

## SUPPORTING INFORMATION

### Synthesis, cytotoxicity and anti-inflammatory activity of rhamnose-containing ursolic and betulinic acid saponins

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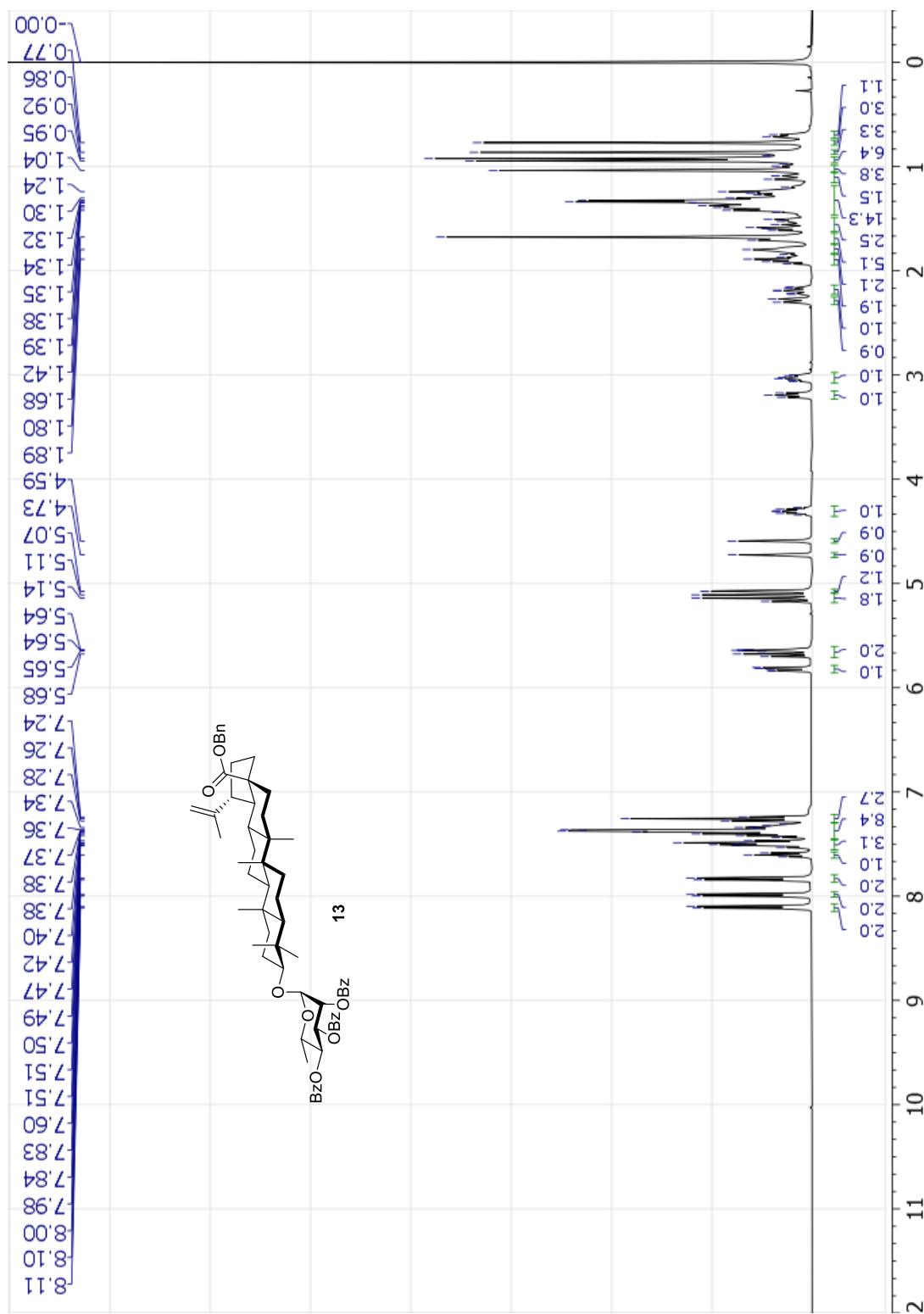
E-mail: andre.pichette@uqac.ca

<sup>b</sup>Institut des Sciences de la Forêt tempérée, Université du Québec en Outaouais, 58, rue Principale, Ripon (Québec), Canada, J0V 1V0.

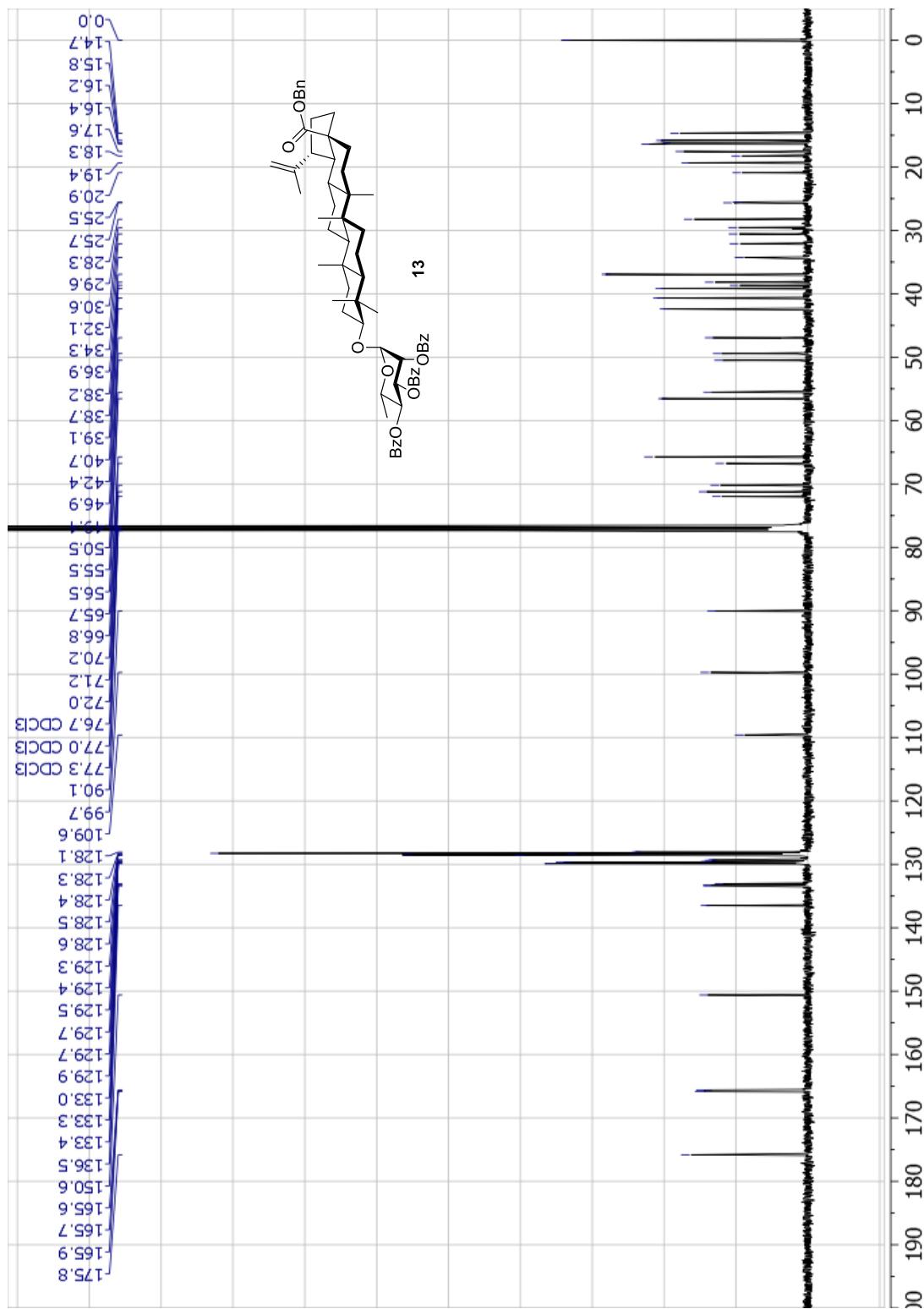
<sup>c</sup>Centre Armand-Frappier Santé Biotechnologie, Institut national de la recherche scientifique (INRS), 531, boul. des Prairies, Laval (Québec), Canada, H7V 1B7.

E-mail: charles.gauthier@iaf.inrs.ca

**Figure S1.**  $^1\text{H}$  NMR spectrum of **13** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S2.**  $^{13}\text{C}$  NMR spectra of **13** ( $\text{CDCl}_3$ , 100 MHz)

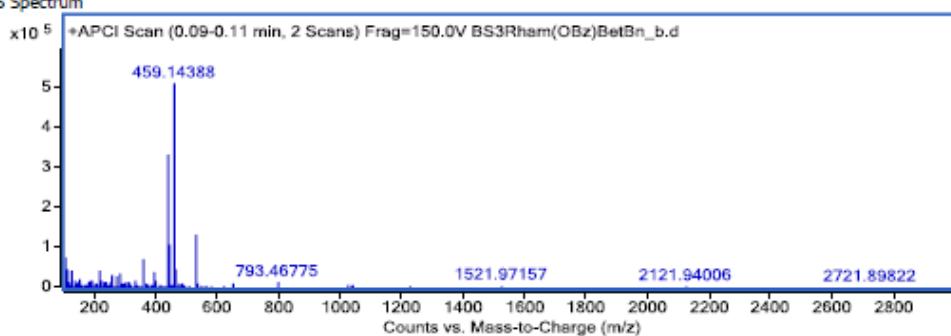


**Figure S3.** HRMS spectra of **13**

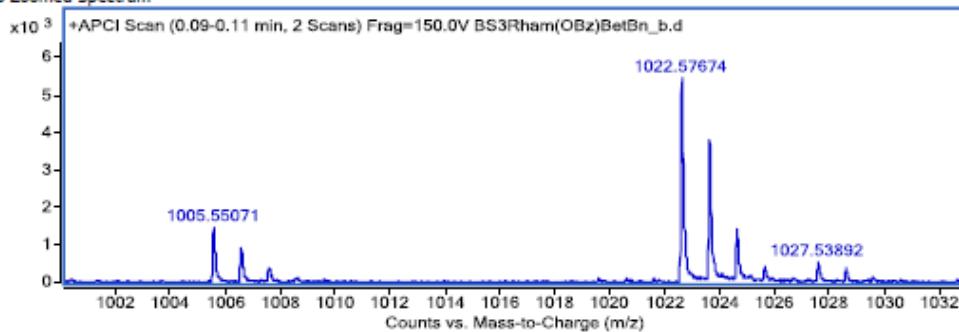
### Rapport de masse exacte

Data File BS3Rham(OBz)BetBn\_b.d      Sample Name BS3Rham(OBz)BetBn  
 Sample Type Sample      Position  
 Analysis Date 9/17/2019 1:48:39 PM      User Name MCT  
 Acq Method APCI\_POS\_DI.m      InstrumentName TOF 6224  
 Comment

MS Spectrum

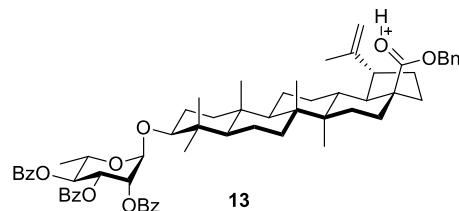


MS Zoomed Spectrum



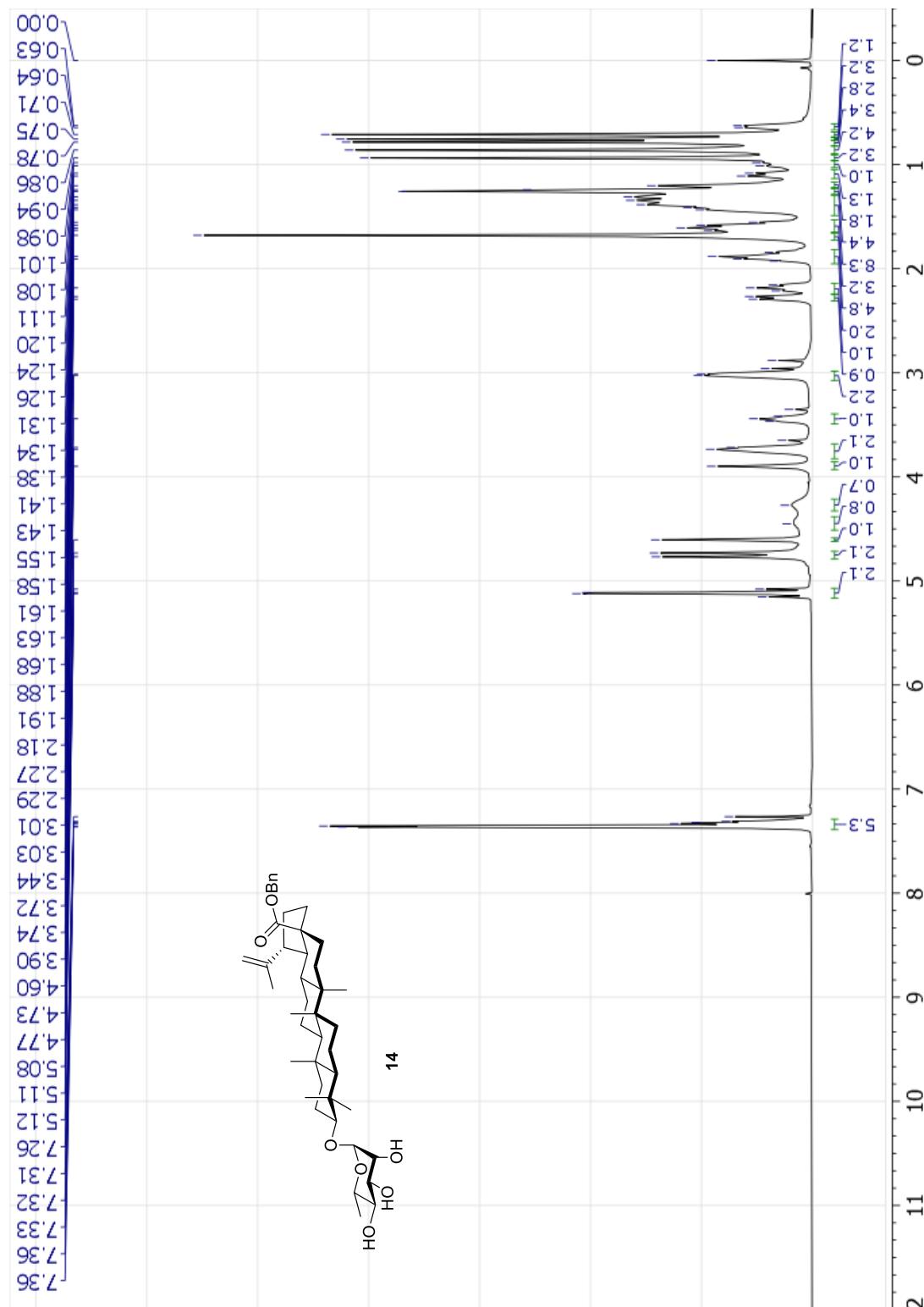
MS Spectrum Peak List

Ion	Ion Formula	Expe. m/z	Calc. m/z	Diff(ppm)
(M+H) <sup>+</sup>	C <sub>64</sub> H <sub>77</sub> O <sub>10</sub>	1005.55071	1005.55113	0.41
(M+NH <sub>4</sub> ) <sup>+</sup>	C <sub>64</sub> H <sub>76</sub> O <sub>10</sub> Na	1022.57674	1022.57767	0.91

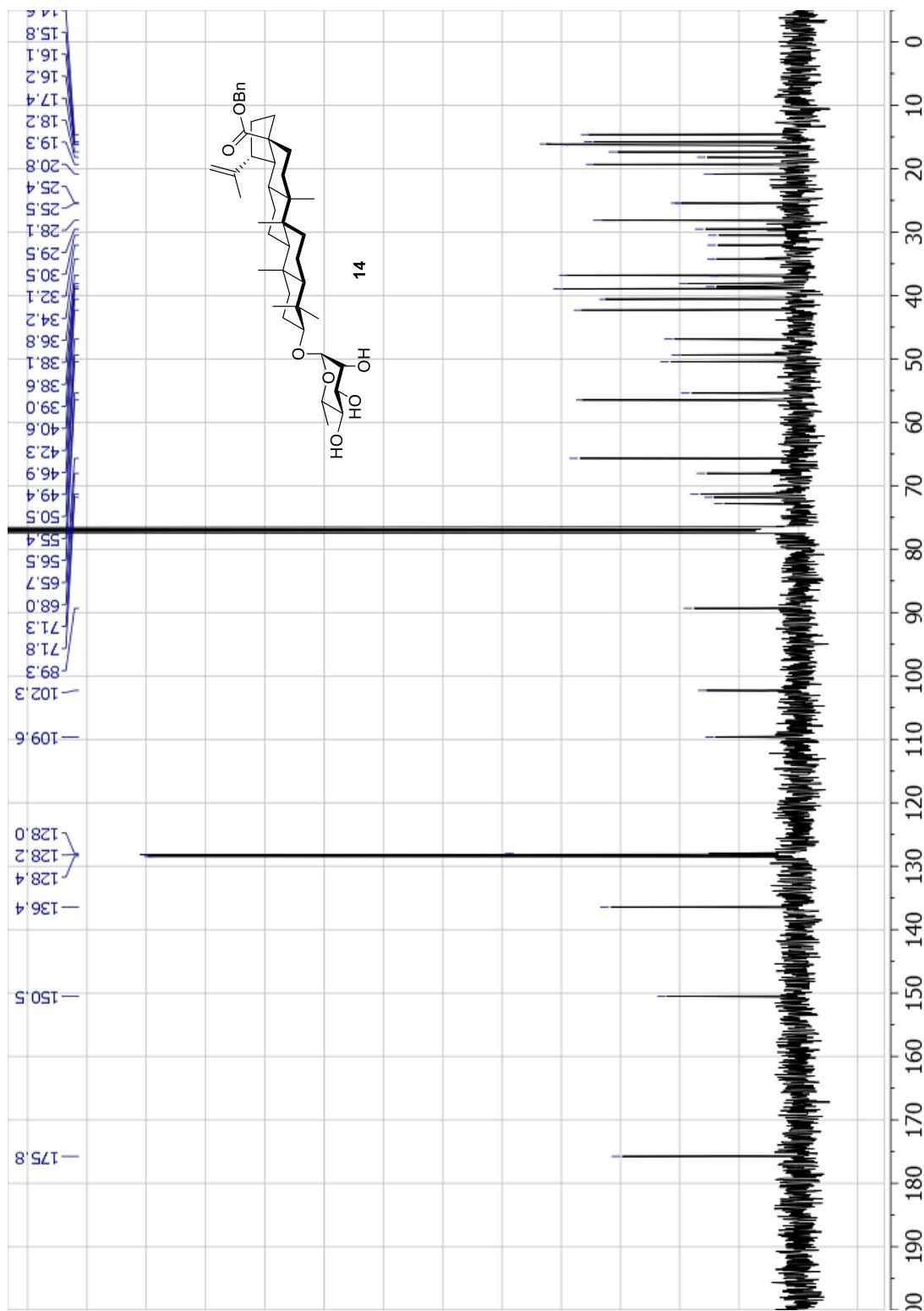


Chemical Formula: C<sub>64</sub>H<sub>77</sub>O<sub>10</sub><sup>+</sup>  
 Exact Mass: 1005.5511  
 Molecular Weight: 1006,2896

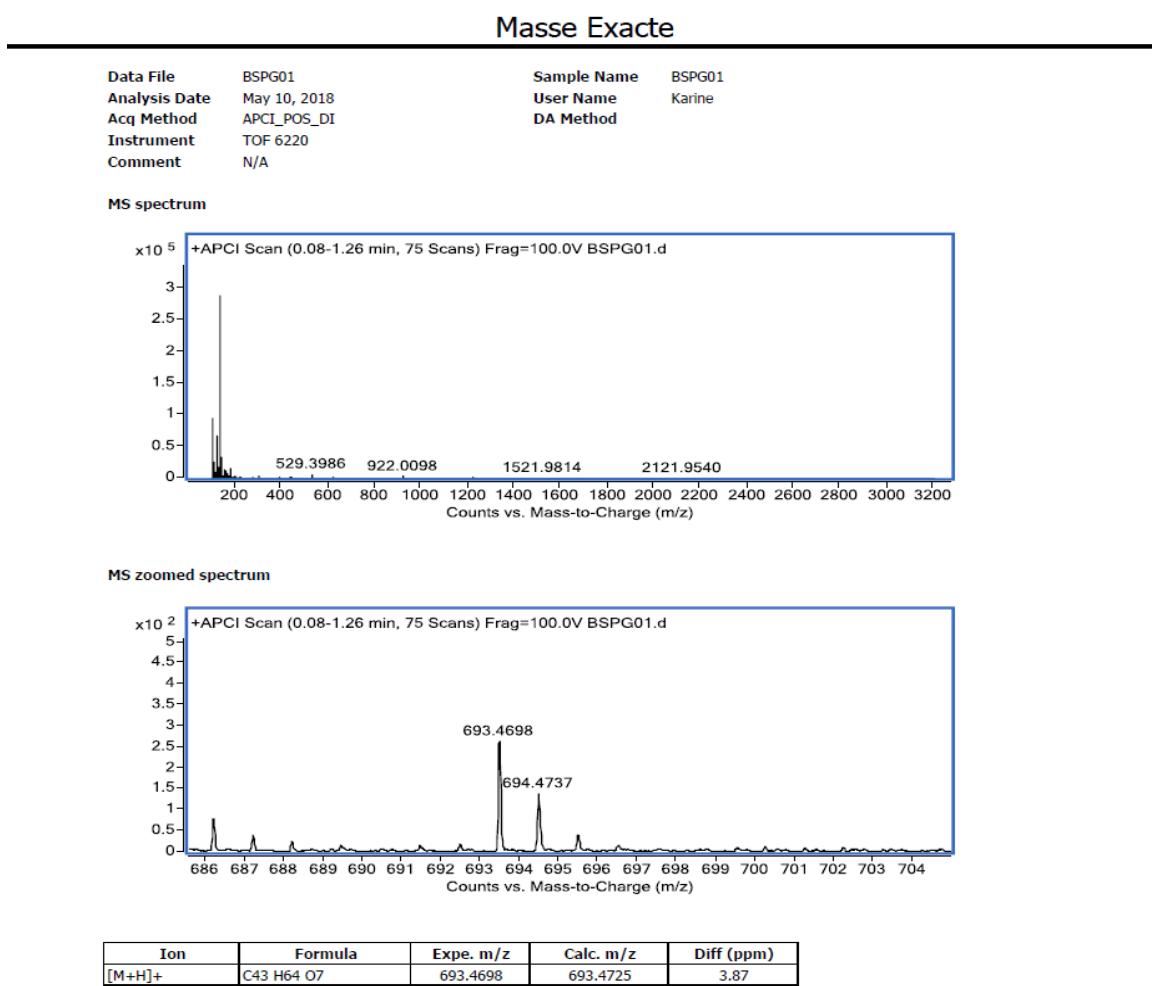
**Figure S4.**  $^1\text{H}$  NMR spectrum of **14** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S5.**  $^{13}\text{C}$  NMR spectra of **14** ( $\text{CDCl}_3$ , 100 MHz)

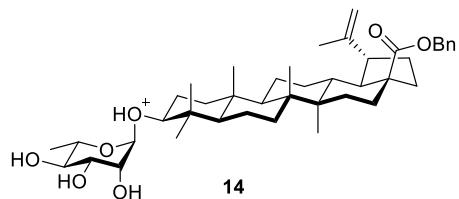


**Figure S6.** HRMS spectra of **14**



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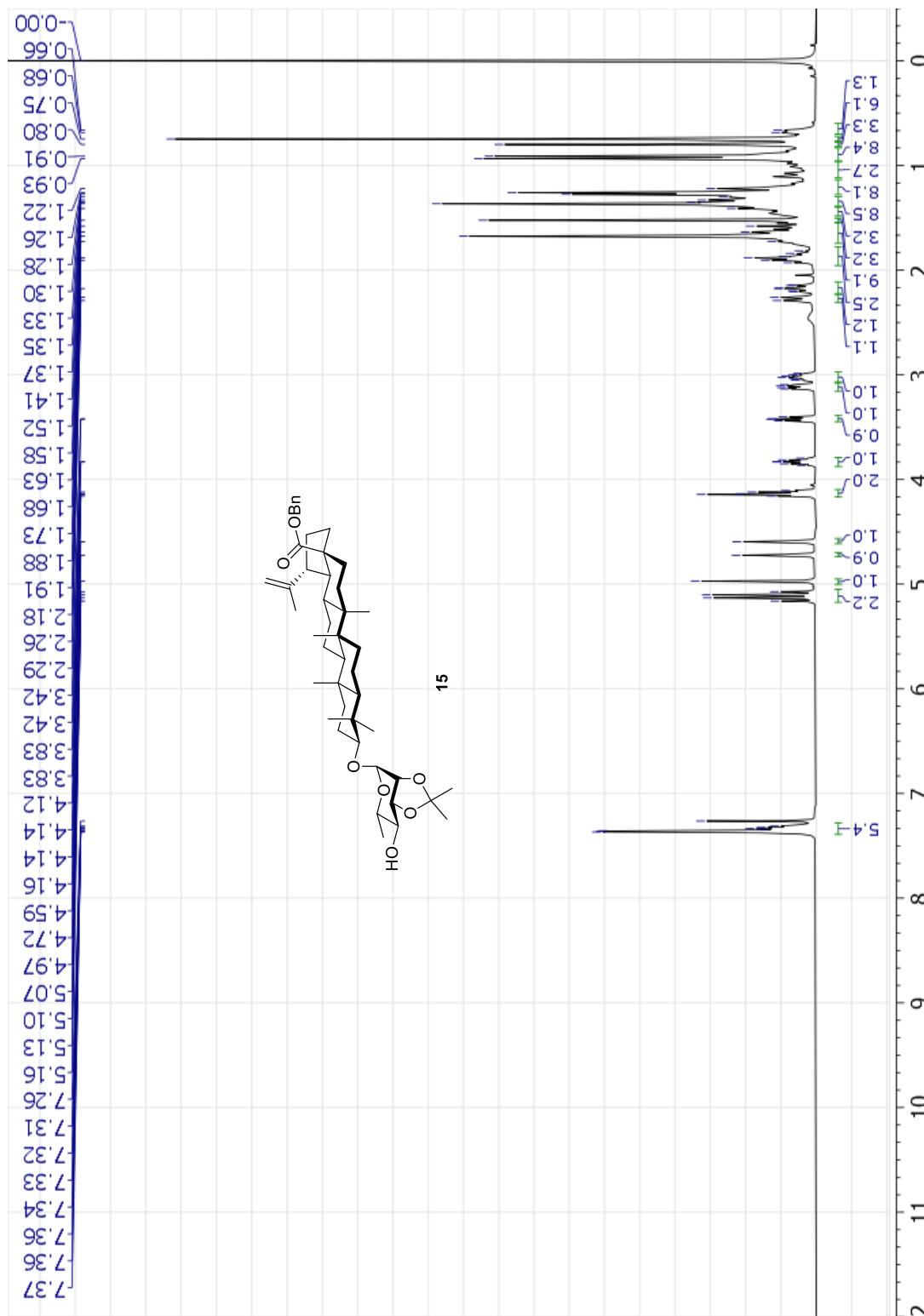


Chemical Formula: C<sub>43</sub>H<sub>65</sub>O<sub>7</sub><sup>+</sup>

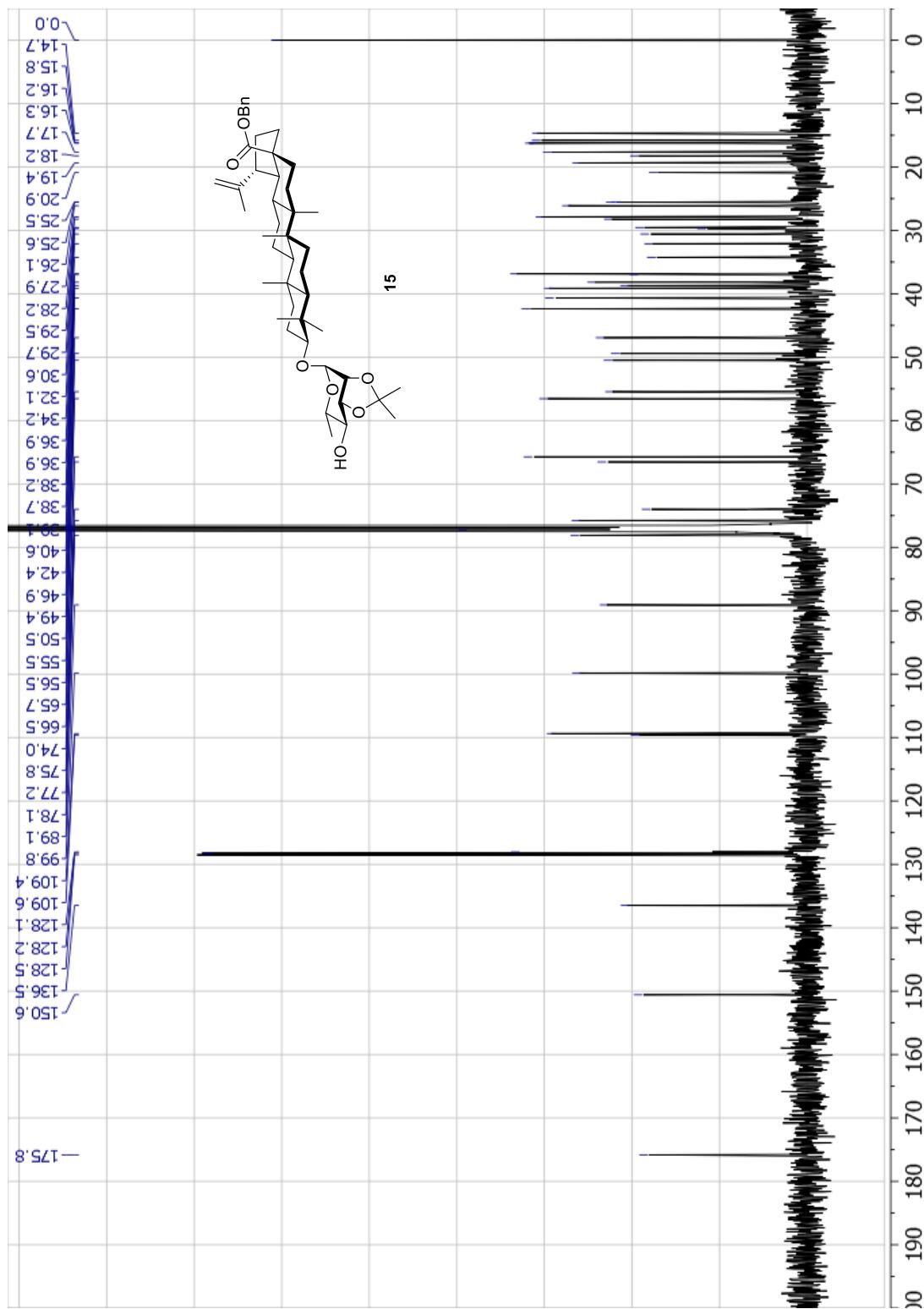
Exact Mass: 693.4725

Molecular Weight: 693.9855

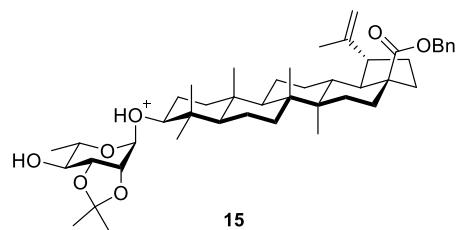
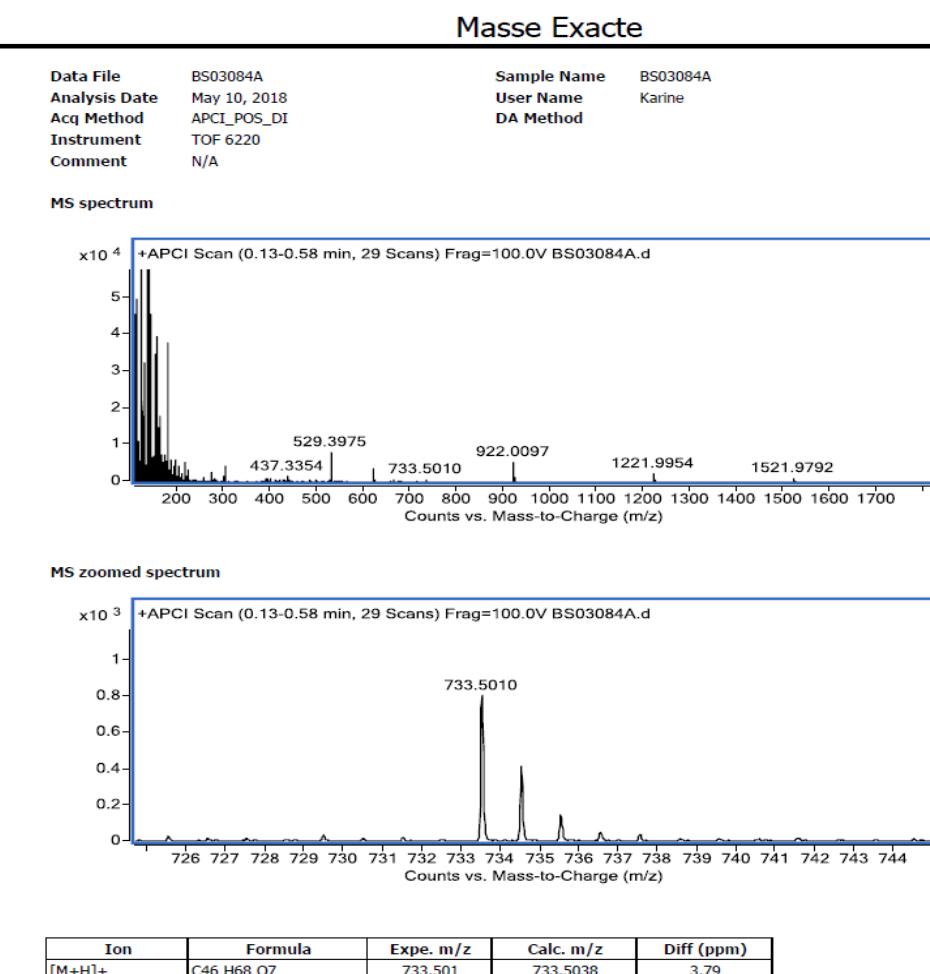
**Figure S7.**  $^1\text{H}$  NMR spectrum of **15** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S8.**  $^{13}\text{C}$  NMR spectra of **15** ( $\text{CDCl}_3$ , 100 MHz)

