

## Supporting Information

### **Traceless Reductive Ligation at Tryptophan Site: a Facile Access to $\beta$ -Hydroxytryptophan appended Peptides**

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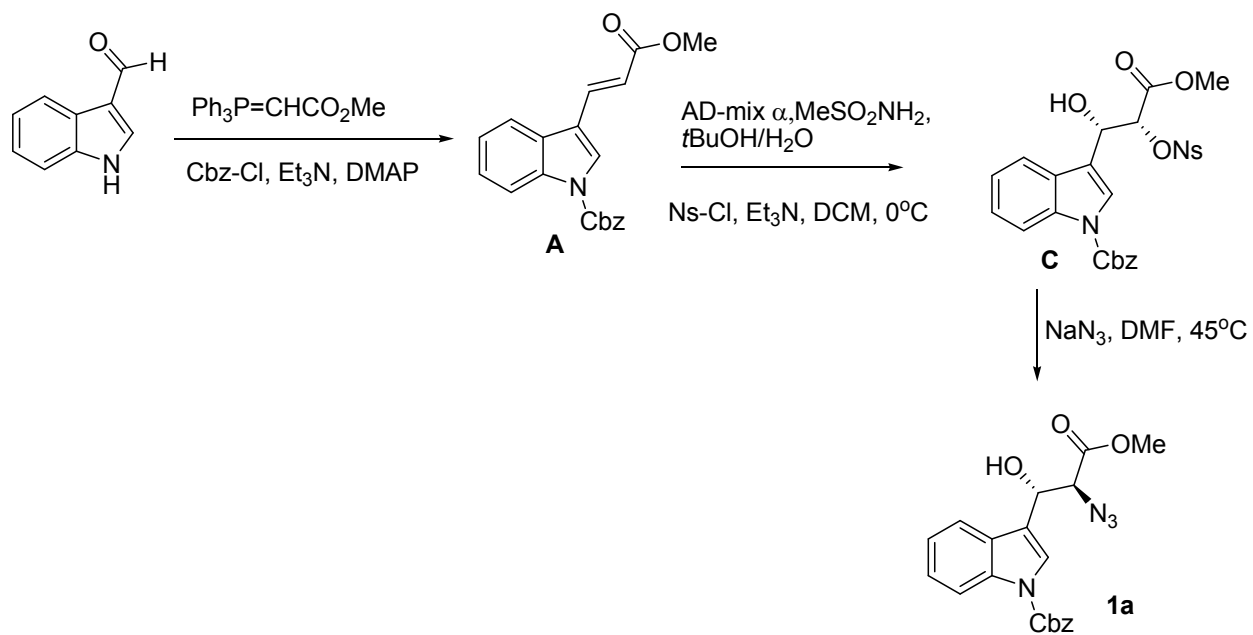
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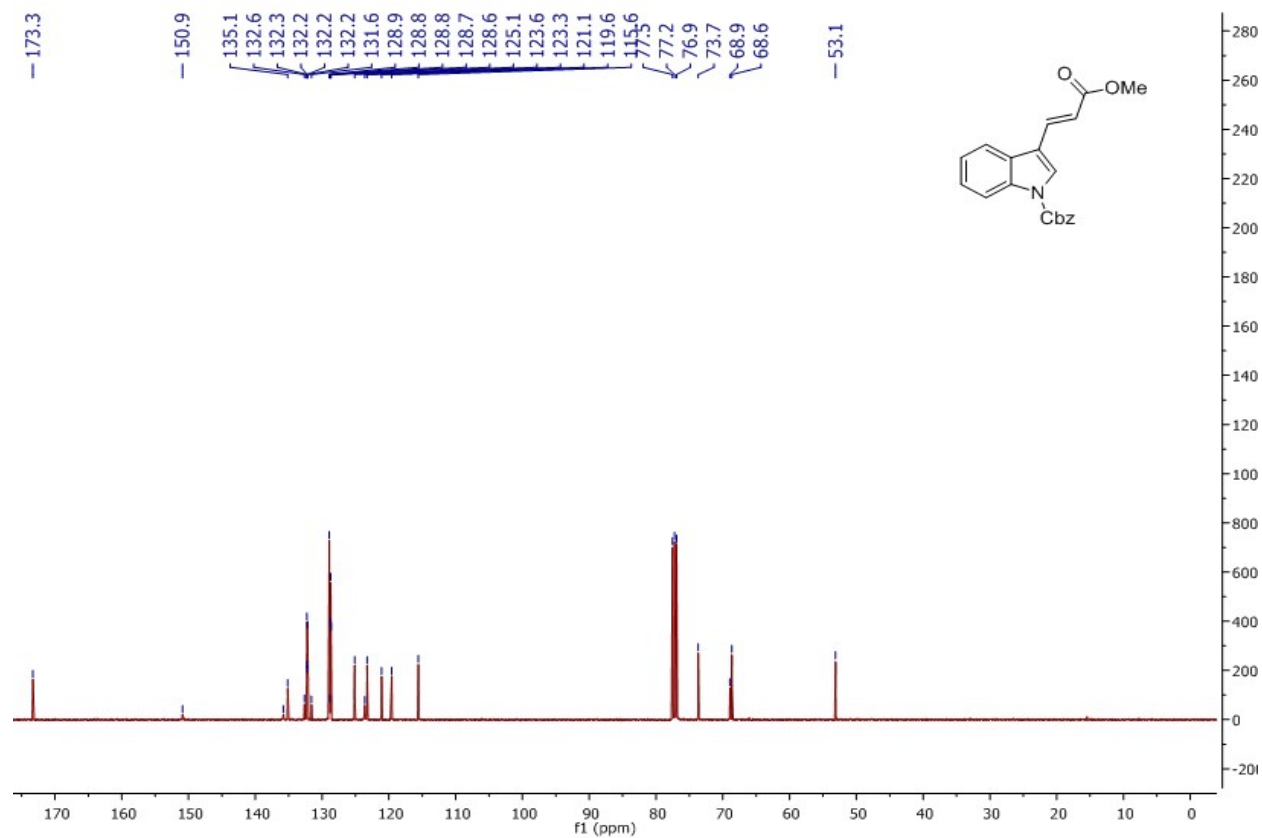
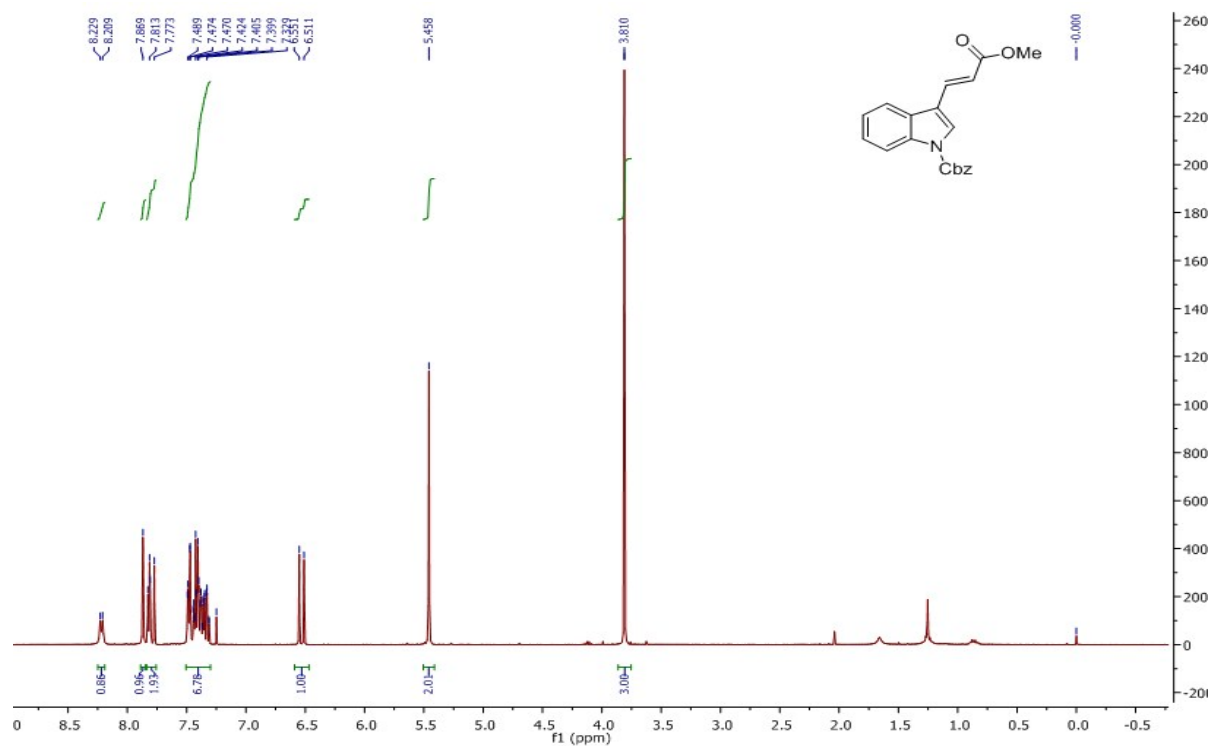
- 1. General procedure for the synthesis of 1a.**
- 2. Spectral data 3a-k and 4a-k**

General synthesis of compound **1a**: Compound **1a** was synthesized by the literature method. (Scheme 1)

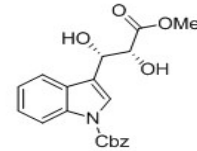
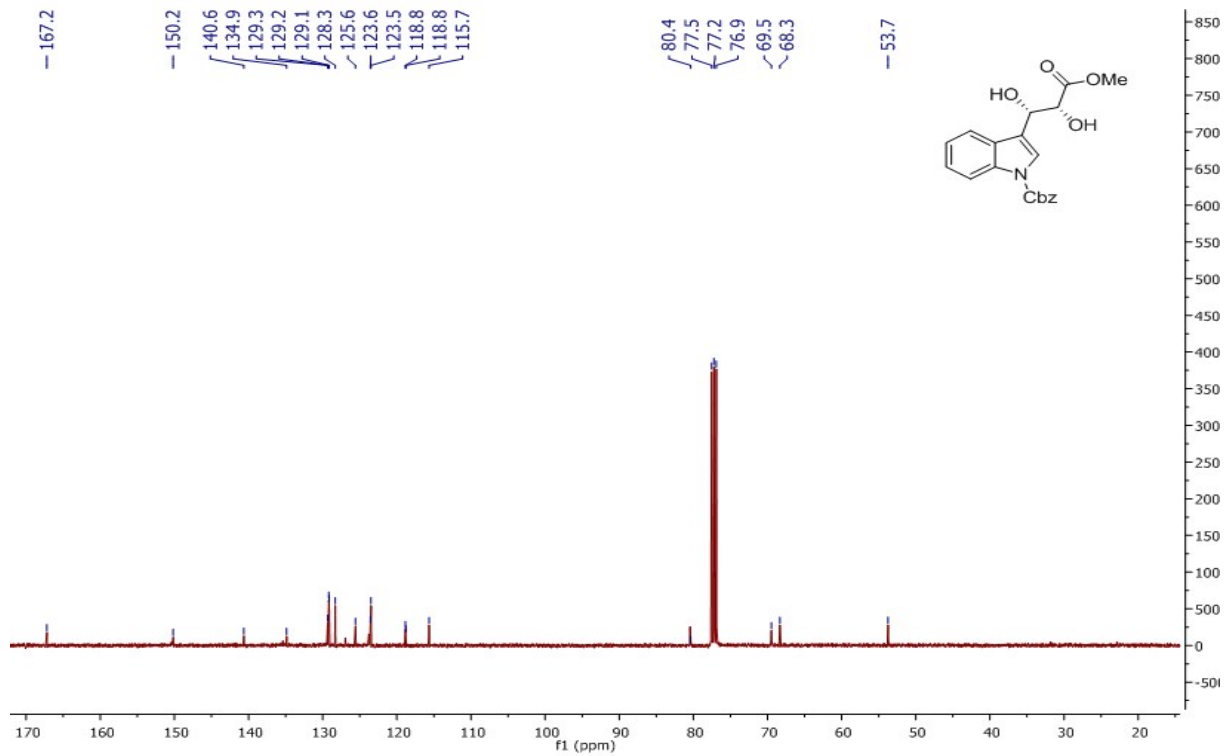
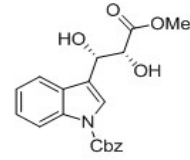
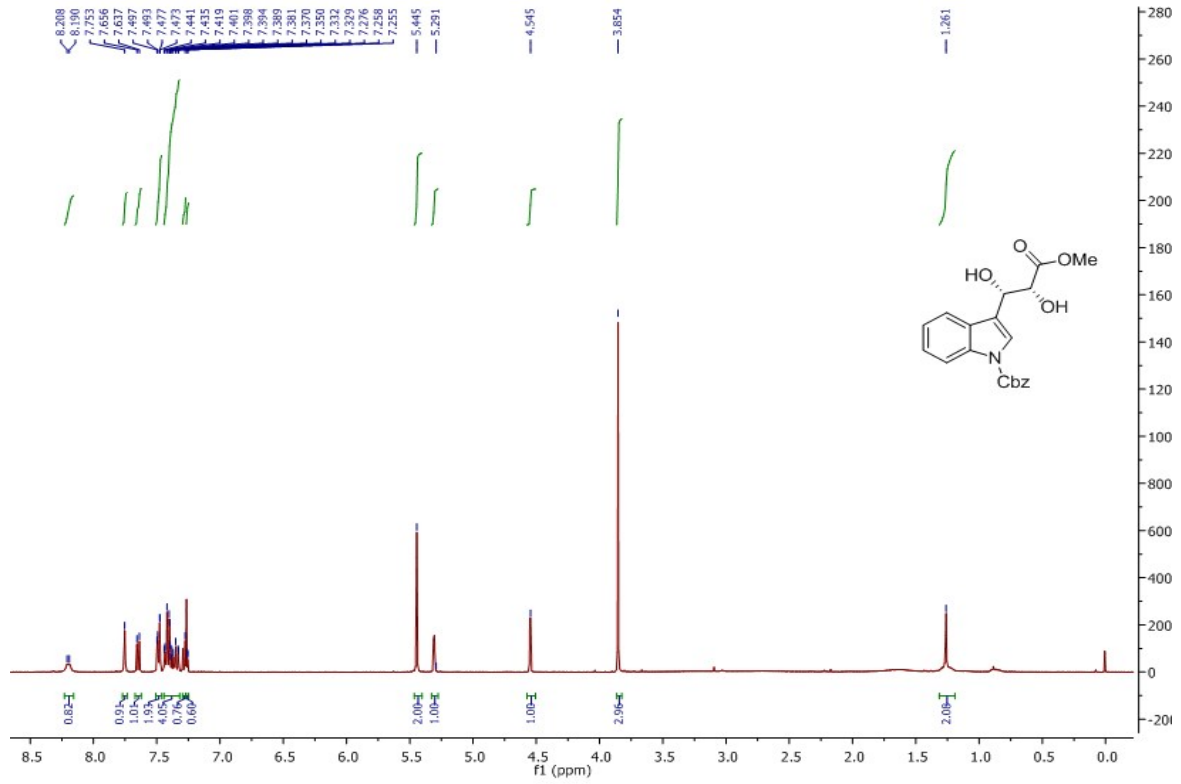


Scheme 1. Synthesis of functionalized tryptophan precursor **1a**.

