

Supporting information

Green synthesis of 1-deoxynojirimycin derivatives by reductive amination in water and “borrowing hydrogen” without solvent

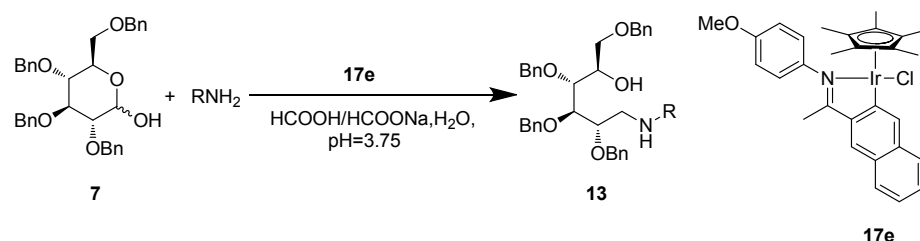
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I. Experimental Details:

General:

All the air or moisture sensitive reactions and manipulations were performed under an inert atmosphere in oven-dried glassware. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 spectrometer using TMS as an internal reference. Coupling constant (J) values are given in Hz. Optical rotation analyses were performed on a Perkin-Elmer Model 343 Polarimeter. HRMS were recorded on a ZAB-HS spectrometer with ES ionization (ESI). All commercially available reagents were used as received. Complexed **17e**,¹ $[\text{IrCp}^*\text{I}_2]_2$,² and $[\text{Cp}^*\text{Ir}(\text{NH}_3)_3]\text{I}_2$ ³ were prepared according to literature's procedure.

1. General procedure for Reductive Amination:

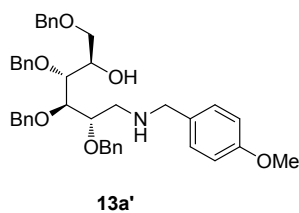


Compound **7** (10 mmol) and complexe **17e** (13.0mg, 0.2% mmol) were charged under argon-atomsphere in a three necked bottle with reflux device. Amine (20 mmol) was then introduced with vigorous stirring for 15 min. To the mixture was added $\text{HCOOH}-\text{HCOONa}$ buffer ($\text{pH} = 3.60$), prepared from HCOOH (88%, 14 mL), $\text{HCOONa} \cdot 2\text{H}_2\text{O}$ (24.5 g) and water (26 mL). The resulting mixture was bubbled with argon for 15 min at room temperature, and was heated at 90°C for 24 h with stirring. The reaction mixture was allowed to cool to room temperature and diluted with ethyl acetate. The organic layer was washed with water and saturated brine solution, dried over anhydrous Na_2SO_4 . The solvent was removed under vacuum and the product was purified by SiO_2 column chromatography (Eluent: Hexane: EtOAc=2:1~1:1).

(2*R*,3*R*,4*R*,5*S*)-6-(benzylamino)-1,3,4,5-tetrakis(benzyloxy)hexan-2-ol (**13a**)

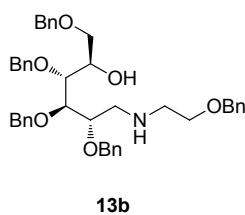
Colorless oil. Yield: 68.0%. ^1H NMR (400 MHz, CDCl_3): $\delta = 7.45 - 7.20$ (m, 25H), 4.78 – 4.48 (m, 8H), 4.08 (dd, $J = 10.3, 5.3$ Hz, 1H), 3.97 (dd, $J = 6.4, 3.6$ Hz, 1H), 3.92 (dd, $J = 10.3, 5.9$ Hz, 1H), 3.74 (dd, $J = 6.6, 3.5$ Hz, 1H), 3.72 – 3.59 (m, 4H), 2.84 (dd, $J = 12.5, 4.1$ Hz, 1H), 2.67 (dd, $J = 12.5, 5.8$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): $\delta = 140.32, 138.50, 138.27, 138.22, 138.14, 128.44, 128.38, 128.34, 128.13, 127.97, 127.92, 127.83, 127.77, 127.75, 127.69, 127.68, 126.90, 79.46, 79.38, 77.71, 74.54, 73.46, 73.16, 73.12, 71.38, 70.78, 53.85, 49.04$. $[\alpha]_D^{20} = +11.0^\circ$ ($c = 1, \text{CHCl}_3$). HRMS (ESI+) m/z calculated for $\text{C}_{41}\text{H}_{45}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 632.3371, found: 632.3384.

(2*R*,3*R*,4*R*,5*S*)-1,3,4,5-tetrakis(benzyloxy)-6-((4-methoxybenzyl)amino)hexan-2-ol (**13a'**)



Light yellow oil. Yield: 69.7%. ¹H NMR (400 MHz, CDCl₃): δ = 7.45 – 7.27 (m, 20H), 7.23 (d, J = 8.5 Hz, 2H), 6.91 (dd, J = 8.5 Hz, 2H), 4.84 (d, J = 11.3 Hz, 1H), 4.76 (dd, J = 11.4, 5.6 Hz, 2H), 4.67 (dd, J = 11.4, 7.8 Hz, 2H), 4.63 – 4.54 (m, 3H), 4.15 (dd, J = 10.1, 5.5 Hz, 1H), 4.04 (dd, J = 6.3, 3.6 Hz, 1H), 3.98 (dd, J = 10.3, 5.8 Hz, 1H), 3.84 (d, J = 3.9 Hz, 3H), 3.84 – 3.79 (m, 1H), 3.78 – 3.71 (m, 2H), 3.69 (d, J = 9.8 Hz, 2H), 2.90 (dd, J = 12.5, 4.0 Hz, 1H), 2.73 (dd, J = 12.5, 5.8 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃): δ = 158.67, 138.61, 138.39, 138.35, 138.24, 132.54, 129.37, 128.49, 128.44, 128.40, 128.15, 128.02, 127.96, 127.80, 127.74, 127.73, 113.79, 79.59, 79.50, 77.88, 74.62, 73.50, 73.23, 73.14, 71.51, 70.87, 55.32, 53.32, 48.99. [α]_D²⁰ = +9.6° (c = 1, CHCl₃). HRMS (ESI+) m/z calculated for C₄₂H₄₇NO₆ [M+H]⁺: 662.3476, found: 662.3481.

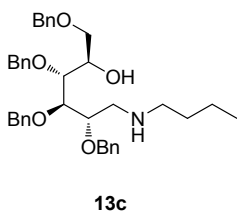
(2R,3R,4R,5S)-1,3,4,5-tetrakis(benzyloxy)-6-((2-(benzyloxy)ethyl)amino)hexan-2-ol (13b)



Light yellow oil. Yield: 67.2%. ¹H NMR (400 MHz, CDCl₃): δ = 7.51 – 7.23 (m, 25H), 4.87 – 4.50 (m, 10H), 4.21 – 3.79 (m, 4H), 3.72 (d, J = 4.3 Hz, 2H), 3.58 (t, J = 5.0 Hz, 2H), 3.16 (s, 2H), 2.93 – 2.69 (m, 4H). ¹³C NMR (101 MHz, CDCl₃): δ = 138.49, 138.41, 138.32, 138.29, 138.23, 128.46, 128.43, 128.39, 128.13, 128.05, 127.92, 127.81, 127.76, 127.72, 127.65, 79.46, 79.01, 77.90, 74.49, 73.47, 73.37, 73.33, 73.18, 71.45, 70.90, 69.45, 49.83, 49.30. [α]_D²⁰ = +15.6° (c = 1, CHCl₃).

HRMS (ESI+) m/z calculated for C₄₃H₄₉NO₆ [M+H]⁺: 676.3633, found: 676.3629.

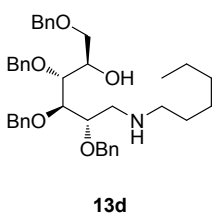
(2R,3R,4R,5S)-1,3,4,5-tetrakis(benzyloxy)-6-(butylamino)hexan-2-ol (13c)



Colorless oil. Yield: 61.7%. ¹H NMR (400 MHz, CDCl₃): δ = 7.63 – 7.03 (m, 20H), 4.90 – 4.52 (m, 8H), 4.26 – 3.67 (m, 6H), 2.94 – 2.83 (m, 1H), 2.79 – 2.77 (m, 1H), 2.52 (t, J = 7.0 Hz, 2H), 1.51 – 1.39 (m, 2H), 1.38 – 1.28 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 138.60, 138.37, 138.26, 128.50, 128.47, 128.44, 128.41, 128.15, 128.08, 127.93, 127.83, 127.77, 127.73, 79.58, 79.22, 77.96, 74.53, 73.48, 73.37, 73.33, 71.52, 70.97, 50.07, 49.77, 32.22, 20.53, 14.15. [α]_D²⁰ = +16.1° (c = 1, CHCl₃).

HRMS (ESI+) m/z calculated for C₃₈H₄₇NO₅ [M+H]⁺: 598.3527, found: 598.3532.

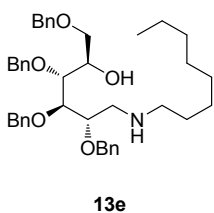
(2R,3R,4R,5S)-1,3,4,5-tetrakis(benzyloxy)-6-(hexylamino)hexan-2-ol (13d)



Light yellow oil. Yield: 62.3%. ¹H NMR (400 MHz, CDCl₃): δ = 7.40 – 7.33 (m, 20H), 4.96 – 4.43 (m, 8H), 4.19 – 3.63 (m, 6H), 2.96 – 2.79 (m, 1H), 2.79 – 2.65 (m, 1H), 2.49 (t, J = 7.2 Hz, 2H), 1.54 – 1.22 (m, 8H), 0.96 (t, J = 6.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 138.55, 138.30, 138.22, 128.48, 128.46, 128.45, 128.42, 128.38, 128.12, 128.06, 127.90, 127.81, 127.76, 127.74, 127.71, 79.52, 79.12, 77.88, 74.47, 73.47, 73.35, 73.32, 71.45, 70.93, 50.06, 31.84, 30.01, 27.06, 22.71, 14.17.

[α]_D²⁰ = +14.7° (c = 1, CHCl₃). HRMS (ESI+) m/z calculated for C₄₀H₅₁NO₅ [M+H]⁺: 626.3840, found: 626.3844.

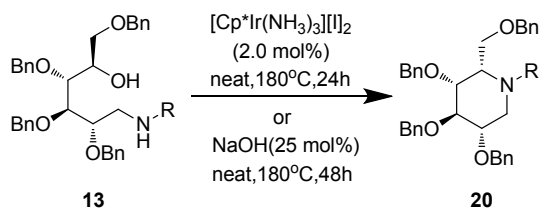
(2R,3R,4R,5S)-1,3,4,5-tetrakis(benzyloxy)-6-(octylamino)hexan-2-ol (13e)



Light yellow oil. Yield: 63.7%. ¹H NMR (400 MHz, CDCl₃): δ = 7.41 – 7.32 (m, 20H), 4.93 – 4.51 (m, 8H), 4.21 – 3.61 (m, 6H), 2.89 – 2.85 (m, 1H), 2.80 – 2.65 (m, 1H), 2.50 (t, J = 6.9 Hz, 2H), 1.55 – 1.21 (m, 12H), 0.98 (t, J = 5.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 138.58, 138.34, 138.24, 128.48, 128.46, 128.43, 128.39, 128.13, 128.06, 127.91, 127.81, 127.75, 127.71, 79.56, 79.20, 77.93, 74.50, 73.47, 73.37, 73.32, 71.49, 70.95, 50.10, 31.94, 30.11, 29.62, 29.39, 27.42, 22.77, 14.23.

[α]_D²⁰ = +14.1° (c = 1, CHCl₃). HRMS (ESI+) m/z calculated for C₄₂H₅₅NO₅ [M+H]⁺: 654.4153, found: 654.4167.

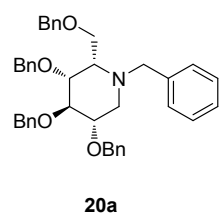
2. General procedure for intramolecular alkylation



Method A: Amino alcohol **13** (5.0 mmol) and $[\text{Cp}^*\text{Ir}(\text{NH}_3)_3][\text{I}]_2$ (63.2mg, 2.0 mol%) were charged under argon-atmosphere in a Schlenk flask. The reaction flask was heated to the 180°C under stirring for 24h, then the reaction mixture was allowed to cool to room temperature and diluted with EtOAc. The organic layer was washed with water and saturated brine solution, dried over Na_2SO_4 . The solvent was removed under vacuum and the product was purified by SiO_2 column chromatography (Eluent: Hexane: EtOAc=9:1~4:1).

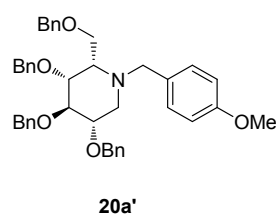
Method B: Amino alcohol **13** (4.0 mmol) and solid NaOH (40 mg, 25 mol%) were added to a glass flask. Then, the reaction mixture was heated to 180°C and vigorously stirred for 48h under Ar_2 atmosphere. The reaction mixture was allowed to cool to room temperature and diluted with EtOAc. The organic layer was washed with water and saturated brine solution, dried over Na_2SO_4 . The solvent was removed under vacuum and the product was purified by SiO_2 column chromatography (Eluent: Hexane: EtOAc=9:1~4:1).

N-benzyl-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (**20a**)

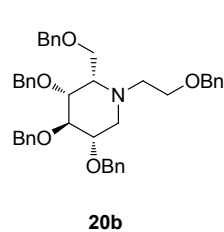


Colorless oil. Yield: 39.5% (Method A), 12.4% (Method B). ^1H NMR (400 MHz, CDCl_3): δ = 7.42 – 7.17 (m, 25H), 4.87 (q, 2H), 4.76 – 4.48 (m, 6H), 4.13 – 3.88 (m, 2H), 3.87 – 3.68 (m, 3H), 3.59 (m, 2H), 3.46 (t, J = 5.7 Hz, 1H), 2.88 (dd, J = 11.8, 4.1 Hz, 1H), 2.63 (t, J = 10.5 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ = 139.68, 139.18, 138.57, 128.36, 128.33, 128.31, 128.26, 128.22, 127.94, 127.75, 127.54, 127.50, 127.40, 126.86, 83.12, 80.37, 79.03, 77.23, 75.45, 73.31, 72.85, 72.61, 64.74, 59.86, 59.08, 48.78, 29.72. $[\alpha]_{\text{D}}^{20}$ = -4.4° (c = 1, CHCl_3). HRMS (ESI+) m/z calculated for $\text{C}_{41}\text{H}_{43}\text{NO}_4$ $[\text{M}+\text{H}]^+$: 614.3265, found: 614.3268.