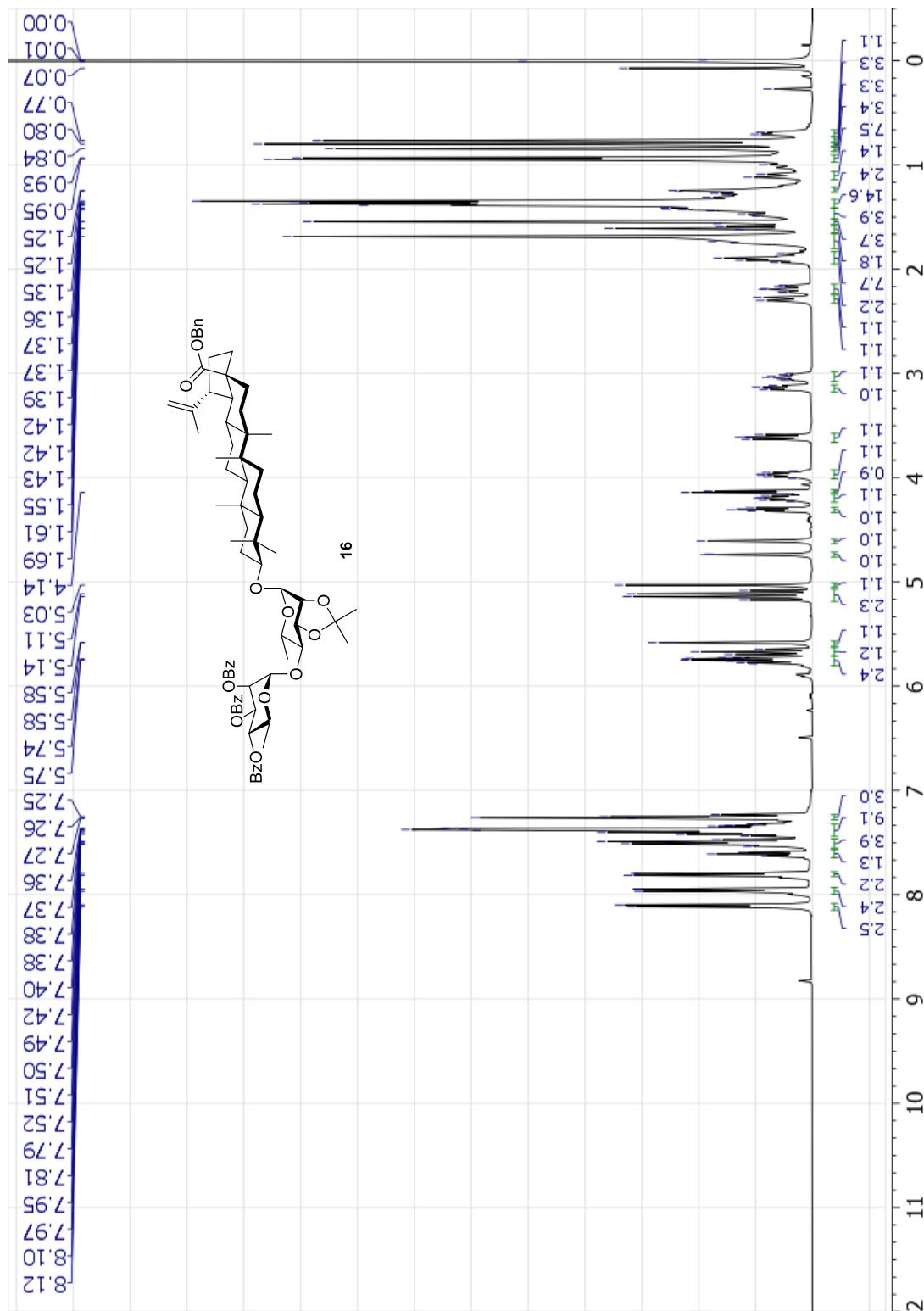


**Figure S9.** HRMS spectra of **15**

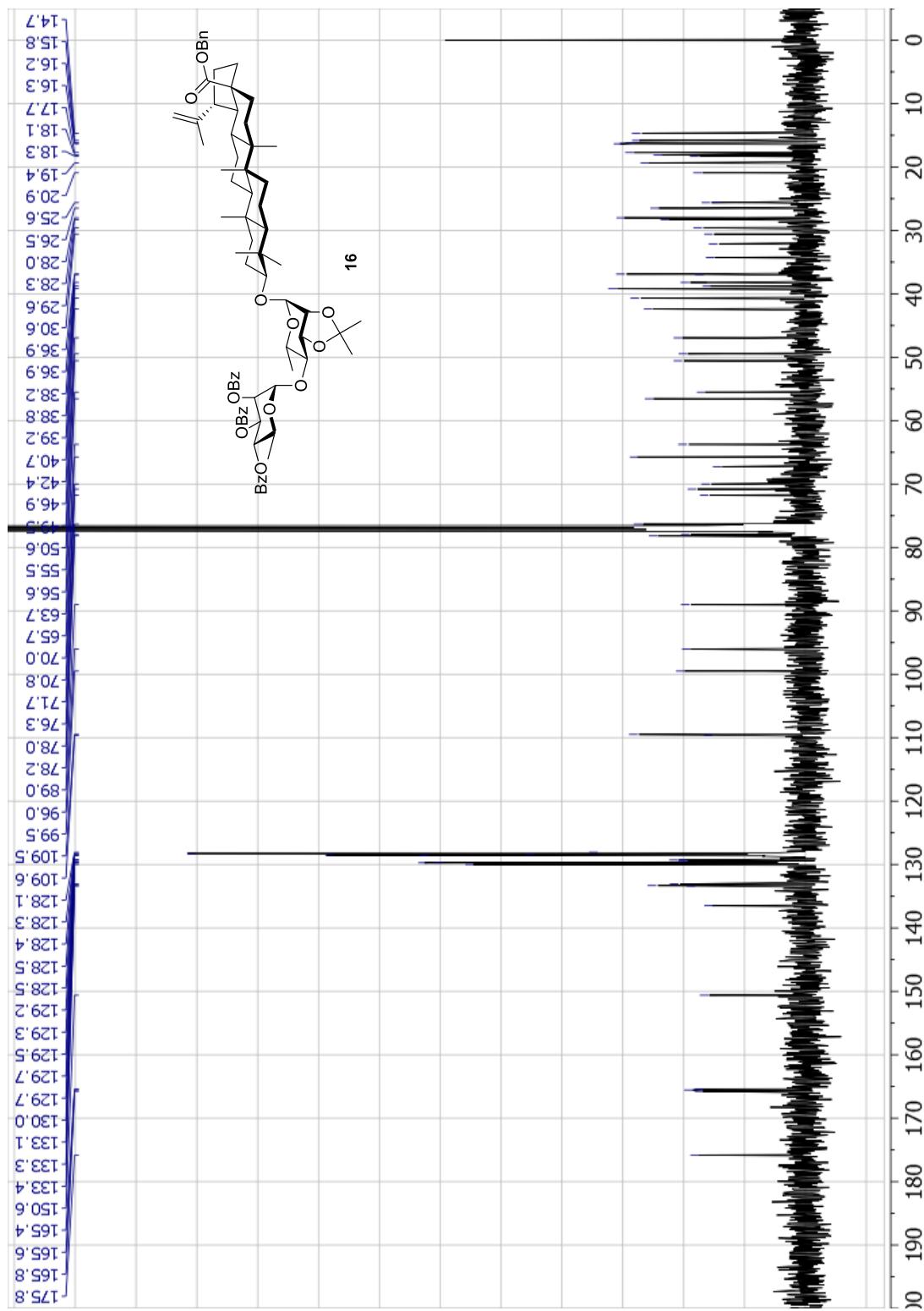


Chemical Formula: C<sub>46</sub>H<sub>68</sub>O<sub>7</sub><sup>+</sup>  
 Exact Mass: 733.5038  
 Molecular Weight: 734.0505

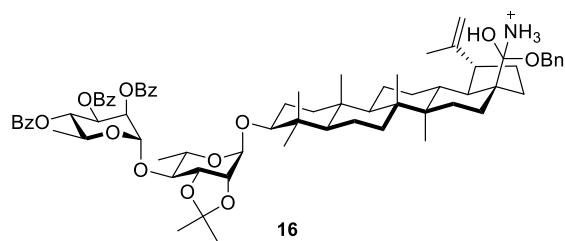
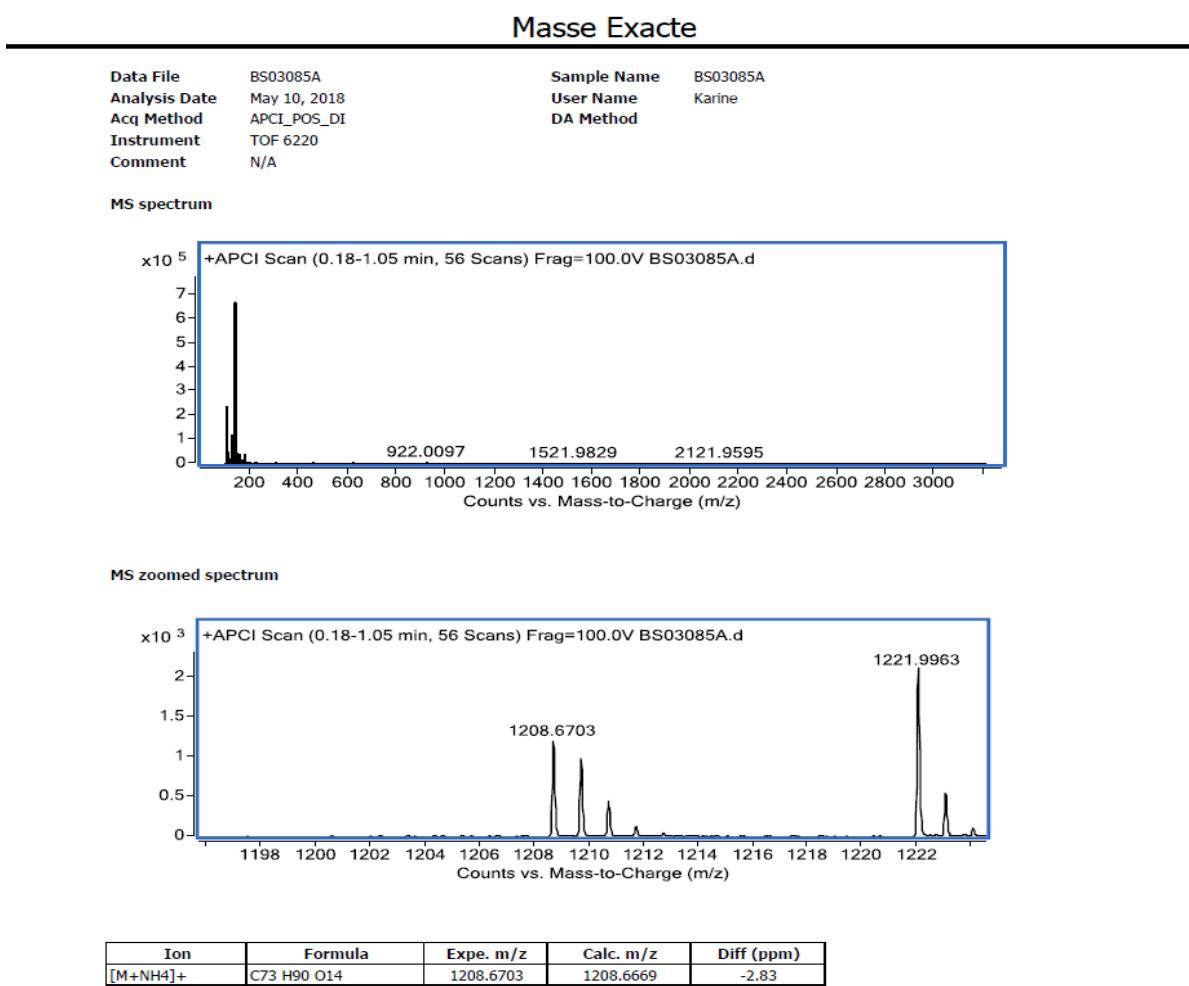
**Figure S10.**  $^1\text{H}$  NMR spectrum of **16** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S11.**  $^{13}\text{C}$  NMR spectra of **16** ( $\text{CDCl}_3$ , 100 MHz)

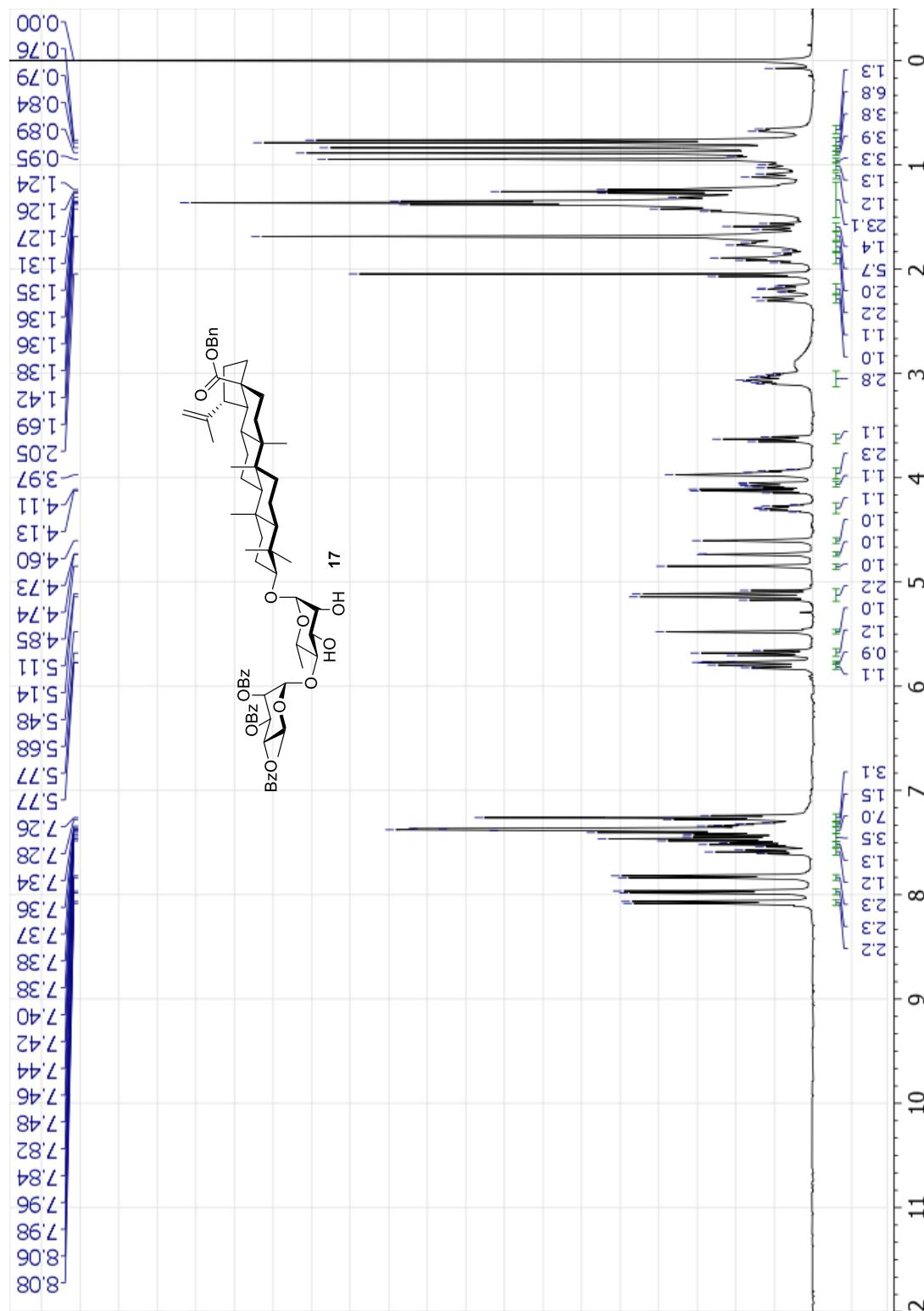


**Figure S12.** HRMS spectra of **16**

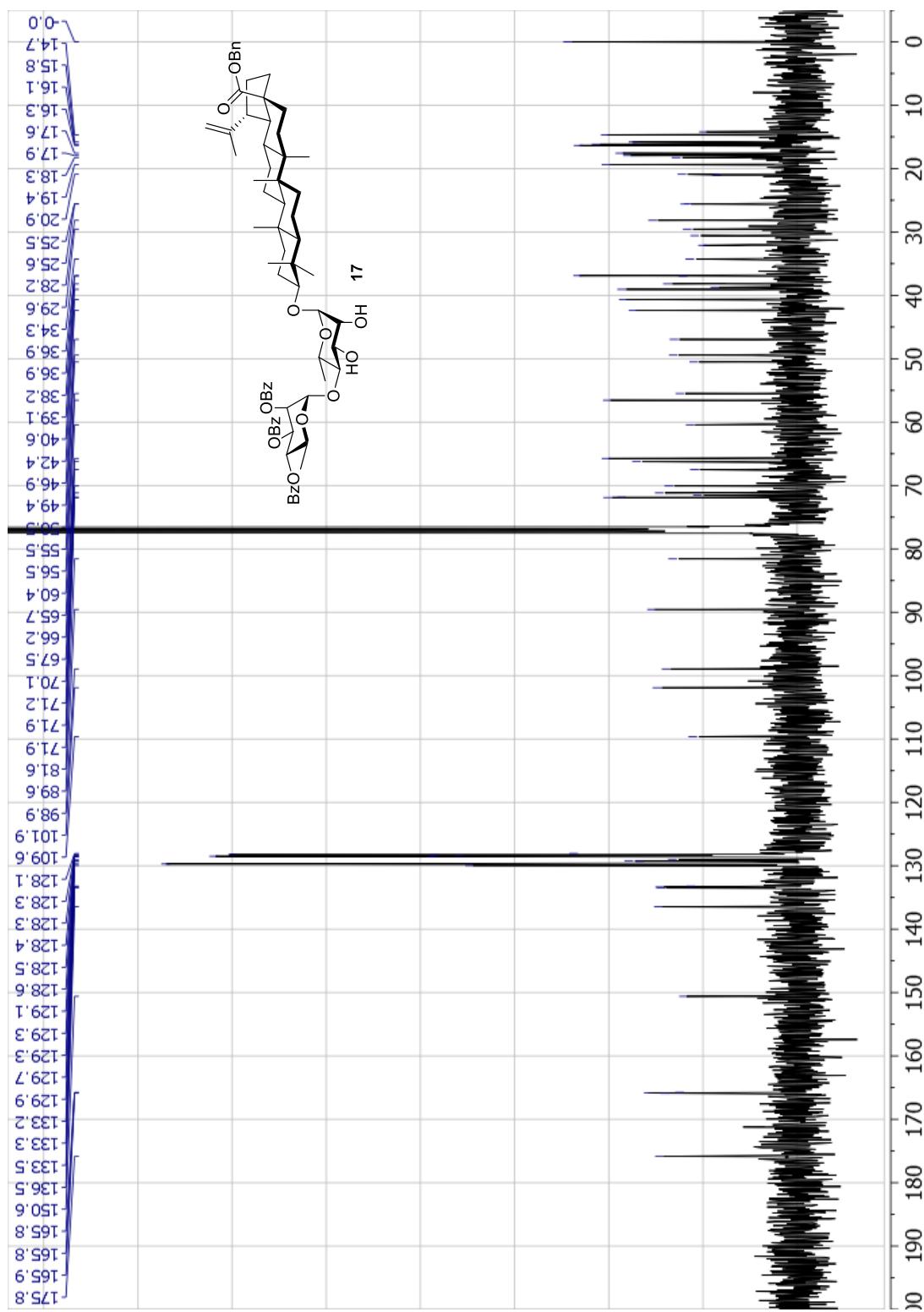


Chemical Formula: C<sub>73</sub>H<sub>94</sub>NO<sub>14</sub><sup>+</sup>  
 Exact Mass: 1208.6669  
 Molecular Weight: 1209.5475

**Figure S13.**  $^1\text{H}$  NMR spectrum of **17** ( $\text{CDCl}_3$ , 400 MHz)



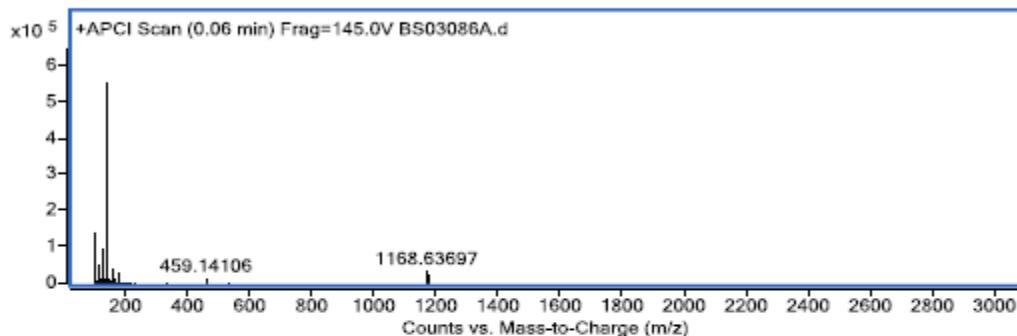
**Figure S14.**  $^{13}\text{C}$  NMR spectra of **17** ( $\text{CDCl}_3$ , 100 MHz)



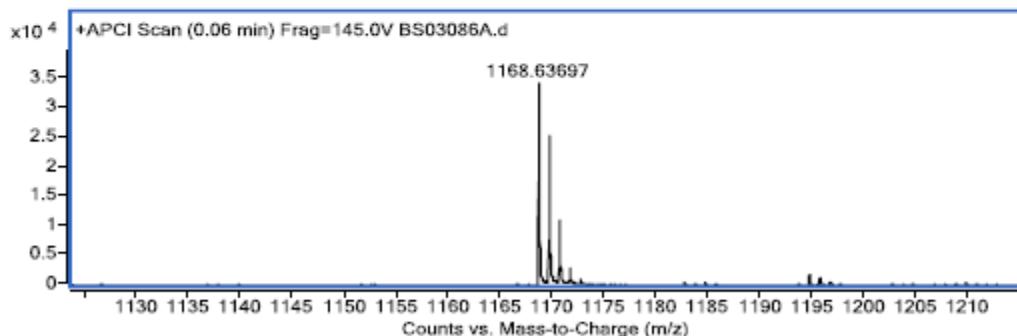
**Figure S15.** HRMS spectra of 17

Data File	BS03086A	Sample Name	BS03086A
Analysis Date	August 31, 2018	User Name	KG
Acq Method	ESI_pos_DI	DA Method	
Instrument	TOF 6224		
Comment	N/A		

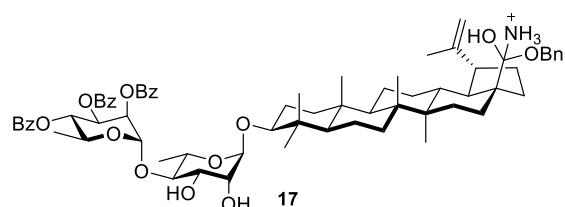
MS spectrum



MS zoomed spectrum



Ion	Formula	Expe. m/z	Calc. m/z	Diff (ppm)
[M+NH4] <sup>+</sup>	C <sub>70</sub> H <sub>86</sub> O <sub>14</sub>	1168.63697	1168.63558	-1.19

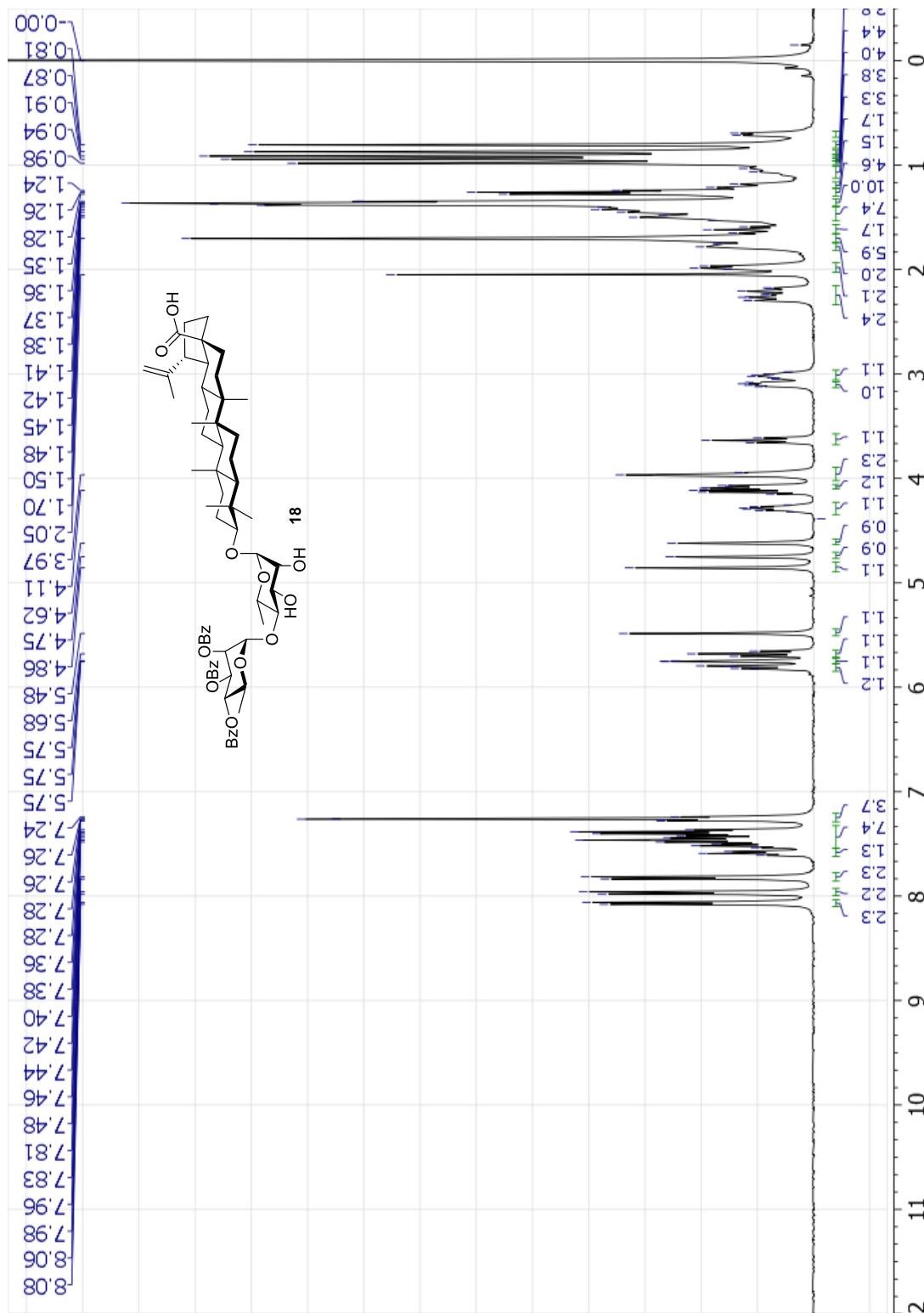


Chemical Formula: C<sub>70</sub>H<sub>86</sub>NO<sub>14</sub><sup>+</sup>

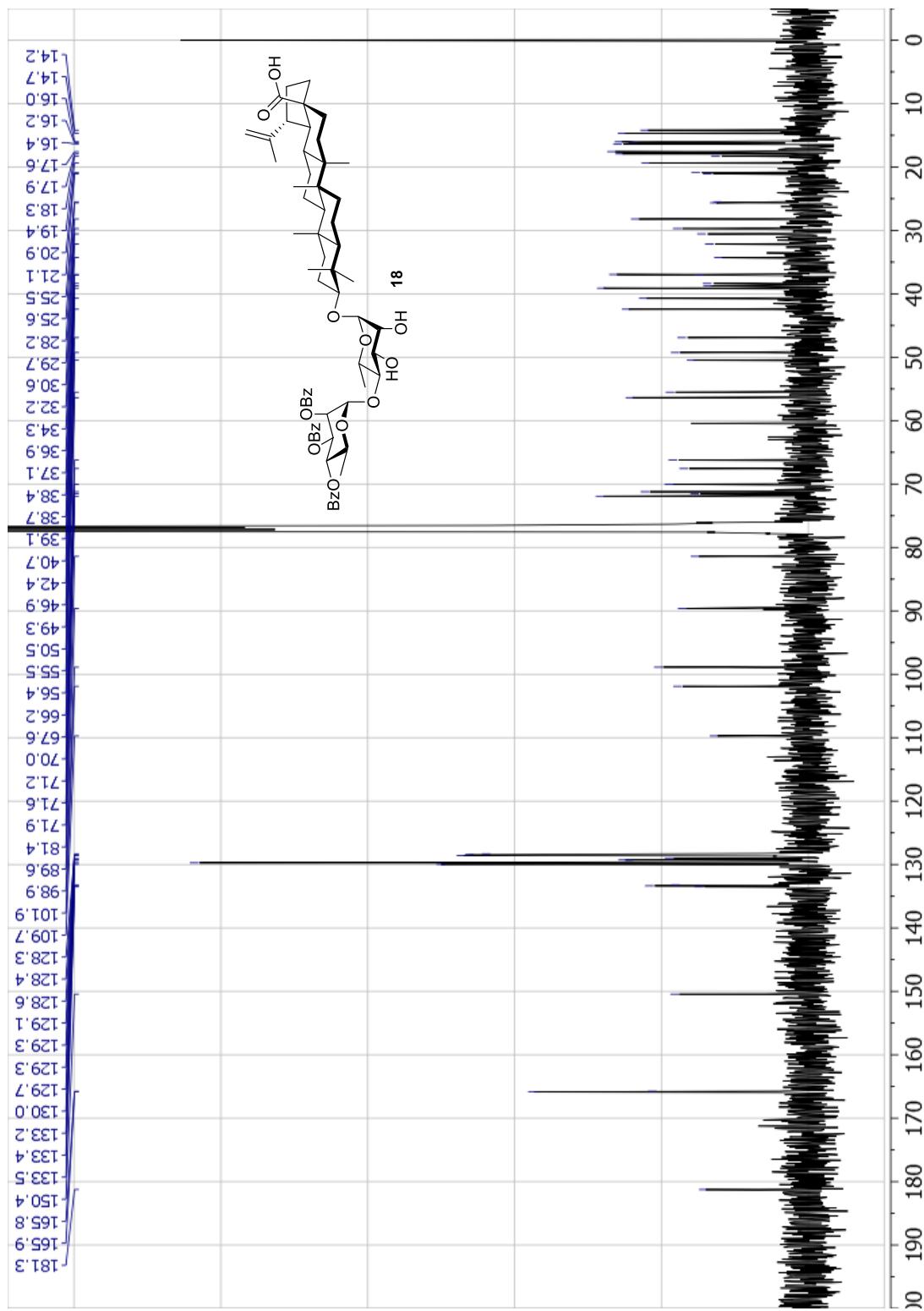
Exact Mass: 1168.6356

Molecular Weight: 1169.4825

**Figure S16.**  $^1\text{H}$  NMR spectrum of **18** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S17.**  $^{13}\text{C}$  NMR spectra of **18** ( $\text{CDCl}_3$ , 100 MHz)

