

Supporting Information for

Design, synthesis and biological evaluation of a novel series of glycosylated platinum(IV) complexes as antitumor agents

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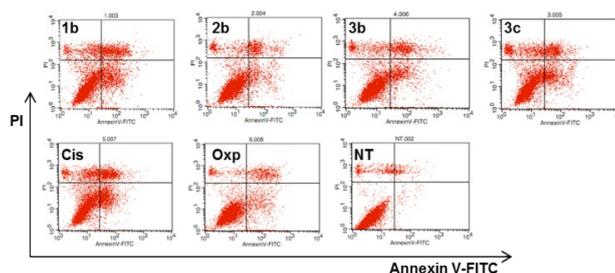
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1. Apoptosis experiments

Table S1 Quantification of apoptosis in HepG2 cells using an annexin V/PI assay.



Compd.	Early apoptosis	Late apoptosis	Necrosis	Sum
1b^a	15.55	12.23	7.37	35.15
2b^a	7.53	7.36	4.98	19.87
3b^a	10.69	9.50	6.72	26.91
3c^a	12.17	9.20	11.02	32.39
Cisplatin ^a	15.31	12.11	10.49	37.91
Oxaliplatin ^b	8.48	7.07	3.05	18.6
Untreated	0.81	2.21	5.34	8.36

^a Concentration of tested compound is 20 μ M; ^b Concentration of tested compound is 50 μ M.

2. Reduction of Pt(IV) complexes by Vc

To investigate the binding properties of DNA with Pt(II) complexes, 5'-GMP was selected as a model of DNA. The cisplatin and oxaliplatin were incubated with 5'-GMP at 37 °C for 24 h respectively. The results (Fig. S1 and S2) revealed that new peaks of cis-Pt(II)-GMP (the conjugated complexes of cisplatin with 5'-GMP) and Oxp-Pt(II)-GMP (the conjugated complexes of oxaliplatin with 5'-GMP) generated by the mixture. It demonstrated the potency of 5'-GMP to combine with Pt(II) complexes.

Further experiments were designed to test the reduction potential of Pt(IV) complexes. Compounds **1b**, **2b** and **3c** were selected. The spectra were given in Fig. S3-S5. Results proved that the glycosylated platinum(IV) complexes could be reduced by Vc and release Pt(II) complexes. Then, the Pt(II) compounds combined with 5'-GMP to form cis-Pt(II)-GMP or Oxp-Pt(II)-GMP, which were confirmed by HRMS.

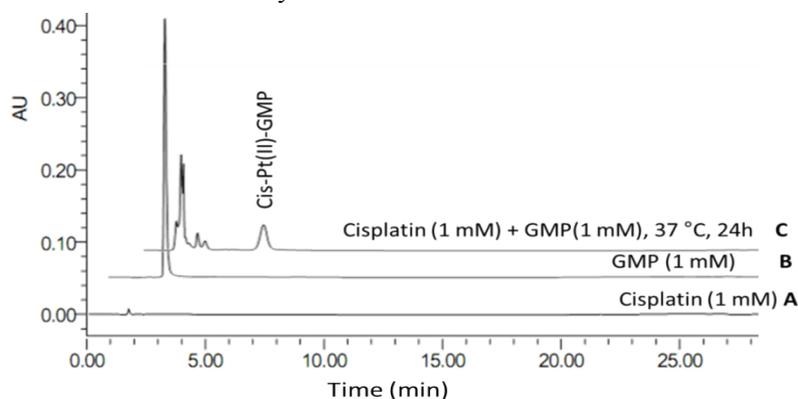


Fig. S1 The reaction of cisplatin with 5'-GMP. (A) Cisplatin (1 mM) in water. (B) 5'-GMP (1 mM)

in water. (C) Solution of cisplatin (1 mM) and GMP (1 mM) in water was incubated in 37 °C for 24h.

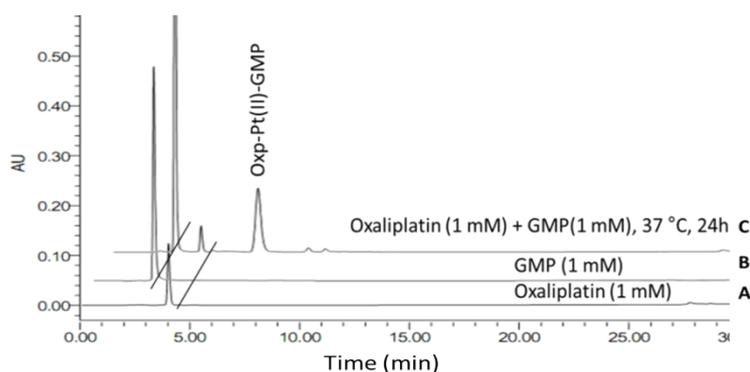
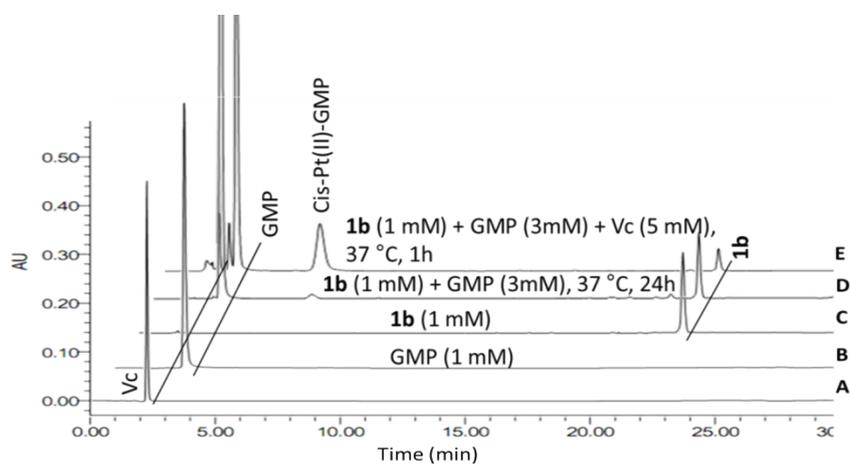


Fig. S2 The reaction of oxaliplatin with 5'-GMP. (A) Oxaliplatin (1 mM) in water. (B) 5'-GMP (1 mM) in water. (C) Solution of oxaliplatin (1 mM) and GMP (1 mM) in water was incubated in 37 °C for 24h.



F

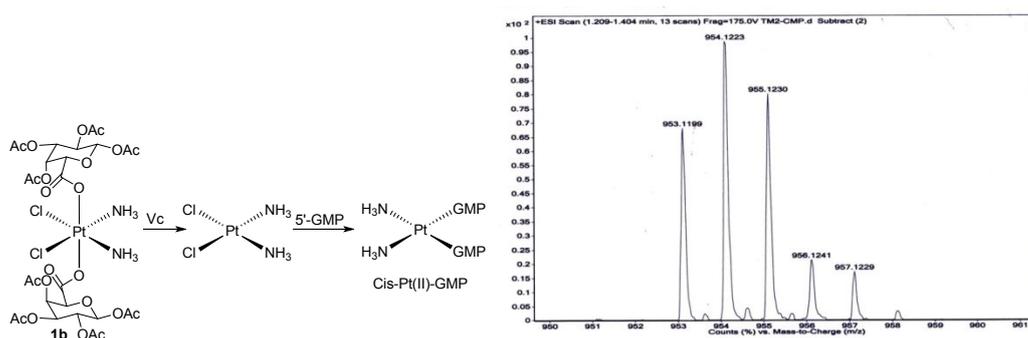
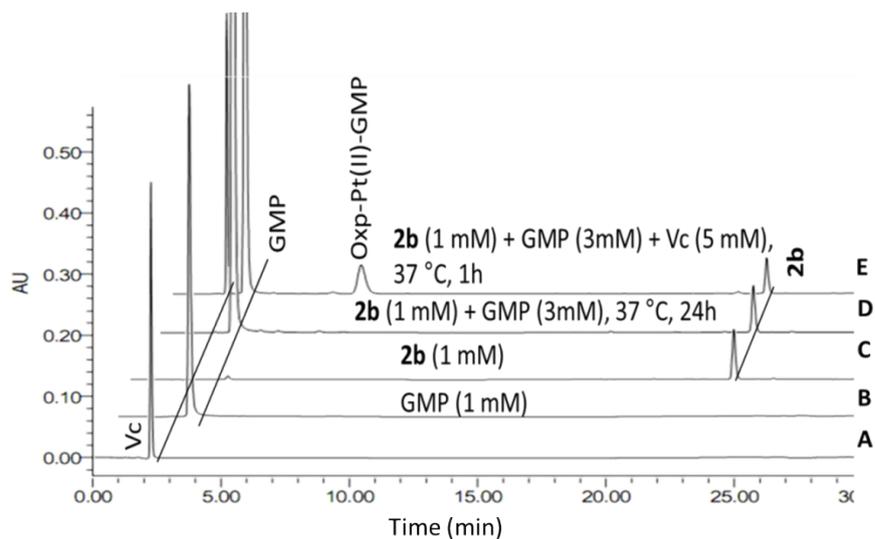


Fig. S3 The reduction of compound **1b**. (A) Ascorbic acid (1 mM) in water. (B) GMP (1 mM) in water. (C) Compound **1b** (1 mM) in water. (D) Solution of compound **1b** (1 mM) and GMP (3 mM) in water was incubated in 37 °C for 24h. (E) Solution of compound **1b** (1 mM), GMP (3 mM) and ascorbic acid (5 mM) in water was incubated in 37 °C for 1h. (F) HRMS of cis-Pt(II)-GMP peak in system E.



F

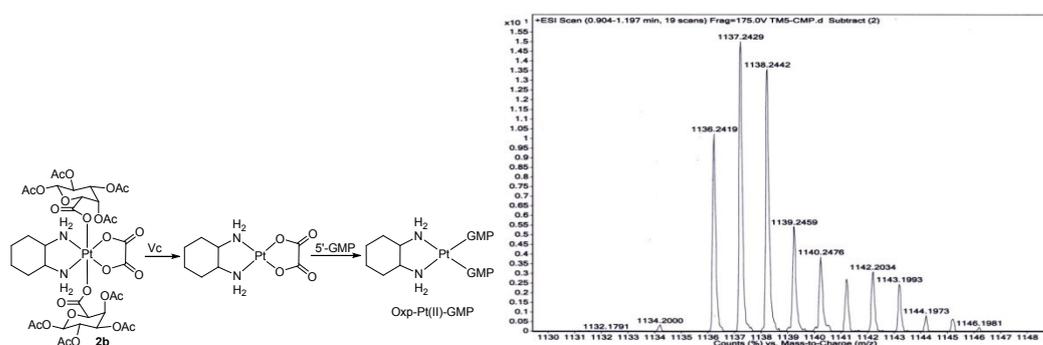
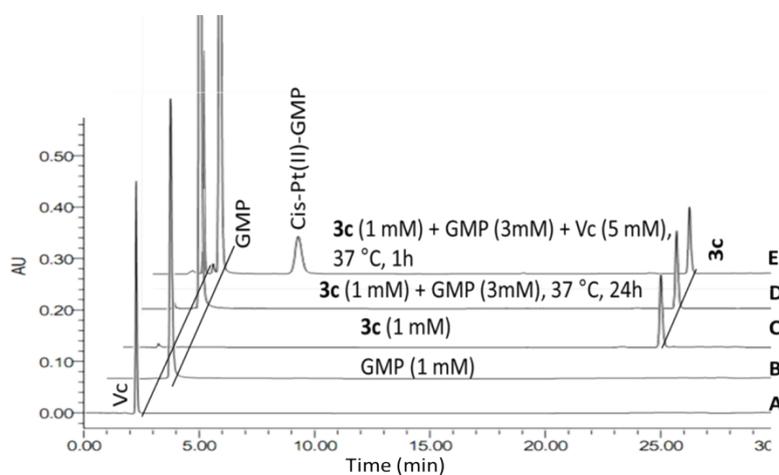


Fig. S4 The reduction of compound **2b**. (A) Ascorbic acid (1 mM) in water. (B) GMP (1 mM) in water. (C) Compound **2b** (1 mM) in water. (D) Solution of compound **2b** (1 mM) and GMP (3 mM) in water was incubated in 37 °C for 24h. (E) Solution of compound **2b** (1 mM), GMP (3 mM) and ascorbic acid (5 mM) in water was incubated in 37 °C for 1h. (F) HRMS of oxp-Pt(II)-GMP peak in system E.



F

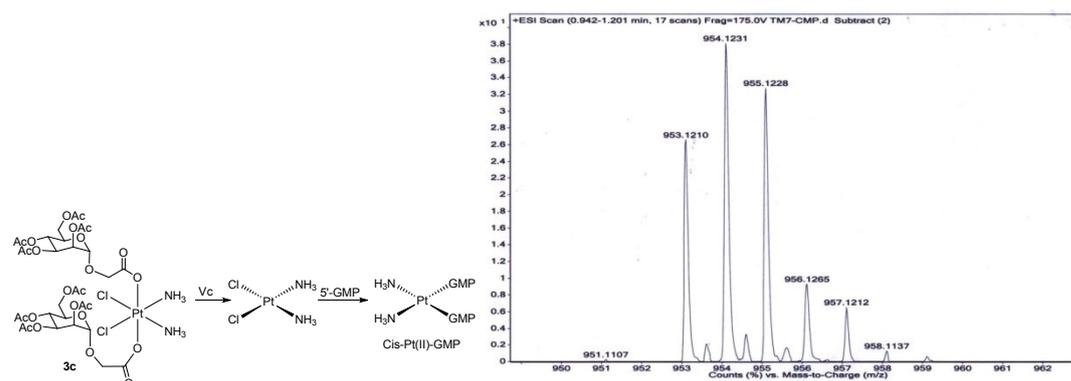
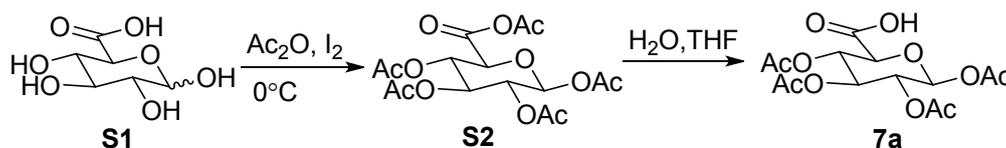


Fig. S5 The reduction of compound **3c**. (A) Ascorbic acid (1 mM) in water. (B) GMP (1 mM) in water. (C) Compound **3c** (1 mM) in water. (D) Solution of compound **3c** (1 mM) and GMP (3 mM) in water was incubated in 37 °C for 24h. (E) Solution of compound **3c** (1 mM), GMP (3 mM) and ascorbic acid (5 mM) in water was incubated in 37 °C for 1h. (F) HRMS of cis-Pt(II)-GMP peak in system E.

3. Synthetic procedures for acids **7a-c** and **8a-f**

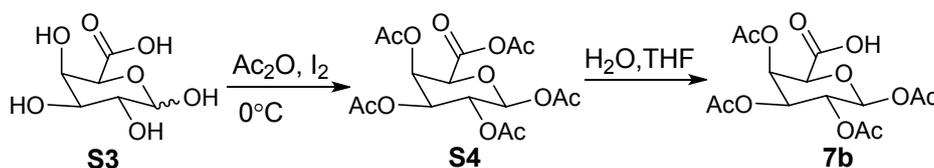
3.1 Preparation of (2*S*,3*S*,4*S*,5*R*,6*S*)-3,4,5,6-tetraacetoxytetrahydro-2H-pyran-2-carboxylic acid (**7a**)



To acetic anhydride 140 mL was added *D*-glucuronic acid **S1** 10.0 g, and the mixture was stirred at 0°C for 20 min. Then iodine 700 mg was added. The reaction mixture was kept at 0°C for 2 h and then turned to 25°C for another 1h. After that, solvent was removed and residue was dissolved in dichloromethane 100 mL and washed twice with $\text{Na}_2\text{S}_2\text{O}_3$ solution 1 M (2×50 mL). The organic layer was dried, concentrated and recrystallized (dichloromethane/ petroleum ether) and pure compound **S2** was obtained as white solid. Compound **S2** was dissolved in a mixture of $\text{H}_2\text{O}/\text{THF}$ (2/1) 400 mL, and the mixture was stirred overnight. Then THF was removed and extracted with dichloromethane. The organic layer was concentrated and the residue was recrystallized (dichloromethane/petroleum ether). Pure compound **7a** 12.7 g was obtained as white solid in yield of 68%.

^1H NMR (400 MHz, CDCl_3) δ 9.49 (br, 1H), 5.81 (d, $J = 7.6$ Hz, 1H), 5.39 – 5.25 (m, 2H), 5.16 (t, $J = 8.2$ Hz, 1H), 4.27 (d, $J = 9.2$ Hz, 1H), 2.14 (s, 3H), 2.07 (s, 3H), 2.06 (s, 3H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.45, 170.08, 169.82, 169.36, 169.00, 91.26, 72.34, 71.73, 70.03, 68.54, 20.78, 20.57, 20.52.

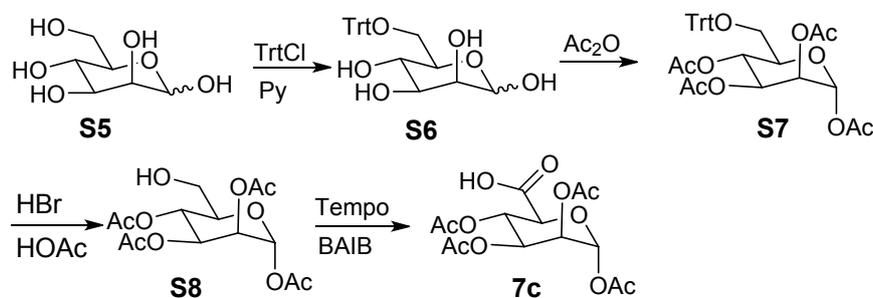
3.2 Preparation of (2*S*,3*R*,4*S*,5*R*,6*S*)-3,4,5,6-tetraacetoxytetrahydro-2H-pyran-2-carboxylic acid (**7b**)



To acetic anhydride 140 mL was added *D*-galacturonic acid **S3** 10.0 g, and the mixture was stirred at 0 °C for 20 min. Then iodine 700 mg was added. The reaction mixture was kept at 0 °C for 2h and then turned to 25 °C for another 1h. After that, solvent was removed and residue was dissolved in dichloromethane 100 mL and washed twice with Na₂S₂O₃ solution 1 M (2×50 mL). The organic layer was dried, concentrated and recrystallized (dichloromethane/ petroleum ether) and pure compound **S4** was obtained as white solid. Compound **S4** was dissolved in a mixture of H₂O/THF (2/1) 400 mL, and the mixture was stirred overnight. Then THF was removed and extracted with dichloromethane. The organic layer was concentrated and the residue was recrystallized (dichloromethane/ petroleum ether). Pure compound **7b** 8.6 g was obtained as white solid in yield of 46%.

¹H NMR (400 MHz, CDCl₃) δ 7.22 (br, 1H), 6.50 (d, *J* = 2.8 Hz, 1H), 5.87 (s, 1H), 5.42 – 5.33 (m, 2H), 4.79 (s, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 170.2, 169.98, 169.93, 168.94, 168.76, 89.37, 70.46, 68.45, 66.98, 65.92, 20.8, 20.61, 20.51 (2C).

3.3 Scheme for the synthesis of (2*S*,3*S*,4*S*,5*S*,6*R*)-3,4,5,6- tetraacetoxytetrahydro-2H-pyran-2- carboxylic acid (**7c**)



Preparation of (2*R*,3*S*,4*S*,5*R*,6*R*)-6-((trityloxy)methyl)tetrahydro-2H-pyran-2,3,4,5- tetrayl tetraacetate (S7**)** *D*-mannose 10.0 g was dissolved in anhydrous pyridine (50 mL) and triphenylmethyl chloride 17.0 g was added. The mixture was stirred at 40 °C for 1.5 h. After cooling down to 0 °C, 30 mL acetic anhydride was added, and the solution was stirred overnight. The mixture was poured into ice-cold water and extracted with dichloromethane. The organic layer was dried over Na₂SO₄ and concentrated to give crude compound. Further recrystallization from ethanol, pure **S7** 21.5 g was afforded with yield of 65.6%.

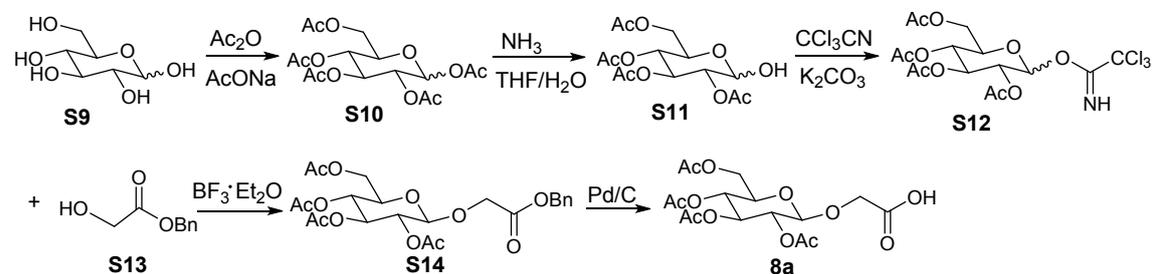
Preparation of (2*R*,3*S*,4*S*,5*R*,6*R*)-6-(hydroxymethyl)tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate (S8**)** Compound **S7** 9.0 g was dissolved in glacial acetic acid 20 mL and 3.0 mL of HBr/HOAc (33%, w/w) was added at 10 °C. The mixture was stirred for 3 min, and white solid formed immediately. The mixture was filtered and the filtrate was poured to ice water and extracted with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate and concentrated. The resulting residue was purified *via* silica gel column chromatography to give pure compound **S8** 4.4 g with yield of 82.3%.

Preparation of (2*S*,3*S*,4*S*,5*S*,6*R*)-3,4,5,6-tetraacetoxytetrahydro-2H-pyran-2-carboxylic acid (7c**)** To a solution of **S8** 2.0 g and TEMPO 150 mg in dichloromethane/water (2/1, v/v) 15 mL was added BAIB 3.4 g, and the mixture was stirred at room temperature overnight. The reaction mixture was extracted with dichloromethane, and the combined organic layer was dried over anhydrous sodium sulfate and concentrated. The resulting residue was purified *via* silica gel column chromatography to give pure compound **7c** as colorless syrup (1.7g, 82%).

¹H NMR (400 MHz, CDCl₃) δ 8.85 (br, 1H), 6.21 (d, *J* = 2.8 Hz, 1H), 5.47 (d, *J* = 9.1 Hz, 1H), 5.42 (d,

$J = 3.3$ Hz, 1H), 5.28 (t, $J = 3.1$ Hz, 1H), 4.44 (d, $J = 8.8$ Hz, 1H), 2.19 (s, 3H), 2.17 (s, 3H), 2.10 (s, 3H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 170.51, 169.95, 169.89 (2C), 168.18, 89.93, 70.92, 68.05, 67.67, 66.37, 20.78, 20.71, 20.63, 20.58.

3.4 Scheme for the synthesis of 2-(((2R,3R,4R,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)acetic acid (**8a**)



Preparation of (3R,4S,5R,6R)-6-(acetoxymethyl)tetrahydro-2H-pyran-2,3,4,5-tetrayl tetraacetate (S10**)** A mixture of *D*-glucose **S9** 25 g and sodium acetate 15 g in acetic anhydride 82 mL was stirred at 80 °C for 8 h. After that, the mixture was poured to ice-water and extracted with dichloromethane. The combined organic layer was washed with saturated sodium bicarbonate solution, dried over anhydrous sodium sulfate and concentrated. The solid obtained was recrystallized with alcohol to afford pure compound **S10** as white solid (43.3 g, 80%).

