

## Supplementary Material

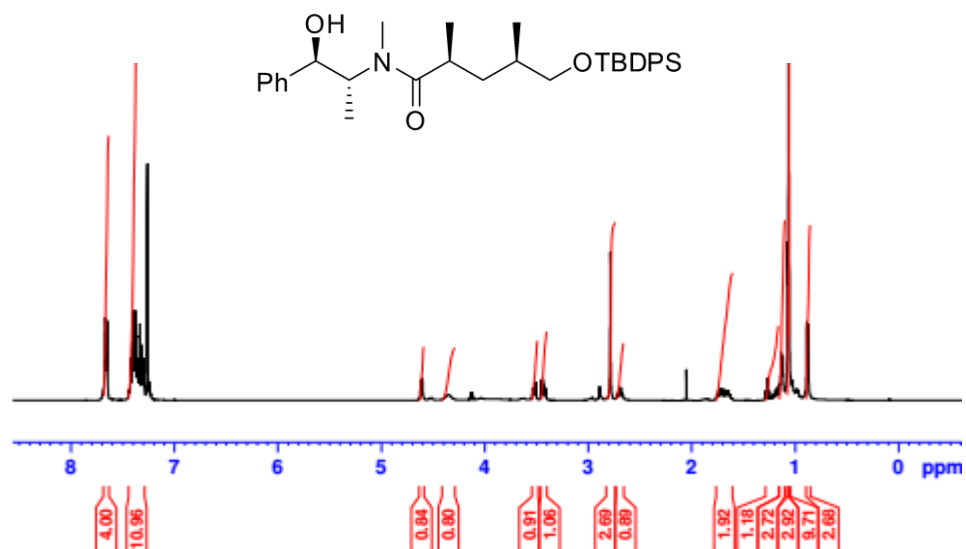
### Stereoselective synthesis of fully functionalized acyclic core of Tianchimycin A

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#### Table of Contents

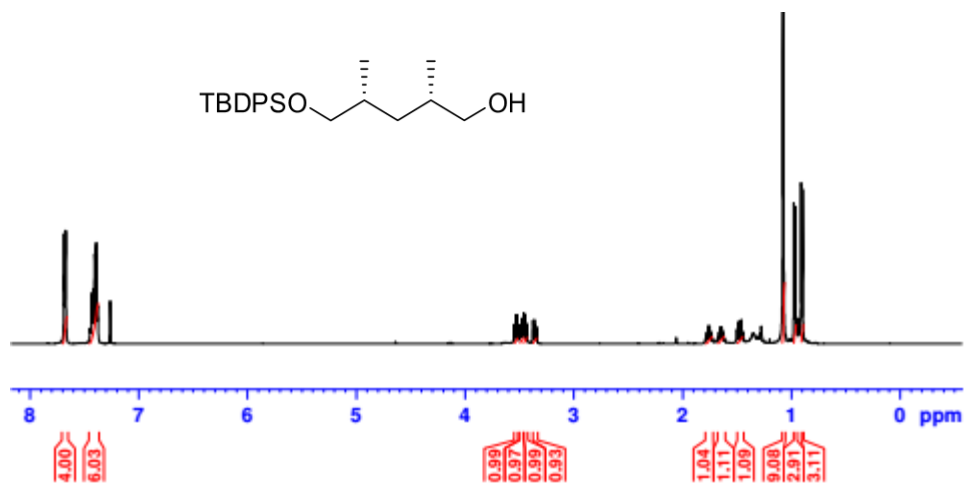
1. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compounds <b>10</b>	S2
2. <sup>1</sup> H & <sup>13</sup> C NMR of spectra of compound <b>6</b>	S3
3. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compounds <b>12 to 17</b>	S4
4. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compound <b>4a</b>	S10
5. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compound <b>8</b>	S11
6. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compounds <b>18 to 21</b>	S12
7. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compound <b>5</b>	S16
8. <sup>1</sup> H & <sup>13</sup> C NMR spectra of compound <b>3</b>	S17



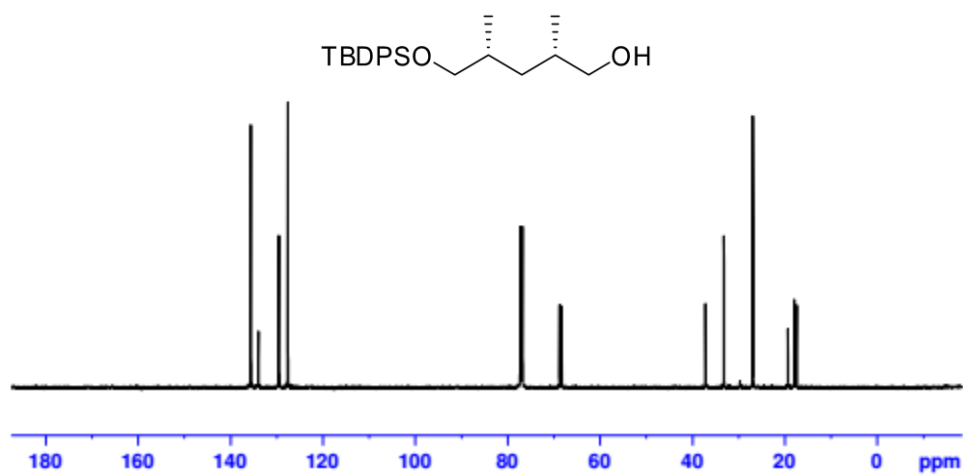
<sup>1</sup>H NMR spectrum of 10 (CDCl<sub>3</sub>, 400 MHz)



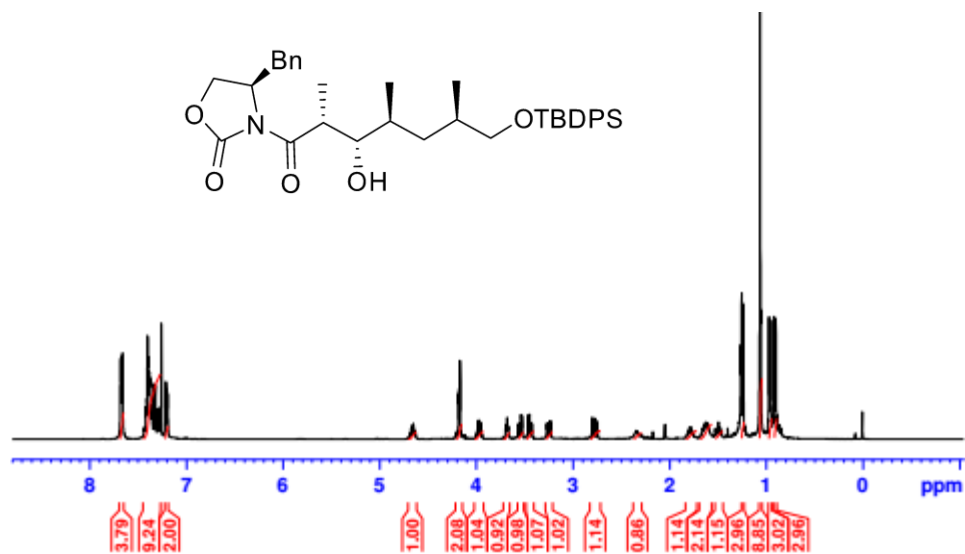
<sup>13</sup>C NMR spectrum of 10 (CDCl<sub>3</sub>, 100 MHz)



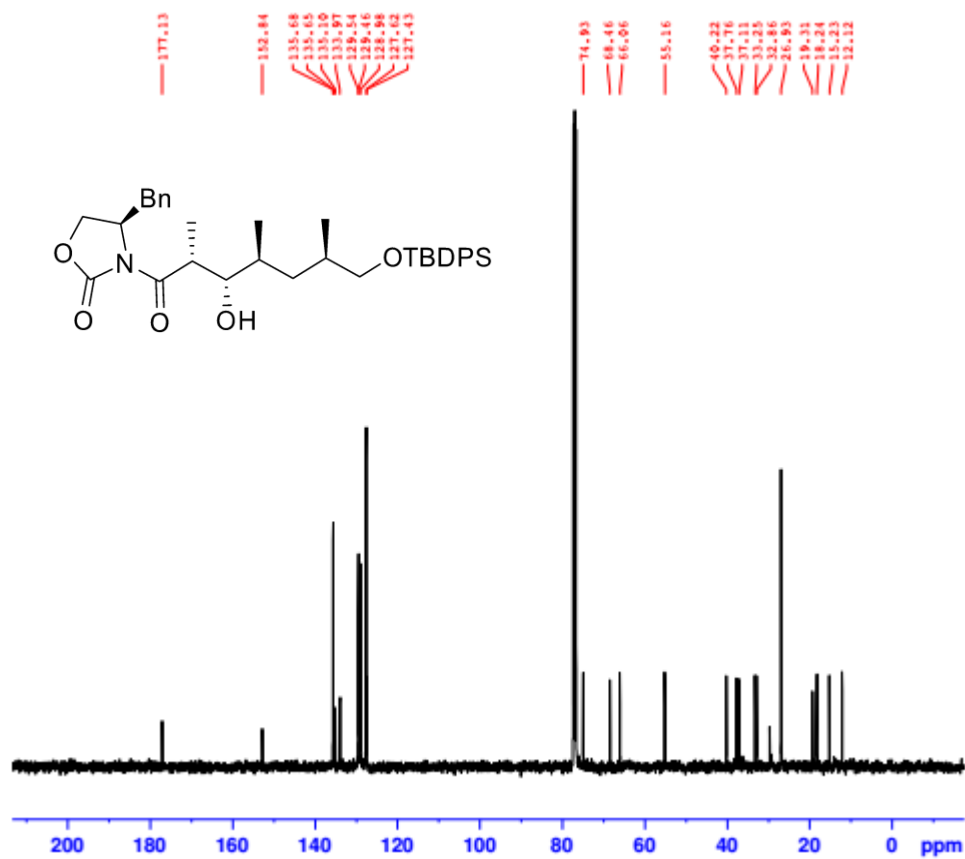
<sup>1</sup>H NMR spectrum of 6 (CDCl<sub>3</sub>, 500 MHz)



