

## Supporting Information

### Synthesis of Optically-pure $\gamma$ PNA Monomers: A Comparative Study

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**Figure 1S.**  $^{19}\text{F}$ -NMR of MTPA-derivatized D- and L-alaninol intermediates.

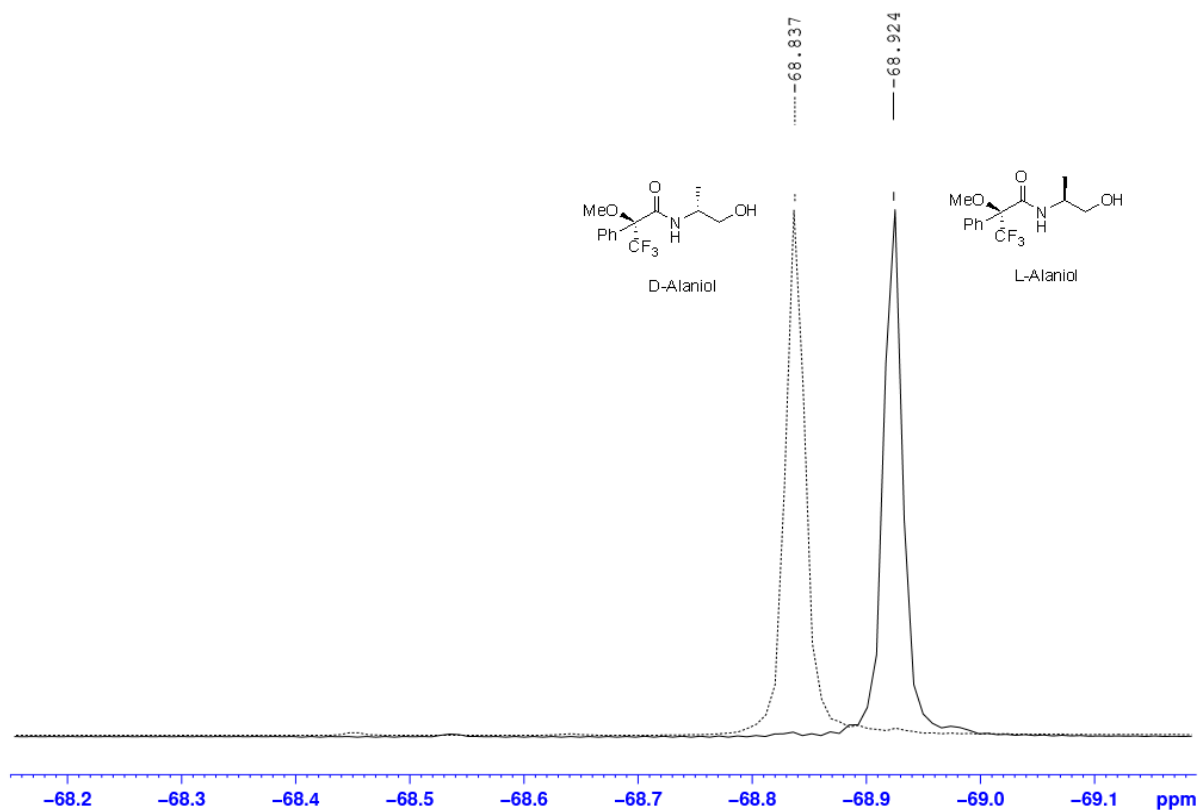


Figure2S.  $^1\text{H}$  NMR Spectrum of compound **2a** ( $\text{CDCl}_3$ , 300 MHz)

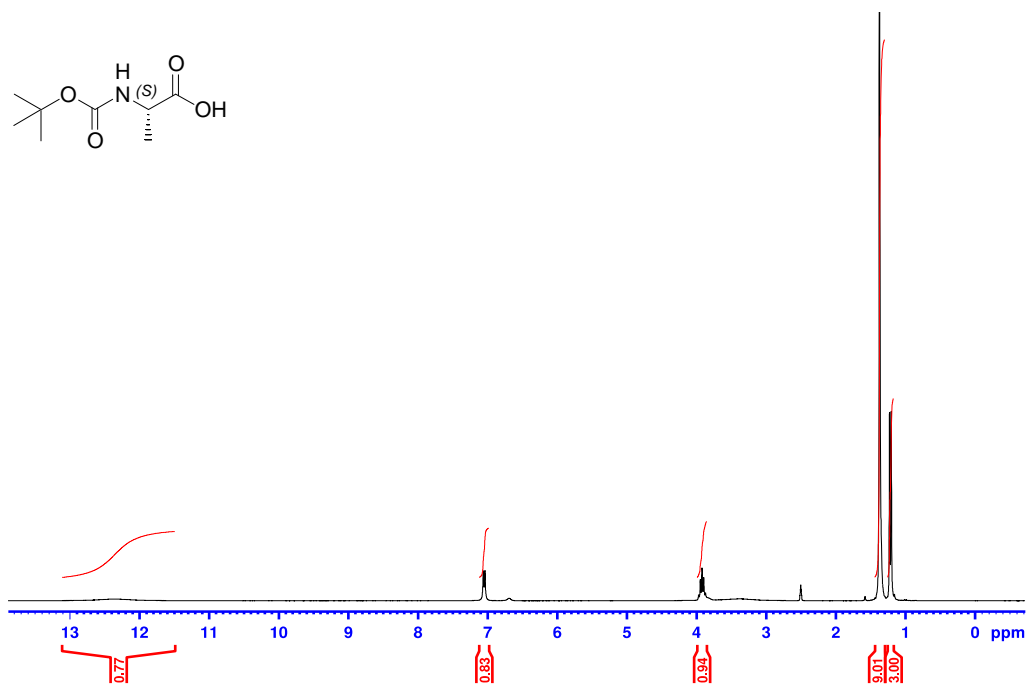
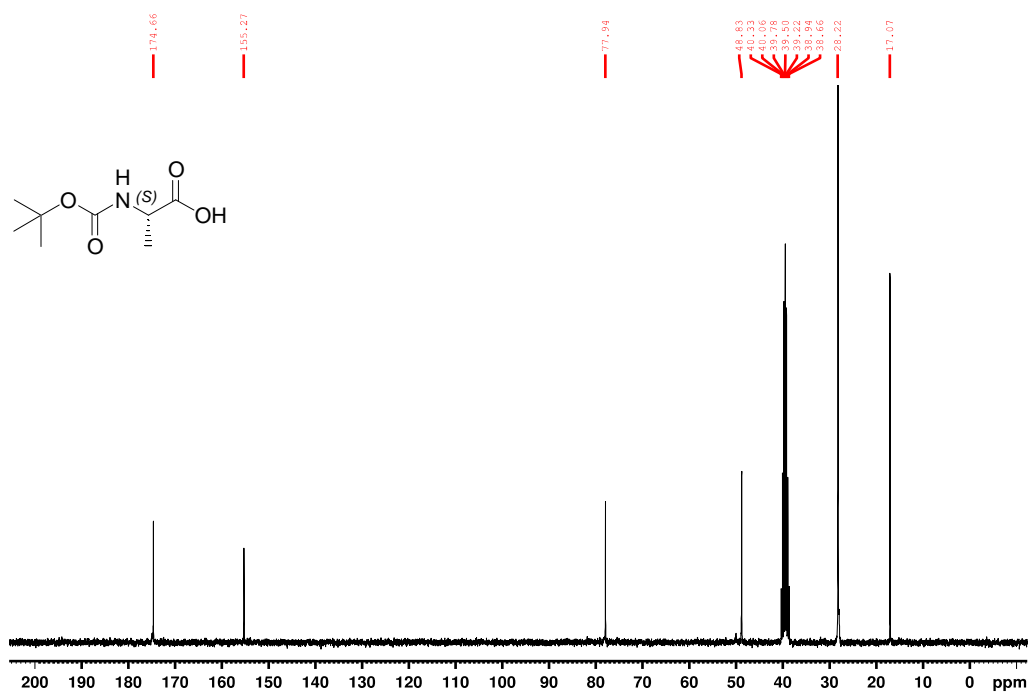
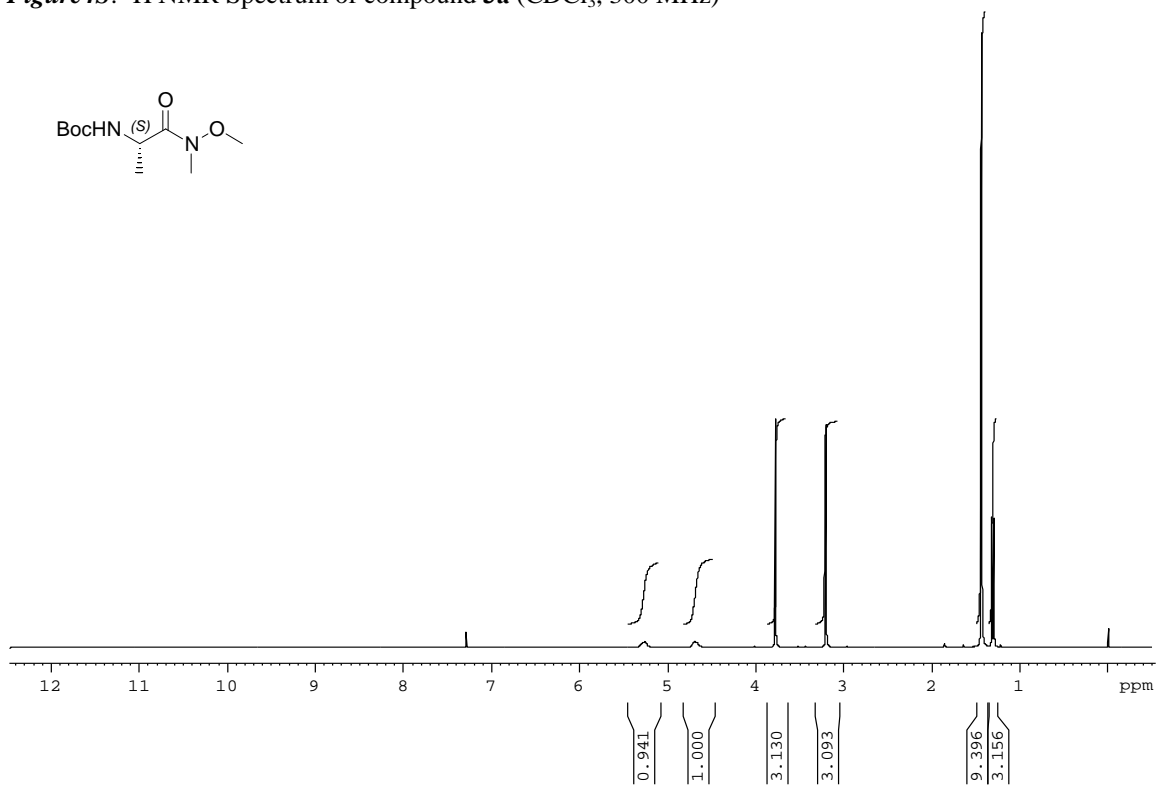


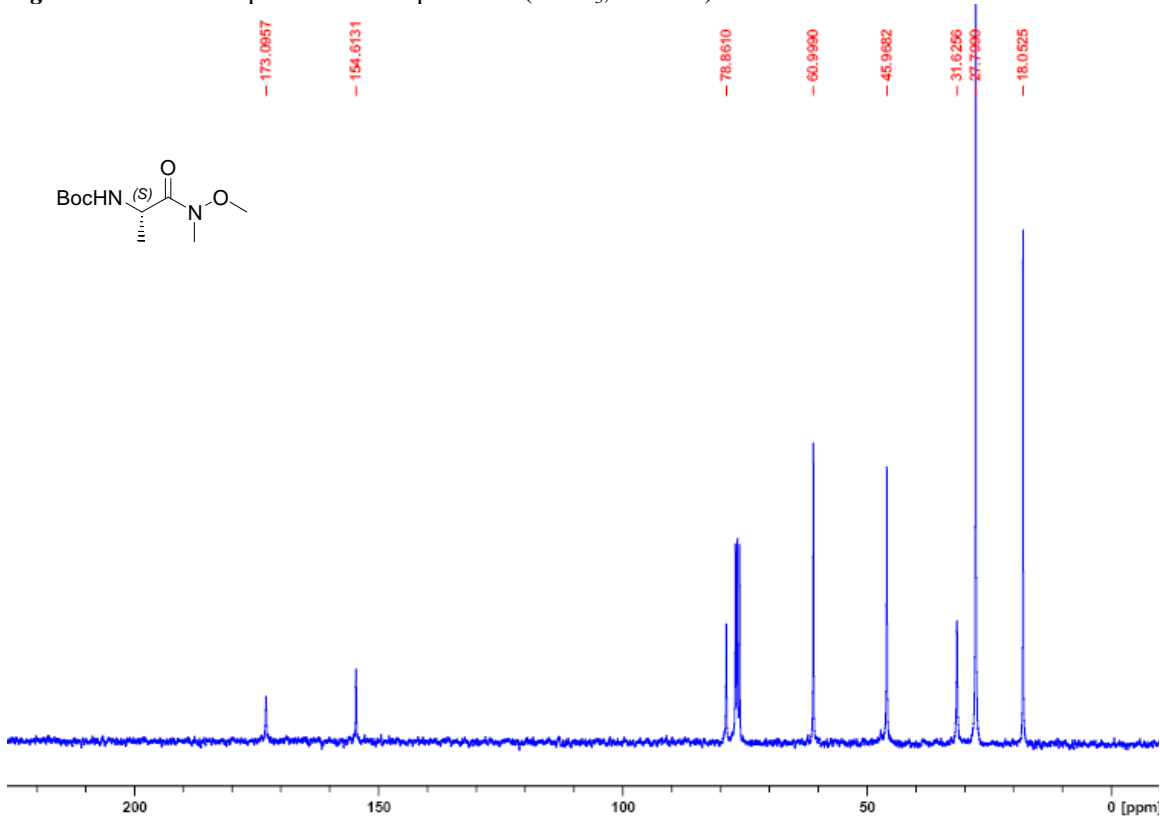
Figure3S.  $^{13}\text{C}$  NMR Spectrum of compound **2a** ( $\text{DMSO-d}_6$ , 75 MHz)



