

Supplementary Information

Regiodivergent Glycosylations of 6-deoxy-Erythronolide B and Oleandomycin-Derived Macrolides Enabled by Chiral Acid Catalysis

Jia-Hui Tay, Alonso J. Argüelles, Matthew D. DeMars II, Paul M. Zimmerman,* David H. Sherman* and Pavel Nagorny.*

Chemistry Department and Life Sciences Institute, University of Michigan, Ann Arbor 48109 USA.

nagorny@umich.edu

Part II – NMR Spectra of Glycosylation Products (^1H , ^{13}C , ^1H - ^{13}C -HSQC, ^1H -COSY, ^1H - ^{13}C -HMBC)

Table of Contents

Nomenclature for compound labelling	S 3
6-dEB-C ₃ - α -A (1)	S 4
6-dEB-C ₅ - α -A (2)	S 11
6-dEB-C ₅ - α -A-C ₁₁ - α -A (3)	S 18
6-dEB-C ₁₁ - α -A	S 25
6-dEB-C ₁₁ - β -A (8a)	S 31
6-dEB-C ₃ - α -B (8b)	S 37
6-dEB-C ₅ - α -B (8c)	S 43
6-dEB-C ₅ - β -B	S 50
7-C ₅ - α -A (8d)	S 56
7-C ₅ - β -A	S 62

X-2- α -A (8e)	S 68
X-2- β -A	S 74
7-C ₃ - α -A (8f)	S 80
7-C ₃ - β -A	S 86
7-C ₃ - β -B (8g)	S 92
7-C ₃ - α -B	S 98
7-C ₁₁ - α -B (8h)	S 104
7-C ₅ - α -B (8i)	S 110
7-C ₅ - β -B	S 116
X-2- α -B (8j)	S 122
X-2- β -B	S 128
7-C ₃ - α -C (8k)	S 134
7-C ₃ - β -C	S 140
7-C ₅ - α -C	S 146
7-C ₅ - β -C	S 152
X-2- α -C	S 158
6-dEB-C ₅ - β -A	S 164

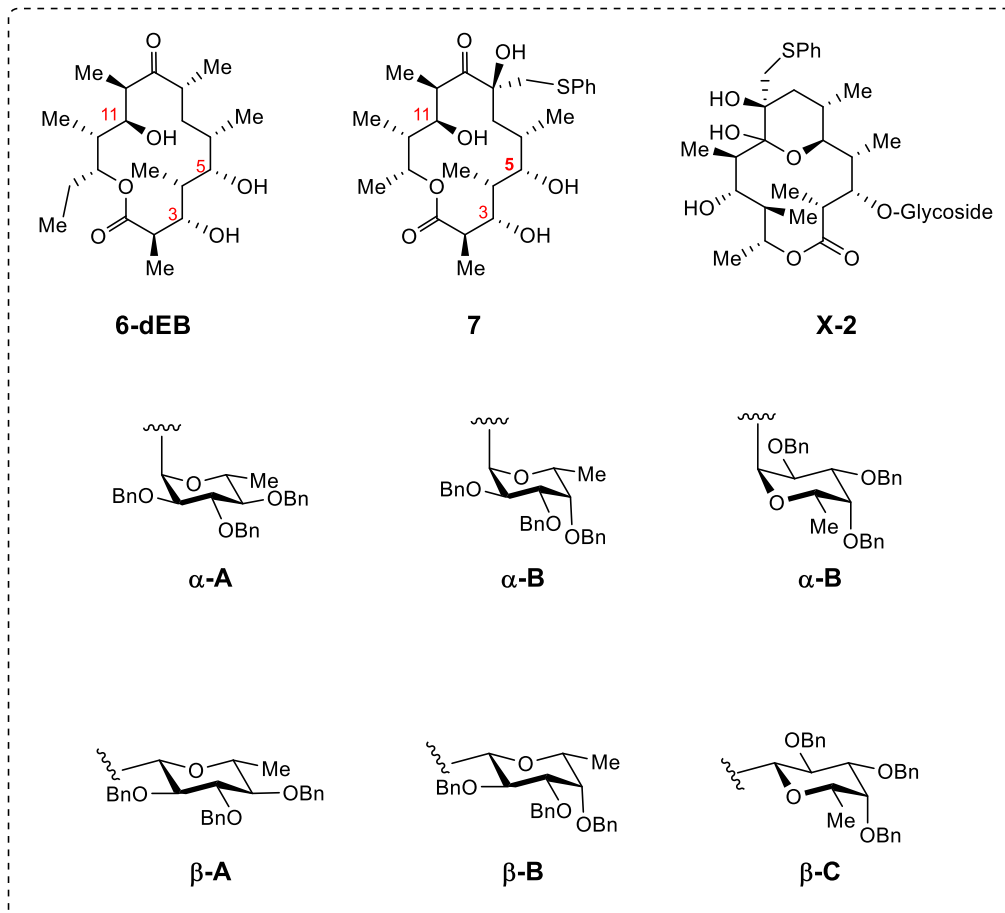
Nomenclature for compound labelling:

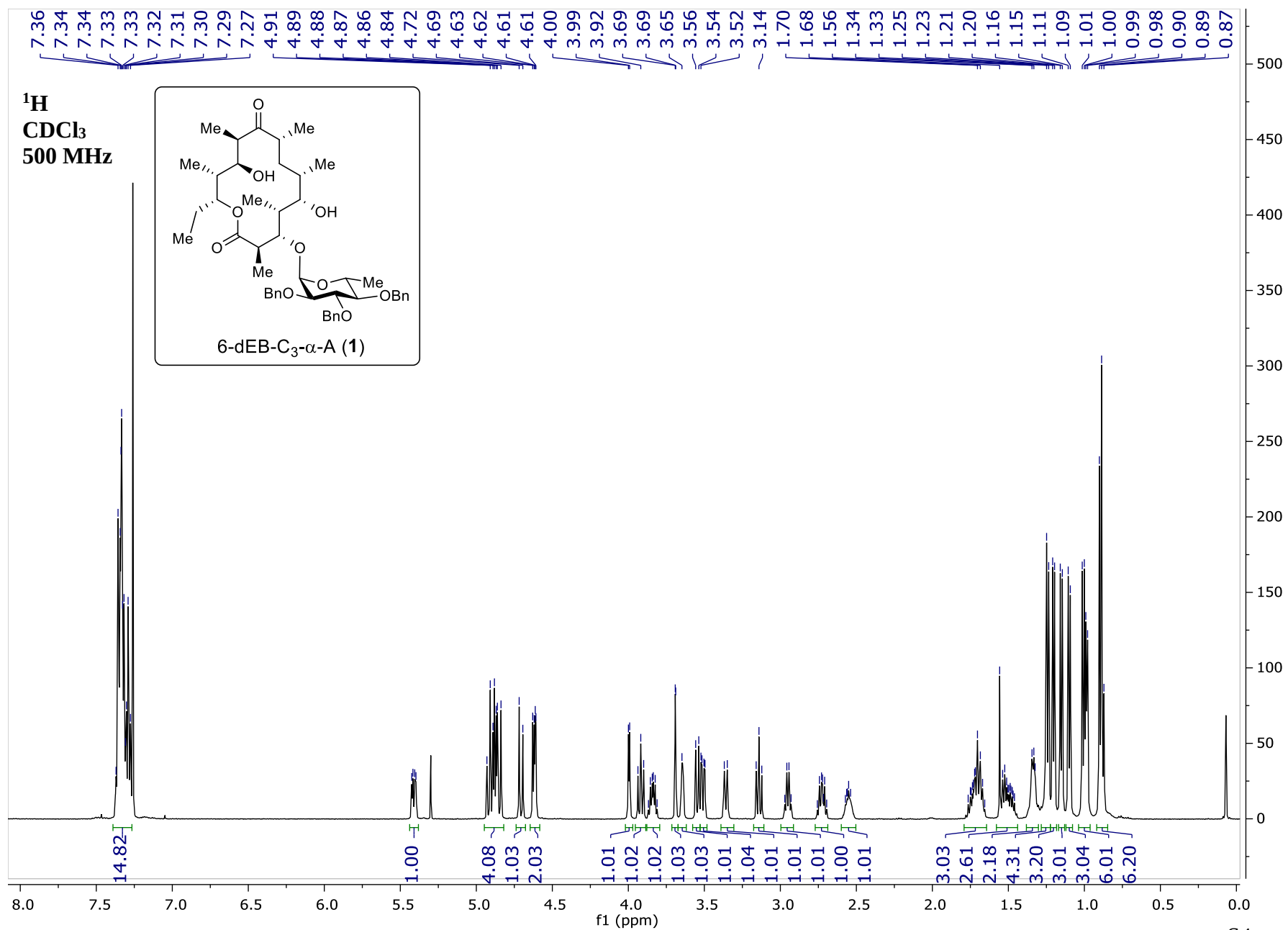
6-dEB-C₃- α -A

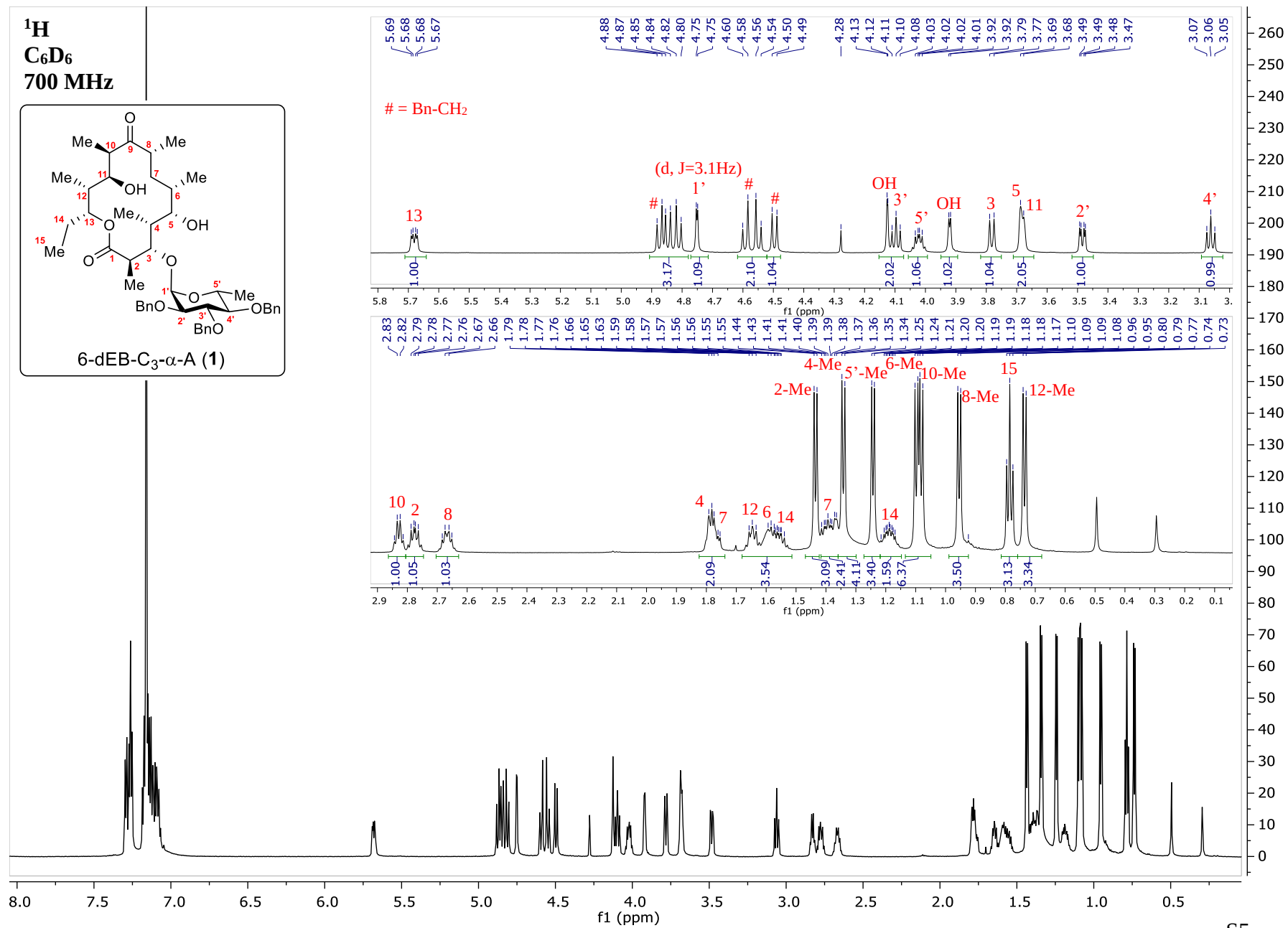
6-dEB-C₃- α -A: structure of macrolide (**6-dEB**, **7**, or **X-2**)

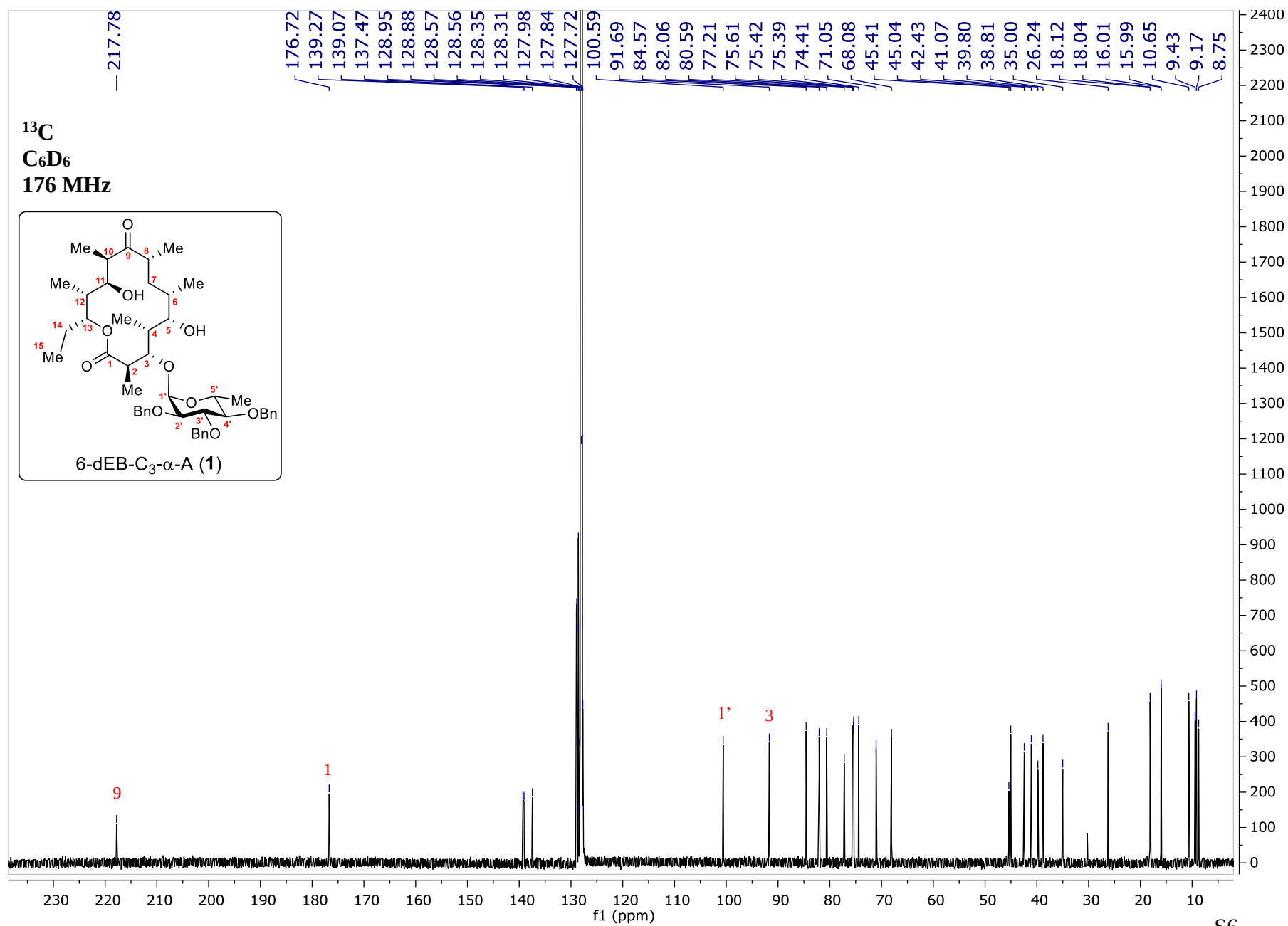
6-dEB-**C₃**- α -A: position of glycoside (C₃, C₅ or C₁₁)

6-dEB-C₃- **α -A**: stereochemistry and structure of glycoside (α or β ; A, B or C)

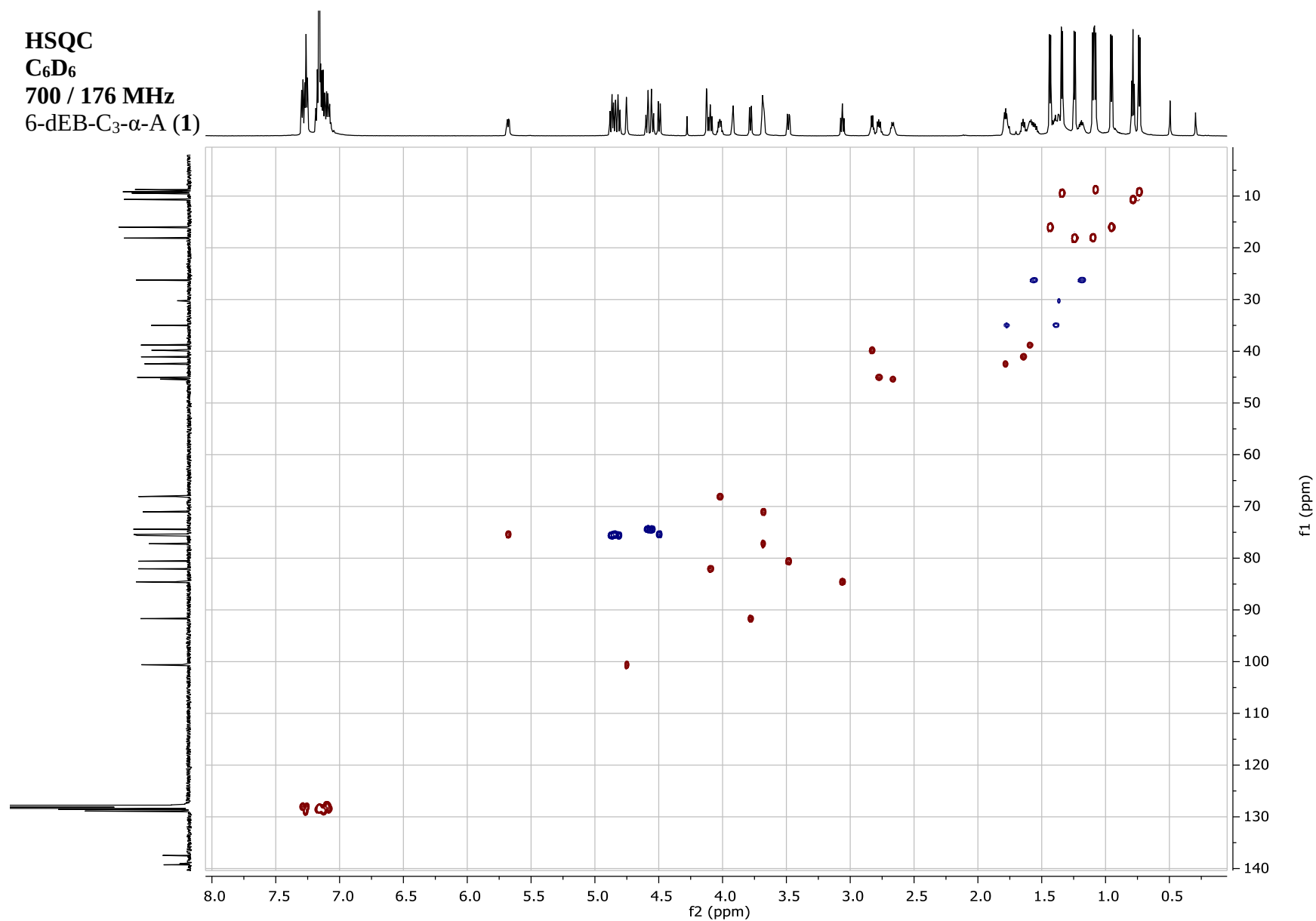








HSQC
C₆D₆
700 / 176 MHz
6-dEB-C₃- α -A (1)

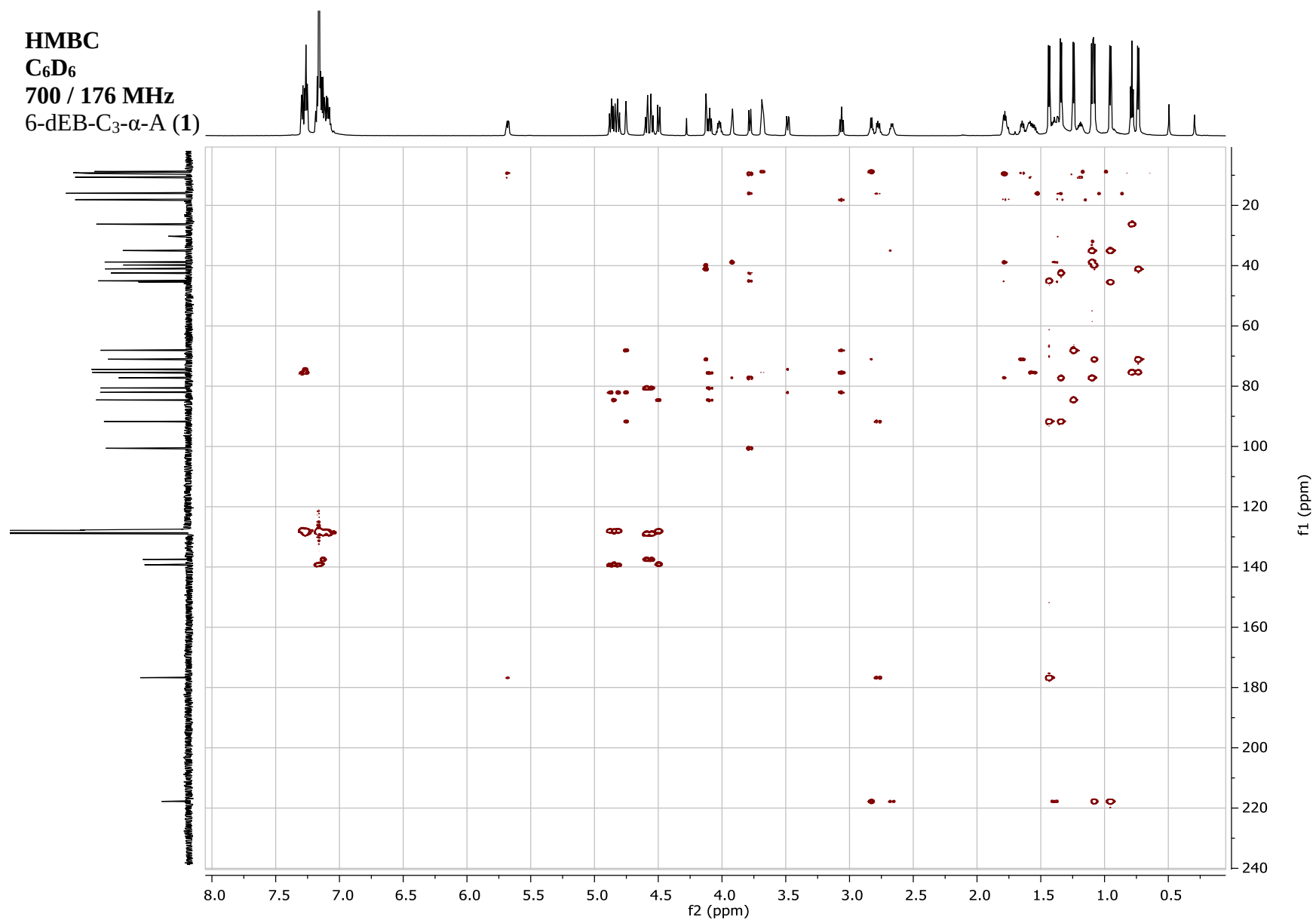


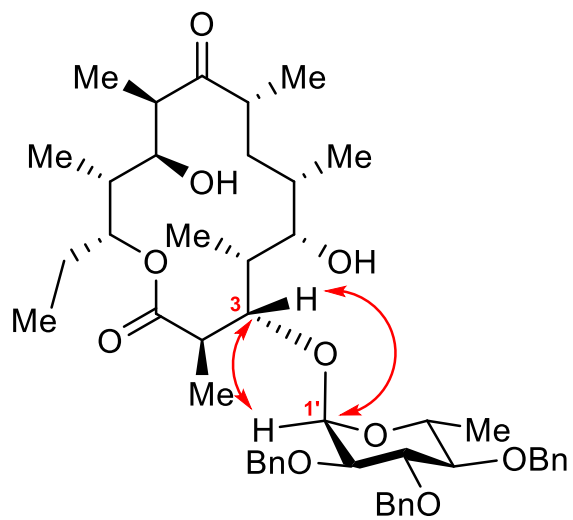
COSY
C₆D₆
700 MHz
6-dEB-C₃-α-A (1)

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

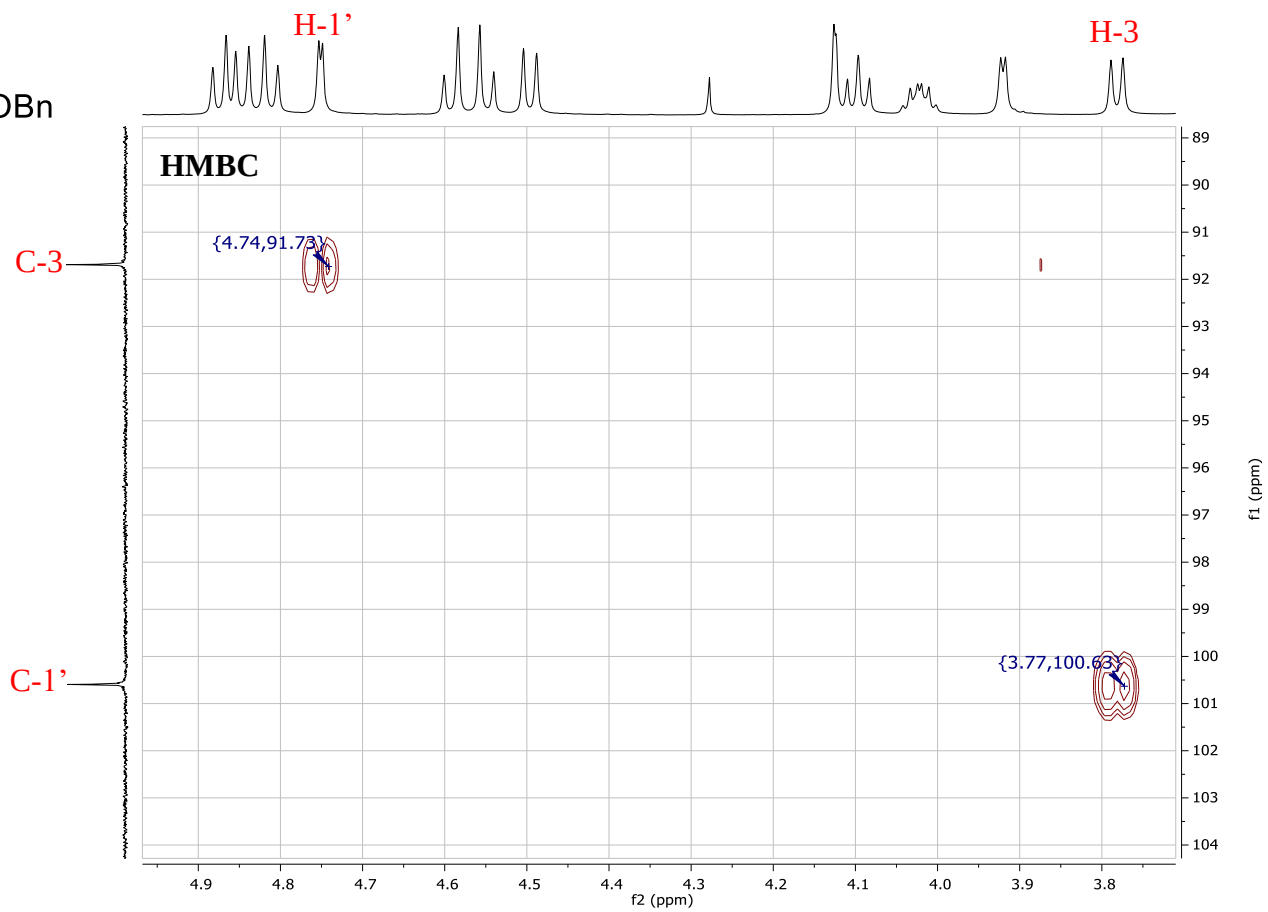
f2 (ppm)

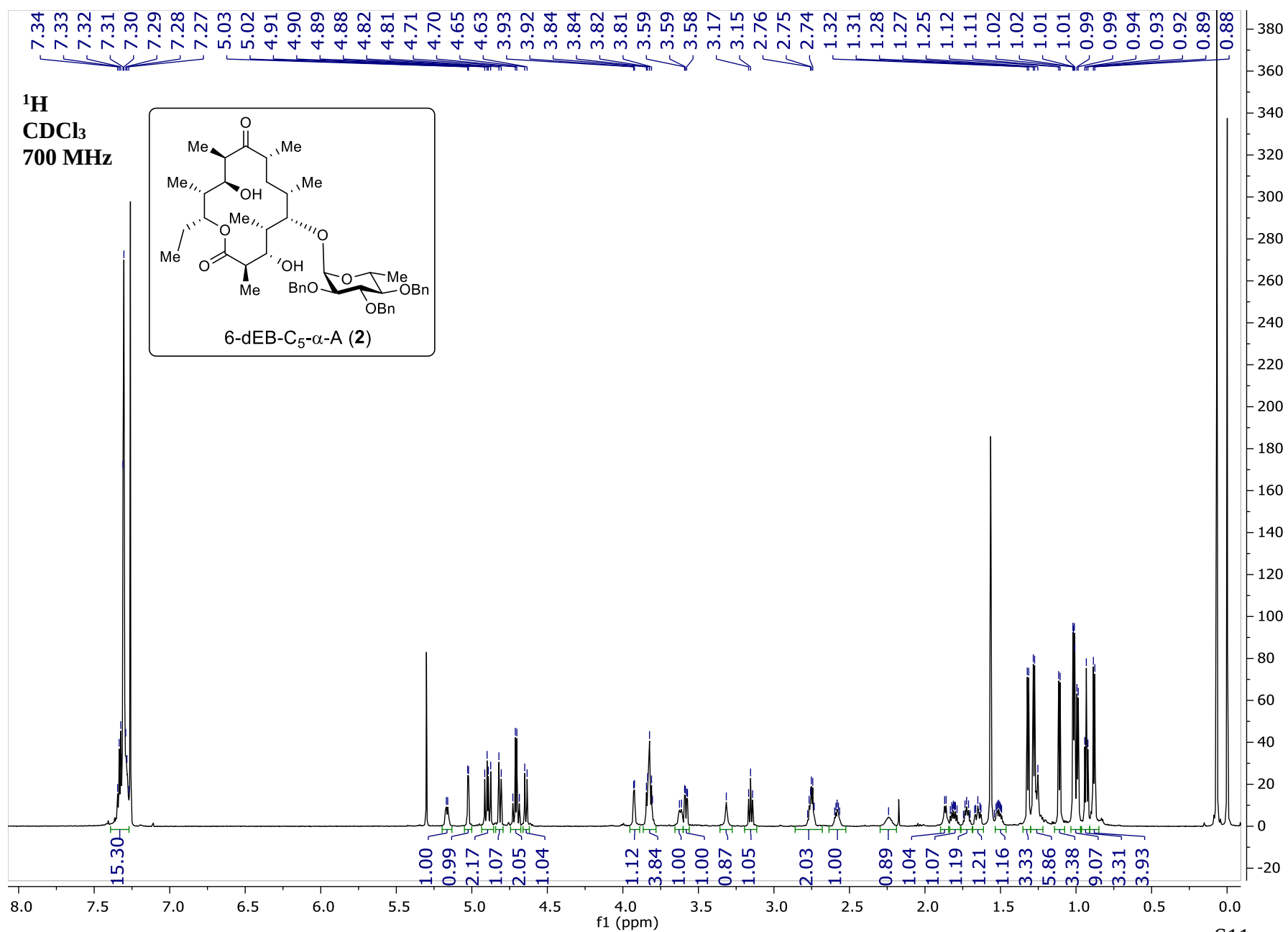
HMBC
C₆D₆
700 / 176 MHz
6-dEB-C₃- α -A (1)

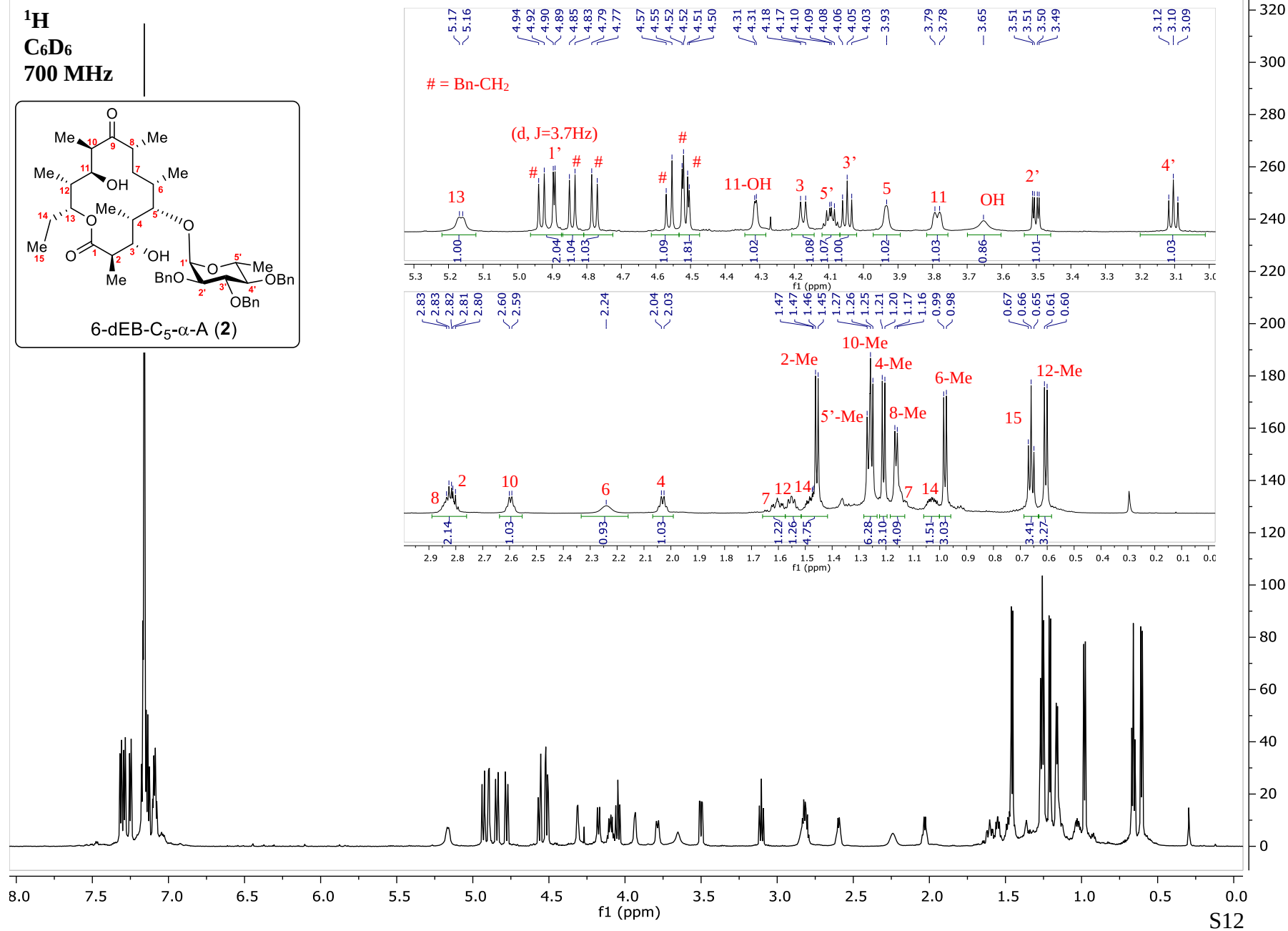


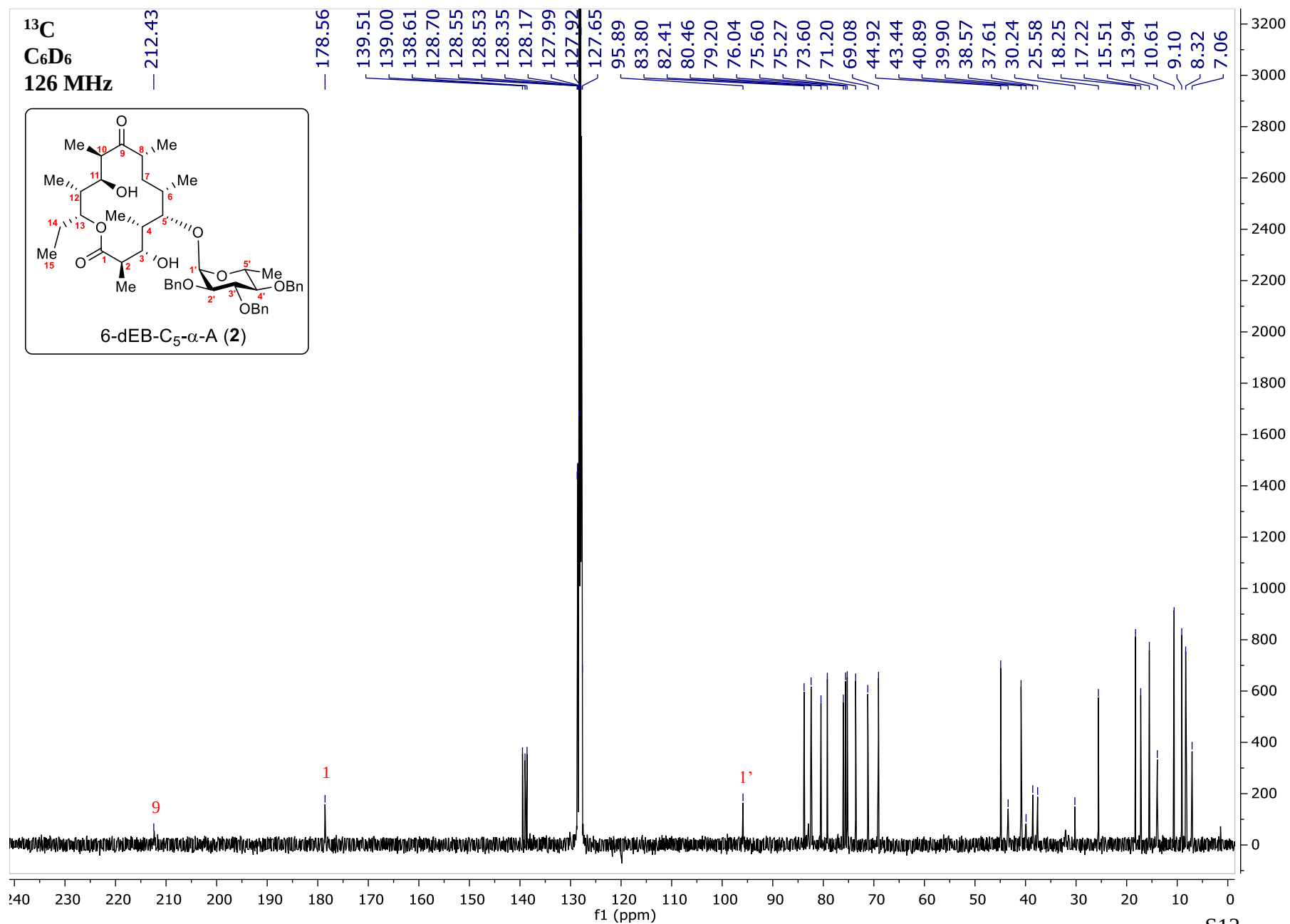


6-dEB-C₃-α-A (1)

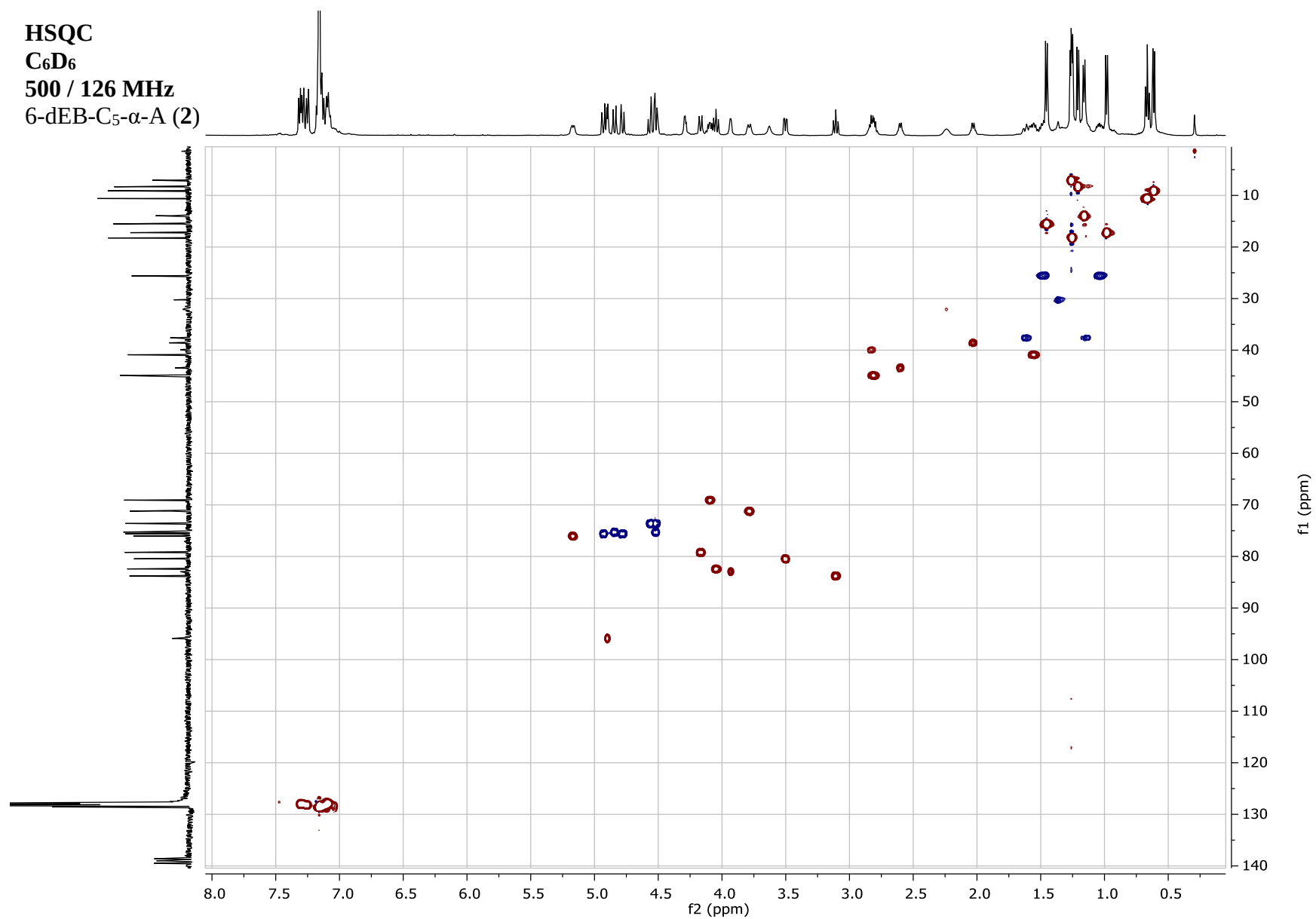




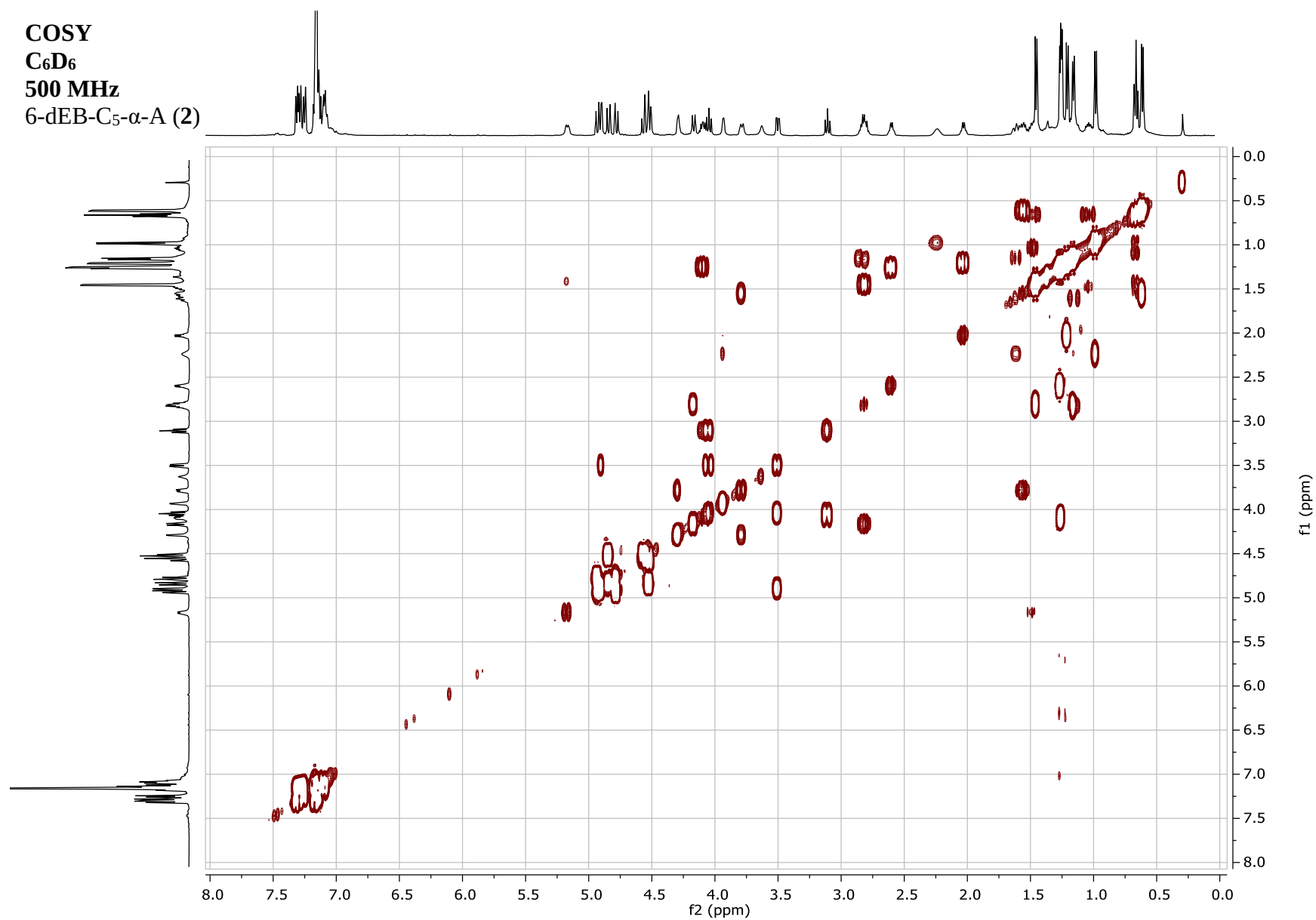




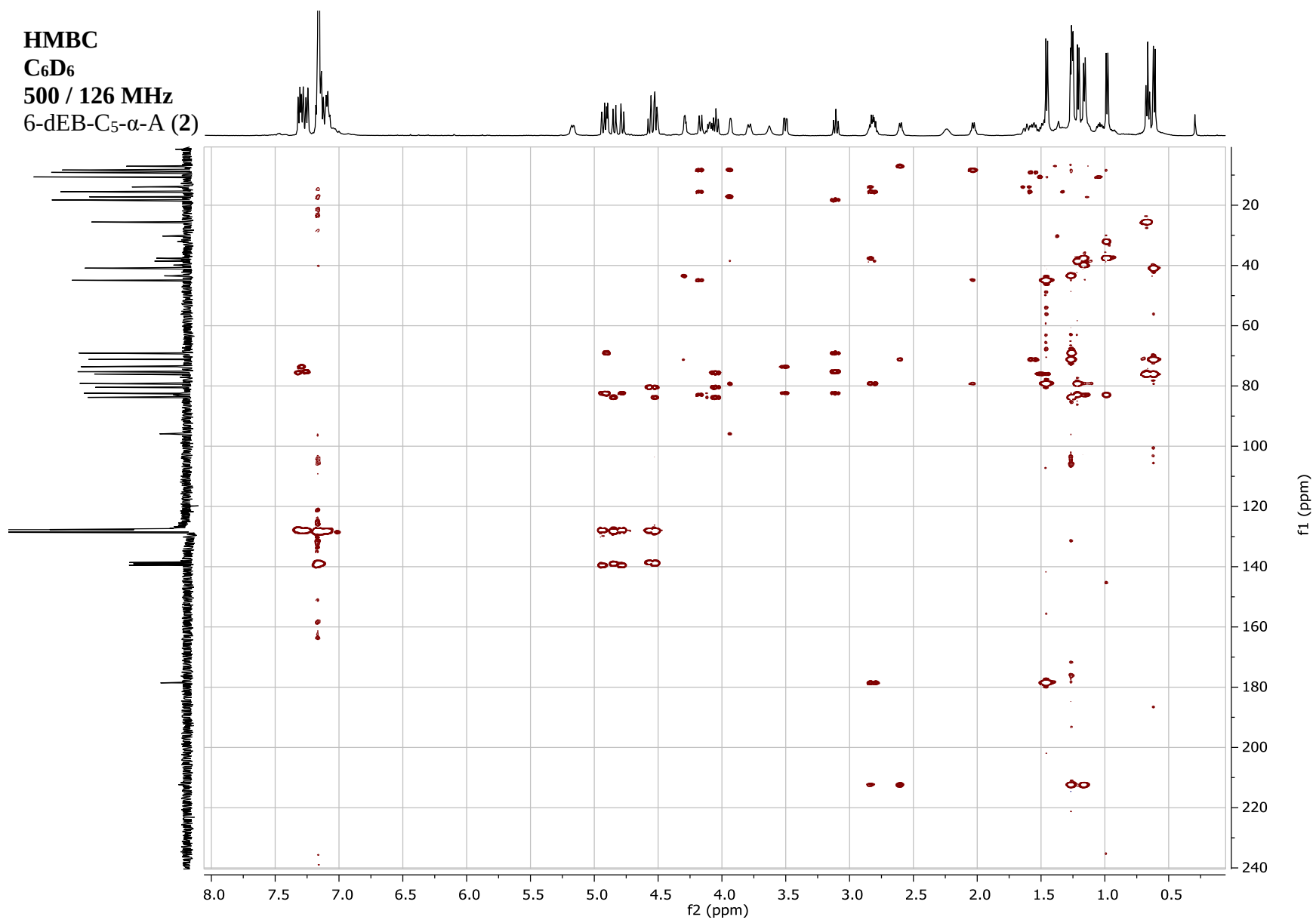
HSQC
C₆D₆
500 / 126 MHz
6-dEB-C₅- α -A (2)

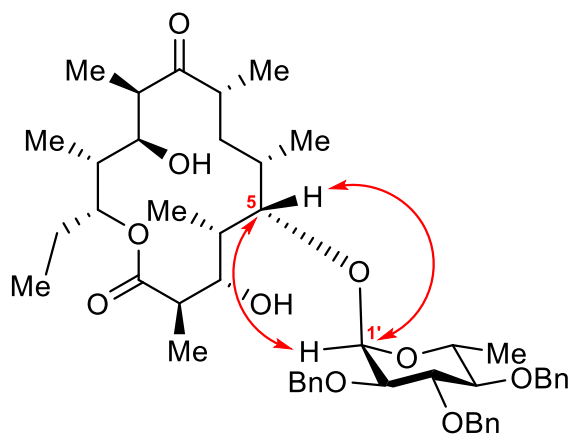


COSY
C₆D₆
500 MHz
6-dEB-C₅- α -A (2)

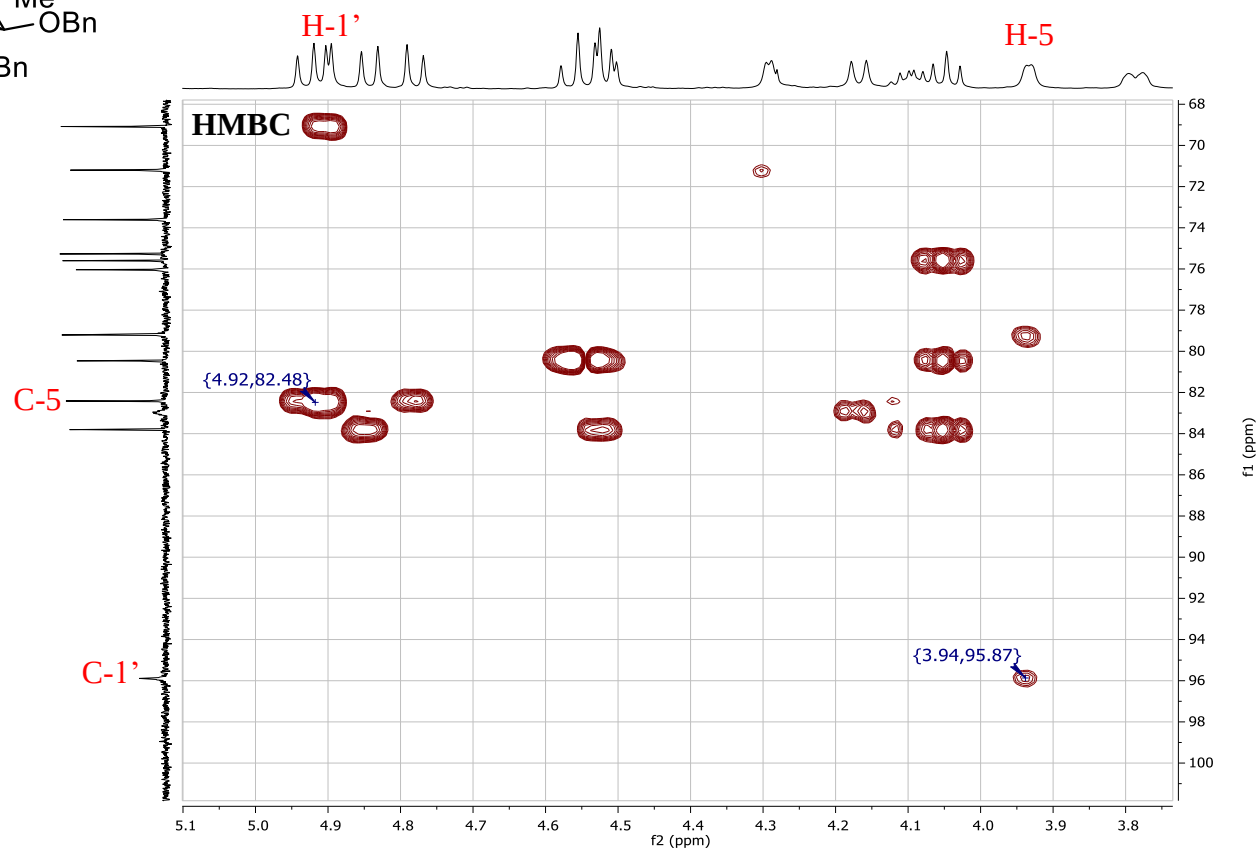


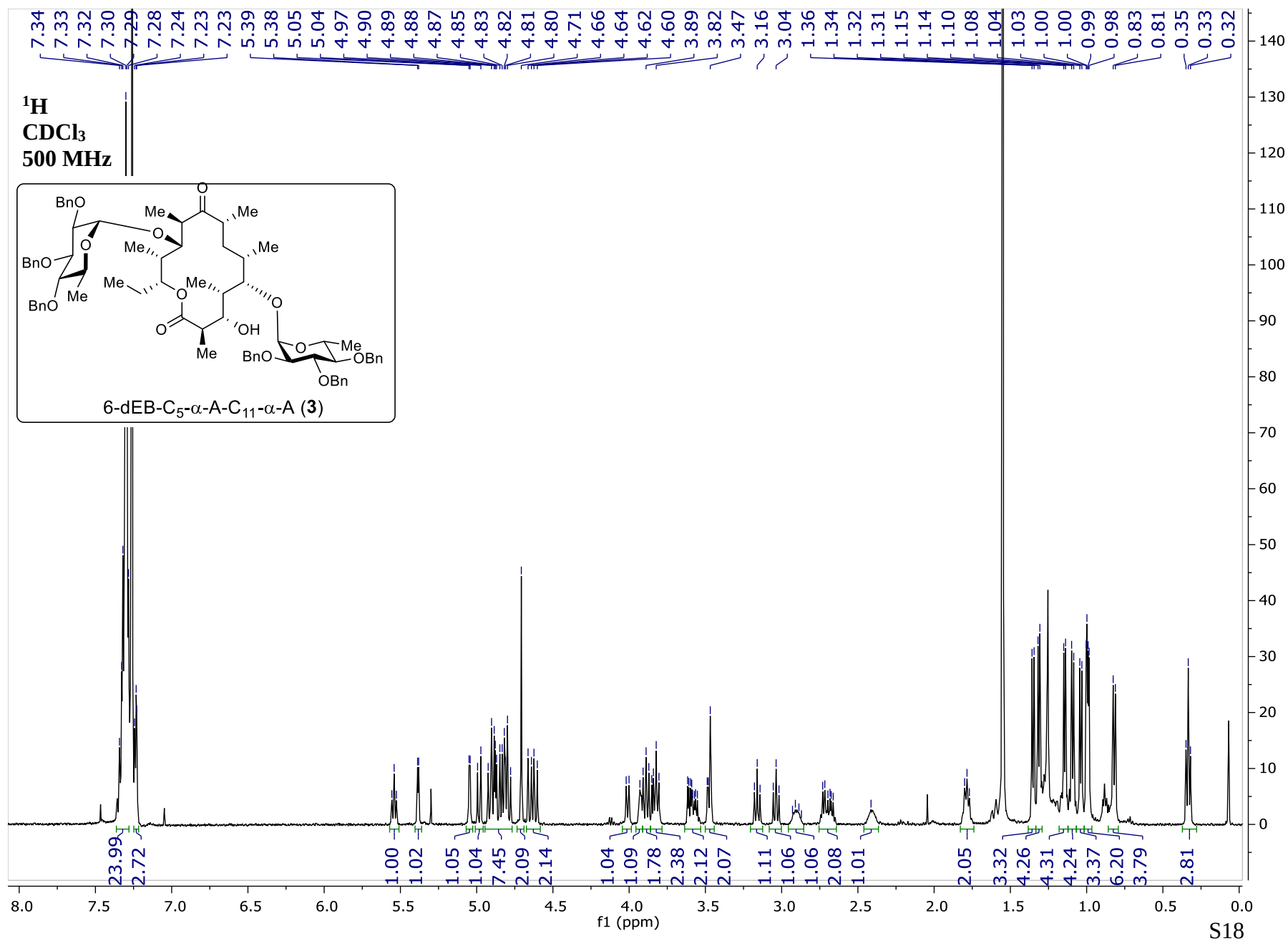
HMBC
C₆D₆
500 / 126 MHz
6-dEB-C₅- α -A (2)



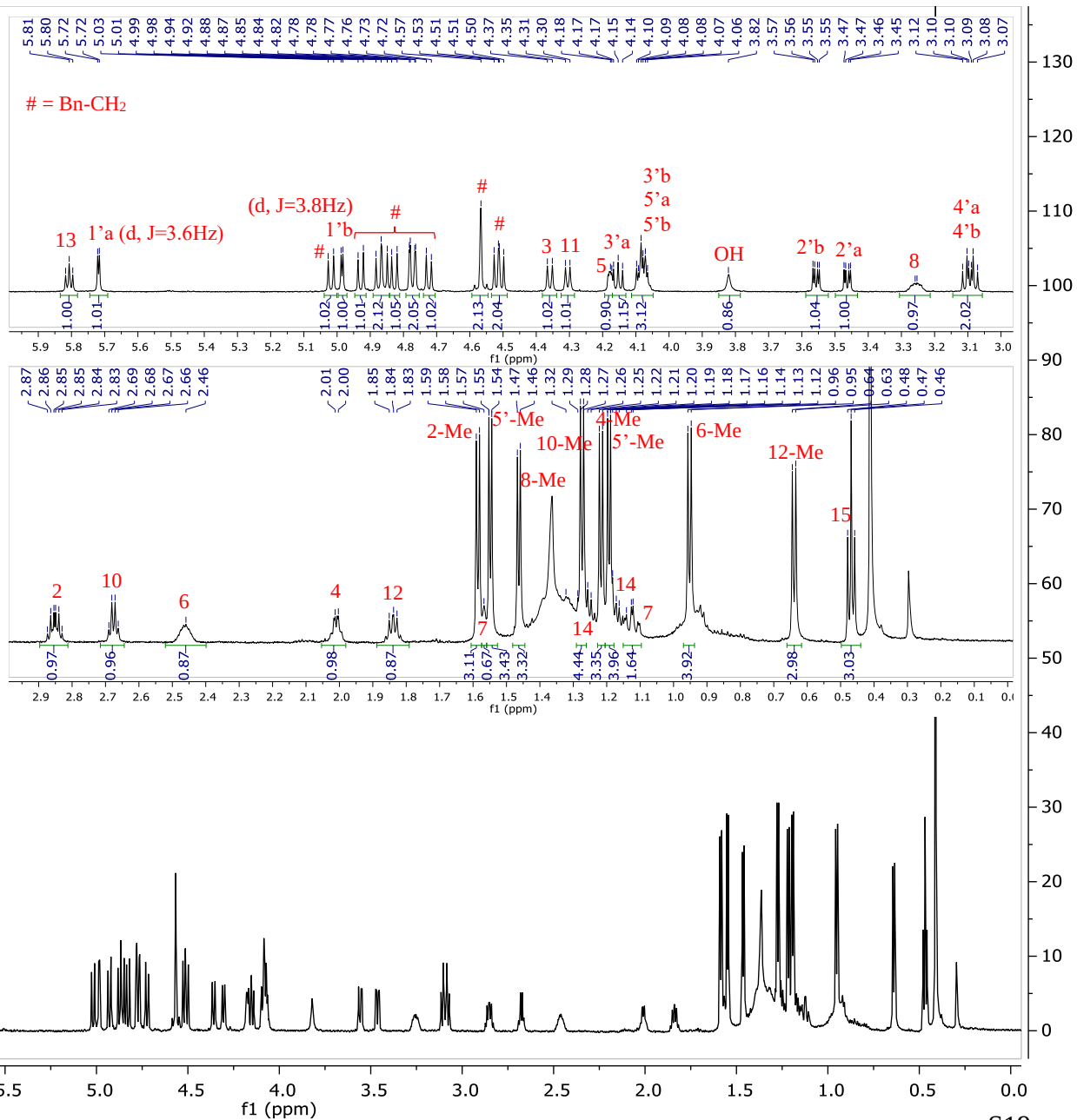
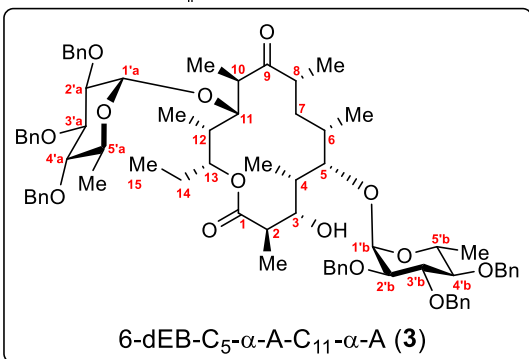


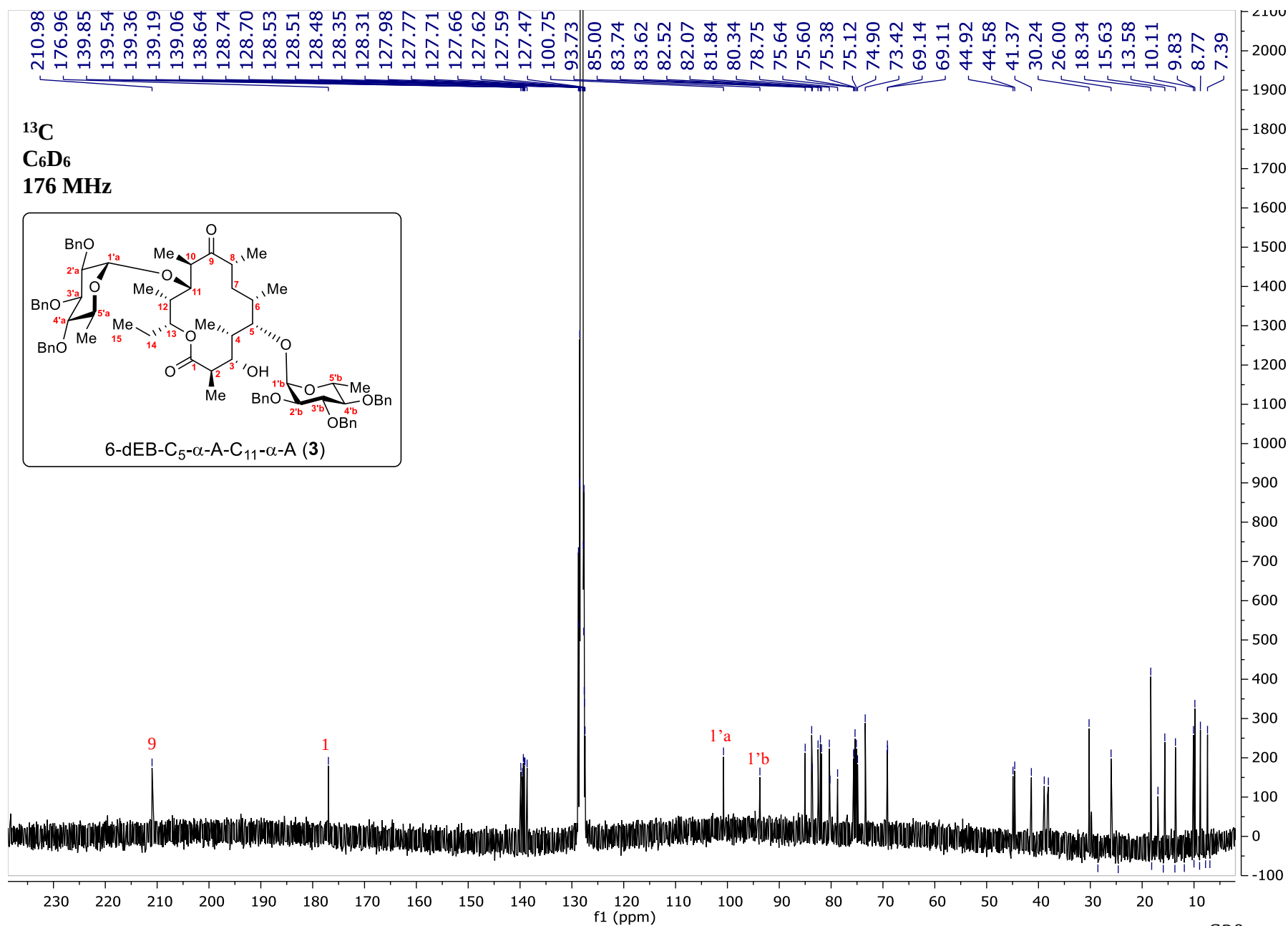
6-dEB-C₅-α-A (2)





¹H
C₆D₆
700 MHz



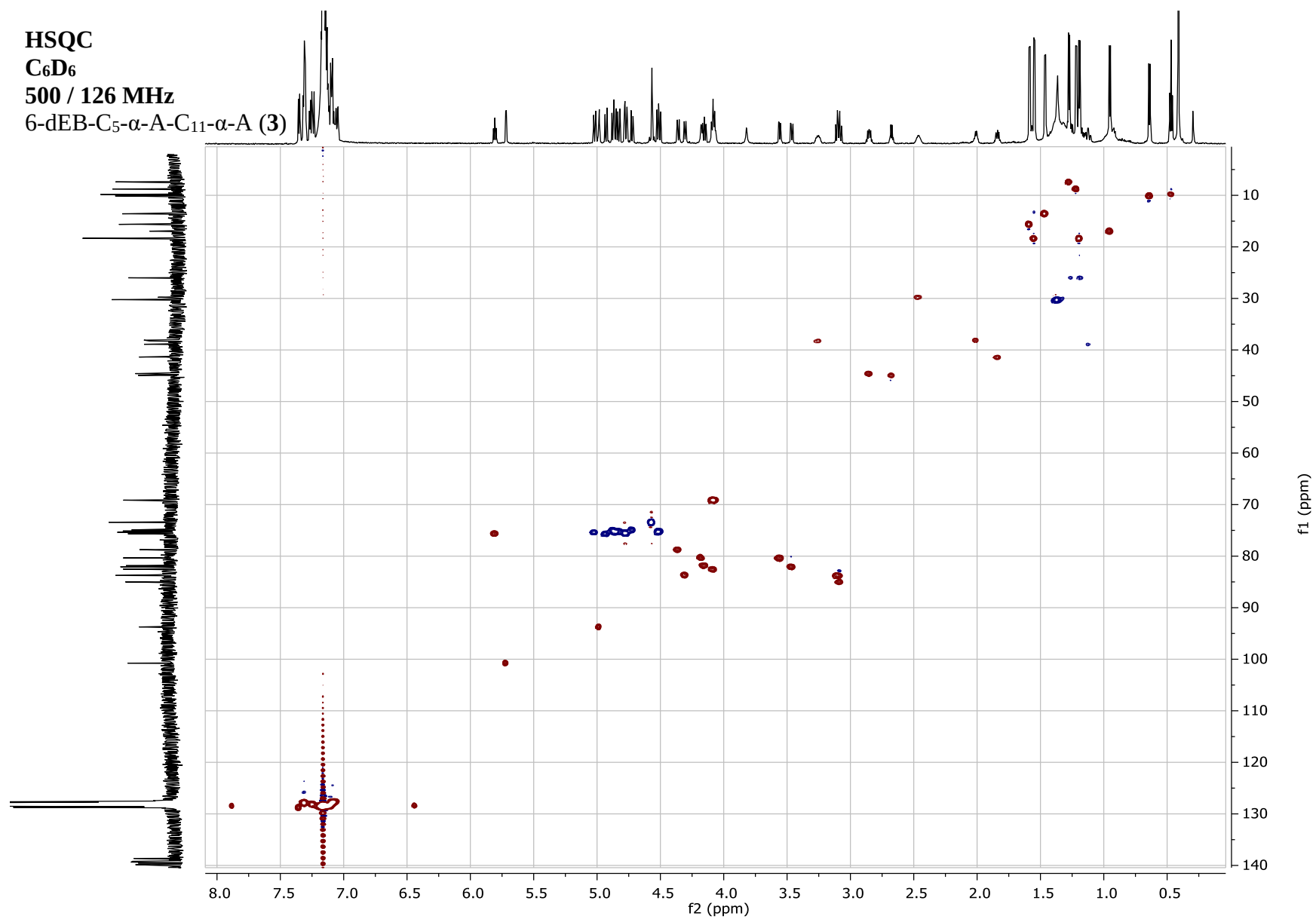


HSQC

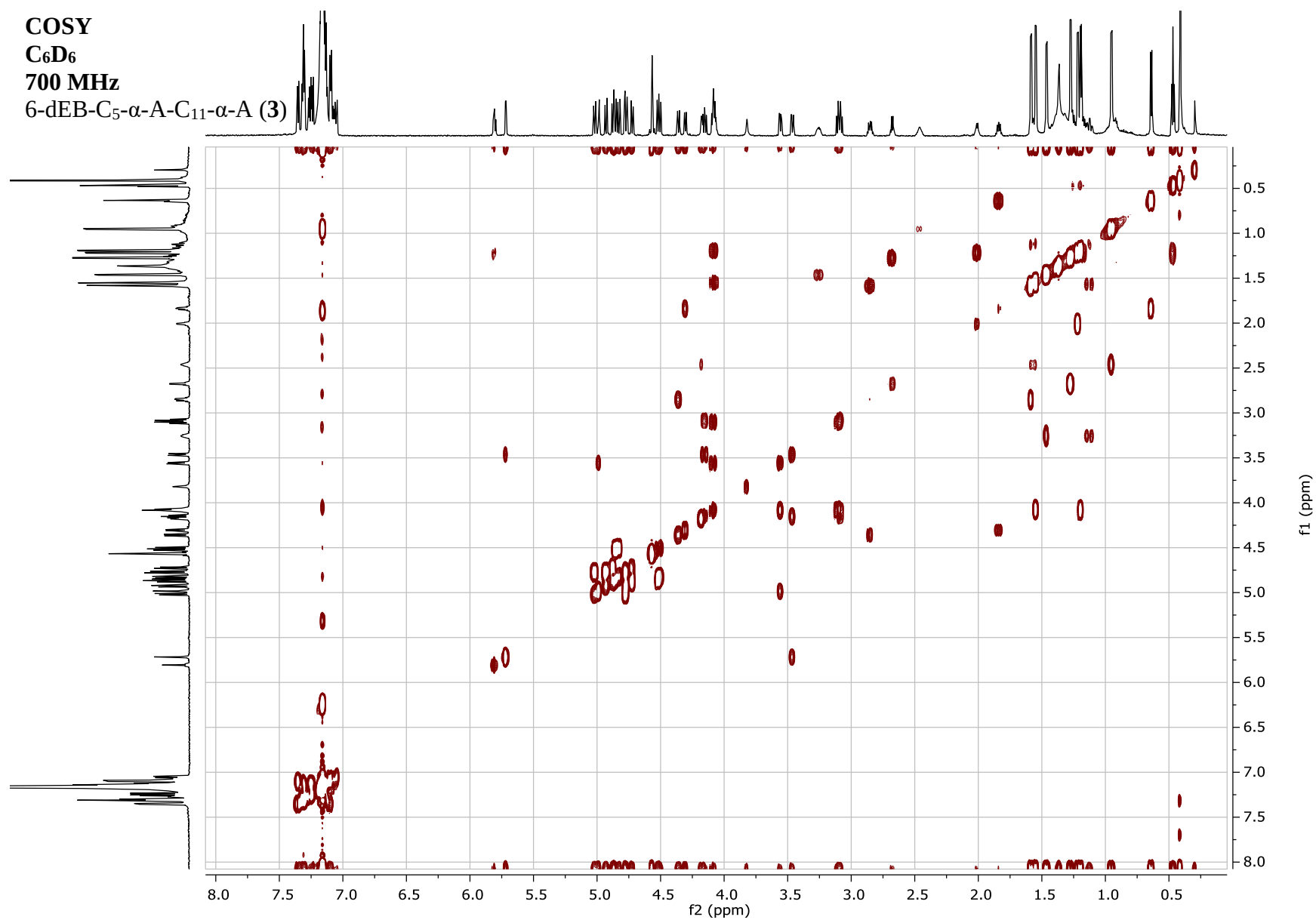
C₆D₆

500 / 126 MHz

6-dEB-C₅- α -A-C₁₁- α -A (3)



COSY
C₆D₆
700 MHz
6-dEB-C₅- α -A-C₁₁- α -A (3)

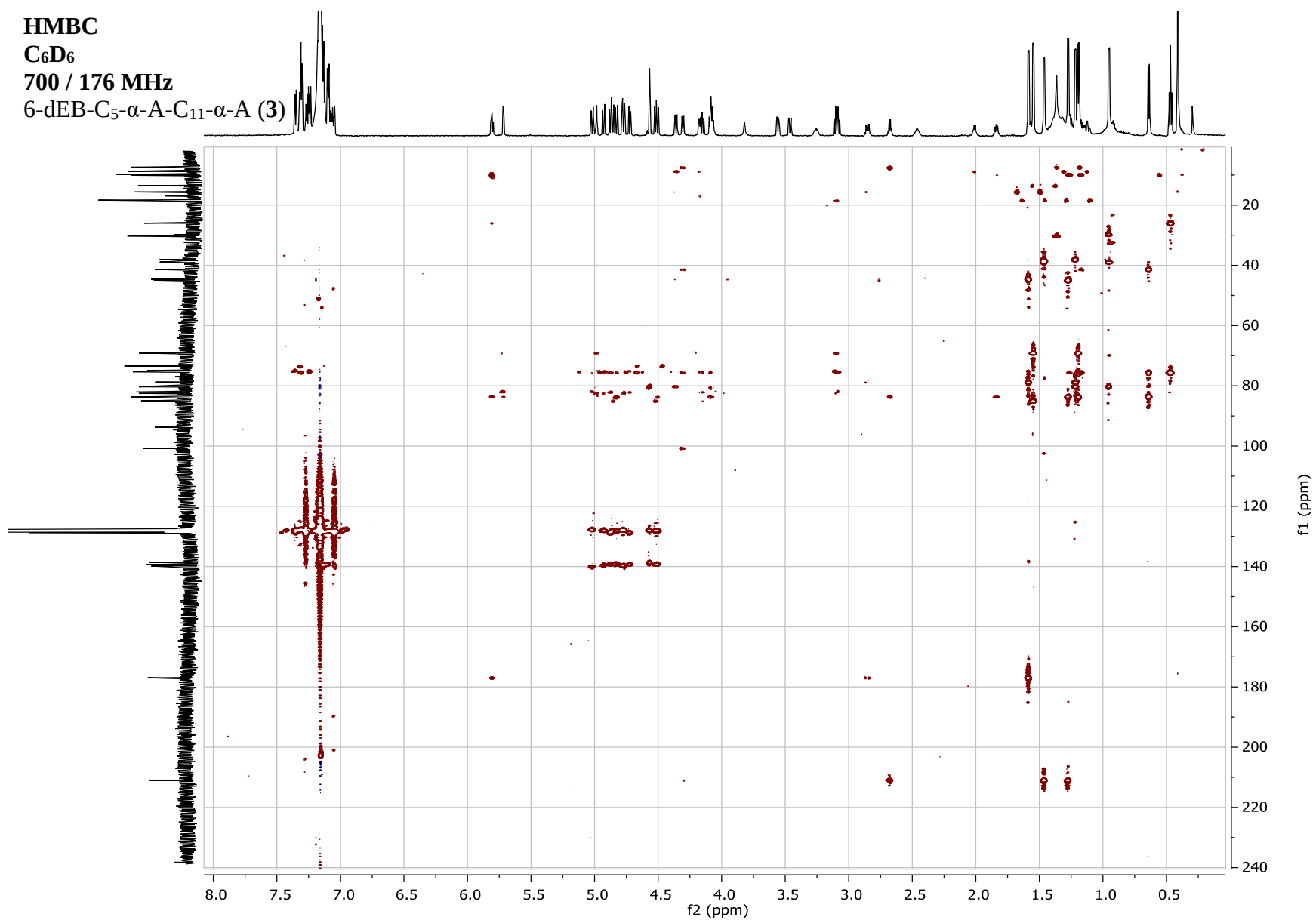


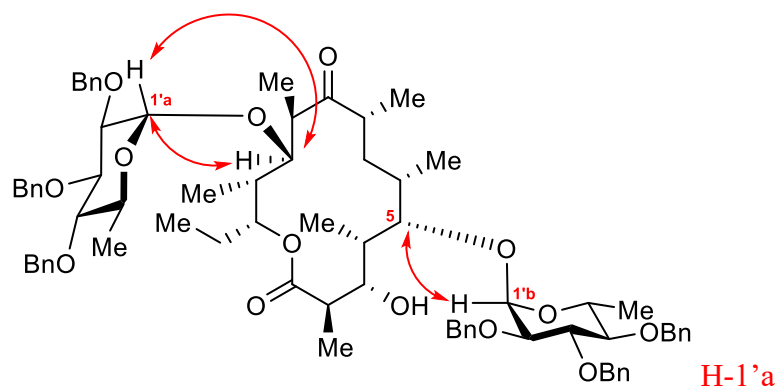
HMBC

C₆D₆

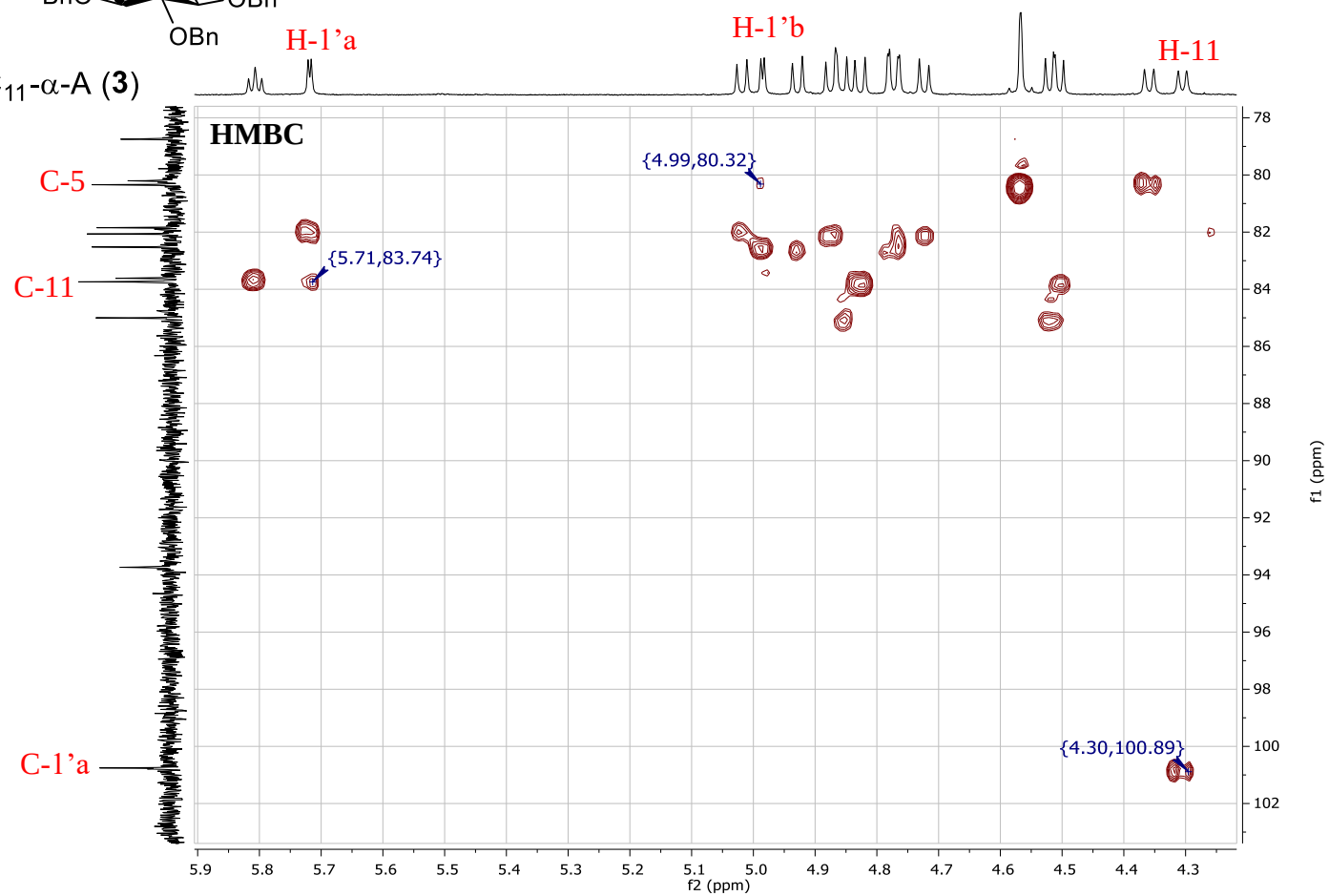
700 / 176 MHz

6-dEB-C₅- α -A-C₁₁- α -A (3)