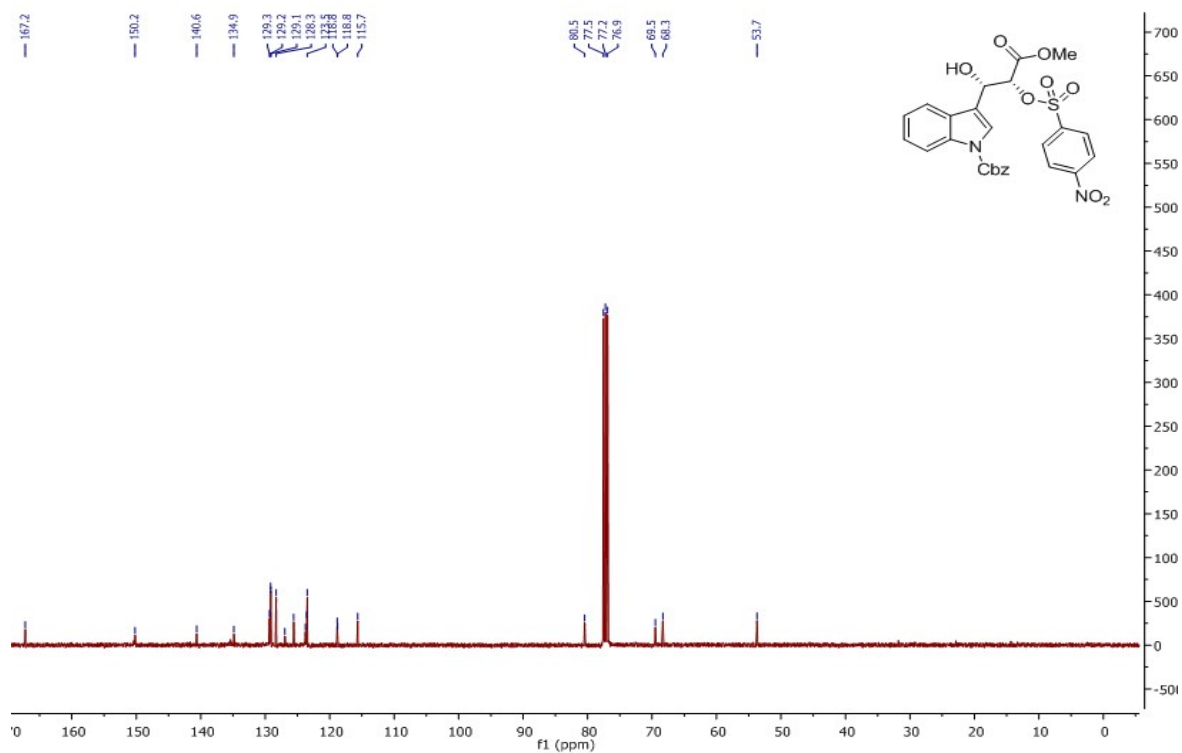
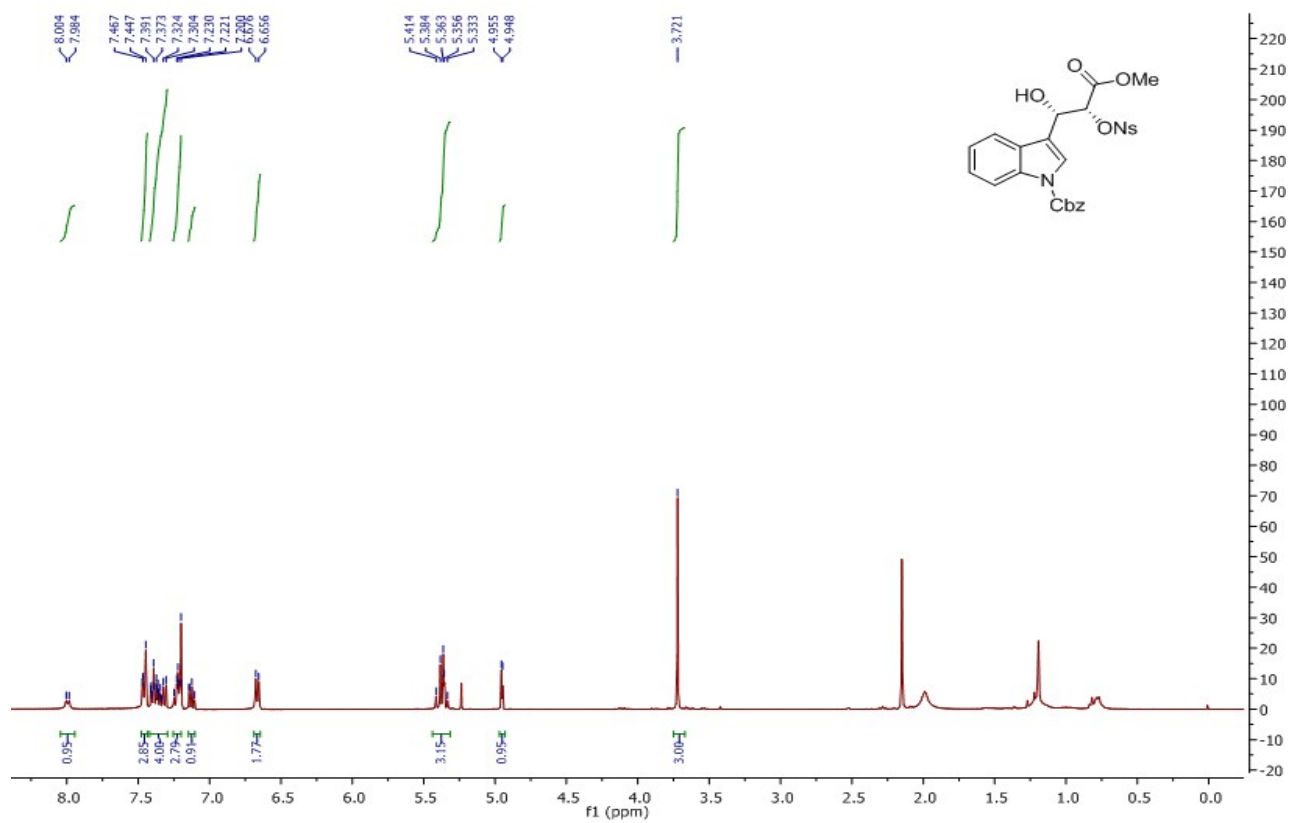
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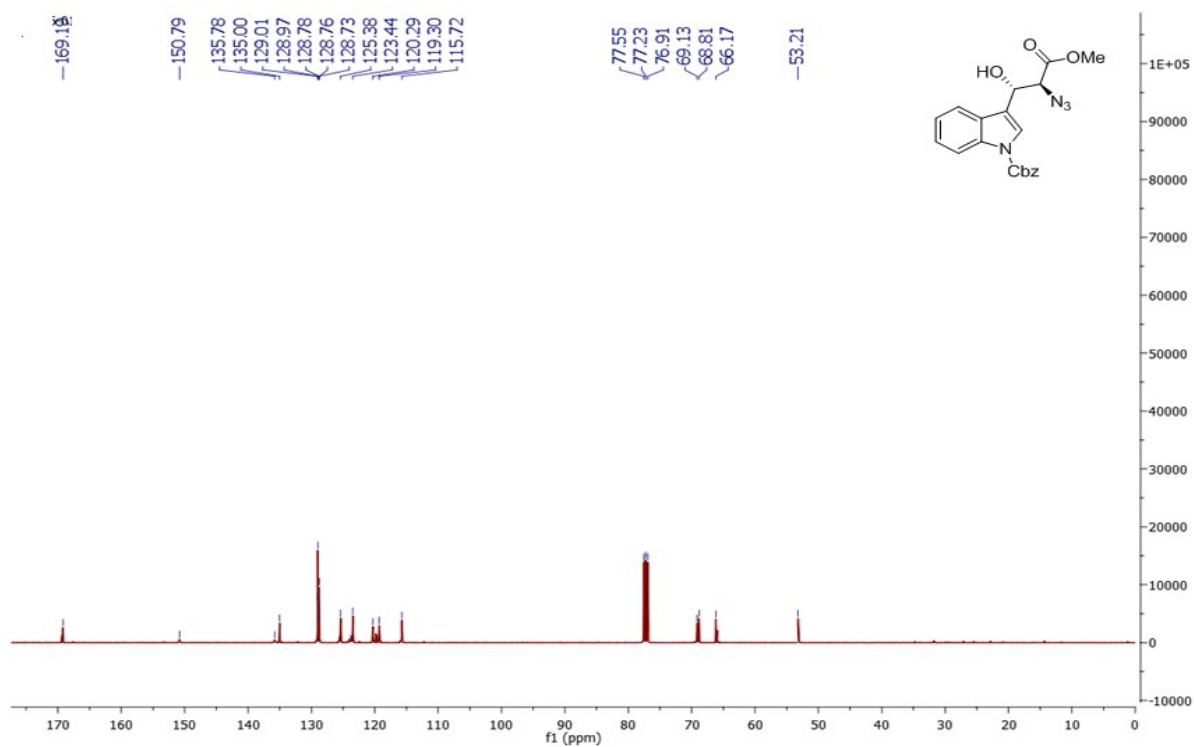
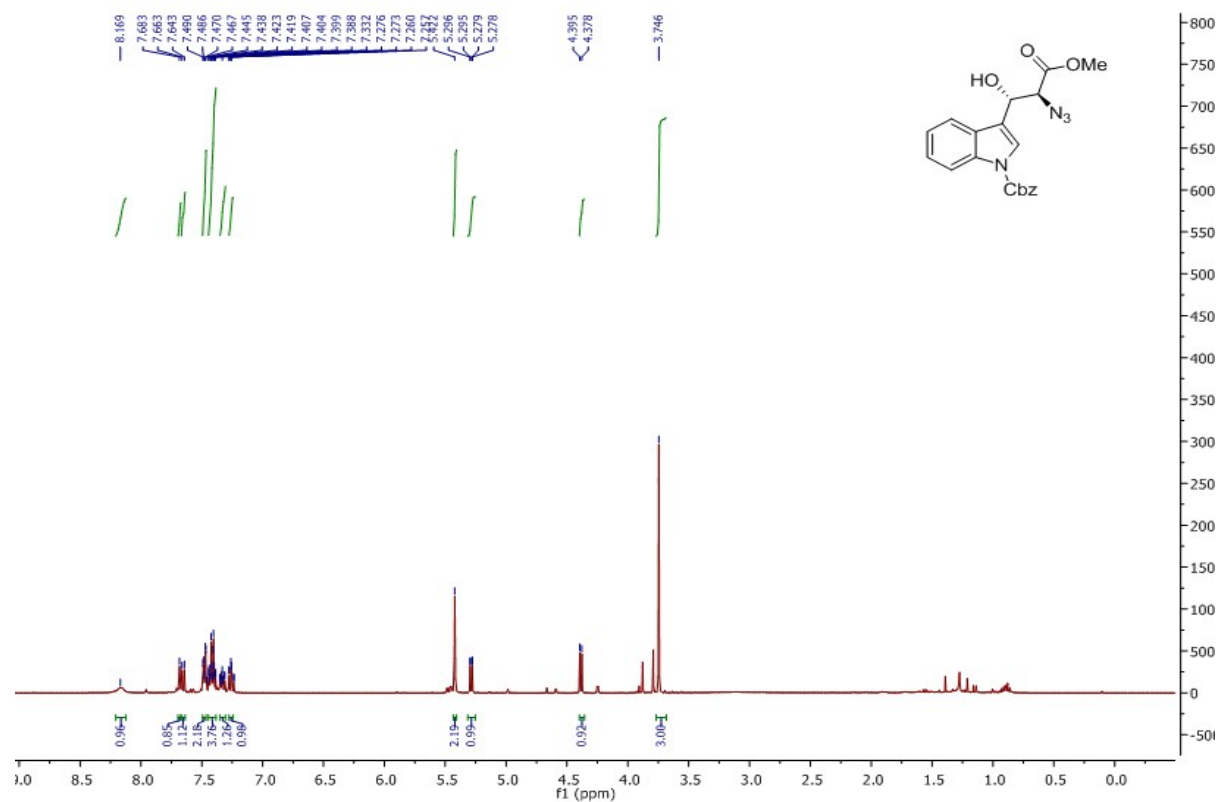
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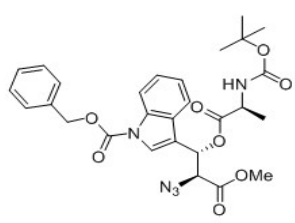
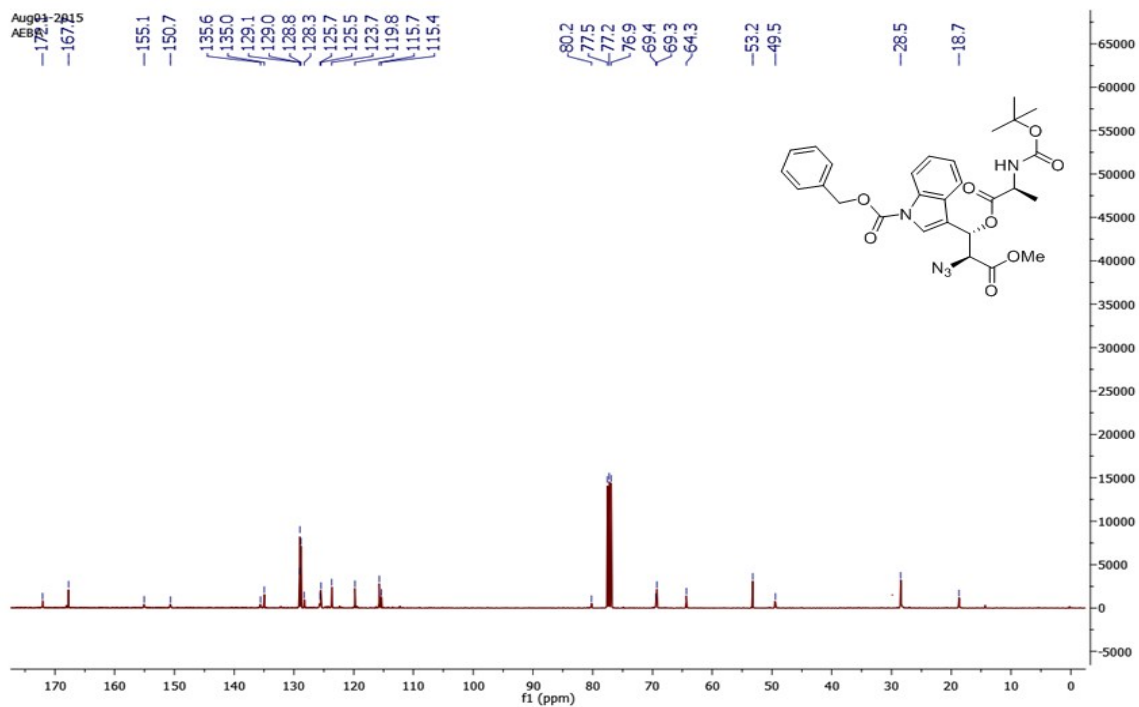
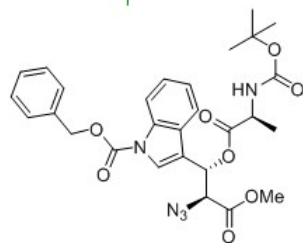
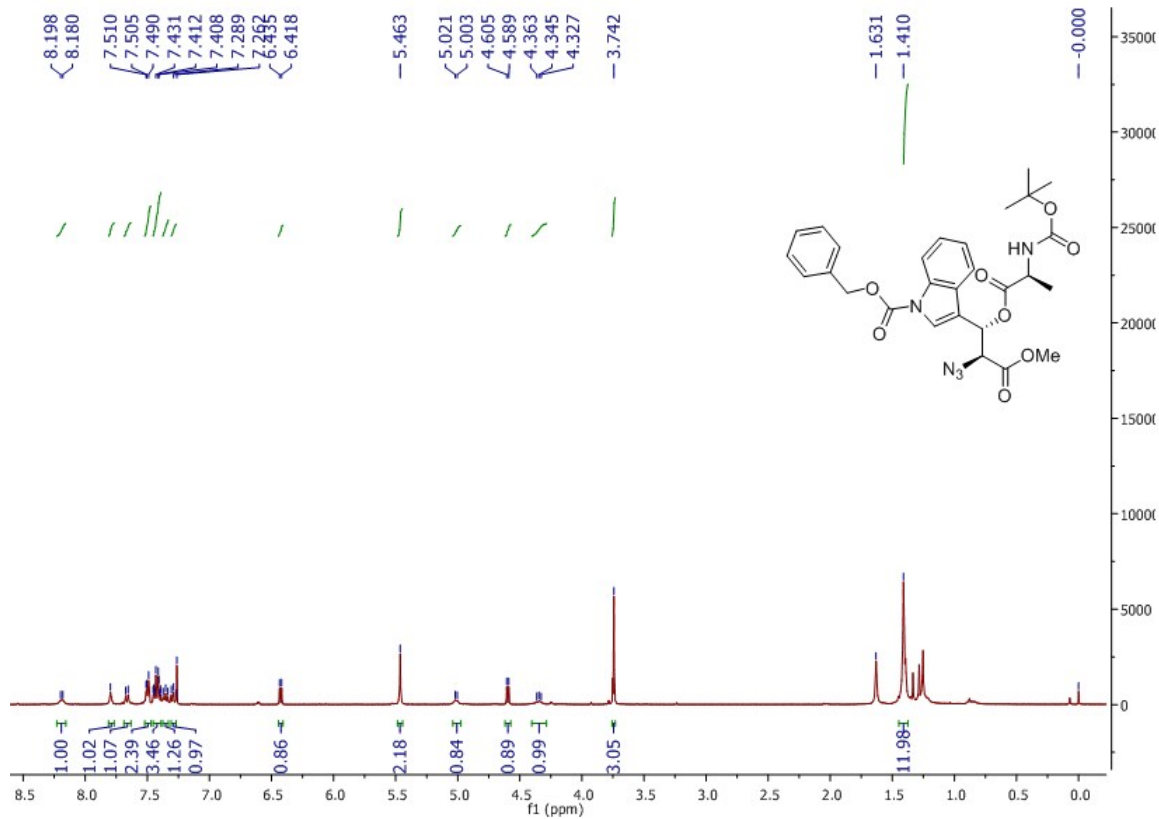
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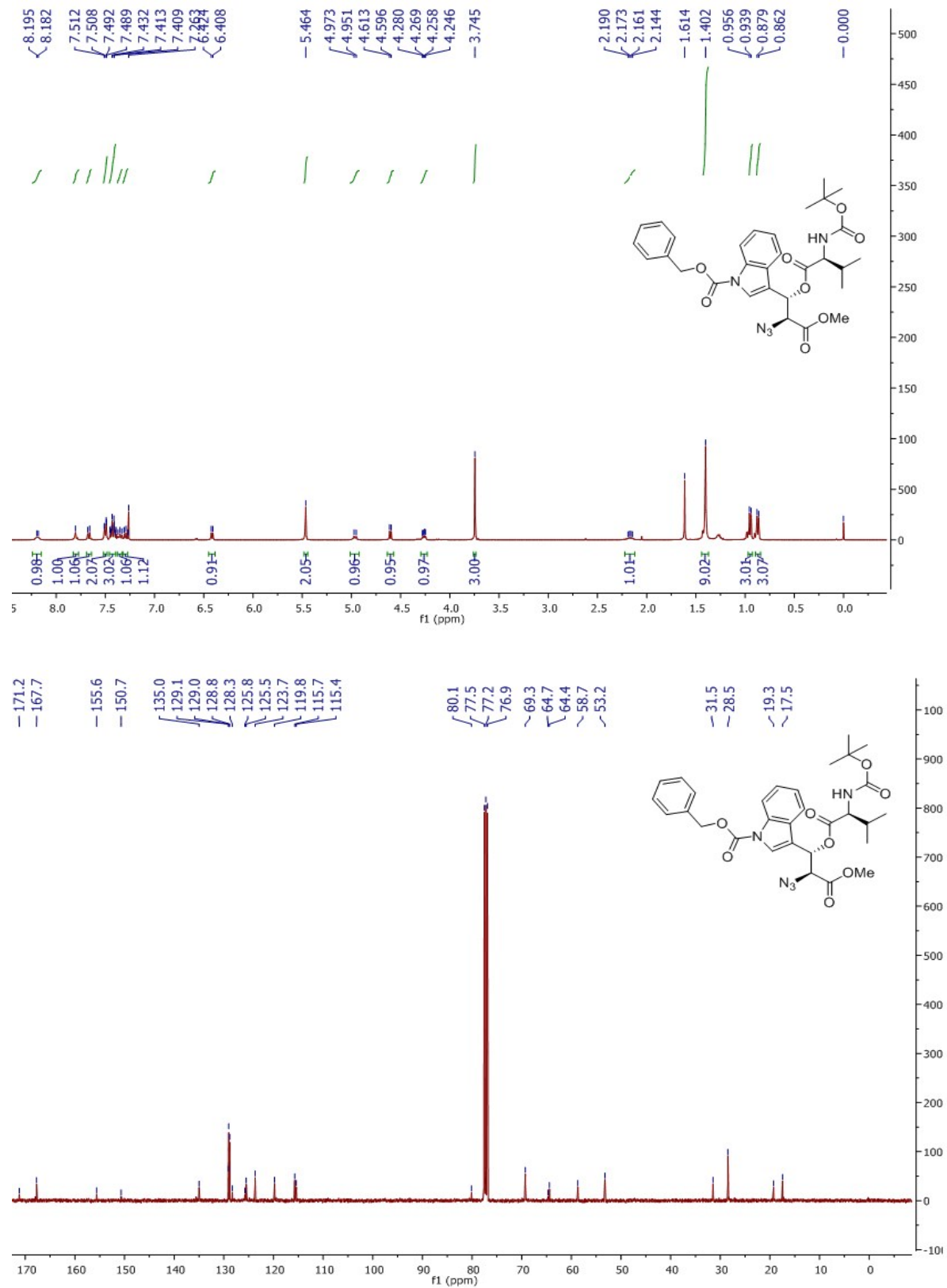
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **1a**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3b**

