

SUPPORTING INFORMATION

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

Balla Sylla,^a Serge Lavoie,^b Jean Legault,^a Charles Gauthier,^{*a,c} and André Pichette^{*a}

^aCentre de recherche sur la Boréale (CREB), Chaire de recherche sur les agents anticancéreux d'origine naturelle, Laboratoire LASEVE, Département des Sciences Fondamentales, Université du Québec à Chicoutimi, 555, boul. de l'Université, Chicoutimi (Québec), Canada, G7H 2B1.

E-mail: andre.pichette@uqac.ca

^bInstitut des Sciences de la Forêt tempérée, Université du Québec en Outaouais, 58, rue Principale, Ripon (Québec), Canada, J0V 1V0.

^cCentre 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. ^1H NMR spectrum of **13** (CDCl_3 , 400 MHz)

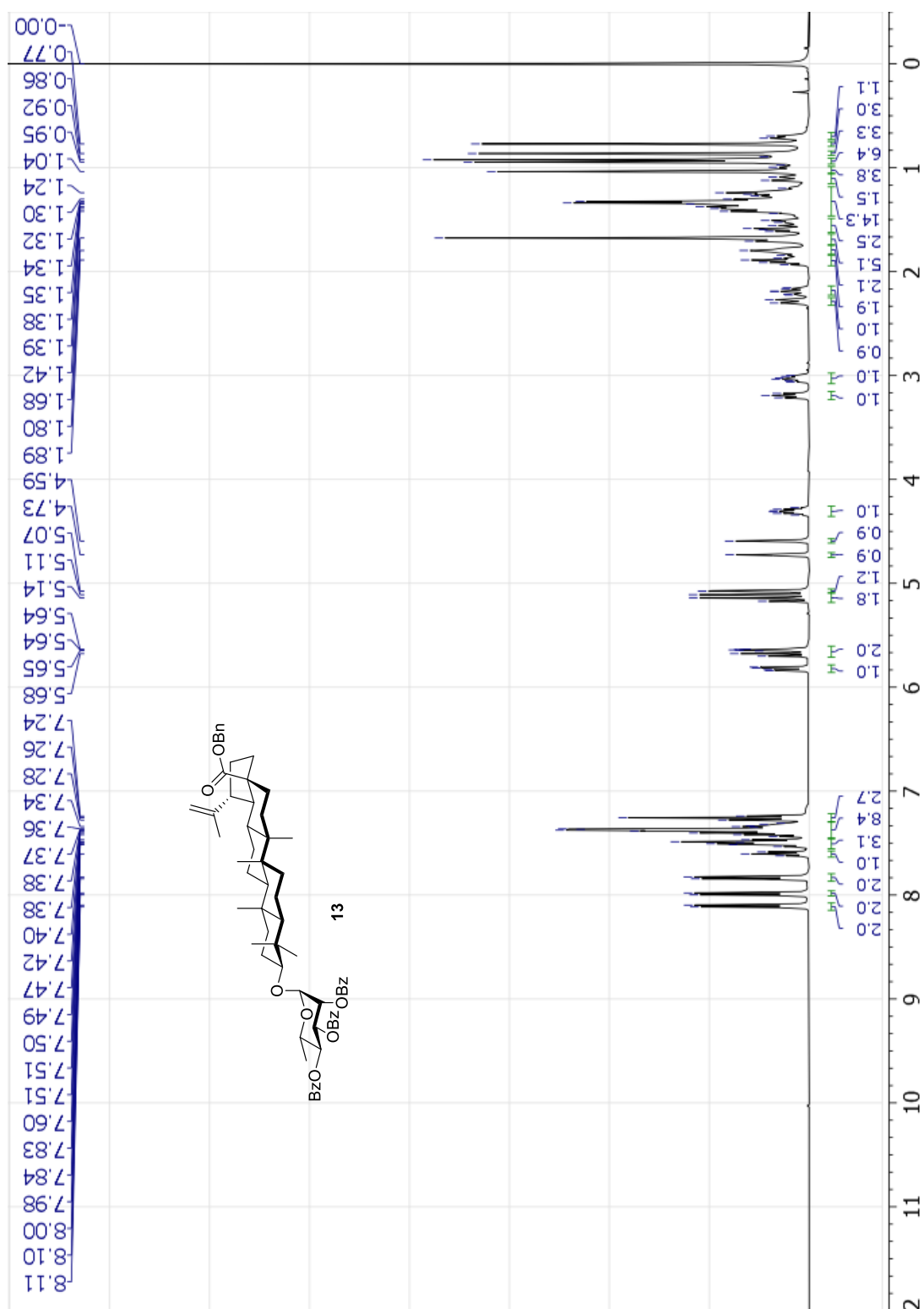


Figure S2. ^{13}C NMR spectra of **13** (CDCl_3 , 100 MHz)

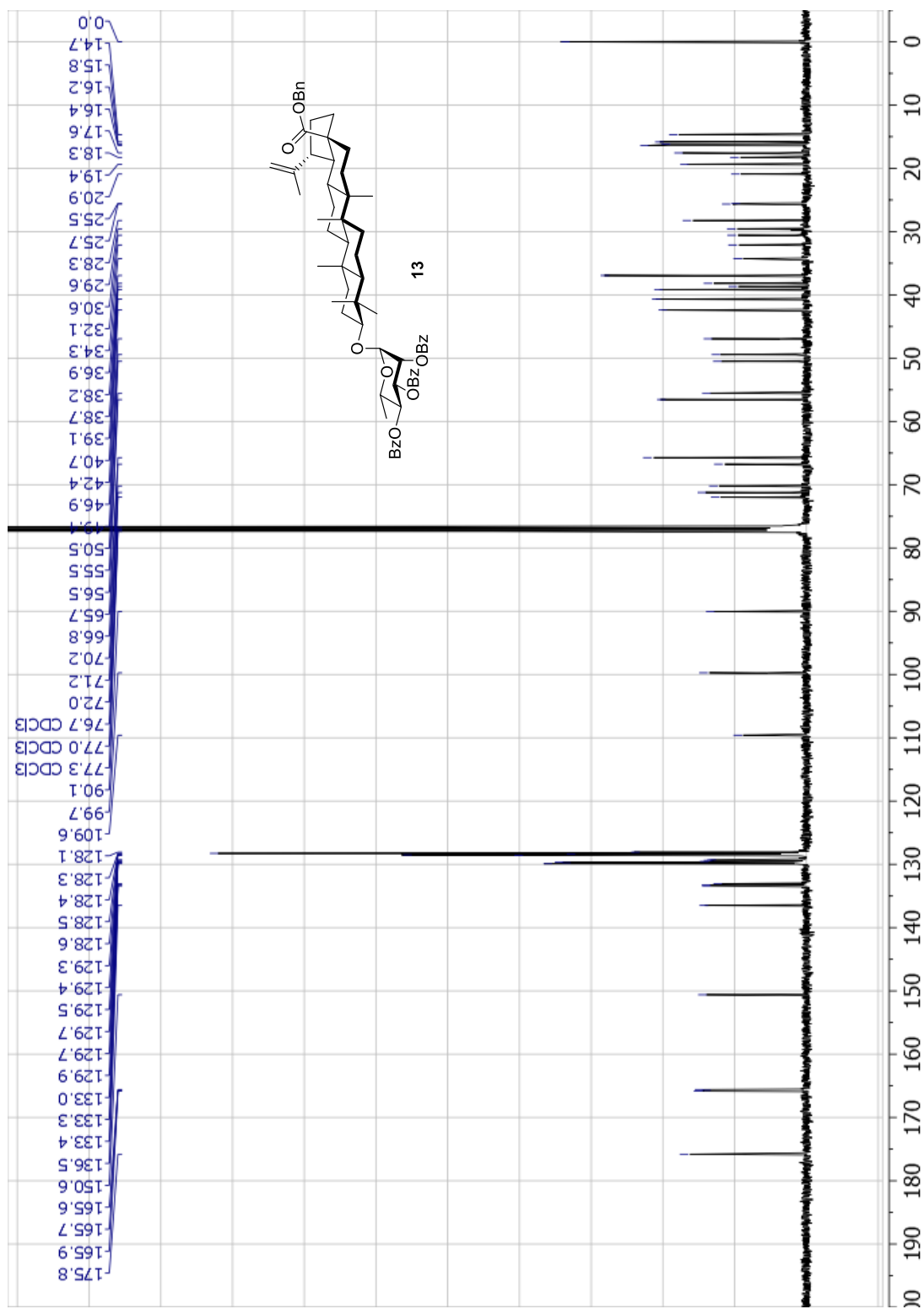
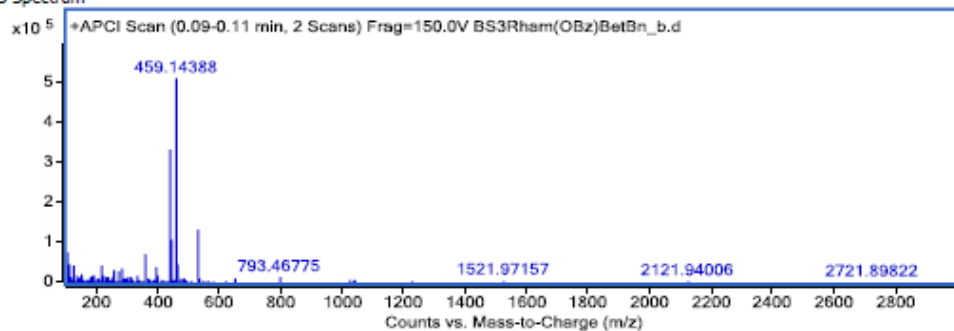


Figure S3. HRMS spectra of 13

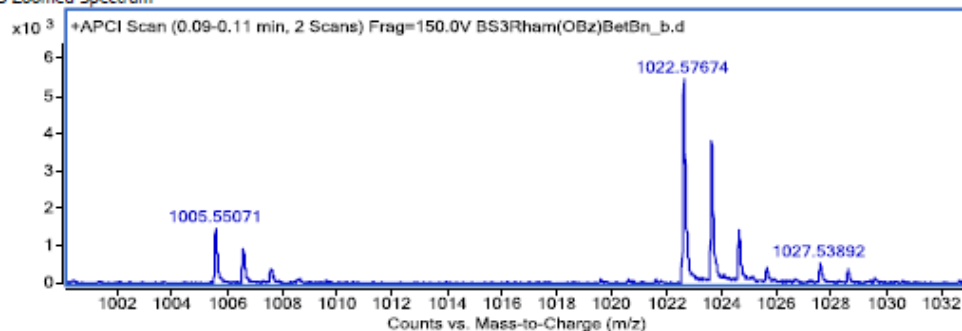
Rapport de masse exacte

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

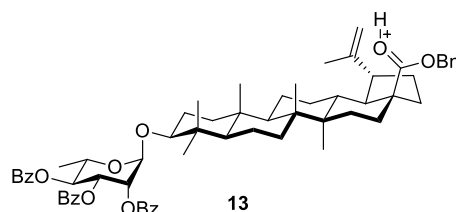


MS Zoomed Spectrum



MS Spectrum Peak List

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



Chemical Formula: C₆₄H₇₇O₁₀⁺
 Exact Mass: 1005,5511
 Molecular Weight: 1006,2896

Figure S4. ^1H NMR spectrum of **14** (CDCl_3 , 400 MHz)

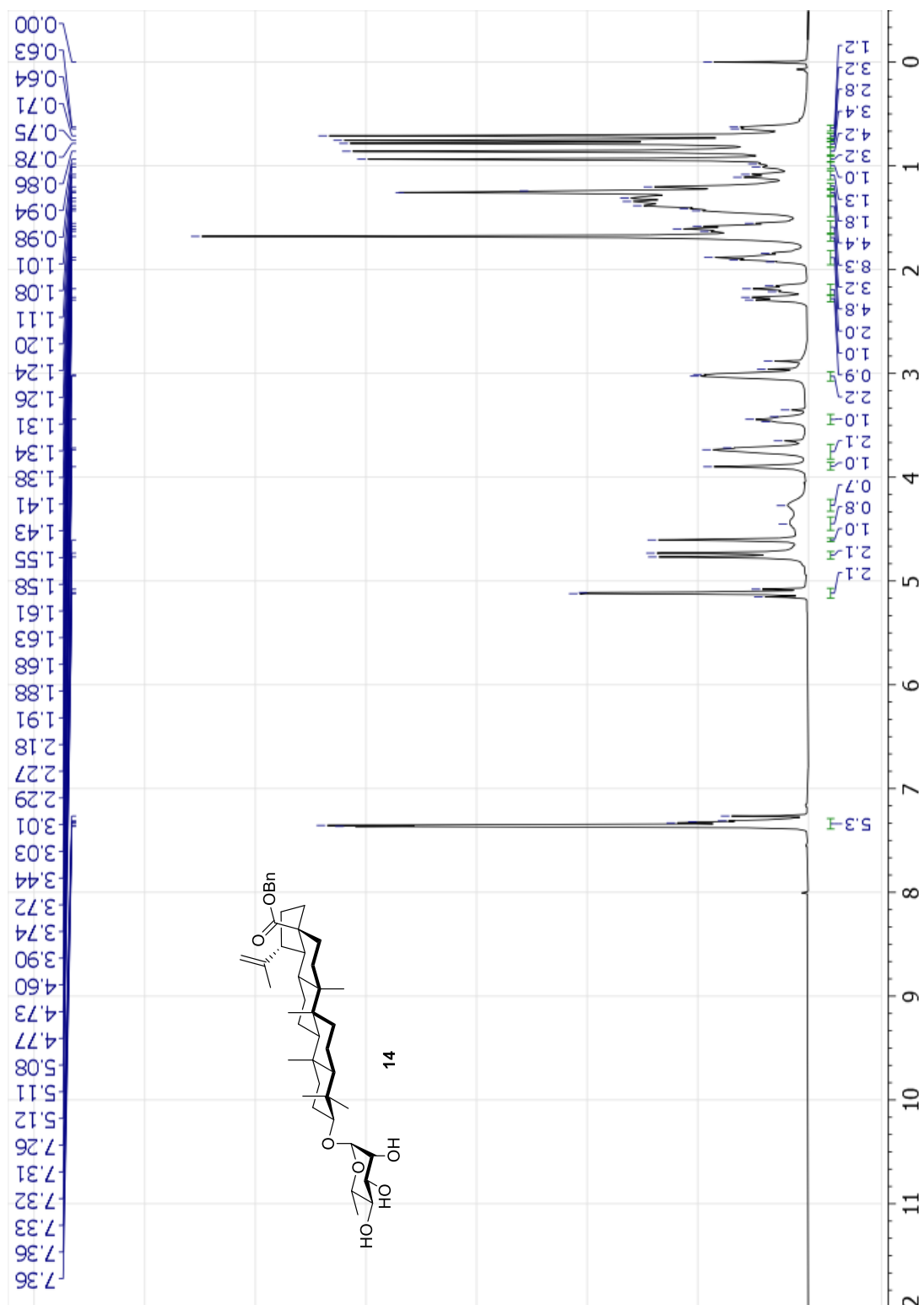


Figure S5. ^{13}C NMR spectra of **14** (CDCl_3 , 100 MHz)

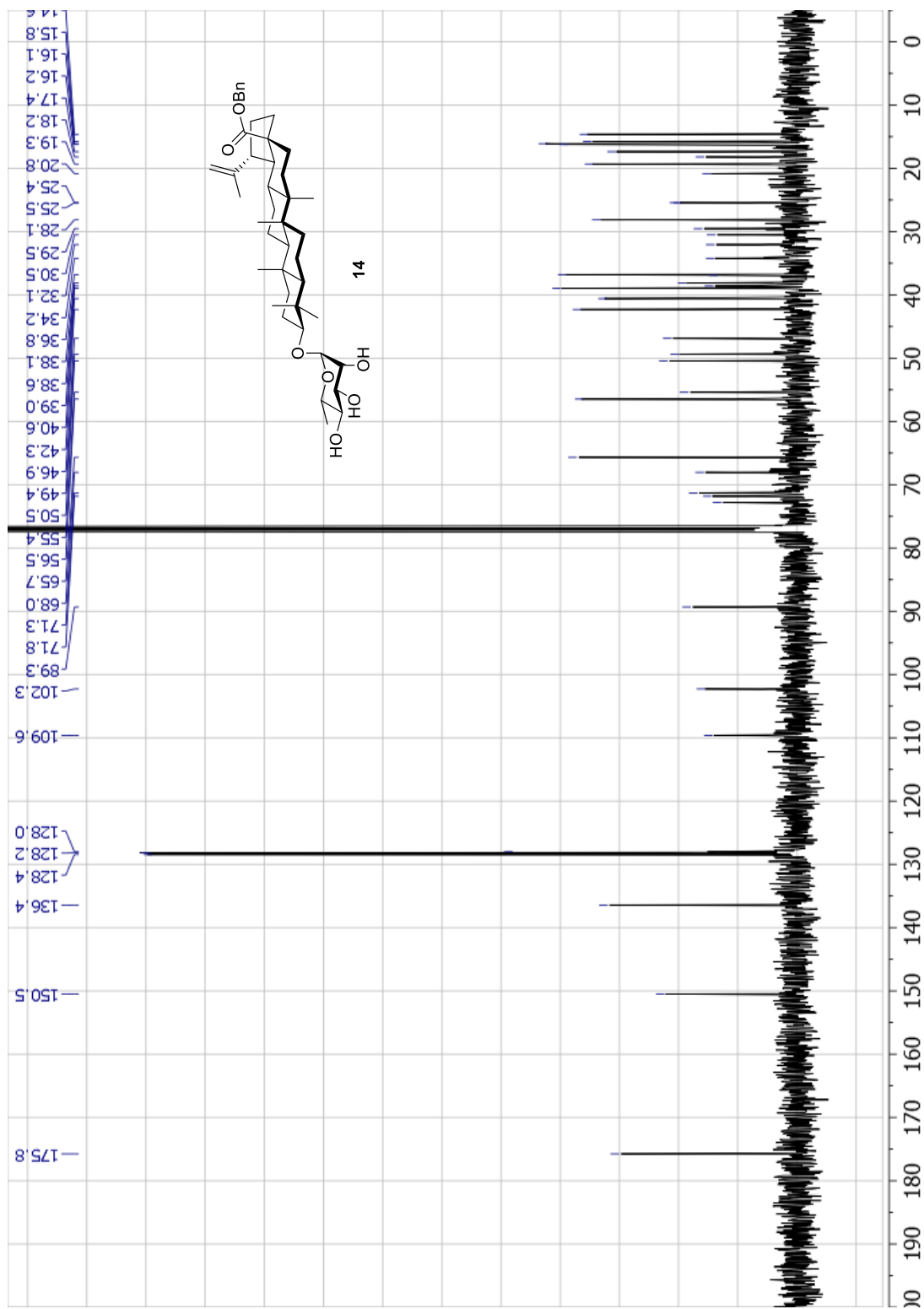
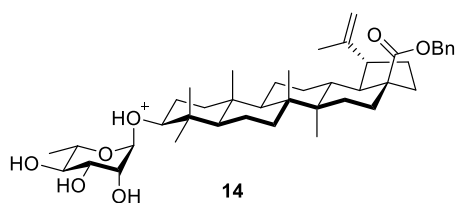
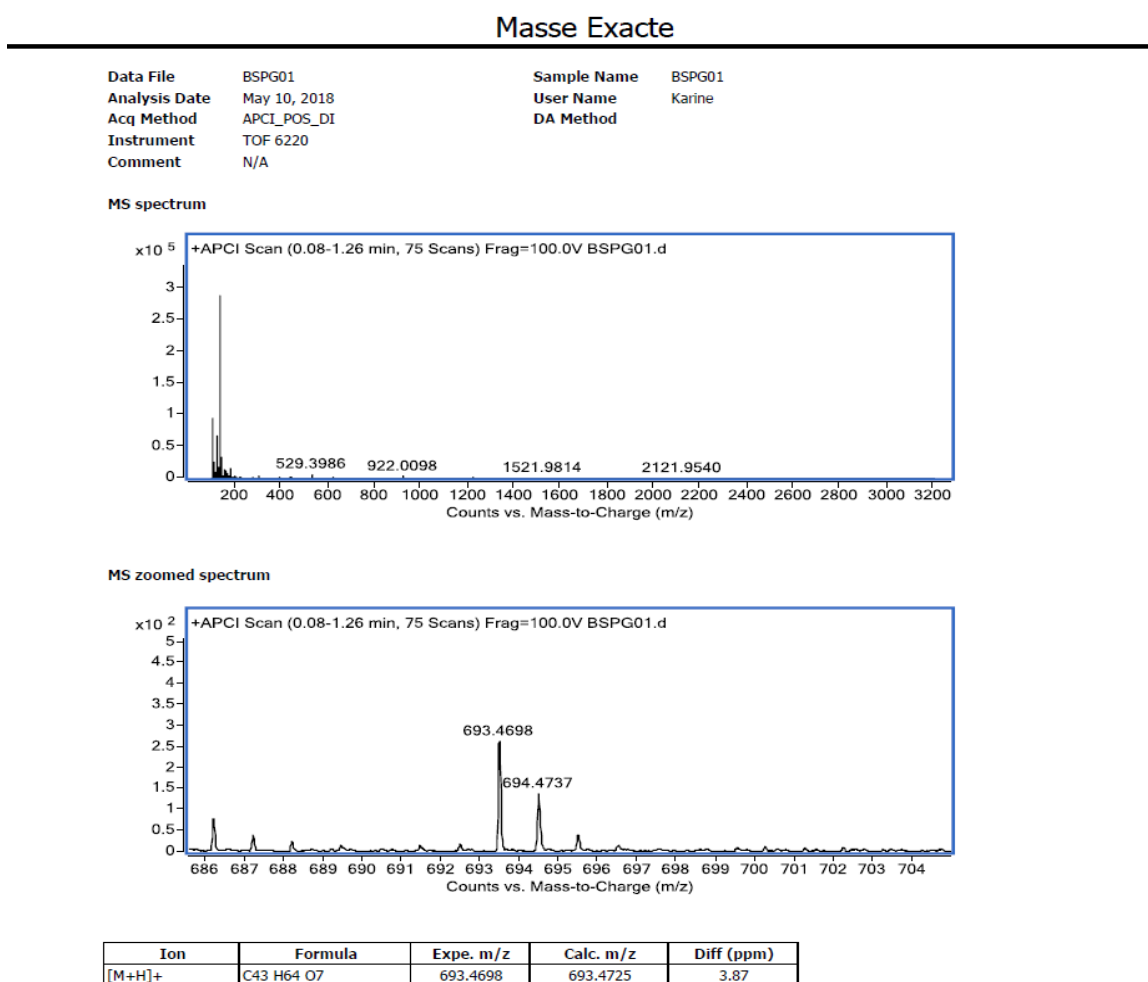


Figure S6. HRMS spectra of 14



Chemical Formula: C₄₃H₆₅O₇⁺
 Exact Mass: 693.4725
 Molecular Weight: 693.9855

Figure S7. ^1H NMR spectrum of **15** (CDCl_3 , 400 MHz)

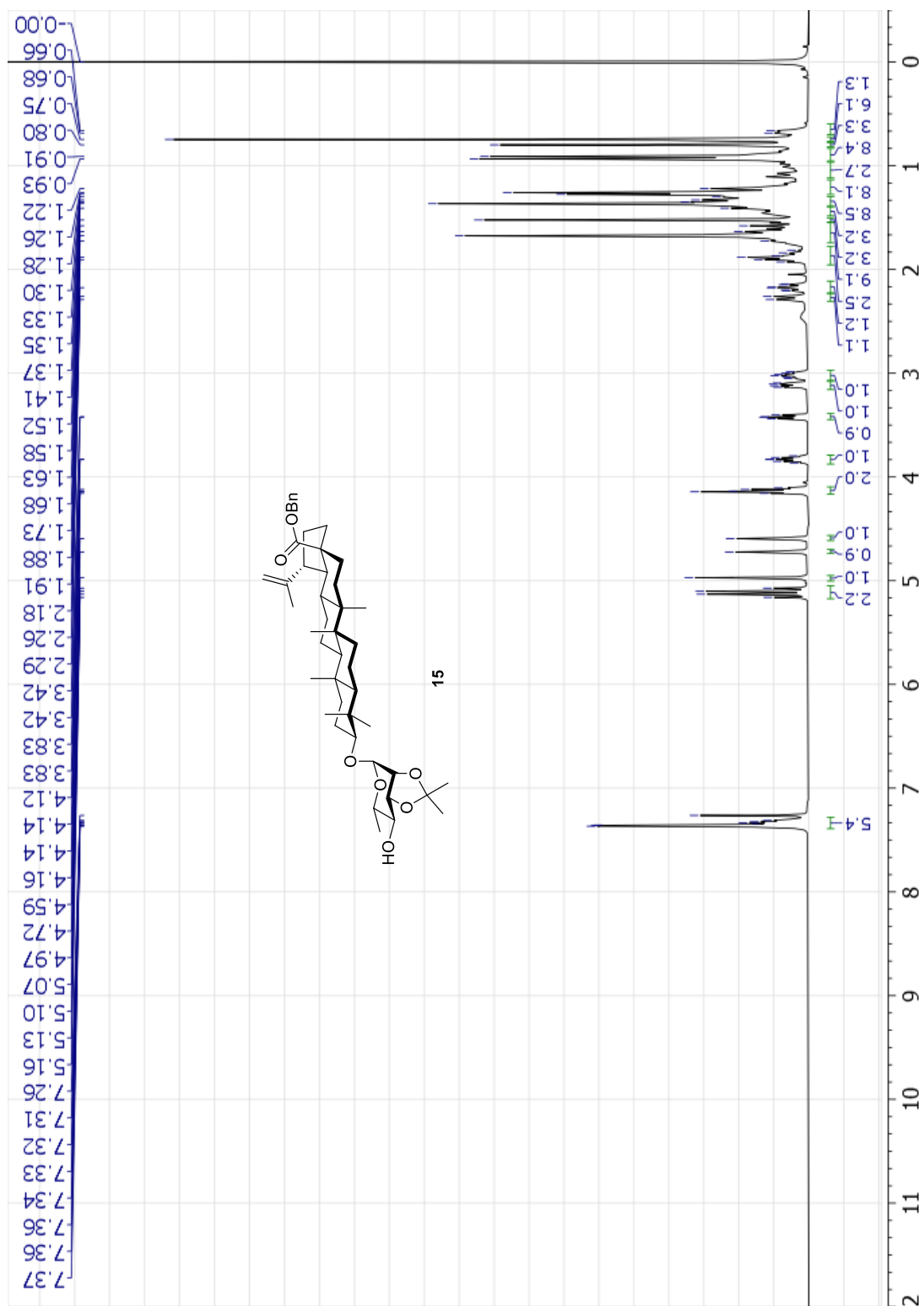


Figure S8. ^{13}C NMR spectra of **15** (CDCl_3 , 100 MHz)

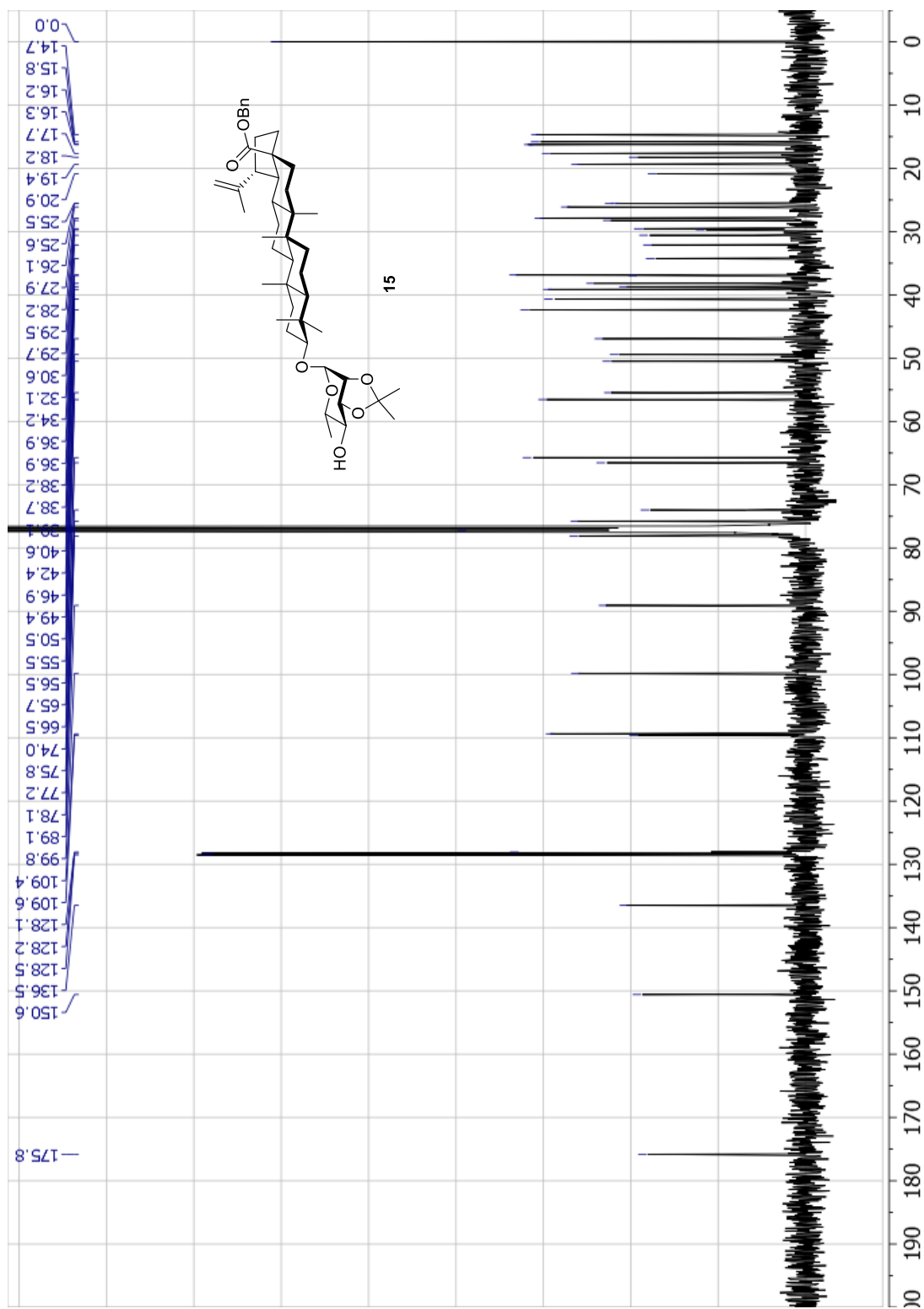


Figure S9. HRMS spectra of **15**

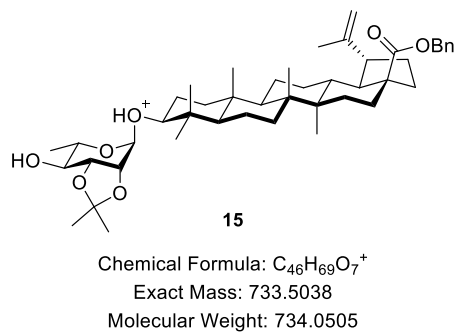
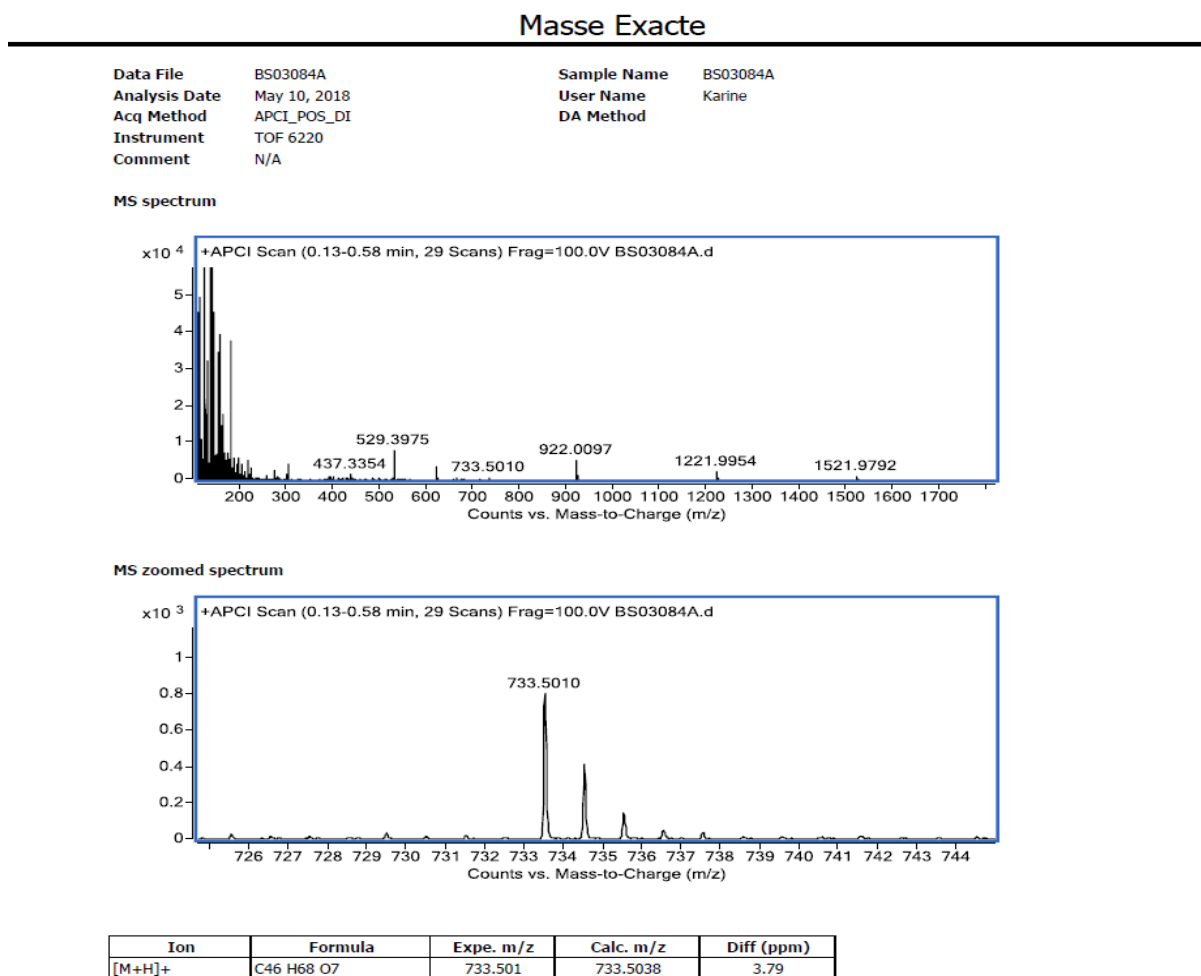


