

# **APPENDIX**

## **CONTROLLING THE INTERFACES OF SUPRAMOLECULAR HYDROGELS FOR TISSUE CULTURE APPLICATION**

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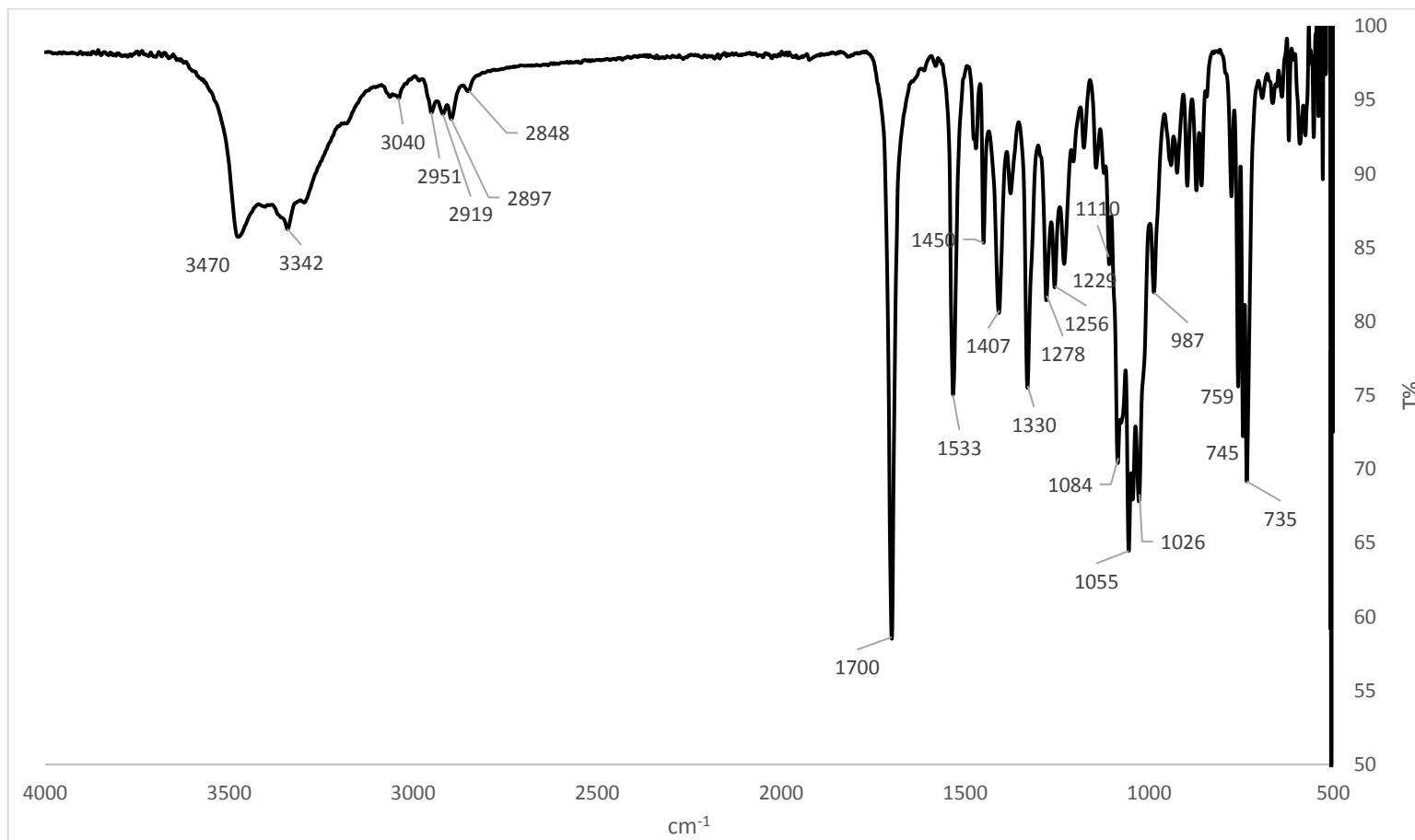
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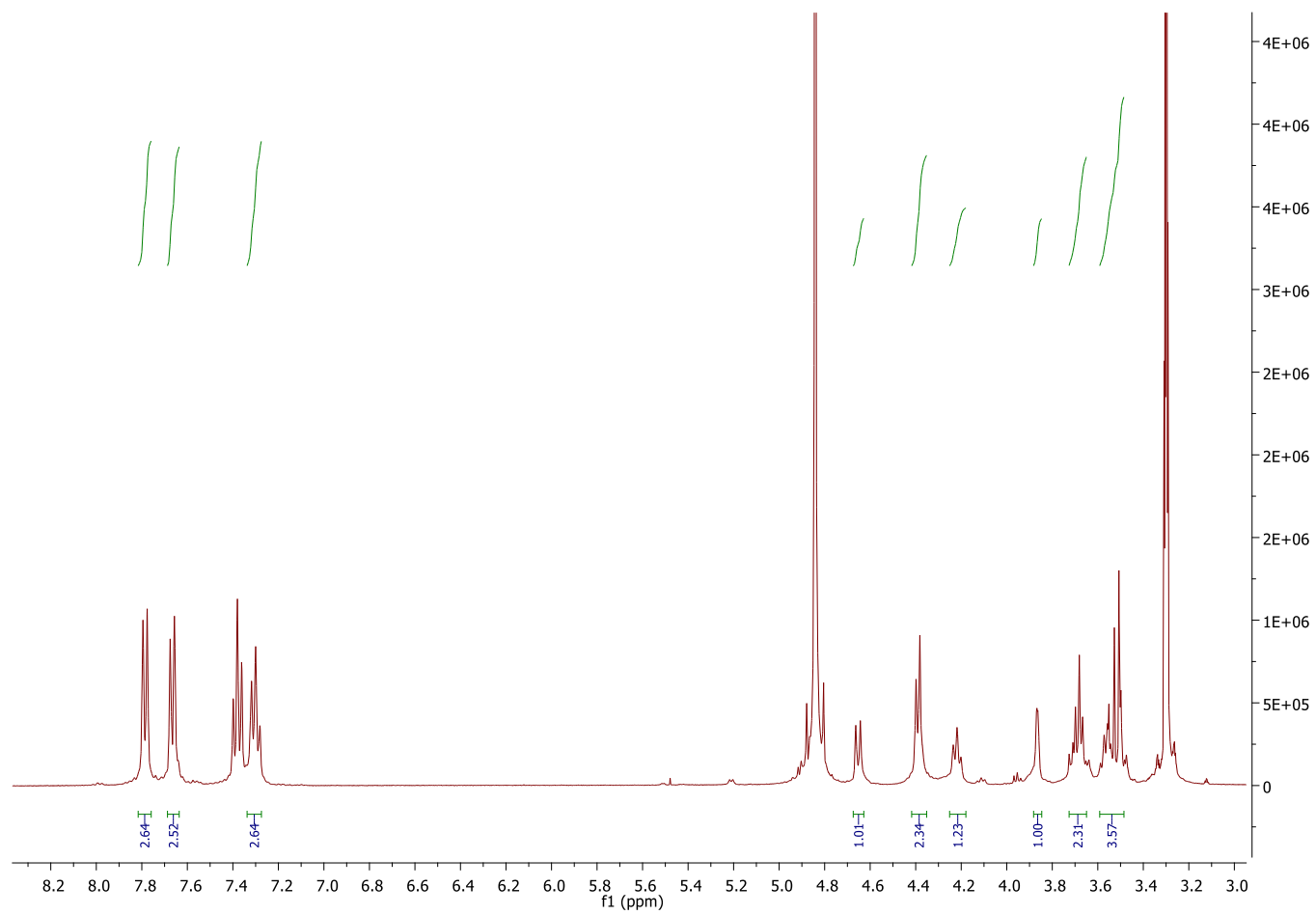
## **SUPPLEMENTARY INFORMATION**

In this section all the spectroscopic data reported in chapter 2 is provided. Two-dimensional NMR spectra (HSQC, HMBC, COSY and NOESY) are not shown herein as were used only for assisting interpretation of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

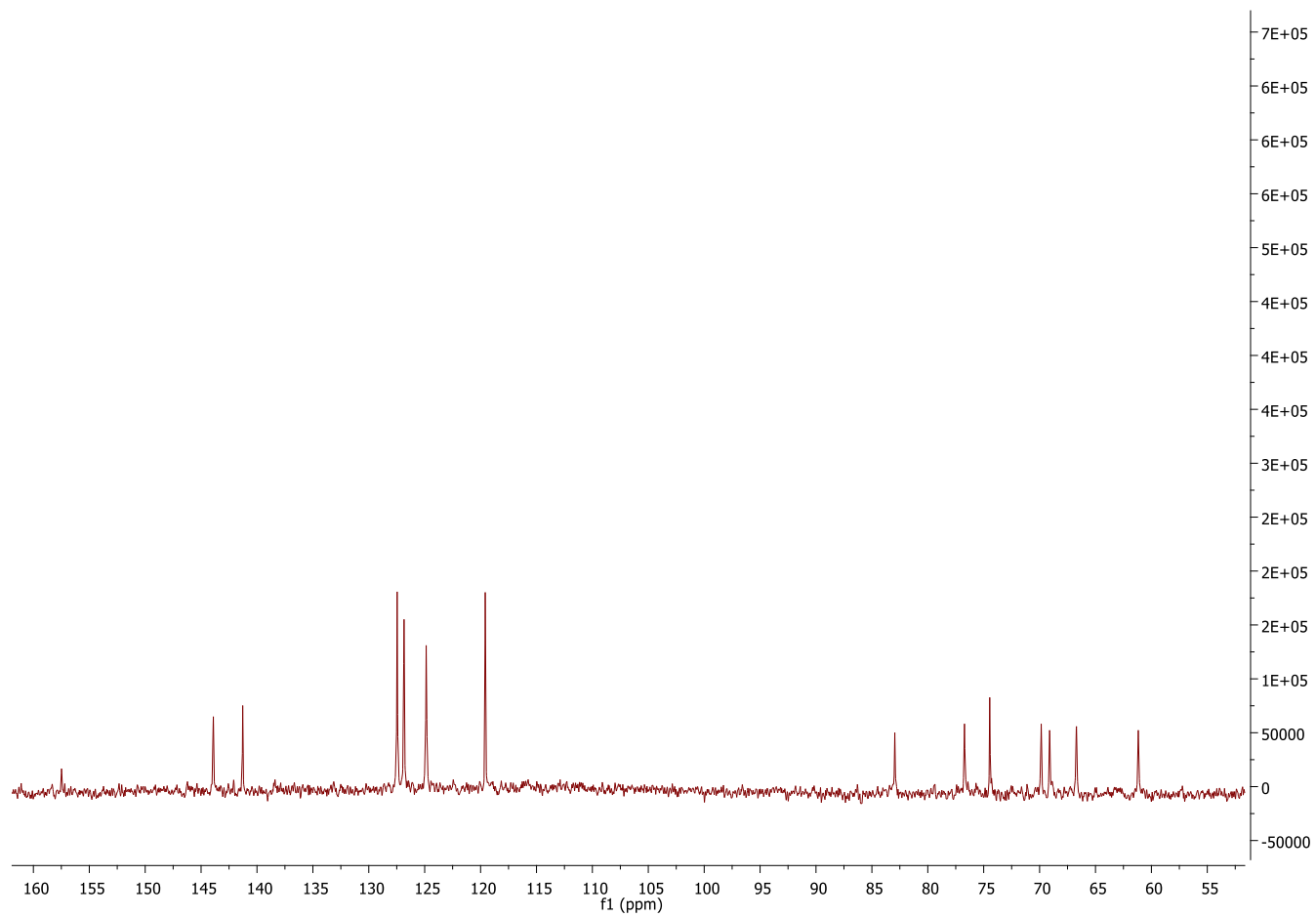
Solution spectra reported in chapter 4 of hydrogelators GalNHFmoc **62**, GlcNHFmoc **63** and Fmoc-F-F **68** in methanol are given to facilitate interpretation of the SRCD studies.



**Figure A 2.1** IR (neat) of *N*-Fmoc-D-galactopyranosylamine **64**

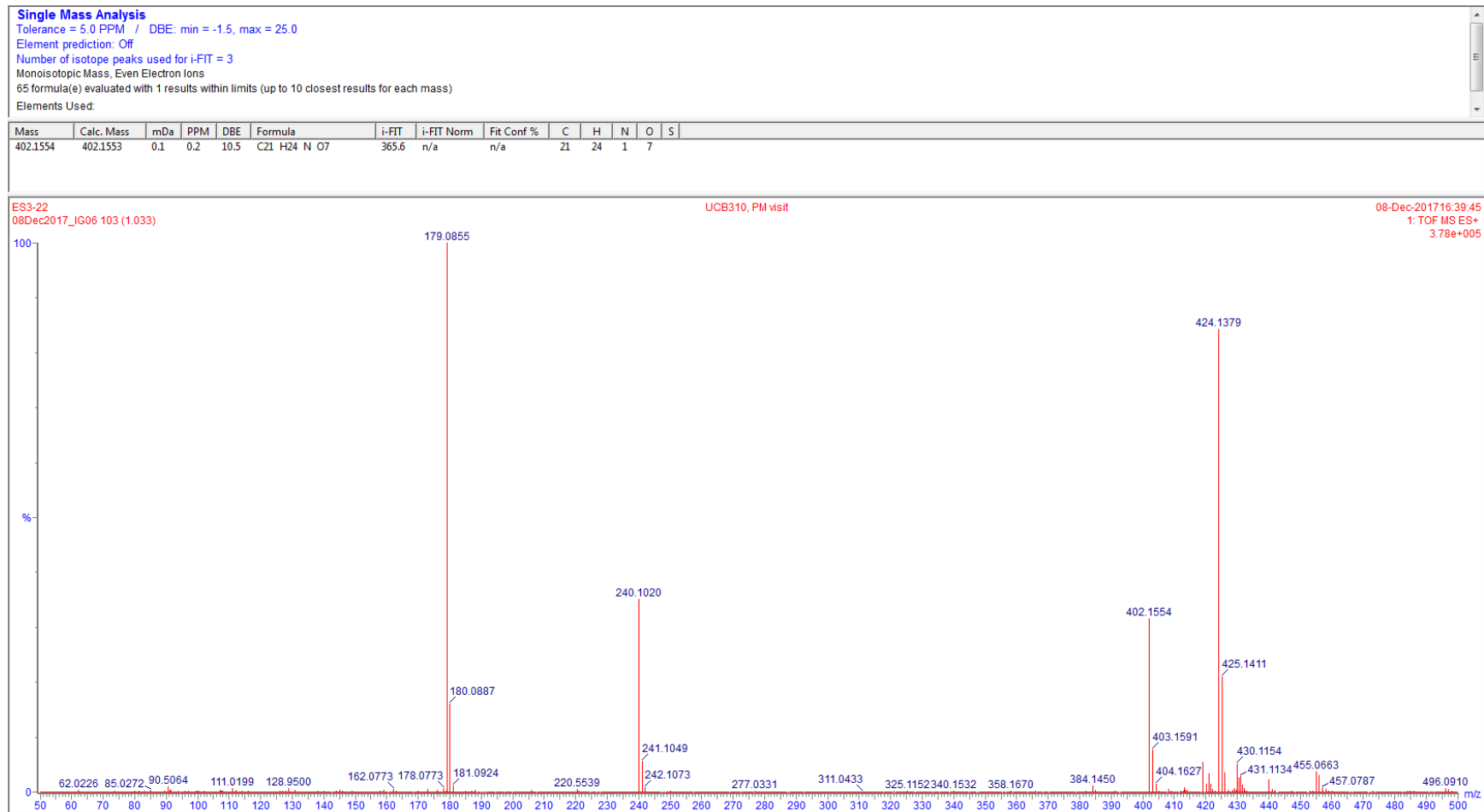


**Figure A 2.2** <sup>1</sup>H NMR (500 MHz, methanol-d<sub>3</sub>) of *N*-Fmoc-D-galactopyranosylamine **64**

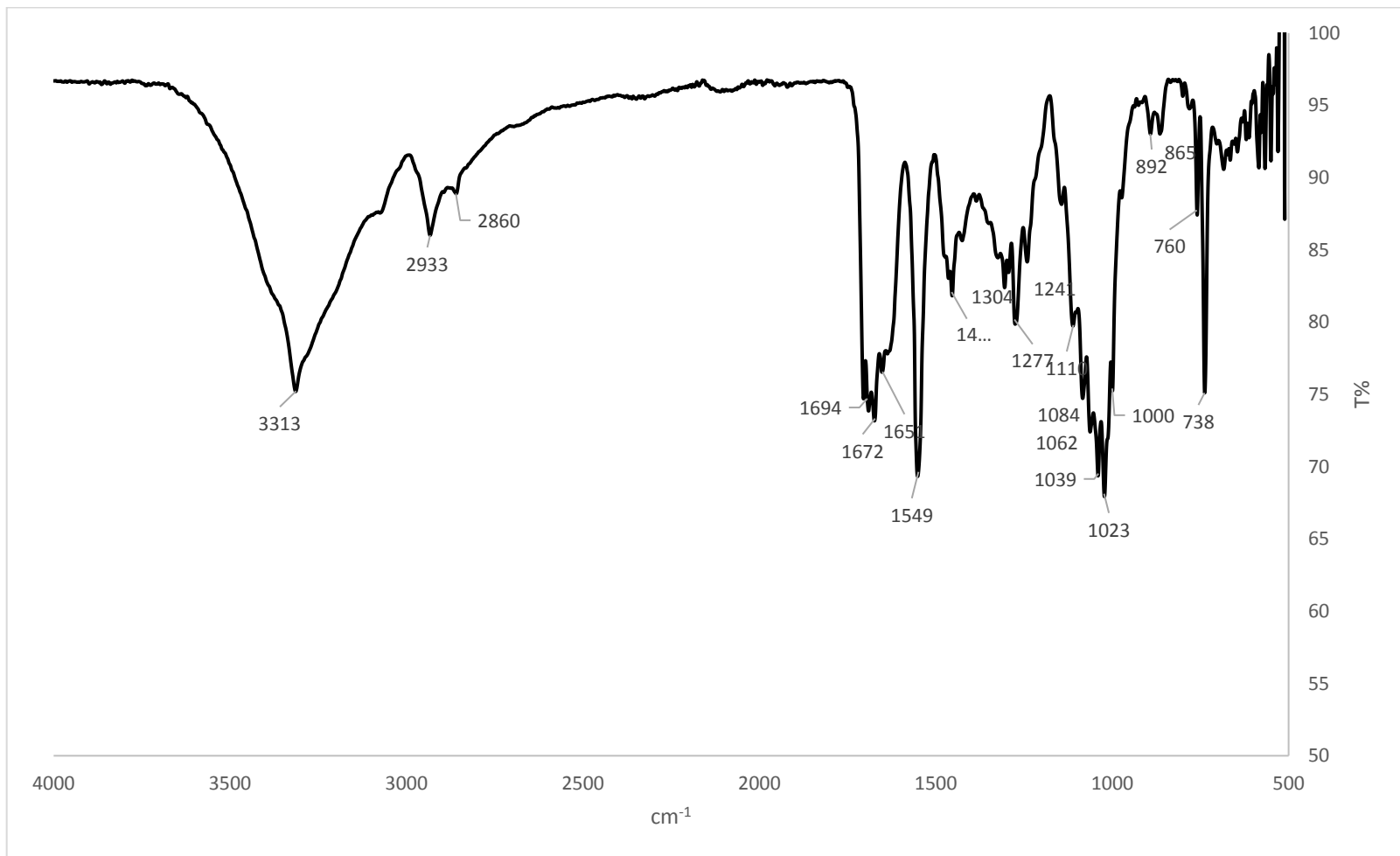


**Figure A 2.3**  $^{13}\text{C}$  NMR (101 MHz, methanol- $\text{d}_3$ ) of *N*-Fmoc-D-galactopyranosylamine **64**

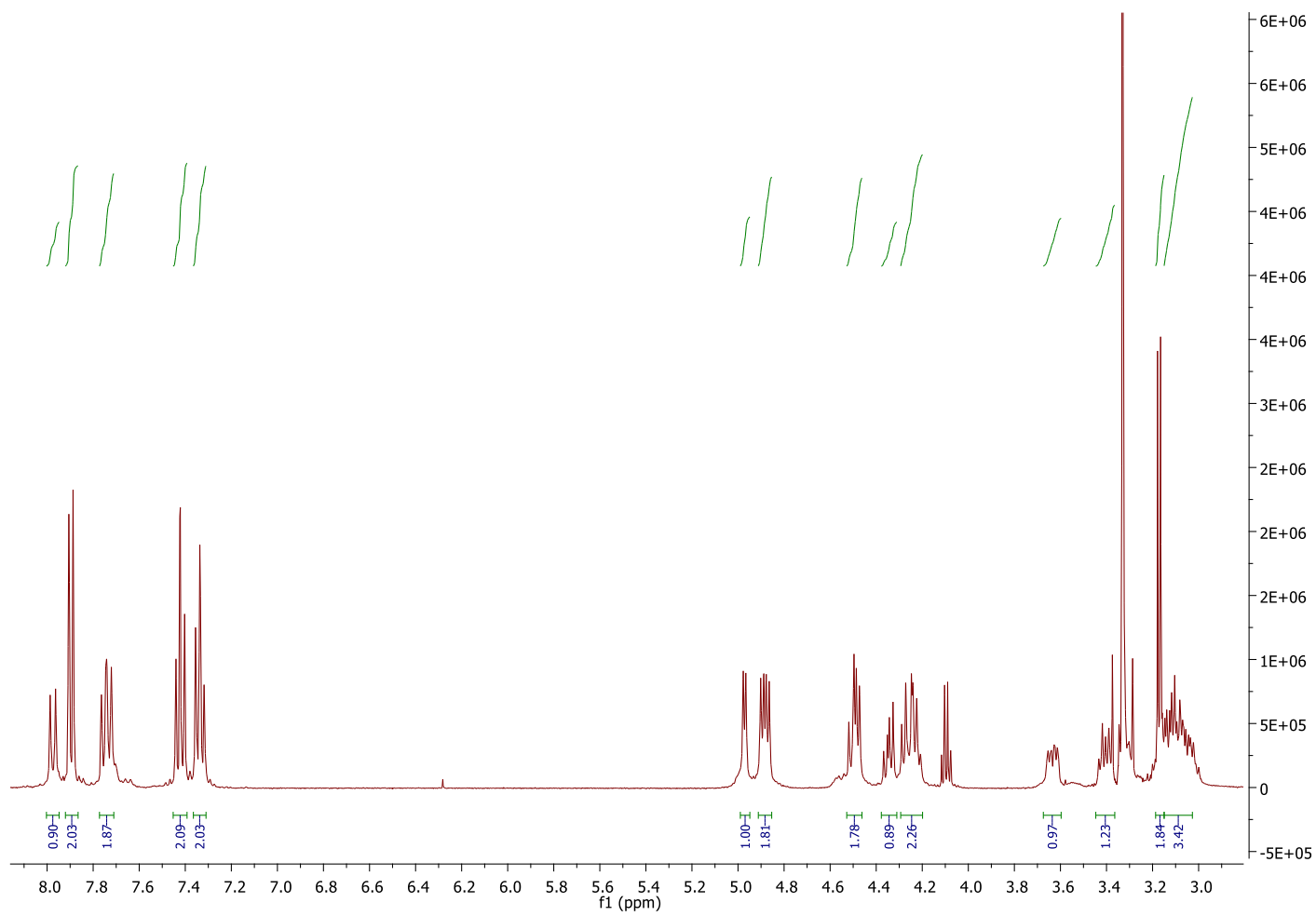




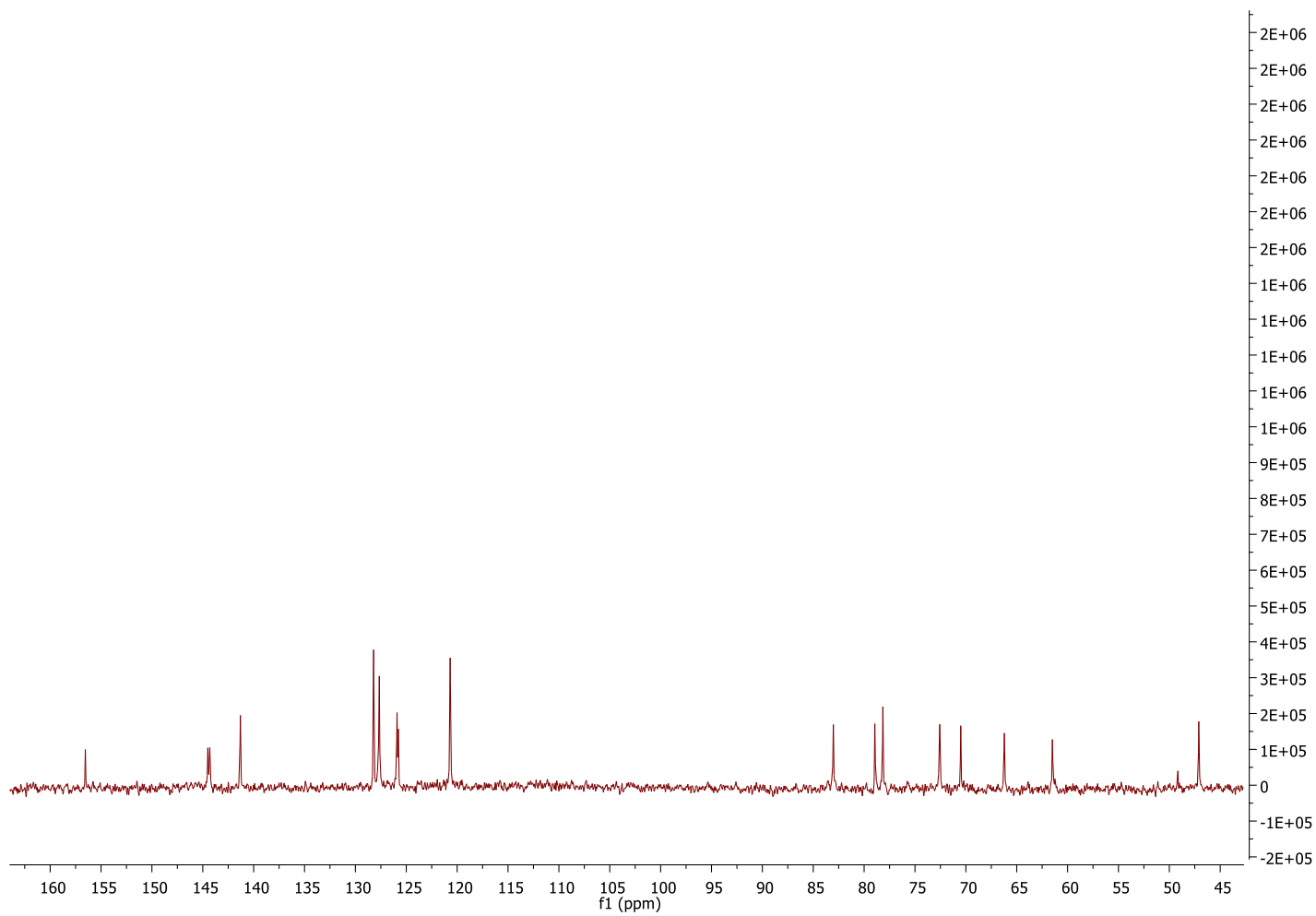
**Figure A 2.4** HR-MS of *N*-Fmoc-D-galactopyranosylamine **64**