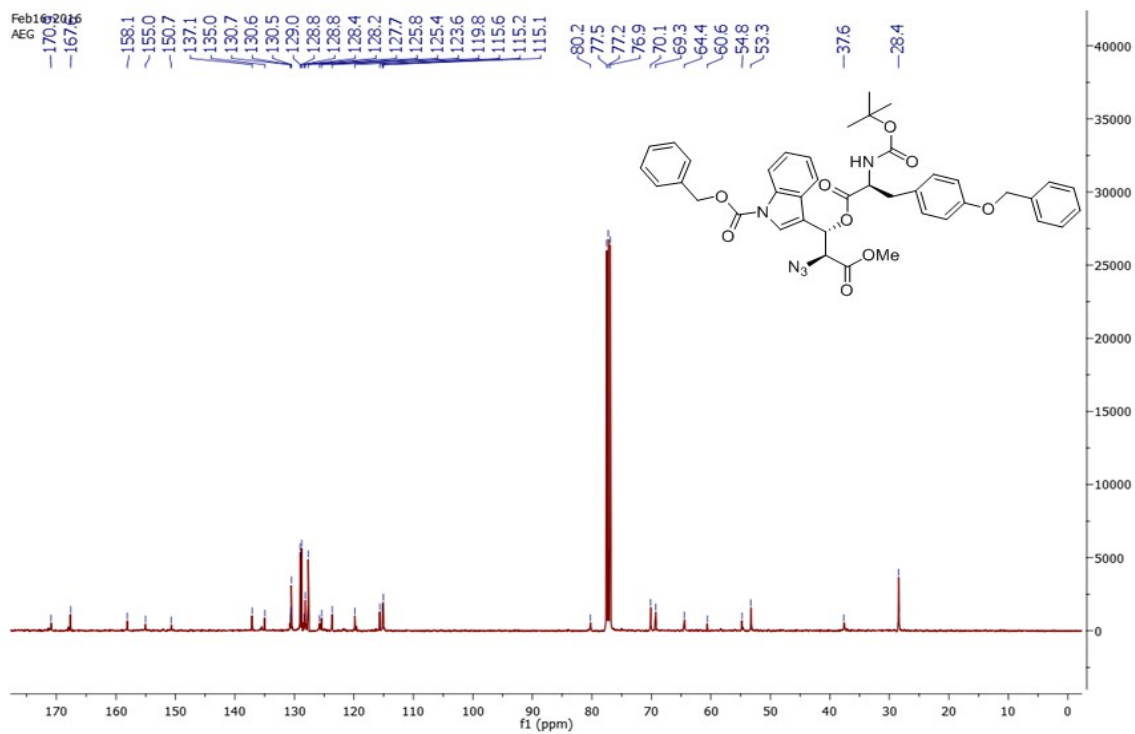
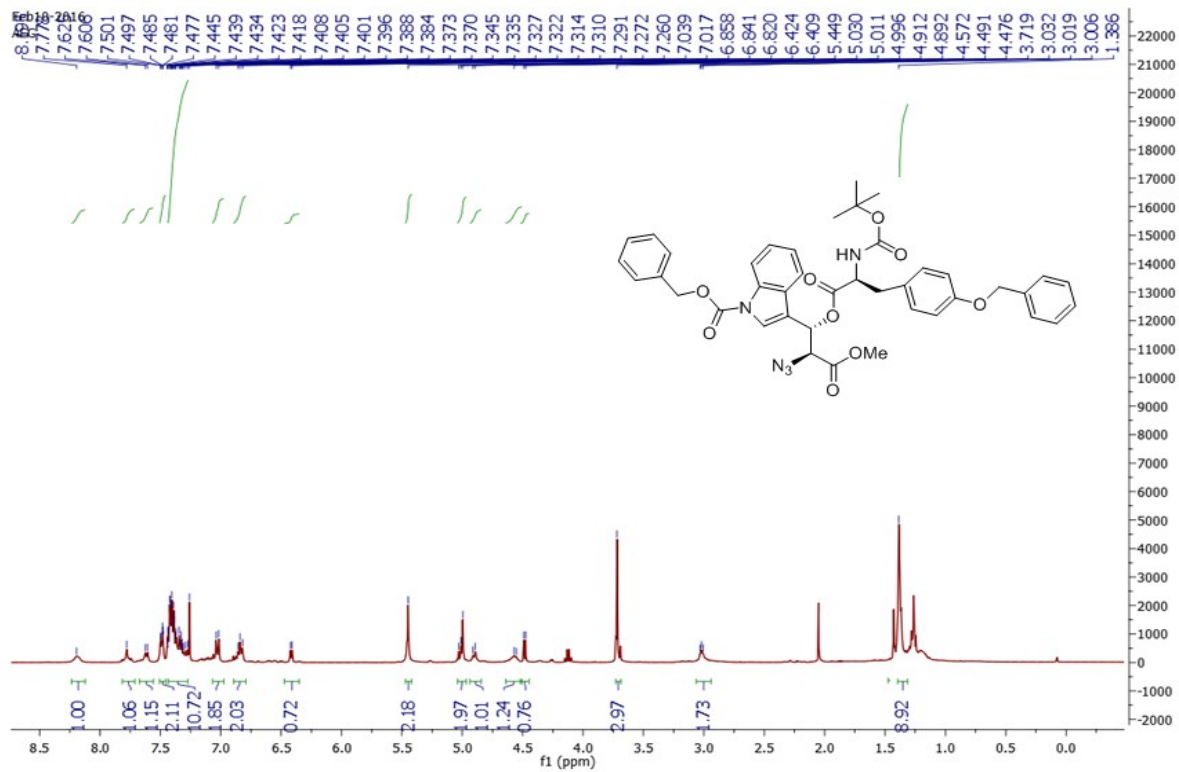


