

# The Use of Remote Acyl Groups for Stereoselective 1,2-*cis*-Glycosylation with Fluorinated Glucosazide Thiodonors

## Supporting Information

### II

#### Copies of NMR spectra

Vojtěch Hamala,<sup>1,2</sup> Lucie Červenková Šťastná,<sup>1</sup> Martin Kurfíř,<sup>1,2</sup> Petra Cuřínová,<sup>1</sup> Martin Dračínský,<sup>3</sup>

Jindřich Karban<sup>1,\*</sup>

<sup>1</sup>*Institute of Chemical Process Fundamentals of the CAS, v. v. i., Rozvojová 135, 16502 Praha 6, Czech*

*Republic.* <sup>2</sup>*University of Chemistry and Technology Prague, Technická 5, 16628 Praha 6, Czech*

*Republic.* <sup>3</sup>*Institute of Organic Chemistry and Biochemistry of the CAS, v. v. i., Flemingovo náměstí*

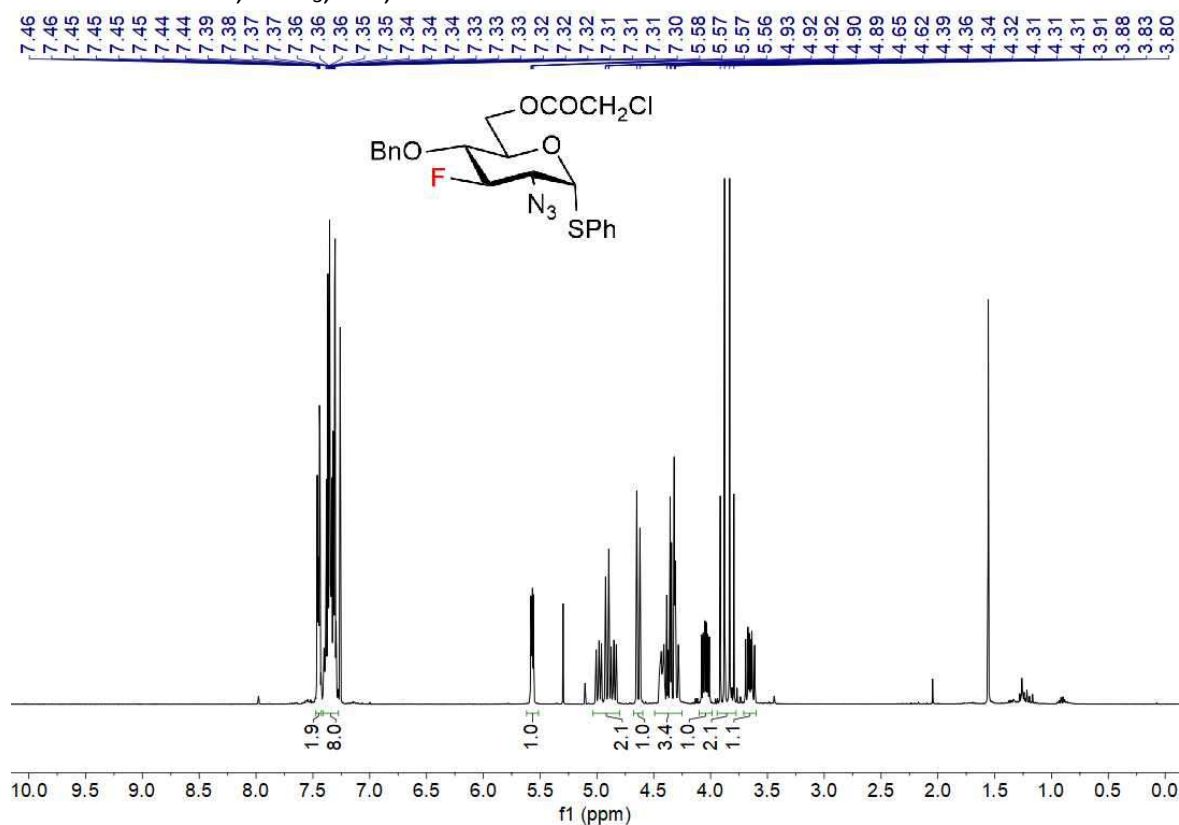
*542/2, 16000, Praha 6, Czech Republic*

\*Email: [karban@icpf.cas.cz](mailto:karban@icpf.cas.cz).

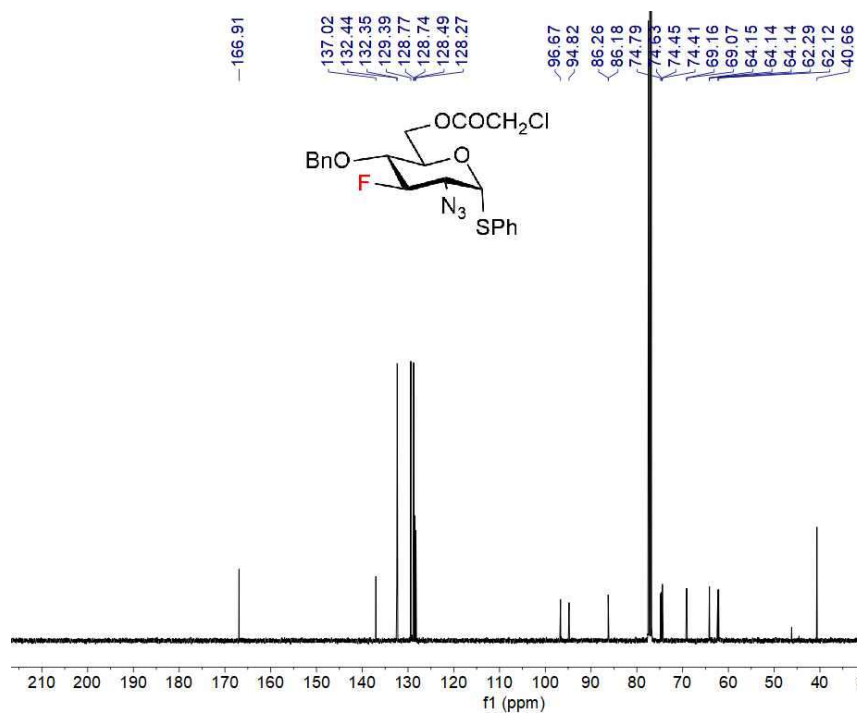
|               |    |
|---------------|----|
| NMR β-9.....  | 6  |
| NMR 10.....   | 9  |
| NMR 11.....   | 12 |
| NMR 12.....   | 15 |
| NMR α-13..... | 18 |
| NMR β-13..... | 21 |
| NMR 14.....   | 24 |
| NMR 15.....   | 27 |
| NMR α-16..... | 30 |
| NMR β-16..... | 33 |
| NMR α-17..... | 36 |
| NMR β-17..... | 39 |
| NMR 20.....   | 42 |
| NMR 21.....   | 45 |
| NMR 23.....   | 48 |
| NMR α-24..... | 50 |
| NMR β-24..... | 53 |
| NMR 25.....   | 56 |

|                                         |     |
|-----------------------------------------|-----|
| NMR 26.....                             | 59  |
| NMR A1.....                             | 62  |
| NMR A9.....                             | 65  |
| NMR A10.....                            | 68  |
| NMR A11- $\alpha$ .....                 | 71  |
| NMR A11, mixture of anomers.....        | 74  |
| NMR A12, enriched $\alpha$ -anomer..... | 77  |
| NMR A12, enriched $\beta$ -anomer.....  | 80  |
| NMR A13, mixture of anomers.....        | 83  |
| NMR B1.....                             | 86  |
| NMR B9- $\alpha$ .....                  | 88  |
| NMR B9- $\beta$ .....                   | 91  |
| NMR B10- $\alpha$ .....                 | 94  |
| NMR B12- $\alpha$ .....                 | 97  |
| NMR C9- $\alpha$ .....                  | 100 |
| NMR D9- $\alpha$ .....                  | 103 |
| NMR E16- $\alpha$ .....                 | 106 |
| NMR E9- $\alpha$ .....                  | 109 |
| NMR A20.....                            | 112 |
| NMR B20- $\alpha$ .....                 | 115 |
| NMR B20- $\beta$ .....                  | 118 |
| NMR E20- $\alpha$ .....                 | 121 |
| NMR E20- $\beta$ .....                  | 124 |
| NMR E21 .....                           | 127 |
| NMR E25- $\alpha$ .....                 | 130 |
| NMR D25- $\alpha$ .....                 | 133 |
| NMR 28.....                             | 136 |
| NMR 29 .....                            | 139 |
| NMR 30 .....                            | 142 |
| NMR 31 .....                            | 145 |
| NMR 32 .....                            | 148 |
| NMR 33 .....                            | 151 |
| NMR 34 .....                            | 154 |
| NMR L-threonine benzyl ester.....       | 157 |
| NMR Phth-Thr-OBn.....                   | 158 |
| NMR Fmoc-Thr-OBn .....                  | 159 |
| NMR $\alpha$ -9                         |     |

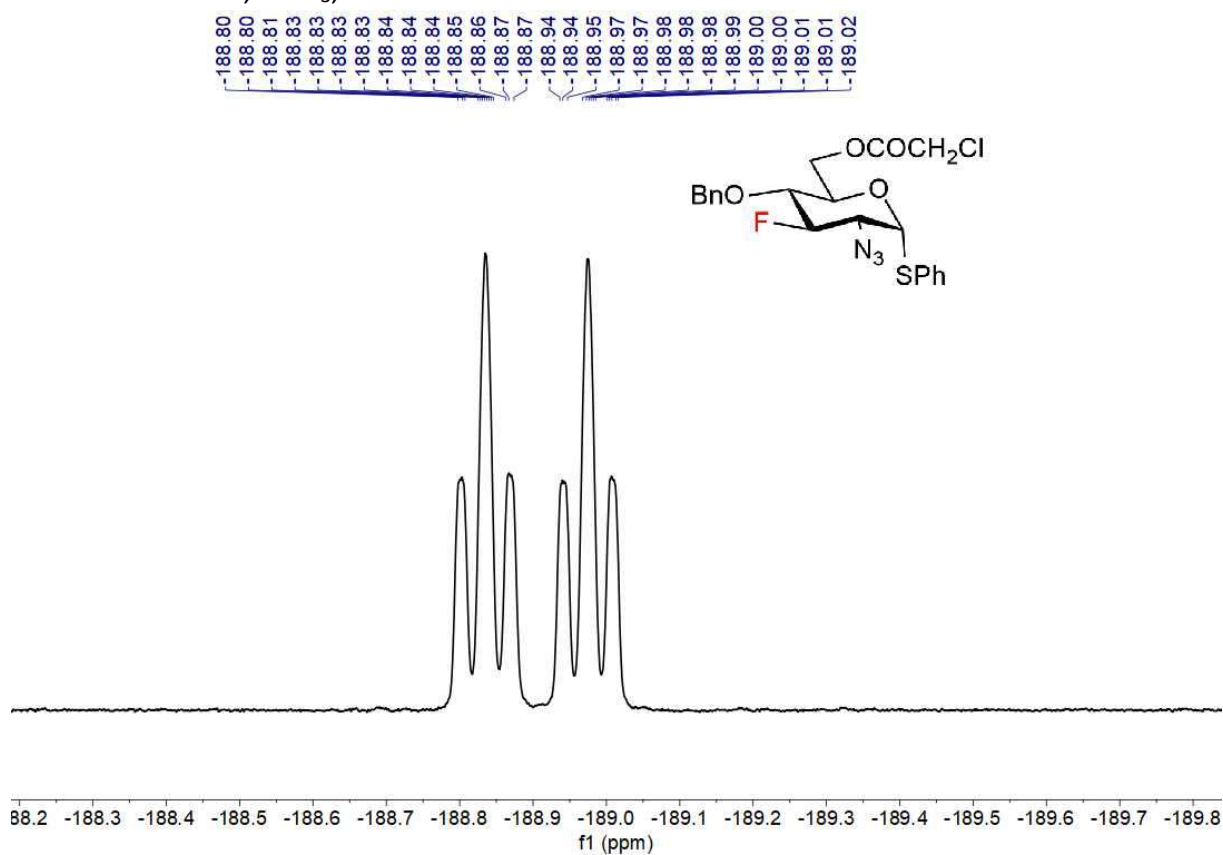
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  $\alpha$ -9,



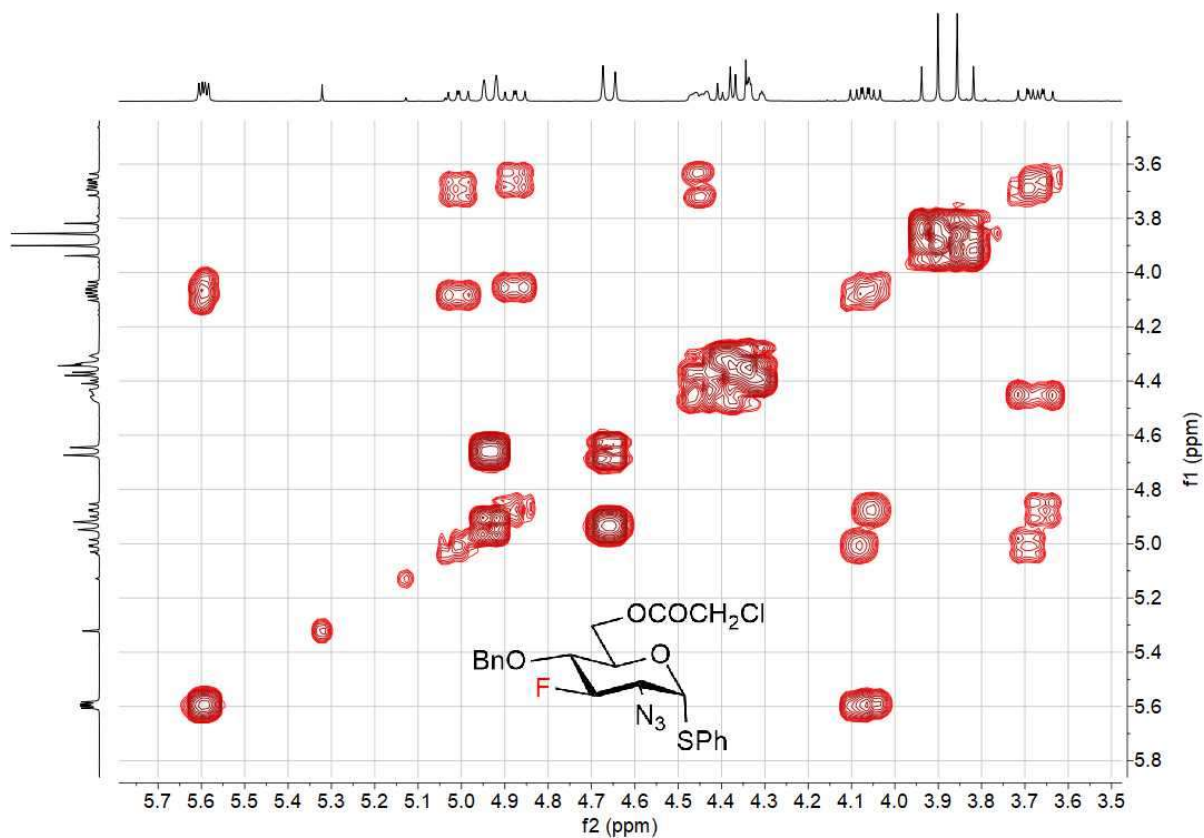
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  $\alpha$ -9



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  $\alpha$ -9

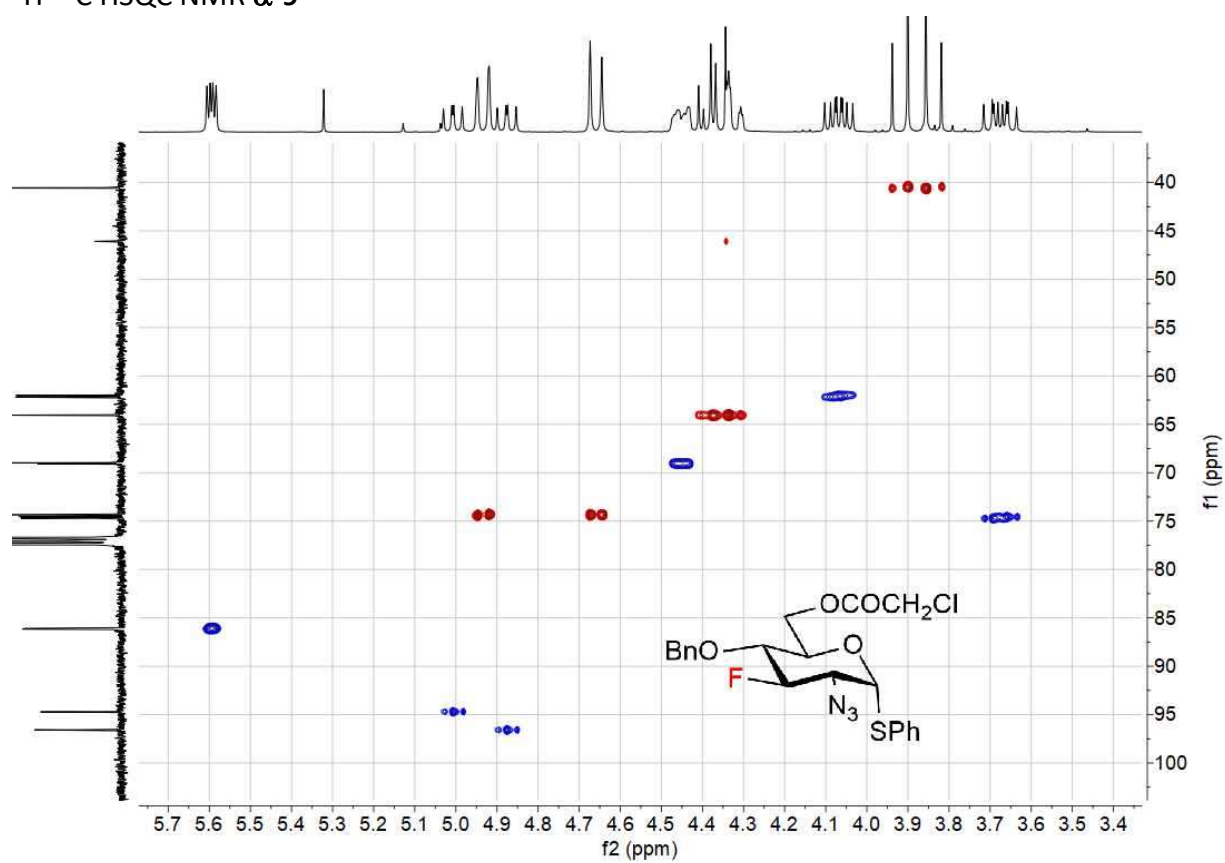


$^1\text{H}$ - $^1\text{H}$  COSY NMR,  $\alpha$ -9



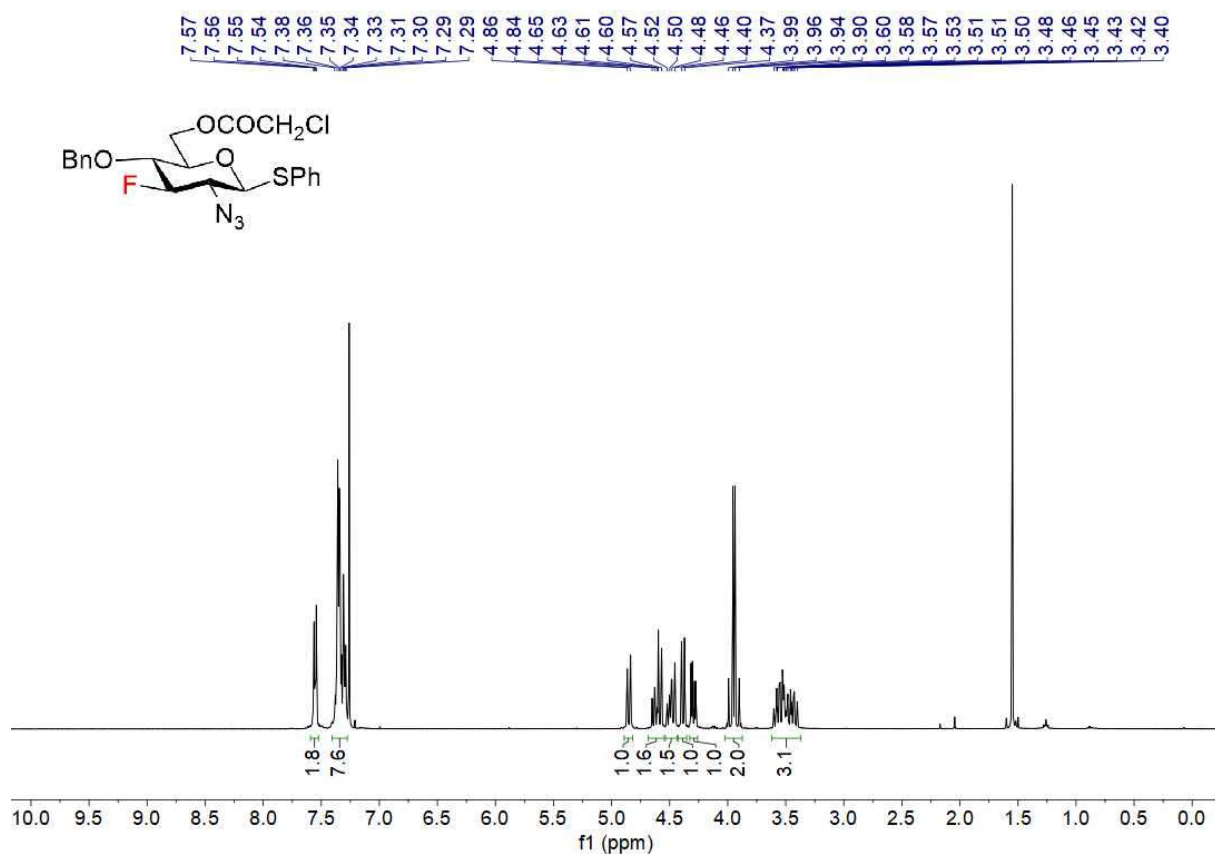


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\alpha$ -9

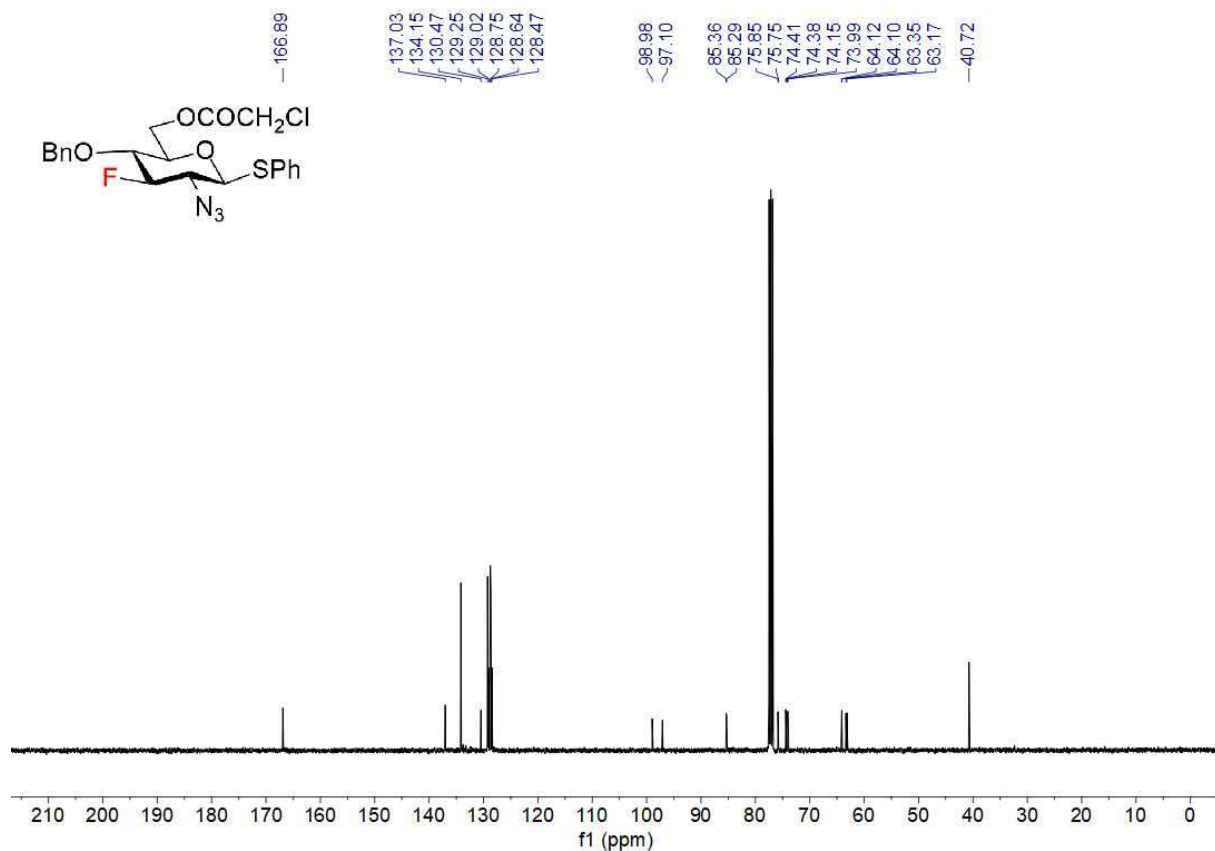


# **NMR $\beta$ -9**

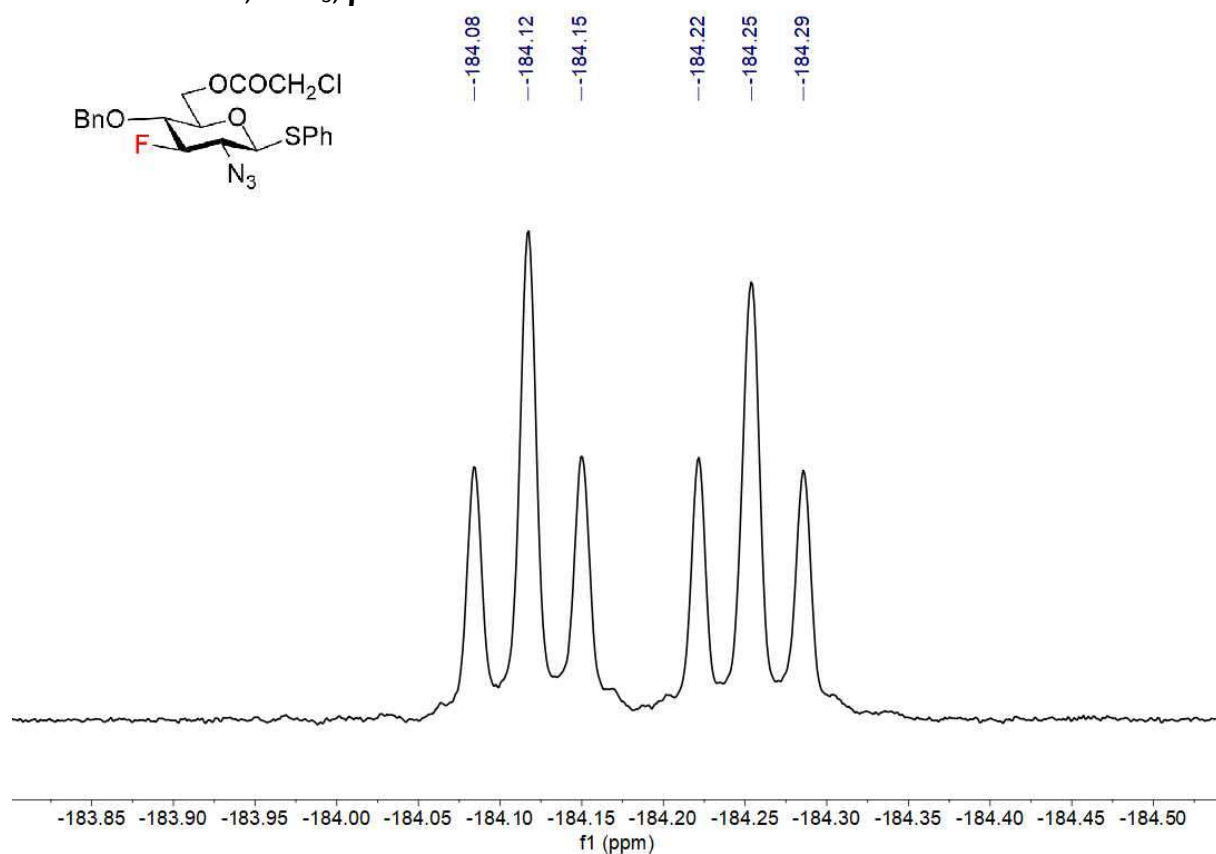
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  $\beta$ -9,



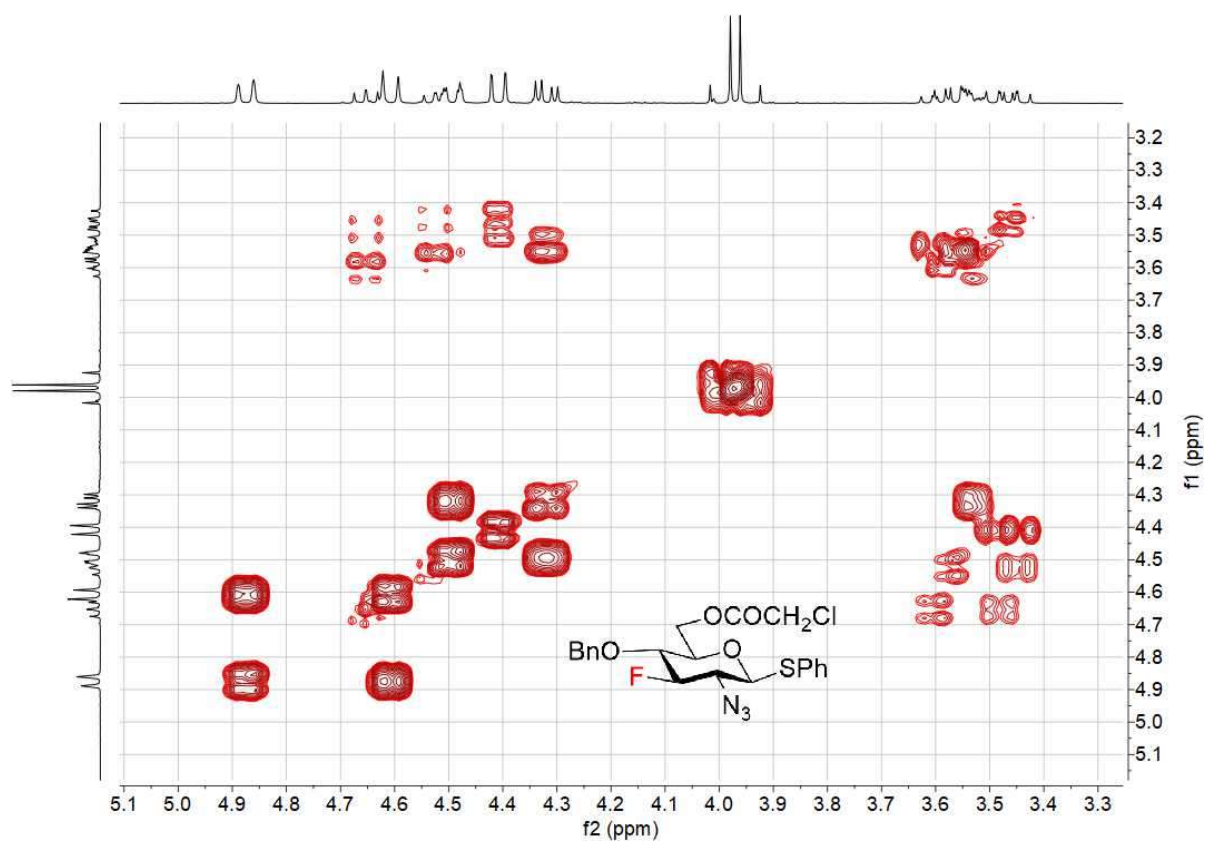
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  $\beta$ -9



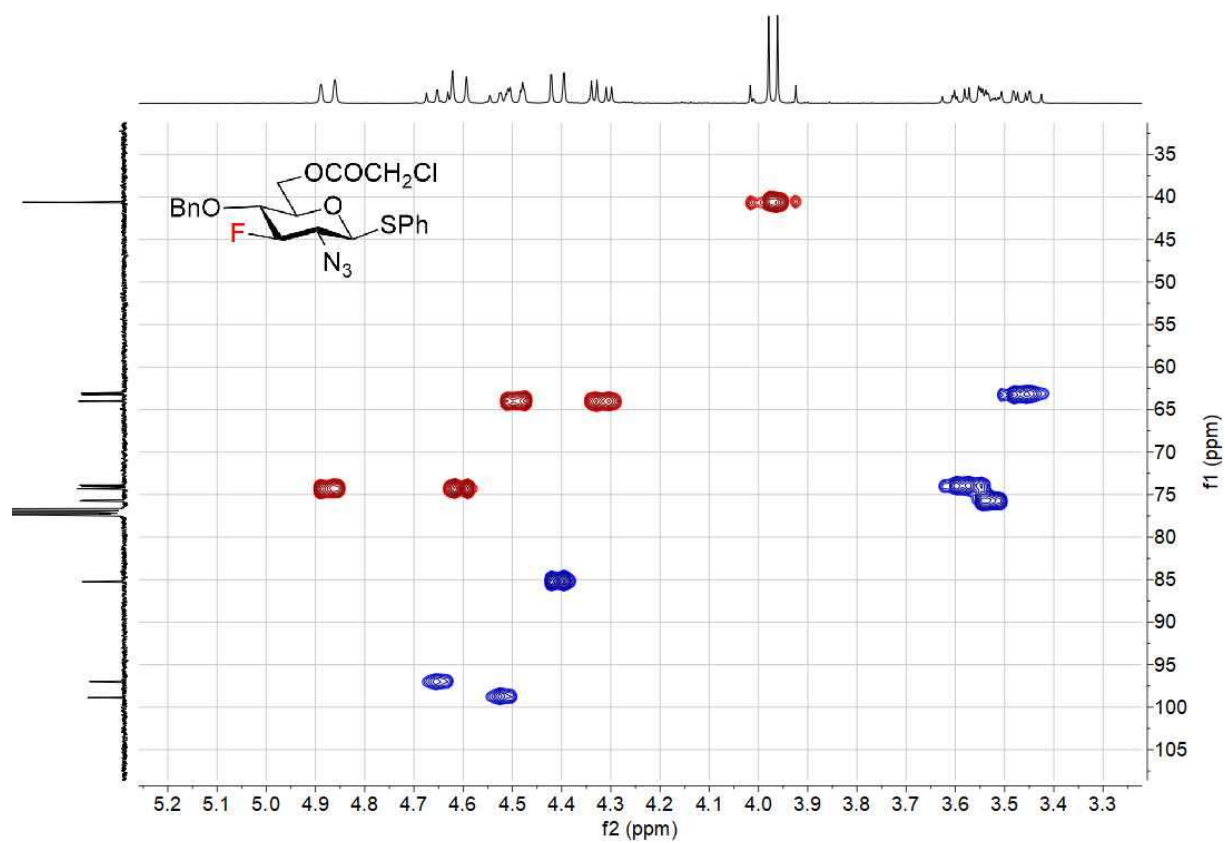
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  $\beta$ -9



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  $\beta$ -9

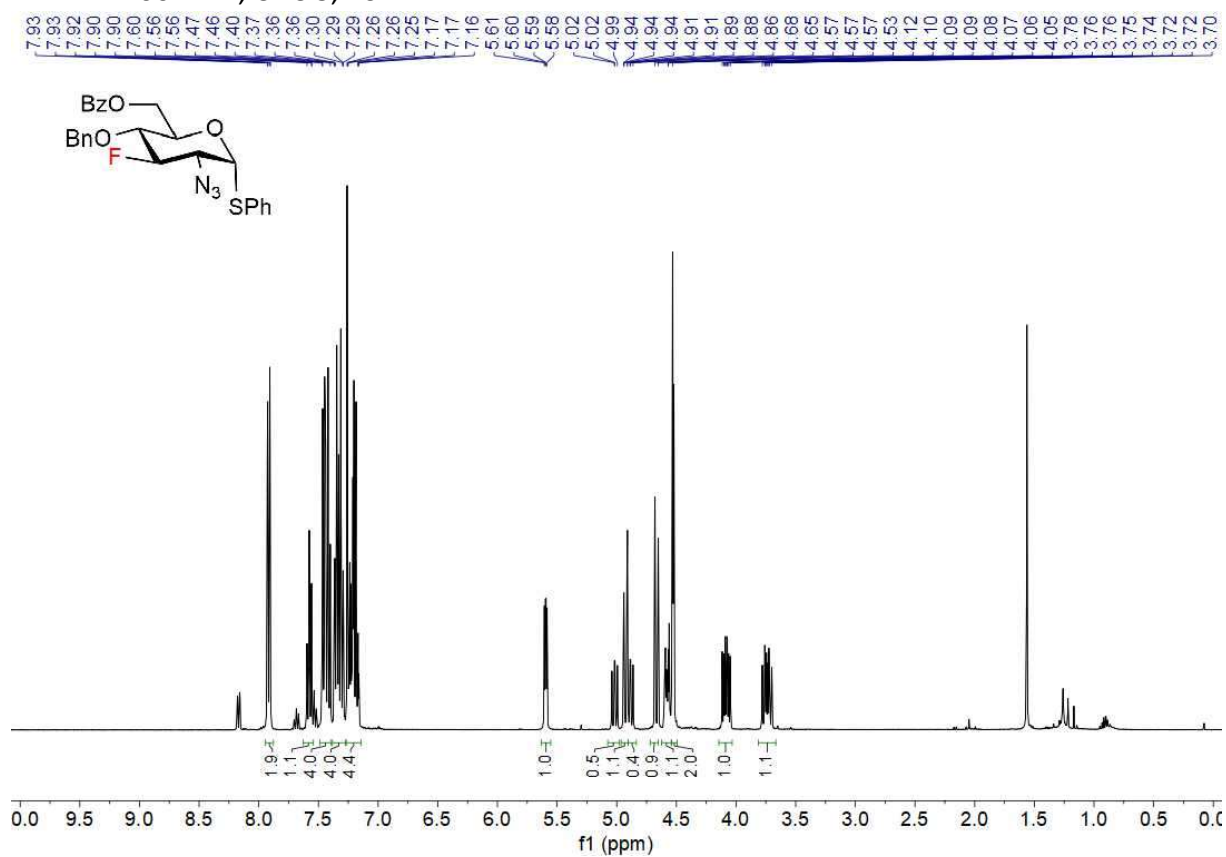


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\beta$ -9

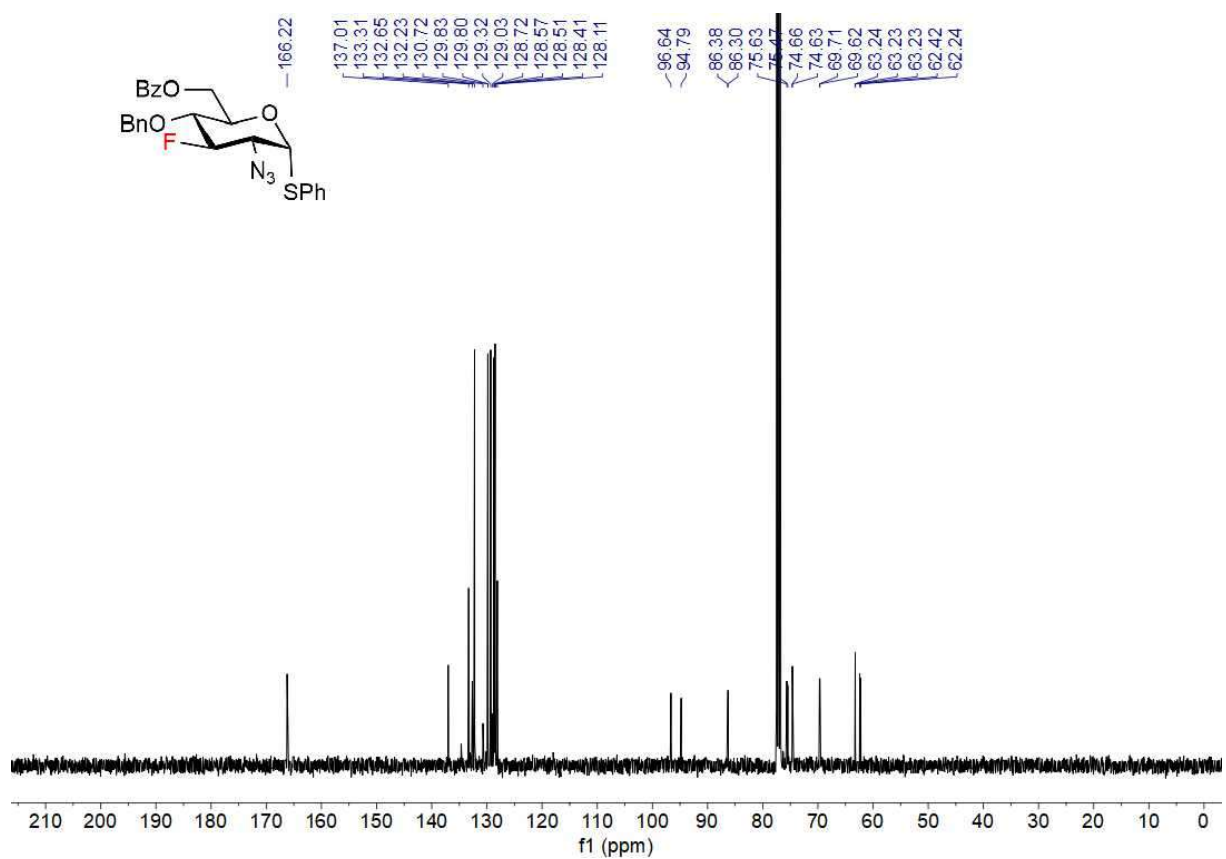


# NMR 10

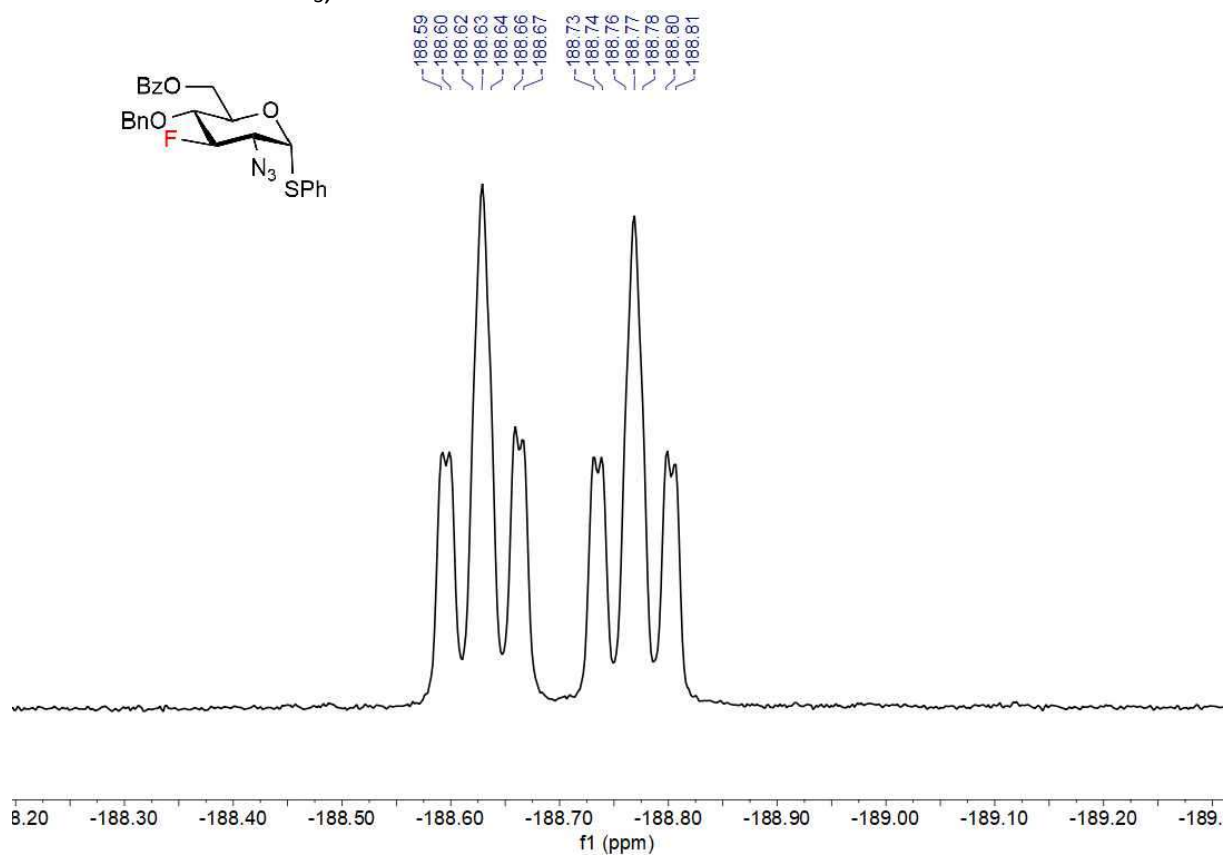
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **10**



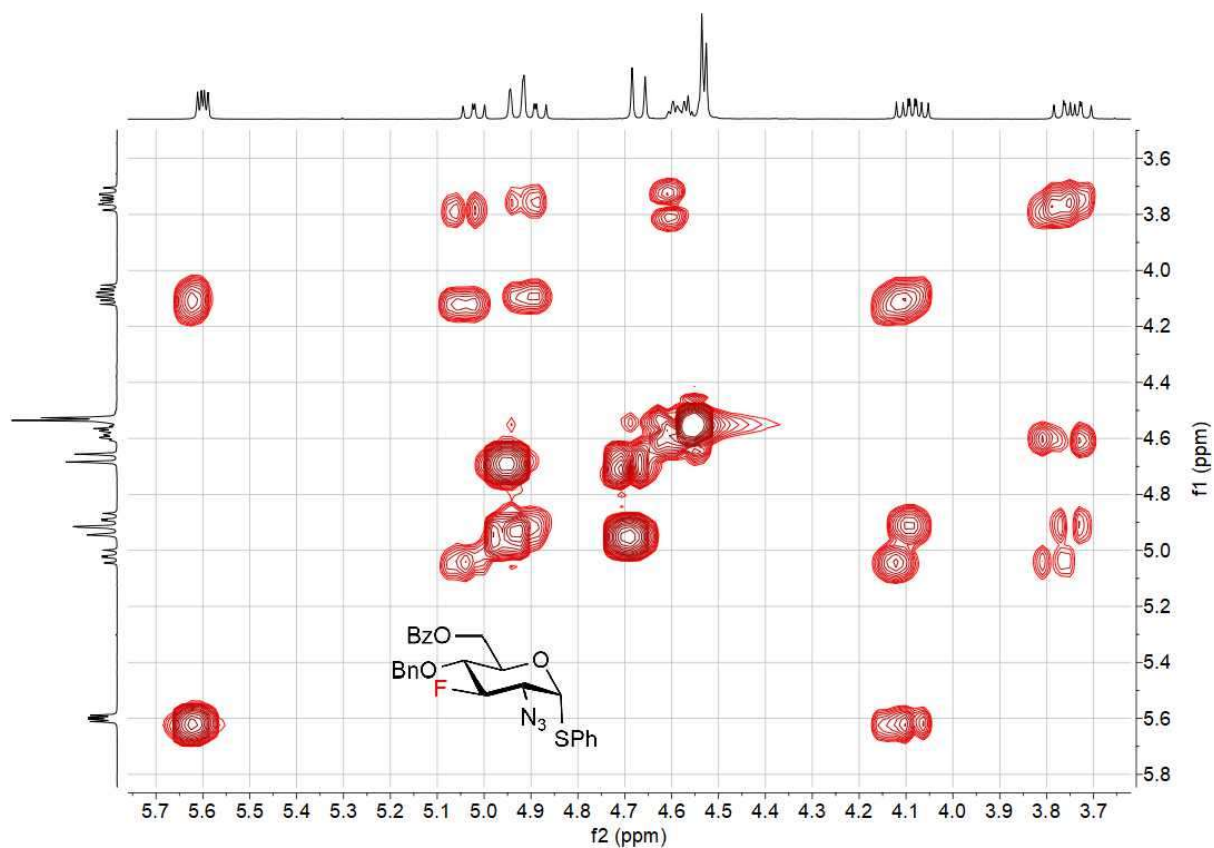
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **10**



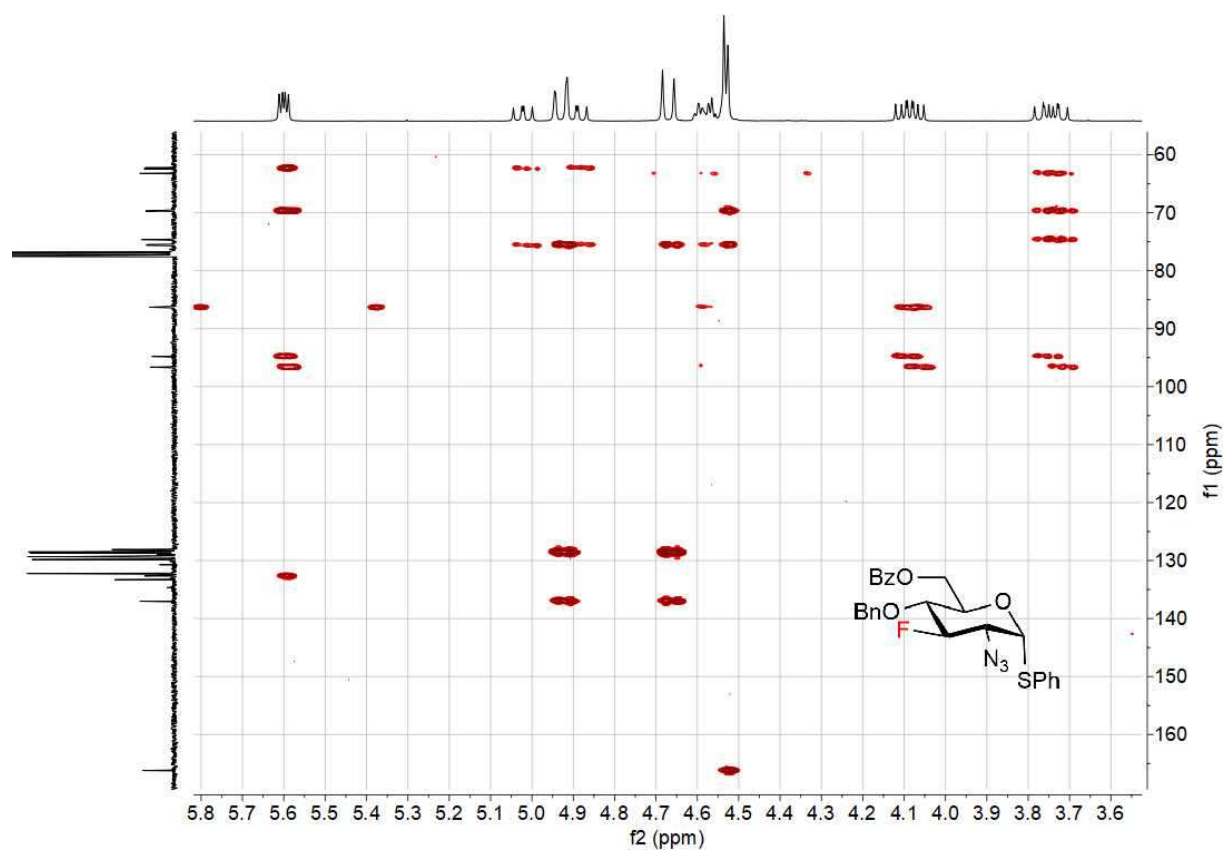
$^{19}\text{F}$  NMR 376 MHz  $\text{CDCl}_3$ , 10



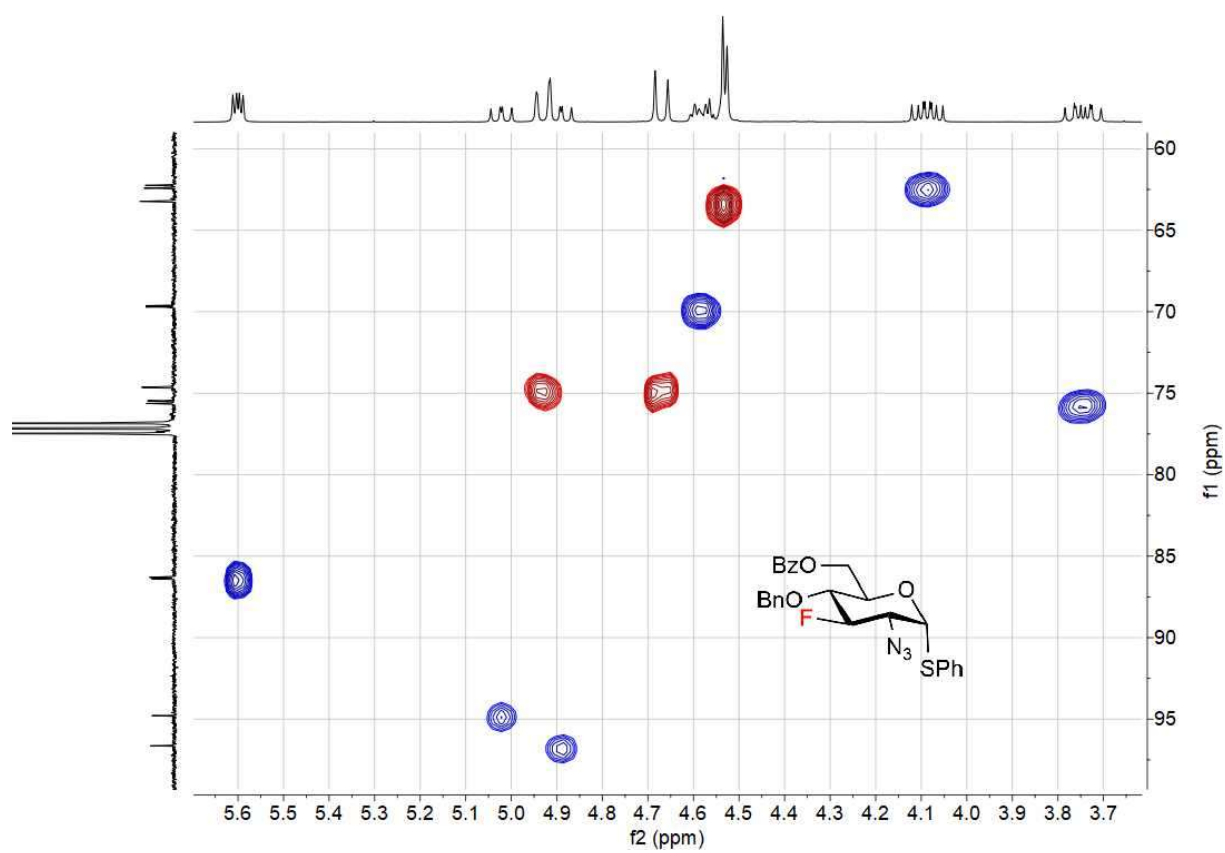
$^1\text{H}$ - $^1\text{H}$  COSY NMR 10



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 10



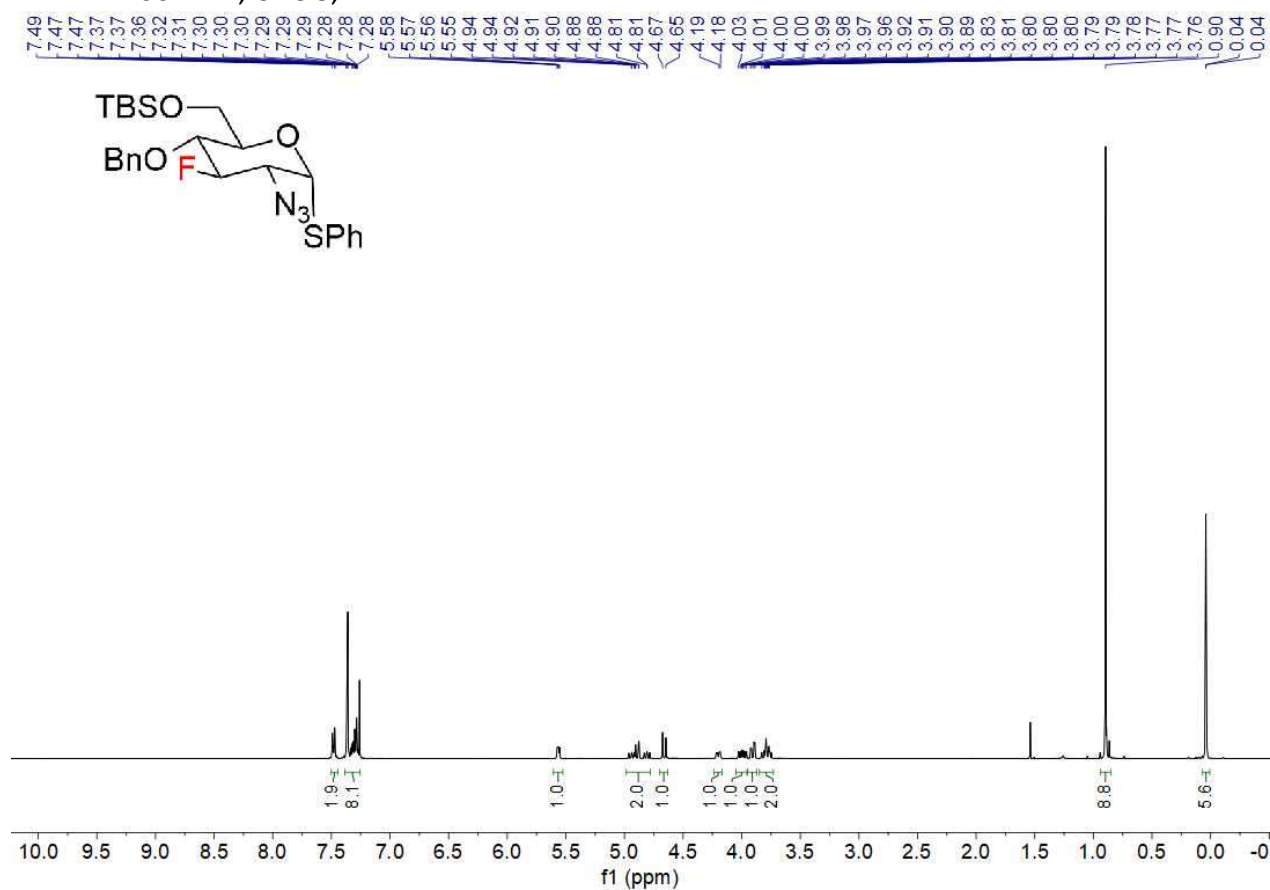
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 10



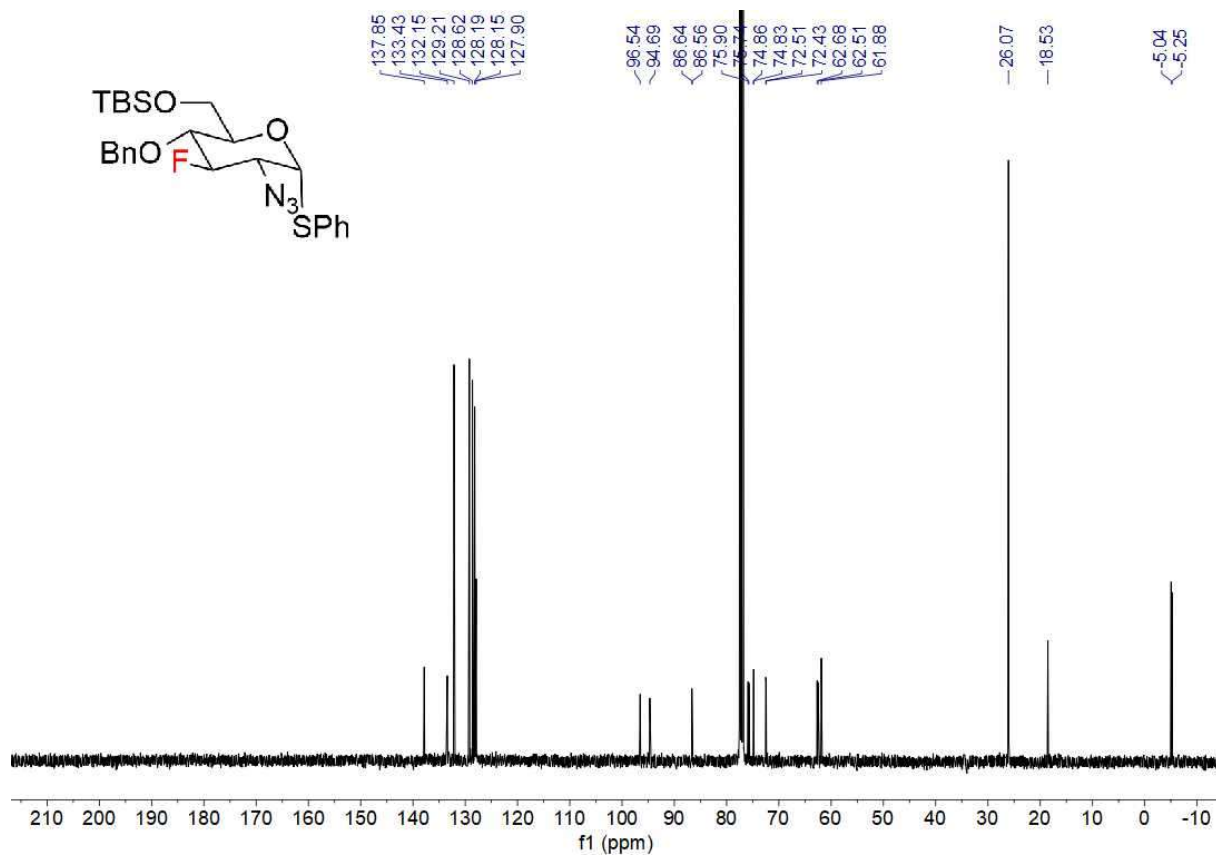


# **NMR 11**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **11**

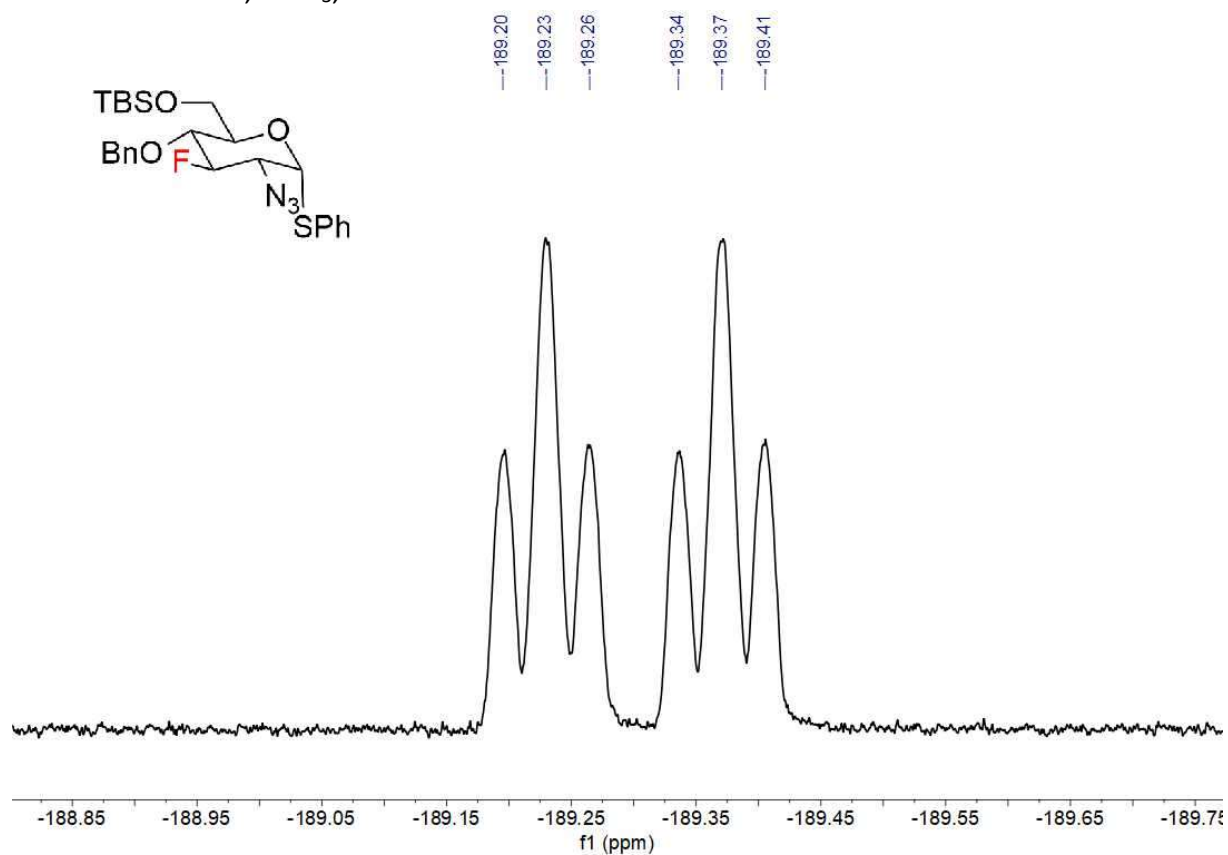


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **11**

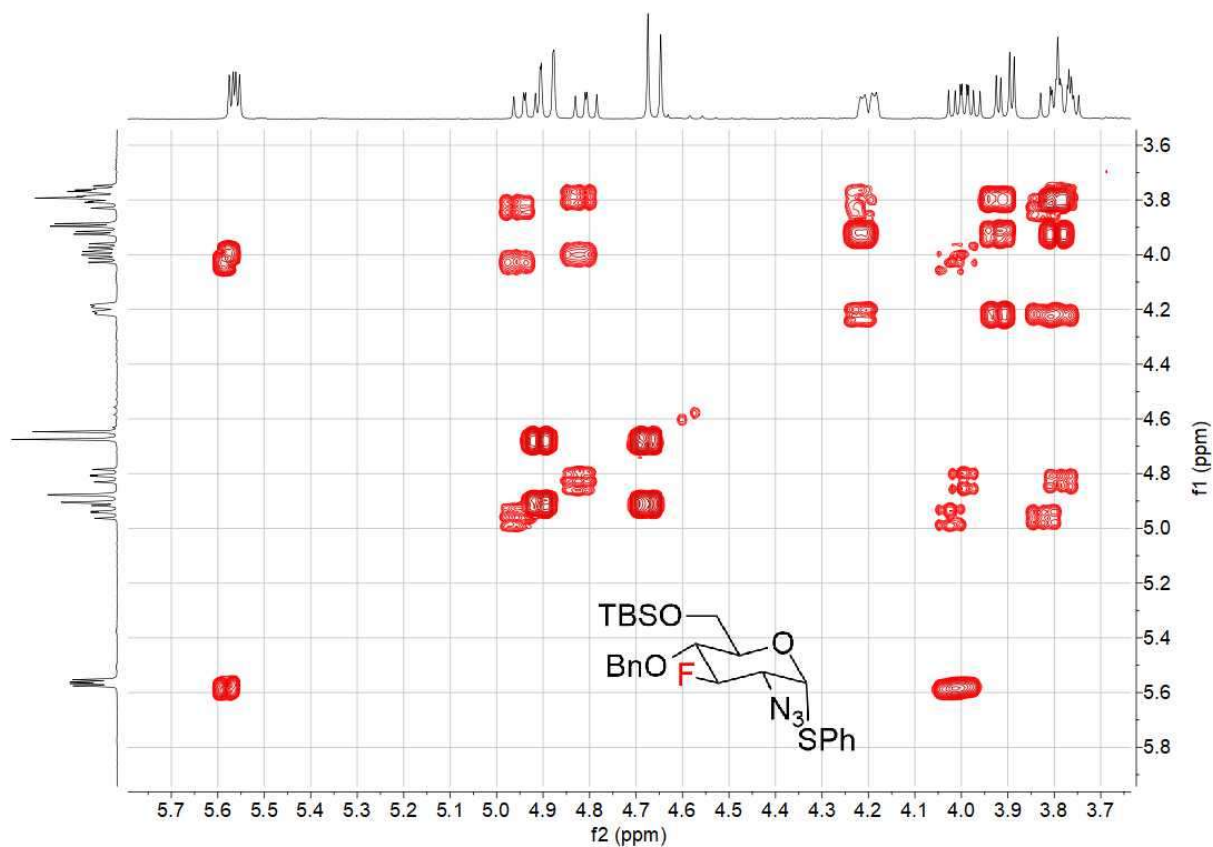




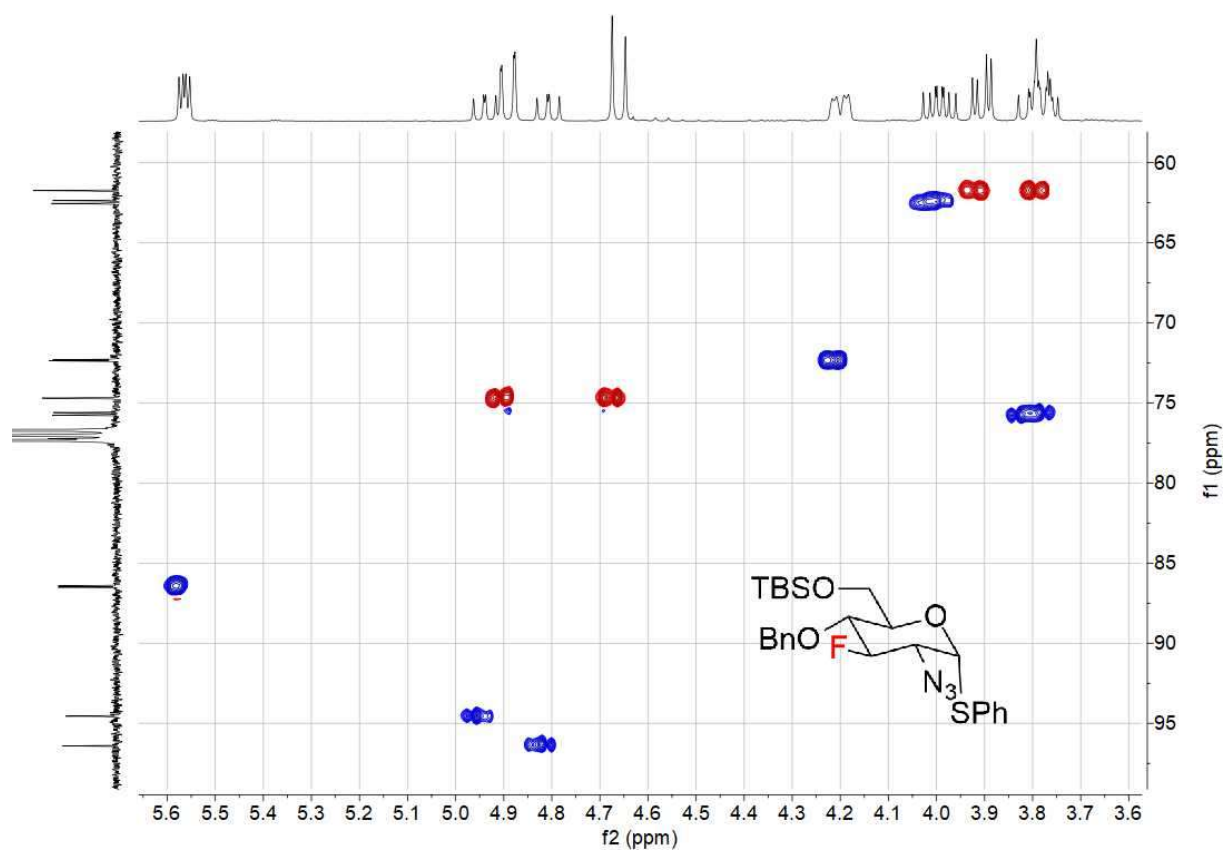
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , 11



$^1\text{H}$ - $^1\text{H}$  COSY NMR 11

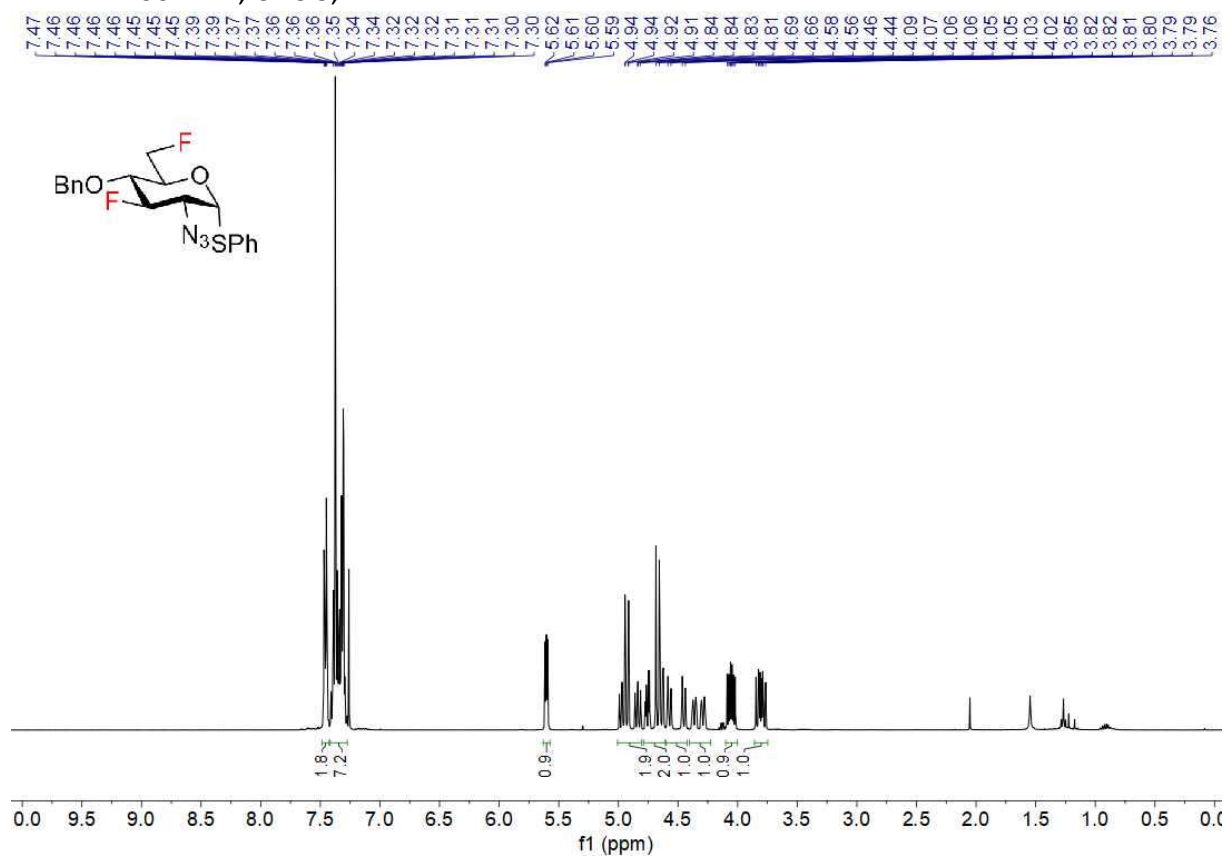


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 11

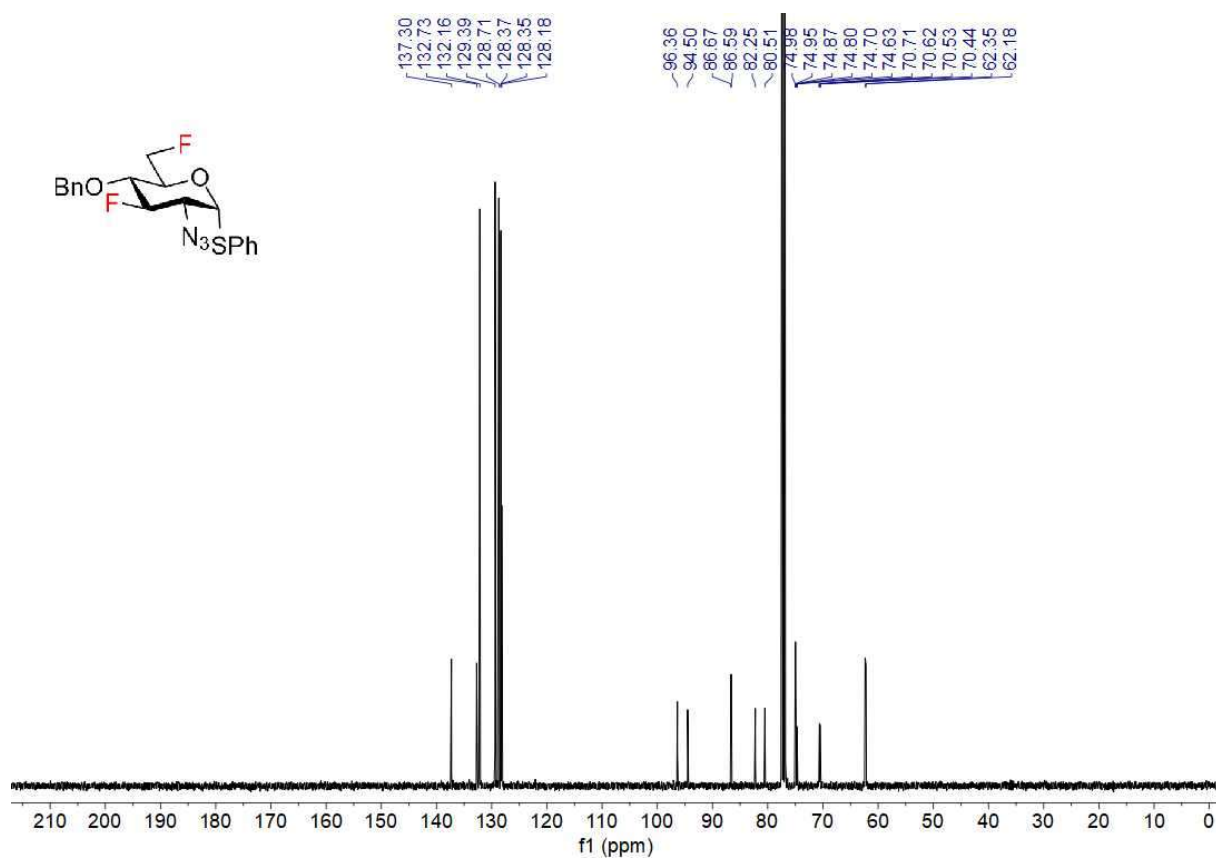


## NMR 12

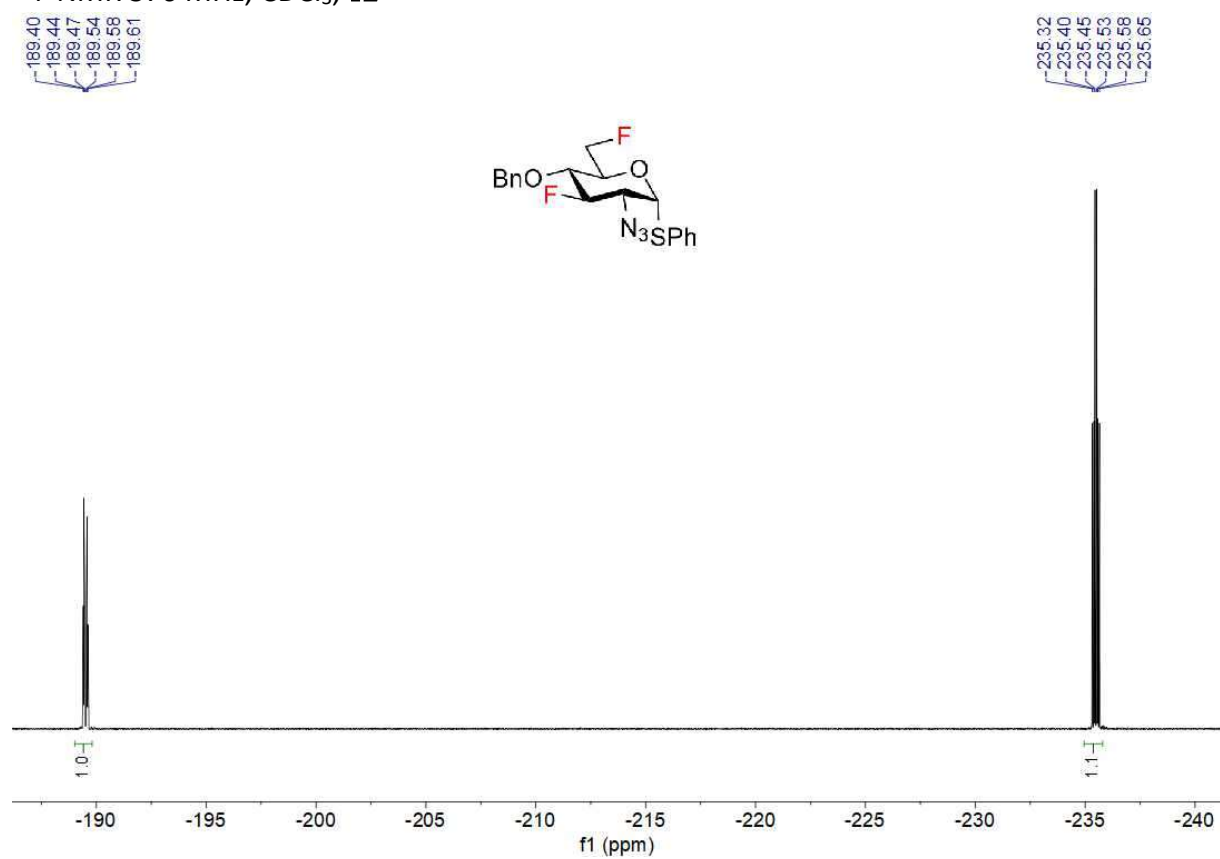
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **12**



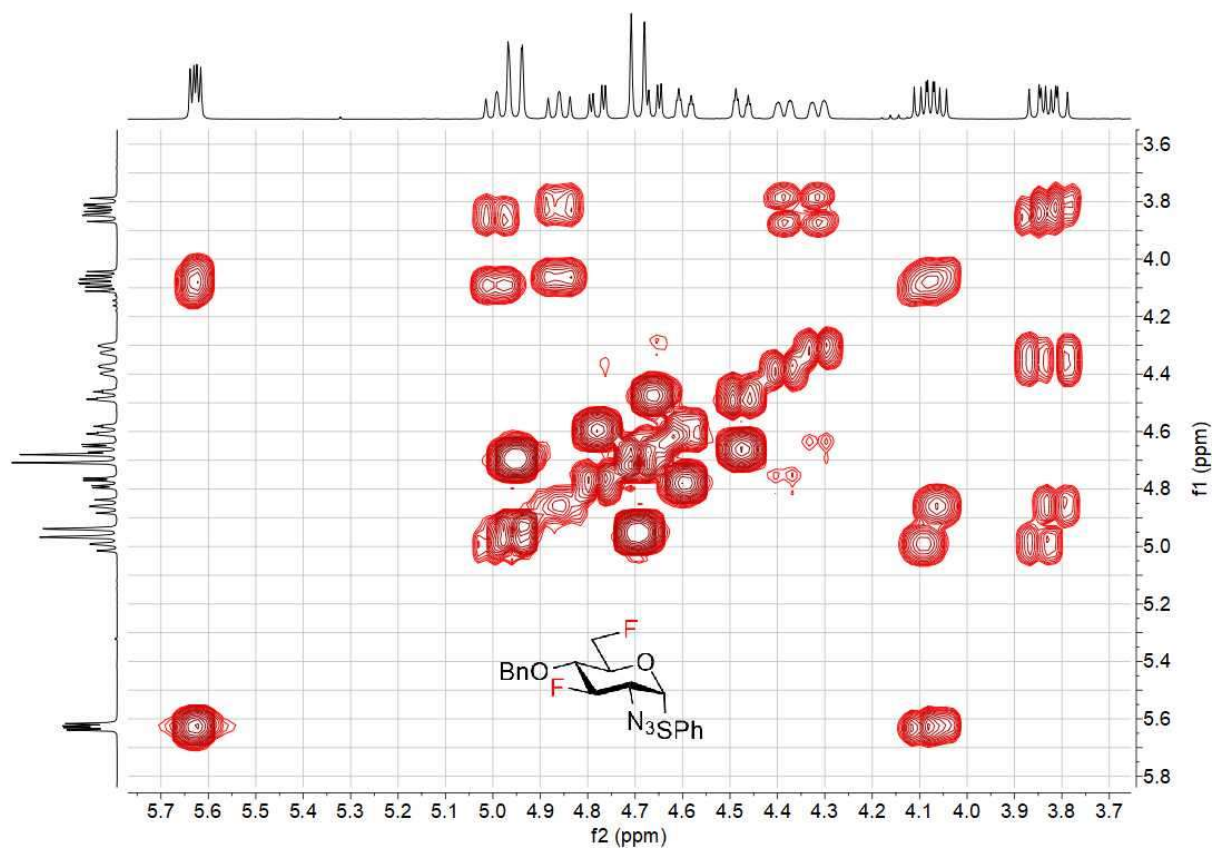
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **12**



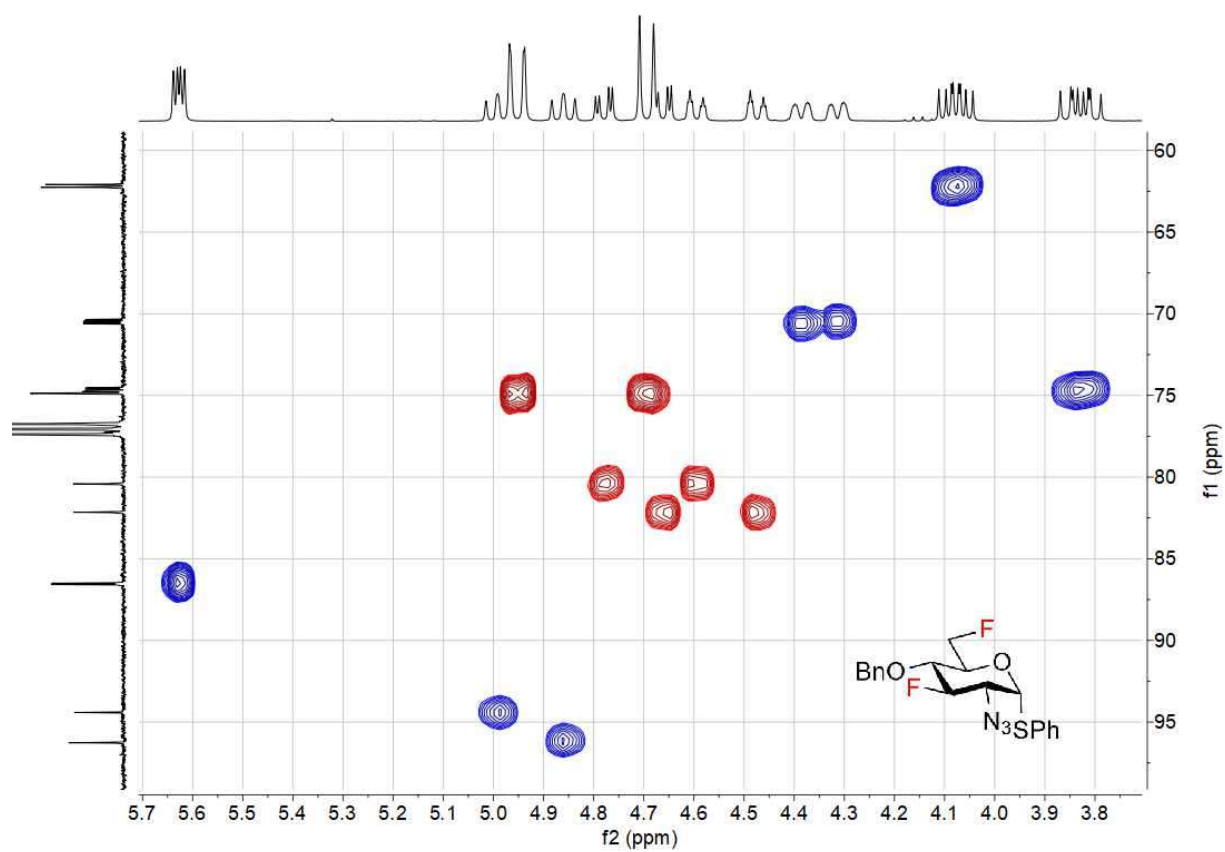
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , 12



$^1\text{H}$ - $^1\text{H}$  COSY NMR, 12

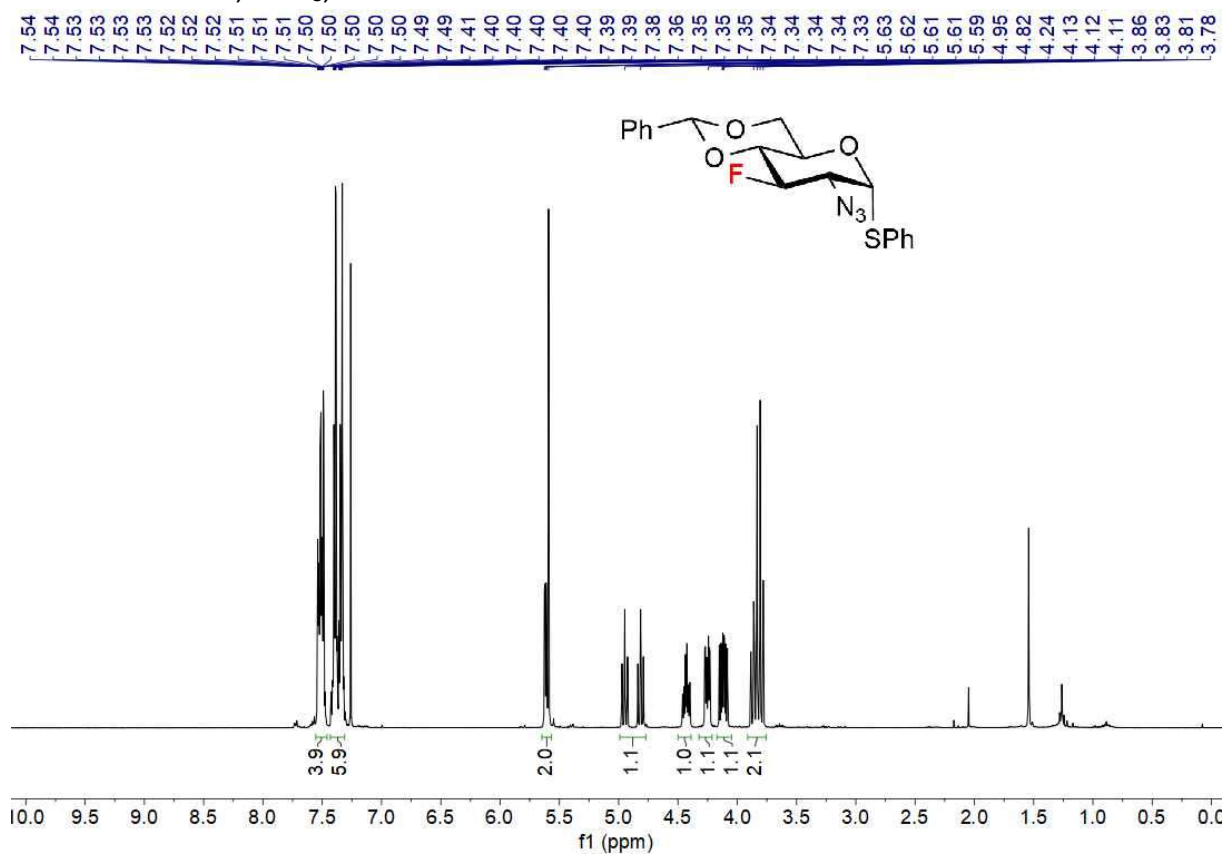


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 12

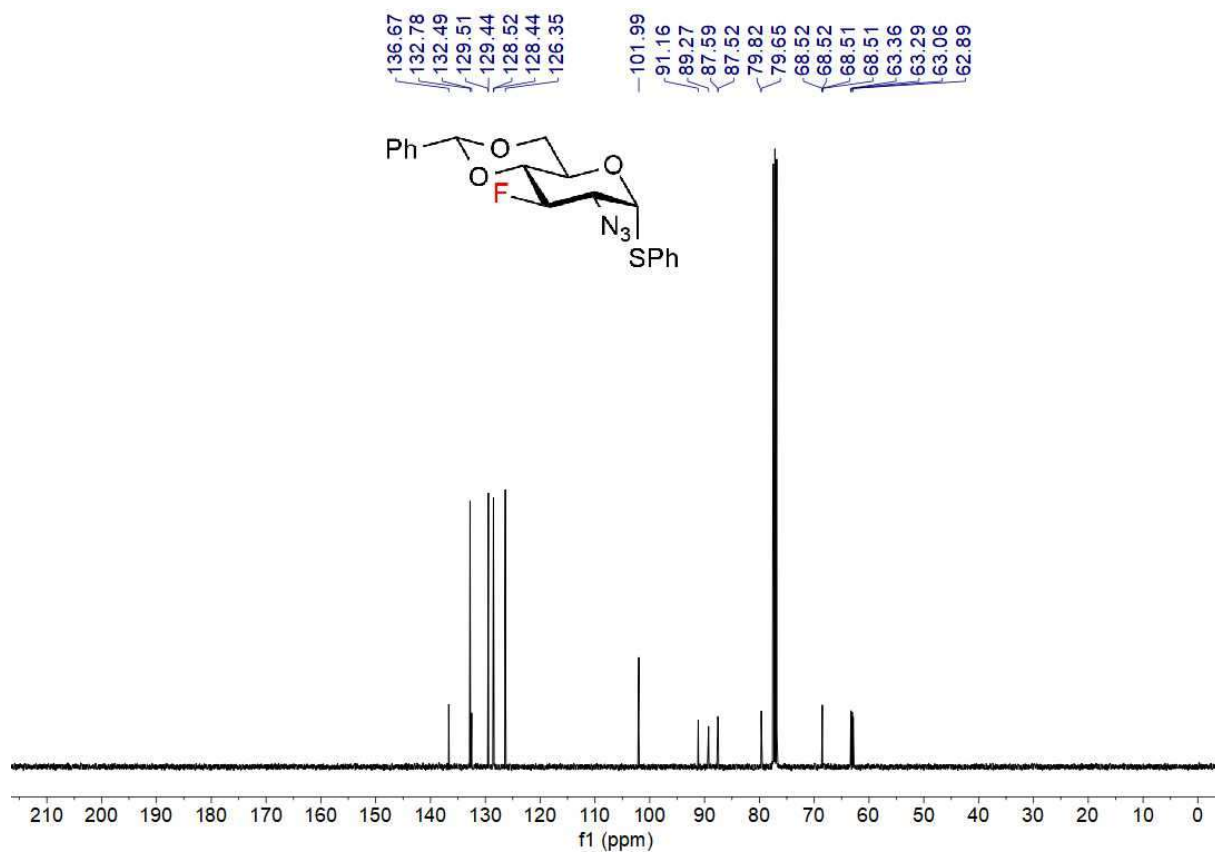


# **NMR $\alpha$ -13**

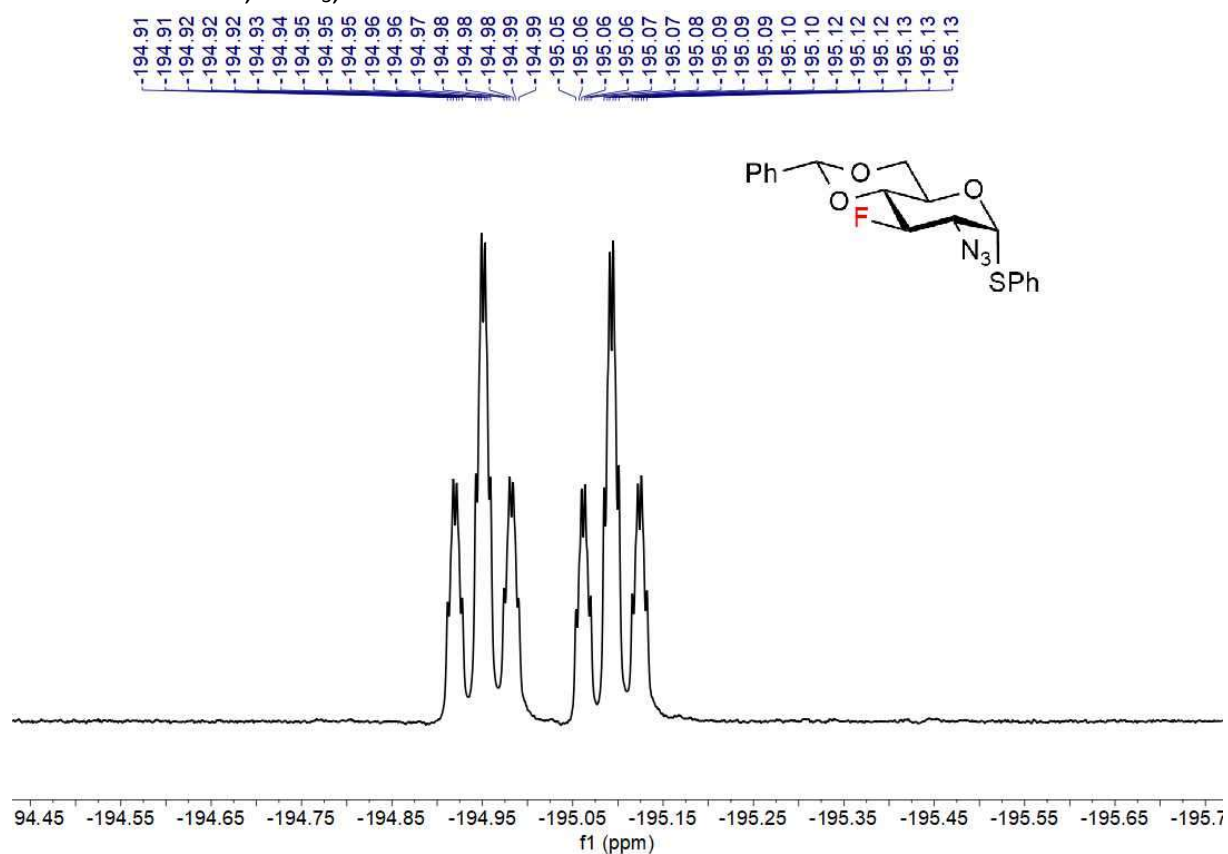
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -13**



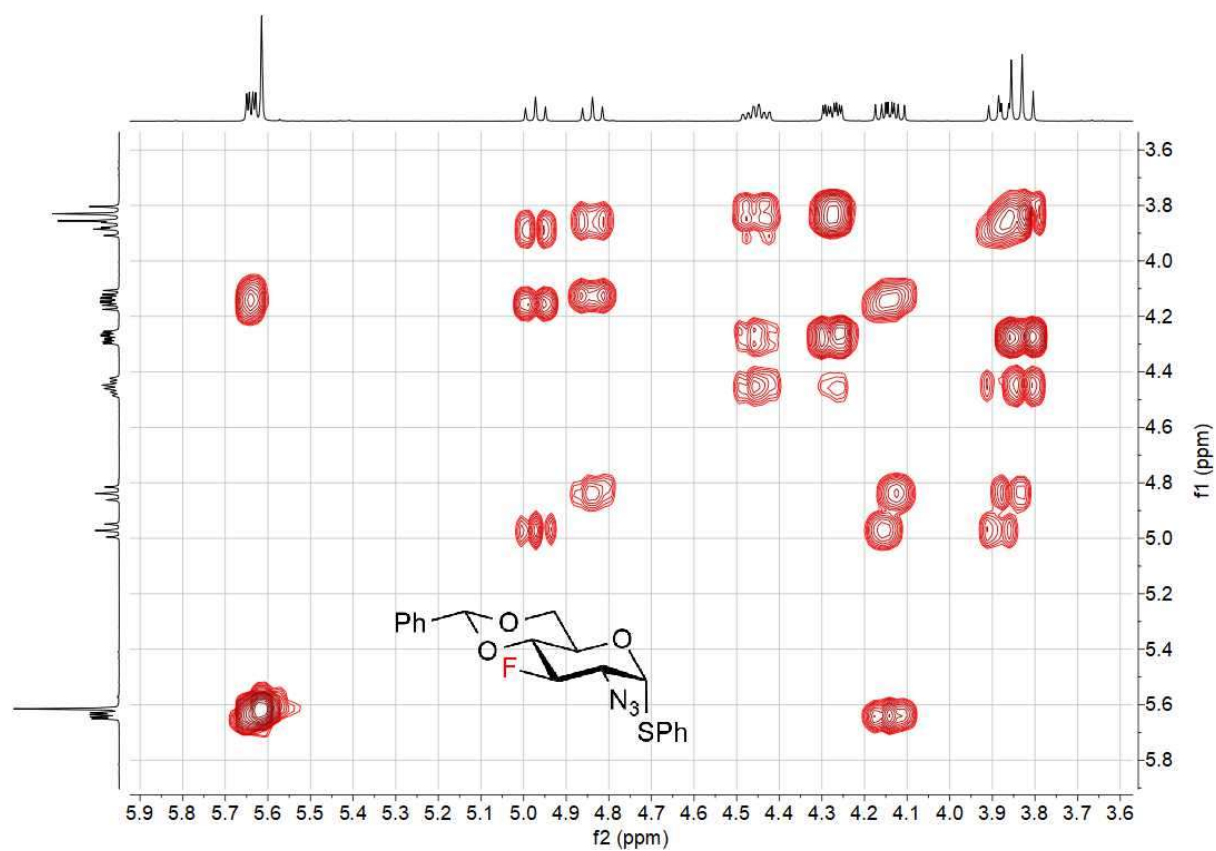
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -13**



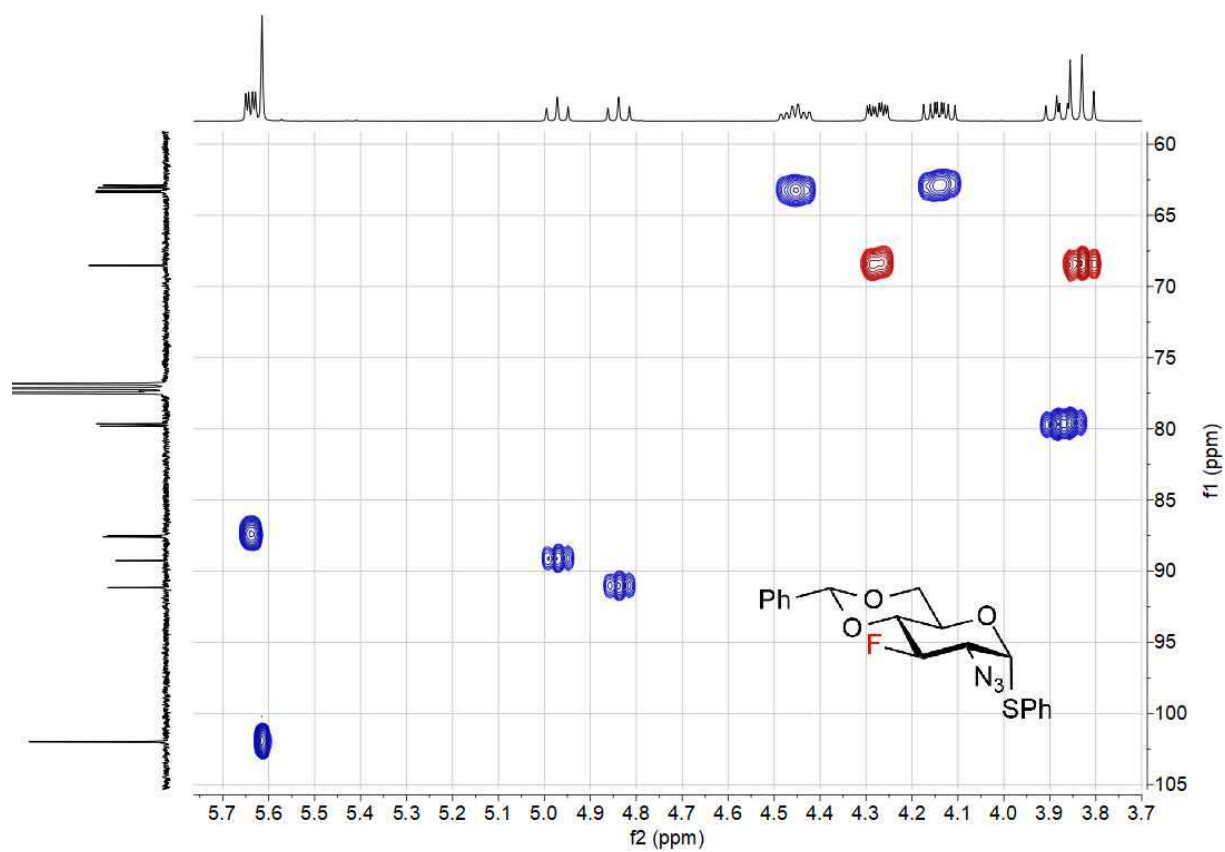
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -13**



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\alpha$ -13**



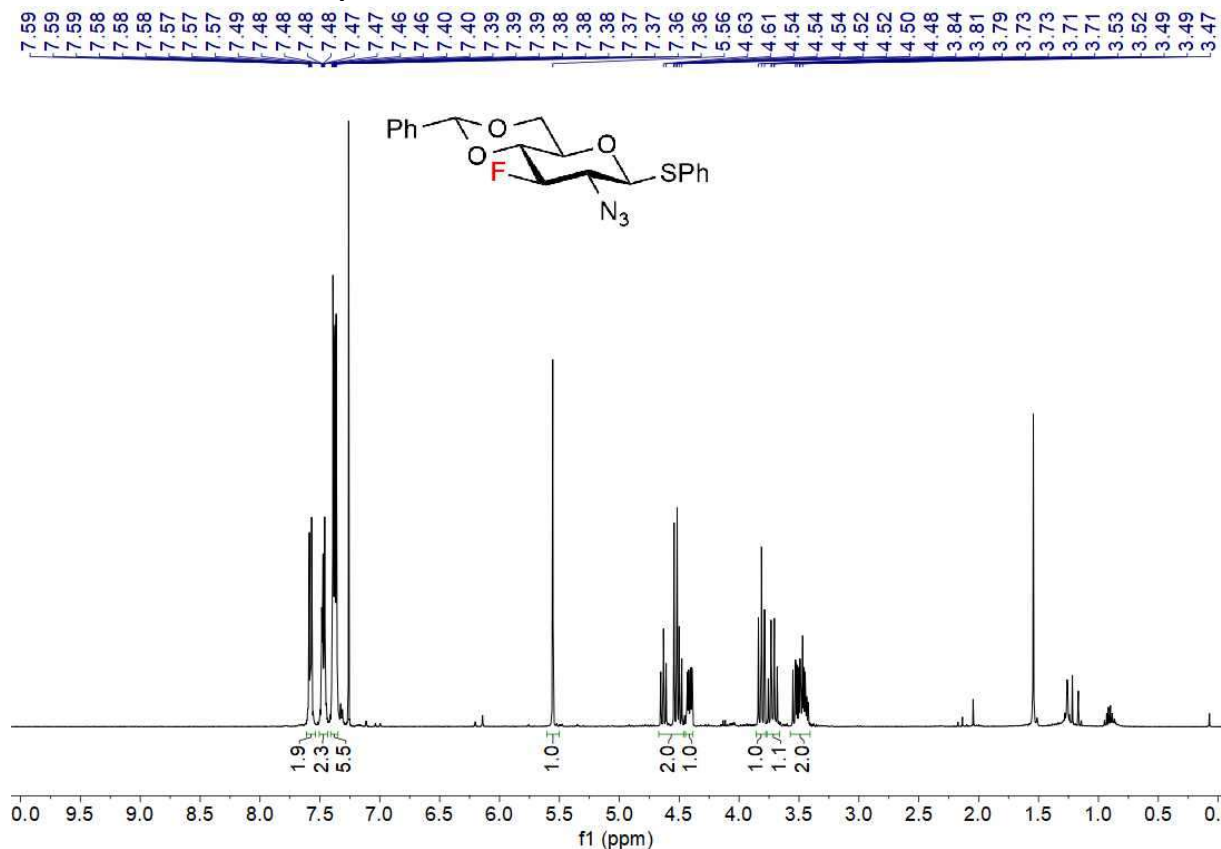
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\alpha$ -13



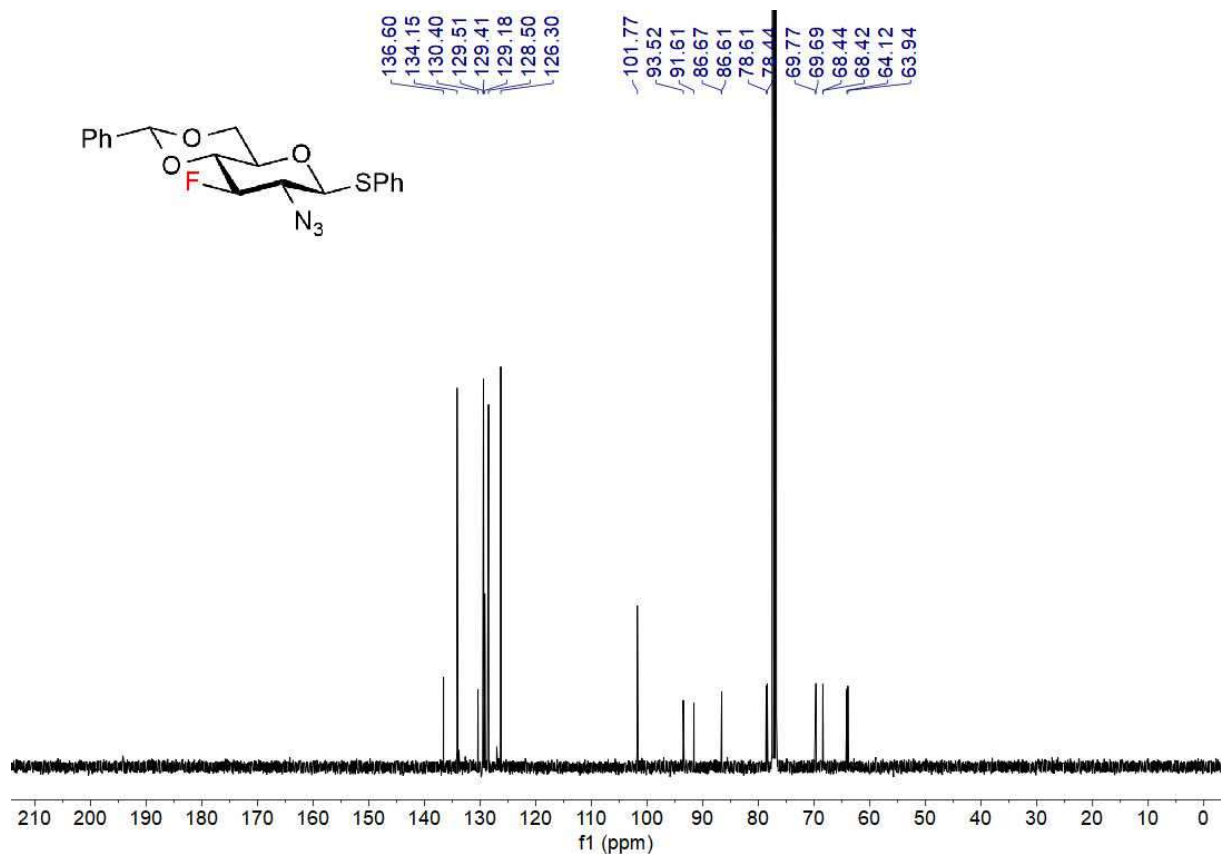


# **NMR $\beta$ -13**

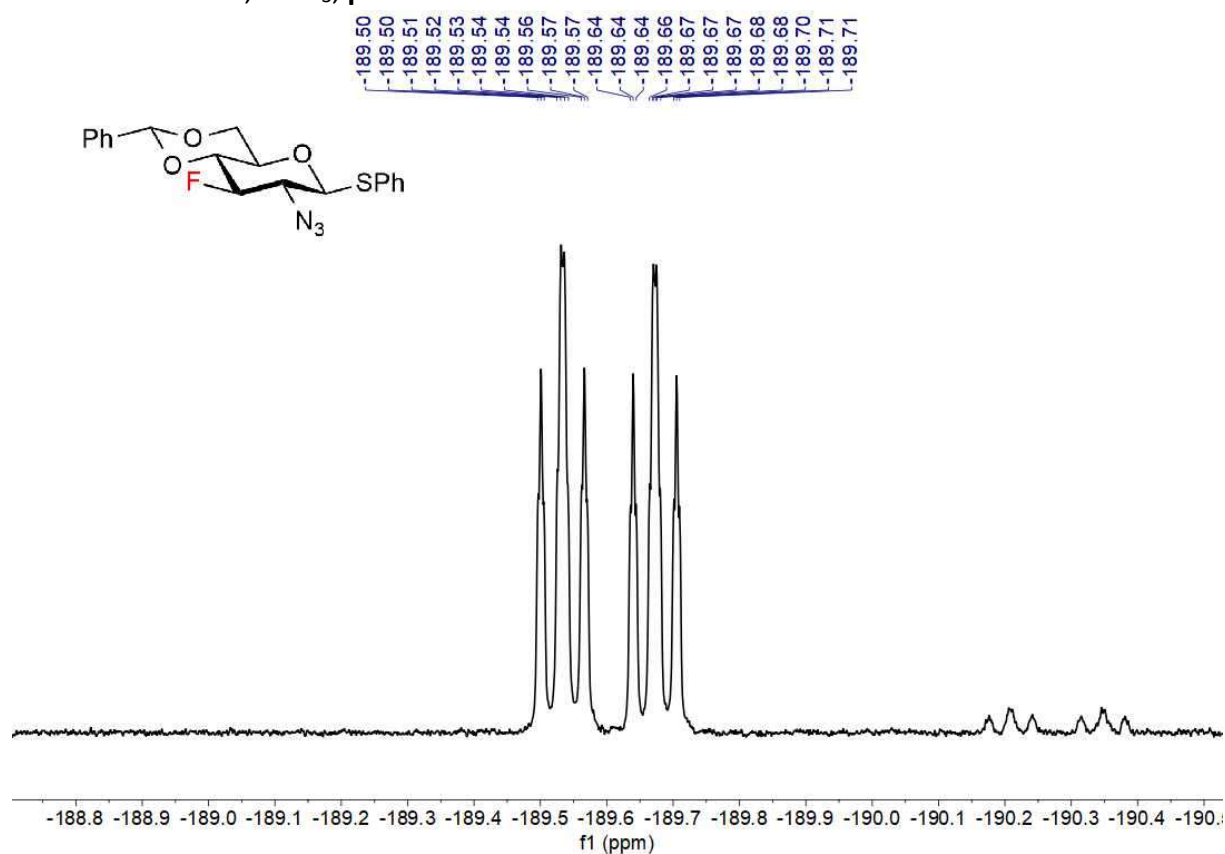
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -13**



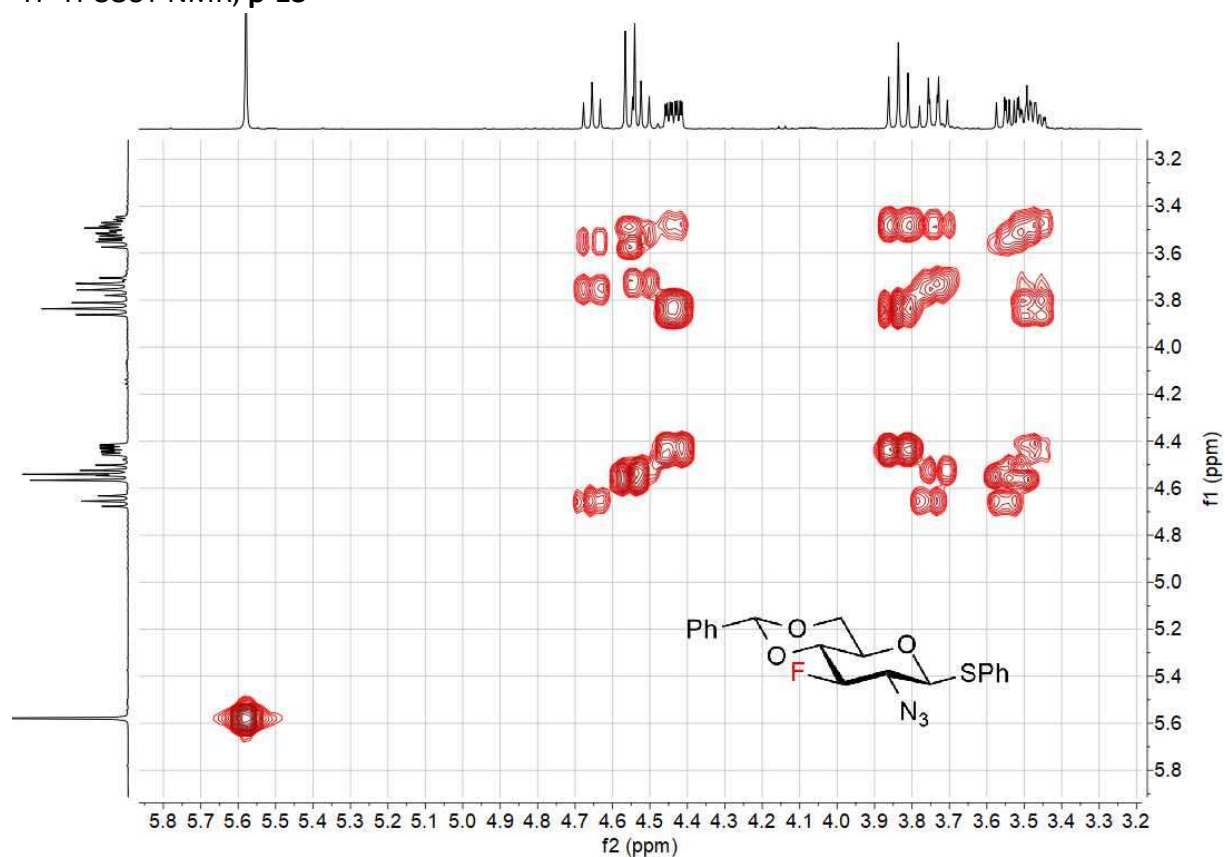
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  **$\beta$ -13**



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -13**



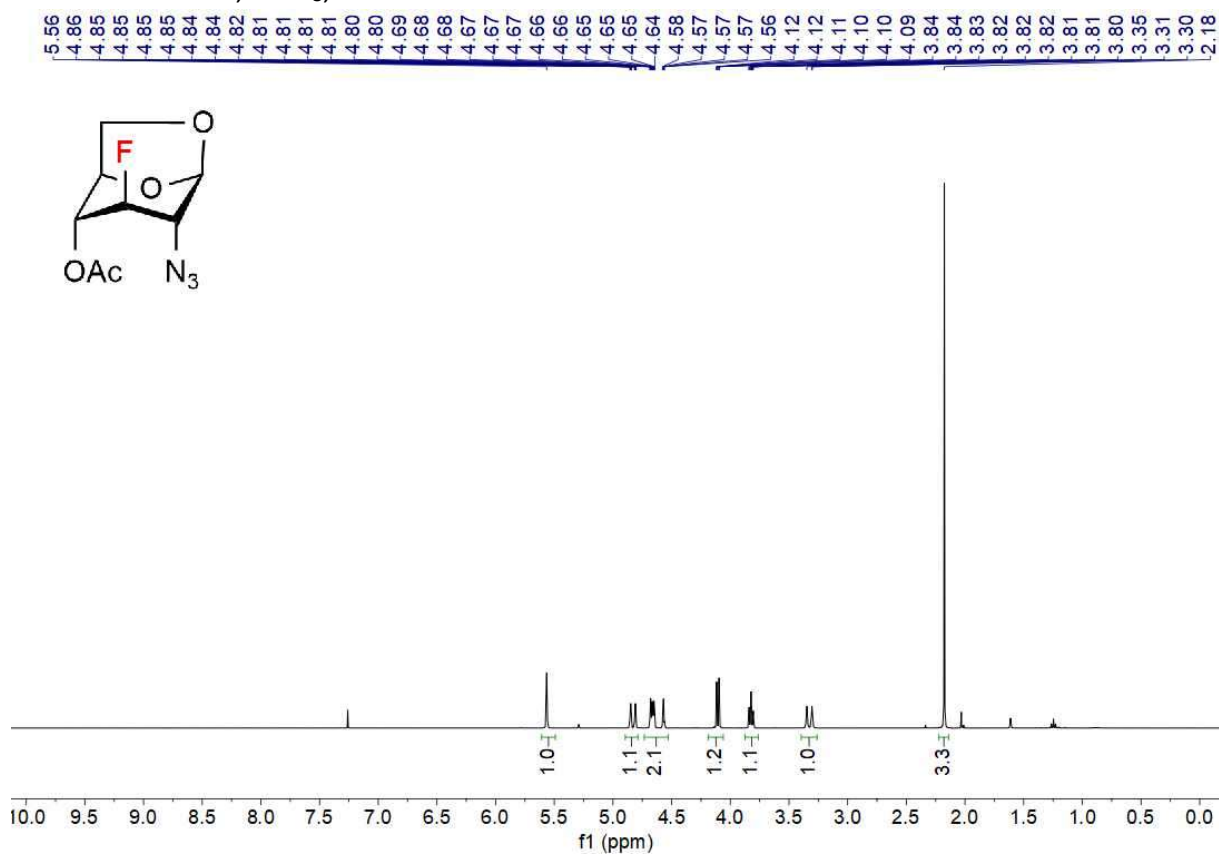
$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\beta$ -13**



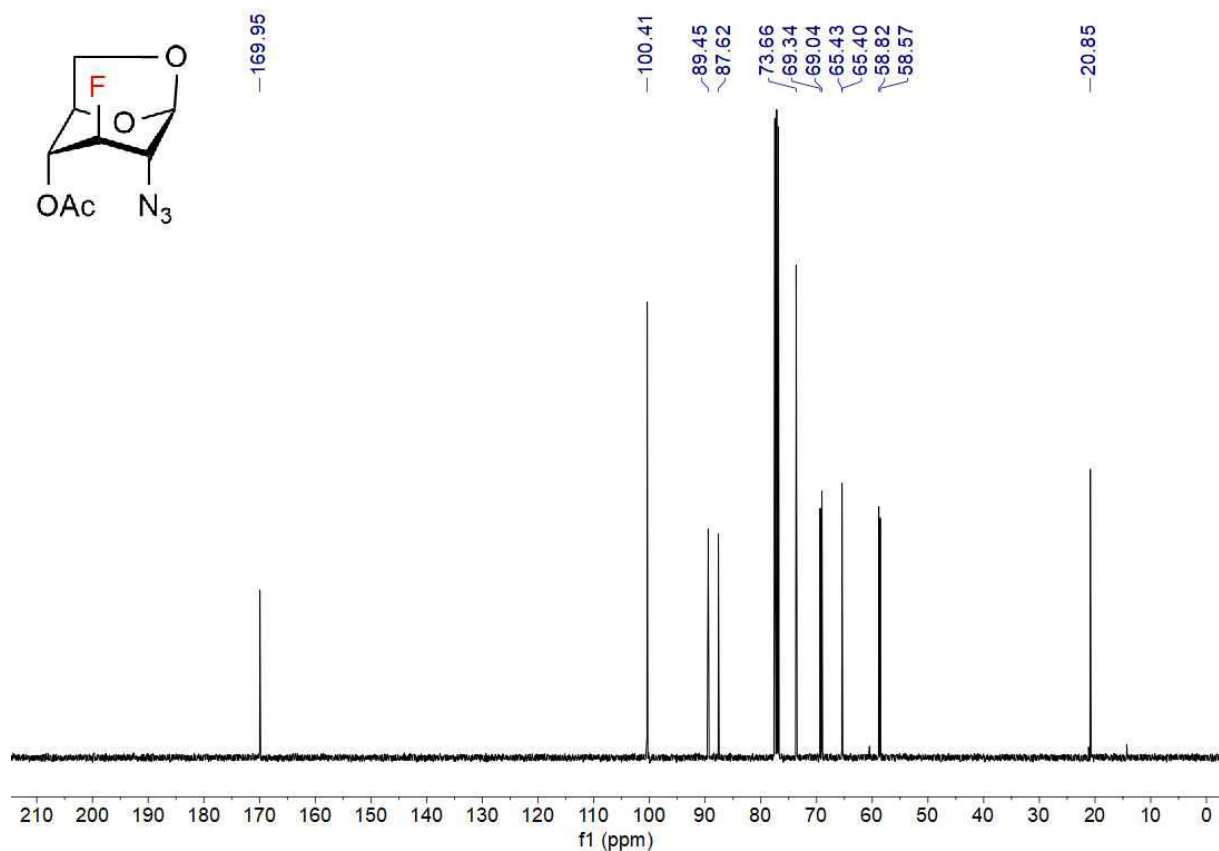


# NMR 14

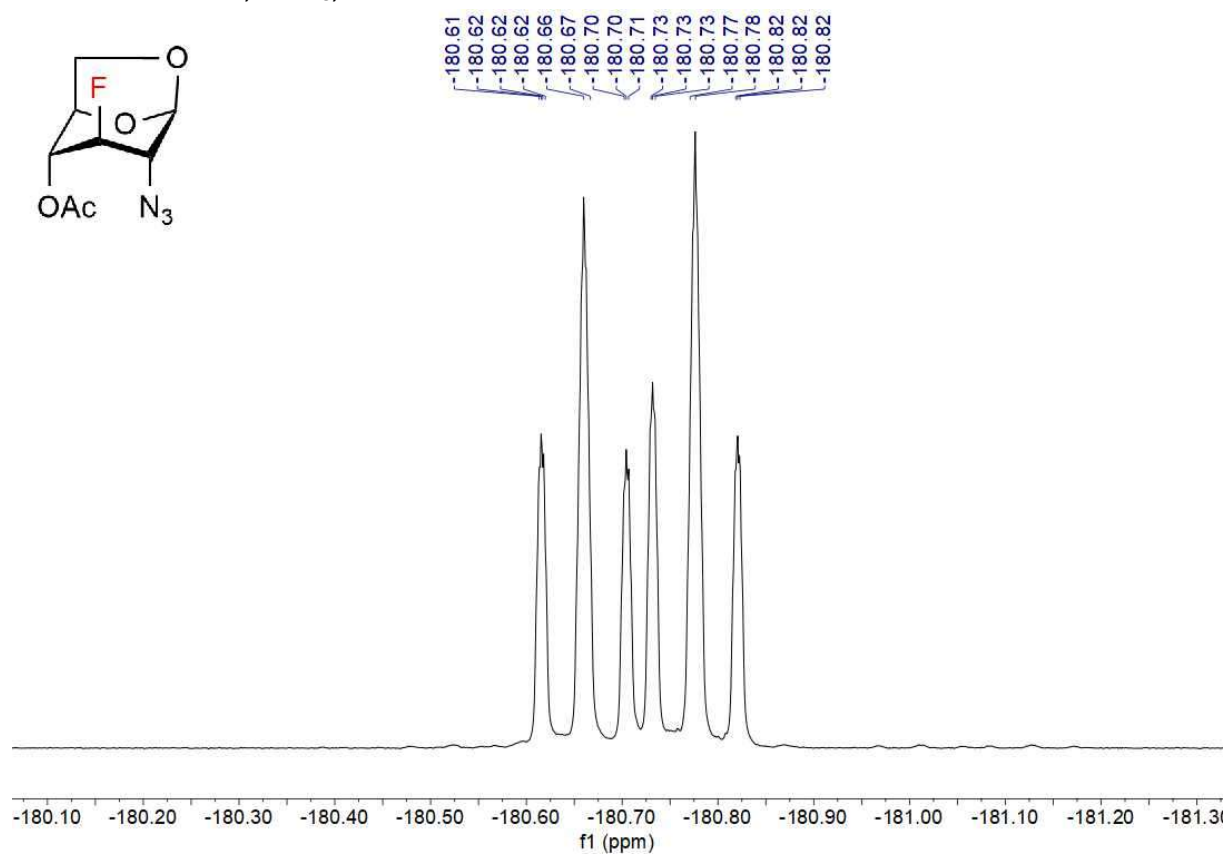
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **14**