**Figure A 2.5** IR (neat) of *N*-Fmoc-D-glucopyranosylamine **65**



**Figure A 2.6**  $^1\text{H}$  NMR (500 MHz,  $\text{dms}\text{-d}_6$ ) of *N*-Fmoc-D-glucopyranosylamine **65**



**Figure A 2.7**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms-}d_6$ ) of *N*-Fmoc-D-glucopyranosylamine **65**

**Single Mass Analysis**  
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 25.0  
Element prediction: Off  
Number of isotope peaks used for i-FIT = 3  
Monoisotopic Mass, Even Electron Ions  
65 formula(e) evaluated with 1 results within limits (up to 10 closest results for each mass)  
Elements Used:

Mass	Calc. Mass	mDa	PPM	DBE	Formula	i-FIT	i-FIT Norm	Fit Conf %	C	H	N	O	S
402.1559	402.1553	0.6	1.5	10.5	C <sub>21</sub> H <sub>24</sub> N <sub>1</sub> O <sub>7</sub>	549.2	n/a	n/a	21	24	1	7	

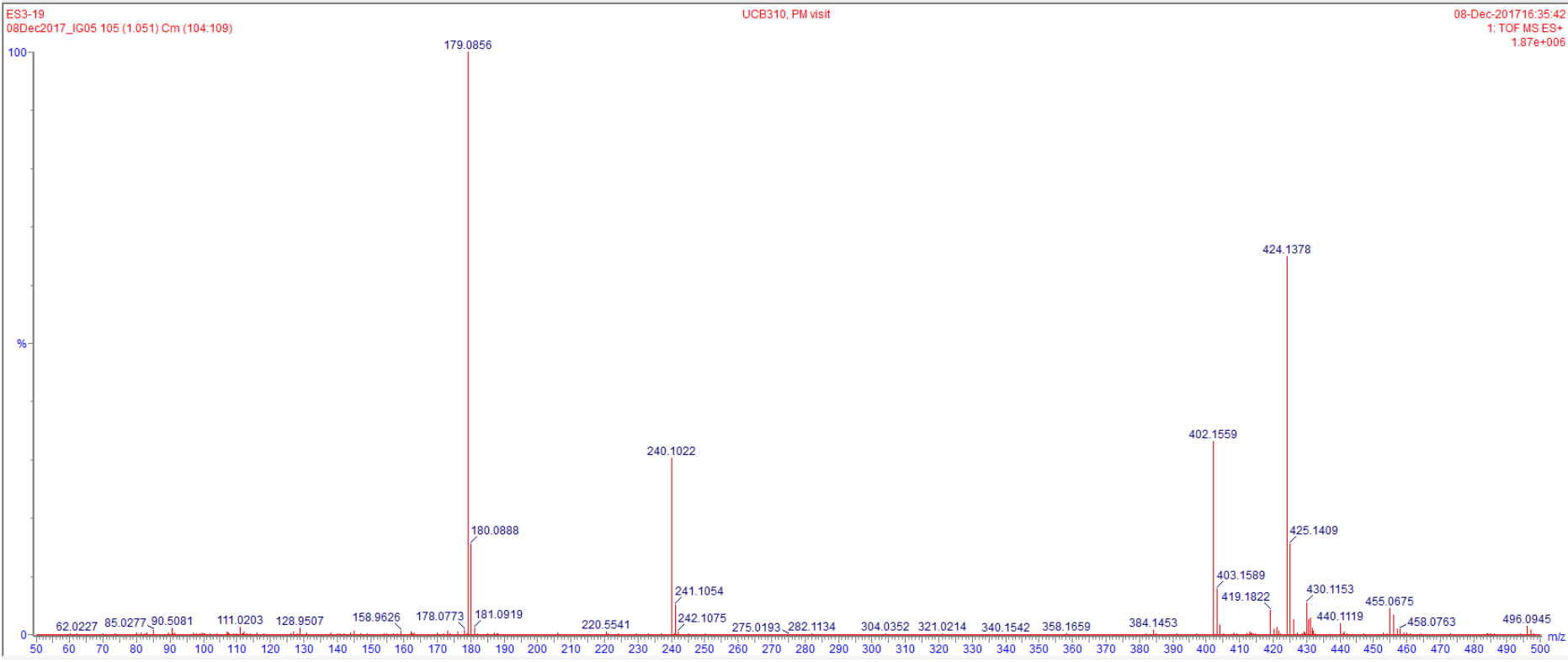
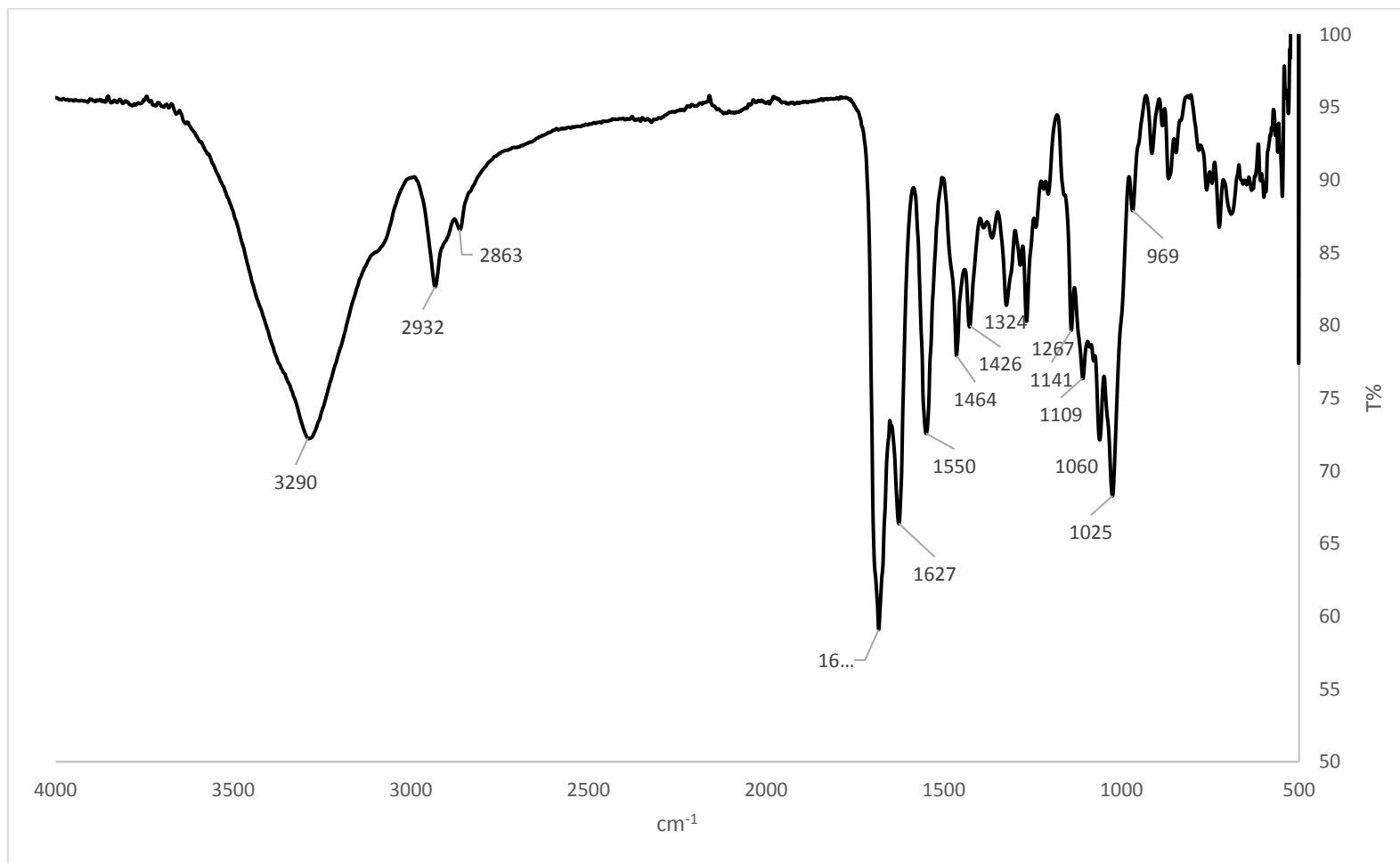
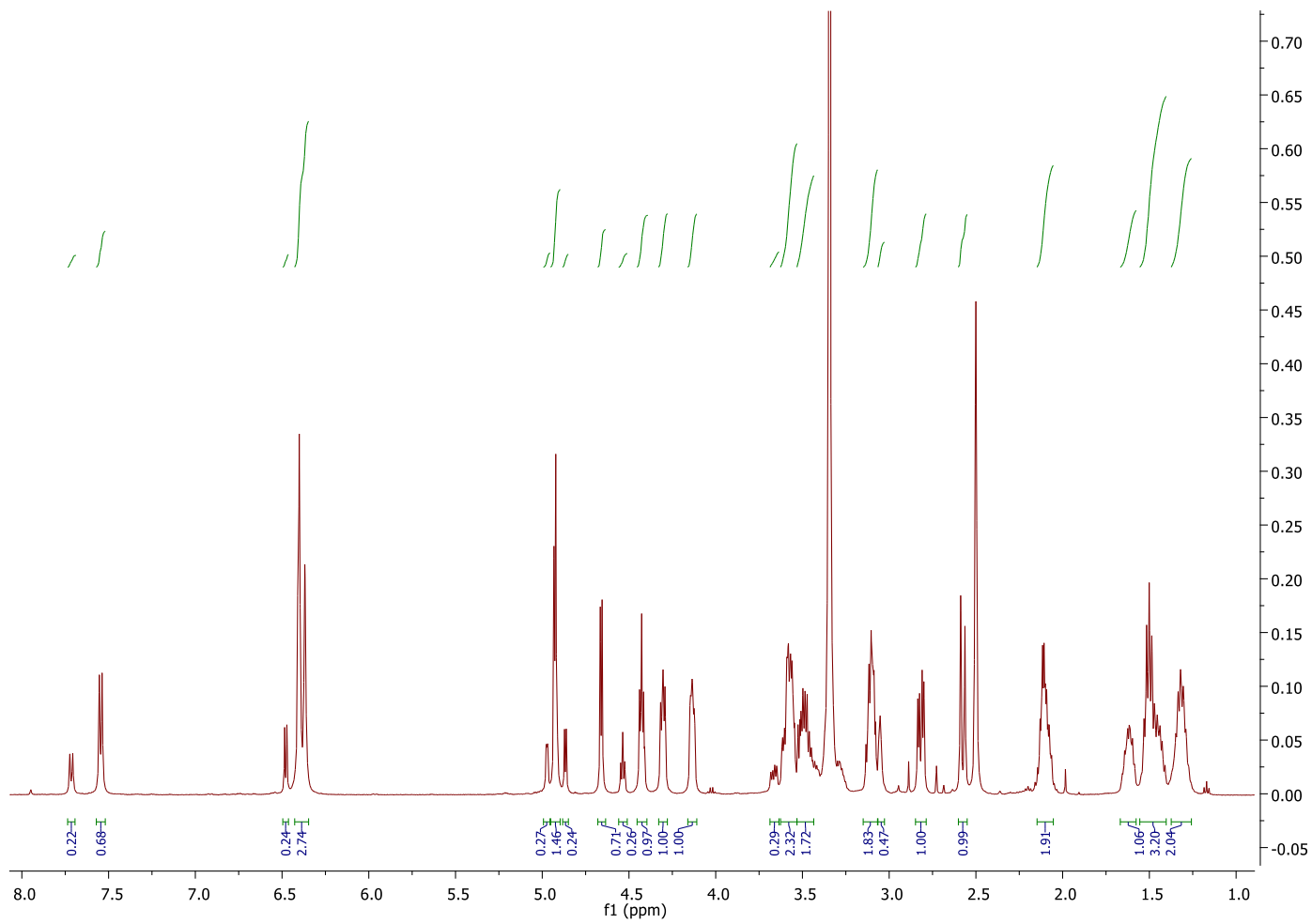


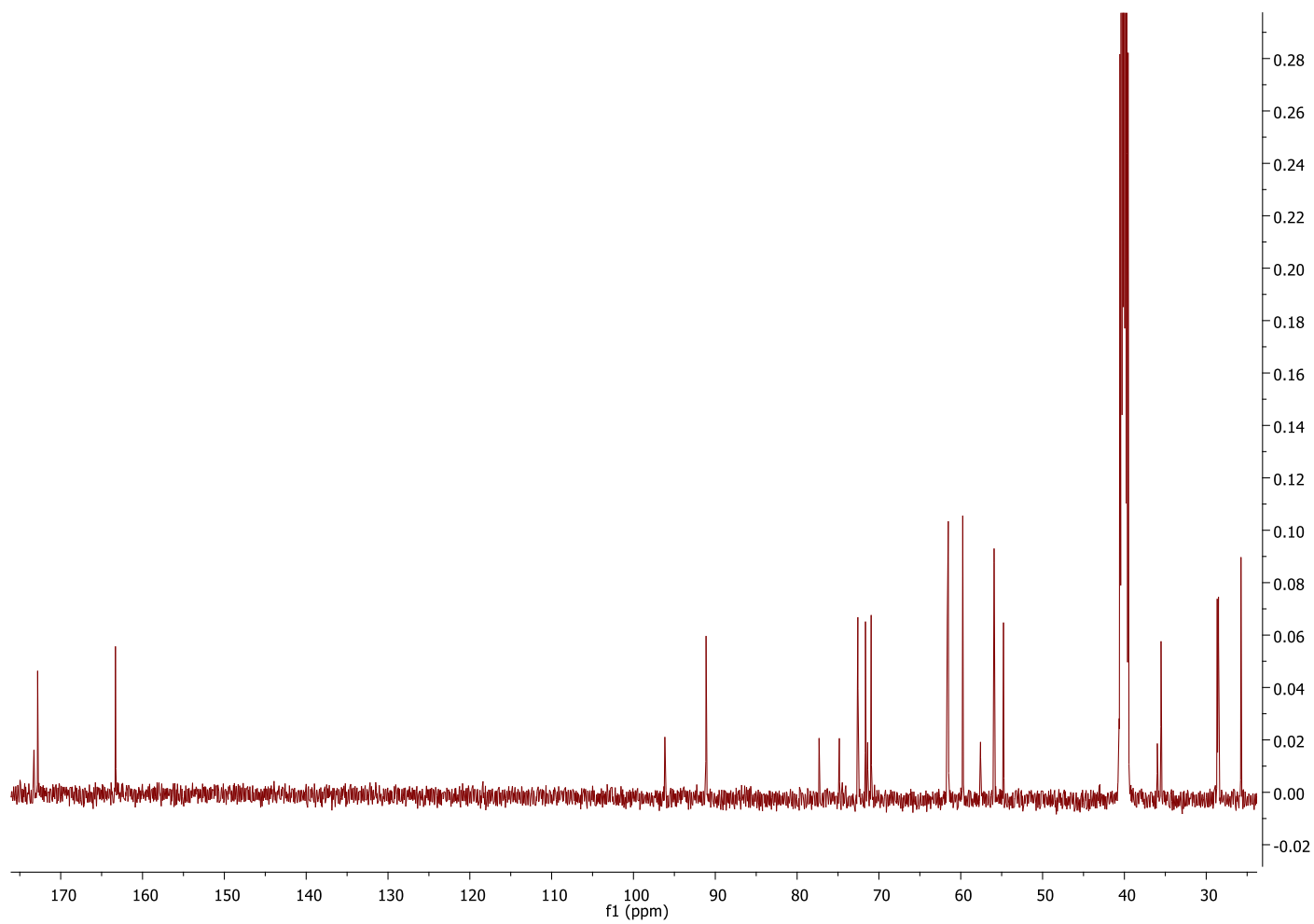
Figure A 2.8 HR-MS of *N*-Fmoc-D-glucopyranosylamine **65**