Preparation of (2R,3R,4S,5R)-2-(acetoxymethyl)-6-hydroxytetrahydro-2H-pyran-3,4,5-triyl triacetate (S11**)** Compound **S10** 10 g was dissolved in THF/MeOH (210 mL/90 mL), and the mixture was stirred in ice bath for 20 min. Then alkaline air was slowly bubbled into the reaction solution. The reaction was monitored by TLC. After the reaction completed, the solvents were quickly removed under vacuum. Then residue was extracted with dichloromethane, and the combined organic layer dried over anhydrous sodium sulfate and concentrated. The resulting residue was purified *via* silica gel column chromatography to give pure compound **S11** as colorless syrup (6.6 g, 74.1%).

Preparation of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2,2,2-trichloro-1-iminoethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (S12**)** A mixture of compound **S11** 1.0 g and anhydrous potassium carbonate 2.0 g in dry DCM was stirred for 20 min, and then trichloroacetonitrile 1.15 mL was injected. The reaction was stirred overnight. Then the mixture was filtered, and the filter-cake was washed with DCM. The organic layer was concentrated and purified *via* silica gel column chromatography to give pure compound **S12** as colorless syrup (1.2 g, 87.8%).

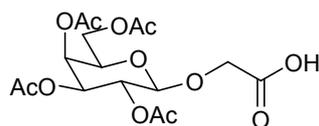
Preparation of (2R,3R,4S,5R,6R)-2-(acetoxymethyl)-6-(2-(benzyloxy)-2-oxoethoxy)tetrahydro-2H-pyran-3,4,5-triyl triacetate (S14**)** A mixture of compound **S12** 1.2 g and compound **S13** 0.6 g in dry DCM was stirred for 20 min at -40 °C, and then $\text{BF}_3 \cdot \text{Et}_2\text{O}$ 0.69 mL was injected. The reaction was stirred for 4h and monitored by TLC. Then the mixture was poured into ice-water and extracted with DCM. Then the organic layer was concentrated and purified *via* silica gel column chromatography to give pure compound **S14** as colorless syrup (0.46 g, 38.4%).

Preparation of 2-(((2R,3R,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)acetic acid (8a**)** To a flask containing **S14** 0.40 g dissolved in methanol 10 mL was added 10% Pd/C 30 mg and ammonium acetate 0.22 g. The mixture was hydrogenated with

H₂ for 1 h, monitoring by TLC. Filtration through celite and removal of solvent in vacuum yielded compound **8a** as white solid (0.27 g, 83.7%).

¹H NMR (400 MHz, CDCl₃) δ 9.05 (br, 1H), 5.26 (t, *J* = 9.4 Hz, 1H), 5.15 – 5.01 (m, 2H), 4.68 (d, *J* = 7.8 Hz, 1H), 4.35 (s, 2H), 4.27 (dd, *J* = 12.3, 3.7 Hz, 1H), 4.16 (d, *J* = 12.3 Hz, 1H), 3.75 (d, *J* = 9.7 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.24, 170.84, 170.30, 169.74, 169.51, 100.23, 72.41, 72.01, 70.93, 68.22, 64.93, 61.75, 20.70, 20.66, 20.57.

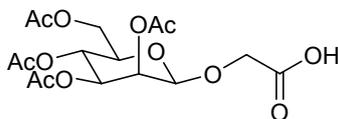
3.5 Preparation of 2-(((2R,3R,4R,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)acetic acid (**8b**)



Compound **8b** was prepared according to the procedure described for compound **8a**, starting from *D*-galactose. The pure product **8b** was obtained as white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.77 (br, 1H), 5.41 (d, *J* = 3.1 Hz, 1H), 5.33 – 5.18 (m, 1H), 5.07 (dd, *J* = 10.5, 3.3 Hz, 1H), 4.64 (d, *J* = 7.9 Hz, 1H), 4.36 (s, 2H), 4.15 (dq, *J* = 6.3, 4.3 Hz, 2H), 3.96 (t, *J* = 6.6 Hz, 1H), 2.17 (s, 3H), 2.10 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.20, 170.61, 170.33, 170.23, 169.98, 100.63, 70.90, 70.55, 68.40, 66.89, 64.73, 61.26, 20.77, 20.66, 20.64, 20.57.

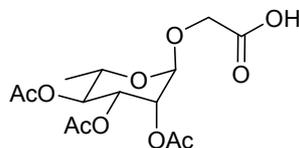
3.6 Preparation of 2-(((2R,3S,4S,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)acetic acid (**8c**)



Compound **8c** was prepared according to the procedure described for compound **8a**, starting from *D*-mannose. The pure product **8c** was obtained as white solid.

¹H NMR (400 MHz, CDCl₃) δ 8.39 (s, 1H), 5.37 (d, *J* = 6.3 Hz, 2H), 5.31 (dd, *J* = 12.4, 7.7 Hz, 1H), 4.96 (s, 1H), 4.29 (m, 3H), 4.13 (m, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 2.06 (s, 3H), 2.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.07, 171.01, 170.10, 169.92, 97.81, 69.14, 68.90, 65.86, 64.13, 62.39, 20.85, 20.74, 20.70, 20.66.

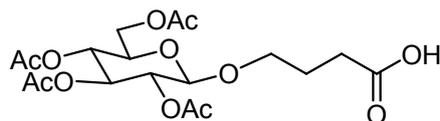
3.7 Preparation of 2-(((2R,3R,4R,5S,6S)-3,4,5-triacetoxy-6-methyltetrahydro-2H-pyran-2-yl)oxy)acetic acid (**8d**)



Compound **8d** was prepared according to the procedure described for compound **8a**, starting from *D*-rhamnose. The pure product **8d** was obtained as colorless oil.

¹H NMR (400 MHz, CDCl₃) δ 7.36 (br, 1H), 5.37 (s, 1H), 5.31 (dd, *J* = 10.1, 3.2 Hz, 1H), 5.09 (t, *J* = 9.9 Hz, 1H), 4.88 (s, 1H), 4.26 (d, *J* = 5.3 Hz, 2H), 3.97 (dd, *J* = 9.7, 6.2 Hz, 1H), 2.16 (s, 3H), 2.07 (s, 3H), 2.00 (s, 3H), 1.23 (d, *J* = 6.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 173.38, 170.25, 170.21, 97.51, 70.76, 69.42, 68.96, 67.11, 63.78, 20.88, 20.80, 20.71, 17.31.

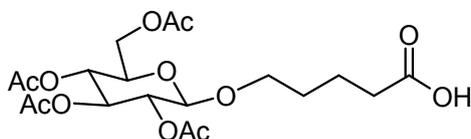
3.8 Preparation of 4-(((2R,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)butanoic acid (**8e**)



Compound **8e** was prepared according to the procedure described for compound **8a**, starting from *D*-glucose. The pure product **8e** was obtained as colorless oil.

^1H NMR (400 MHz, CDCl_3) δ 5.21 (t, $J = 9.5$ Hz, 1H), 5.09 (t, $J = 9.7$ Hz, 1H), 4.99 (dd, $J = 9.6, 8.0$ Hz, 1H), 4.50 (d, $J = 8.0$ Hz, 1H), 4.26 (dd, $J = 12.3, 4.7$ Hz, 1H), 4.14 (dd, $J = 12.3, 2.2$ Hz, 1H), 3.93 (dt, $J = 9.9, 5.7$ Hz, 1H), 3.70 (ddd, $J = 9.9, 4.6, 2.3$ Hz, 1H), 3.57 (dt, $J = 9.6, 6.3$ Hz, 1H), 2.44 (t, $J = 7.2$ Hz, 2H), 2.09 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.96 – 1.85 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 178.73, 170.80, 170.35, 169.46, 100.72, 72.80, 71.76, 71.23, 68.58, 68.37, 61.92, 30.12, 24.46, 20.73, 20.62.

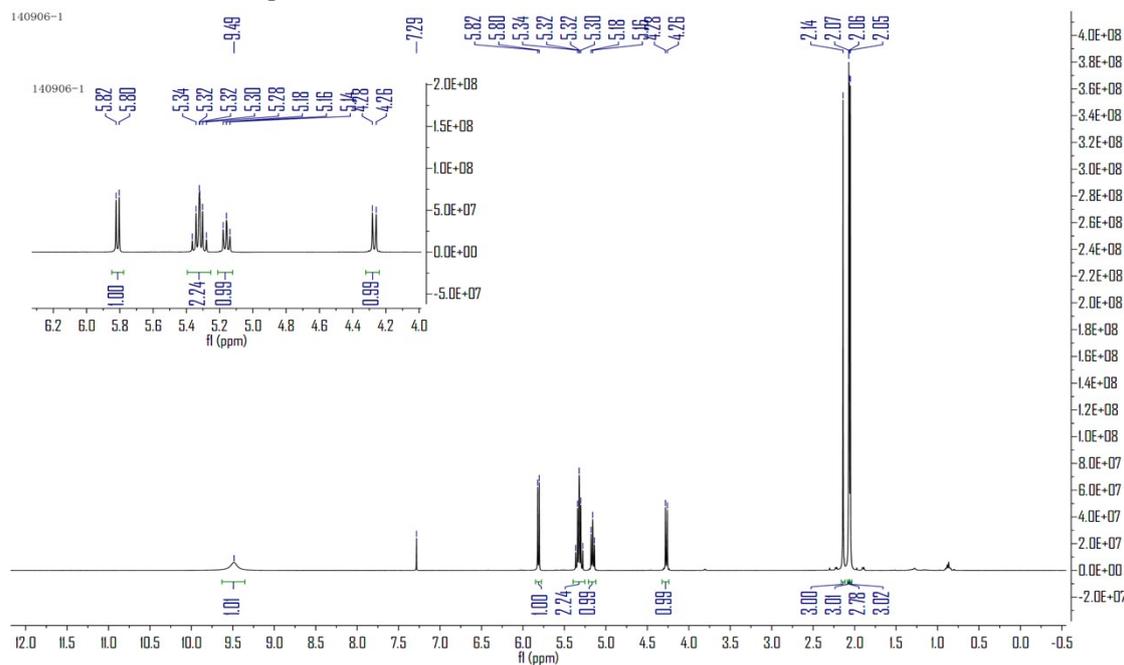
3.9 Preparation of 5-(((2R,5R,6R)-3,4,5-triacetoxy-6-(acetoxymethyl)tetrahydro-2H-pyran-2-yl)oxy)pentanoic acid (**8f**)



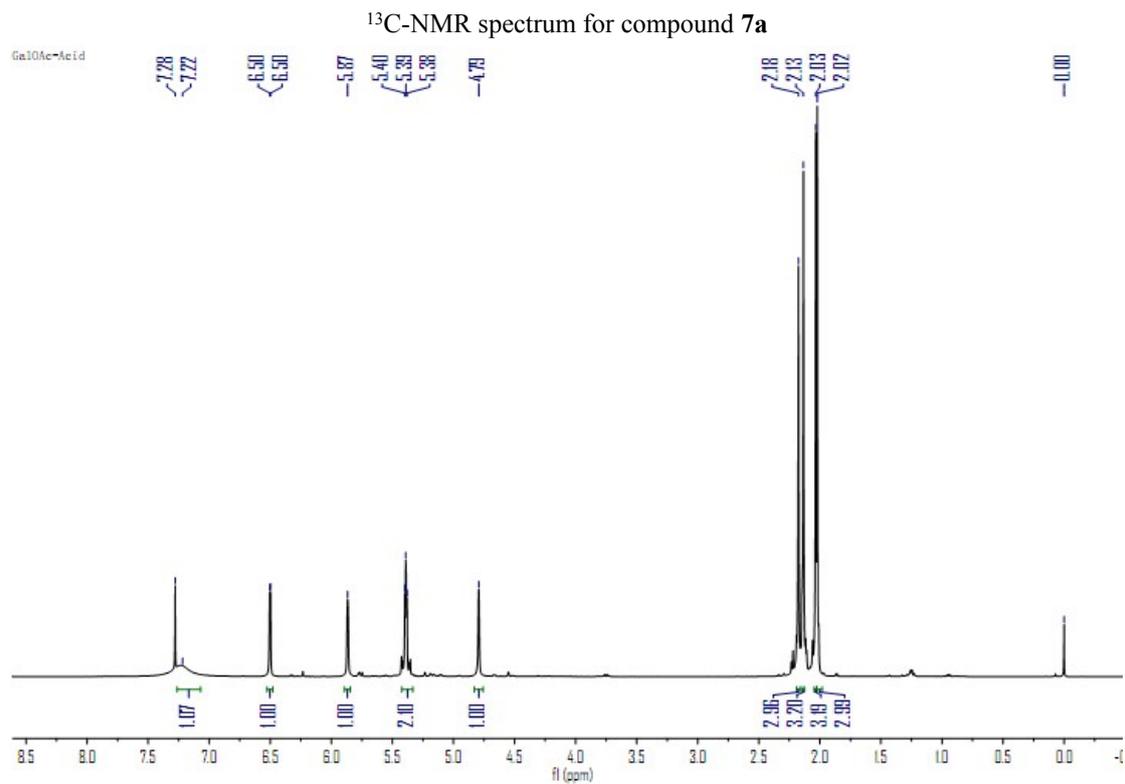
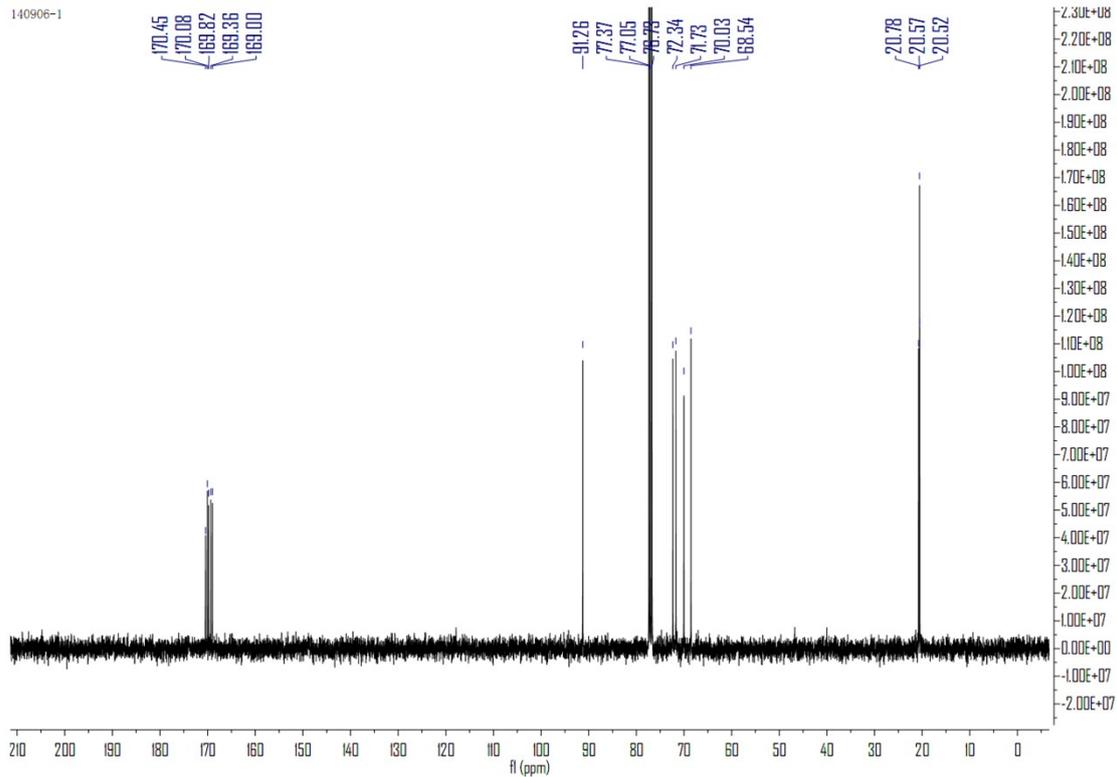
Compound **8f** was prepared according to the procedure described for compound **8a**, starting from *D*-glucose. The pure product **8f** was obtained as colorless oil.

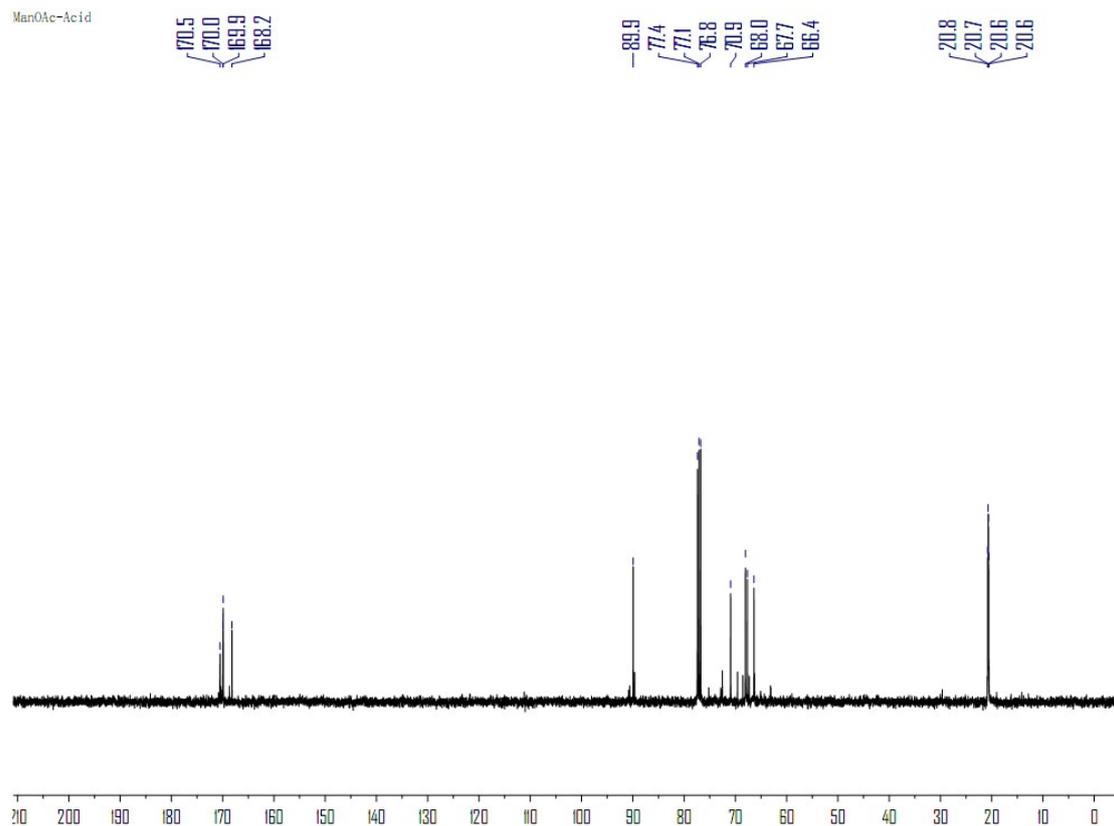
^1H NMR (400 MHz, CDCl_3) δ 5.21 (t, $J = 9.5$ Hz, 1H), 5.09 (t, $J = 9.7$ Hz, 1H), 4.99 (dd, $J = 9.6, 8.0$ Hz, 1H), 4.50 (d, $J = 8.0$ Hz, 1H), 4.26 (dd, $J = 12.3, 4.7$ Hz, 1H), 4.14 (dd, $J = 12.2, 2.3$ Hz, 1H), 3.92 (dd, $J = 9.8, 5.6$ Hz, 1H), 3.69 (m, 1H), 3.55 – 3.46 (m, 1H), 2.37 (t, $J = 7.0$ Hz, 2H), 2.09 (s, 3H), 2.05 (s, 3H), 2.03 (s, 3H), 2.01 (s, 3H), 1.75 – 1.57 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 178.72, 170.80, 170.38, 169.46, 169.44, 100.77, 72.83, 71.77, 71.27, 69.44, 68.41, 61.95, 33.36, 28.62, 21.13, 20.78, 20.65.