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3c**

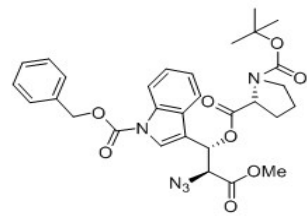
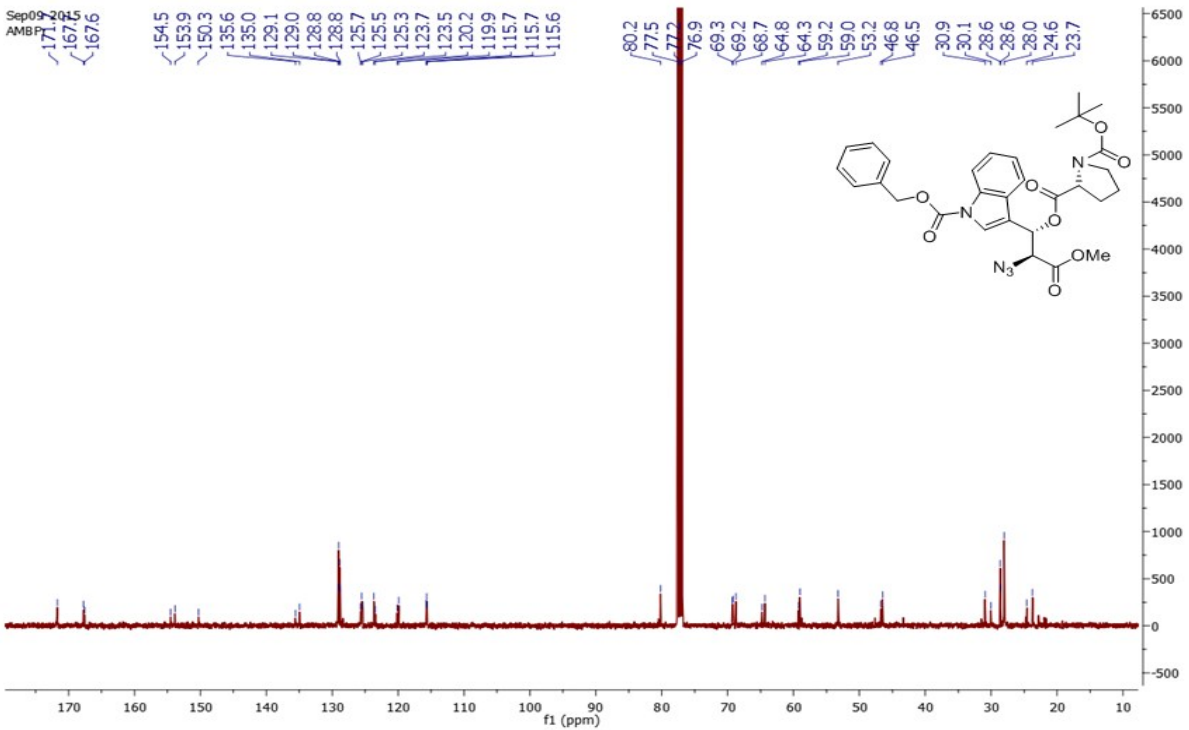
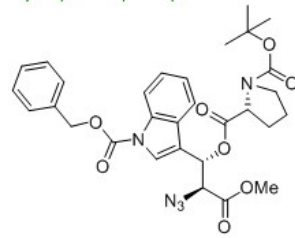
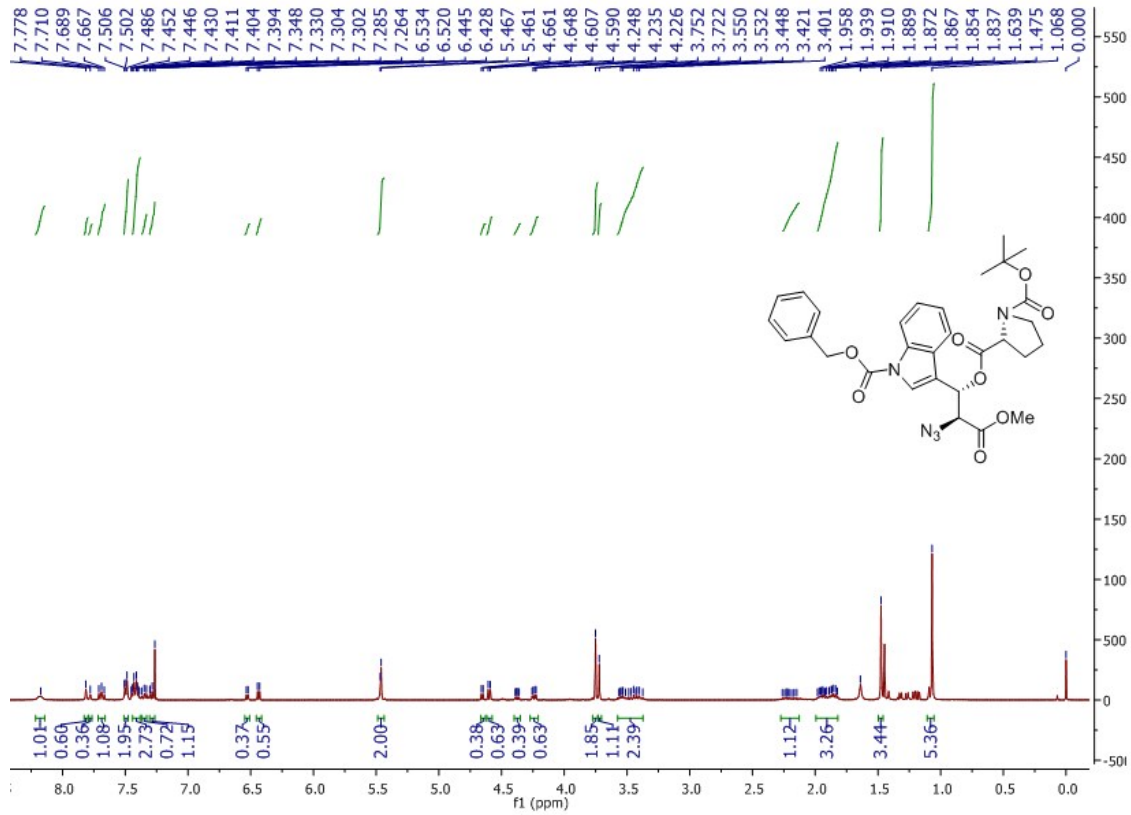




$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3d**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3e**



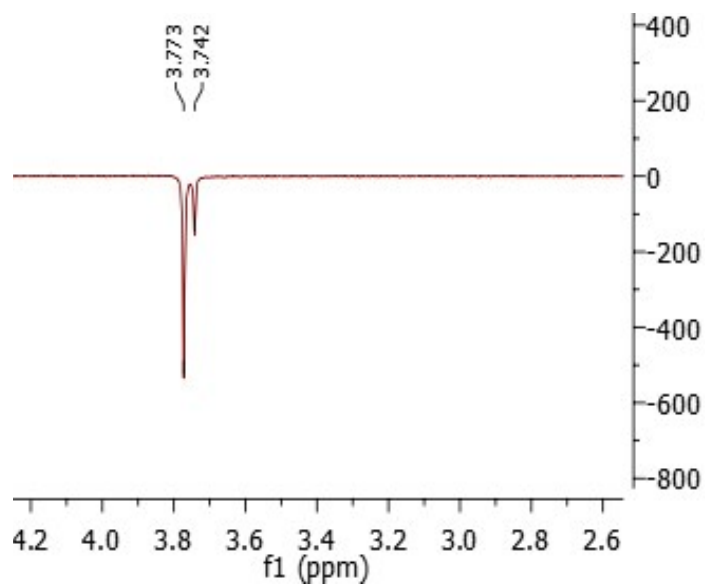


Fig 1a: 1D gradient NOE spectrum of compound **3e** with an initial selective pulse at 3.77 ppm creates a peak at 3.77 ppm as well as a new peak of the same phase at 3.74 ppm due to rotameric chemical exchange.