**Figure A 2.9** IR (neat) of Biotin-D-glucosamine **67**

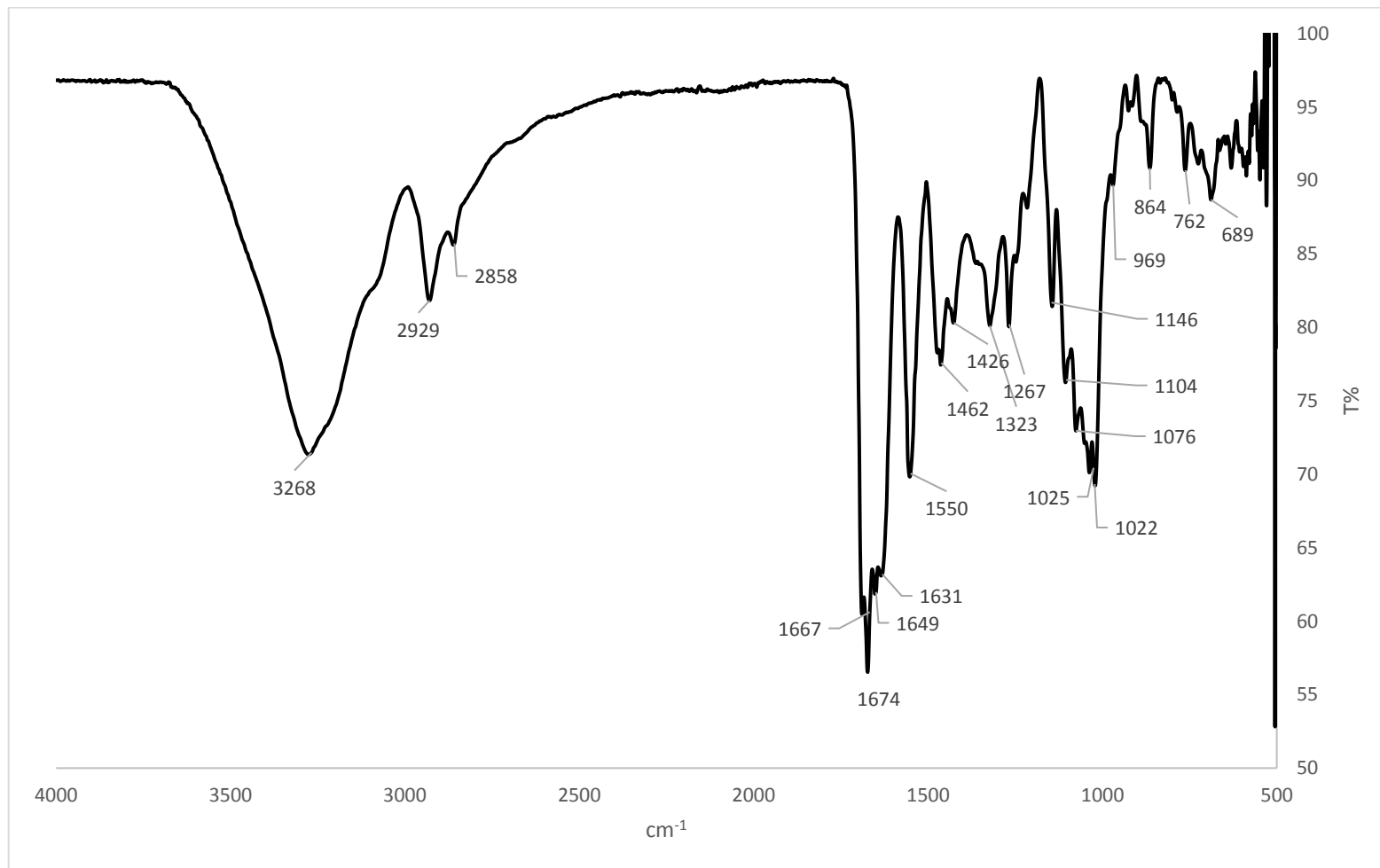


**Figure A 2.10**  $^1\text{H}$  NMR (500 MHz,  $\text{dms}\text{-d}_6$ ) of Biotin-D-glucosamine **67**

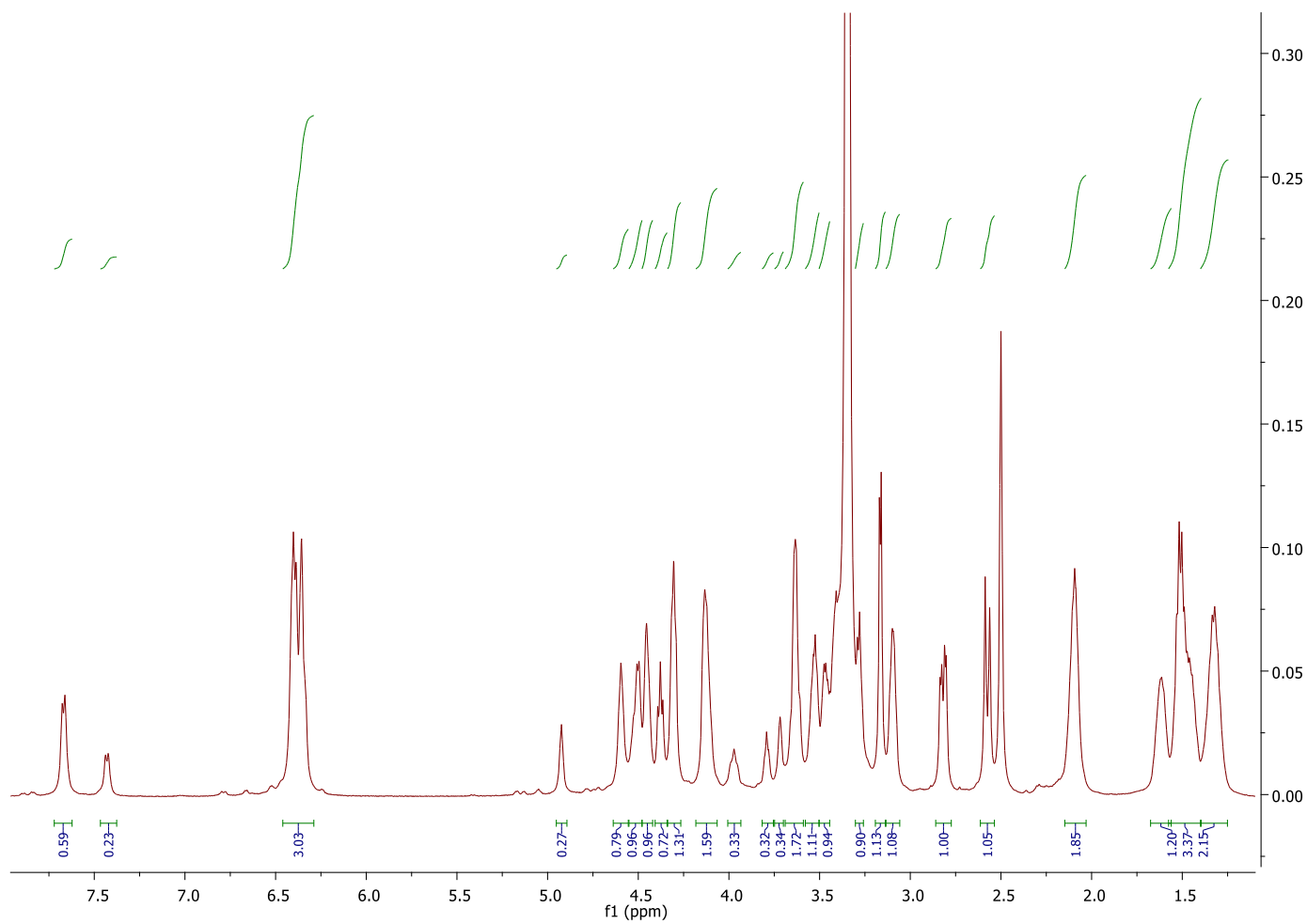


**Figure A 2.11**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms0-d}_6$ ) of Biotin-D-glucosamine **67**

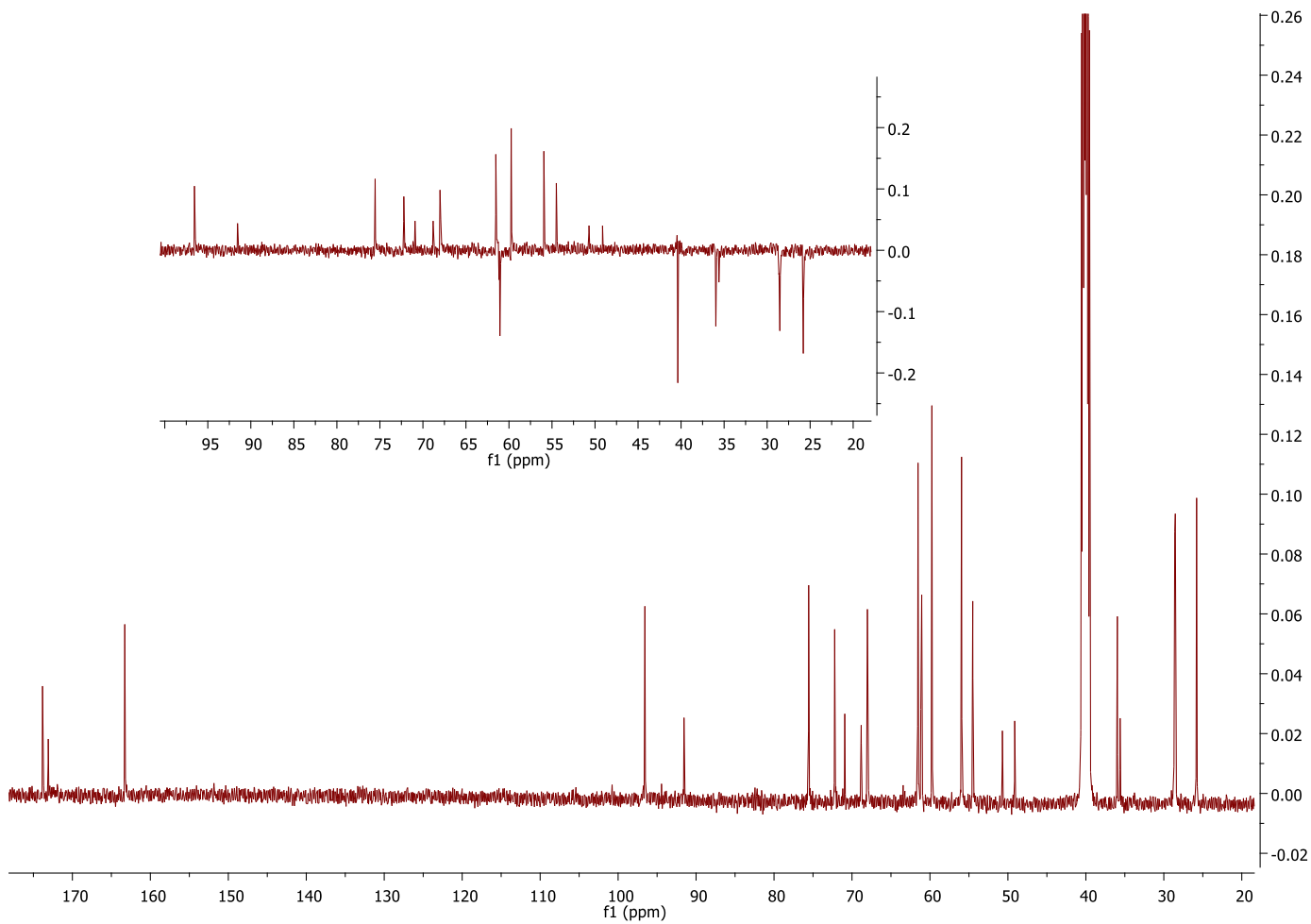




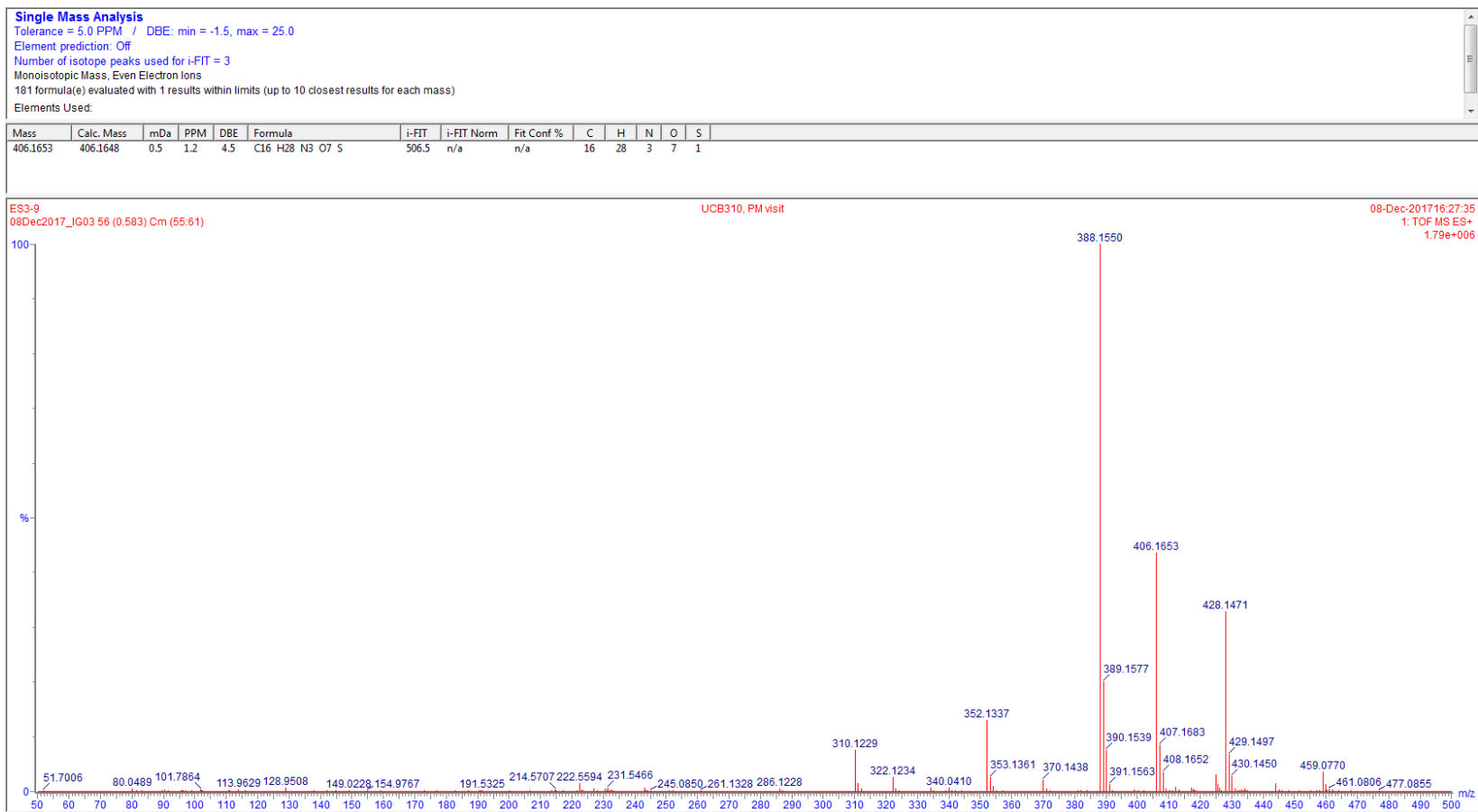
**Figure A 2.12** IR (neat) of Biotin-D-galactosamine **66**



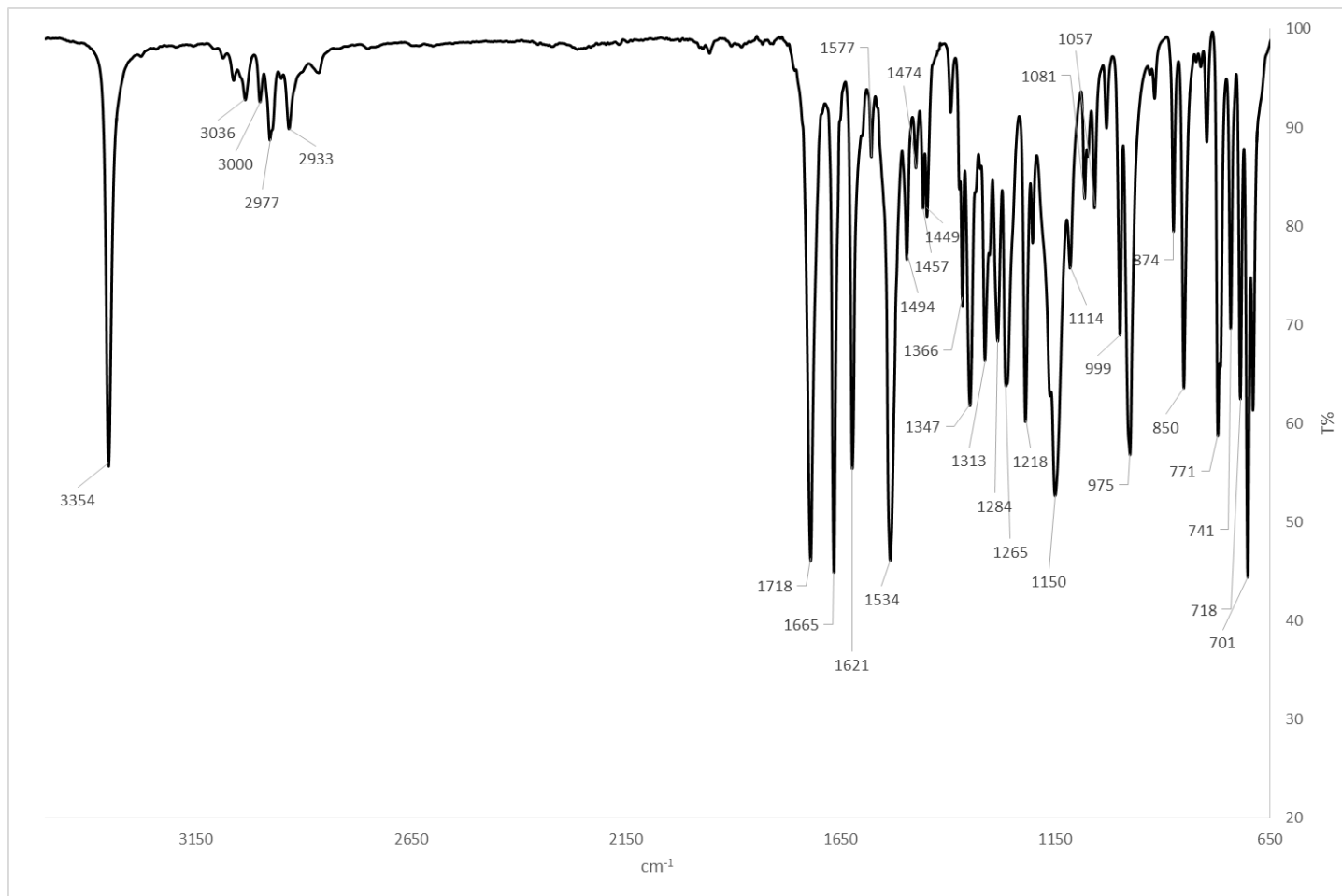
**Figure A 2.13**  $^1\text{H}$  NMR (500 MHz,  $\text{dms}\text{-d}_6$ ) of Biotin-D-galactosamine **66**



**Figure A 2.14**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms}\text{-d}_6$ ) of Biotin-D-galactosamine **66**



**Figure A 2.15 HR-MS of Biotin-D-galactosamine 66**



**Figure A 2.16** IR spectrum (neat) of Cin-F-OrBu 90

Sample 1 Vial 1:13 ID 31A File 08Jun2016\_ES01 PDF and RPT filename GeneralUser114

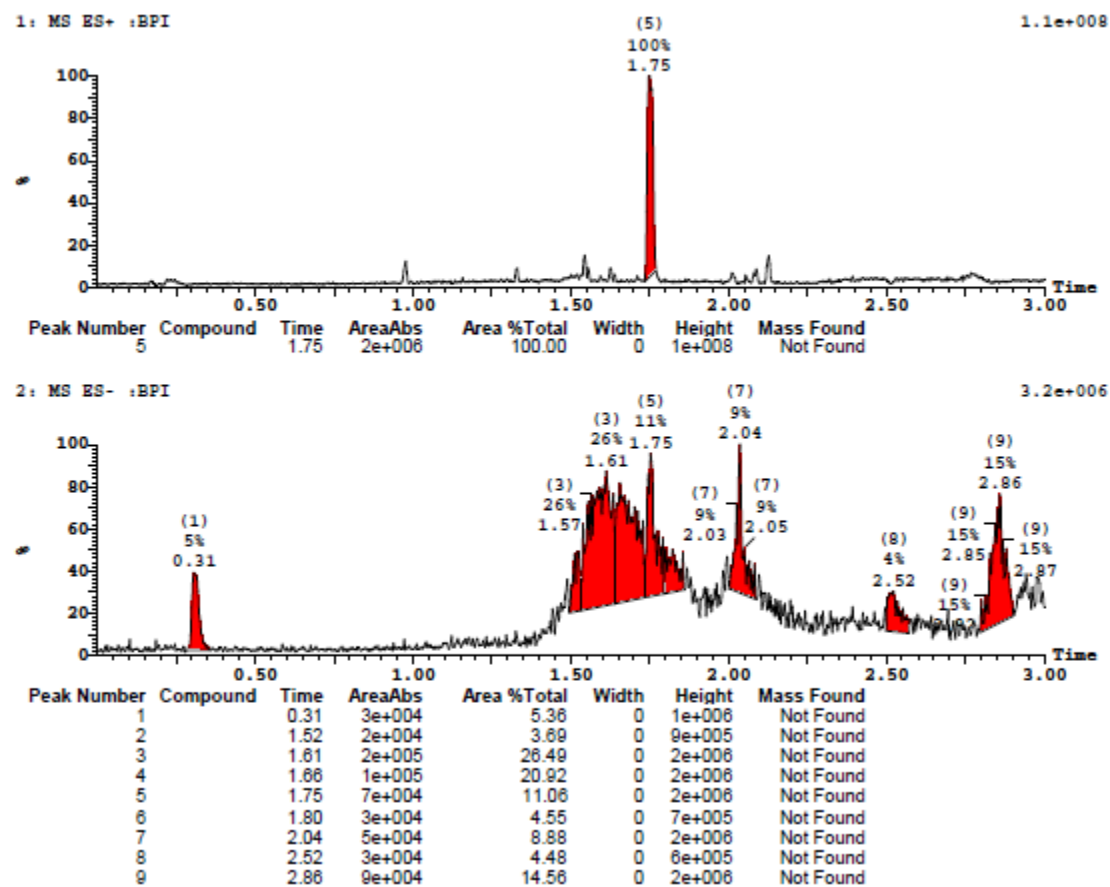
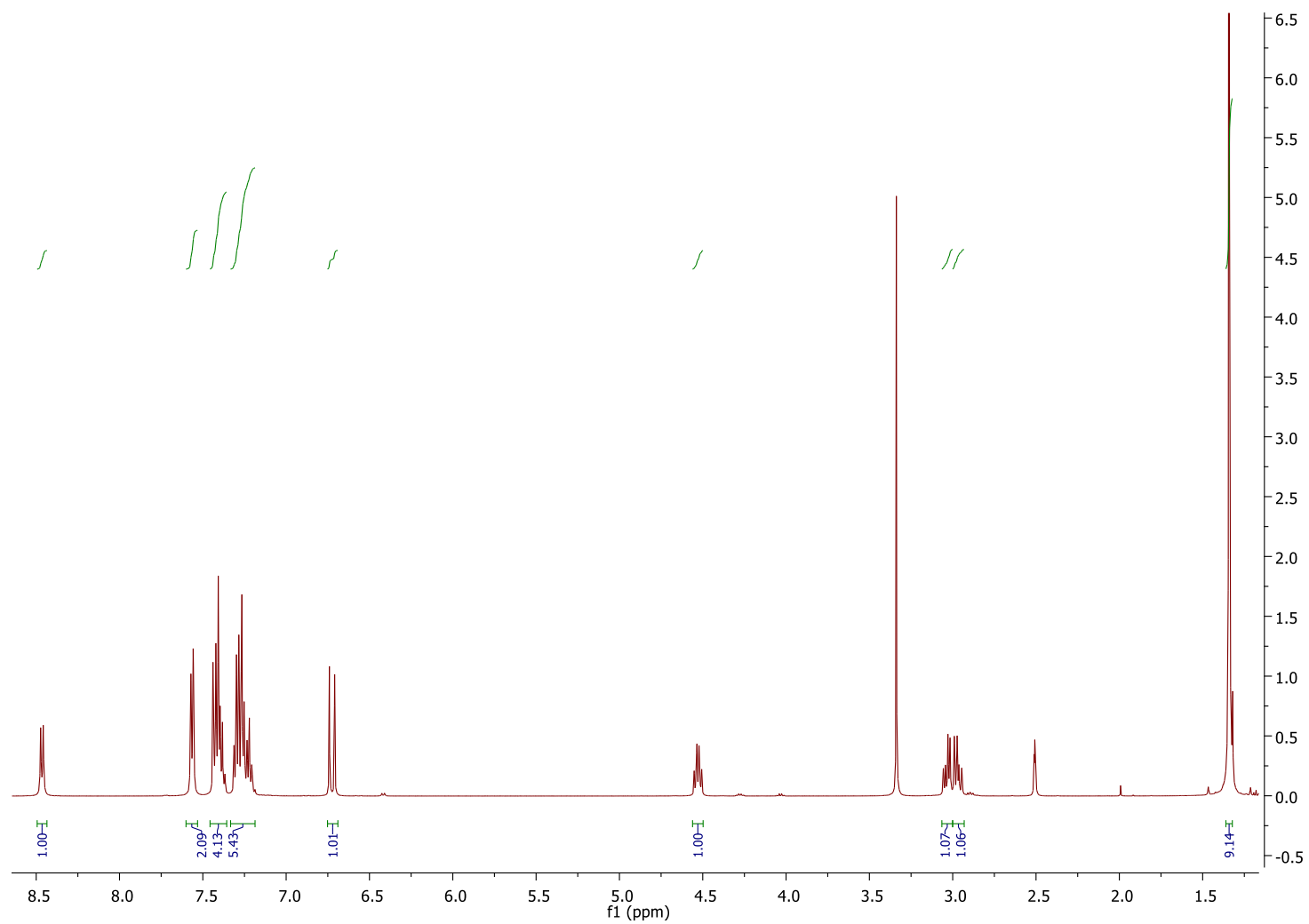


Figure A 2.17 MS (ES<sup>+</sup>) of Cin-F-*o*tBu ester **90**. Mass was not found



**Figure A 2.18**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) of Cin-F-OtBu **90**

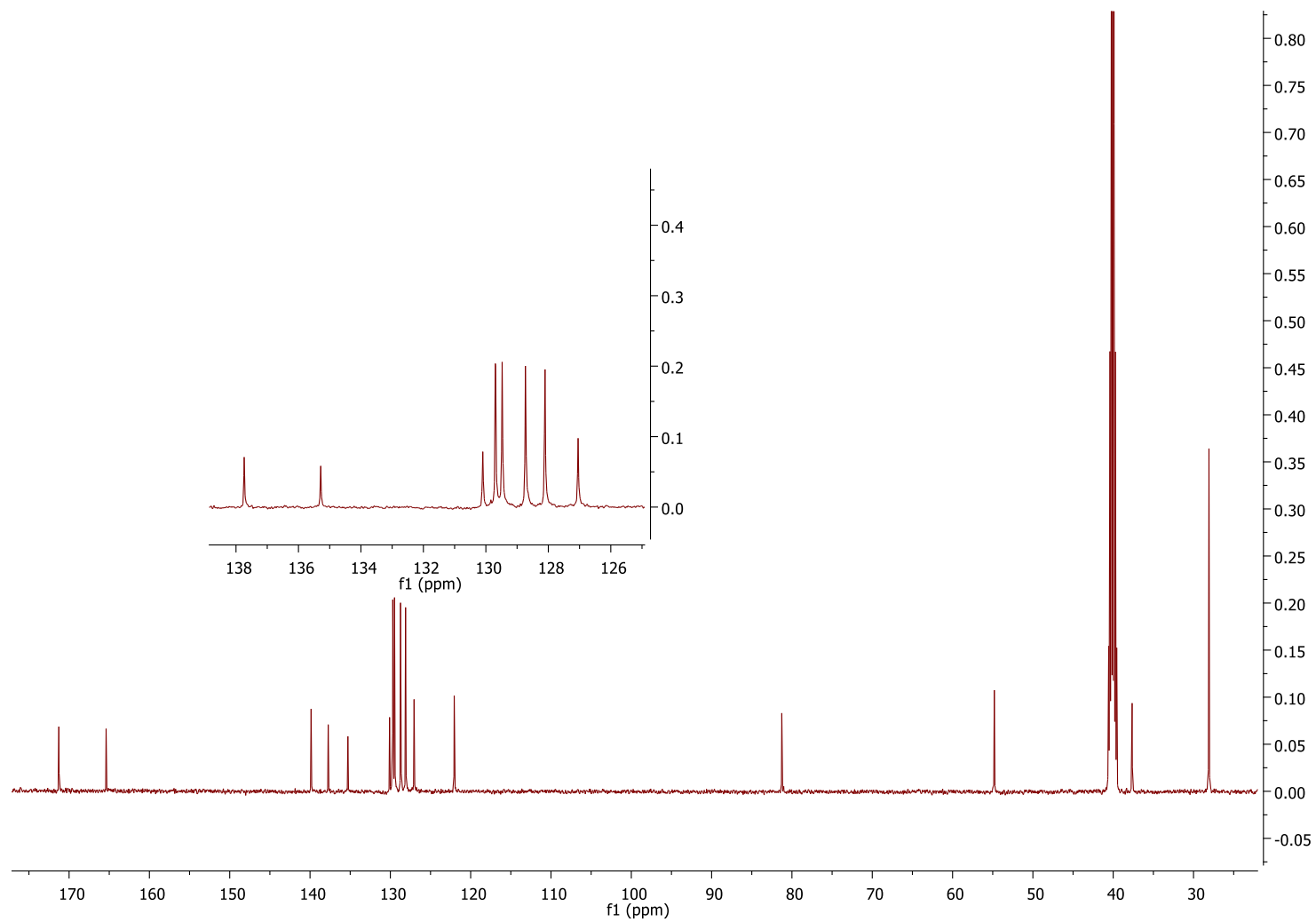
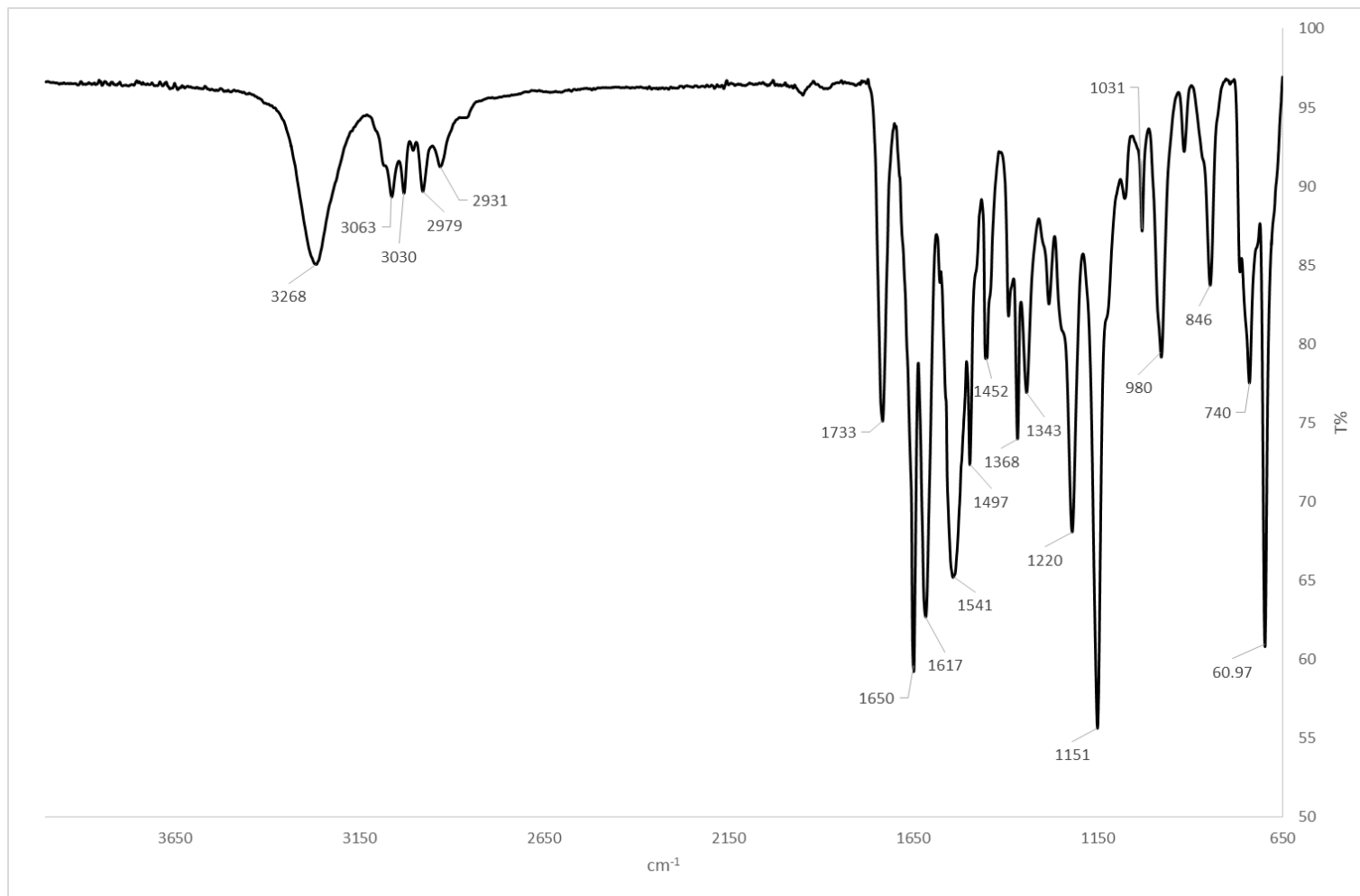


Figure A 2.19  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms0-d}_6$ ) of Cin-F-OtBu **90**