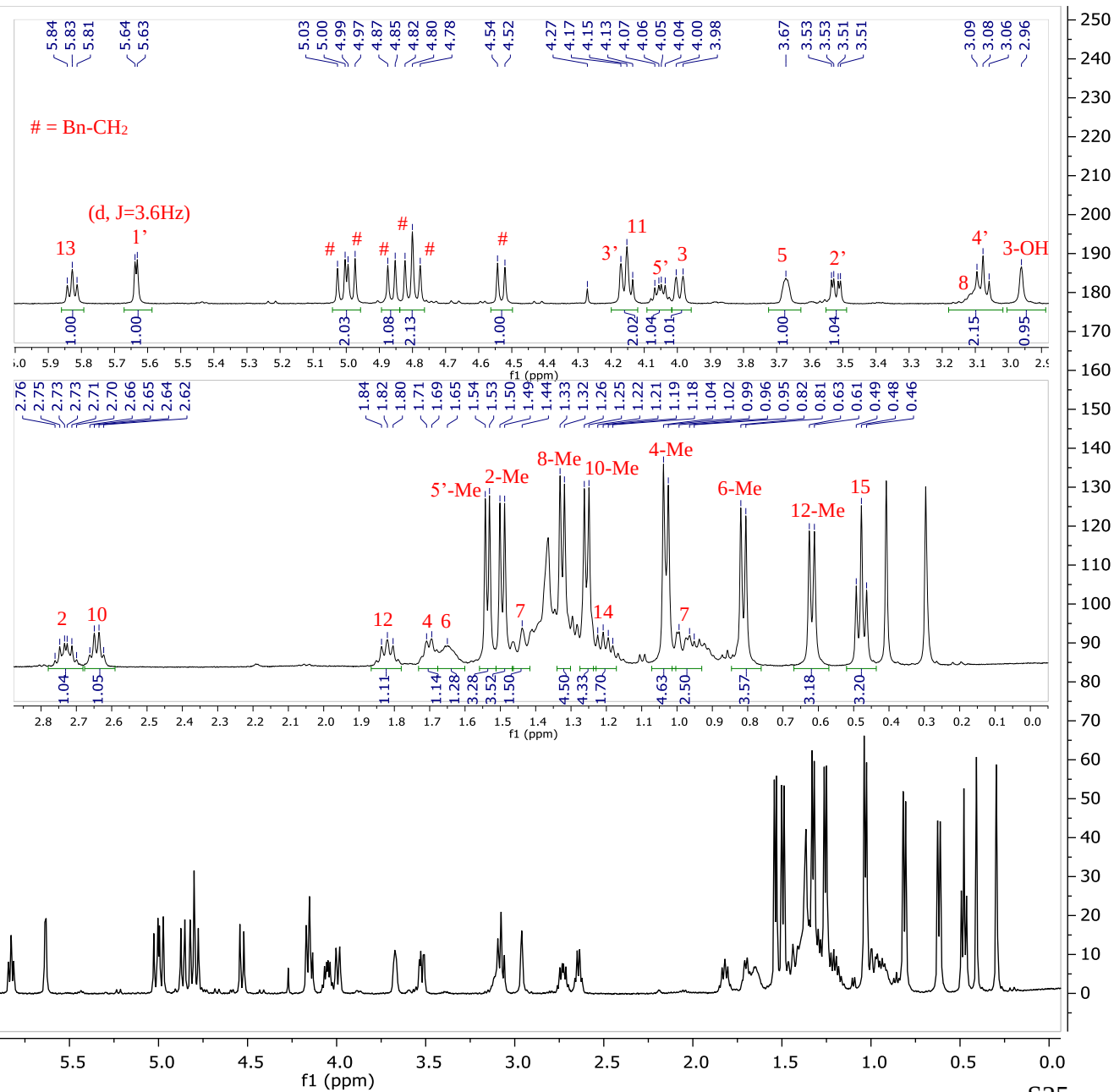
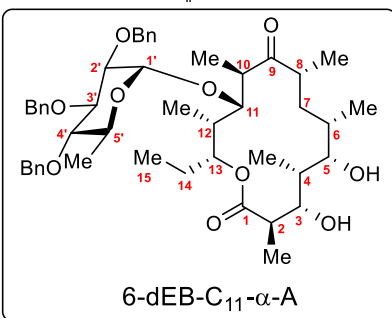


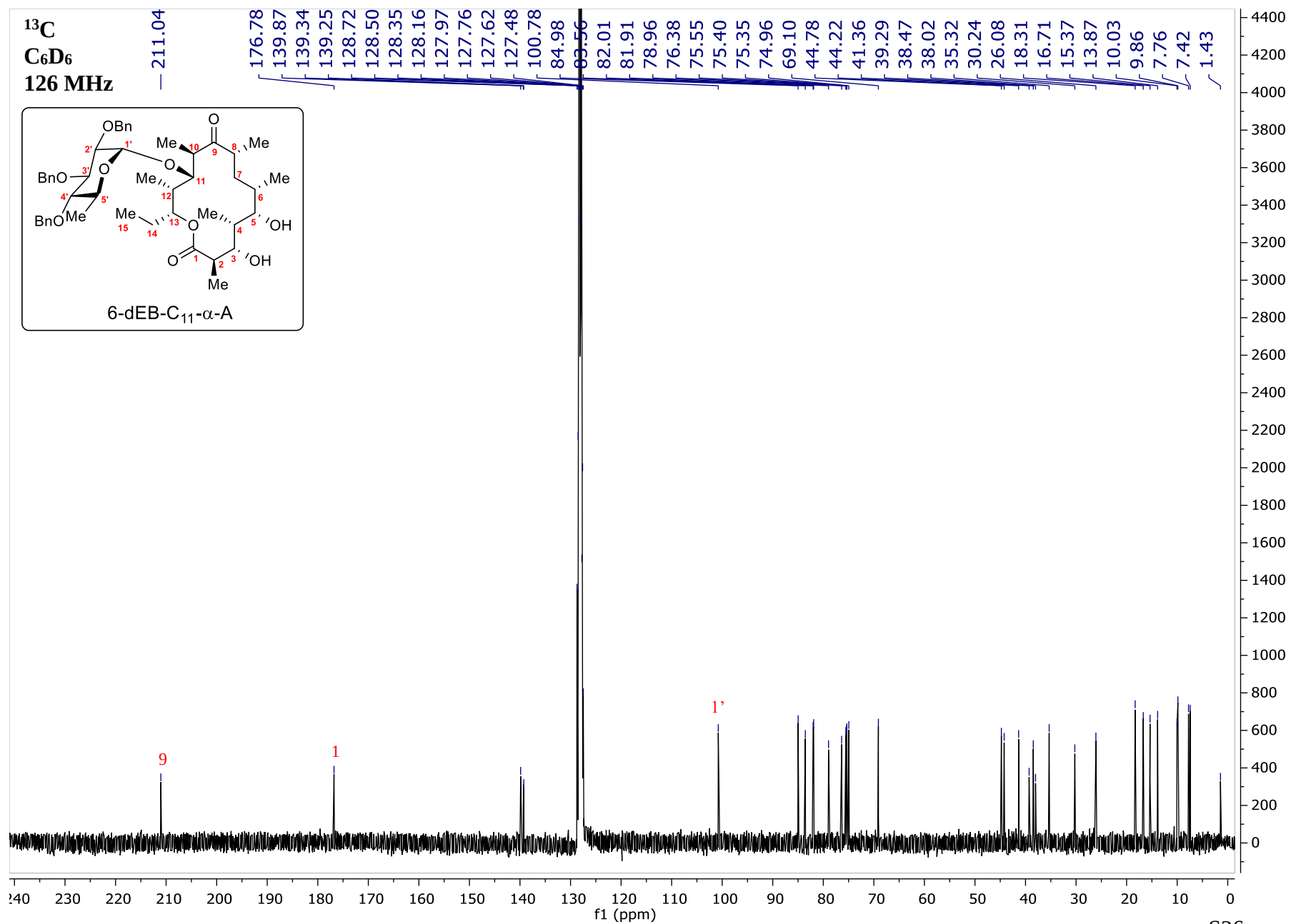


6-dEB-C₅-α-A-C₁₁-α-A (3)

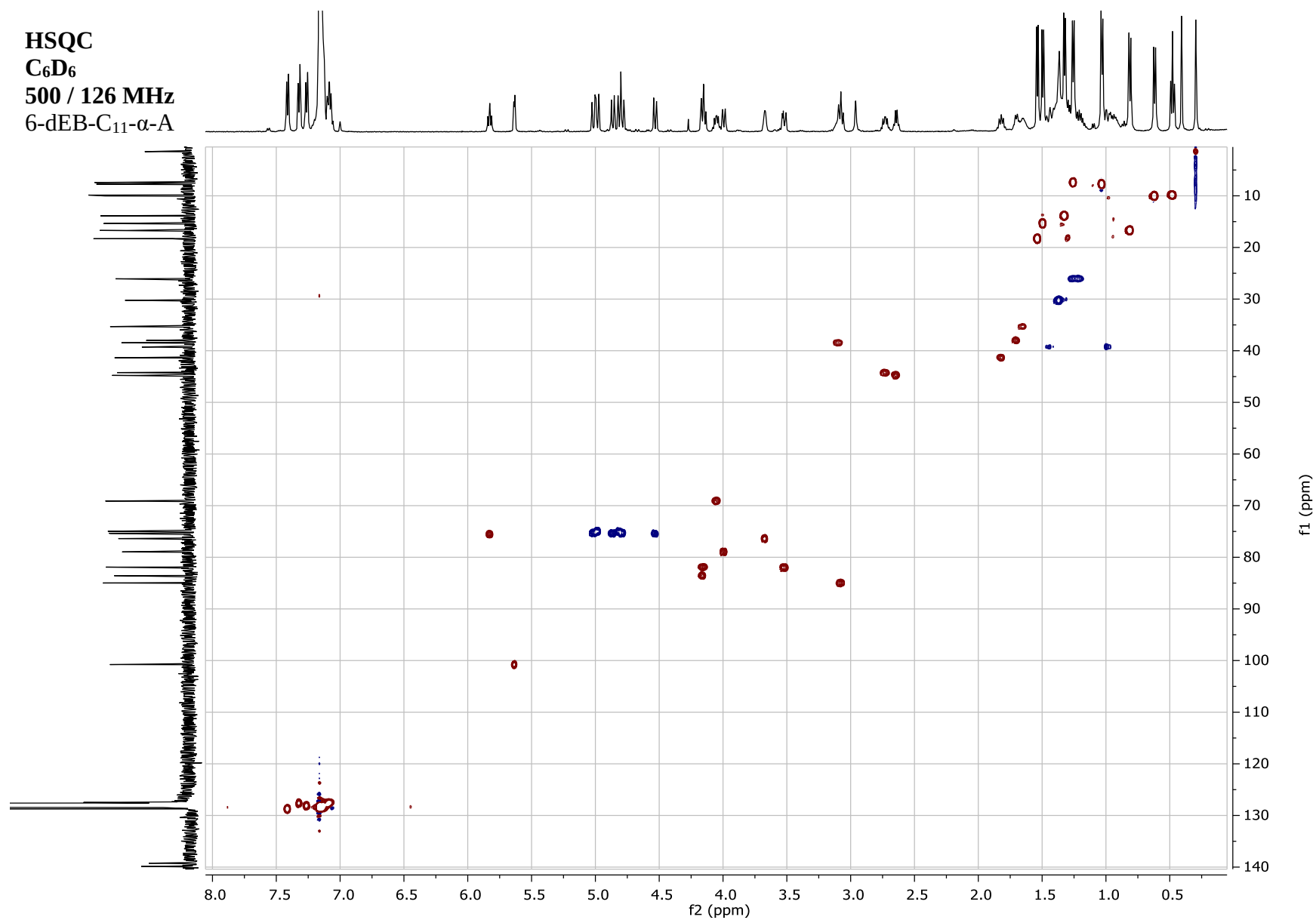


¹H
C₆D₆
500 MHz

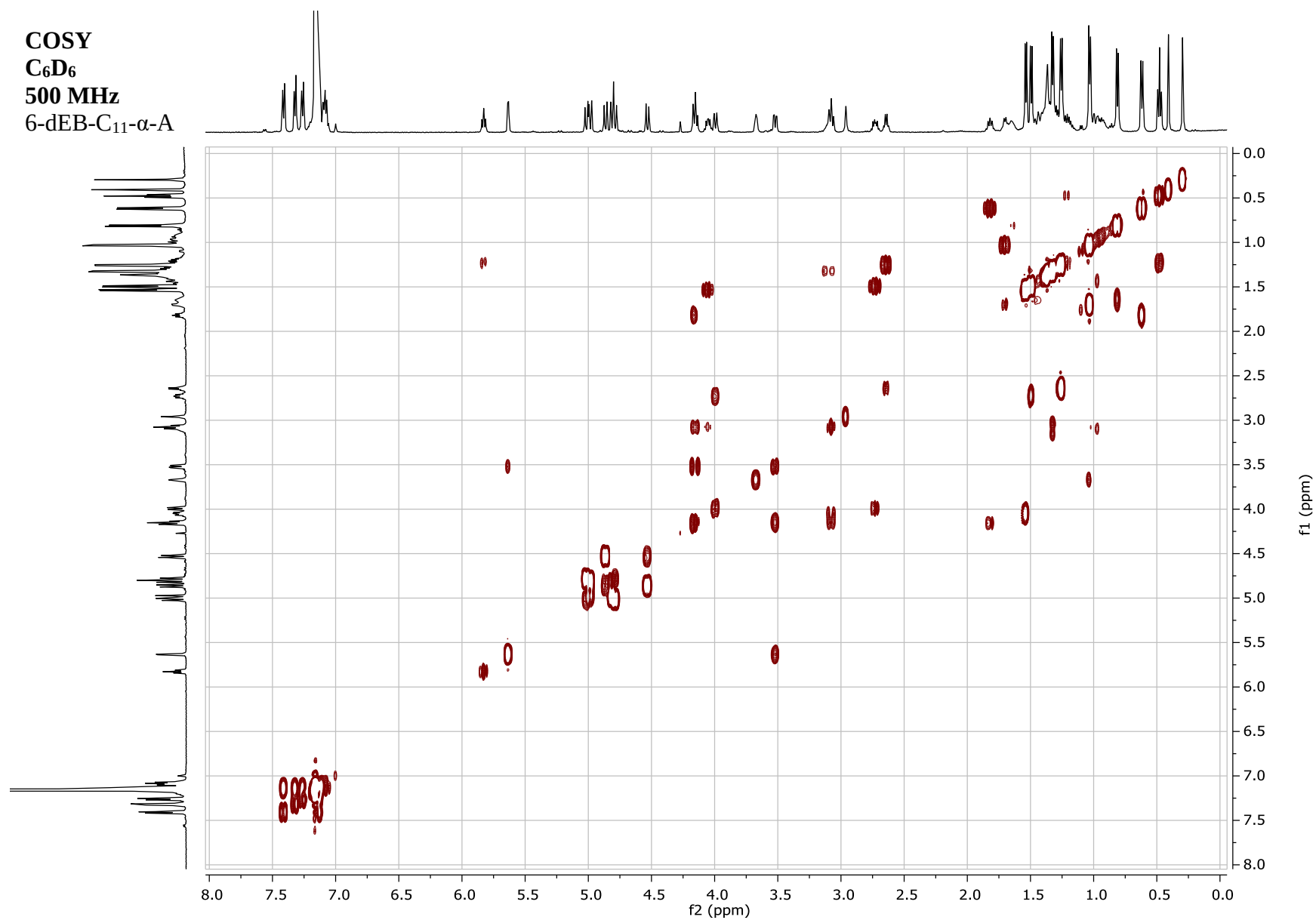




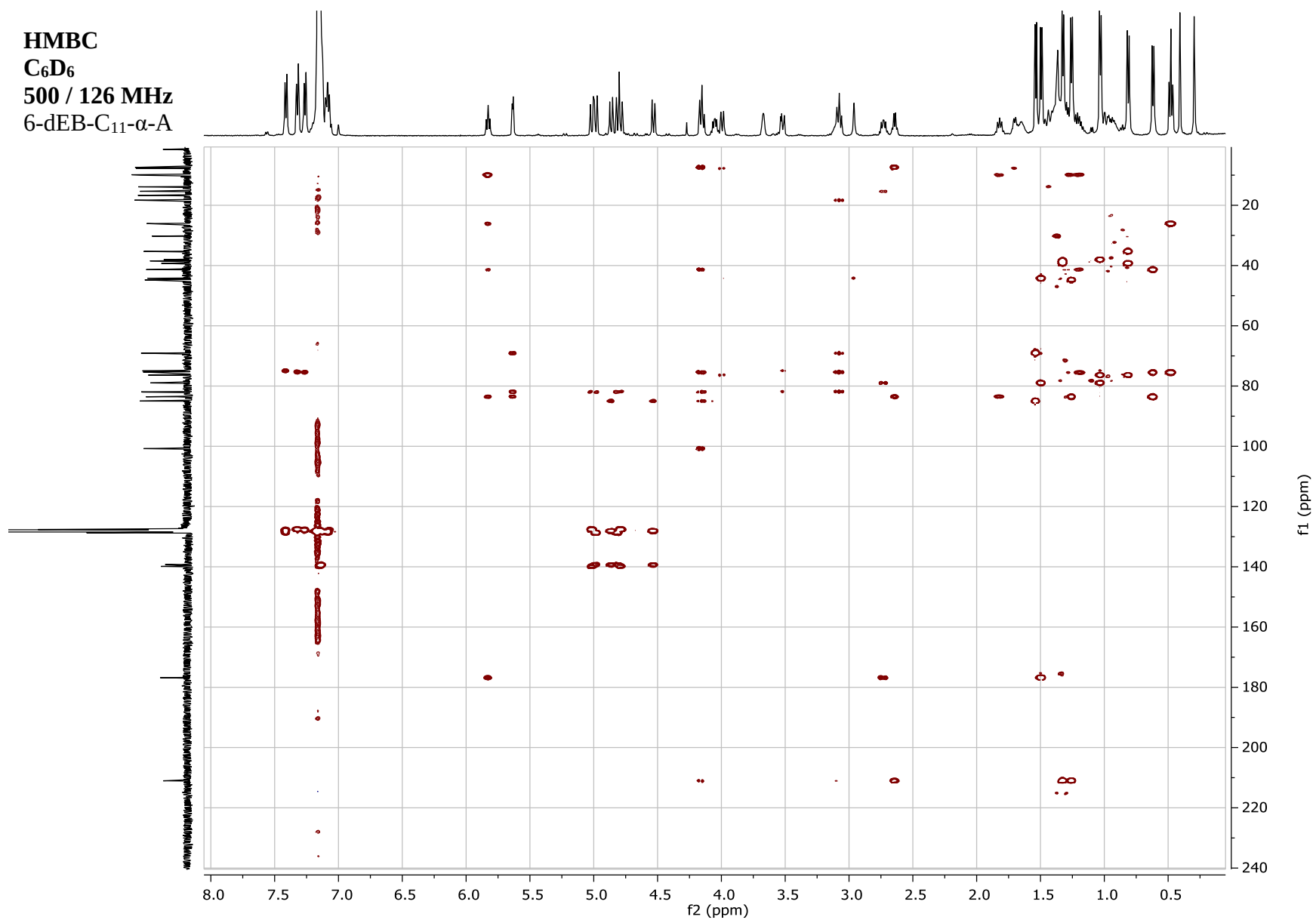
HSQC
C₆D₆
500 / 126 MHz
6-dEB-C₁₁- α -A

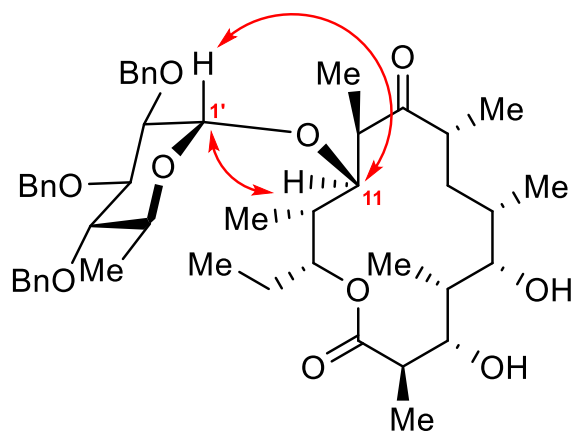


COSY
C₆D₆
500 MHz
6-dEB-C₁₁-α-A

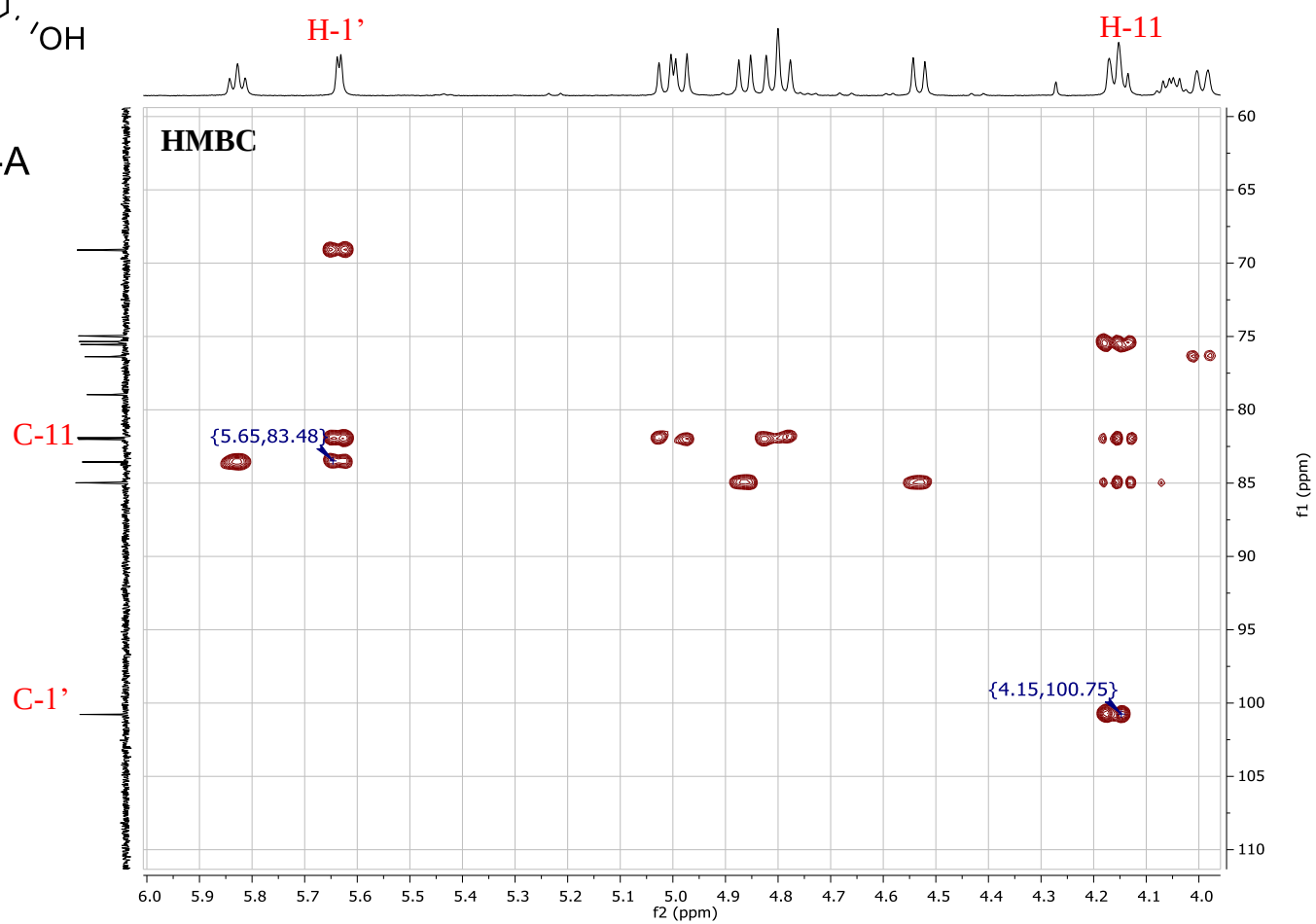


HMBC
C₆D₆
500 / 126 MHz
6-dEB-C₁₁- α -A

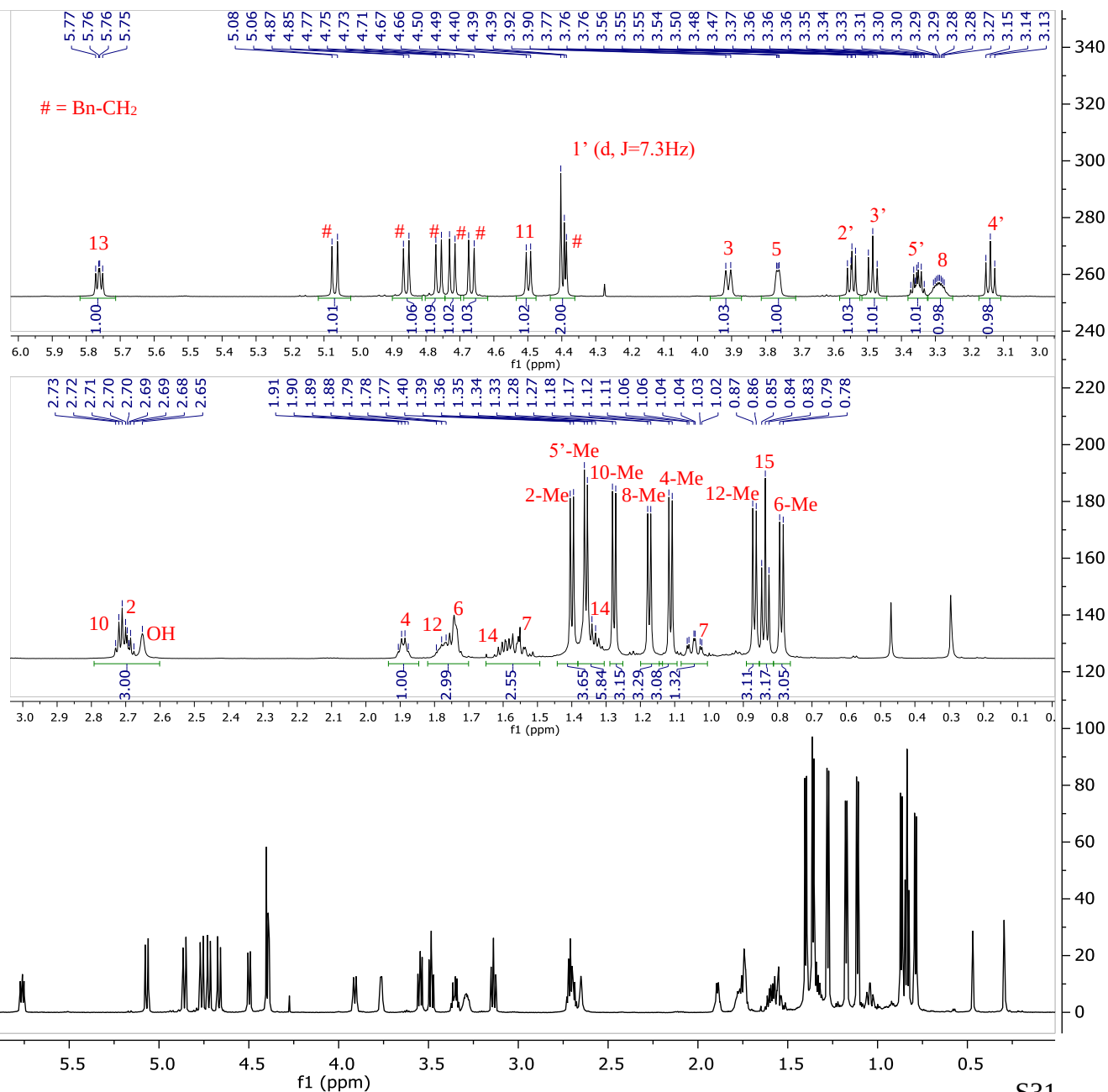
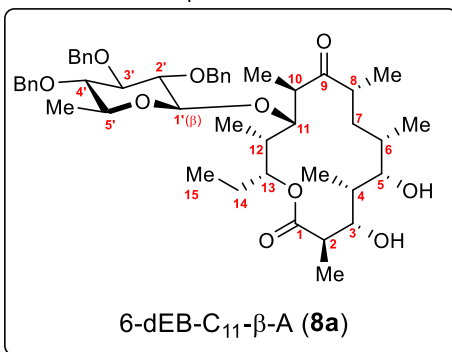


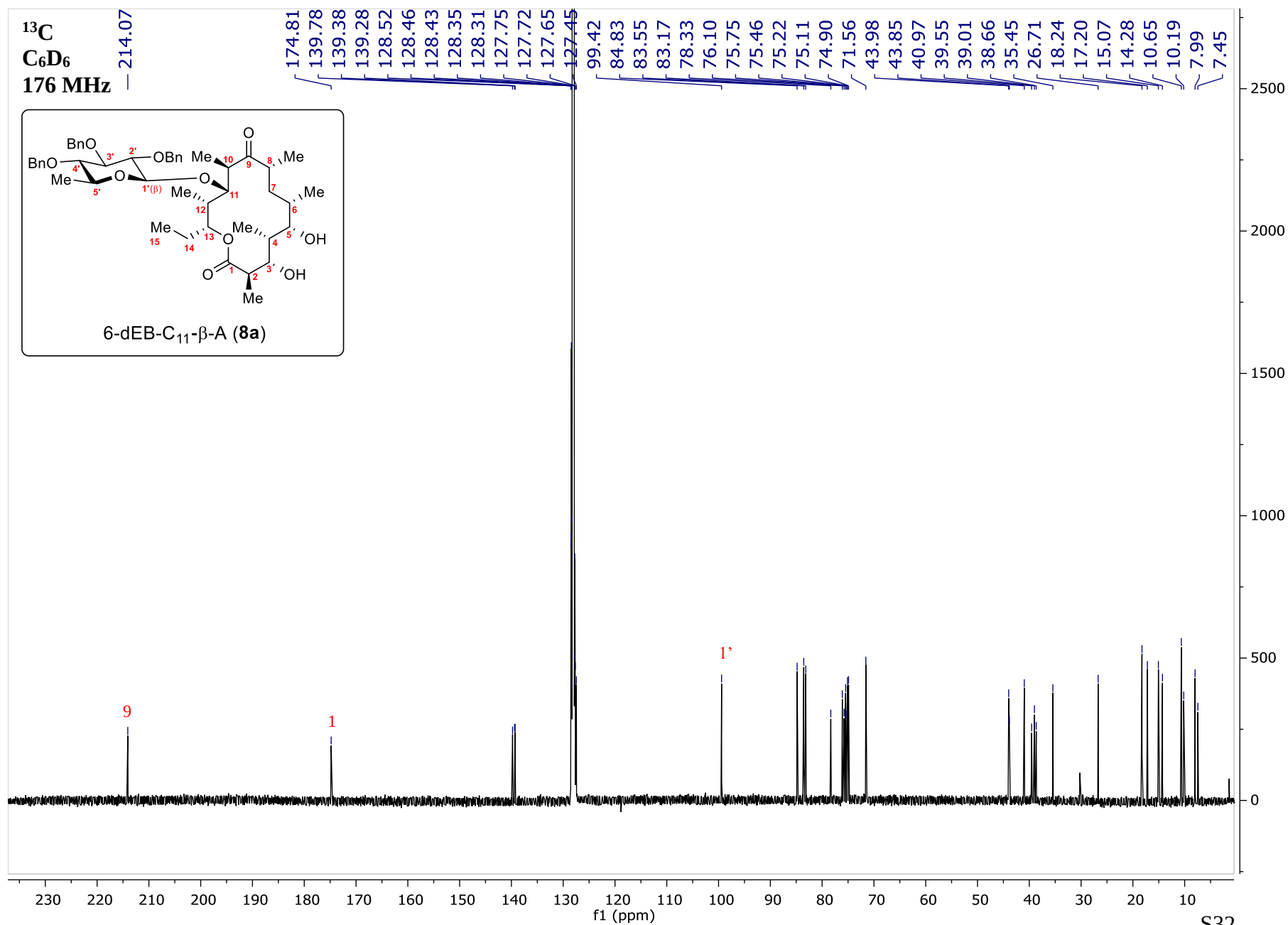


6-dEB-C₁₁-α-A

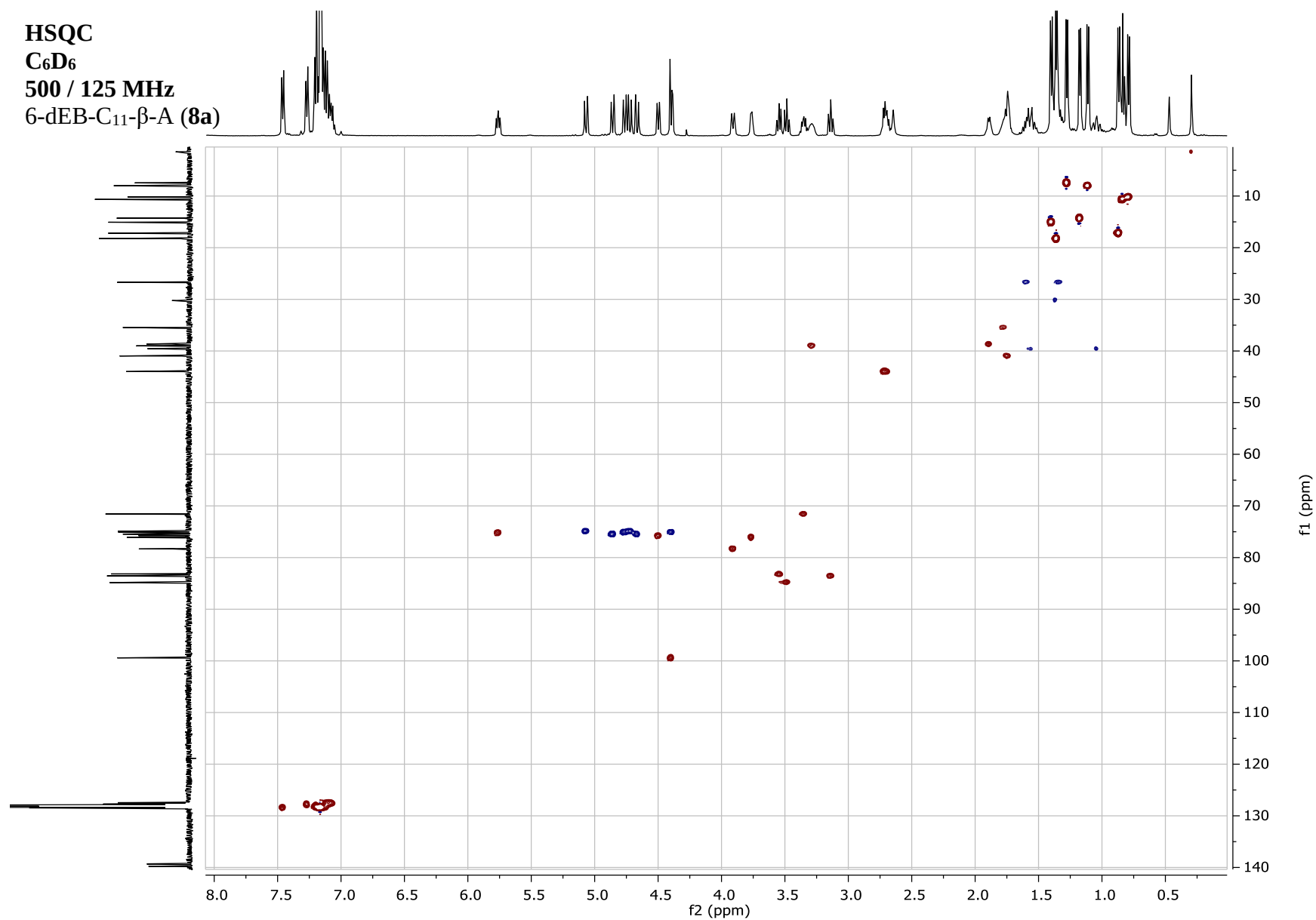


¹H
C₆D₆
700 MHz

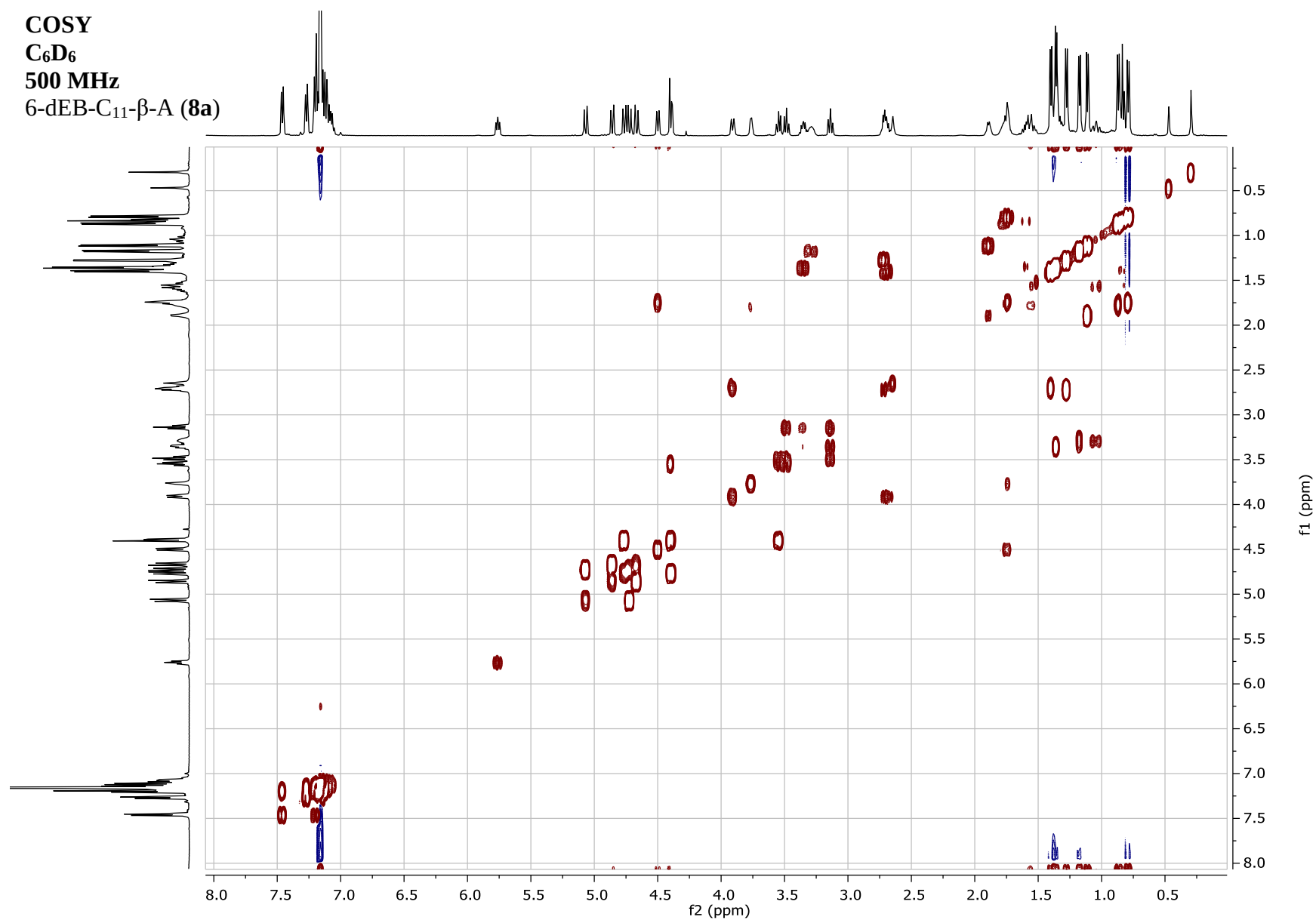




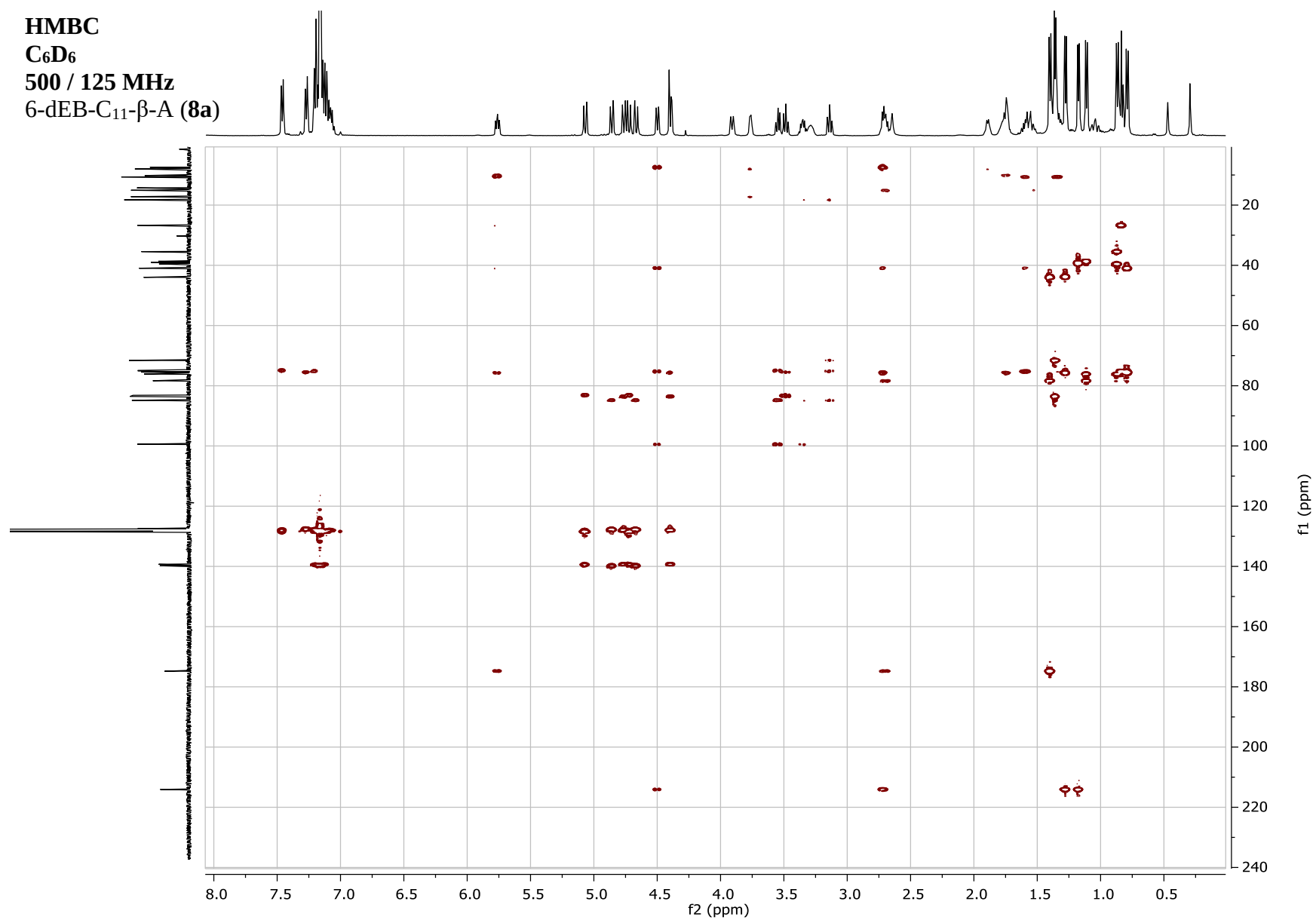
HSQC
C₆D₆
500 / 125 MHz
6-dEB-C₁₁-β-A (8a)

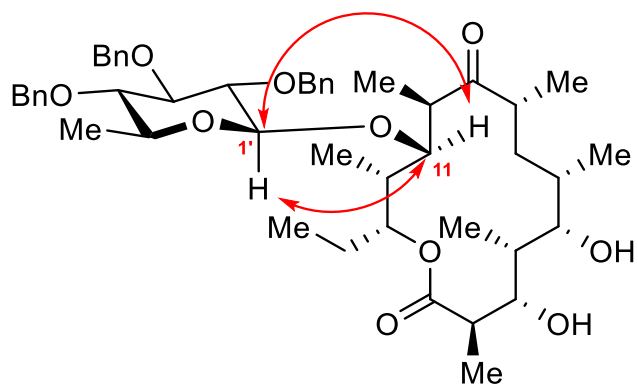


COSY
C₆D₆
500 MHz
6-dEB-C₁₁-β-A (8a)

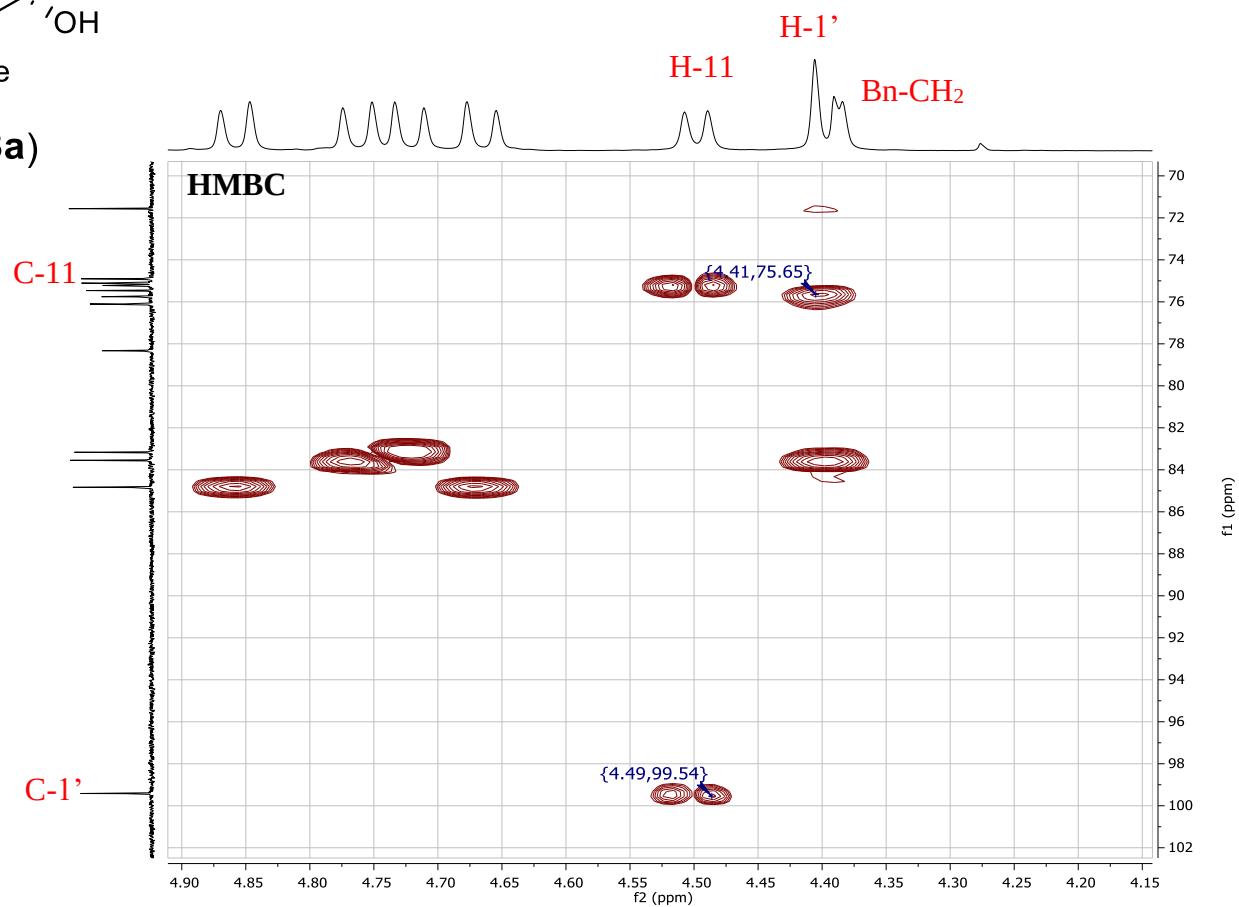


HMBC
C₆D₆
500 / 125 MHz
6-dEB-C₁₁-β-A (8a)



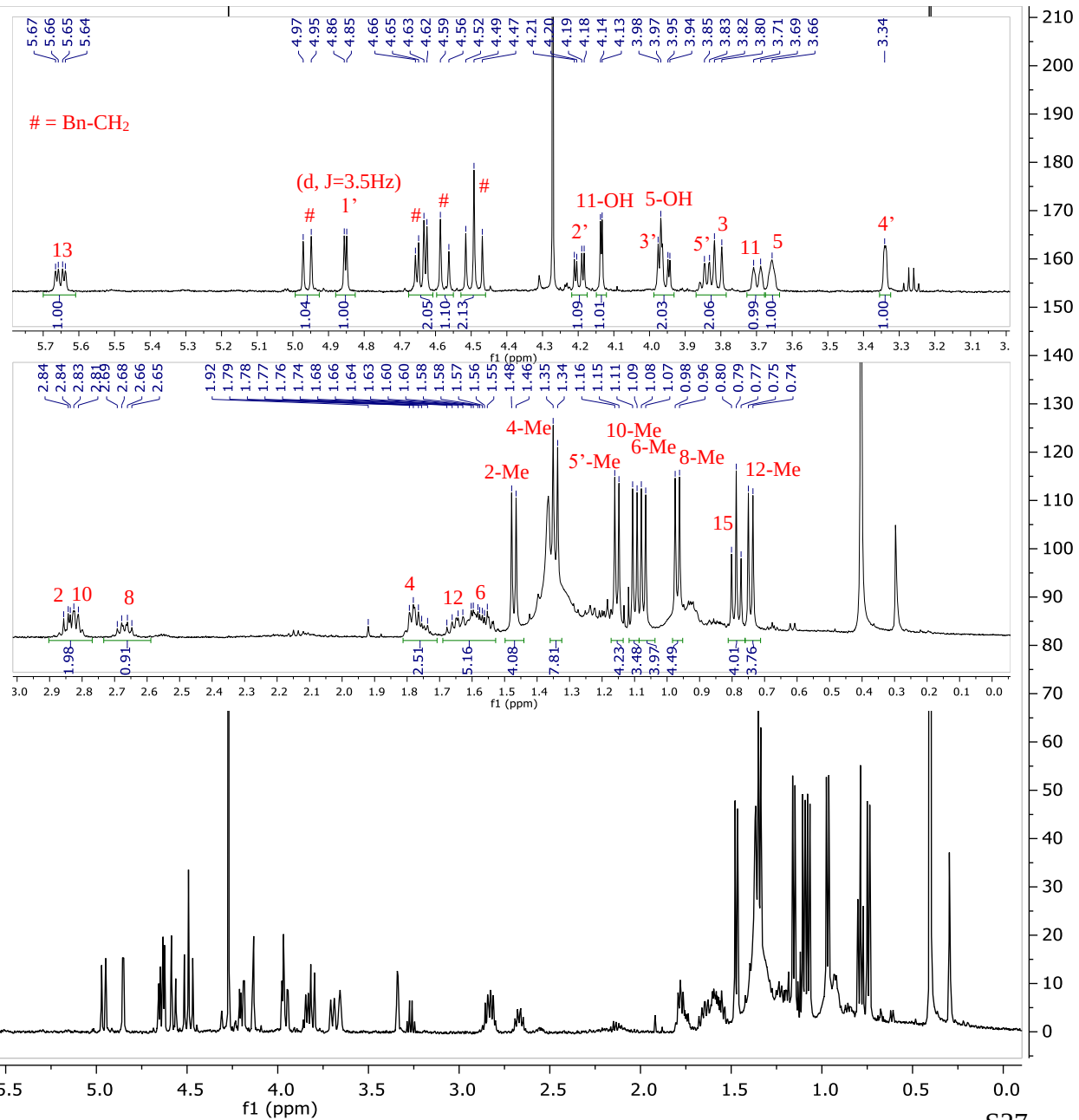
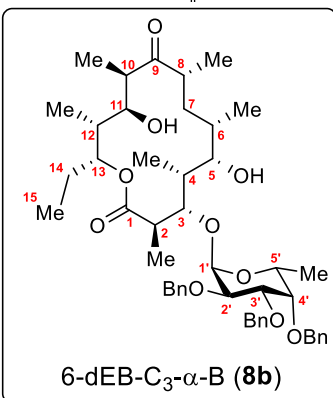


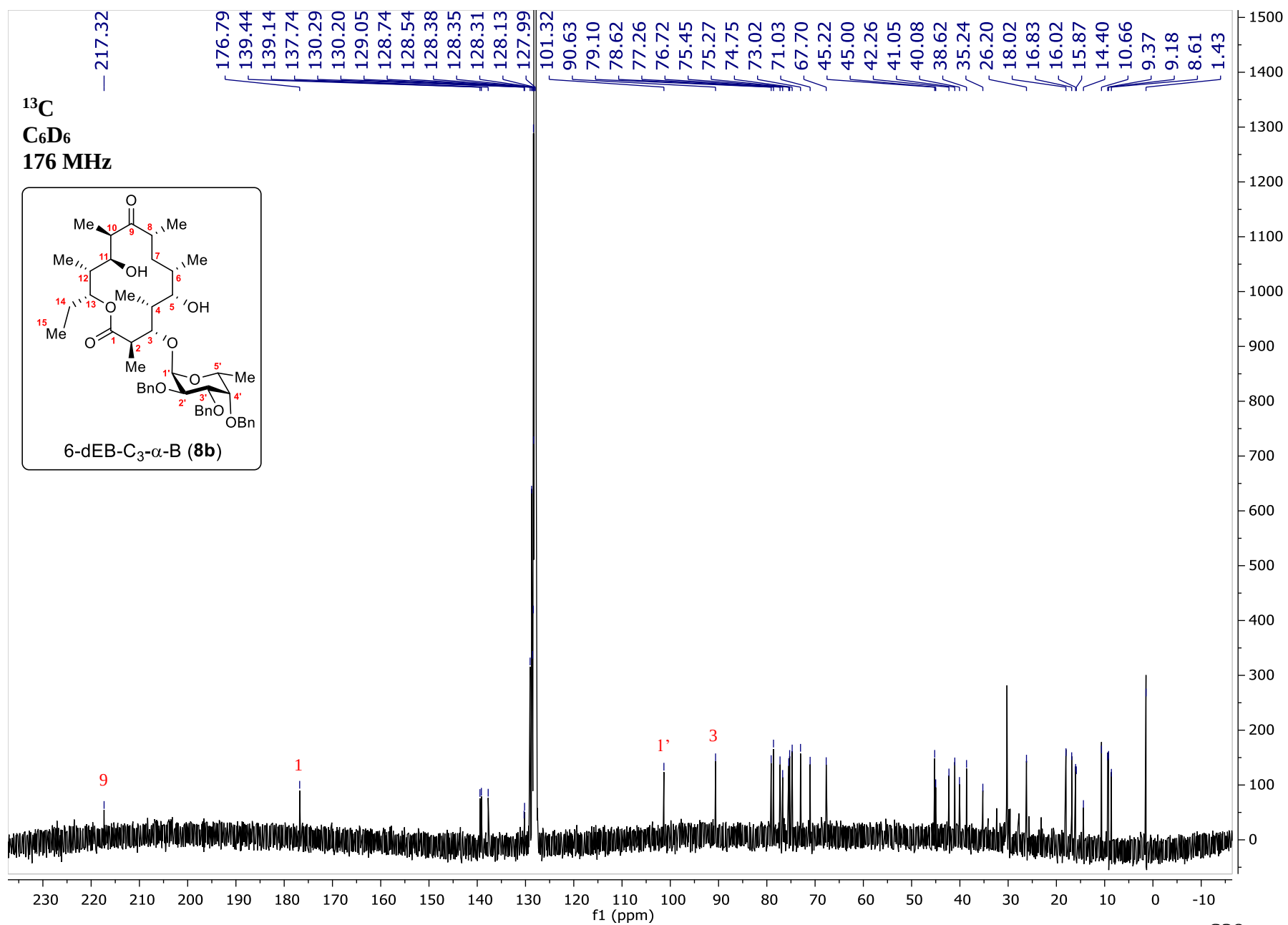
6-dEB-C₁₁-β-A (8a)



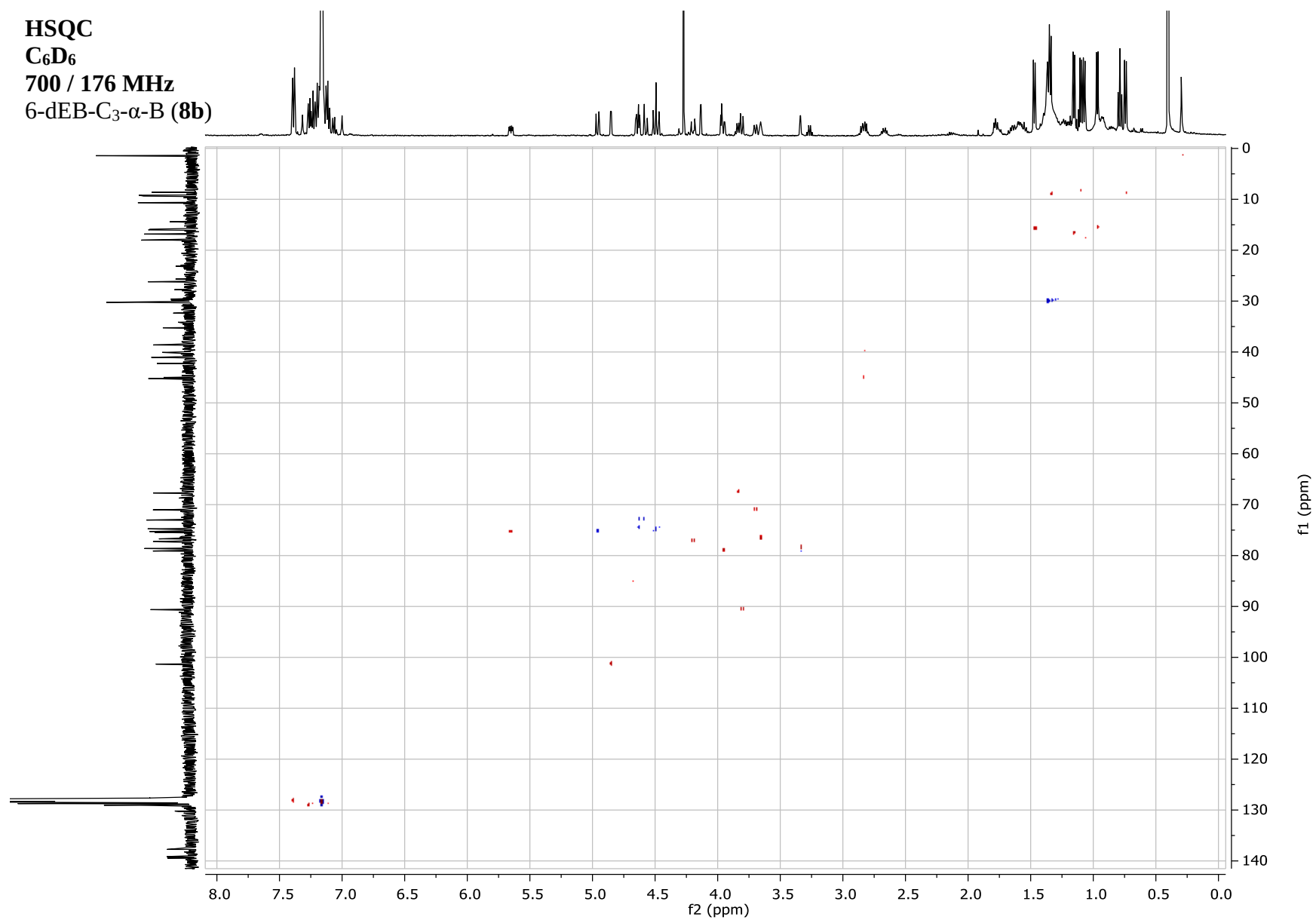
$$^1\text{H}$$

$$\text{C}_6\text{D}_6$$

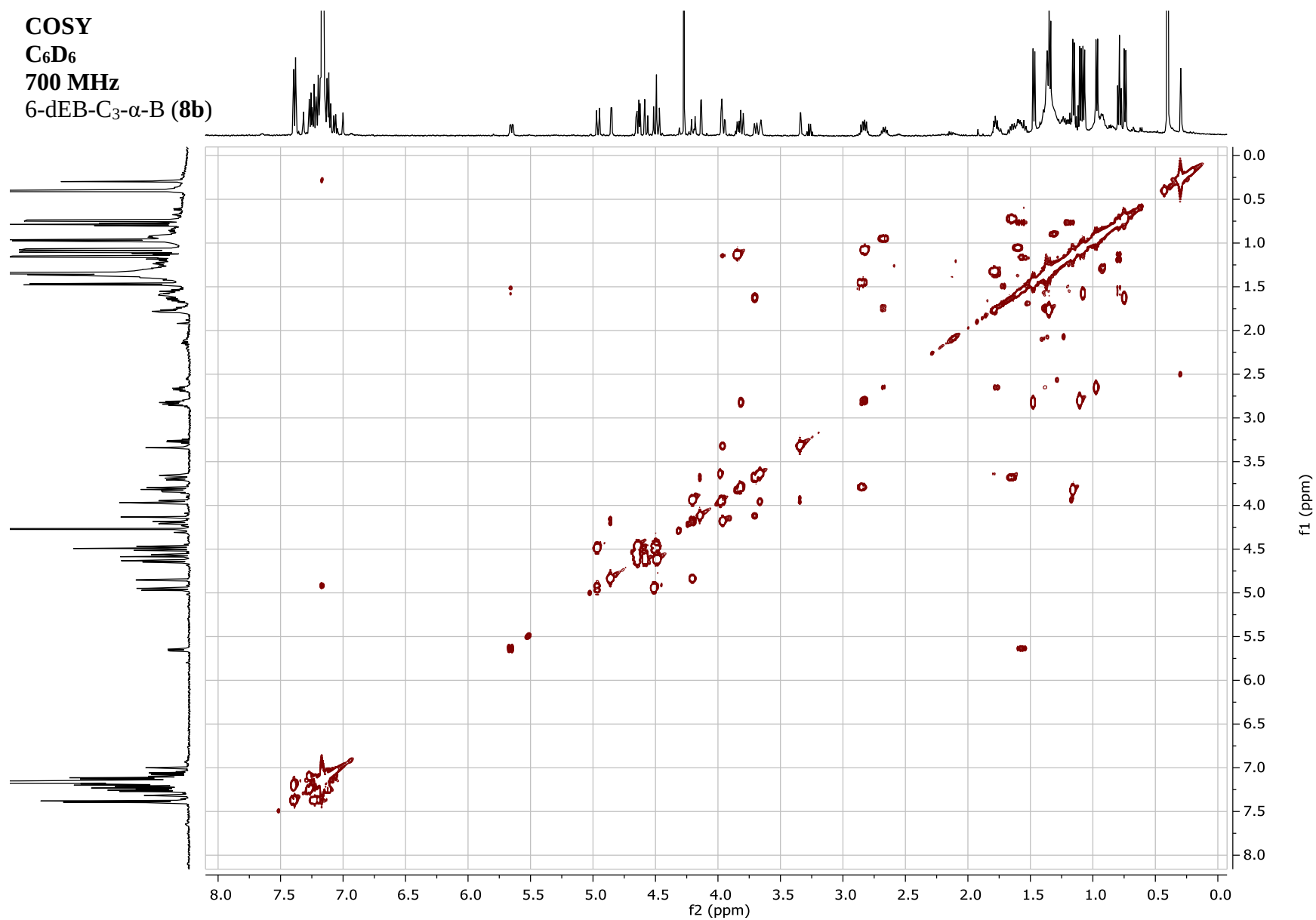
$$500 \text{ MHz}$$




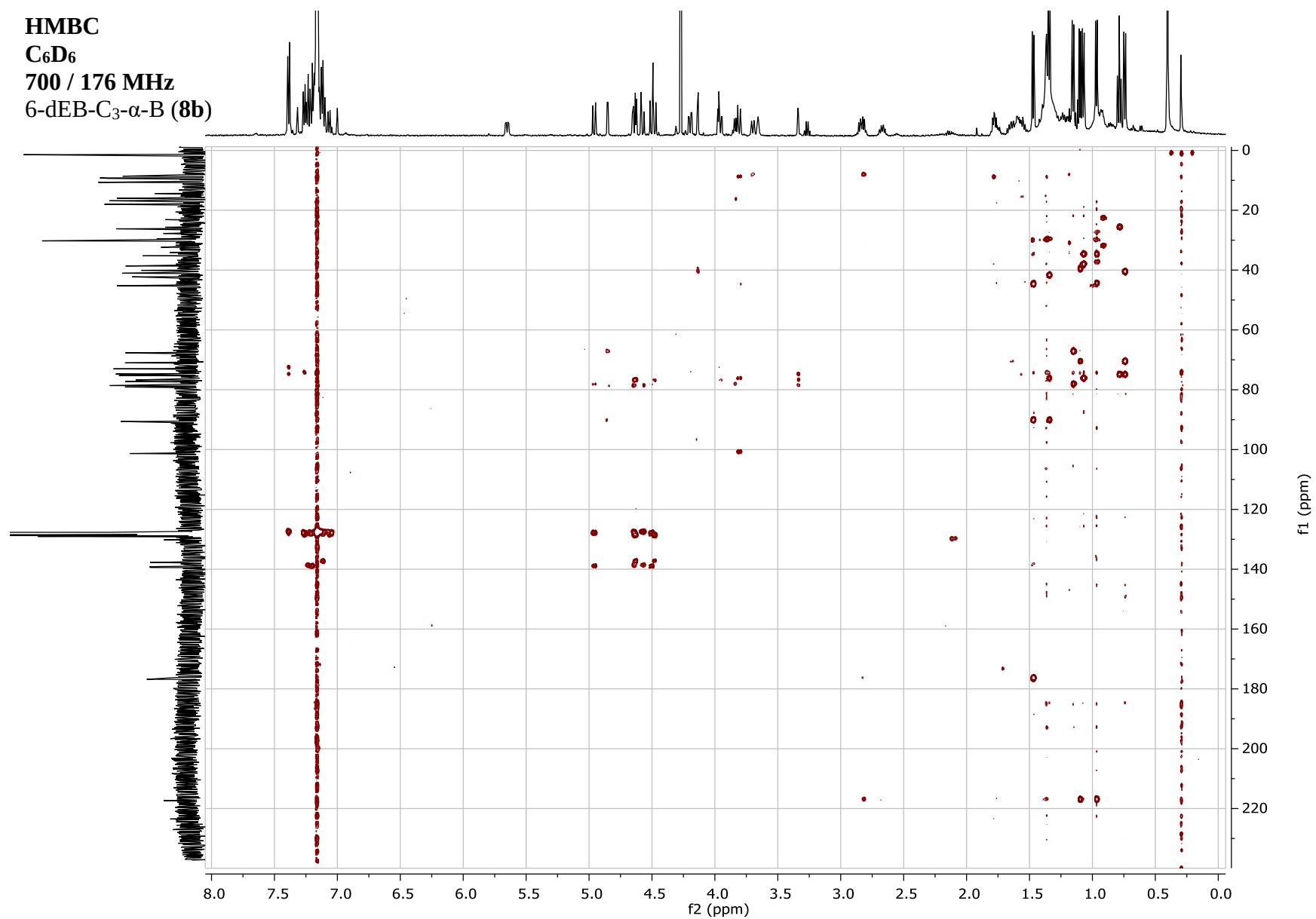
HSQC
C₆D₆
700 / 176 MHz
6-dEB-C₃- α -B (8b)

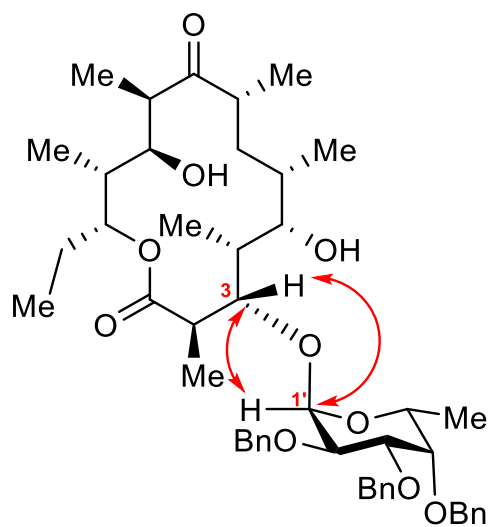


COSY
C₆D₆
700 MHz
6-dEB-C₃- α -B (**8b**)

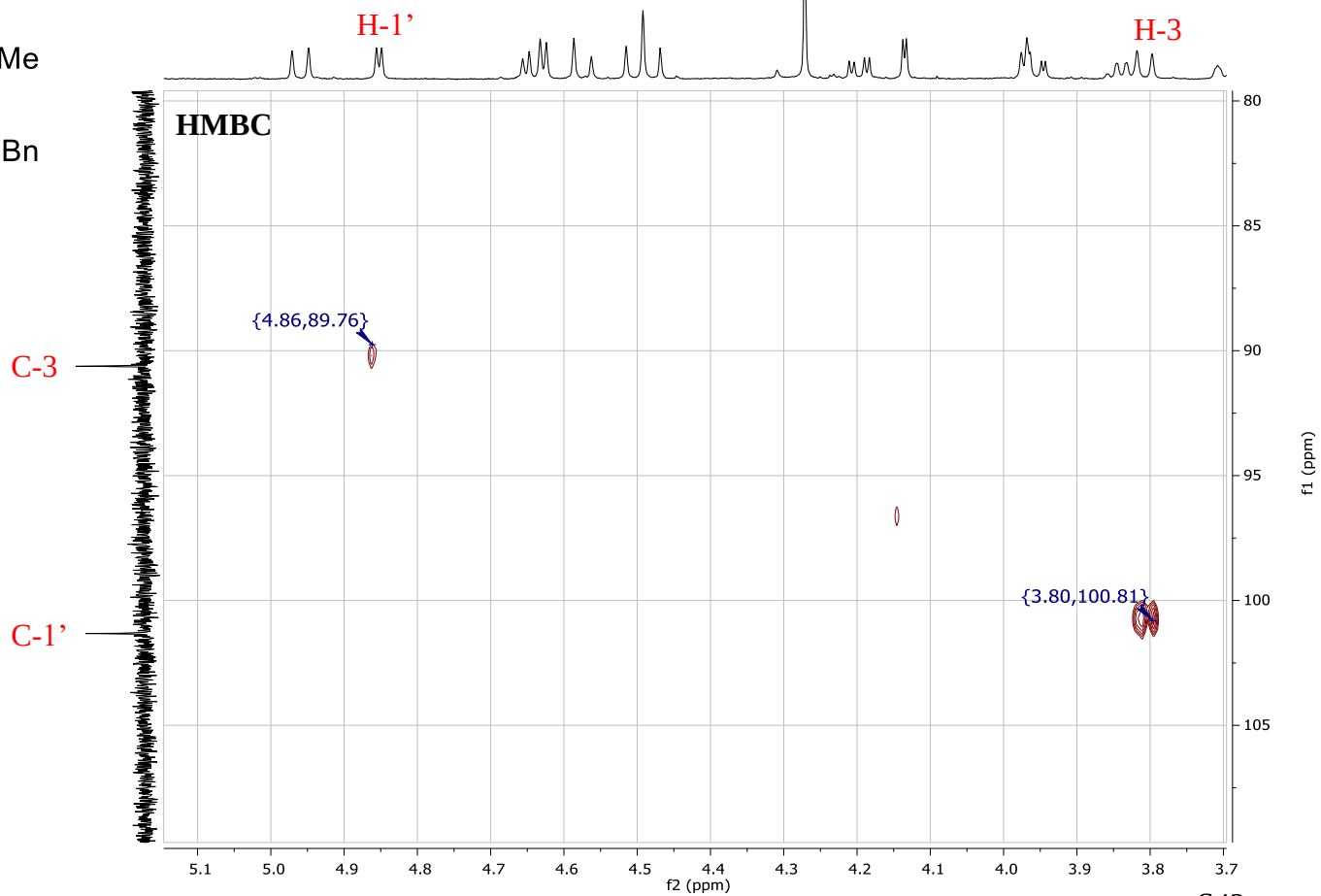


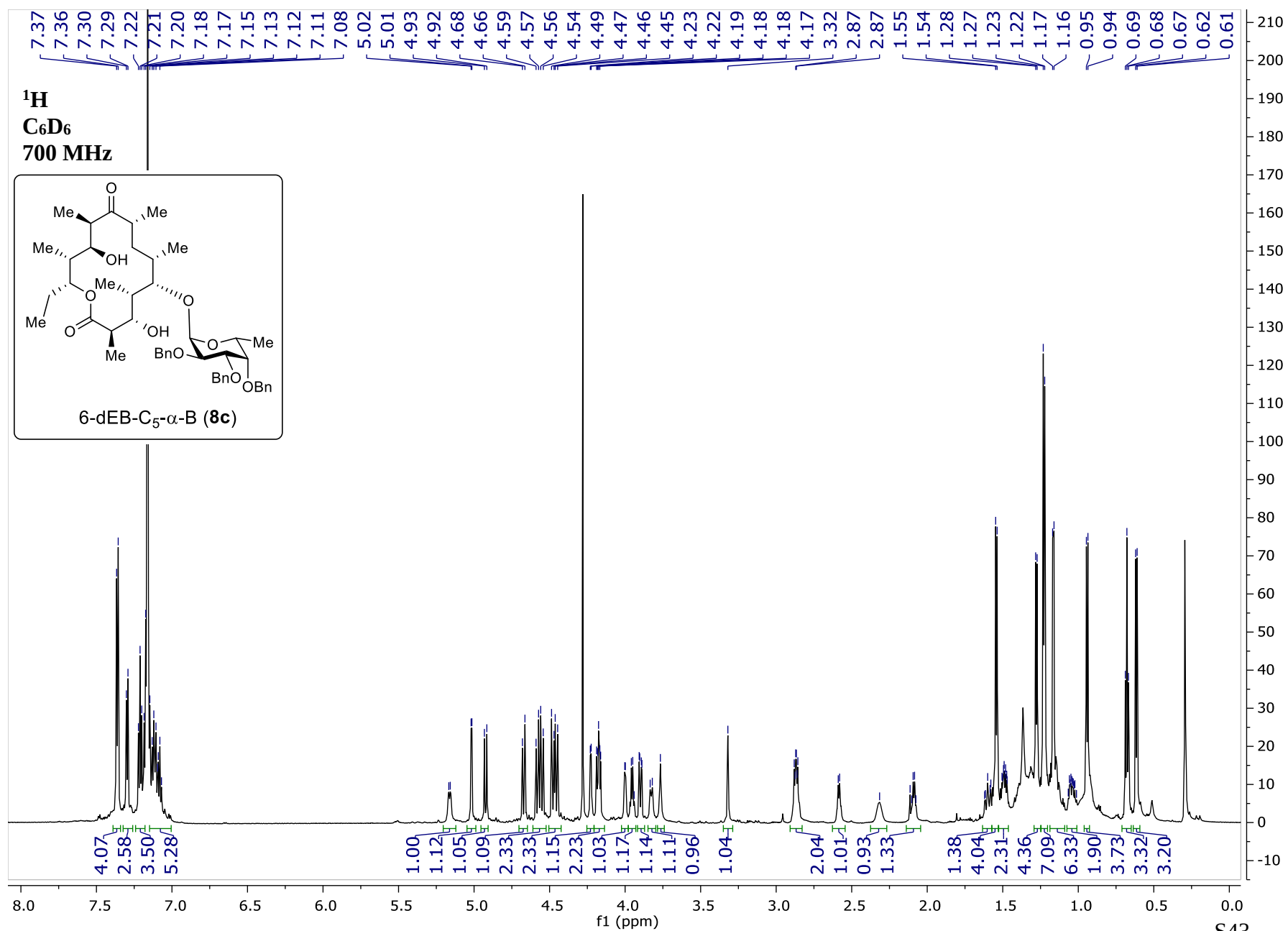
HMBC
C₆D₆
700 / 176 MHz
6-dEB-C₃- α -B (8b)