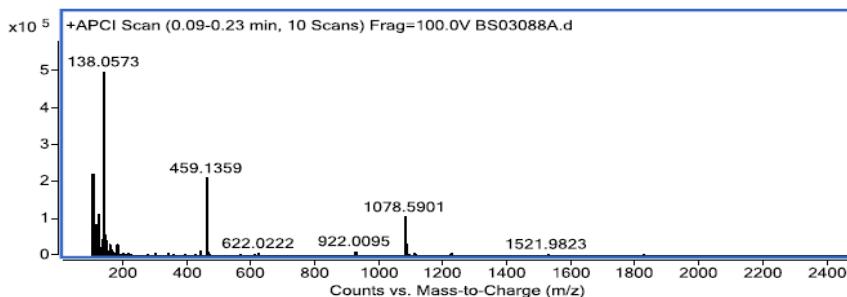


**Figure S18.** HRMS spectra of **18**

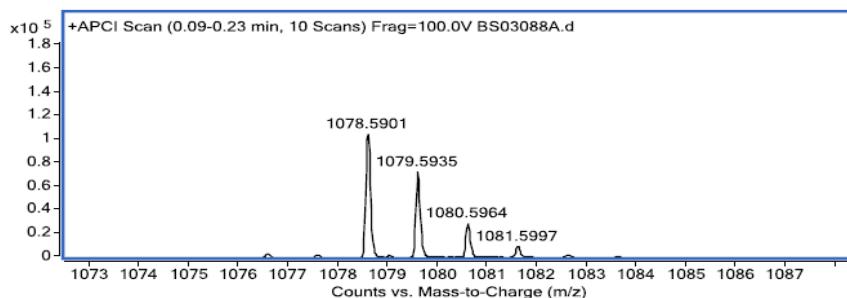
masse Exacte

Data File	BS03088A	Sample Name	BS03088A
Analysis Date	May 10, 2018	User Name	Karine
Acq Method	APCI_POS_DI	DA Method	
Instrument	TOF 6220		
Comment	N/A		

MS spectrum



MS zoomed spectrum

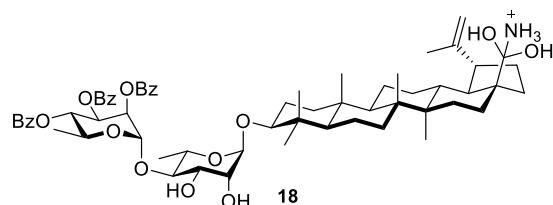


Ion	Formula	Expe. m/z	Calc. m/z	Diff (ppm)
[M+NH4] <sup>+</sup>	C <sub>63</sub> H <sub>80</sub> O <sub>14</sub>	1078.5901	1078.5886	-1.36



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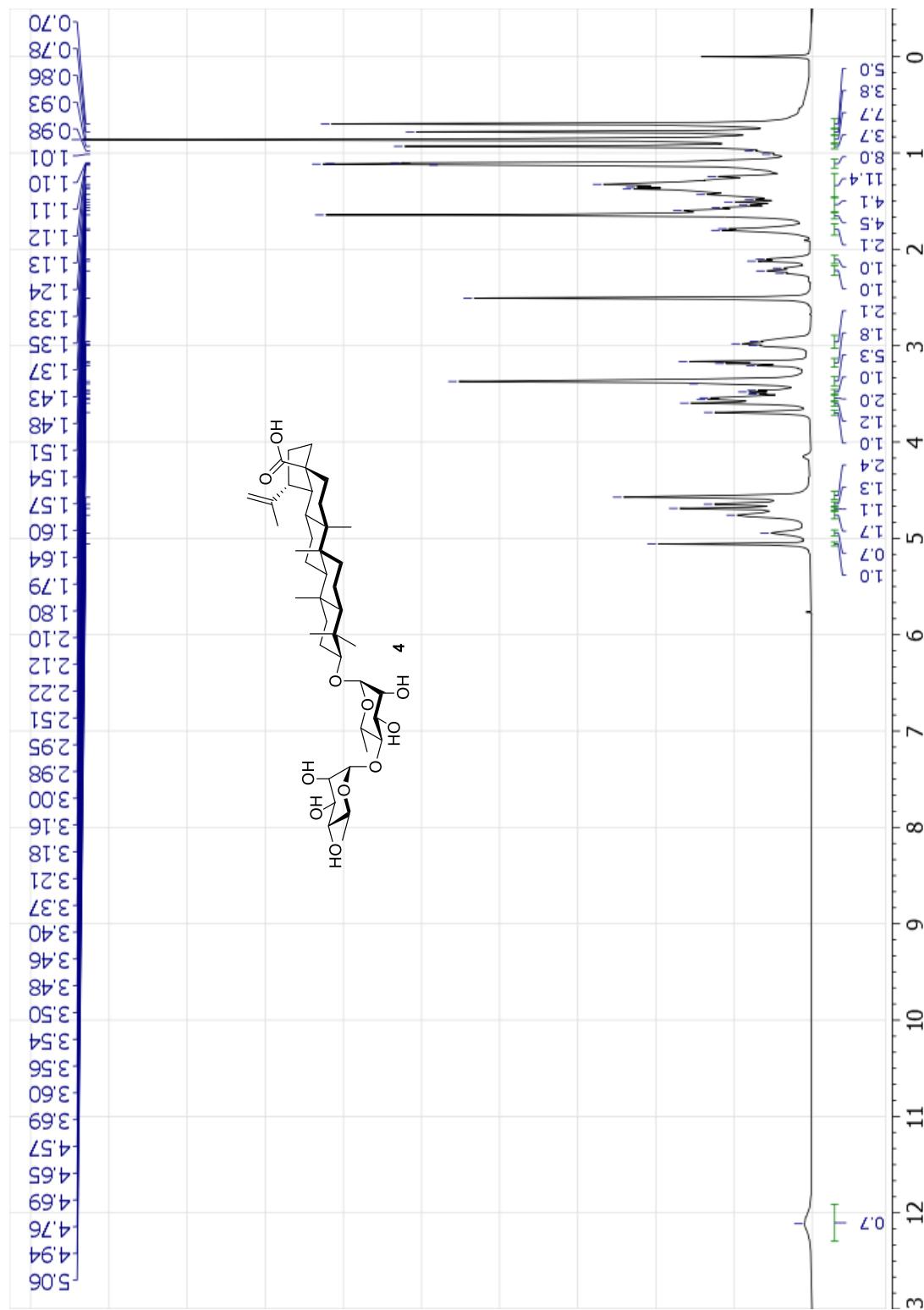


Chemical Formula: C<sub>63</sub>H<sub>84</sub>NO<sub>14</sub><sup>+</sup>

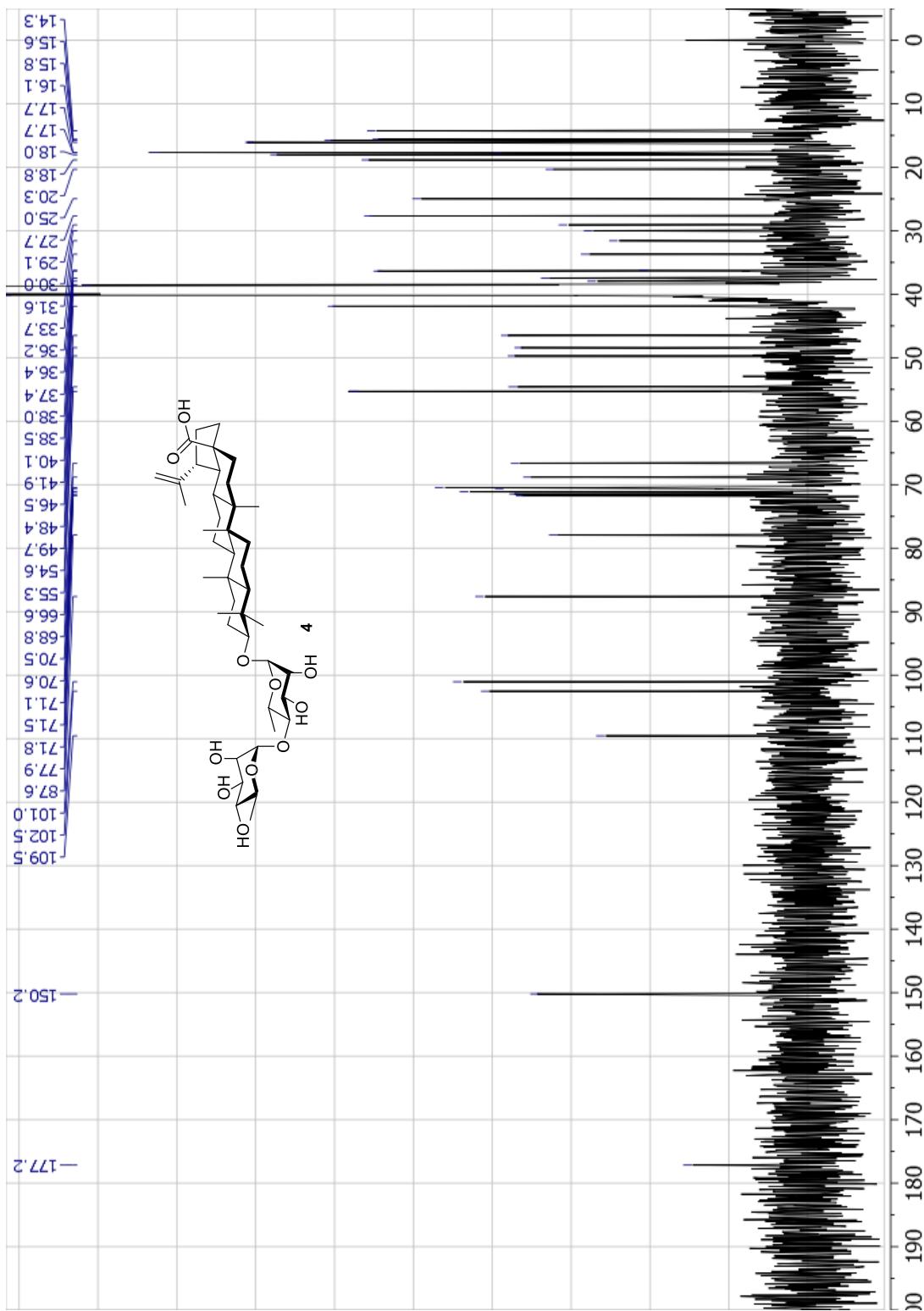
Exact Mass: 1078.5886

Molecular Weight: 1079.3575

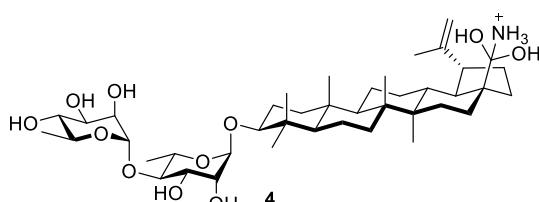
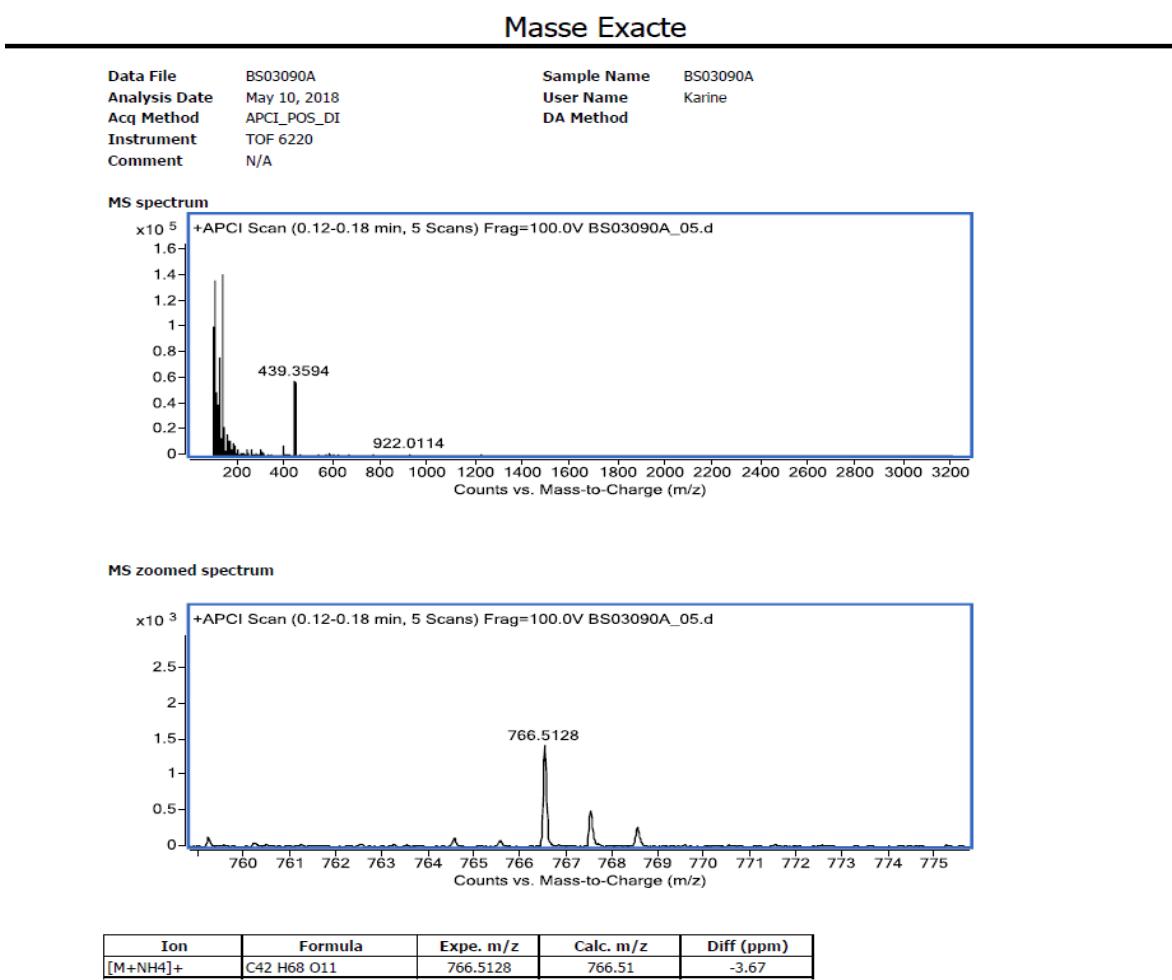
**Figure S19.**  $^1\text{H}$  NMR spectrum of **4** (DMSO- $d_6$ , 400 MHz)



**Figure S20.**  $^{13}\text{C}$  NMR spectra of **4** (DMSO- $d_6$ , 100 MHz)



**Figure S21.** HRMS spectra of **4**

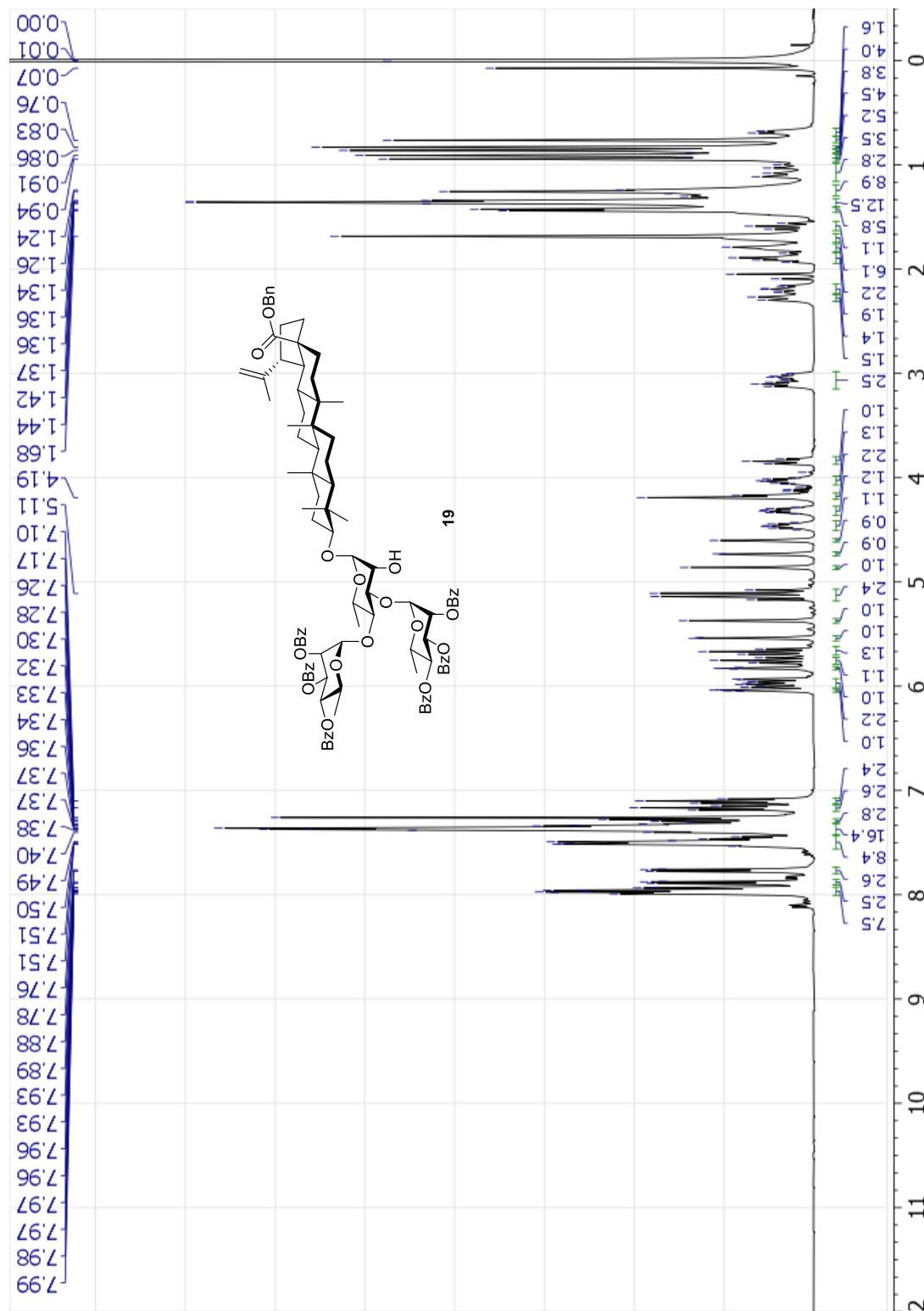


Chemical Formula: C<sub>42</sub>H<sub>72</sub>NO<sub>11</sub><sup>+</sup>

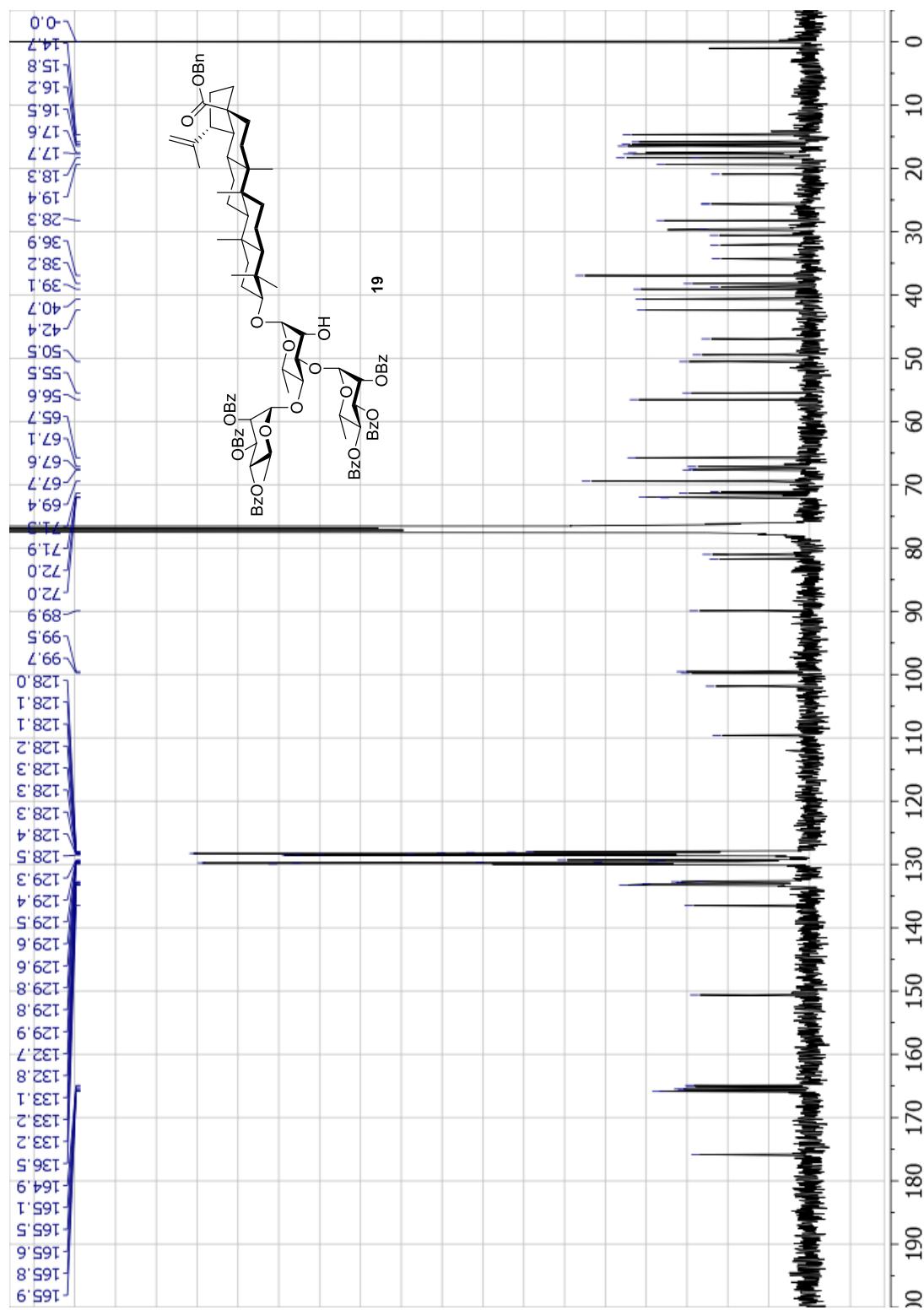
Exact Mass: 766.5100

Molecular Weight: 767.0335

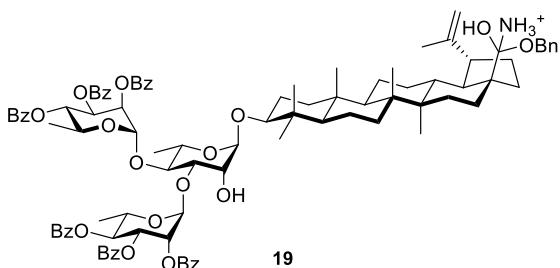
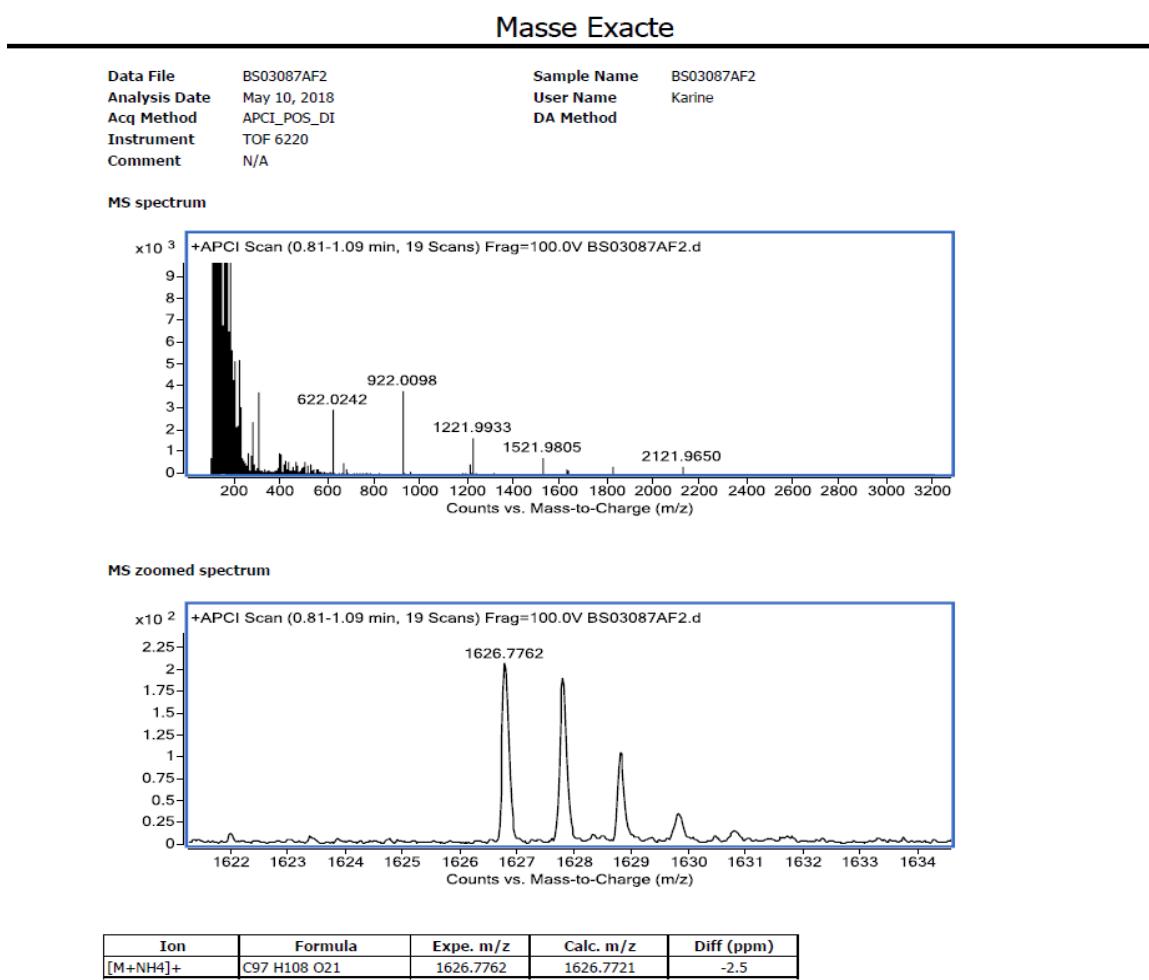
**Figure S22.**  $^1\text{H}$  NMR spectrum of **19** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S23.**  $^{13}\text{C}$  NMR spectra of **19** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S24.** HRMS spectra of **19**