4. NMR and HRMS spectra

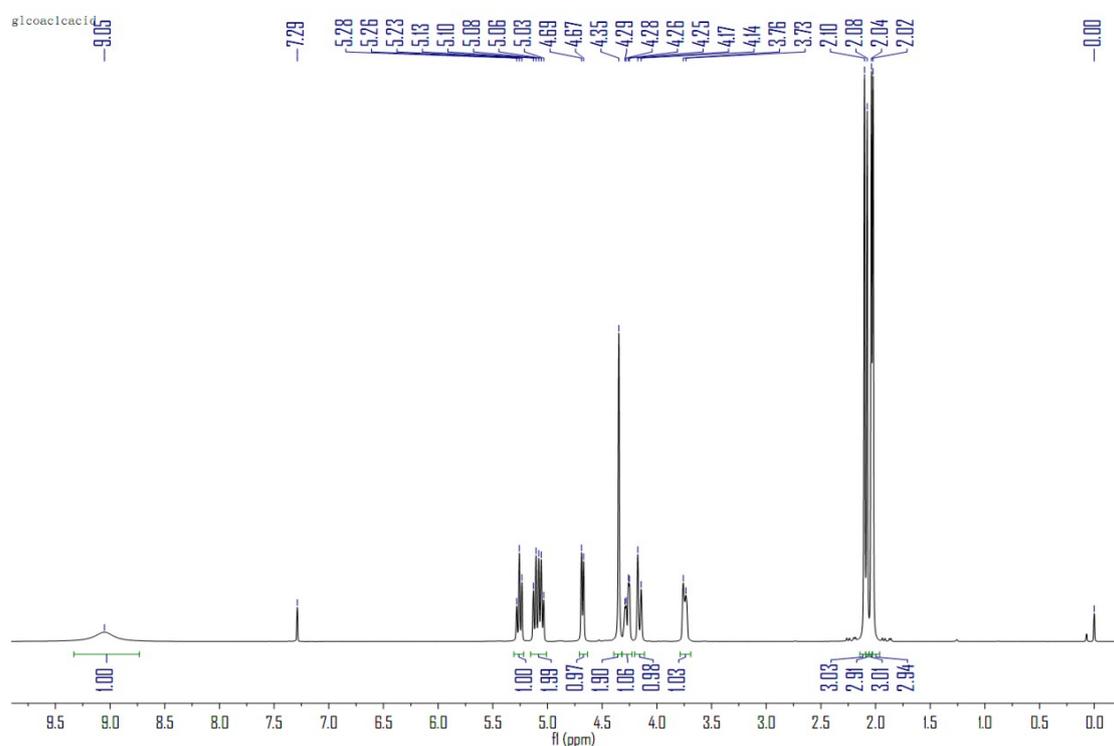


^1H -NMR spectrum for compound **7a**

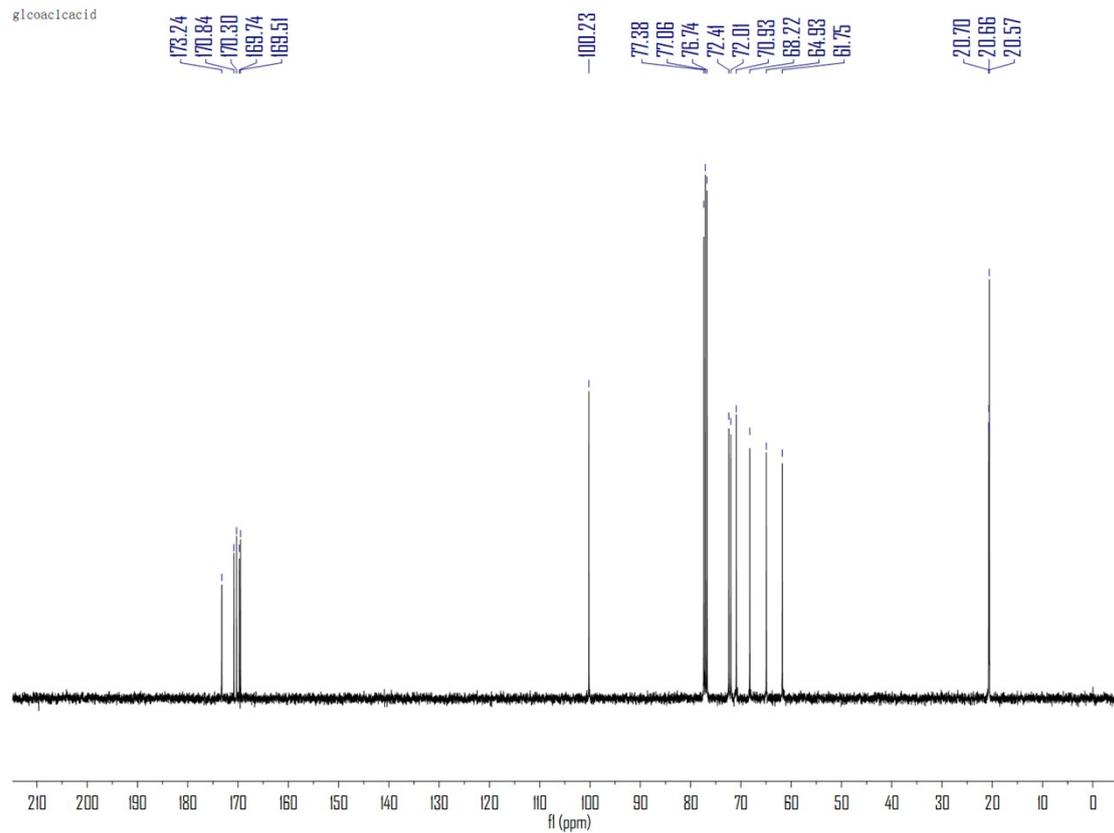




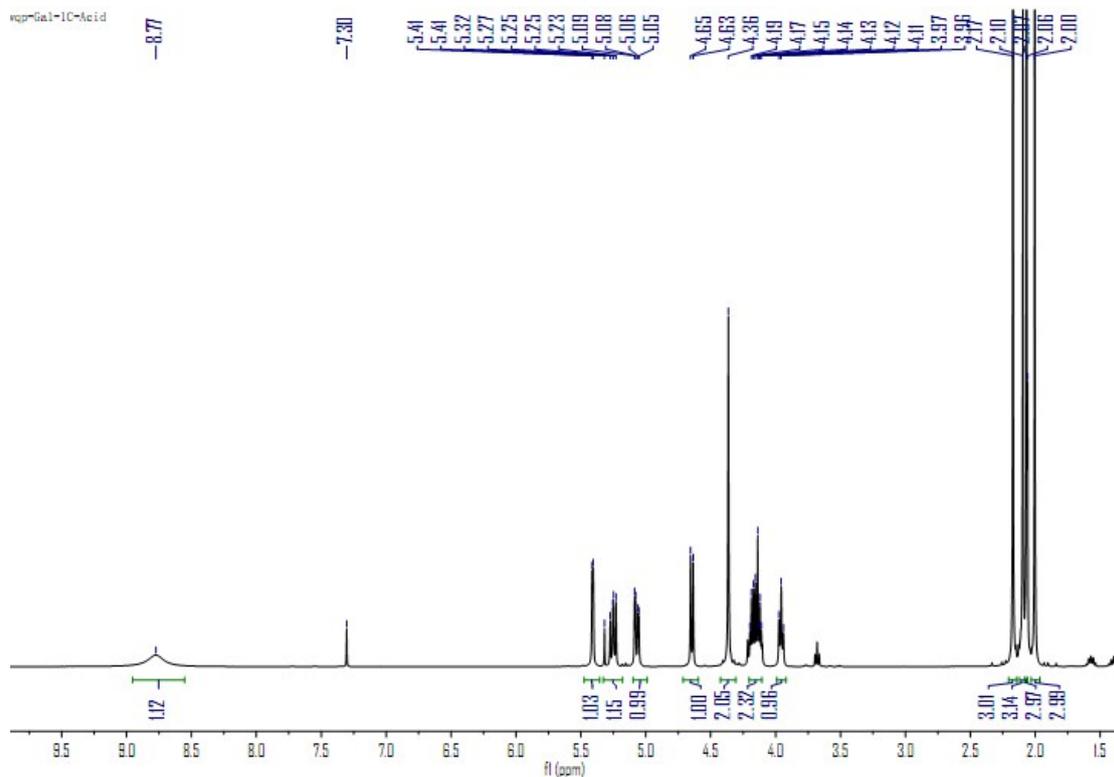
^{13}C -NMR spectrum for compound **7c**



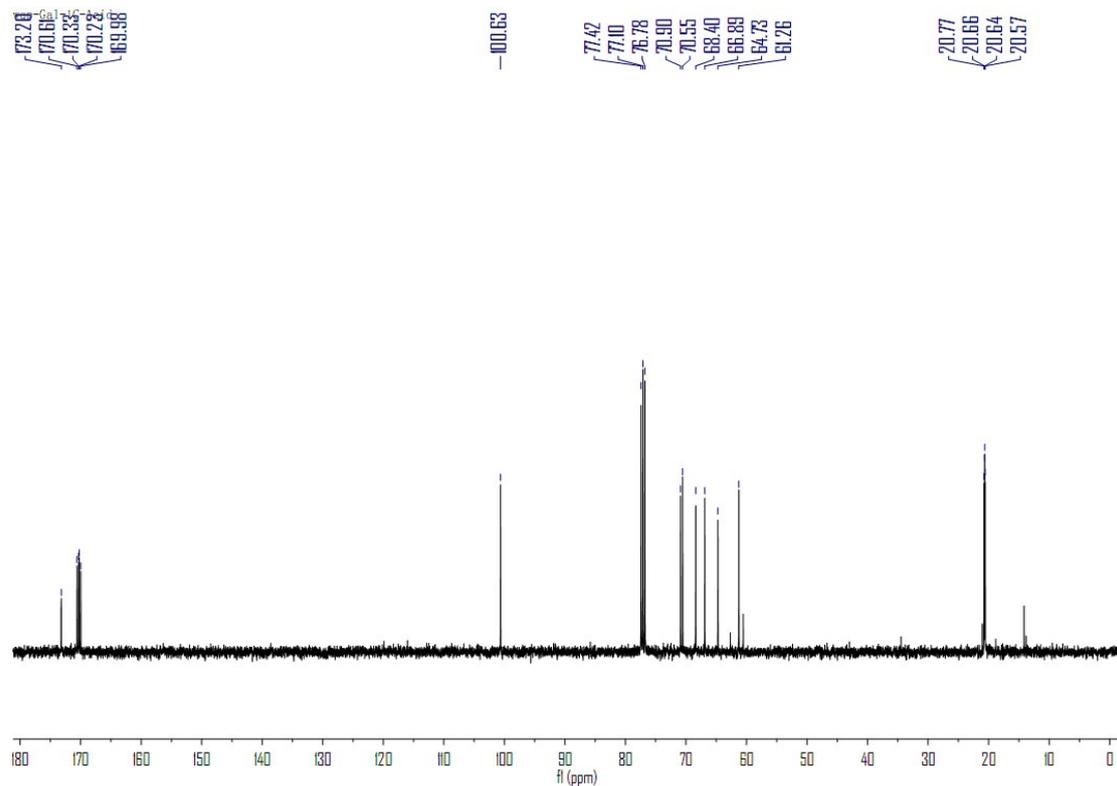
^1H -NMR spectrum for compound **8a**



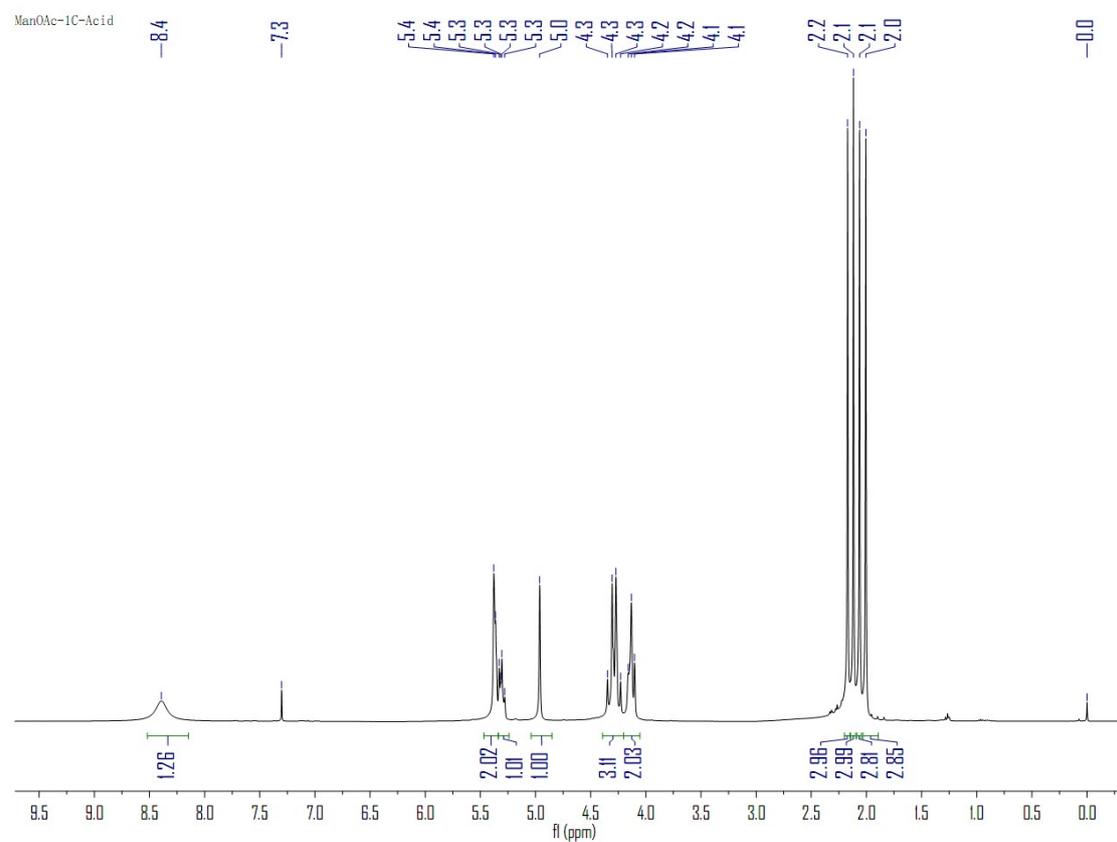
¹³C-NMR spectrum for compound **8a**



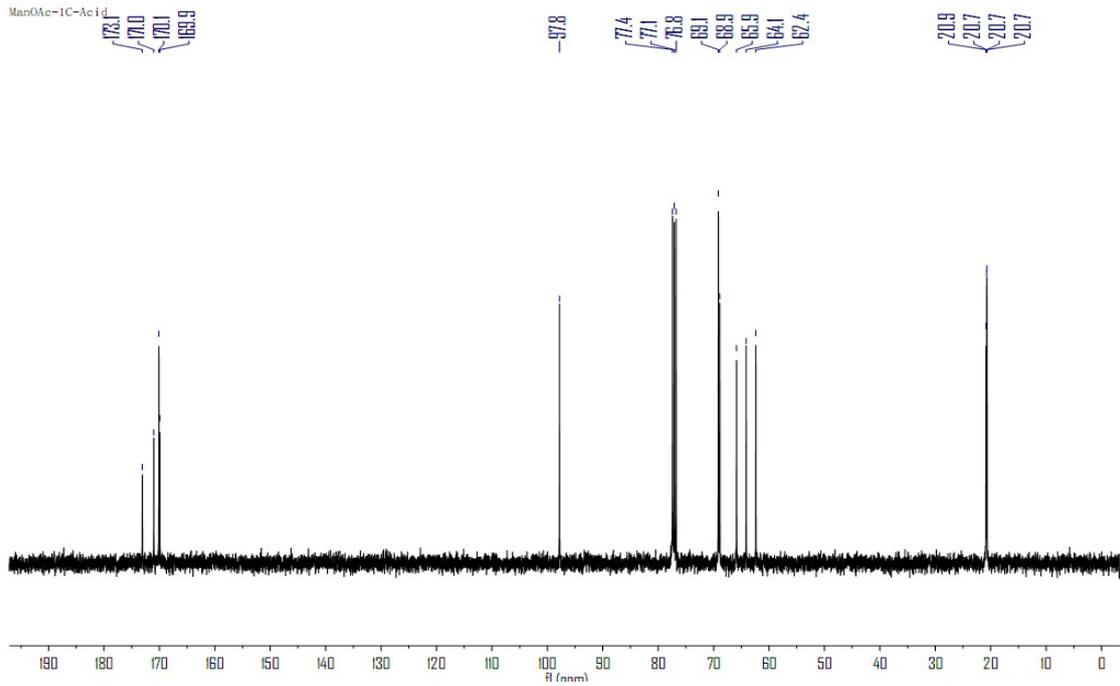
¹H-NMR spectrum for compound **8b**



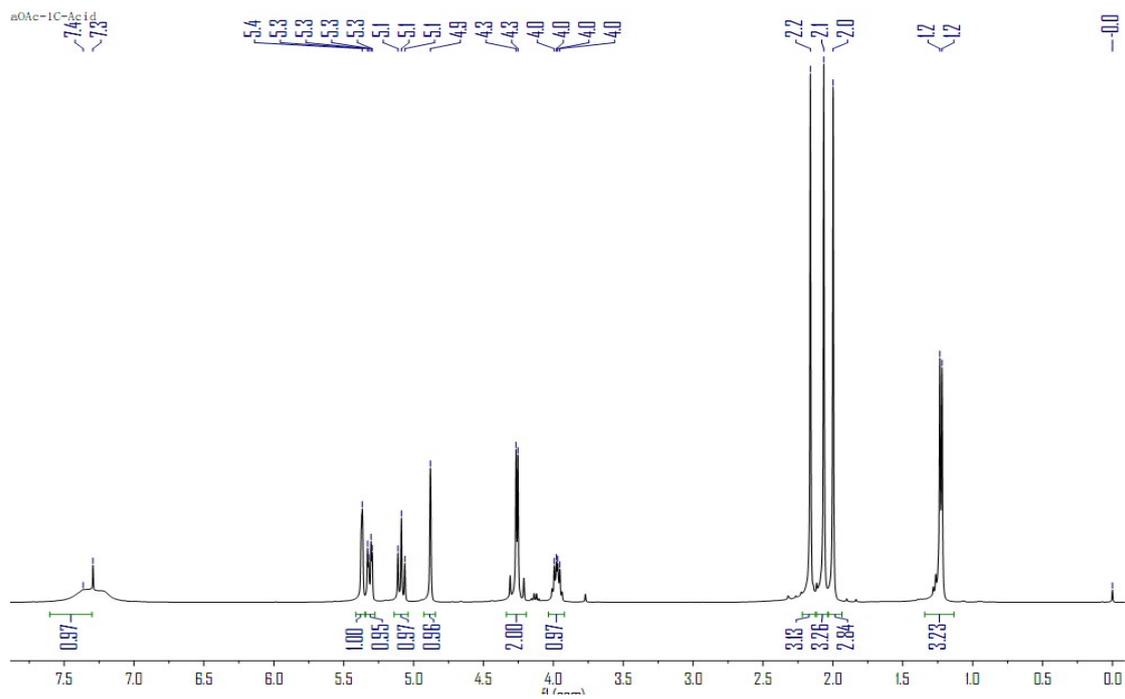
¹³C-NMR spectrum for compound **8b**



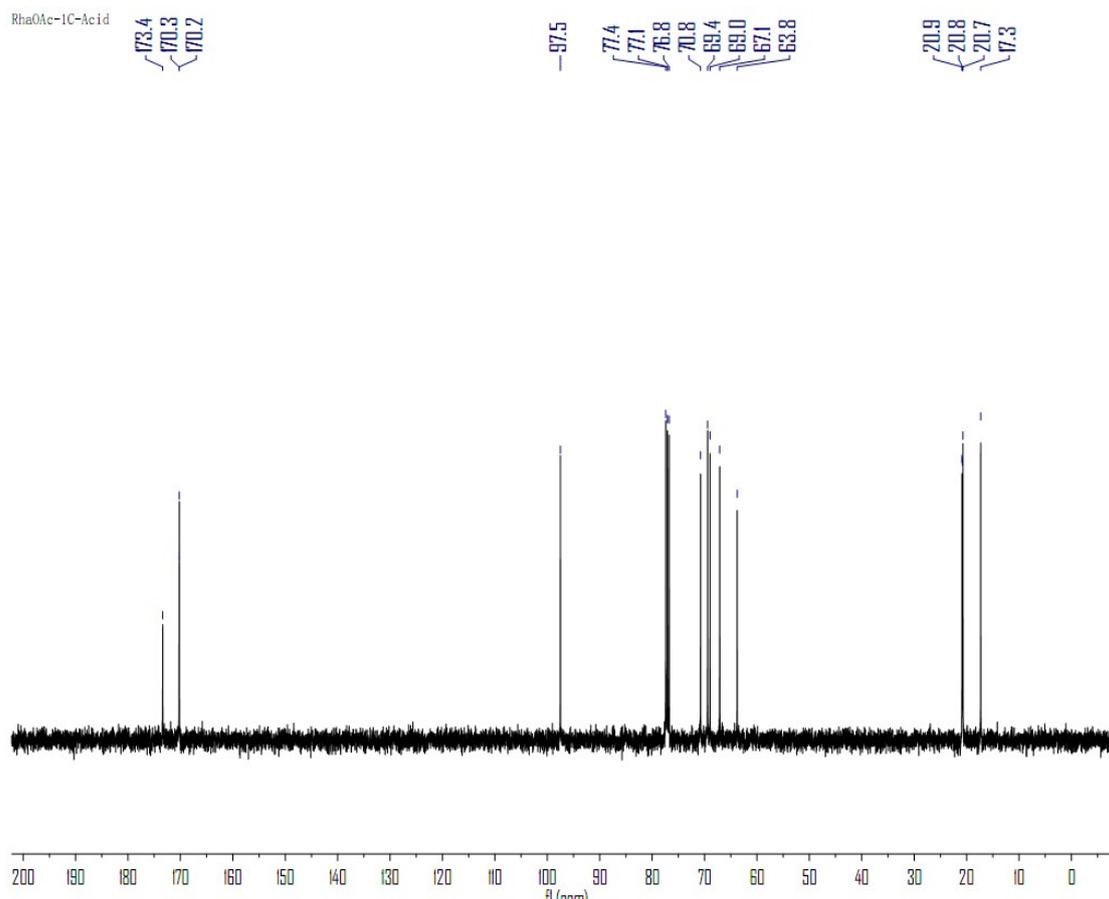
¹H-NMR spectrum for compound **8c**



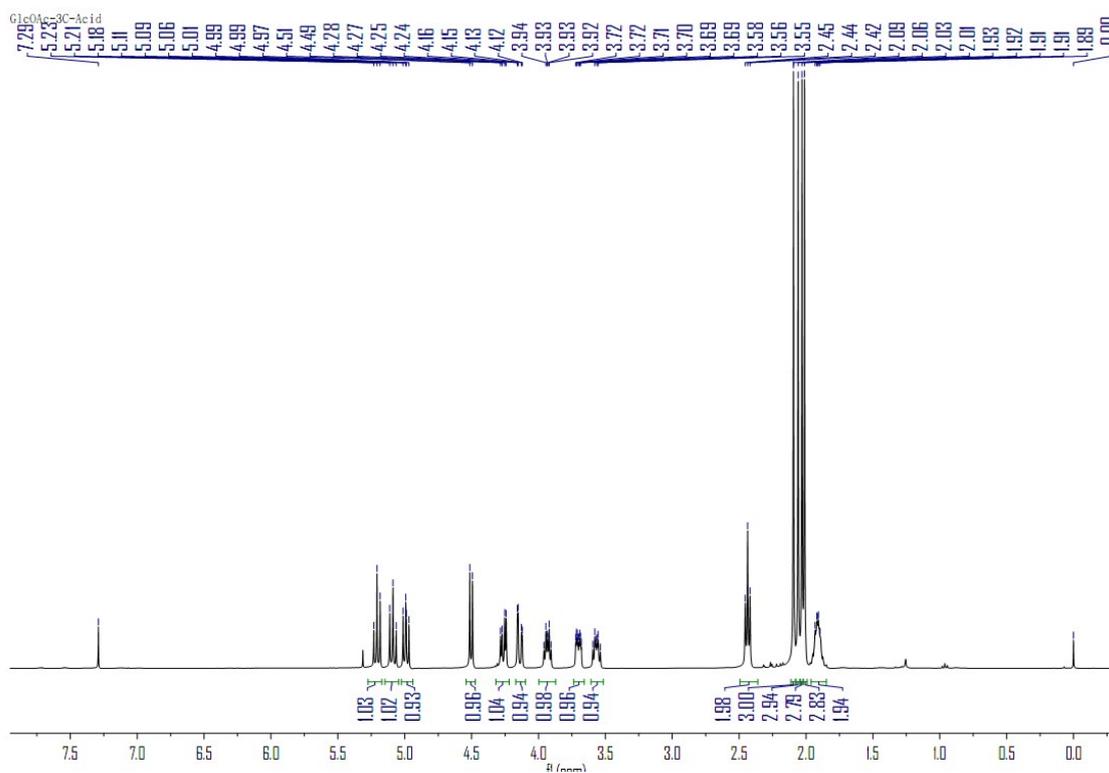
^{13}C -NMR spectrum for compound **8c**



