ($CDCl_3$, 400 MHz) of **7c**

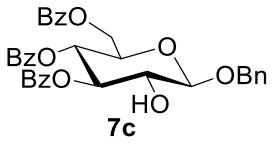




7c

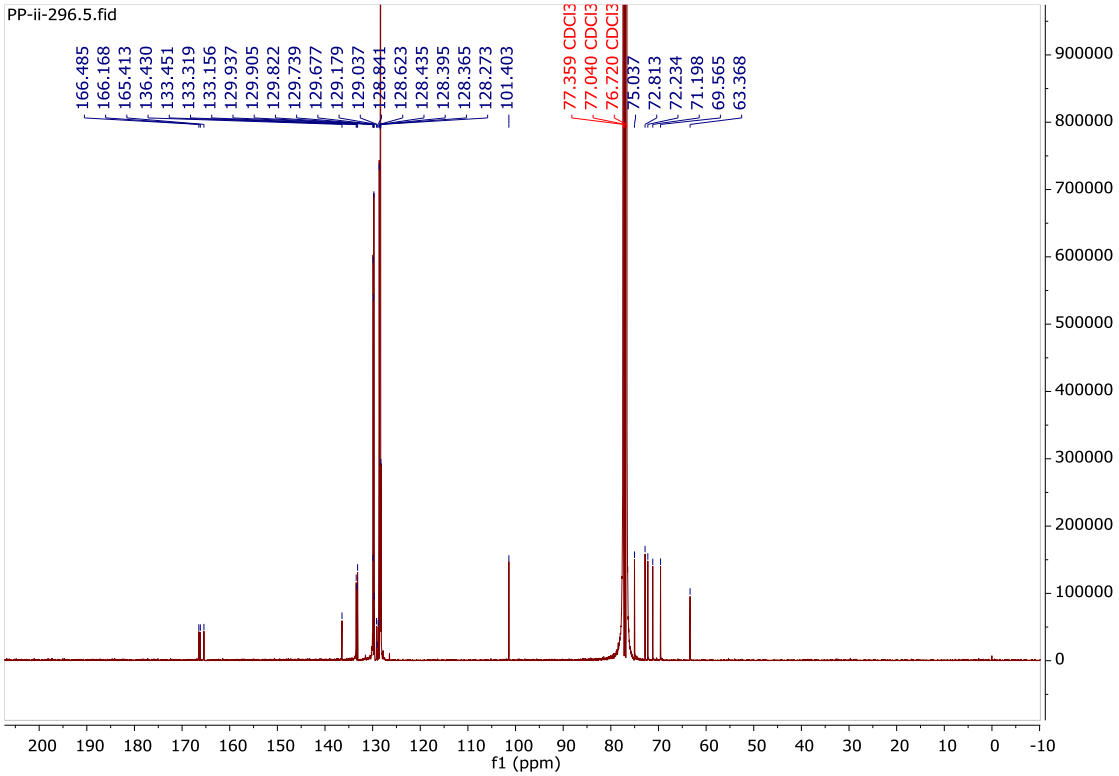
gHSQC ($CDCl_3$, 400 MHz) of **7c**

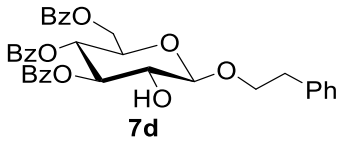




7c

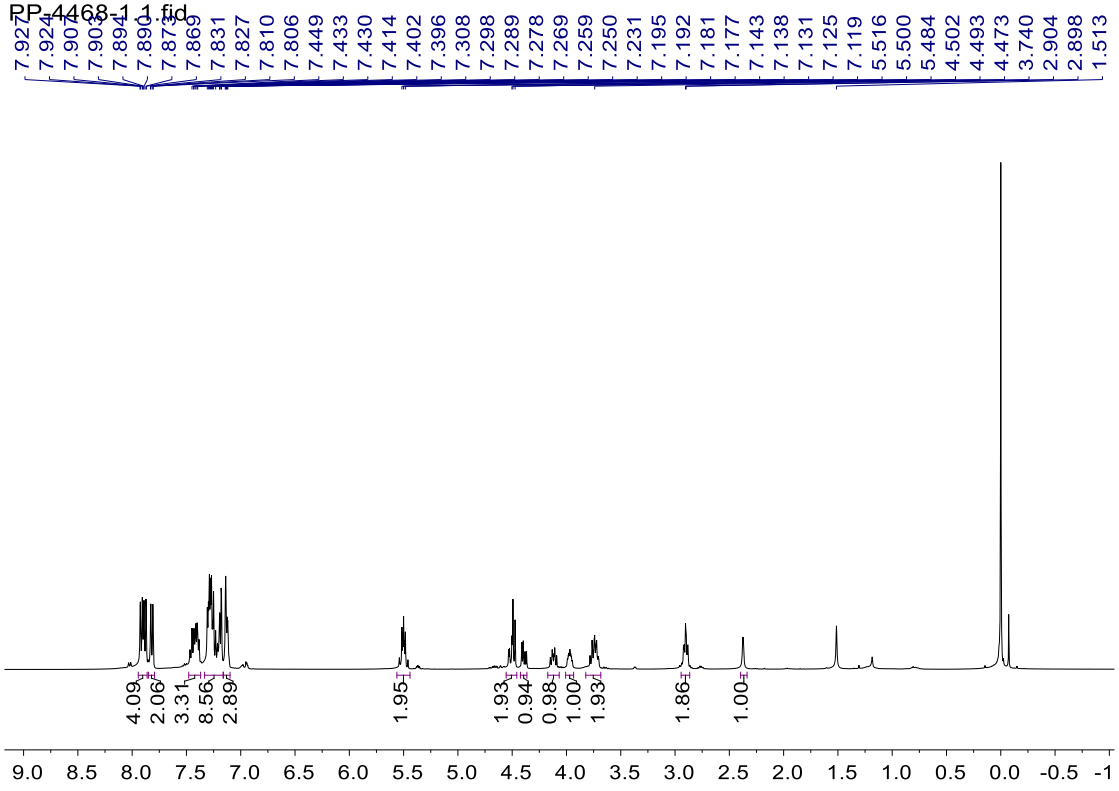
^{13}C NMR ($CDCl_3$, 101 MHz) of **7c**

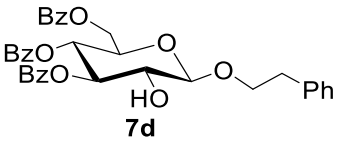




7d

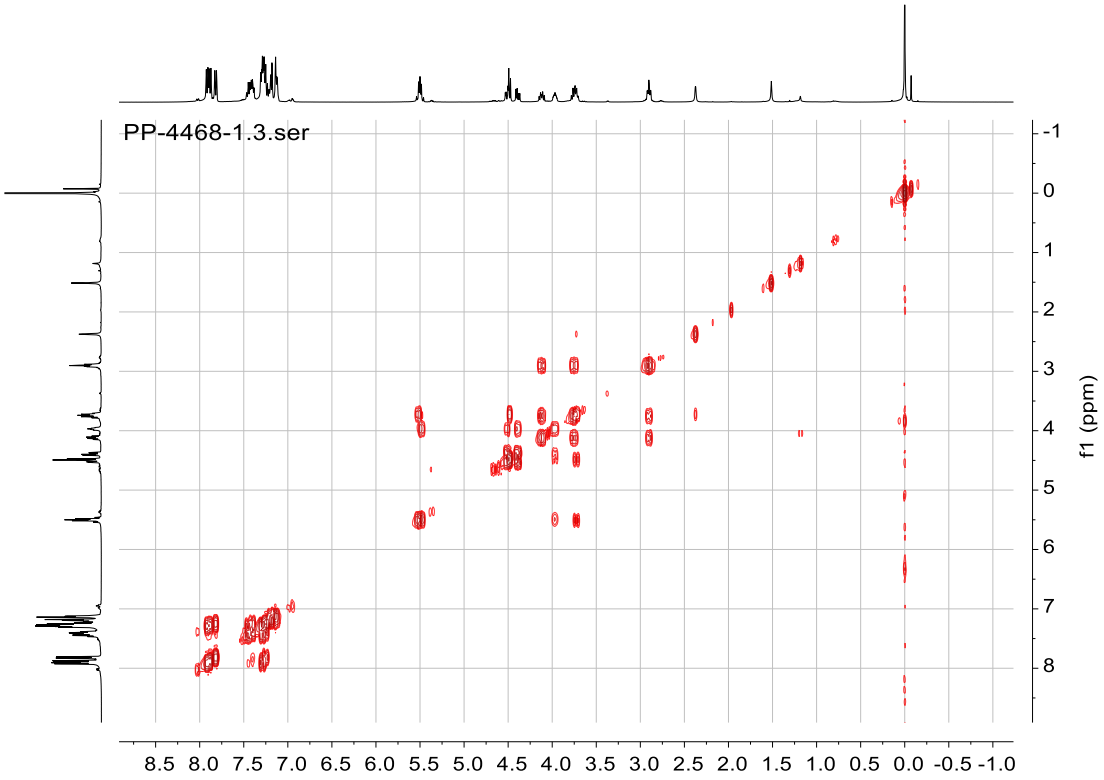
^{1}H NMR ($CDCl_3$, 400 MHz) of **7d**

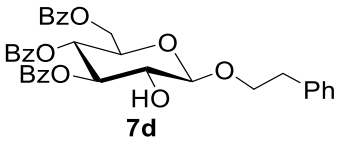




7d

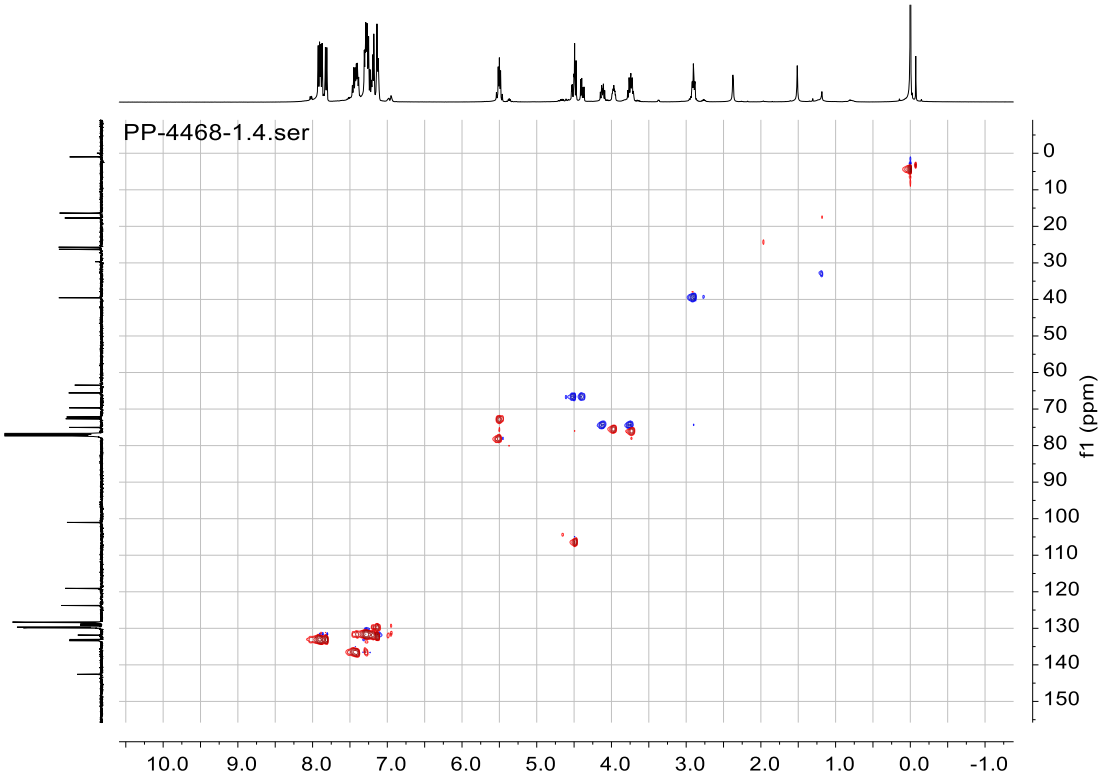
gCOSY ($CDCl_3$, 400 MHz) of **7d**

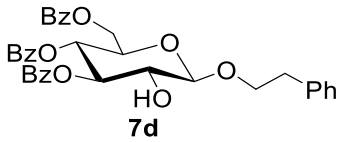




7d

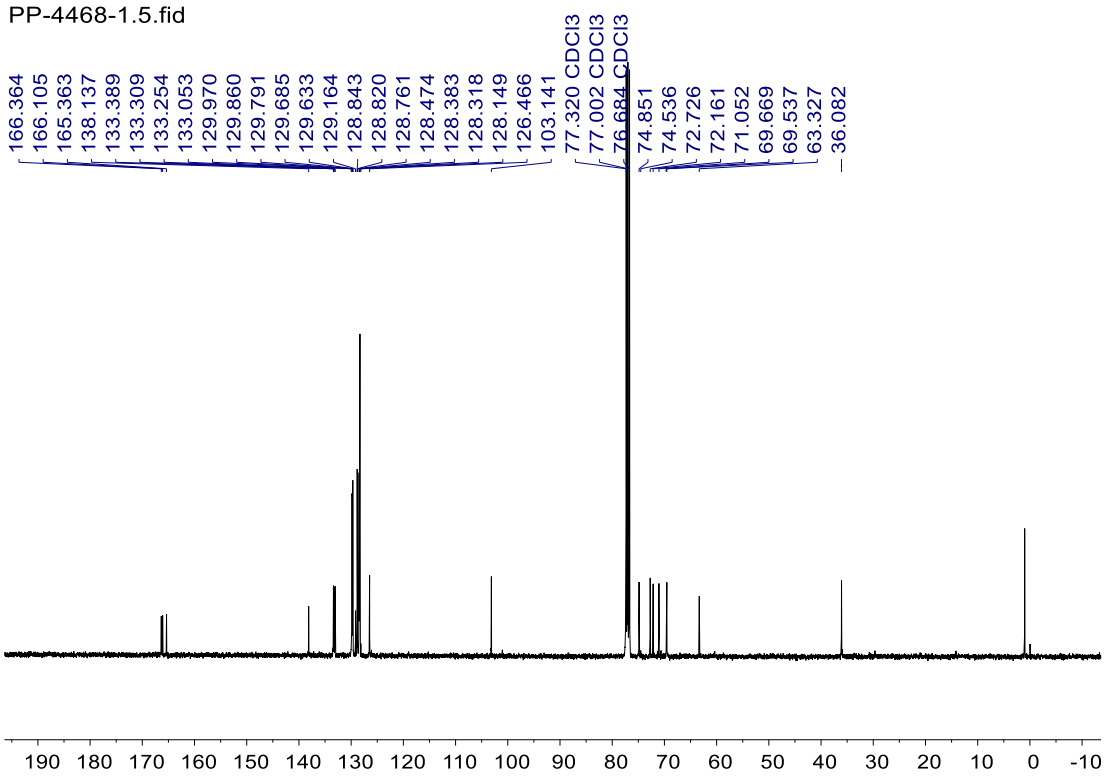
gHSQC ($CDCl_3$, 400 MHz) of **7d**

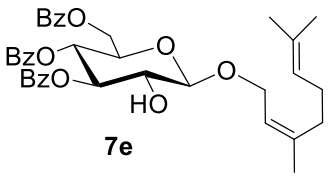




7d

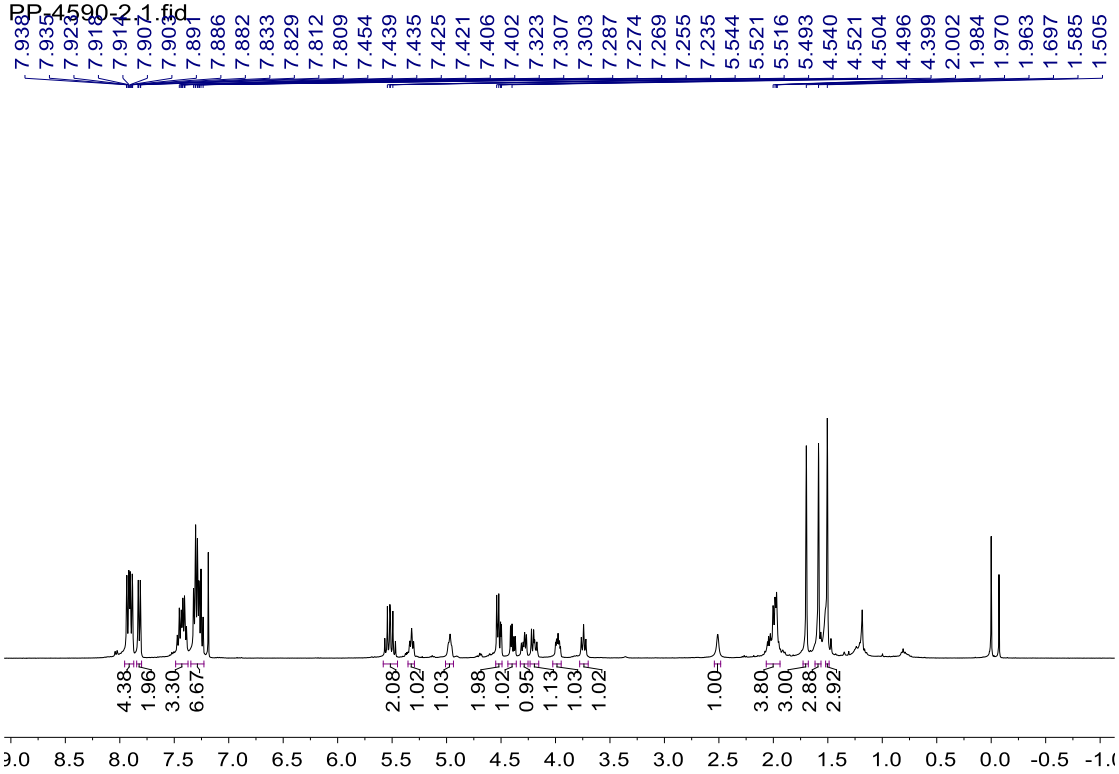
^{13}C NMR ($CDCl_3$, 101 MHz) of **7d**