Figure S10. ^1H NMR spectrum of **16** (CDCl_3 , 400 MHz)

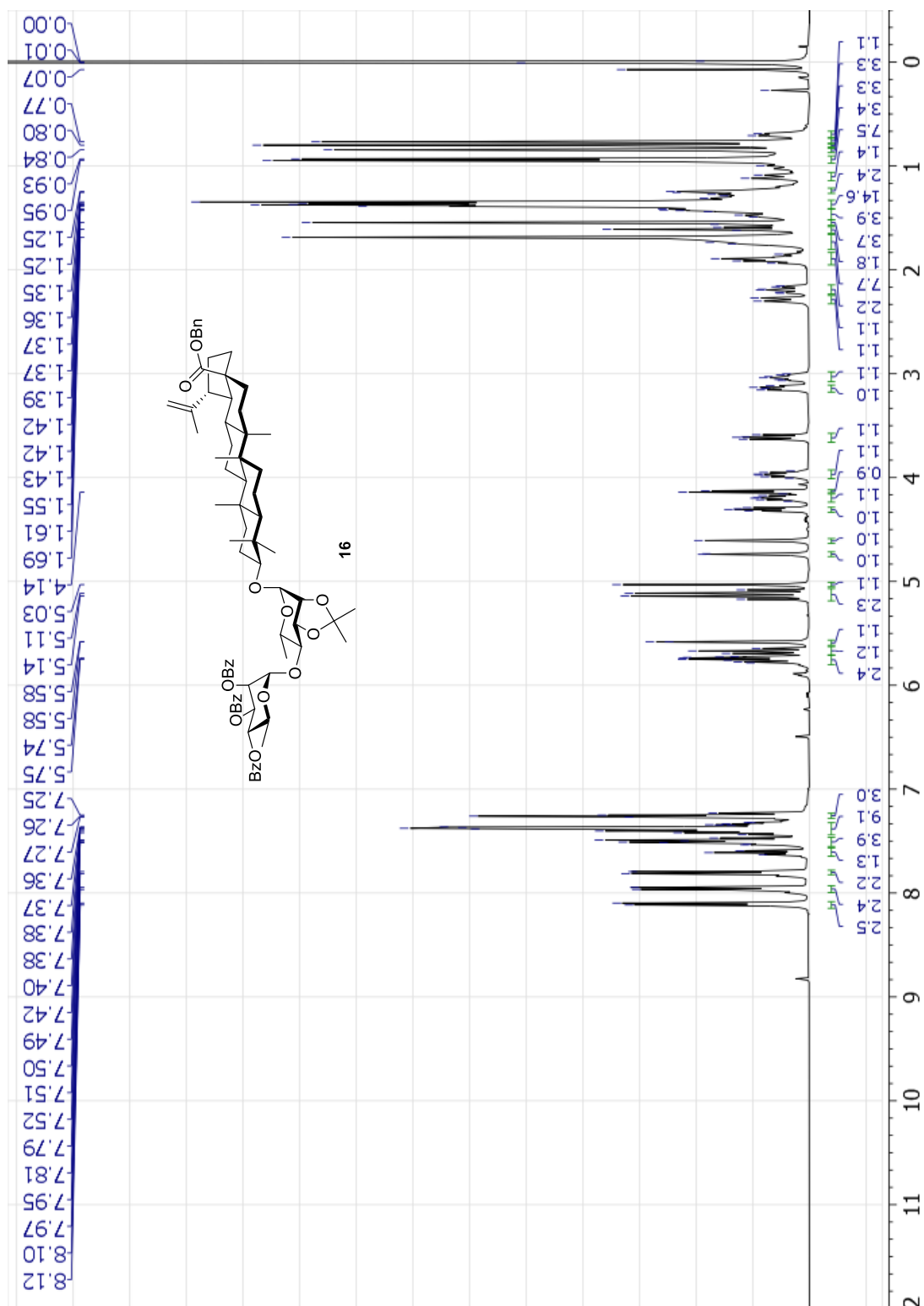


Figure S11. ^{13}C NMR spectra of **16** (CDCl_3 , 100 MHz)

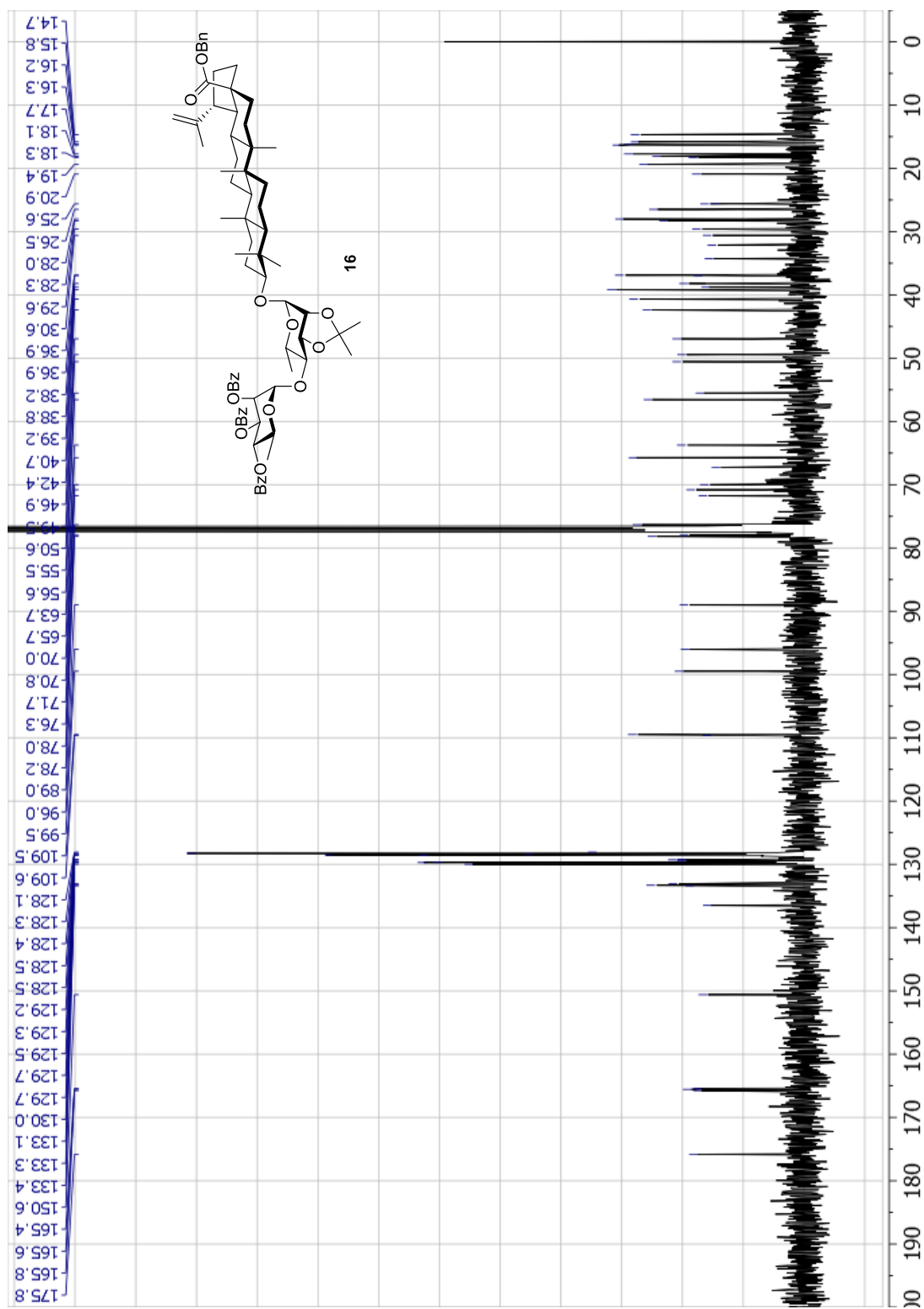
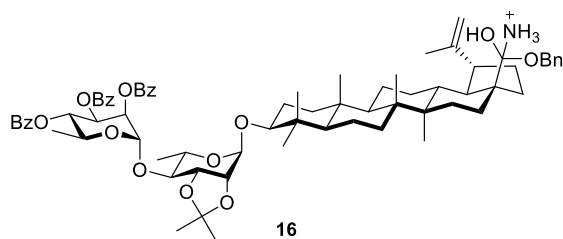
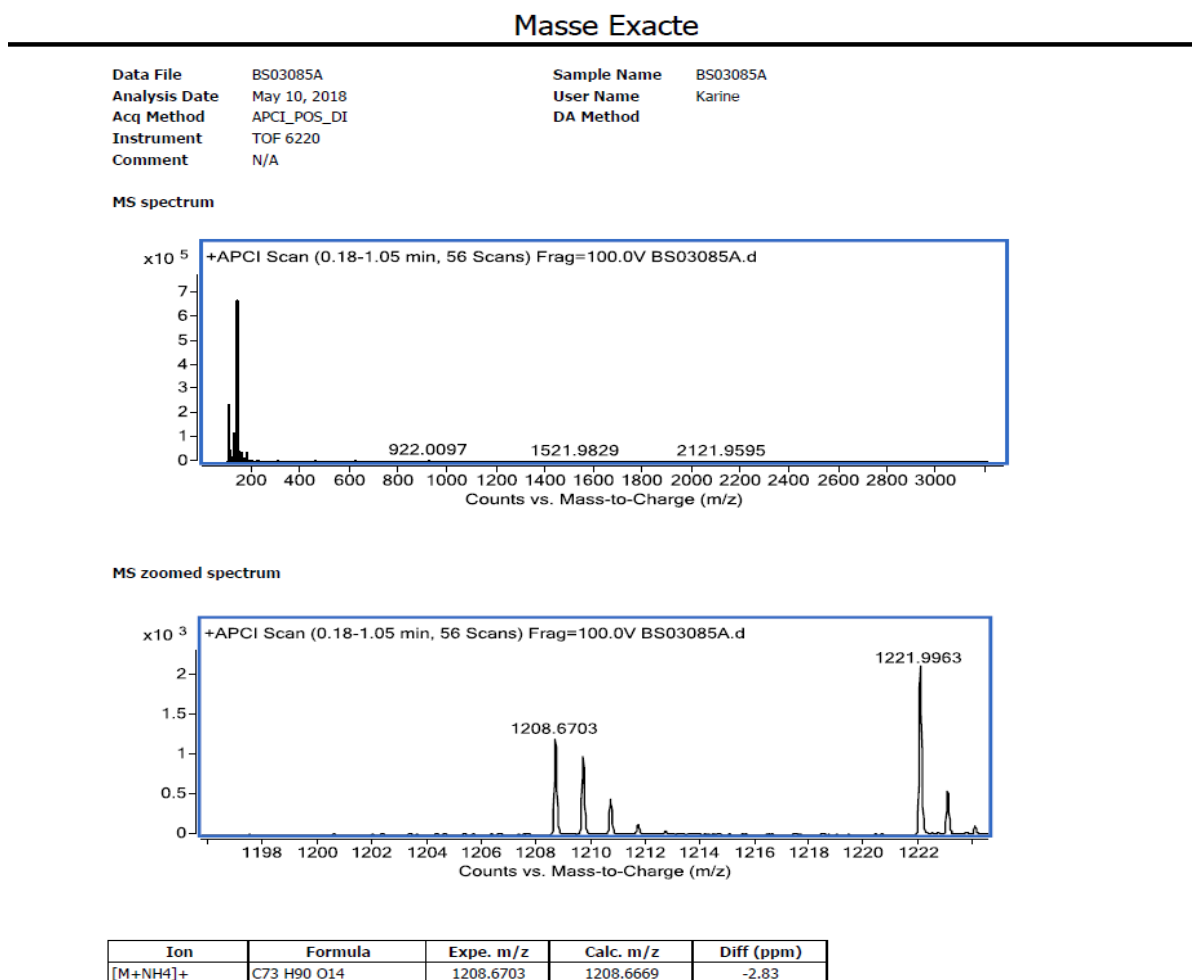


Figure S12. HRMS spectra of **16**



Chemical Formula: C₇₃H₉₄NO₁₄⁺
 Exact Mass: 1208.6669
 Molecular Weight: 1209.5475

Figure S13. ^1H NMR spectrum of **17** (CDCl_3 , 400 MHz)

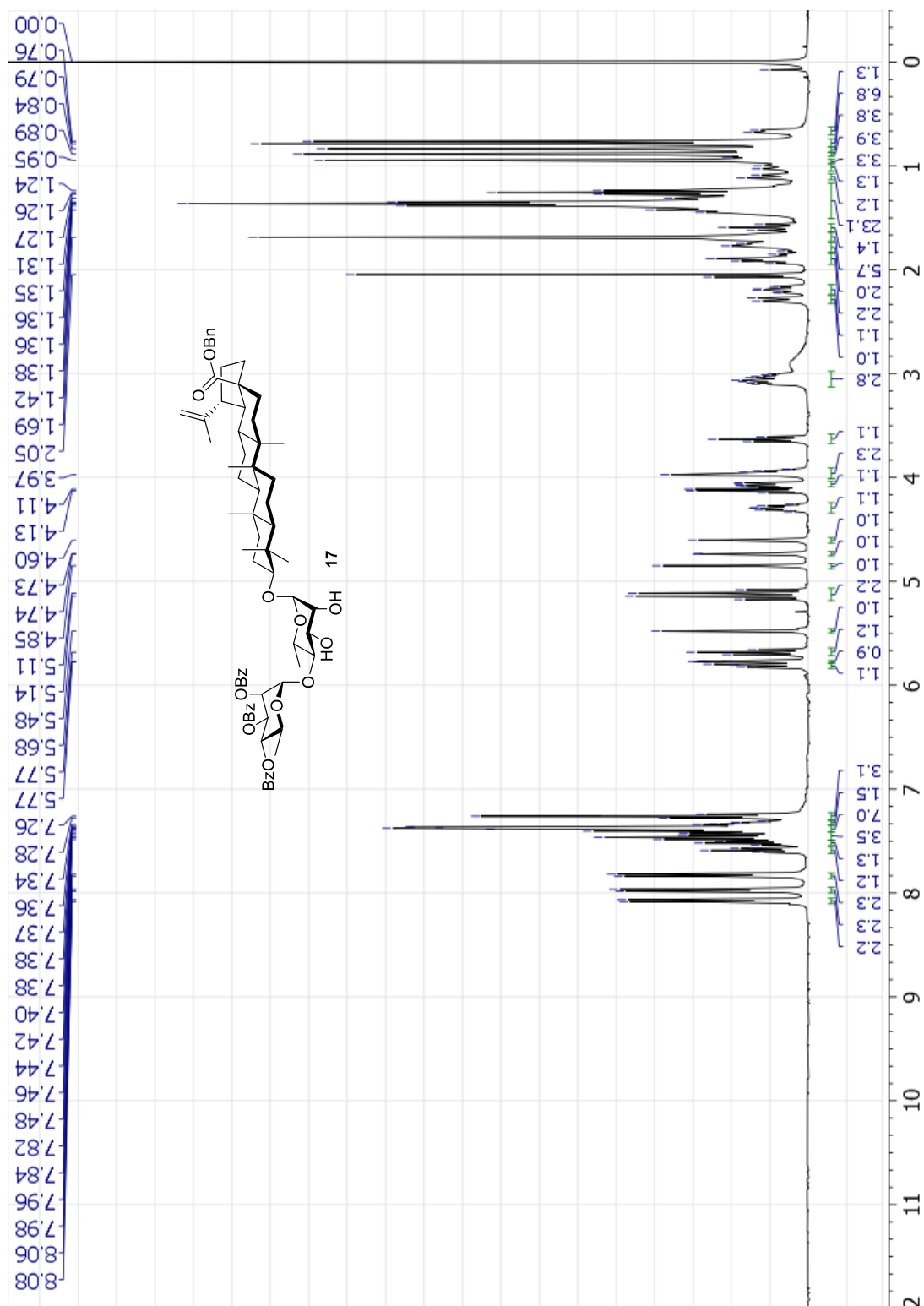


Figure S14. ^{13}C NMR spectra of **17** (CDCl_3 , 100 MHz)

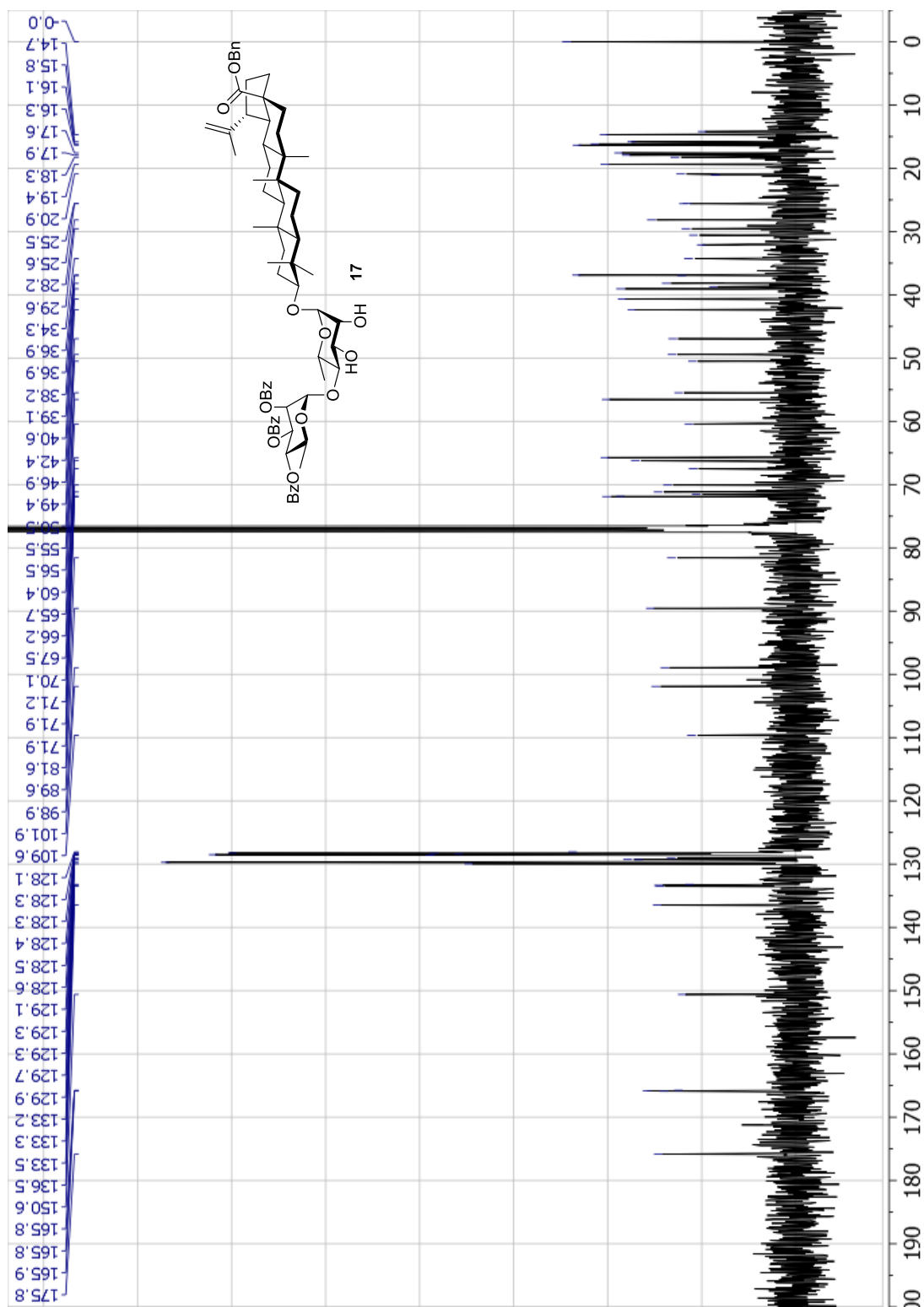
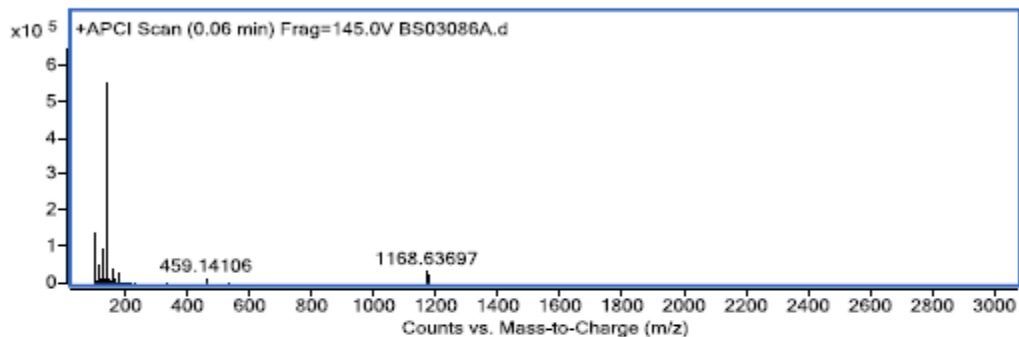


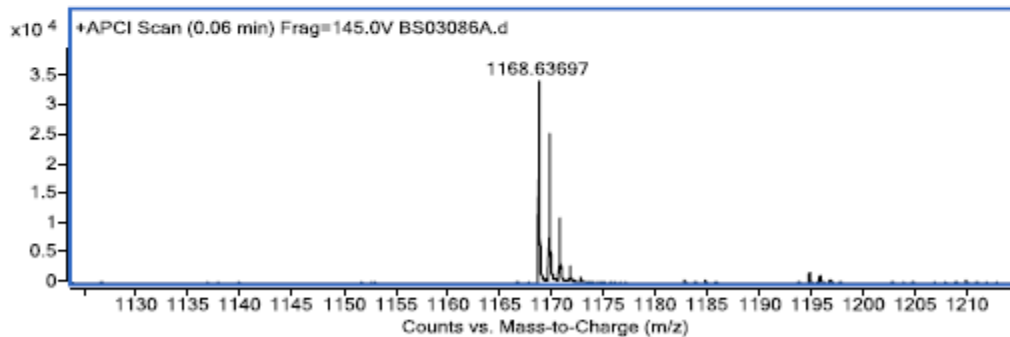
Figure S15. HRMS spectra of **17**

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		

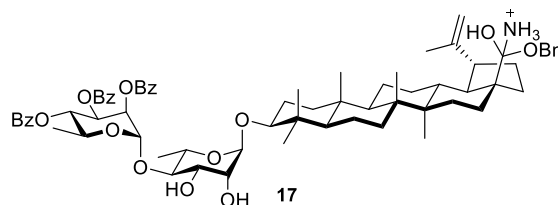
MS spectrum



MS zoomed spectrum

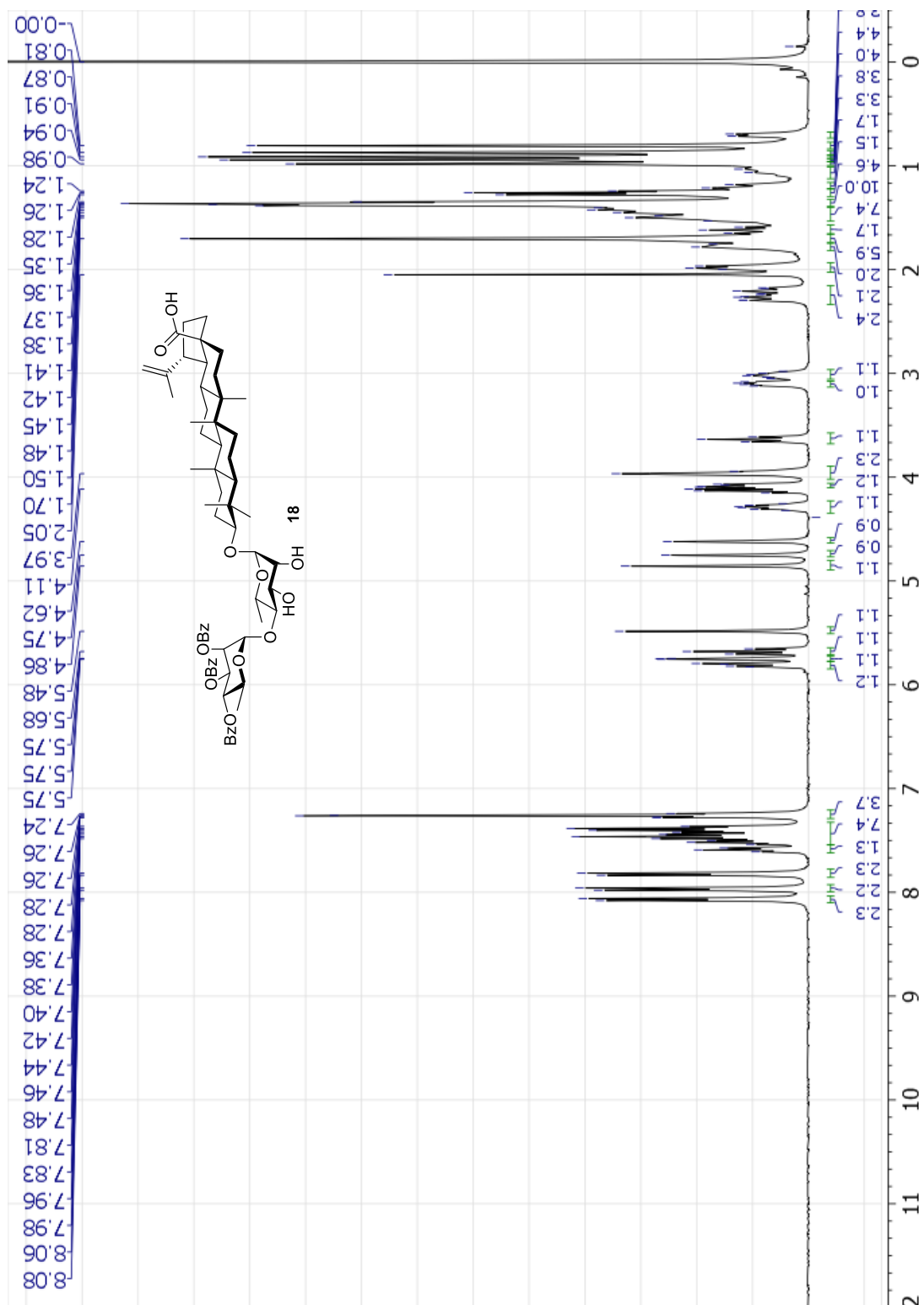


Ion	Formula	Expe. m/z	Calc. m/z	Diff (ppm)
[M+NH ₄] ⁺	C ₇₀ H ₈₆ O ₁₄	1168.63697	1168.63558	-1.19



Chemical Formula: C₇₀H₉₀NO₁₄⁺
 Exact Mass: 1168.6356
 Molecular Weight: 1169.4825

Figure S16. ^1H NMR spectrum of **18** (CDCl_3 , 400 MHz)



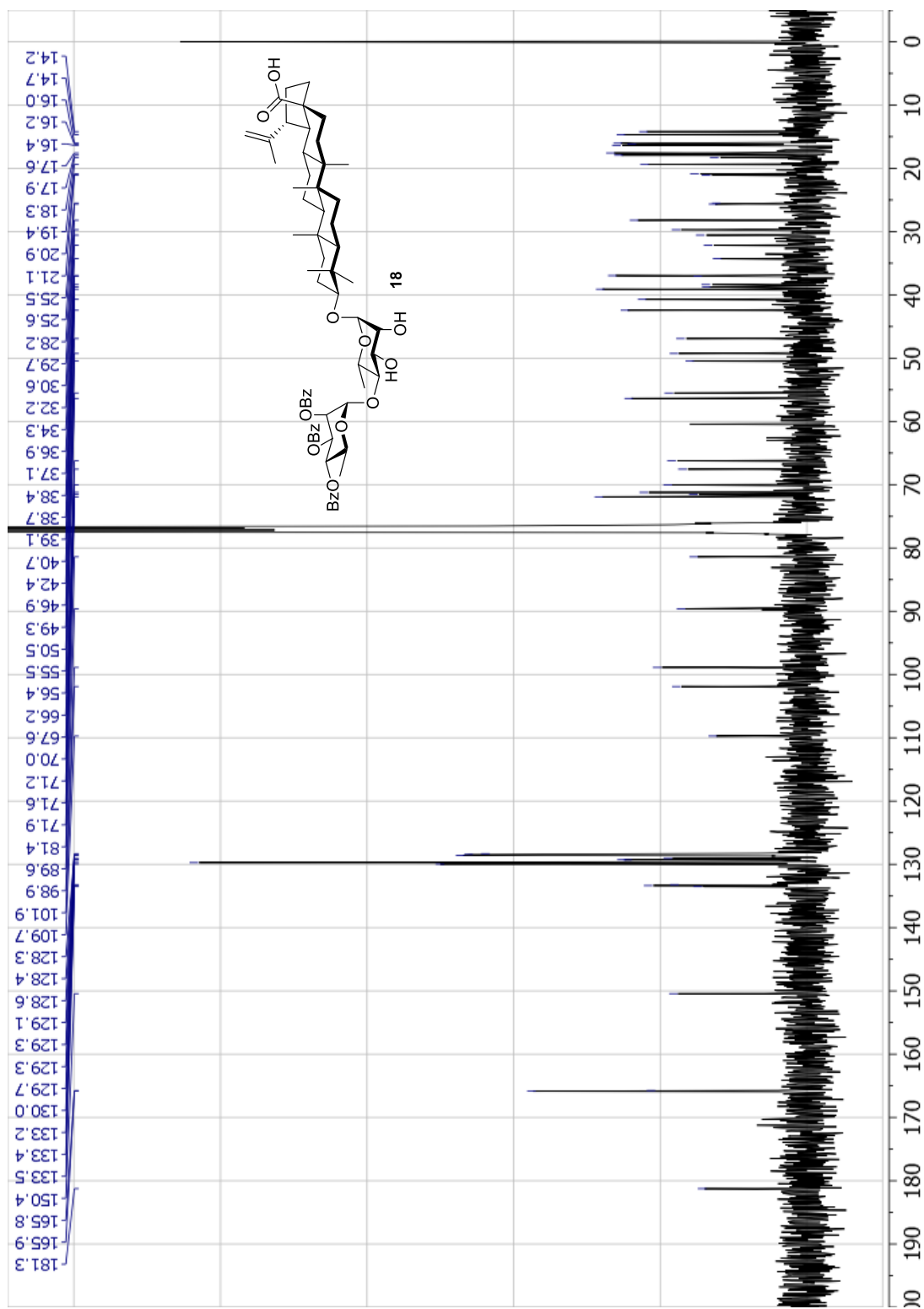
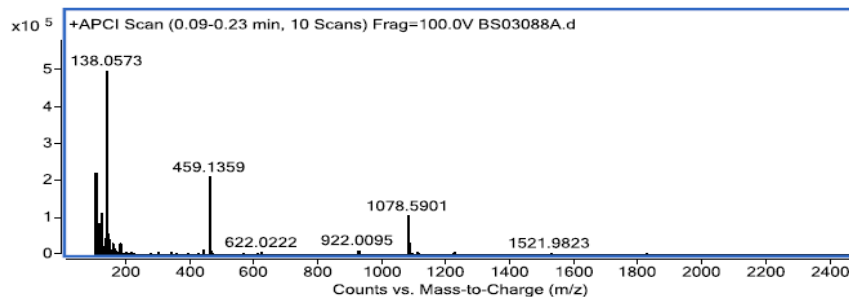