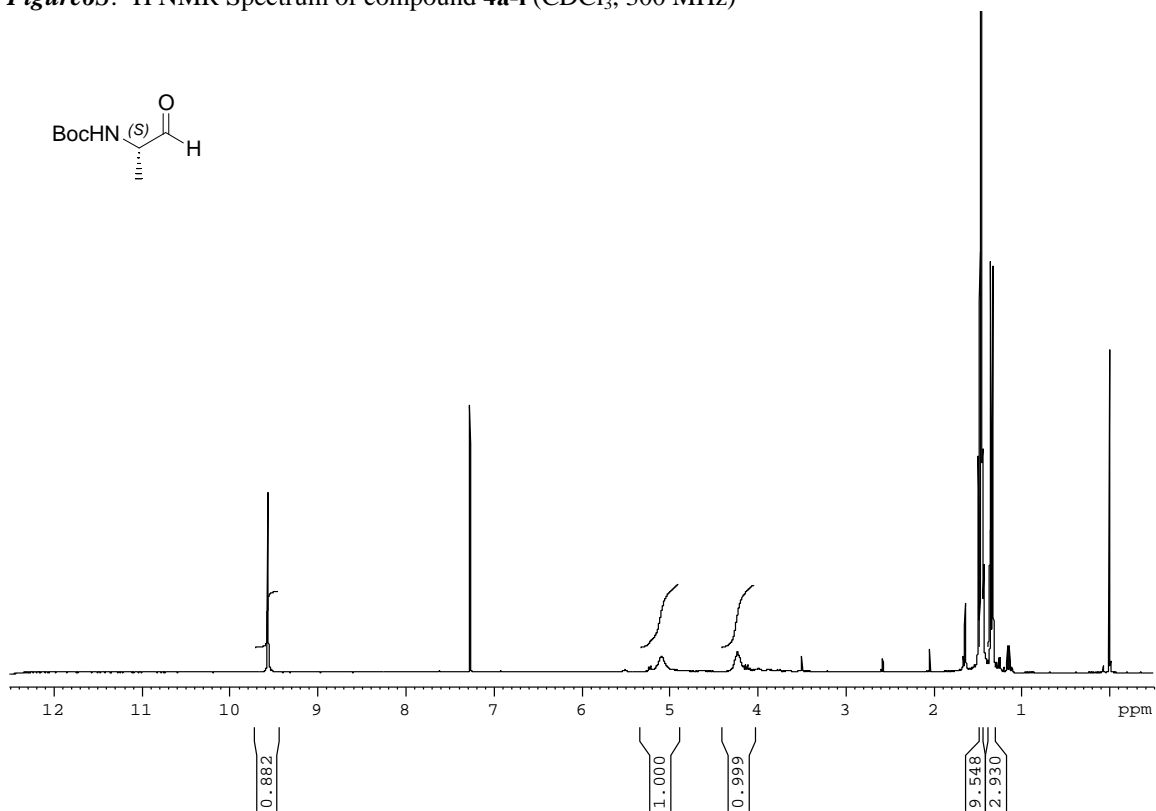
**Figure4S.**  $^1\text{H}$  NMR Spectrum of compound **3a** ( $\text{CDCl}_3$ , 300 MHz)



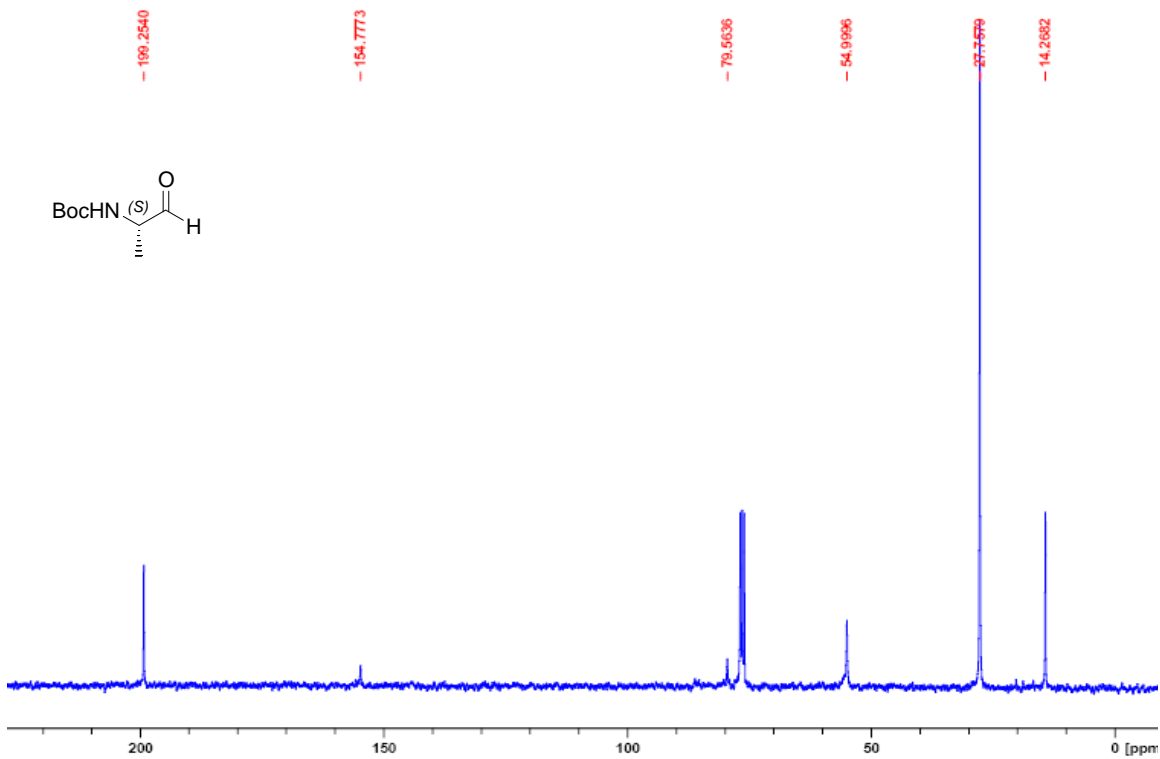
**Figure5S.**  $^{13}\text{C}$  NMR Spectrum of compound **3a** ( $\text{CDCl}_3$ , 75 MHz)



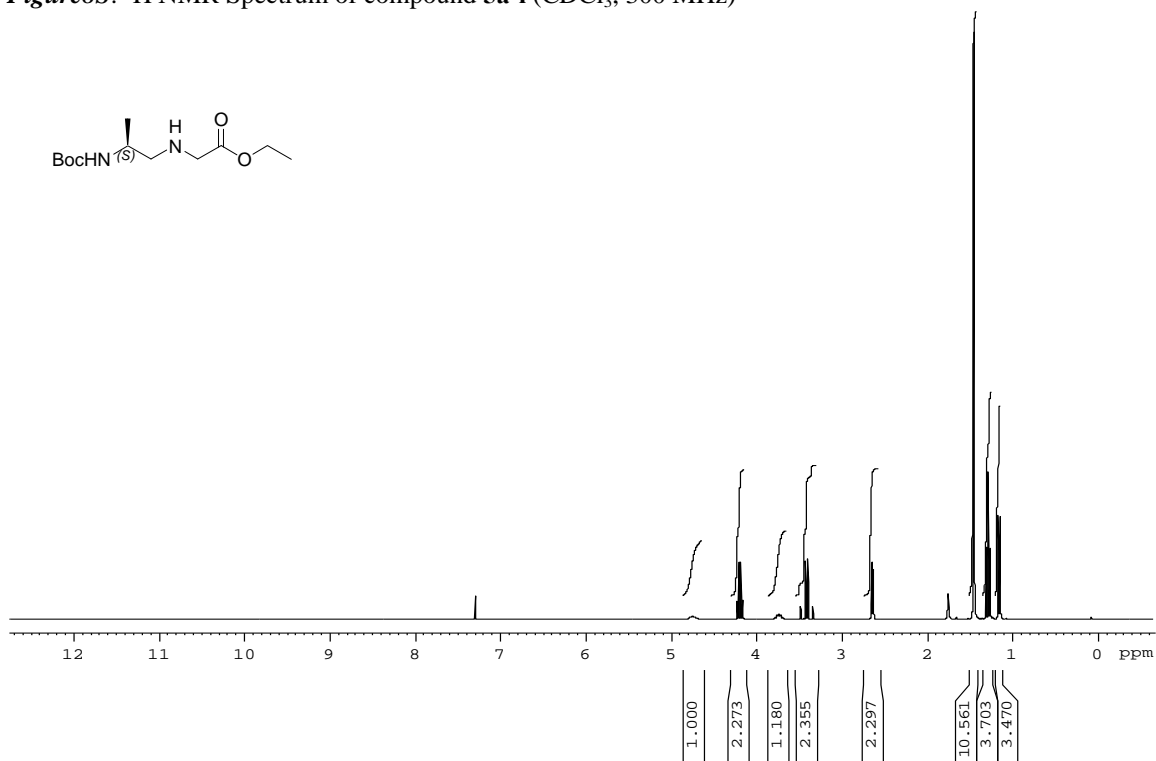
**Figure6S.**  $^1\text{H}$  NMR Spectrum of compound **4a-i** ( $\text{CDCl}_3$ , 300 MHz)



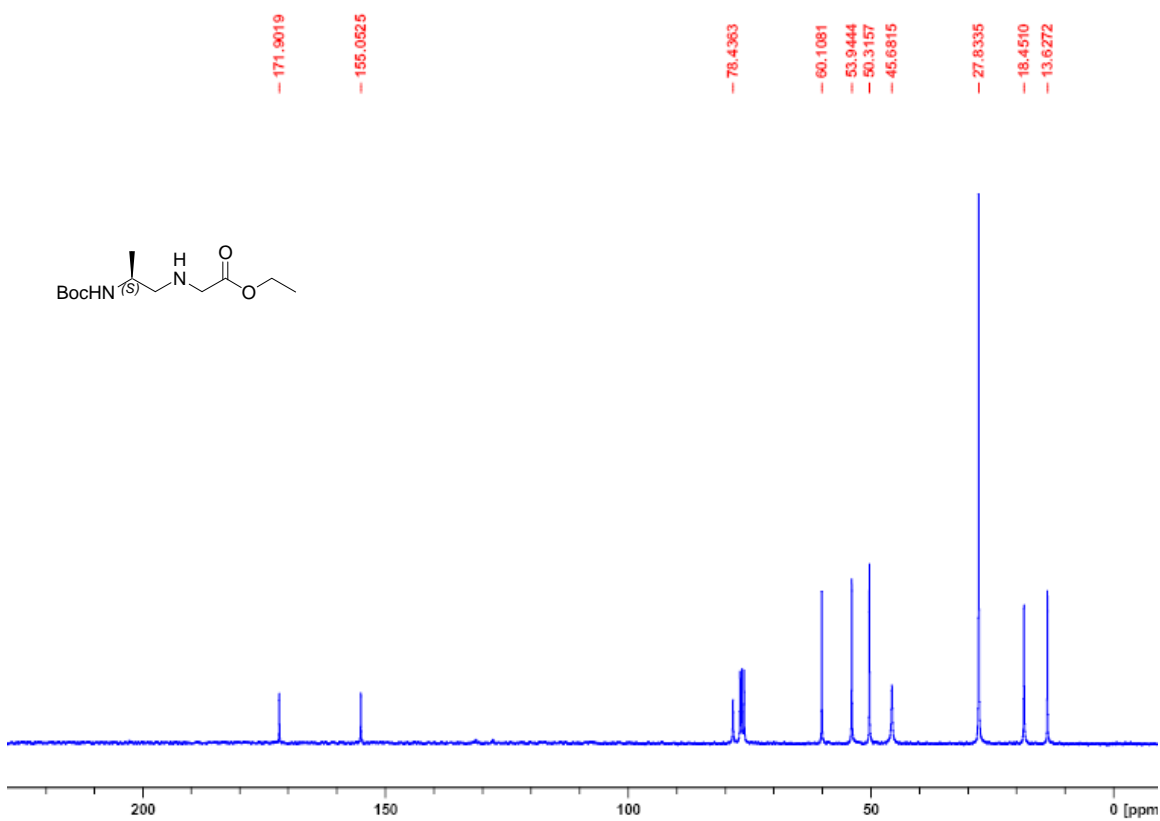
**Figure7S.**  $^{13}\text{C}$  NMR Spectrum of compound **4a-i** ( $\text{CDCl}_3$ , 75 MHz)



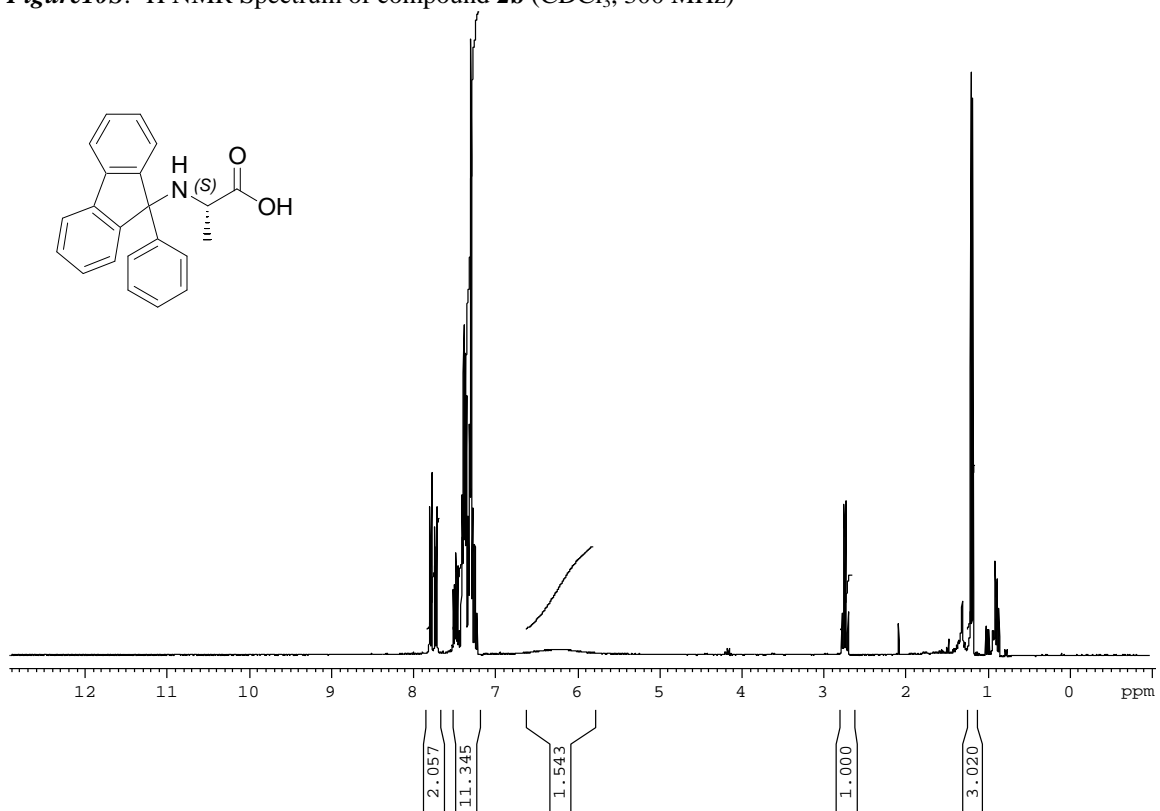
**Figure8S.**  $^1\text{H}$  NMR Spectrum of compound **5a-i** ( $\text{CDCl}_3$ , 300 MHz)