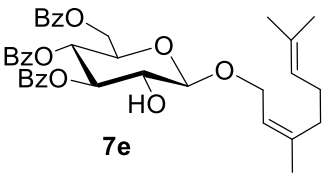




7e

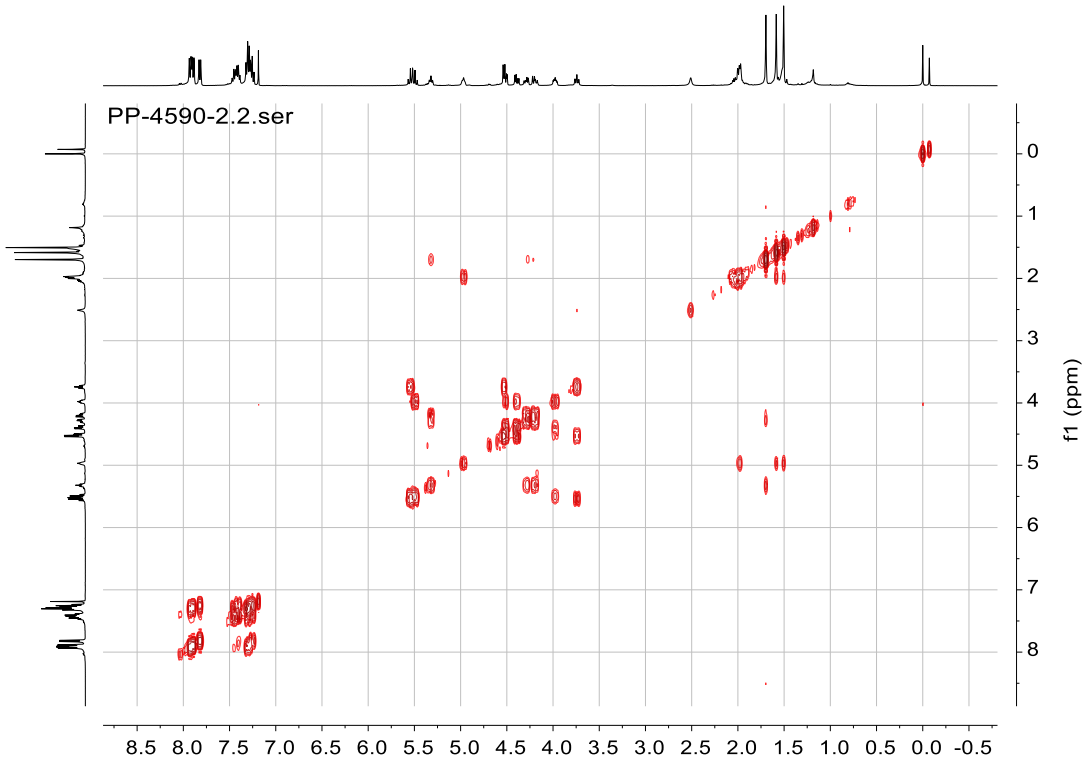
^{1}H NMR ($CDCl_3$, 400 MHz) of **7e**

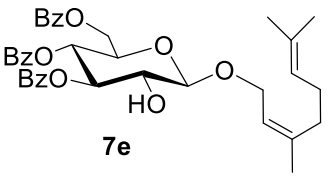




7e

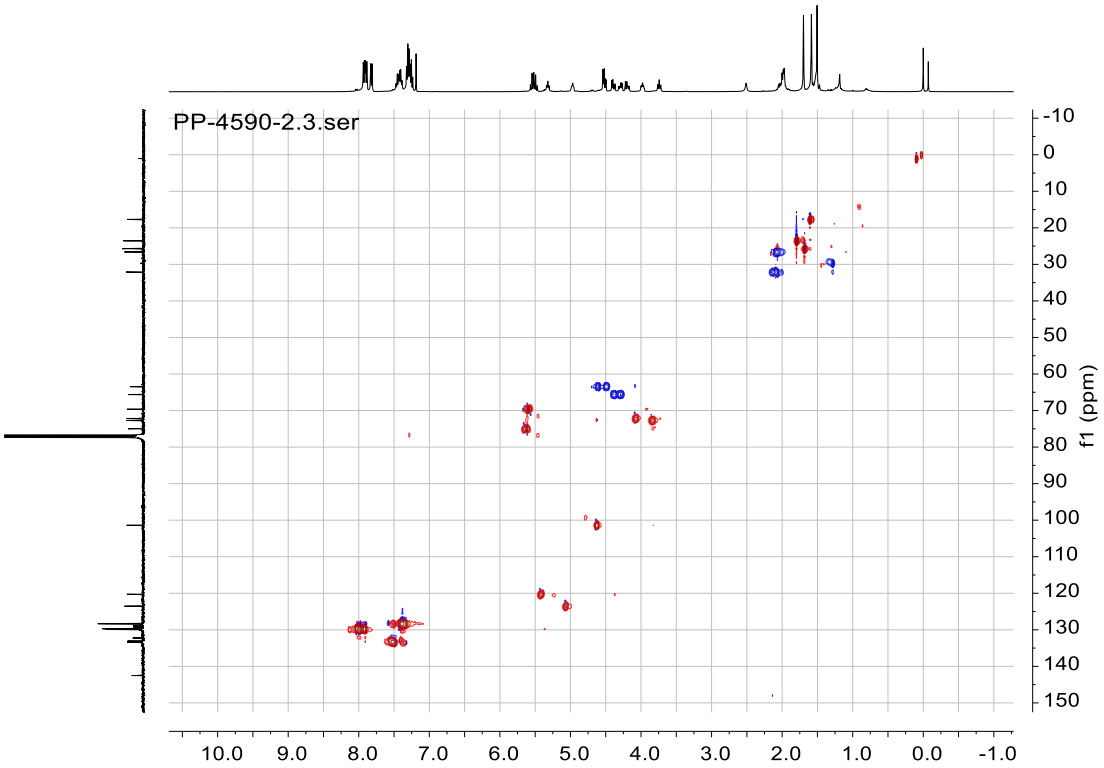
gCOSY ($CDCl_3$, 400 MHz) of **7e**

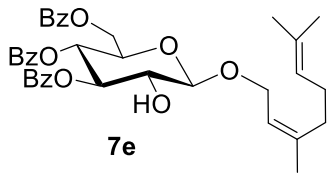




7e

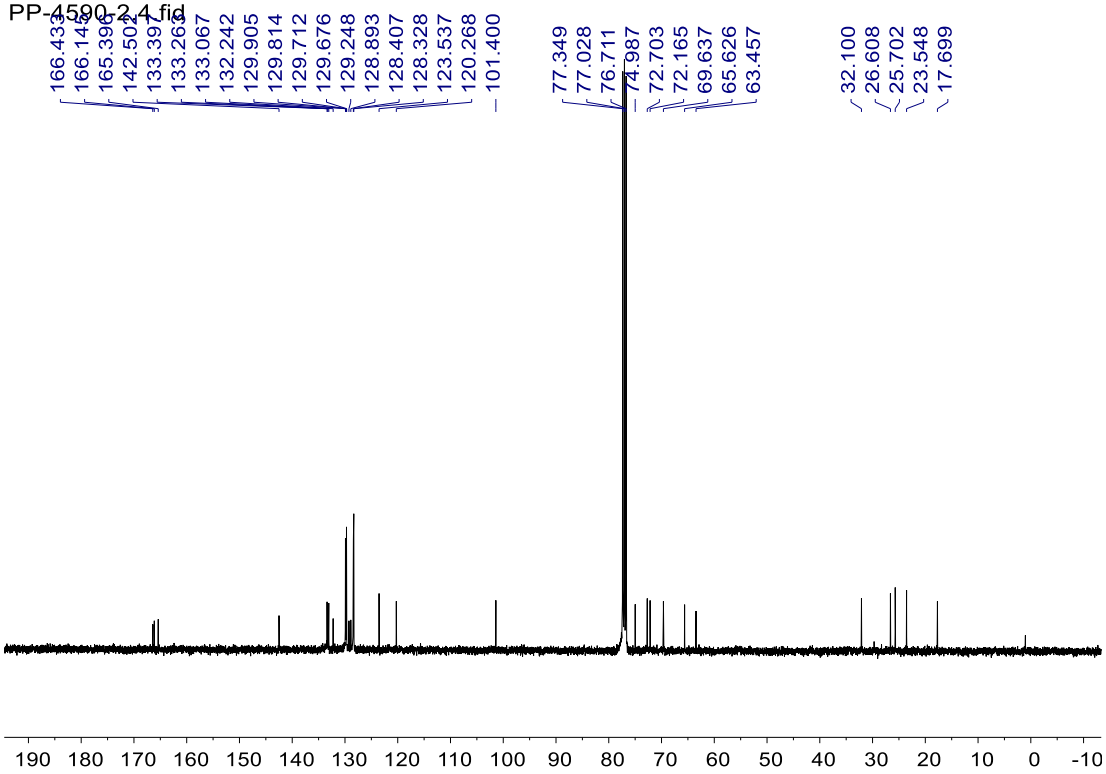
gHSQC ($CDCl_3$, 400 MHz) of **7e**

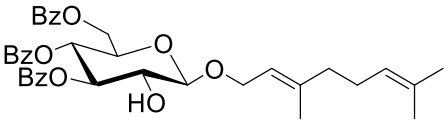




7e

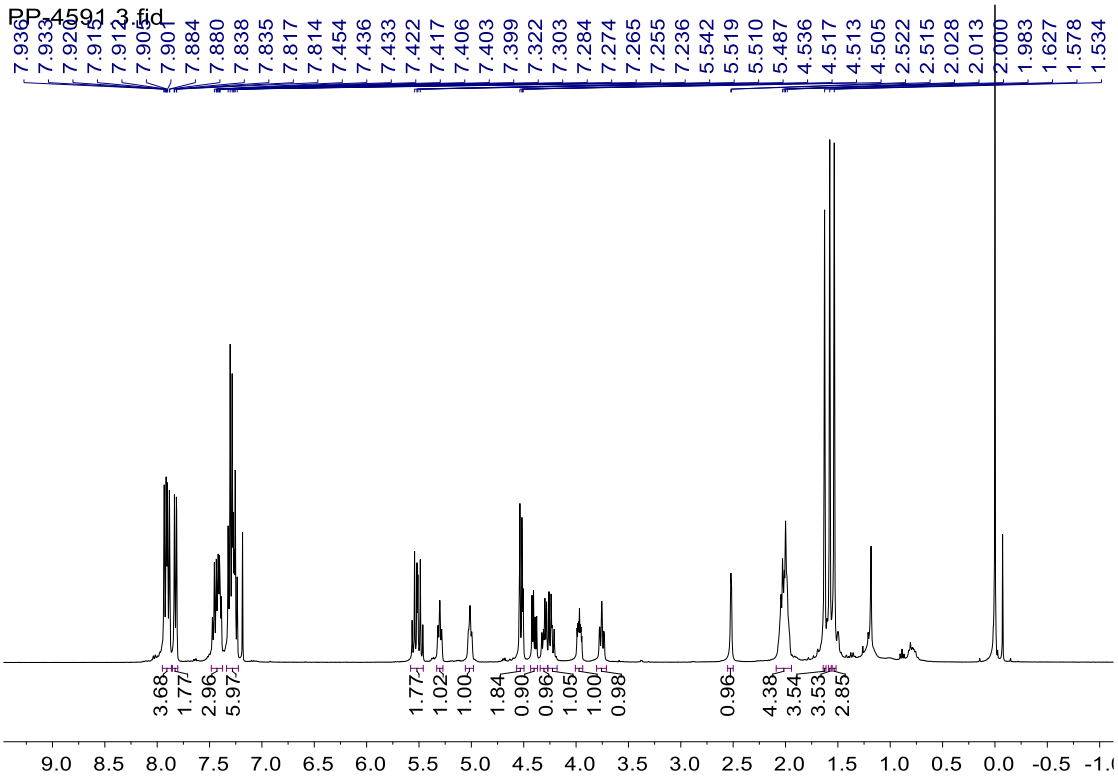
^{13}C NMR ($CDCl_3$, 101 MHz) of **7e**