Figure S18. HRMS spectra of **18**

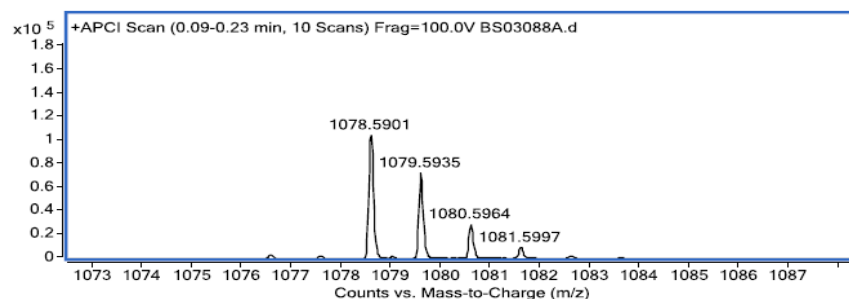
Masse Exacte

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		

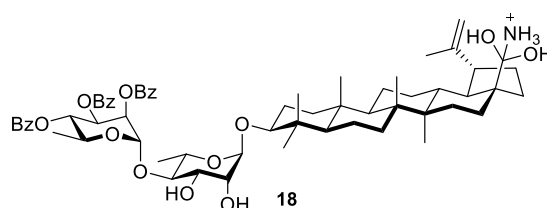
MS spectrum



MS zoomed spectrum



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



Chemical Formula: C₆₃H₈₄NO₁₄⁺
 Exact Mass: 1078.5886
 Molecular Weight: 1079.3575

Figure S19. ^1H NMR spectrum of **4** (DMSO- d_6 , 400 MHz)

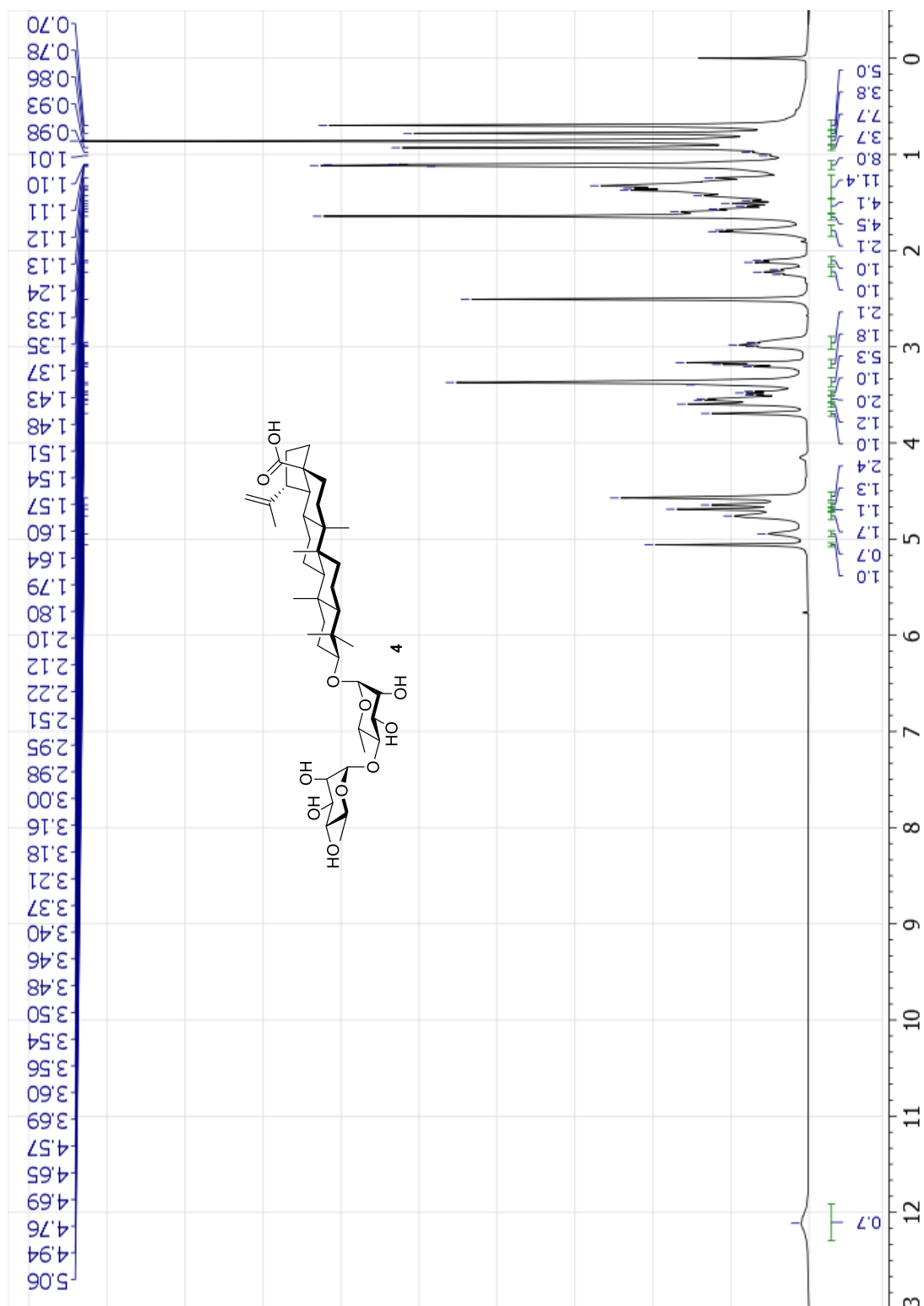


Figure S20. ^{13}C NMR spectra of **4** (DMSO- d_6 , 100 MHz)

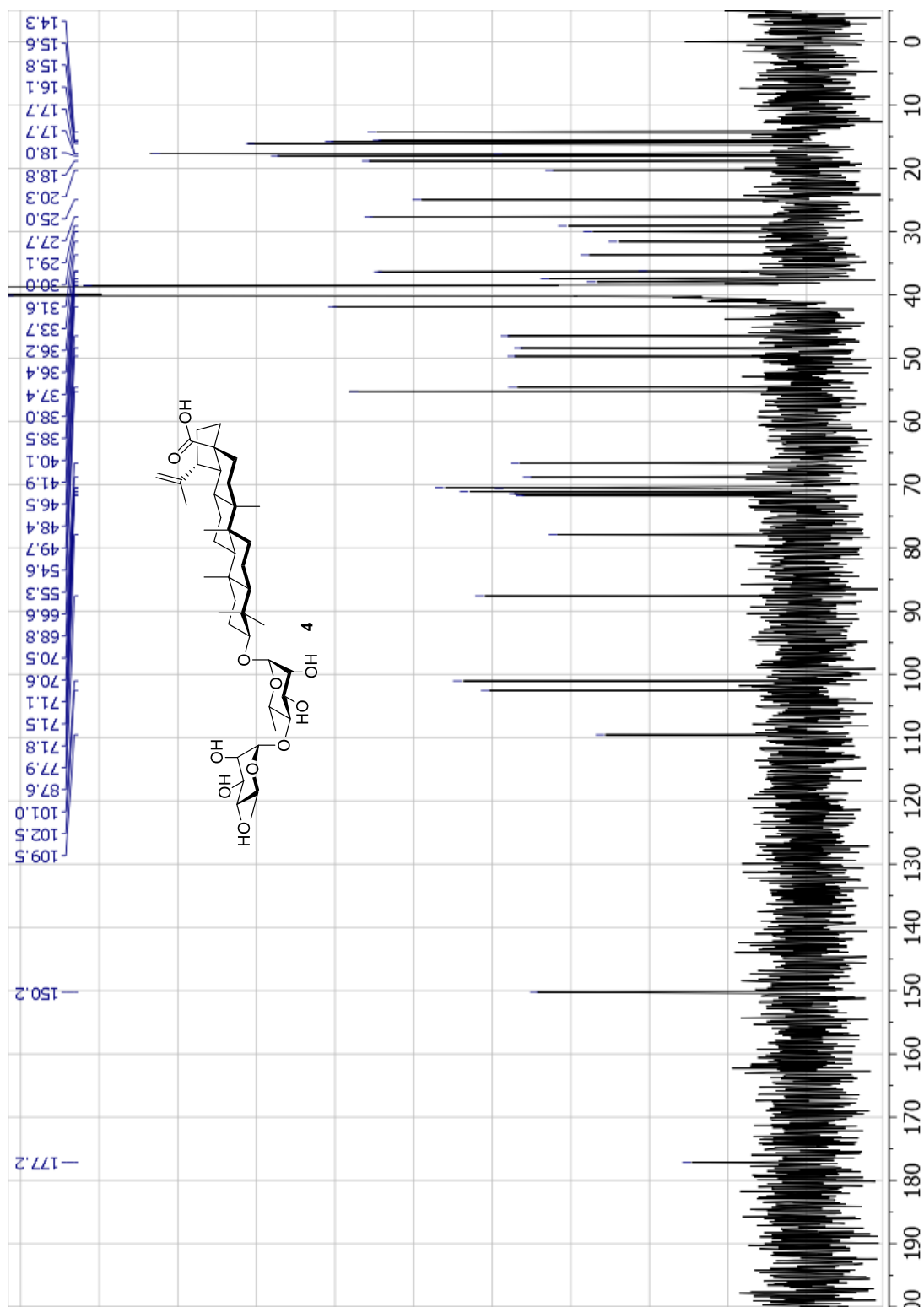
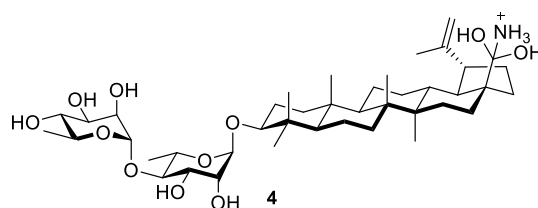
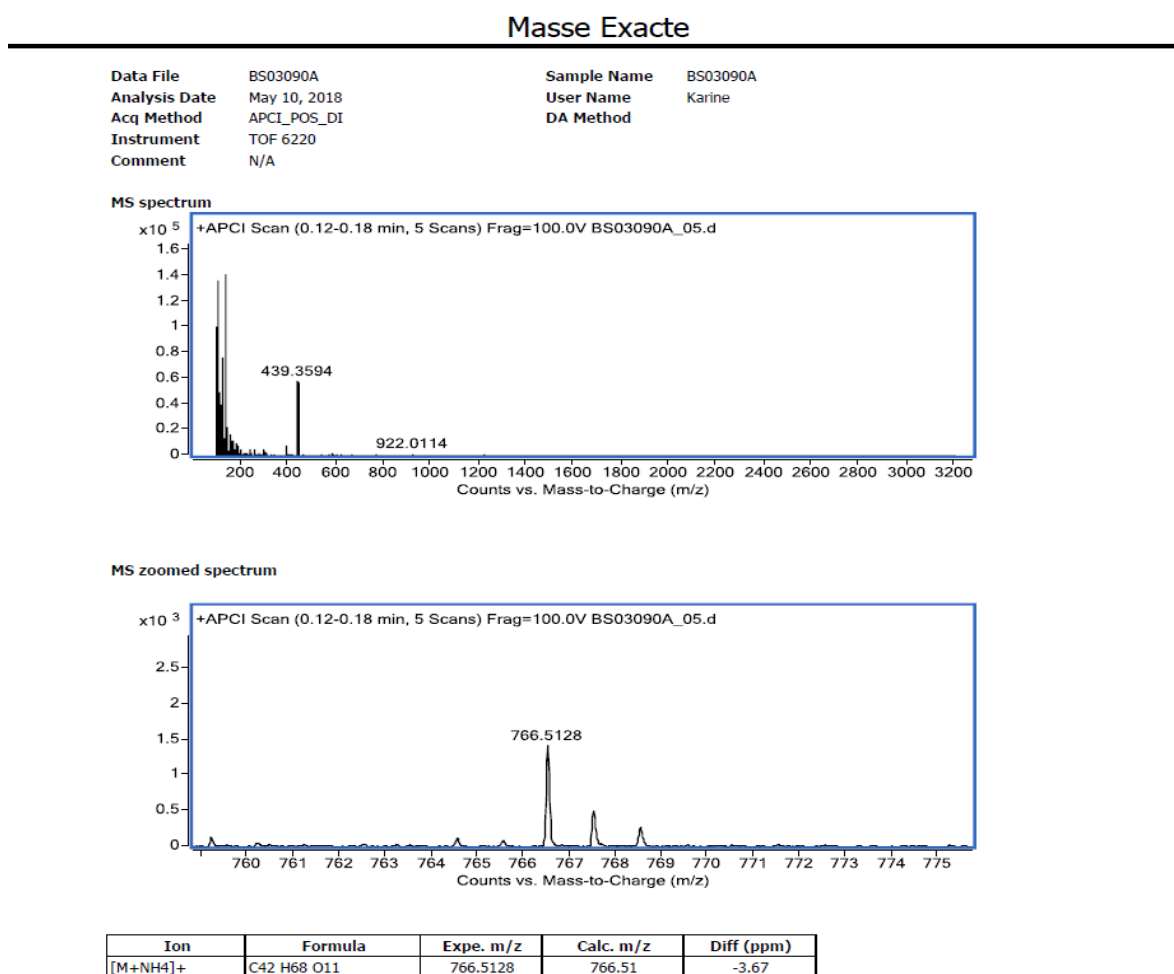


Figure S21. HRMS spectra of **4**



Chemical Formula: C₄₂H₇₂NO₁₁⁺
 Exact Mass: 766.5100
 Molecular Weight: 767.0335

Figure S22. ^1H NMR spectrum of **19** (CDCl_3 , 400 MHz)

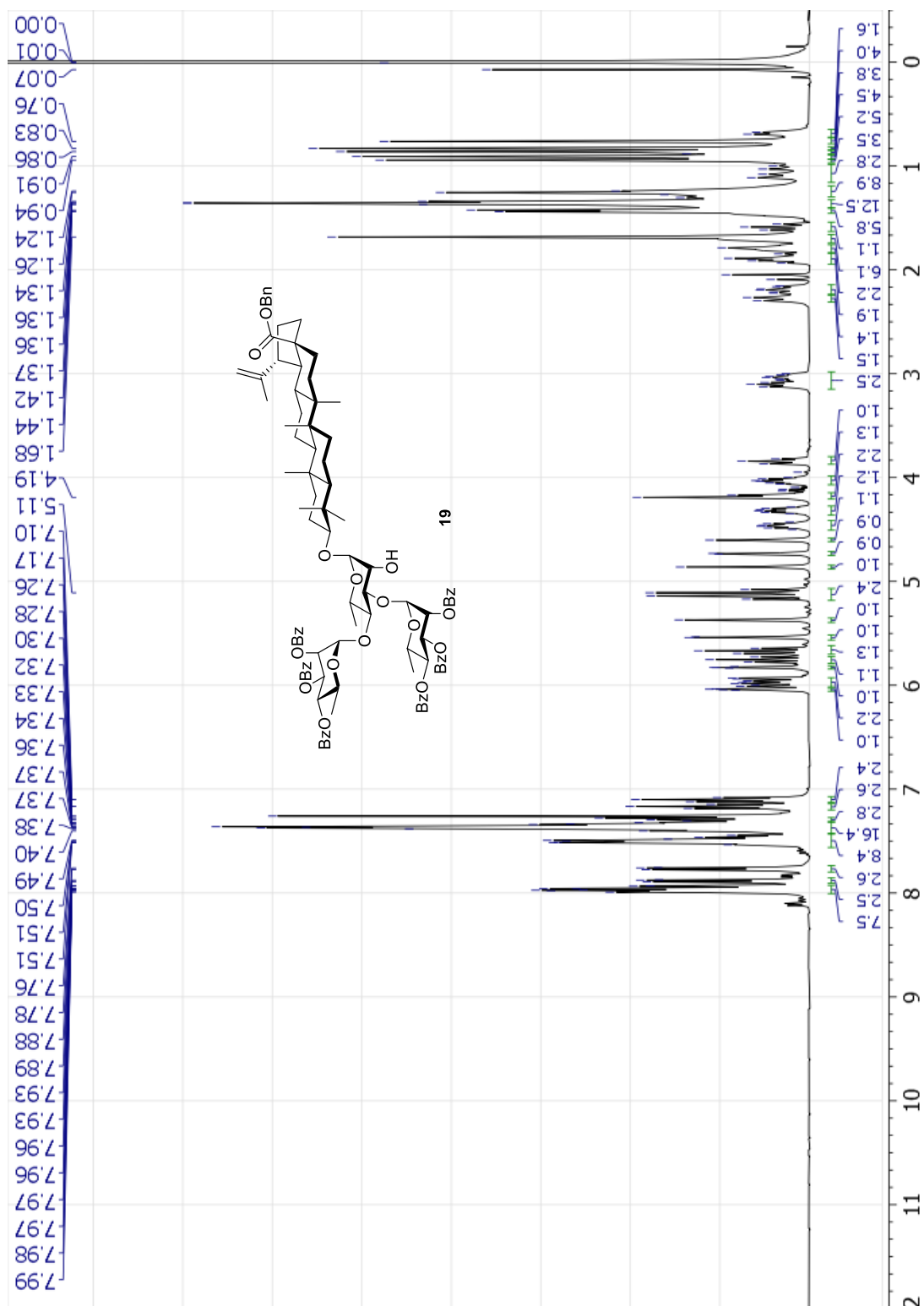


Figure S23. ^{13}C NMR spectra of **19** (CDCl_3 , 100 MHz)

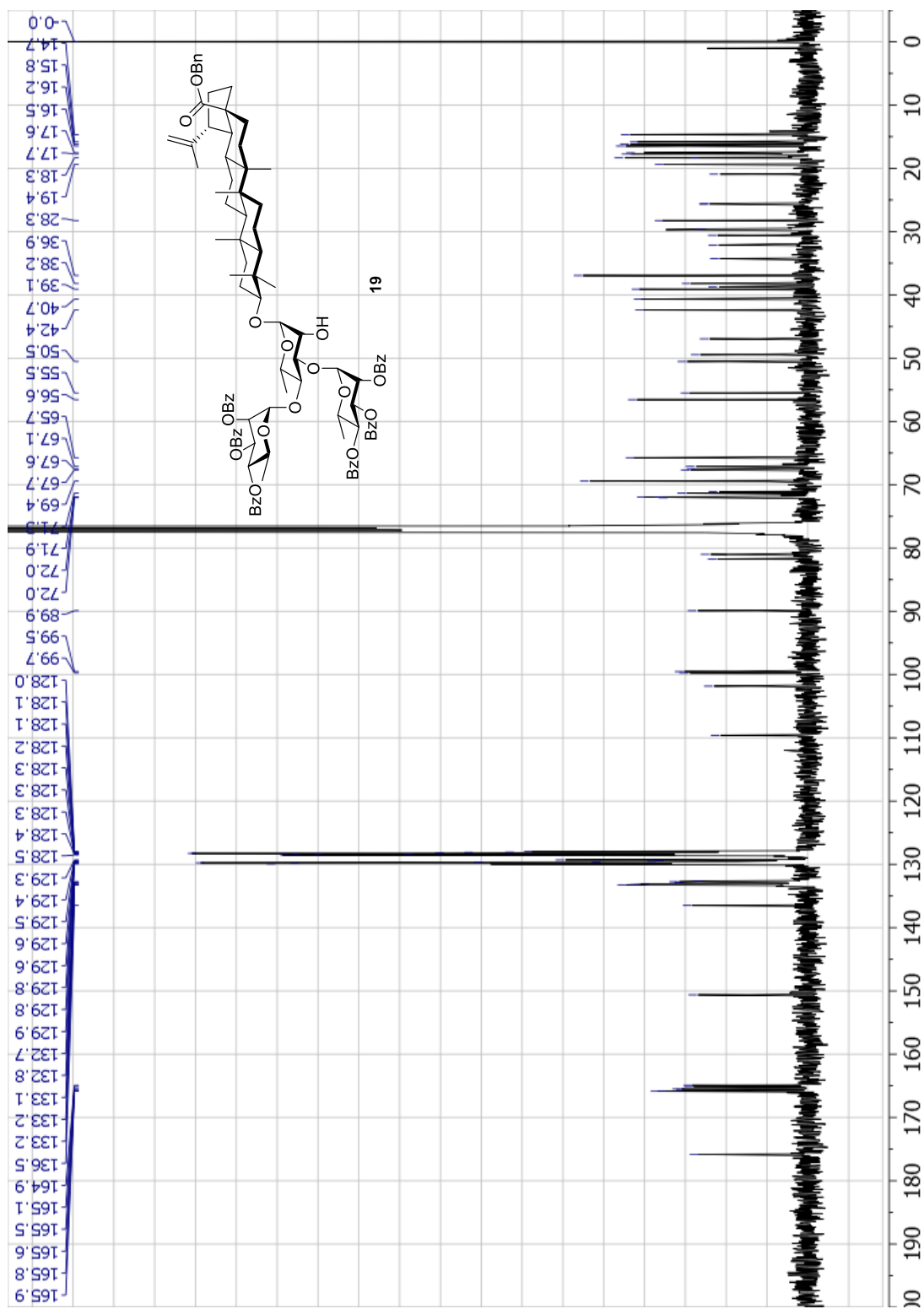
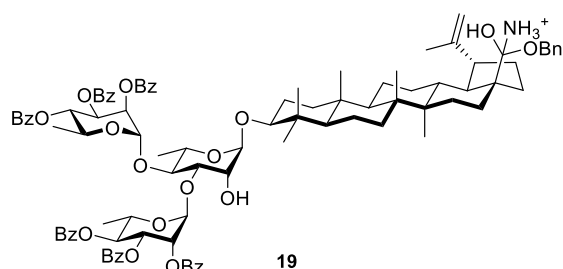
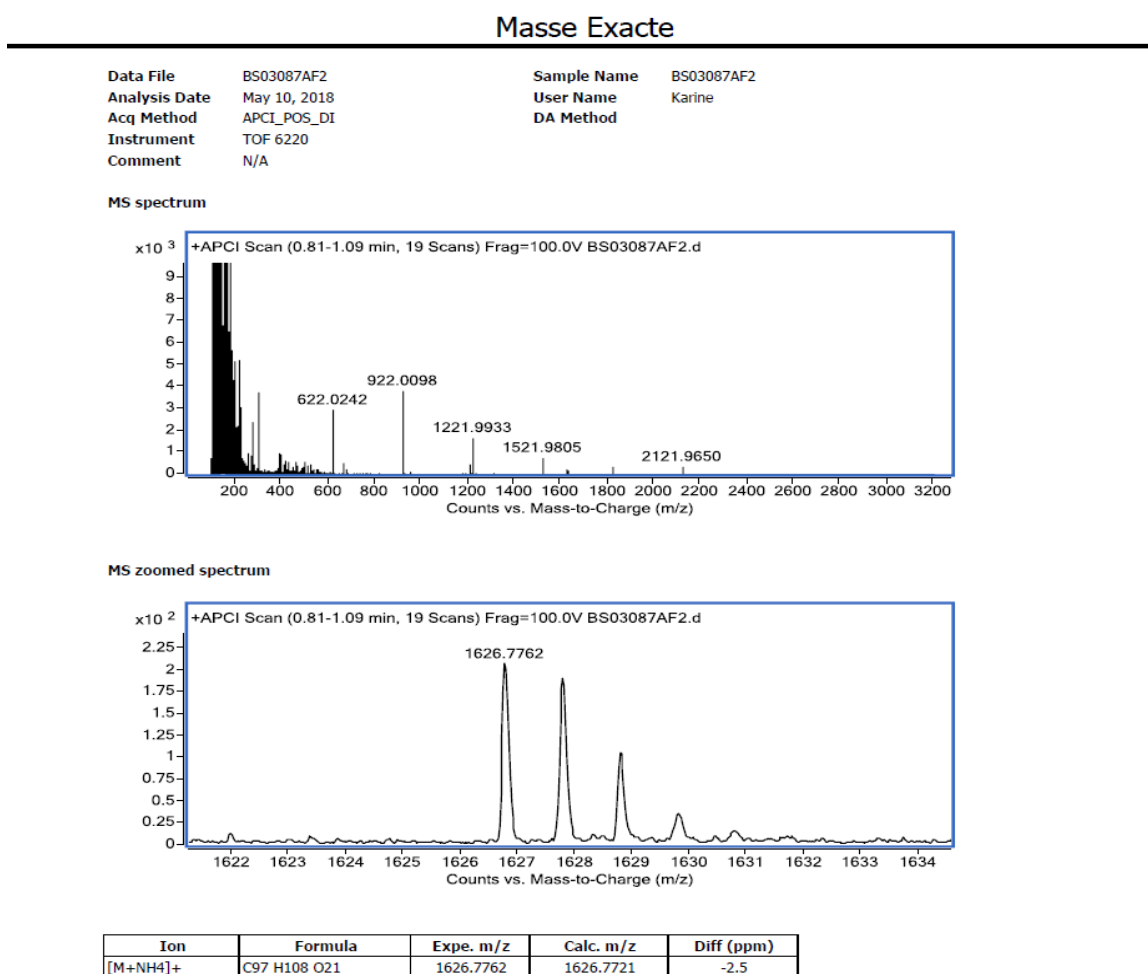


Figure S24. HRMS spectra of **19**



Chemical Formula: C₉₇H₁₁₂NO₂₁⁺
 Exact Mass: 1626.7721
 Molecular Weight: 1627.9485

Figure S25. ^1H NMR spectrum of **5** ($\text{DMSO-}d_6$ + 1 drop H_2O , 400 MHz)

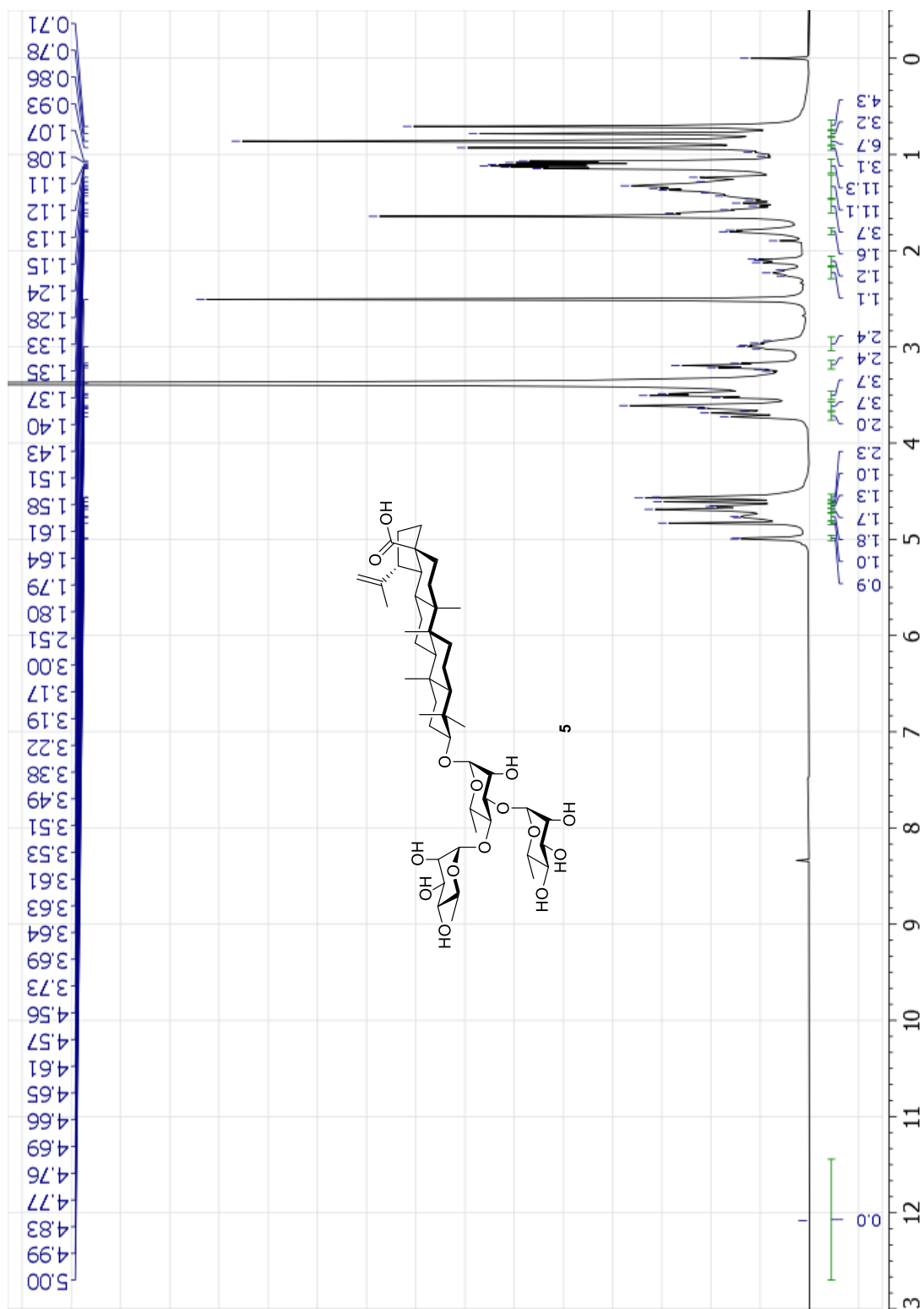


Figure S26. ^{13}C NMR spectra of **5** (DMSO- d_6 + 1 drop H_2O , 100 MHz)