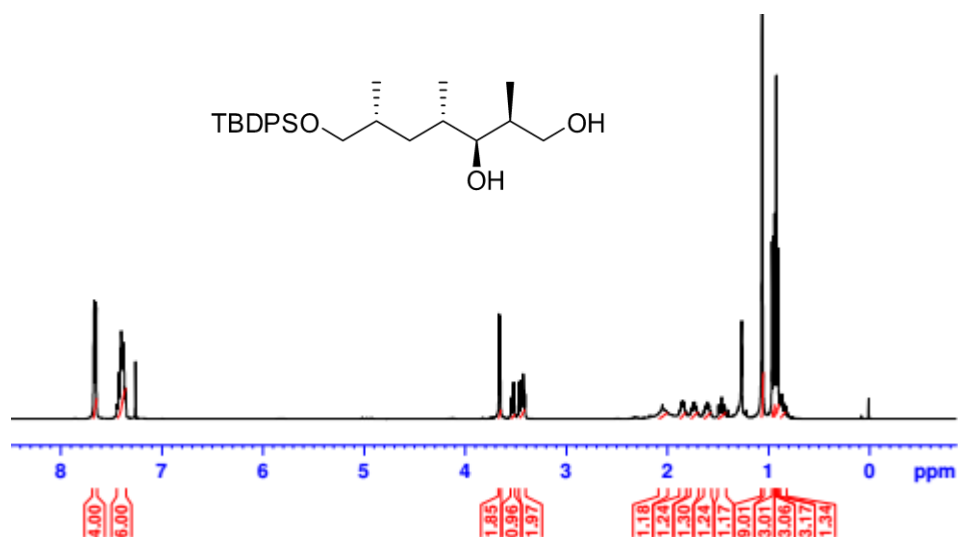
<sup>13</sup>C NMR spectrum of 6 (CDCl<sub>3</sub>, 125 MHz)



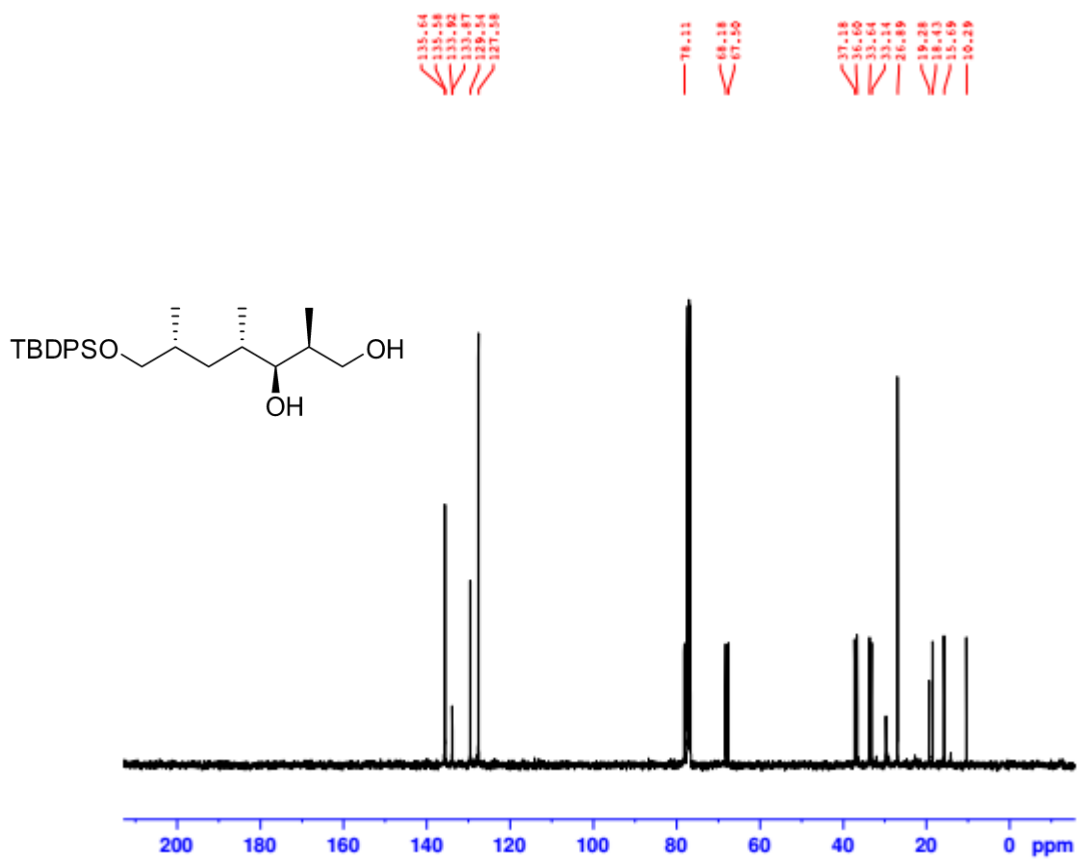
<sup>1</sup>H NMR spectrum of 12 (CDCl<sub>3</sub>, 400 MHz)



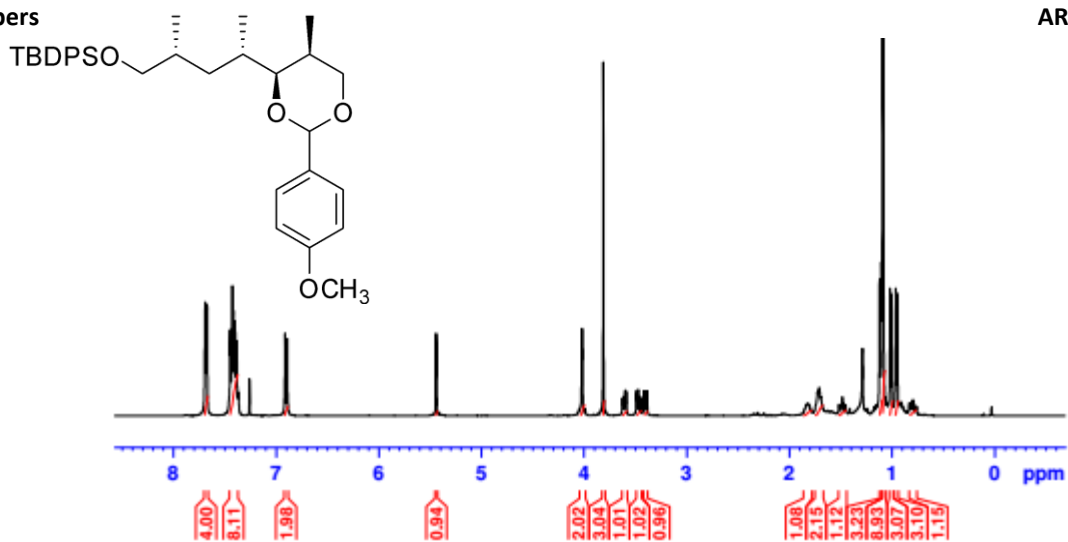
<sup>13</sup>C NMR spectrum of 12 (CDCl<sub>3</sub>, 100 MHz)