^1H -NMR spectrum for compound **8d**

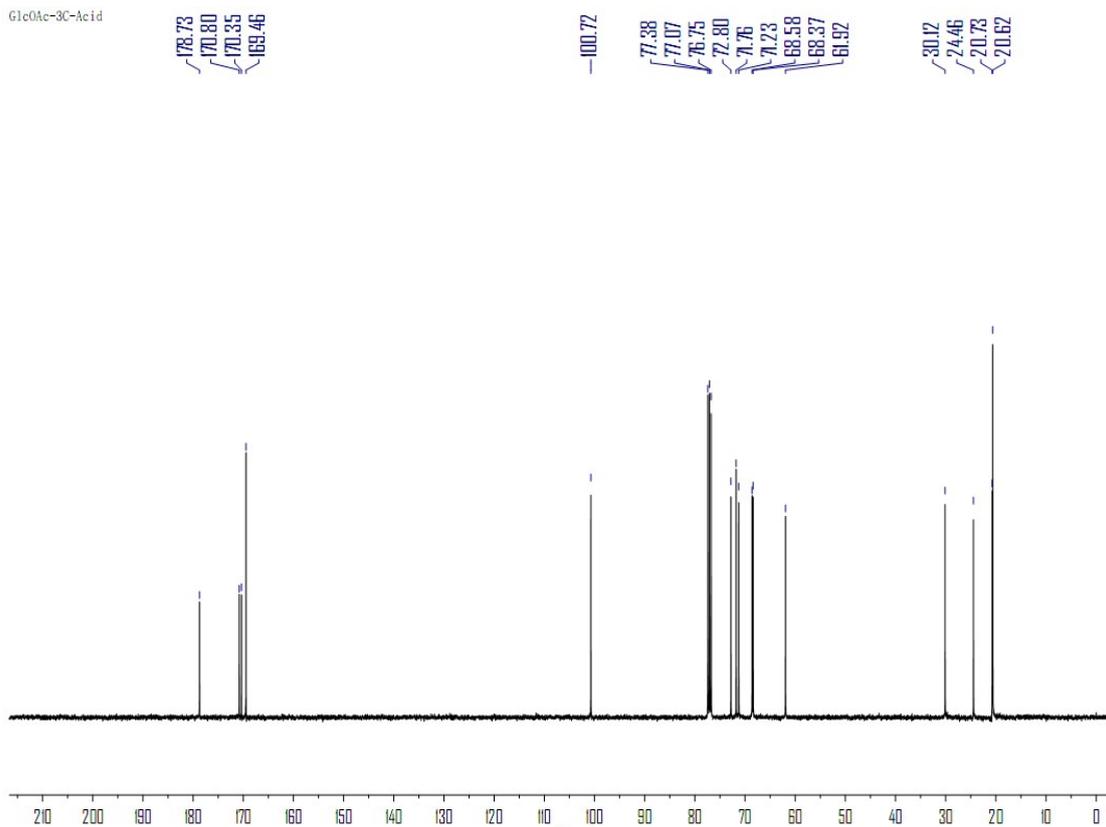


^{13}C -NMR spectrum for compound **8d**

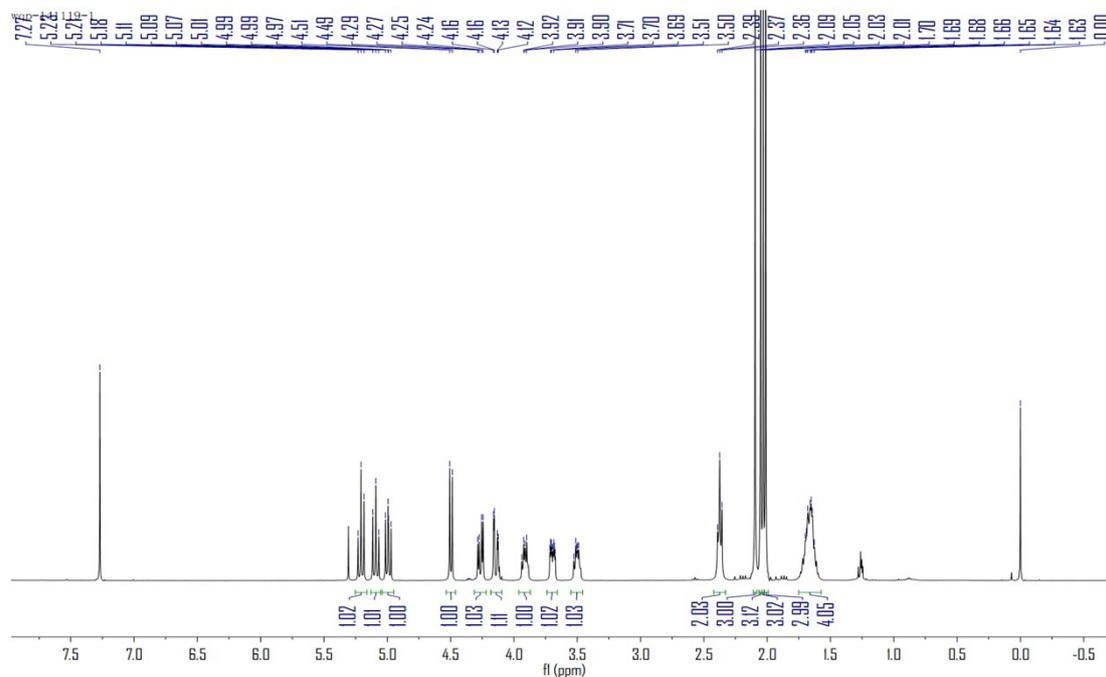


^1H -NMR spectrum for compound **8e**

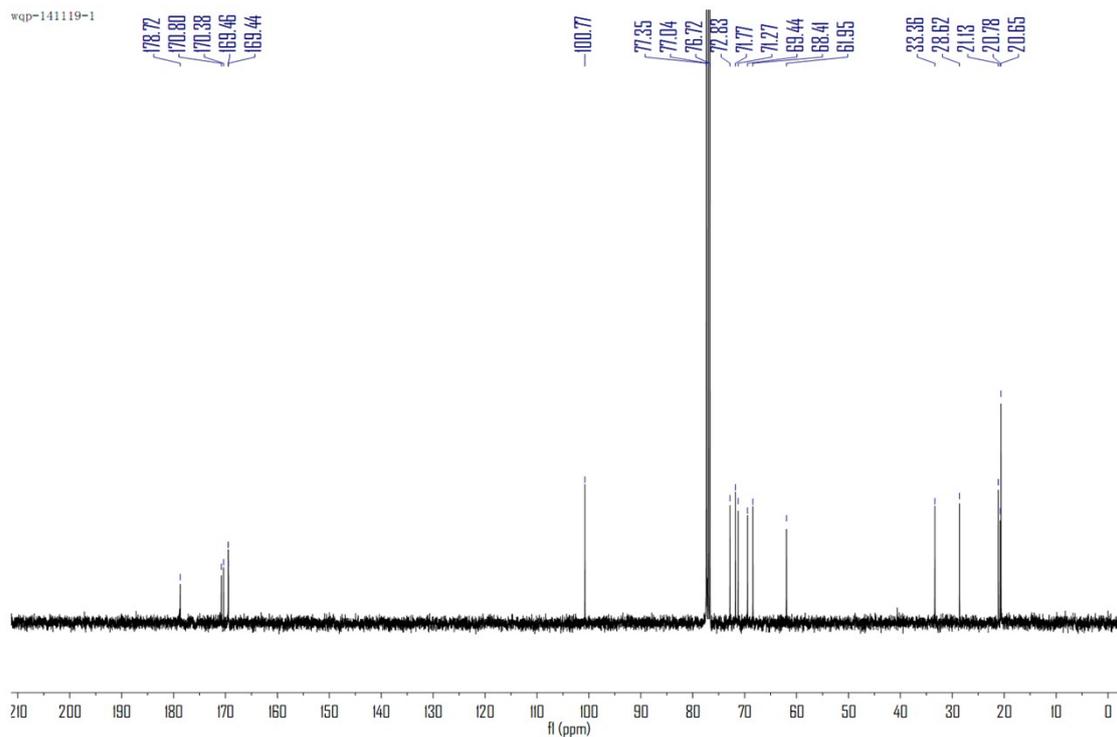
GlcOAc-3C-Acid



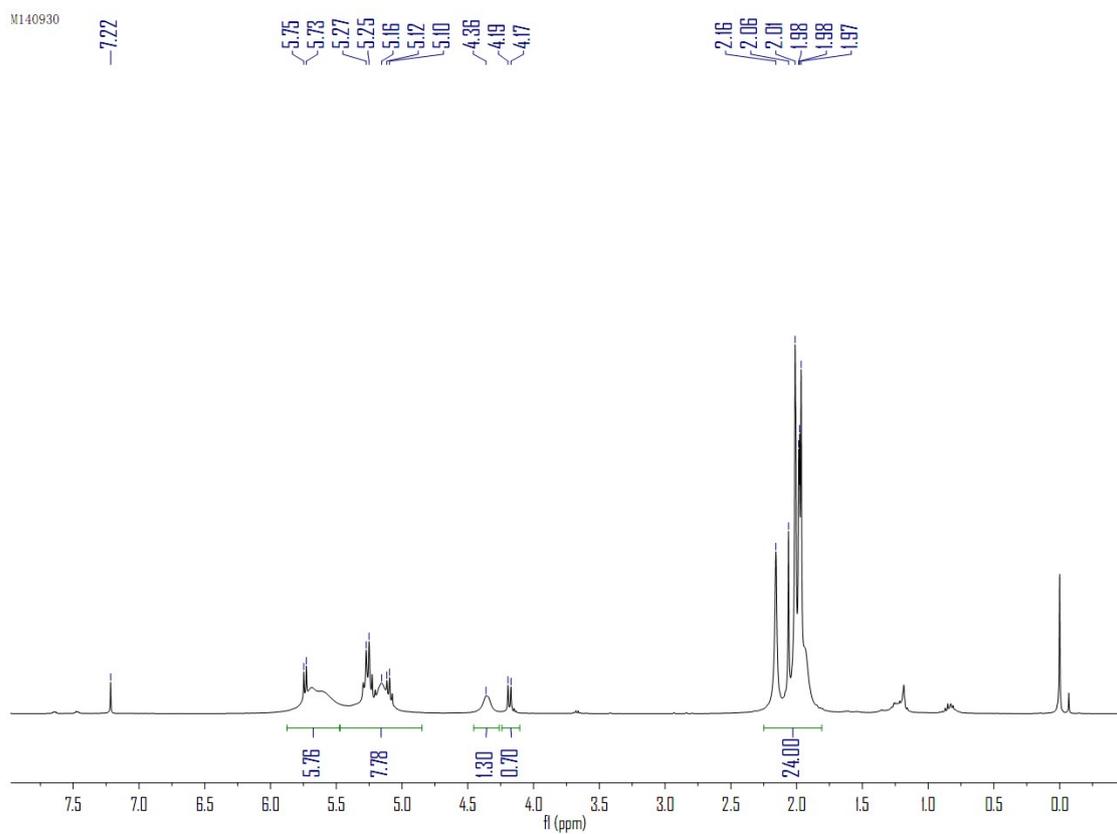
¹³C-NMR spectrum for compound **8e**



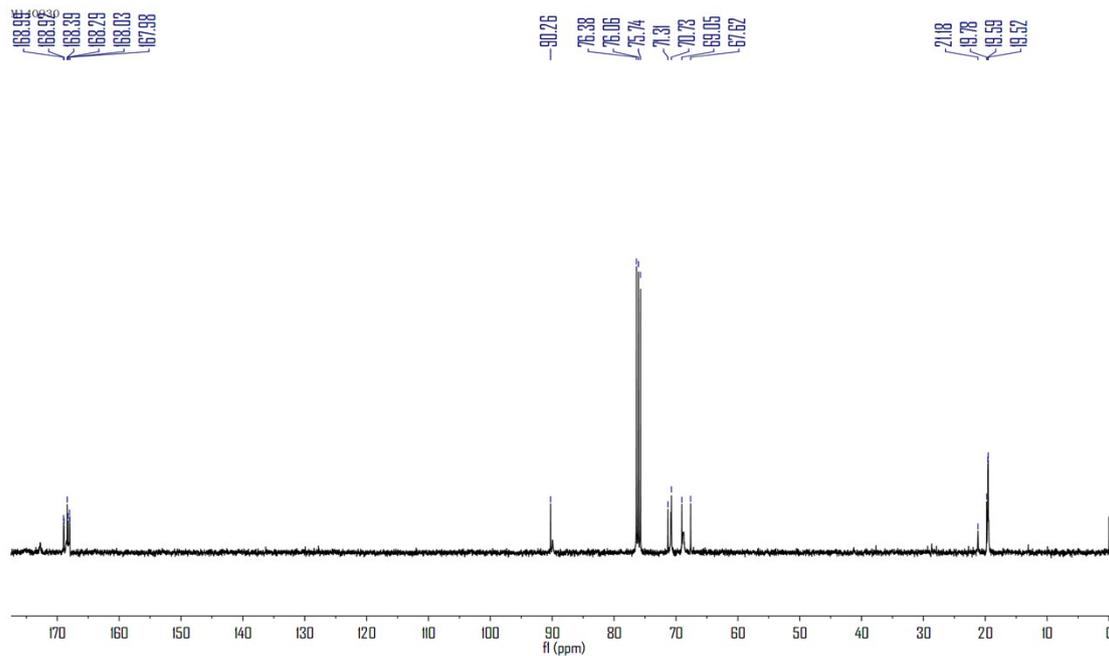
¹H-NMR spectrum for compound **8f**



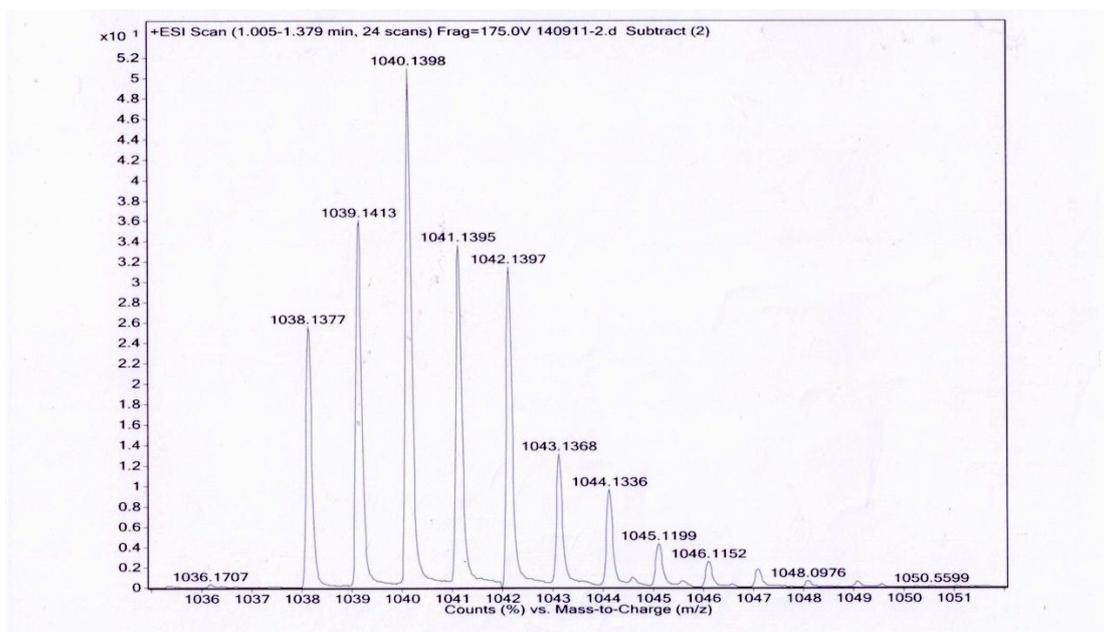
¹³C-NMR spectrum for compound **8f**



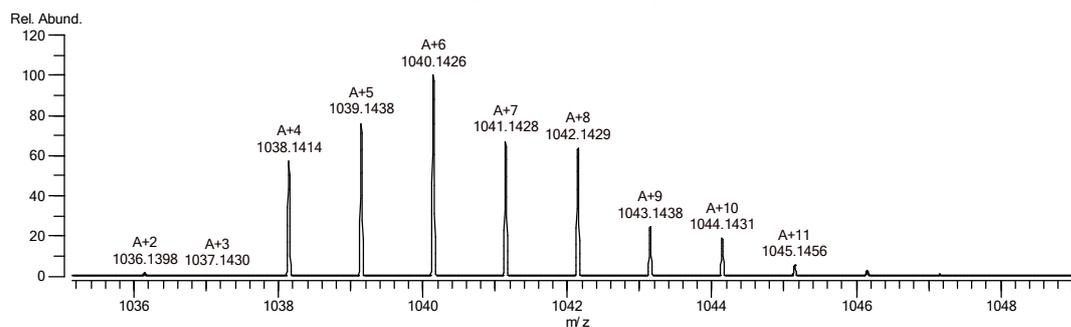
¹H-NMR spectrum for compound **1a**



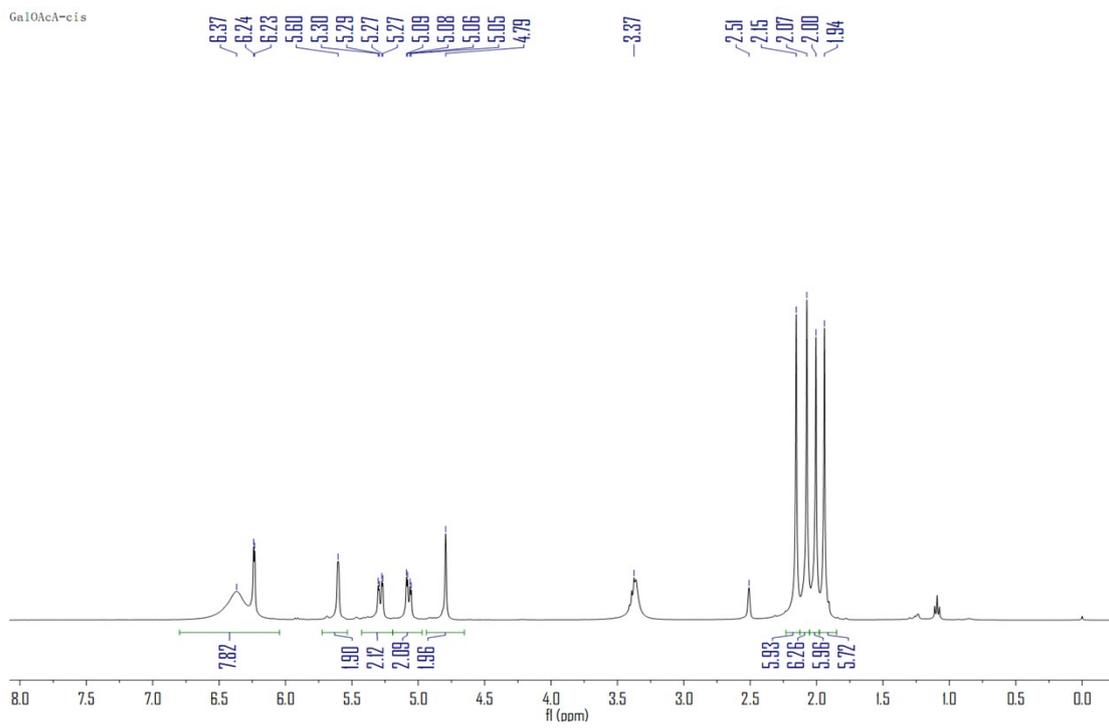
¹³C-NMR spectrum for compound **1a**



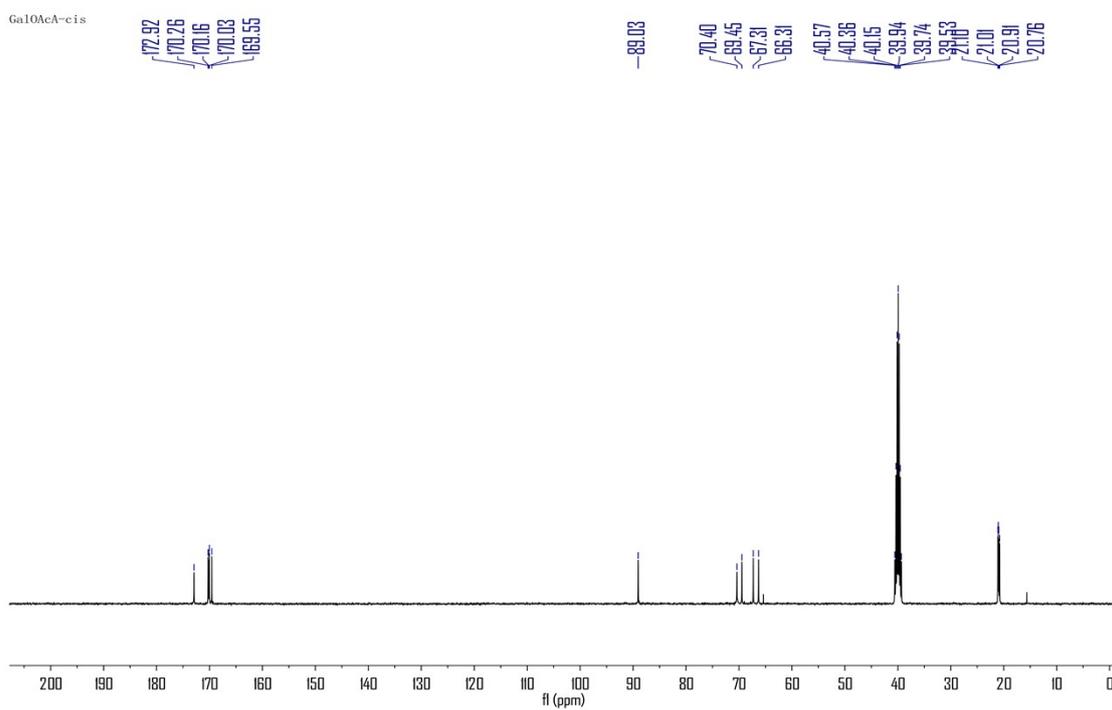
HRMS spectrum for compound **1a**



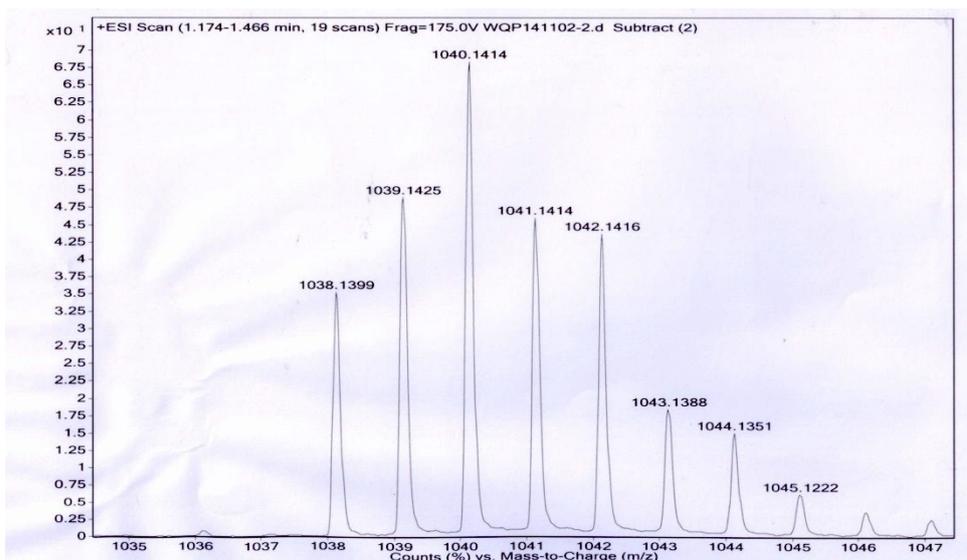
Calculated HRMS spectrum for compound **1a**