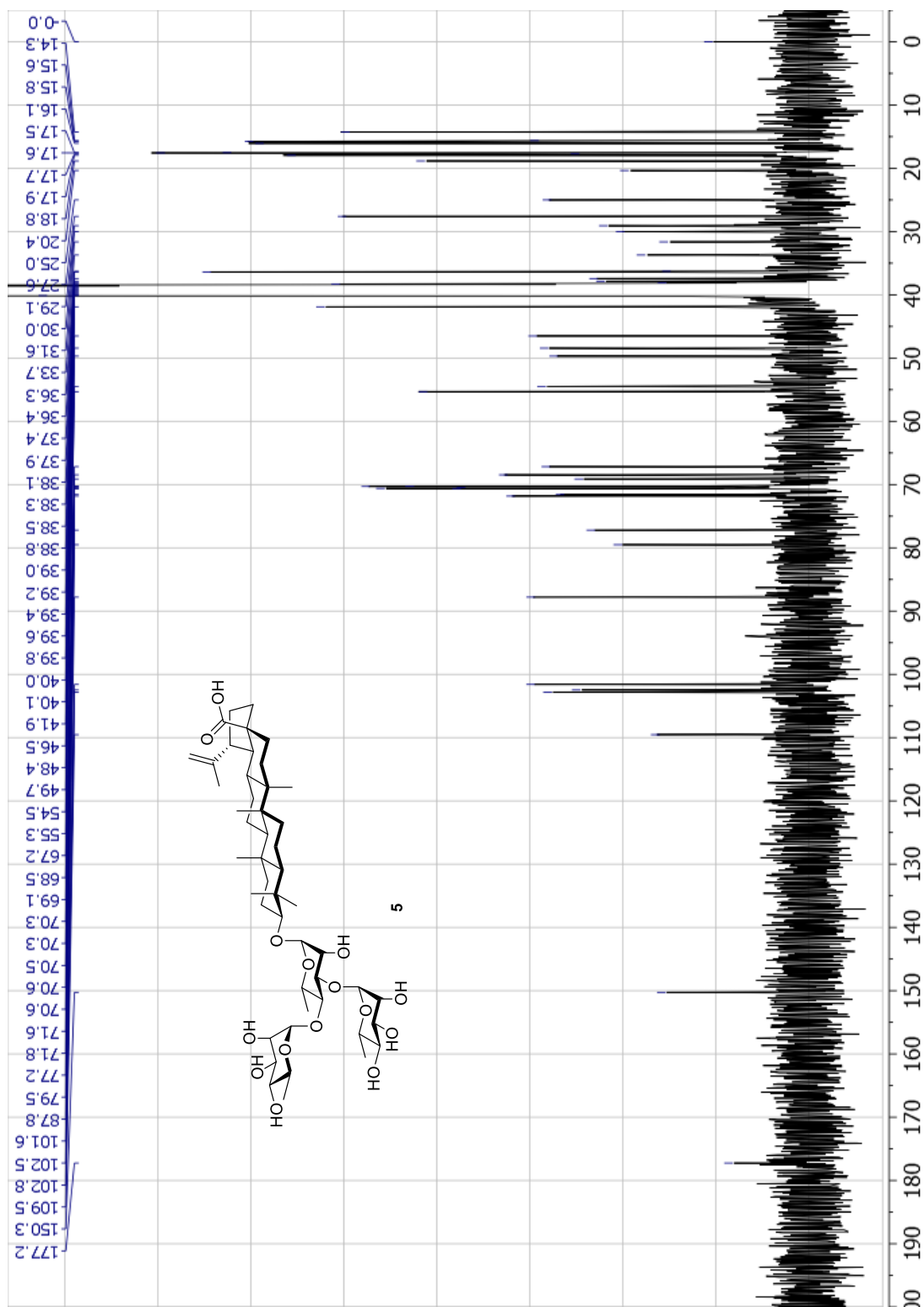


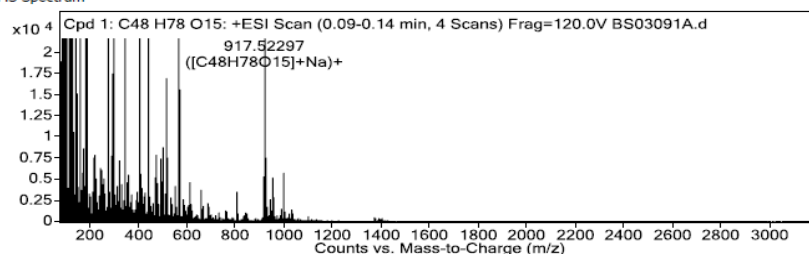
Figure S27. HRMS spectra of **5**

Rapport de masse exacte

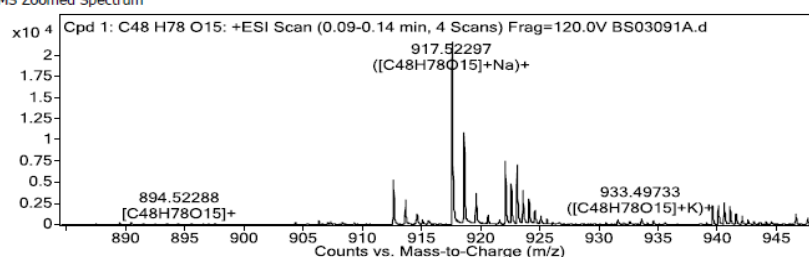
Data File BS03091A.d Sample Name BS03091A
Sample Type Sample Position P1-C2
Analysis Date 5/23/2018 2:50:04 PM User Name TNT
Acq Method ESI_POS_DI.m InstrumentName TOF 6224

Comment

MS Spectrum



MS Zoomed Spectrum



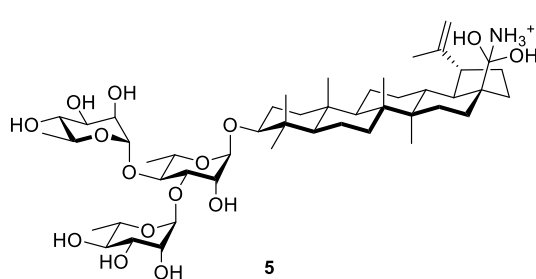
MS Spectrum Peak List

Ion	Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+NH4)+	C48H78O15	5316.61	912.56823	912.5679	-0.36
(M+Na)+	C48H78O15	21660.78	917.52297	917.52329	0.35

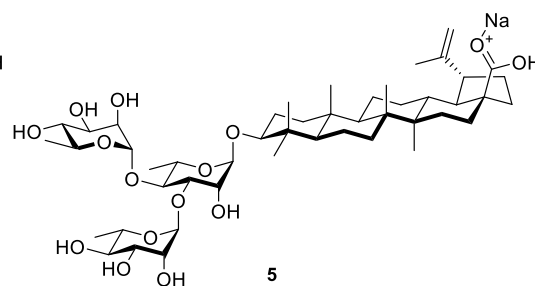
 Centre Regional de Spectrometrie de Masse
Université de Montreal

Sous la supervision de Dr. Furtos

Page 1 of 1



Chemical Formula: $C_{48}H_{82}NO_{15}^{+}$
Exact Mass: 912.5679
Molecular Weight: 913.1755



Chemical Formula: $C_{48}H_{78}NaO_{15}^{+}$
Exact Mass: 917.5233
Molecular Weight: 918.1262

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

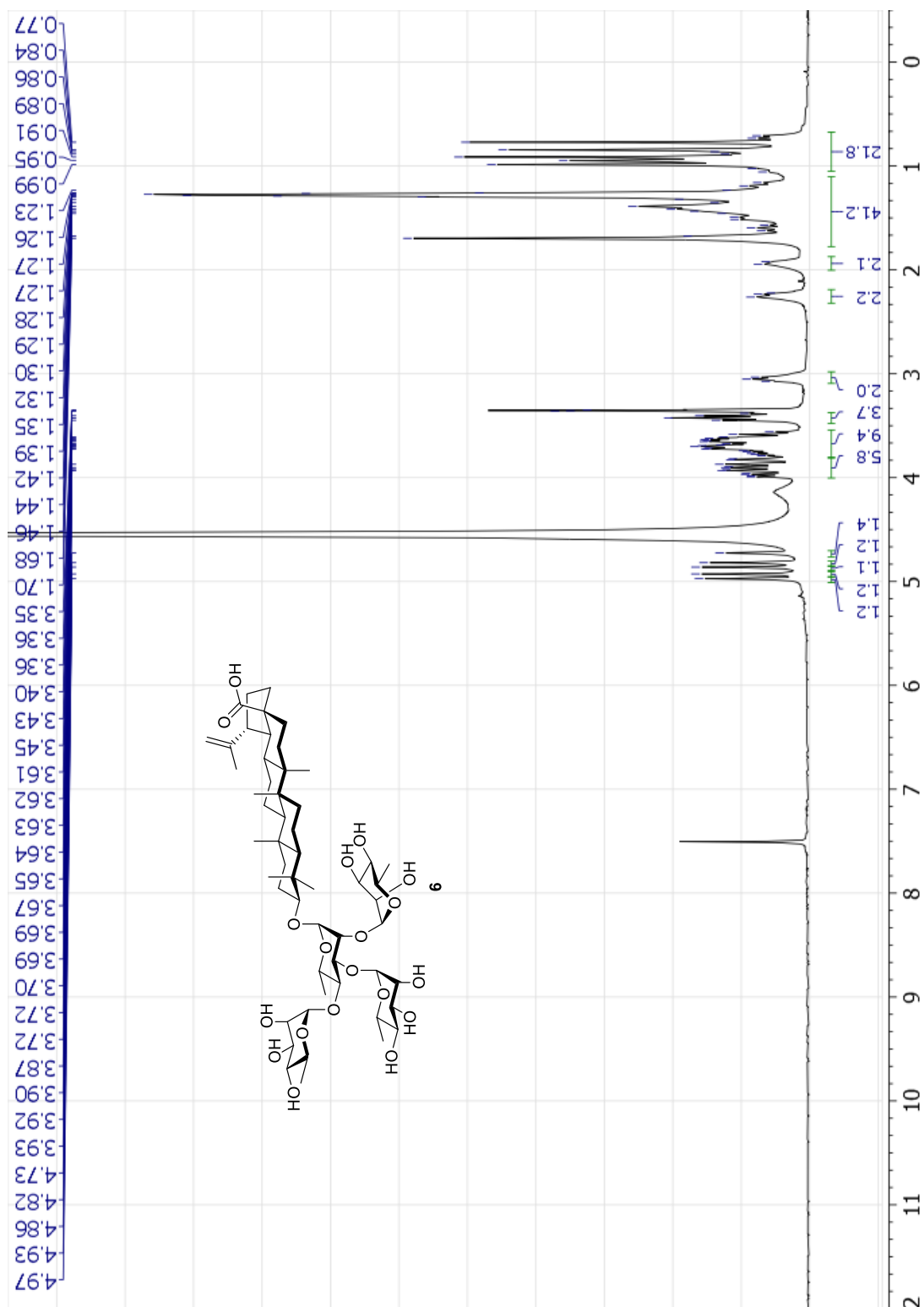


Figure S29. ^{13}C NMR spectra of **6** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 100 MHz)

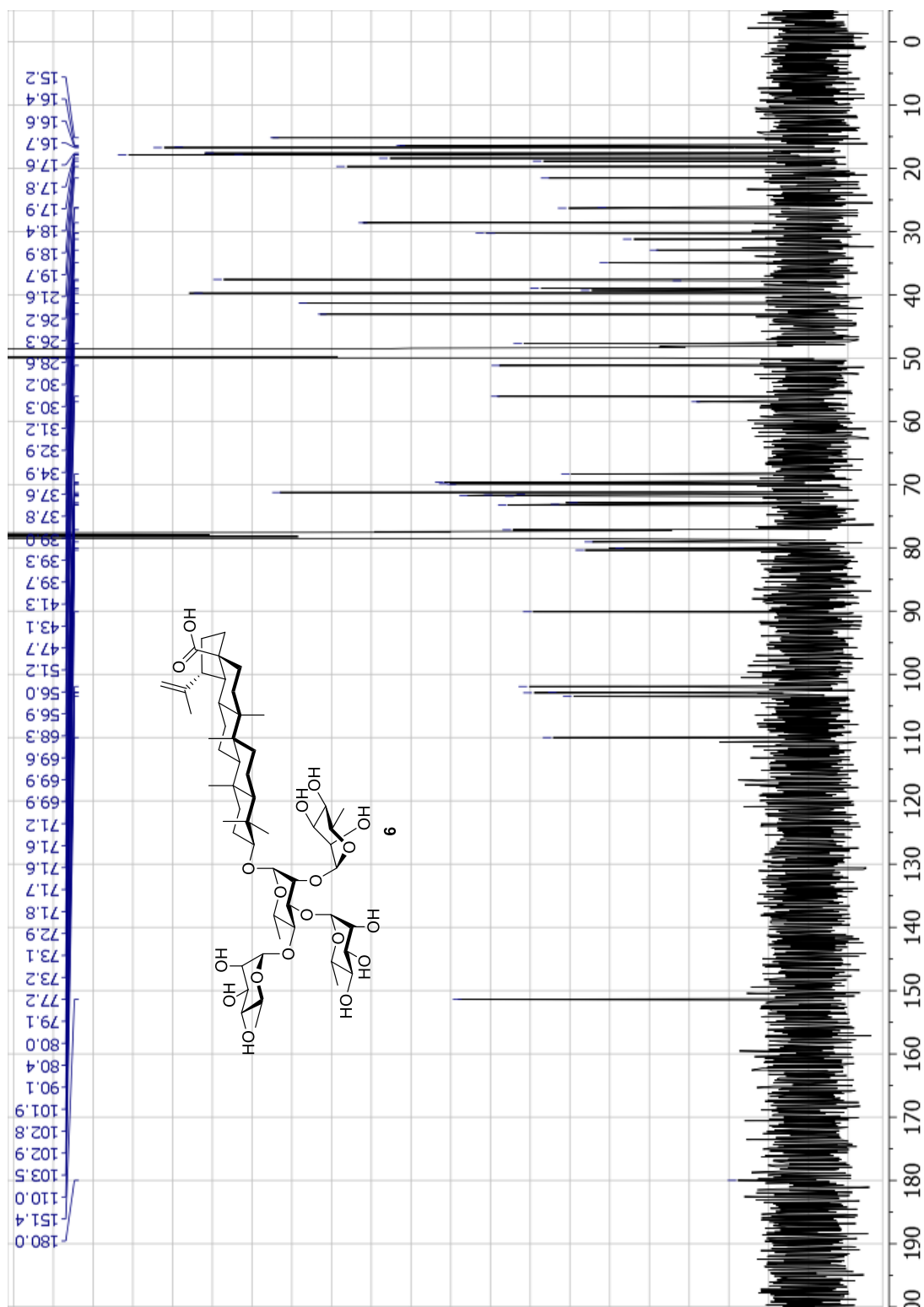
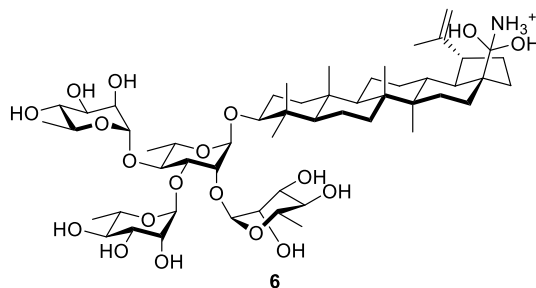
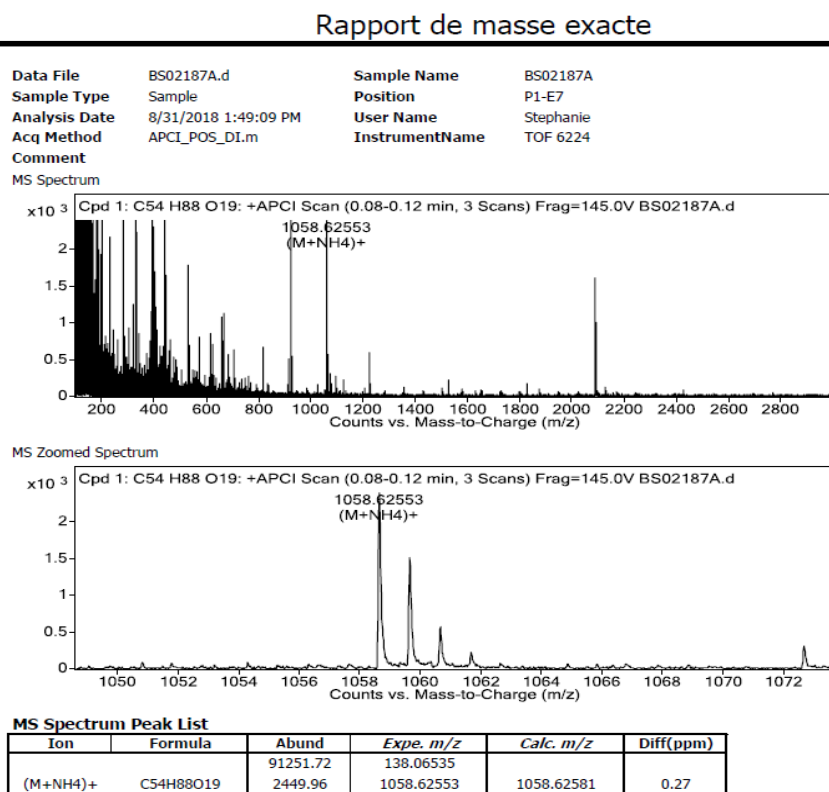


Figure S30. HRMS spectra of **6**



Chemical Formula: C₅₄H₉₂NO₁₉⁺
 Exact Mass: 1058.6258
 Molecular Weight: 1059.3175

Figure S31. ^1H NMR spectrum of **21** (CDCl_3 , 400 MHz)

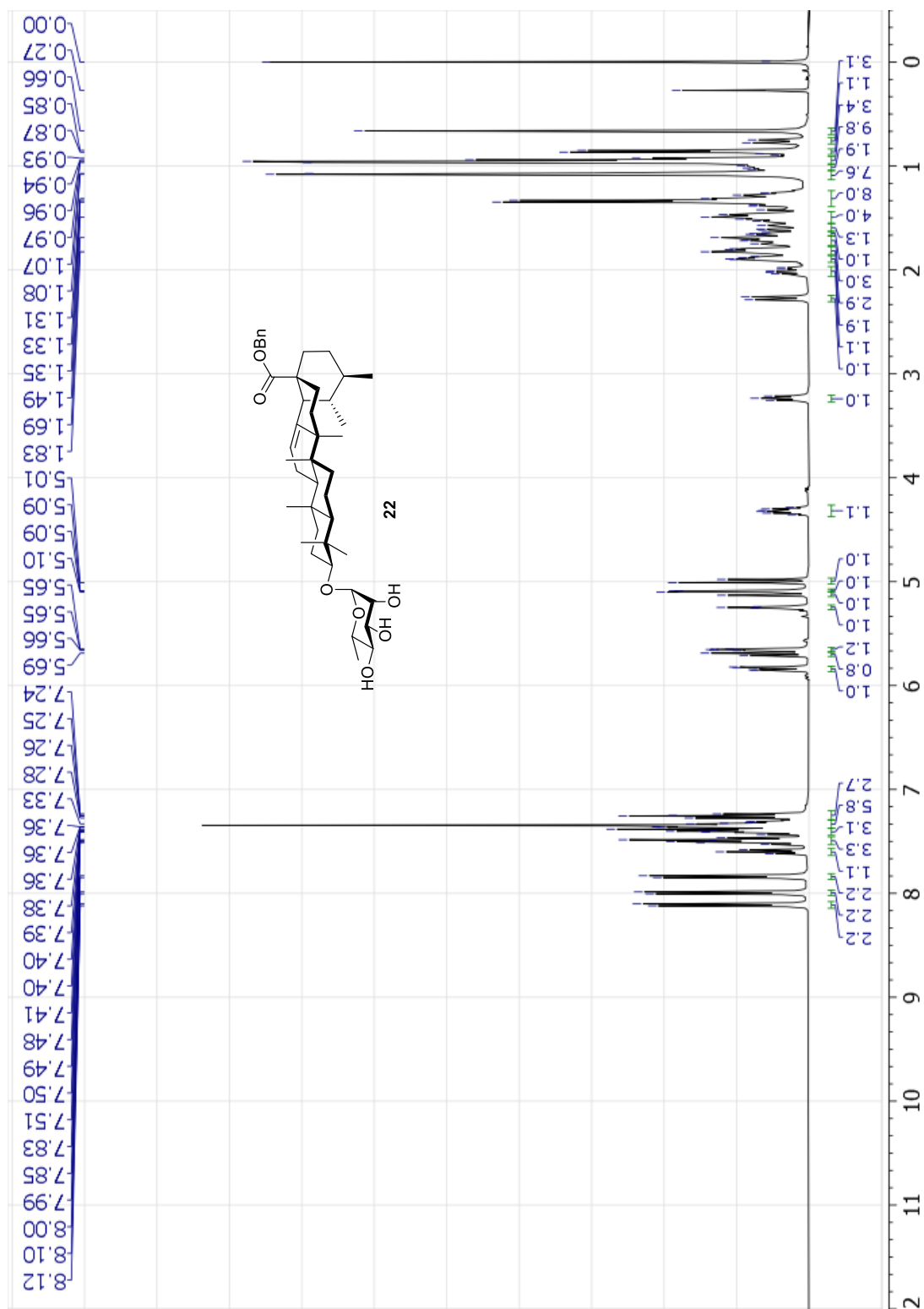


Figure S32. ^{13}C NMR spectra of **21** (CDCl_3 , 100 MHz)

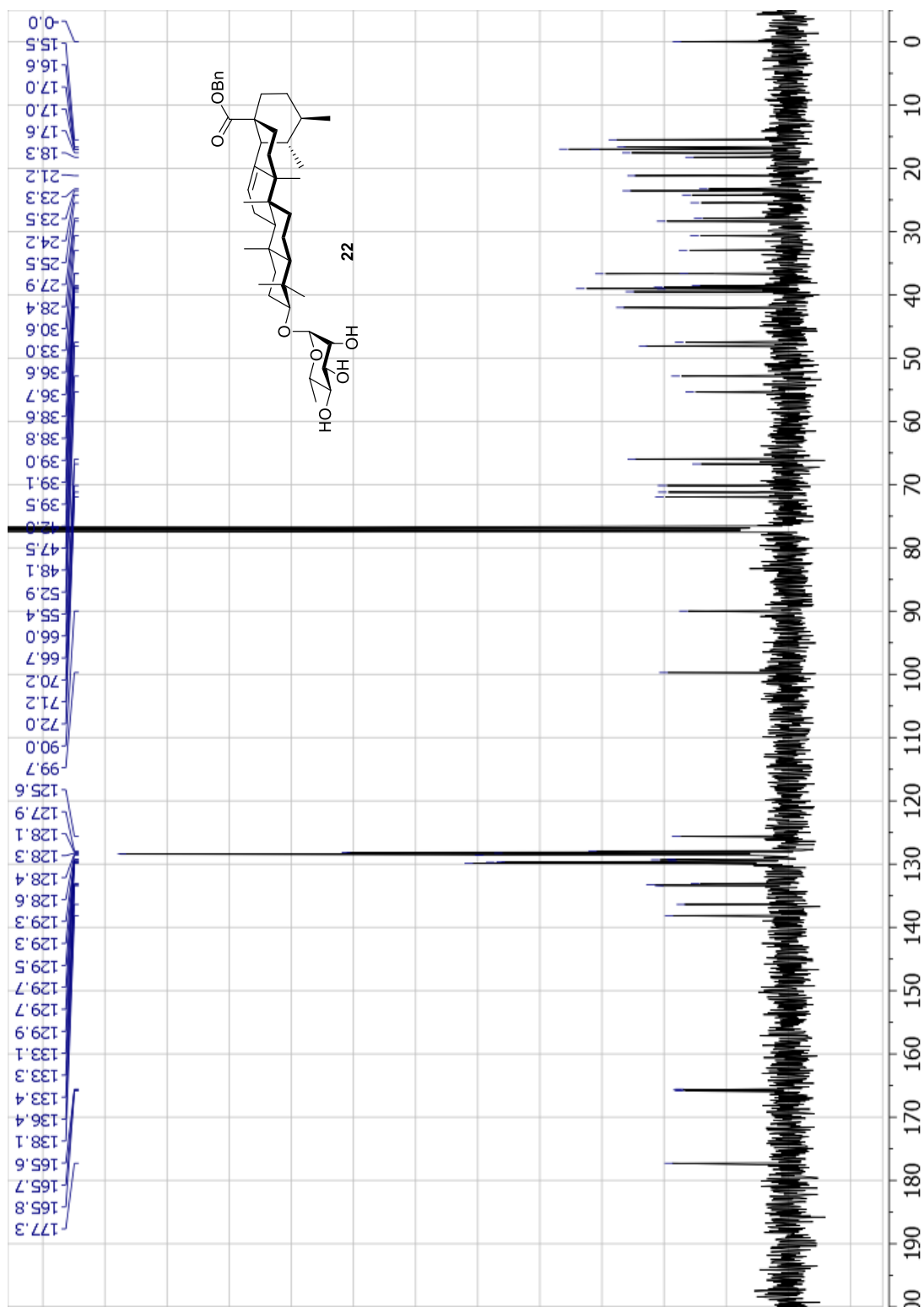


Figure S33. HRMS spectra of **21**

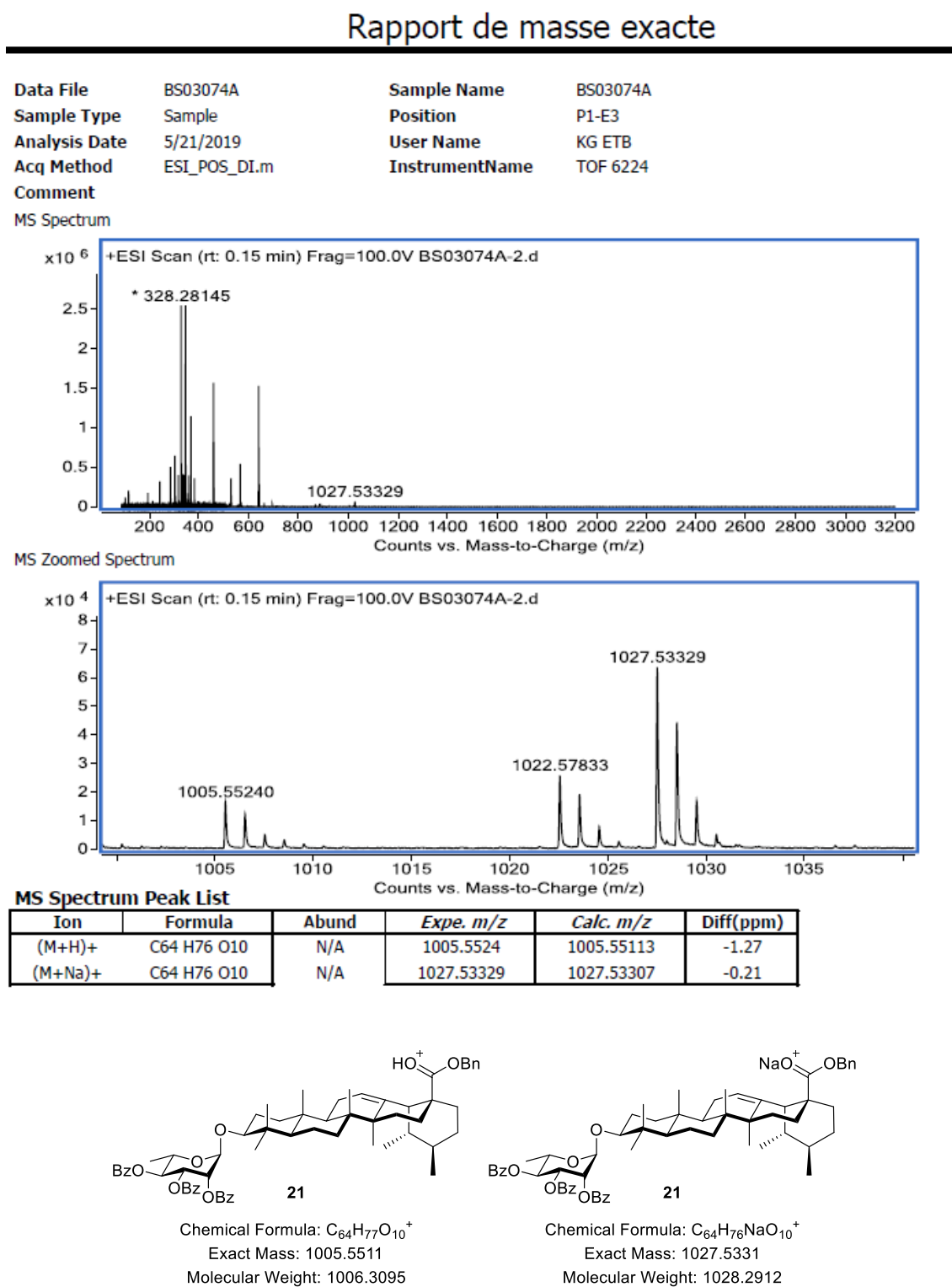


Figure S34. ^1H NMR spectrum of **22** (CDCl_3 , 400 MHz)

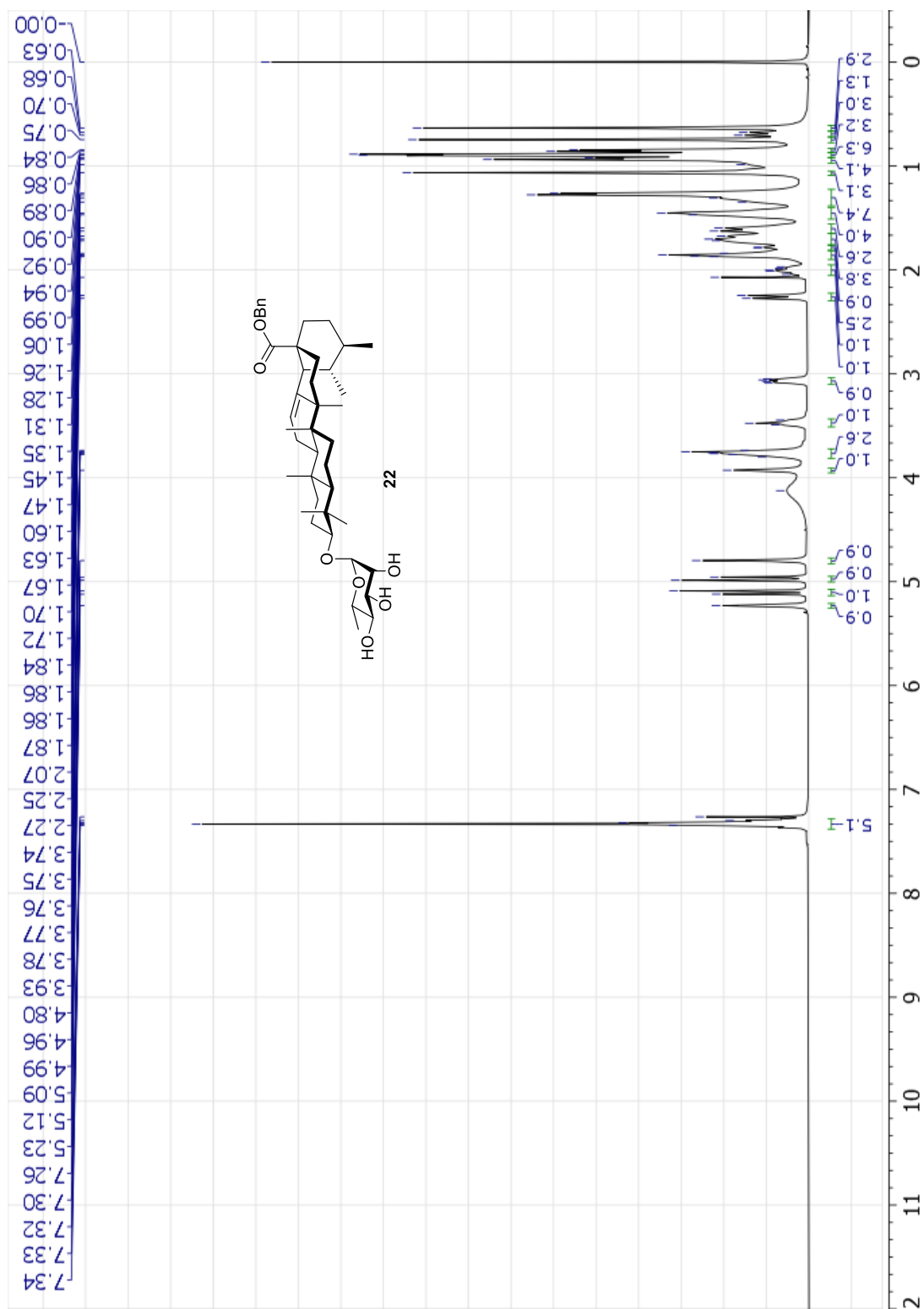


Figure S35. ^{13}C NMR spectra of **22** (CDCl_3 , 100 MHz)