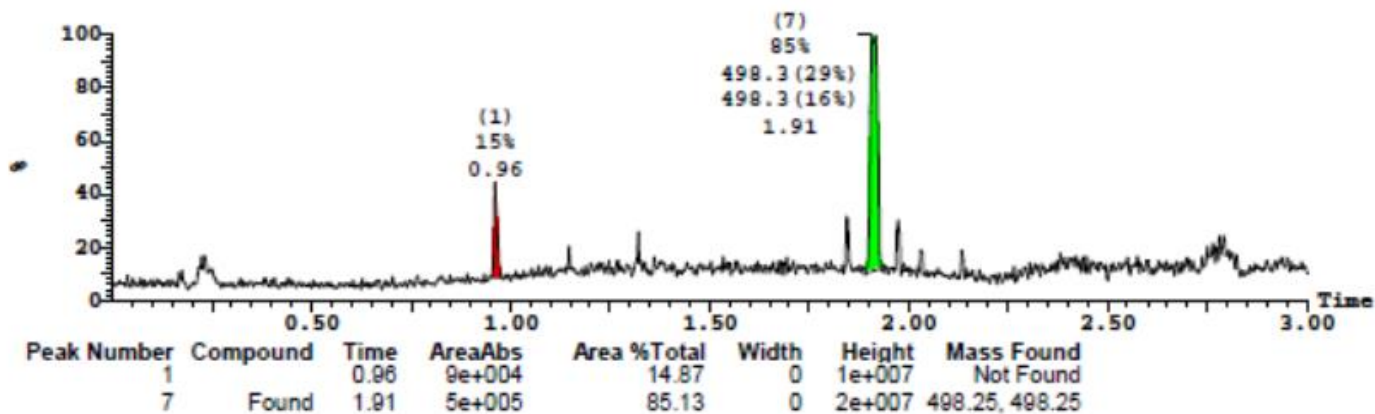




**Figure A 2.20** IR spectrum (neat) of Cin-L-F-L-FOtBu **91** and Cin-D-F-L-FOtBu **92** mixture (2:1 ratio)

1: MS ES+ :BPI

2.7e+007



Peak ID Time  
7 1.91

1:MS ES+  
1.1e+007

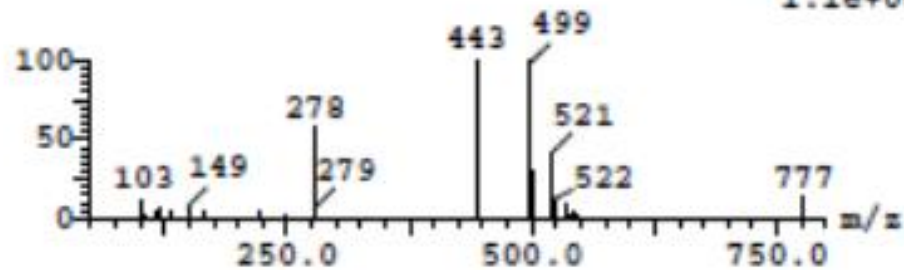
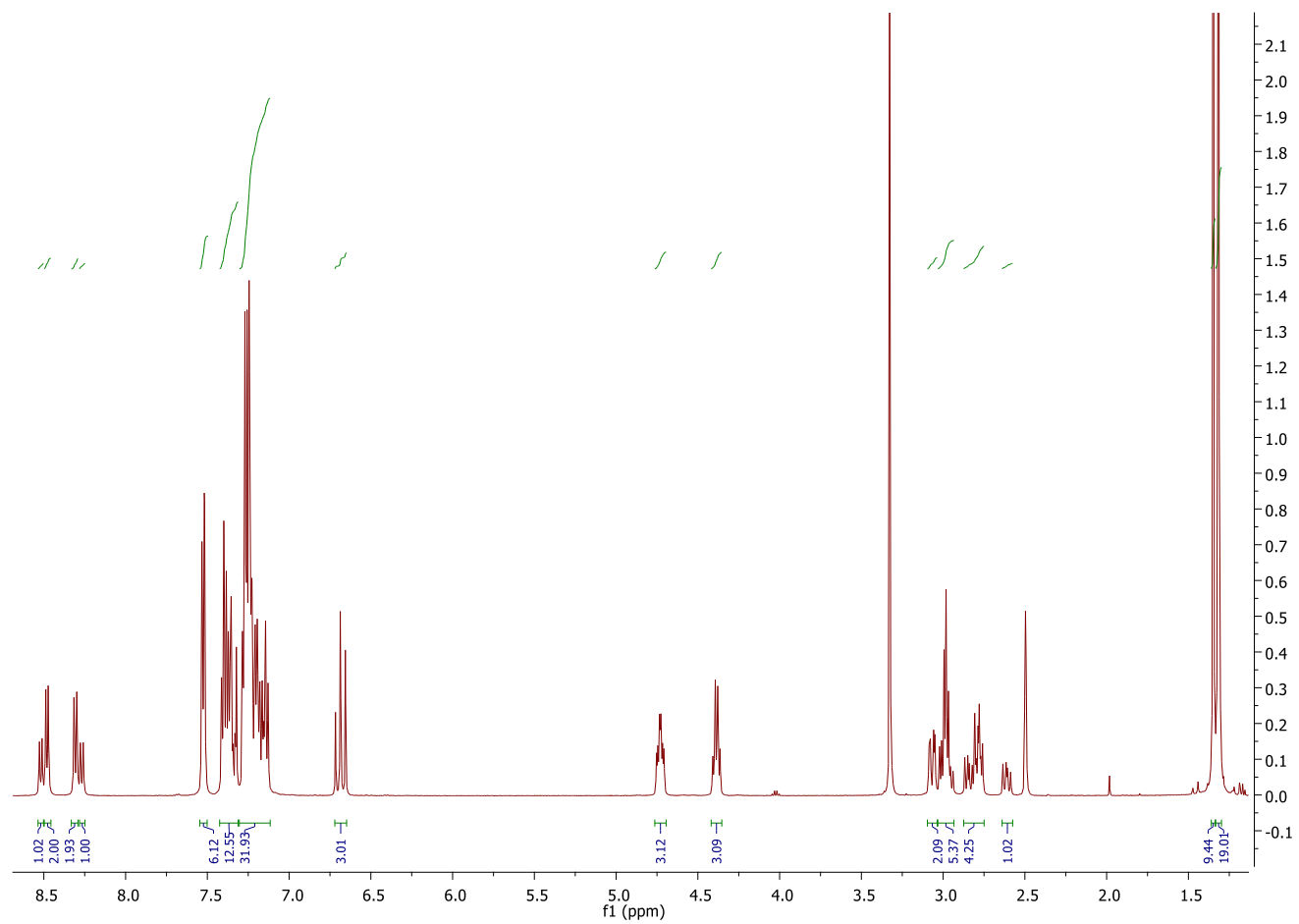
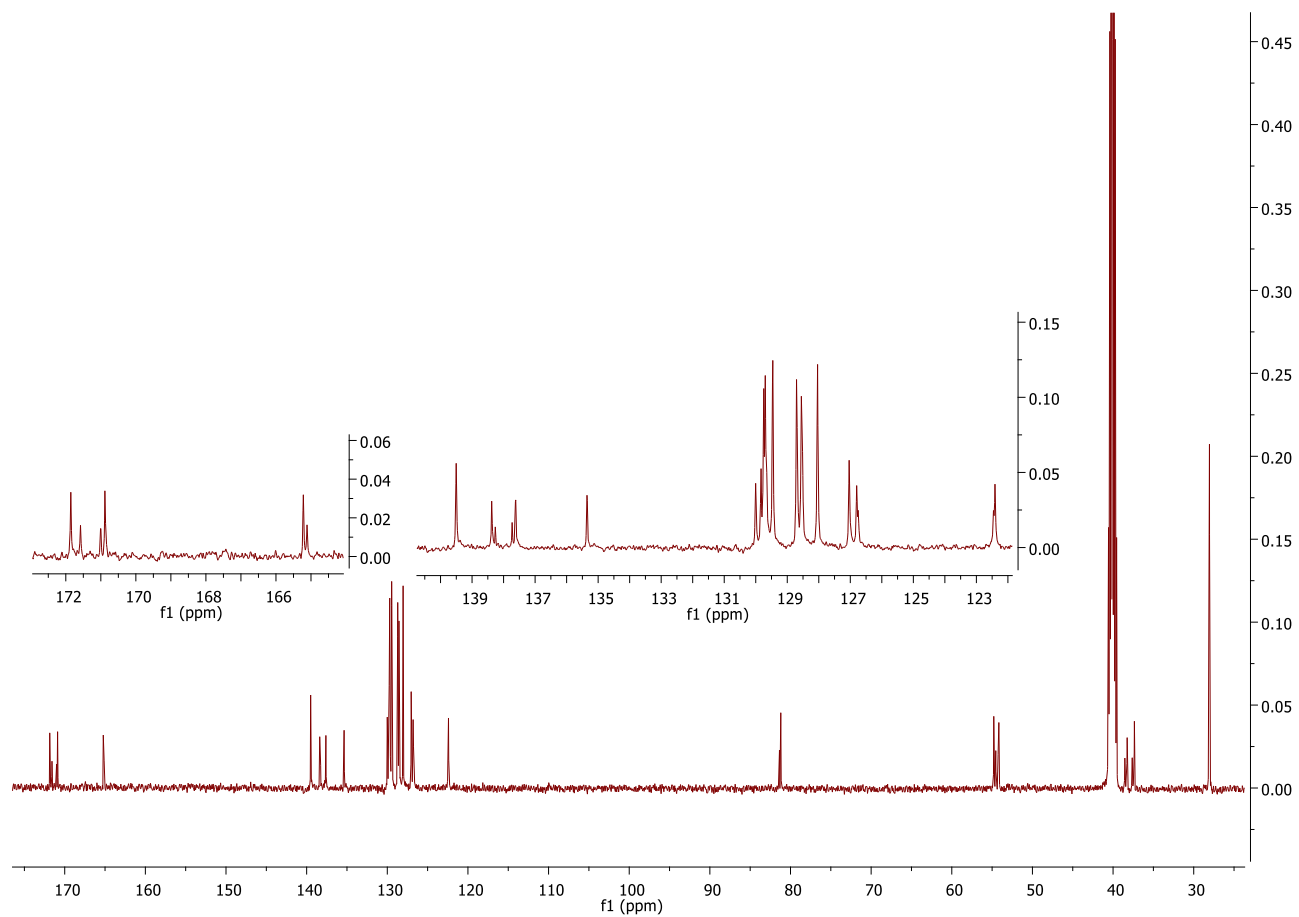


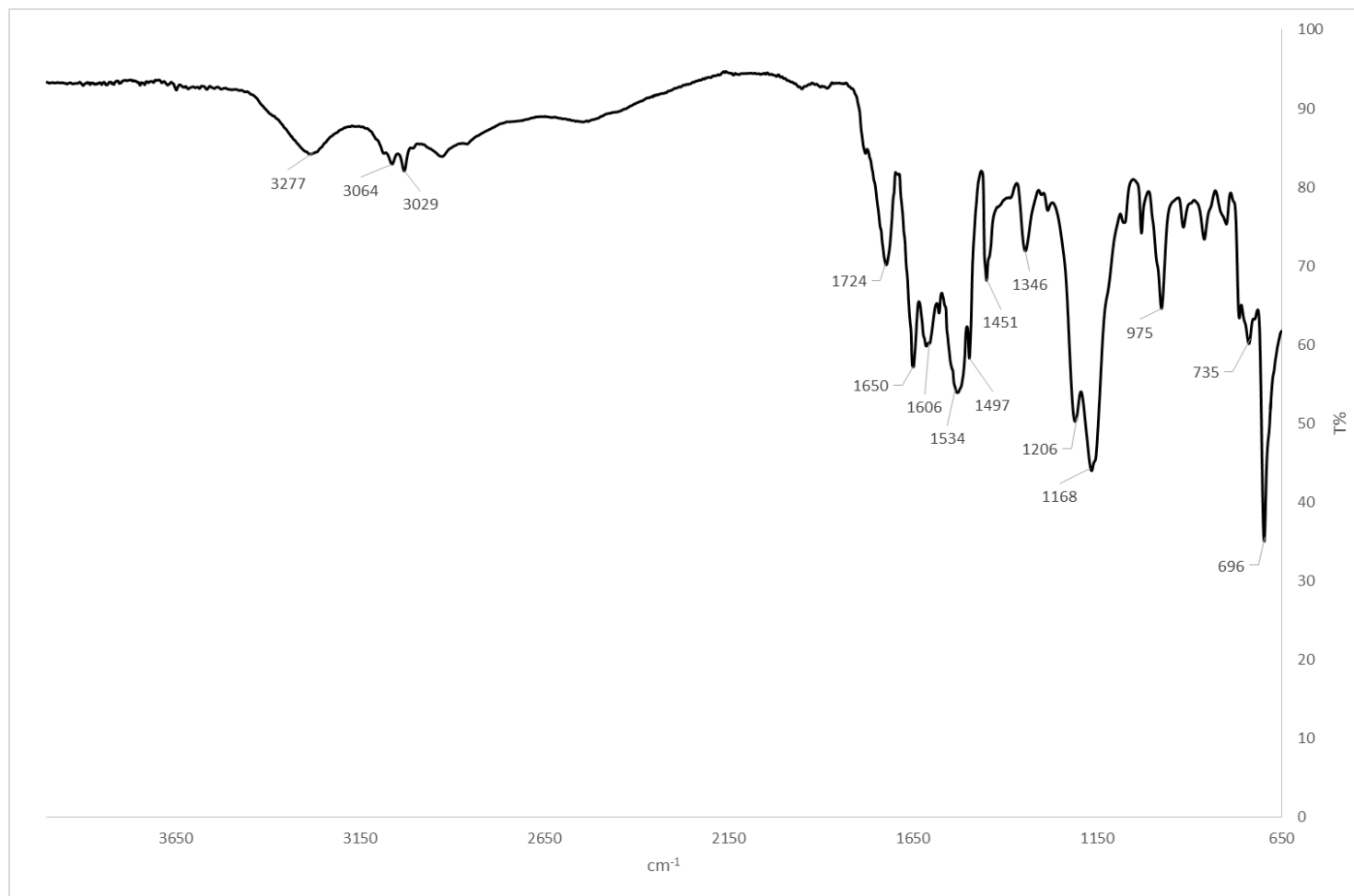
Figure A 2.21 MS (ES<sup>+</sup>) of Cin-L-F-L-FOtBu **91** and Cin-D-F-L-FOtBu **92** mixture (2:1 ratio)



**Figure A 2.22**  $^1\text{H}$  NMR (500 MHz,  $\text{dms}\text{-d}_6$ ) spectrum of Cin-L-F-L-FO/Bu **91** and Cin-D-F-L-FO/Bu **92** mixture (2:1 ratio)



**Figure A 2.23**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms}\text{-d}_6$ ) spectrum of Cin-L-F-L-FOtBu **91** and Cin-D-F-L-FOtBu **92** mixture (2:1 ratio)



**Figure A 2.24** IR spectrum (neat) of Cin-L-F-L-F **70** and Cin-D-F-L-F **93** mixture (2:1 ratio)

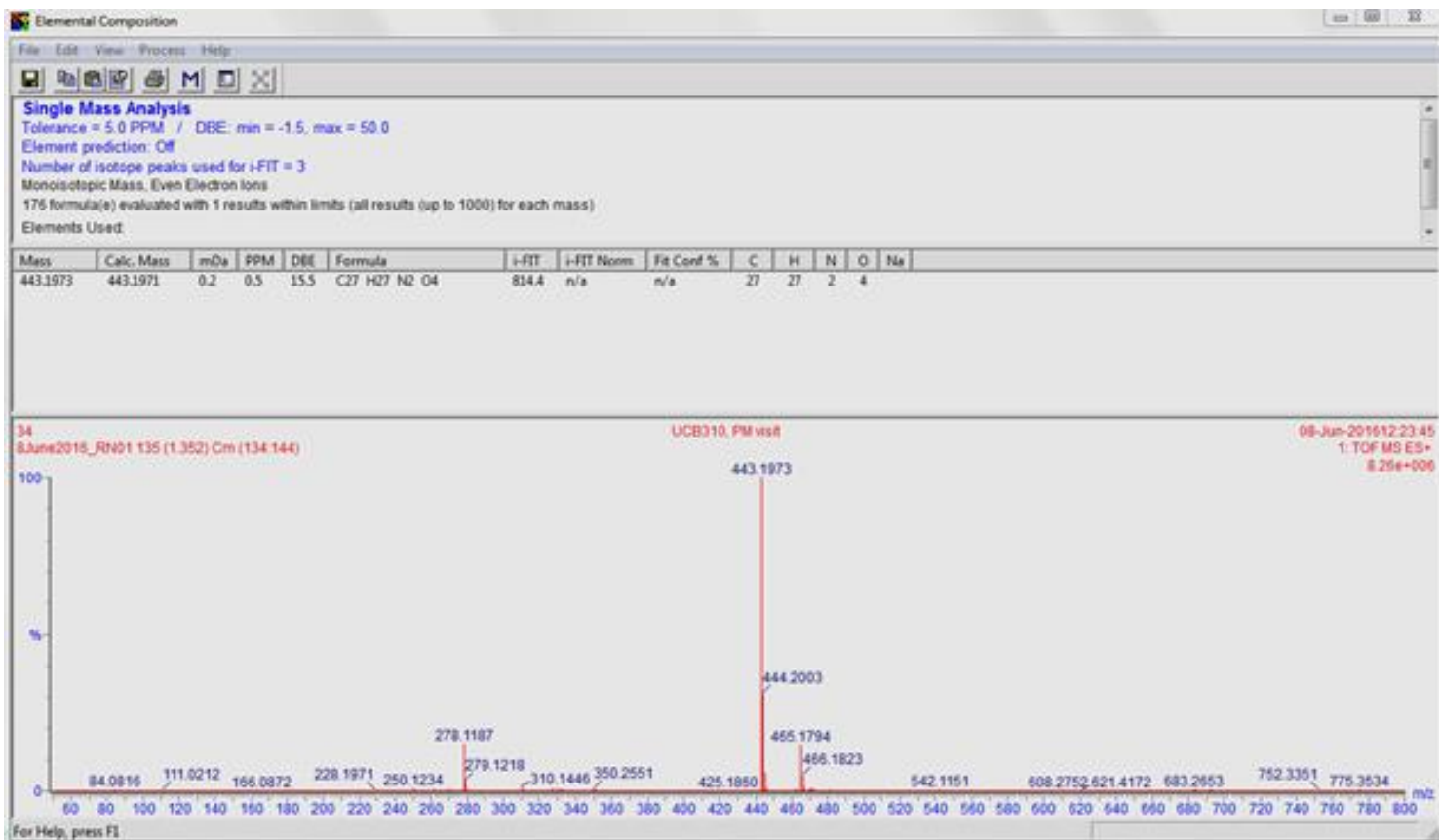


Figure A 2.25 HR-MS  $[M+H]^+$  of Cin-L-F-L-F **70** and Cin-D-F-L-F **93** mixture (2:1 ratio)

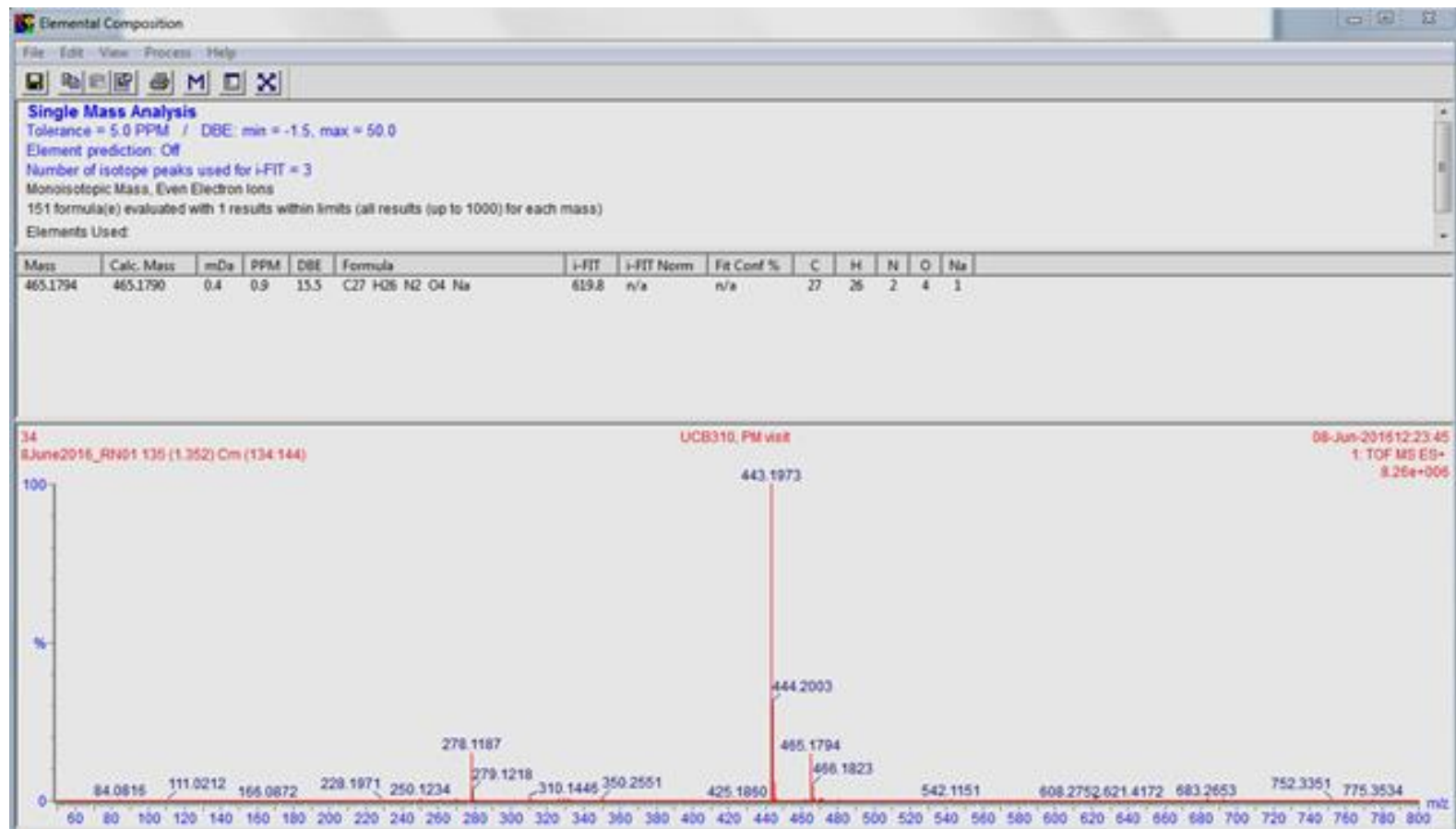
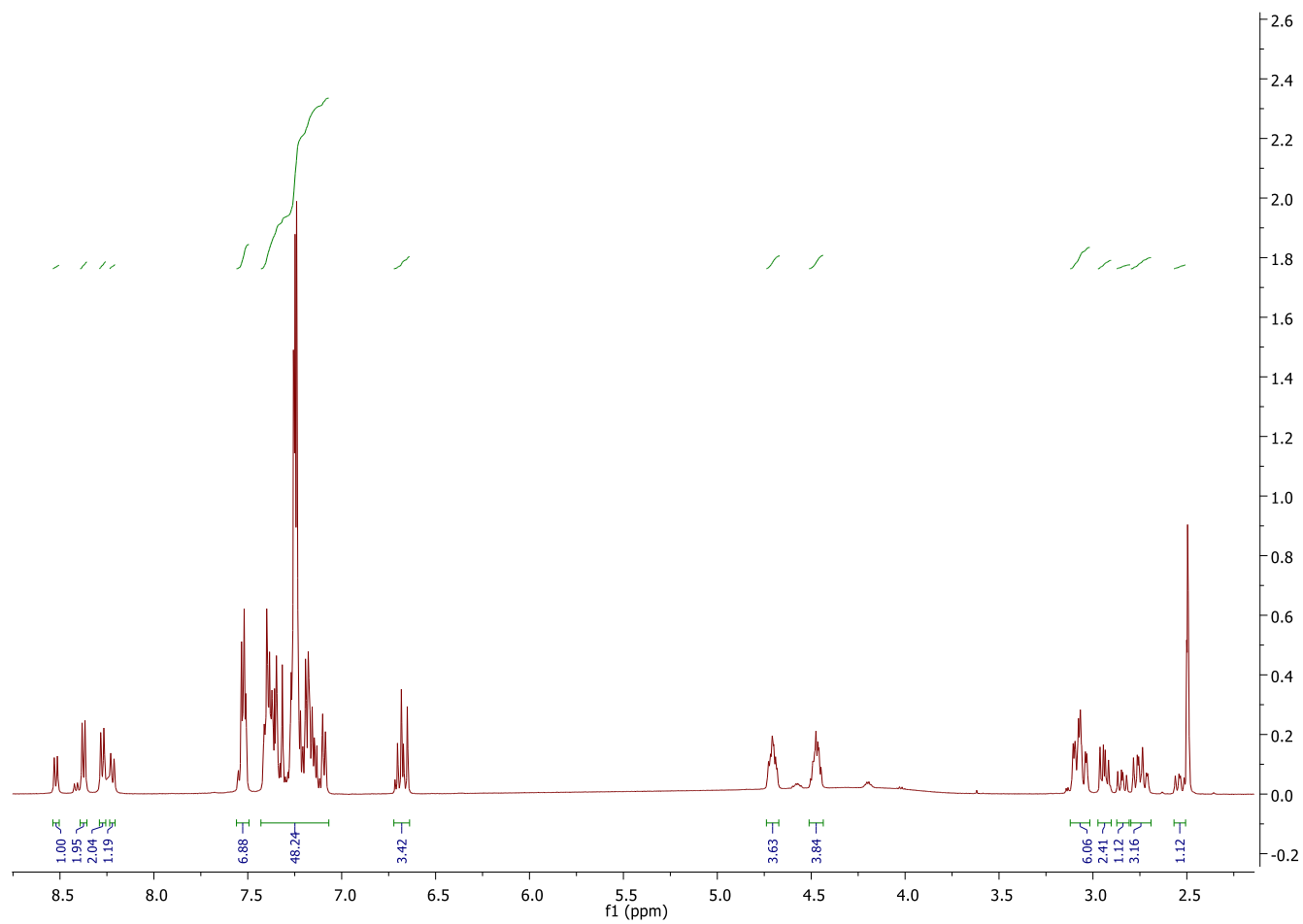
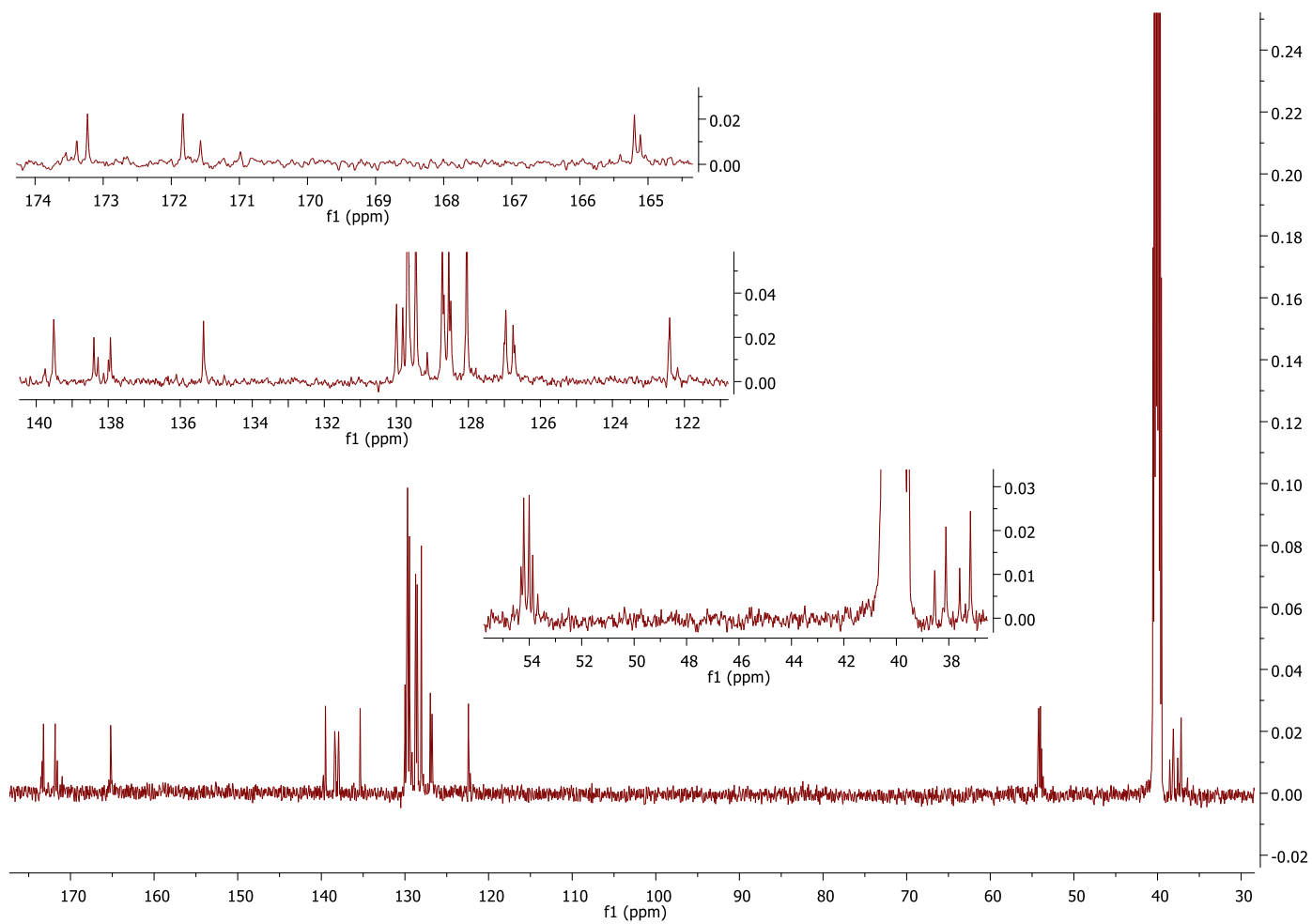