N-(4-methoxybenzyl)-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (**20a'**)

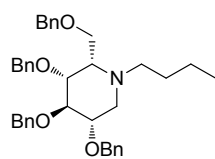


Colorless oil. Yield: 38.7% (Method A), 9.6% (Method B). ^1H NMR (400 MHz, CDCl_3): δ = 7.48 – 7.30 (m, 20H), 7.24 (d, J = 8.3 Hz, 2H), 6.89 (d, J = 8.3 Hz, 2H), 4.90 (q, J = 10.9 Hz, 2H), 4.80 – 4.53 (m, 6H), 4.08 – 3.66 (m, 9H), 3.62 (d, J = 5.3 Hz, 2H), 2.91 (dd, J = 11.7, 3.9 Hz, 1H), 2.65 (t, J = 13.1, 7.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ = 158.63, 139.24, 138.64, 138.61, 132.03, 131.68, 129.47, 128.39, 128.36, 128.34, 128.30, 127.98, 127.78, 127.58, 127.55, 127.53, 127.43, 114.37, 113.67, 83.22, 80.40, 79.09, 75.46, 73.33, 72.88, 72.62, 64.77, 59.62, 58.46, 55.61, 55.29, 48.77. $[\alpha]_{\text{D}}^{20}$ = -1.8° (c = 1, CHCl_3). HRMS (ESI+) m/z calculated for $\text{C}_{42}\text{H}_{45}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 644.3371, found: 644.3370.



N-(2-(benzyloxy)ethyl)-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (20b**)**
 Colorless oil. Yield: 31.9% (Method A), 9.1% (Method B). ^1H NMR (400 MHz, CDCl_3): δ = 7.54 – 7.31 (m, 25H), 5.06 – 4.50 (m, 10H), 4.03 – 3.44 (m, 8H), 3.26 – 3.05 (m, 2H), 3.05 – 2.89 (m, 1H), 2.83 – 2.64 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3): δ = 139.28, 138.79, 138.72, 138.62, 128.64, 128.55, 128.48, 128.42, 128.37, 128.06, 127.87, 127.75, 127.70, 127.64, 127.59, 127.52, 83.00, 80.26, 78.94, 75.46, 73.38, 73.19, 73.04, 72.78, 69.06, 64.73, 60.47, 54.64, 50.26. $[\alpha]_{\text{D}}^{20}$ = -16.4° (c = 1, CHCl_3). HRMS (ESI+) m/z

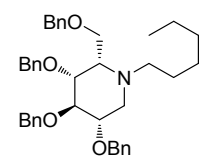
calculated for C₄₃H₄₇NO₅ [M+H]⁺: 658.3527, found: 658.3525.



20c

N-butyl-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (20c)

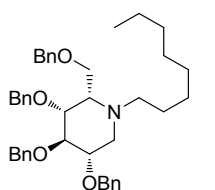
Colorless oil. Yield: 42.3% (Method A), 11.9% (Method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.57 - 7.12 (m, 20H), 4.85 (dd, J = 24.1, 11.0 Hz, 2H), 4.76 - 4.62 (m, 4H), 4.59 - 4.48 (m, 2H), 3.84 (dd, J = 10.1, 6.4 Hz, 1H), 3.78 - 3.65 (m, 2H), 3.64 - 3.44 (m, 2H), 3.39 (t, J = 4.9 Hz, 1H), 2.90 (dd, J = 11.9, 5.4 Hz, 1H), 2.73 (ddd, J = 12.5, 8.8, 6.2 Hz, 1H), 2.54 (t, 2H), 1.54 - 1.37 (m, 2H), 1.37 - 1.19 (m, 2H), 0.91 (t, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 139.26, 138.78, 138.72, 138.66, 128.41, 128.35, 128.30, 128.00, 127.83, 127.63, 127.55, 127.49, 127.47, 127.43, 83.20, 80.38, 78.99, 75.39, 73.29, 73.06, 72.71, 64.50, 59.84, 54.53, 49.93, 30.25, 20.49, 14.10. α_D²⁰ = -14.4° (c = 1, CHCl₃). HRMS (ESI⁺) m/z calculated for C₃₈H₄₅NO₄ [M+H]⁺: 580.3422, found: 580.3426.



20d

N-hexyl-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (20d)

Colorless oil. Yield: 41.8% (Method A), 10.7% (Method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.37 - 7.20 (m, 20H), 4.92 - 4.46 (m, 8H), 3.88 - 3.80 (m, 1H), 3.77 - 3.65 (m, 2H), 3.63 - 3.46 (m, 2H), 3.43 - 3.36 (m, 1H), 2.90 (dd, J = 7.2 Hz, 1H), 2.77 - 2.67 (m, 1H), 2.55 (t, J = 10.4 Hz, 2H), 1.57 - 1.48 (m, 2H), 1.37 - 1.32 (m, 6H), 0.96 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 139.26, 138.79, 138.72, 138.66, 128.46, 128.41, 128.35, 128.29, 128.00, 127.83, 127.63, 127.55, 127.49, 127.47, 127.43, 83.19, 80.36, 78.97, 75.39, 73.30, 73.05, 72.72, 64.50, 59.79, 54.83, 49.95, 31.81, 28.01, 26.99, 22.73, 14.16. [α]_D²⁰ = -17.1° (c = 1, CHCl₃). HRMS (ESI⁺) m/z calculated for C₄₀H₄₉NO₄ [M+H]⁺: 608.3735, found: 608.3738.

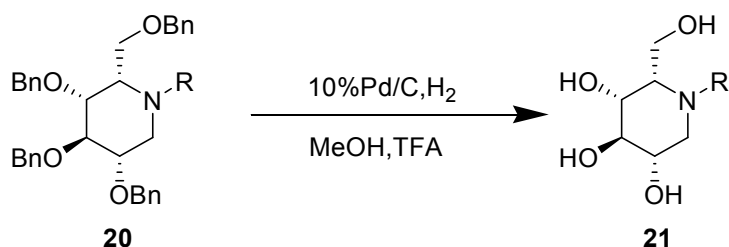


20e

N-octyl-2,3,4,6-Tetra-O-benzyl-L-ido-1-deoxynojirimycin (20e)

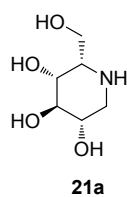
Colorless oil. Yield: 40.6% (Method A), 11.5% (Method B). ¹H NMR (400 MHz, CDCl₃): δ = 7.39 - 7.26 (m, 20H), 4.94 - 4.46 (m, 8H), 3.84 (dd, J = 10.1, 6.4 Hz, 1H), 3.77 - 3.65 (m, 2H), 3.55 (ddd, J = 22.0, 16.1, 8.9 Hz, 2H), 3.39 (t, J = 4.6 Hz, 1H), 2.90 (dd, J = 11.8, 5.4 Hz, 1H), 2.78 - 2.48 (m, 3H), 1.48 - 1.17 (m, 12H), 0.93 (t, J = 6.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃): δ = 139.22, 138.75, 138.69, 138.63, 128.49, 128.43, 128.38, 128.35, 128.32, 128.26, 127.97, 127.80, 127.60, 127.52, 127.46, 83.16, 80.33, 78.94, 75.36, 73.27, 73.04, 72.70, 64.47, 59.76, 54.80, 49.92, 31.90, 29.53, 29.36, 29.29, 27.31, 22.71, 14.16. [α]_D²⁰ = -26.3° (c = 1, CHCl₃). HRMS (ESI⁺) m/z calculated for C₄₂H₅₃NO₄ [M+H]⁺: 636.4048, found: 636.4042.

3. General procedure for debenzylation:



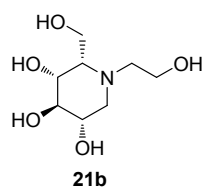
To a solution of compounds **20** (1 mmol) in methanol (14 mL) was bubbled with nitrogen for 30 min at room temperature, then the solution was added to dried and degassed 10% Pd/C (1.0g) followed by 0.2 mL TFA. The mixture was stirred at room temperature with a hydrogen balloon for 24 h until TLC monitored the complete consumption of starting material. After filtered with Celite, the residue was washed with methanol for three times and water two time. The combined filtrate was concentrated and coevaporated with MeOH.

The residue was purified by flash column chromatography with aluminum oxide (MeOH: CHCl₃ = 3 : 1 ~ 1 : 1 or MeOH:EtOAc:NH₄OH=10:12:3) to afford Compound 21.



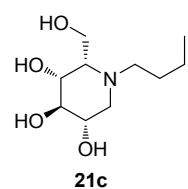
L-ido-1-Deoxynojirimycin (21a)

Colorless oil. Yield: 90.1% (from **20a**), 85.8% (from **20a'**). ¹H NMR (400MHz, D₂O): δ = 3.98 – 3.94 (m, 1H), 3.93 – 3.89 (m, 2H), 3.88 – 3.72 (m, 2H), 3.55 – 3.42 (m, 1H), 3.34 (dd, J = 13.6 Hz, 1H), 3.30 – 3.22 (m, 1H). ¹³C NMR (101 MHz, D₂O): δ = 67.26, 67.15, 66.25, 58.68, 56.47, 44.99. [α]_D²⁰ = -1.5° (c = 1, H₂O). LRMS: (ES+) *m/z* = 164.2[M+1].



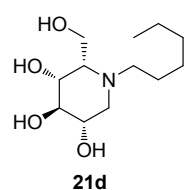
N-Hydroxyethyl-L-ido-1-deoxynojirimycin (21b)

Colorless oil. Yield: 86.9%. ¹H NMR (400 MHz, D₂O): δ = 3.85 – 3.71 (m, 3H), 3.68 – 3.53 (m, 3H), 3.39 (t, J = 9.1 Hz, 1H), 3.07 (d, J = 5.2 Hz, 1H), 2.95 – 2.74 (m, 3H), 2.60 (t, J = 11.7 Hz, 1H). ¹³C NMR (101 MHz, D₂O): δ = 74.32, 70.19, 69.02, 63.43, 59.01, 55.89, 55.36, 50.51. [α]_D²⁰ = -14.3° (c = 1, H₂O). HRMS: (ESI+) *m/z* calculated for C₈H₁₇NO₅ [M+Na]⁺ 230.0999, found 230.0992.



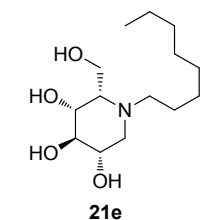
N-Butyl-L-ido-1-deoxynojirimycin (21c)

Colorless oil. Yield: 91.7%. ¹H NMR (400 MHz, MeOD): δ = 4.00 – 3.85 (m, 3H), 3.80 (d, J = 3.7 Hz, 1H), 3.74 – 3.62 (m, 1H), 3.44 – 3.29 (m, 1H), 3.29 – 3.18 (m, 1H), 3.16 – 3.00 (m, 3H), 1.78 – 1.57 (m, 2H), 1.49 – 1.36 (m, 2H), 1.00 (t, J = 7.3 Hz, 3H). ¹³C NMR (101 MHz, MeOD): δ = 70.83, 70.38, 68.45, 62.61, 57.81, 53.65, 52.16, 26.49, 19.76, 12.70. [α]_D²⁰ = +55.6° (c = 1, MeOH). HRMS: (ES+) *m/z* = 220.2 [M+1].



N-Hexyl-L-ido-1-deoxynojirimycin (21d)

Colorless oil. Yield: 94.0%. ¹H NMR (400 MHz, MeOD): δ = 3.99 – 3.73 (m, 3H), 3.68 – 3.60 (m, 1H), 3.50 (t, J = 7.3 Hz, 1H), 3.16 (d, J = 4.7 Hz, 1H), 3.05 – 2.68 (m, 4H), 1.71 – 1.50 (m, 2H), 1.44 – 1.26 (m, 6H), 0.93 (t, J = 6.0 Hz, 3H). ¹³C NMR (101 MHz, MeOD): δ = 73.13, 71.17, 69.36, 62.77, 56.79, 54.13, 51.72, 31.42, 26.54, 26.25, 22.29, 13.03. [α]_D²⁰ = +13.4° (c = 1, MeOH). LRMS: (ES+) *m/z* = 248.2 [M+1].



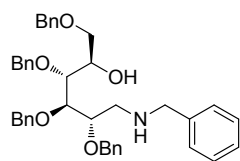
N-Octyl-L-ido-1-deoxynojirimycin (21e)

Colorless oil. Yield: 94.3%. ¹H NMR (400 MHz, MeOD): δ = 3.94 – 3.69 (m, 3H), 3.62 – 3.52 (m, 1H), 3.45 (s, 1H), 3.05 (s, 1H), 2.86 – 2.49 (m, 4H), 1.58 – 1.44 (m, 2H), 1.39 – 1.23 (m, 10H), 0.89 (t, J = 6.4 Hz, 3H). ¹³C NMR (101 MHz, MeOD): δ = 74.57, 71.30, 69.62, 62.44, 56.38, 54.31, 51.37, 31.66, 29.30, 29.11, 27.34, 27.13, 22.41, 13.42. [α]_D²⁰ = +24.8° (c = 1, MeOH). LRMS: (ES+) *m/z* = 276.2 [M+1].