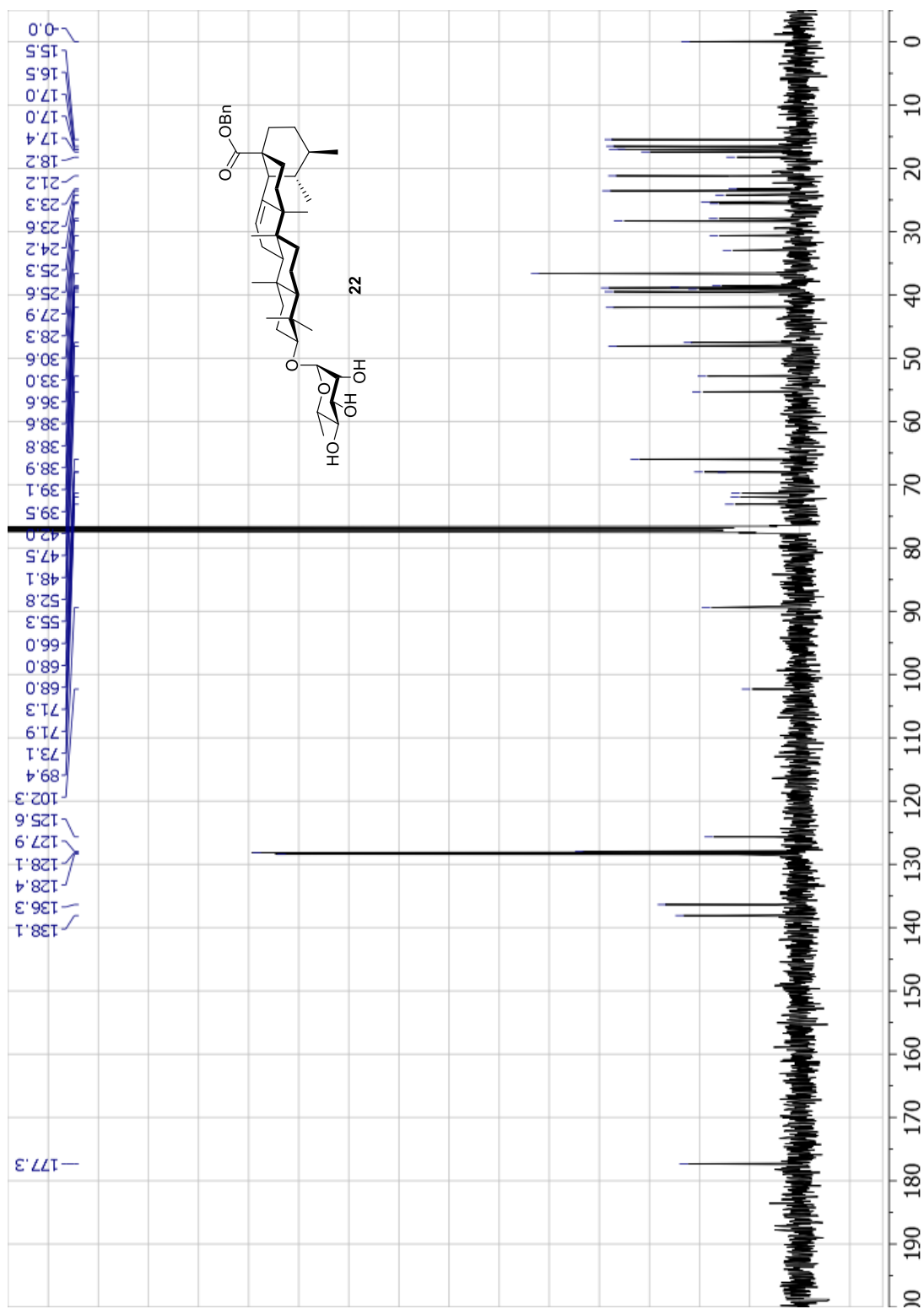


Figure S36. HRMS spectra of **22**

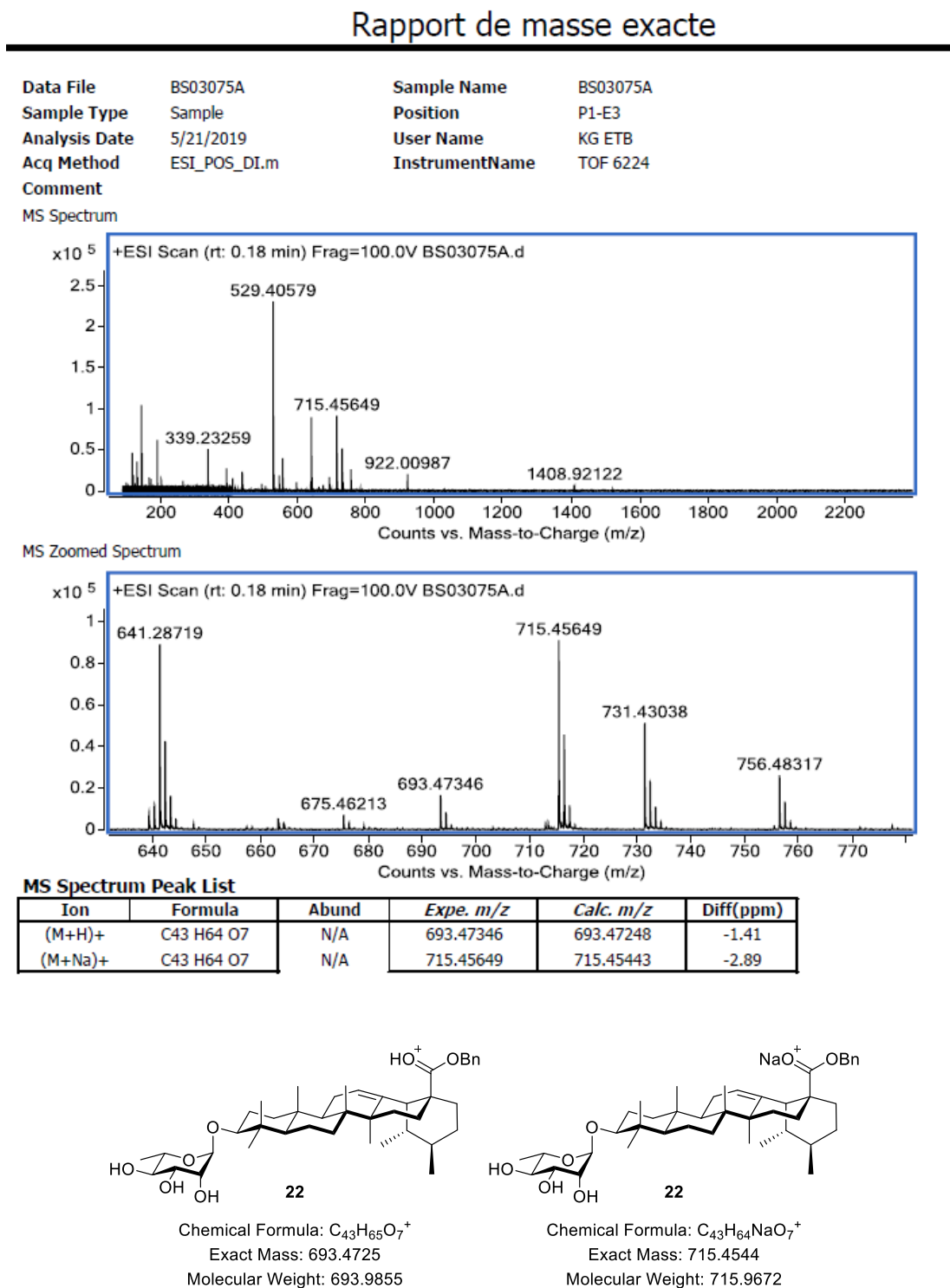


Figure S37. ^1H NMR spectrum of **7** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 400 MHz)

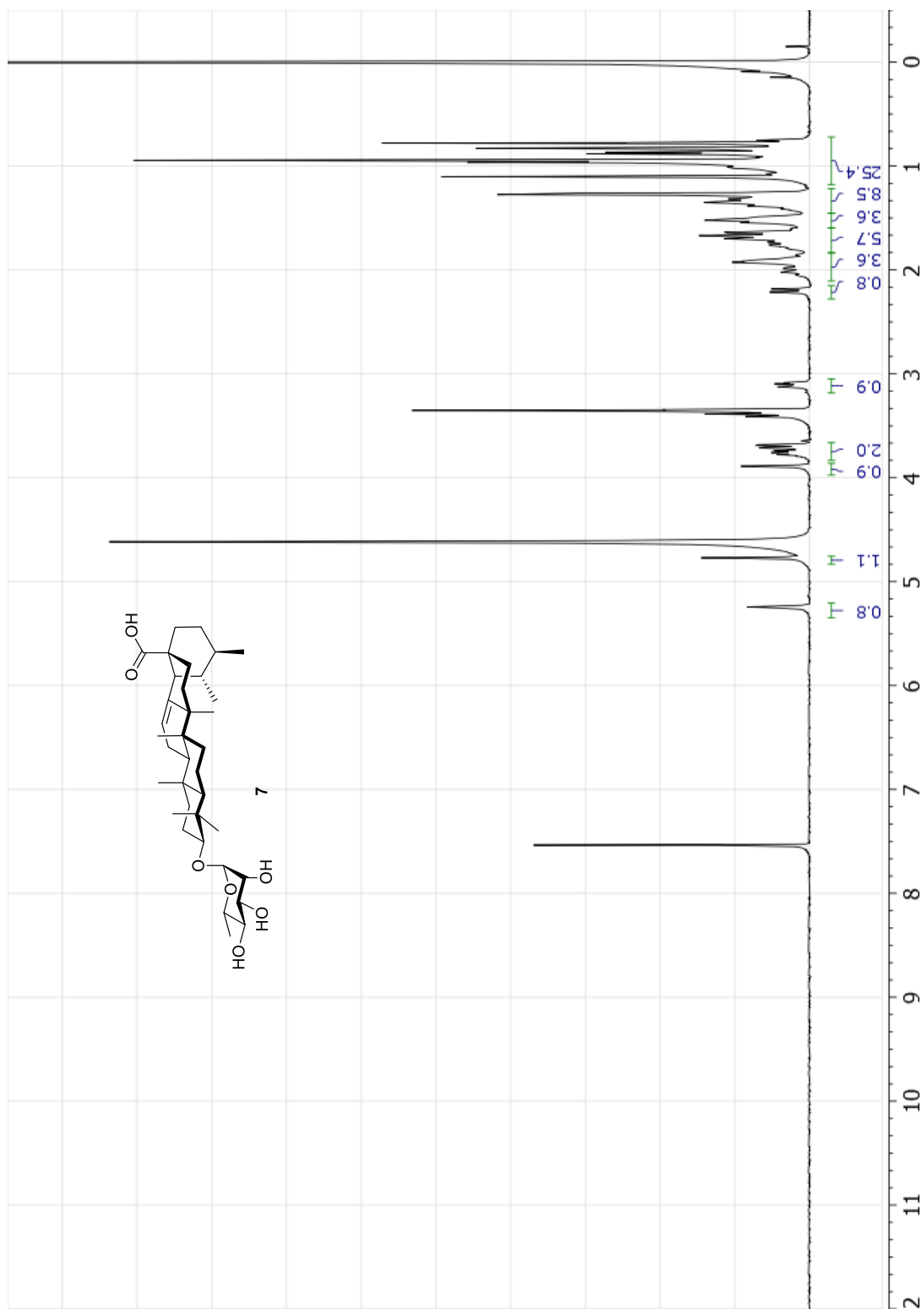


Figure S38. ^{13}C NMR spectra of **7** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 100 MHz)

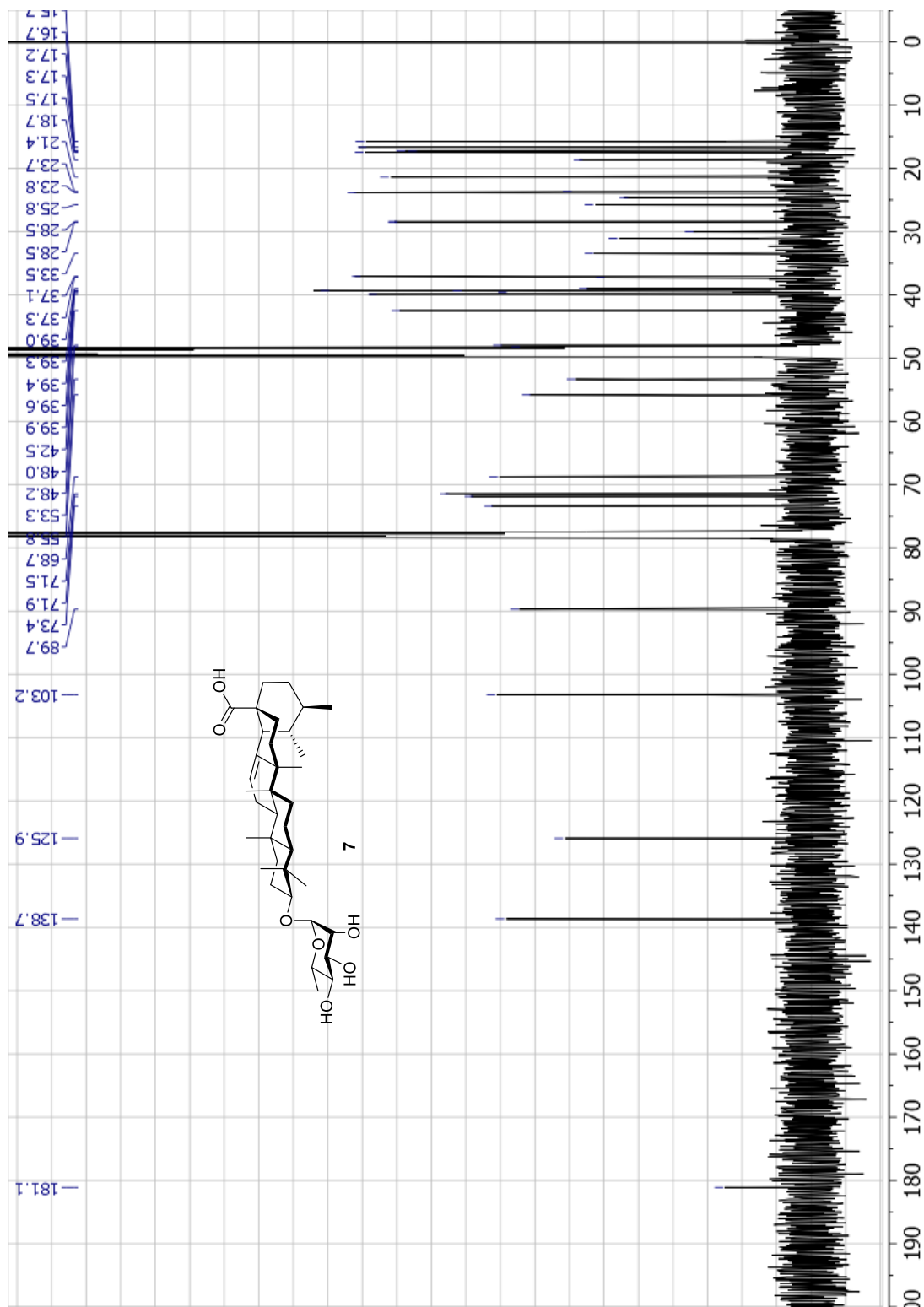
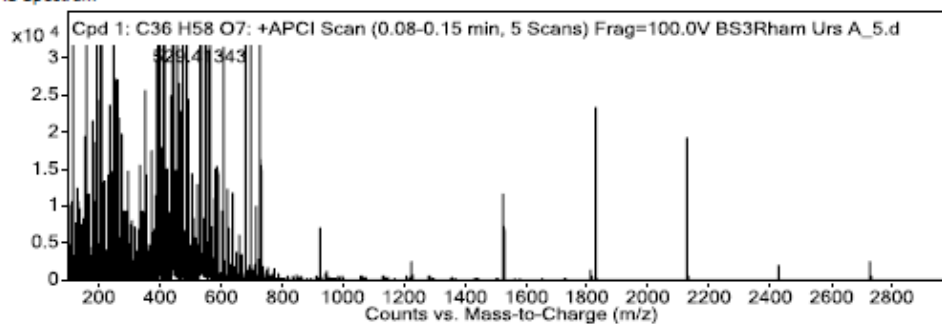


Figure S39. HRMS spectra of **7**

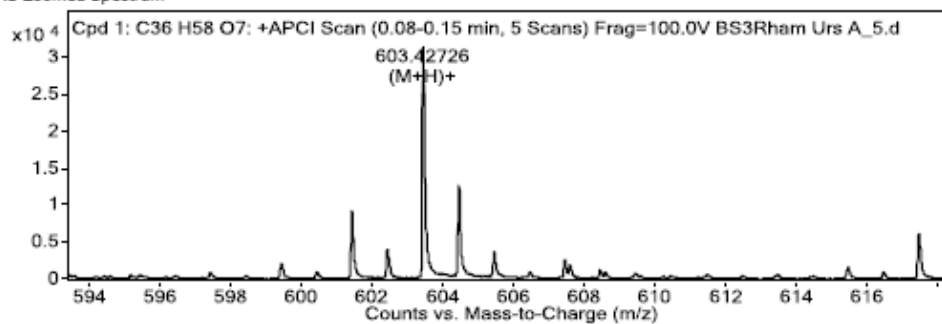
Rapport de masse exacte

Data File	BS3Rham Urs A_5.d	Sample Name	BS3Rham Urs A
Sample Type	Sample	Position	P1-C7
Analysis Date	9/6/2019 9:22:10 AM	User Name	Im
Acq Method	APCI_POS_DI.m	InstrumentName	TOF 6224
Comment			

MS Spectrum

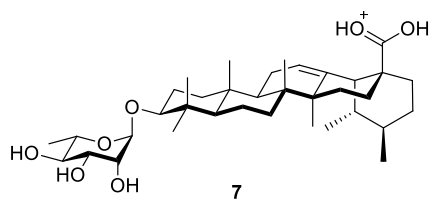


MS Zoomed Spectrum



MS Spectrum Peak List

Ion	Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+H) ⁺	C ₃₆ H ₅₈ O ₇	1659762.15	529.41343	603.42553	-2.86
		31522.25	603.42726		



Chemical Formula: C₃₆H₅₉O₇⁺

Exact Mass: 603,4255

Molecular Weight: 603,8489

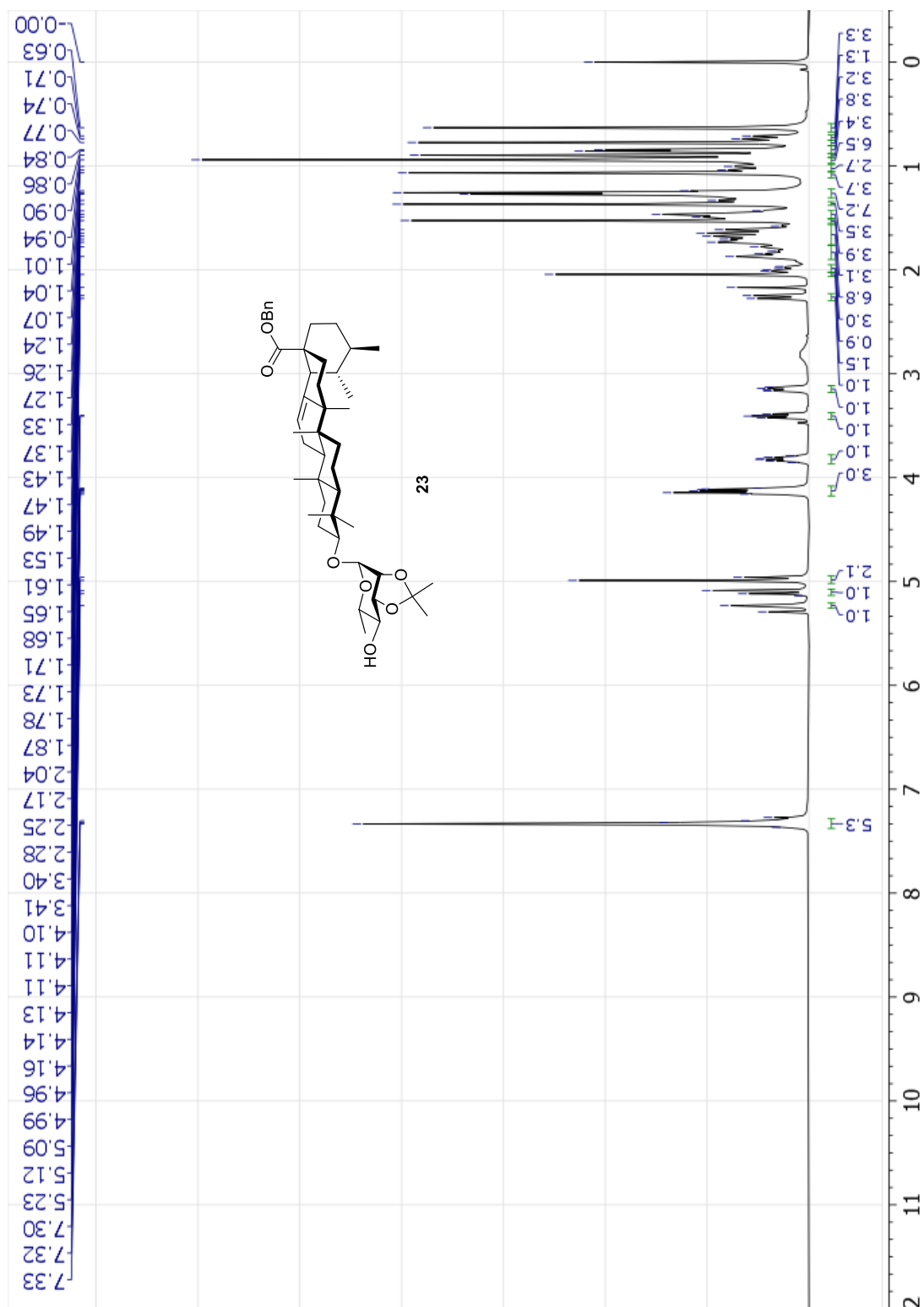


Figure S41. ^{13}C NMR spectra of **23** (CDCl_3 , 100 MHz)

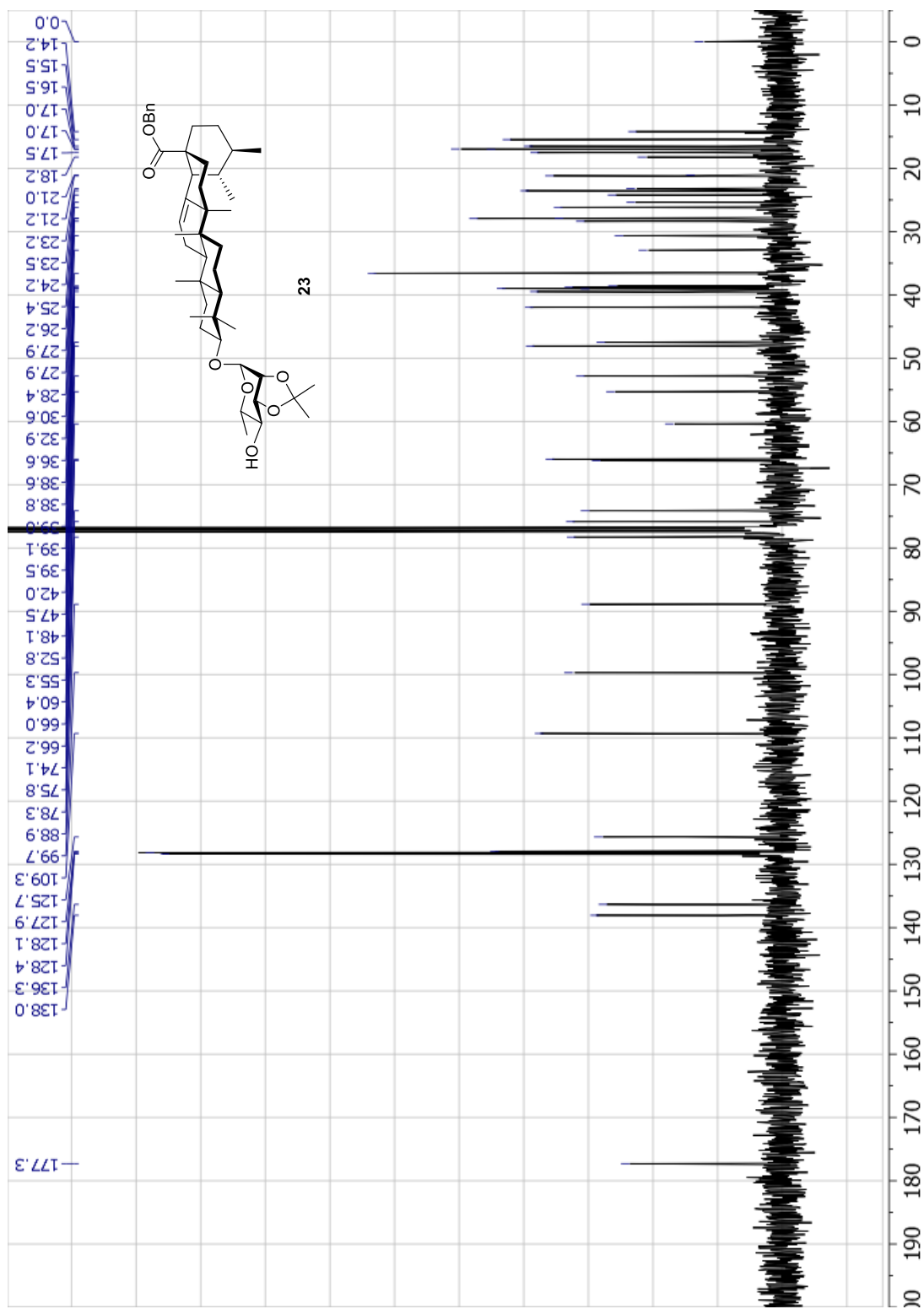


Figure S42. HRMS spectra of **23**

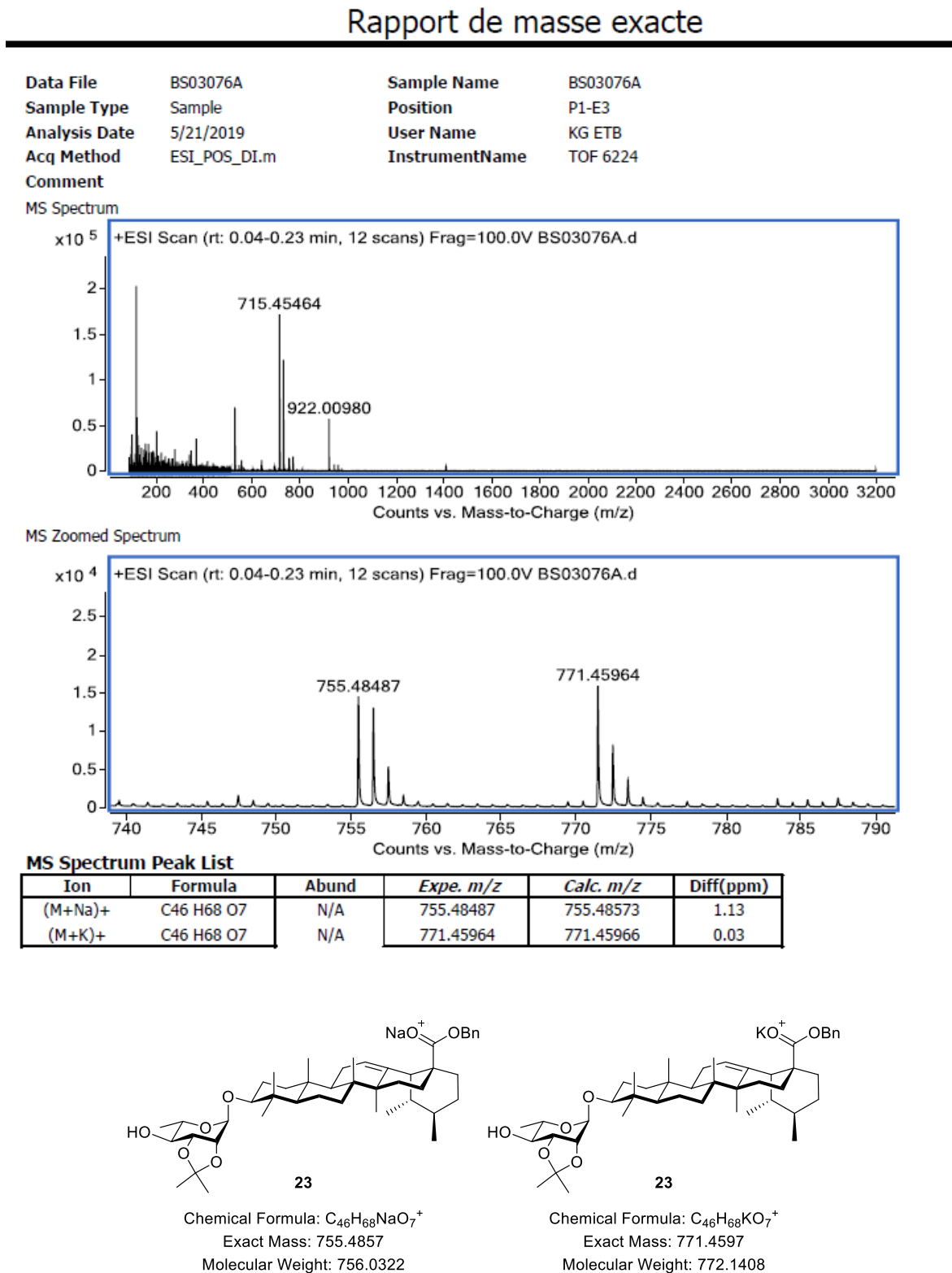
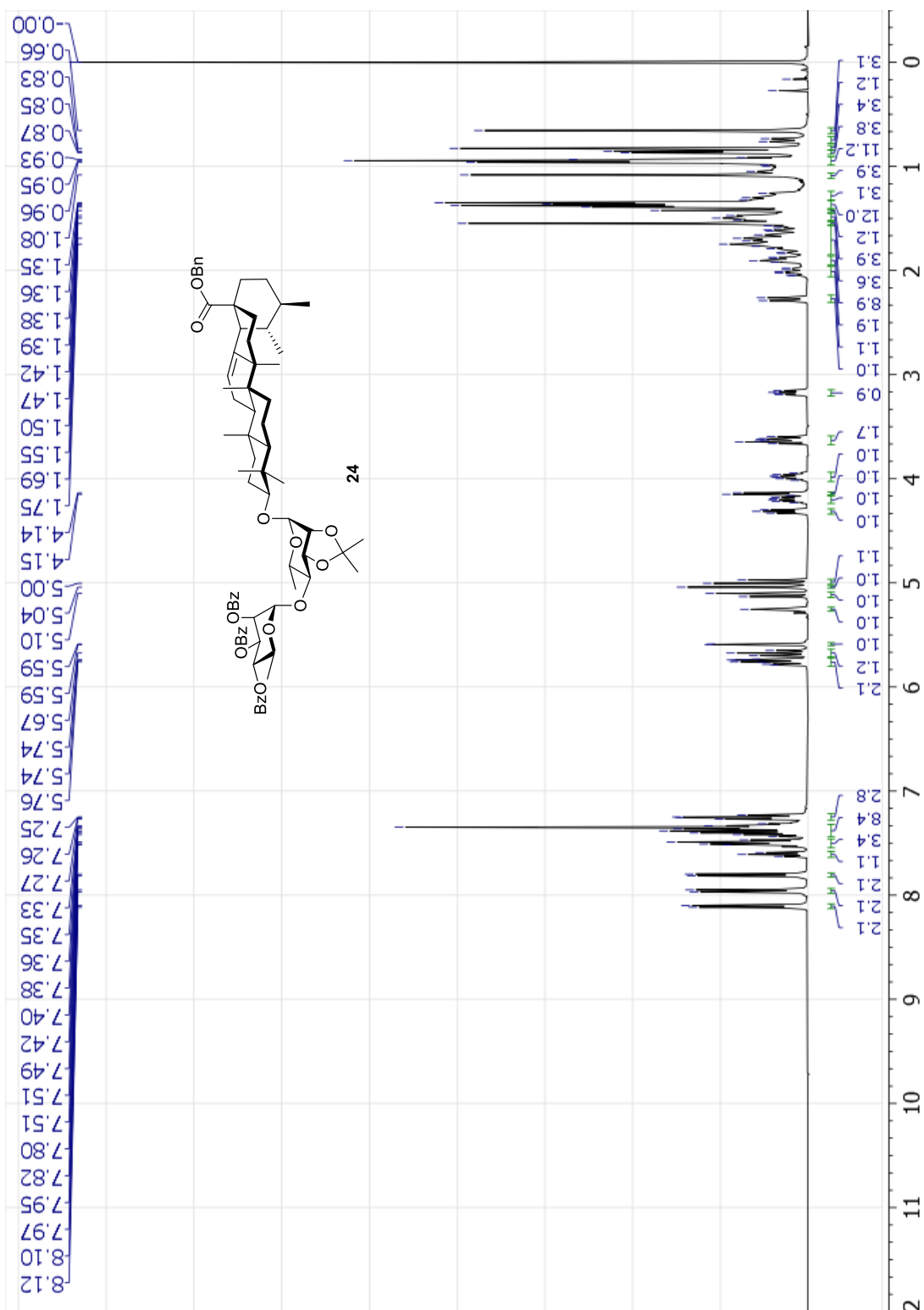


