

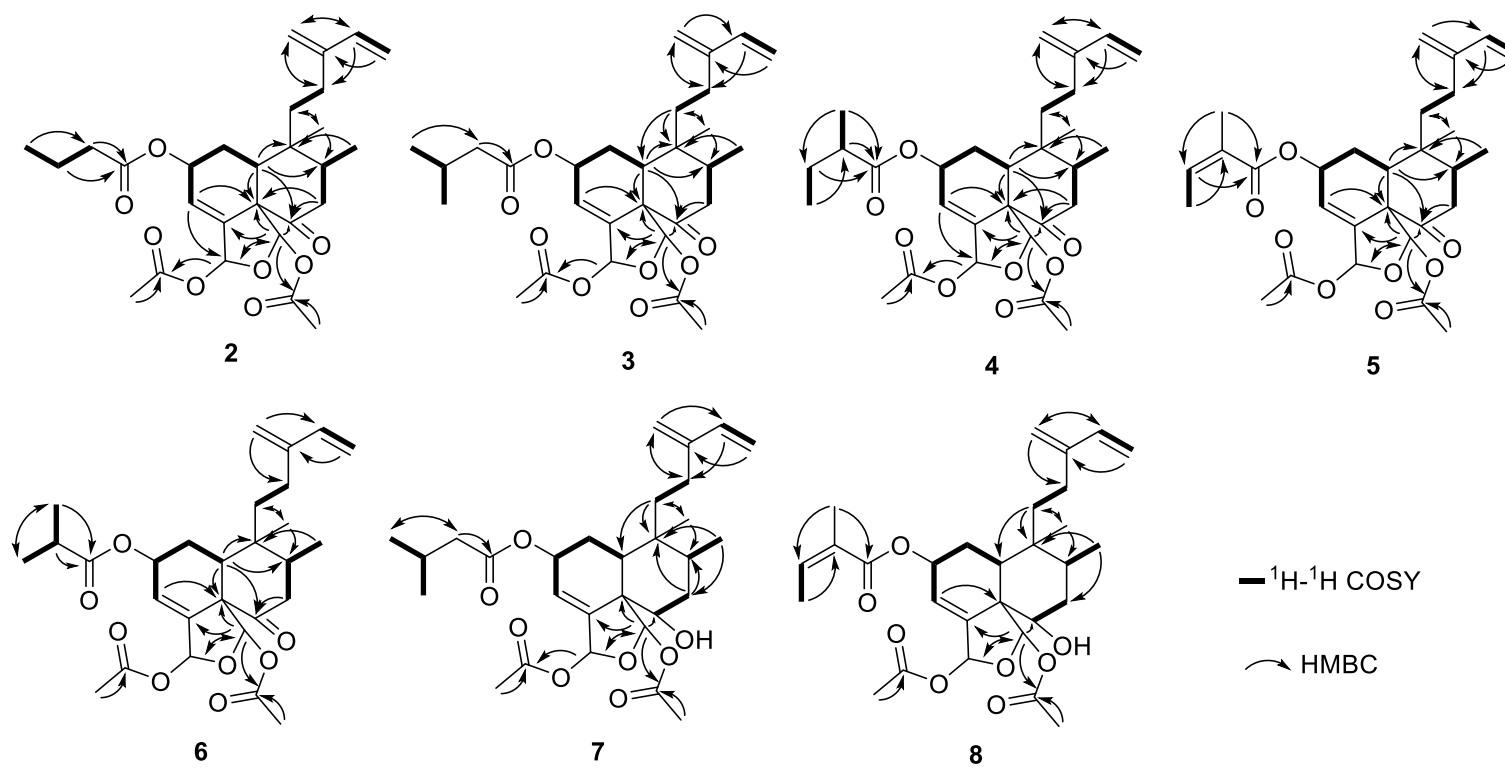
Supporting information - Figure S1-S68

## List of Contents

<b>Figure S1.</b> Selected $^1\text{H}$ - $^1\text{H}$ COSY and HMBC correlations of compounds <b>2-8</b> .....	S4
<b>Figure S2.</b> Selected ROESY correlations of compounds <b>2-5</b> and <b>7</b> .....	S5
<b>Figure S3.</b> ECD curves of compounds <b>2, 3,</b> and <b>5-8</b> .....	S6
<b>Figure S4.</b> Comparison of experimental and calculated VCD spectra of Anacolosin B ( <b>2</b> ) .....	S7
<b>Figure S5.</b> Selected ion extraction of the reaction residue of hydrolysate of Anacolosin D ( <b>4</b> ) and $\alpha$ -bromo-2-acetonaphthone ( <b>11</b> ) .....	S8
<b>Figure S6.</b> C18 and chiral HPLC analysis of <b>13</b> from <i>S</i> and <i>R/S</i> - <b>12</b> and Anacolosin D ( <b>4</b> ) .....	S9
<b>Figure S7.</b> $\Delta\delta_{\text{H}}$ ( <i>S</i> - <i>R</i> ) values (ppm) calculated from O-MTPA esters of Corymbulosin ( <b>7</b> ) .....	S10
<b>Figure S8.</b> $^1\text{H}$ NMR (400 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S11
<b>Figure S9.</b> $^{13}\text{C}$ NMR (100 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S12
<b>Figure S10.</b> $^1\text{H}$ - $^1\text{H}$ COSY (500 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S13
<b>Figure S11.</b> HSQC (500 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S14
<b>Figure S12.</b> HMBC (500 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S15
<b>Figure S13.</b> ROESY (600 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{DMSO-}d_6$ .....	S16
<b>Figure S14.</b> ROESY (500 MHz) spectrum of Anacolosin A ( <b>1</b> ) in $\text{CDCl}_3$ .....	S17
<b>Figure S15.</b> HRESIMS spectrum of Anacolosin A ( <b>1</b> ) .....	S18
<b>Figure S16.</b> $^1\text{H}$ NMR (600 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S19
<b>Figure S17.</b> $^{13}\text{C}$ NMR (100 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S20
<b>Figure S18.</b> $^1\text{H}$ - $^1\text{H}$ COSY (500 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S21
<b>Figure S19.</b> HSQC (500 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S22
<b>Figure S20.</b> HMBC (500 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S23
<b>Figure S21.</b> ROESY (500 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{MeOH-}d_4$ .....	S24
<b>Figure S22.</b> ROESY (500 MHz) spectrum of Anacolosin B ( <b>2</b> ) in $\text{CDCl}_3$ .....	S25
<b>Figure S23.</b> HRESIMS spectrum of Anacolosin B ( <b>2</b> ) .....	S26
<b>Figure S24.</b> $^1\text{H}$ NMR (600 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S27
<b>Figure S25.</b> $^{13}\text{C}$ NMR (150 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S28
<b>Figure S26.</b> $^1\text{H}$ - $^1\text{H}$ COSY (500 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S29
<b>Figure S27.</b> HSQC (500 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S30
<b>Figure S28.</b> HMBC (500 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S31
<b>Figure S29.</b> ROESY (500 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{MeOH-}d_4$ .....	S32
<b>Figure S30.</b> ROESY (500 MHz) spectrum of Anacolosin C ( <b>3</b> ) in $\text{CDCl}_3$ .....	S33
<b>Figure S31.</b> HRESIMS spectrum of Anacolosin C ( <b>3</b> ) .....	S34
<b>Figure S32.</b> $^1\text{H}$ NMR (600 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S35
<b>Figure S33.</b> $^{13}\text{C}$ NMR (150 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S36
<b>Figure S34.</b> $^1\text{H}$ - $^1\text{H}$ COSY (500 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S37
<b>Figure S35.</b> HSQC (500 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S38
<b>Figure S36.</b> HMBC (500 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S39
<b>Figure S37.</b> ROESY (500 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{MeOH-}d_4$ .....	S40
<b>Figure S38.</b> ROESY (500 MHz) spectrum of Anacolosin D ( <b>4</b> ) in $\text{CDCl}_3$ .....	S41

<b>Figure S39.</b> HRESIMS spectrum of Anacolosin D ( <b>4</b> ) .....	S42
<b>Figure S40.</b> <sup>1</sup> H NMR (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S43
<b>Figure S41.</b> <sup>13</sup> C NMR (100 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S44
<b>Figure S42.</b> <sup>1</sup> H- <sup>1</sup> H COSY (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S45
<b>Figure S43.</b> HSQC (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S46
<b>Figure S44.</b> HMBC (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S47
<b>Figure S45.</b> ROESY (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S48
<b>Figure S46.</b> ROESY (500 MHz) spectrum of Anacolosin E ( <b>5</b> ) in CDCl <sub>3</sub> .....	S49
<b>Figure S47.</b> HRESIMS spectrum of Anacolosin E ( <b>5</b> ) .....	S50
<b>Figure S48.</b> <sup>1</sup> H NMR (500 MHz) spectrum of Anacolosin F ( <b>6</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S51
<b>Figure S49.</b> <sup>1</sup> H- <sup>1</sup> H COSY (500 MHz) spectrum of Anacolosin F ( <b>6</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S52
<b>Figure S50.</b> HSQC (500 MHz) spectrum of Anacolosin F ( <b>6</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S53
<b>Figure S51.</b> HMBC (500 MHz) spectrum of Anacolosin F ( <b>6</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S54
<b>Figure S52.</b> HRESIMS spectrum of Anacolosin F ( <b>6</b> ) .....	S55
<b>Figure S53.</b> <sup>1</sup> H NMR (500 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S56
<b>Figure S54.</b> <sup>13</sup> C NMR (100 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S57
<b>Figure S55.</b> <sup>1</sup> H- <sup>1</sup> H COSY (500 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S58
<b>Figure S56.</b> HSQC (500 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S59
<b>Figure S57.</b> HMBC (500 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S60
<b>Figure S58.</b> ROESY (500 MHz) spectrum of Corymbulosin X ( <b>7</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S61
<b>Figure S59.</b> HRESIMS spectrum of Corymbulosin X ( <b>7</b> ) .....	S62
<b>Figure S60.</b> <sup>1</sup> H NMR (500 MHz) spectrum of Corymbulosin Y ( <b>8</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S63
<b>Figure S61.</b> <sup>1</sup> H- <sup>1</sup> H COSY (500 MHz) spectrum of Corymbulosin Y ( <b>8</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S64
<b>Figure S62.</b> HSQC (500 MHz) spectrum of Corymbulosin Y ( <b>8</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S65
<b>Figure S63.</b> HMBC (500 MHz) spectrum of Corymbulosin Y ( <b>8</b> ) in MeOH- <i>d</i> <sub>4</sub> .....	S66
<b>Figure S64.</b> HRESIMS spectrum of Corymbulosin Y ( <b>8</b> ) .....	S67
<b>Figure S65.</b> <sup>1</sup> H NMR (400 MHz) spectrum of the synthetic standard <i>R/S</i> - <b>13</b> in MeOH- <i>d</i> <sub>4</sub> .....	S68
<b>Figure S66.</b> <sup>13</sup> C NMR (100 MHz) spectrum of the synthetic standard <i>R/S</i> - <b>13</b> in MeOH- <i>d</i> <sub>4</sub> .....	S69
<b>Figure S67.</b> <sup>1</sup> H NMR (400 MHz) spectrum of the synthetic standard <i>S</i> - <b>13</b> in MeOH- <i>d</i> <sub>4</sub> .....	S70
<b>Figure S68.</b> <sup>13</sup> C NMR (100 MHz) spectrum of the synthetic standard <i>S</i> - <b>13</b> in MeOH- <i>d</i> <sub>4</sub> .....	S71

**Figure S1.** Selected  $^1\text{H}$ - $^1\text{H}$  COSY and HMBC correlations of compounds **2-8**





**Figure S2.** Selected ROESY correlations of compounds **2-5** and **7**

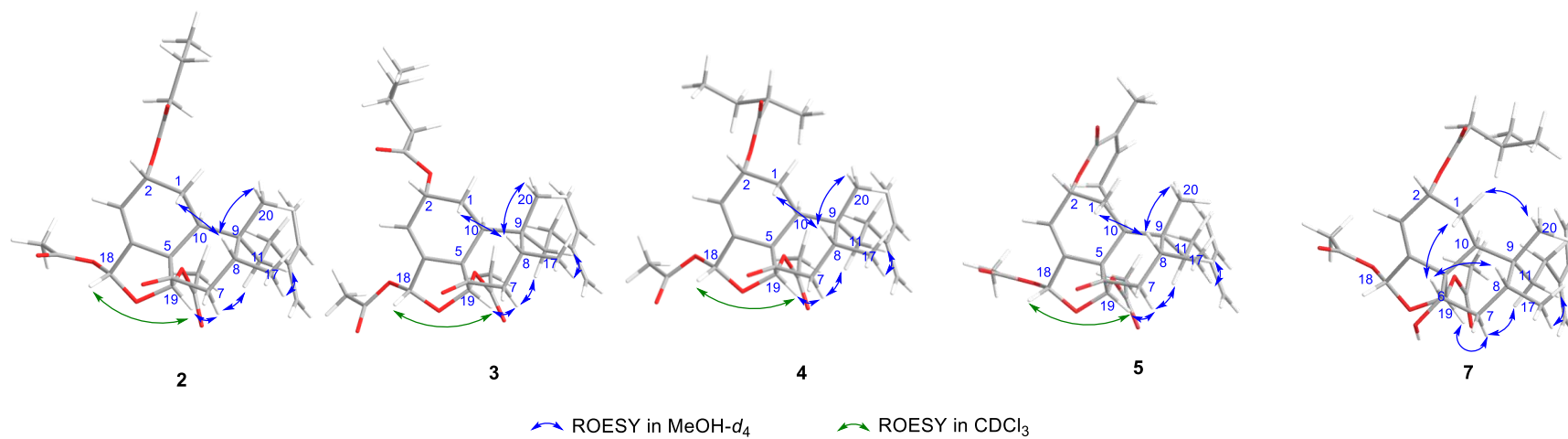
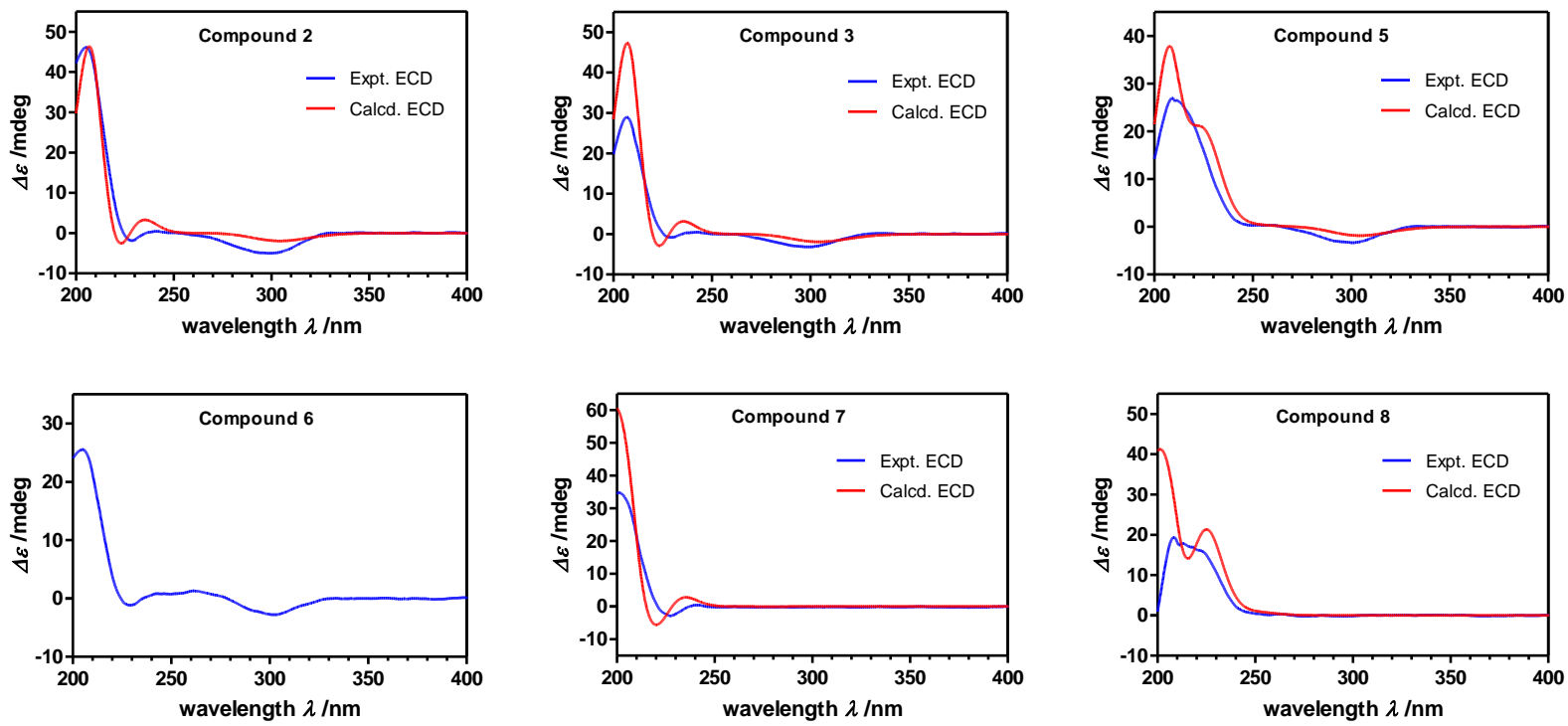
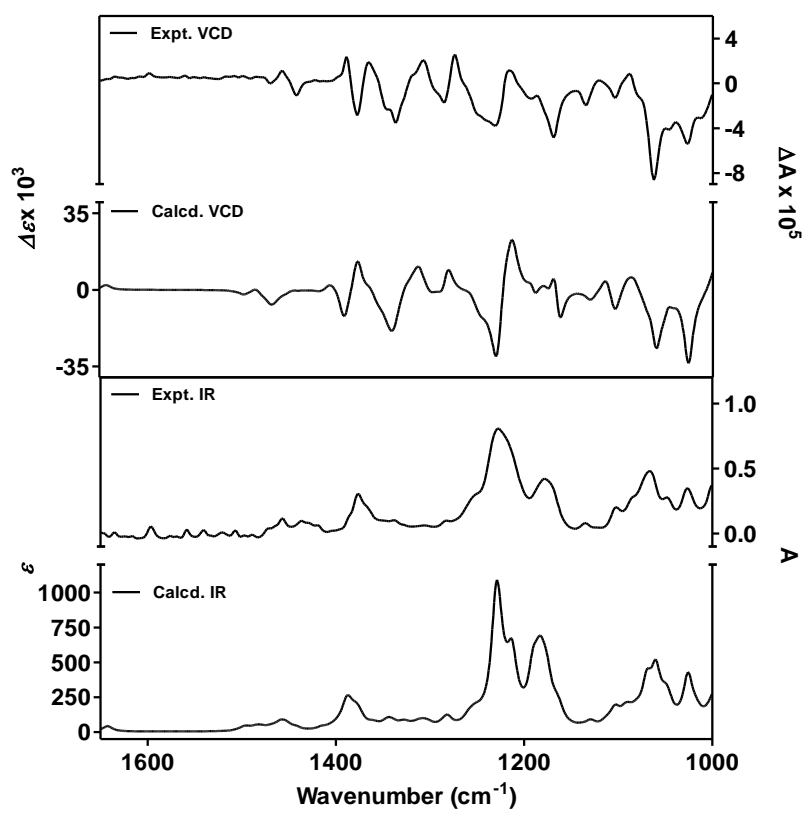


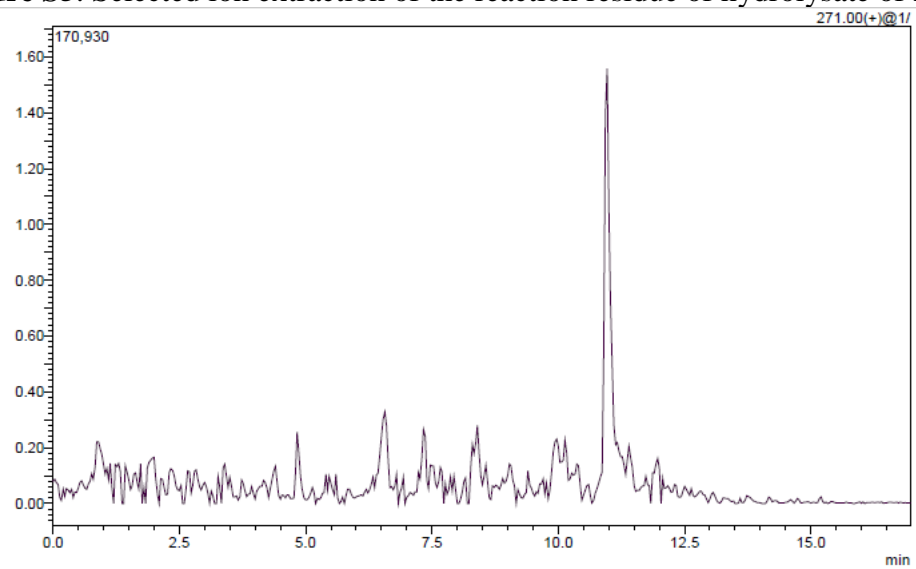
Figure S3. ECD curves of compounds 2, 3, and 5-8



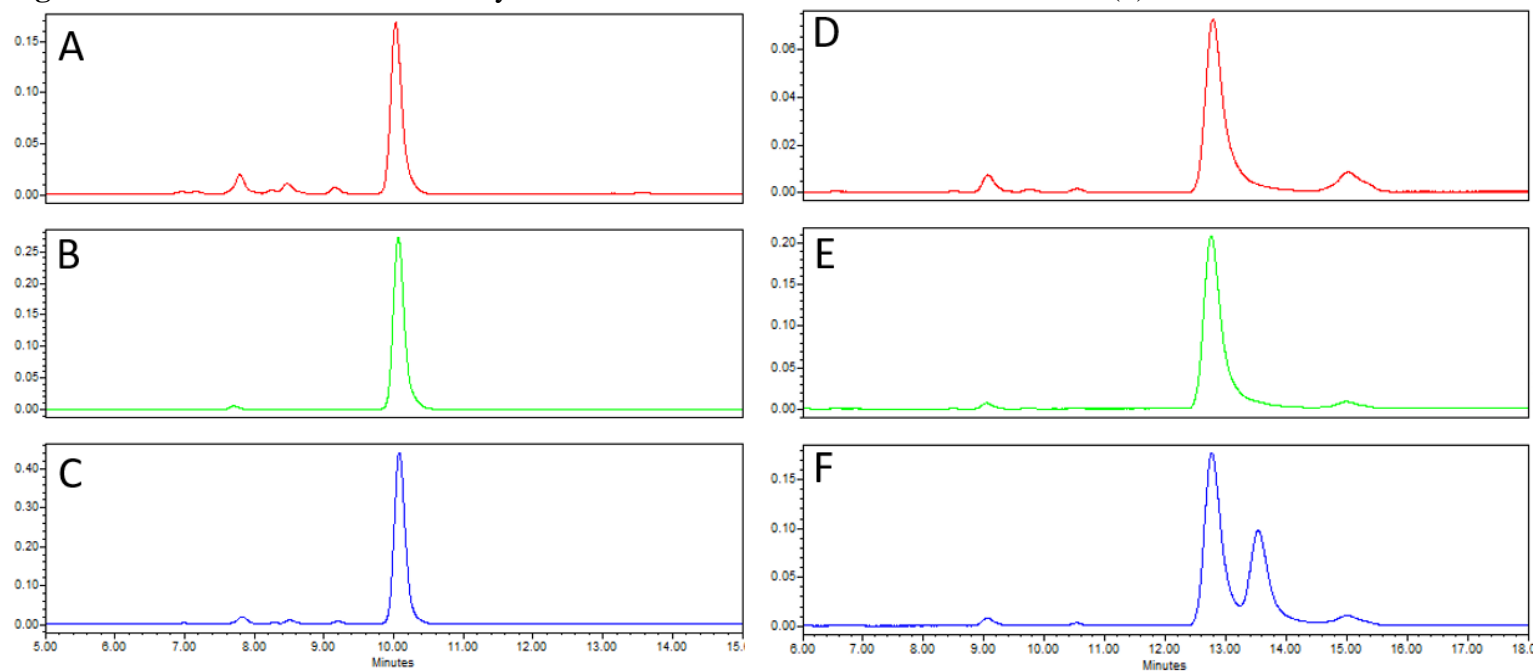
**Figure S4.** Comparison of experimental and calculated VCD spectra of Anacolosin B (2)



**Figure S5.** Selected ion extraction of the reaction residue of hydrolysate of Anacolosin D (**4**) and  $\alpha$ -bromo-2-acetonaphthone (**11**)



**Figure S6.** C18 and chiral HPLC analysis of **13** from *S* and *R/S*-**12** and Anacolosin D (**4**)



A: C18 HPLC analysis of 2-methylbutyric acid 2-naphthacyl ester (**13**) from Anacolosin D (**4**)

B: C18 HPLC analysis of **13** from *S*-**12** (2-methylbutyric acid)

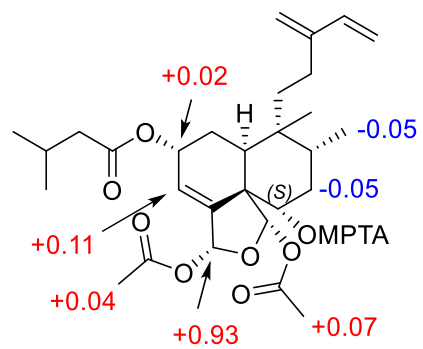
C: Co-injection of **13** from Anacolosin D (**4**) and from *S*-**12** on C18 HPLC

D: Chiral HPLC analysis of **13** from Anacolosin D (**4**) on Phenomenex Cellulose-3 column

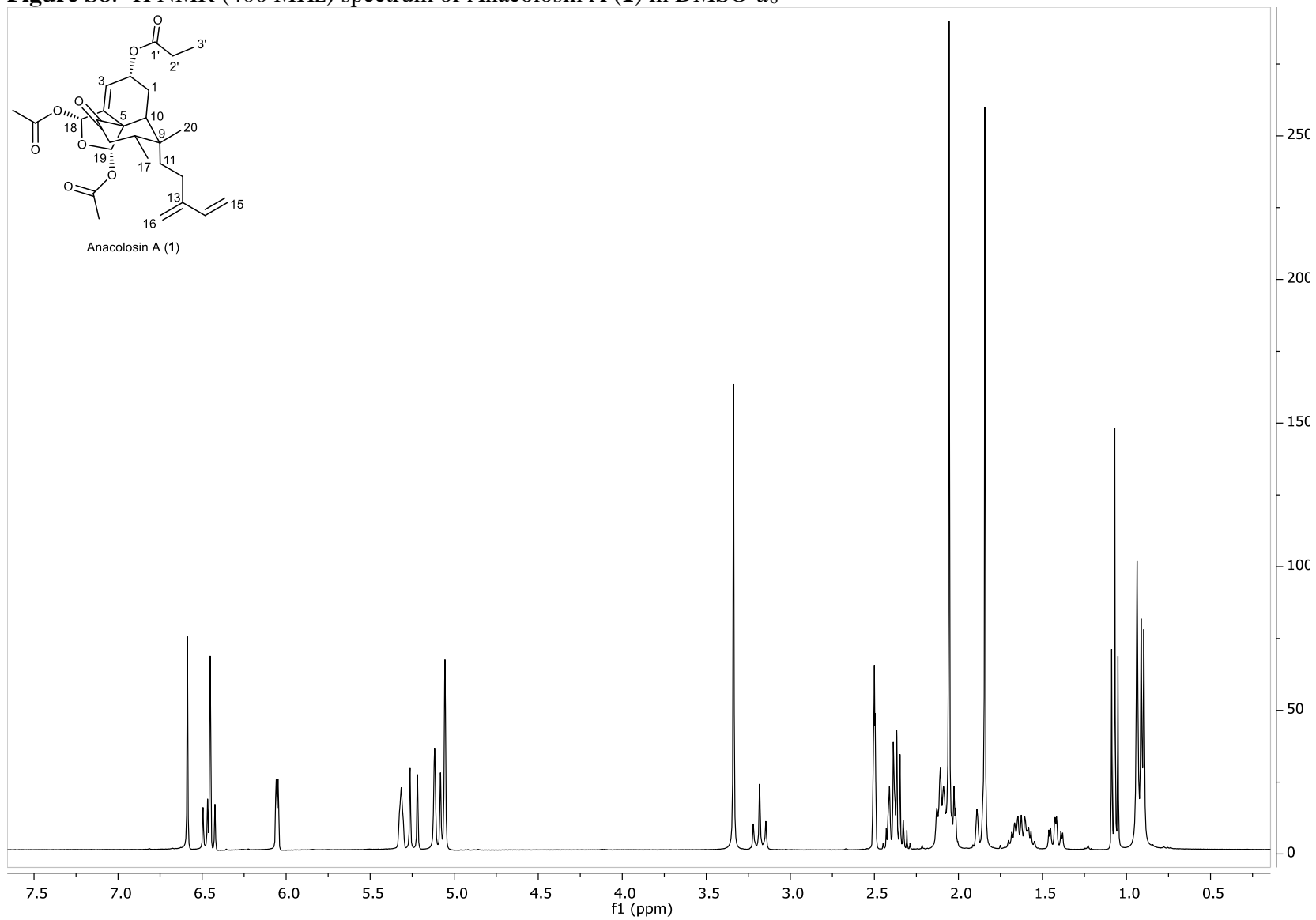
E: Co-injection of **13** from the Anacolosin D (**4**) and from *S*-**12** on Phenomenex Cellulose-3 column

F: Co-injection of **13** from the Anacolosin D (**4**) and from *R/S*-**12** on Phenomenex Cellulose-3 column