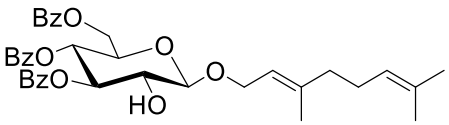




7f

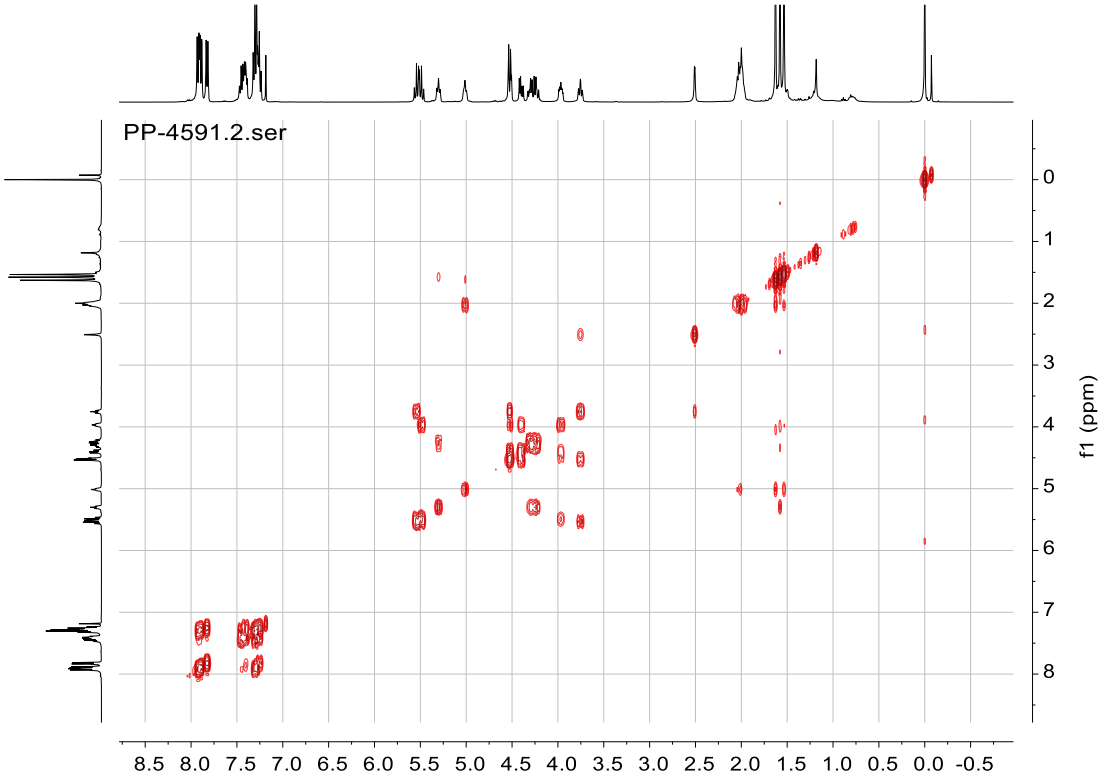
^{1}H NMR ($CDCl_3$, 400 MHz) of **7f**

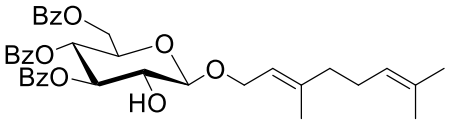




7f

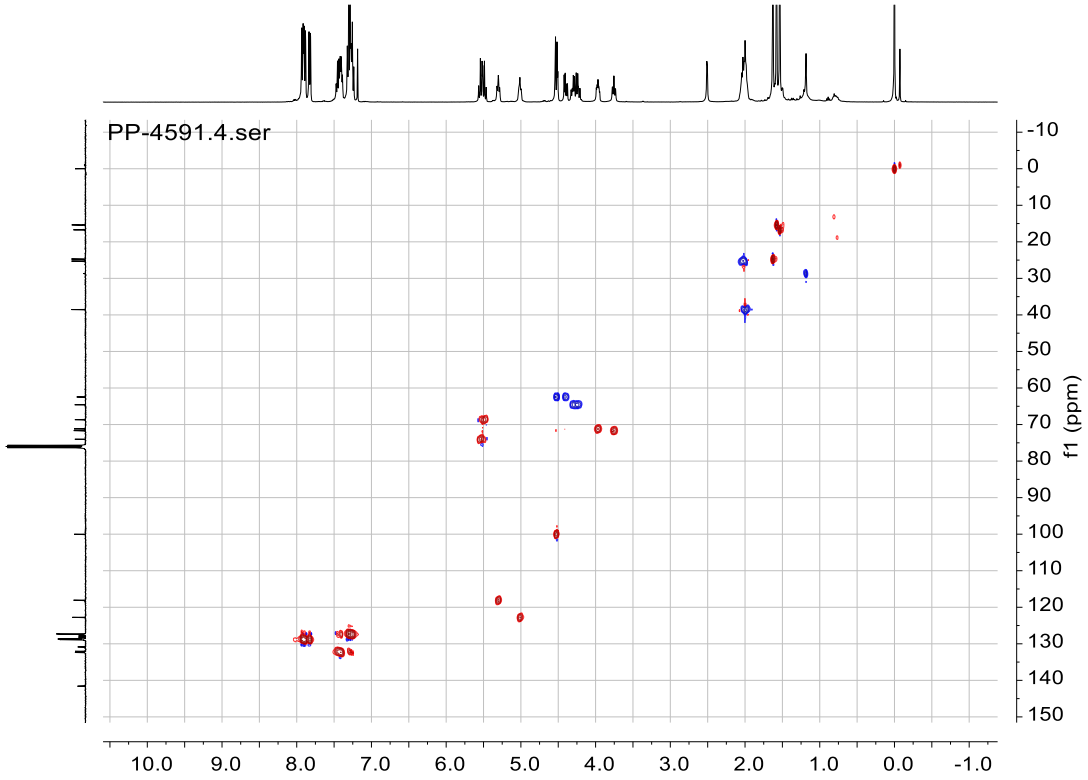
gCOSY ($CDCl_3$, 400 MHz) of **7f**

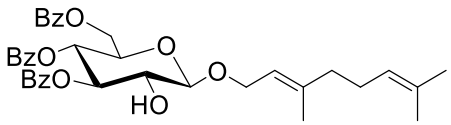




7f

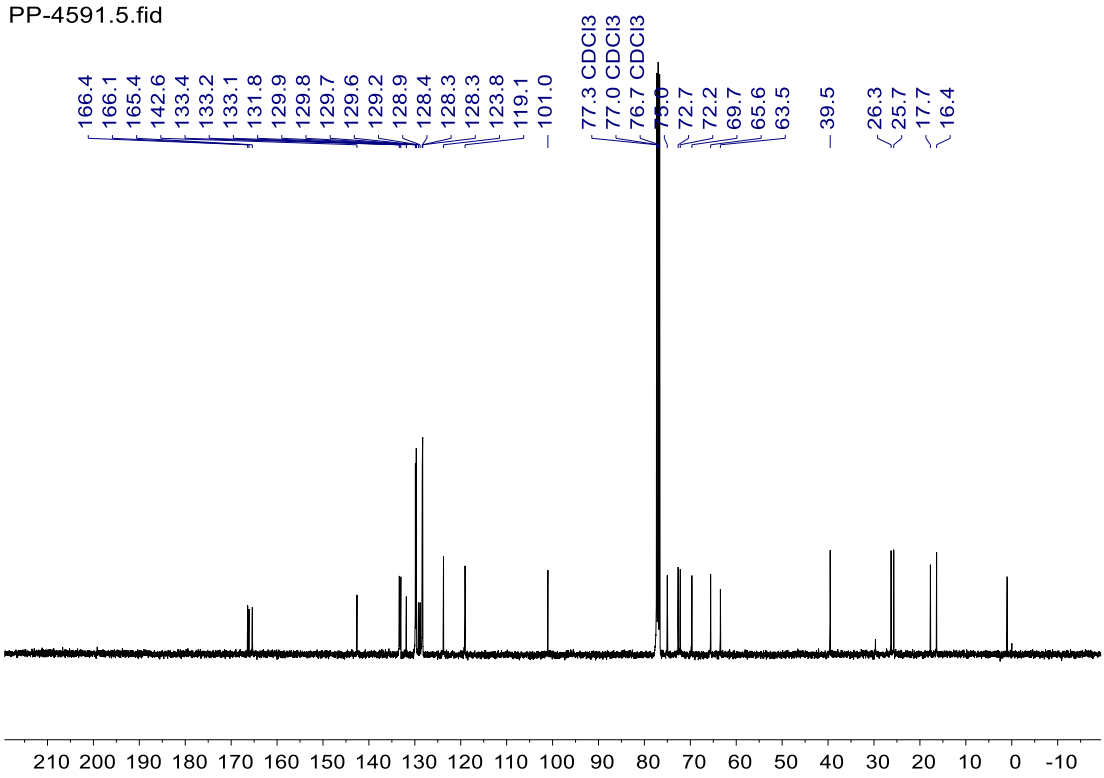
gHSQC ($CDCl_3$, 400 MHz) of **7f**

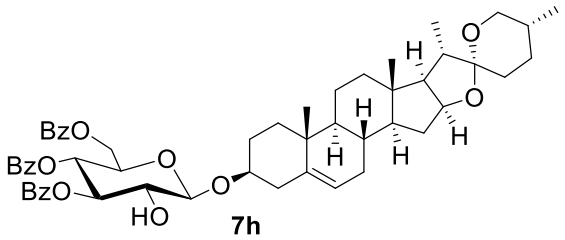




7f

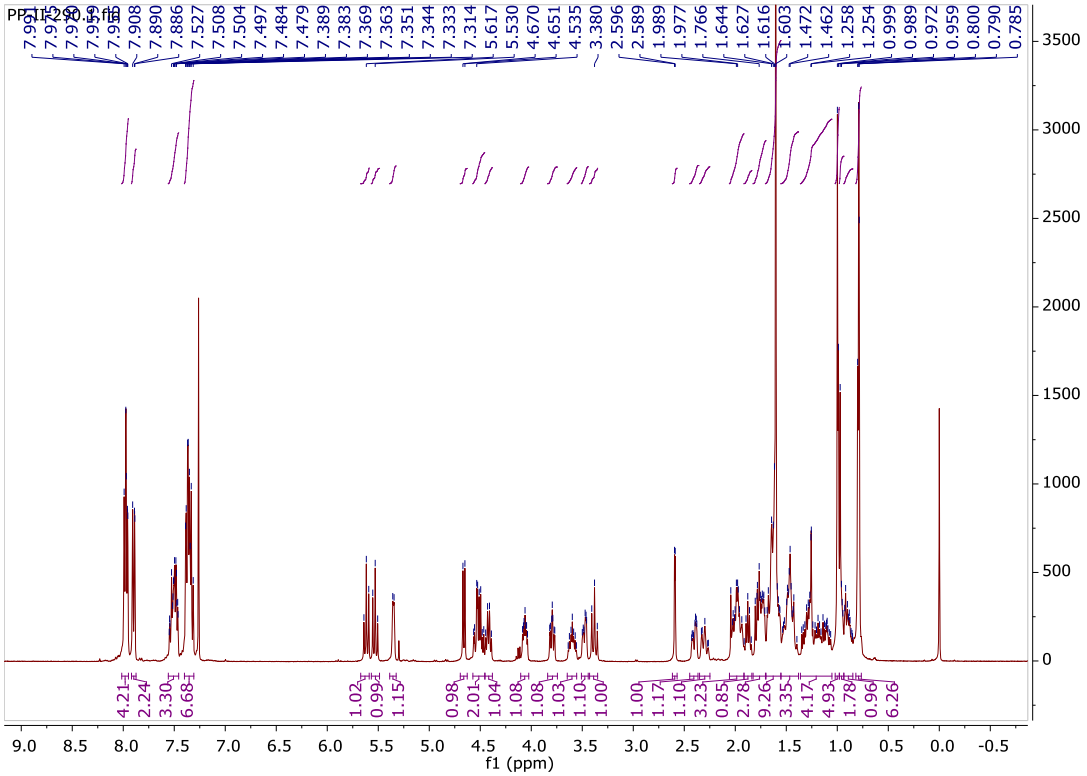
^{13}C NMR ($CDCl_3$, 101 MHz) of **7f**