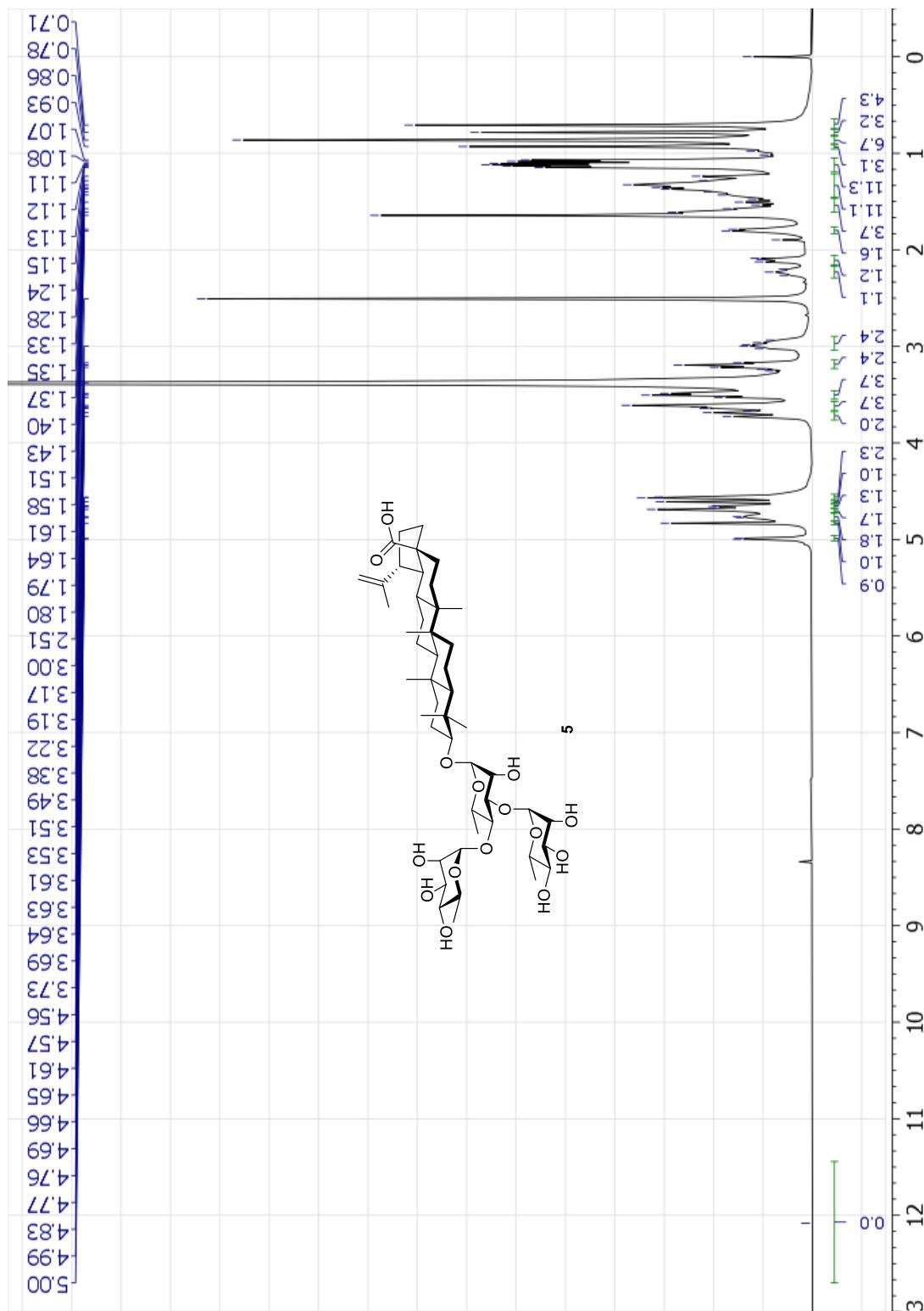


Chemical Formula: C<sub>97</sub>H<sub>112</sub>NO<sub>21</sub><sup>+</sup>

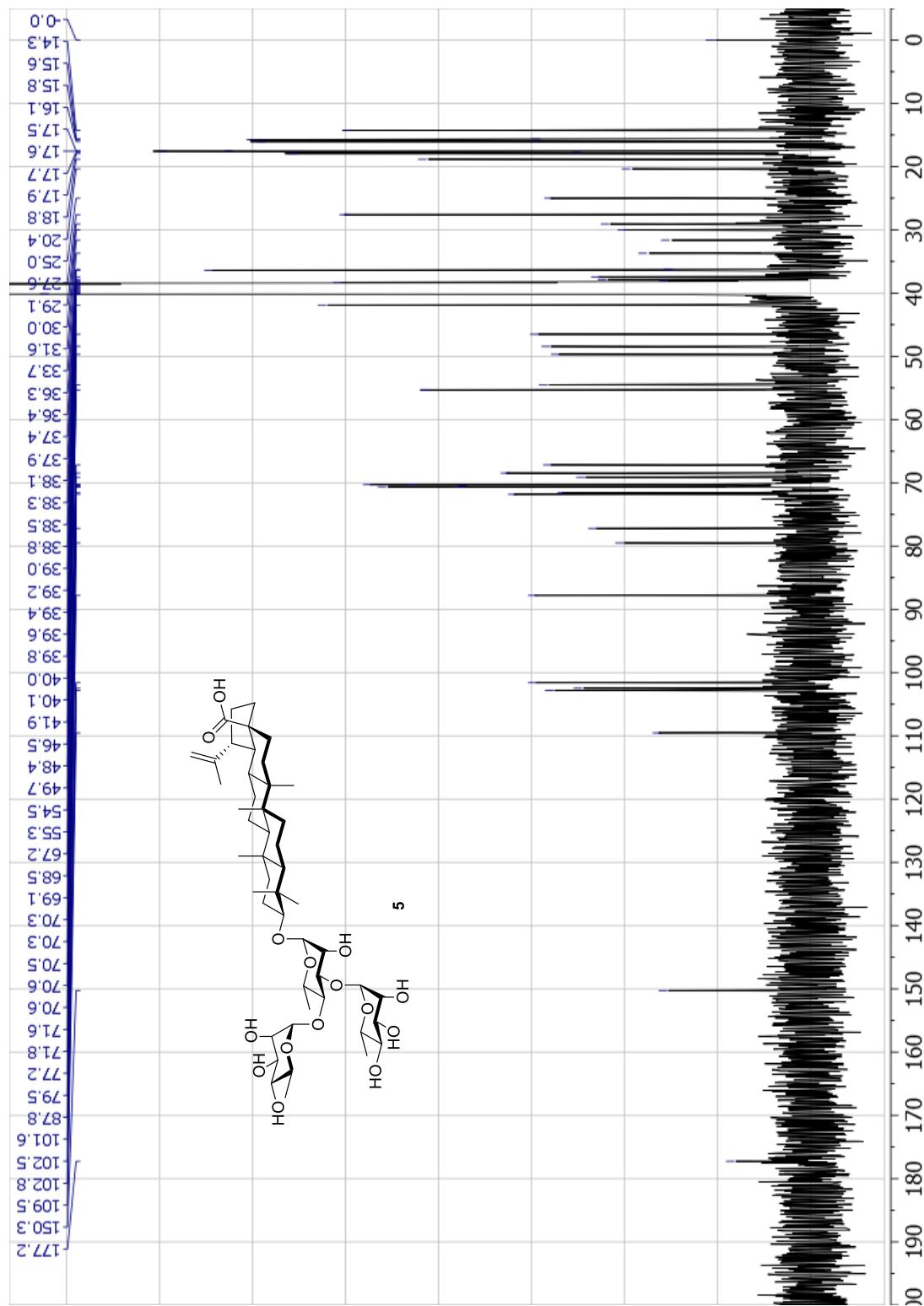
Exact Mass: 1626.7721

Molecular Weight: 1627.9485

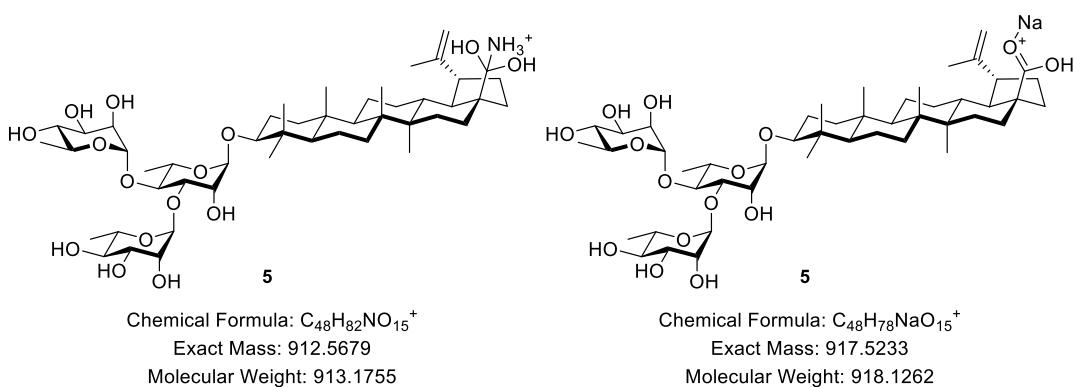
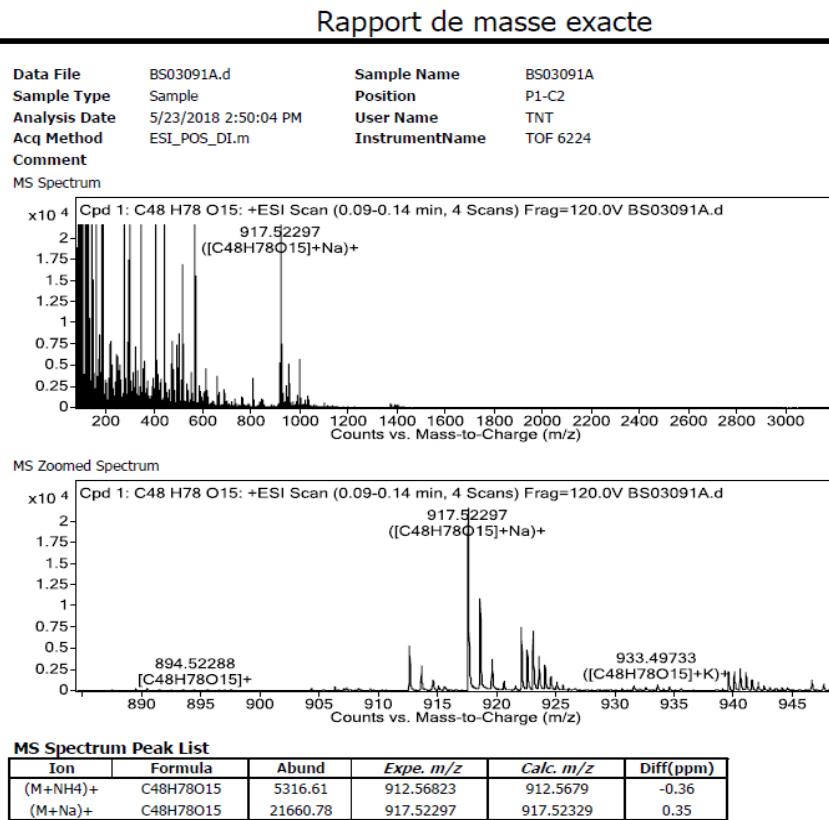
**Figure S25.**  $^1\text{H}$  NMR spectrum of **5** (DMSO- $d_6$  + 1 drop H<sub>2</sub>O, 400 MHz)



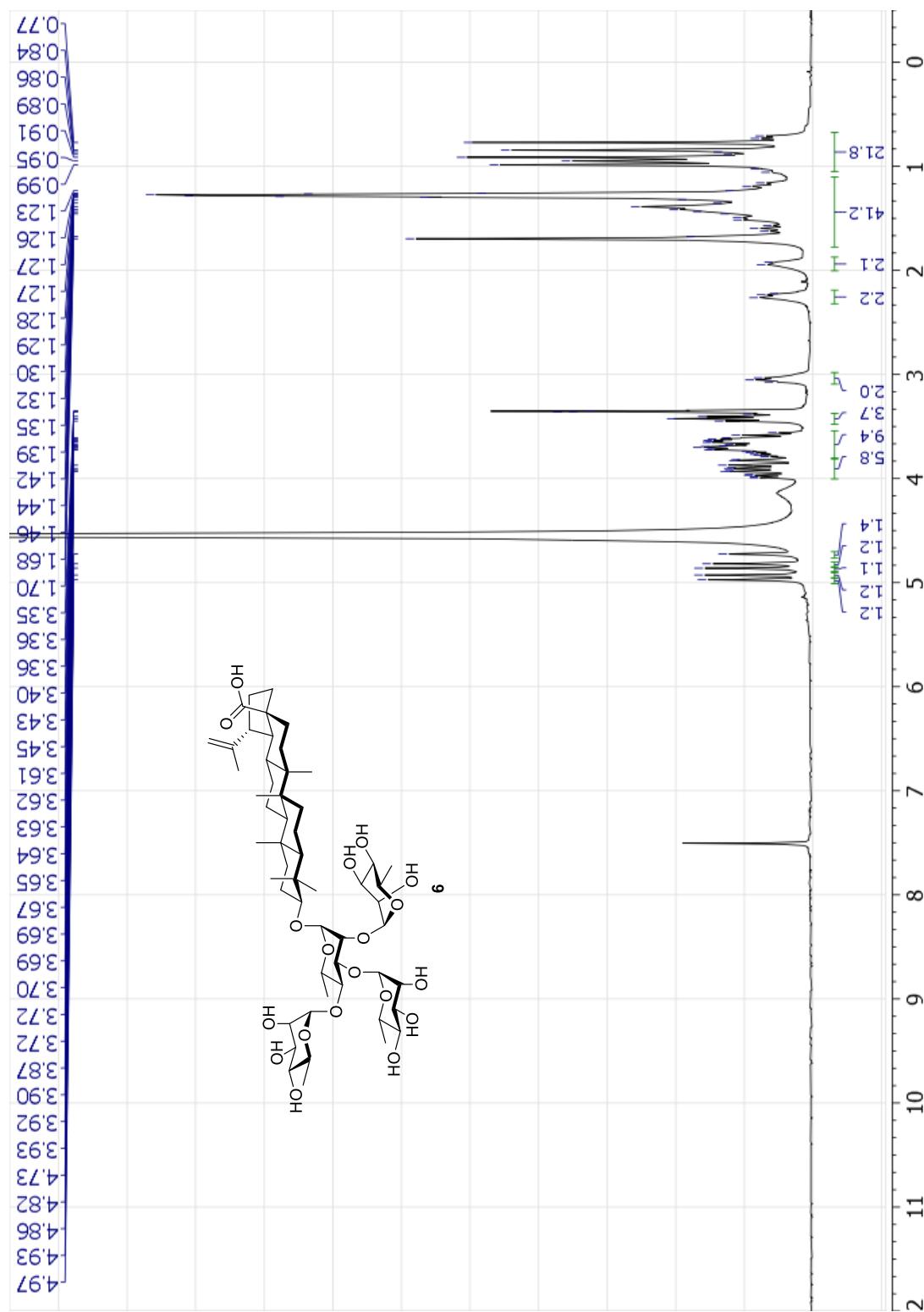
**Figure S26.**  $^{13}\text{C}$  NMR spectra of **5** (DMSO- $d_6$  + 1 drop  $\text{H}_2\text{O}$ , 100 MHz)



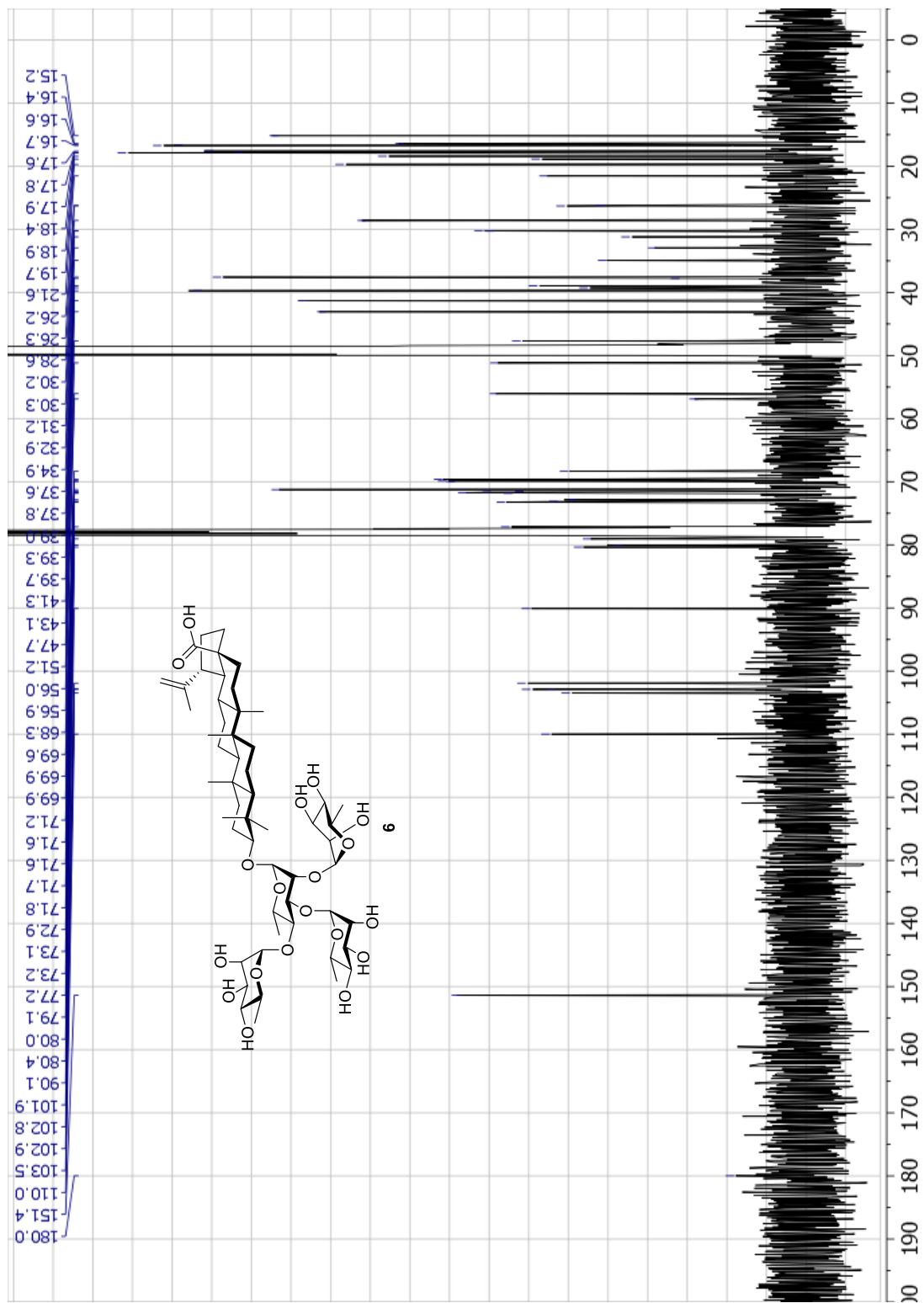
**Figure S27.** HRMS spectra of 5



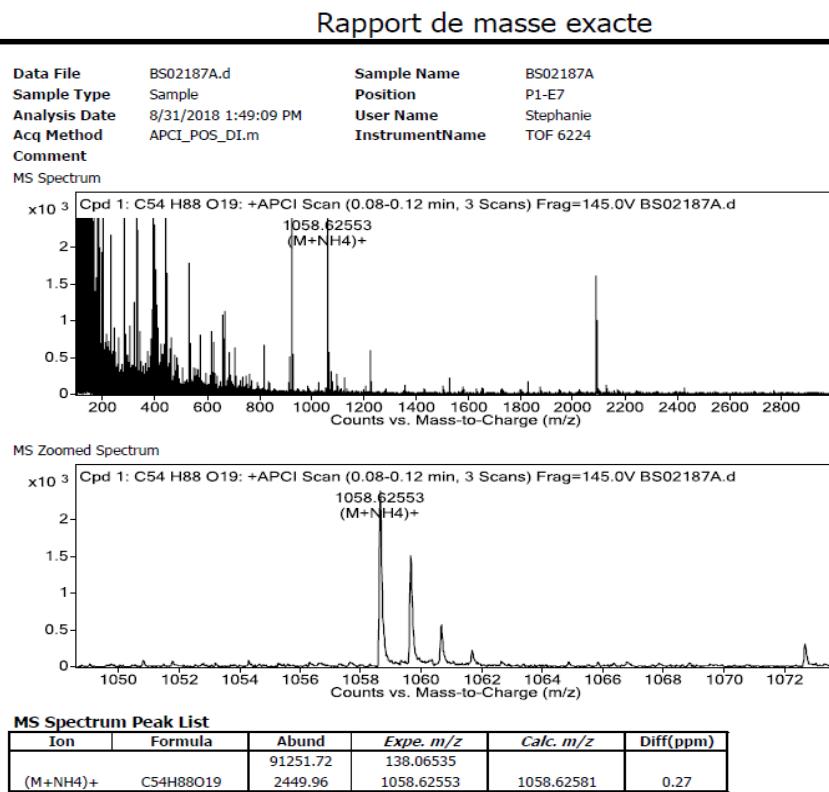
**Figure S28.**  $^1\text{H}$  NMR spectrum of **6** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 400 MHz)



**Figure S29.**  $^{13}\text{C}$  NMR spectra of **6** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 100 MHz)



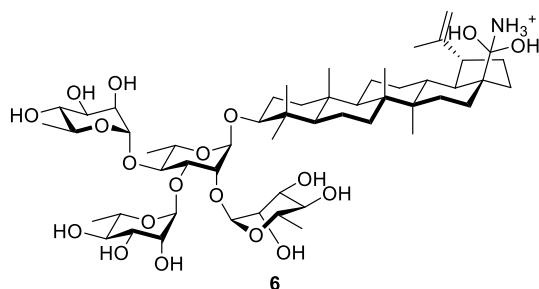
**Figure S30.** HRMS spectra of **6**



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Sous la supervision de Dr. Furtos

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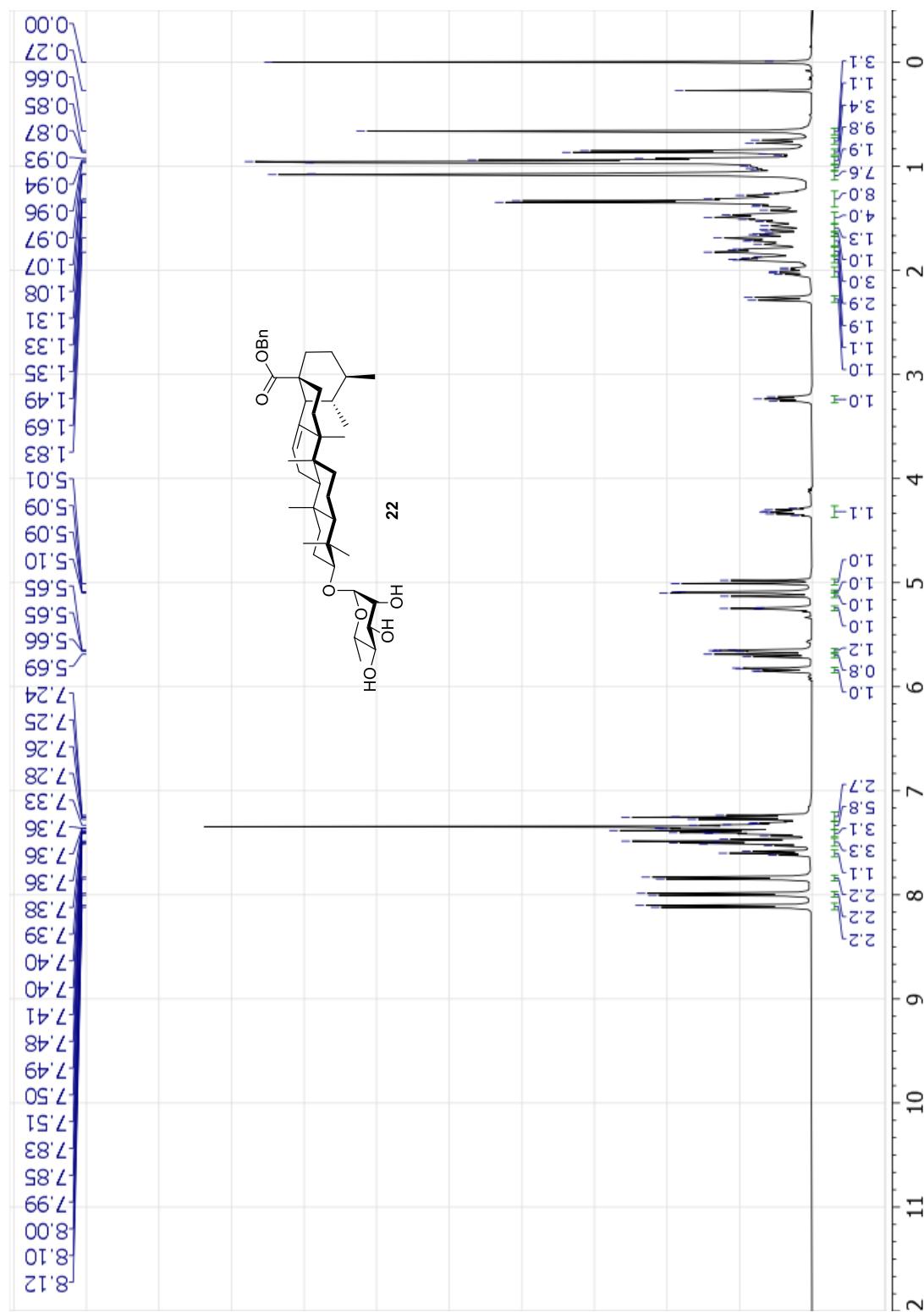


Chemical Formula: C<sub>54</sub>H<sub>92</sub>NO<sub>19</sub><sup>+</sup>

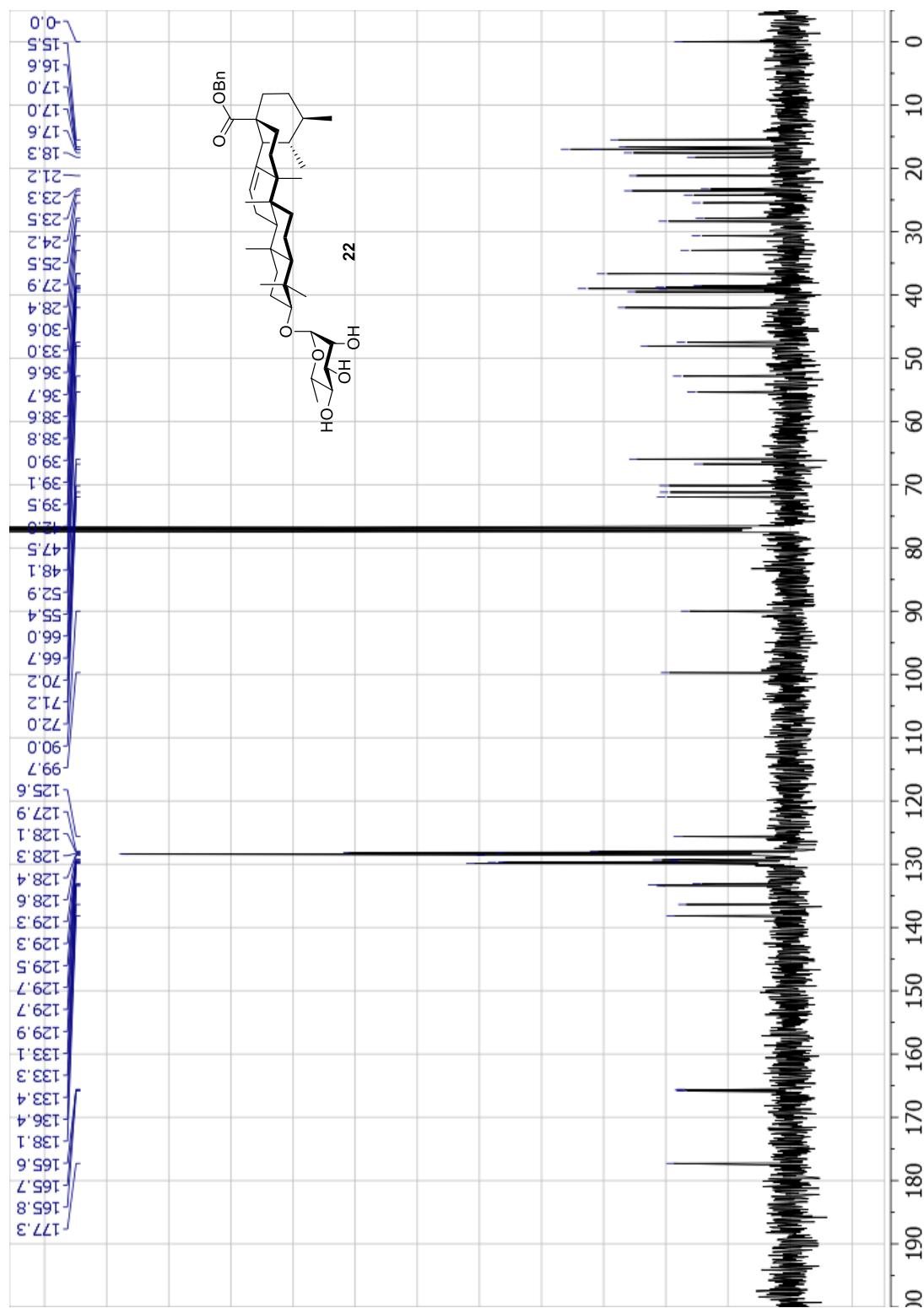
Exact Mass: 1058.6258

Molecular Weight: 1059.3175

**Figure S31.**  $^1\text{H}$  NMR spectrum of **21** ( $\text{CDCl}_3$ , 400 MHz)

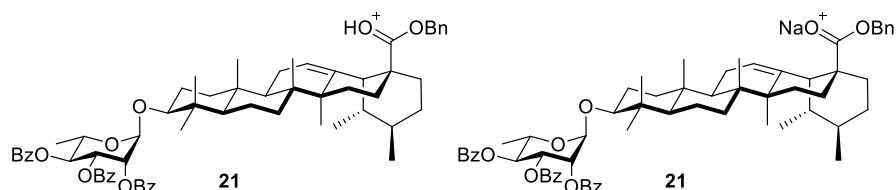
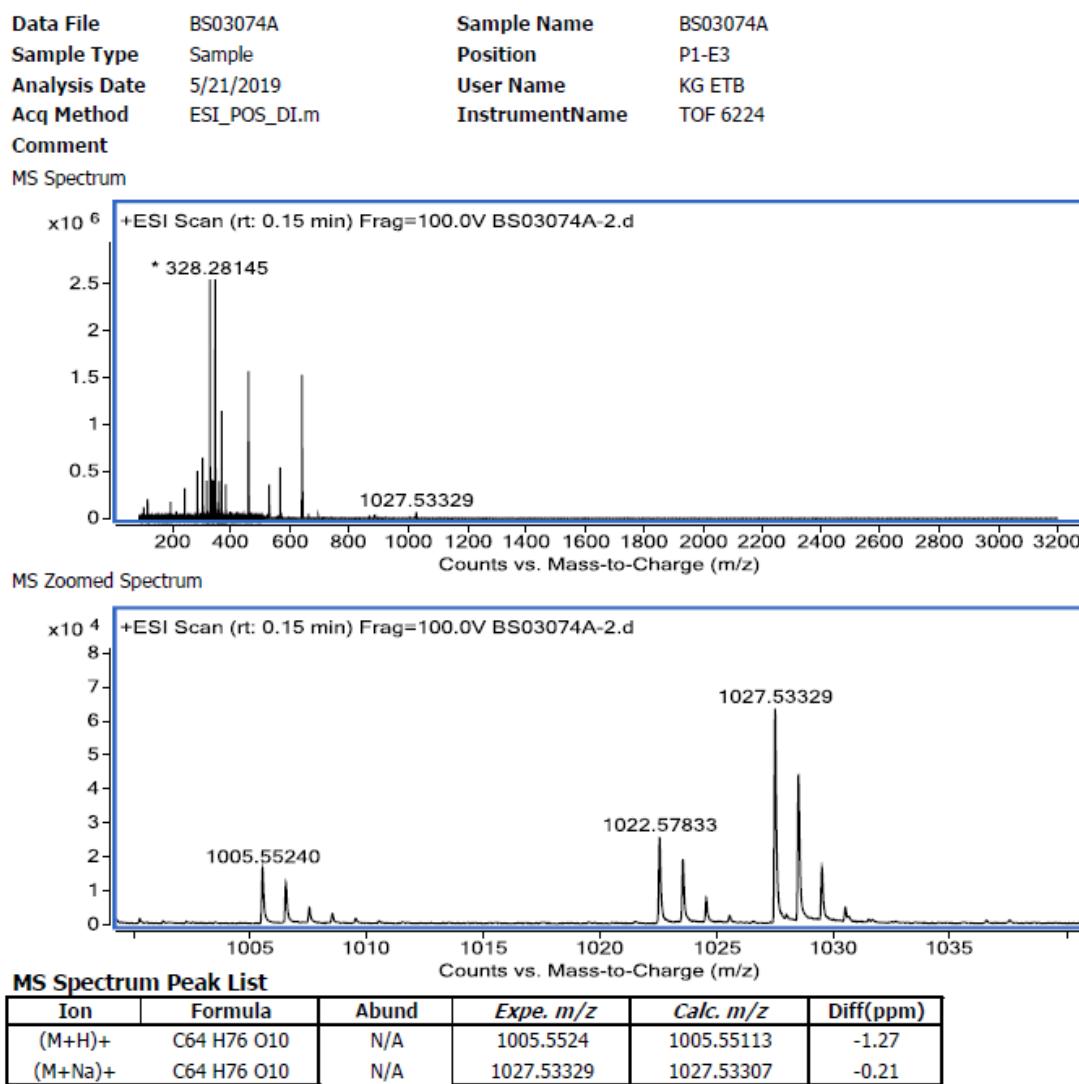


**Figure S32.**  $^{13}\text{C}$  NMR spectra of **21** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S33.** HRMS spectra of **21**