**Figure9S.**  $^{13}\text{C}$  NMR Spectrum of compound **5a-i** ( $\text{CDCl}_3$ , 75 MHz)



**Figure 10S.**  $^1\text{H}$  NMR Spectrum of compound **2b** ( $\text{CDCl}_3$ , 300 MHz)



**Figure 11S.**  $^{13}\text{C}$  NMR Spectrum of compound **2b** ( $\text{DMSO-d}_6$ , 75 MHz)

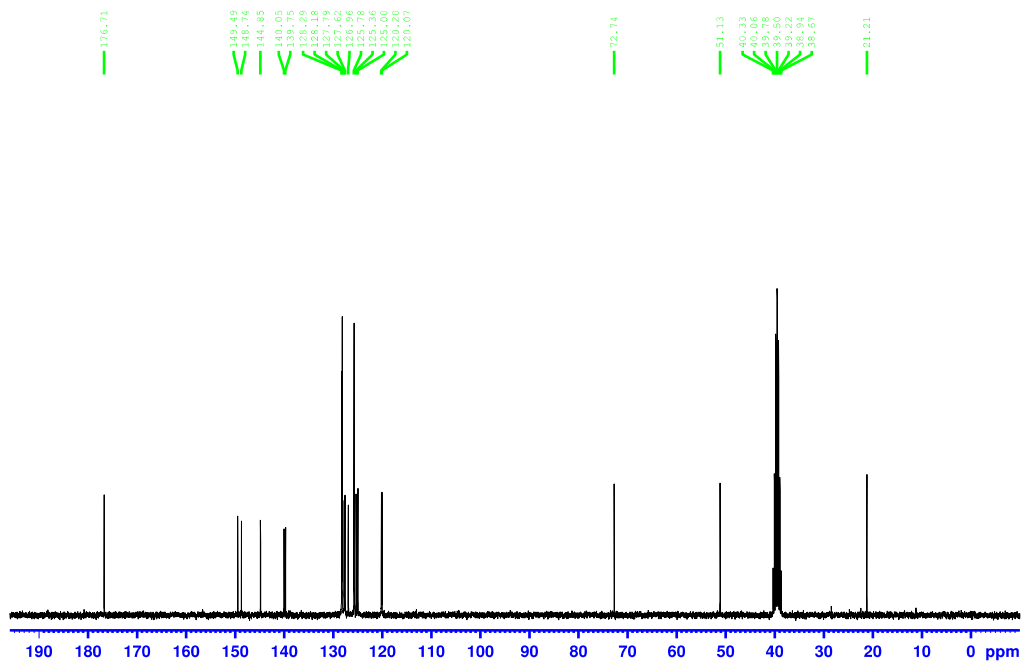


Figure 12S. <sup>1</sup>H NMR Spectrum of compound **3b** (CDCl<sub>3</sub>, 300 MHz)

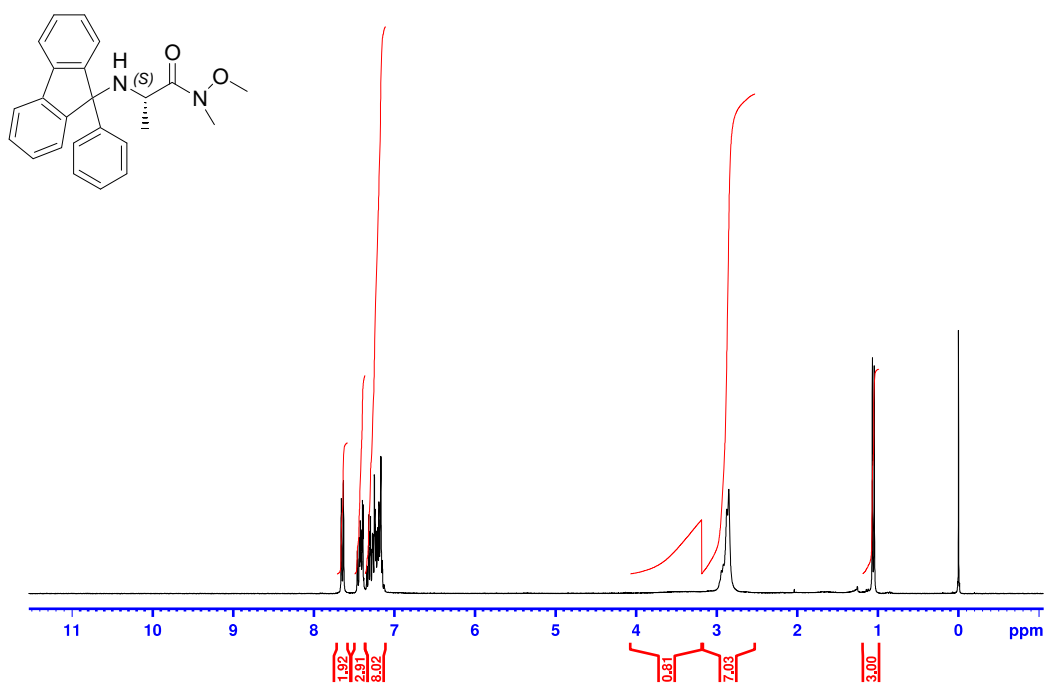


Figure 13S. <sup>13</sup>C NMR Spectrum of compound **3b** (CDCl<sub>3</sub>, 75 MHz)

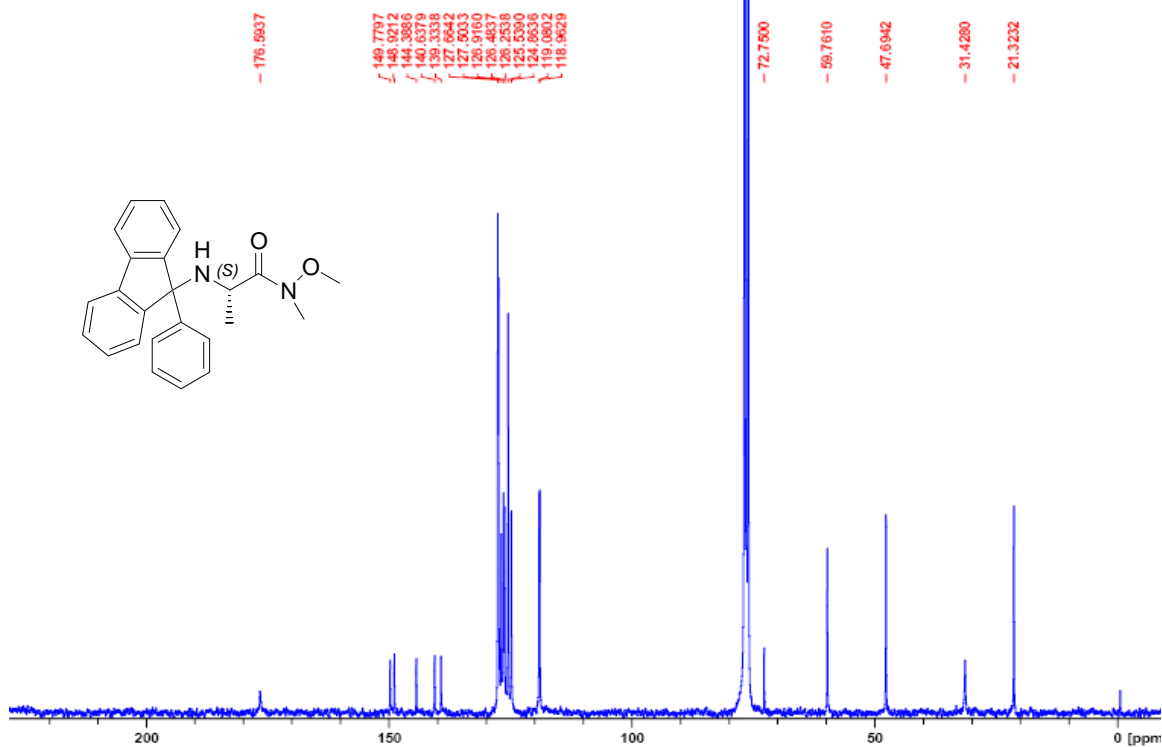




Figure 14S.  $^1\text{H}$  NMR Spectrum of compound **4b** ( $\text{CDCl}_3$ , 300 MHz)

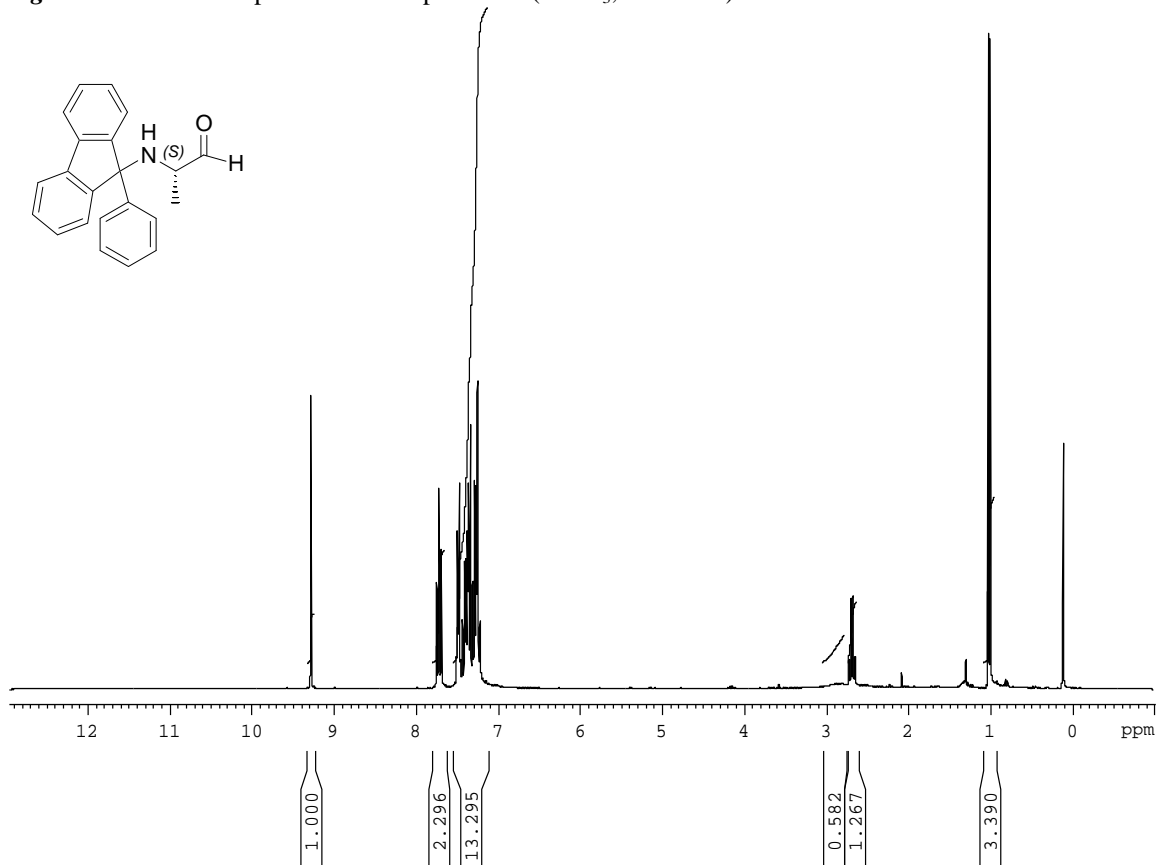


Figure15S. <sup>1</sup>H NMR Spectrum of compound 5b (CDCl<sub>3</sub>, 300 MHz)