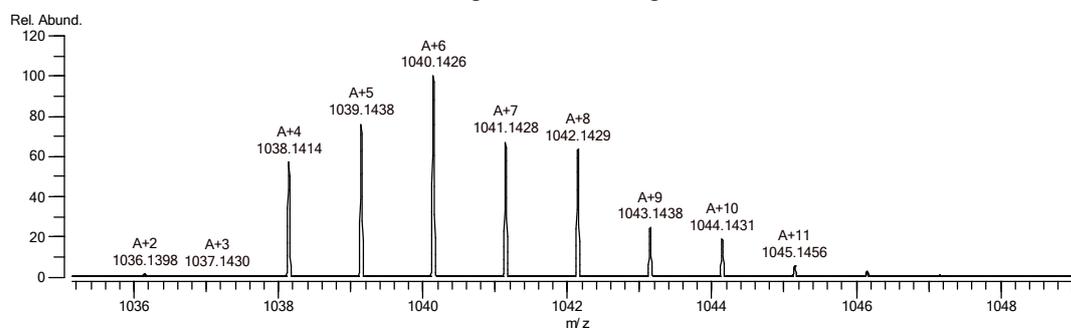
¹H-NMR spectrum for compound **1b**



¹³C-NMR spectrum for compound **1b**

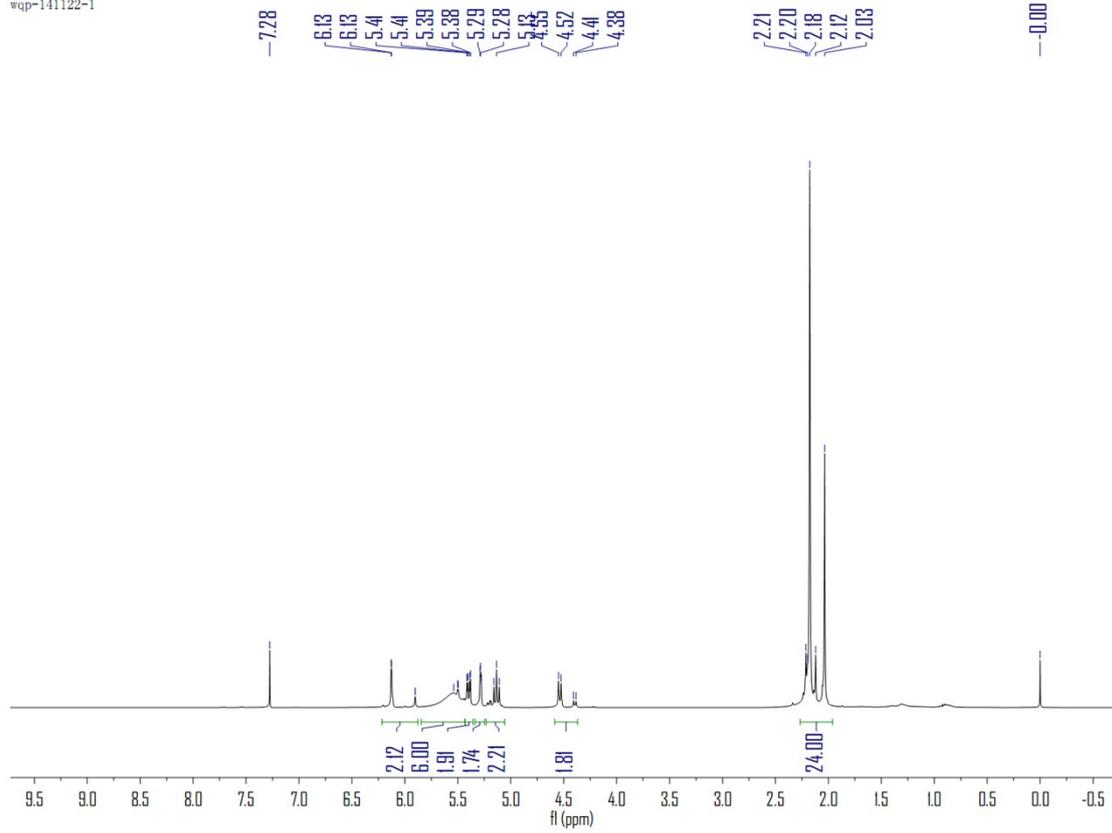


HRMS spectrum for compound **1b**



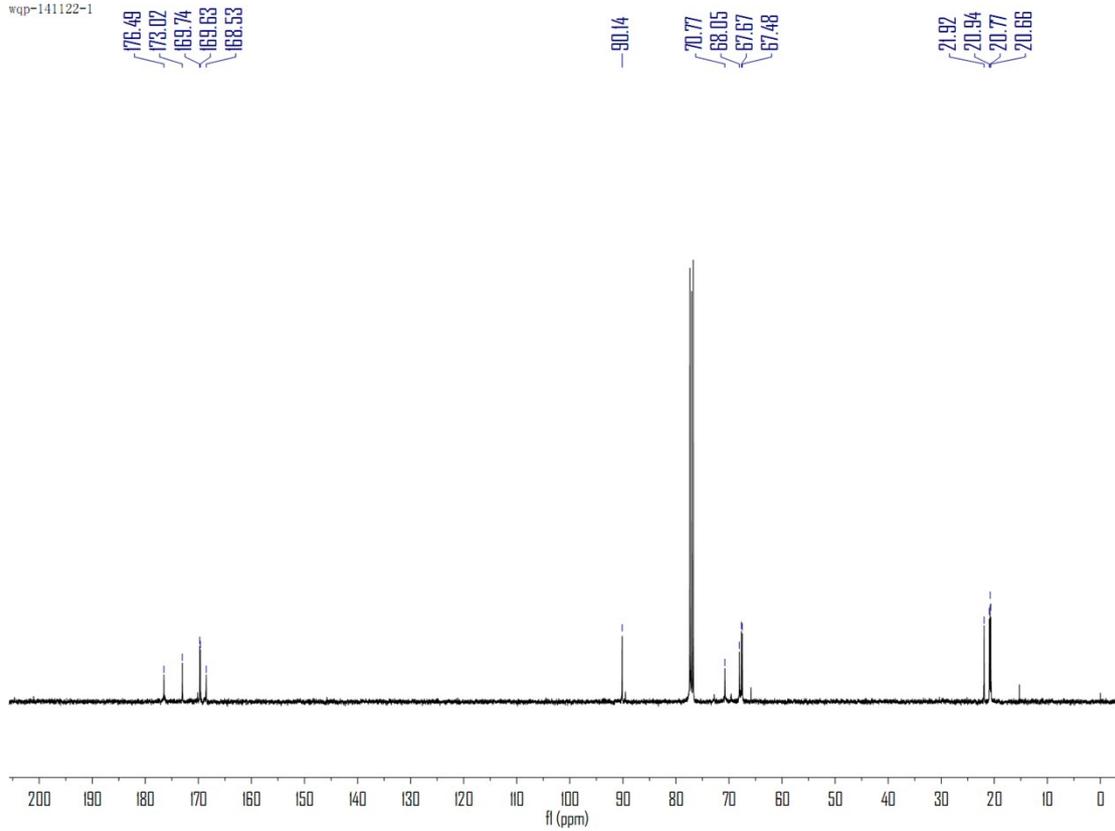
Calculated HRMS spectrum for compound **1b**

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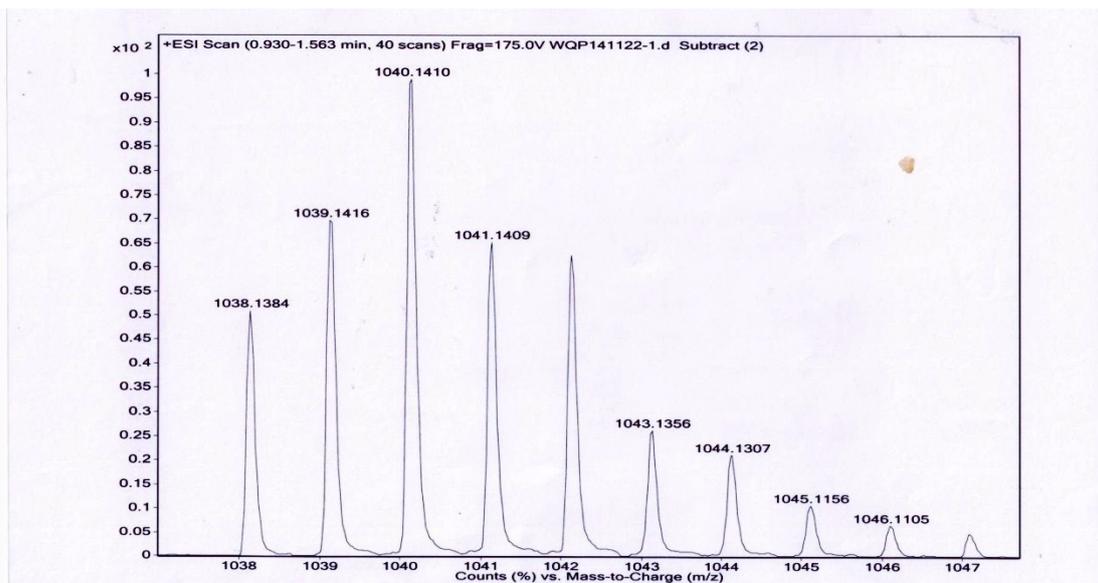


¹H-NMR spectrum for compound **1c**

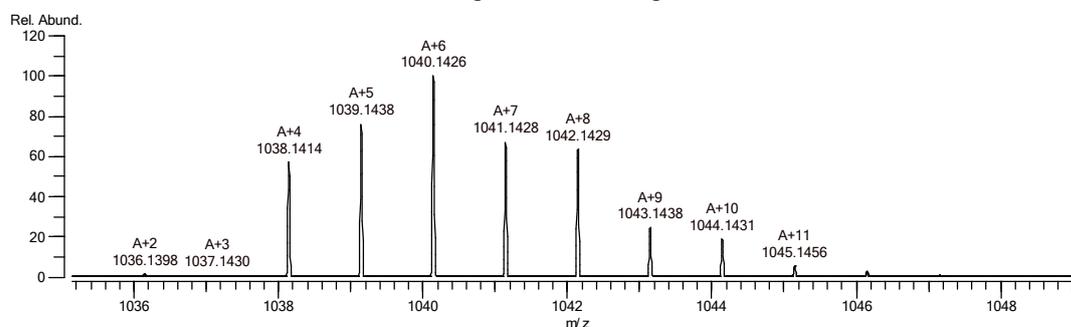
wqp-141122-1



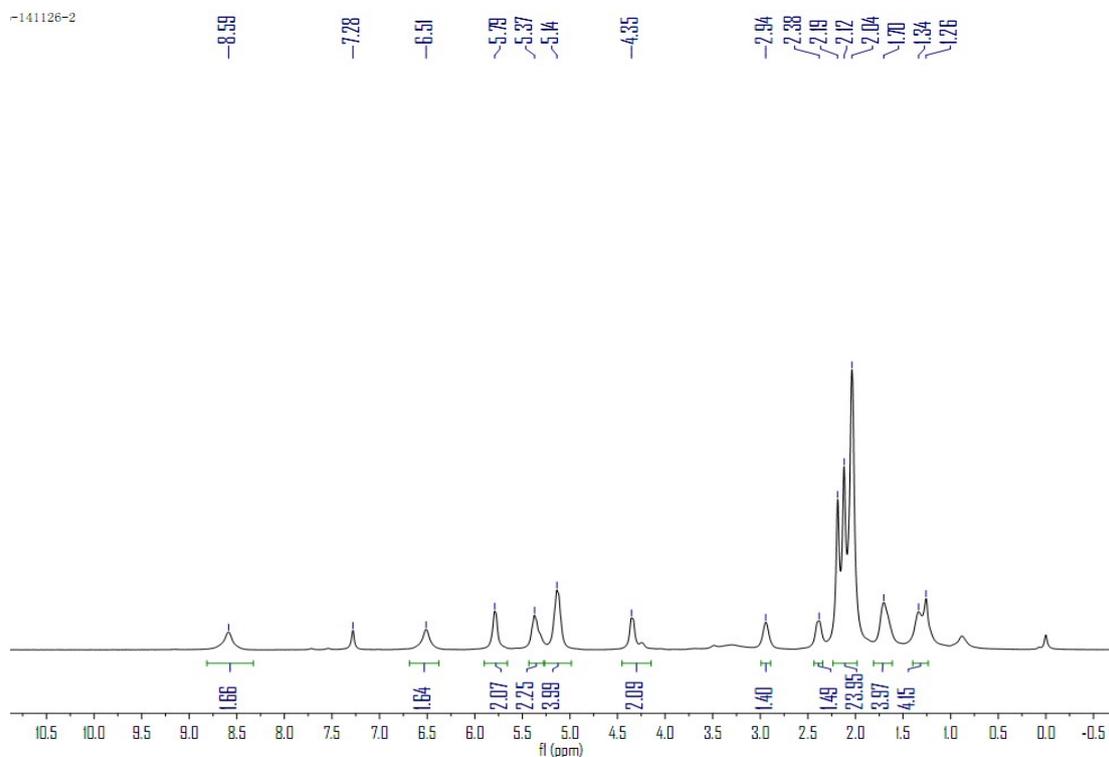
¹³C-NMR spectrum for compound **1c**



HRMS spectrum for compound **1c**

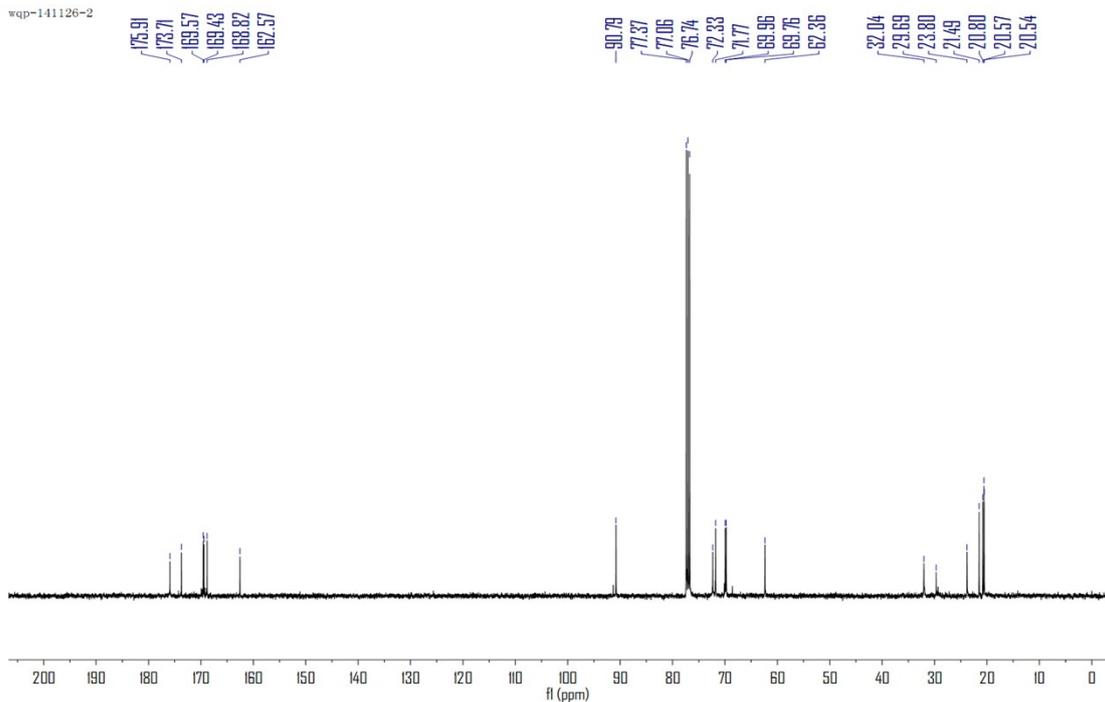


Calculated HRMS spectrum for compound **1c**

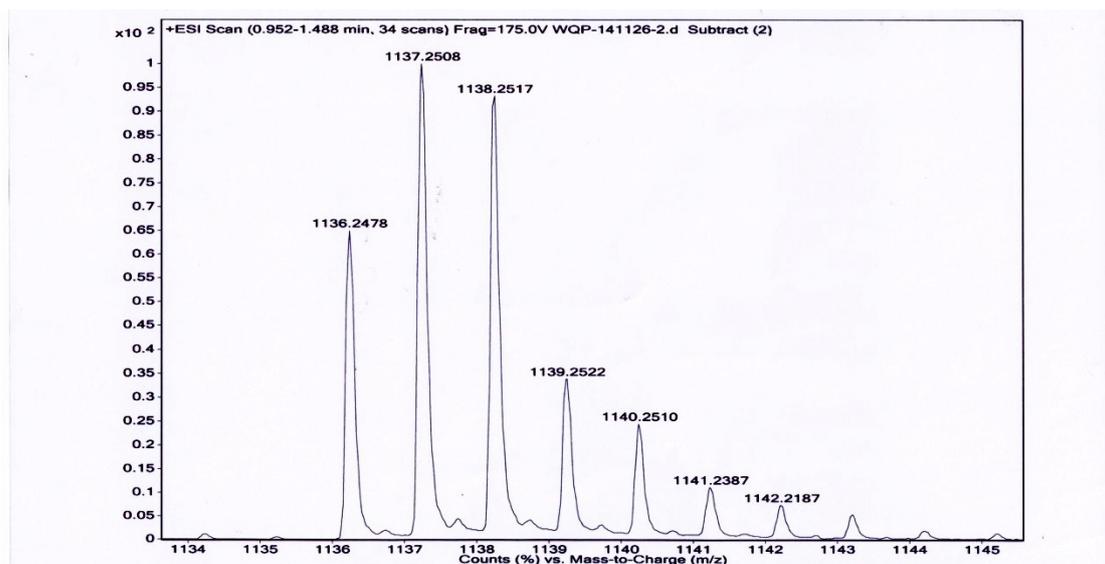


¹H-NMR spectrum for compound **2a**

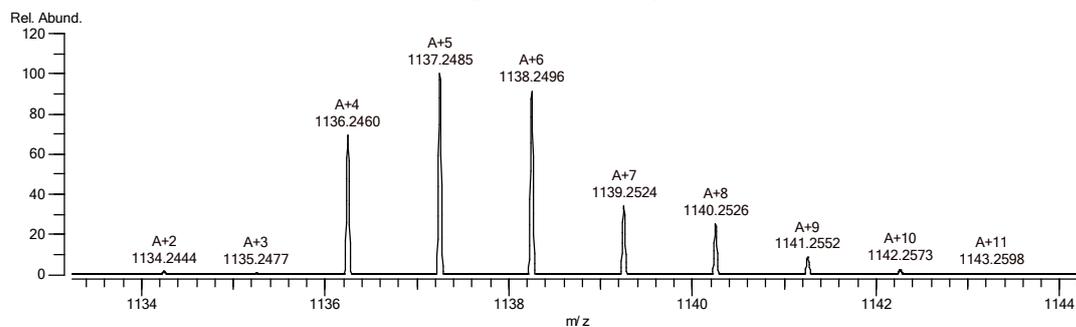
wqp-141126-2



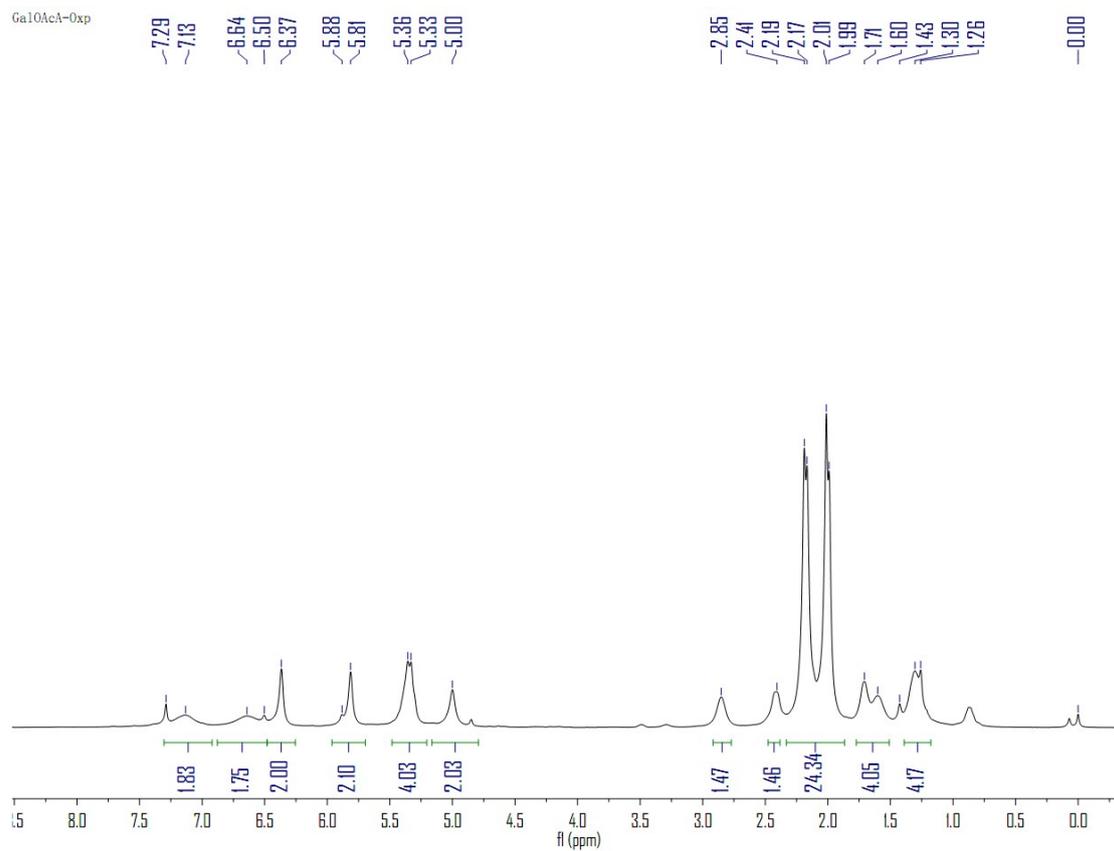
¹³C-NMR spectrum for compound 2a



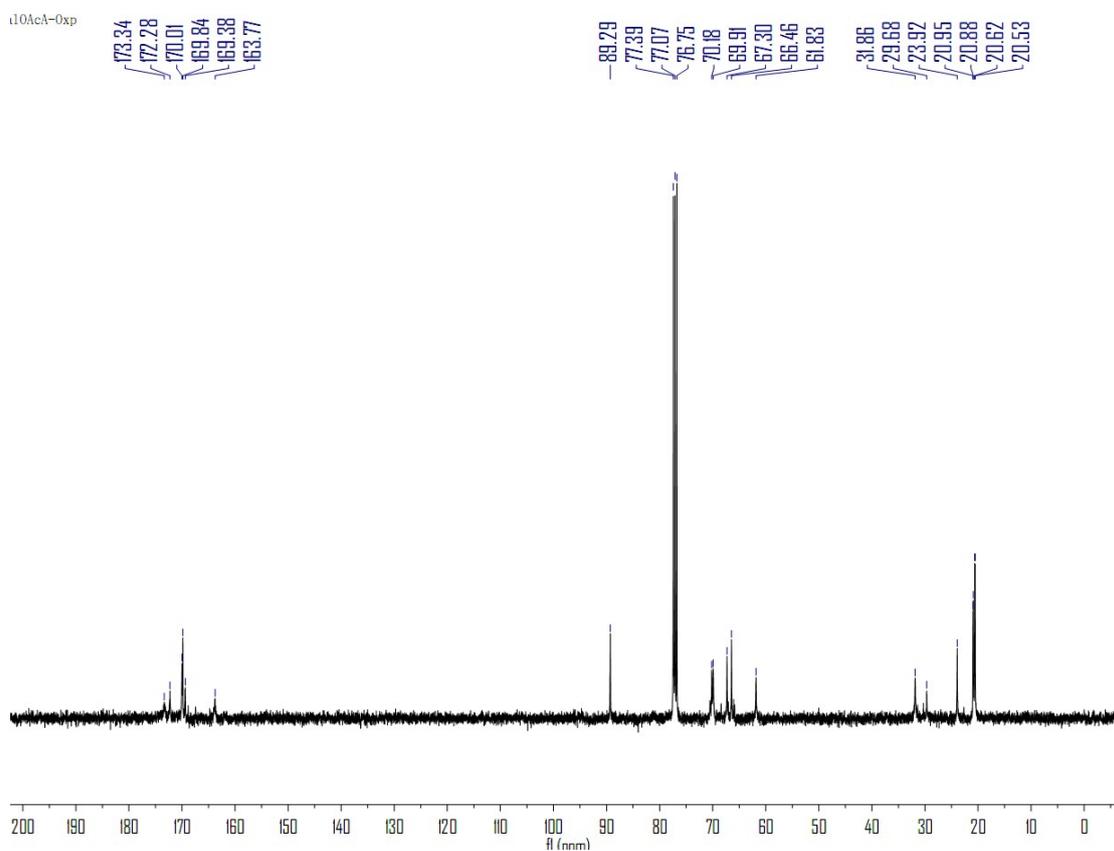
HRMS spectrum for compound 2a



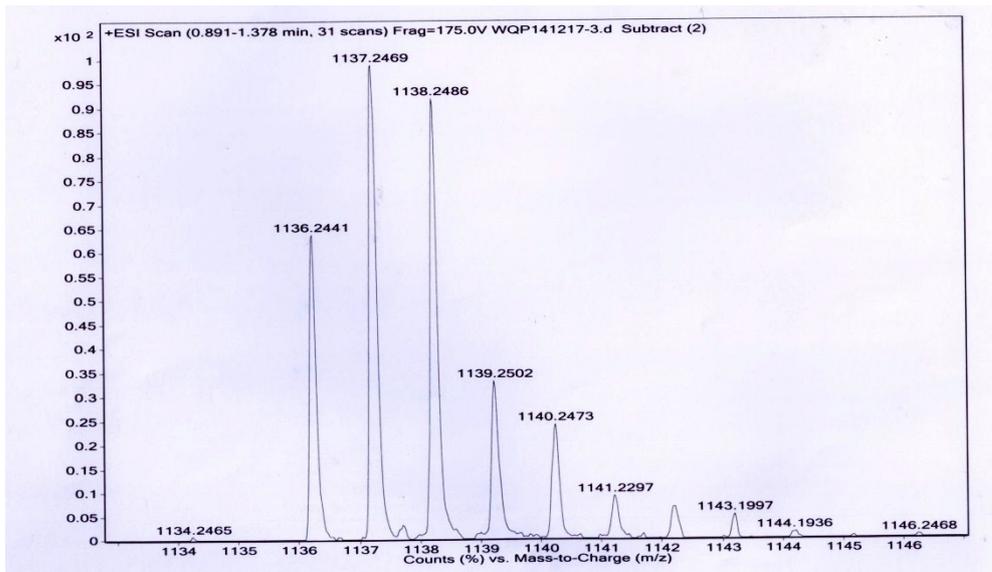
Calculated HRMS spectrum for compound 2a