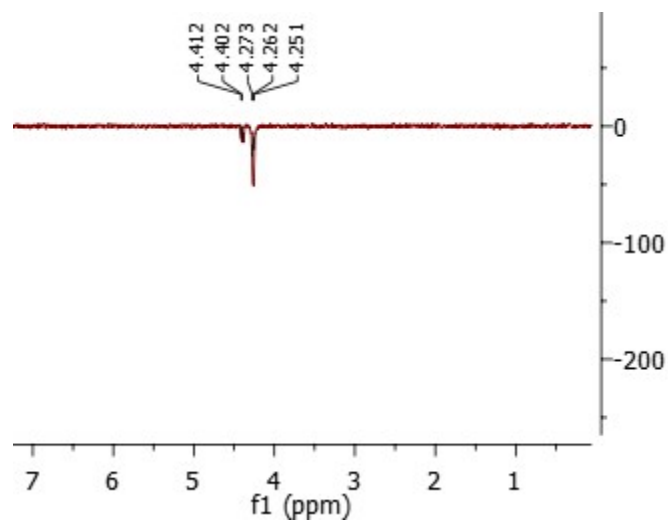
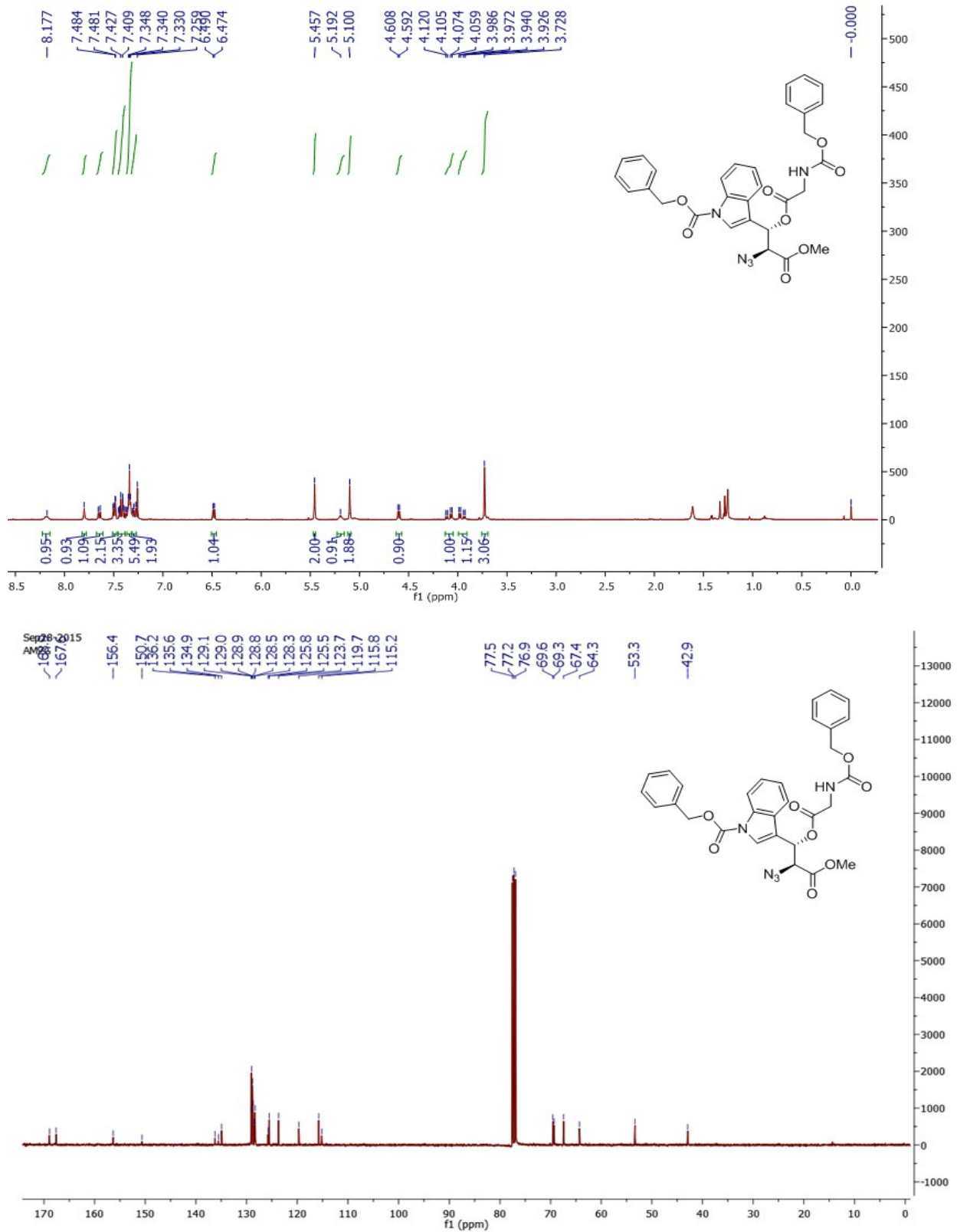
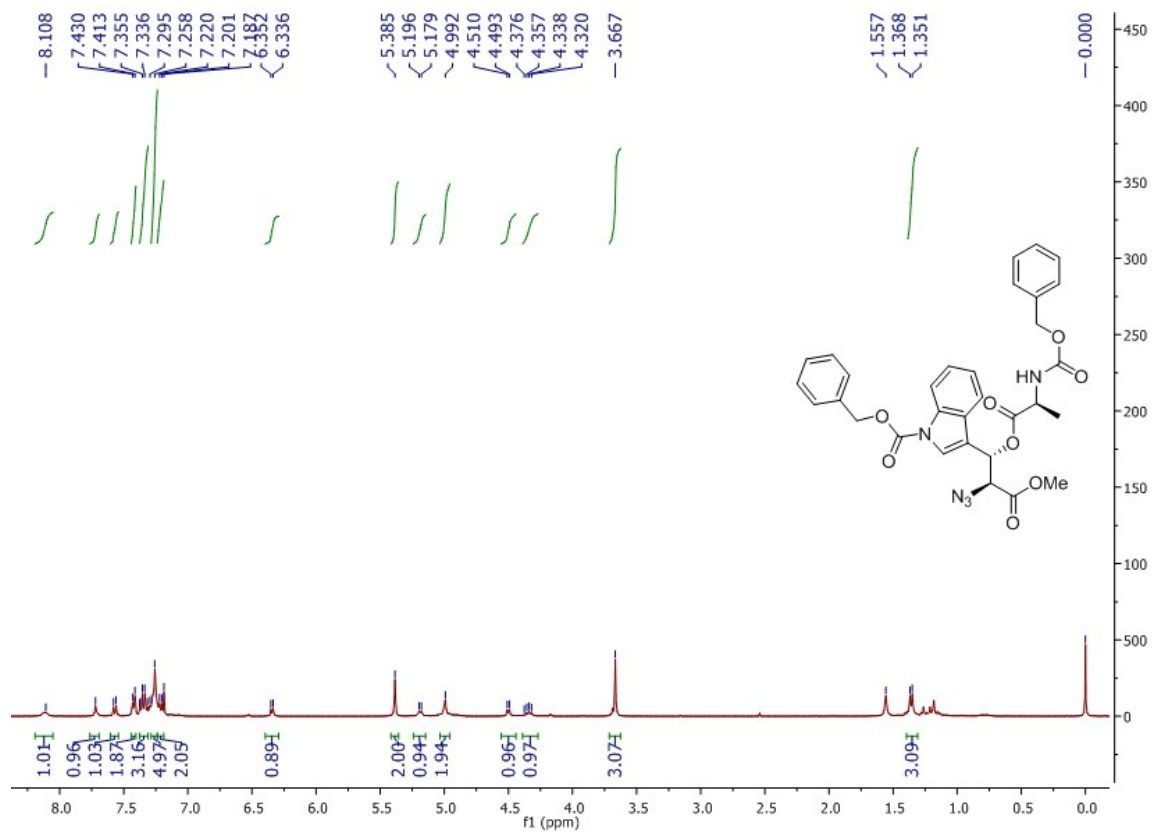


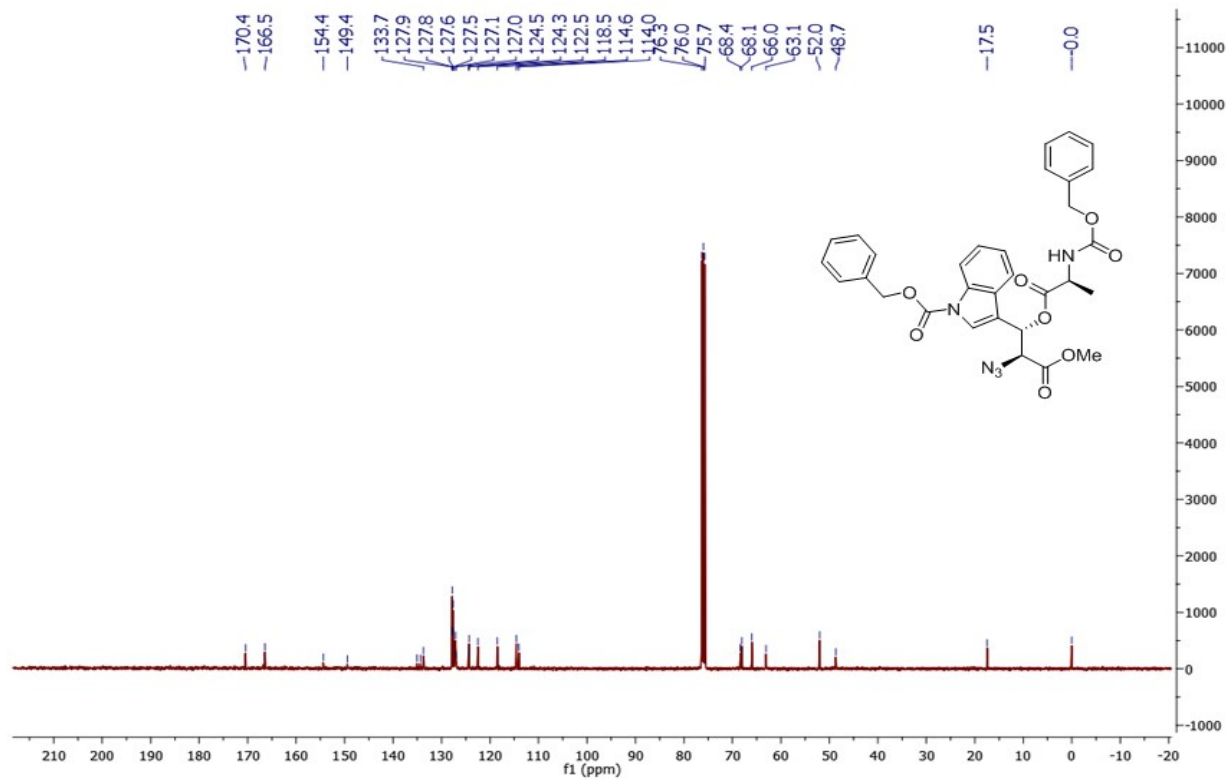
Fig 1b: 1D gradient NOE spectrum of compound **3e** with an initial selective pulse at 4.26 ppm creates a new peak of the same phase at 4.41 ppm due to rotameric chemical exchange.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3f**