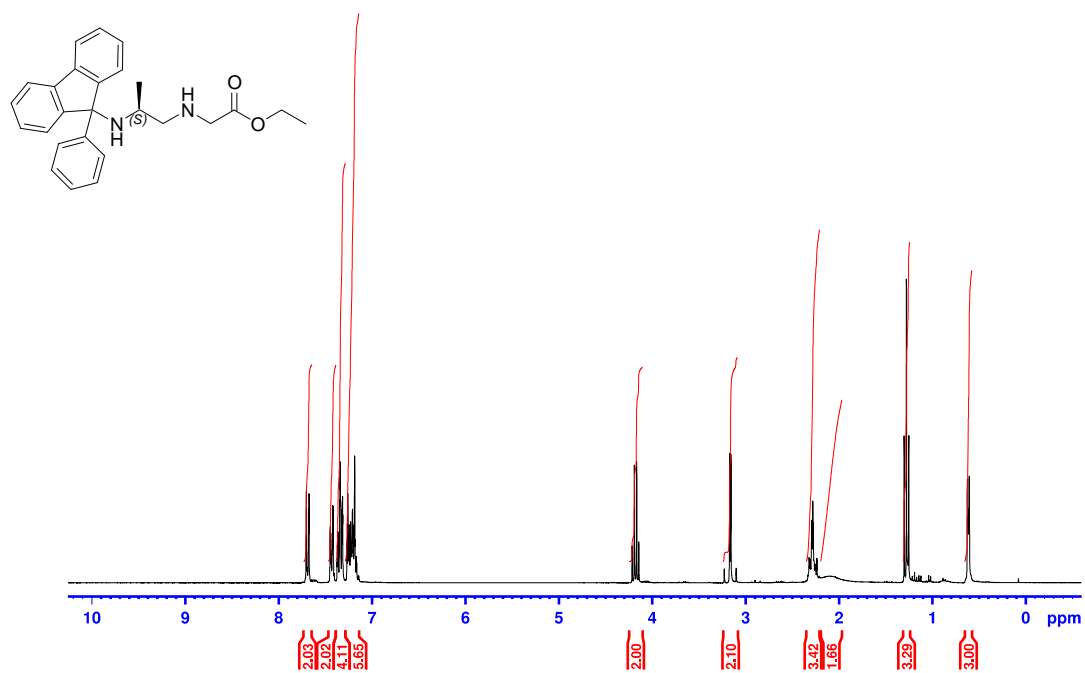


Figure16S. <sup>13</sup>C NMR Spectrum of compound 5b (CDCl<sub>3</sub>, 75 MHz)

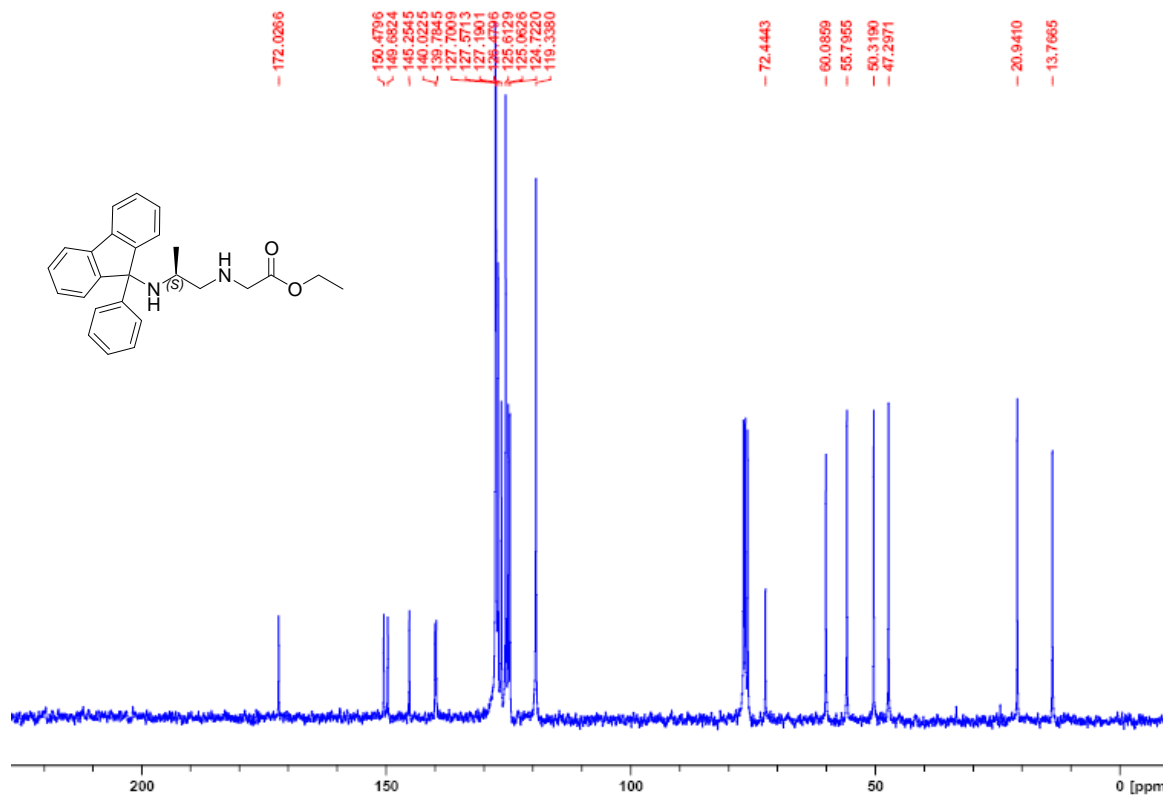


Figure 17S.  $^1\text{H}$  NMR Spectrum of compound **6** ( $\text{CDCl}_3$ , 300 MHz)

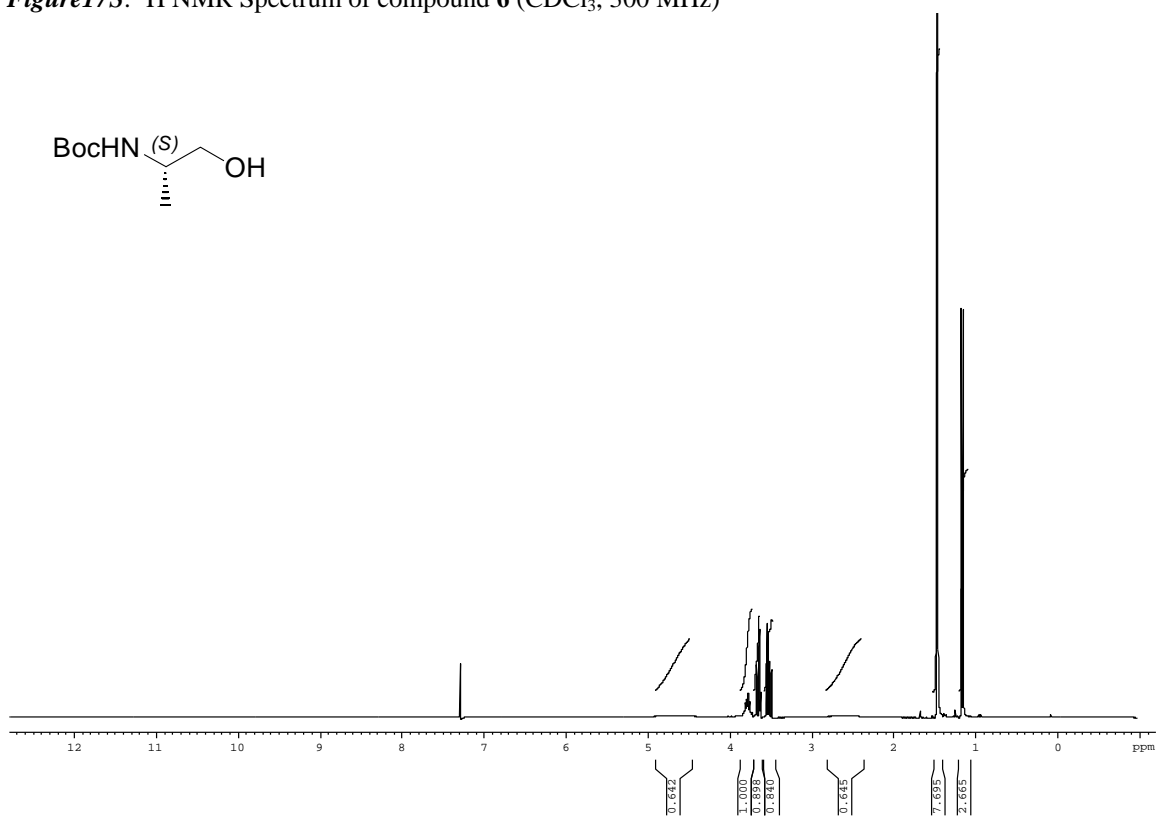


Figure 18S.  $^{13}\text{C}$  NMR Spectrum of compound **6** ( $\text{CDCl}_3$ , 75 MHz)

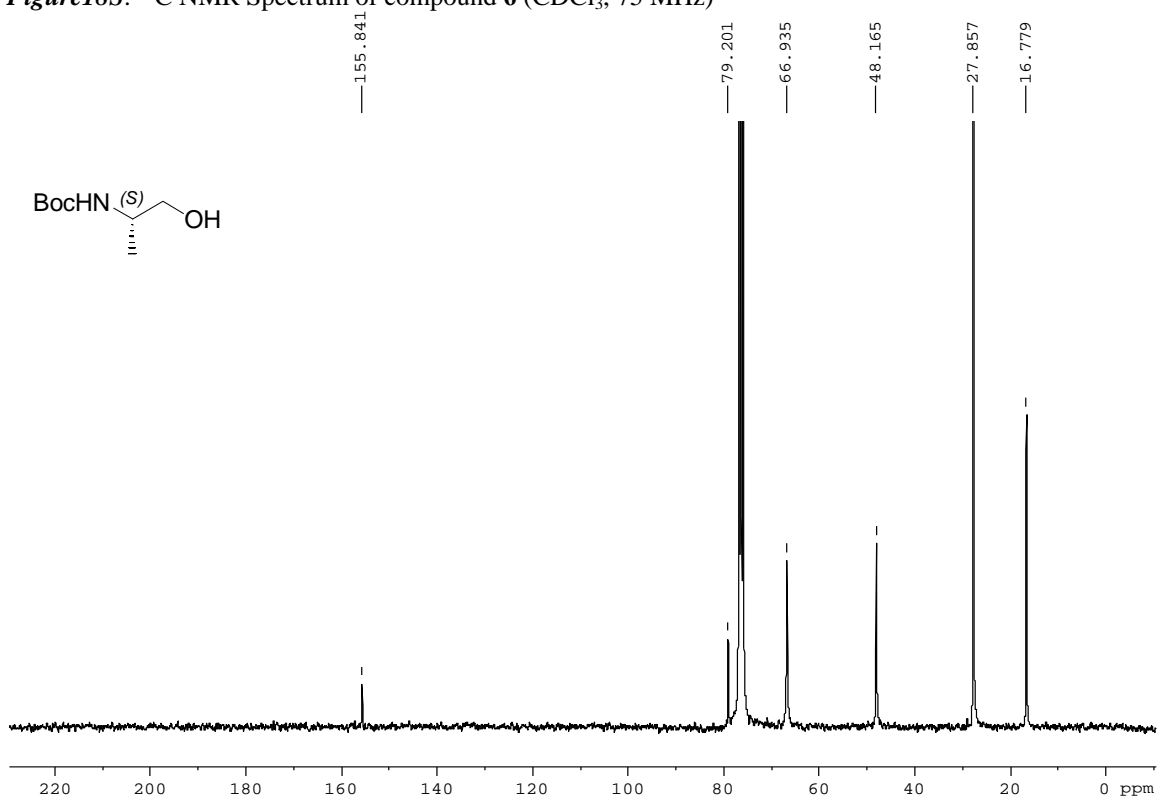


Figure19S.  $^1\text{H}$  NMR of compound **8** ( $\text{CDCl}_3$ , 300 MHz)

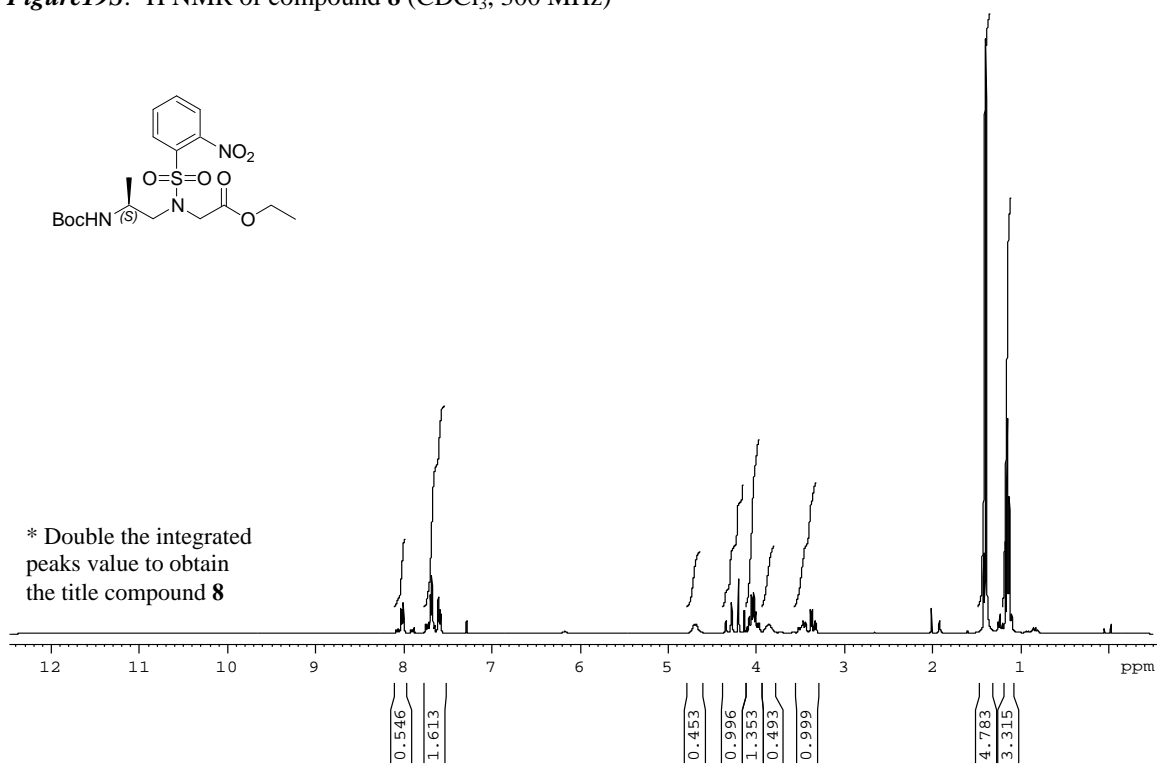


Figure20S.  $^{13}\text{C}$  NMR of compound **8** ( $\text{CDCl}_3$ , 75 MHz)

