Electronic Supplementary Information

Non-classical *C*-saccharides linkage of dehydroalanine: synthesis of *C*-glycoamino acids and *C*-glycopeptides

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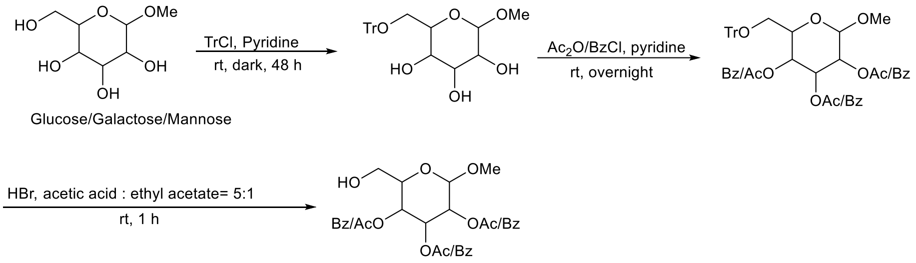
1. General information

All commercially available reagents were used without further purification unless otherwise stated. All solvents were purified and dried according to standard methods prior to use. ^{1}H NMR, ^{19}F NMR, and ^{13}C NMR spectra were recorded on a Bruker 300 instrument spectrometer in $CDCl_3$ unless otherwise noted. Data for ^{1}H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, and brs = broad signal, and coupling constant(s) in Hz integration). Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). Reactions were monitored by thin layer chromatography (TLC) and column chromatography purifications were carried out using silica gel. Melting points were measured on a SCW X-4 and values are uncorrected. Emission intensities were recorded by using a PerkinElmer spectrofluorophotometer LS 55. All new compounds were further characterized by high resolution mass spectra (HRMS, ESI source). Semi preparative HPLC was performed on Hanbon Sci.& Tech HPLC analysis were performed on Waters e2695. HPLC was performed on Waters 1525 Binary HPLC, using CHIRALCEL IA or IC chiral column, eluted with a mixture of hexane and ethanol.

2. The synthesis of substrates

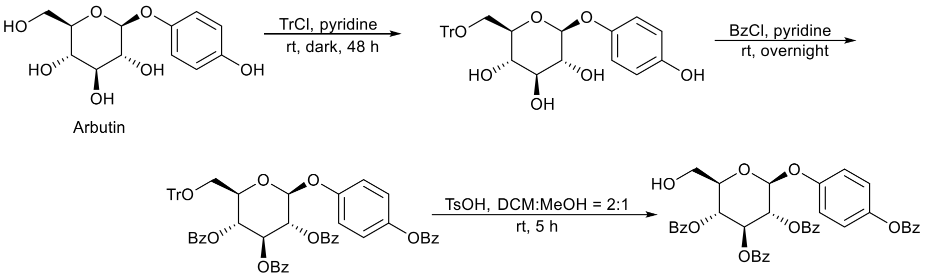
2.1 The synthesis of alcohol[1-4]



Scheme S1 General procedure of Ac/Bz protected hexose derivatives.

The solution of methyl-α-*D*-glucopyranoside/methyl-α-*D*-mannopryanoside/methyl-α-*D*-galactopryanoside (30 mmol, 1.0 equiv), trityl chloride (8.49 g, 1.1 equiv) in pyridine (70 ml) was stirred 48 h at room temperature under nitrogen in the dark. After completion of reaction through TLC determination, benzoyl chloride (15.7mL, 4.5 equiv) or acetic anhydride (11.3mL, 4.0 equiv) was added and stirred at room temperature for 12 h. After completion of reaction, the pyridine was removed under reduced pressure, and extracted by ethyl acetate (100 mL × 3), washed by 2 N HCl (100 mL × 3). The combined organic layers were dried with Na_2SO_4, filtered and evaporated under reduced pressure.

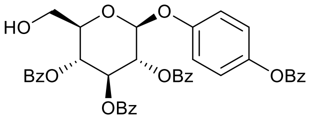
The crude residue from above step was dissolved in acetic acid (50 mL) and ethyl acetate (10 mL), then hydrobromic acid was added dropwise, the white precipitate was formed immediately. The mixture was stirred at room temperature until TLC indicated complete conversion. The solution was removed under reduced pressure, and the residue was diluted by ethyl acetate (100 mL), then sat. Na_2CO_3 was added to adjust pH above 7, and the solution was extracted by ethyl acetate (100 mL × 3), washed by brine (75 mL × 3), dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The residue was purified by chromatography on a silica gel column to give the alcohol (Petroleum ether : ethyl acetate = 3:1). The Characterization data of Ac/Bz protected hexose derivatives were consistent with those previously reported[10].



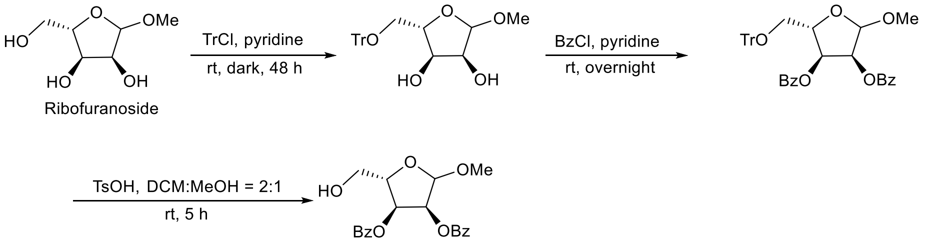
Scheme S2 General procedure of Bz protected arbutin.

The solution of arbutin (30 mmol, 1.0 equiv), trityl chloride (8.49g, 1.1 equiv) in pyridine (70 ml) was stirred 48 h at room temperature under nitrogen in the dark. After completion of reaction through TLC determination, benzoyl chloride (21 mL, 6.0 equiv) was added and stirred at room temperature for 12 h. After completion of reaction, the pyridine was removed under reduced pressure, and extracted by ethyl acetate (100 mL × 3), washed by 2 N HCl (100 mL × 3). The combined organic layers were dried with Na_2SO_4, filtered and evaporated under reduced pressure.

The crude residue from above step was dissolved in DCM:MeOH = 2:1 (30 mL) followed by addition of TsOH (2.58 g, 0.5 equiv). The mixture was stirred at room temperature for 5 h. The solution was quenched by sat. Na_2CO_3, and the solution was extracted by DCM (70 mL × 3), washed by brine (60 mL × 3), dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The residue was purified by chromatography on a silica gel column to give the alcohol (Petroleum ether : ethyl acetate = 3:1).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 2H), 7.97 (d, *J* = 7.8 Hz, 4H), 7.90-7.87 (m, 2H), 7.49-7.24 (m, 12H), 7.13-7.06 (m, 4H), 6.07 (t, *J* = 9.0 Hz, 1H), 5.83 (t, *J* = 9.0 Hz, 1H), 5.62 (t, *J* = 9.0 Hz, 1H), 5.45 (d, *J* = 6.0 Hz, 1H), 3.99-3.76 (m, 3H), 3.05 (br, 1H). **HRMS (ESI)** $C_{40}H_{32}NaO_{11}^+$ [M+Na] calcd: 711.1842, found: 711.1839.

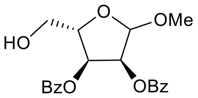


Scheme S3 General procedure of Bz protected ribofuranoside.

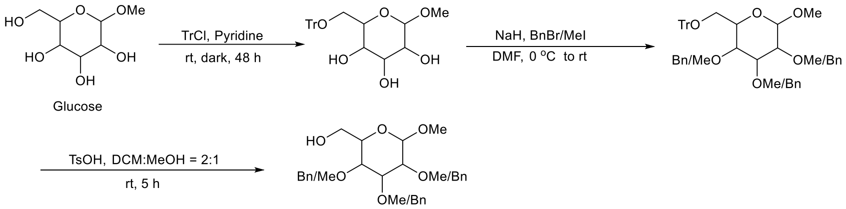
The solution of Methyl-*D*-ribofuranoside (α and β mixture, 30 mmol, 1.0 equiv), trityl chloride (8.49 g, 1.1 equiv) in pyridine (70 ml) was stirred 48 h at room temperature under nitrogen in the dark. After completion of reaction through TLC determination, benzoyl chloride (10.5 mL, 3.0 equiv) was added and stirred at room temperature for 12 h. After completion of reaction, the pyridine was removed under reduced pressure, and extracted by ethyl acetate (100 mL × 3), washed by 2 N HCl

(100 mL × 3). The combined organic layers were dried with Na_2SO_4, filtered and evaporated under reduced pressure.

The crude residue from above step was dissolved in DCM:MeOH = 2:1 (30 mL) followed by addition of TsOH (2.58 g, 0.5 equiv). The mixture was stirred at room temperature for 5 h. The solution was quenched by sat. Na_2CO_3, and the solution was extracted by DCM (70 mL × 3), washed by brine (60 mL × 3), dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The residue was purified by chromatography on a silica gel column to give the alcohol (Petroleum ether : ethyl acetate = 3:1).



^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.91-7.88 (m, 2H), 7.60-7.49 (m, 2H), 7.44-7.39 (m, 2H), 7.35-7.30 (m, 2H), 5.73 (t, *J* = 6.0 Hz, 1H), 5.63-5.62 (m, 1H), 5.16 (s, 1H), 3.96-3.92 (m, 1H), 3.85-3.77 (m, 1H), 3.52(s, 3H), 3.47 (s, 1H), 2.55-2.51 (m, 1H). **HRMS (ESI)** $C_{20}H_{20}NaO_7^+$ [M+Na] calcd: 395.1107, found: 395.1103.



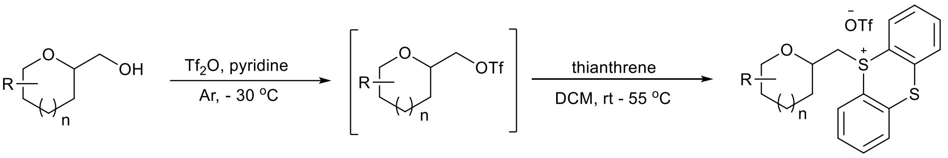
Scheme S4 General procedure of Me/Bn protected hexose derivatives.

To a solution of methyl-α-*D*-glucopyranoside or methyl-α-*D*-mannopryanoside (30 mmol, 1.0 equiv) in pyridine (70 mL) was added trityl chloride (8.49 g, 1.1 equiv) and the reaction mixture was stirred at room temperature for 48 h in the dark. The solvent was removed in *vacuo*. The residue was extracted by ethyl acetate (100 mL × 3), and washed by brine (75 mL × 3). Organic phase was dried by Na_2SO_4 and concentrated to afford desired product.

The obtained compound from above step was dissolved in DMF (150 mL) and cooled to 0 °C. Sodium hydride (9.6 g, 60% in mineral oil, 8.0 equiv) was added portion-wise under Ar atmosphere. After 1 h, BnBr/MeI (6.0 equiv) was added dropwise under Ar atmosphere at 0 °C. The mixture was stirred overnight and allowed to warm to room temperature. The reaction was quenched with sat. AcOH (~10 mL) / NH_4Cl (~20 mL). The solvents were evaporated in *vacuo* and the residue was dissolved in Et_2O (70 mL), and then washed with water (70 mL). The aqueous phase was extracted with Et_2O (70 mL × 2), the combined organic phases were washed with water (70 mL × 2), dried over Na_2SO_4, filtered, and concentrated in *vacuo* to obtain crude product as an oil or foam. Purification by flash column chromatography (Petroleum ether : ethyl acetate = 10:1) yielded product as a white foam.

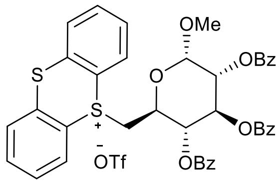
The crude residue from above step was dissolved in DCM:MeOH = 2:1 (30 mL) followed by addition of TsOH (2.58 g, 0.5 equiv). The mixture was stirred at room temperature for 5 h. The solution was quenched by sat. Na_2CO_3, and the solution was extracted by DCM (70 mL × 3), washed by brine (60 mL × 3), dried by Na_2SO_4, combined the organic phase and concentrated with reduced pressure. The residue was purified by chromatography on a silica gel column to give the alcohol (Petroleum ether : ethyl acetate = 3:1). The Characterization data of Me/Bn protected hexose derivatives were consistent with those previously reported[11].

2.2 The synthesis of glycosyl thianthrenium salt[5]

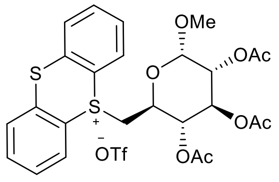


A flame-dried 100 mL flask was placed under an atmosphere of nitrogen and charged with a stir bar and alcohol (5.0 mmol, 1.0 equiv). The alcohol was dissolved in CH_2Cl_2 (20.0 mL) and cooled to -30 °C before adding pyridine (0.48 mL, 6.0 mmol, 1.2 equiv). While stirring, triflic anhydride (1.0 mL, 6.0 mmol, 1.2 equiv) was added dropwise, and then the reaction mixture stirred for 3 h while remaining at -5 °C. While the flask was still in a -5 °C bath, 0.5 M H_2SO_4 (30 mL) was added. The flask was removed from the cold bath, and the mixture was transferred to a separatory funnel and extracted with 3 × 20 mL of CH_2Cl_2. The organic layers were combined and washed 1 × 50 mL of distilled water. The collected organic layers were then dried over $MgSO_4$, then filtered and concentrated to a 10 mL liquid under vacuum (without heating), which was used directly in the next step.

Flame-dried 25 mL Schlenk tube was added thianthrene (1.08 g, 5.0 mmol), then the above liquid was added. The mixture was stired at 55 °C for 5-20 h. The mixture was carefully condensed under reduced pressure at 25 ºC and subjected to silica gel chromatography with DCM/MeOH.

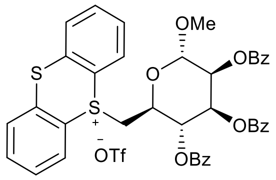


5-(((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzoyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 2.3g, yield: 55%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.93-7.87 (m, 6H), 7.82-7.73 (m, 5H), 7.70-7.66 (m, 3H), 7.48 (br, 2H), 7.34-7.25 (m, 7H), 6.12 (t, *J* = 9.6 Hz, 1H), 5.36-5.30 (m, 1H), 5.19-5.14 (m, 2H), 4.86 (br, 1H), 4.11-4.09 (m, 1H), 3.95-3.90(m, 1H), 3.64 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.93, 165.76, 165.42, 136.65, 136.08, 135.06, 134.98, 134.43, 134.36, 134.14, 133.97, 133.63, 133.30, 130.65, 130.38, 130.08, 129.87, 129.74, 129.59, 128.85, 128.61, 128.53, 128.49, 128.33, 127.84, 119.33,118.77, 97.51, 71.49, 69.29, 65.85, 60.39, 57.15, 43.78. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.05. **HRMS (ESI)** $C_{40}H_{33}O_8S_2^+$ [M-OTf] calcd: 705.1611, found: 705.1630.

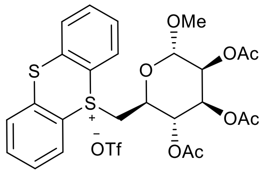


5-(((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-triacetoxy-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.3g, yield: 40%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ

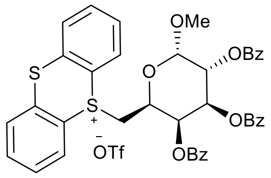
8.51 (d, *J* = 7.5 Hz, 1H), 8.16 (d, *J* = 7.8 Hz, 1H), 7.90-7.84 (m, 2H), 7.79-7.66 (m, 4H), 5.45 (t, *J* = 9.3 Hz, 1H), 4.77-4.76 (m, 1H), 4.68-4.64 (m, 2H), 4.23-4.15 (m, 2H), 3.94-3.89 (m, 1H), 3.56(s, 3H), 2.06 (s, 3H), 2.02 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 170.81, 170.26, 169.49, 136.78, 136.04, 135.05, 134.35, 134.29, 134.14, 130.90, 130.62, 130.29, 129.63, 119.40, 118.88, 97.11, 70.94, 68.73, 68.14, 65.70, 56.94, 43.53, 38.71, 30.34, 28.91. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.19. **HRMS (ESI)** $C_{25}H_{27}O_8S_2^+$ [M-OTf] calcd: 519.1142, found: 519.1153.



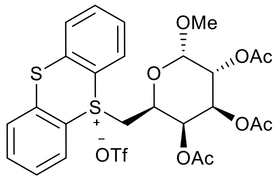
5-(((2*S*,3*S*,4*S*,5*S*,6*S*)-3,4,5-tris(benzoyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 2.1g, yield: 50%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.1 Hz, 12.6 Hz, 2H), 8.00 (d, *J* = 7.5 Hz, 2H), 7.90 (d, *J* = 7.5 Hz, 2H), 7.84-7.75 (m, 4H), 7.72-7.64 (m, 3H), 7.62-7.48 (m, 5H), 7.42-7.32 (m, 3H), 7.26-7.21 (m, 2H), 5.86-5.81 (m, 1H), 5.66-5.60 (m, 2H), 4.92 (s, 1H), 4.81-4.74 (m, 1H), 4.24-4.12 (m, 1H), 4.10-4.05 (m, 1H), 3.68 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 165.19, 165.36, 165.10, 136.36, 136.18, 134.73, 134.60, 134.50, 134.24, 134.06, 133.94, 133.43, 130.57, 130.50, 130.01, 129.94, 129.86, 129.74, 129.60, 128.97, 128.83, 128.71, 128.60, 128.37, 127.92, 119.03, 118.31, 98.97, 70.18, 69.11, 68.93, 66.56, 56.97, 44.00. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.04. **HRMS (ESI)** $C_{40}H_{33}O_8S_2^+$ [M-OTf] calcd: 705.1611, found: 705.1596.



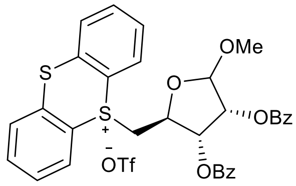
5-(((2*S*,3*S*,4*S*,5*S*,6*S*)-3,4,5-triacetoxy-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.4g, yield: 42%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 7.90-7.85 (m, 2H), 7.76-7.67 (m, 4H), 5.34-5.23 (m, 2H), 5.04 (t, *J* = 9.3 Hz, 1H), 4.54 (s, 1H), 4.44 (br, 1H), 4.07 (s, 2H), 3.50(s, 3H), 2.13 (s, 3H), 2.05 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 171.19, 169.67, 169.48, 136.68, 136.18, 135.03, 134.39, 134.26, 134.10, 130.58, 130.34, 129.96, 129.70, 119.41, 118.87, 98.87, 71.24, 68.83, 67.91, 66.76, 56.67, 46.85, 44.06, 29.69, 29.32. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.27. **HRMS (ESI)** $C_{25}H_{27}O_8S_2^+$ [M-OTf] calcd: 519.1142, found: 519.1148.



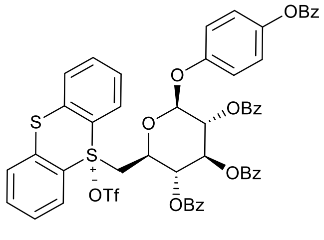
5-(((2*S*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzoyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 2.0g, yield: 48%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.46 (d, *J* = 6.9 Hz, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.84 (t, *J* = 7.8 Hz, 4H), 7.69-7.67 (m, 2H), 7.61-7.57 (m, 6H), 7.42-7.36 (m, 3H), 7.30-7.25 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 2H), 5.84 (dd, *J* = 3.0 Hz, 7.8 Hz, 1H), 5.66 (s, 1H), 5.38 (dd, *J* = 3.3 Hz, 7.5 Hz, 1H), 5.11-5.10 (m, 1H), 5.02-4.99 (m, 1H), 4.18 (t, *J* = 11.4 Hz, 1H), 3.73 (d, *J* = 2.4 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 164.96, 164.40, 164.04, 135.05, 134.78, 133.90, 133.40, 133.31, 133.04, 132.55, 132.23, 129.40, 129.33, 129.13, 128.84, 128.78, 128.52, 127.78, 127.67, 127.45, 127.37, 127.21, 126.67, 121.87, 118.42, 117.62, 117.24, 97.21, 69.16, 67.62, 66,48, 64.27, 56.46, 40.79. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.06. **HRMS (ESI)** $C_{40}H_{33}O_8S_2^+$ [M-OTf] calcd: 705.1611, found: 705.1597.



5-(((2*S*,3*R*,4*S*,5*R*,6*S*)-3,4,5-triacetoxy-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.3g, yield: 40%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.42 (d, *J* = 7.5 Hz, 1H), 8.23 (d, *J* = 7.5 Hz, 1H), 7.90-7.82 (m, 2H), 7.76-7.65 (m, 4H), 5.30-5.24 (m, 2H), 5.04 (t, *J* = 9.0 Hz, 1H), 4.46 (s, 1H), 4.43-4.40 (m, 1H), 4.06-4.07 (m, 2H), 3.49(s, 3H), 2.14 (s, 3H), 2.04 (s, 3H), 1.97 (s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 171.19, 169.67, 169.48, 136.68, 136.18, 135.03, 134.39, 134.26, 134.10, 130.58, 130.34, 129.96, 129.70, 119.41, 118.87, 98.87, 71.24, 68.83, 67.91, 66.76, 56.67, 46.85, 44.06, 29.69, 29.32. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.25. **HRMS (ESI)** $C_{25}H_{27}O_8S_2^+$ [M-OTf] calcd: 519.1142, found: 519.1149.

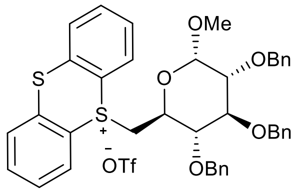


5-(((2*S*,3*S*,4*R*)-3,4-bis(benzoyloxy)-5-methoxytetrahydrofuran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.6g, yield: 45%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.52 (d, *J* = 7.5 Hz, 1H), 8.35 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.2 Hz, 2H), 7.88-7.78 (m, 4H), 7.75-7.55 (m, 5H),7.48-7.40 (m, 3H), 7.34-7.25 (m, 2H), 5.52-5.51 (m, 1H), 5.40-5.36 (m, 1H), 5.03-4.95 (m, 2H), 4.33 (t, *J* = 11.1 Hz, 1H), 4.09-4.05 (m, 1H), 3.03(s, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 171.17, 165.86, 165.27, 165.15, 136.36, 135.84, 135.17, 134.99, 134.55, 134.47, 133.75, 133.68, 130.22, 129.95, 129.90, 129.77, 128.69, 128.61, 128.40, 128.16, 122.94, 118.82, 118.69, 118.06, 107.18, 76.60, 74.94, 74.56, 60.39, 55.77, 53.54, 47.04. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.09. **HRMS (ESI)** $C_{32}H_{27}O_6S_2^+$ [M-OTf] calcd: 571.1244, found:571.1244.

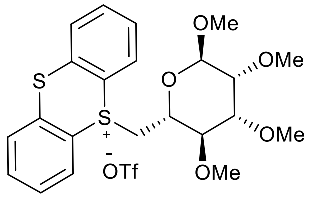


5-(((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzoyloxy)-6-(4-(benzoyloxy)phenoxy)tetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 2.2g, yield: 43%. **^{1}H NMR** (300

MHz, $CDCl_3$) δ. 8.44 (d, J = 8.1 Hz, 1H), 8.17 (d, J = 7.8 Hz, 2H), 7.93 (dd, J = 7.8 Hz, 10.8 Hz, 4H), 7.78 (q, J = 8.1 Hz, 4H), 7.66-7.57 (m, 3H), 7.52-7.47 (m, 5H), 7.42-7.23 (m, 13H), 6.08-5.97 (m, 2H), 5.70 (t, J= 8.4 Hz, 1H), 5.53-5.47 (m, 1H), 5.38-5.30 (m, 1H), 4.34-4.27 (m, 1H), 3.88-3.82 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 166.19, 165.68, 165.23, 165.10, 153.42, 146.24, 136.44, 136.15, 134.76, 134.52, 134.15, 134.07, 133.68, 133.52, 133.28, 130.37, 130.23, 130.16, 129.98, 129.86, 129.69, 128.66, 128.60, 128.46, 128.31, 127.72, 123.30, 120.05, 119.81, 116.79, 96.61, 71.95, 71.91, 71.10, 69.92, 46.28. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.06. **HRMS (ESI)** $C_{52}H_{39}O_{10}S_2^+$ [M-OTf] calcd: 887.1979, found: 887.1970.



5-(((2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.5g, yield: 37%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.31 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 8.1 Hz, 1H), 7.78-7.55 (m, 7H), 7.32-7.26 (m, 9H), 7.20-7.14 (m, 5H), 4.93 (d, J = 11.1 Hz, 1H), 4.81 (d, J = 11.4 Hz, 1H), 4.75-4.69 (m, 2H), 4.63-4.56 (m, 2H), 4.49 (d, J = 11.7 Hz, 1H), 3.87-3.79 (m, 2H), 3.61-3.55 (m, 2H), 3.49-3.39 (m, 4H), 3.23 (t, J = 9.0 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ. 138.27, 137.73, 137.47, 135.85, 135.64, 135.01, 134.82, 134.41, 134.19, 130.23, 129.95, 129.86, 128.59, 128.57, 128.54, 128.43, 128.13, 127.89. 90.79, 80.90, 79.71, 79.39, 75.68, 74.91, 73.53, 68.16, 65.79, 57.01. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.12. **HRMS (ESI)** $C_{40}H_{39}O_5S_2^+$ [M-OTf] calcd: 663.2233, found: 663.2215.

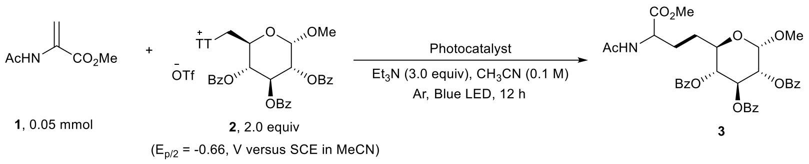


5-(((2*R*,3*R*,4*R*,5*R*,6*R*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)methyl)-5H-thianthren-5-ium trifluoromethanesulfonate. 1.2g, yield: 41%. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.41 (d, J = 7.8 Hz, 1H), 8.24 (d, J = 7.5 Hz, 1H), 7.89-7.87 (m, 2H), 7.80-7.67 (m, 4H), 4.77 (s, 1H), 4.07-4.03 (m, 2H), 3.81-3.74 (m, 1H), 3.54-3.40(m, 14H), 3.04(t, J = 9.6 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ.136.14, 135.92, 134.74, 134.63, 130.37, 130.33, 130.10, 129.97, 128.68, 127.71, 118.30, 117.87, 98.68, 80.65, 77.89, 76.33, 66.92, 60.56, 58.93, 57.41, 56.37, 43.17. **^{19}F NMR** (282 MHz, $CDCl_3$) δ -78.15. **HRMS (ESI)** $C_{12}H_{27}O_5S_2^+$ [M-OTf] calcd: 435.1294, found: 435.1290.

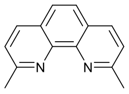
3. General procedures

3.1 Optimization of reaction conditions.

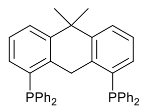
Table S1 Photocatalyst screening



Entry	Photocatalyst	$E_{1/2}$(PC/PC$^-$) (V vs SCE)	Isolated Yield (%)
1	Ir[dF(CF$_3$)ppy]$_2$(5,5'-CF$_3$bpy)PF$_6$ (1 mol%)	-0.69 V	30%
2	Ir[dF(CF$_3$)ppy]$_2$(dtbpy)PF$_6$ (1 mol%)	-1.37 V	0
3	Ir(ppy)$_2$(dtbbpy)PF$_6$ (1 mol%)	-1.51 V	5%
4	CzIPN (5 mol%)	-1.16 V	trace
5	Eosin Y (10 mol%)	-1.11 V	8%
6	Ru(bpy)$_3$Cl$_2$·6H$_2$O (1 mol%)	-1.33 V	7%
7	Cu(OAc)$_2$ (5 mol%) + **L1** (6 mol%) + **L2** (6 mol%)	-1.86 V	0



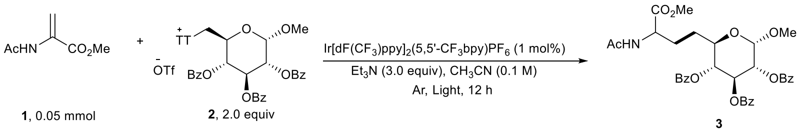
L1, dmp



L2, xantphos

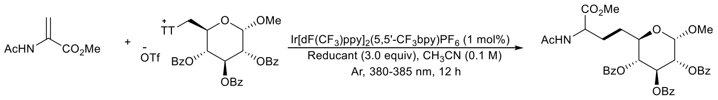
Note: In this study, we used several types of photocatalysts with different reduction potential. However, only Ir[dF(CF$_3$)ppy]$_2$(5,5'-CF$_3$bpy)PF$_6$ gave acceptable yield. The results indicates that the generation of strongly reducing species is not necessary for the outcome of the reaction.