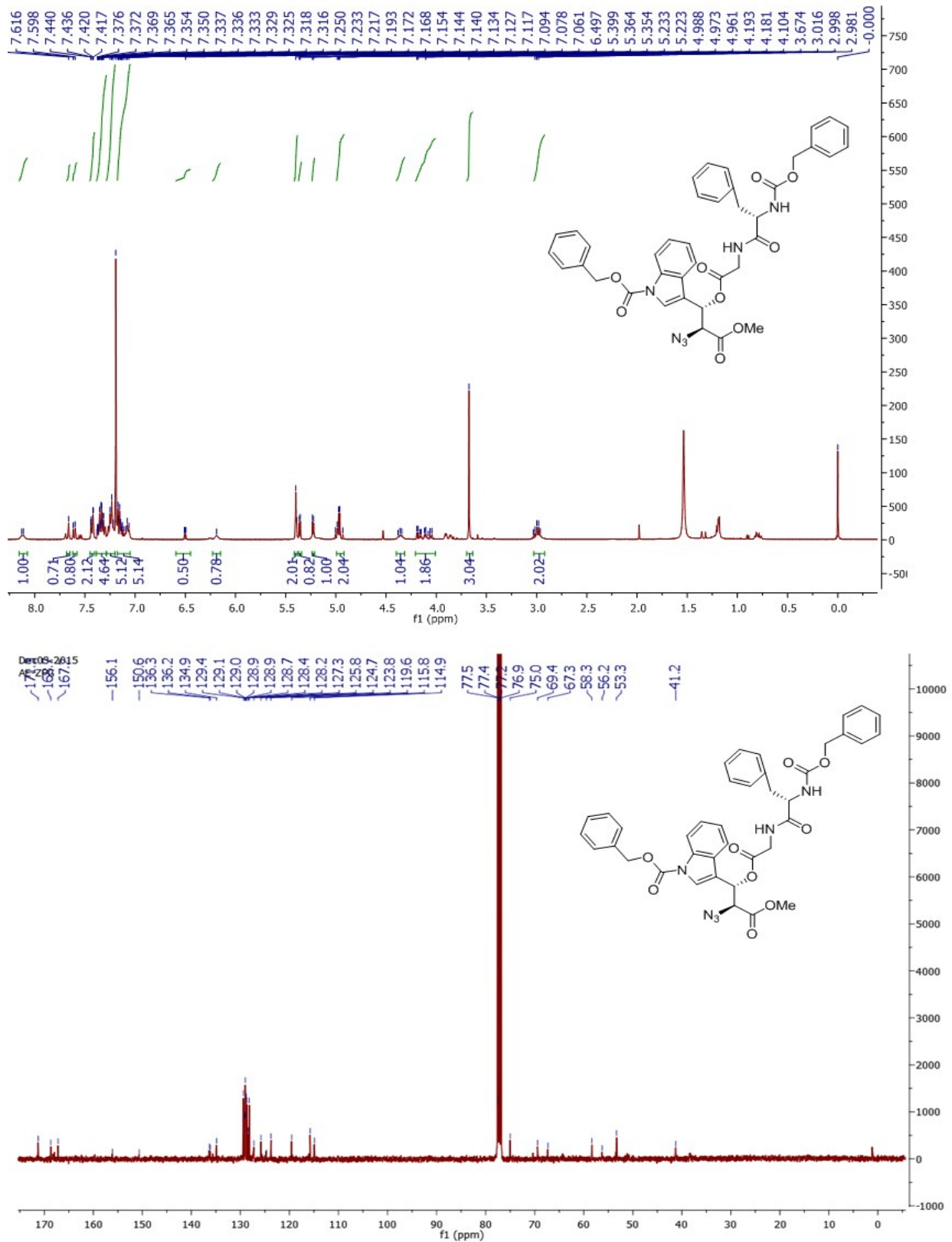




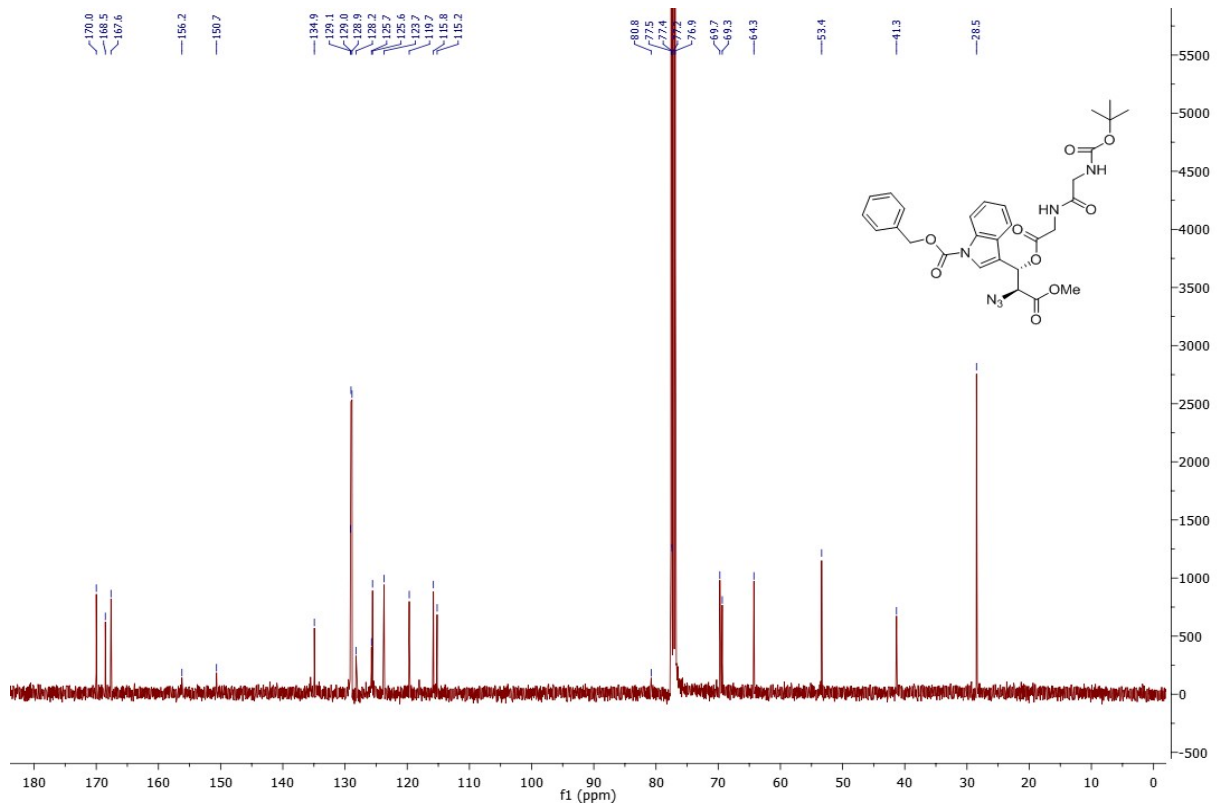
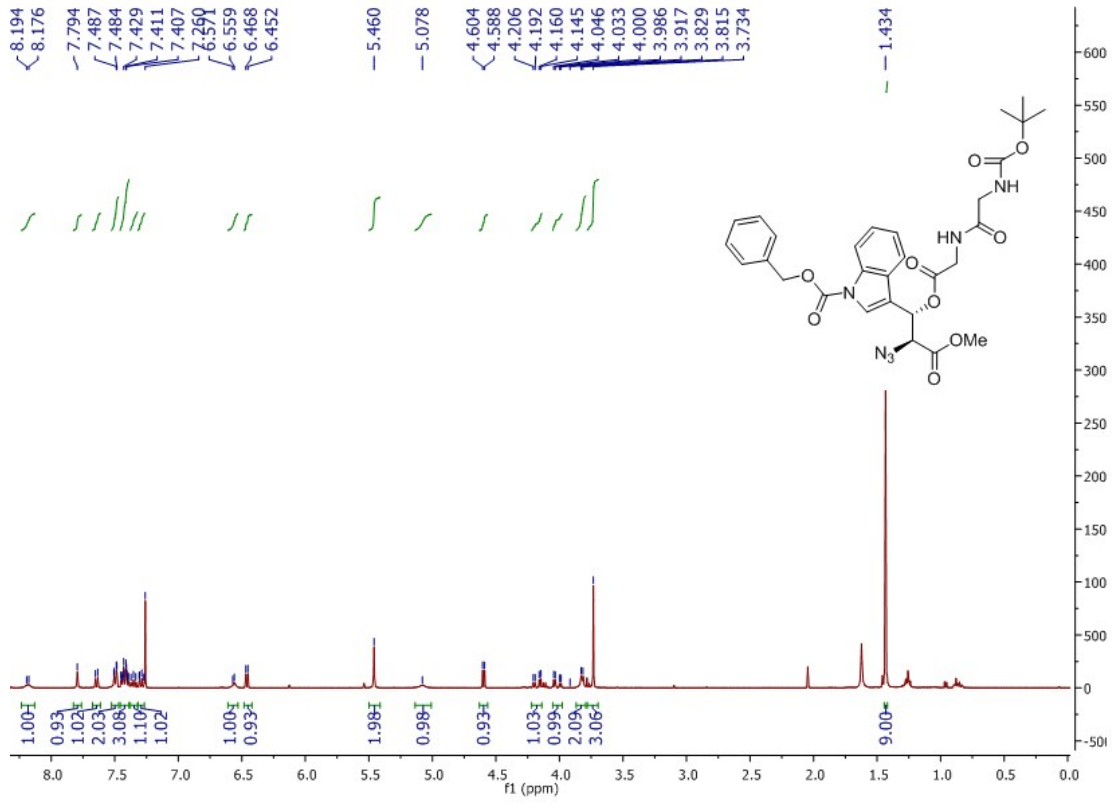
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of compound 3g**



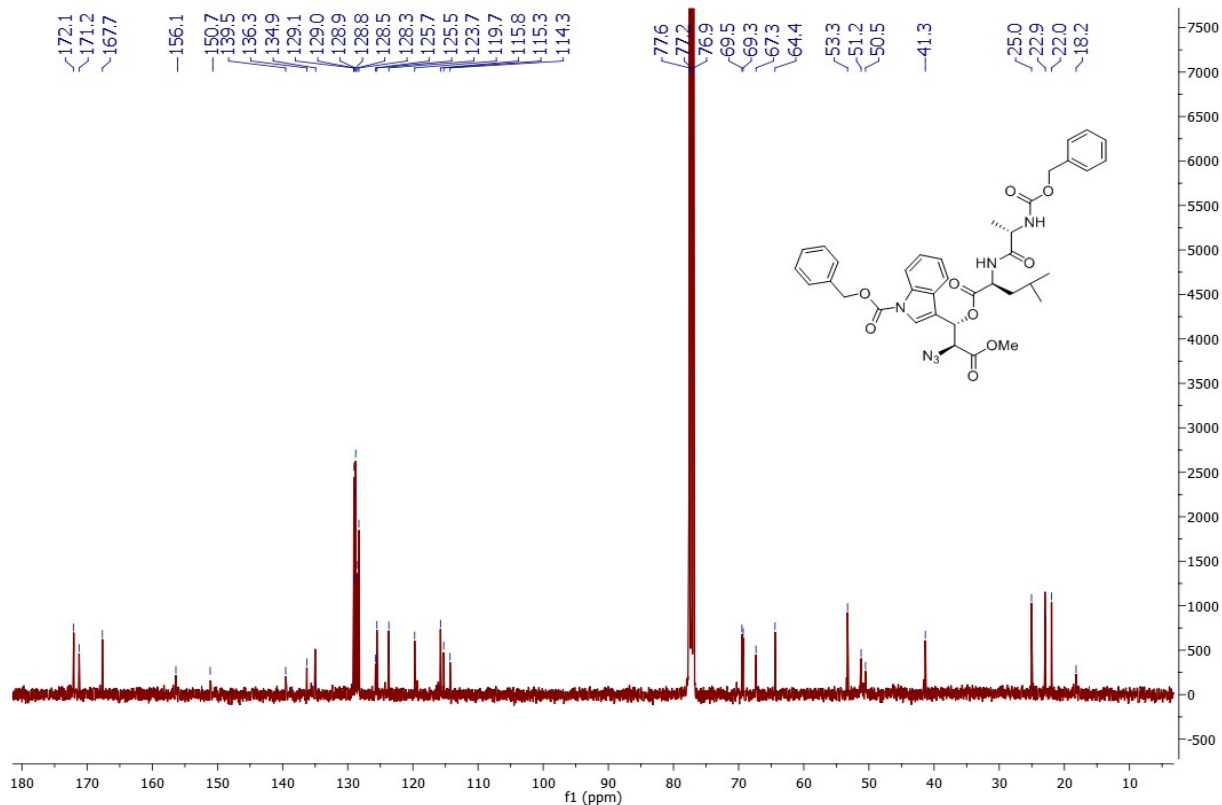
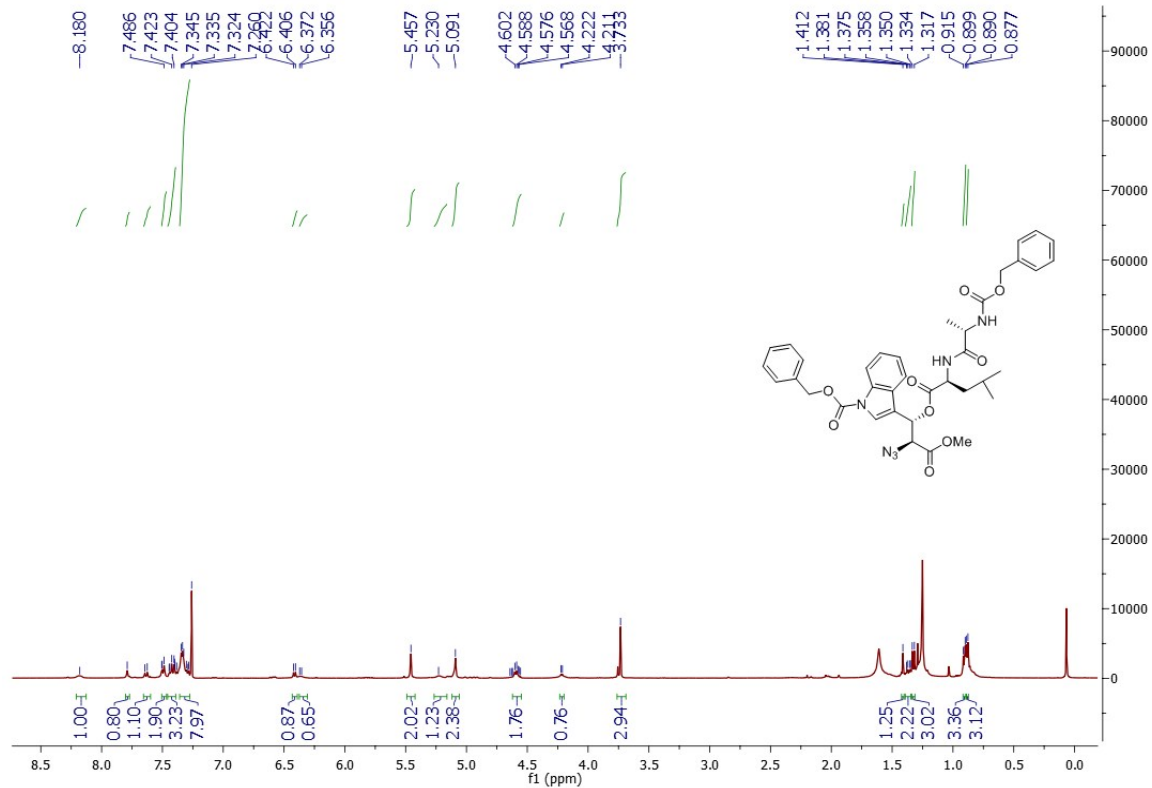
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3h**



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3i**

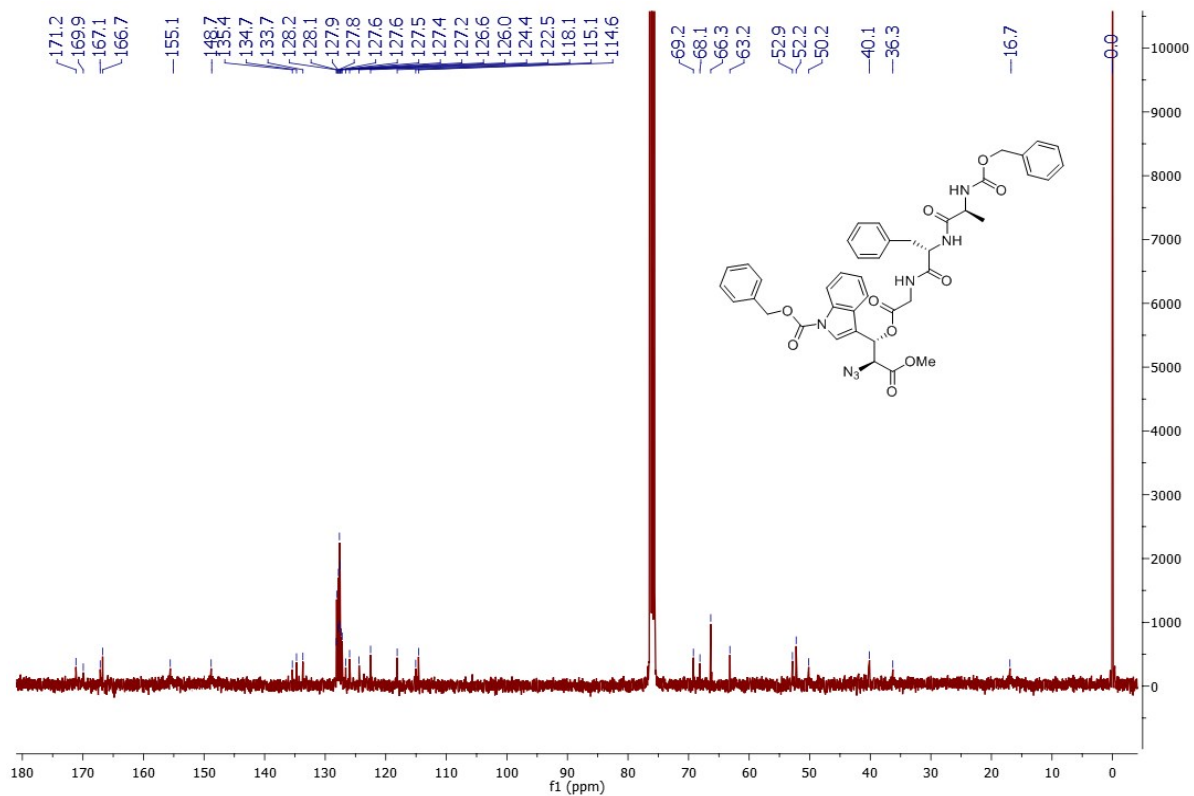
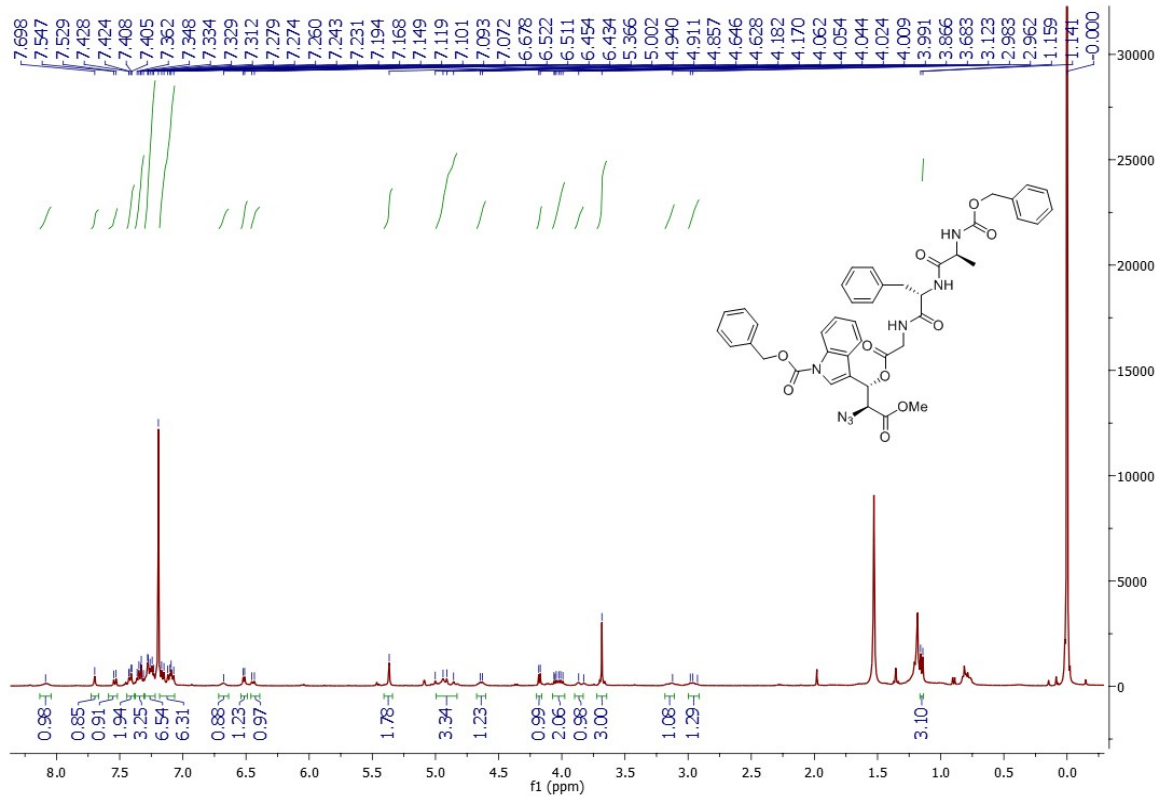