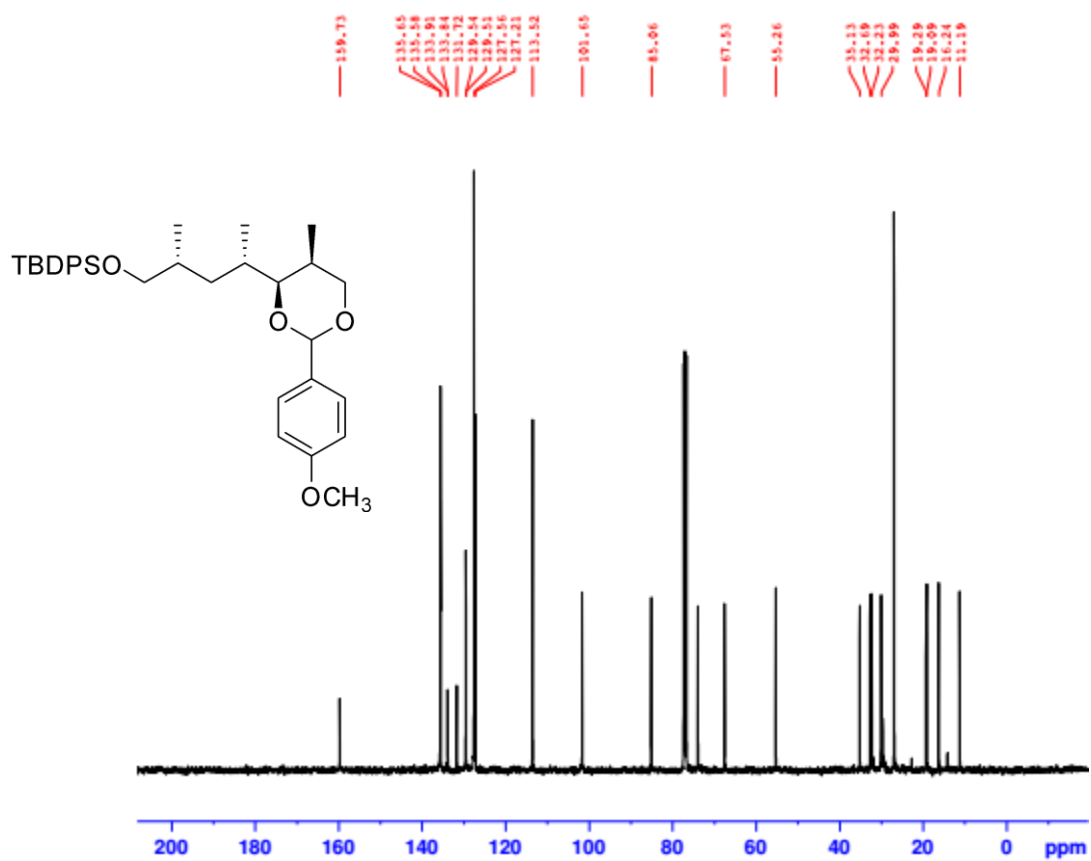
<sup>1</sup>H NMR spectrum of 13 (CDCl<sub>3</sub>, 400 MHz)



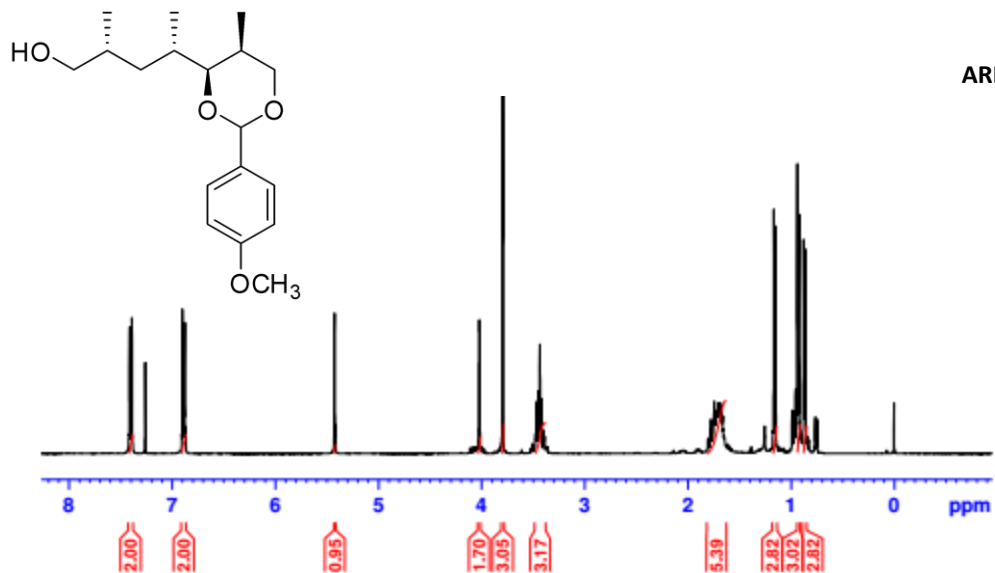
<sup>13</sup>C NMR spectrum of 13 (CDCl<sub>3</sub>, 100 MHz)



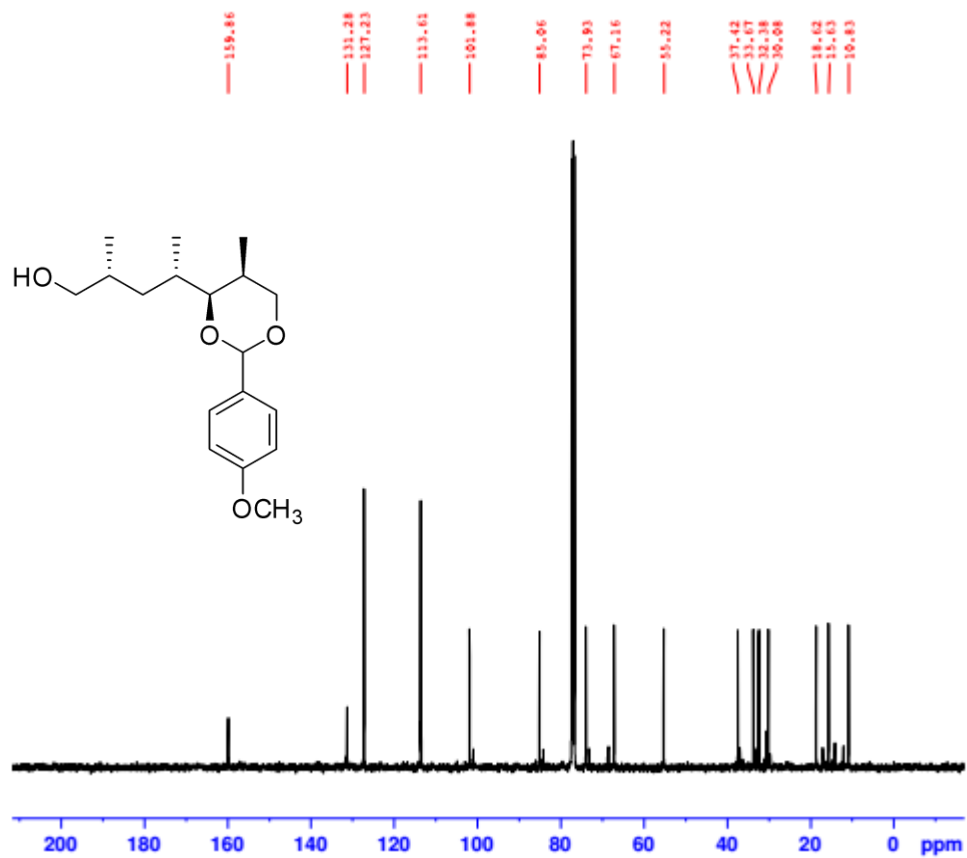
<sup>1</sup>H NMR spectrum of 14 (CDCl<sub>3</sub>, 400 MHz)



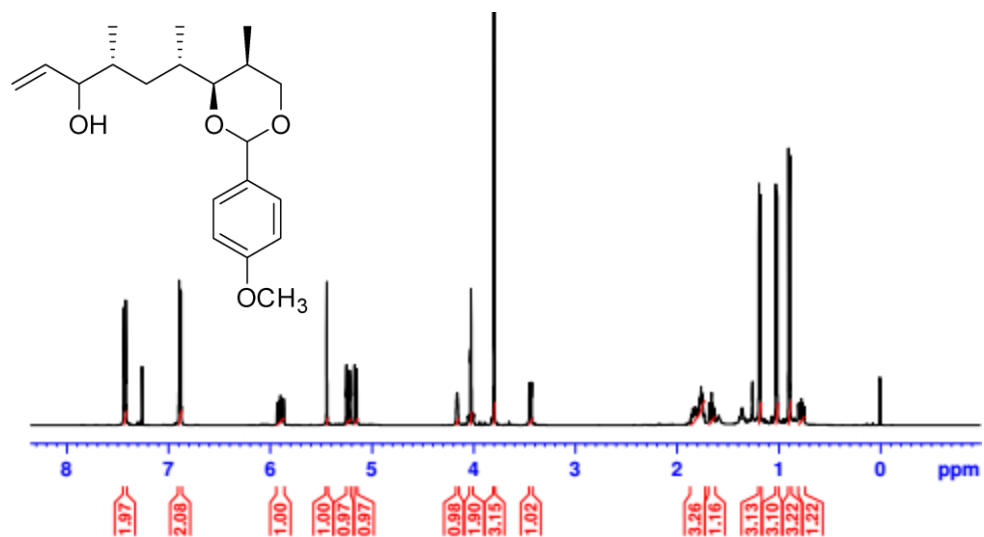
<sup>13</sup>C NMR spectrum of 14 (CDCl<sub>3</sub>, 100 MHz)