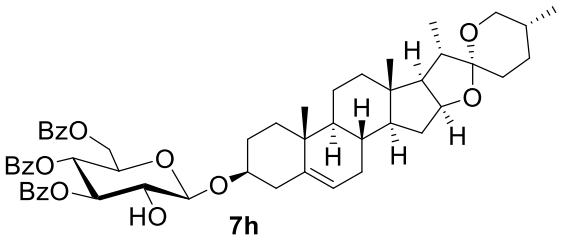




7h

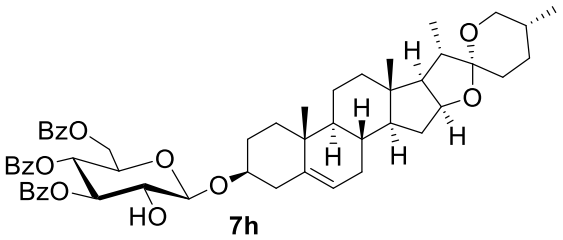
^{1}H NMR ($CDCl_3$, 400 MHz) of **7h**





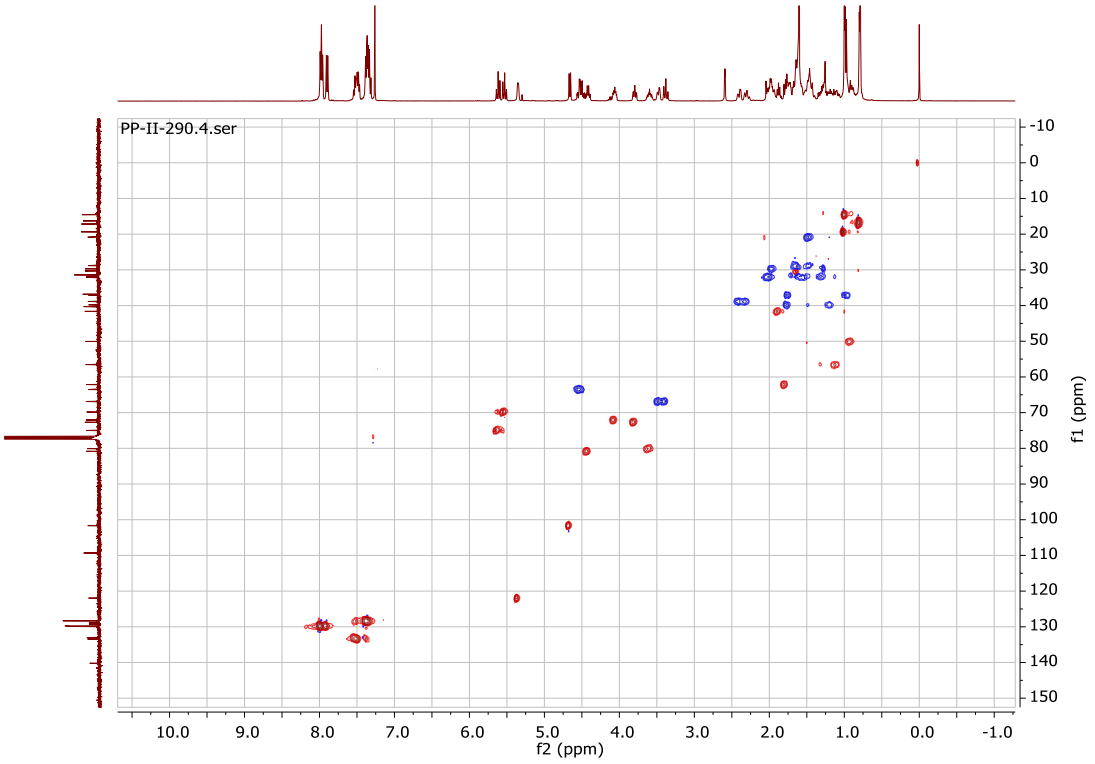
7h

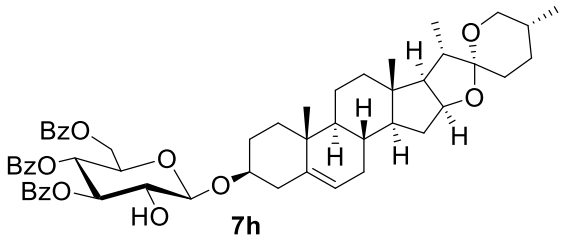
gCOSY ($CDCl_3$, 400 MHz) of **7h**



7h

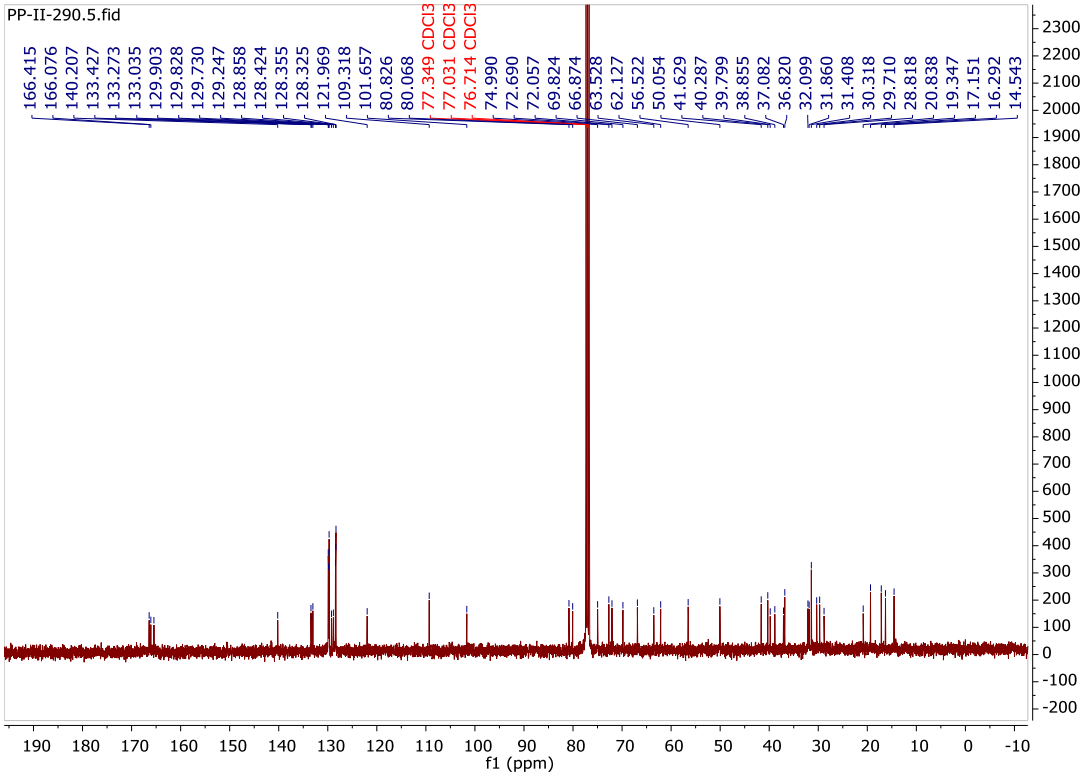
gHSQC ($CDCl_3$, 400 MHz) of **7h**

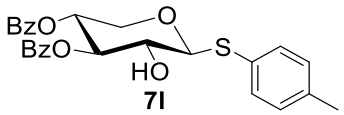




7h

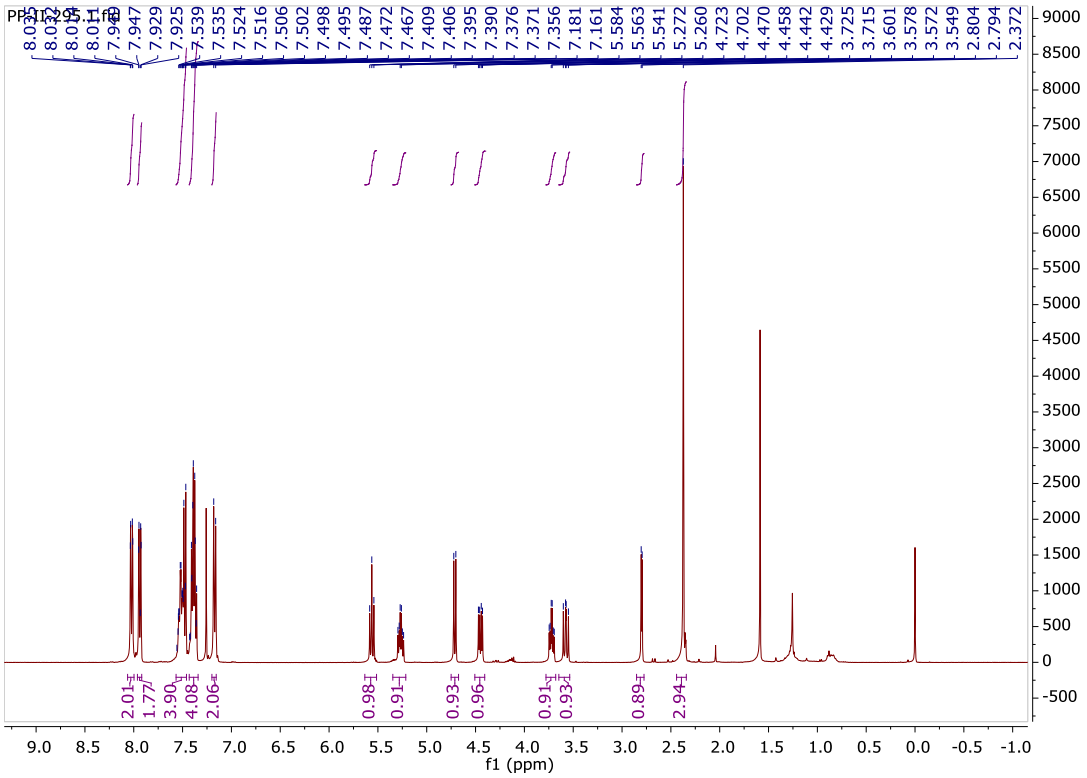
^{13}C NMR ($CDCl_3$, 101 MHz) of **7h**

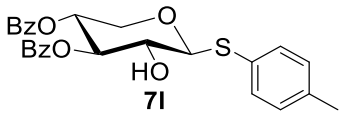




7l

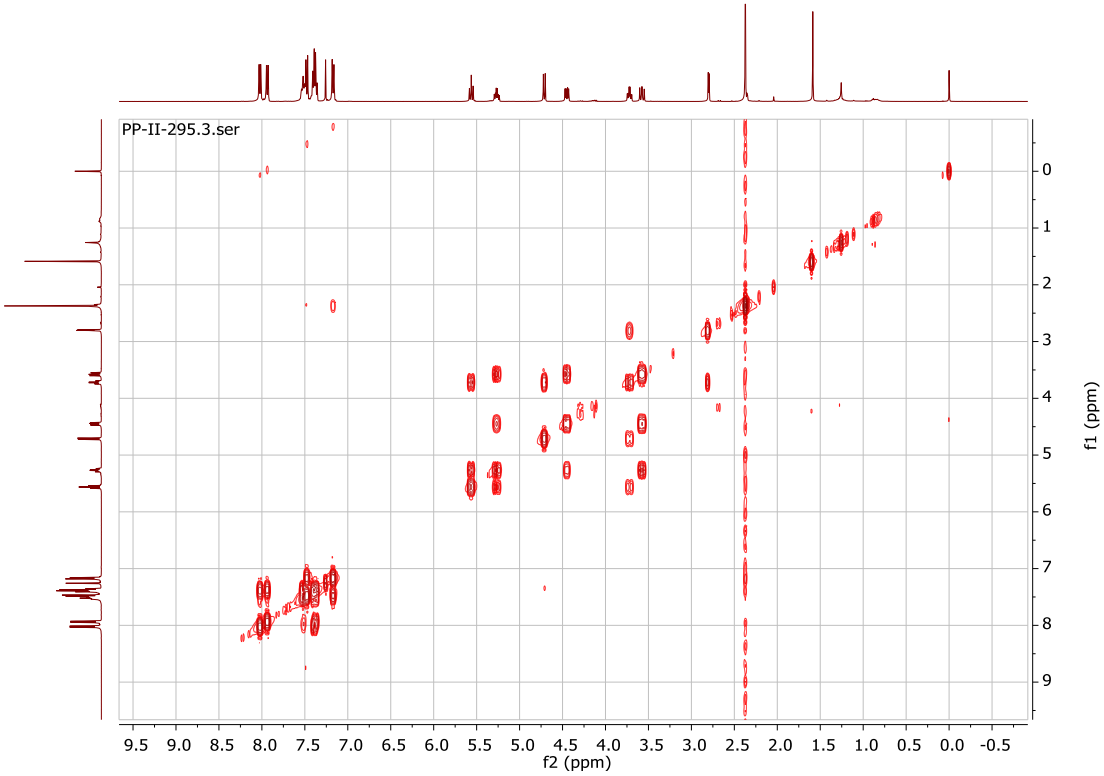
^{1}H NMR ($CDCl_3$, 400 MHz) of **7l**

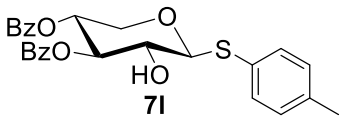




7l

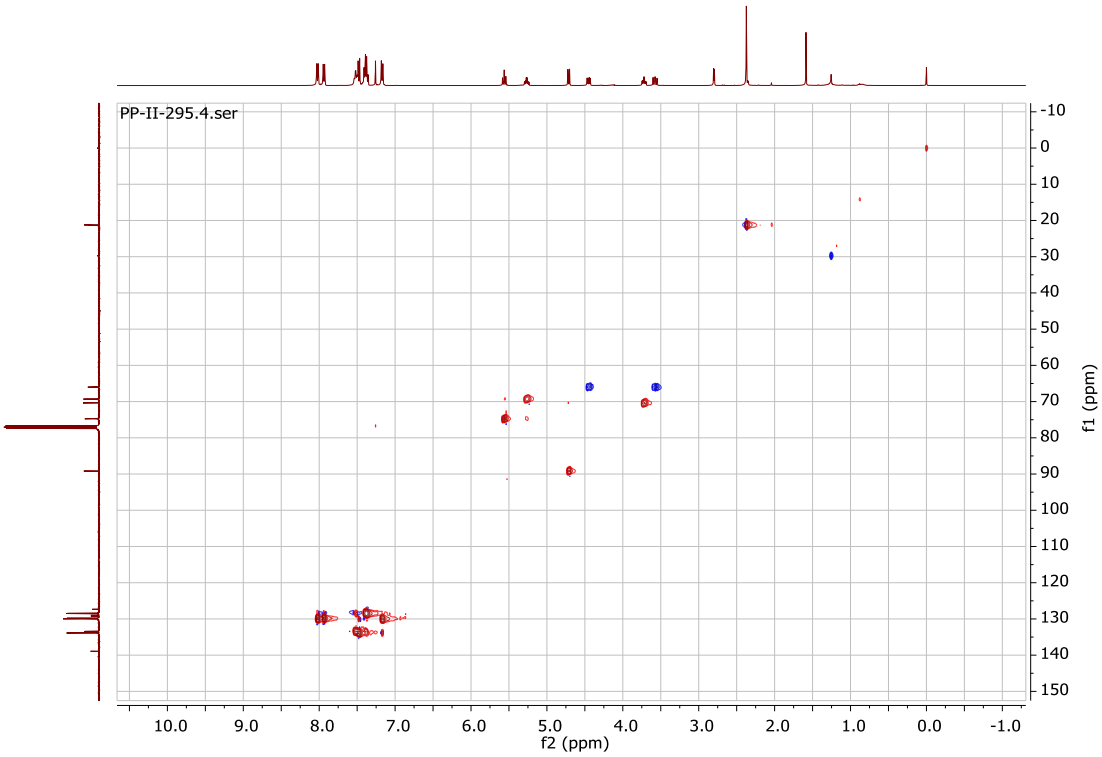
gCOSY ($CDCl_3$, 400 MHz) of **7l**

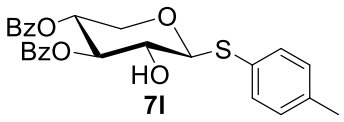




7l

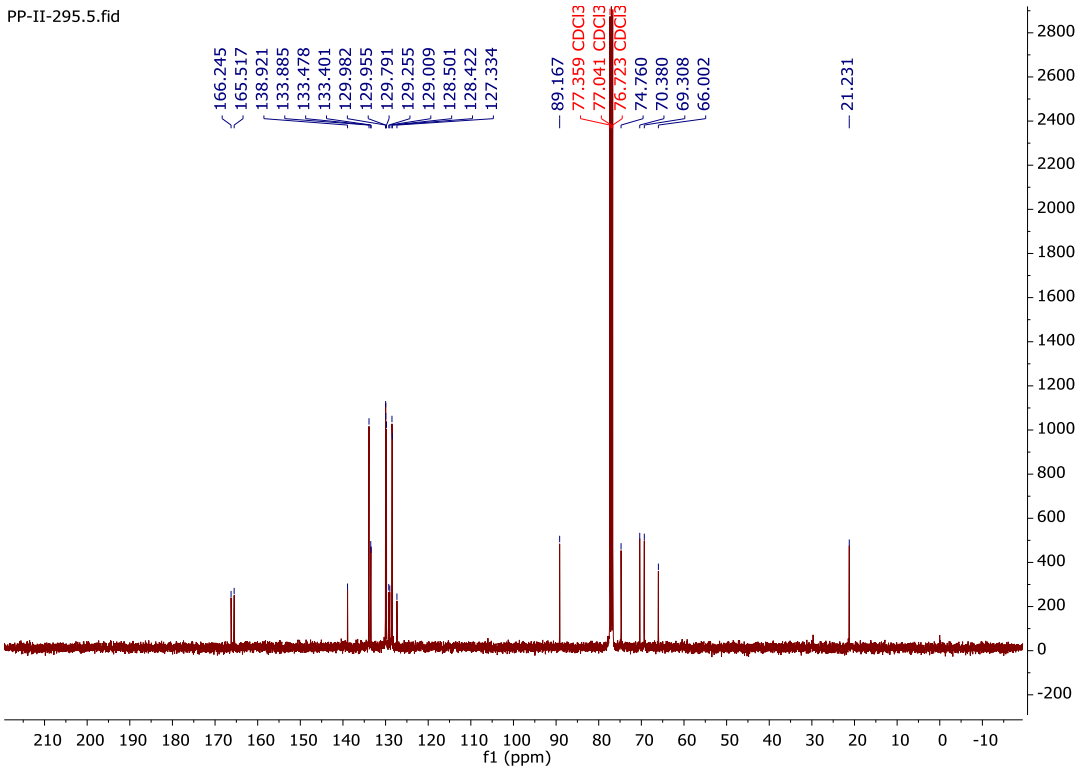
gHSQC ($CDCl_3$, 400 MHz) of **7l**

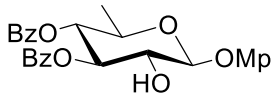




7l

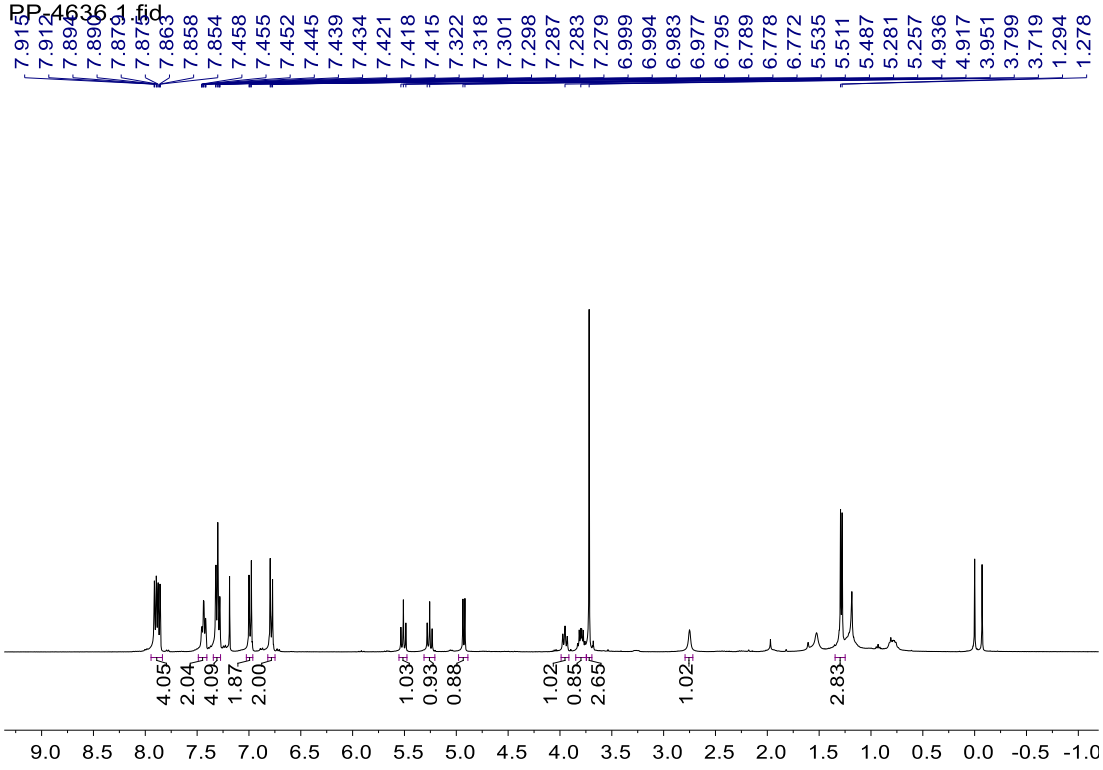
^{13}C NMR ($CDCl_3$, 101 MHz) of **7l**