Figure A 2.26 HR-MS  $[M+Na]^+$  of Cin-L-F-L-F **70** and Cin-D-F-L-F **93** mixture (2:1 ratio)

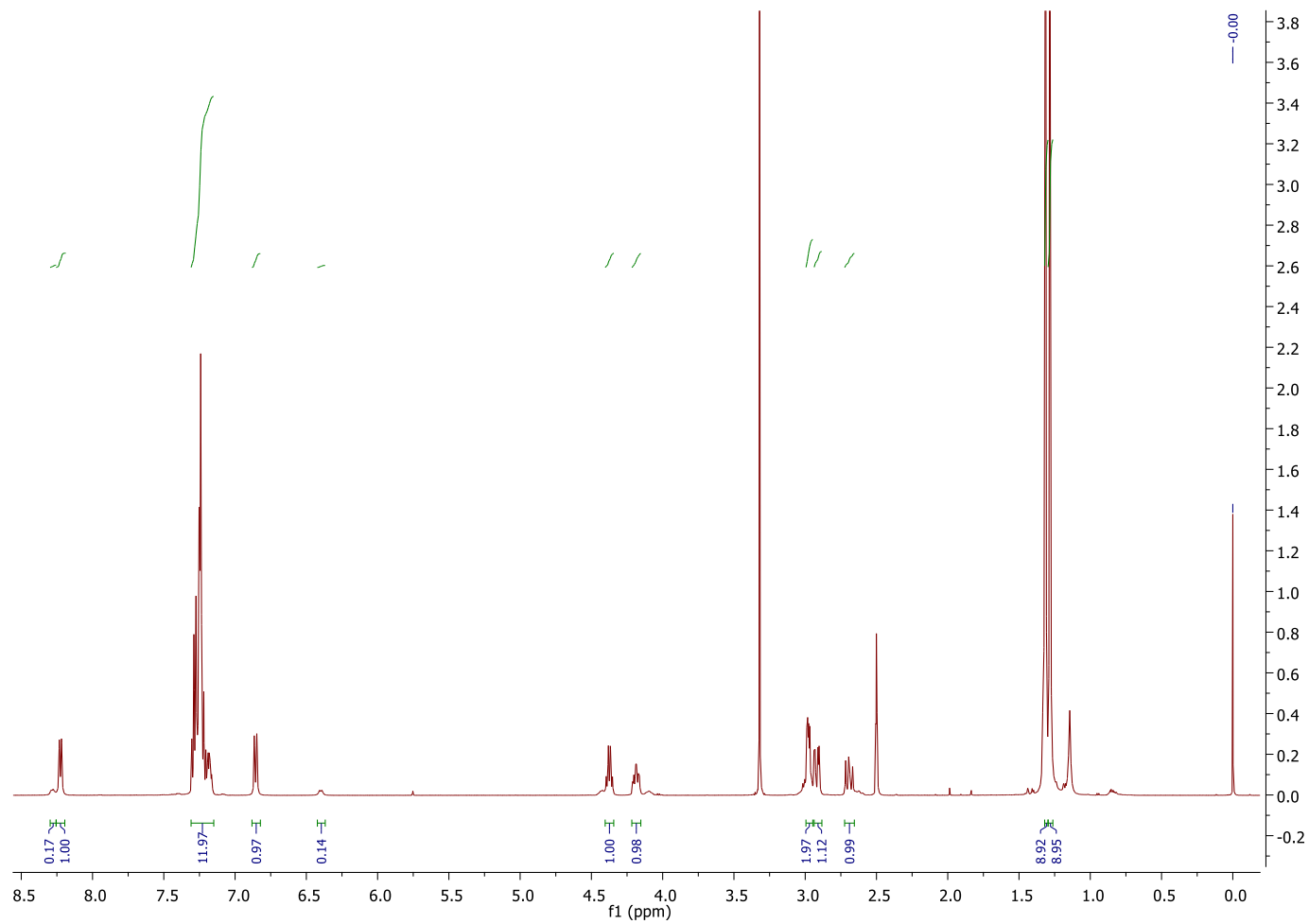


**Figure A 2.27** <sup>1</sup>H NMR (500 MHz, dms<sub>o</sub>-d<sub>6</sub>) spectrum of Cin-L-F-L-F **70** and Cin-D-F-L-F **93** mixture (2:1 ratio)

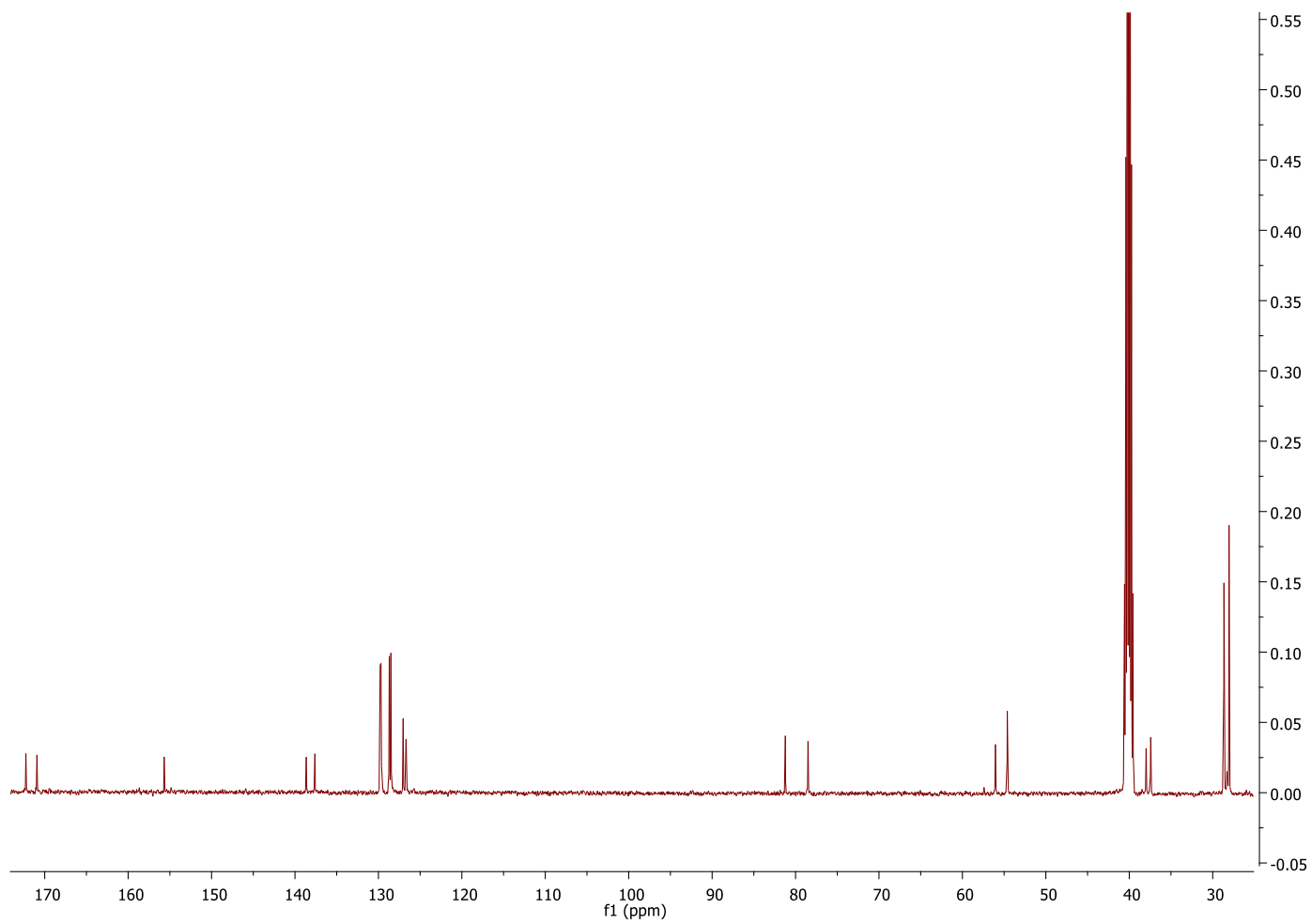




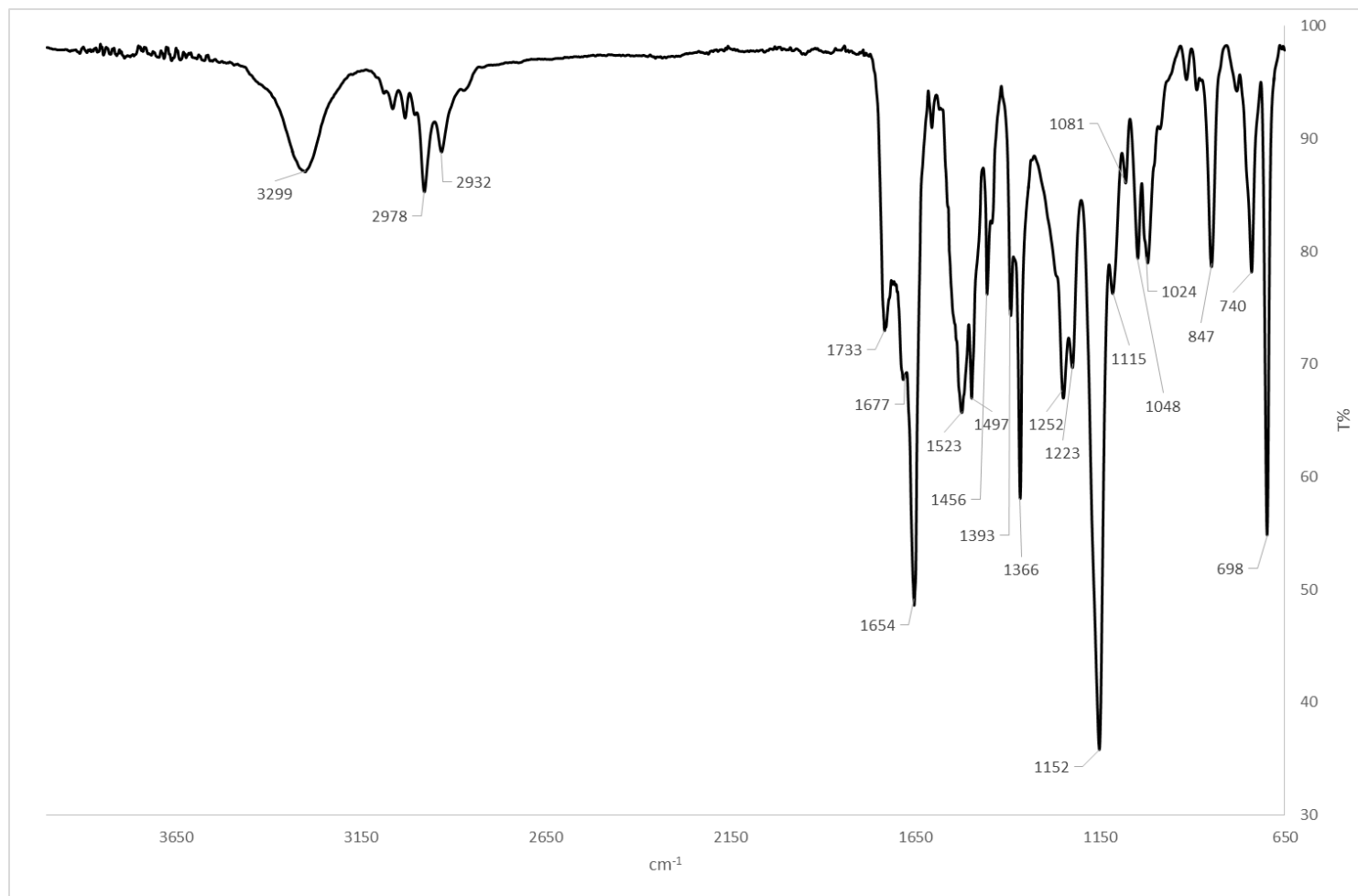
**Figure A 2.28**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms0-d}_6$ ) spectrum of Cin-L-F-L-F **70** and Cin-D-F-L-F **93** mixture (2:1 ratio)



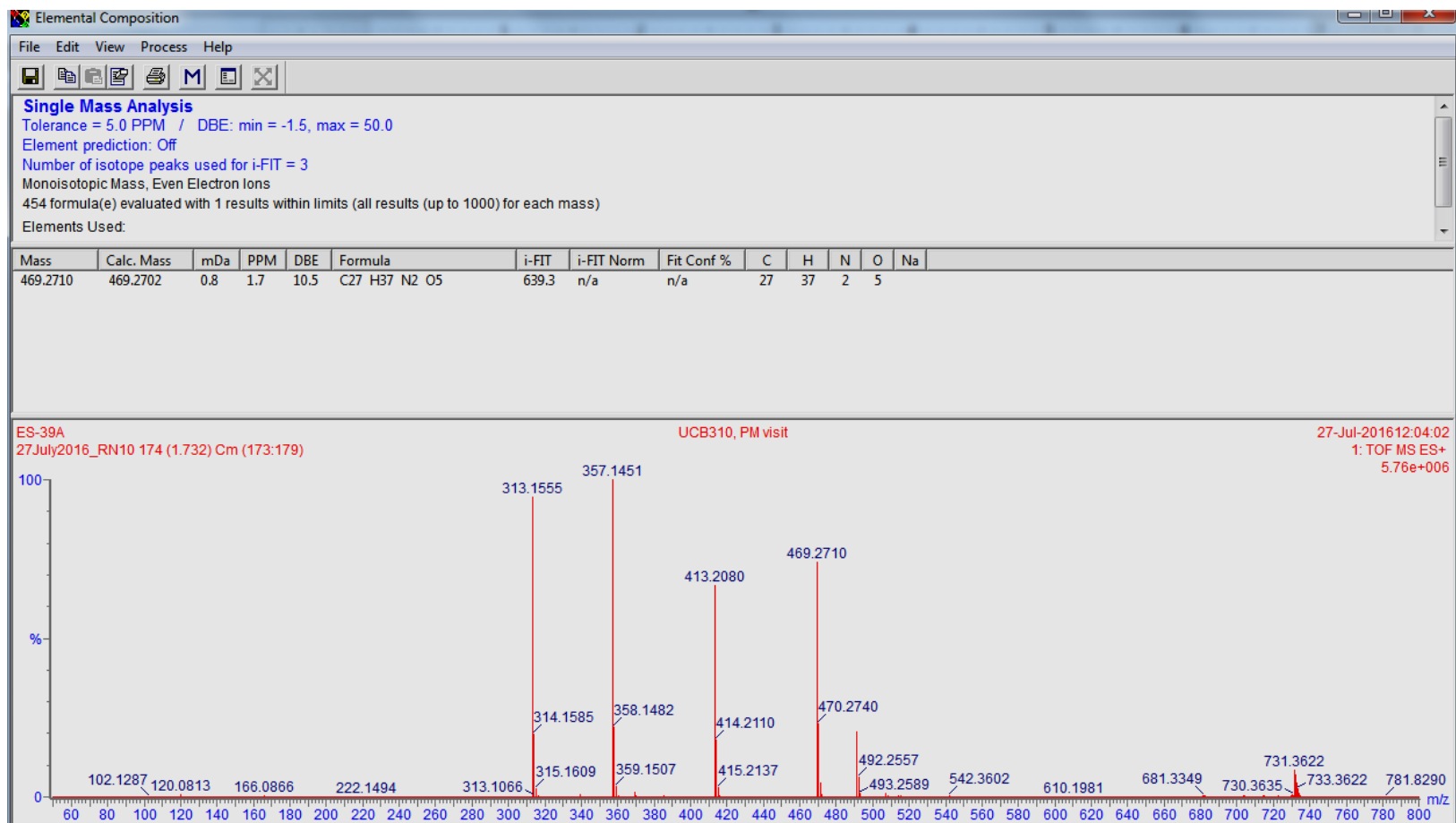
**Figure A 2.29**  $^1\text{H}$  NMR (500 MHz,  $\text{dmsso-d}_6$ ) spectrum of Boc-F-FOtBu **102**



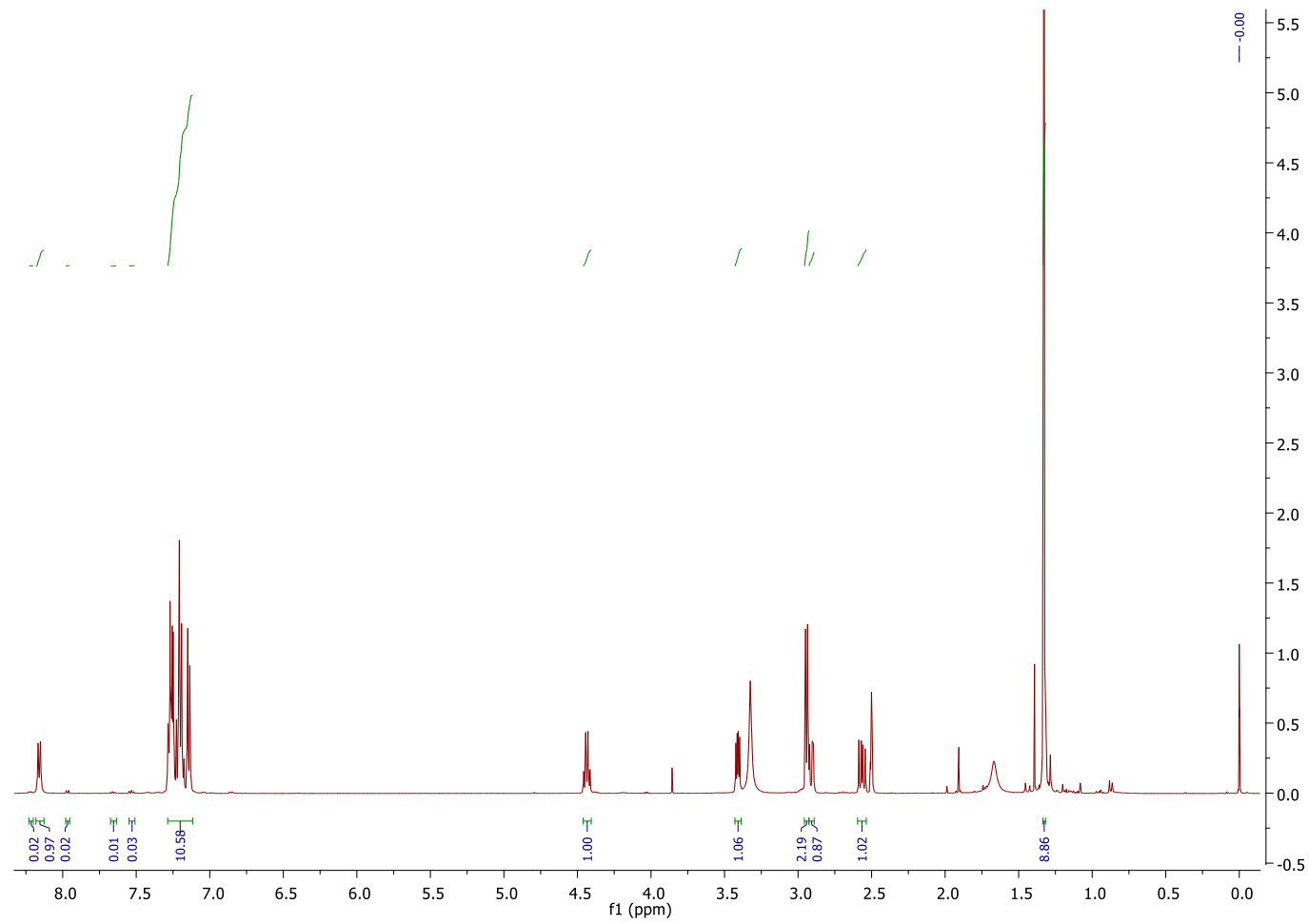
**Figure A 2.30**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms}\text{-d}_6$ ) spectrum of *Boc-F-FOtBu* **102**



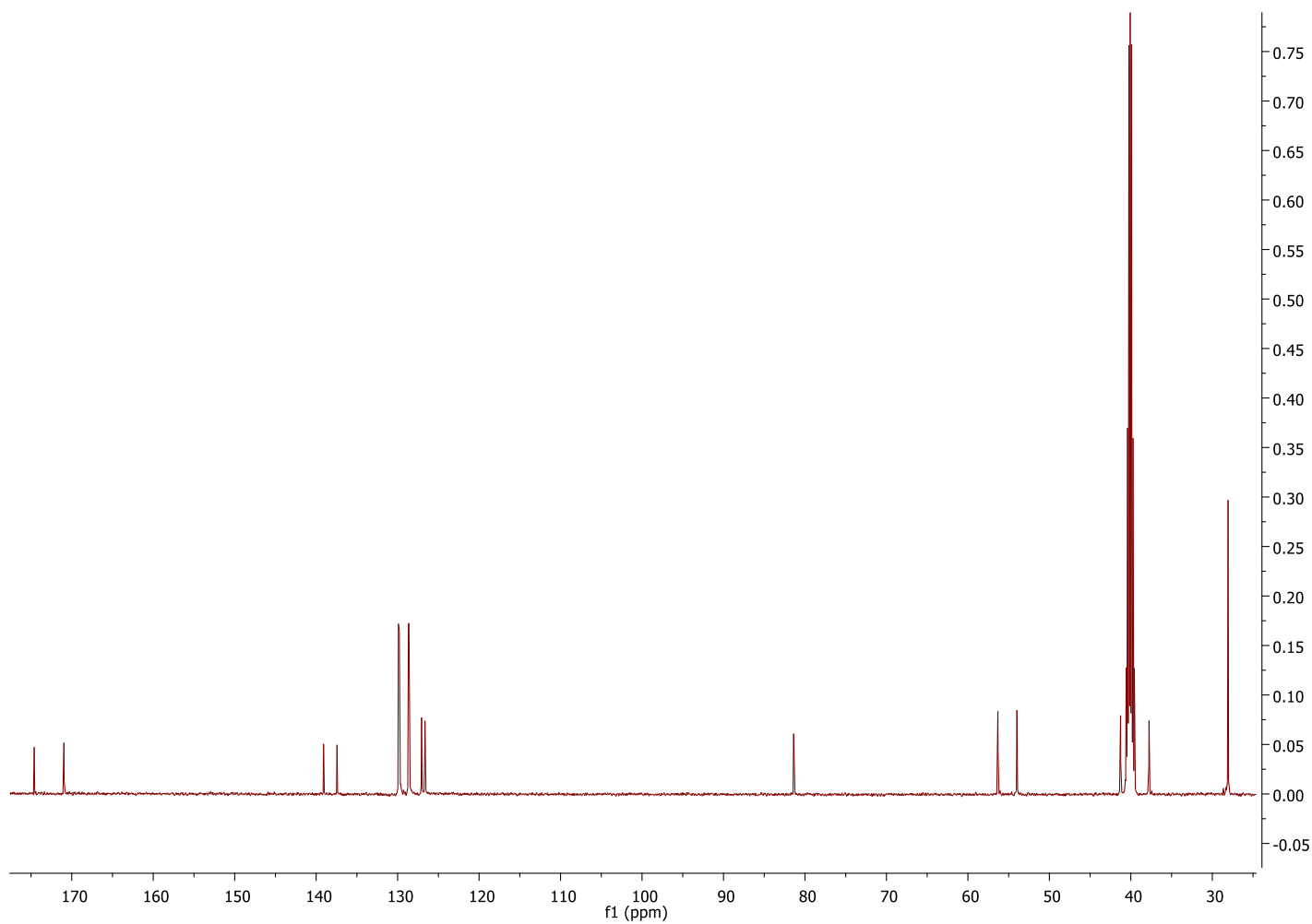
**Figure A 2.31** IR spectrum (neat) of *Boc-F-FOtBu 102*