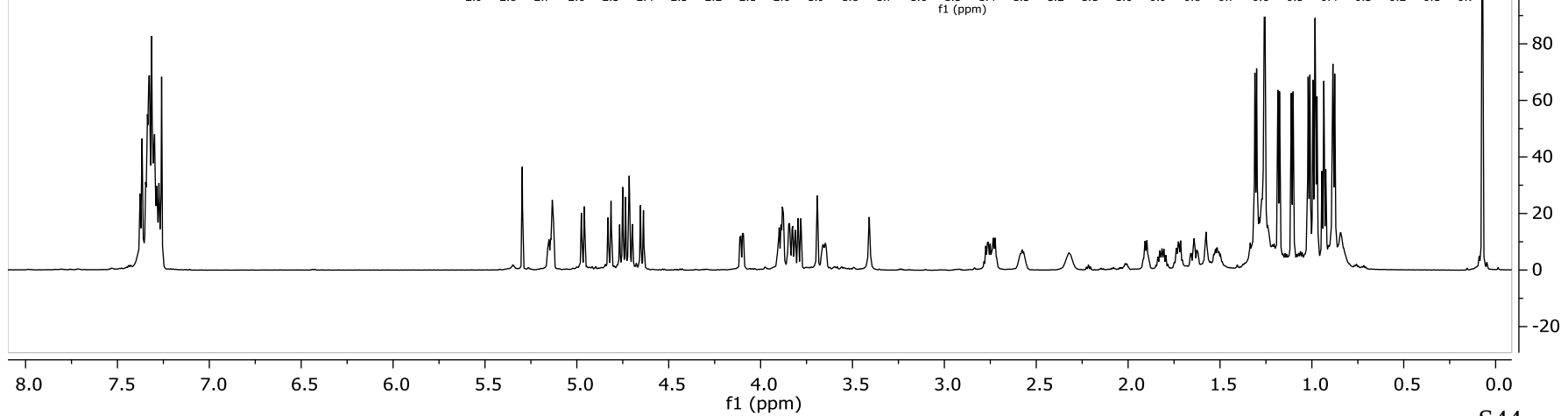
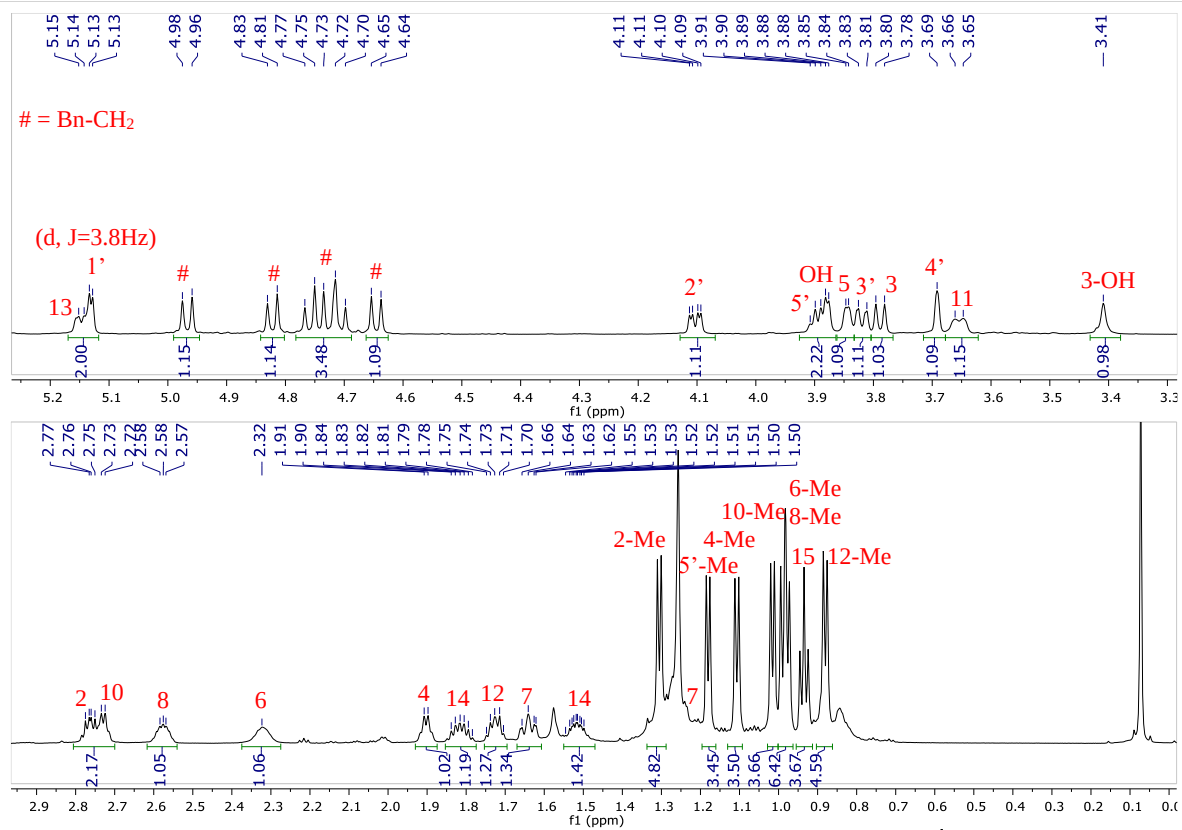
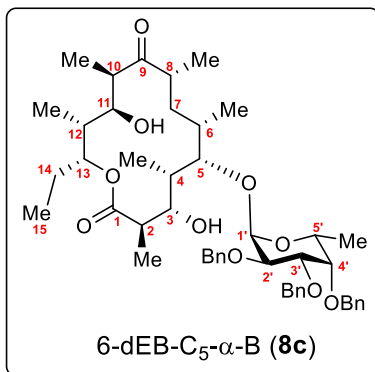


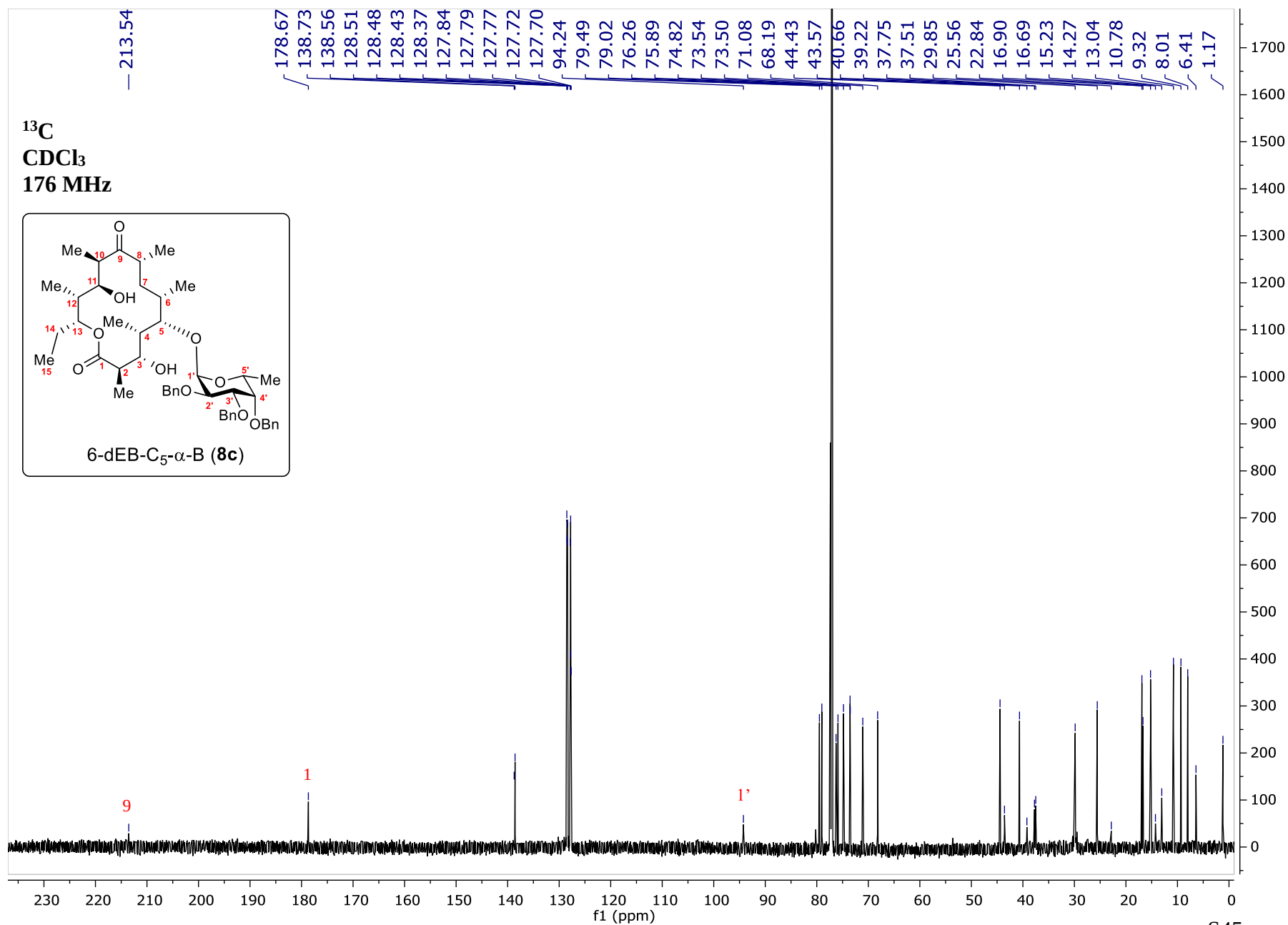
6-dEB-C₃-α-B (8b)



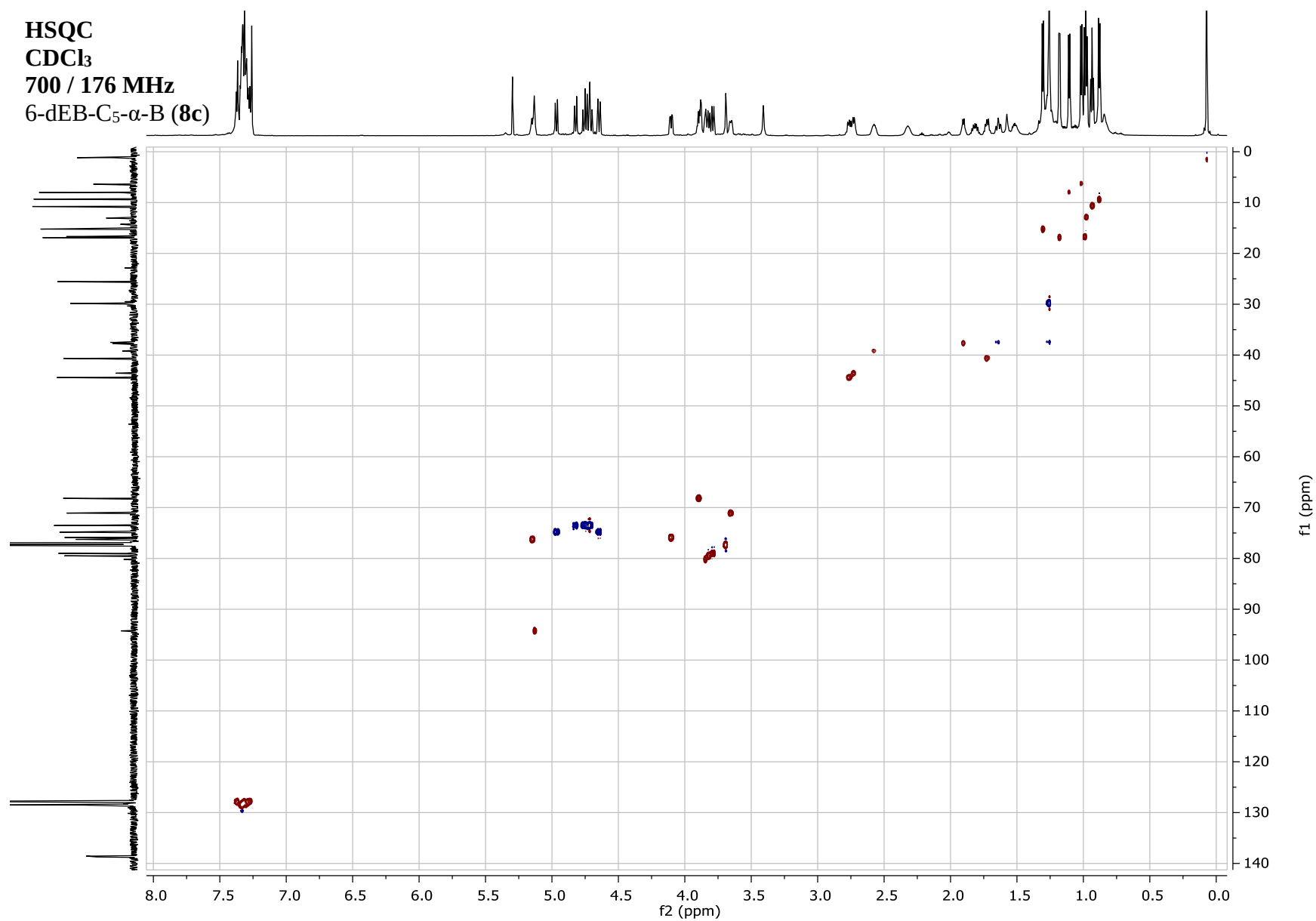


¹H
CDCl₃
700 MHz

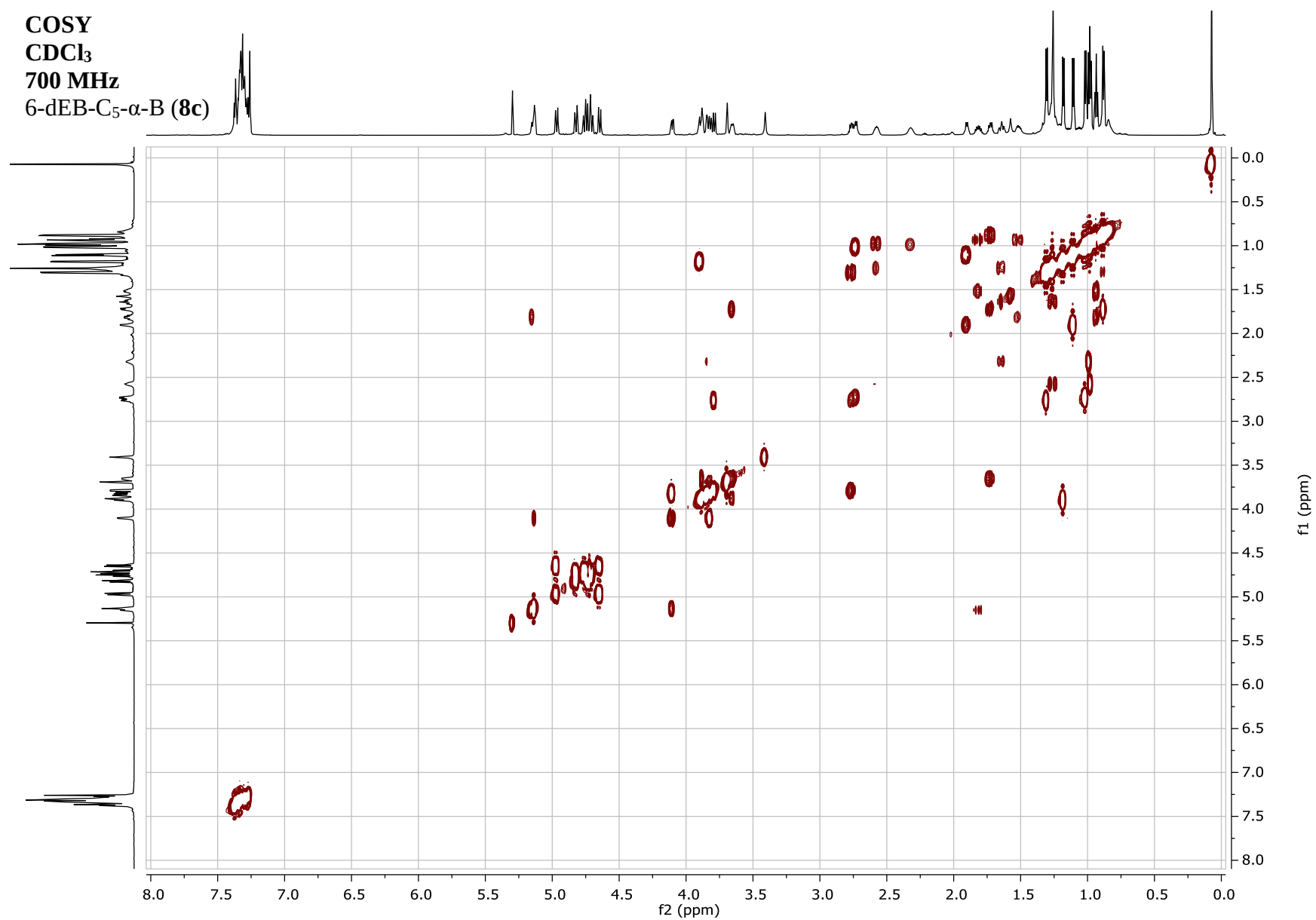




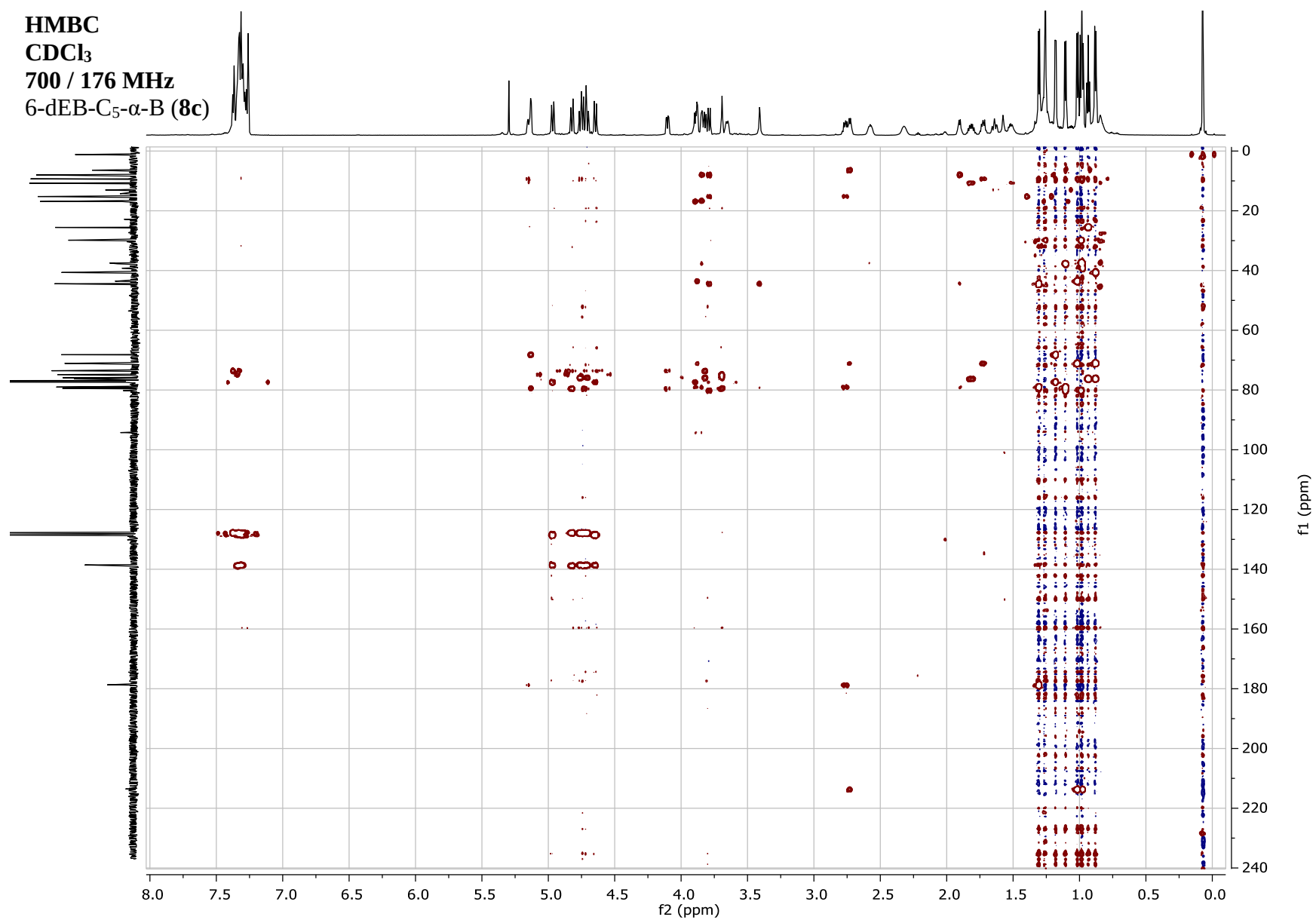
HSQC
CDCl₃
700 / 176 MHz
6-dEB-C₅-α-B (8c)

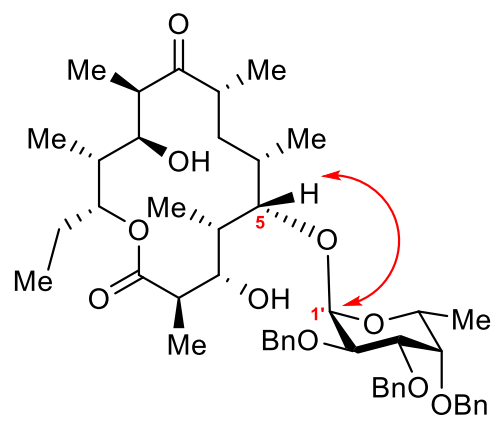


COSY
CDCl₃
700 MHz
6-dEB-C₅-α-B (8c)

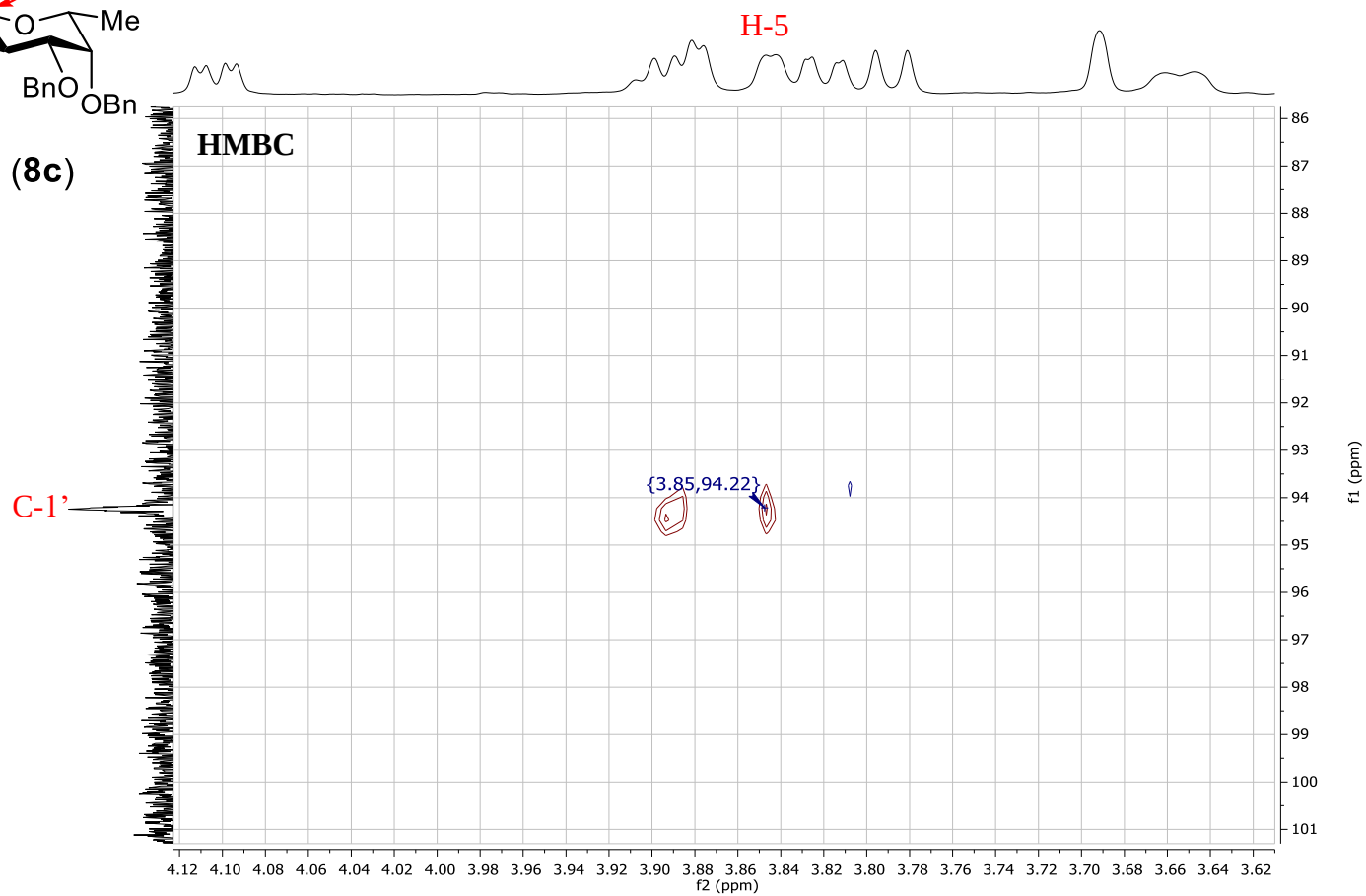


HMBC
CDCl₃
700 / 176 MHz
6-dEB-C₅-α-B (8c)

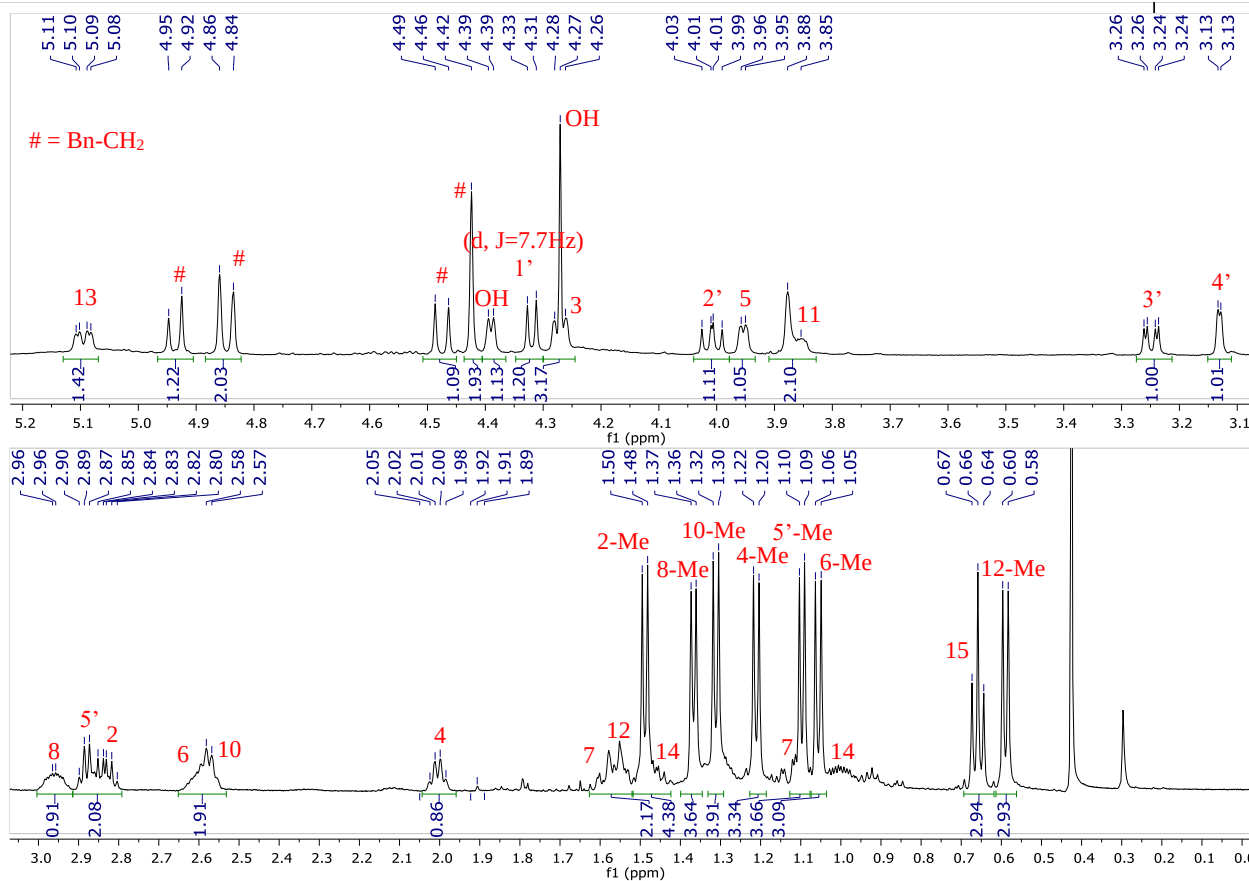
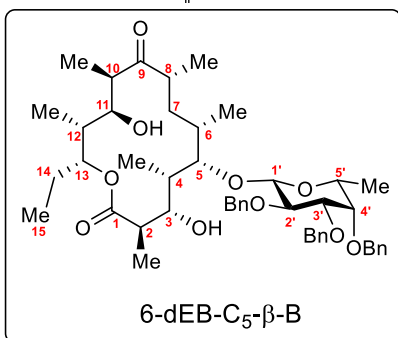


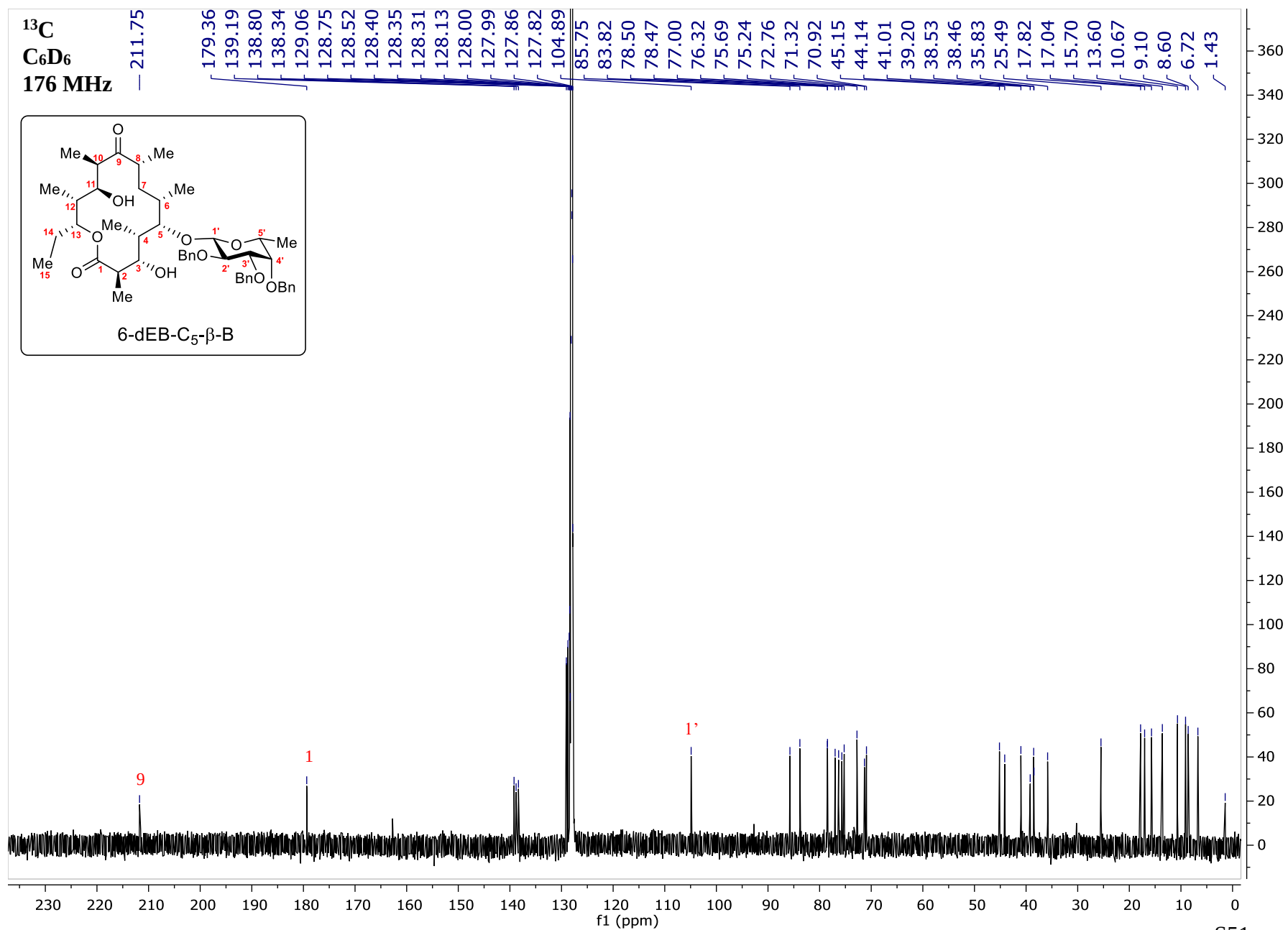


6-dEB-C₅-α-B (8c)

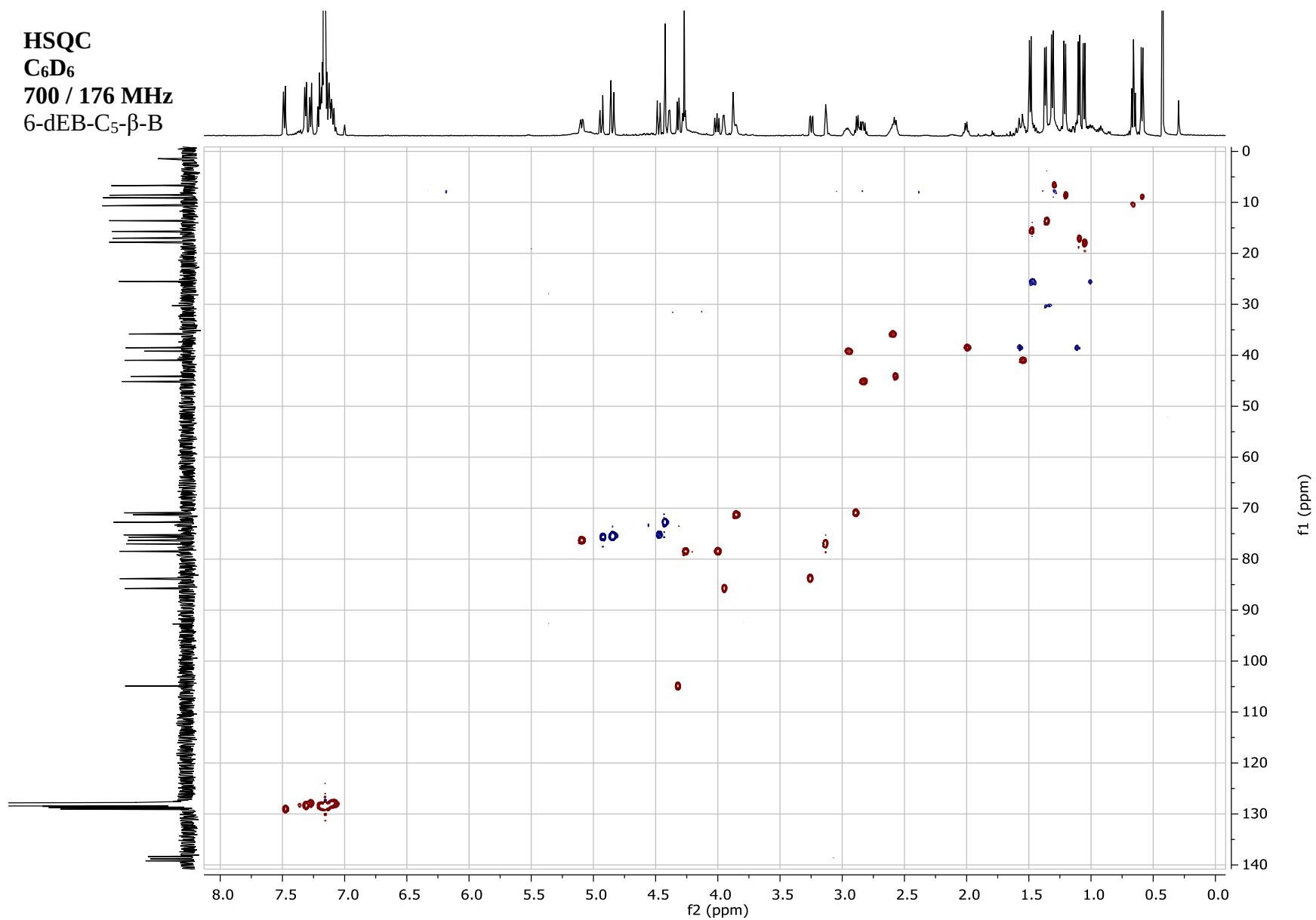


¹H
C₆D₆
500 MHz

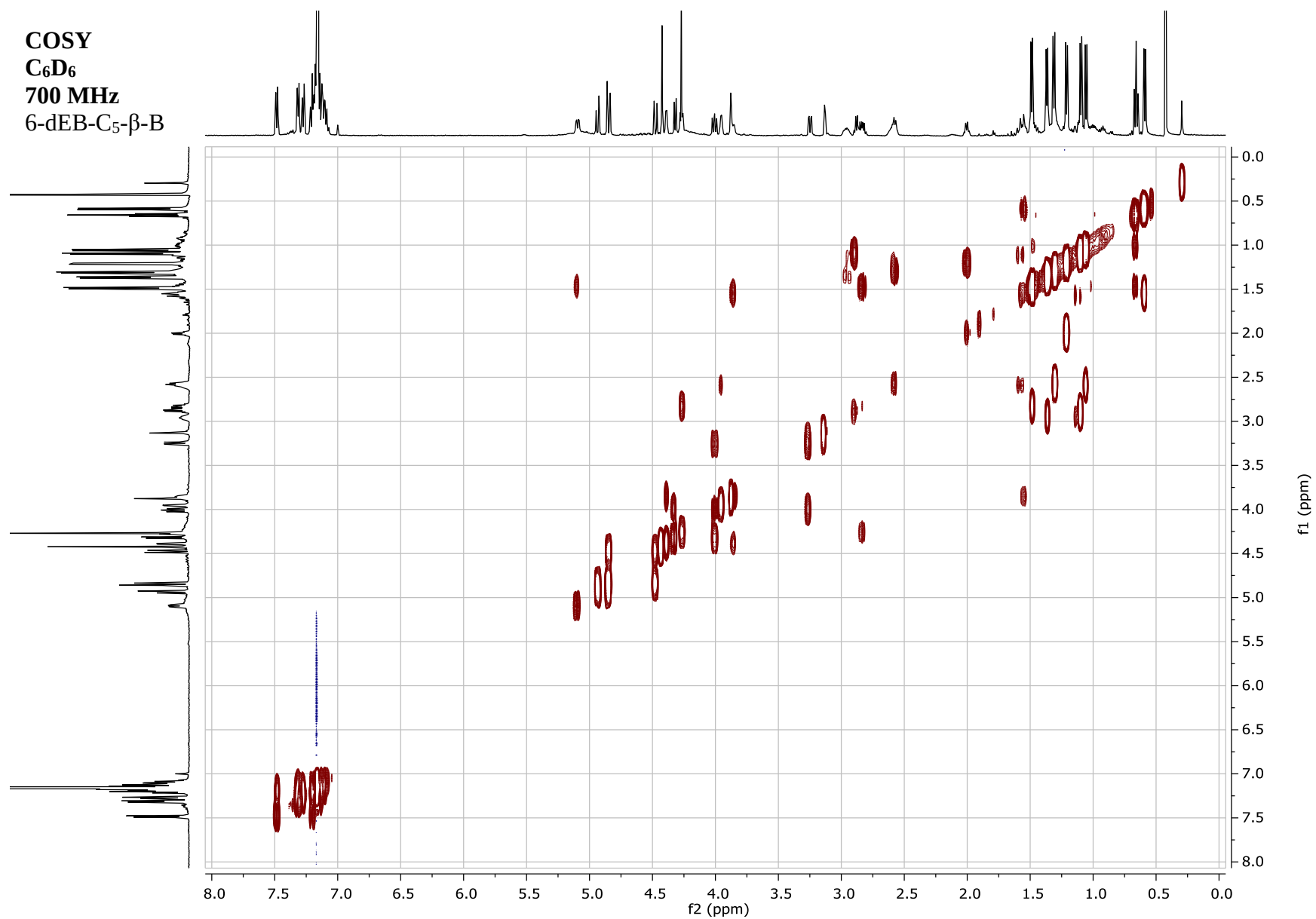




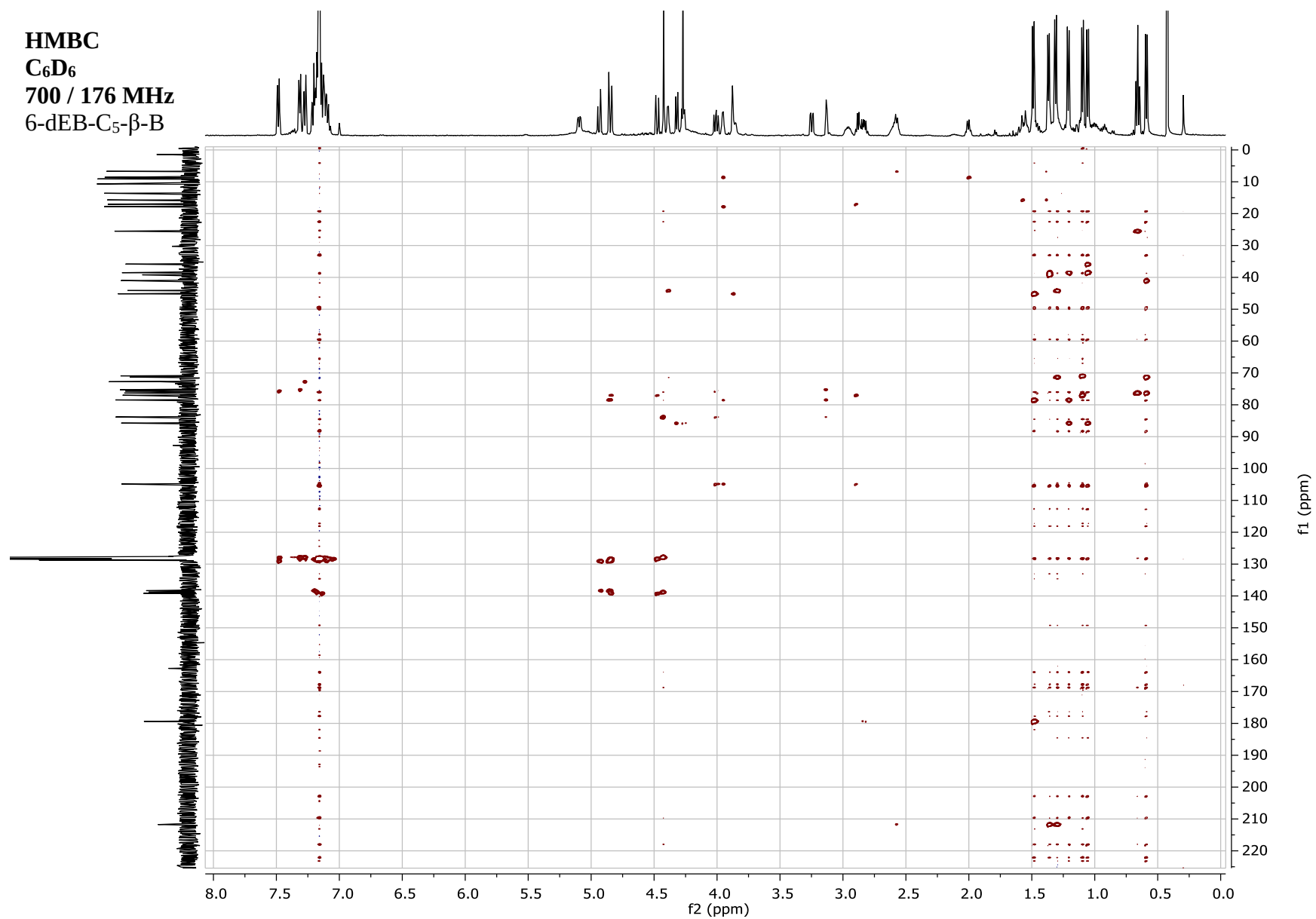
HSQC
C₆D₆
700 / 176 MHz
6-dEB-C₅-β-B

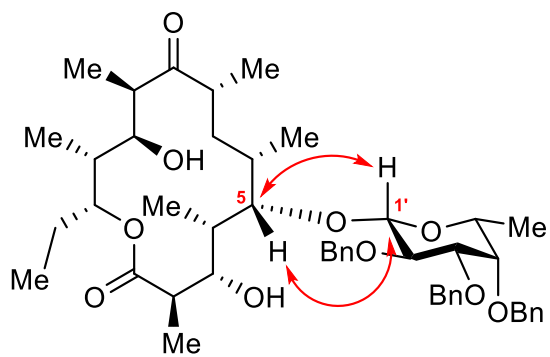


COSY
C₆D₆
700 MHz
6-dEB-C₅-β-B



HMBC
C₆D₆
700 / 176 MHz
6-dEB-C₅-β-B

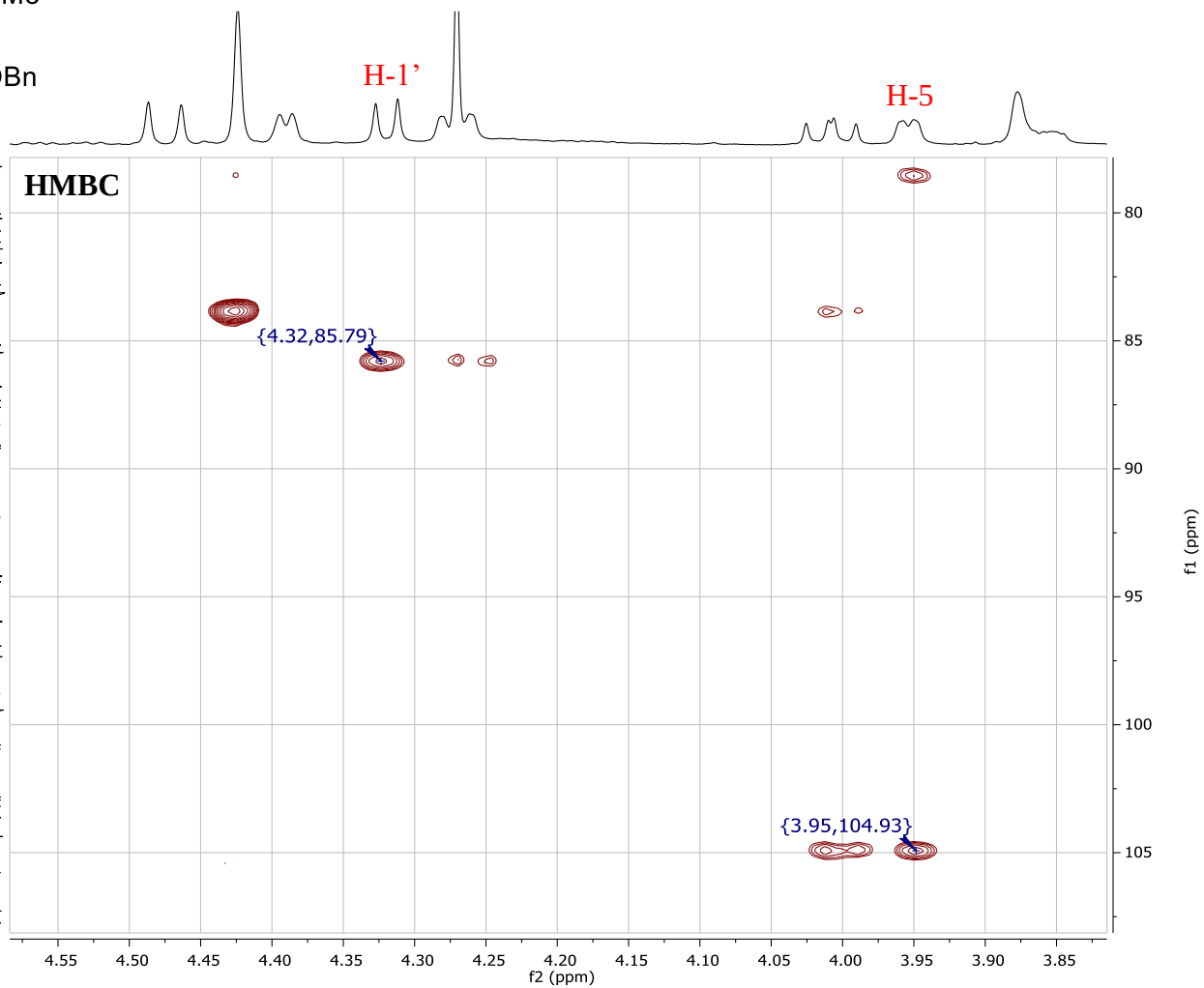




6-dEB-C₅-β-B

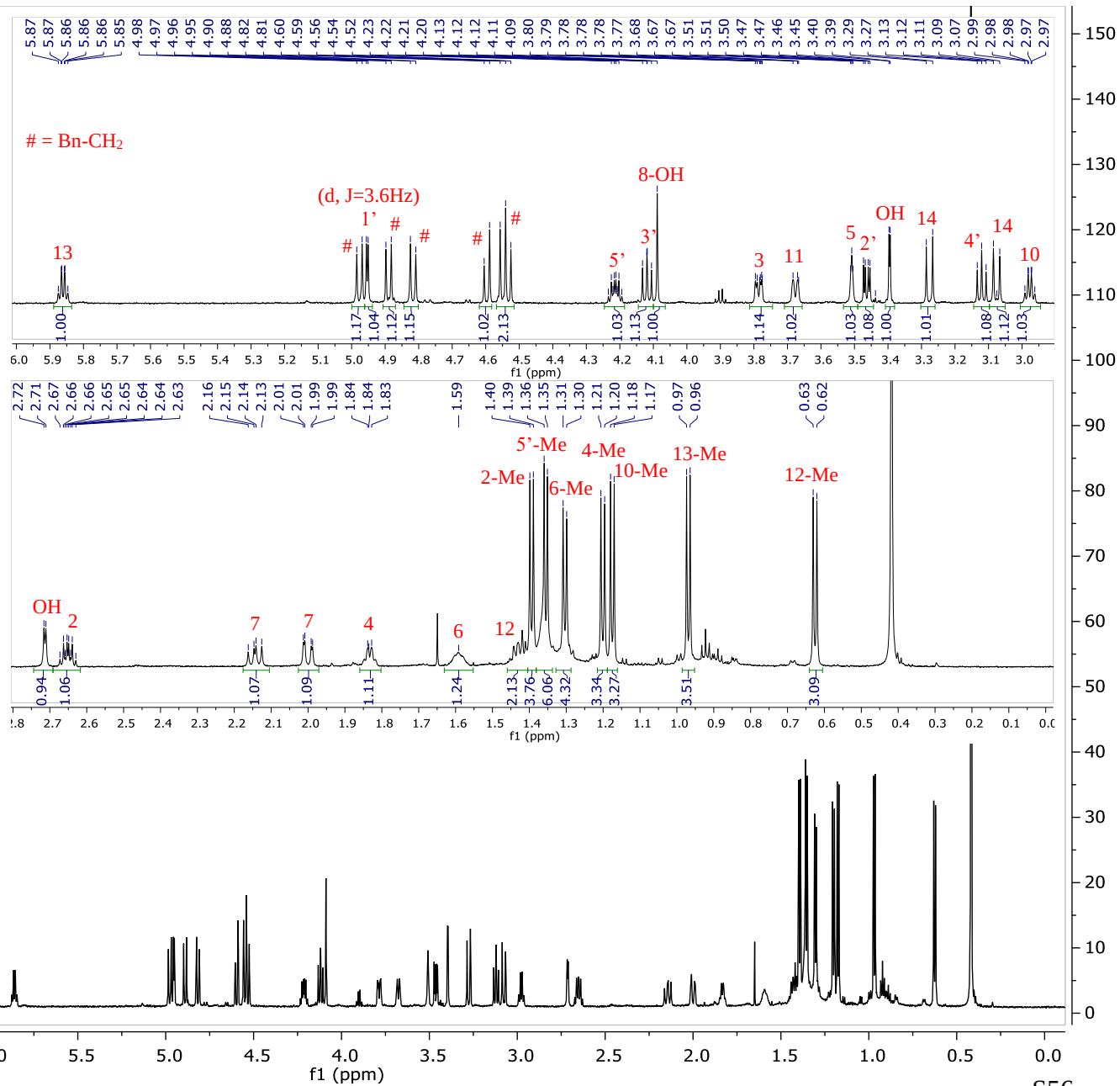
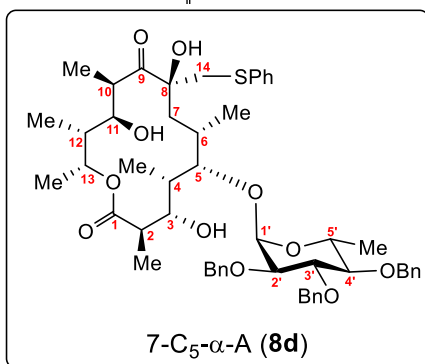
C-5

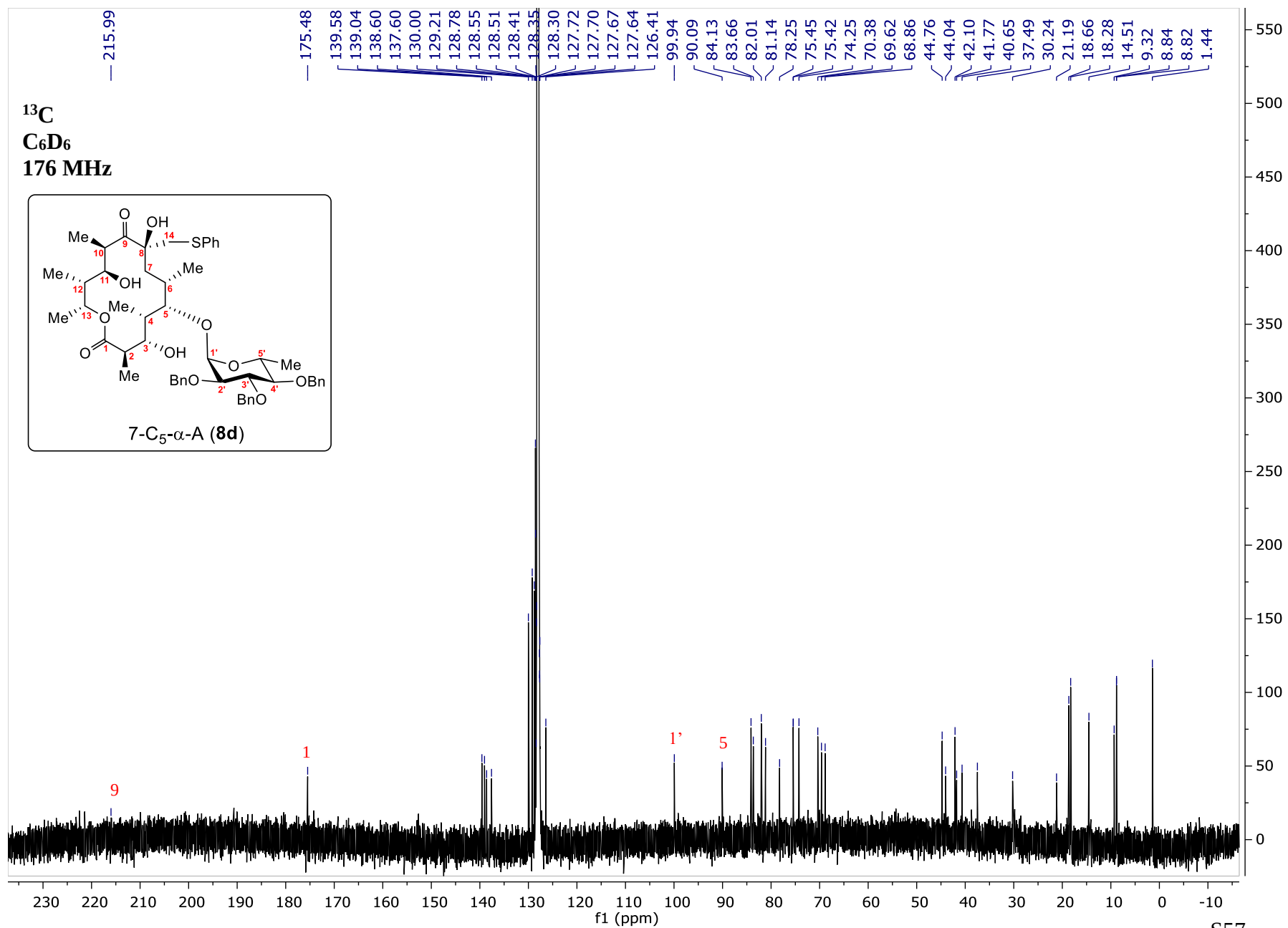
C-1'



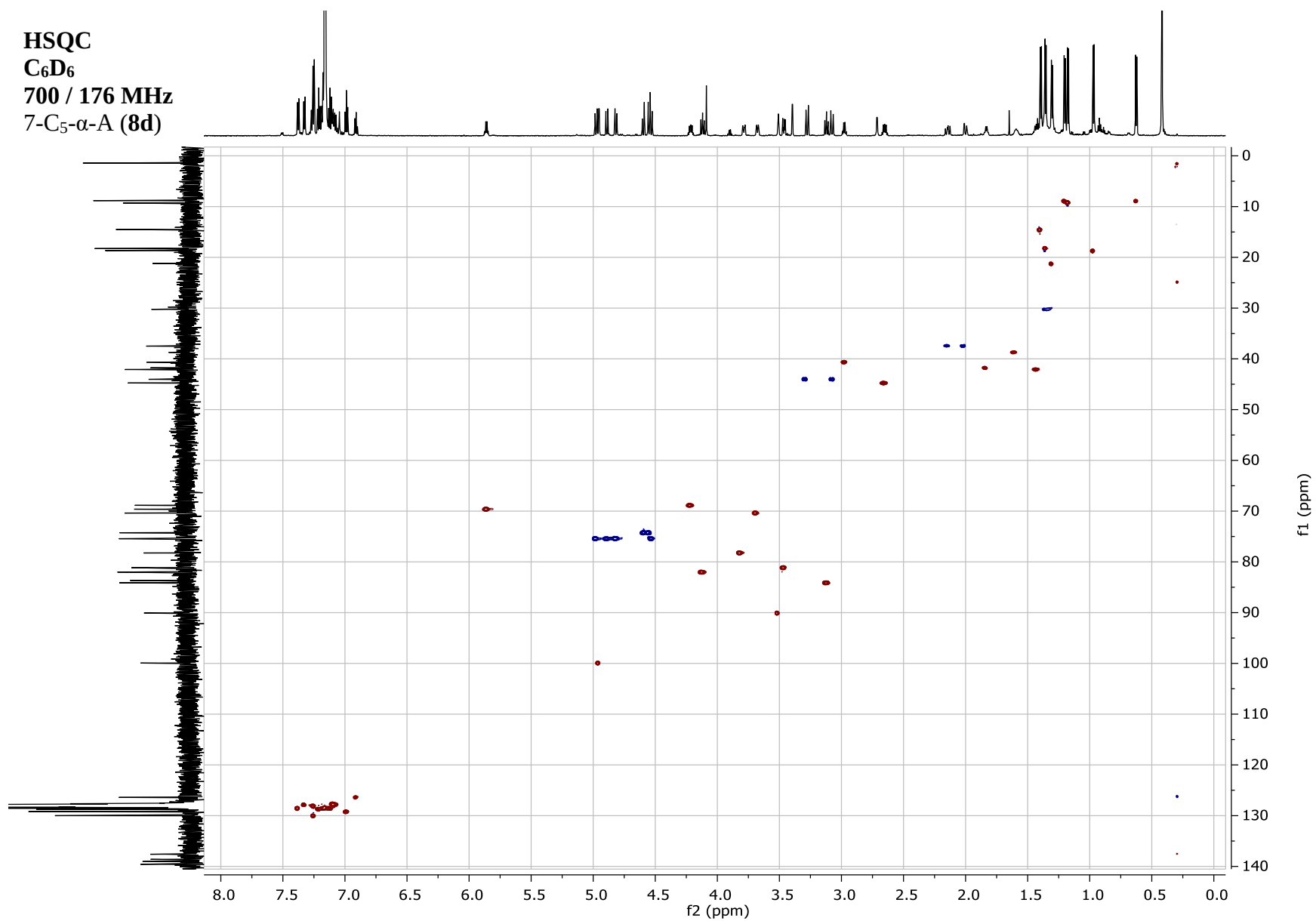
$$^1\text{H}$$

$$\text{C}_6\text{D}_6$$

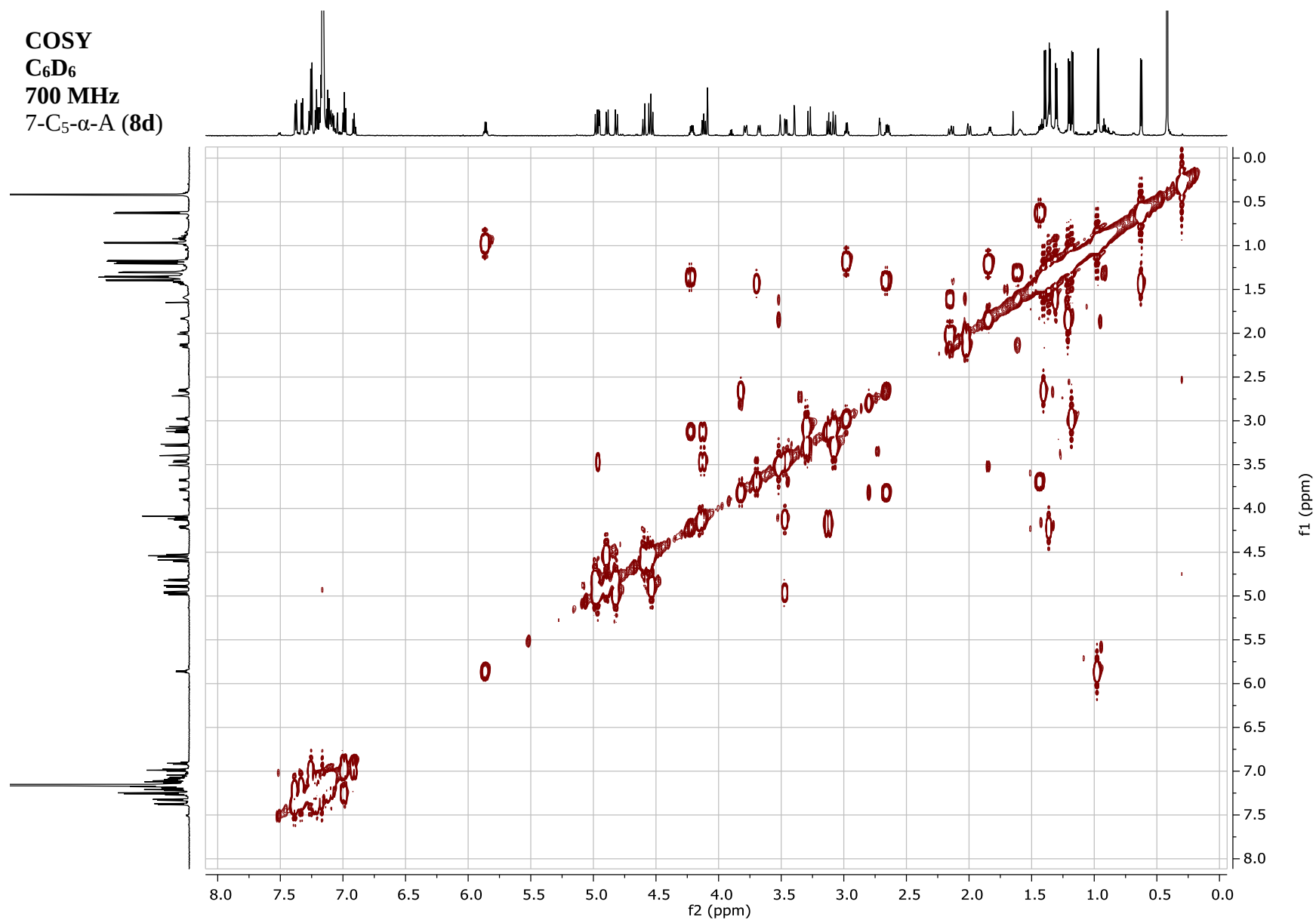
$$700 \text{ MHz}$$




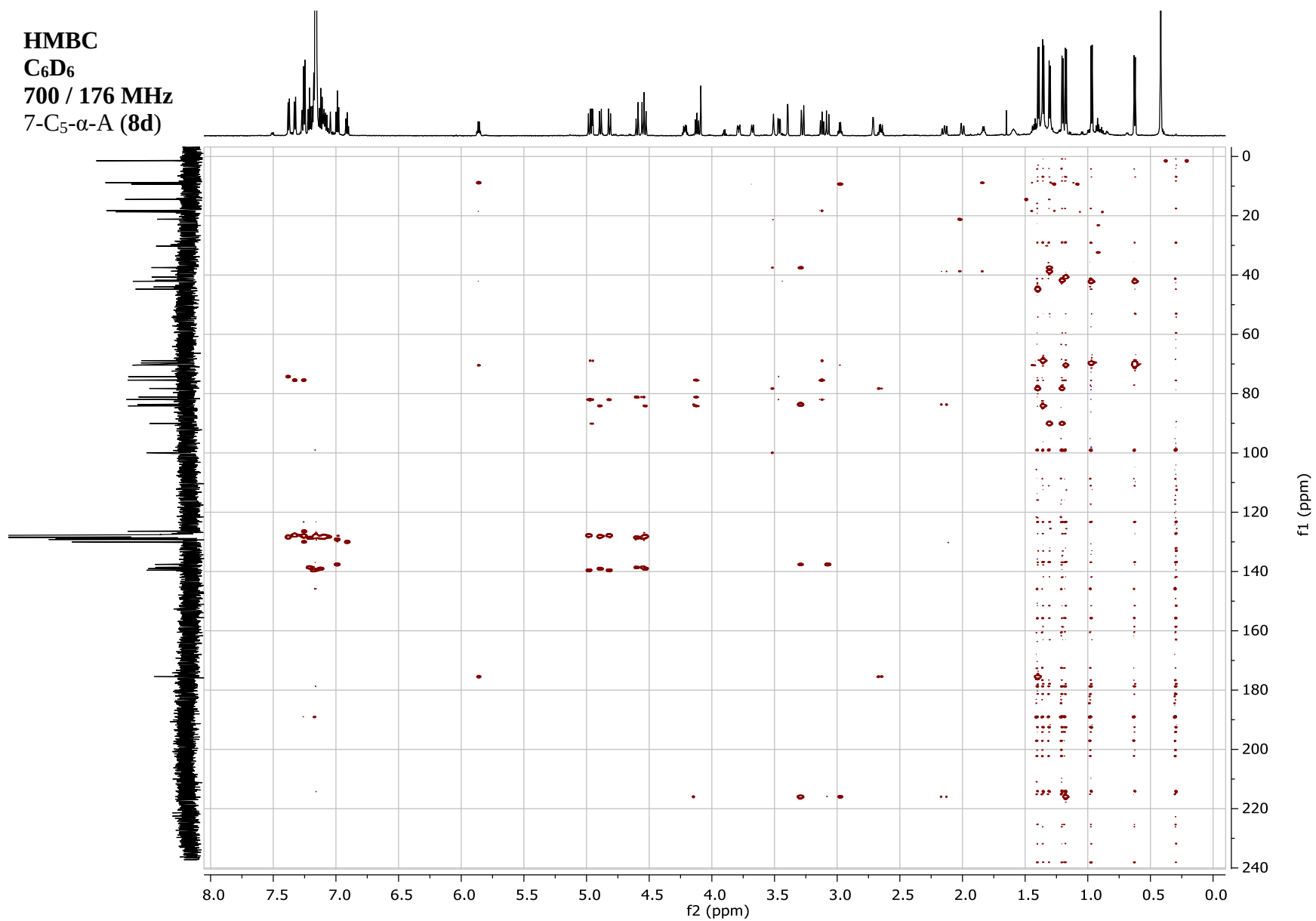
HSQC
C₆D₆
700 / 176 MHz
7-C₅- α -A (8d)

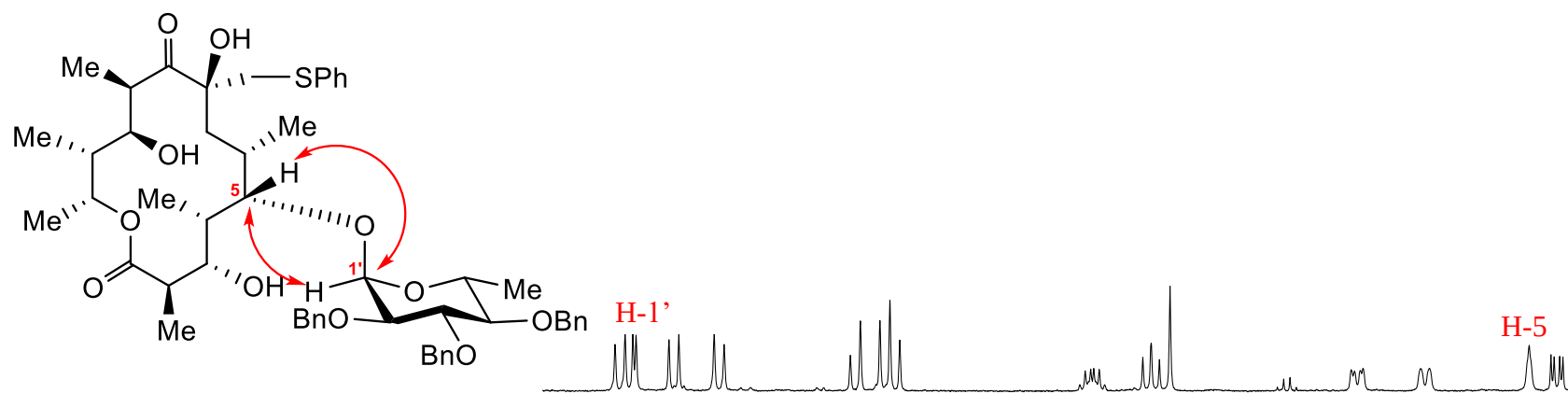


COSY
C₆D₆
700 MHz
7-C₅- α -A (8d)

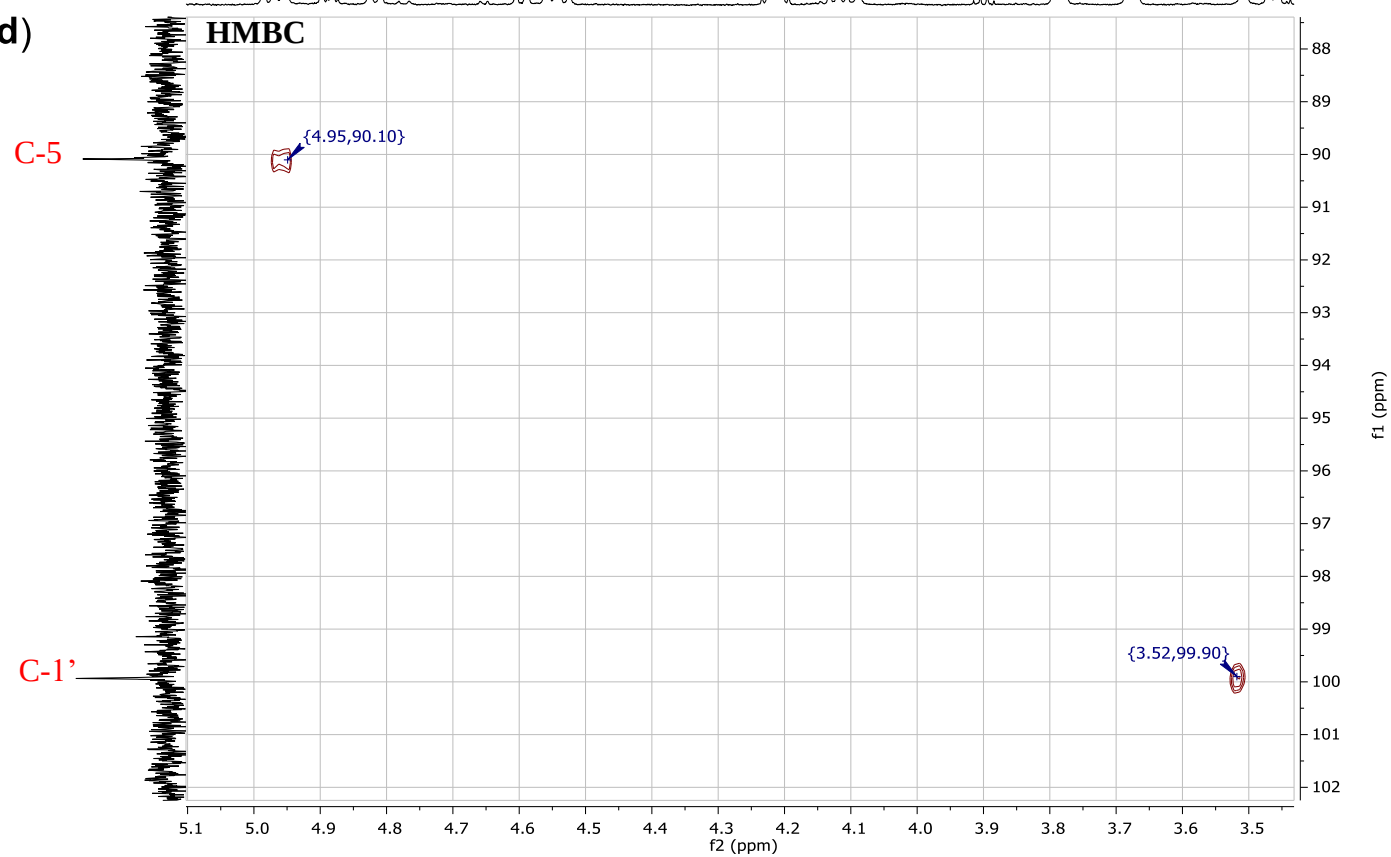


HMBC
C₆D₆
700 / 176 MHz
7-C₅- α -A (8d)

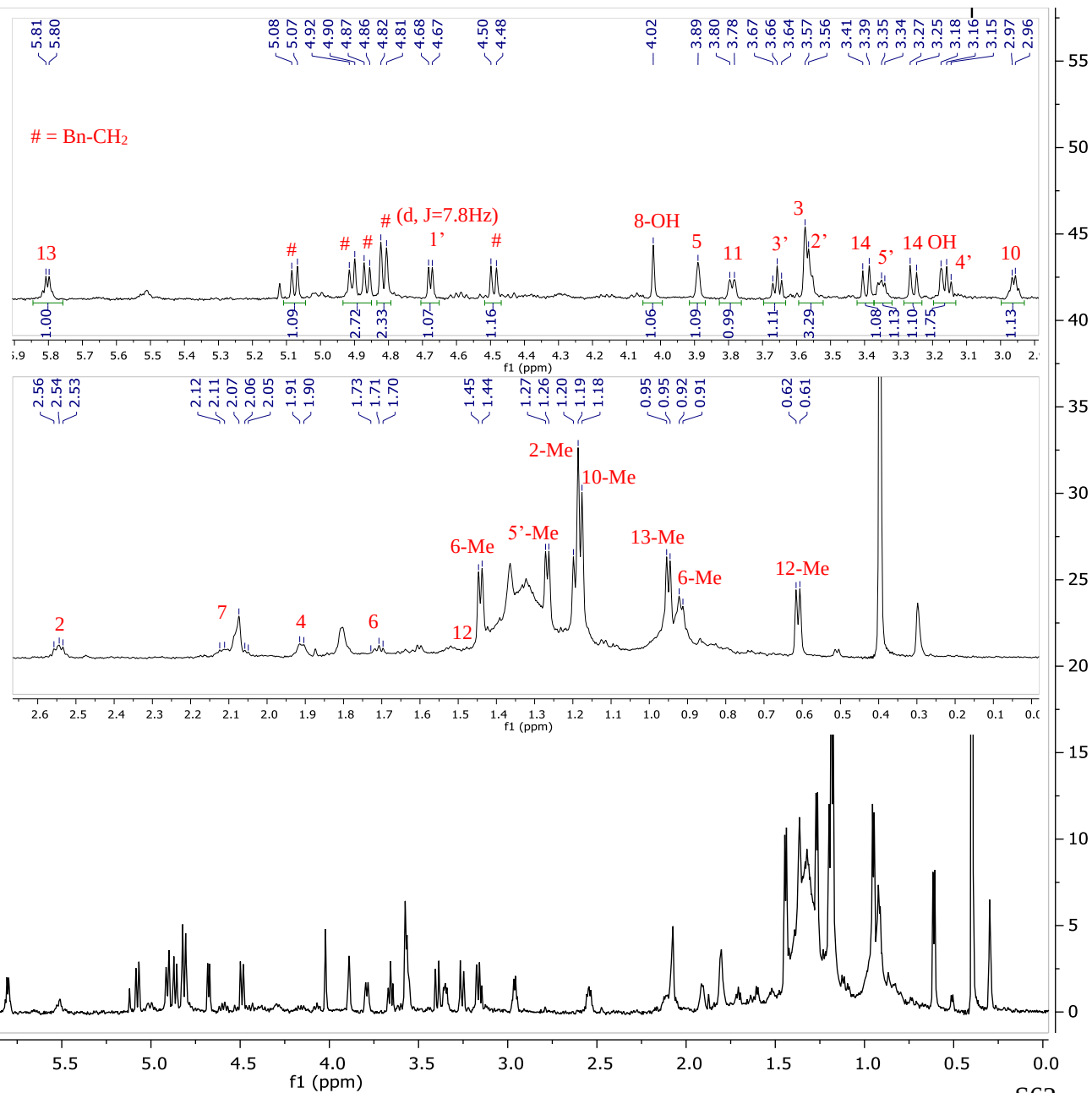
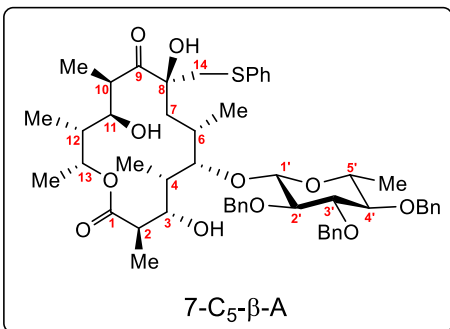


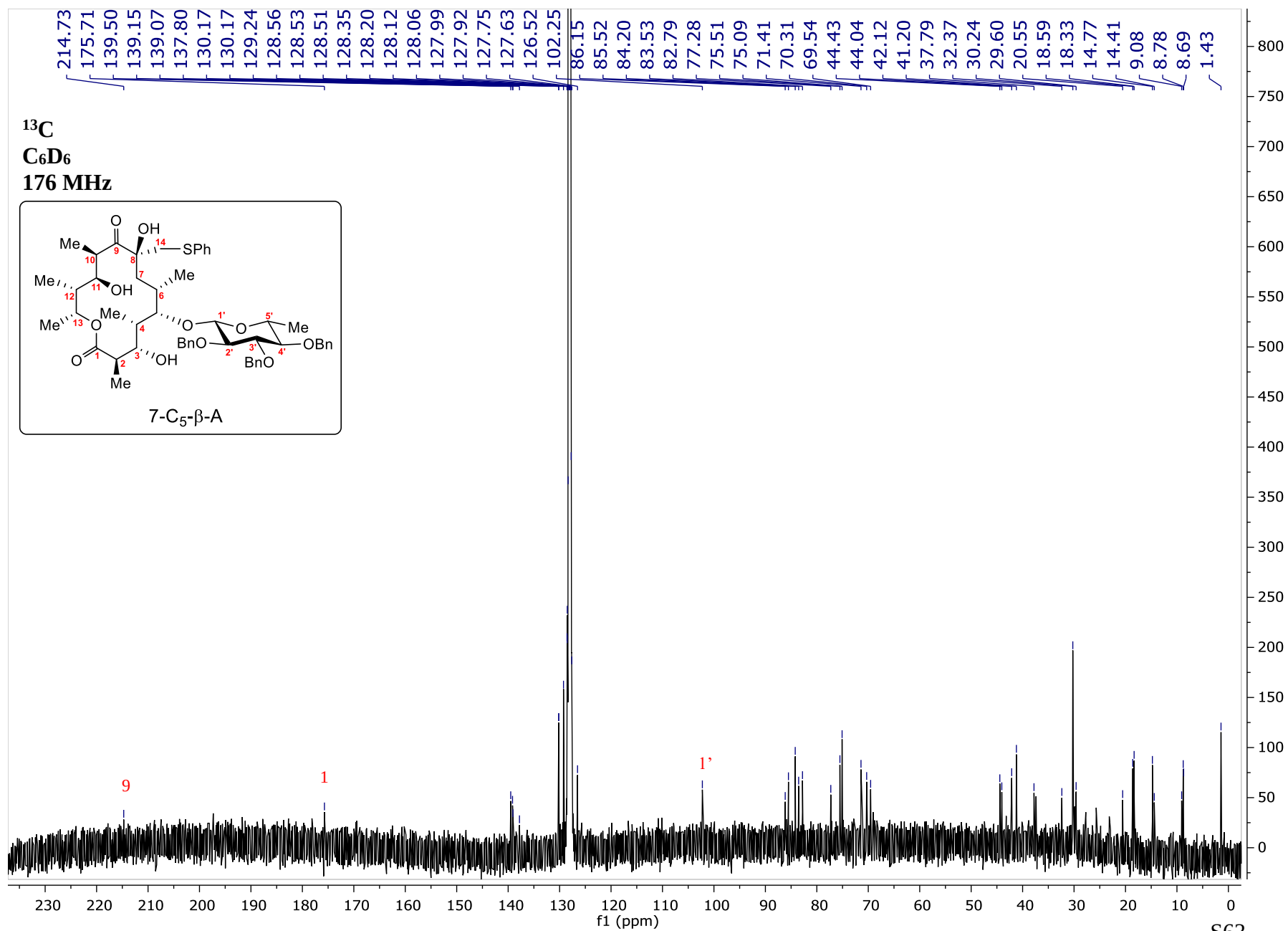


7-C₅-α-A (8d)