Figure S43. ^1H NMR spectrum of **24** (CDCl_3 , 400 MHz)



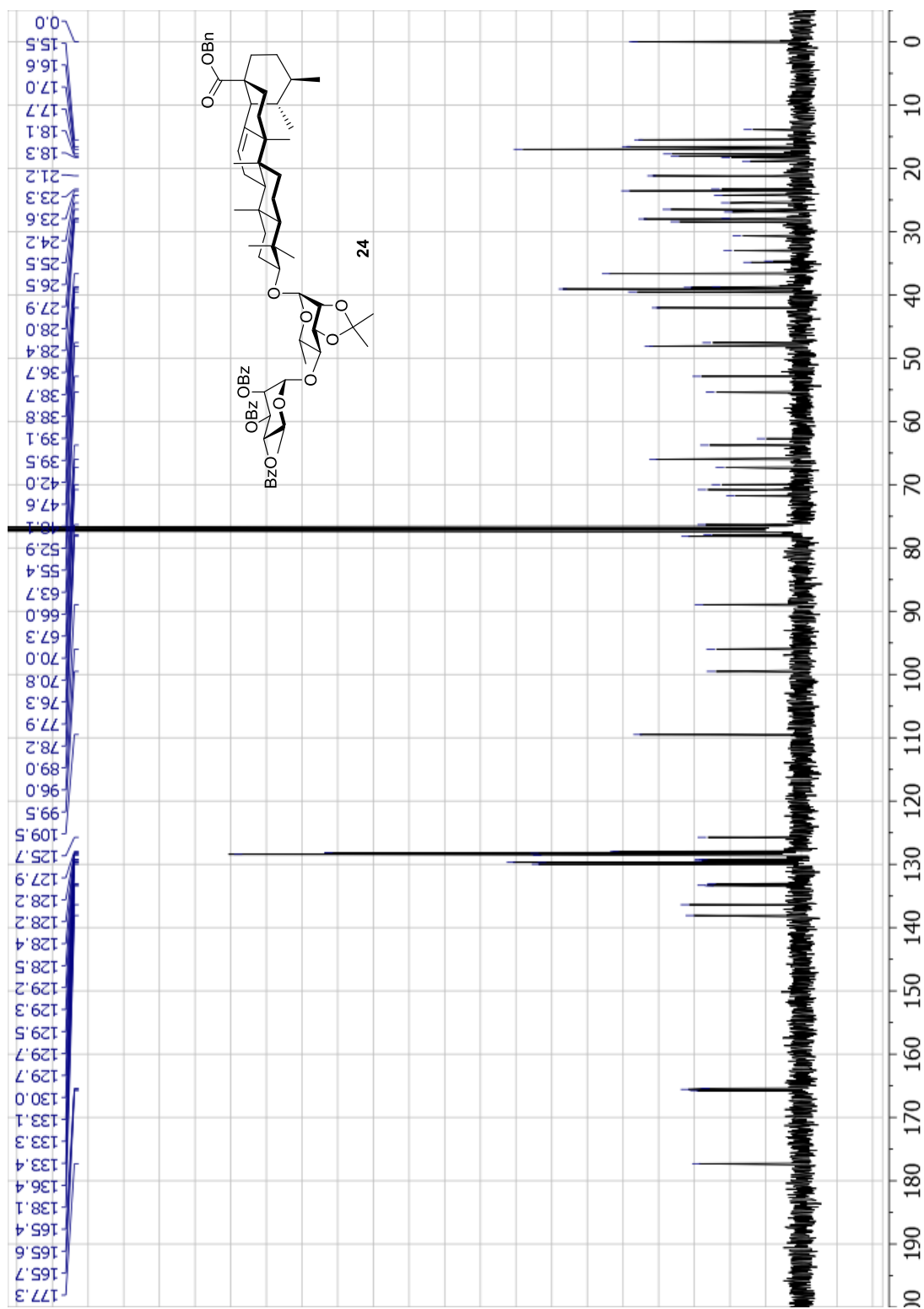
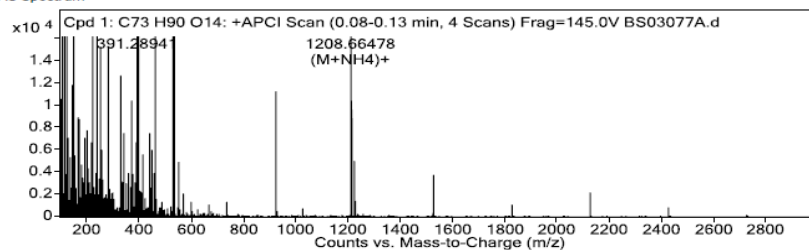


Figure S45. HRMS spectra of 24

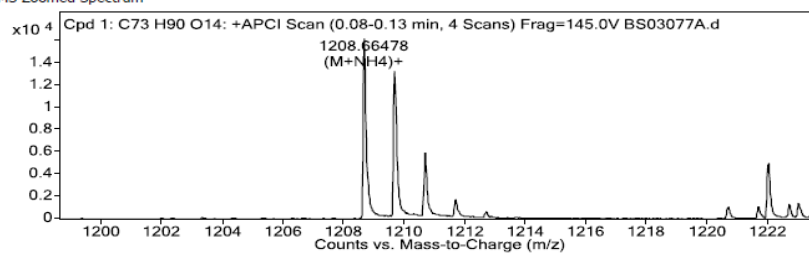
Rapport de masse exacte

Data File BS03077A.d Sample Name BS03077A
Sample Type Sample Position P2-C5
Analysis Date 3/21/2018 11:27:11 AM User Name KG
Acq Method APCI_POS_DI.m InstrumentName TOF 6224
Comment

MS Spectrum



MS Zoomed Spectrum



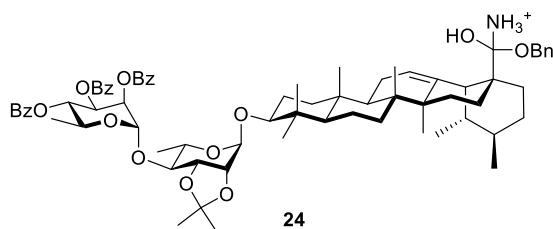
MS Spectrum Peak List

Ion	Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+NH4)+	C73H90O14	236071.89	391.28941		
		16633.2	1208.66478	1208.66688	1.74

 Centre Régional de Spectrométrie de Masse
Université de Montréal

Sous la supervision de Dr. Furtos

Page 1 of 1



Chemical Formula: C₇₃H₉₄NO₁₄⁺
Exact Mass: 1208.6669
Molecular Weight: 1209.5475

Figure S46. ^1H NMR spectrum of **25** (CDCl_3 , 400 MHz)

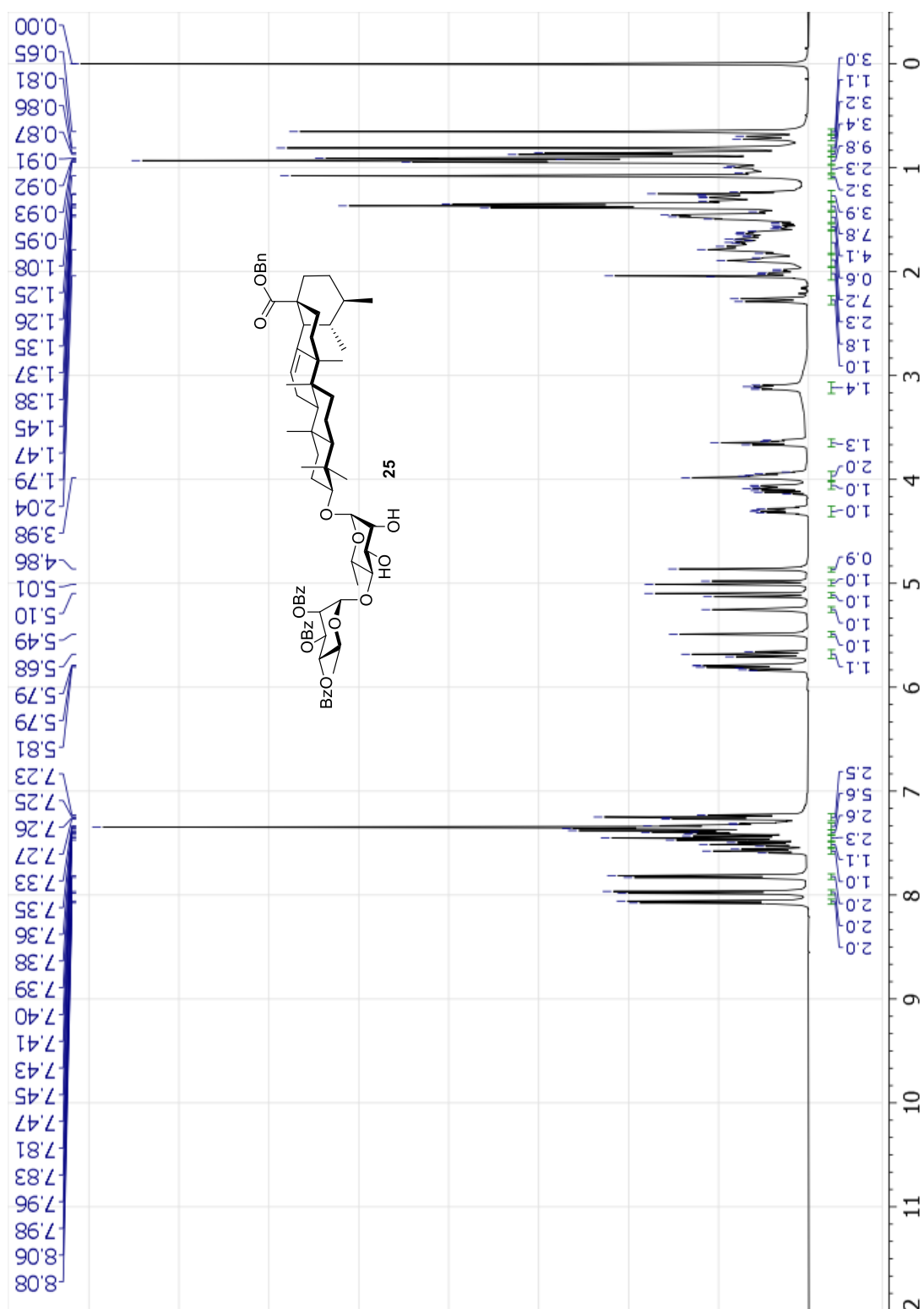


Figure S47. ^{13}C NMR spectra of **25** (CDCl_3 , 100 MHz)

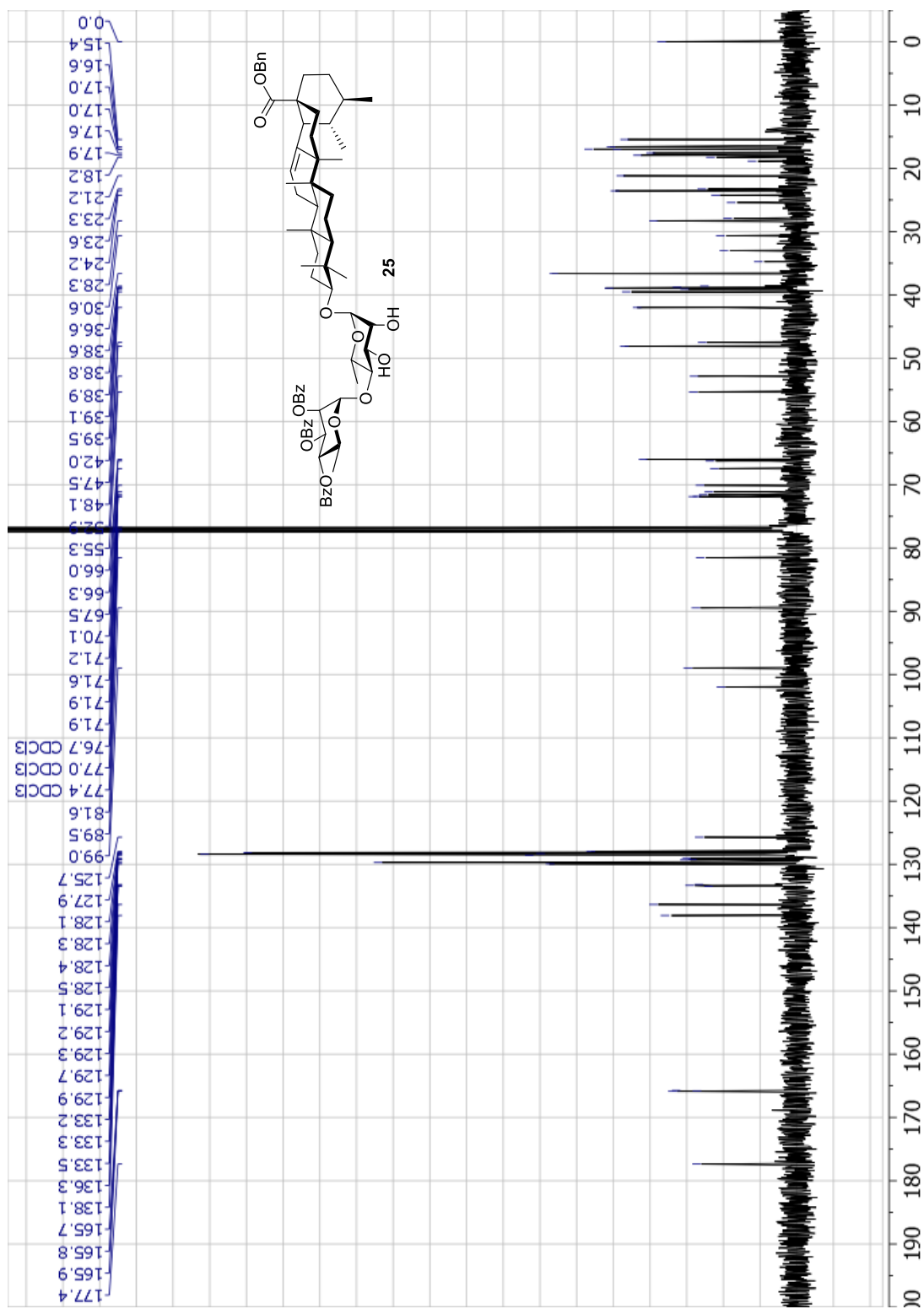
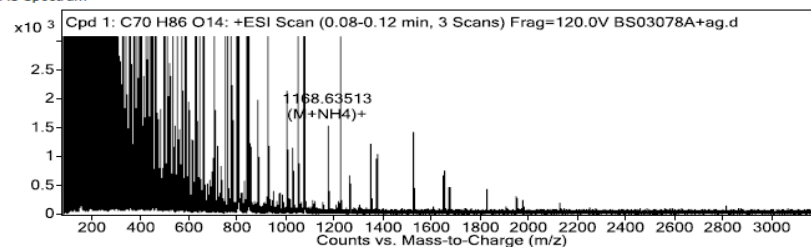


Figure S48. HRMS spectra of **25**

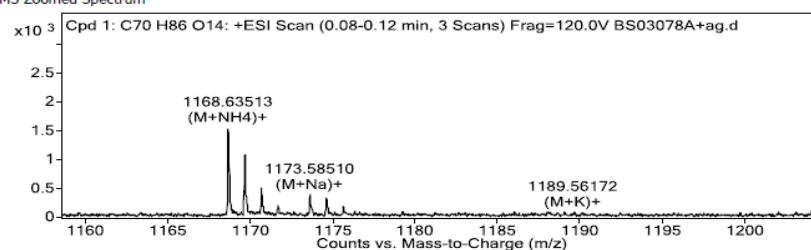
Rapport de masse exacte

Data File BS03078A+ag.d Sample Name BS03078A+ag
Sample Type Sample Position P2-C6
Analysis Date 3/9/2018 11:01:27 AM User Name KG
Acq Method ESI_POS_DI.m InstrumentName TOF 6224
Comment

MS Spectrum



MS Zoomed Spectrum



MS Spectrum Peak List

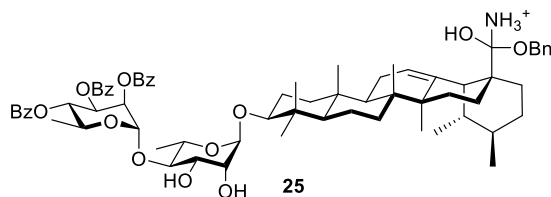
Ion	Formula	Abund	Expe. m/z	Calc. m/z	Diff(ppm)
(M+NH4)+	C70H86O14	1573.47	1168.63513	1168.63558	0.39
(M+Na)+	C70H86O14	410.76	1173.5851	1173.59098	5.01



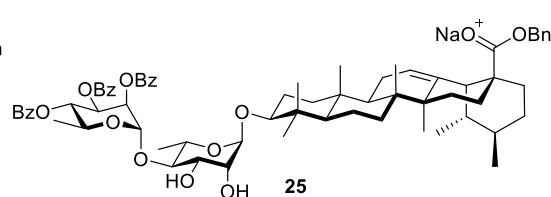
Centre Regional de Spectrométrie de Masse
Université de Montréal

Sous la supervision de Dr. Furtos

Page 1 of 1



Chemical Formula: C₇₀H₉₀NO₁₄⁺
Exact Mass: 1168.6356
Molecular Weight: 1169.4825



Chemical Formula: C₇₀H₈₆NaO₁₄⁺
Exact Mass: 1173.5910
Molecular Weight: 1174.4332

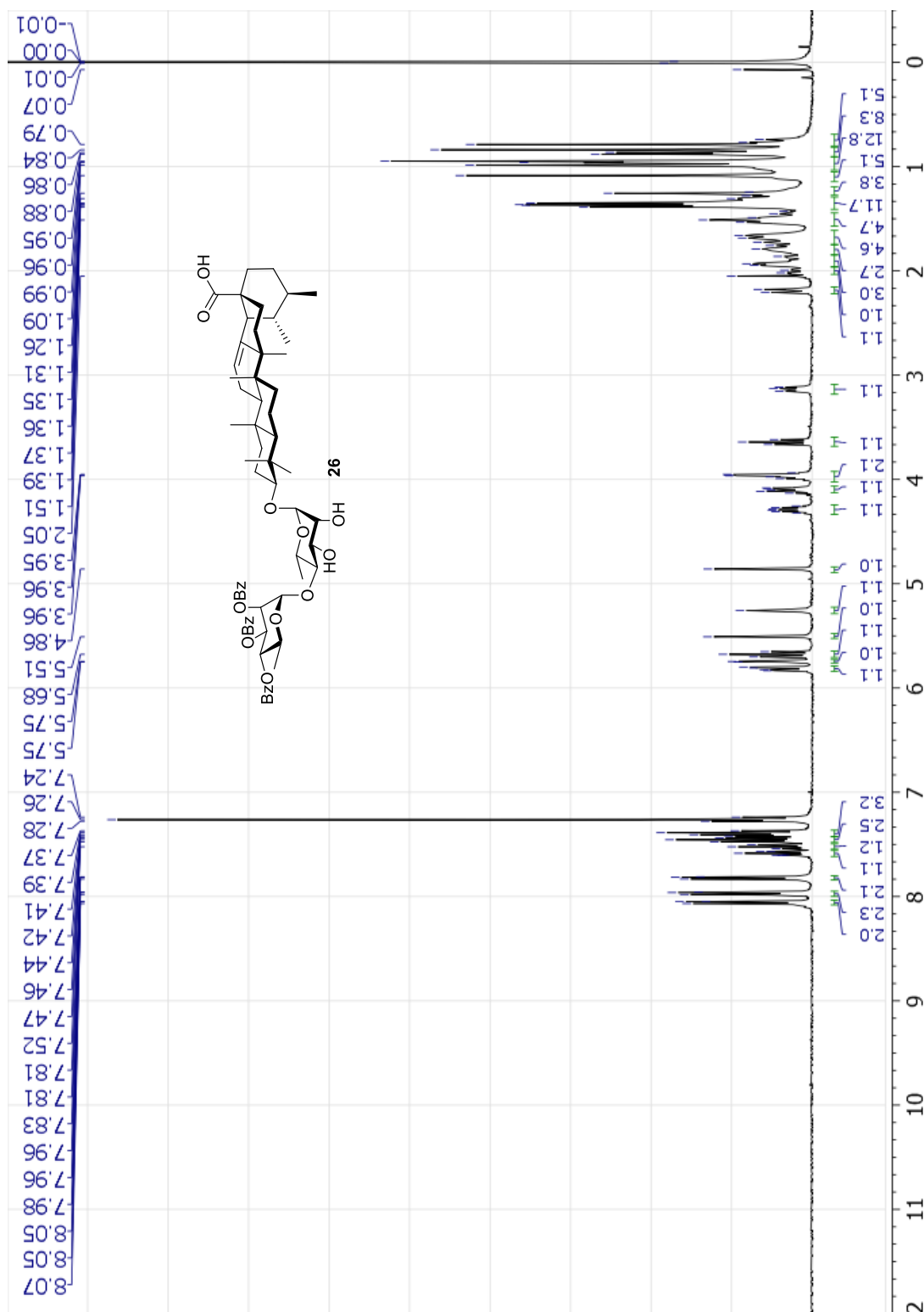


Figure S50. ^{13}C NMR spectra of **26** (CDCl_3 , 100 MHz)

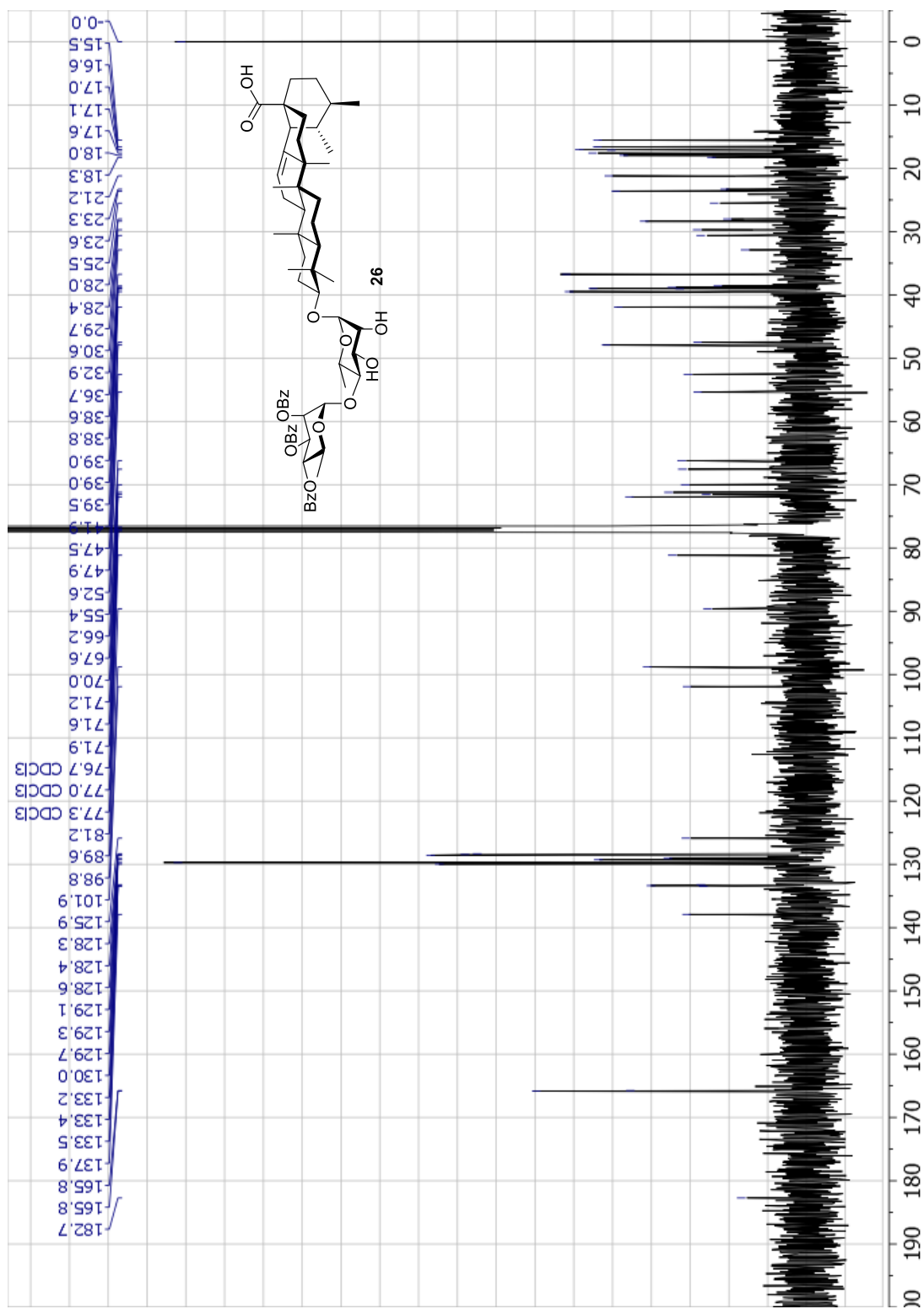
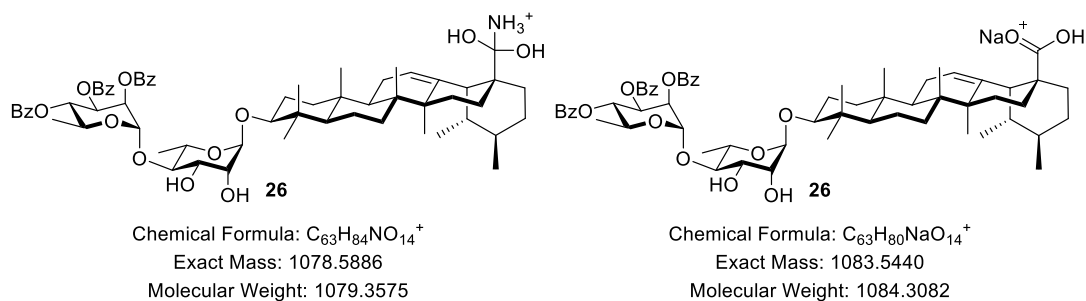
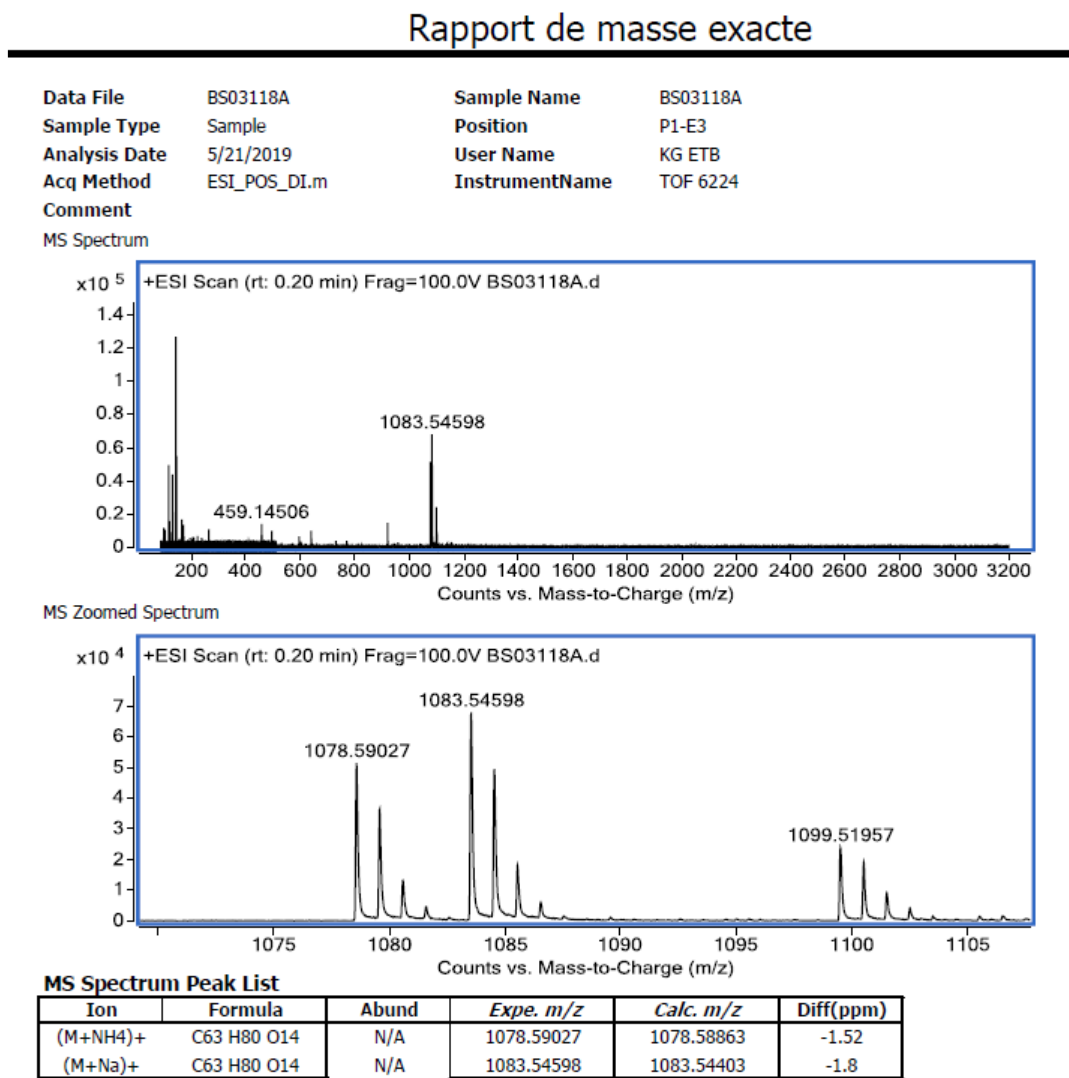