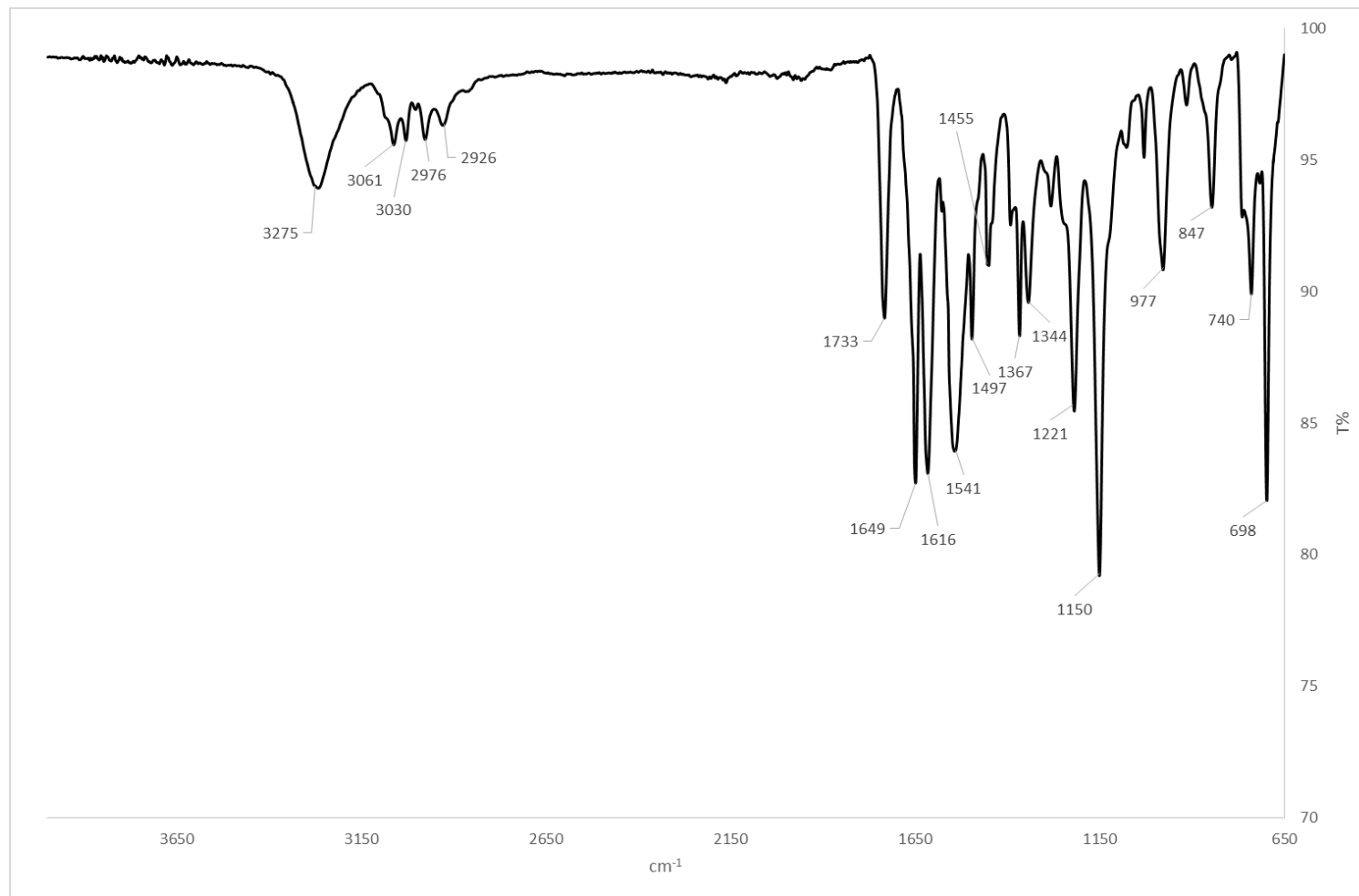
**Figure A 2.32** HR MS  $[M+H]^+$  of *Boc-F-FOtBu 102*. Mass found  $m/z$  491 (tentative)



**Figure A 2.33**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of F-FOtBu **103**



**Figure A 2.34**  $^{13}\text{C}$  NMR (126 MHz, dms0-d<sub>6</sub>) spectrum of F-FOtBu **103**

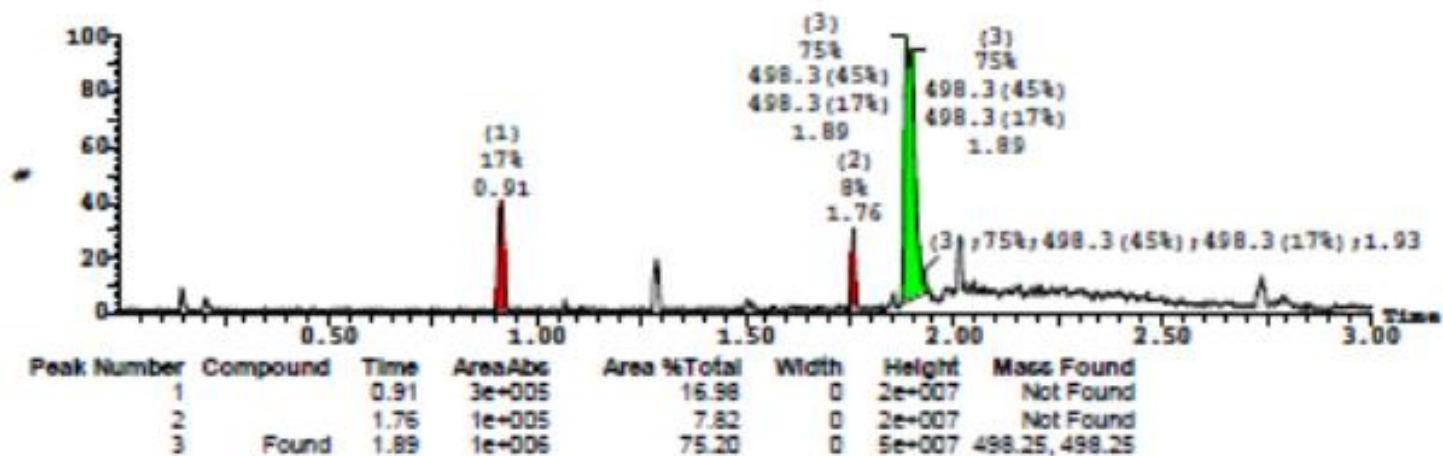


**Figure A 2.35** IR spectrum (neat) of Cin-F-FOtBu **91**

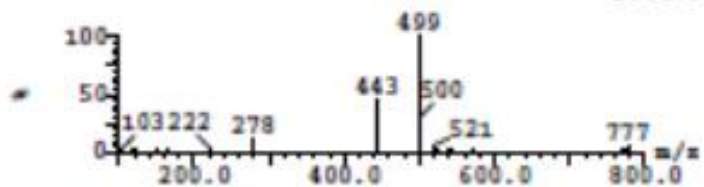


1: MS ES+ :BPI

5.4e+007



Peak ID Time  
3 1.89



Peak ID Time  
3 1.89

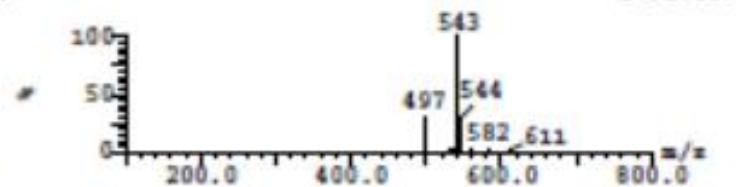
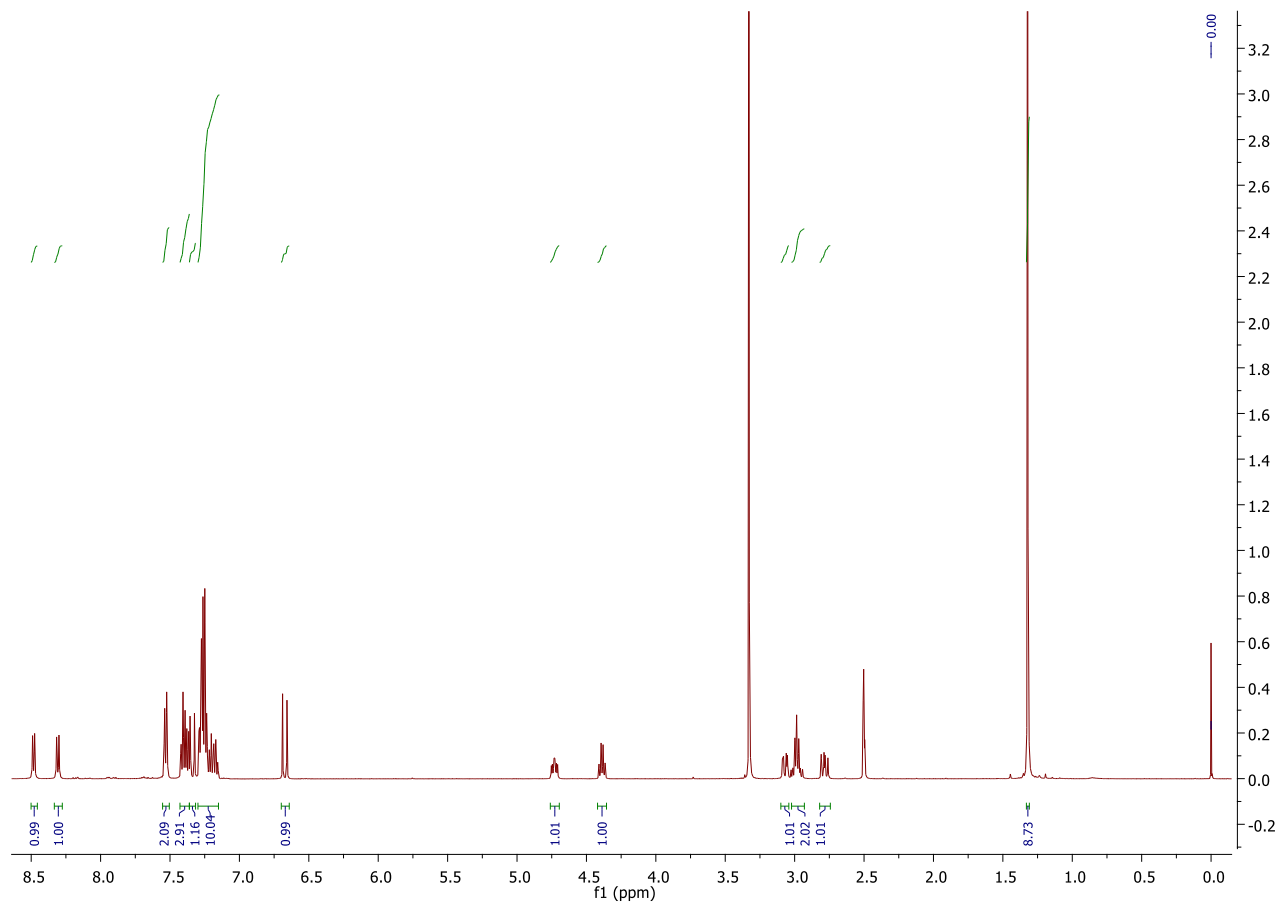
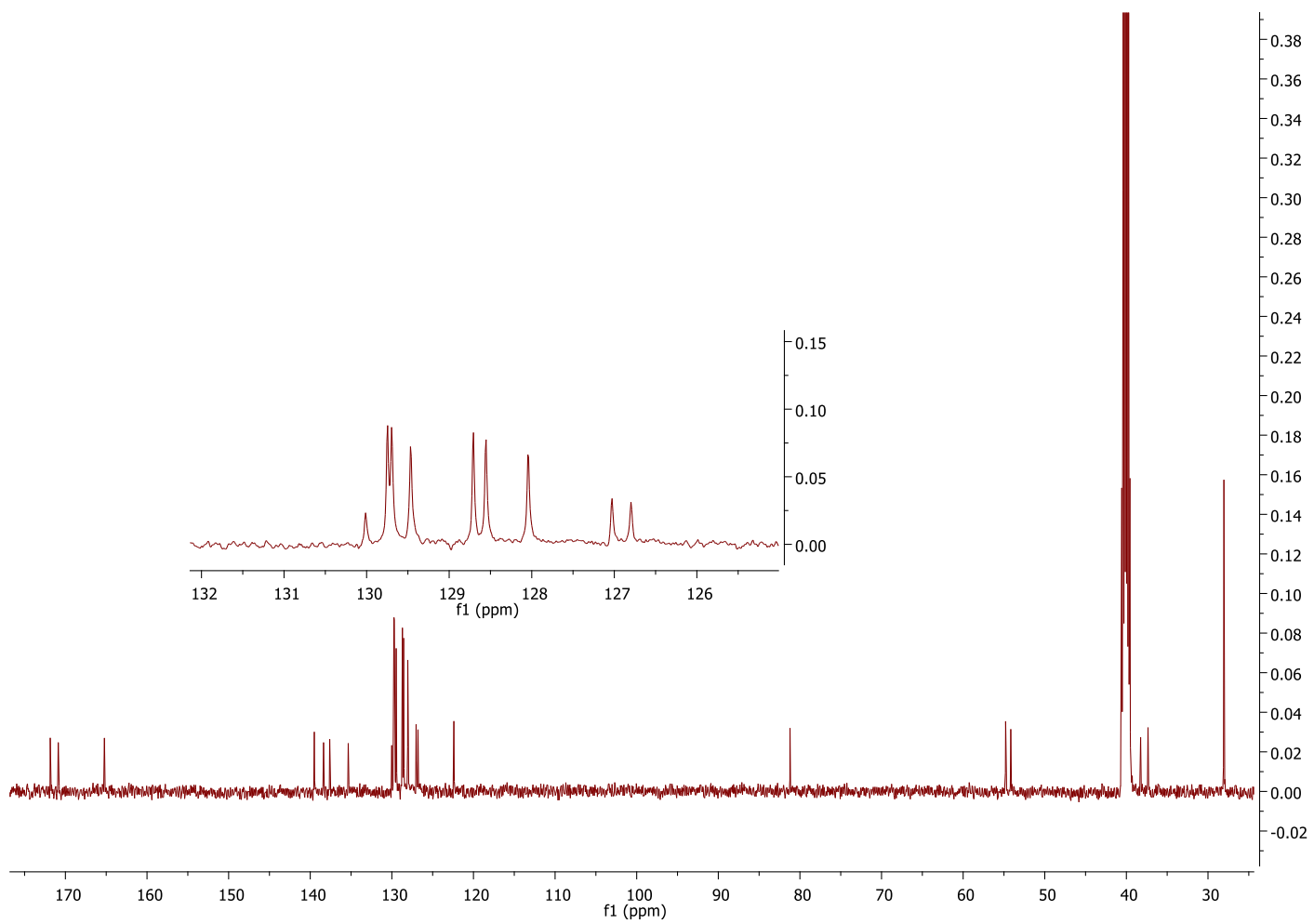


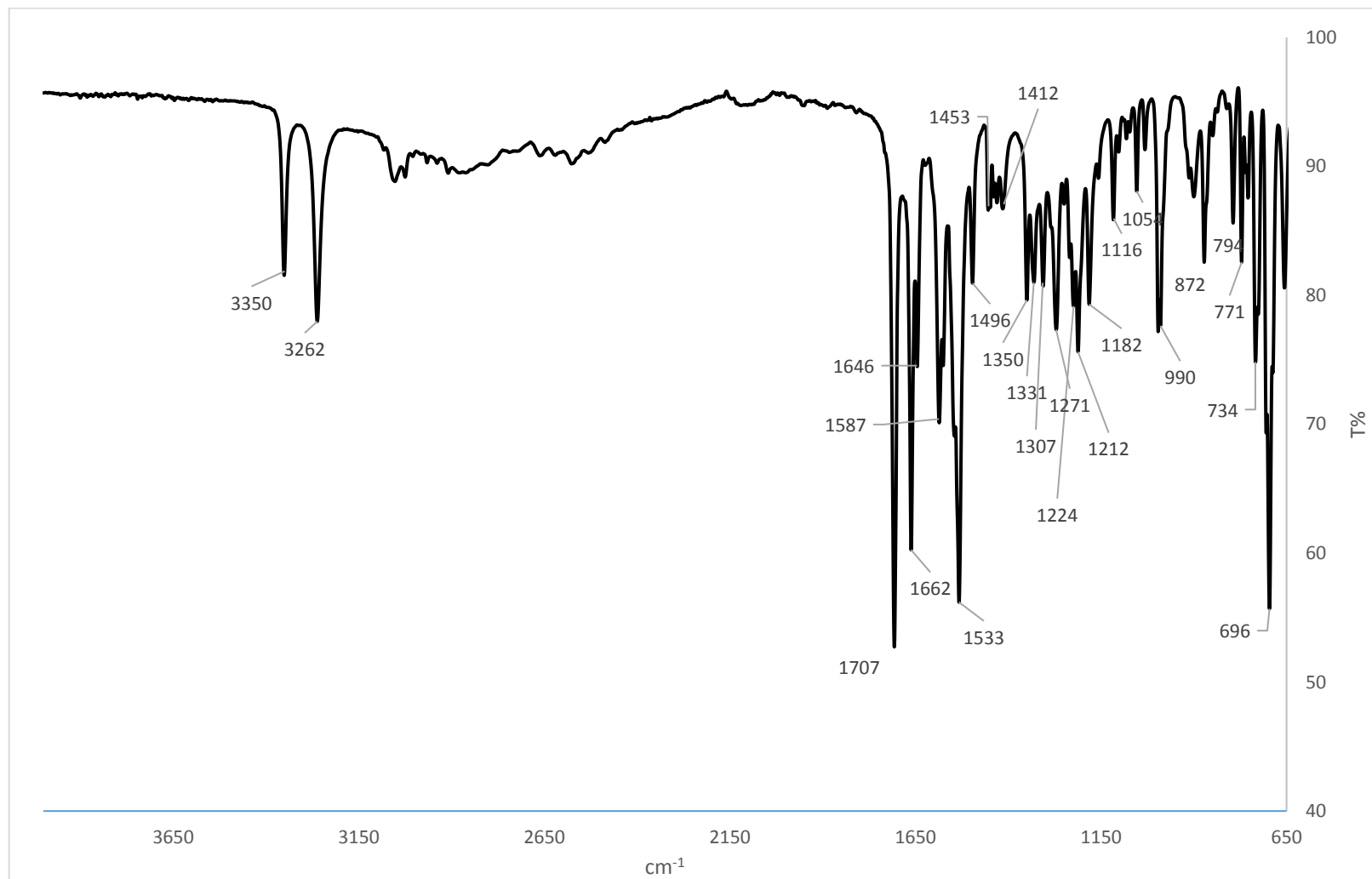
Figure A 2.36 MS (ES<sup>+</sup>) and (ES<sup>-</sup>): of Cin-F-FOtBu 91



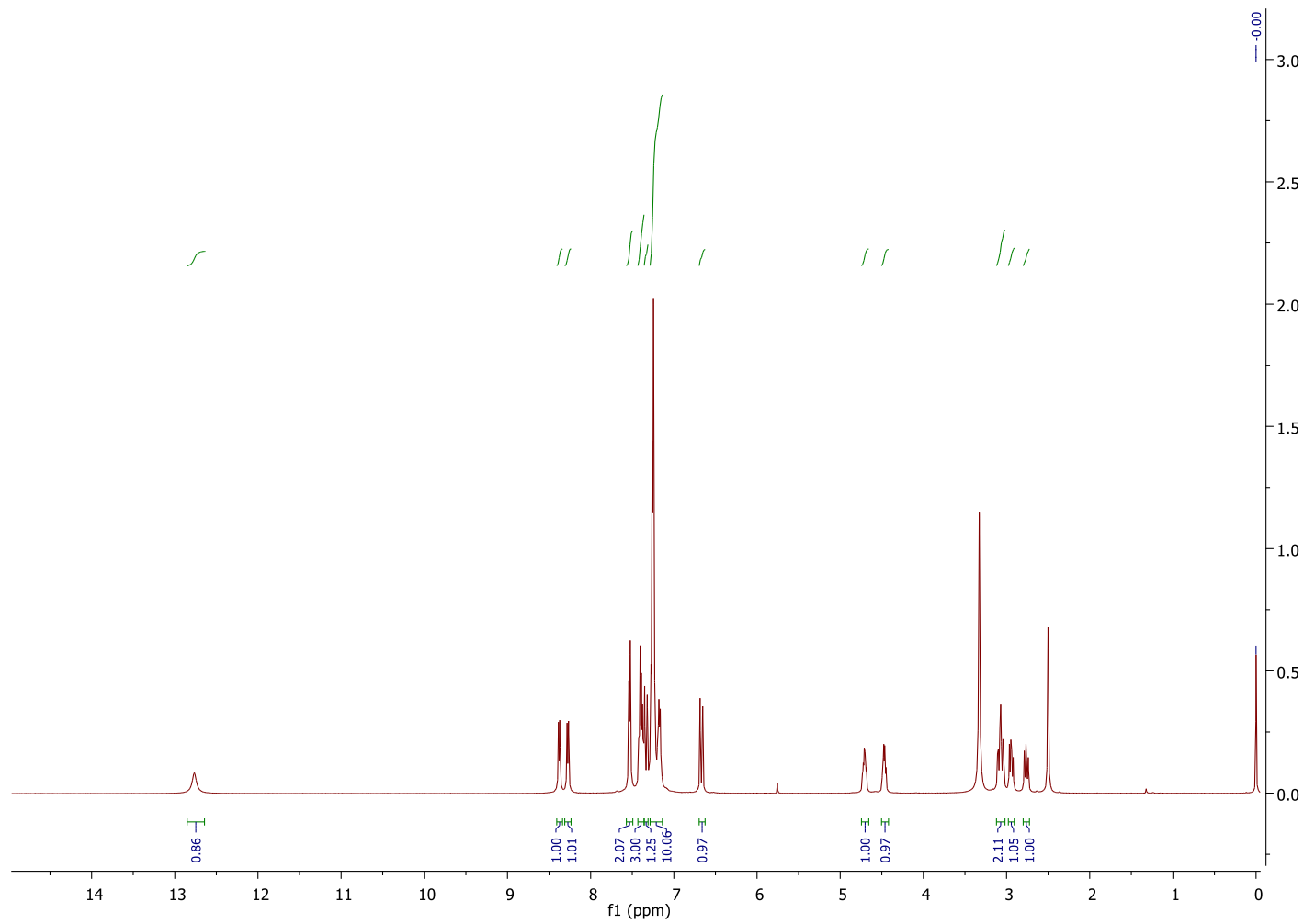
**Figure A 2.37**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of Cin-F-FOtBu **91**



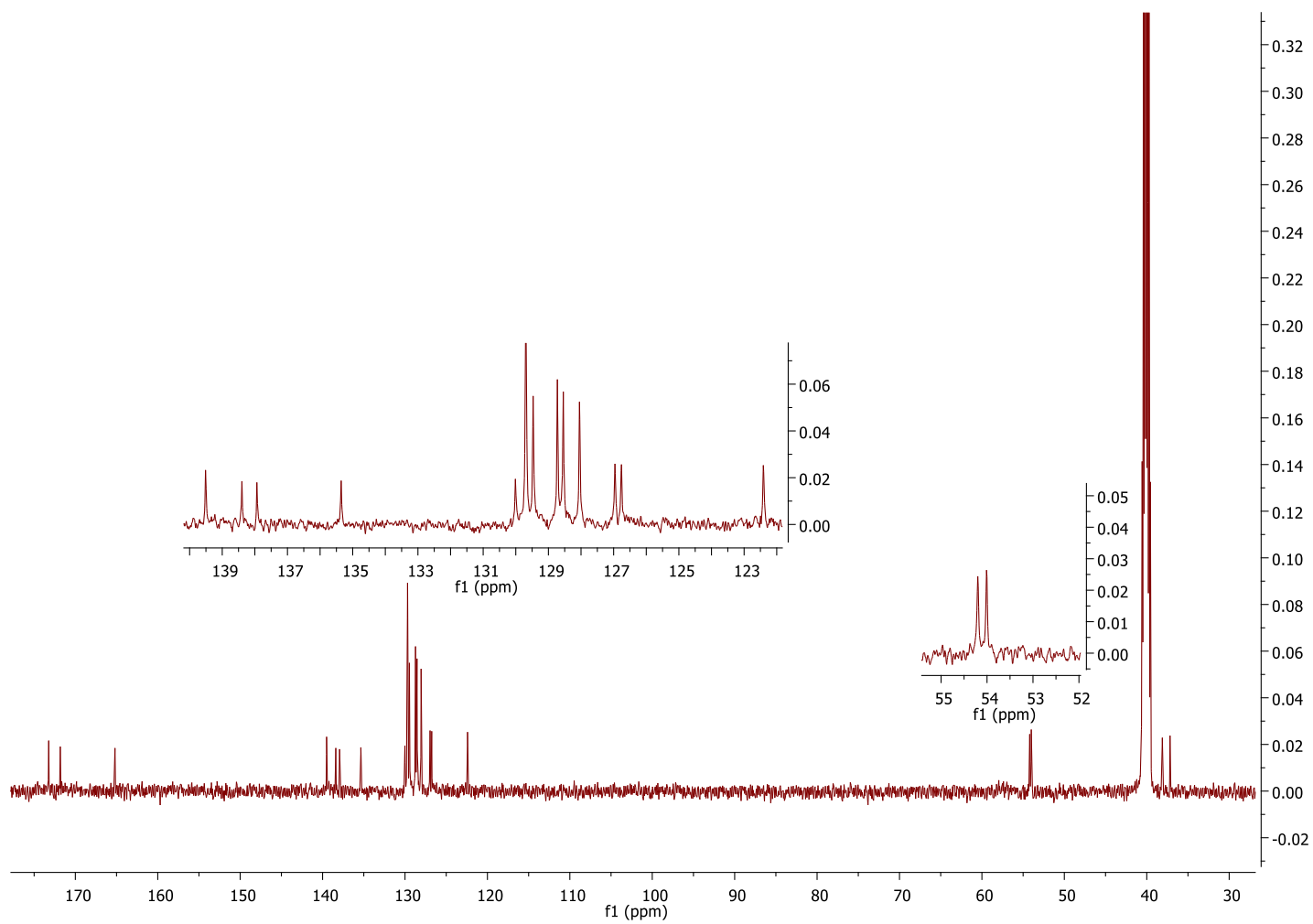
**Figure A 2.38**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms}\text{-d}_6$ ) spectrum of Cin-F-FOtBu **91**