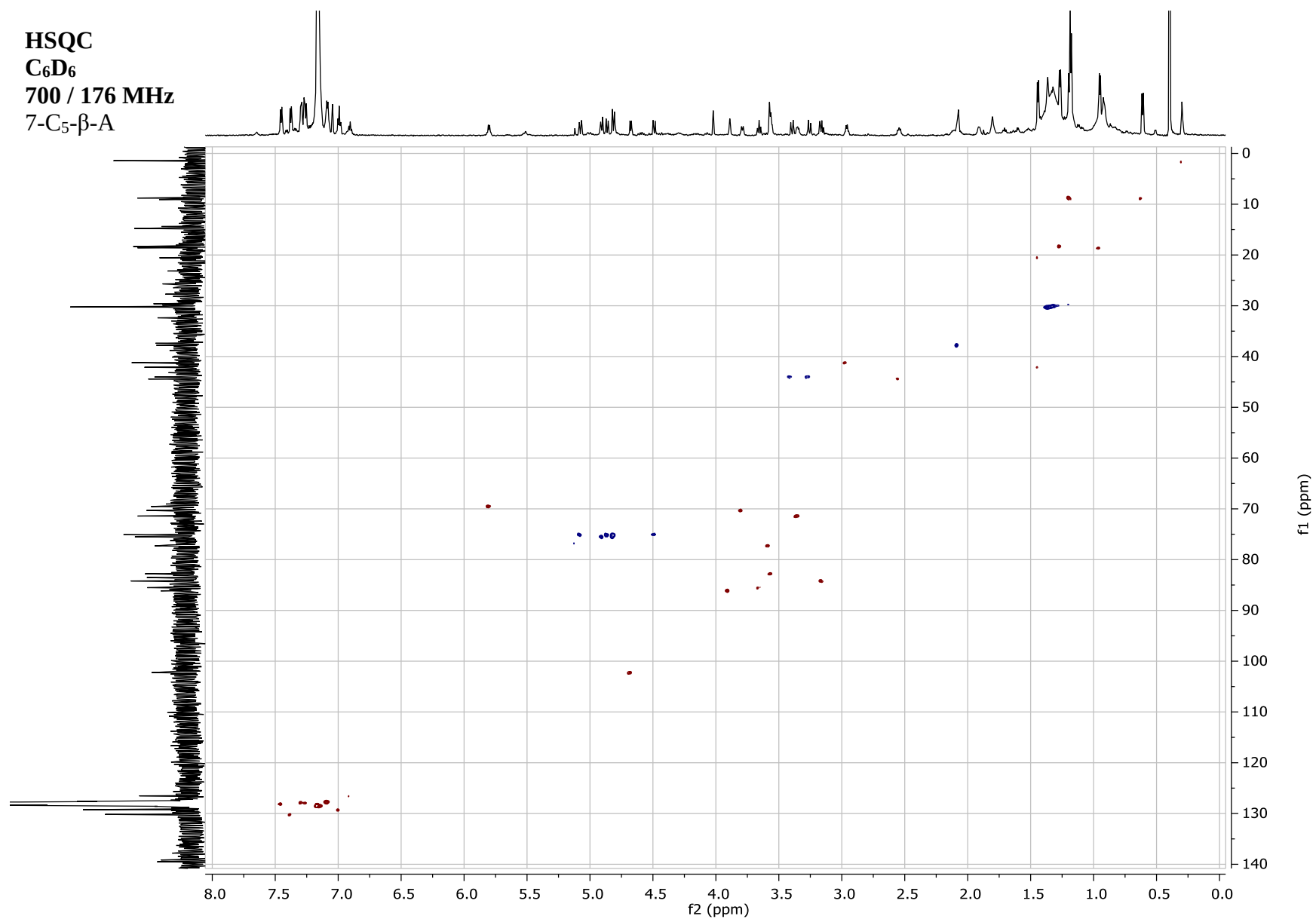


¹H
C₆D₆
700 MHz

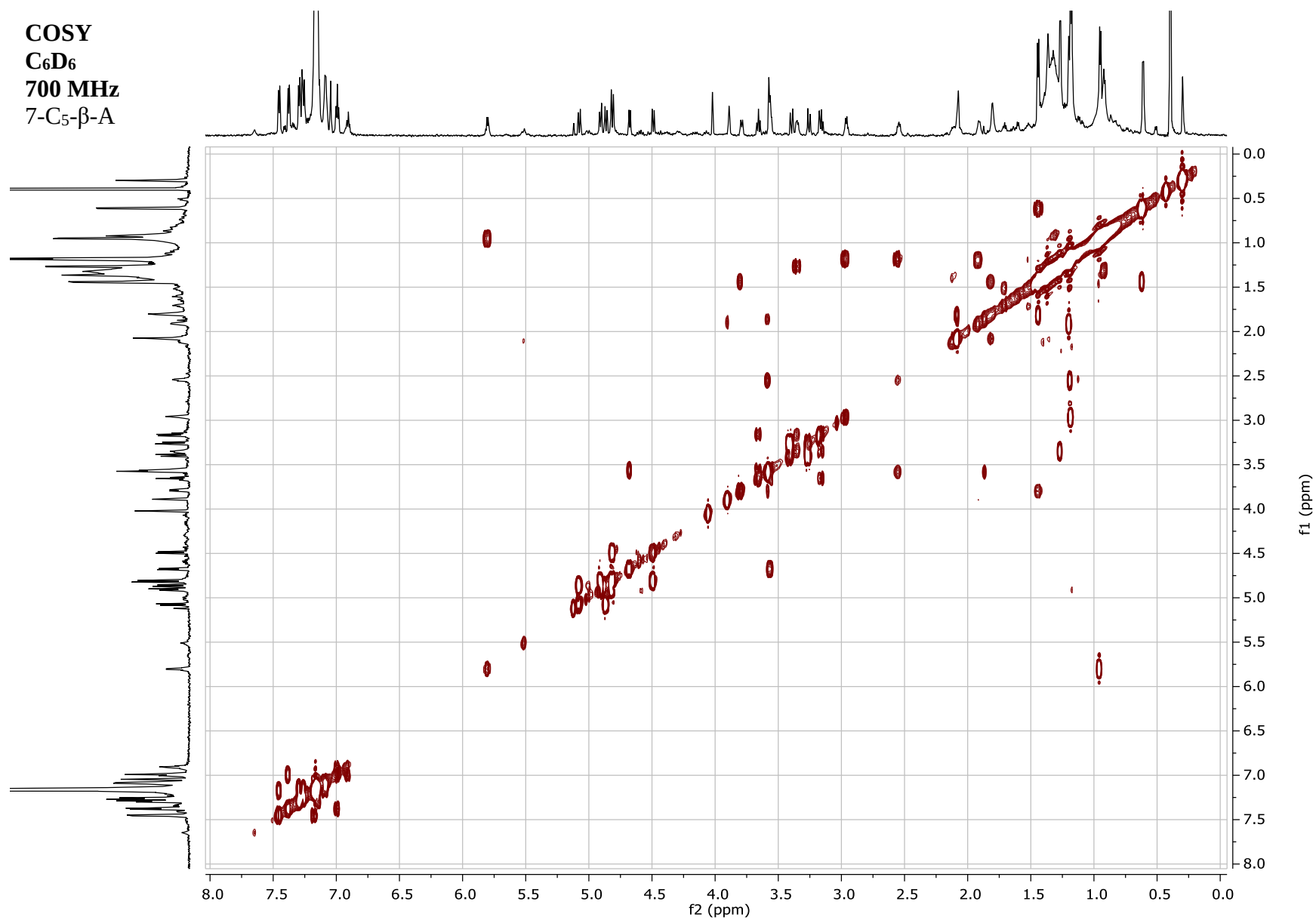




HSQC
C₆D₆
700 / 176 MHz
7-C₅-β-A



COSY
C₆D₆
700 MHz
7-C₅-β-A

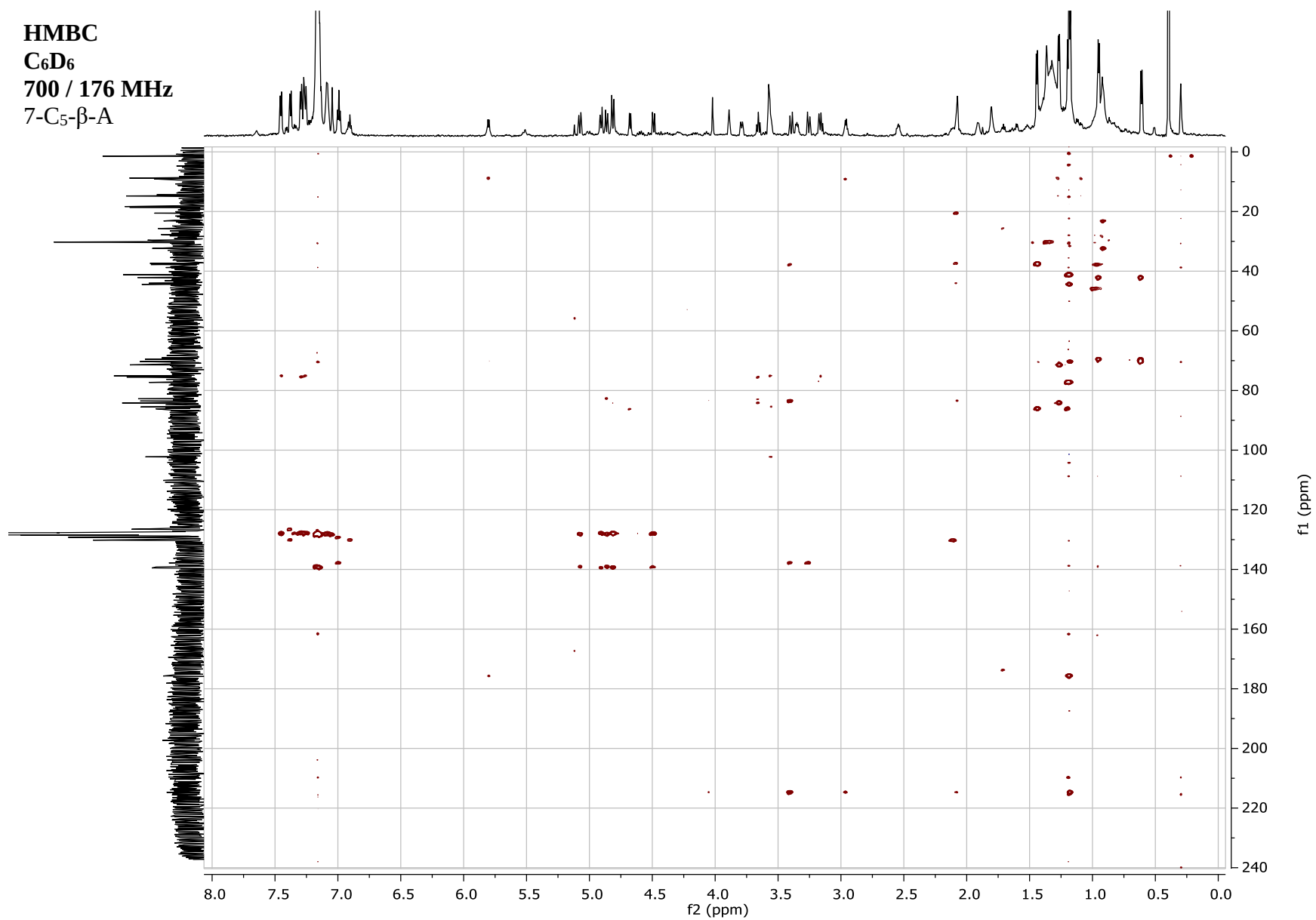


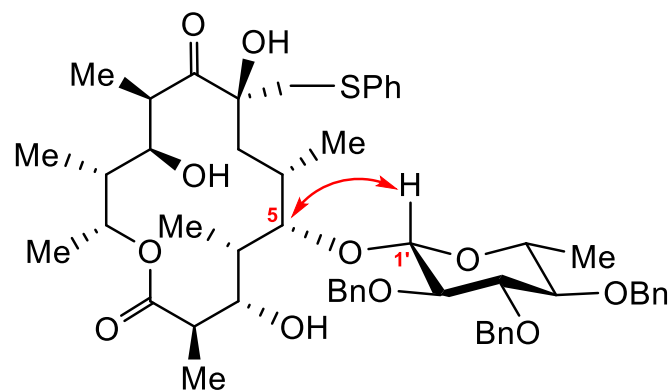
HMBC

C₆D₆

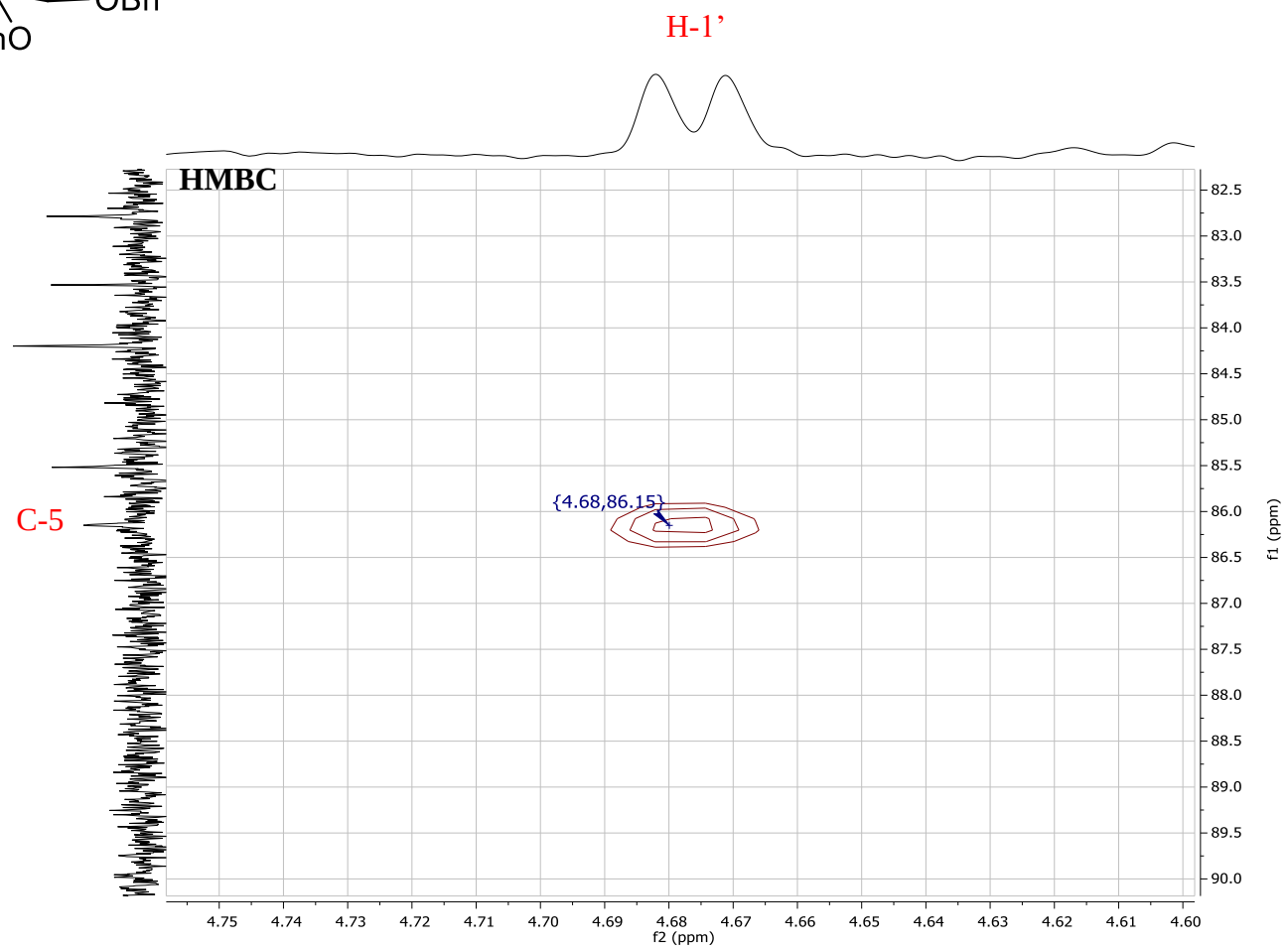
700 / 176 MHz

7-C₅-β-A

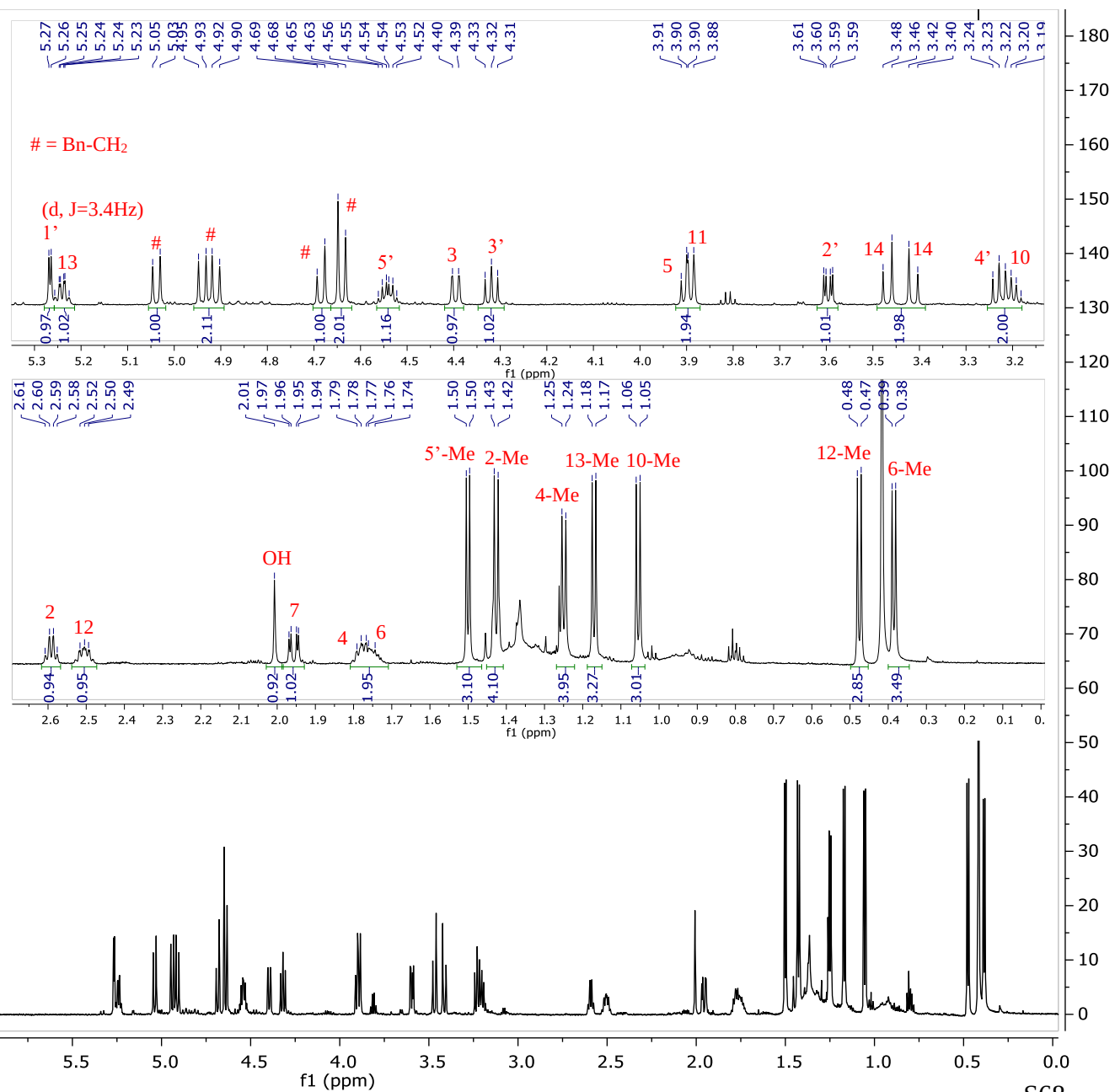
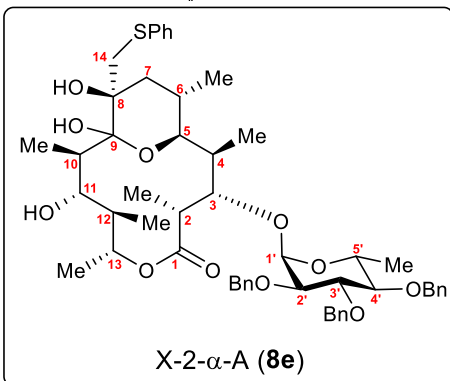


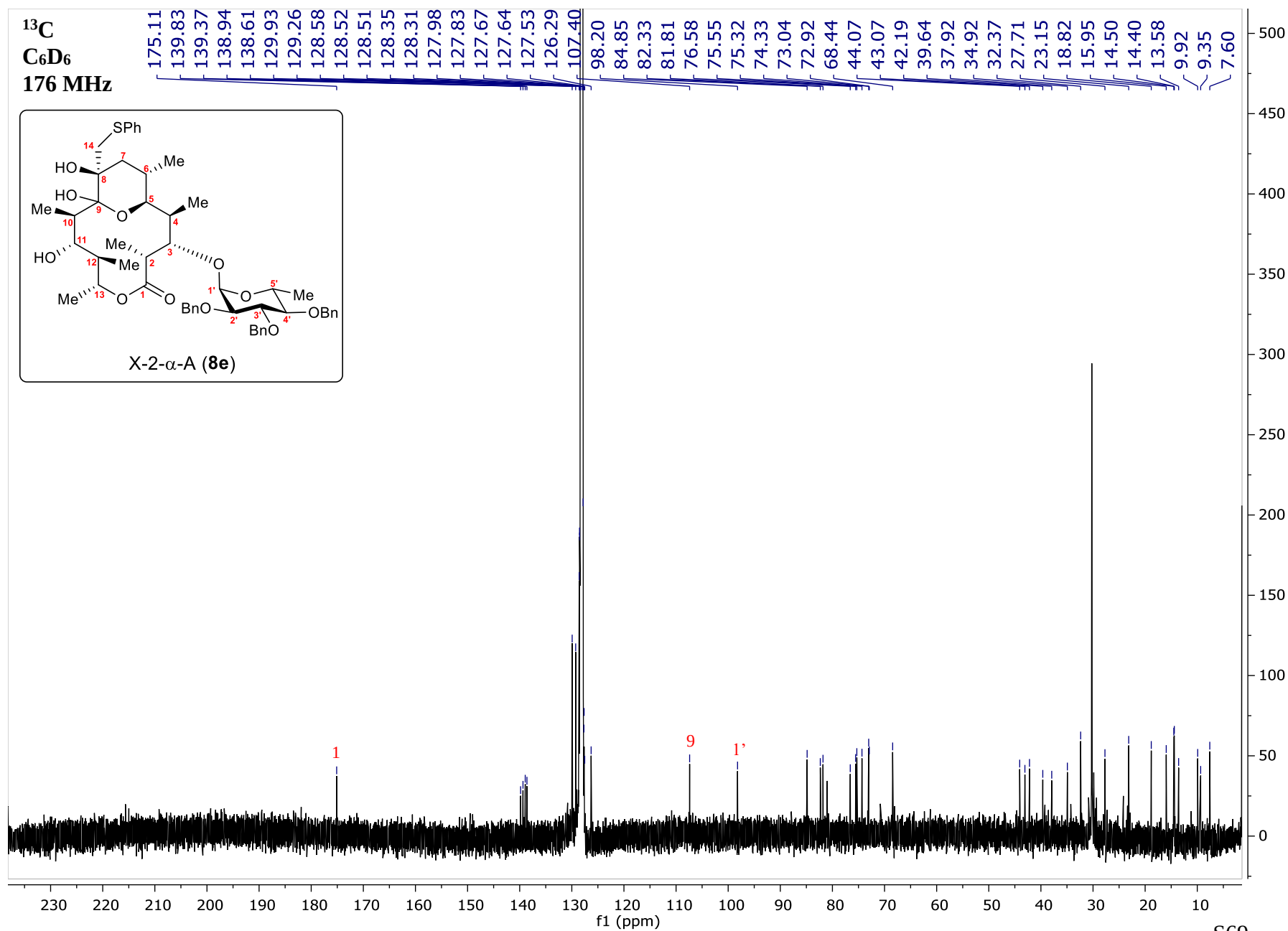


7-C₅-β-A



¹H
C₆D₆
700 MHz



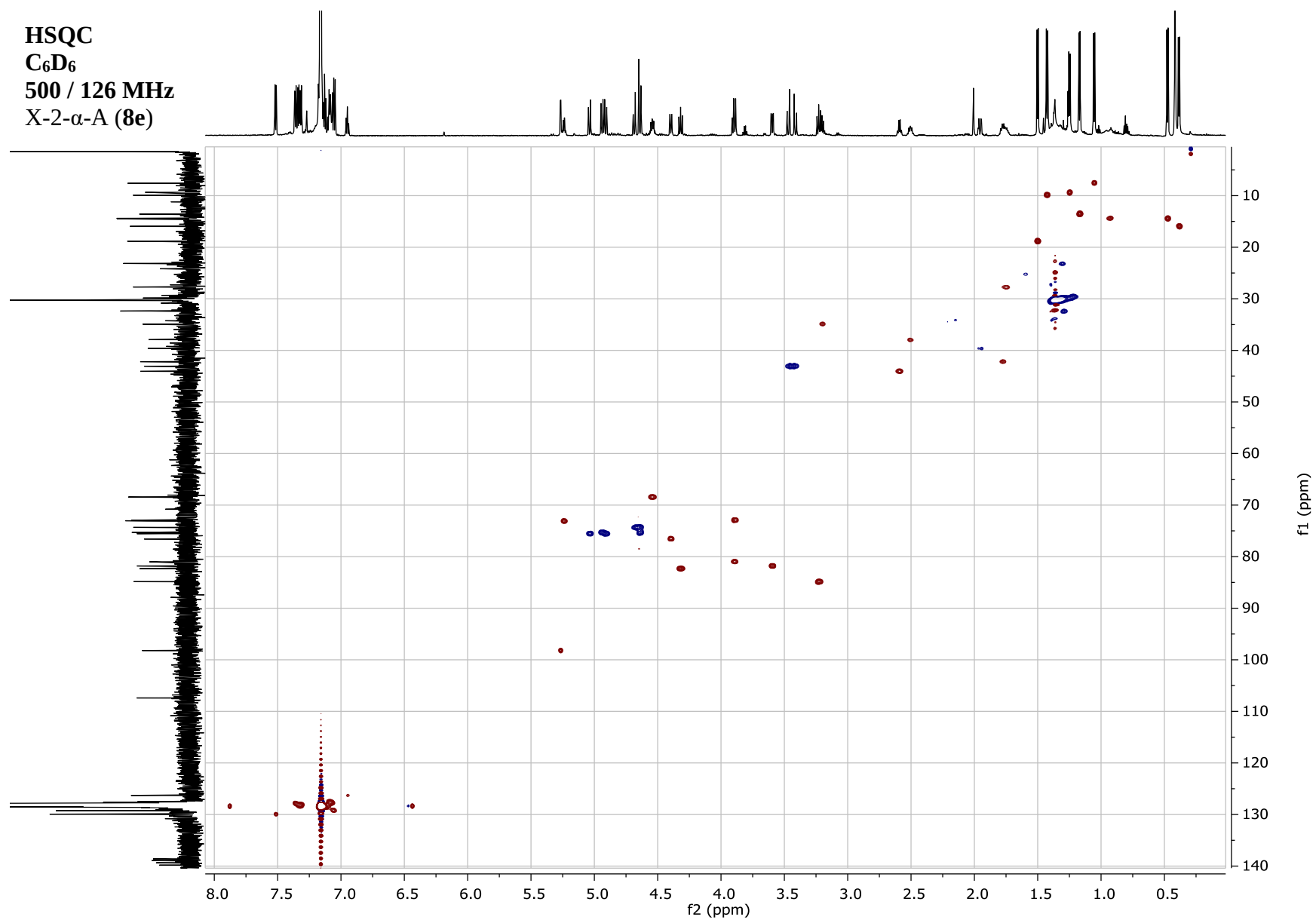


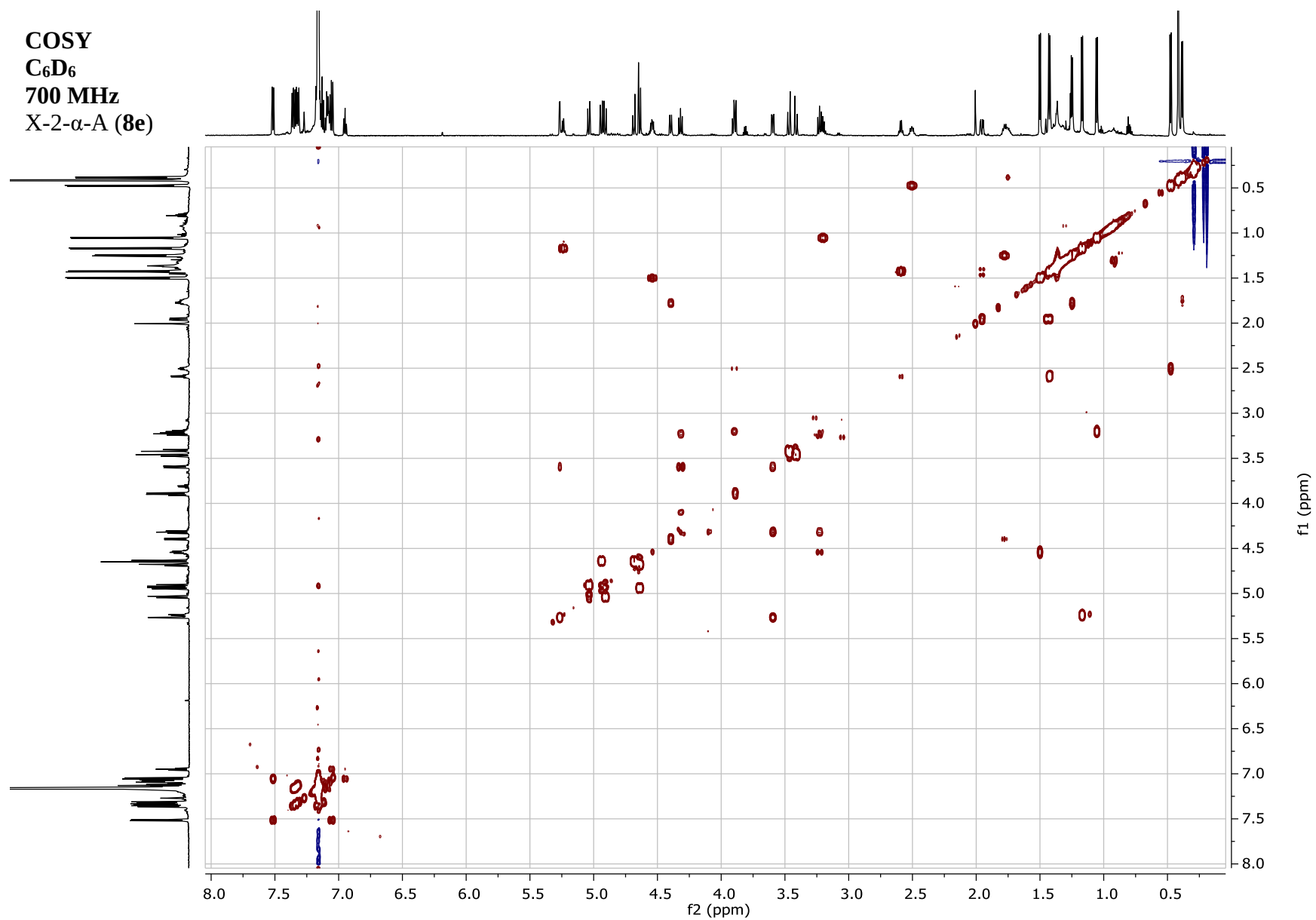
HSQC

C₆D₆

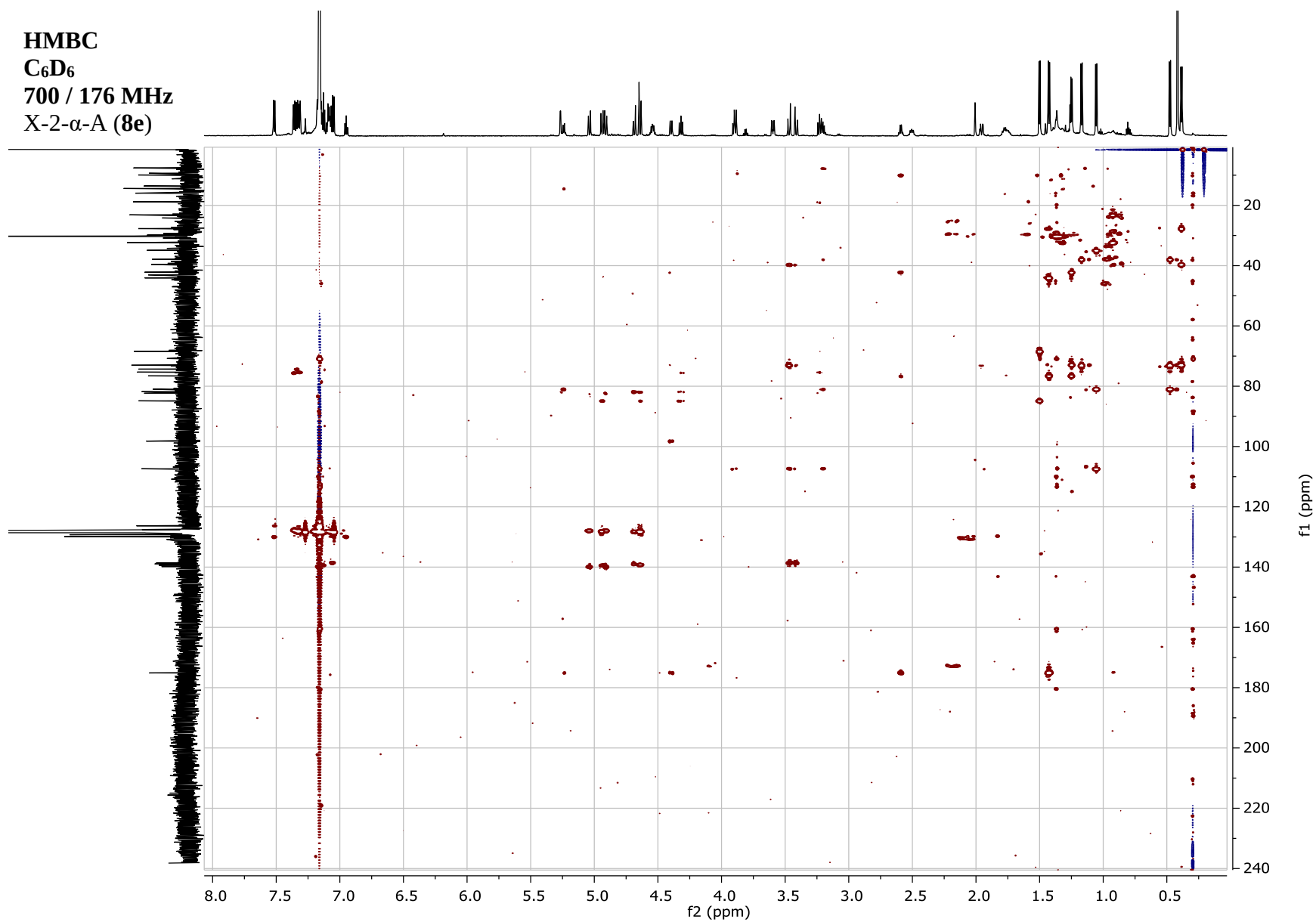
500 / 126 MHz

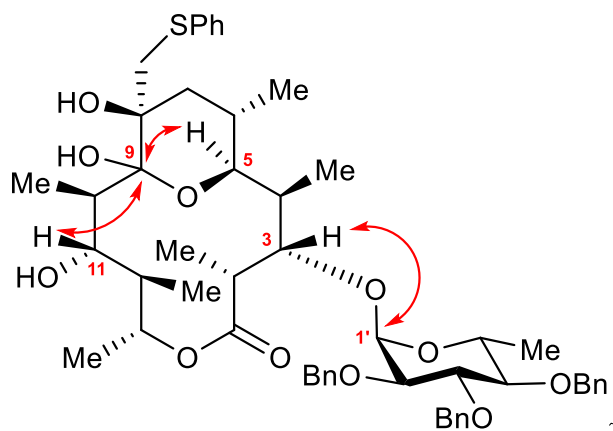
X-2- α -A (8e)



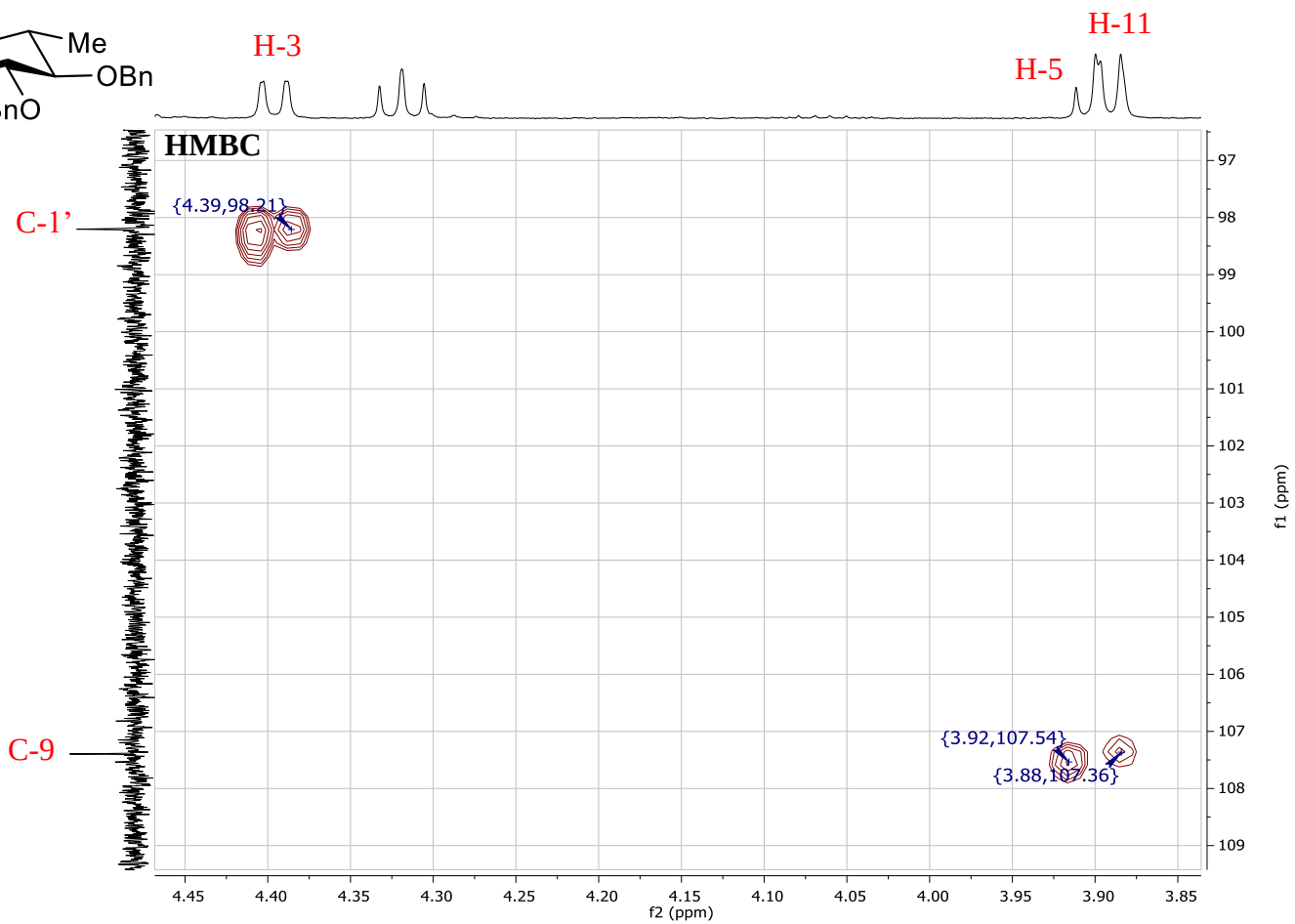


HMBC
C₆D₆
700 / 176 MHz
X-2- α -A (8e)

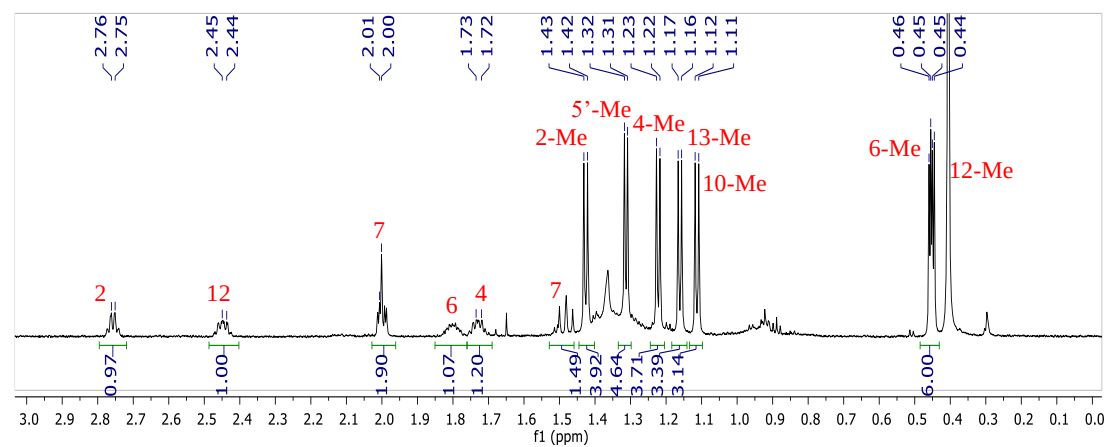
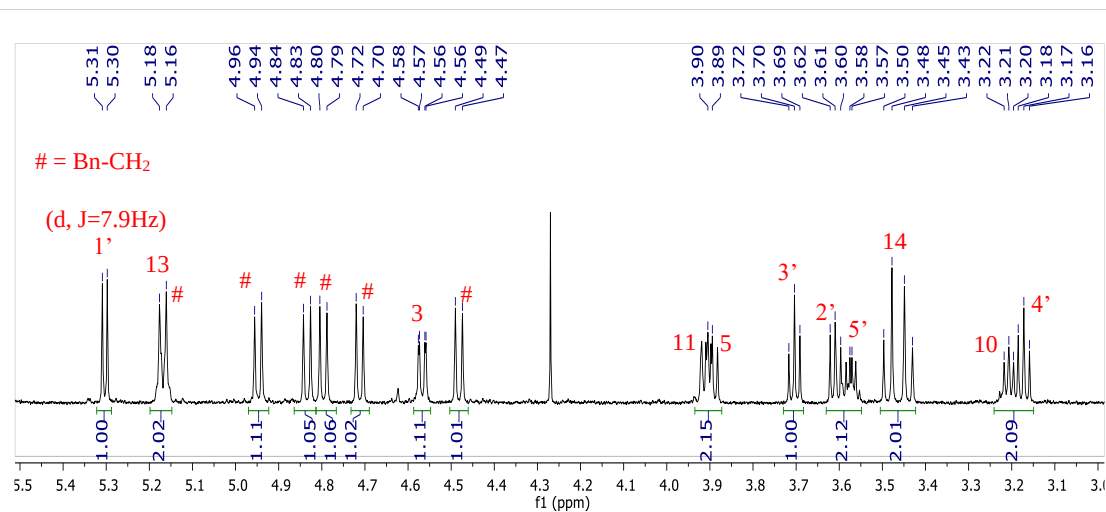
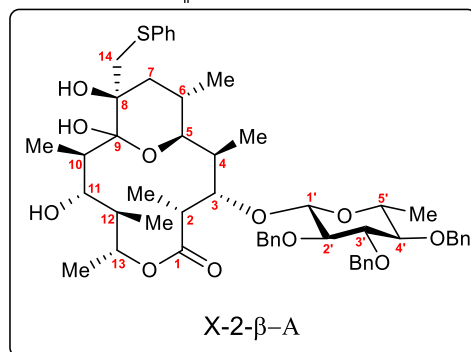




X-2- α -A (8e)

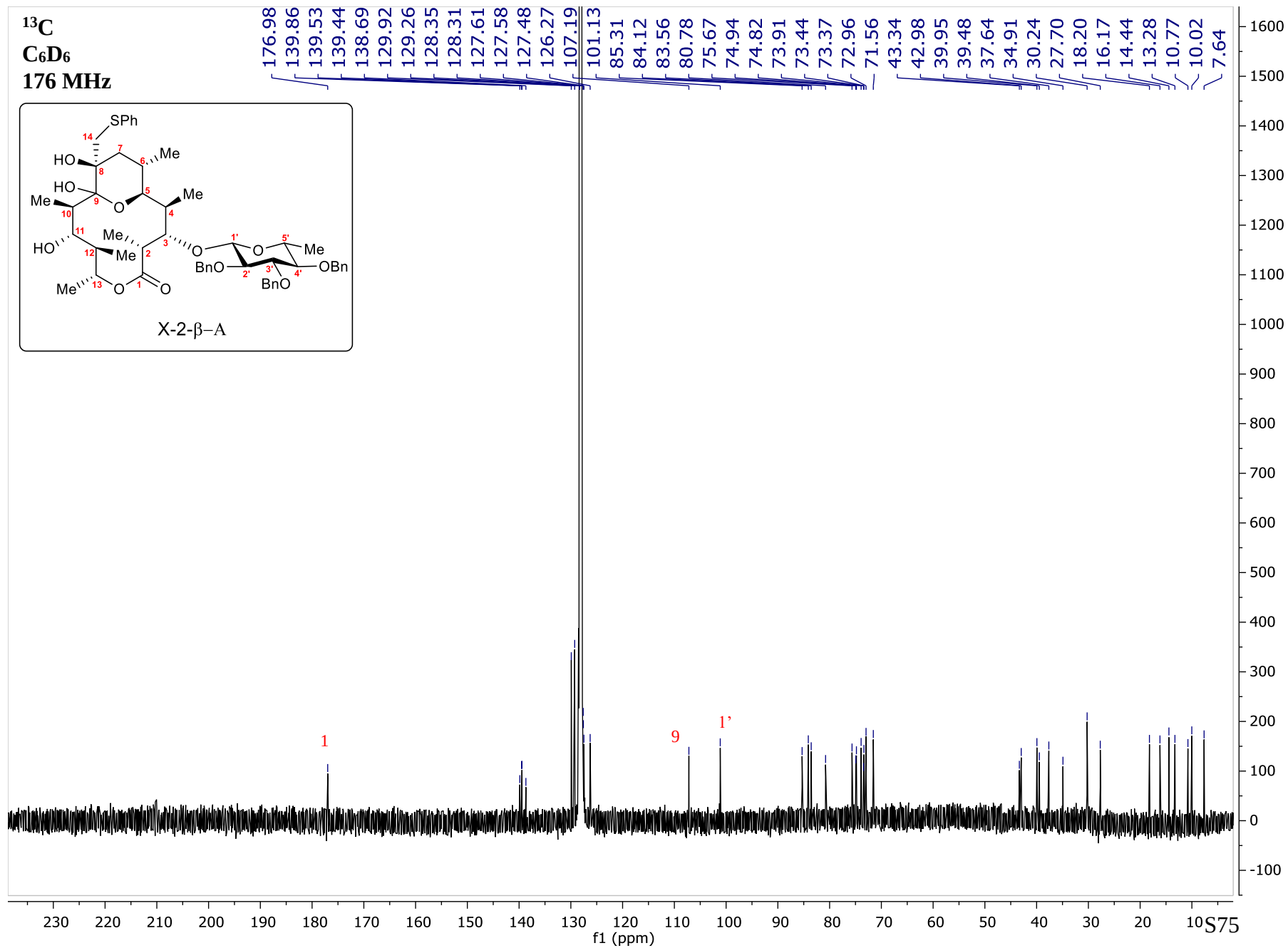


¹H
C₆D₆
700 MHz

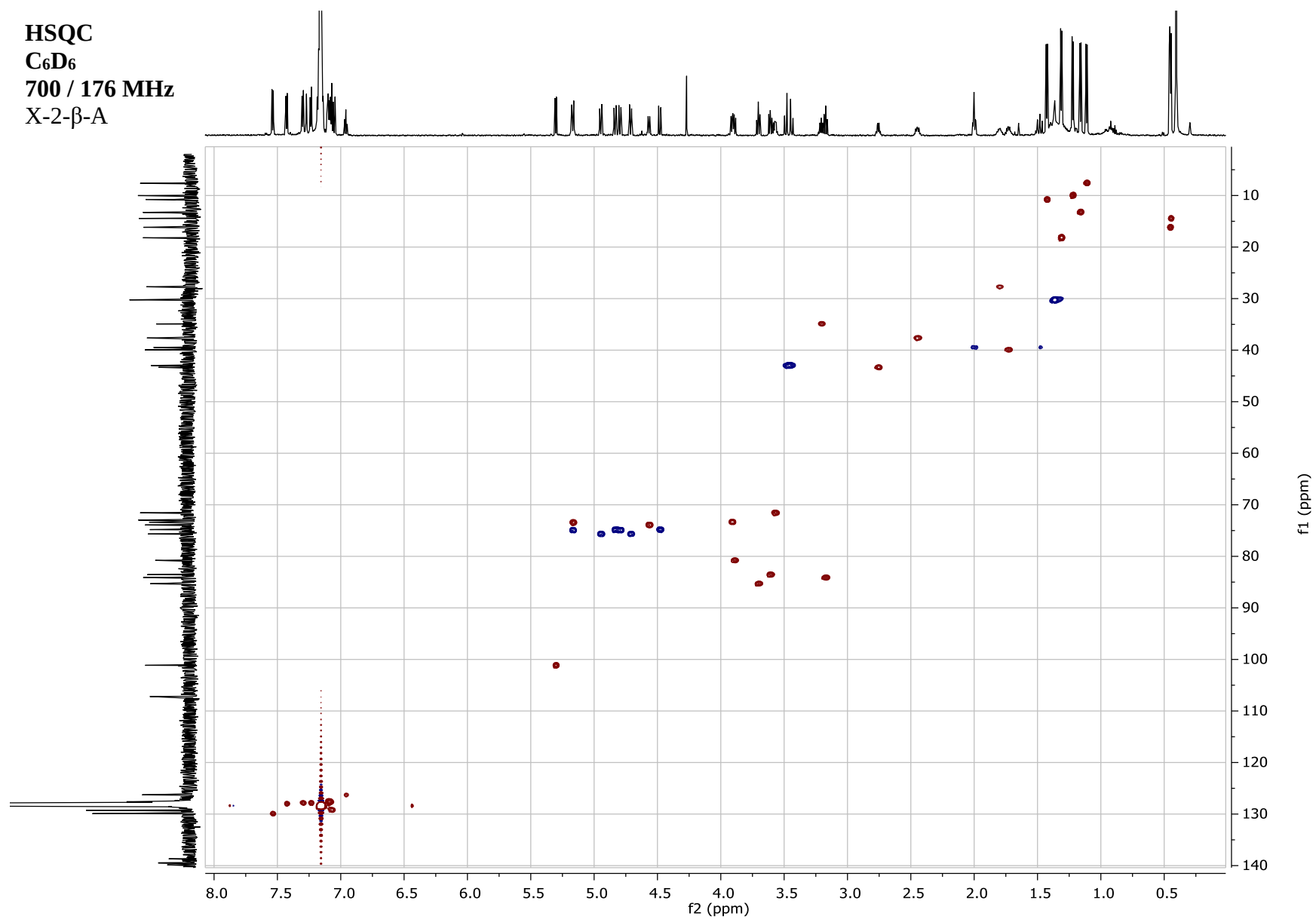


8.0, 7.5, 7.0, 6.5, 6.0, 5.5, 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0, 0.5, f1 (ppm)

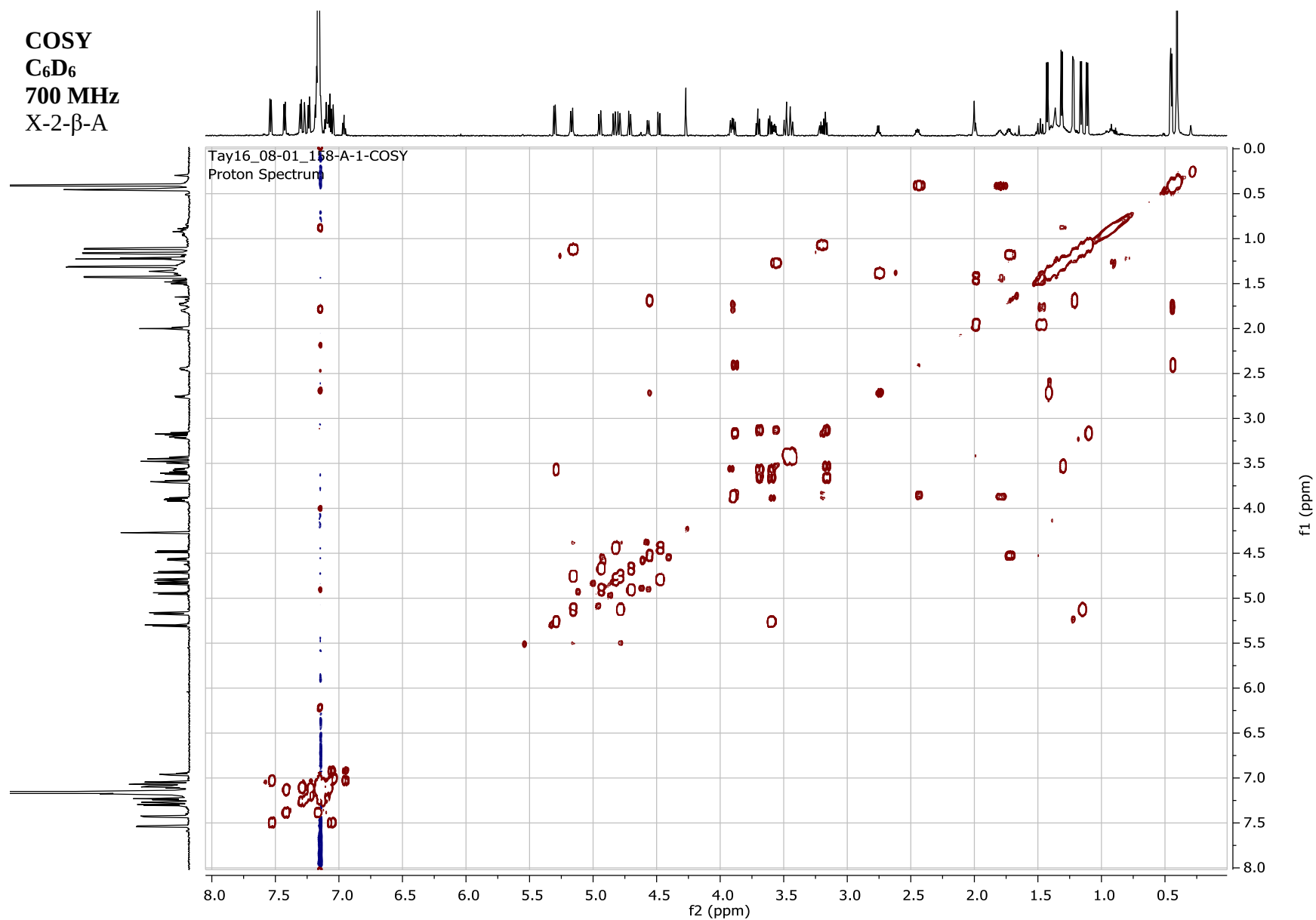
S74



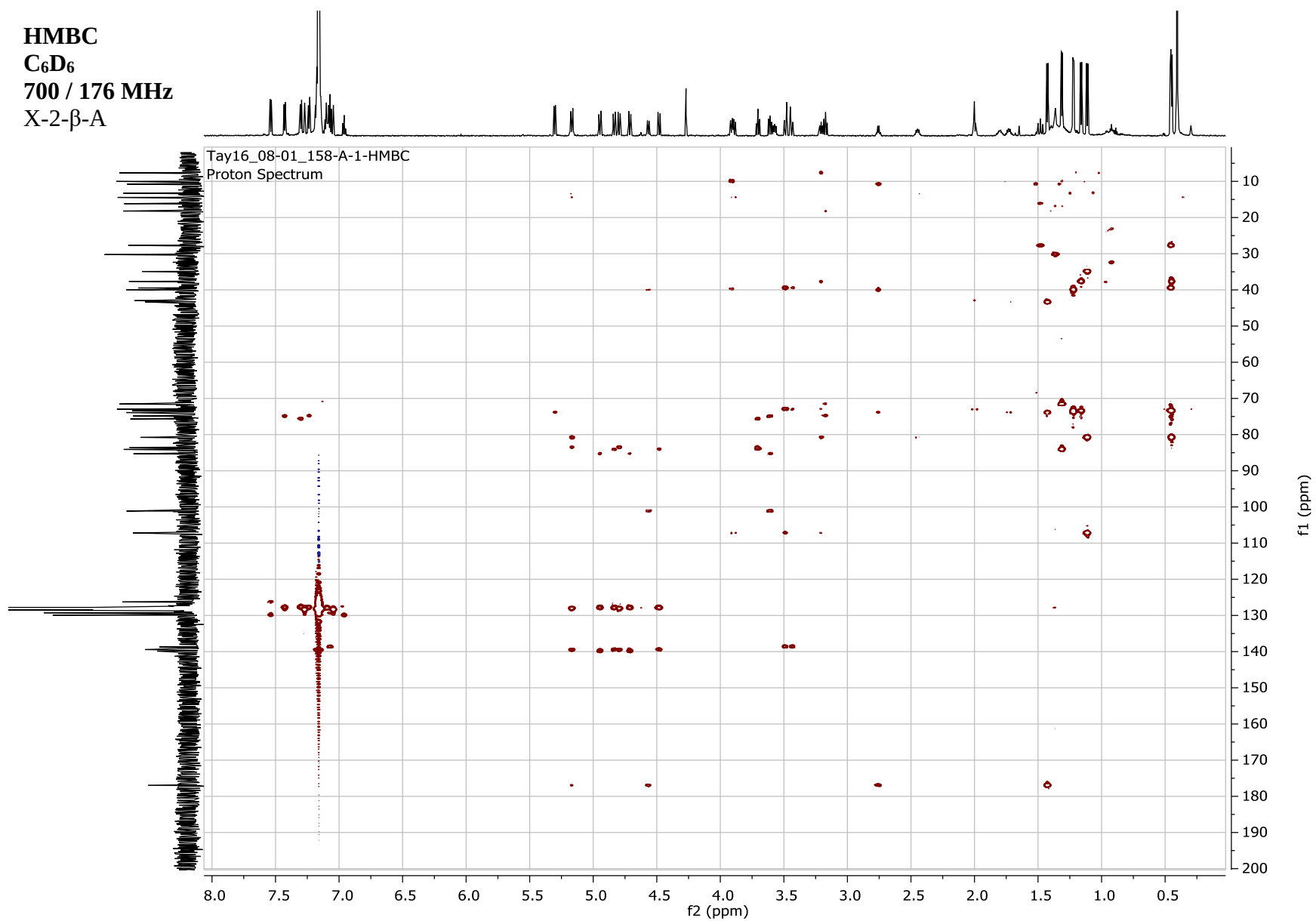
HSQC
C₆D₆
700 / 176 MHz
X-2-β-A

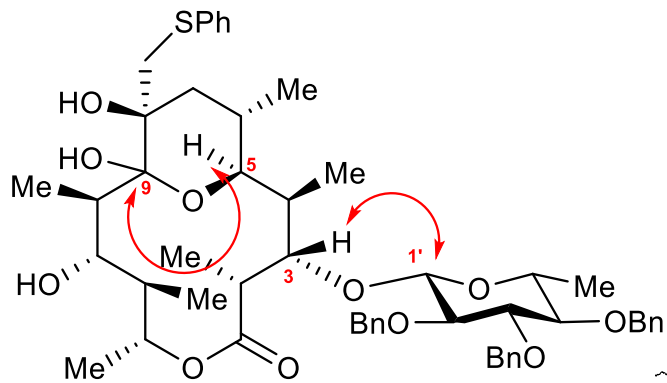


COSY
C₆D₆
700 MHz
X-2-β-A

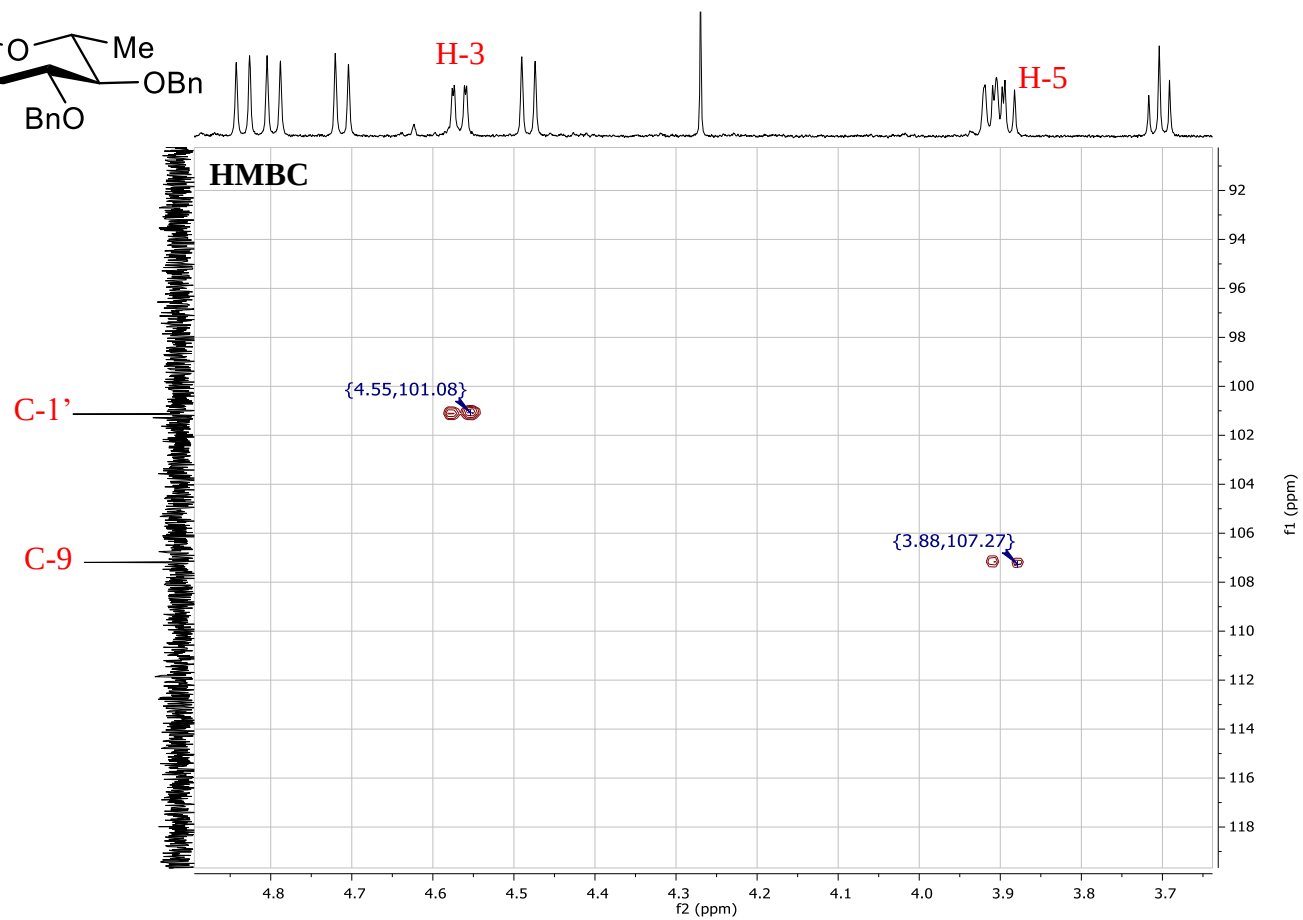


HMBC
C₆D₆
700 / 176 MHz
X-2-β-A

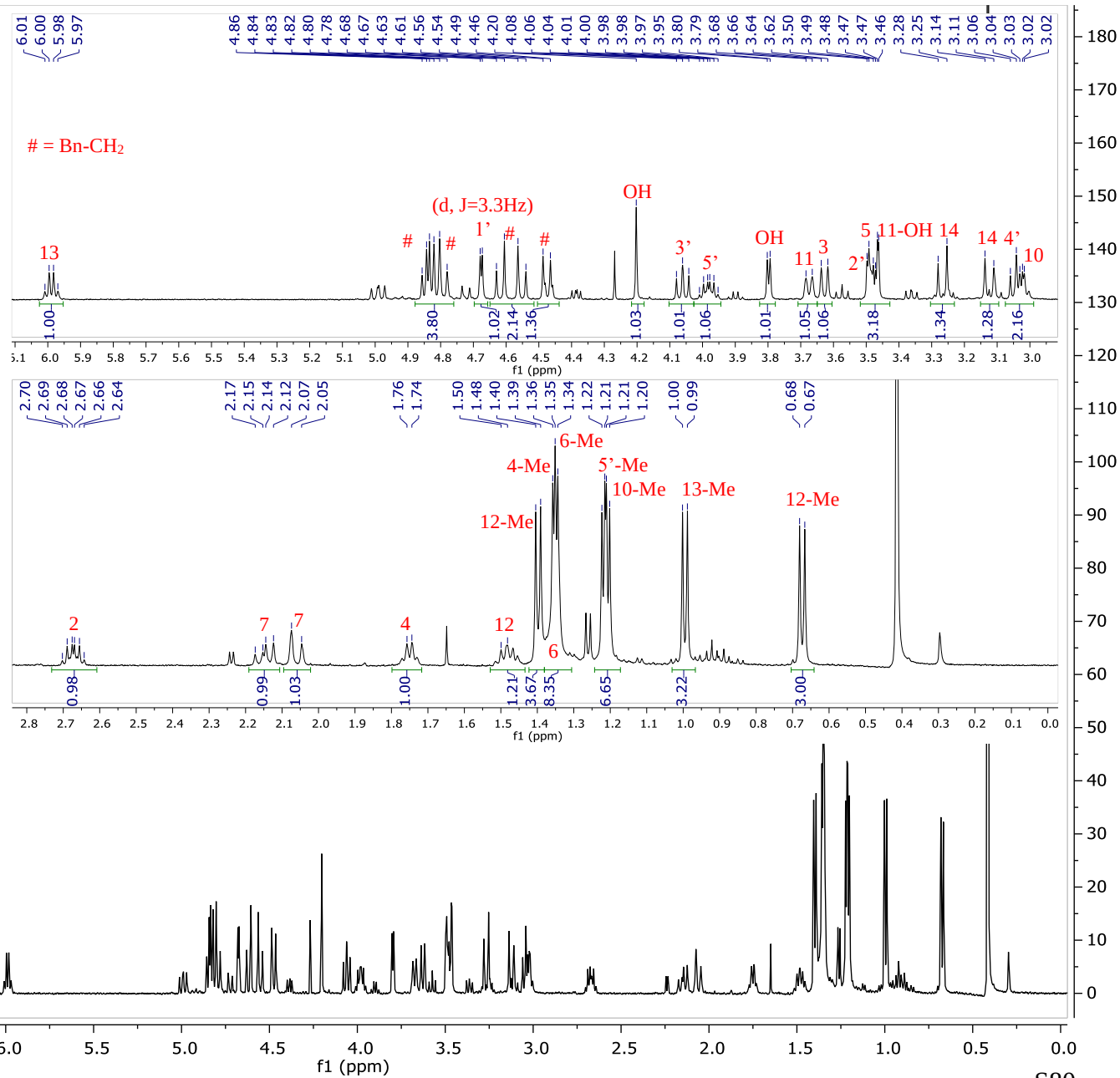
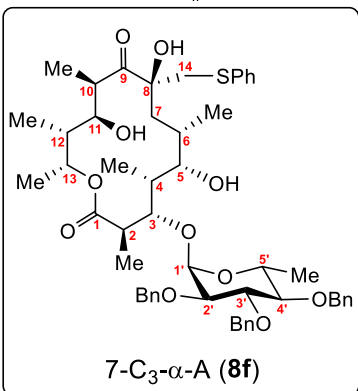


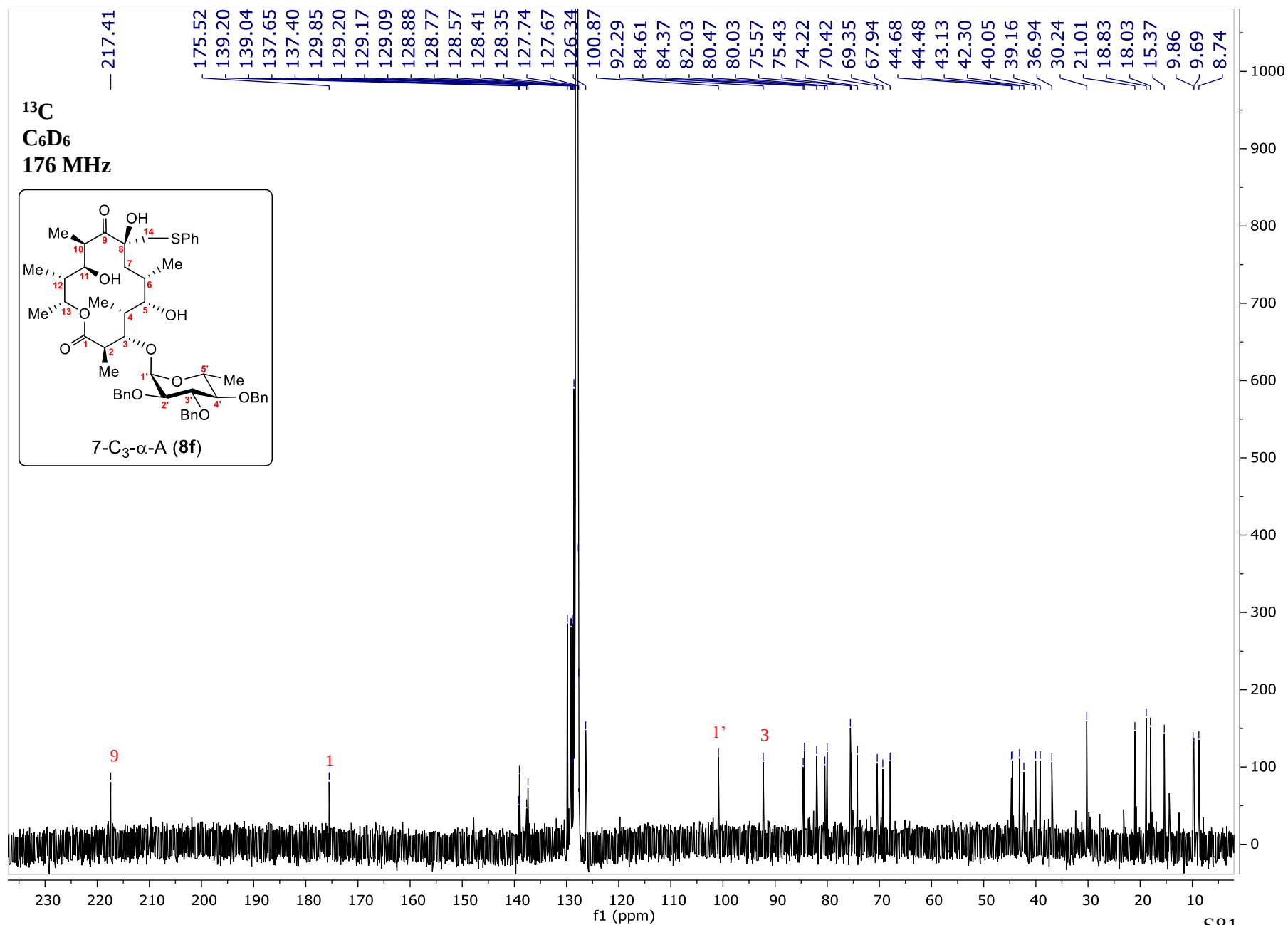


X-2-β-A

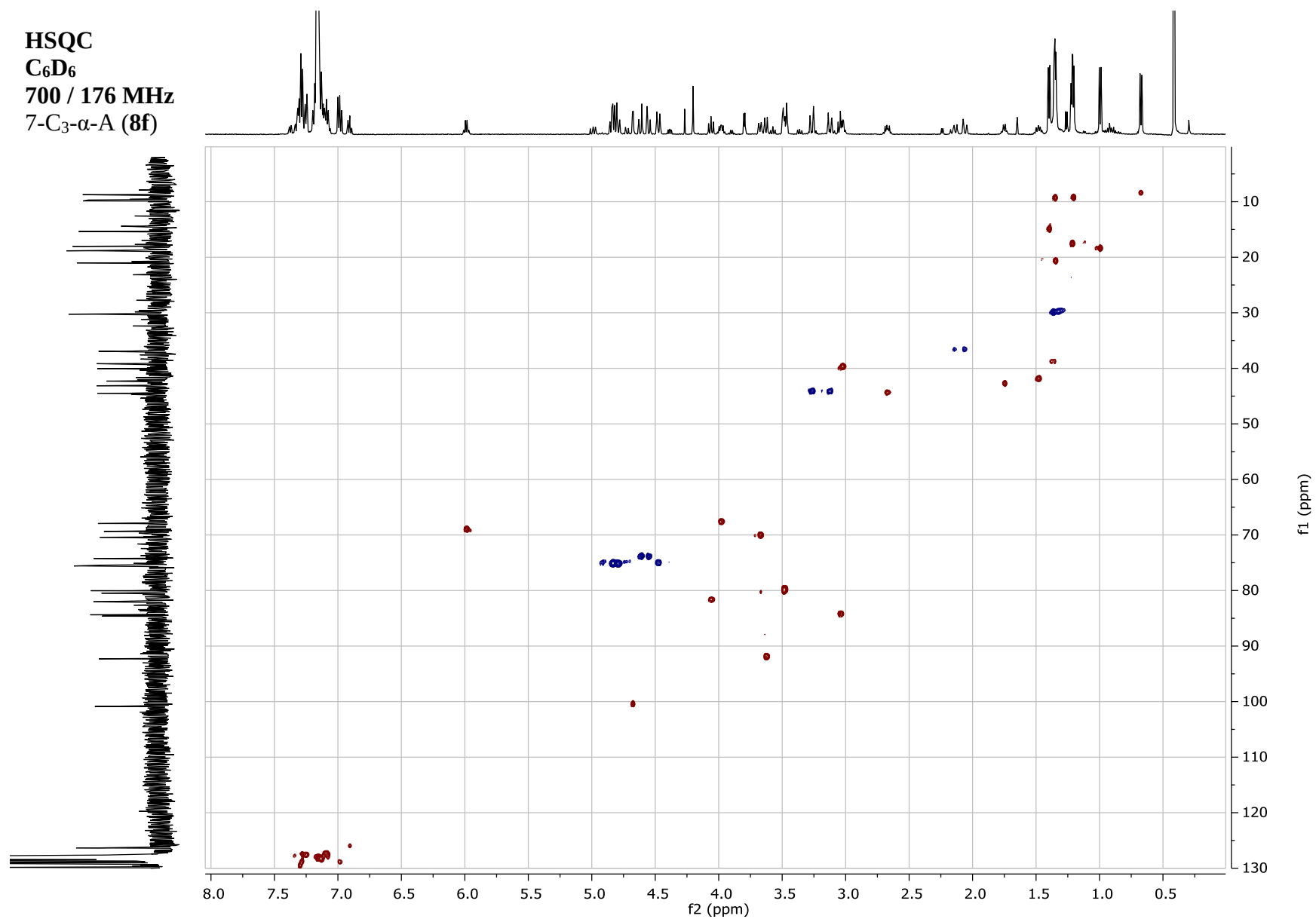


¹H
C₆D₆
500 MHz

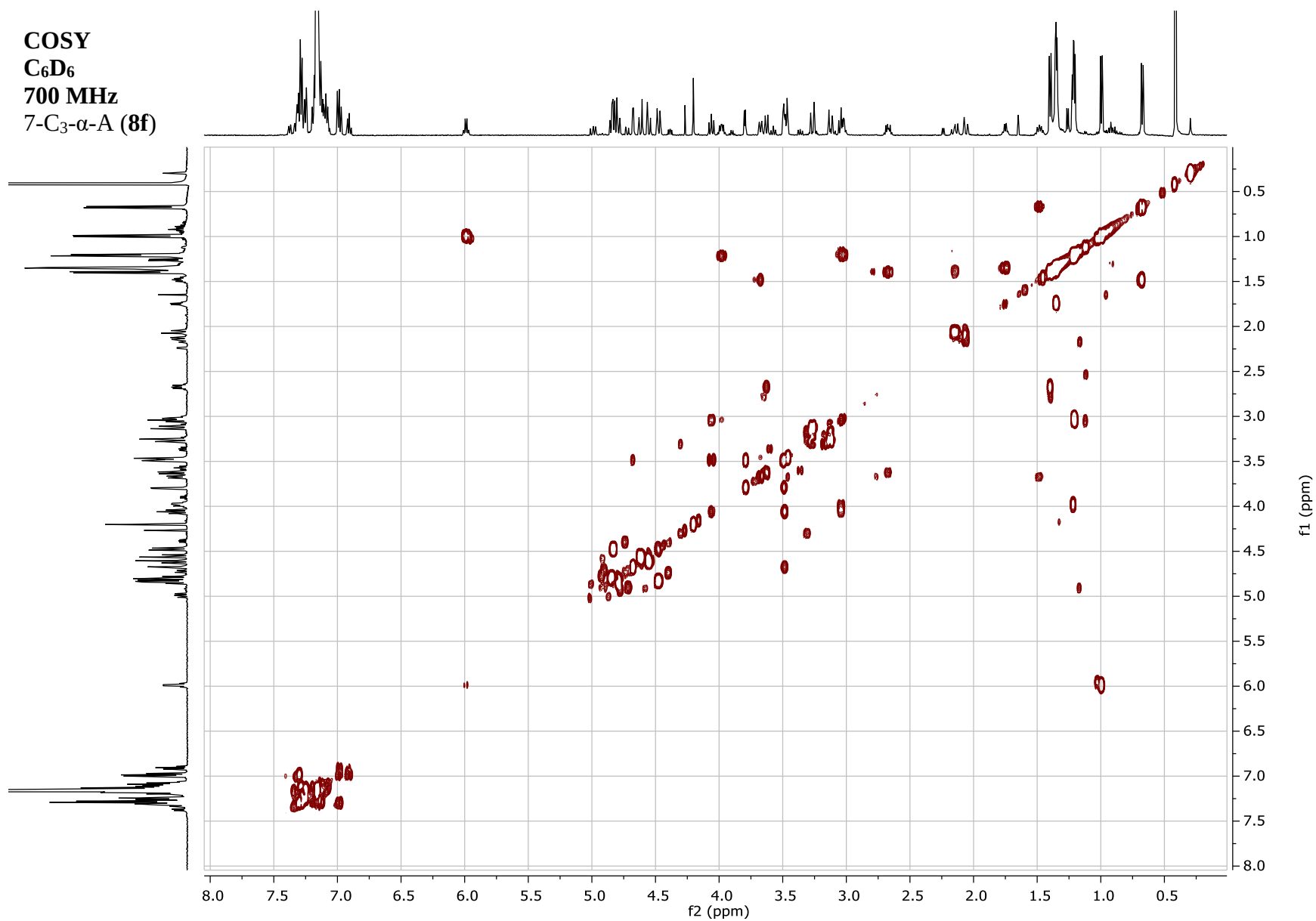




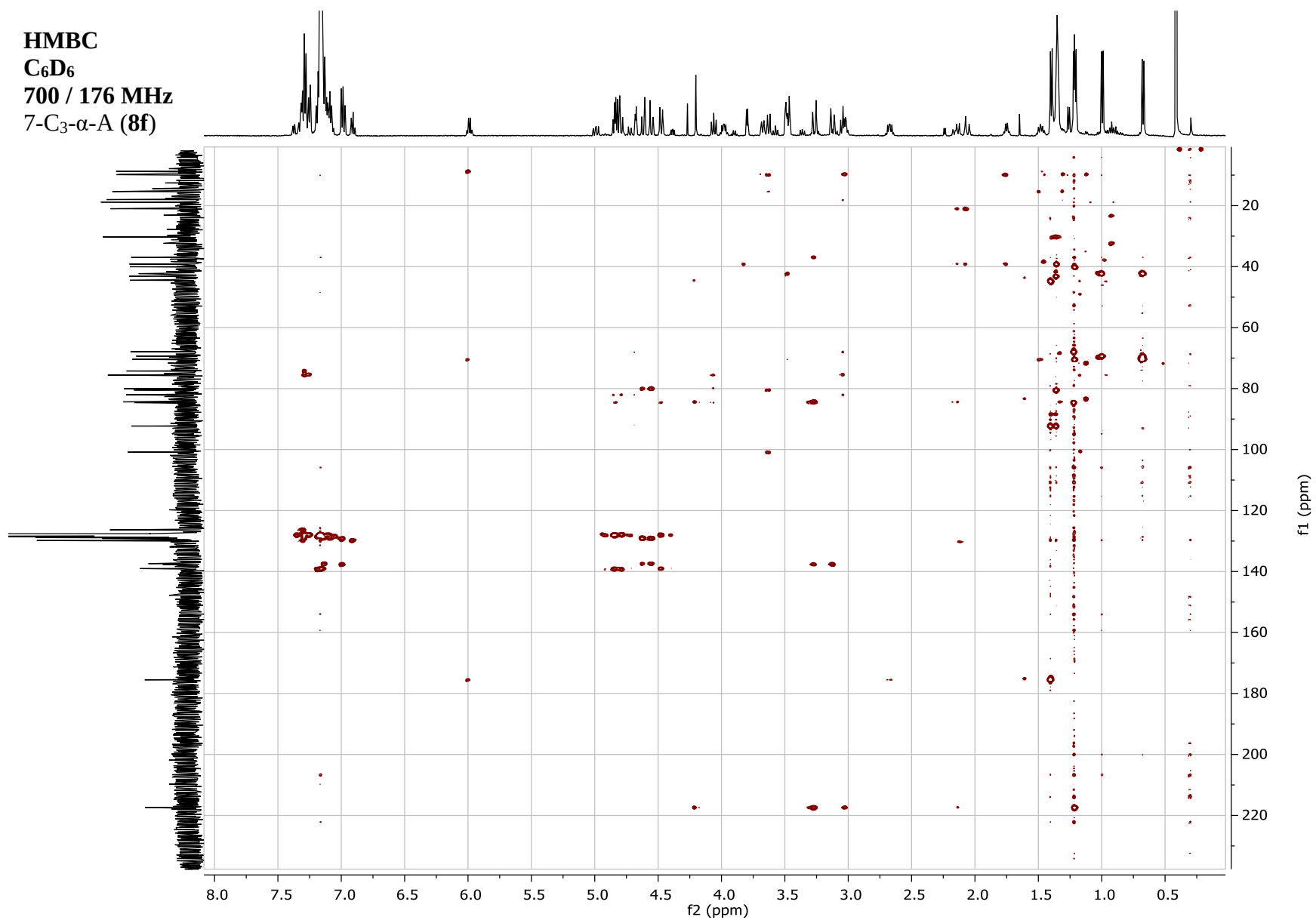
HSQC
C₆D₆
700 / 176 MHz
7-C₃- α -A (8f)