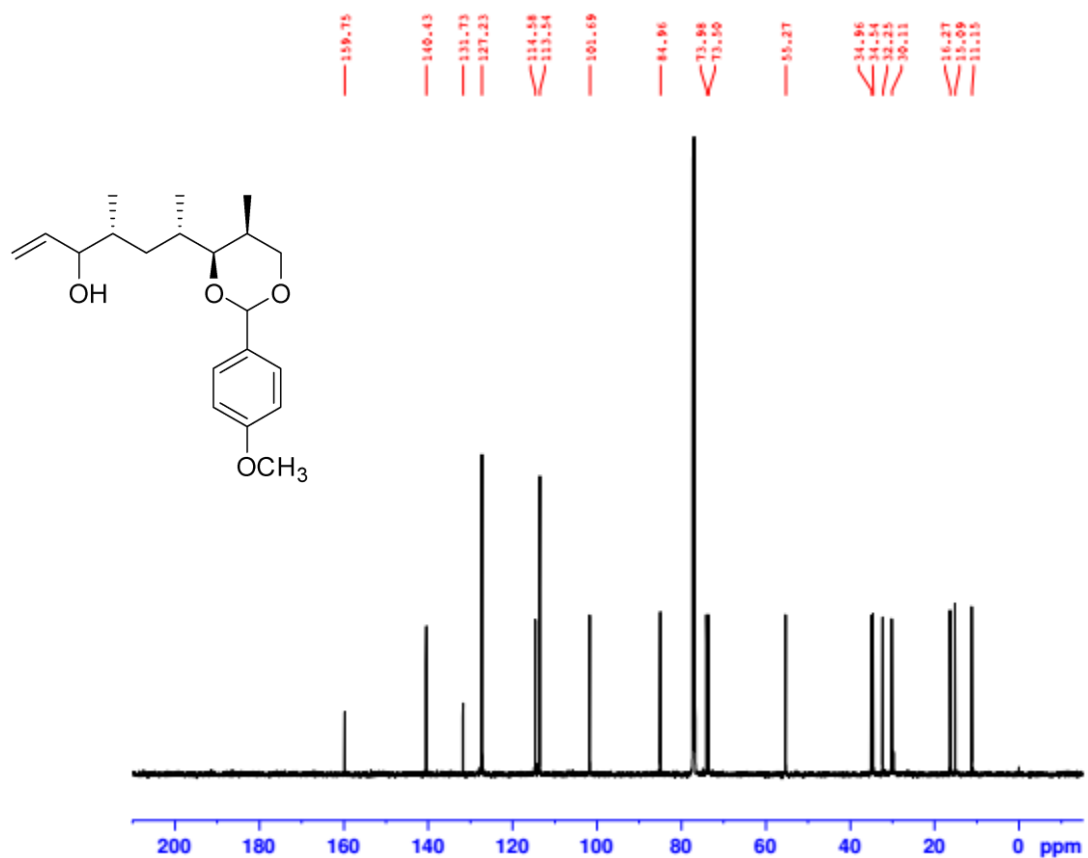
<sup>1</sup>H NMR spectrum of 15 (CDCl<sub>3</sub>, 400 MHz)



<sup>13</sup>C NMR spectrum of 15 (CDCl<sub>3</sub>, 100 MHz)