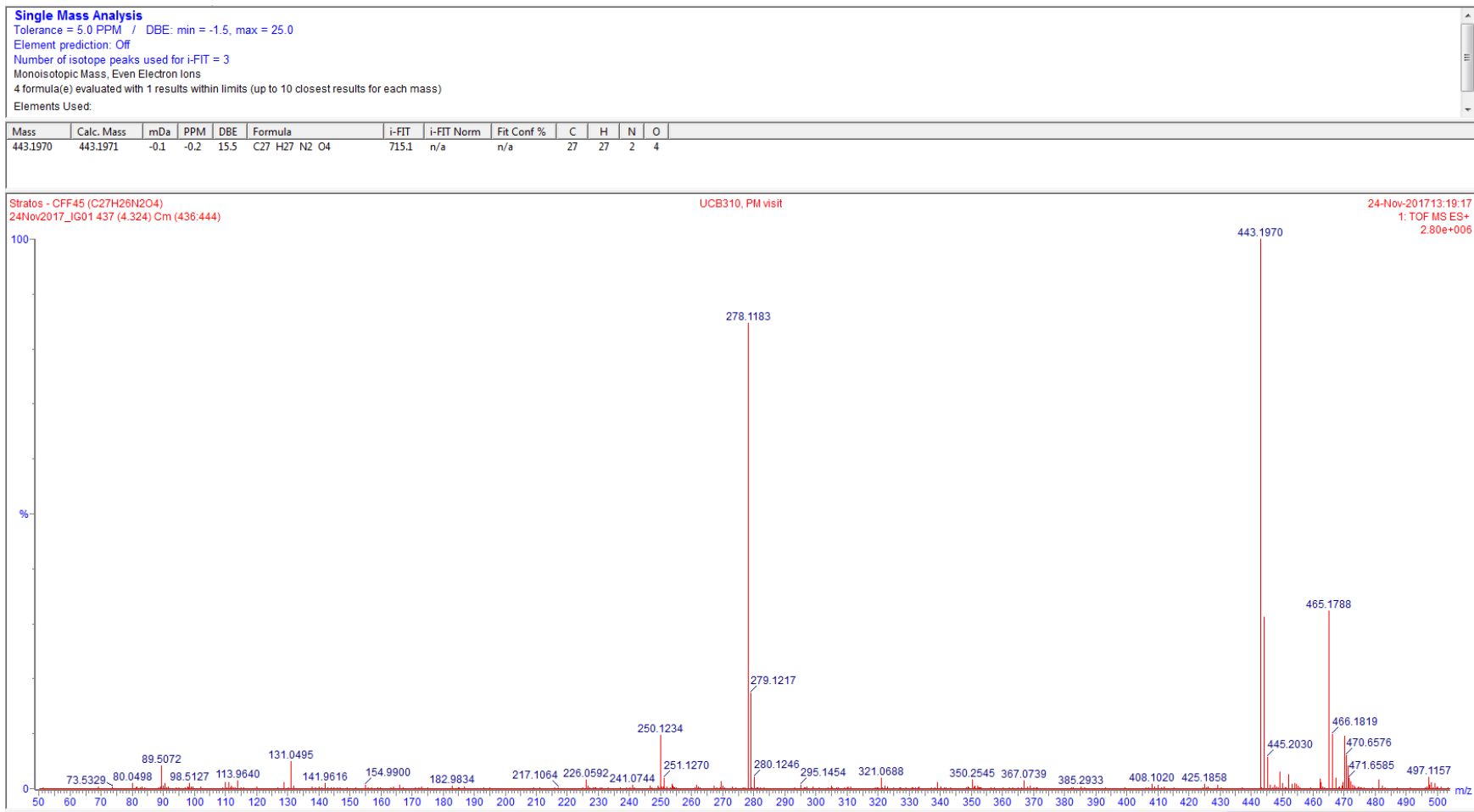
**Figure A 2.39** IR (neat) of Cin-F-F 70



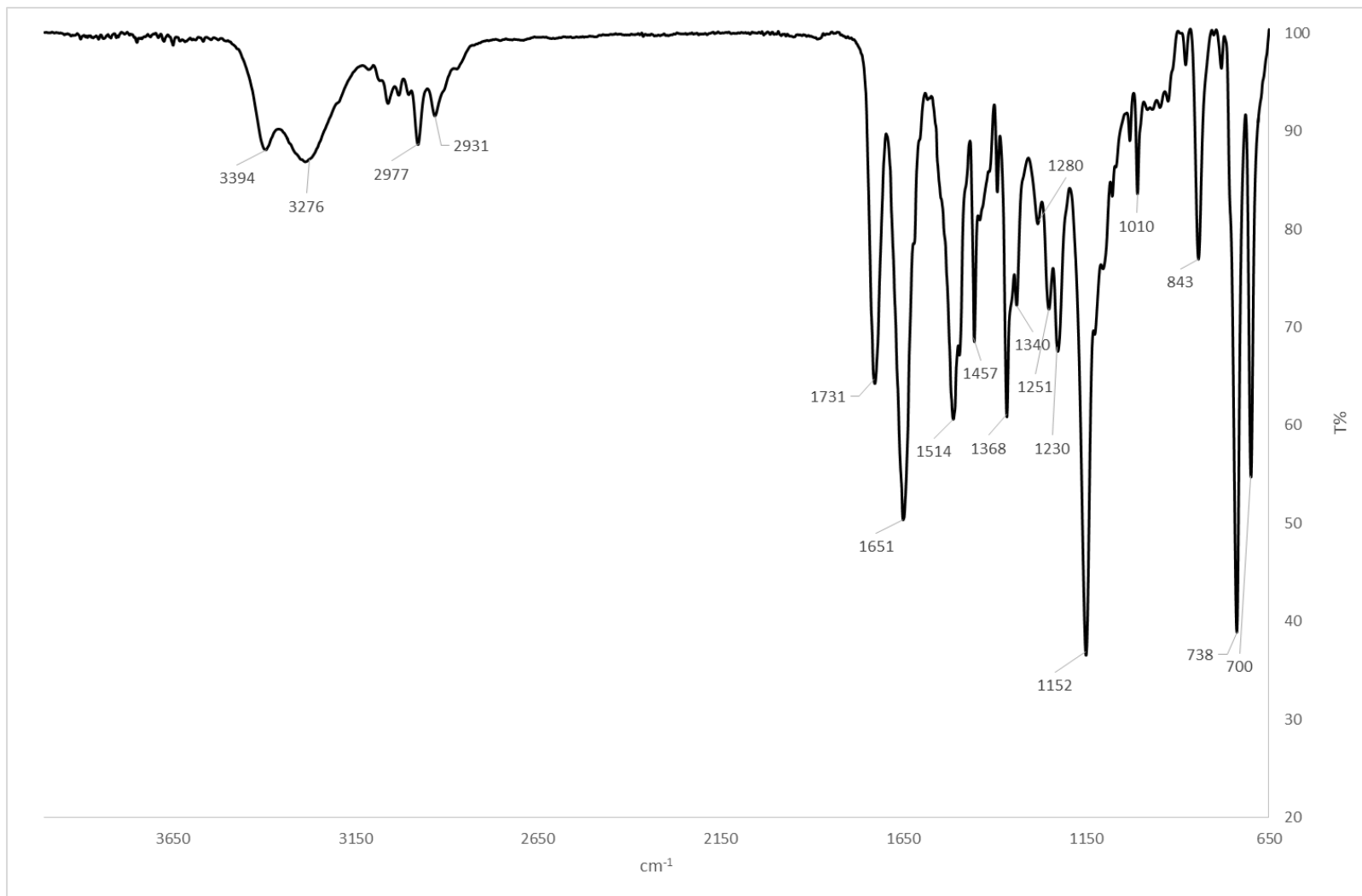
**Figure A 2.40**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of Cin-F-F 70



**Figure A 2.41**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms0-d}_6$ ) spectrum of Cin-F-F 70



**Figure A 2.42 HR-MS of Cin-F-F 70**



**Figure A 2.43** IR spectrum (neat) of Ind-FOtBu **108**



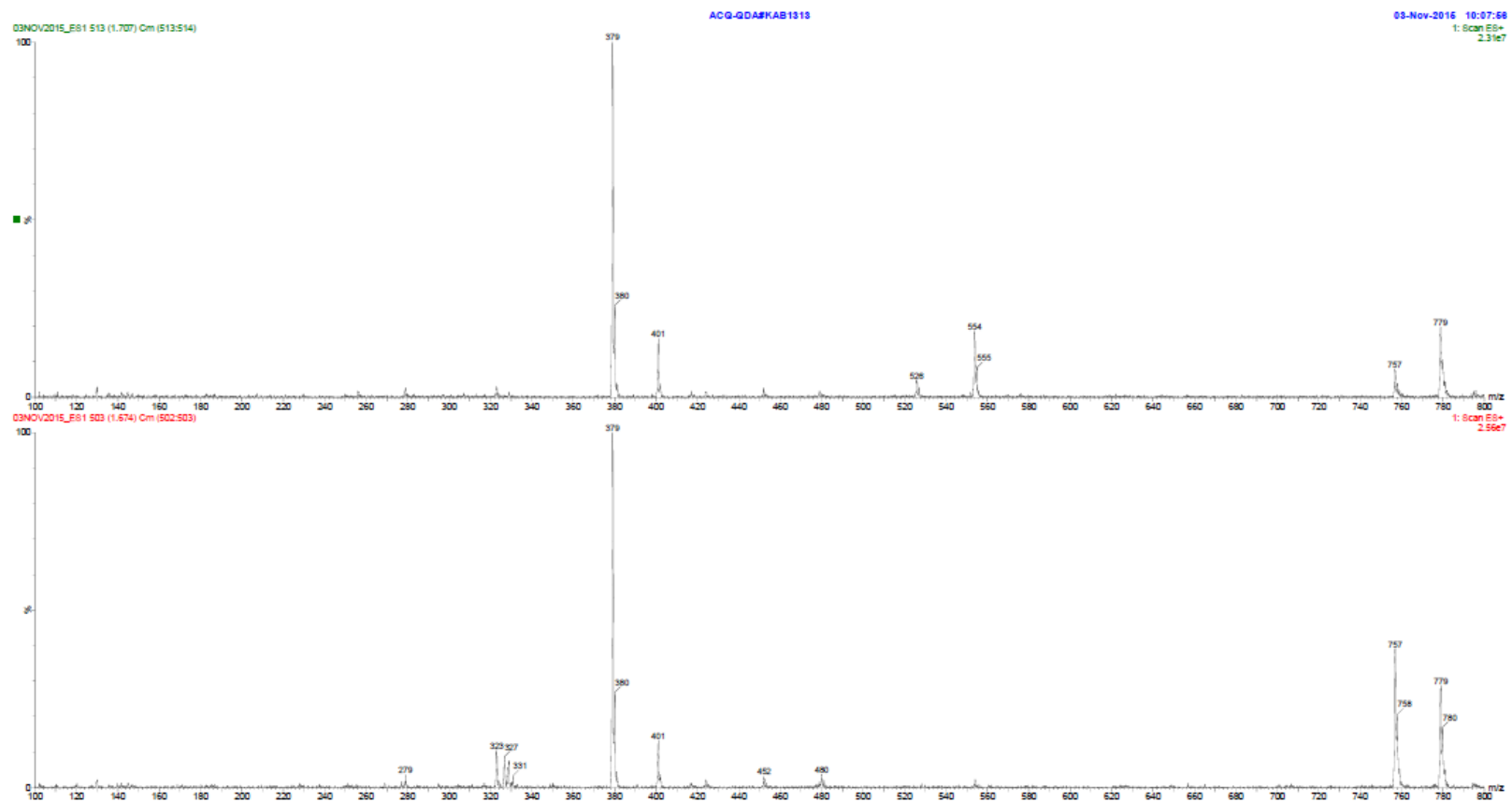


Figure A 2.44 MS (ES<sup>+</sup>) of Ind-FOtBu 108

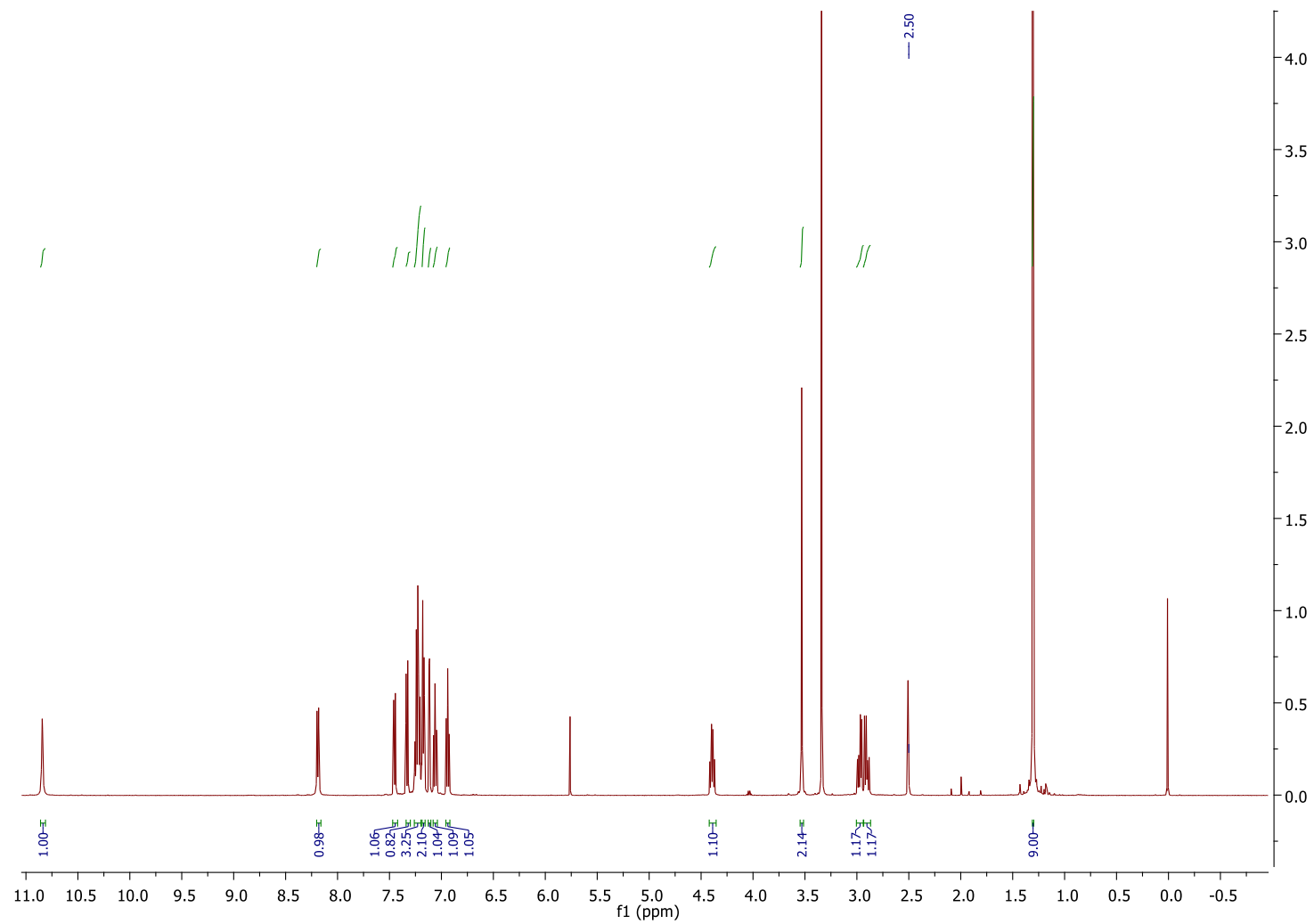
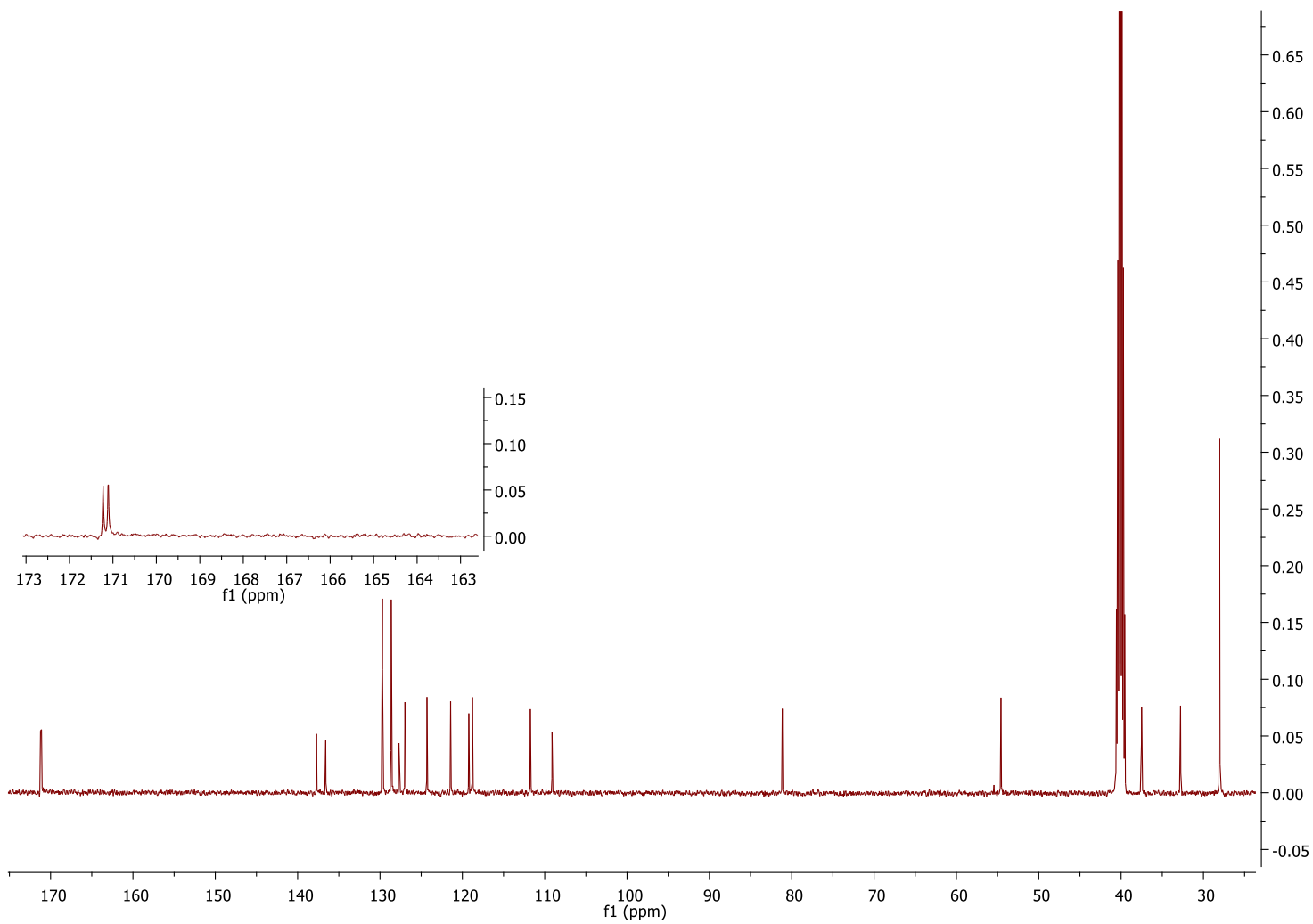
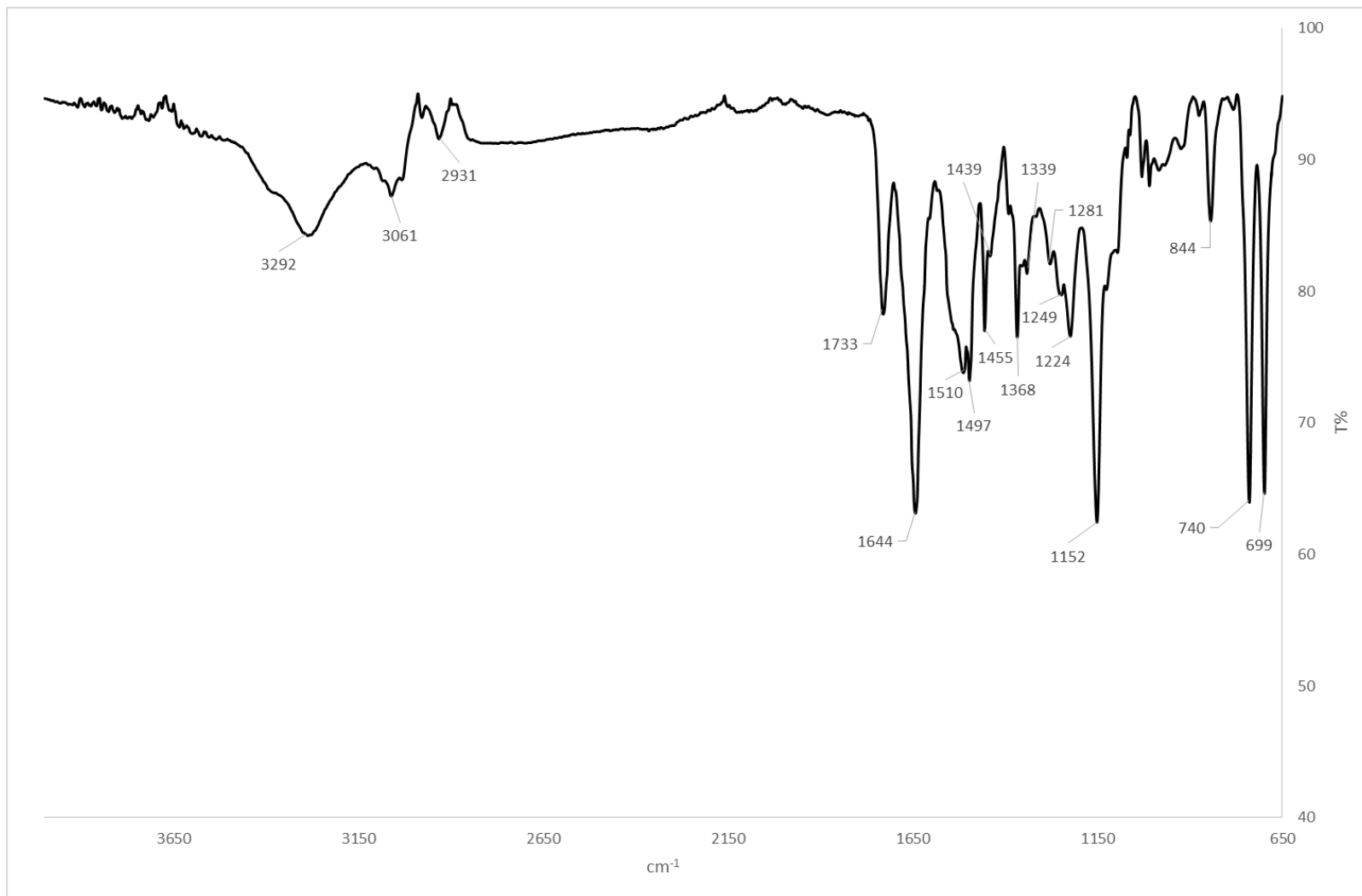


Figure A 2.45  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of Ind-FOtBu **108**



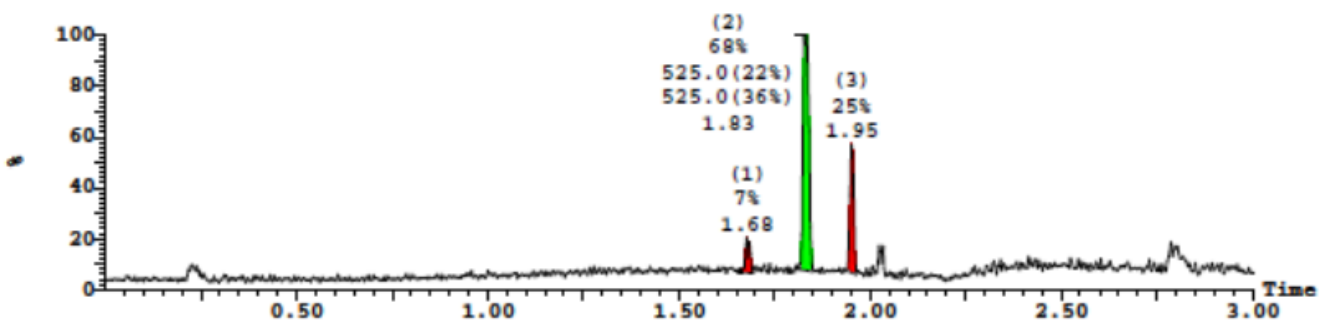
**Figure A 2.46**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dmsO-d}_6$ ) spectrum of Ind-FOtBu **108**



**Figure A 2.47** IR spectrum (neat) of Ind-F-FOtBu **110**

1: MS ES+ :BPI

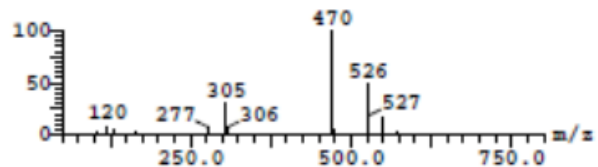
4.4e-007



Peak Number	Compound	Time	AreaAbs	Area %Total	Width	Height	Mass Found
1		1.68	8e+004	7.29	0	6e+006	Not Found
2	Tentative	1.83	7e+005	67.81	0	4e+007	525.00, 525.00
3		1.95	3e+005	24.91	0	2e+007	Not Found