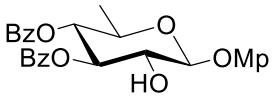




7n

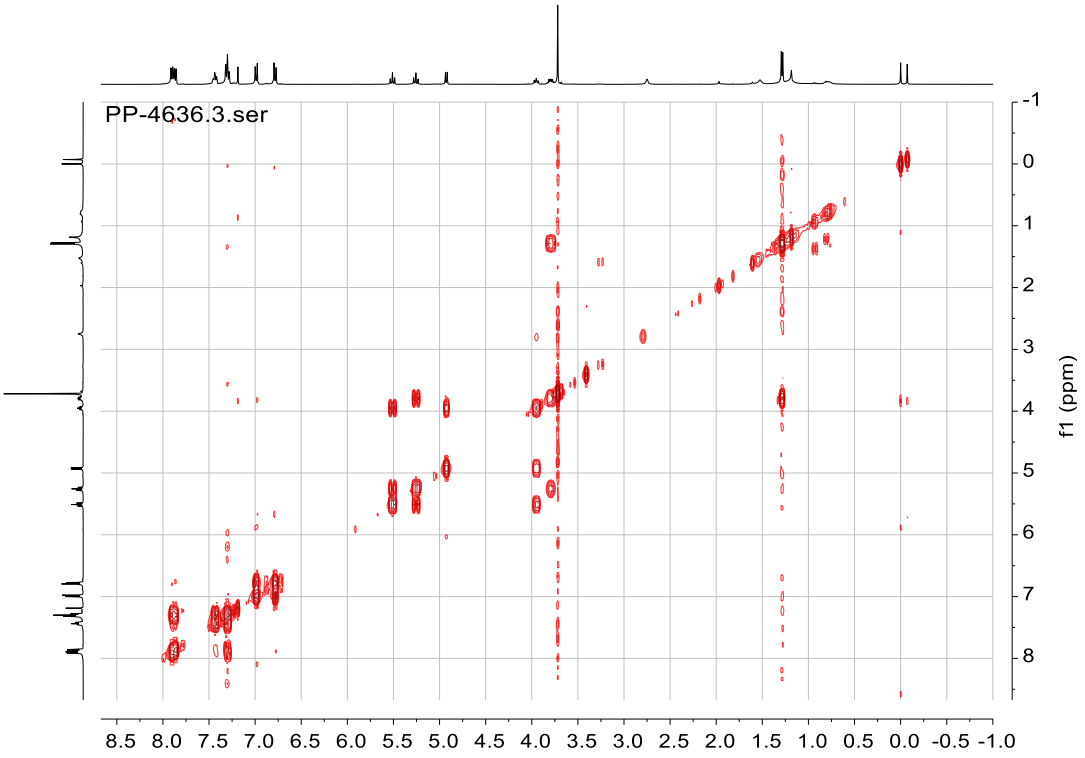
^{1}H NMR ($CDCl_3$, 400 MHz) of **7n**

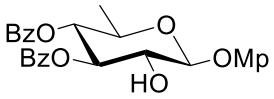




7n

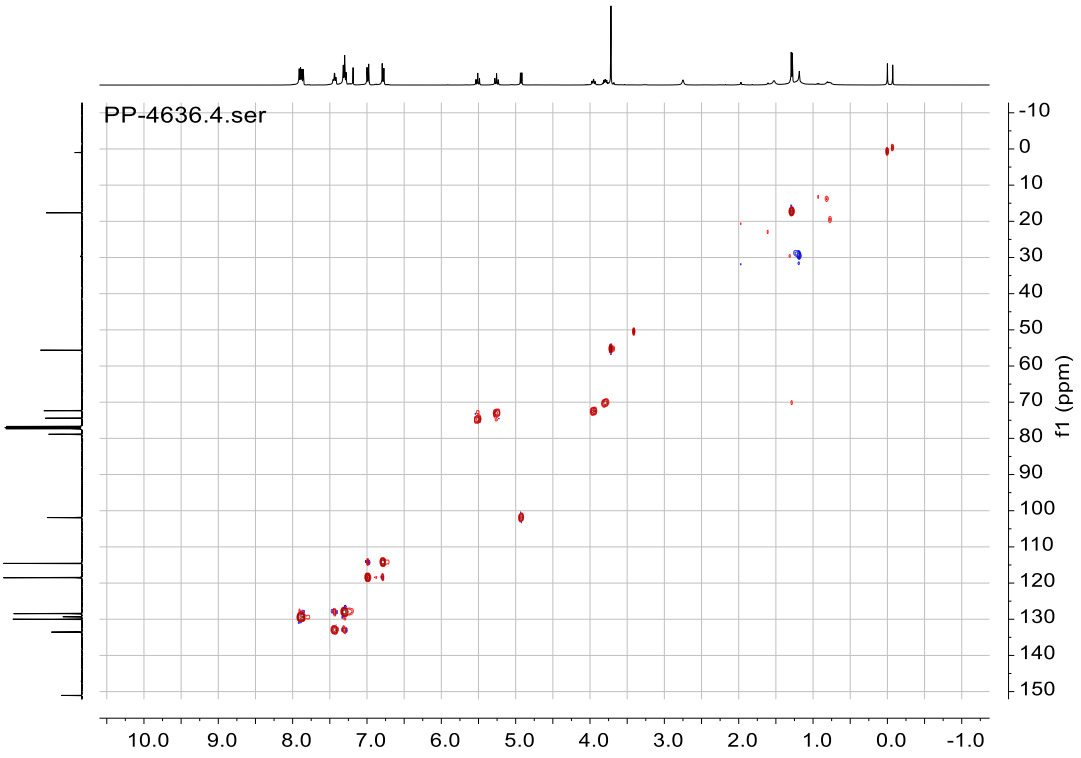
gCOSY ($CDCl_3$, 400 MHz) of **7n**

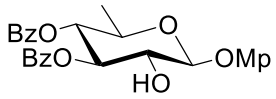




7n

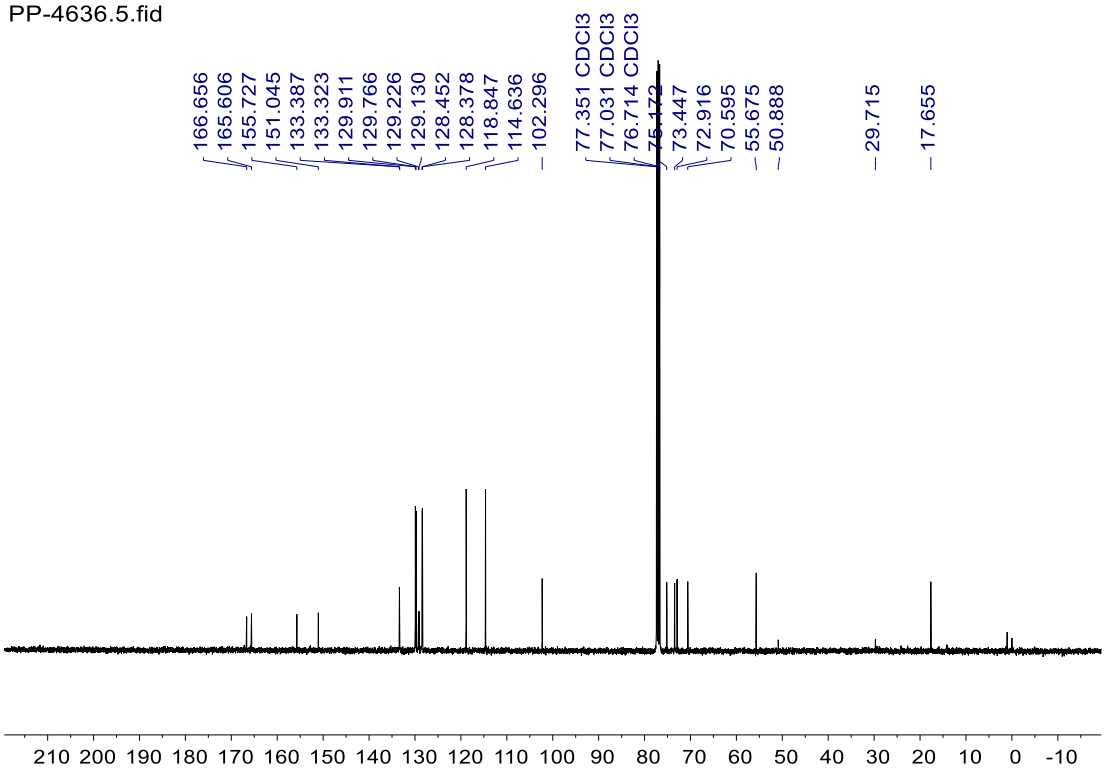
gHSQC ($CDCl_3$, 400 MHz) of **7n**

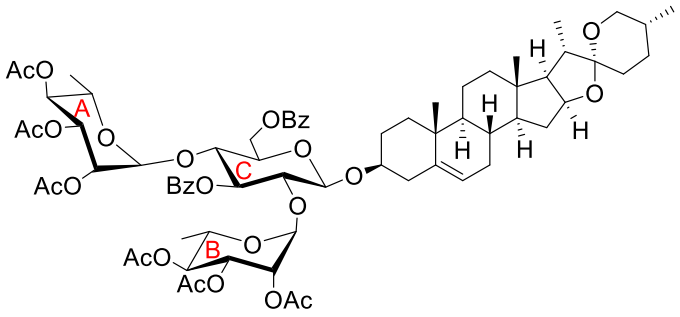




7n

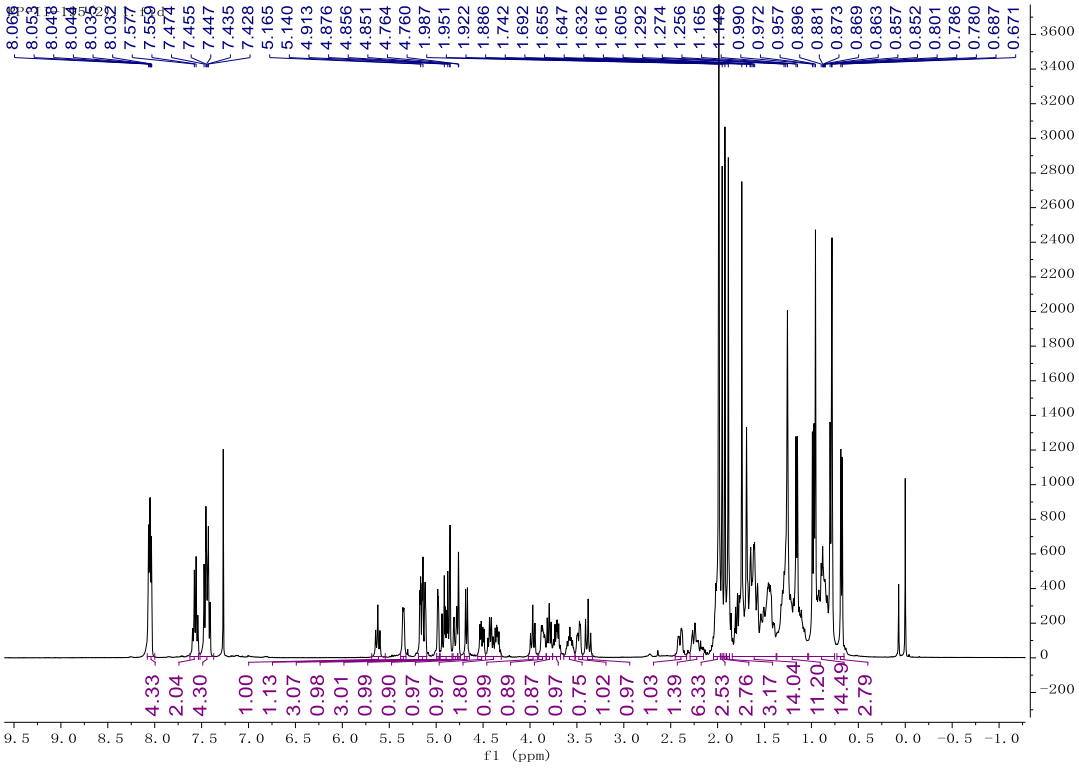
^{13}C NMR ($CDCl_3$, 101 MHz) of **7n**