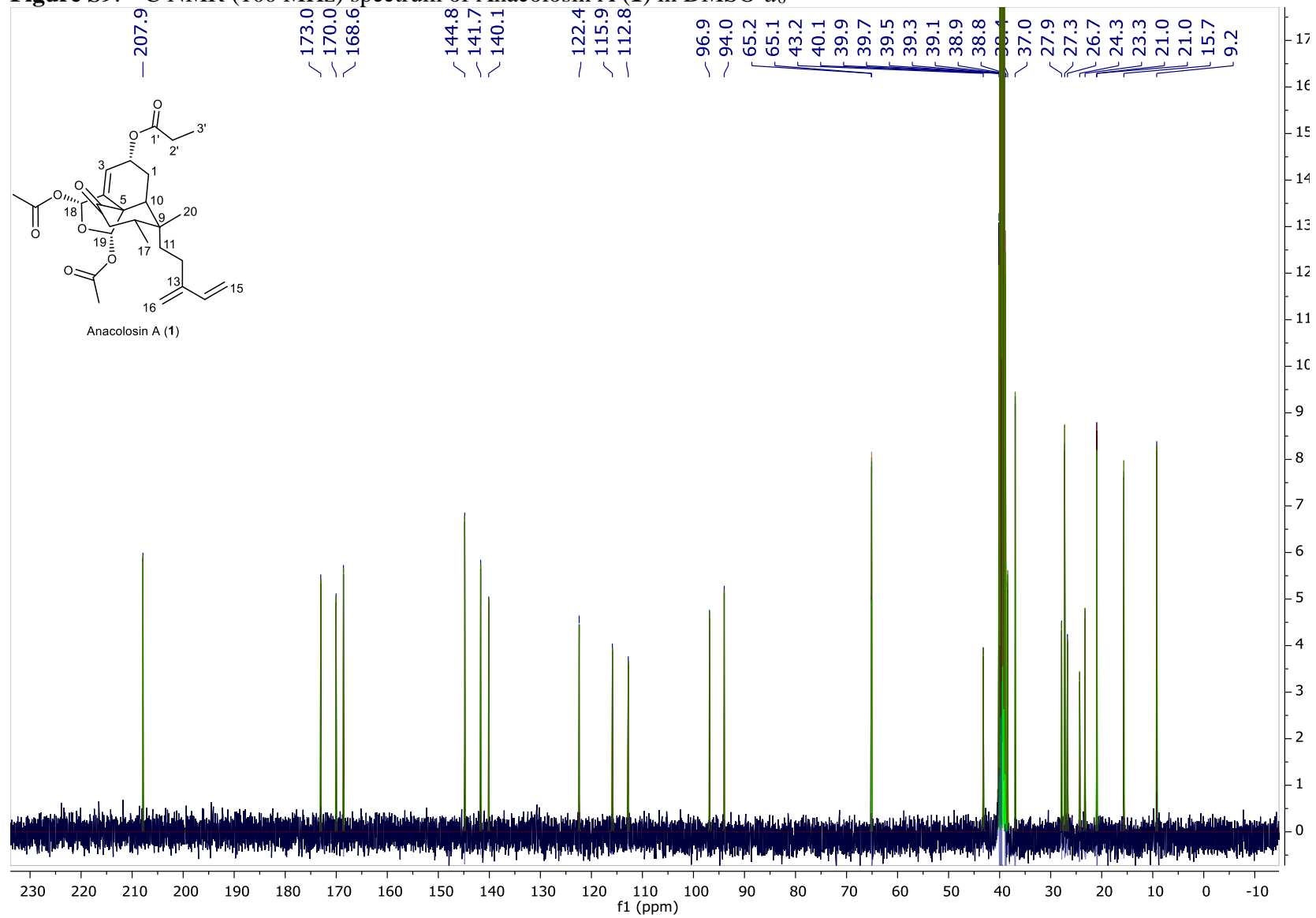
**Figure S7.**  $\Delta\delta_{\text{H}}$  (*S*-*R*) values (ppm) calculated from O-MTPA esters of Corymbulosin (**7**)



**Figure S8.**  $^1\text{H}$  NMR (400 MHz) spectrum of Anacolosin A (**1**) in  $\text{DMSO-}d_6$

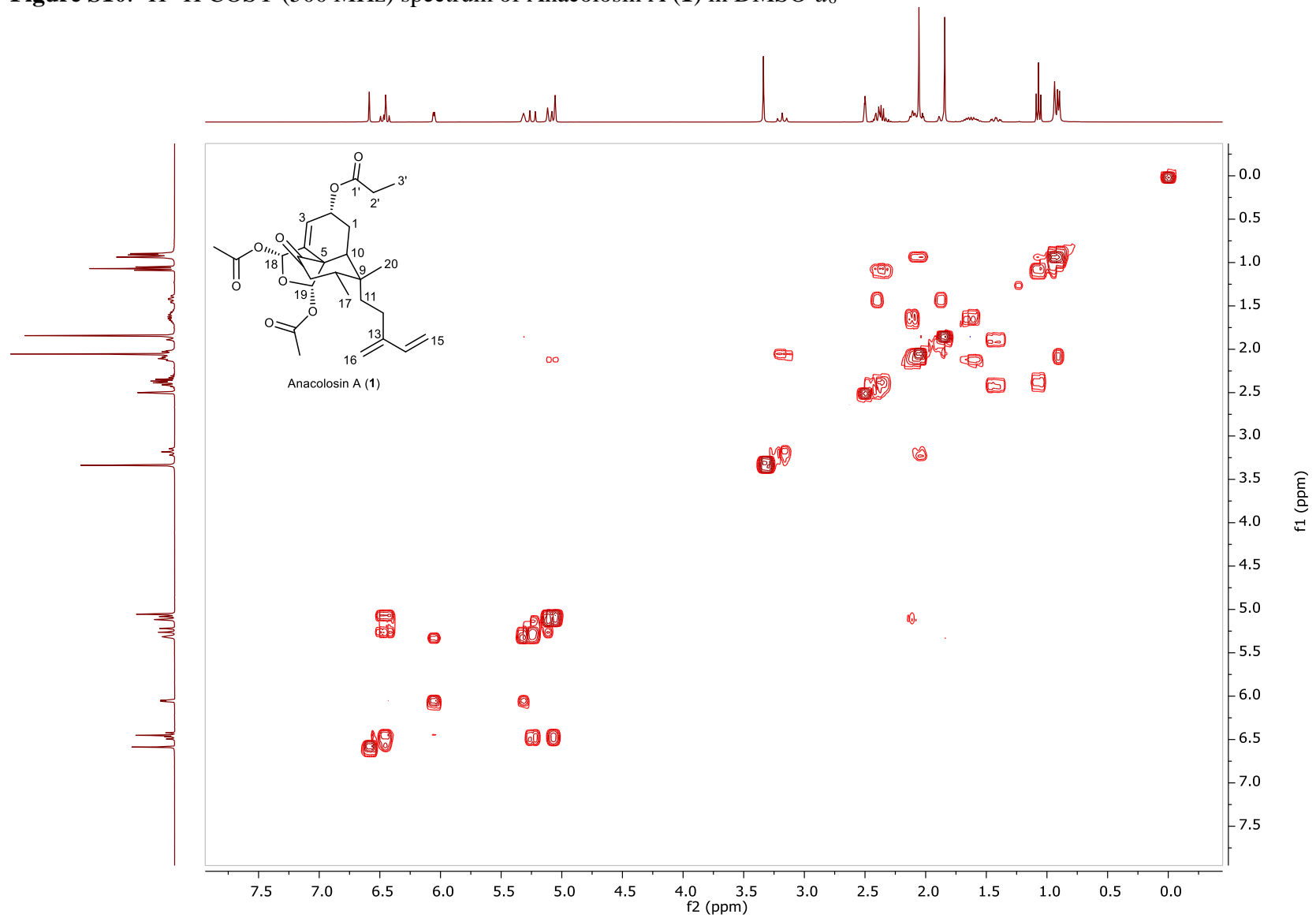


**Figure S9.**  $^{13}\text{C}$  NMR (100 MHz) spectrum of Anacolosin A (**1**) in  $\text{DMSO-}d_6$

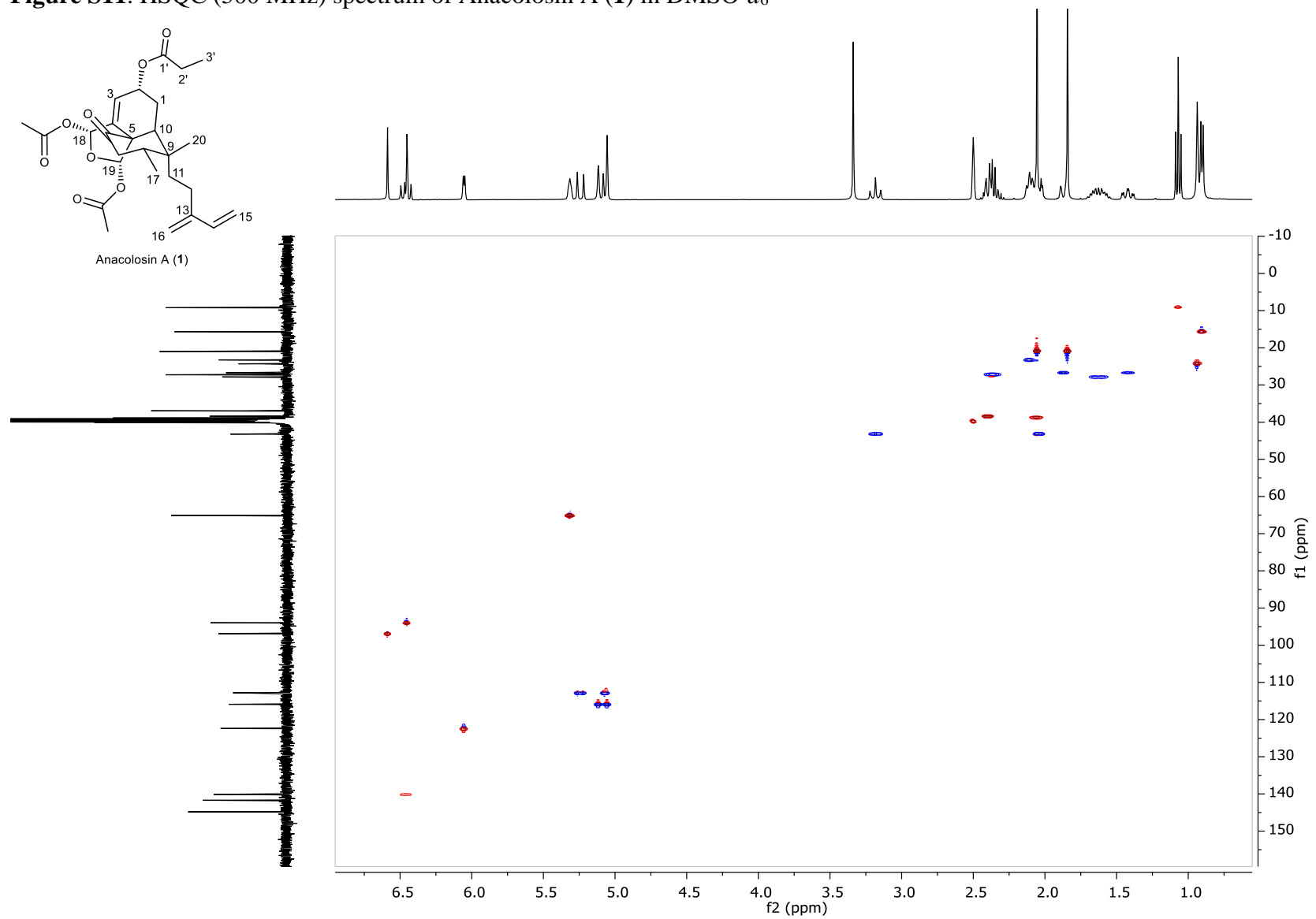




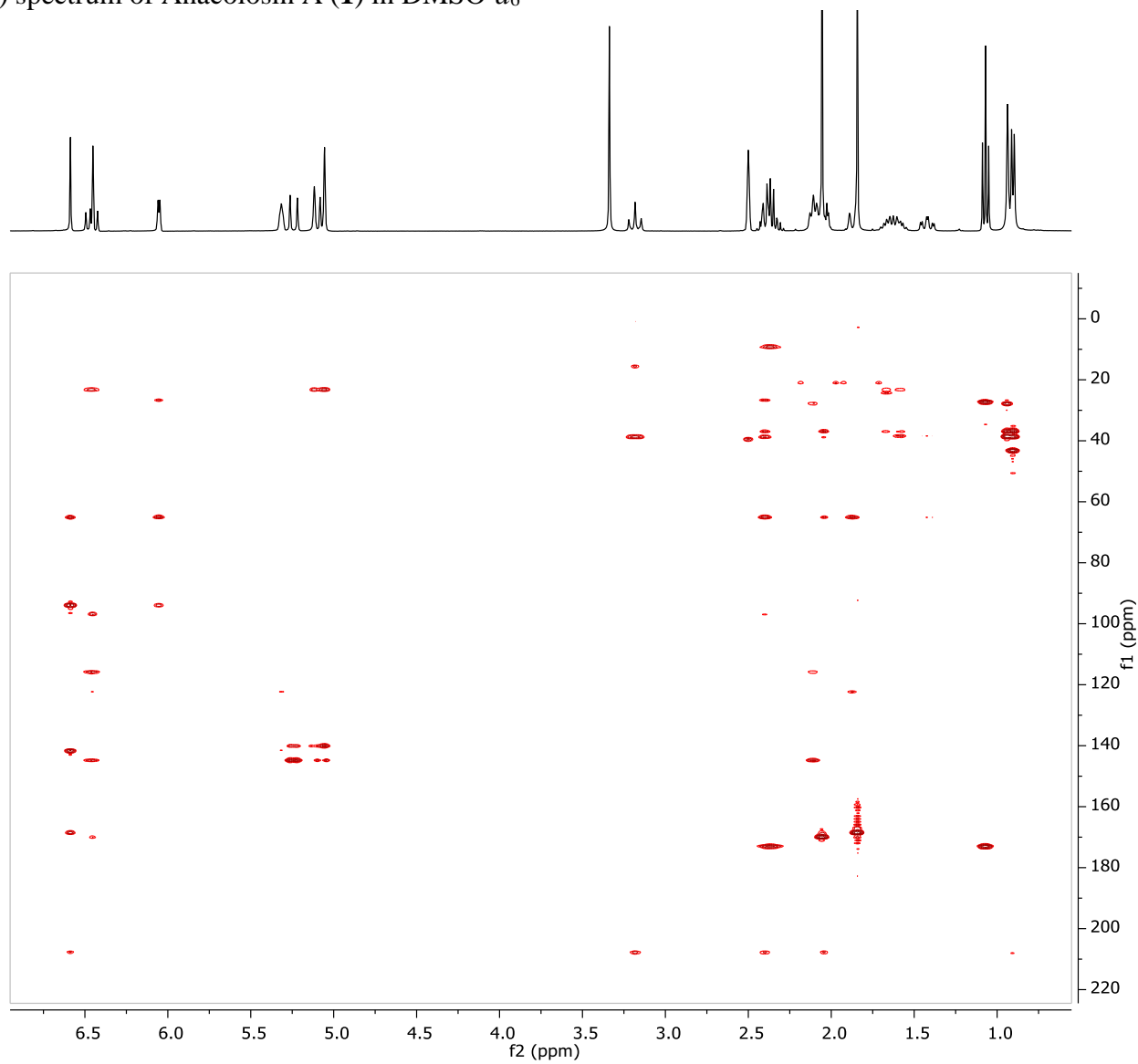
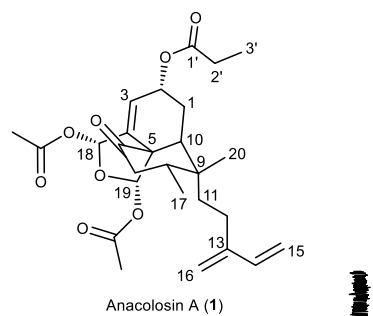
**Figure S10.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Anacolosin A (**1**) in  $\text{DMSO-}d_6$



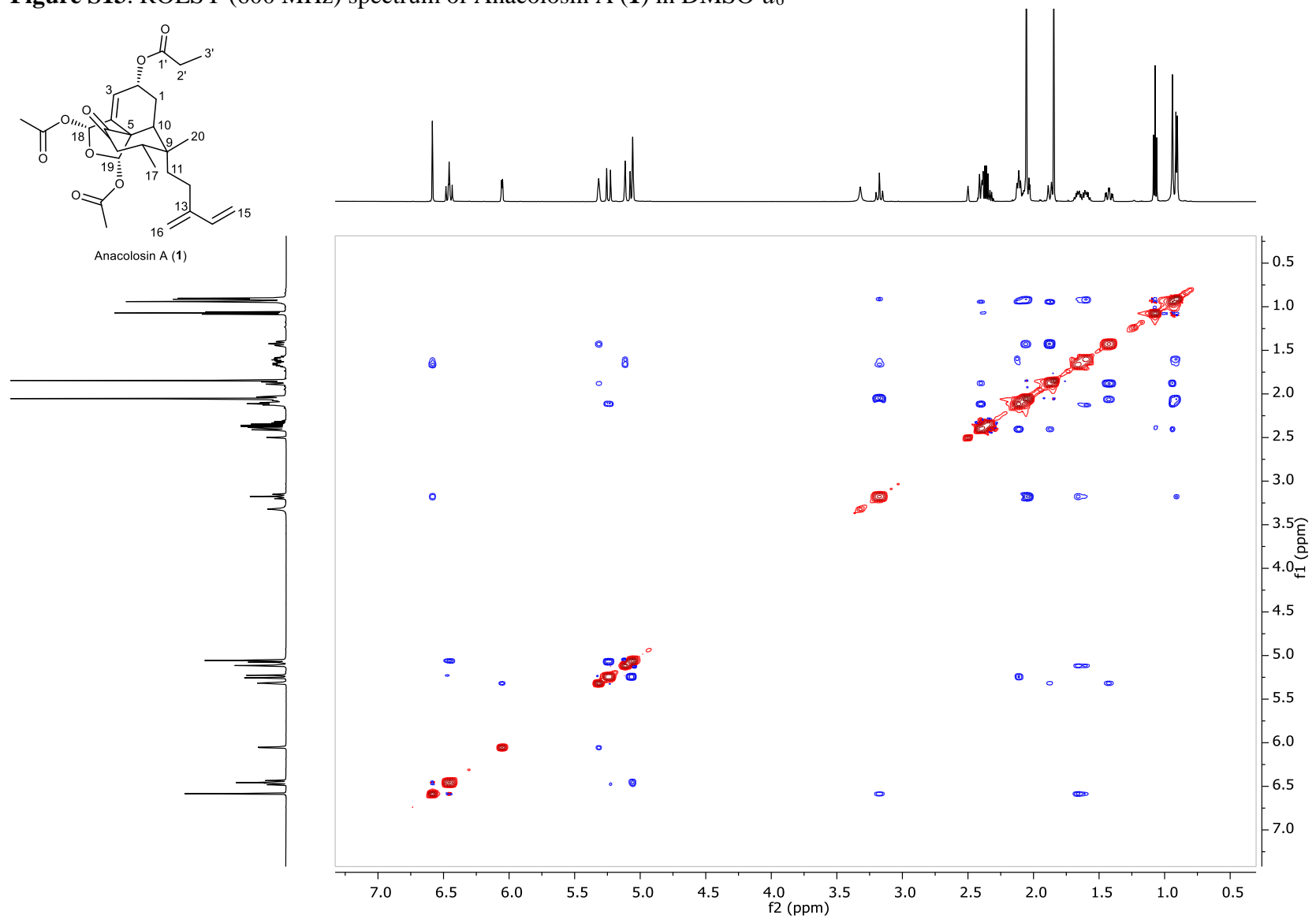
**Figure S11.** HSQC (500 MHz) spectrum of Anacolosin A (**1**) in DMSO-*d*<sub>6</sub>



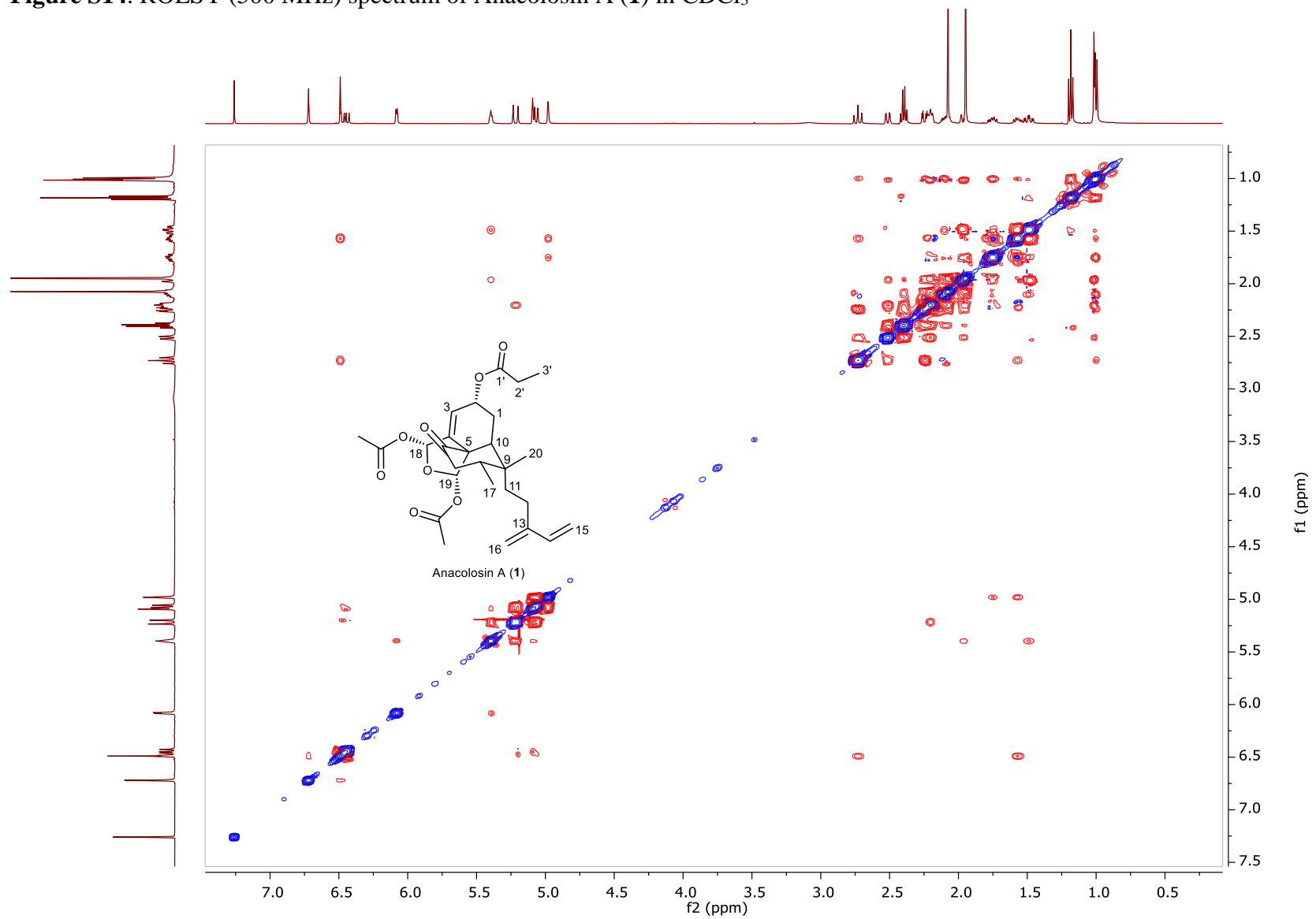
**Figure S12.** HMBC (500 MHz) spectrum of Anacolosin A (**1**) in DMSO-*d*<sub>6</sub>



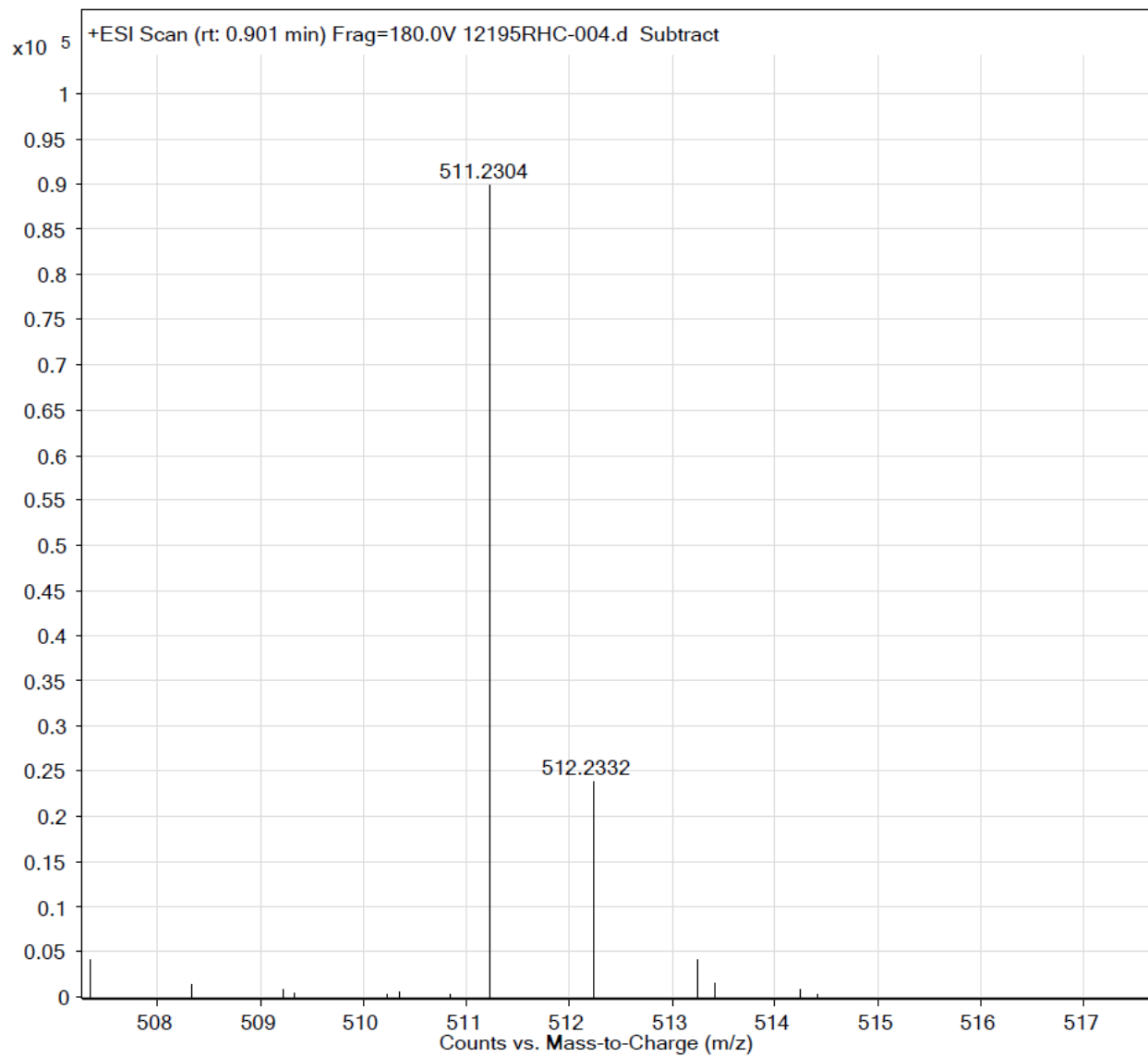
**Figure S13.** ROESY (600 MHz) spectrum of Anacolosin A (**1**) in DMSO-*d*<sub>6</sub>