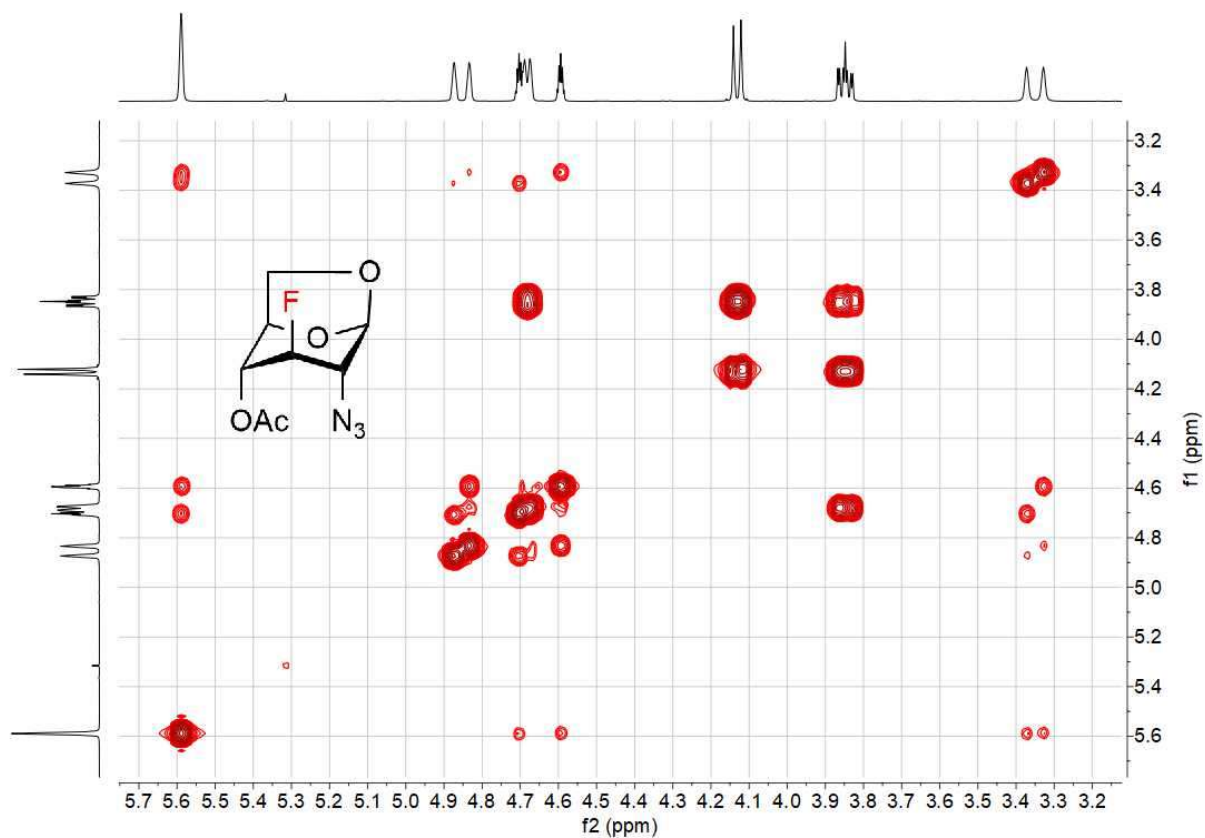
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **14**



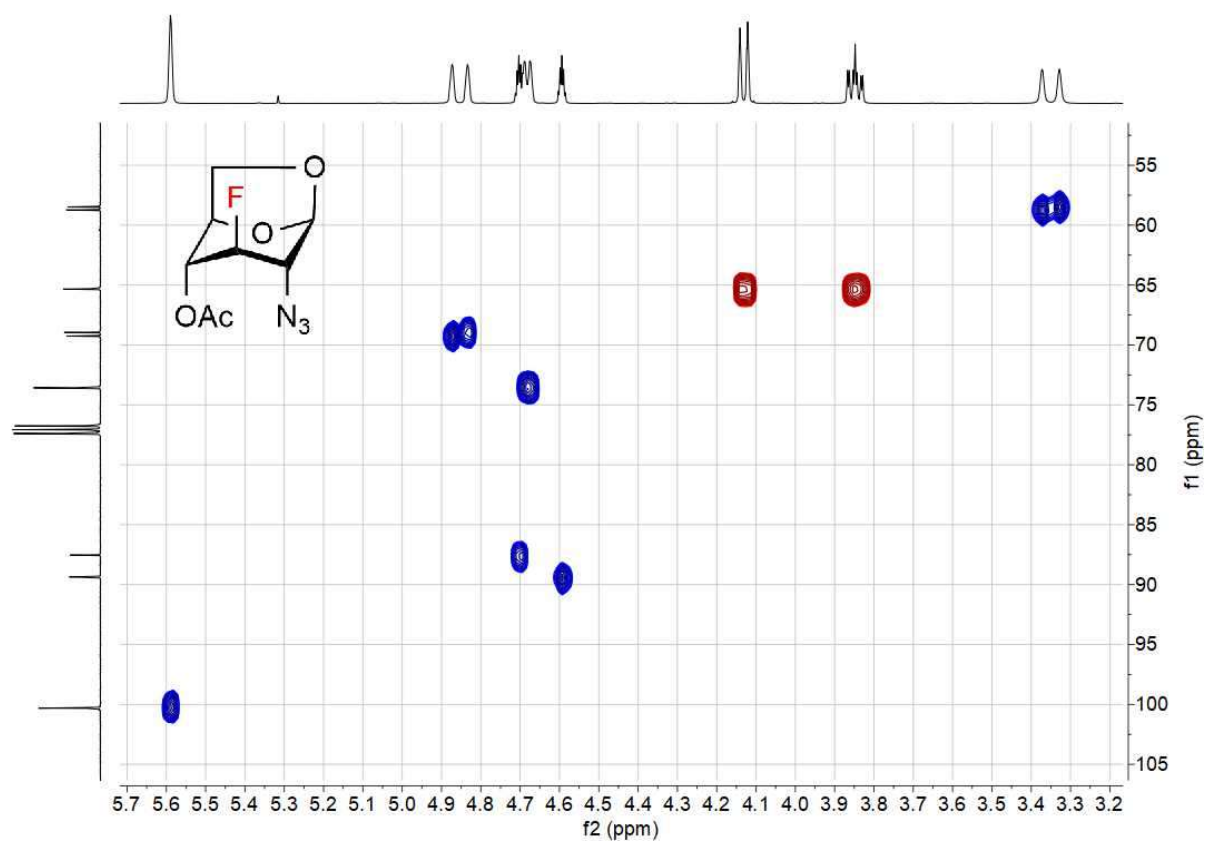
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **14**



$^1\text{H}$ - $^1\text{H}$  COSY NMR, **14**

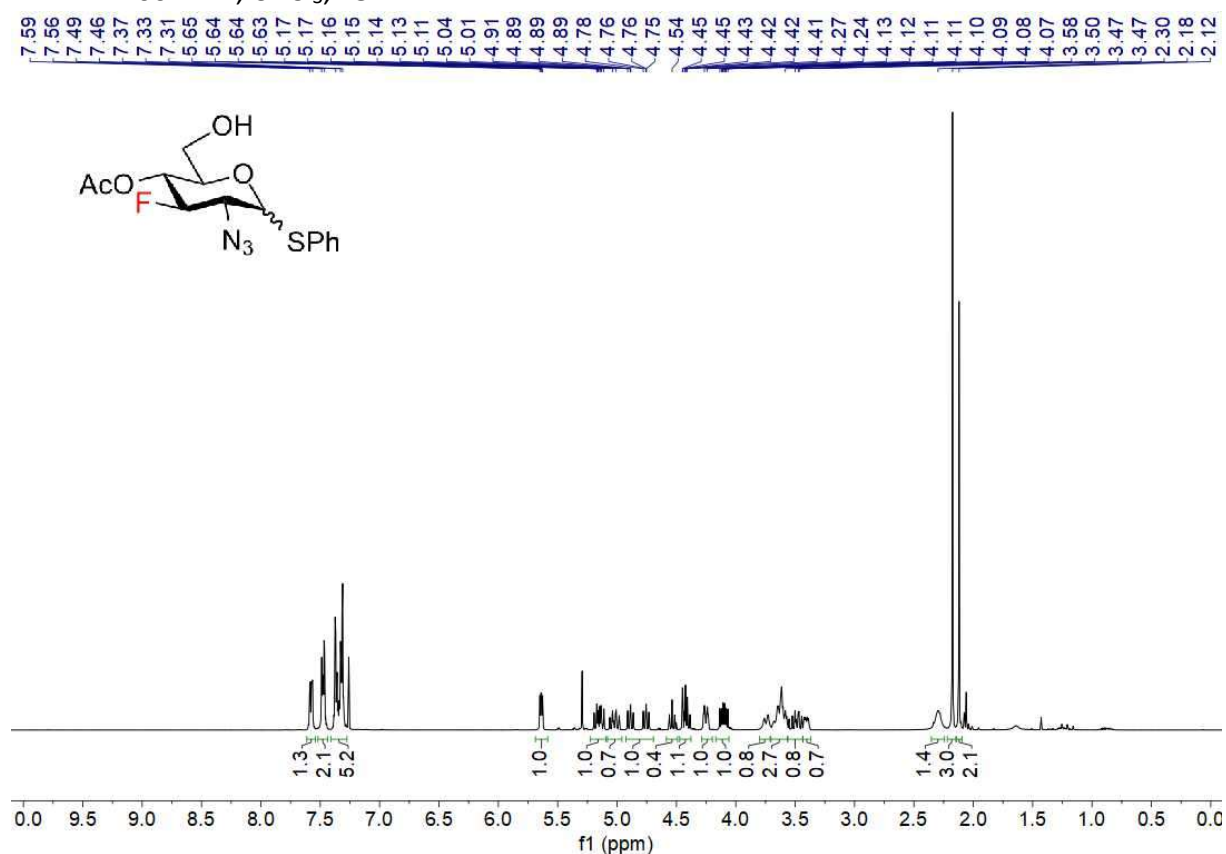


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 14

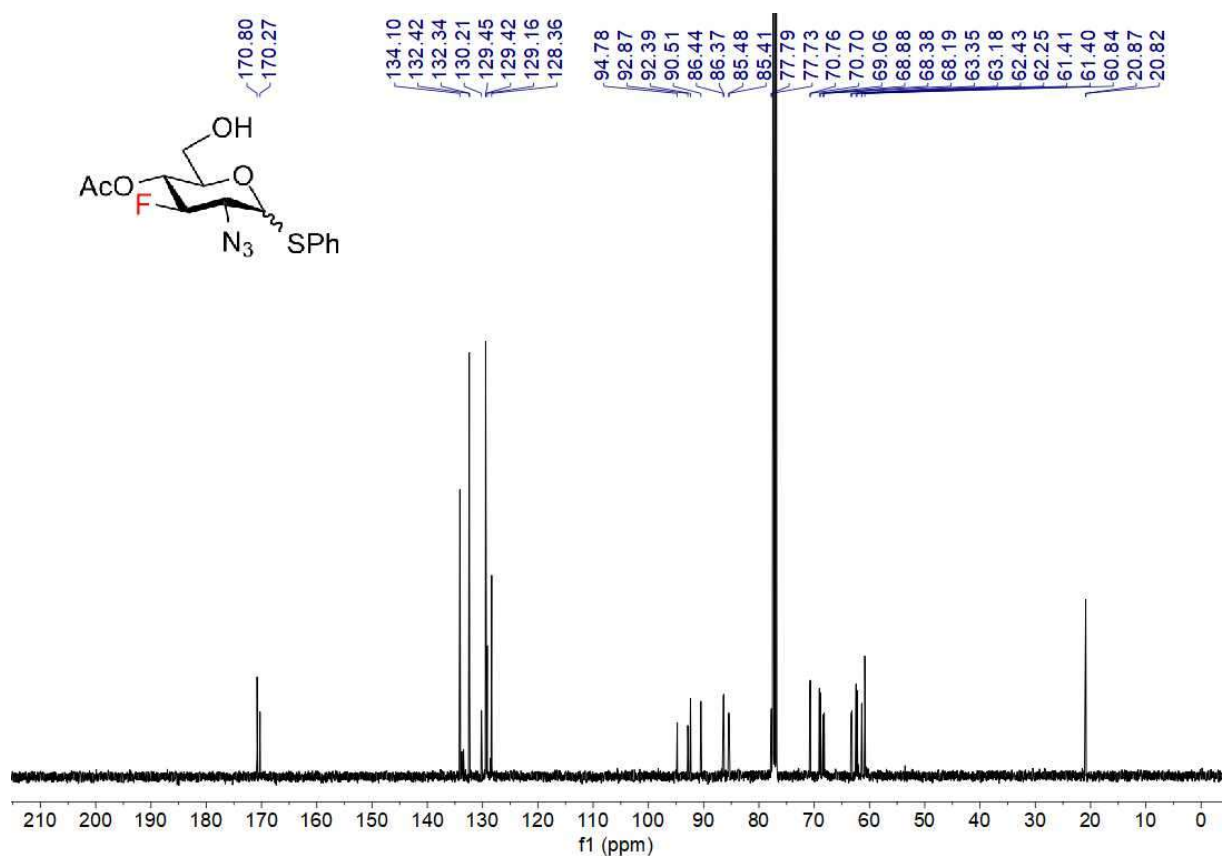


# **NMR 15**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **15**

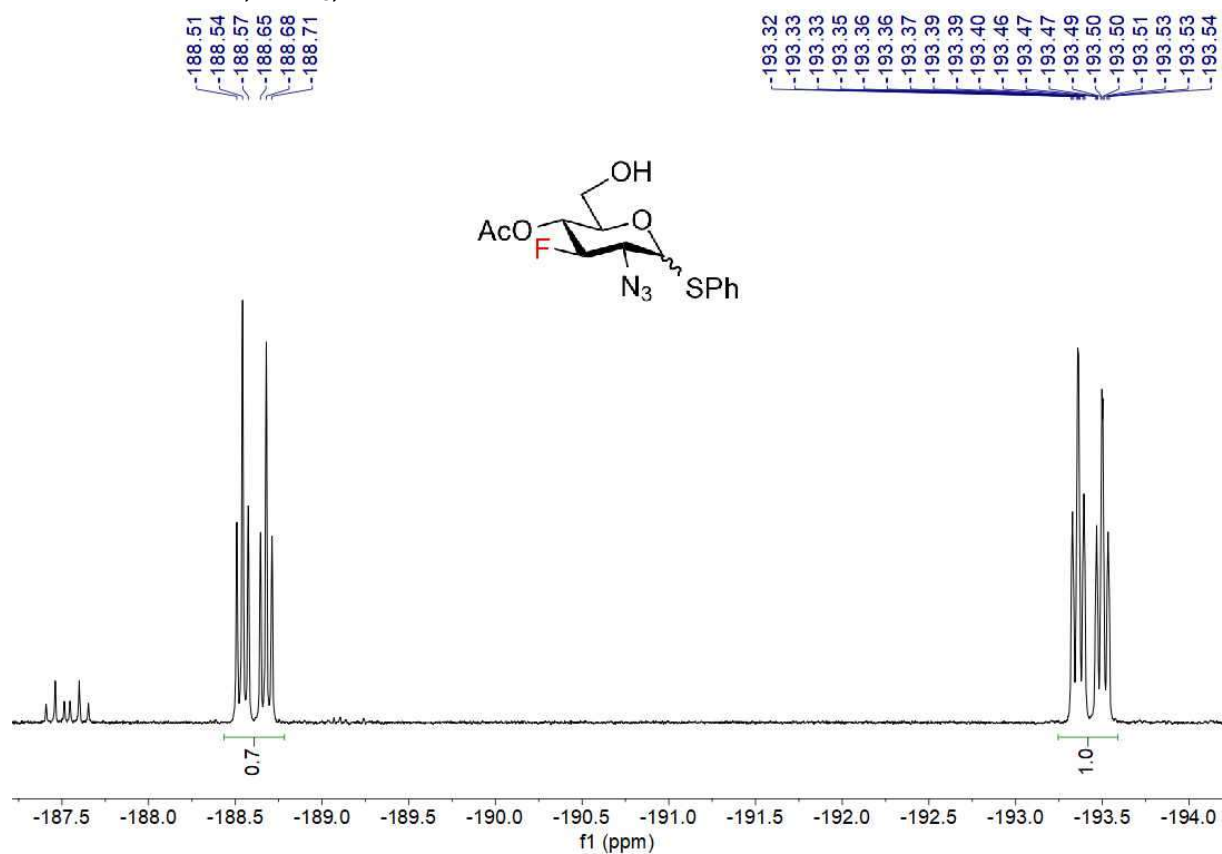


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **15**

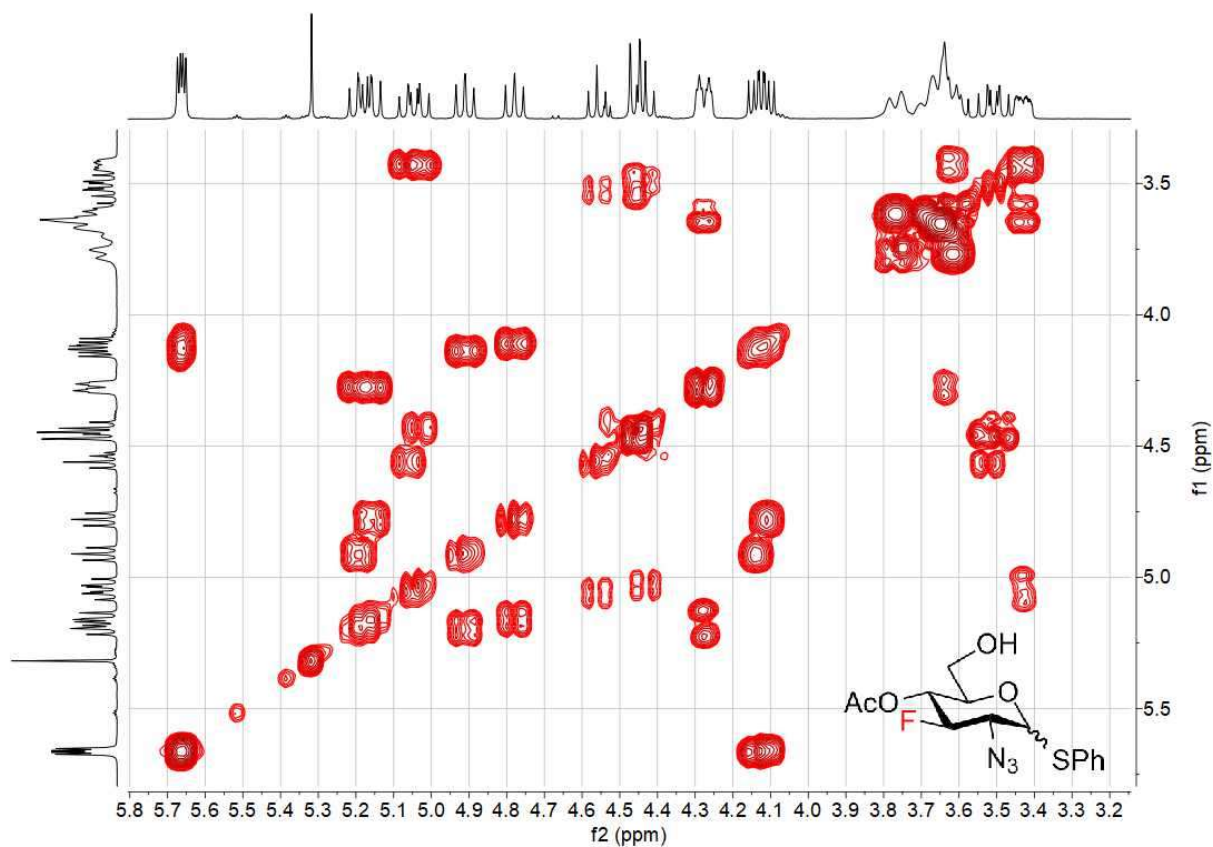




$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **15**

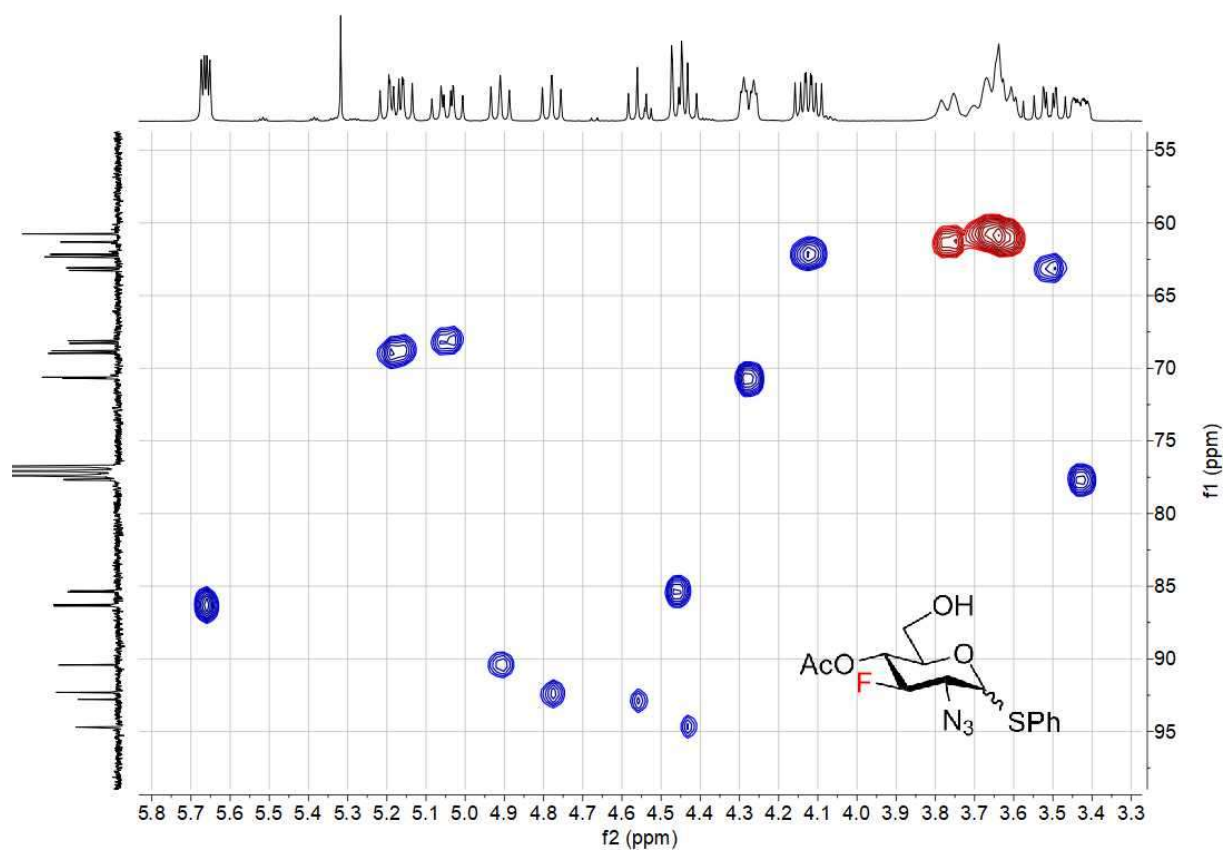


$^1\text{H}$ - $^1\text{H}$  COSY NMR, **15**



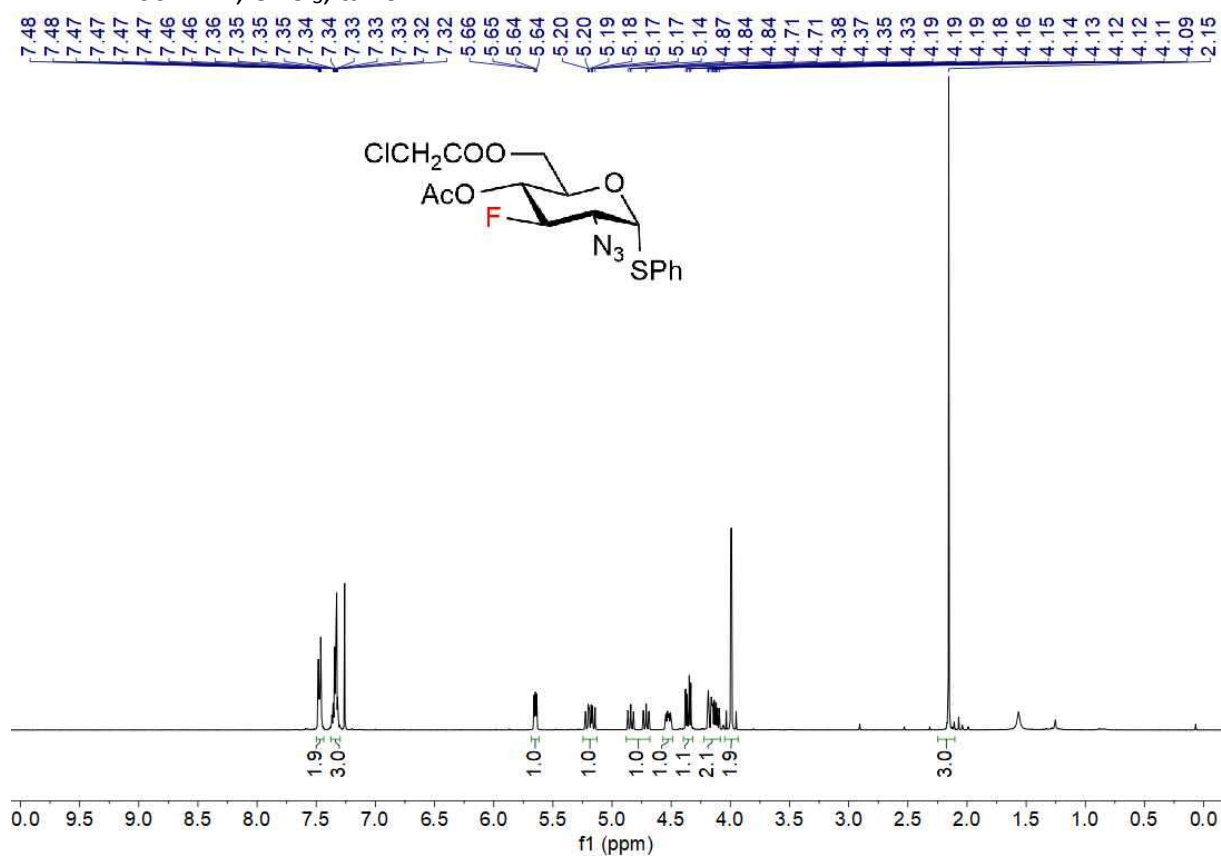


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 15

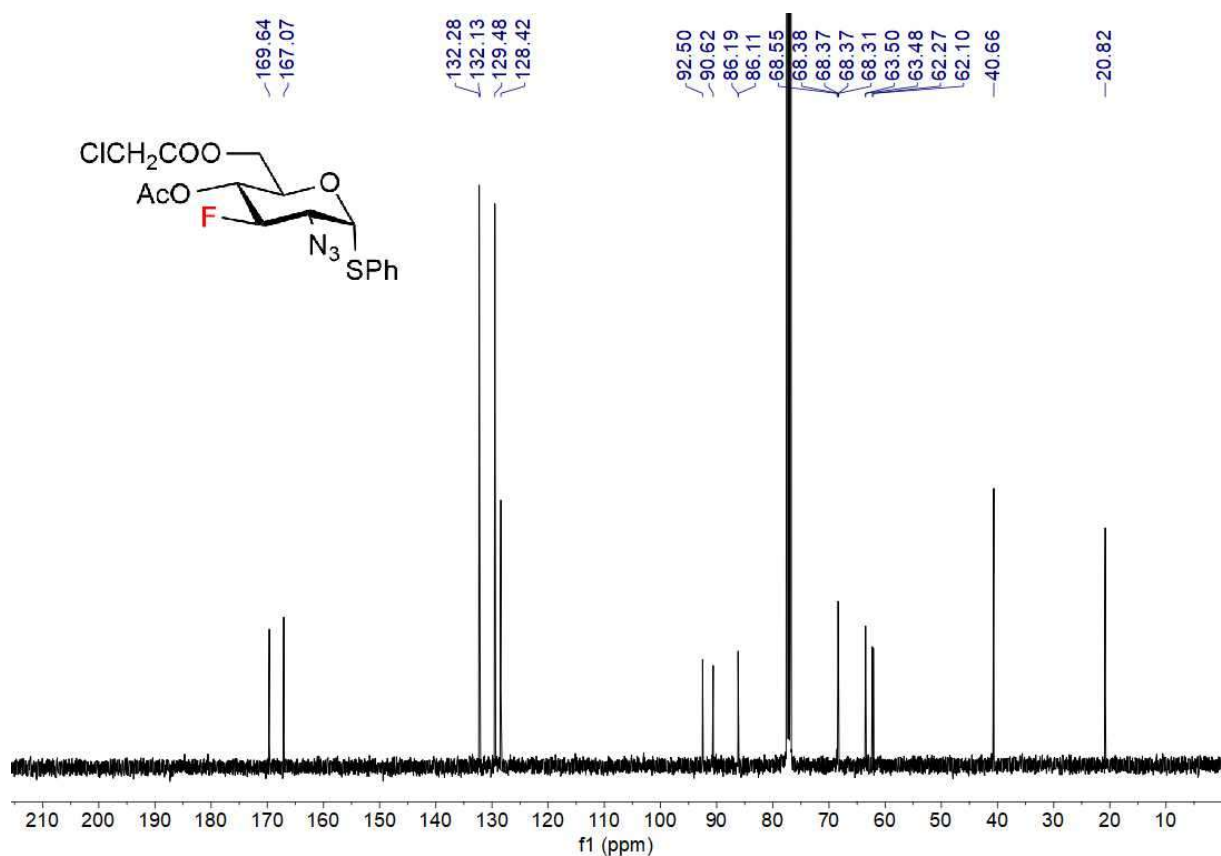


# **NMR $\alpha$ -16**

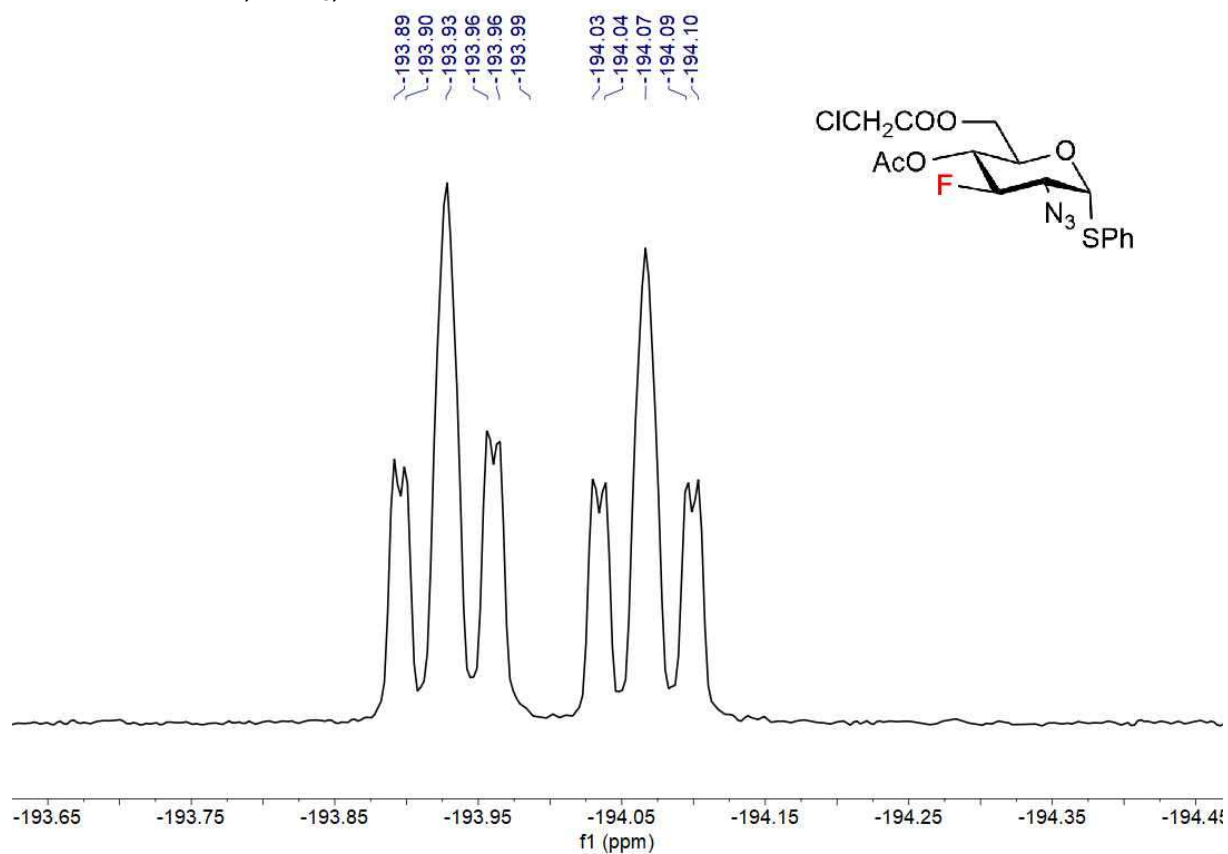
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -16**



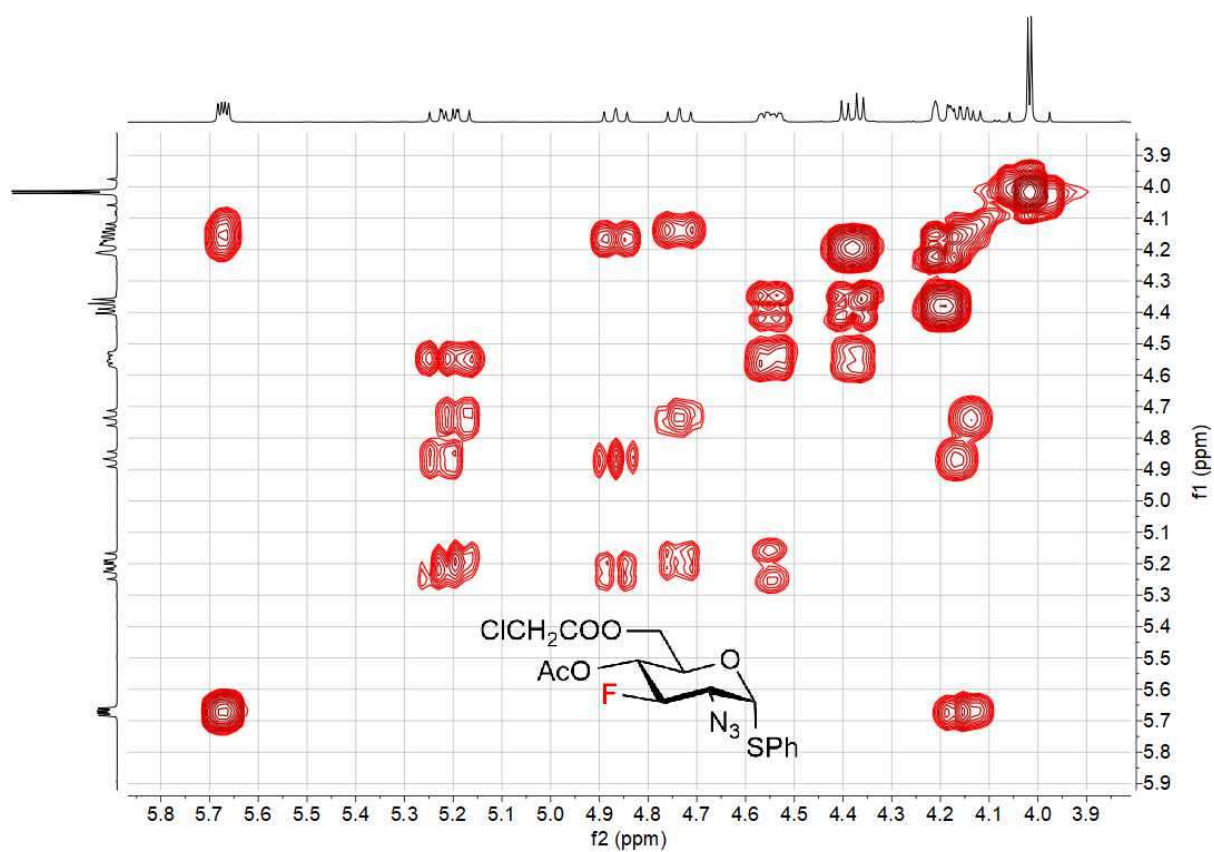
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -16**



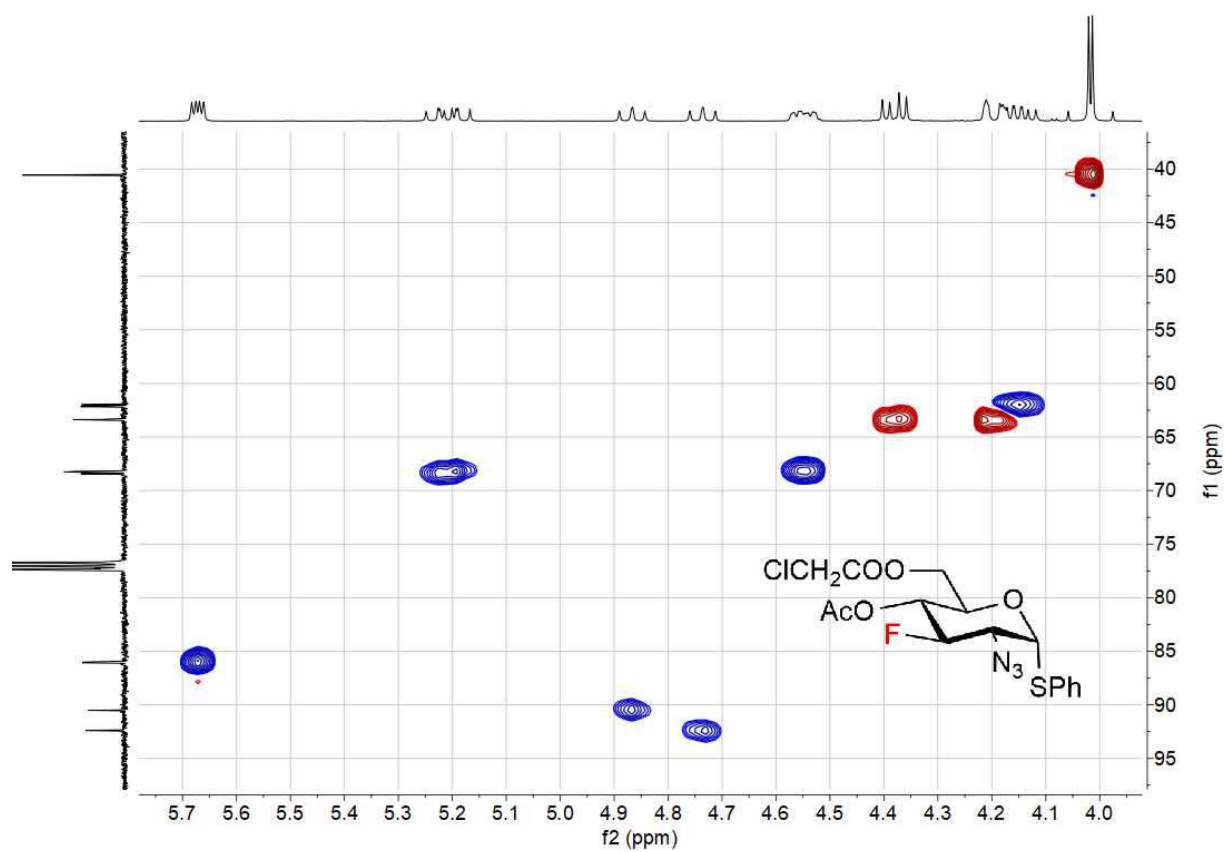
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -16**



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\alpha$ -16**

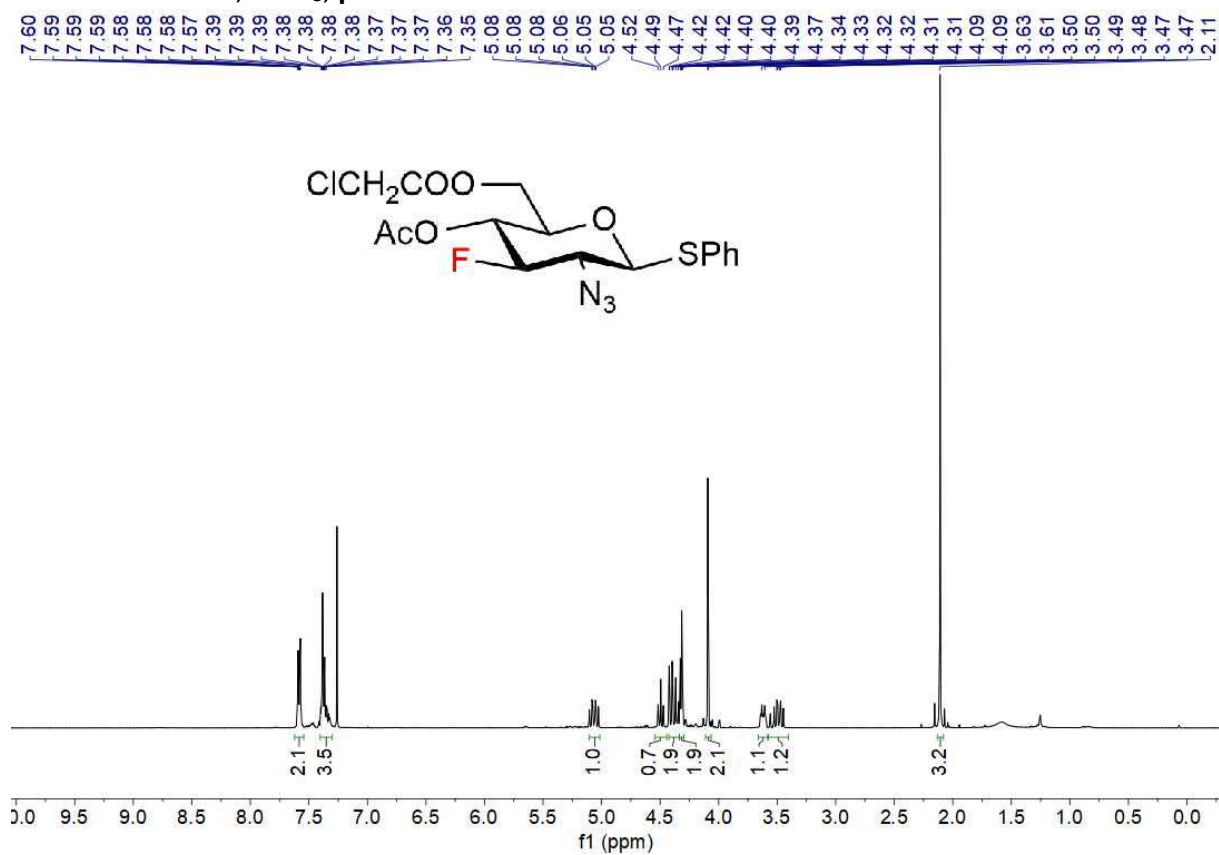


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  **$\alpha$ -16**

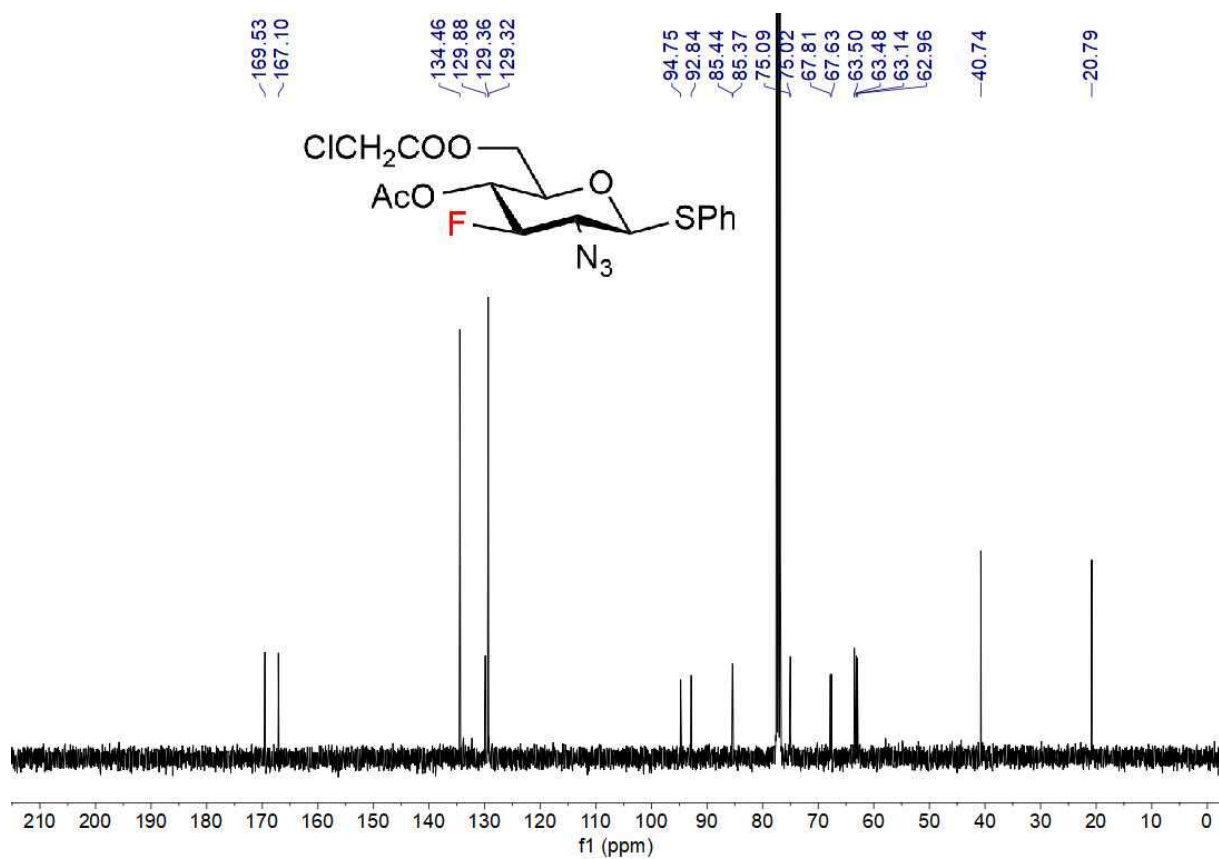


# **NMR $\beta$ -16**

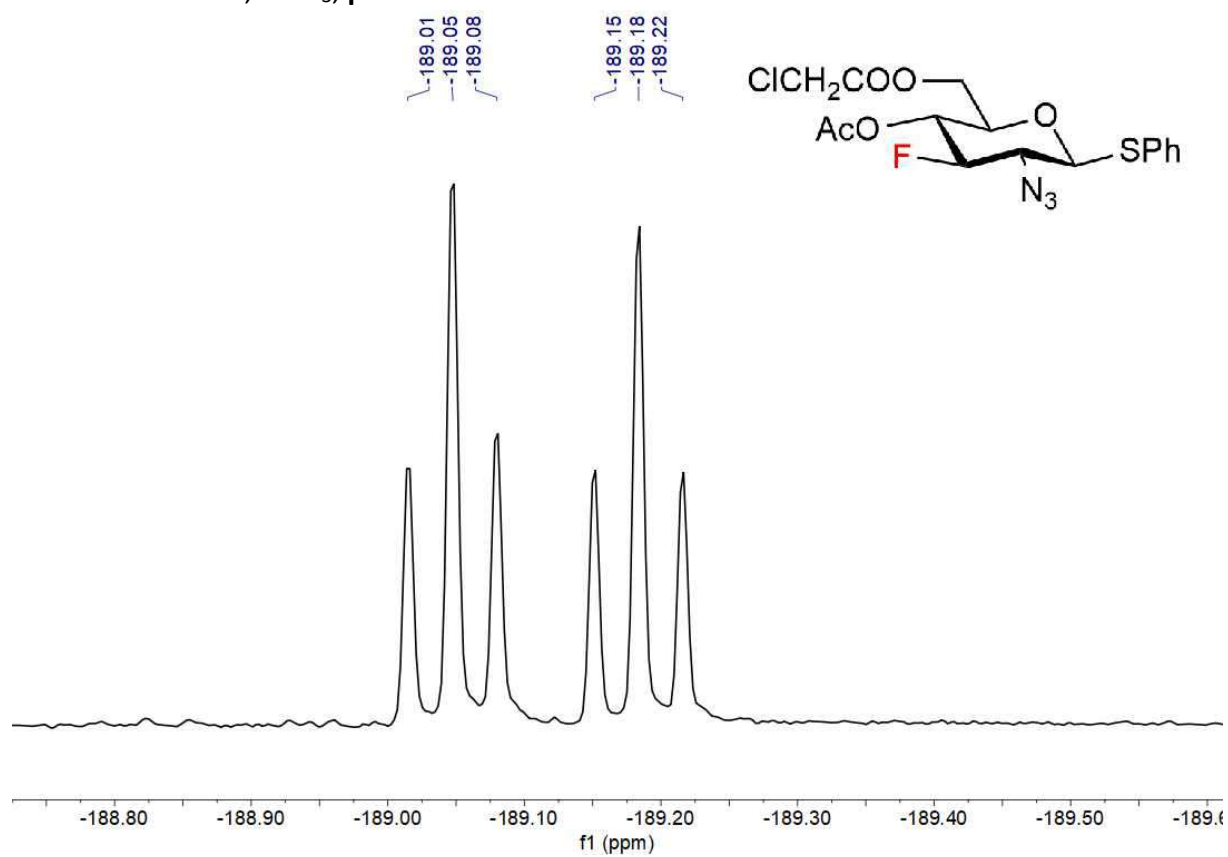
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -16**



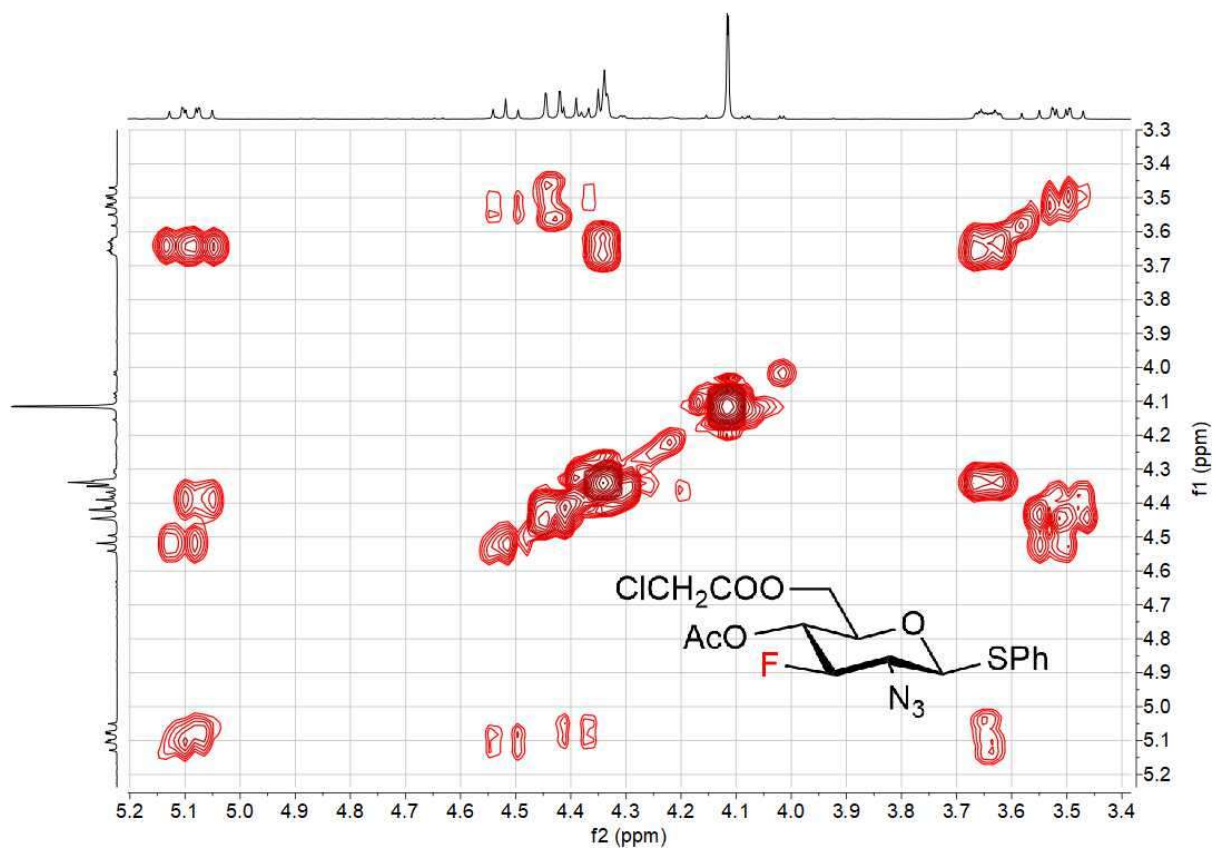
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  **$\beta$ -16**



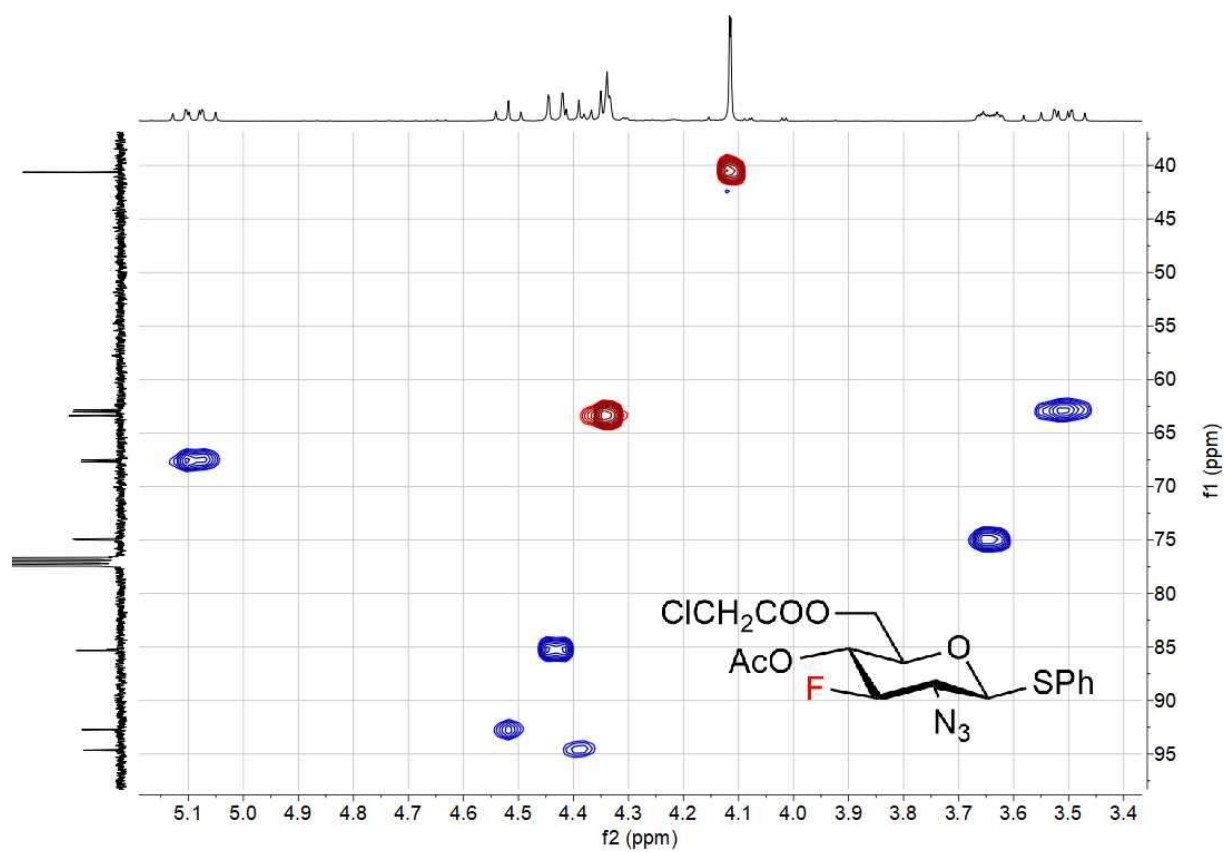
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -16**



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\beta$ -16**

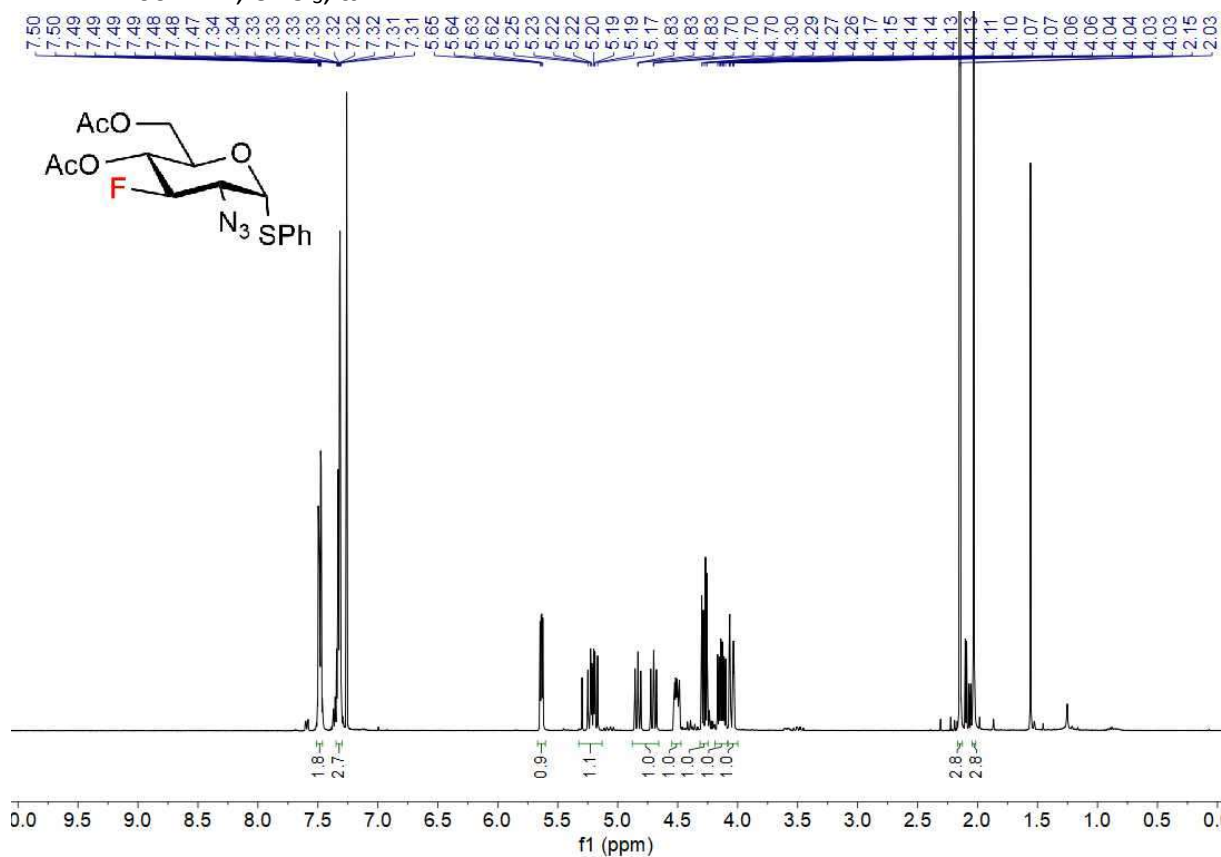


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  **$\beta$ -16**

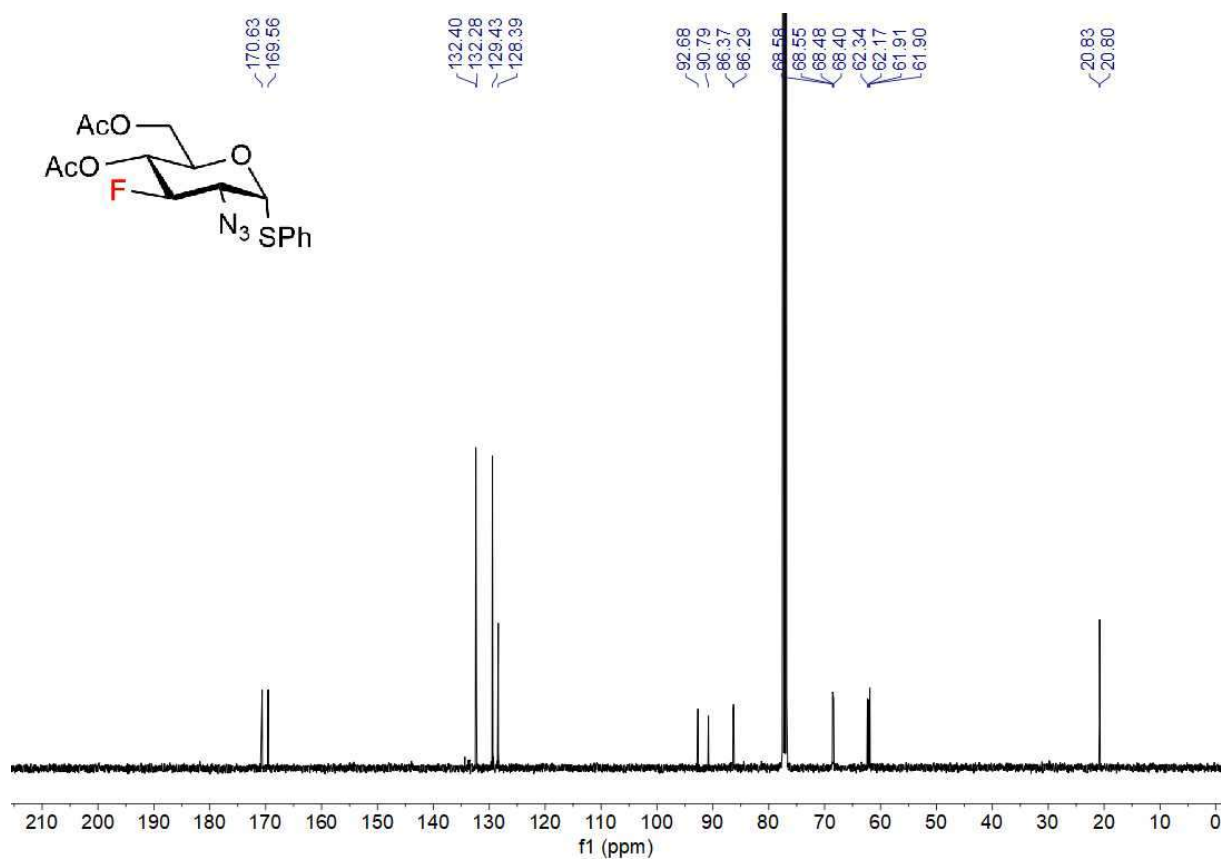


# **NMR $\alpha$ -17**

$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -17**

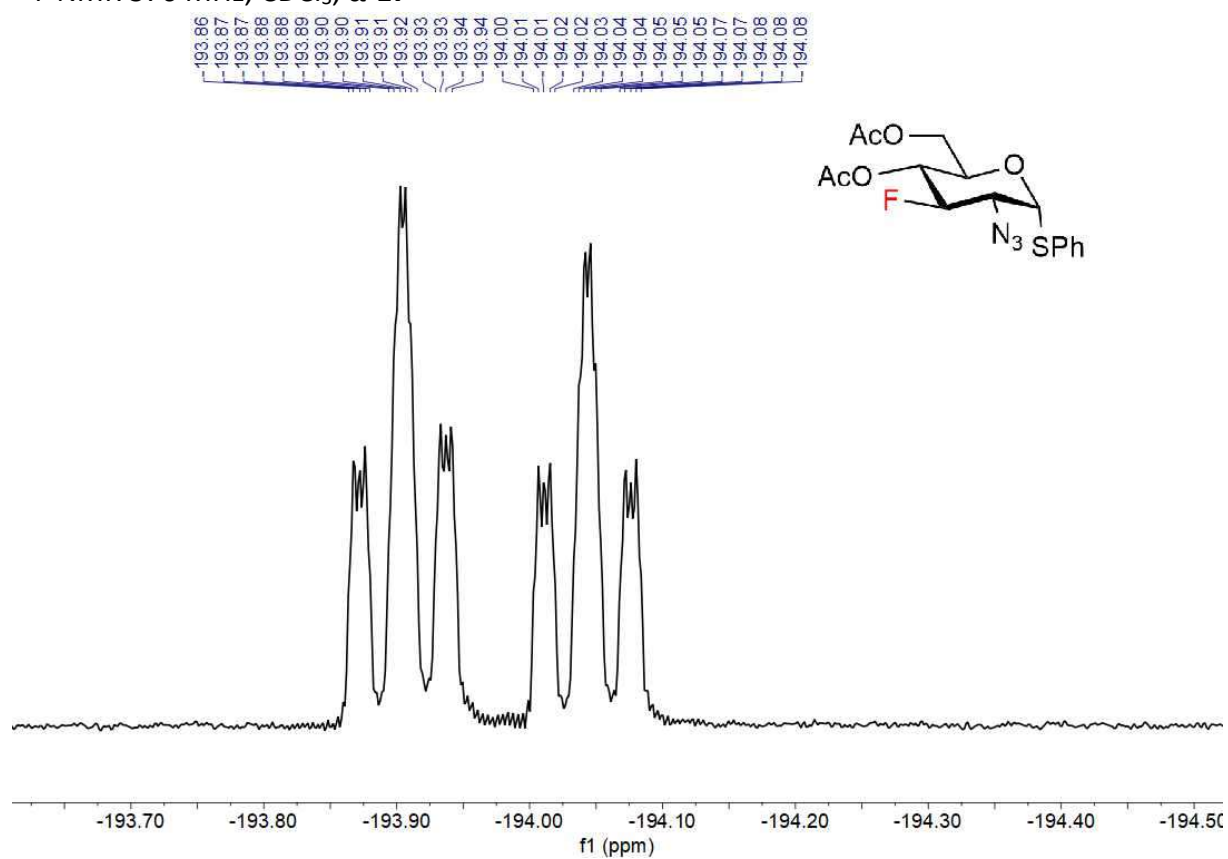


$^{13}\text{C}$  { $^1\text{H}$ } NMR 100MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -17**

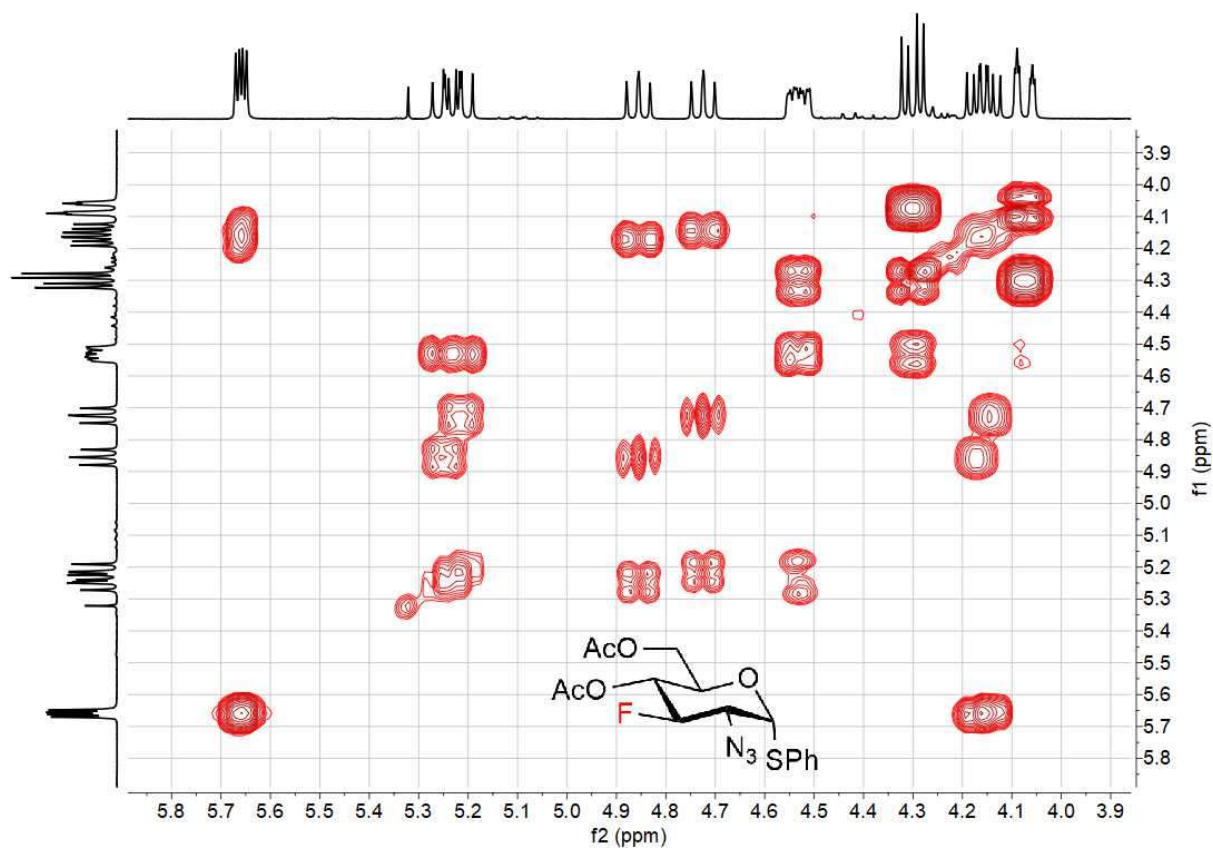




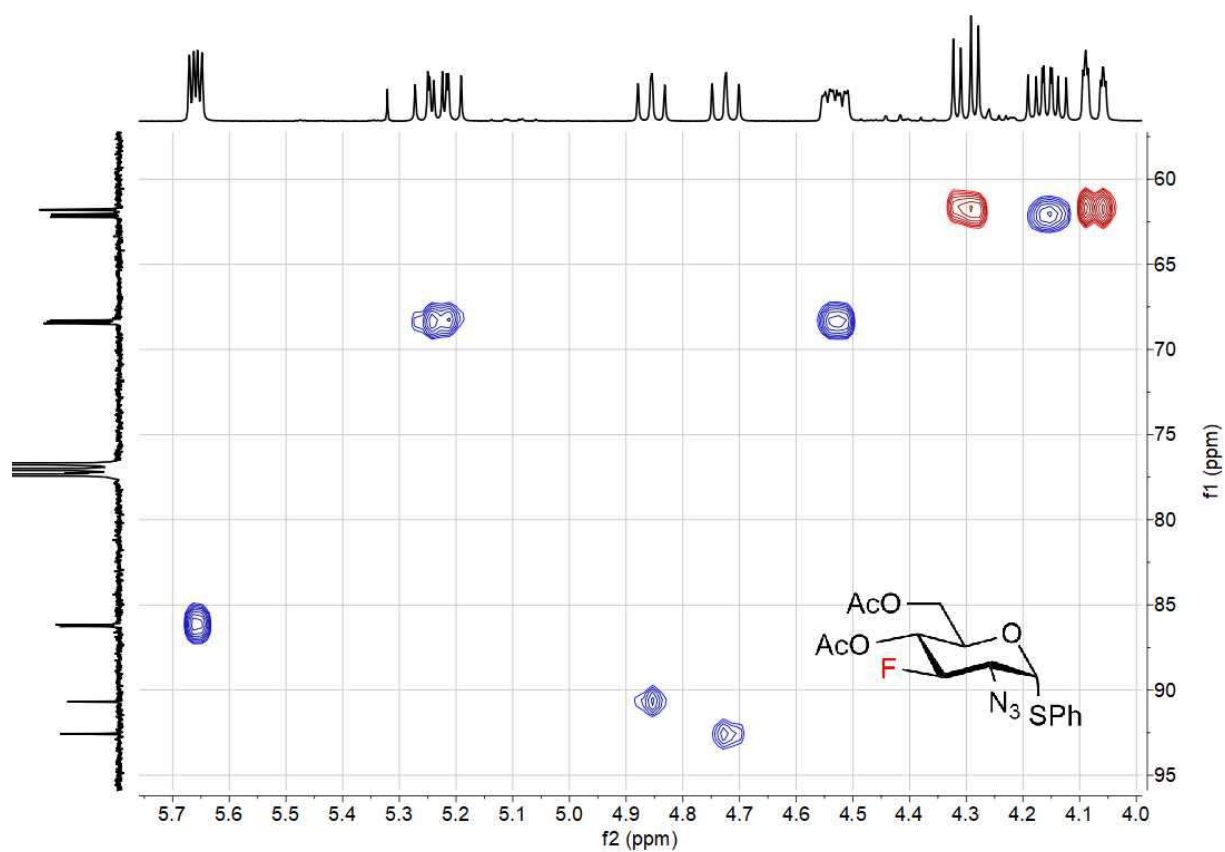
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  $\alpha$ -17



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  $\alpha$ -17

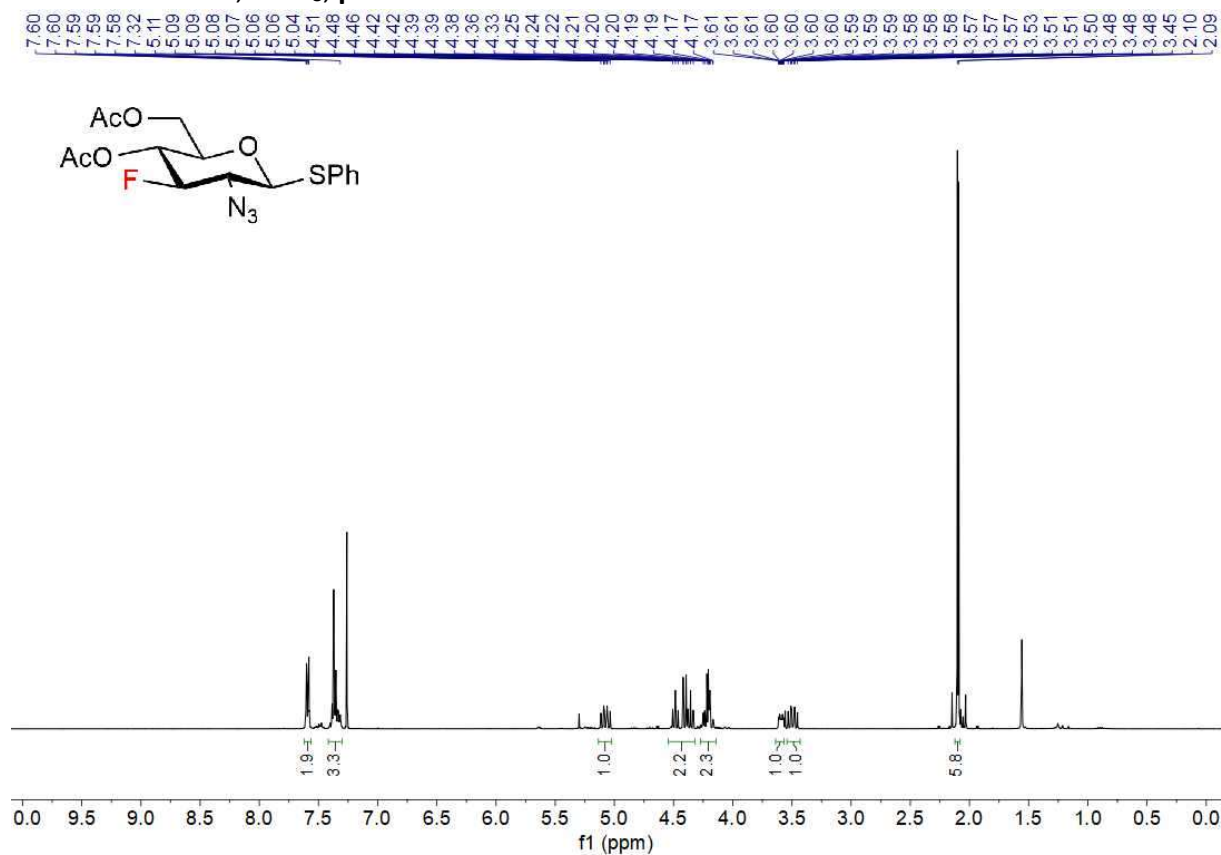


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\alpha$ -17

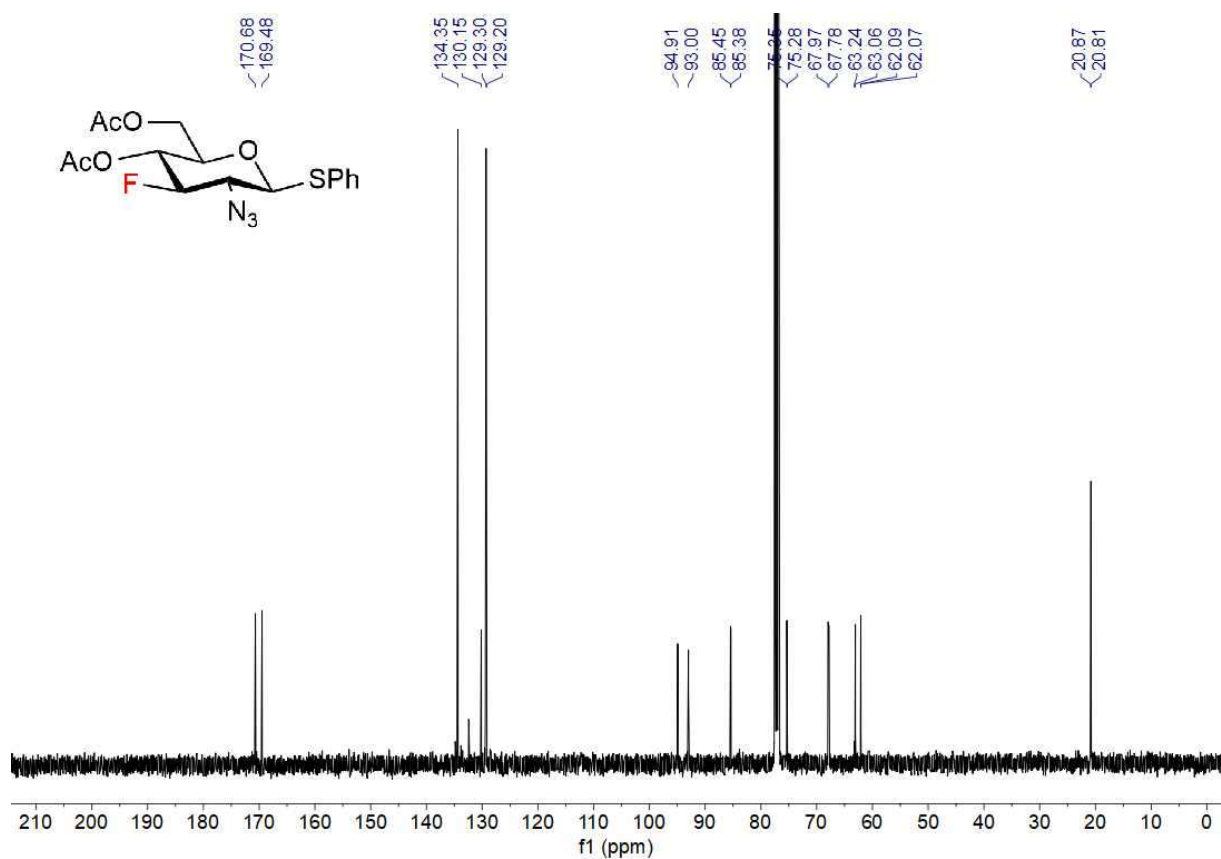


# NMR $\beta$ -17

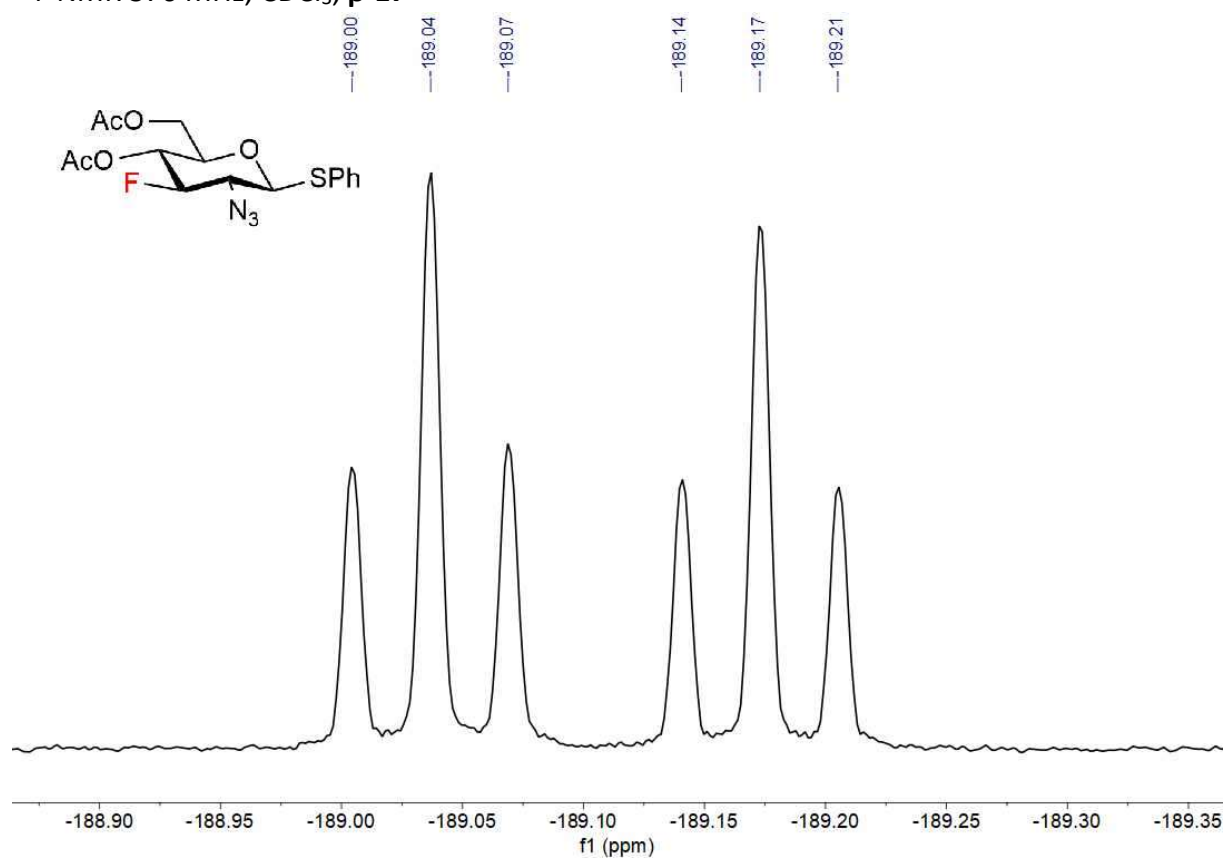
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  $\beta$ -17



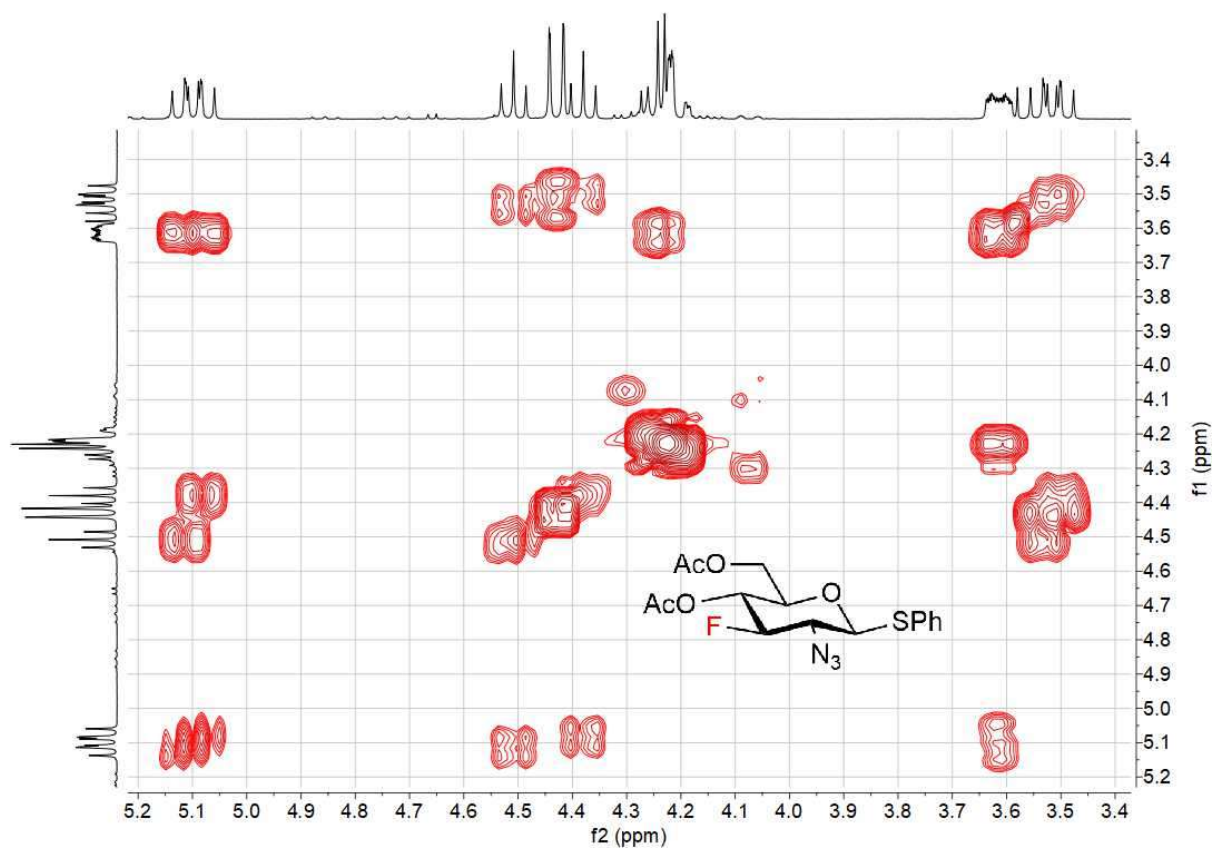
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  $\beta$ -17



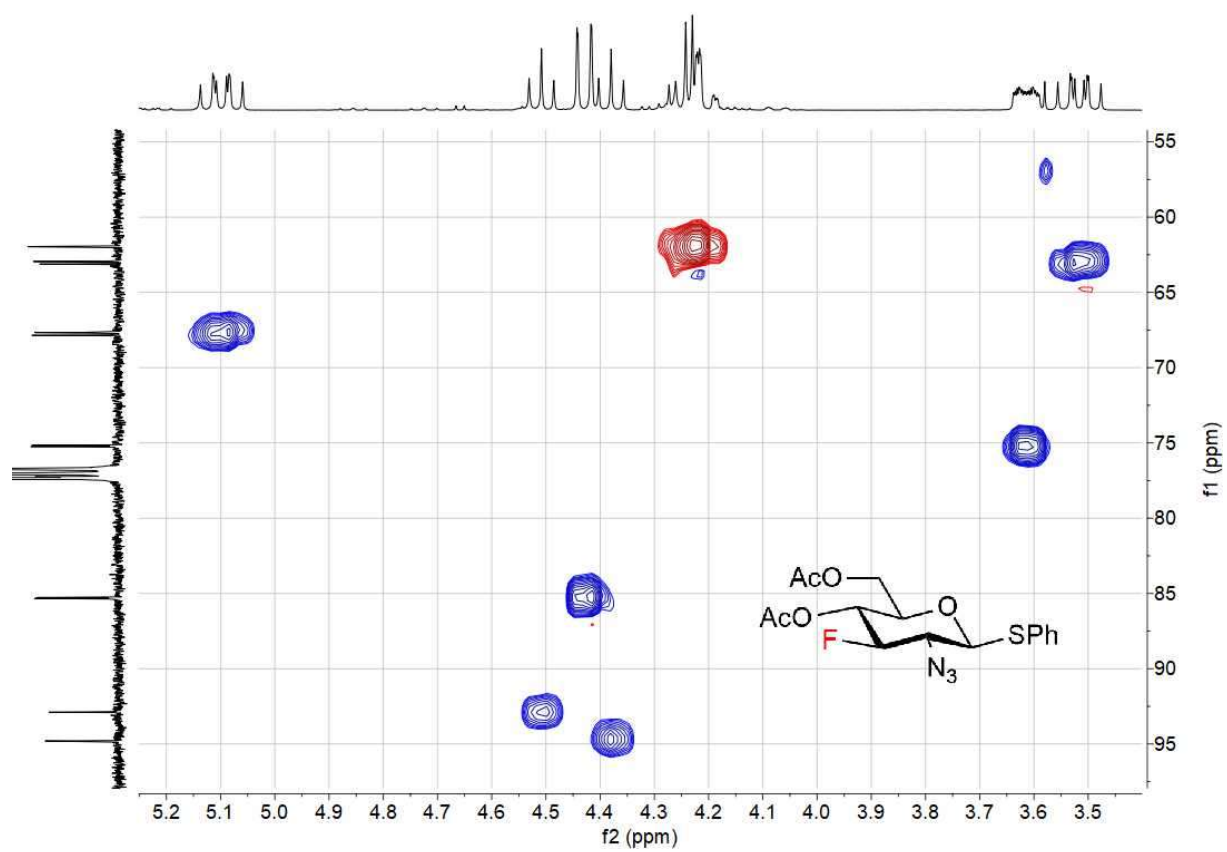
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -17**



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\beta$ -17**

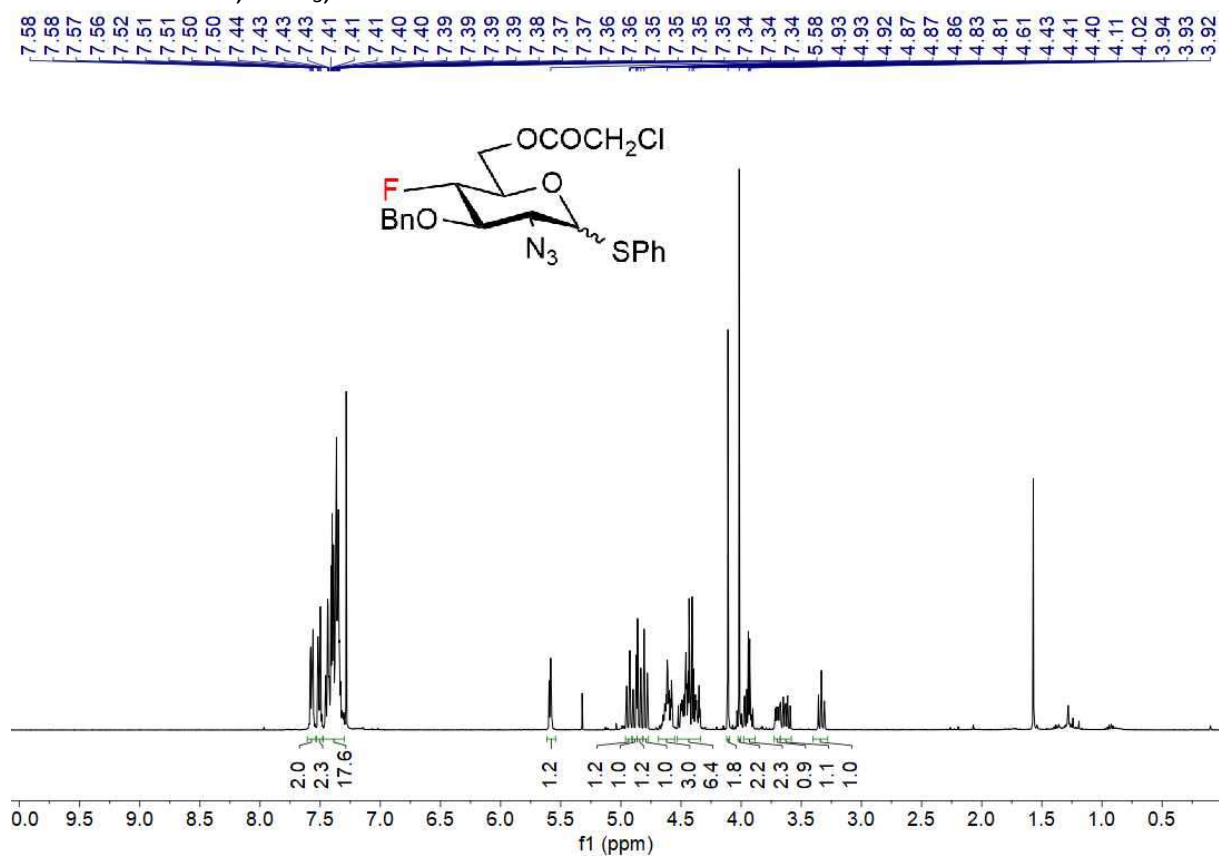


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\beta$ -17

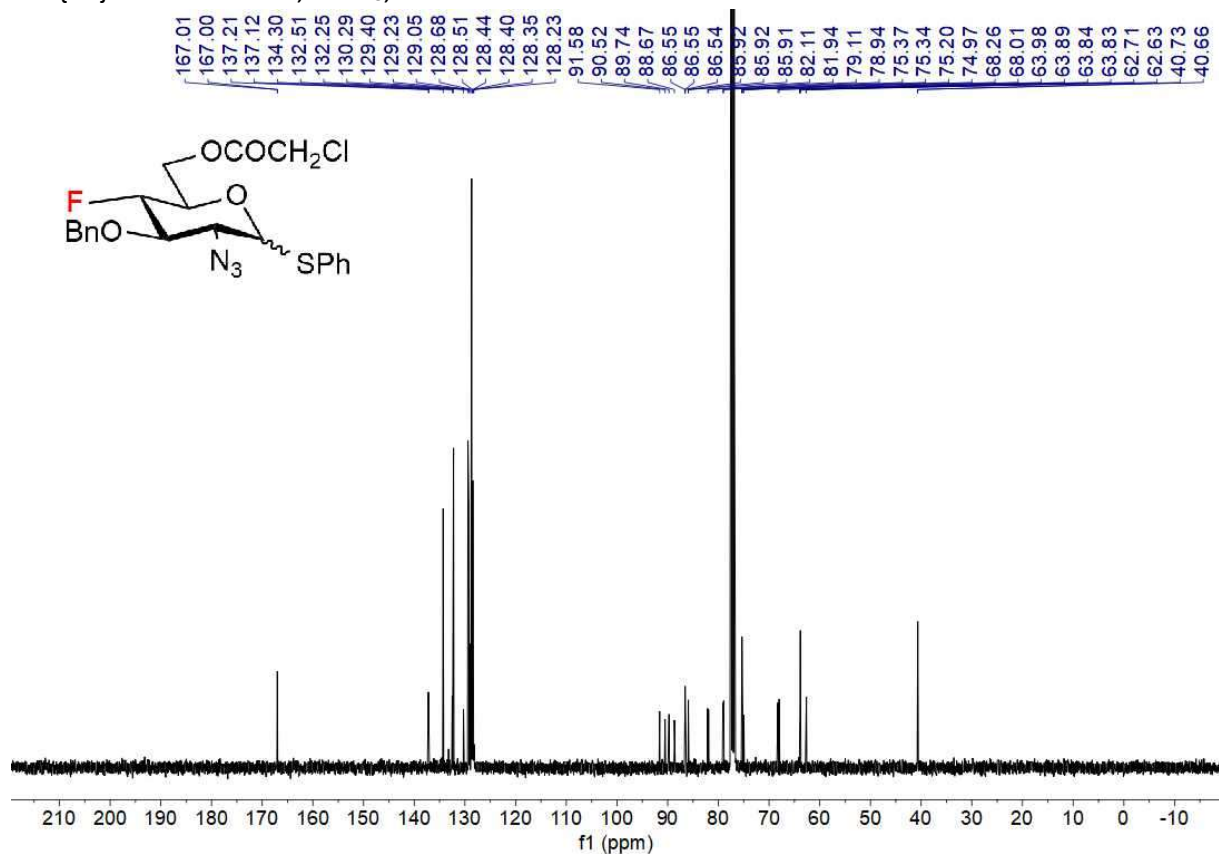


# **NMR 20**

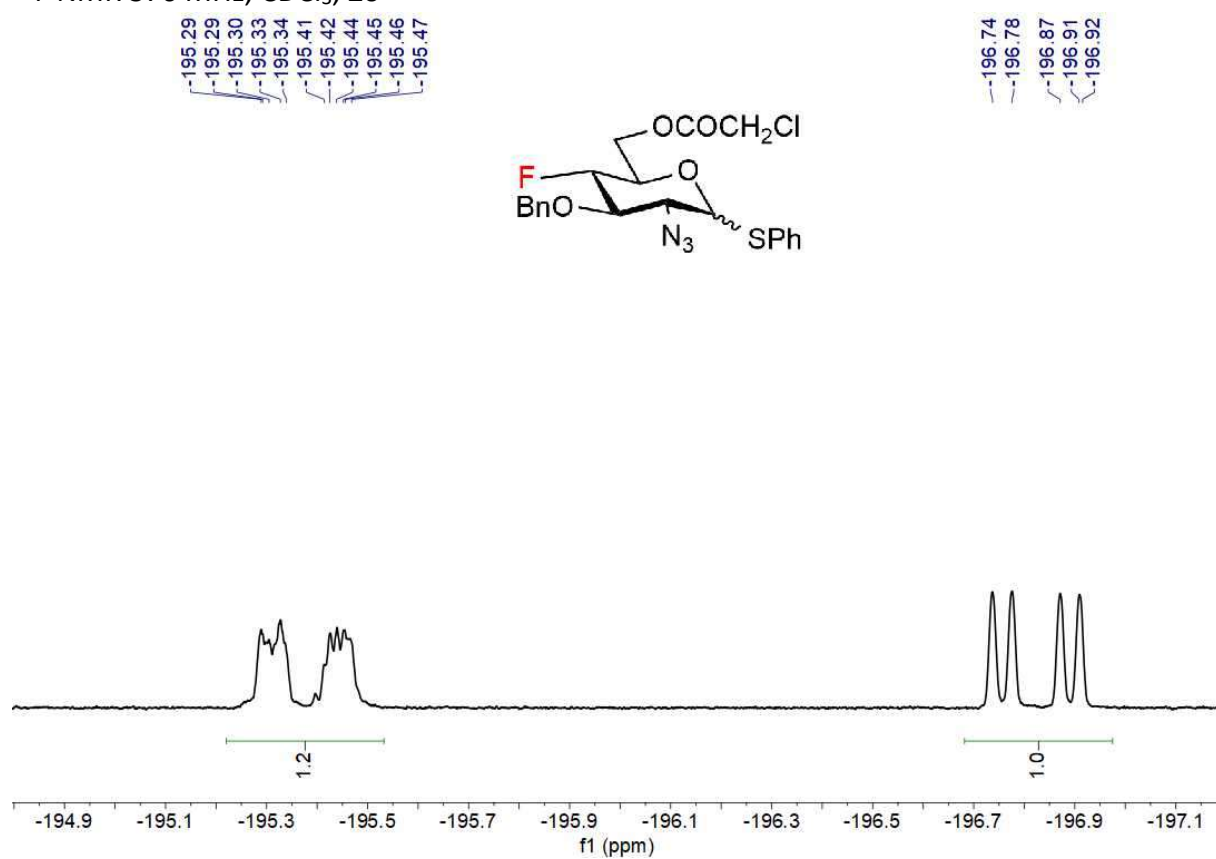
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **20**



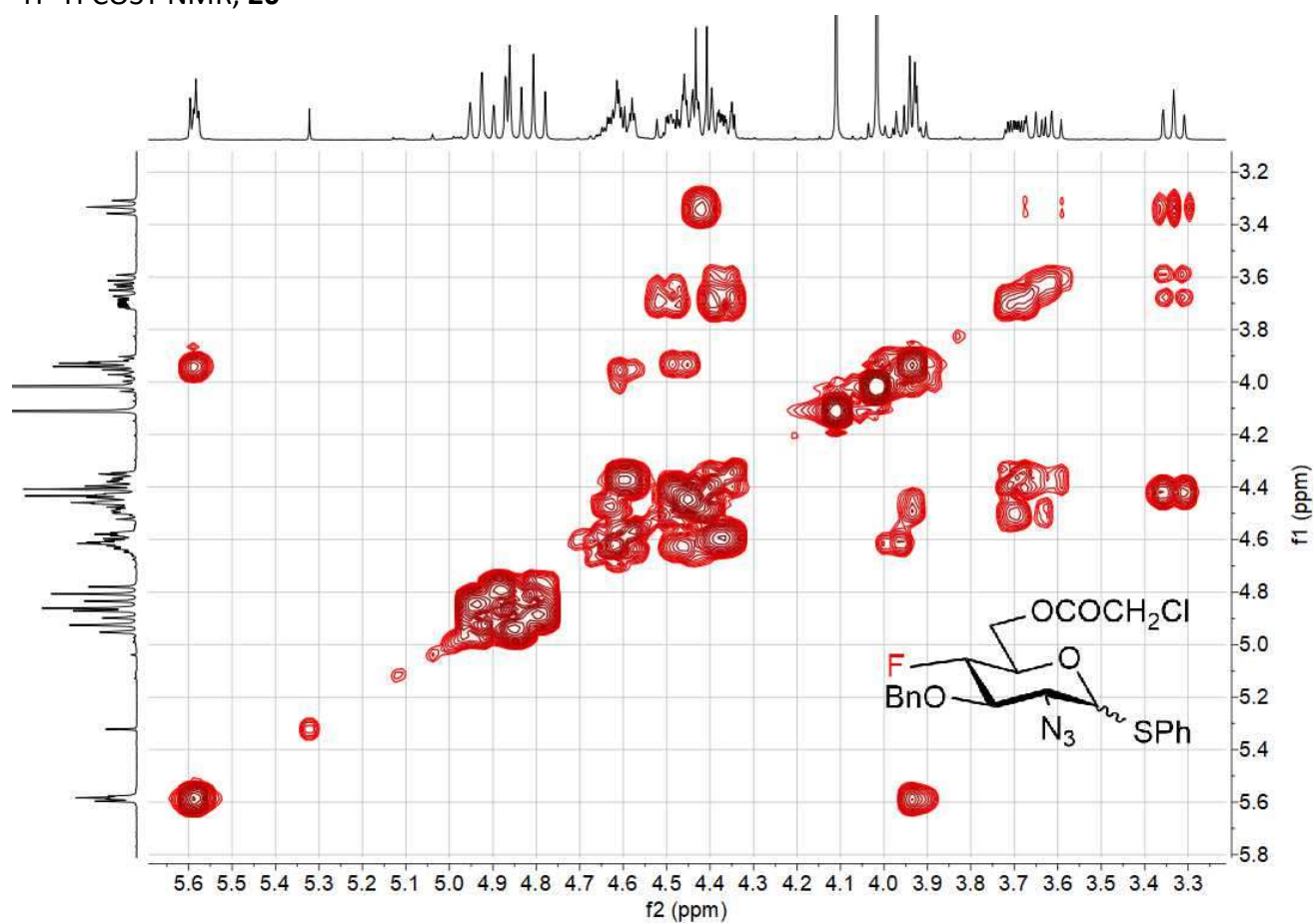
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **20**



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **20**

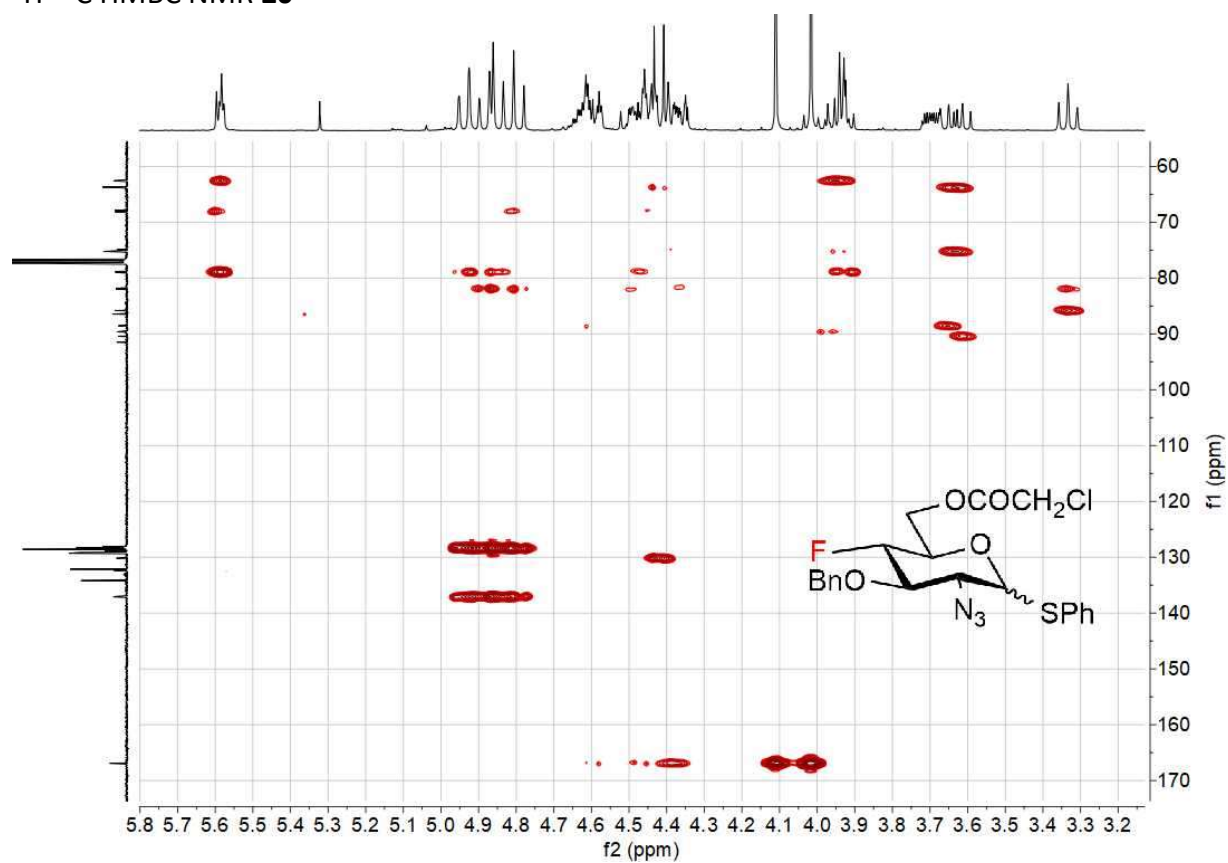


$^1\text{H}$ - $^1\text{H}$  COSY NMR, **20**

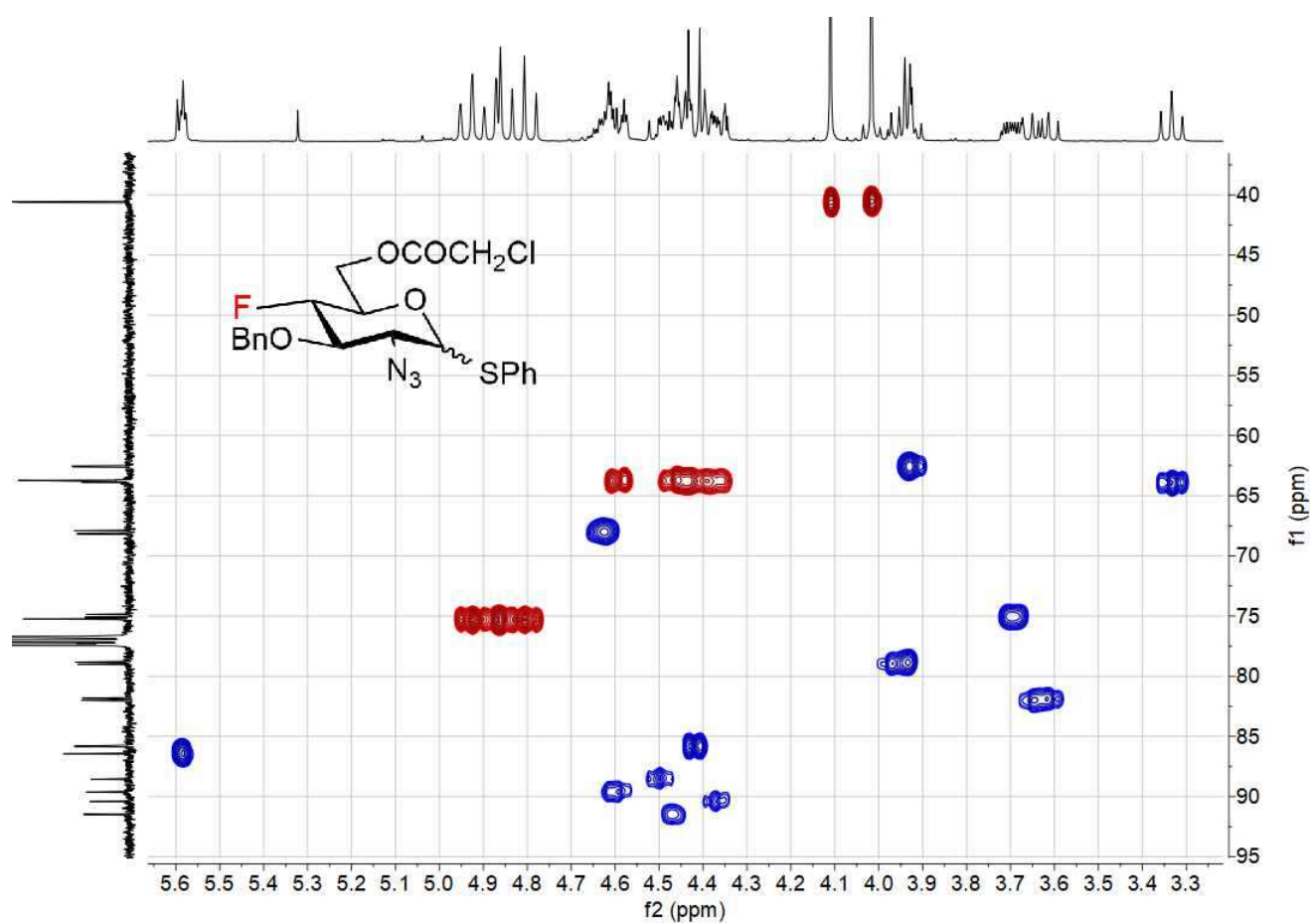




$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 20



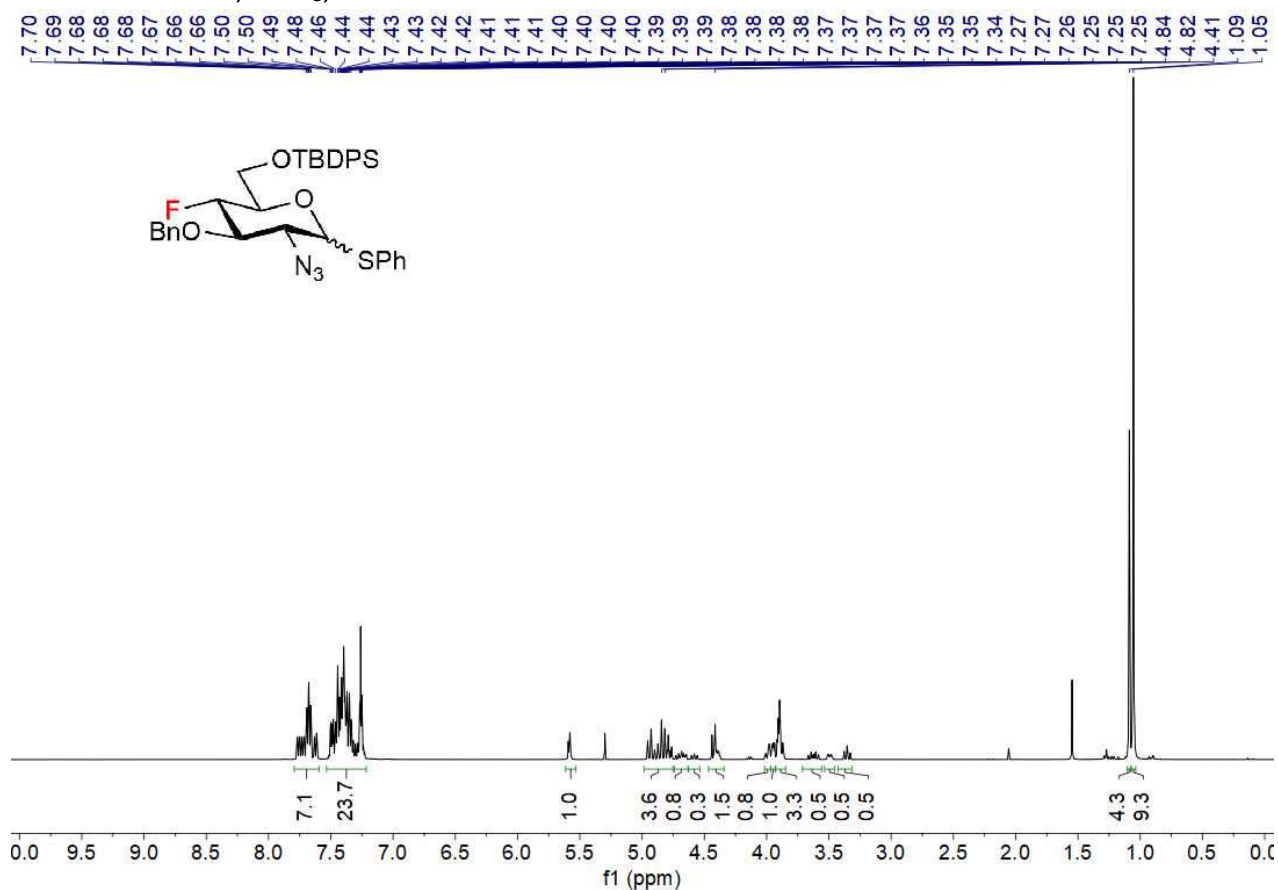
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 20



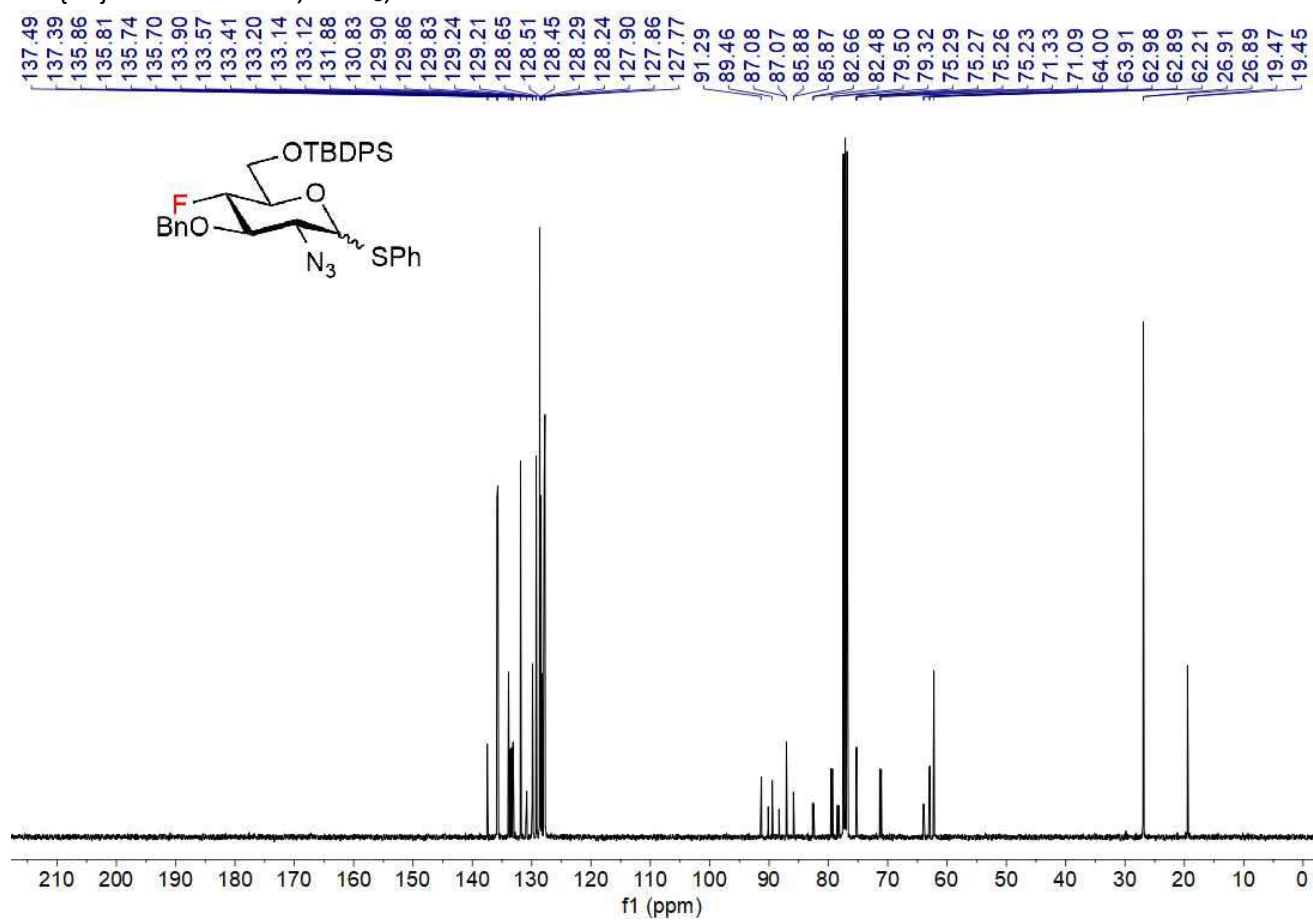


# **NMR 21**

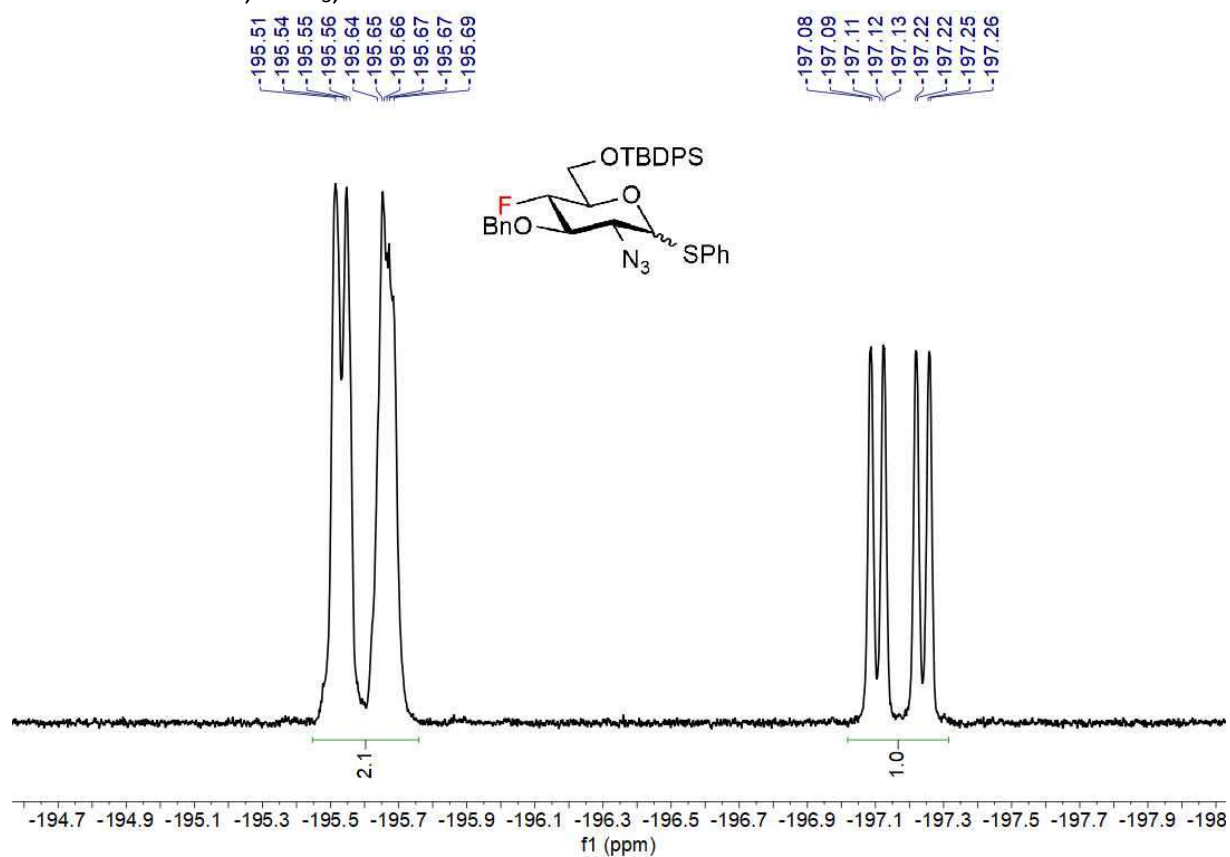
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **21**



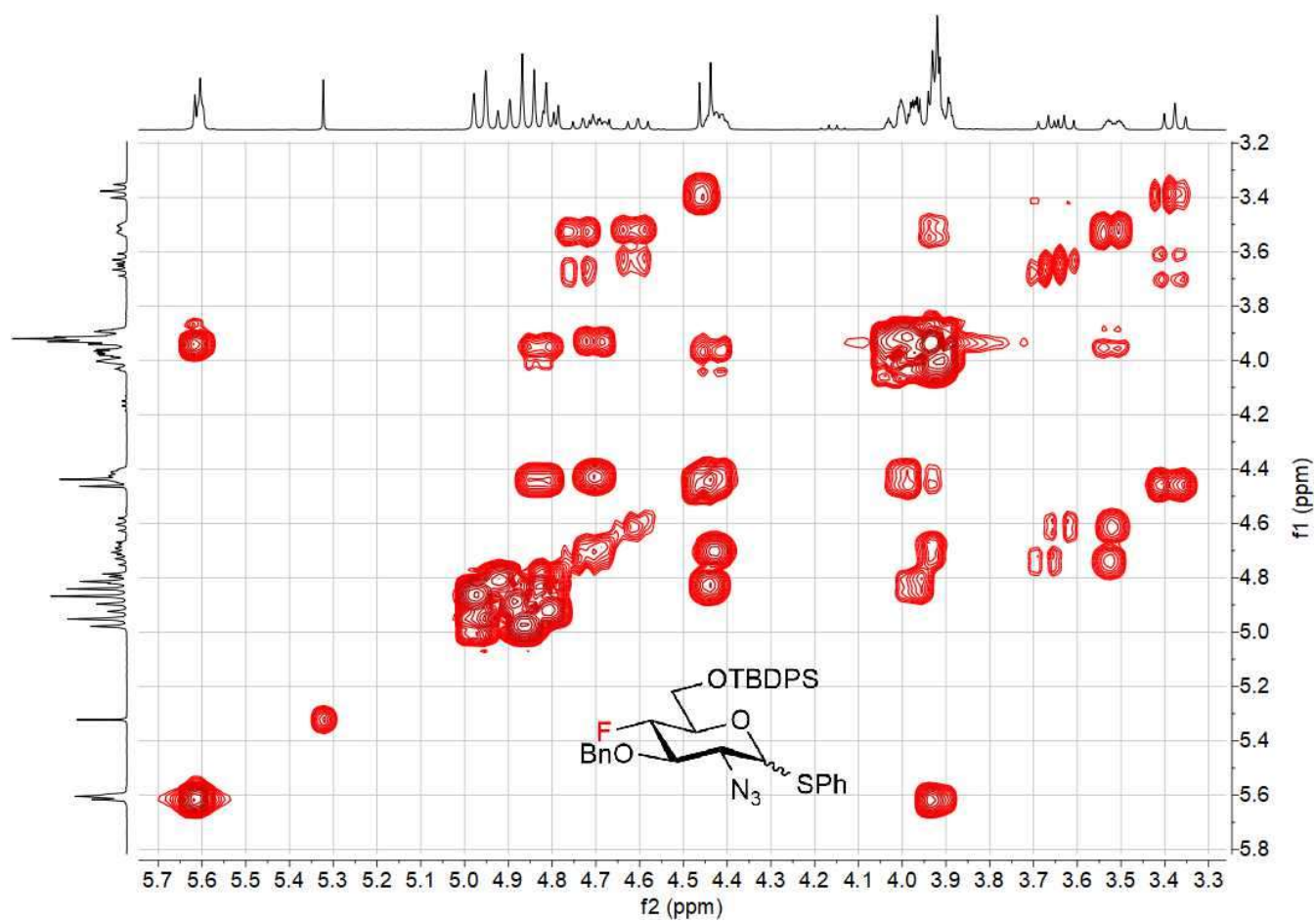
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **21**