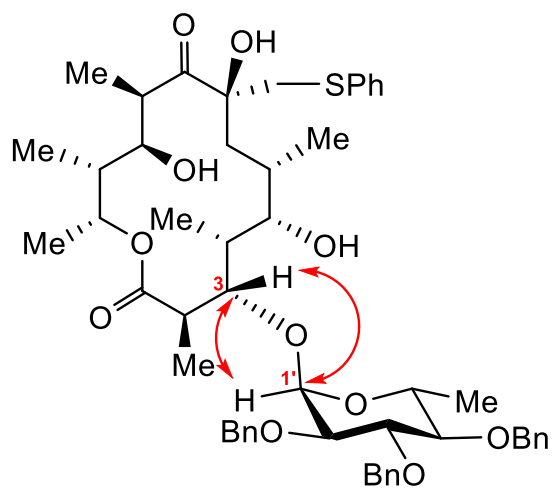


COSY
C₆D₆
700 MHz
7-C₃- α -A (8f)

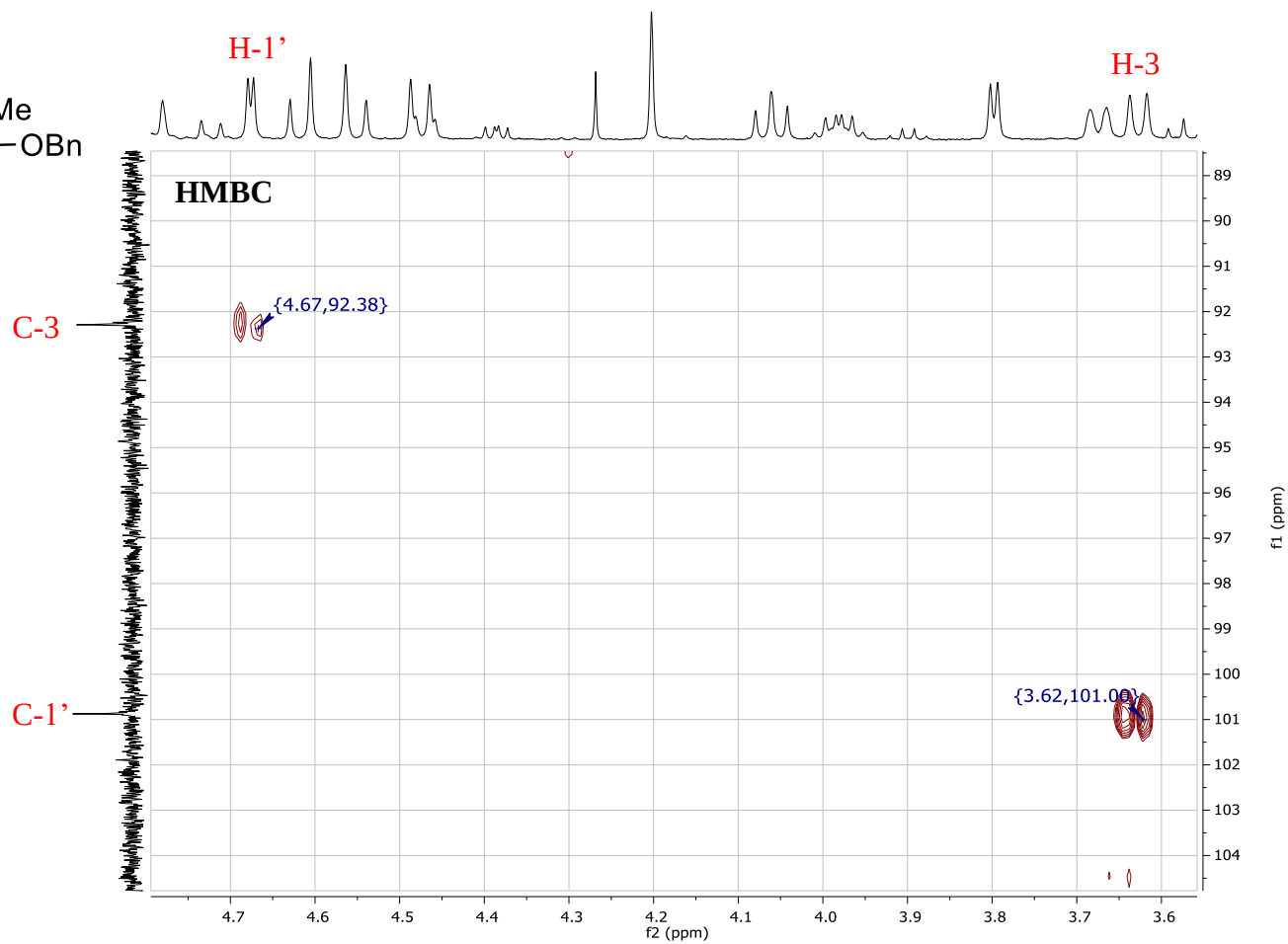


HMBC
C₆D₆
700 / 176 MHz
7-C₃- α -A (8f)



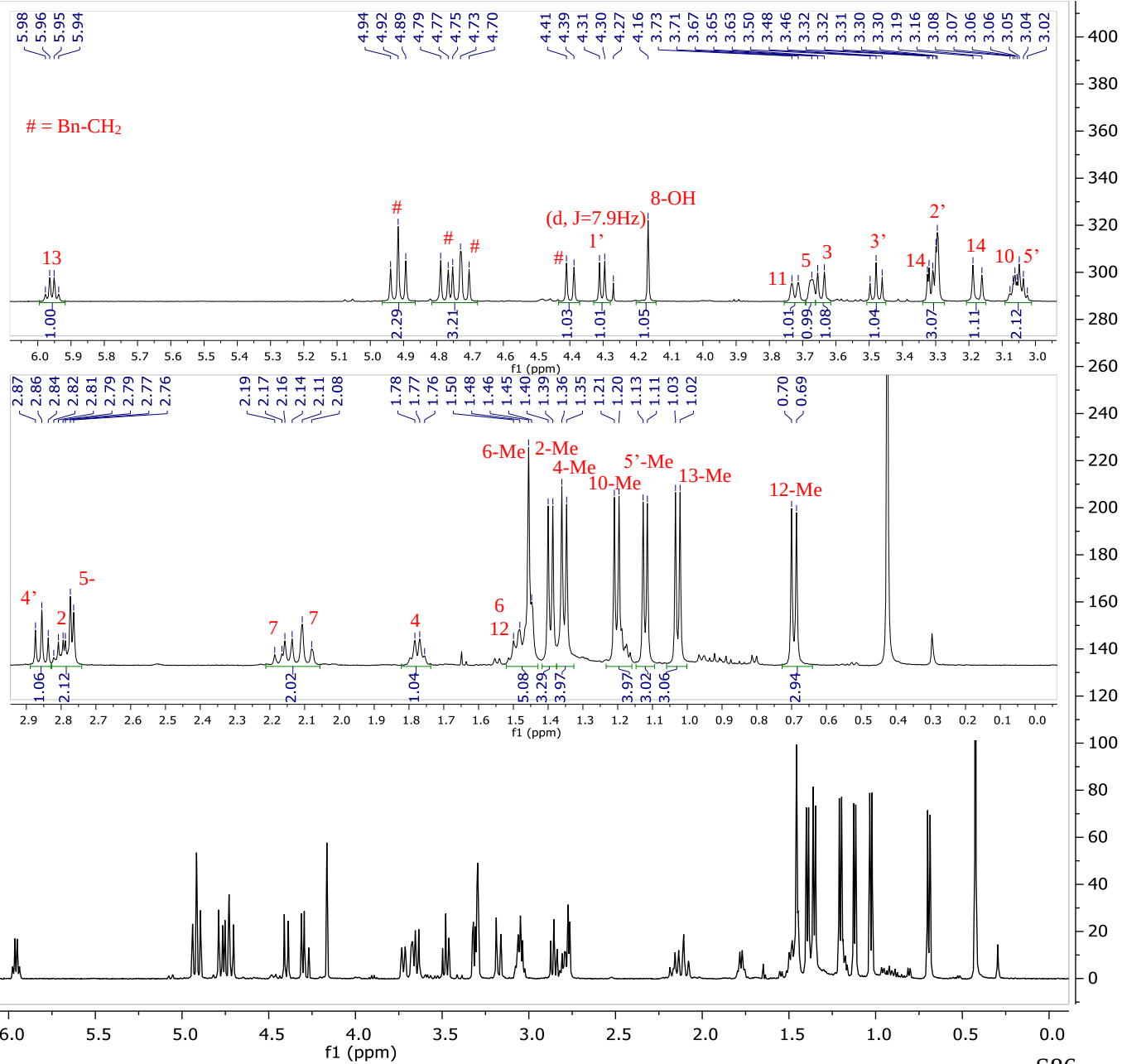
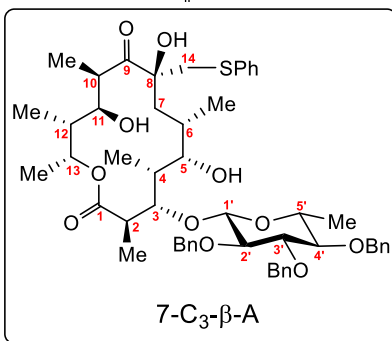


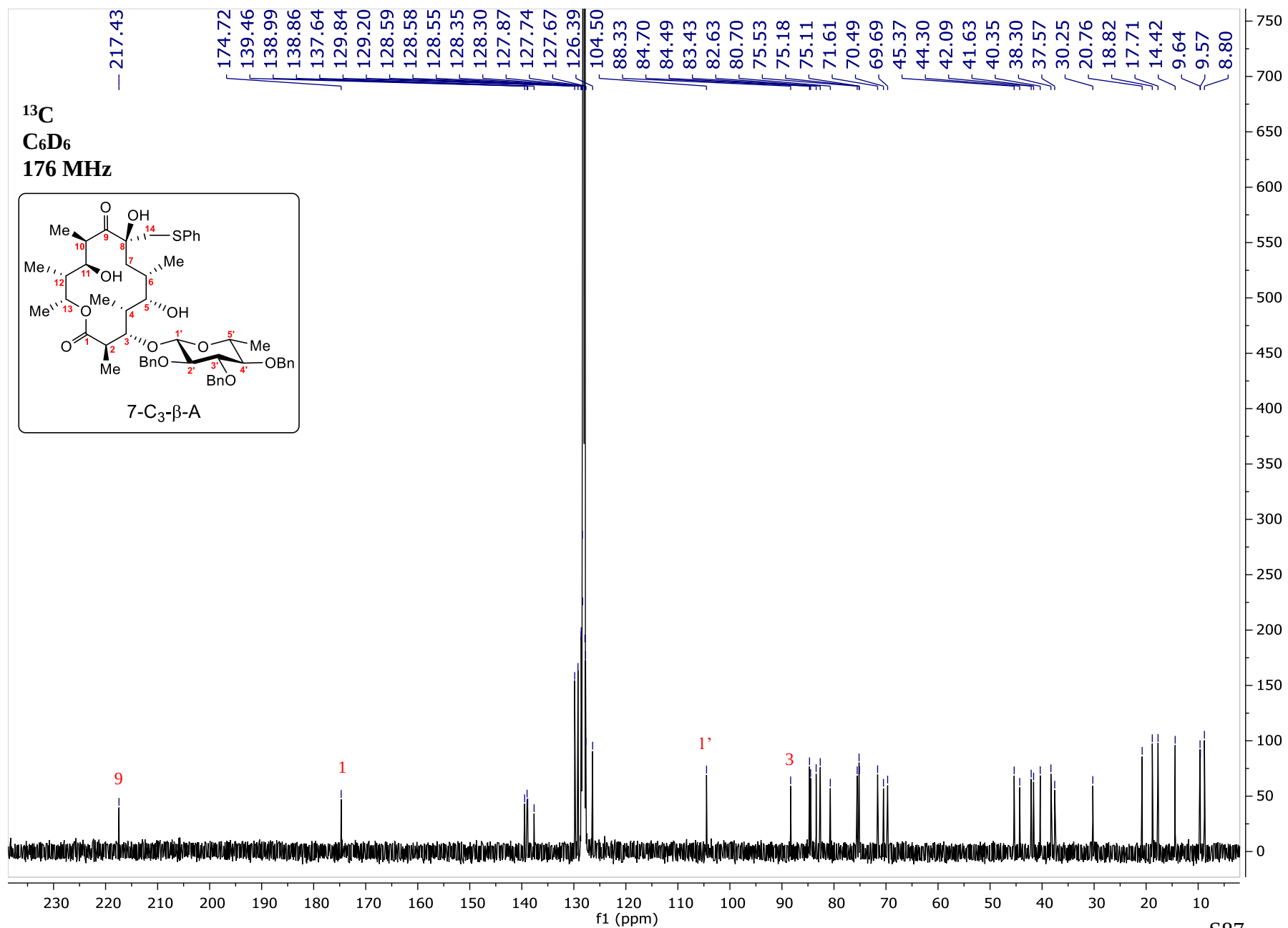
7-C₃-α-A (8f)



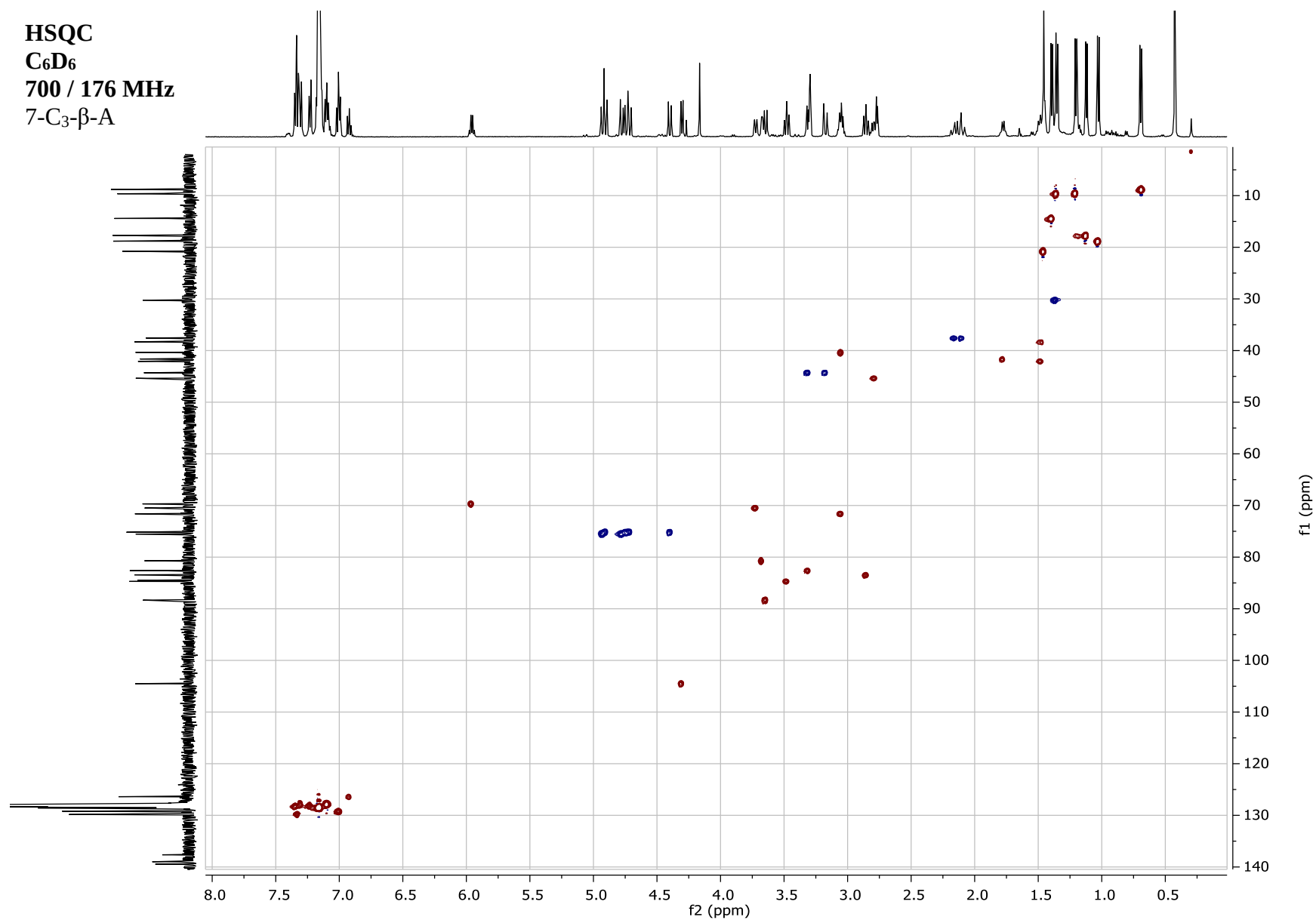
$$^1\text{H}$$

$$\text{C}_6\text{D}_6$$

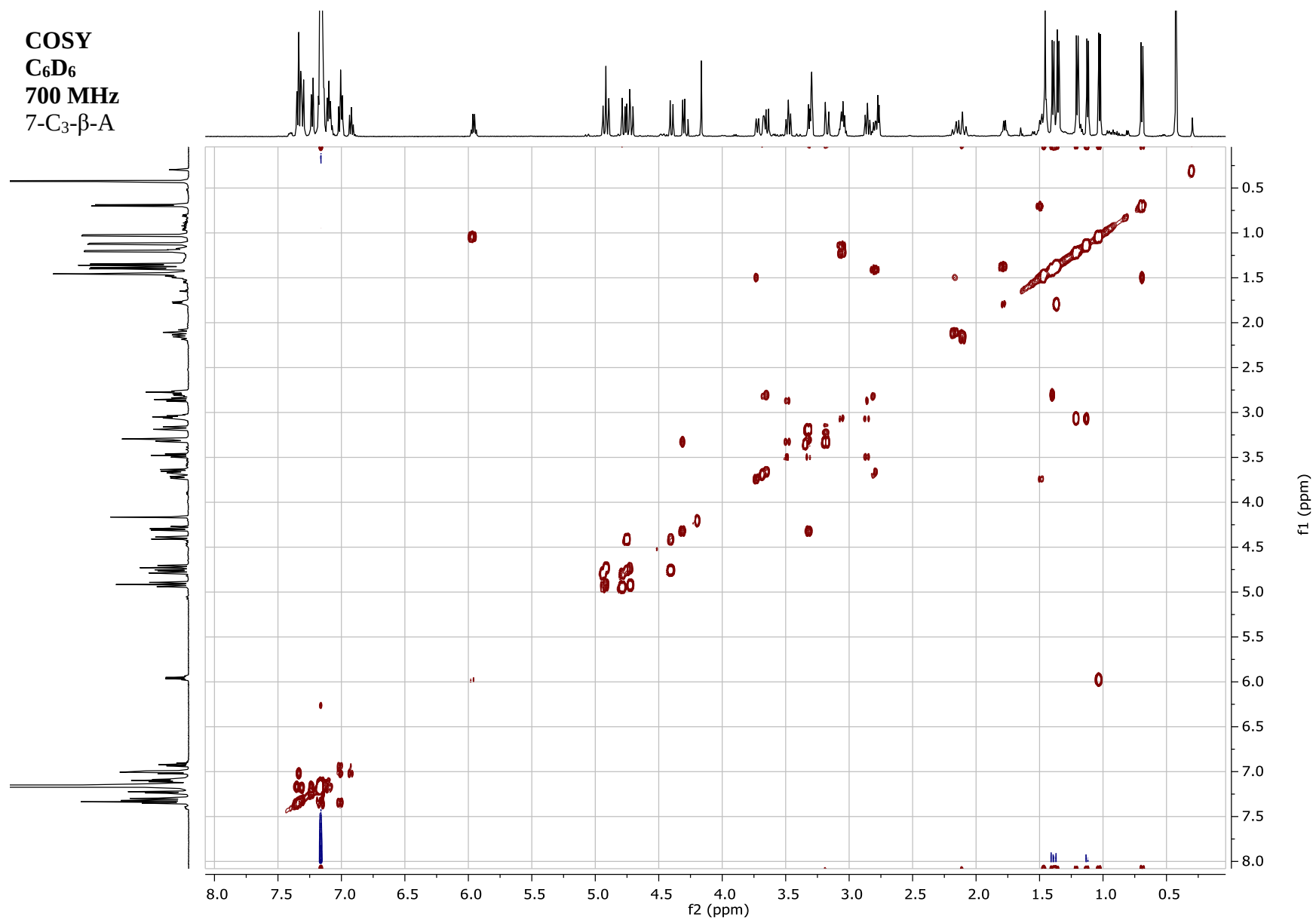
$$500 \text{ MHz}$$




HSQC
C₆D₆
700 / 176 MHz
7-C₃-β-A



COSY
C₆D₆
700 MHz
7-C₃-β-A

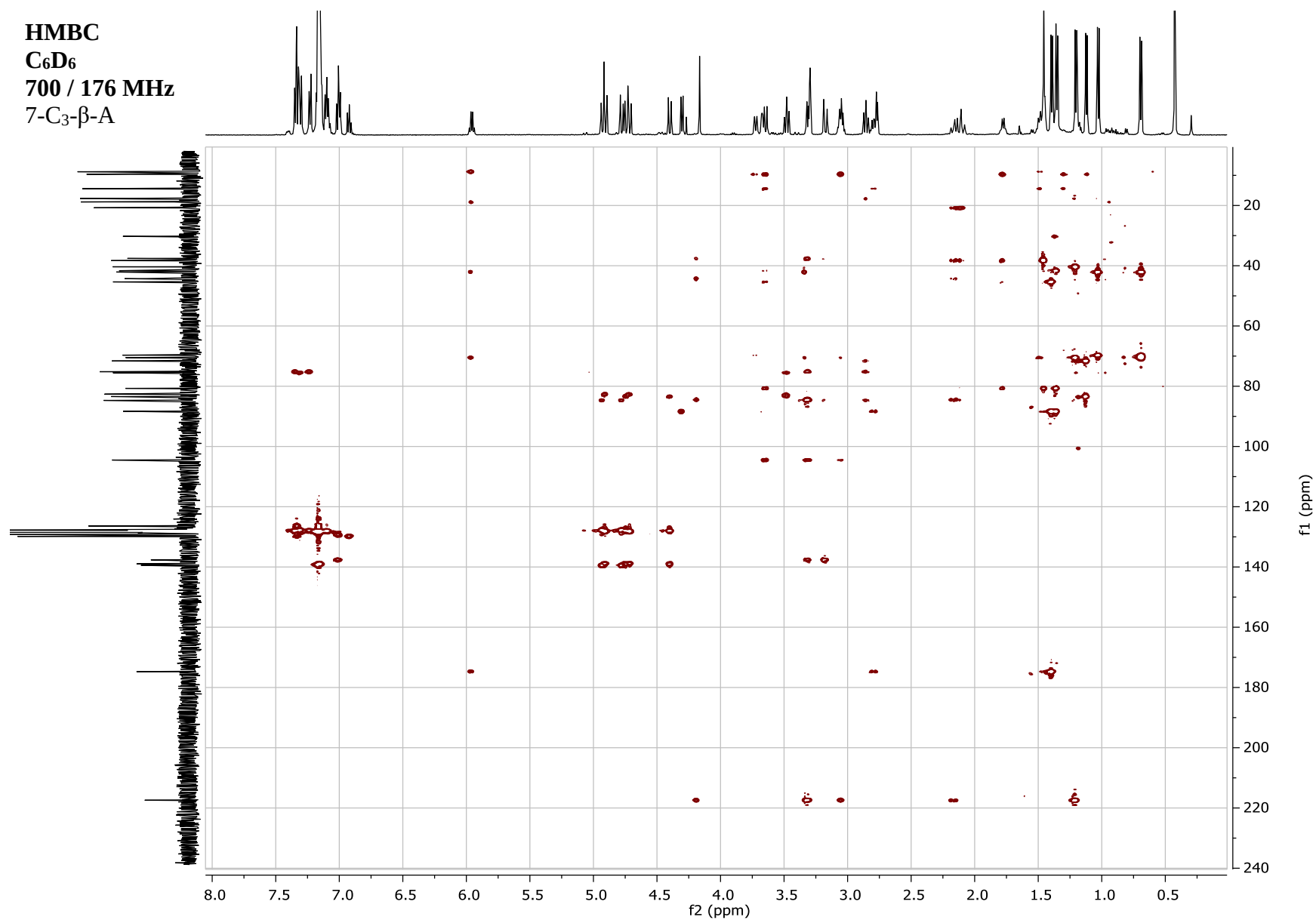


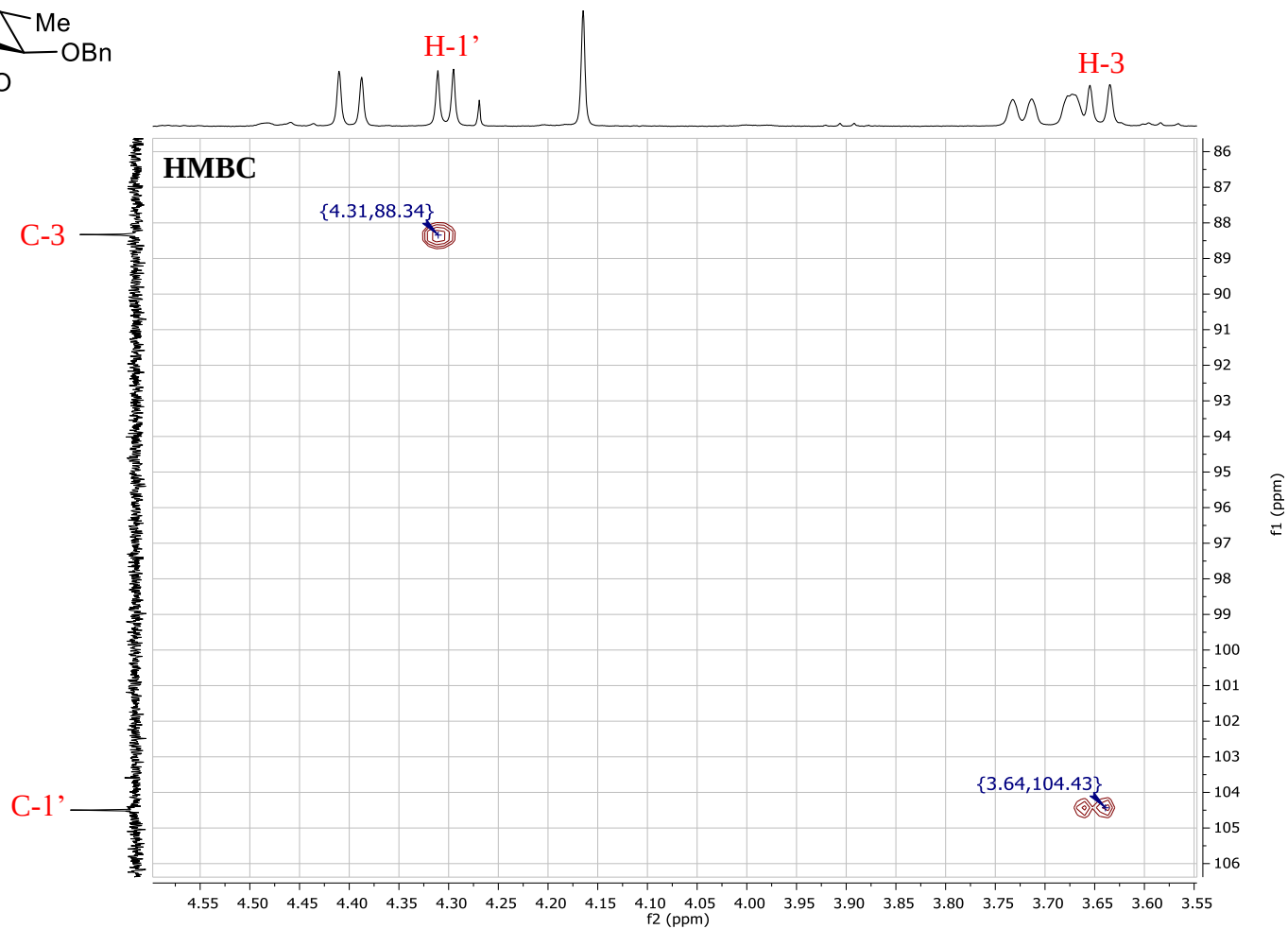
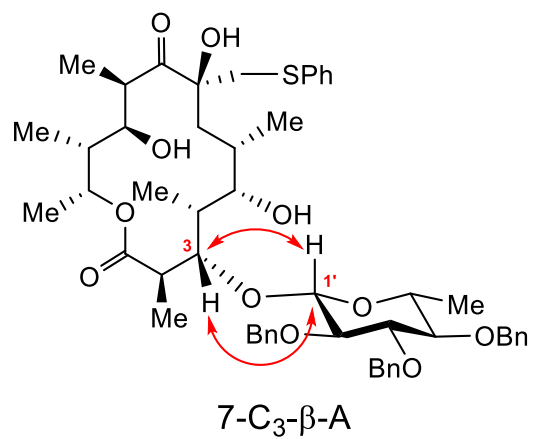
HMBC

C₆D₆

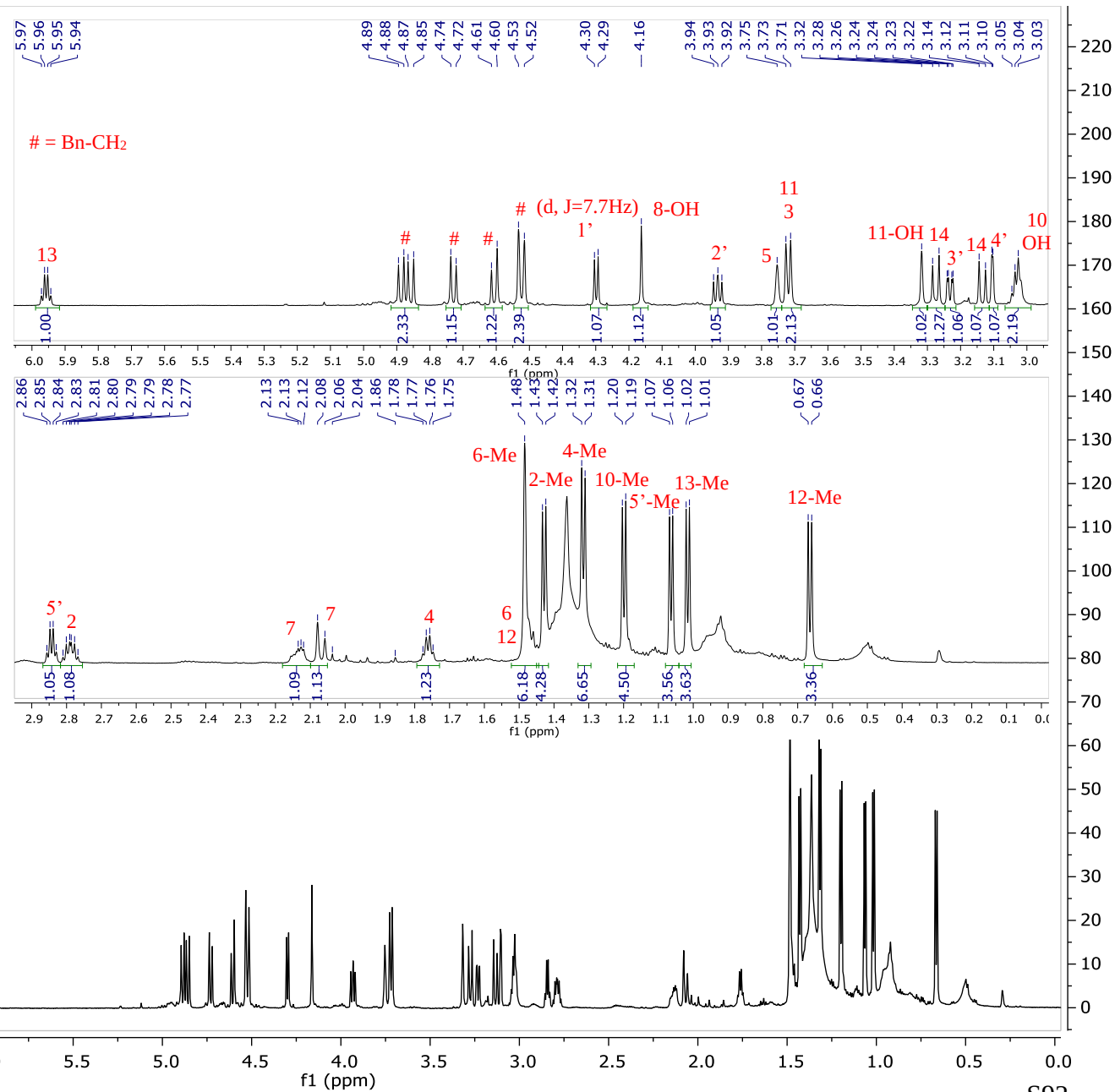
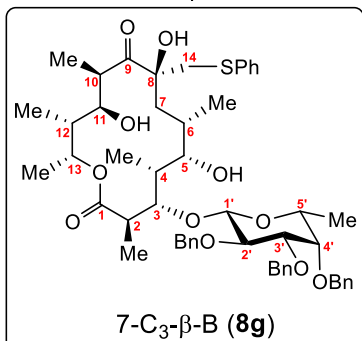
700 / 176 MHz

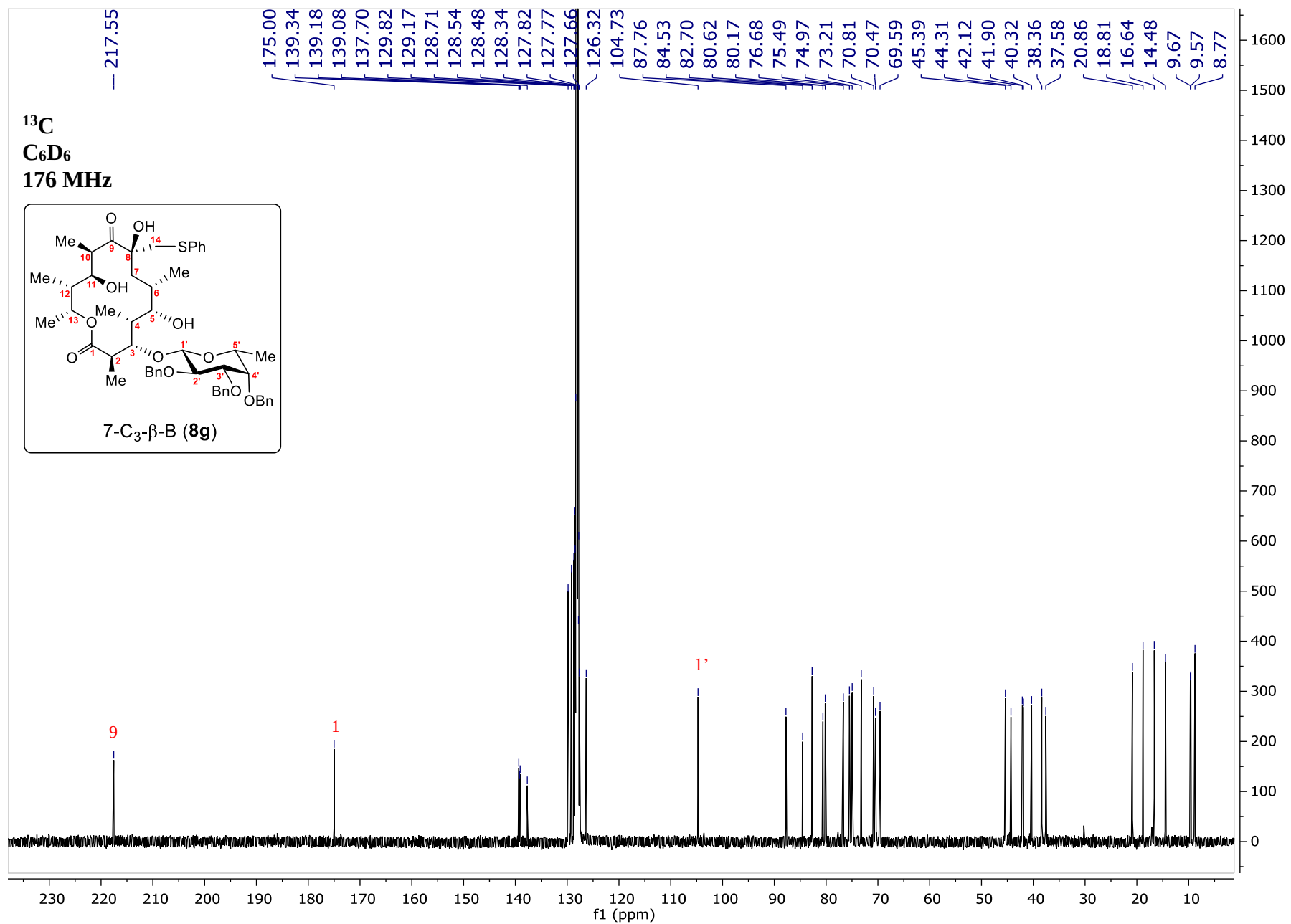
7-C₃-β-A





¹H
C₆D₆
700 MHz





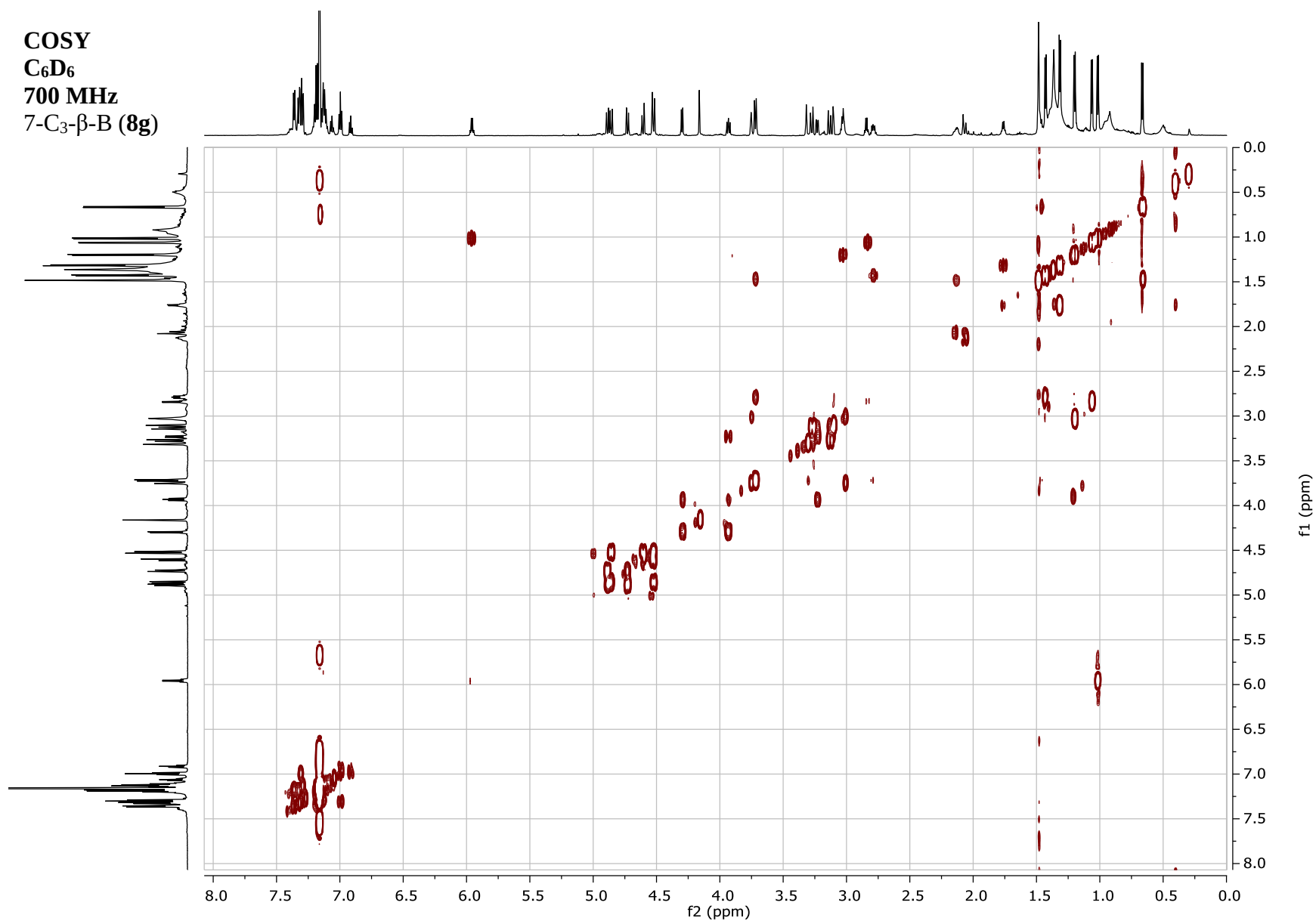
HSQC
C₆D₆
500 / 126 MHz
7-C₃-β-B (8g)

8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

f2 (ppm)

10 20 30 40 50 60 70 80 90 100 110 120 130 140

COSY
C₆D₆
700 MHz
7-C₃-β-B (8g)

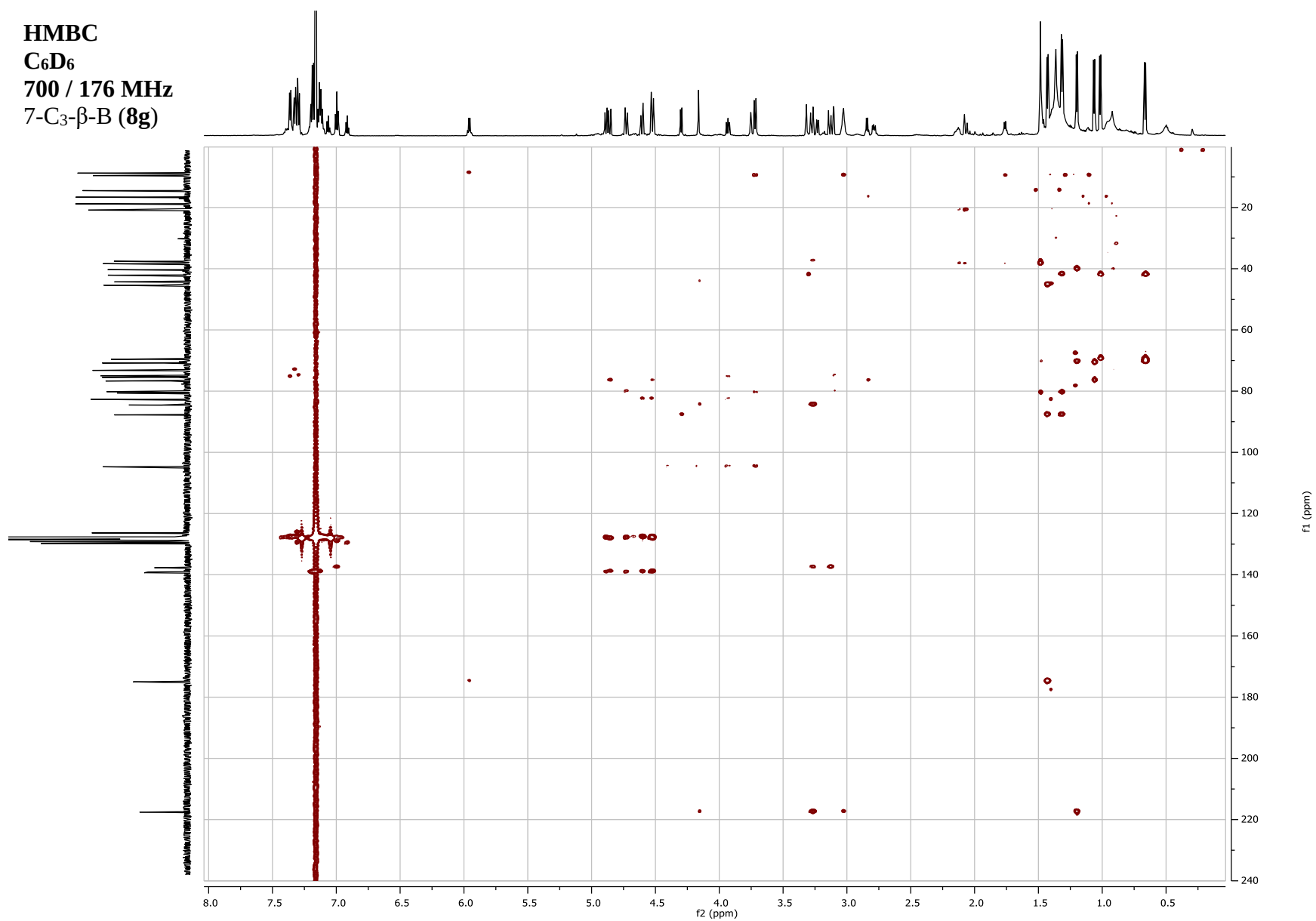


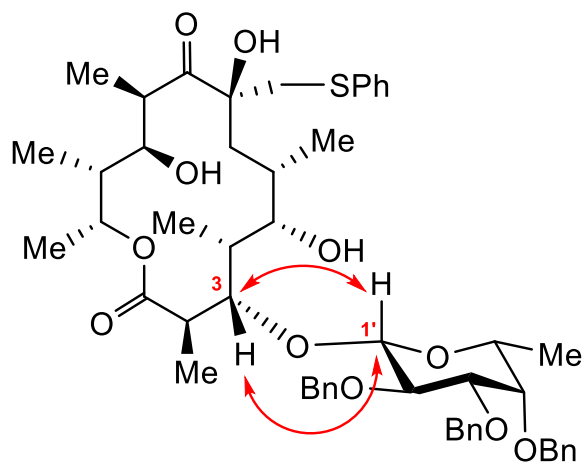
HMBC

C₆D₆

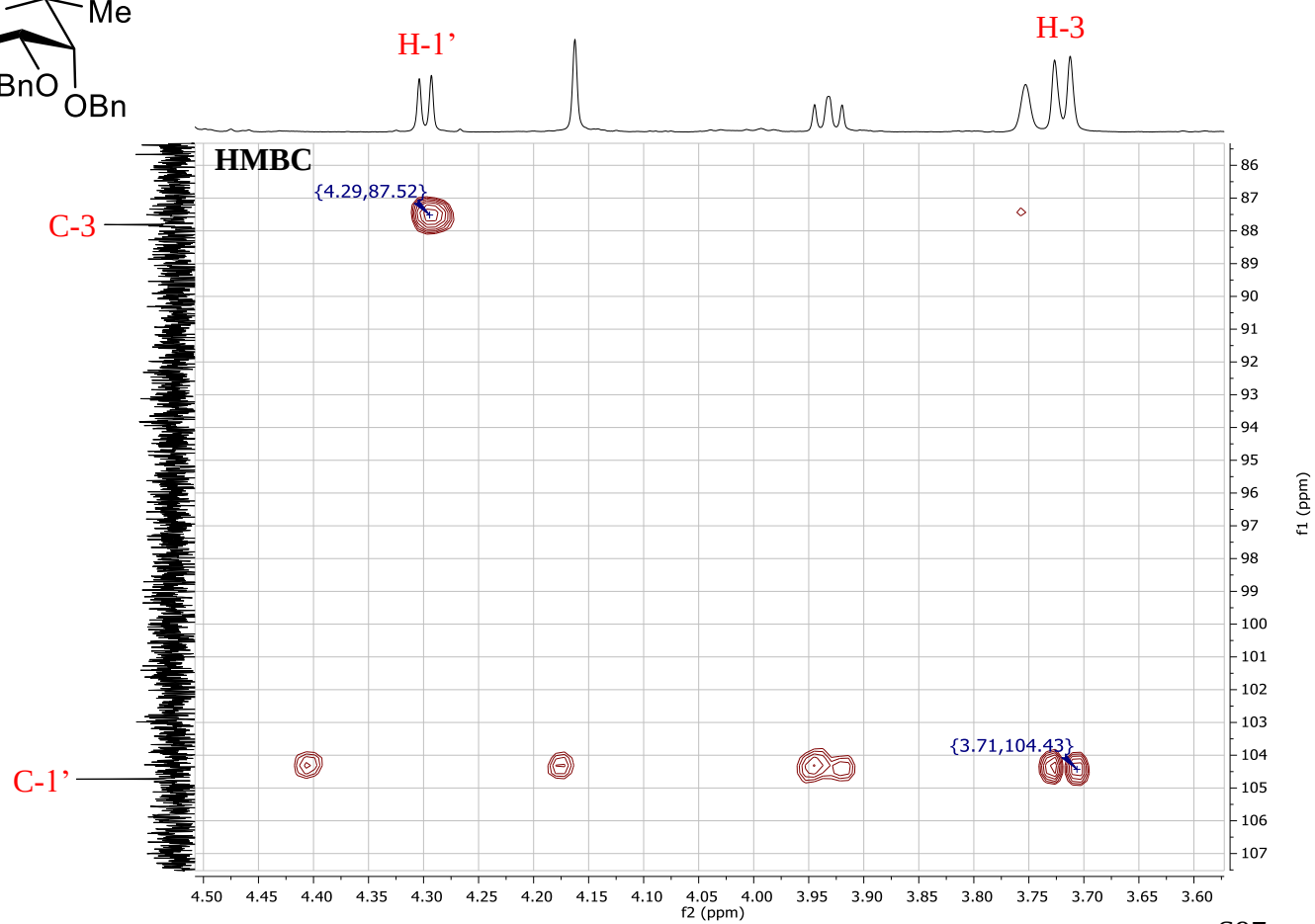
700 / 176 MHz

7-C₃-β-B (8g)

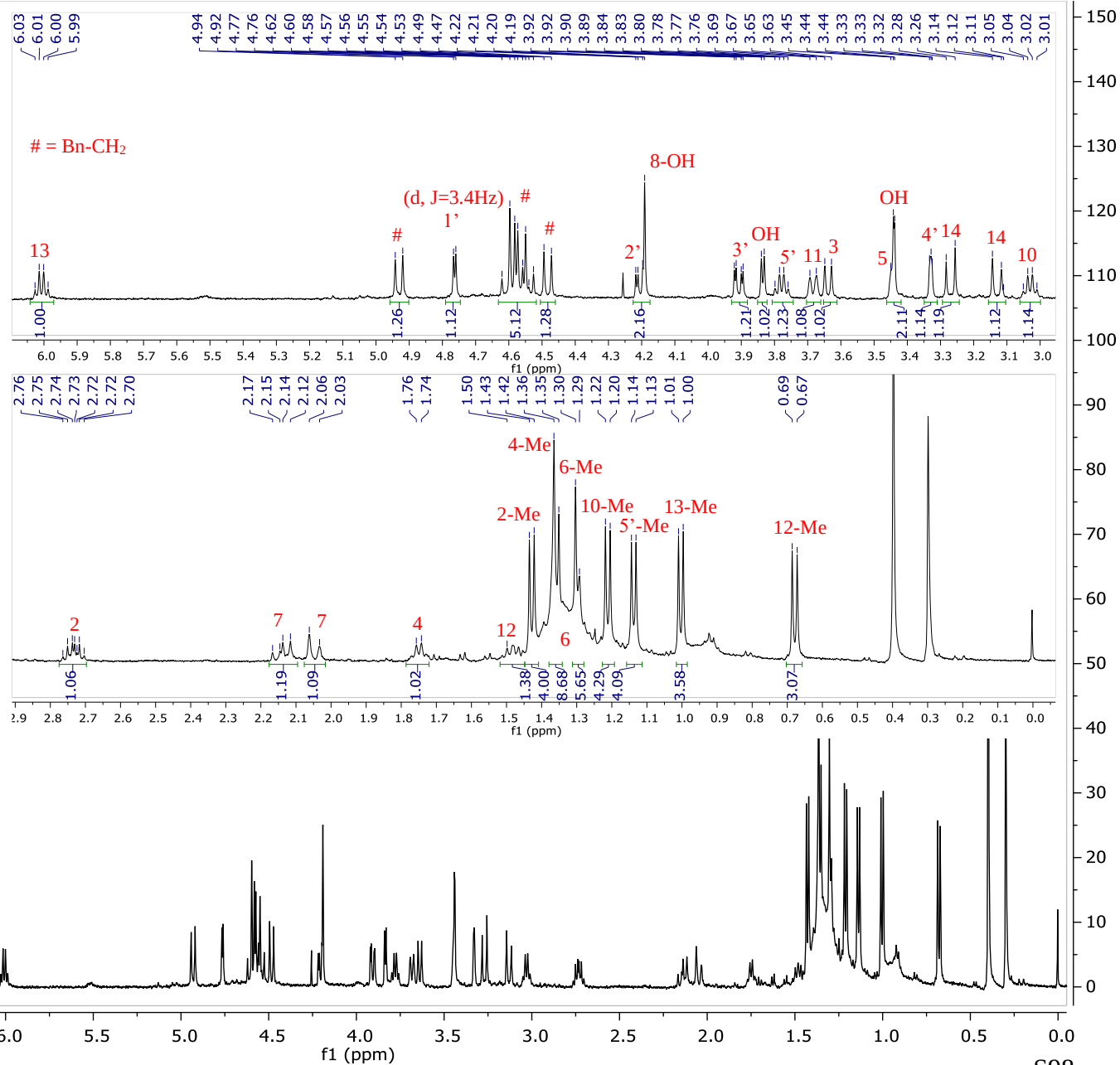
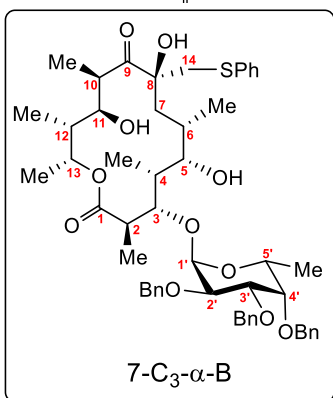


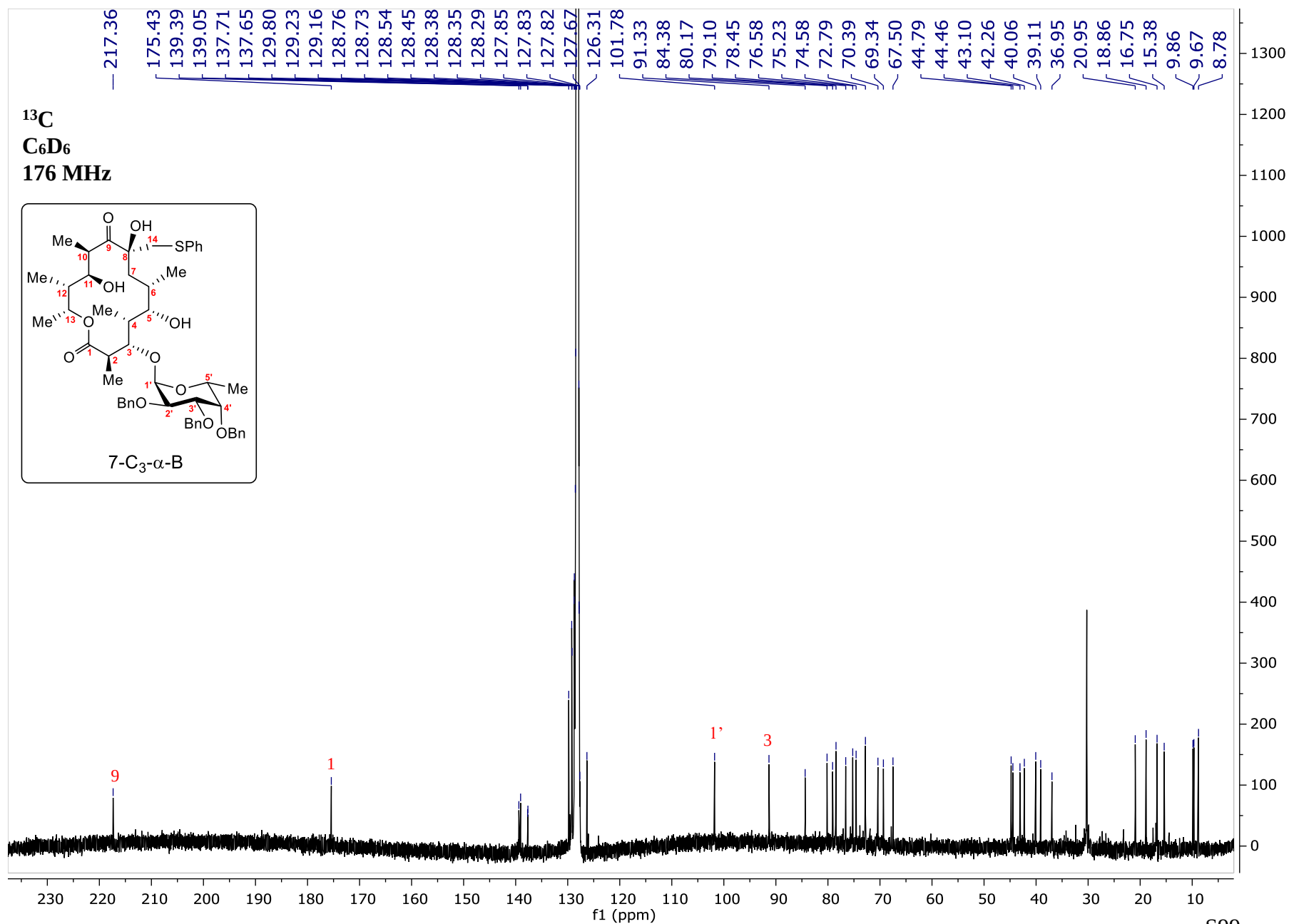


7-C₃-β-B (8g)