**<sup>1</sup>H NMR spectrum of 16 (CDCl<sub>3</sub>, 500 MHz)**

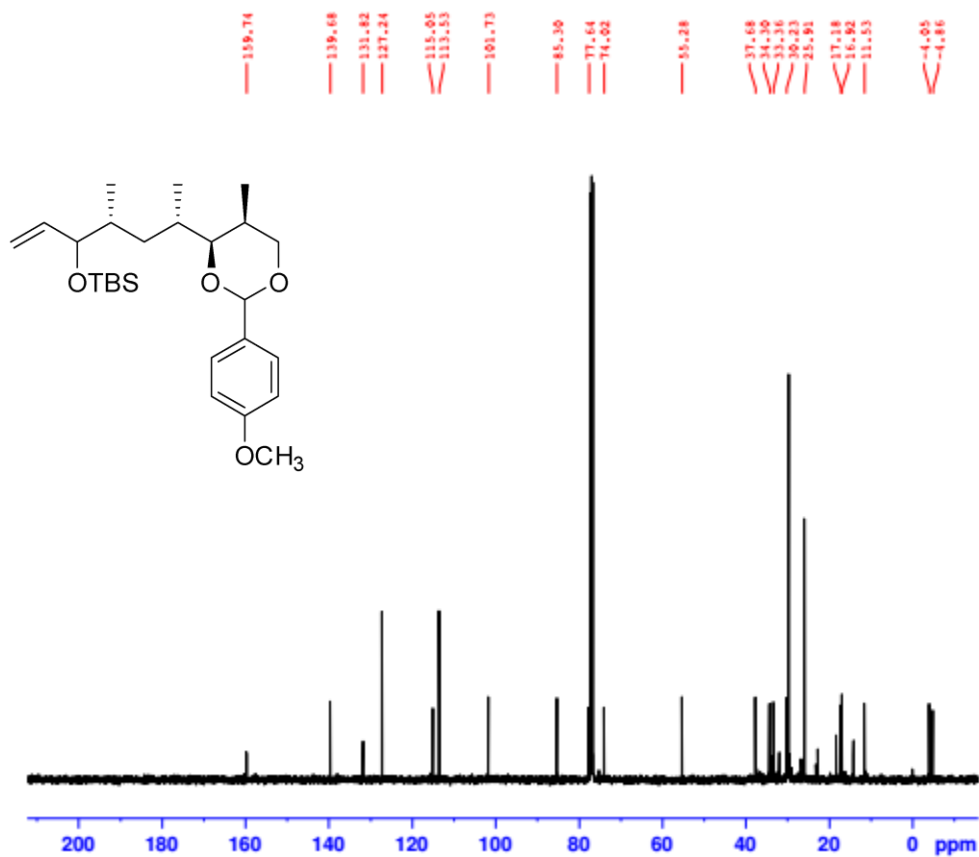


**<sup>13</sup>C NMR spectrum of 16 (CDCl<sub>3</sub>, 125 MHz)**

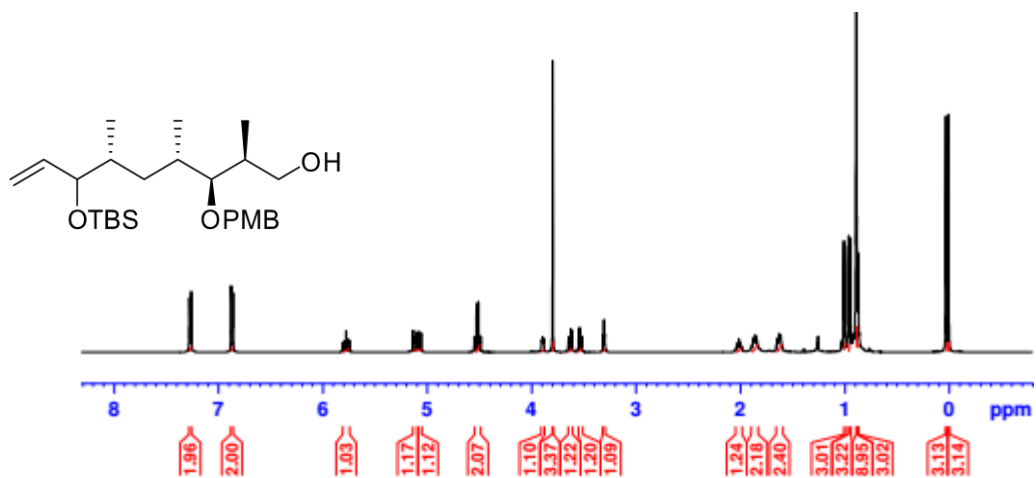




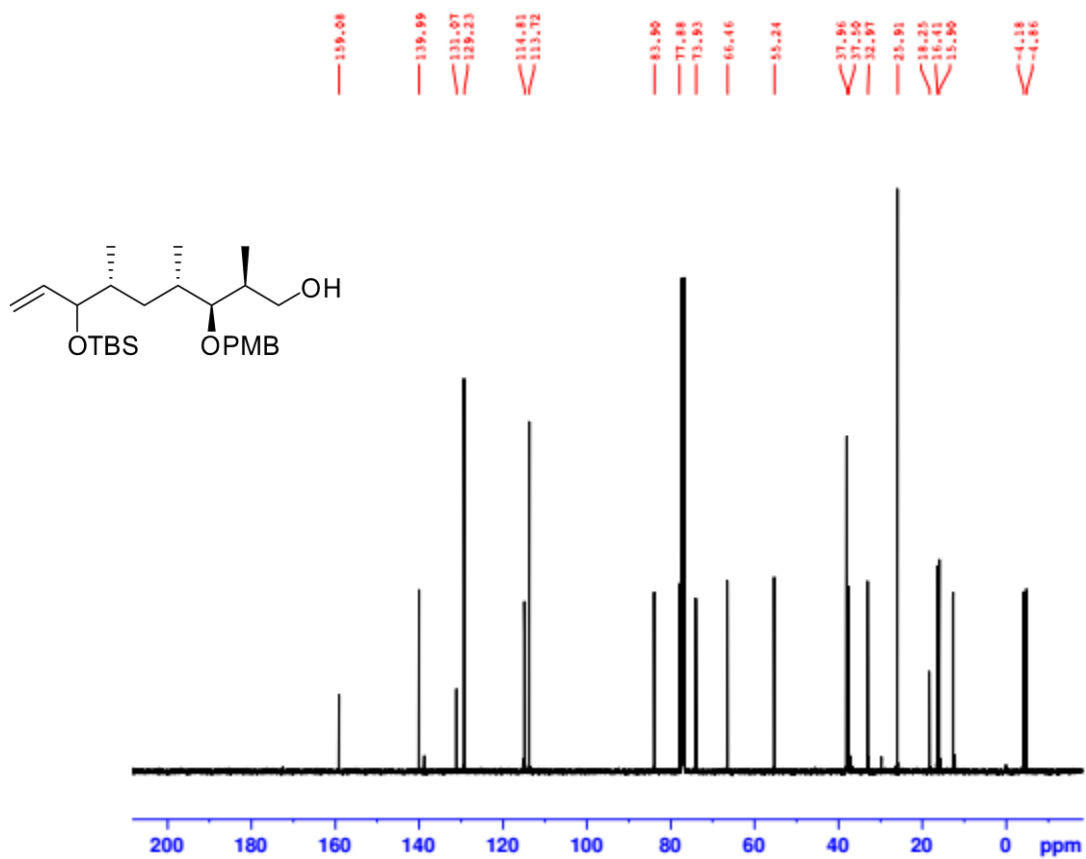
$^1\text{H}$  NMR spectrum of 17 ( $\text{CDCl}_3$ , 400 MHz)



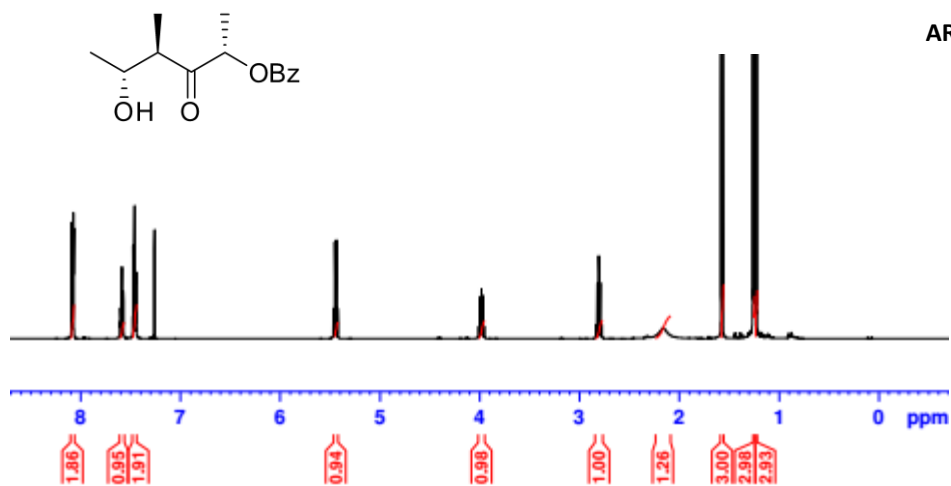
$^{13}\text{C}$  NMR spectrum of 17 ( $\text{CDCl}_3$ , 125 MHz)



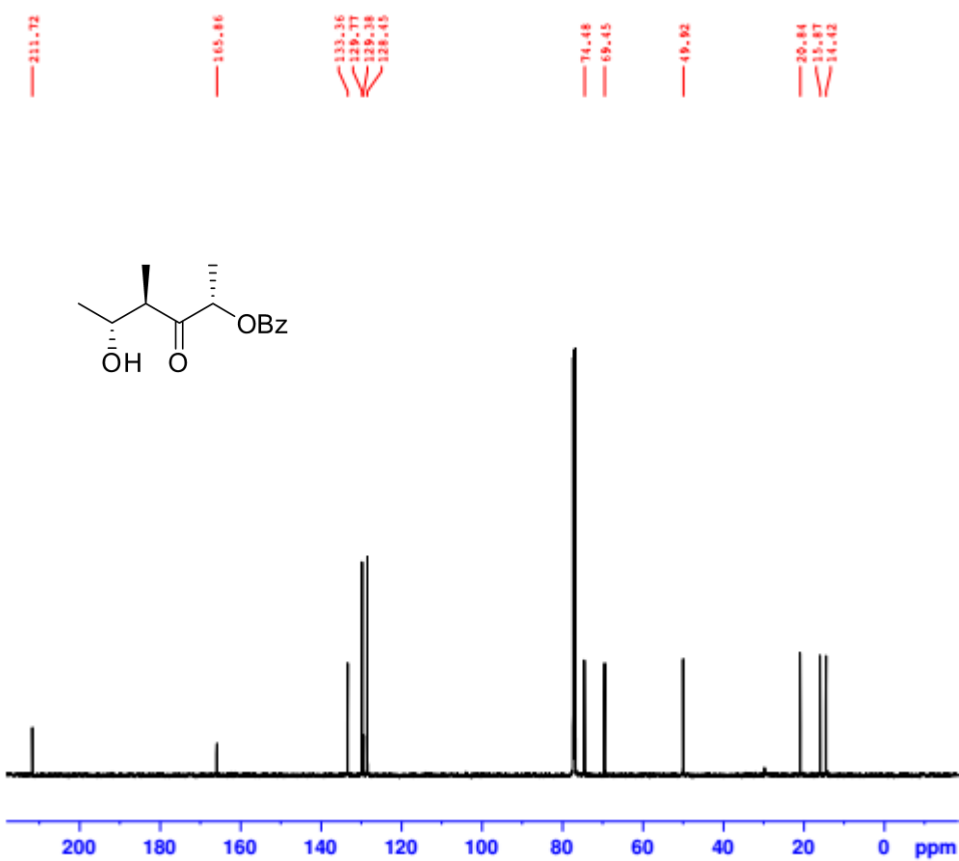
$^1\text{H}$  NMR spectrum of 4a ( $\text{CDCl}_3$ , 500 MHz)



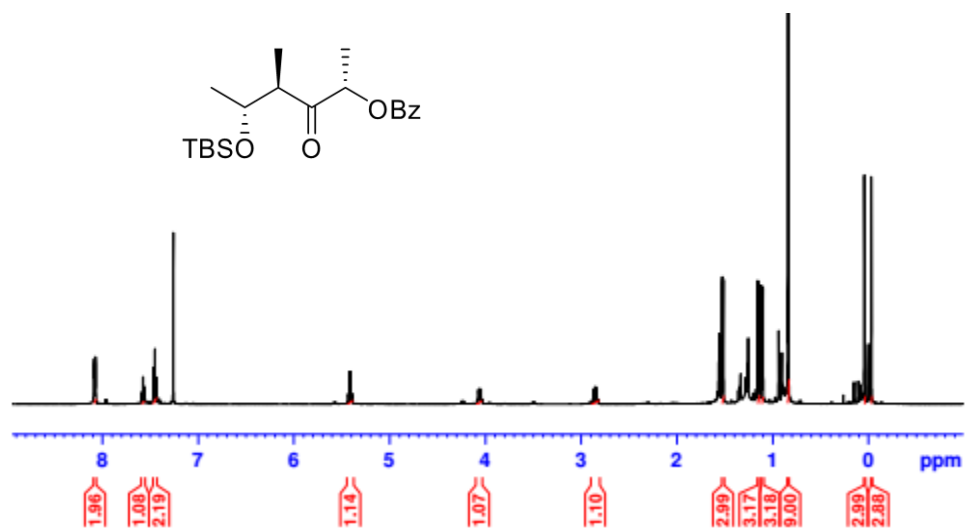
$^{13}\text{C}$  NMR spectrum of 4a ( $\text{CDCl}_3$ , 125 MHz)