Table S2 Light source screening



Entry	Light	Isolated Yield (%)
1	White LED	30%
2	Green LED	trace
3	420-430 nm	35%
4	410-420 nm	30%
5	400-410 nm	32%
6	395-400 nm	35%
7	380-385 nm	37%

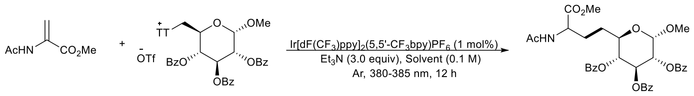
Table S3 Reductant screening



1, 0.05 mmol; **2**, 2.0 equiv; **3**

Entry	Reducant	Isolated Yield (%)	Entry	Reducant	Isolated Yield (%)
1	DIPEA	22%	6	TMG	12%
2	TMEDA	16%	7	Morpholine	16%
3	Et_2NH	33%	8	PPh_3	11%
4	HMPA	7%	9	Hantzsch ester	29%
5	TEOA	24%			

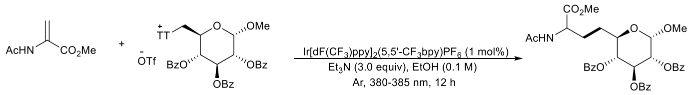
Table S4 Solvent screening



1, 0.05 mmol; **2**, 2.0 equiv; **3**

Entry	Solvent	Isolated Yield (%)	Entry	Solvent	Isolated Yield (%)
1	Acetone	0	11	MeOH	47%
2	THF	26%	12	EA	11%
3	Toluene	9%	13	1,3-Dioxolane	0
4	DMF	0	14	Et_2O	0
5	DMAc	0	15	$HFIPH_2$	0
6	DCM	0	16	EtOH	51%
7	1,4-Dioxane	trace	17	CF_3CH_2OH	20%
8	DMSO	0	18	i-PrOH	15%
9	CH_3Cl	trace	19	NMP	0
10	DCE	7%	20	DMPU	0

Table S5 Screening the loading of glycosyl thianthrenium salt

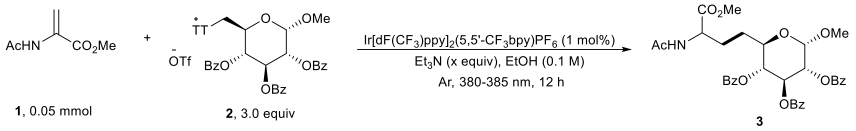


1, 0.05 mmol; **2**, x equiv; **3**

Entry	x (equiv)	Isolated Yield (%)	Entry	x (equiv)	Isolated Yield (%)
1	1.2 equiv	36%	5	3.0 equiv	60%
2	1.5 equiv	38%	6	4.0 equiv	52%
3	2.0 equiv	50%	7	5.0 equiv	50%
4	2.5 equiv	46%			

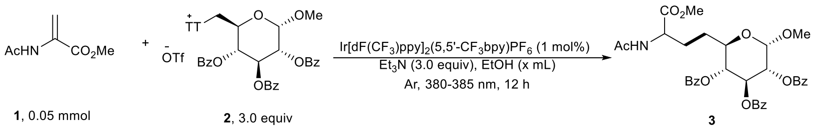
Note: The glycosyl thianthrenium salt was almost completely consumed under standard conditions with methyl 2,3,4-tri-O-benzoyl-6-deoxy-α-D-glucopyranoside formed as the main by-product (30-40% isolated yield based **2**). When the concentration of substrate was too high (4 or 5 equiv of glycosyl thianthrenium salt was used), the photocatalyst in the reaction mixture might not be able to effectively absorb the light energy, which would cause the decease of catalytic efficiency and diminish the yield of desire product.

Table S6 Screening the loading of Et_3N



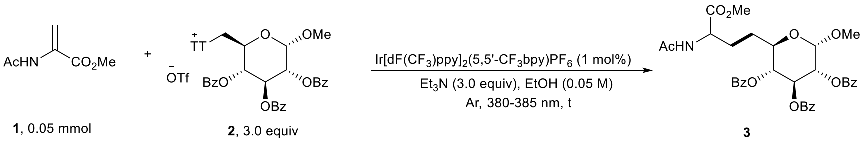
Entry	x (equiv)	Isolated Yield (%)
1	1.0 equiv	28%
2	2.0 equiv	40%
3	4.0 equiv	46%
4	5.0 equiv	41%

Table S7 Screening the concentration of reaction mixtures



Entry	x (mL)	Isolated Yield (%)
1	0.25 mL	47%
2	0.75 mL	63%
3	1.0 mL	70%
4	1.5 mL	52%

Table S8 Influences of reaction time



Entry	t (h)	Isolated Yield (%)
1	3.0 h	29%
2	6.0 h	50%
3	9.0 h	62%
4	15.0 h	81%
5	18.0 h	76%
6	24.0 h	78%

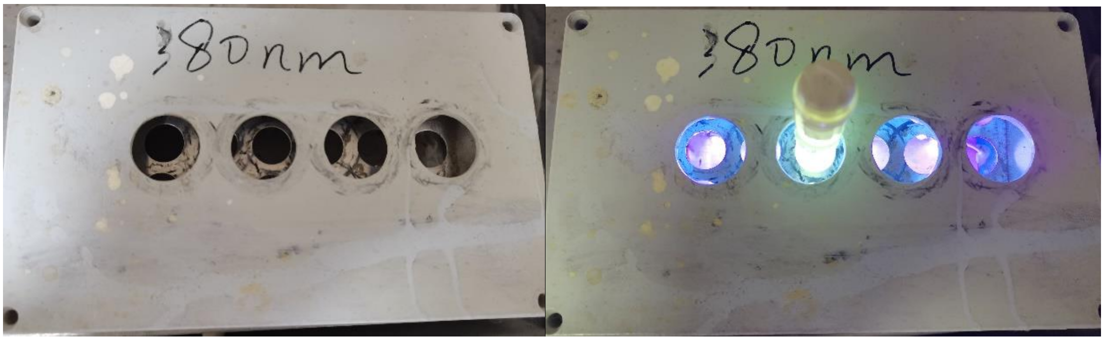
3.2 General procedure for the synthesis of 3-28

To an oven-dried 10 mL quartz test tube with a stirring bar was added alkene (0.2 mmol), glycosyl thianthrenium salt (0.6 mmol, 3.0 equiv), and $Ir[dF(CF_3)ppy]_2(5,5'\text{-}CF_3bpy)PF_6$ (2.3 mg, 1.0 mol%). Then, air was withdrawn and backfilled with Ar (three times). EtOH (4 mL) and Et_3N (60.7 mg, 0.6 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm), where it was irradiated for 15 h. Then, the reaction was concentrated in *vacuo*, and purified by column chromatography (hexane/ethyl acetate) to afford the product (**3-28**).

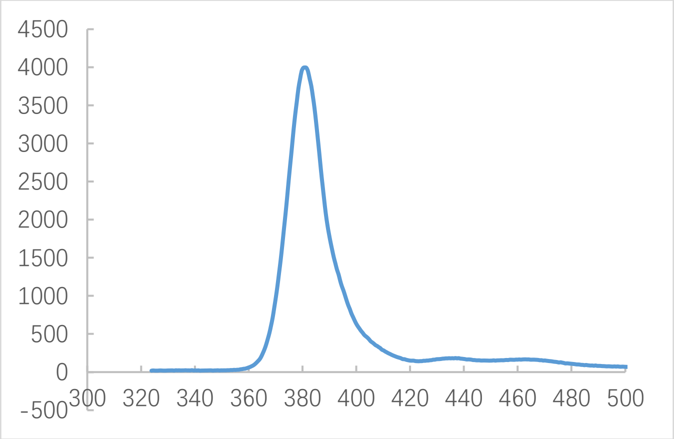
3.3 General procedure for the synthesis of 29-32

To an oven-dried 10 mL quartz test tube with a stirring bar was added hexapeptide (0.05 mmol, 36.8 mg), glycosyl thianthrenium salt (0.15 mmol, 3.0 equiv), and Ir[dF(CF$_3$)ppy]$_2$(5,5'-CF$_3$bpy)PF$_6$ (0.6 mg, 1.0 mol%). Then, air was withdrawn and backfilled with Ar (three times). EtOH (1 mL) and Et$_3$N (15.2 mg, 0.15 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm), where it was irradiated for 15 h. Then, the reaction was concentrated in *vacuo*, the resulted thianthrene was removed by column chromatography (DCM/MeOH) and the product was isolated by Semi preparative HPLC purification (**29-32**).

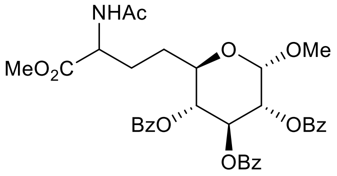
Picture of the reaction photo set-up (380-385 nm)



We also measured the wavelength of the LED light by ourselves (recorded on an AVANTES® AvaSpec-ULS2048 spectrometer instrument). The result was shown as follow:



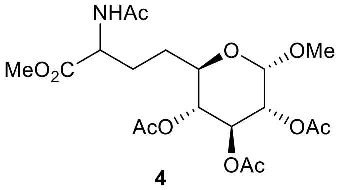
4. Characterization of products



3

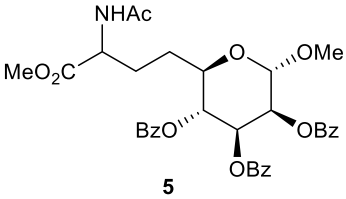
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 102.5 mg, yield: 81%. d. r. = 1:1. White solid, M. p. 80-82 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.99-7.95 (m, 4H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.52-7.48 (m, 2H), 7.43-7.34 (m, 5H), 7.29-7.27 (m, 2H), 6.24-6.08 (m, 2H), 5.38 (t, *J* = 9.6 Hz, 1H), 5.24-5.17 (m, 2H), 4.65-4.49

(m, 1H), 4.13-4.03 (m, 1H), 3.71(s, 1.5H), 3.61 (s, 1.5H), 3.45 (s, 3H), 2.18-2.07 (m, 1H), 1.98(s, 1.5H), 1.90-1.57 (m, 4.5H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 172.85, 172.62, 170.12, 169.83, 165.90, 165.83, 165.72, 133.61, 133.40, 133.11, 129.92, 129.85,129.62, 129.20, 129.01, 128.81, 128.53, 128.43, 128.28, 96.86, 77.30, 72.23, 71.89, 70.29, 68.41, 68.01, 55.65, 55.59, 52.48, 52.34, 51.79, 51.69, 27.24, 26.48, 23.13, 23.00. **HRMS (ESI)** $C_{34}H_{35}NNaO_{11}$ $[M+Na]^+$ calcd: 656.2102, found: 656.2092.



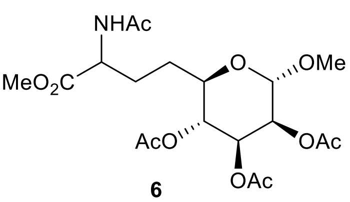
4

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl triacetate: 74.2 mg, yield: 83%. d. r. = 1.2:1. White solid, M. p. 60-63 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 6.17-6.08 (m,1H), 5.47-5.39 (m, 1H), 4.87-4.80 (m, 3H), 4.63-4.54 (m, 1H), 3.87-3.75 (m, 4H), 3.39 (s, 3H), 2.07-2.00 (m, 12H), 1.94-1.40 (m, 4H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ172.74, 172.62, 170.24, 170.21, 170.06,169.99, 169.88, 169.78, 96.47, 77.28, 71.92, 71.75, 71.03, 70.98, 70.02, 69.95, 67.91, 67.63, 55.37, 55.34, 52.49, 52.43, 51.80, 51.72, 28.06, 27.57, 26.51, 23.15, 23.08, 20.74, 20.60. **HRMS (ESI)** $C_{19}H_{29}NNaO_{11}$ $[M+Na]^+$ calcd: 470.1633, found: 470.1643.



5

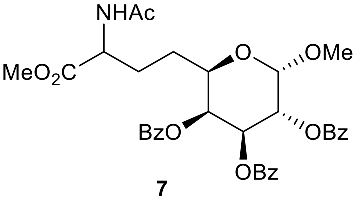
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 91.2 mg, yield: 72%. d. r. = 1.2:1. White solid, M. p. 65-68 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 8.09 (d, *J* = 7.5 Hz, 2H), 7.97 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 7.5 Hz, 2H), 7.65-7.60 (m, 1H), 7.55-7.48 (m, 3H), 7.44-7.37 (m, 3H), 7.27-7.23(m, 2H), 6.20-6.12 (m, 1H), 5.87-5.81 (m, 1H), 5.74-5.65(m, 2H), 4.92 (s, 1H), 4.67-4.59(m, 1H), 4.10-4.06(m, 1H), 3.69 (s, 1.35H), 3.61 (s, 1.65H), 3.50 (s, 3H), 2.20-1.63(m, 7H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ172.82, 172.57, 170.01, 169.73, 165.96, 165.75, 165.44, 165.42, 165.34, 165.30, 133.48, 133.43, 133.07, 129.78, 129.69, 129.65, 129.59, 129.39, 129.24, 129.01, 128.93, 128.83, 128.56, 128.45, 128.42, 128.19, 98.35, 77.21, 70.52, 69.88, 69.83, 69.52, 69.38, 68.94, 55.42, 55.38, 52.34, 52.23, 51.70, 51.58, 27.93, 27.25, 26.70, 26.61, 23.02, 22.91. **HRMS (ESI)** $C_{34}H_{35}NNaO_{11}$ $[M+Na]^+$ calcd: 656.2102, found: 656.2107.



6

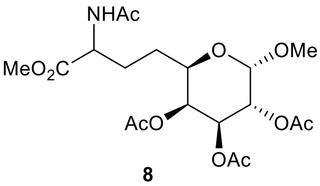
(2*R*,3*R*,4*S*,5*S*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-

3,4,5-triyl triacetate : 69.7 mg, yield: 78%, d. r. = 1:1. Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.20 (d, *J* = 7.5 Hz, 0.5H), 6.14 (d, *J* = 7.5 Hz, 0.5H), 5.32-5.23 (m, 2H), 5.12-5.05 (m, 1H), 4.64-4.58 (m, 2H), 3.76 (brs, 4H), 3.38 (s, 3H), 2.15 (s, 3H), 2.04 (d, *J* = 6.0 Hz, 6H), 1.99 (s, 3H), 1.93-1.77 (m, 2H), 1.75-1.49 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.74, 172.57,170.15, 169.94, 169.70, 98.27, 77.20, 69.50, 69.19, 69.02, 68.93, 68.80, 55.14, 52.30, 51.79, 51.64, 28.08, 27.52, 26.63, 23.05, 22.97, 20.81, 20.71, 20.59. **HRMS (ESI)** $C_{19}H_{29}NNaO_{11}$ $[M+Na]^+$ calcd: 470.1633, found: 470.1643.



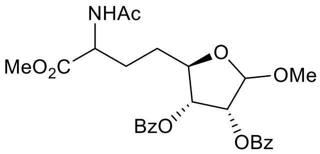
7

(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 86.1 mg, yield: 68%. d. r. = 1:1. White solid, M. p. 70-73 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.2 Hz, 2H), 7.98 (d, *J* = 7.5 Hz, 2H), 7.78 (d, *J* = 7.8 Hz, 2H), 7.65-7.60 (m, 1H), 7.52-7.47 (m, 3H), 7.45-7.35 (m, 3H), 7.24-7.21 (m ,2H), 6.02 (t, *J* = 7.8 Hz, 1H), 5.92 (d, *J* = 10.8 Hz, 1H), 5.78(s, 1H), 5.63 (d, *J* = 10.5 Hz, 1H), 5.24 (s, 1H), 4.67-4.61 (m, 1H), 4.21-4.14 (m, 1H), 3.68 (s, 1.5H), 3.64 (s, 1.5H), 3.46 (s, 3H), 2.13-1.94 (m, 4H), 1.77-1.48 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.53, 172.48, 169.89, 166.01, 165.97, 165.86, 165.77, 165.46, 165.39 133.50, 133.41, 133.24, 132.99, 129.73, 129.69, 129.57, 129.49, 129.13, 129.06, 128.55, 128.51, 128.29, 128.12, 97.38, 77.20, 71.09, 70.70, 69.30, 69.23, 68.53, 68.49, 68.13, 67.78, 55.61, 55.56, 52.31, 52.28, 51.64, 51.48, 28.38, 28.33, 26.02, 25.93, 22.90. **HRMS (ESI)** $C_{34}H_{35}NNaO_{11}$ $[M+Na]^+$ calcd: 656.2102, found: 656.2095.



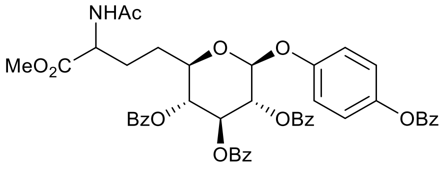
8

(2*R*,3*S*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl triacetate: 62.6 mg, yield: 70%. d. r. = 1:1. Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 6.16 (d, *J* = 7.5 Hz, 0.45H), 6.11 (d, *J* = 7.5 Hz, 0.42H), 5.47-5.40 (m, 1H), 4.87-4.80 (m, 3H), 4.61-4.57 (m, 1H), 3.75 (brs, 4H), 3.39 (s, 3H), 2.22-2.12 (m, 1H), 2.07-2.00 (m, 12H), 1.94-1.42 (m, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.69, 172.56, 170.18, 170.15, 169.99, 169.93, 169.82, 169.74, 96.45, 71.89, 71.71, 71.00, 70.95, 69.99, 69.92, 67.87, 67.60, 55.33, 52.43, 52.37, 51.77, 51.69, 28.01, 27.52, 26.49, 23.09, 23.02, 20.67, 20.62. **HRMS (ESI)** $C_{19}H_{30}NO_{11}$ $[M+H]^+$ calcd: 448.1813, found: 448.1817.



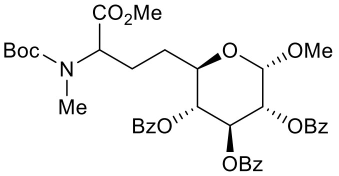
9

(2*R*,3*R*,4*R*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-5-methoxytetrahydrofuran-3,4-diyl dibenzoate: 62.9 mg, yield: 63%. d. r. = 1:1:1:1. Yellow oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00-7.87 (m, 4H), 7.57-7.24 (m, 6H), 6.38-6.16 (m, 1H), 5.81-5.80 (m, 0.5H), 5.57-5.50 (m ,1H), 5.39-5.10 (m, 1.5H), 4.69-4.62 (m, 1H), 4.40-4.28 (m, 1H), 3.76 (s, 0.7H), 3.71 (s, 0.8H), 3.66(s, 0.7H), 3,61 (s, 0.8H), 3.45 (s, 3H), 2.12-1.70 (m, 7H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.66, 169.88, 165.41, 165.20, 165.10, 133.34, 133.24, 129.79, 129.67, 129.60, 129.16, 129.08, 129.01, 128.37, 128.27, 128.17, 106.24, 105.72, 105.65, 80.58, 75.64, 75.01, 74.72, 72.74, 72.69, 71.40, 55.48, 55.38, 55.30, 52.30, 52.23, 52.19, 51.83, 51.73, 30.31, 28.78, 28.39, 25.43, 23.01, 22.90. **HRMS (ESI)** $C_{26}H_{29}NNaO_9$ $[M+Na]^+$ calcd: 522.1735, found: 522.1737.



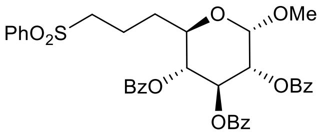
10

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-4-oxobutyl)-6-(4-(benzoyloxy)phenoxy)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 122.2 mg, yield: 75%. d. r. = 1.3:1. White solid, M. p. 85-87 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.18 (d, J = 7.5 Hz, 2H), 7.96 (d, J = 7.2 Hz, 4H), 7.85 (d, J = 7.5 Hz, 2H), 7.63-7.60 (m, 1H), 7.53-7.46 (m, 4H), 7.41-7.35 (m, 5H), 7.31-7.29 (m ,2H), 7.09 (dd, J = 8.4 Hz, 15.6 Hz, 4H), 6.16 (dd, J = 7.2 Hz, 14.4 Hz, 1H), 5.98-5.91 (m, 1H), 5.76 (t, J = 8.7 Hz, 1H), 5.49 (t, J = 9.6 Hz, 1H), 5.38 (d, J = 7.8 Hz, 1H), 4.63-4.57 (m, 1H), 4.07-4.01 (m, 1H), 3.71 (s, 1.3H), 3.59 (s, 1.7H), 2.16-2.04 (m, 1H), 1.94-1.79 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.66, 172.43, 170.01, 169.73, 165.67, 165.53, 165.36, 165.24, 165.05 154.57, 154.50, 146.38, 133.58, 133.28, 133.19, 130.07, 129.73, 129.68, 129.31, 128.99, 128.72, 128.63, 128.52, 128.44, 128.36, 128.24, 122.68, 118.07, 117.93, 99.81, 77.20, 73.35, 72.98, 72.76, 71.87, 71.74, 52.46, 52.24, 51.53, 51.11, 27.76, 27.29, 26.99, 26.67, 22.94, 22.85. **HRMS (ESI)** $C_{46}H_{41}NNaO_{13}$ $[M+Na]^+$ calcd: 838.2470, found: 838.2453.



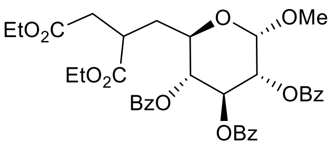
11

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((tert-butoxycarbonyl)(methyl)amino)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 110.0 mg, yield: 78%. d. r. = 2:1. White solid, M. p. 63-65 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00-7.93 (m, 4H), 7.86 (d, J = 7.5 Hz, 2H), 7.53-7.48 (m, 2H), 7.43-7.35 (m, 5H), 7.30-7.25 (m ,2H), 6.11 (t, J = 9.6 Hz, 1H), 5.41 (t, J = 9.6 Hz, 1H), 5.26-5.20 (m, 2H), 4.82-4.69 (m, 0.53H), 4.49-4.39 (m, 0.47H), 4.15-4.06 (m, 1H), 3.67 (s, 2H), 3.66 (s, 1H), 3.46 (s, 3H), 2.77 (d, J = 15.3 Hz, 3H), 2.36-2.26 (m, 0.57 H), 2.19-2.04 (m, 0.7H), 1.86-1.66 (m, 2.8H), 1.40-1.37 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.15, 171.92, 165.78, 165.70, 165.43, 165.32, 156.03, 155.38, 133.35, 133.28, 132.98, 129.83, 129.70, 129.53, 129.15, 128.96, 128.89, 128.83, 128.32, 128.17, 96.75, 80.31, 79.95, 77.20, 72.20, 70.33, 68.82, 67.96, 67.82, 59.51, 58.69, 57.74, 57.08, 55.47, 52.03, 51.98, 31.39, 30.78, 30.05, 28.17, 27.48, 25.04, 24.78, 23.60. **HRMS (ESI)** $C_{38}H_{43}NNaO_{12}$ $[M+Na]^+$ calcd: 728.2677, found: 728.2673.



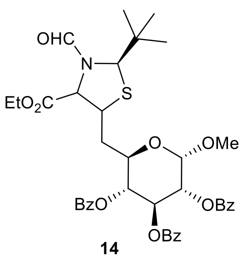
12

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-methoxy-6-(3-(phenylsulfonyl)propyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 98.7 mg, yield: 75%. White solid, M. p. 55-57 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96-7.82 (m, 8H), 7.66-7.63(m, 1H), 7.61-7.57 (m, 4H), 7.54-7.36 (m, 5H), 7.30-7.25 (m ,2H), 6.07 (t, *J* = 9.6 Hz, 1H), 5.30 (t, *J* = 9.6 Hz, 1H), 5.21-5.14 (m, 2H), 4.01-3.94 (m, 1H), 3.40 (s, 3H), 3.23-3.05 (m, 2H), 2.08-1.98 (m, 1H), 1.93-1.80 (m, 1H), 1.70-1.62 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.83, 165.71, 165.46, 138.96, 133.72, 133.47, 133.37, 133.06, 129.89, 129.81, 129.59, 129.27, 129.14, 128.97, 128.81, 128.44, 128.40, 128.24, 128.02, 96.80, 72.33, 72.13, 70.18, 68.57, 56.04, 55.57, 29.58, 18.88. **HRMS (ESI)** $C_{36}H_{34}NNaO_{10}S$ $[M+Na]^+$ calcd: 681.1765, found: 681.1769.



13

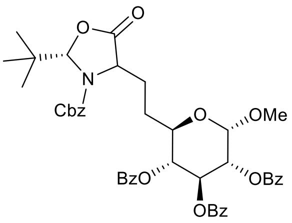
diethyl 2-(((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzoyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)methyl)succinate: 92.7 mg, yield: 70%. d. r. = 2.4:1. Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (t, *J* = 9.0 Hz, 4H), 7.85 (t, *J* = 7.8 Hz, 2H), 7.54-7.49(m, 2H), 7.44-7.35 (m, 5H), 7.31-7.28 (m, 2H), 6.09 (t, *J* = 9.9 Hz, 1H), 5.37 (t, *J* = 10.2Hz, 1H), 5.30-5.18 (m, 2H), 4.20-4.04 (m, 5H), 3.50 (s, 0.88H), 3.49 (s, 2.12H), 3.19-3.03 (m, 1H), 2.77-2.68 (m, 1H), 2.56-2.44 (m, 1H), 2.18-1.95 (m, 1H), 1.86-1.79 (m, 1H), 1.27-1.16 (m, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 174.30, 174.13, 171.55, 165.86, 165.78, 165.47, 133.44, 133.37, 133.08, 129.93, 129.83, 129.65, 129.25, 129.22, 129.04, 128.94, 128.43, 128.27, 97.03, 72.69, 72.15, 70.24, 67.44, 67.01, 60.91, 60.83, 60.69, 56.08, 38.54, 35.83, 33.07, 14.14. **HRMS (ESI)** $C_{36}H_{38}NaO_{12}$ $[M+Na]^+$ calcd: 685.2255, found: 685.2258.



14

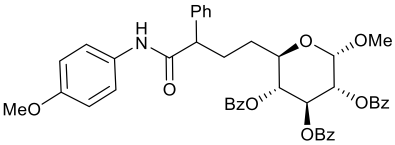
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(((2*R*)-2-(tert-butyl)-4-(ethoxycarbonyl)-3-formylthiazolidin-5-yl)methyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 124.6 mg, yield: 85%. r. r. = 5.9:1. White solid, M. p. 76-78 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.29 (s, 0.86H), 8.22 (s, 0.14H) 7.99-7.93(m, 4H), 7.87-7.79 (m, 2H), 7.52-7.49 (m, 2H), 7.44-7.36 (m, 5H),7.30-7.28 (m, 2H), 6.11 (t, *J* = 9.6 Hz, 0.86H), 5.86 (t, *J* = 9.3 Hz, 0.14H), 5.38 (t, *J* = 9.6 Hz, 1H), 5.29-5.21 (m, 2H), 4.73 (s, 1H), 4.44-4.37 (m, 1H), 4.32-4.21 (m, 2H), 4.18-4.08 (m, 2H), 3.55 (s, 3H), 2.54-2.36 (m, 1H), 1.89-1.80 (m, 1H), 1.31 (t, J = 7.5 Hz, 3H), 1.06 (s, 7.7H), 0.97 (s, 1.3H). **^{13}C NMR** (75 MHz,

$CDCl_3$) δ 169.01, 165.78, 165.68, 165.41, 162.22, 133.44, 133.34, 133.05, 129.87, 129.83, 129.57, 129.10, 128.94, 128.75, 128.42, 128.37, 128.22, 96.89, 77.20, 74.79, 72.34, 72.02, 70.10, 68.02, 66.51, 61.82, 55.84, 45.37, 38.53, 36.32, 26.34, 14.08. **HRMS (ESI)** $C_{39}H_{43}NNaO_{11}S$ $[M+Na]^+$ calcd: 756.2449, found: 756.2445.



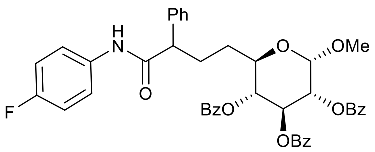
15

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(2-((2S)-3-((benzyloxy)carbonyl)-2-(tert-butyl)-5-oxooxazolidin-4-yl)ethyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 123 mg, yield: 79%. d. r. > 20:1. White solid, M. p. 75-78 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.00-7.93 (m, 4H), 7.87 (d, *J* = 7.8 Hz, 2H), 7.53-7.48 (m, 2H), 7.44-7.35 (m, 10H), 7.30-7.28 (m ,2H), 6.11 (t, *J* = 9.9 Hz, 1H), 5.53 (s, 1H), 5.40 (t, *J* = 9.9 Hz, 1H), 5.24-5.07 (m, 4H), 4.33-4.28 (m, 1H), 4.08-4.03 (m, 1H), 3.42 (s, 3H), 2.36-2.24 (m, 1H), 2.09-1.85 (m, 3H), 0.92 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.15, 165.78, 165.72, 165.38, 155.84, 135.14, 133.28, 132.99, 129.84, 129.72, 129.56, 129.18, 128.99, 128.64, 128.58, 128.41, 128.35, 128.19, 96.77, 96.24, 77.20, 72.17, 71.96, 70.31, 68.64, 68.25, 56.86, 55.48, 36.79, 28.62, 27.35, 24.79. **HRMS (ESI)** $C_{44}H_{45}NNaO_{12}$ $[M+Na]^+$ calcd: 802.2834, found: 802.2804.