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **21**



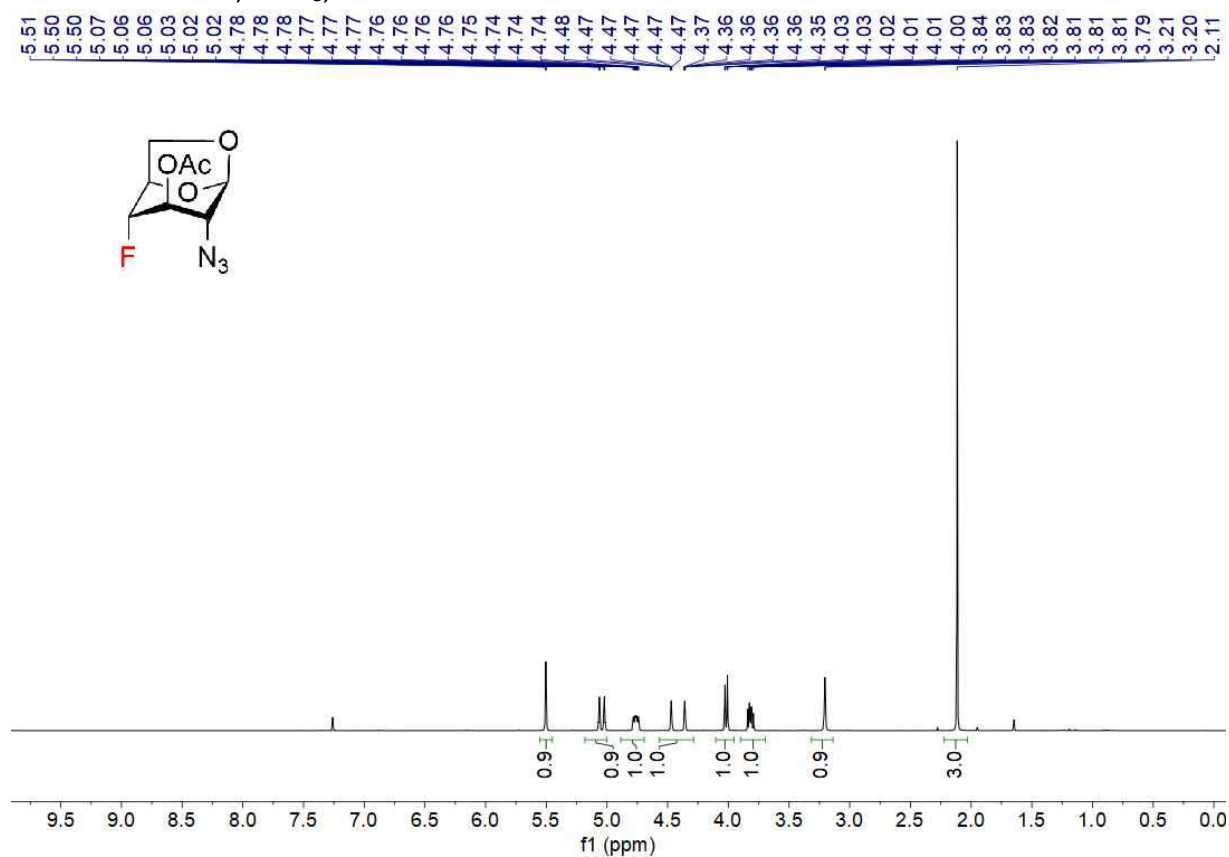
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **21**



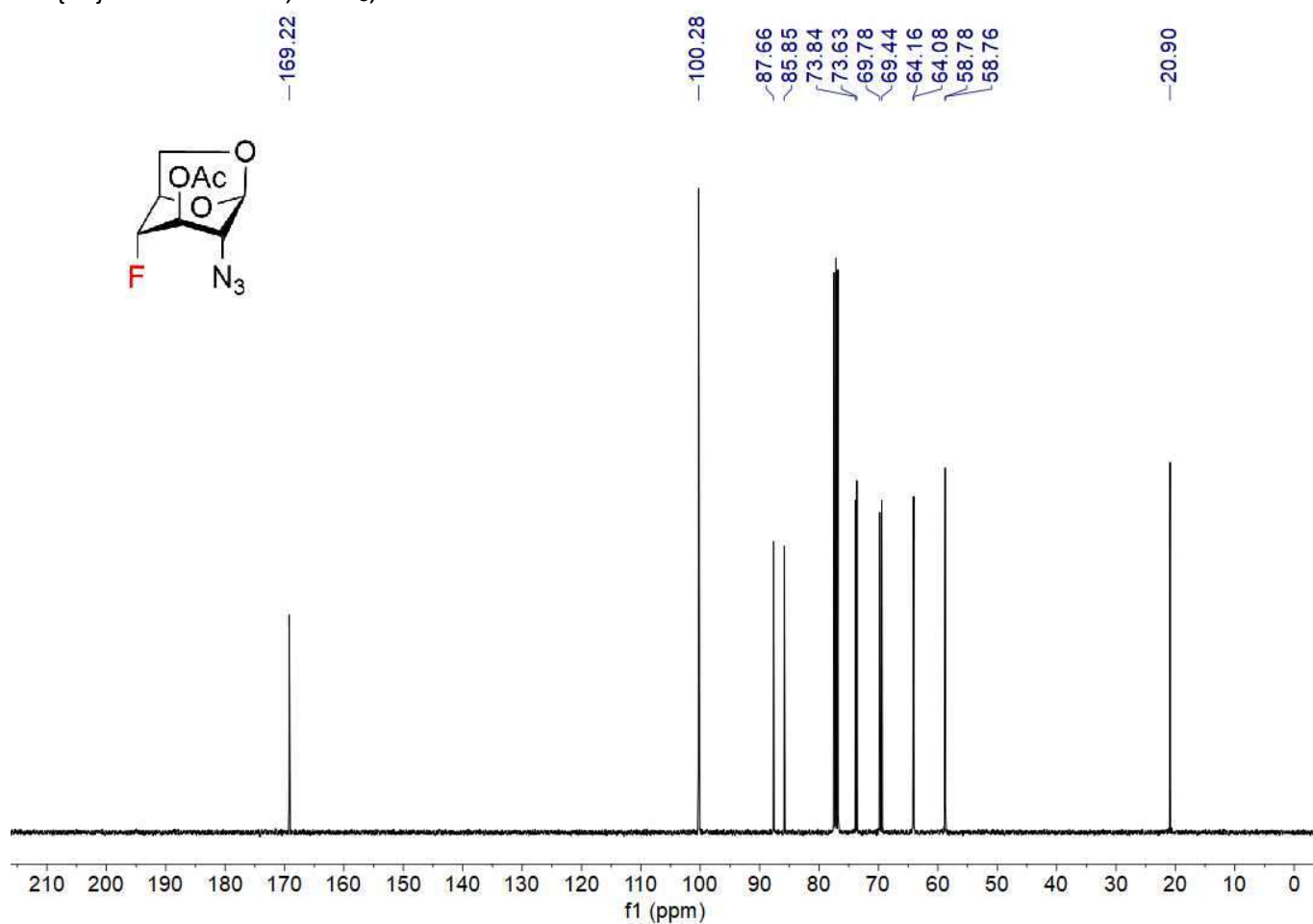


# **NMR 23**

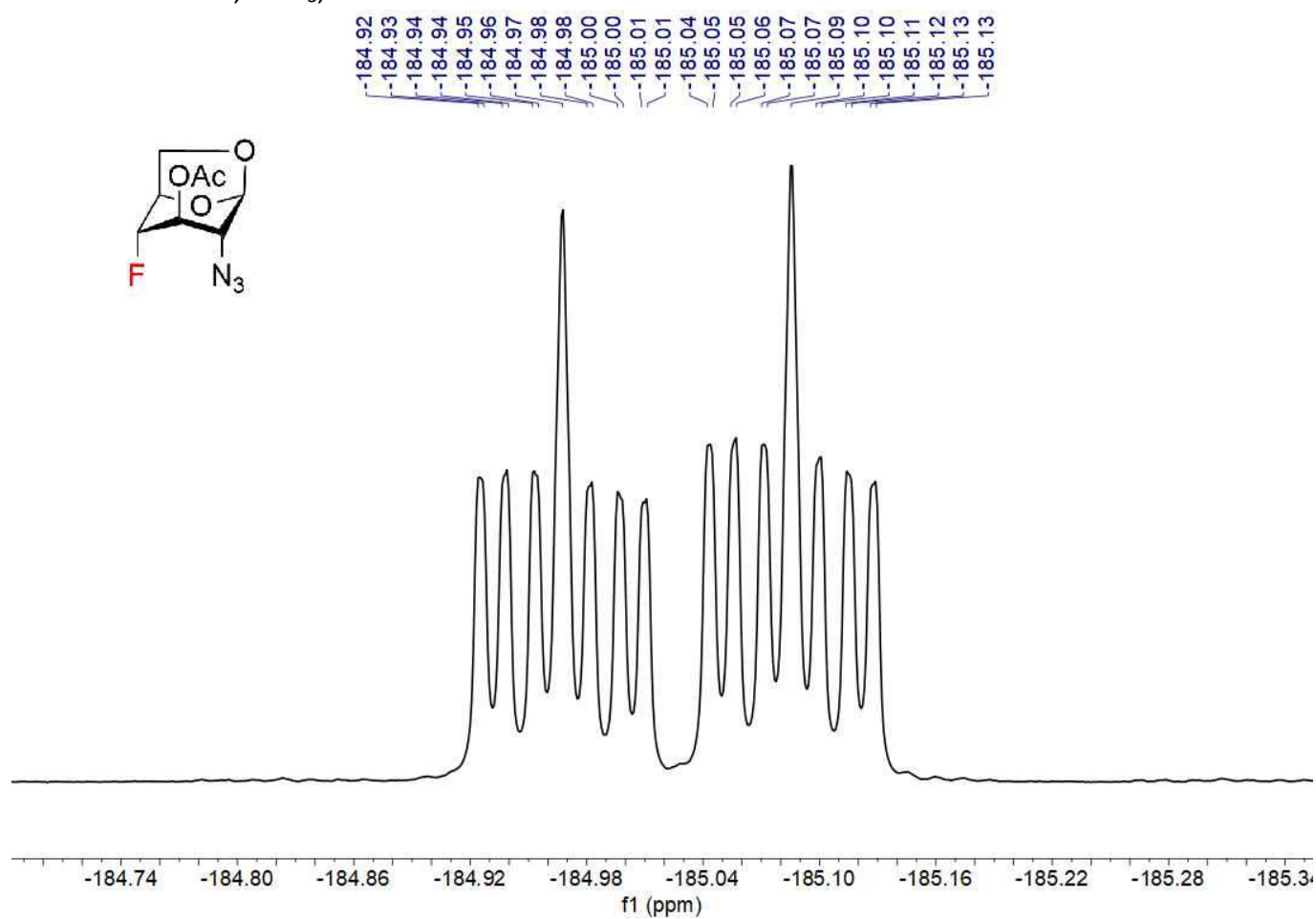
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **23**



<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **23**

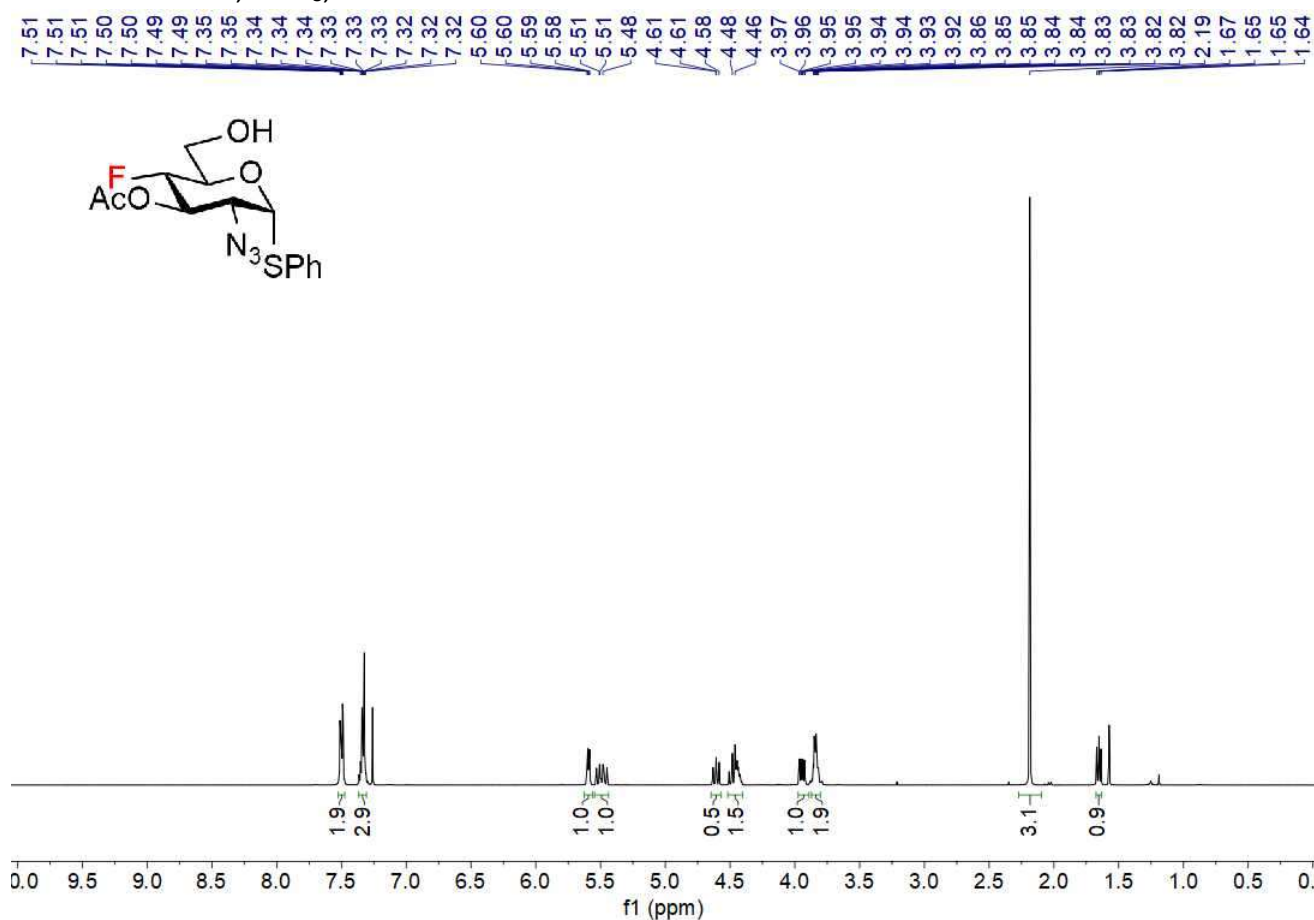


$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **23**

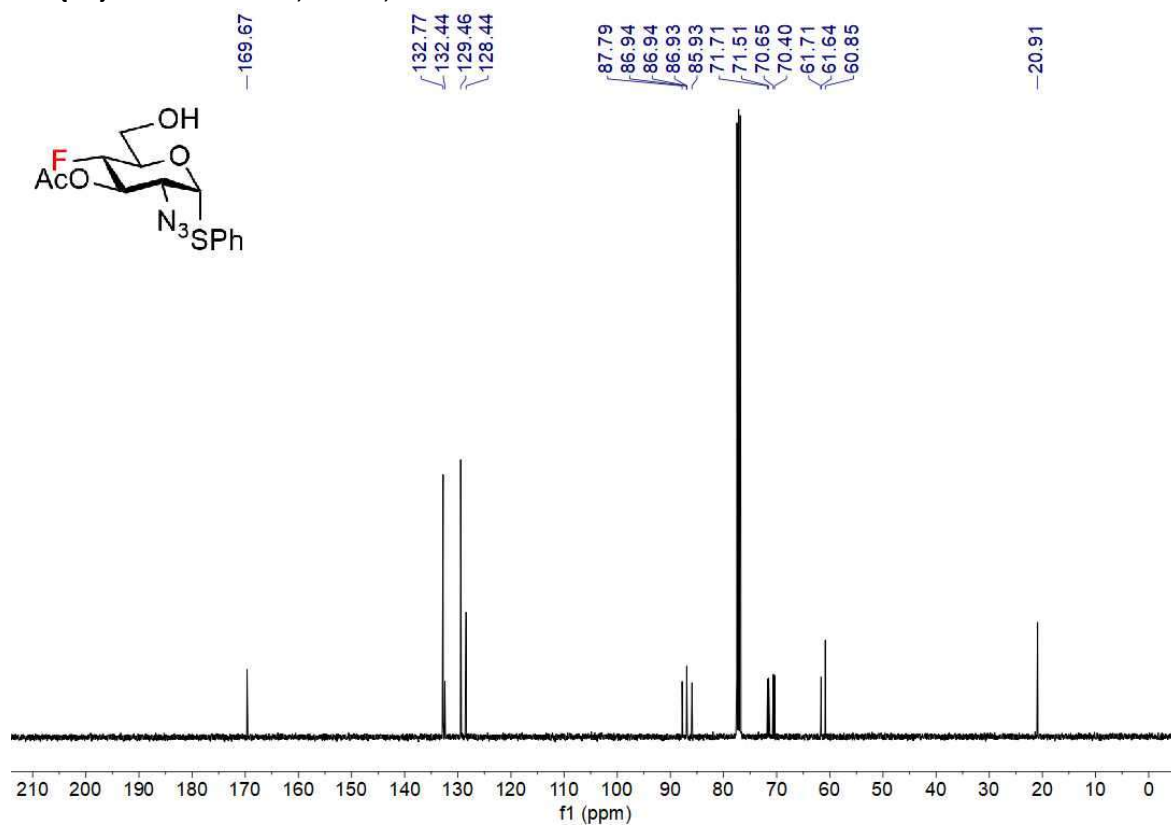


# **NMR $\alpha$ -24**

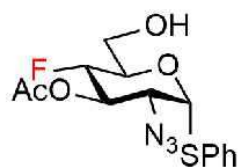
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -24**



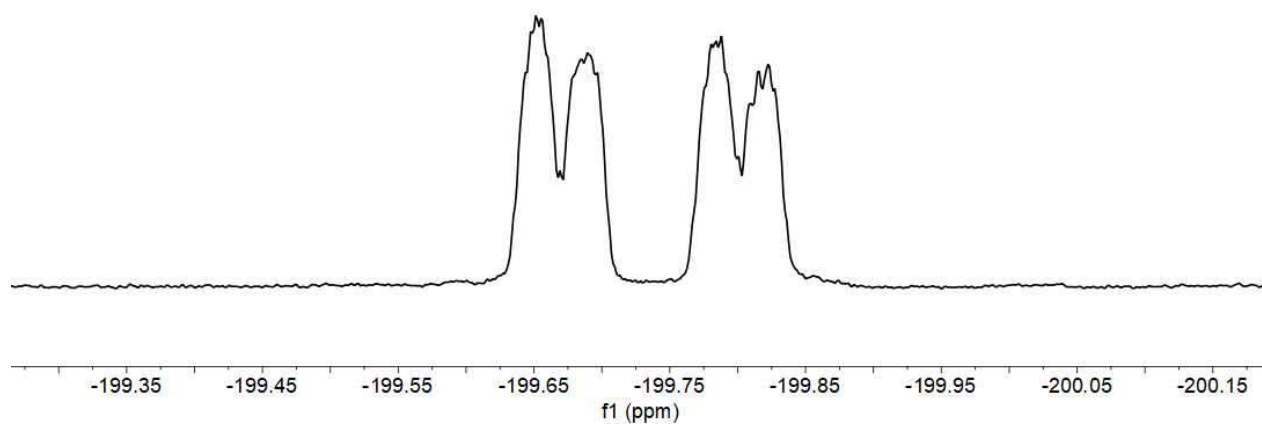
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -24**



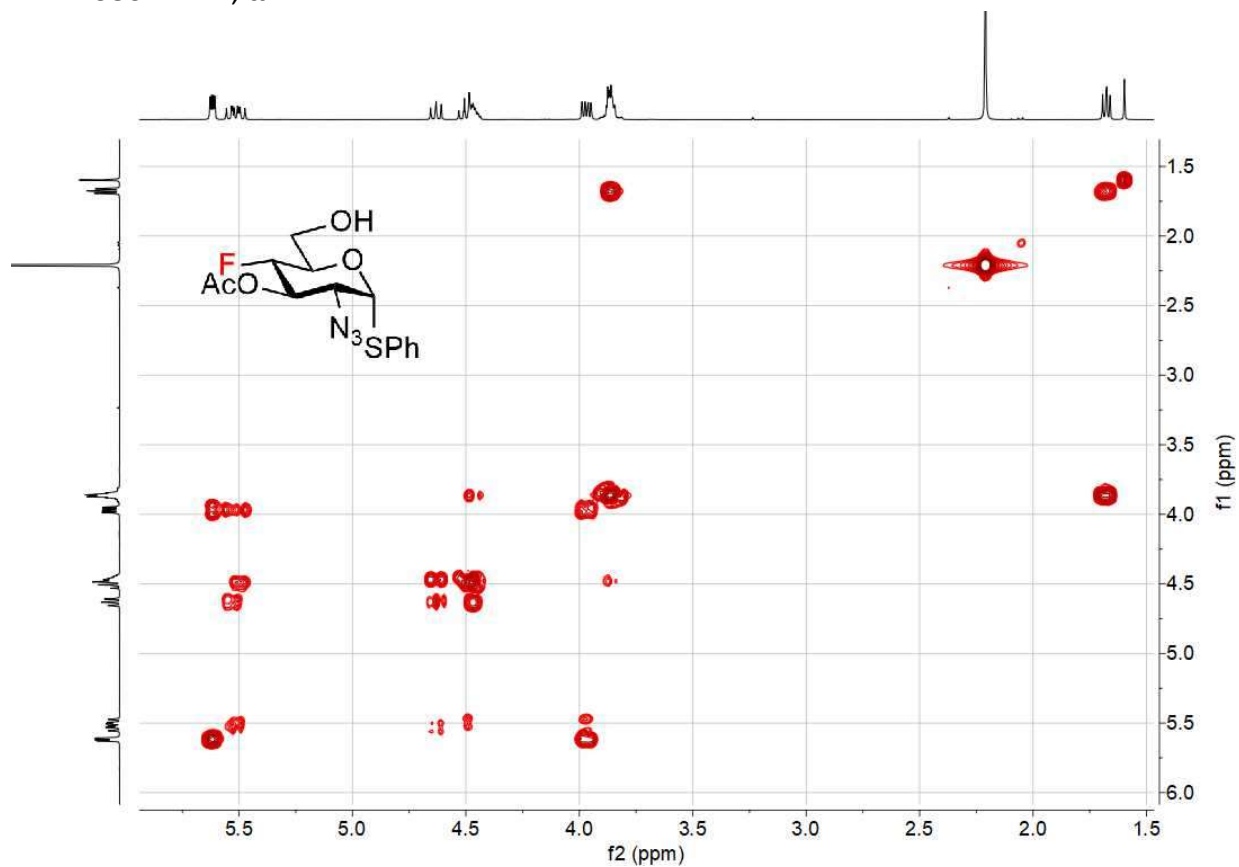
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\alpha$ -24**



-199.64  
-199.65  
-199.65  
-199.66  
-199.68  
-199.69  
-199.70  
-199.77  
-199.78  
-199.79  
-199.79  
-199.81  
-199.81  
-199.82  
-199.83

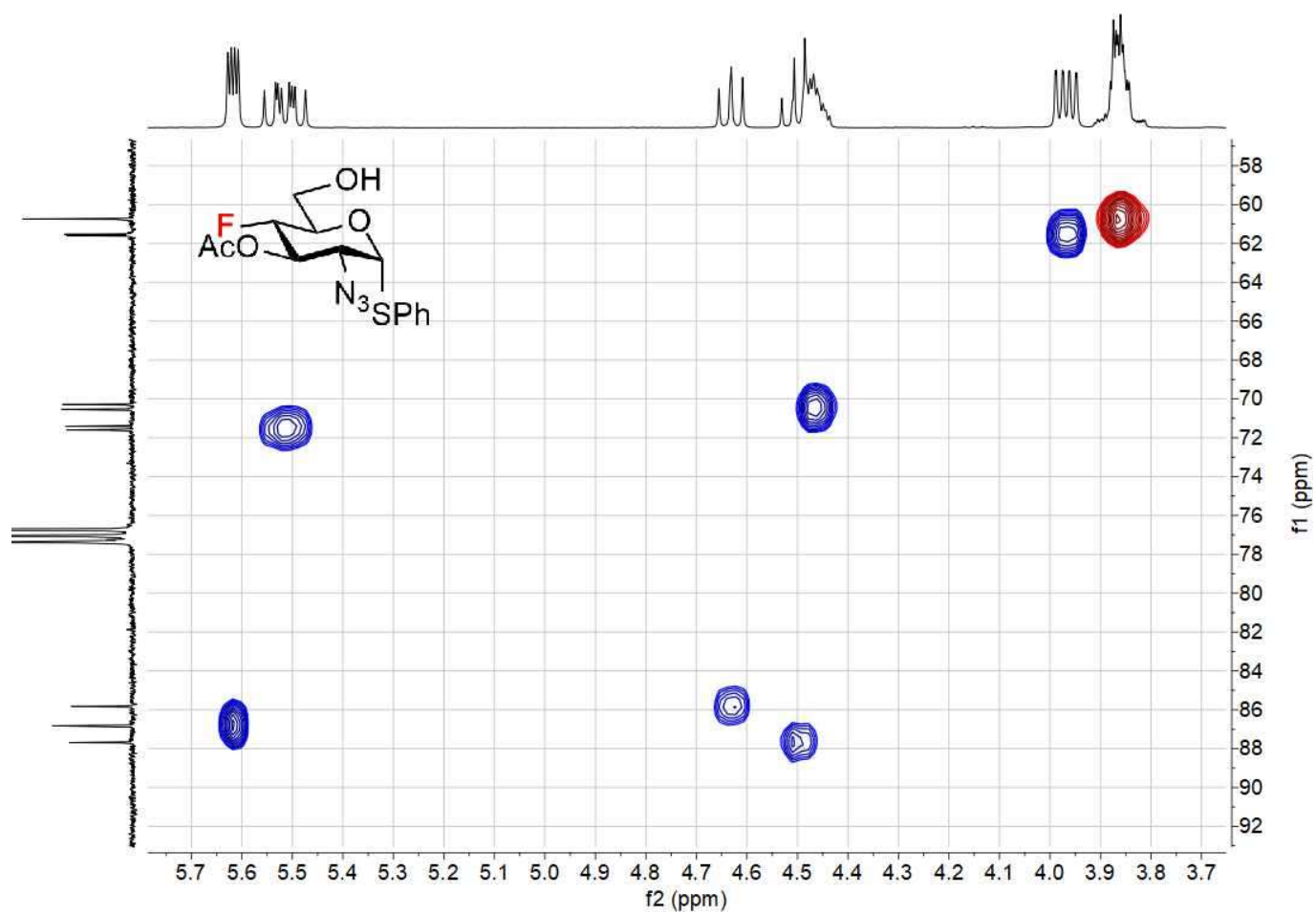


$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\alpha$ -24**



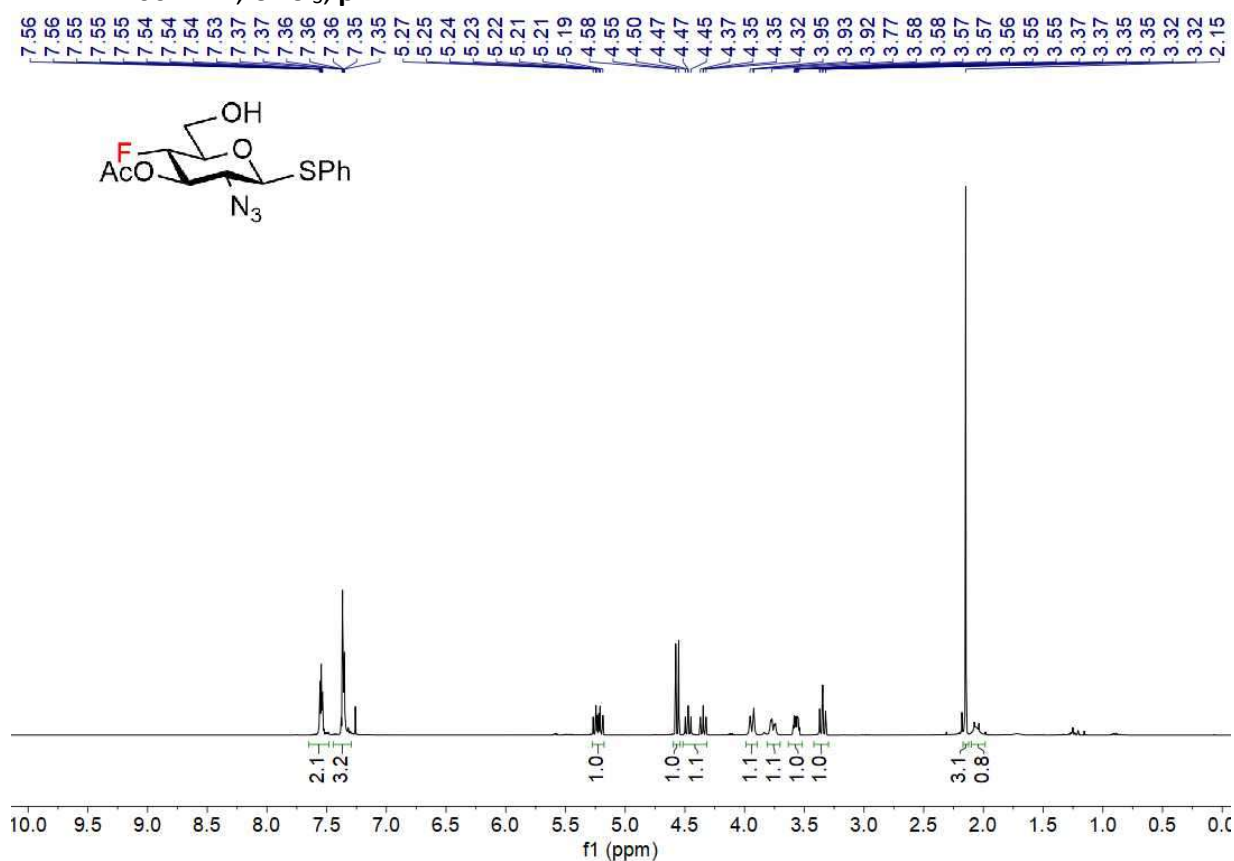


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  $\alpha$ -24

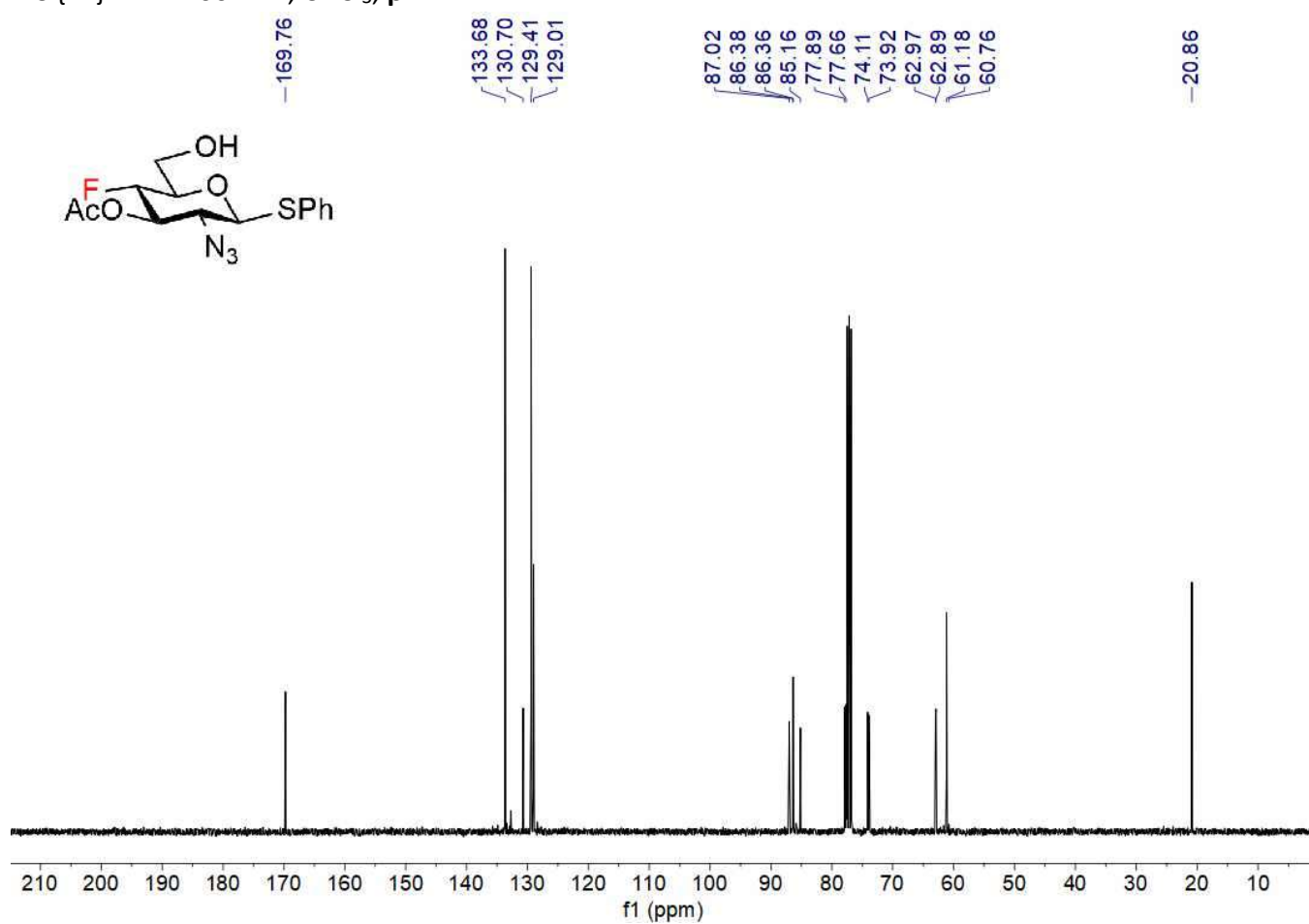


# NMR $\beta$ -24

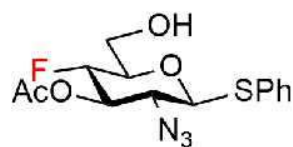
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ ,  $\beta$ -24



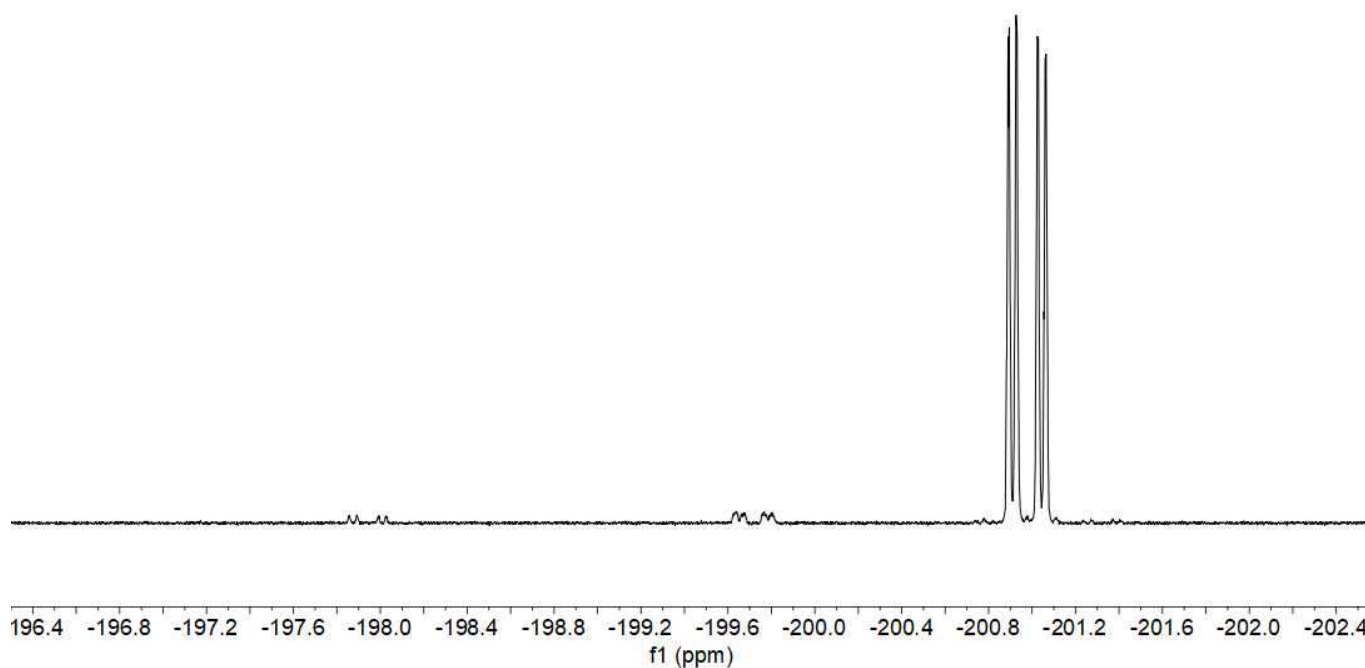
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ ,  $\beta$ -24



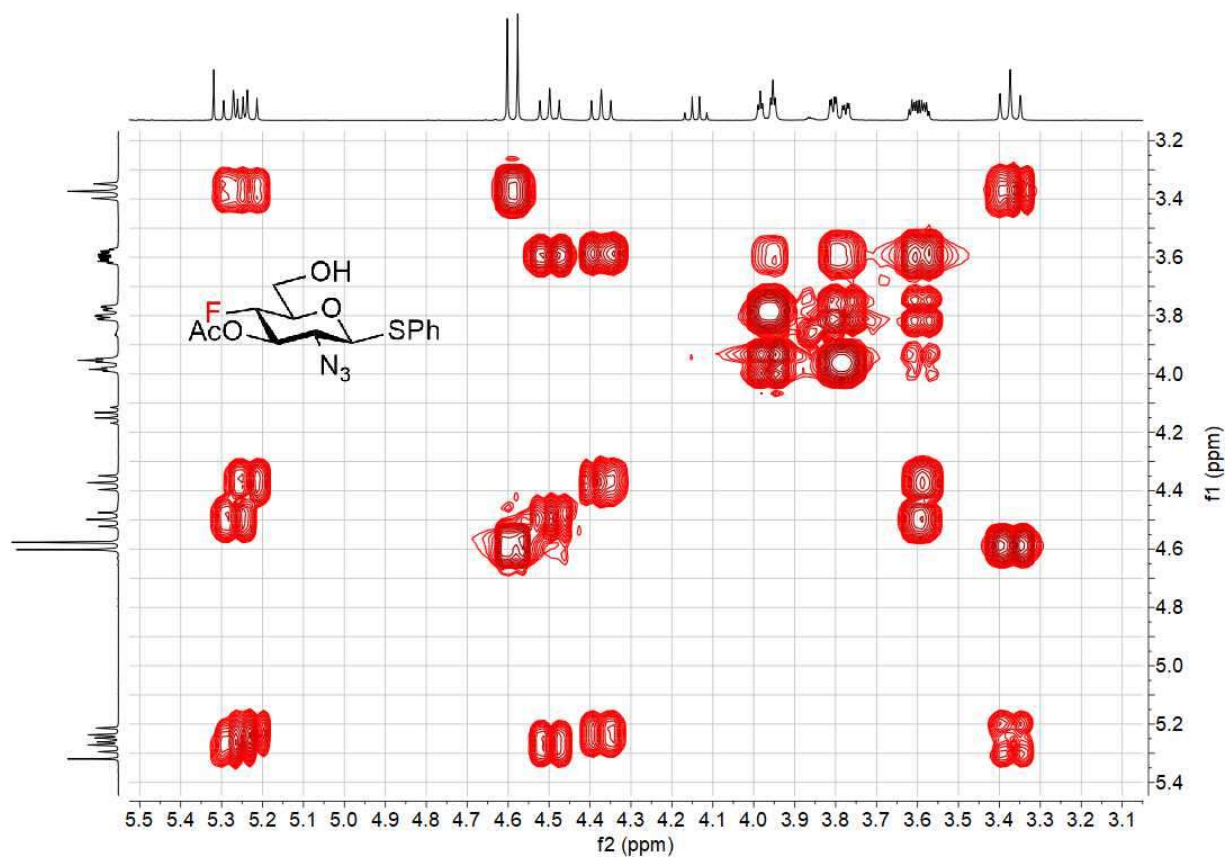
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ ,  **$\beta$ -24** (traces of the  $\alpha$ -anomer at  $\delta$  -199.74)



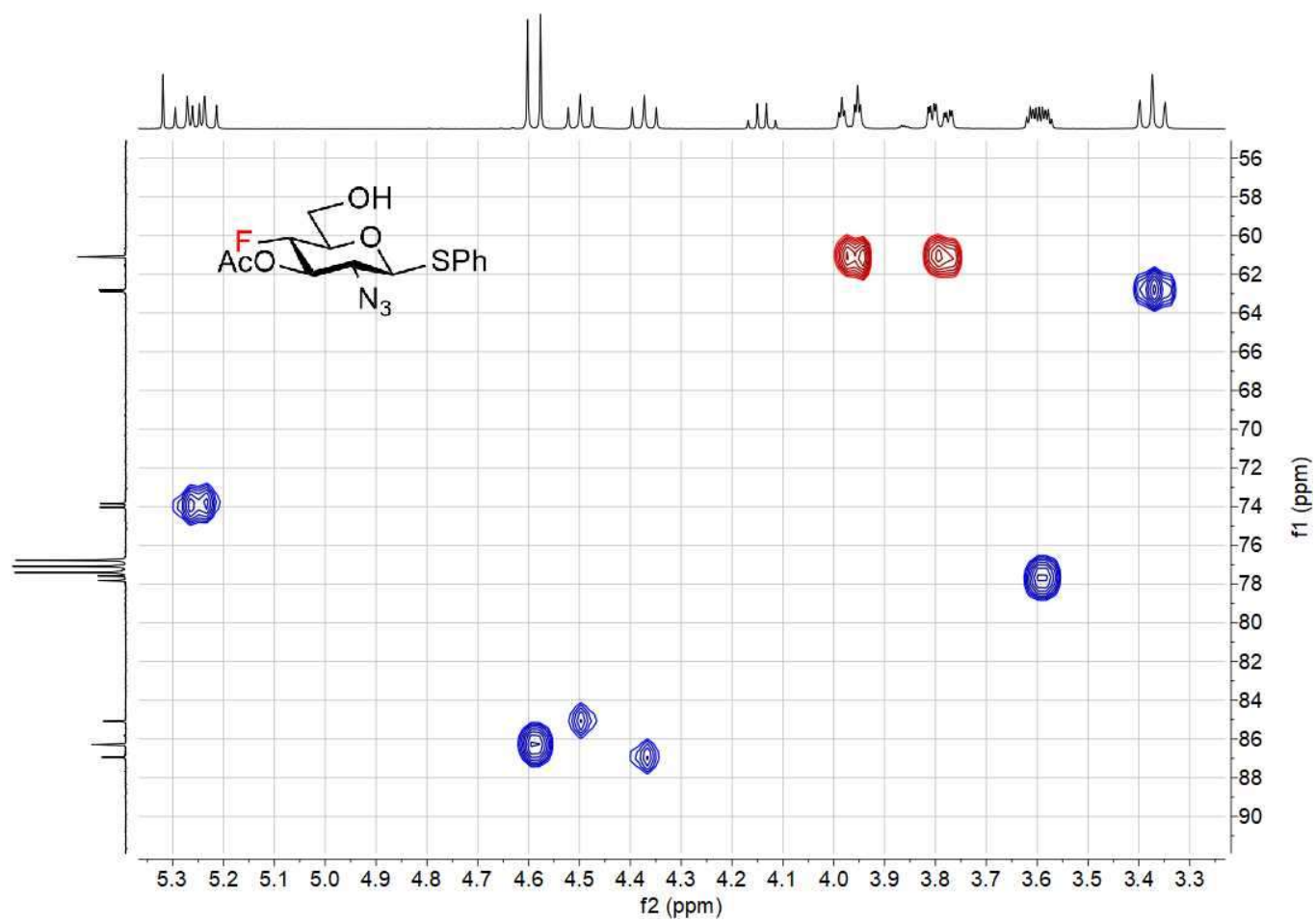
-200.88  
-200.89  
-200.90  
-200.90  
-200.92  
-200.93  
-200.93  
-200.94  
-201.02  
-201.02  
-201.03  
-201.04  
-201.05  
-201.06  
-201.07



$^1\text{H}$ - $^1\text{H}$  COSY NMR,  **$\beta$ -24**

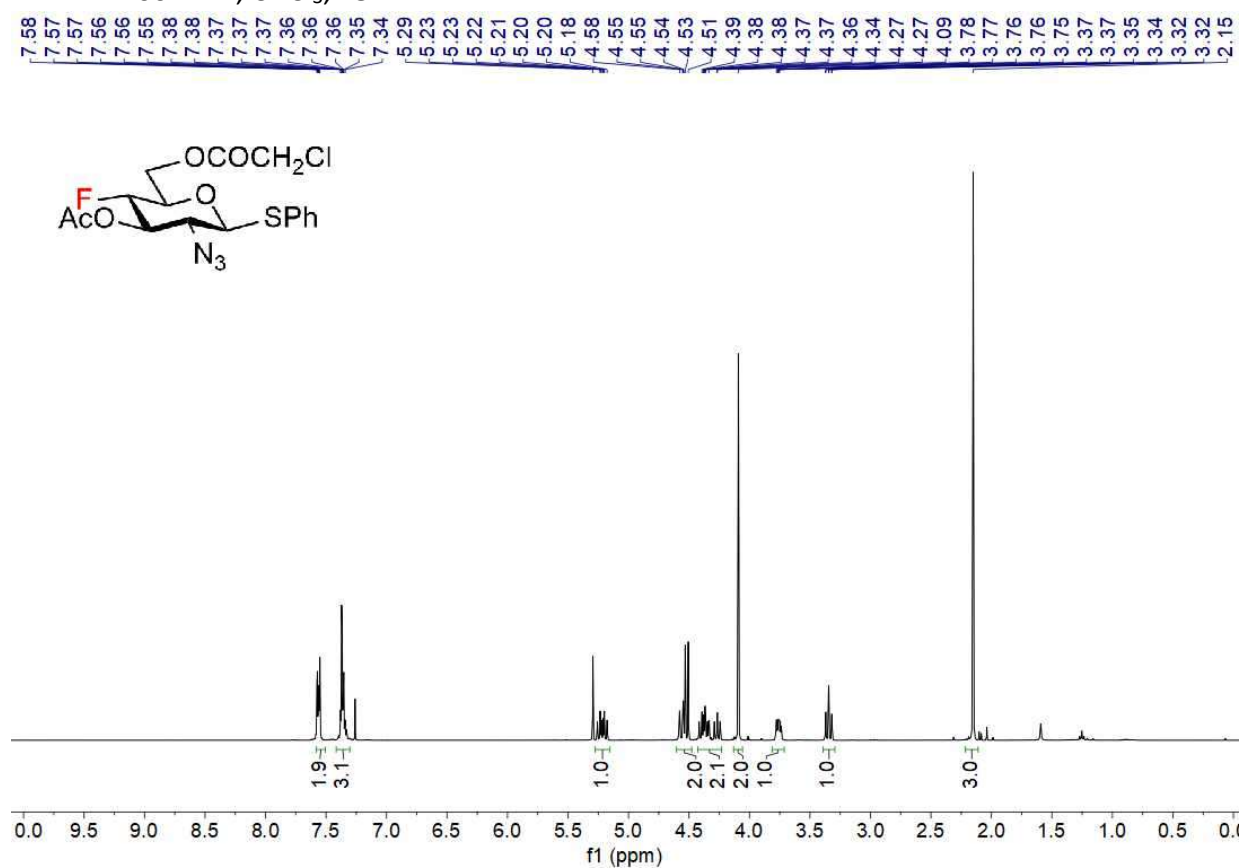


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR  **$\beta$ -24**

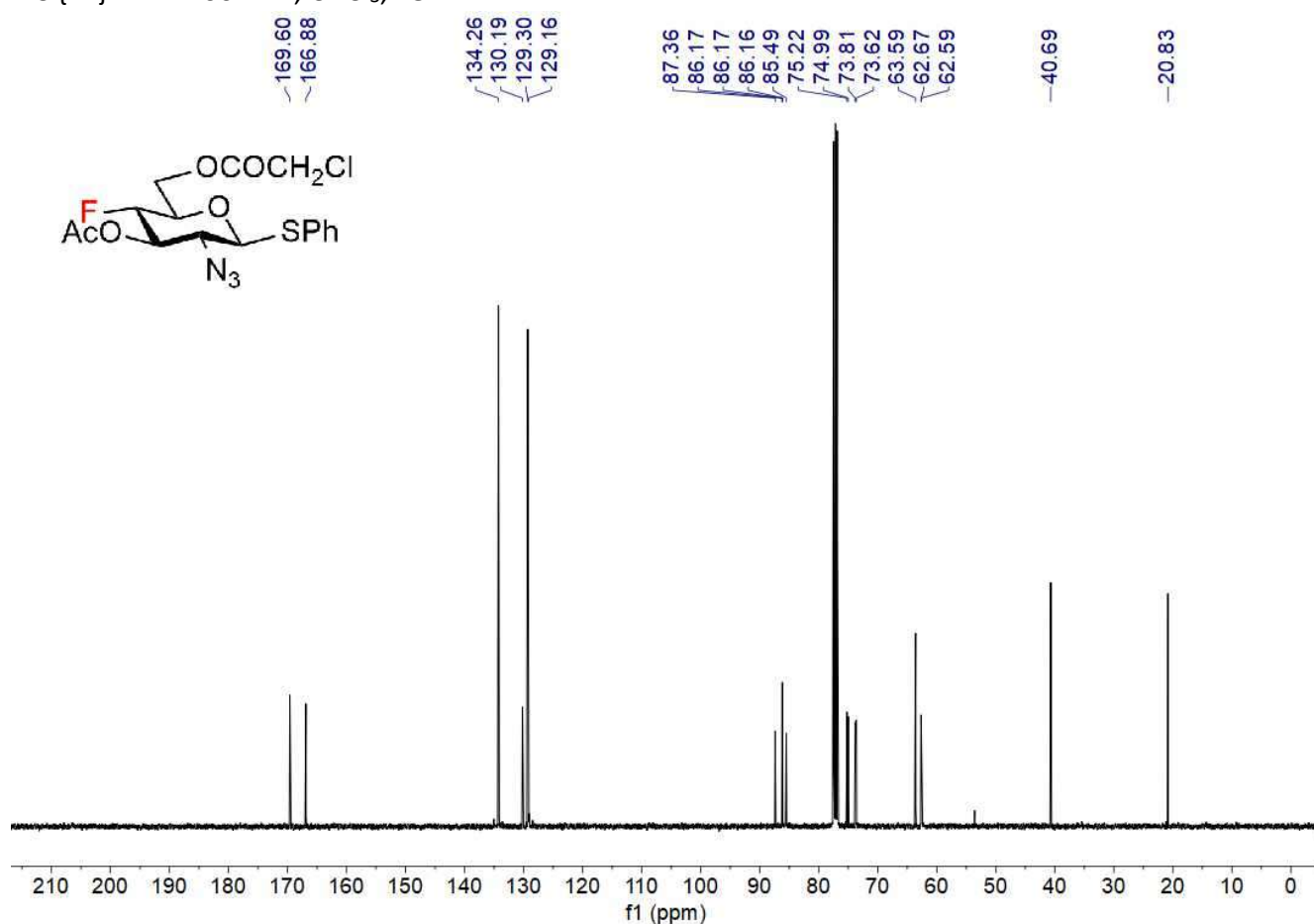


# **NMR 25**

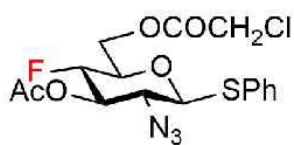
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **25**



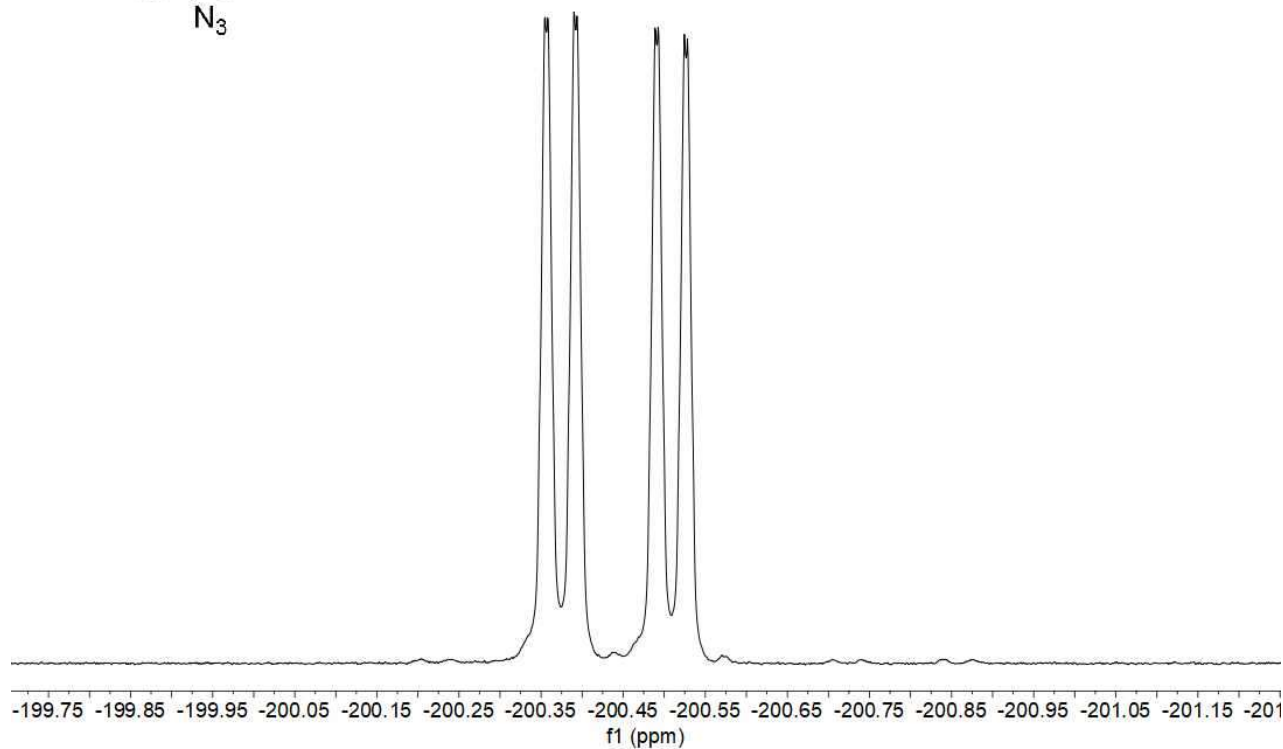
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **25**



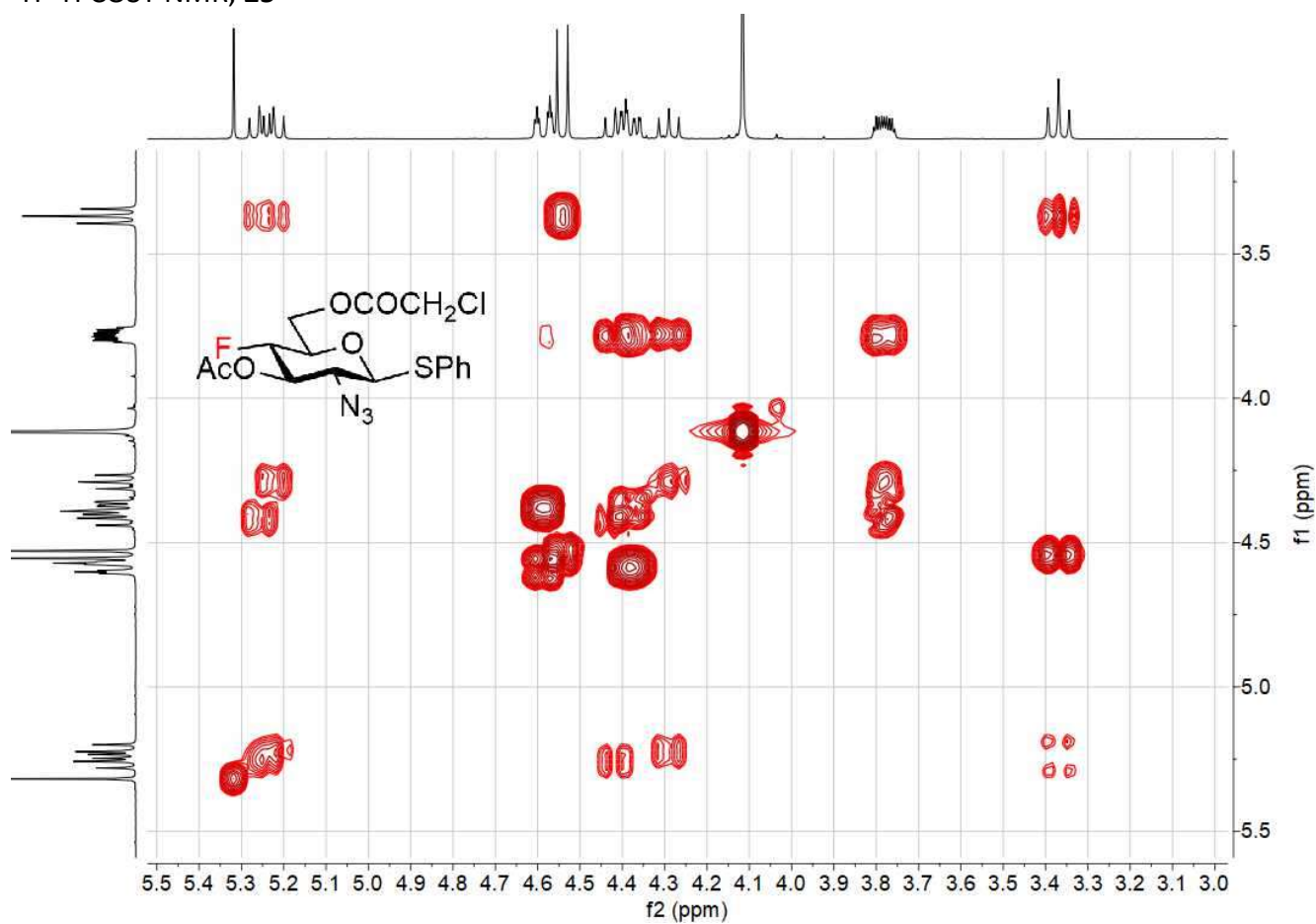
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **25**



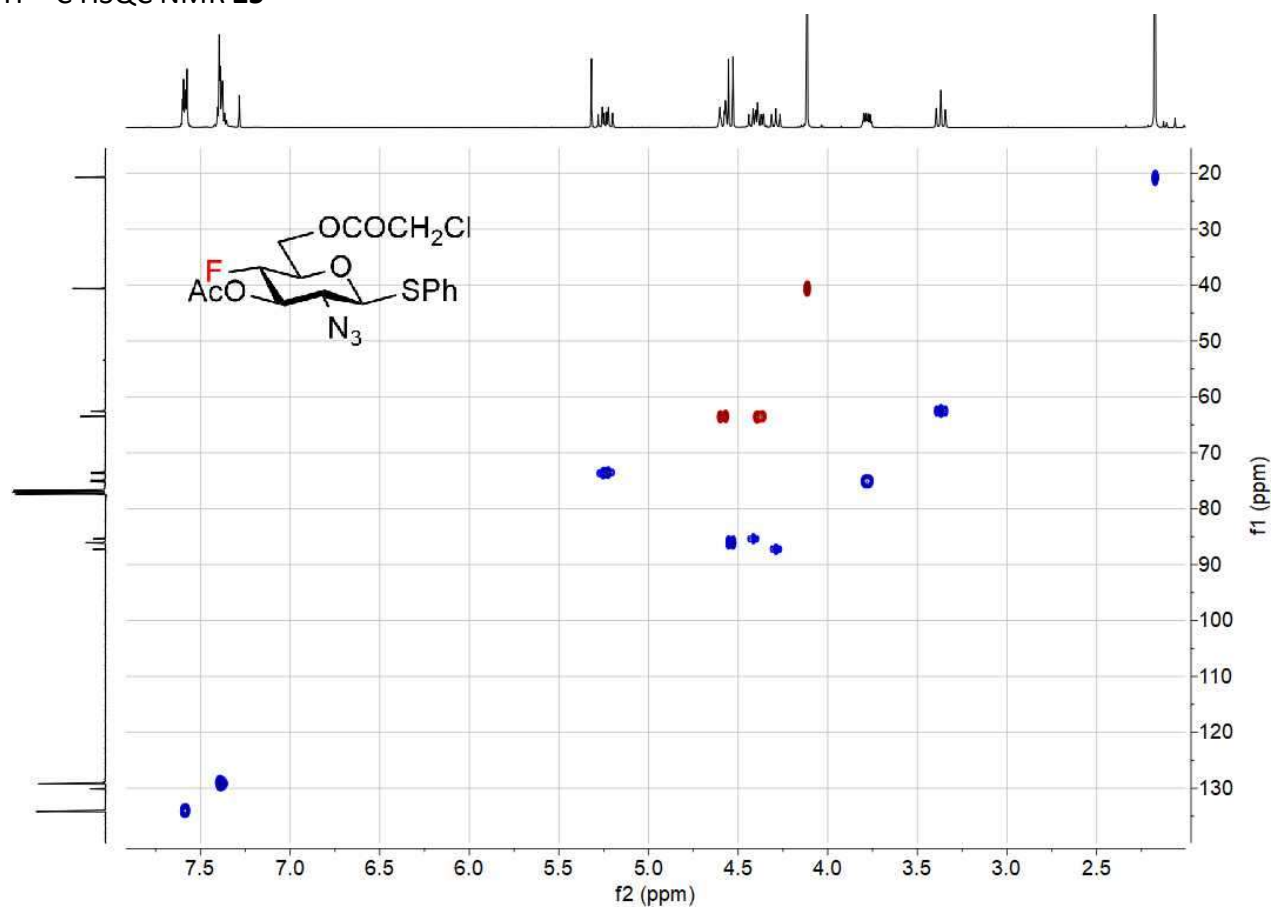
200.35  
200.35  
200.36  
200.36  
200.38  
200.38  
200.39  
200.39  
200.48  
200.48  
200.49  
200.49  
200.52  
200.52  
200.53  
200.53



$^1\text{H}$ - $^1\text{H}$  COSY NMR, **25**



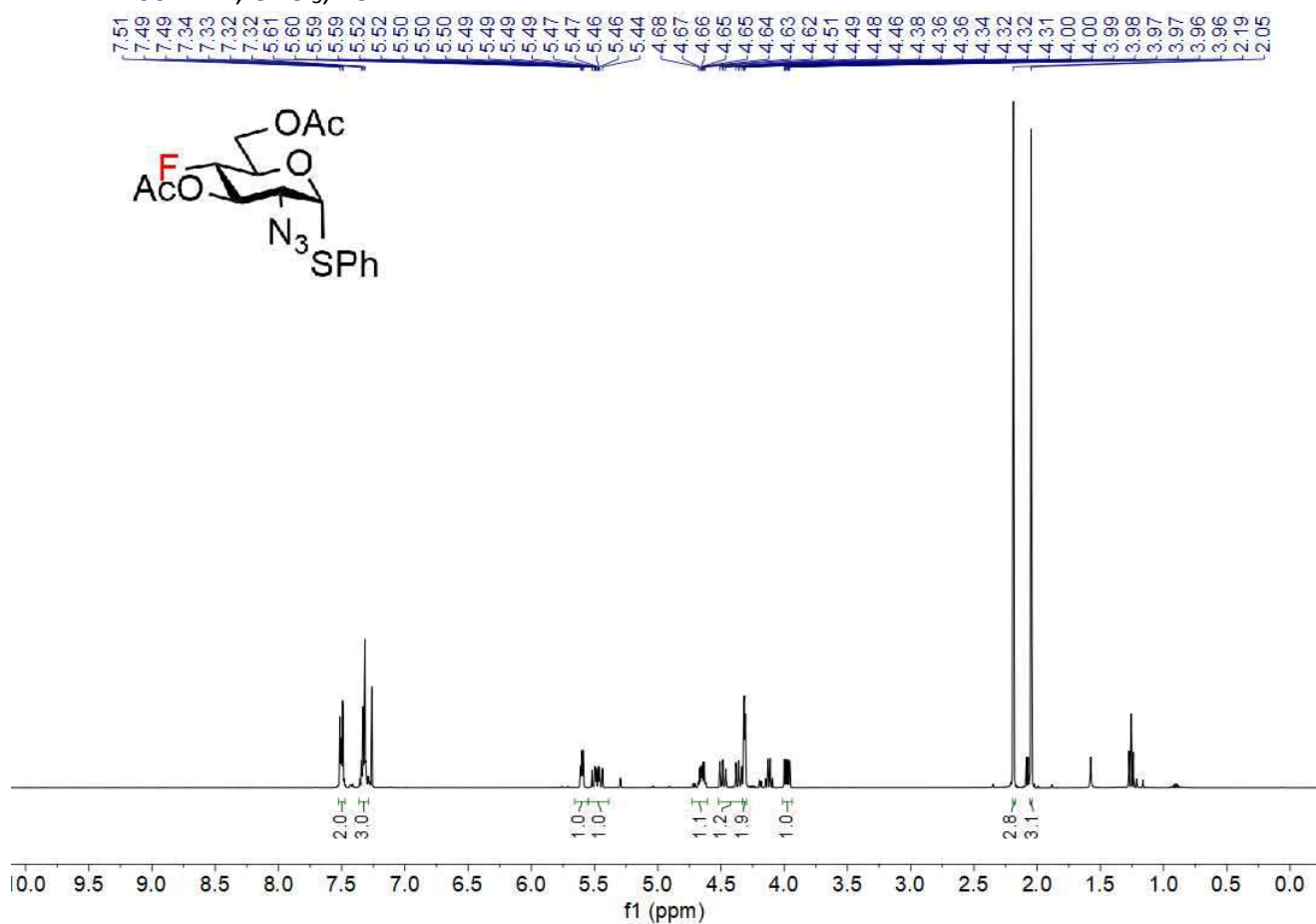
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 25



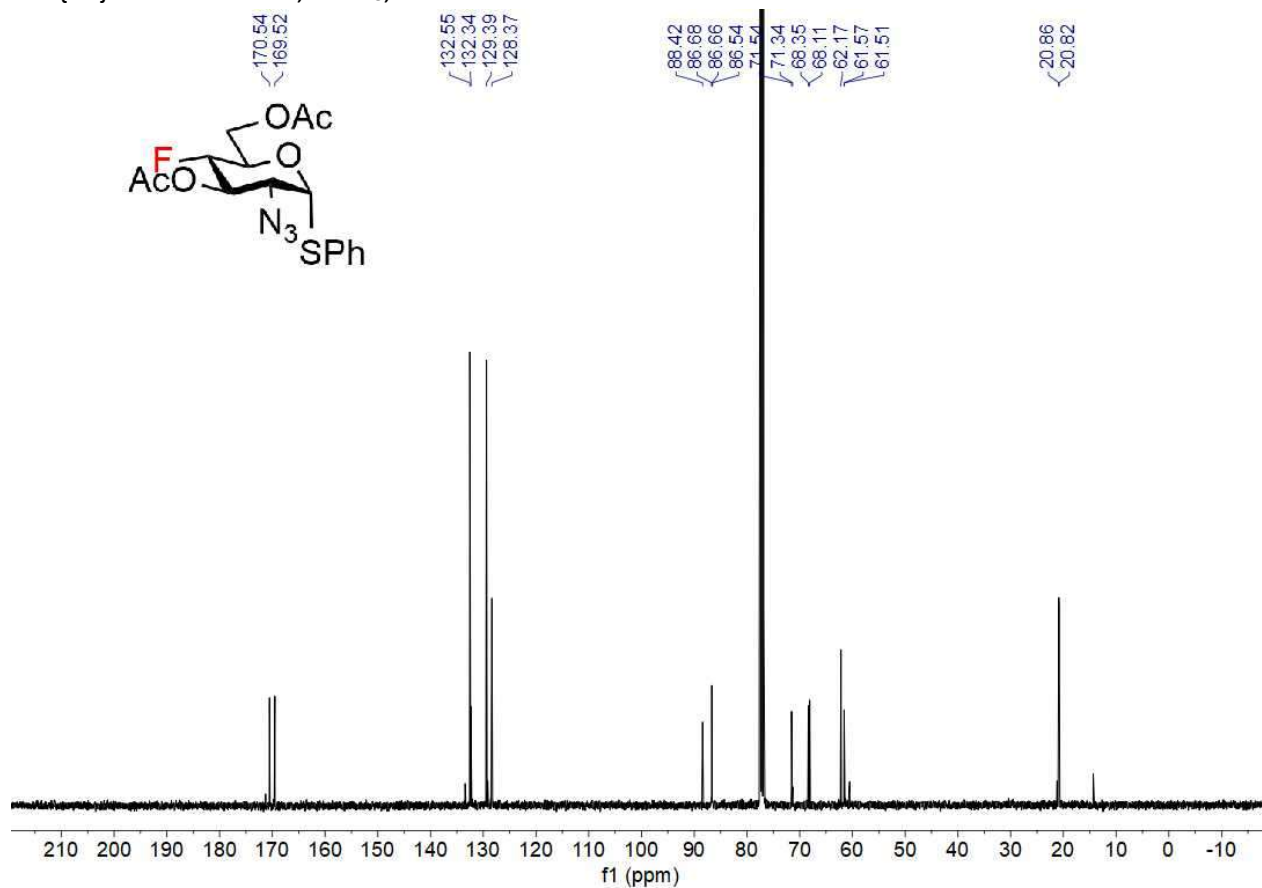


# **NMR 26**

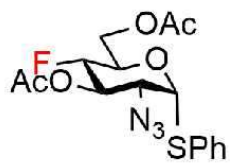
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **26**



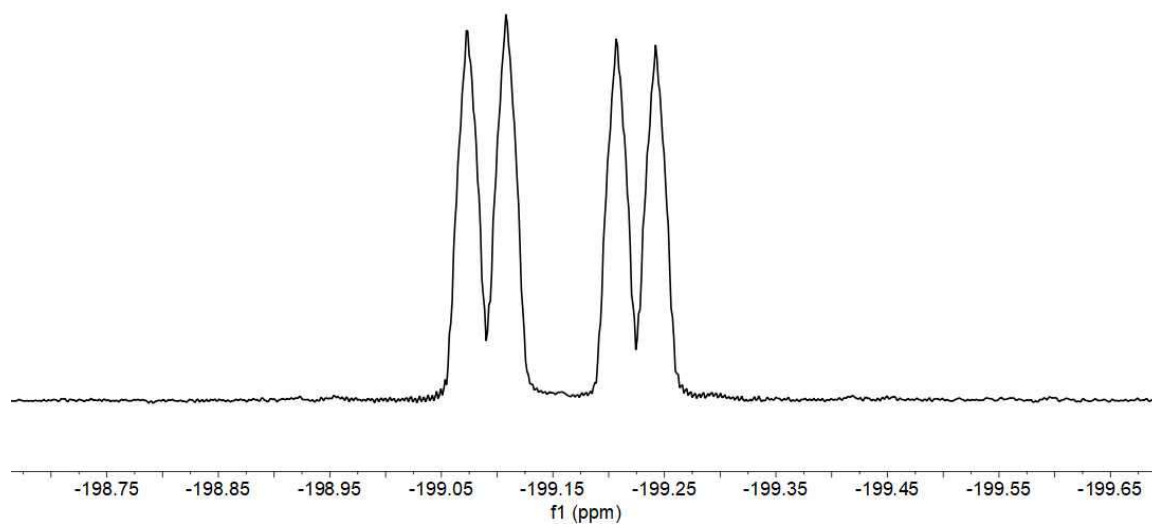
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **26**



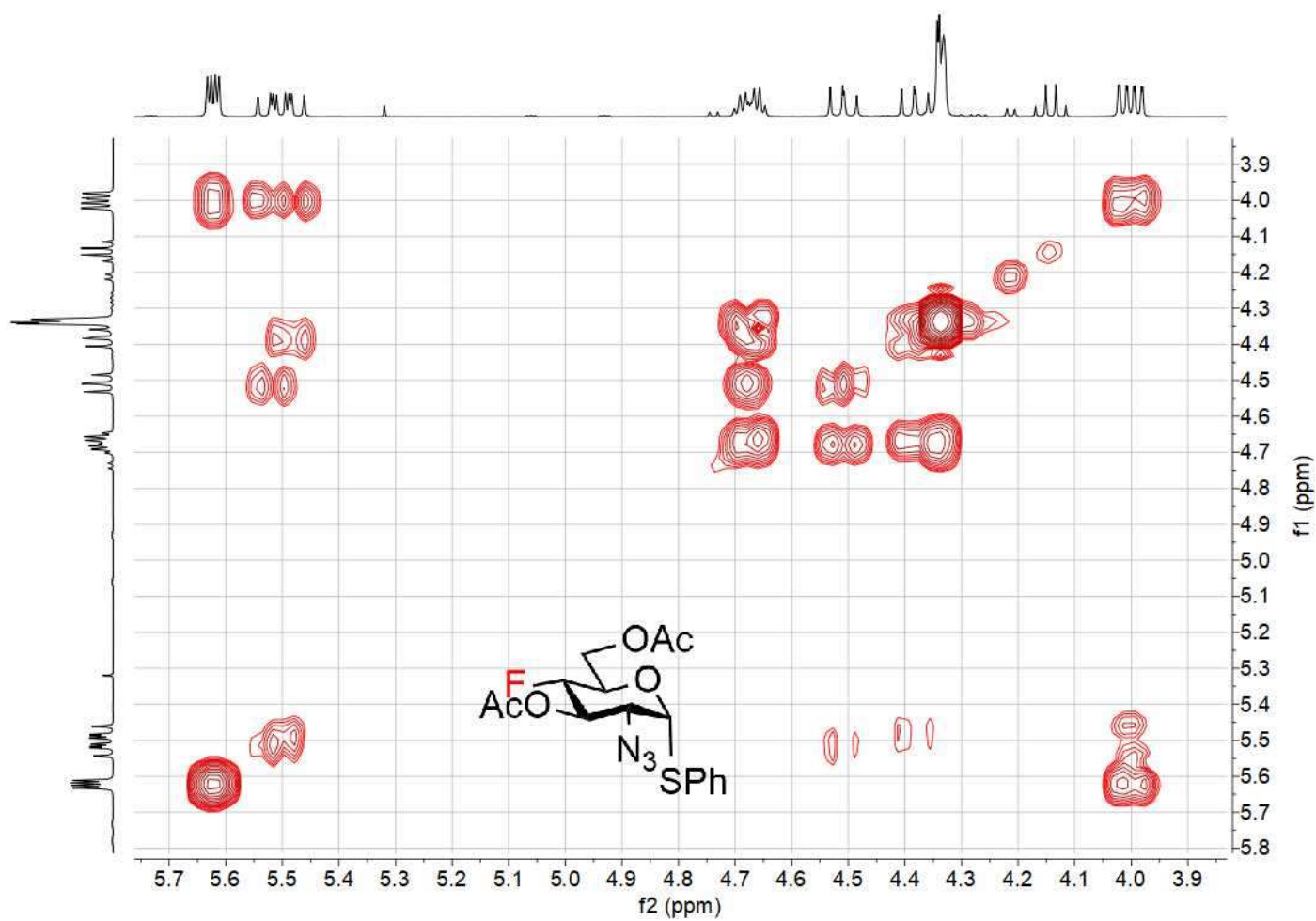
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **26**

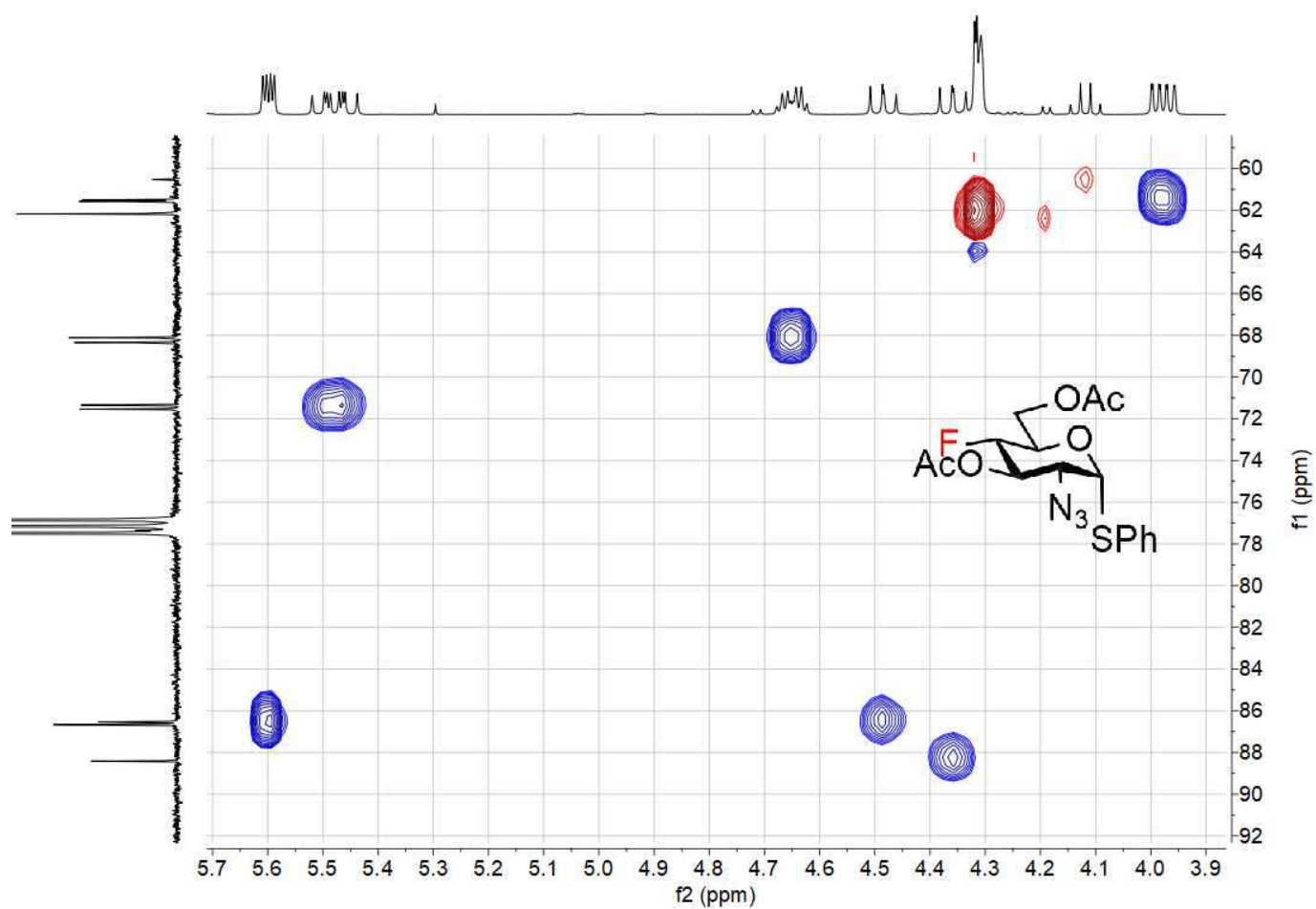


199.07  
199.07  
199.08  
199.11  
199.12  
  
199.21  
199.21  
199.24  
199.24  
199.25



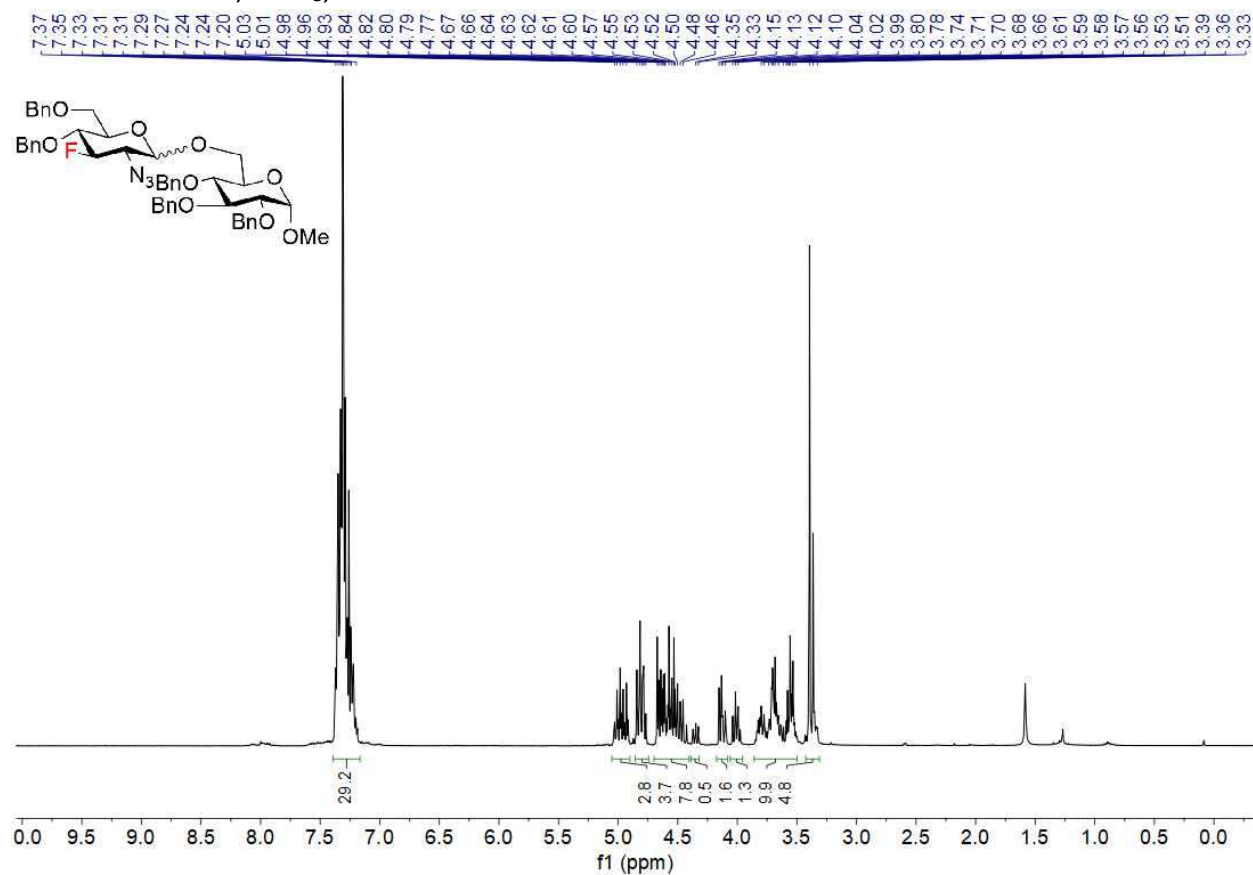
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **26**



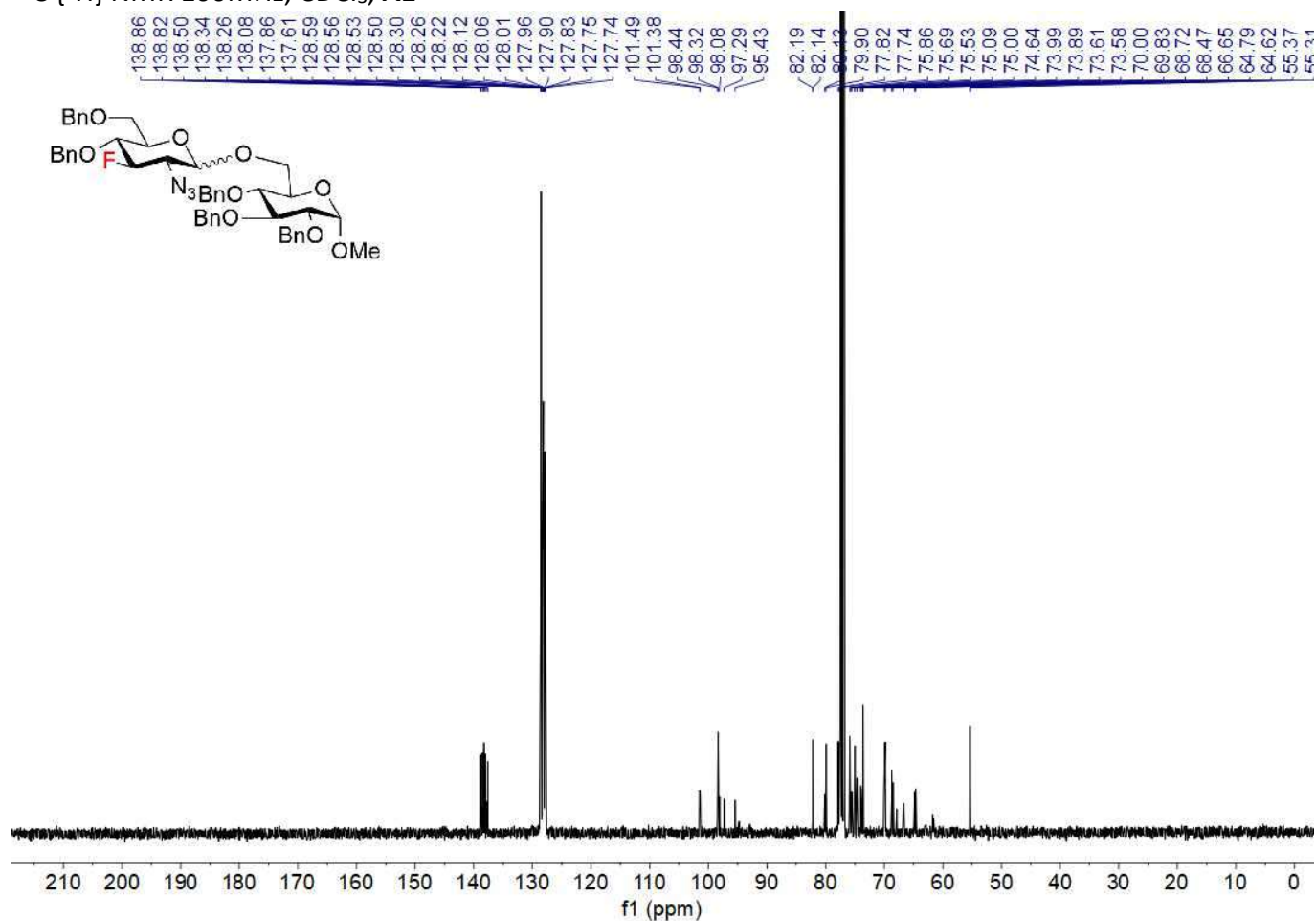


# NMR A1

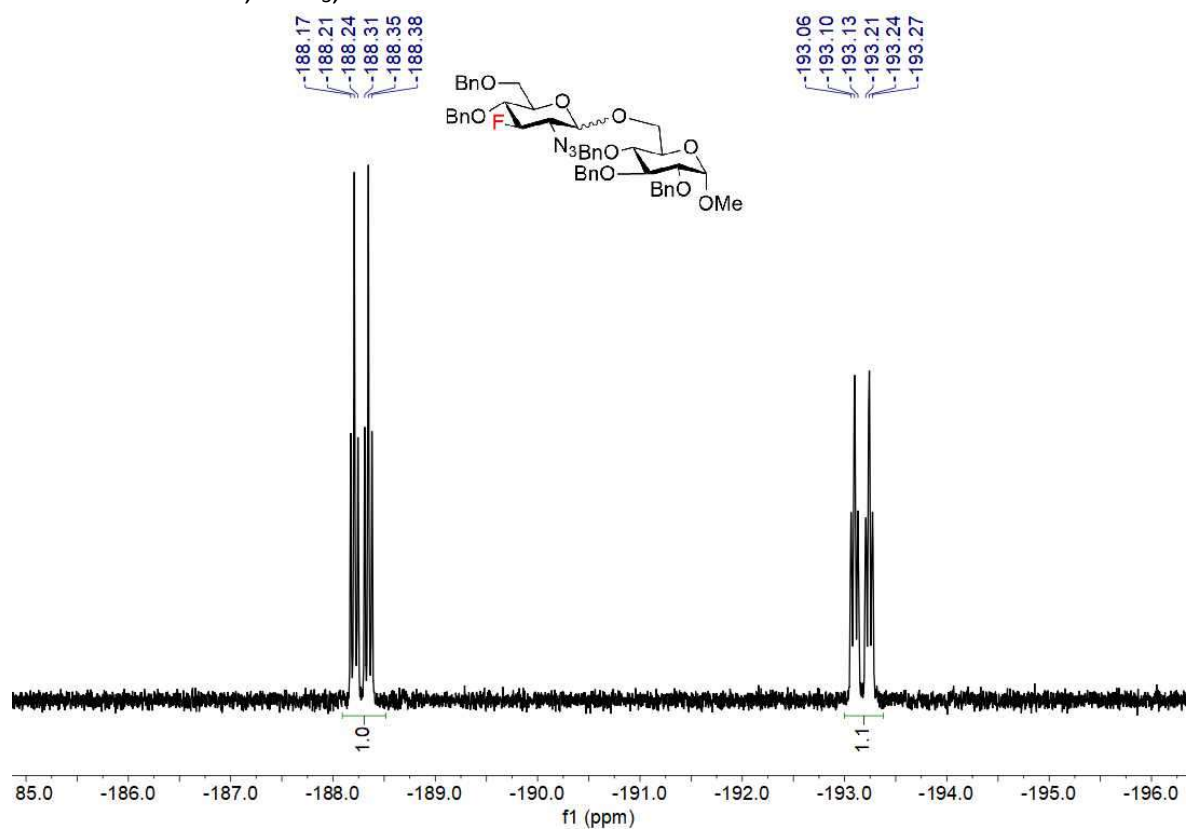
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, A1



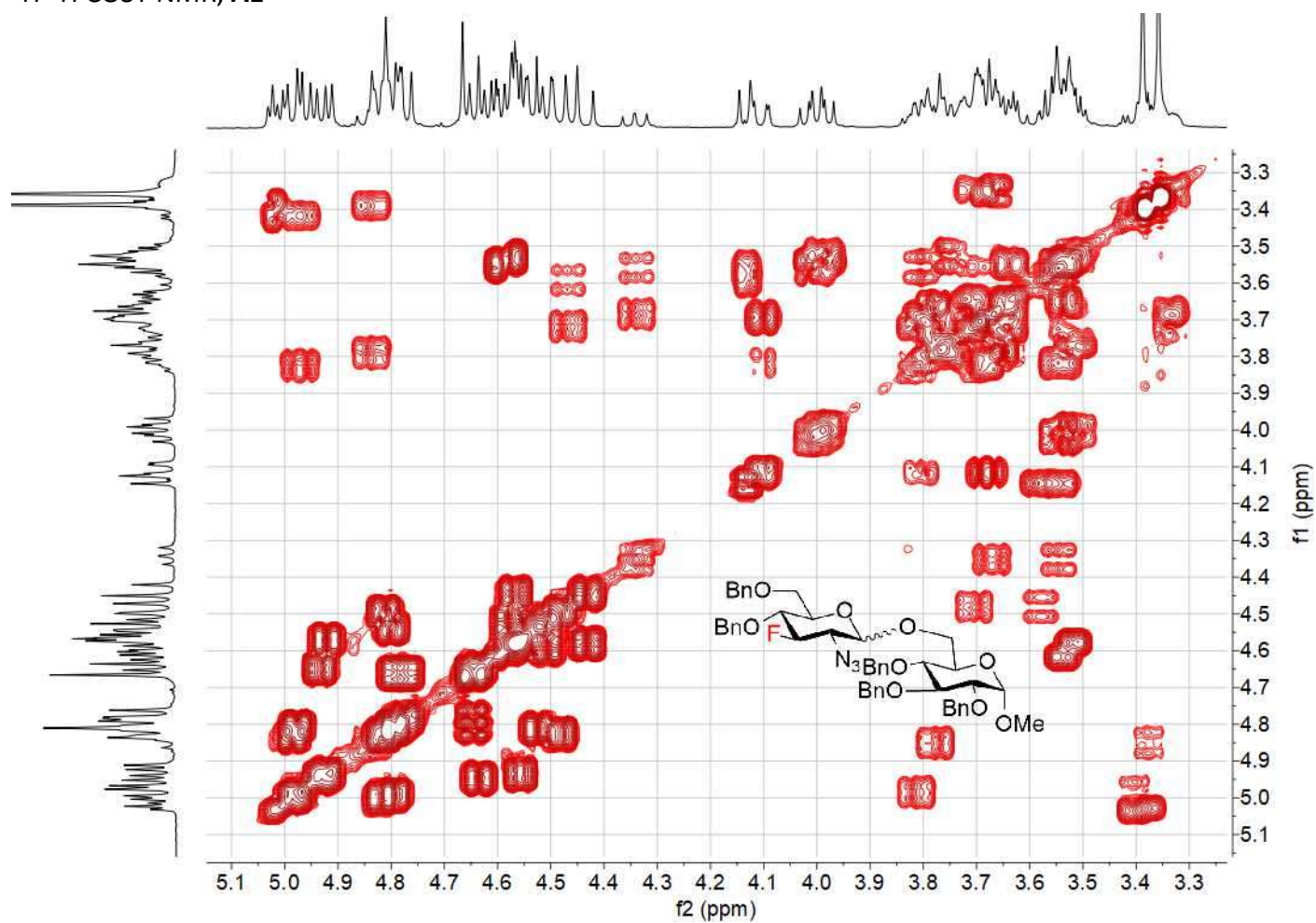
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, A1



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A1**

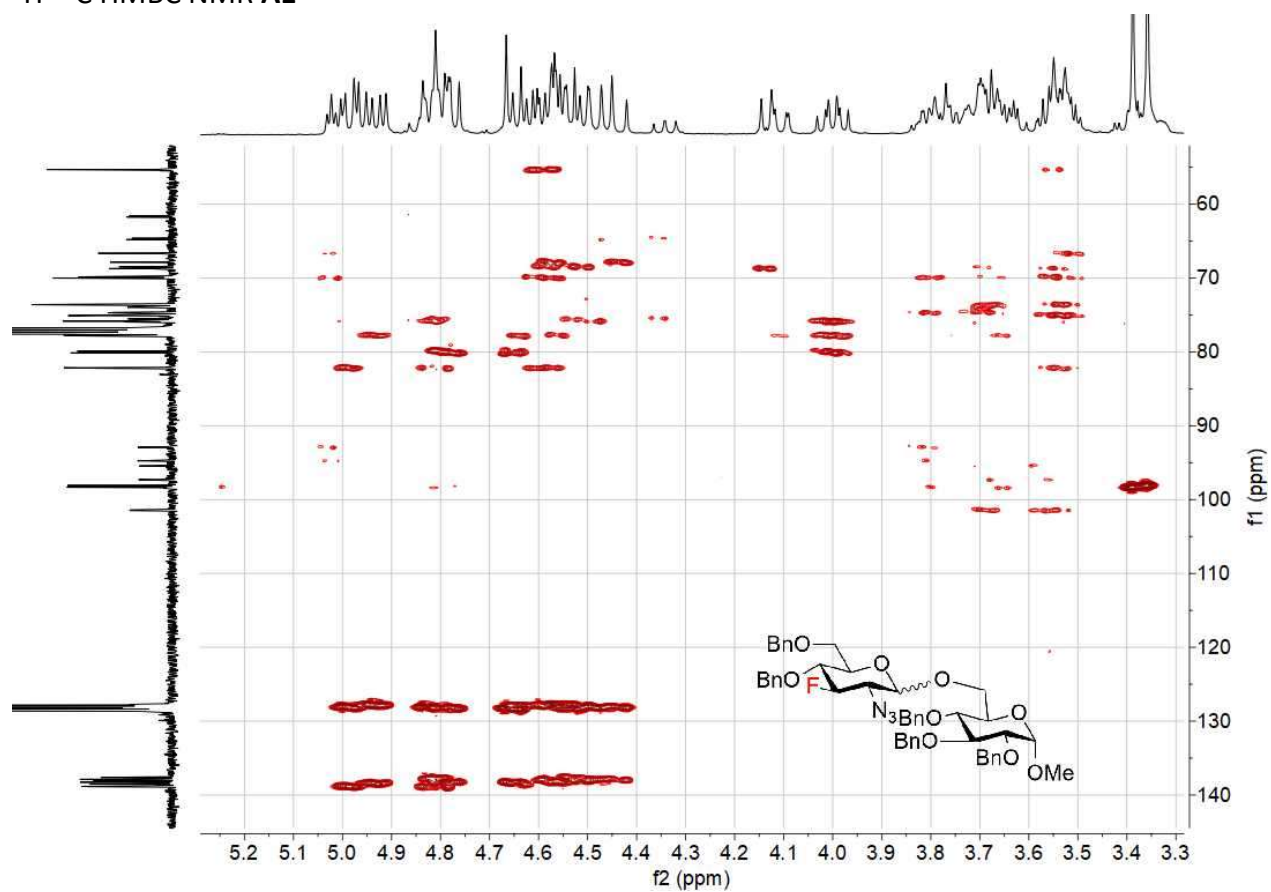


$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A1**

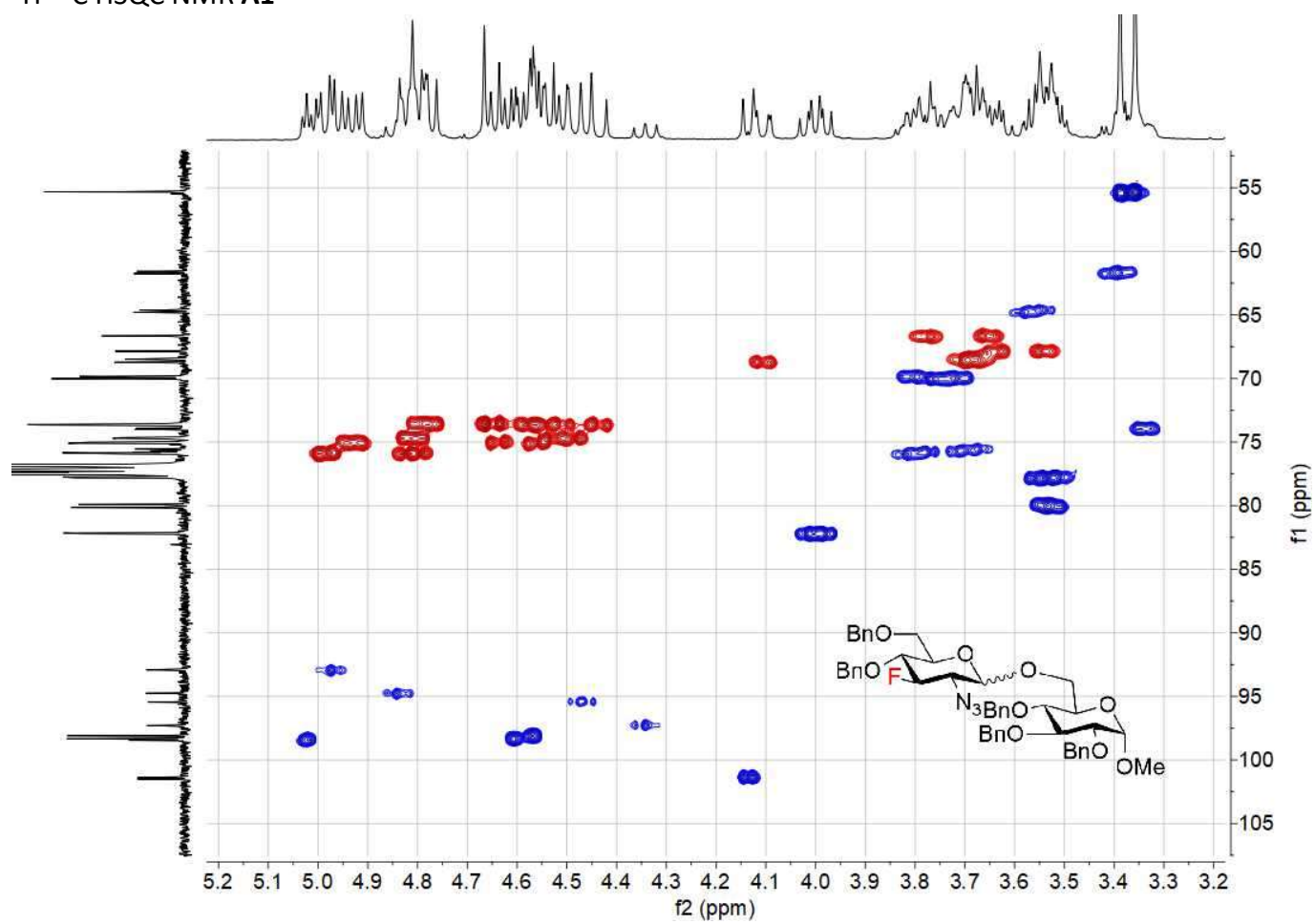




$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR A1

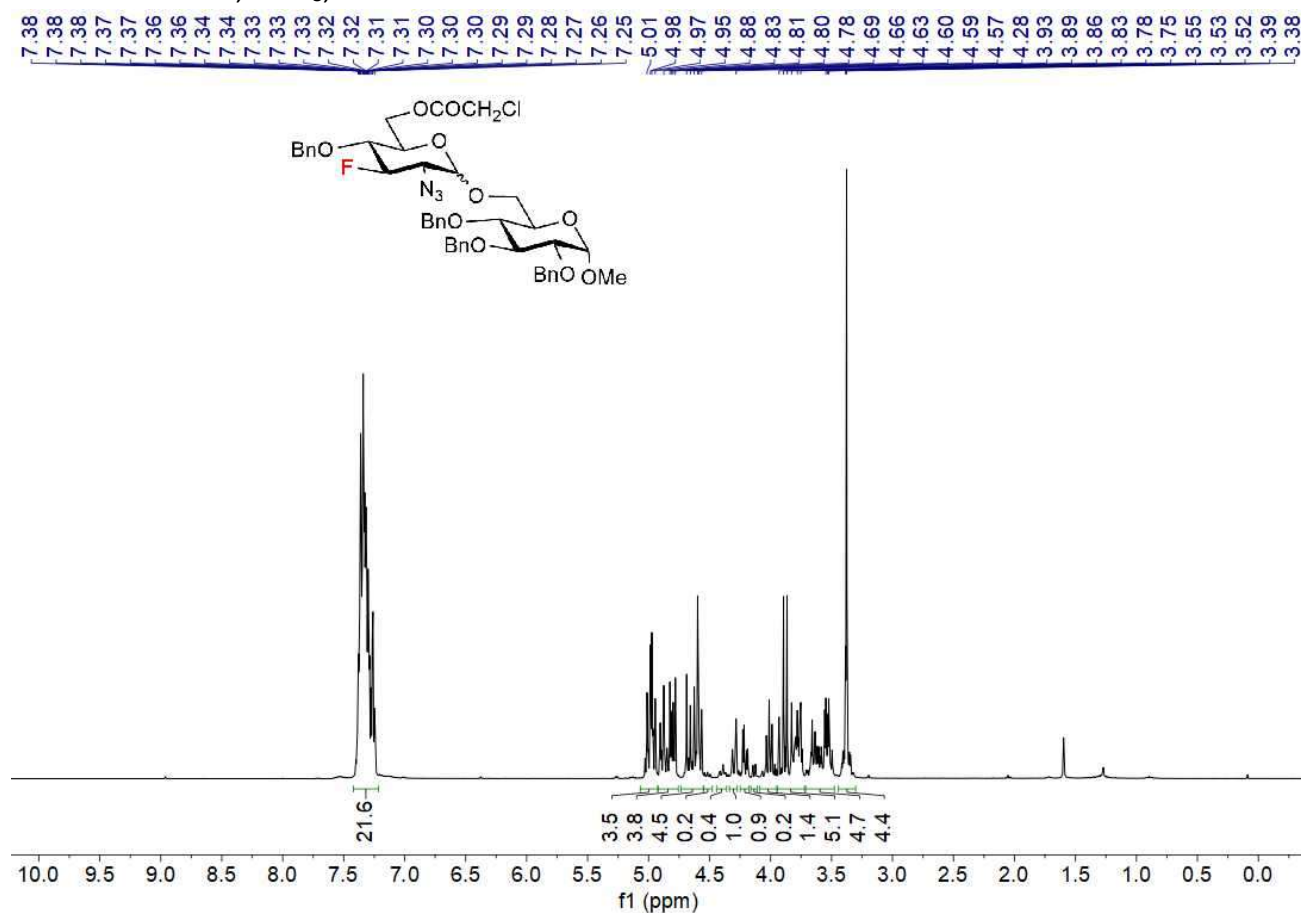


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR A1

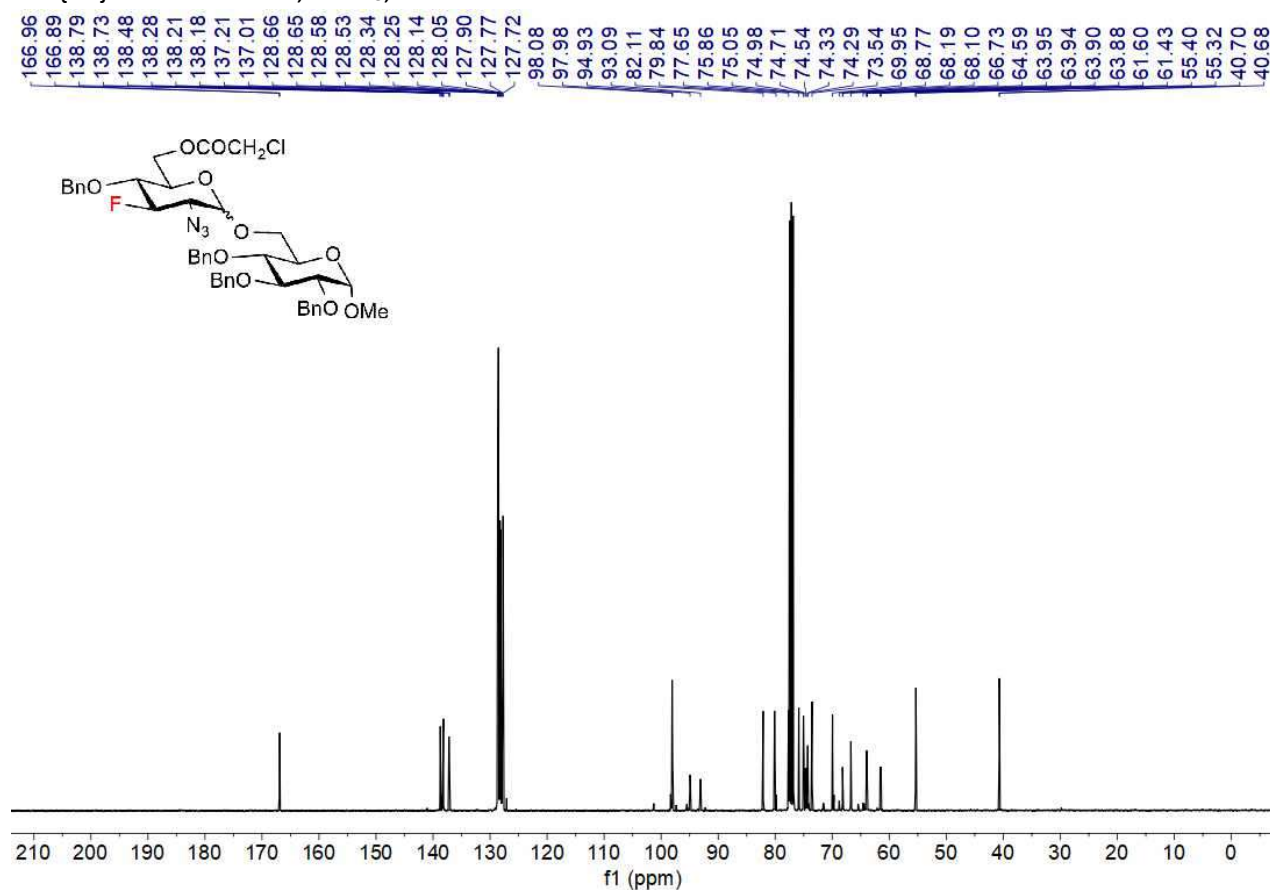


# **NMR A9**

**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, A9**

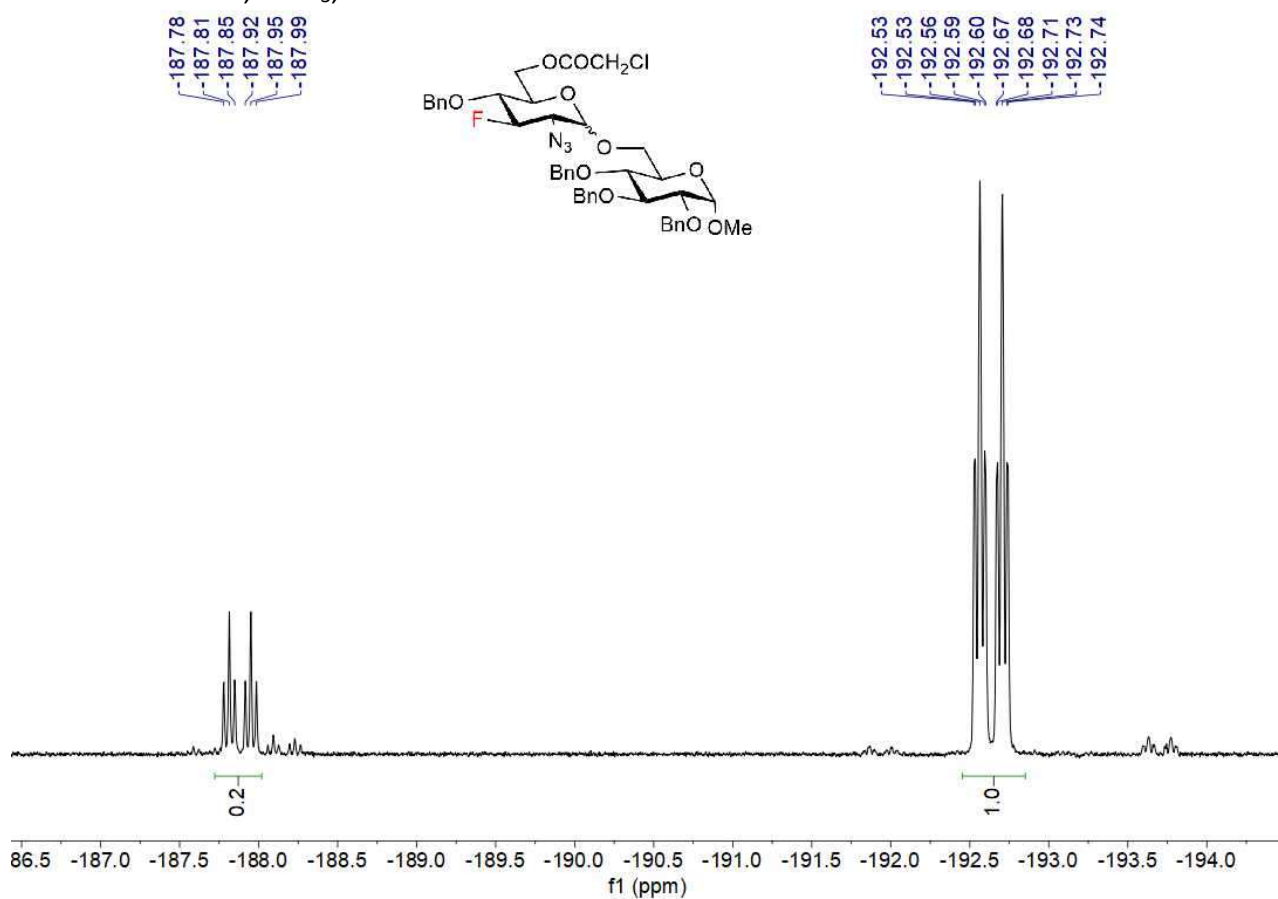


**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, A9**

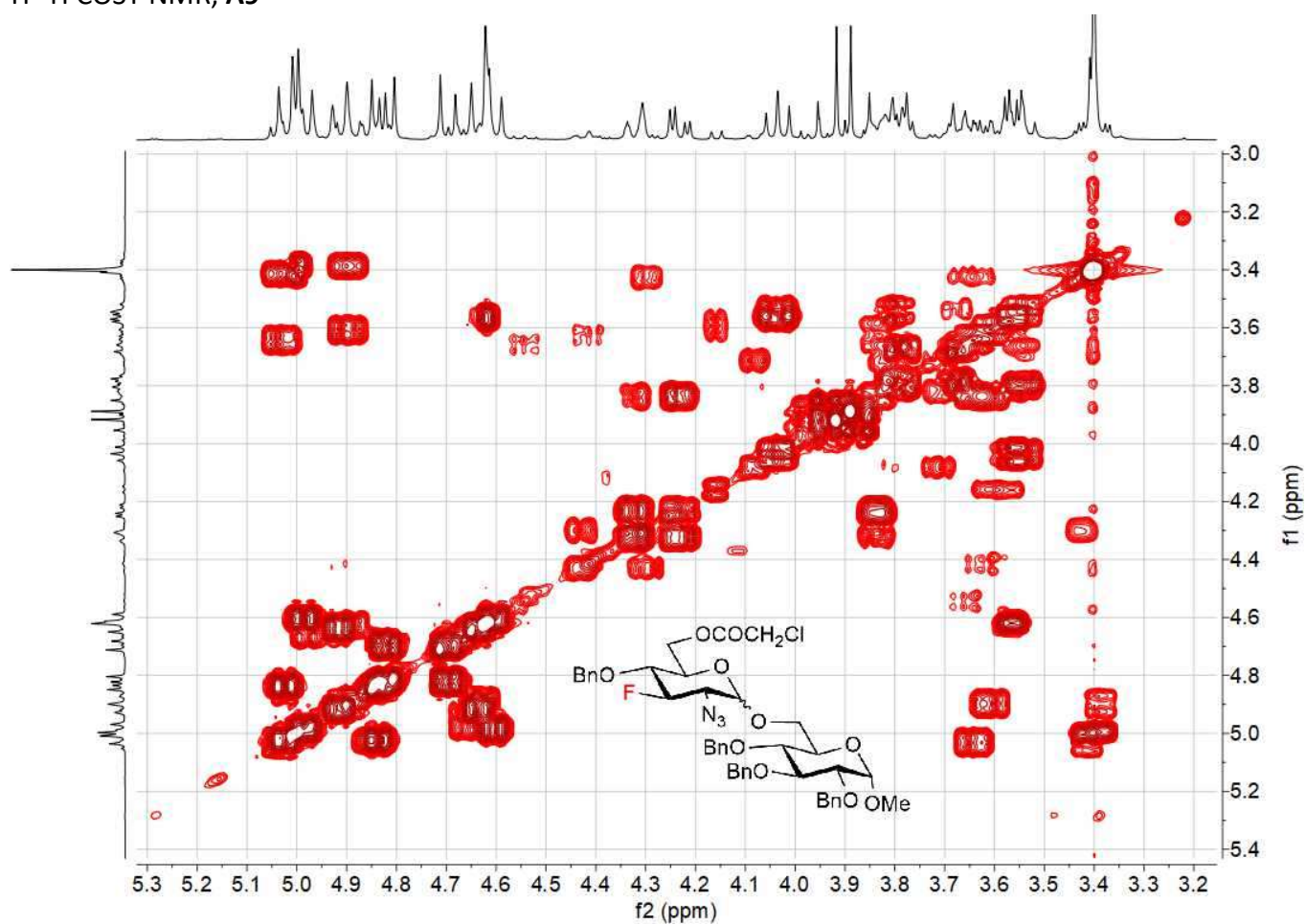




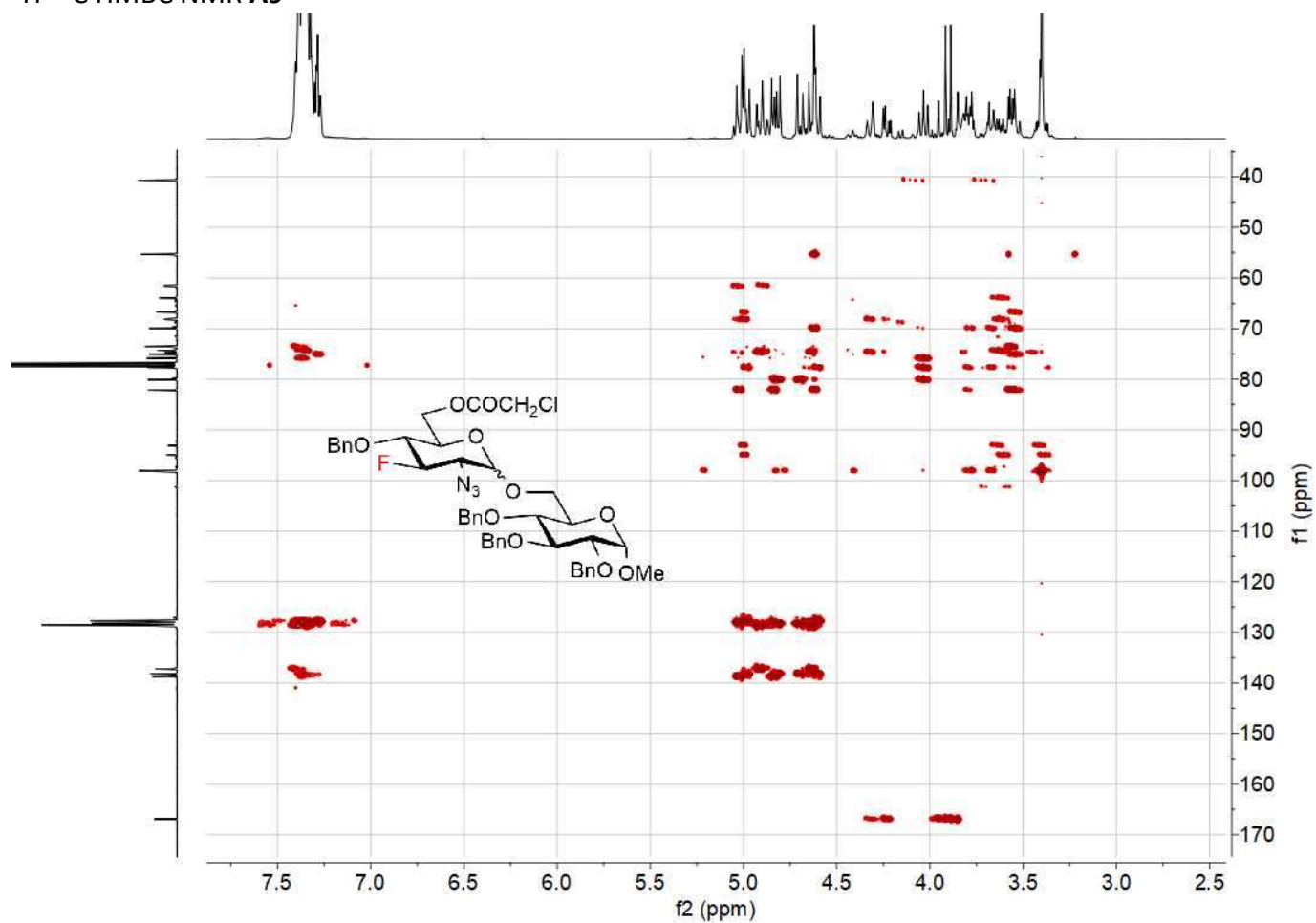
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A9**



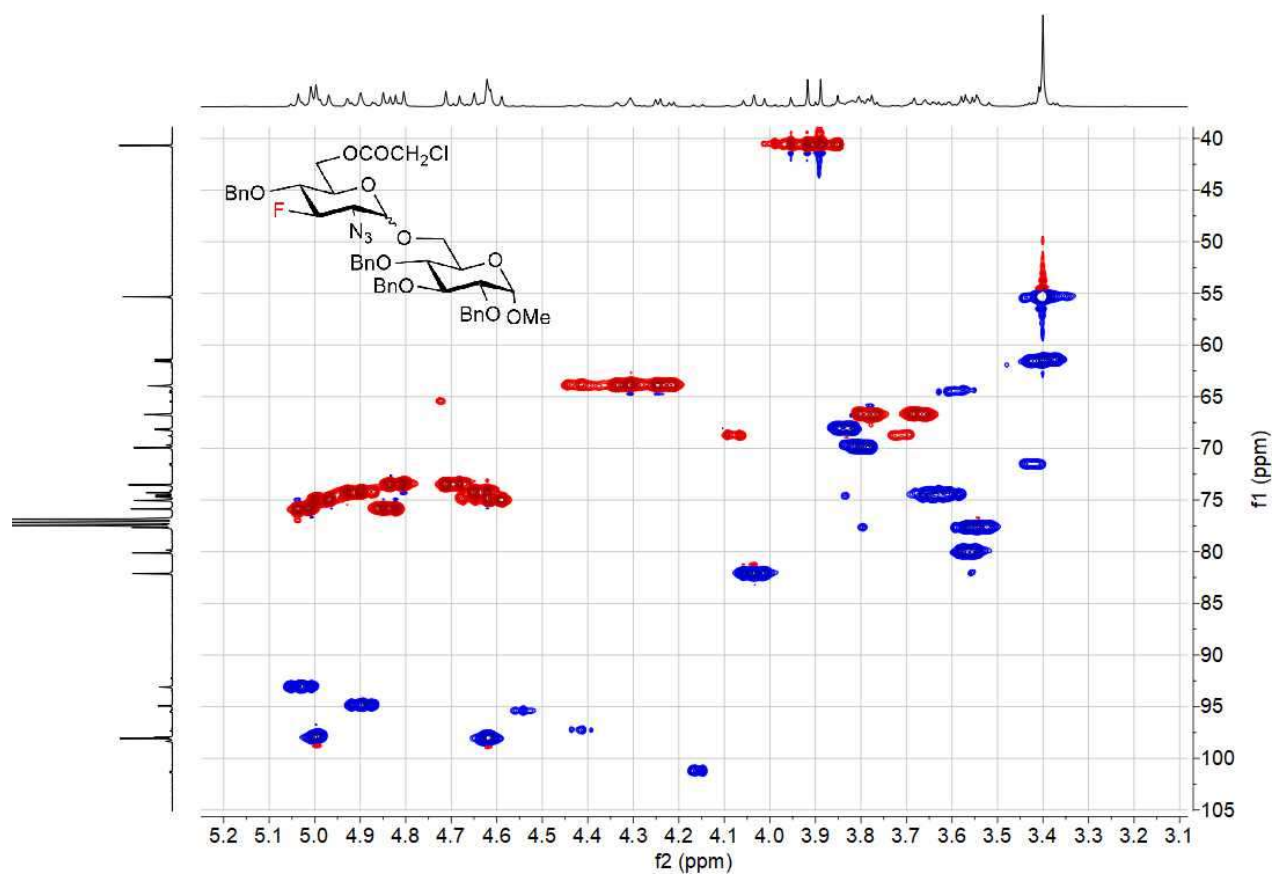
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A9**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR A9