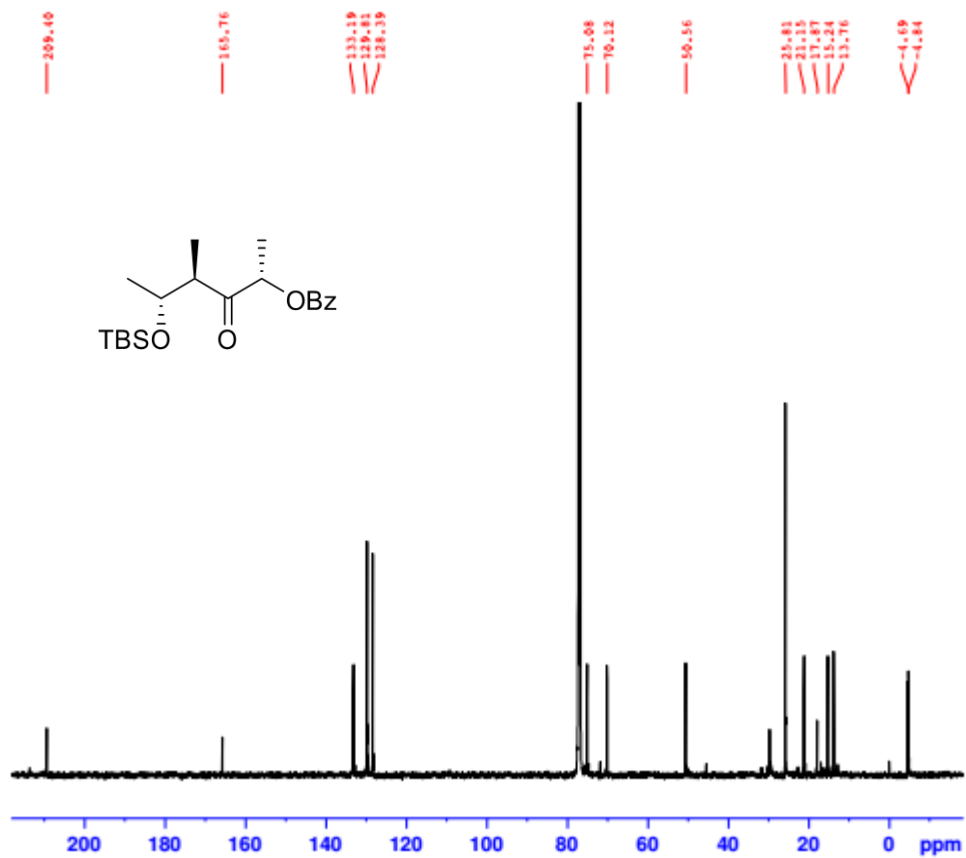
<sup>1</sup>H NMR spectrum of 8 (CDCl<sub>3</sub>, 500 MHz)

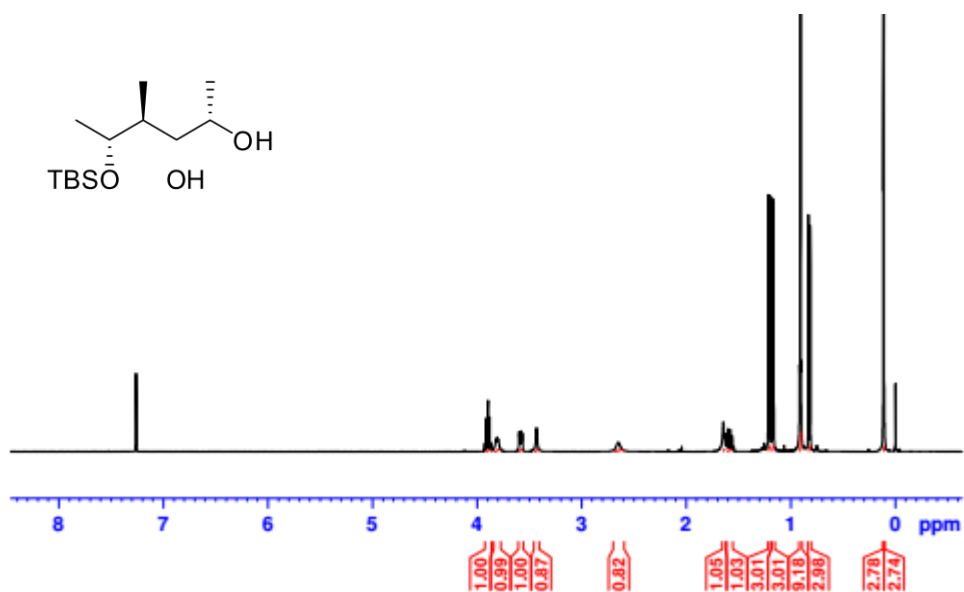
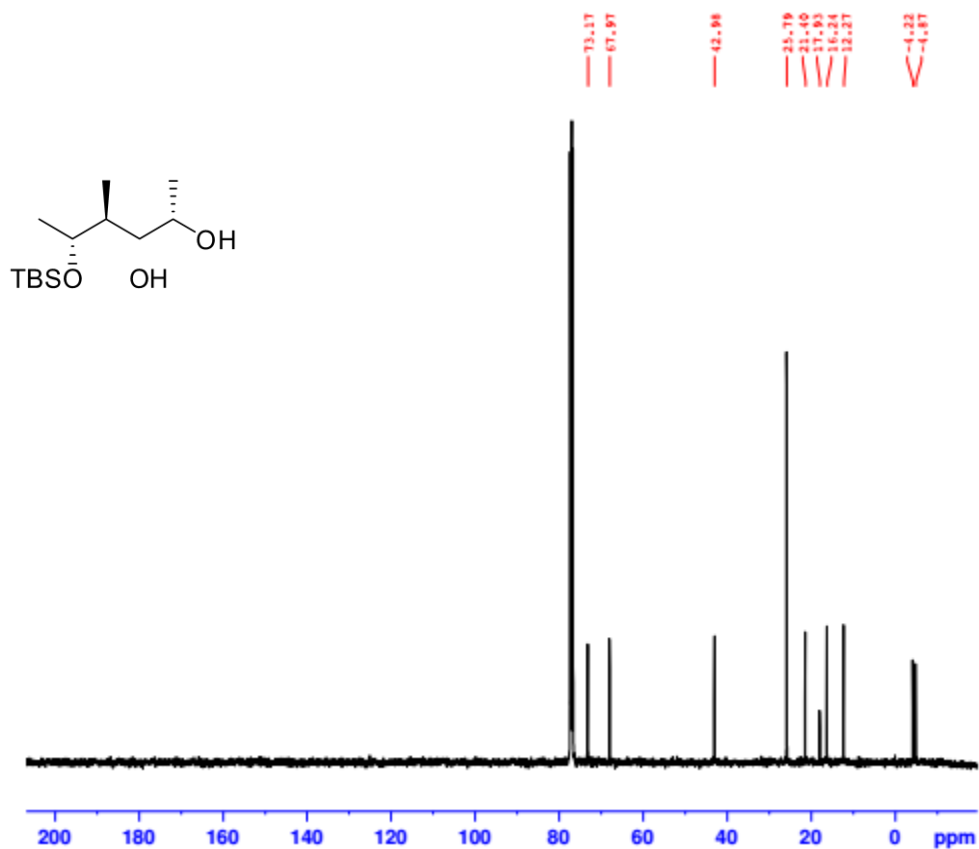


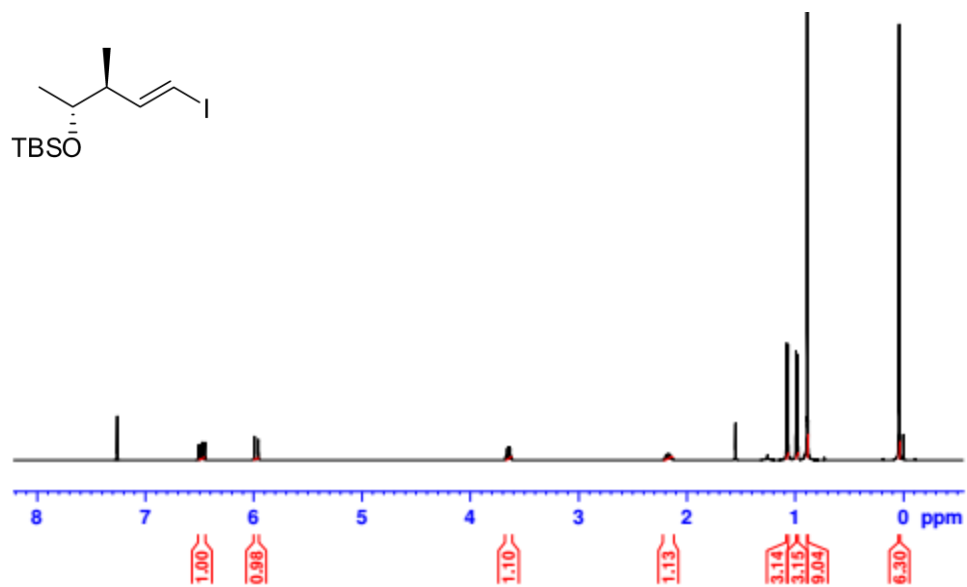
<sup>13</sup>C NMR spectrum of 8 (CDCl<sub>3</sub>, 125 MHz)