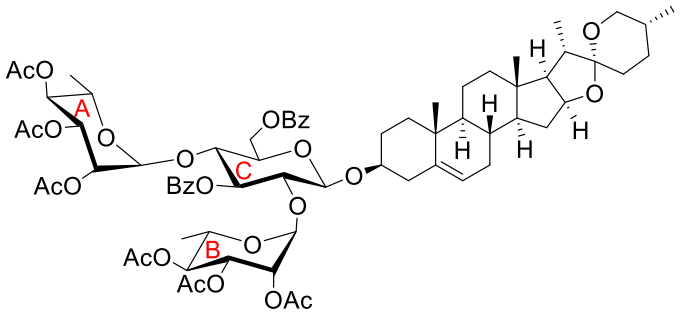




11

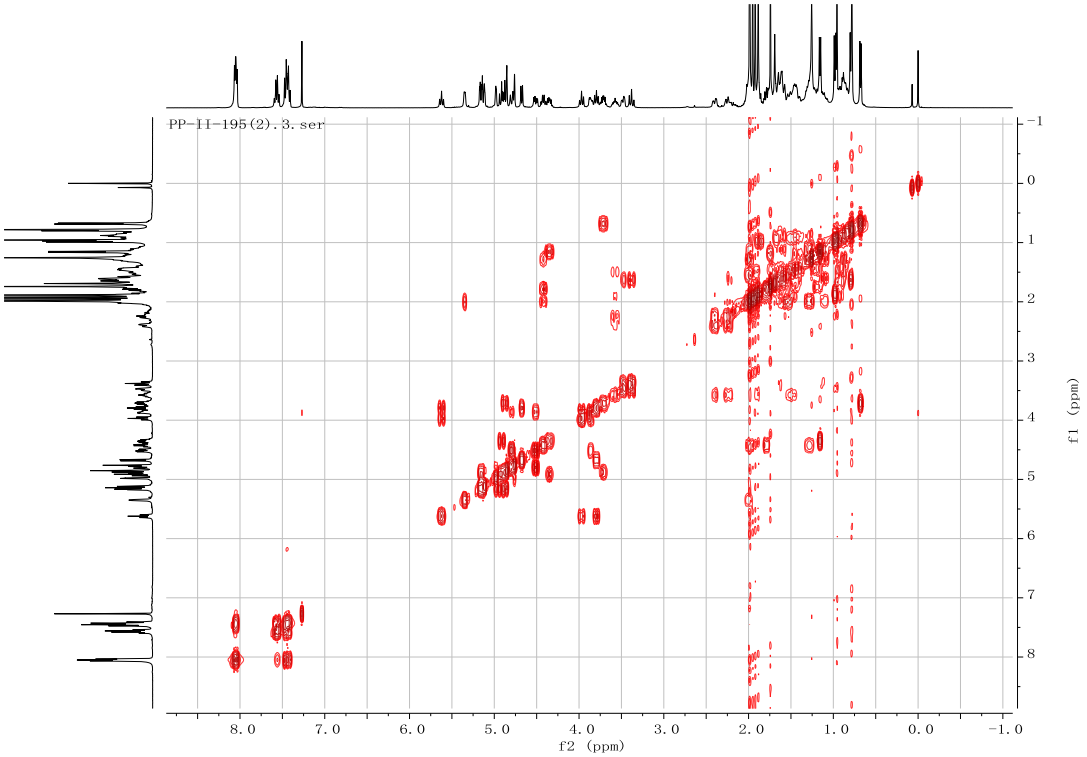
^{1}H NMR ($CDCl_3$, 400 MHz) of **11**

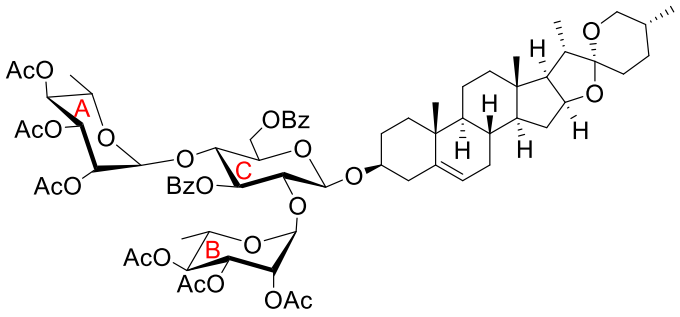




11

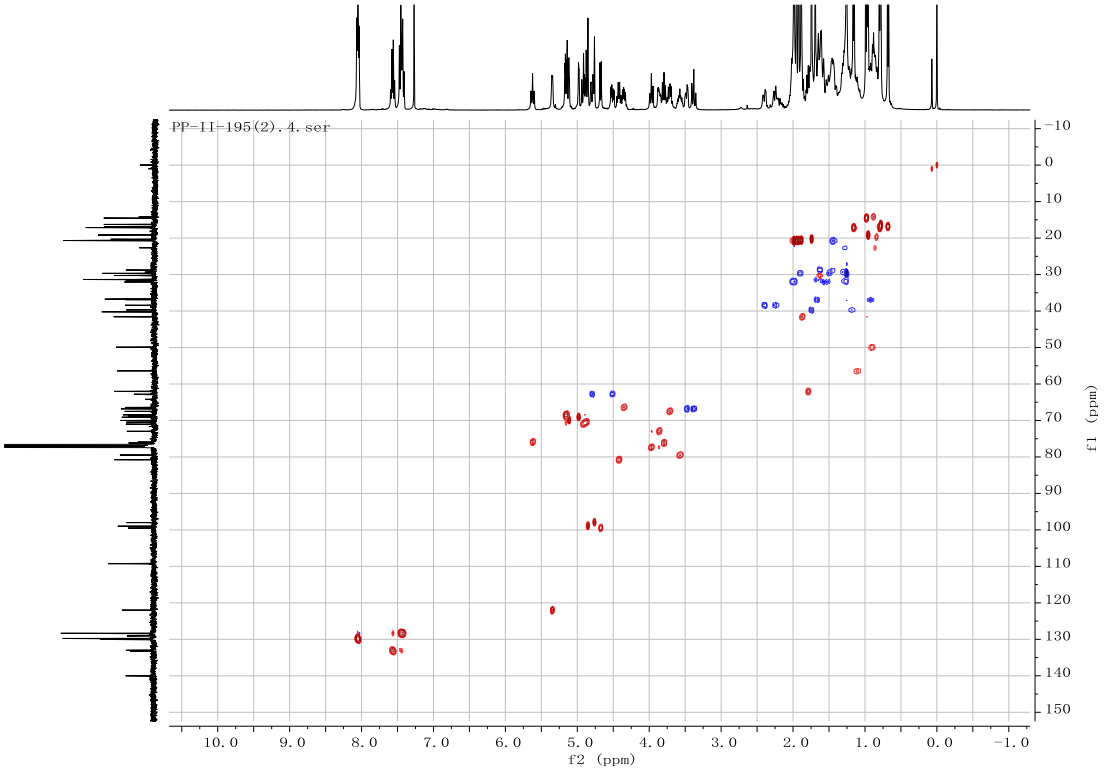
gCOSY ($CDCl_3$, 400 MHz) of **11**

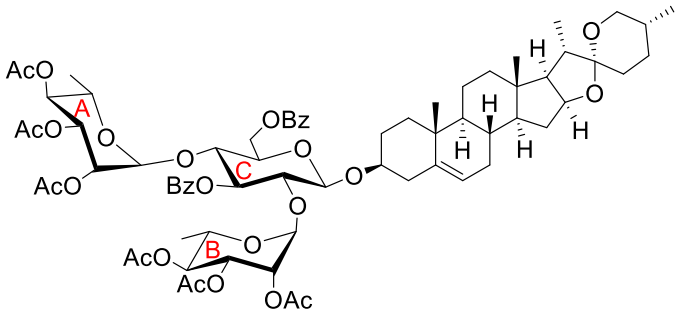




11

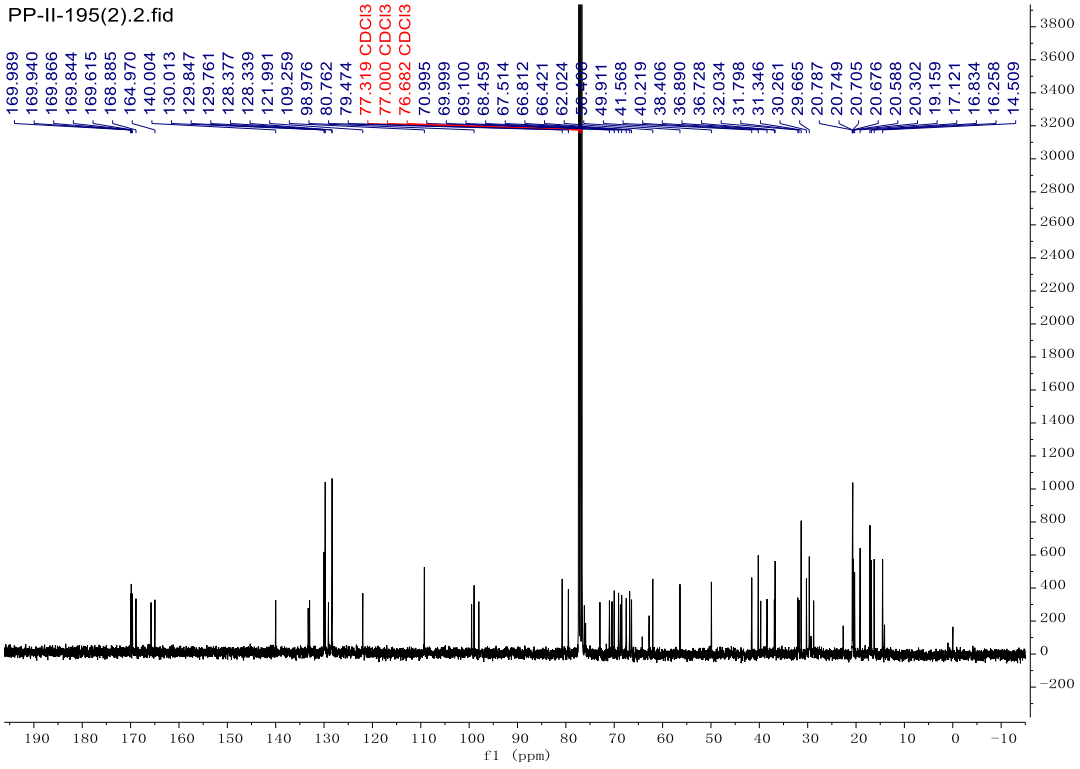
gHSQC ($CDCl_3$, 400 MHz) of **11**

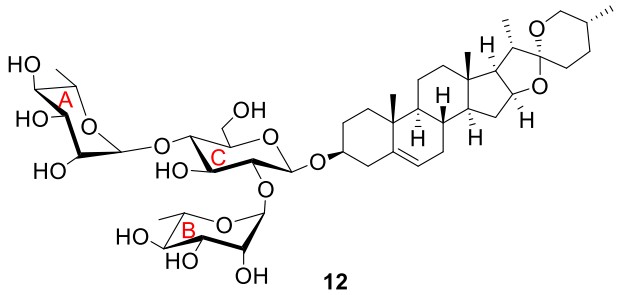




11

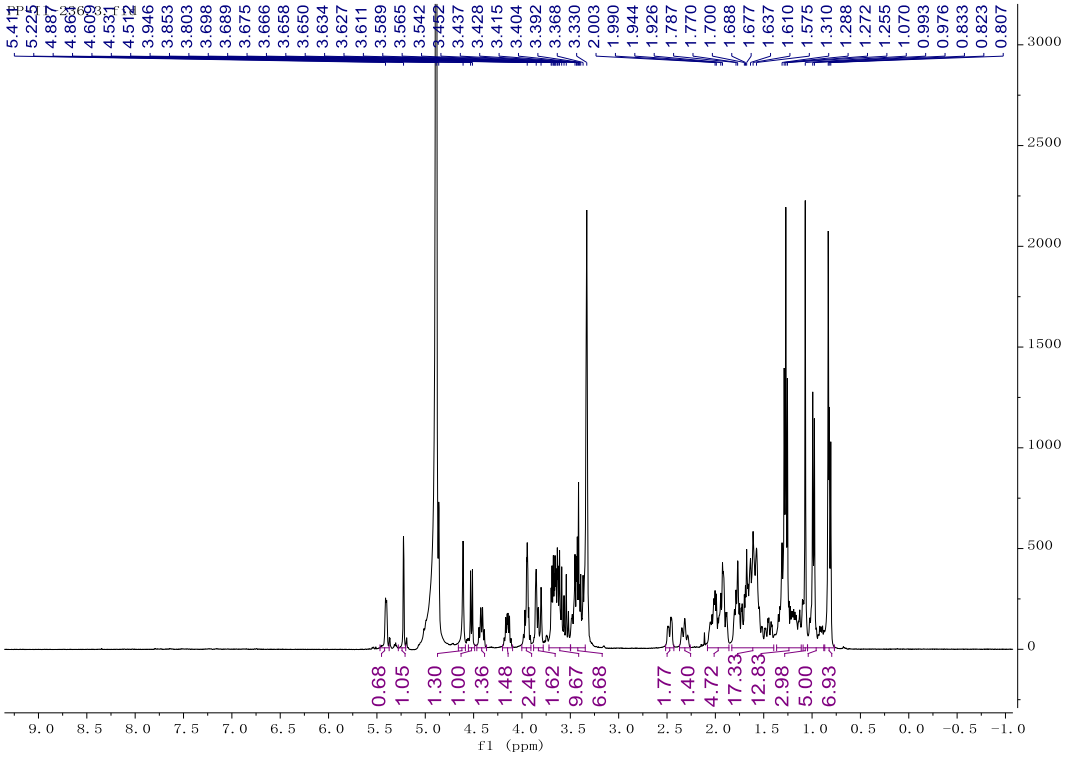
^{13}C NMR ($CDCl_3$, 101 MHz) of **11**