Figure S51. HRMS spectra of **26**



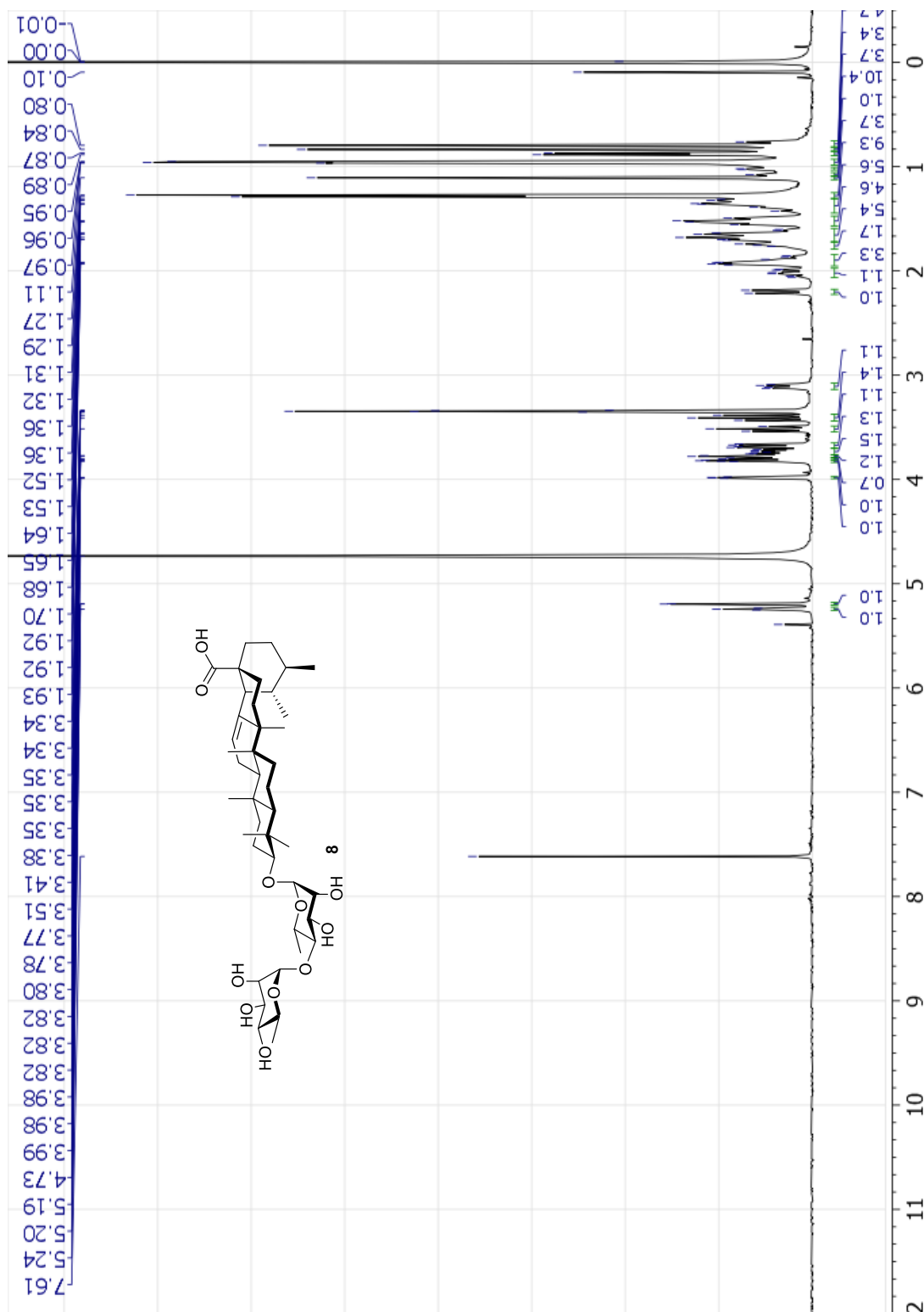


Figure S53. ^{13}C NMR spectra of **8** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 100 MHz)

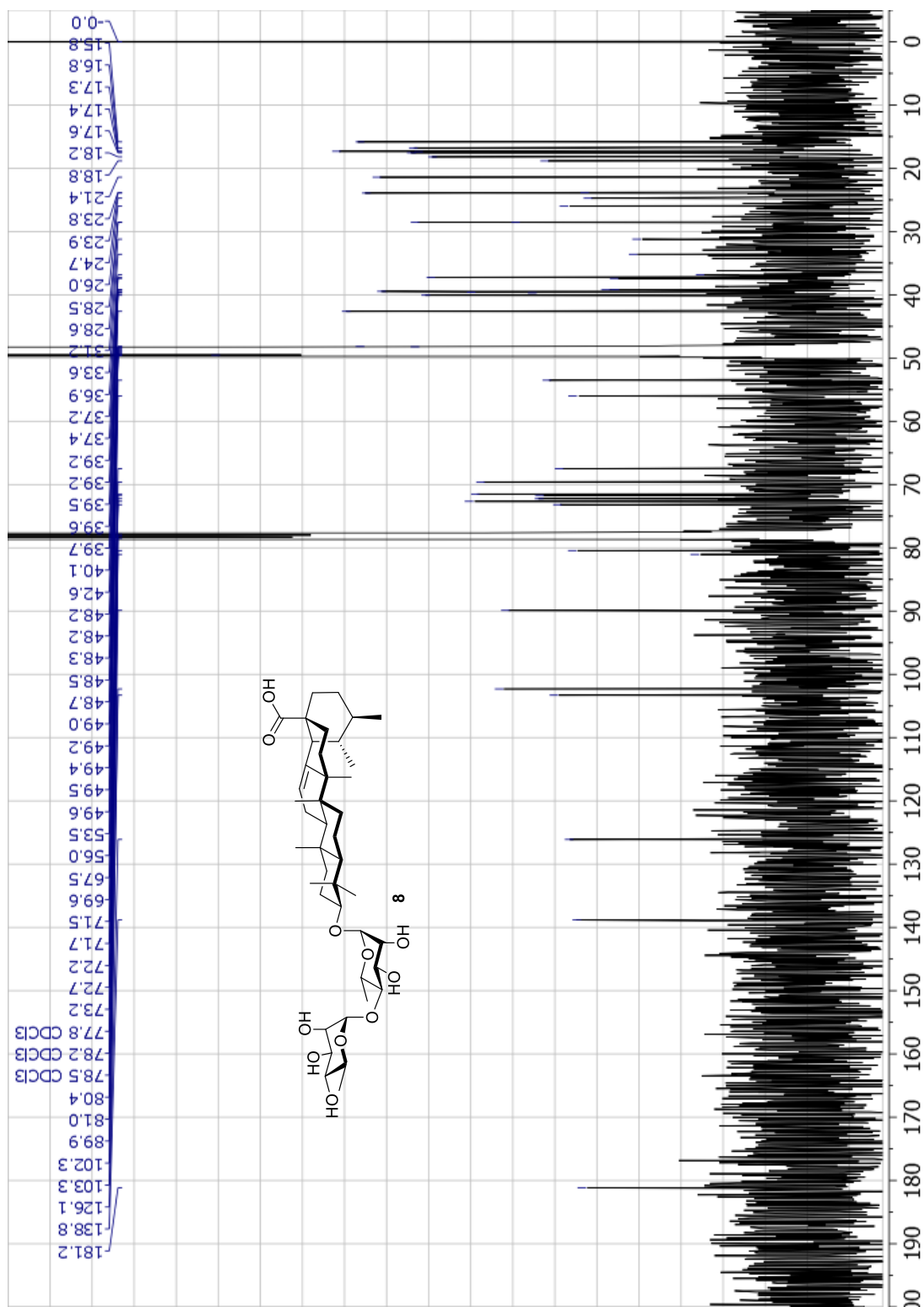


Figure S54. HRMS spectra of **8**

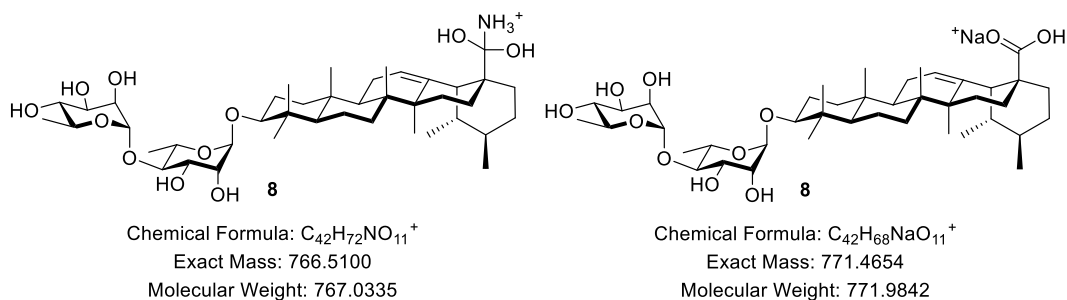
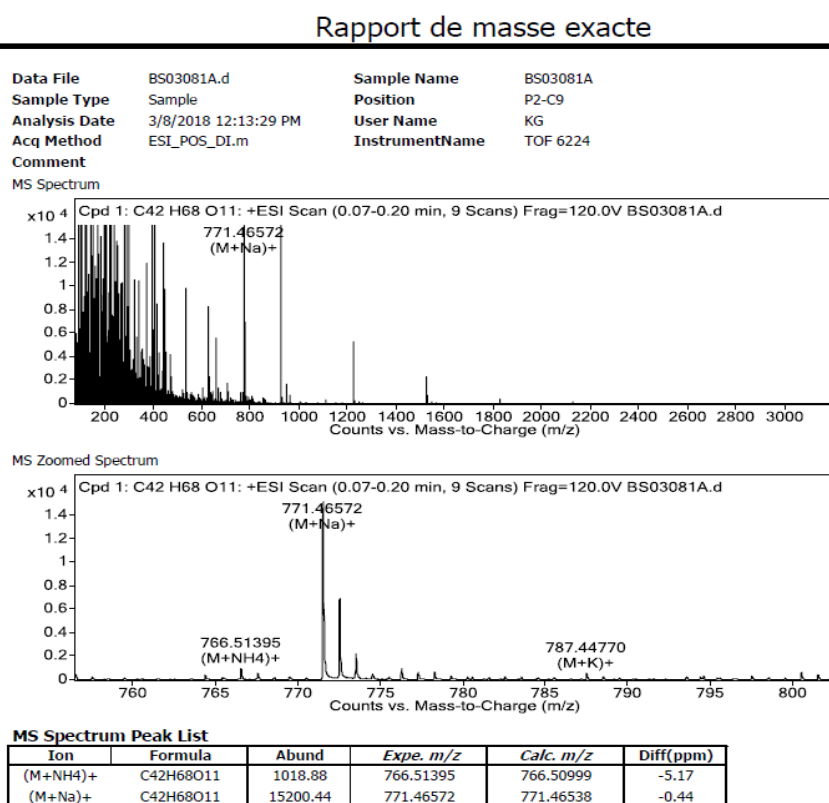


Figure S55. ^1H NMR spectrum of **27** (CDCl_3 , 400 MHz)

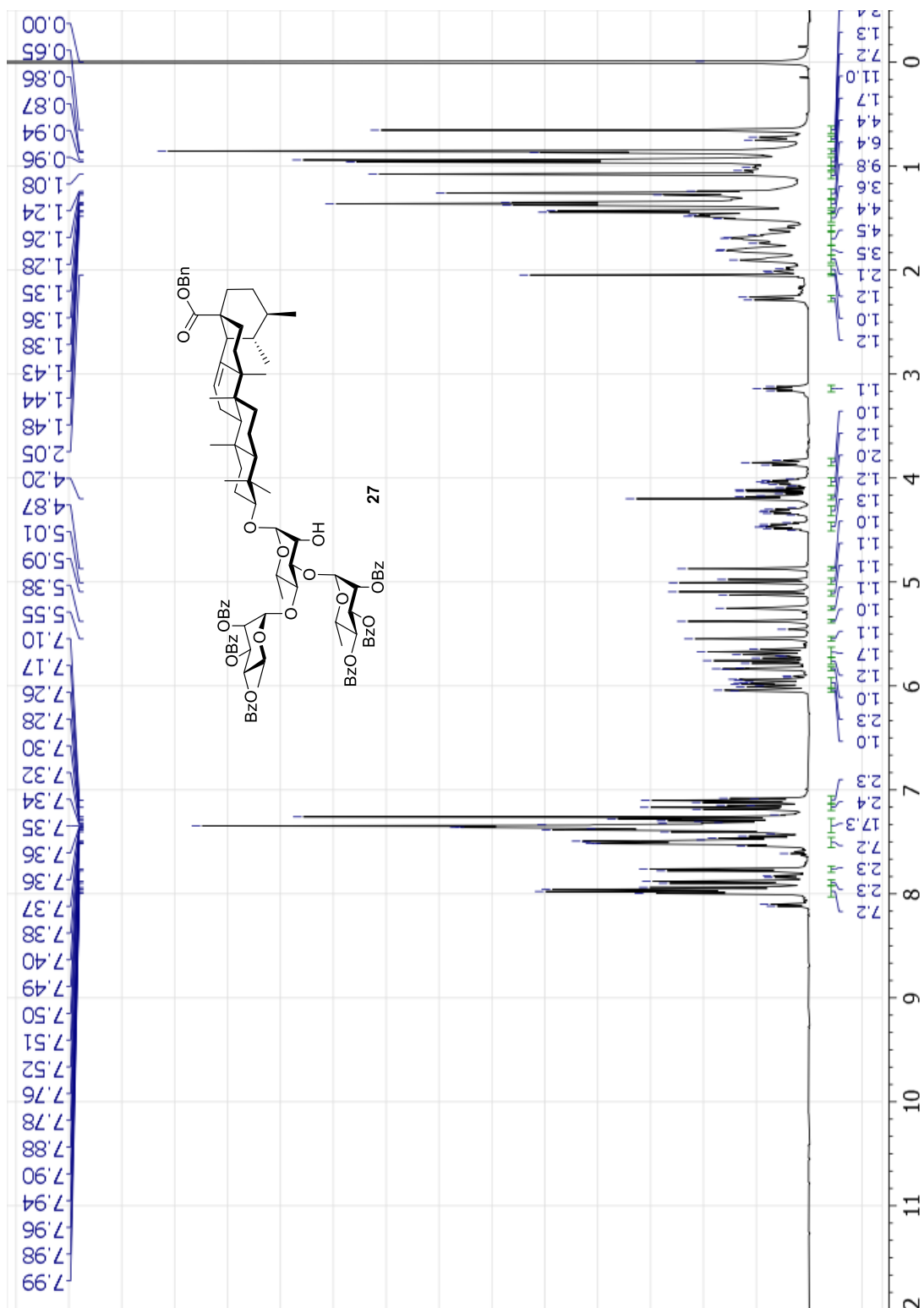


Figure S56. ^{13}C NMR spectra of **27** (CDCl_3 , 100 MHz)

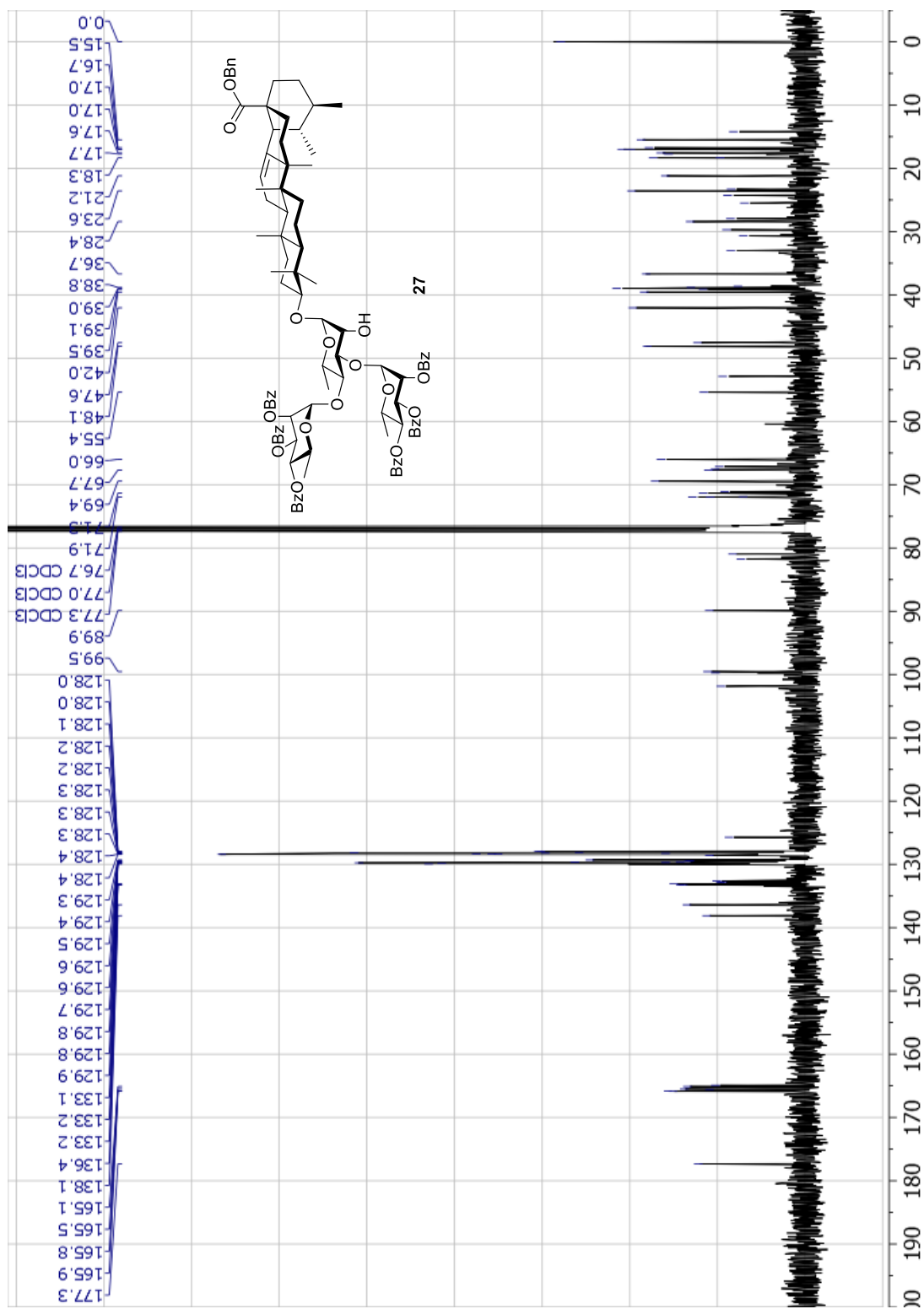
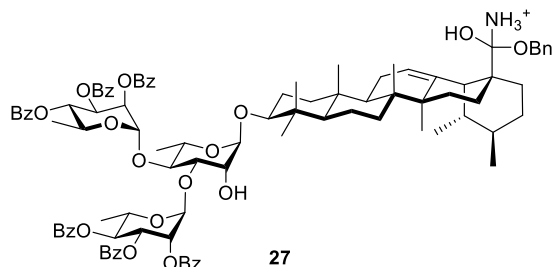
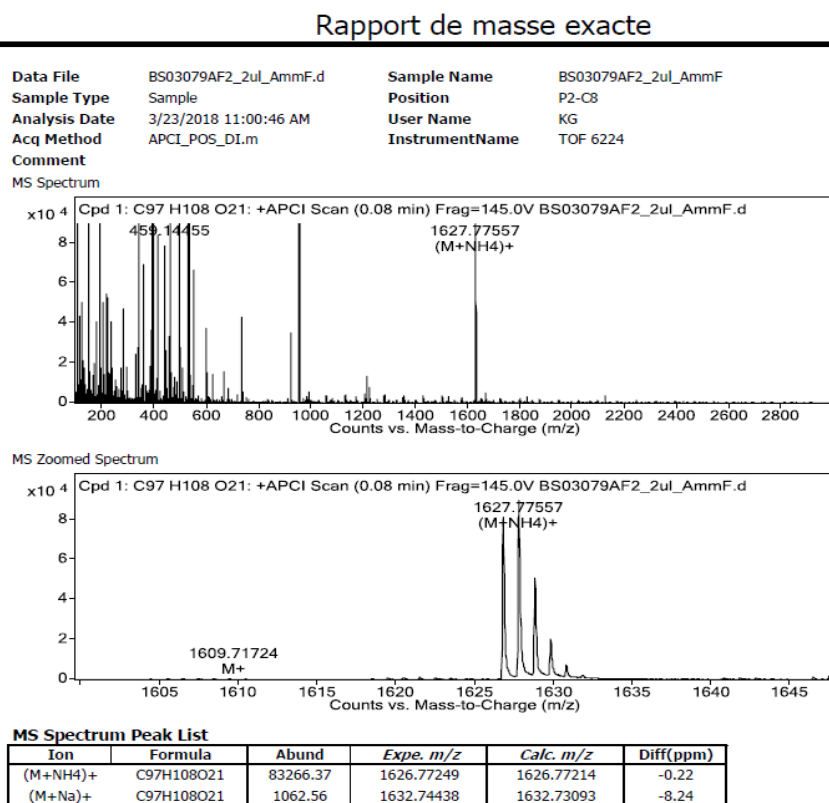
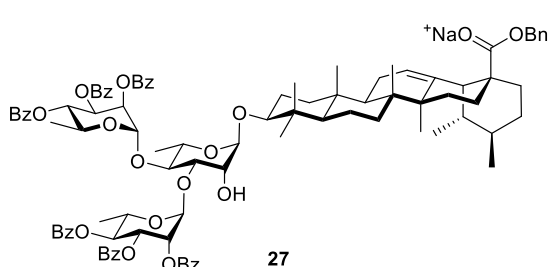


Figure S57. HRMS spectra of **27**



Chemical Formula: C₉₇H₁₁₂NO₂₁⁺
 Exact Mass: 1626.7721
 Molecular Weight: 1627.9485



Chemical Formula: C₉₇H₁₀₈NaO₂₁⁺
 Exact Mass: 1631.7275
 Molecular Weight: 1632.8992

Figure S58. ^1H NMR spectrum of **28** (CDCl_3 , 400 MHz)

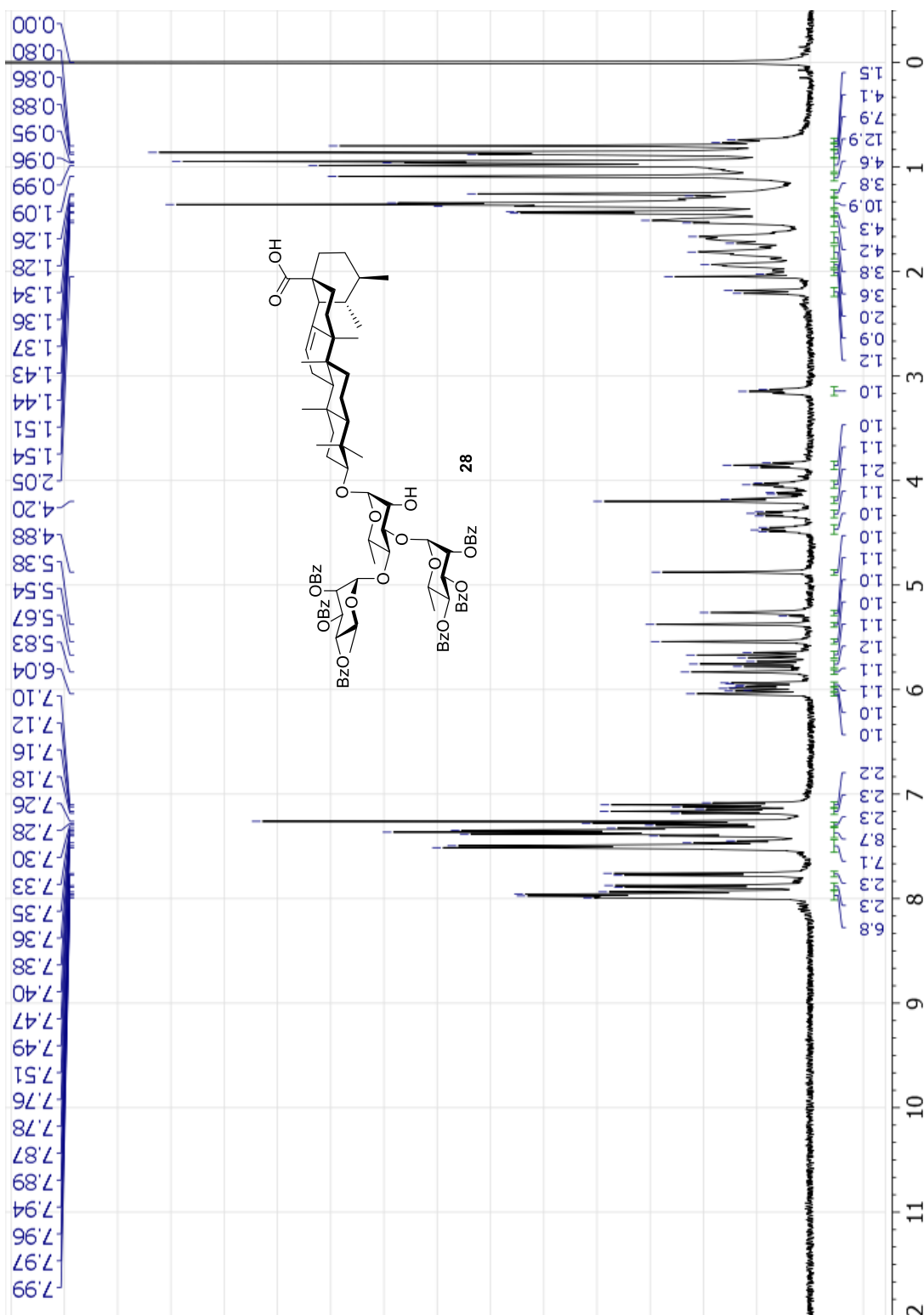


Figure S59. ^{13}C NMR spectrum of **28** (CDCl_3 , 100 MHz)

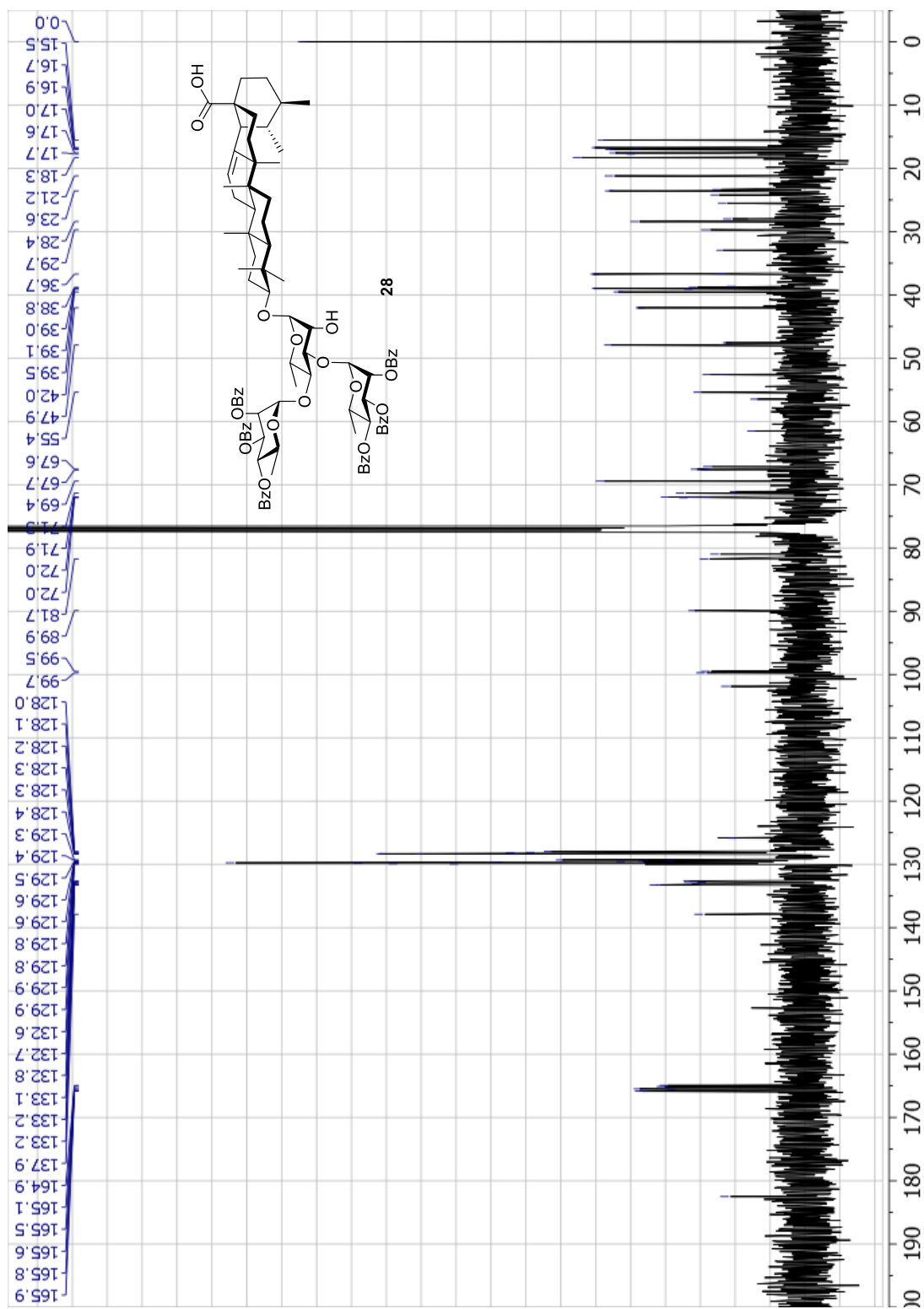
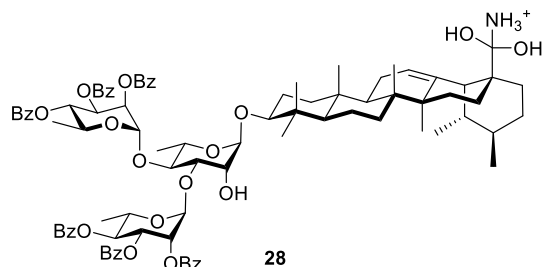
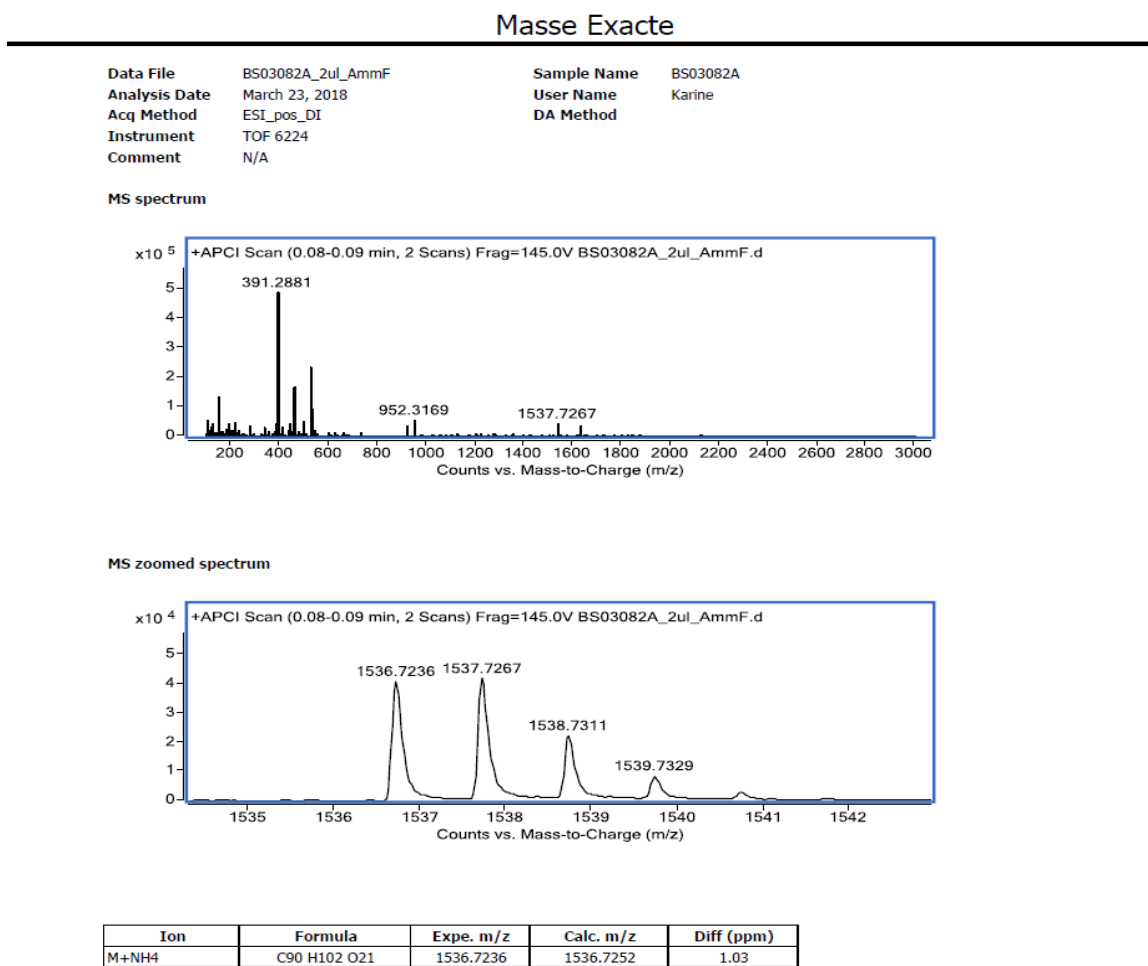