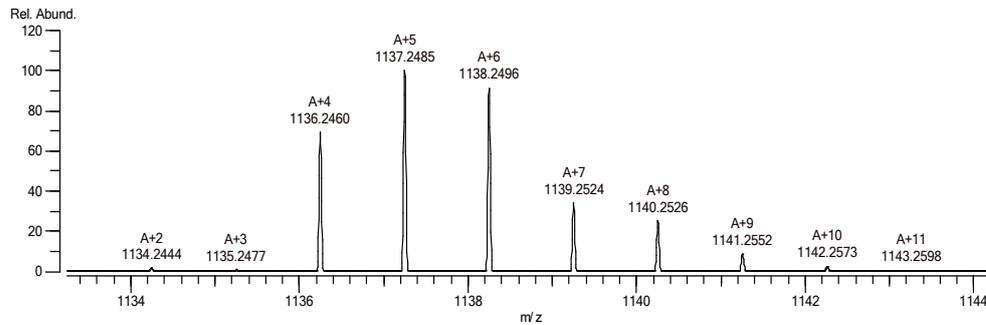
¹H-NMR spectrum for compound **2b**



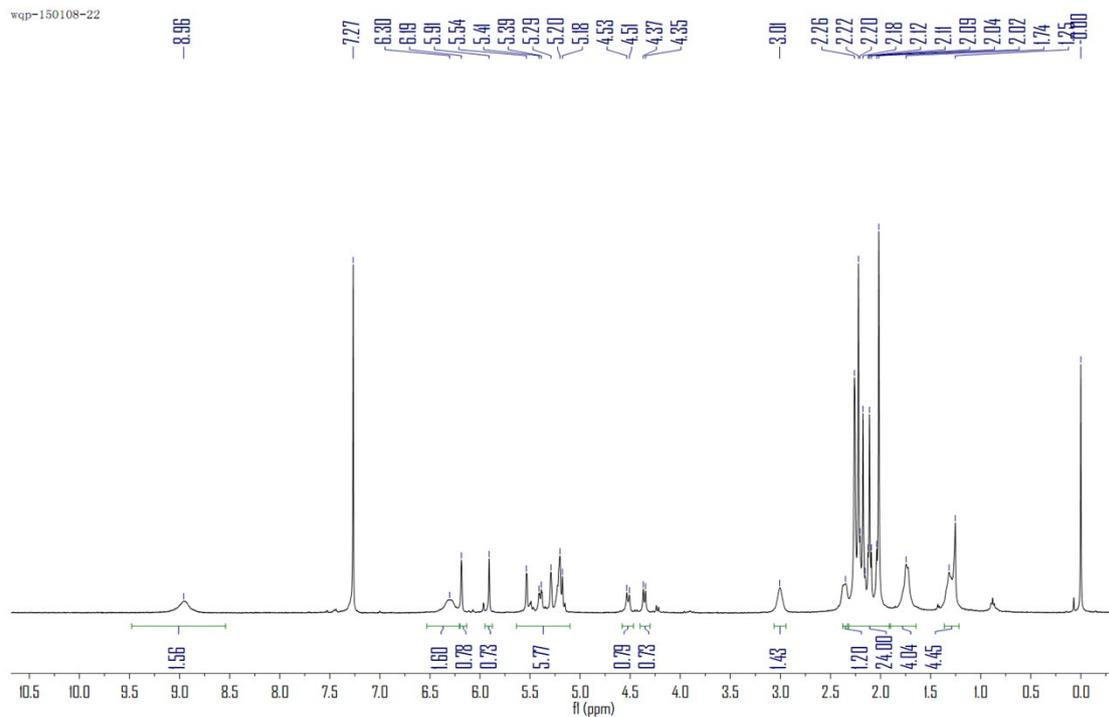
¹³C-NMR spectrum for compound **2b**



HRMS spectrum for compound **2b**

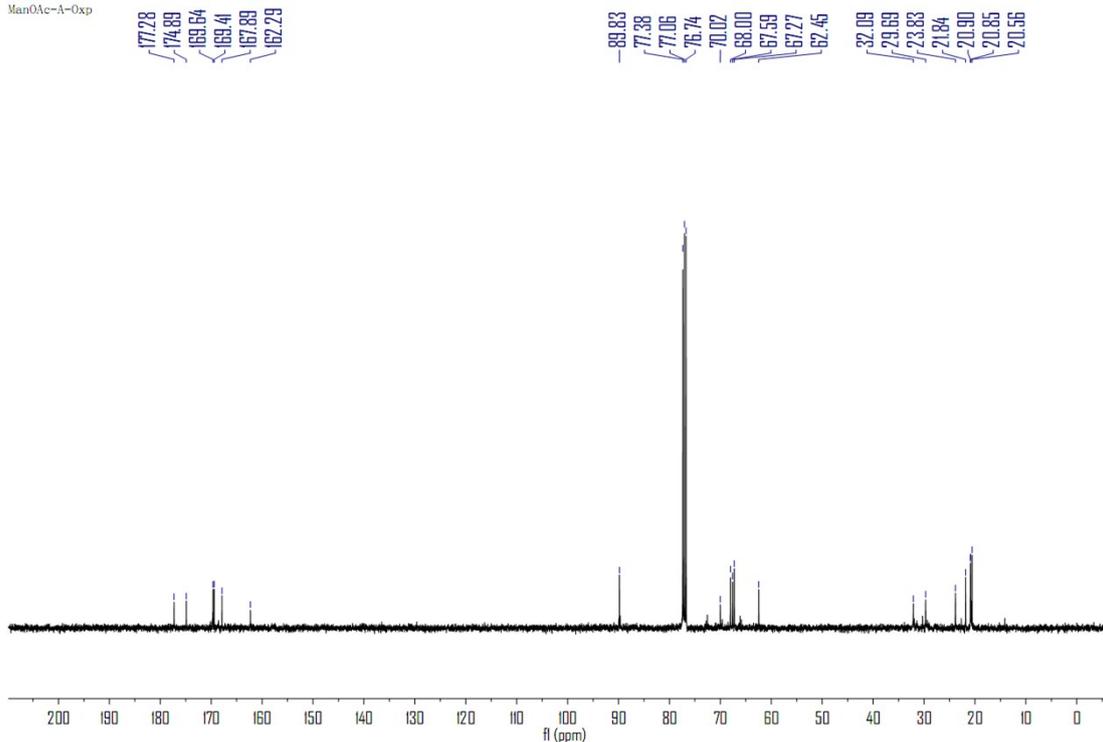


Calculated HRMS spectrum for compound **2b**

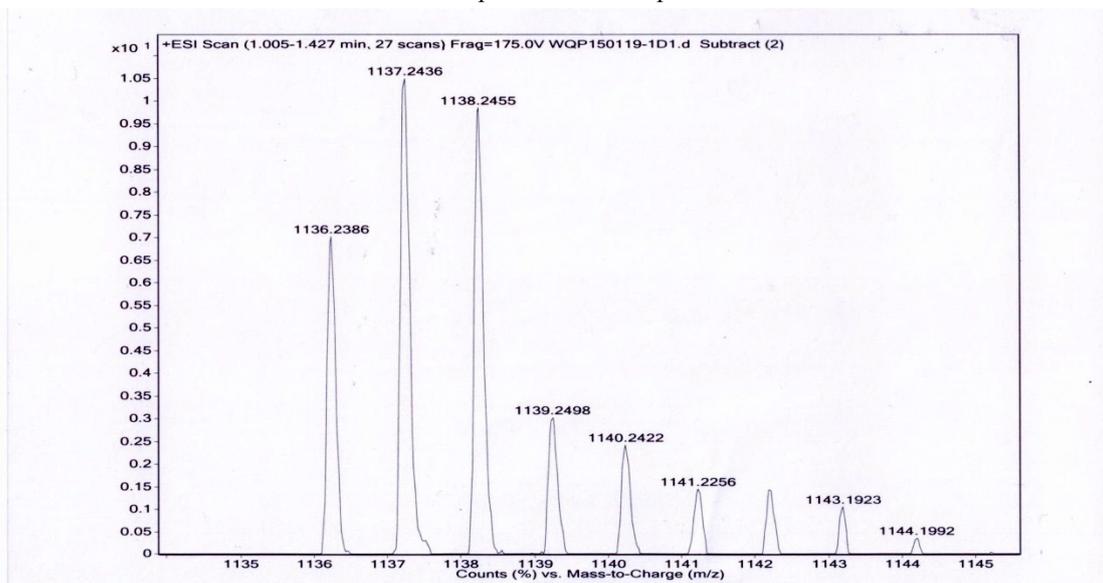


$^1\text{H-NMR}$ spectrum for compound **2c**

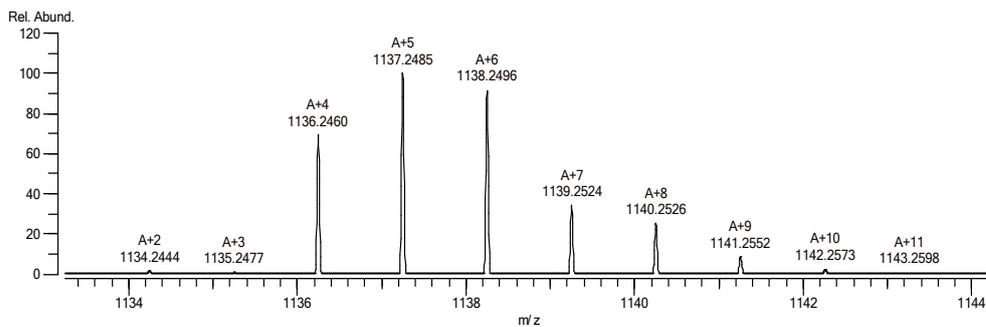
Man0Ac-A-Oxp



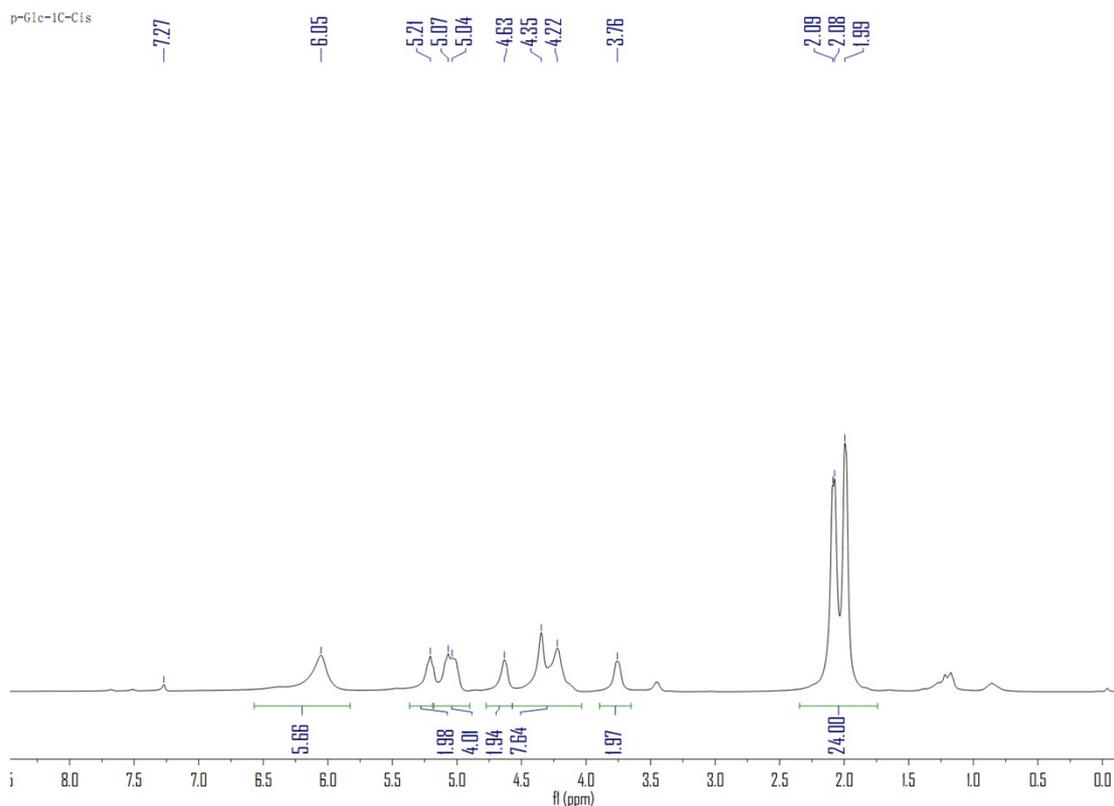
^{13}C -NMR spectrum for compound **2c**



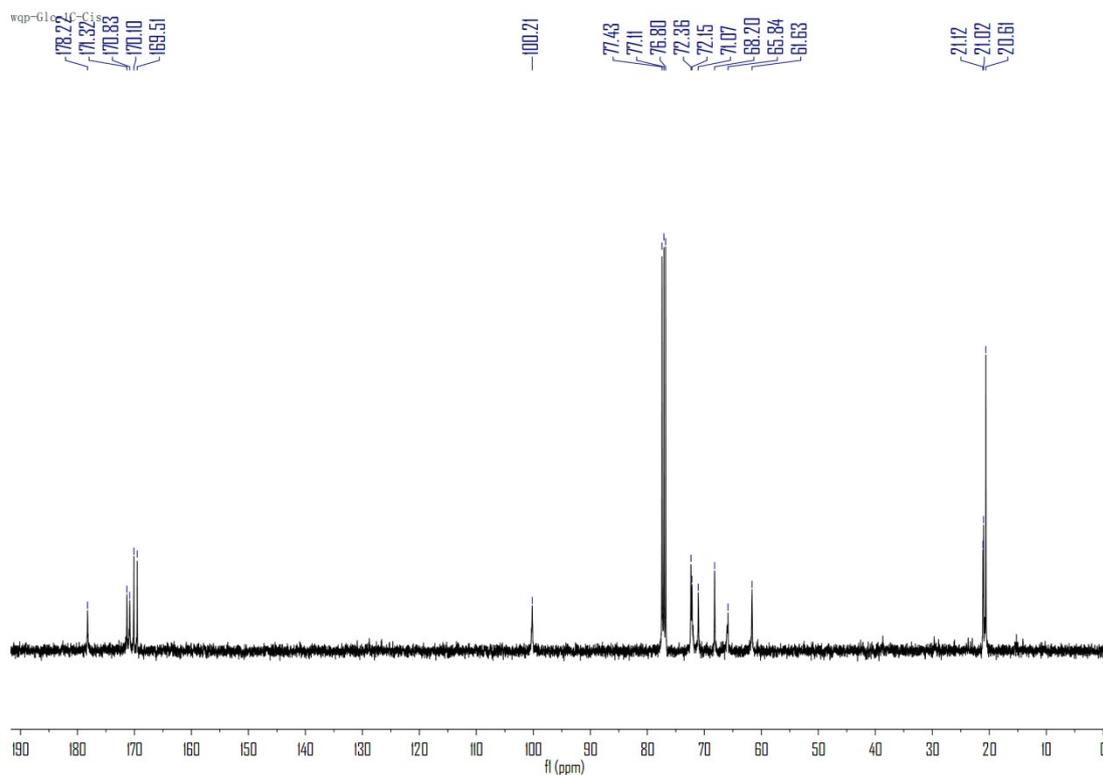
HRMS spectrum for compound **2c**



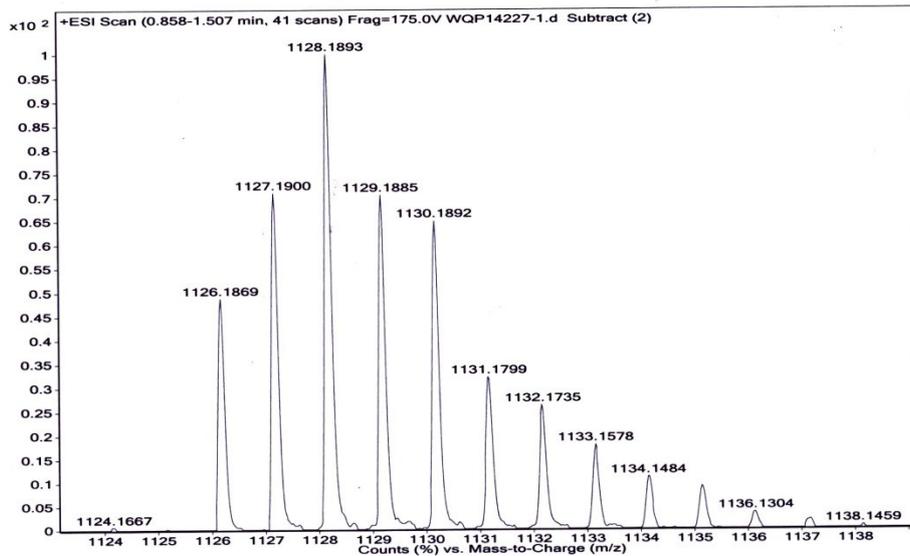
Calculated HRMS spectrum for compound **2c**