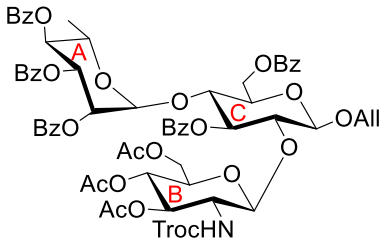




12

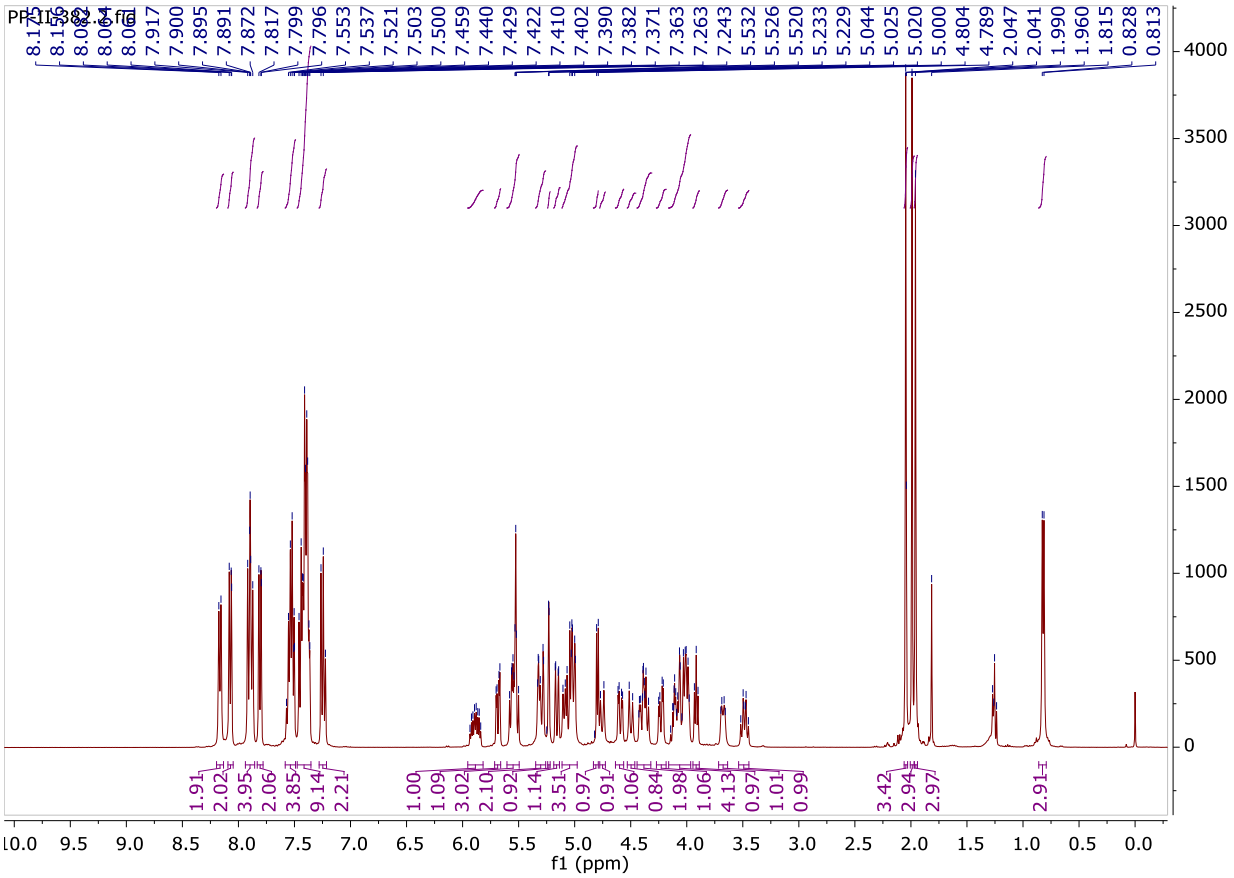
^{1}H NMR ($CDCl_3$, 400 MHz) of **12**

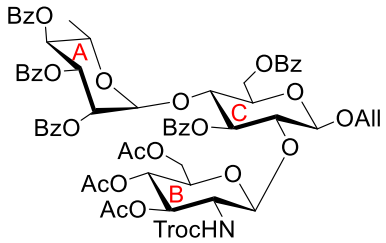




15

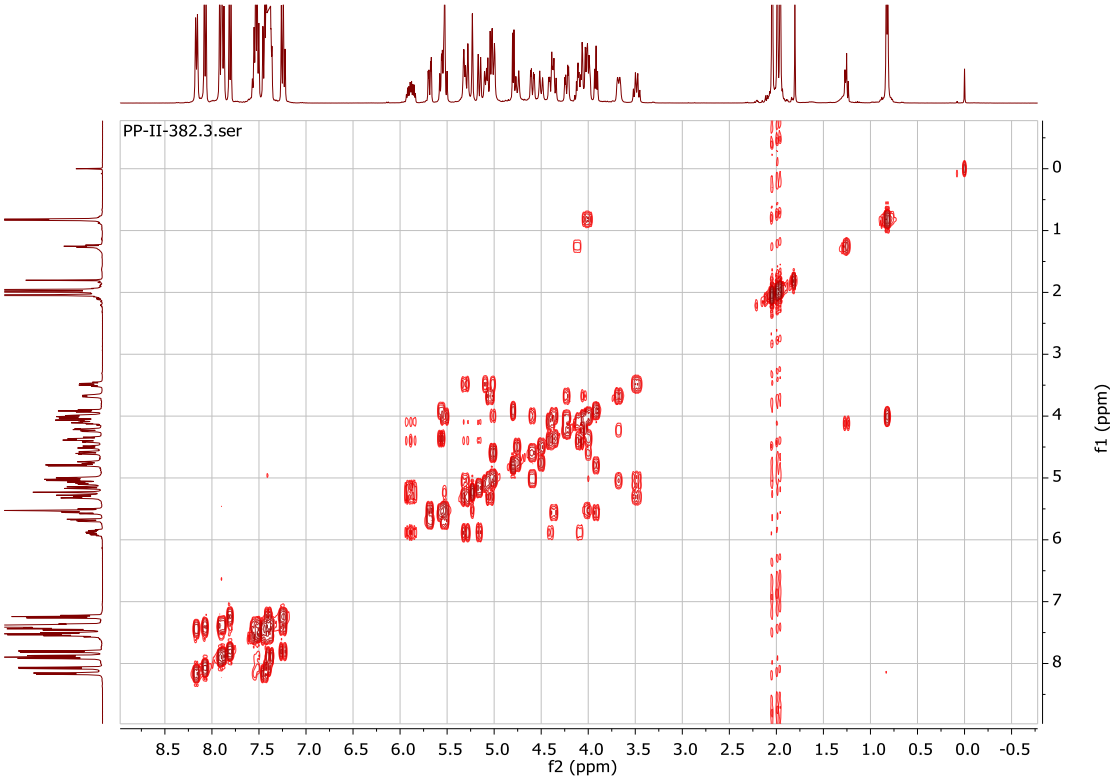
^{1}H NMR ($CDCl_3$, 400 MHz) of **15**

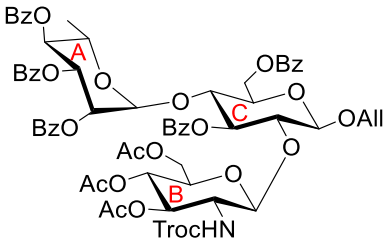




15

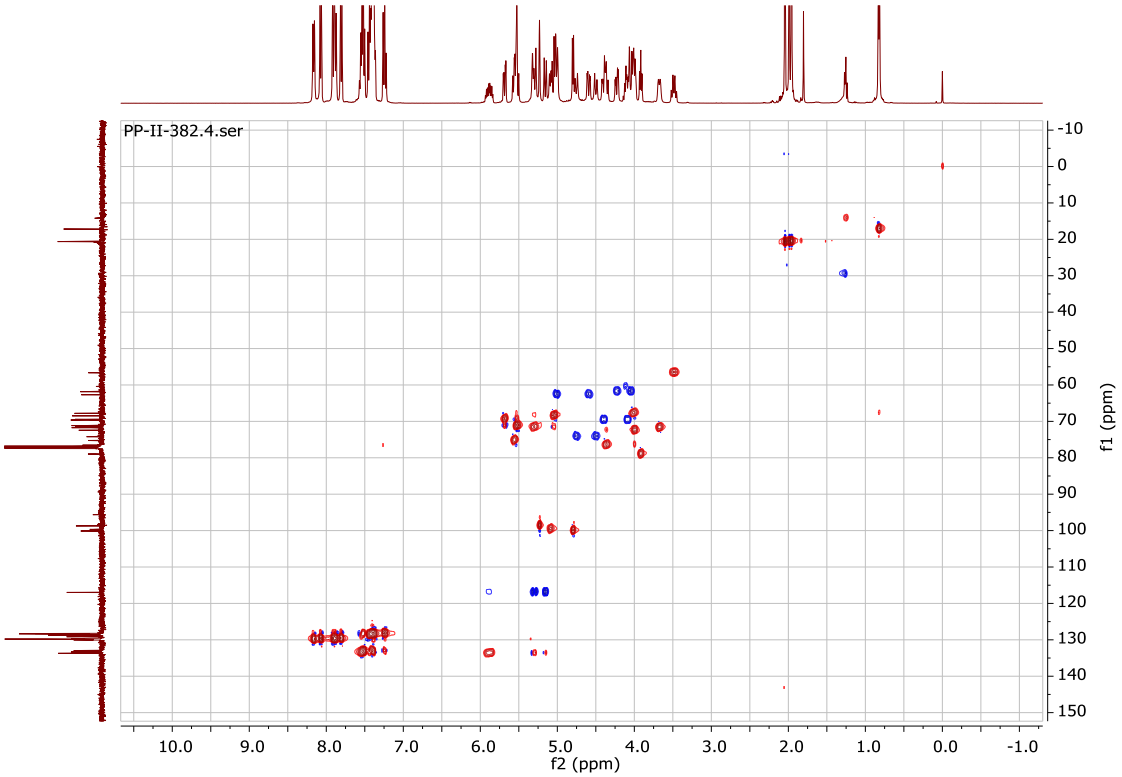
gCOSY ($CDCl_3$, 400 MHz) of **15**

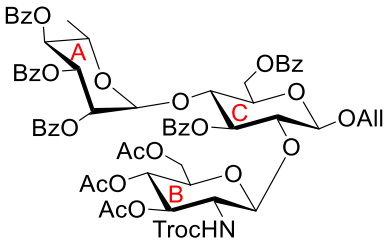




15

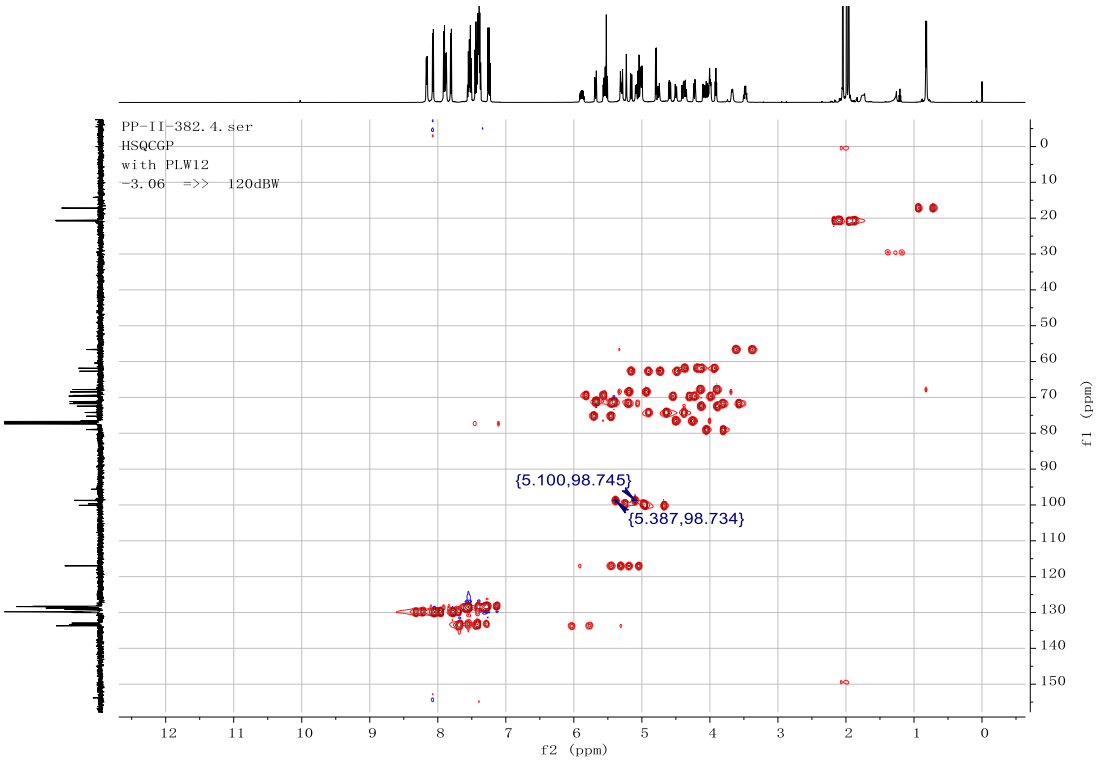
gHSQC ($CDCl_3$, 400 MHz) of **15**

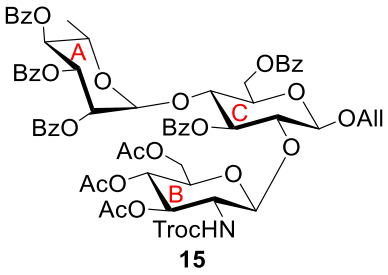




15

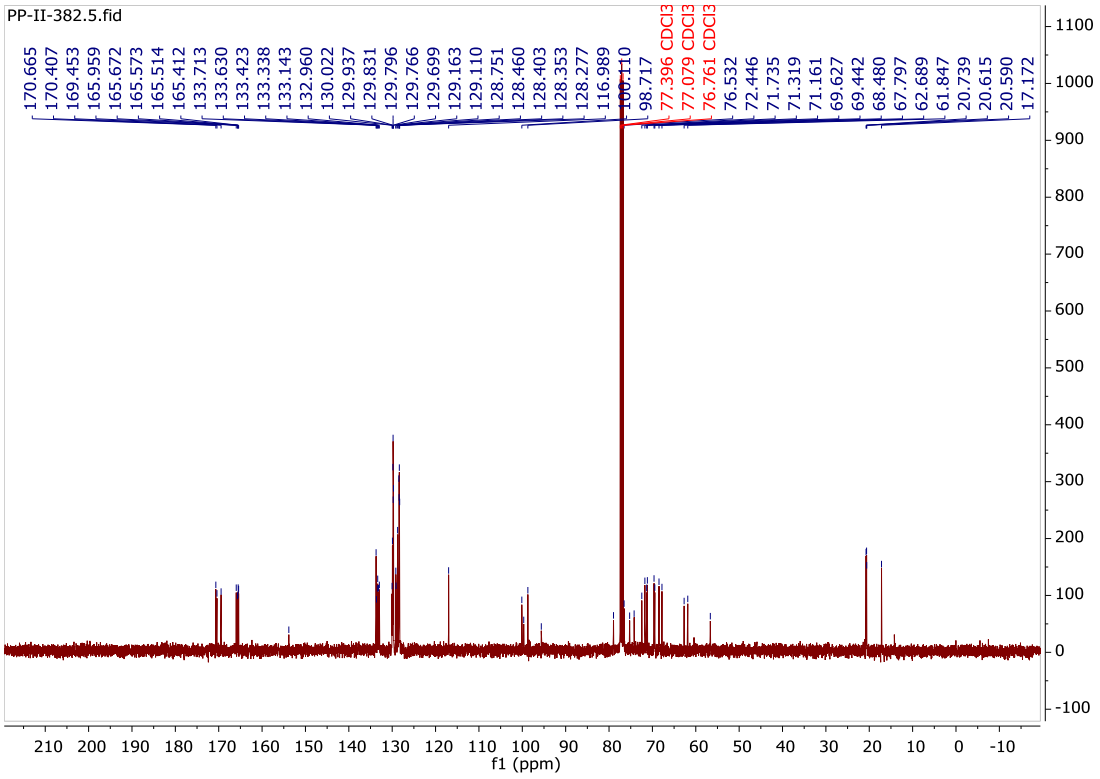
Coupled gHSQC ($CDCl_3$, 400 MHz) of **15**

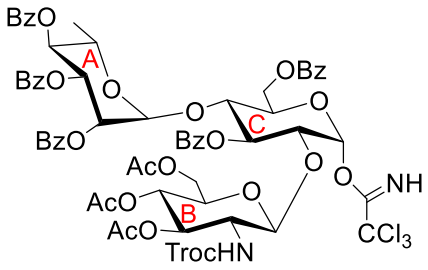




15

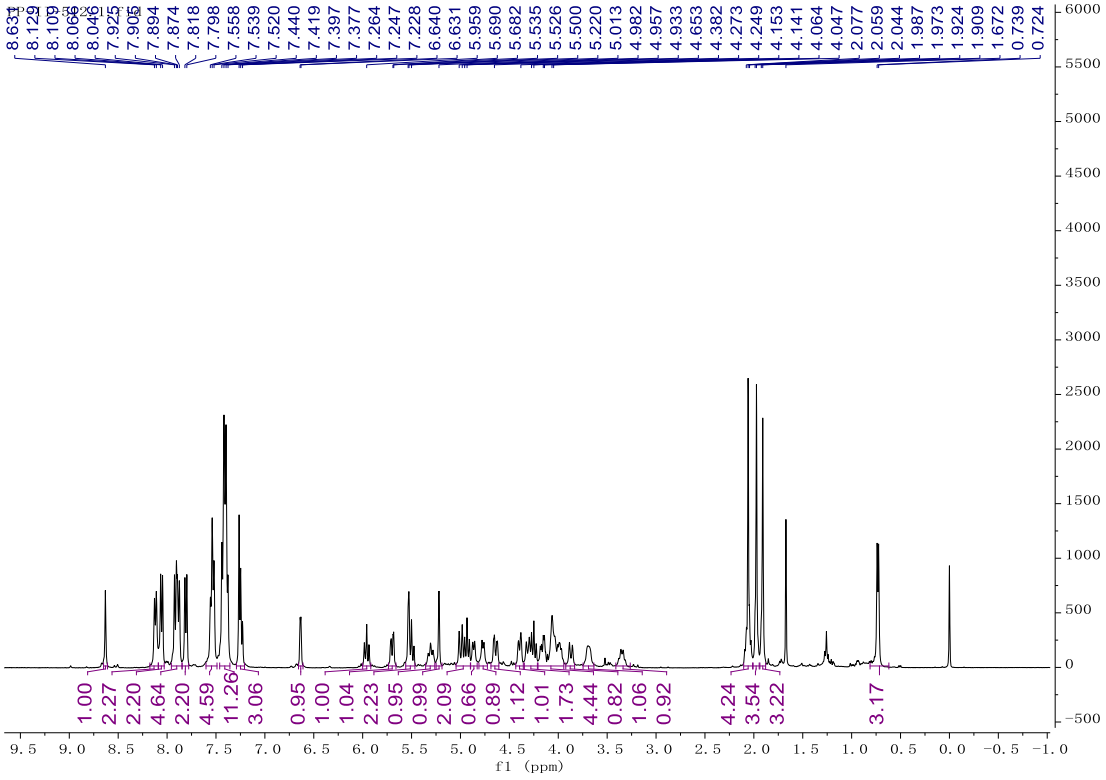
^{13}C NMR ($CDCl_3$, 101 MHz) of **15**