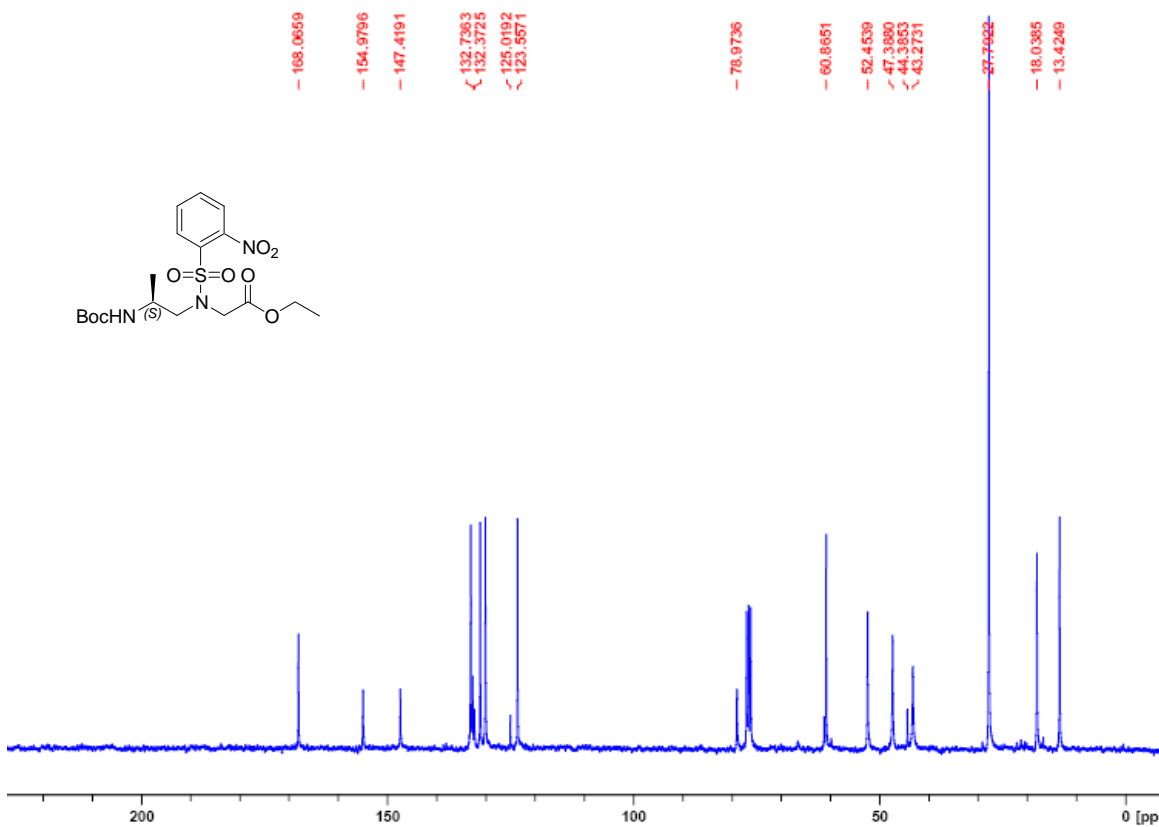


Figure 21S. <sup>1</sup>H NMR Spectrum of compound 9a-i (DMSO-d<sub>6</sub>, 300 MHz)

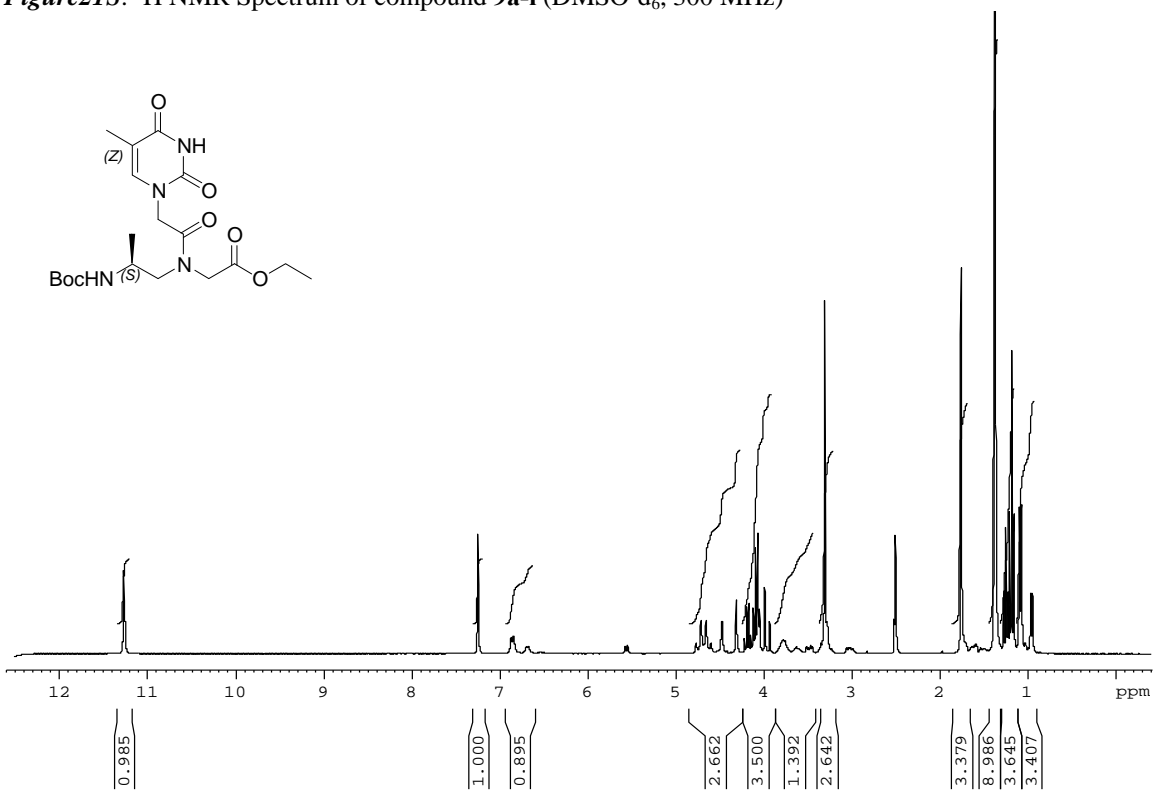


Figure 22S. <sup>13</sup>C NMR Spectrum of compound 9a-i (DMSO-d<sub>6</sub>, 75 MHz)

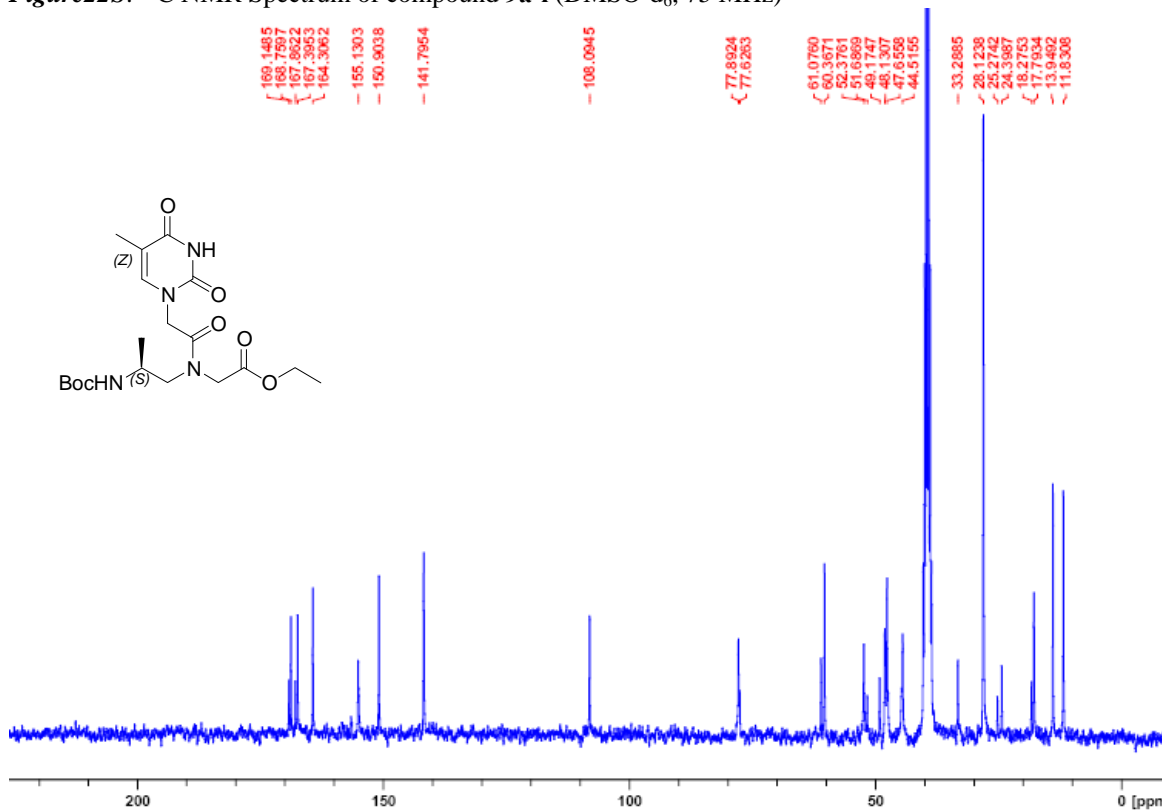


Figure 23S.  $^1\text{H}$  NMR Spectrum of compound **10a-i** (DMSO- $d_6$ , 300 MHz)

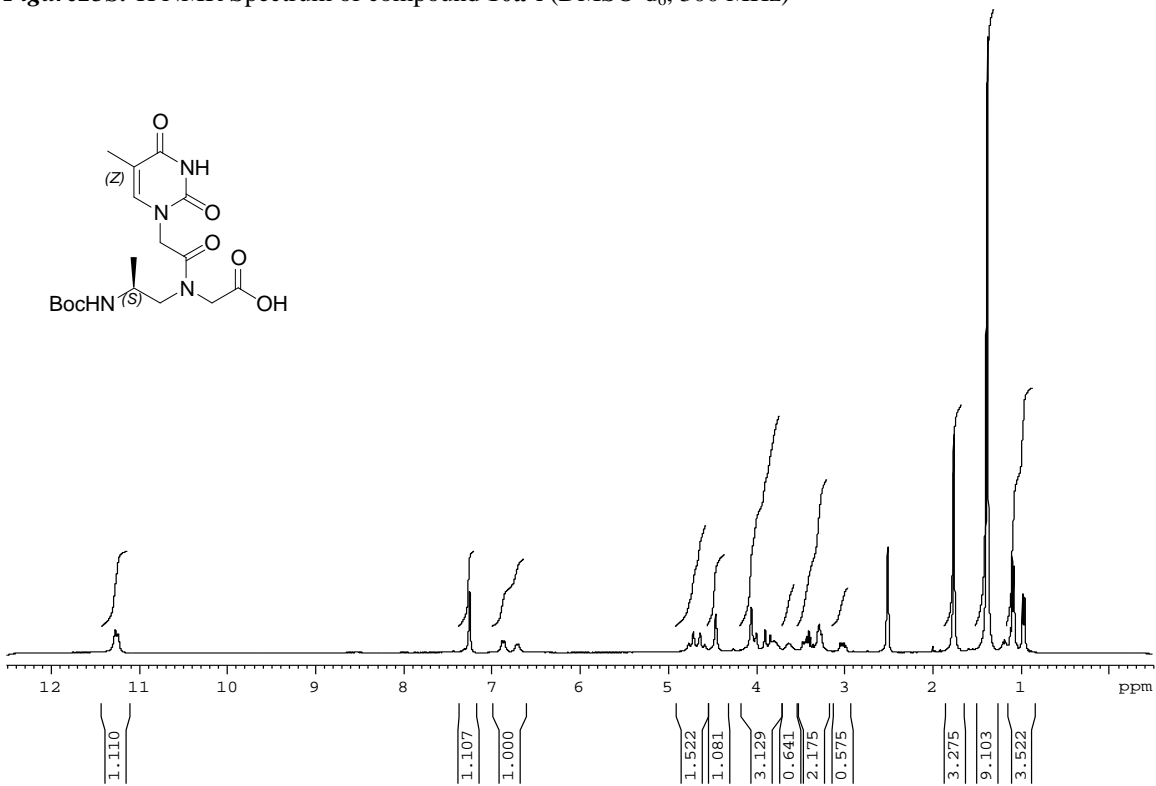


Figure 24S.  $^{13}\text{C}$  NMR Spectrum of compound **10a-i** (DMSO- $d_6$ , 75 MHz)

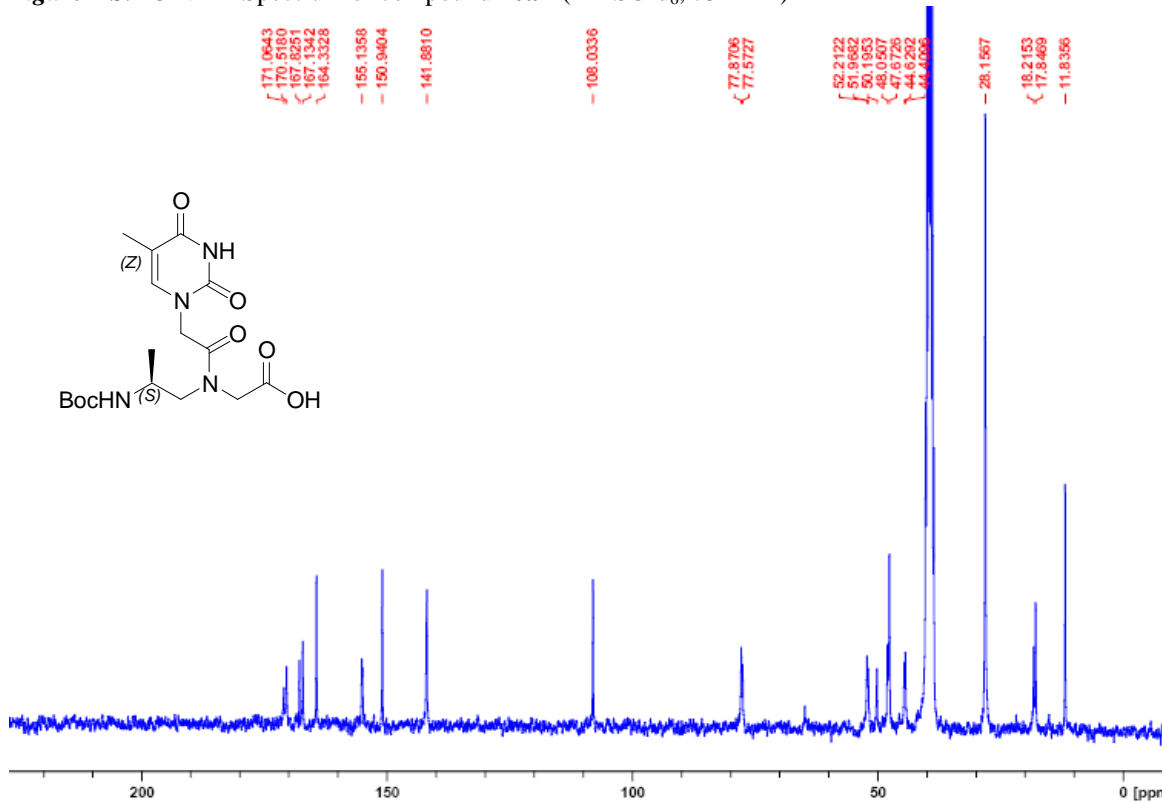


Figure25S. <sup>1</sup>H NMR Spectrum of compound **9b** (CDCl<sub>3</sub>, 300 MHz)