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3j**

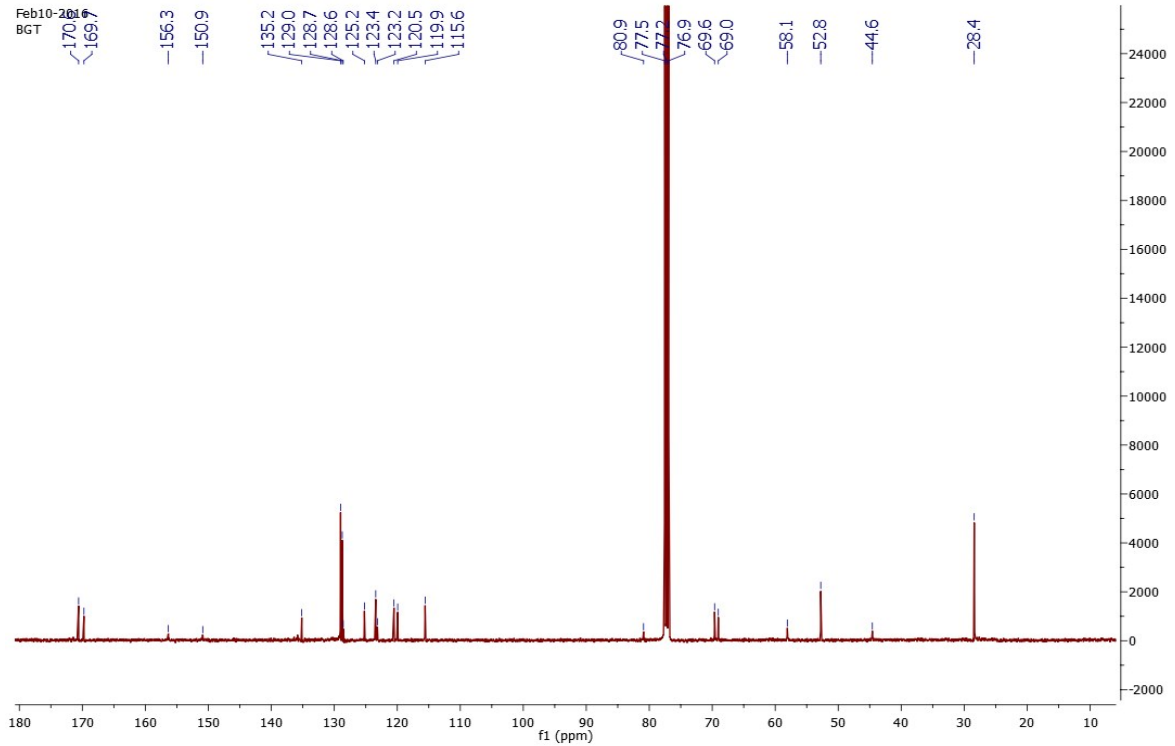
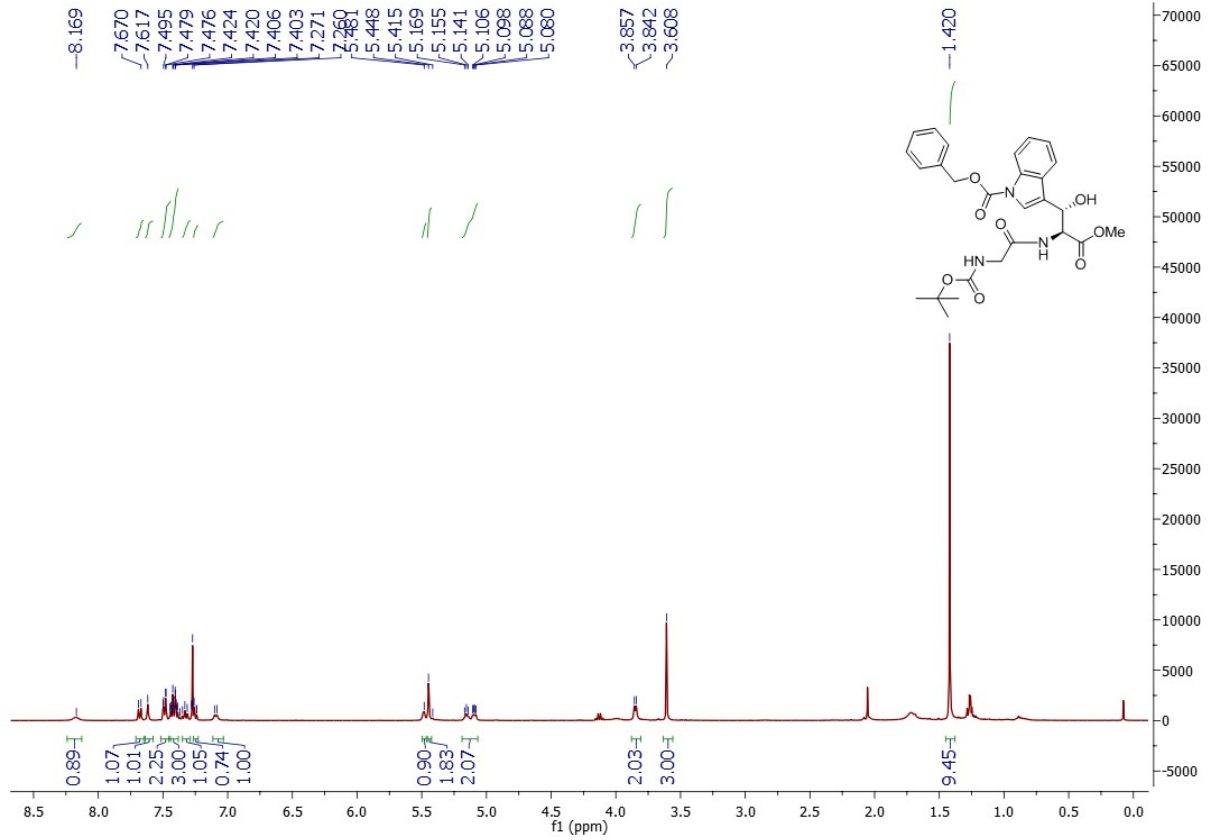




$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of compound **3k**

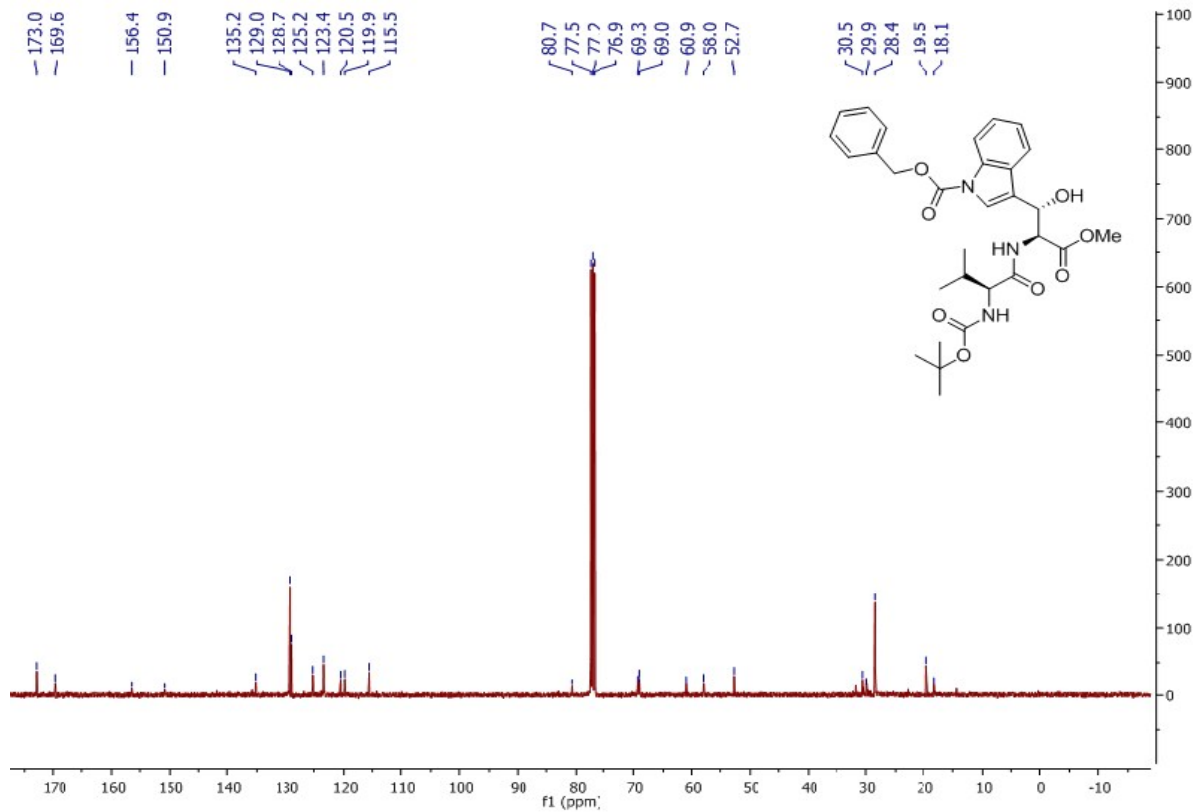
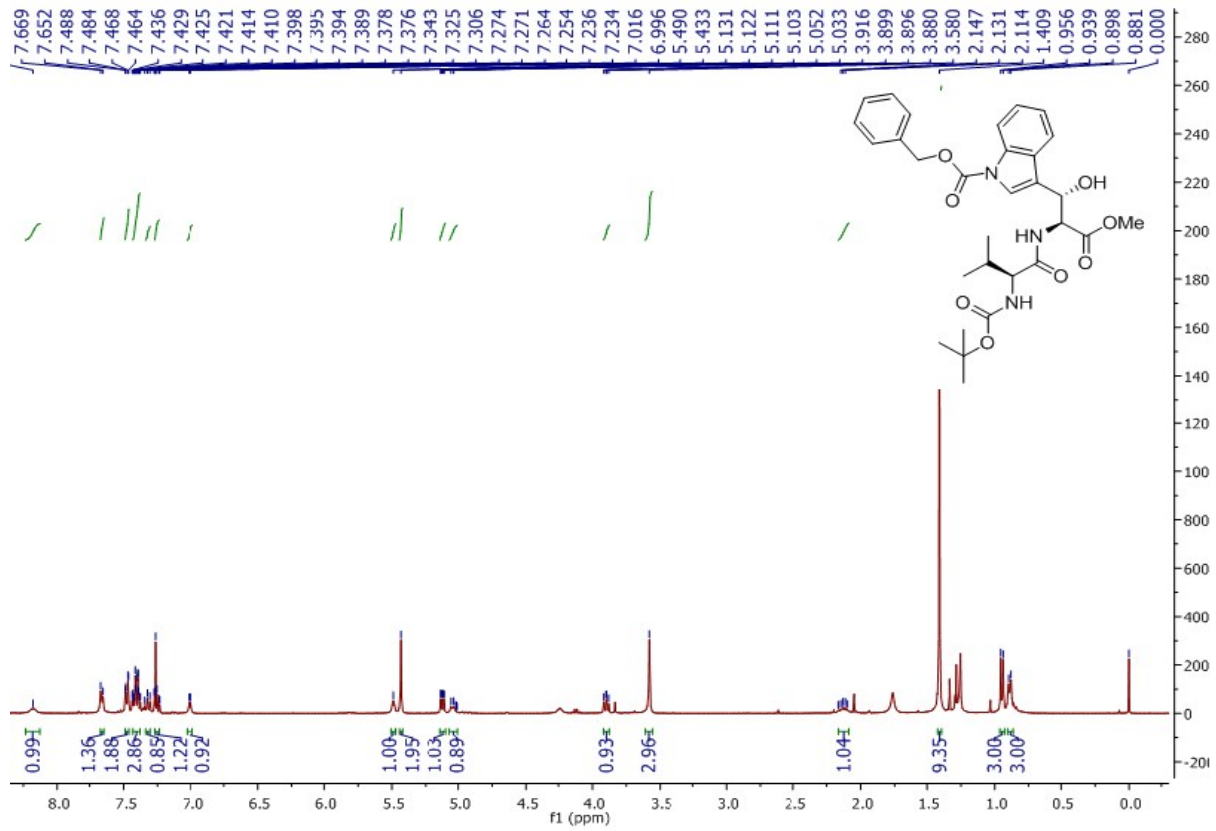