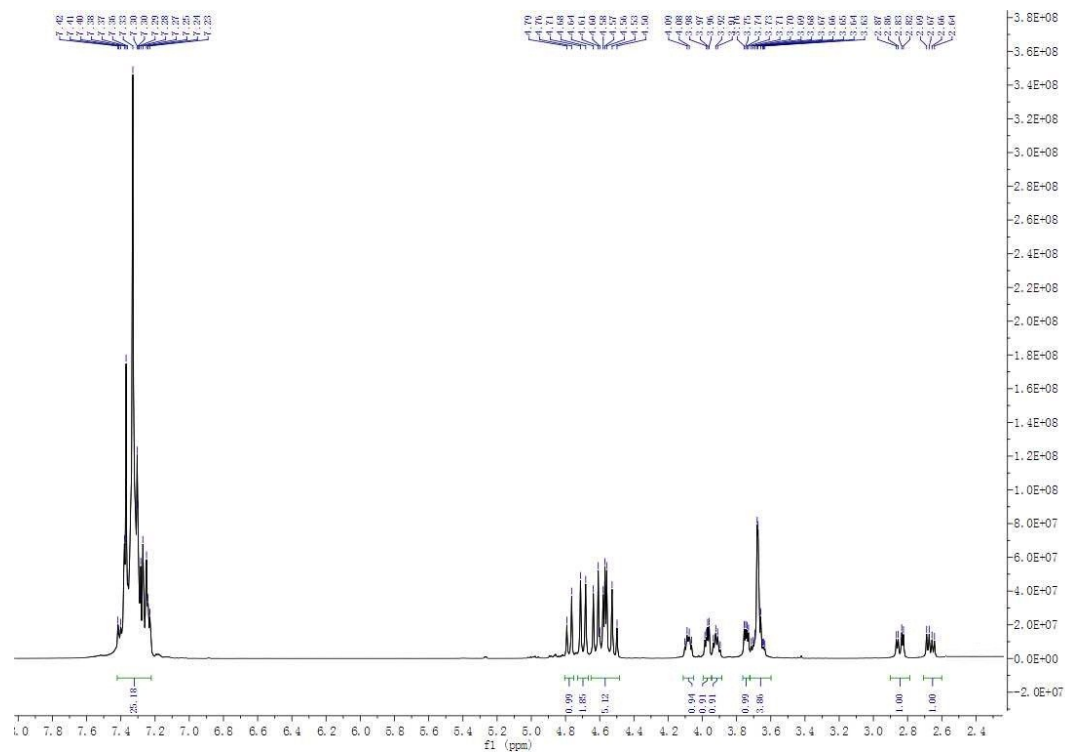
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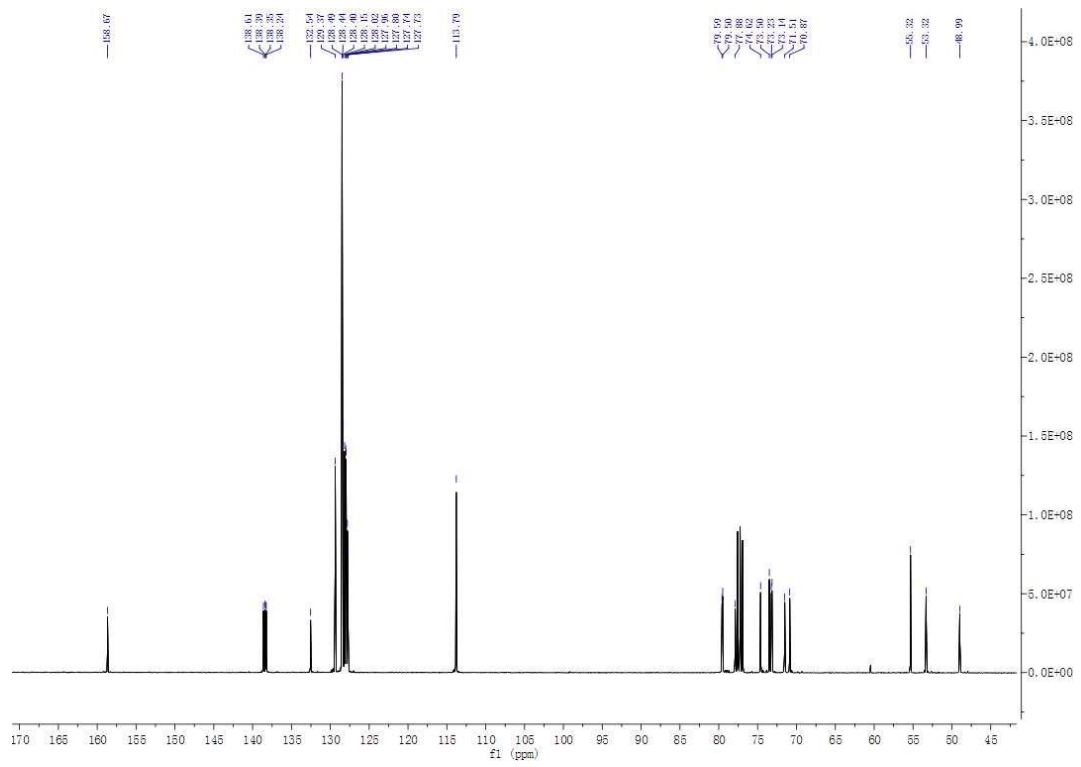
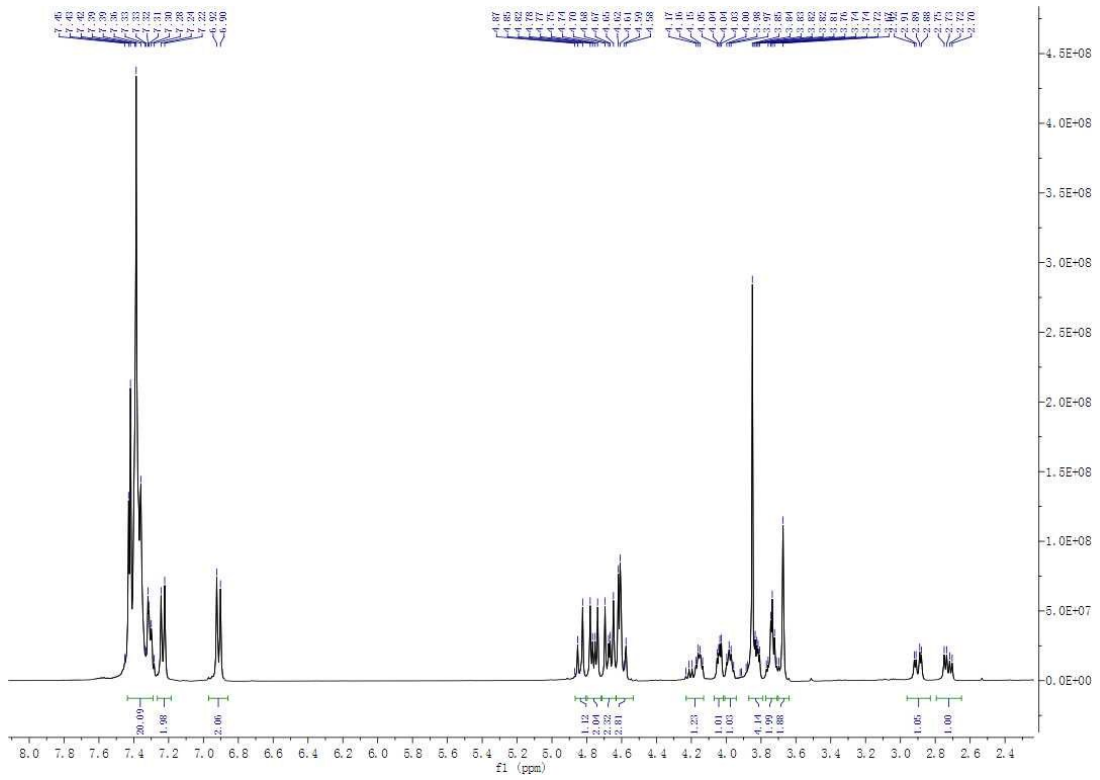
1. C. Wang, A. Pettman, J. Bacsá, J. Xiao, *Angew. Chem. Int. Ed.* **2010**, *49*, 7548-7552.
2. A. J. Blacker, M. J. Stirling, M. I. Page, *Org. Process Res. Dev.* **2007**, *11*, 642-648.
3. R. Kawahara, K. Fujita and R. Yamaguchi, *J. Am. Chem. Soc.* **2010**, *132*, 15108-15111.

II. Spectra Data:



13a





Display Report

Analysis Info

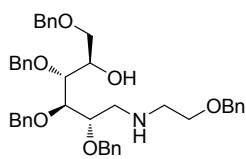
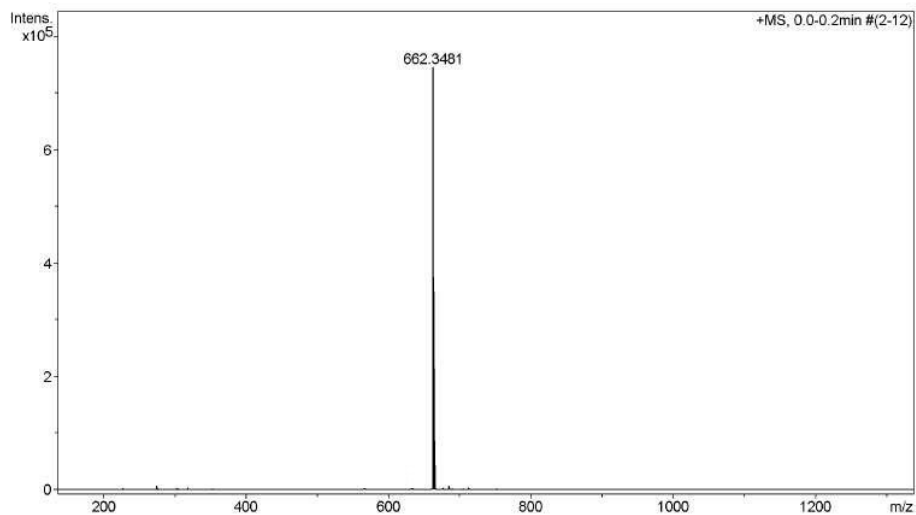
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 Sample Name
 Comment

Acquisition Date 2016-5-4 16:17:54

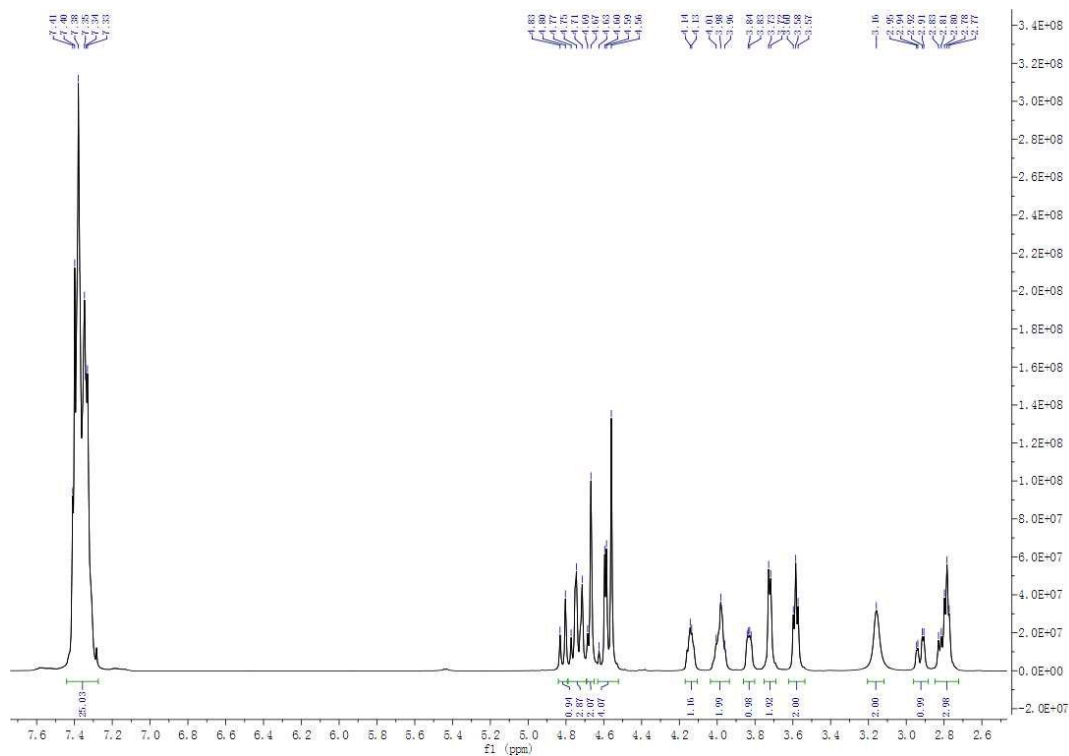
Operator NWU
 Instrument micrOTOF-Q II 10280

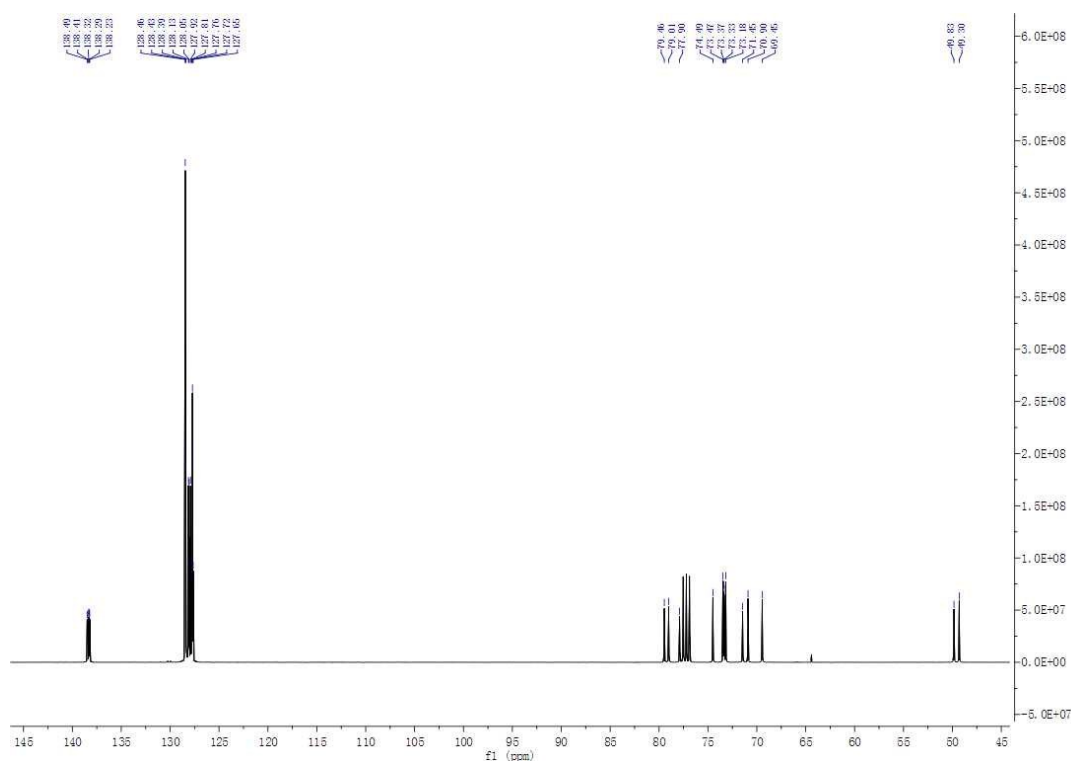
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13b

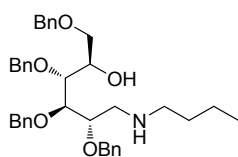
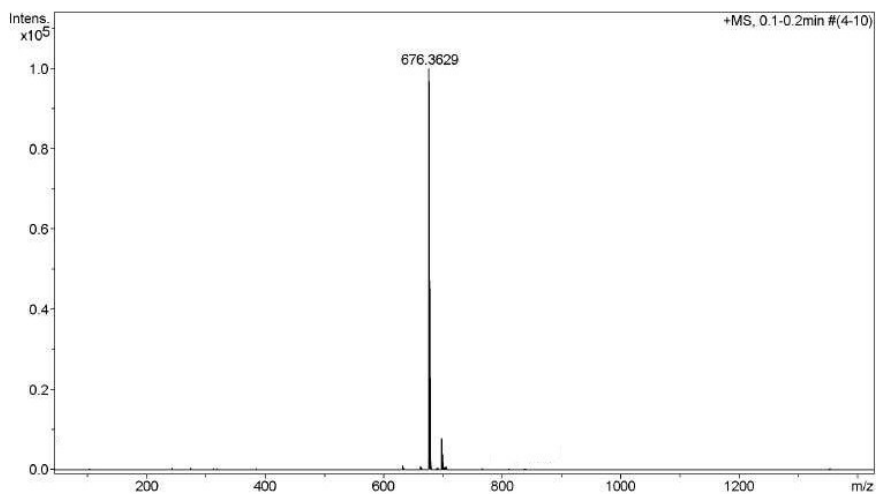