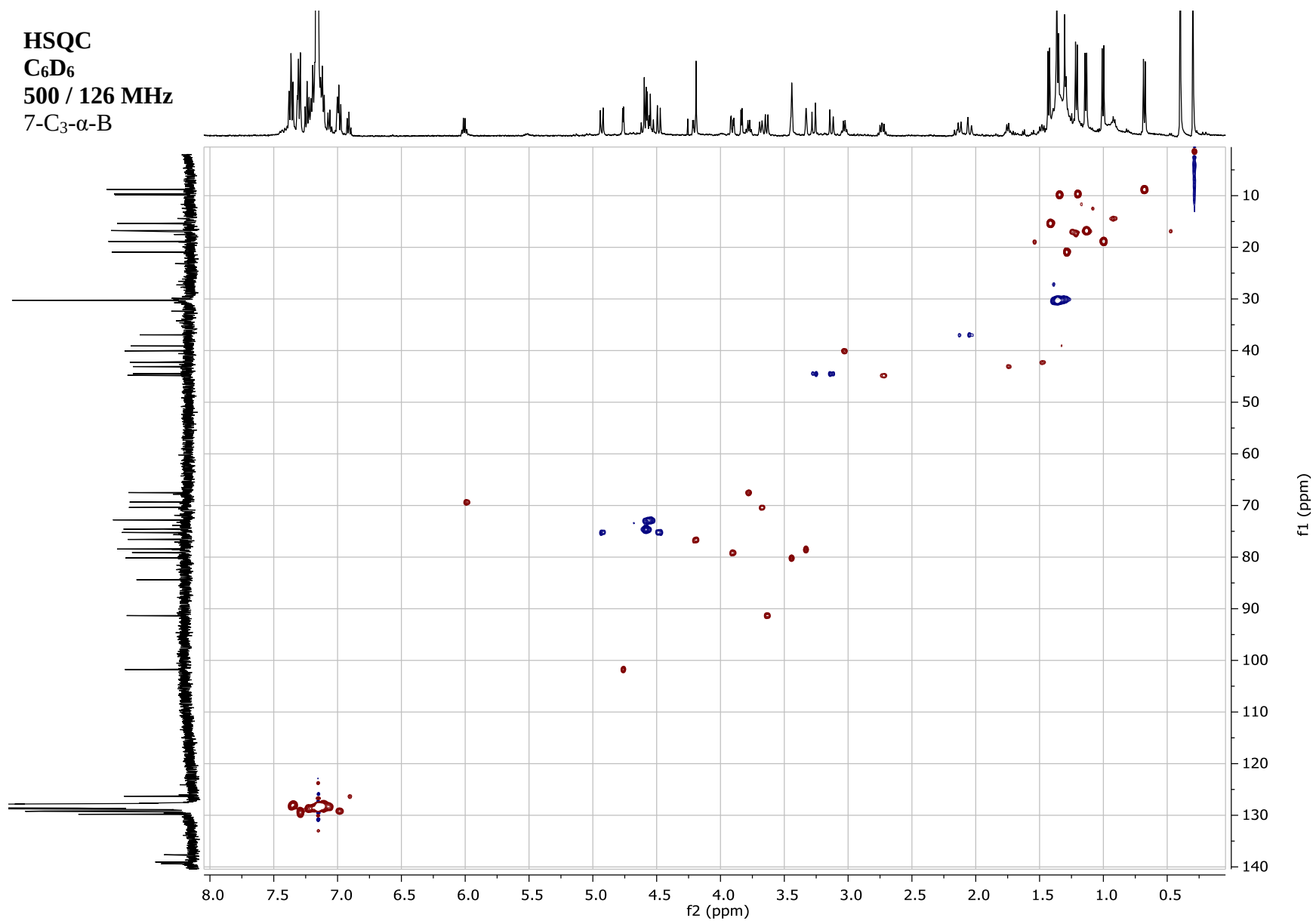


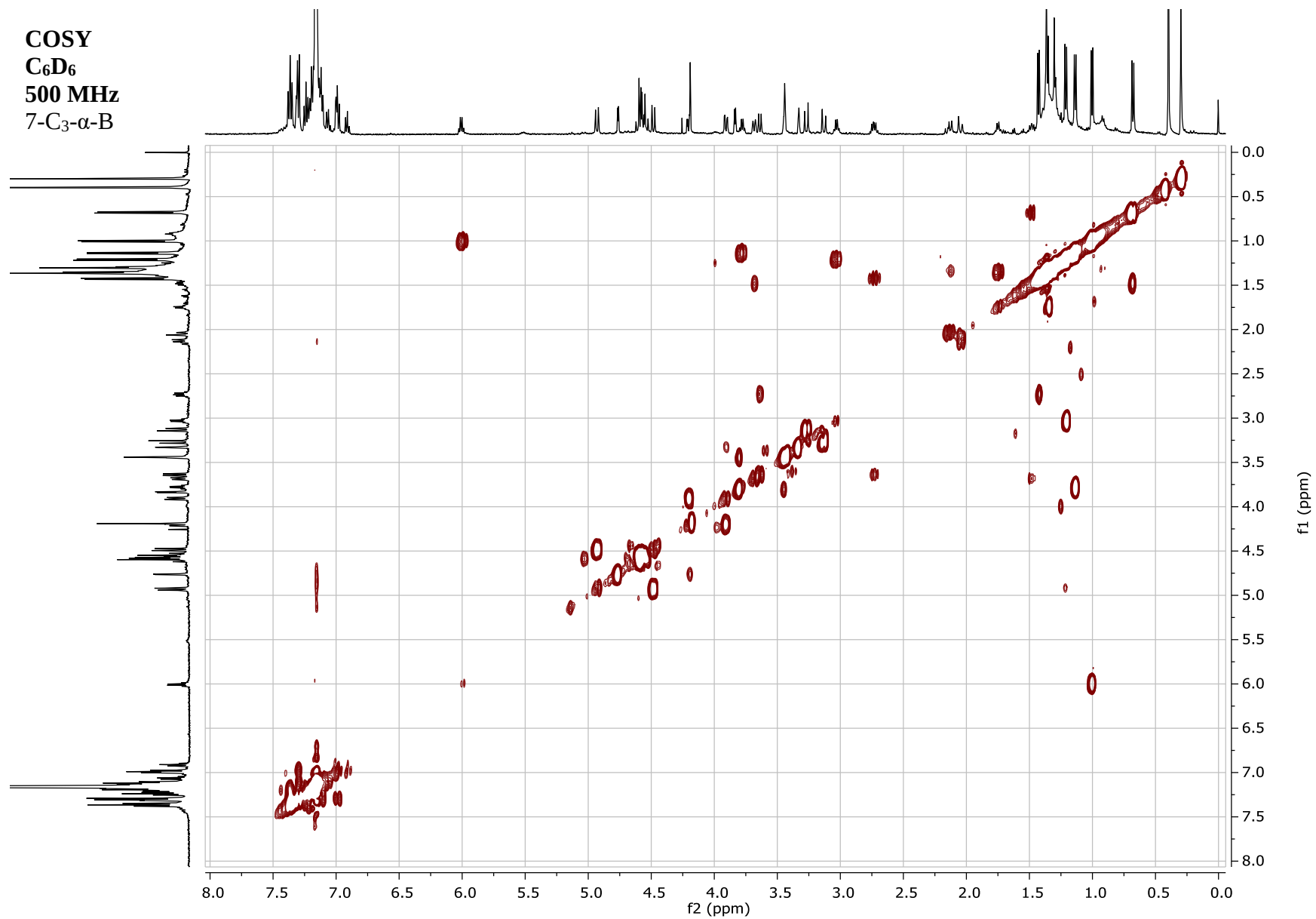
¹H
C₆D₆
500 MHz





HSQC
C₆D₆
500 / 126 MHz
7-C₃- α -B



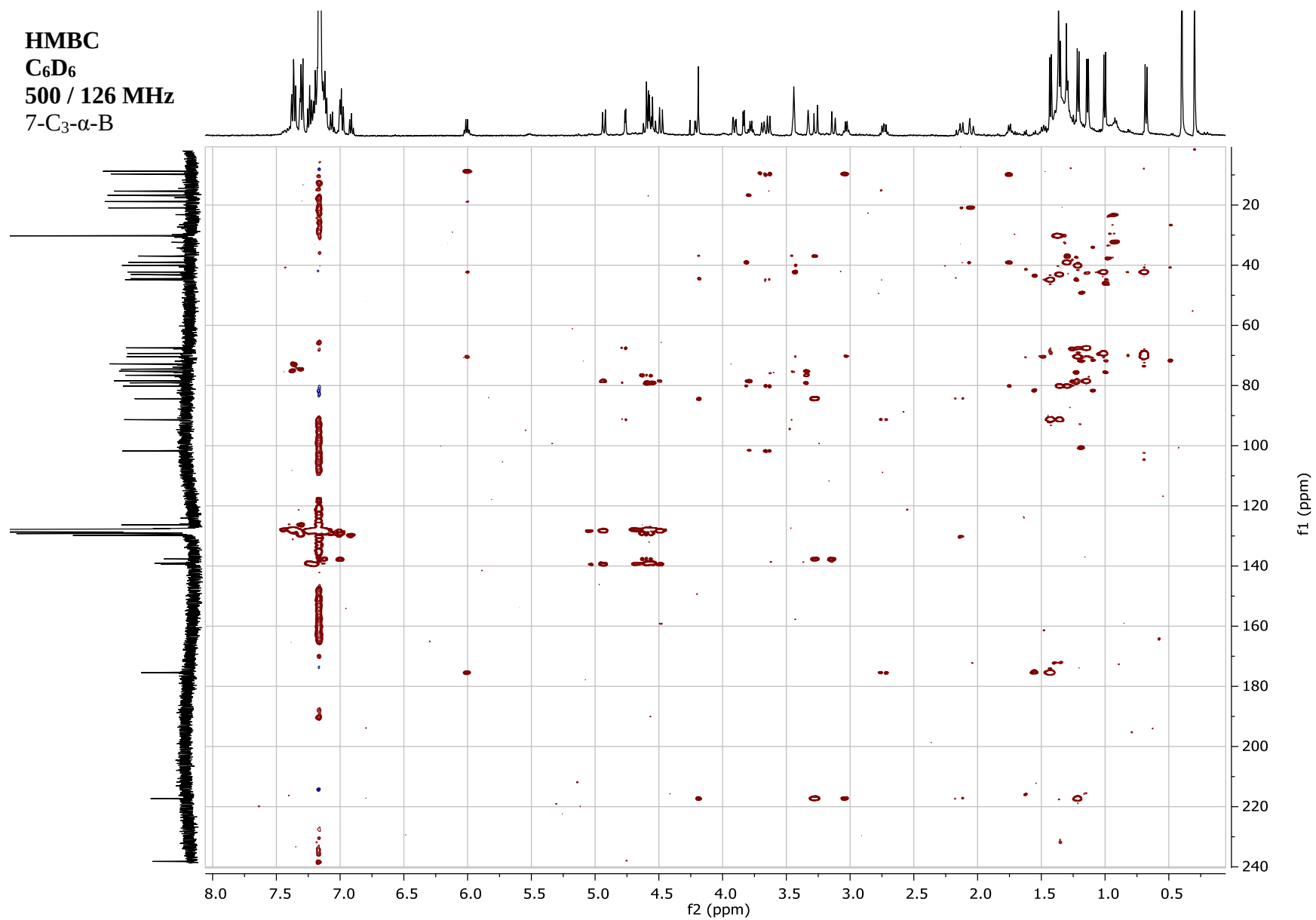


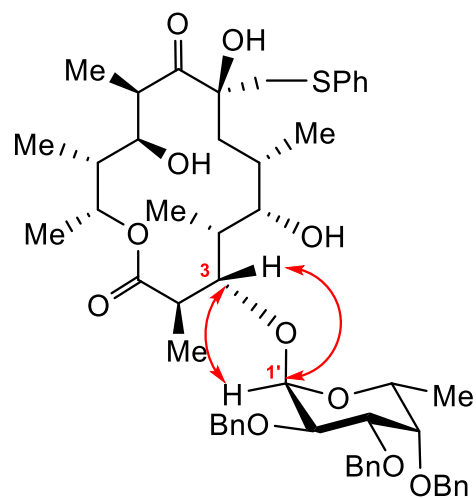
HMBC

C₆D₆

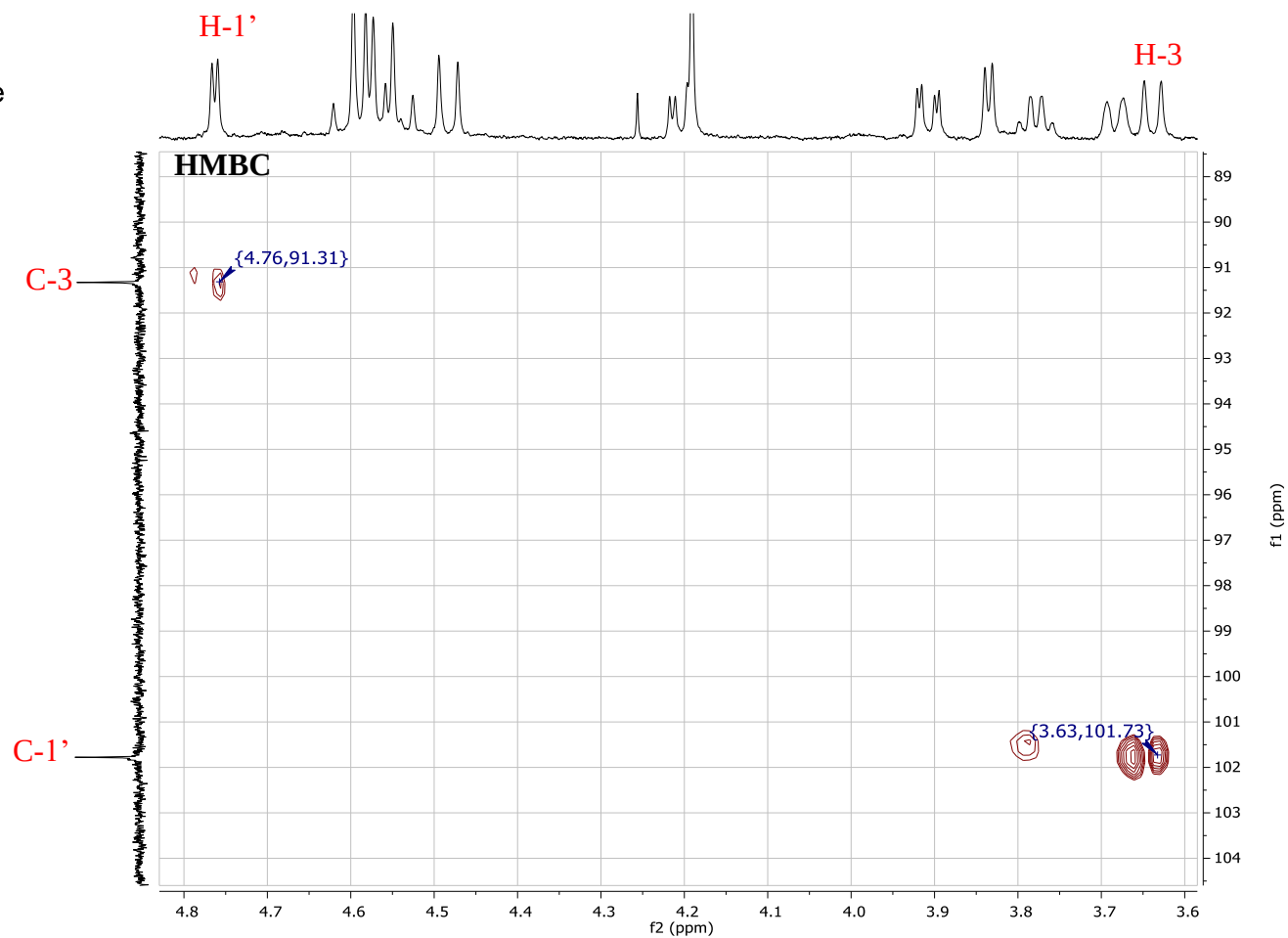
500 / 126 MHz

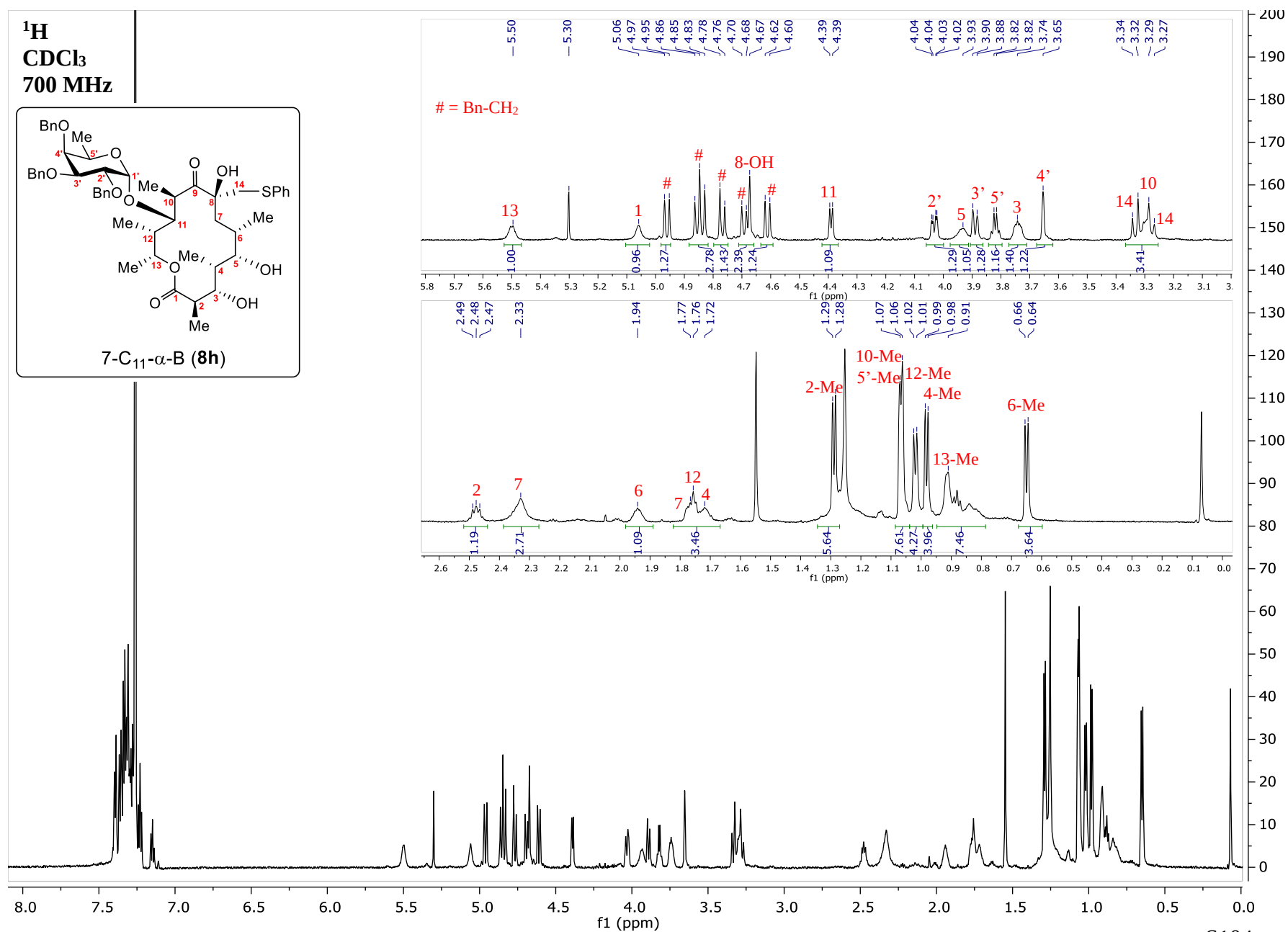
7-C₃- α -B

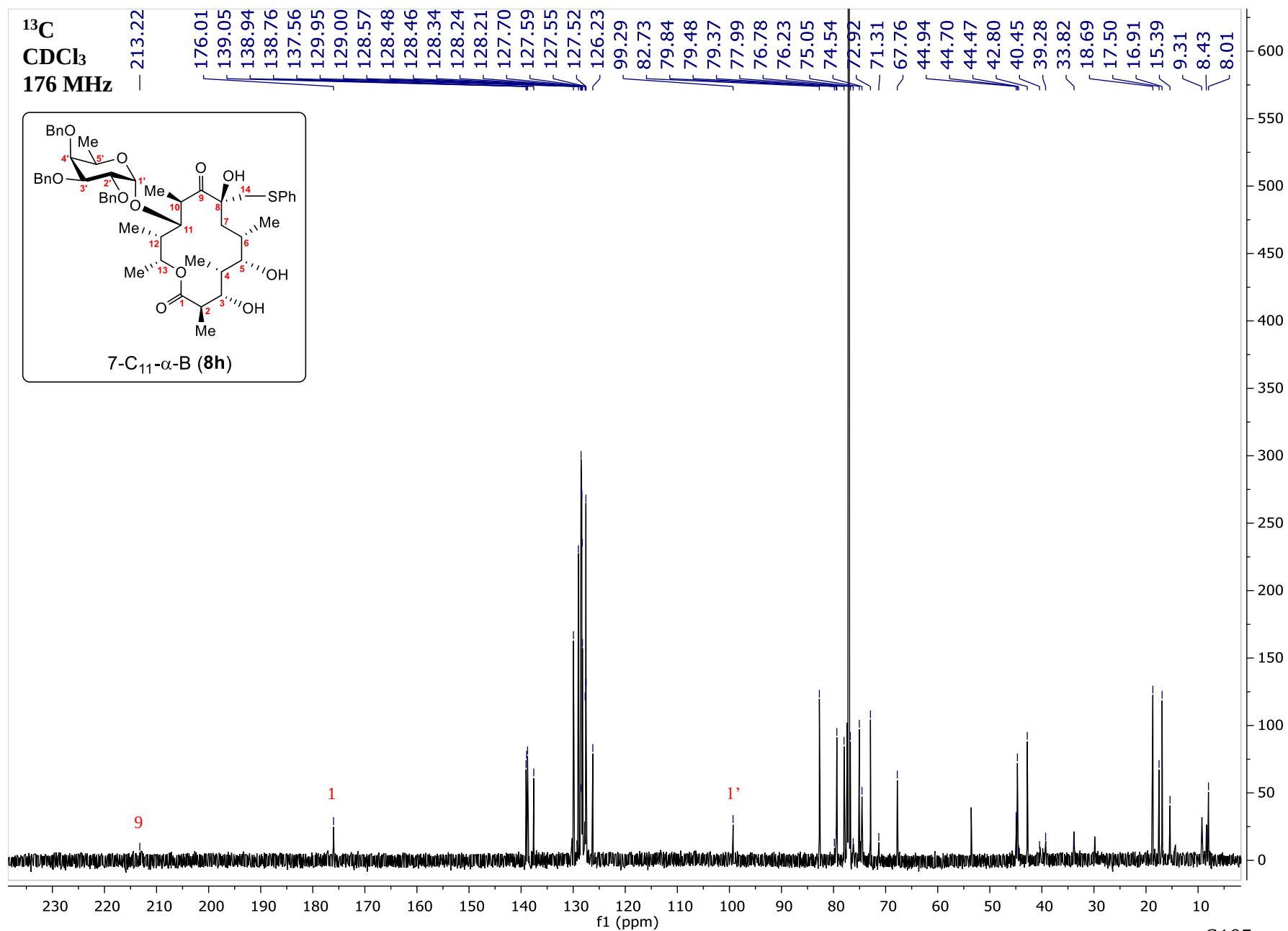




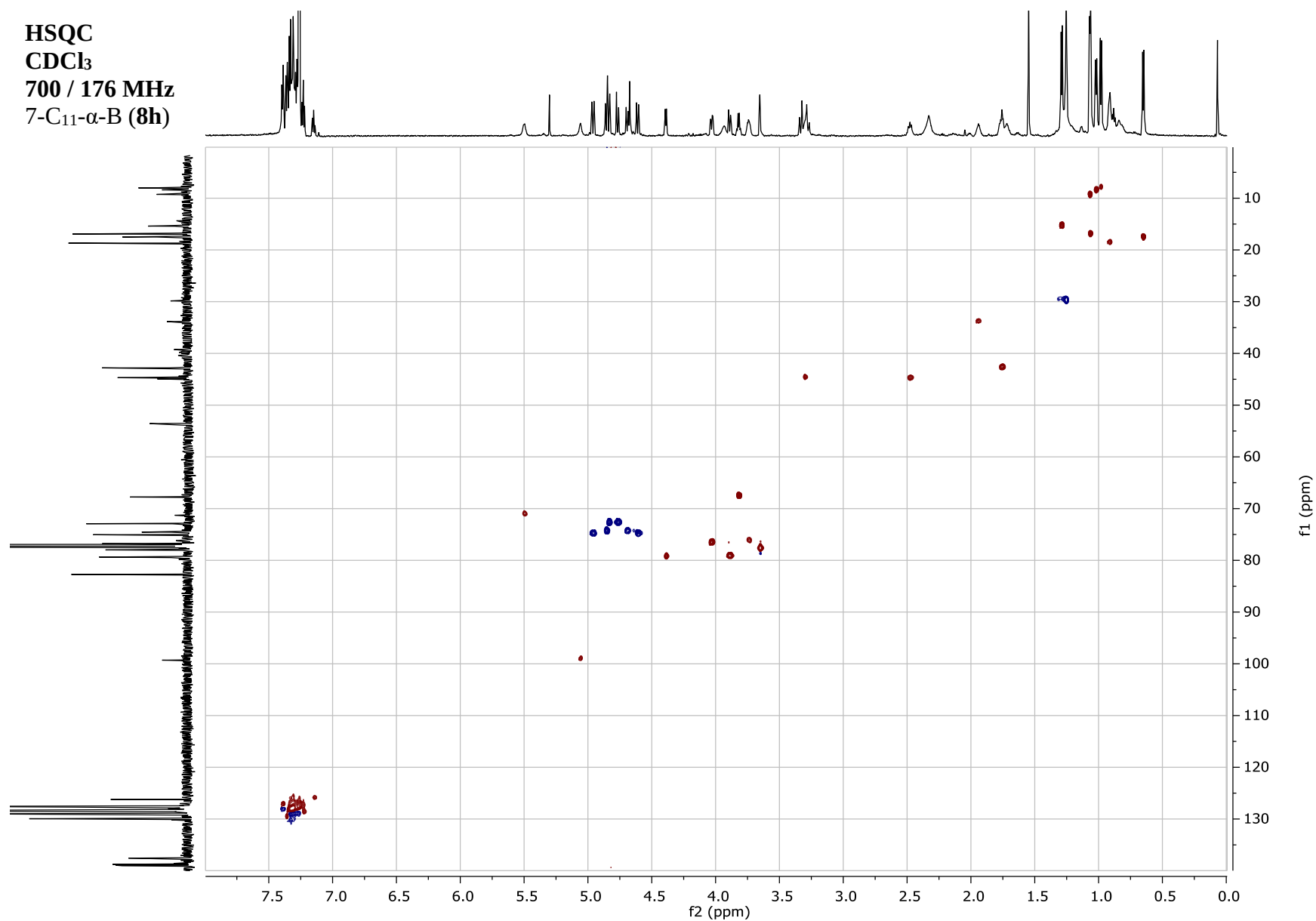
7-C₃-α-B



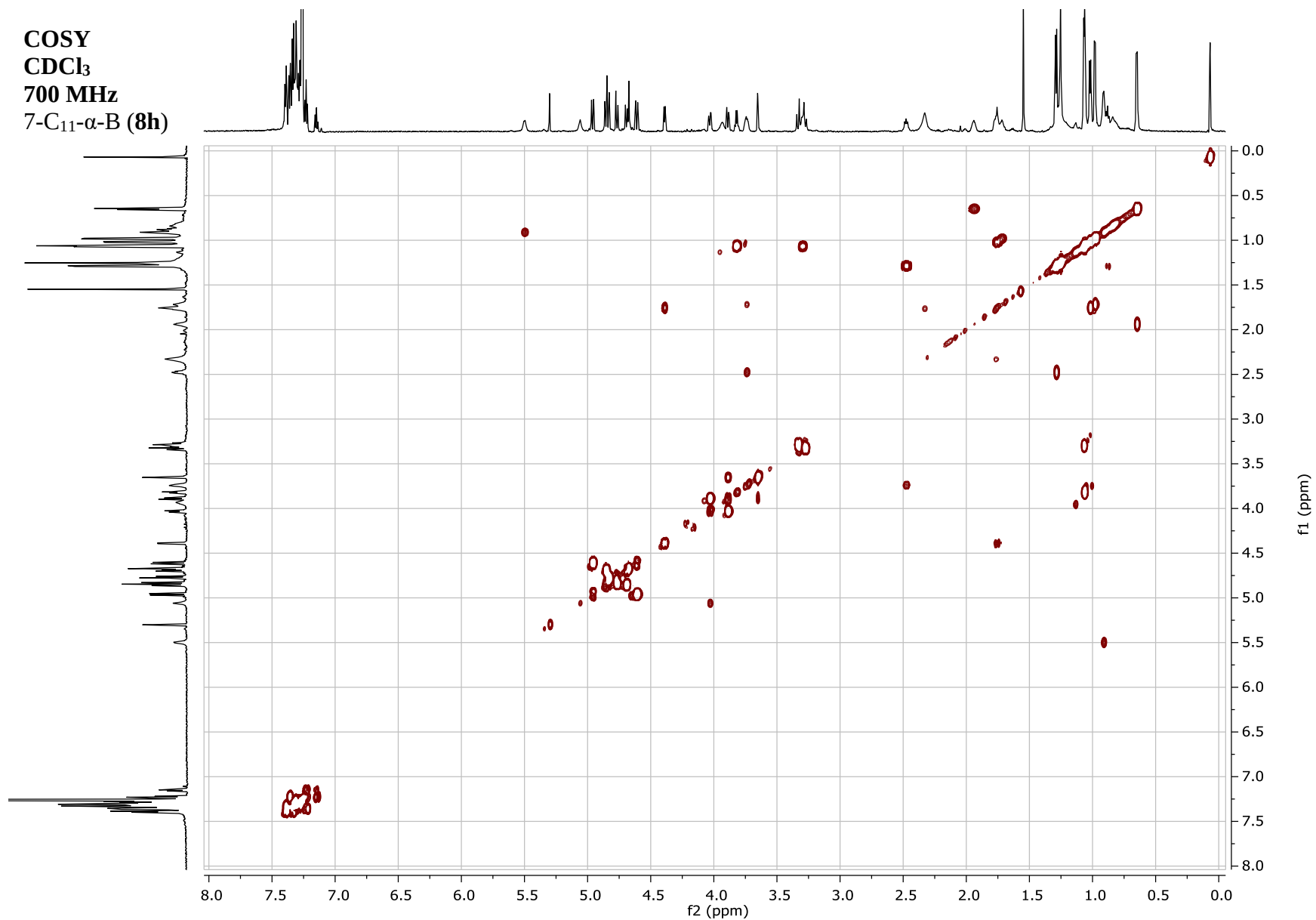




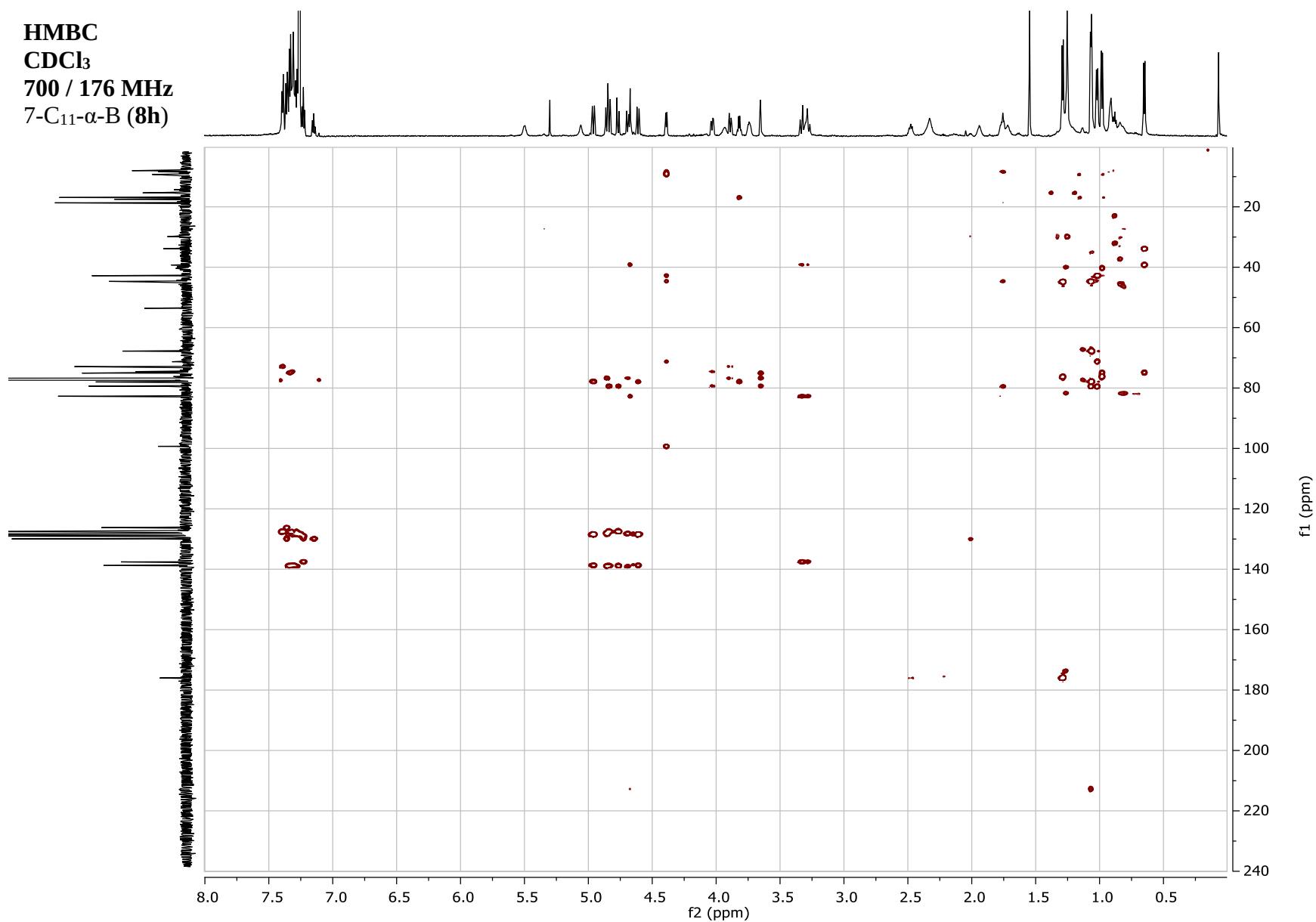
HSQC
CDCl₃
700 / 176 MHz
7-C₁₁-α-B (8h)

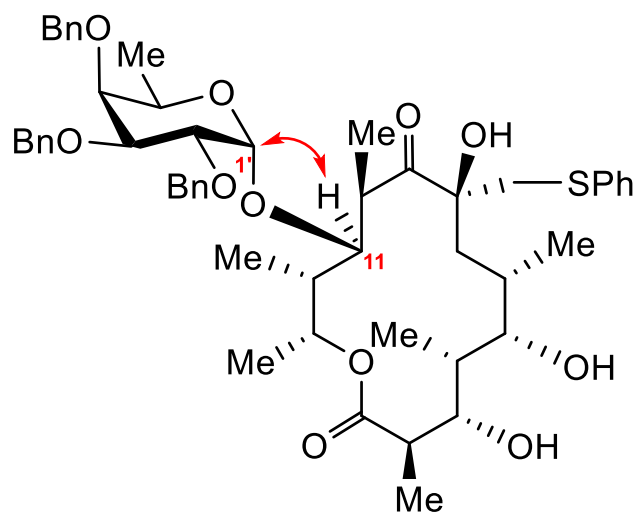


COSY
CDCl₃
700 MHz
7-C₁₁- α -B (8h)

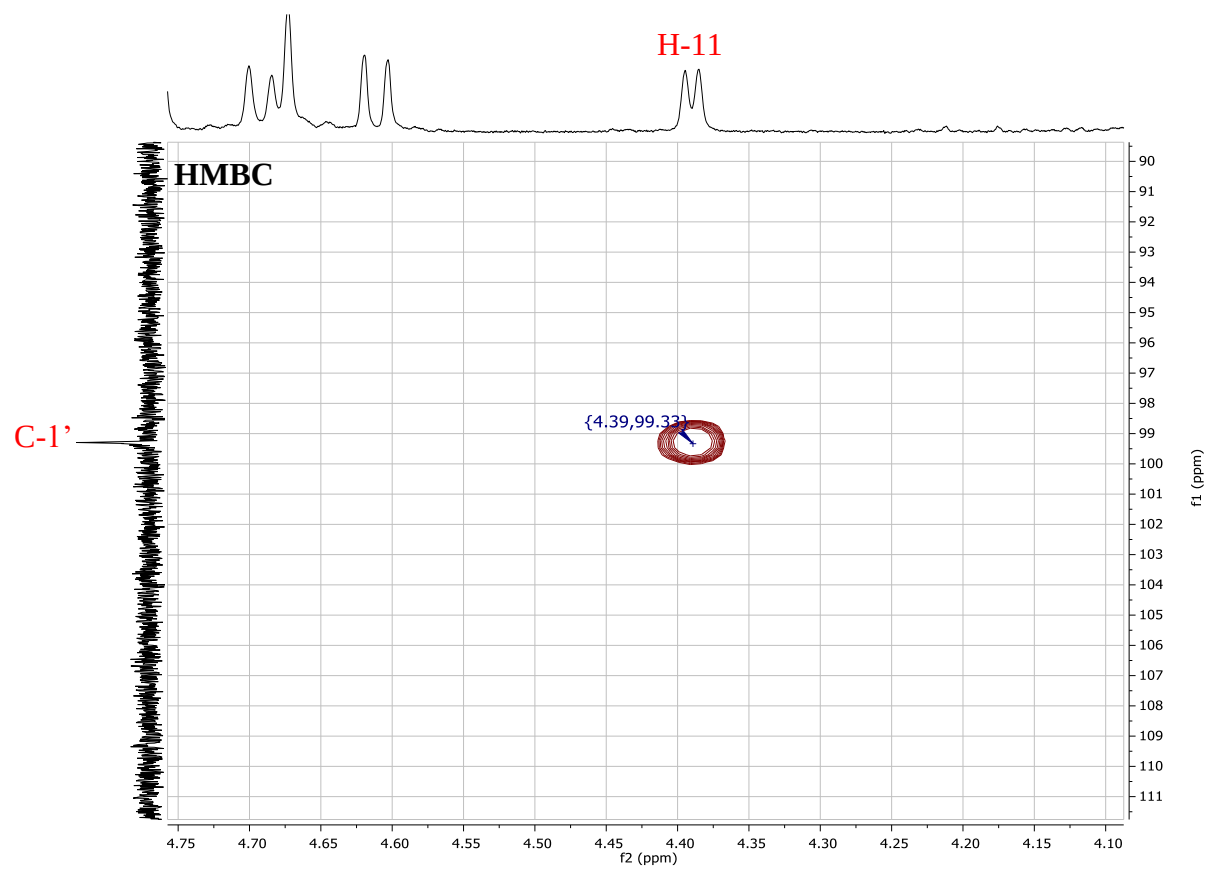


HMBC
CDCl₃
700 / 176 MHz
7-C₁₁- α -B (8h)



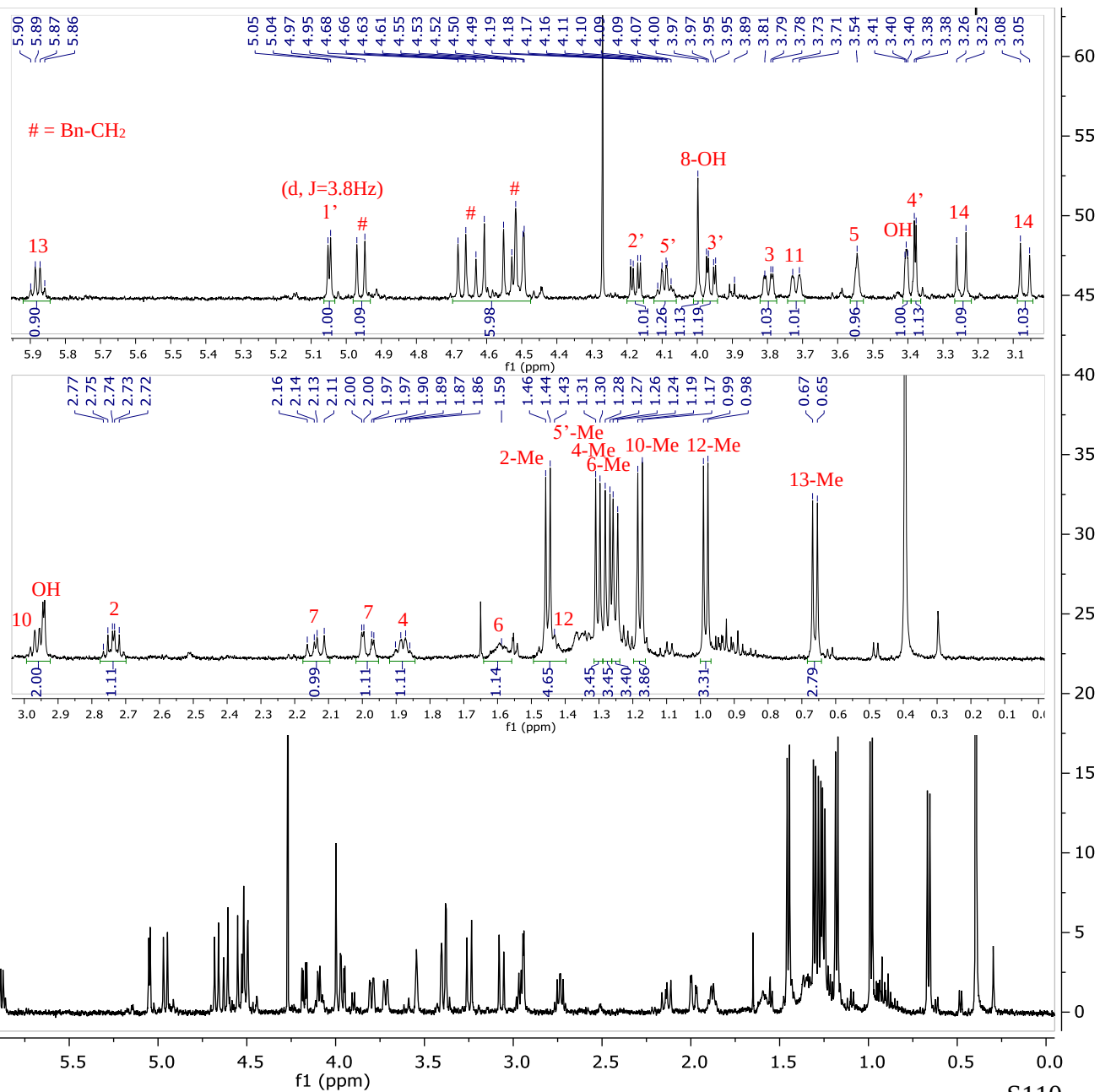
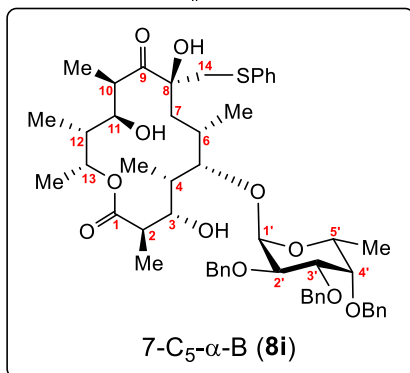


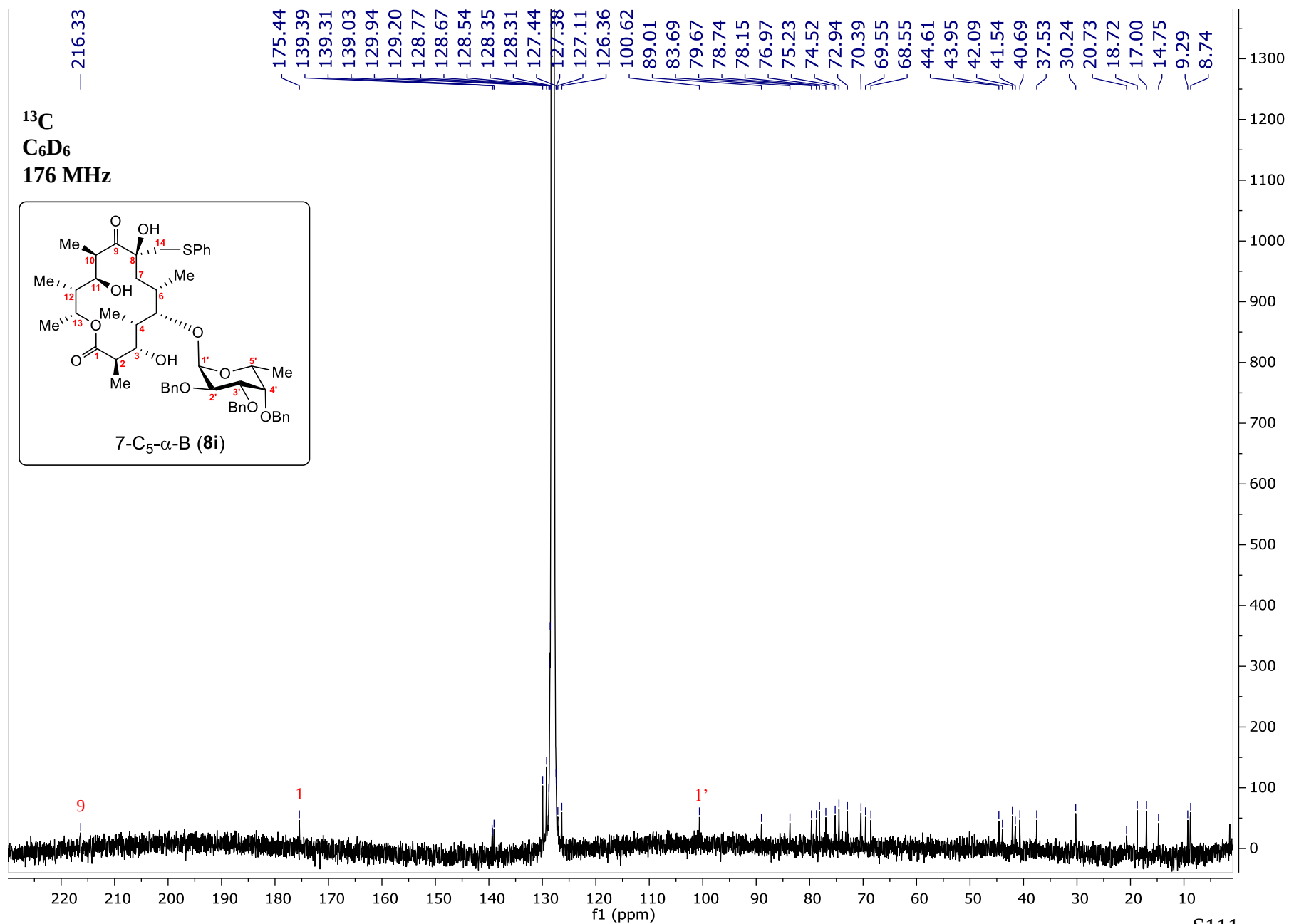
7-C₁₁-α-B (8h)



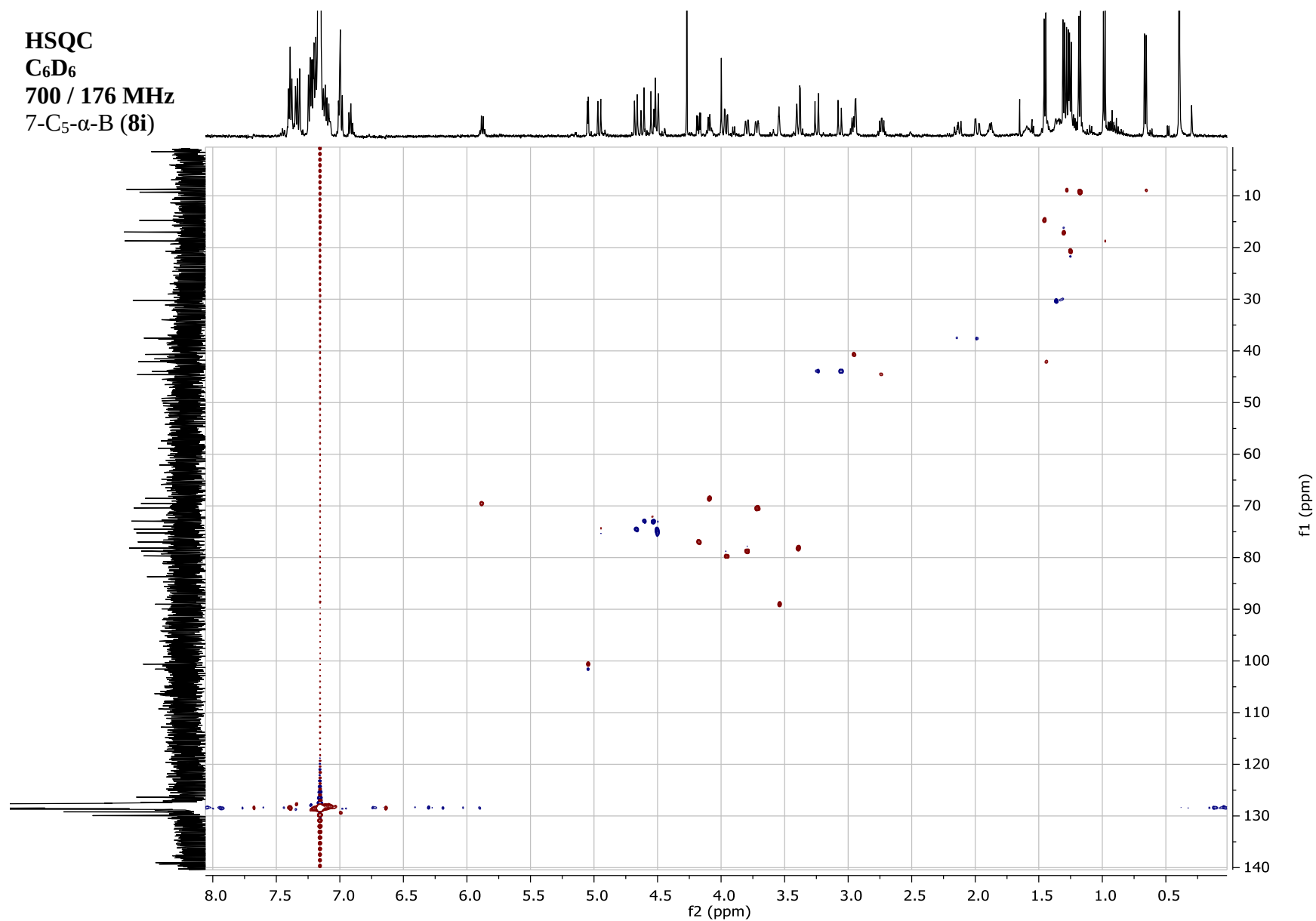
$$^1\text{H}$$

$$\text{C}_6\text{D}_6$$

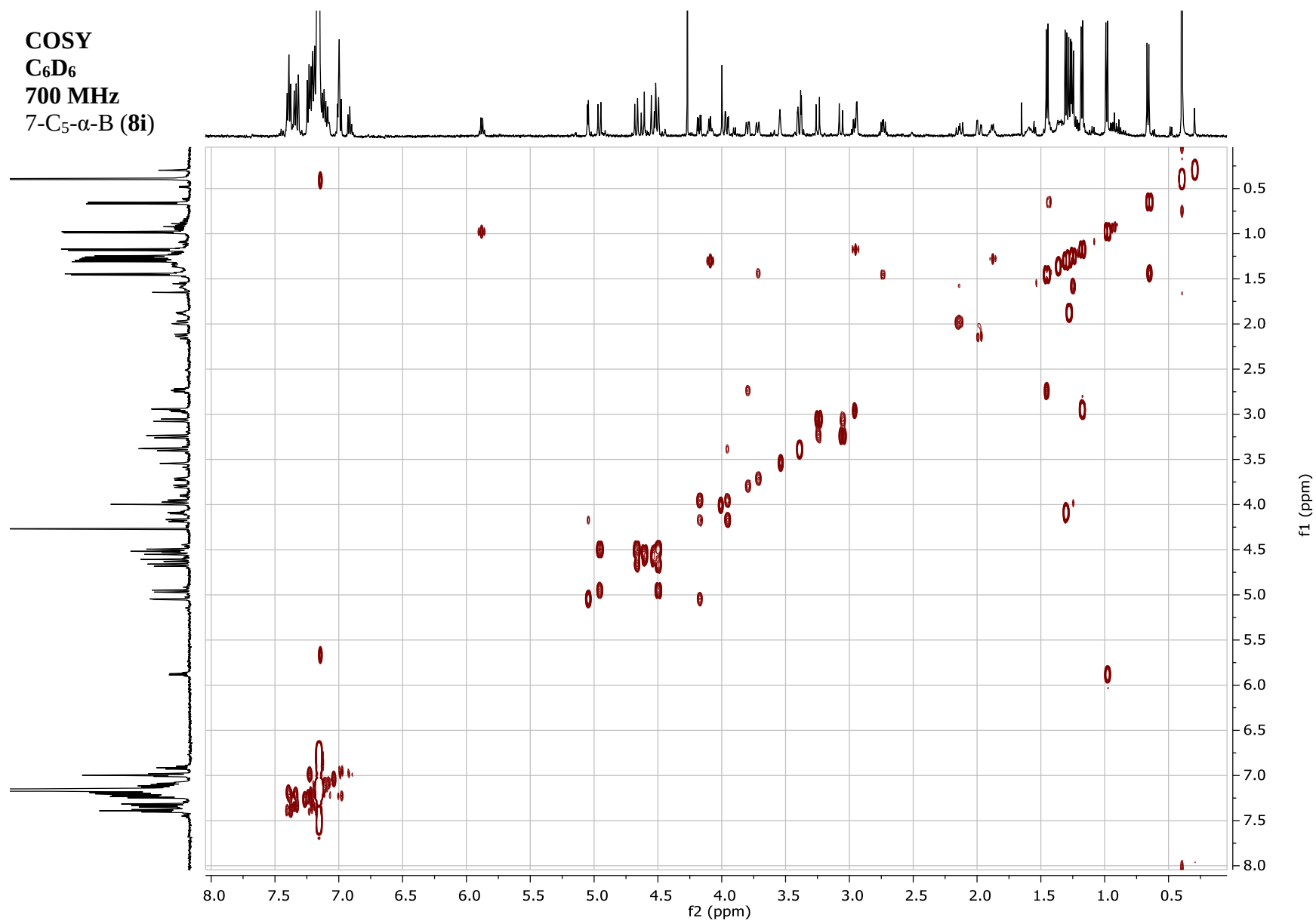
$$500 \text{ MHz}$$




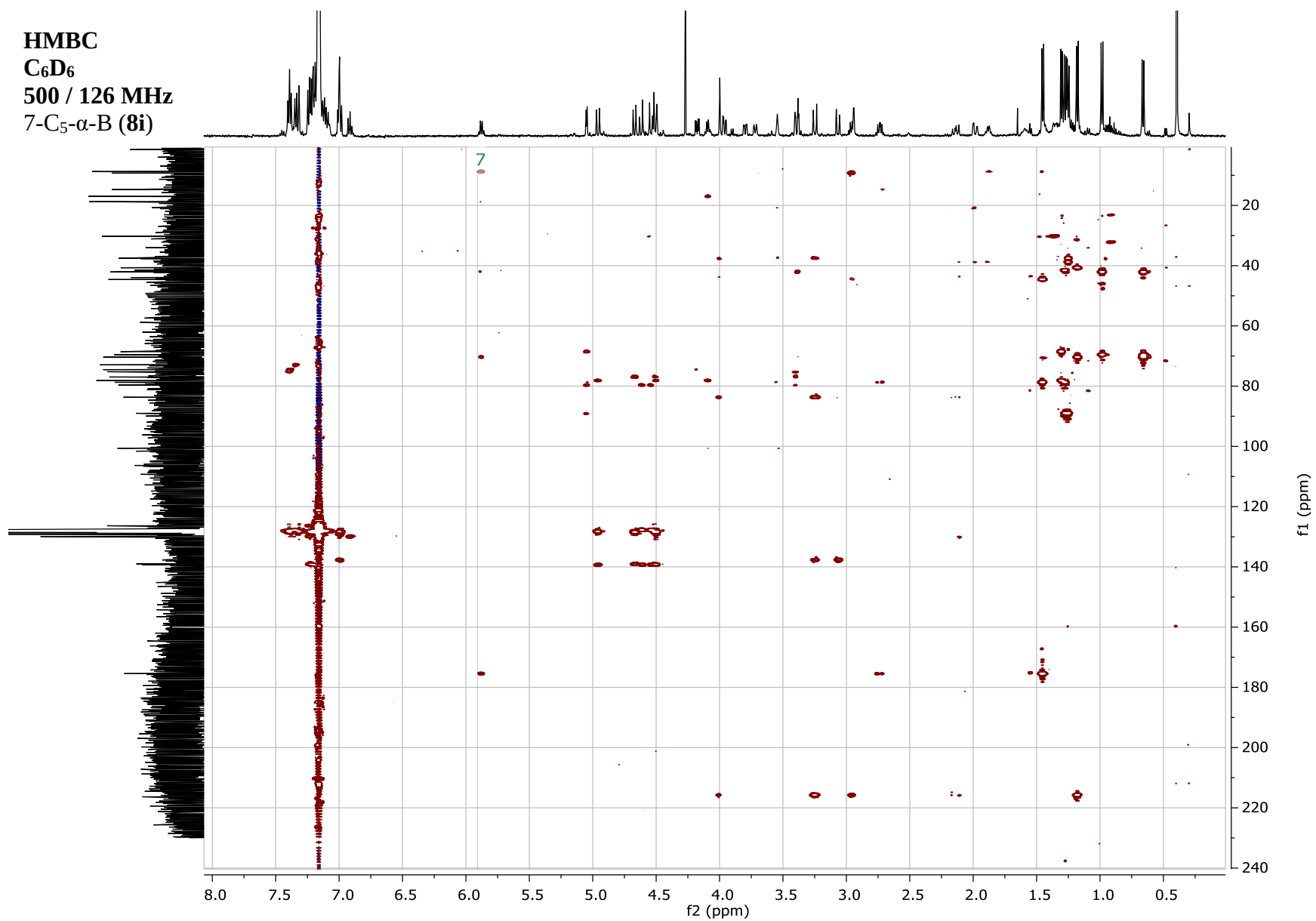
HSQC
C₆D₆
700 / 176 MHz
7-C₅- α -B (8i)

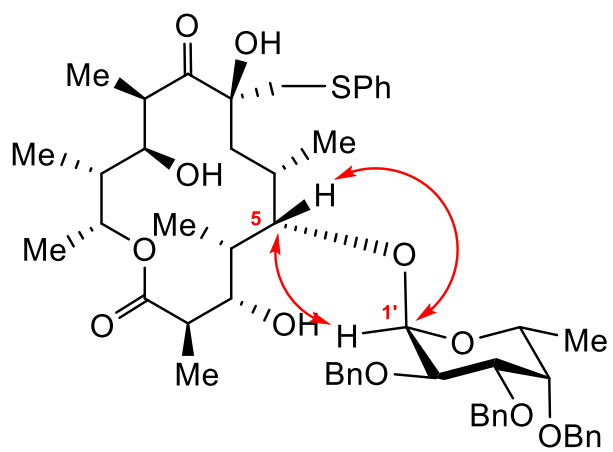


COSY
C₆D₆
700 MHz
7-C₅- α -B (8i)

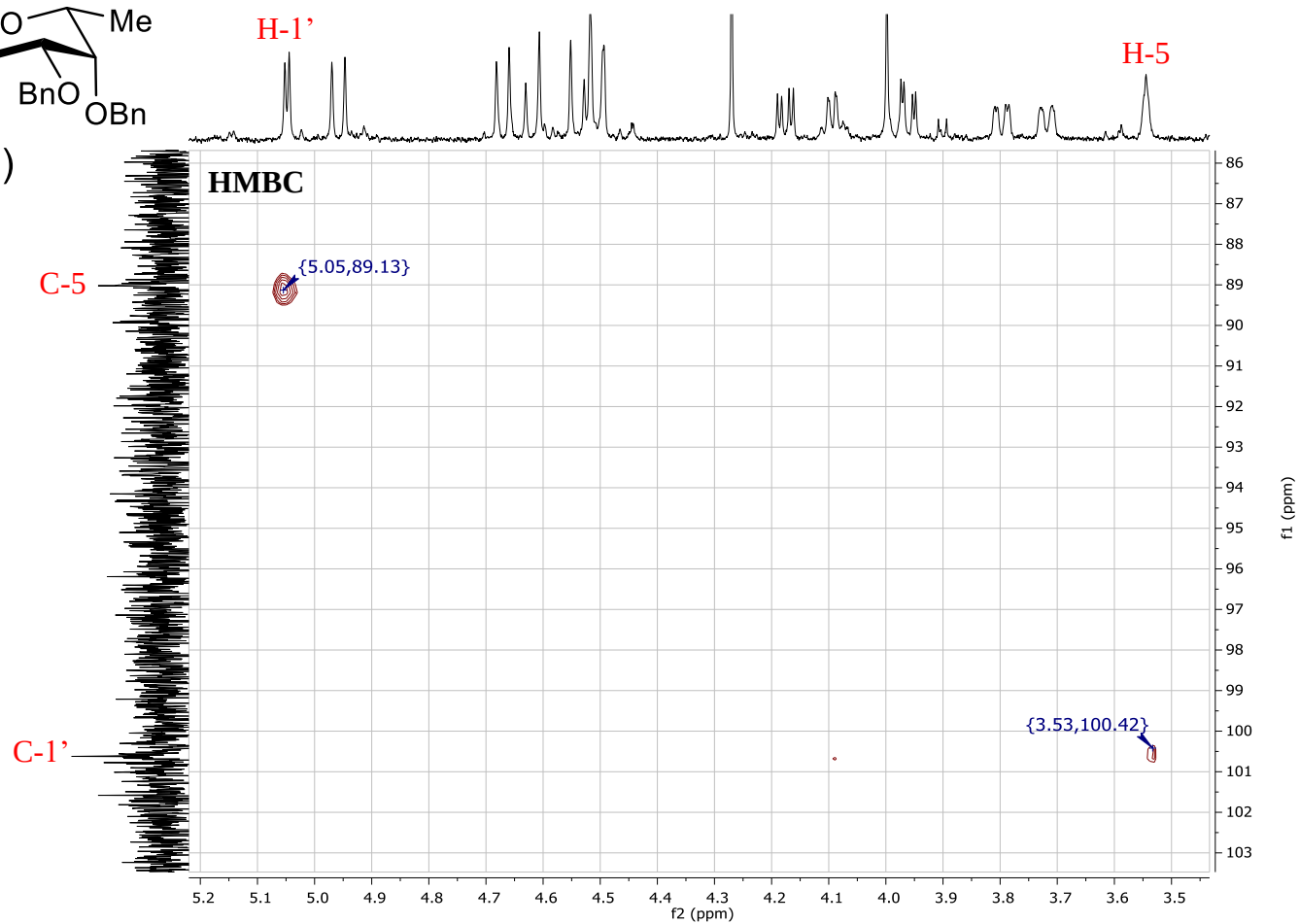


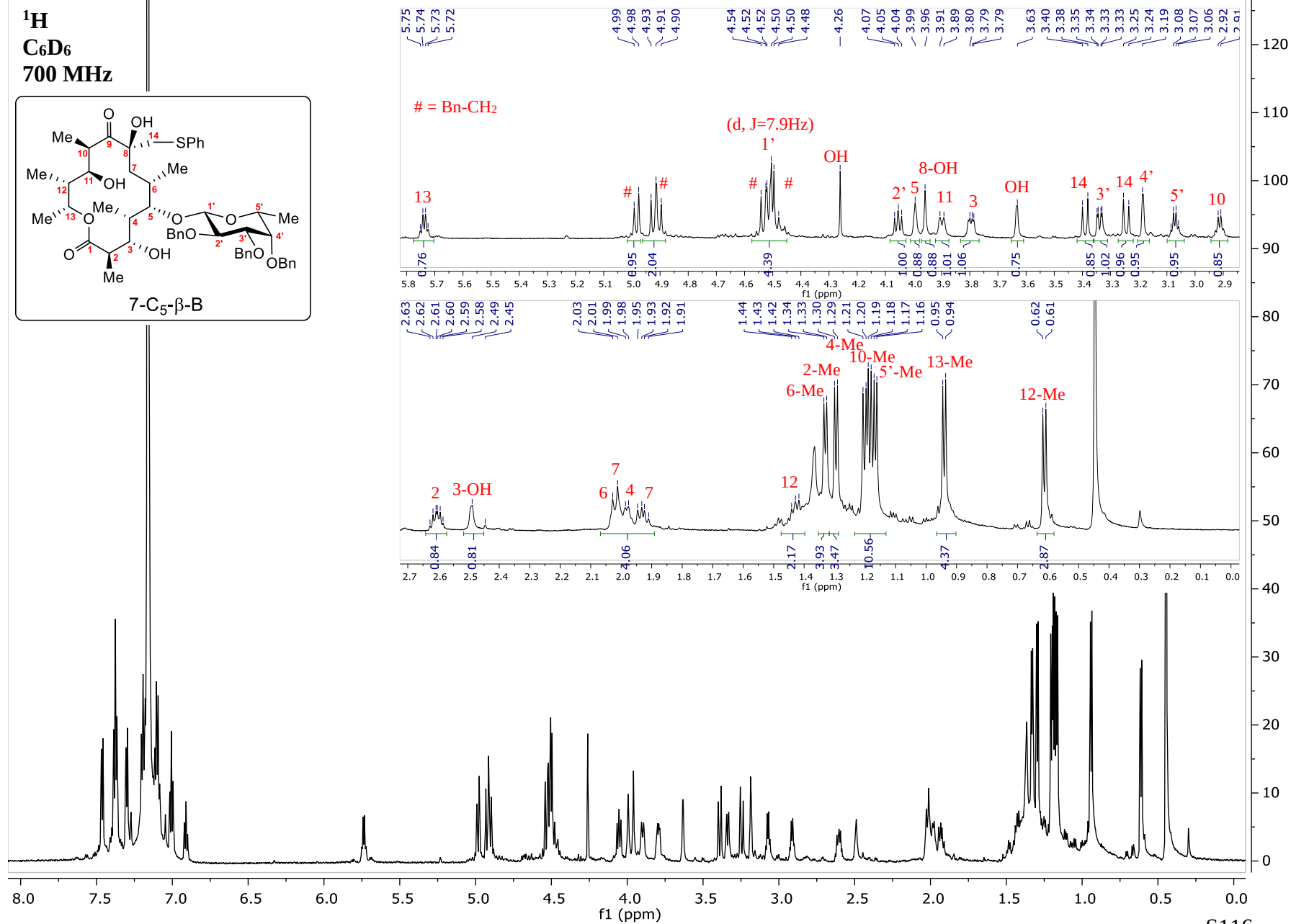
HMBC
C₆D₆
500 / 126 MHz
7-C₅- α -B (8i)

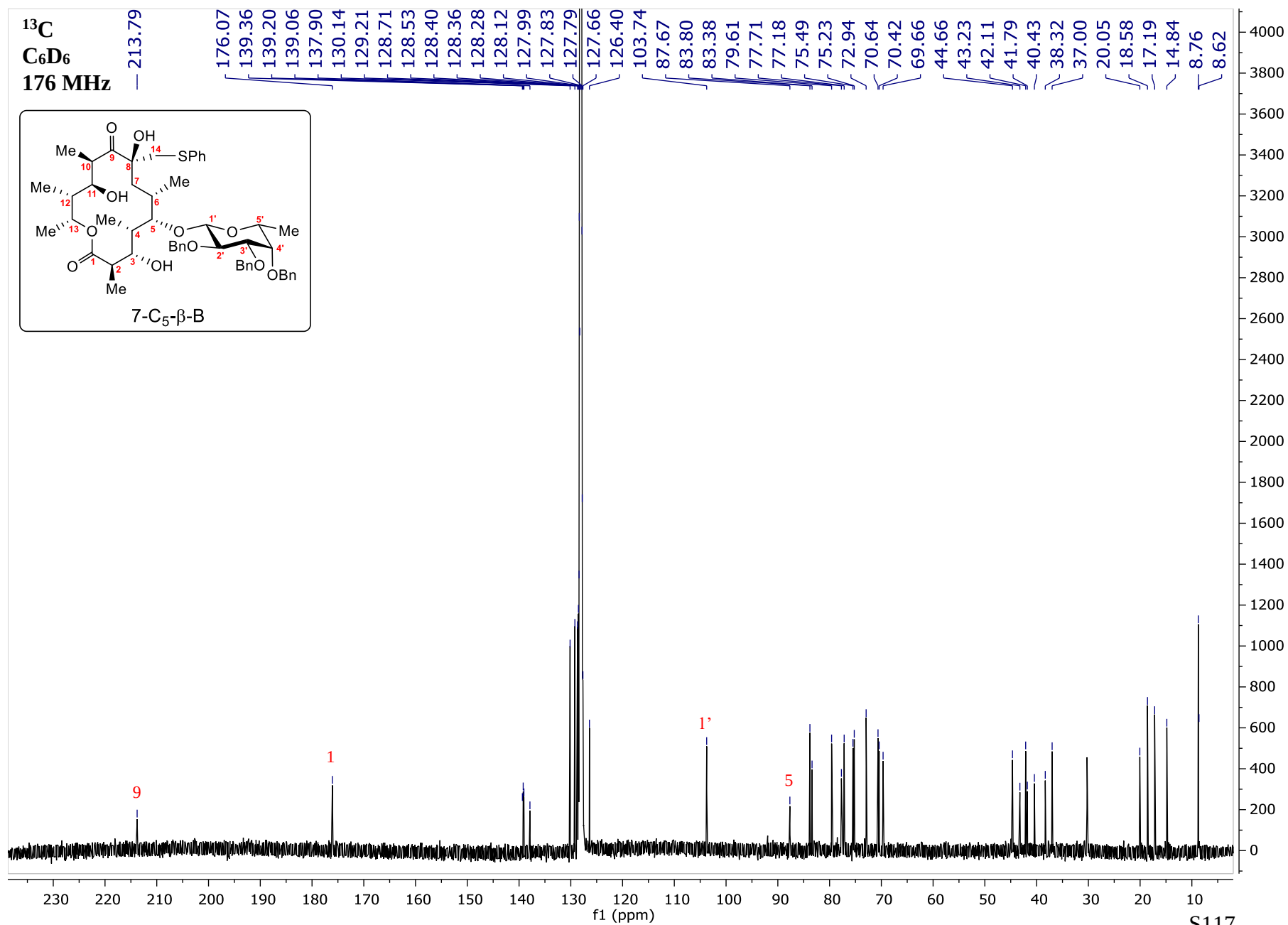




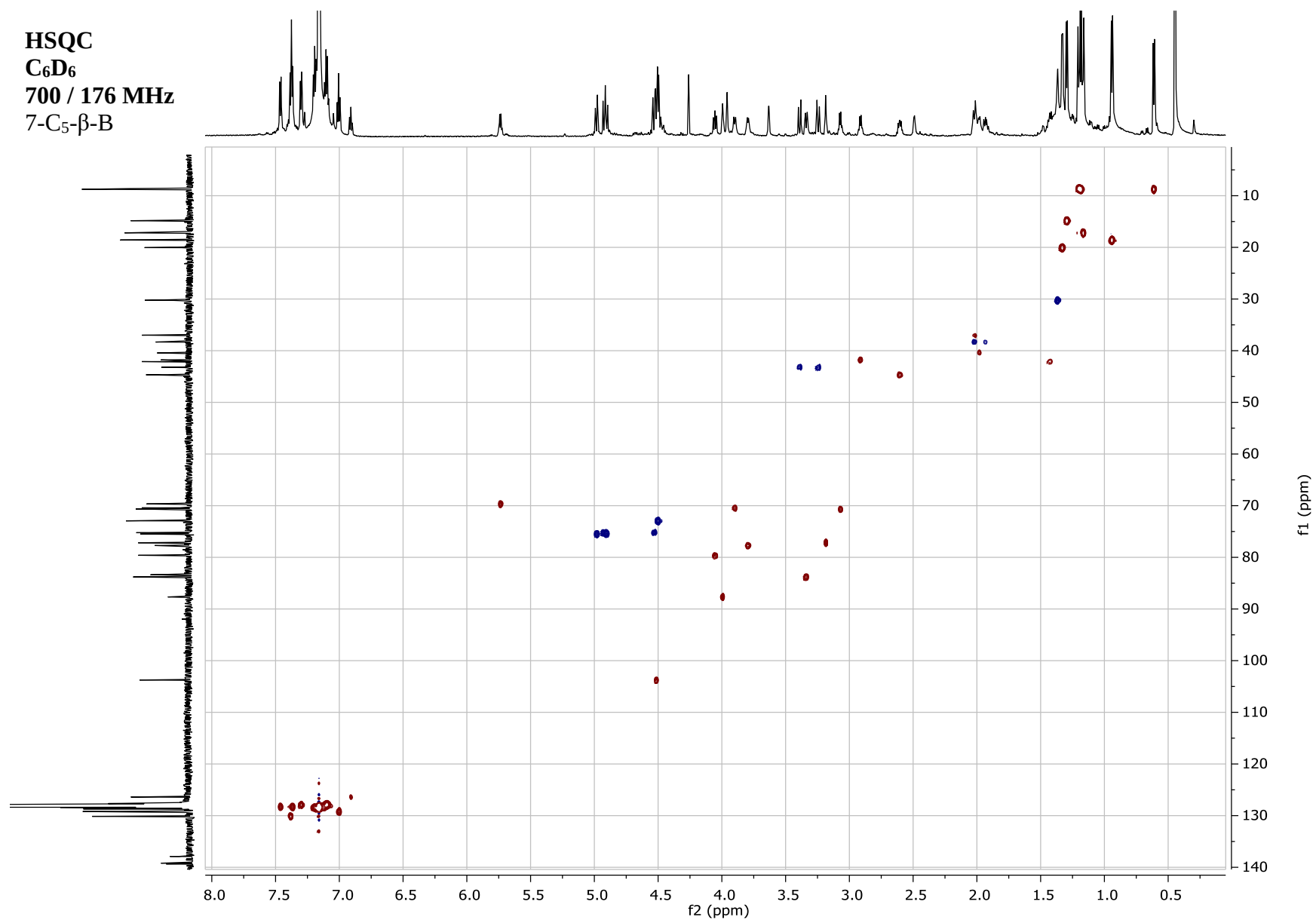
7-C₅-α-B (8i)

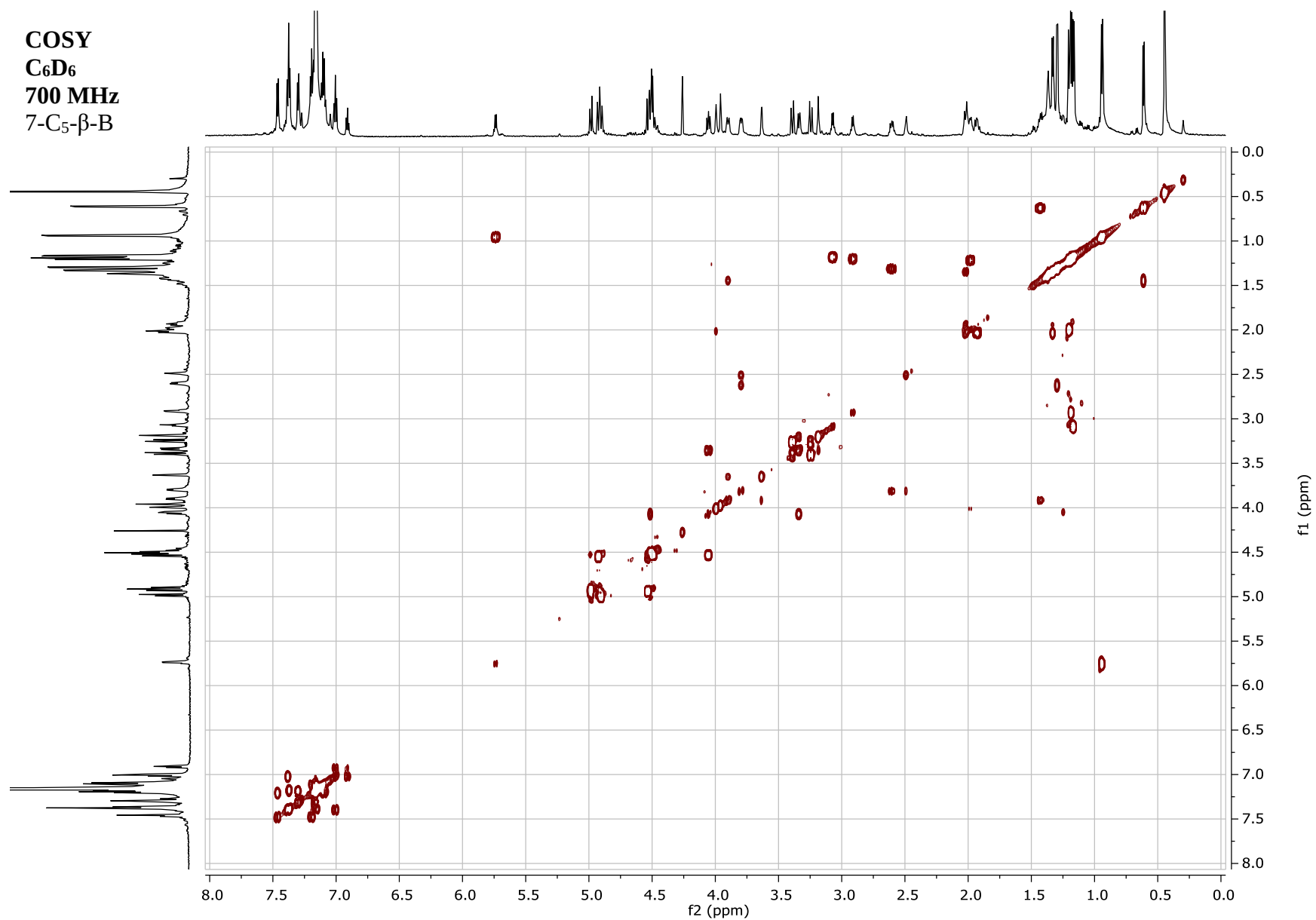




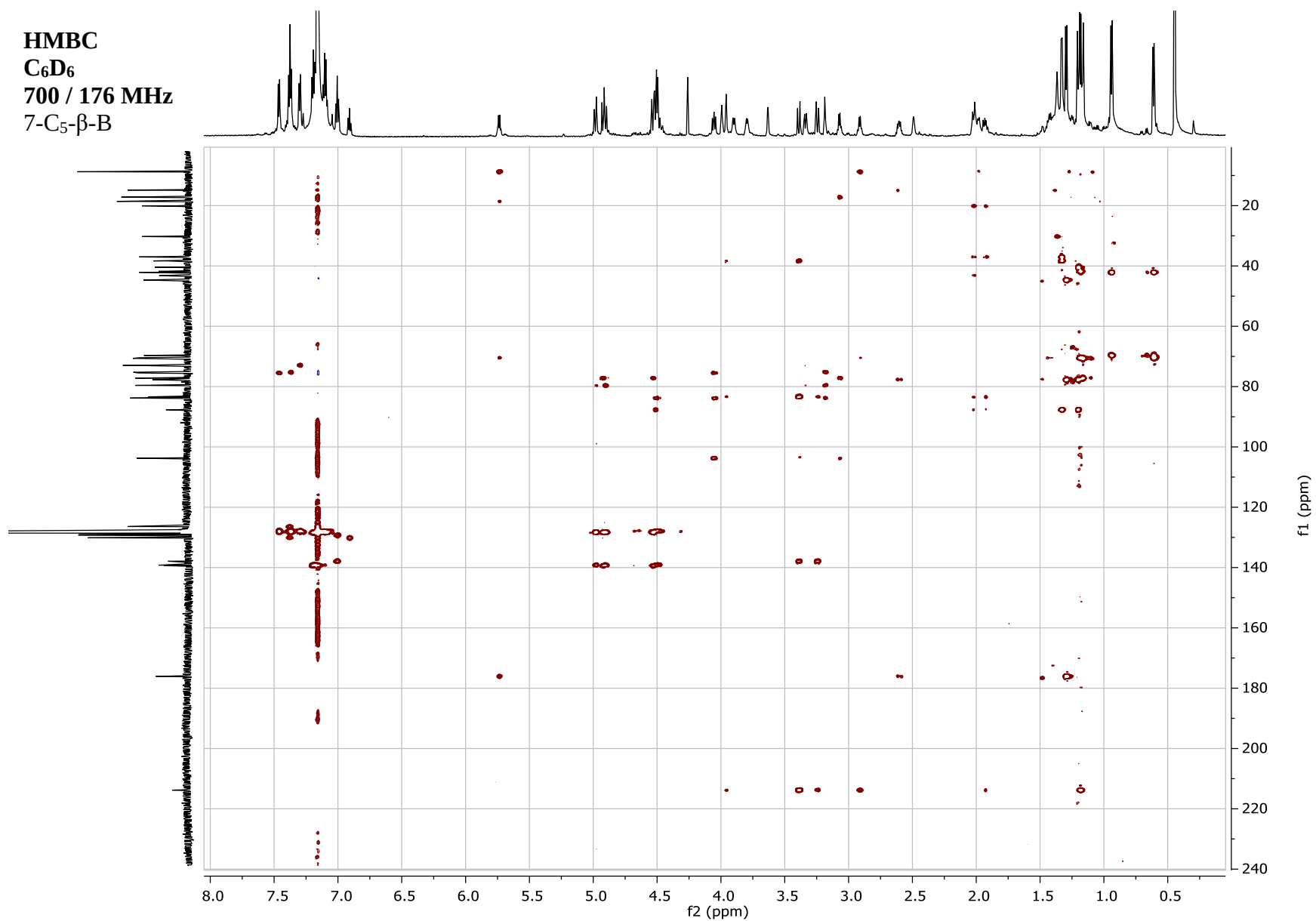


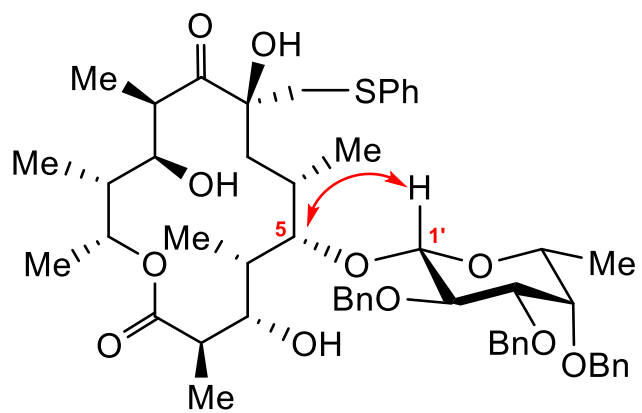
HSQC
C₆D₆
700 / 176 MHz
7-C₅-β-B



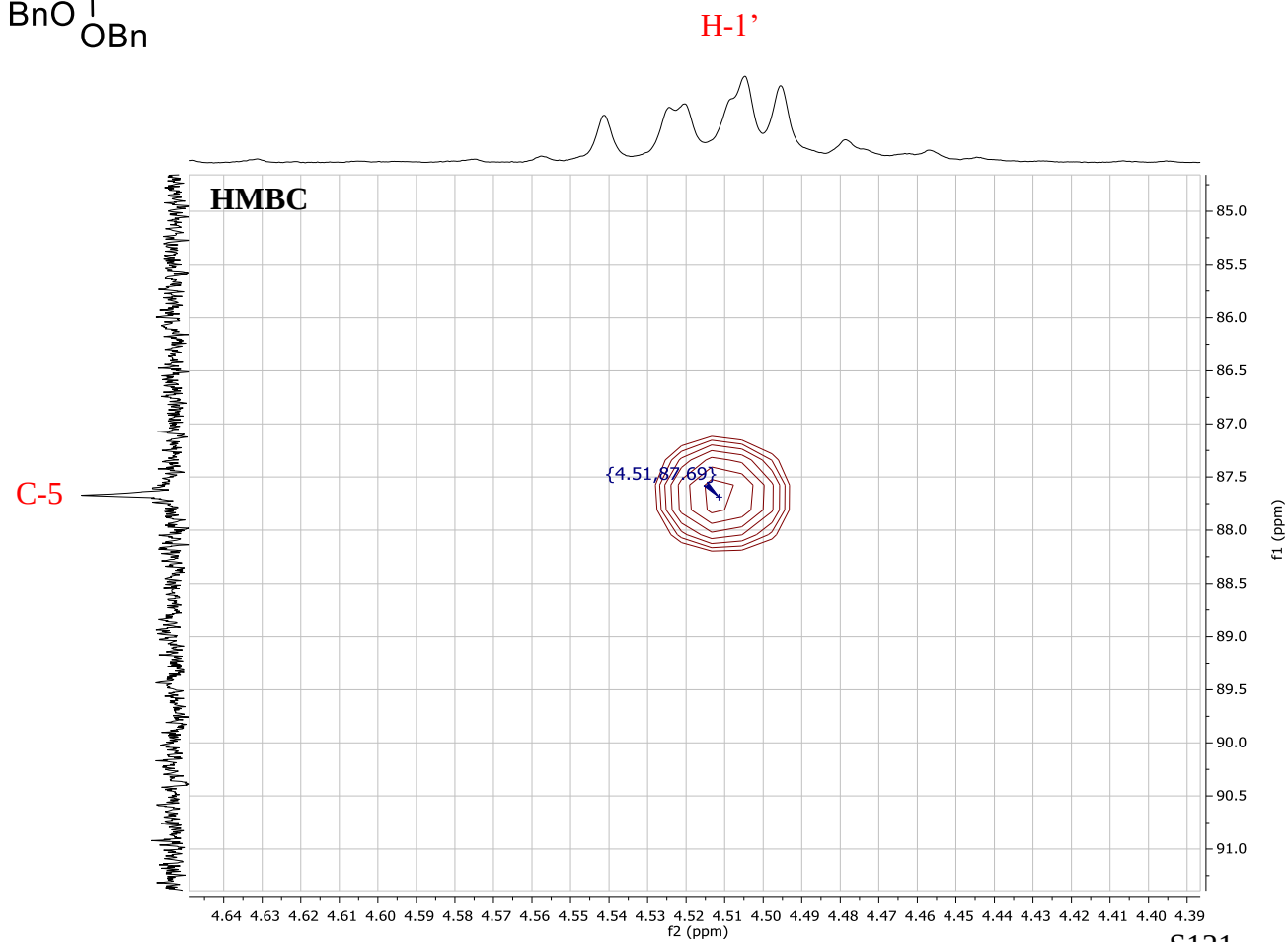


HMBC
C₆D₆
700 / 176 MHz
7-C₅-β-B

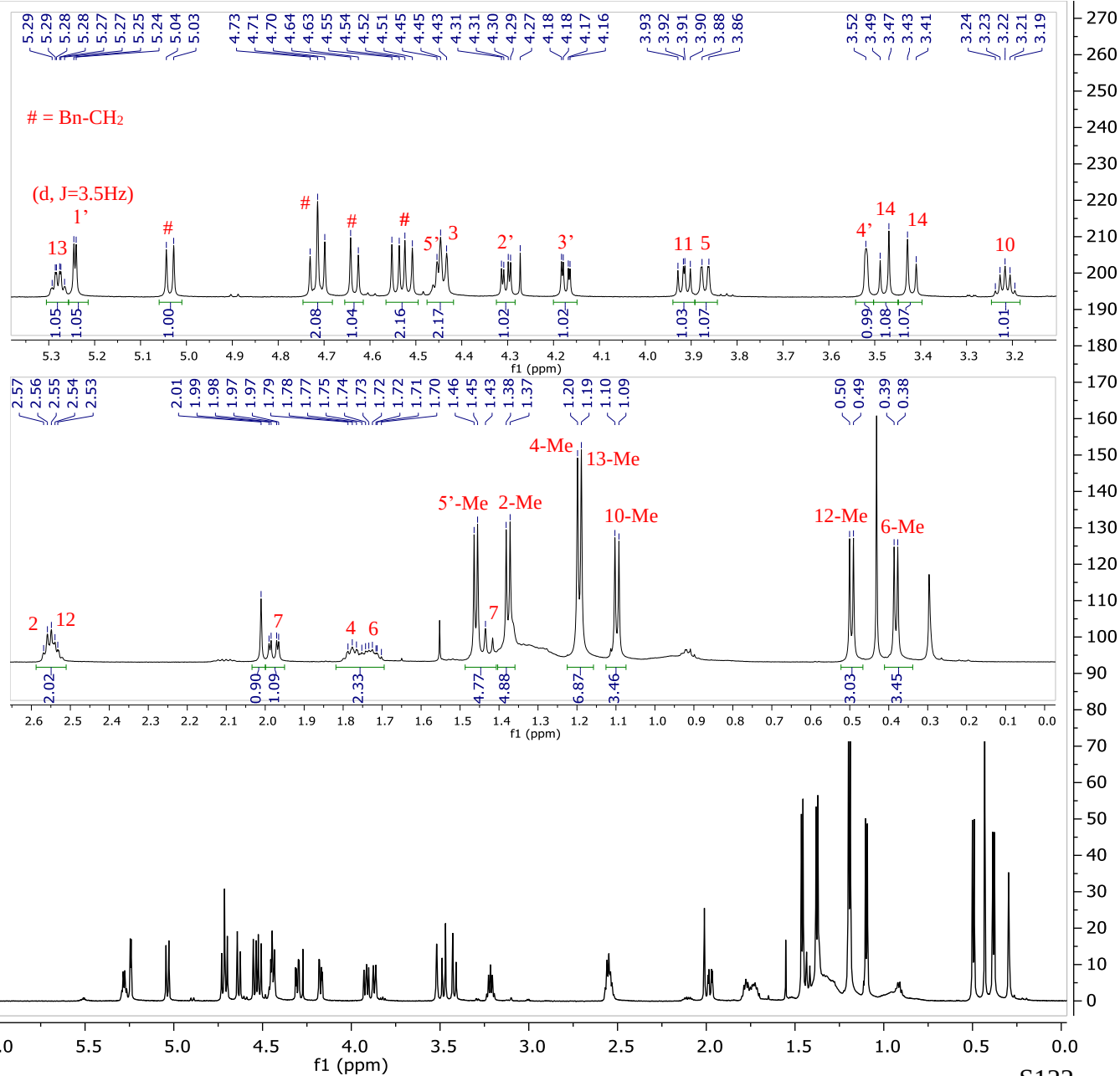
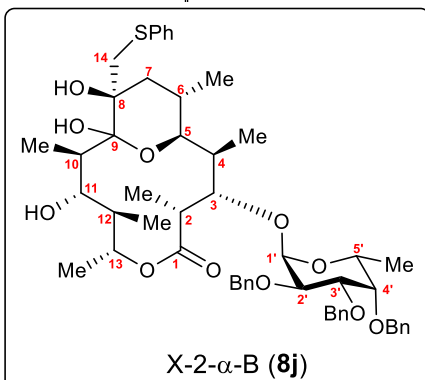


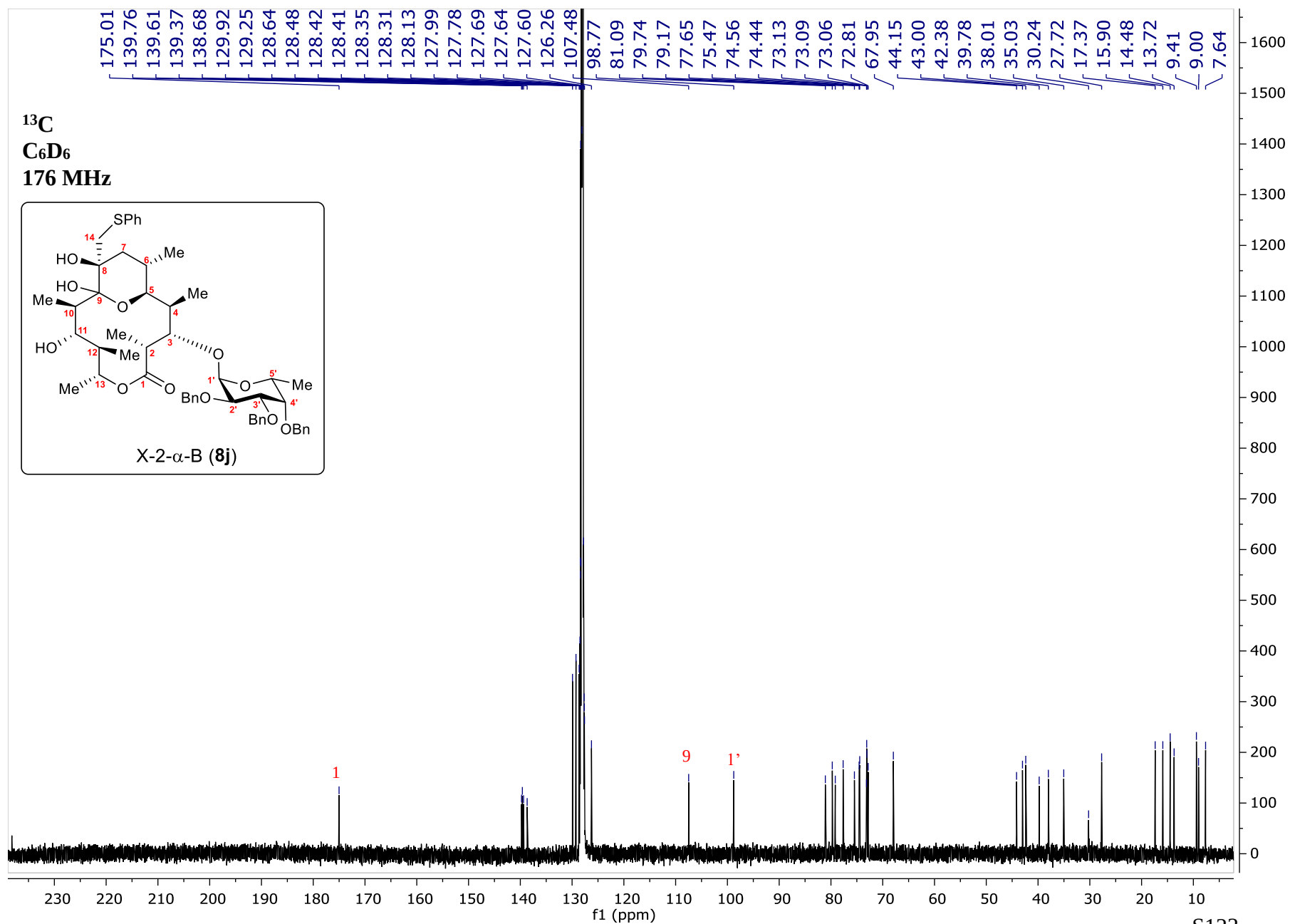


7-C₅-β-B

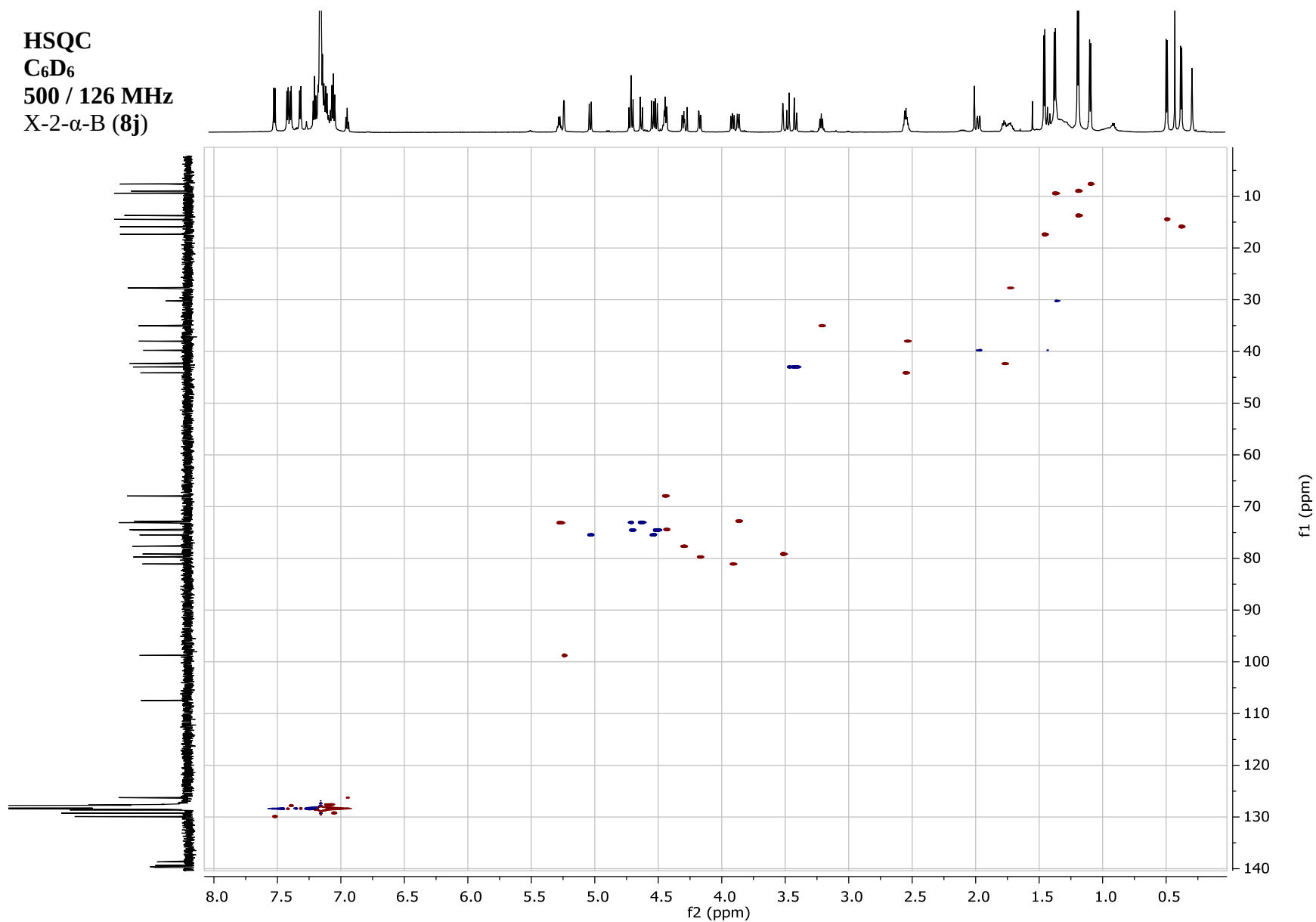


¹H
C₆D₆
700 MHz

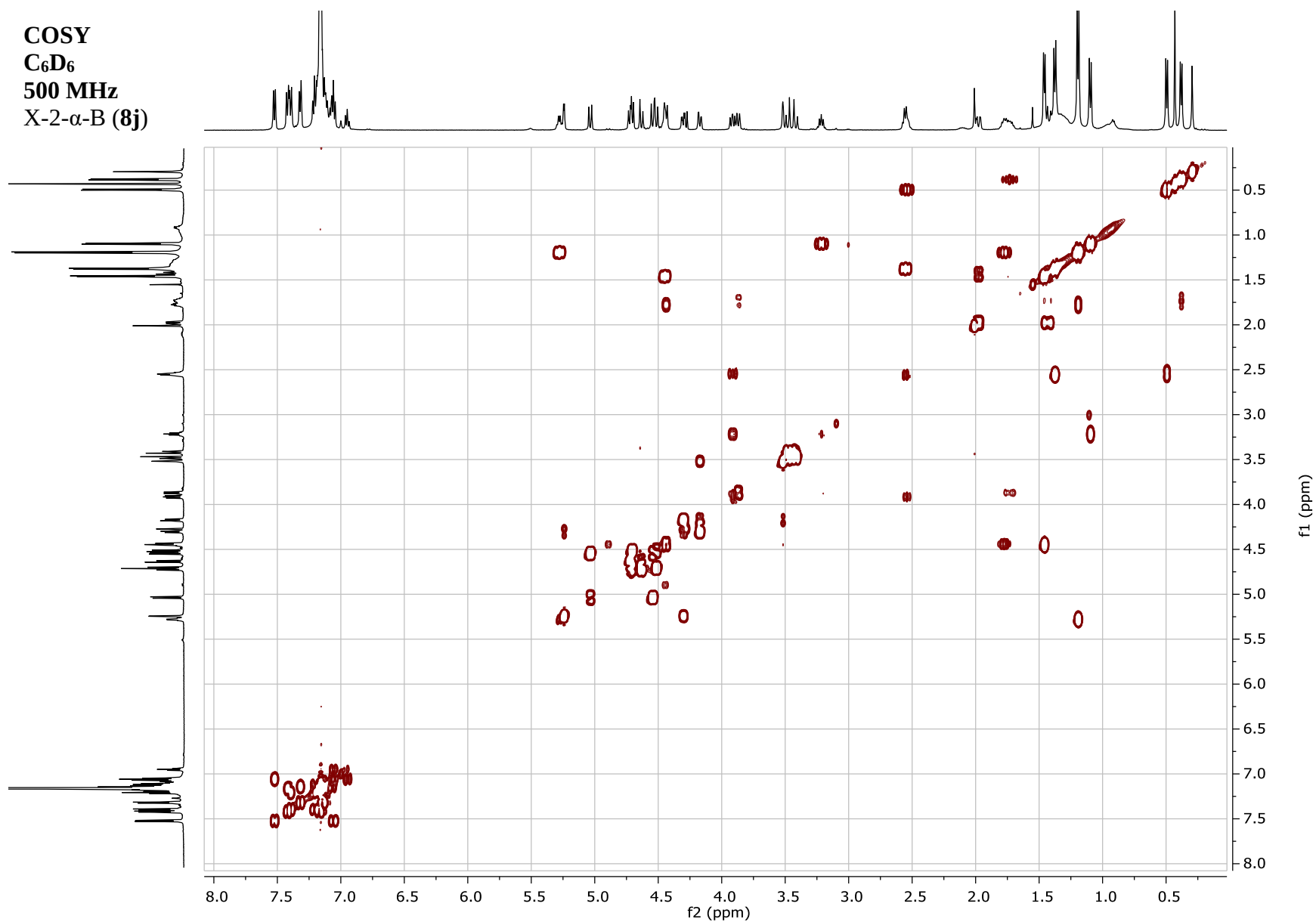




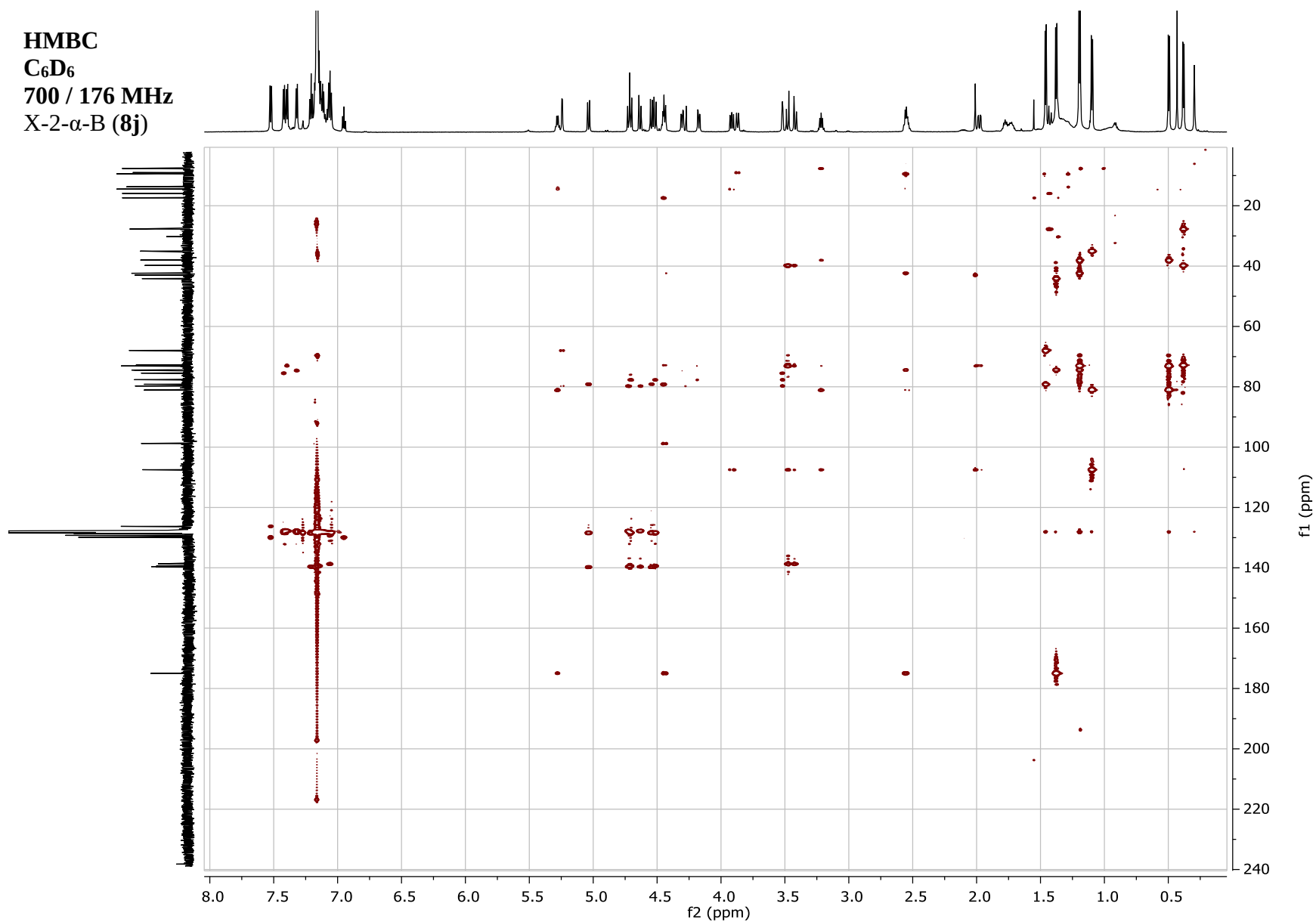
HSQC
C₆D₆
500 / 126 MHz
X-2- α -B (8j)