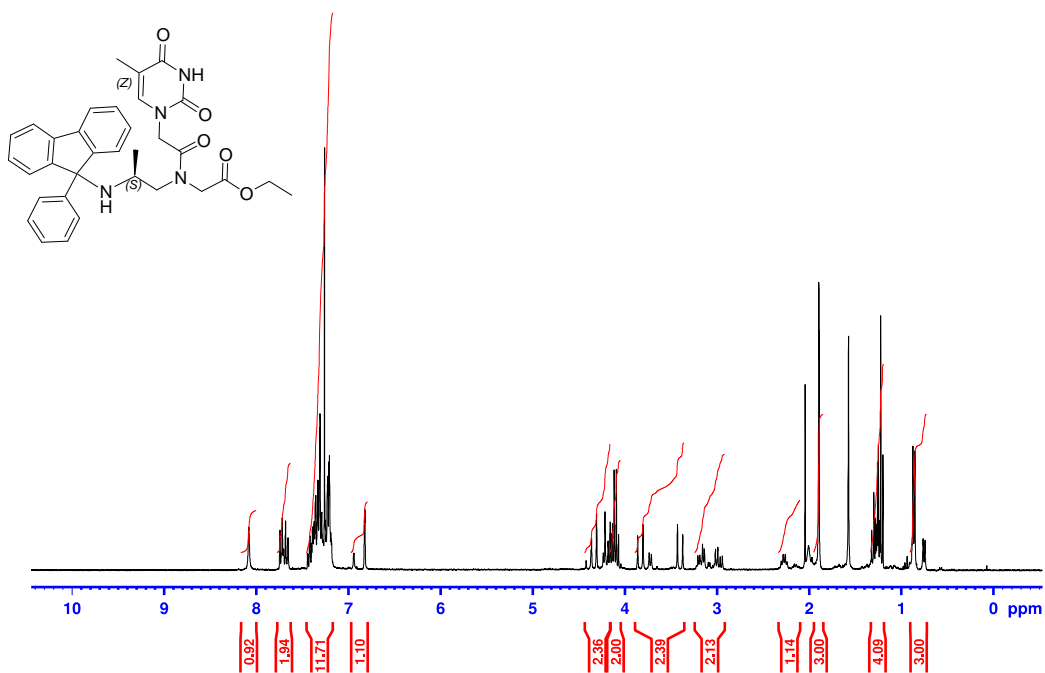


Figure26S. <sup>13</sup>C NMR Spectrum of compound **9b** (DMSO-d<sub>6</sub>, 75 MHz)

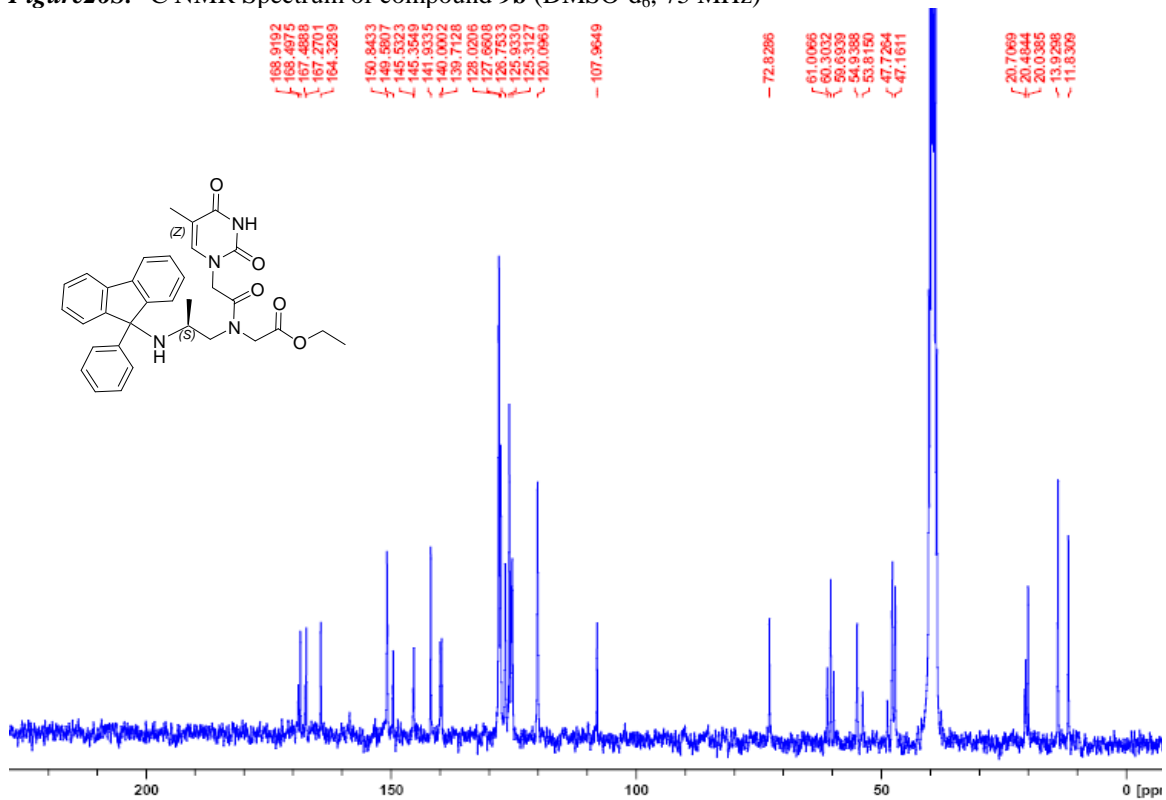


Figure 27S. <sup>1</sup>H NMR Spectrum of compound 10b (DMSO-d<sub>6</sub>, 300 MHz)

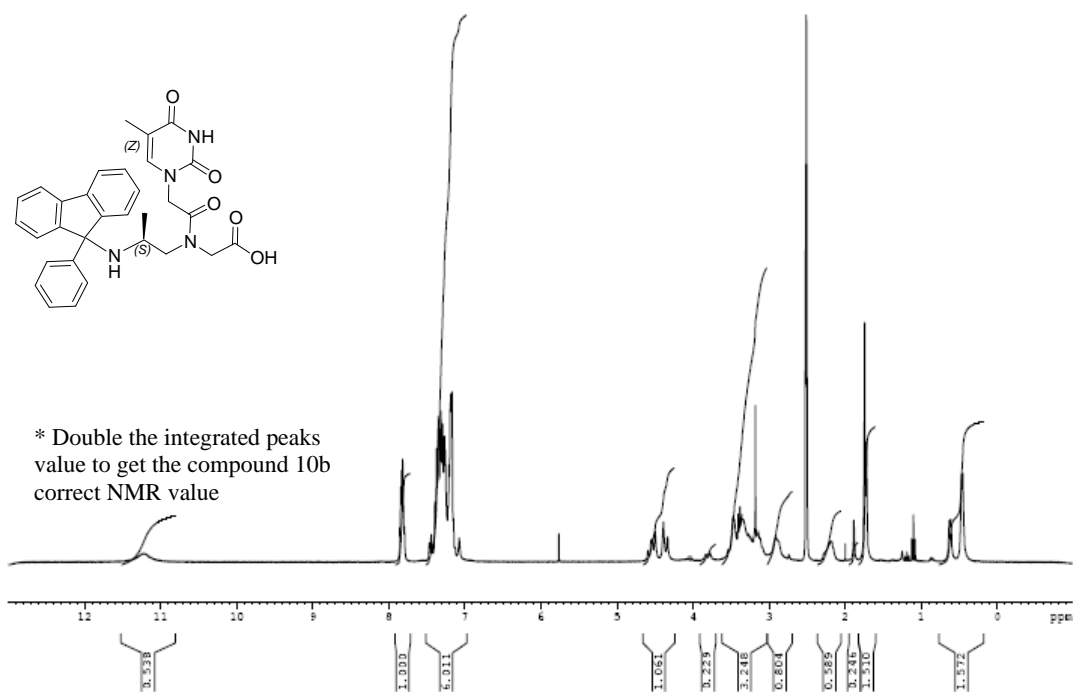


Figure 28S. <sup>13</sup>C NMR Spectrum of compound 10b (DMSO-d<sub>6</sub>, 75 MHz)

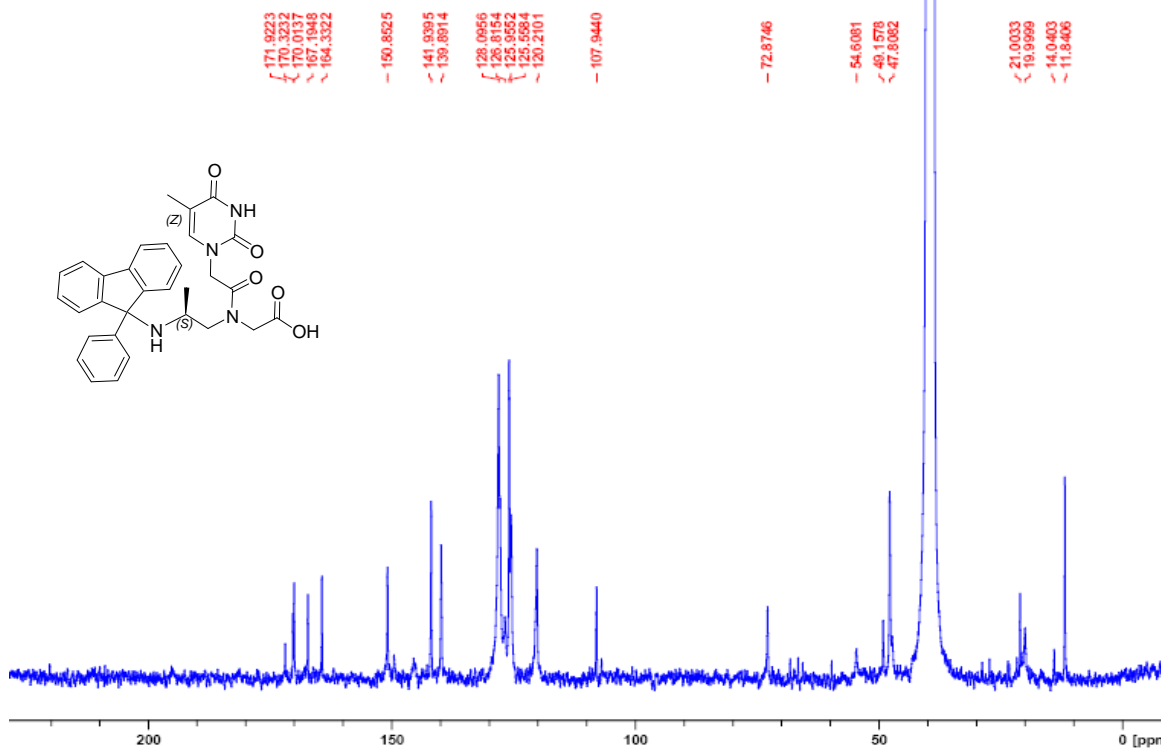




Figure 29S. <sup>1</sup>H NMR Spectrum of compound 11a-i, 11a-ii (DMSO-d<sub>6</sub>, 300 MHz)

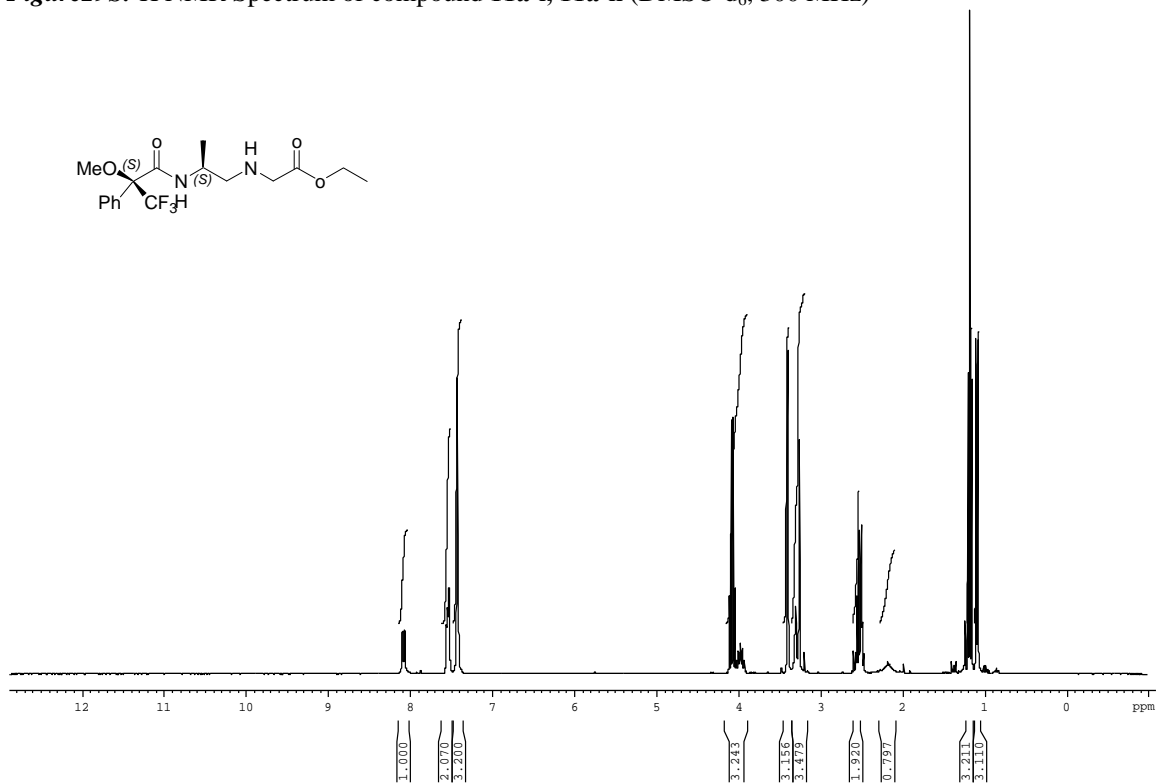


Figure 30S. <sup>13</sup>C NMR Spectrum of compound 11a-i, 11a-ii (DMSO-d<sub>6</sub>, 75 MHz)