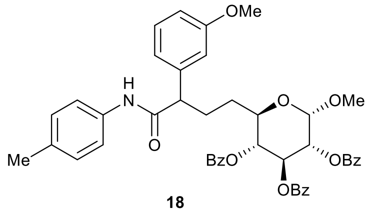
16

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-methoxy-6-(4-((4-methoxyphenyl)amino)-4-oxo-3-phenylbutyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 124.8 mg, yield: 84%. d. r. = 1:1. White solid, M. p. 65-67 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.97 (d, *J* = 7.5 Hz, 2H), 7.89-7.83(m, 4H), 7.49-7.42 (m, 2H), 7.38-7.12 (m, 15H), 6.77-6.73 (m ,2H), 6.13-6.05 (m, 1H), 5.39-5.30 (m, 1H), 5.24-5.18 (m, 2H), 4.11-3.98 (m, 1H), 3.73 (s, 3H), 3.54-3.44 (m, 4H), 2.58-2.54 (m, 0.5H), 2.33-2.18 (m, 1H), 1.93-1.86 (m, 0.5H), 1.68-1.52 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.10, 170.94, 165.81, 165.73, 165.53, 165.48, 156.29, 139.26, 138.99, 133.27, 133.17, 132.96, 130.86, 130.71, 129.84, 129.73, 129.66, 129.56, 129.21, 129.02, 128.88, 128.33, 128.27, 128.18, 127.98, 127.84,127.53, 127.42, 121.67, 121.57, 113.91, 96.71, 77.20, 72.44, 72.36, 72.24, 70.48, 70.43, 69.07, 68.64, 55.48, 55.37, 53.67, 29.10, 29.02, 28.72. **HRMS (ESI)** $C_{44}H_{41}NNaO_{10}$ $[M+Na]^+$ calcd: 766.2623, found: 766.2603.



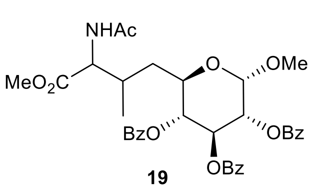
17

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(4-((4-fluorophenyl)amino)-4-oxo-3-phenylbutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 115.5 mg, yield: 79%. d. r. = 1:1 White solid, M. p. 53-55 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.89-7.83(m, 4H), 7.49-7.47 (m, 2H), 7.42-7.18 (m, 15H), 6.93-6.86 (m ,2H), 6.09 (td, *J* = 3.0 Hz, 9.3Hz, 1H), 5.35 (dd, *J* = 9.6 Hz, 6.6Hz, 1H), 5.26-5.19 (m, 2H), 4.12-4.00 (m, 1H), 3.52-3.44 (m, 4H), 2.65-2.53 (m, 0.5H), 2.41-2.14 (m, 1H), 1.99-1.87 (m, 0.5H), 1.68-1.52 (m, 2H). **^{19}F NMR** (282 MHz, CDCl$_3$) δ -117.95, -118.08· **^{13}C NMR** (75 MHz, CDCl$_3$) δ 171.26, 171.11, 165.83, 165.75, 165.58, 165.51, 139.01, 138.76, 133.68, 133.58, 133.30, 133.24, 133.00, 129.86, 129.73, 129.66, 129.57, 129.18, 129.11, 128.98, 128.36, 128.30, 128.20, 127.96, 127.82, 127.68, 127.57, 121.67, 121.59, 121.49, 115.55, 115.25, 96.73, 77.20, 72.39, 72.34, 72.22, 70.44, 70.39, 68.99, 68.66, 55.50, 53.74, 28.99, 28.71. **HRMS (ESI)** C$_{43}$H$_{38}$FNNaO$_9$ [M+Na]$^+$ calcd: 754.2423, found: 754.2411.



18

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-methoxy-6-(3-(3-methoxyphenyl)-4-oxo-4-(p-tolylamino)butyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 113.6 mg, yield: 75%. d. r. = 1:1. White solid, M. p. 65-67 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.97 (d, *J* = 7.8 Hz, 2H), 7.89-7.83(m, 4H), 7.51-7.46 (m, 2H), 7.42-7.22 (m, 9H),7.19-7.14 (m, 2H),7.04-7.00 (m, 2H), 6.90-6.86 (m ,2H), 6.78-6.70 (m, 1H), 6.09 (d, *J* = 9.6 Hz, 1H), 5.34-5.31 (m, 1H), 5.25-5.18 (m, 2H), 4.11-3.99 (m, 1H), 3.76 (s, 1.5H), 3.72 (s, 1.5H), 3.50-3.44 (m, 4H), 2.58-2.52 (m, 0.5H), 2.34-2.14 (m, 4H), 1.97-1.85 (m, 0.5H), 1.68-1.52 (m, 2H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 170.96, 170.81, 165.80, 165.72, 165.50, 165.46, 159.98, 159.88, 140.72, 140.44, 135.18, 135.05, 133.78, 133.69, 133.25, 133.18, 132.95, 130.03, 129.83, 129.71, 129.64, 129.54, 129.25, 129.20, 129.01, 128.97, 128.32, 128.28, 128.17, 120.29, 120.16, 119.79, 119.73, 113.63, 113.47, 112.87, 112.80, 96.70, 77.20, 72.44, 72.26, 70.49, 70.42, 69.09, 68.61, 55.47, 55.10, 53.79, 28.94, 28.46, 20.75. **HRMS (ESI)** C$_{45}$H$_{43}$NNaO$_{10}$ [M+Na]$^+$ calcd: 780.2779, found: 780.2767.



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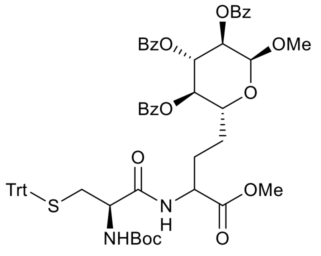
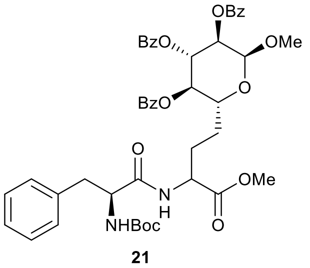
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-acetamido-4-methoxy-2-methyl-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 71.2 mg, yield: 55%. d. r. not determined. Yellow solid, M. p. 65-67 °C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 8.03-7.94 (m, 4H), 7.87-7.85(m, 2H), 7.54-7.49 (m, 2H), 7.44-7.38 (m, 5H), 7.31-7.24 (m ,2H), 6.90-6.85 (m, 0.25H), 6.29 (d, *J* = 7.8 Hz, 0.08H), 6.19-6.10 (m, 1H), 6.07-6.02 (m, 0.48H), 5.88-5.83 (m, 0.26H), 5.51-5.45 (m, 0.19 H), 5.39-5.33 (m, 0.96H), 5.24-5.19 (m, 1.74H), 4.89 (d, *J* = 7.6 Hz, 0.23H), 4.81-4.77 (m, 0.15H), 4.69-4.66 (m, 0.46H), 4.57(t, *J* = 6.6 Hz, 0.19H), 4.38-4.31 (m, 0.21H), 4.25 (t, *J* = 9.6 Hz, 0.28H), 4.17-4.05 (m, 0.57H), 3.72-3.70 (m, 1.18H), 3.66 (s, 0.64H), 3.56-3.54 (m, 1.8H), 3.48 (s, 1.26H), 3.39-3.37 (m, 1.13H), 2.53 (brs, 0.3H), 2.32 (brs, 0.7H), 1.99 (s, 2H), 1.77 (s, 1H), 1.68-1.56 (m, 1H), 1.47-1.34 (m, 1H), 0.97 (d, *J* = 6.3Hz, 2H), 0.86 (d, *J* = 6.9 Hz, 1H) **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.75, 172.20, 171.72, 170.13, 169.95, 169.51, 165.98, 165.81, 165.57, 133.48, 133.36, 133.05, 132.94, 130.04, 129.91, 129.83, 129.78, 129.63, 129.55, 129.20, 129.04, 128.48, 128.41, 128.35, 128.26, 115.35, 97.11, 96.94, 77.24, 72.84, 72.50, 72.17, 70.37, 70.24, 67.51, 66.76, 56.83, 56.27, 55.94, 55.63, 54.99, 52.98, 52.49, 52.21, 51.89, 34.89, 33.15, 32.30, 29.70, 23.21, 22.89, 16.88, 16.11, 15.88, 15.39. **HRMS (ESI)** $C_{35}H_{37}NNaO_{11}$ $[M+Na]^+$ calcd: 670.2259, found: 670.2252.



20

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((*R*)-2-((tert-butoxycarbonyl)amino)-3-(tritylthio)propanamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 134.7 mg, yield: 65%. d. r. = 1.3:1. White solid, M. p. = 85-87 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (t, *J* = 9.3 Hz, 4H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.53-7.48(m, 2H), 7.46-7.41 (m, 11H), 7.39-7.19 (m, 11H), 6.64-6.50 (m, 1H), 6.08 (t, *J* = 9.3 Hz, 1H), 5.36-5.28 (m, 1H), 5.18-5.12 (m, 2H), 4.74 (brs, 1H), 4.54-4.47 (m, 1H), 4.05-4.00 (m, 1H), 3.77 (brs, 1H), 3.64 (s, 1.7H), 3.57 (s, 1.3H), 3.41 (s, 3H), 2.73-2.44 (m, 2H), 2.14-1.80 (m, 2H), 1.63-1.62 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.11, 171.81, 170.27, 170.02, 165.80, 165.70, 165.46, 155.21, 144.34, 133.35, 133.29, 132.98, 129.86, 129.77, 129.57, 129.50, 129.24, 129.22, 129.04, 128.94, 128.39, 128.35, 128.20, 128.02, 126.86, 126.83, 96.73, 80.26, 77.21, 72.20, 72.11, 70.41, 68.31, 67.99, 67.09, 55.47, 53.31, 52.29, 52.21, 51.89, 51.67, 33.54, 28.17, 27.78, 26.54. **HRMS (ESI)** $C_{59}H_{60}N_2NaO_{13}S$ $[M+Na]^+$ calcd: 1059.3708, found: 1059.3675.



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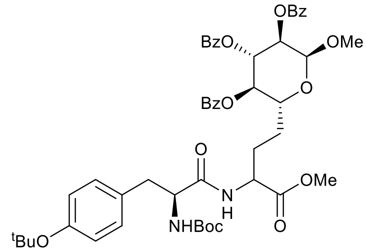
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((*S*)-2-((tert-butoxycarbonyl)amino)-3-phenylpropanamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 114.2 mg, yield: 68%. d. r. = 1.2:1. White solid, M. p. = 70-73 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99 (m, 4H), 7.86-7.84 (m, 2H), 7.53-7.49(m, 2H), 7.44-7.35 (m, 5H), 7.30-7.17 (m, 6H), 7.10 (s, 1H), 6.48 (d, *J* = 7.5 Hz, 0.42H), 6.30 (d, *J* = 7.5 Hz, 0.5H), 6.10 (t, *J* = 9.6 Hz, 1H), 5.32 (dd, *J* = 9.0 Hz, 7.2 Hz, 1H), 5.22-5.16 (m, 2H), 4.98 (brs, 0.9H), 4.57-4.47 (m, 1H), 4.33-4.31 (m, 1H), 4.03-3.98 (m, 1H), 3.67(s, 1.63H), 3.59 (s, 1.37H), 3.45 (s, 3H), 3.05-2.90 (m, 2H), 2.13-1.80 (m, 2H), 1.60-1.58 (m, 2H), 1.39 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.22, 171.85, 171.11, 170.95, 165.88, 165.85, 165.75, 165.63, 165.52, 155.19, 136.55, 133.44, 133.36, 133.06, 129.91, 129.82, 129.62, 129.35, 129.25, 129.05, 128.90, 128.66, 128.62, 128.46, 128.41, 128.26, 127.68, 126.91, 96.83, 80.20, 72.20, 70.35, 68.37, 68.01, 55.62, 53.59, 52.42, 52.29, 51.91, 51.75, 38.29, 29.70, 28.23, 28.04, 27.43, 26.57. **HRMS (ESI)** $C_{46}H_{50}N_2NaO_{13}$ $[M+Na]^+$ calcd: 861.3205, found: 861.3123.



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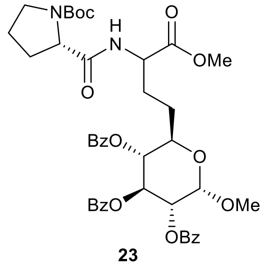
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((S)-3-(4-(tert-butoxy)phenyl)-2-((tert-butoxycarbonyl)amino)propanamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 127.5 mg, yield: 70%. d. r. = 1.4:1. White solid, M. p. = 86-88 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.99-7.93 (m, 4H), 7.87-7.84 (m, 2H), 7.53-7.48(m, 2H), 7.43-7.37 (m, 5H), 7.30-7.25 (m, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.90 (t, *J* = 8.4 Hz, 2H), 6.51 (d, *J* = 7.5 Hz, 0.42H), 6.32 (d, *J* = 7.5 Hz, 0.58H), 6.15-6.07 (m, 1H), 5.35 (t, *J* = 9.6 Hz, 1H), 5.25-5.18 (m, 2H), 4.99 (brs, 0.94H), 4.55-4.49 (m, 1H), 4.29 (brs, 1H), 4.06-4.01 (m, 1H), 3.66 (s, 1.8H), 3.59 (s, 1.2H), 3.45 (s, 3H), 3.05-2.79 (m, 2H), 2.13-1.77 (m, 2H), 1.61-1.54 (m, 2H), 1.39 (s, 9H), 1.33 (s, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.14, 171.78, 171.10, 170.95, 165.77, 165.67, 165.54, 165.42, 155.14, 154.20, 133.37, 133.26, 132.96, 131.31, 129.83, 129.73, 129.66, 129.53, 129.19, 129.00, 128.84, 128.36, 128.32, 128.16, 124.31, 124.26, 96.72, 79.87, 78.29, 77.20, 72.15, 72.07, 70.31, 68.29, 67.90, 55.53, 55.46, 52.33, 52.21, 51.80, 51.61, 37.84, 28.75, 28.16, 28.03, 27.51, 26.60, 26.47. **HRMS (ESI)** $C_{50}H_{58}N_2NaO_{14}$ $[M+Na]^+$ calcd: 933.3780, found: 933.3658.



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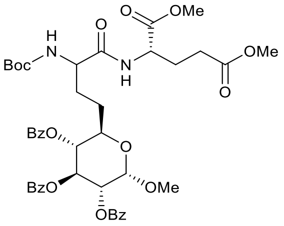
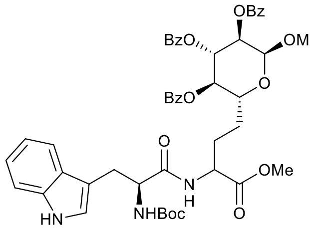
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((*S*)-1-(tert-butoxycarbonyl)pyrrolidine-2-carboxamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 86.7 mg, yield: 55%. d. r. = 1.5:1. Colorless oil. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (t, *J* = 7.8 Hz, 4H), 7.85 (d, *J* = 7.8 Hz, 2H), 7.53-7.49 (m, 2H), 7.44-7.35 (m, 5H), 7.30-7.27 (m, 2.6H), 6.50 (brs, 0.4H), 6.09 (t, *J* = 9.6 Hz, 1H), 5.36 (t, *J* = 9.3 Hz, 1H), 5.22-5.18 (m, 2H), 4.60 (brs, 1H), 4.19-4.04 (m, 2H), 3.69-3.64 (m, 3H), 3.45 (s, 3H), 3.32 (brs, 2H), 2.17-2.00 (m, 3H), 1.81-1.64 (m, 5H), 1.46-1.44 (m, 9H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 172.63, 172.46, 165.87, 165.77, 165.45, 165.38, 133.41, 133.33, 133.02, 129.92, 129.89, 129.81, 129.63, 129.30, 129.08, 128.40, 128.32, 128.24, 96.85, 80.52, 72.33, 72.25, 70.62, 70.46, 68.49, 68.06, 62.77, 57.06, 55.58, 52.35, 52.27, 51.54, 47.00, 28.46, 28.33, 27.99, 26.95. **HRMS (ESI)** $C_{42}H_{48}N_2NaO_{13}$ $[M+Na]^+$ calcd: 811.3049, found: 811.3039.



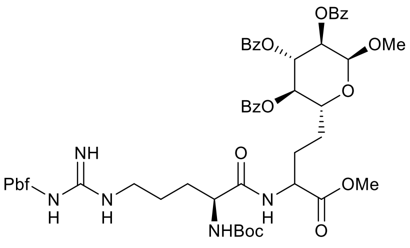
24

dimethyl (2-((tert-butoxycarbonyl)amino)-4-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzoyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)butanoyl)-L-glutamate: 113.5 mg, yield: 68%. d. r. = 1.25:1. White solid, M. p. = 75-77 °C..^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.99-7.93 (m, 4H), 7.86-7.84 (m, 2H), 7.53-7.51 (m, 2H), 7.48-7.35 (m, 5H), 7.30-7.27 (m, 2H), 6.15 (d, *J* = 9.3 Hz, 0.4H), 6.09 (d, *J* = 9.6 Hz, 0.5H), 6.16-6.07 (m, 1H), 5.43-5.30 (m, 1H), 5.24-5.19 (m, 2H), 4.64-4.54 (m ,1H), 4.11-4.03 (m, 2H), 3.83-3.59 (m, 6.9H), 3.45 (s, 3H), 2.43-2.33 (m, 2H), 2.23-2.14 (m, 1H), 2.05-1.91 (m, 2H), 1.78-1.64 (m, 3H), 1.41 (s, 9H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 173.18, 173.06, 171.97, 171.75, 171.64, 165.80, 165.74, 165.50, 155.57, 133.45, 133.31, 133.03, 133.00, 129.88, 129.82, 129.58, 129.20, 129.03, 128.85, 128.36, 128.31, 96.81, 80.15, 77.20, 72.18, 70.39, 70.25, 68.81, 68.43, 55.68, 55.58, 52.51, 52.46, 51.80, 51.56, 51.44, 29.82, 28.17, 27.99, 27.23, 27.12, 26.70. **HRMS (ESI)** $C_{43}H_{50}N_2NaO_{15}$ $[M+Na]^+$ calcd: 857.3103, found: 857.3087



25

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((*S*)-2-((tert-butoxycarbonyl)amino)-3-(1H-indol-3-yl)propanamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 101.5 mg, yield: 58%. d. r. = 1.5:1. White solid, M. p. = 105-108 °C..^{1}**H NMR** (300 MHz, $CDCl_3$) δ 8.45-8.39 (m, 1H), 7.99-7.93 (m, 4H), 7.89-7.87 (m, 2H), 7.70-7.68 (m, 1H), 7.52-7.50 (m, 2H), 7.46-7.38 (m, 6H), 7.31-7.22 (m, 2.4H), 7.19-7.12 (m, 2H), 6.92 (s, 0.6H), 6.25 (d, *J* = 7.8 Hz, 0.4H), 6.05 (t, *J* = 9.6 Hz, 1H), 5.94 (d, *J* = 7.5 Hz, 0.6H), 5.30-5.15 (m, 3H), 5.04-5.02 (m, 1H), 4.47-4.32 (m ,2H), 3.92-3.81 (m, 1H), 3.64 (s, 1.9H), 3.55 (s, 1.1H), 3.38 (s, 3H), 3.26-3.01 (m, 2H), 1.98-1.64 (m, 2H), 1.50-1.32 (m, 11H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 172.06, 171.76, 171.65, 171.42, 165.88, 165.81, 165.72, 165.64, 155.17, 136.19, 136.13, 133.60, 133.47, 133.33, 133.05, 129.84, 129.74, 129.53, 129.14, 128.95, 128.78, 128.49, 128.43, 128.36, 128.26, 128.22, 127.26, 123.52, 123.07, 122.22, 122.15, 119.67, 118.82, 111.32, 111.24, 110.43, 96.72, 96.65, 79.89, 77.20, 72.34, 72.25, 72.02, 71.94, 70.37, 70.27, 68.30, 67.85, 55.52, 52.29, 52.14, 51.95, 51.85, 28.23, 27.53, 27.09, 26.42, 26.13. **HRMS (ESI)** $C_{48}H_{51}N_3NaO_{13}$ $[M+Na]^+$ calcd: 900.3314, found: 900.3300.



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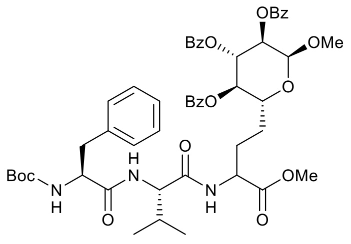
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-(3-((*S*)-2-((tert-butoxycarbonyl)amino)-5-(3-((2,2,4,6,7-pentamethyl-2,3-dihydrobenzofuran-5-yl)sulfonyl)guanidino)pentanamido)-4-methoxy-4-oxobutyl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 114.3 mg, yield: 52%. d. r. = 1.2:1. White solid, M. p. = 100-103 °C..^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.98-7.77 (m, 6H), 7.51-7.49 (m, 2H), 7.43-7.35 (m, 5H), 7.29-7.14 (m, 4H), 6.23-6.05 (m, 3H), 5.46-5.15 (m, 4H), 4.49 (brs, 1H), 4.22-4.05 (m, 2H), 3.64 (s, 1.4H), 3.61 (s, 1.6H), 3.53 (s, 0.3H), 3.50 (s, 0.2H), 3.43 (s, 1.1H), 3.39 (s, 1.4H), 3.20-3.15 (m, 2H), 2.94 (s, 2H), 2.58 (s, 3H), 2.52 (s, 3H), 2.14-1.91 (m, 5H), 1.69-1.51 (m, 5H), 1.45 (s, 6H), 1.39-1.26 (m, 10H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ172.41, 172.36, 165.82, 165.69, 165.61, 158.66, 156.29, 156.15, 138.32, 133.32, 133.05, 132.88, 132.81, 132.25, 129.87, 129.79, 129.56, 129.18, 128.99, 128.89, 128.77, 128.45, 128.37, 128.22, 124.54, 117.40, 96.74, 86.31, 80.06, 77.20, 72.43, 72.17, 70.36, 68.38, 67.86, 55.54, 52.38, 52.32, 51.80, 43.17, 40.59, 29.66, 28.55, 28.24, 27.18, 25.00, 19.27, 17.90, 12.45. **HRMS (ESI)** $C_{56}H_{69}N_5NaO_{16}S$ $[M+Na]^+$ calcd: 1122.4352, found: 1122.4235.



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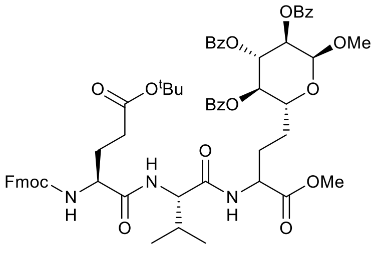
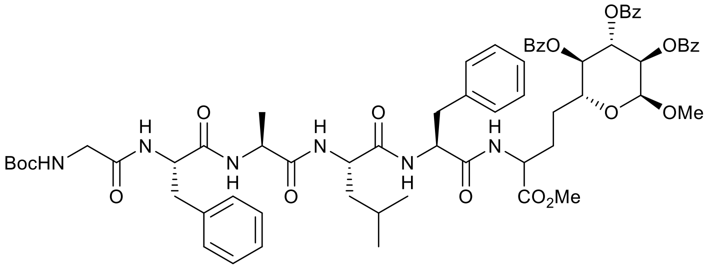
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((6*S*,9*S*)-6-benzyl-9-isopropyl-12-(methoxycarbonyl)-2,2-dimethyl-4,7,10-trioxo-3-oxa-5,8,11-triazatetradecan-14-yl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: 108.7 mg, yield: 58%, d. r. = 1.8:1. White solid, M. p = 105-108°C. ^{1}**H NMR** (300 MHz, $CDCl_3$) δ 7.96 (t, *J* = 6.3 H z, 4H), 7.84 (d, *J* = 7.5 Hz, 2H), 7.53-7.48 (m, 2H), 7.39-7.35 (m, 5H), 7.29-7.15 (m, 7H), 6.81-6.74 (m, 1H), 6.58 (d, *J* = 8.4 Hz, 0.36H), 6.46 (d, *J* = 8.4 Hz, 0.64H), 6.11 (t, *J* = 9.6 Hz, 1H), 5.38 (t, *J* = 9.6 Hz, 1H), 5.24-5.17 (m, 2H), 5.09-5.03 (m, 1H), 4.58-4.50 (m, 1H), 4.38-4.20 (m, 2H), 4.06-4.04 (m, 1H), 3.70 (s, 1.87H), 3.63 (s, 1.14H), 3.44 (s, 3H), 3.07-3.01 (m, 2H), 2.21-1.88 (m, 3H), 1.71-1.62 (m, 2H), 1.39 (s, 9H), 0.84 (dd, *J* = 6.3 Hz, *J* = 12.0 Hz, 2H), 0.71 (d, *J* = 6.3 Hz, 4H). ^{13}**C NMR** (75 MHz, $CDCl_3$) δ 172.17, 171.98, 171.26, 171.13, 170.63, 170.50, 165.81, 165.68, 165.49, 155.55, 136.50, 136.33, 133.39, 133.32, 133.28, 132.96, 129.85, 129.55, 129.21, 129.02, 128.91, 128.86, 128.65, 128.34, 128.17, 126.91, 96.78, 80.42, 77.20, 72.20, 72.12, 70.37, 68.32, 68.04, 58.42, 58.20, 55.63, 55.49, 52.35, 52.21, 51.94, 51.83, 37.67, 30.54, 28.17, 27.42, 27.06, 26.61, 19.03, 17.63, 17.27. **HRMS (ESI)** $C_{51}H_{59}N_3NaO_{14}$ $[M+Na]^+$ calcd: 960.3895, found: 960.3895.



28

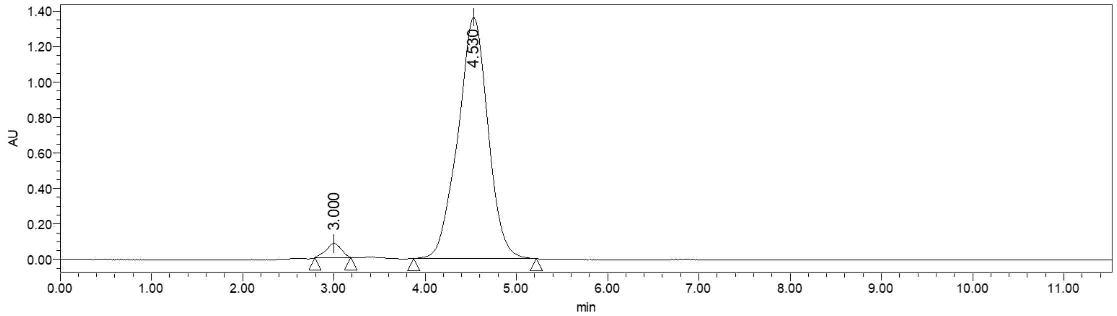
(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((5*S*,8*S*)-5-(3-(tert-butoxy)-3-oxopropyl)-1-(9H-fluoren-9-yl)-8-isopropyl-11-(methoxycarbonyl)-3,6,9-trioxo-2-oxa-4,7,10-triazatridecan-13-yl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate:114 mg, yield: 52%, d. r. = 1.25:1. White solid, M. p = 115-118°C. **^{1}H NMR** (300 MHz, CDCl$_3$) δ 7.98-7.96 (m, 4H), 7.84-7.82 (m, 2H), 7.76 (d, *J* = 7.2 Hz, 2H), 7.58 (brs, 2H), 7.50-7.48 (m, 2H), 7.39-7.26 (m, 11H), 6.94 (d, *J* = 7.5 Hz, 0.4H), 6.77-6.74 (m, 1.5H), 6.10 (t, *J* = 9.6 Hz, 1H), 5.97 (d, *J* = 5.4 Hz, 0.5H), 5.87 (t, *J* = 6.6 Hz, 0.4H), 5.37 (t, *J* = 9.0 Hz, 1H), 5.23-5.16 (m, 2H), 4.62-4.53 (m, 1H), 4.39-4.37 (m, 2H), 4.31-4.21 (m, 2.4H), 4.04 (brs, 1.6H), 3.65 (s, 3H), 3.43 (s, 3H), 2.40-2.29 (m, 2H), 2.07-2.05 (m, 4H), 1.67 (brs, 3H), 1.46 (s, 9H), 0.93-0.87 (m, 3H), 0.77 (brs, 3H). **^{13}C NMR** (75 MHz, CDCl$_3$) δ 173.27, 172.25, 172.11, 171.42, 171.24, 170.77, 170.64, 165.88, 165.74, 165.52, 156.40, 143.72, 141.28, 133.50, 133.36, 133.07, 129.93, 129.88, 129.62, 129.24, 129.08, 128.92, 128.46, 128.41, 128.26, 127.73, 127.10, 125.11, 119.99, 96.88, 81.26, 77.25, 72.25, 71.95, 70.47, 68.38, 68.74, 67.28, 58.59, 58.19, 55.67, 55.53, 55.02, 52.41, 52.29, 51.97, 51.86, 47.07, 31.87, 28.07, 27.54, 26.97, 26.56, 19.22, 17.65, 17.24. **HRMS (ESI)** $C_{61}H_{68}N_3O_{16}$ [M+H]$^+$ calcd: 1098.4600, found: 1098.4607.