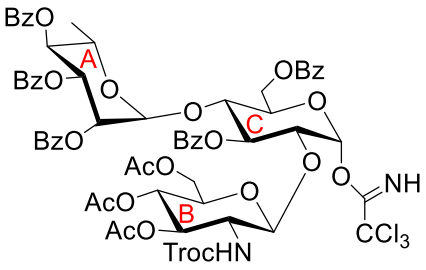




17

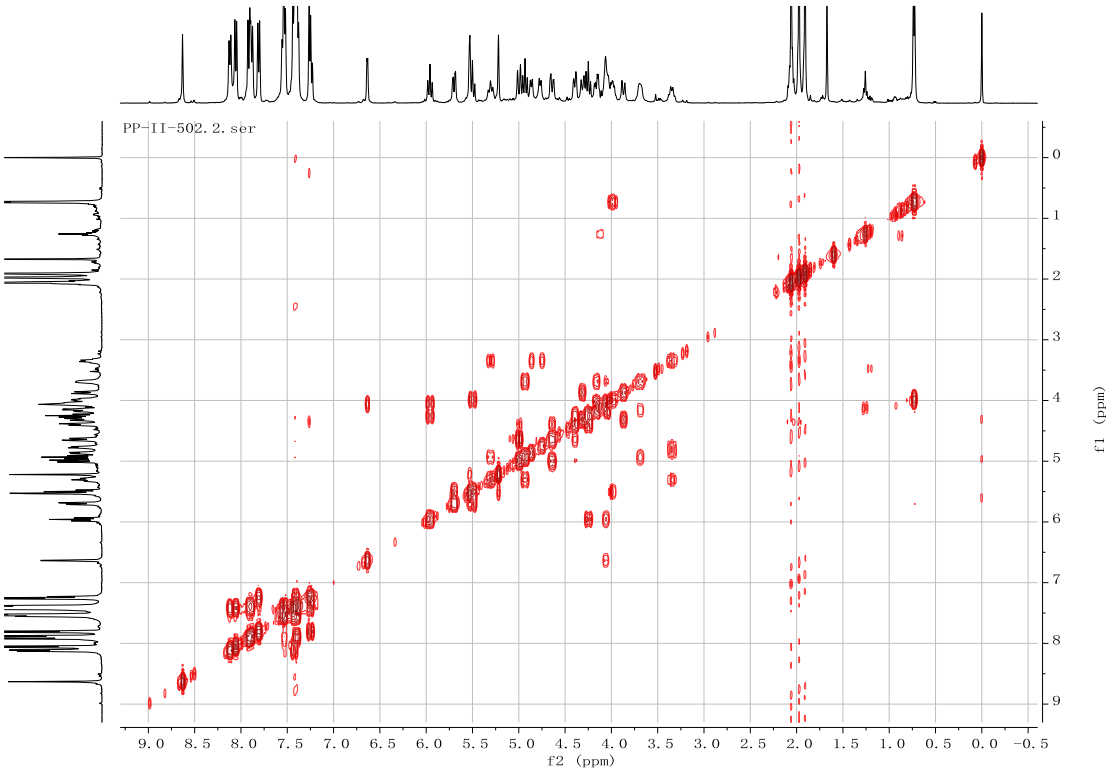
^{1}H NMR ($CDCl_3$, 400 MHz) of **17**

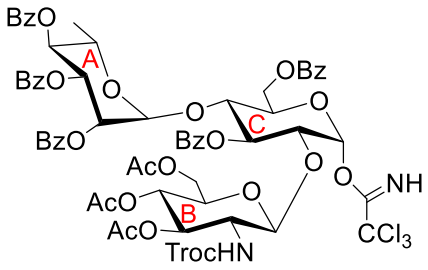




17

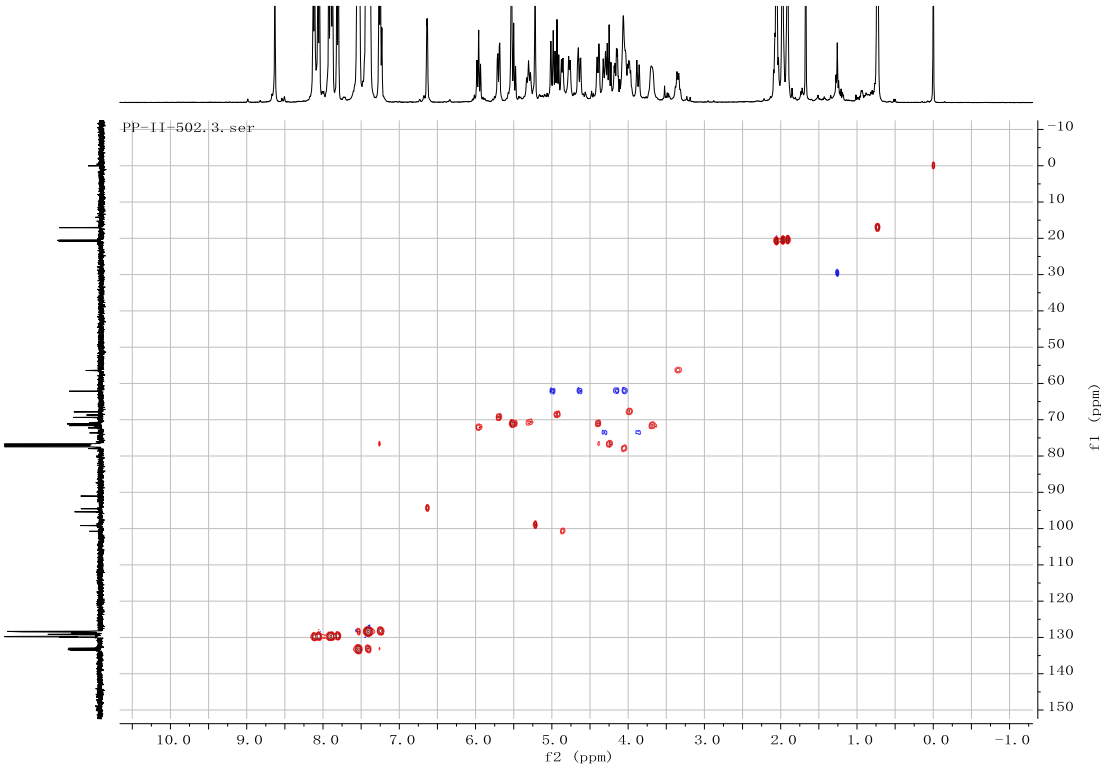
gCOSY ($CDCl_3$, 400 MHz) of **17**

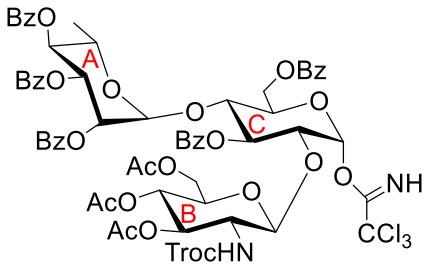




17

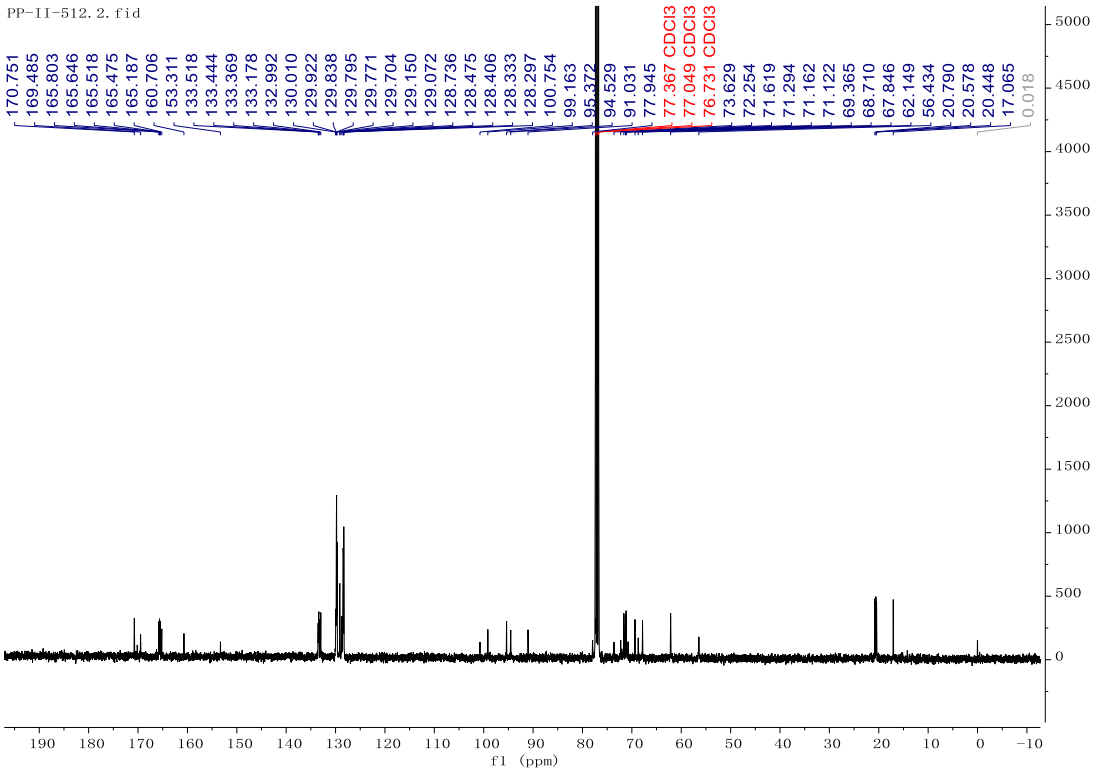
gHSQC ($CDCl_3$, 400 MHz) of **17**

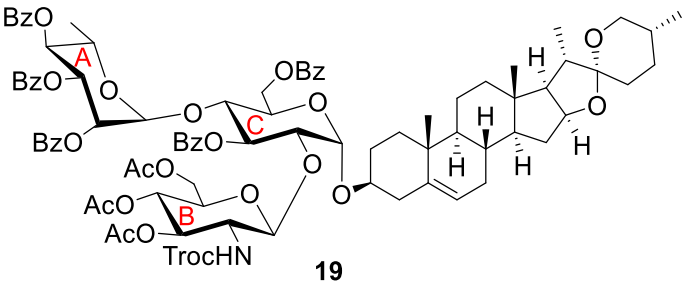




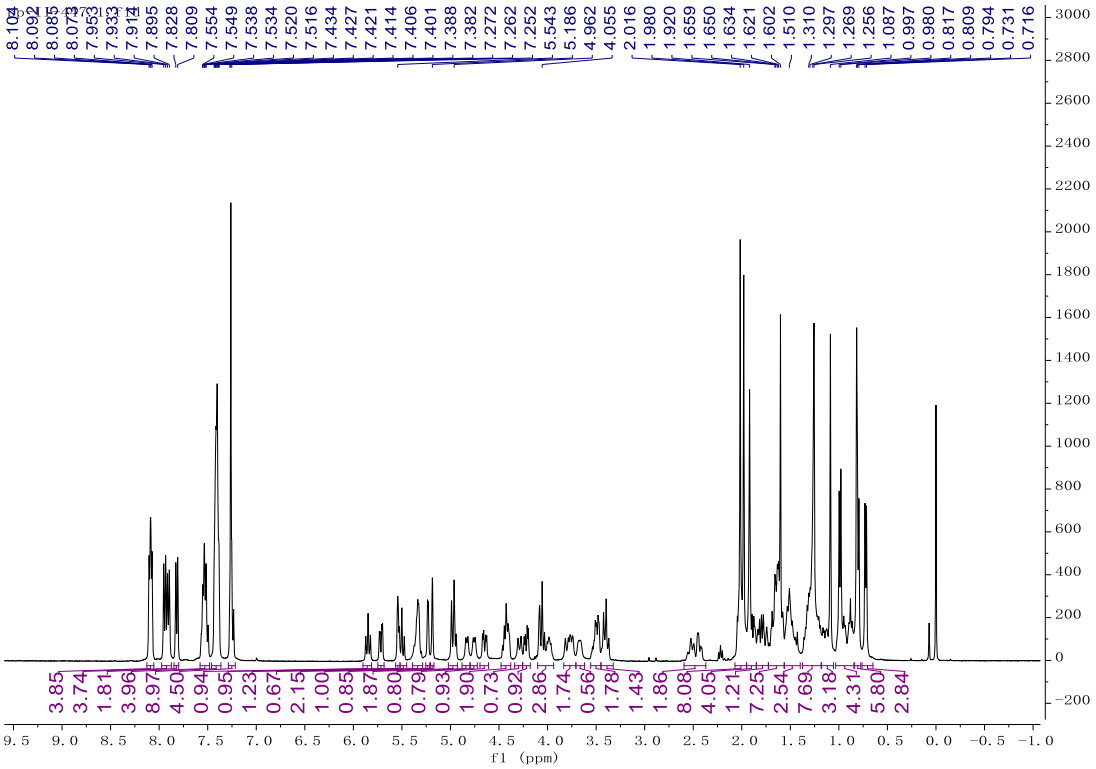
17

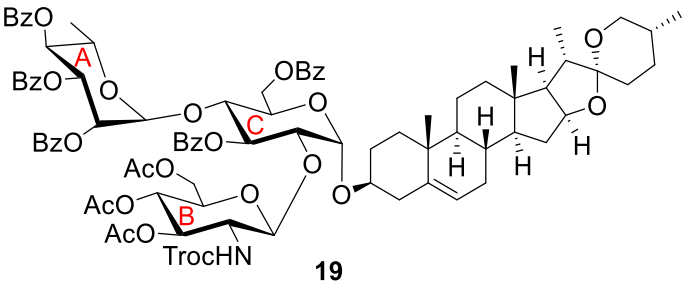
^{13}C NMR ($CDCl_3$, 101 MHz) of **17**





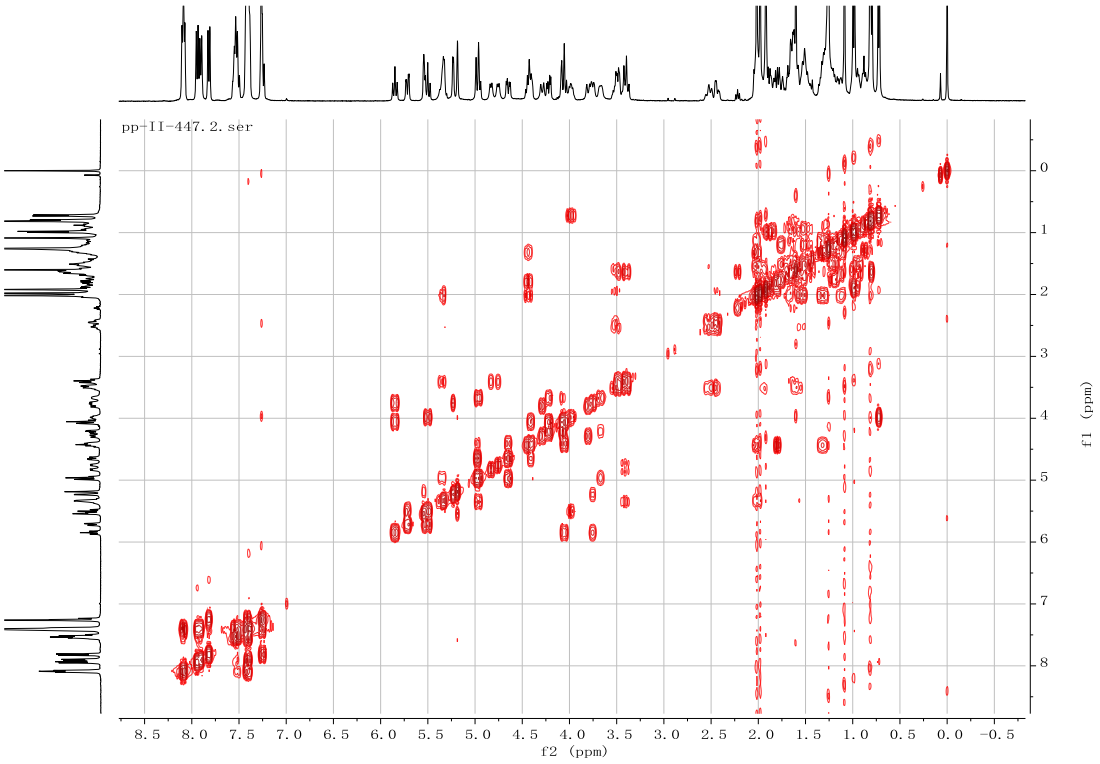
^{1}H NMR ($CDCl_3$, 400 MHz) of **19**

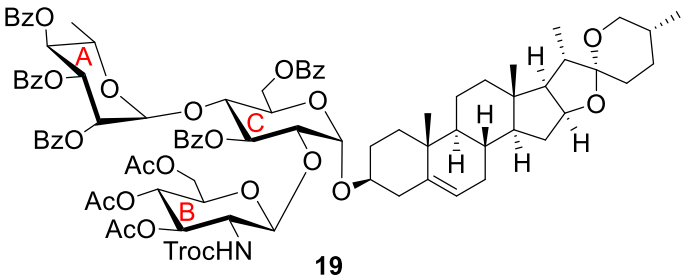




19

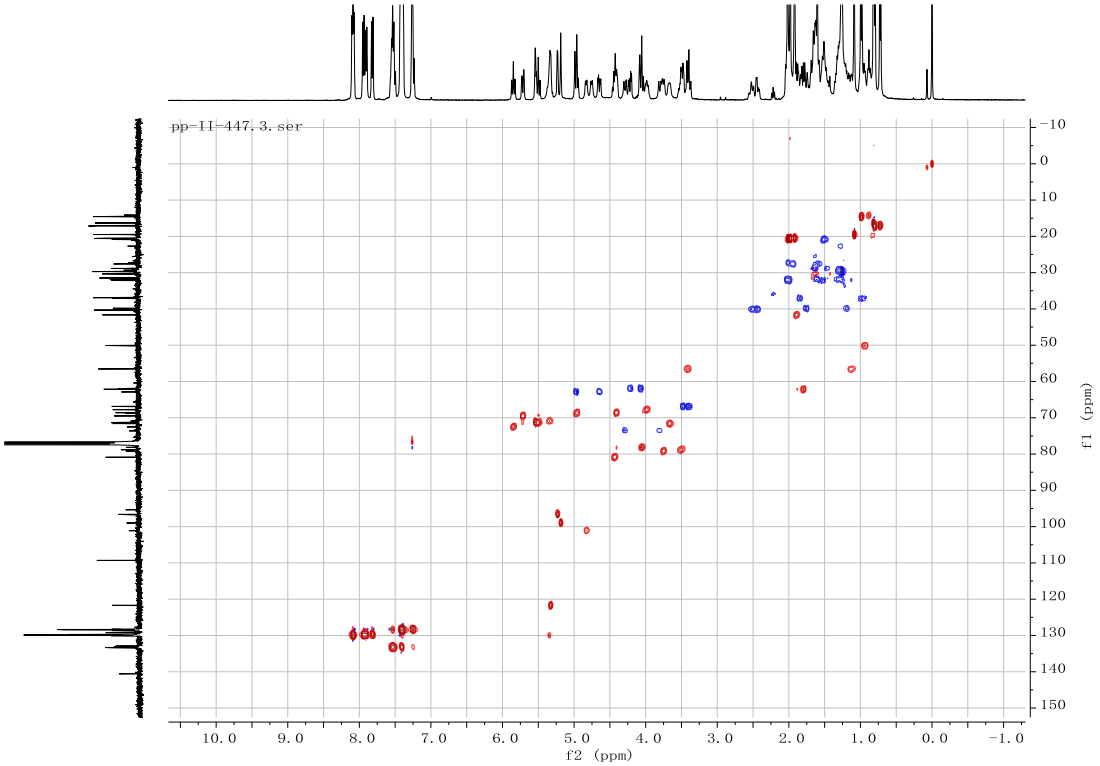
gCOSY ($CDCl_3$, 400 MHz) of **19**

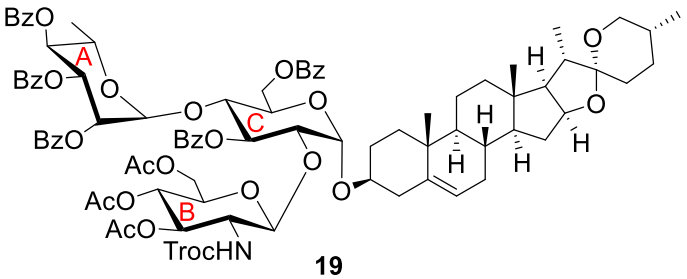




19

gHSQC ($CDCl_3$, 400 MHz) of **19**





19

^{13}C NMR ($CDCl_3$, 101 MHz) of **19**