## Rapport de masse exacte



Chemical Formula: C<sub>64</sub>H<sub>76</sub>O<sub>10</sub><sup>+</sup>

Exact Mass: 1005.5511

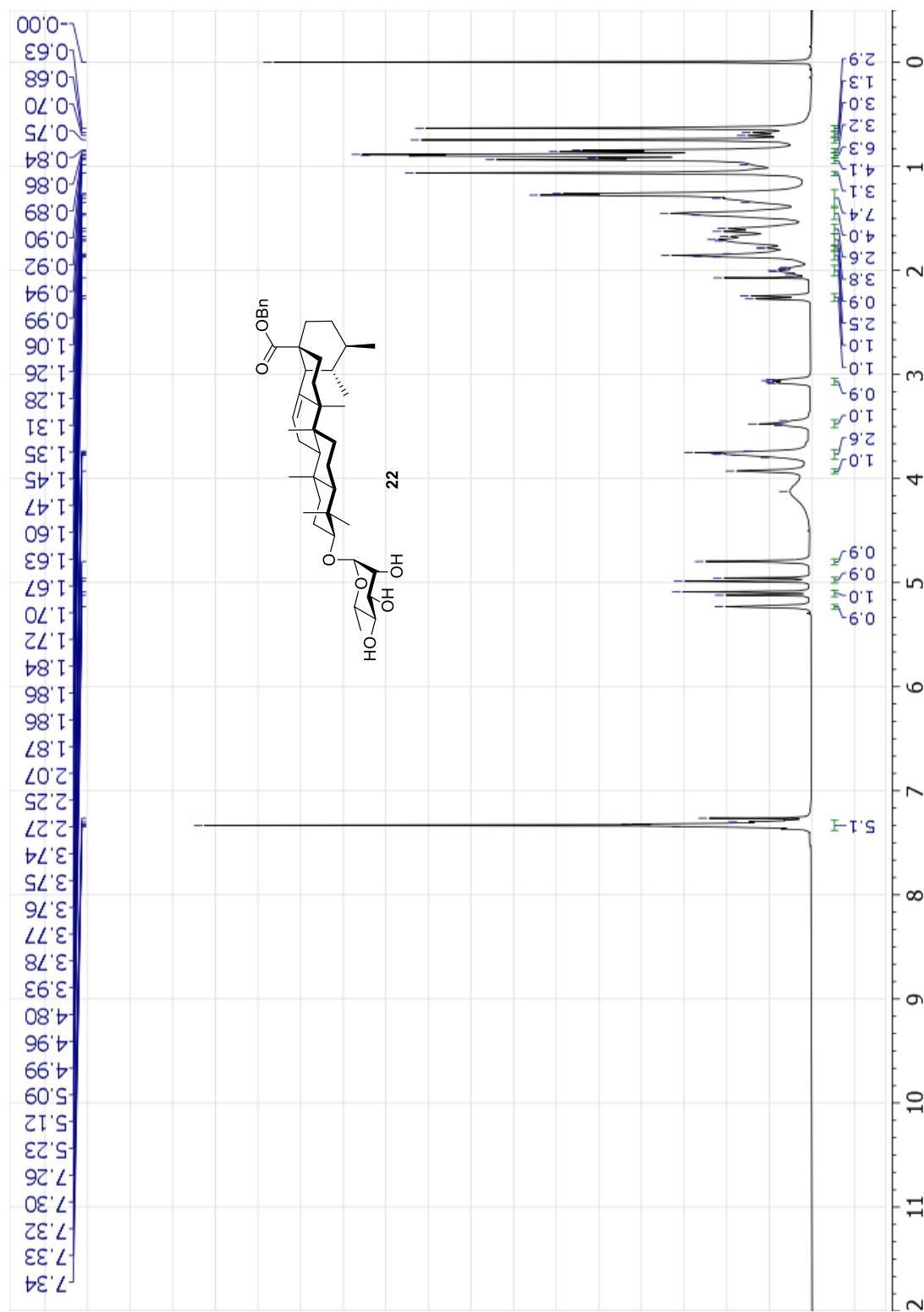
Molecular Weight: 1006.3095

Chemical Formula: C<sub>64</sub>H<sub>76</sub>NaO<sub>10</sub><sup>+</sup>

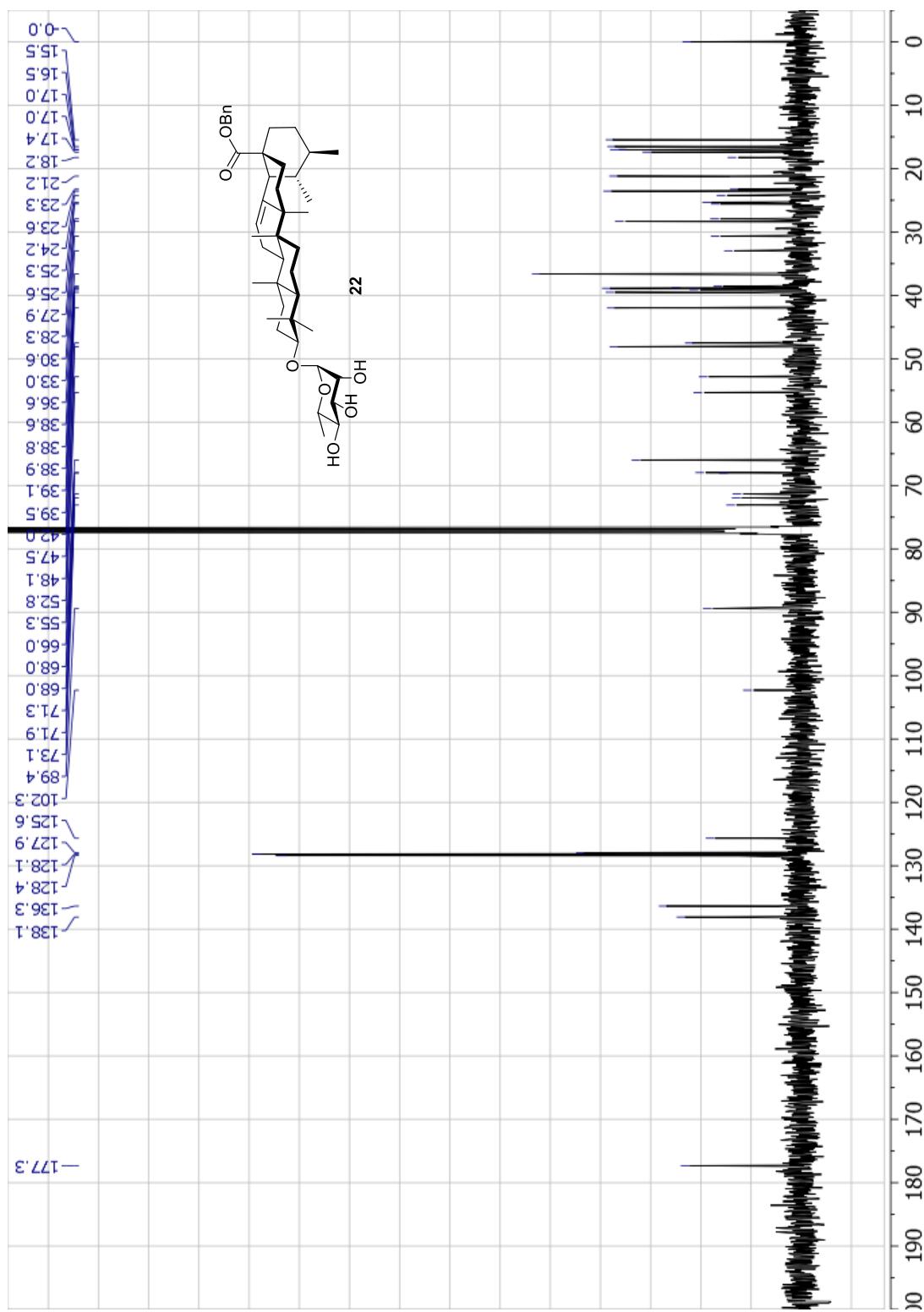
Exact Mass: 1027.5331

Molecular Weight: 1028.2912

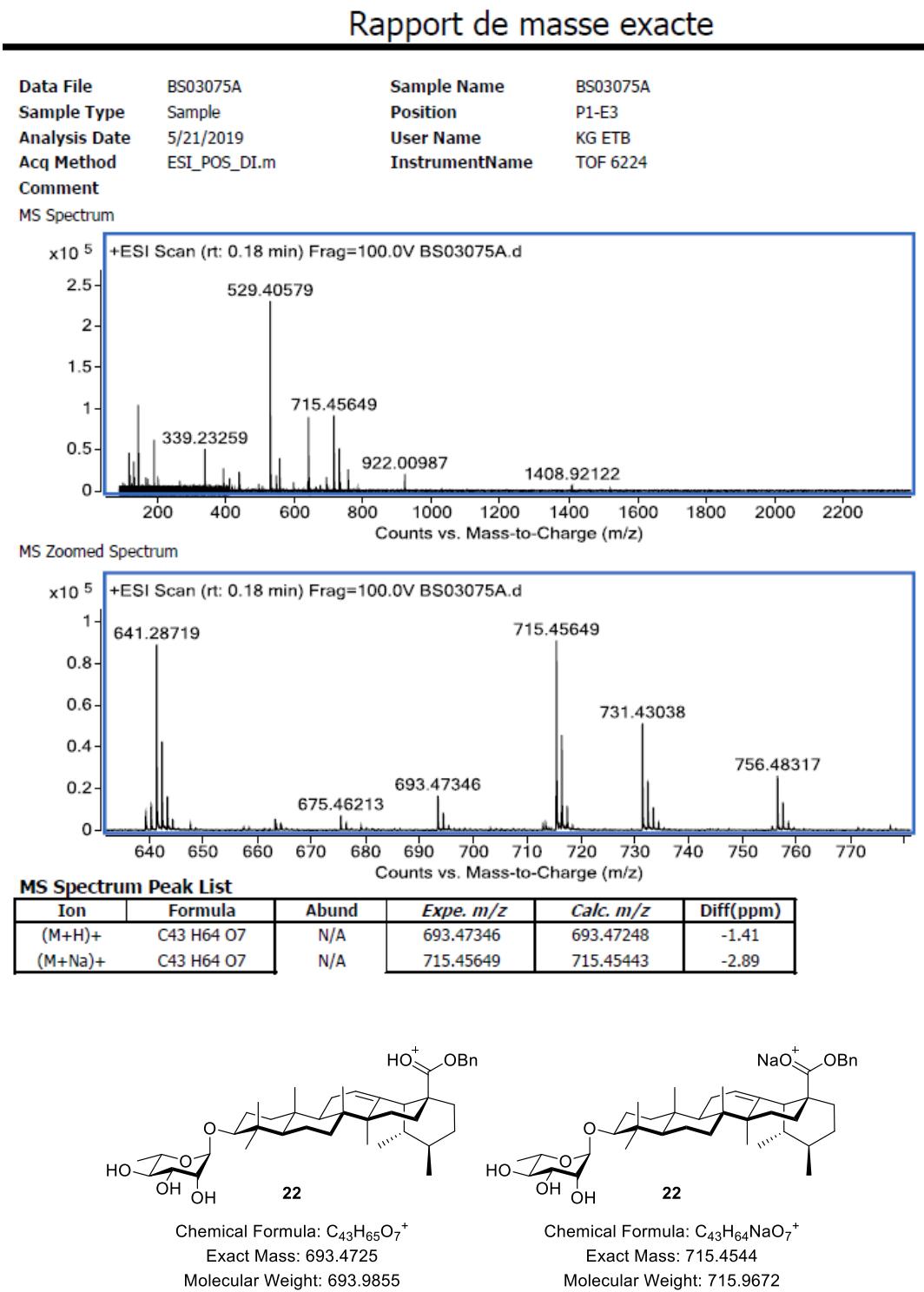
**Figure S34.**  $^1\text{H}$  NMR spectrum of **22** ( $\text{CDCl}_3$ , 400 MHz)



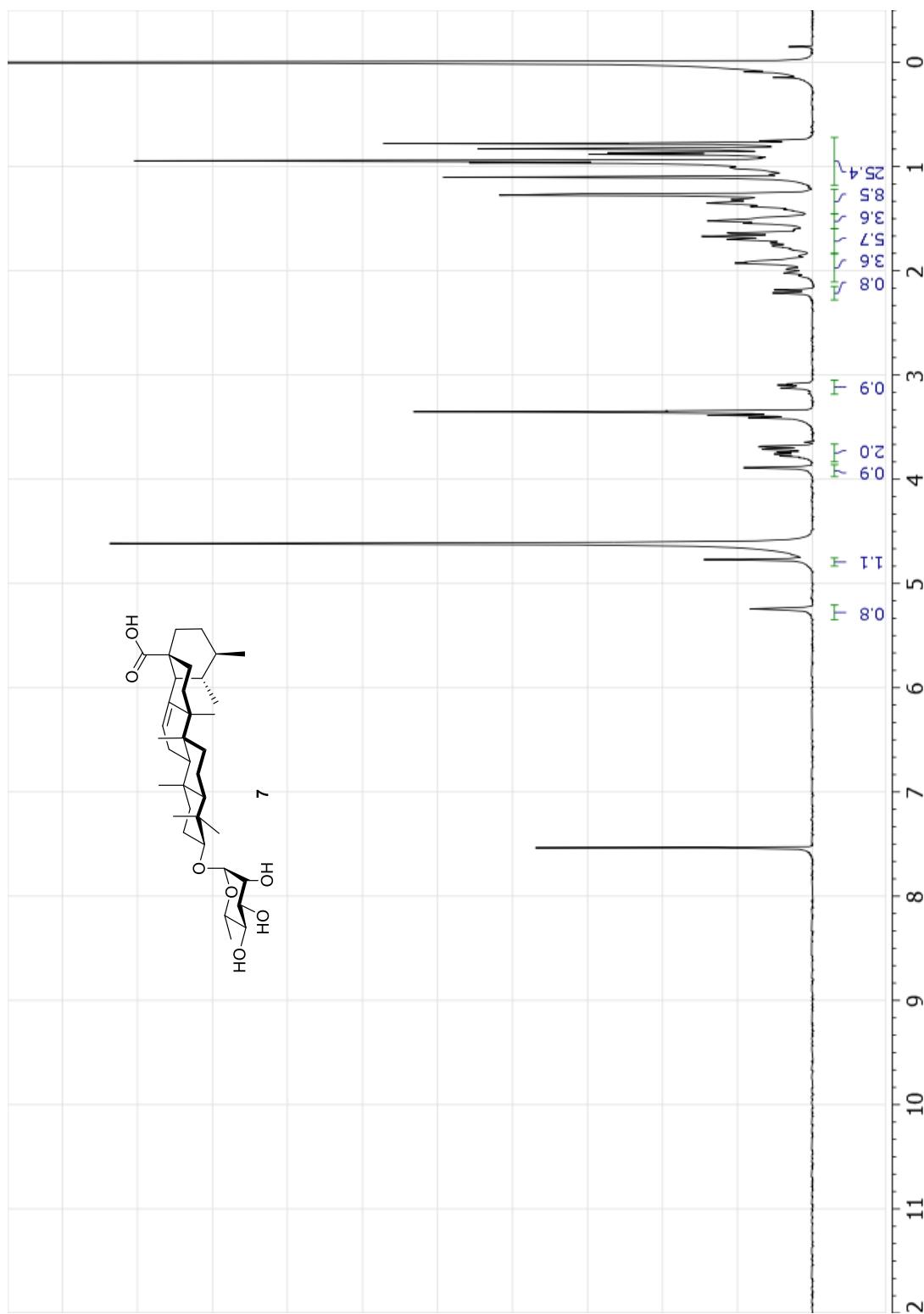
**Figure S35.**  $^{13}\text{C}$  NMR spectra of **22** ( $\text{CDCl}_3$ , 100 MHz)



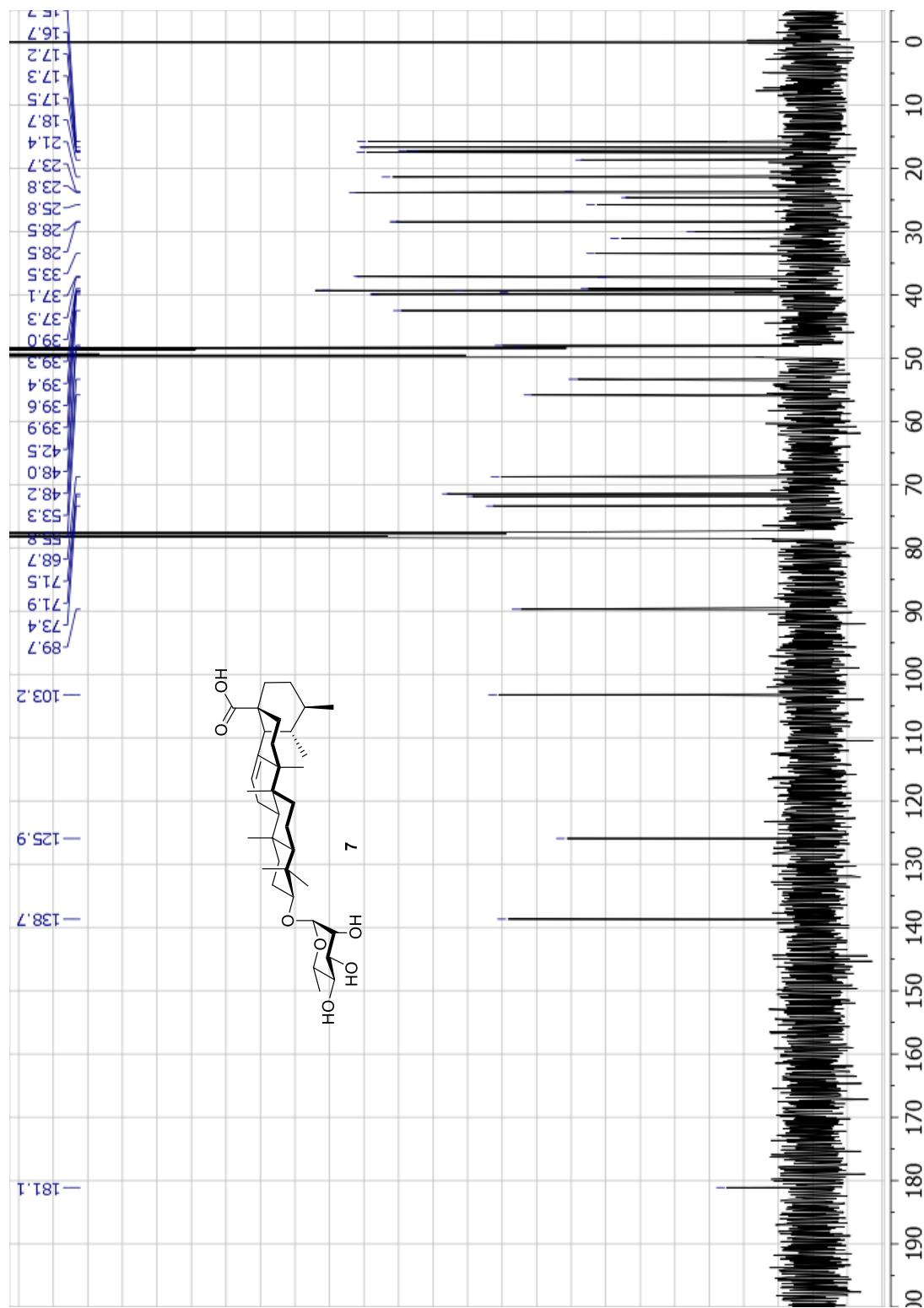
**Figure S36.** HRMS spectra of 22



**Figure S37.**  $^1\text{H}$  NMR spectrum of **7** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 400 MHz)

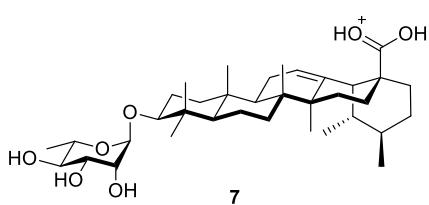
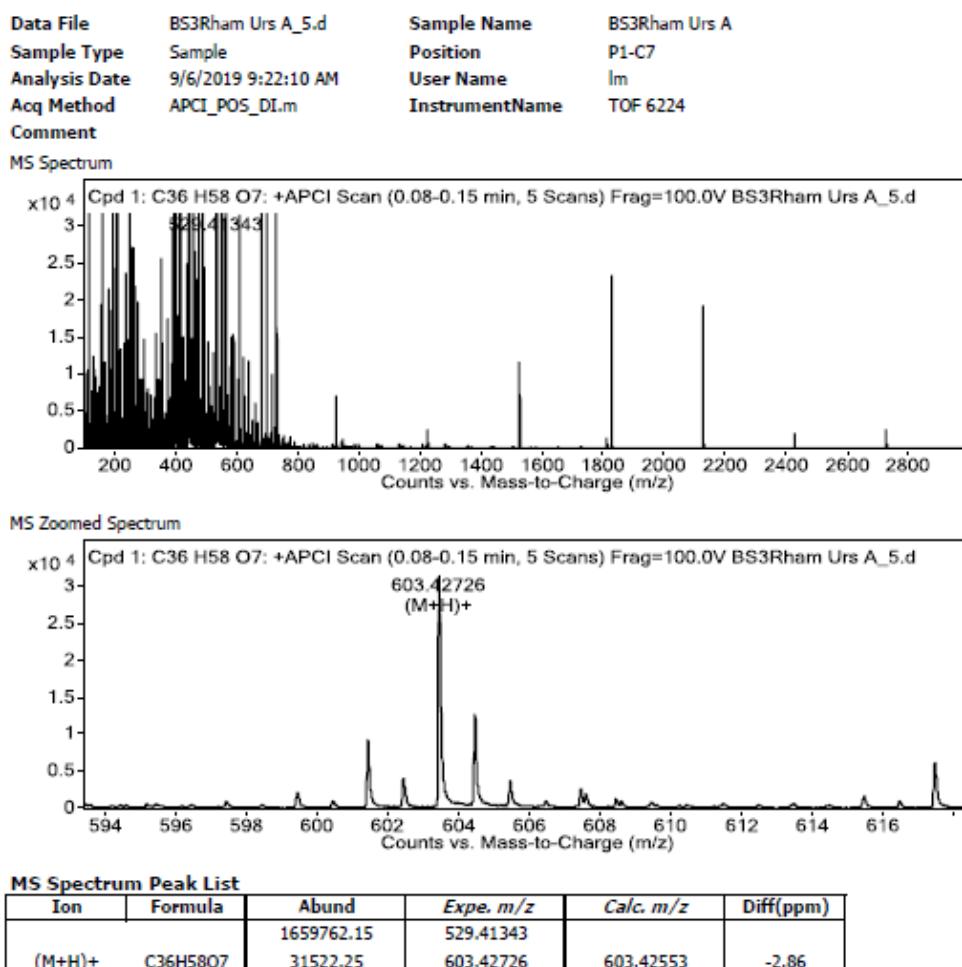


**Figure S38.**  $^{13}\text{C}$  NMR spectra of **7** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 100 MHz)



**Figure S39.** HRMS spectra of 7

### Rapport de masse exacte

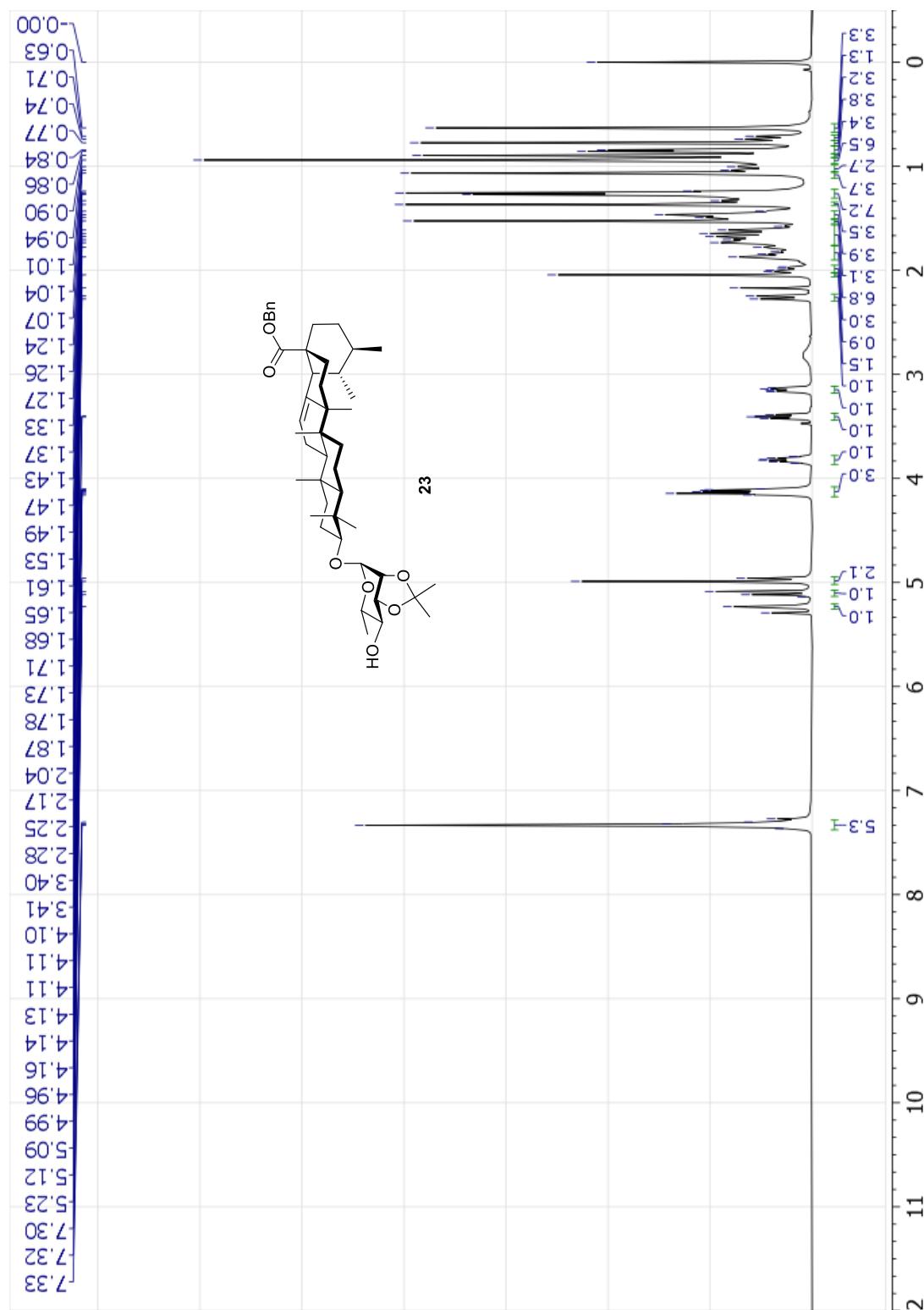


Chemical Formula: C<sub>36</sub>H<sub>59</sub>O<sub>7</sub><sup>+</sup>

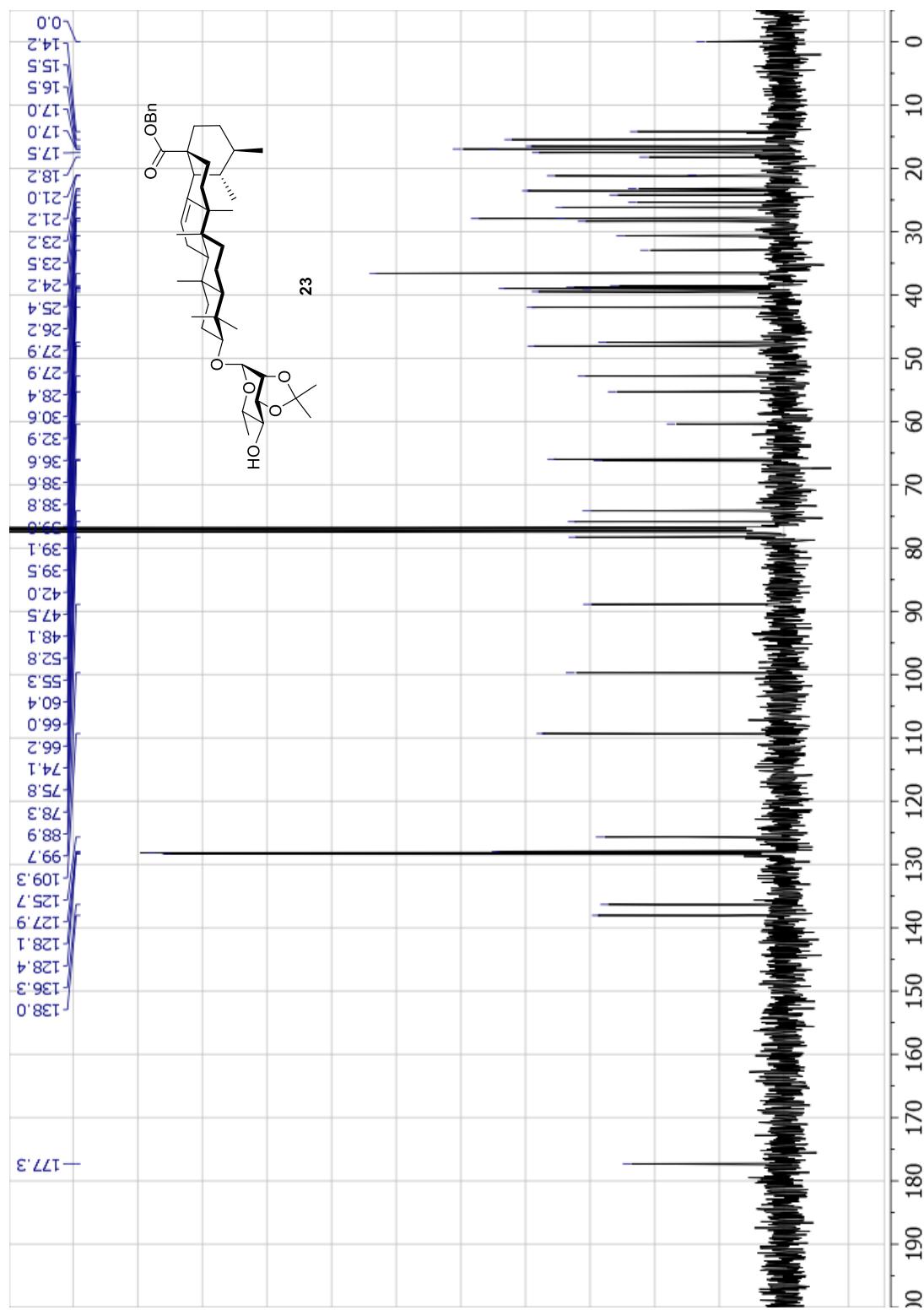
Exact Mass: 603.4255

Molecular Weight: 603,8489

**Figure S40.**  $^1\text{H}$  NMR spectrum of **23** ( $\text{CDCl}_3$ , 400 MHz)

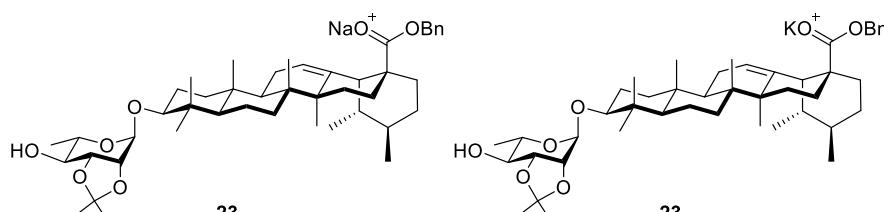
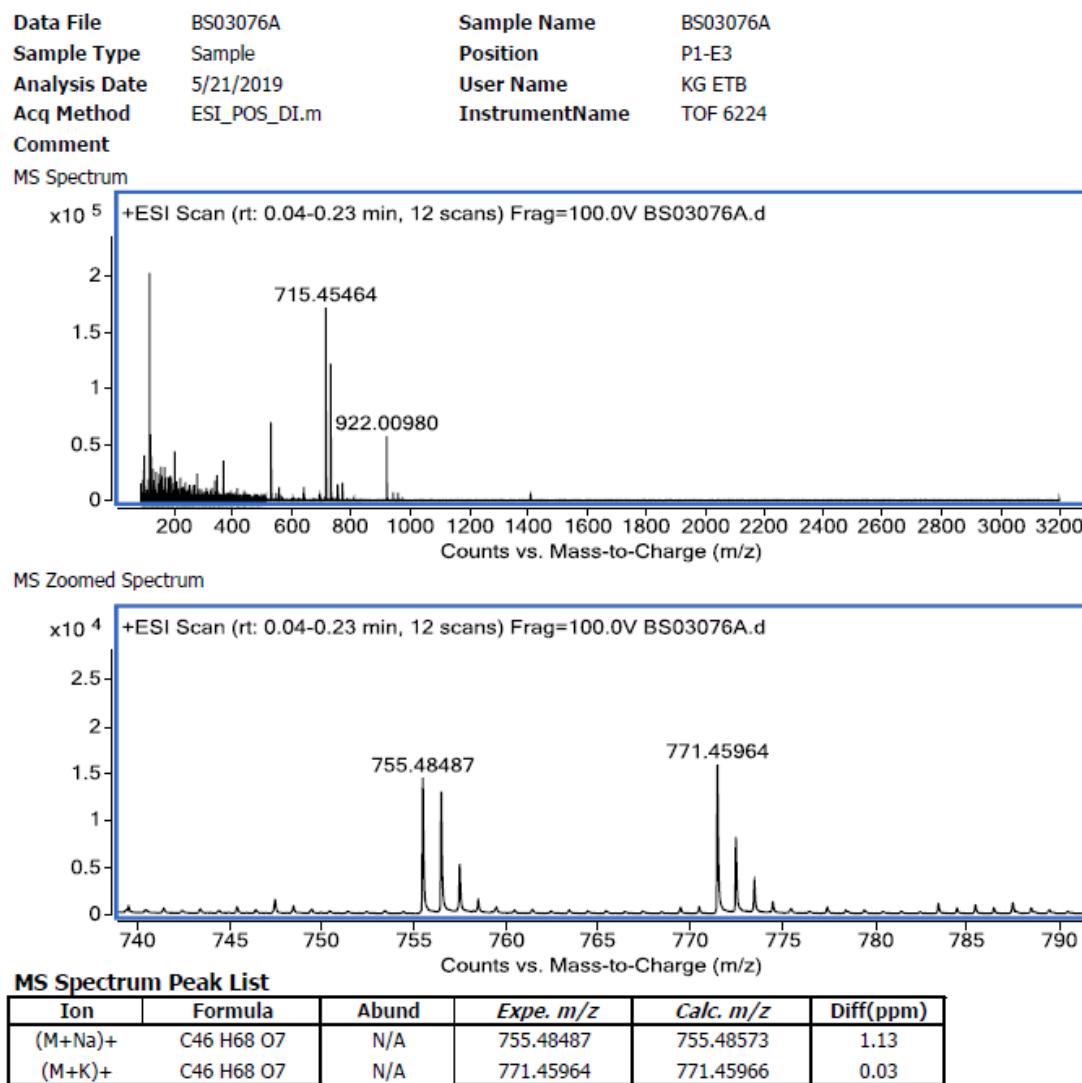


**Figure S41.**  $^{13}\text{C}$  NMR spectra of **23** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S42.** HRMS spectra of **23**