29

(2*R*,3*R*,4*S*,5*R*,6*S*)-2-((9*S*,12*S*,15*S*,18*S*)-9,18-dibenzyl-15-isobutyl-21-(methoxycarbonyl)-2,2,12-trimethyl-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazatricosan-23-yl)-6-methoxytetrahydro-2H-pyran-3,4,5-triyl tribenzoate: Prepared following the general procedure outlined using methyl (9S,12S,15S,18S)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-21-methylene-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate (36.8 mg, 0.05 mmol, 1.0 equiv), glycosyl thianthrenium salt (0.15 mmol, 3.0 equiv), and Ir[dF(CF$_3$)ppy]$_2$(5,5'-CF$_3$bpy)PF$_6$ (1 mmol %). Then, air was withdrawn and backfilled with Ar (three times). EtOH (1 mL) and Et$_3$N (0.15 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm). After 15 h, the reaction mixture was removed from light irradiation and concentrated in *vacuo*, the resulted thianthrene was removed by column chromatography (DCM/MeOH) and the product was isolated by Semi preparative HPLC, conditions: Hanbon Sci.& Tech (Dubhe, C$_{18}$, 10μ), length 20 mm*250 mm, 30-100% CH$_3$CN/H$_2$O + 0.1% trifluoroacetic acid. The product was obtained as a white solid (21.5 mg, isolated yield: 35%), and subjected to HPLC analysis, conditions: Waters e2695 (BEH, C$_{18}$, 10μ, 130Å), length 4.6 mm*250 mm, 93% CH_3CN/H_2O + 0.1% trifluoroacetic acid. The d. r. = 1:1, (d. r. were measured by HPLC, IA, hexane : ethanol = 1:6). **HRMS (ESI)** $C_{66}H_{78}N_6NaO_{17}$ $[M+Na]^+$ calcd: 1249.5316, found: 1249.5203.

Preparative reverse phase HPLC data for purified peptide



No	Ret. Time	Area	Rel. Area (%)	Height
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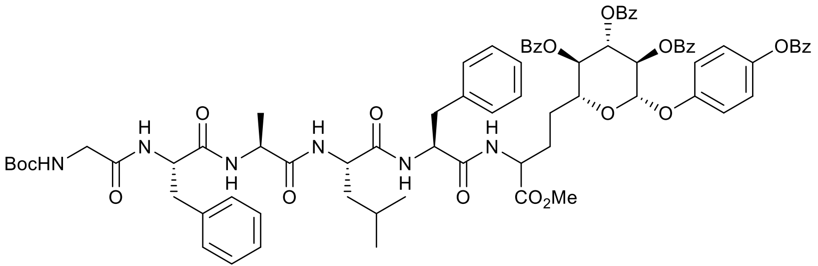
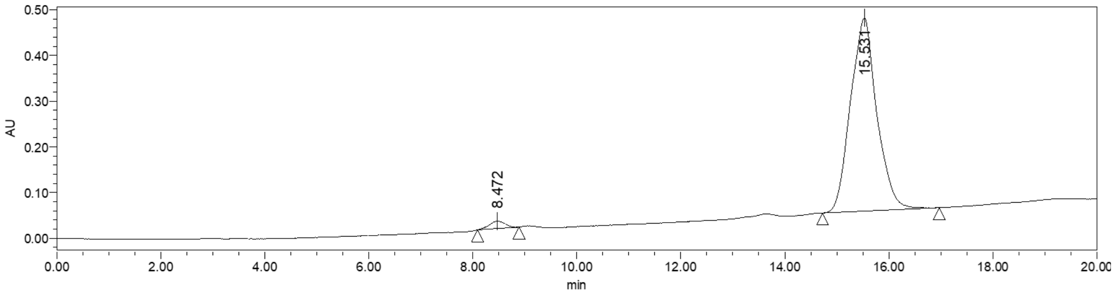
2	4.530	30348728	97.16	1325383



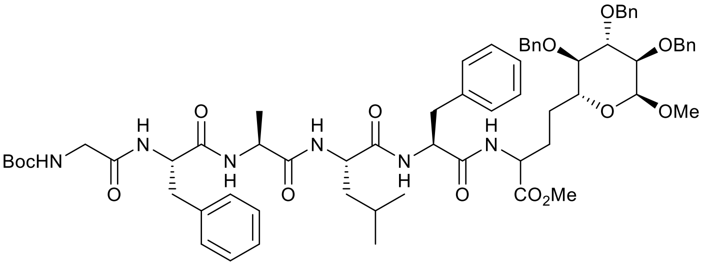
30

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-(4-(benzoyloxy)phenoxy)-6-((9*S*,12*S*,15*S*,18*S*)-9,18-dibenzyl-15-isobutyl-21-(methoxycarbonyl)-2,2,12-trimethyl-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazatricosan-23-yl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: Prepared following the general procedure outlined using methyl (9S,12S,15S,18S)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-21-methylene-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate (36.8 mg, 0.05 mmol, 1.0 equiv), glycosyl thianthrenium salt (0.15 mmol, 3.0 equiv), and $Ir[dF(CF_3)ppy]_2(5,5'\text{-}CF_3bpy)PF_6$ (1 mmol %). Then, air was withdrawn and backfilled with Ar (three times). EtOH (1 mL) and Et_3N (0.15 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm). After 15 h, the reaction mixture was removed from light irradiation and concentrated in *vacuo*, the resulted thianthrene was removed by column chromatography (DCM/MeOH) and the product was isolated by Semi preparative HPLC, conditions: Hanbon Sci.& Tech (Dubhe, C_{18}, 10μ), length 20 mm*250 mm, 30-100% CH_3CN/H_2O + 0.1% trifluoroacetic acid The product was obtained as a white solid (22.4 mg, isolated yield: 32%), and subjected to HPLC analysis, conditions: Waters e2695 (BEH, C_{18}, 10μ, 130Å), length 4.6 mm*250 mm, 93% CH_3CN/H_2O + 0.1% trifluoroacetic acid. The d. r. = 1:1, (d. r. were measured by HPLC, IC, hexane : ethanol = 1:4). **HRMS (ESI)** $C_{78}H_{84}N_6NaO_{19}$ $[M+Na]^+$ calcd: 1431.5683, found: 1431.5526.

Preparative reverse phase HPLC data for purified peptide



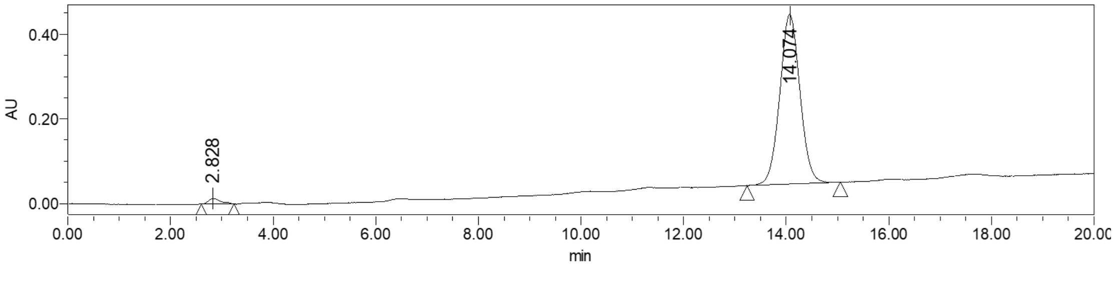
No	Ret. Time	Area	Rel. Area (%)	Height
1	8.472	333074	2.19	16030
2	15.531	14842839	97.81	422844



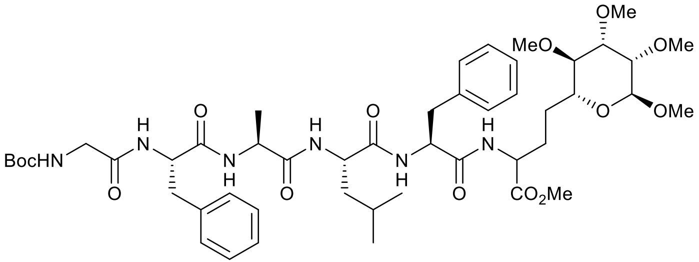
31

methyl (9*S*,12*S*,15*S*,18*S*)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-4,7,10,13,16,19-hexaoxo-21-(2-((2*R*,3*R*,4*S*,5*R*,6*S*)-3,4,5-tris(benzyloxy)-6-methoxytetrahydro-2H-pyran-2-yl)ethyl)-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate: Prepared following the general procedure outlined using methyl (9S,12S,15S,18S)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-21-methylene-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate (36.8 mg, 0.05 mmol, 1.0 equiv), glycosyl thianthrenium salt (0.15 mmol, 3.0 equiv), and Ir[dF(CF_3)ppy]$_2$(5,5'-CF_3bpy)PF_6 (1 mmol %). Then, air was withdrawn and backfilled with Ar (three times). EtOH (1 mL) and Et_3N (0.15 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm). After 15 h, the reaction mixture was removed from light irradiation and concentrated in *vacuo*, the resulted thianthrene was removed by column chromatography (DCM/MeOH) and the product was isolated by Semi preparative HPLC, conditions: Hanbon Sci.& Tech (Dubhe, C_{18}, 10μ), length 20 mm*250 mm, 30-100% CH_3CN/H_2O + 0.1% trifluoroacetic acid The product was obtained as a white solid (17.0 mg, isolated yield: 29%), and subjected to HPLC analysis, conditions: Waters e2695 (BEH, C_{18}, 10μ, 130Å), length 4.6 mm*250 mm, 70%-100% CH_3CN/H_2O + 0.1% trifluoroacetic acid. The d. r. = 1:1, (d. r. were measured by HPLC, IA, hexane : ethanol = 1:6). **HRMS (ESI)** $C_{66}H_{84}N_6NaO_{14}$ $[M+Na]^+$ calcd: 1207.5938, found: 1207.5823.

Preparative reverse phase HPLC data for purified peptide



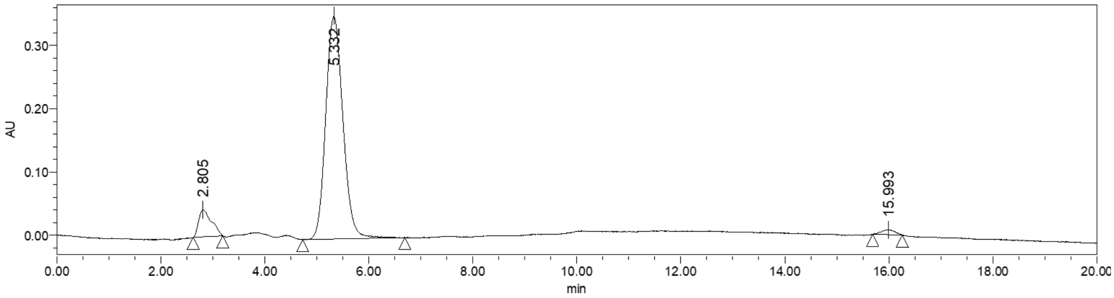
No	Ret. Time	Area	Rel. Area (%)	Height
1	2.828	223513	2.01	13143
2	14.074	10921759	97.99	400825



32

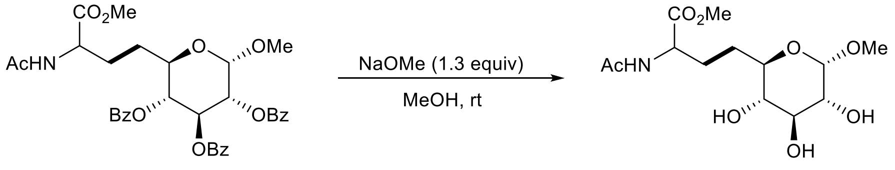
methyl (9*S*,12*S*,15*S*,18*S*)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-4,7,10,13,16,19-hexaoxo-21-(2-((2*R*,3*R*,4*S*,5*S*,6*S*)-3,4,5,6-tetramethoxytetrahydro-2H-pyran-2-yl)ethyl)-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate: Prepared following the general procedure outlined using methyl (9S,12S,15S,18S)-9,18-dibenzyl-15-isobutyl-2,2,12-trimethyl-21-methylene-4,7,10,13,16,19-hexaoxo-3-oxa-5,8,11,14,17,20-hexaazadocosan-22-oate (36.8 mg, 0.05 mmol, 1.0 equiv), glycosyl thianthrenium salt (0.15 mmol, 3.0 equiv), and Ir[dF(CF_3)ppy]$_2$(5,5'-CF_3bpy)PF_6 (1 mmol %). Then, air was withdrawn and backfilled with Ar (three times). EtOH (1 mL) and Et_3N (0.15 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm). After 15 h, the reaction mixture was removed from light irradiation and concentrated in *vacuo*, the resulted thianthrene was removed by column chromatography (DCM/MeOH) and the product was isolated by Semi preparative HPLC, conditions: Hanbon Sci.& Tech (Dubhe, C_{18}, 10μ), length 20 mm*250 mm, 30-100% CH_3CN/H_2O + 0.1% trifluoroacetic acid The product was obtained as a white solid (12.0 mg, isolated yield: 25%), and subjected to HPLC analysis, conditions: Waters e2695 (BEH, C_{18}, 10μ, 130Å), length 4.6 mm*250 mm, 70%-100% CH_3CN/H_2O + 0.1% trifluoroacetic acid. The d. r. = 1:1 (d. r. were measured by HPLC, IC, hexane : ethanol = 1:4). **HRMS (ESI)** $C_{48}H_{72}N_6NaO_{14}$ $[M+Na]^+$ calcd: 979.4999, found: 979.4912.

Preparative reverse phase HPLC data for purified peptide



No	Ret. Time	Area	Rel. Area (%)	Height
1	2.805	736155	8.22	42738
2	5.332	8085094	90.23	352168
3	15.993	139222	1.55	7709

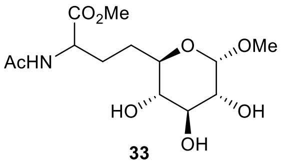
5. Synthetic application[6]



3

33, 82% yield, 1:1 d.r.

Compound **3** (0.1 mmol, 63.3 mg) was exposed to 1.3 equivalents of NaOMe in MeOH (4 mL) at ambient temperature. After six hours, The resulting solution was evaporated in *vacuo*. The product **33** was purified by silica gel column chromatography using DCM/MeOH as eluent.

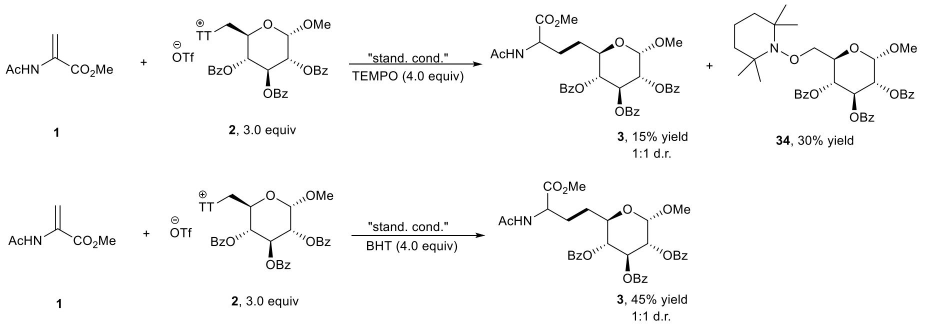


33

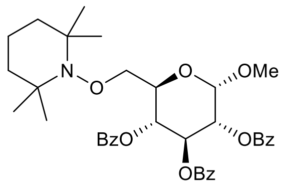
2-acetamido-4-((2*R*,3*S*,4*S*,5*R*,6*S*)-3,4,5-trihydroxy-6-methoxytetrahydro-2H-pyran-2-yl)butanoic acid: 26.2 mg, 82% yield, d. r. =1:1 , colorless oil. **^{1}H NMR** (300 MHz, MeOD) δ 4.63 (d, *J* = 3.3Hz, 1H), 4.43-4.39 (m, 1H), 3.71 (s, 3H), 3.59-3.35 (m, 7H), 3.04 (t, *J* = 9.3 Hz, 1H), 2.19-1.62 (m, 6H), 1.51-1.36 (m, 1H). **^{13}C NMR** (75 MHz, MeOD) δ 174.31, 174.27, 173.51, 173.46, 101.21, 75.62, 75.05, 75.01, 73.68, 73.65, 72.21, 71.35, 55.63, 55.59, 54.09, 53.65, 52.70, 29.06, 28.87, 28.48, 22.30. **HRMS (ESI)** $C_{13}H_{23}NNaO_8$ [M+Na]$^+$ calcd: 344.1321, found: 344.1317.

6. The mechanistic studies

6.1. Radical trapping experiments



To an oven-dried 10 mL quartz test tube with a stirring bar was added **1** (0.2 mmol, 28.6 mg), glycosyl thianthrenium salt (511.8 mg, 0.6 mmol, 3.0 equiv), and $Ir[dF(CF_3)ppy]_2(5,5'\text{-}CF_3bpy)PF_6$ (2.3 mg, 1.0 mol%), TEMPO or BHT (0.8 mmol, 4.0 equiv). Then, air was withdrawn and backfilled with Ar (three times). EtOH (4 mL) and Et_3N (60.7 mg, 0.6 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm), where it was irradiated for 15 h. Then, the reaction was concentrated in *vacuo*, and purified by column chromatography. When 4.0 equiv of TEMPO was added under standard conditions, the yield of corresponding product **3** dramatically decreased to 15%, and the TEMPO-glycosy adduct **34** was isolated in 30% yield. When 4.0 equiv of BHT were added under standard conditions, the corresponding glycosyl product **3** (45% yield) was observed. These results indicated that glycosyl radical was formed in the reaction process.

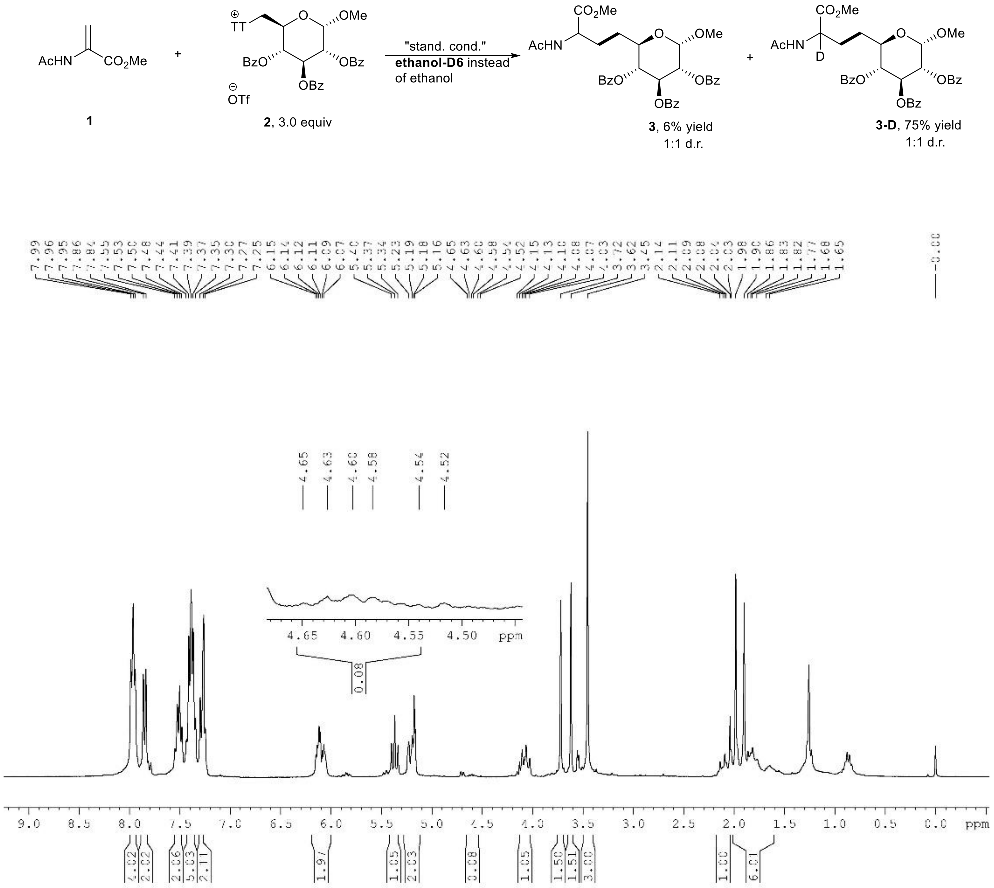


34

(2*S*,3*R*,4*S*,5*R*,6*R*)-2-methoxy-6-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)methyl)tetrahydro-2H-pyran-3,4,5-triyl tribenzoate: ^{1}H NMR (300MHz, $CDCl_3$): δ 8.00-7.92 (m, 4H), 7.88 (d, *J* = 7.5 Hz, 2H), 7.49-7.47 (m, 2H), 7.39-7.33 (m, 5H), 7.30-7.25 (m, 2H), 6.11 (t, *J* = 9.3 Hz, 1H), 5.52 (t, *J* = 9.3 Hz, 1H), 5.27-5.23 (m, 2H), 4.28-4.23 (m, 1H), 4.08-4.03 (m, 1H), 3.92-3.89 (m, 1H), 3.49 (s, 3H), 1.42-1.26 (m, 6H), 1.09 (s, 12H). **HRMS (ESI)** $C_{37}H_{43}NNaO_9$ $[M+Na]^+$ calcd: 668.2830, found: 668.2823.

6.2 Isotope labeling experiments

H/D labeling experiment



Scheme S5 H/D Labeling experiments.

To an oven-dried 10 mL quartz test tube with a stirring bar was added **1** (0.1 mmol, 14.3 mg), glycosyl thianthrenium salt (255.9 mg, 0.3 mmol, 3.0 equiv), and $Ir[dF(CF_3)ppy]_2(5,5'-CF_3bpy)PF_6$ (1.2 mg, 1.0 mol%). Then, air was withdrawn and backfilled with Ar (three times). Ethanol-D6 (2 mL) and Et_3N (30.4 mg, 0.3 mmol, 3 equiv) were added. The mixture was transferred to a violet LED photoreactor (24-W, 380-385 nm), where it was irradiated for 15 h. Then, the reaction was concentrated in *vacuo*, and purified by column chromatography (hexane/ethyl acetate) to afford the product (yield: 81%), the yield of deuterated product **7a-D** was 75%.

6.3. Stern-Volmer fluorescence quenching study

DMF was degassed with a stream of argon for 30 min. Ir[dF(CF_3)ppy]$_2$(5,5'-CF_3bpy)PF_6 (1.0 μmol) was added to each of a set of 5 volumetric flasks (10 mL). Subsequently, the solution of quencher in DMF (10 mL, 0.01 M) was added in increasing amounts (0, 100 μL, 1.0 mL, 2.0 mL, 3.0 mL) to the volumetric flasks and the volume of volumetric flasks were adjusted to 10 mL by adding DMF. Emission intensities were recorded by using a PerkinElmer spectrofluorophotometer LS 55. All solutions were excited at 390 nm and the fluorescence emission spectra were recorded.

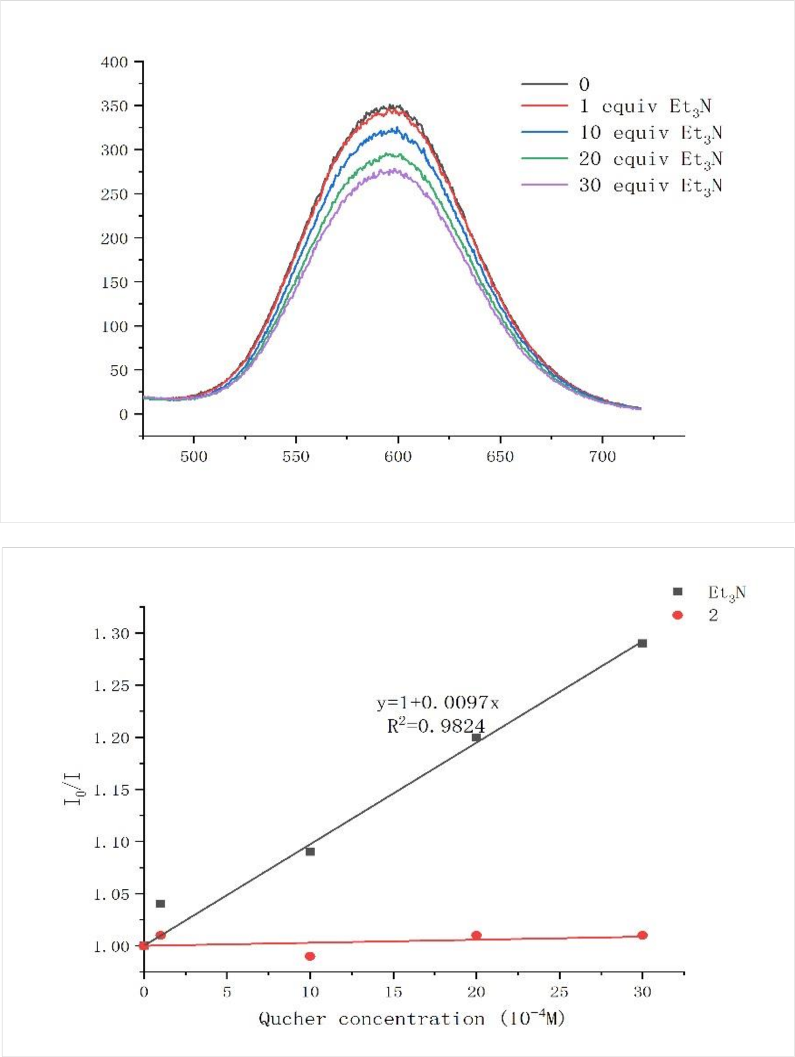


Figure S1 Stern-Volmer plot for the emission quenching of Ir[dF(CF_3)ppy]$_2$(5,5'-CF_3bpy)PF_6 by various concentrations of quencher.

NOTE: The result indicated that the Et_3N quenched the excited state of Ir[dF(CF_3)ppy]$_2$(5,5'-CF_3bpy)PF_6, where it presumably engaged in SET event with the photosensitizer Ir.

6.4. Cyclic Voltammetry experiments

Cyclic Voltammetry was performed on a CH Instruments Electrochemical Workstation model CHI760E. A solution of the sample in MeCN (0.001 M) was tested with 0.1 M Bu_4NPF_6 as the supporting electrolyte, using a glassy carbon as the working electrode, a Pt as the counter electrode, and a saturated calomel electrode reference electrode. Scan rate = 0.05 V/s, 2 sweep segments, a sample interval of 0.001 V.

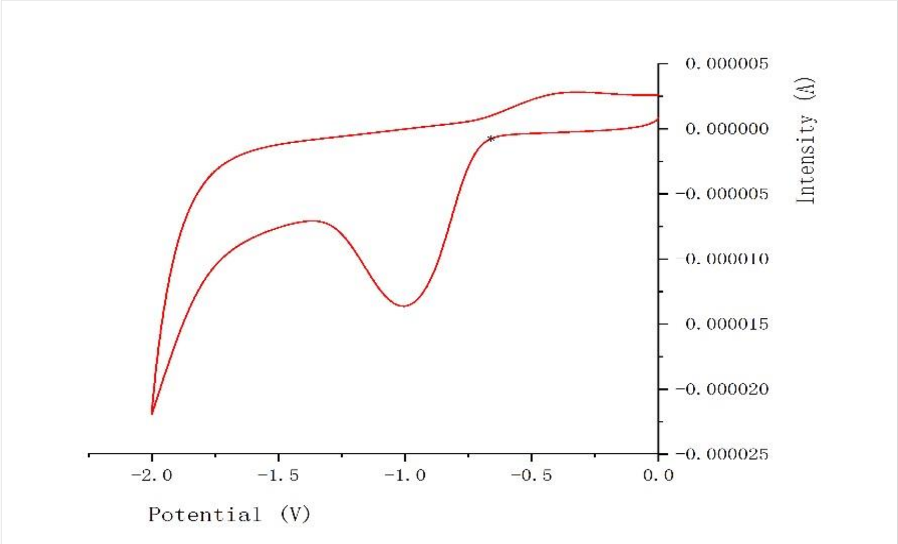


Figure S2 Cyclic Voltammetry of thianthrenium salt **2**.

$$E_{p/2} = (-1.007\ V - 0.328\ V)/2 = -0.663\ V\ (vs\ SCE)$$

7. X-ray crystallography

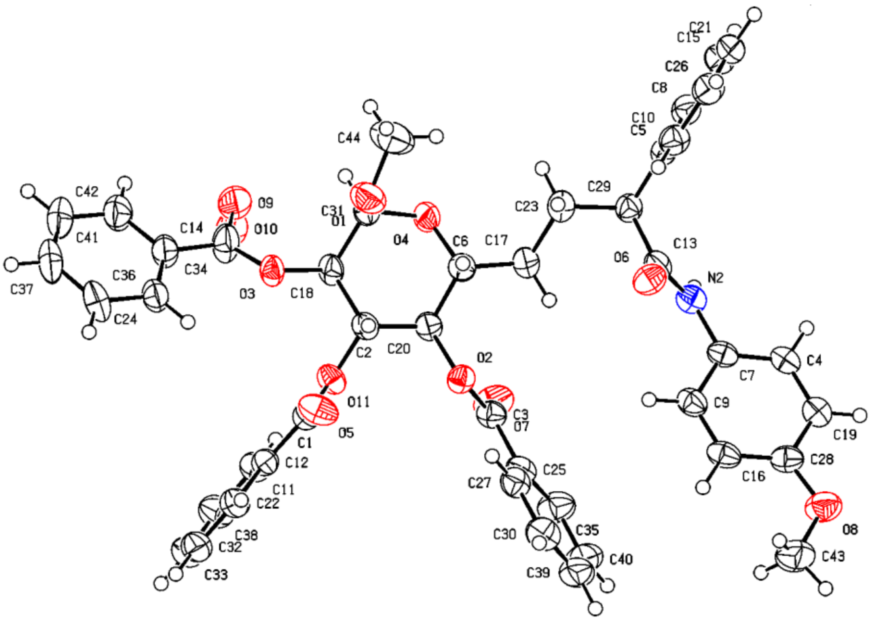


Figure S3 Views of the structure of **16**.

7.1 Experimental methods

A suitable crystal of **16** was selected and mounted on a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 149.99 (10) K during data collection. Using Olex2[7], the structure was solved with the SHELXT[8] structure solution program using Intrinsic Phasing and refined with the SHELXL[9] refinement package using Least Squares minimisation.