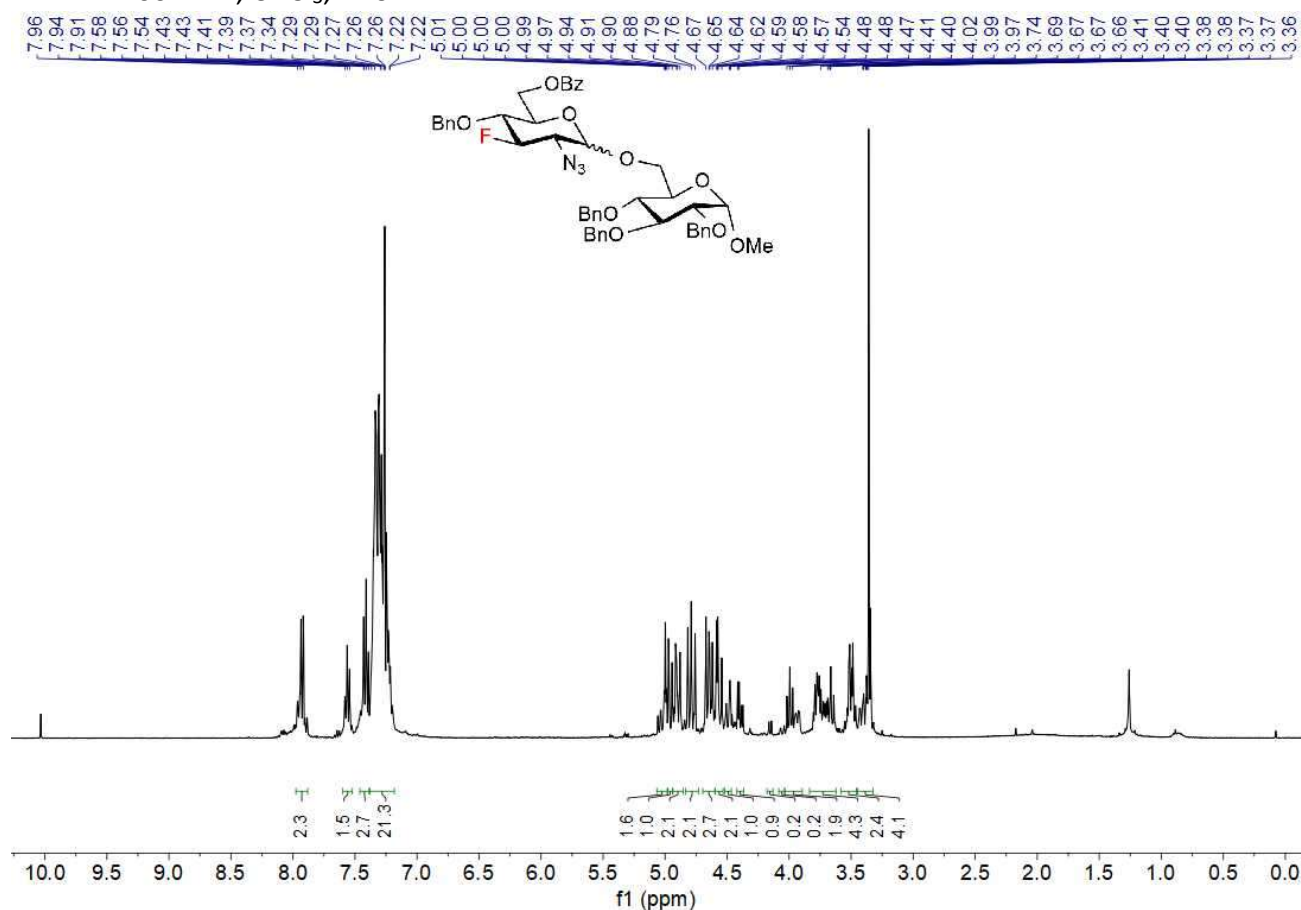


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR A9

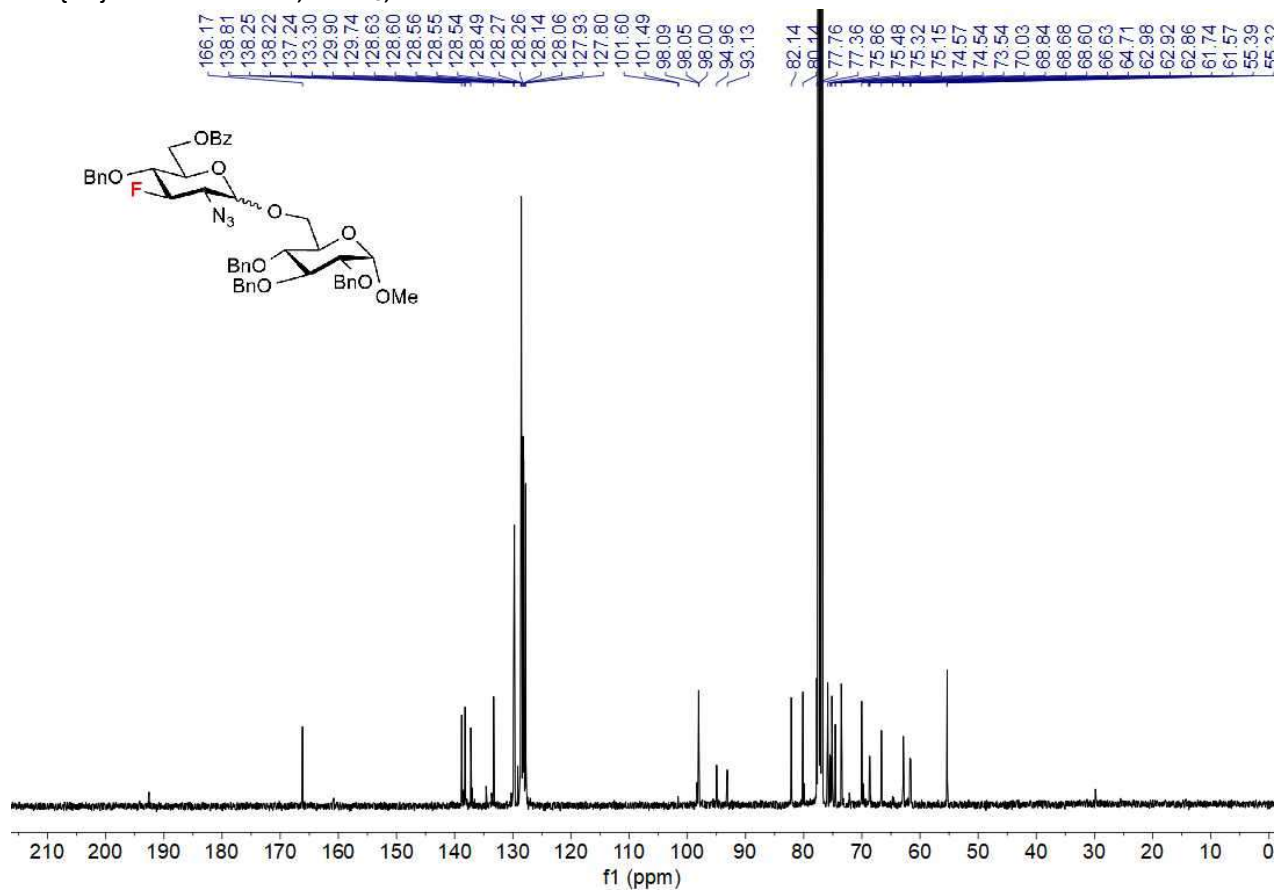


# NMR A10

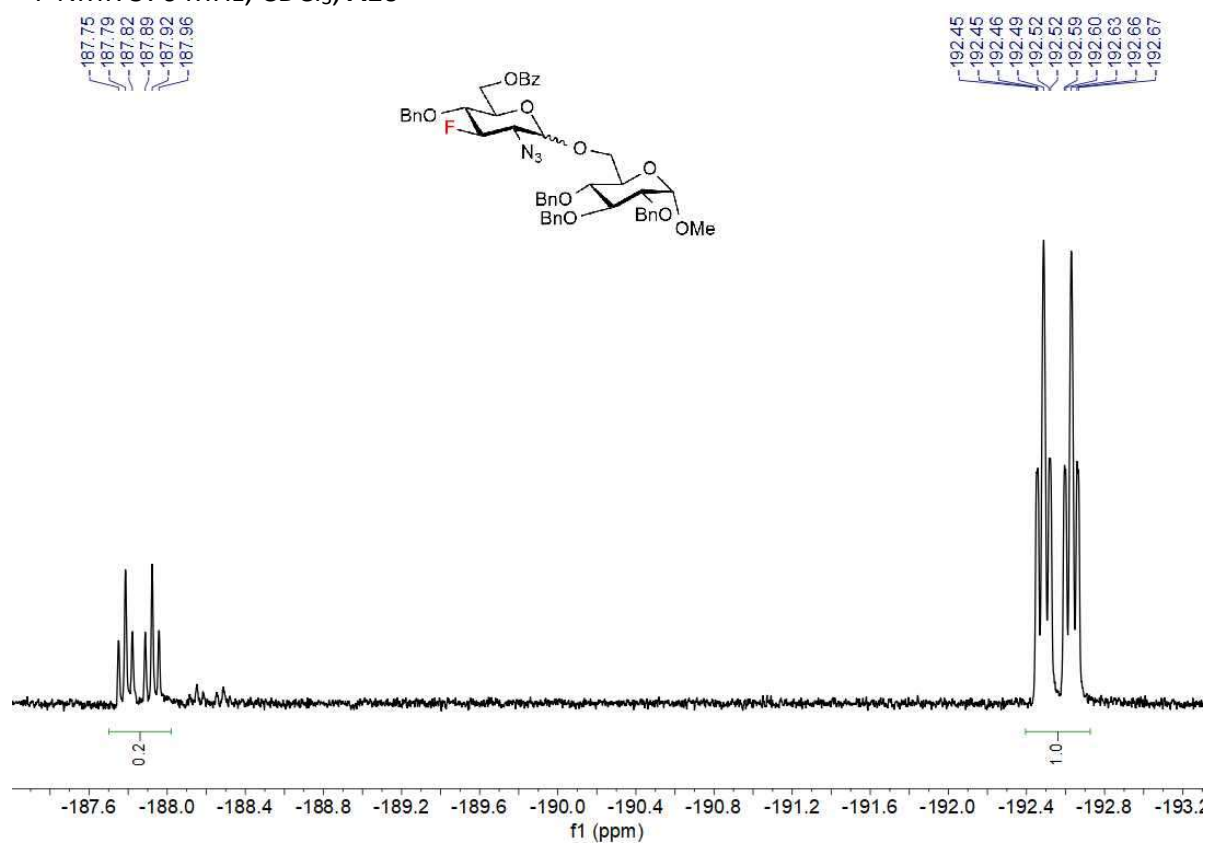
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, A10



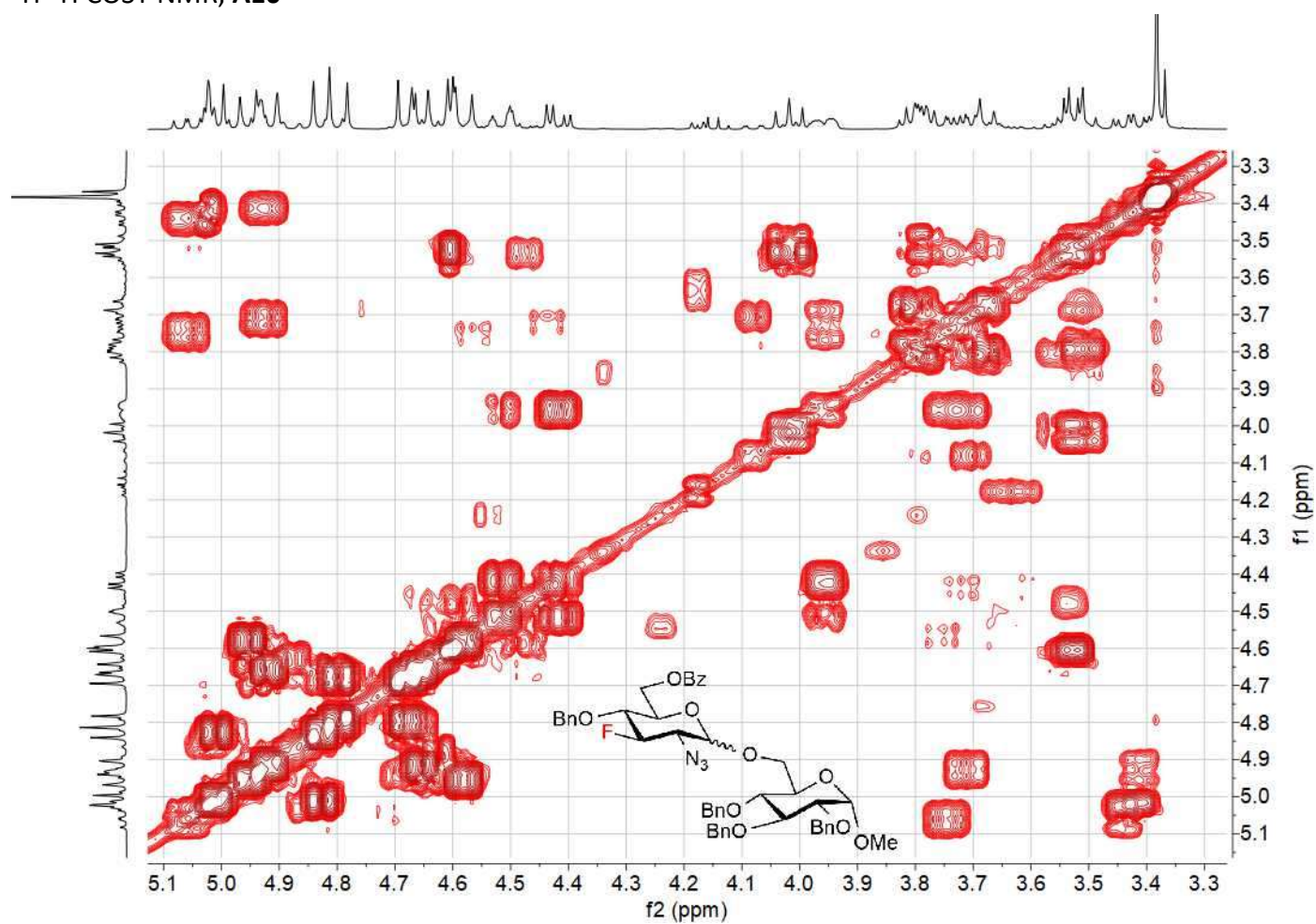
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, A10



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A10**

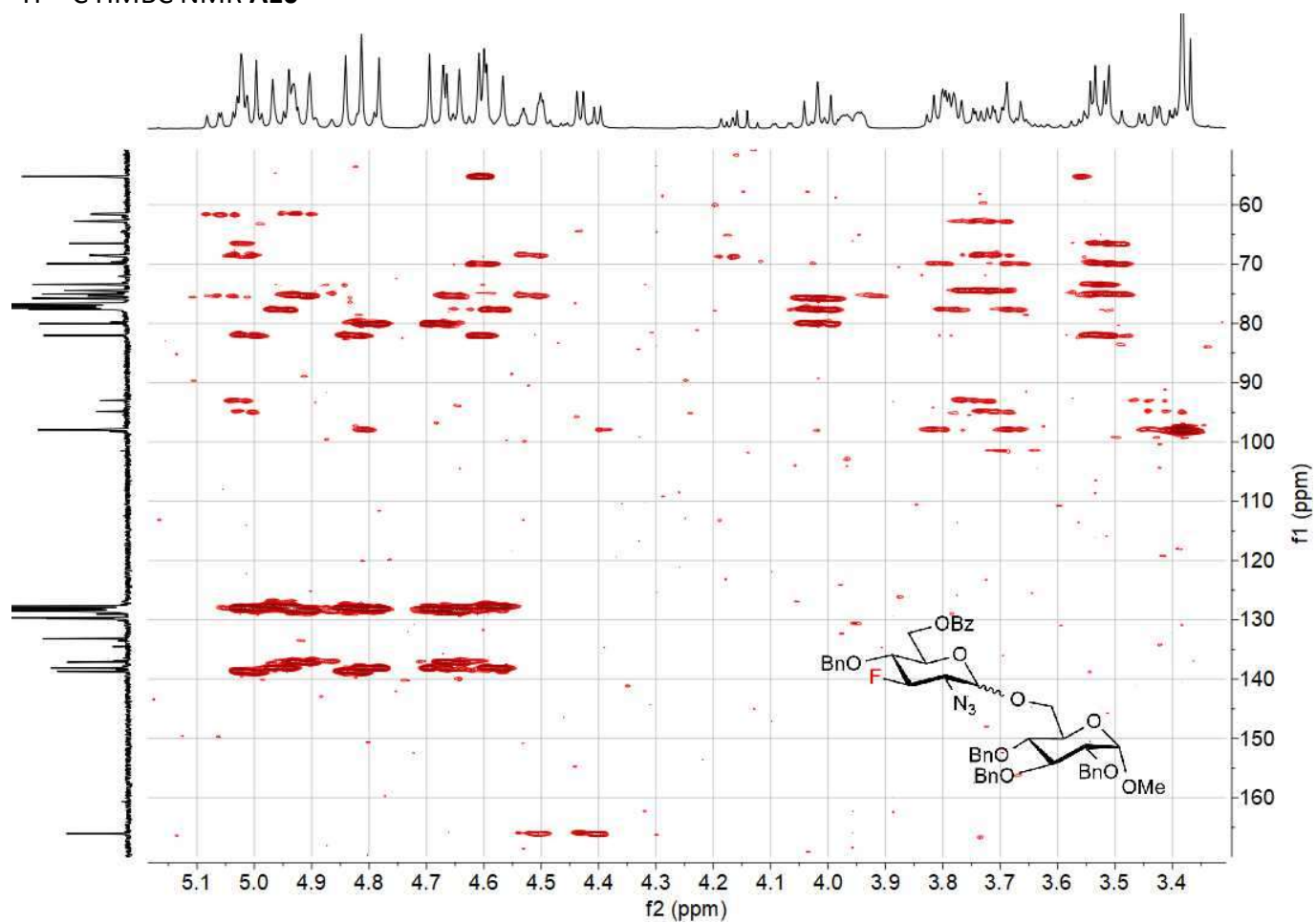


$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A10**

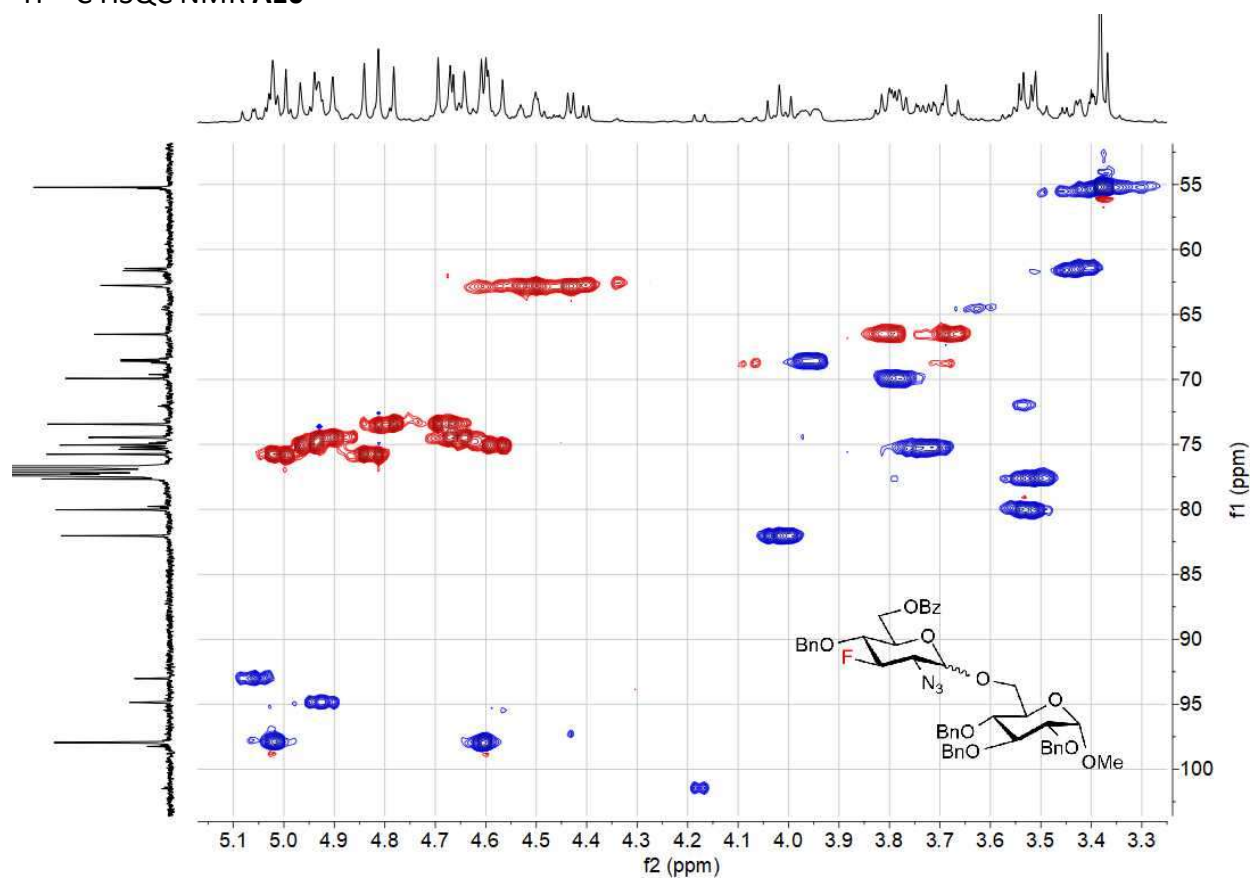




$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR A10

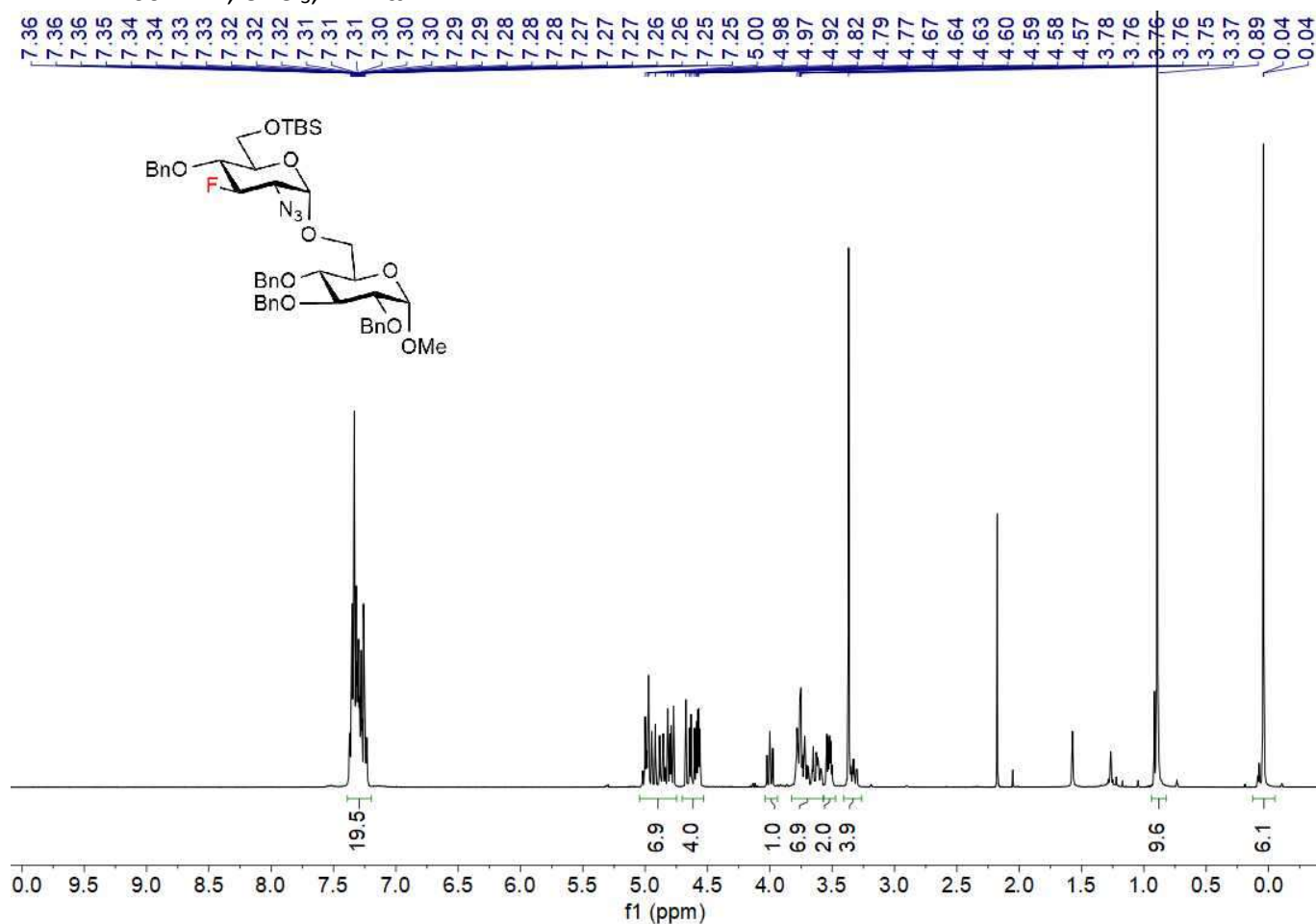


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR A10

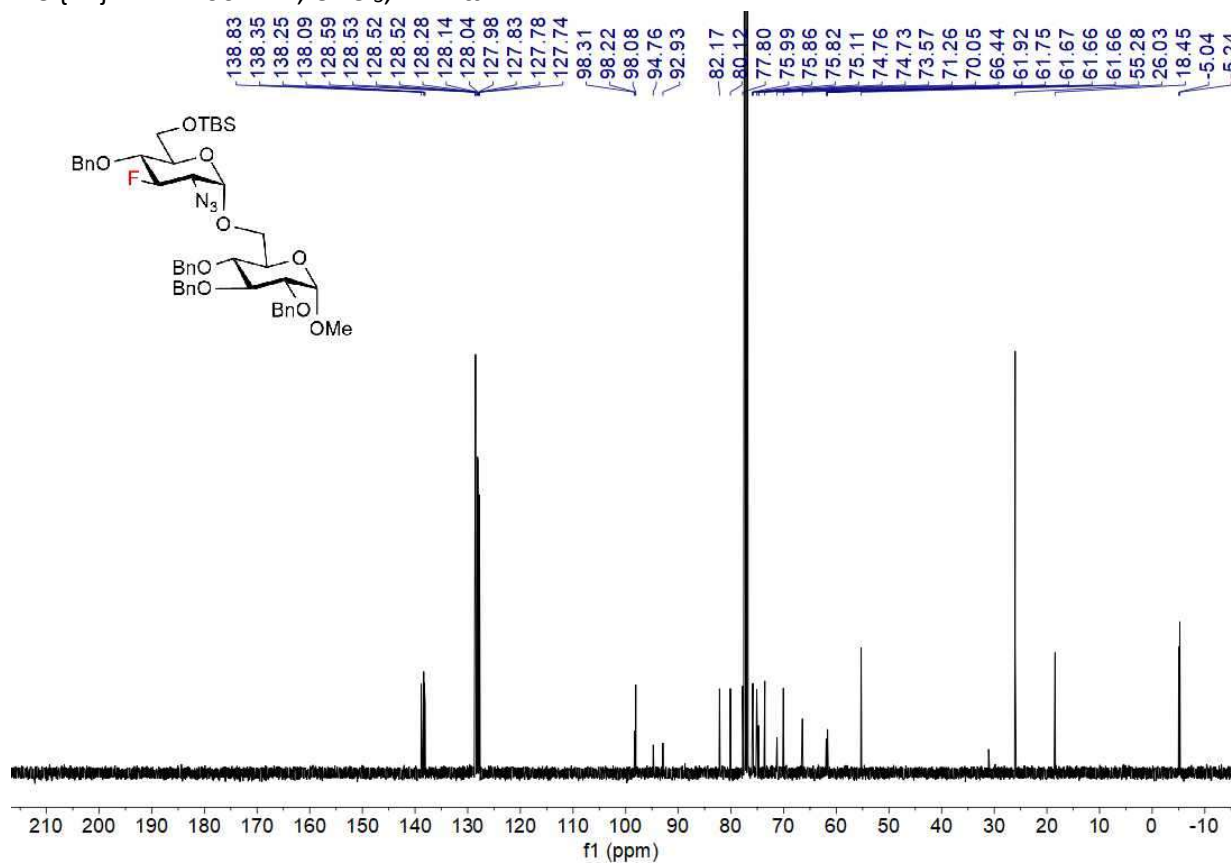


# **NMR A11- $\alpha$**

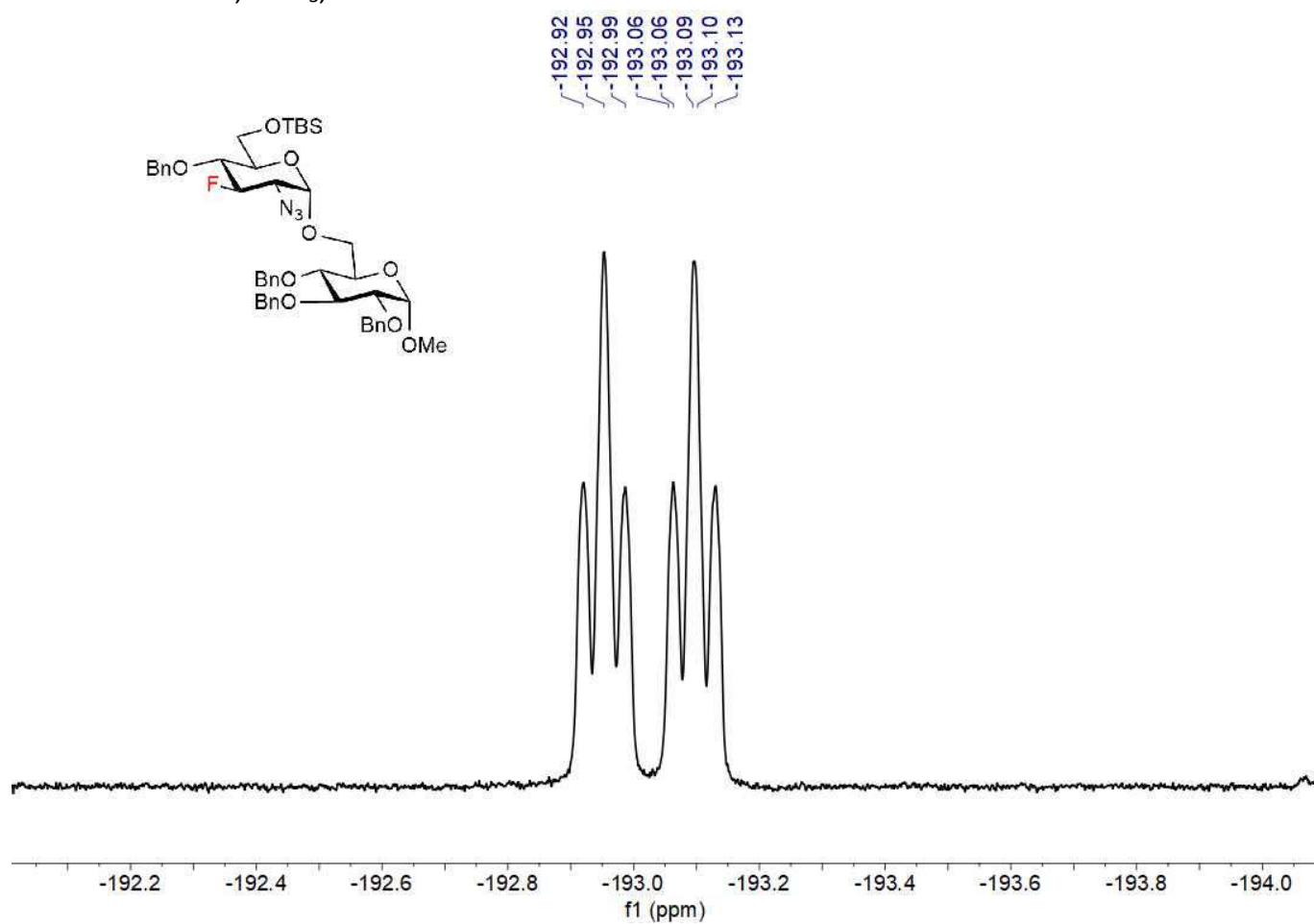
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **A11- $\alpha$**



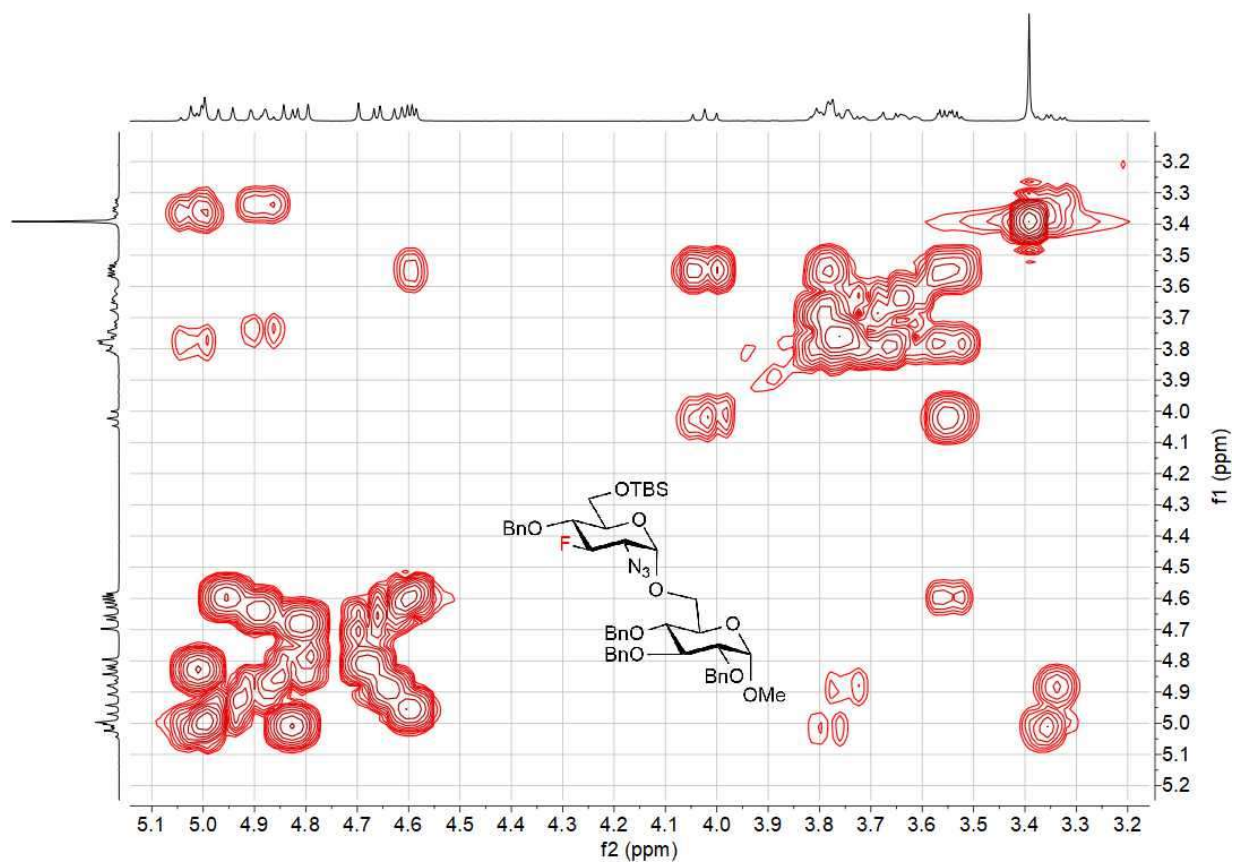
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **A11- $\alpha$**



$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A11- $\alpha$**

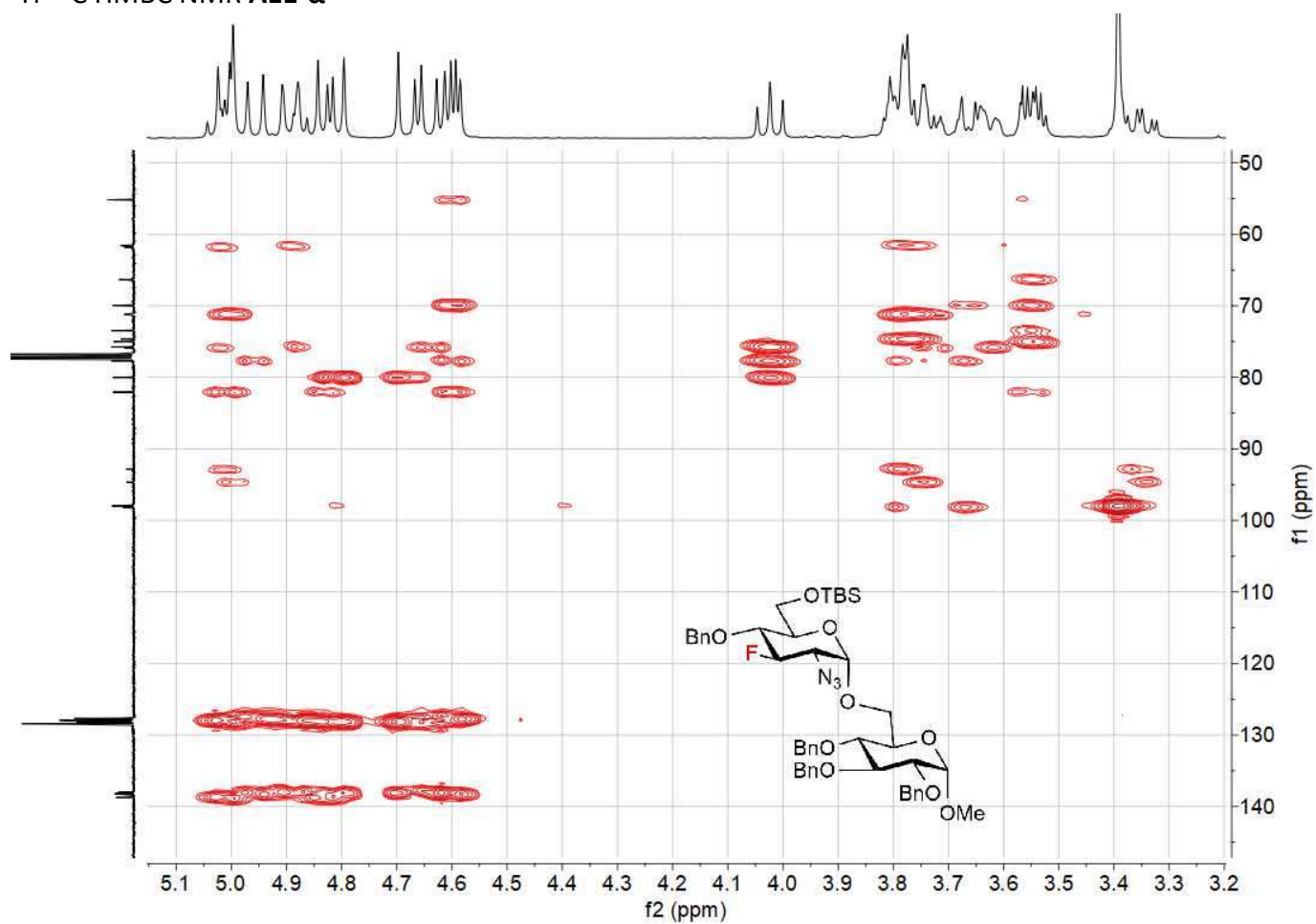


$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A11- $\alpha$**

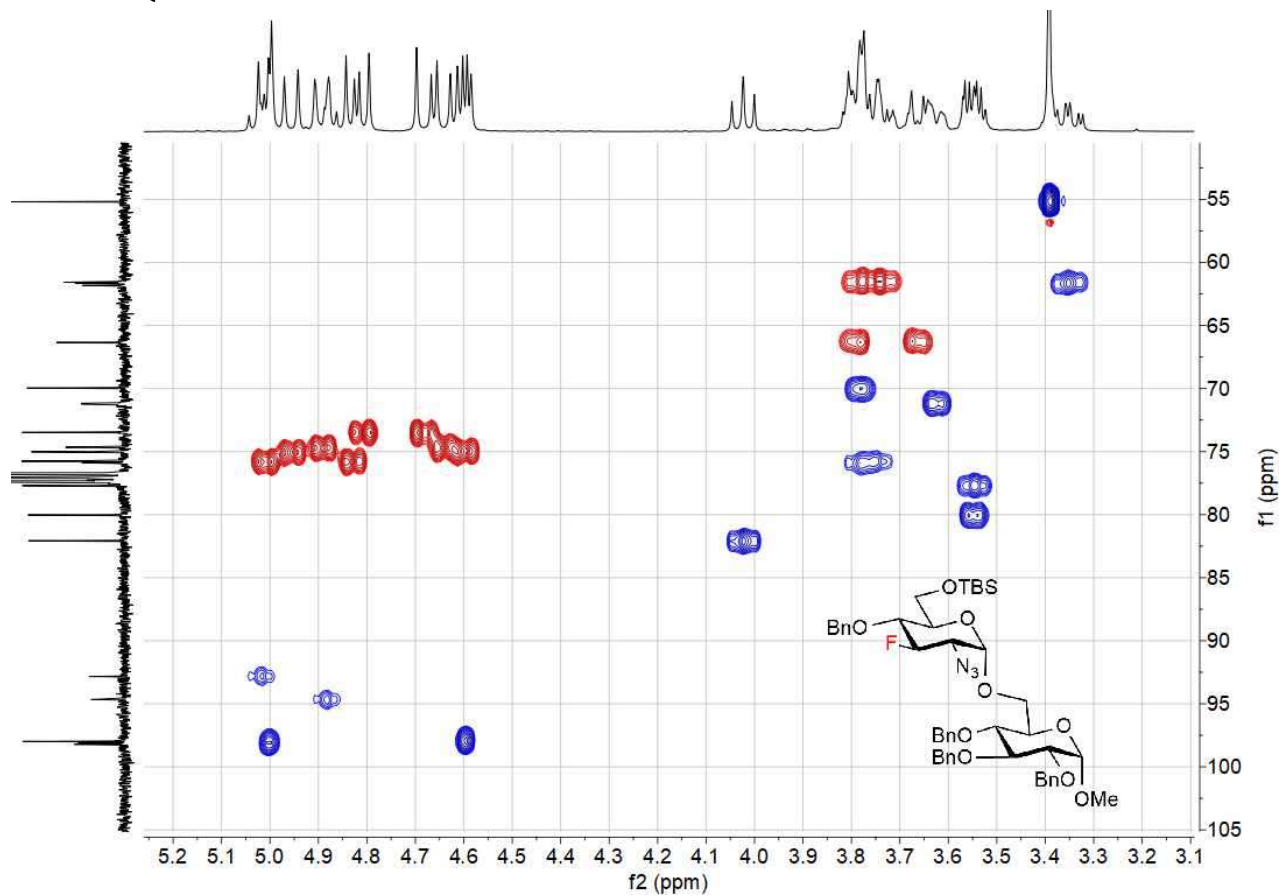


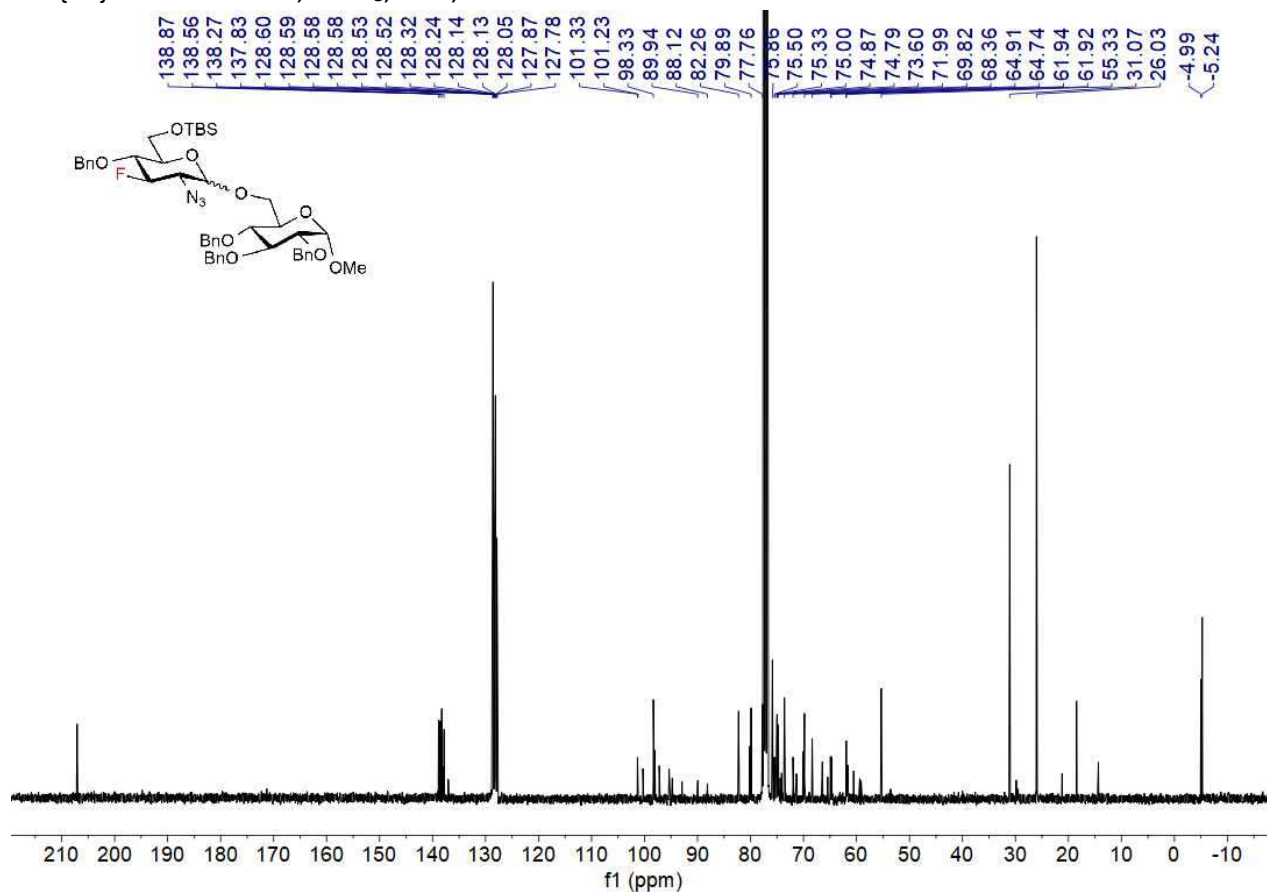
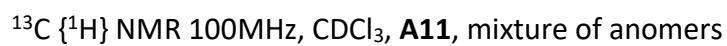


$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **A11- $\alpha$**

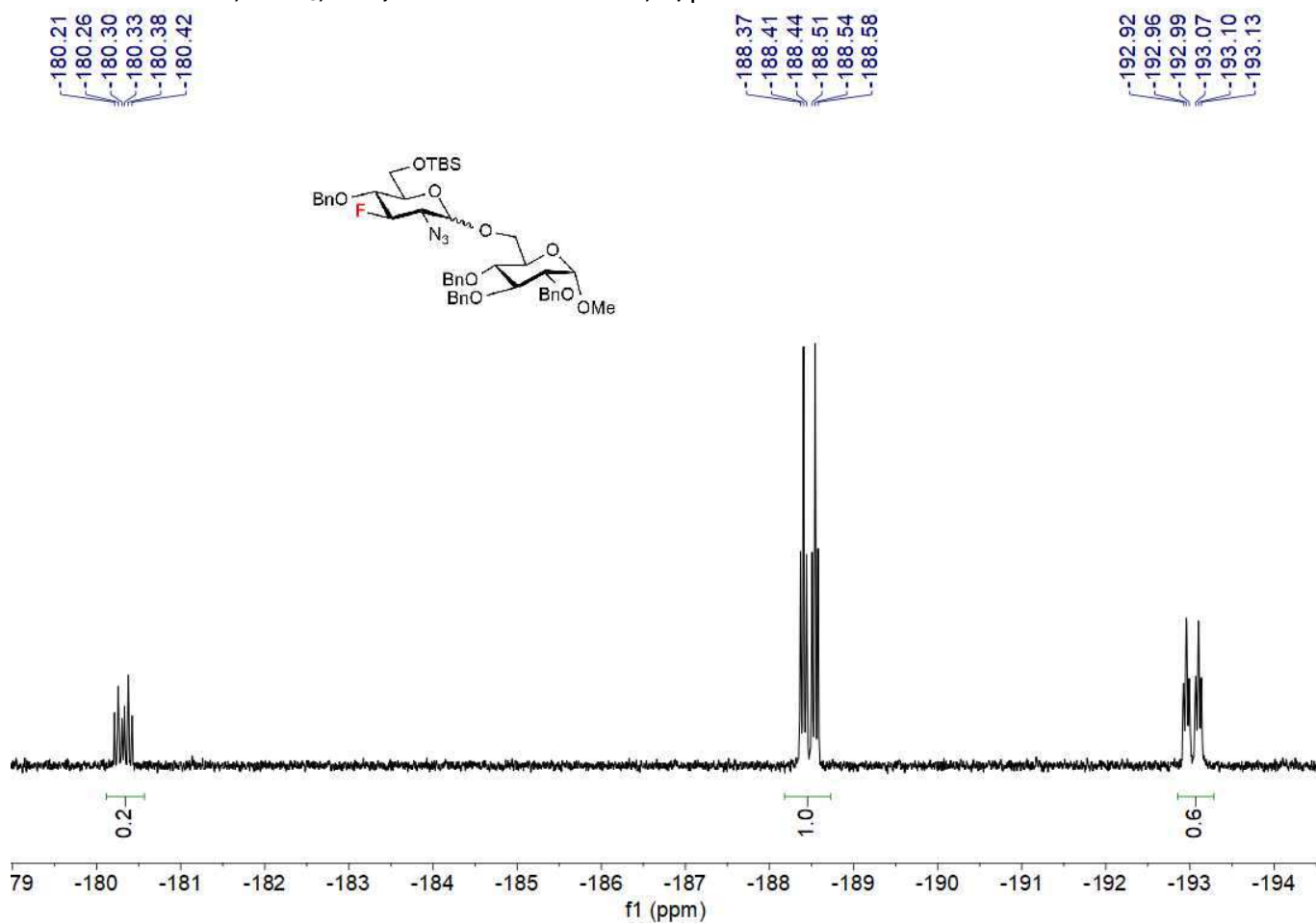


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **A11- $\alpha$**

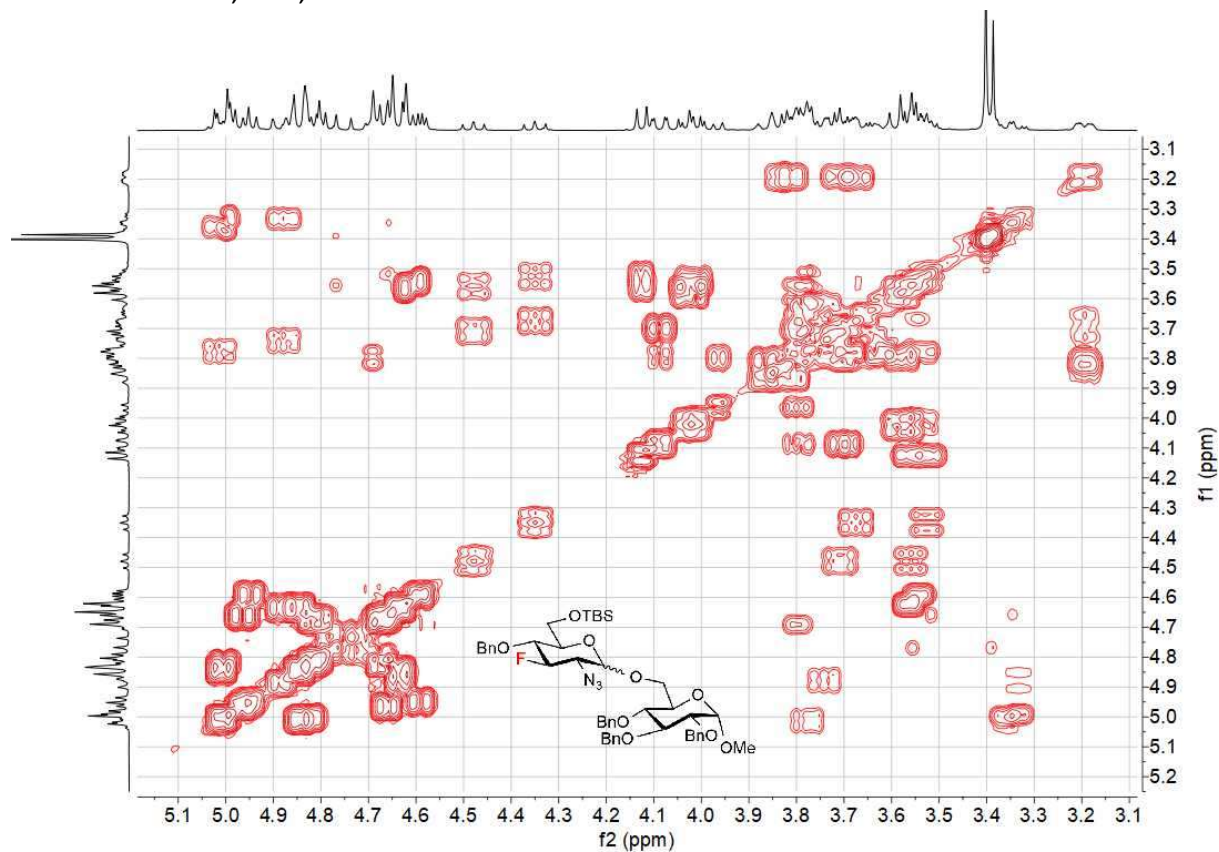


<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **A11**, mixture of anomers

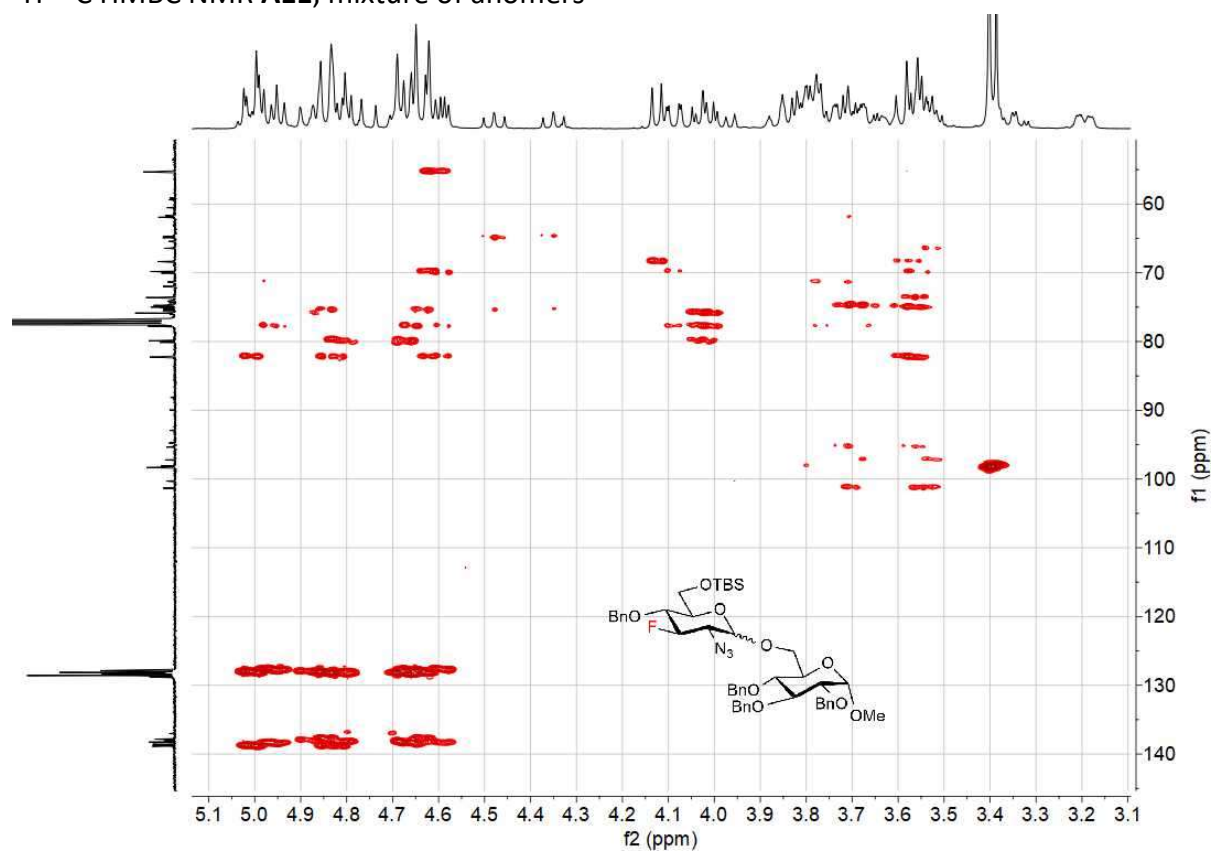
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A11**, mixture of anomers,  $\alpha/\beta$  3:5



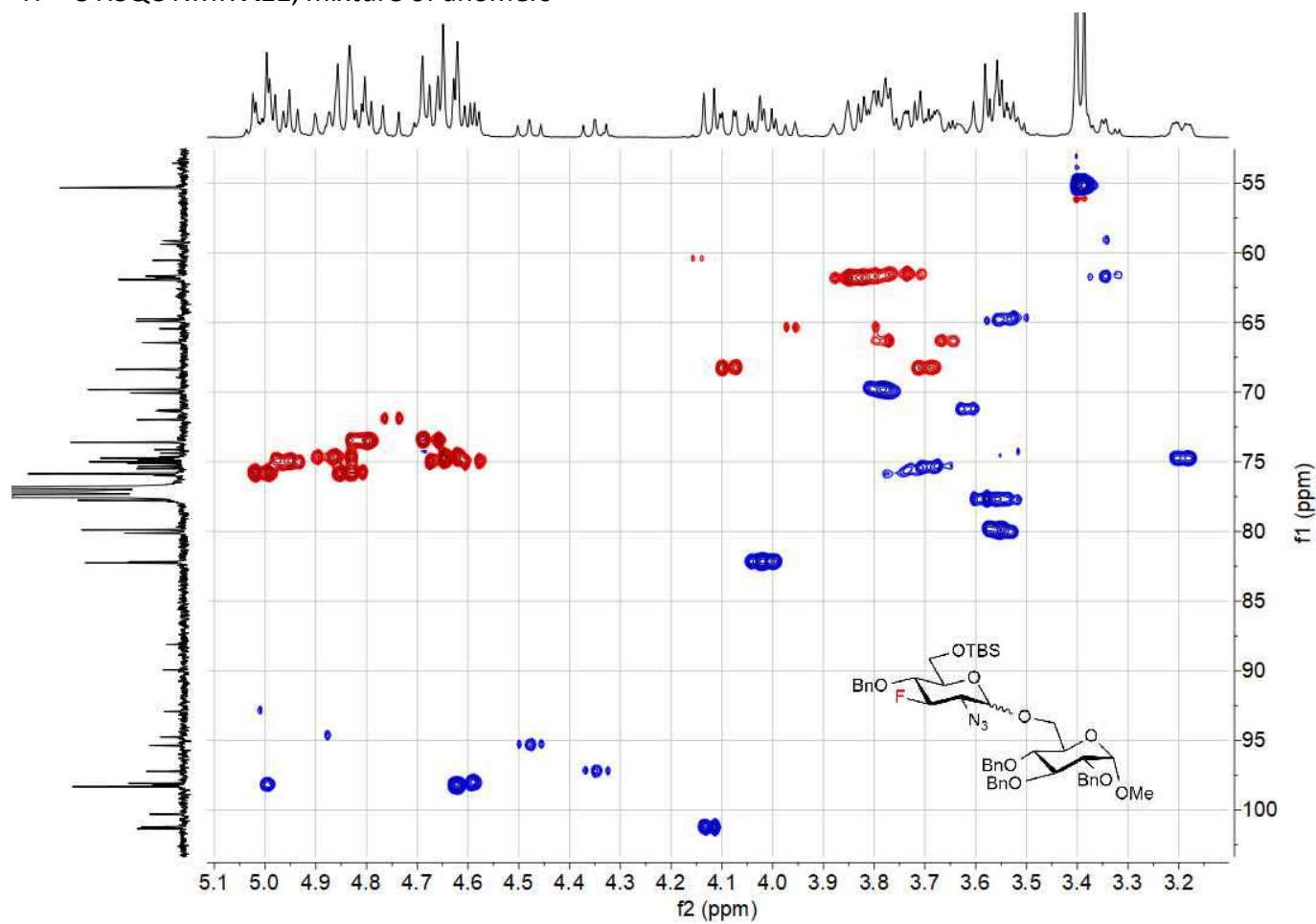
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A11**, mixture of anomers

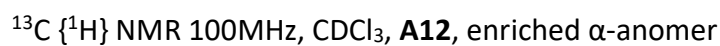


$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **A11**, mixture of anomers



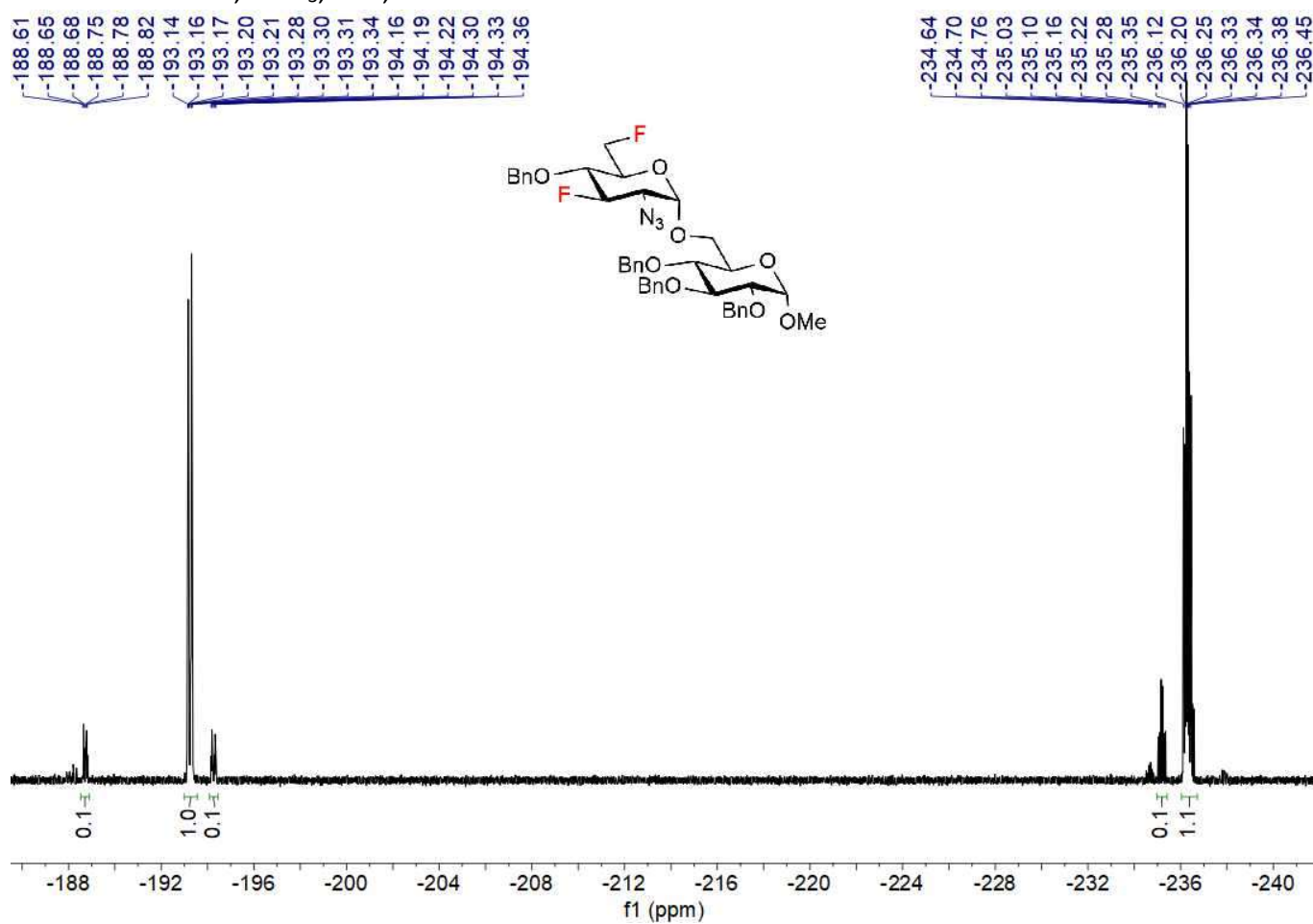
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **A11**, mixture of anomers



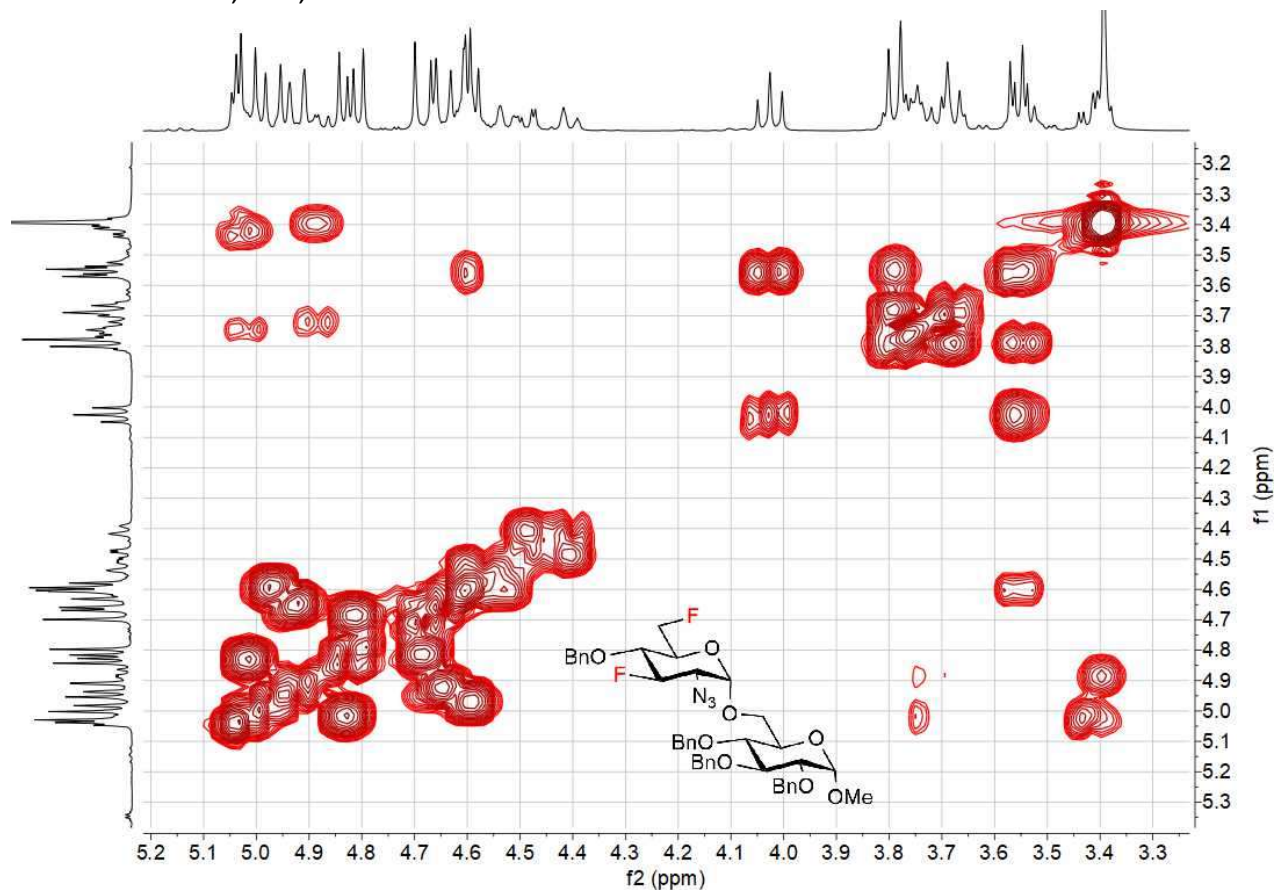
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **A12**, enriched α-anomer



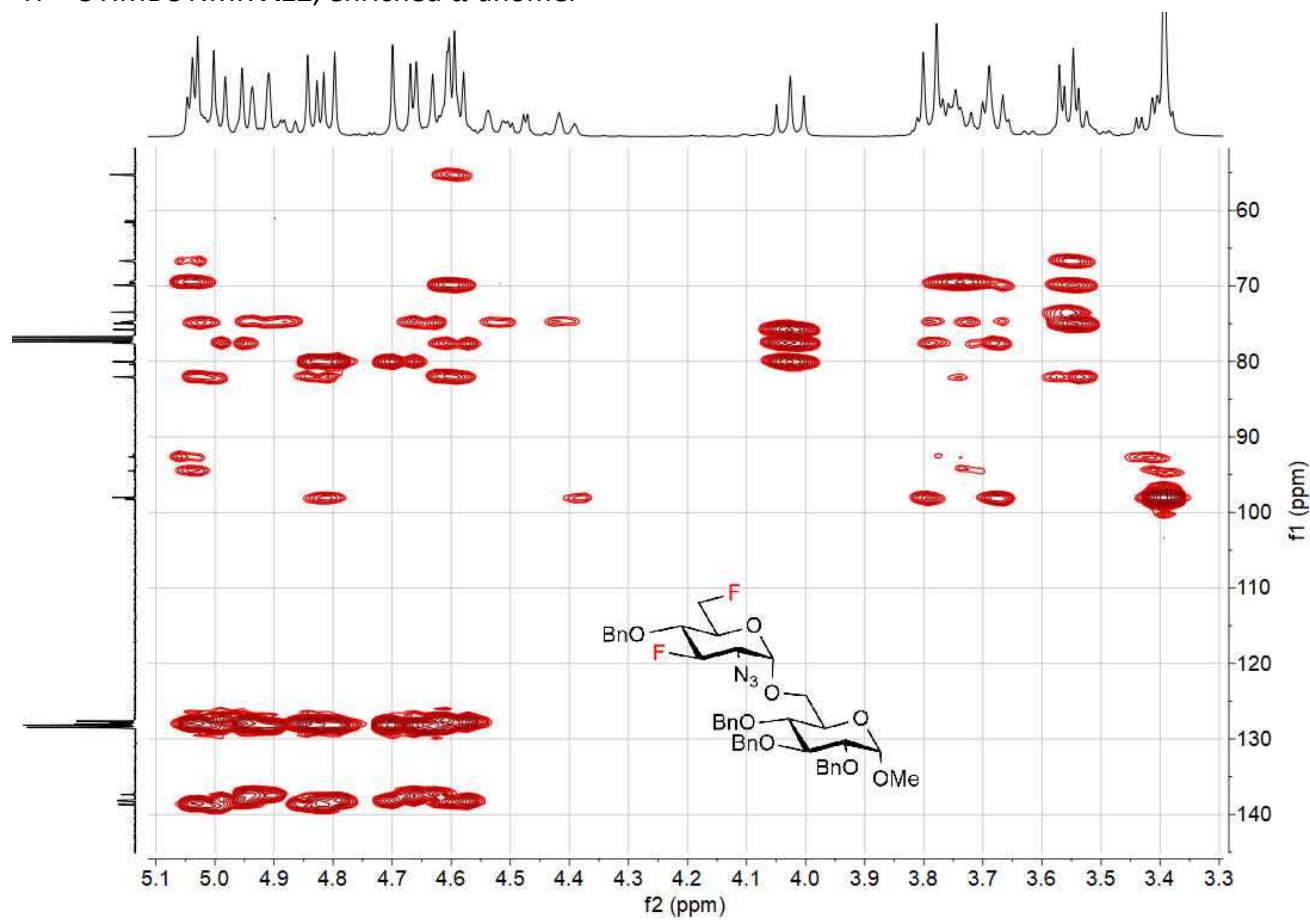
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A12**, enriched  $\alpha$ -anomer



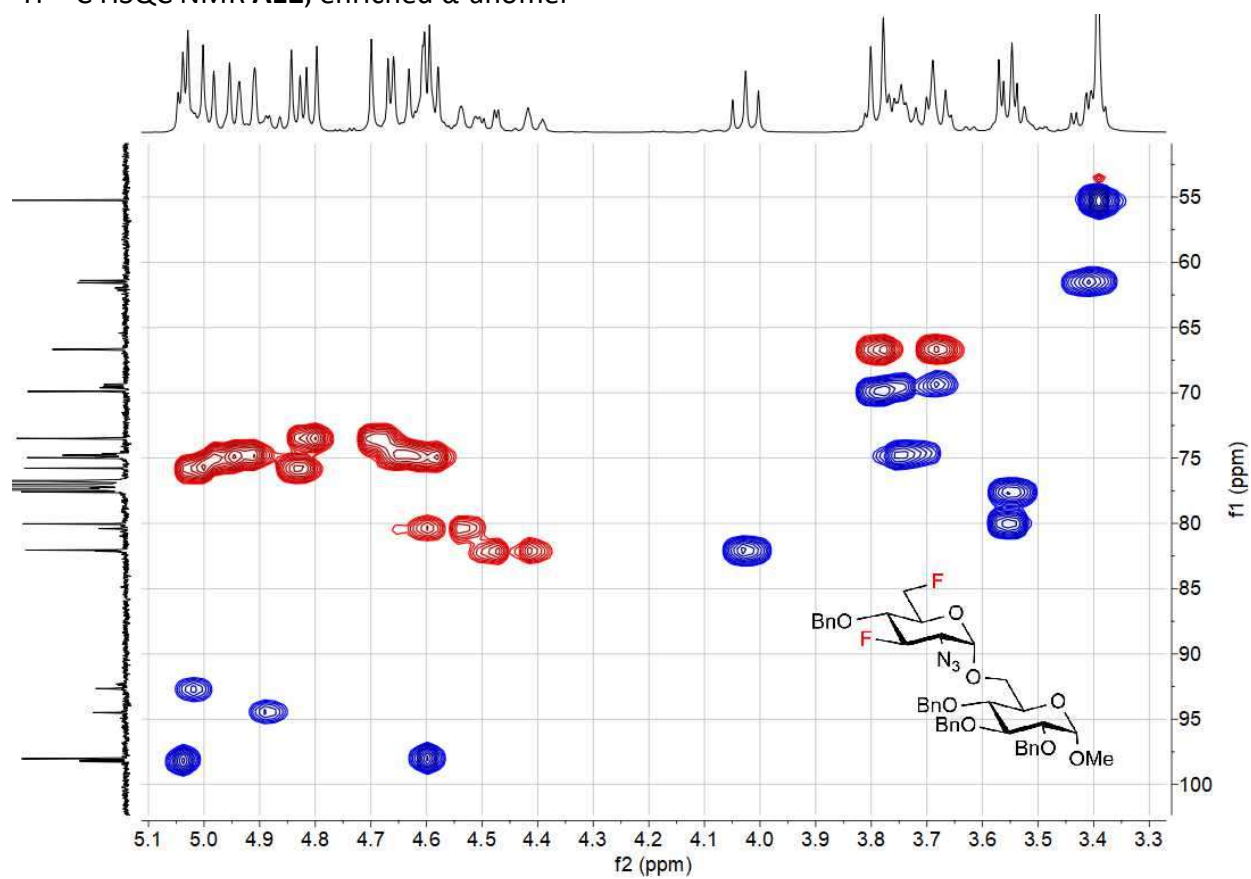
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A12**, enriched  $\alpha$ -anomer



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **A12**, enriched  $\alpha$ -anomer



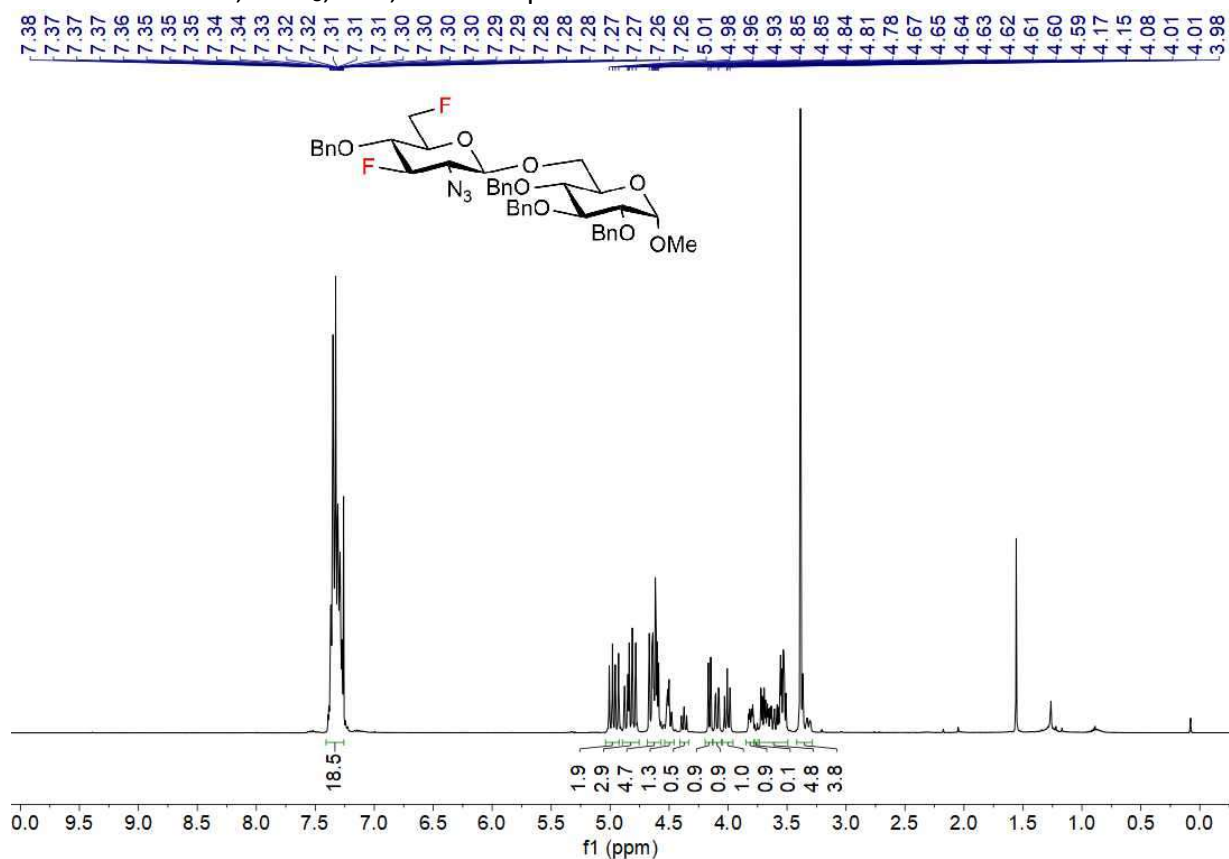
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **A12**, enriched  $\alpha$ -anomer



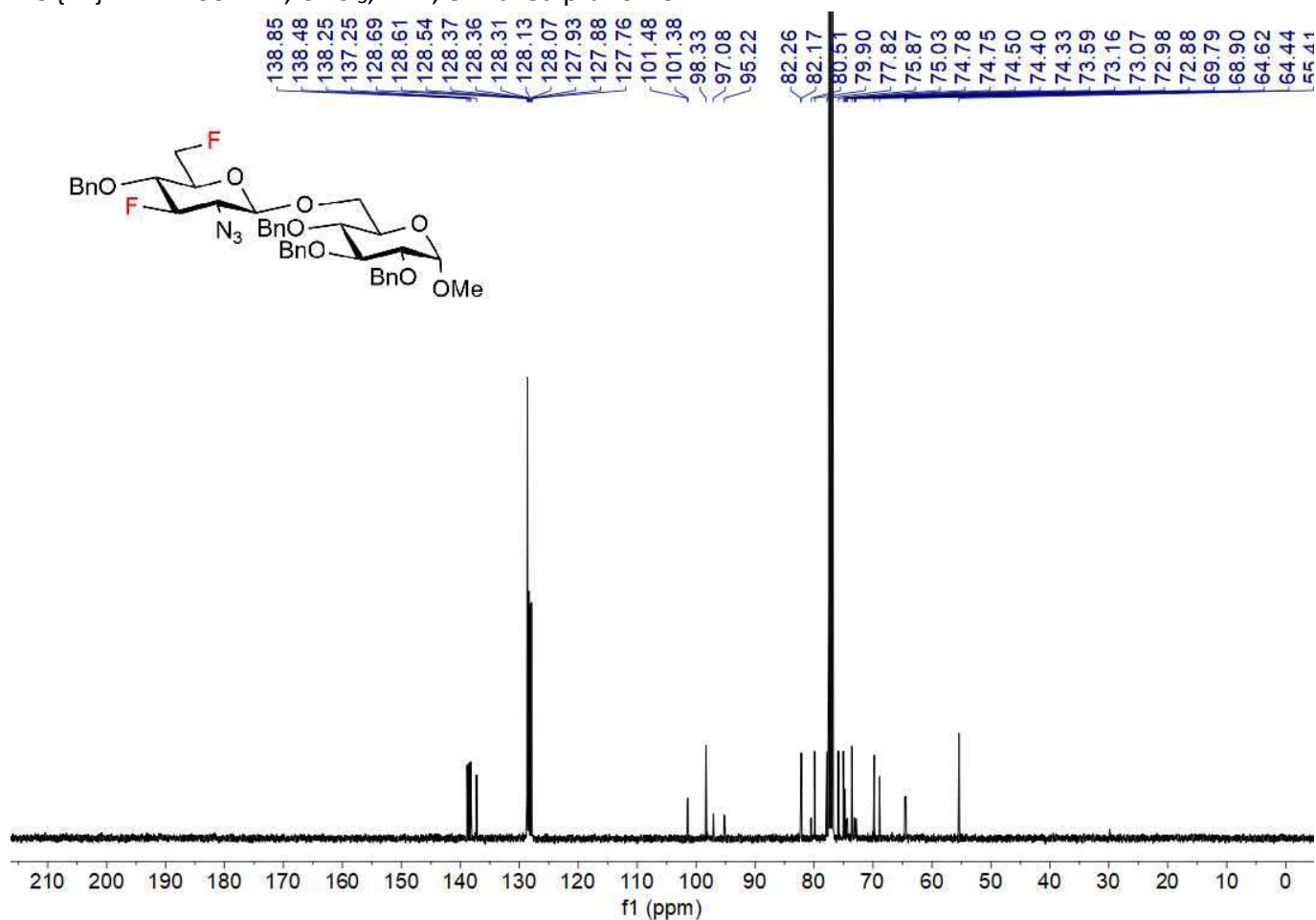


# **NMR A12, enriched $\beta$ -anomer**

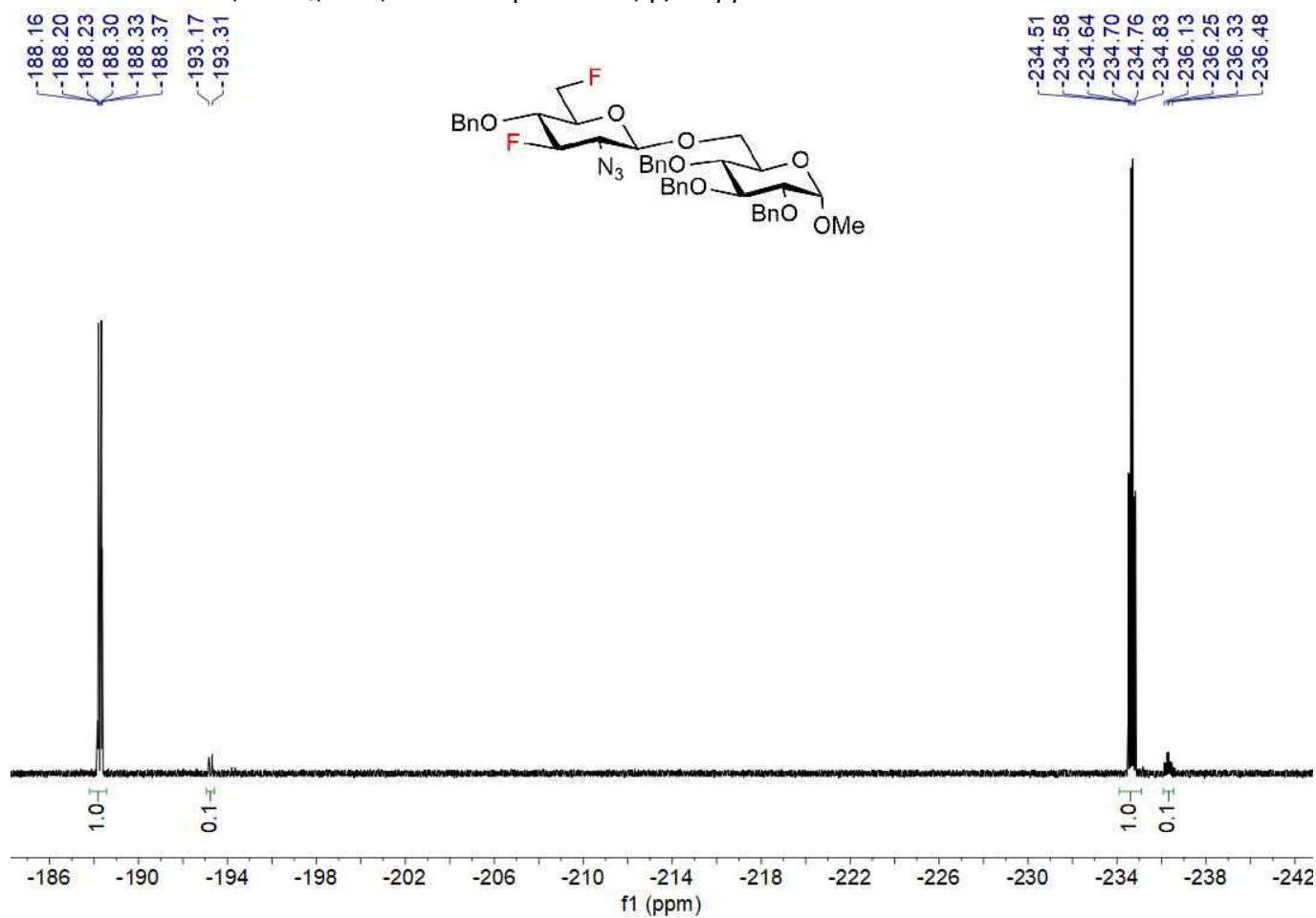
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **A12**, enriched  $\beta$ -anomer



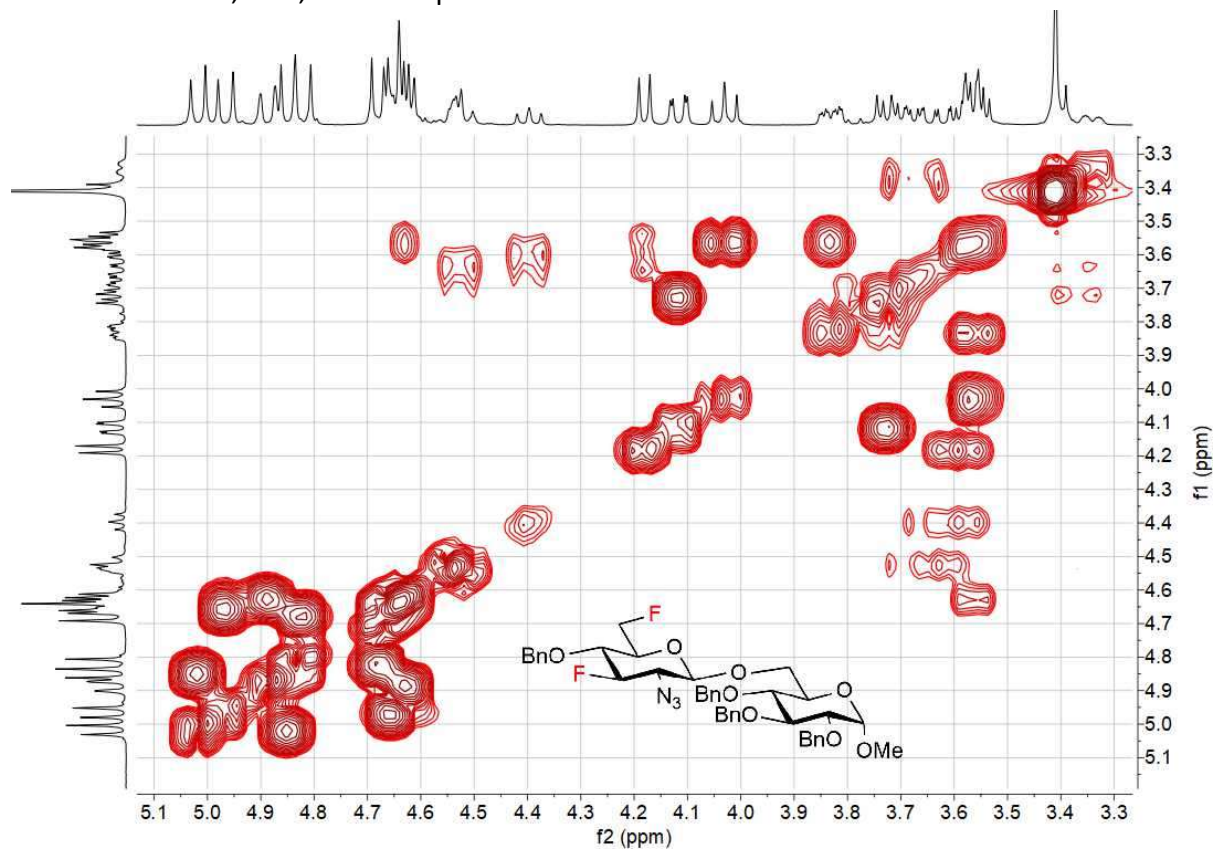
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **A12**, enriched  $\beta$ -anomer



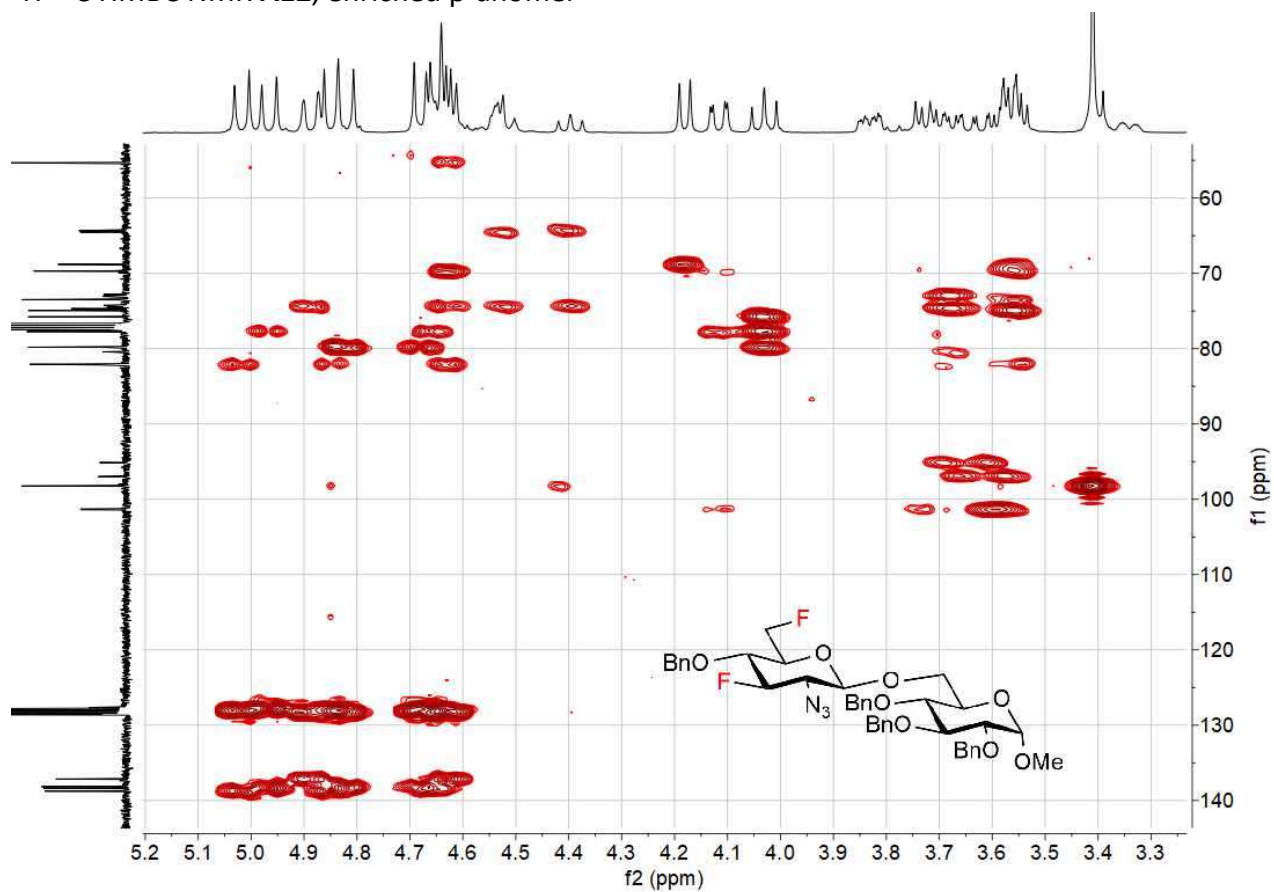
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A12**, enriched  $\beta$ -anomer,  $\beta/\alpha$  approx. 10:1



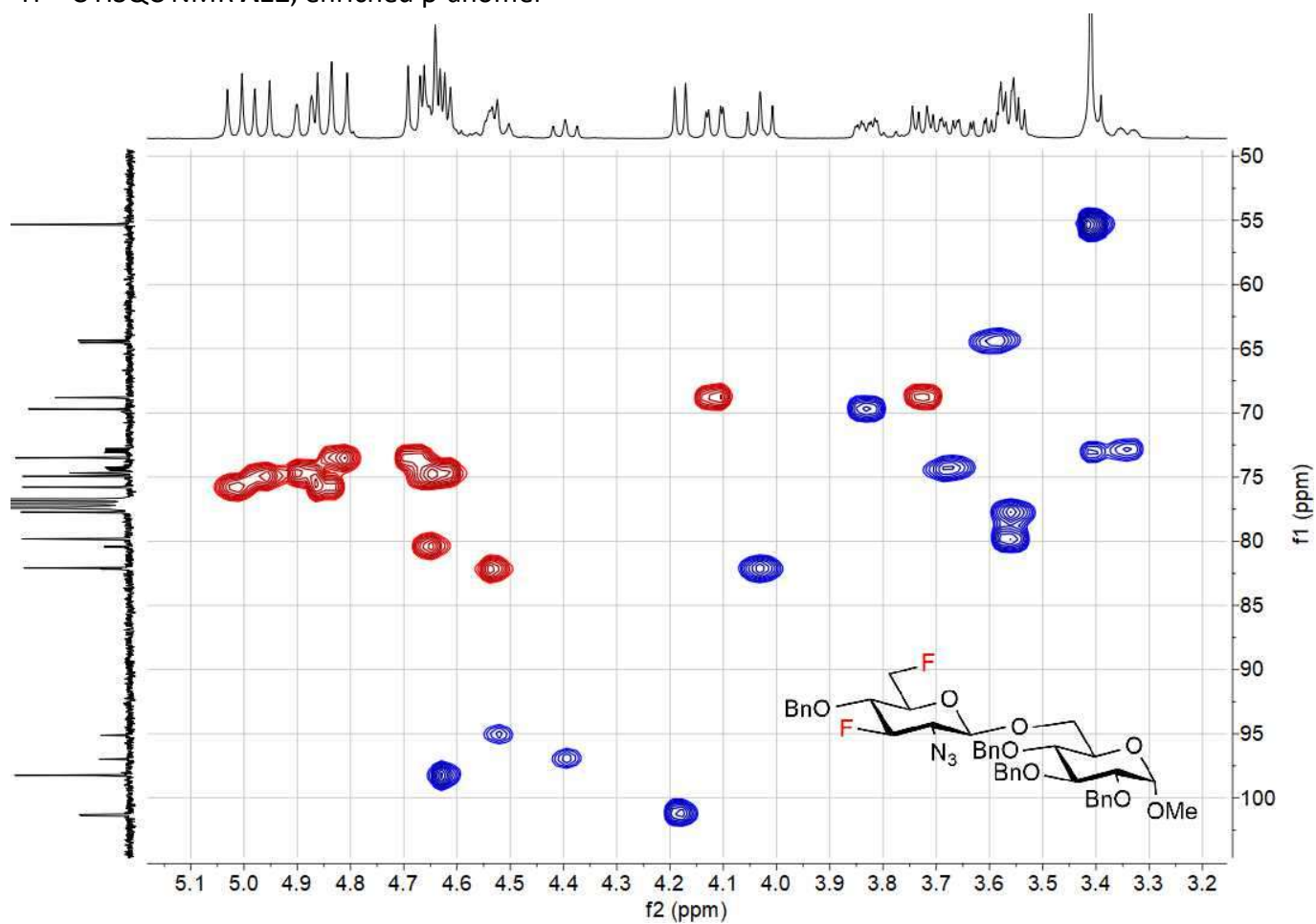
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A12**, enriched  $\beta$ -anomer



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **A12**, enriched  $\beta$ -anomer

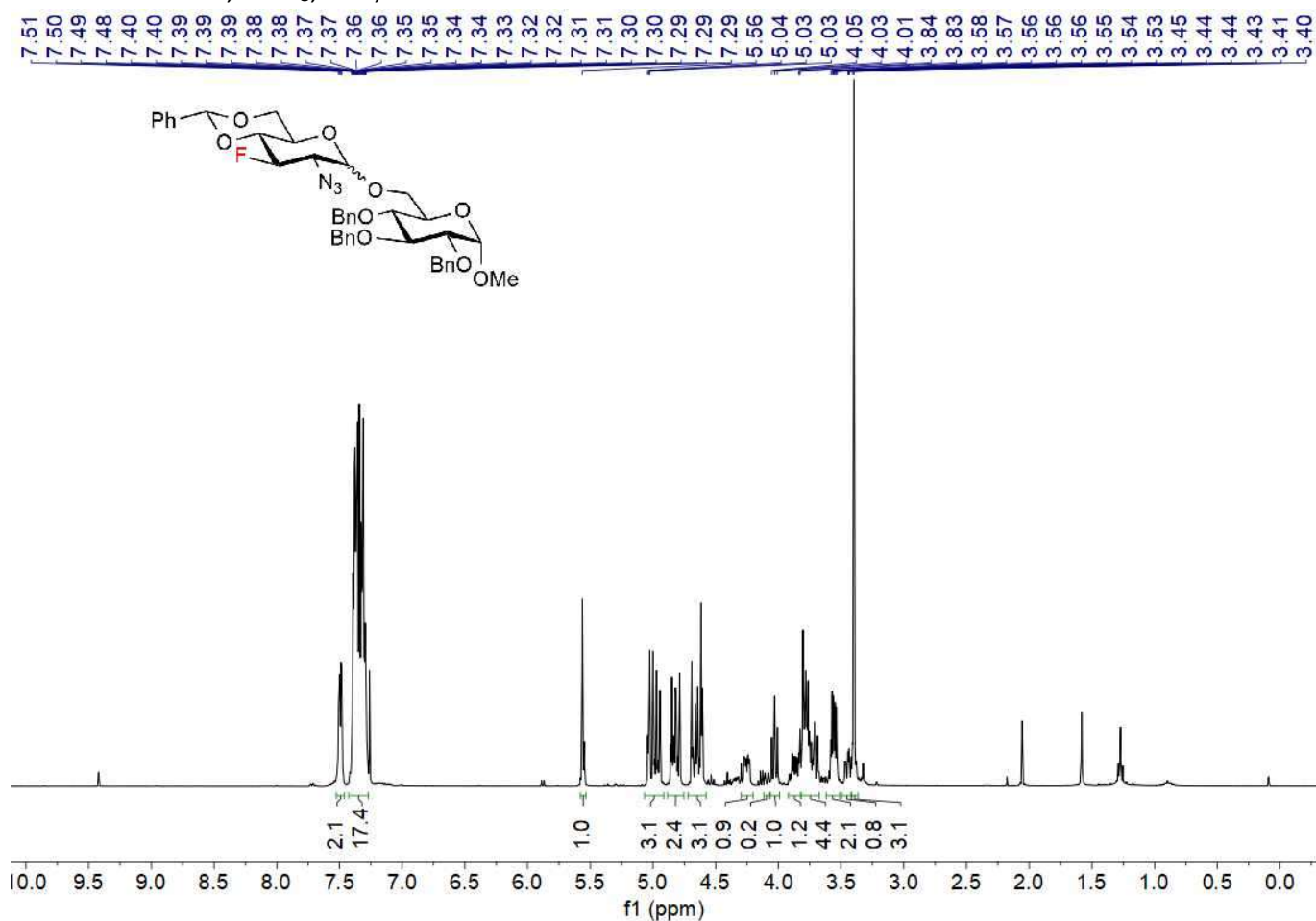


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **A12**, enriched  $\beta$ -anomer

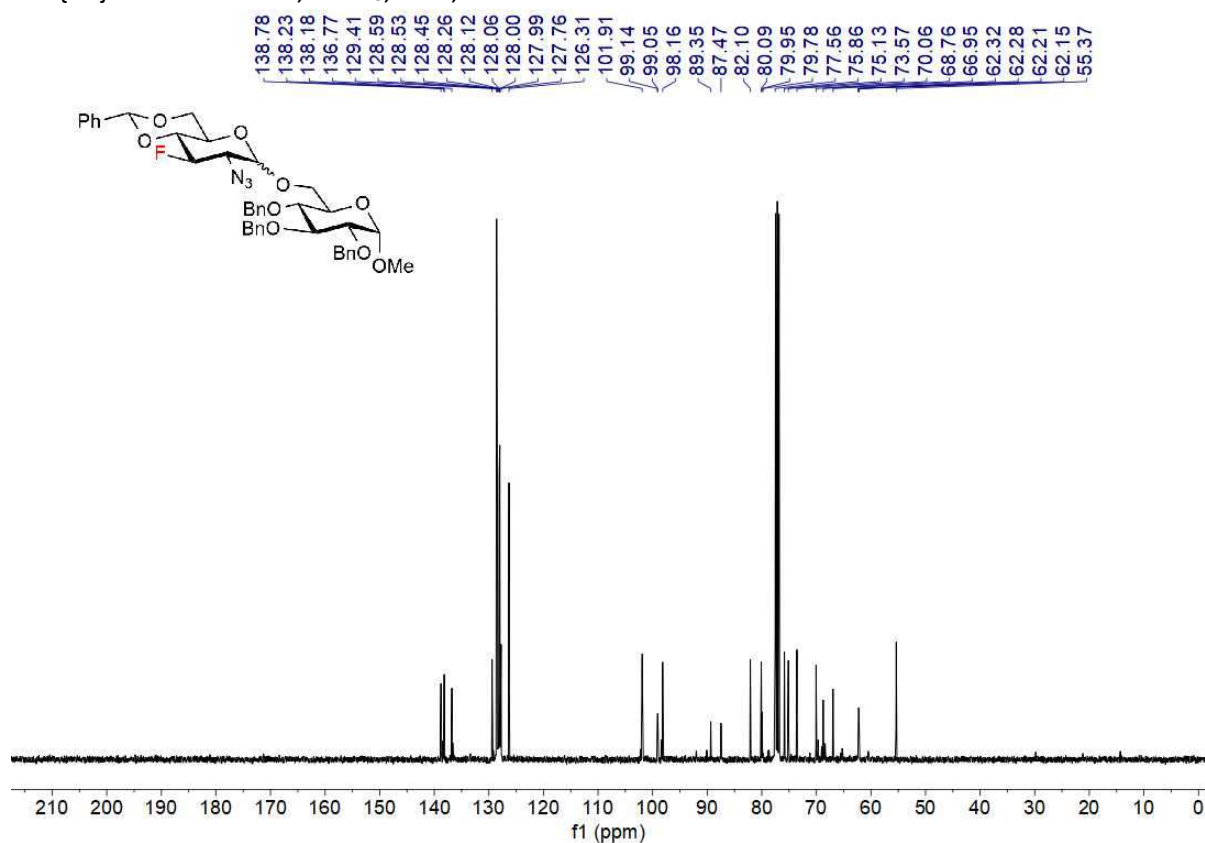


**NMR A13, mixture of anomers**

$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **A13**, mixture of anomers

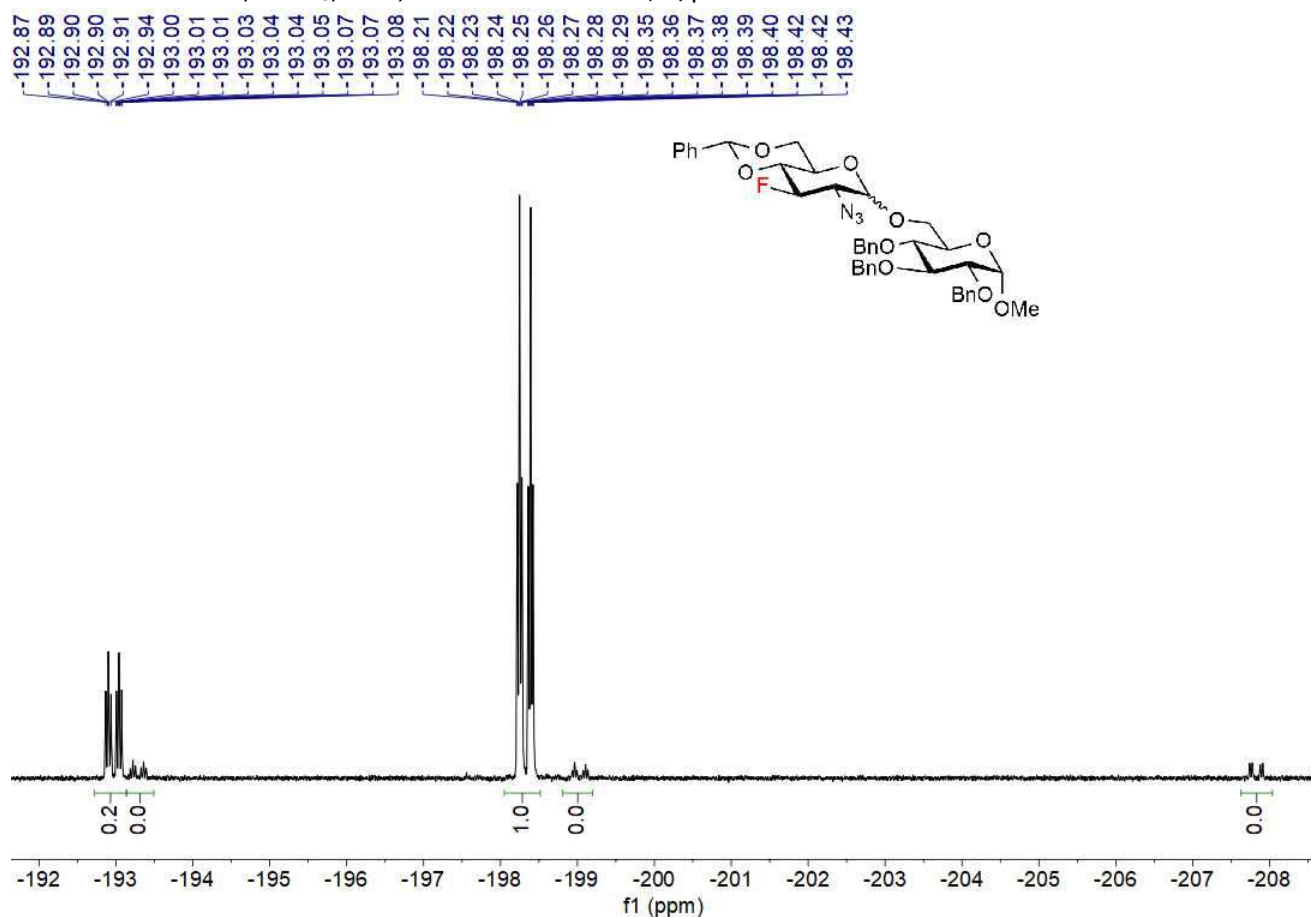


$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **A13**, mixture of anomers

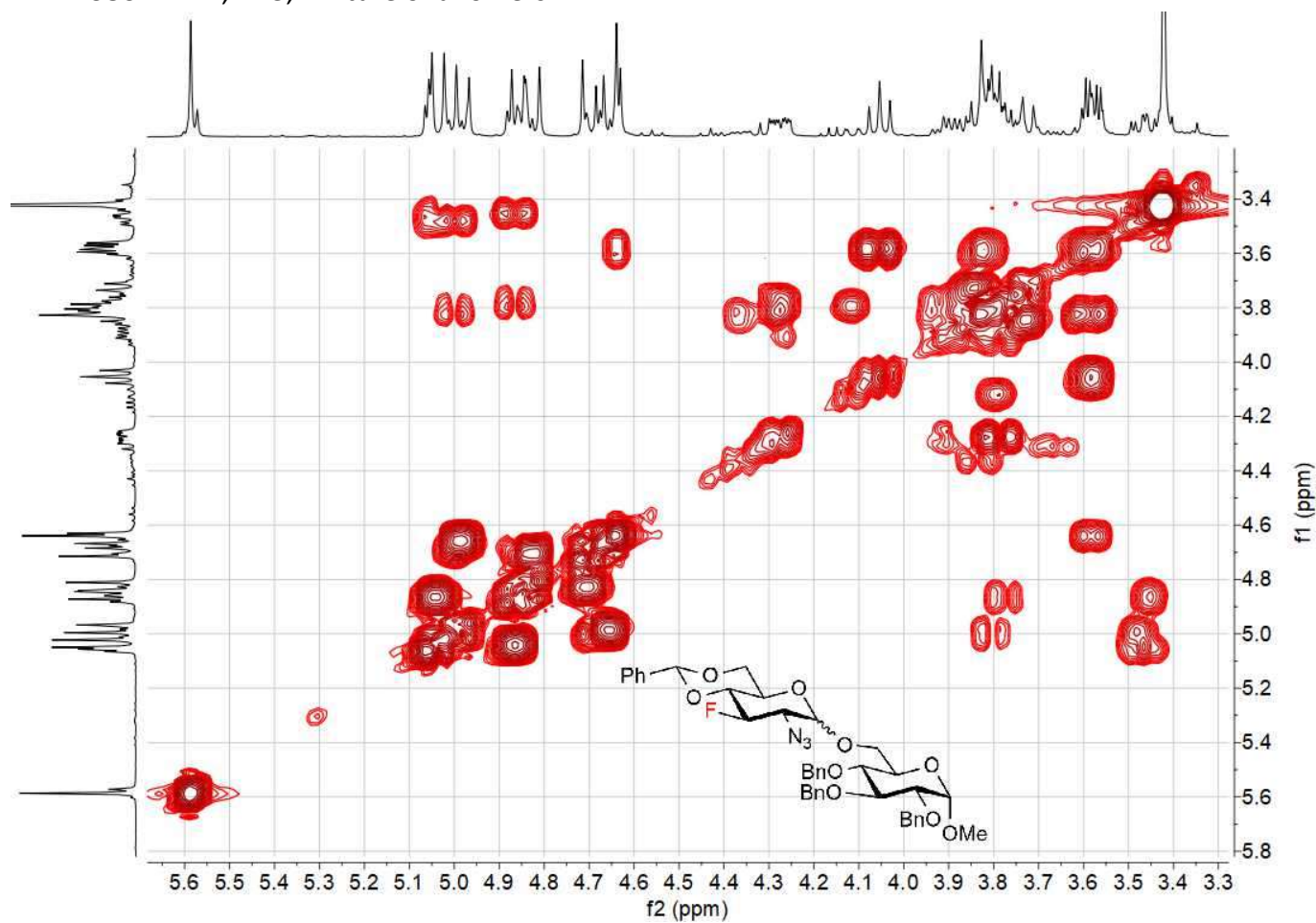




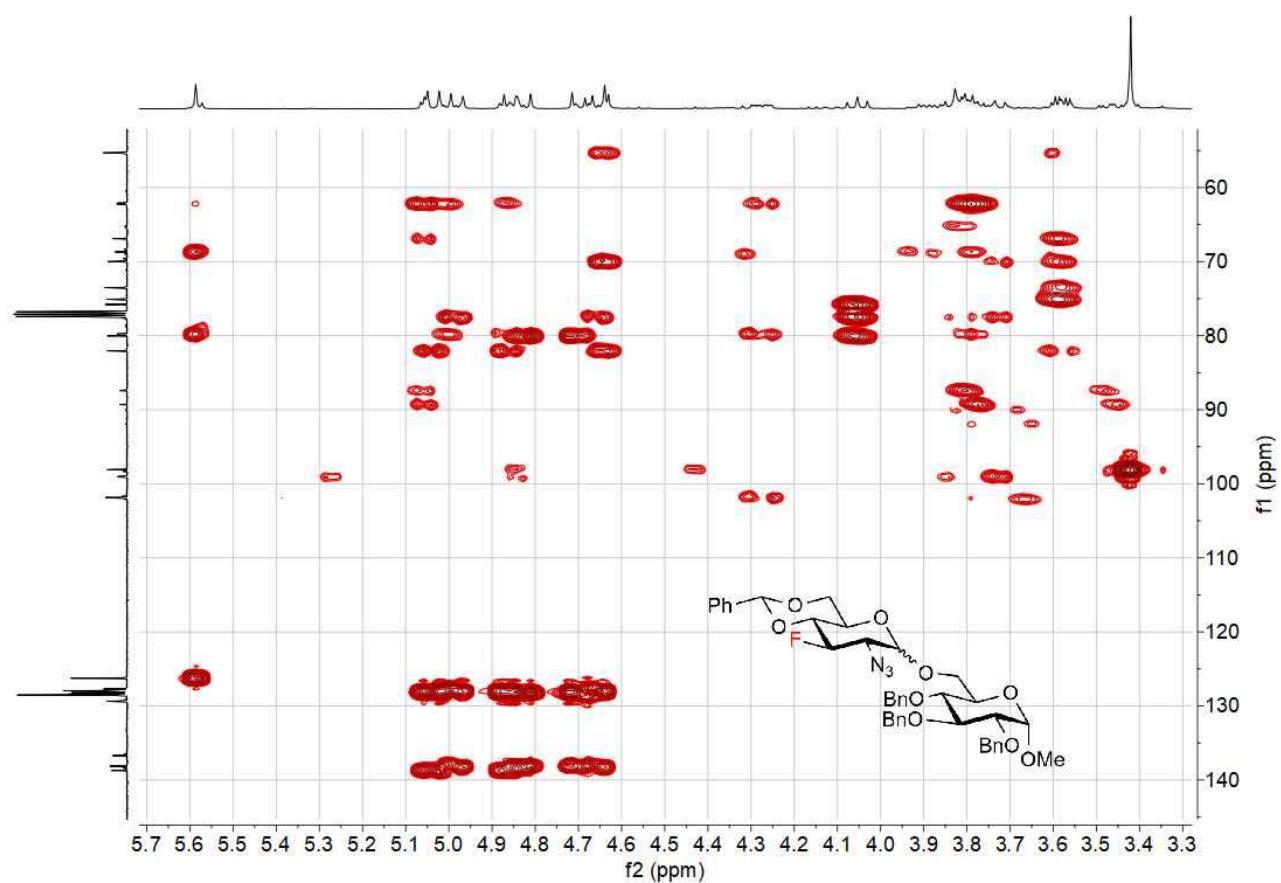
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A13**, mixture of anomers,  $\alpha/\beta$  5:1



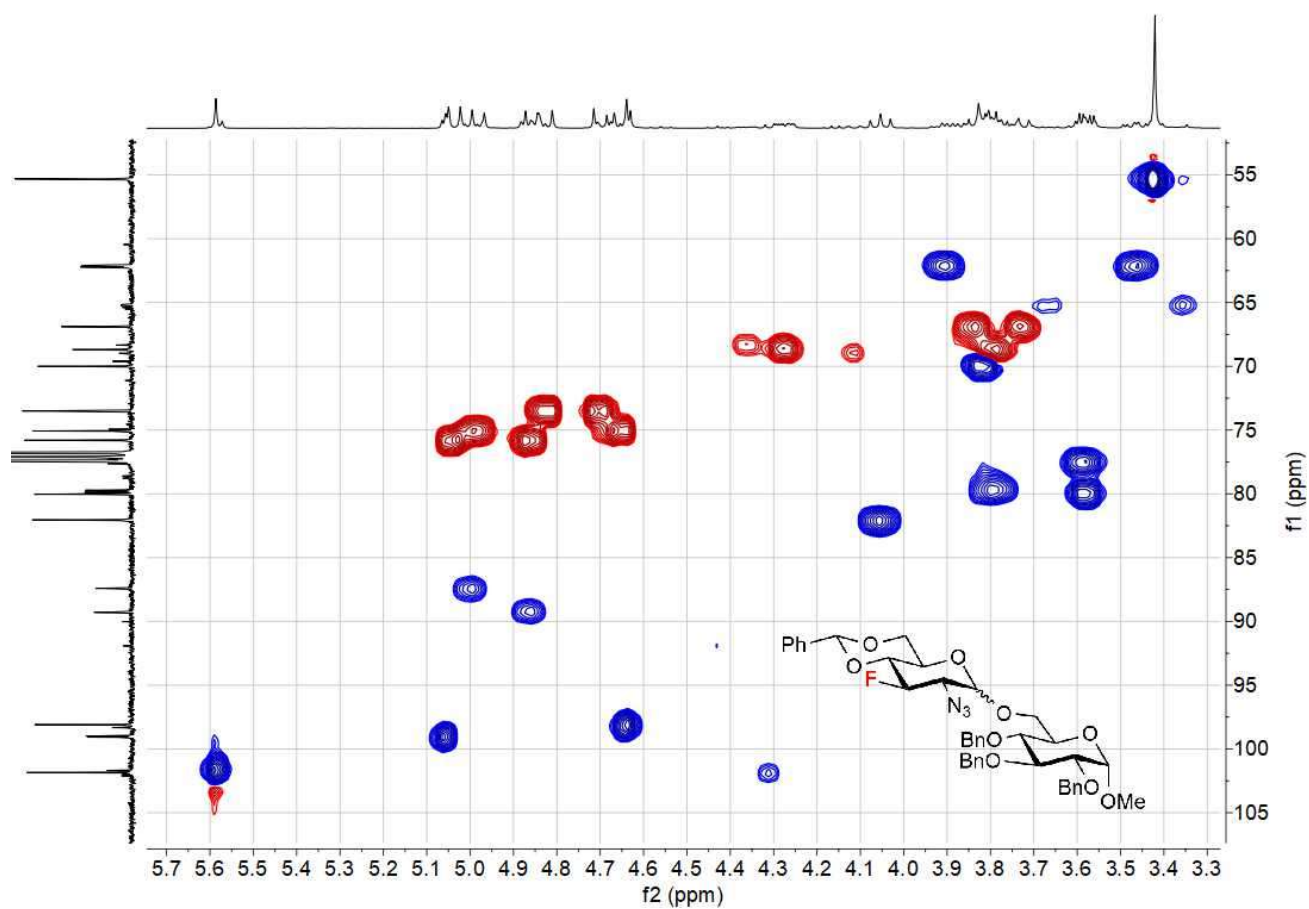
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A13**, mixture of anomers



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **A13**, mixture of anomers



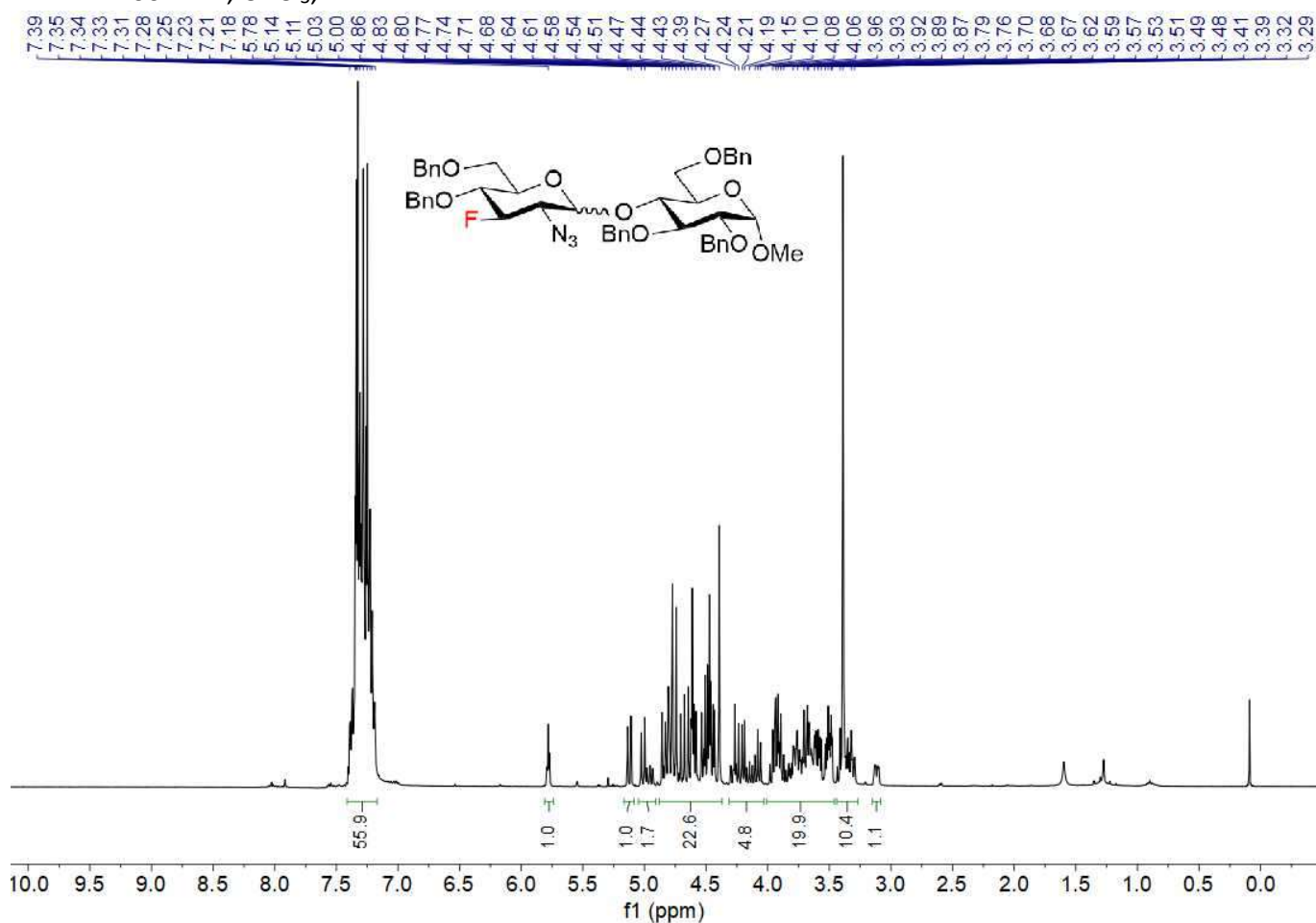
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **A13**, mixture of anomers



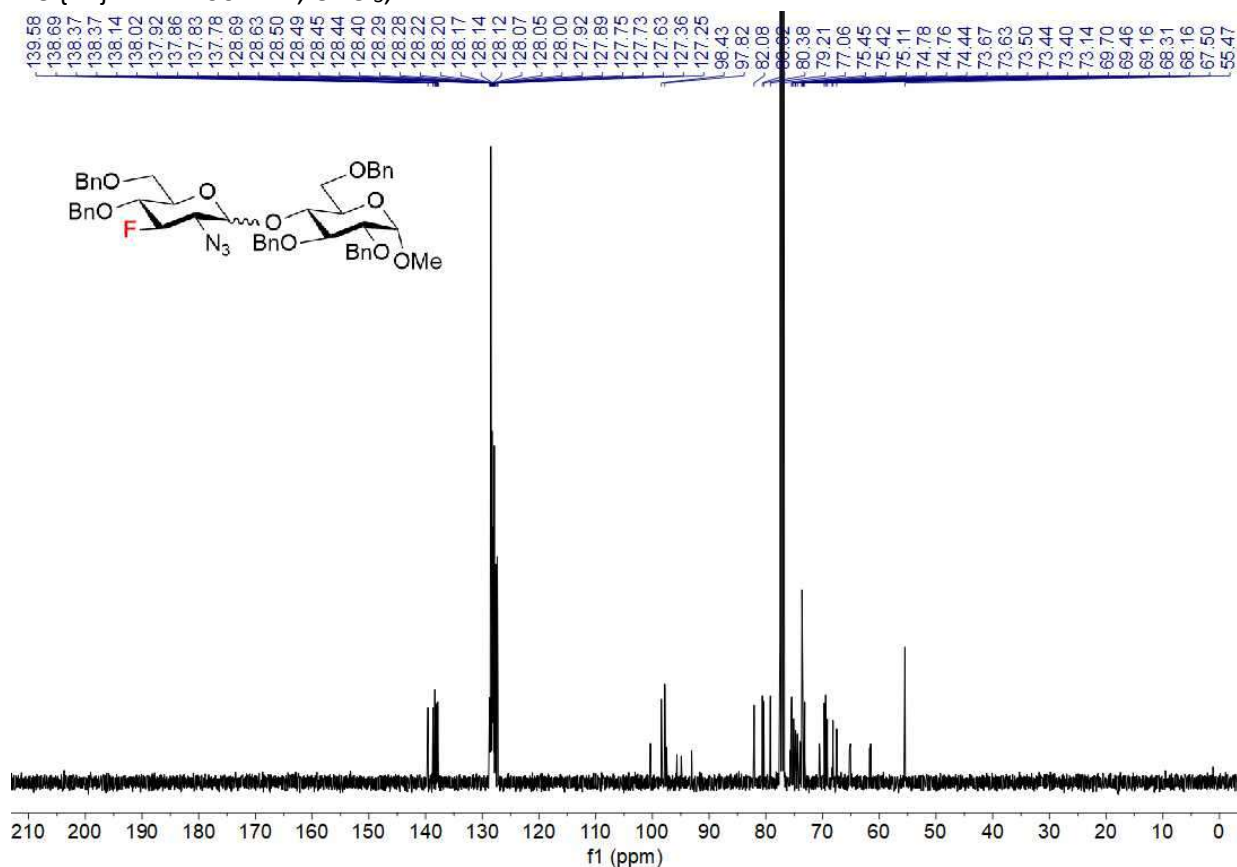


# **NMR B1**

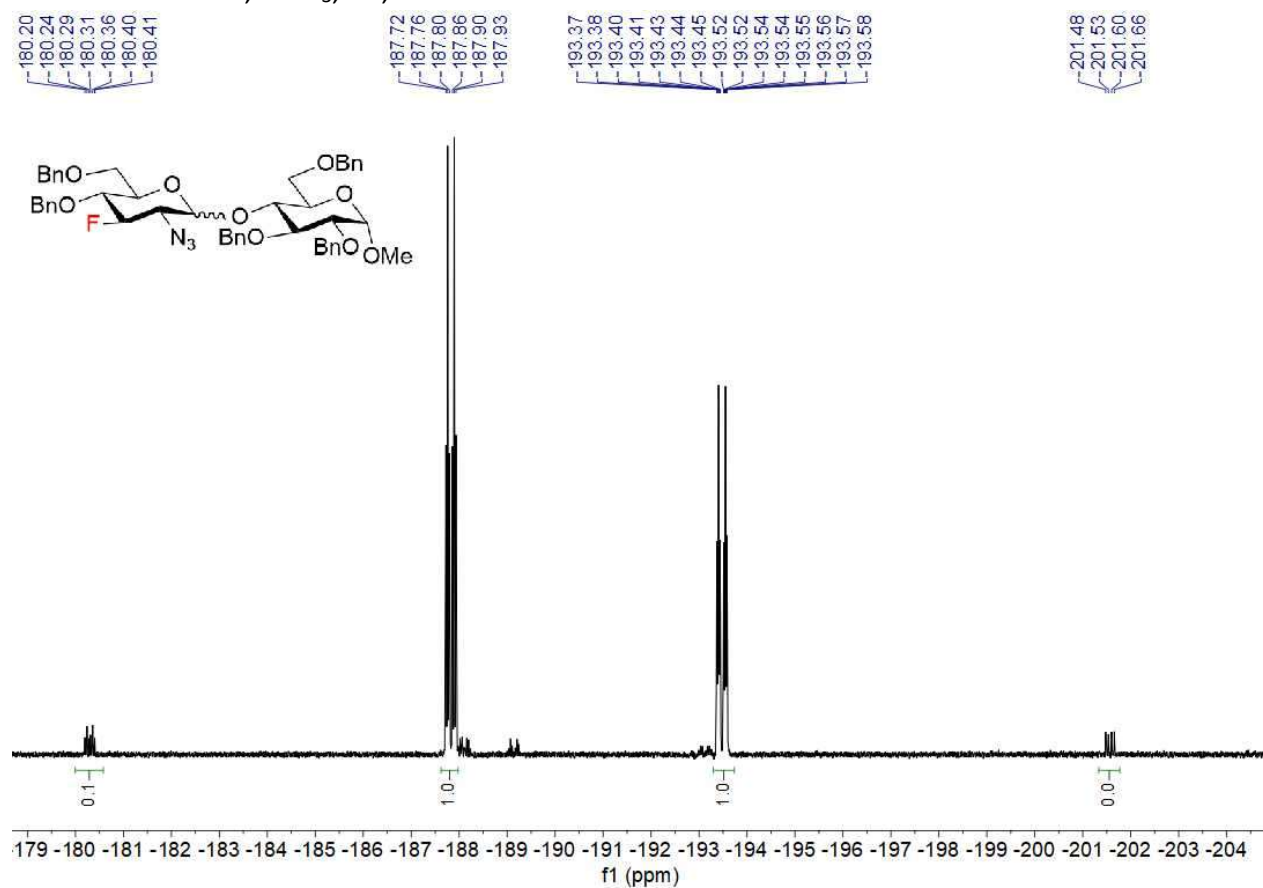
**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, B1**