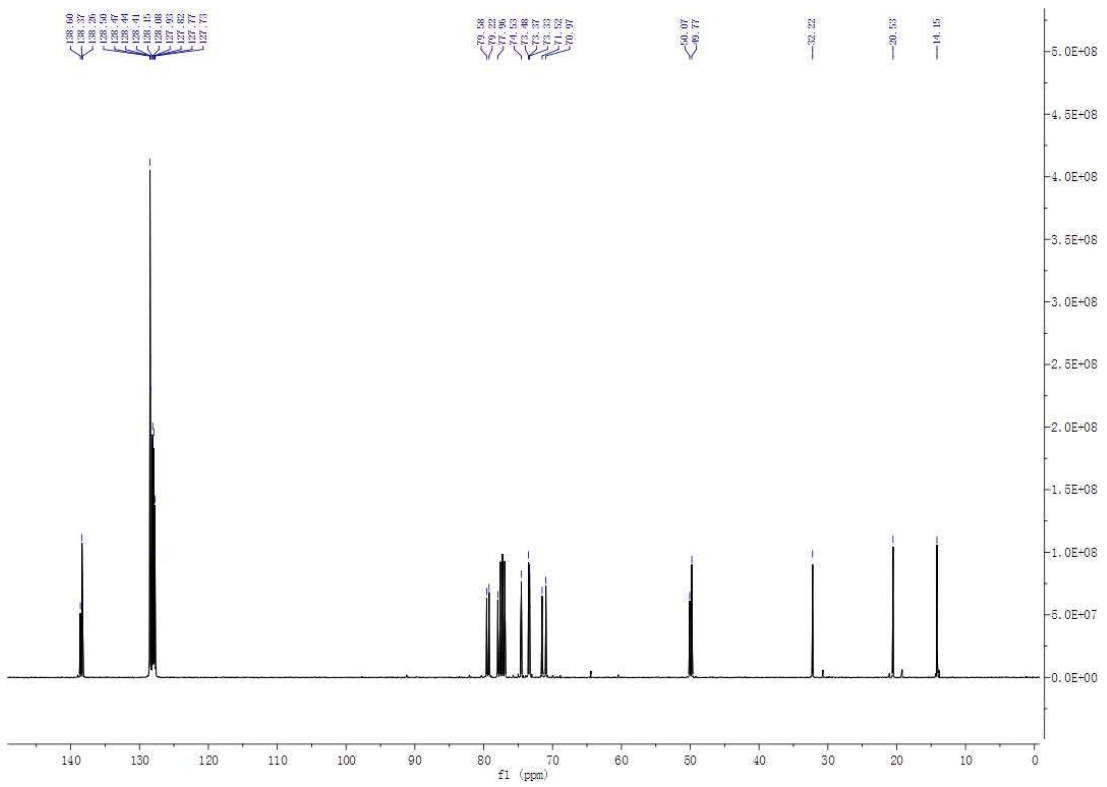
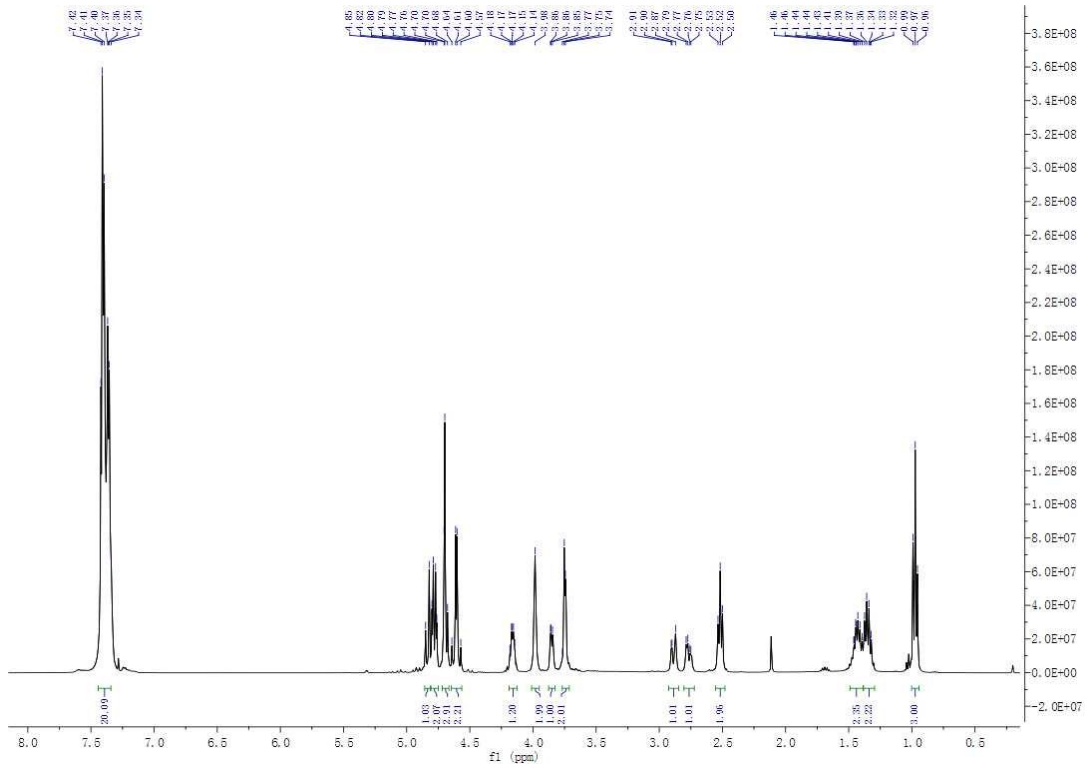
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| Comment | | |
| | Operator | NWU |
| | Instrument | micrOTOF-Q II 10280 |

| | | | | | |
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13c



Display Report

Analysis Info

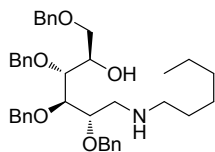
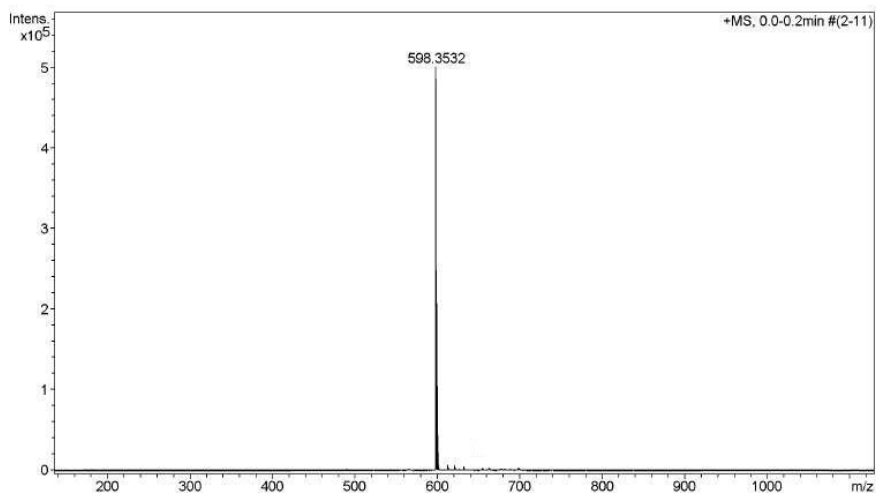
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Sample Name
Comment

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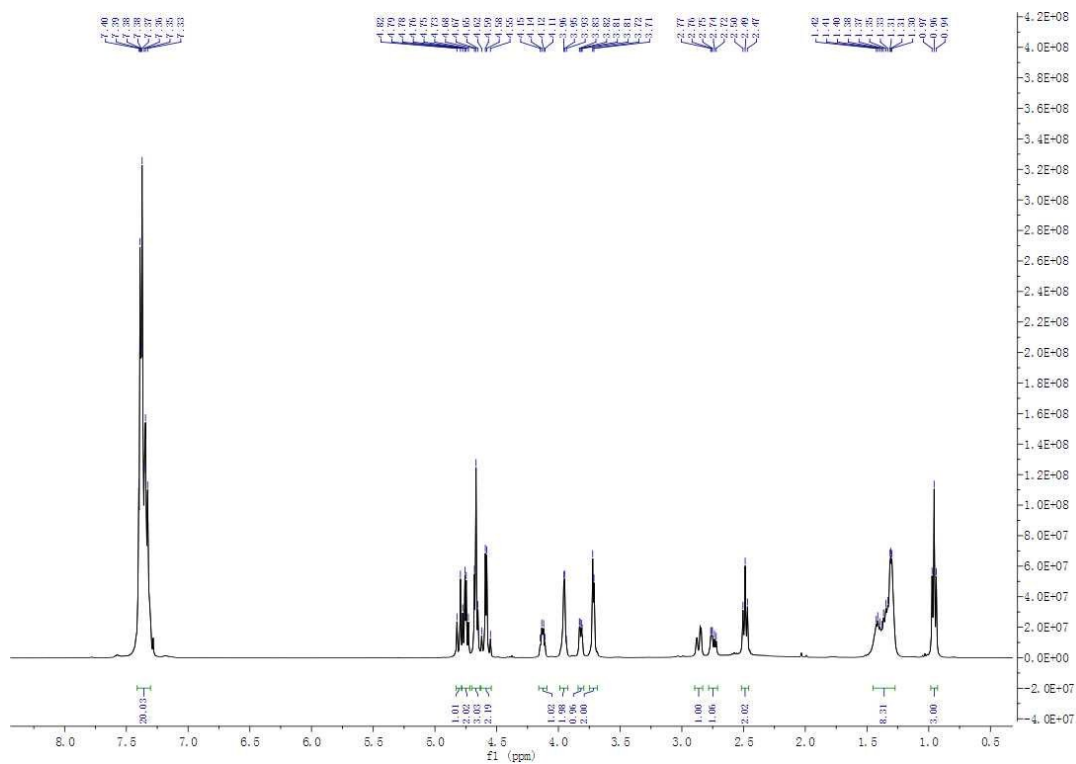
Operator NWU
Instrument micrOTOF-Q II 10280

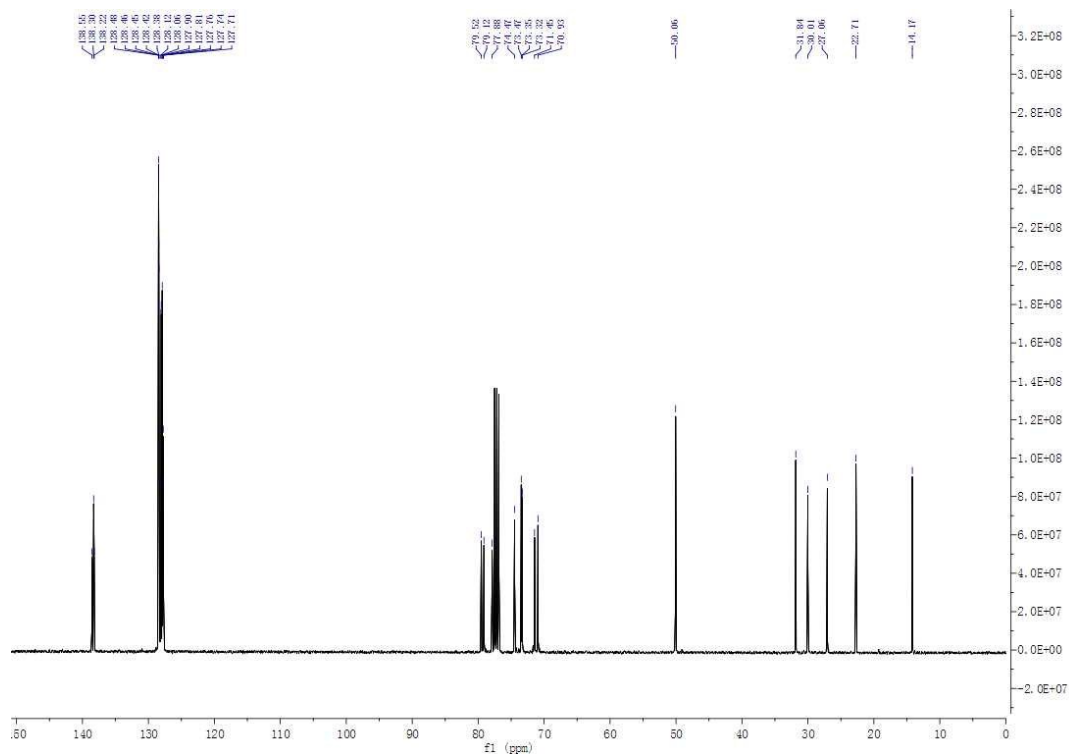
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13d