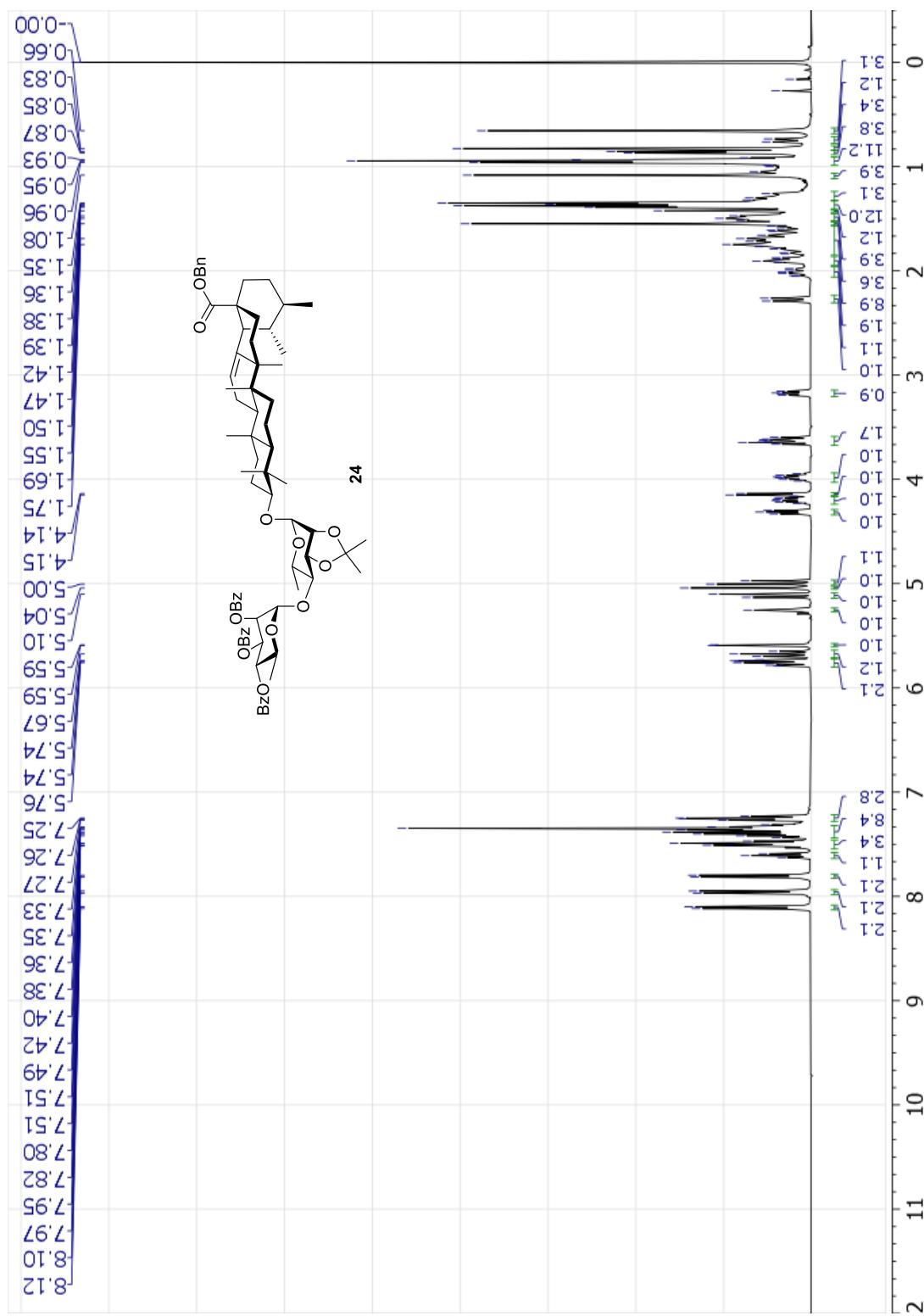
### Rapport de masse exacte



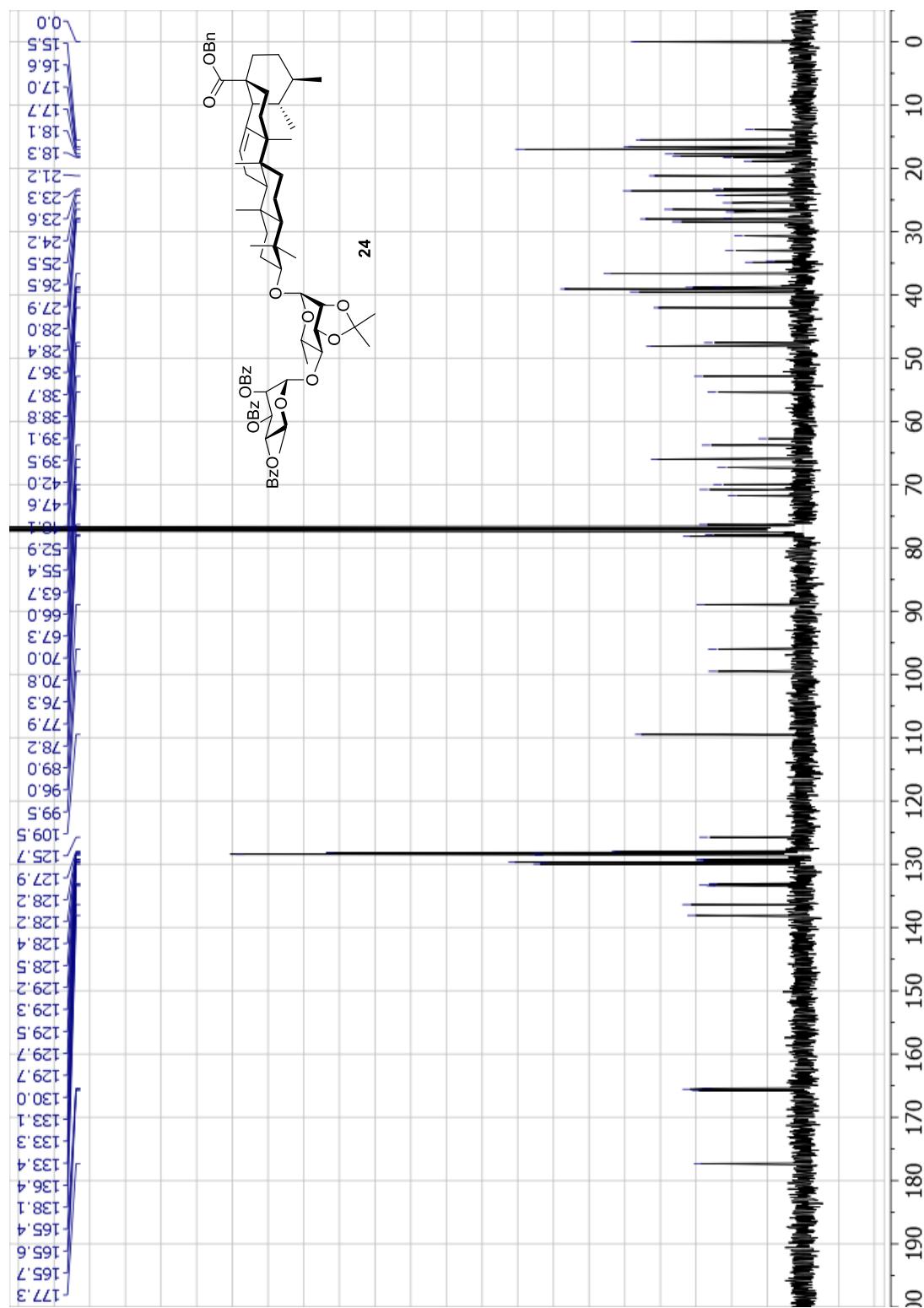
Chemical Formula: C<sub>46</sub>H<sub>68</sub>NaO<sub>7</sub><sup>+</sup>  
 Exact Mass: 755.4857  
 Molecular Weight: 756.0322

Chemical Formula: C<sub>46</sub>H<sub>68</sub>KO<sub>7</sub><sup>+</sup>  
 Exact Mass: 771.4597  
 Molecular Weight: 772.1408

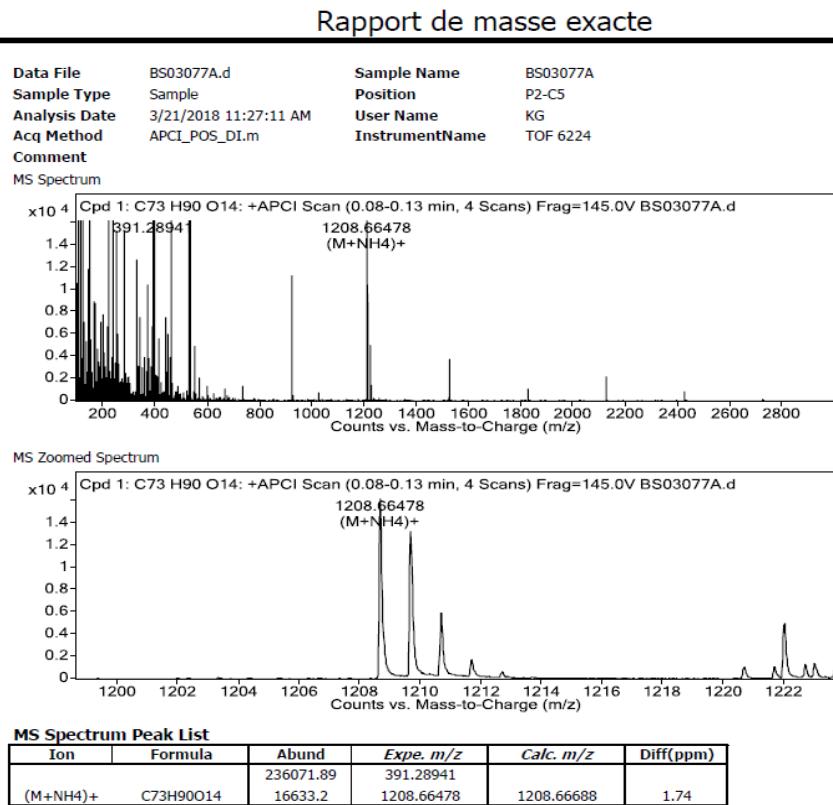
**Figure S43.**  $^1\text{H}$  NMR spectrum of **24** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S44.**  $^{13}\text{C}$  NMR spectra of **24** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S45.** HRMS spectra of **24**

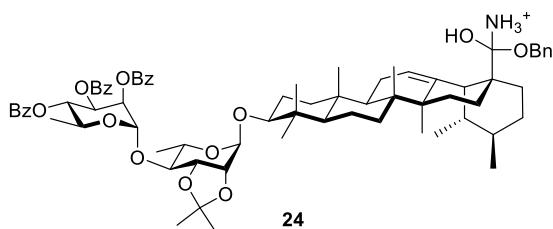


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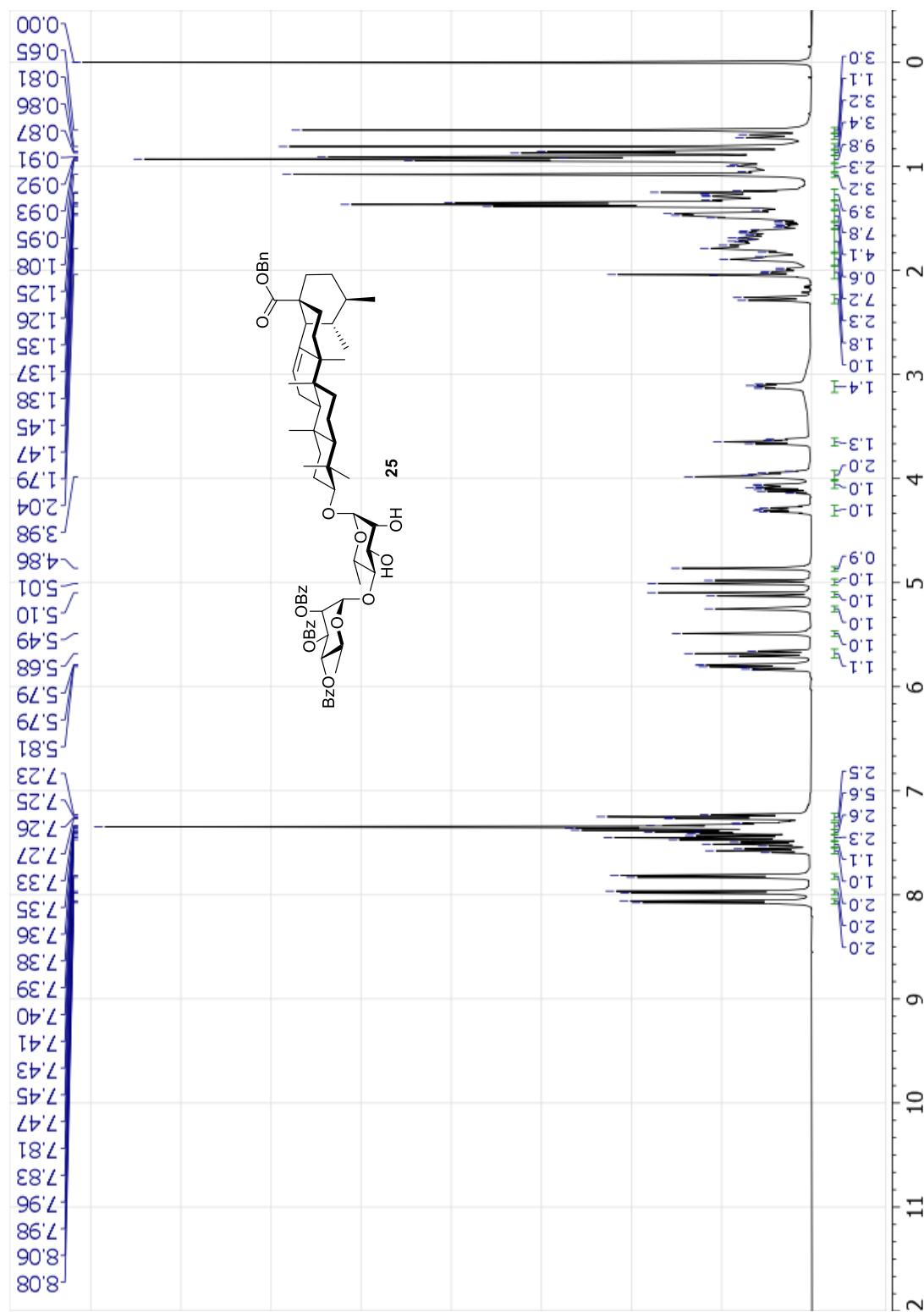


Chemical Formula: C<sub>73</sub>H<sub>94</sub>NO<sub>14</sub><sup>+</sup>

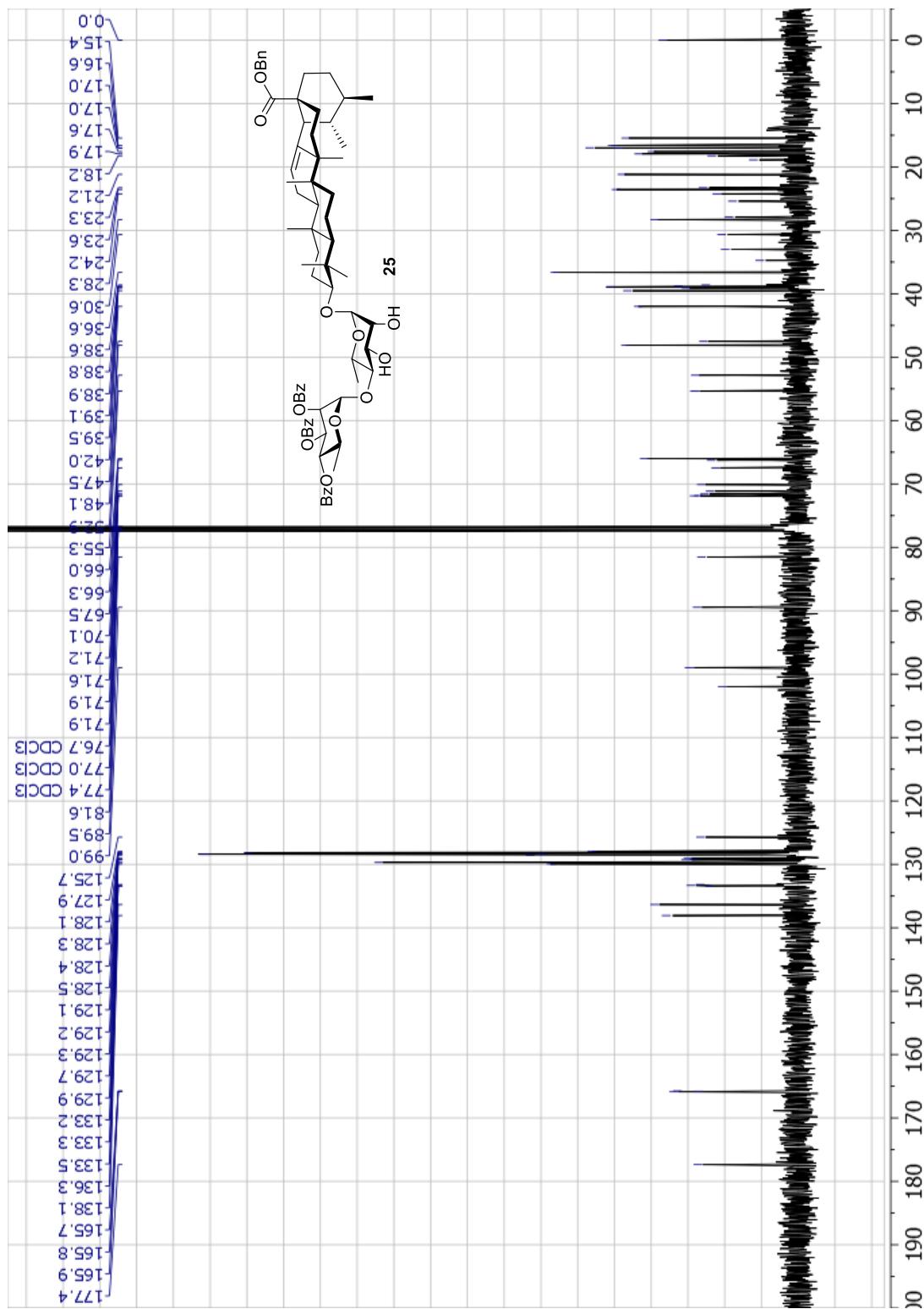
Exact Mass: 1208.6669

Molecular Weight: 1209.5475

**Figure S46.**  $^1\text{H}$  NMR spectrum of **25** ( $\text{CDCl}_3$ , 400 MHz)

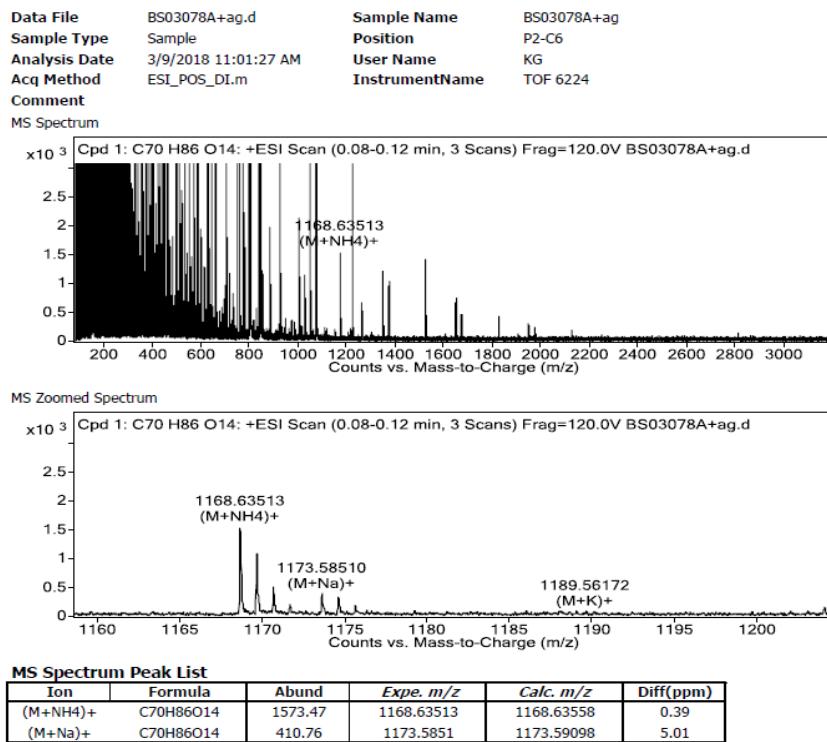


**Figure S47.**  $^{13}\text{C}$  NMR spectra of **25** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S48.** HRMS spectra of **25**

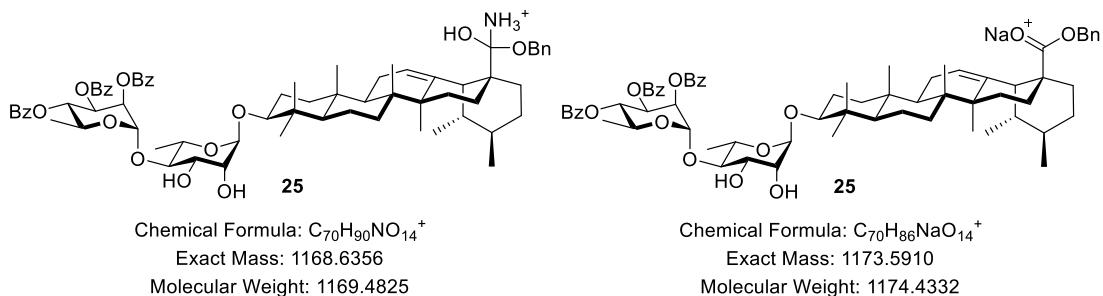
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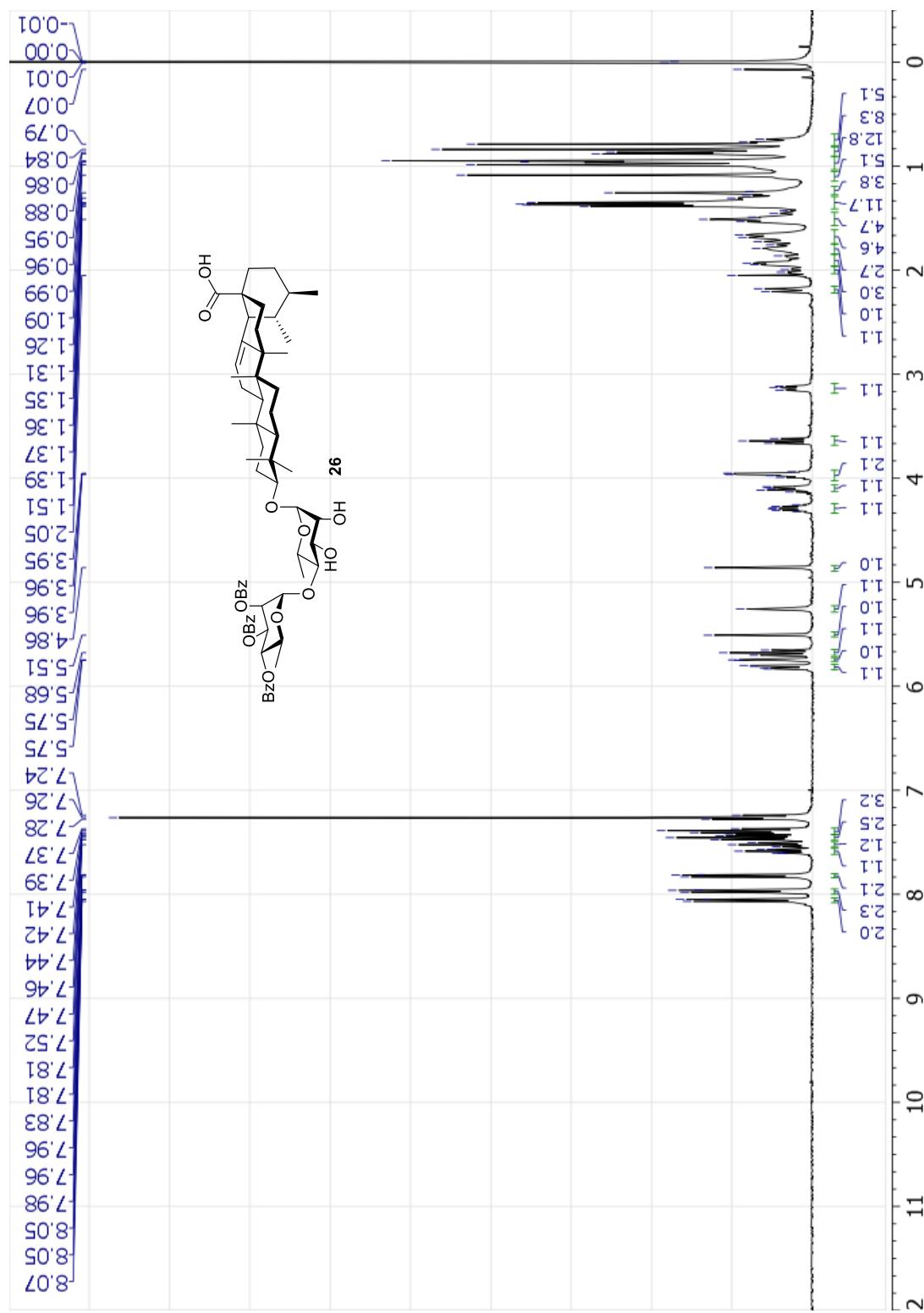
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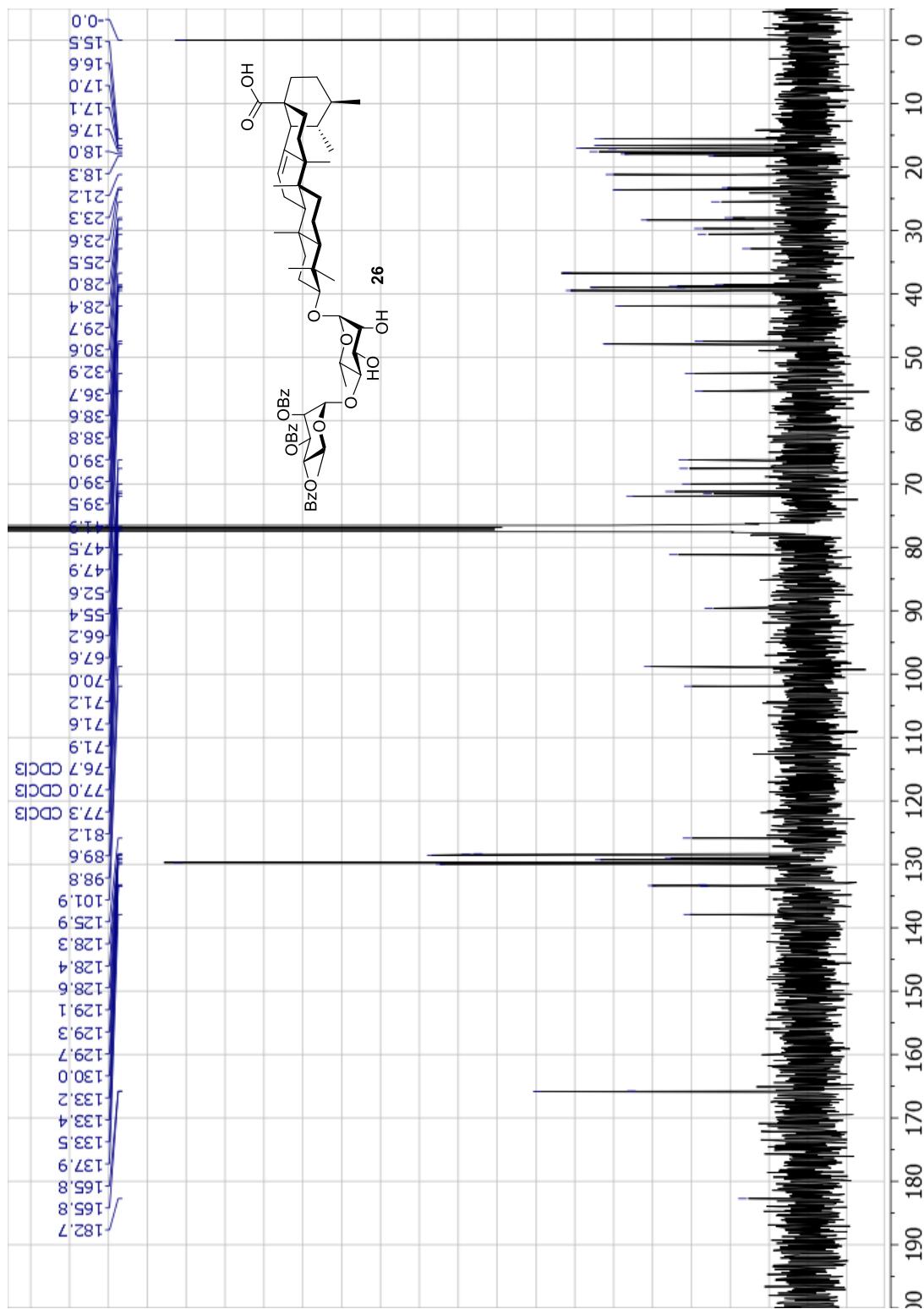
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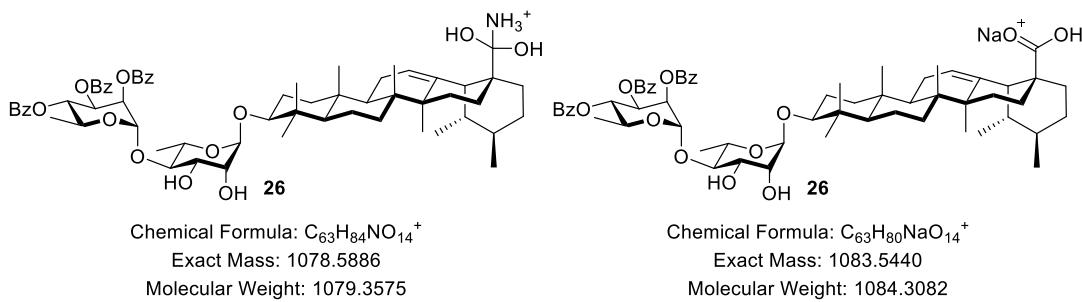
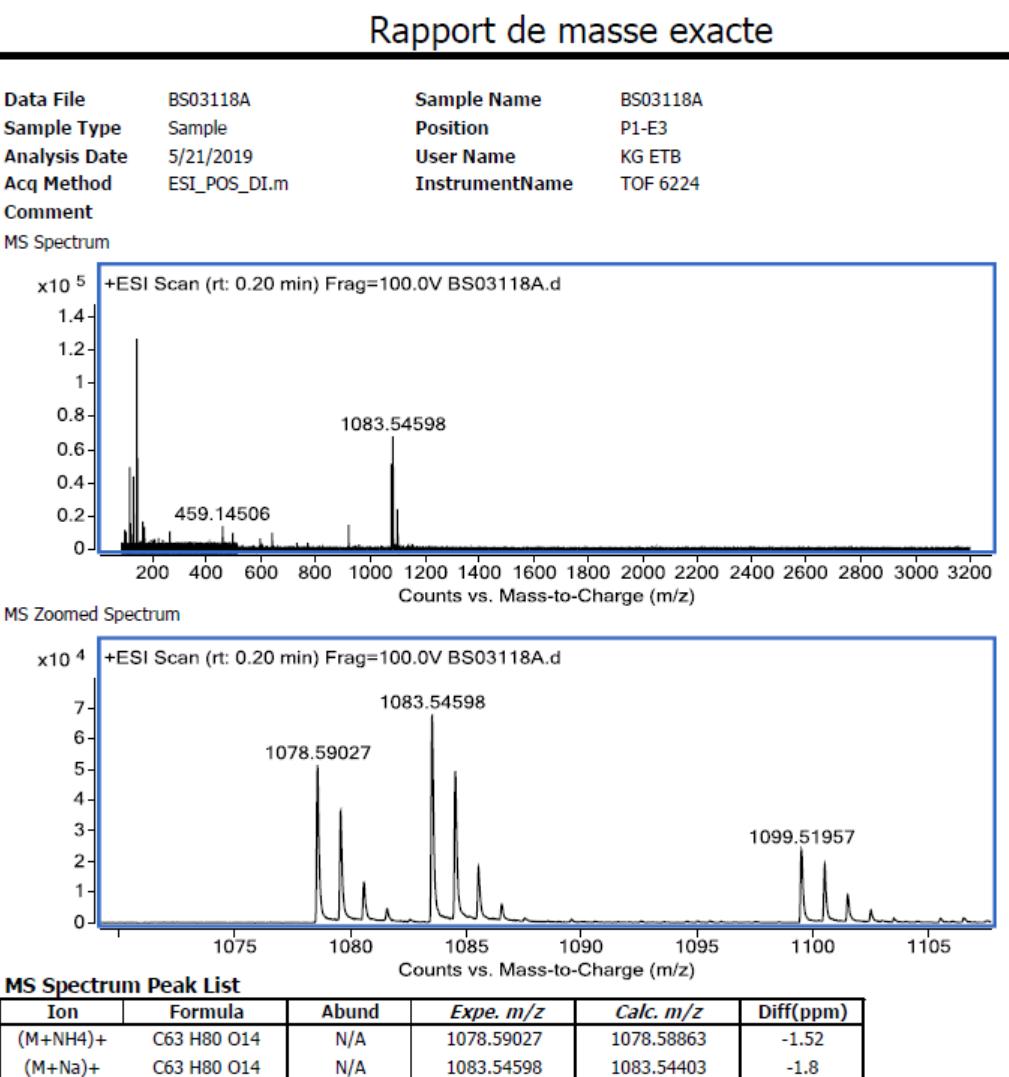
**Figure S49.**  $^1\text{H}$  NMR spectrum of **26** ( $\text{CDCl}_3$ , 400 MHz)