**Figure S14.** ROESY (500 MHz) spectrum of Anacolosin A (**1**) in CDCl<sub>3</sub>



**Figure S15.** HRESIMS spectrum of Anacolosin A (**1**)



**Figure S16.**  $^1\text{H}$  NMR (600 MHz) spectrum of Anacolosin B (**2**) in  $\text{MeOH-}d_4$

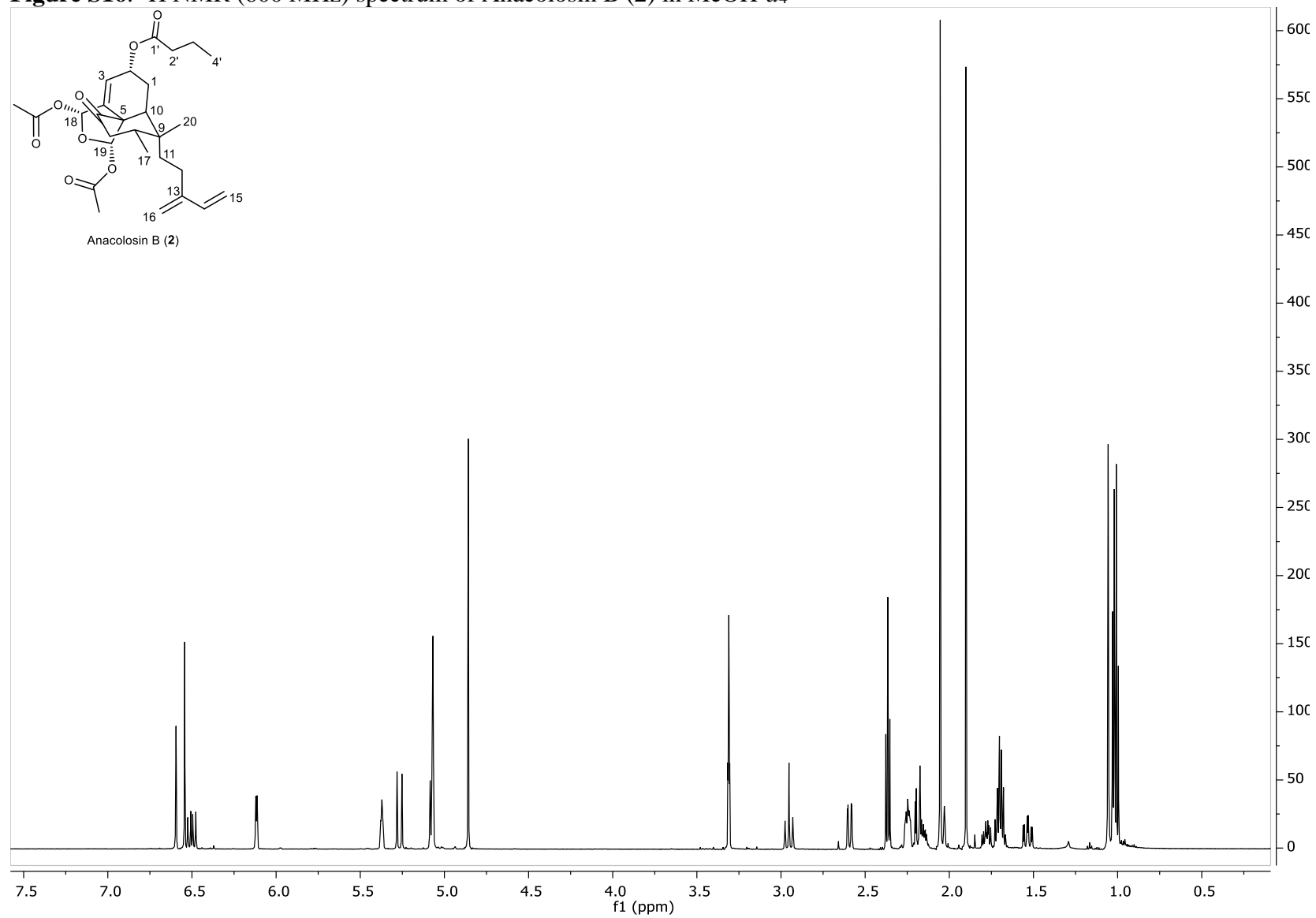
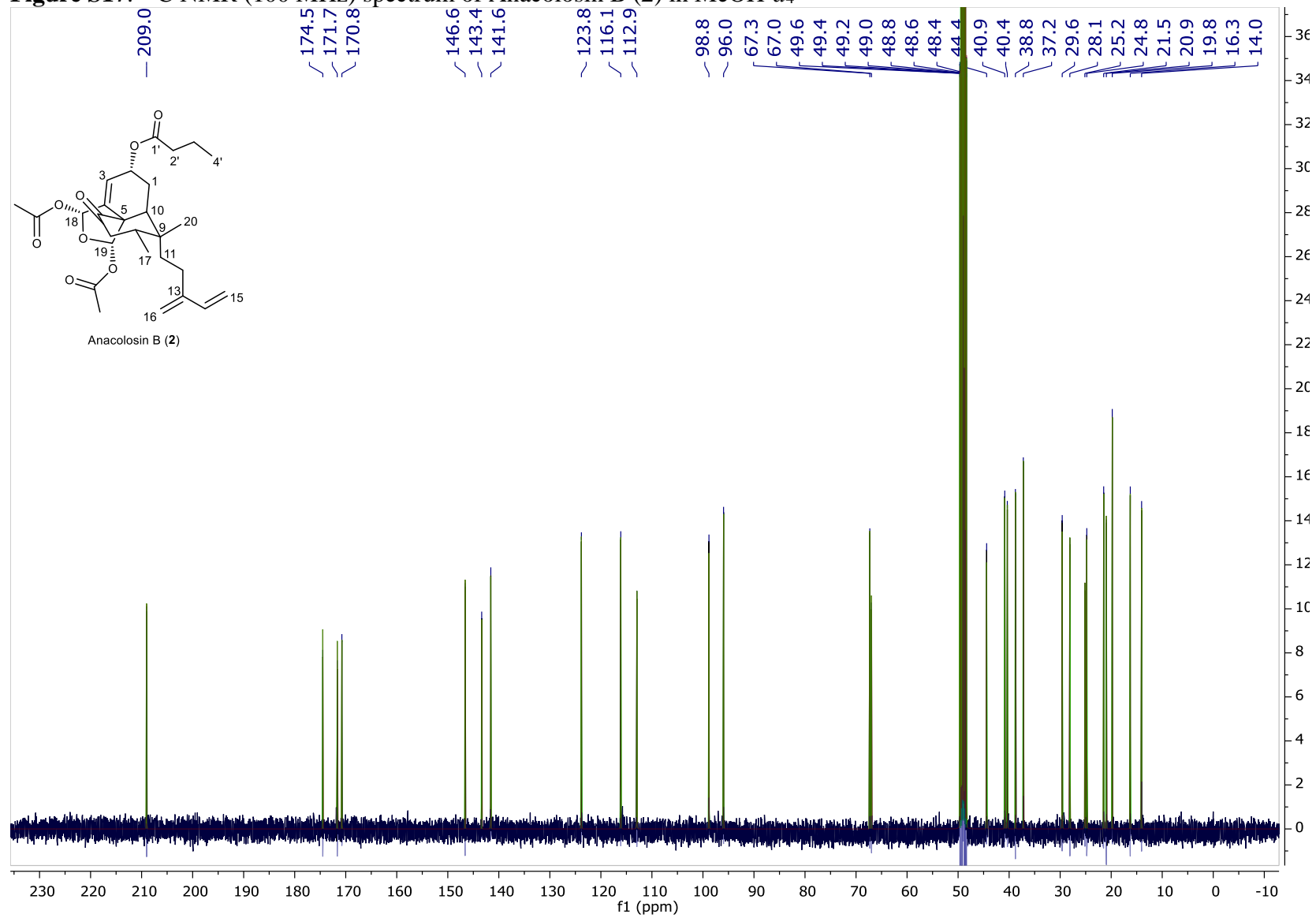
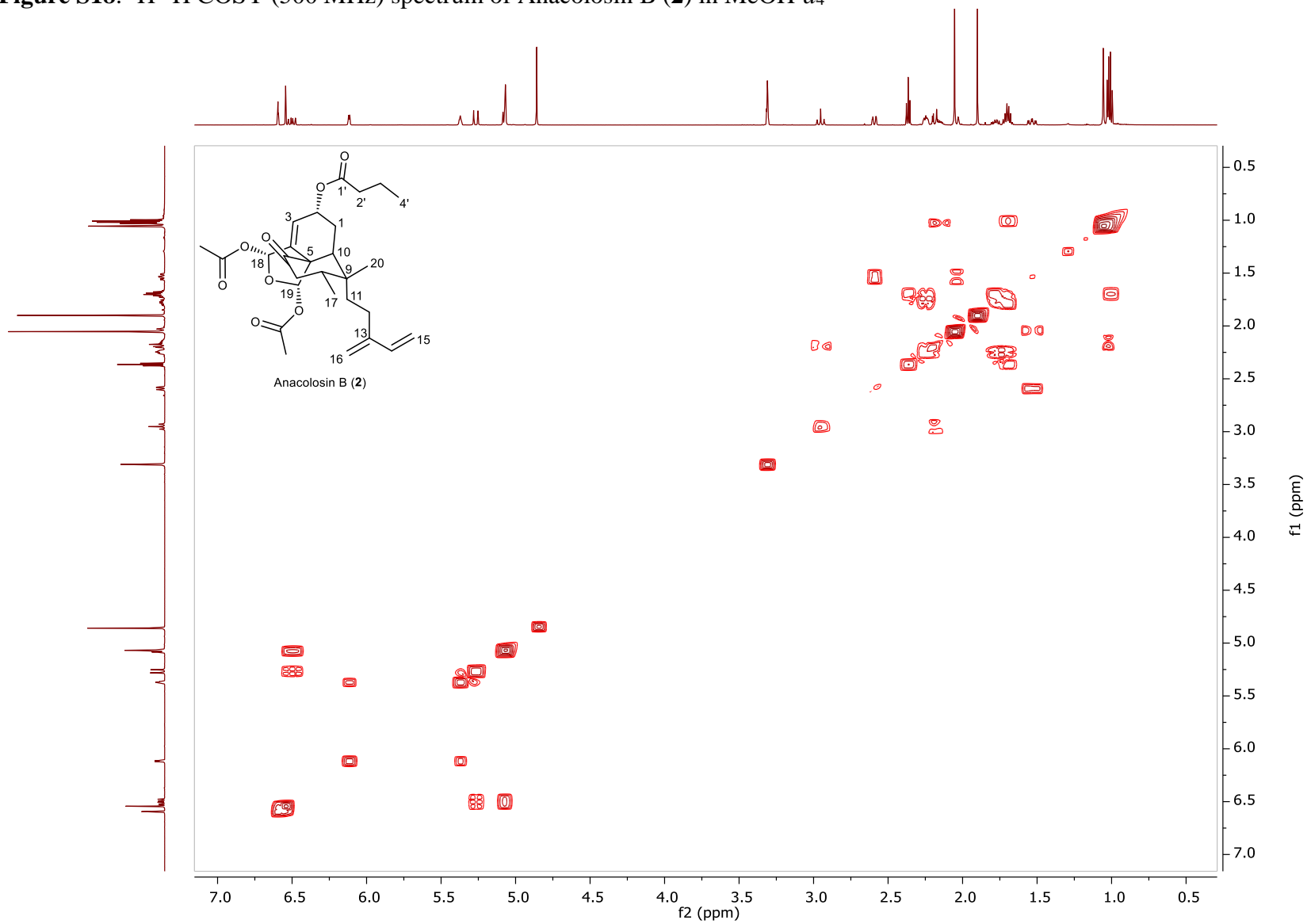


Figure S17.  $^{13}\text{C}$  NMR (100 MHz) spectrum of Anacolosin B (2) in  $\text{MeOH-}d_4$

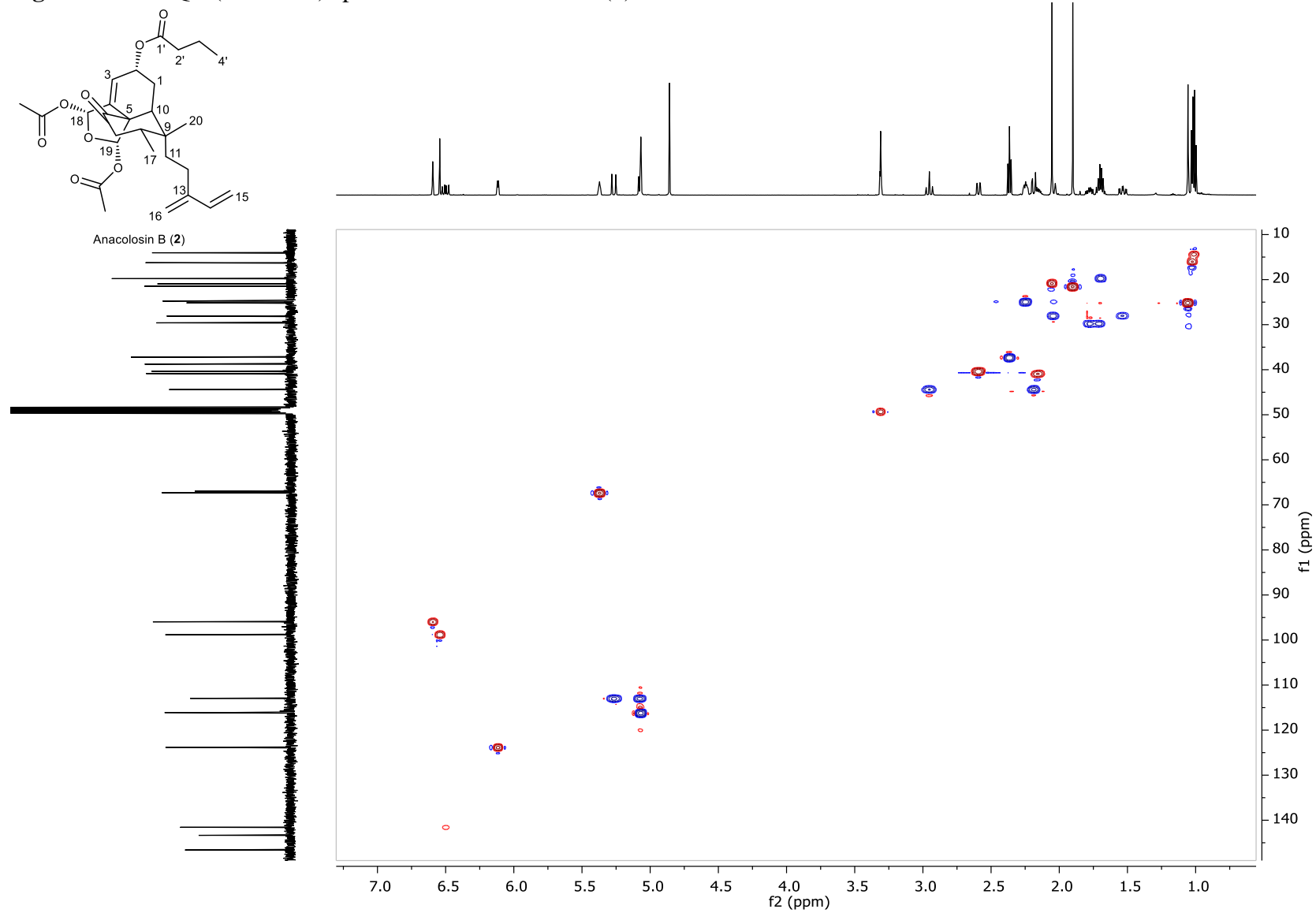




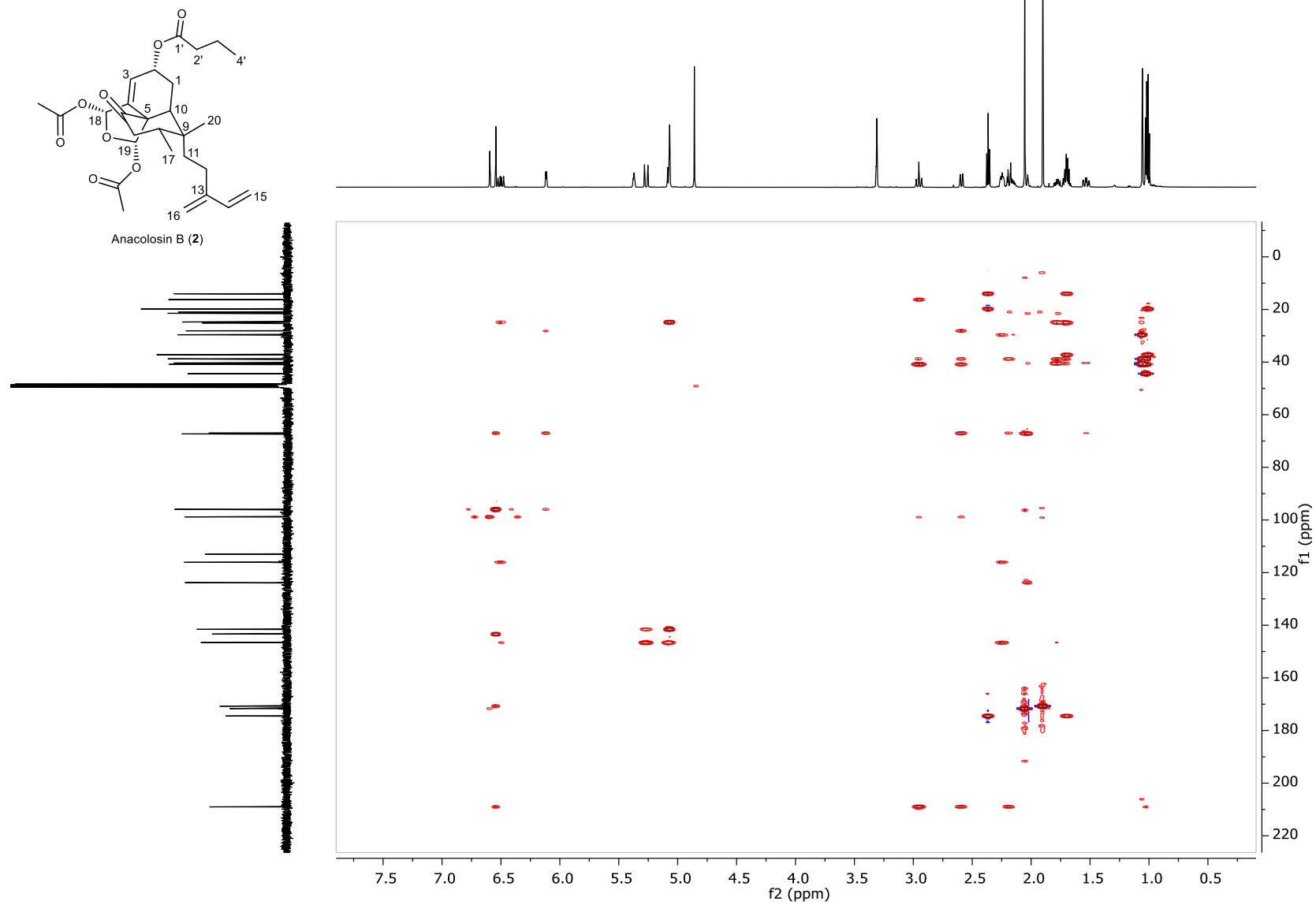
**Figure S18.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Anacolosin B (**2**) in  $\text{MeOH-}d_4$



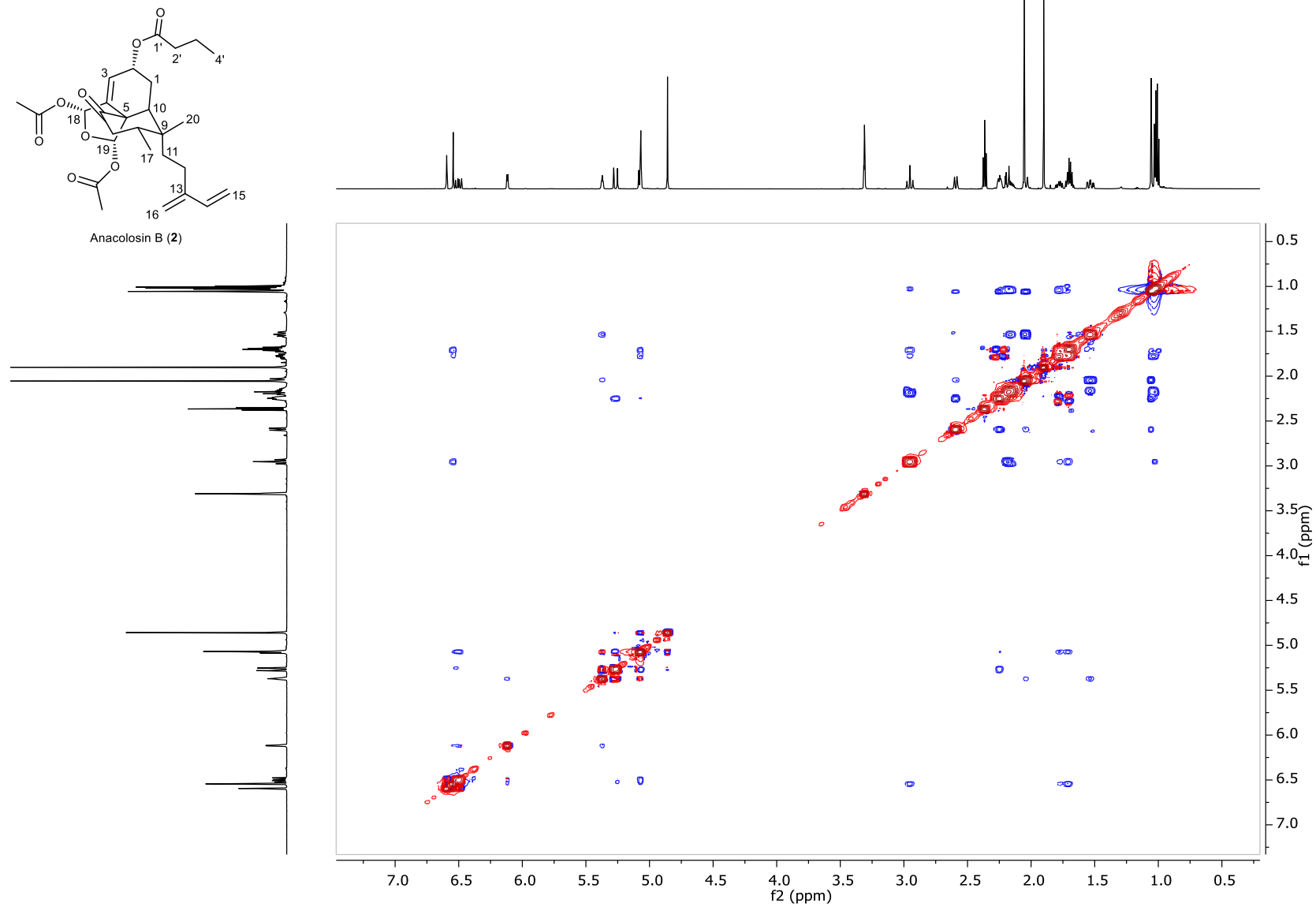
**Figure S19.** HSQC (500 MHz) spectrum of Anacolosin B (**2**) in MeOH-*d*<sub>4</sub>



**Figure S20.** HMBC (500 MHz) spectrum of Anacolosin B (**2**) in MeOH-*d*<sub>4</sub>

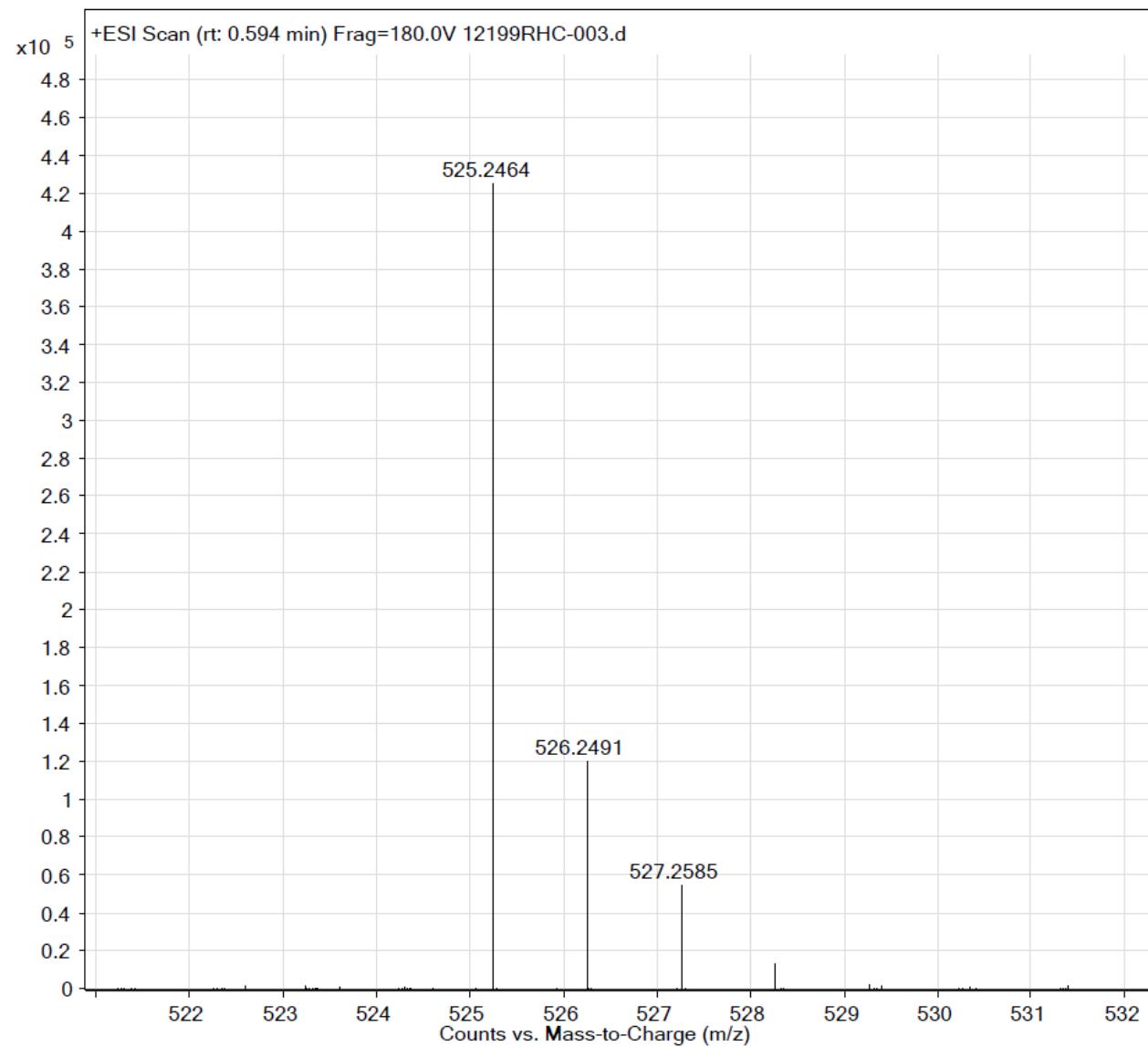


**Figure S21.** ROESY (500 MHz) spectrum of Anacolosin B (**2**) in MeOH-*d*<sub>4</sub>





**Figure S23.** HRESIMS spectrum of Anacolosin B (2)



**Figure S24.**  $^1\text{H}$  NMR (600 MHz) spectrum of Anacolosin C (**3**) in  $\text{MeOH-}d_4$

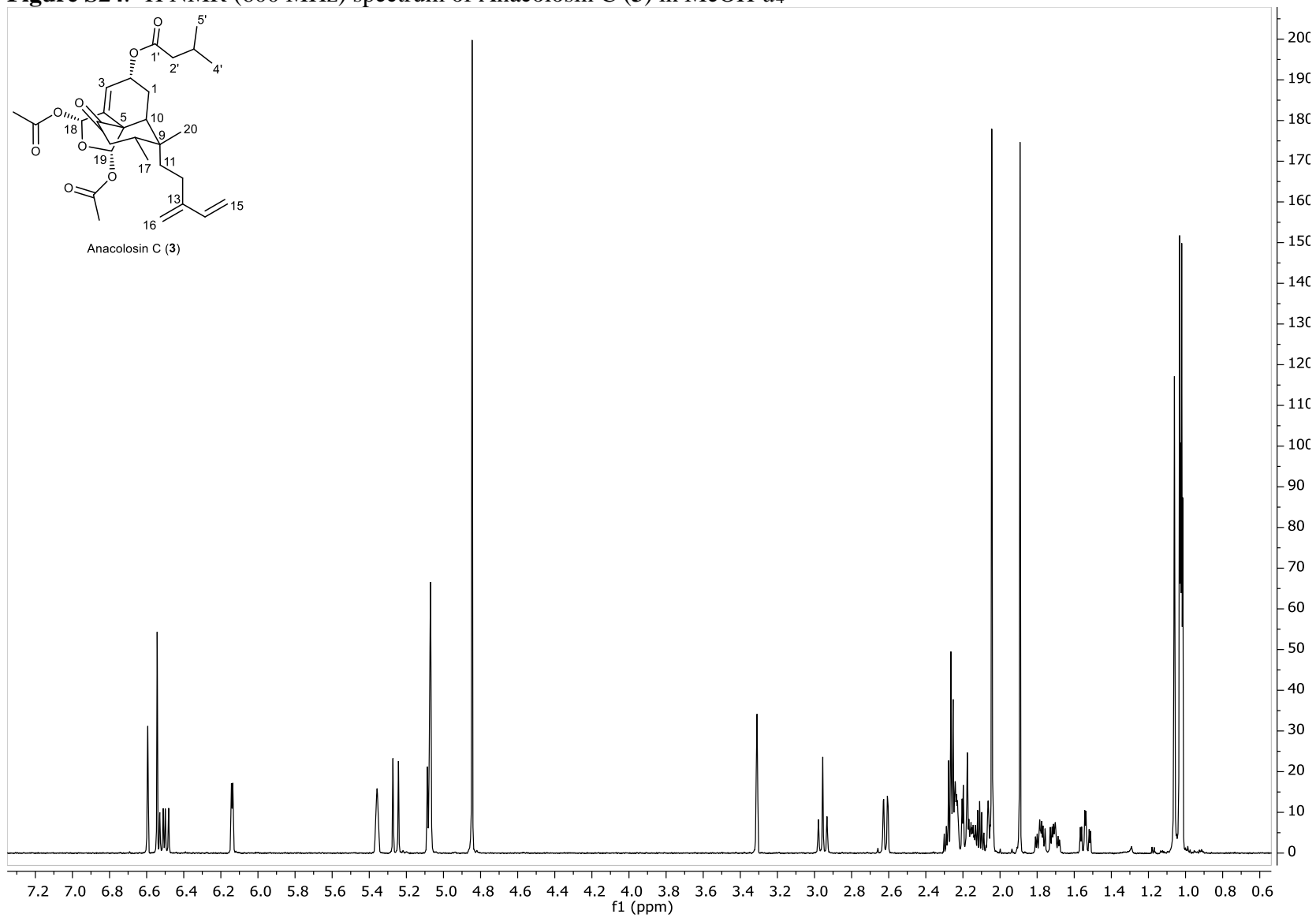


Figure S25.  $^{13}\text{C}$  NMR (150 MHz) spectrum of Anacolosin C (**3**) in  $\text{MeOH-}d_4$

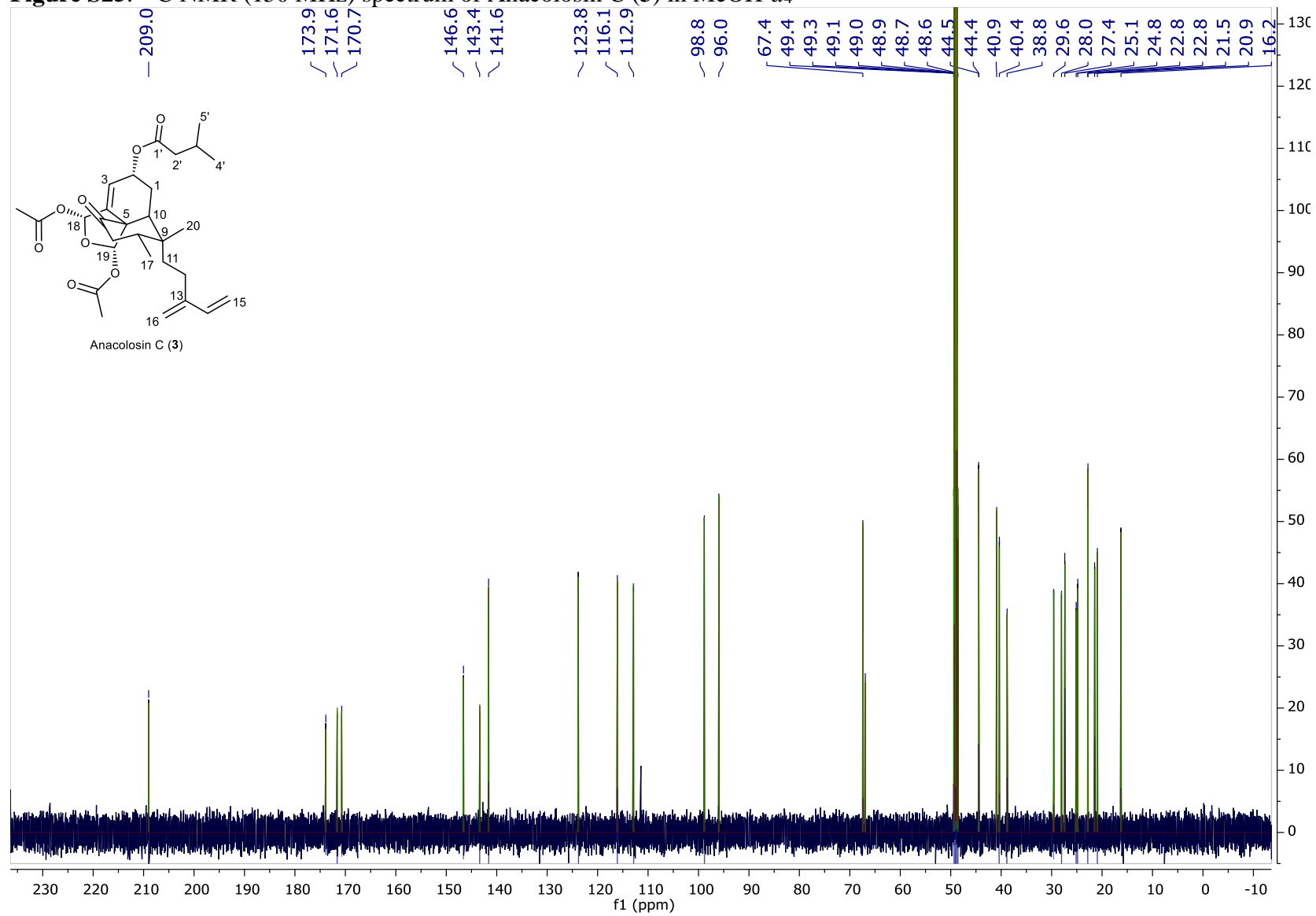
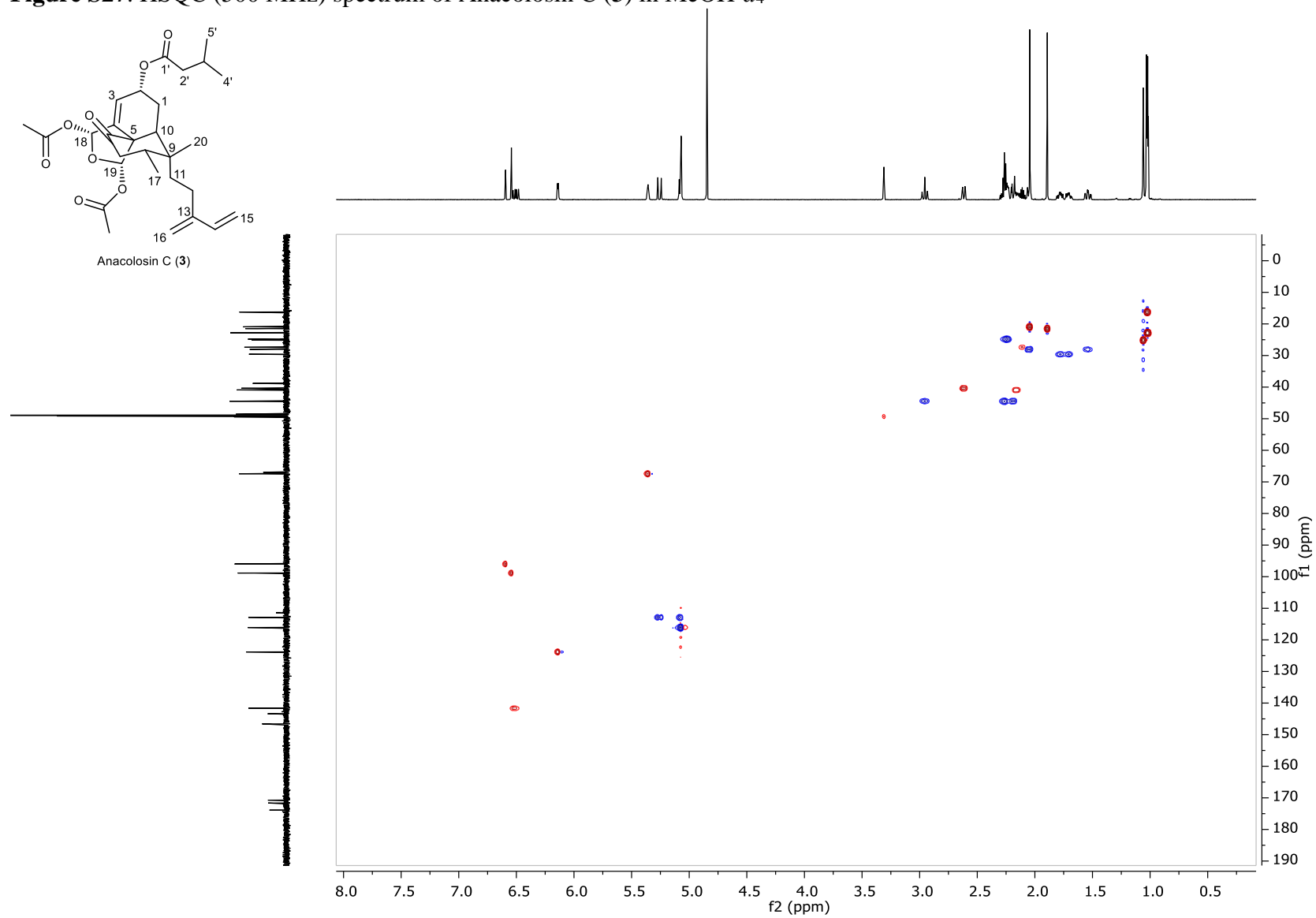