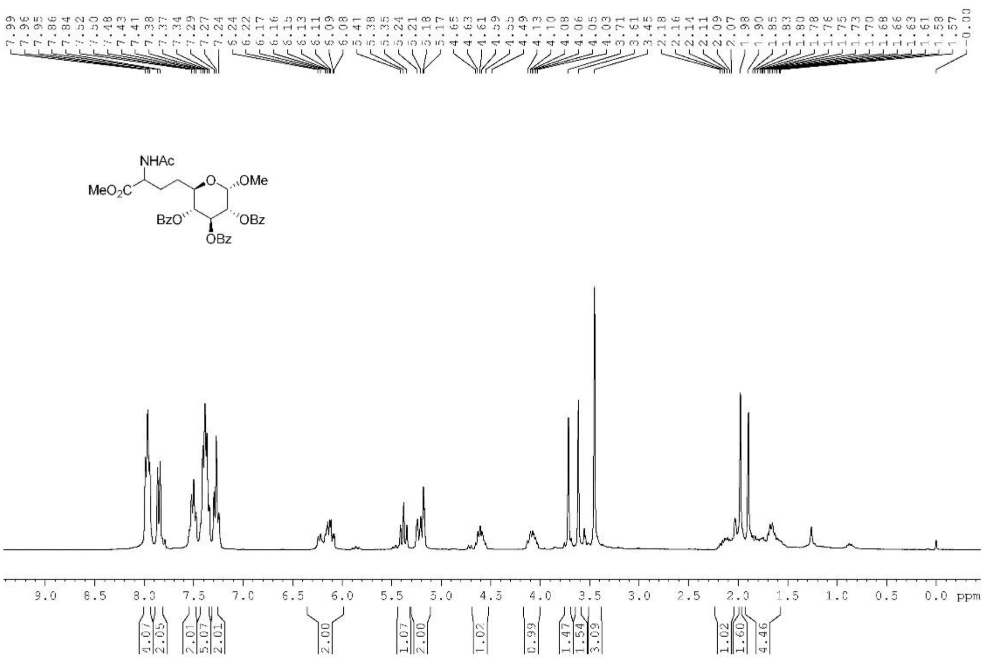
7.2 Summary of crystal data

Table S9 Crystal data and structure refinement for **16**

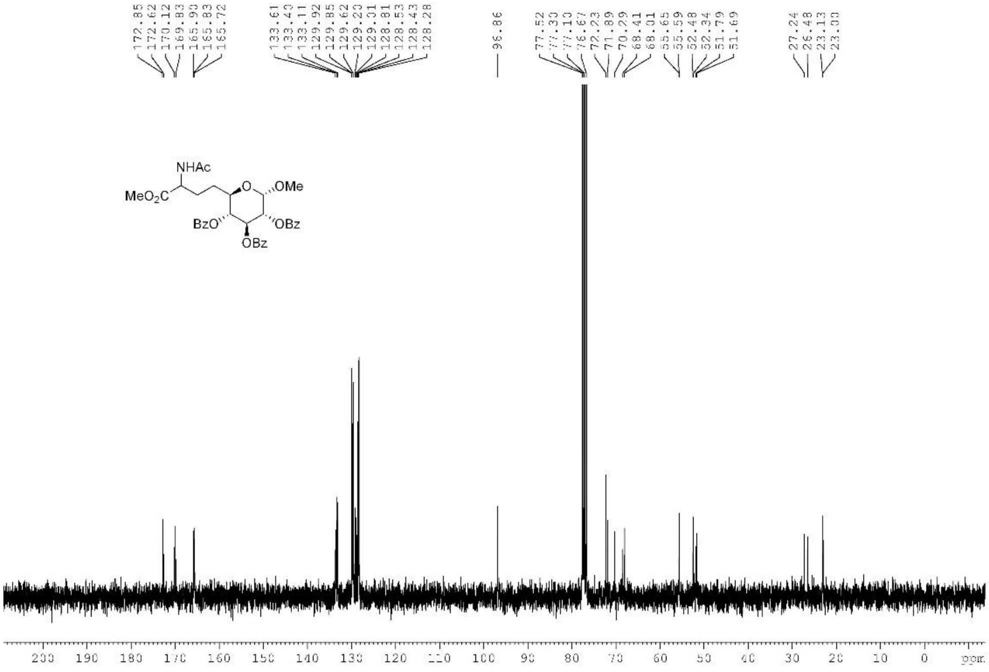
Compound	**16**
Empirical formula	$C_{44}H_{41}NO_{10}$
CCDC Number	2205739
Formula weight	743.78
Temperature/K	149.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.4574(2)
b/Å	10.5099(2)
c/Å	39.2952(6)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3905.80(13)
Z	4
ρ_{calc}g/cm^3	1.265
μ/mm^{-1}	0.737
F(000)	1568
Crystal size/mm^3	0.18 × 0.13 × 0.08
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.498 to 154.738
Index ranges	$-11 \leq h \leq 11$, $-6 \leq k \leq 12$, $-49 \leq l \leq 49$
Reflections collected	14695
Independent reflections	7108 [R_{int} = 0.0501, R_{sigma} = 0.0454]
Data/restraints/parameters	7108/13/507
Goodness-of-fit on F^2	1.097
Final R indexes [I>=2σ (I)]	R_1 = 0.0736, wR_2 = 0.1985
Final R indexes [all data]	R_1 = 0.0781, wR_2 = 0.2018
Largest diff. peak/hole / e Å^{-3}	0.55/-0.29
Flack parameter	-0.8(4)

8. NMR spectra of products

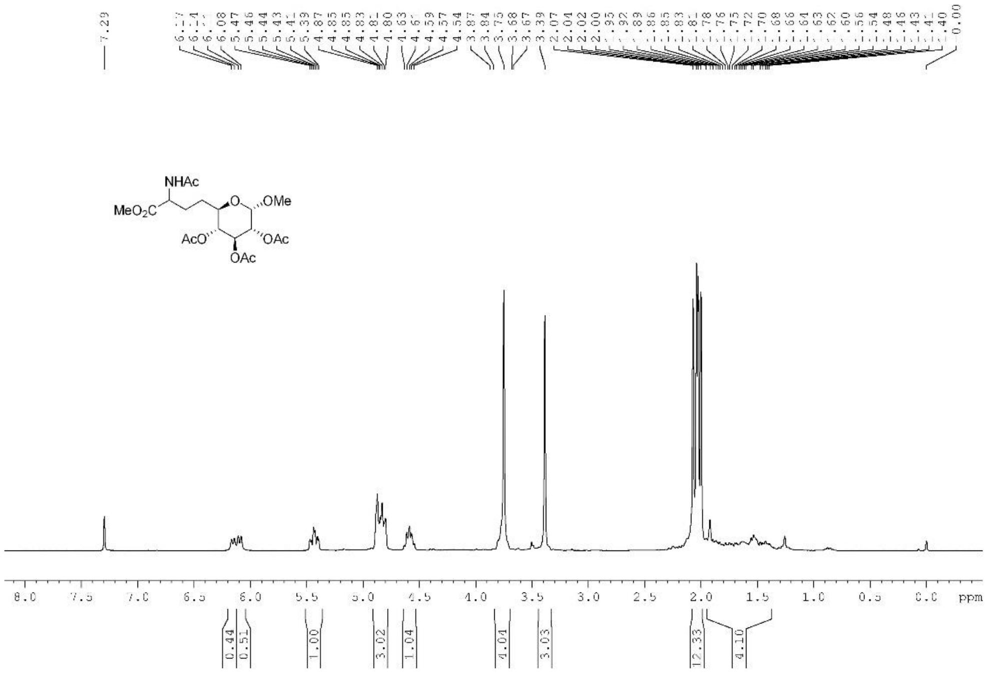
The ^{1}H NMR spectrum of **3**



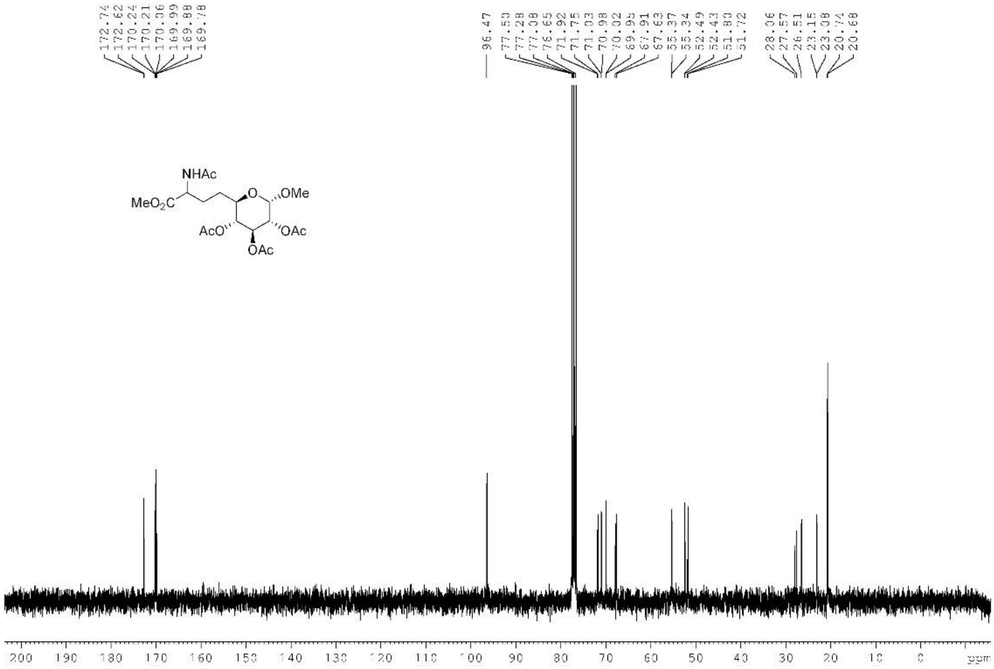
The ^{13}C NMR spectrum of **3**



The ^{1}H NMR spectrum of **4**



The ^{13}C NMR spectrum of **4**



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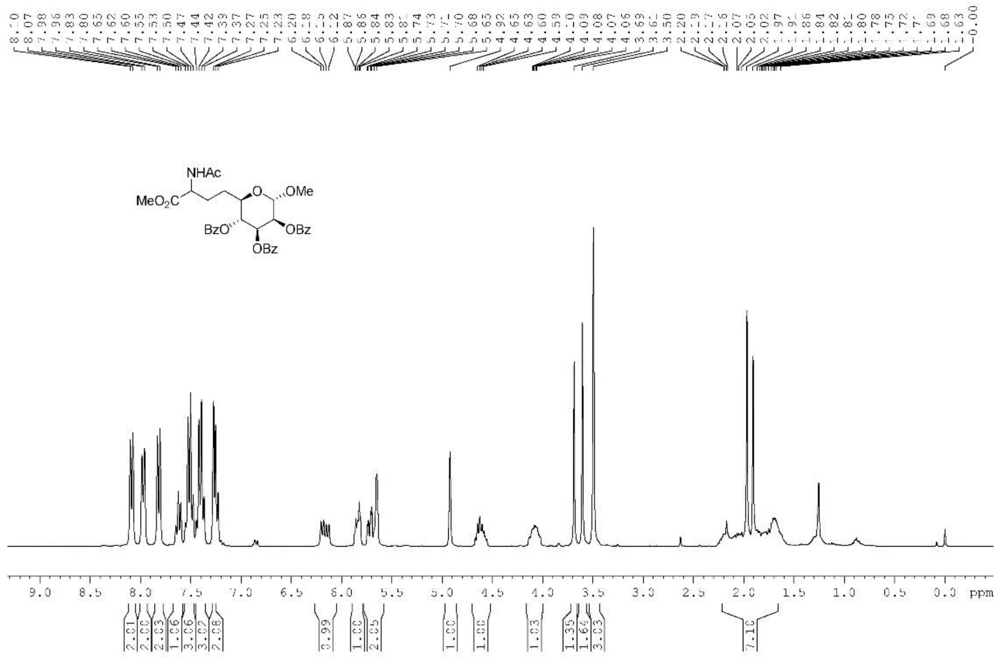

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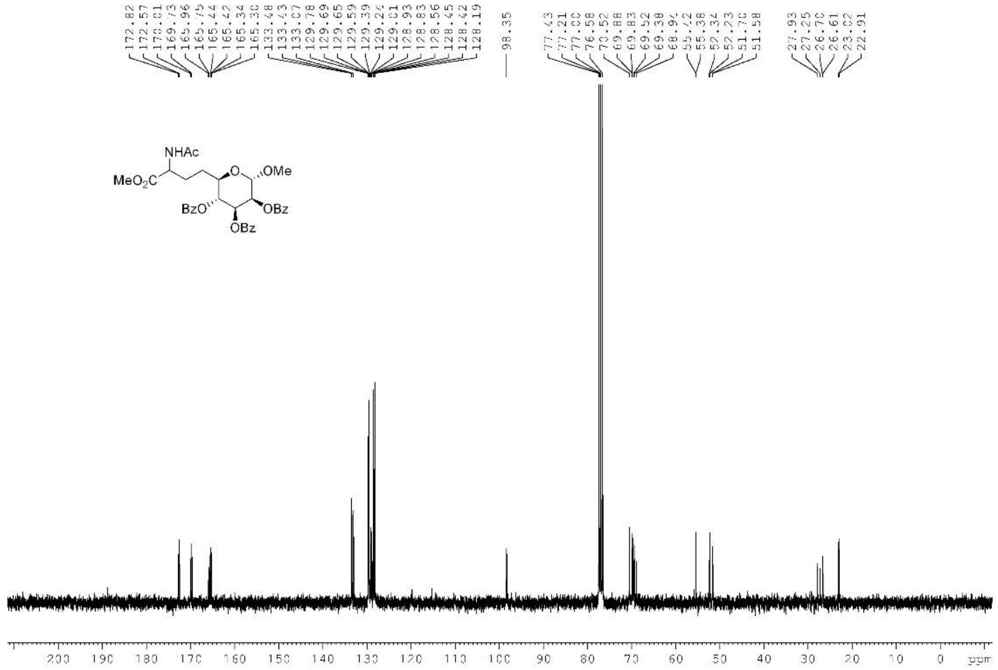

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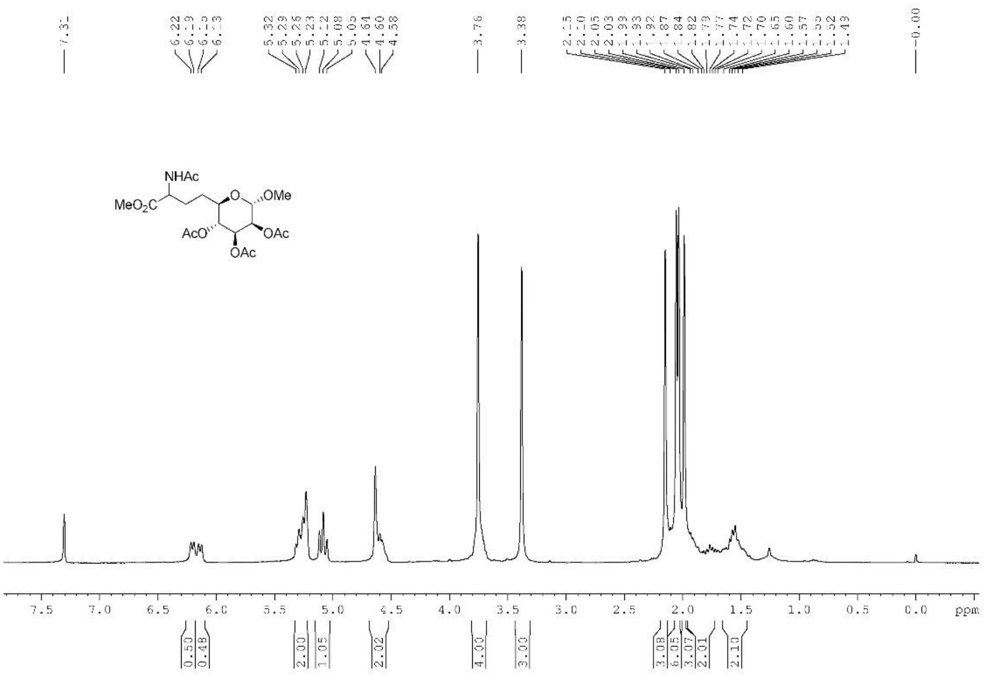
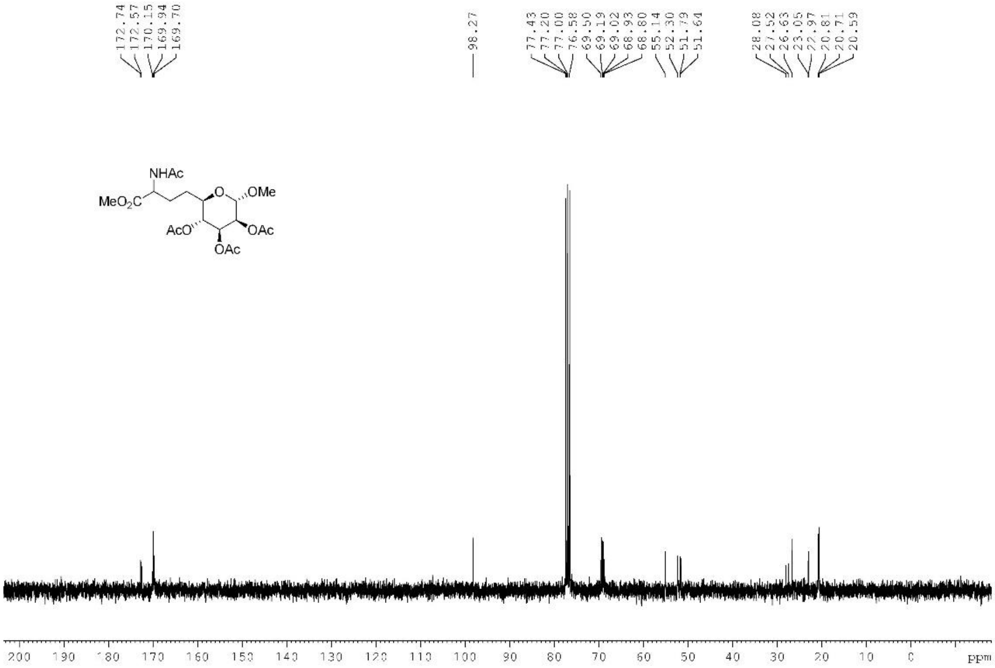


The ^{13}C NMR spectrum of **6**



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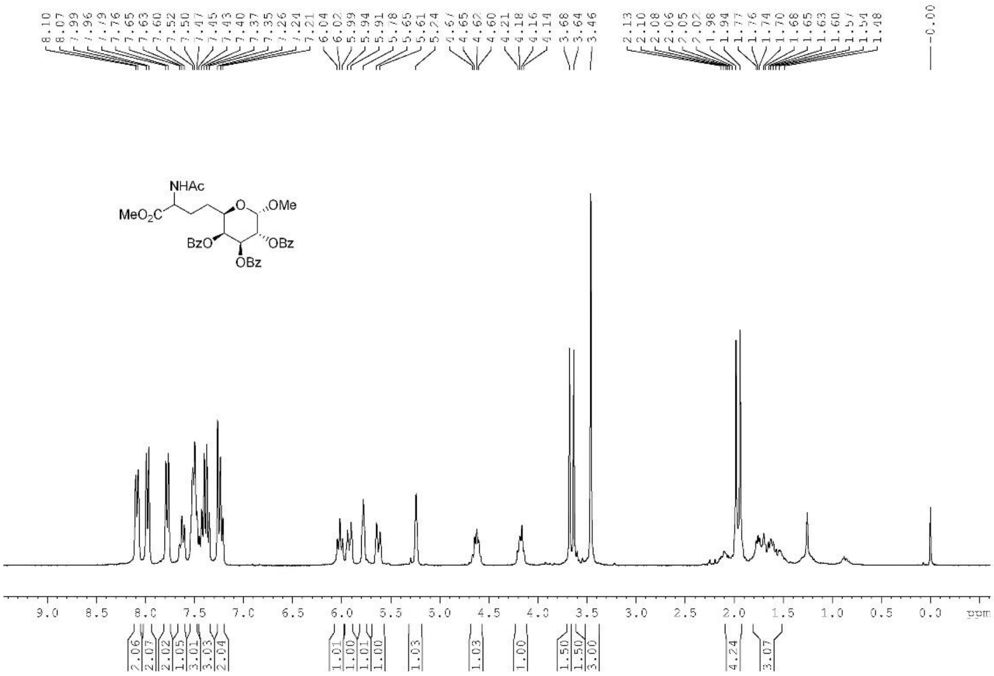

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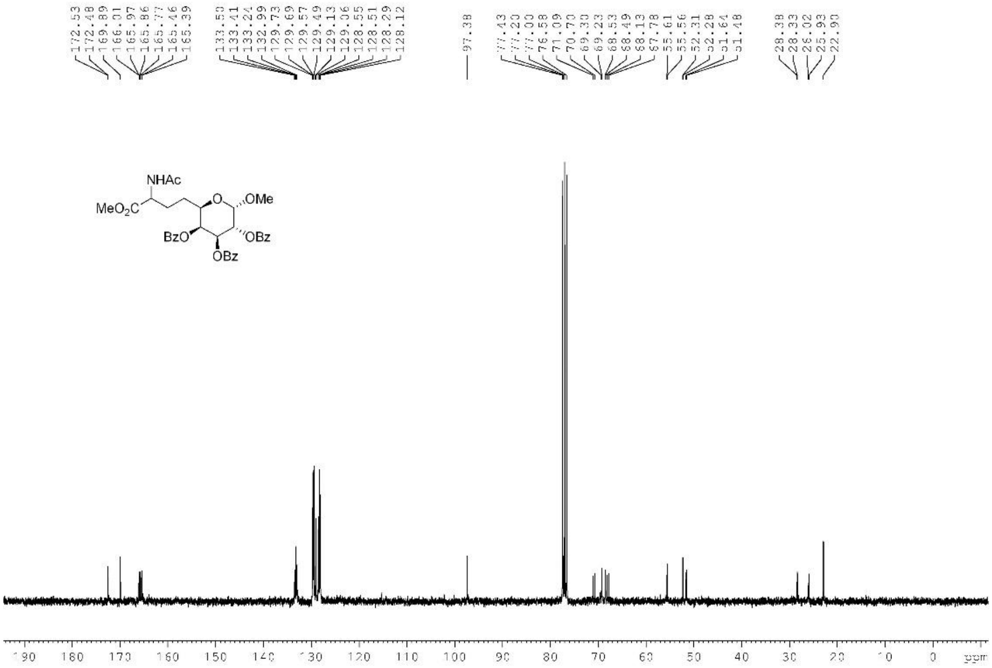

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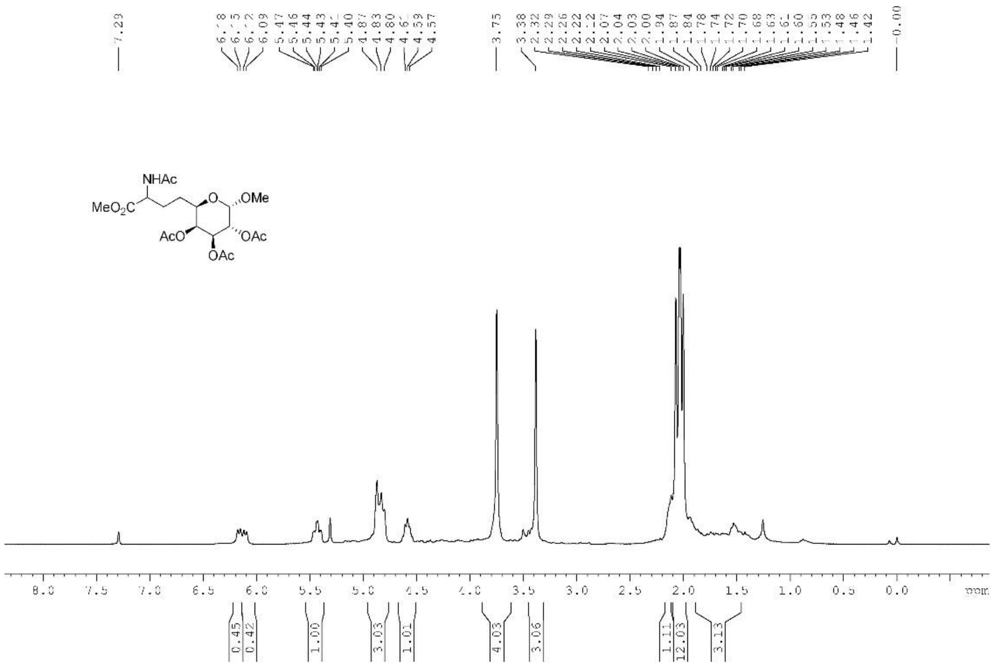

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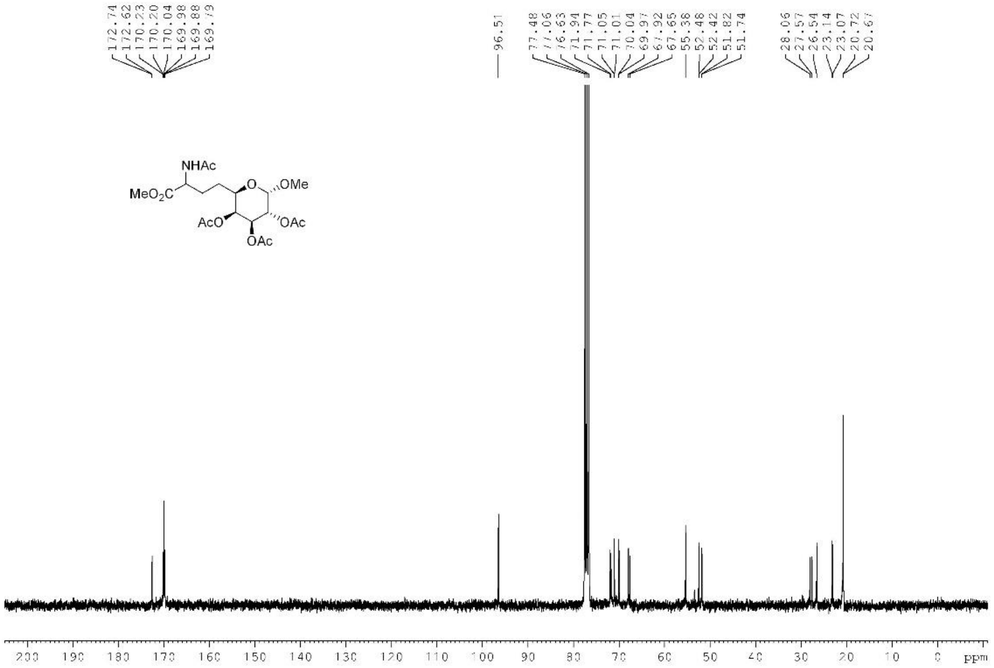

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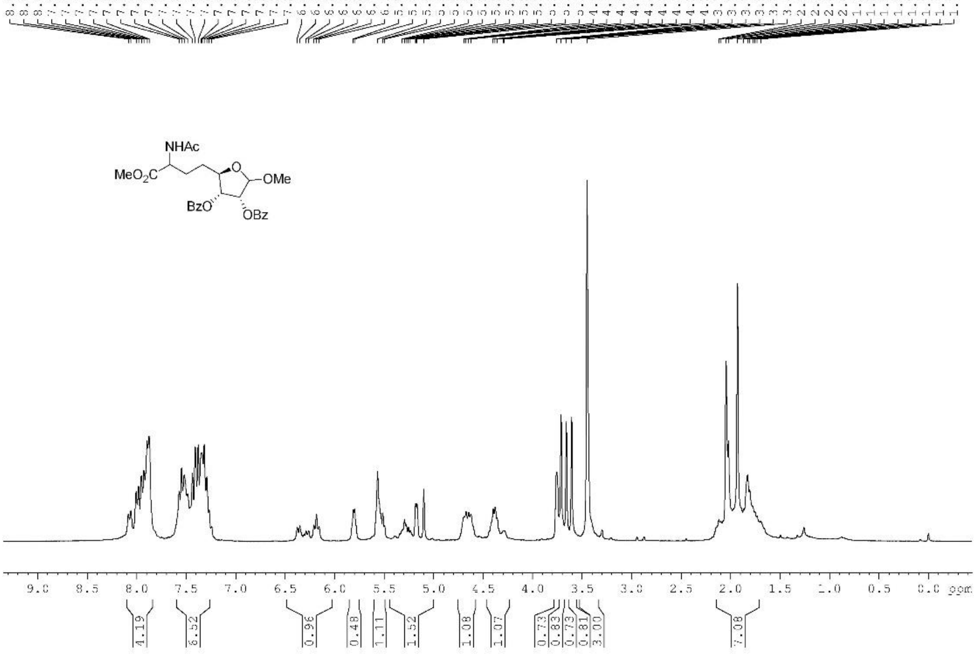