Peak ID 2  
Time 1.83

1:MS ES+  
1.8e+007



Peak ID 2  
Time 1.83

2:MS ES-  
2.9e+006

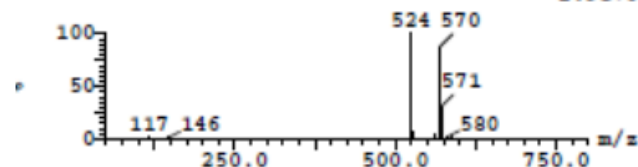
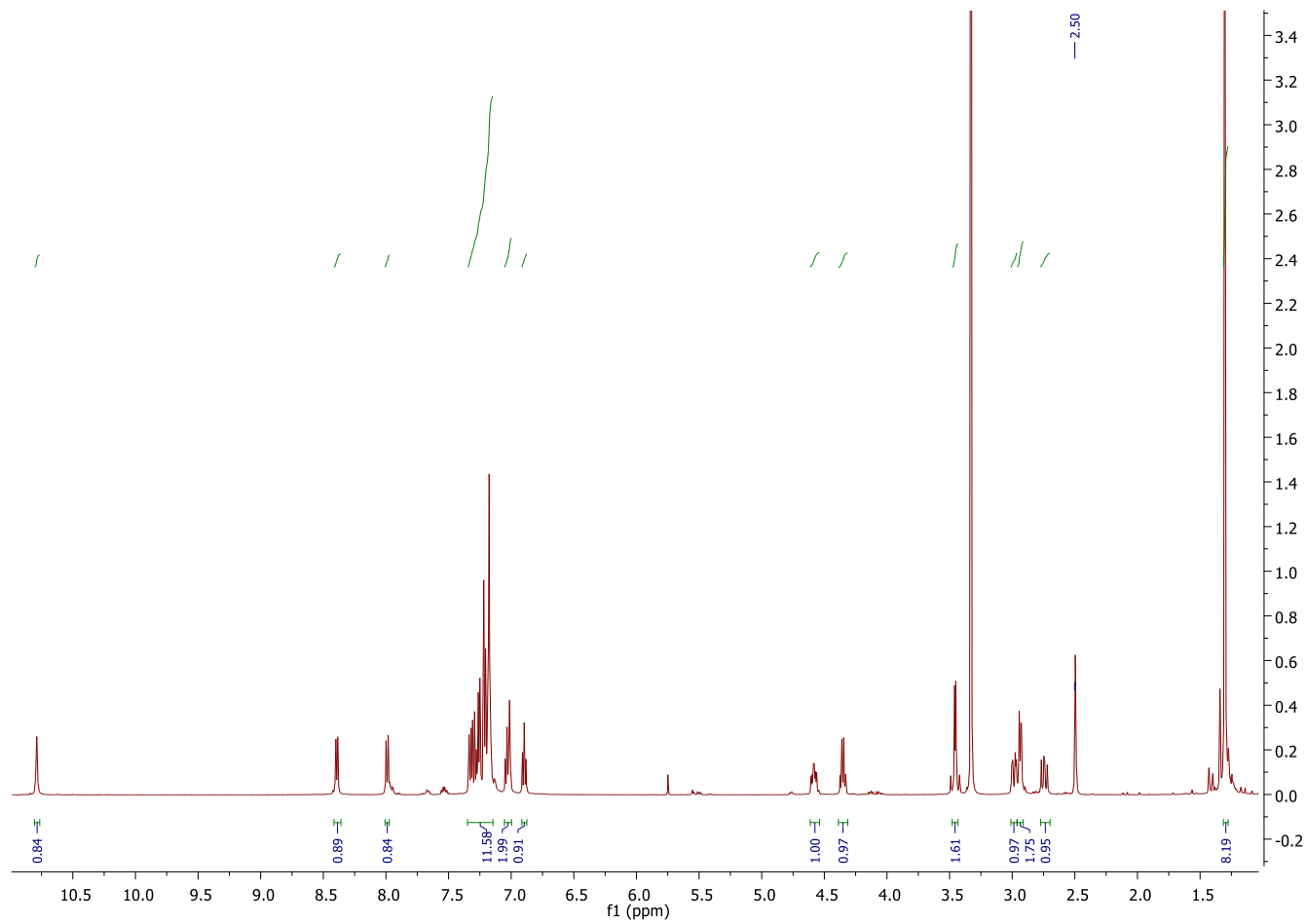
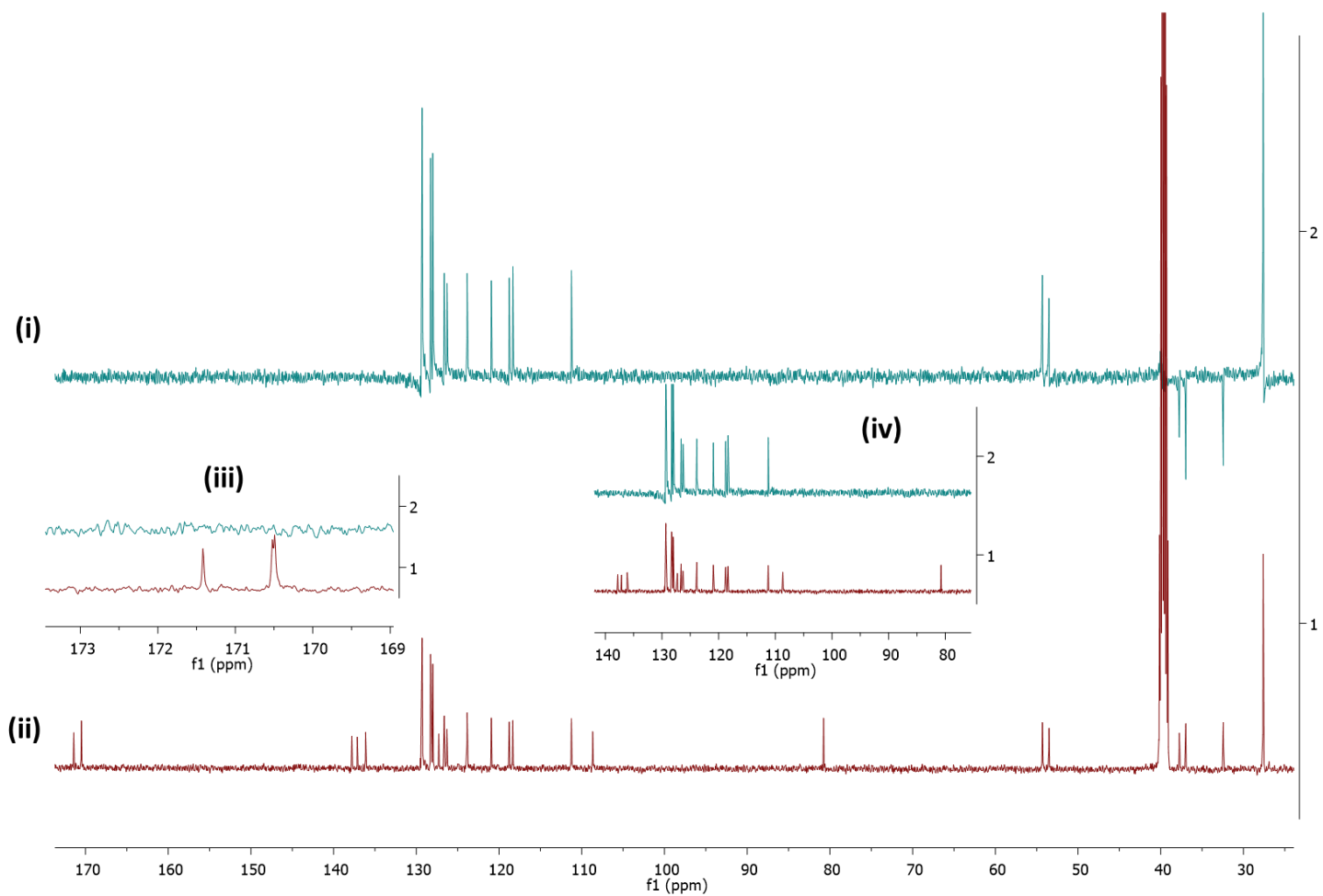


Figure A 2.48 MS (ES<sup>+</sup>) and (ES<sup>-</sup>) of Ind-F-FO/Bu 110



**Figure A 2.49**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of Ind-F-FOtBu **110**



**Figure A 2.50** DEPT-135 (i) and  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms}\text{-d}_6$ ) (ii) spectrum of Ind-F-FOtBu **110**. Enlarged areas (iii) and (iv)

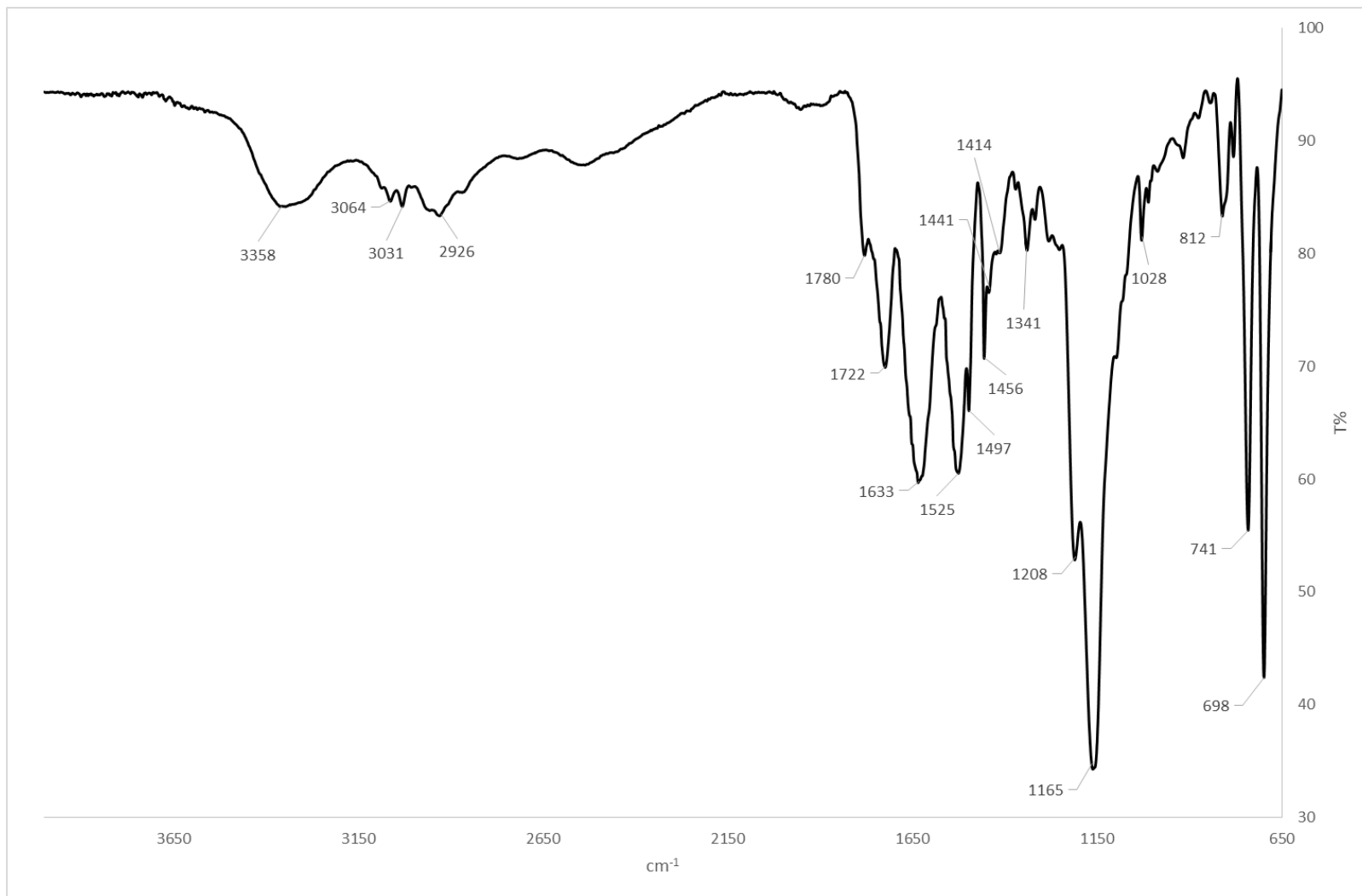


Figure A 2.51 IR spectrum (neat) of Ind-F-F 69



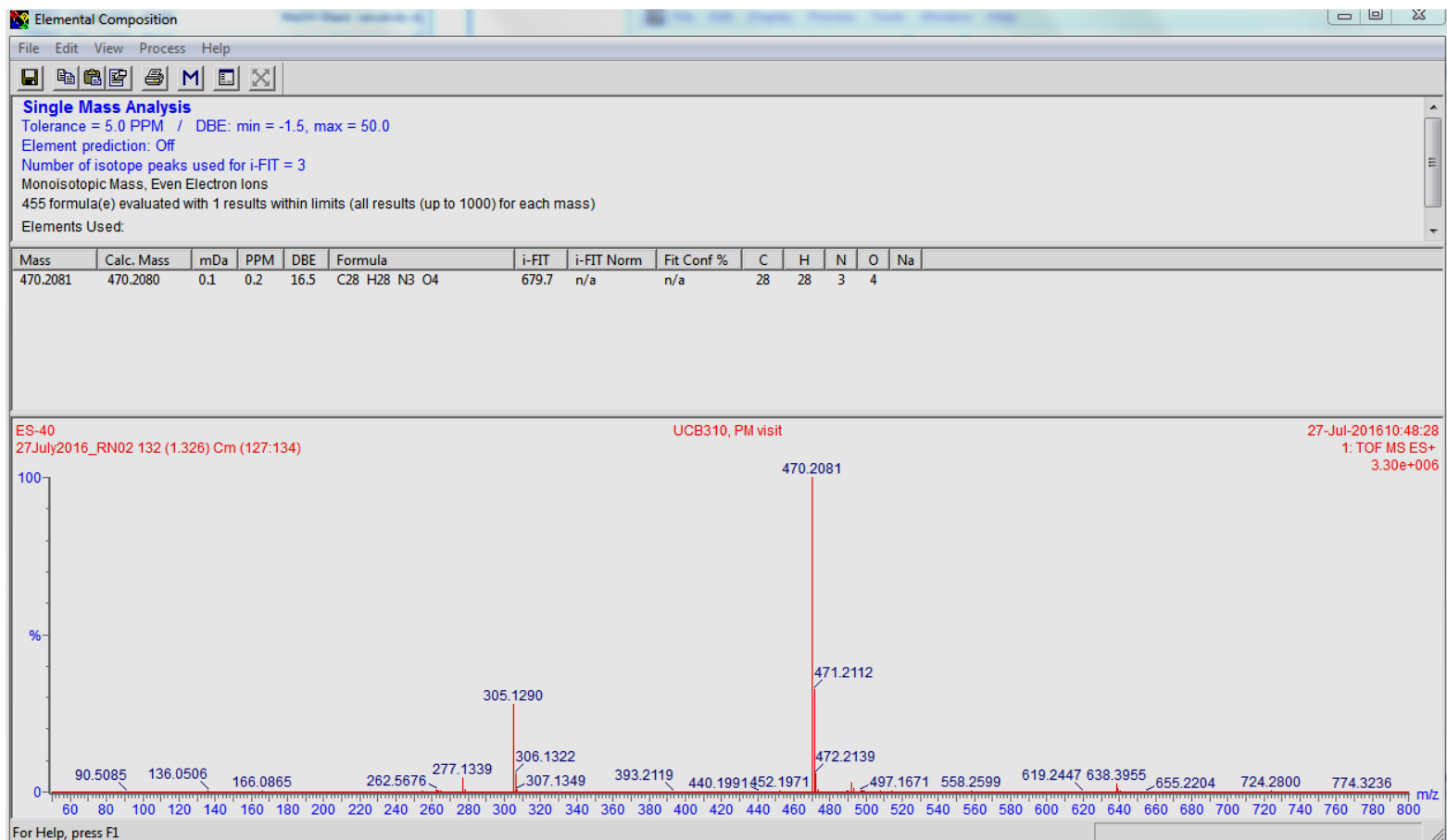
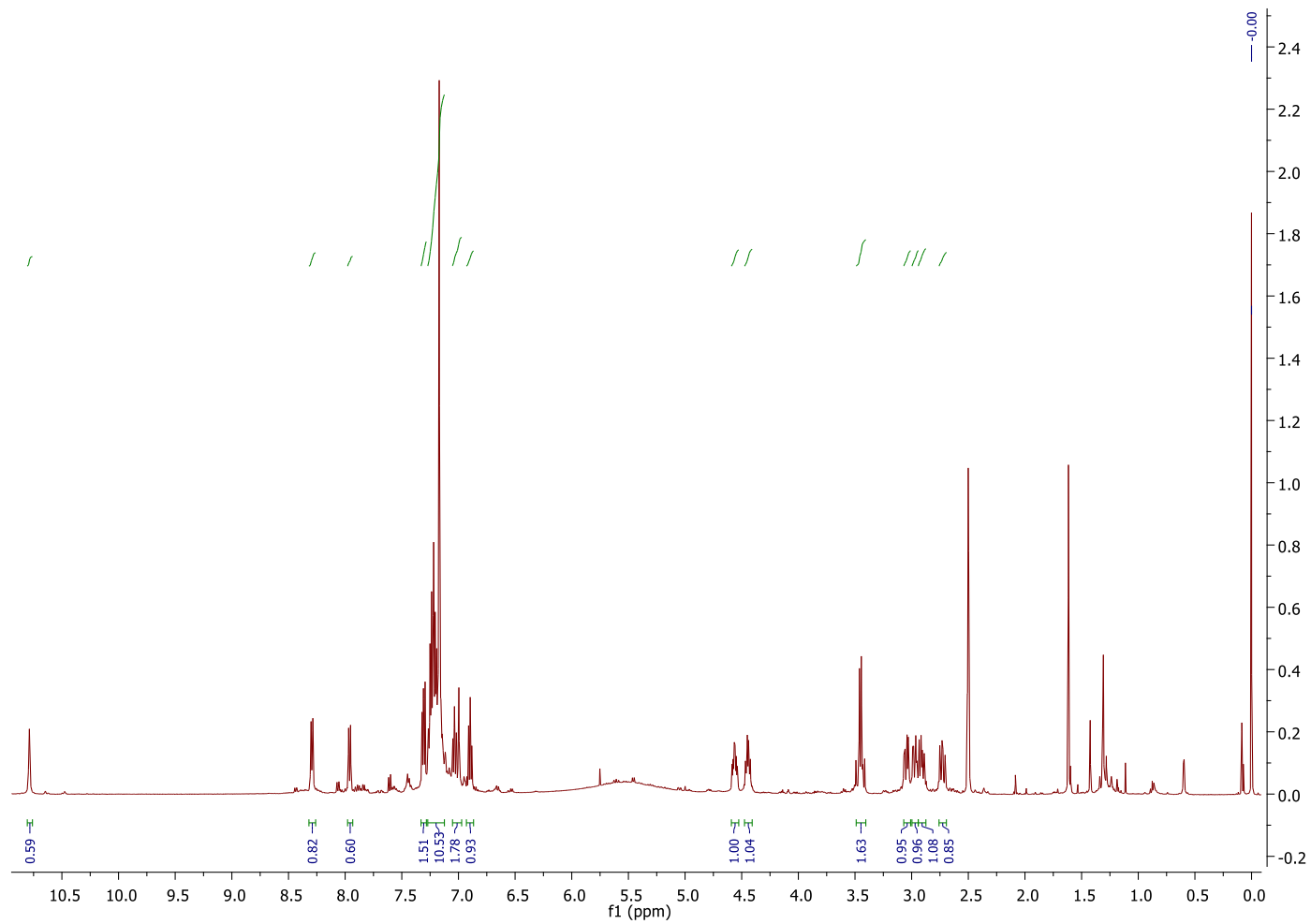
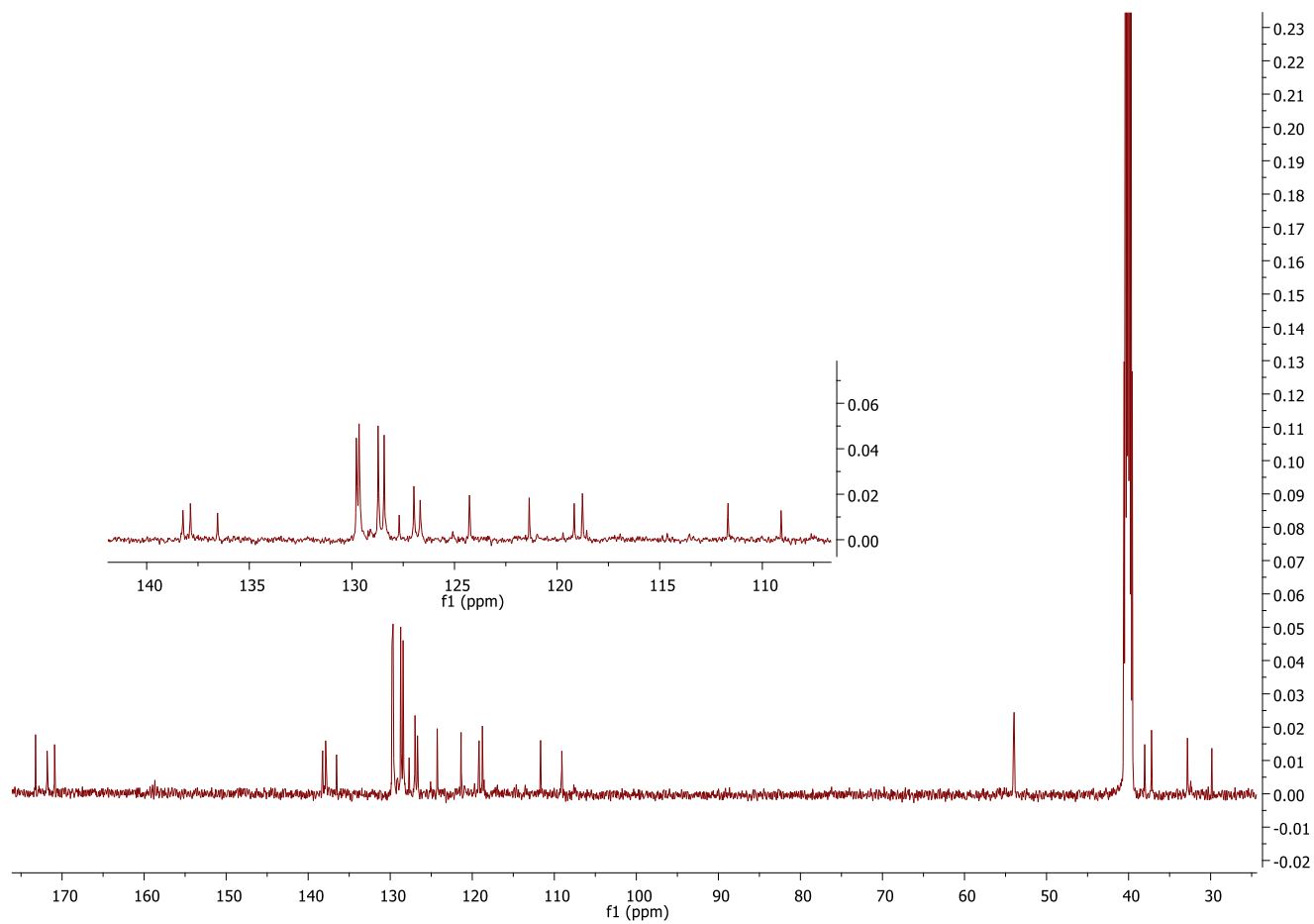


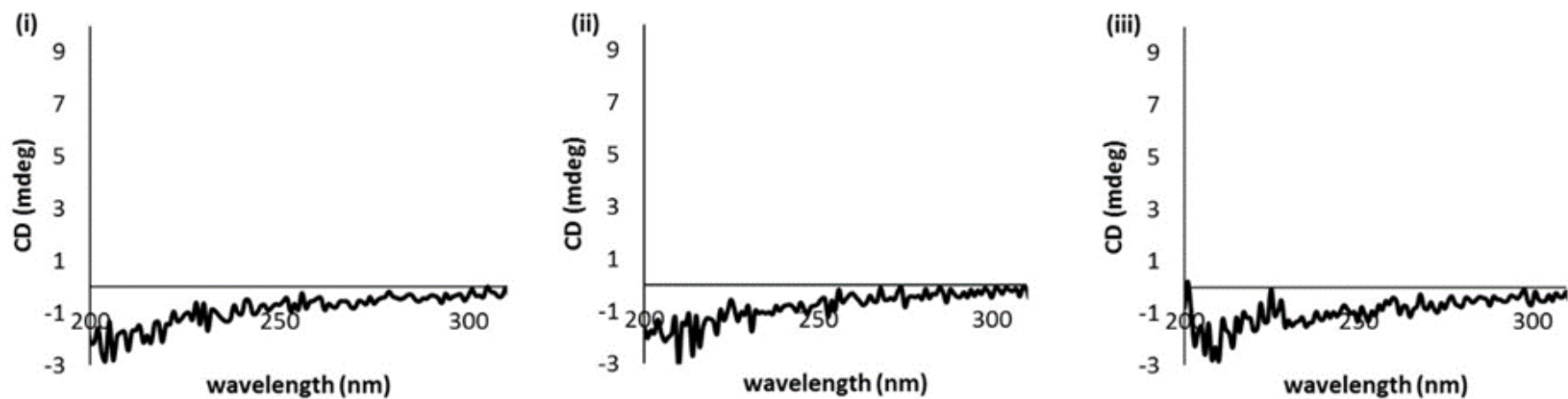
Figure A 2.52 HR-MS of Ind-F-F 69



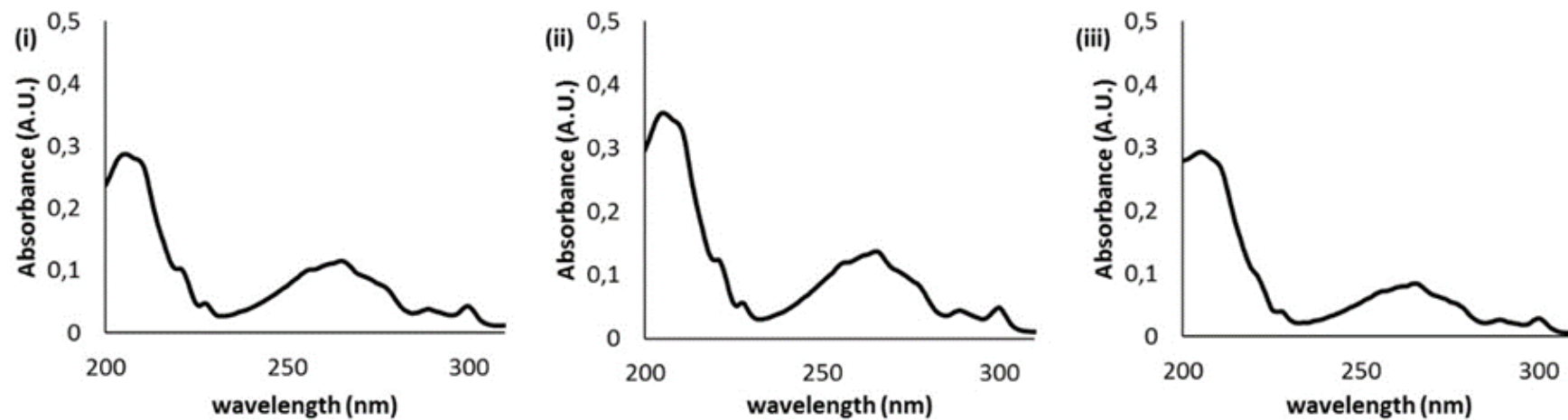
**Figure A 2.53**  $^1\text{H}$  NMR (500 MHz,  $\text{dms0-d}_6$ ) spectrum of Ind-F-F **69**



**Figure A 2.54**  $^{13}\text{C}$  NMR (126 MHz,  $\text{dms0-d}_6$ ) spectrum of Ind-F-F **69**



**Figure A 4.1** CD spectra of hydrogelators **62**, **63**, **68** in methanol. (i) GalNHFmoc **62**; (ii) GlcNHFmoc **63**; (iii) Fmoc-F-F **68**. All samples were recorded in a cylindrical non-demountable cell of the path length 0.1 mm at a concentration of 0.2 mg/mL.



**Figure A 4.2** Absorbance spectra of hydrogelators **62**, **63**, **68** in methanol. (i) GalNHFmoc **62**; (ii) GlcNHFmoc **63**; (iii) Fmoc-F-F **68**. All samples were recorded in a cylindrical non-demountable cell of the path length 0.1 mm at a concentration of 0.2 mg/mL.