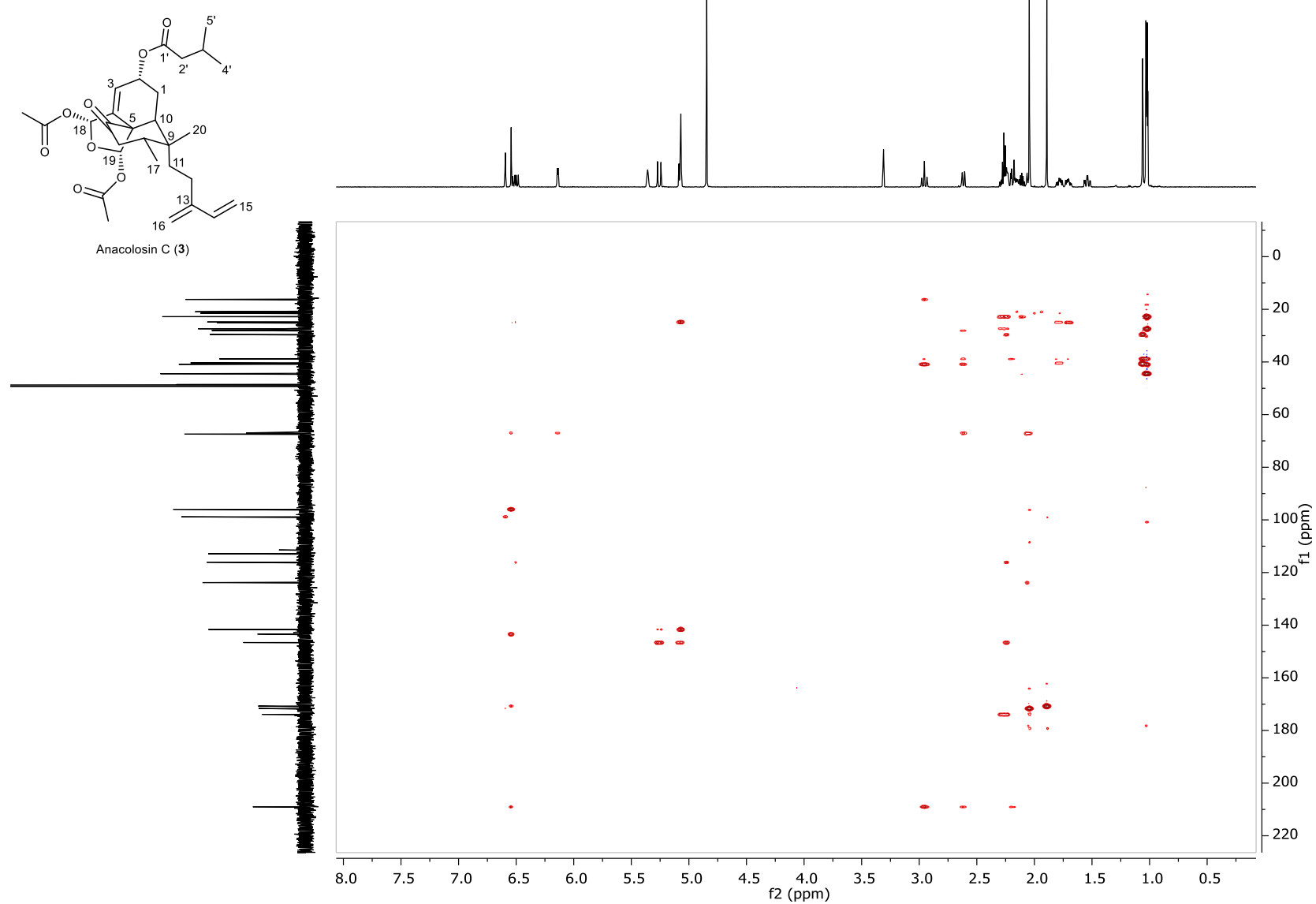




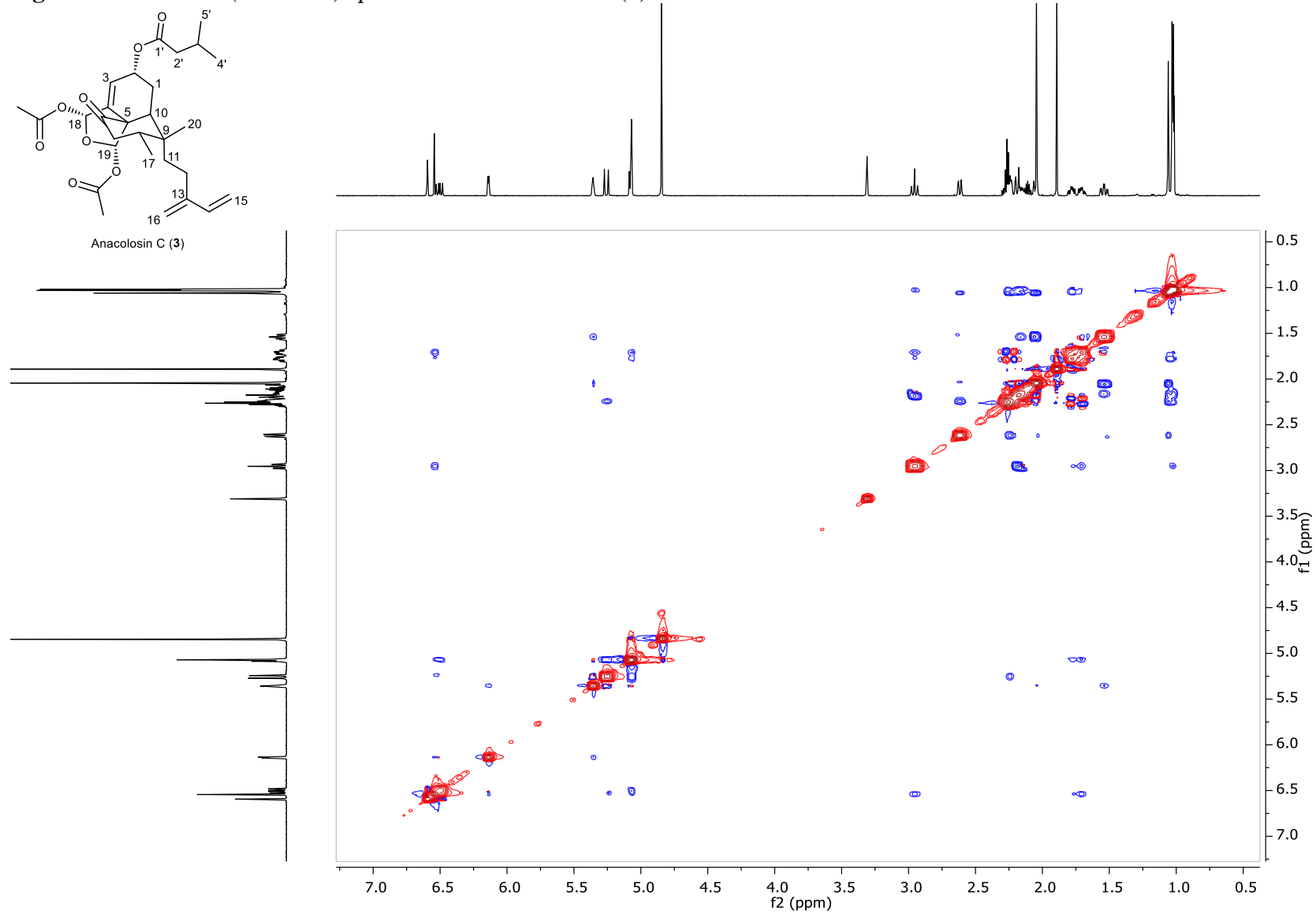
Figure S27. HSQC (500 MHz) spectrum of Anacolosin C (**3**) in MeOH-*d*<sub>4</sub>



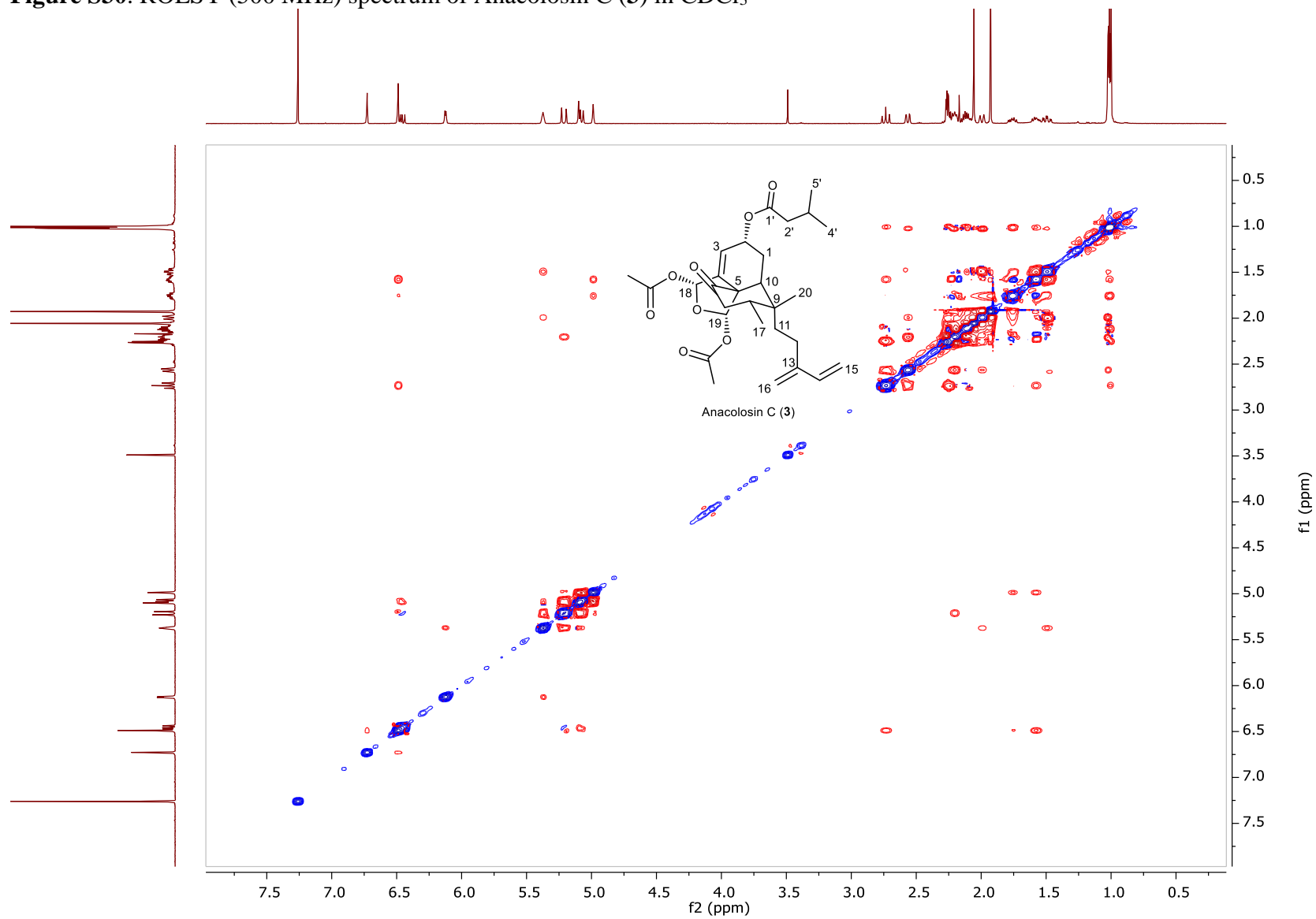
**Figure S28.** HMBC (500 MHz) spectrum of Anacolosin C (**3**) in MeOH-*d*<sub>4</sub>



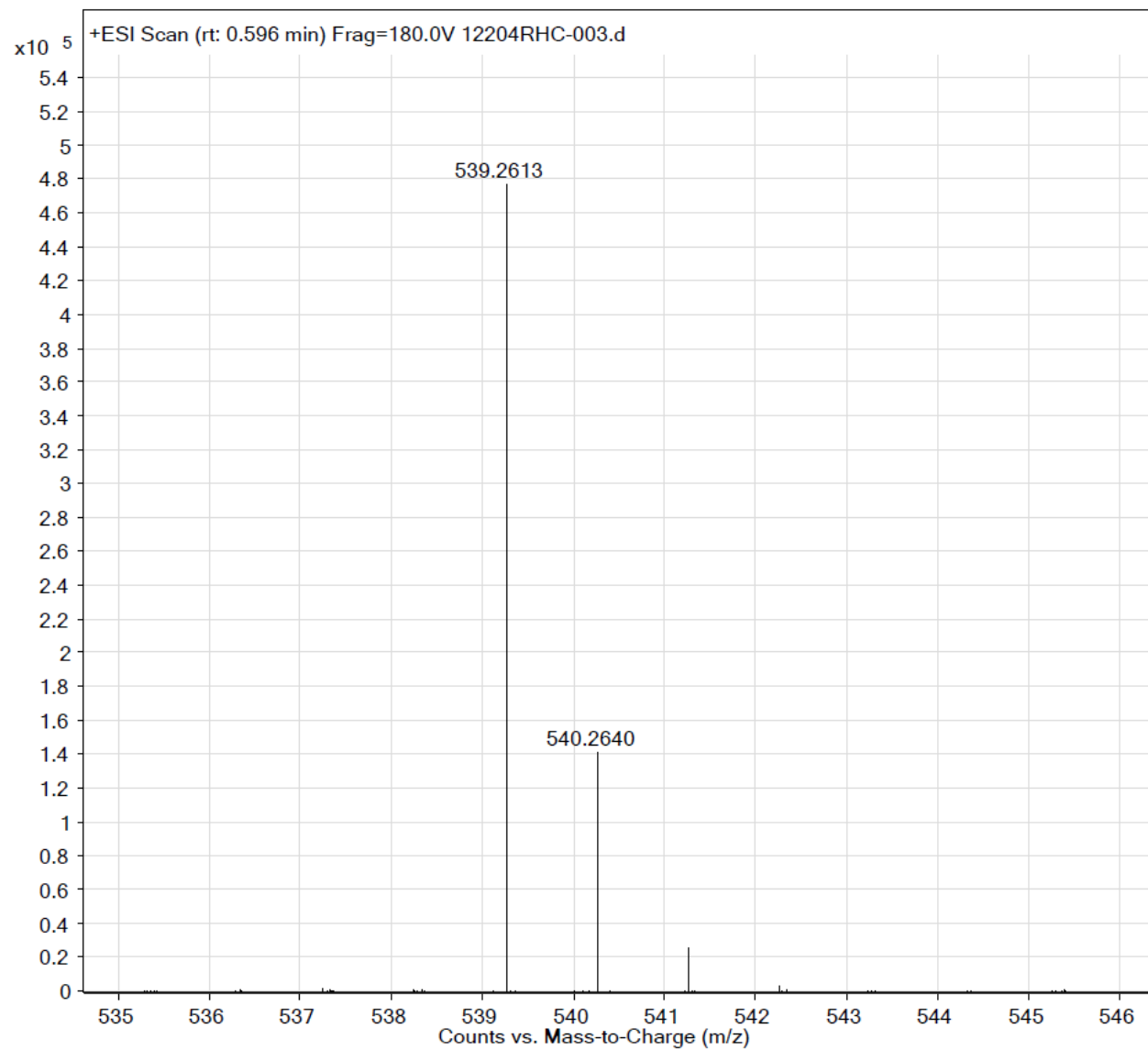
**Figure S29.** ROESY (500 MHz) spectrum of Anacolosin C (**3**) in MeOH-*d*<sub>4</sub>



**Figure S30.** ROESY (500 MHz) spectrum of Anacolosin C (**3**) in CDCl<sub>3</sub>



**Figure S31.** HRESIMS spectrum of Anacolosin C (**3**)



**Figure S32.**  $^1\text{H}$  NMR (600 MHz) spectrum of Anacolosin D (**4**) in  $\text{MeOH-}d_4$

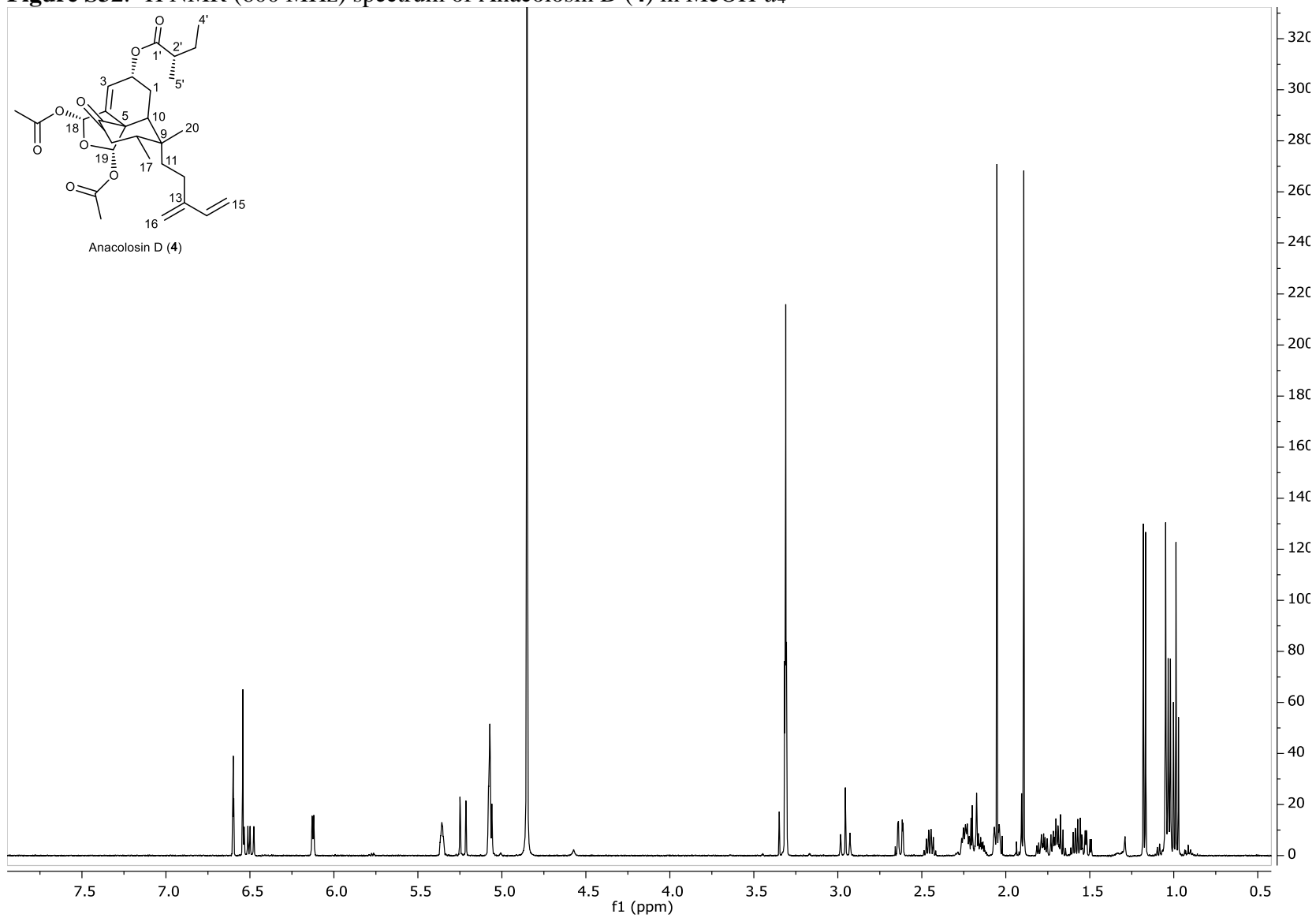
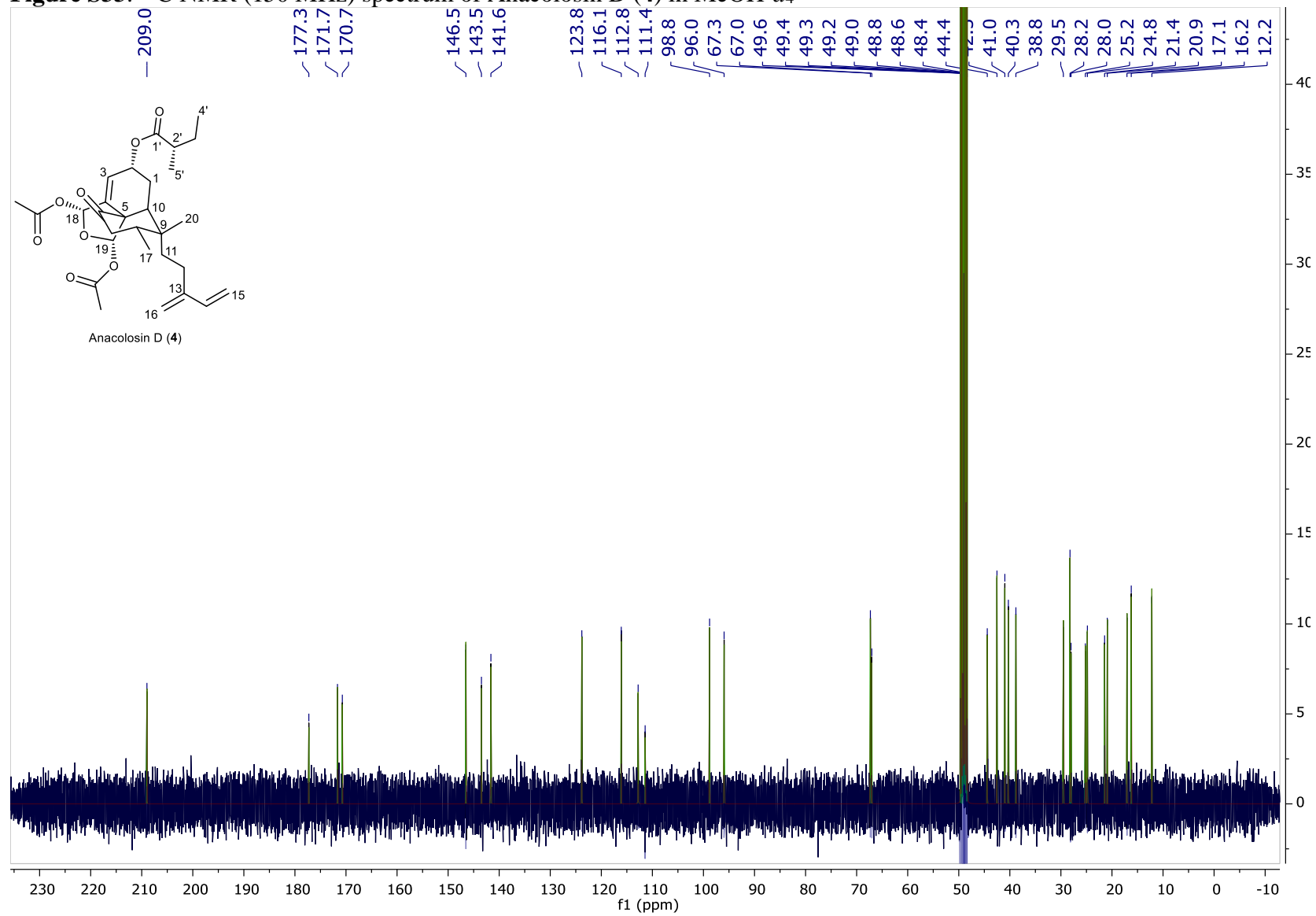
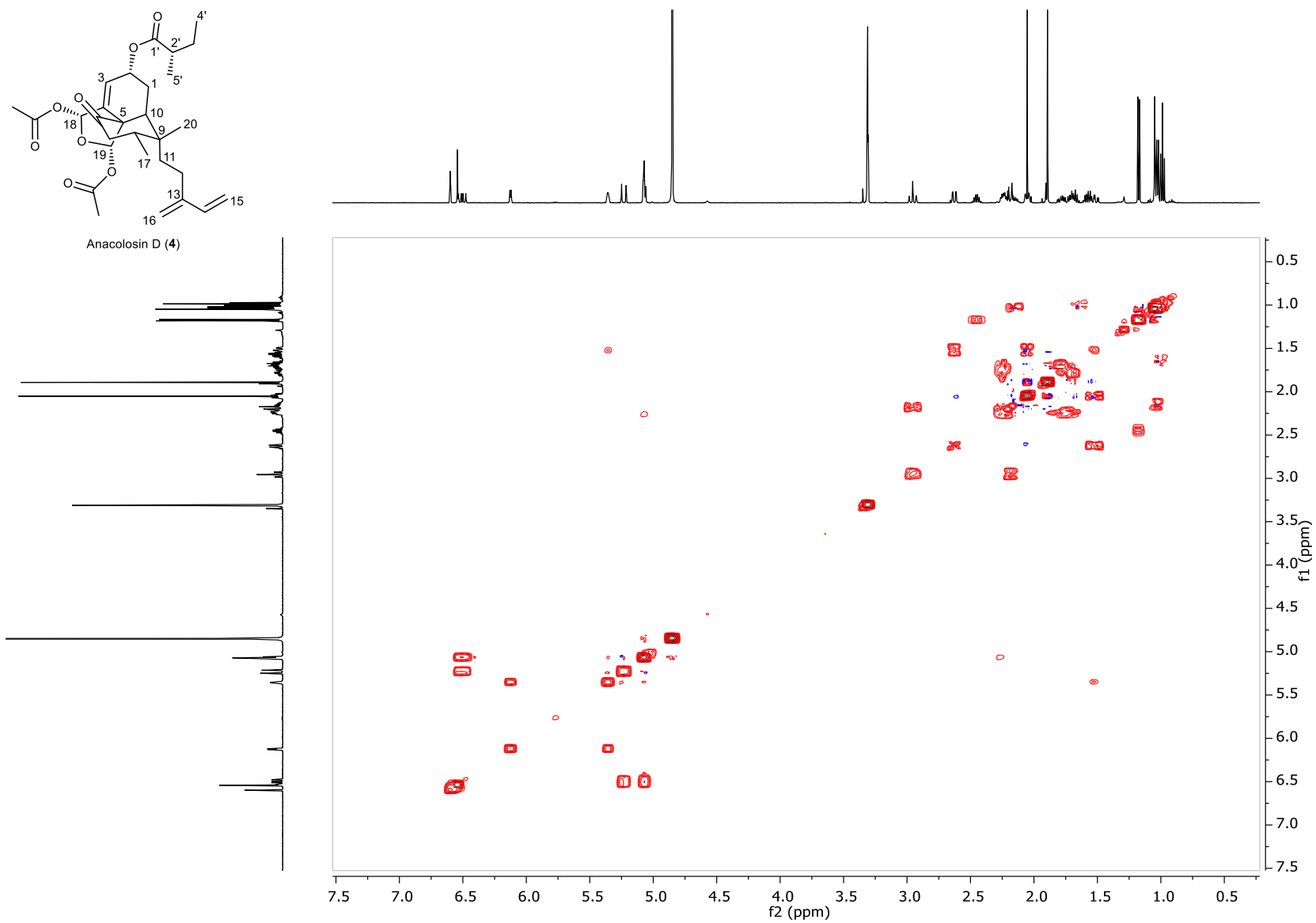


Figure S33.  $^{13}\text{C}$  NMR (150 MHz) spectrum of Anacolosin D (**4**) in  $\text{MeOH-}d_4$