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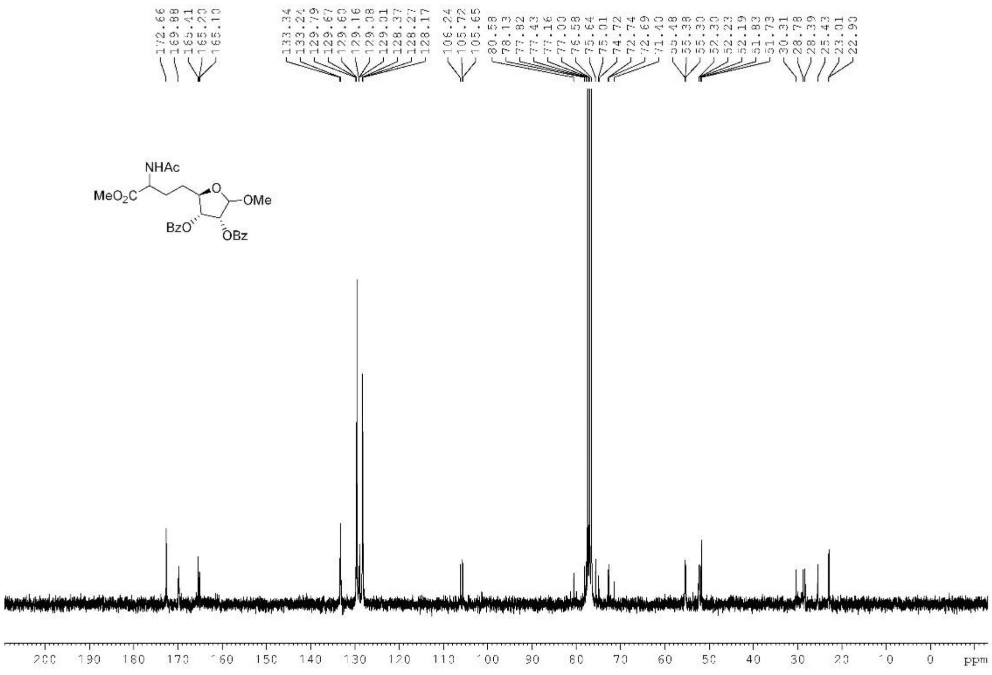

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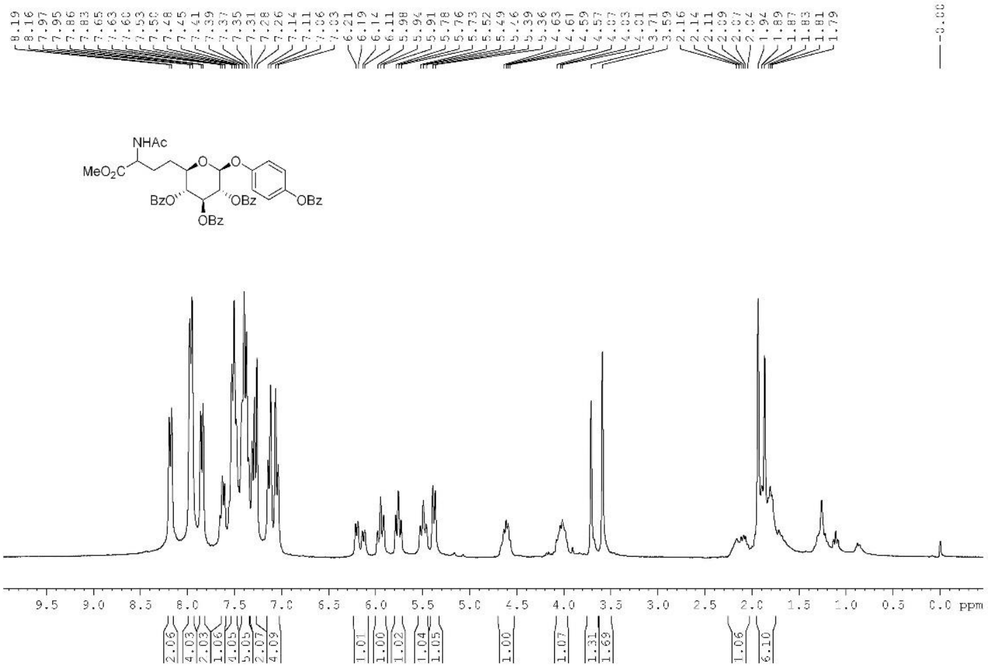

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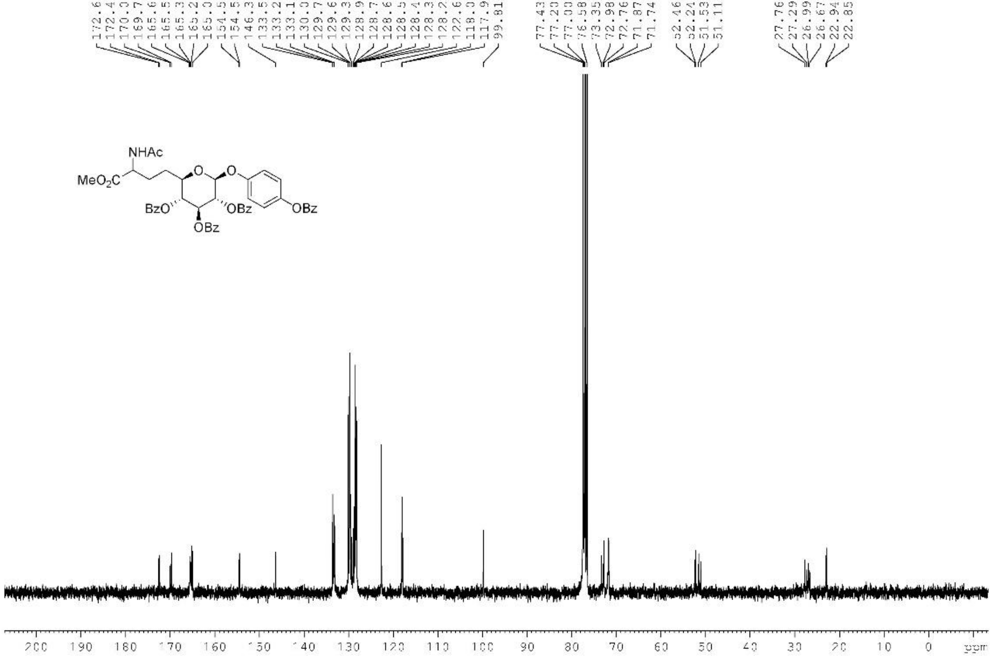

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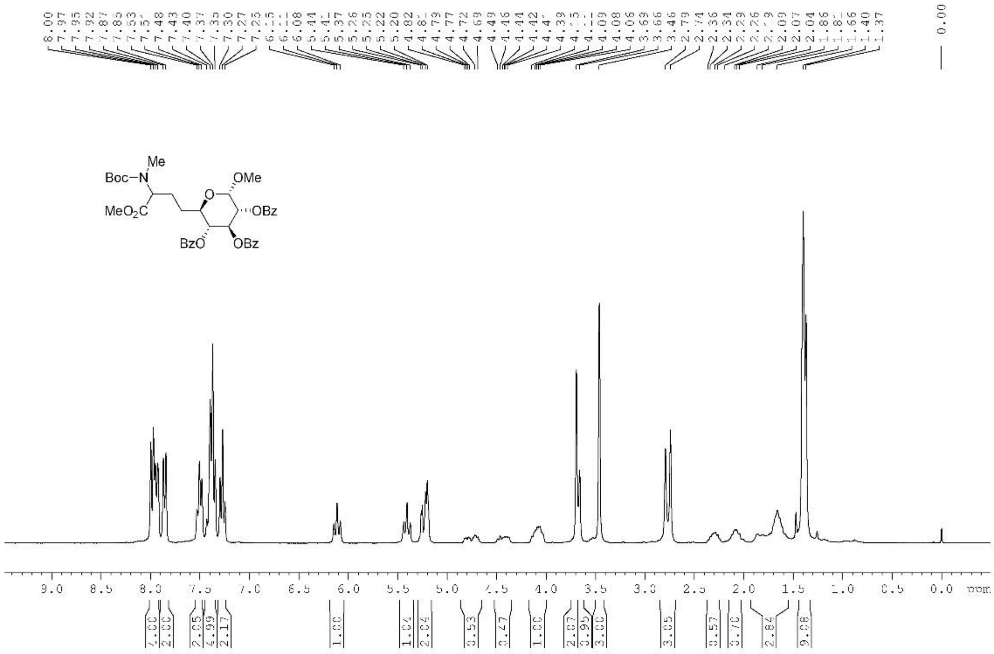

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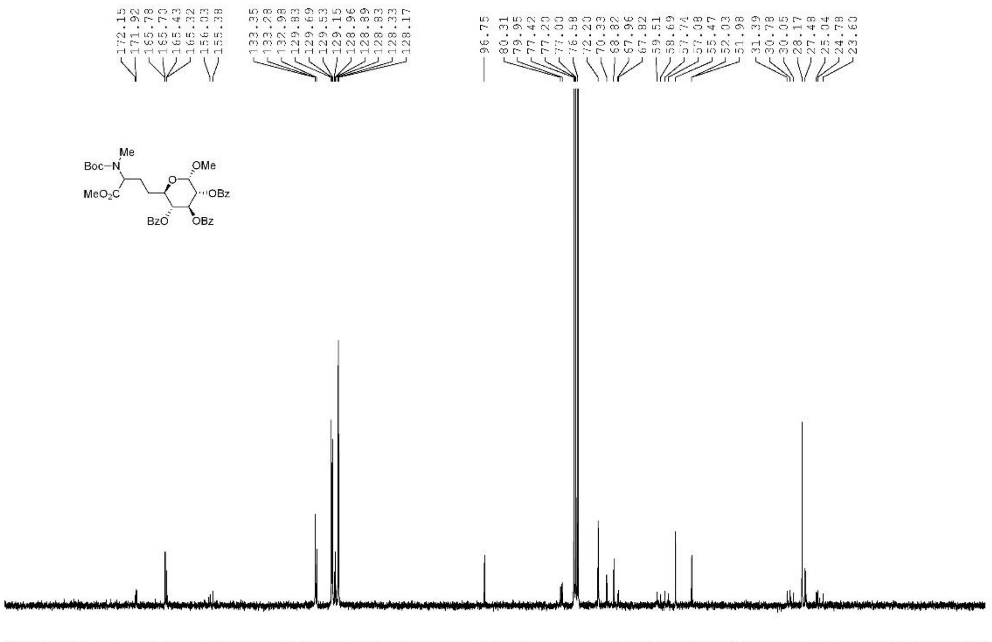

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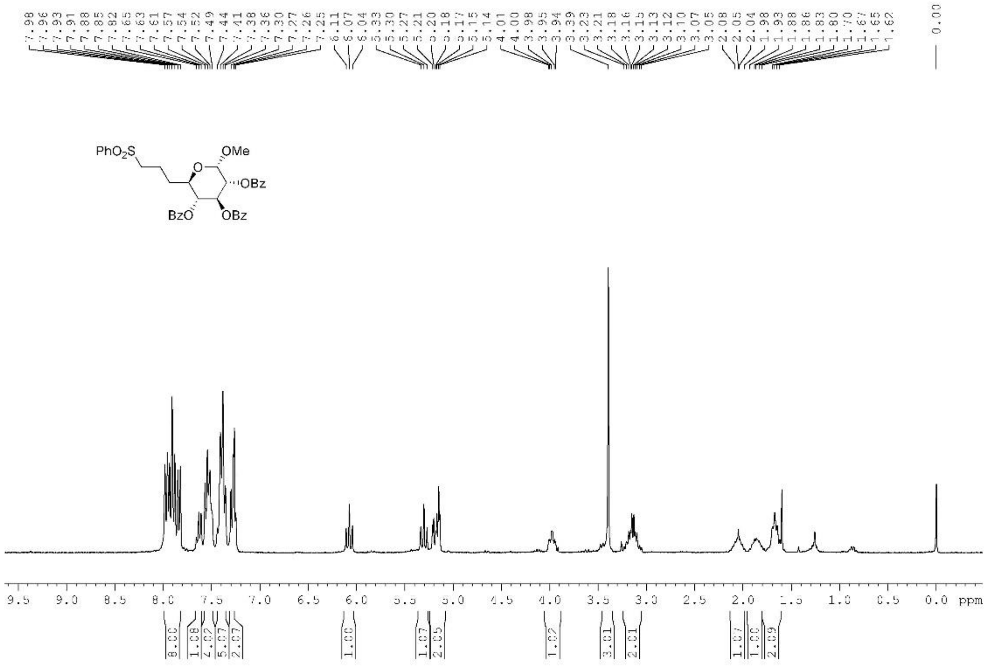

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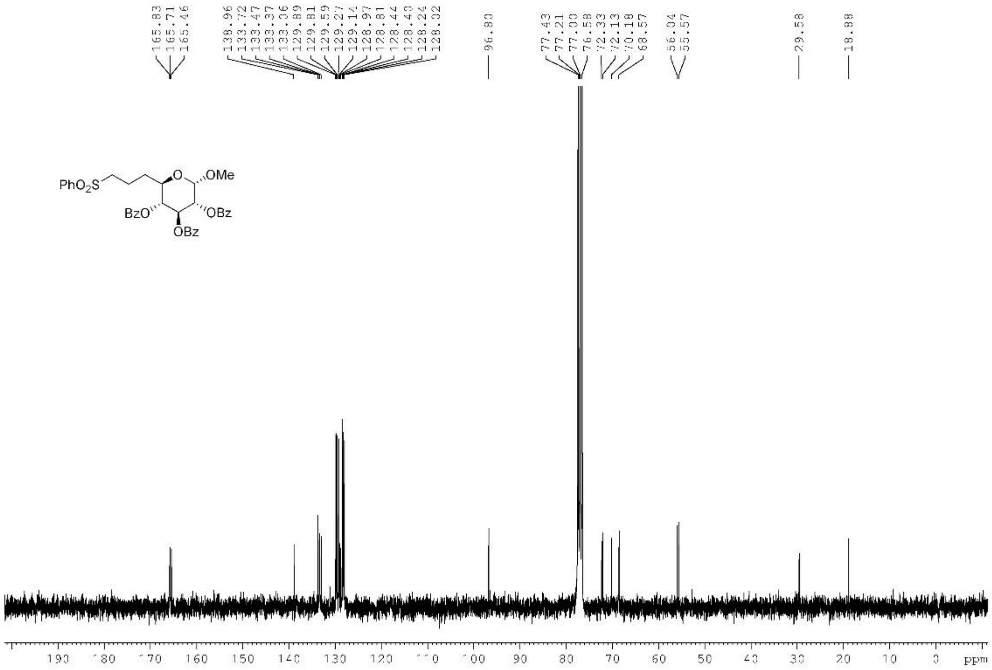

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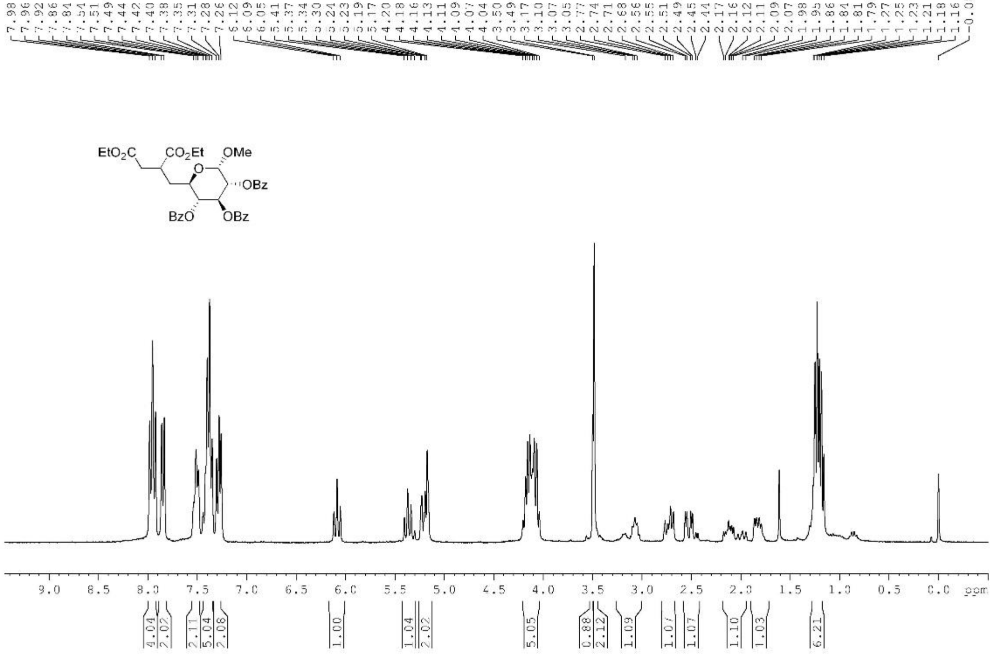

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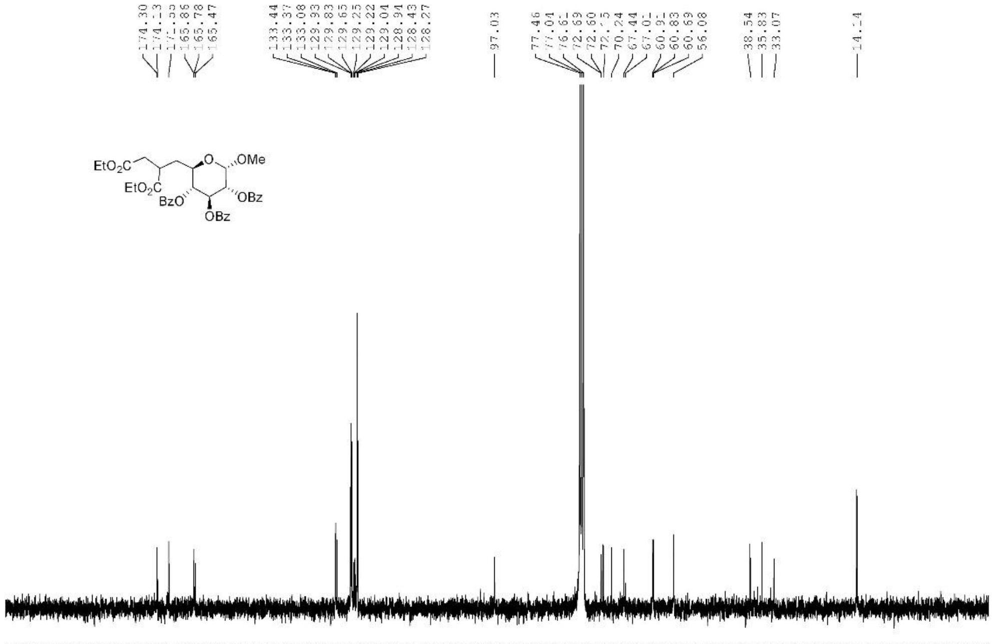

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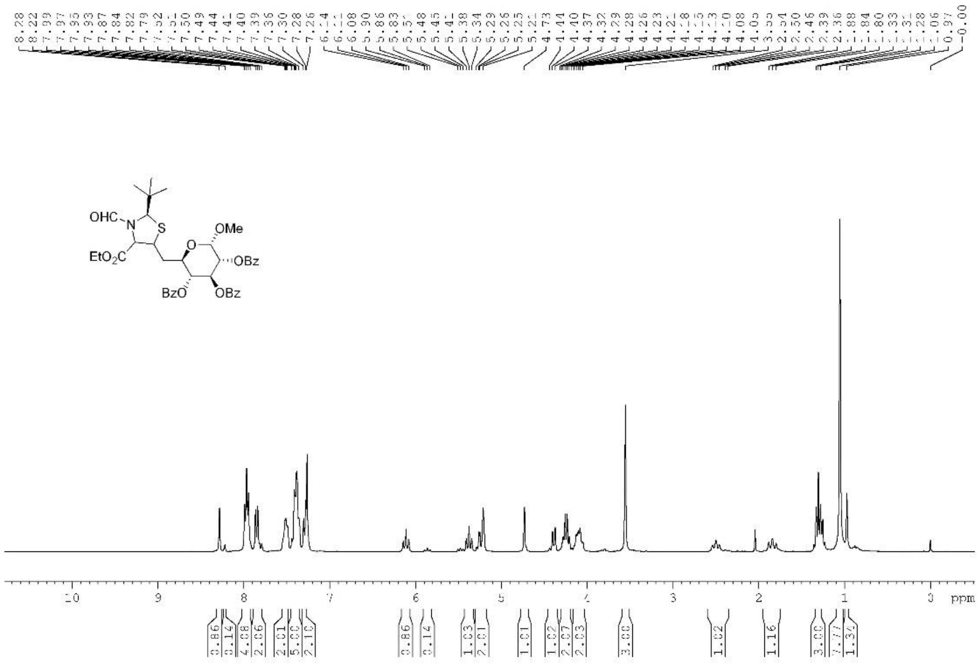

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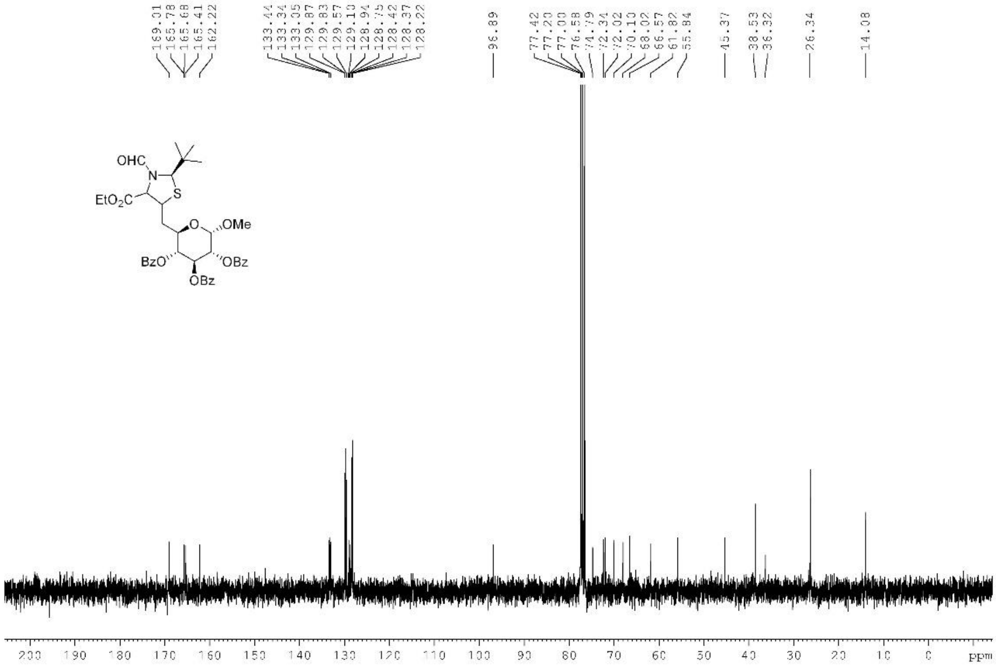

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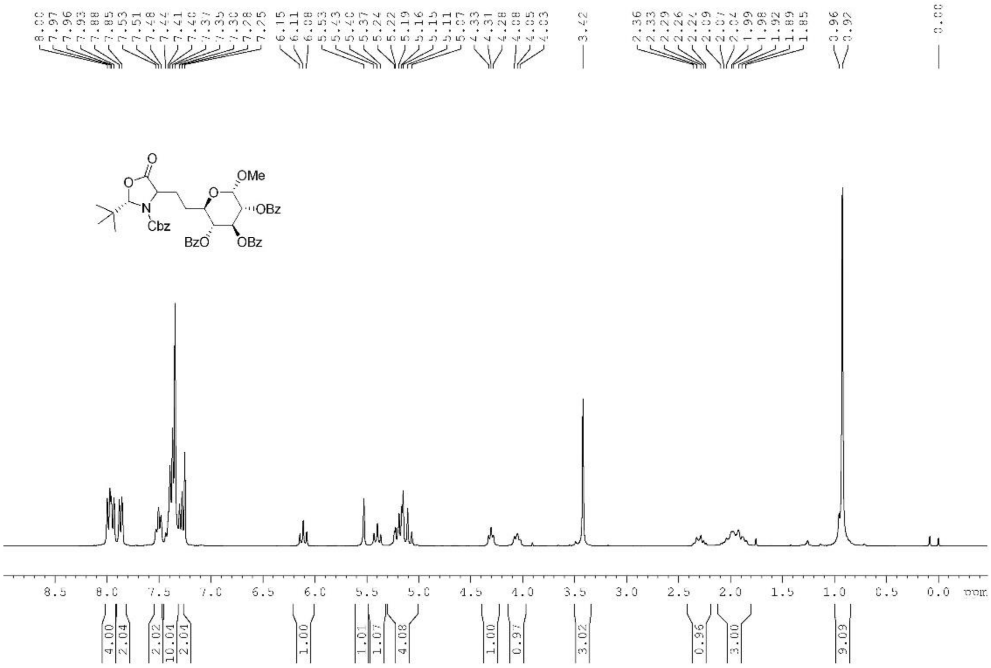

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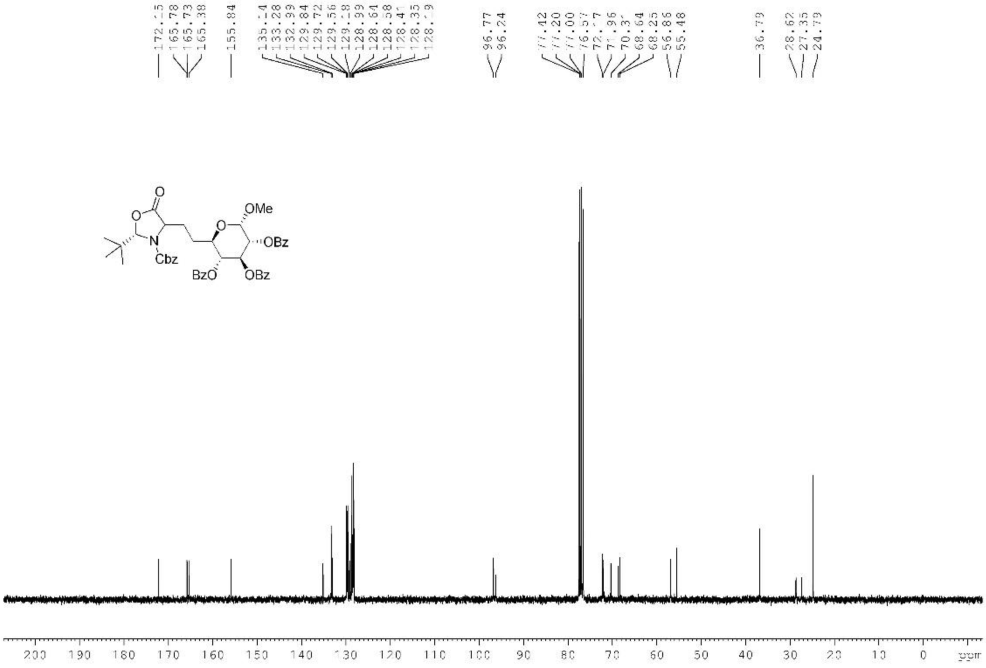

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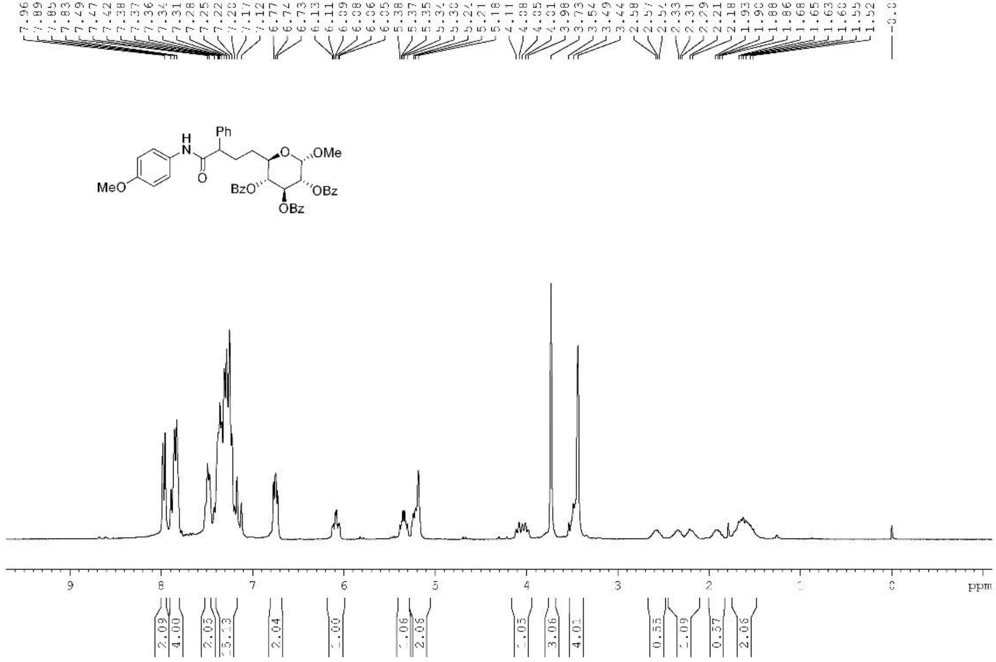