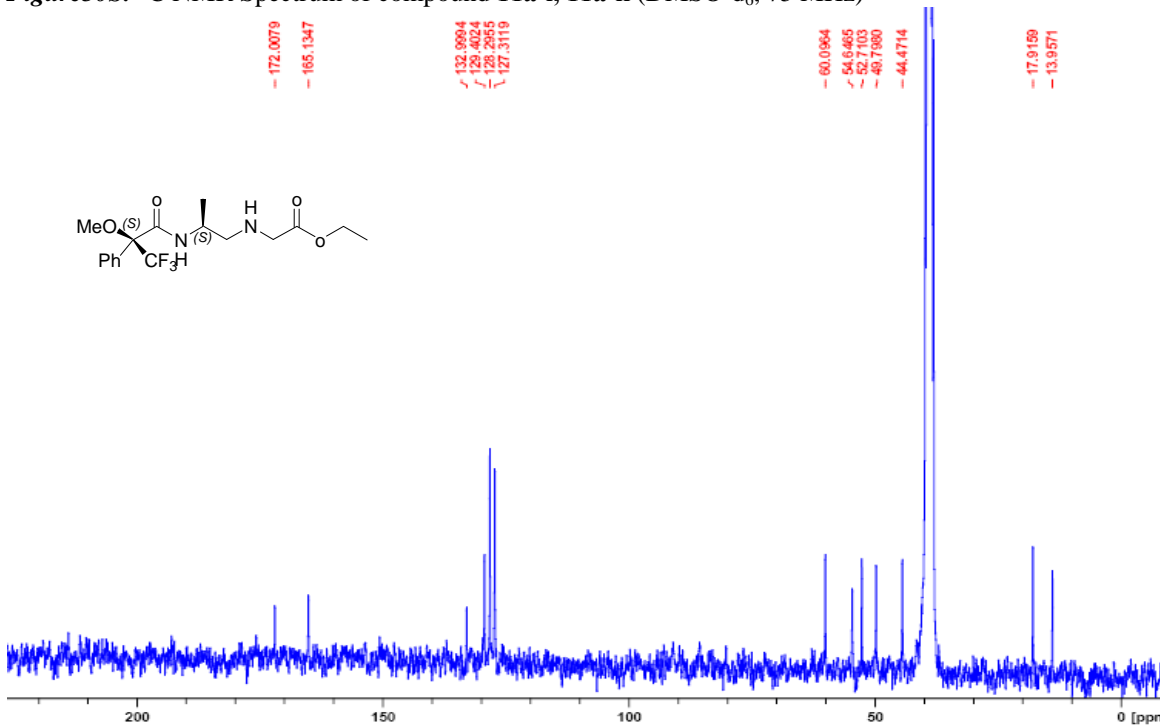


Figure 31S. <sup>1</sup>H NMR Spectrum of compound 12a-i, 12a-ii (DMSO-d<sub>6</sub>, 300 MHz)

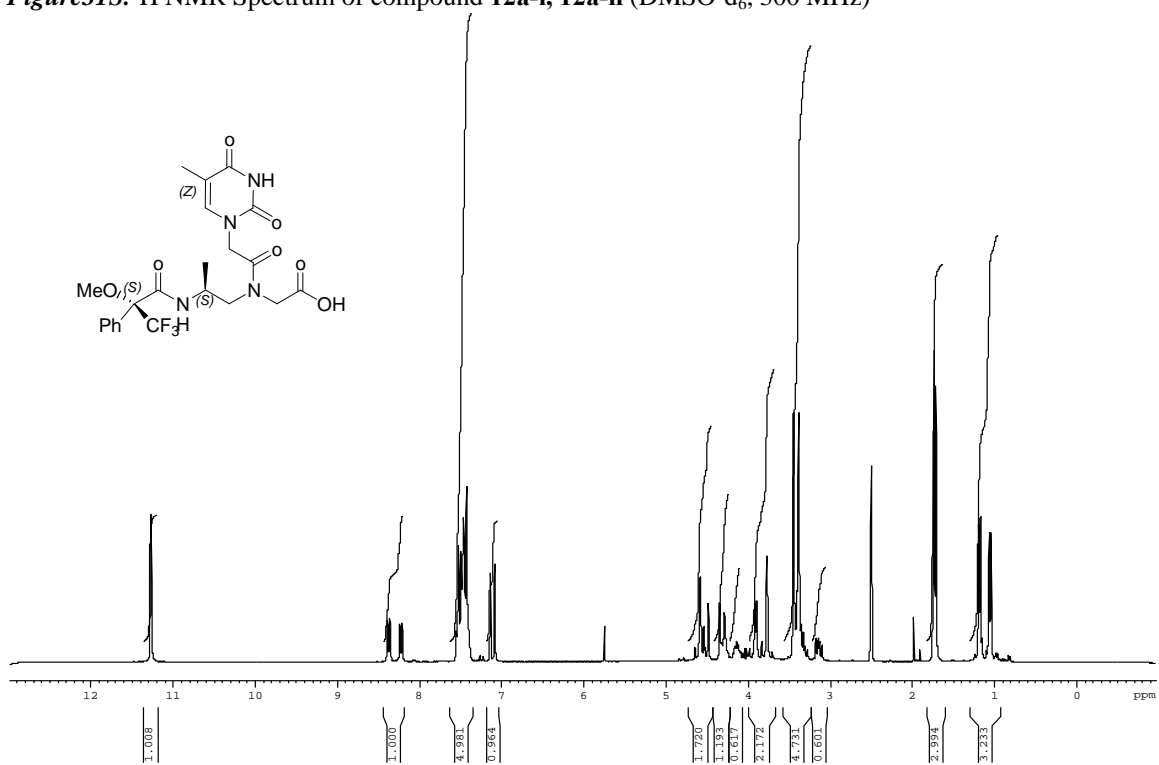


Figure 32S. <sup>13</sup>C NMR Spectrum of compound 12a-i, 12a-ii (DMSO-d<sub>6</sub>, 75 MHz)

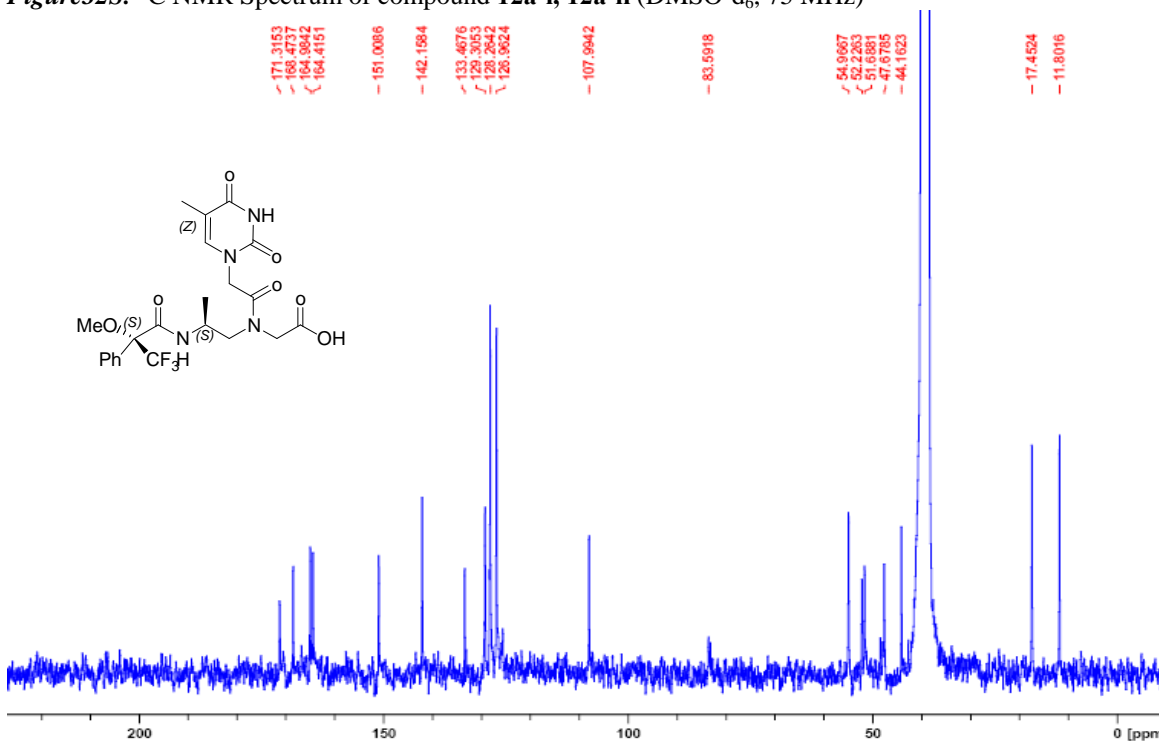


Figure33S.MALDI-TOF Spectrum of oligomer, PNA2a

Voyager Spec #1[BP = 2919.6, 5978]

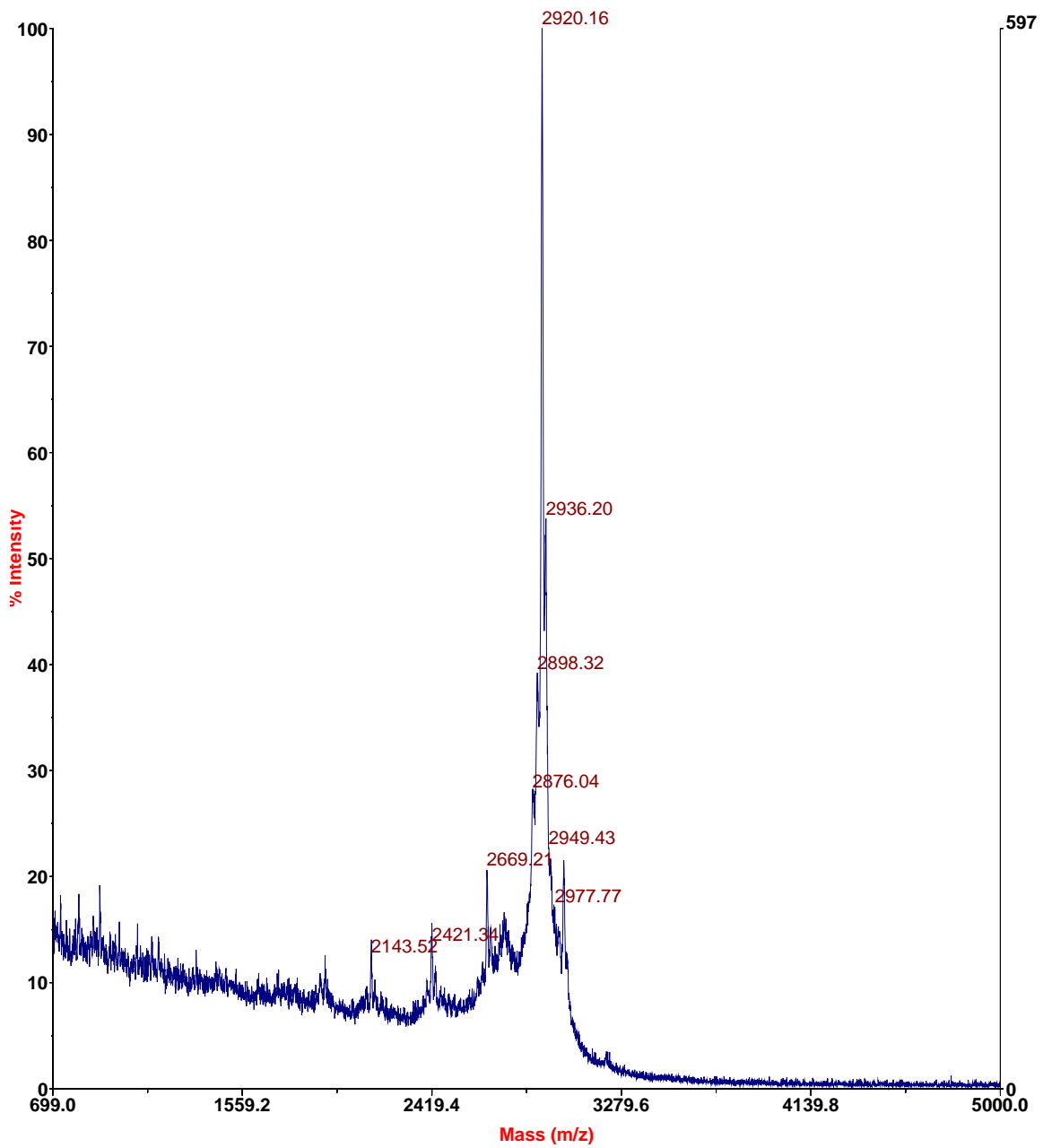


Figure 34S. MALDI-TOF Spectrum of oligomer, PNA2b

Voyager Spec #1 [BP = 2901.7, 3108]