Display Report

Analysis Info

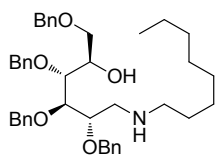
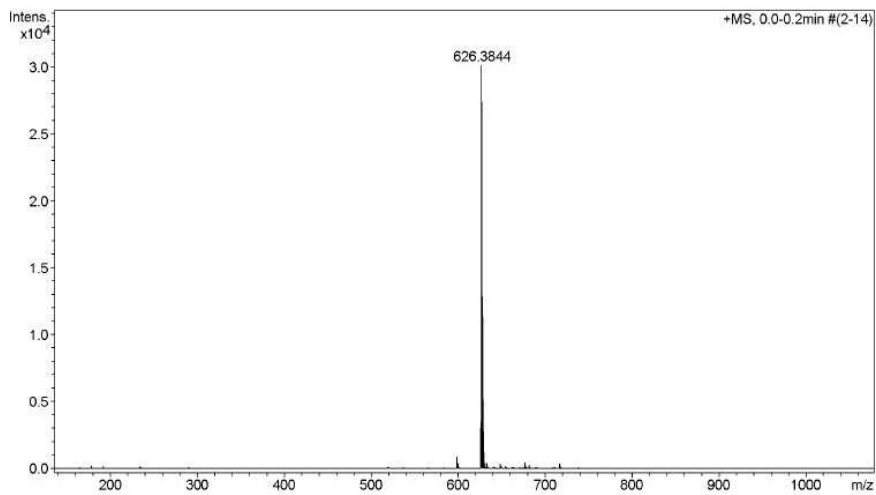
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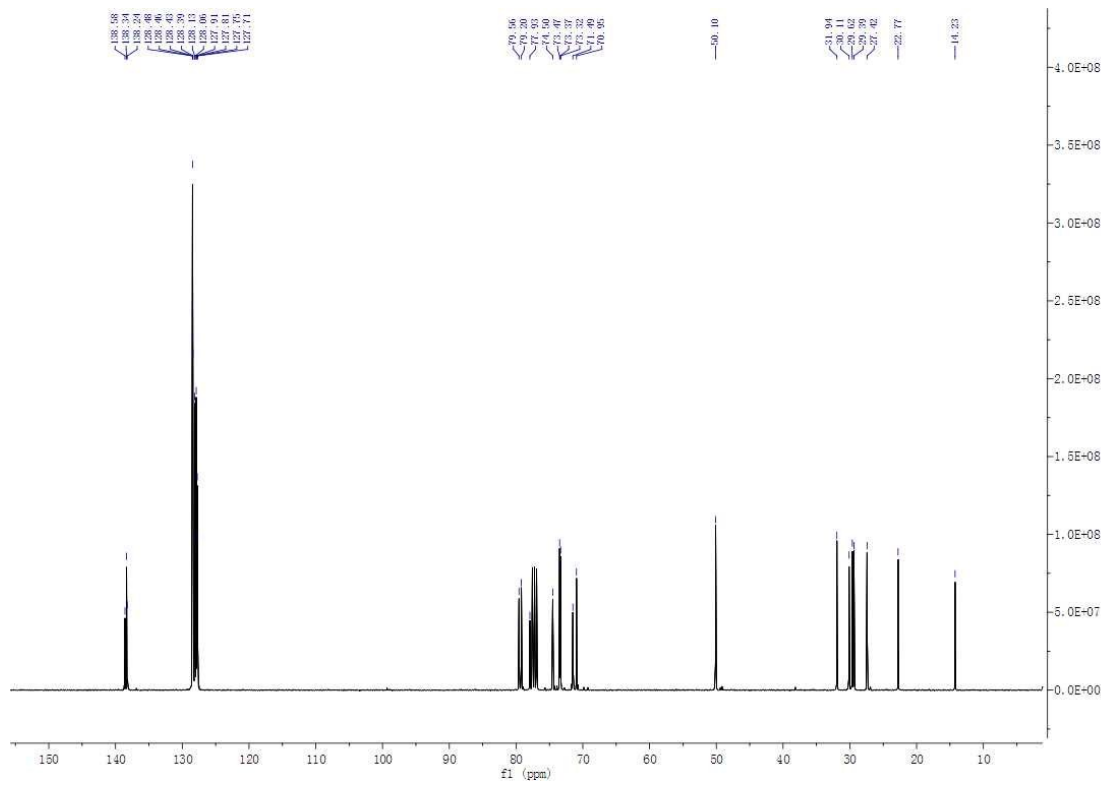
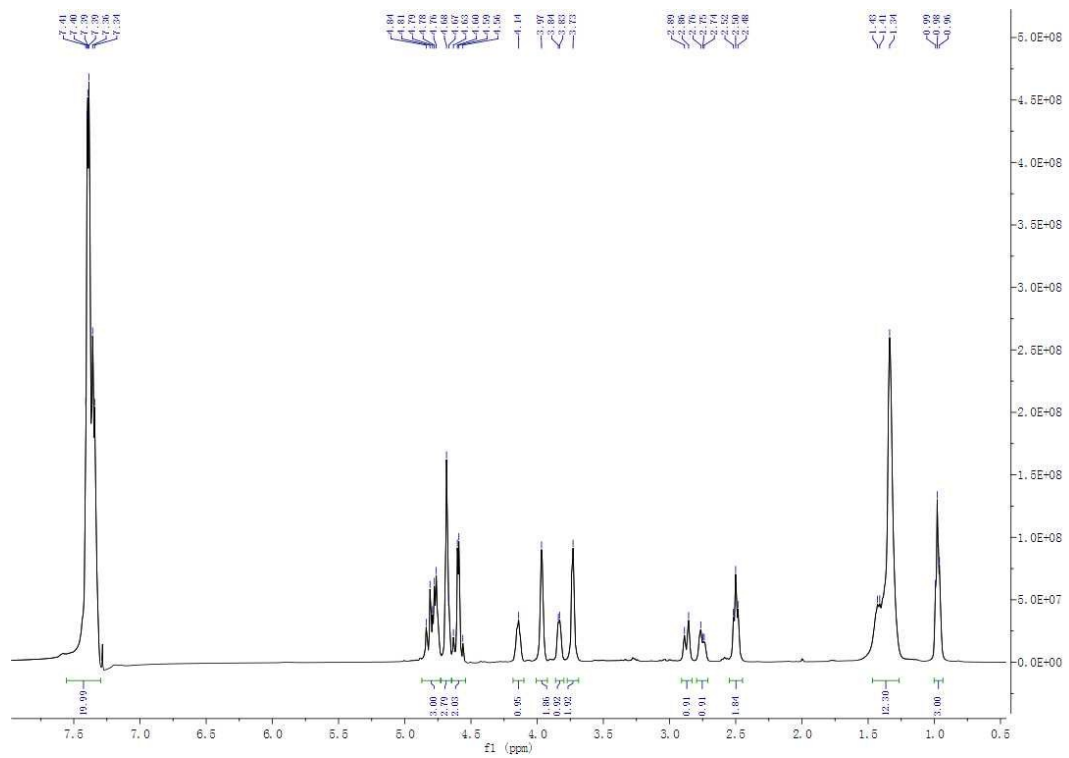
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13e



Display Report

Analysis Info

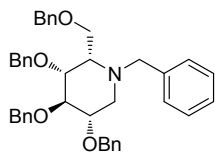
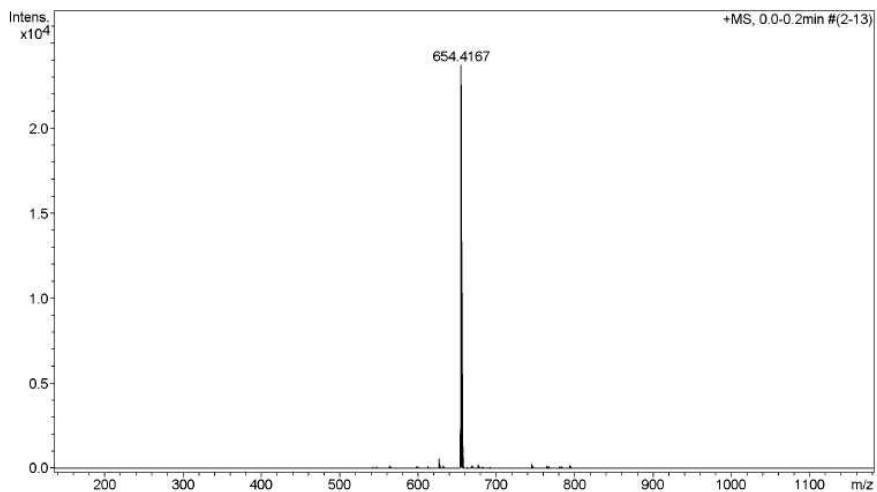
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Sample Name
Comment

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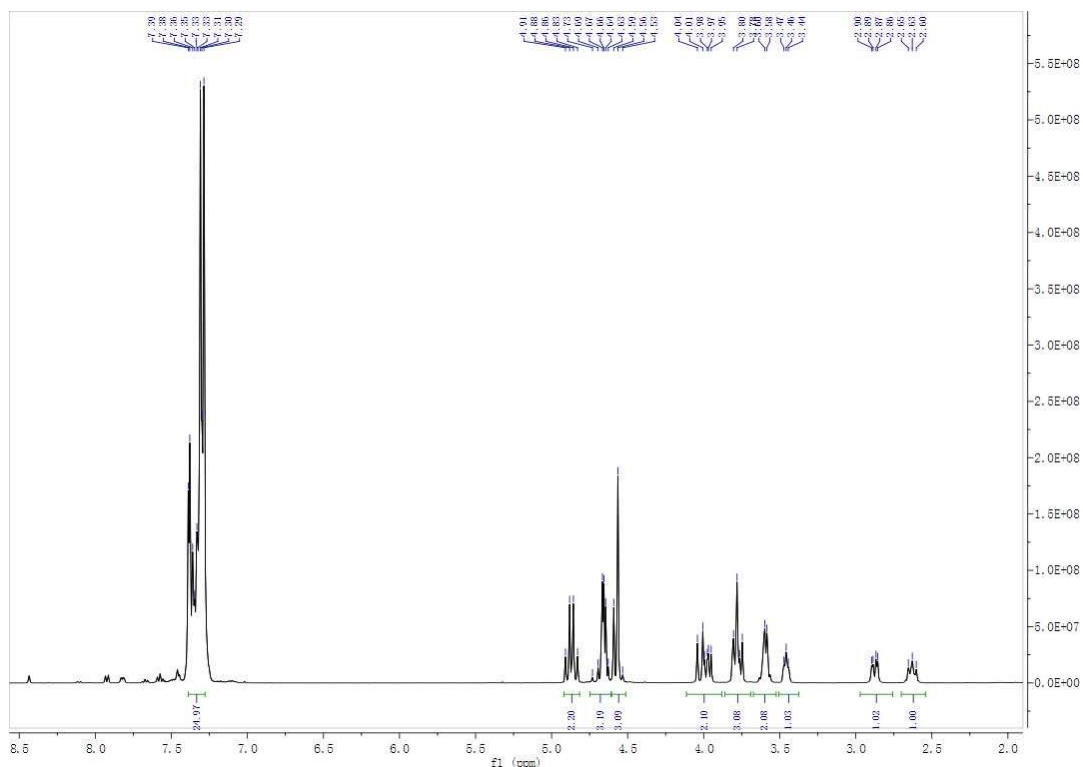
Operator NWU
Instrument micrOTOF-Q II 10280

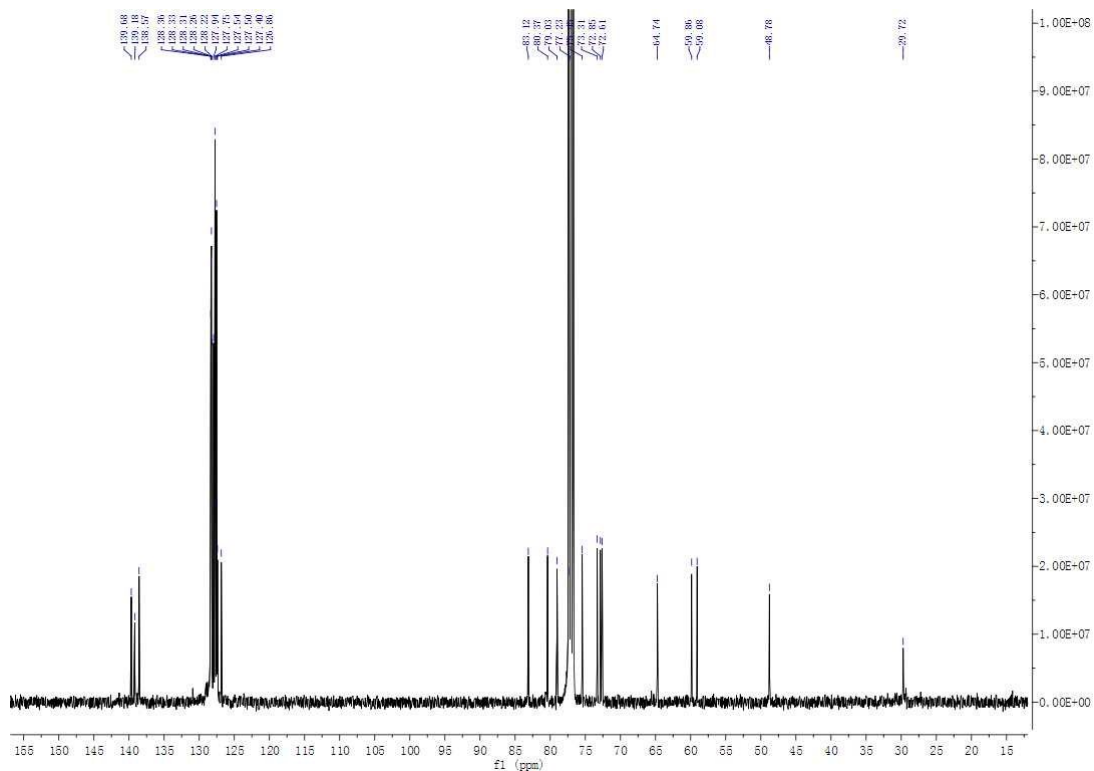
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20a





Display Report

Analysis Info

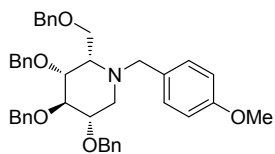
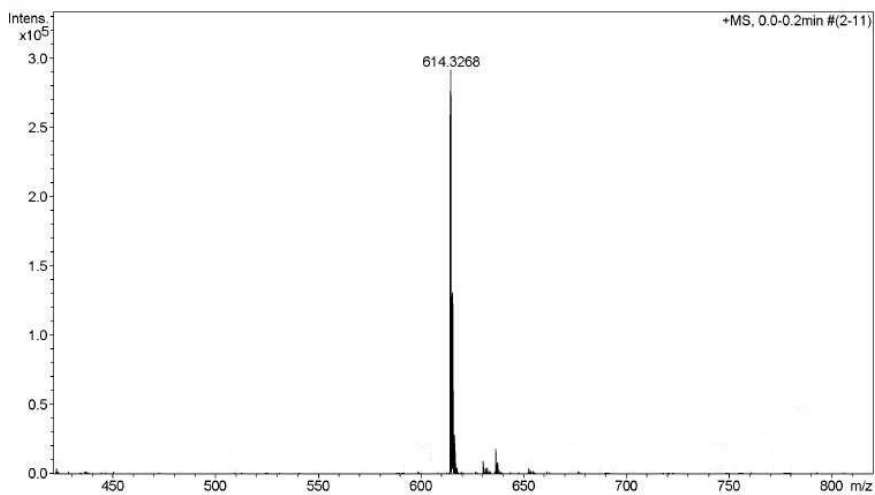
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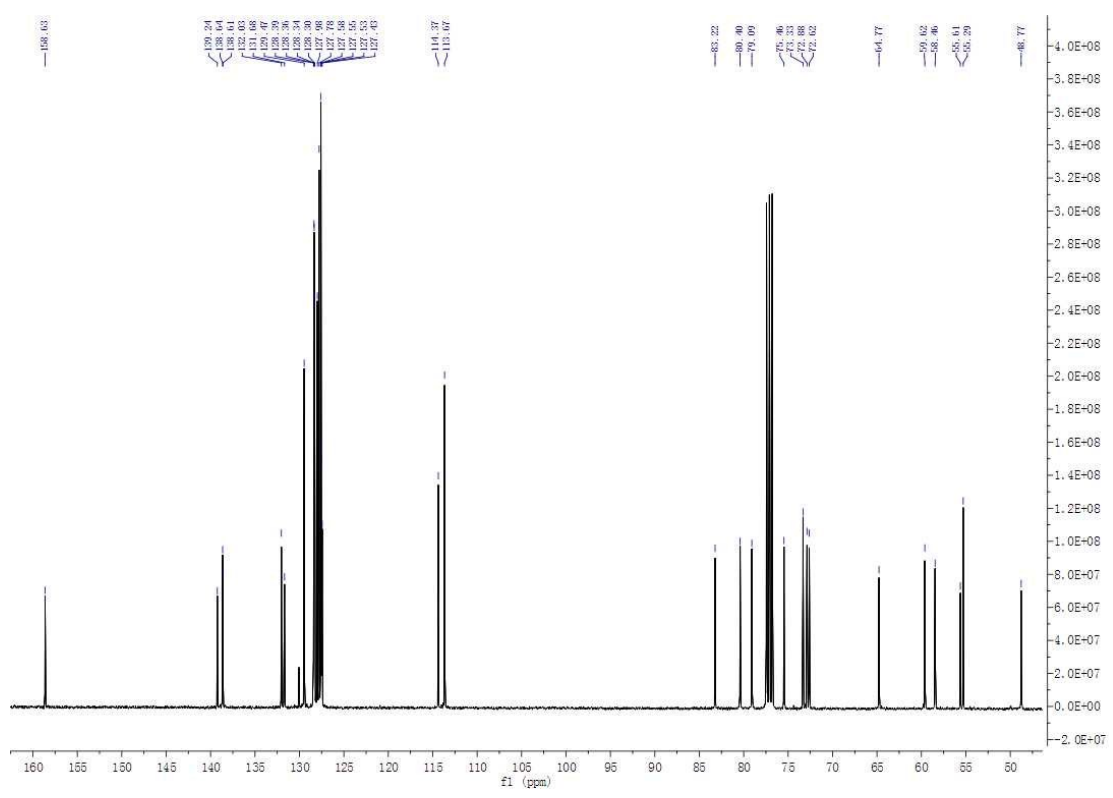
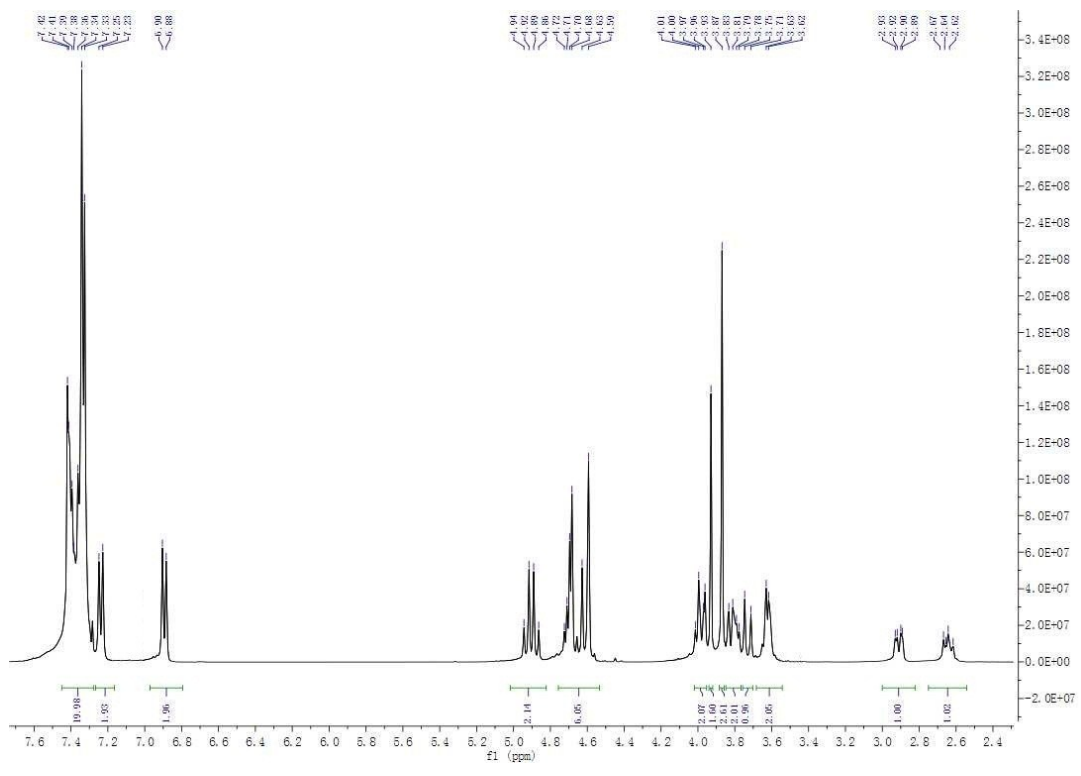
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 Instrument: micrOTOF-Q II 10280