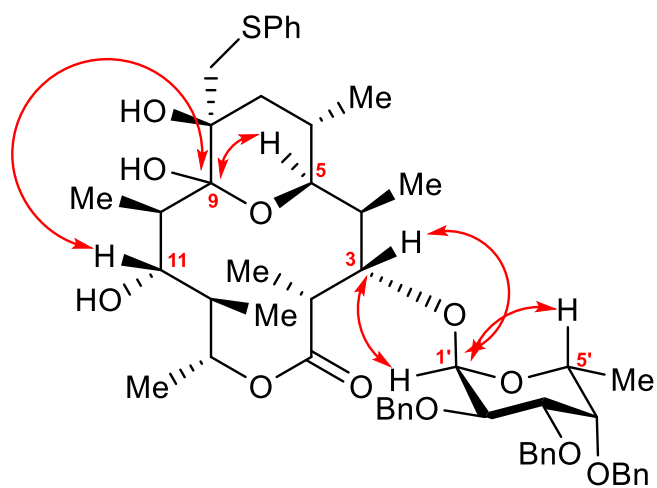


COSY
C₆D₆
500 MHz
X-2- α -B (8j)

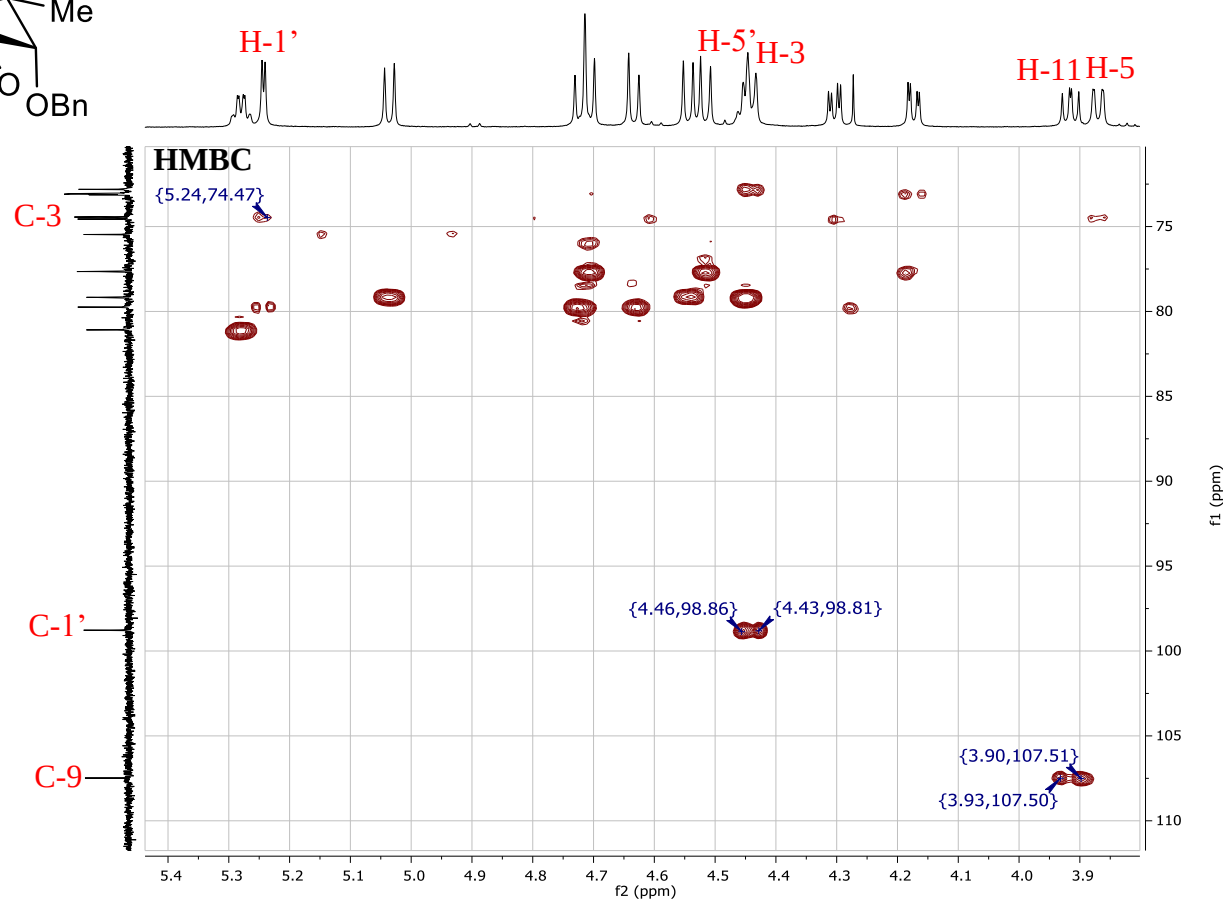


HMBC
C₆D₆
700 / 176 MHz
X-2-α-B (8j)

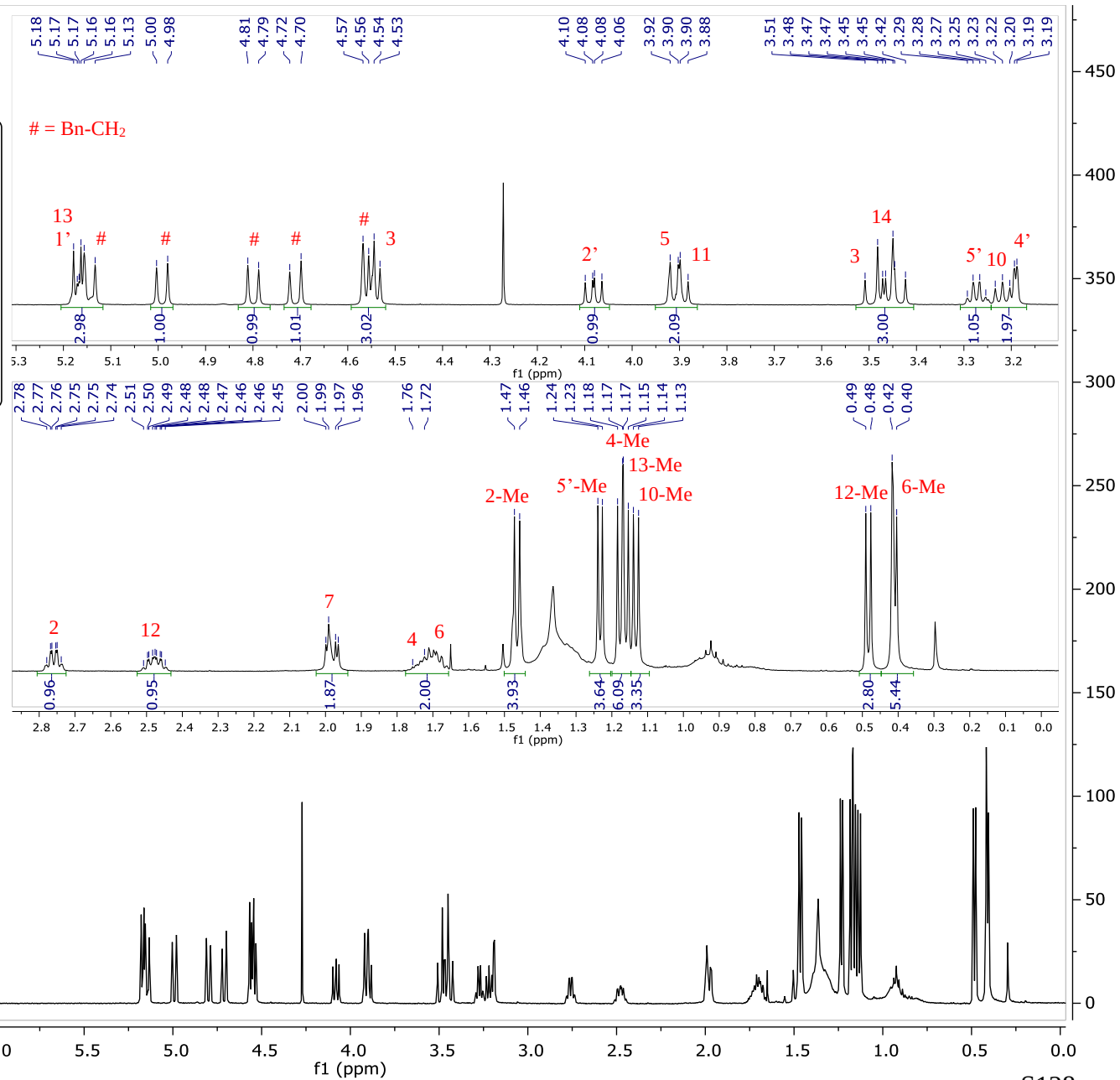
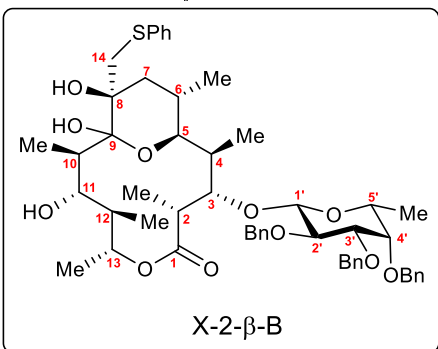


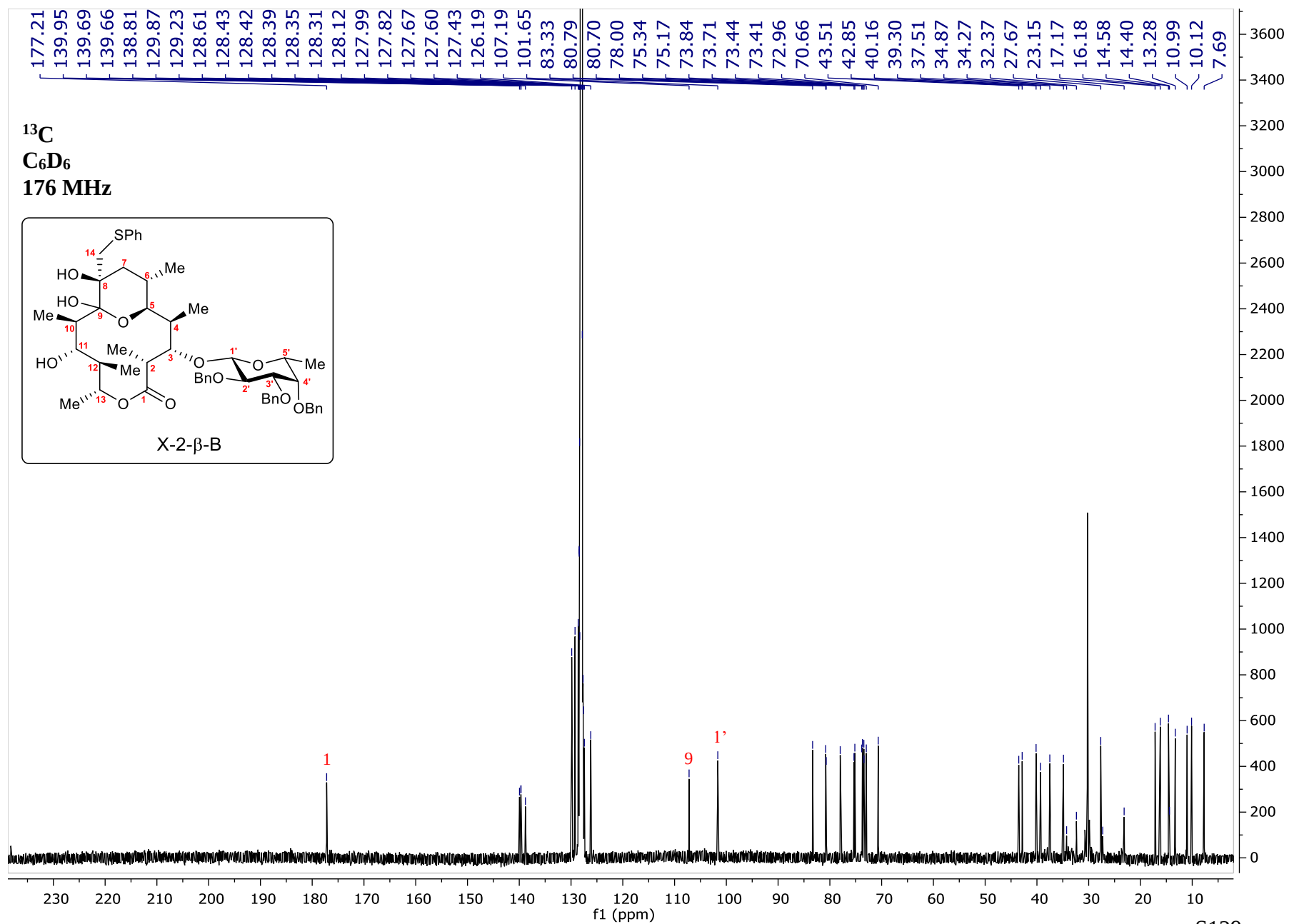


X-2- α -B (8j)



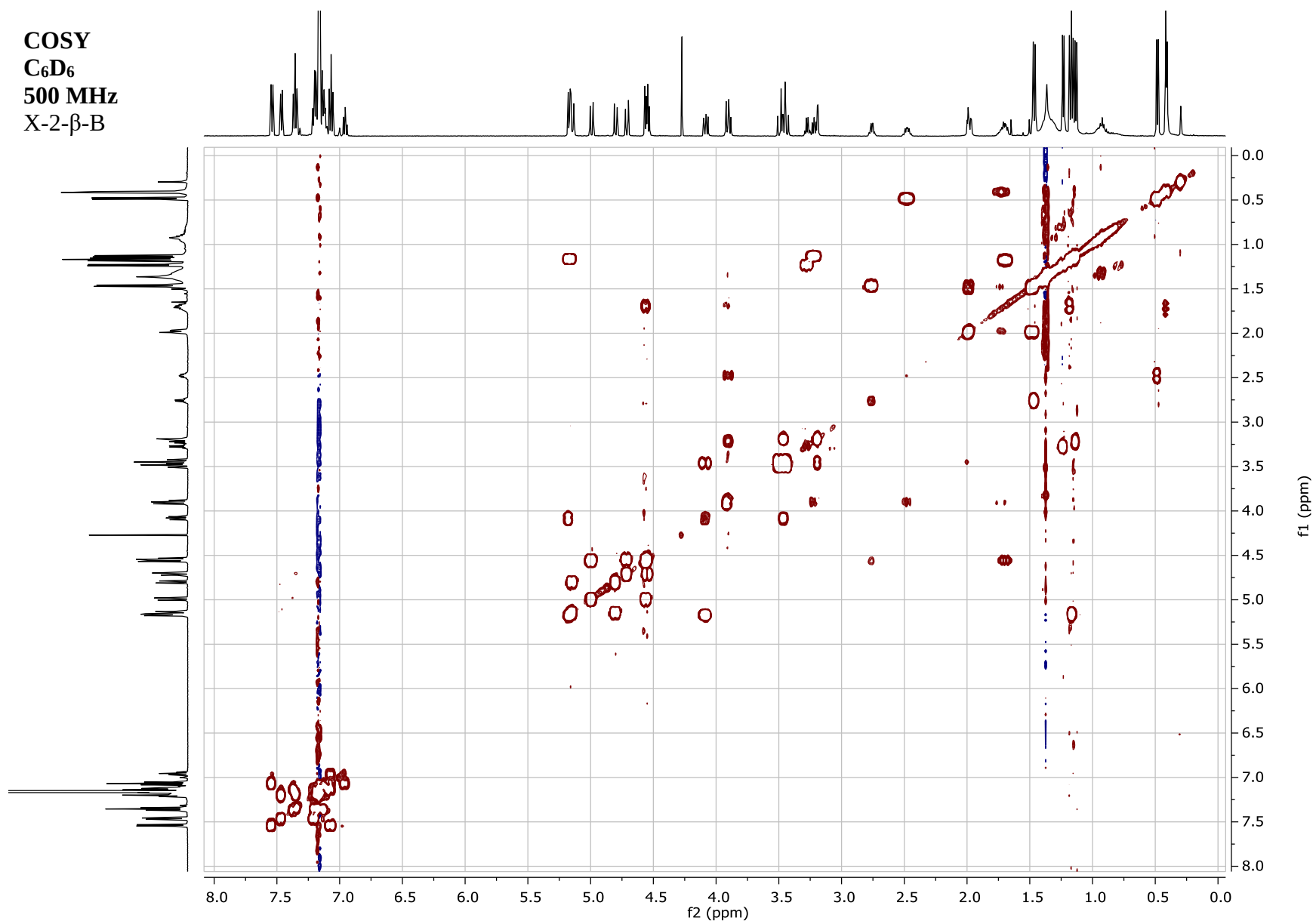
¹H
C₆D₆
500 MHz



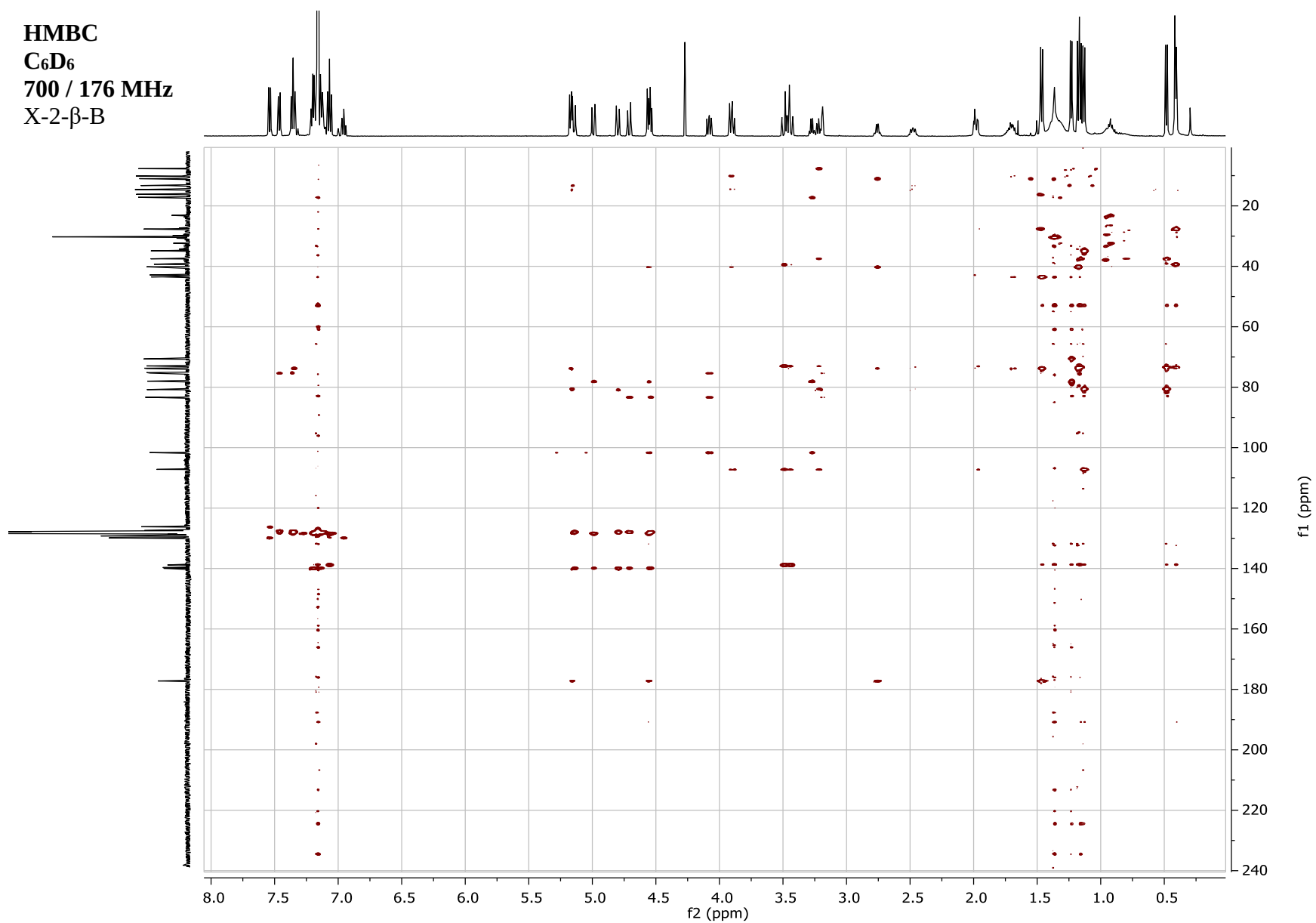


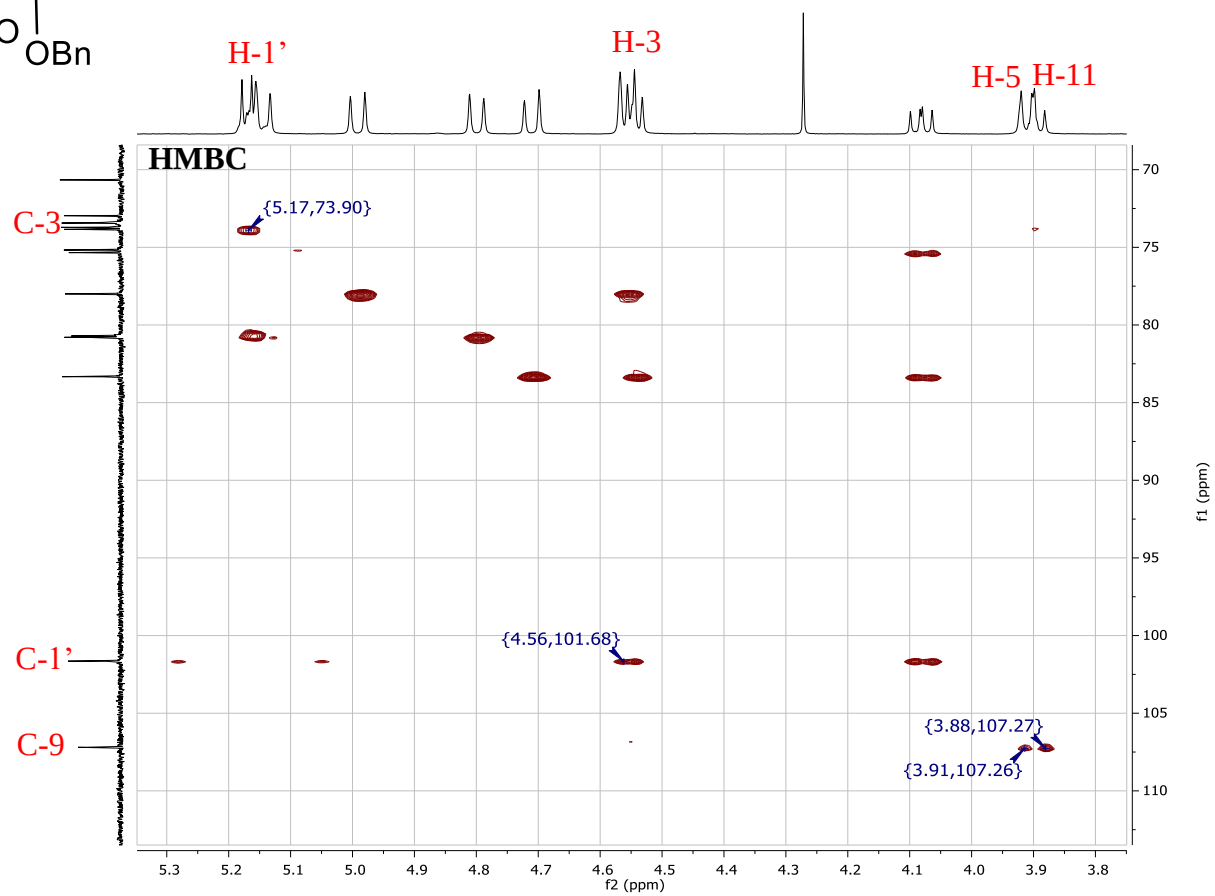
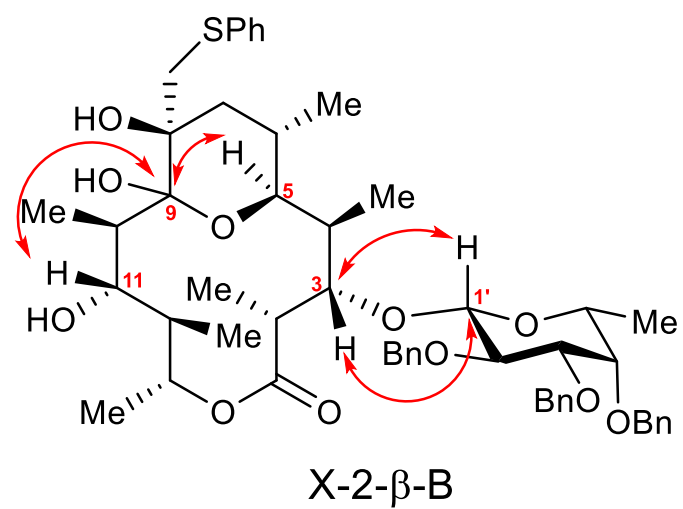
HSQC
C₆D₆
500 / 126 MHz
X-2-β-B

COSY
C₆D₆
500 MHz
X-2-β-B

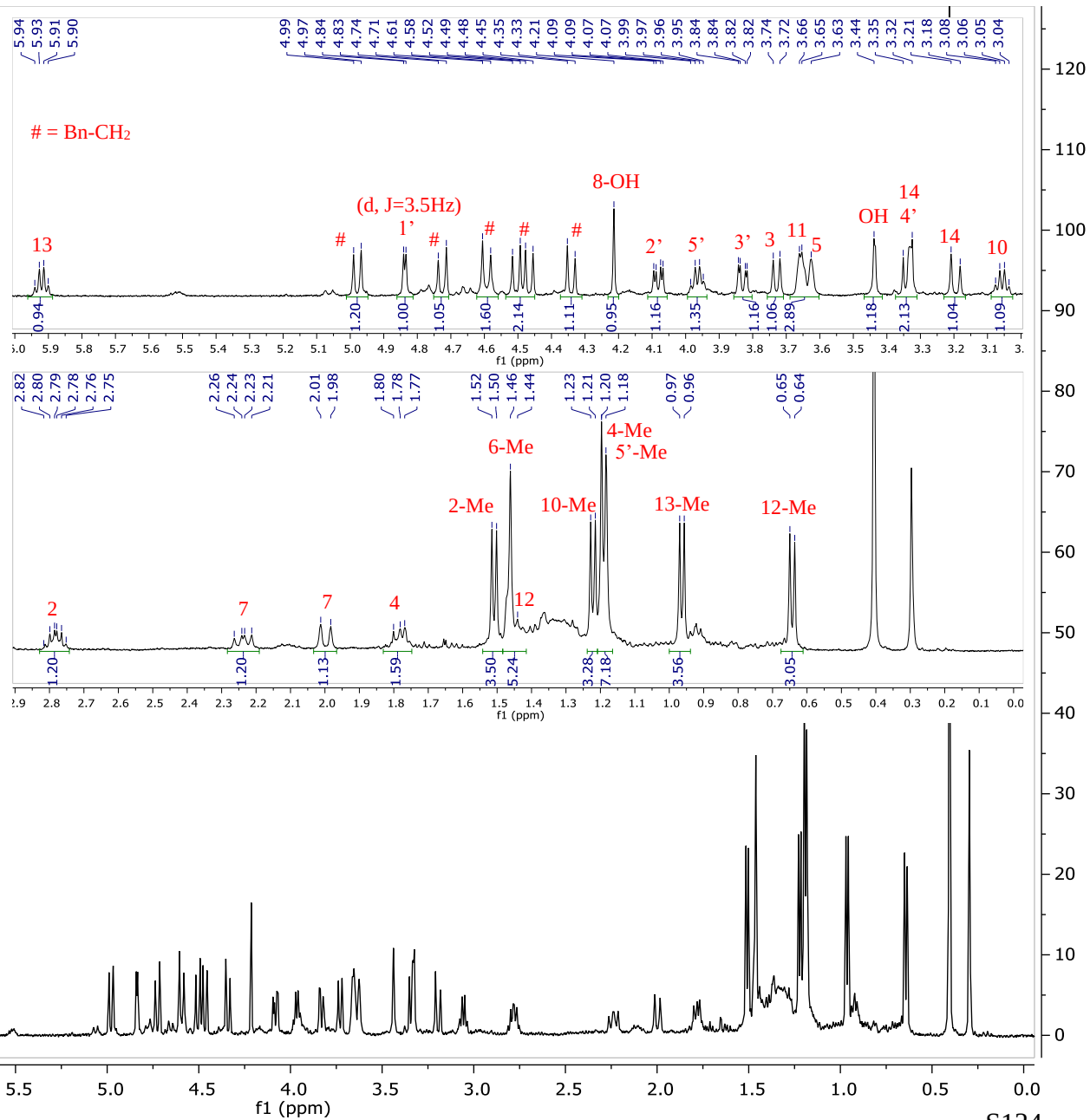
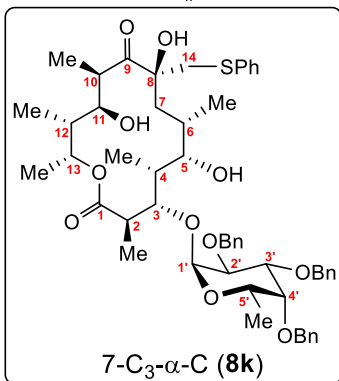


HMBC
C₆D₆
700 / 176 MHz
X-2-β-B

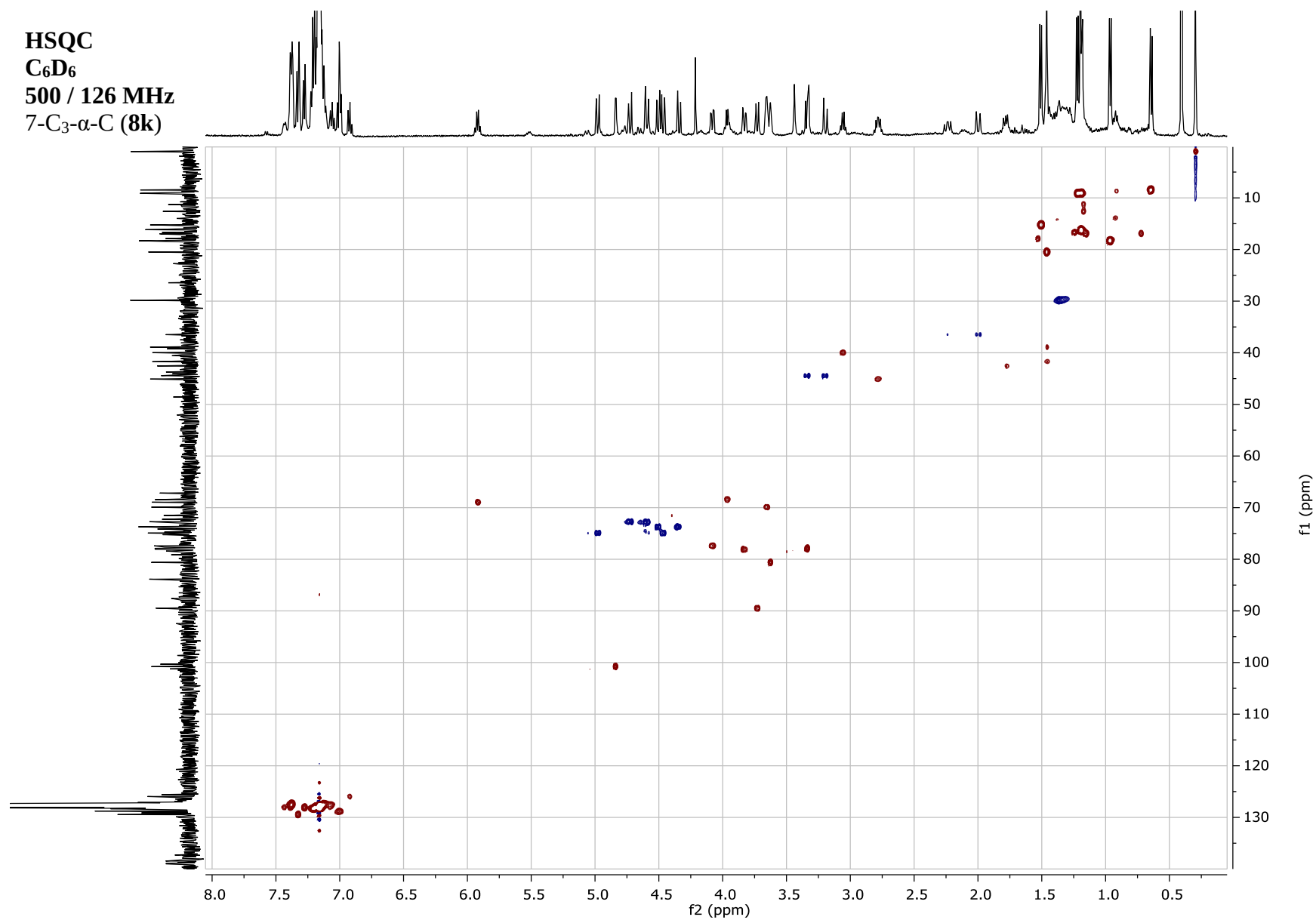




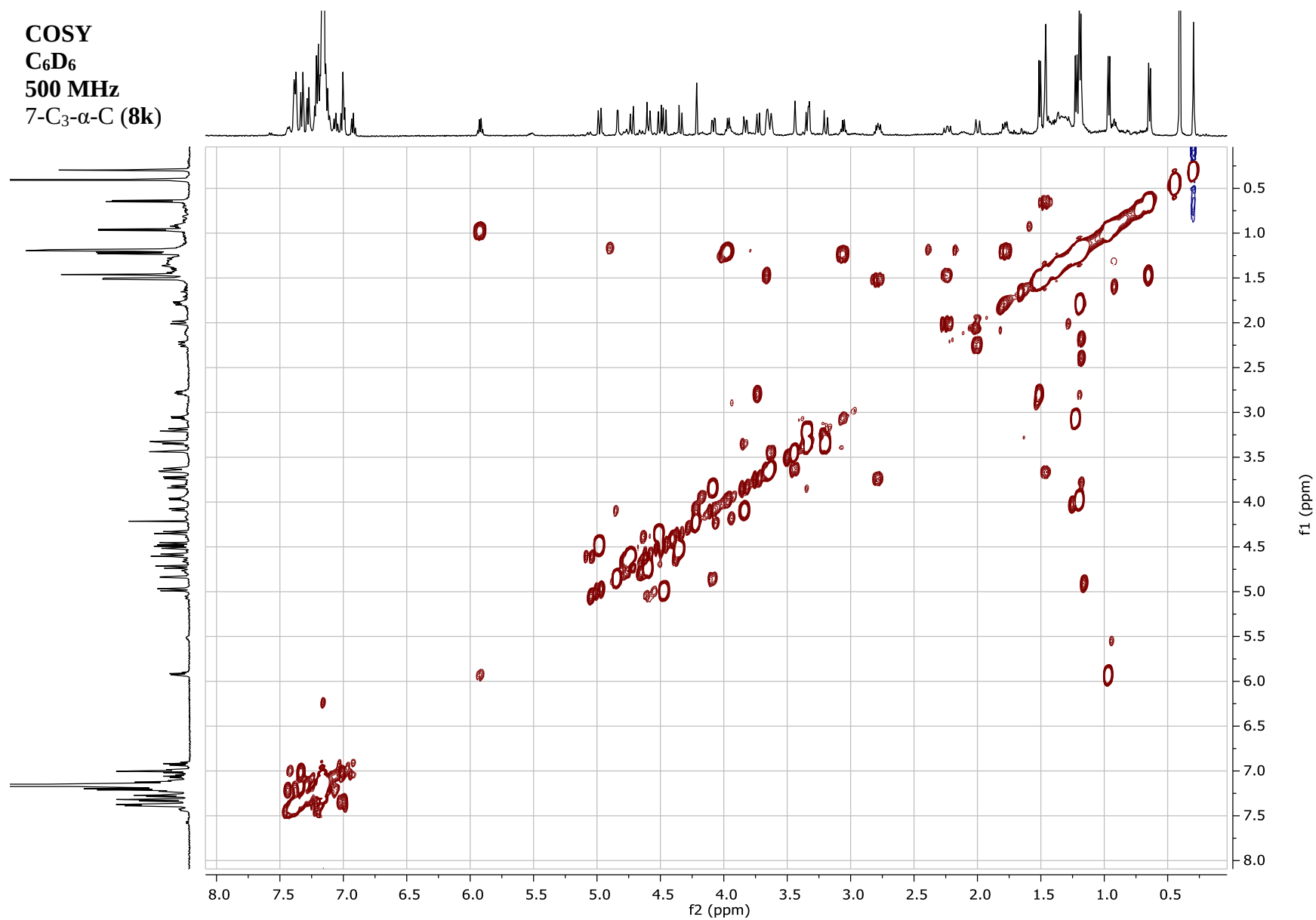
¹H
C₆D₆
500 MHz



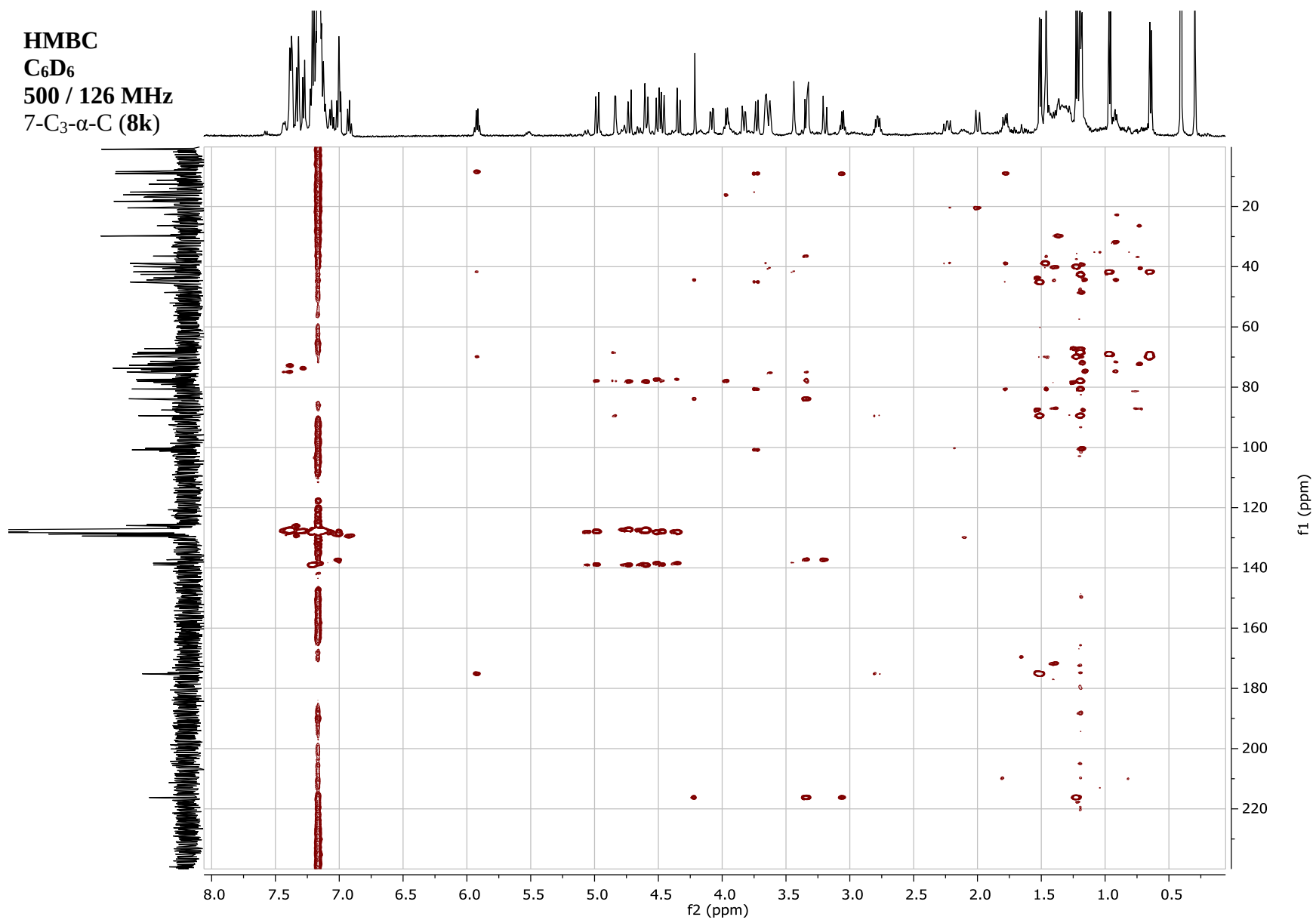
HSQC
C₆D₆
500 / 126 MHz
7-C₃- α -C (8k)

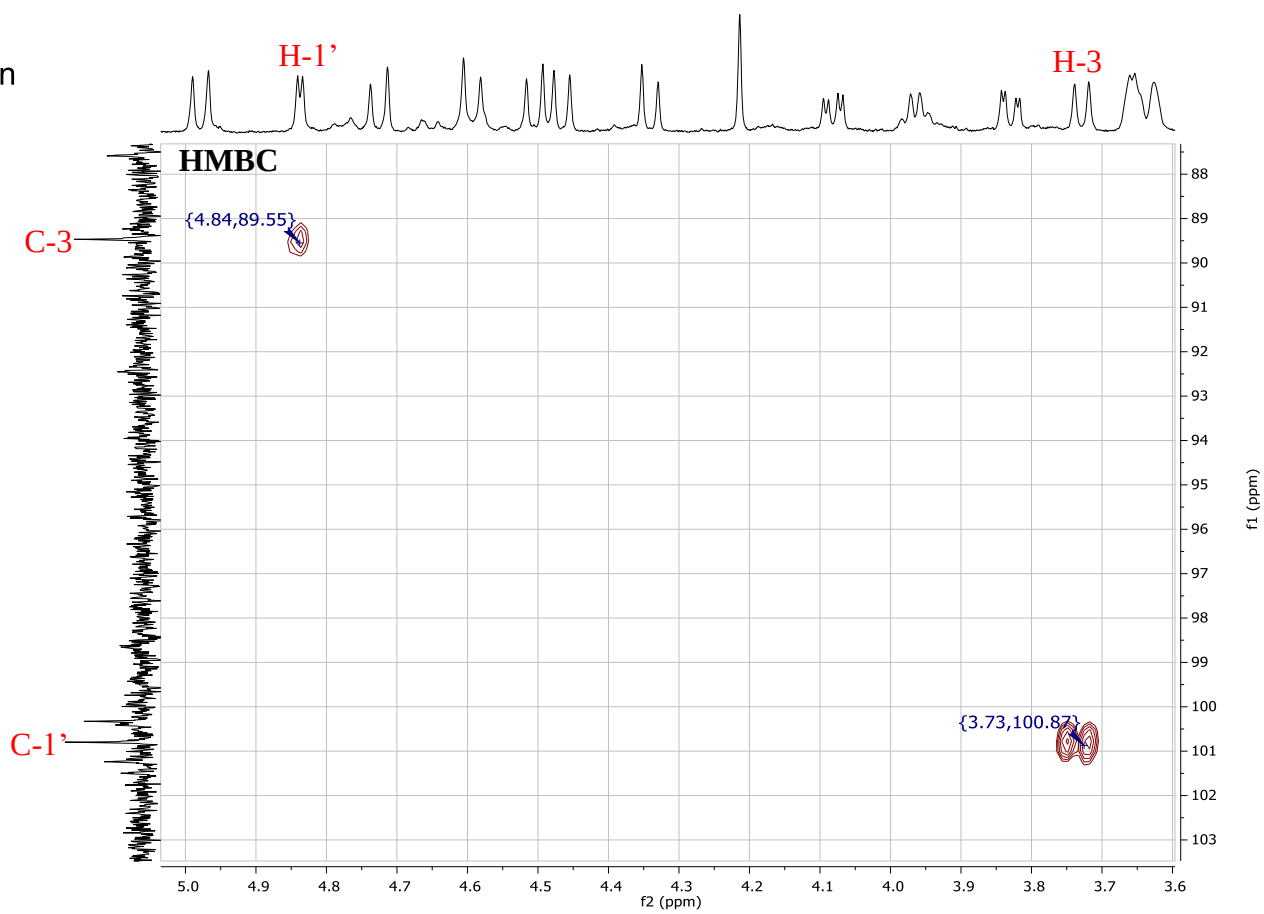
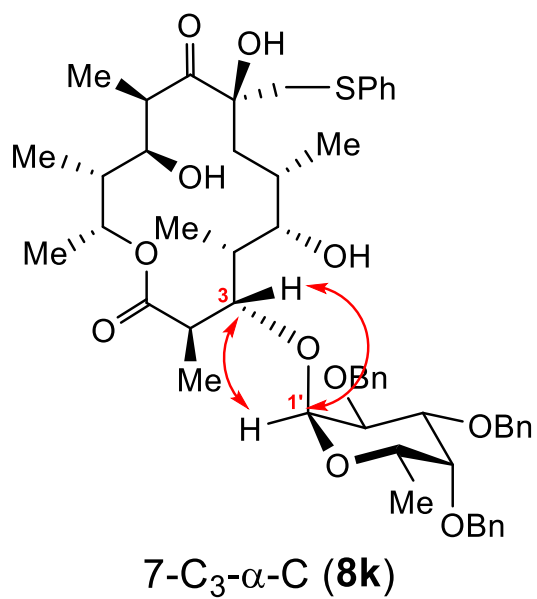


COSY
C₆D₆
500 MHz
7-C₃- α -C (8k)



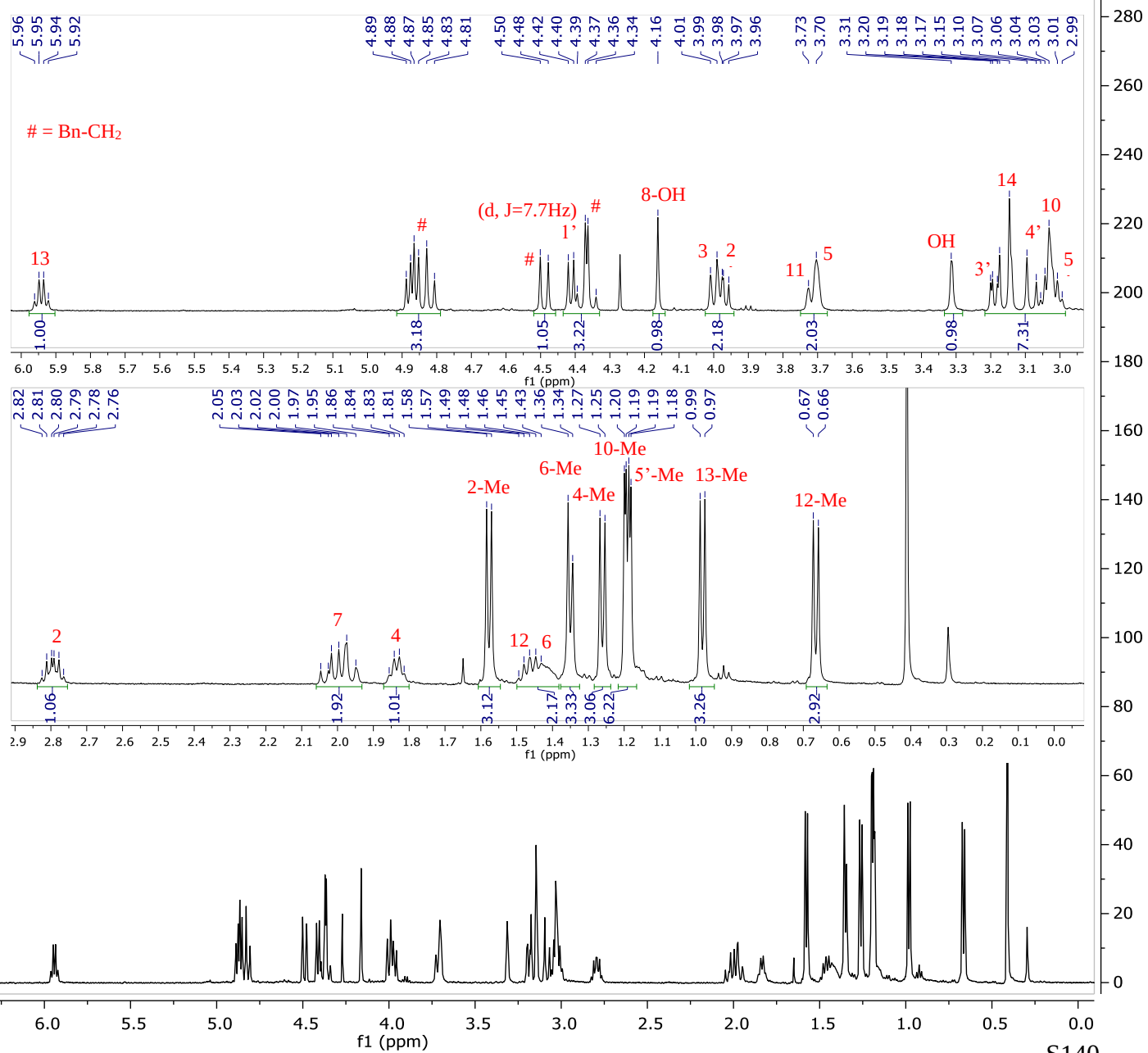
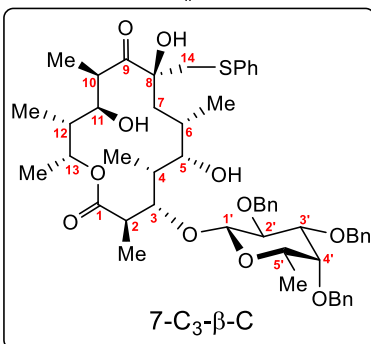
HMBC
C₆D₆
500 / 126 MHz
7-C₃- α -C (8k)