**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, B1**

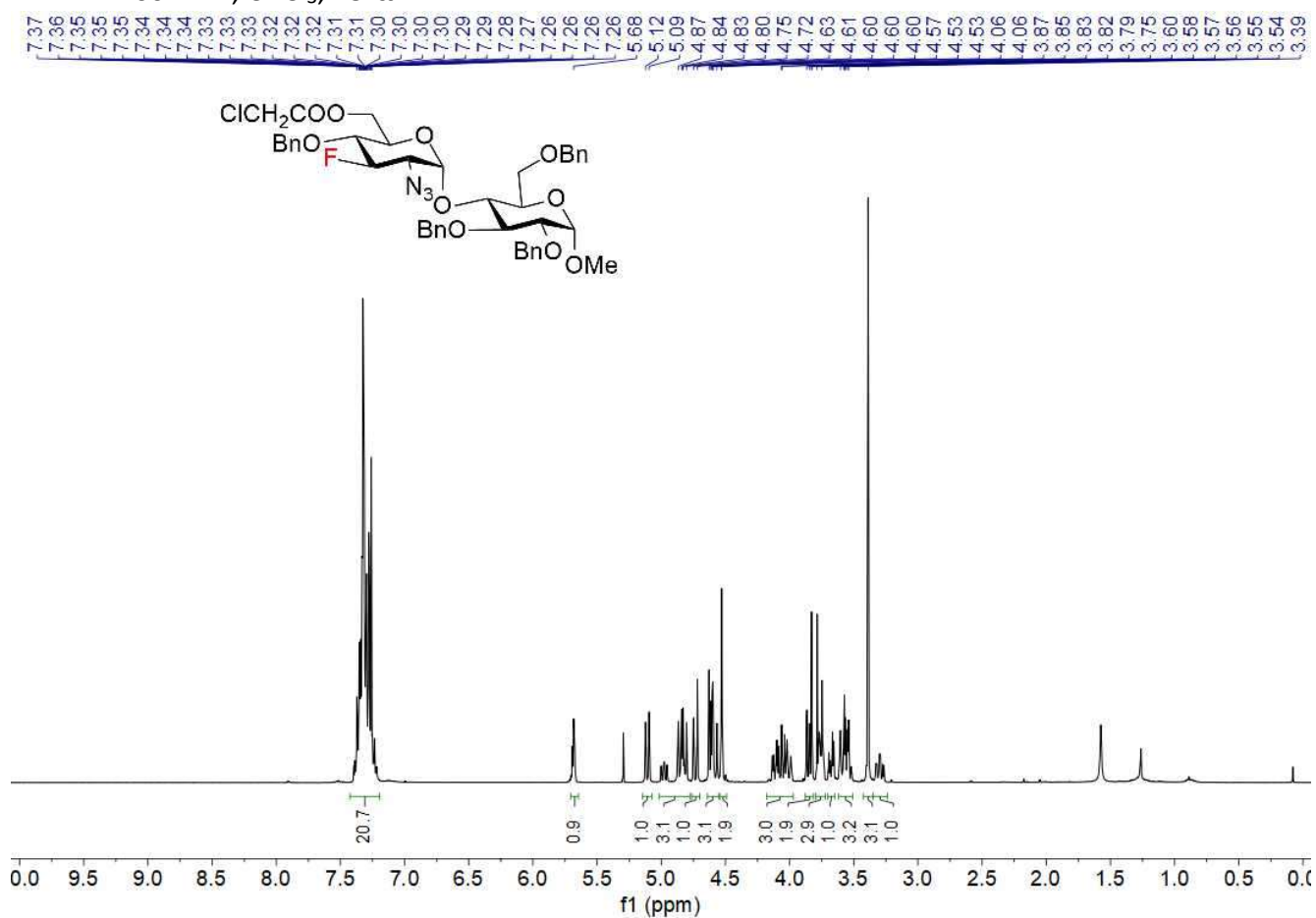


$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B1**,

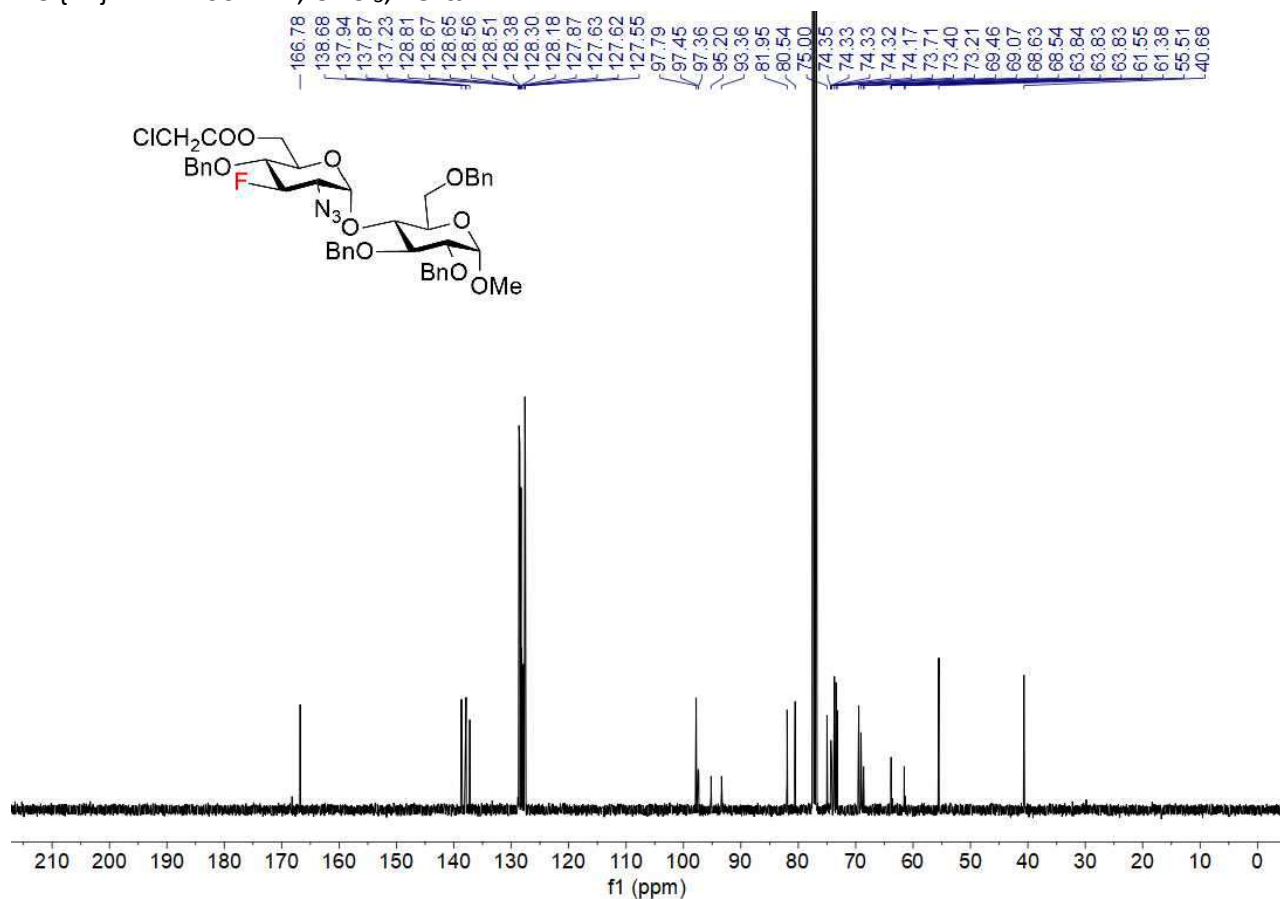


# **NMR B9- $\alpha$**

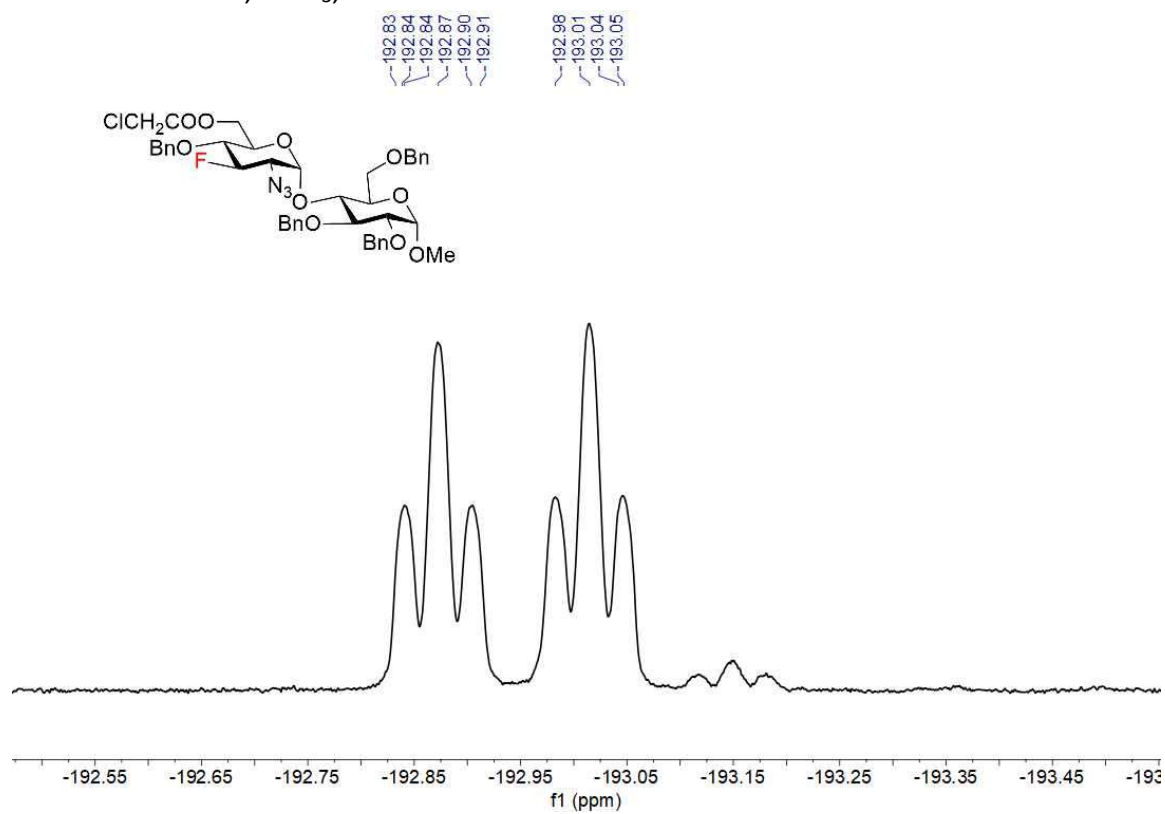
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **B9- $\alpha$**



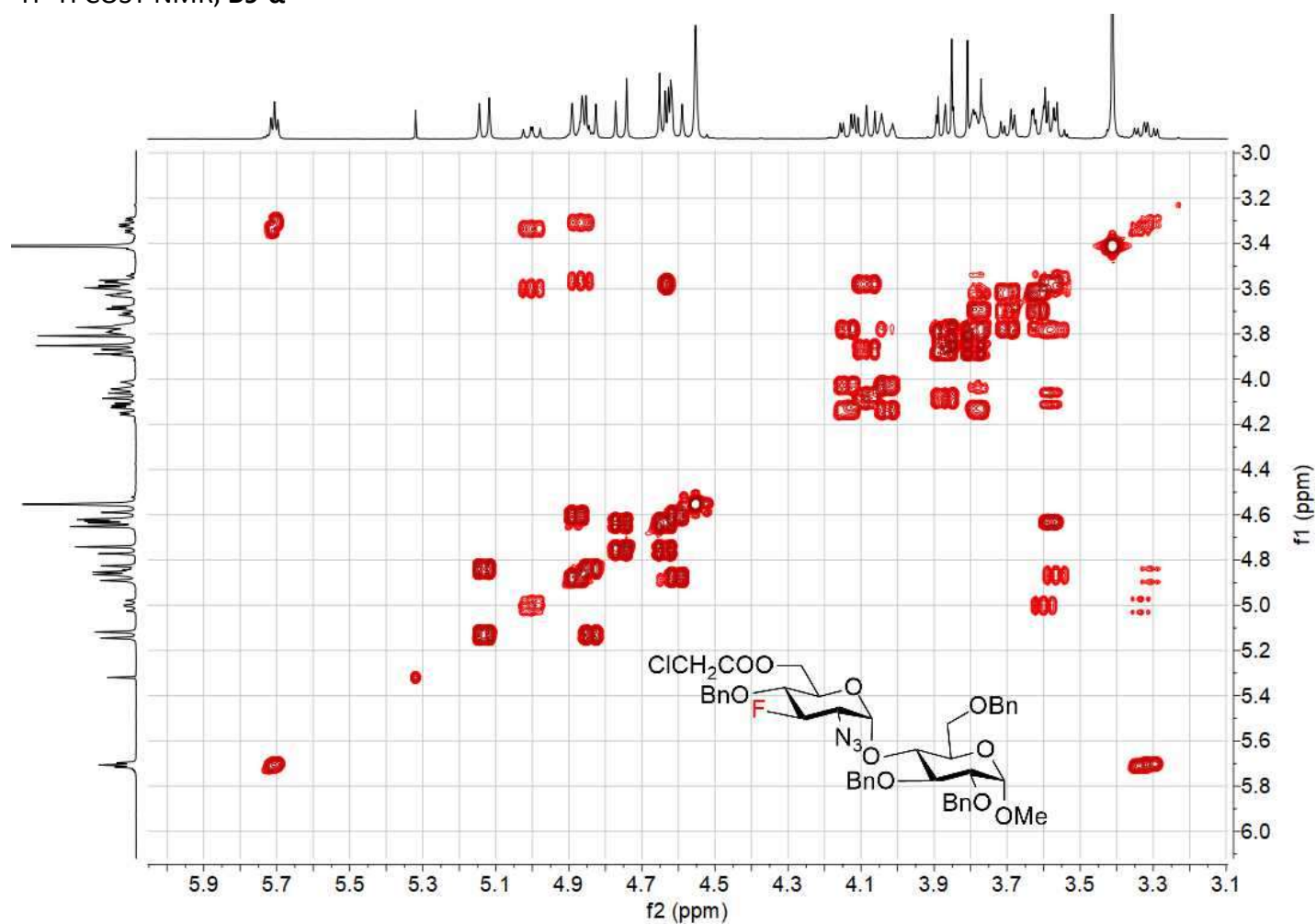
$^{13}\text{C}$  { $^1\text{H}$ } NMR 100MHz,  $\text{CDCl}_3$ , **B9- $\alpha$**



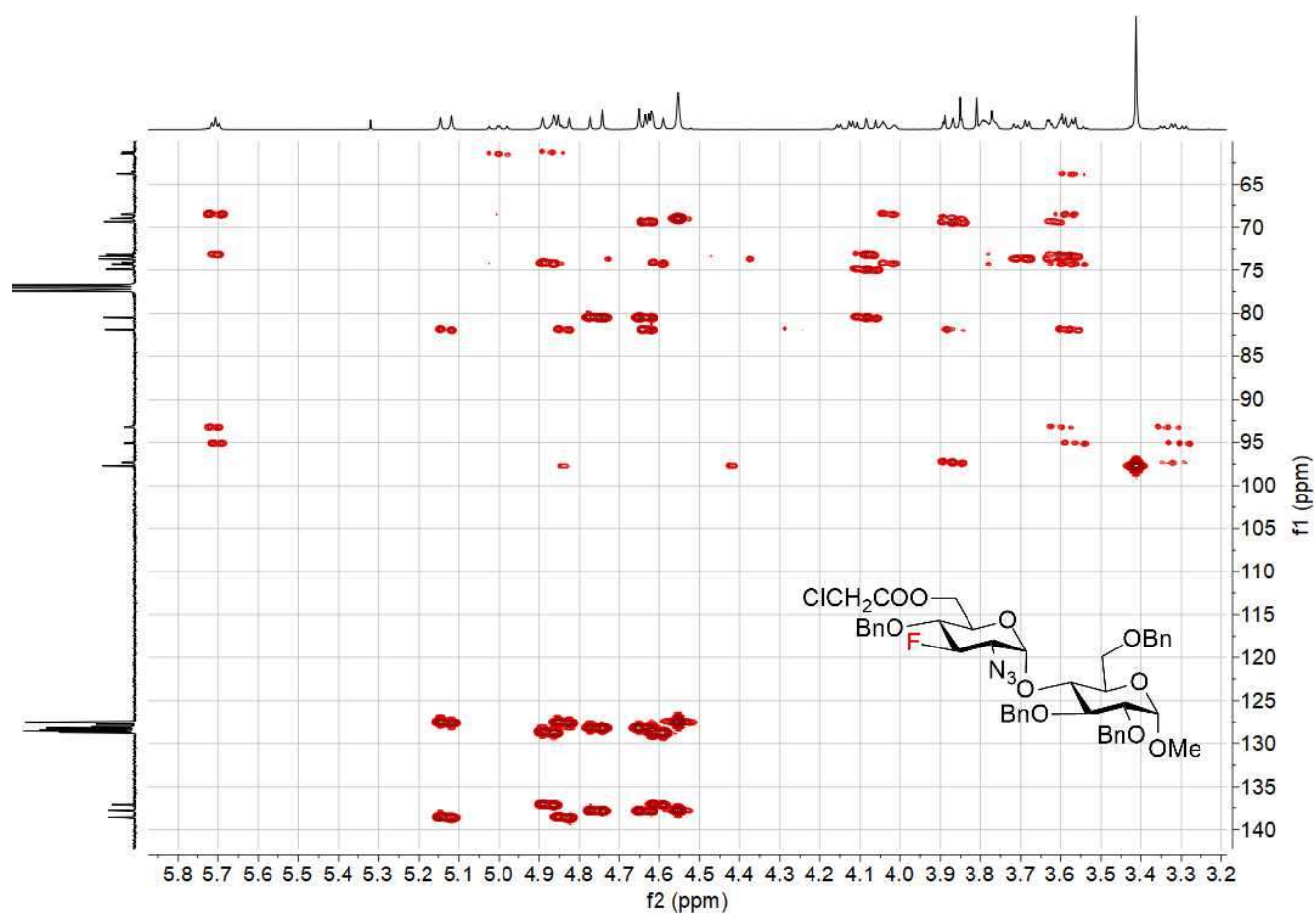
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B9- $\alpha$**



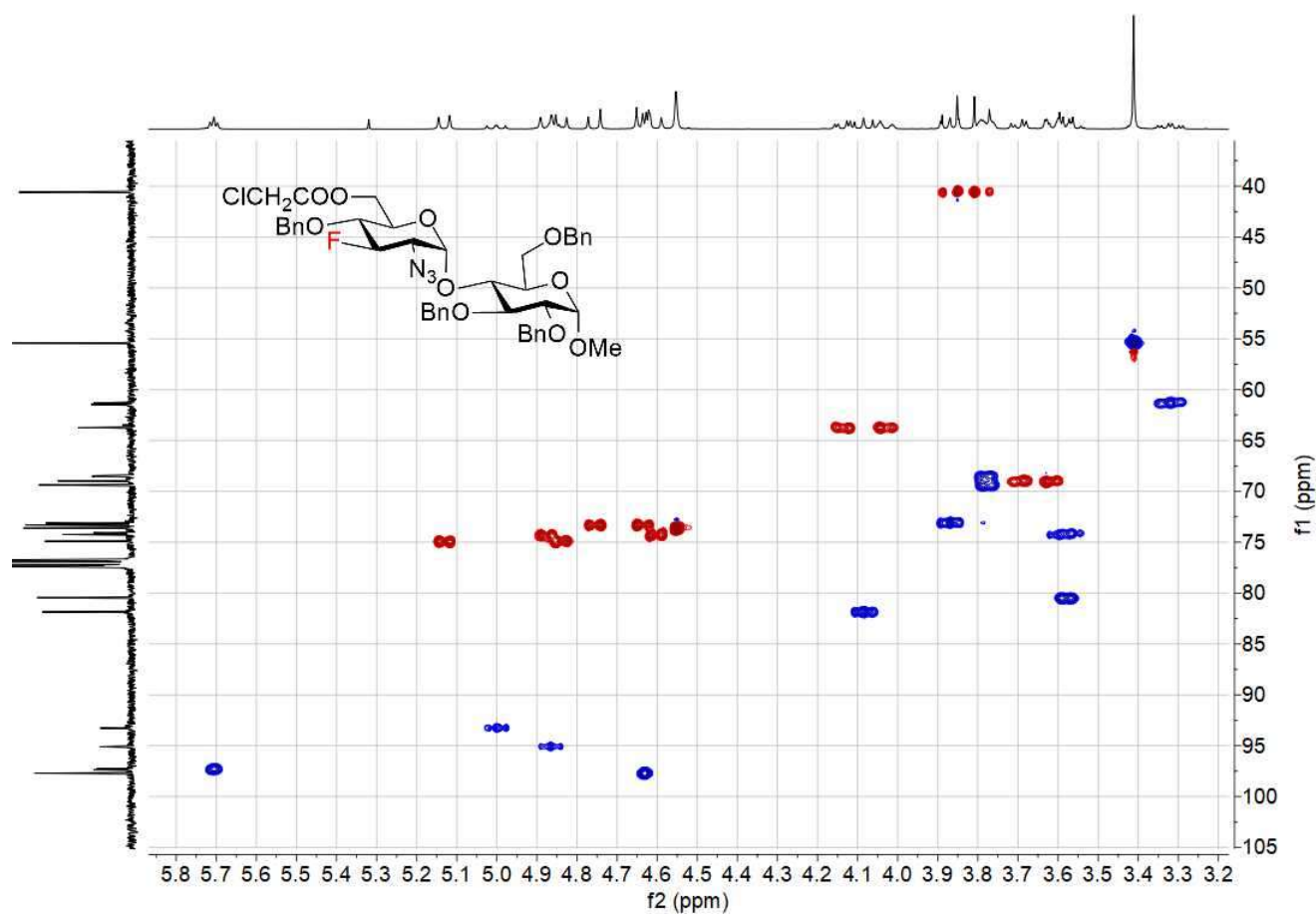
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B9- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **B9- $\alpha$**



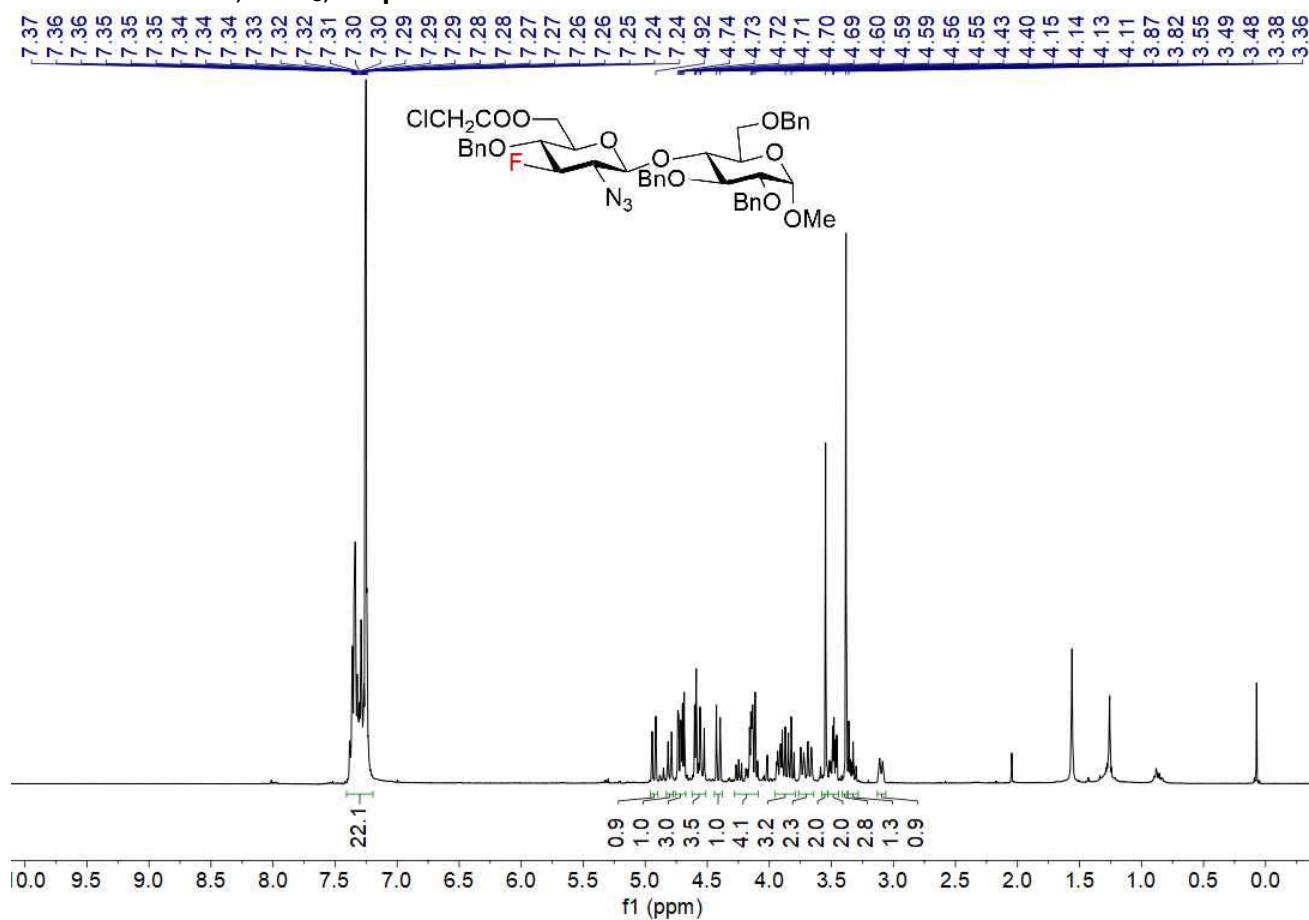
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **B9- $\alpha$**



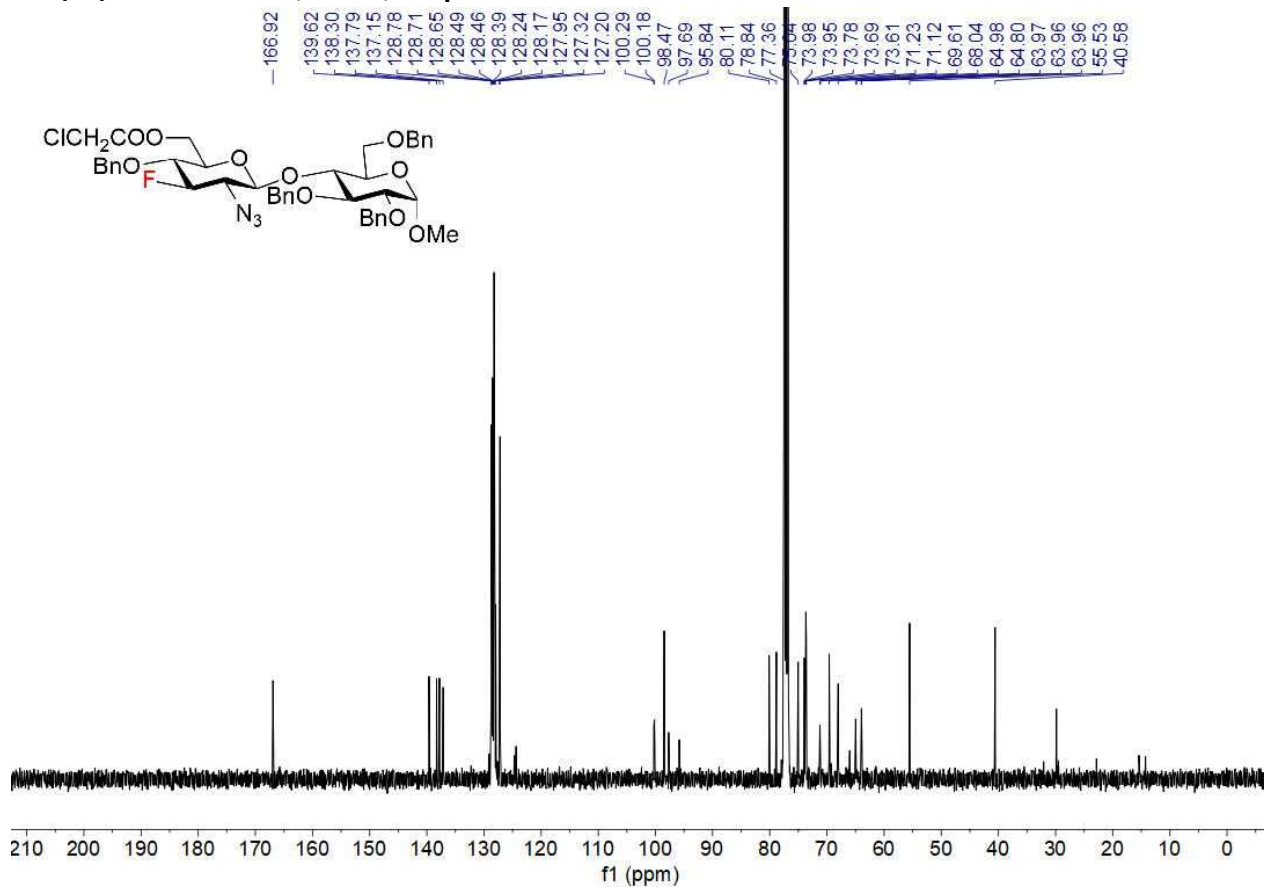


# **NMR B9-β**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **B9-β**

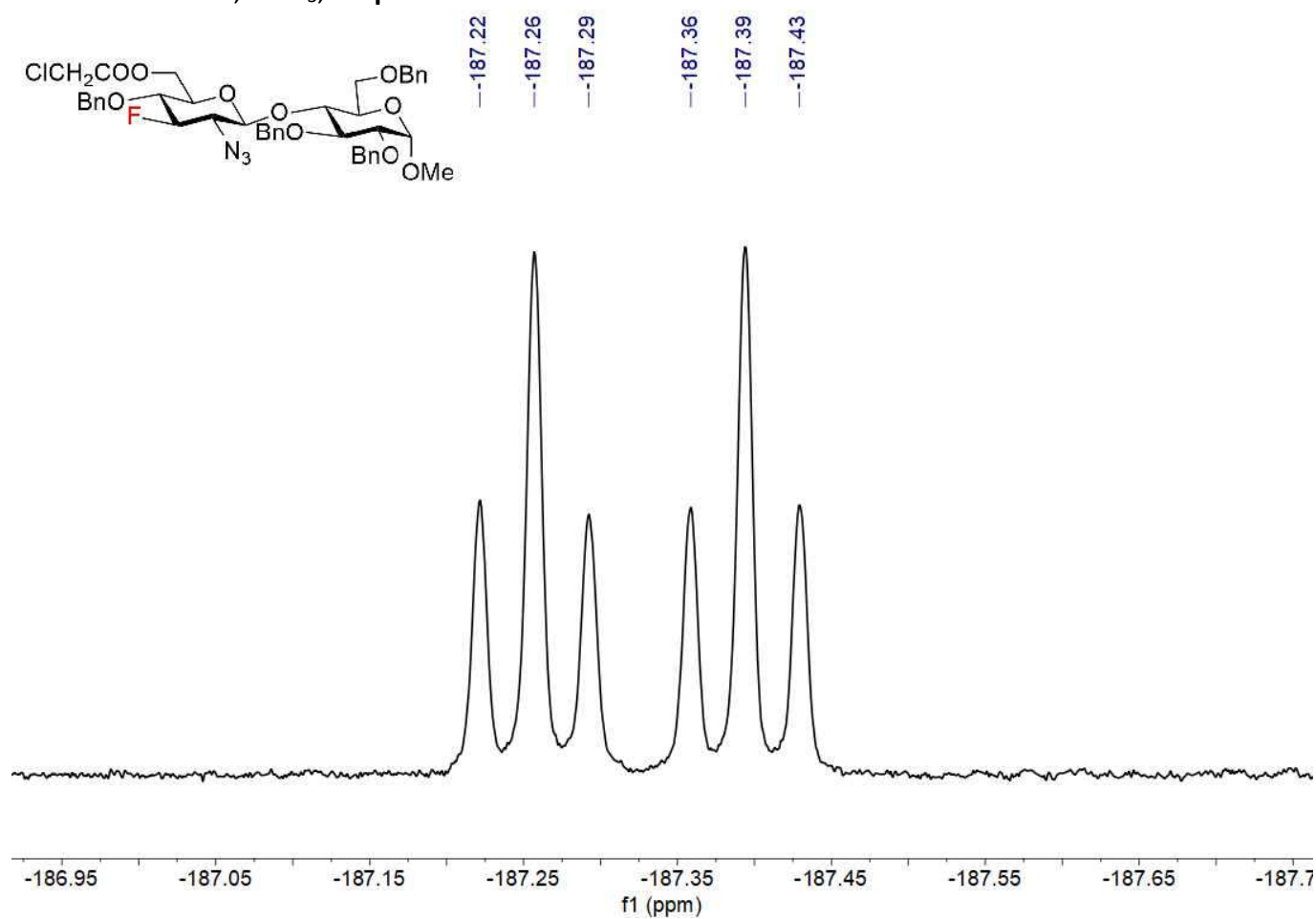


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **B9-β**

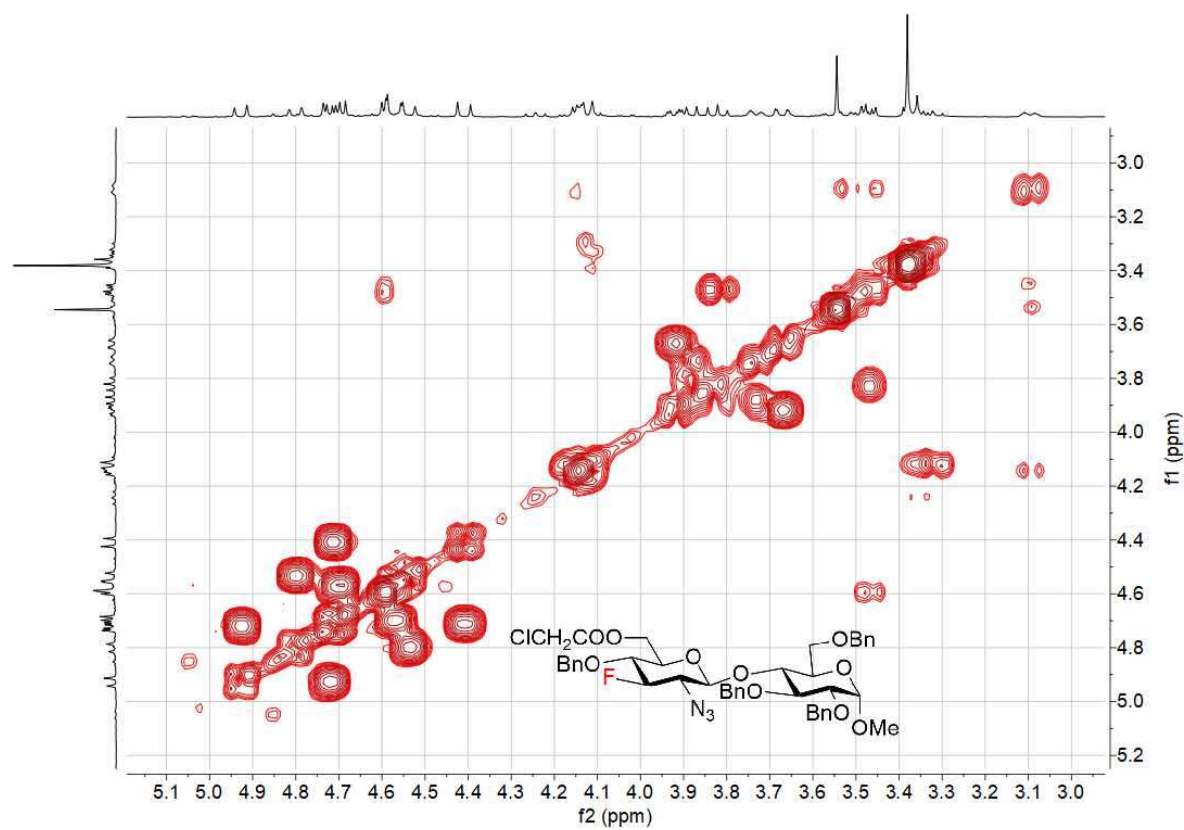




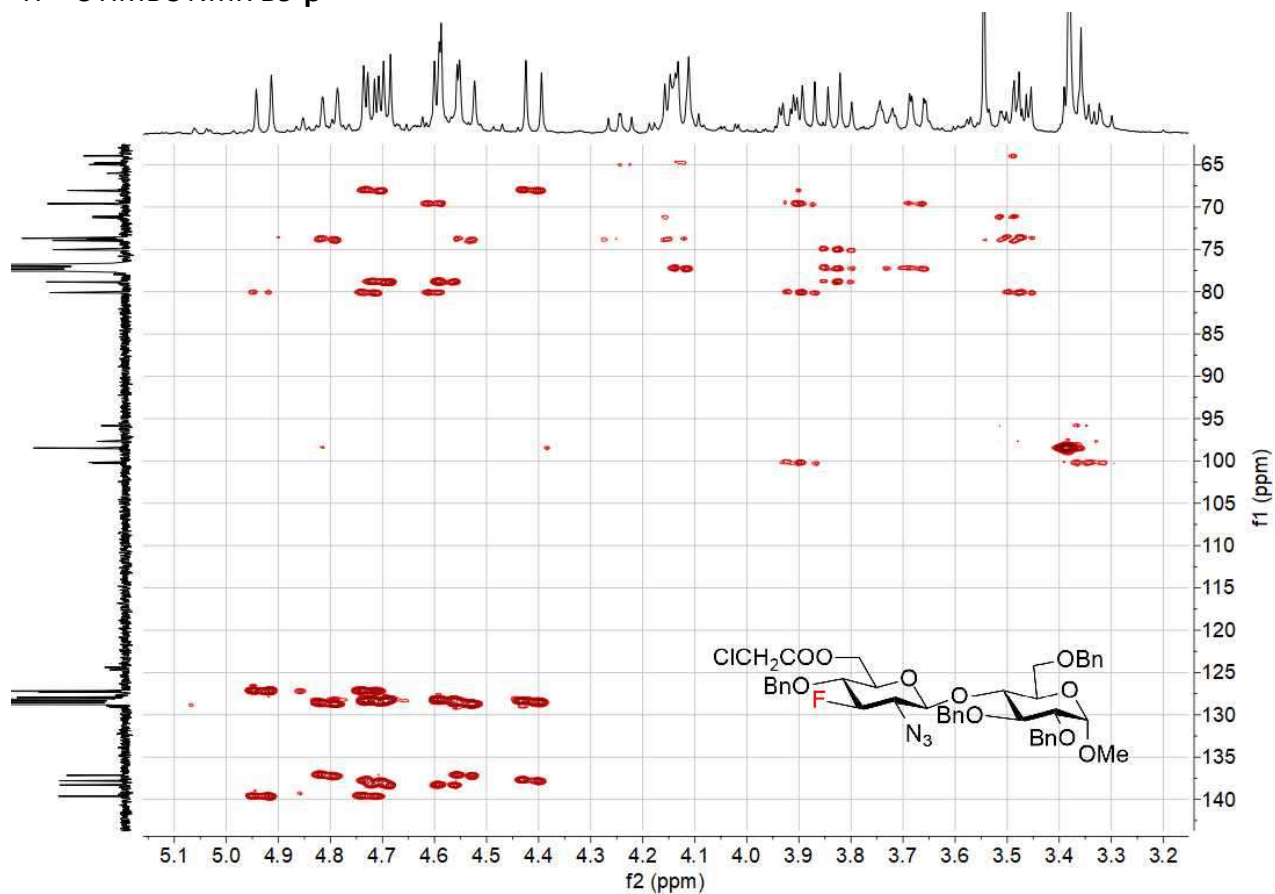
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B9- $\beta$**



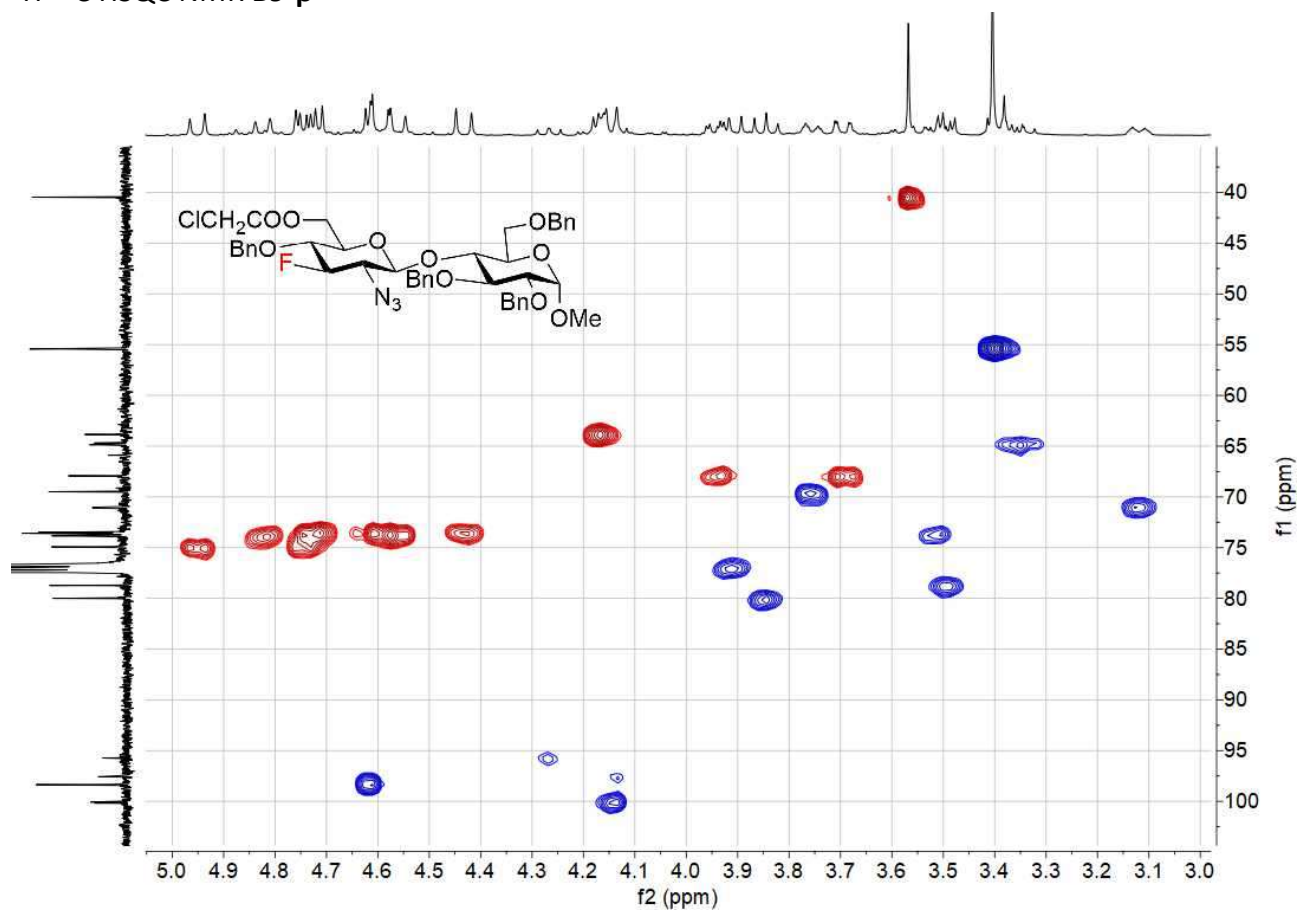
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B9- $\beta$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **B9- $\beta$**

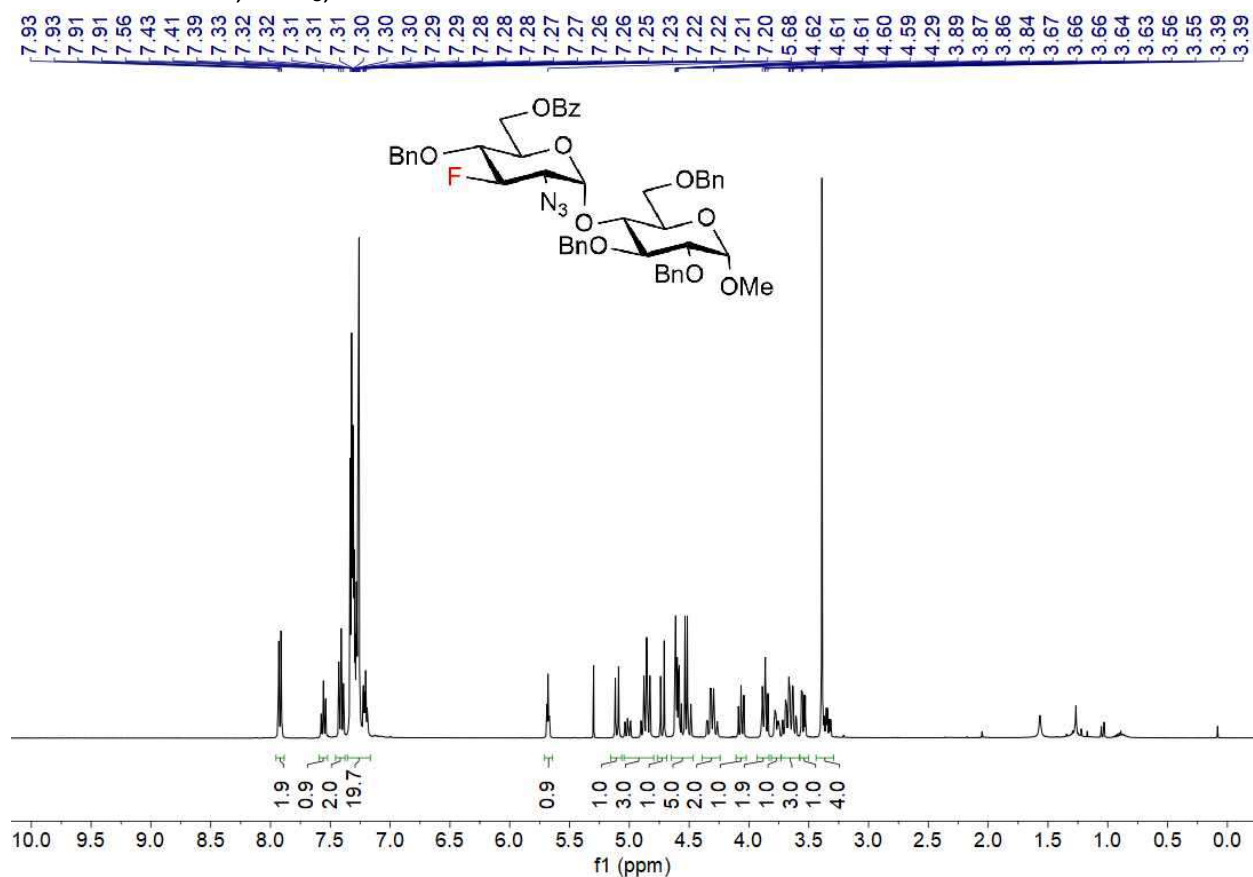


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **B9- $\beta$**

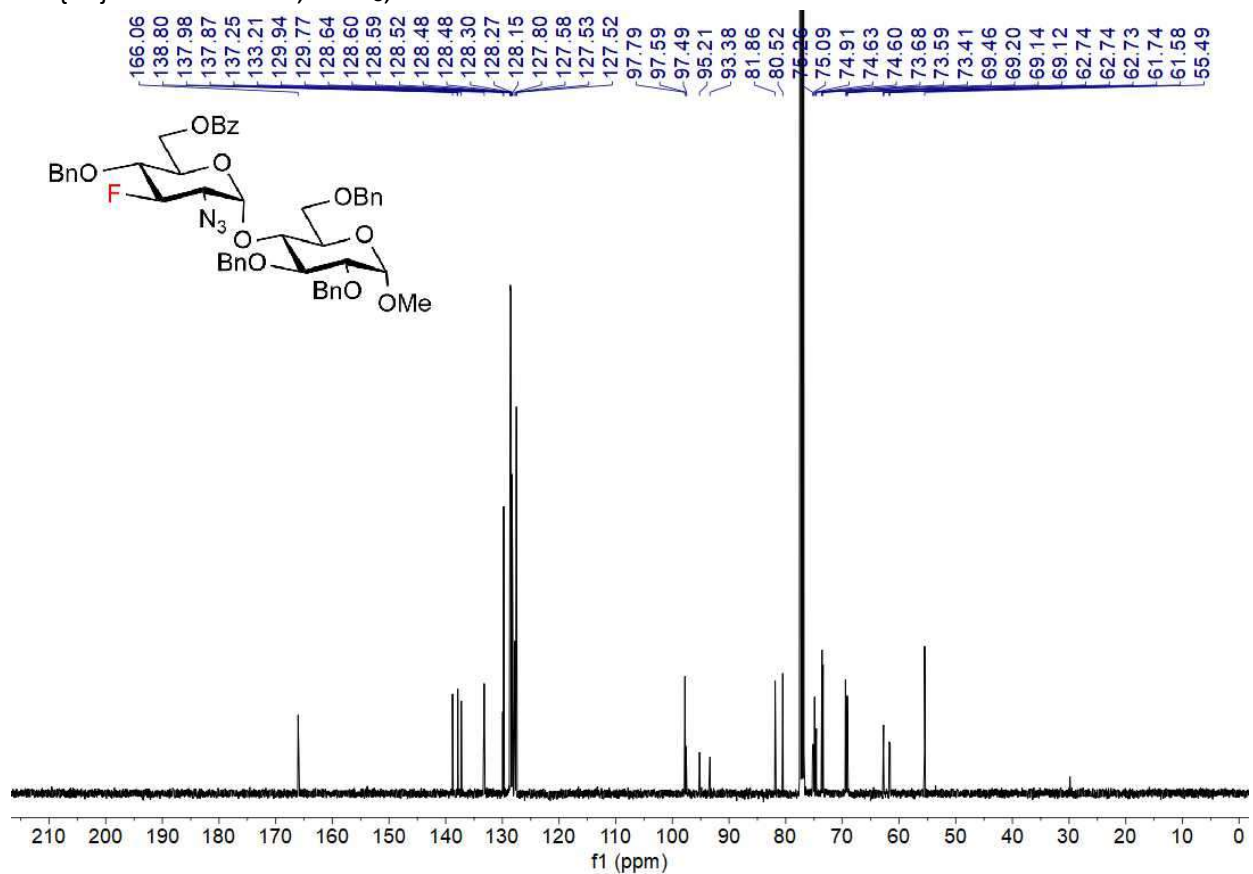


# **NMR B10- $\alpha$**

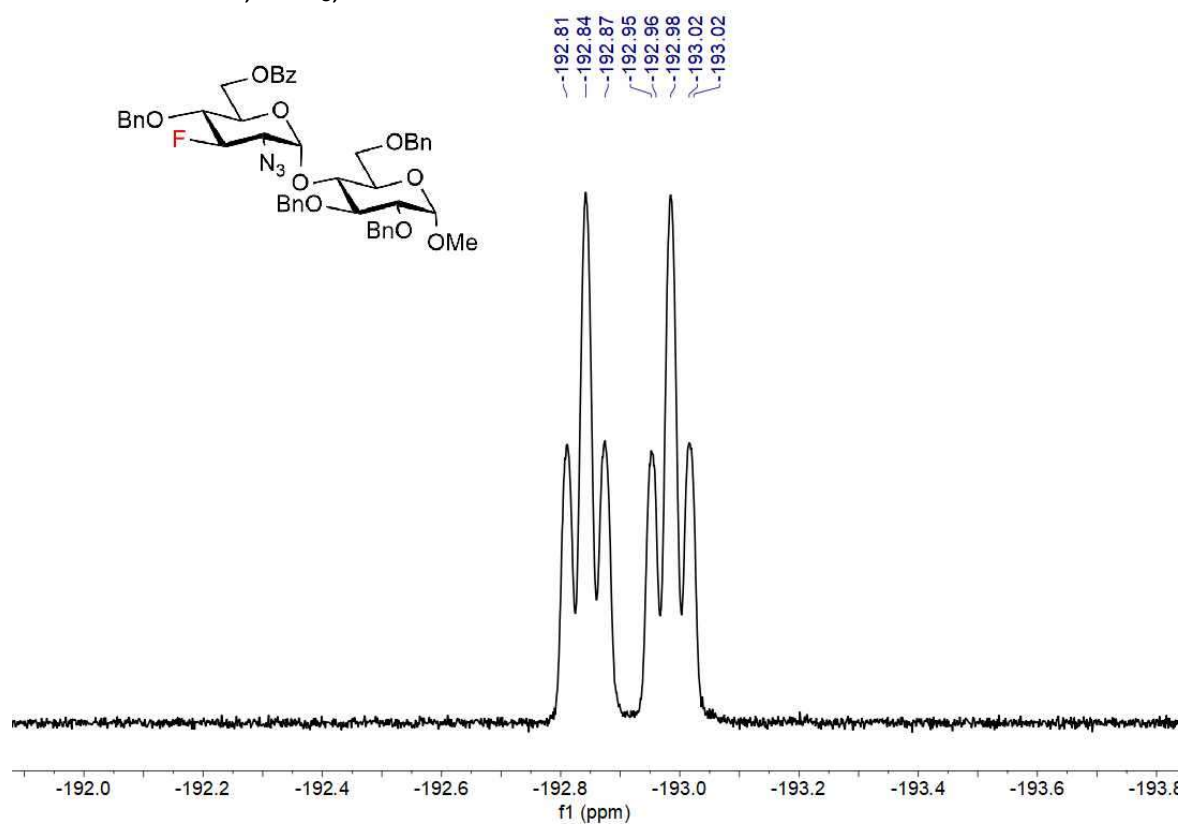
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **B10- $\alpha$**



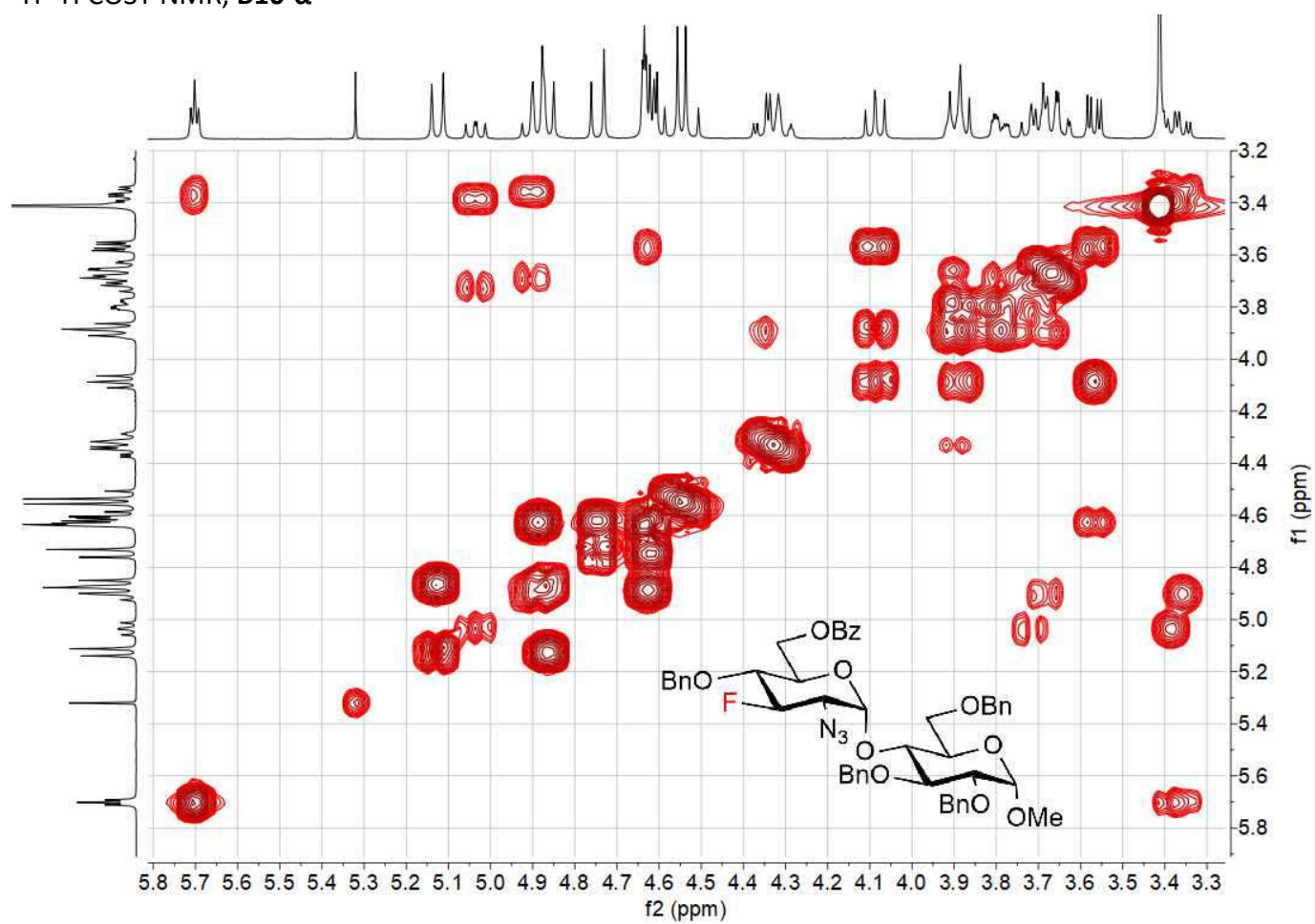
$^{13}\text{C}$  { $^1\text{H}$ } NMR 100MHz,  $\text{CDCl}_3$ , **B10- $\alpha$**



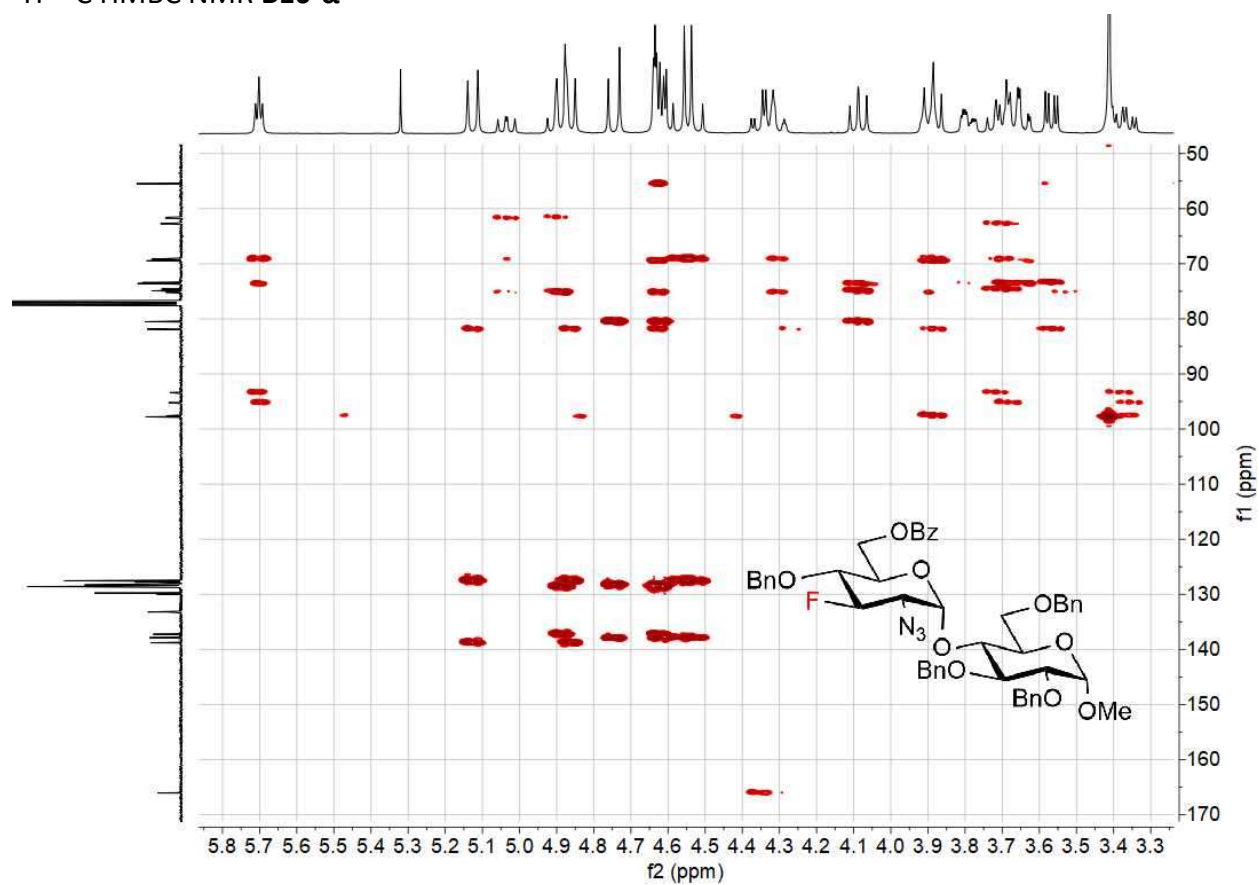
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B10- $\alpha$**



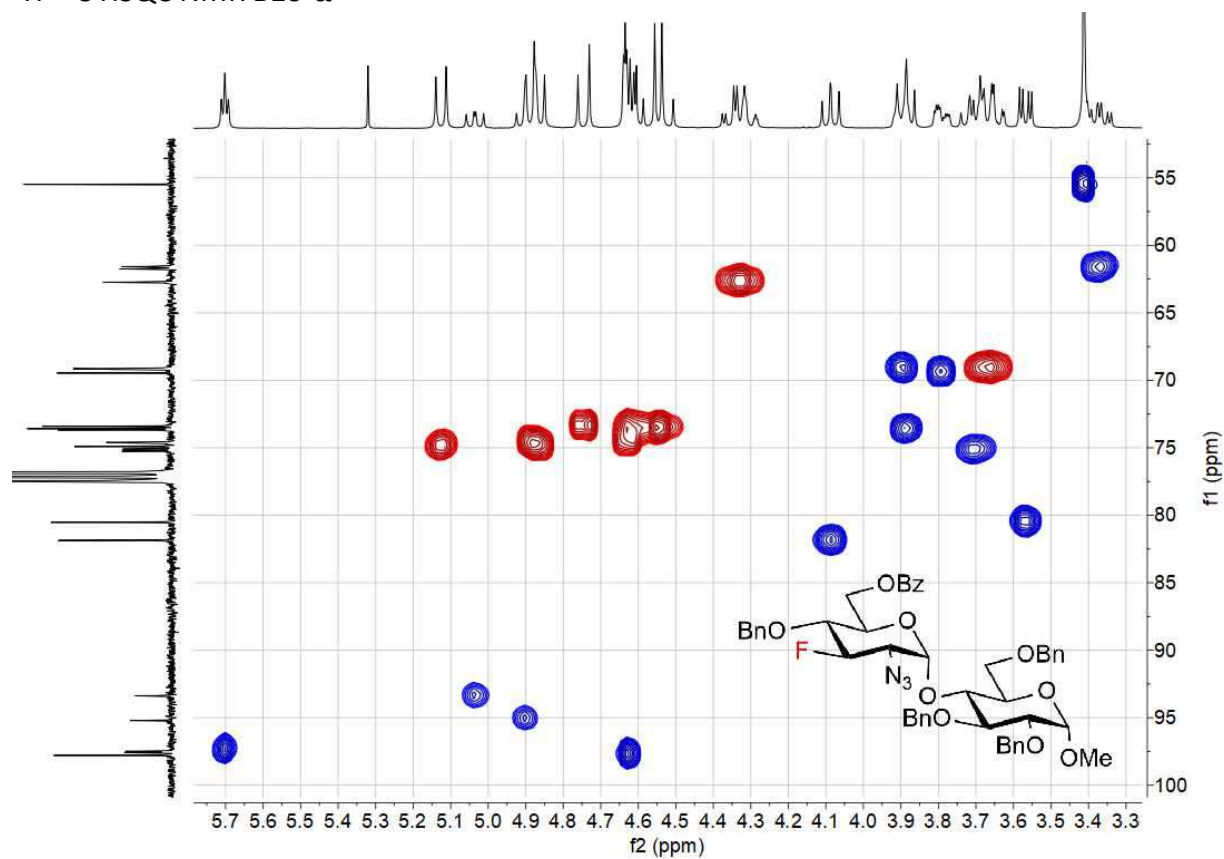
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B10- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **B10- $\alpha$**



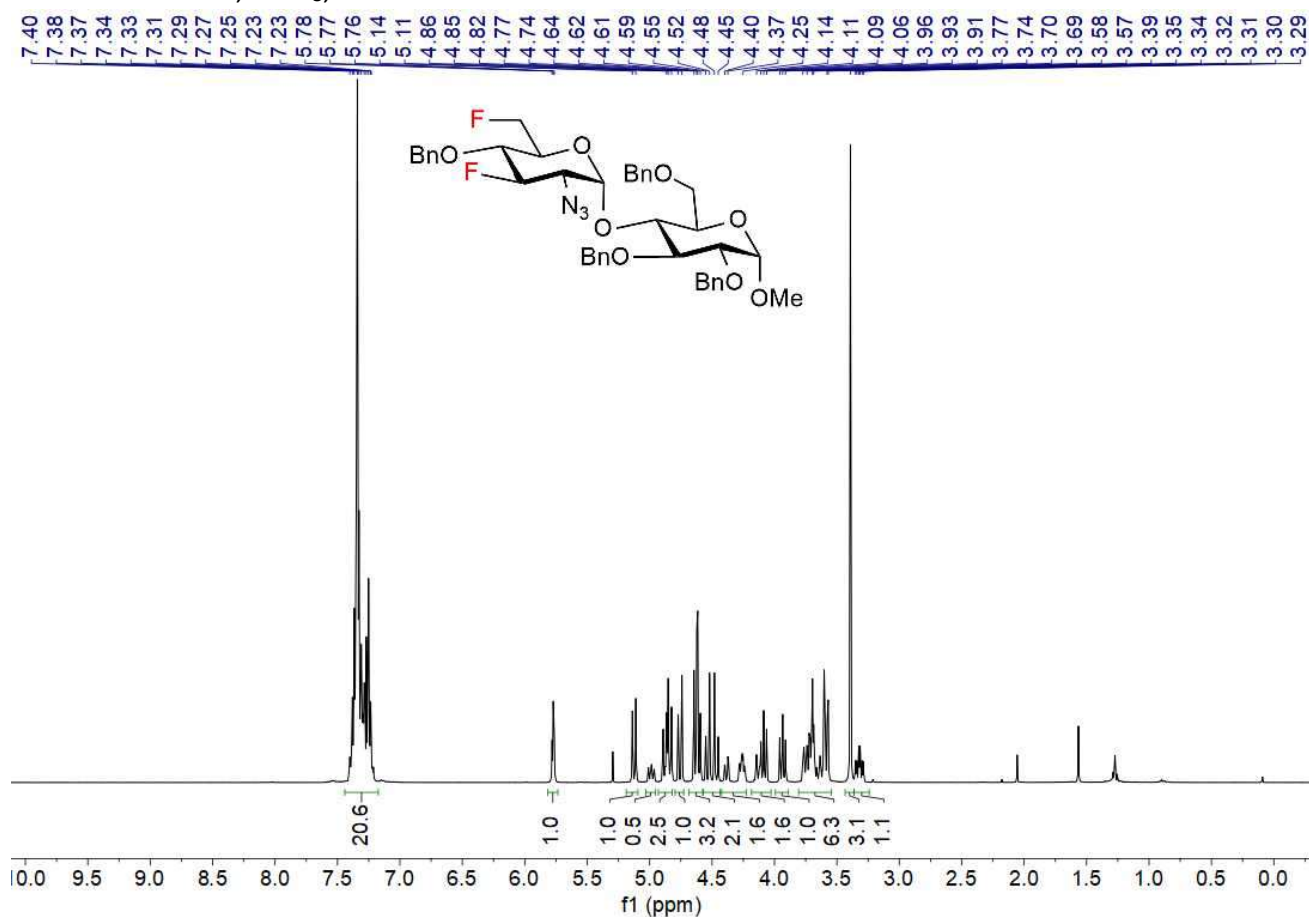
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **B10- $\alpha$**



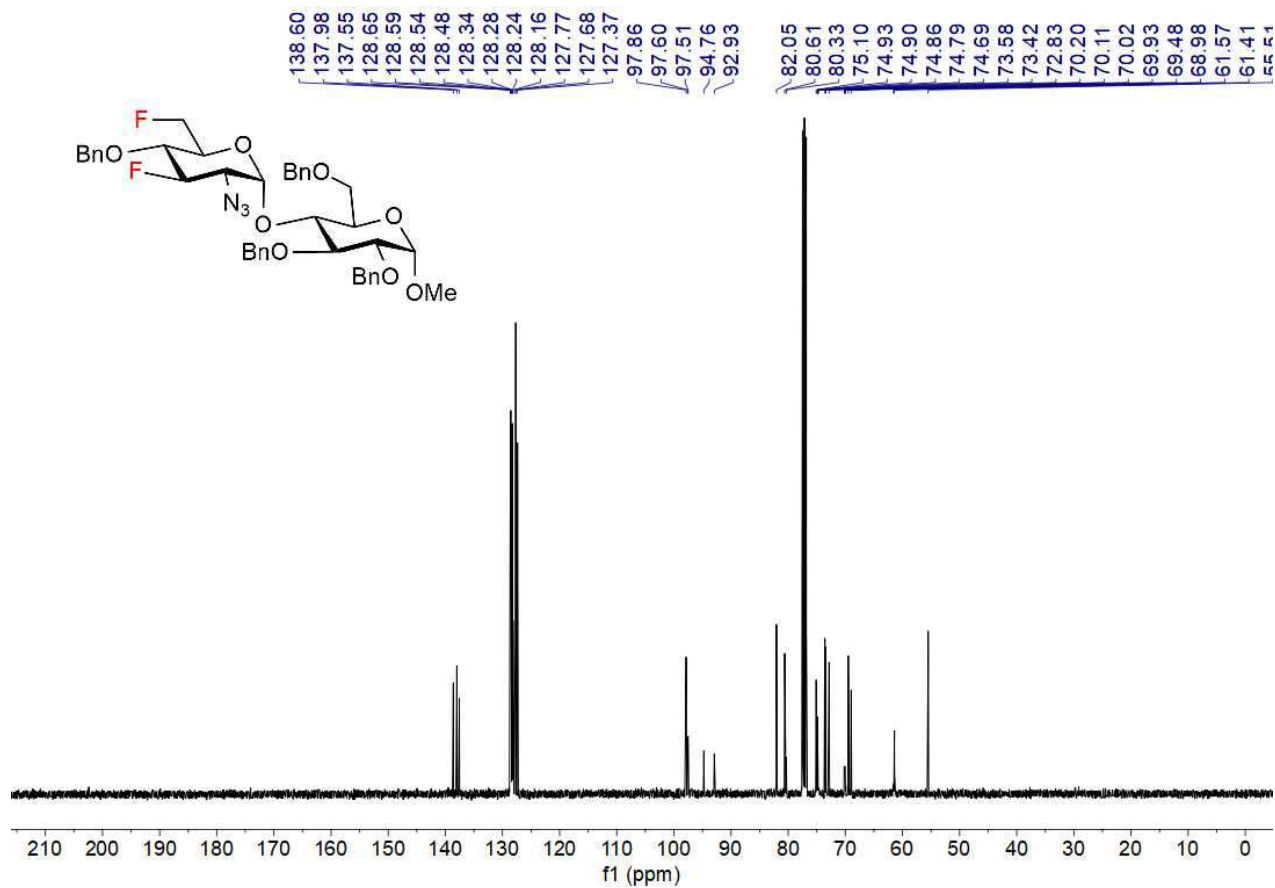


# **NMR B12- $\alpha$**

$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **B12- $\alpha$**

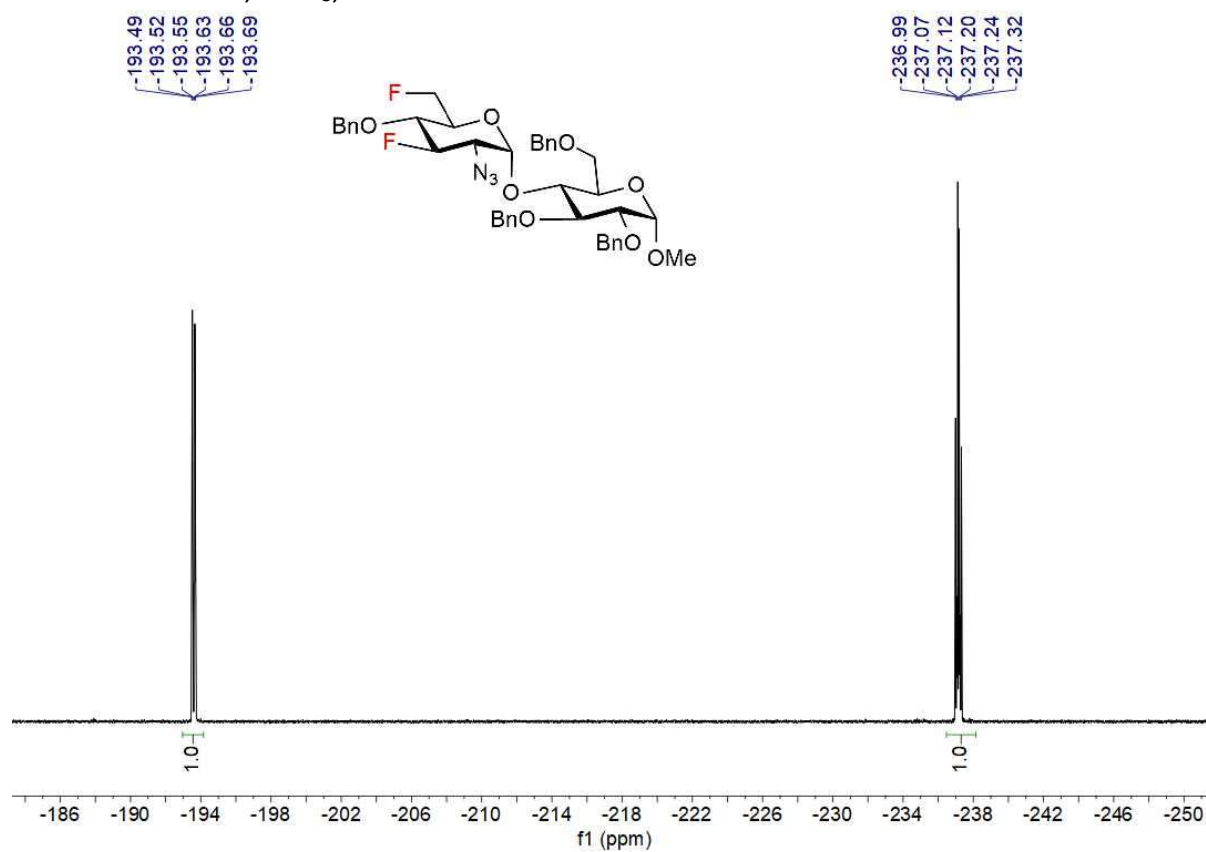


$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **B12- $\alpha$**

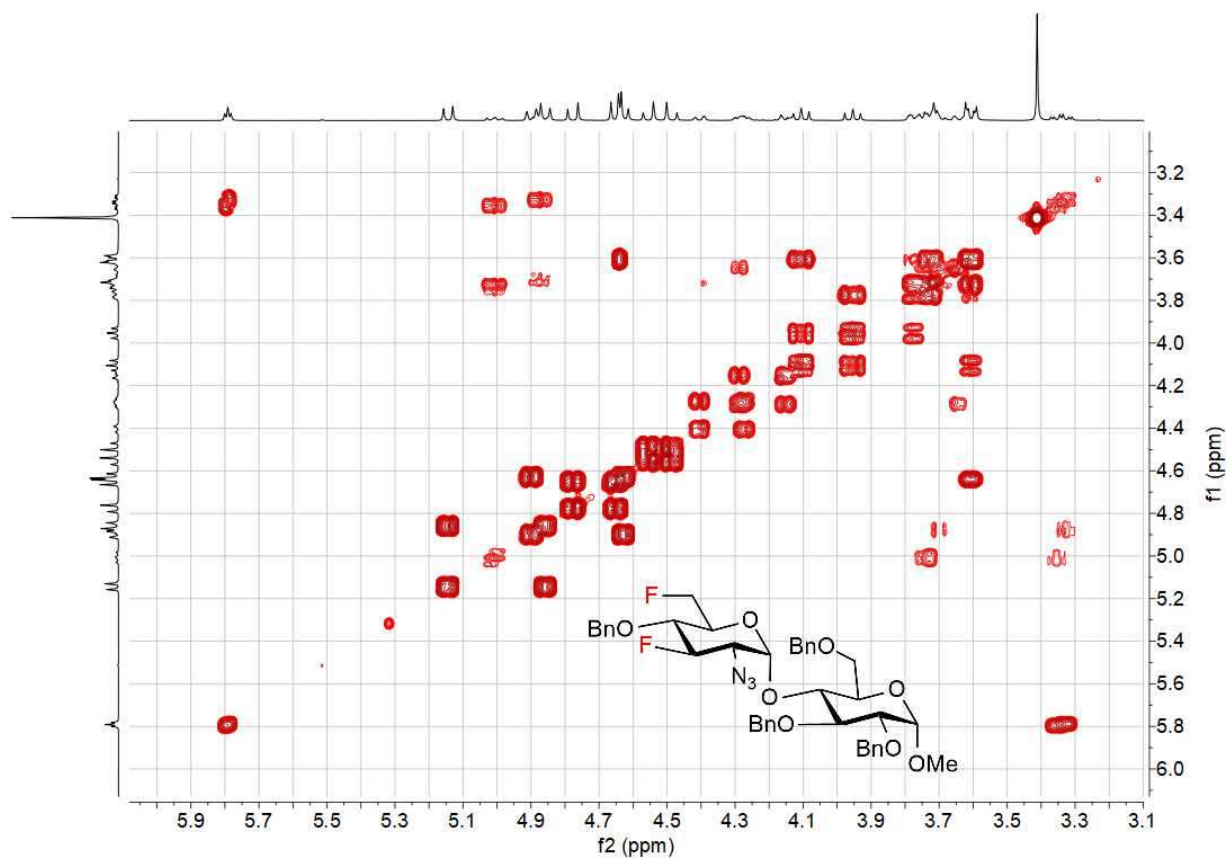




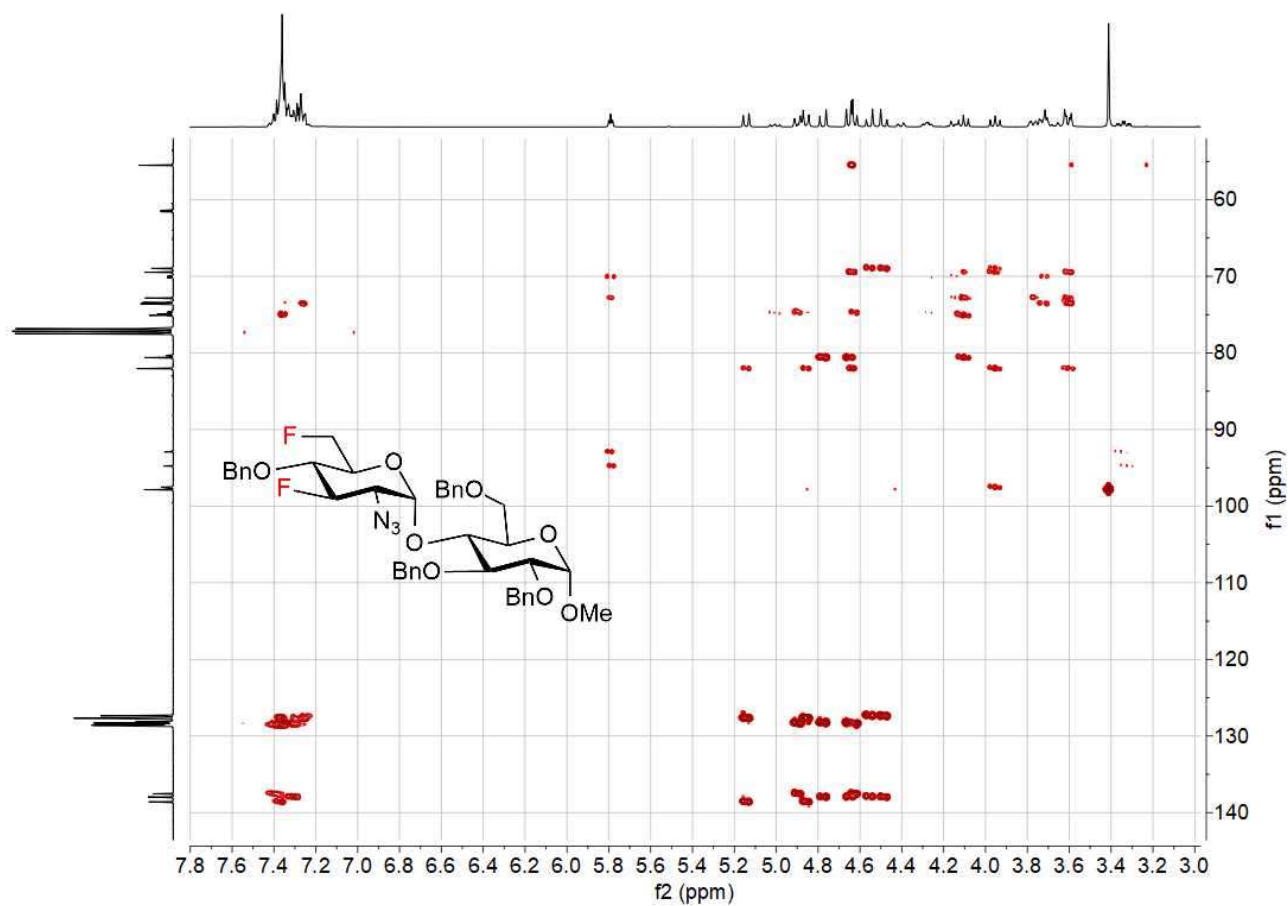
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B12- $\alpha$**



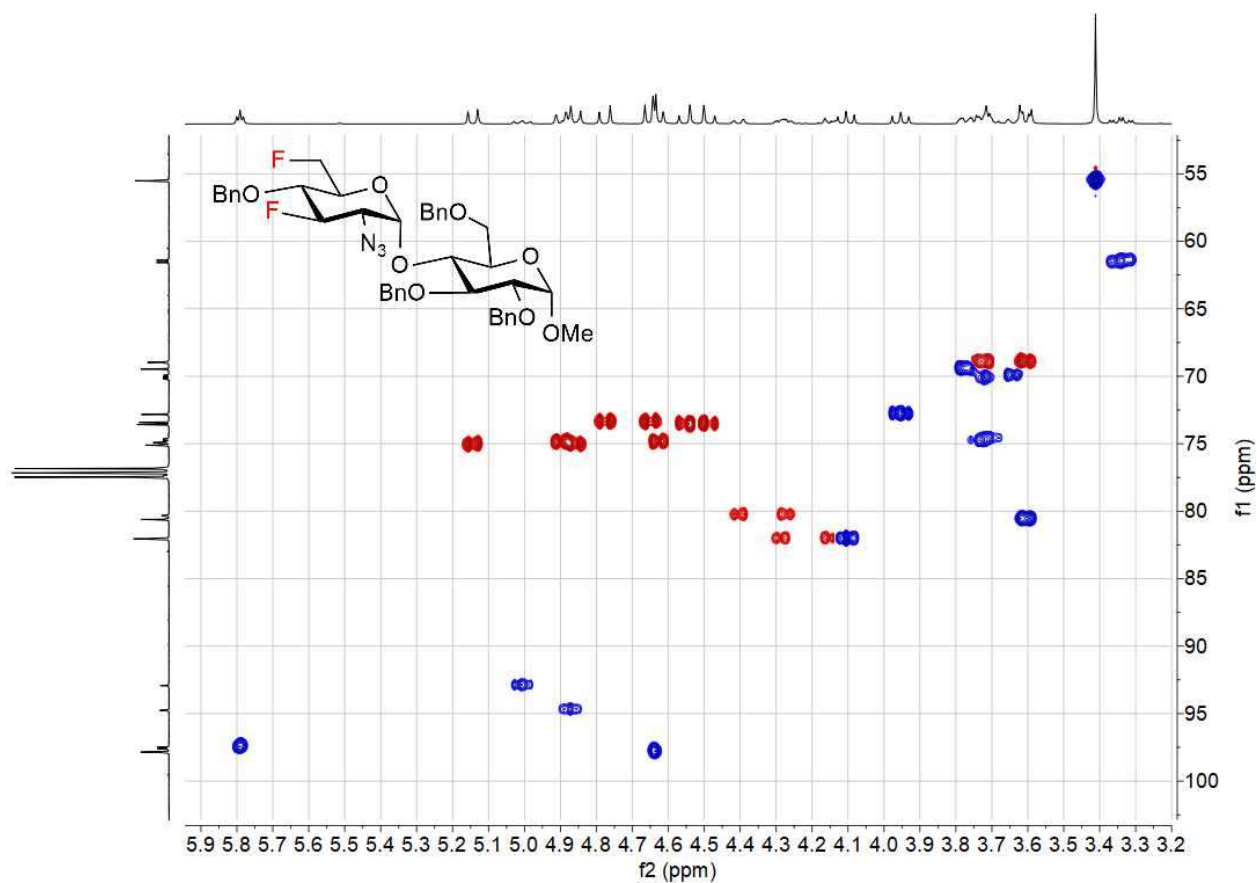
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B12- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **B12- $\alpha$**

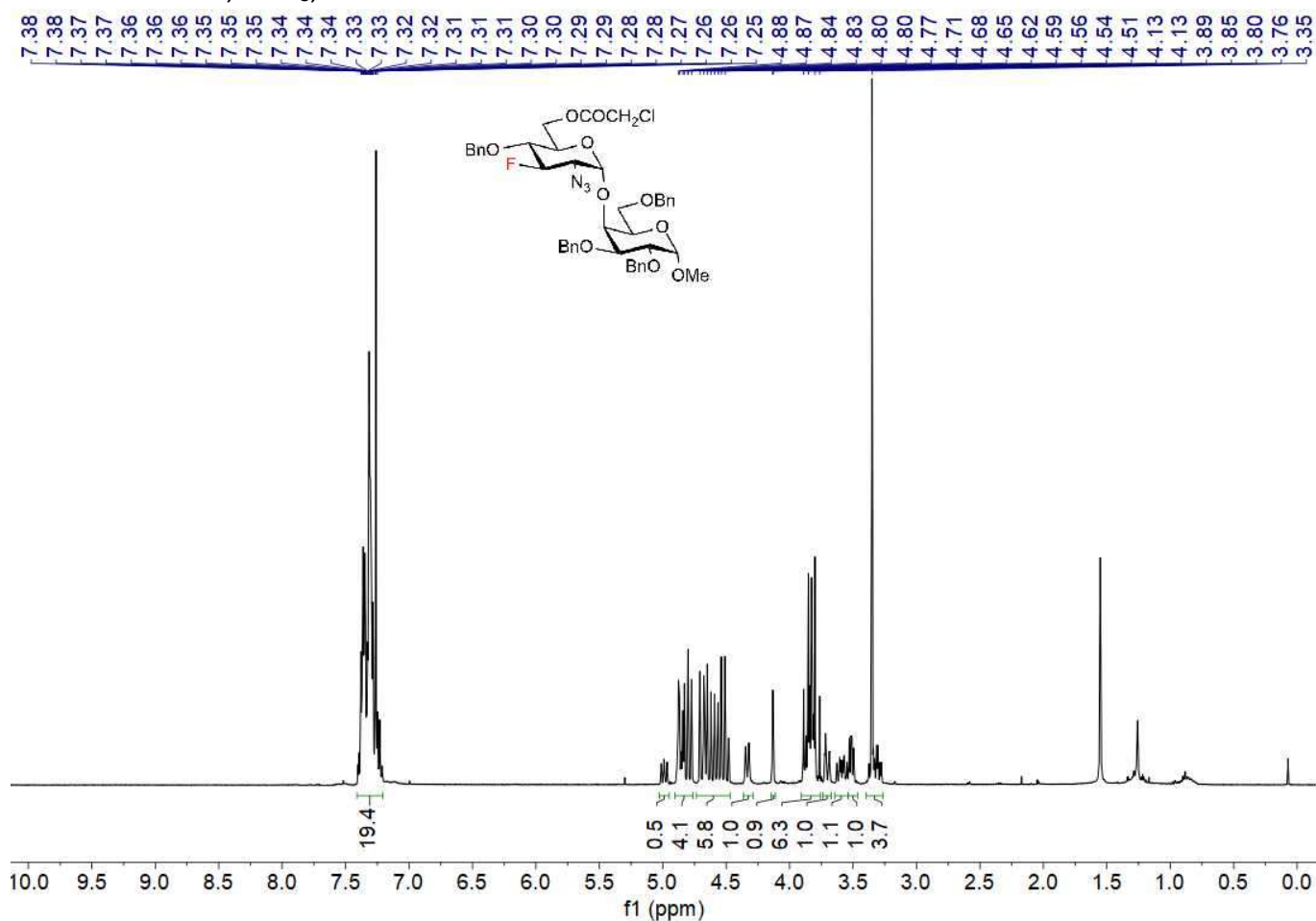


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **B12- $\alpha$**

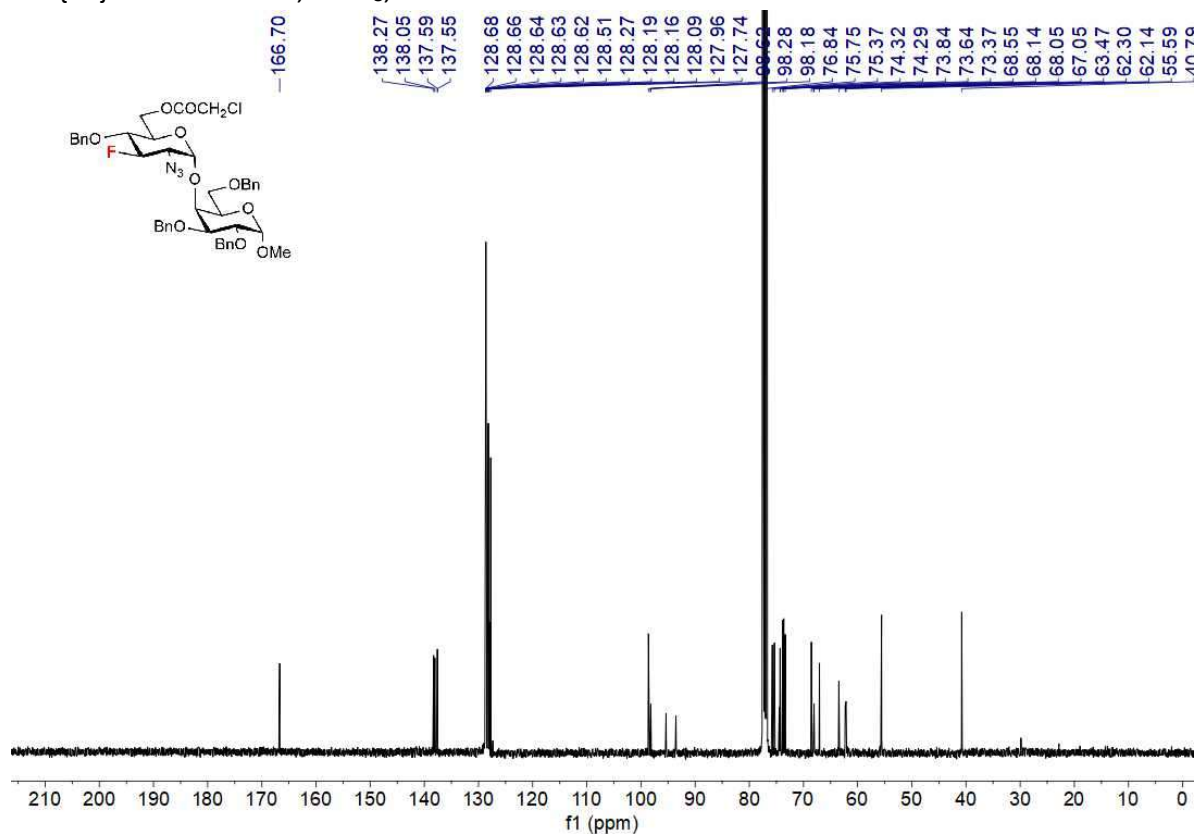


# **NMR C9- $\alpha$**

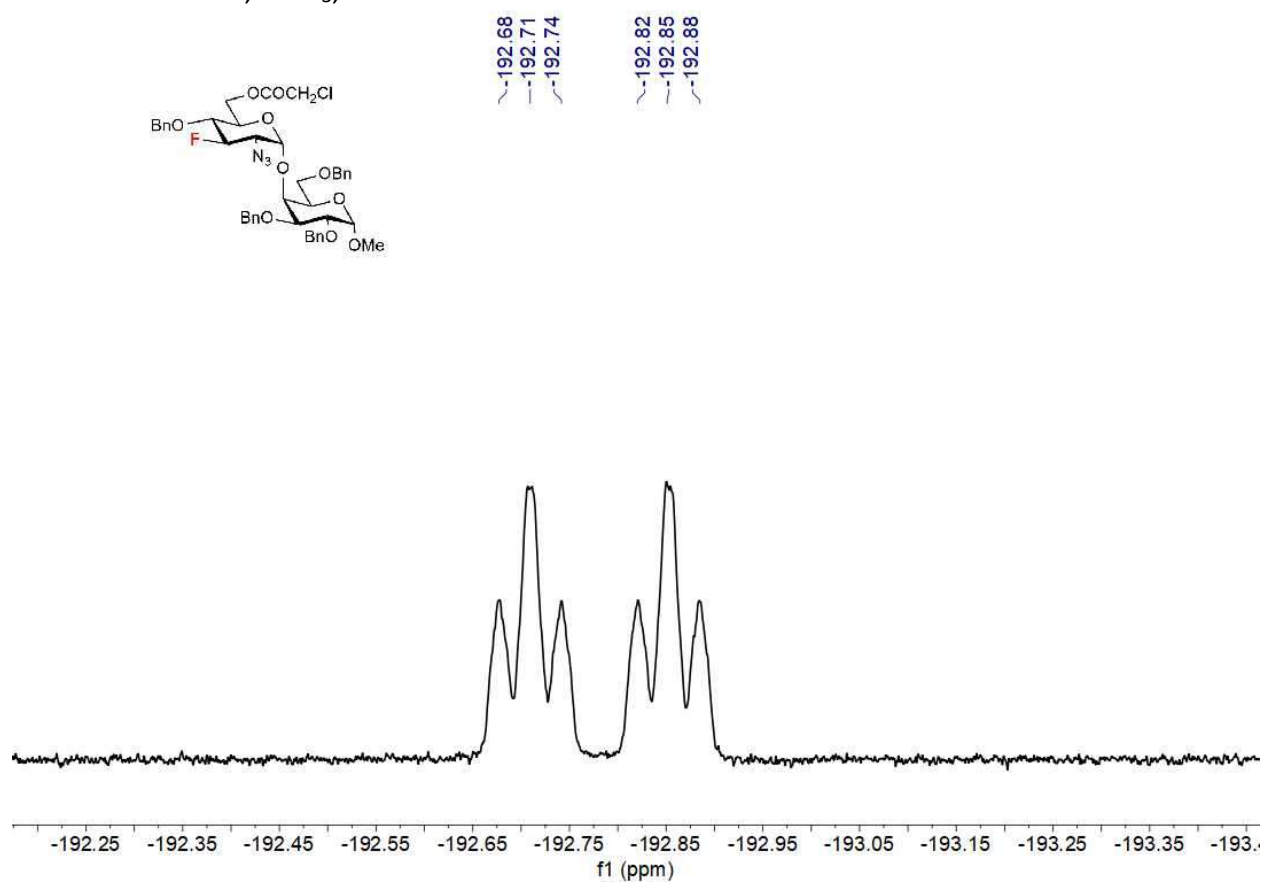
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **C9- $\alpha$**



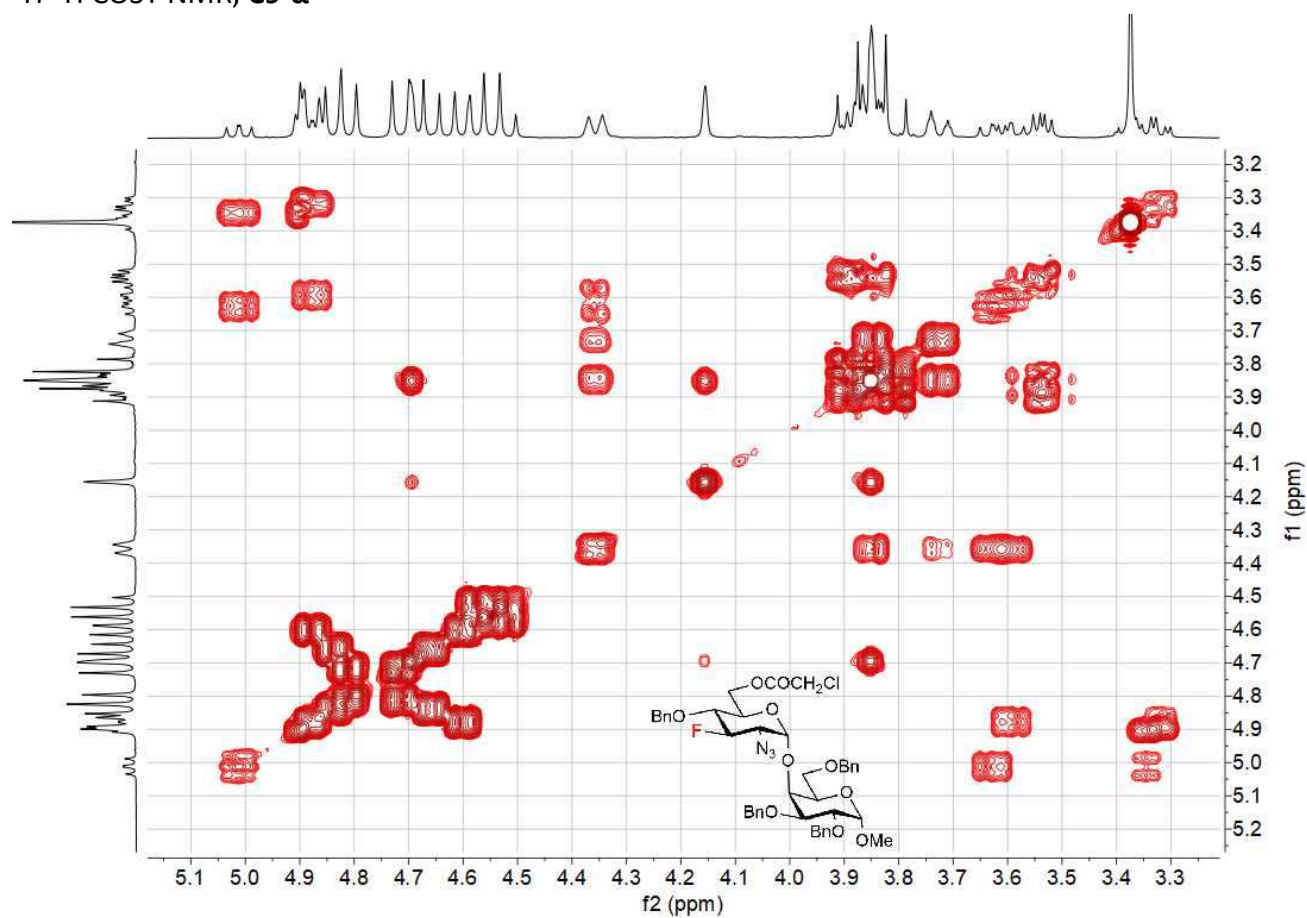
$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **C9- $\alpha$**



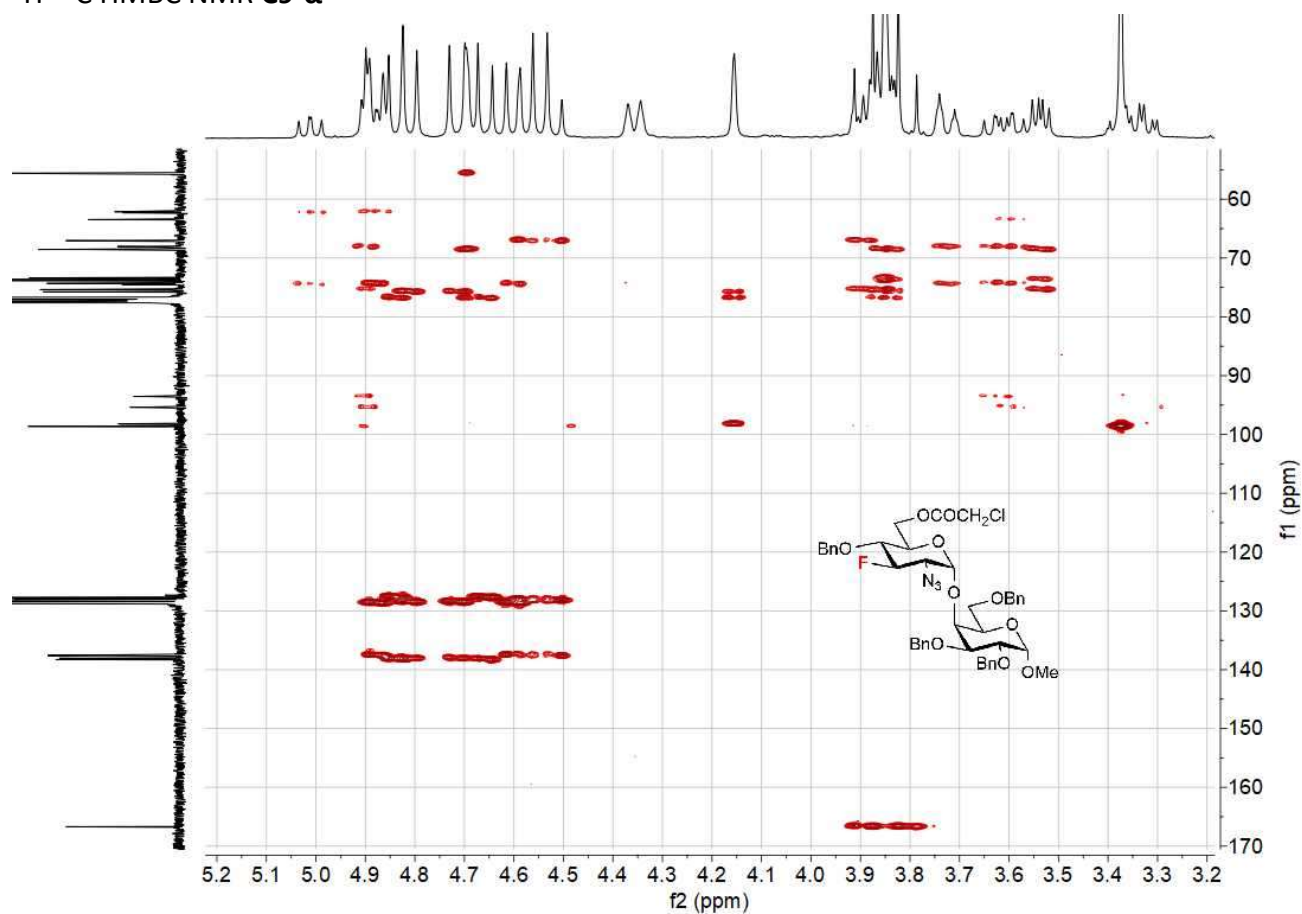
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **C9- $\alpha$**



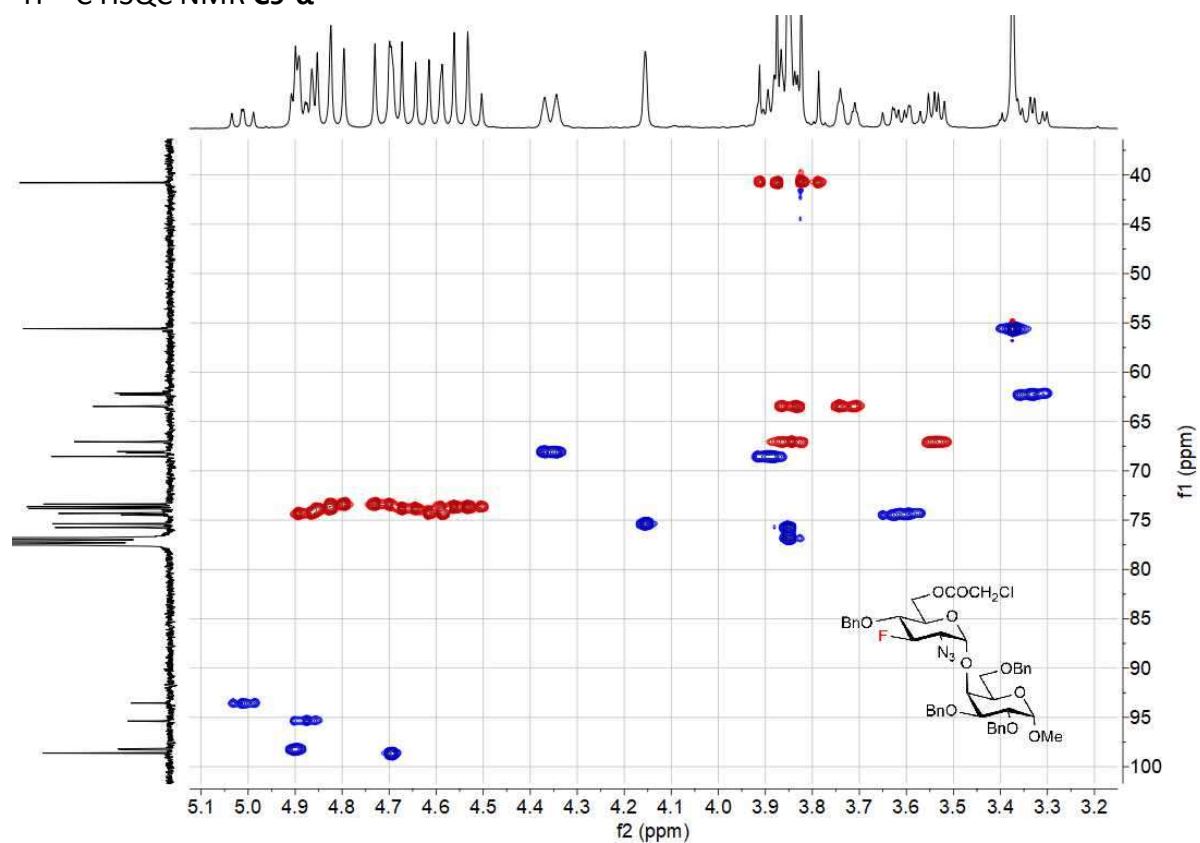
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **C9- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR C9- $\alpha$



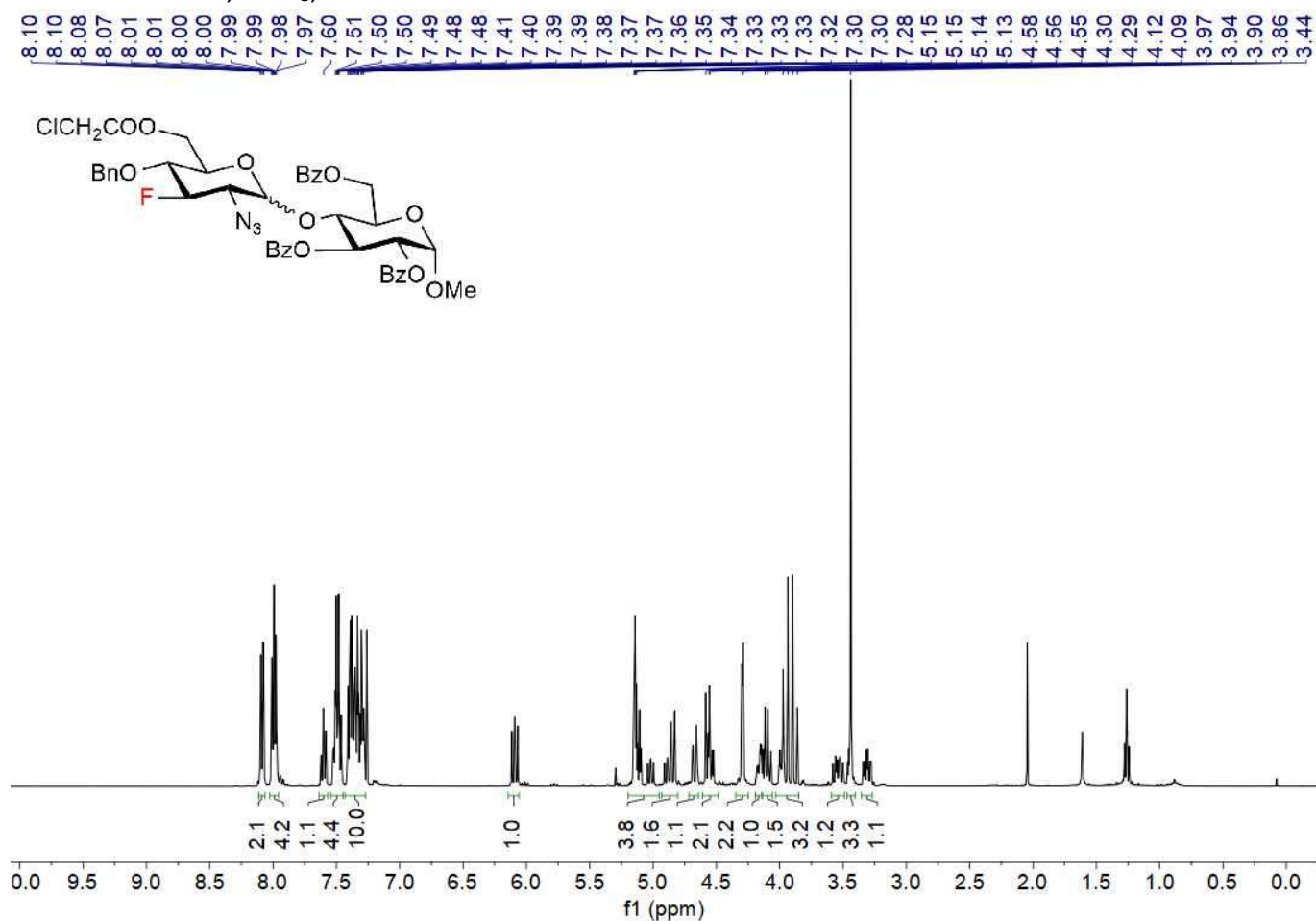
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR C9- $\alpha$



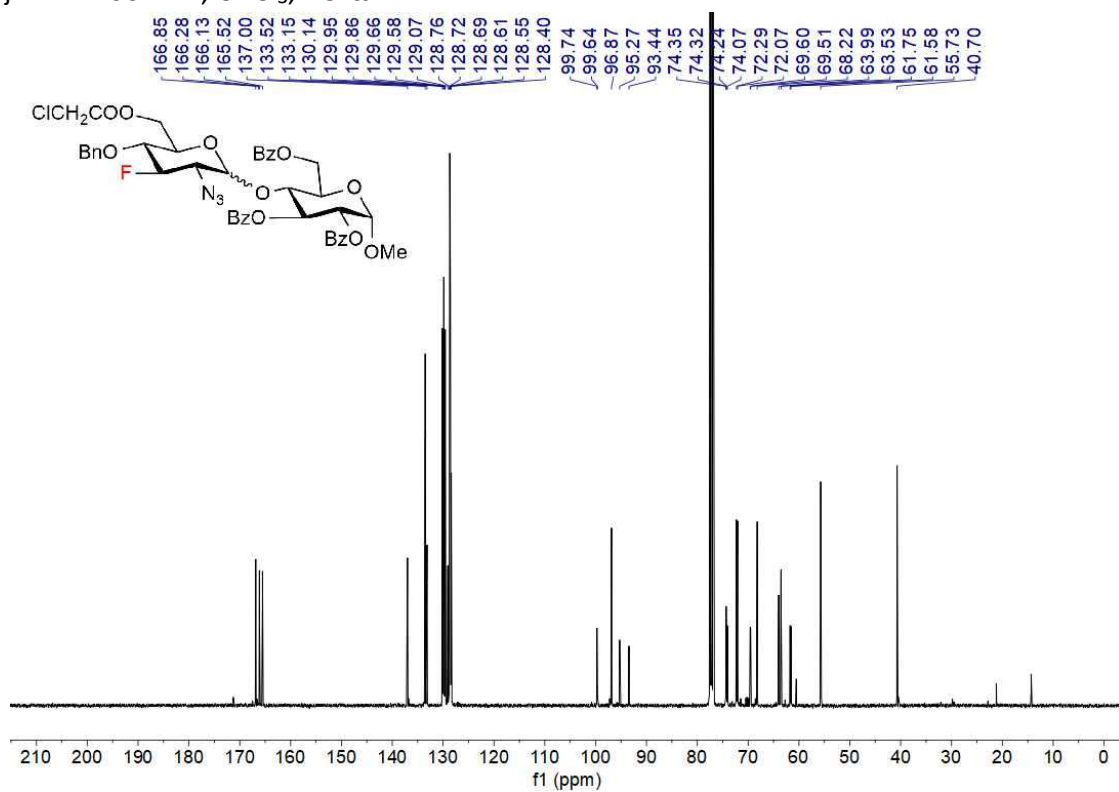


# NMR D9- $\alpha$

$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **D9- $\alpha$**

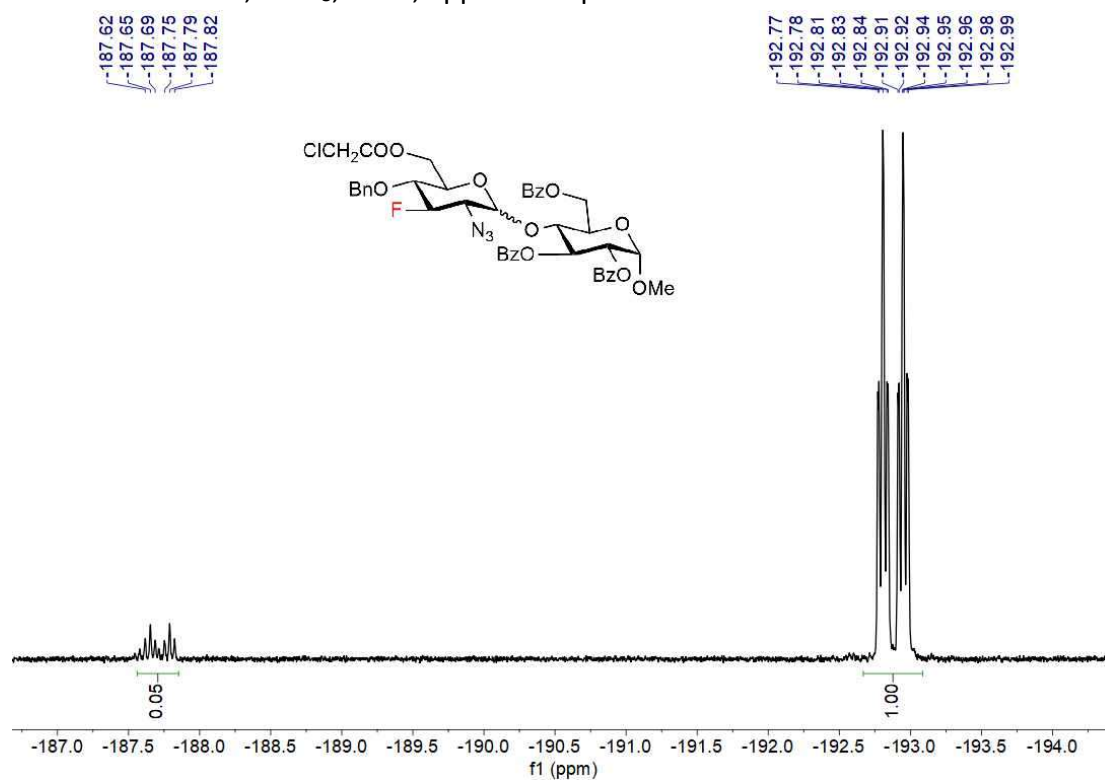


$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **D9- $\alpha$**

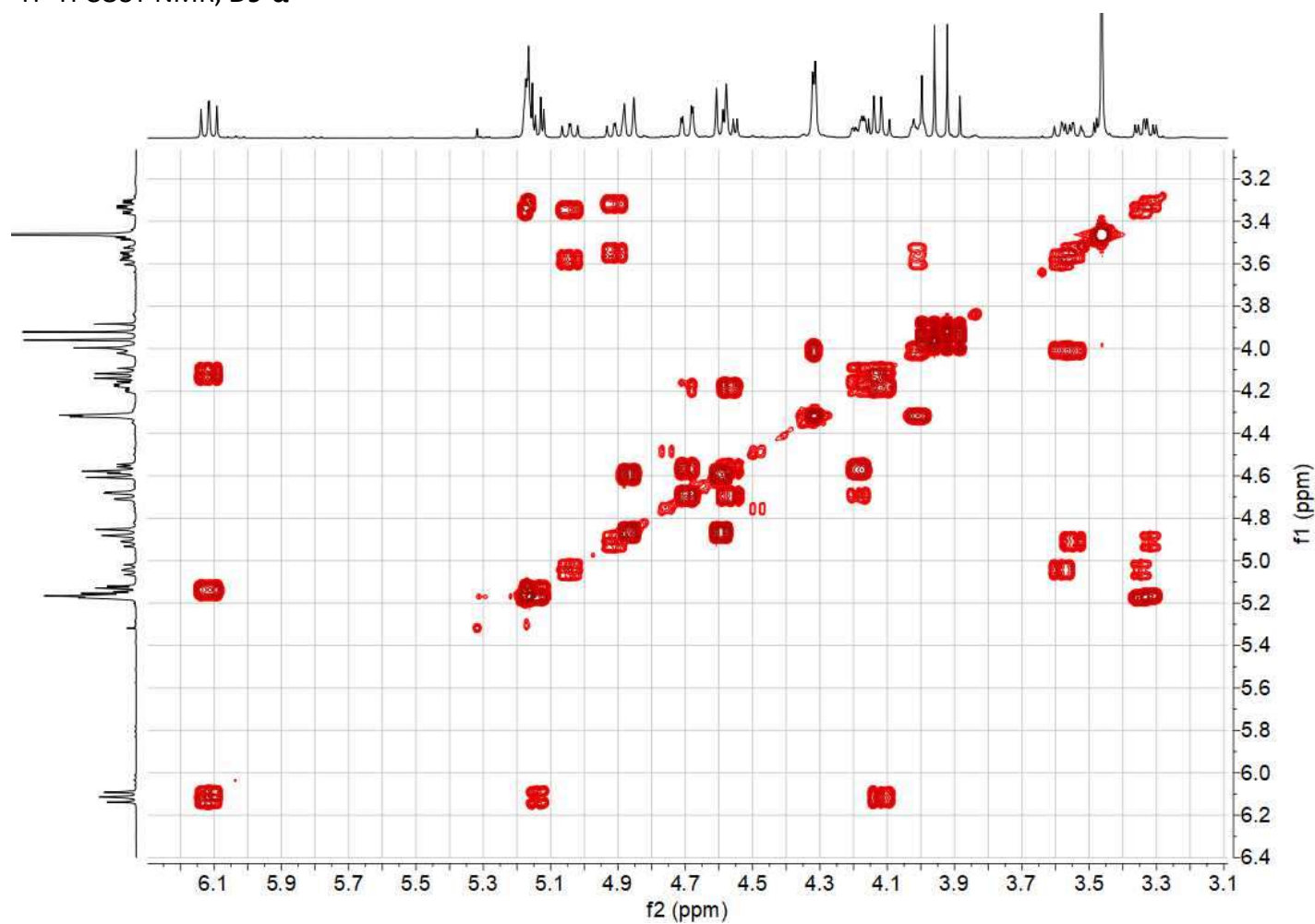




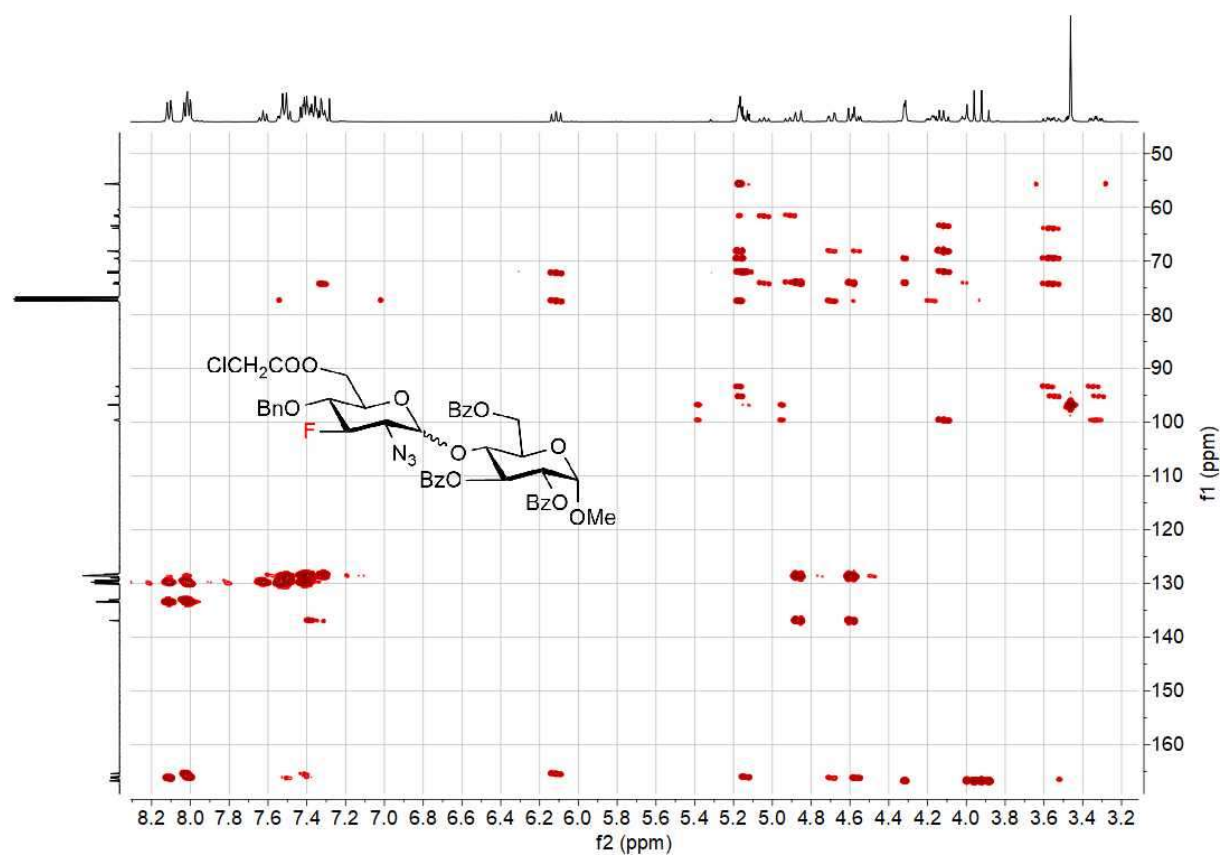
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **D9- $\alpha$** , approx. 5%  $\beta$ -anomer at  $\delta$  -187.72