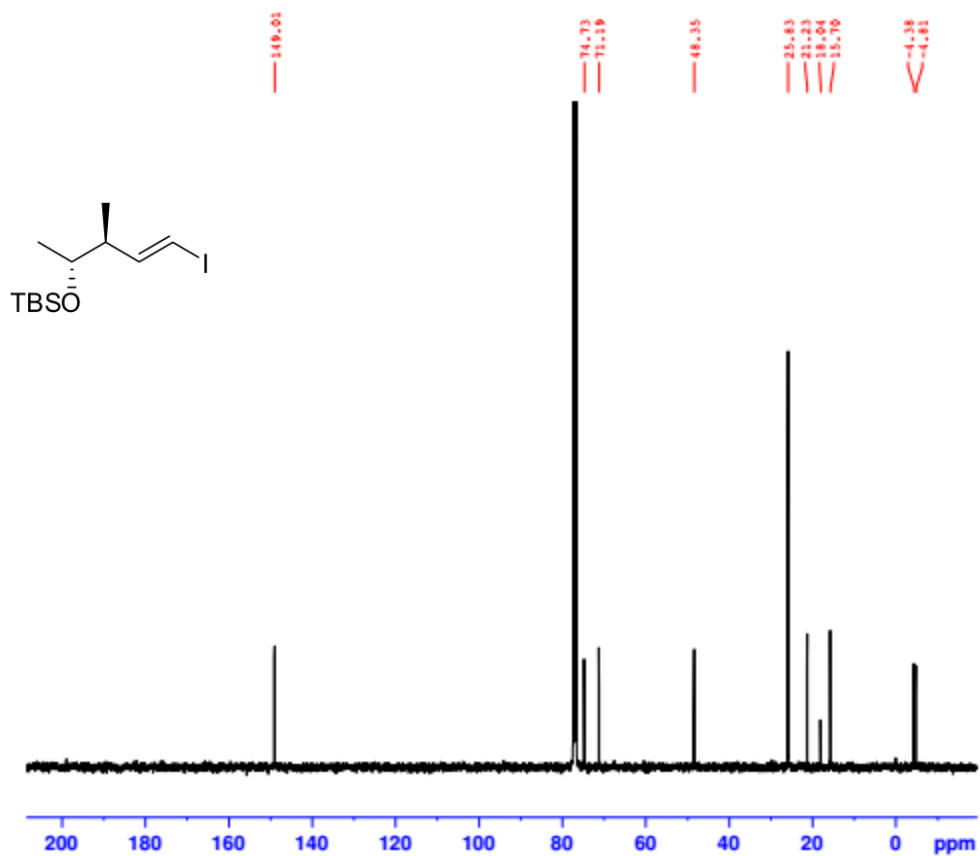
$^1\text{H}$  NMR spectrum of 18 ( $\text{CDCl}_3$ , 500 MHz)



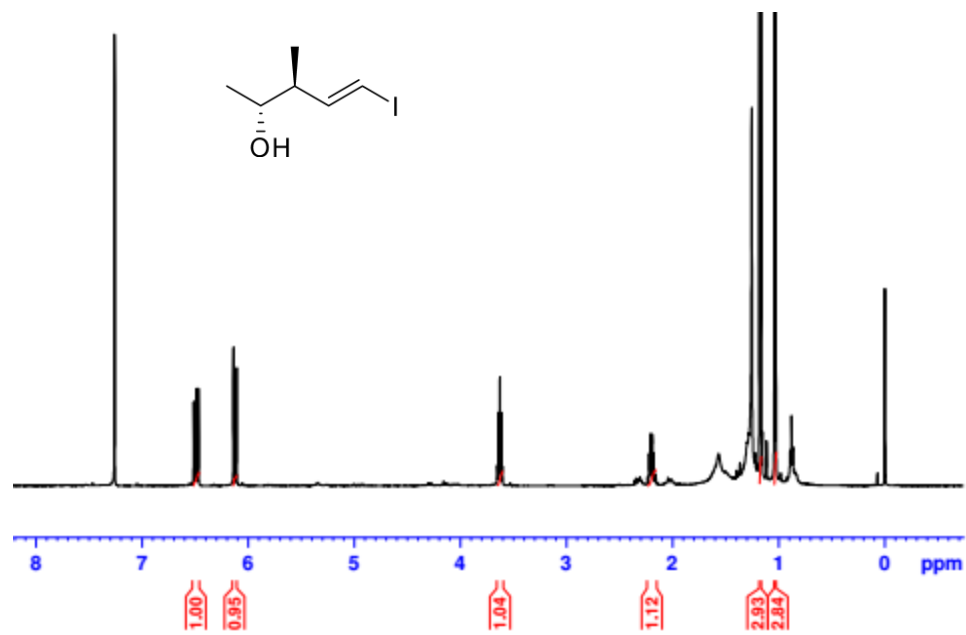
$^{13}\text{C}$  NMR spectrum of 18 ( $\text{CDCl}_3$ , 125 MHz) $^1\text{H}$  NMR spectrum of 19 ( $\text{CDCl}_3$ , 400 MHz) $^{13}\text{C}$  NMR spectrum of 19 ( $\text{CDCl}_3$ , 100 MHz)



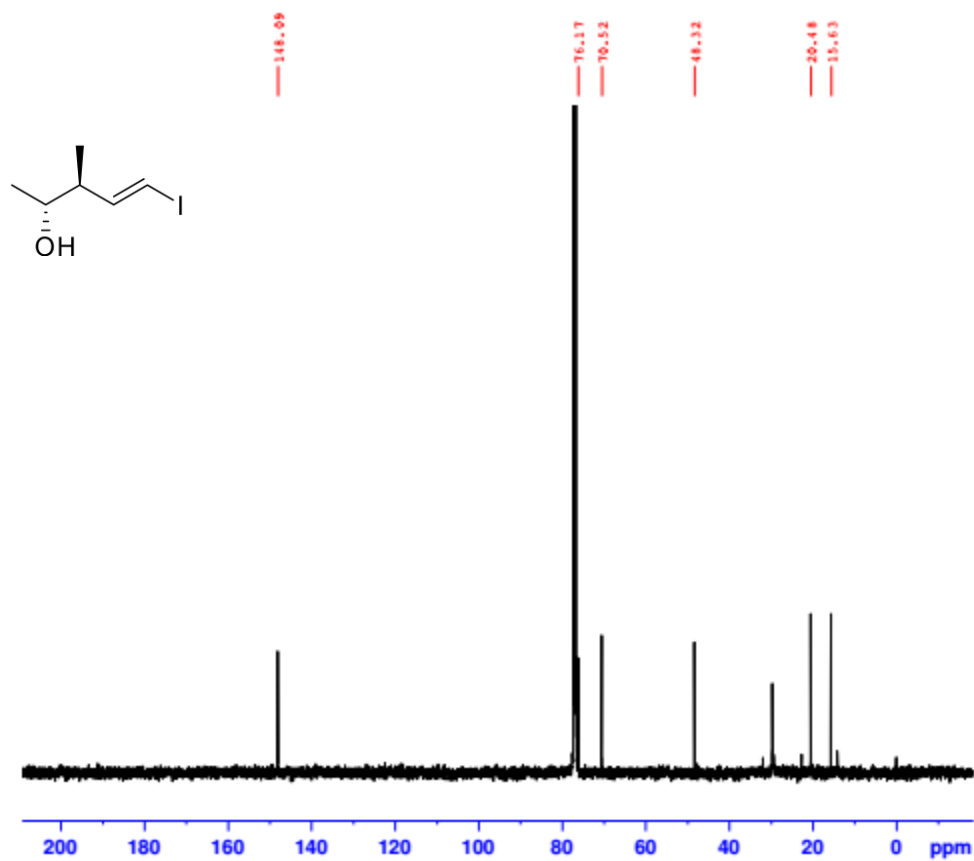
<sup>1</sup>H NMR spectrum of 20 (CDCl<sub>3</sub>, 400 MHz)