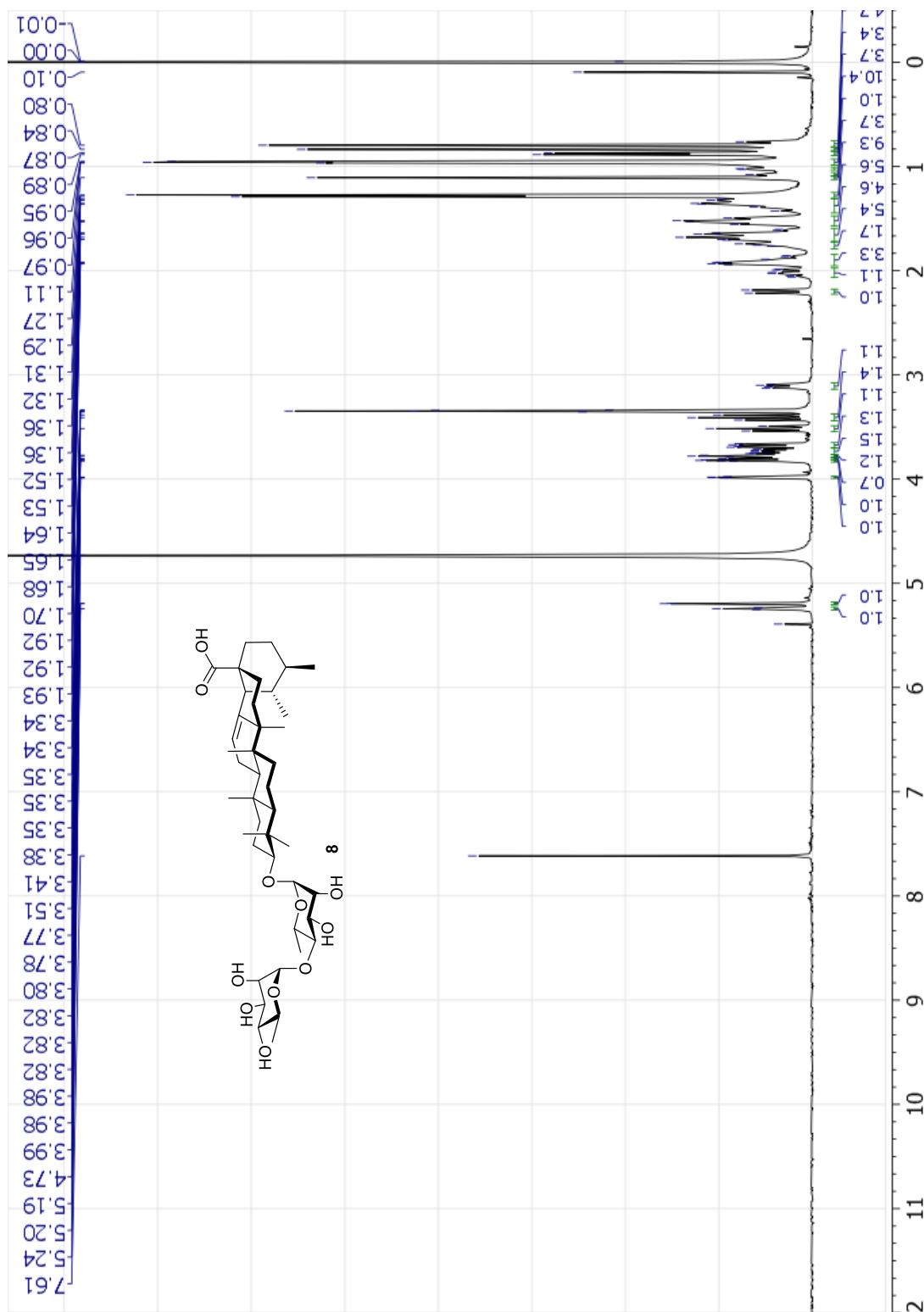
**Figure S50.**  $^{13}\text{C}$  NMR spectra of **26** ( $\text{CDCl}_3$ , 100 MHz)



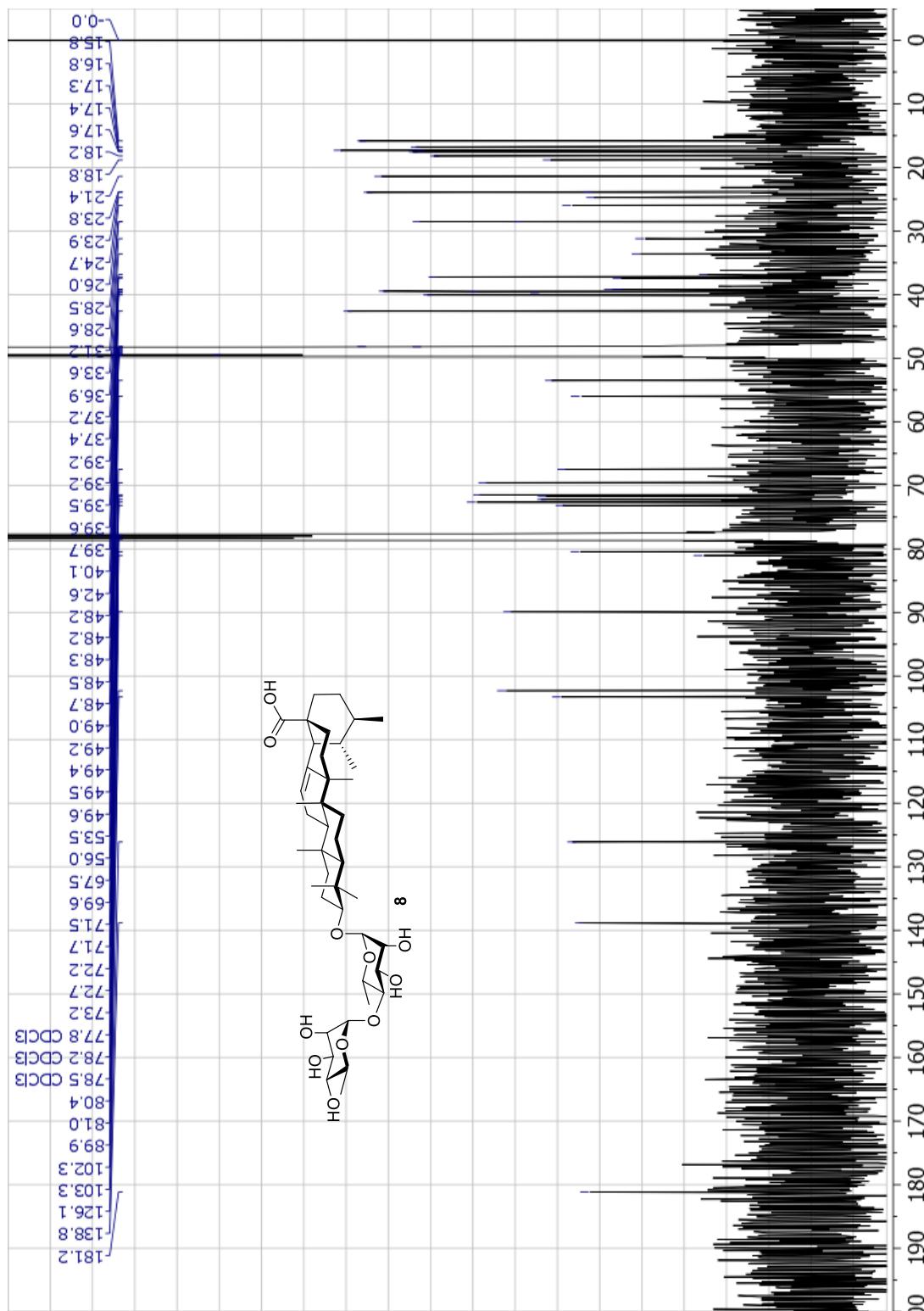
**Figure S51.** HRMS spectra of **26**



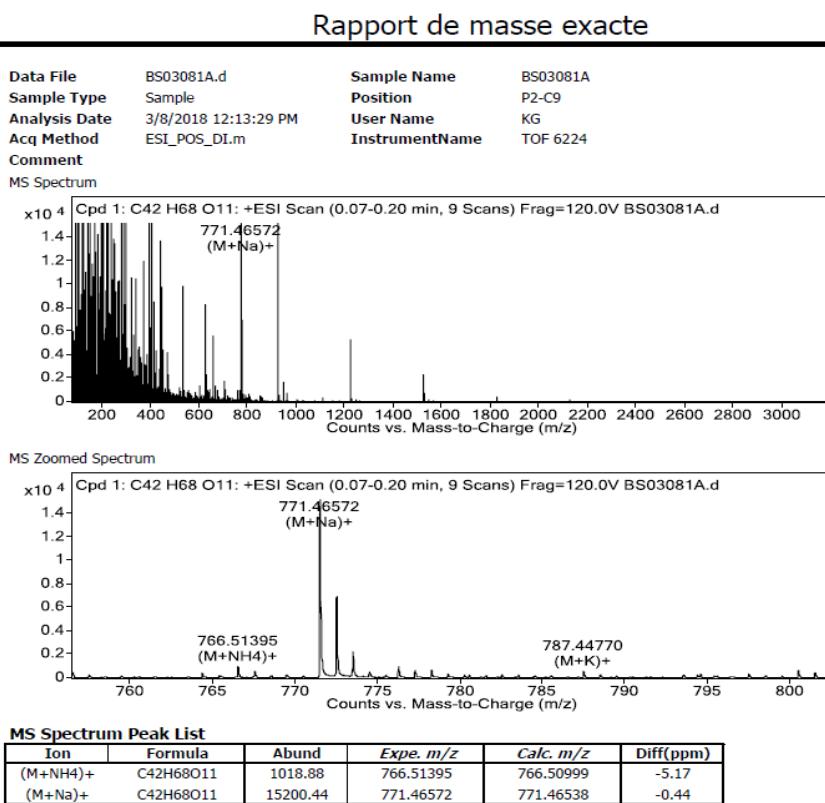
**Figure S52.**  $^1\text{H}$  NMR spectrum of **8** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 400 MHz)



**Figure S53.**  $^{13}\text{C}$  NMR spectra of **8** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 100 MHz)



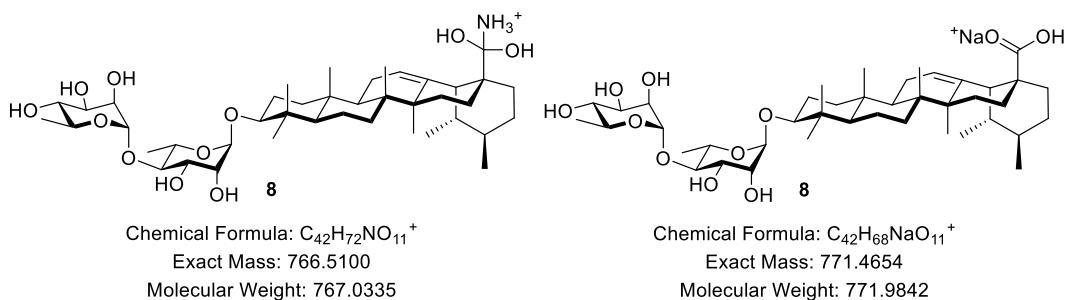
**Figure S54.** HRMS spectra of **8**



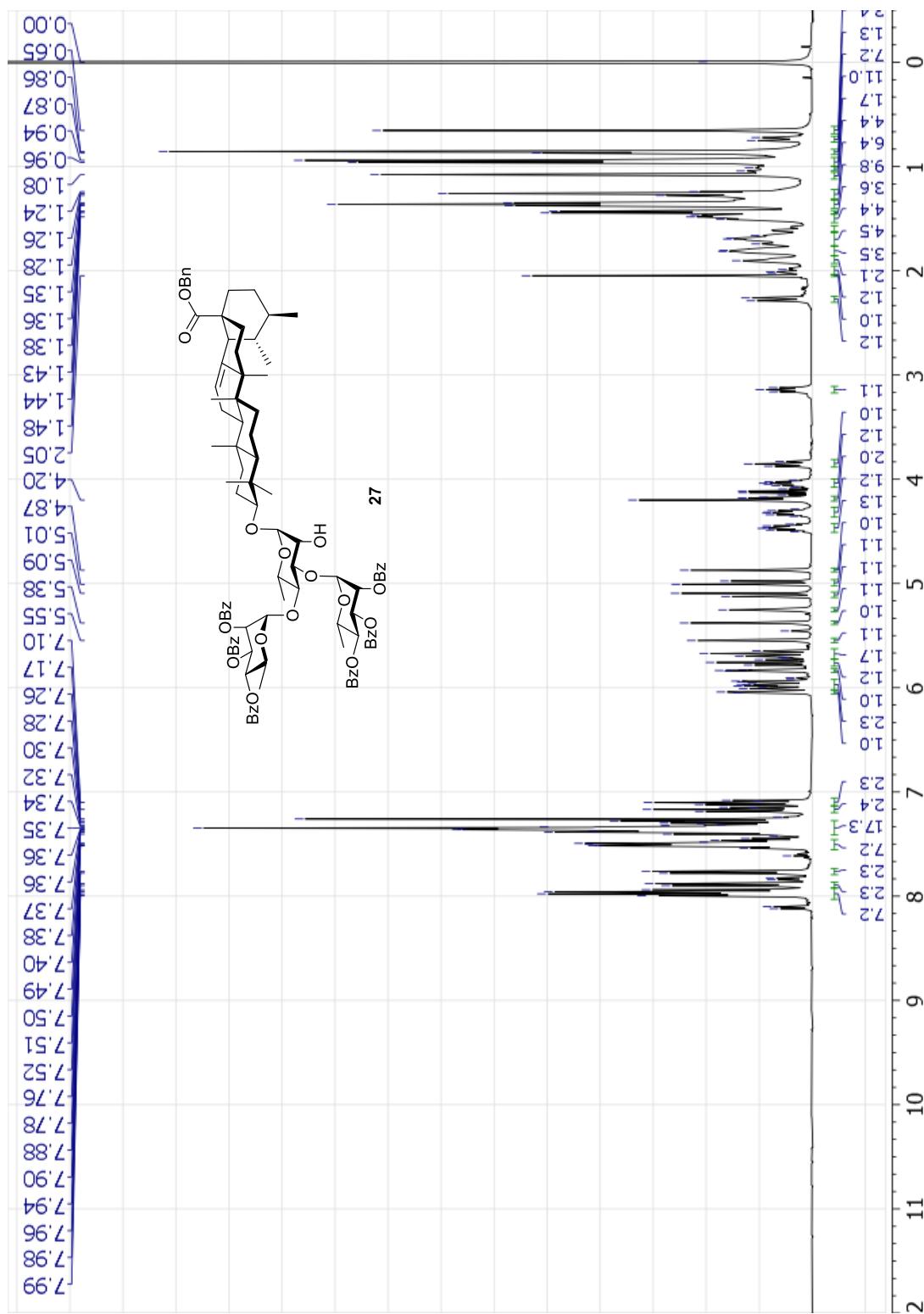
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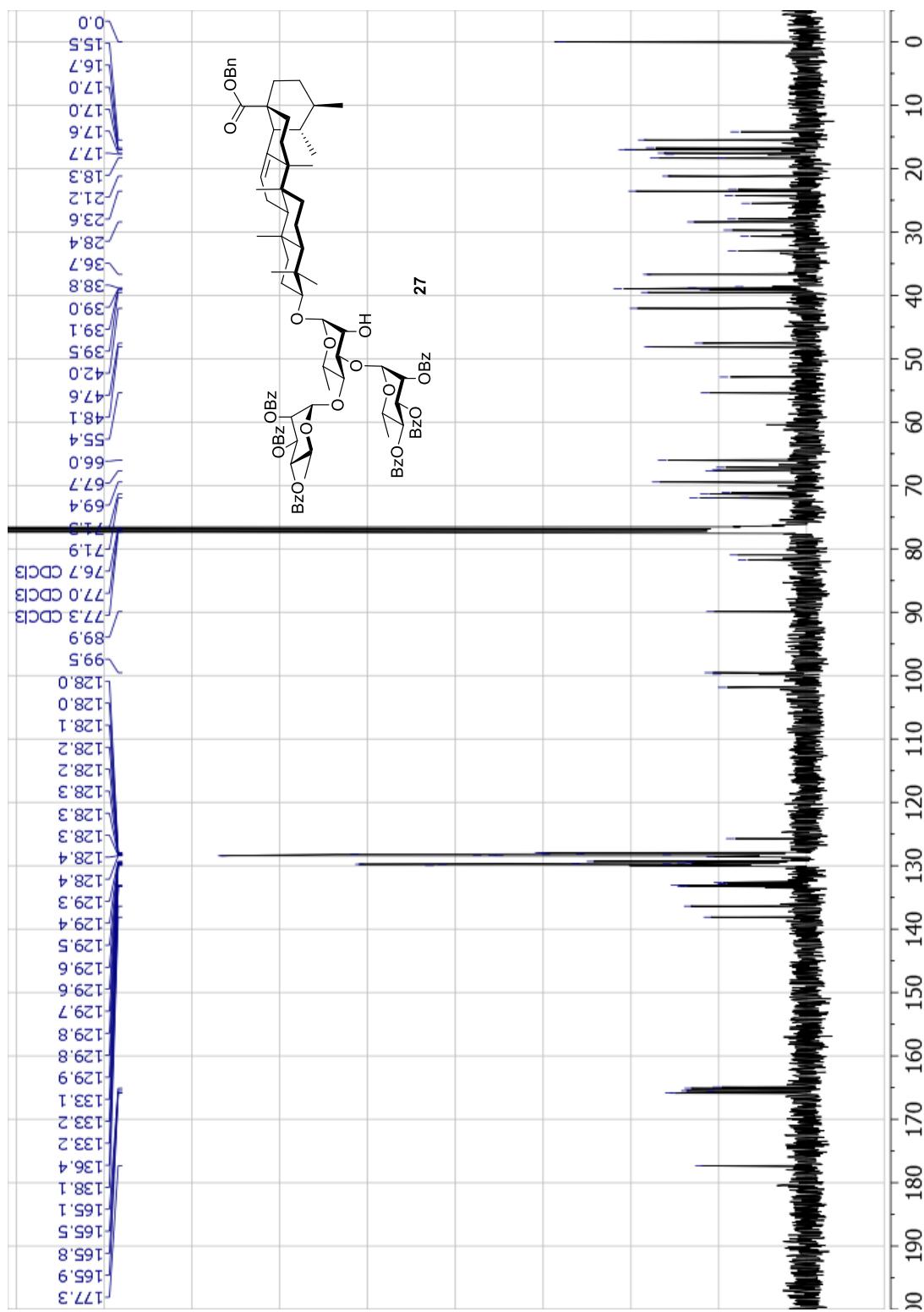
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**Figure S55.**  $^1\text{H}$  NMR spectrum of **27** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S56.**  $^{13}\text{C}$  NMR spectra of **27** ( $\text{CDCl}_3$ , 100 MHz)



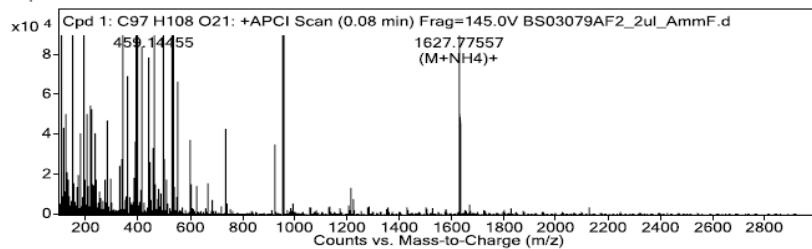
**Figure S57.** HRMS spectra of **27**

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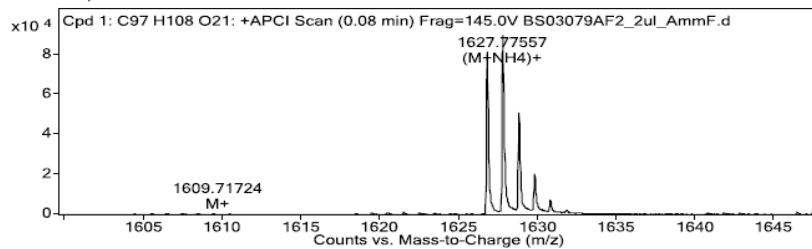
Data File	BS03079AF2_2ul_AmmF.d	Sample Name	BS03079AF2_2ul_AmmF
Sample Type	Sample	Position	P2-C8
Analysis Date	3/23/2018 11:00:46 AM	User Name	KG
Acq Method	APCI_POS_DI.m	InstrumentName	TOF 6224

Comment

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

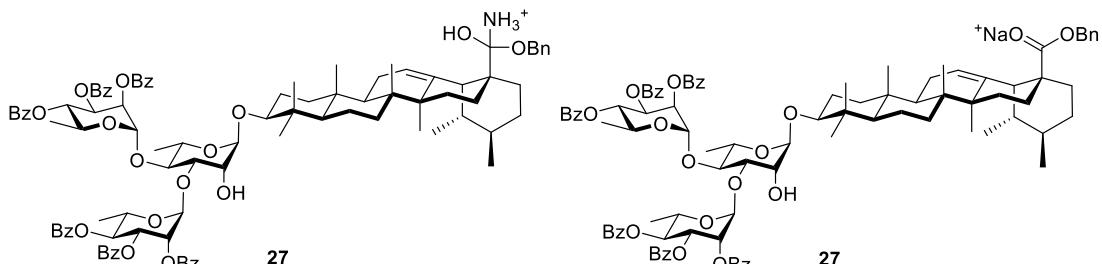
Ion	Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+NH <sub>4</sub> ) <sup>+</sup>	C <sub>97</sub> H <sub>108</sub> O <sub>21</sub>	83266.37	1626.77249	1626.77214	-0.22
(M+Na) <sup>+</sup>	C <sub>97</sub> H <sub>108</sub> O <sub>21</sub>	1062.56	1632.74438	1632.73093	-8.24

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Chemical Formula: C<sub>97</sub>H<sub>112</sub>NO<sub>21</sub><sup>+</sup>

Exact Mass: 1626.7721

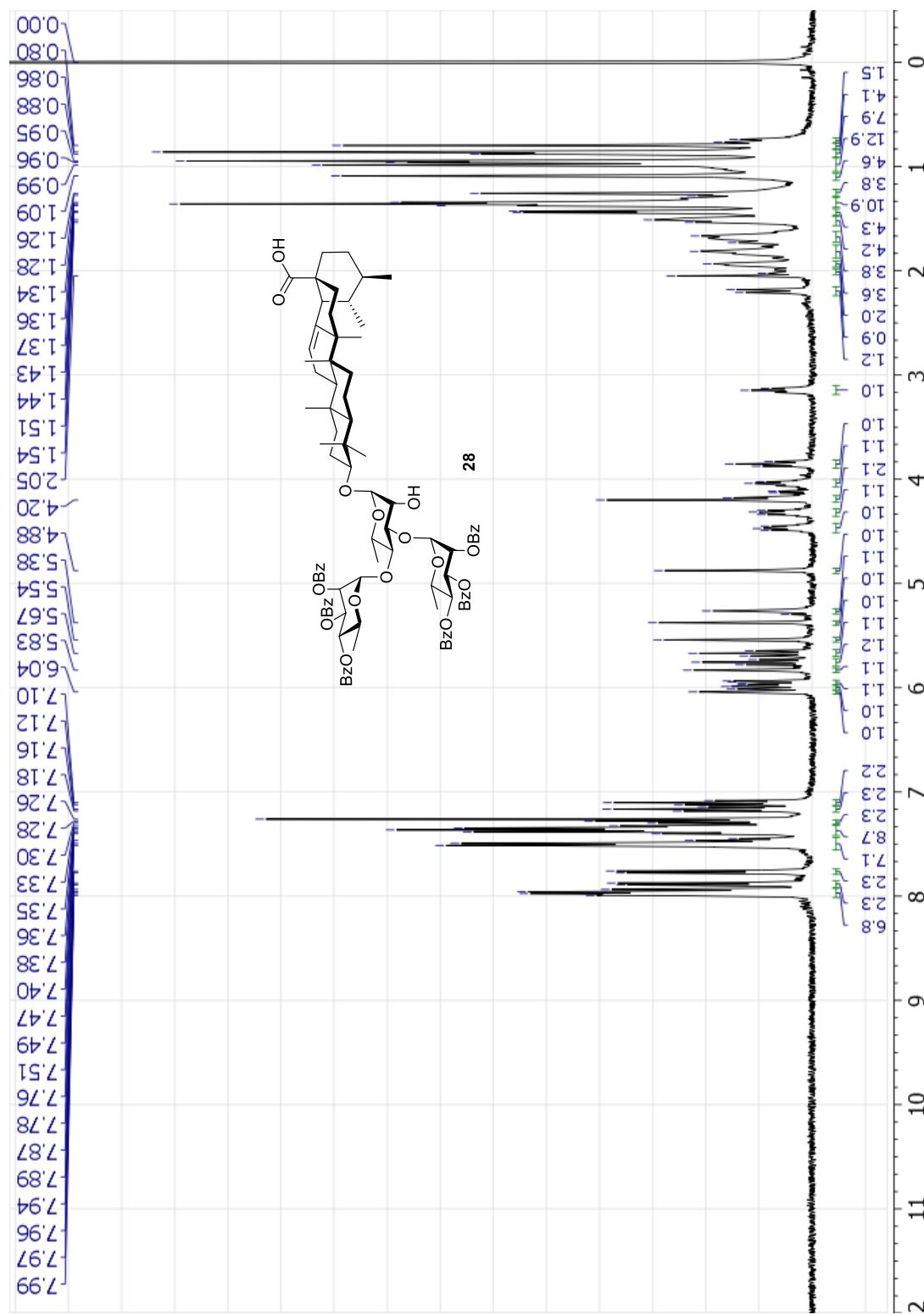
Molecular Weight: 1627.9485

Chemical Formula: C<sub>97</sub>H<sub>108</sub>NaO<sub>21</sub><sup>+</sup>

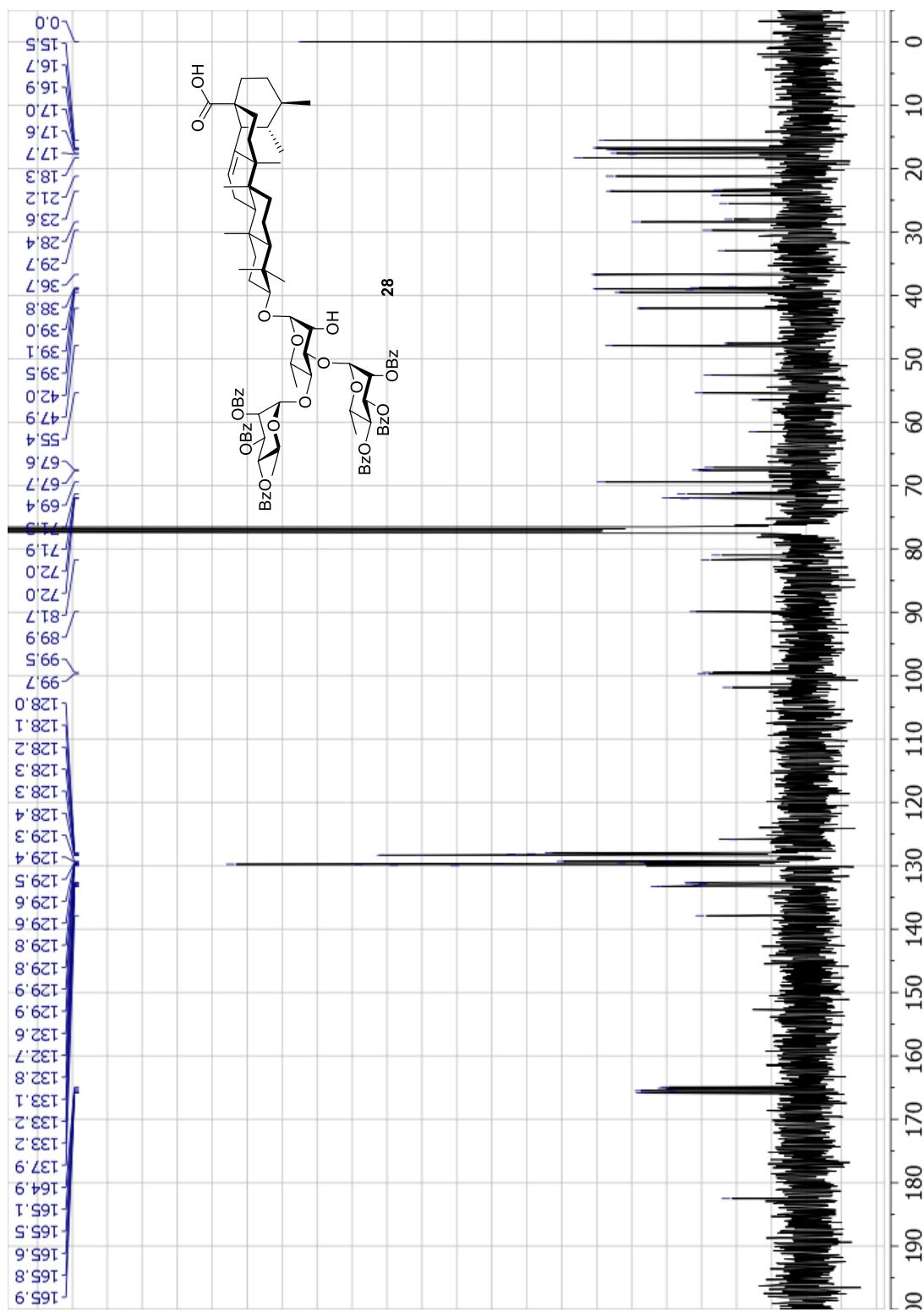
Exact Mass: 1631.7275

Molecular Weight: 1632.8992

**Figure S58.**  $^1\text{H}$  NMR spectrum of **28** ( $\text{CDCl}_3$ , 400 MHz)



**Figure S59.**  $^{13}\text{C}$  NMR spectrum of **28** ( $\text{CDCl}_3$ , 100 MHz)



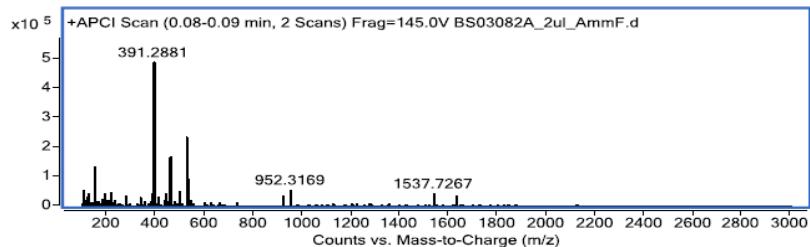
**Figure S60.** HRMS spectra of **28**

Masse Exacte

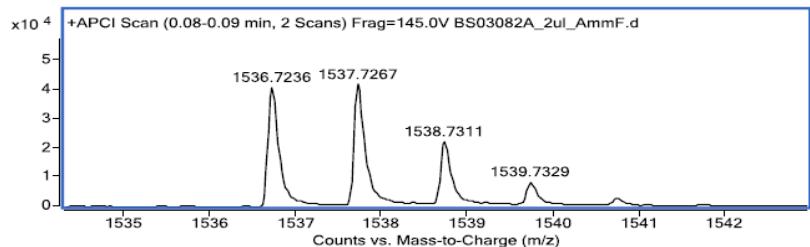
Data File BS03082A\_2ul\_AmmF  
 Analysis Date March 23, 2018  
 Acq Method ESI\_pos\_DI  
 Instrument TOF 6224  
 Comment N/A