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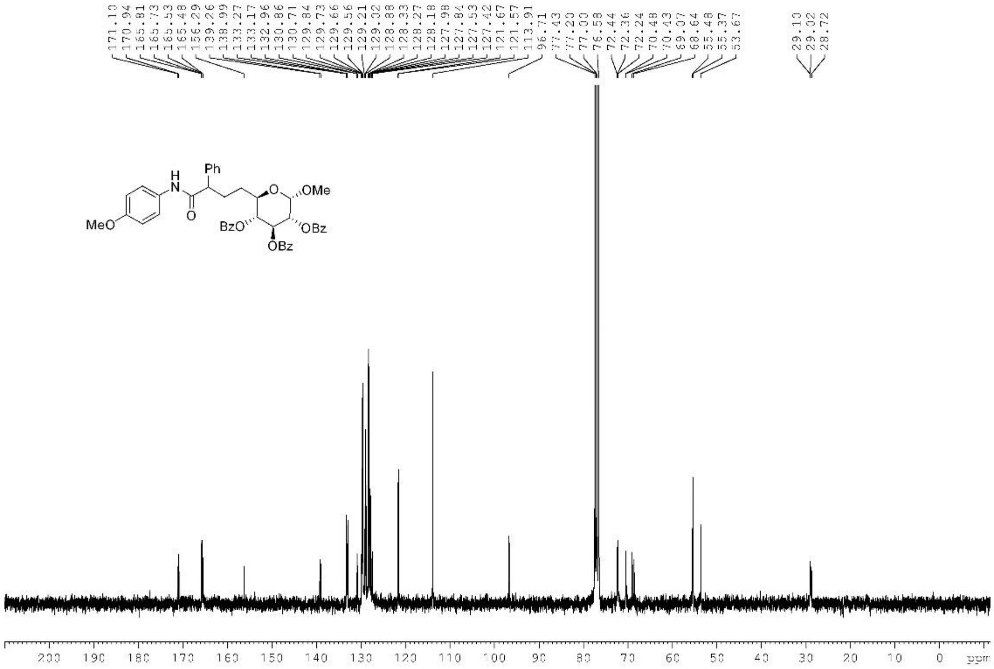

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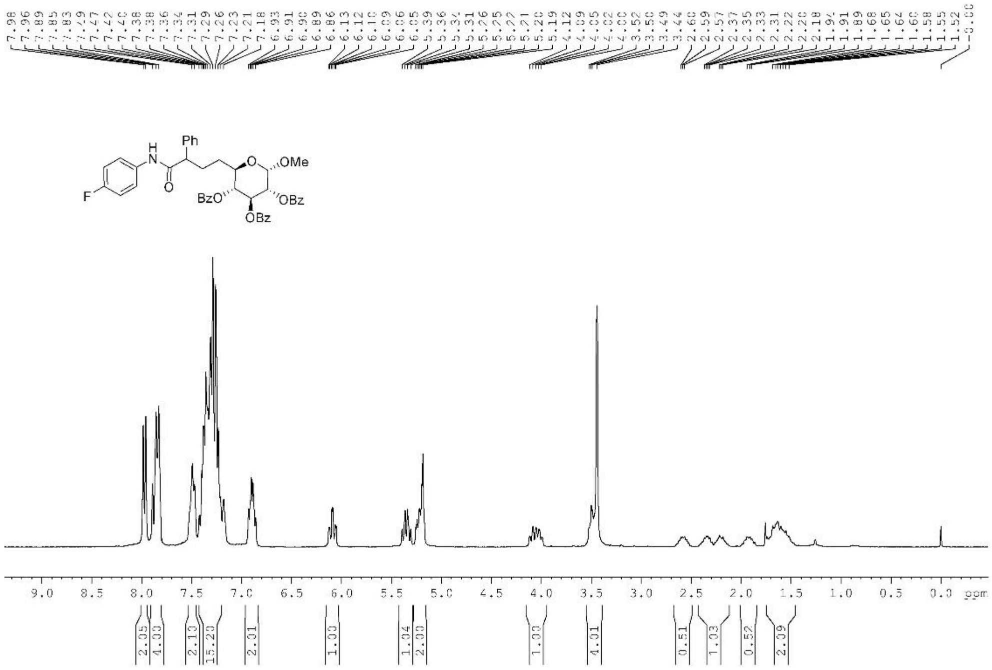

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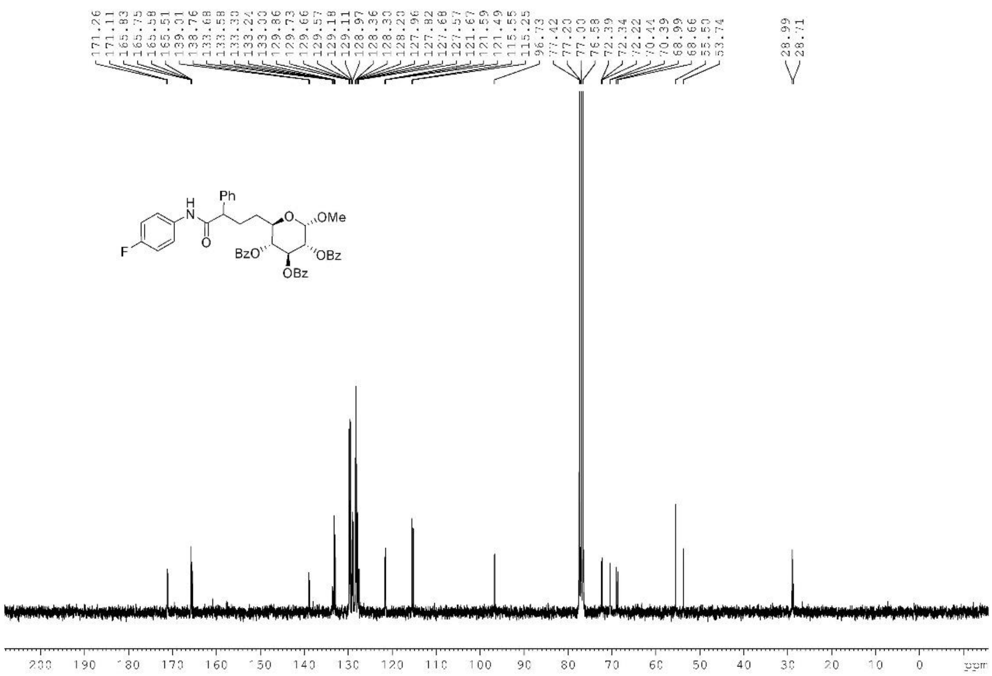

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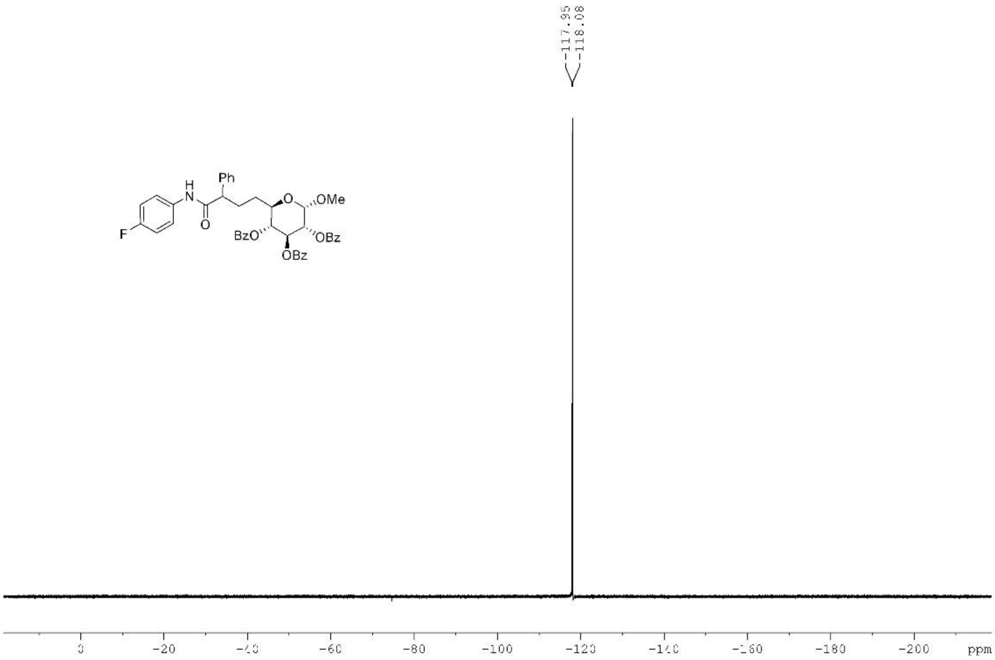

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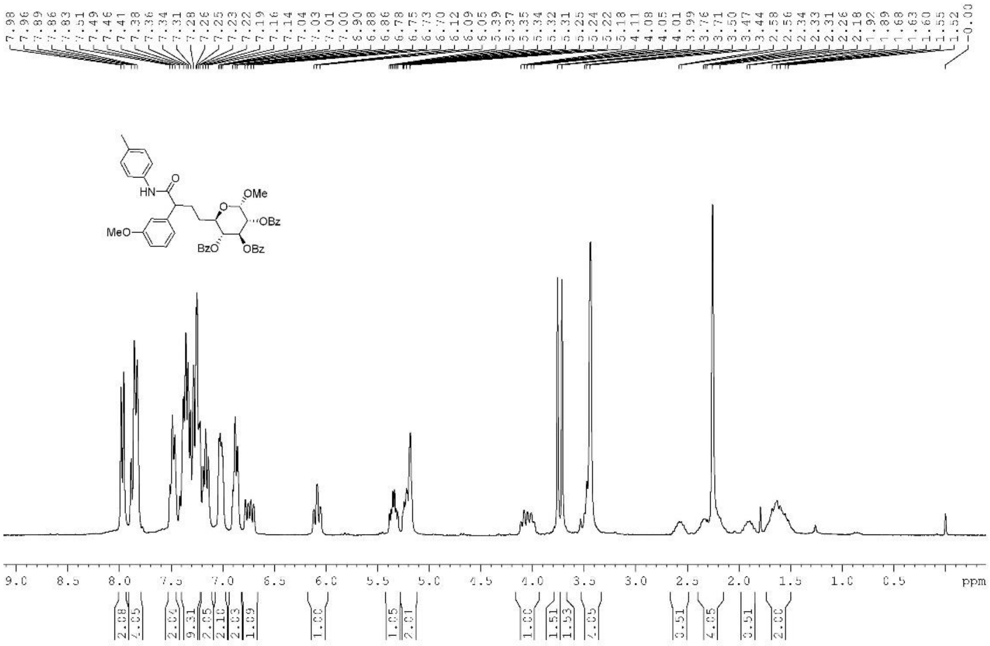

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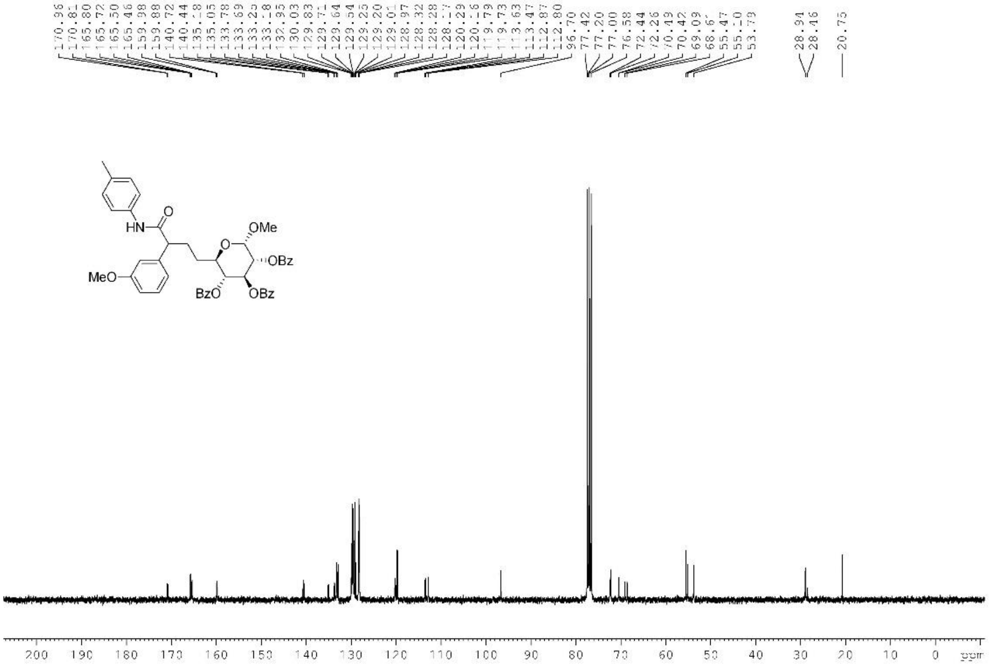

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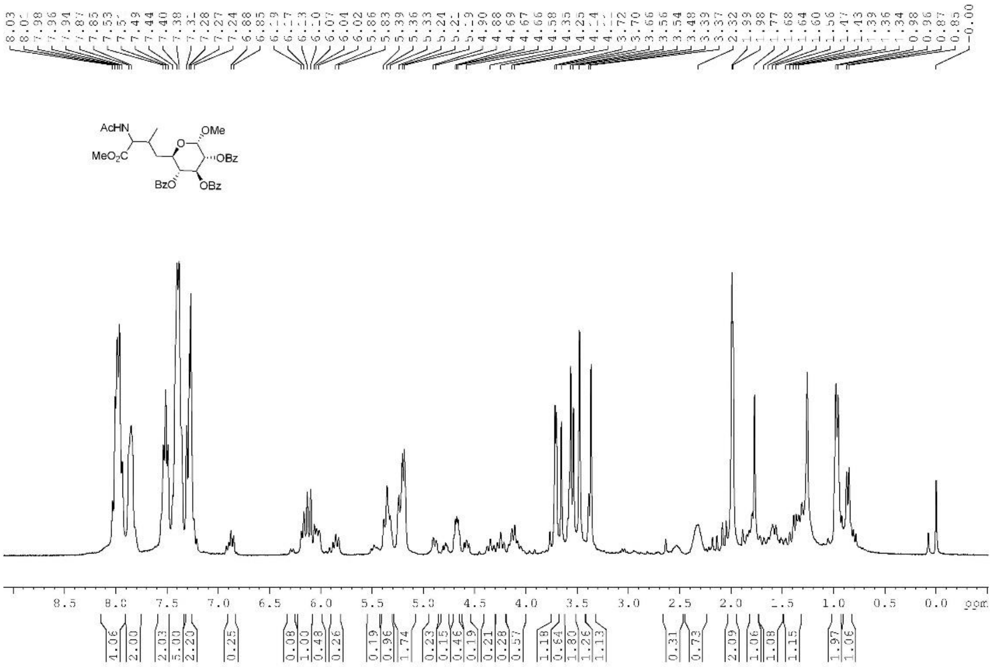
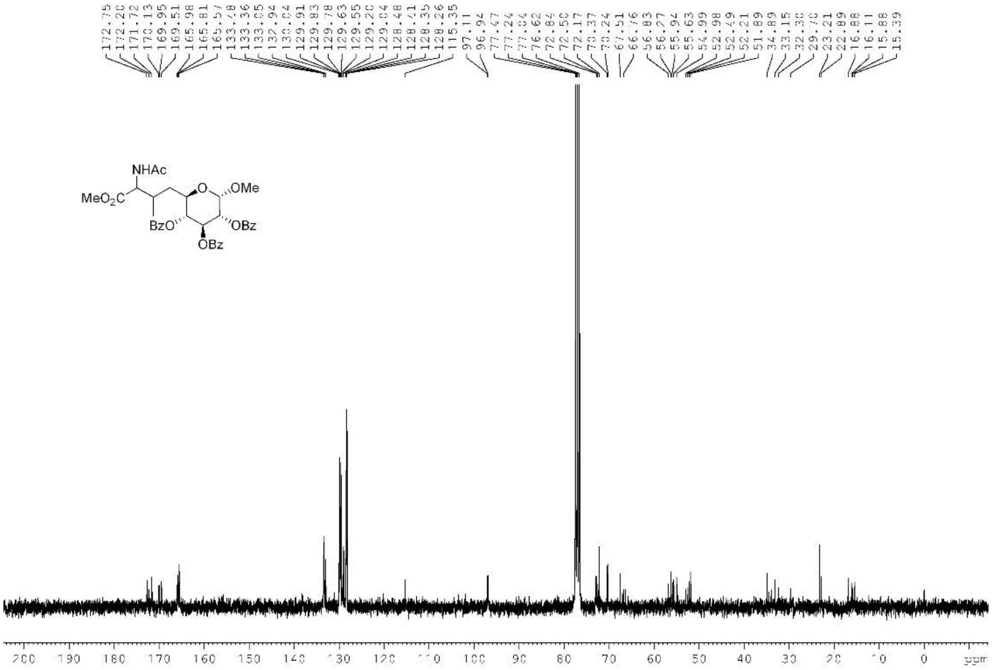


The ^{13}C NMR spectrum of **19**



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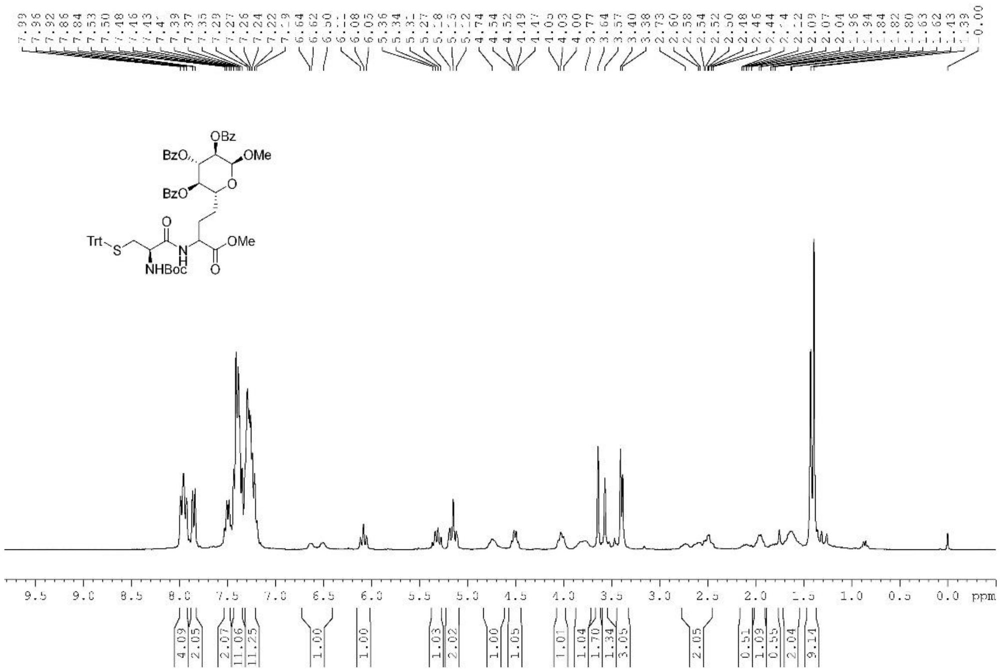

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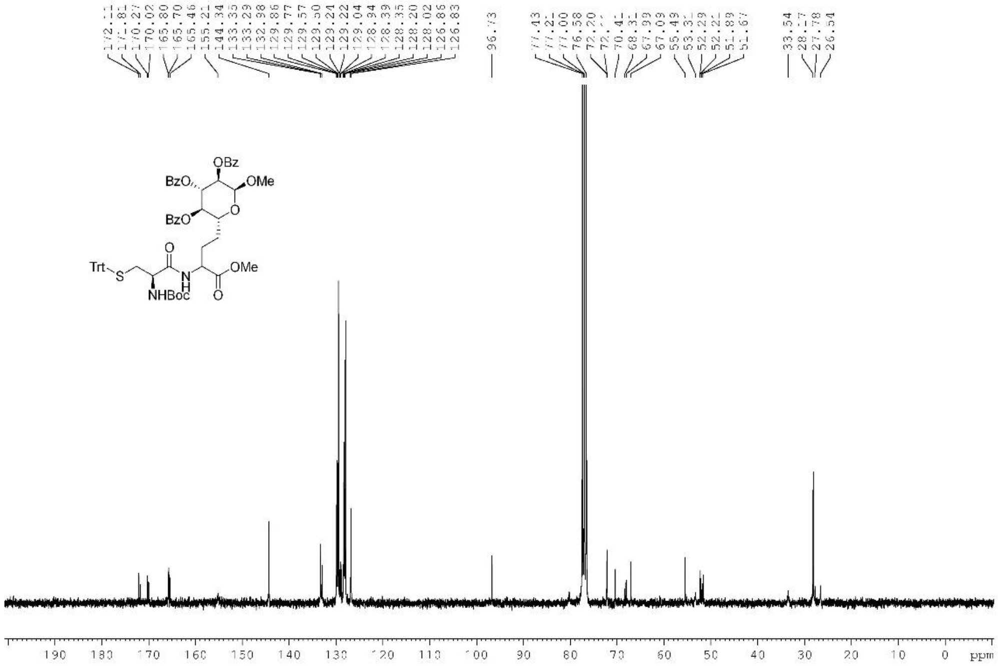

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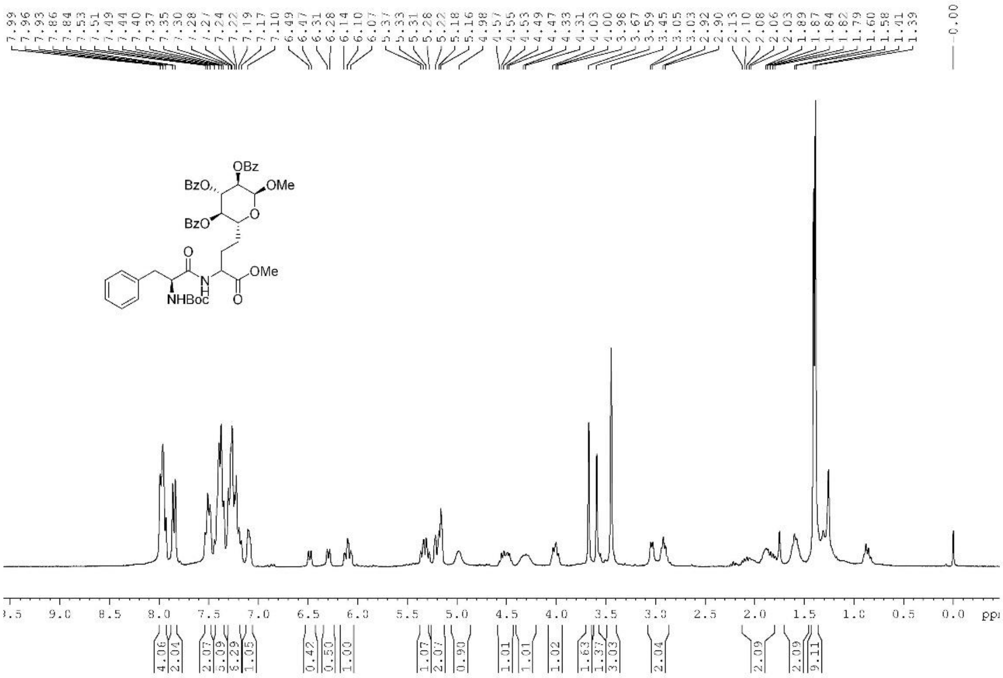

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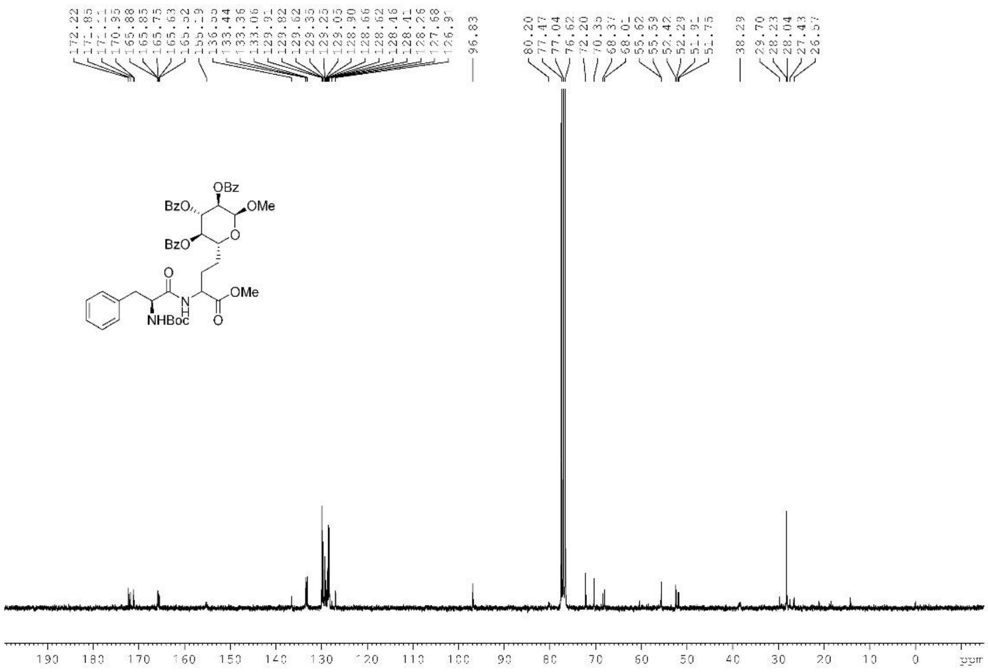

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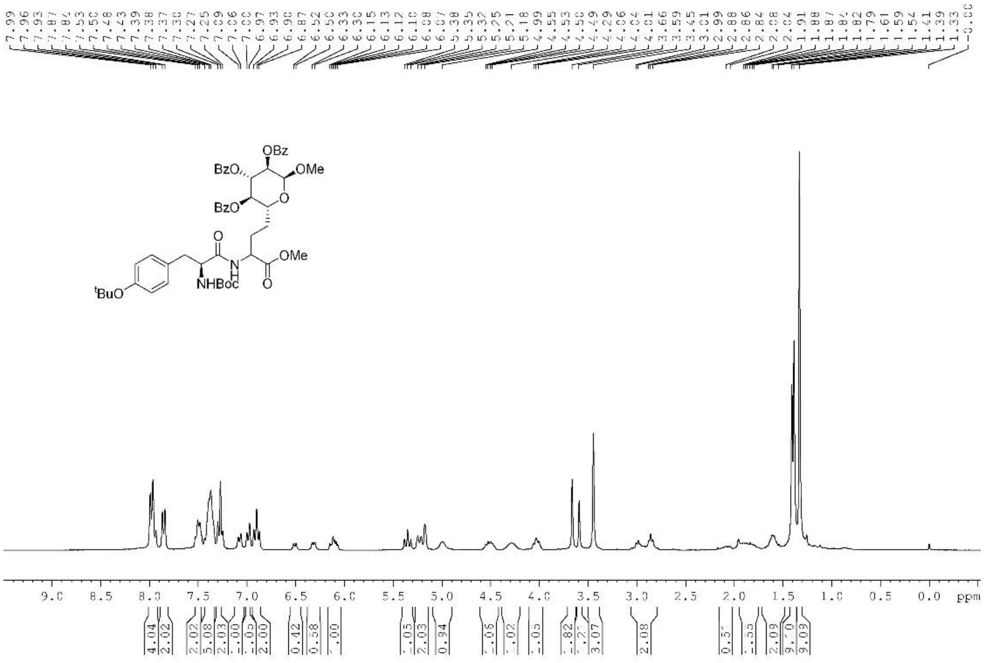

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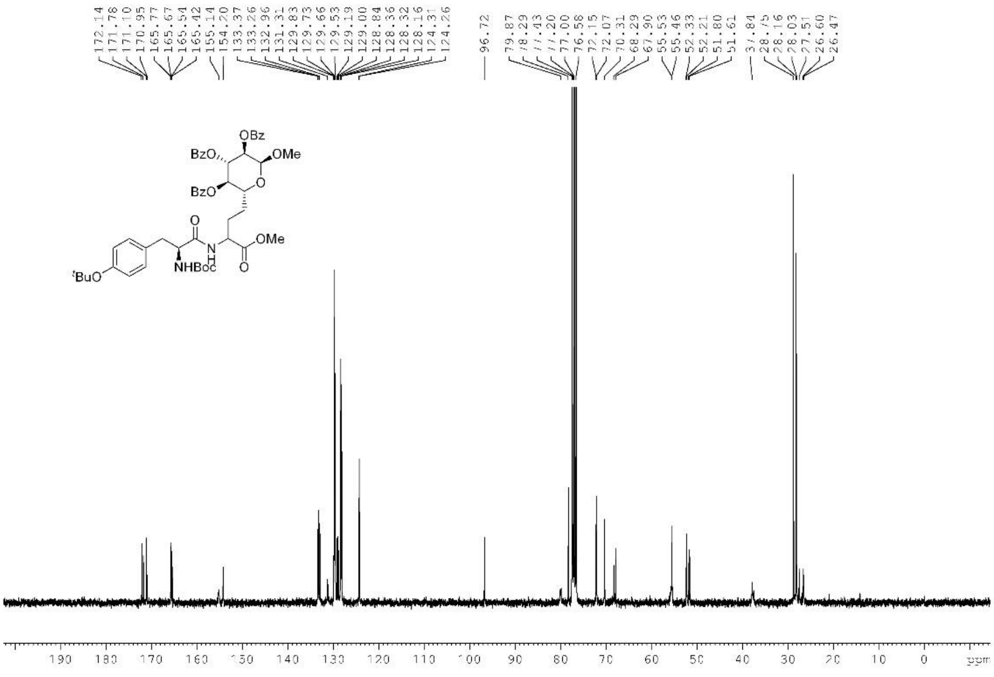