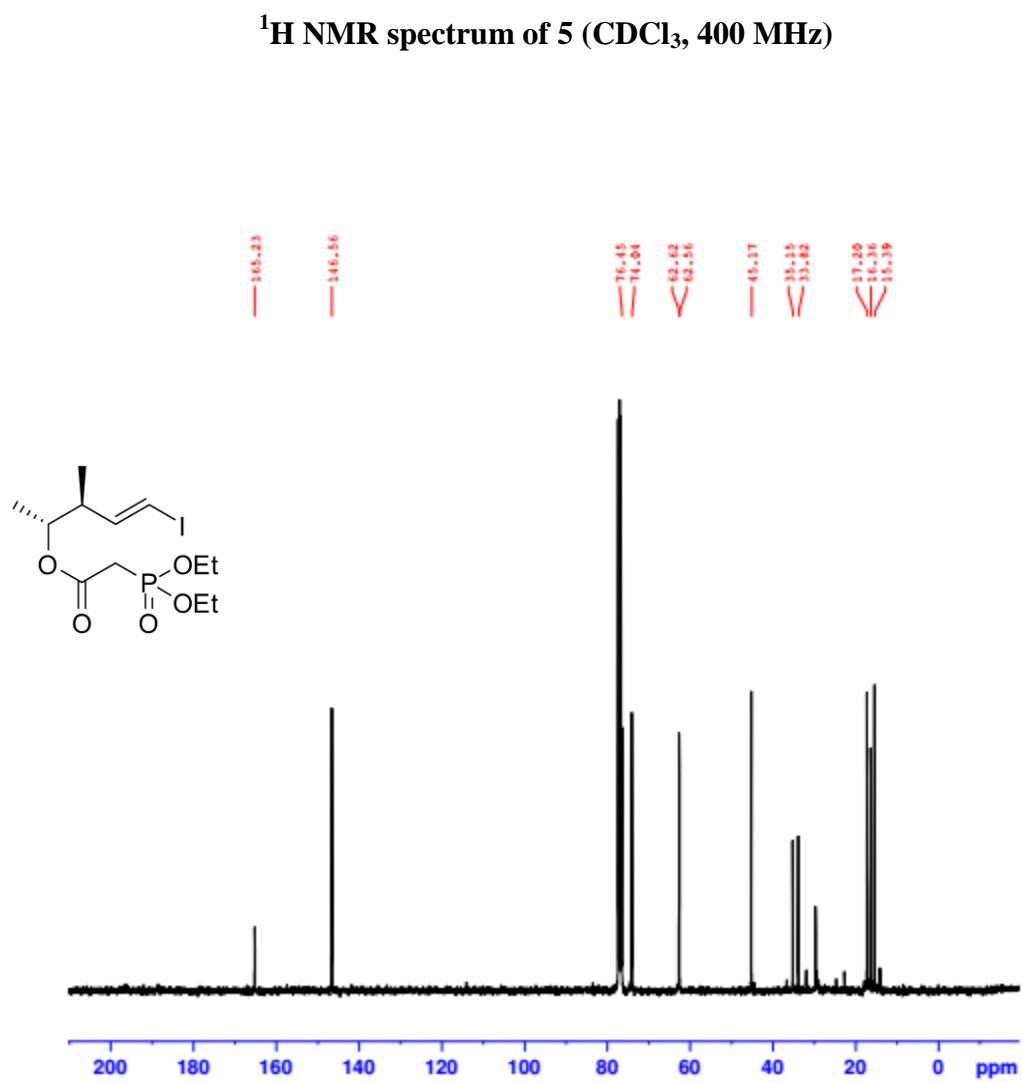
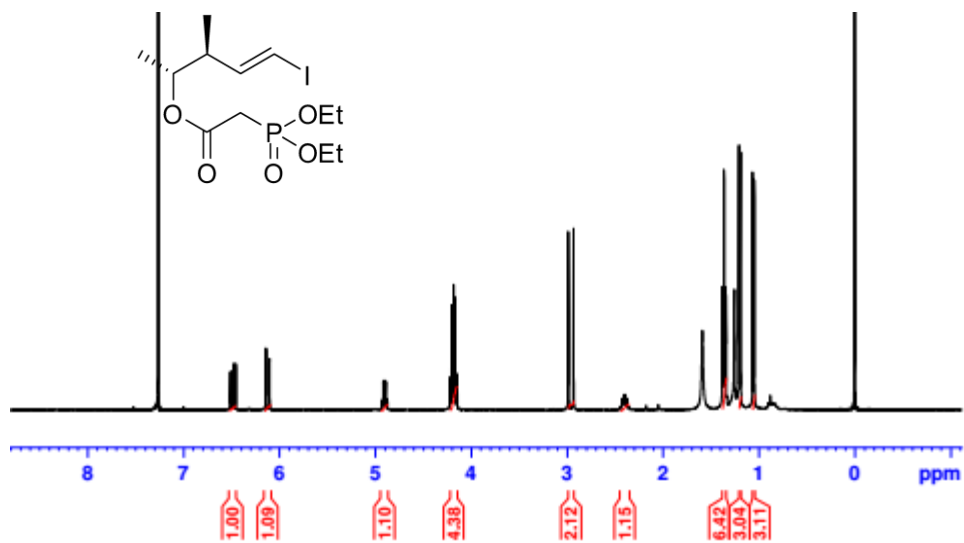
<sup>13</sup>C NMR spectrum of 20 (CDCl<sub>3</sub>, 100 MHz)



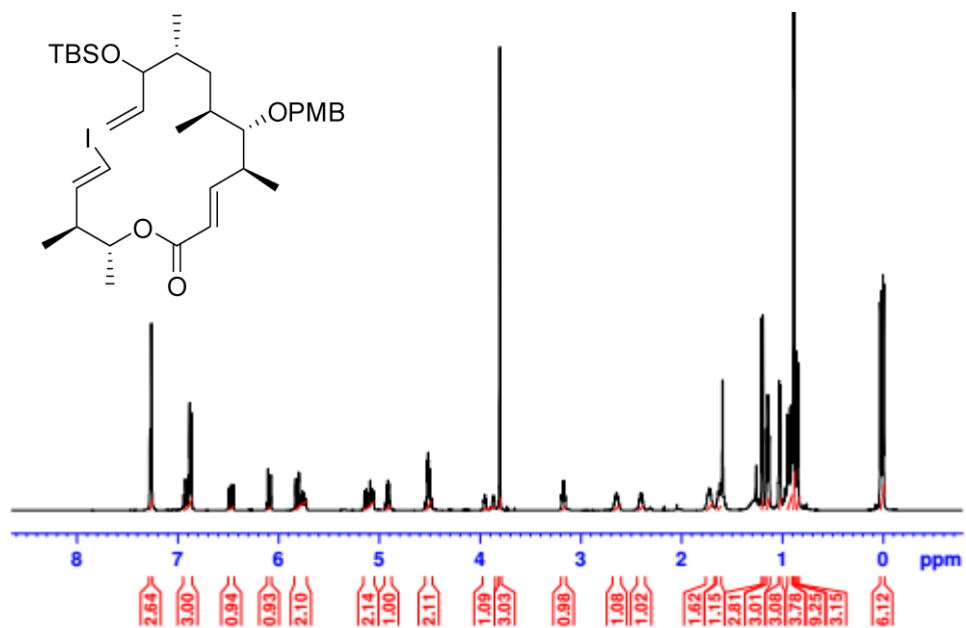
<sup>1</sup>H NMR spectrum of 21 (CDCl<sub>3</sub>, 500 MHz)



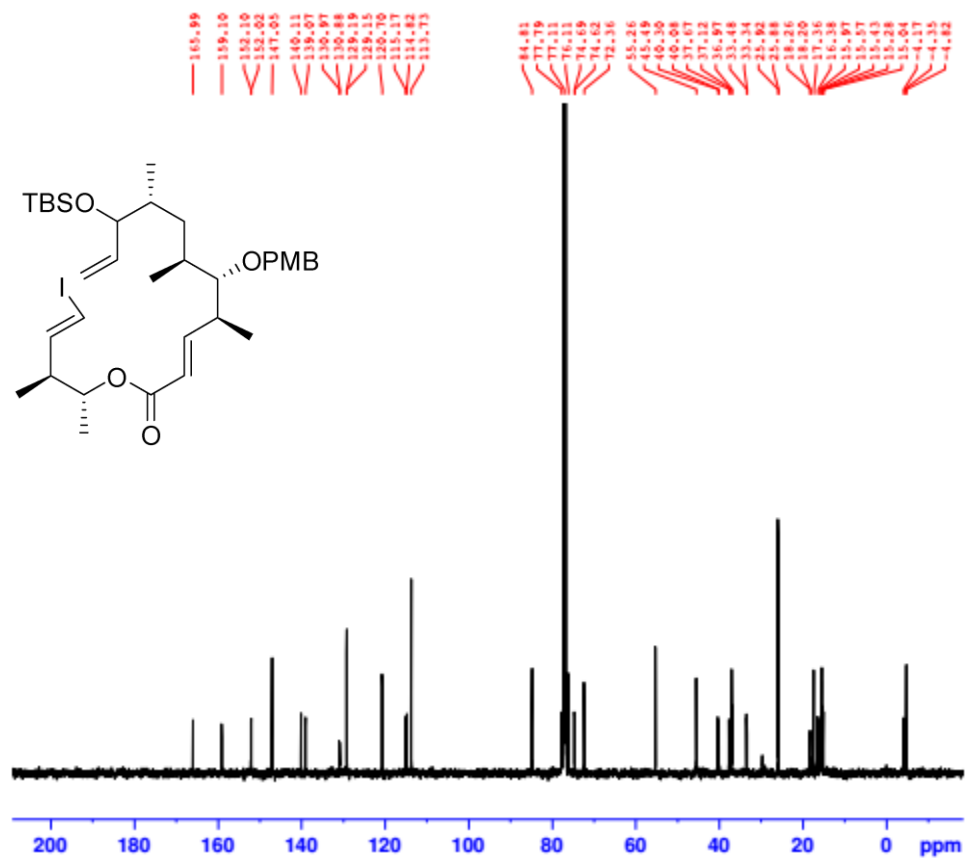
<sup>13</sup>C NMR spectrum of 21 (CDCl<sub>3</sub>, 125 MHz)







**<sup>1</sup>H NMR spectrum of 3 (CDCl<sub>3</sub>, 500 MHz)**



**<sup>13</sup>C NMR spectrum of 3 (CDCl<sub>3</sub>, 125 MHz)**