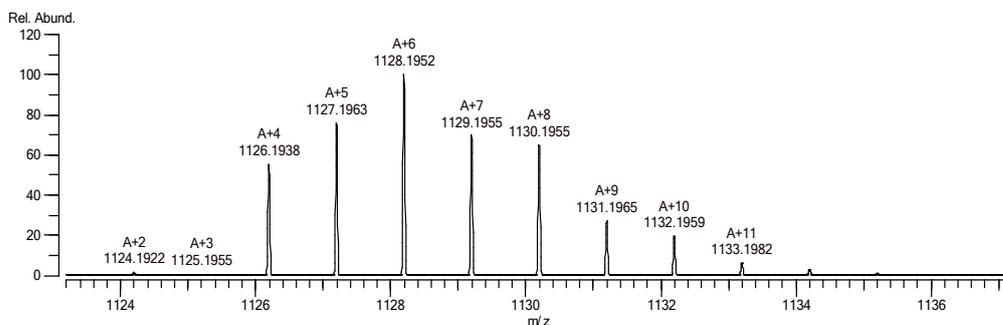
¹H-NMR spectrum for compound **3a**



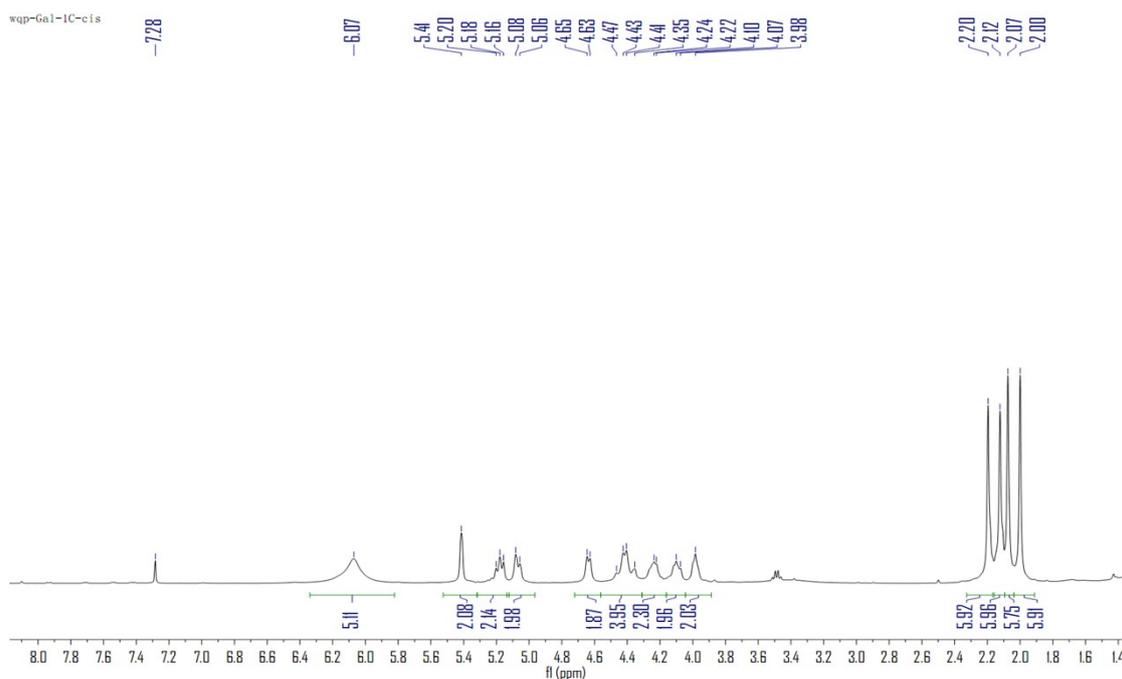
¹³C-NMR spectrum for compound **3a**



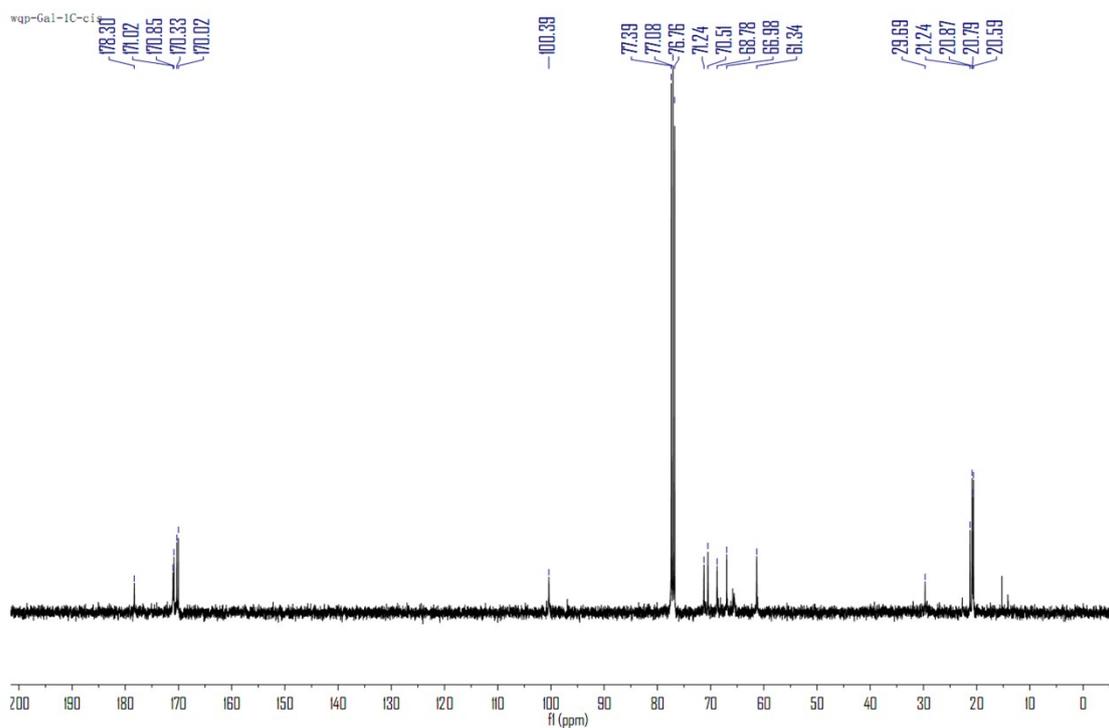
HRMS spectrum for compound **3a**



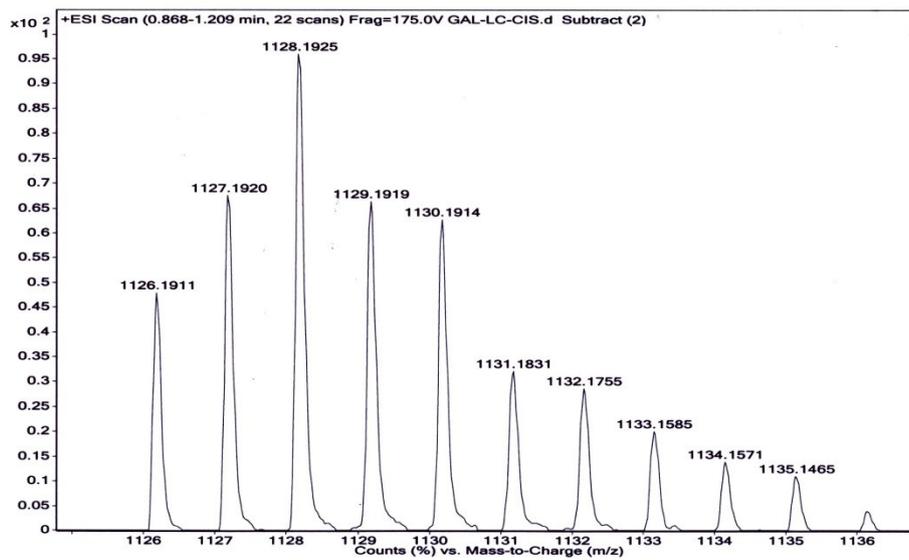
Calculated HRMS spectrum for compound **3a**



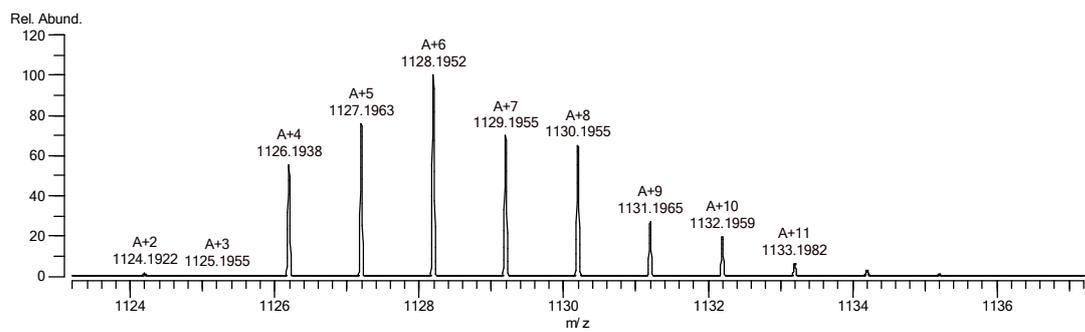
¹H-NMR spectrum for compound **3b**



^{13}C -NMR spectrum for compound **3b**

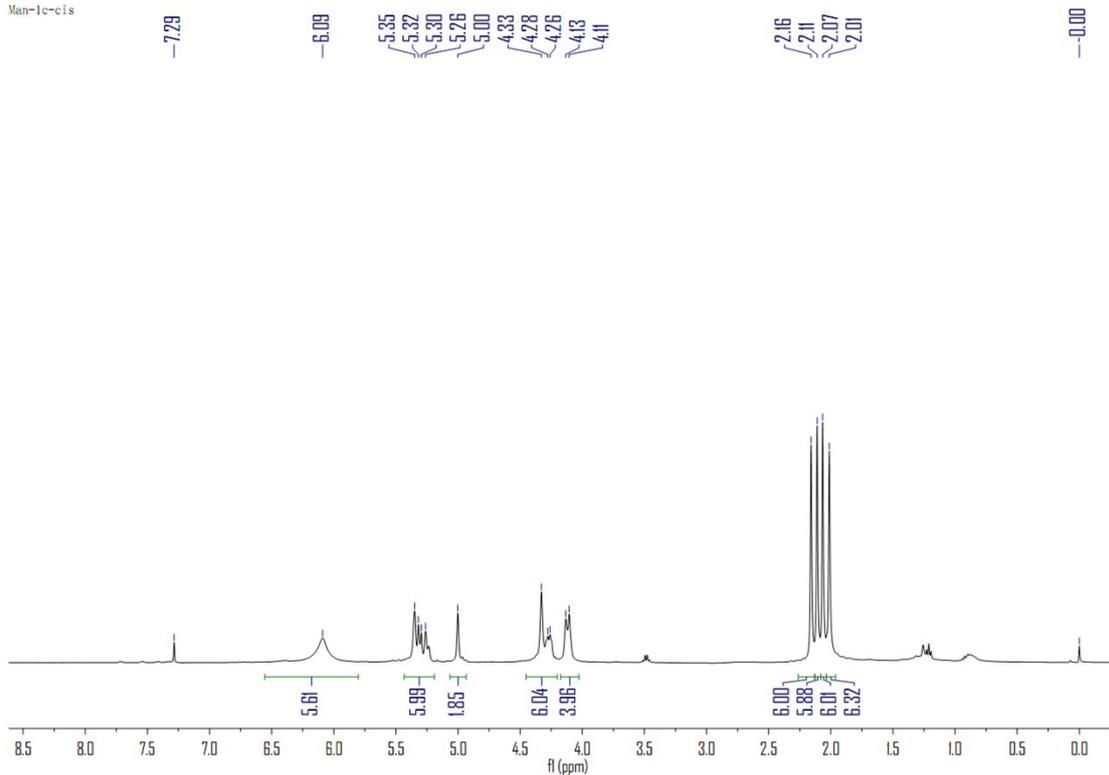


HRMS spectrum for compound **3b**



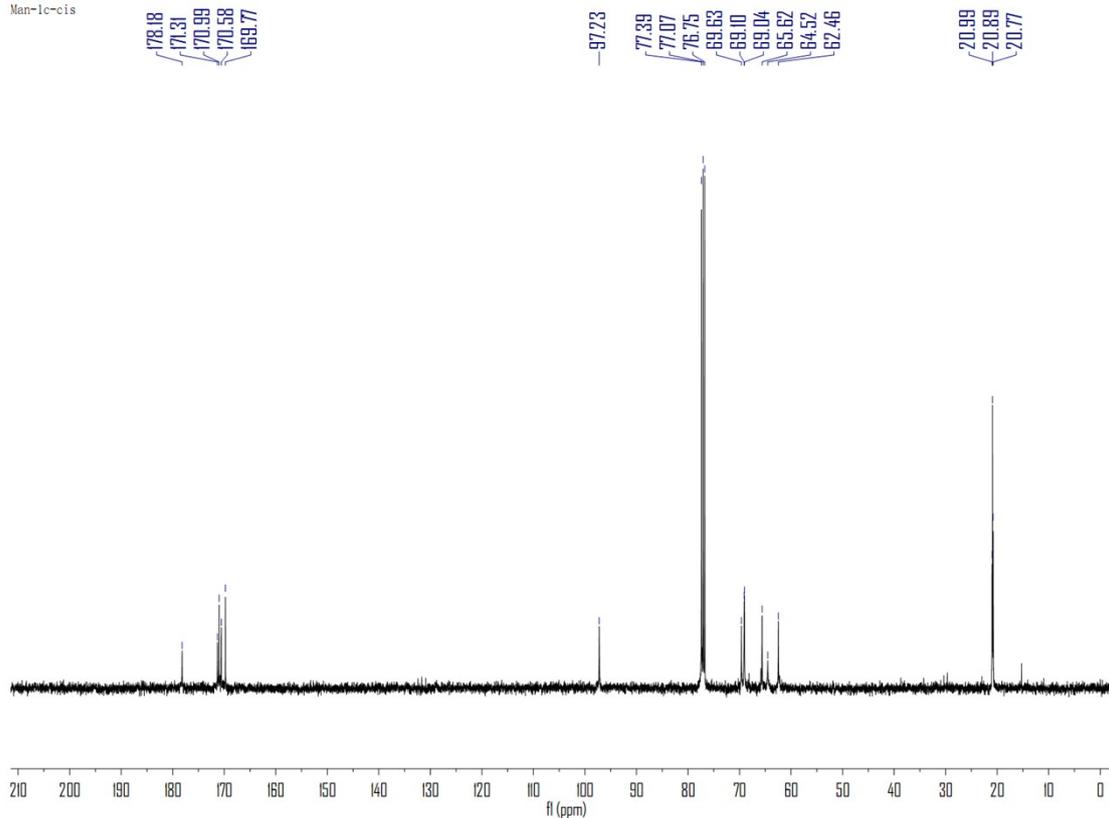
Calculated HRMS spectrum for compound **3b**

Man-1c-cis

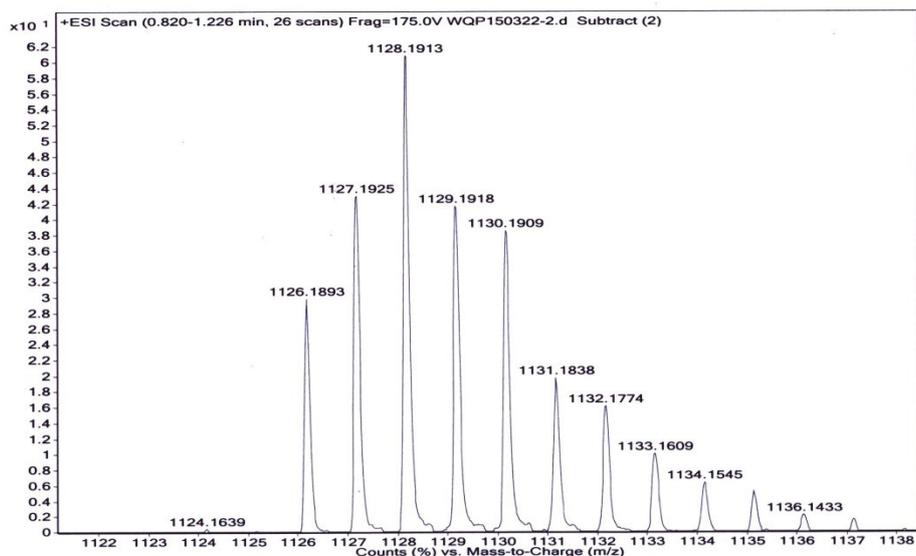


¹H-NMR spectrum for compound **3c**

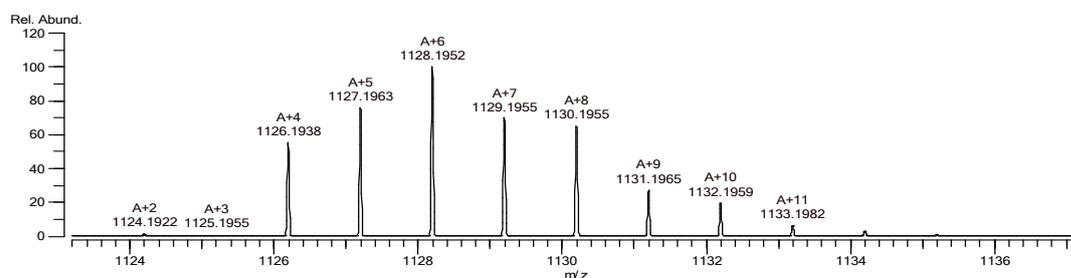
Man-1c-cis



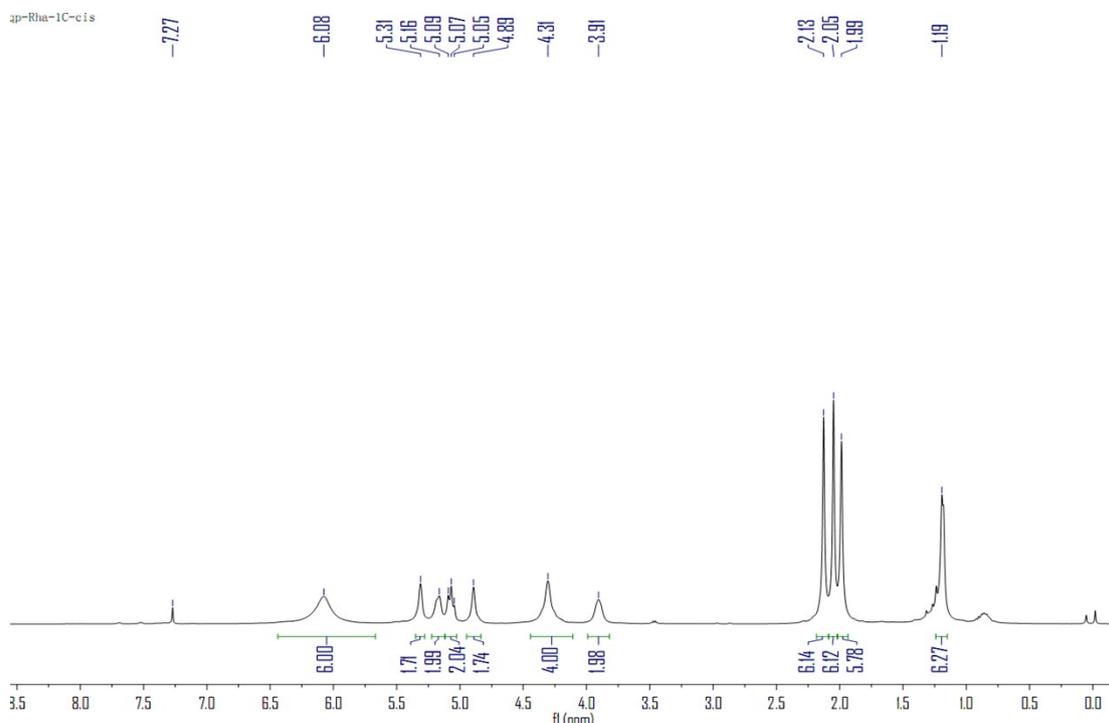
¹³C-NMR spectrum for compound **3c**



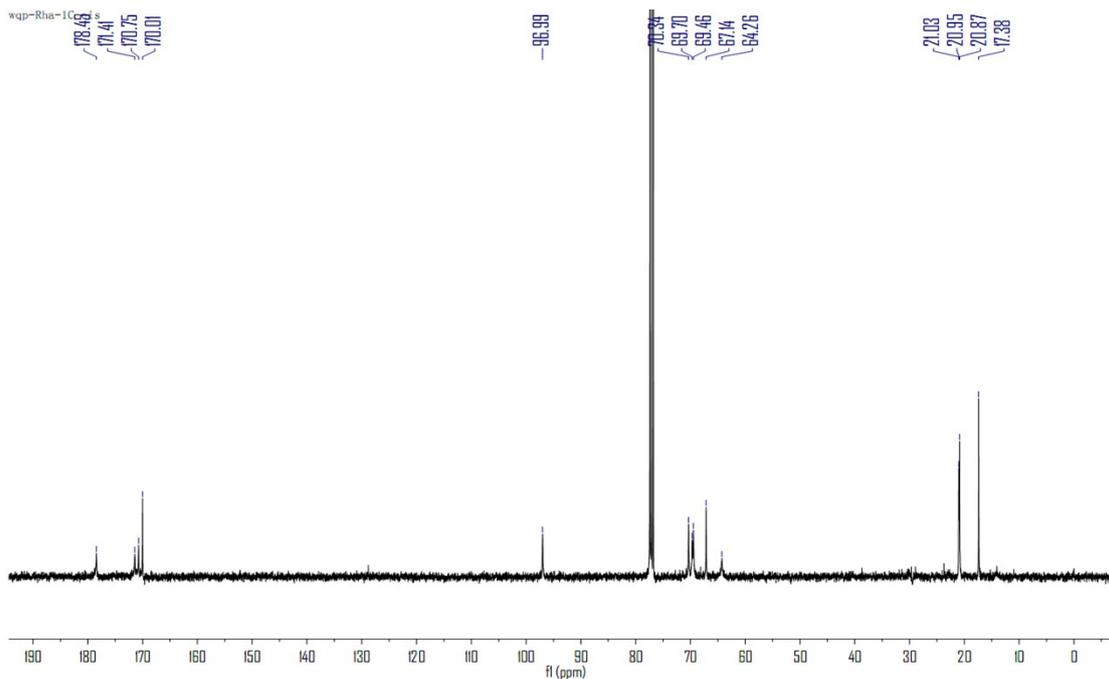
HRMS spectrum for compound **3c**



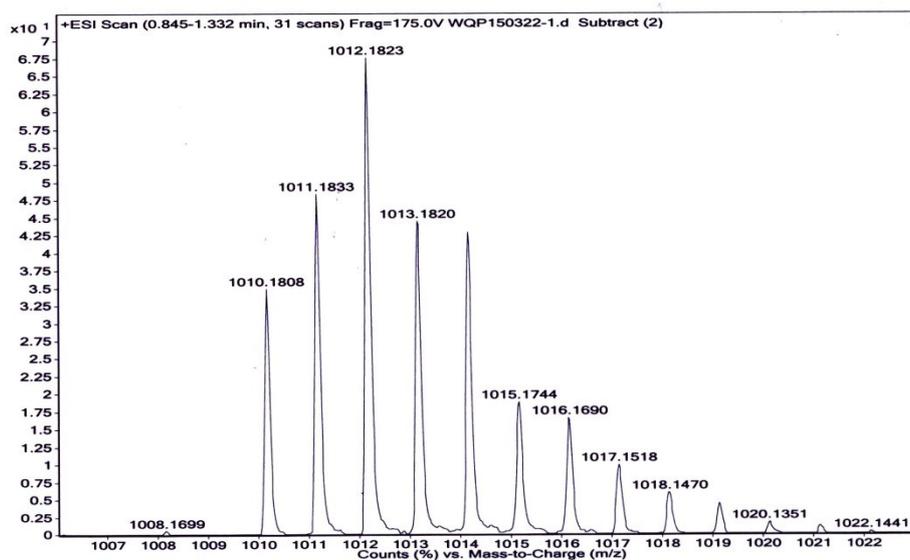
Calculated HRMS spectrum for compound **3c**



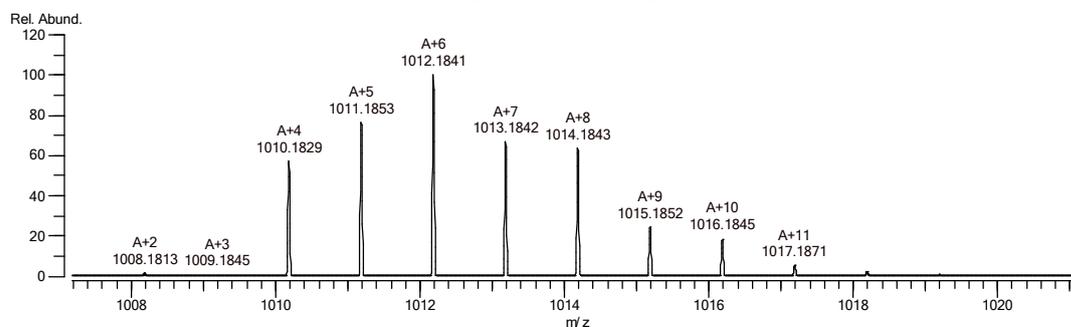
¹H-NMR spectrum for compound **3d**



¹³C-NMR spectrum for compound **3d**

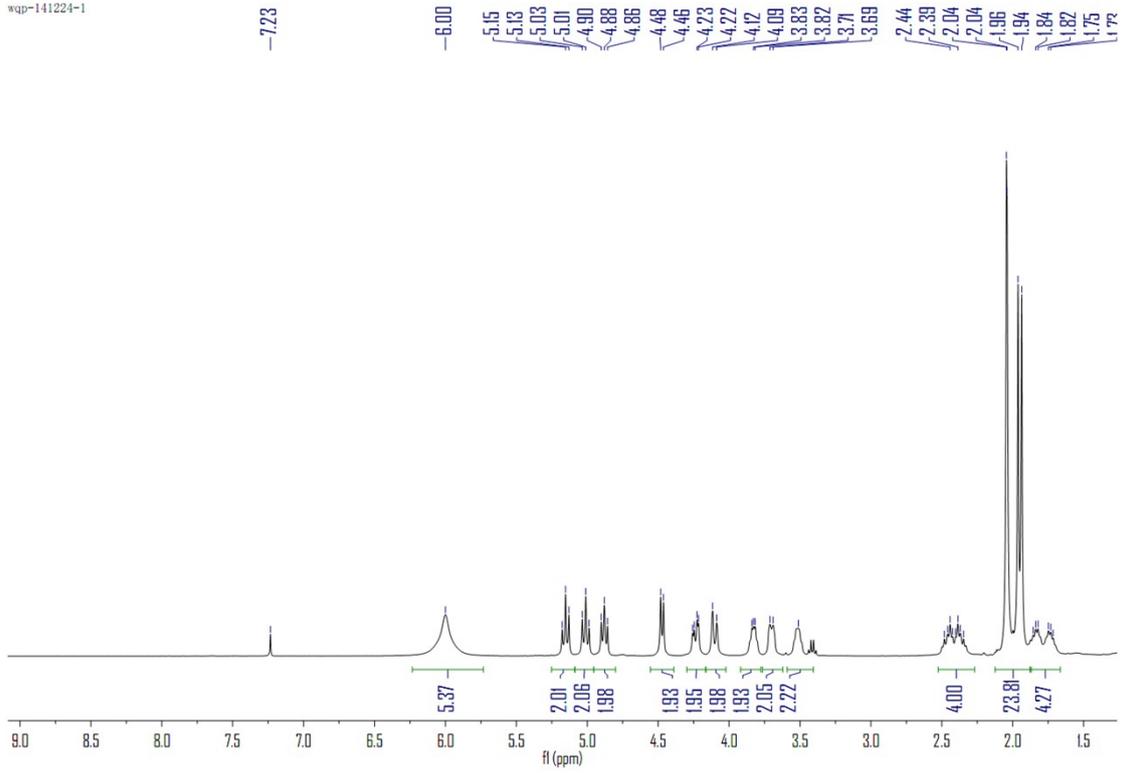


HRMS spectrum for compound **3d**



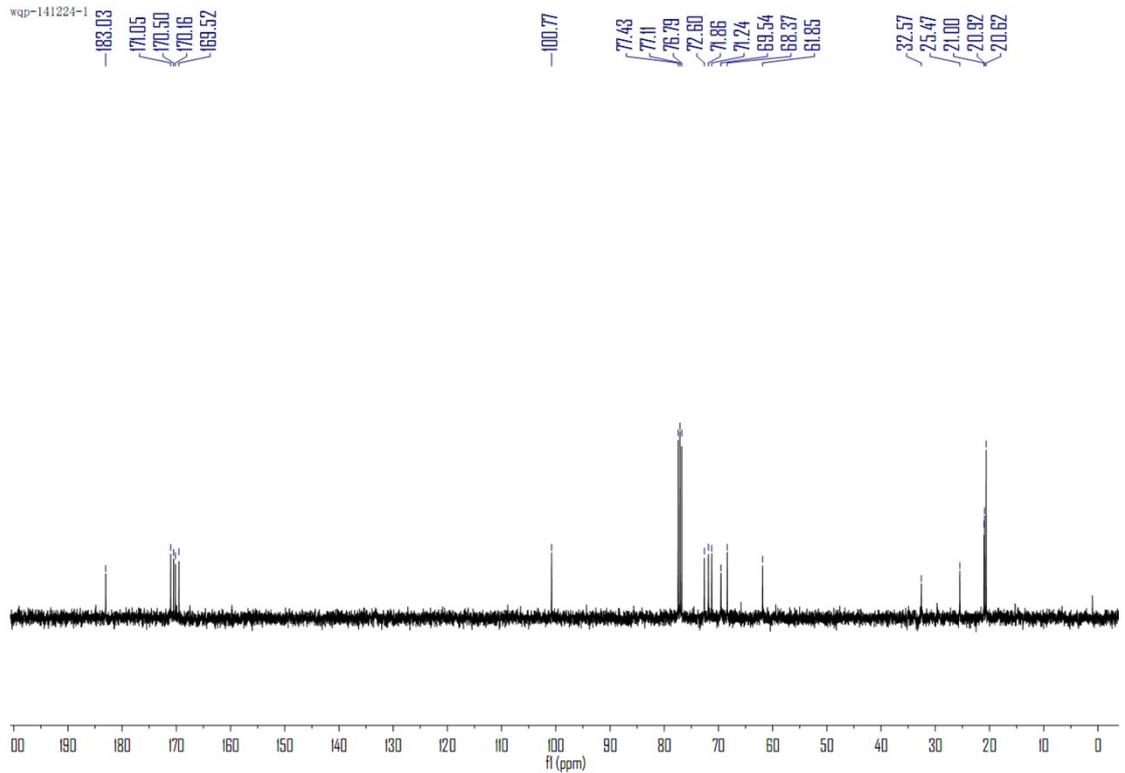
Calculated HRMS spectrum for compound **3d**