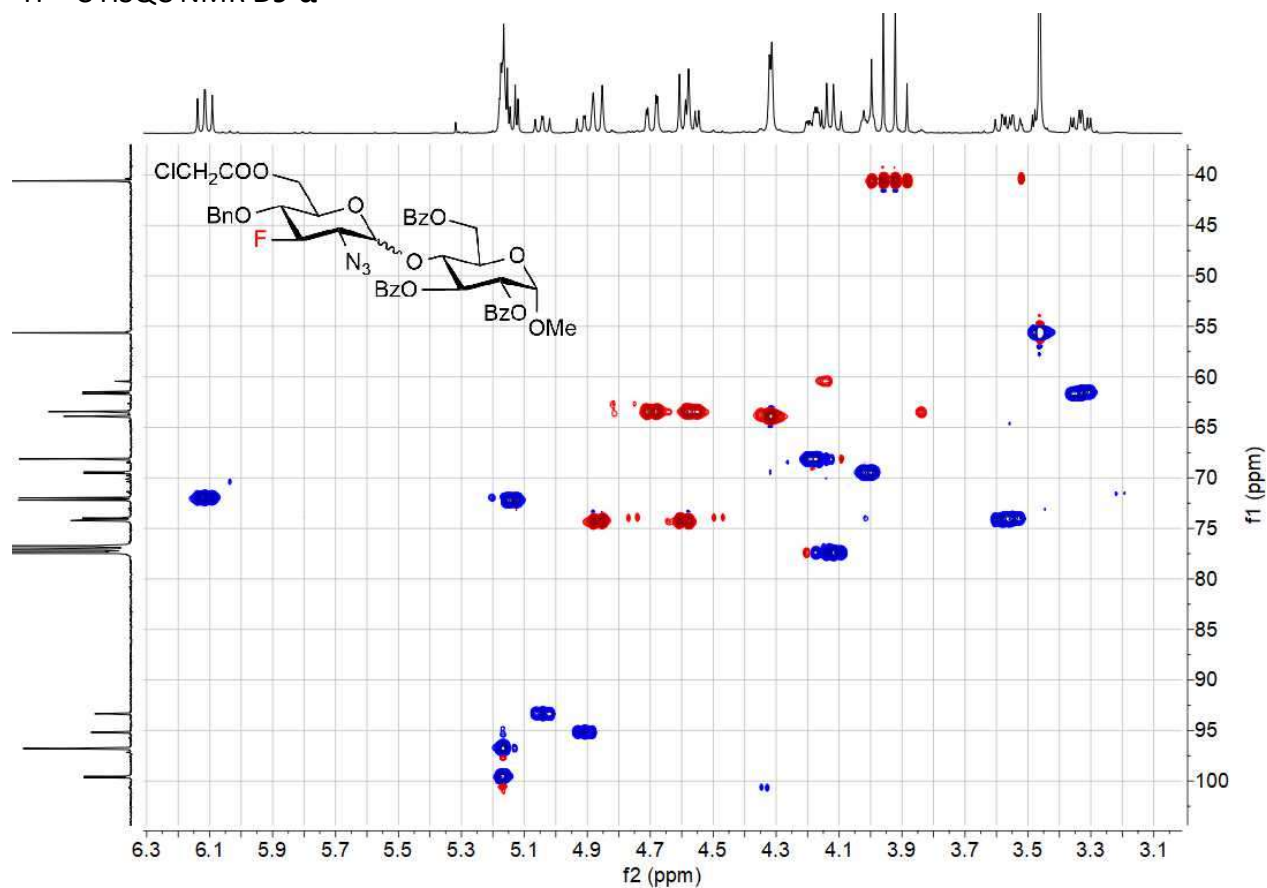
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **D9- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **D9- $\alpha$**

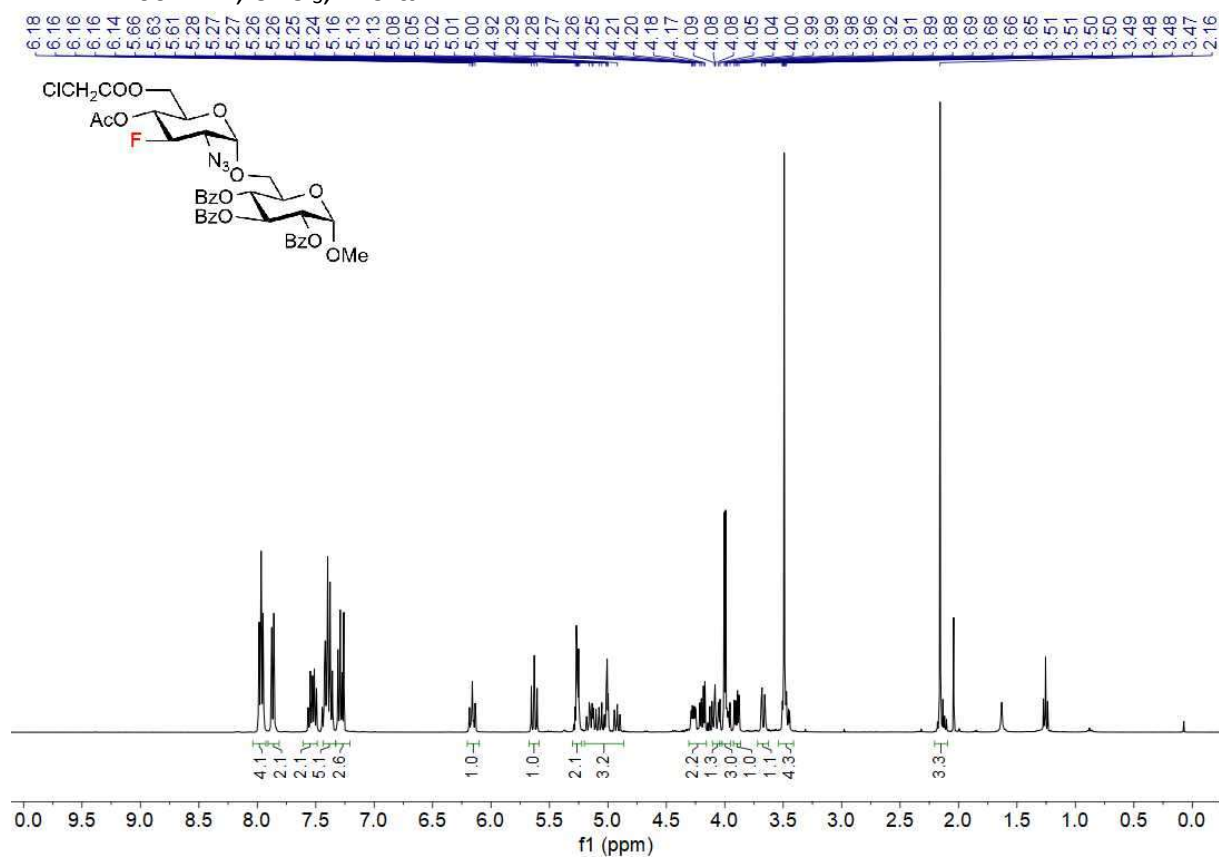


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **D9- $\alpha$**

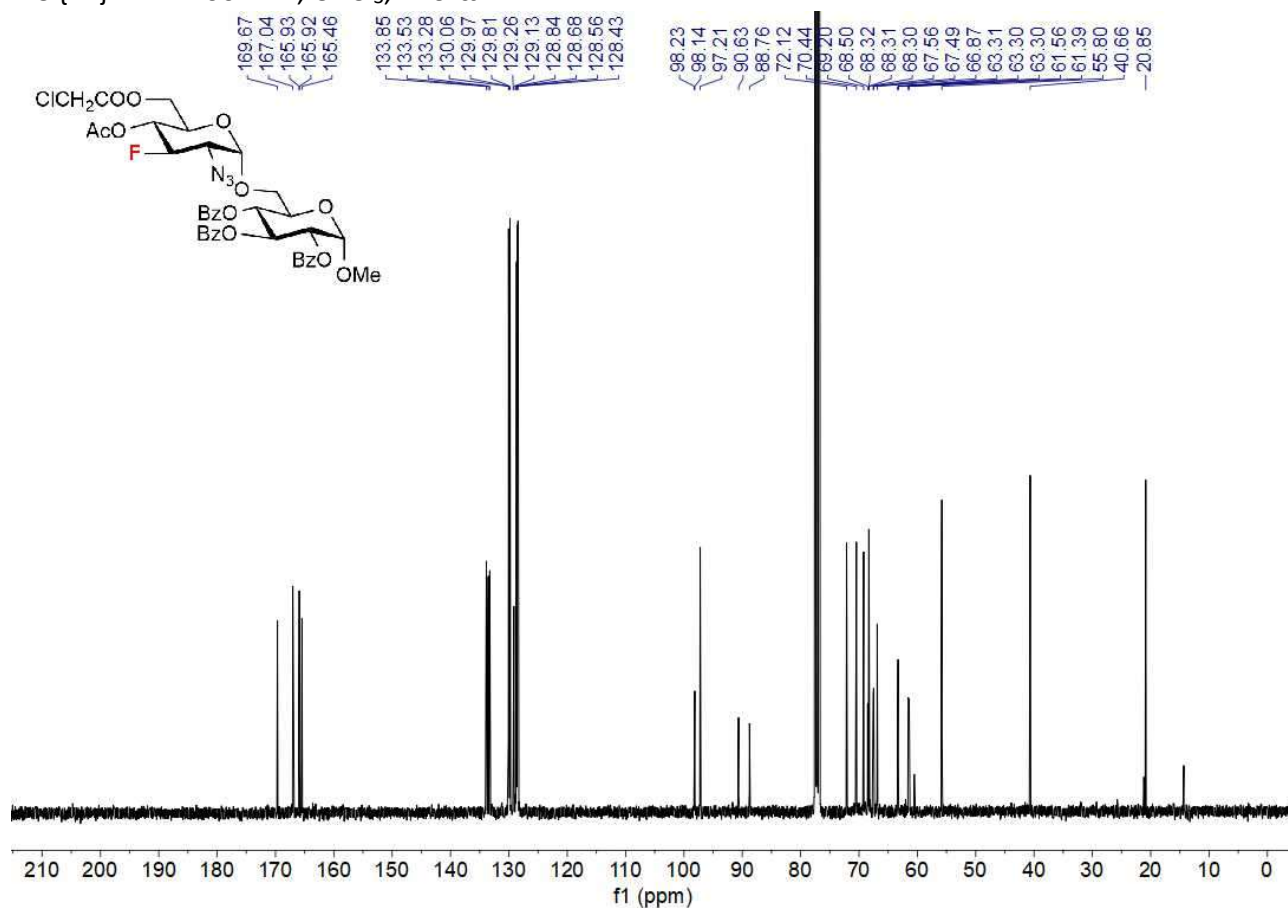


# **NMR E16-α**

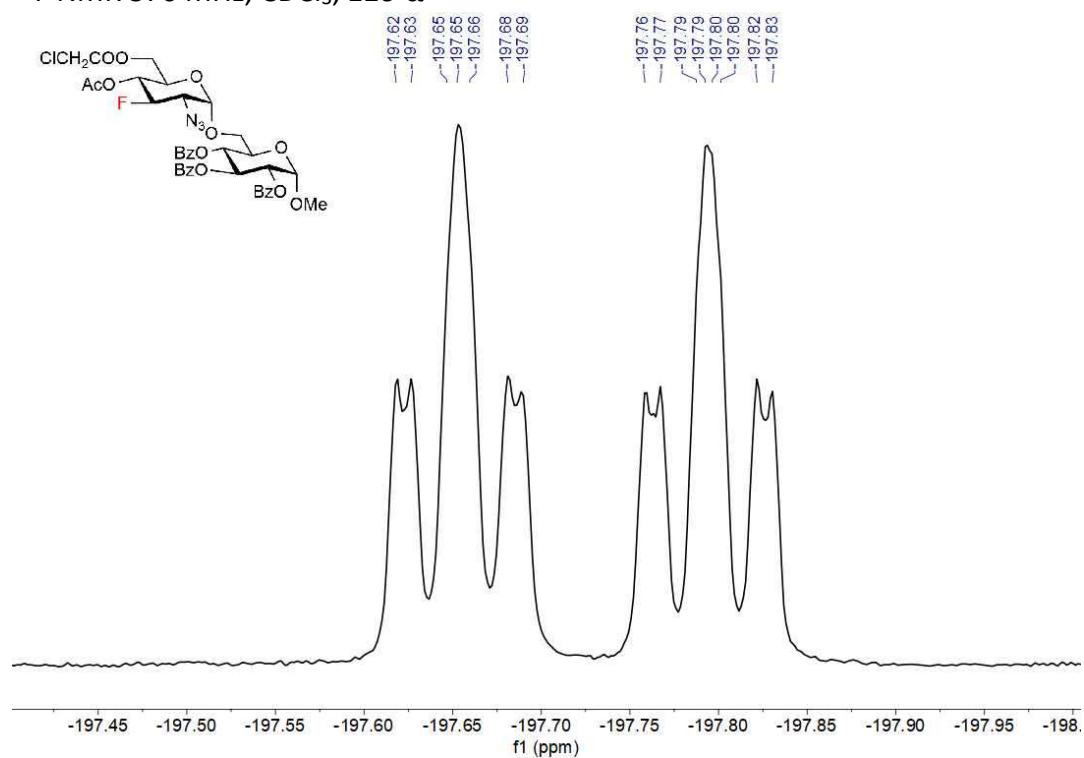
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E16-α**



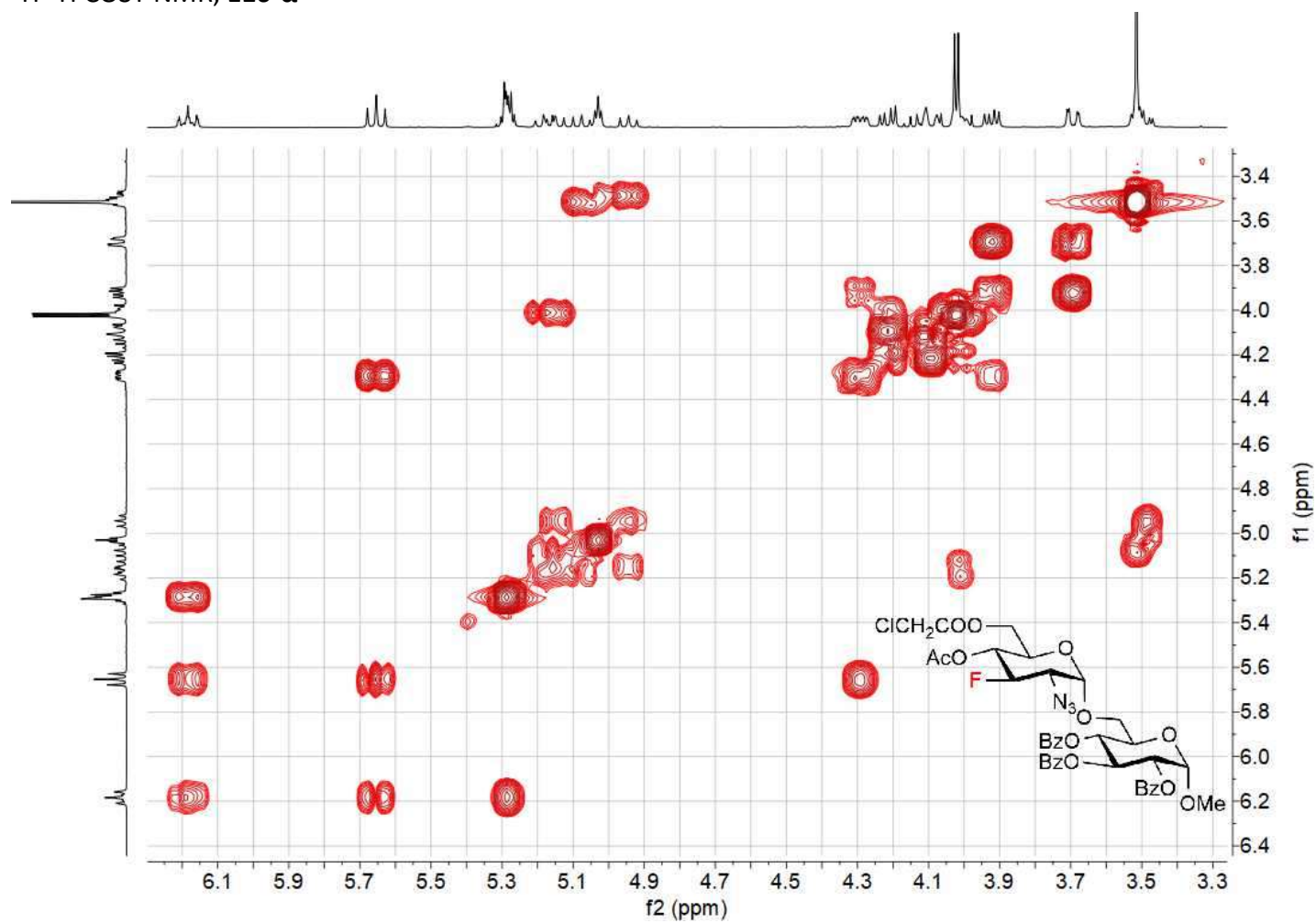
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E16-α**



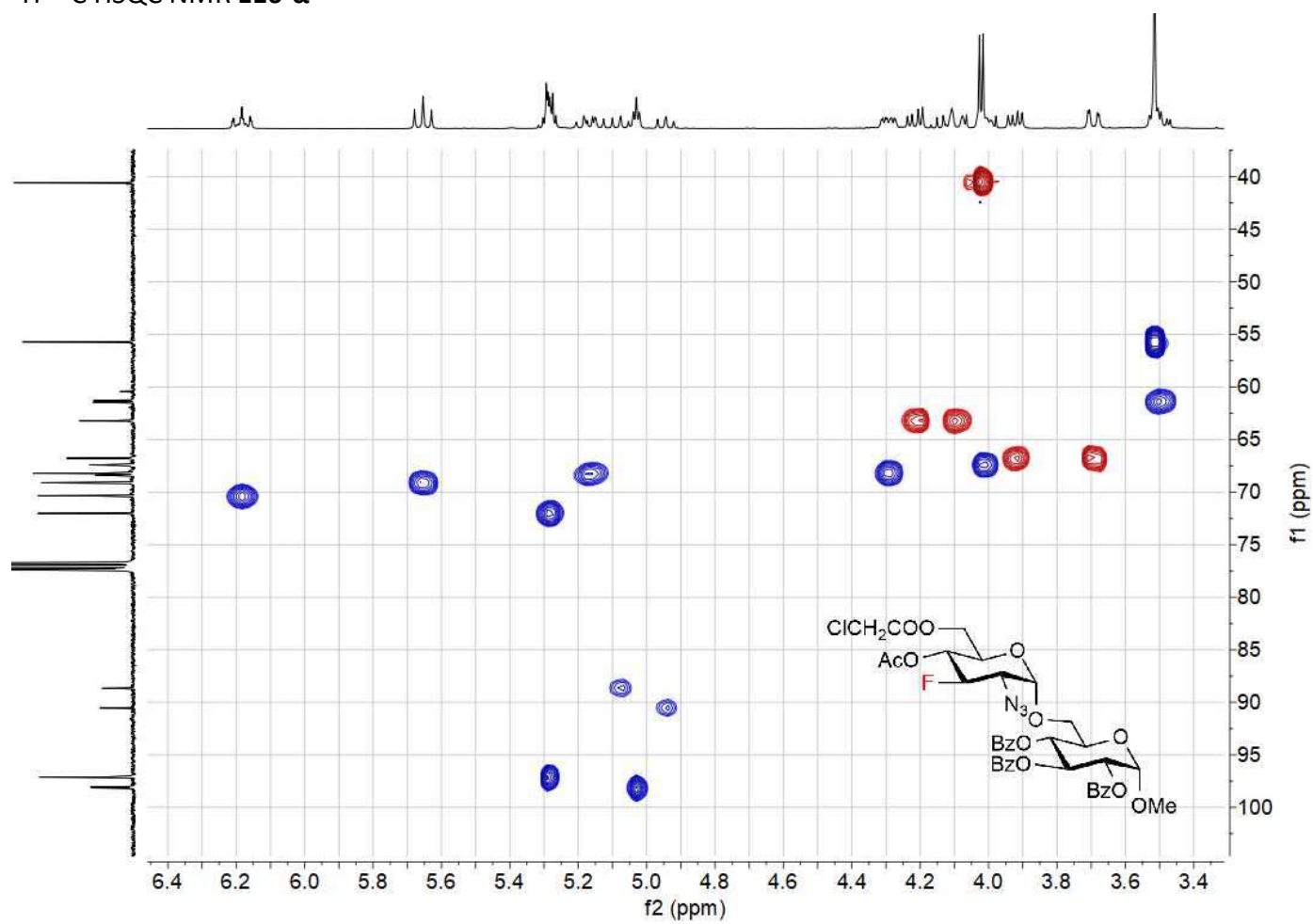
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E16- $\alpha$**



$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E16- $\alpha$**

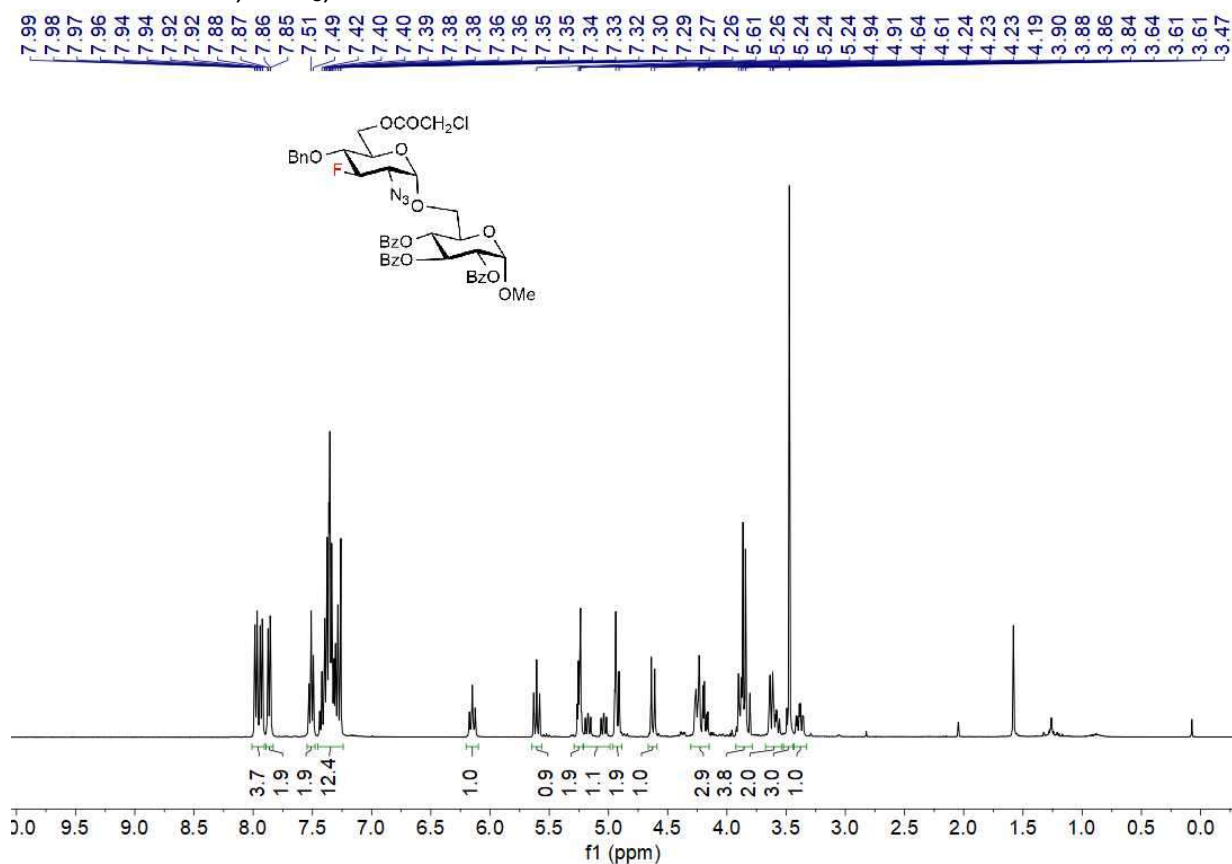


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR E16- $\alpha$

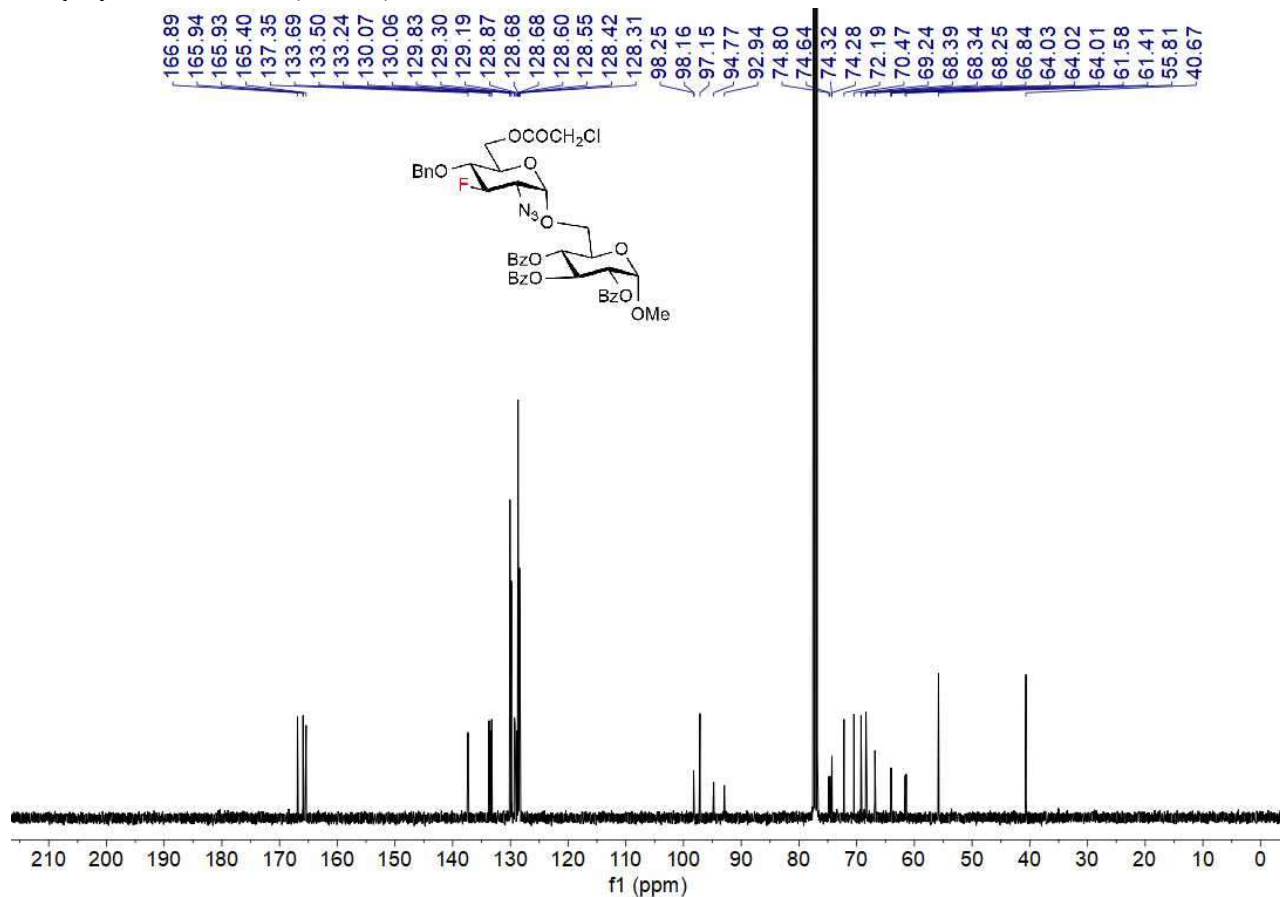


# **NMR E9-α**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E9-α**

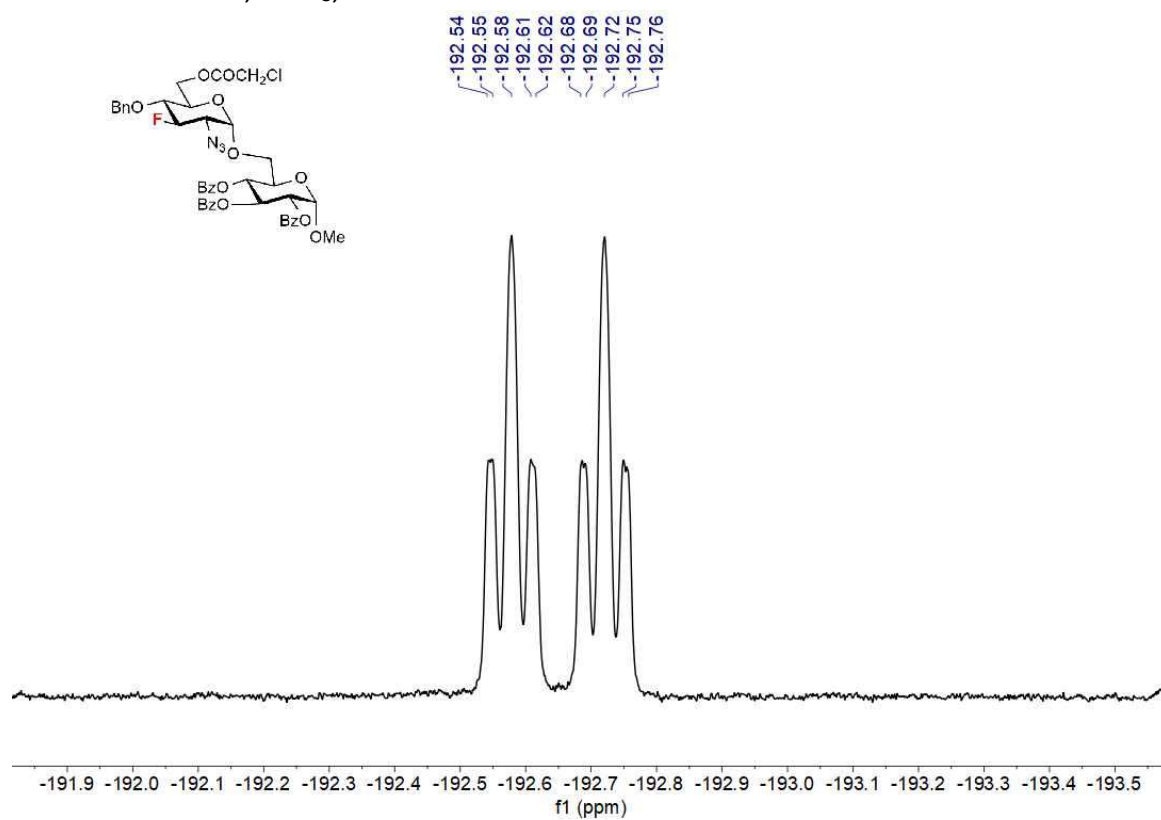


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E9-α**

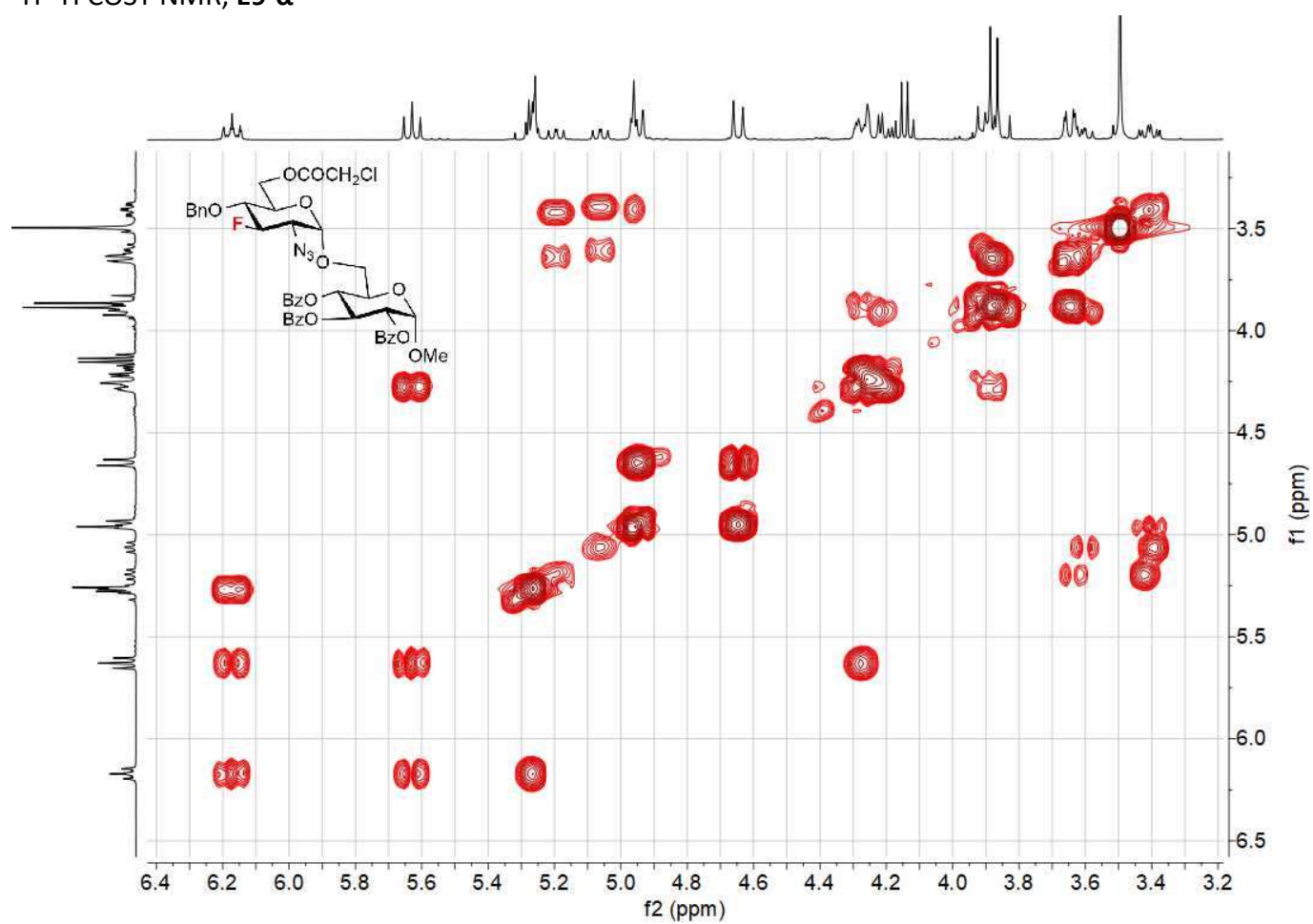




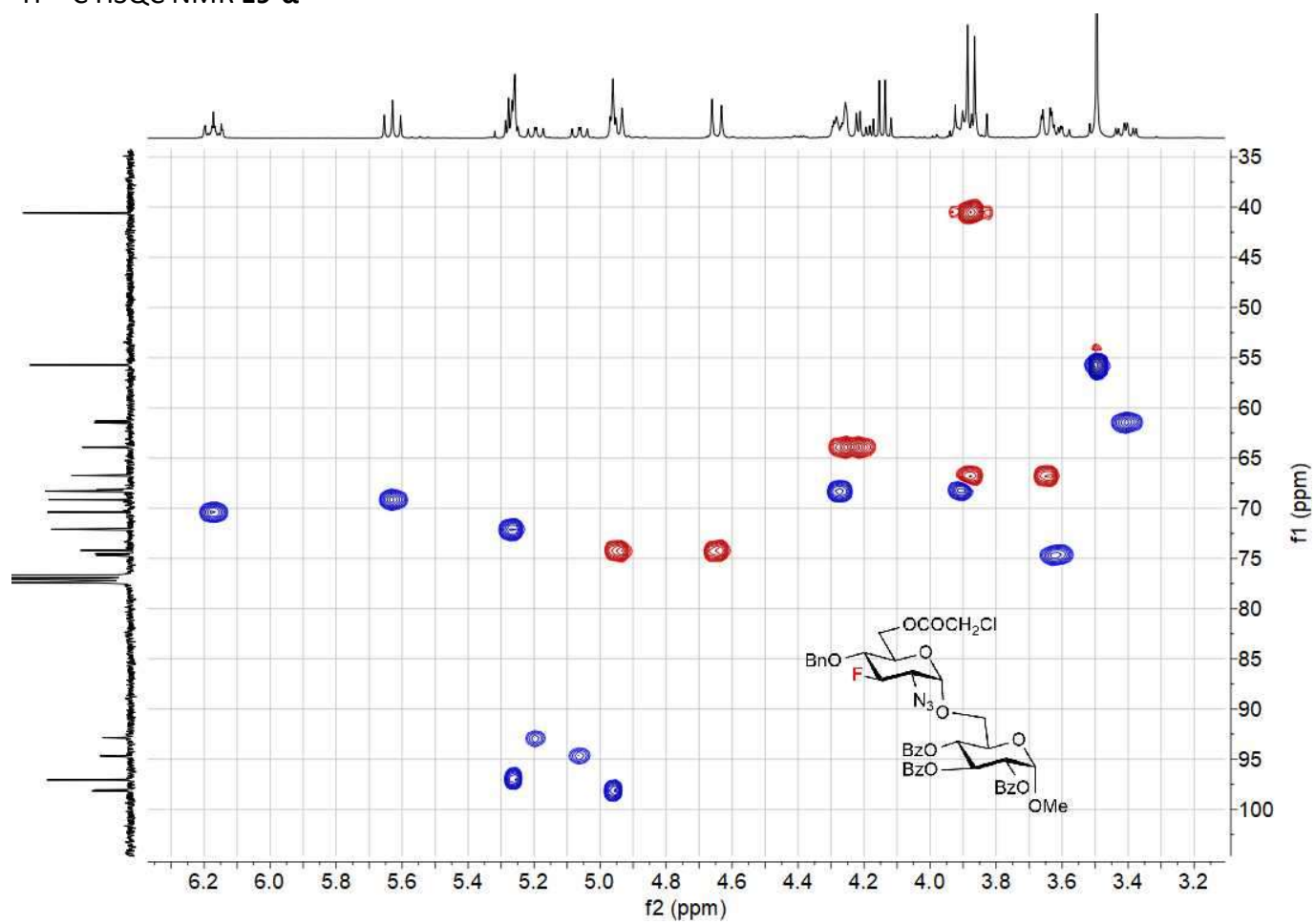
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E9- $\alpha$**



$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E9- $\alpha$**

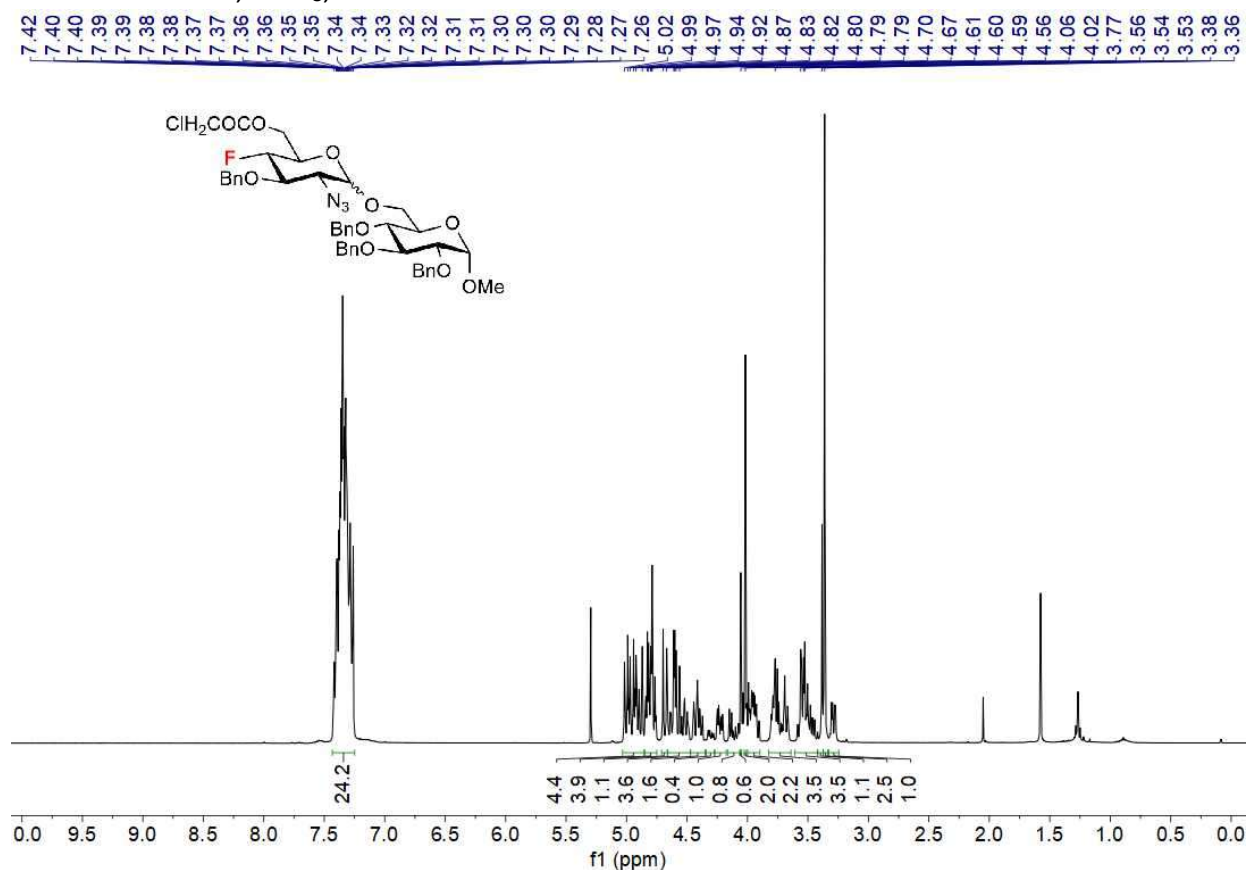


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR E9- $\alpha$

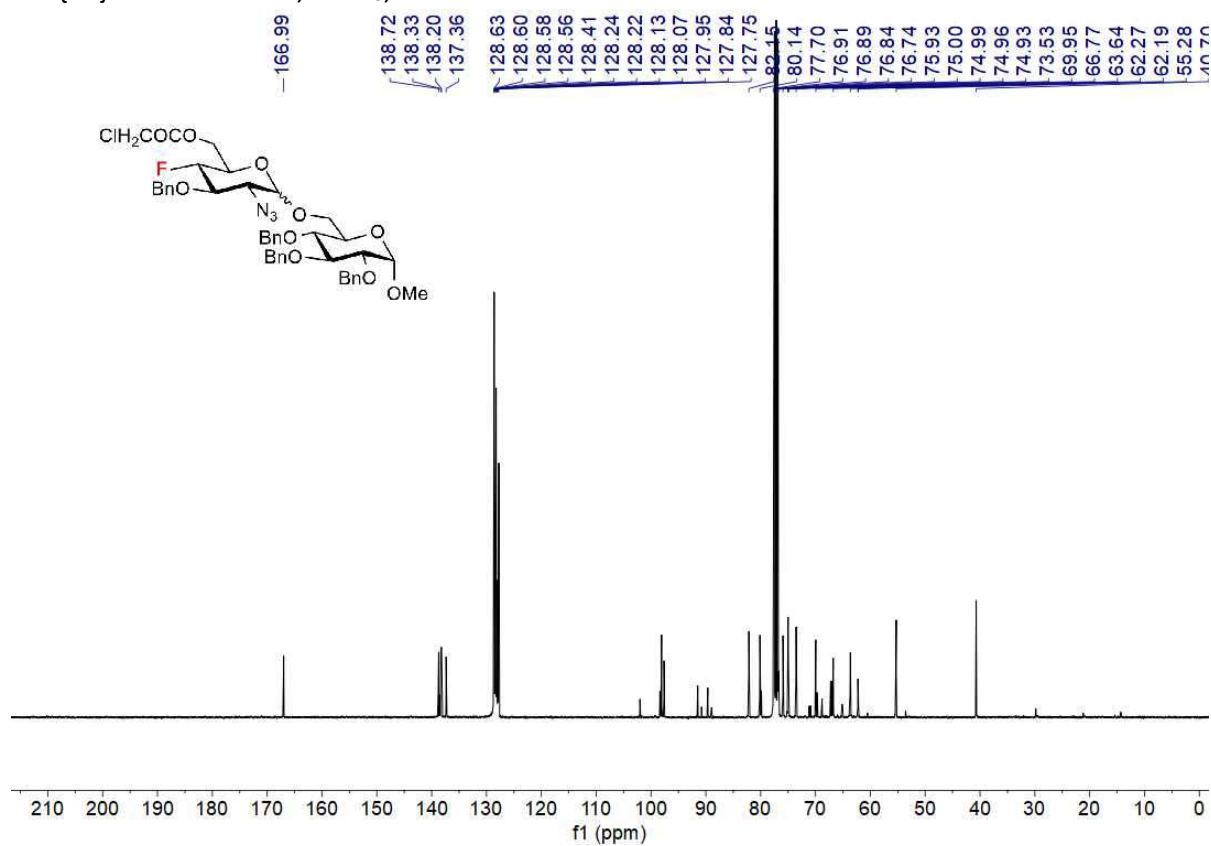


# NMR A20

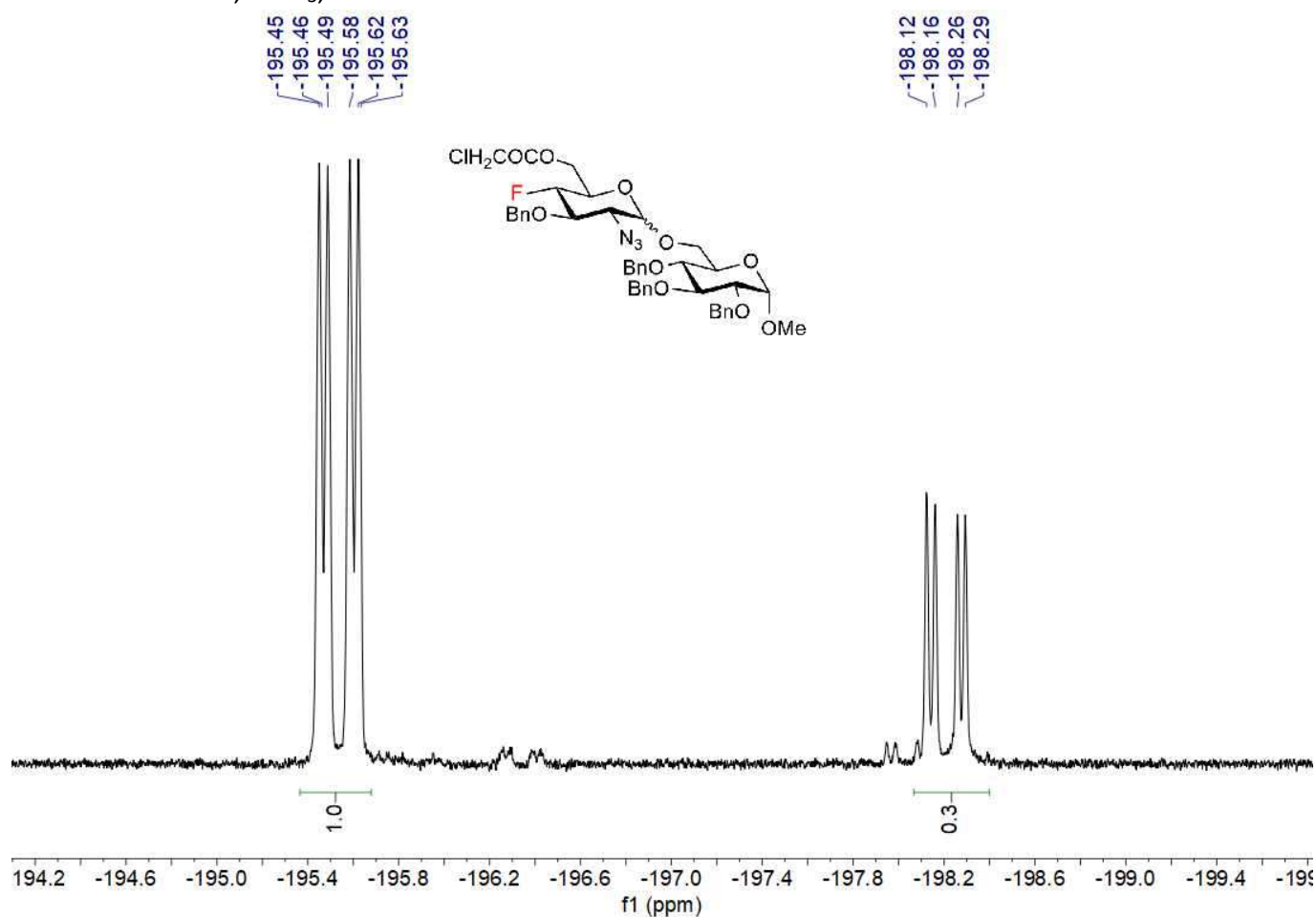
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, A20



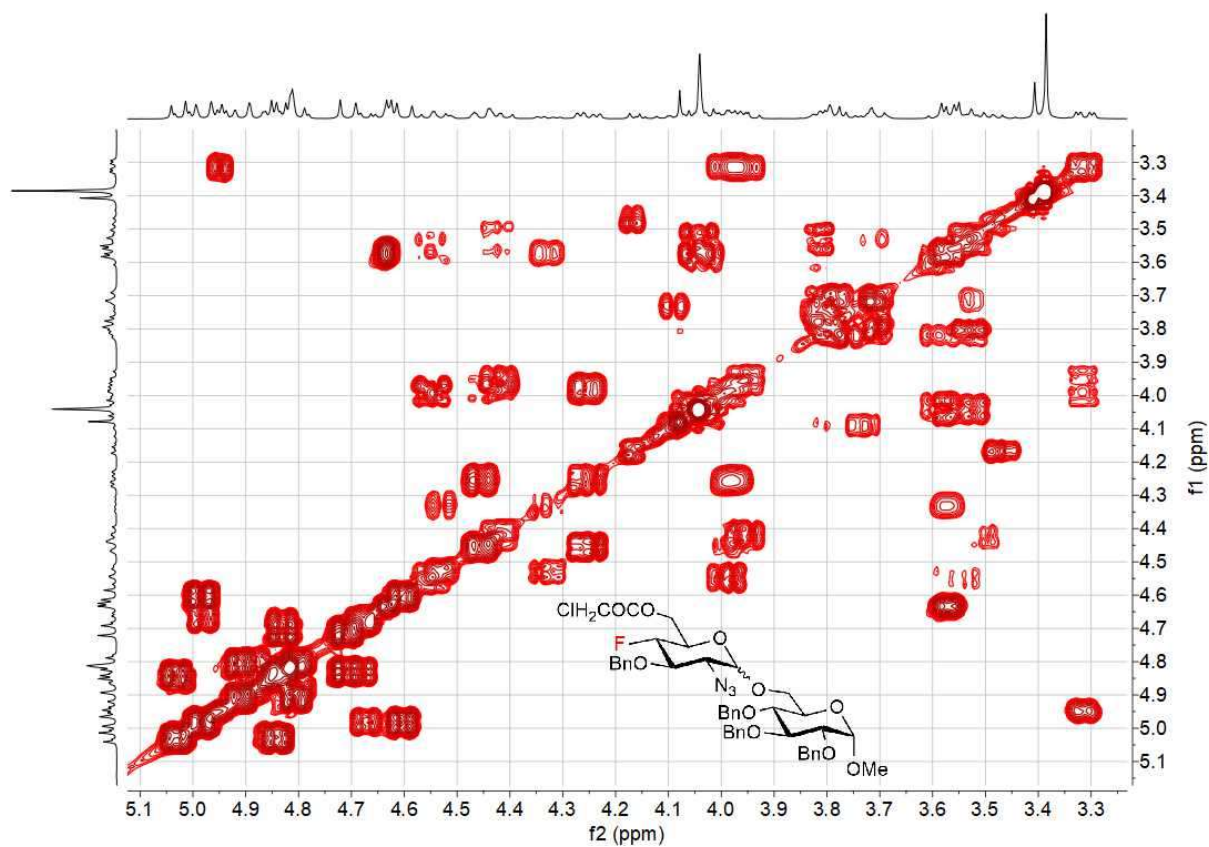
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, A20



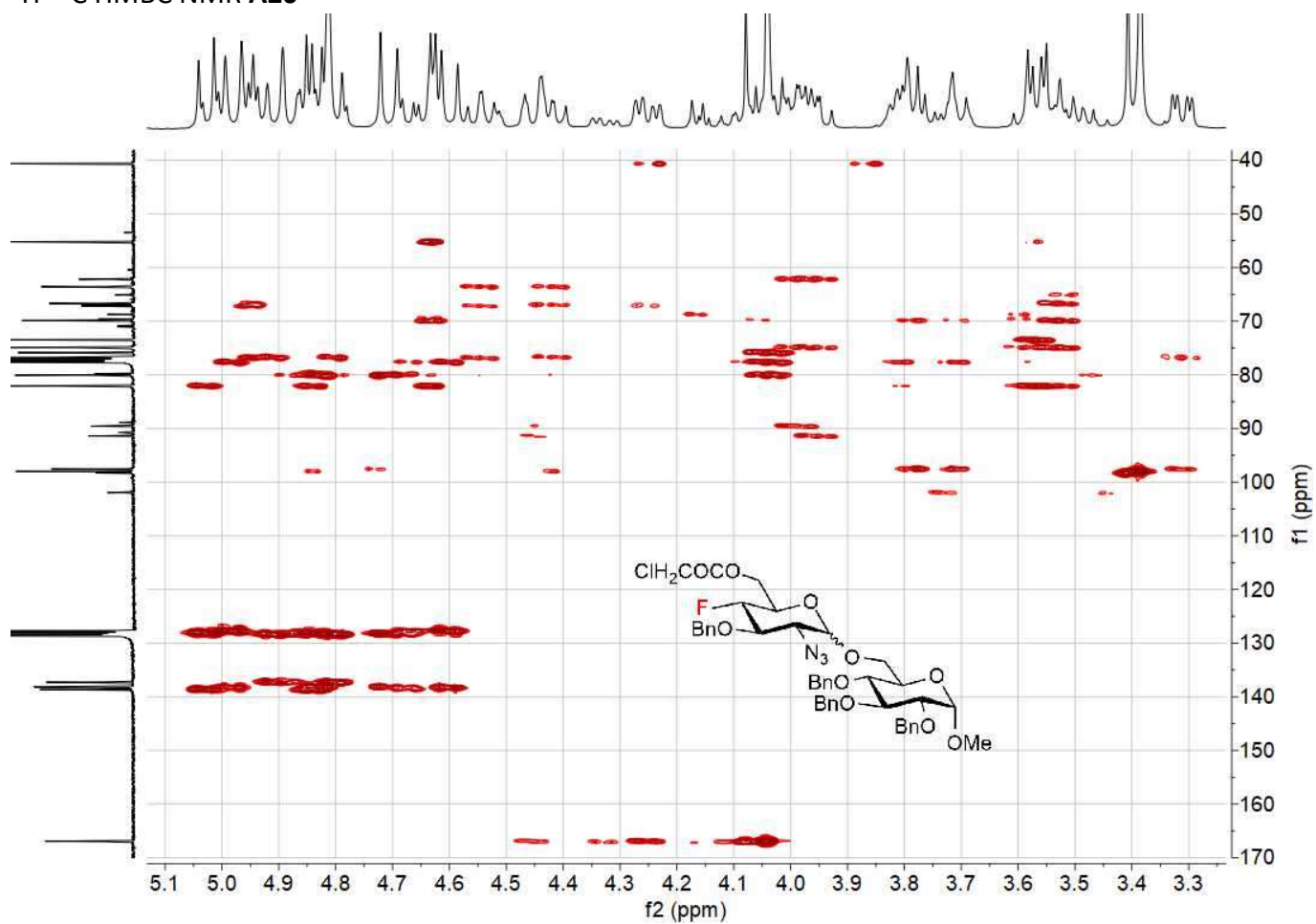
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **A20**



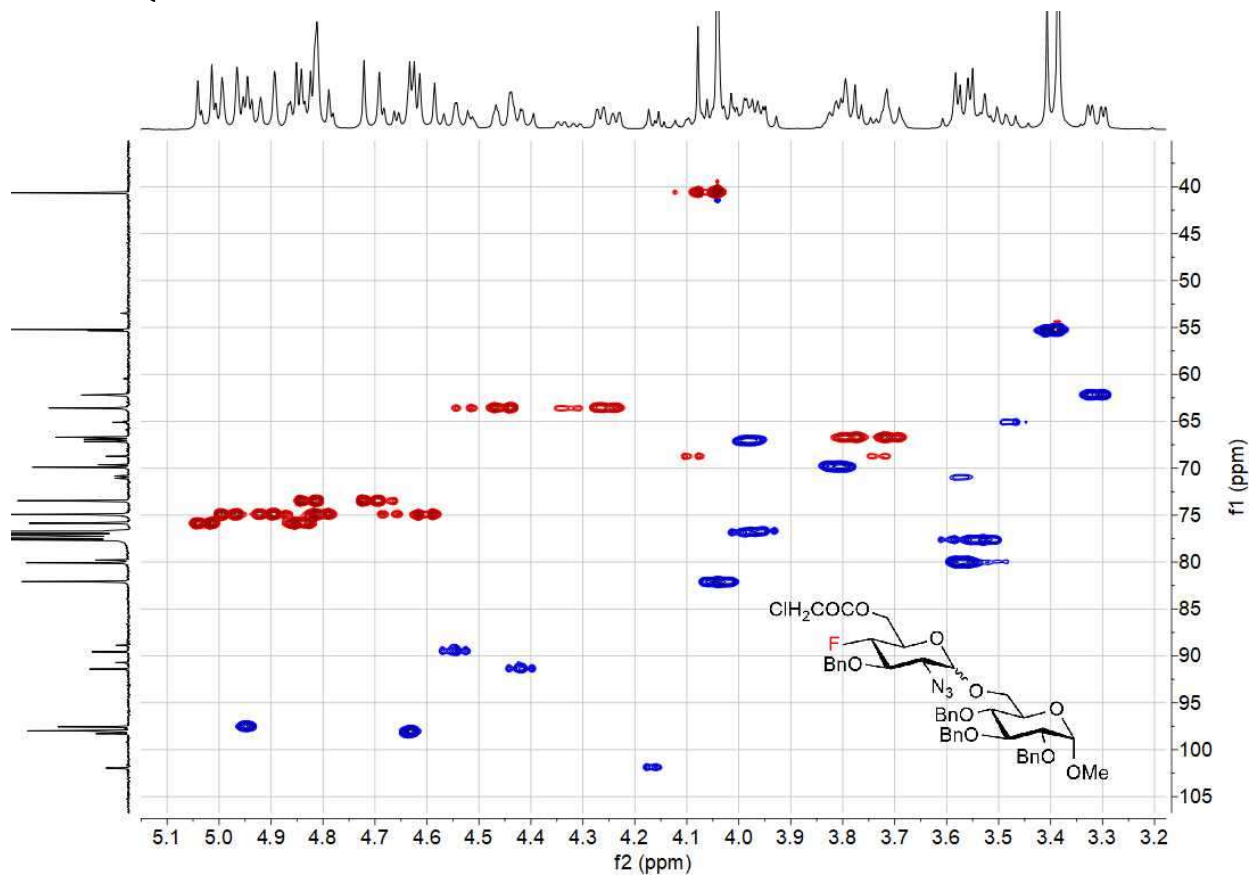
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **A20**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR A20



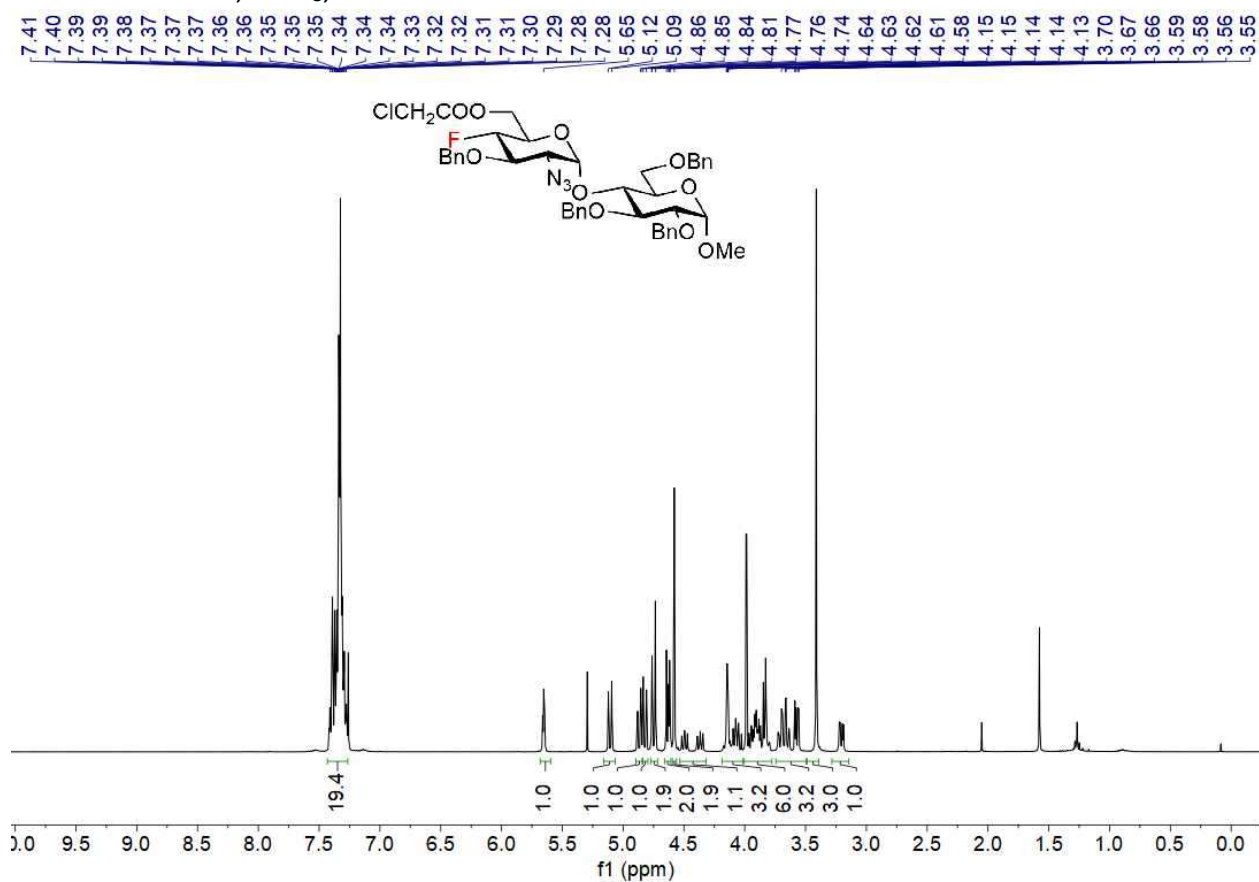
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR A20



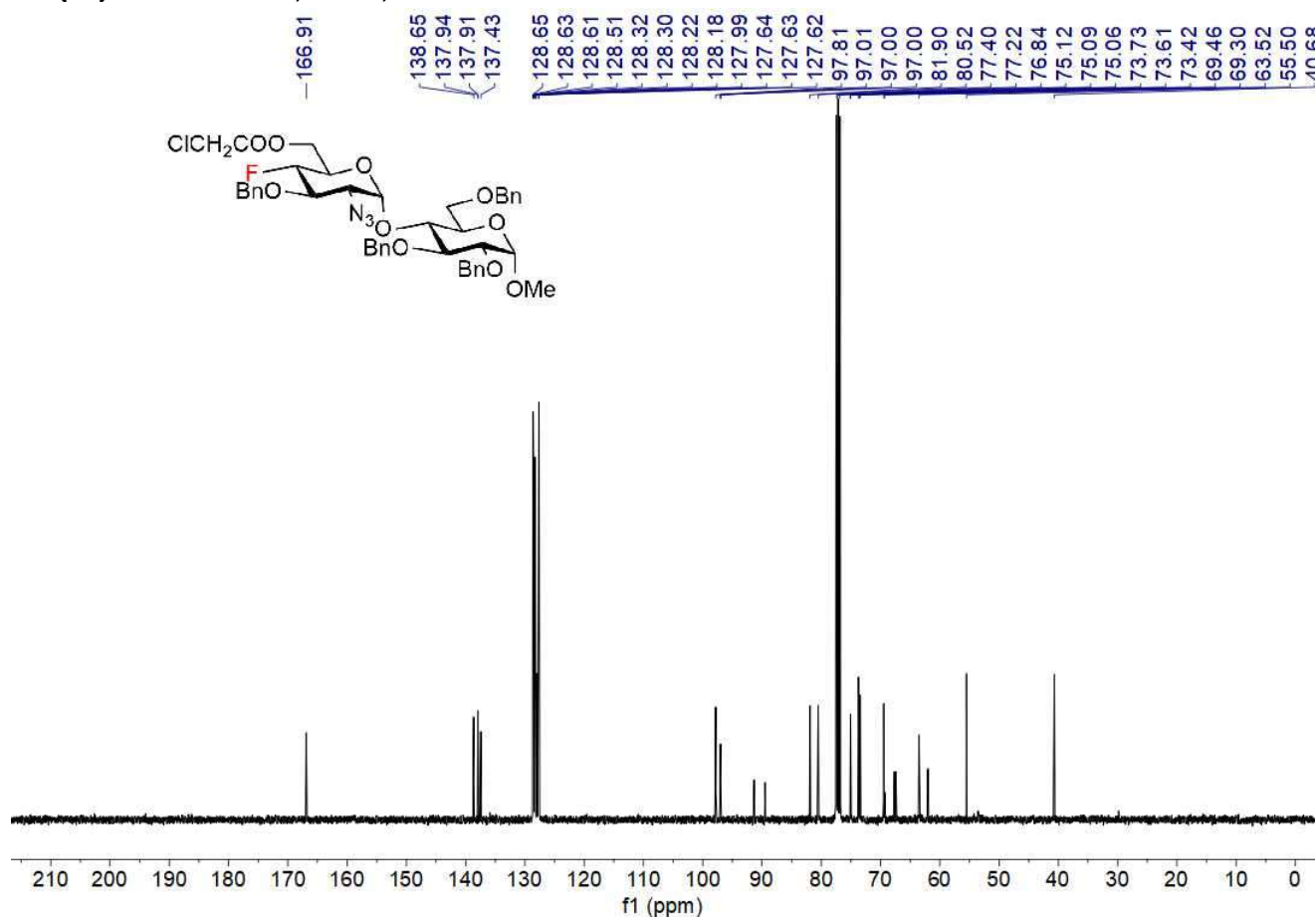


# **NMR B20-α**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **B20-α**

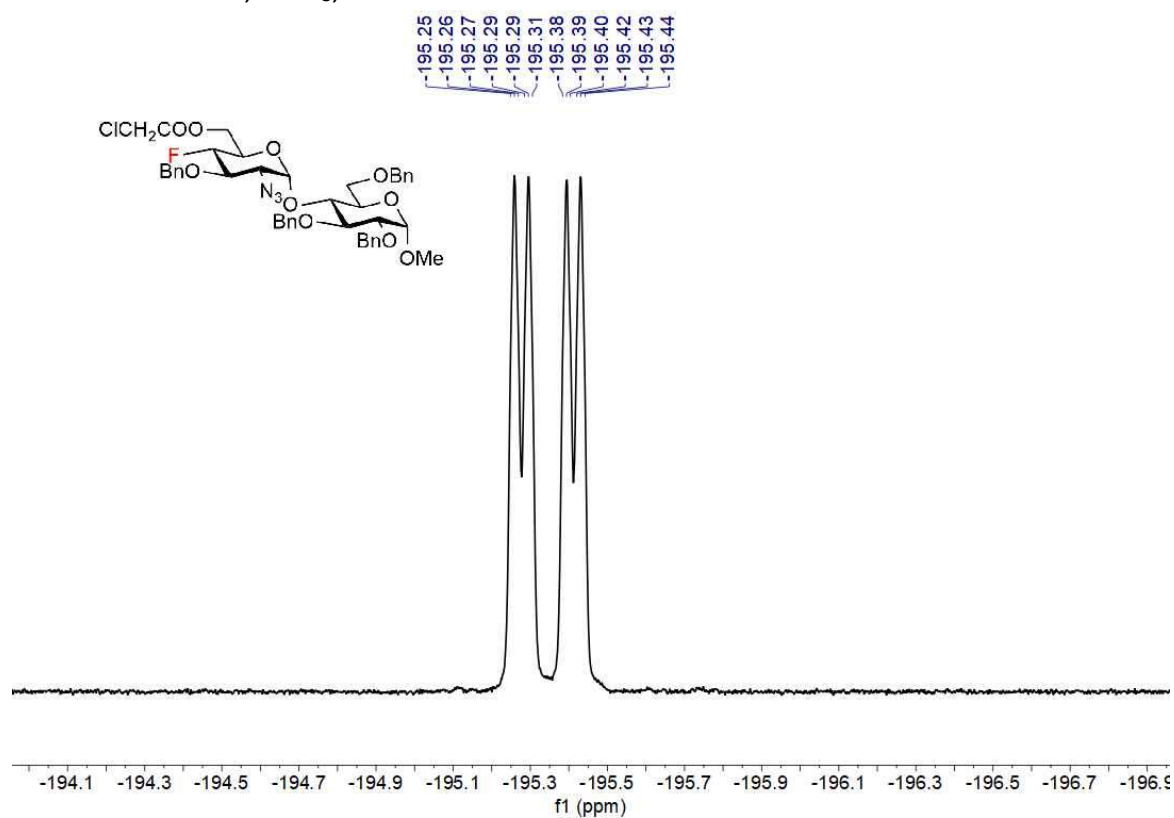


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **B20-α**

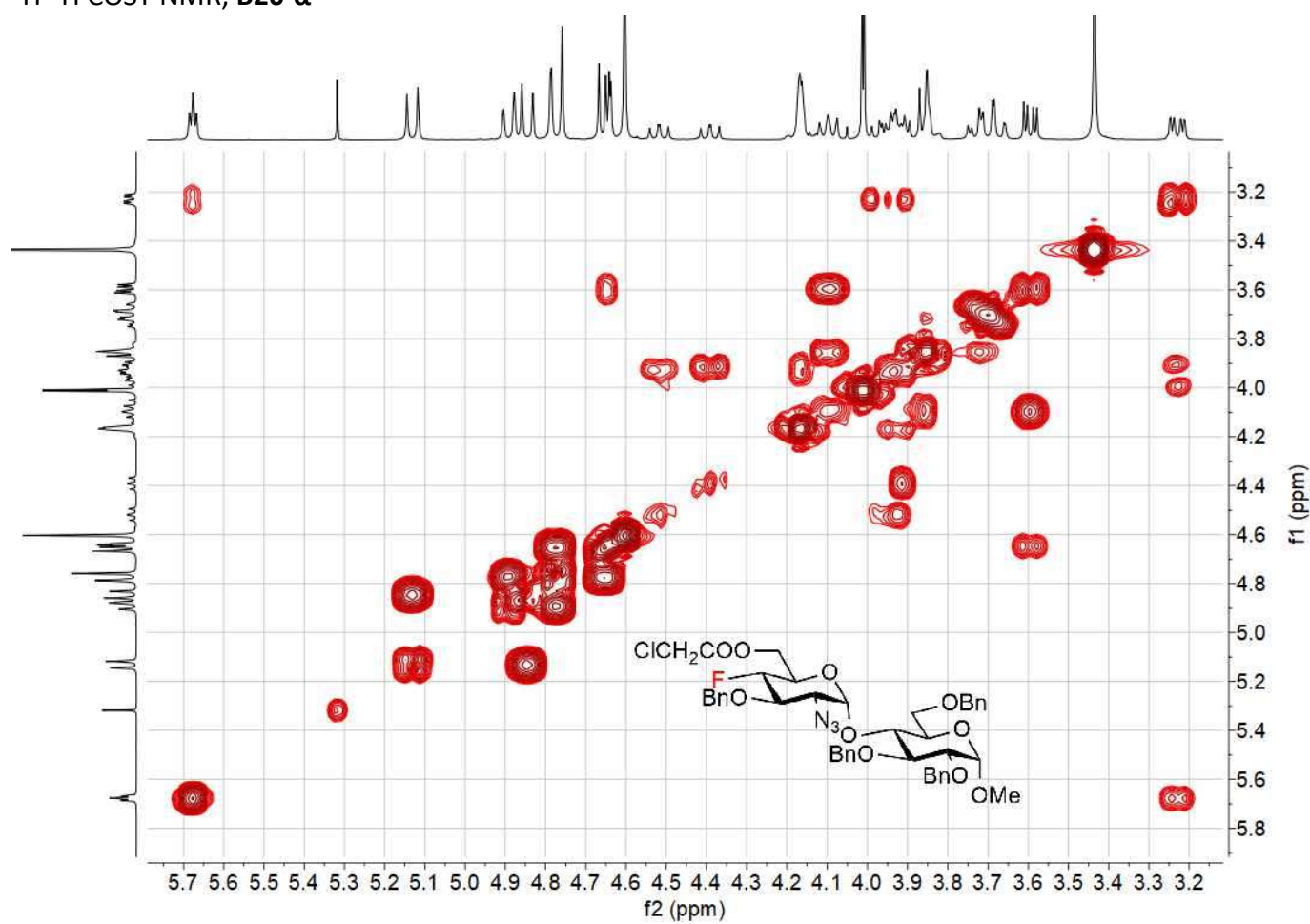




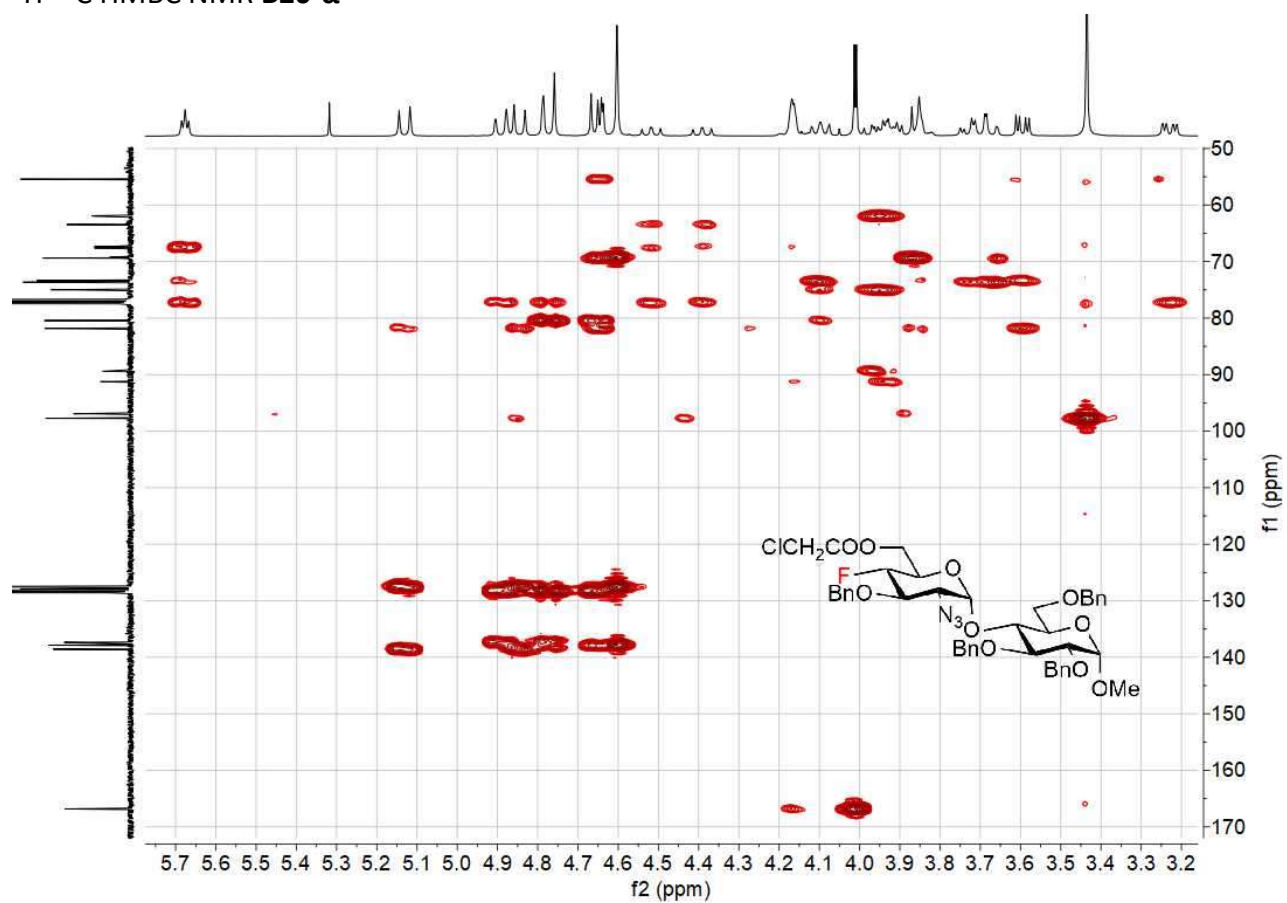
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B20- $\alpha$**



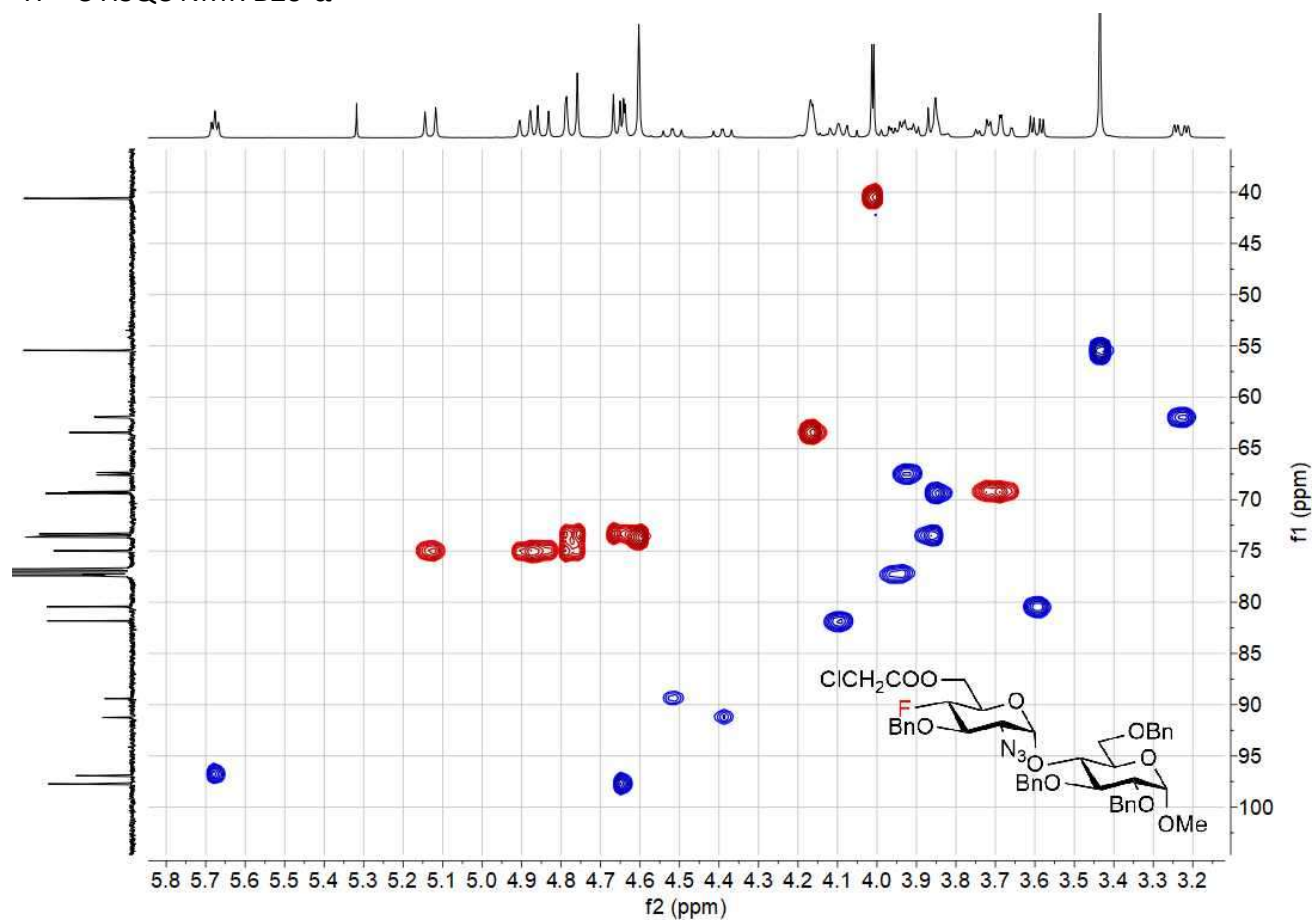
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B20- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **B20- $\alpha$**

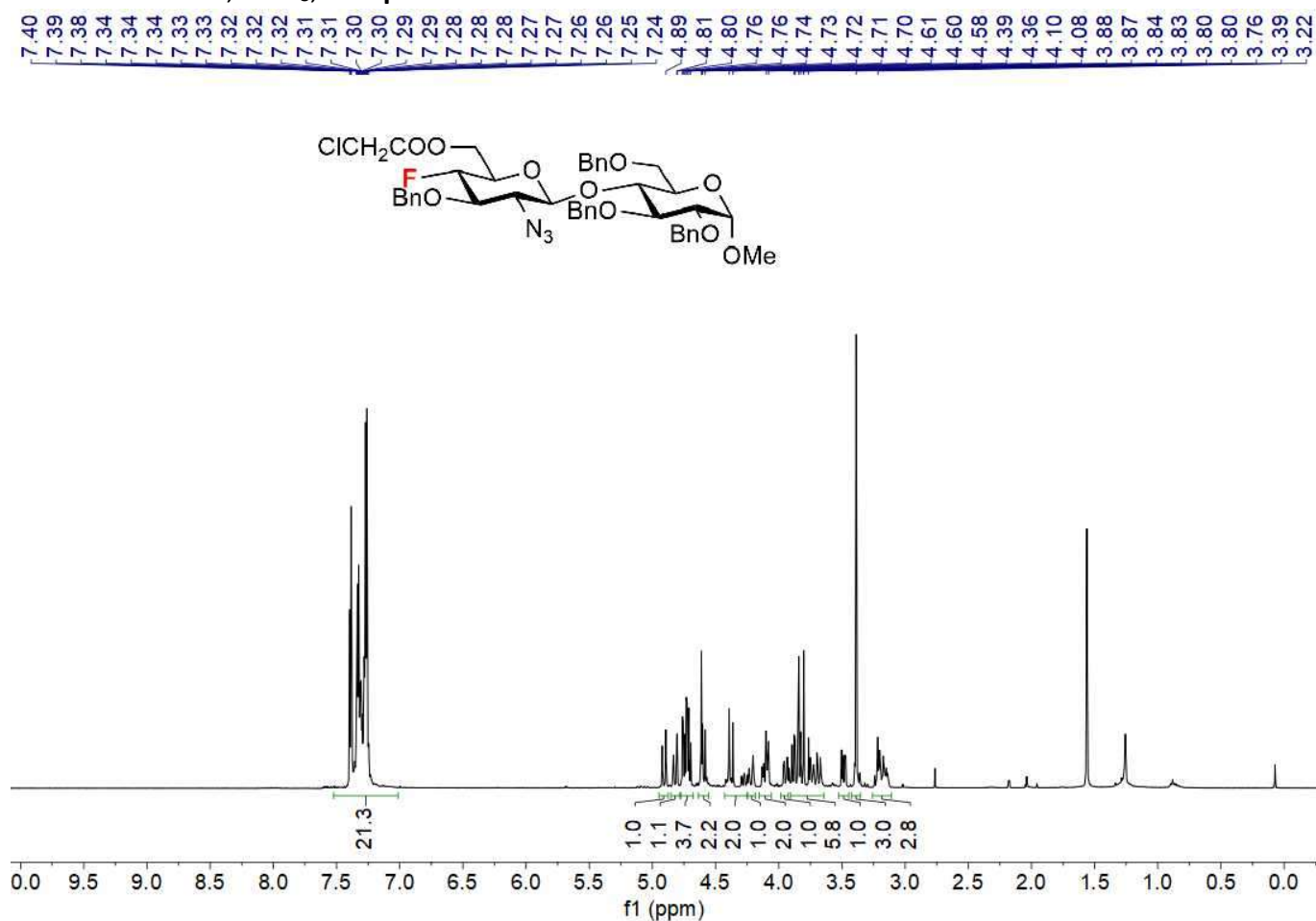


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **B20- $\alpha$**

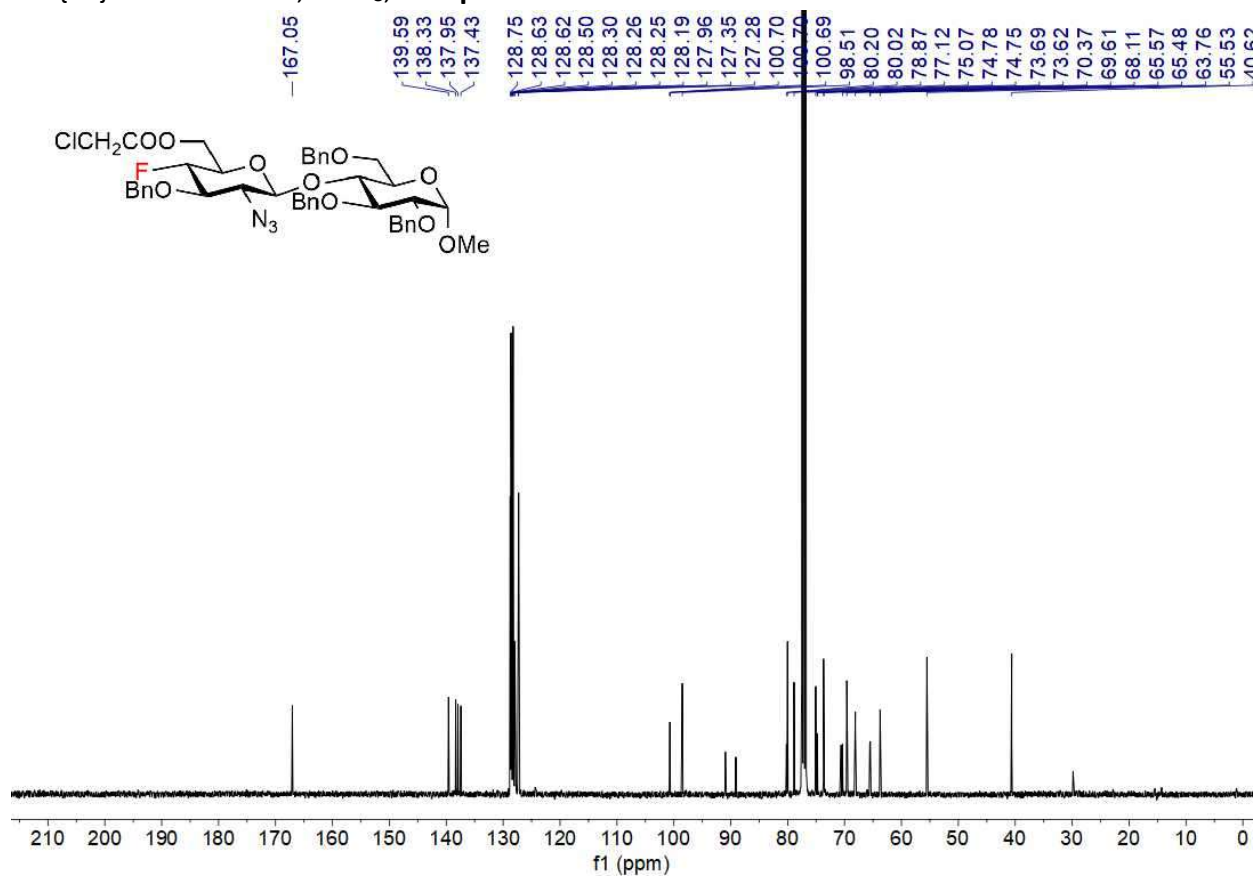


# **NMR B20-β**

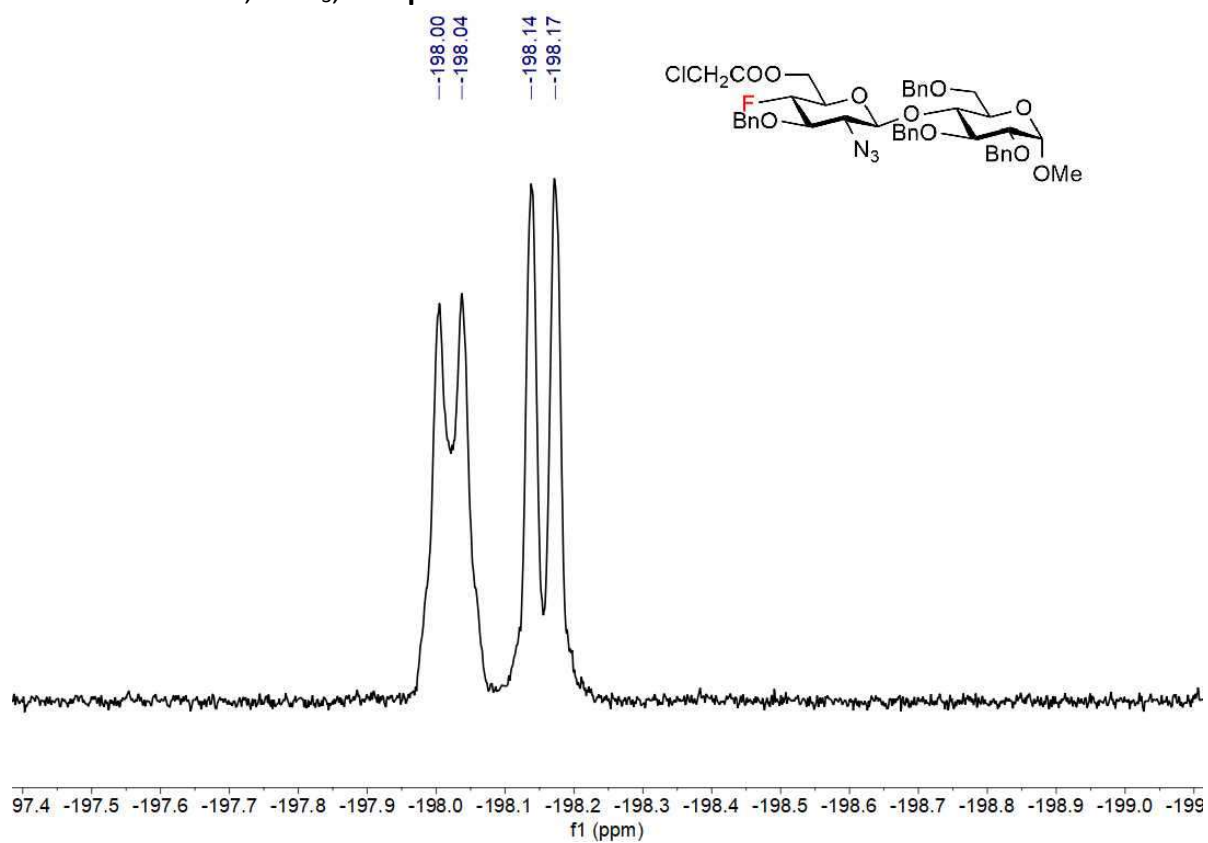
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **B20-β**



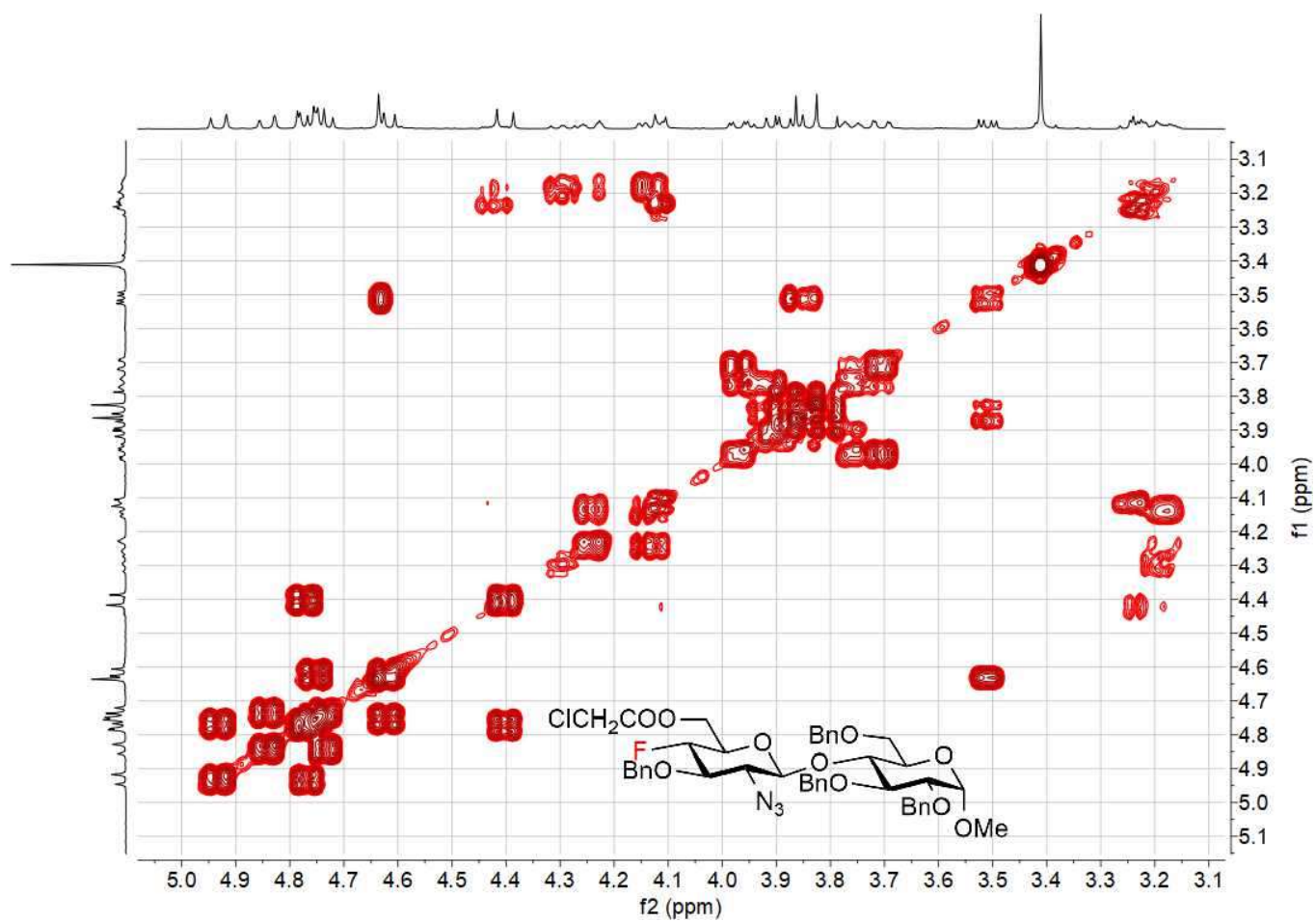
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **B20-β**



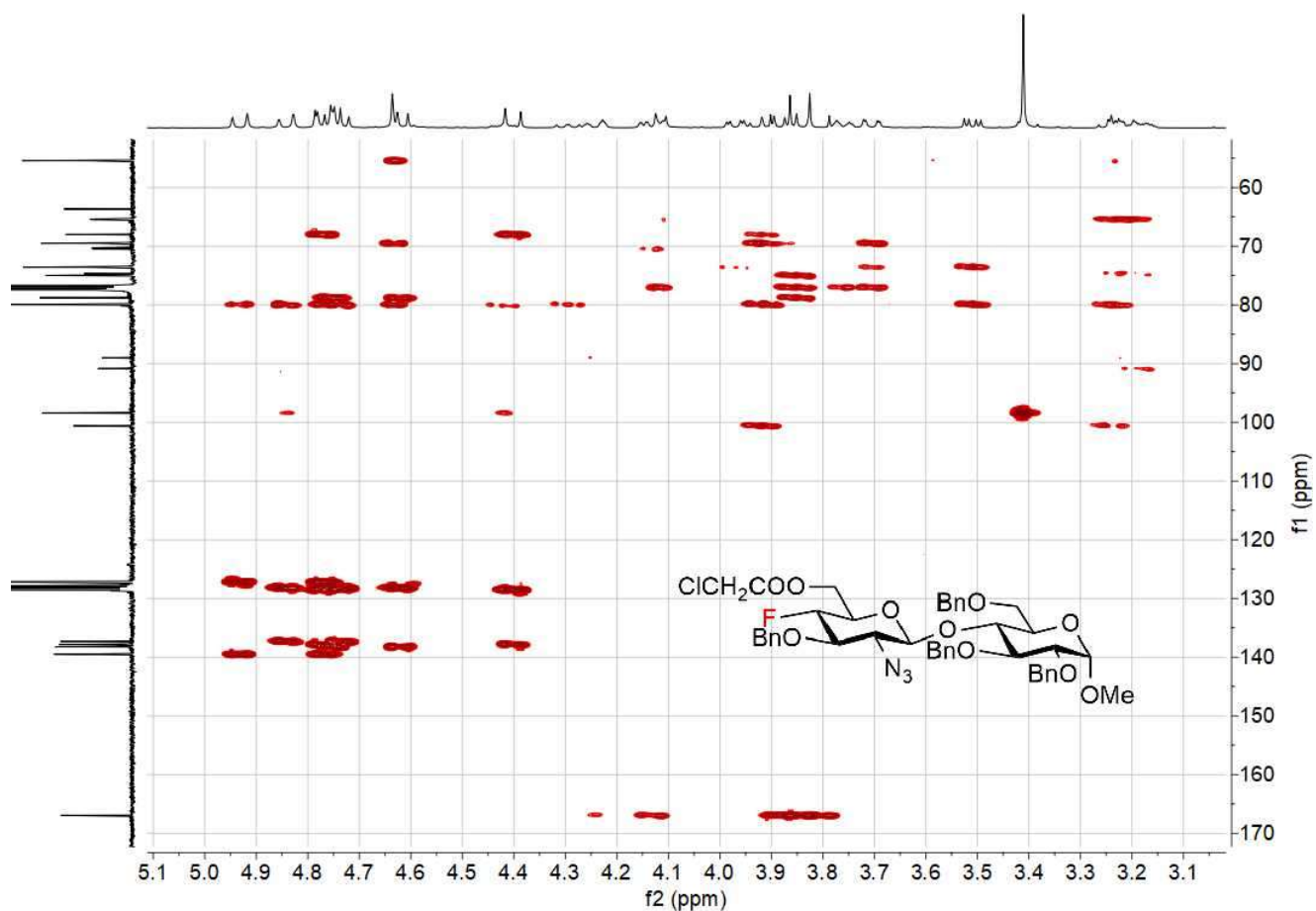
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **B20- $\beta$**



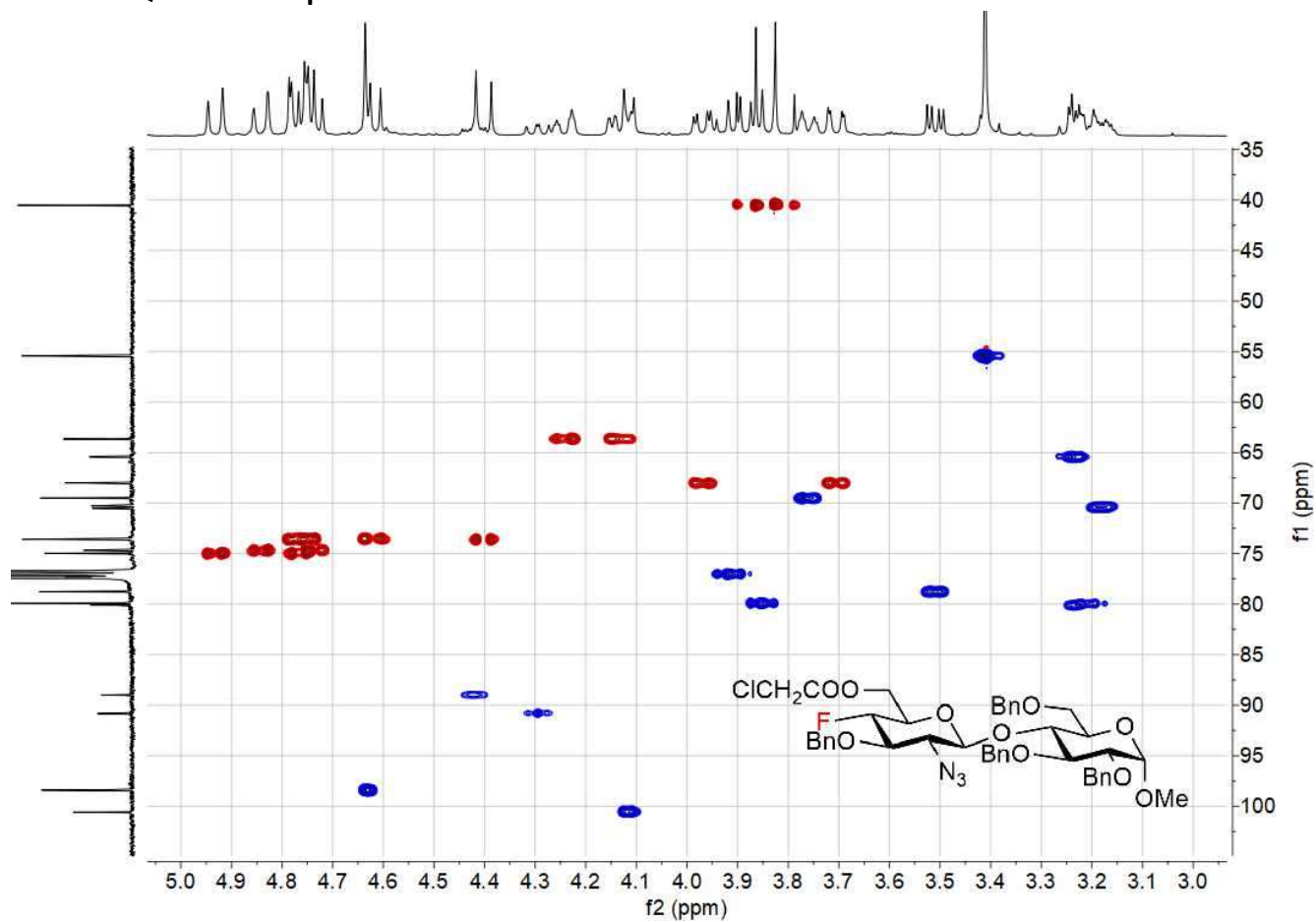
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **B20- $\beta$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR B20- $\beta$



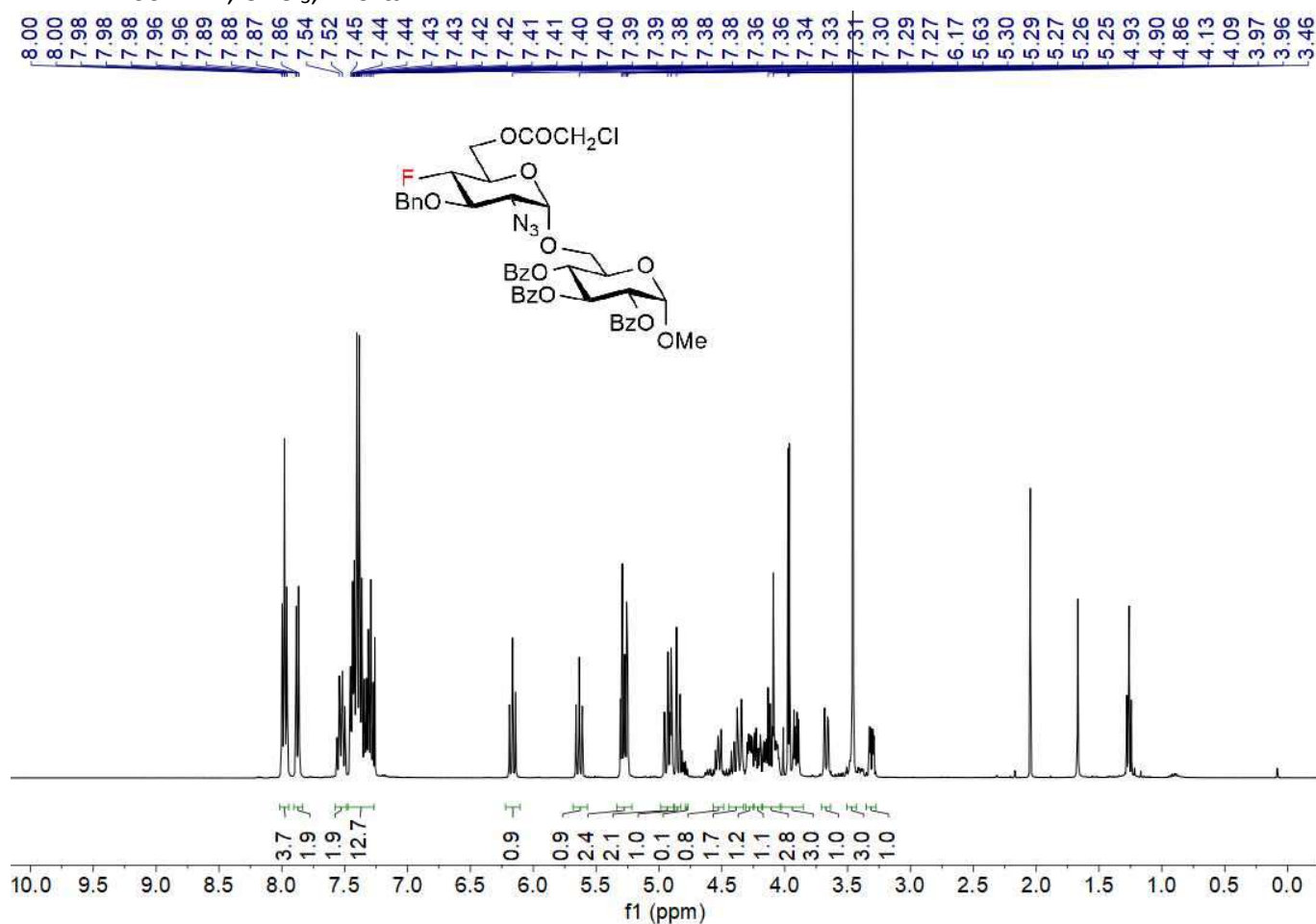
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR B20- $\beta$



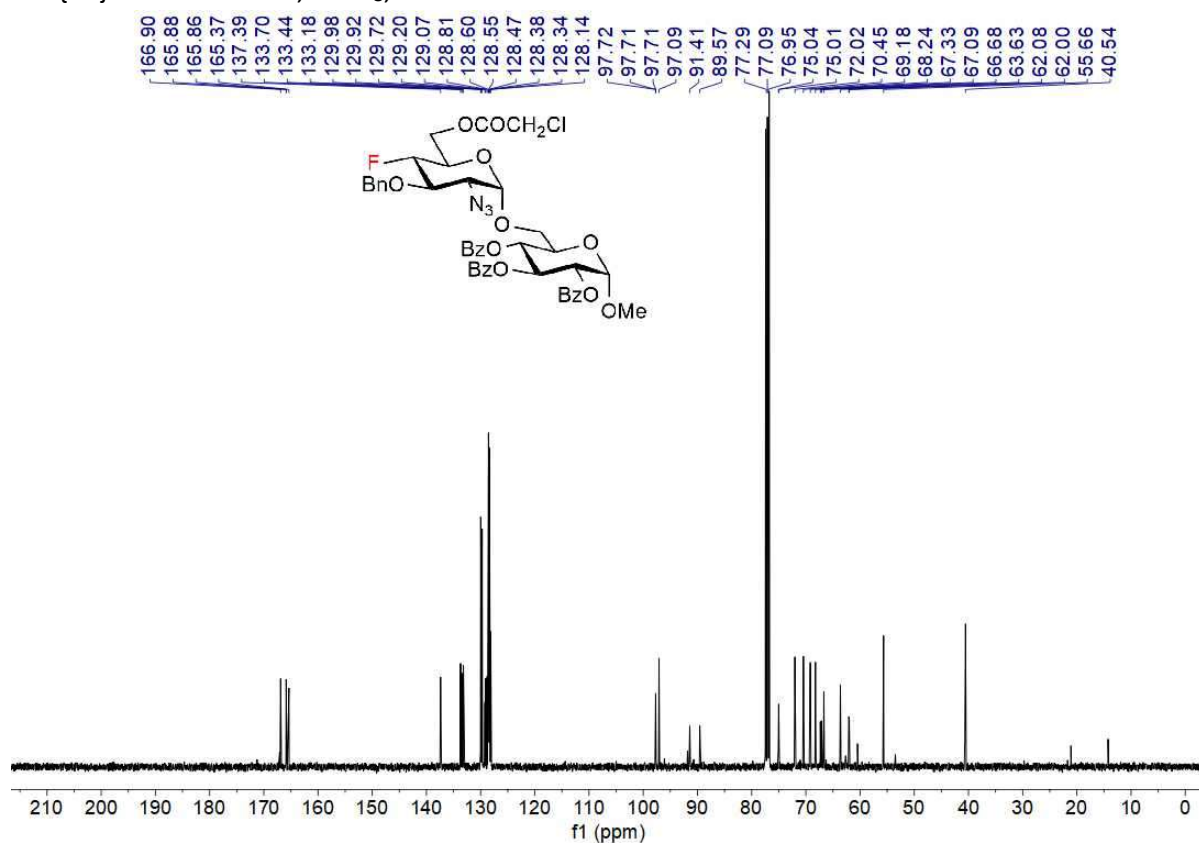


# **NMR E20-α**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E20-α**

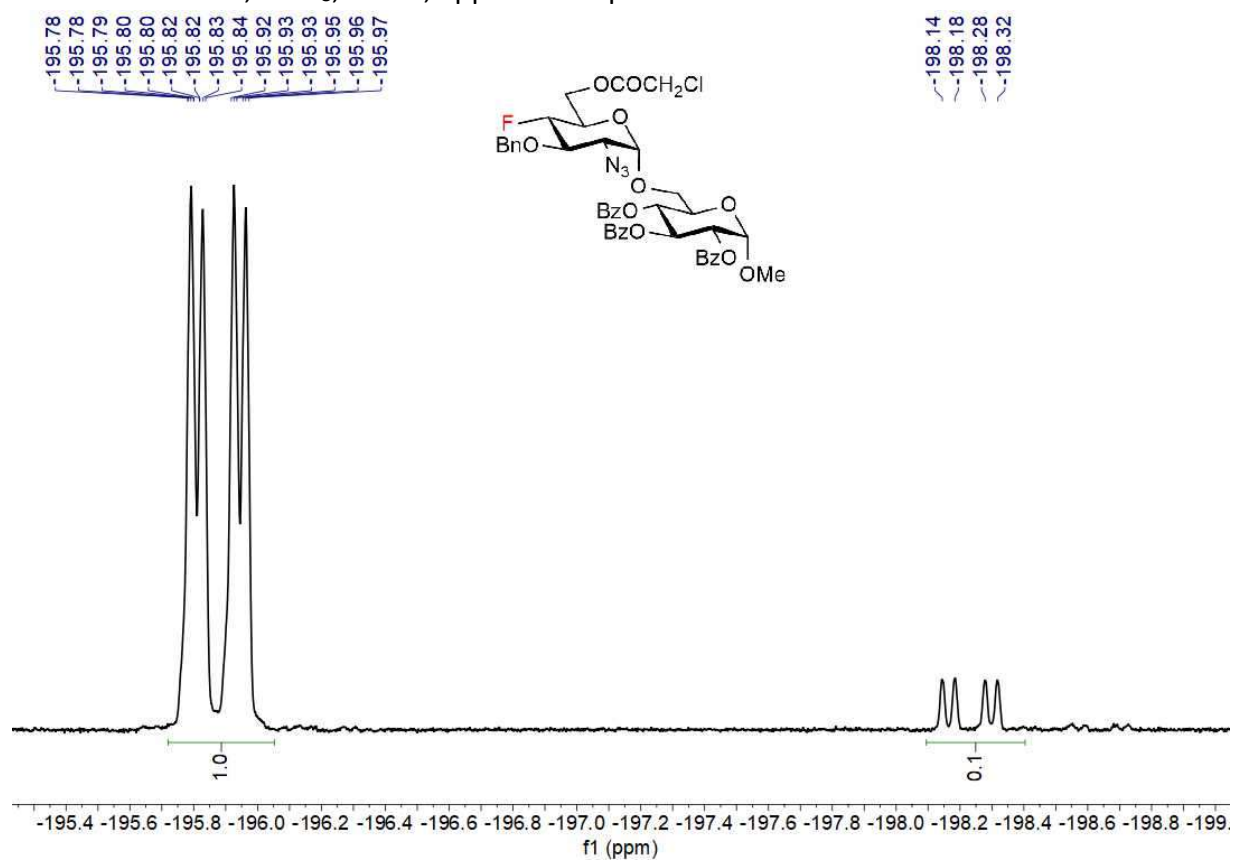


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E20-α**

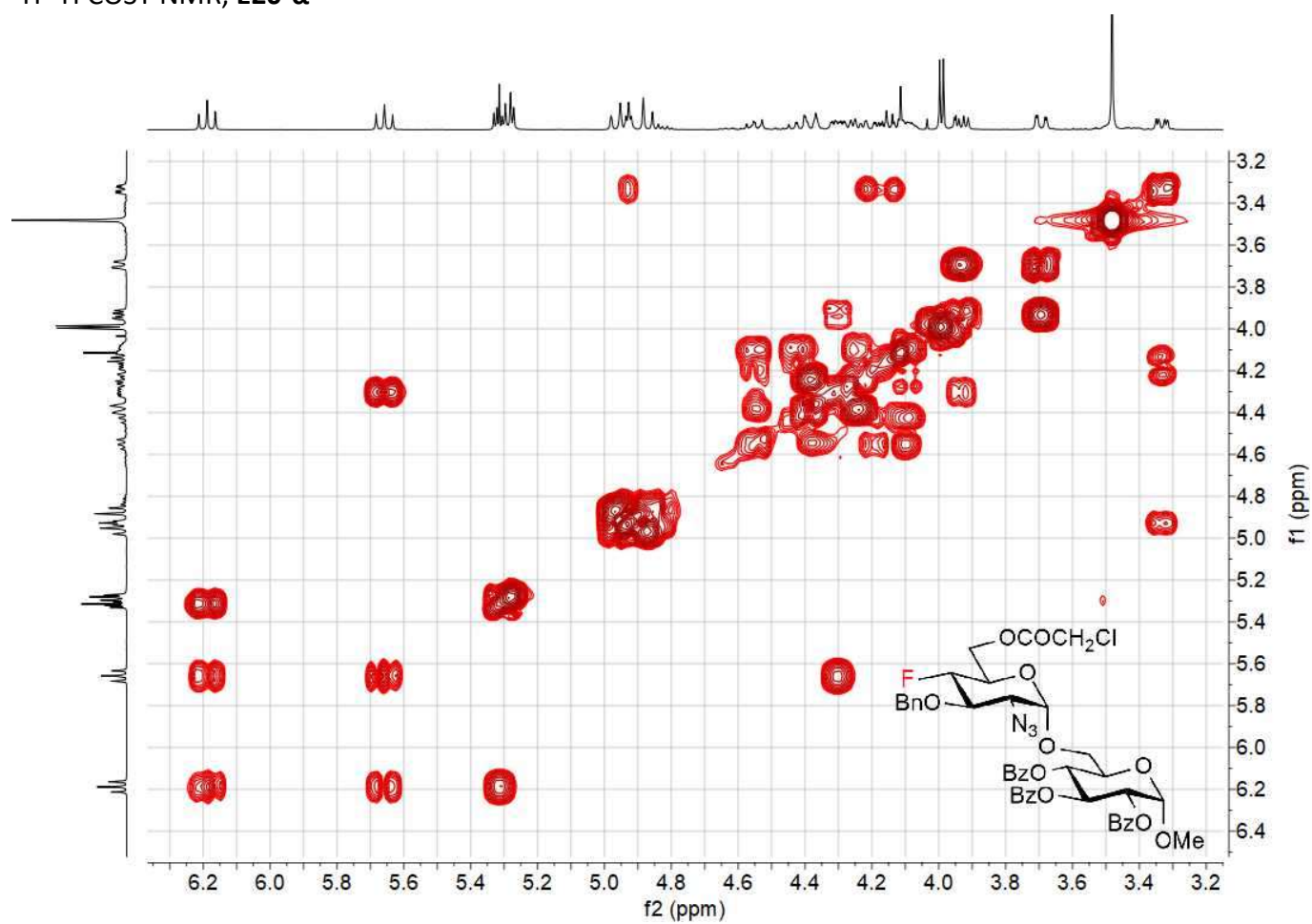




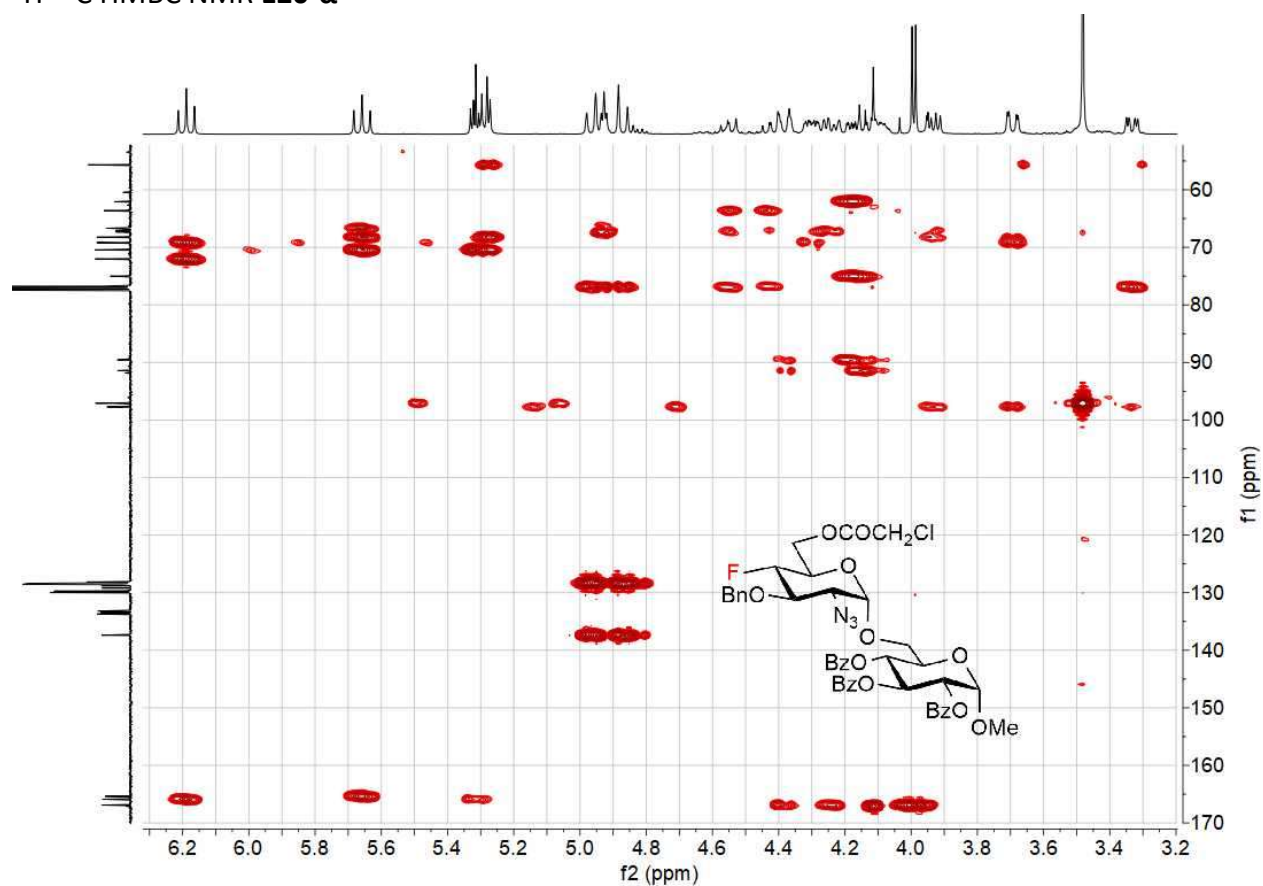
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E20- $\alpha$** , approx. 10%  $\beta$ -anomer



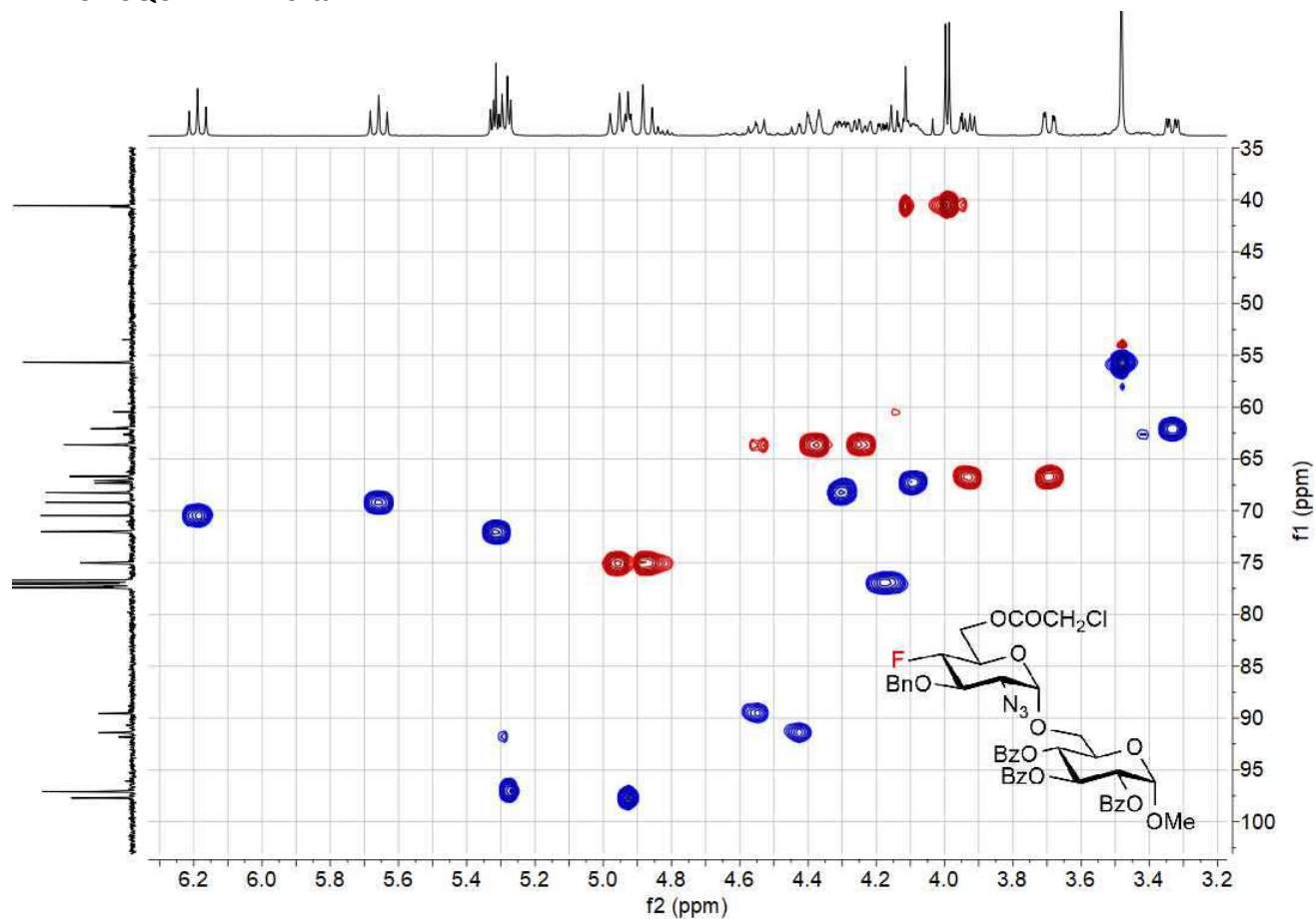
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E20- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **E20- $\alpha$**