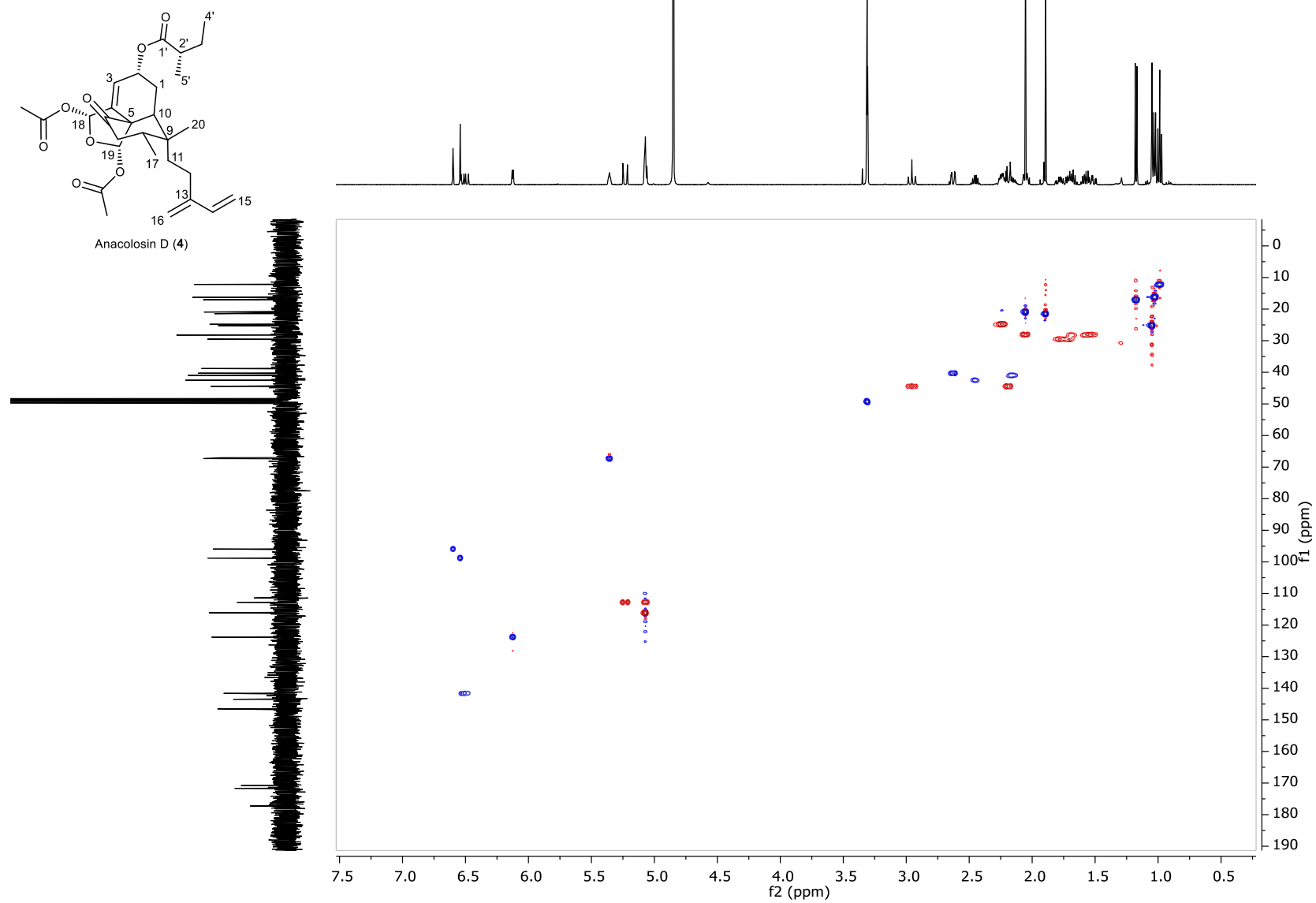




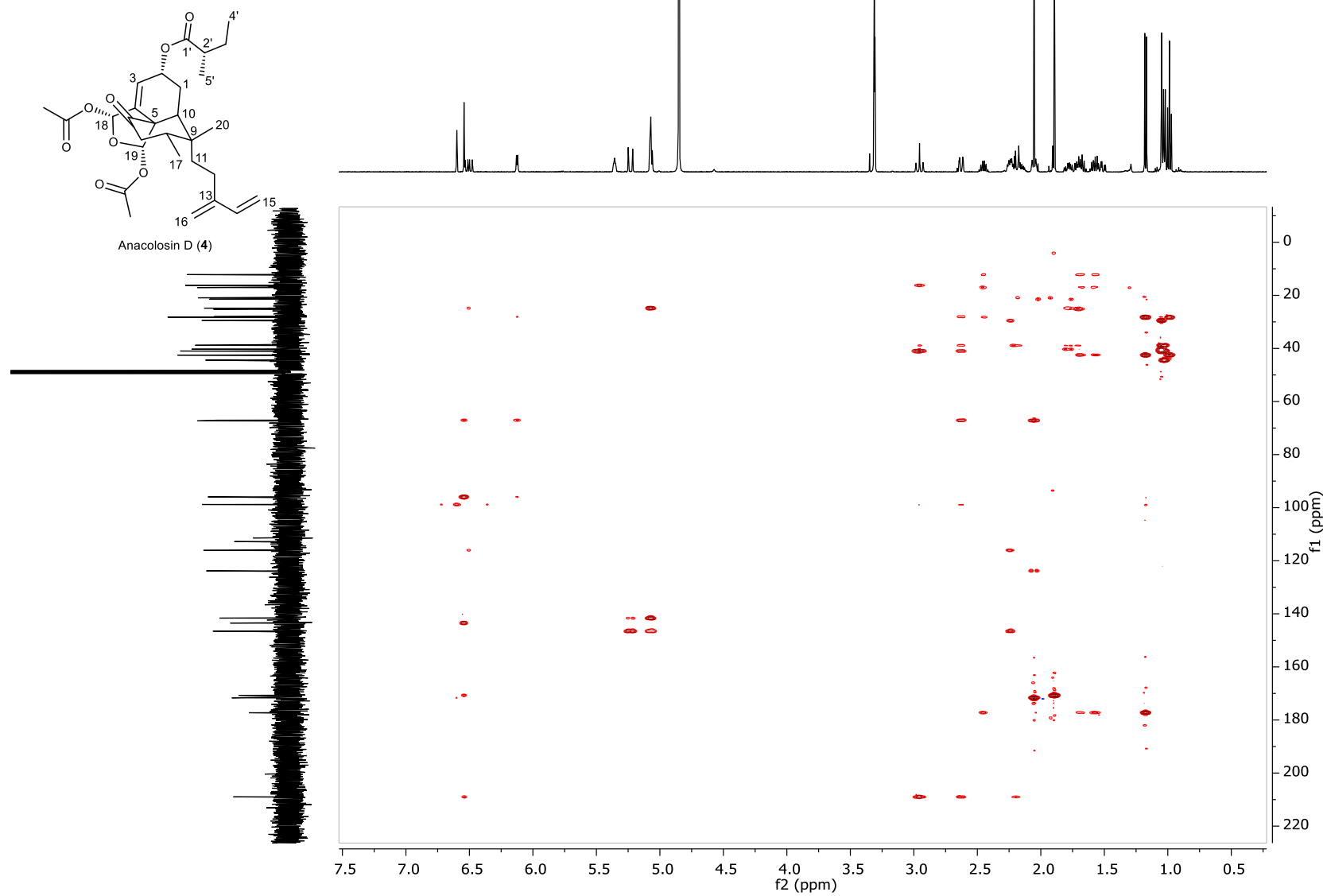
**Figure S34.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Anacolosin D (**4**) in  $\text{MeOH-}d_4$



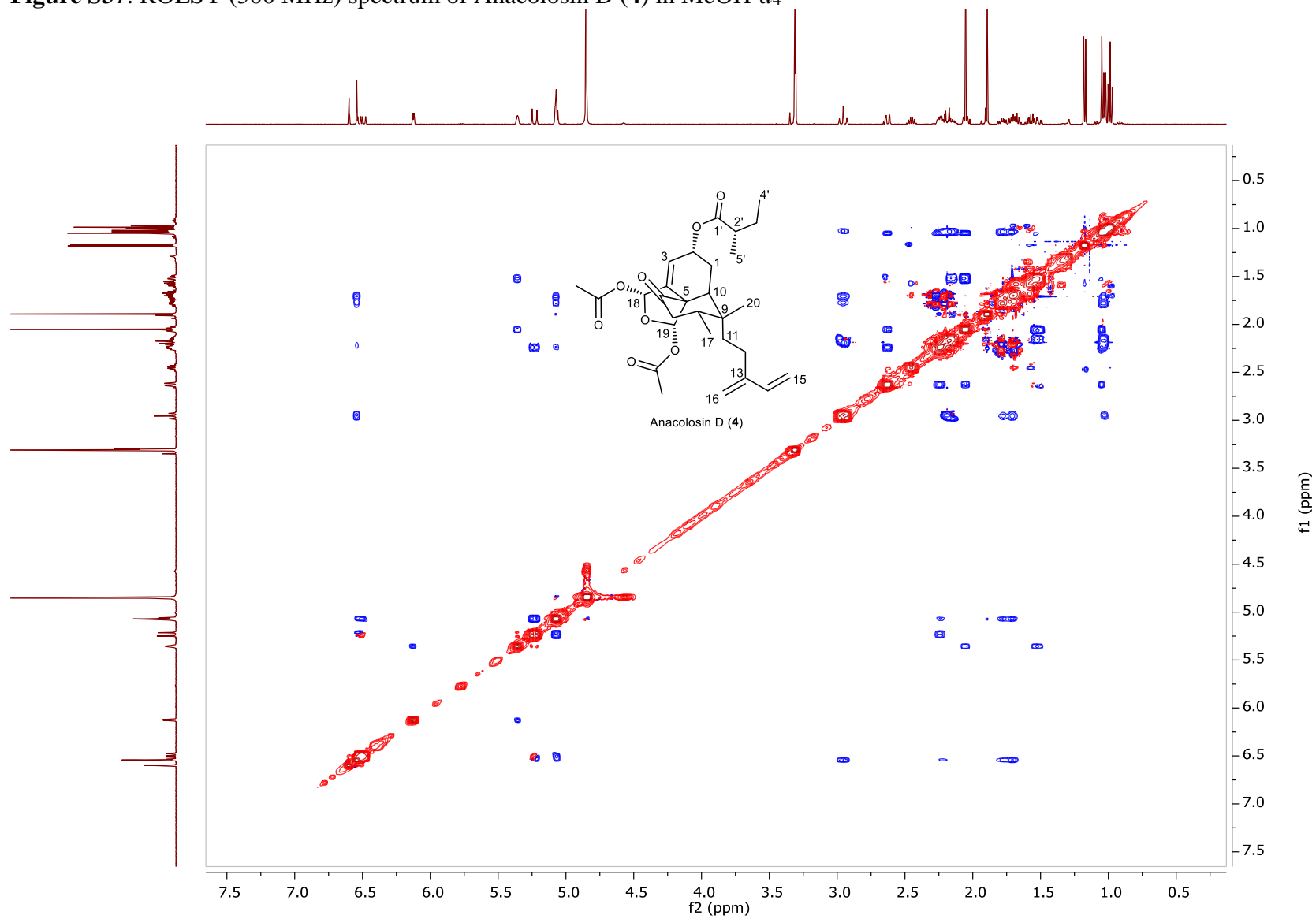
**Figure S35.** HSQC (500 MHz) spectrum of Anacolosin D (**4**) in MeOH-*d*<sub>4</sub>



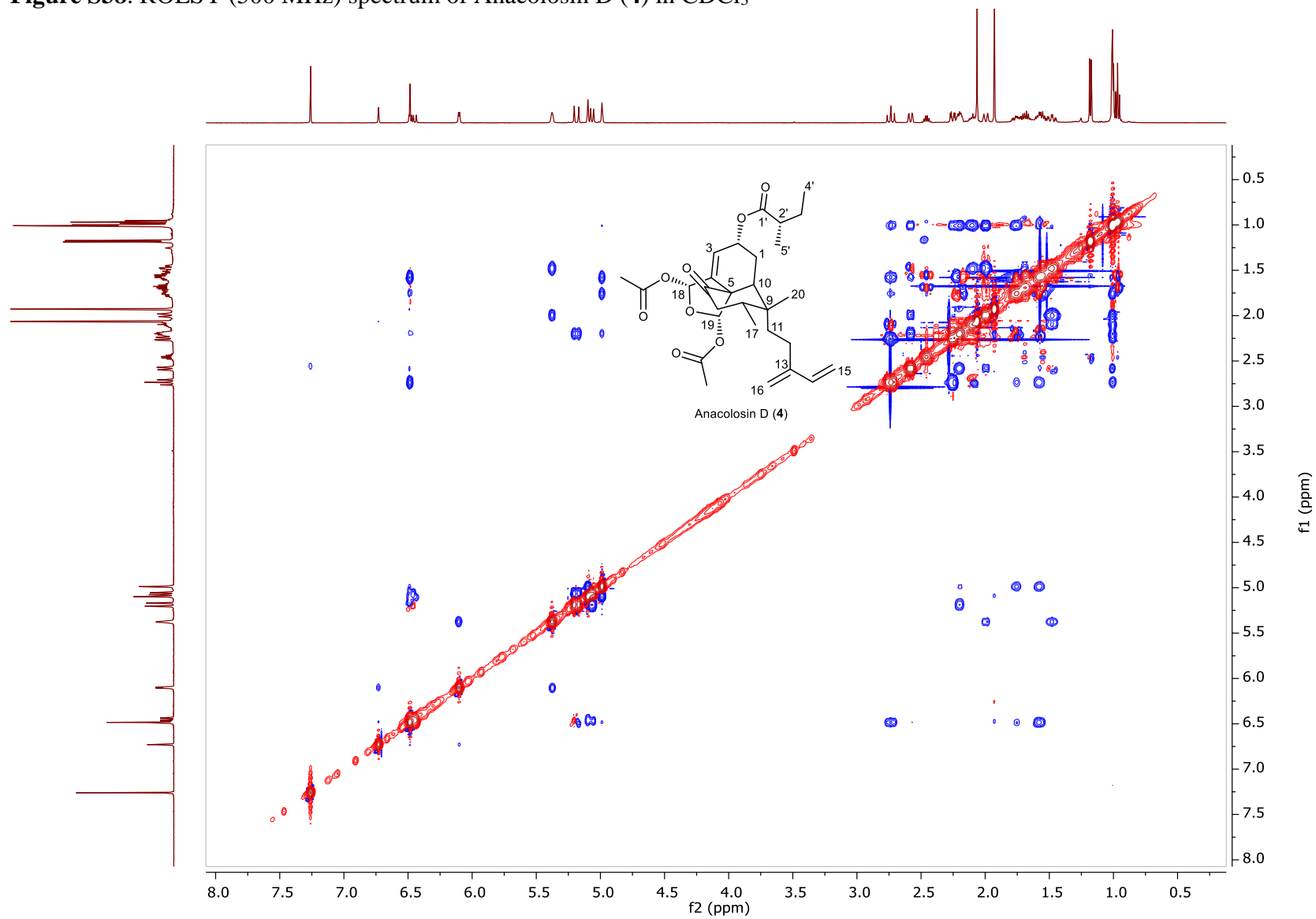
**Figure S36.** HMBC (500 MHz) spectrum of Anacolosin D (**4**) in MeOH-*d*<sub>4</sub>



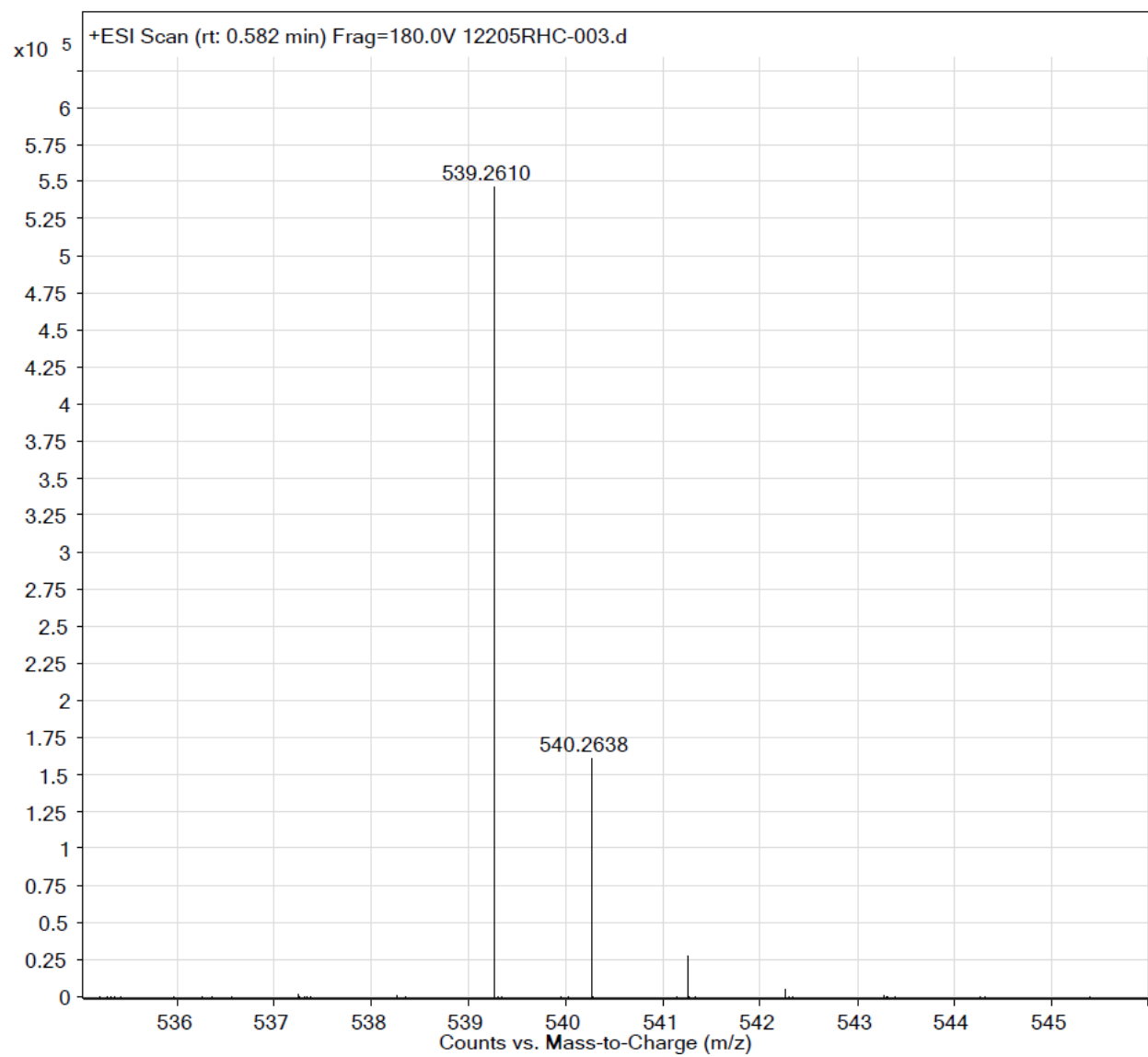
**Figure S37.** ROESY (500 MHz) spectrum of Anacolosin D (**4**) in MeOH-*d*<sub>4</sub>



**Figure S38.** ROESY (500 MHz) spectrum of Anacolosin D (**4**) in CDCl<sub>3</sub>



**Figure S39.** HRESIMS spectrum of Anacolosin D (4)



**Figure S40.**  $^1\text{H}$  NMR (500 MHz) spectrum of Anacolosin E (**5**) in  $\text{MeOH-}d_4$

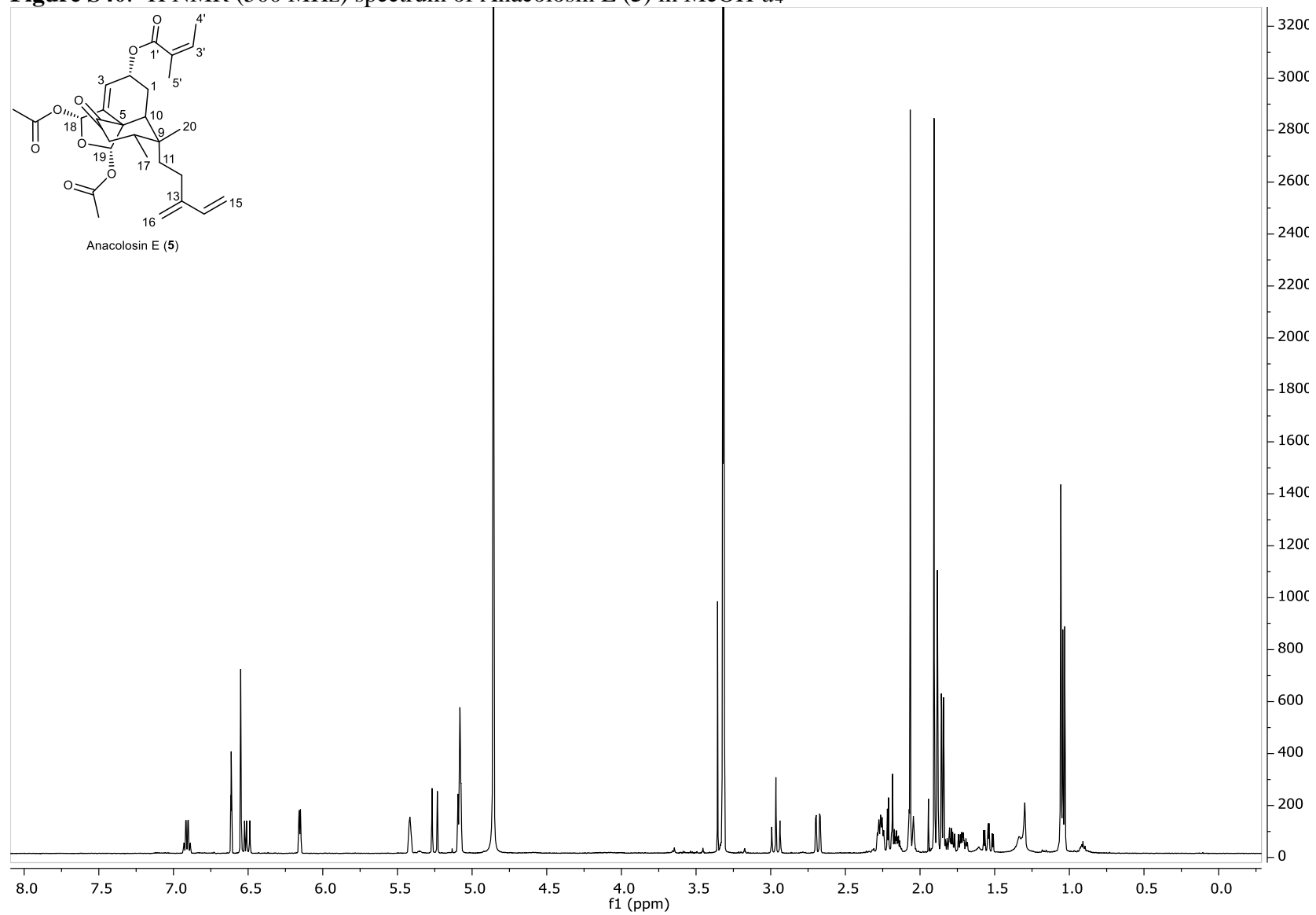
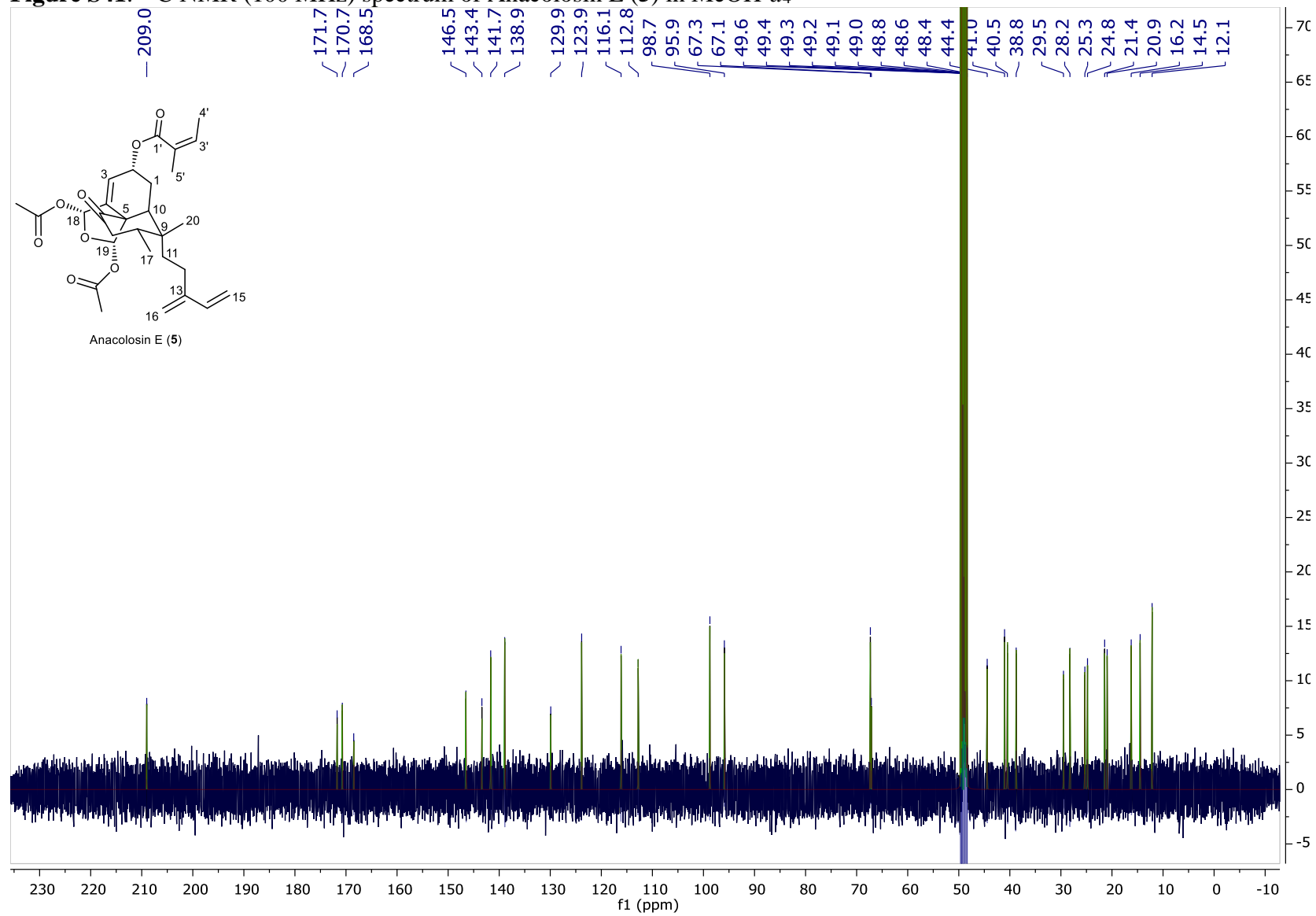
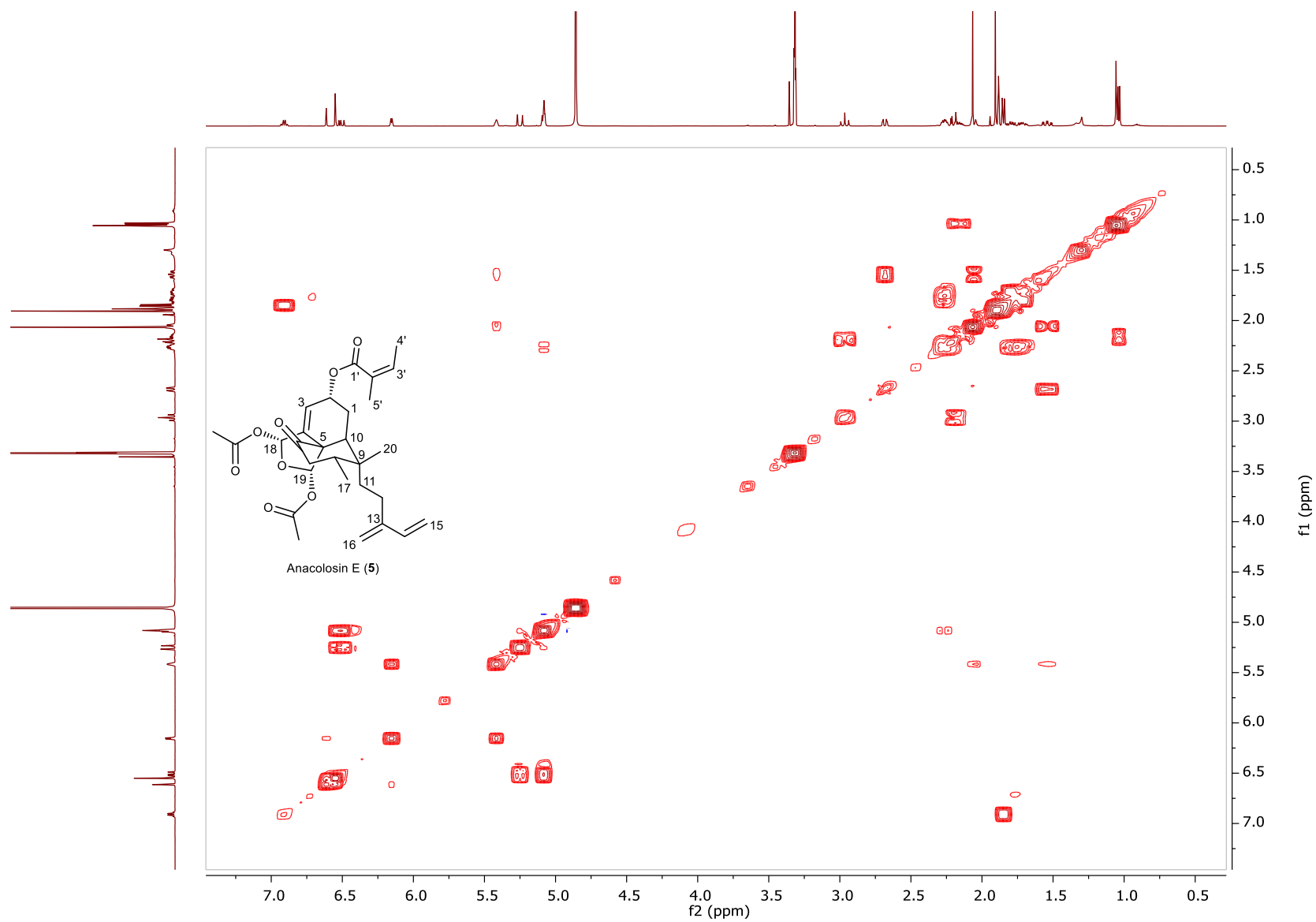


Figure S41.  $^{13}\text{C}$  NMR (100 MHz) spectrum of Anacolosin E (5) in  $\text{MeOH-}d_4$