Acquisition Parameter

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20a'



Display Report

Analysis Info

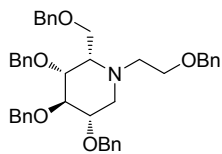
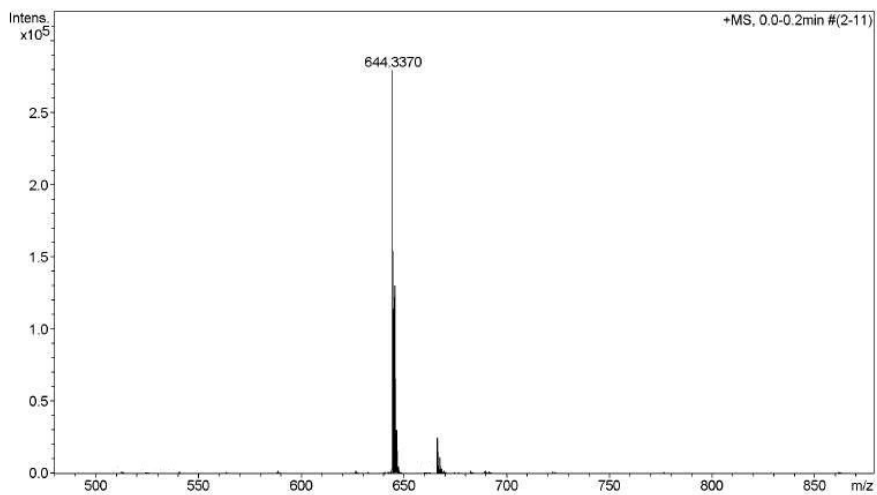
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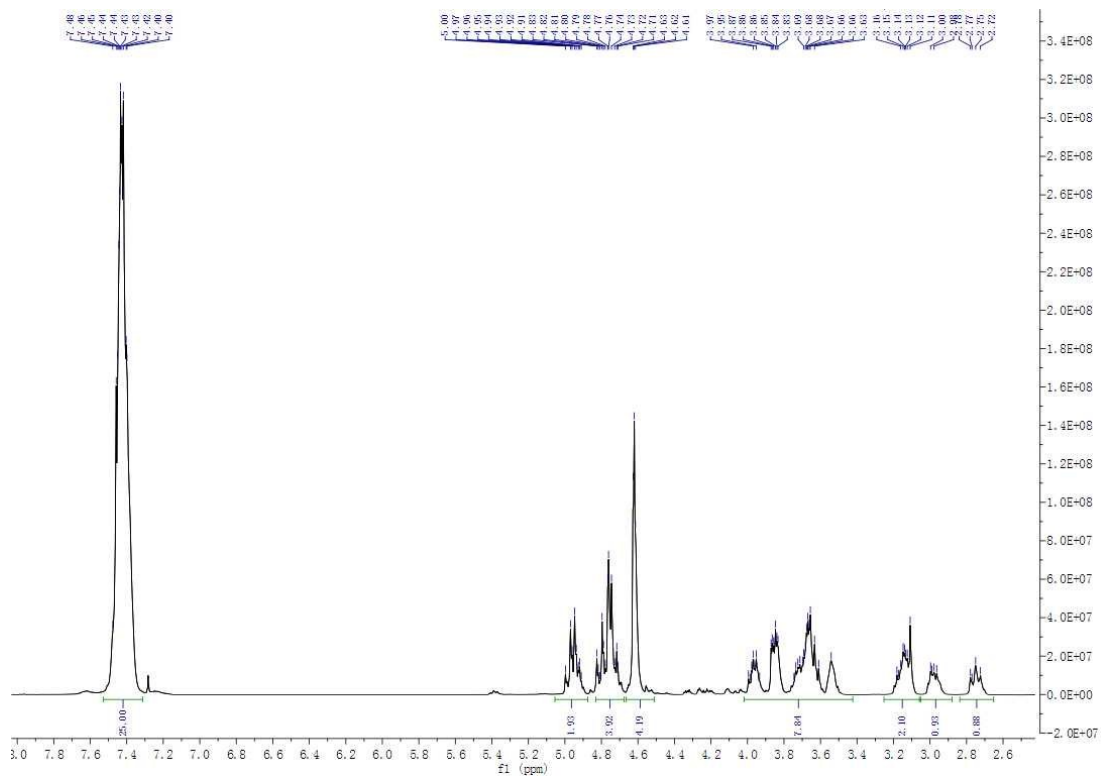
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 Instrument: micrOTOF-Q II 10280

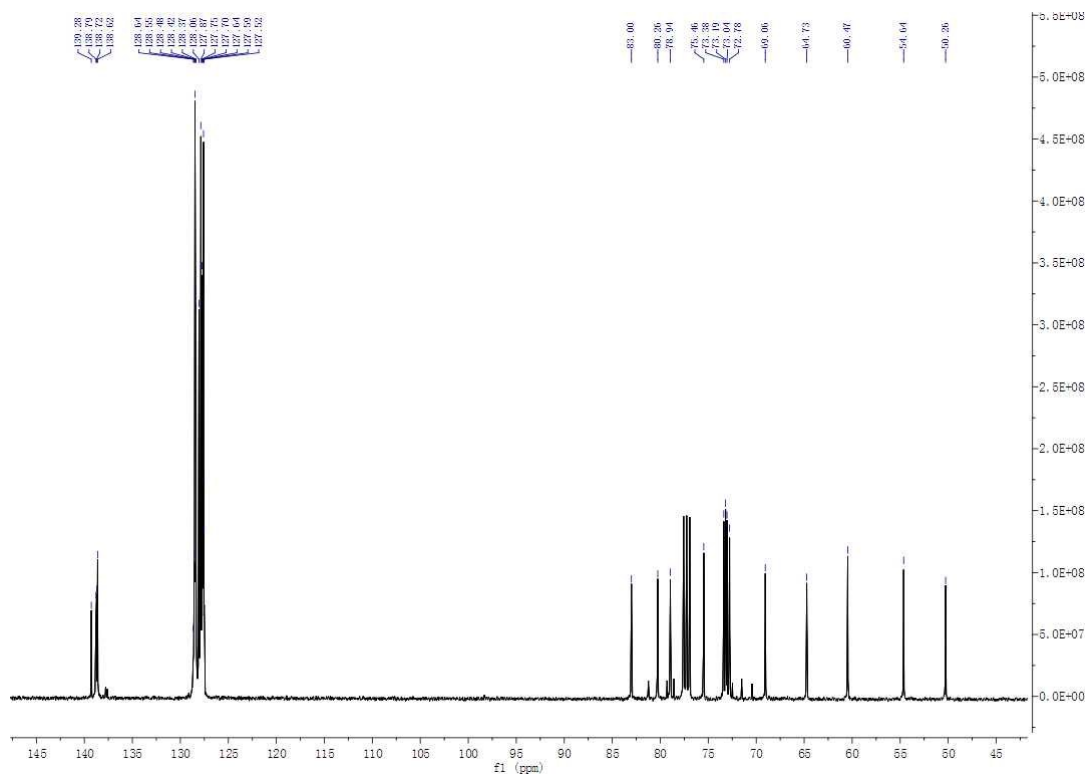
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20b

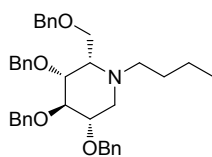
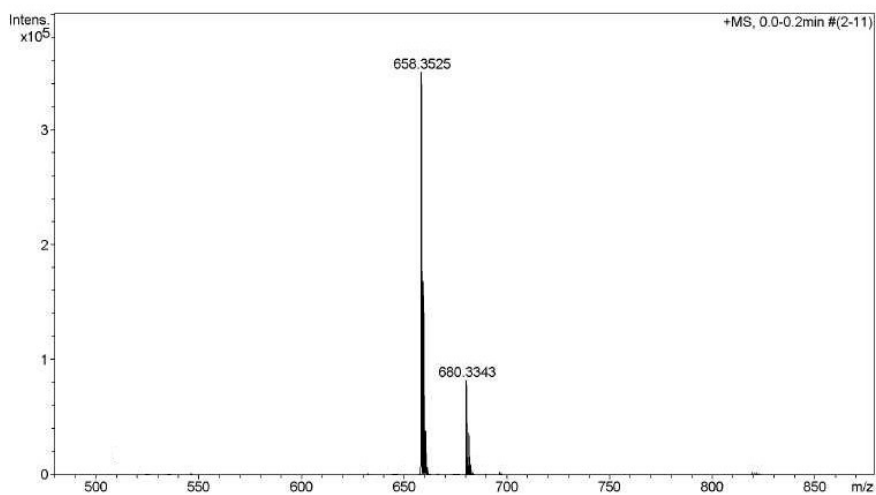




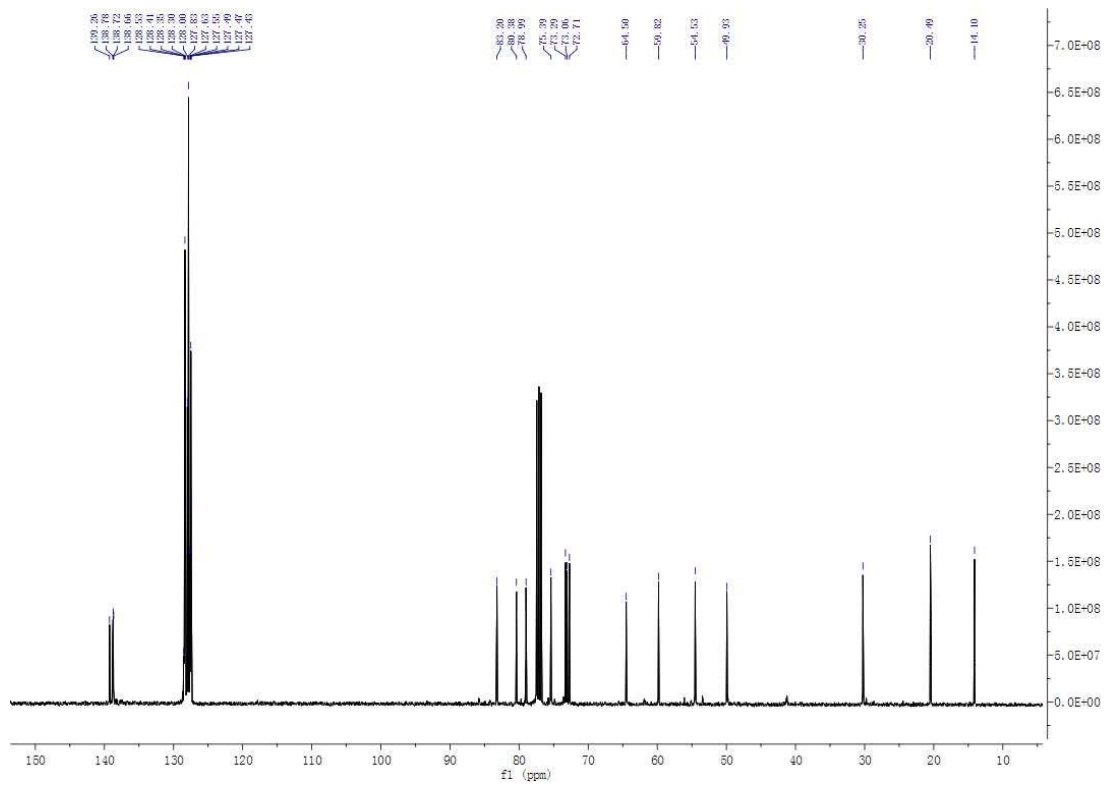
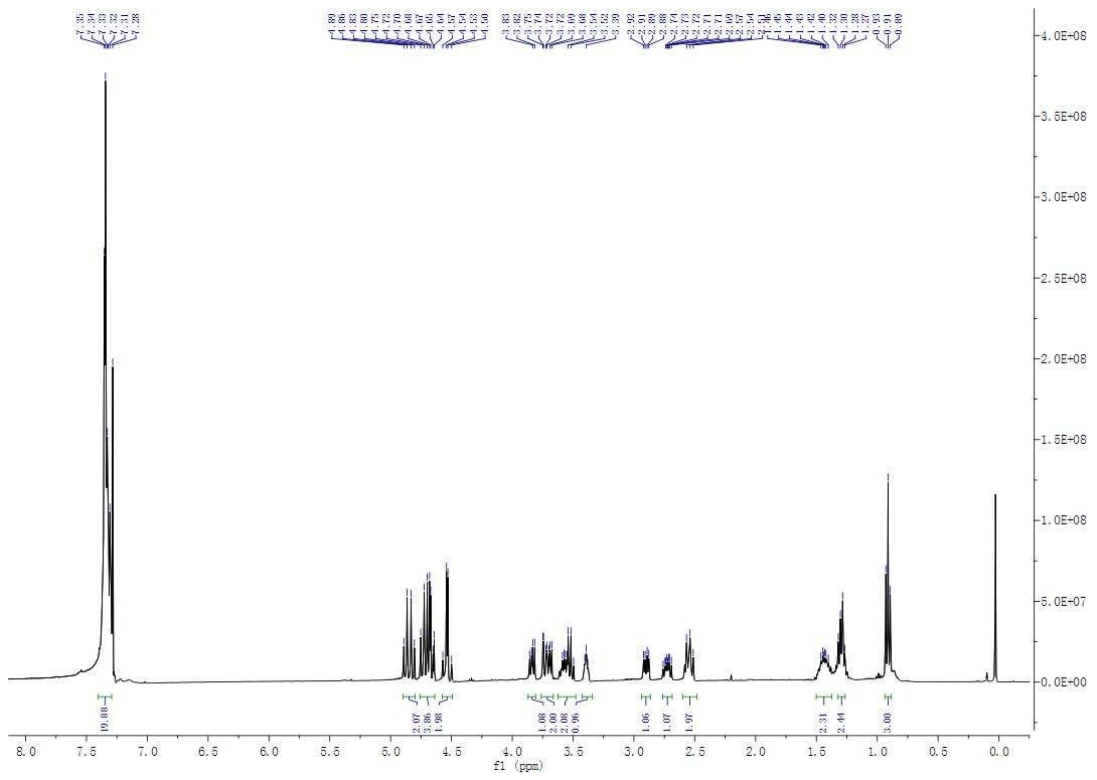
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| Sample Name | | Instrument | micrOT-OF-Q II 10280 |
| Comment | | | |