Figure S60. HRMS spectra of **28**



Chemical Formula: C₉₀H₁₀₆NO₂₁⁺
 Exact Mass: 1536.7252
 Molecular Weight: 1537.8235

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

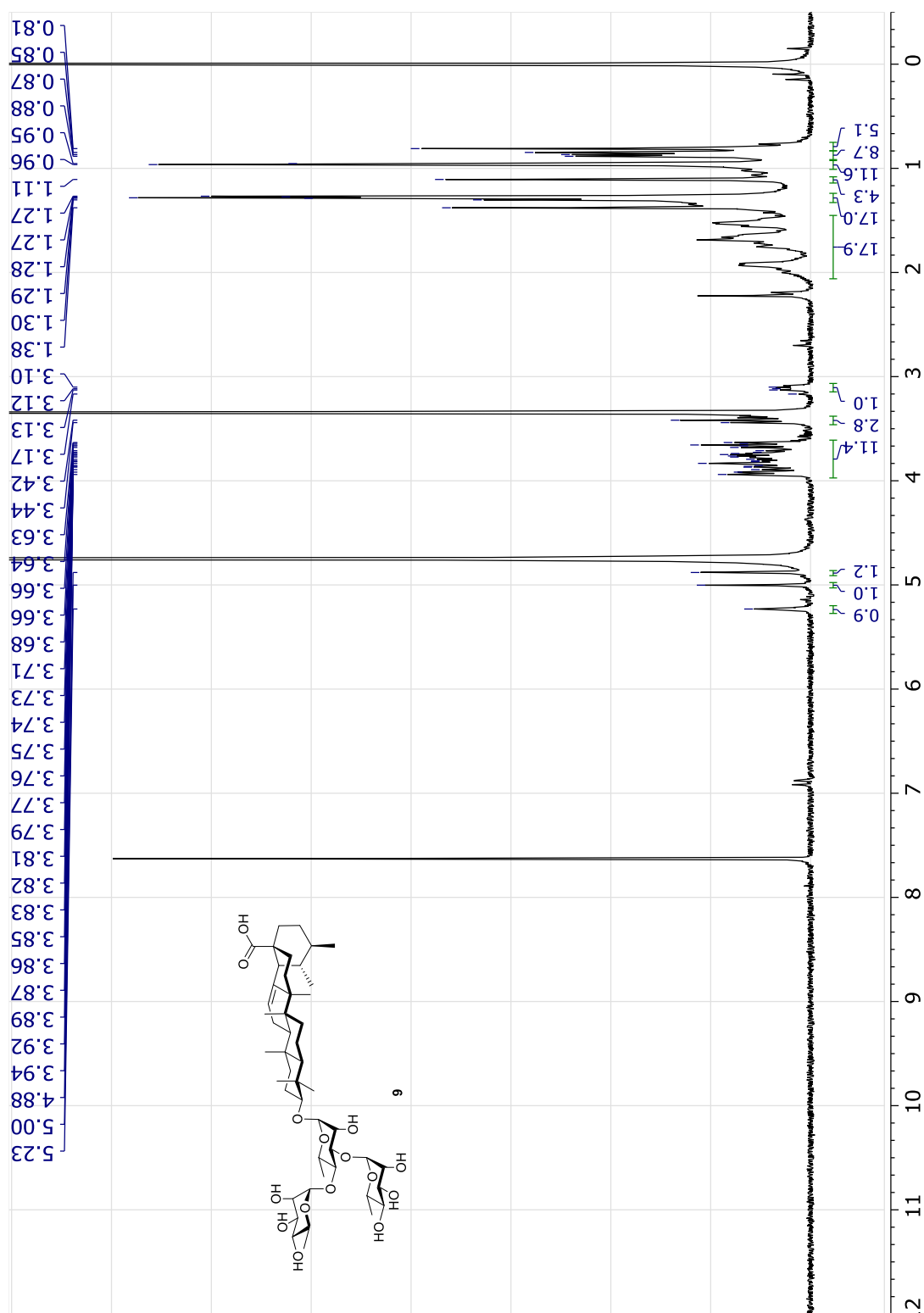


Figure S62. ^{13}C NMR spectrum of **9** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 100 MHz)

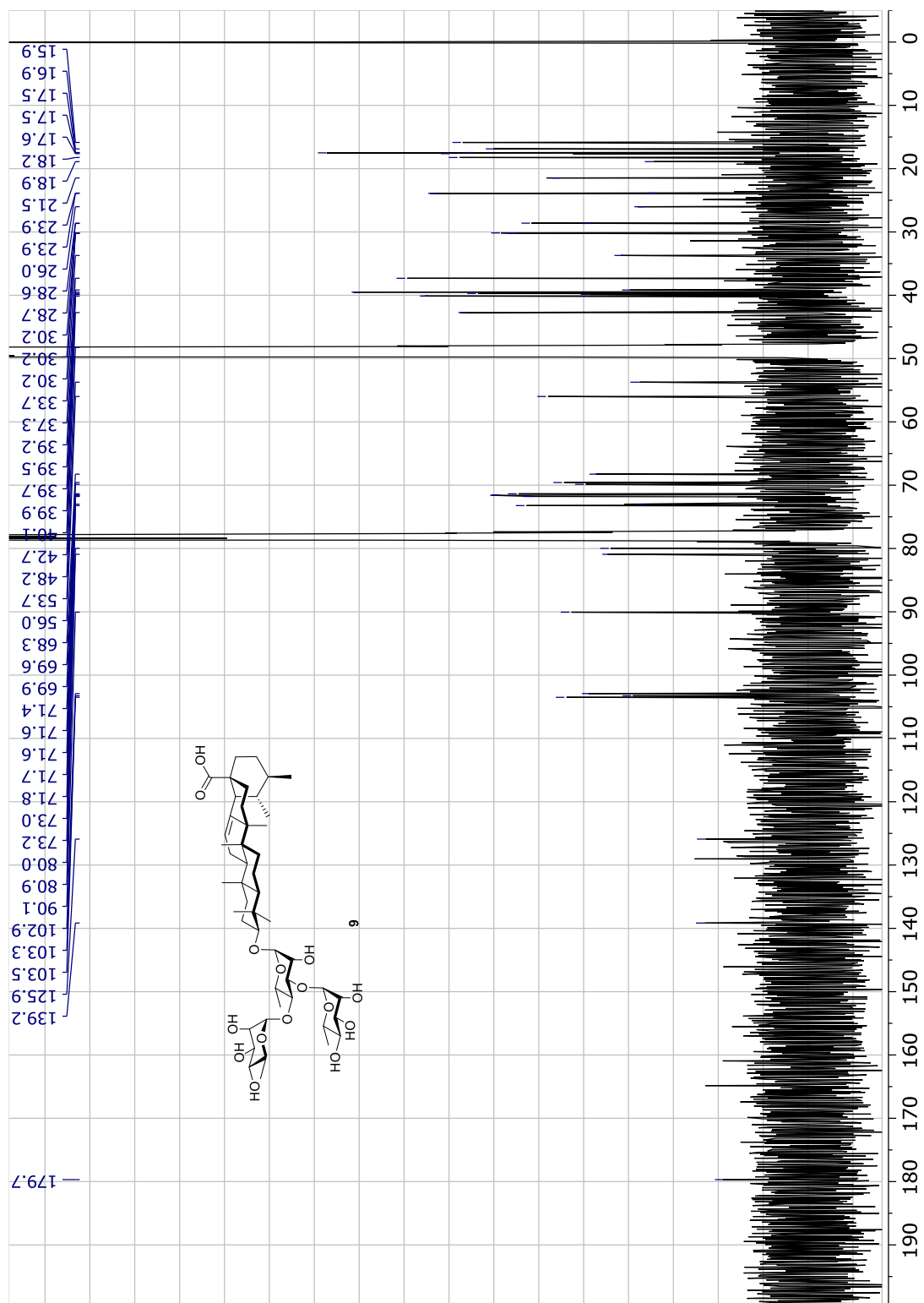


Figure S63. HRMS spectra of **9**

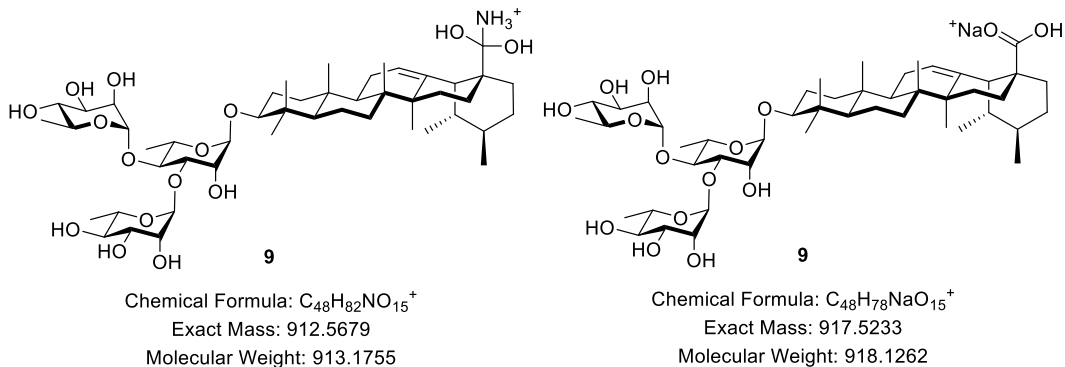
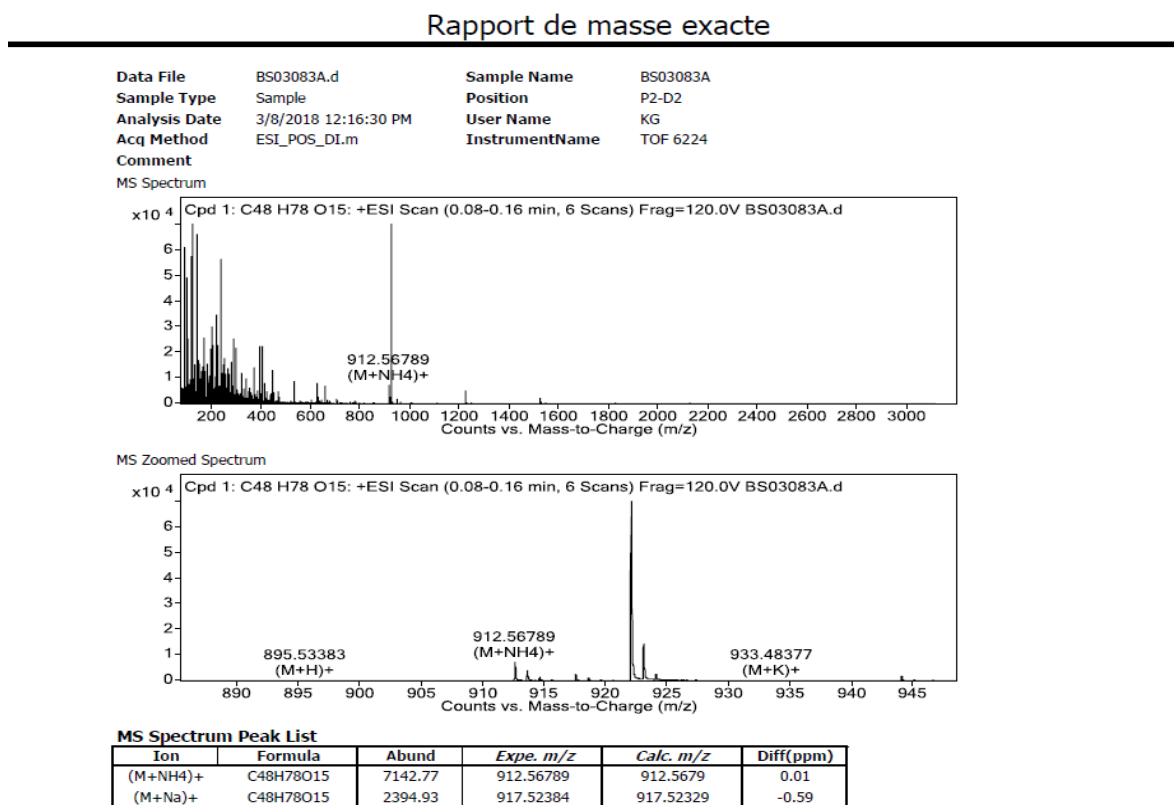


Figure S64. ^1H NMR spectrum of **29** (CDCl_3 , 400 MHz)

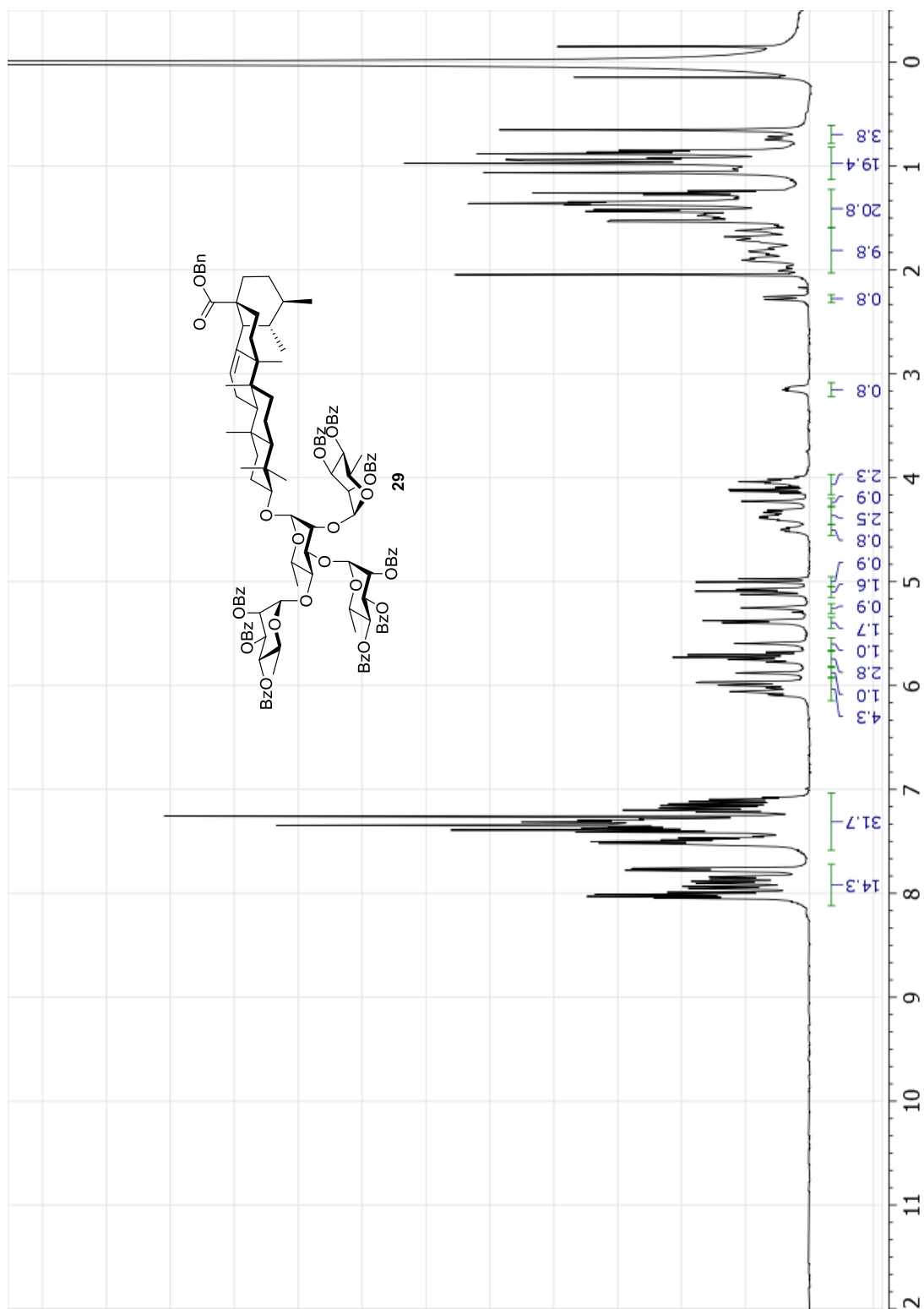


Figure S65. ^{13}C NMR spectrum of **29** (CDCl_3 , 100 MHz)

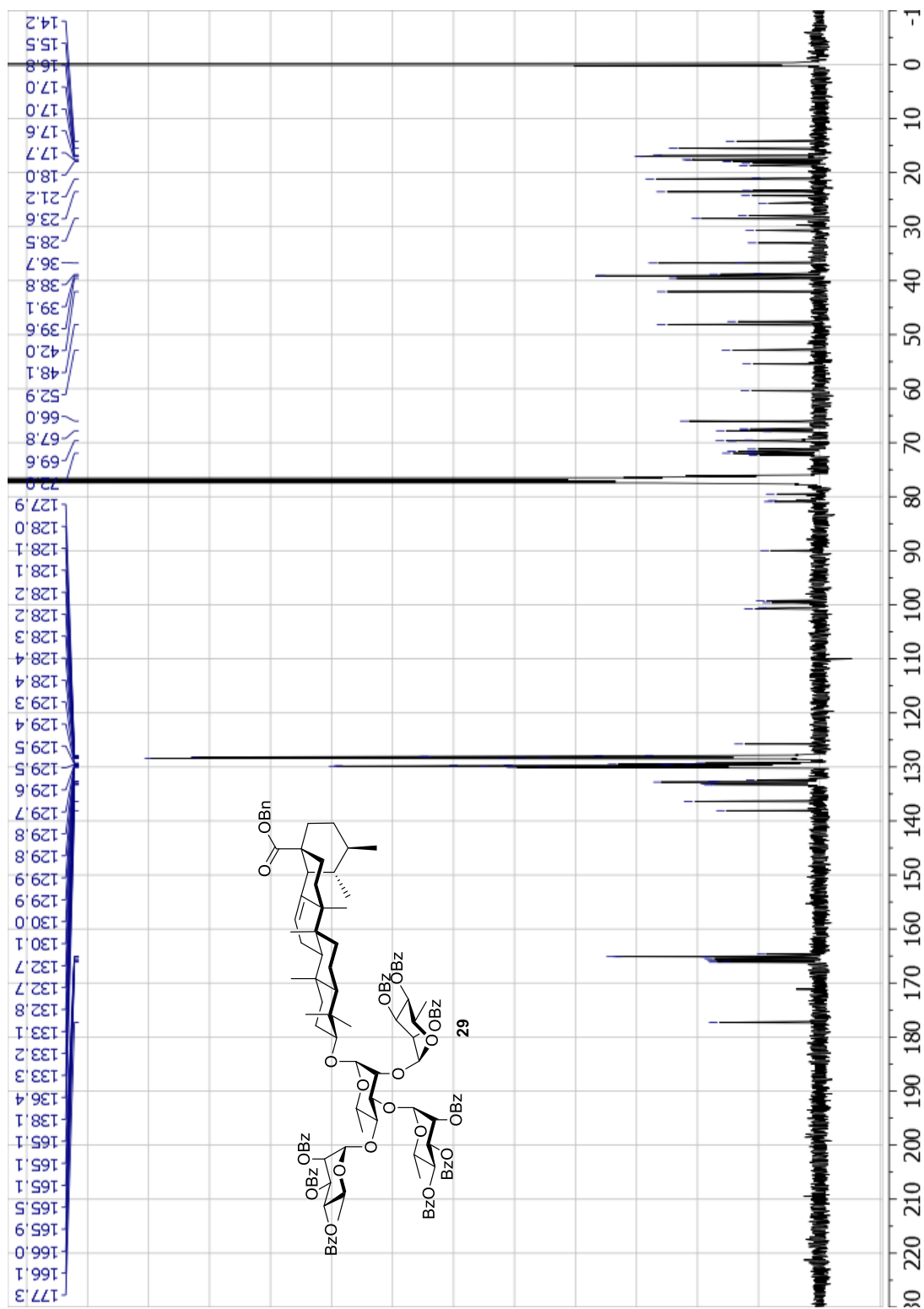
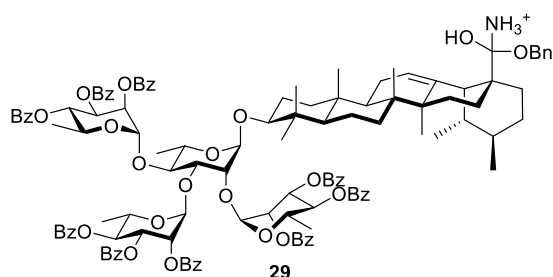
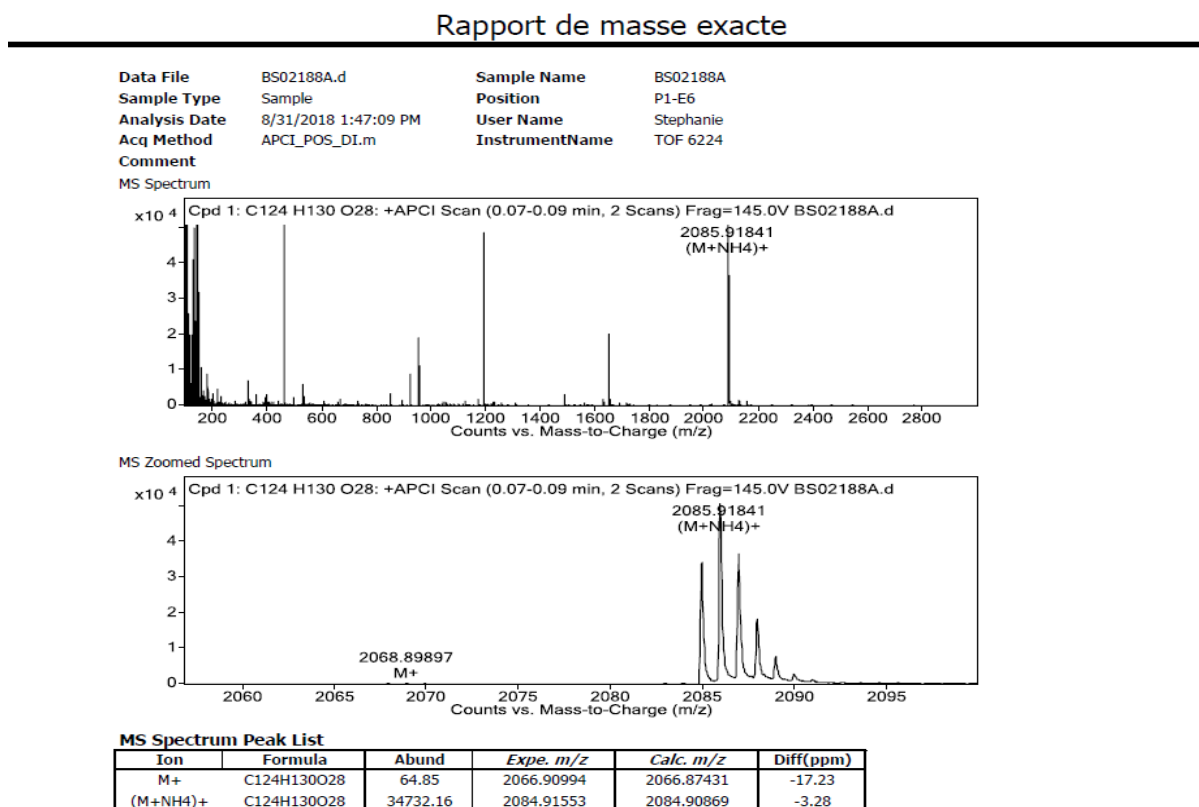


Figure S66. HRMS spectra of **29**



Chemical Formula: C₁₂₄H₁₃₄NO₂₈⁺
 Exact Mass: 2084.9087
 Molecular Weight: 2086.4145

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

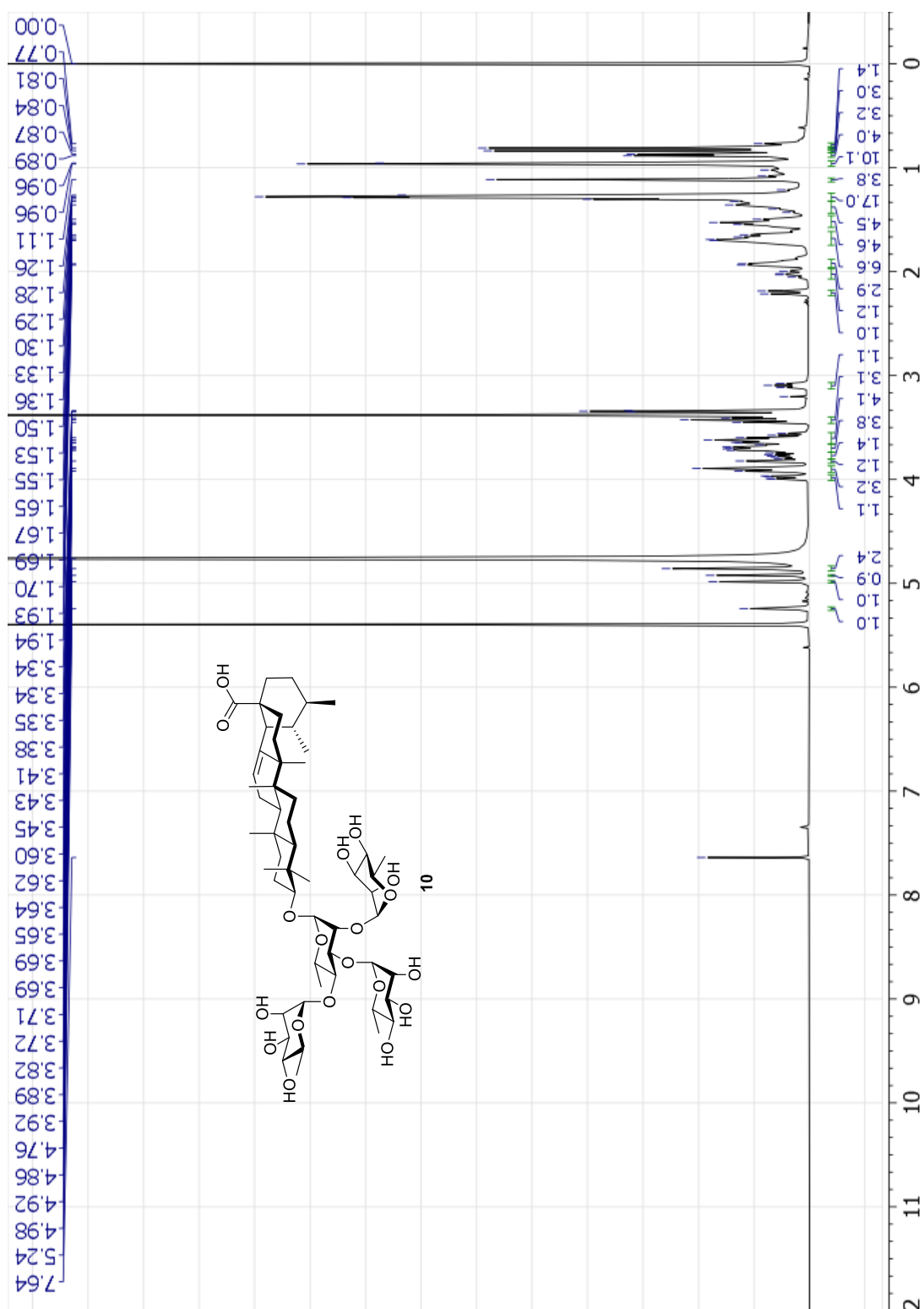


Figure S68. ^1H NMR spectrum of **10** ($\text{CD}_3\text{OD}/\text{CDCl}_3$ 1:1, 100 MHz)

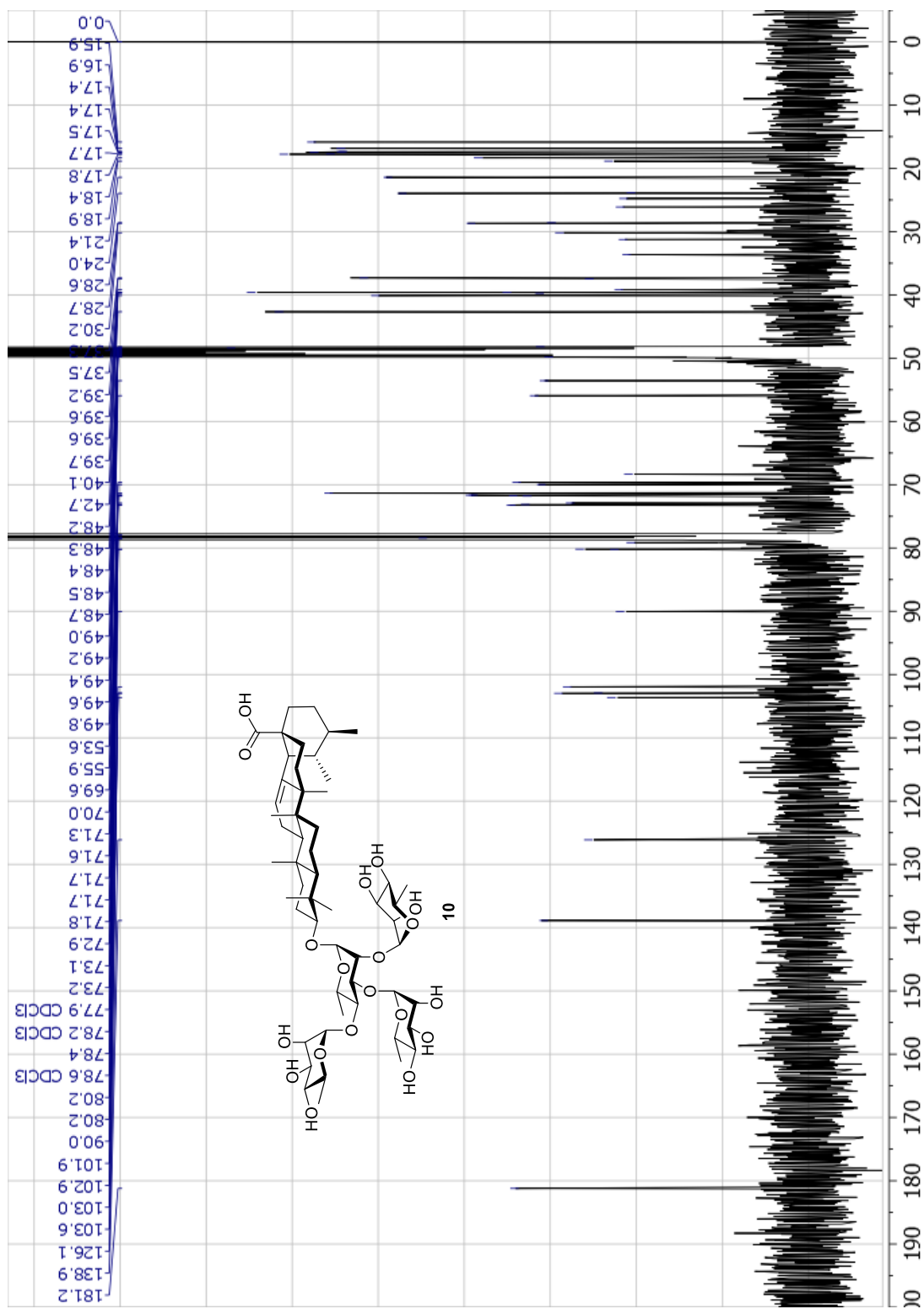


Figure S69. HRMS spectra of **10**