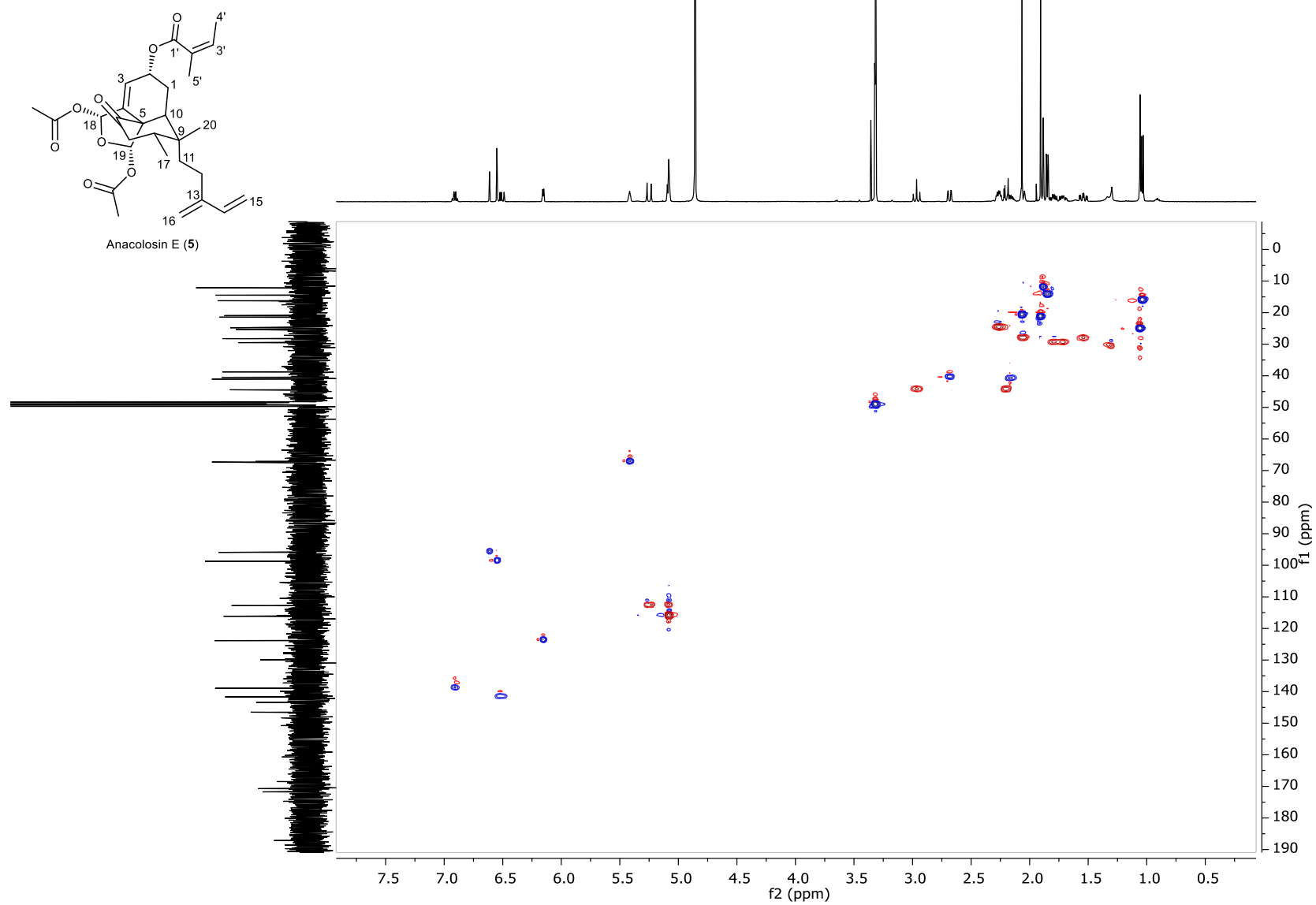




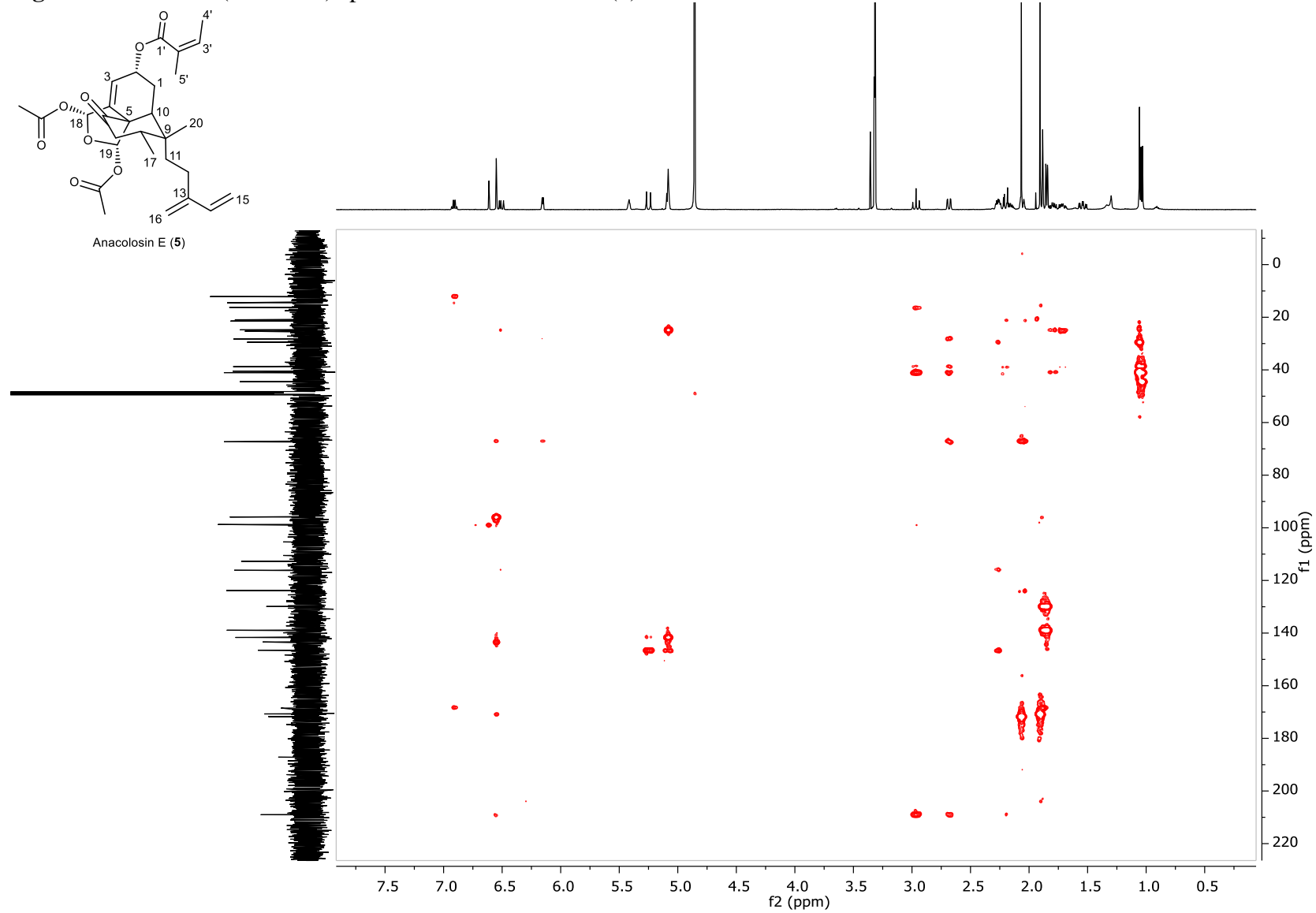
**Figure S42.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Anacolosin E (**5**) in  $\text{MeOH-}d_4$



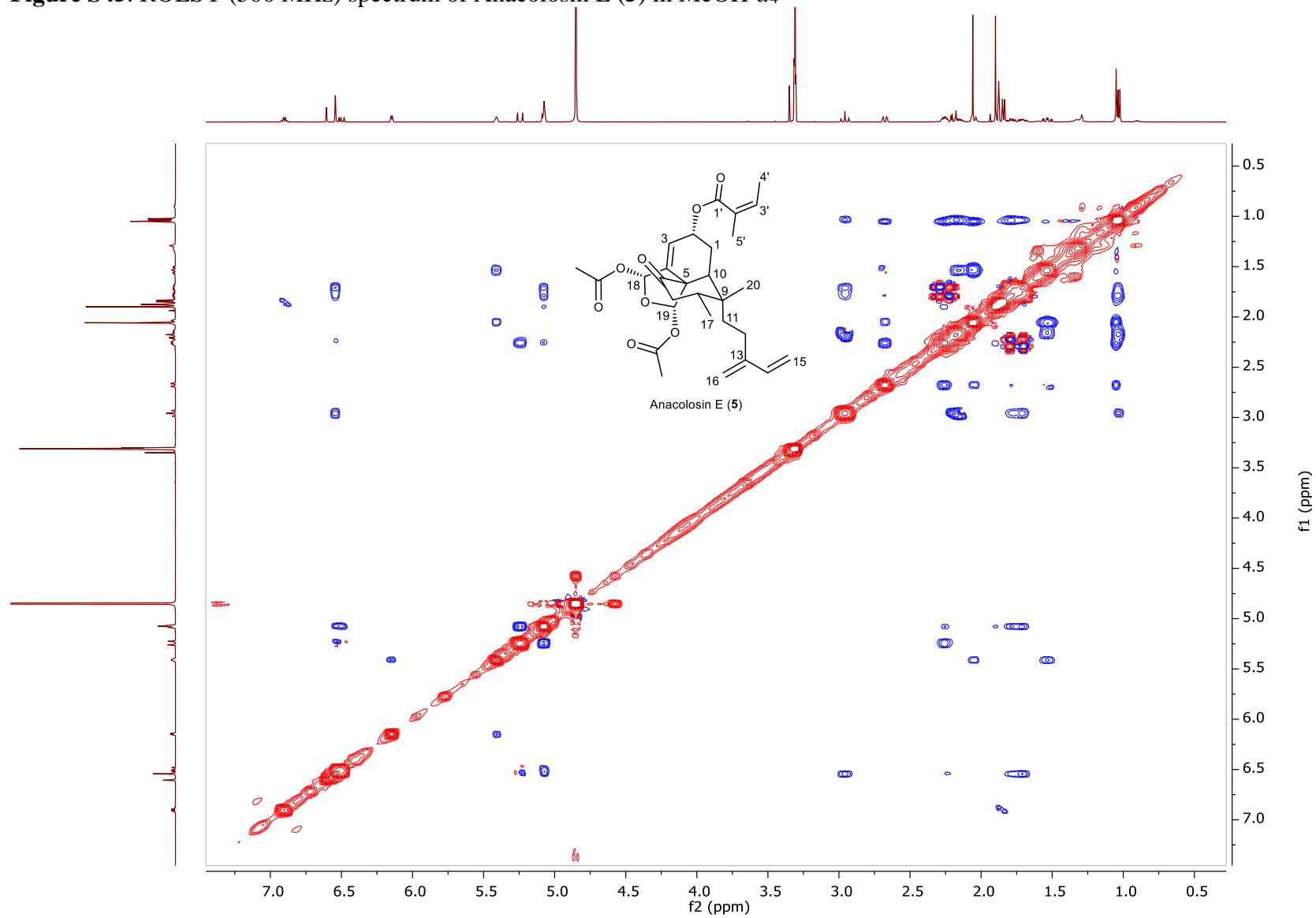
**Figure S43.** HSQC (500 MHz) spectrum of Anacolosin E (**5**) in MeOH-*d*<sub>4</sub>



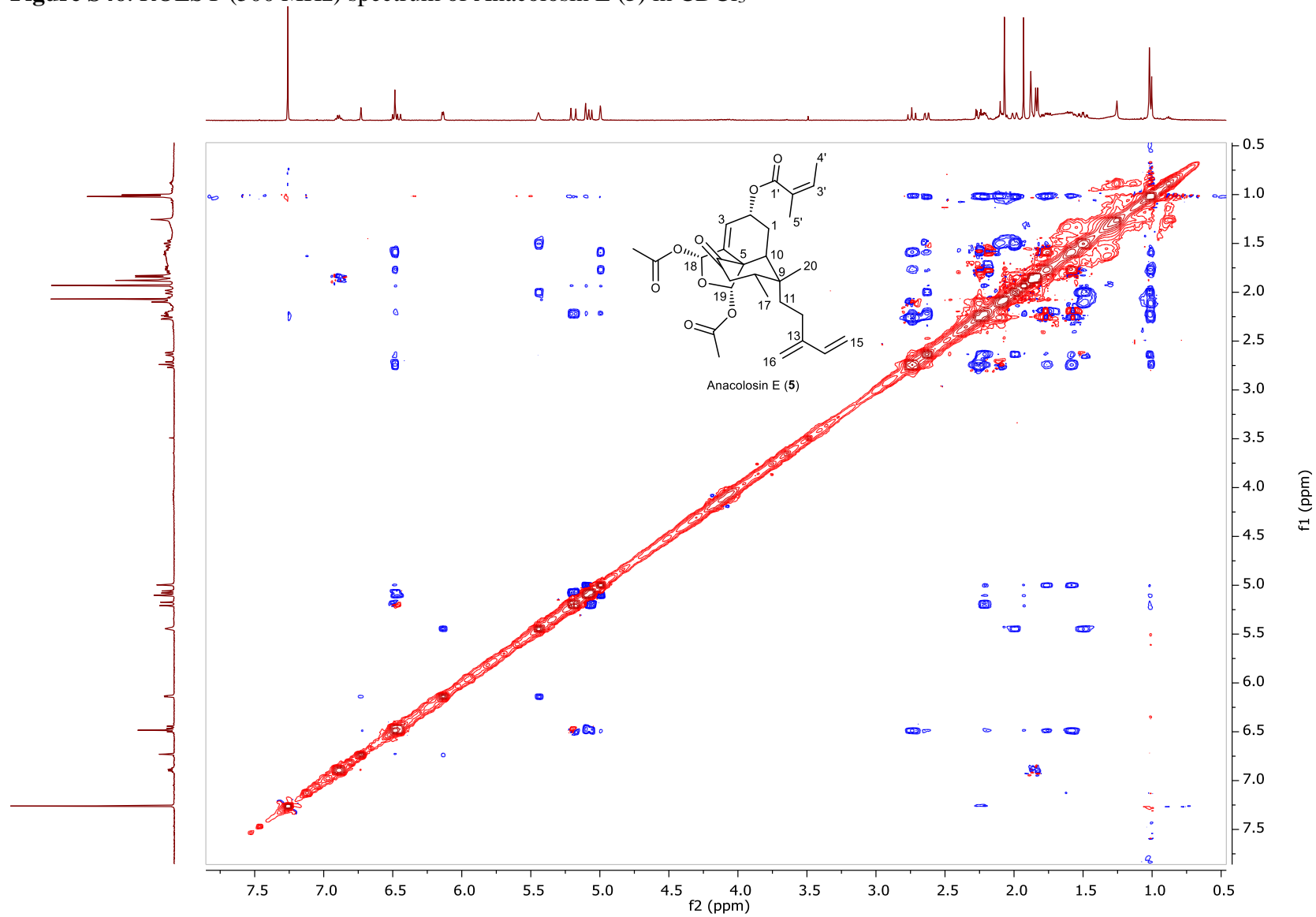
**Figure S44.** HMBC (500 MHz) spectrum of Anacolosin E (**5**) in MeOH-*d*<sub>4</sub>



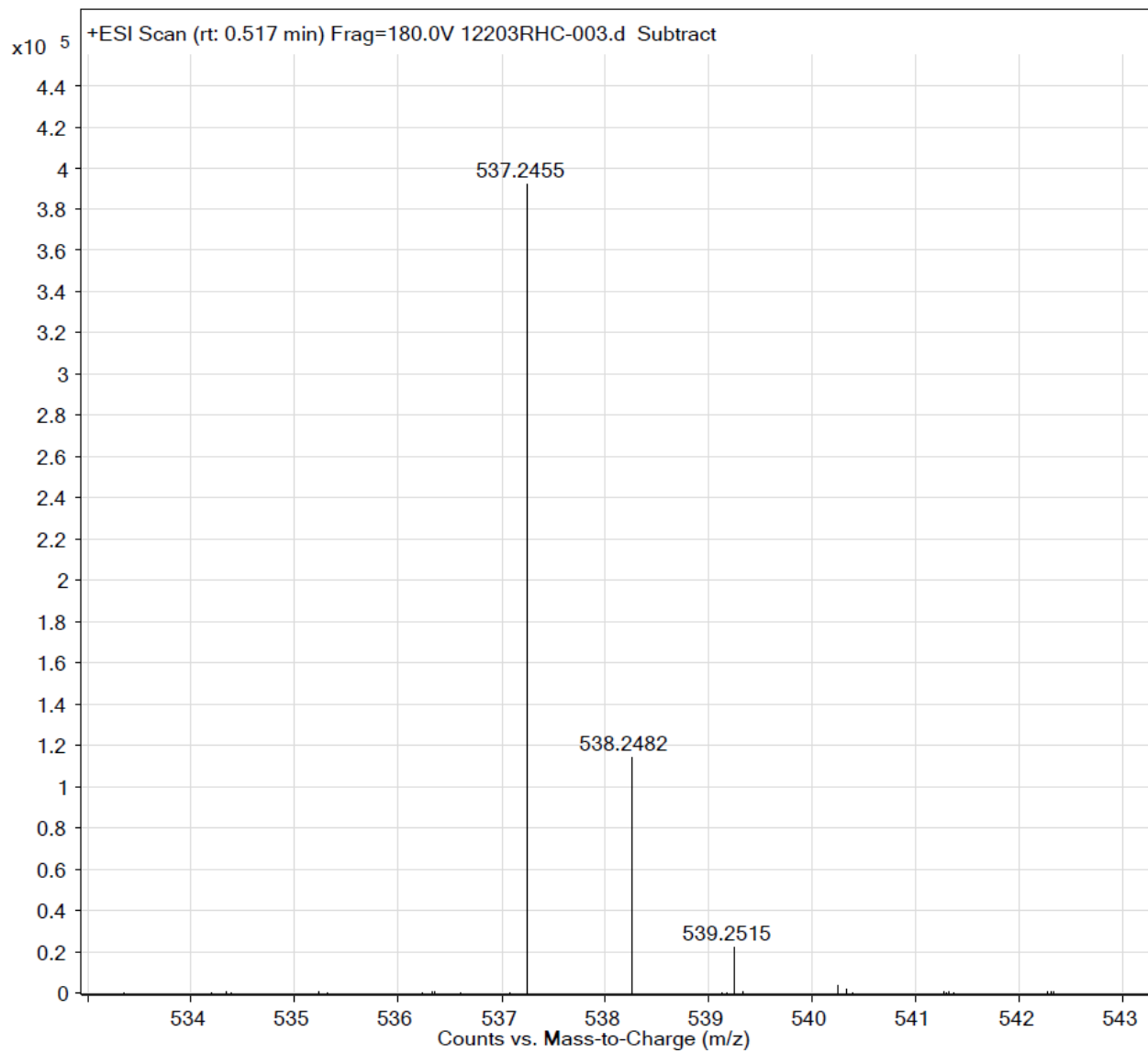
**Figure S45.** ROESY (500 MHz) spectrum of Anacolosin E (**5**) in MeOH-*d*<sub>4</sub>



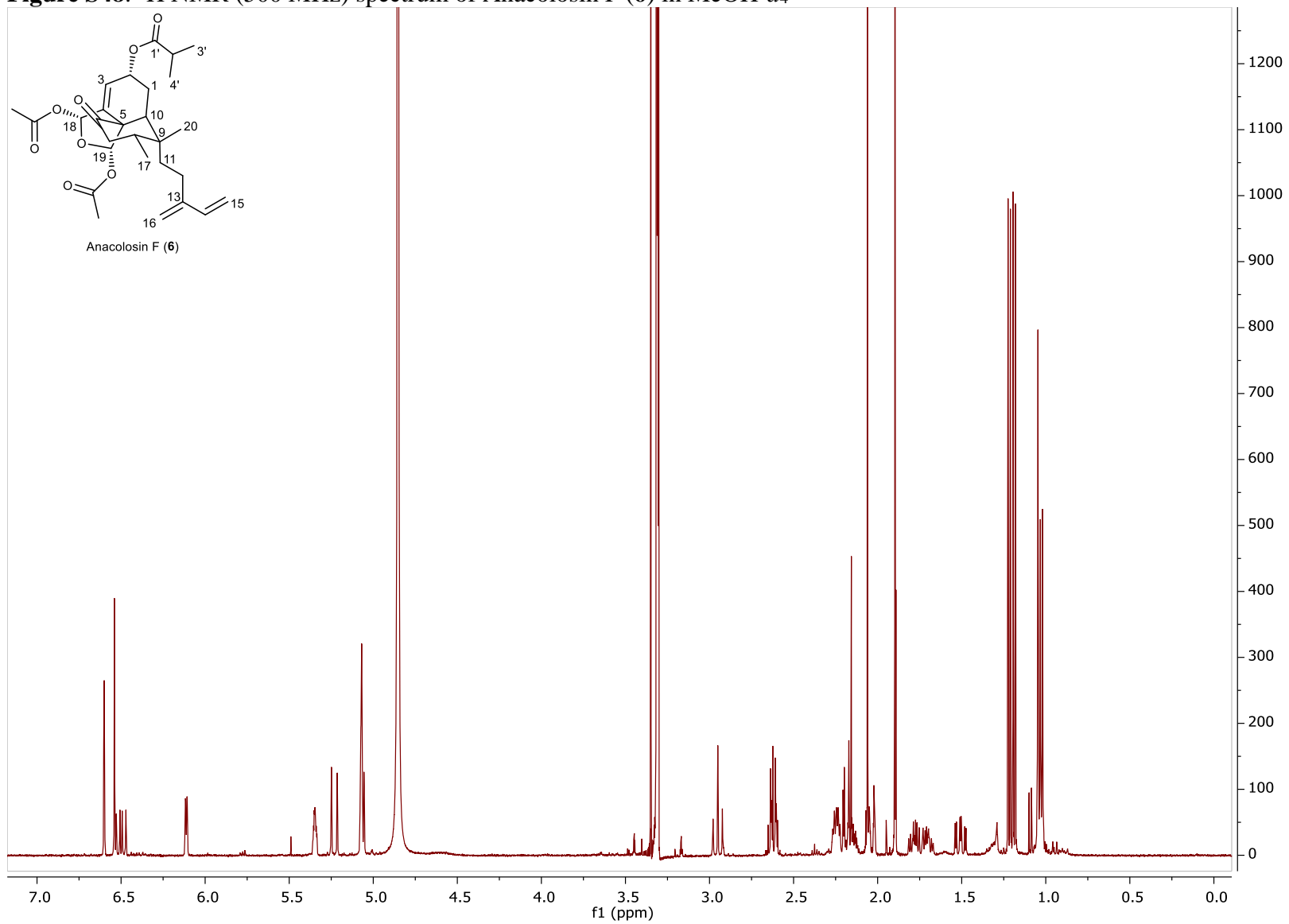
**Figure S46.** ROESY (500 MHz) spectrum of Anacolosin E (**5**) in CDCl<sub>3</sub>



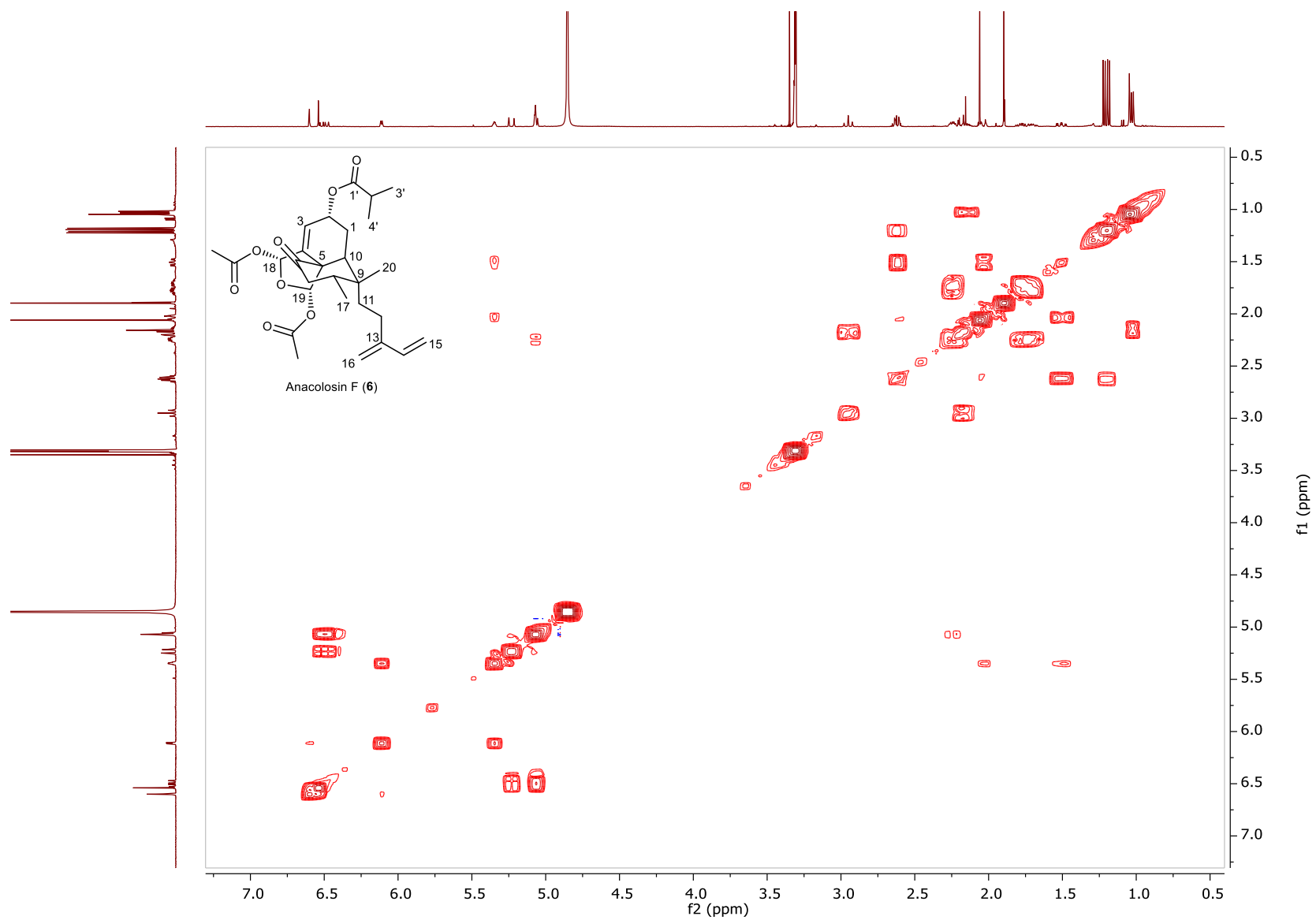
**Figure S47.** HRESIMS spectrum of Anacolosin E (**5**)



**Figure S48.**  $^1\text{H}$  NMR (500 MHz) spectrum of Anacolosin F (**6**) in  $\text{MeOH-}d_4$

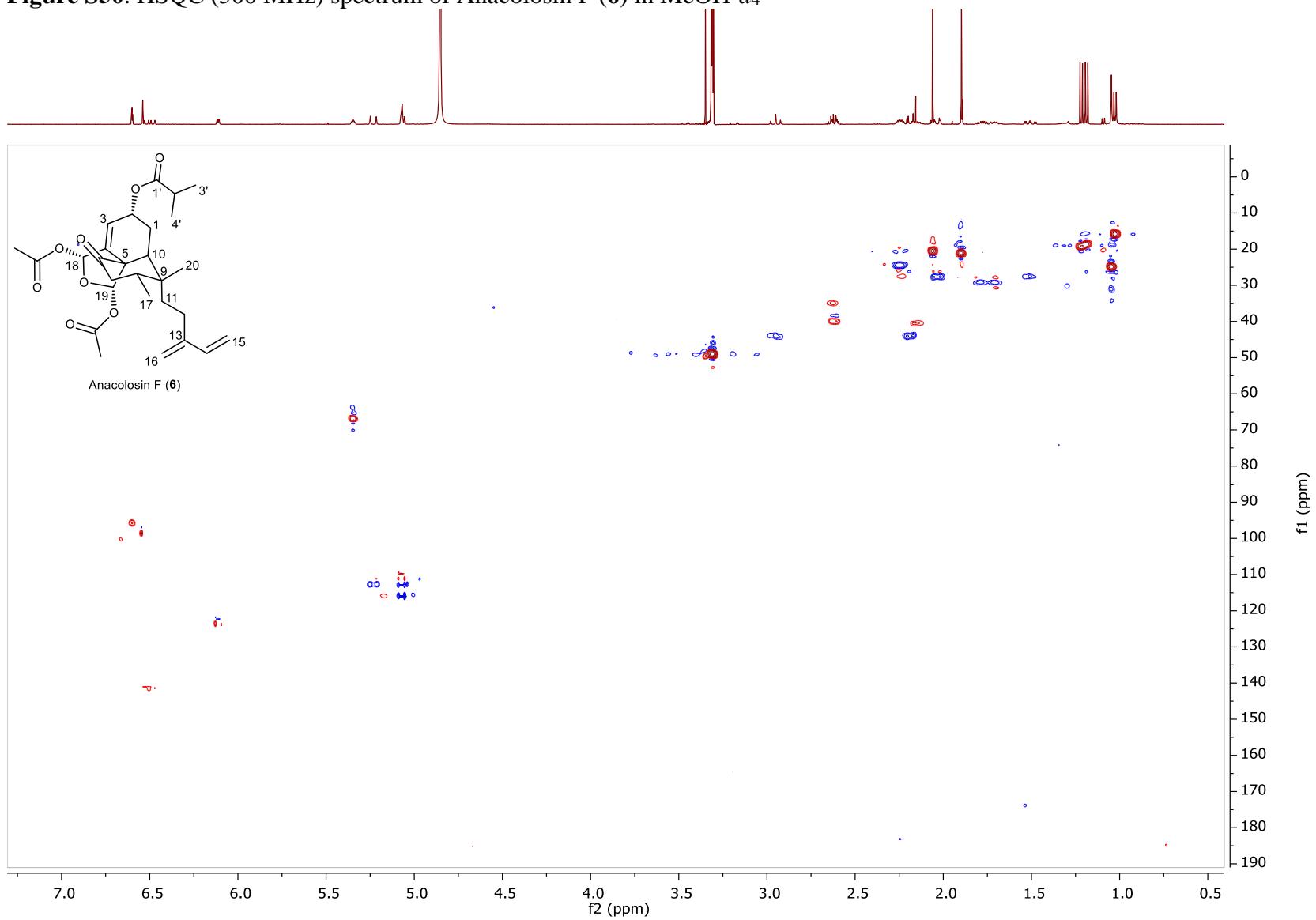


**Figure S49.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Anacolosin F (**6**) in  $\text{MeOH-}d_4$

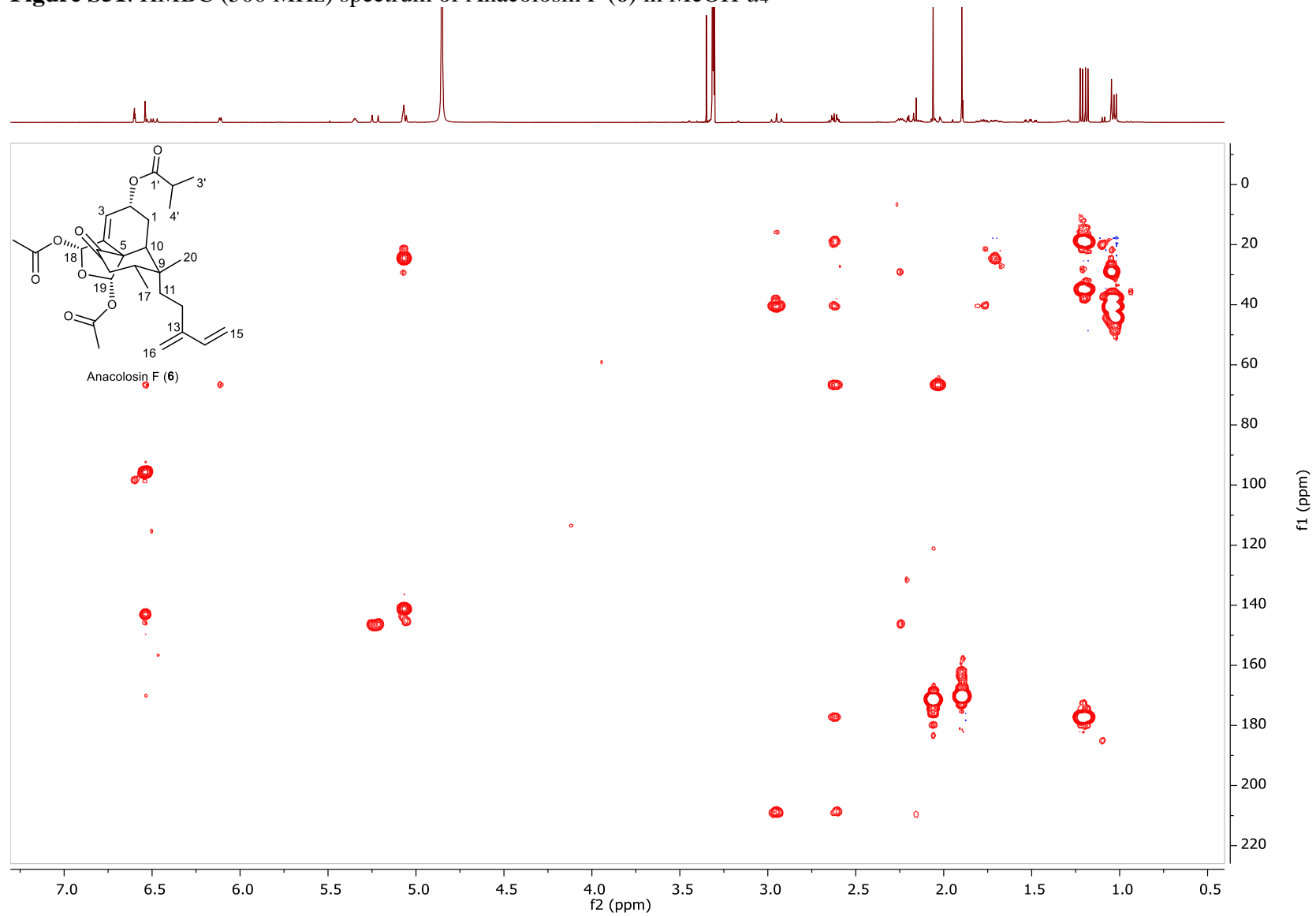




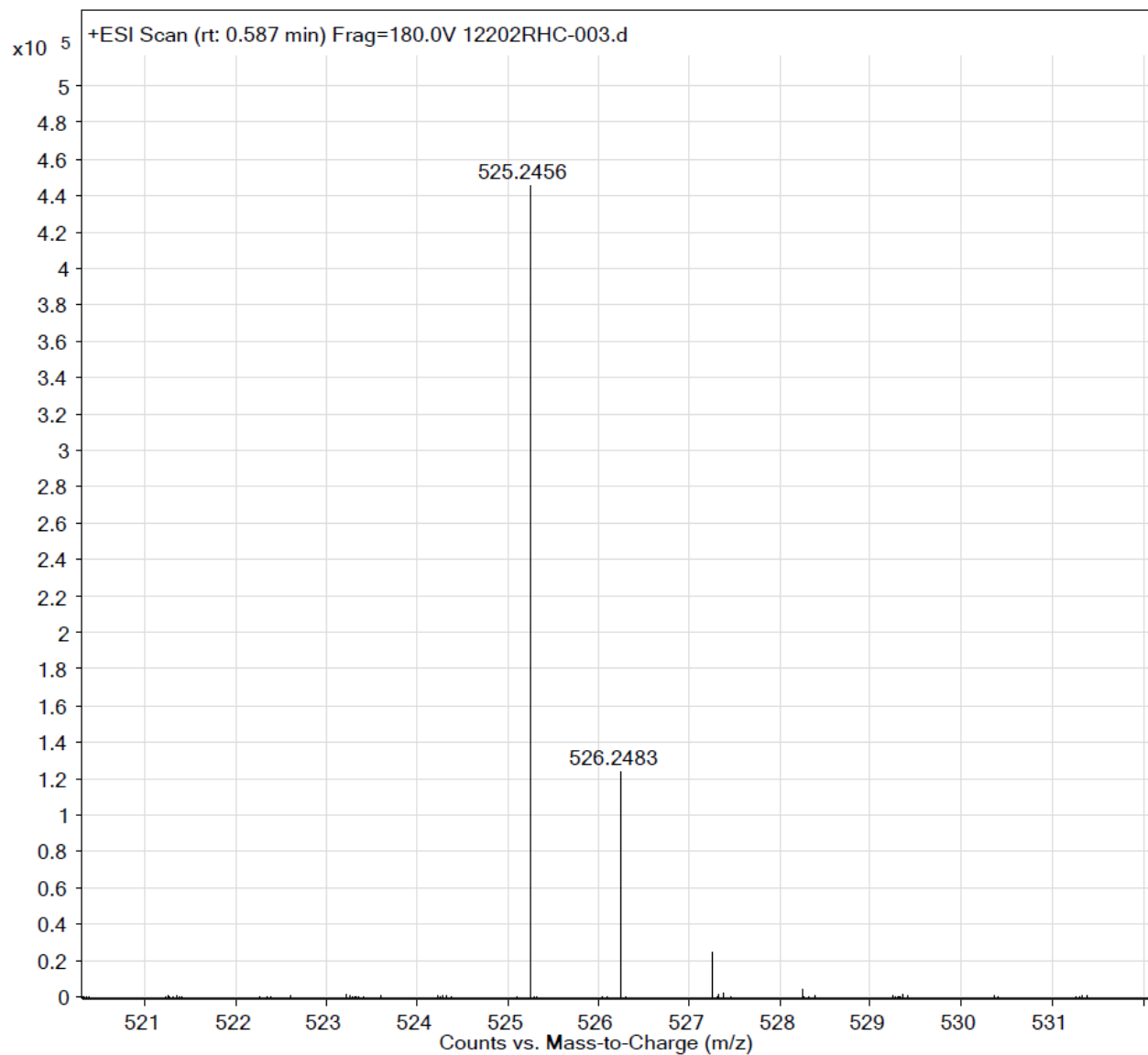
**Figure S50.** HSQC (500 MHz) spectrum of Anacolosin F (**6**) in MeOH-*d*<sub>4</sub>