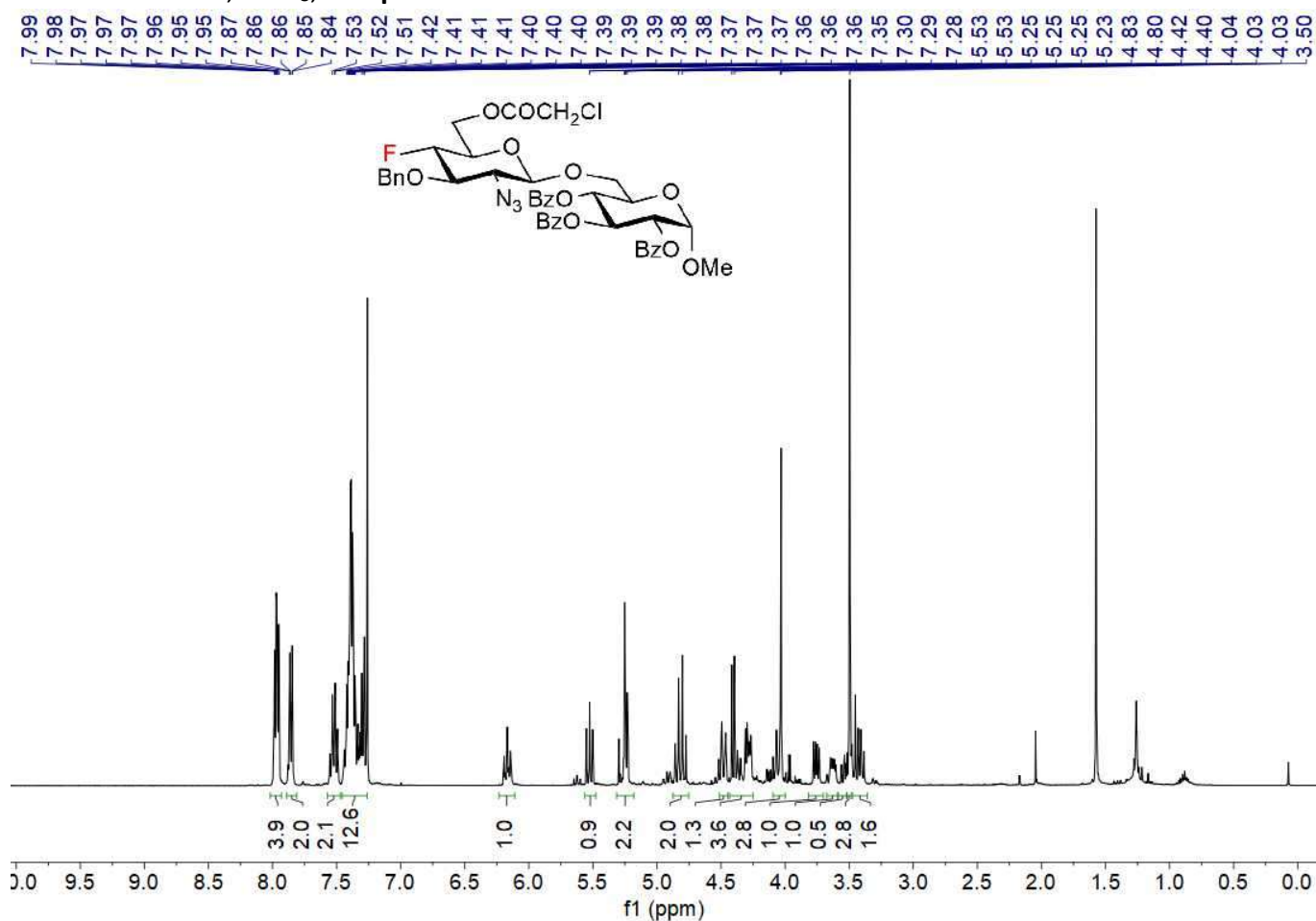


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **E20- $\alpha$**

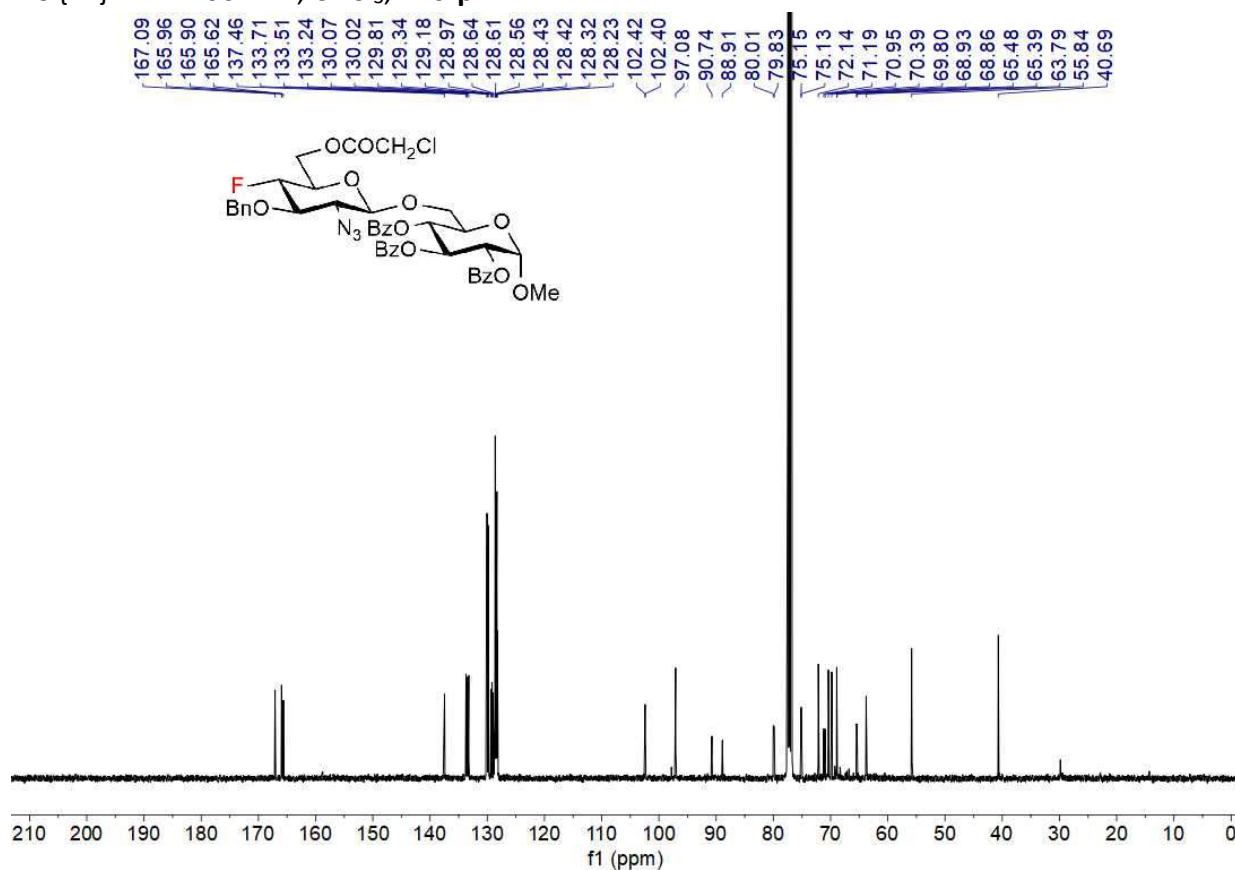


# **NMR E20-β**

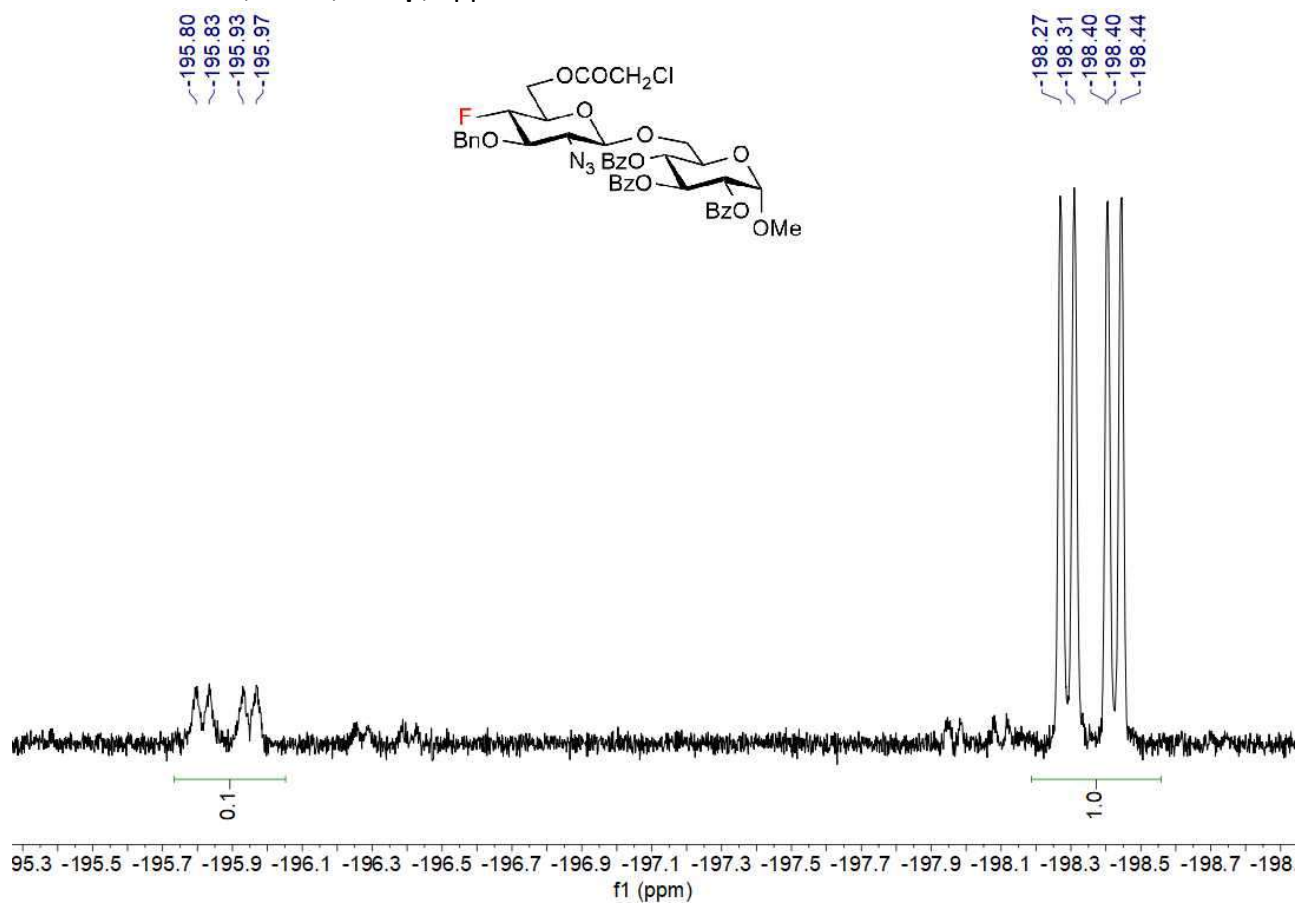
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E20-β**



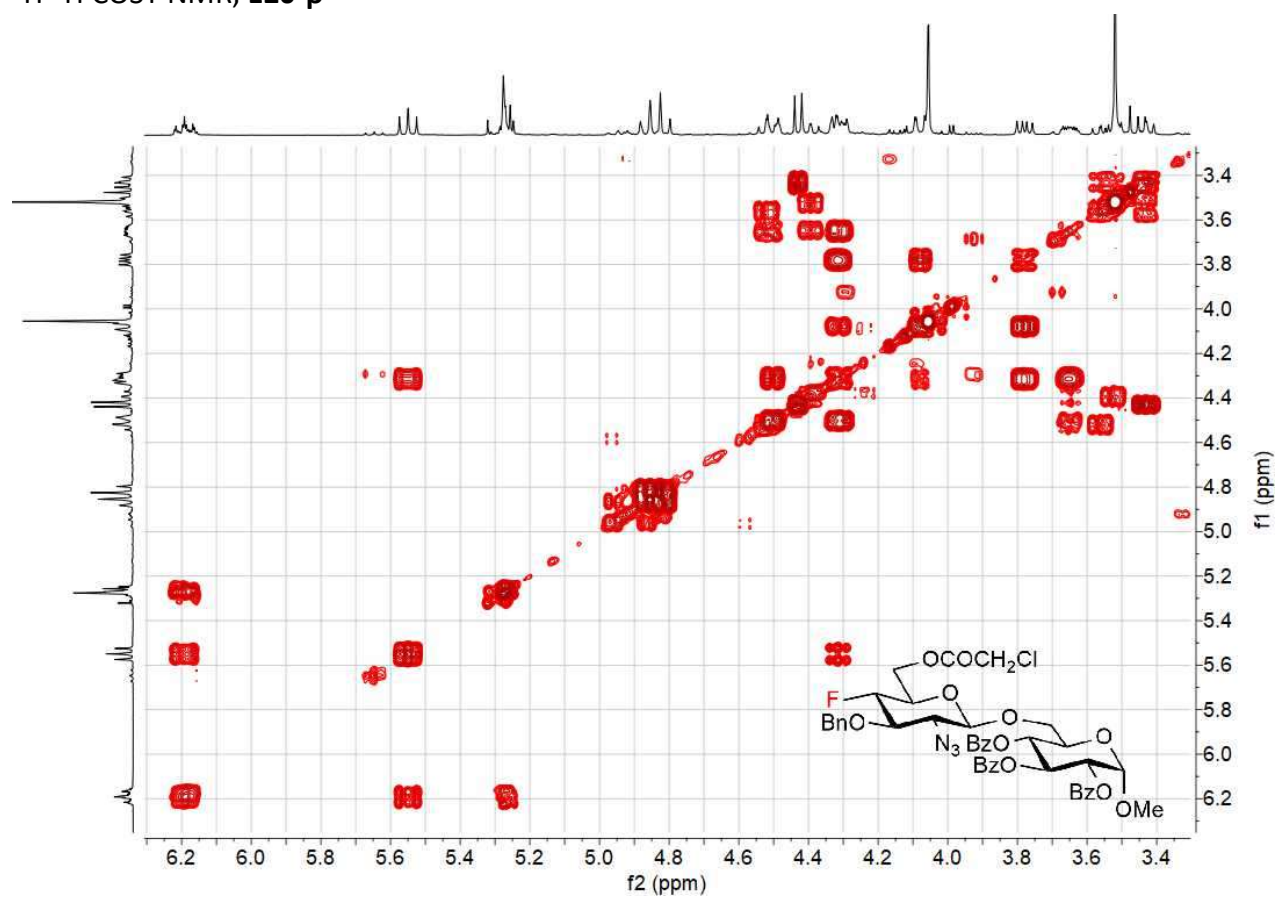
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E20-β**



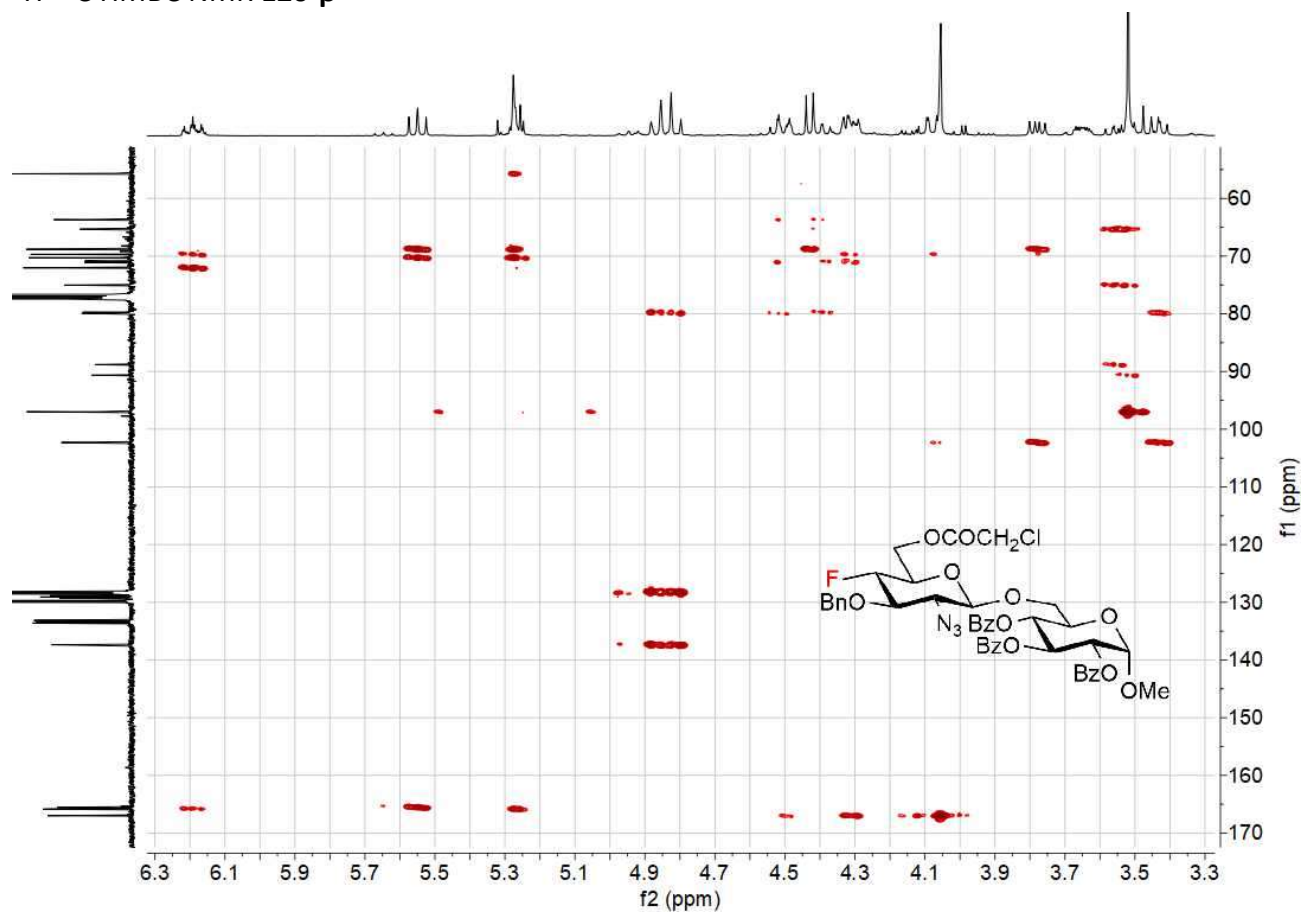
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E20- $\beta$** , approx. 10%  $\alpha$ -anomer



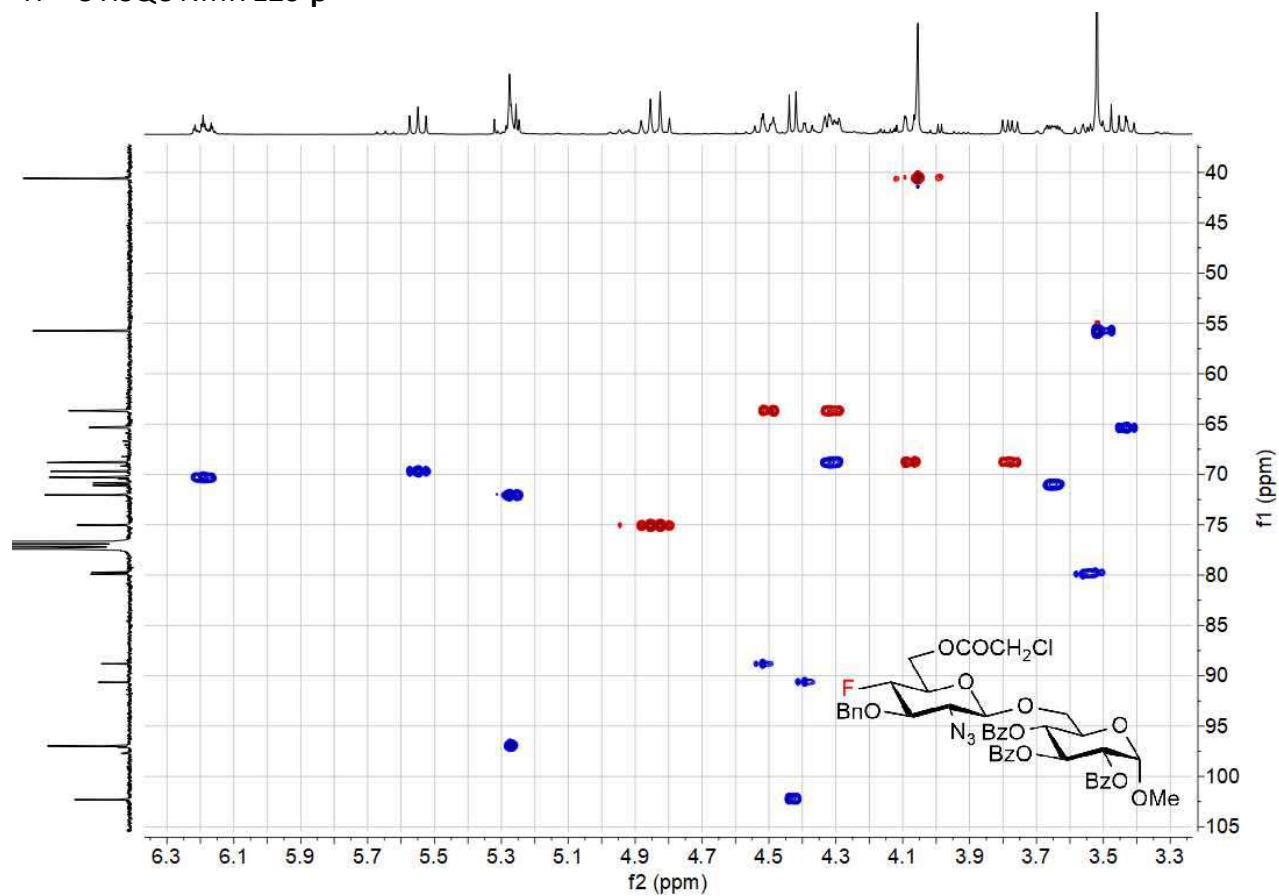
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E20- $\beta$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR E20- $\beta$



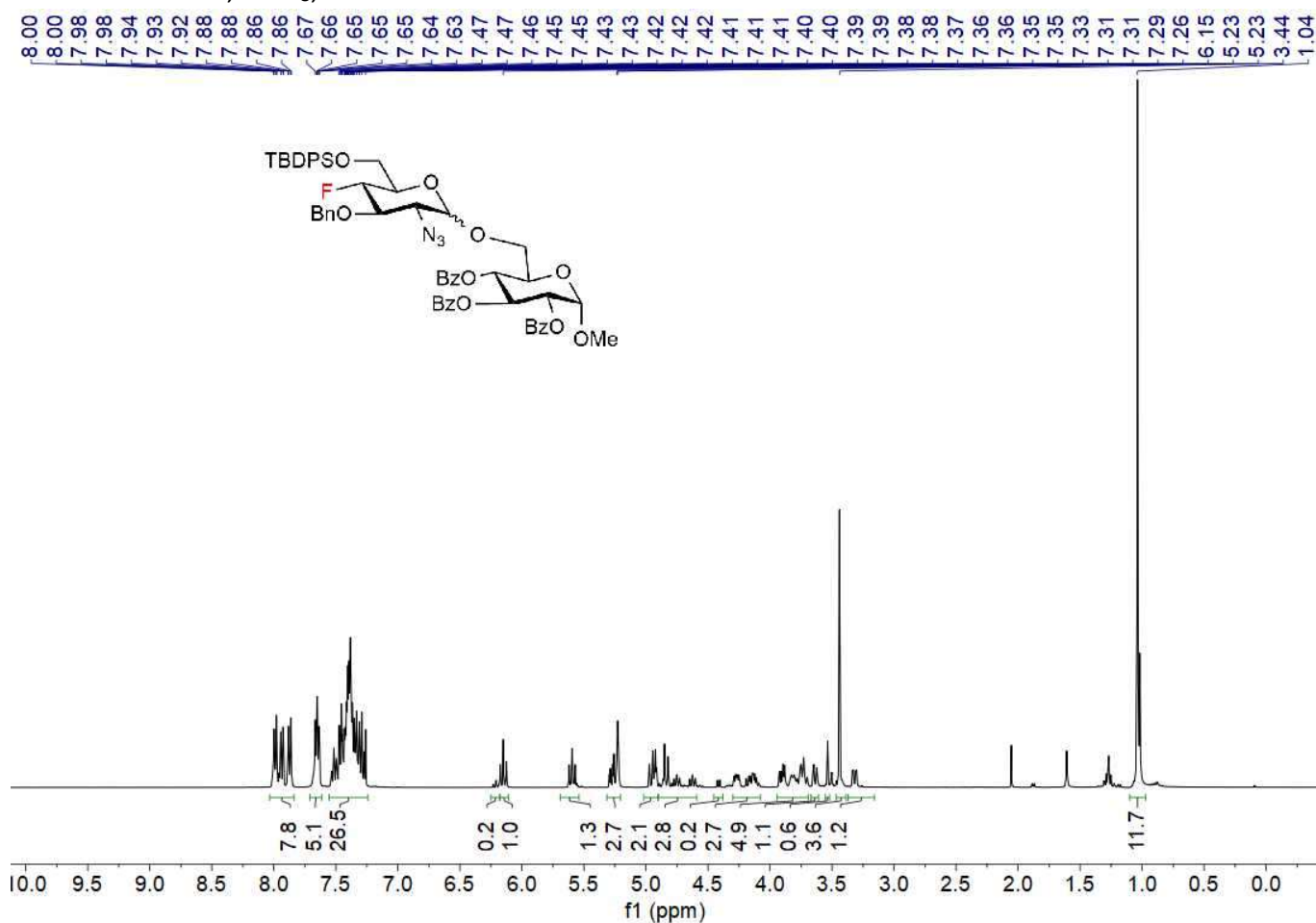
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR E20- $\beta$



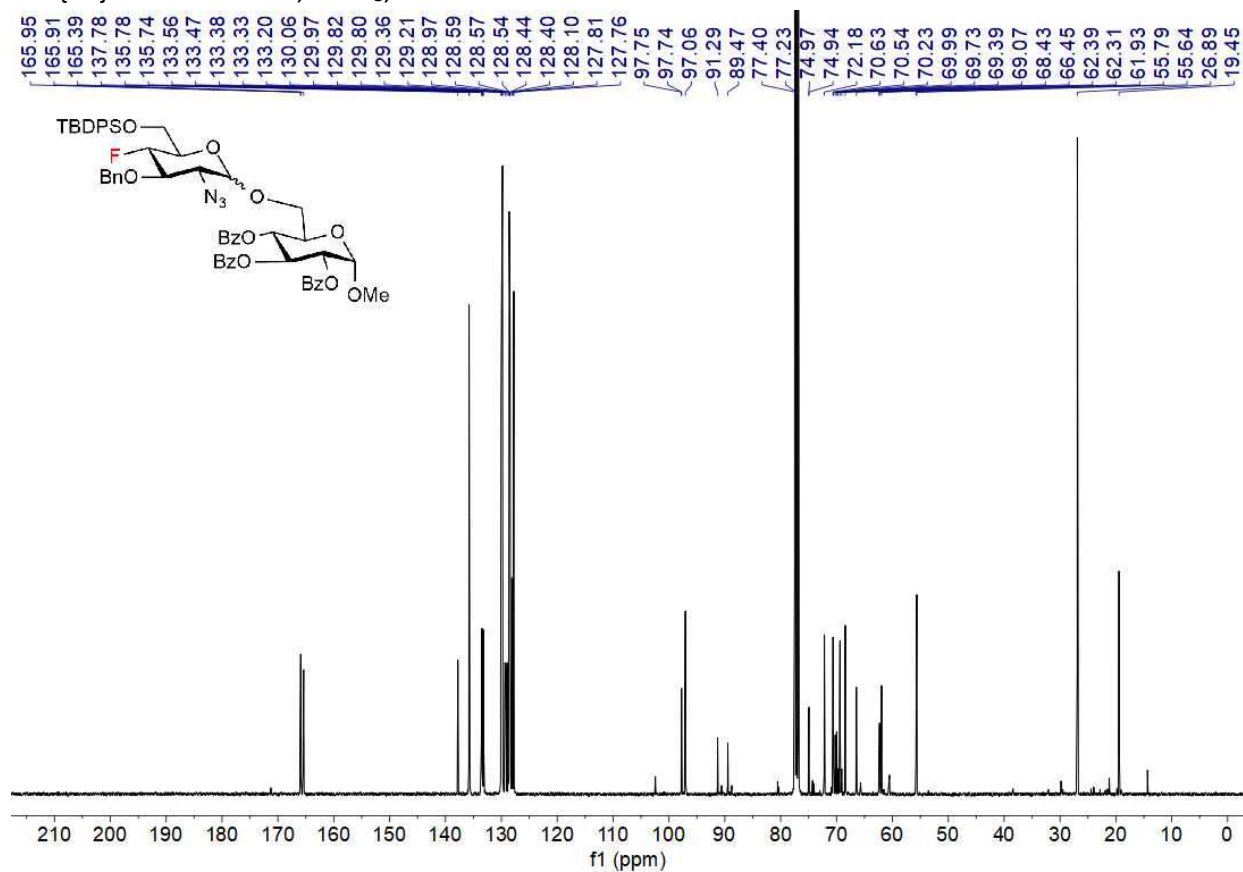


# **NMR E21**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E21**

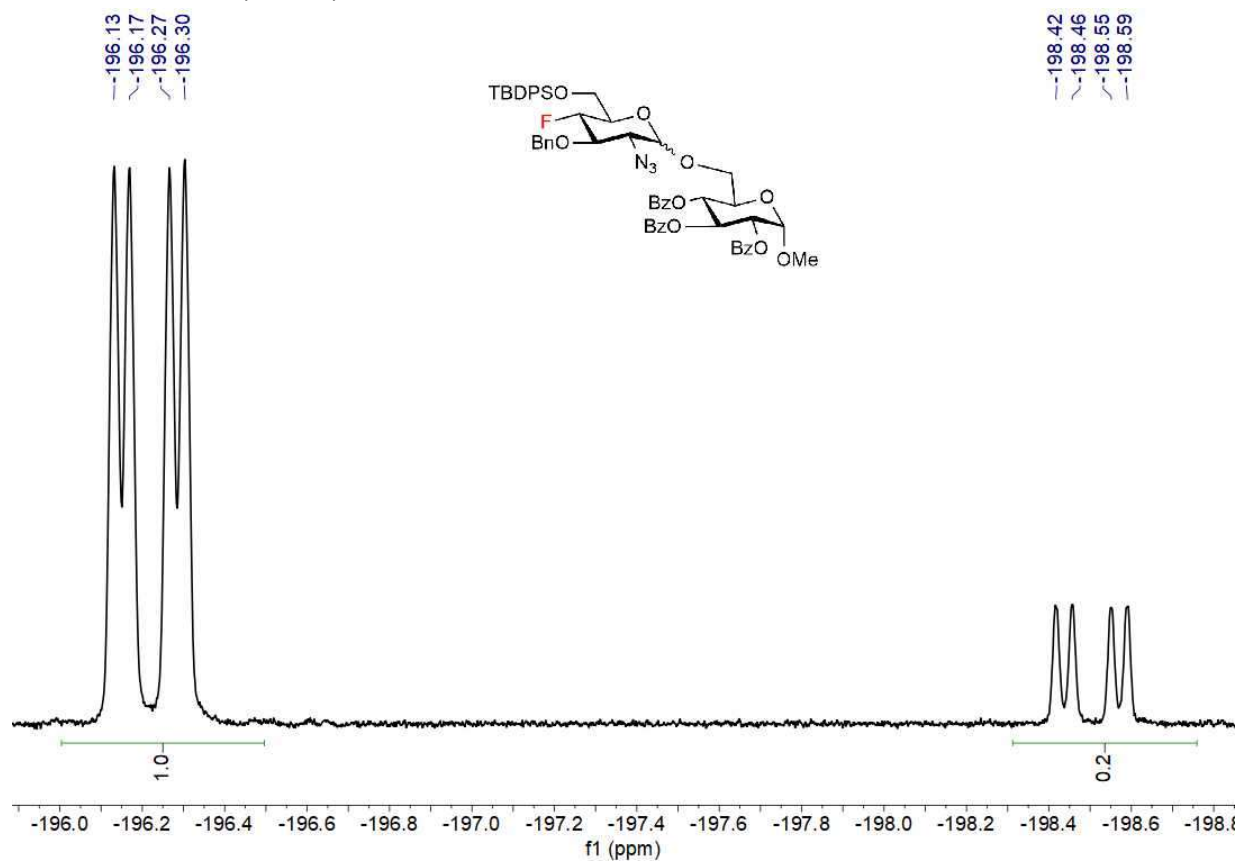


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E21**

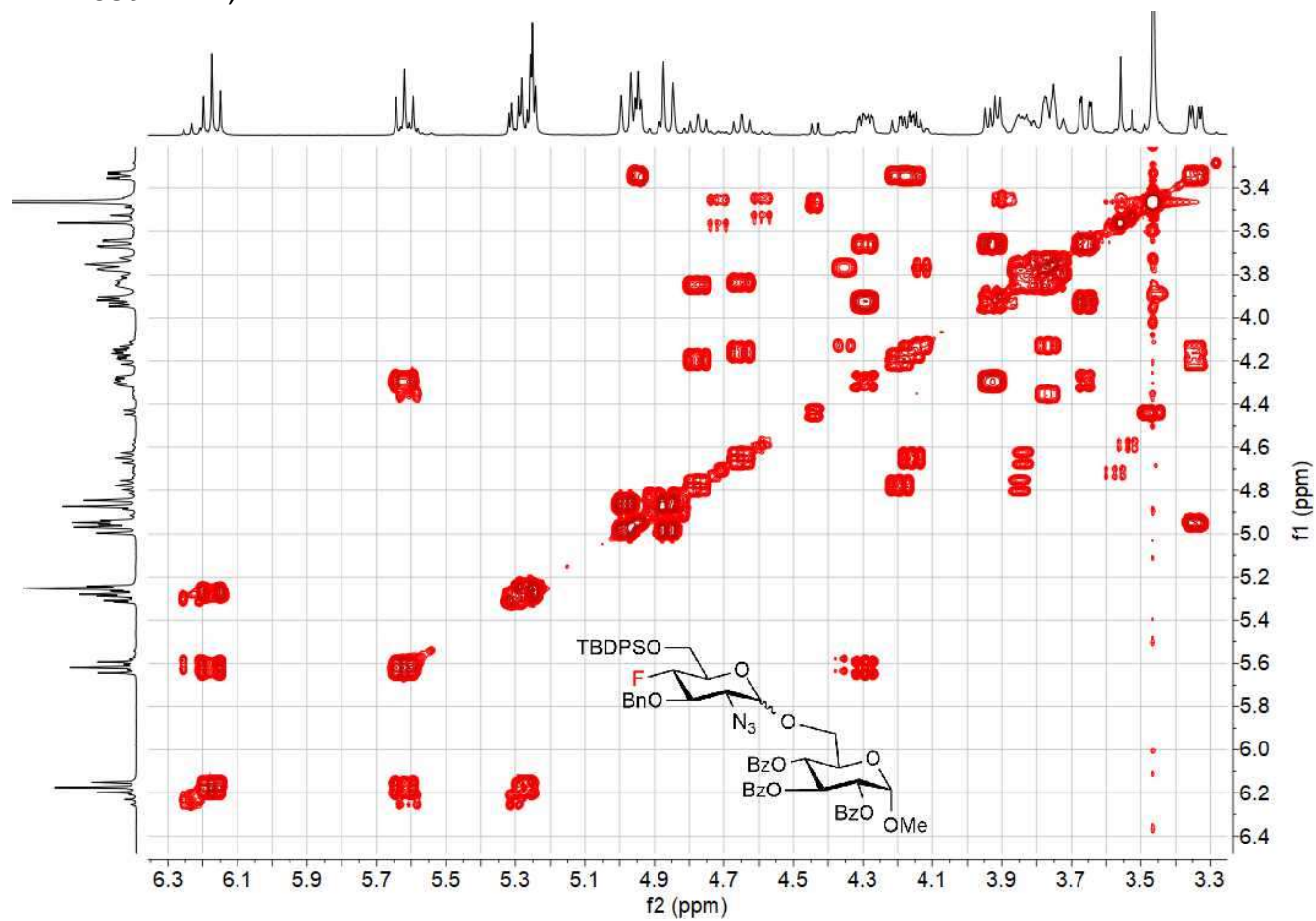




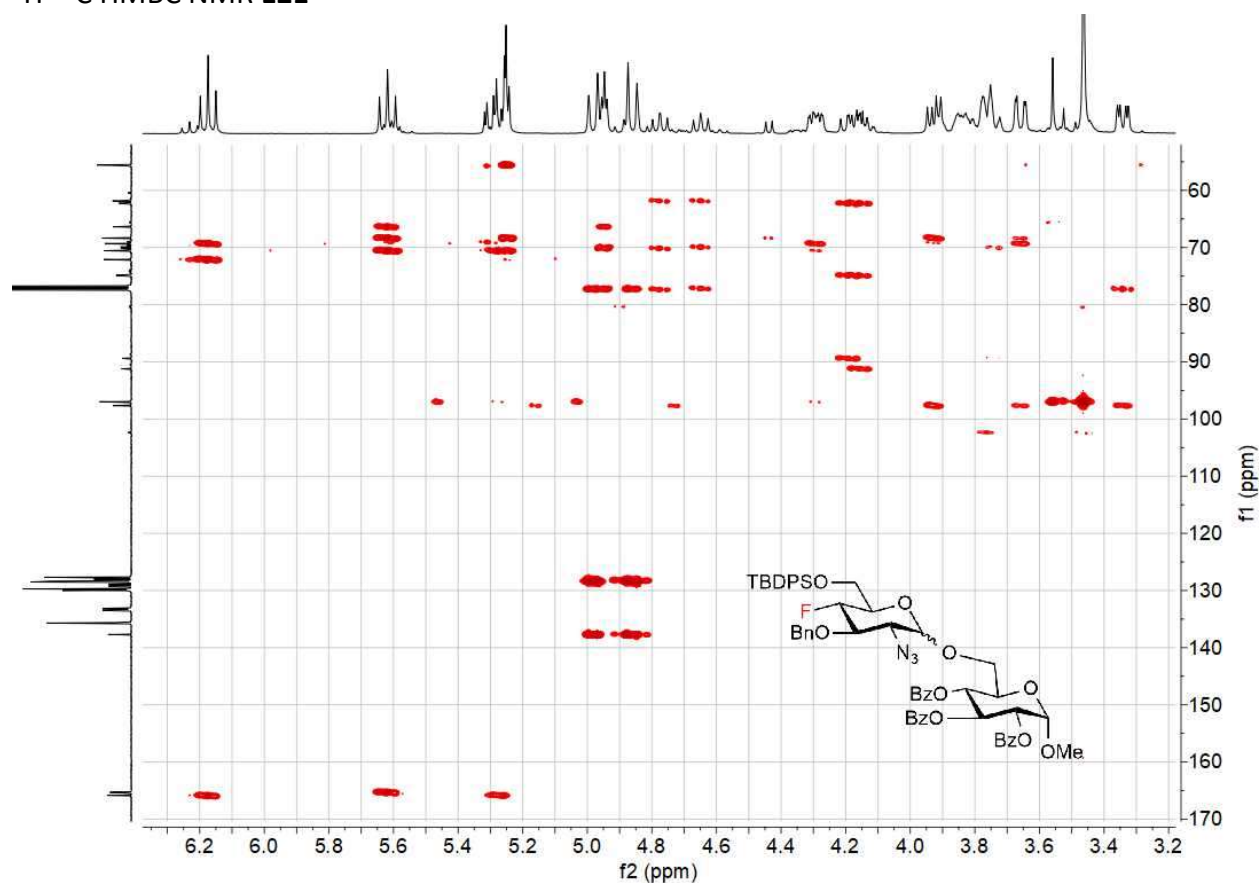
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E21**



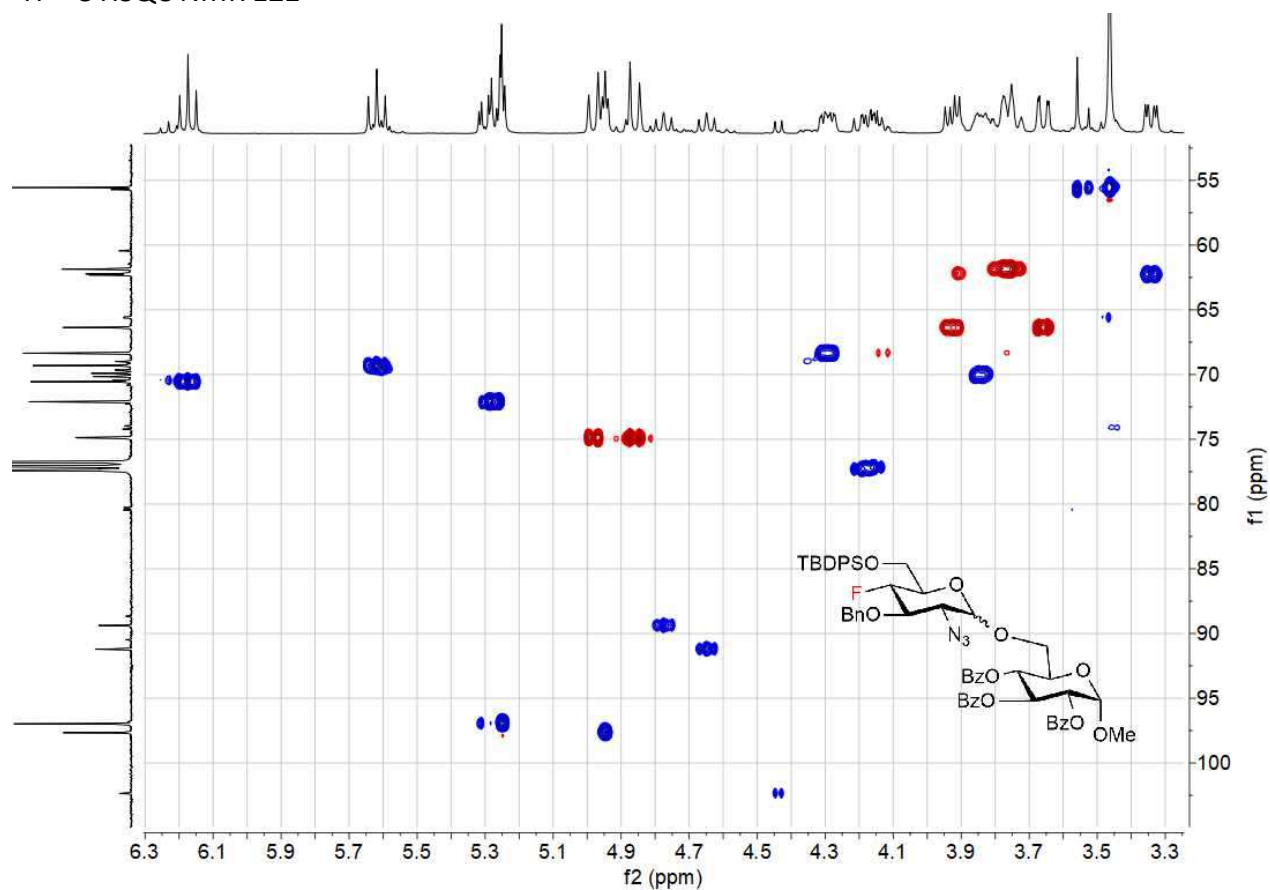
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E21**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR E21

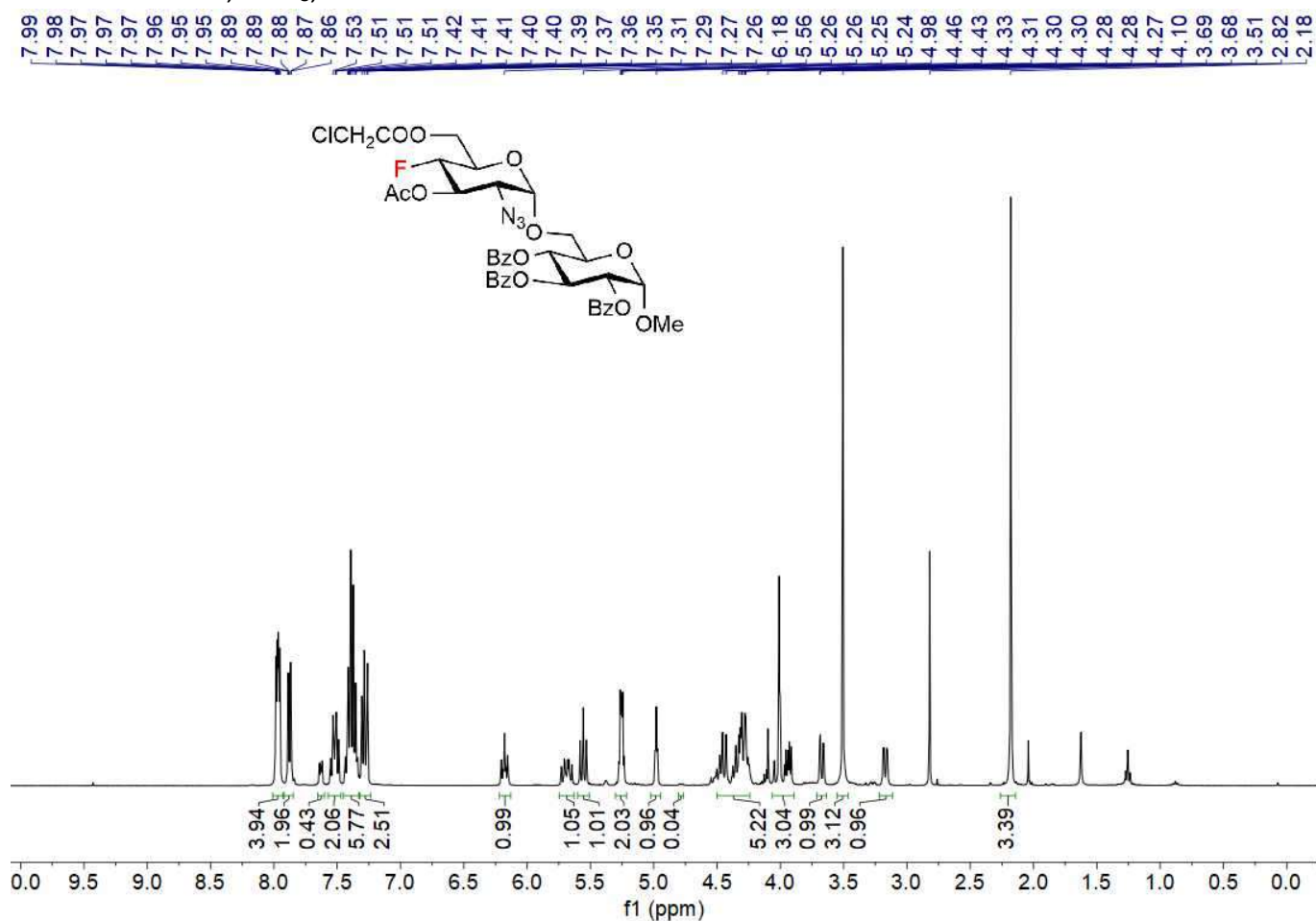


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR E21

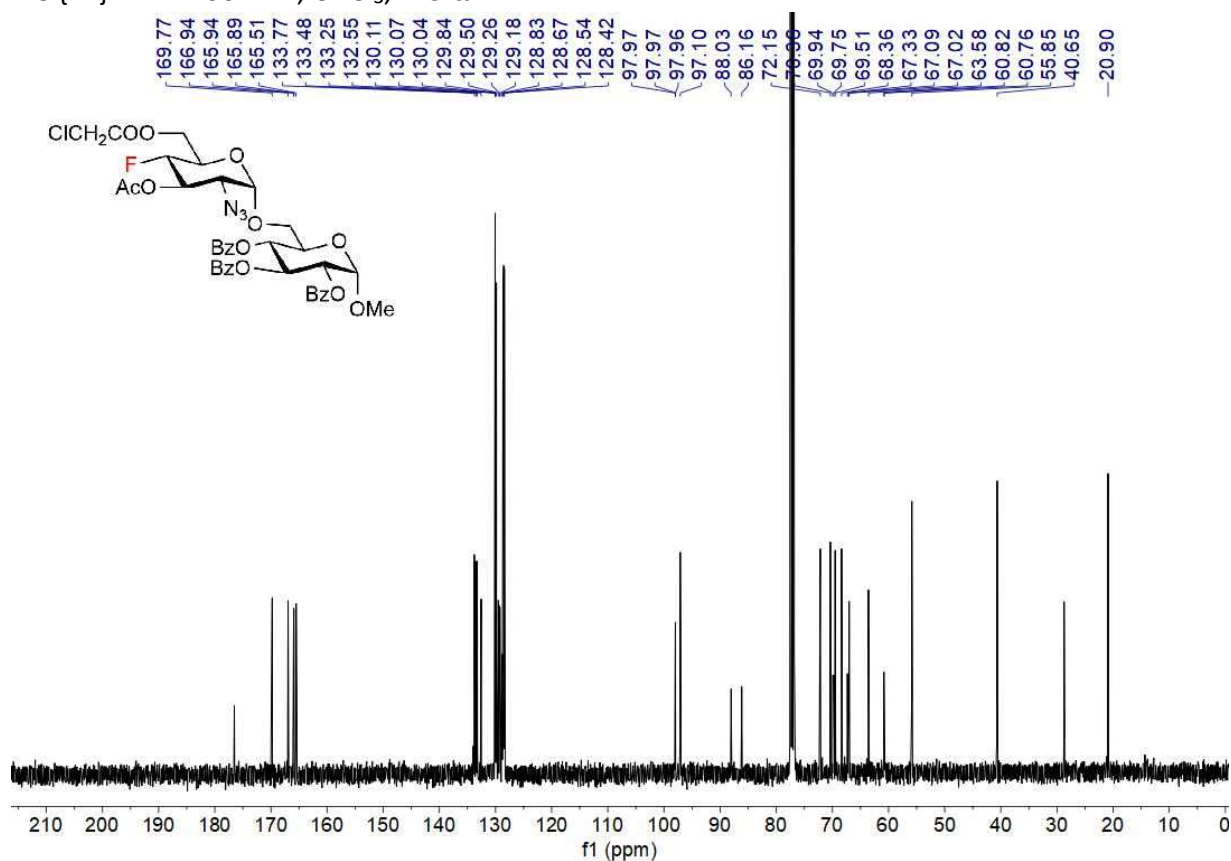


# **NMR E25-α**

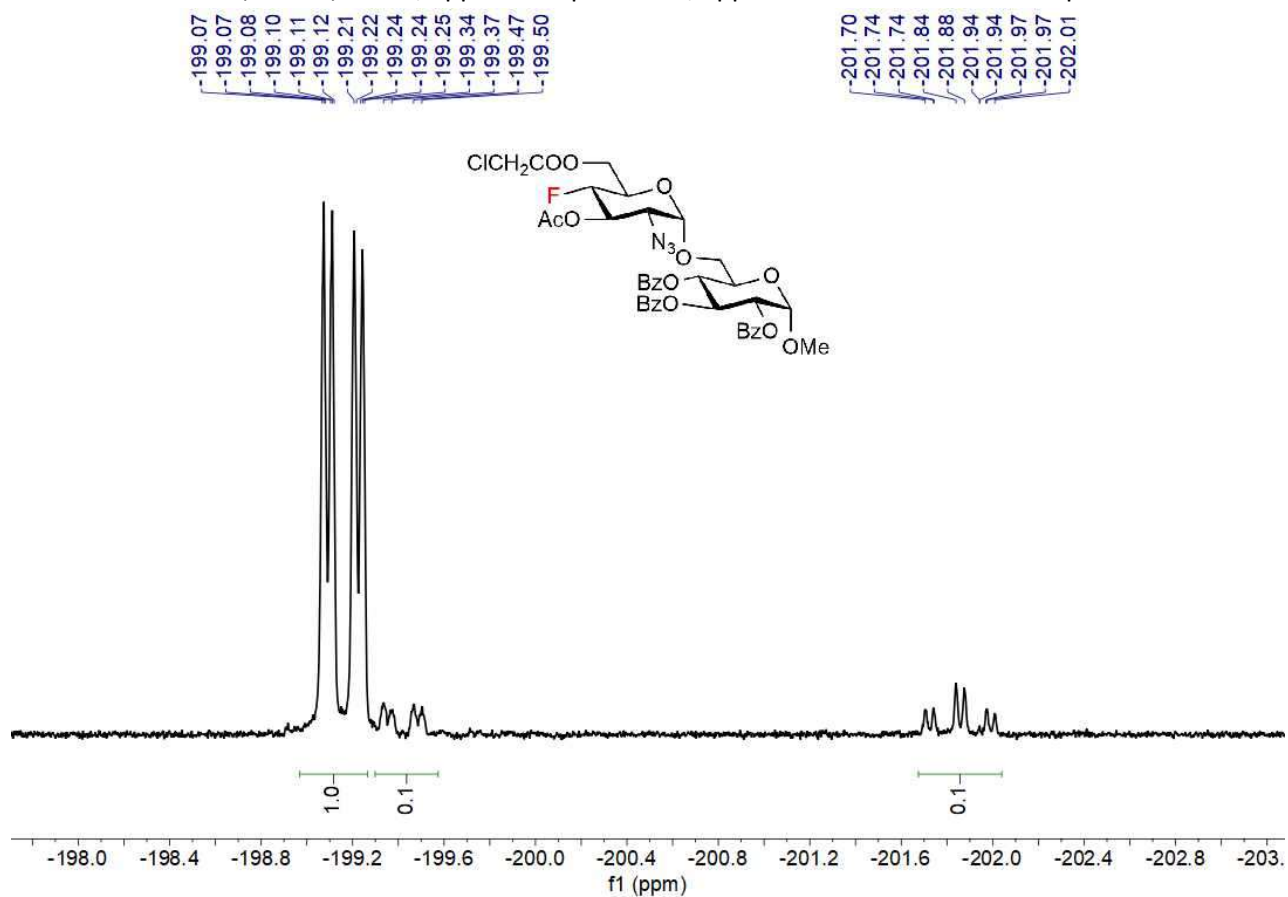
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **E25-α**



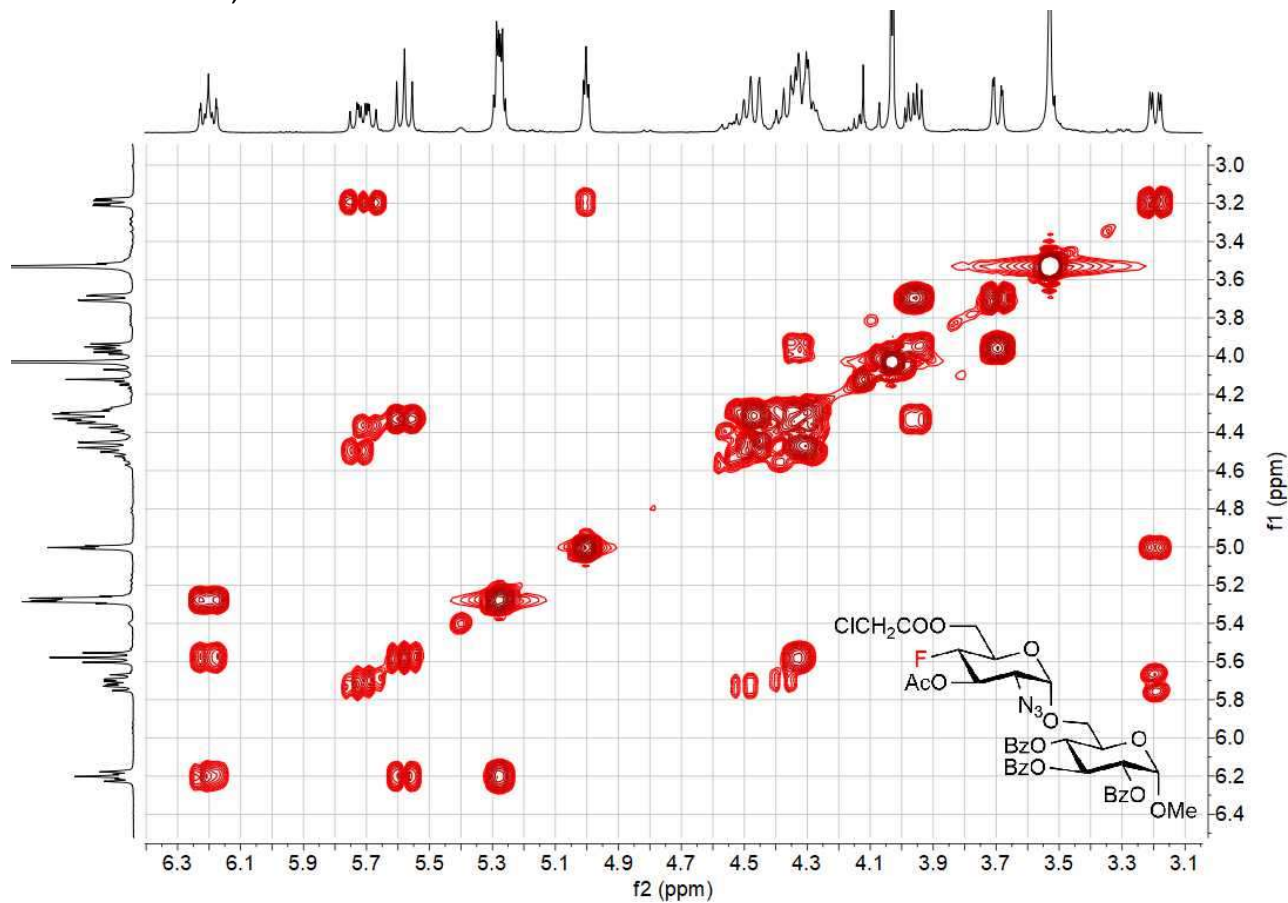
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **E25-α**



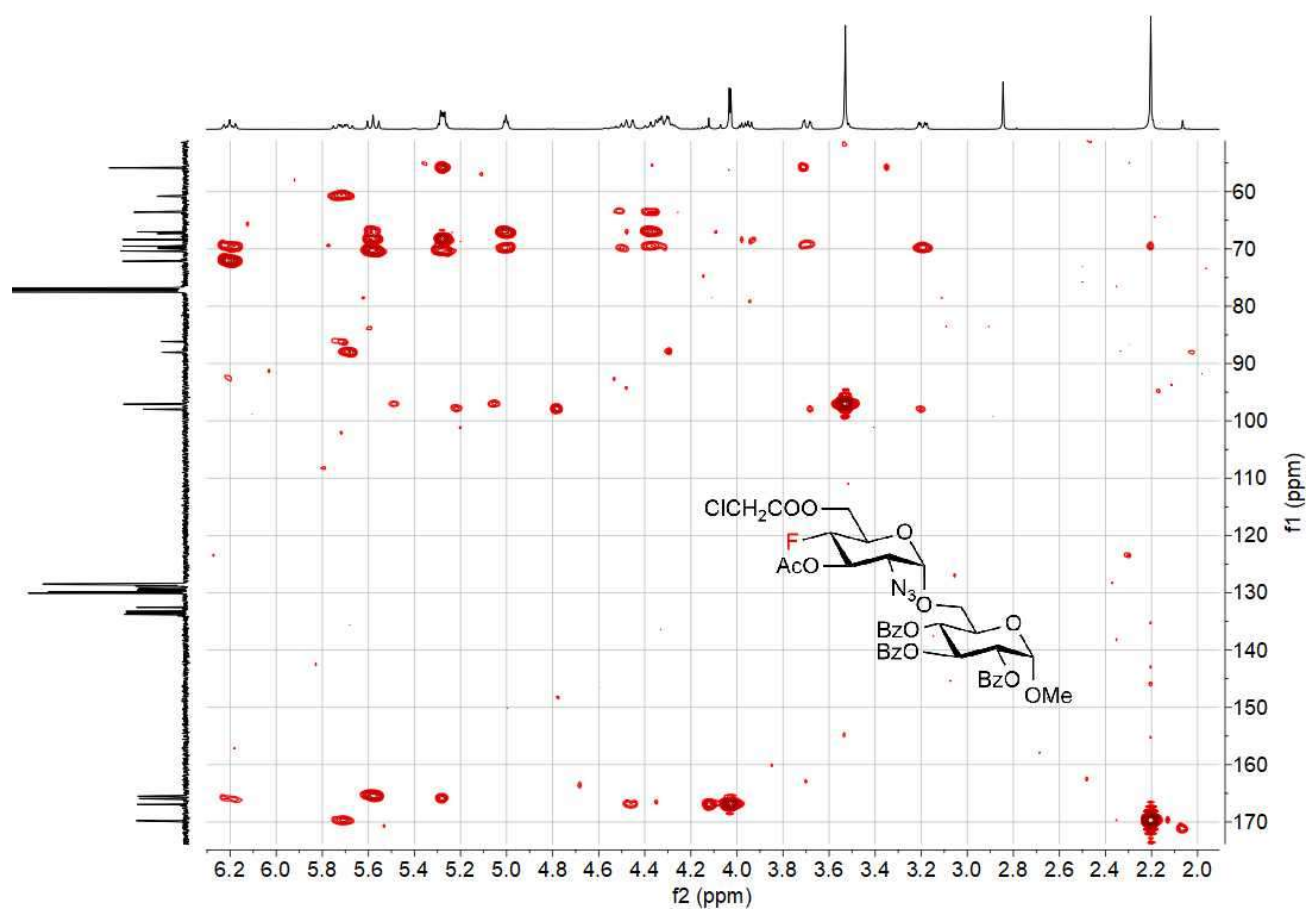
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **E25- $\alpha$** , approx. 5%  $\beta$ -anomer, approx. 15% unidentified side-products



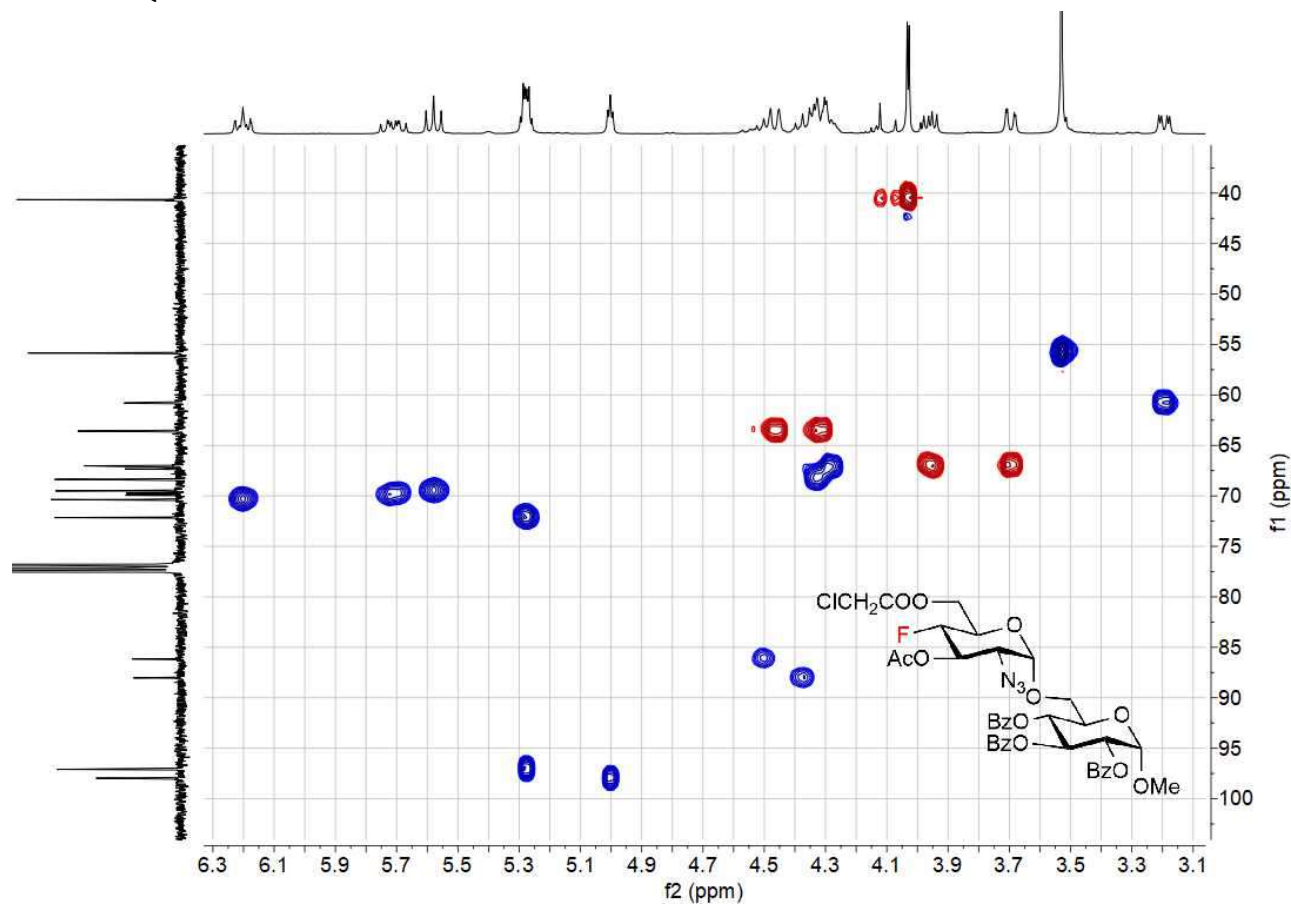
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **E25- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR E25- $\alpha$



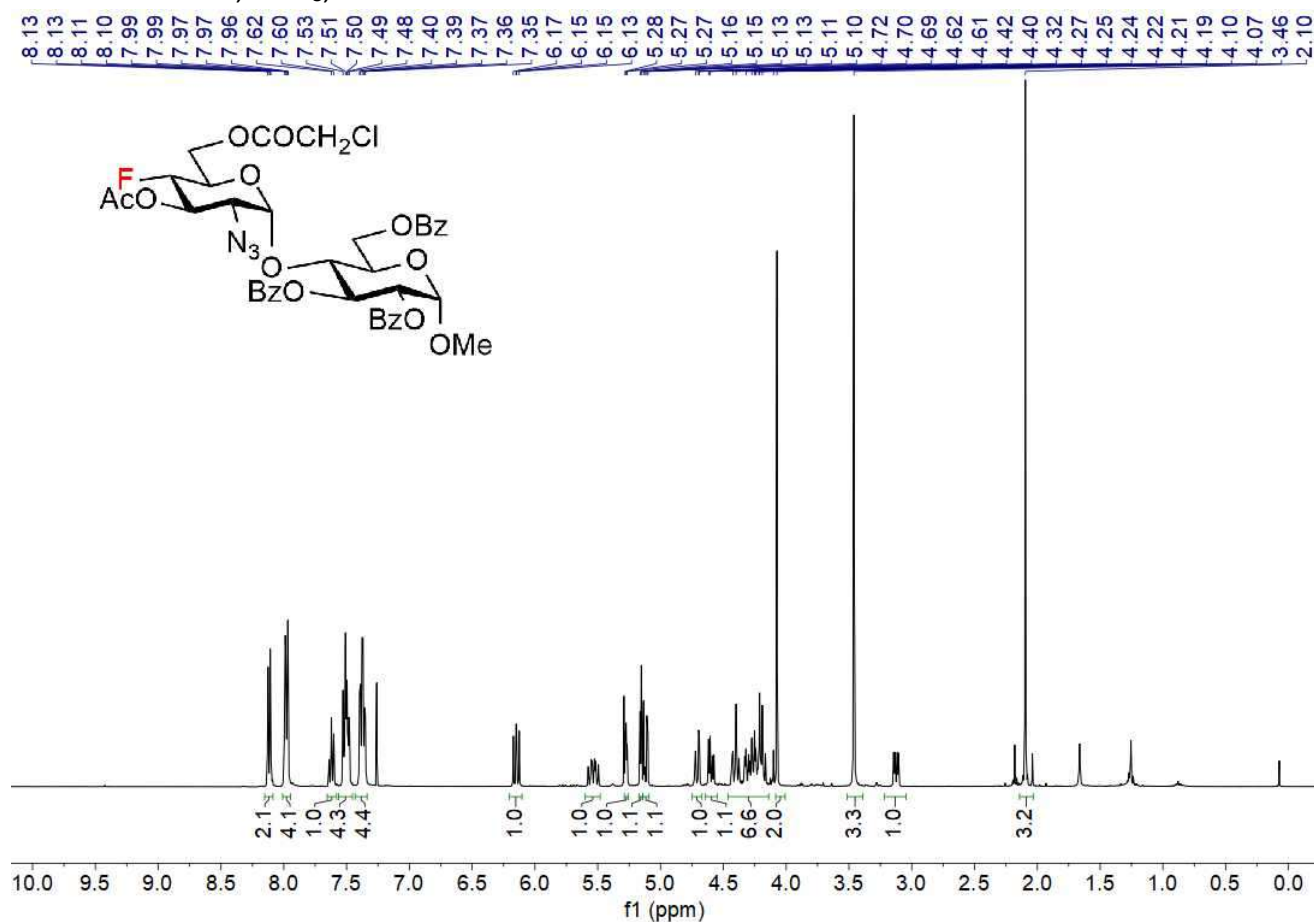
$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR E25- $\alpha$



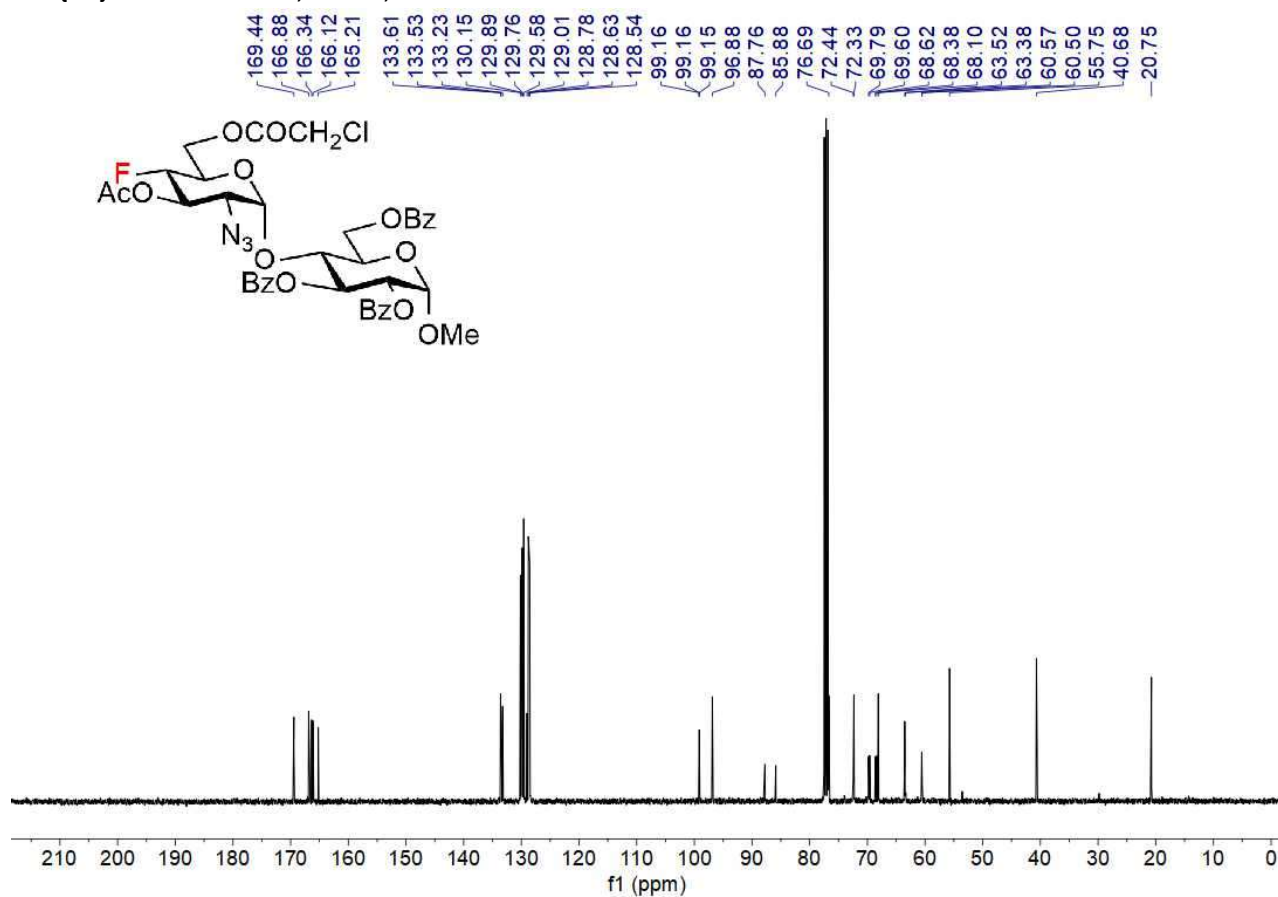


# **NMR D25- $\alpha$**

$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , **D25- $\alpha$**

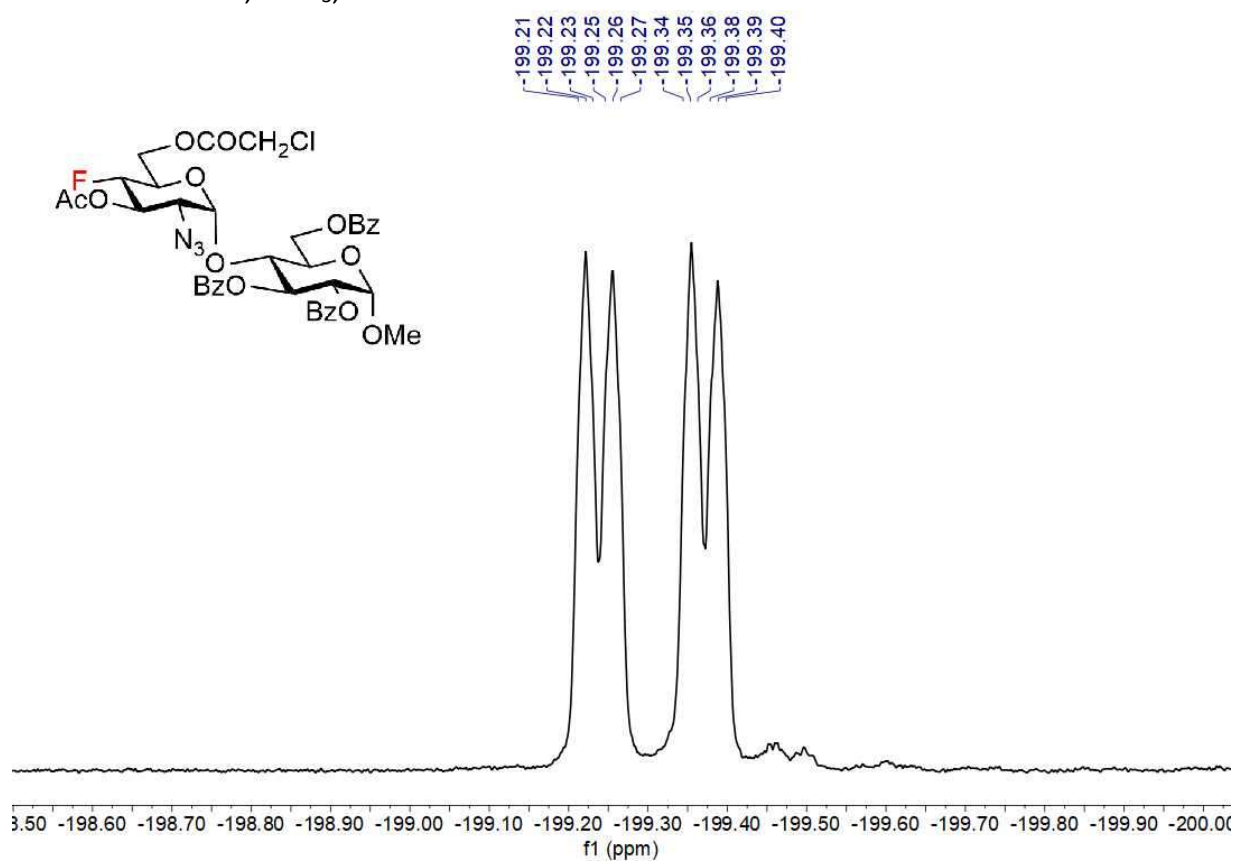


$^{13}\text{C}$   $\{^1\text{H}\}$  NMR 100MHz,  $\text{CDCl}_3$ , **D25- $\alpha$**

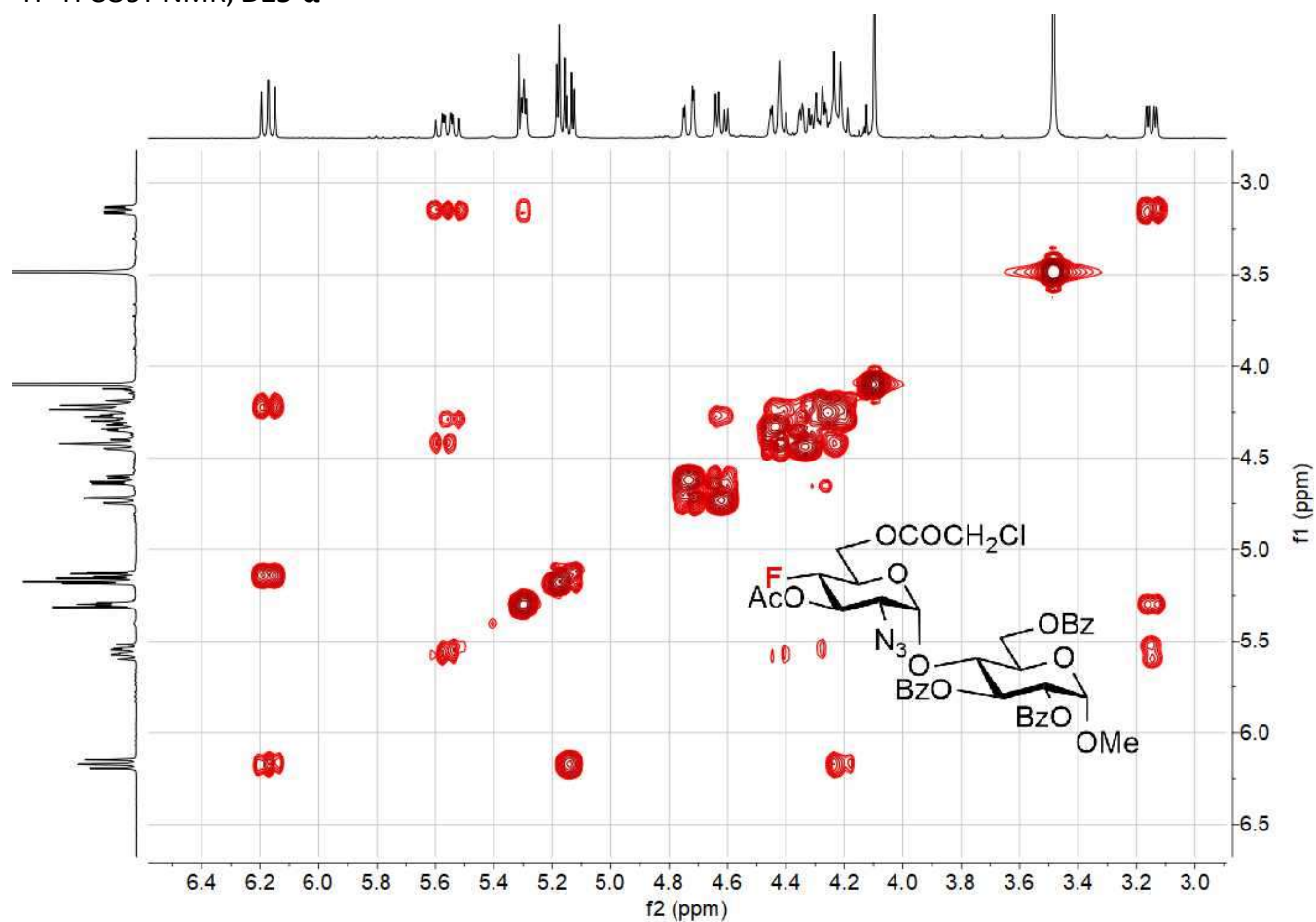




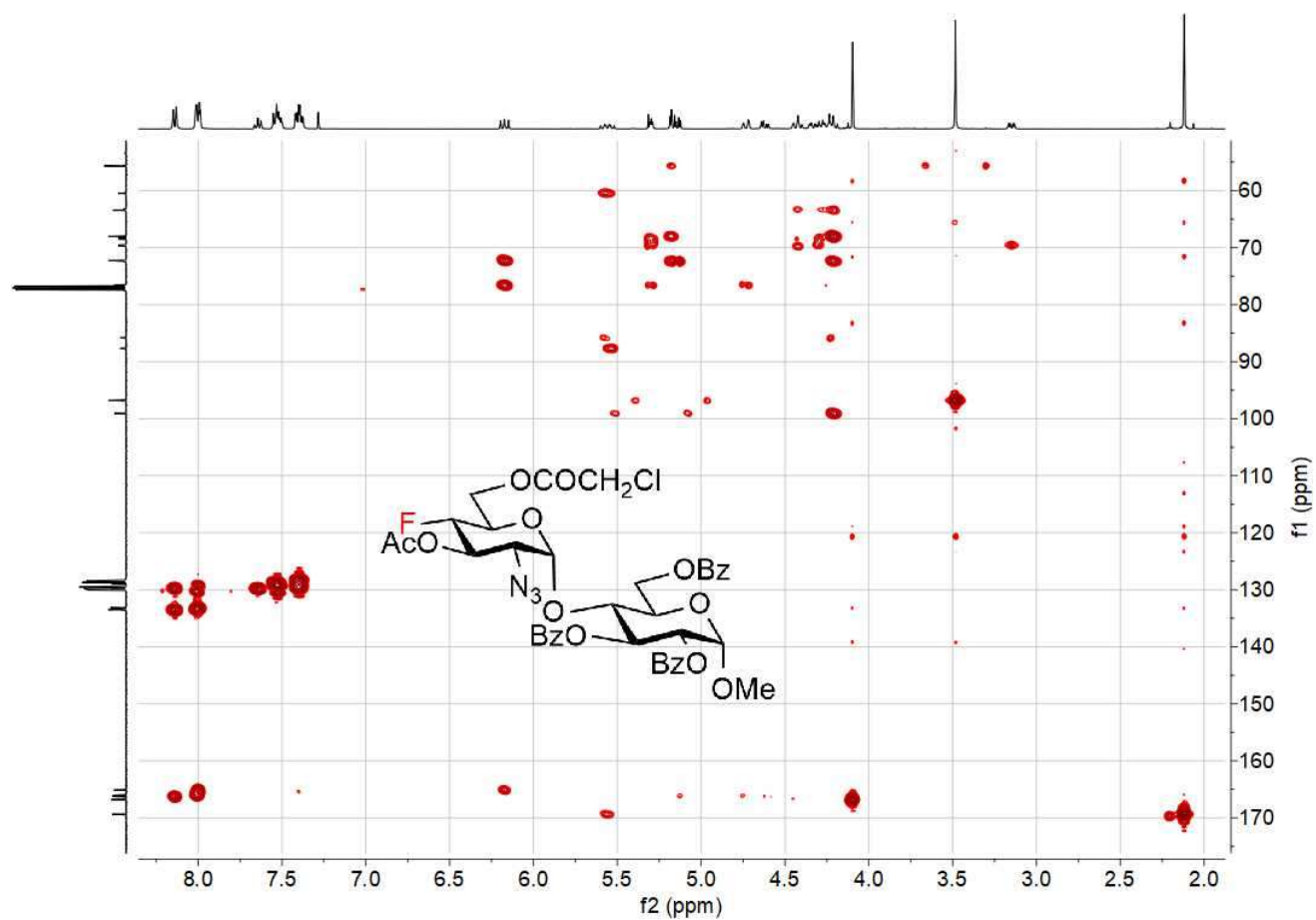
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **D25- $\alpha$**



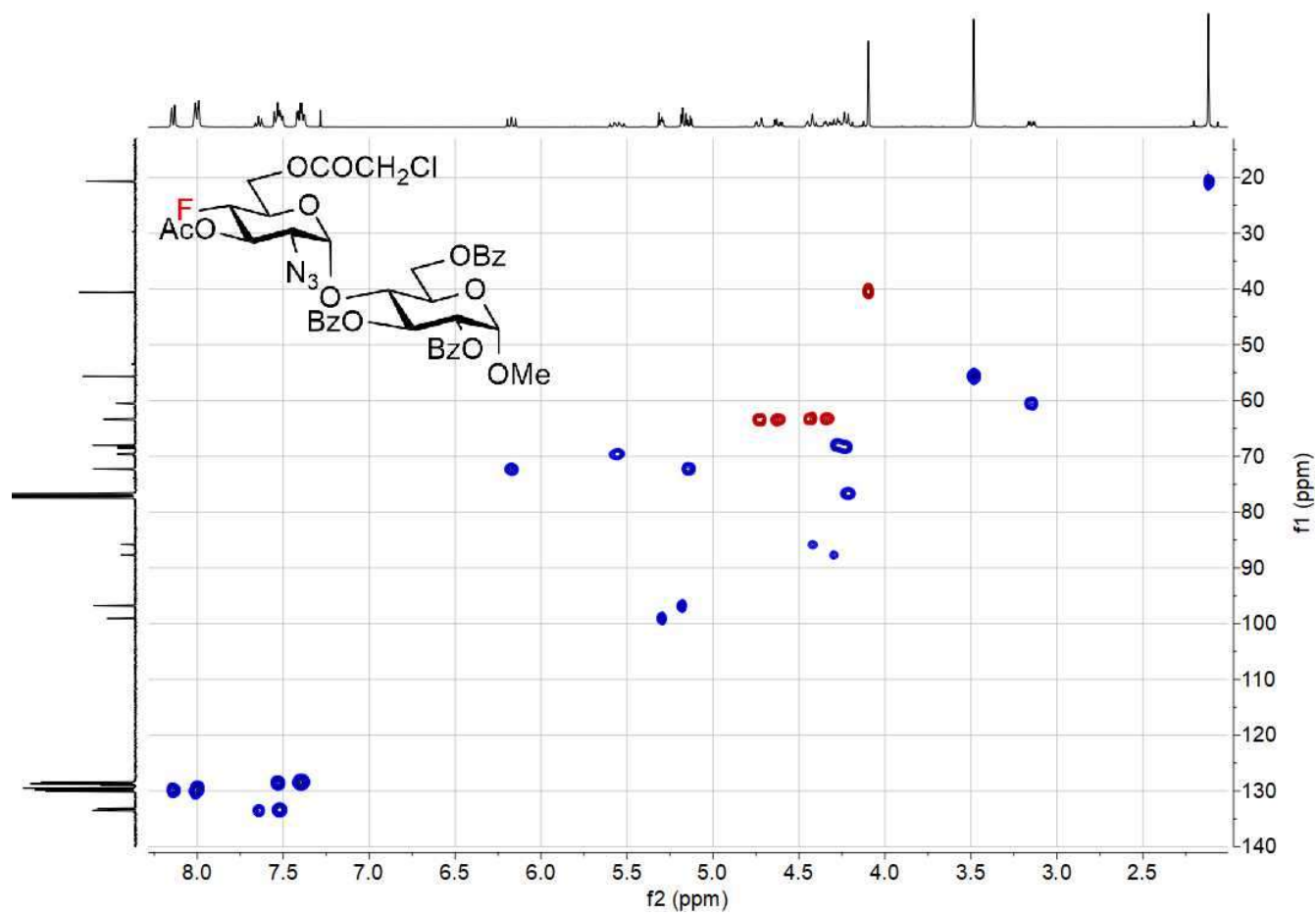
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **D25- $\alpha$**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **D25- $\alpha$**

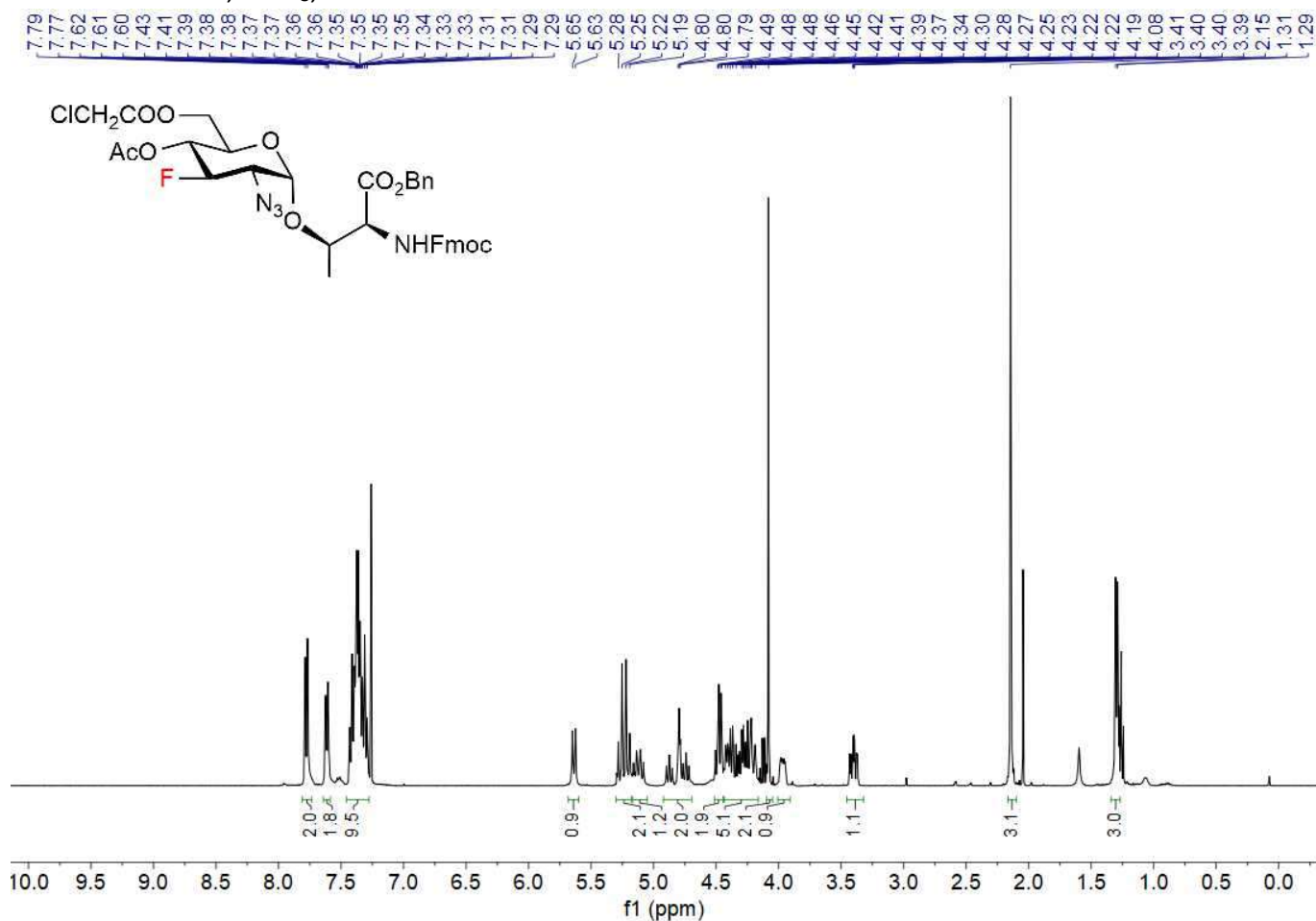


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **D25- $\alpha$**

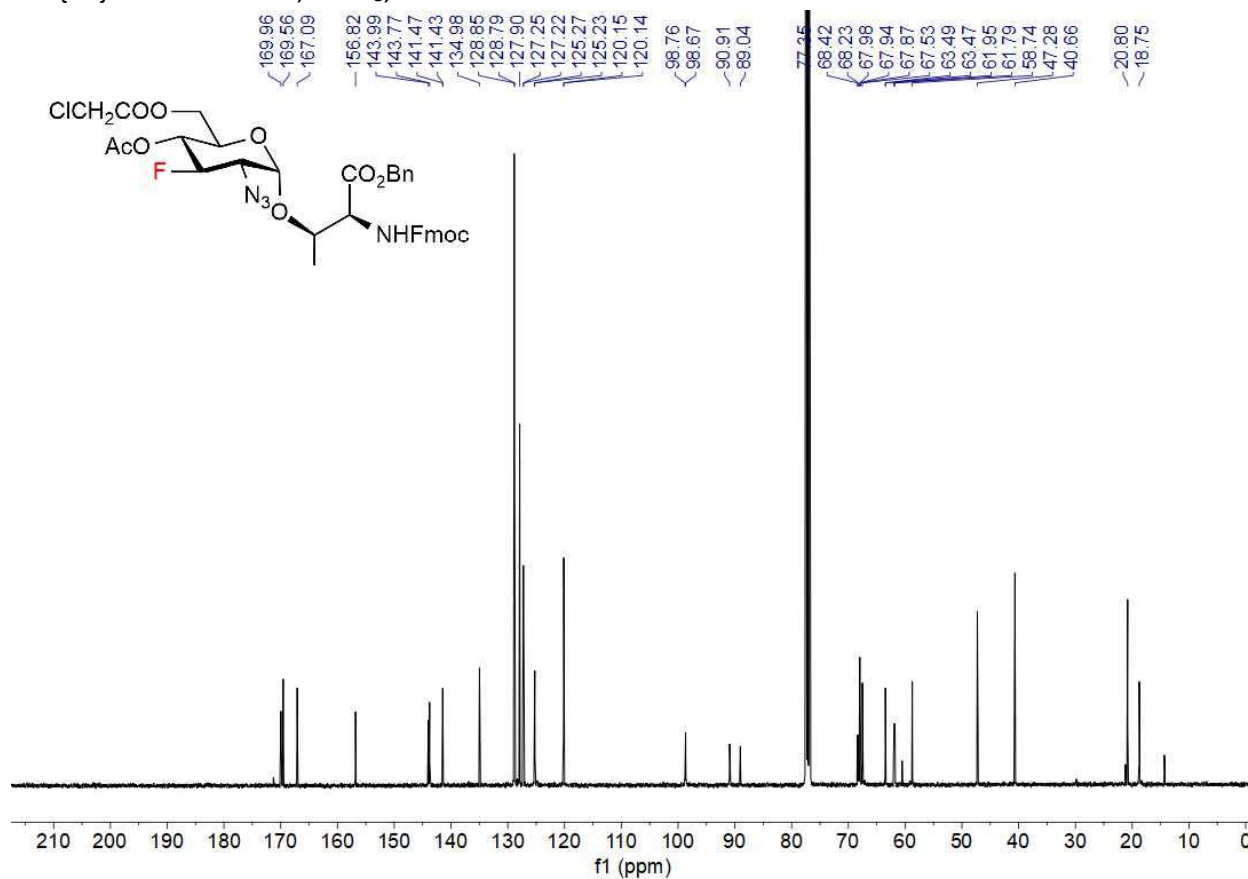


# **NMR 28**

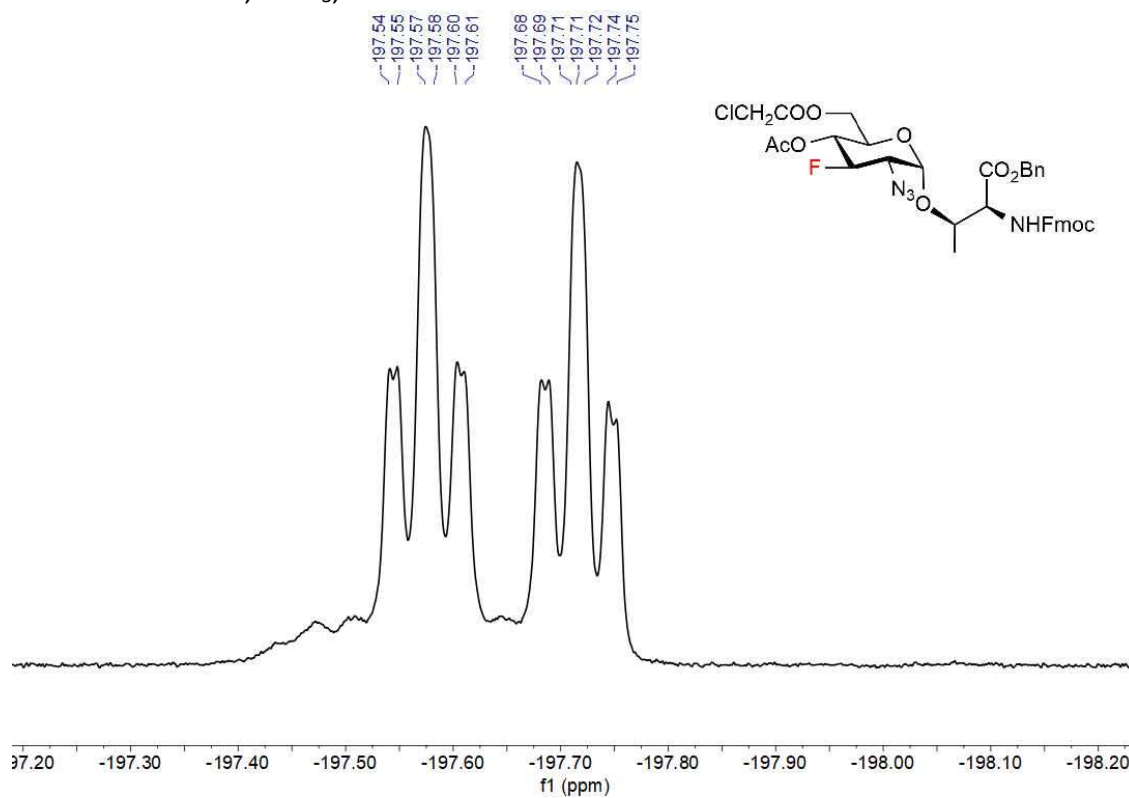
<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **28**



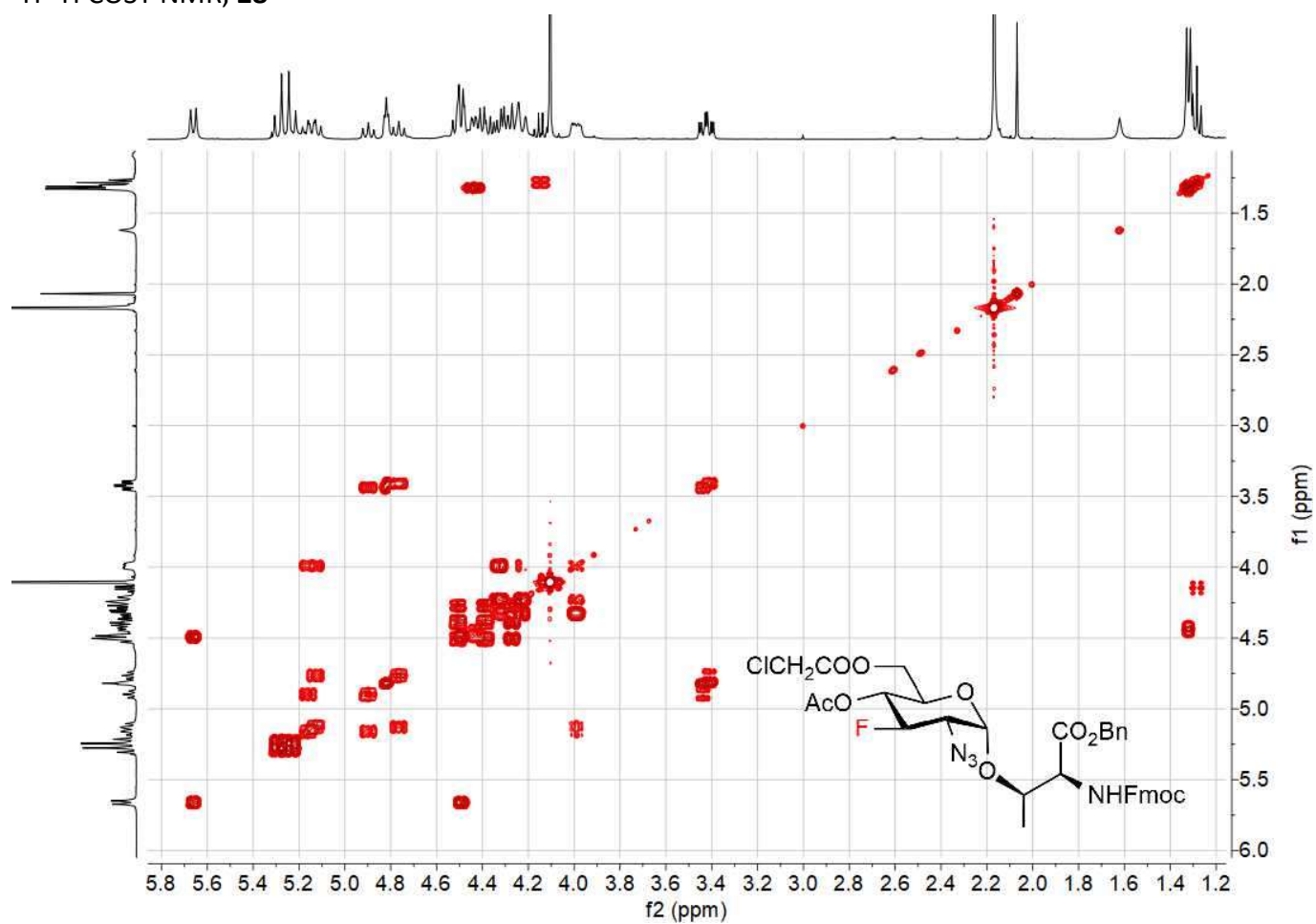
<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **28**



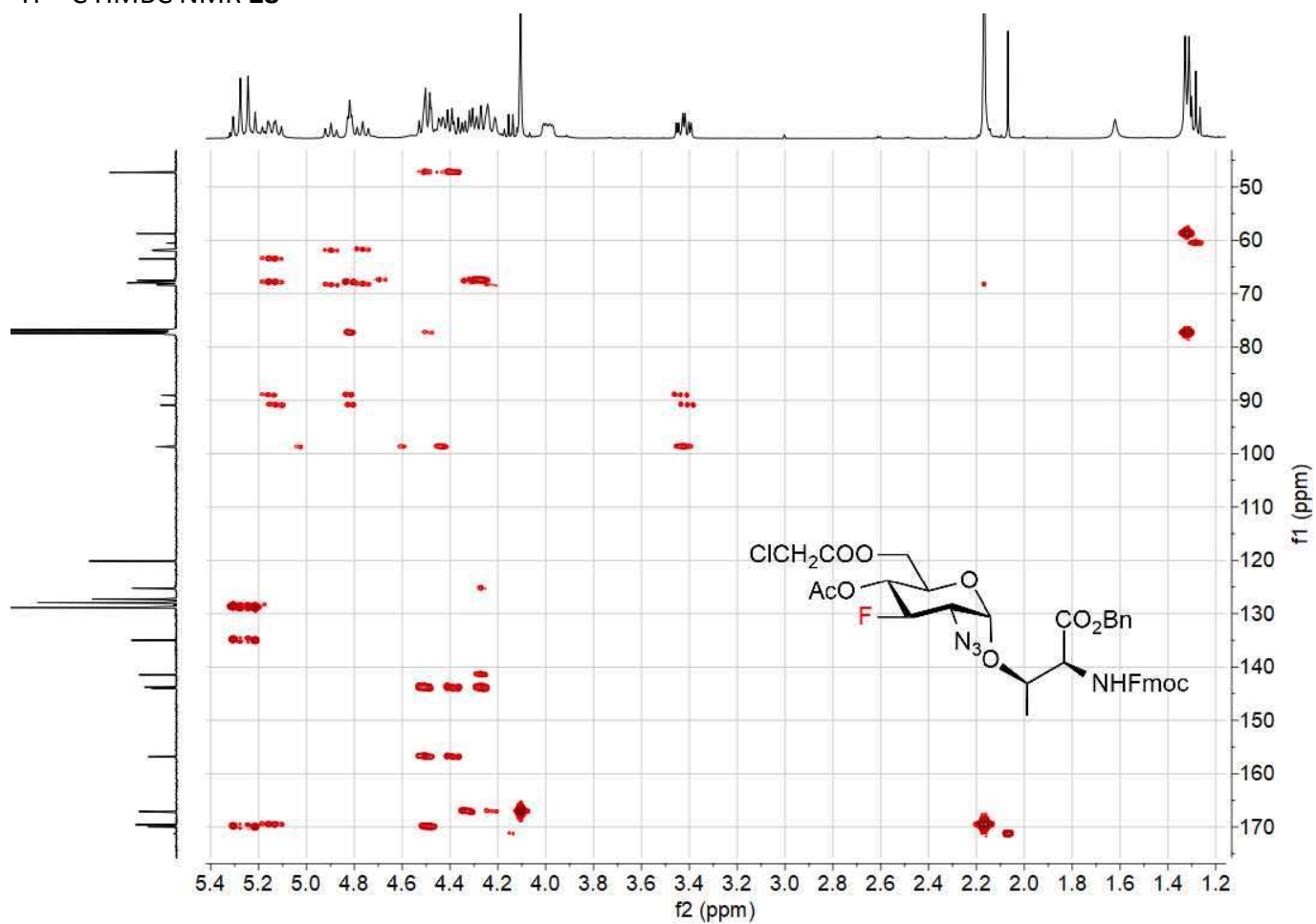
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **28**



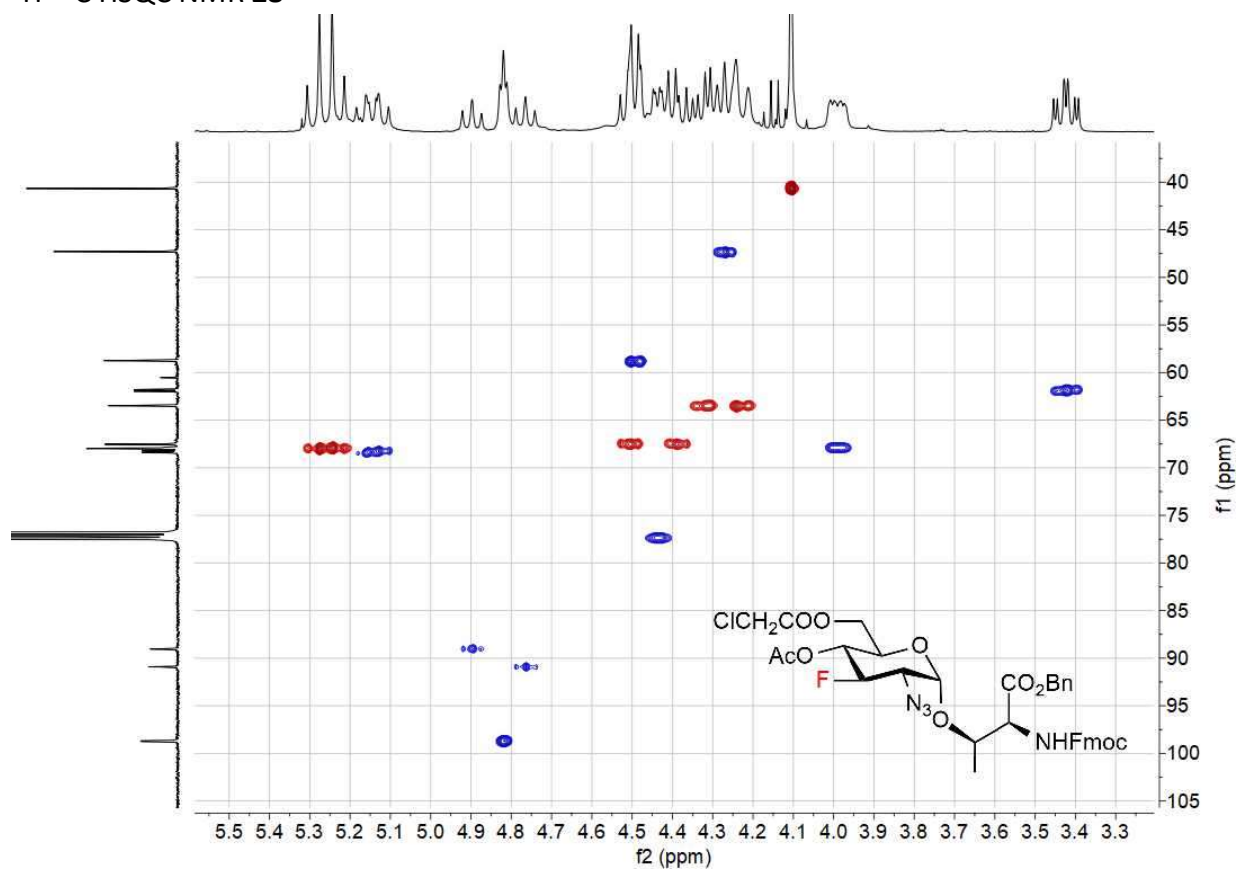
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **28**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 28

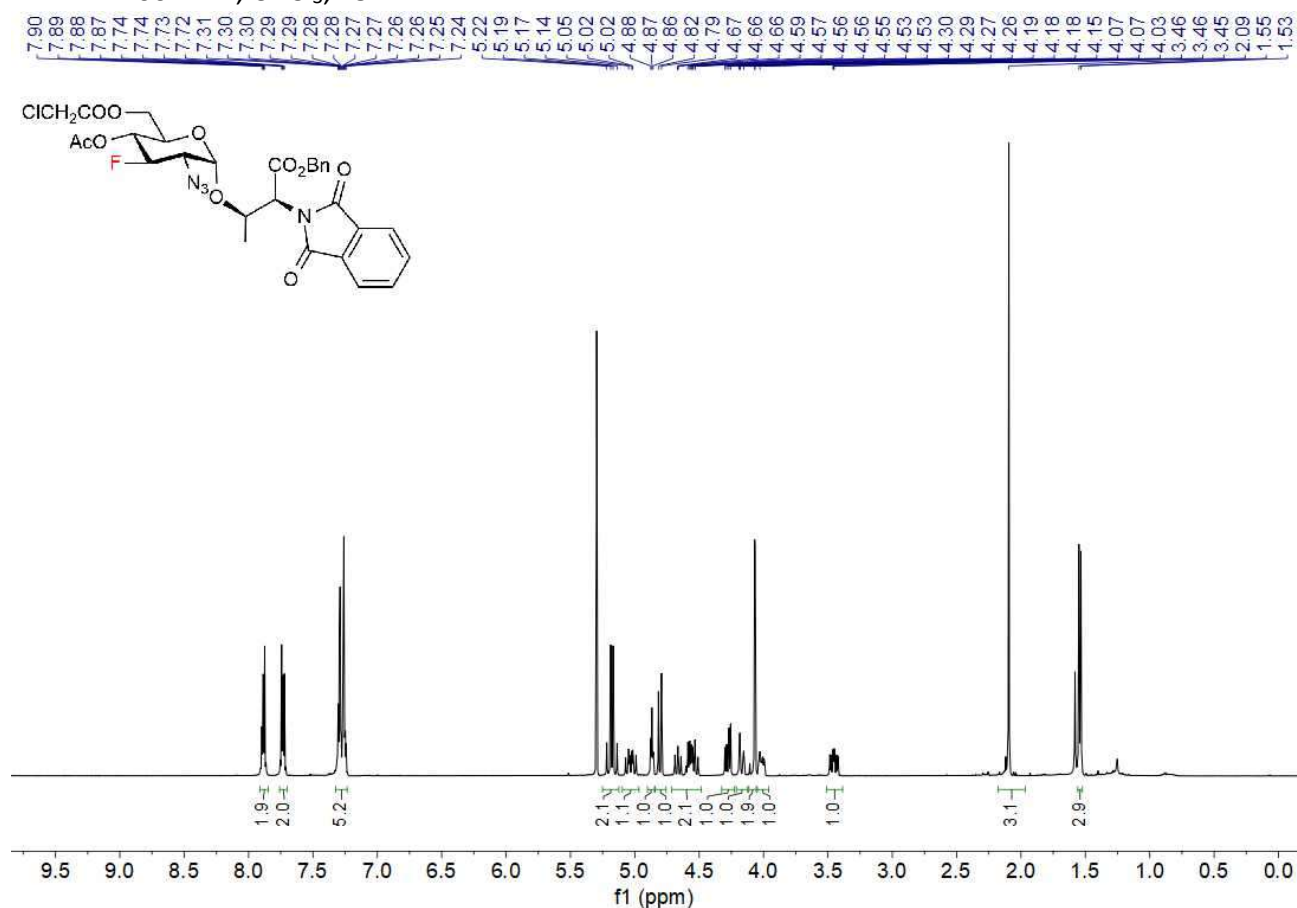


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 28

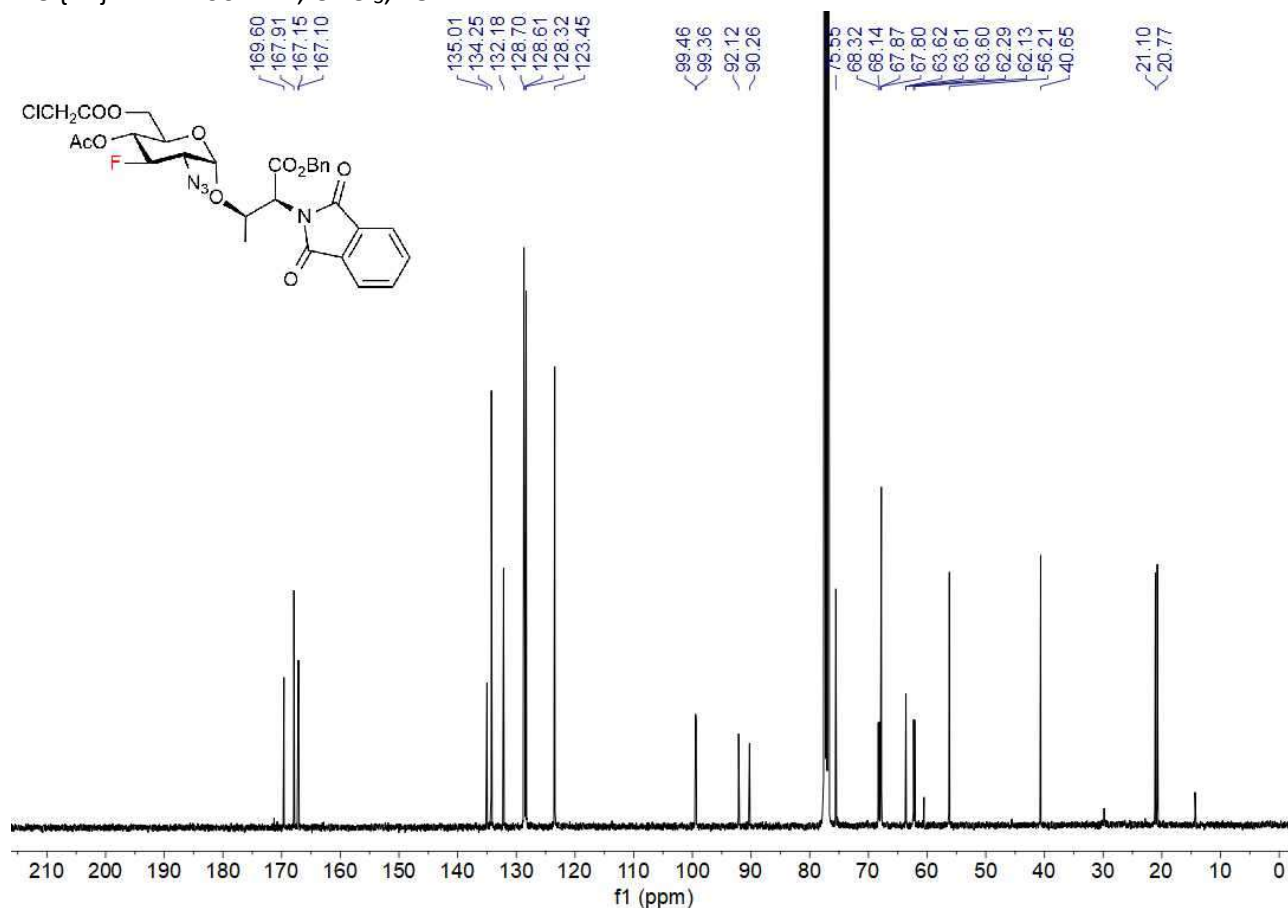


# **NMR 29**

**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, 29**

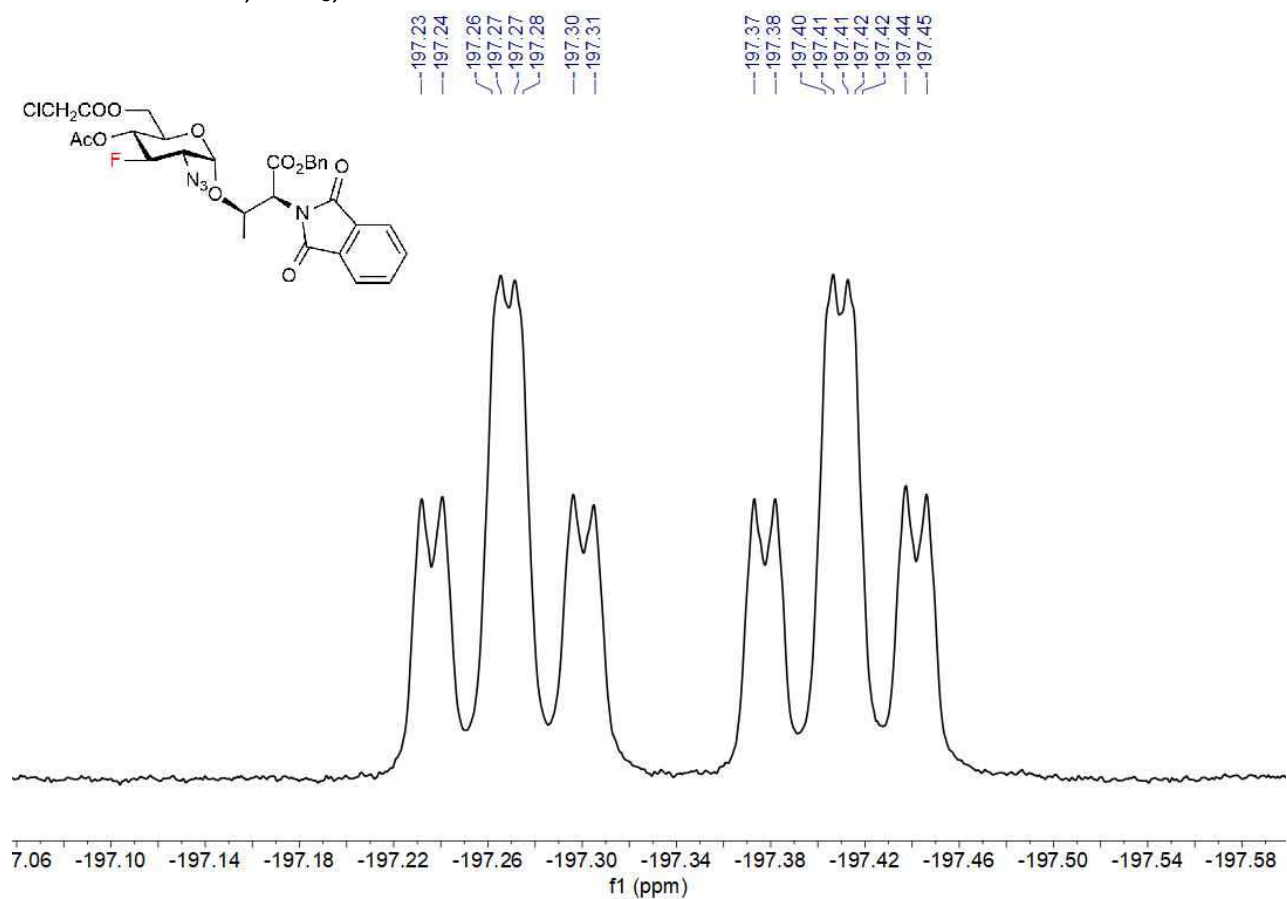


**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, 29**

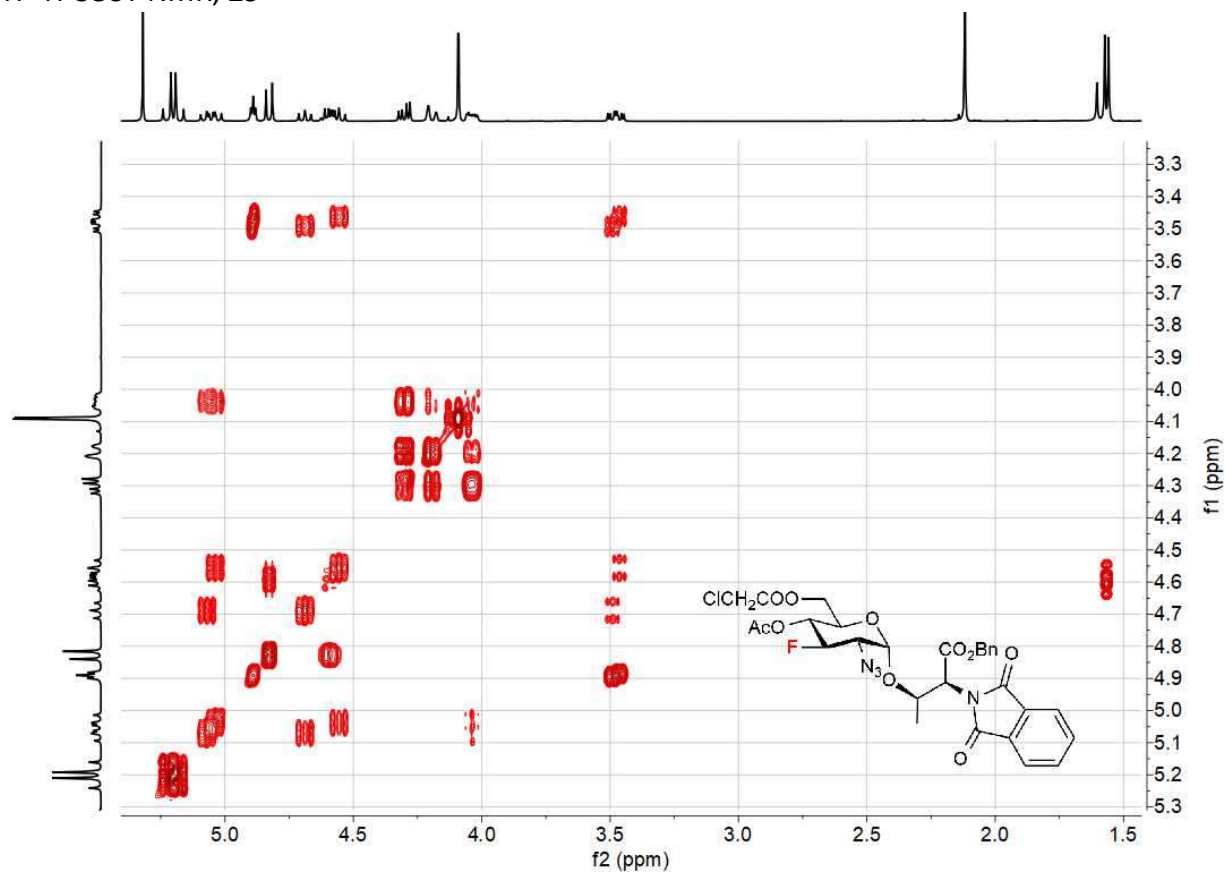




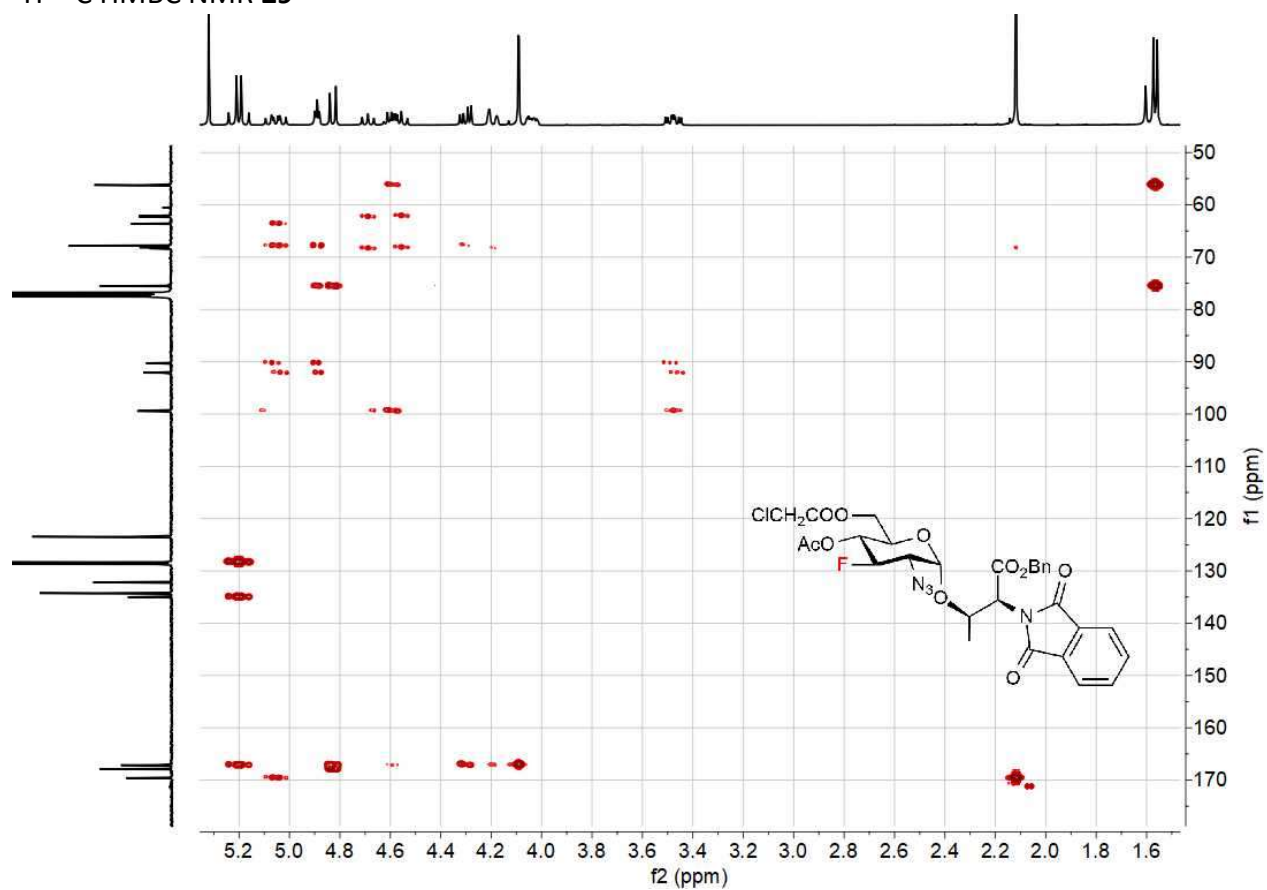
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **29**



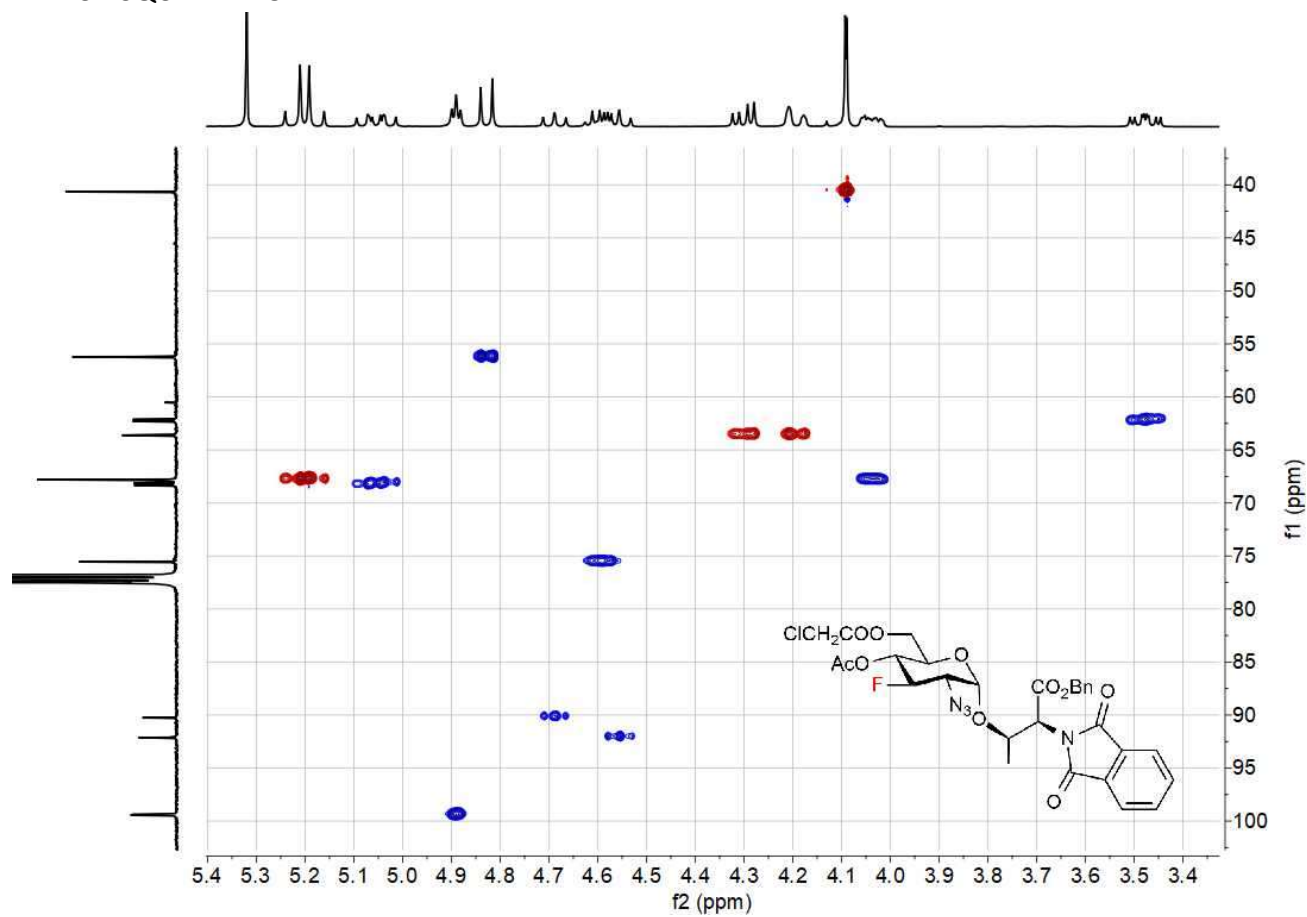
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **29**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 29