Sample Name BS03082A  
 User Name Karine  
 DA Method

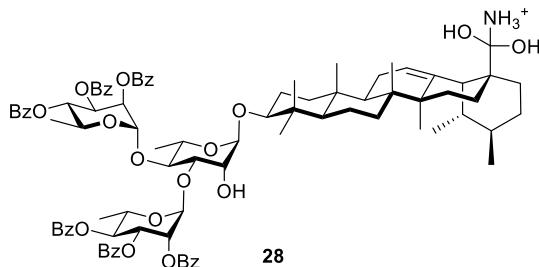
MS spectrum



MS zoomed spectrum

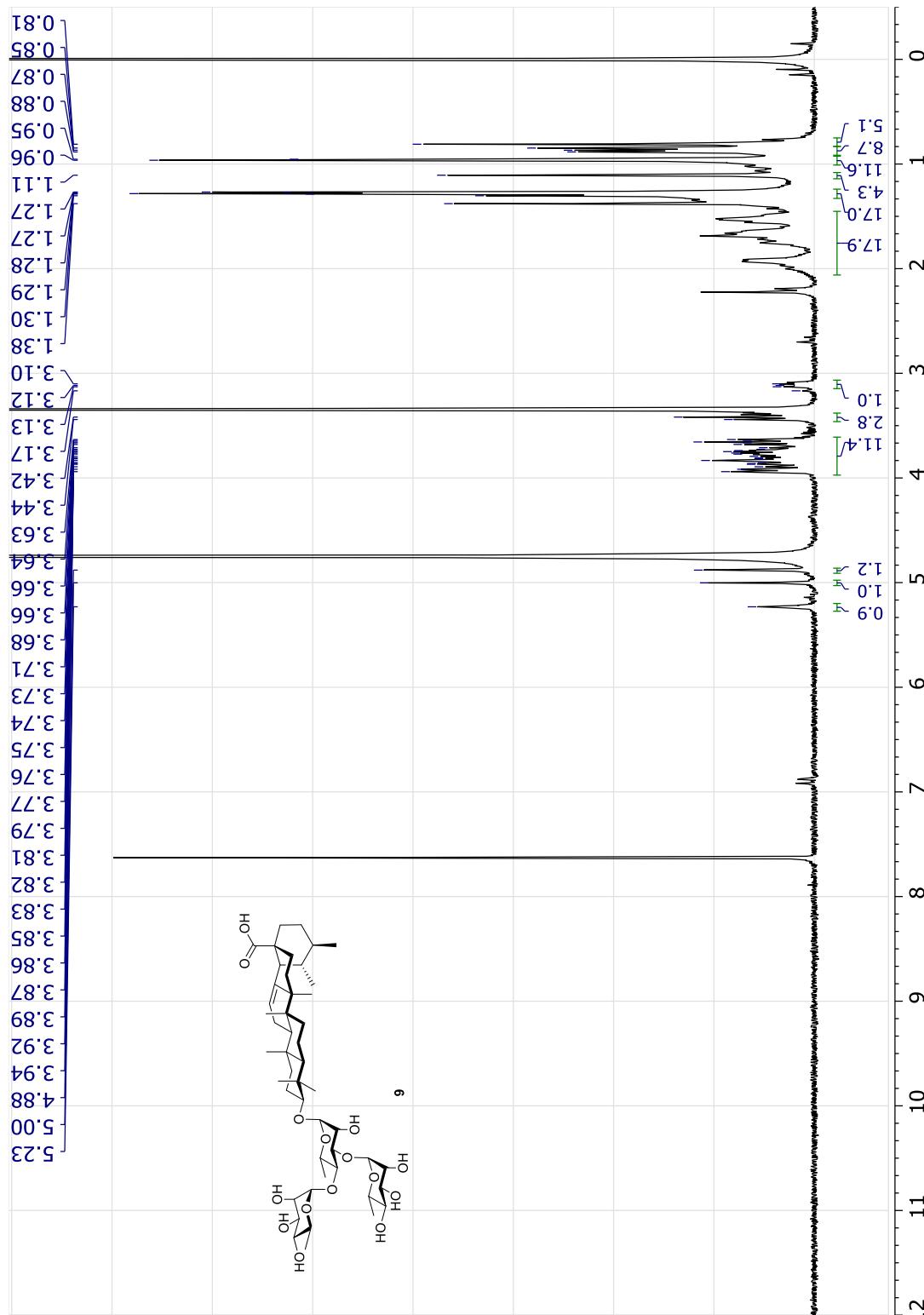


Ion	Formula	Expe. m/z	Calc. m/z	Diff (ppm)
M+NH4	C90 H102 O21	1536.7236	1536.7252	1.03

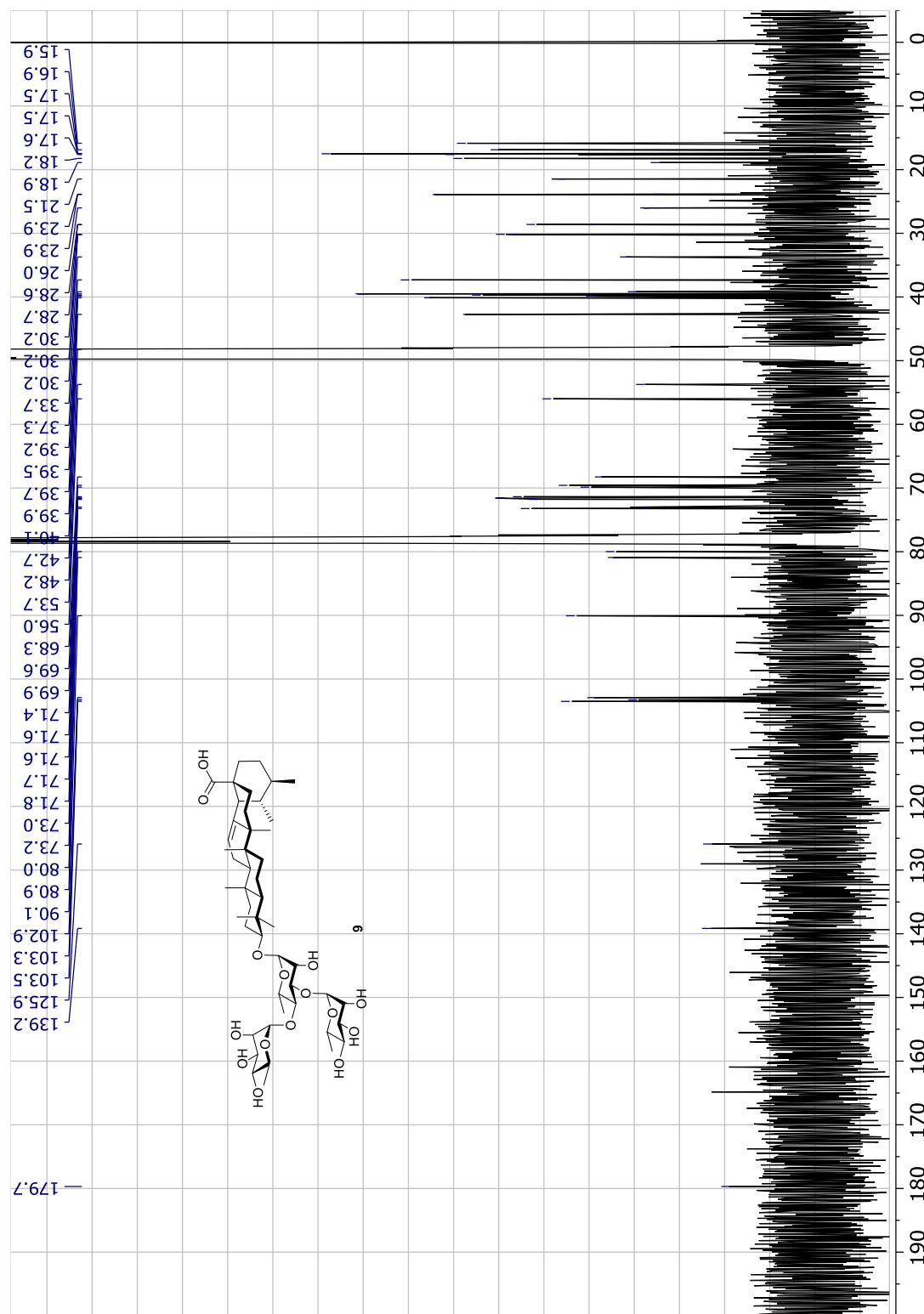


Chemical Formula: C<sub>90</sub>H<sub>106</sub>NO<sub>21</sub><sup>+</sup>  
 Exact Mass: 1536.7252  
 Molecular Weight: 1537.8235

**Figure S61.**  $^1\text{H}$  NMR spectrum of **9** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 400 MHz)

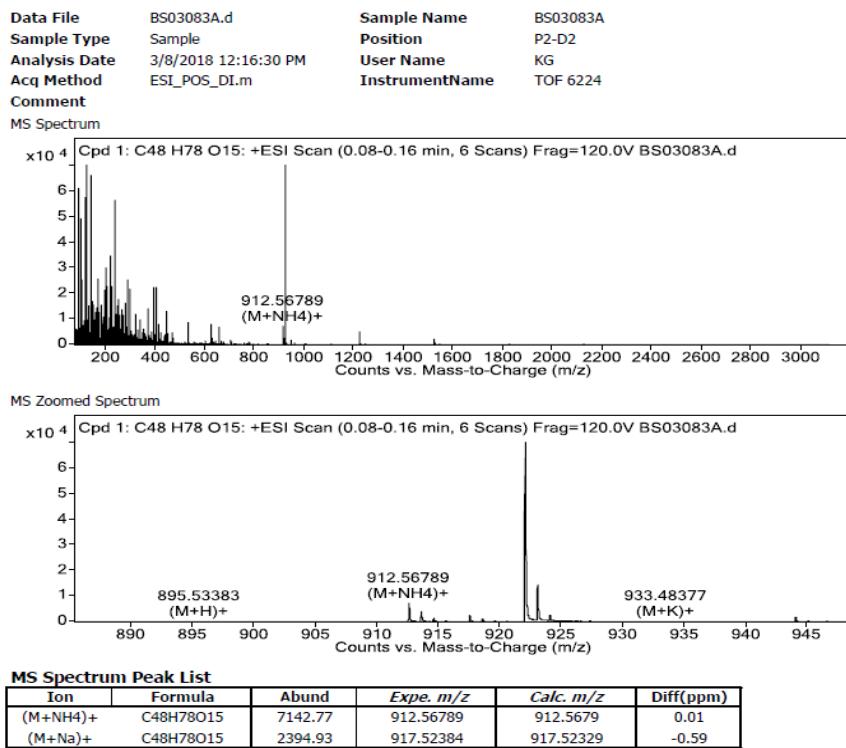


**Figure S62.**  $^{13}\text{C}$  NMR spectrum of **9** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 100 MHz)



**Figure S63.** HRMS spectra of **9**

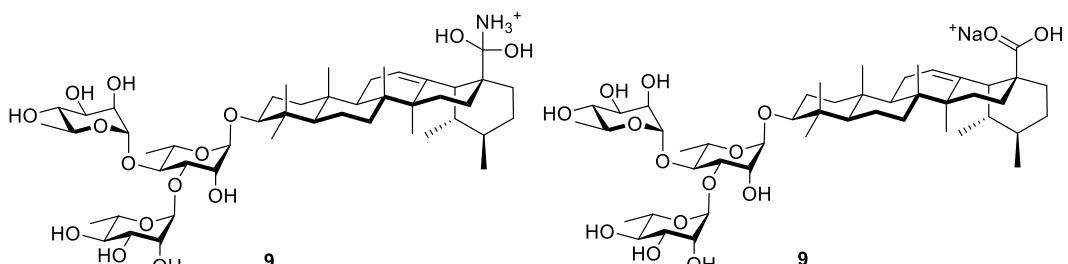
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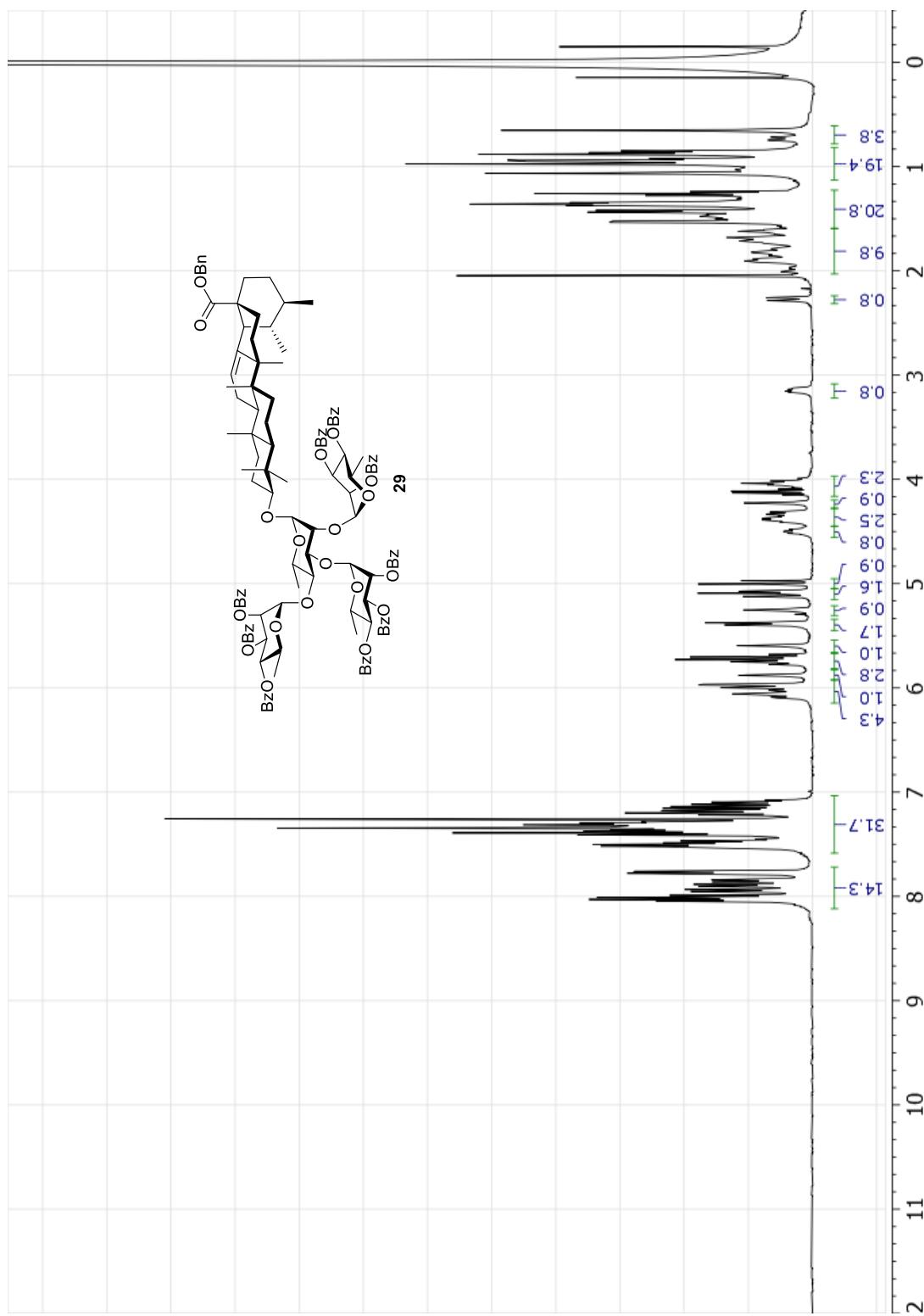
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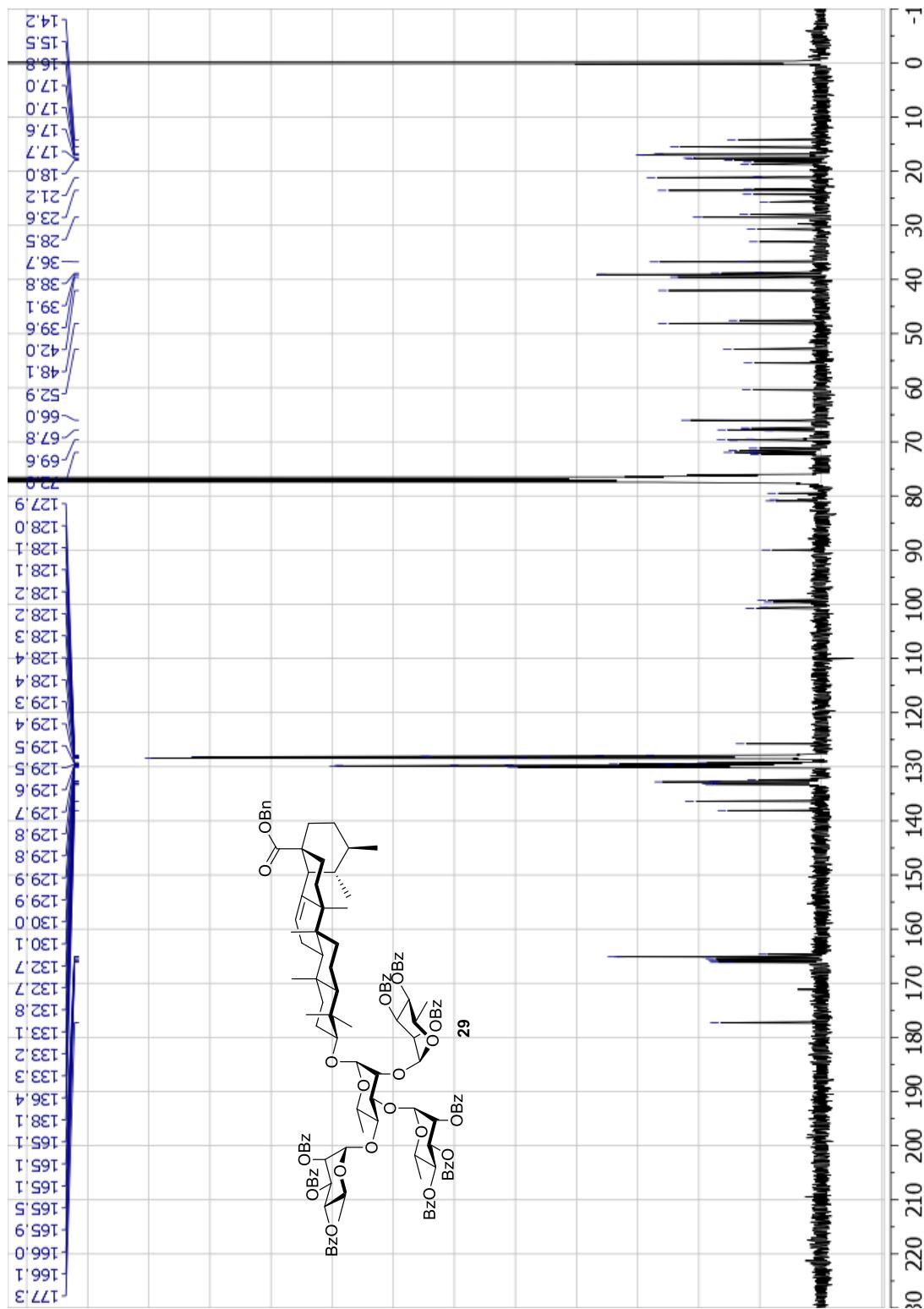
Chemical Formula: C<sub>48</sub>H<sub>82</sub>NO<sub>15</sub><sup>+</sup>  
Exact Mass: 912.5679  
Molecular Weight: 913.1755

Chemical Formula: C<sub>48</sub>H<sub>78</sub>NaO<sub>15</sub><sup>+</sup>  
Exact Mass: 917.5233  
Molecular Weight: 918.1262

**Figure S64.**  $^1\text{H}$  NMR spectrum of **29** ( $\text{CDCl}_3$ , 400 MHz)

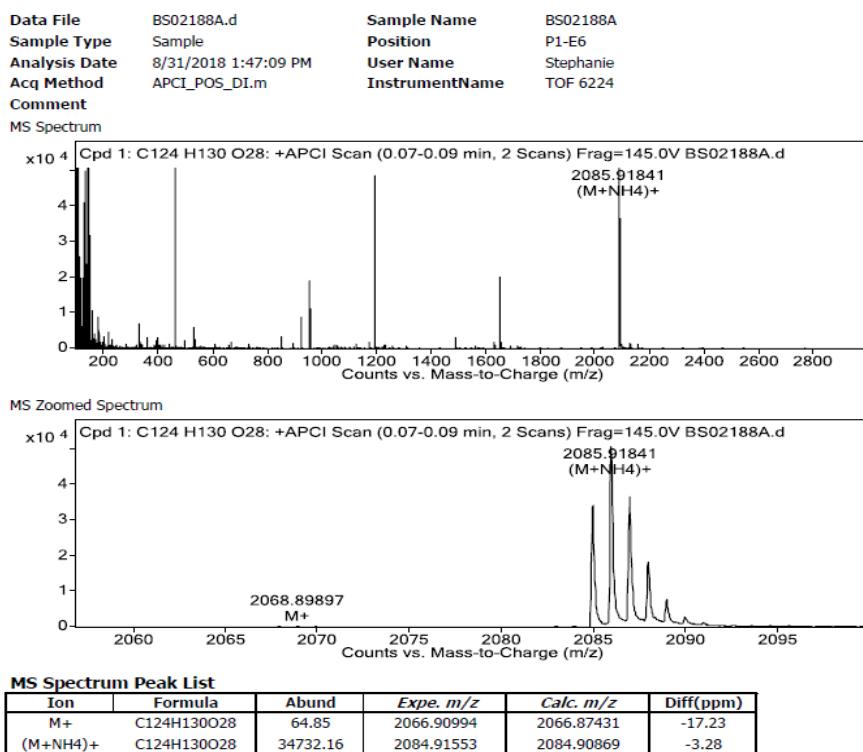


**Figure S65.**  $^{13}\text{C}$  NMR spectrum of **29** ( $\text{CDCl}_3$ , 100 MHz)



**Figure S66.** HRMS spectra of **29**

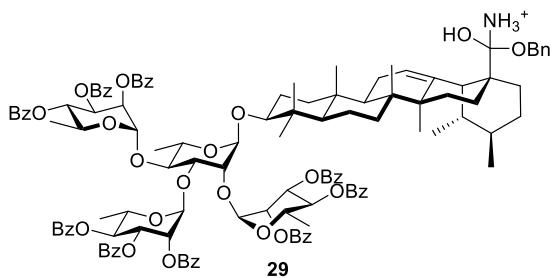
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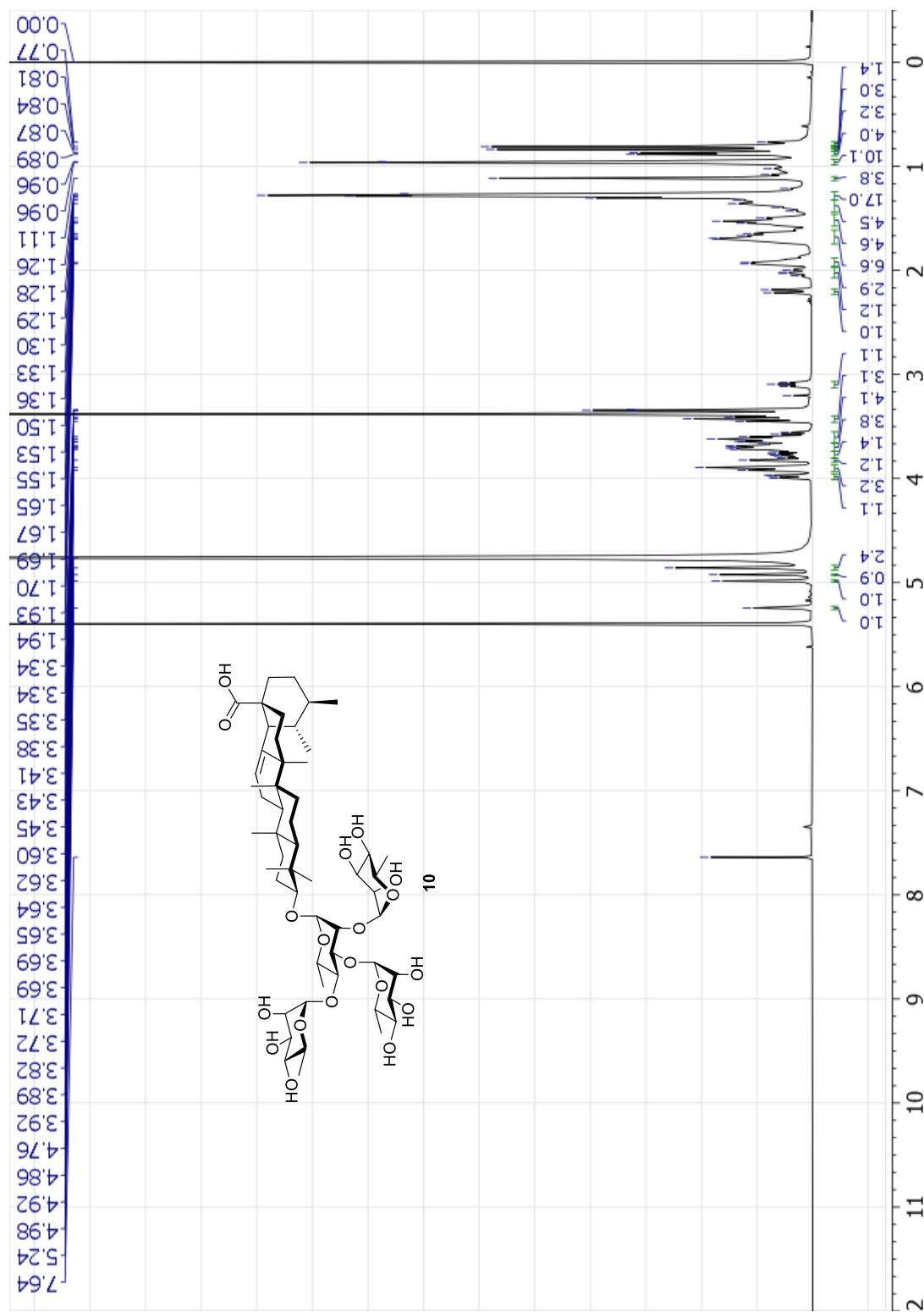


Chemical Formula: C<sub>124</sub>H<sub>134</sub>NO<sub>28</sub><sup>+</sup>

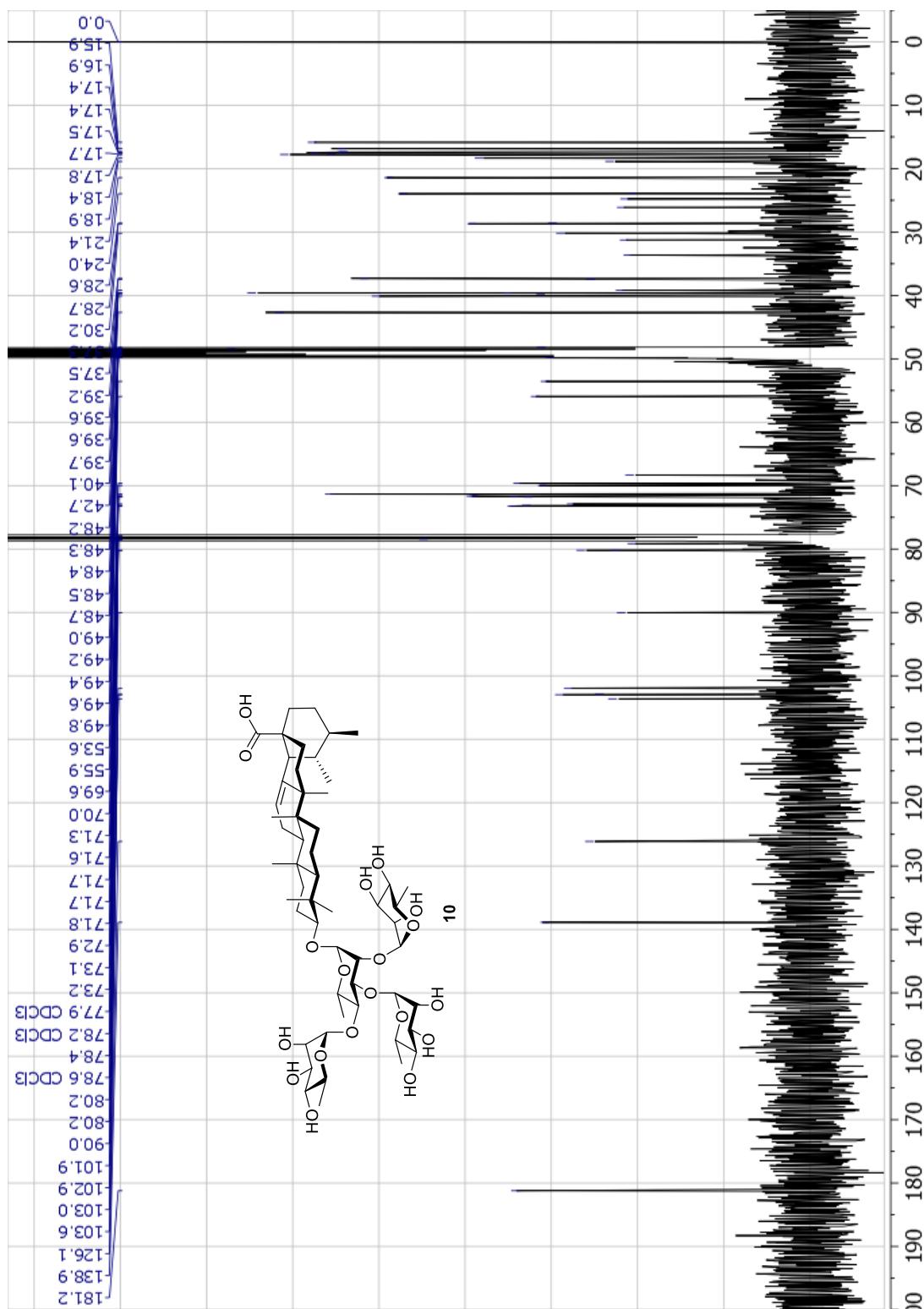
Exact Mass: 2084.9087

Molecular Weight: 2086.4145

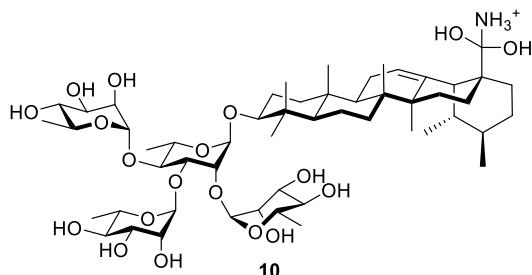
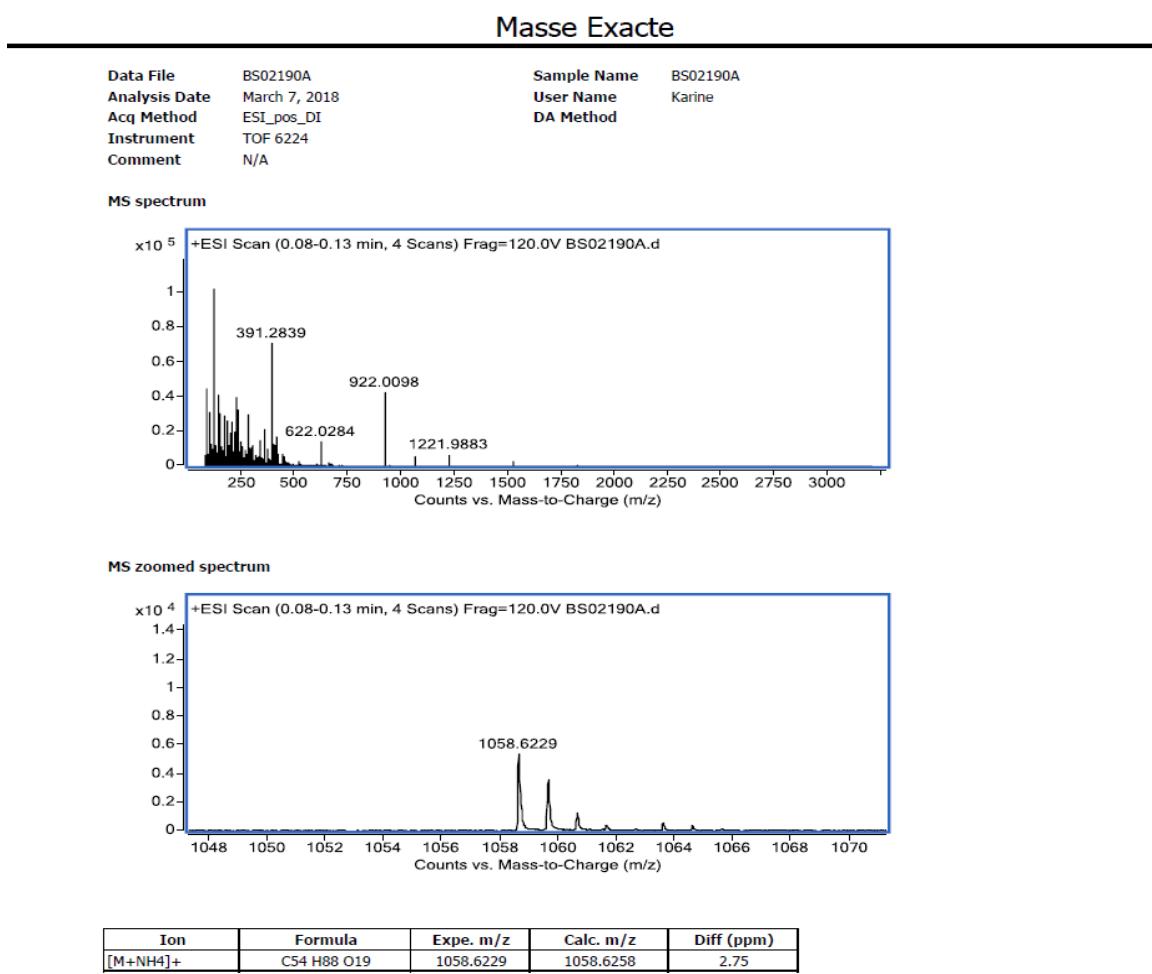
**Figure S67.**  $^1\text{H}$  NMR spectrum of **10** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 400 MHz)



**Figure S68.**  $^1\text{H}$  NMR spectrum of **10** ( $\text{CD}_3\text{OD}/\text{CDCl}_3$  1:1, 100 MHz)



**Figure S69.** HRMS spectra of **10**



Chemical Formula: C<sub>54</sub>H<sub>92</sub>NO<sub>19</sub><sup>+</sup>

Exact Mass: 1058.6258

Molecular Weight: 1059.3175