| Acquisition Parameter | | | | | |
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20c



Display Report

Analysis Info

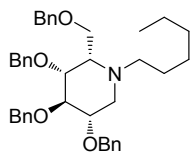
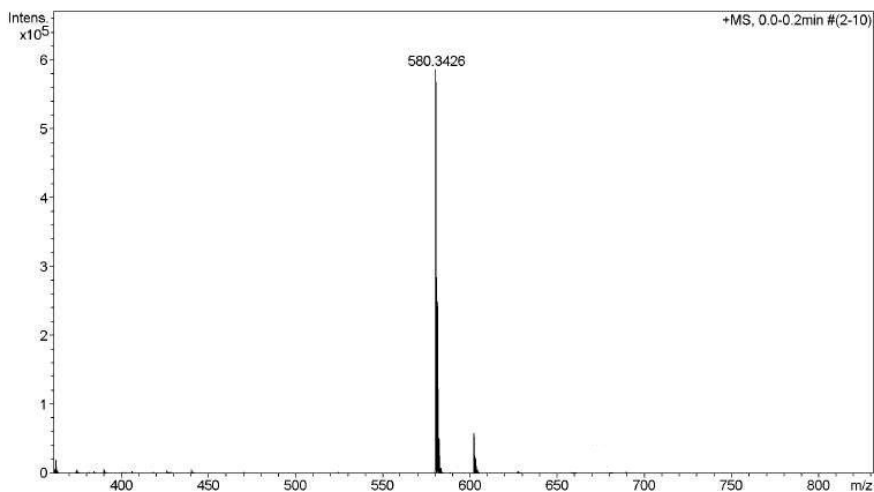
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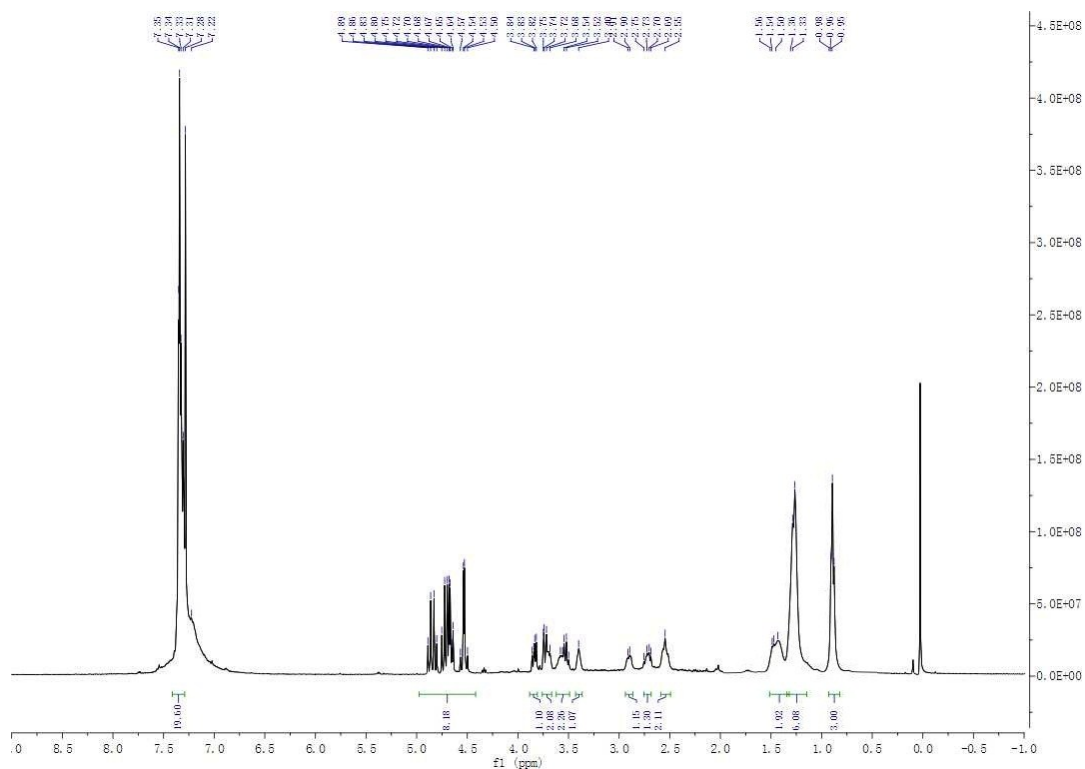
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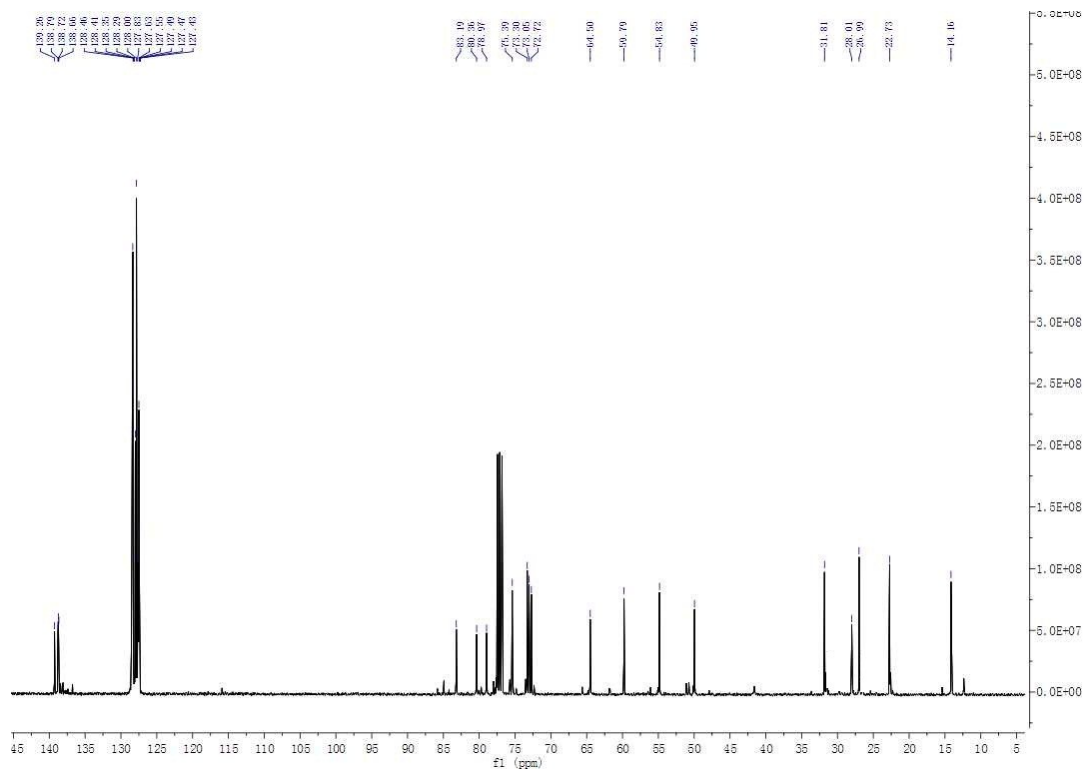
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20d





Display Report

Analysis Info

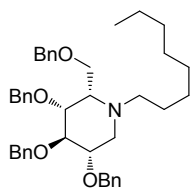
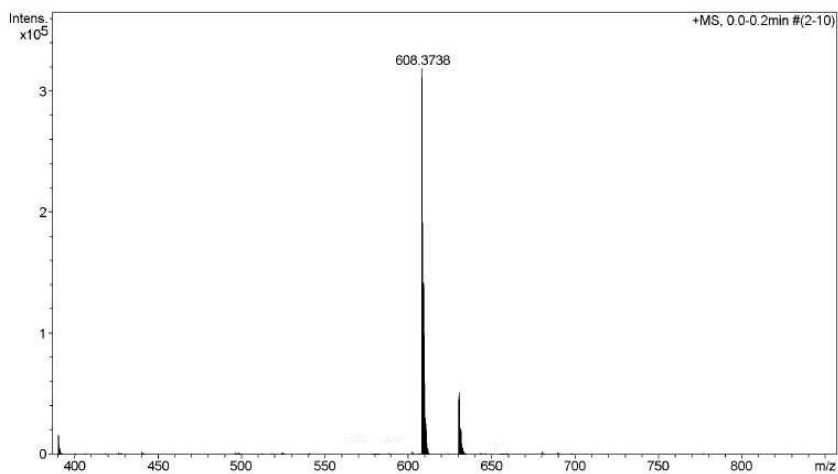
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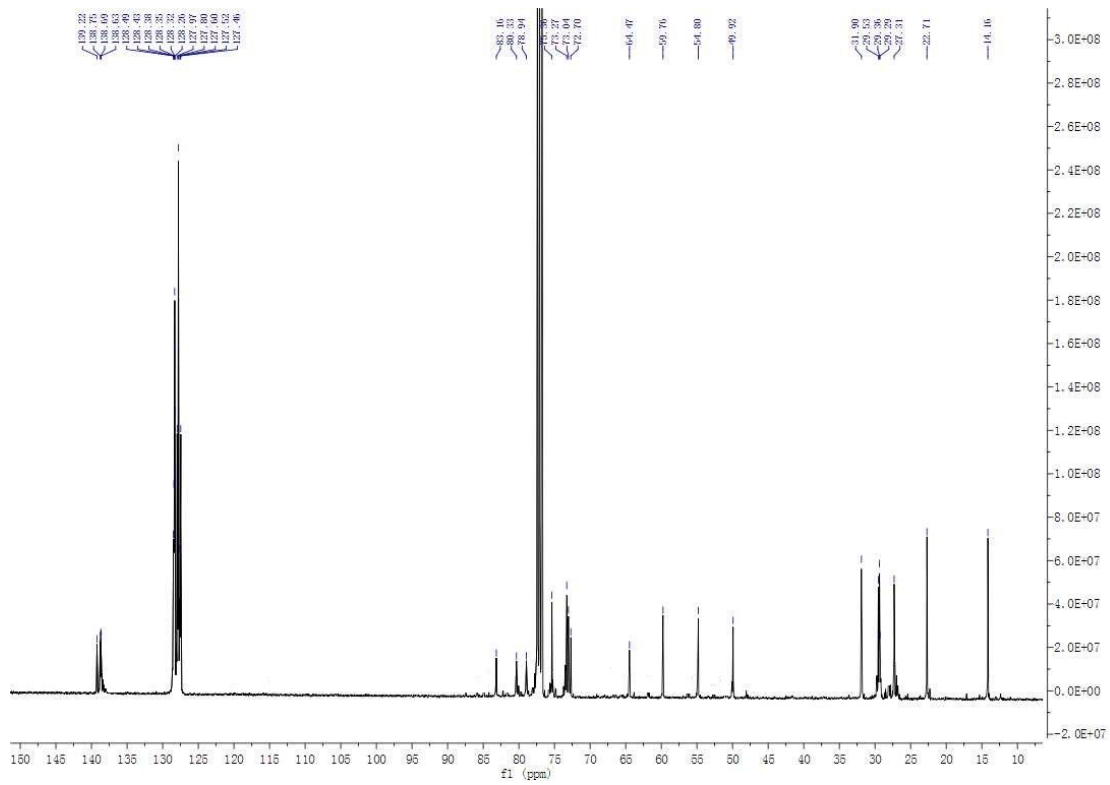
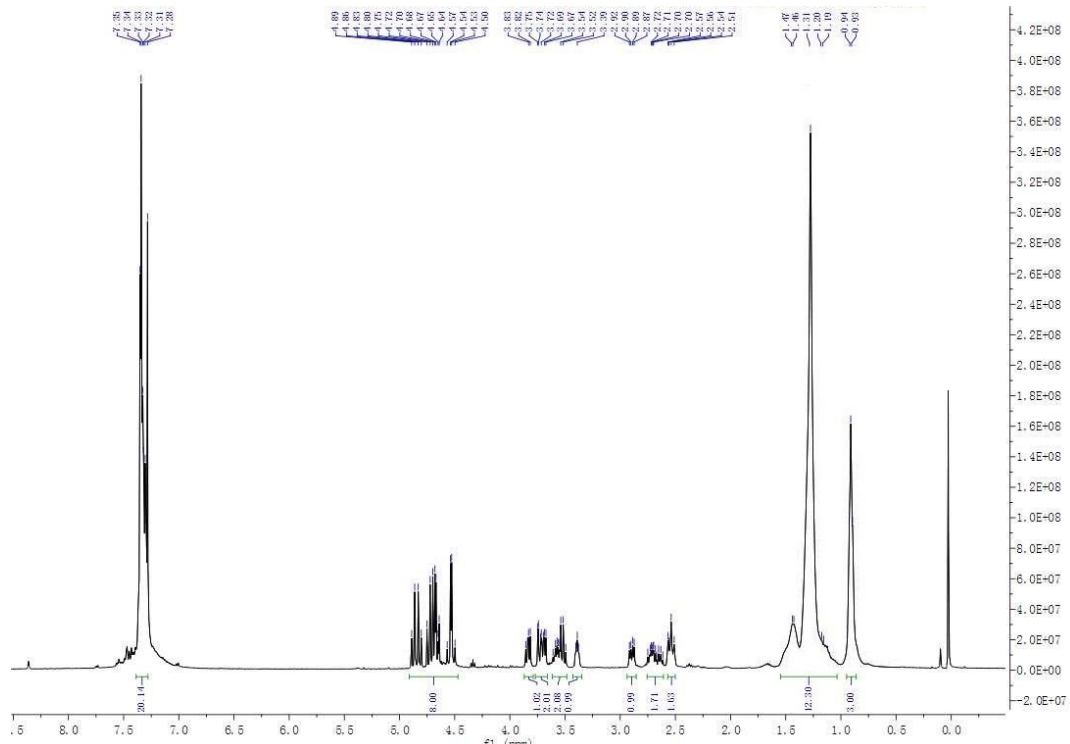
Operator NWU
 Instrument micrOTOF-Q II 10280