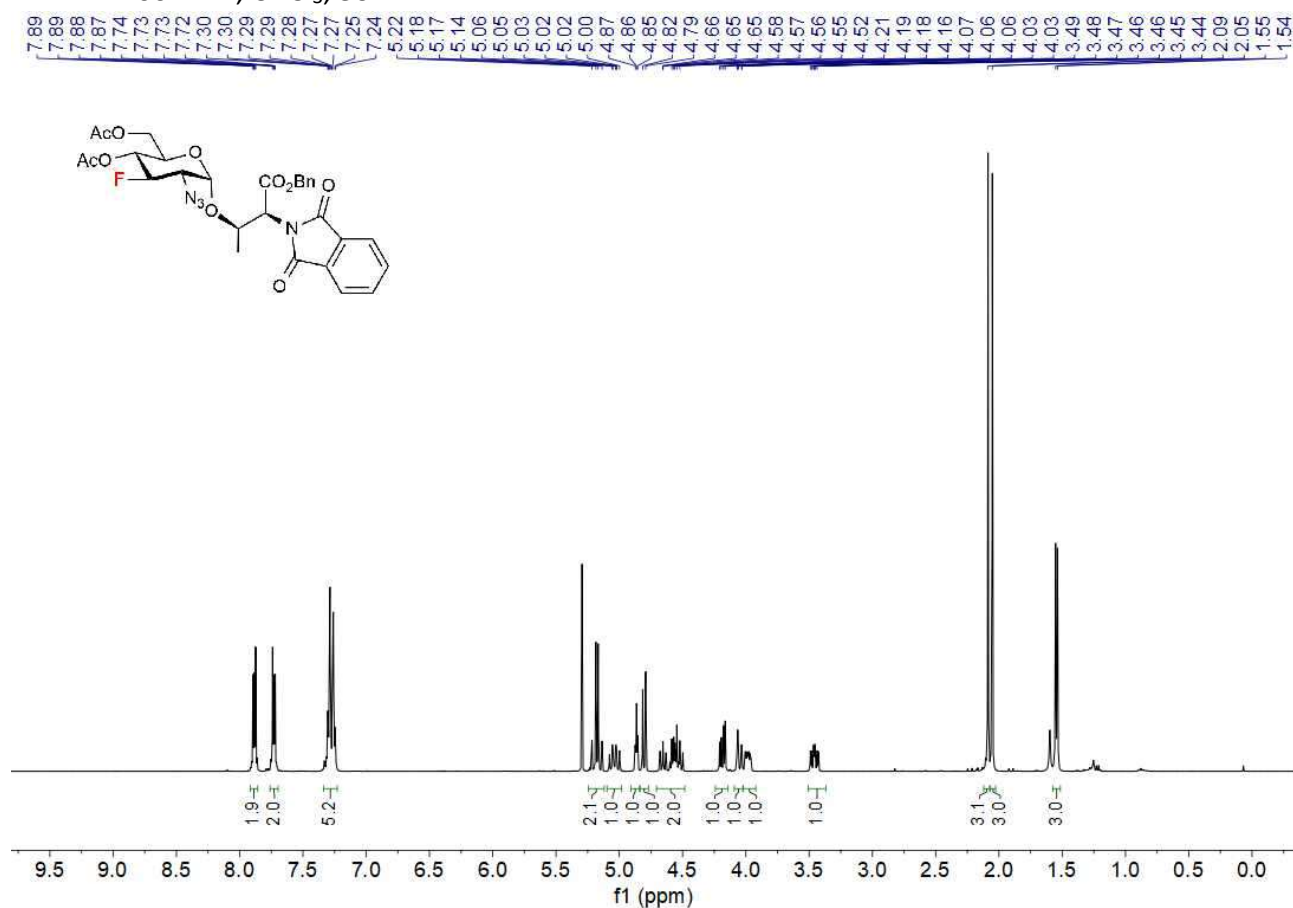


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 29

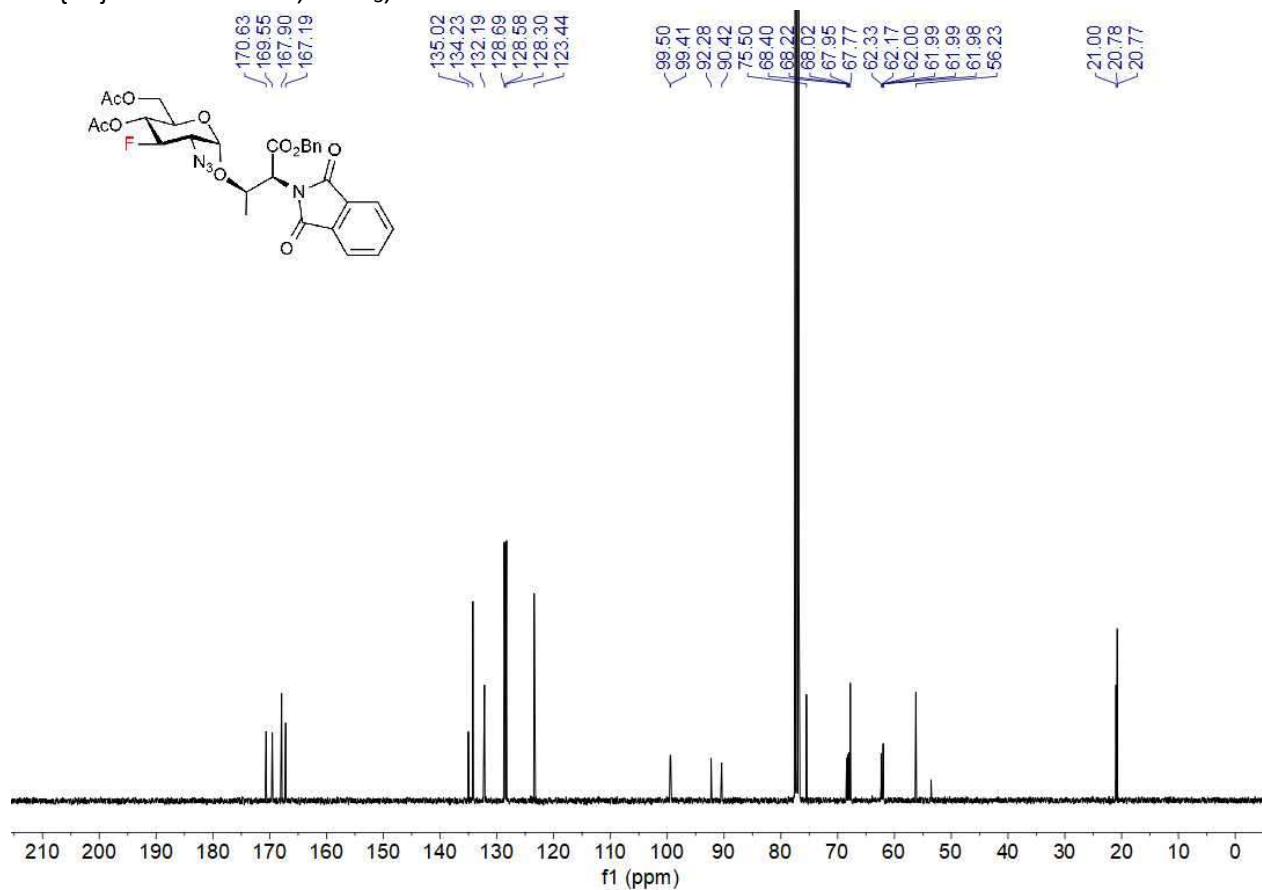


# **NMR 30**

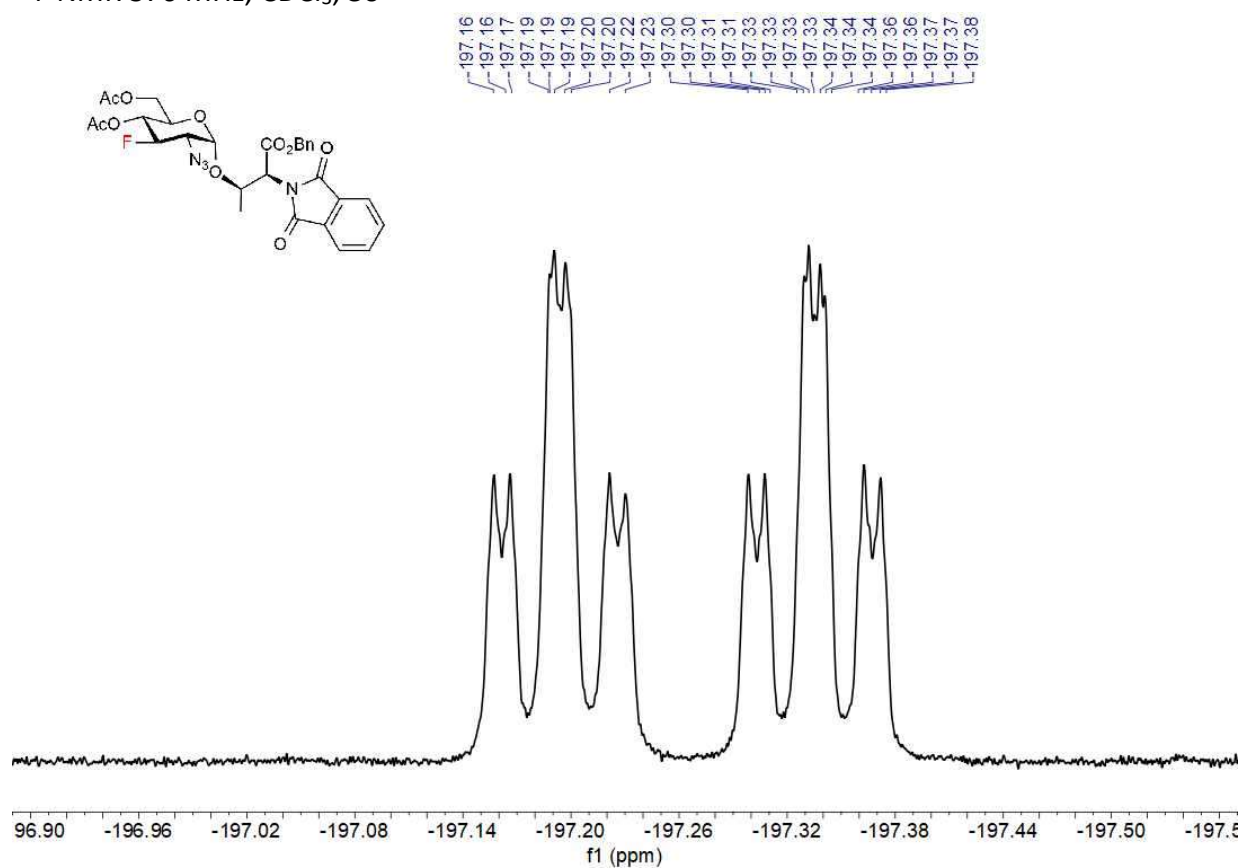
**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, 30**



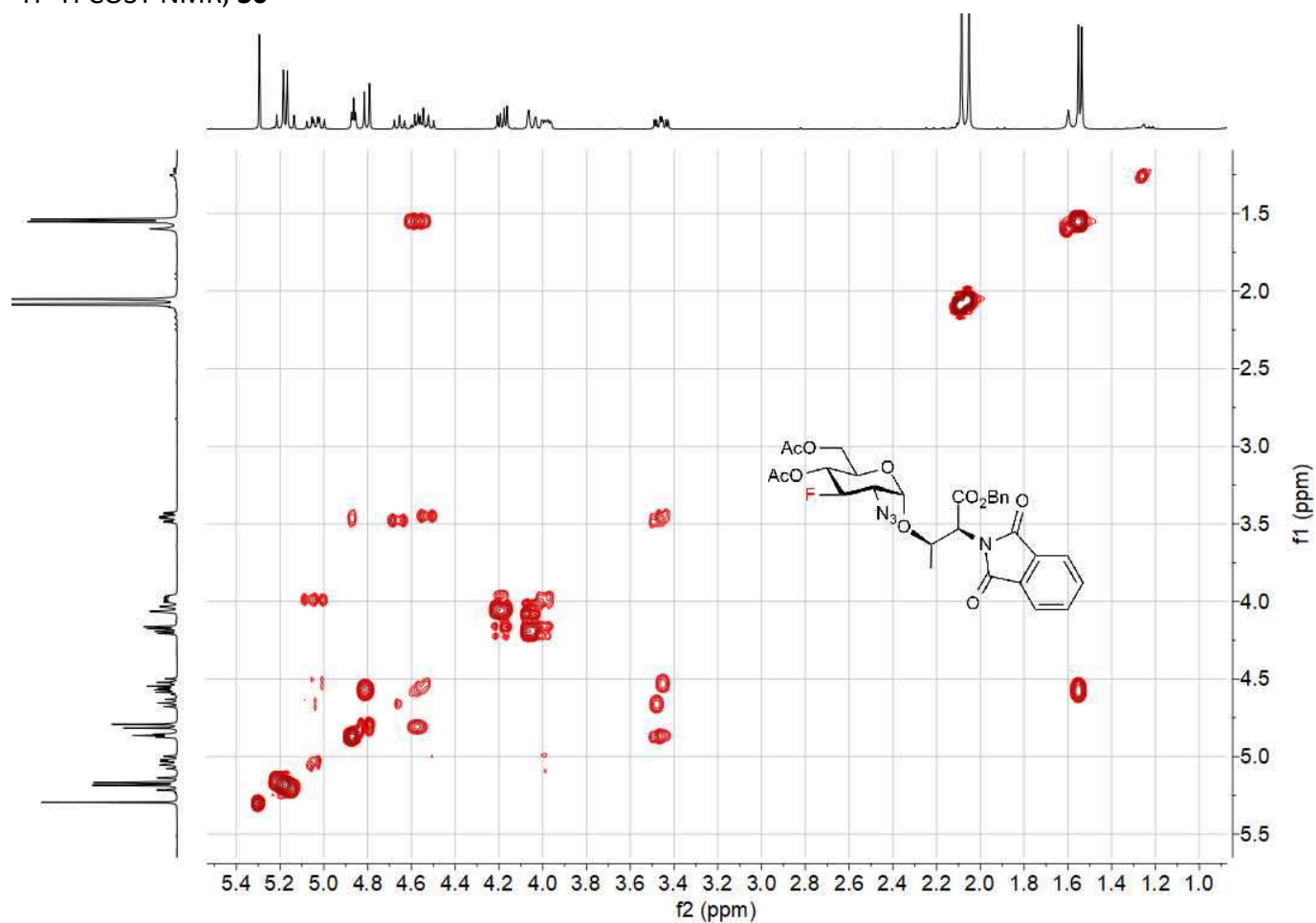
**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, 30**



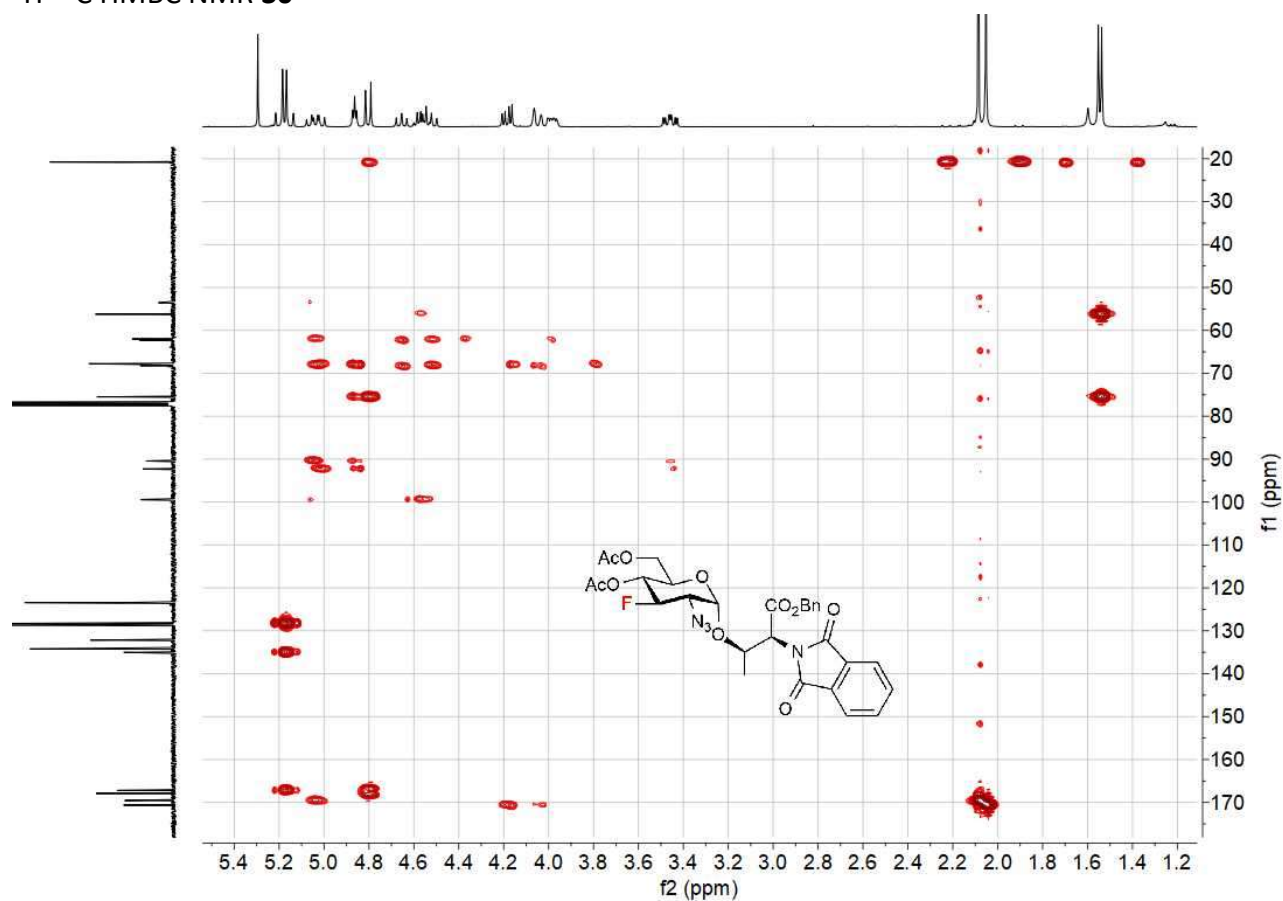
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **30**



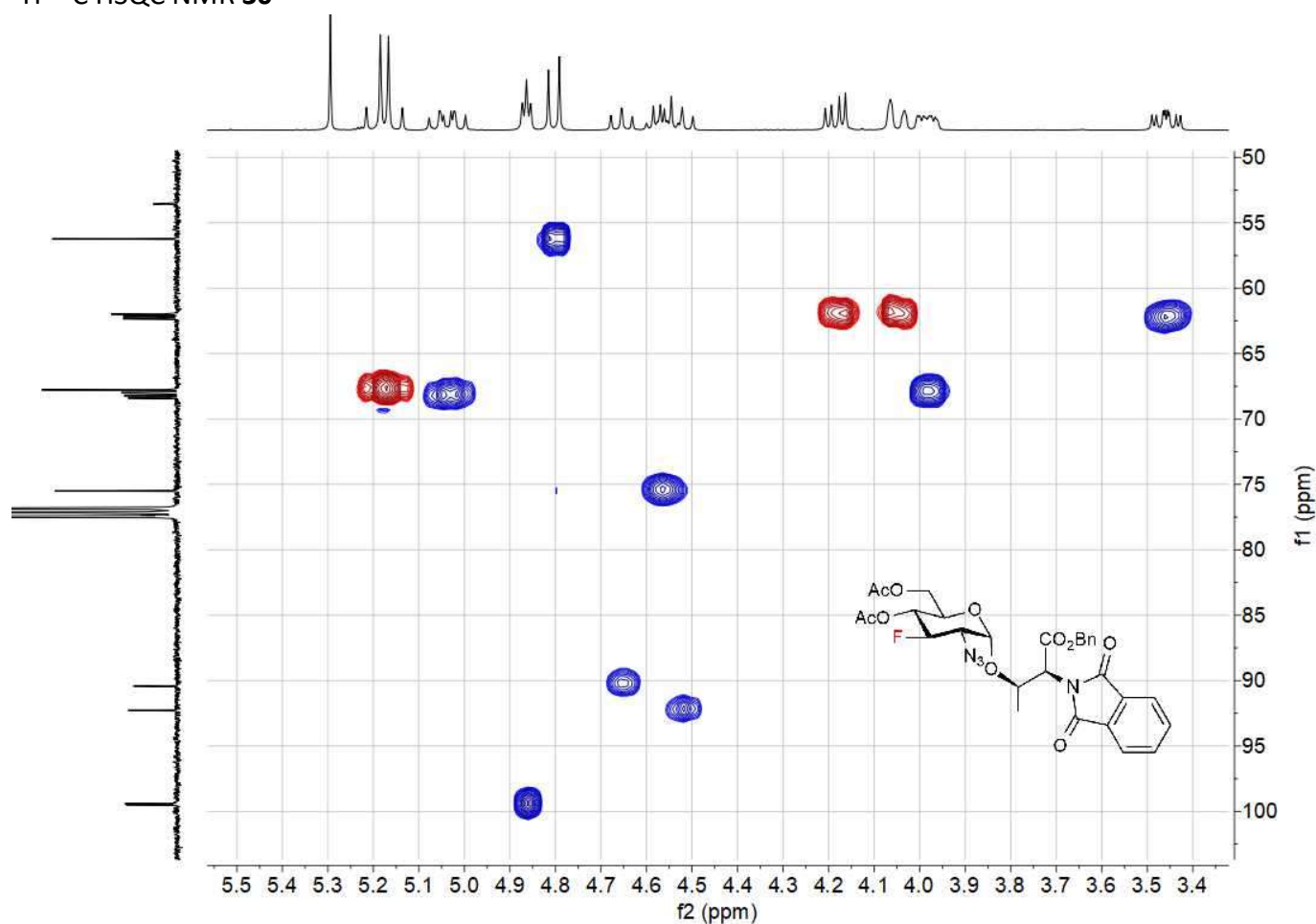
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **30**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **30**

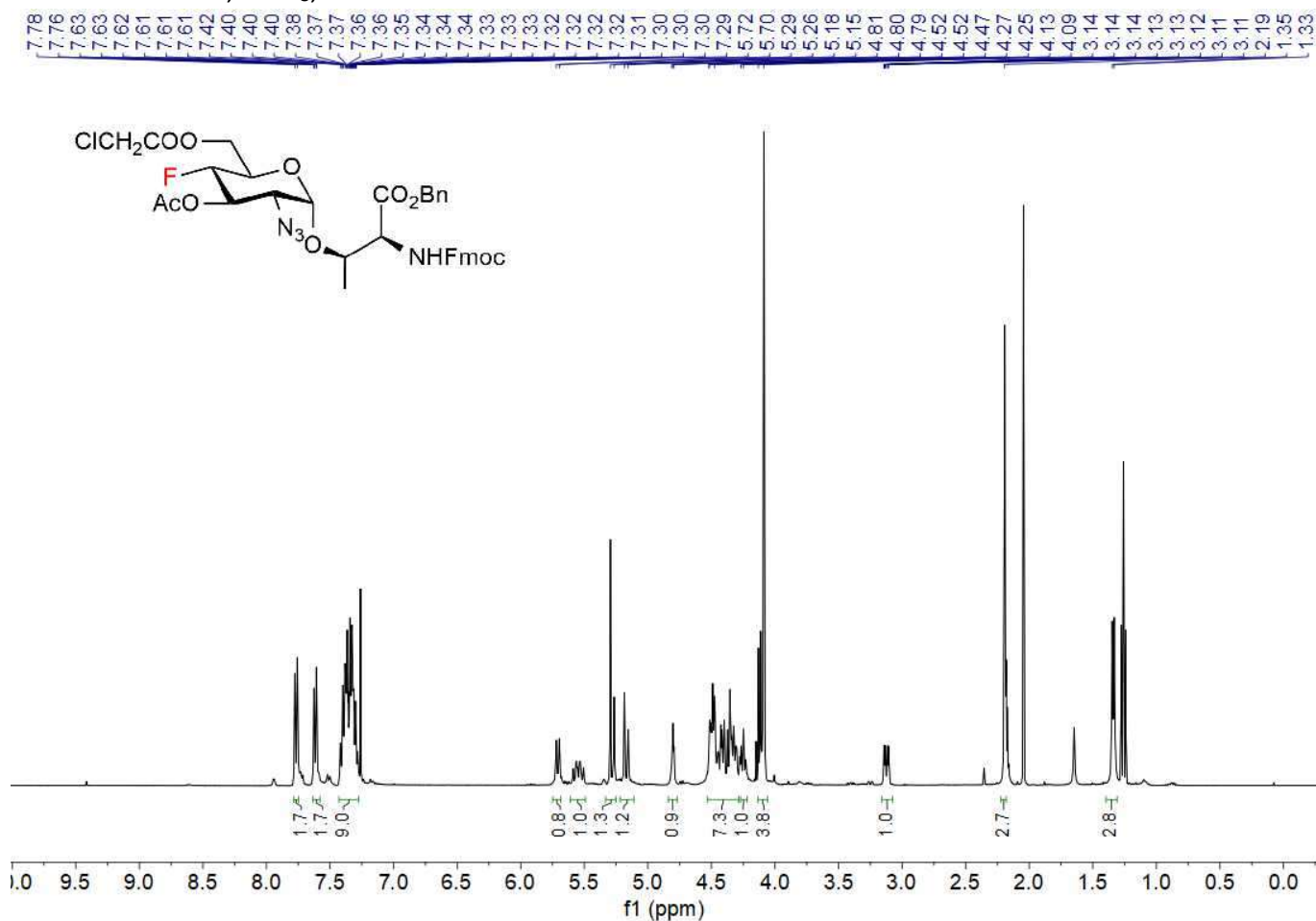


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **30**

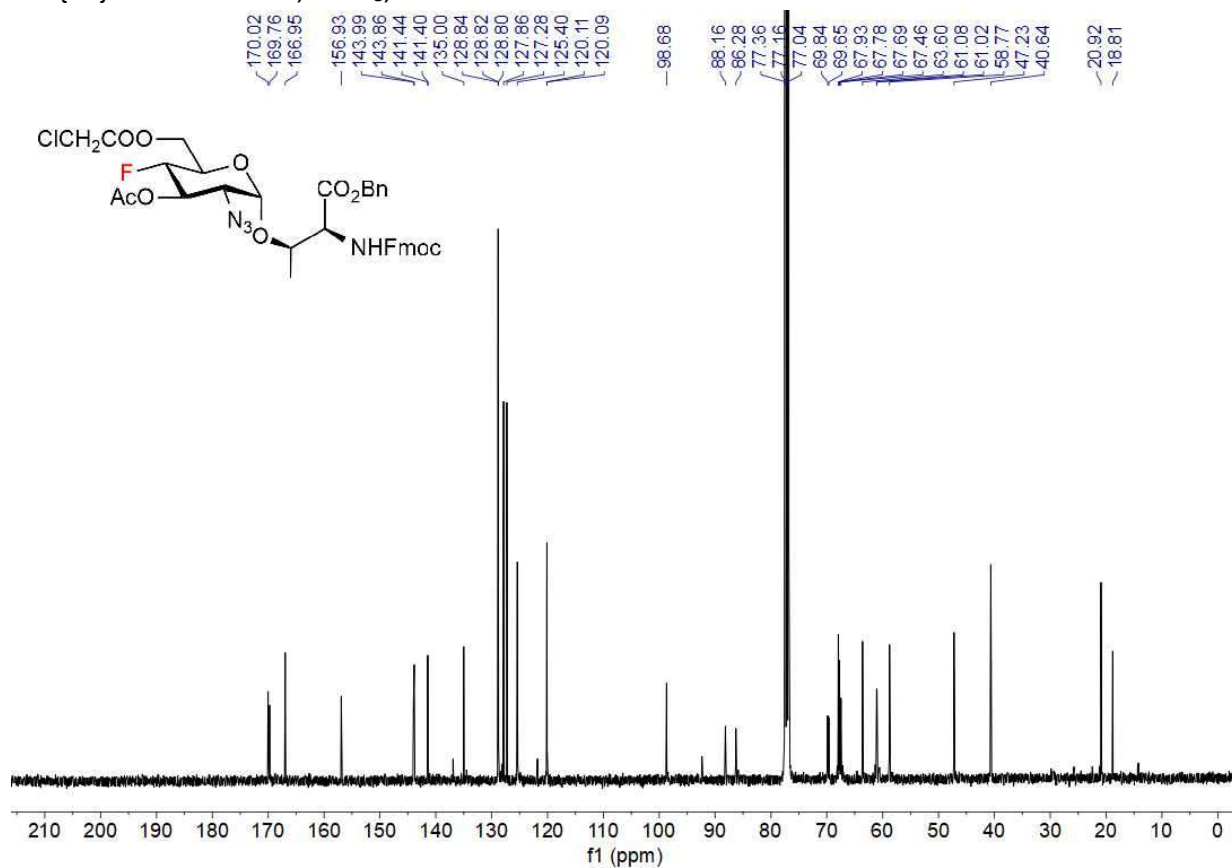


# **NMR 31**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **31**

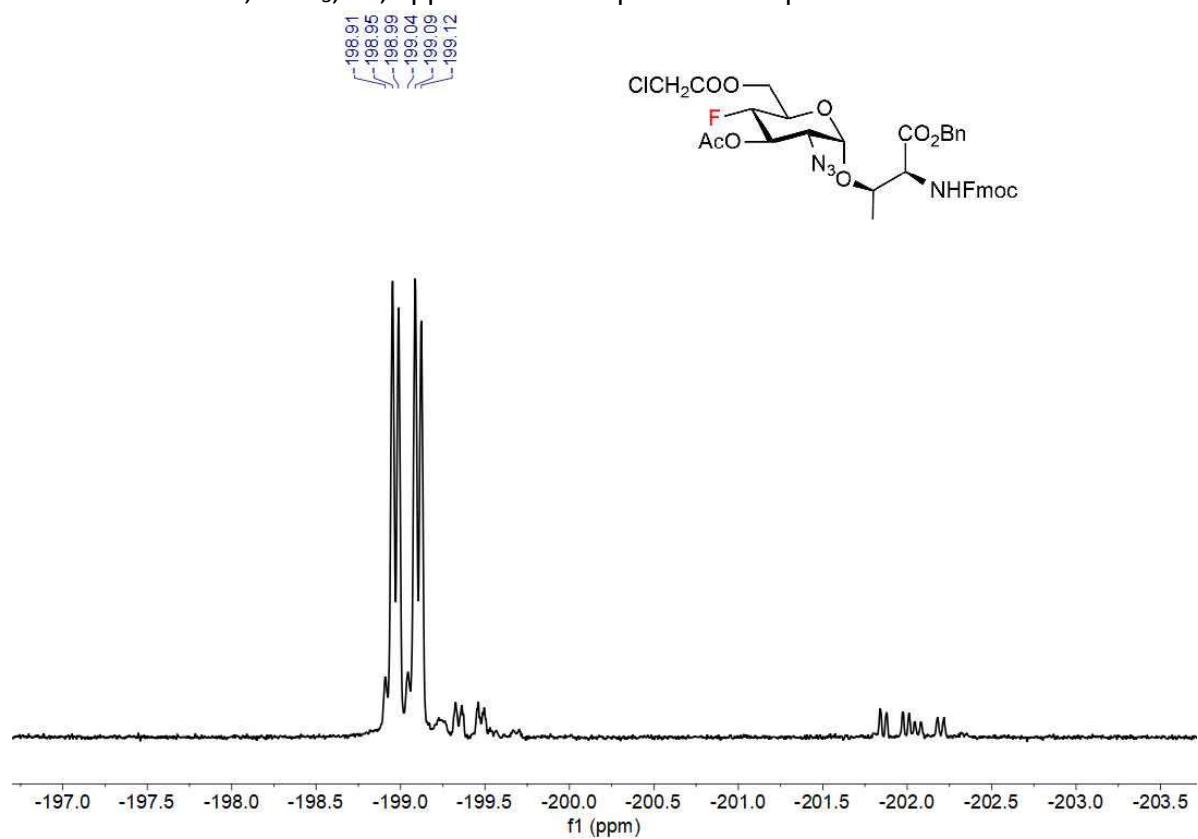


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **31**

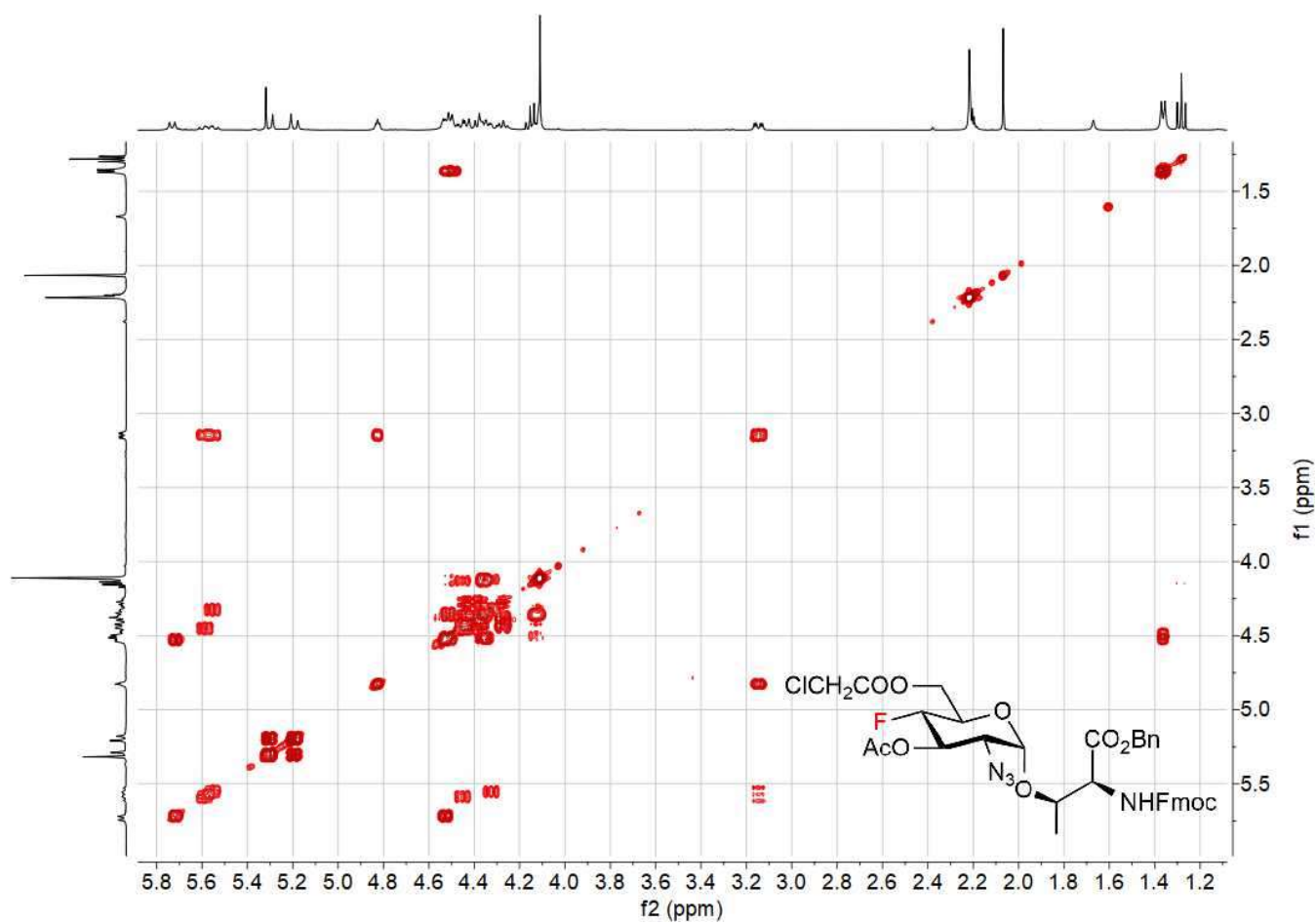




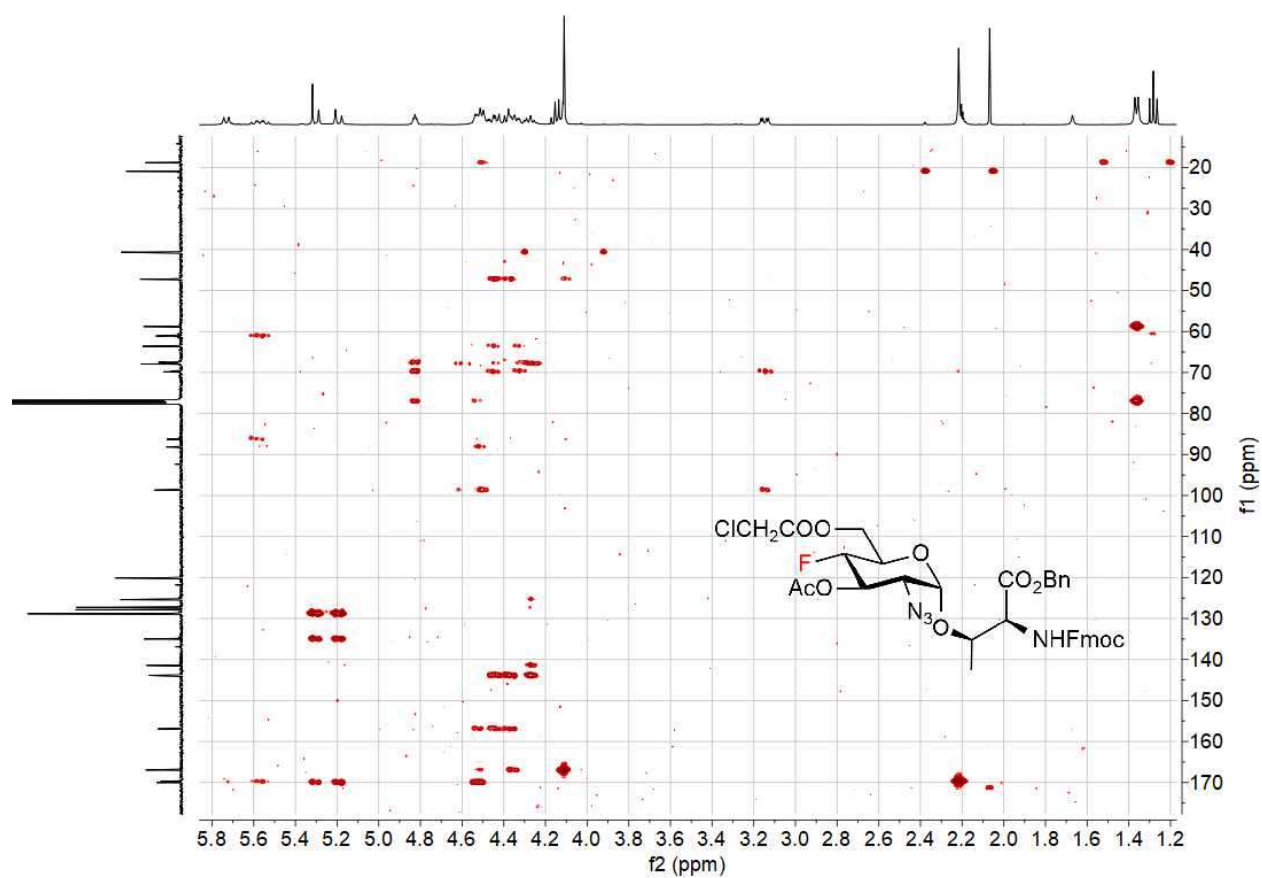
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **31**, approx. 17% inseparable side-products detected



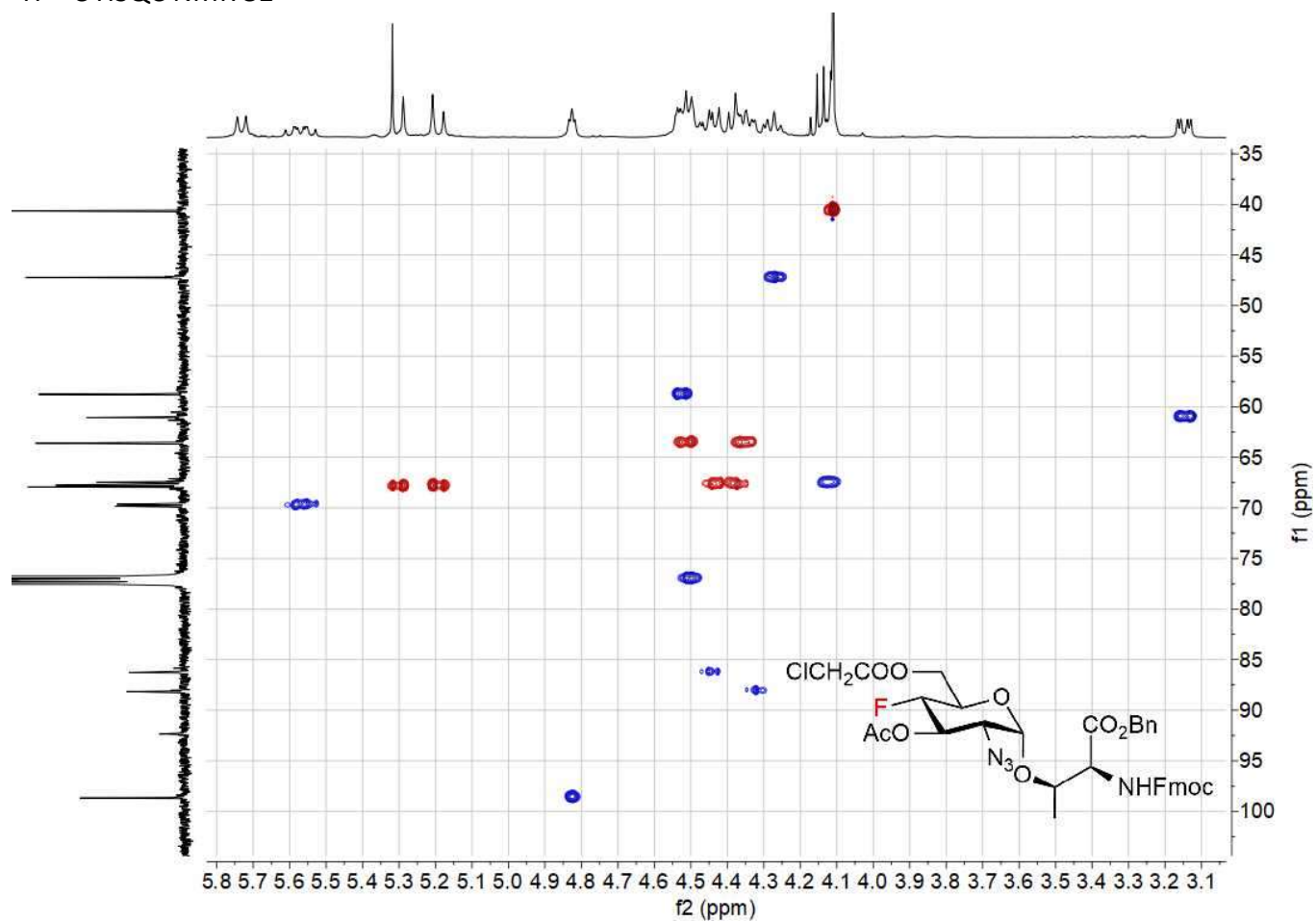
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **31**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 31

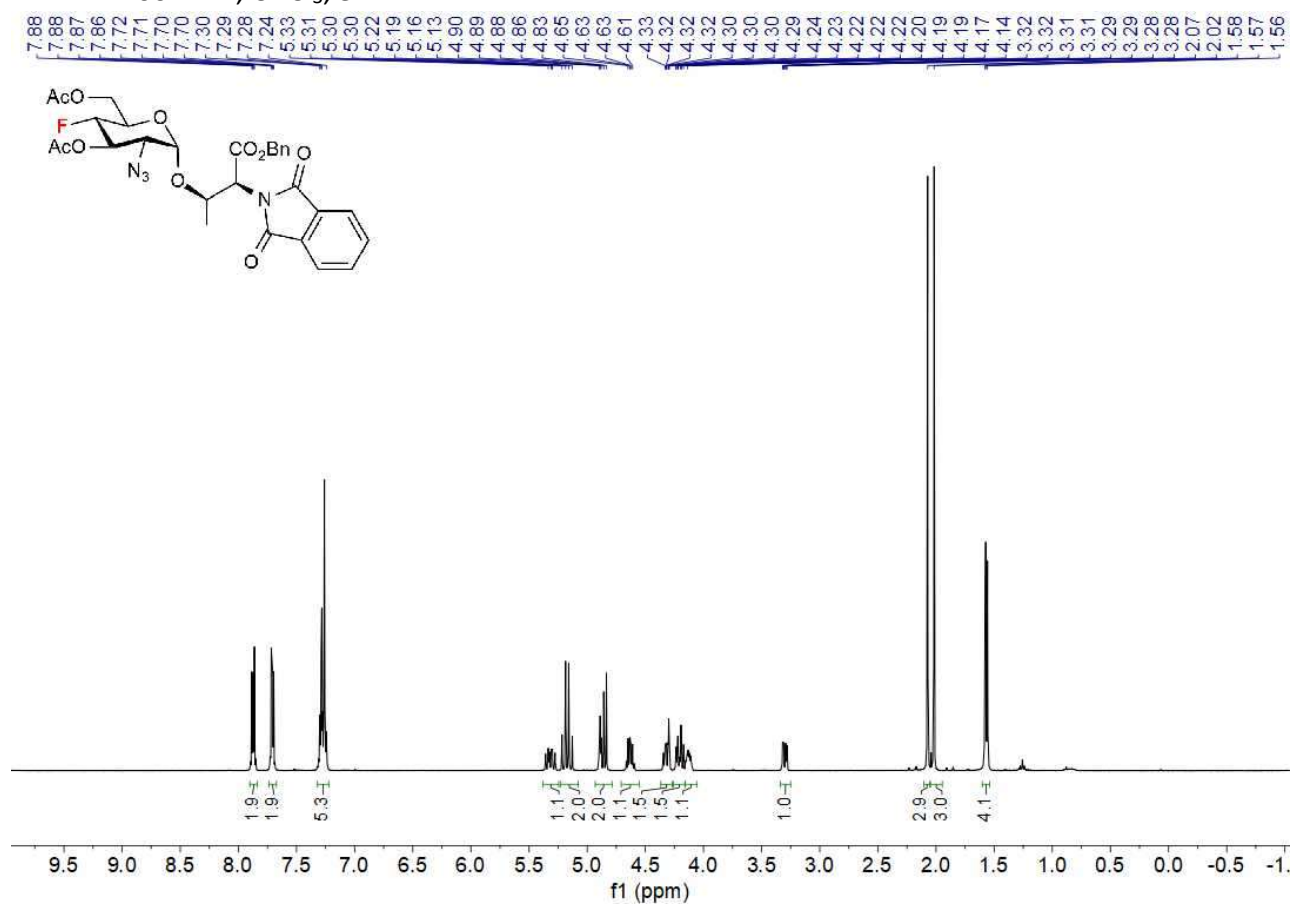


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 31

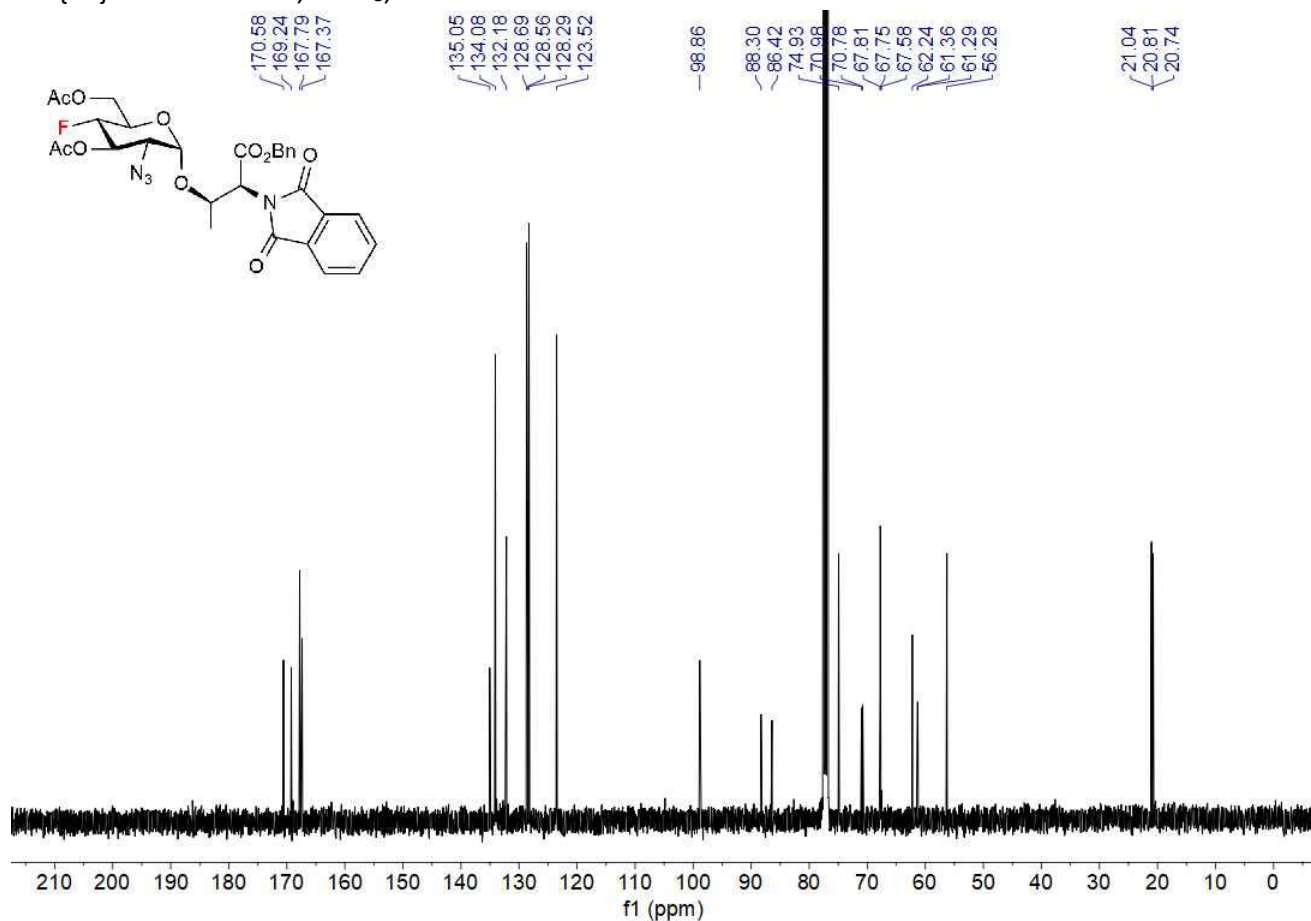


# **NMR 32**

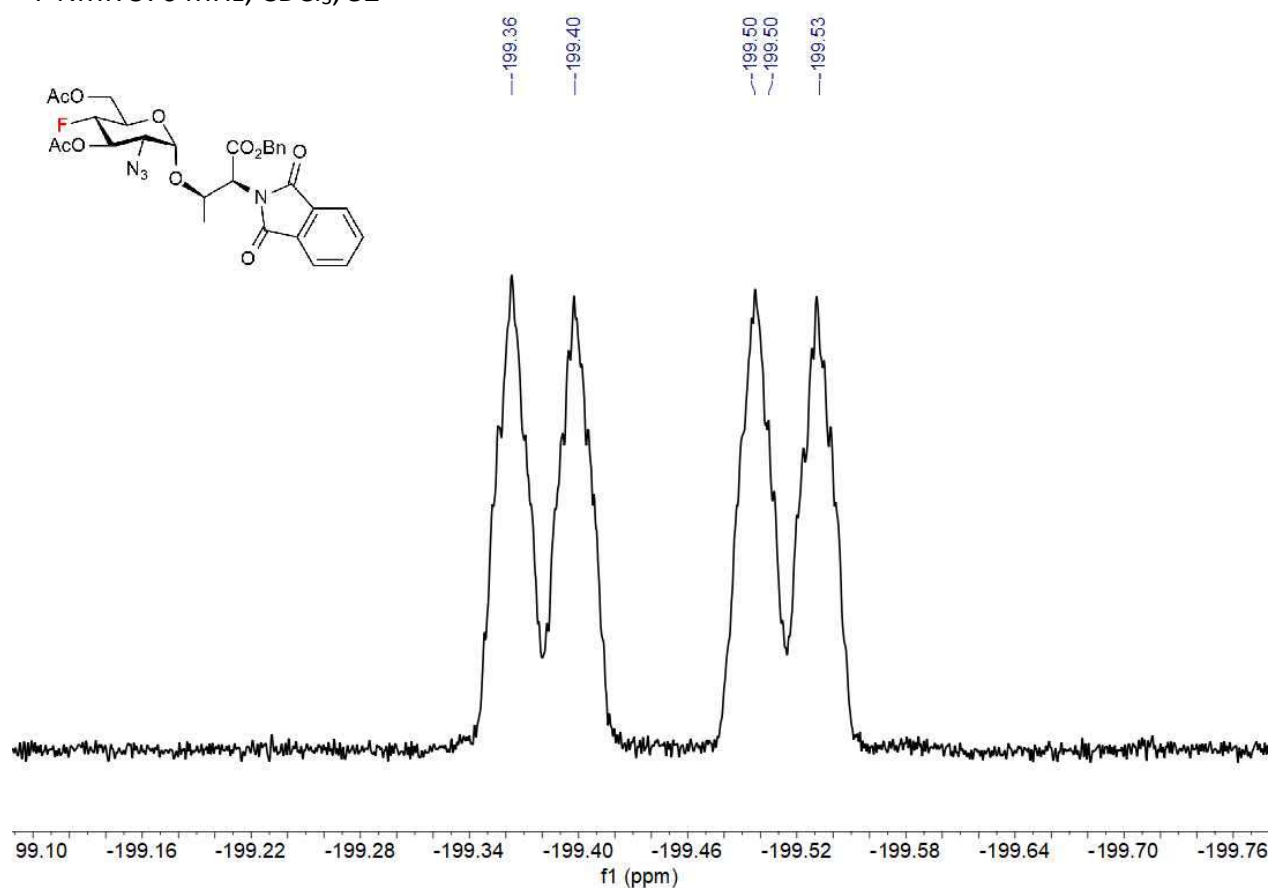
**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, 32**



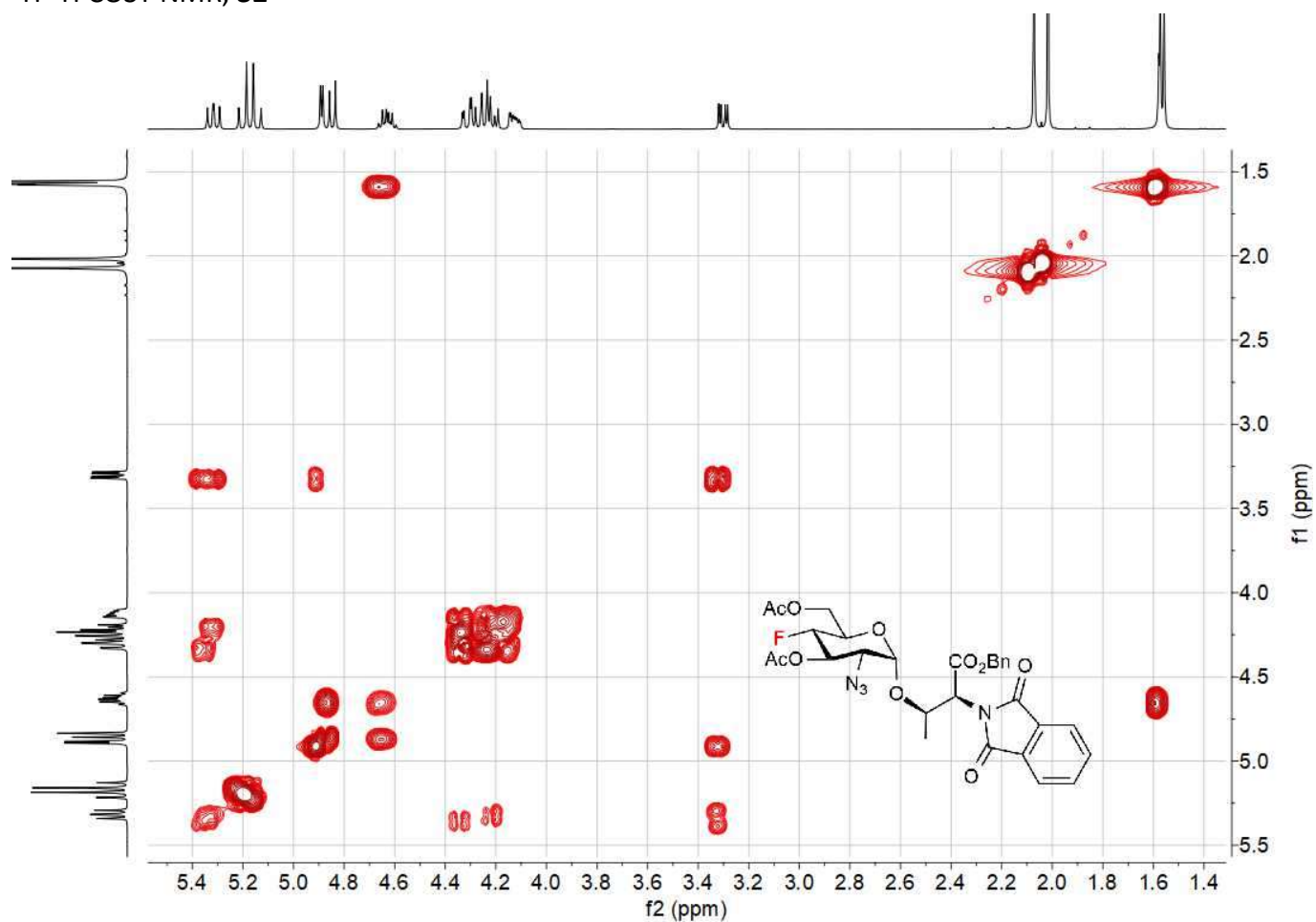
**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, 32**



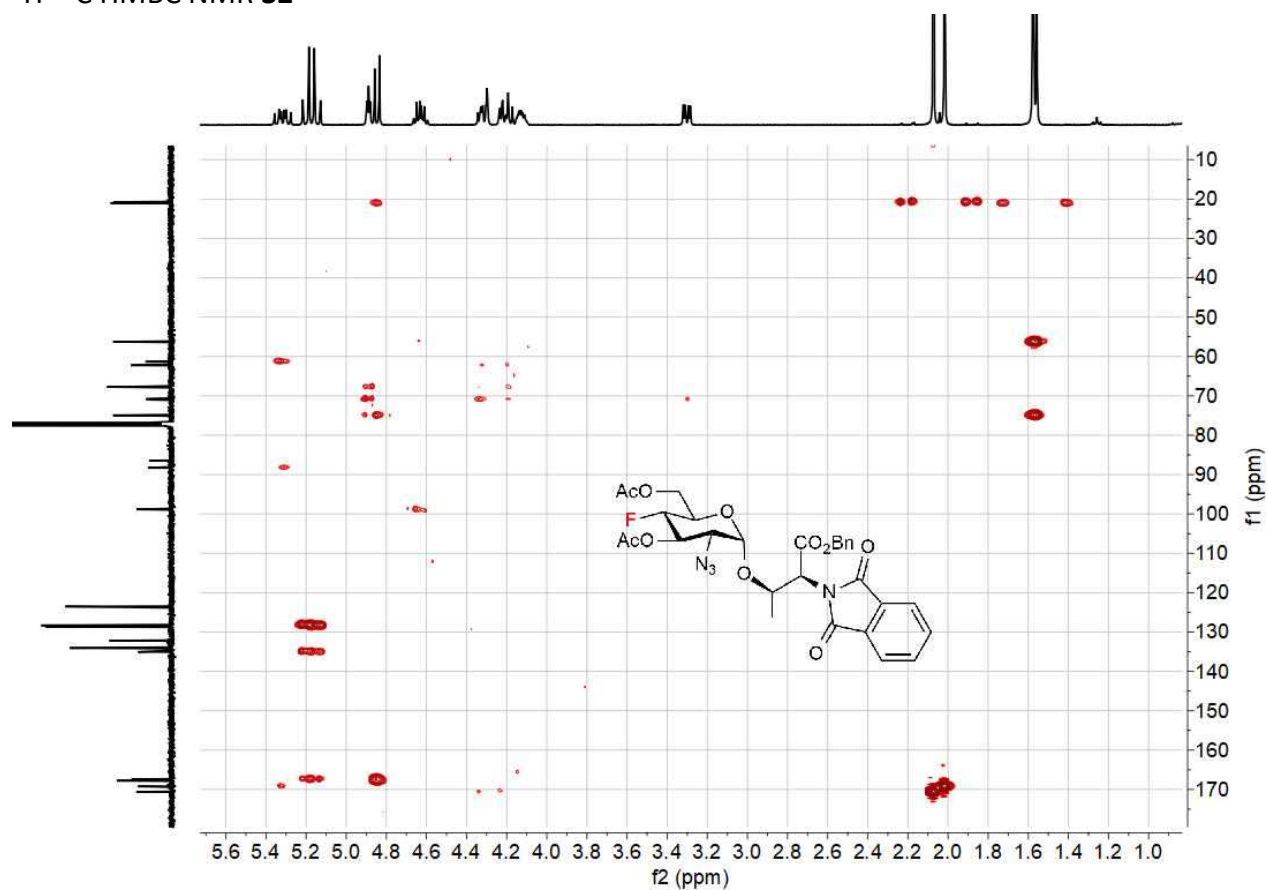
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **32**



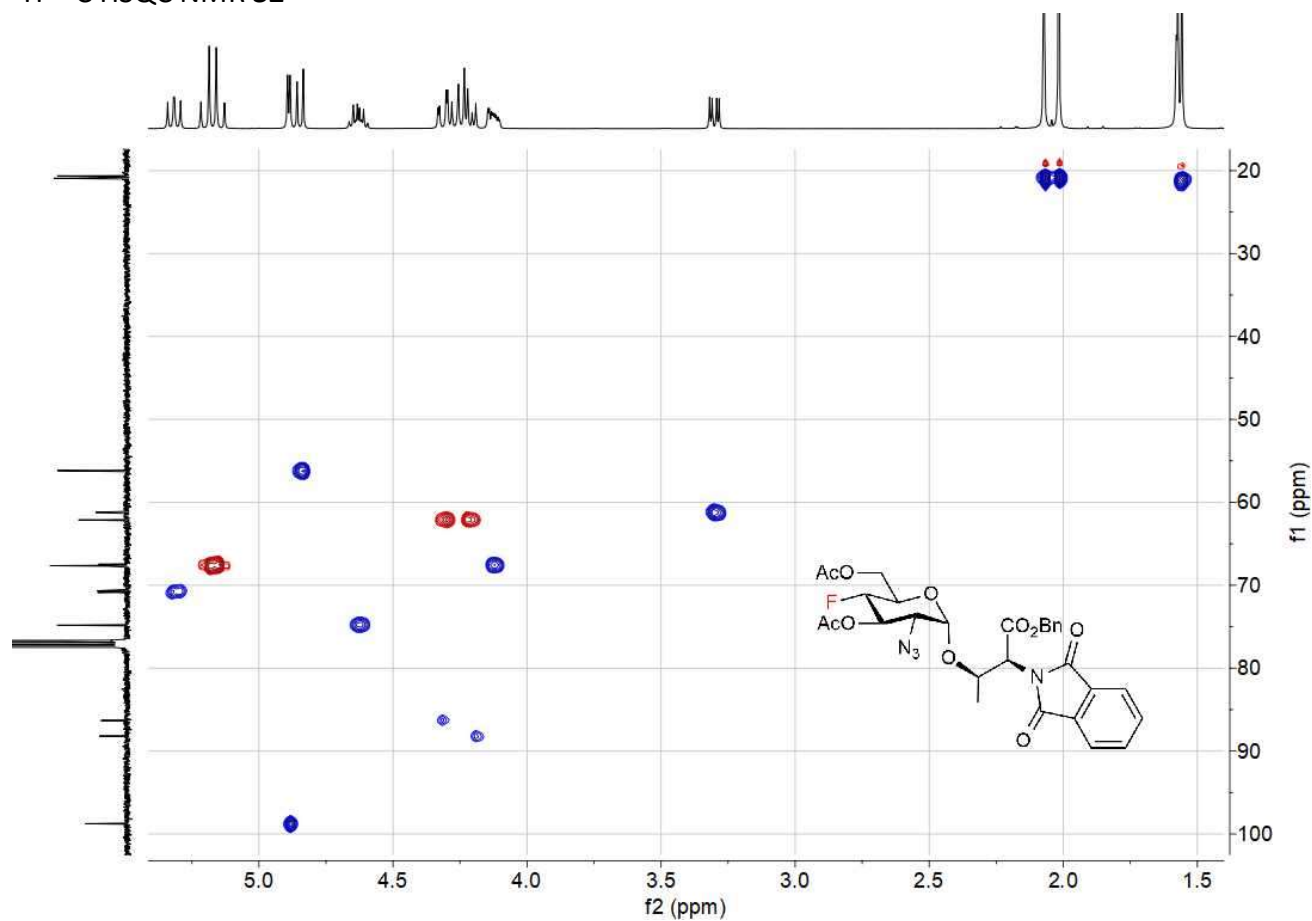
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **32**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **32**

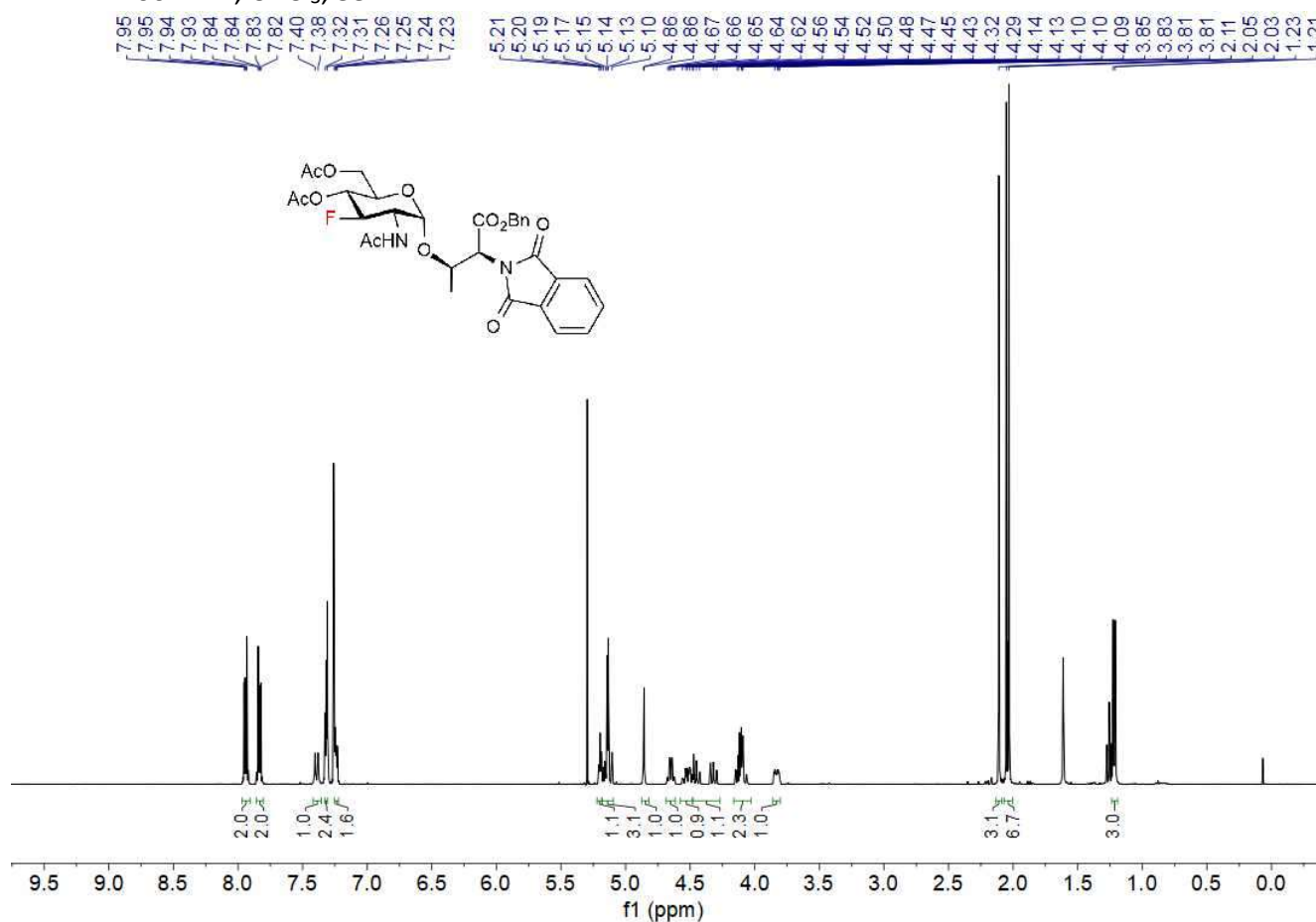


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **32**

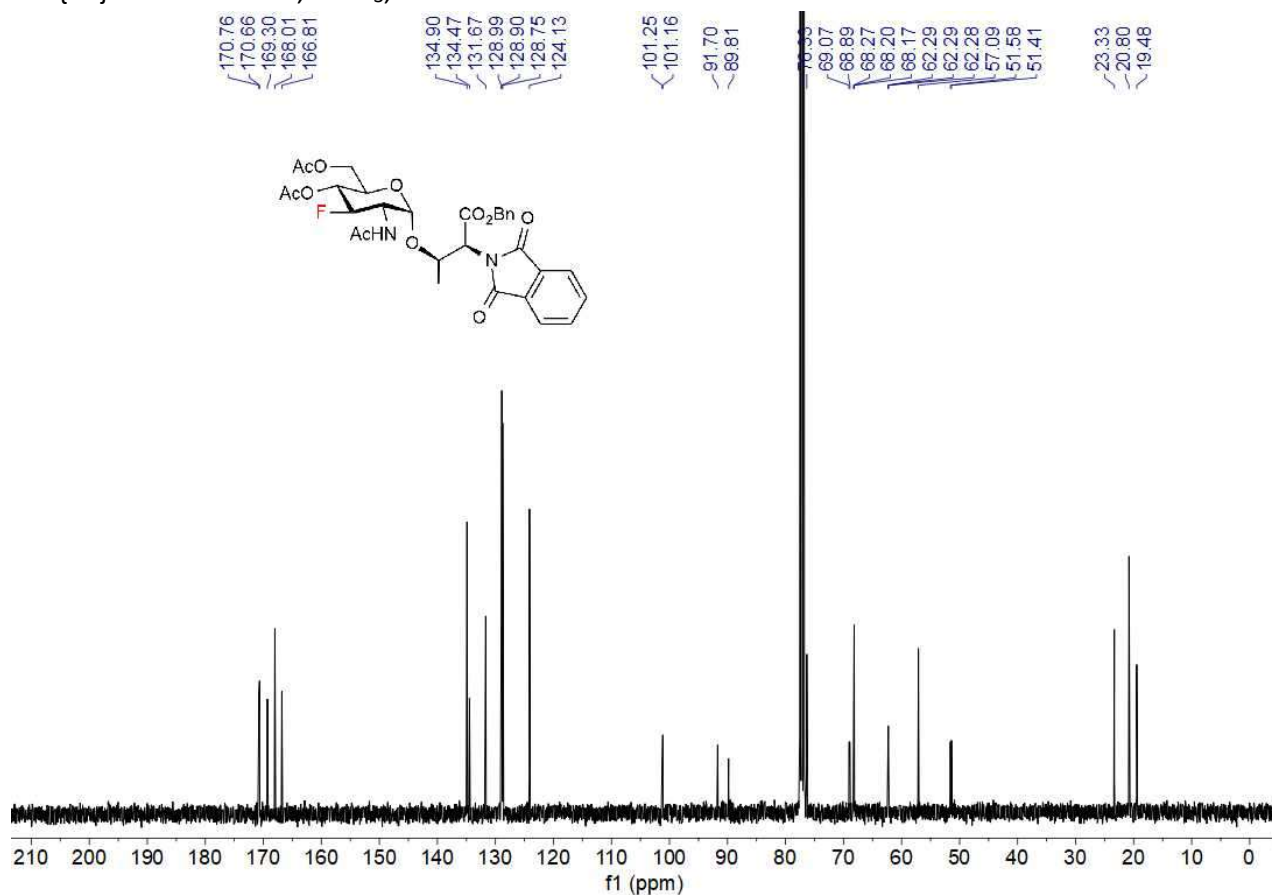


# **NMR 33**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **33**

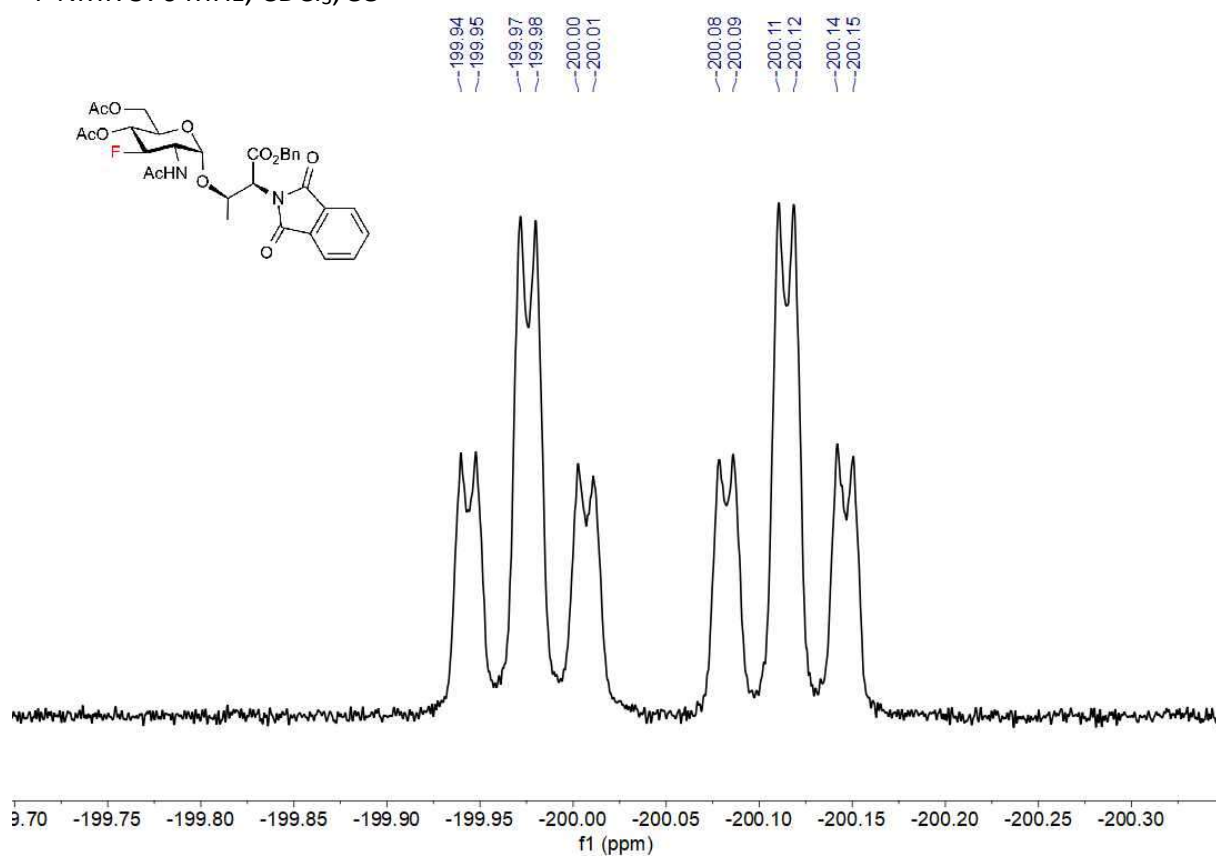


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **33**

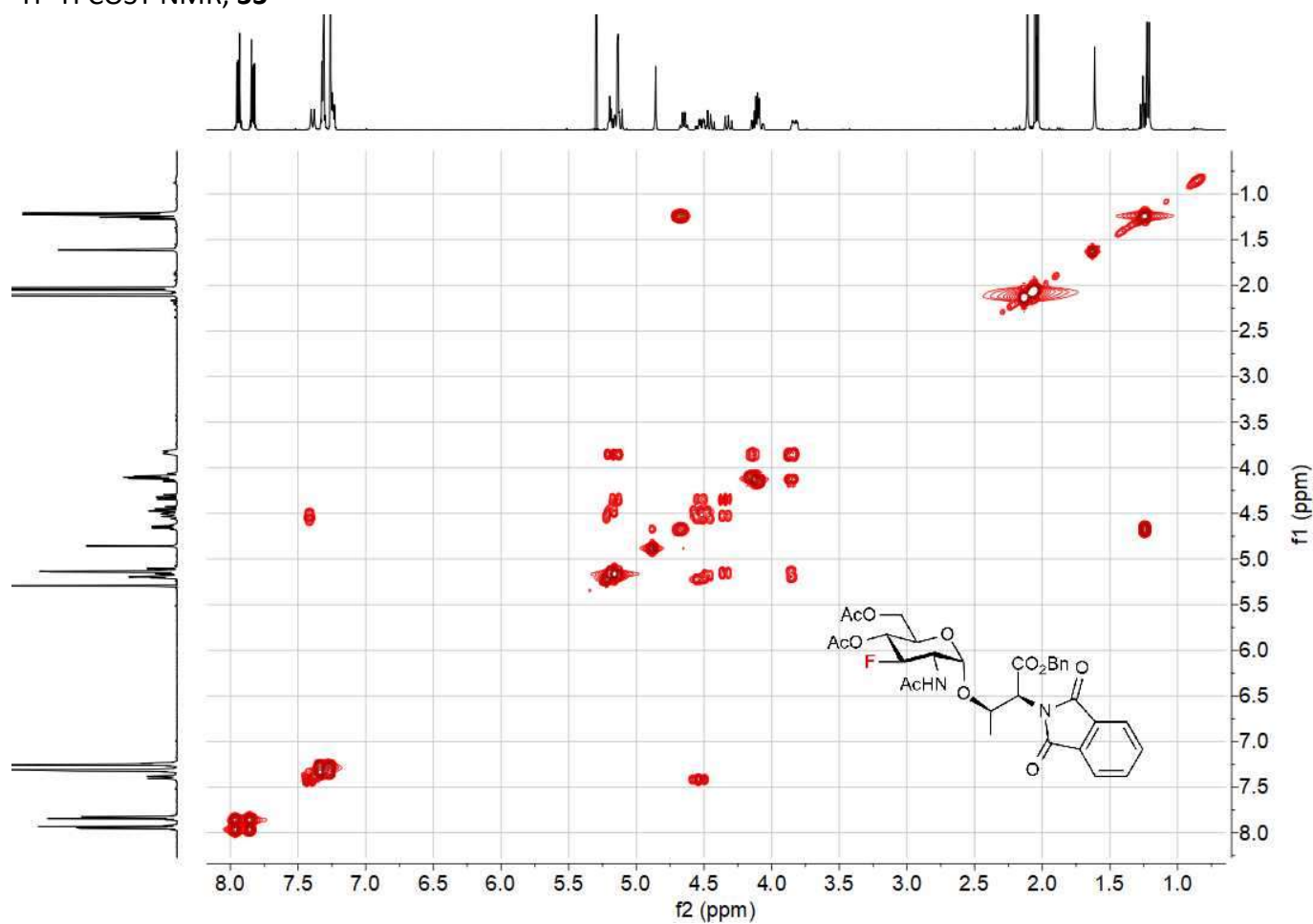




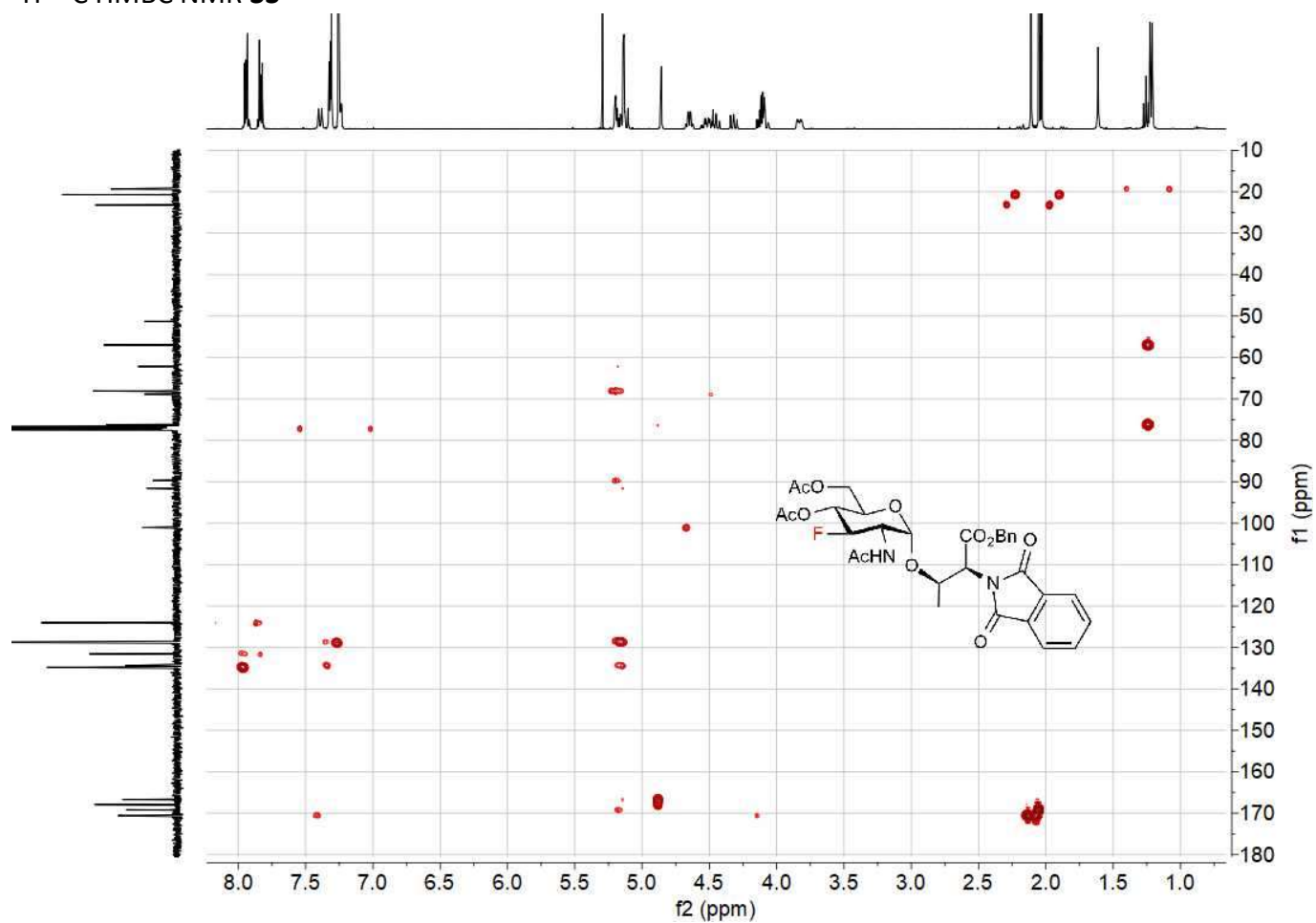
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **33**



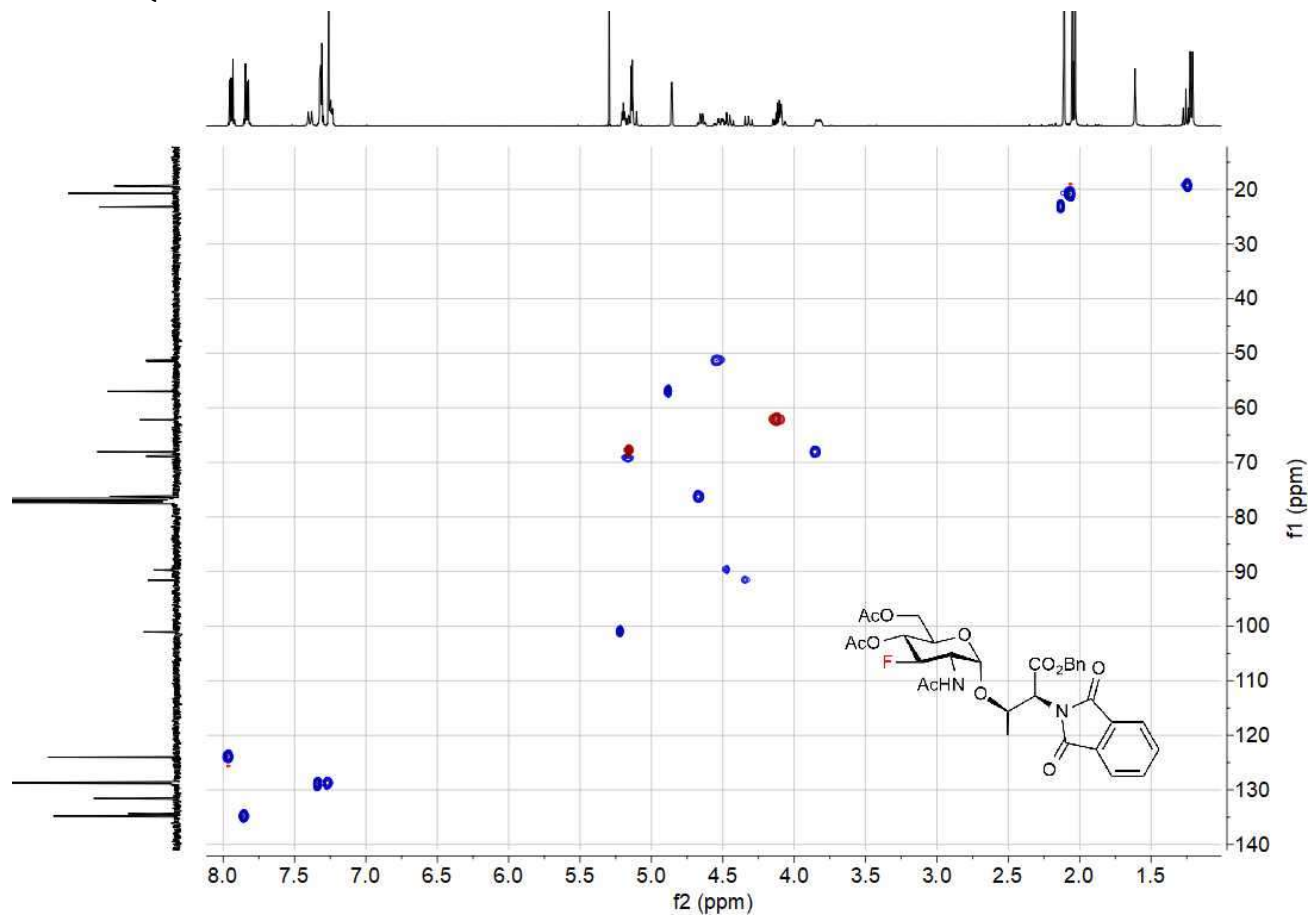
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **33**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR 33

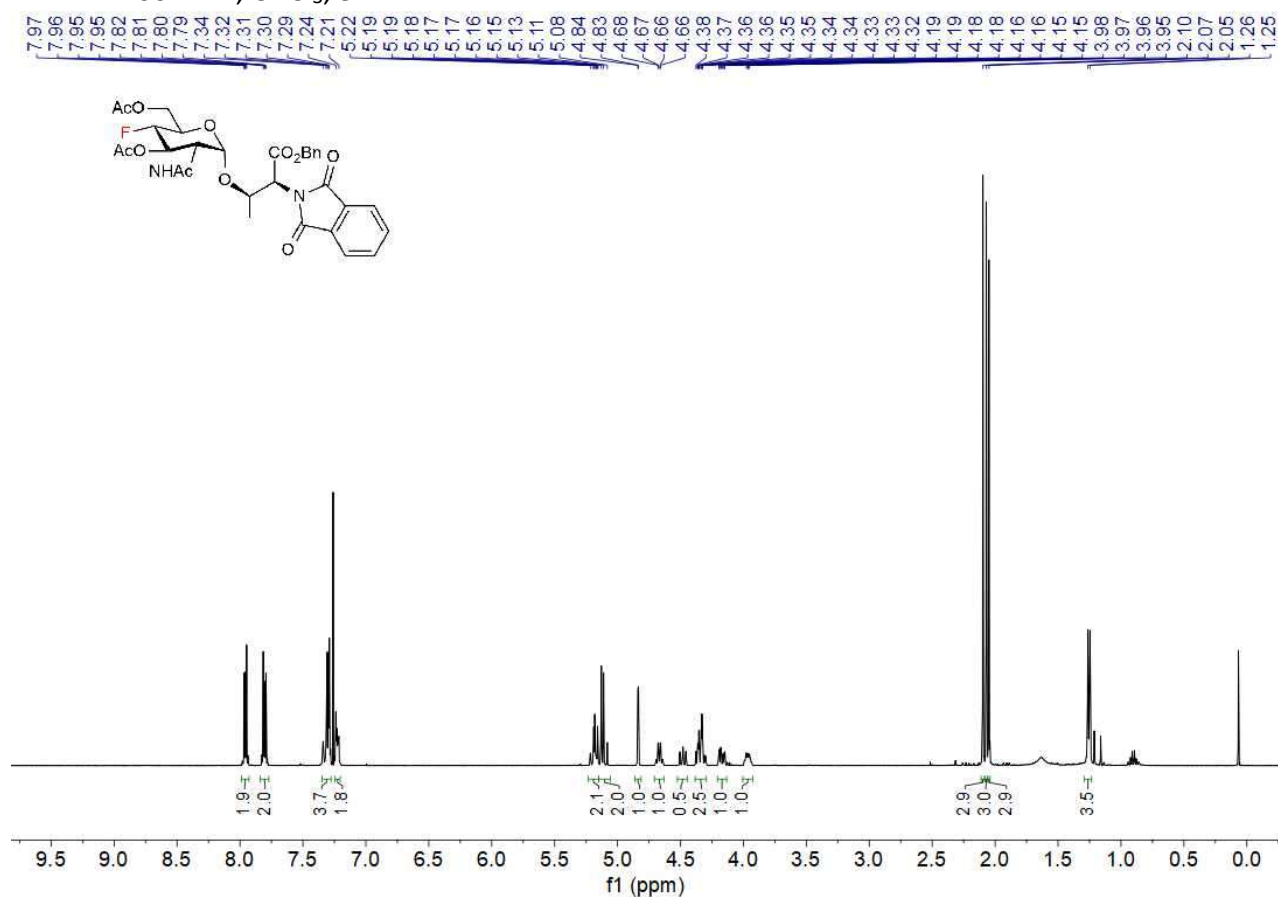


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR 33

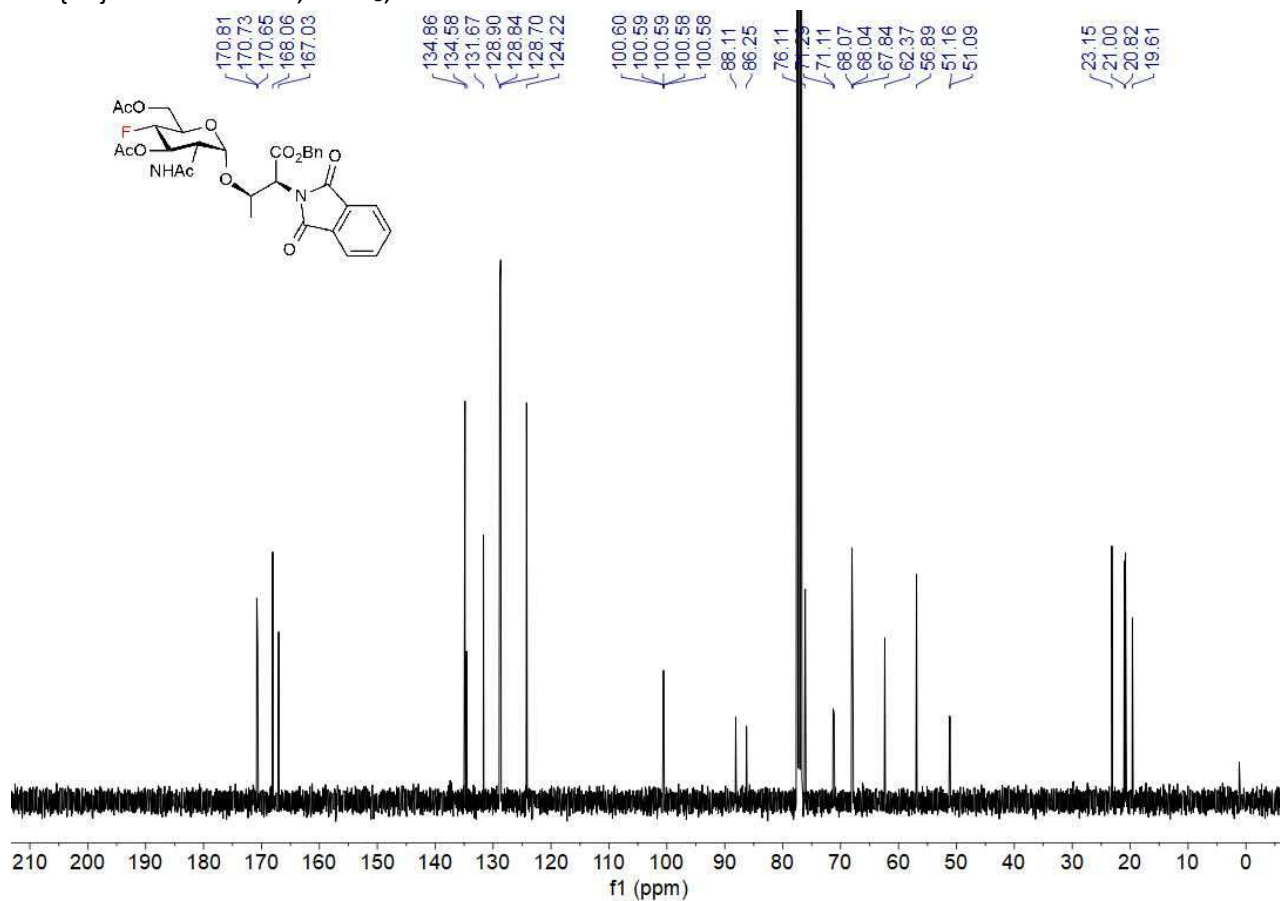


# **NMR 34**

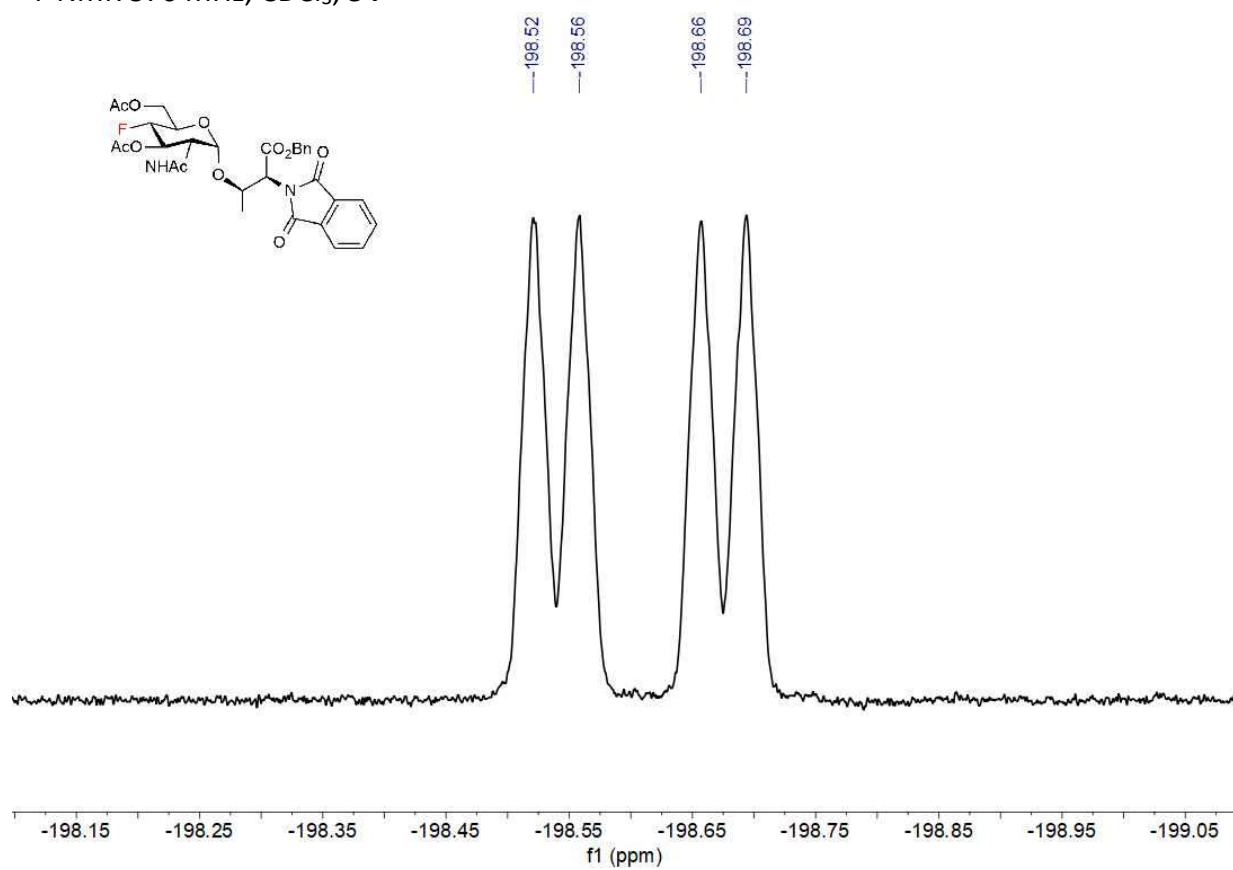
**<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, 34**



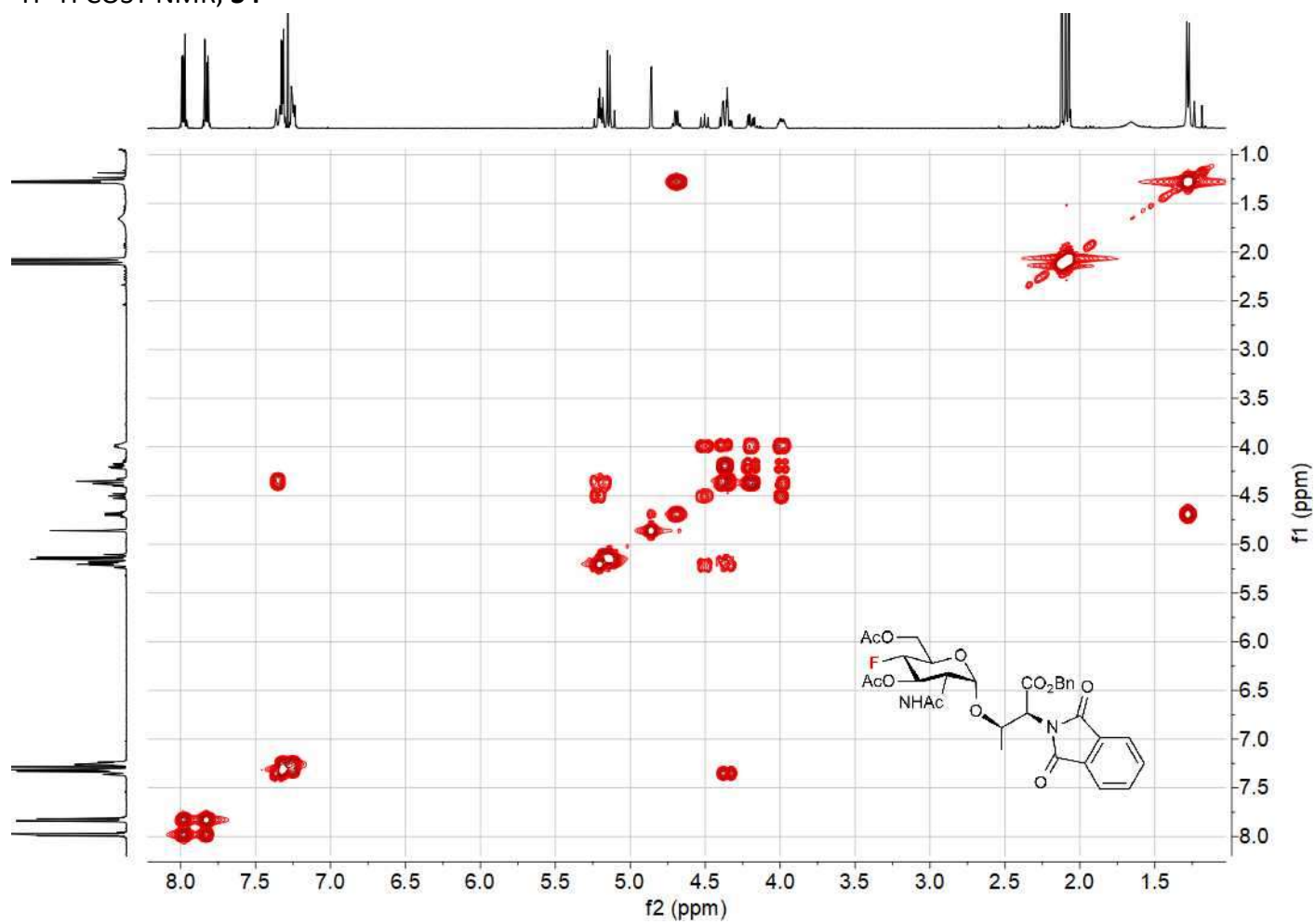
**<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, 34**



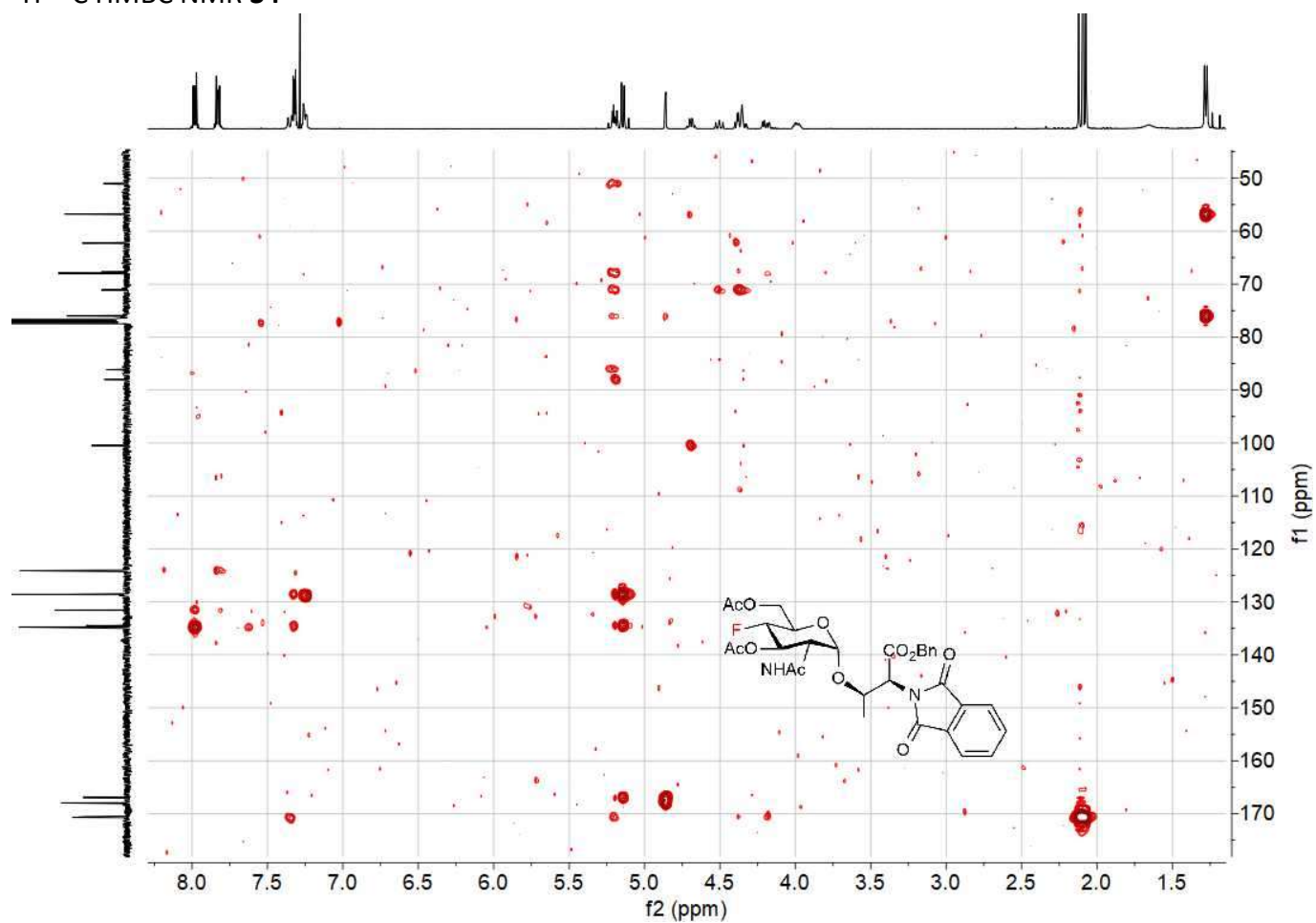
$^{19}\text{F}$  NMR 376 MHz,  $\text{CDCl}_3$ , **34**



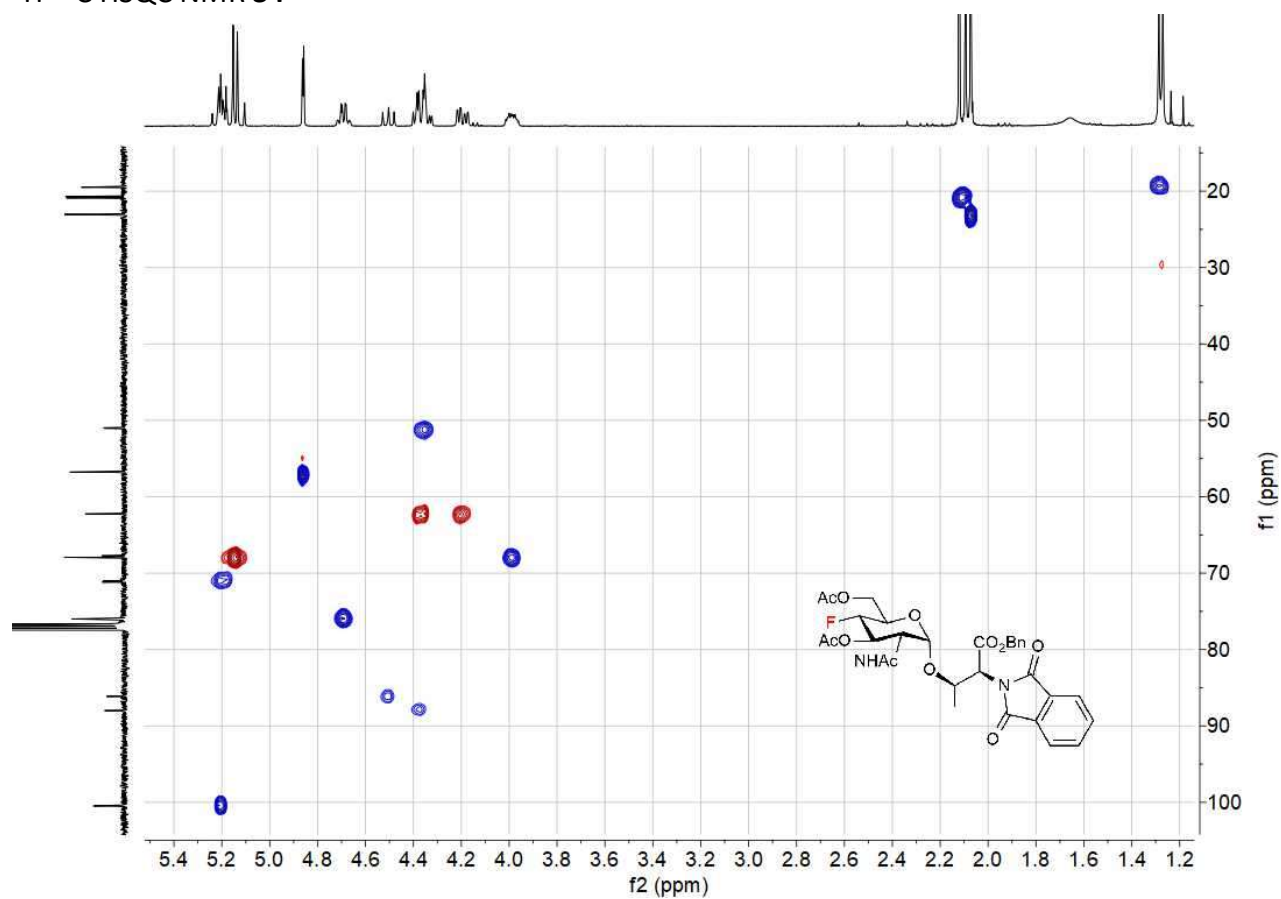
$^1\text{H}$ - $^1\text{H}$  COSY NMR, **34**



$^1\text{H}$ - $^{13}\text{C}$  HMBC NMR **34**

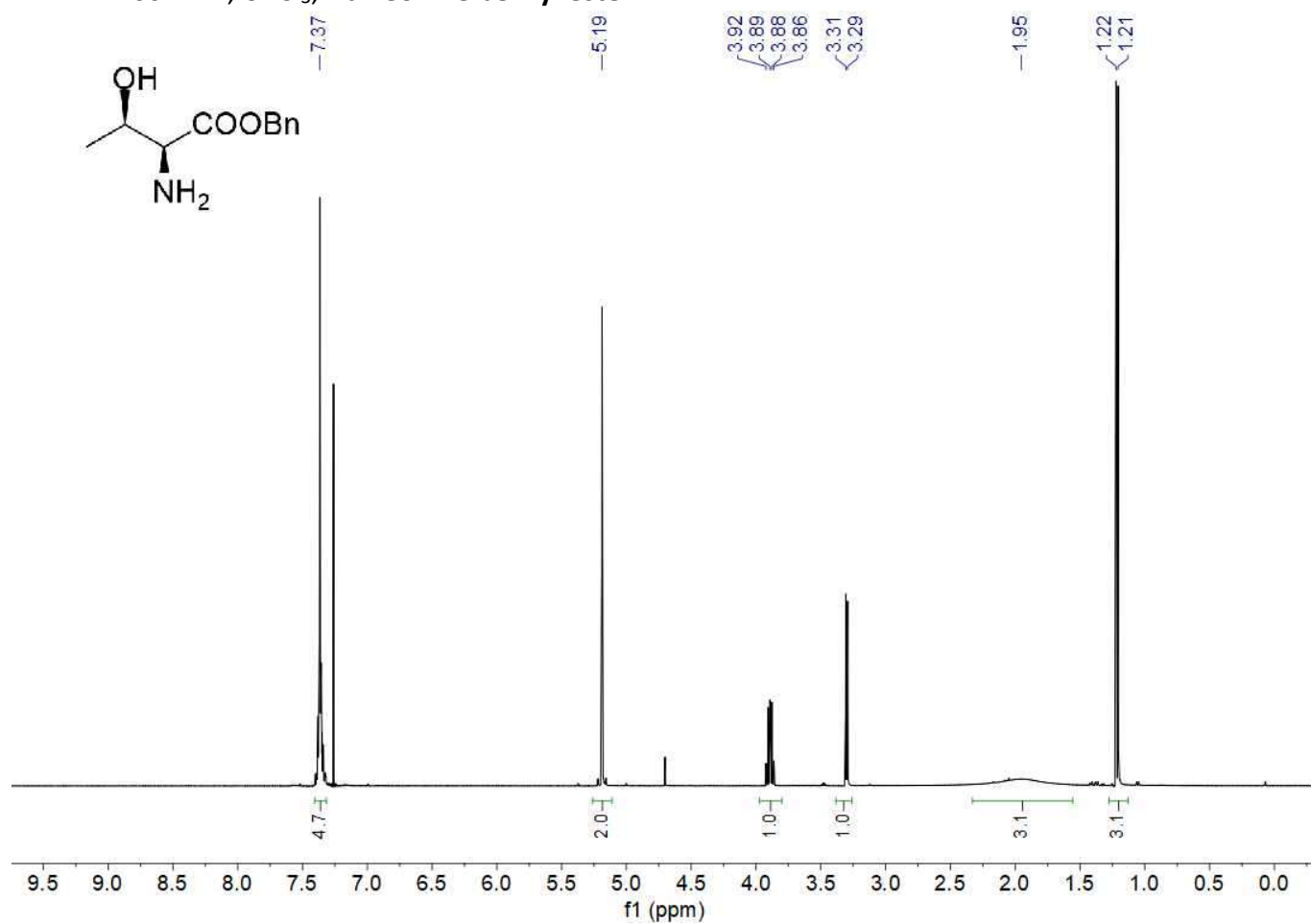


$^1\text{H}$ - $^{13}\text{C}$  HSQC NMR **34**



# NMR L-threonine benzyl ester

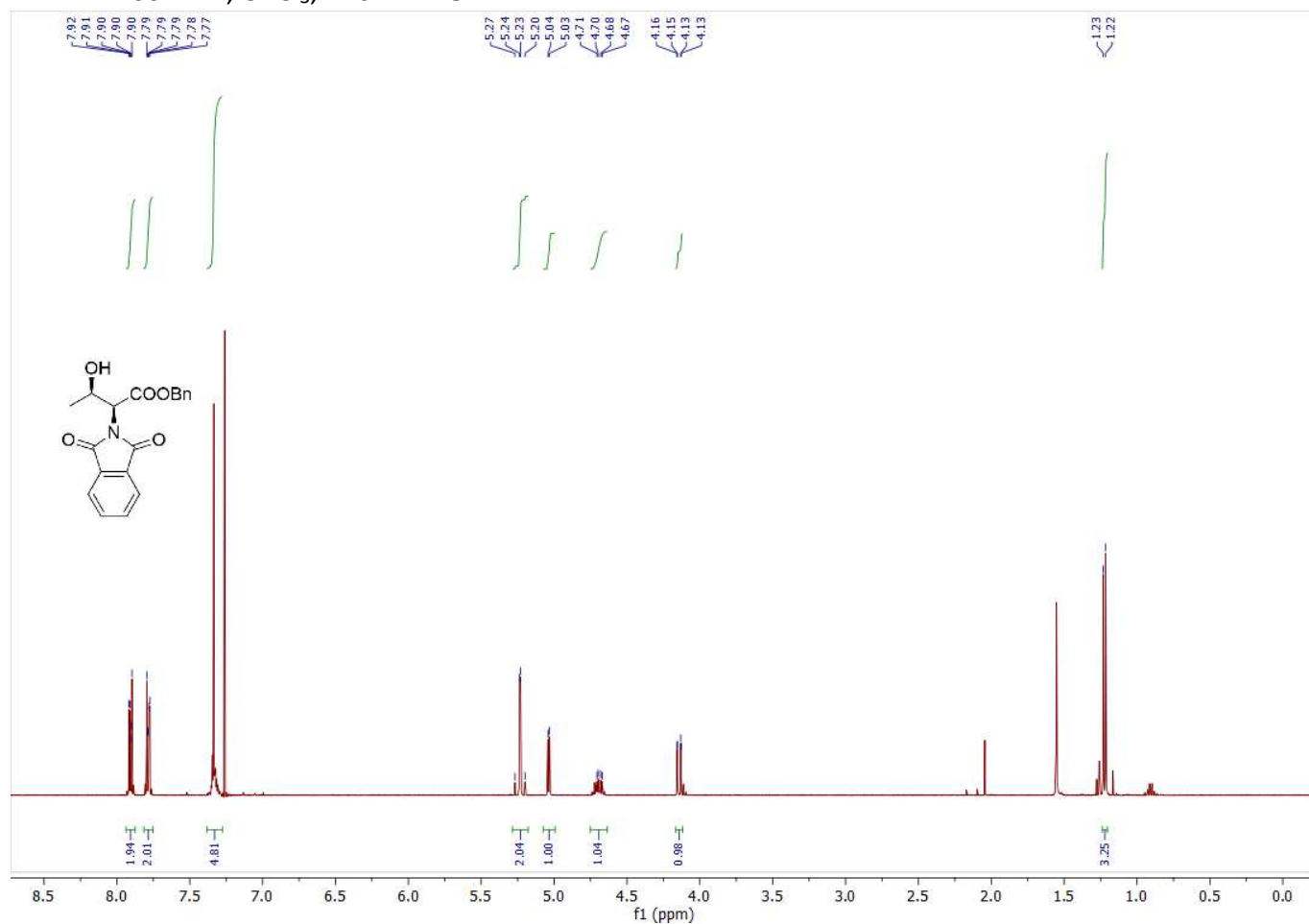
$^1\text{H}$  NMR 400 MHz,  $\text{CDCl}_3$ , L-threonine benzyl ester



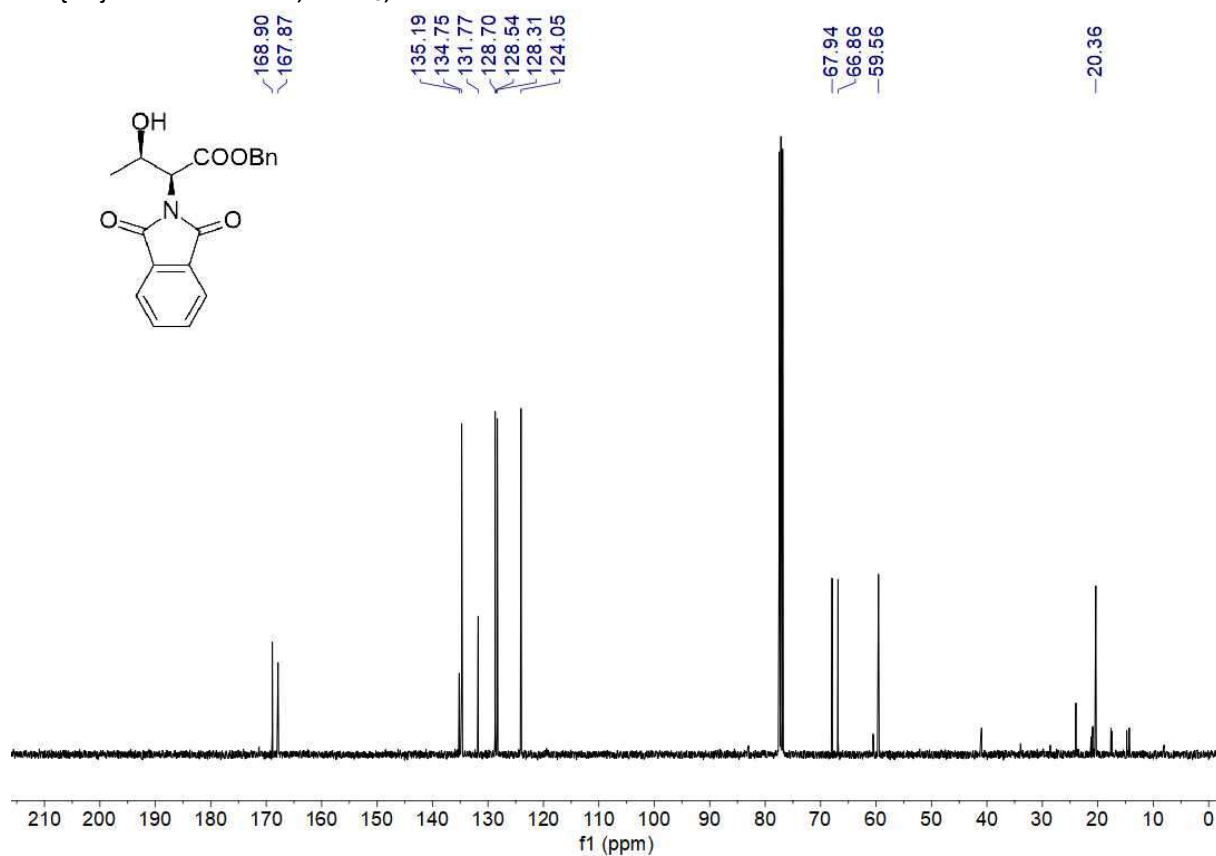


# **NMR Phth-Thr-OBn**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **Phth-Thr-OBn**

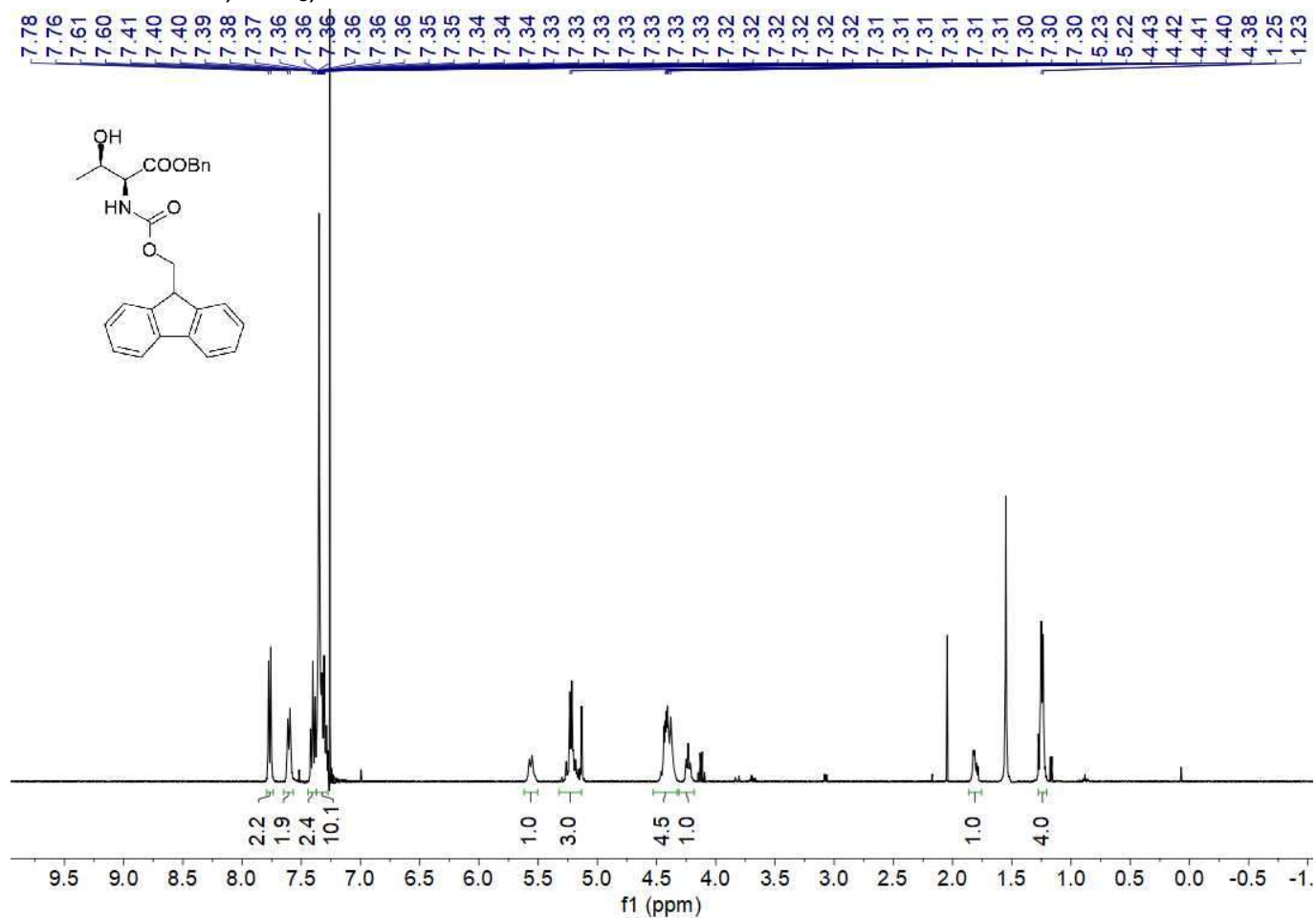


<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub>, **Phth-Thr-OBn**



# **NMR Fmoc-Thr-OBn**

<sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub>, **Fmoc-Thr-OBn**



<sup>13</sup>C {<sup>1</sup>H} NMR 100MHz, CDCl<sub>3</sub> **Fmoc-Thr-OBn**