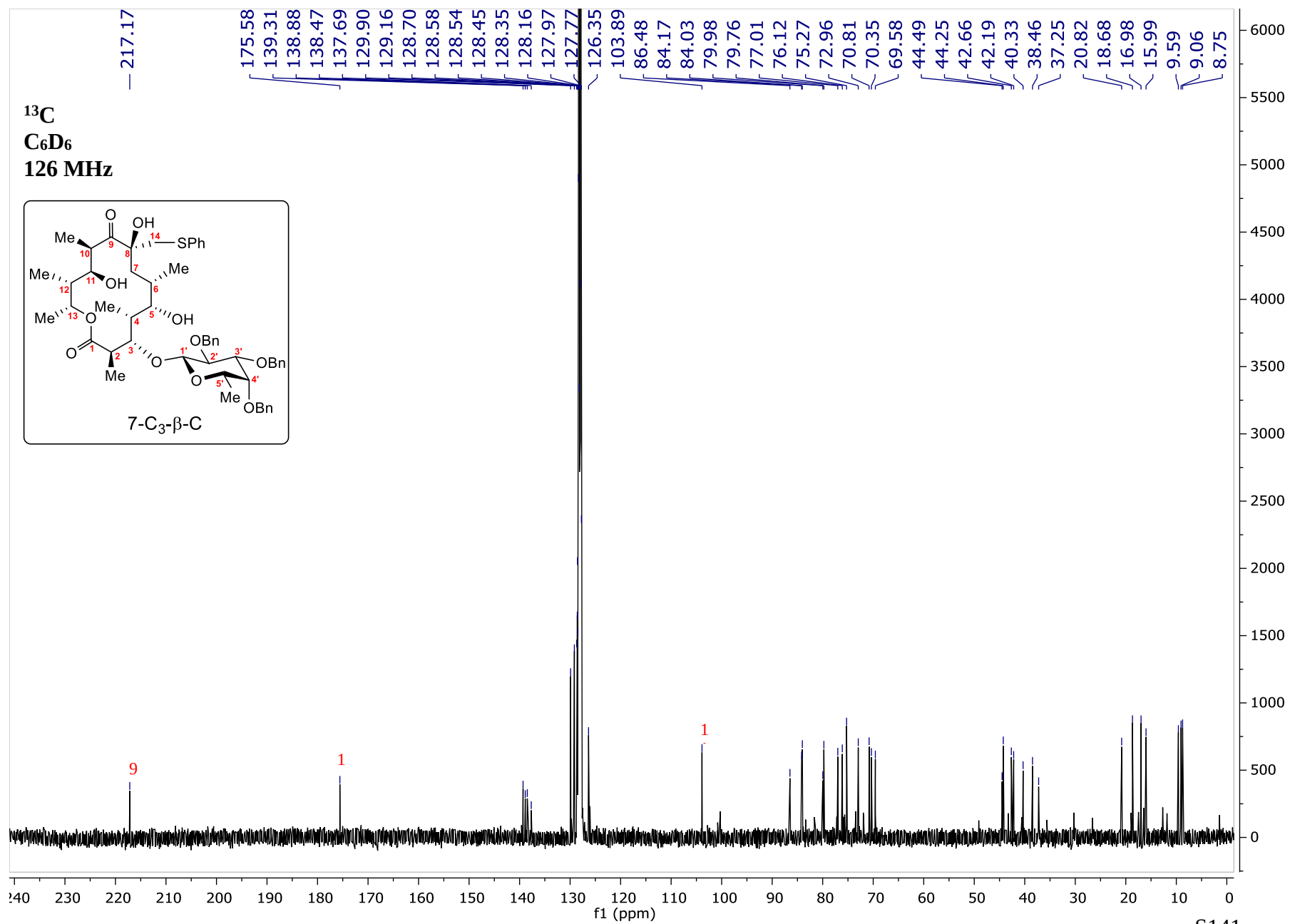


$$^1\text{H}$$

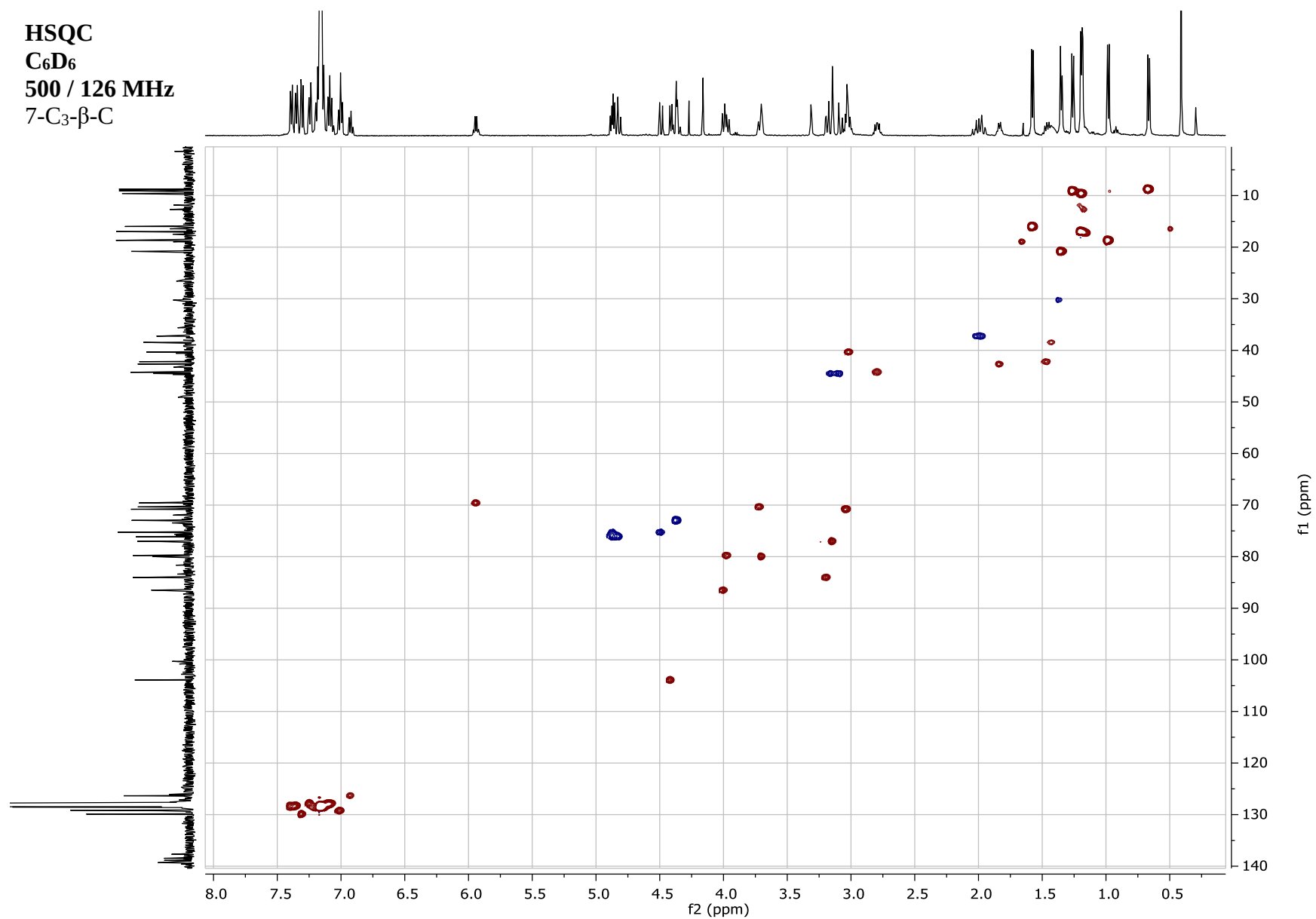
$$\text{C}_6\text{D}_6$$

$$500 \text{ MHz}$$


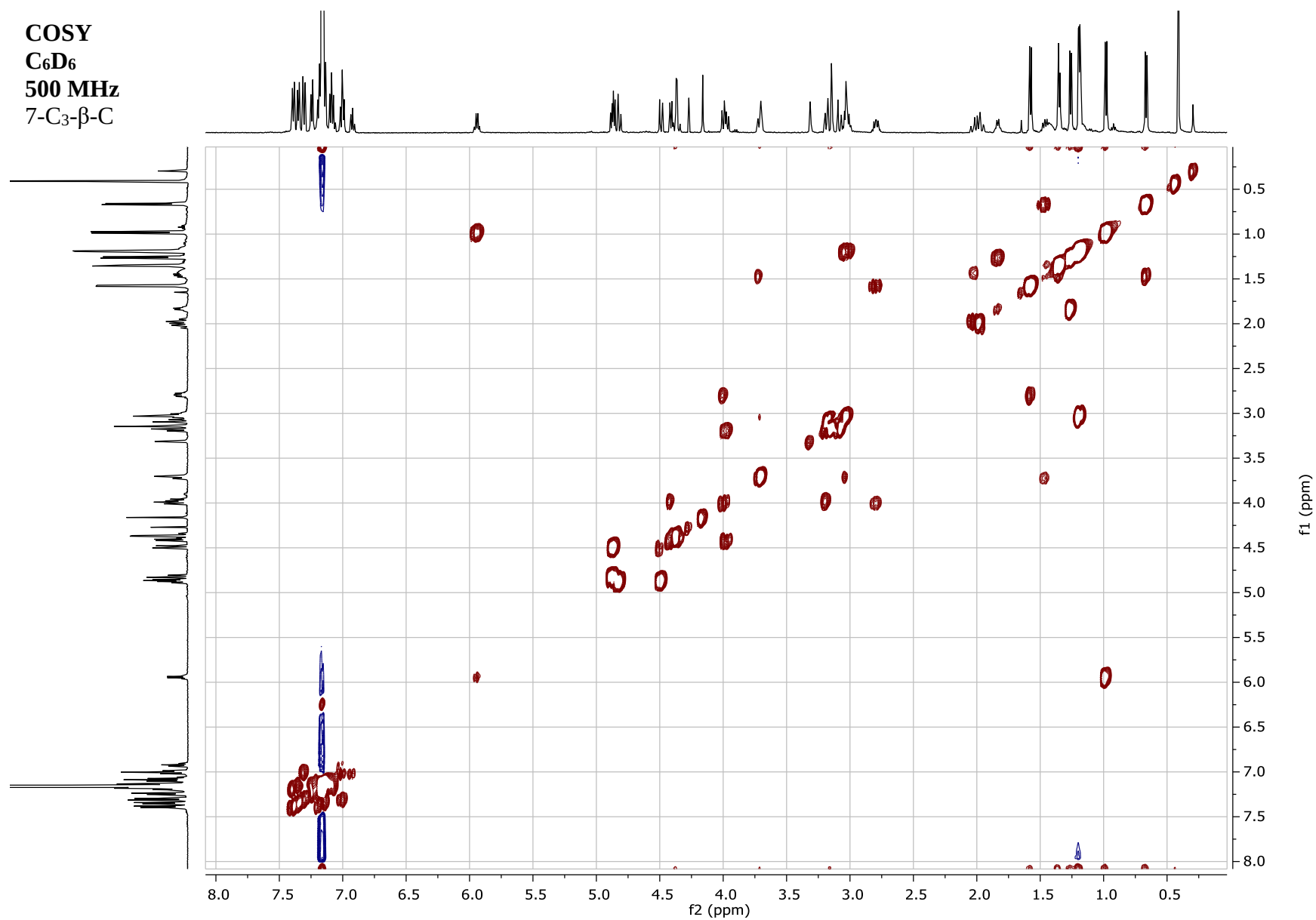
S140



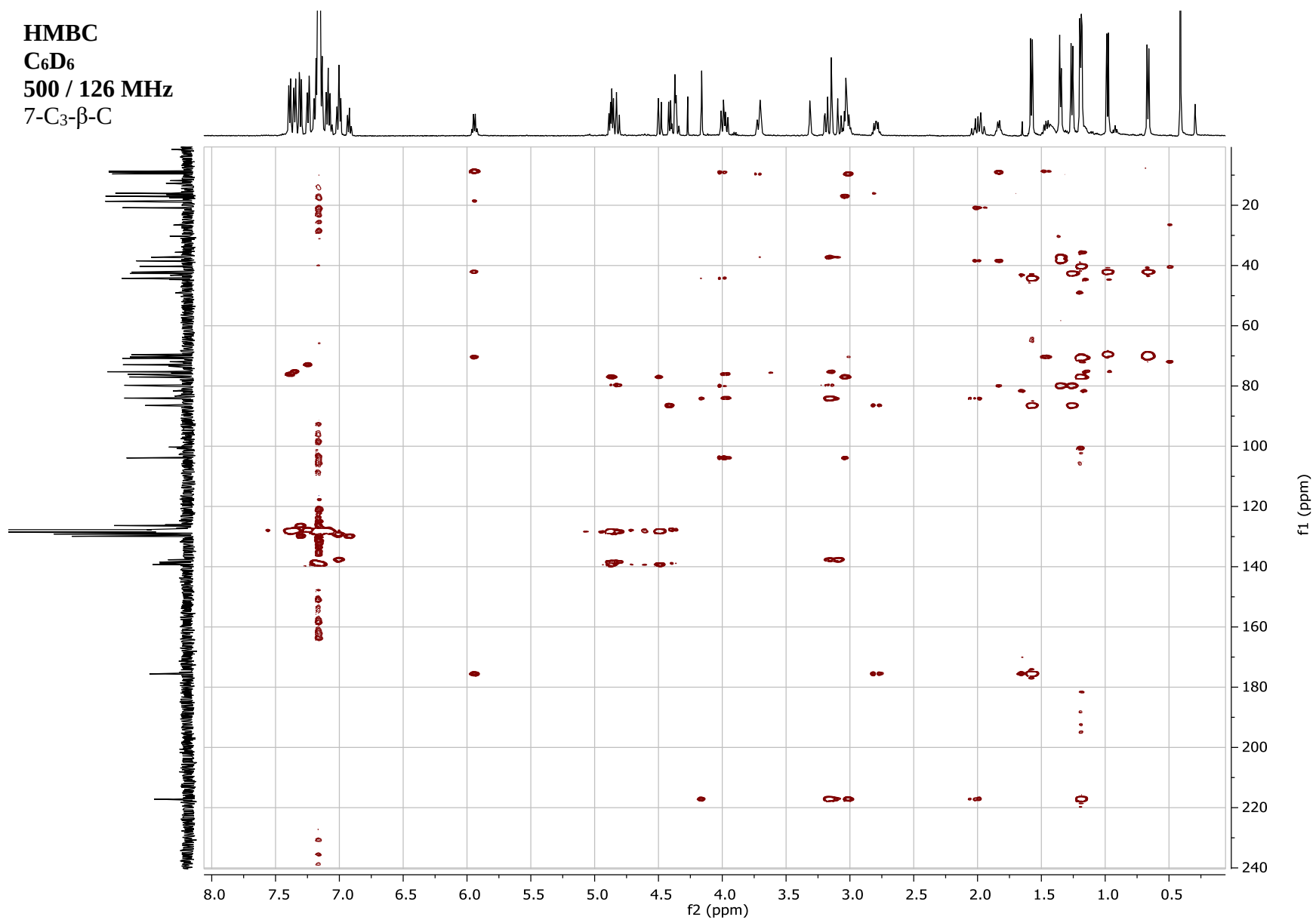
HSQC
C₆D₆
500 / 126 MHz
7-C₃-β-C

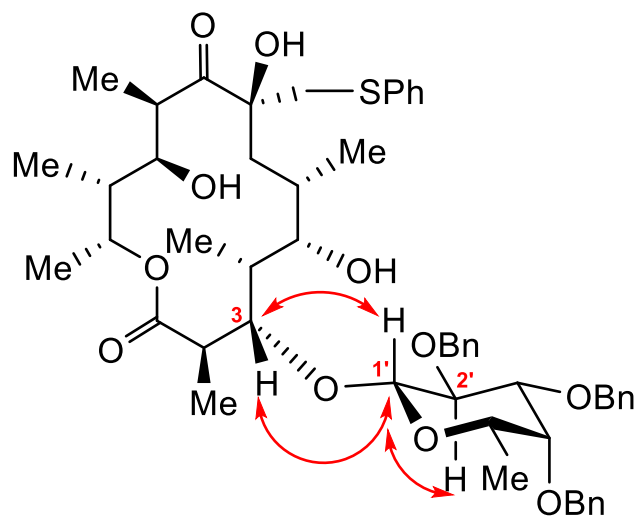


COSY
C₆D₆
500 MHz
7-C₃-β-C

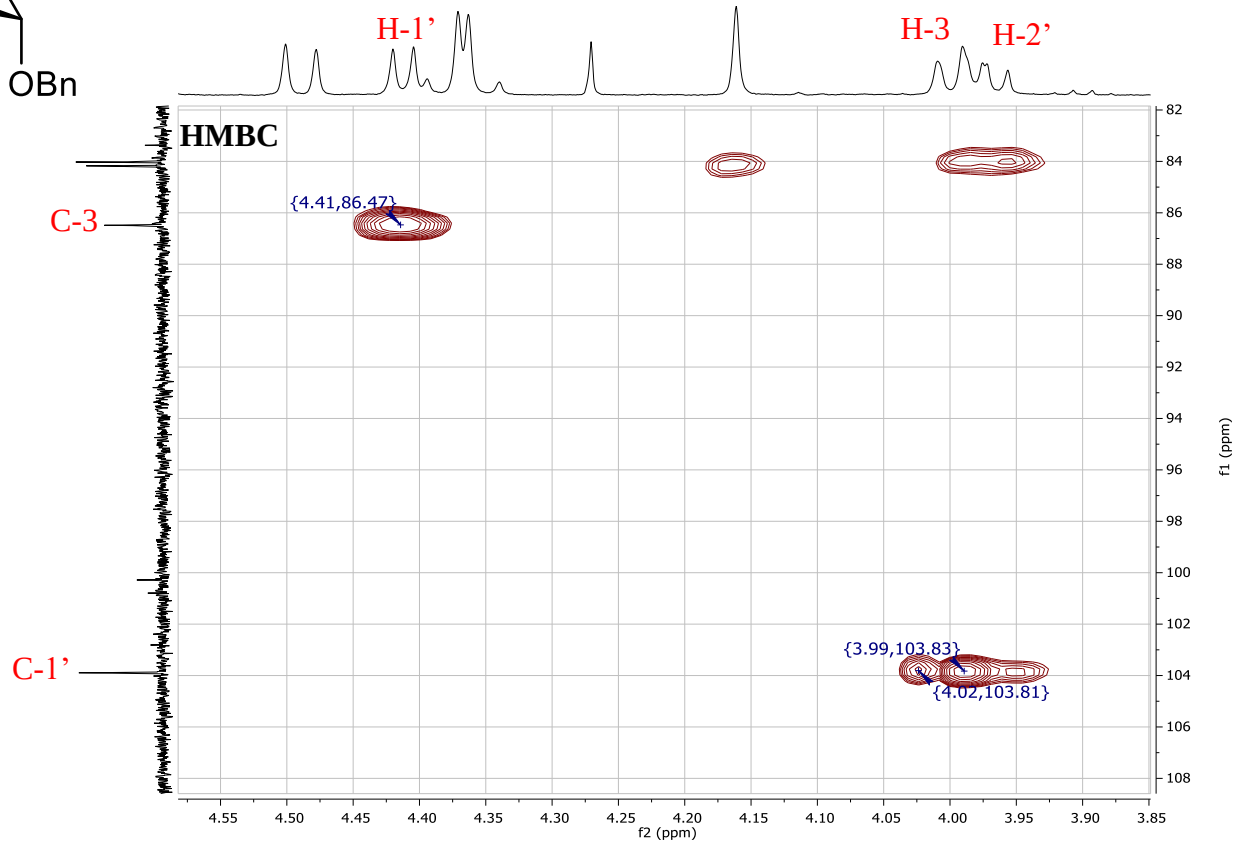


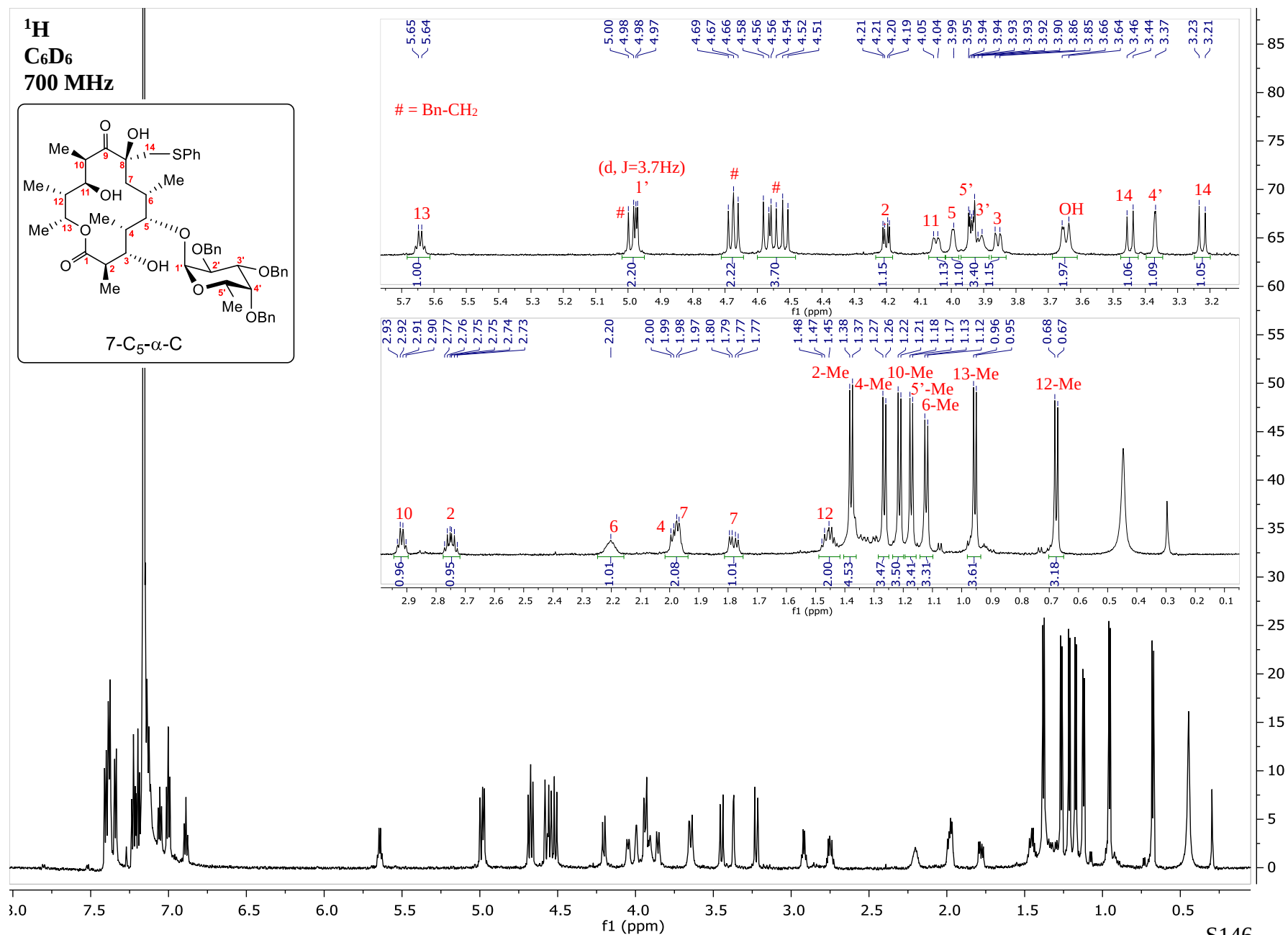
HMBC
C₆D₆
500 / 126 MHz
7-C₃-β-C

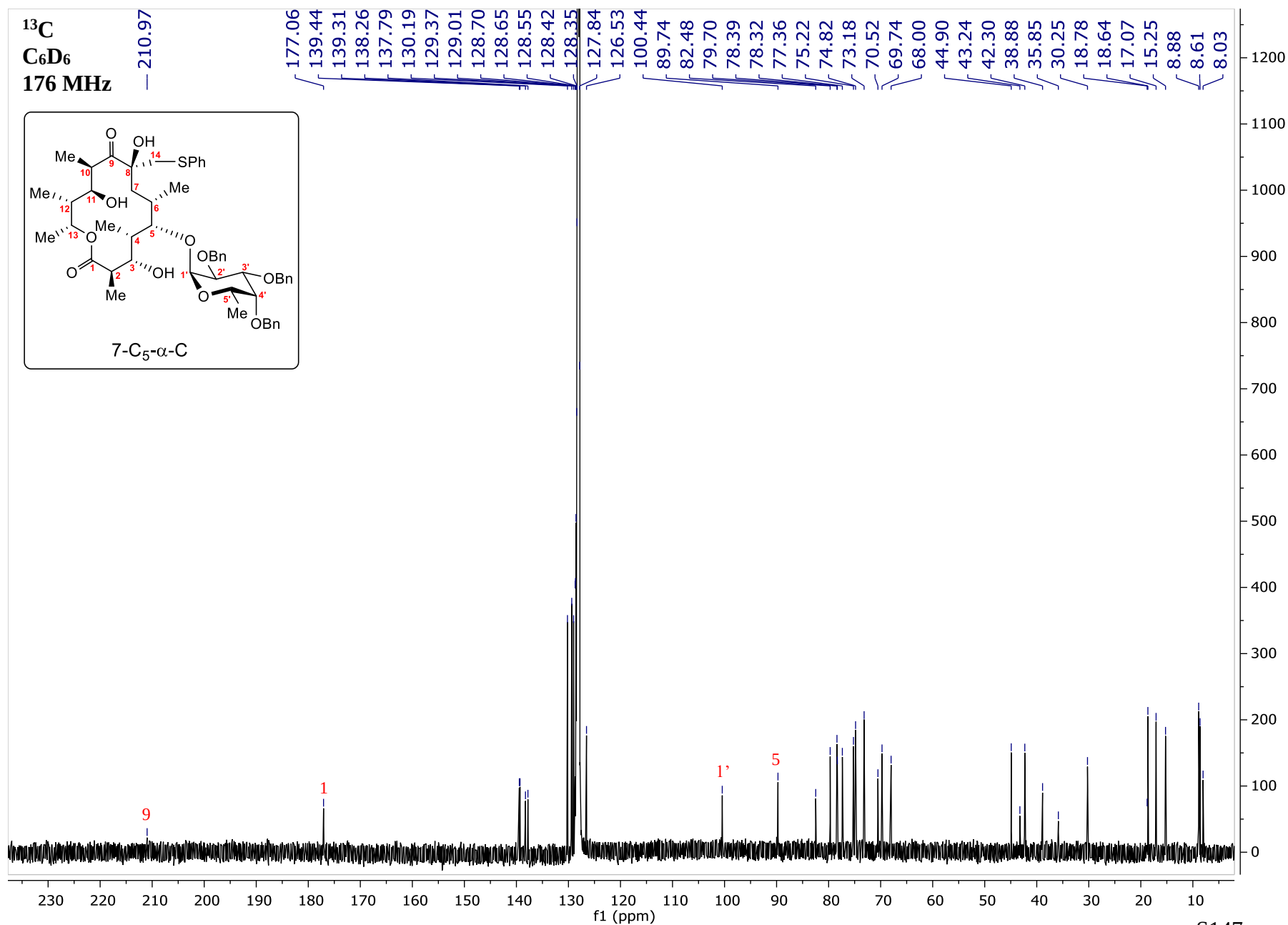




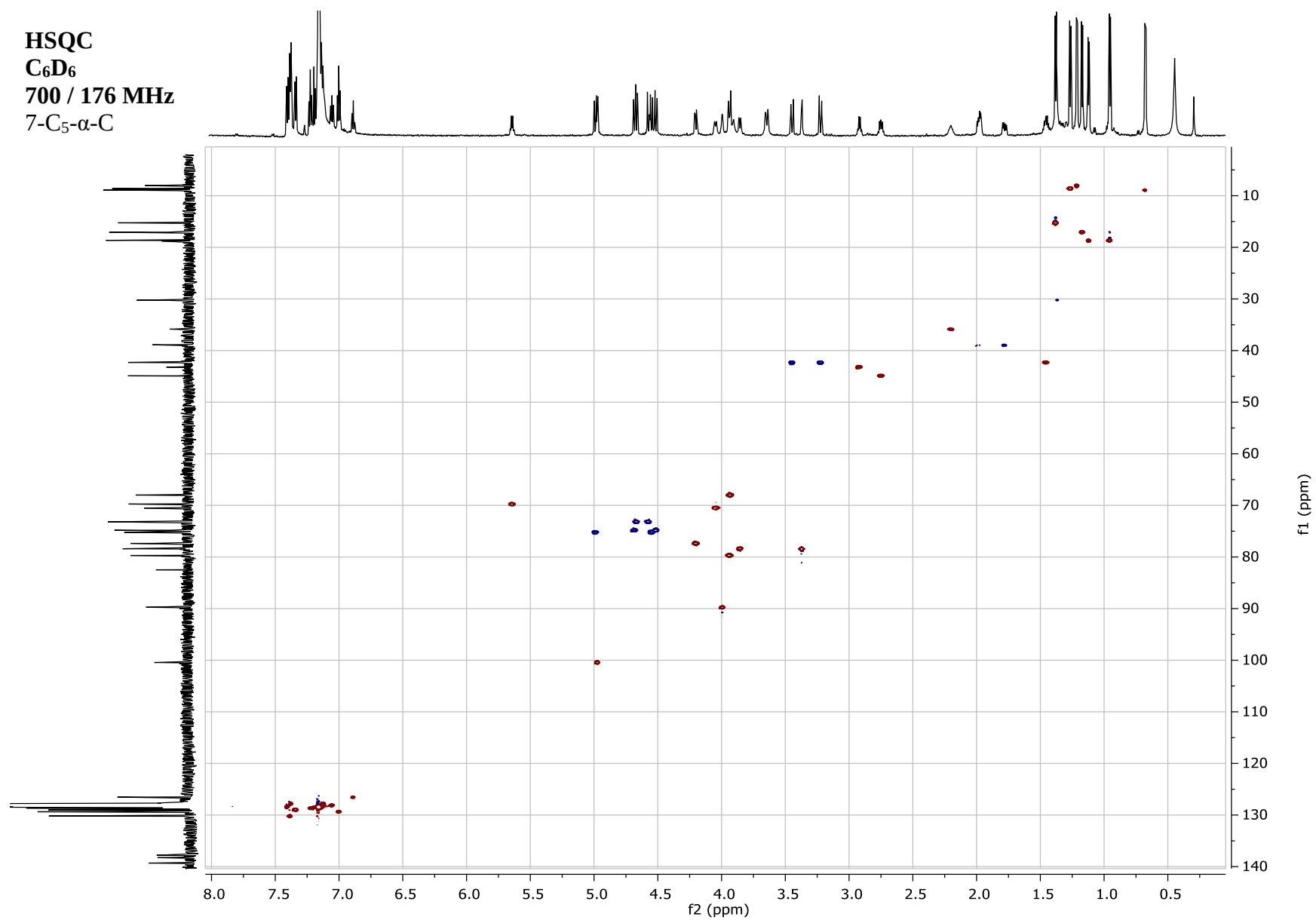
7-C₃-β-C



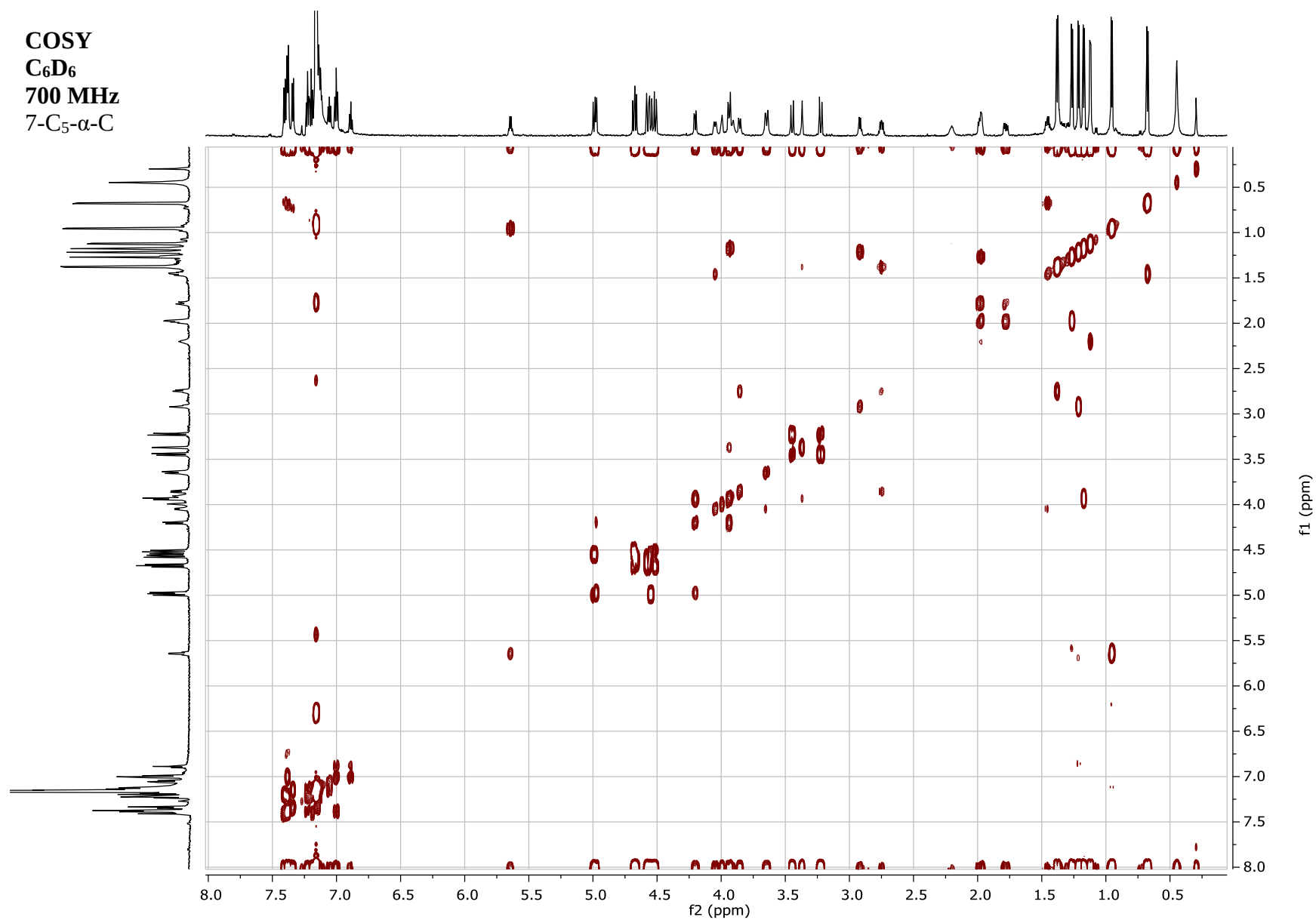




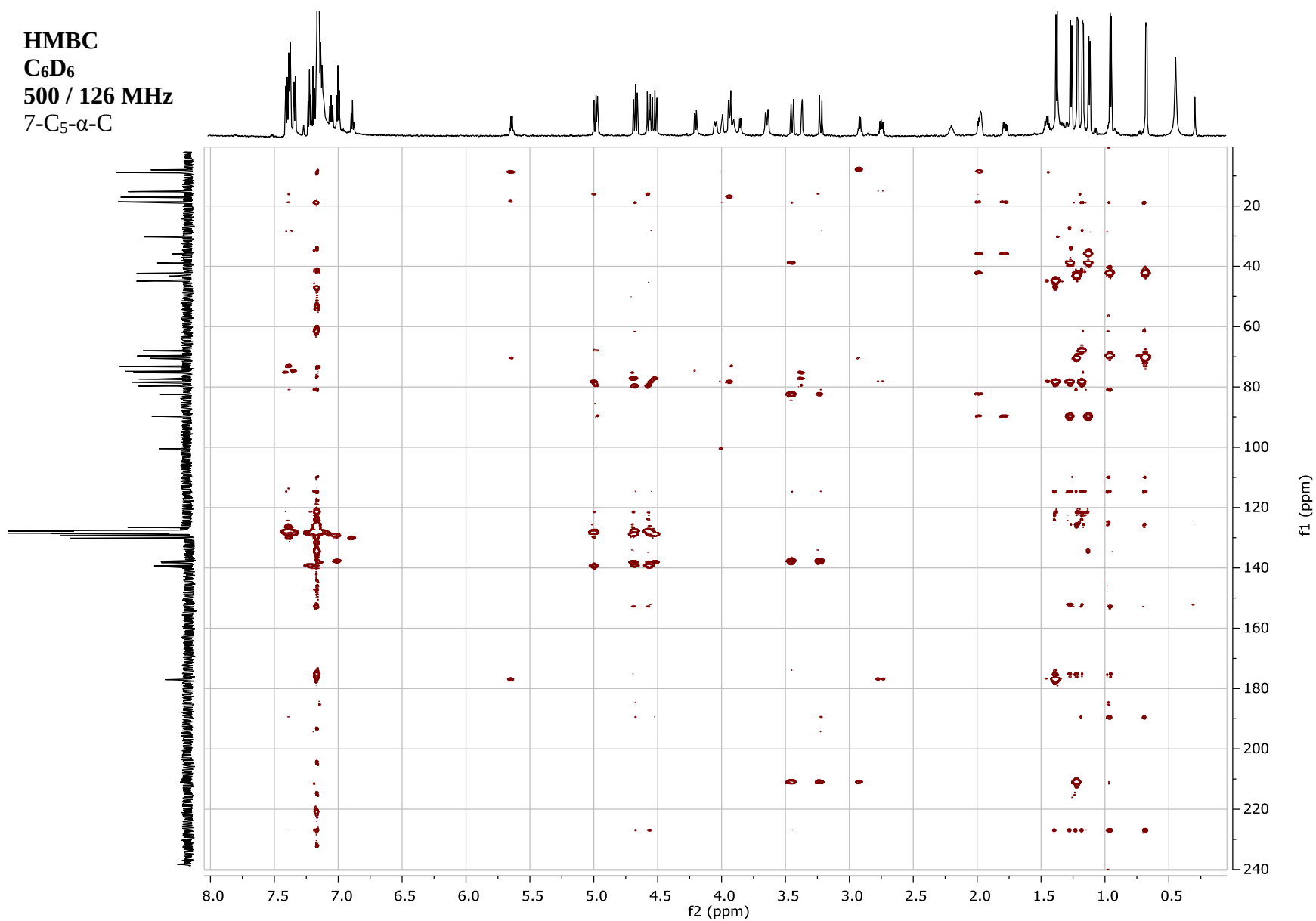
HSQC
C₆D₆
700 / 176 MHz
7-C₅- α -C

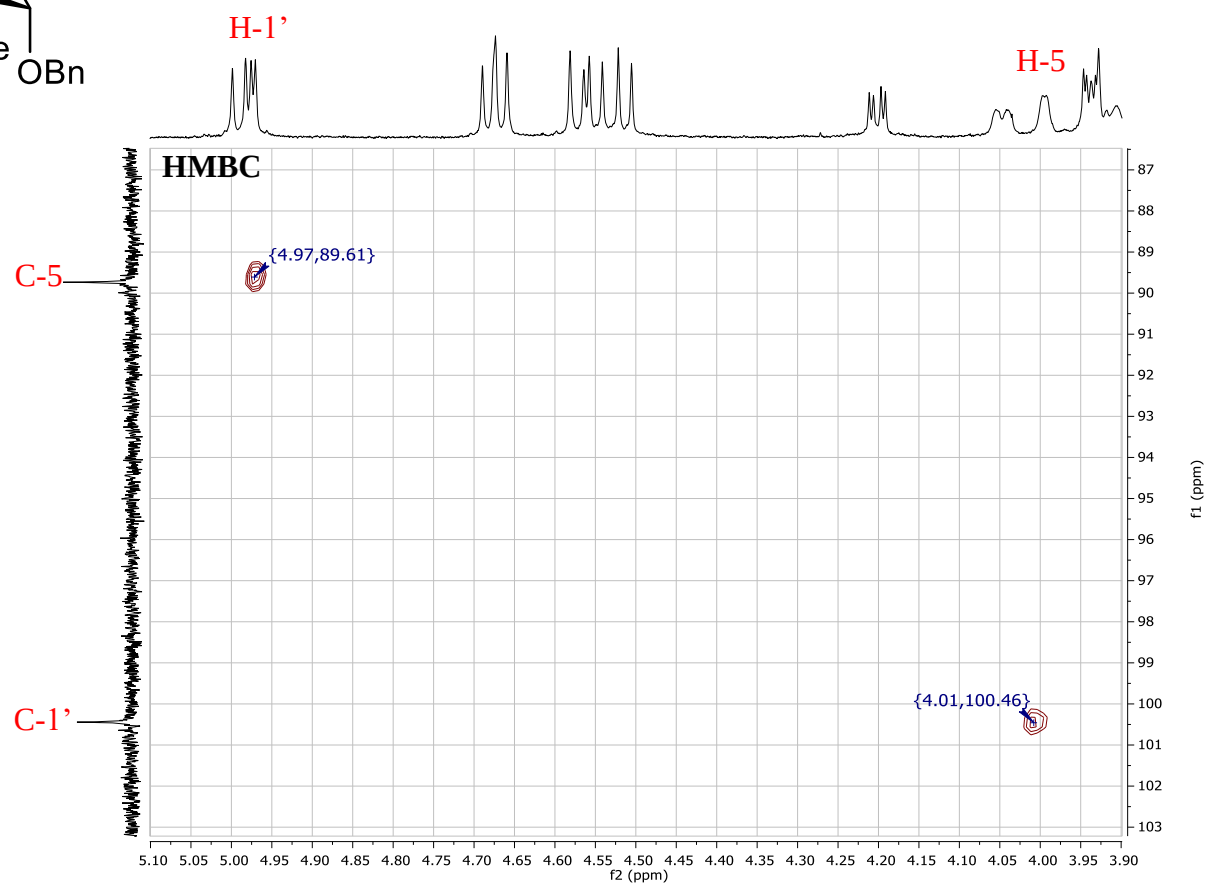
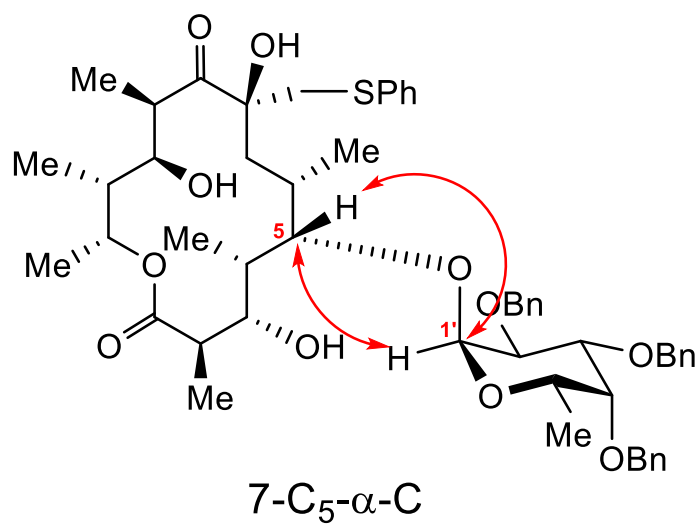


COSY
C₆D₆
700 MHz
7-C₅- α -C

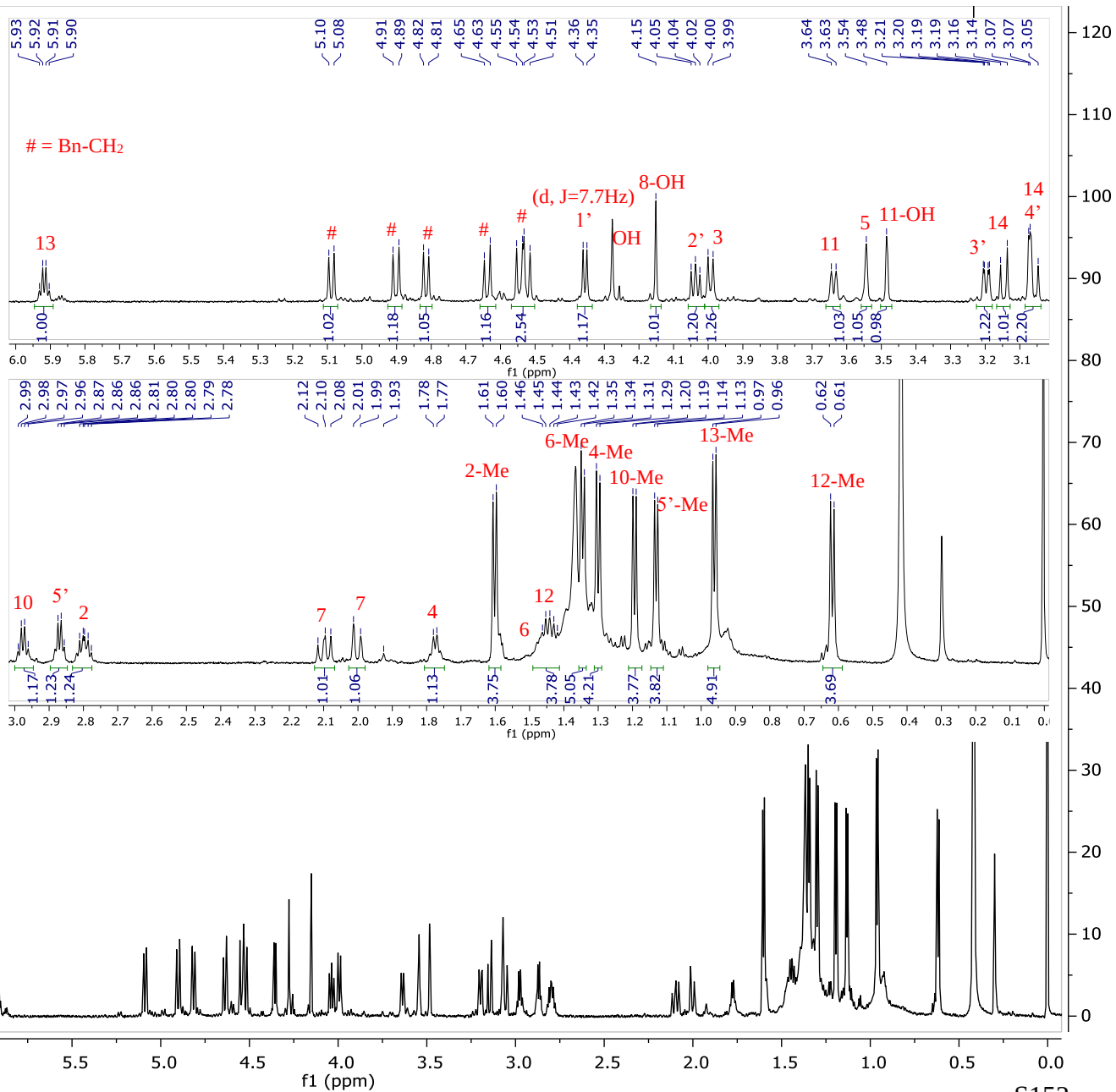
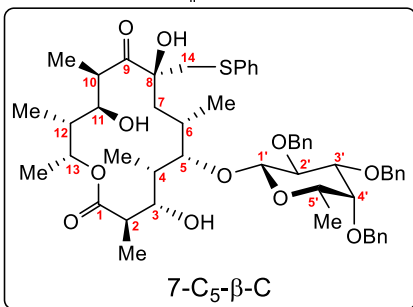


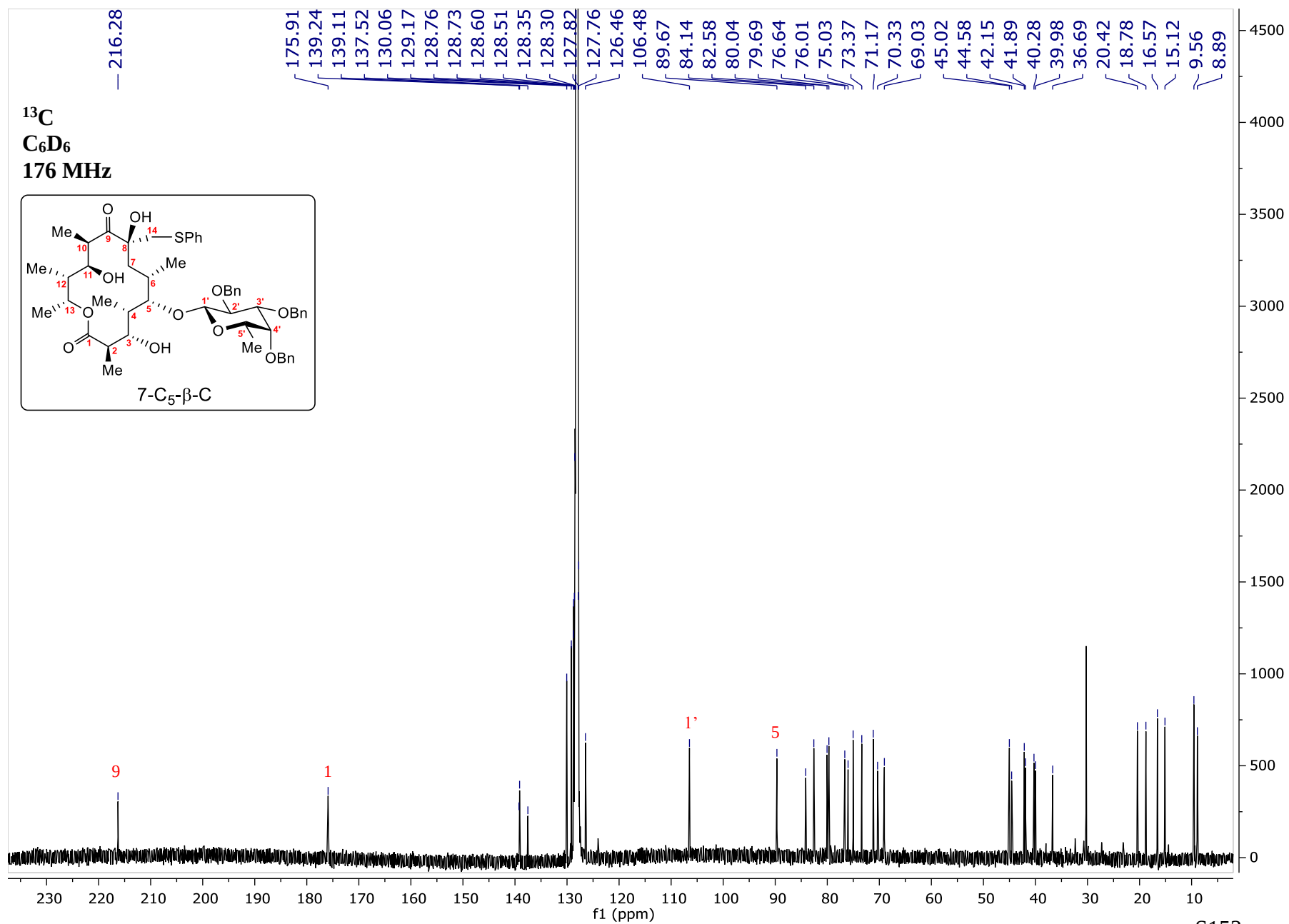
HMBC
C₆D₆
500 / 126 MHz
7-C₅-α-C



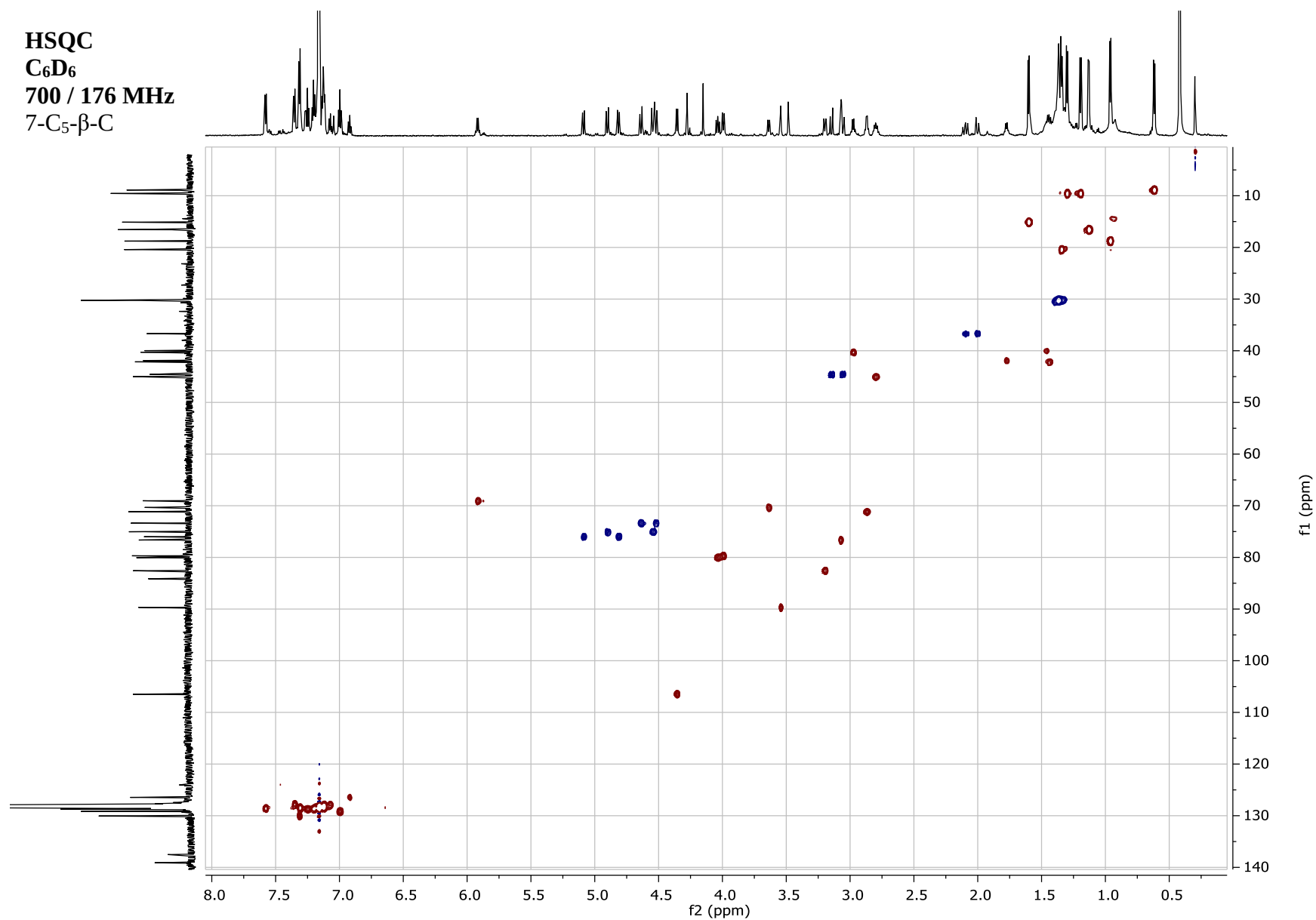


¹H
C₆D₆
700 MHz

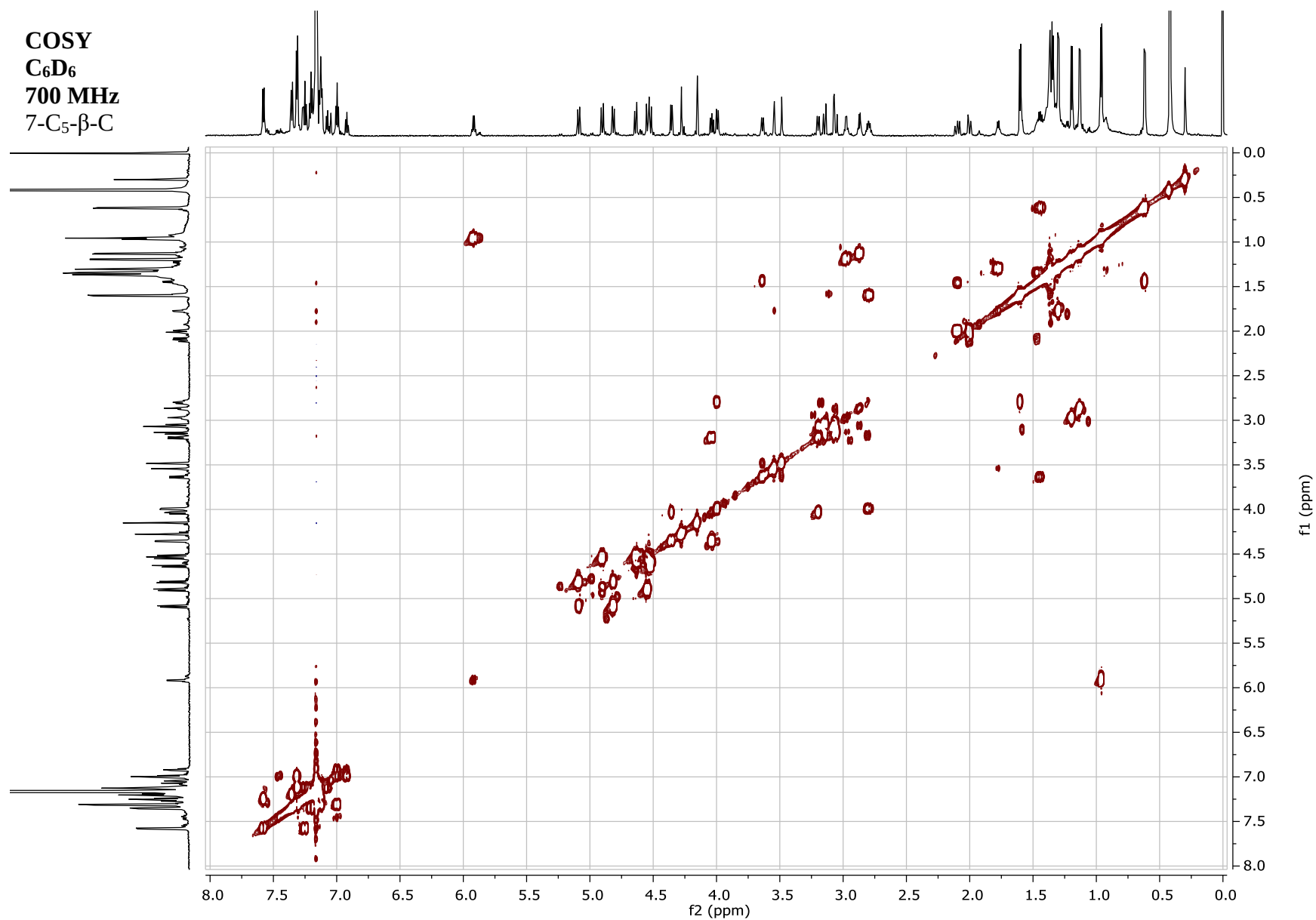




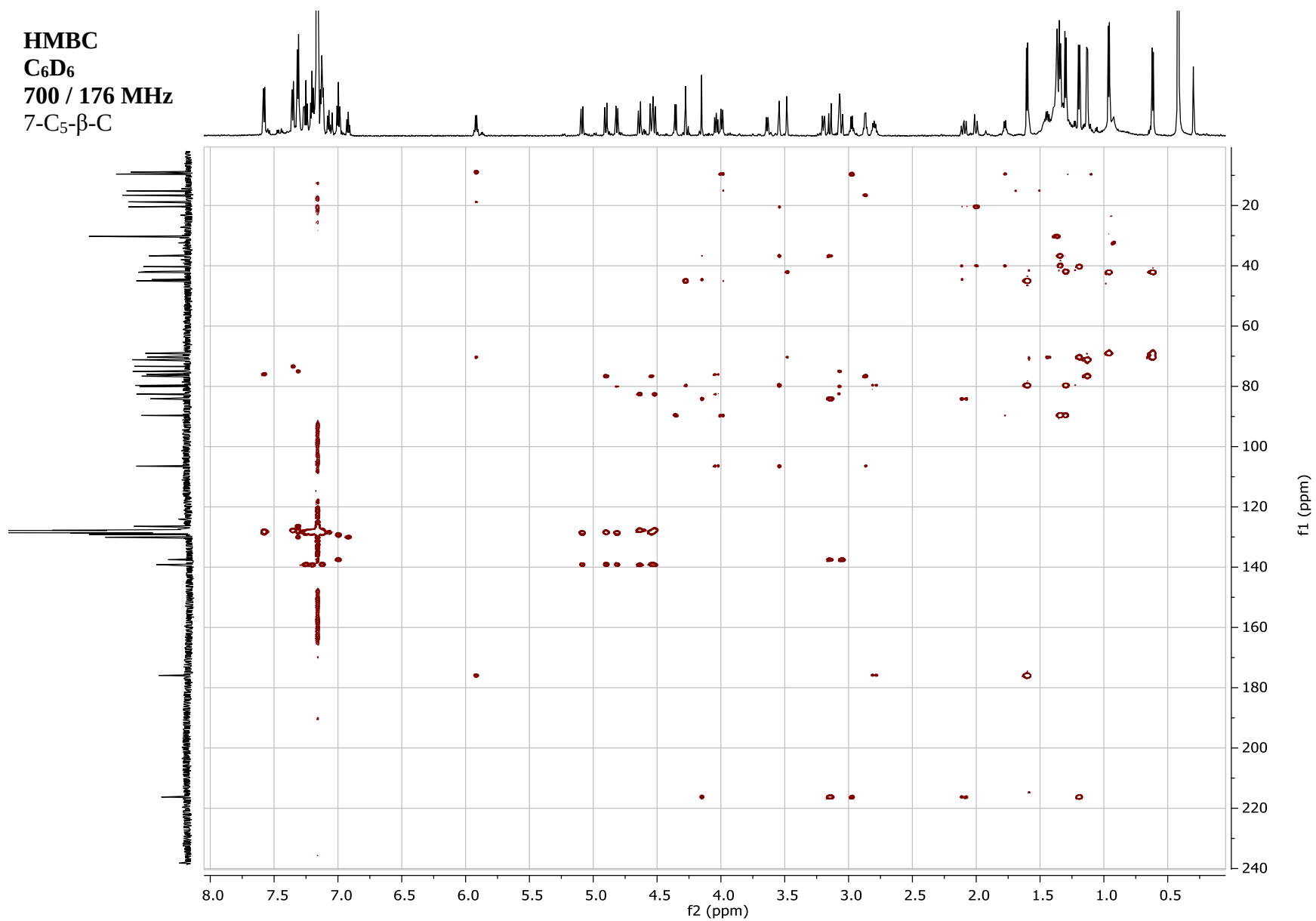
HSQC
C₆D₆
700 / 176 MHz
7-C₅-β-C

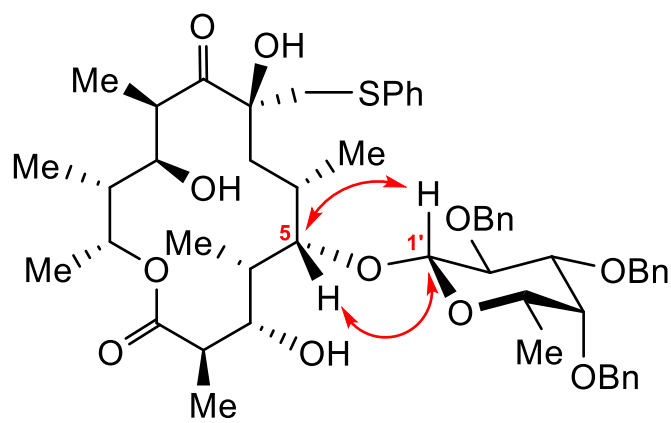


COSY
C₆D₆
700 MHz
7-C₅-β-C

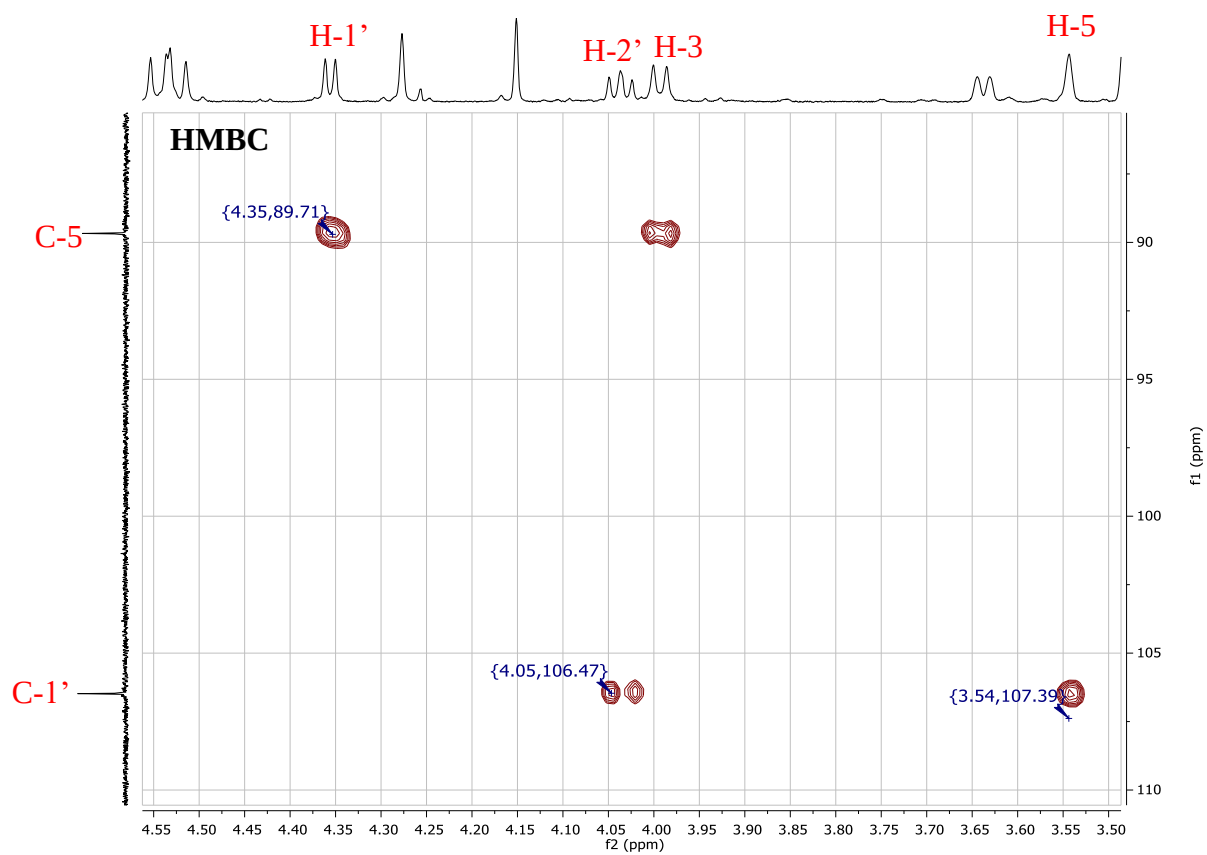


HMBC
C₆D₆
700 / 176 MHz
7-C₅-β-C

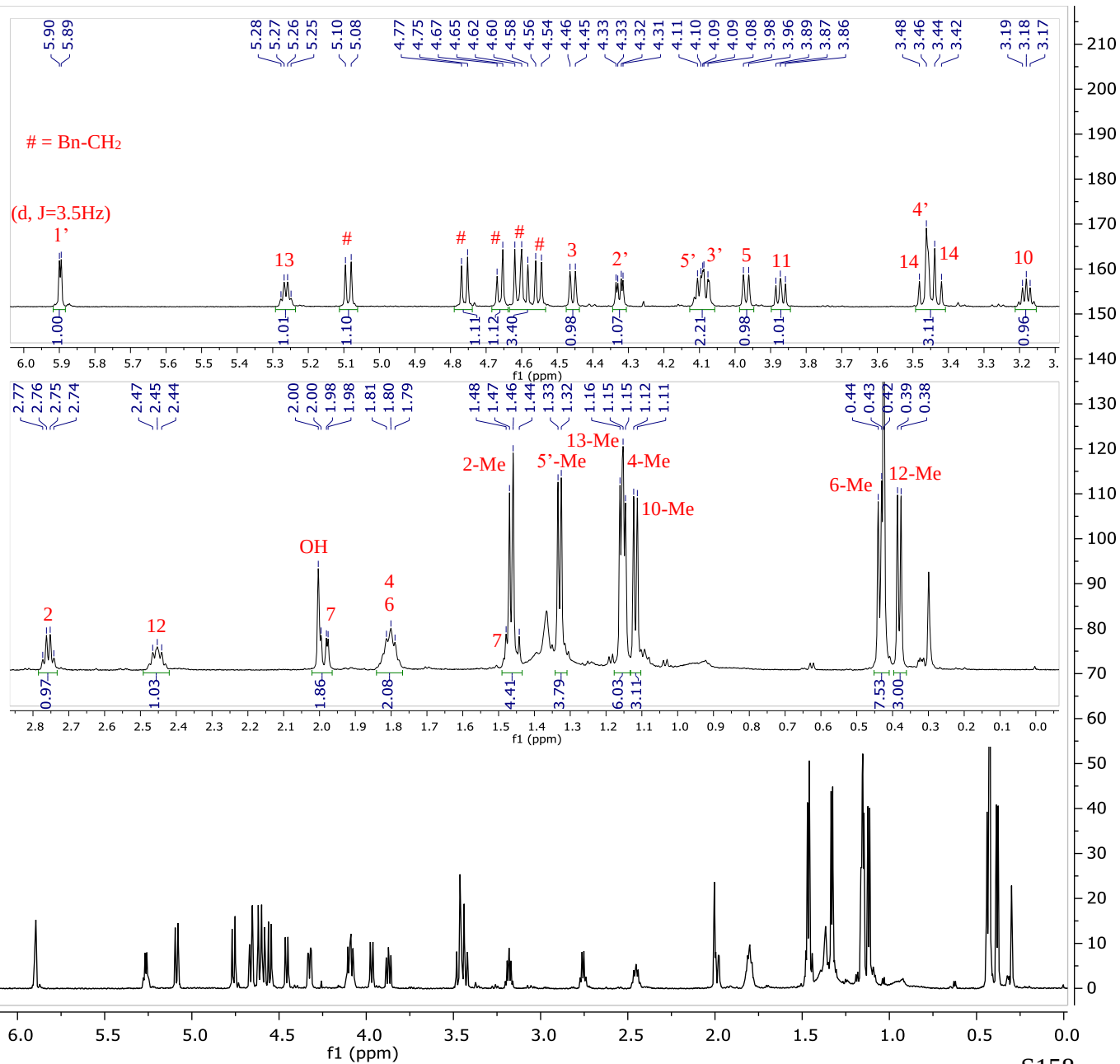
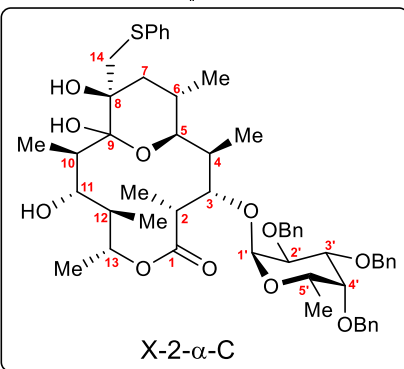


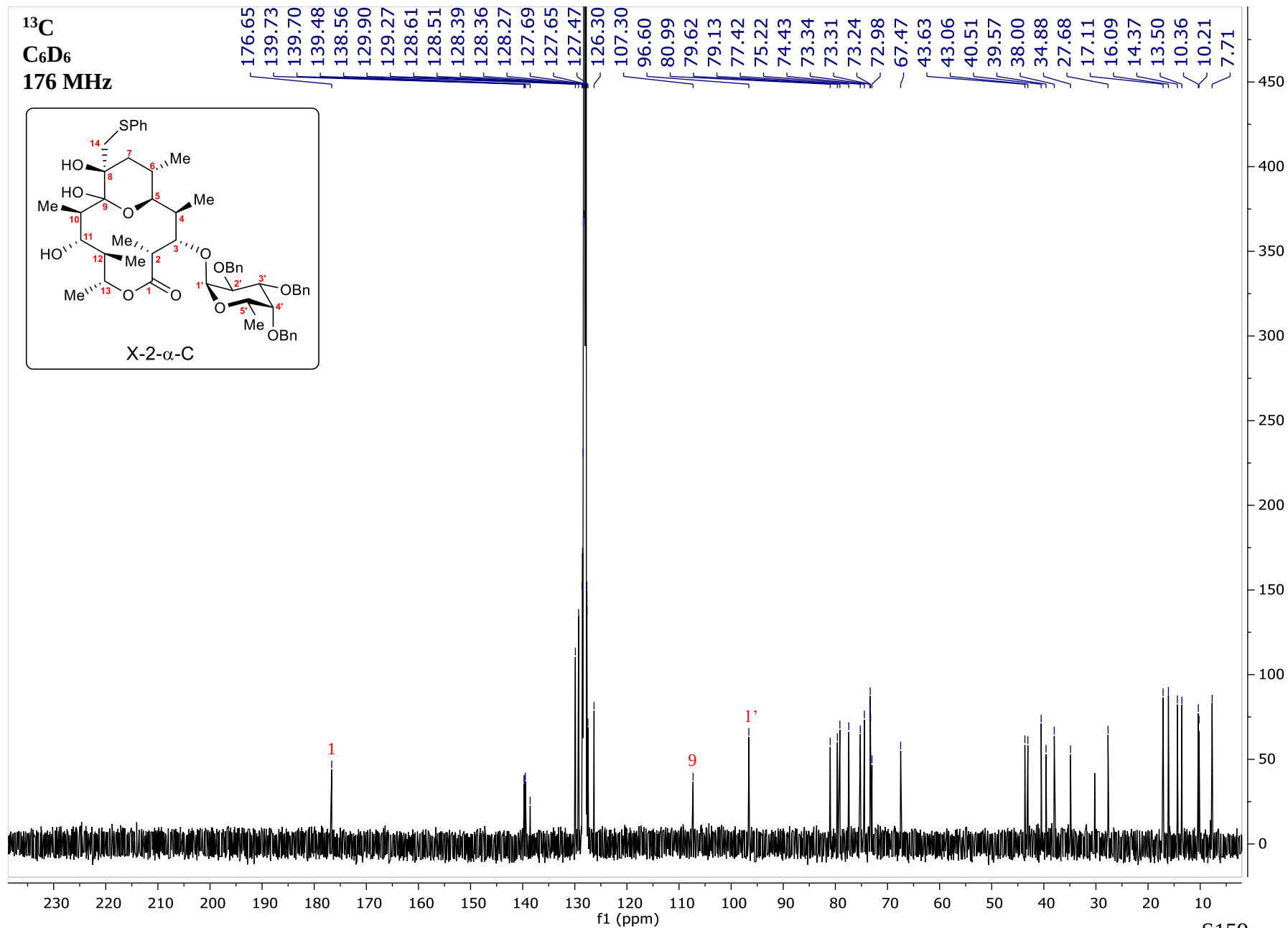


7-C₅-β-C

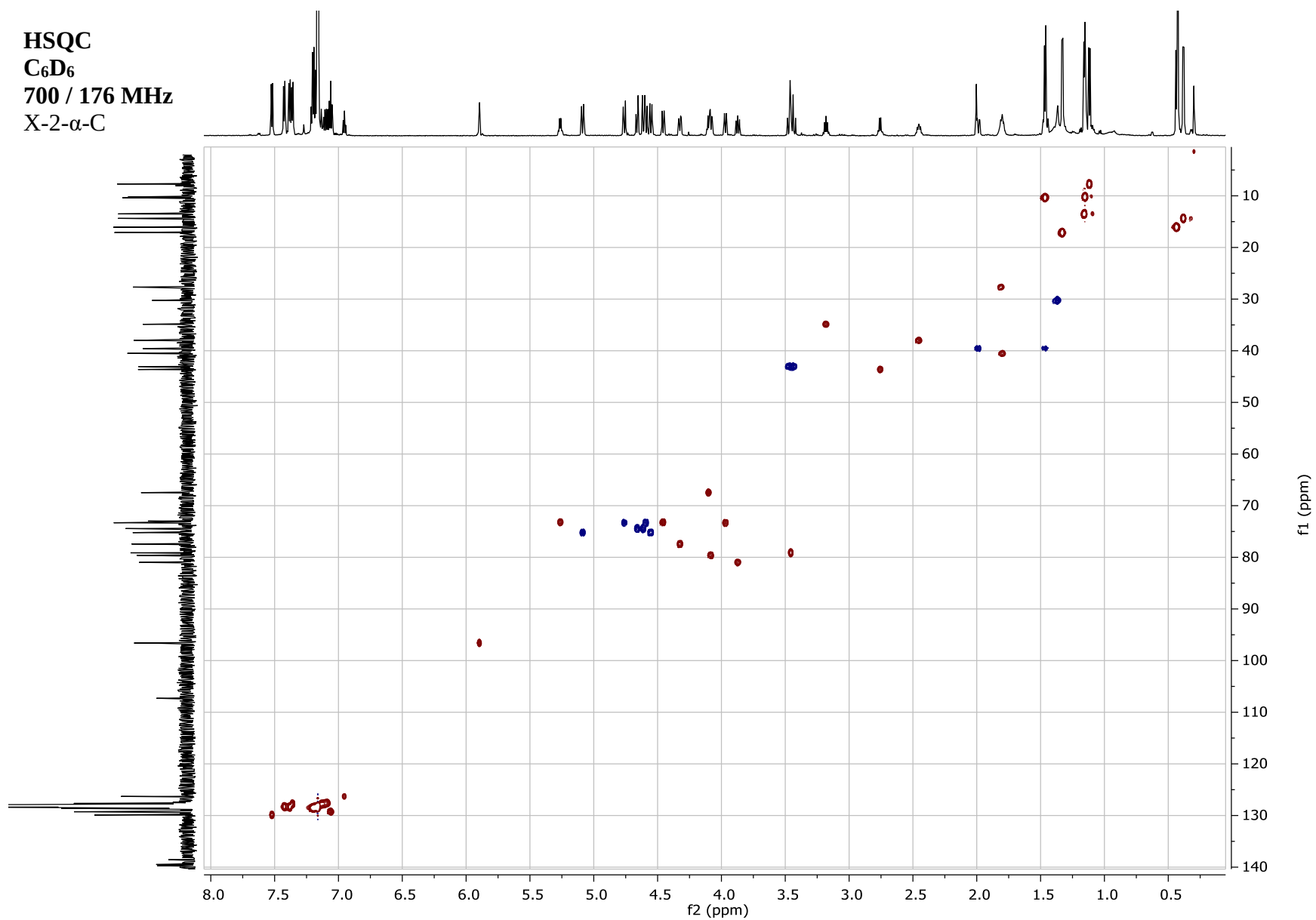


¹H
C₆D₆
700 MHz

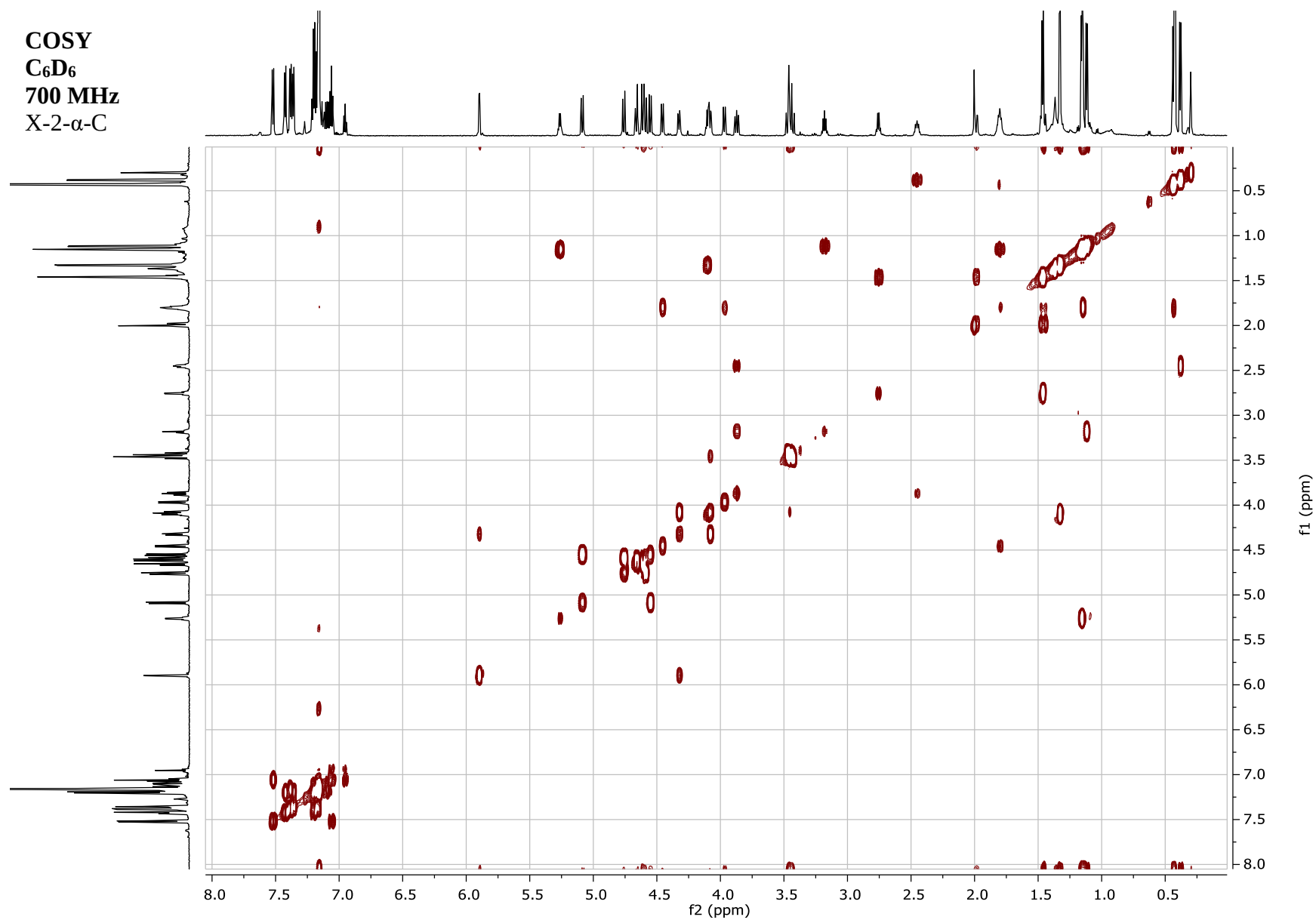




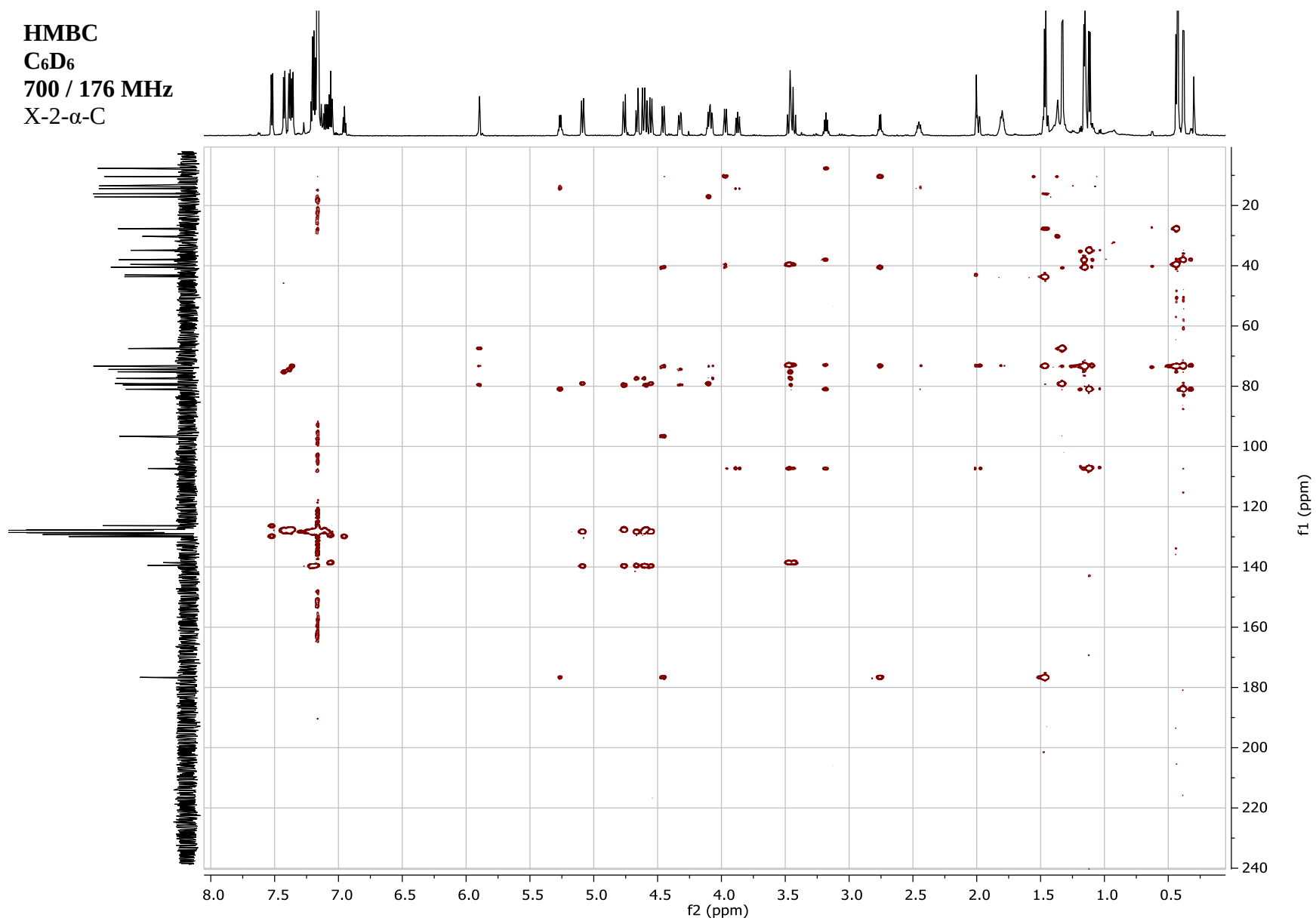
HSQC
C₆D₆
700 / 176 MHz
X-2- α -C

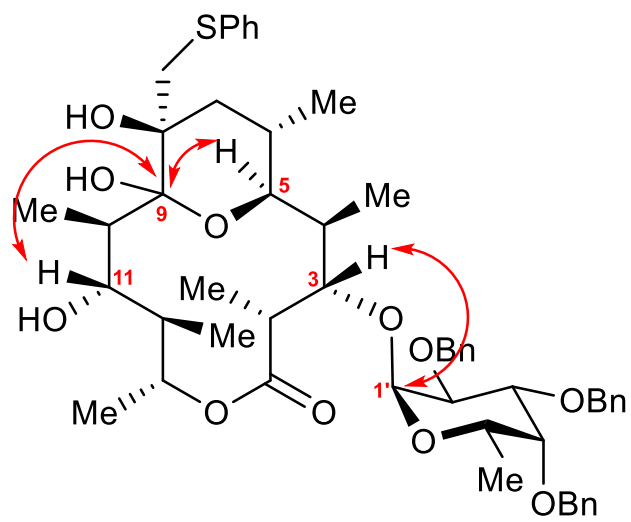


COSY
C₆D₆
700 MHz
X-2- α -C

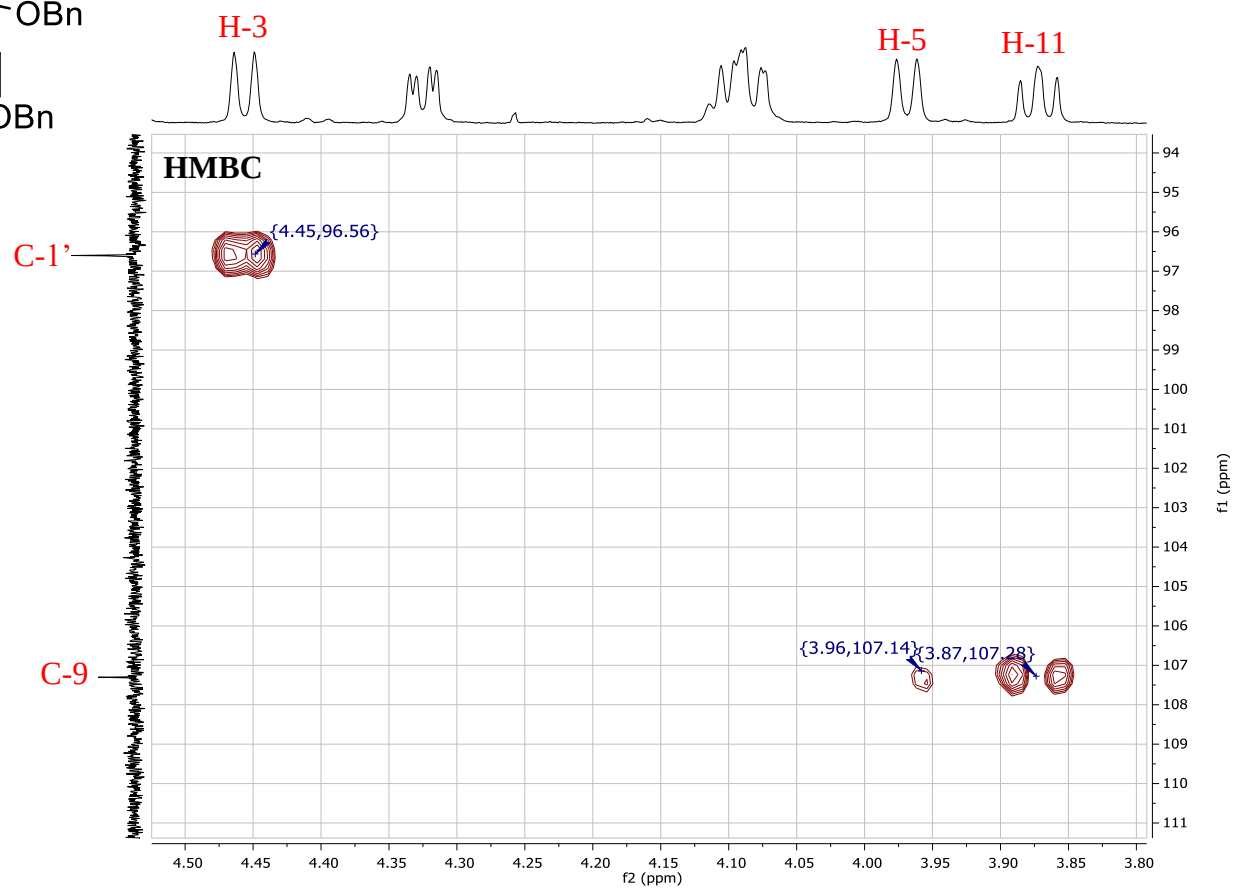


HMBC
C₆D₆
700 / 176 MHz
X-2- α -C

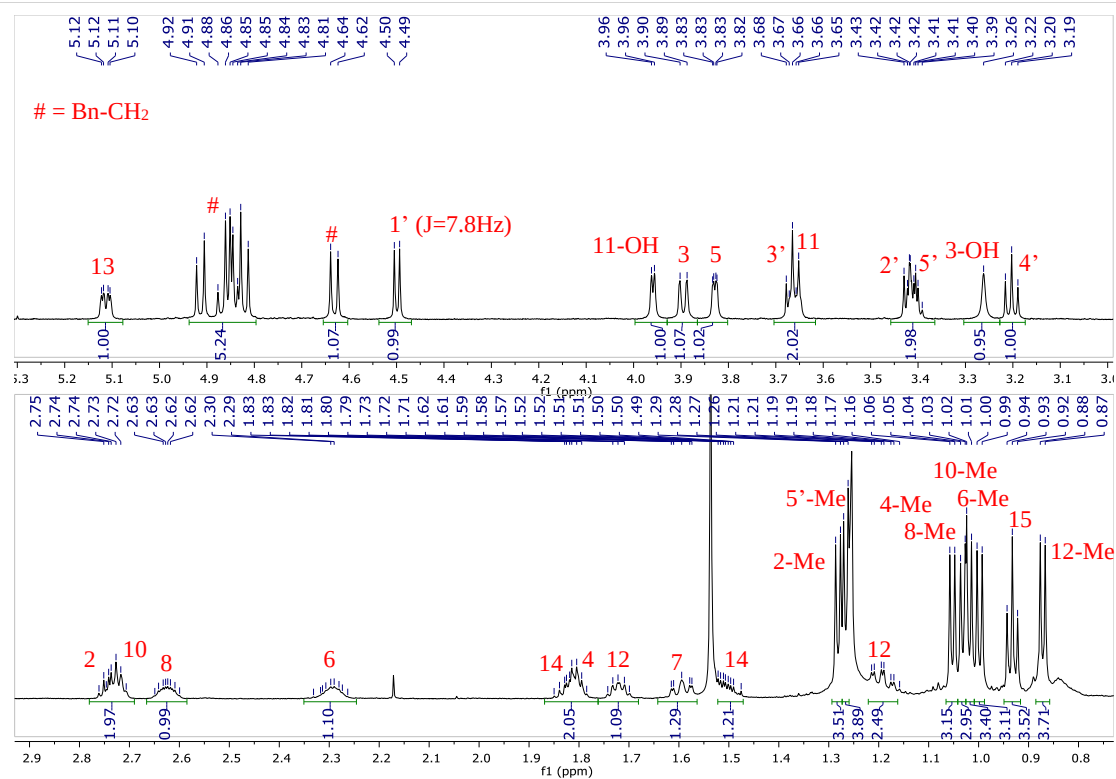
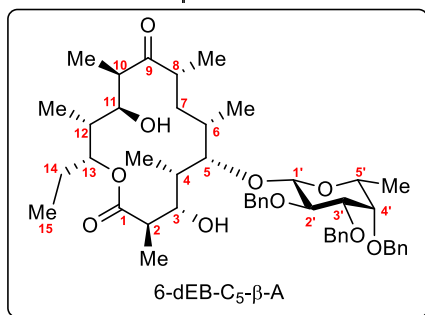


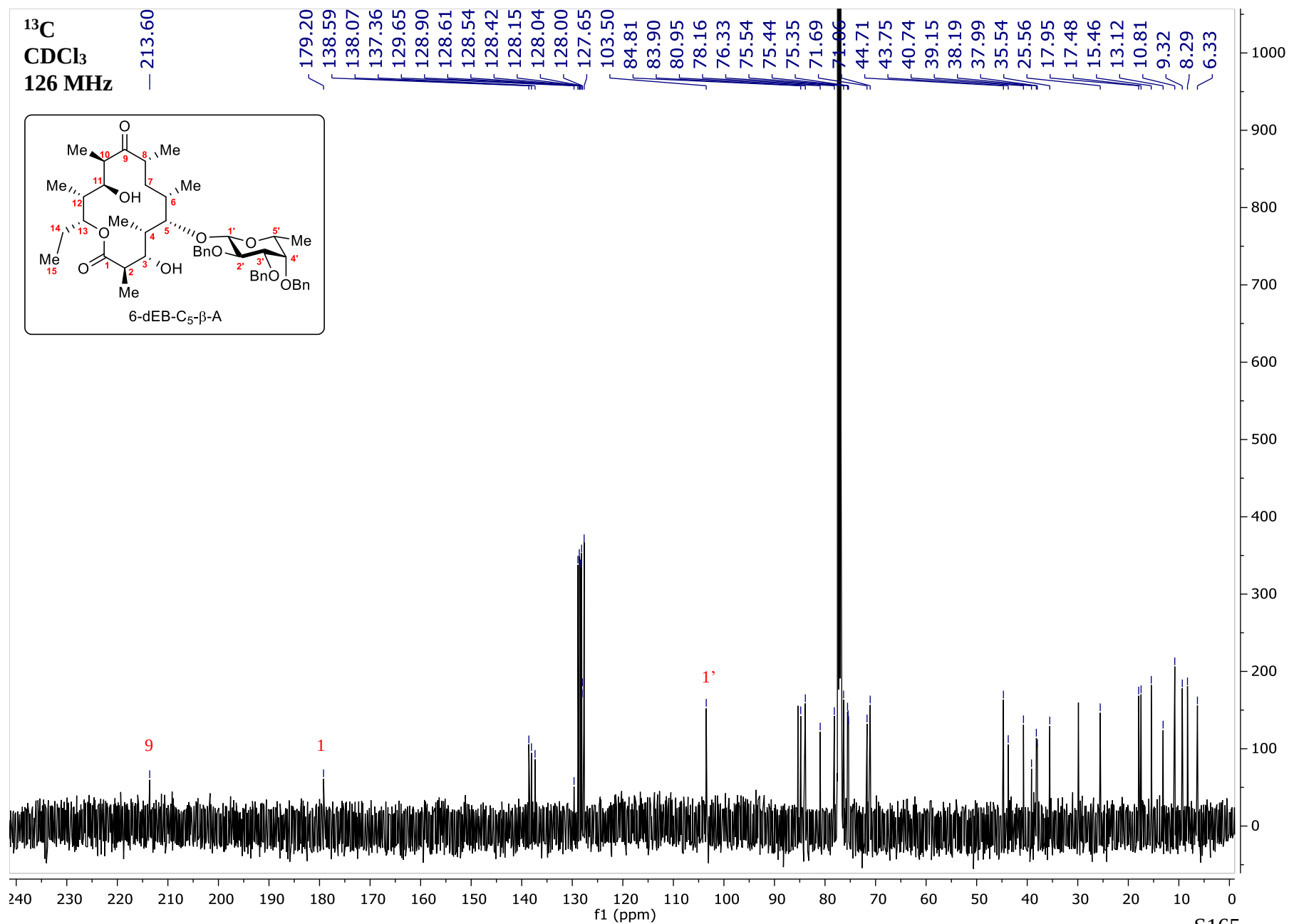


X-2- α -C

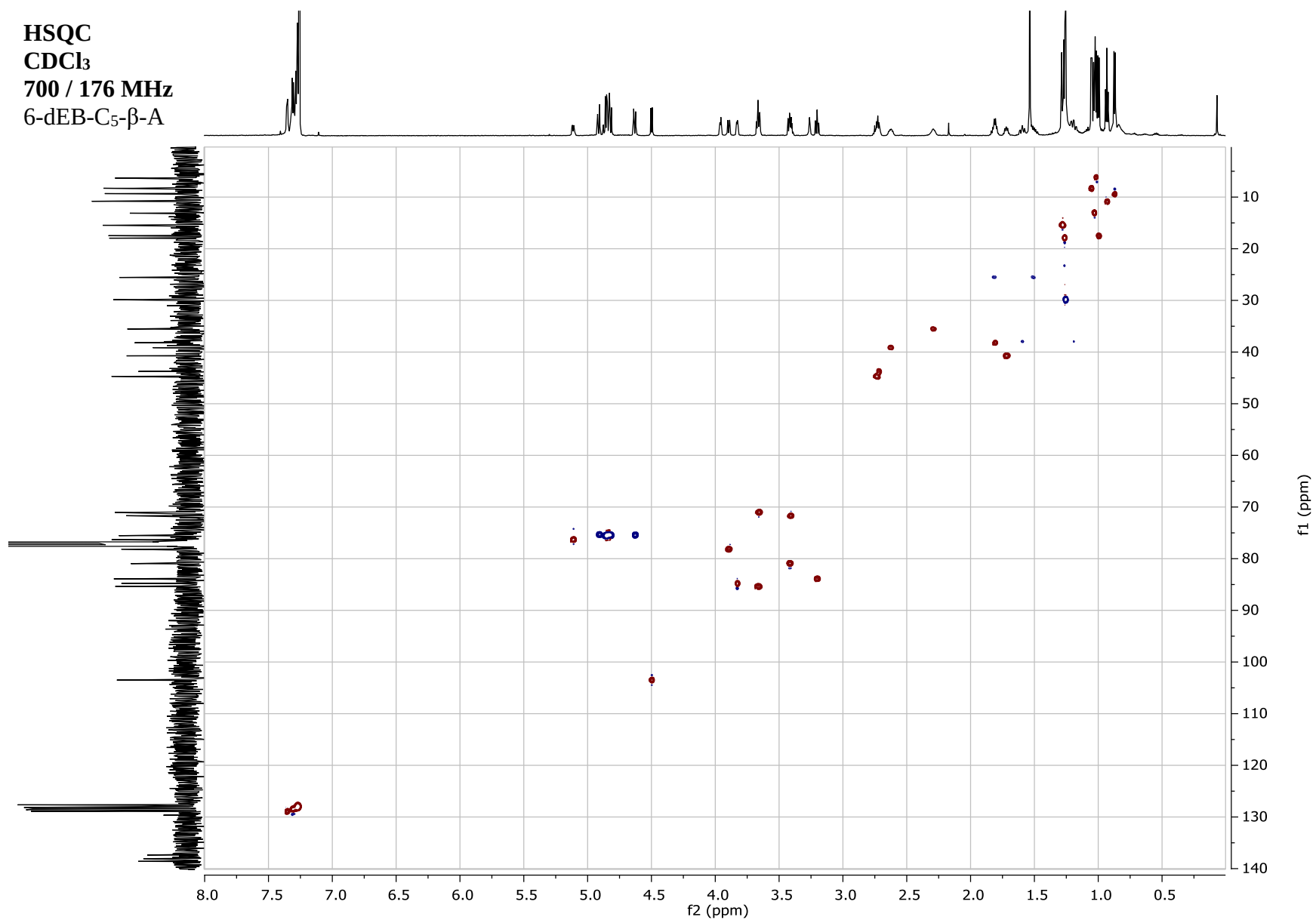


¹H
CDCl₃
700 MHz

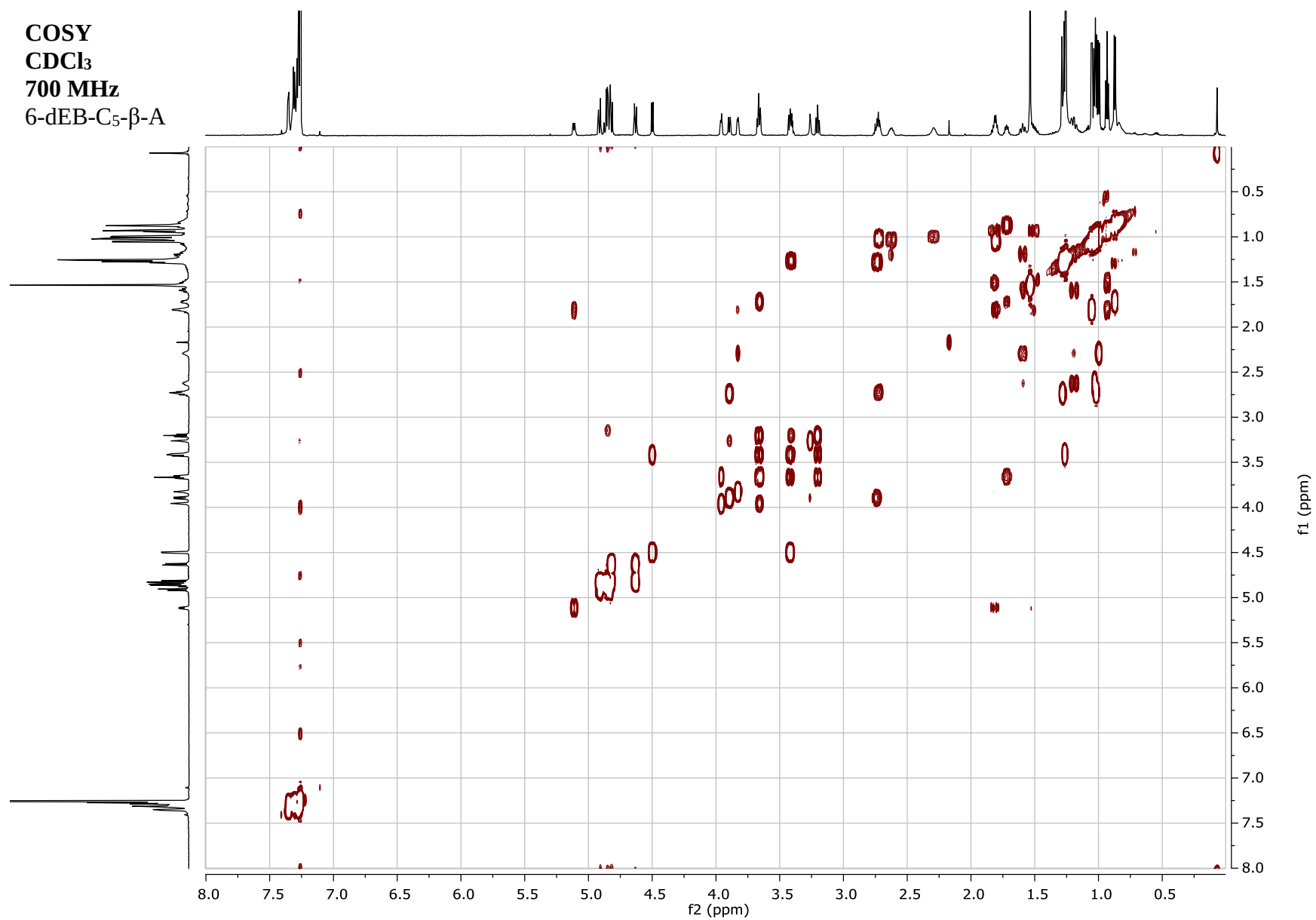




HSQC
CDCl₃
700 / 176 MHz
6-dEB-C₅-β-A



COSY
CDCl₃
700 MHz
6-dEB-C₅-β-A



HMBC
CDCl₃
500 / 126 MHz
6-dEB-C₅-β-A