Acquisition Parameter

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20e



Display Report

Analysis Info

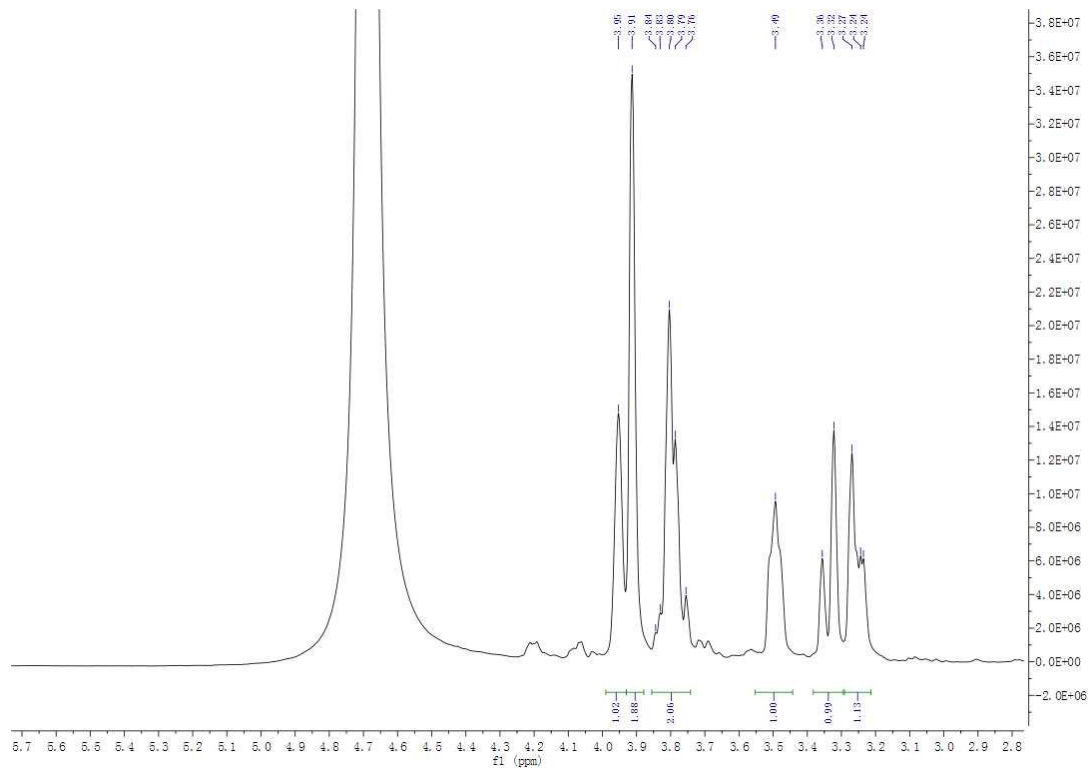
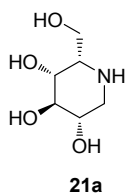
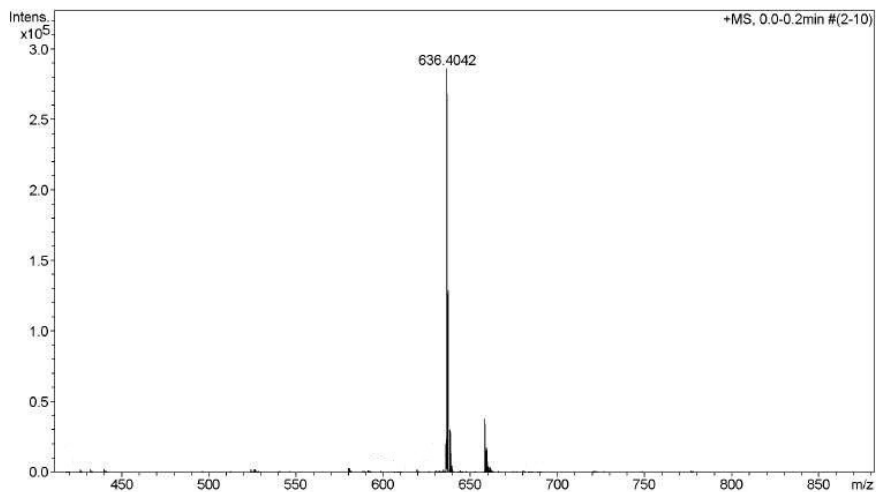
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Sample Name
Comment

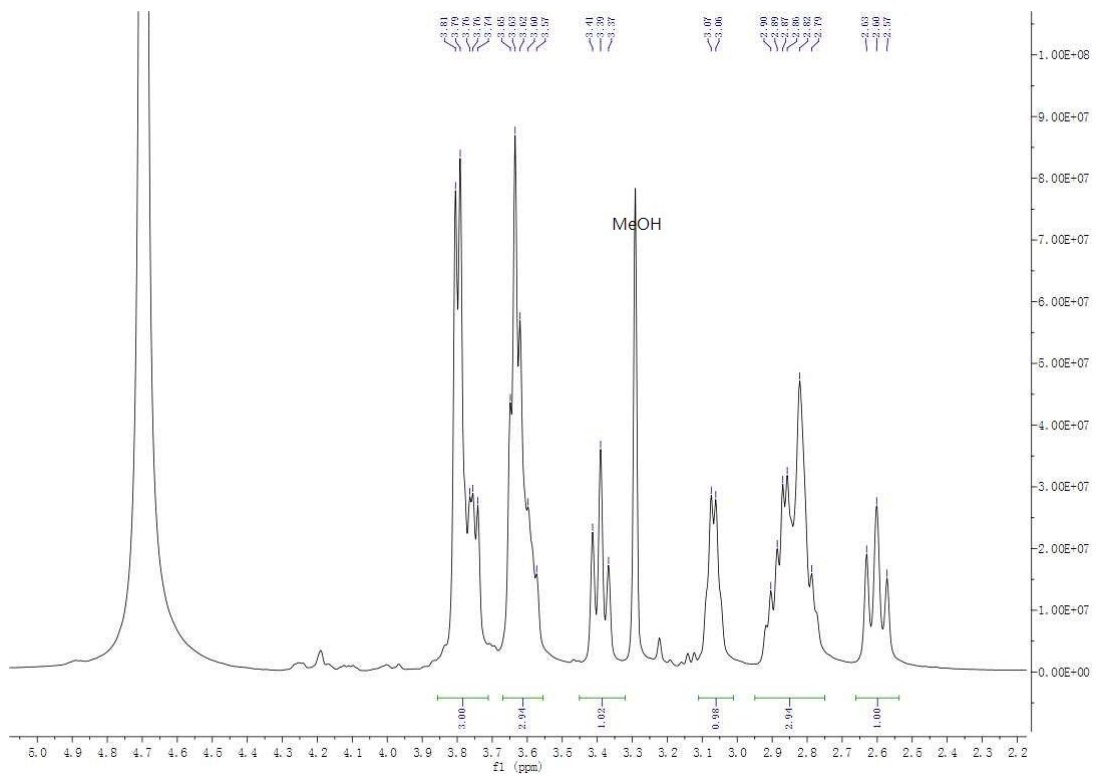
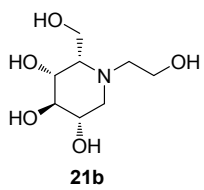
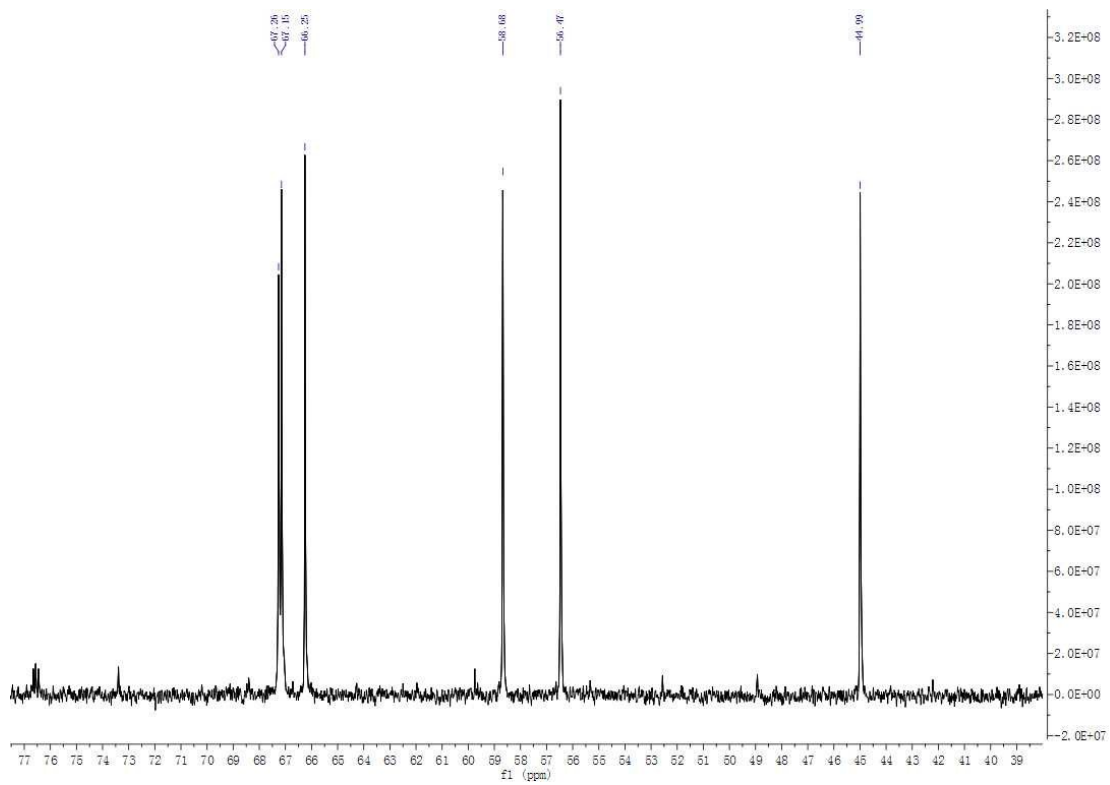
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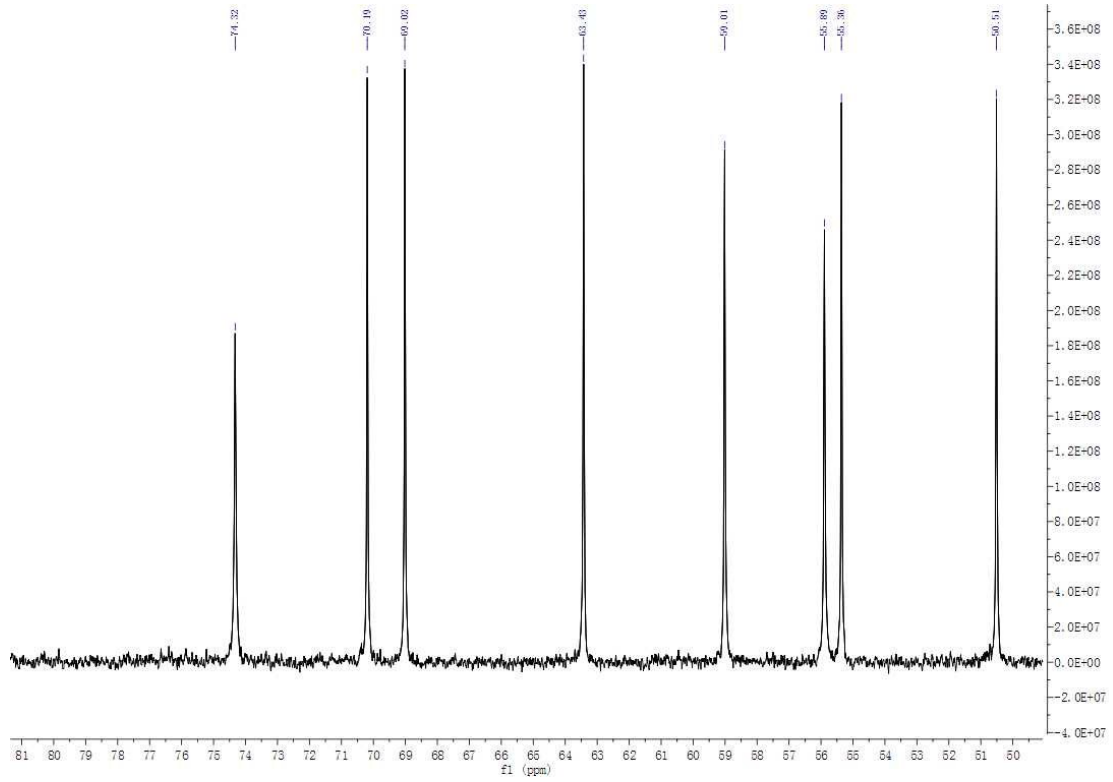
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Instrument micrOTOF-Q II 10280

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Display Report

Analysis Info

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 Sample Name
 Comment

Acquisition Date 2016-5-4 17:00:06

Operator NWU
 Instrument micrOTOF-Q II 10280

Acquisition Parameter

| | | | | | |
|-------------|------------|-----------------------|-----------|------------------|-----------|
| Source Type | ESI | Ion Polarity | Positive | Set Nebulizer | 0.4 Bar |
| Focus | Not active | Set Capillary | 4500 V | Set Dry Heater | 180 °C |
| Scan Begin | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 4.0 l/min |
| Scan End | 3000 m/z | Set Collision Cell RF | 110.0 Vpp | Set Divert Valve | Source |