**Figure S51.** HMBC (500 MHz) spectrum of Anacolosin F (**6**) in MeOH-*d*<sub>4</sub>



**Figure S52.** HRESIMS spectrum of Anacolosin F (**6**)



**Figure S53.**  $^1\text{H}$  NMR (500 MHz) spectrum of Corymbulosin X (7) in  $\text{MeOH-}d_4$

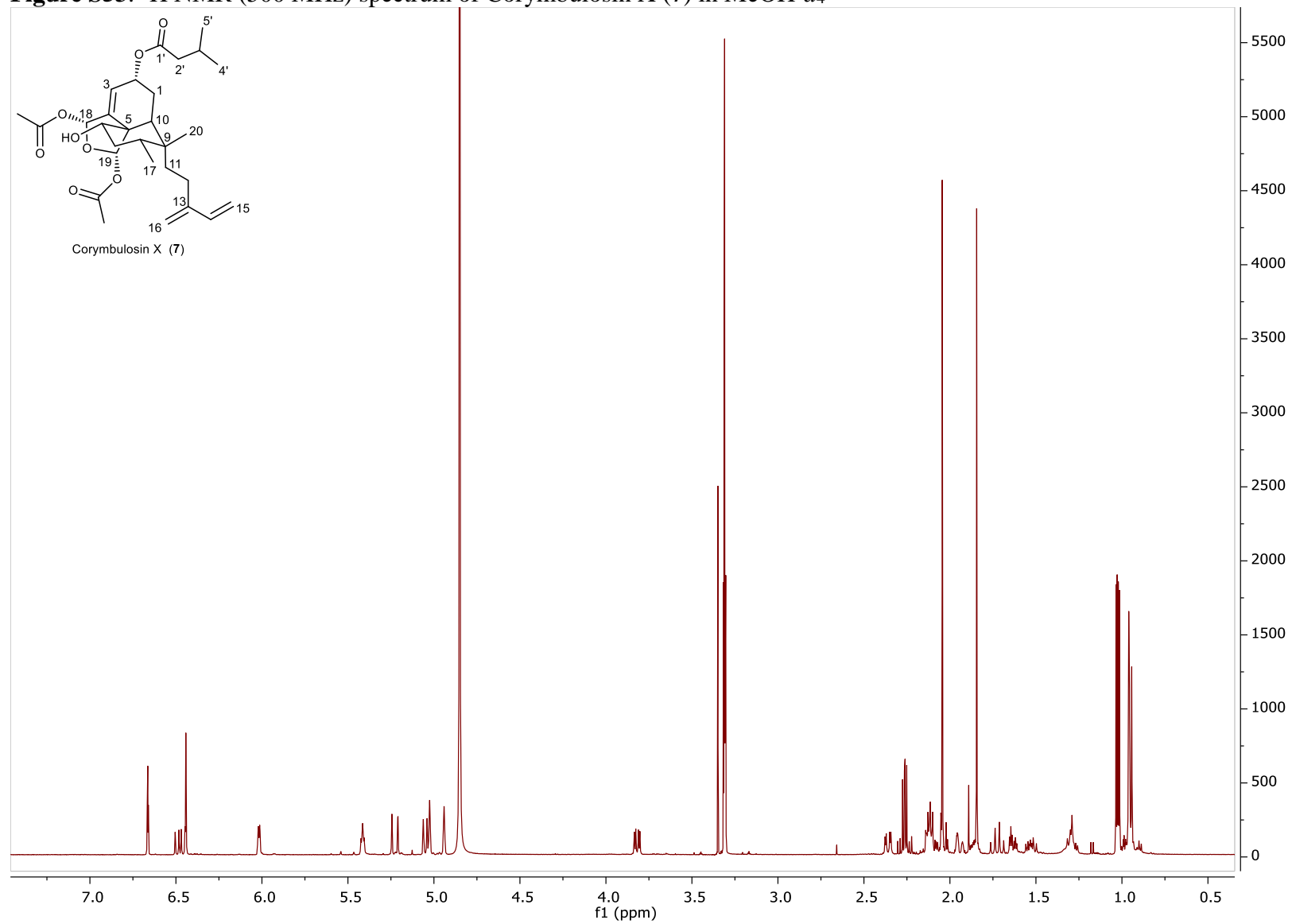
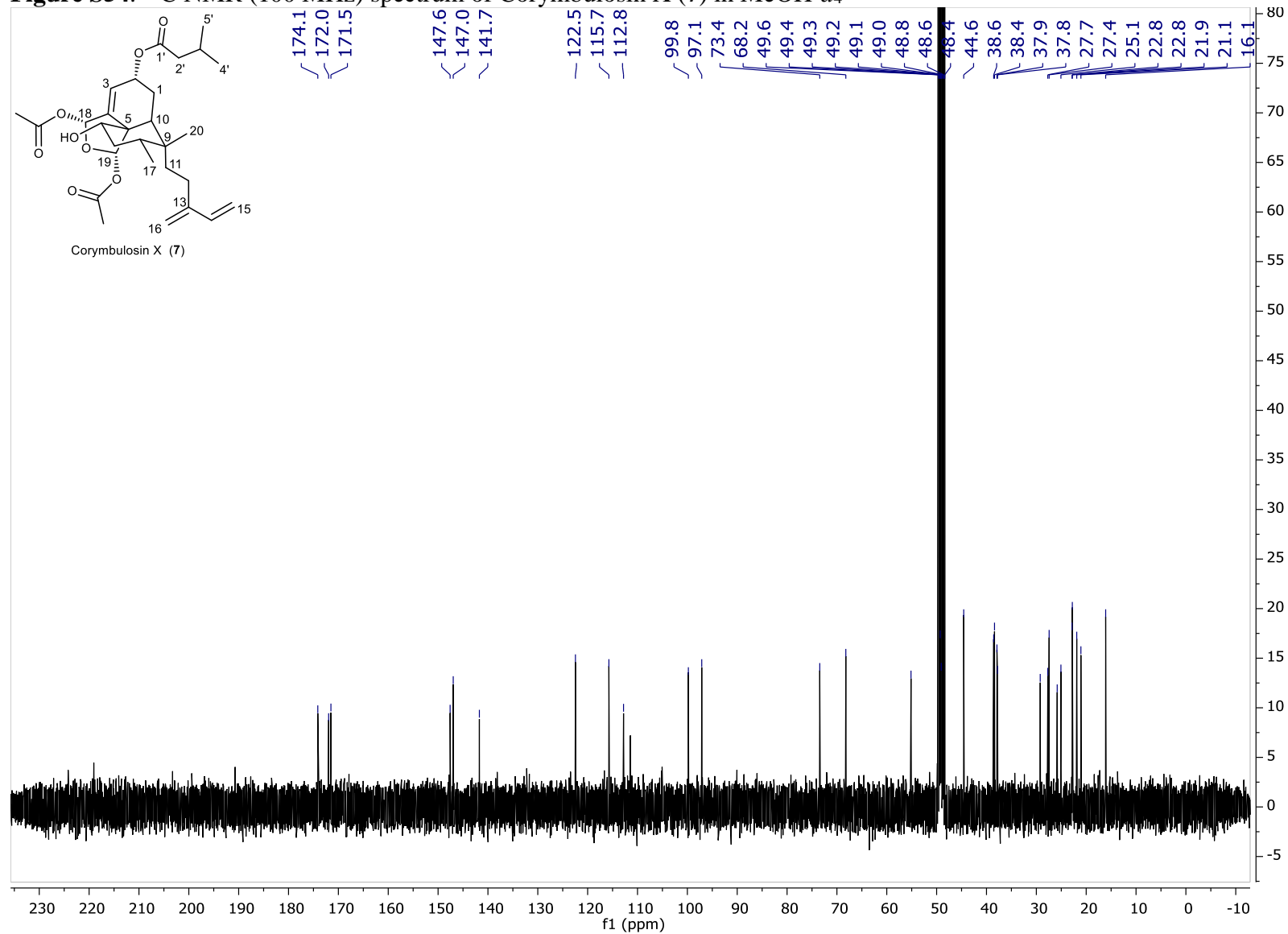


Figure S54.  $^{13}\text{C}$  NMR (100 MHz) spectrum of Corymbulosin X (7) in  $\text{MeOH-}d_4$



**Figure S55.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Corymbulosin X (**7**) in  $\text{MeOH-}d_4$

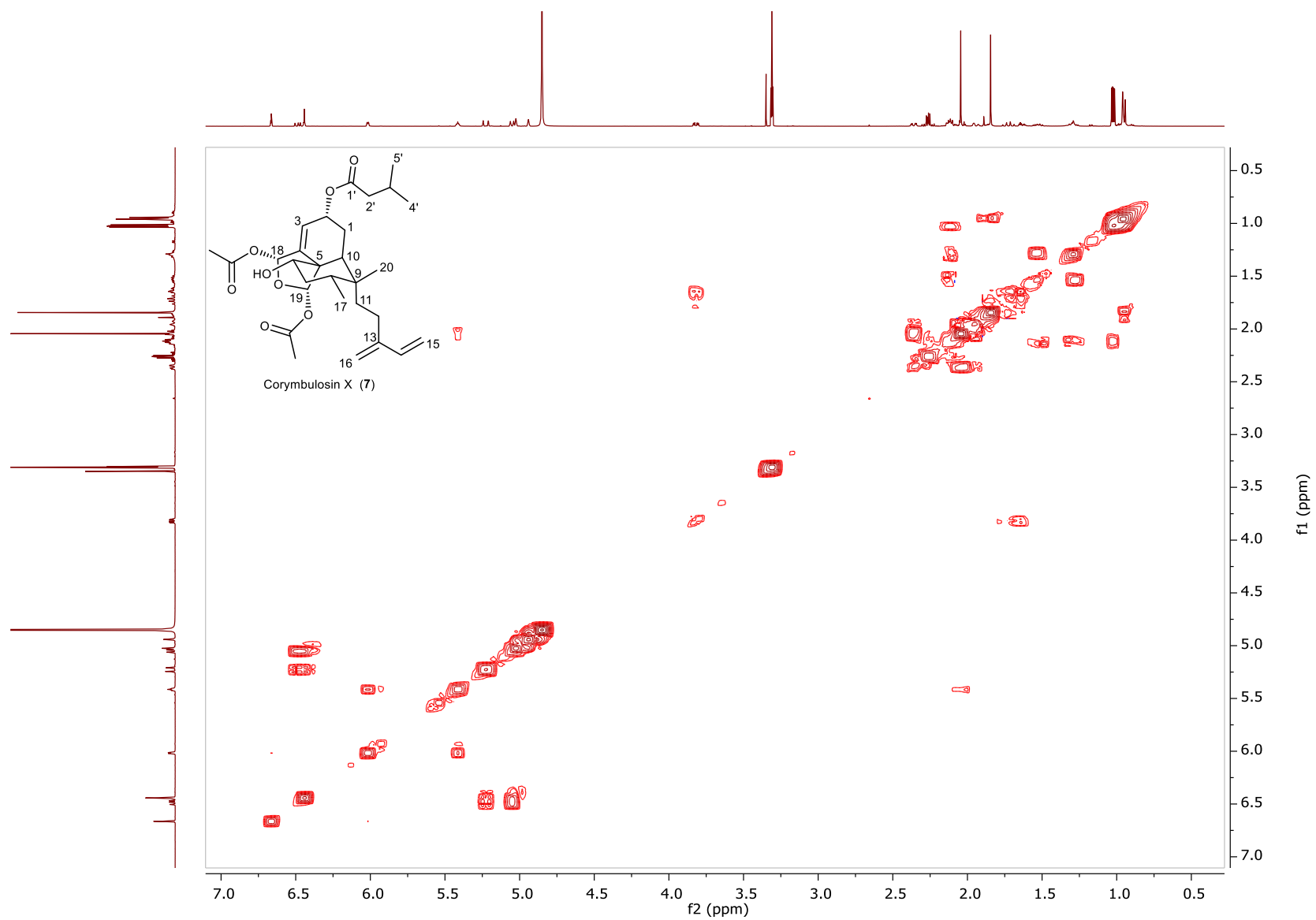


Figure S56. HSQC (500 MHz) spectrum of Corymbulosin X (7) in MeOH-*d*<sub>4</sub>

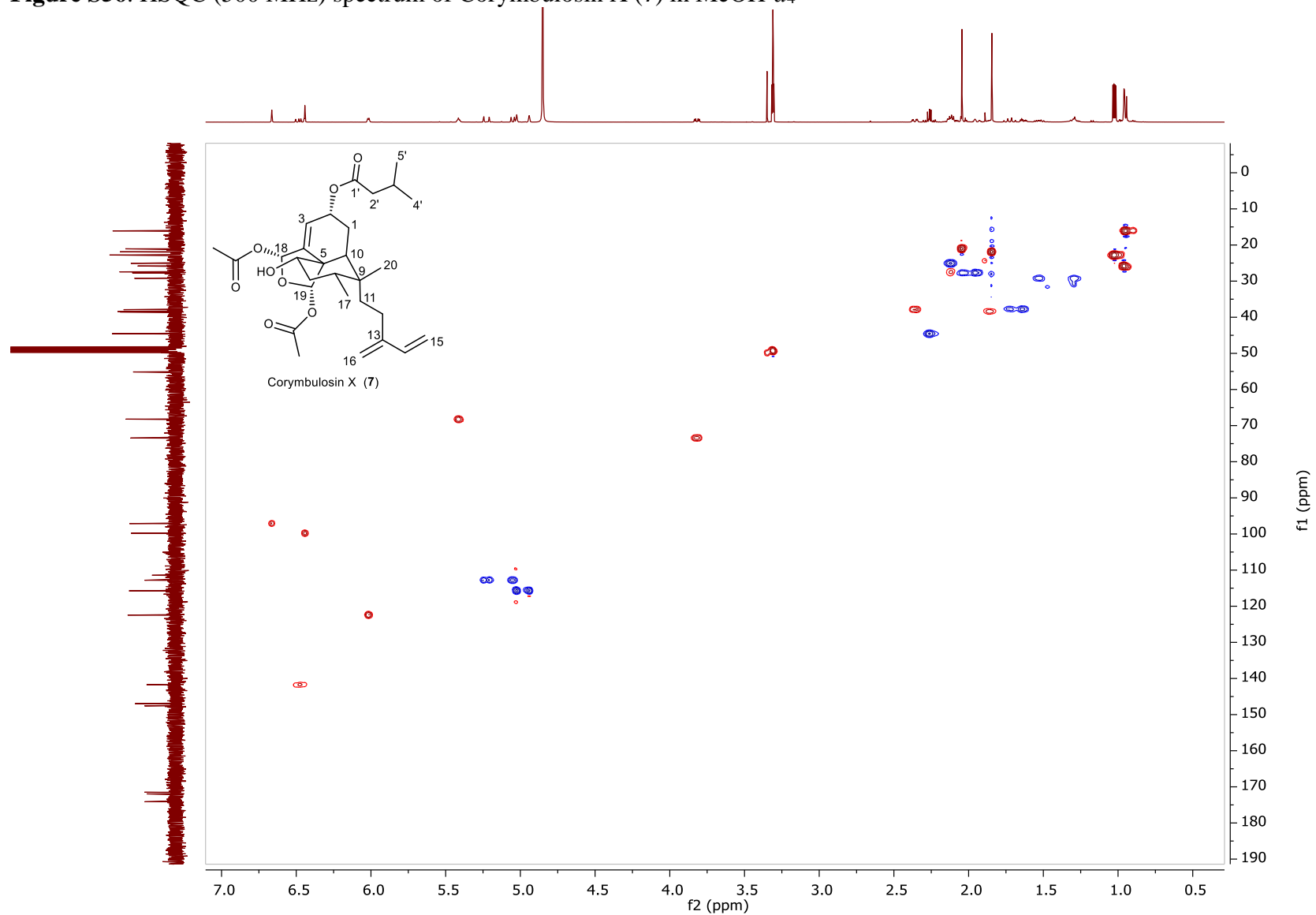
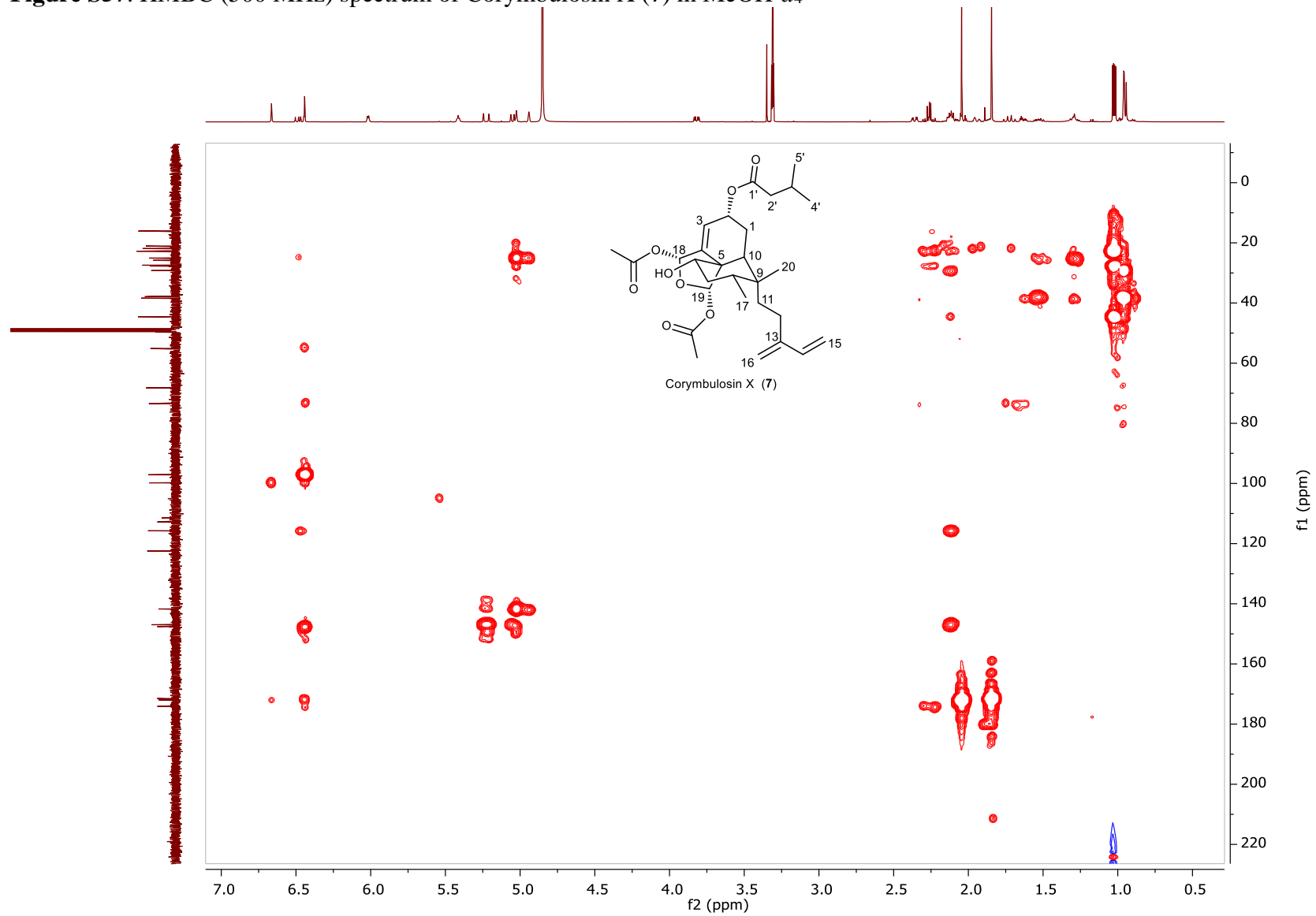
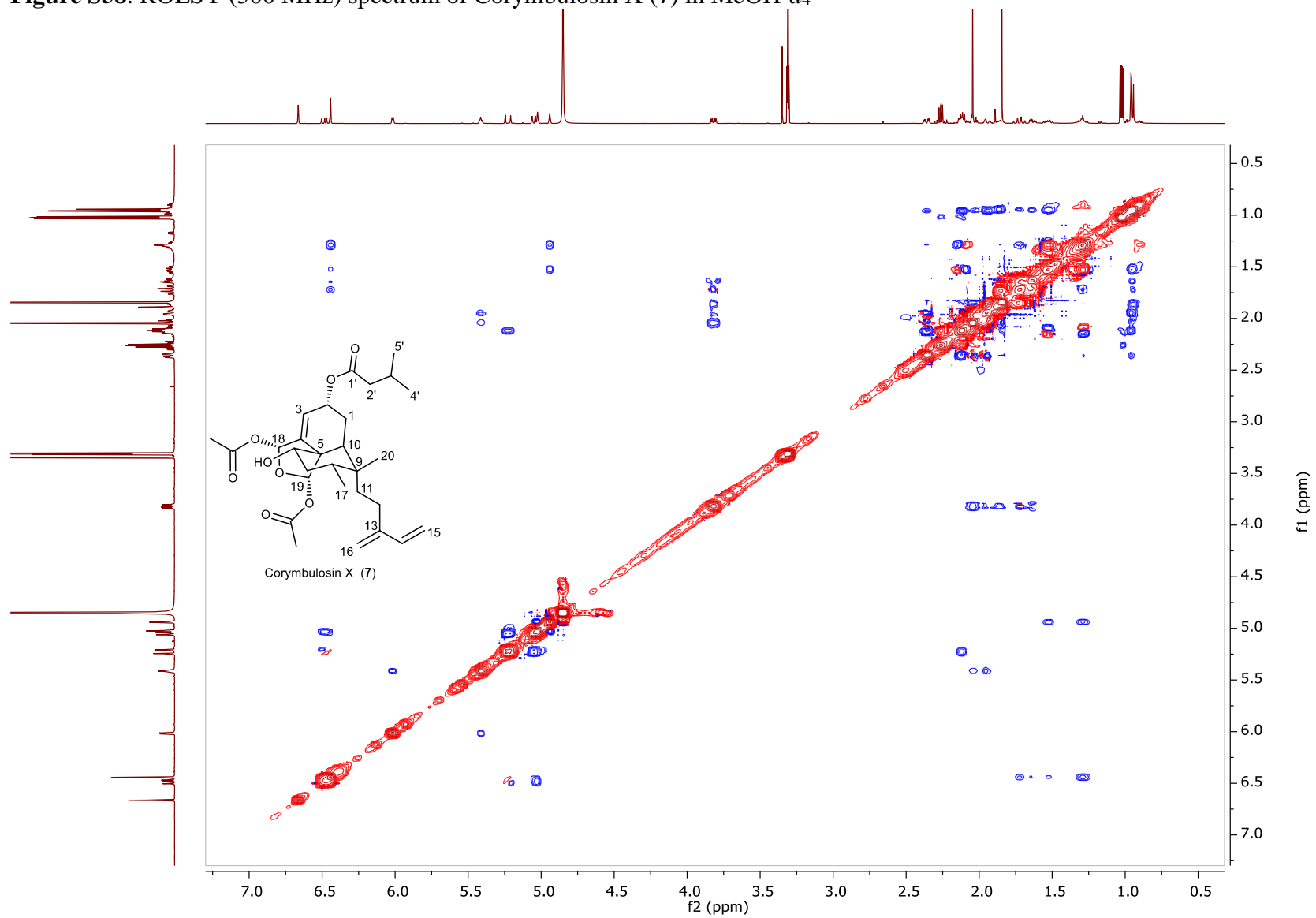


Figure S57. HMBC (500 MHz) spectrum of Corymbulosin X (7) in MeOH-*d*<sub>4</sub>

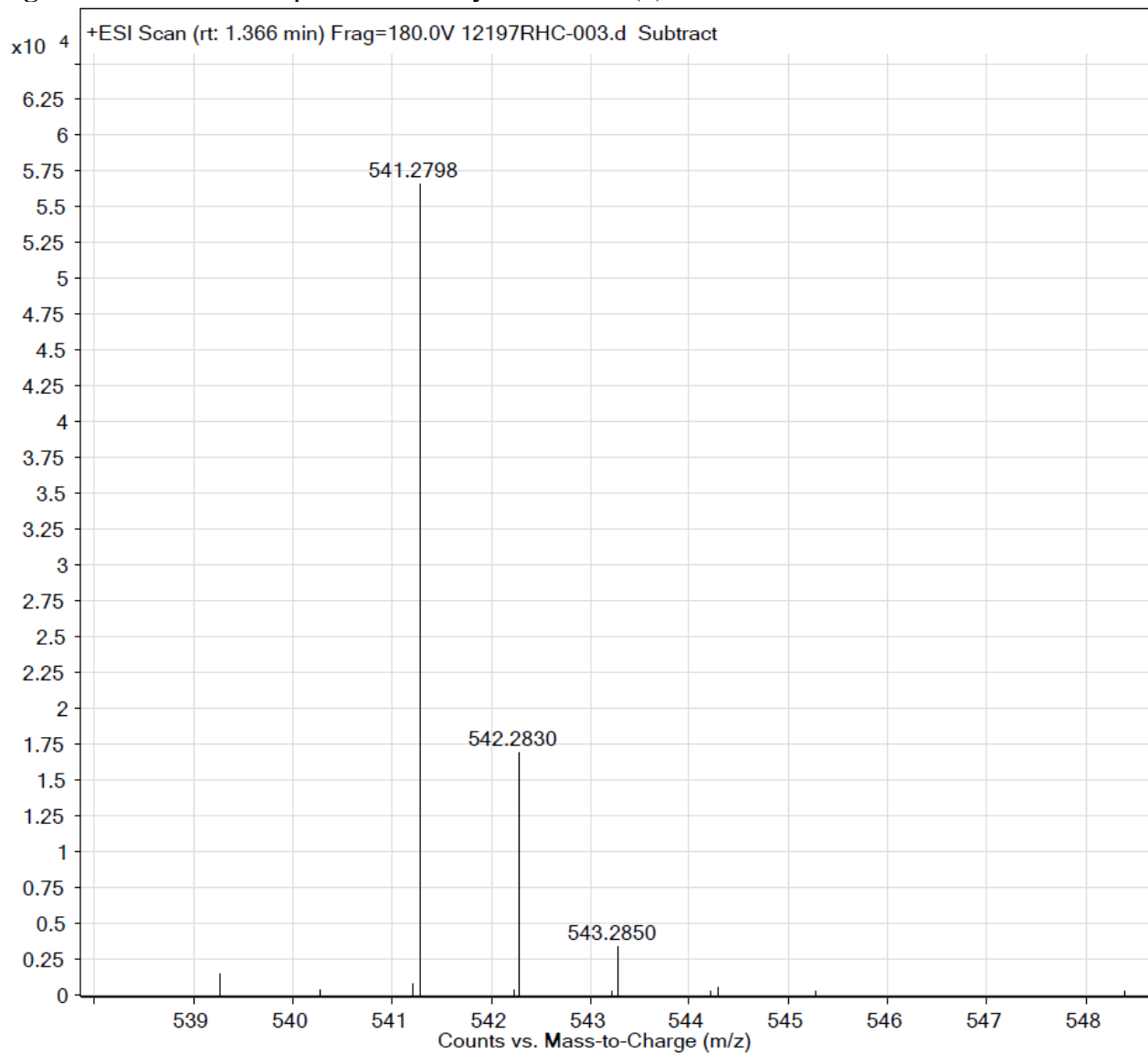




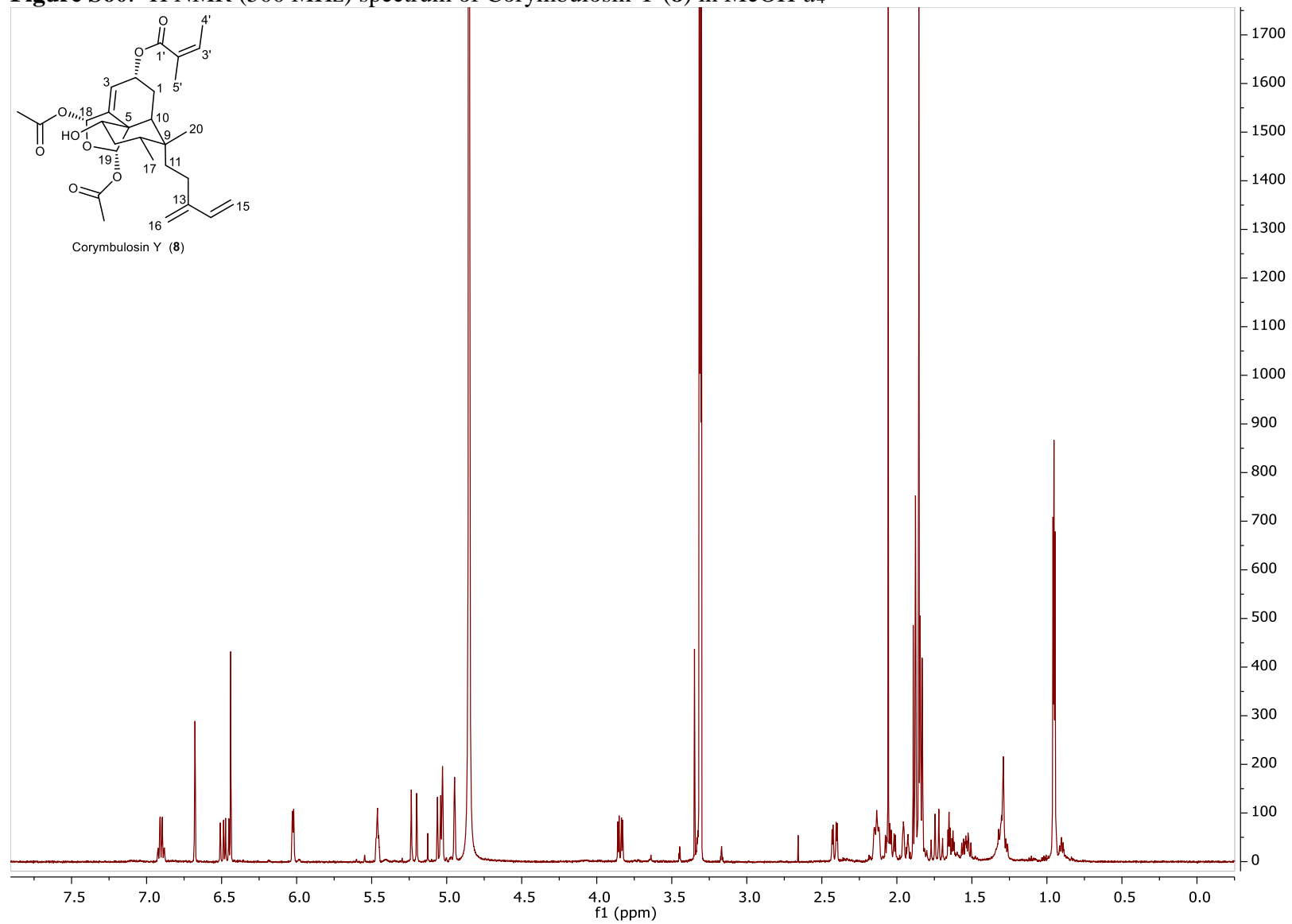
**Figure S58.** ROESY (500 MHz) spectrum of Corymbulosin X (7) in MeOH-*d*<sub>4</sub>