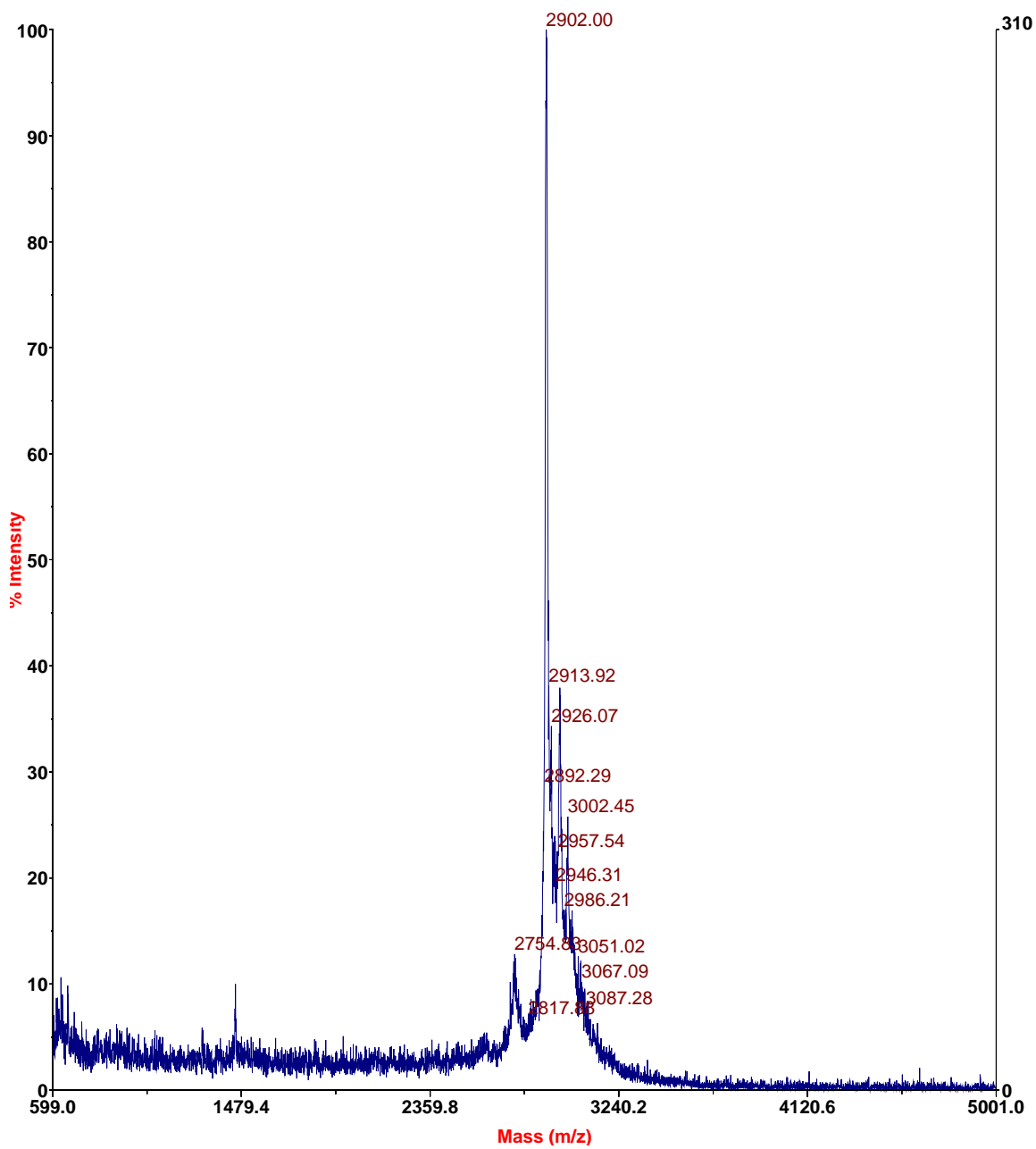


Figure35S.MALDI-TOF Spectrum of oligomer, PNA3a

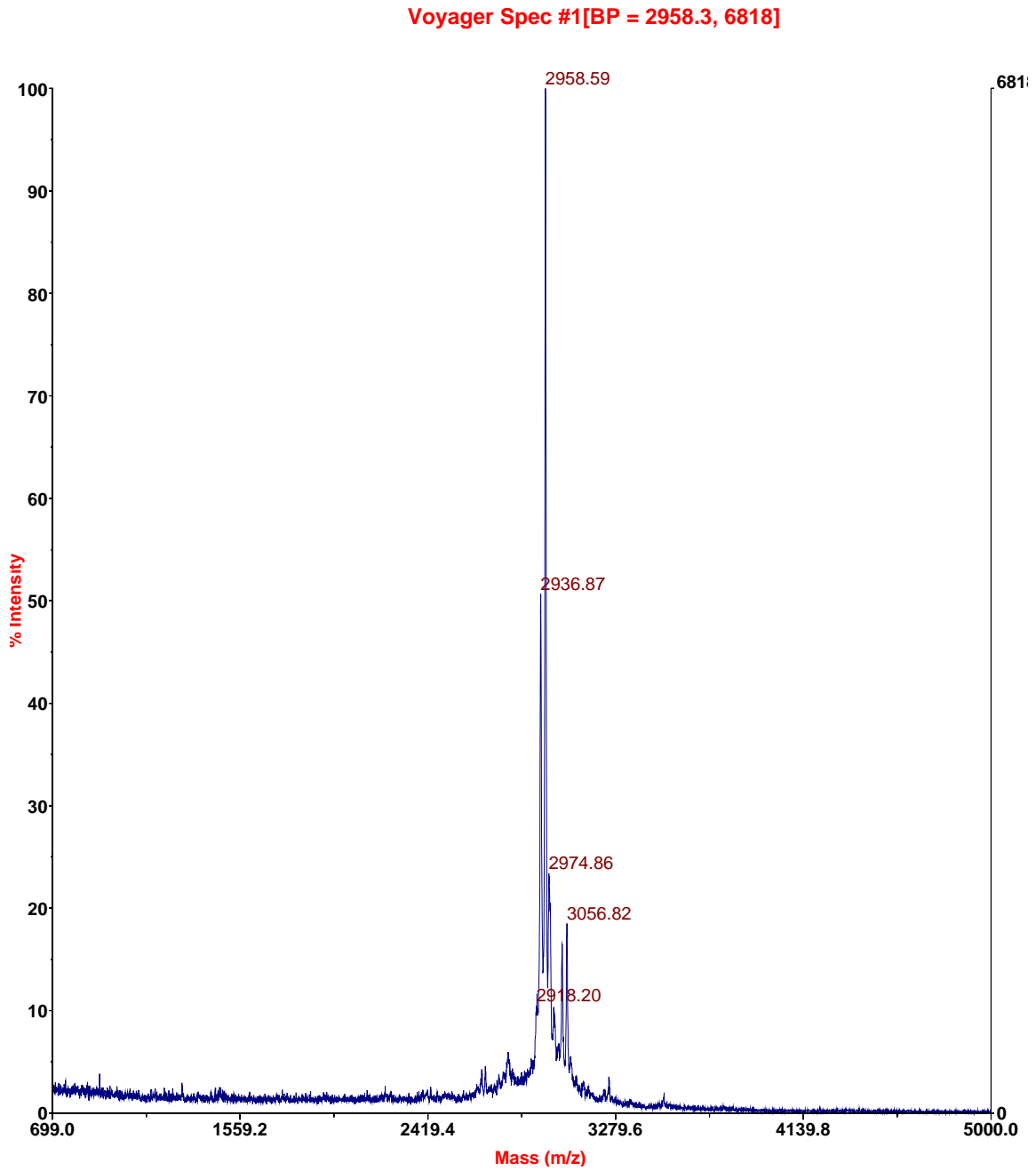
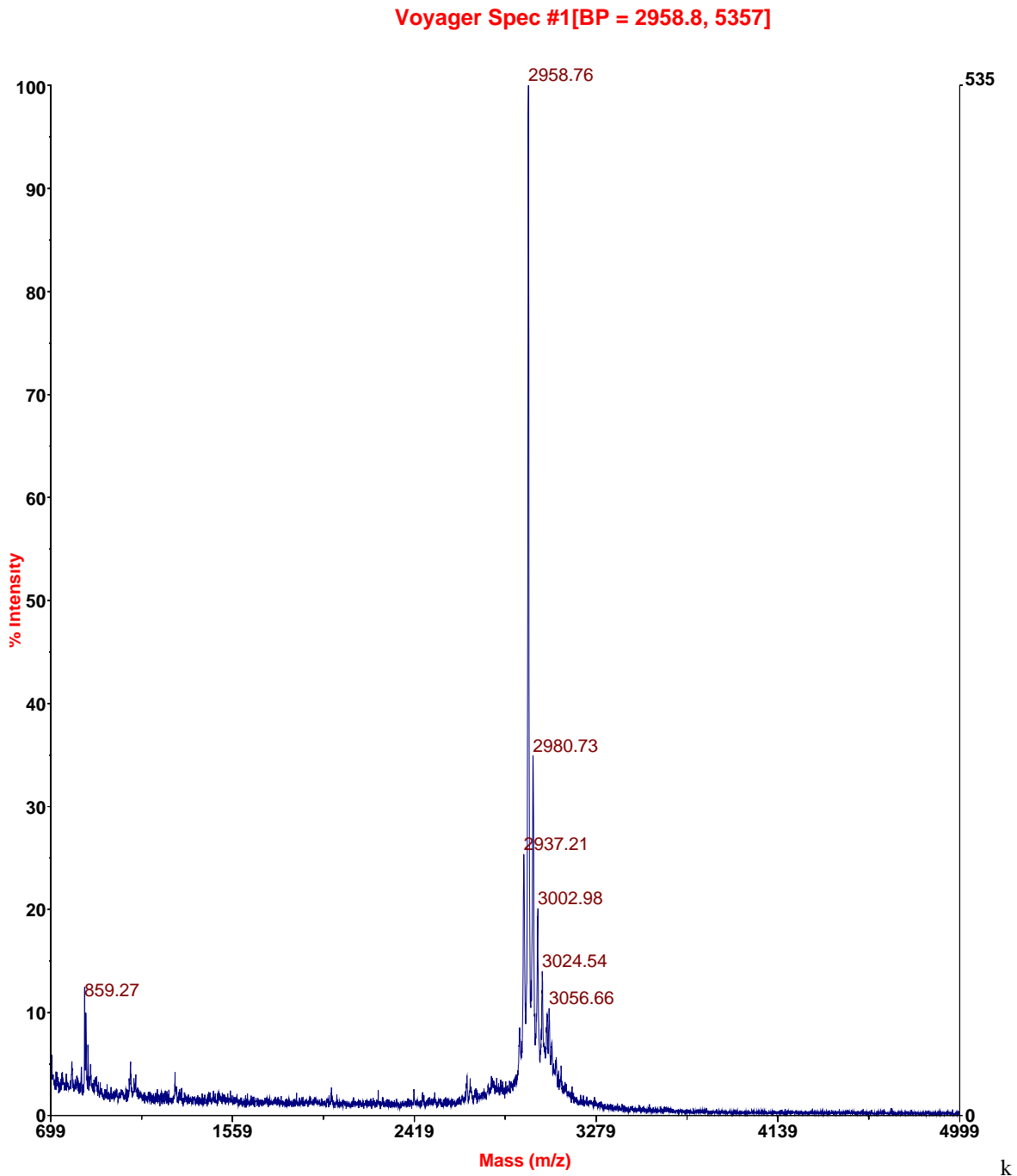
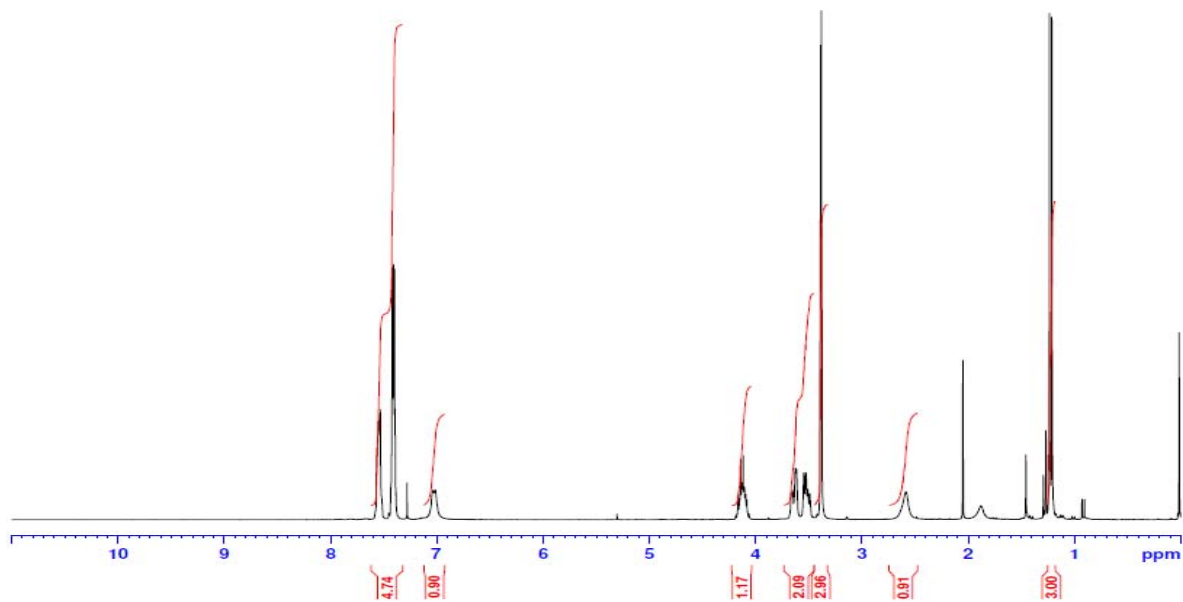
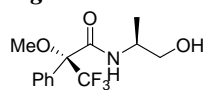


Figure36S.MALDI-TOF Spectrum of oligomer, PNA3b



**Figure 37S.**  $^1\text{H}$  NMR Spectrum of compound **14a-i** ( $\text{CDCl}_3$ , 300 MHz)



**Figure 38S.**  $^{13}\text{C}$  NMR Spectrum of compound **14a-i** ( $\text{CDCl}_3$ , 75 MHz)