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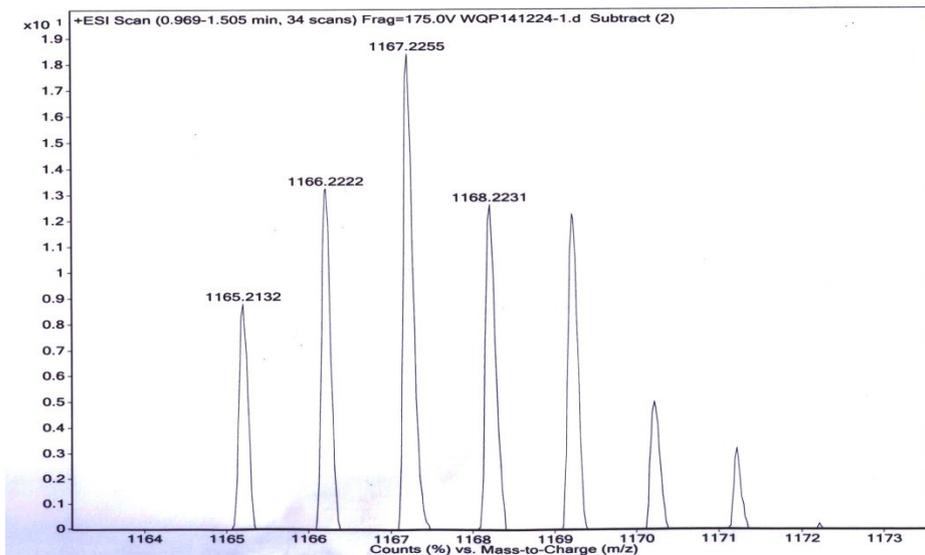


¹H-NMR spectrum for compound **3e**

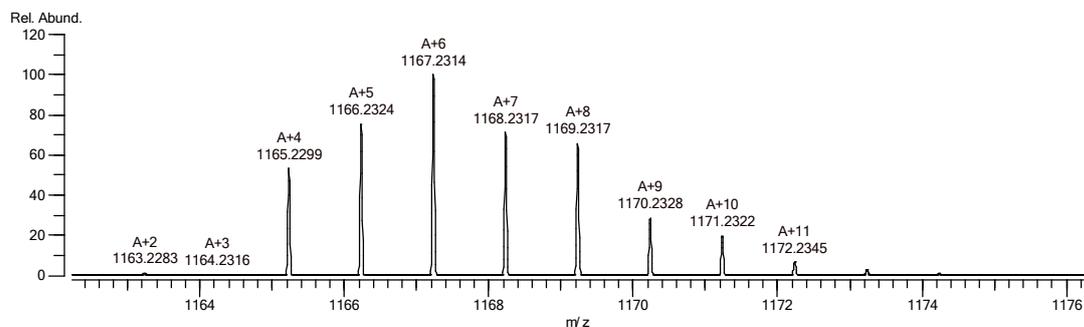
wqp-141224-1



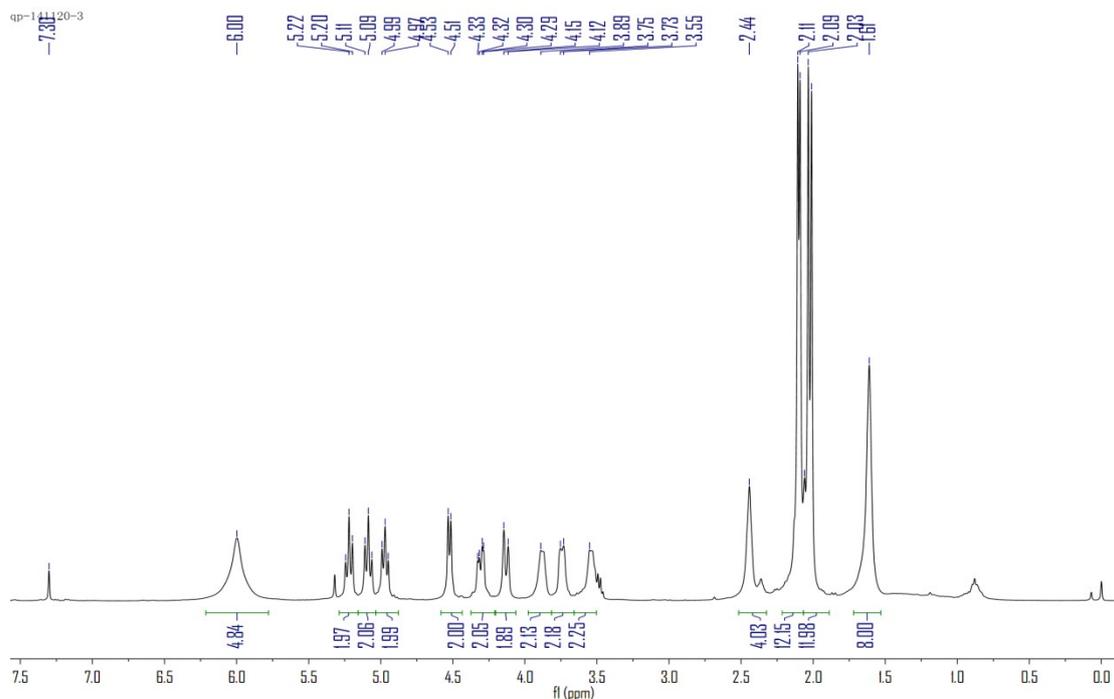
¹³C-NMR spectrum for compound **3e**



HRMS spectrum for compound **3e**

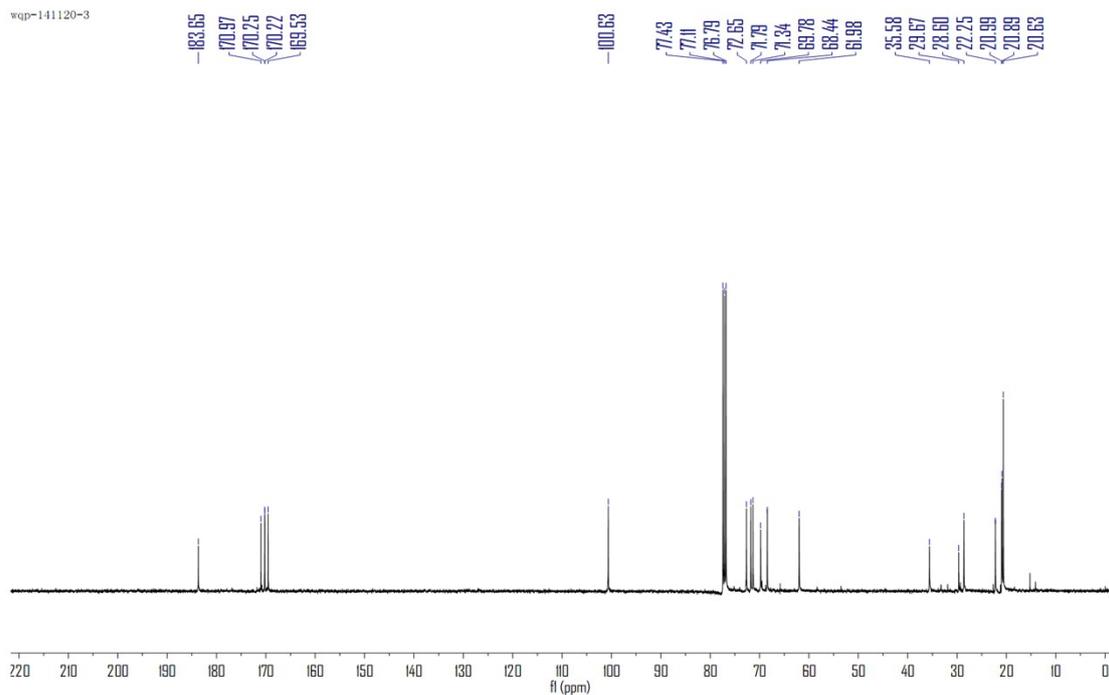


Calculated HRMS spectrum for compound **3e**

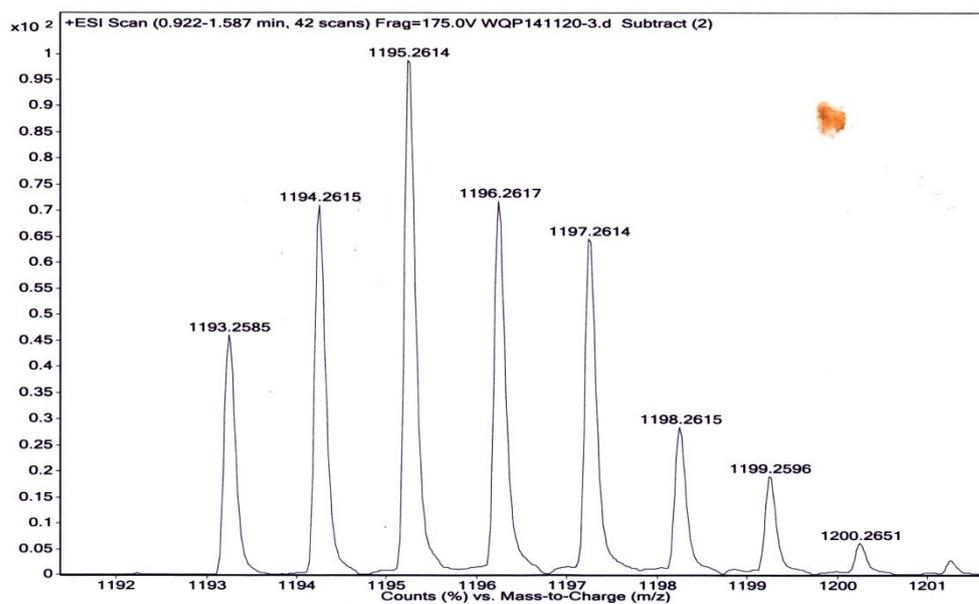


¹H-NMR spectrum for compound **3f**

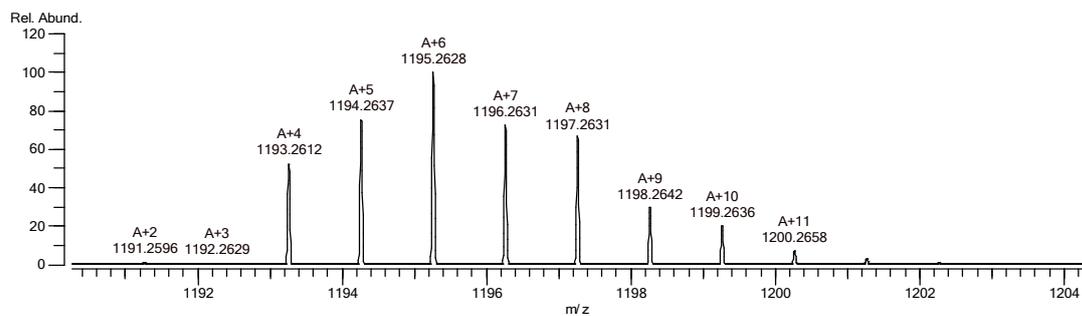
wqp-141120-3



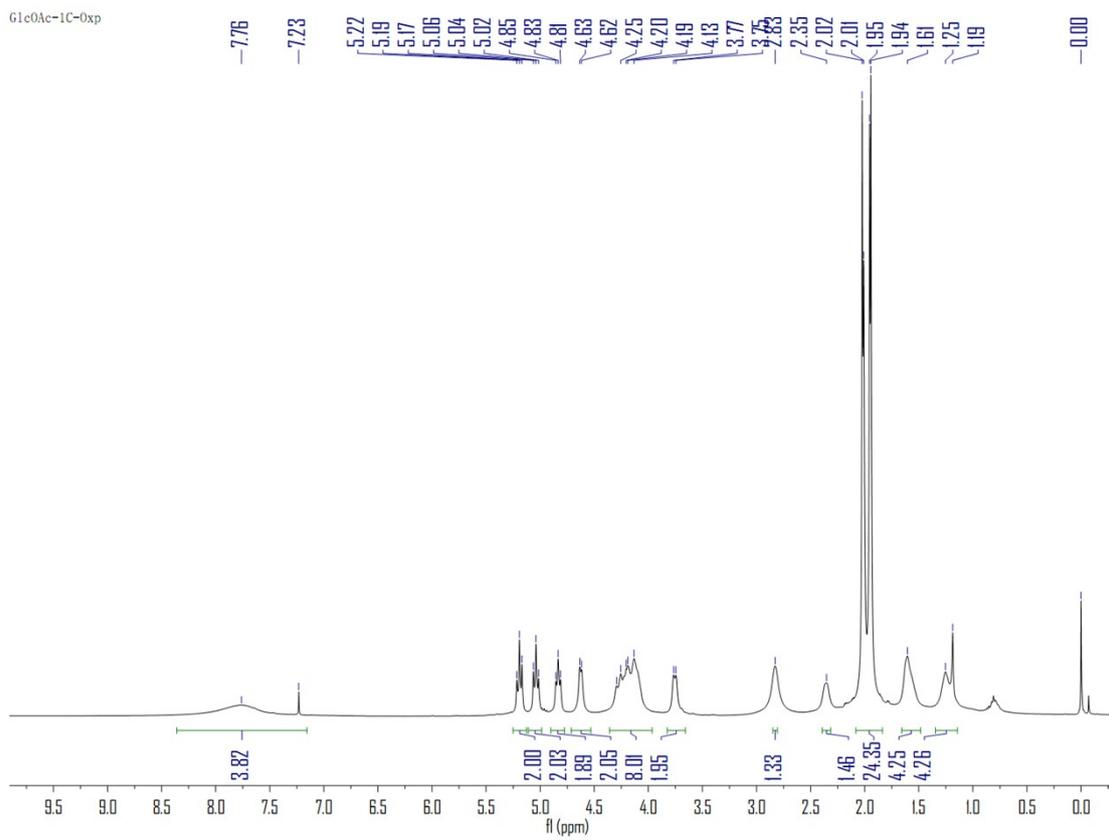
^{13}C -NMR spectrum for compound **3f**



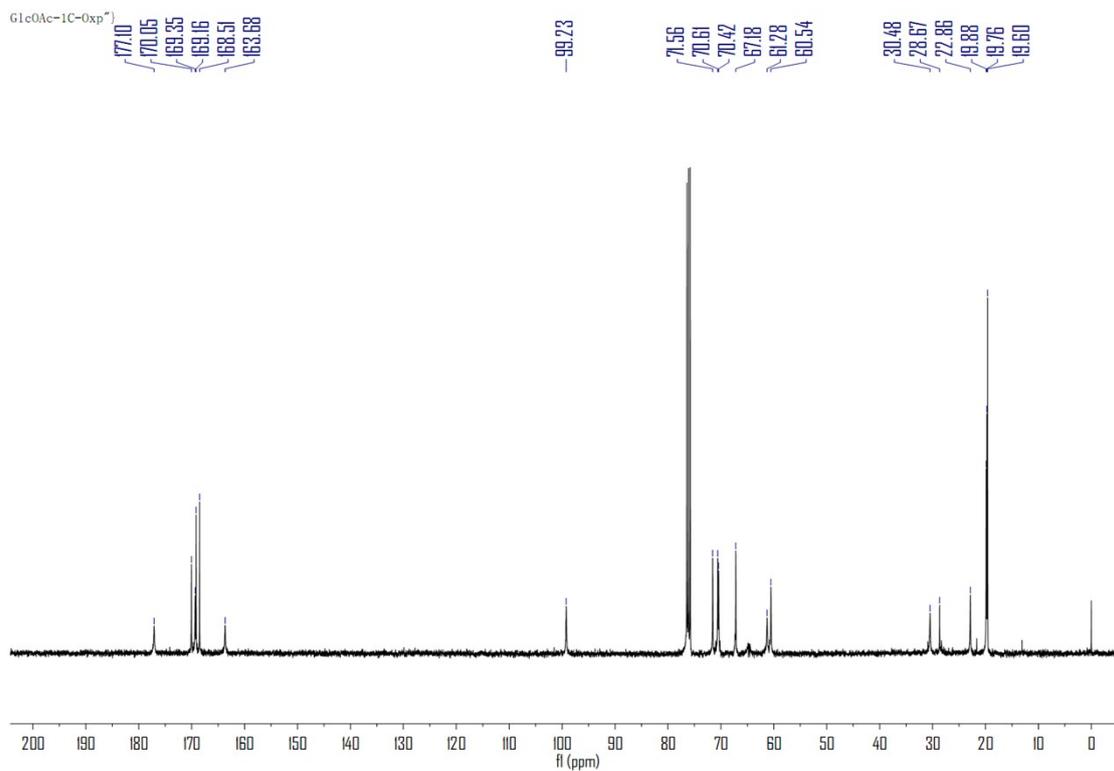
HRMS spectrum for compound **3f**



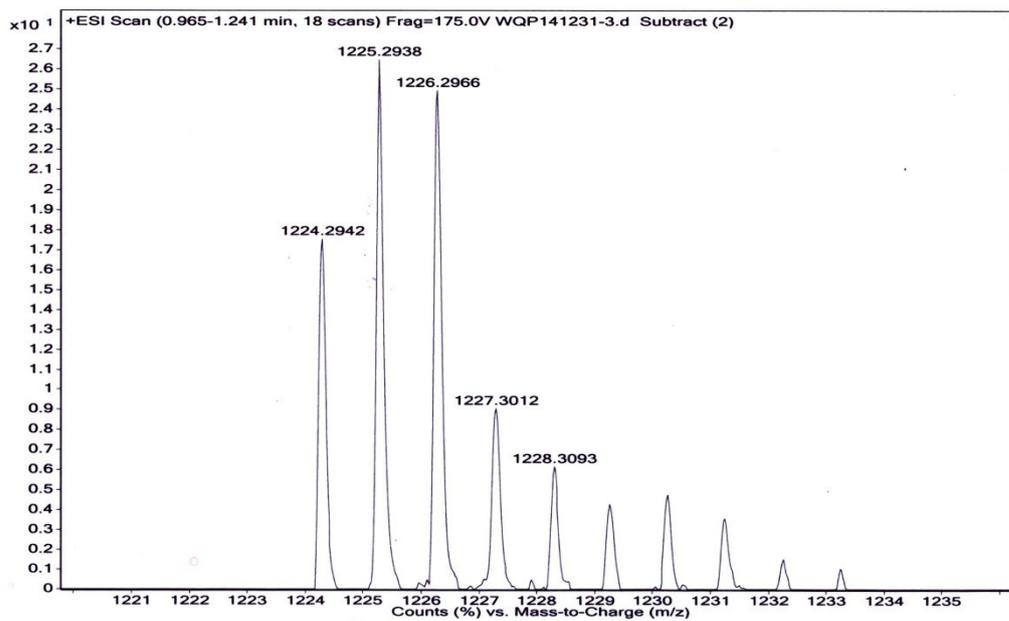
Calculated HRMS spectrum for compound **3f**



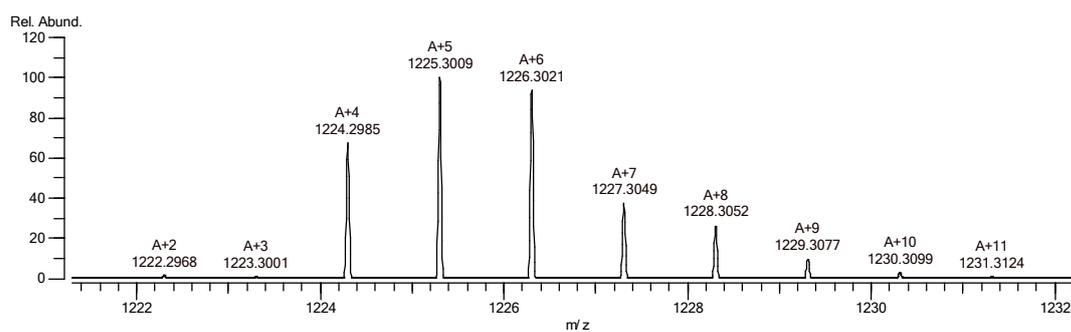
¹H-NMR spectrum for compound 4



¹³C-NMR spectrum for compound 4



HRMS spectrum for compound 4



Calculated HRMS spectrum for compound 4