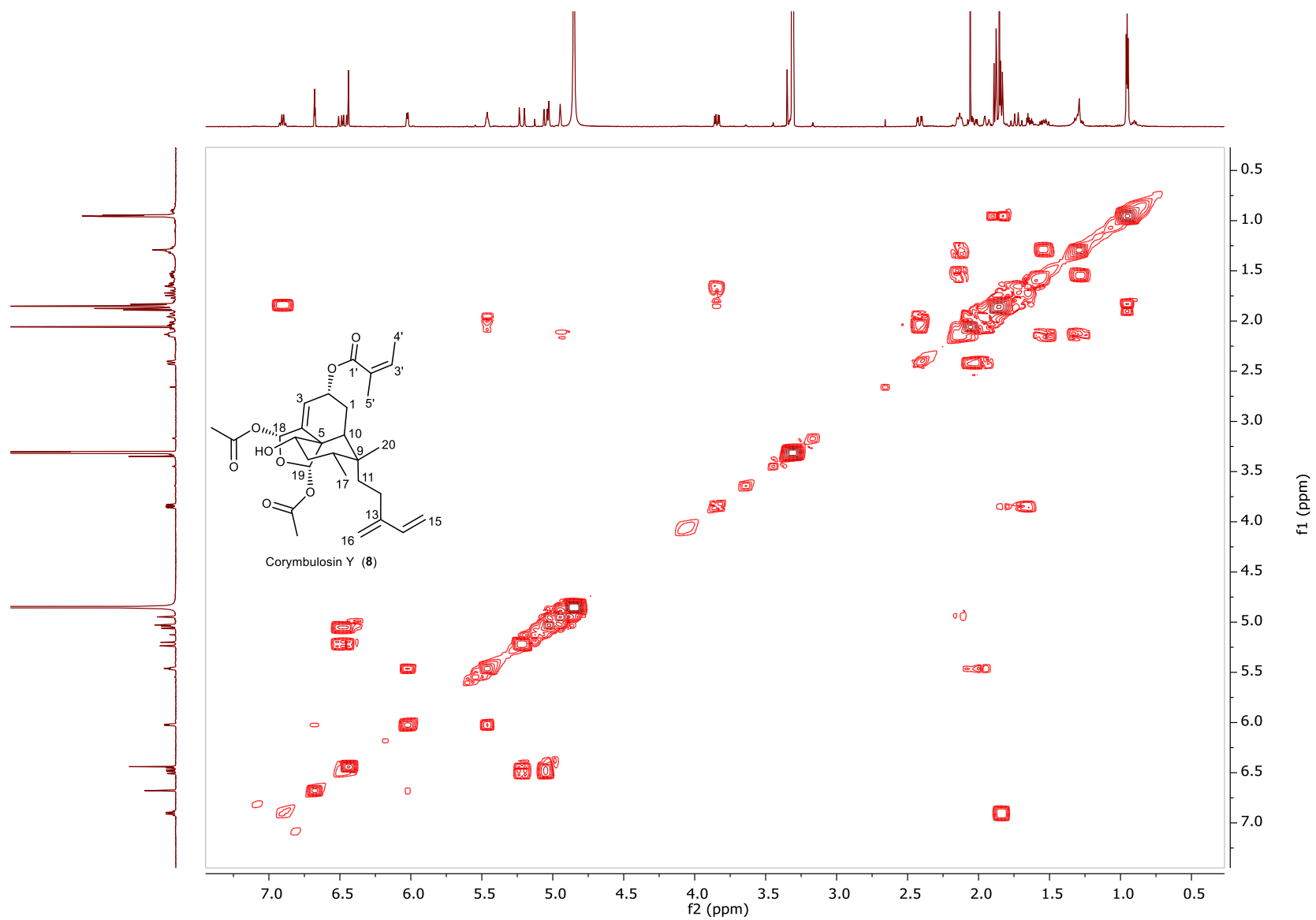
**Figure S59.** HRESIMS spectrum of Corymbulosin X (7)



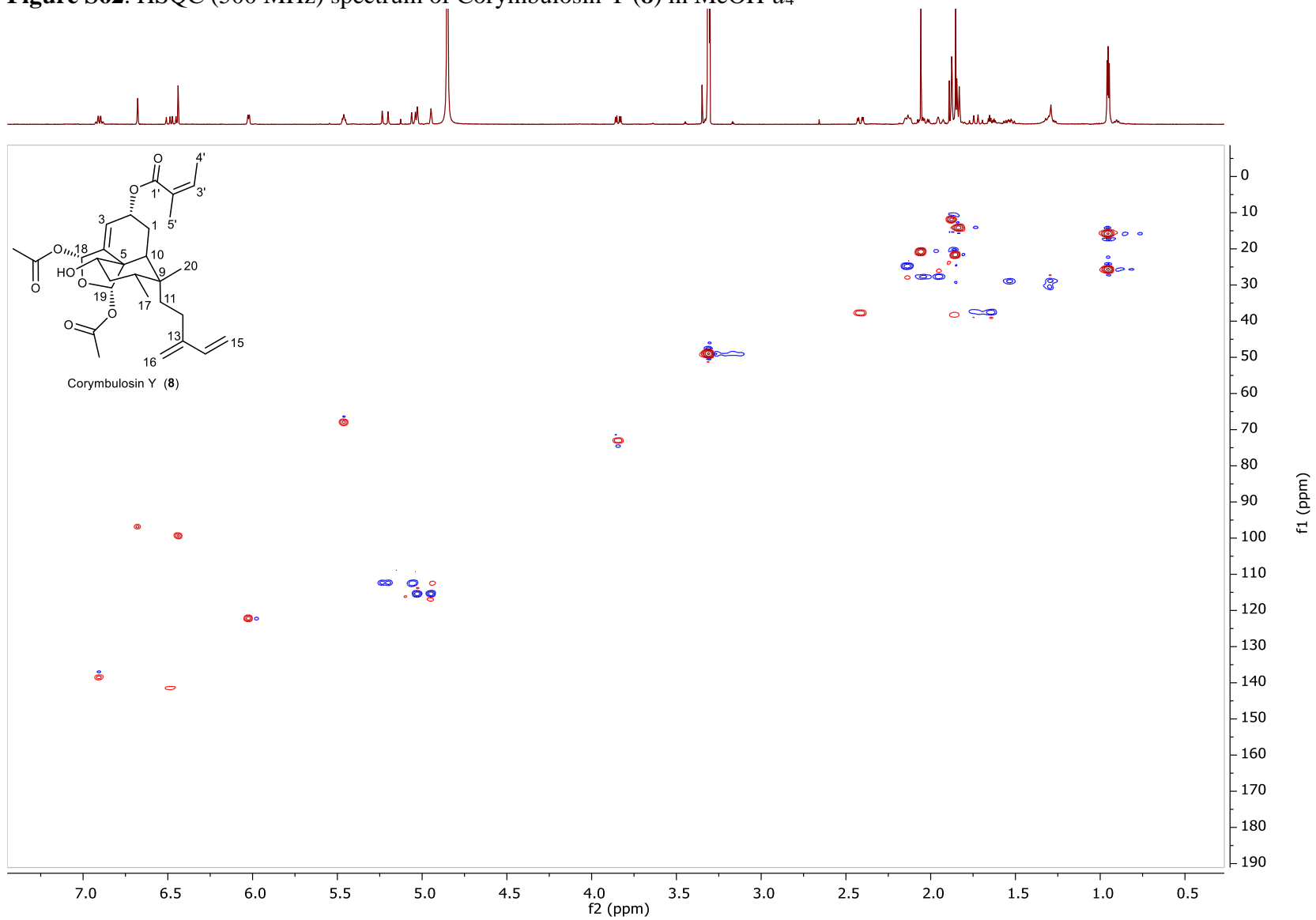
**Figure S60.**  $^1\text{H}$  NMR (500 MHz) spectrum of Corymbulosin Y (**8**) in  $\text{MeOH-}d_4$



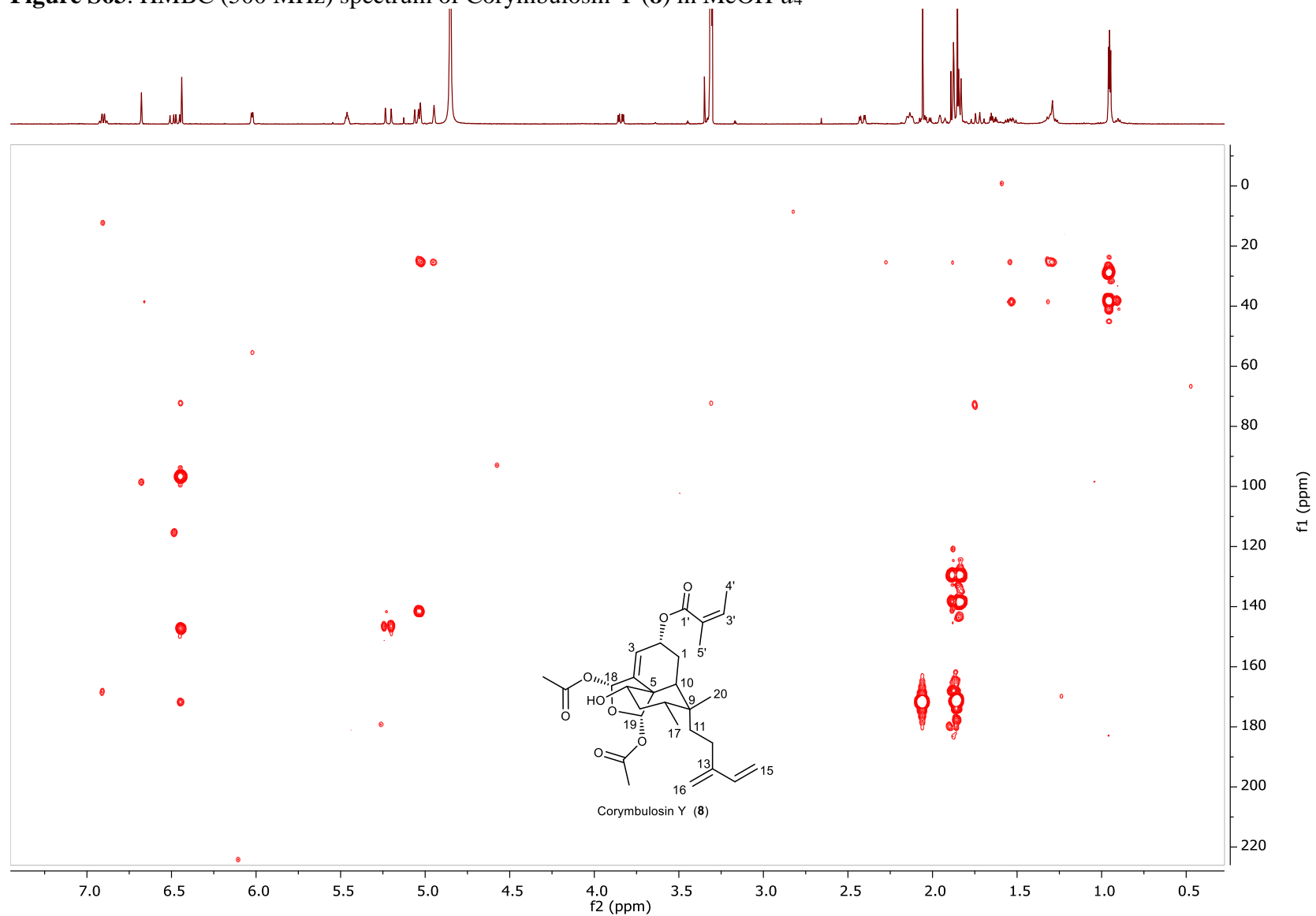
**Figure S61.**  $^1\text{H}$ - $^1\text{H}$  COSY (500 MHz) spectrum of Corymbulosin Y (**8**) in  $\text{MeOH-}d_4$



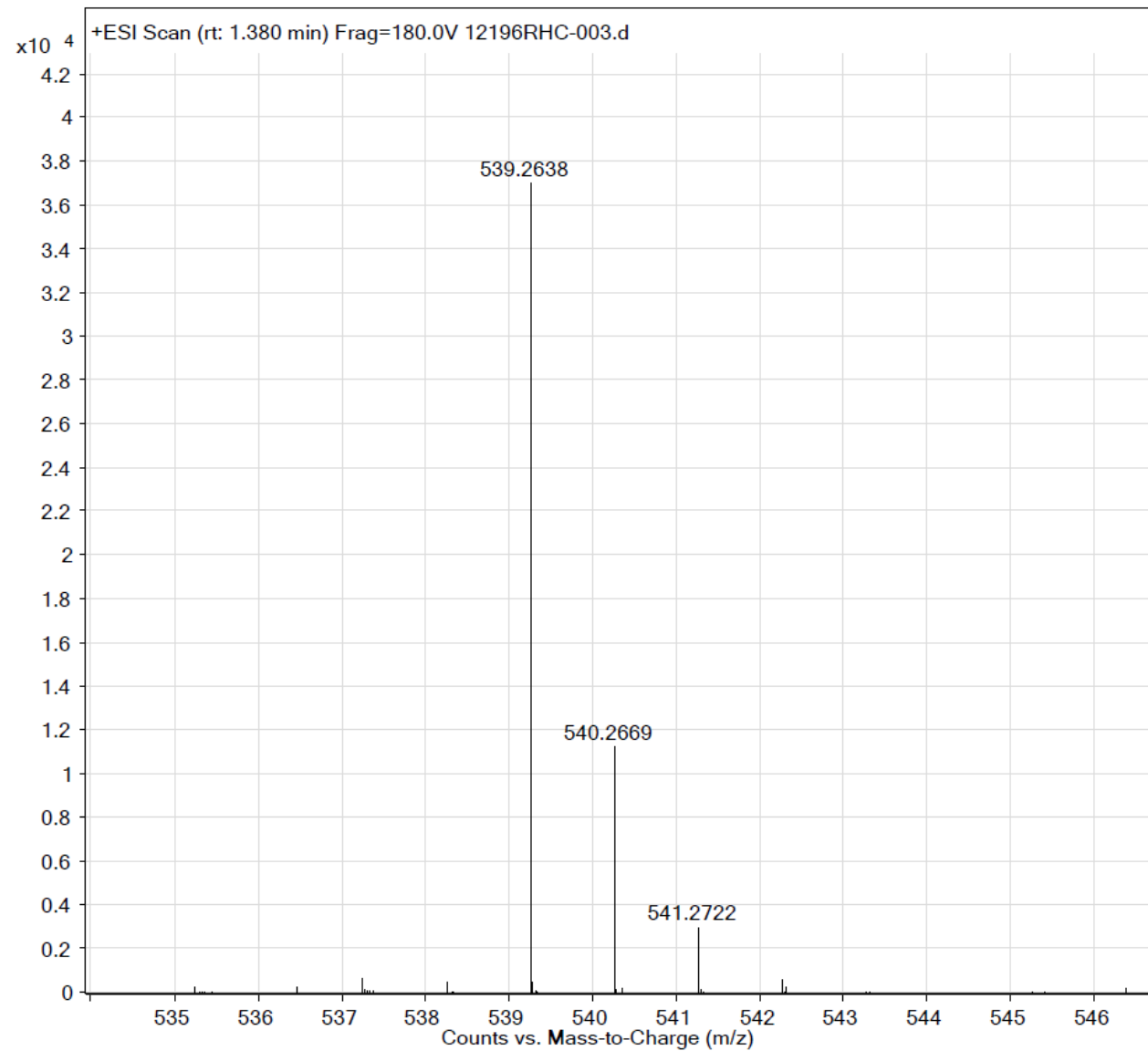
**Figure S62.** HSQC (500 MHz) spectrum of Corymbulosin Y (**8**) in MeOH-*d*<sub>4</sub>



**Figure S63.** HMBC (500 MHz) spectrum of Corymbulosin Y (**8**) in MeOH-*d*<sub>4</sub>



**Figure S64.** HRESIMS spectrum of Corymbulosin Y (**8**)



**Figure S65.**  $^1\text{H}$  NMR (400 MHz) spectrum of the synthetic standard *R/S*-**13** in  $\text{MeOH-}d_4$

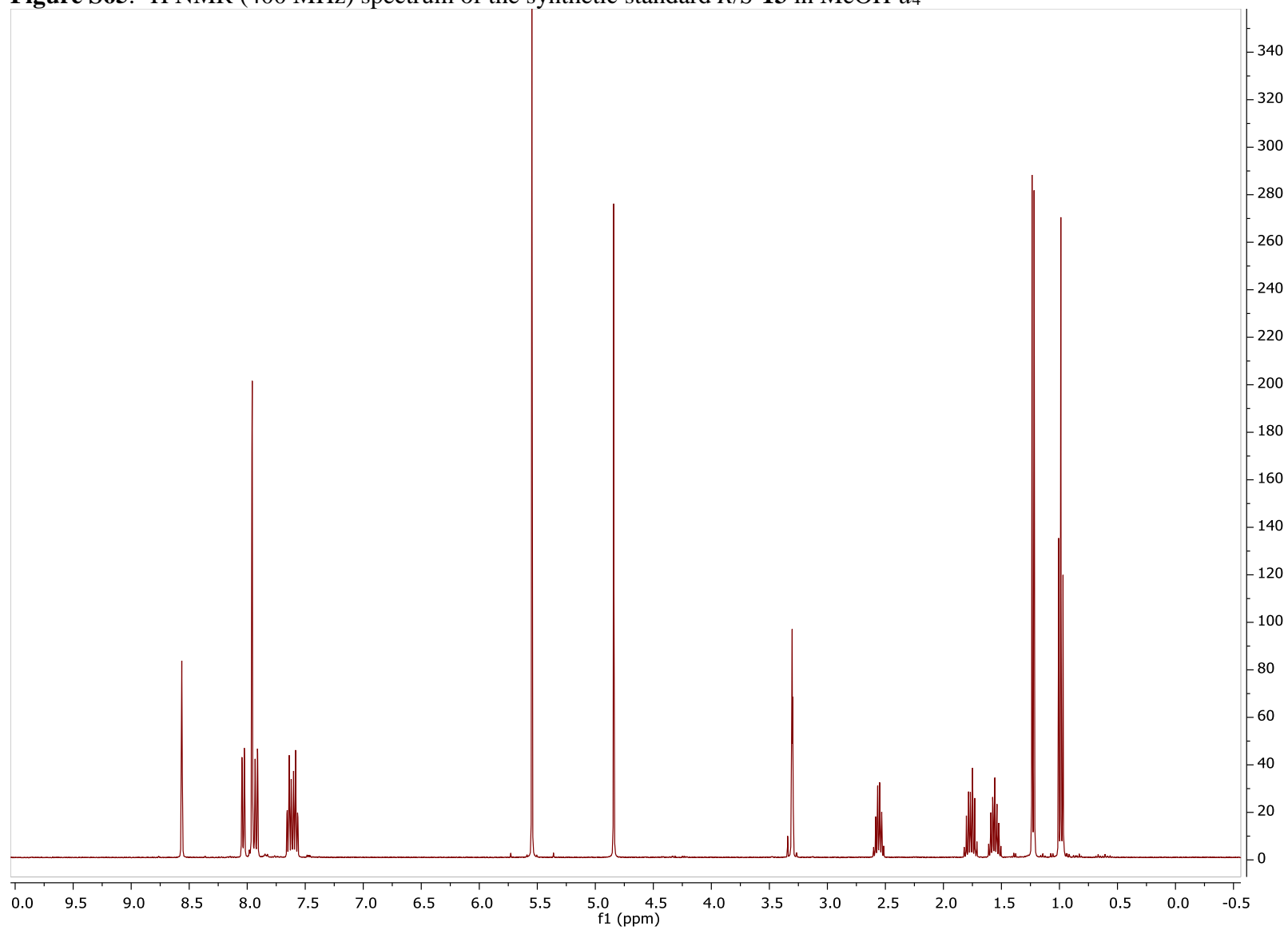
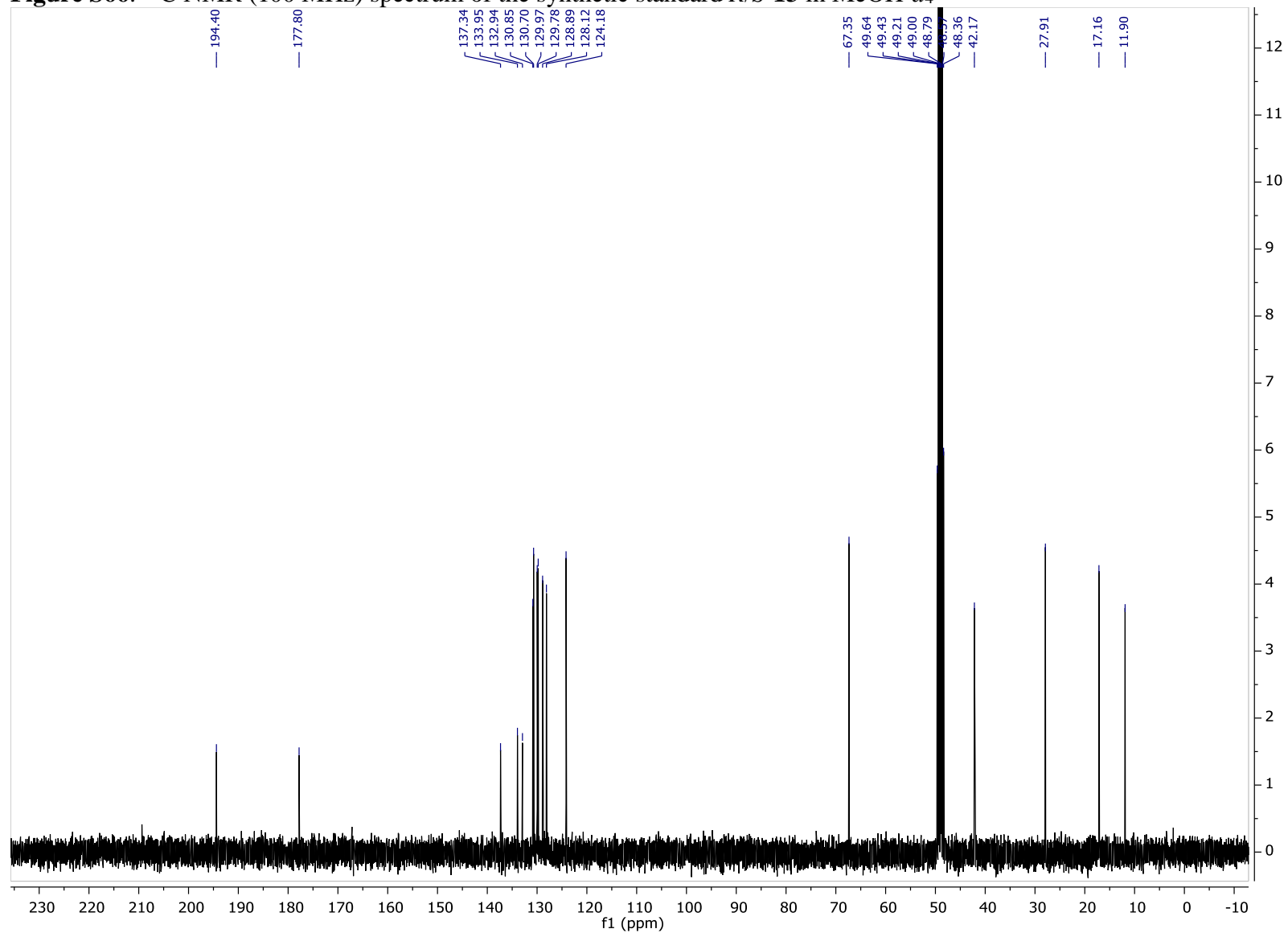




Figure S66.  $^{13}\text{C}$  NMR (100 MHz) spectrum of the synthetic standard *R/S*-13 in  $\text{MeOH-}d_4$



**Figure S67.**  $^1\text{H}$  NMR (400 MHz) spectrum of the synthetic standard **S-13** in  $\text{MeOH-}d_4$

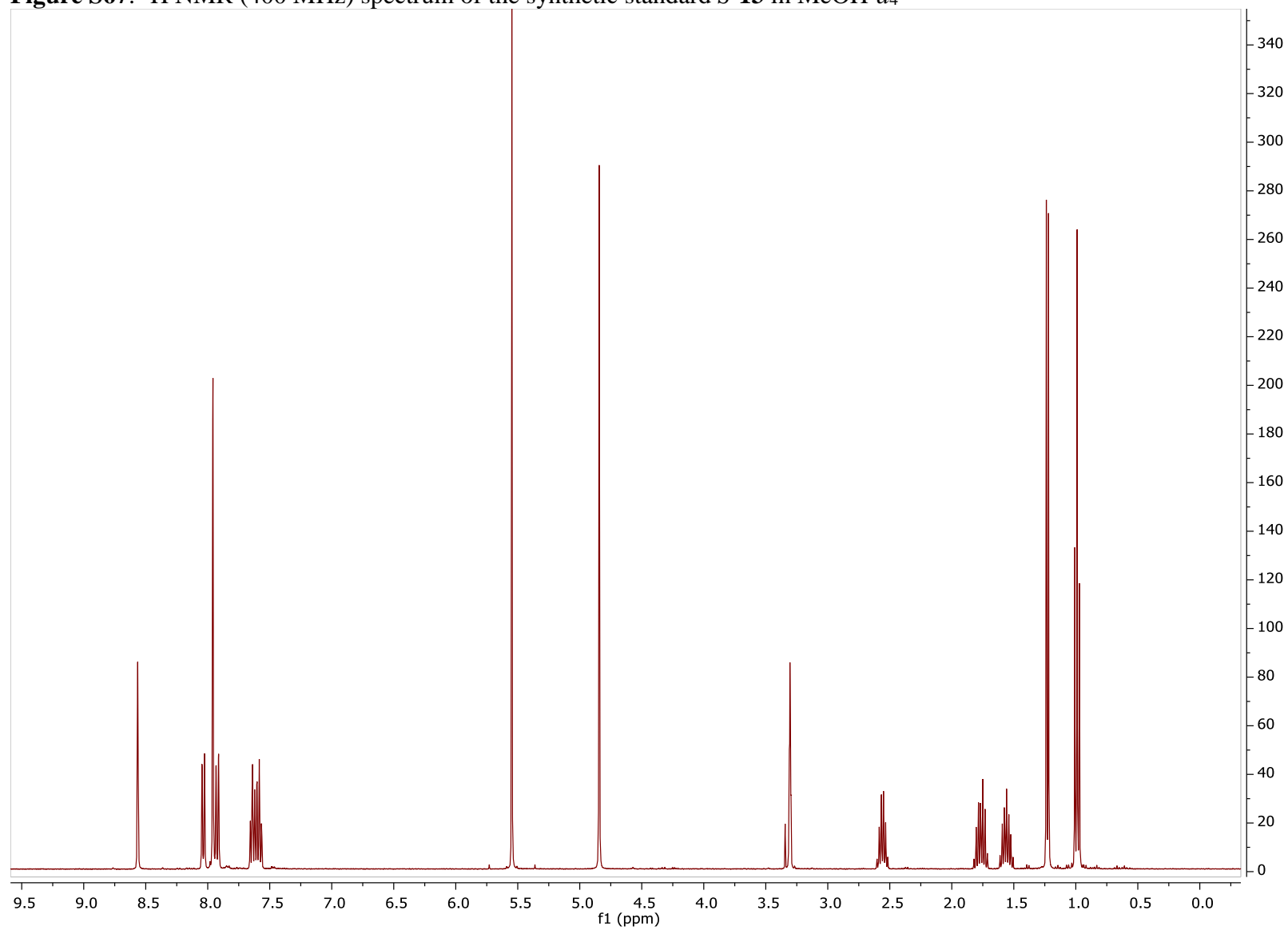


Figure S68.  $^{13}\text{C}$  NMR (100 MHz) spectrum of the synthetic standard *S-13* in  $\text{MeOH-}d_4$