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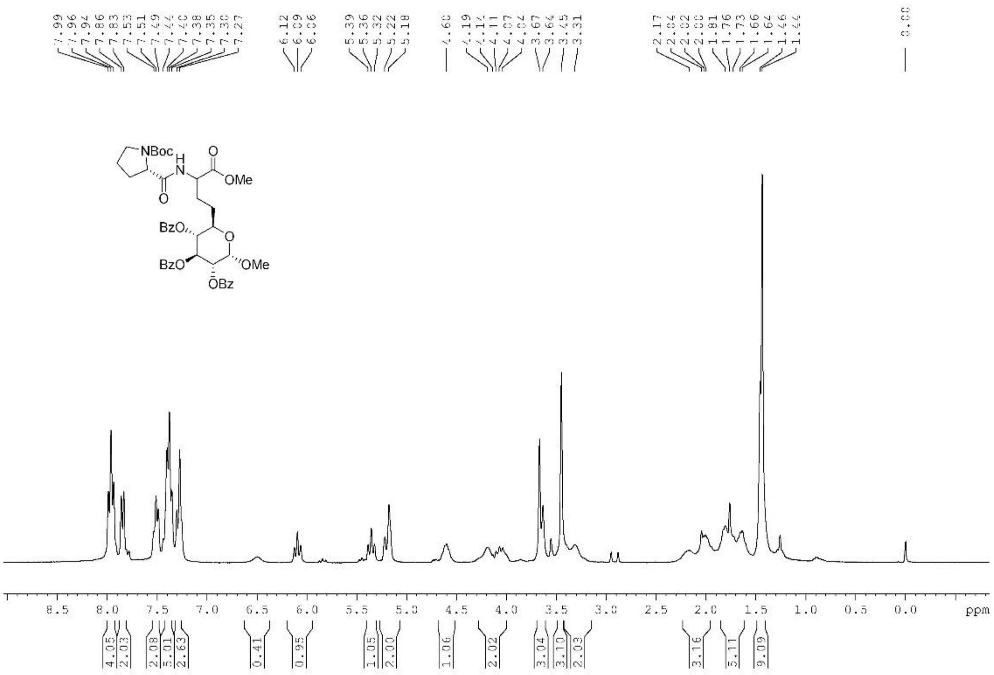

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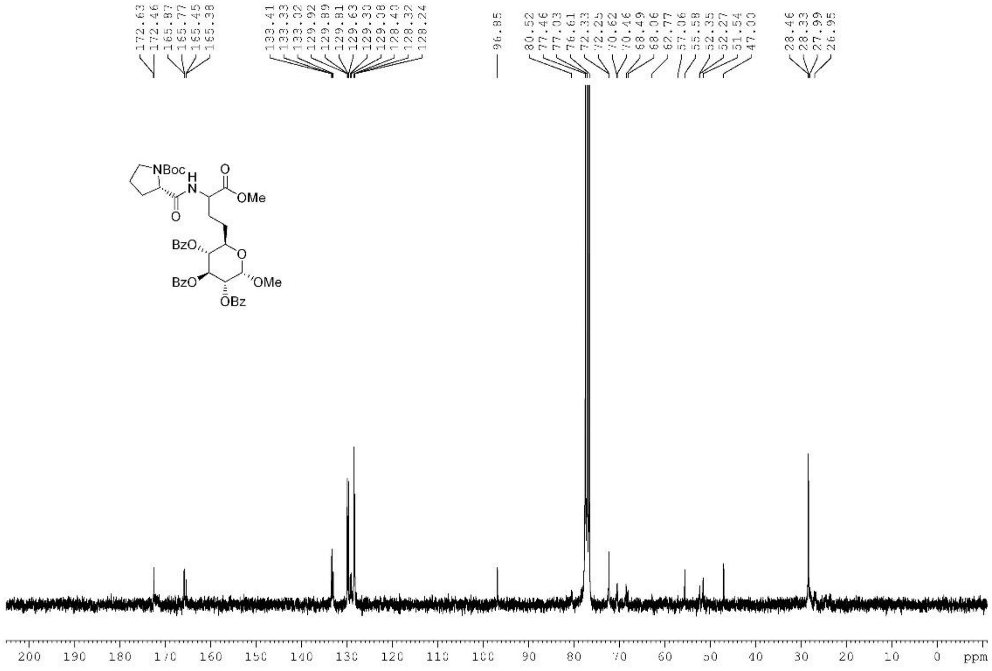

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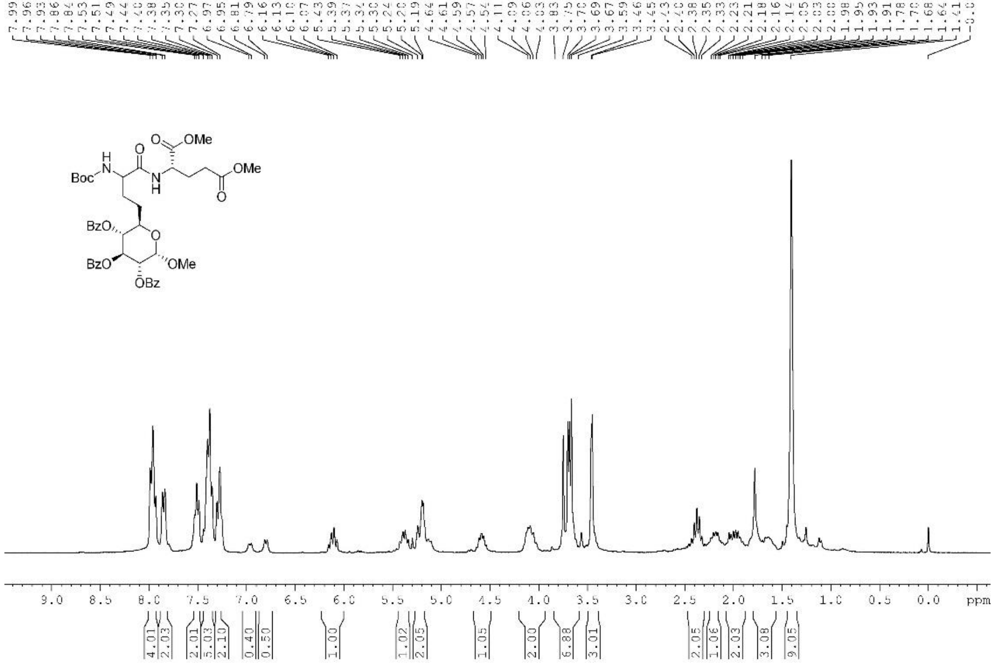

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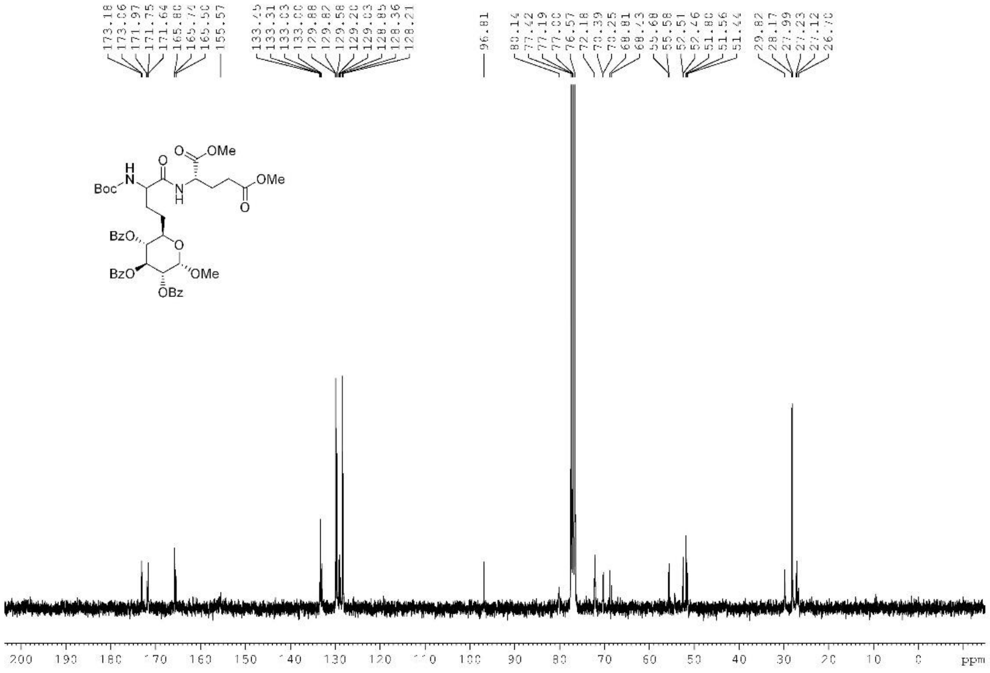

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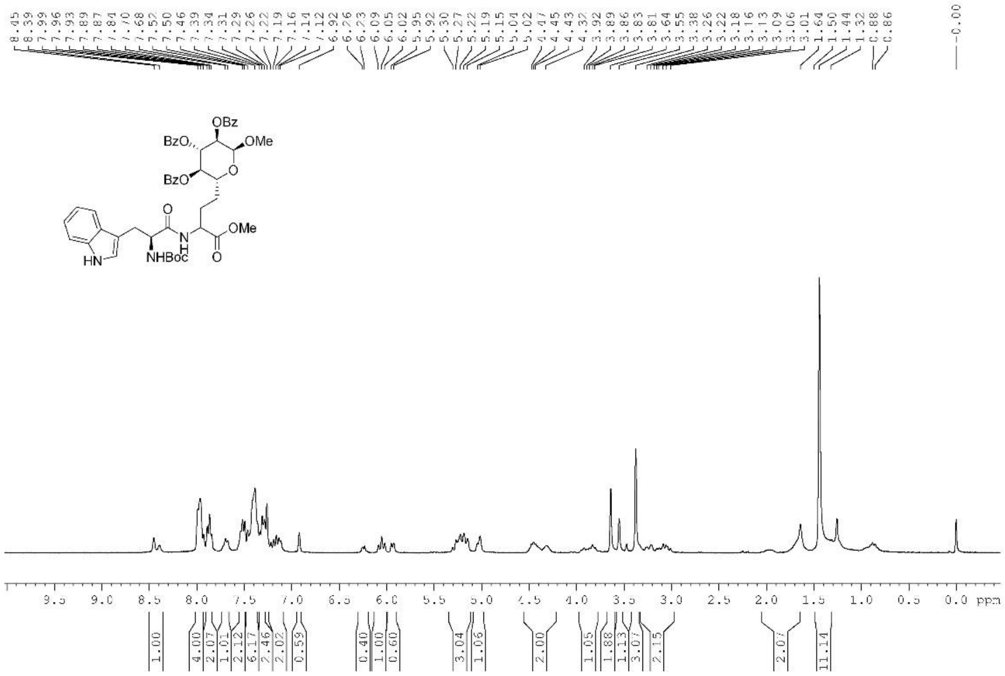
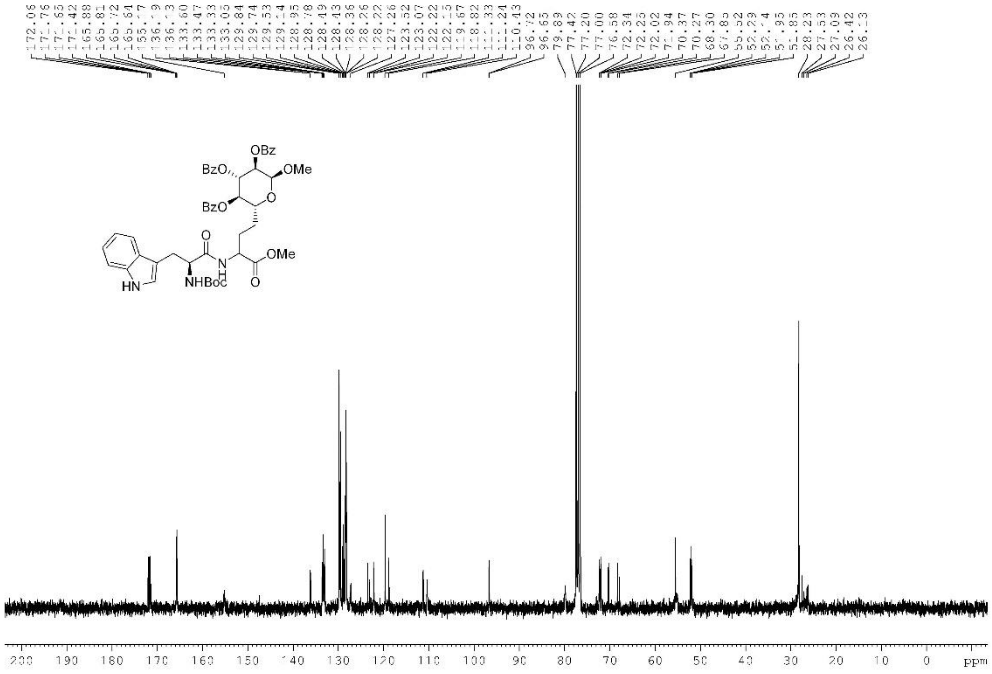


The ^{13}C NMR spectrum of **25**



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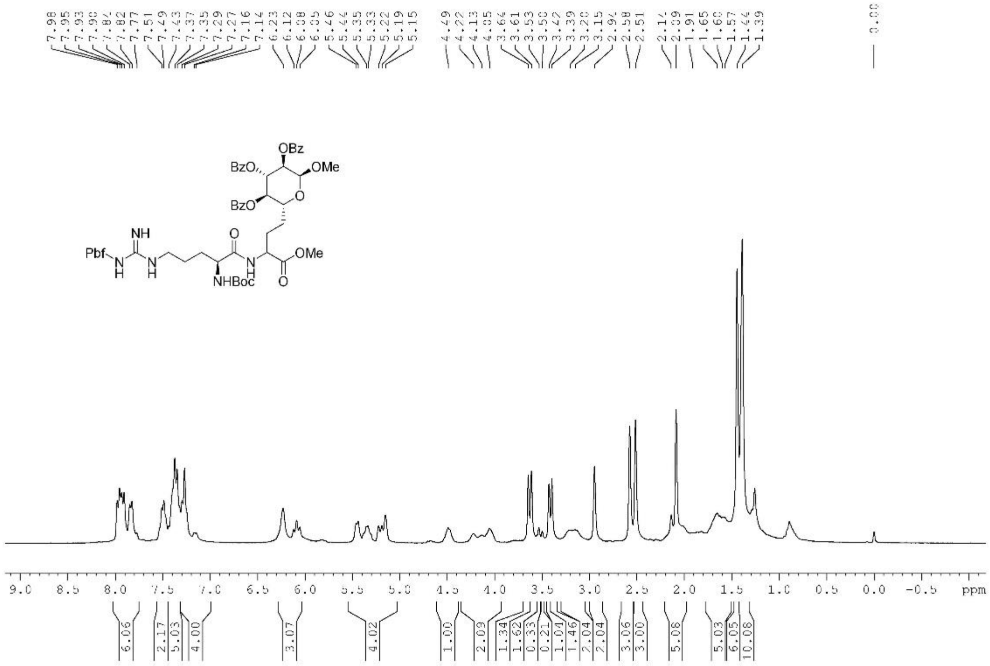
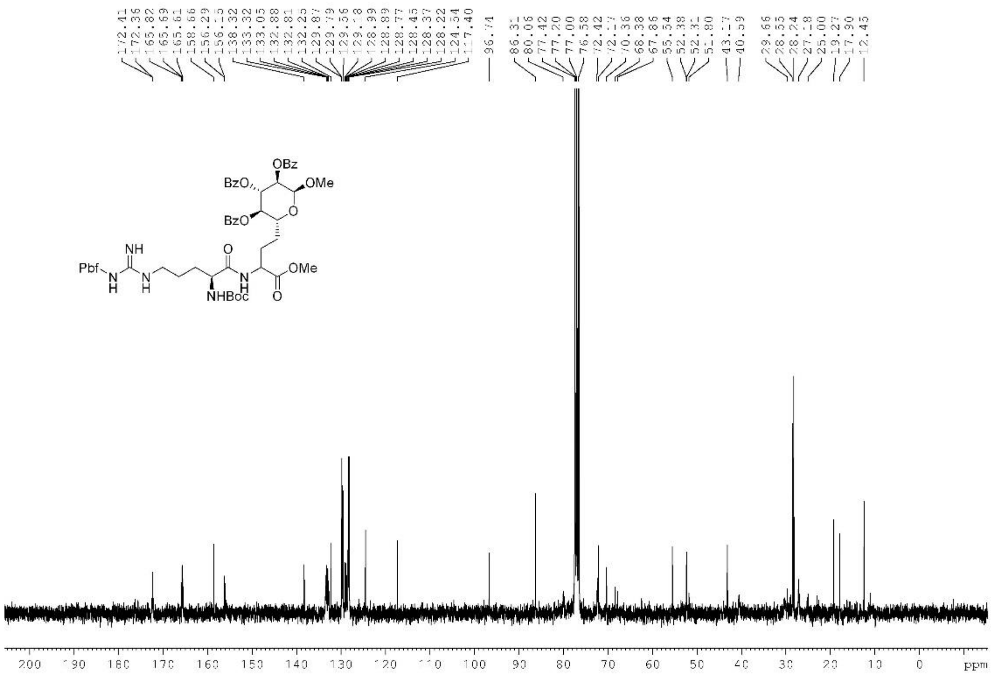


The ^{13}C NMR spectrum of **26**



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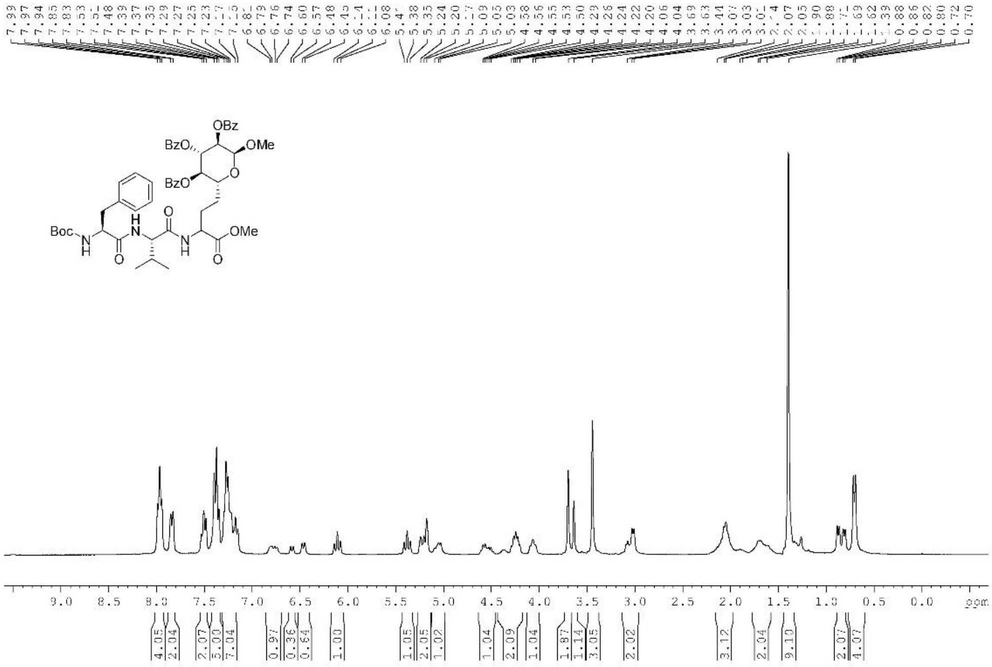
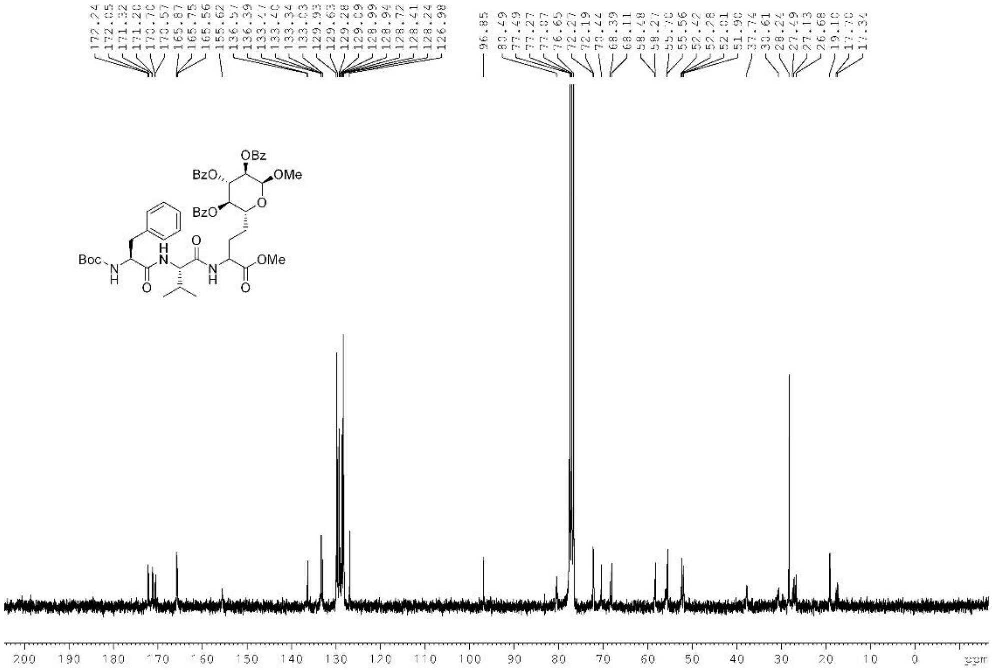


The ^{13}C NMR spectrum of **27**



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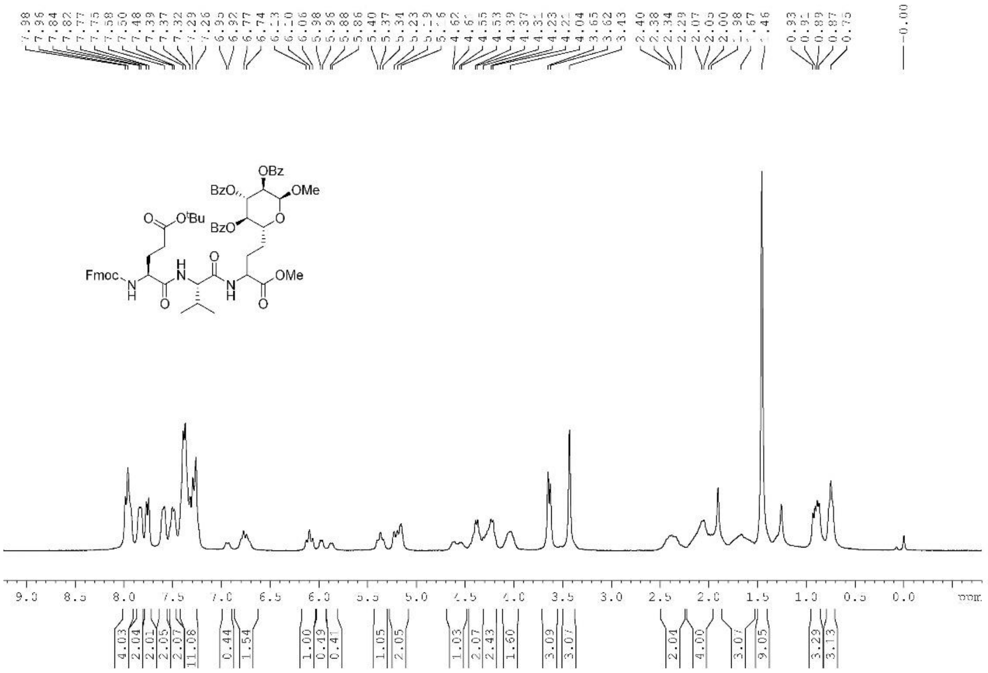

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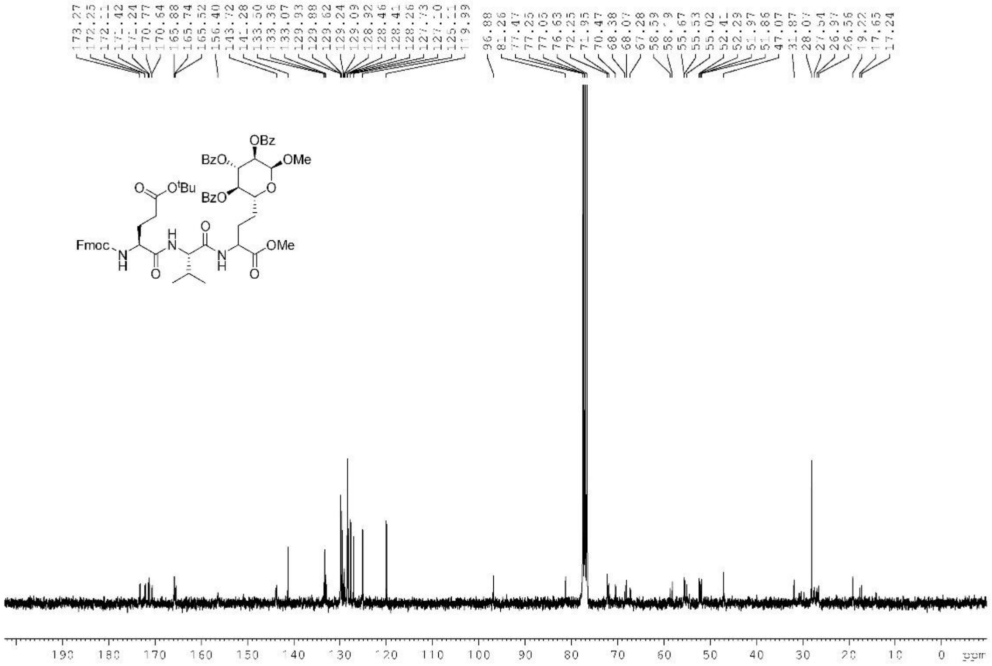

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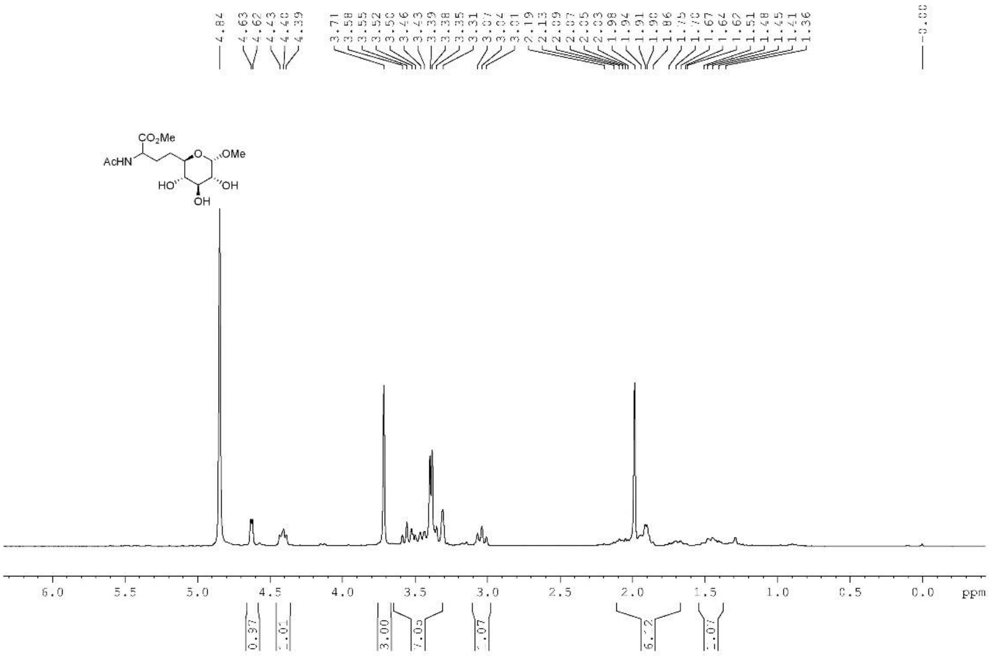

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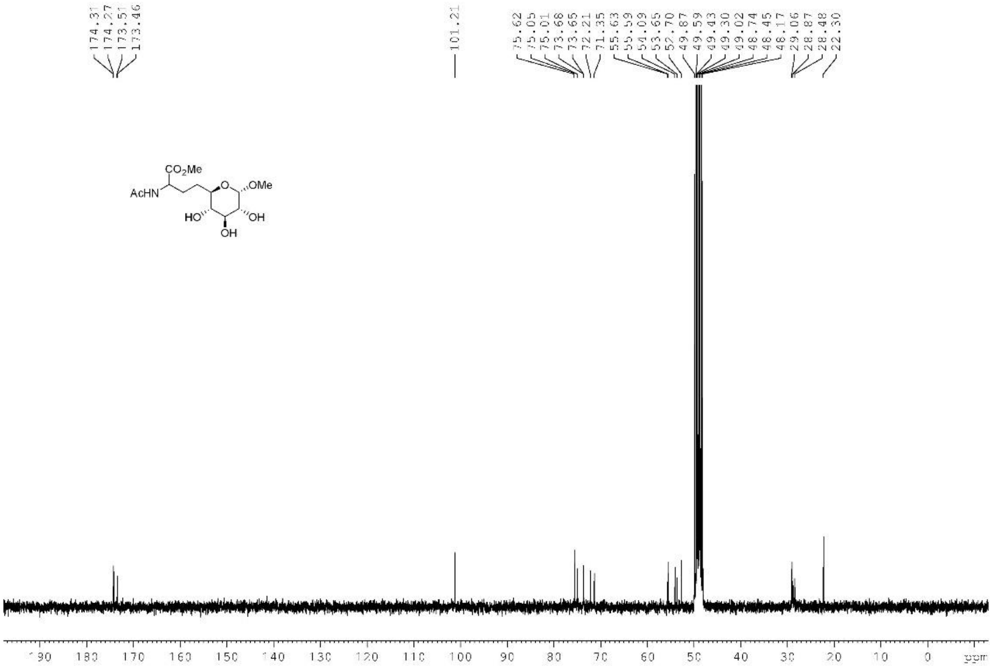

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