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of Ligated product **4a**

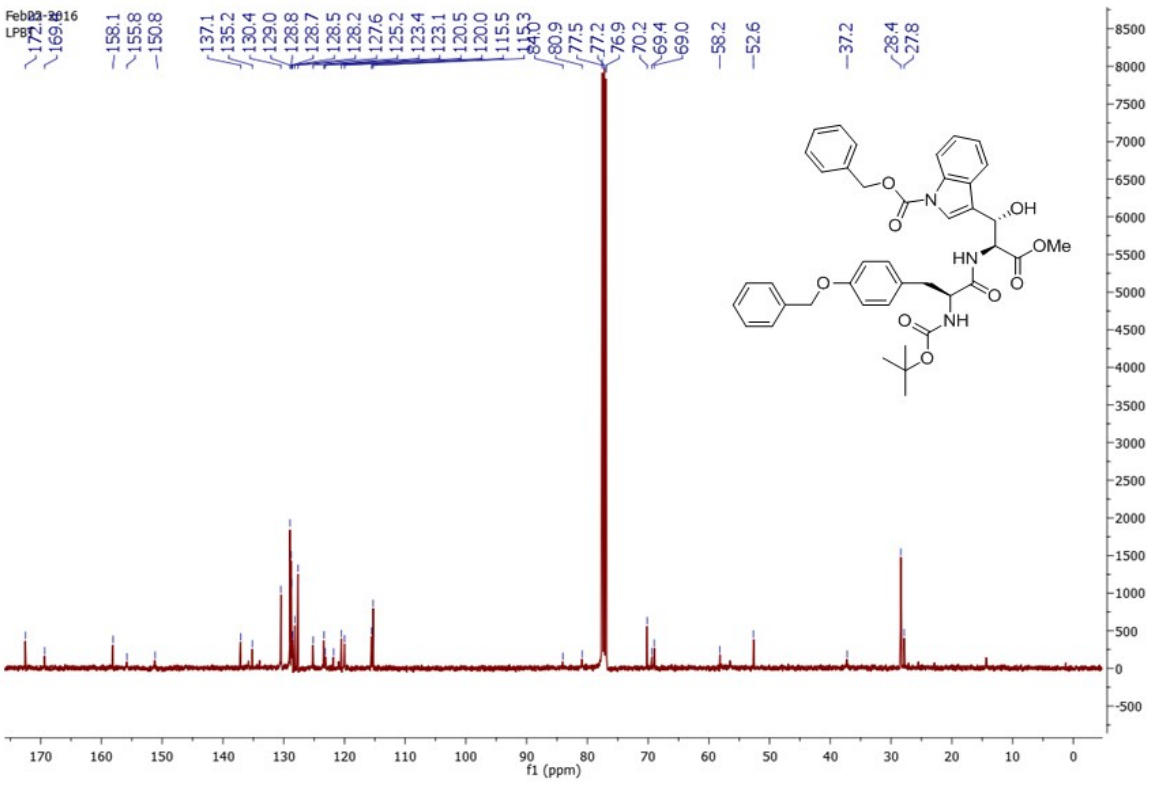
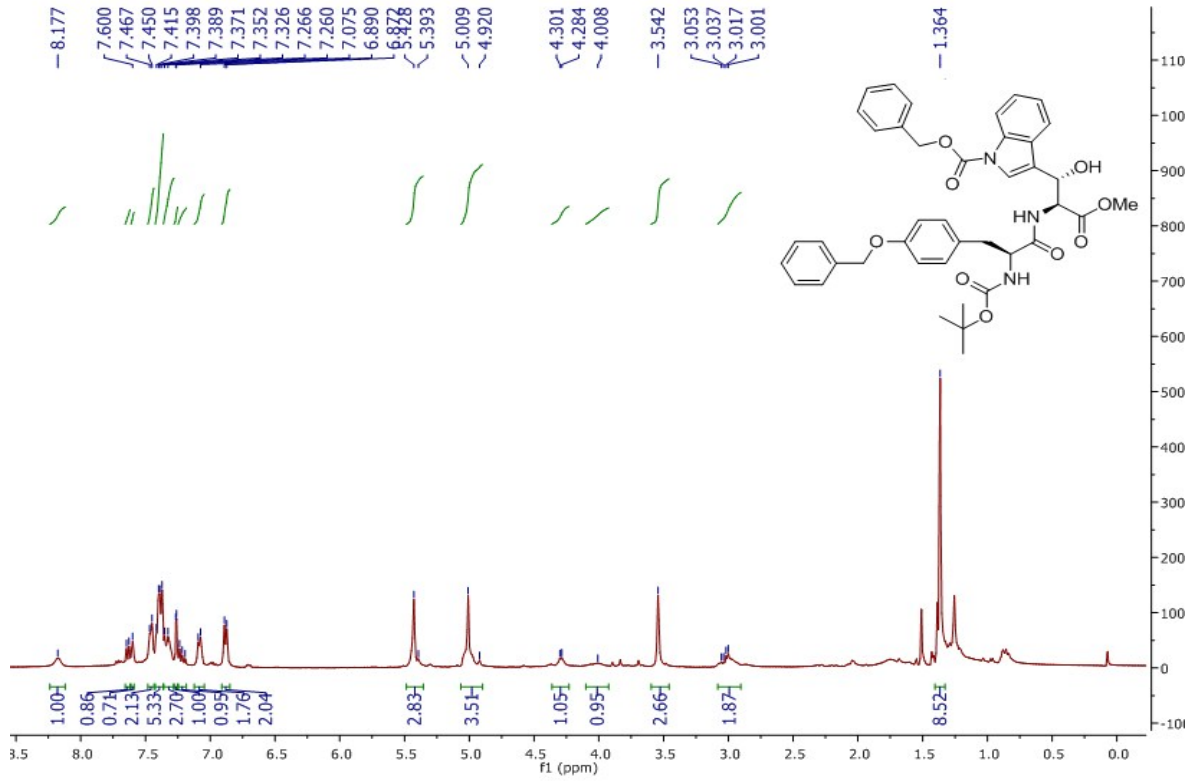




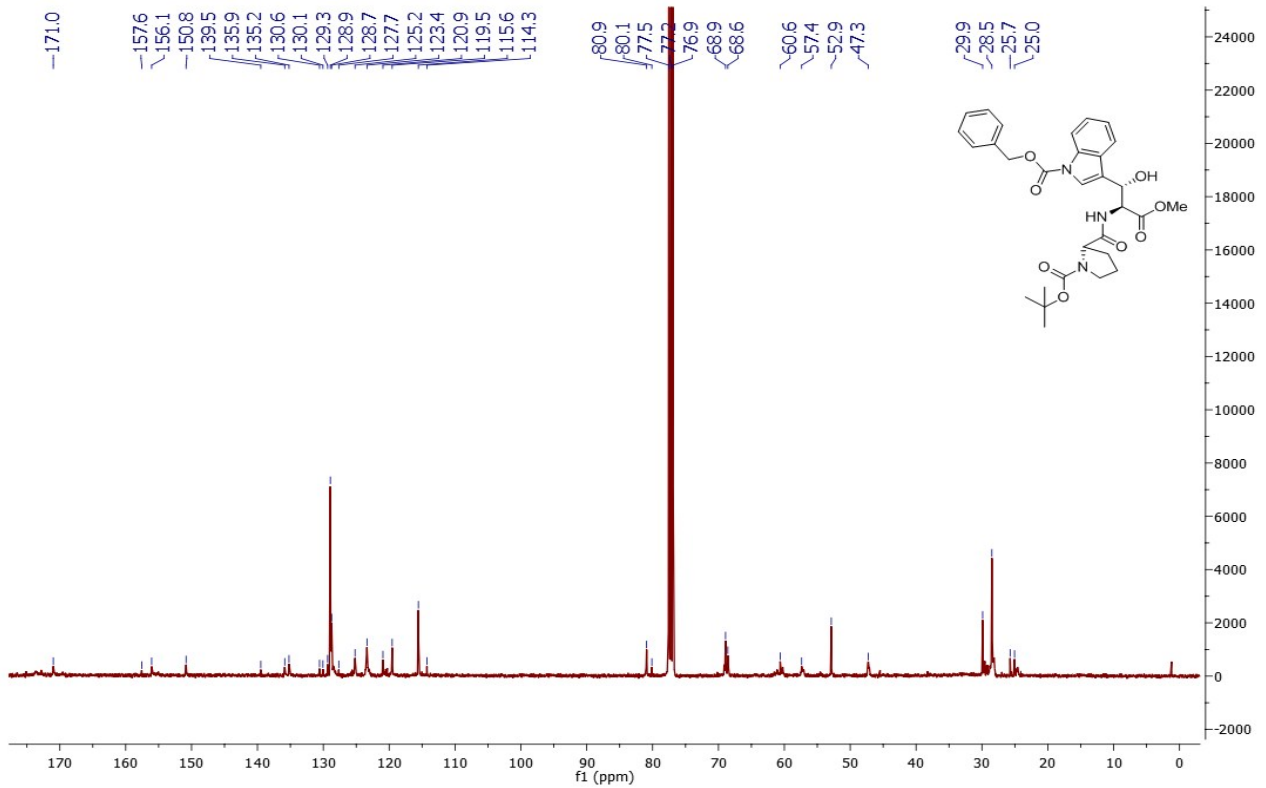
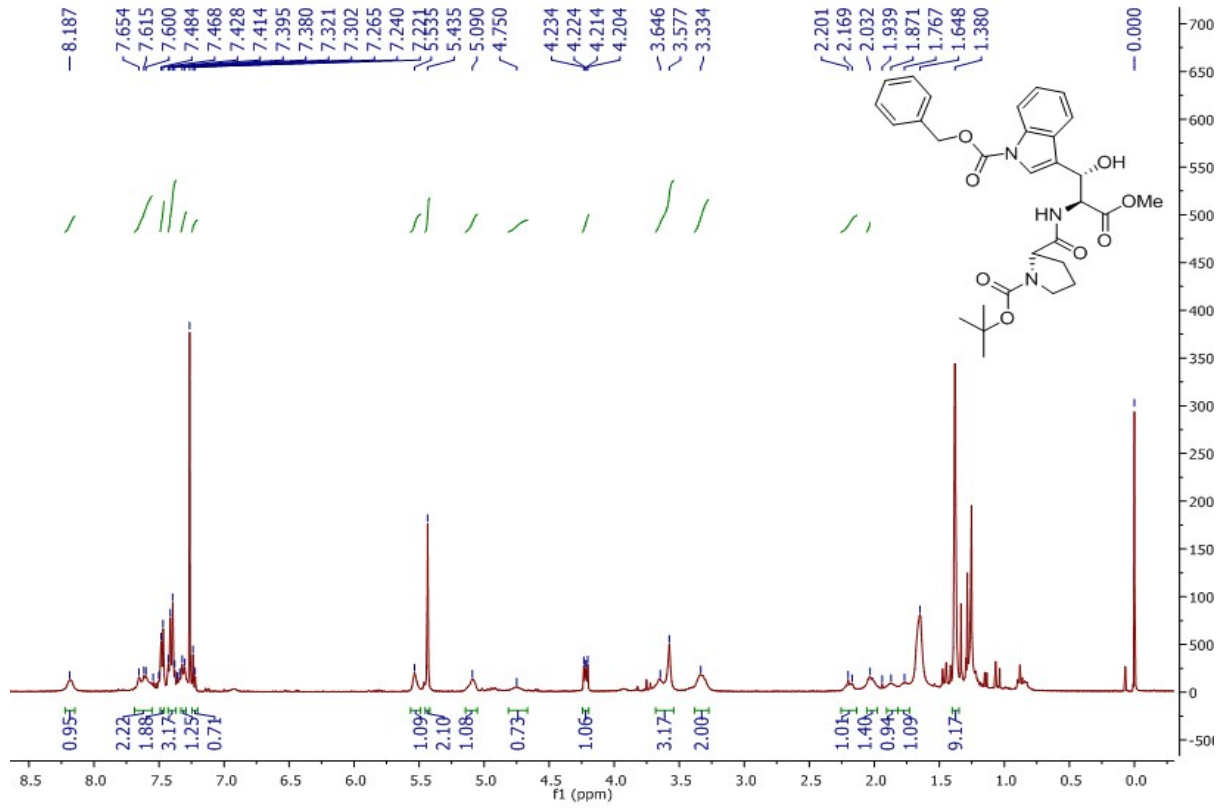
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of Ligated product **4c**



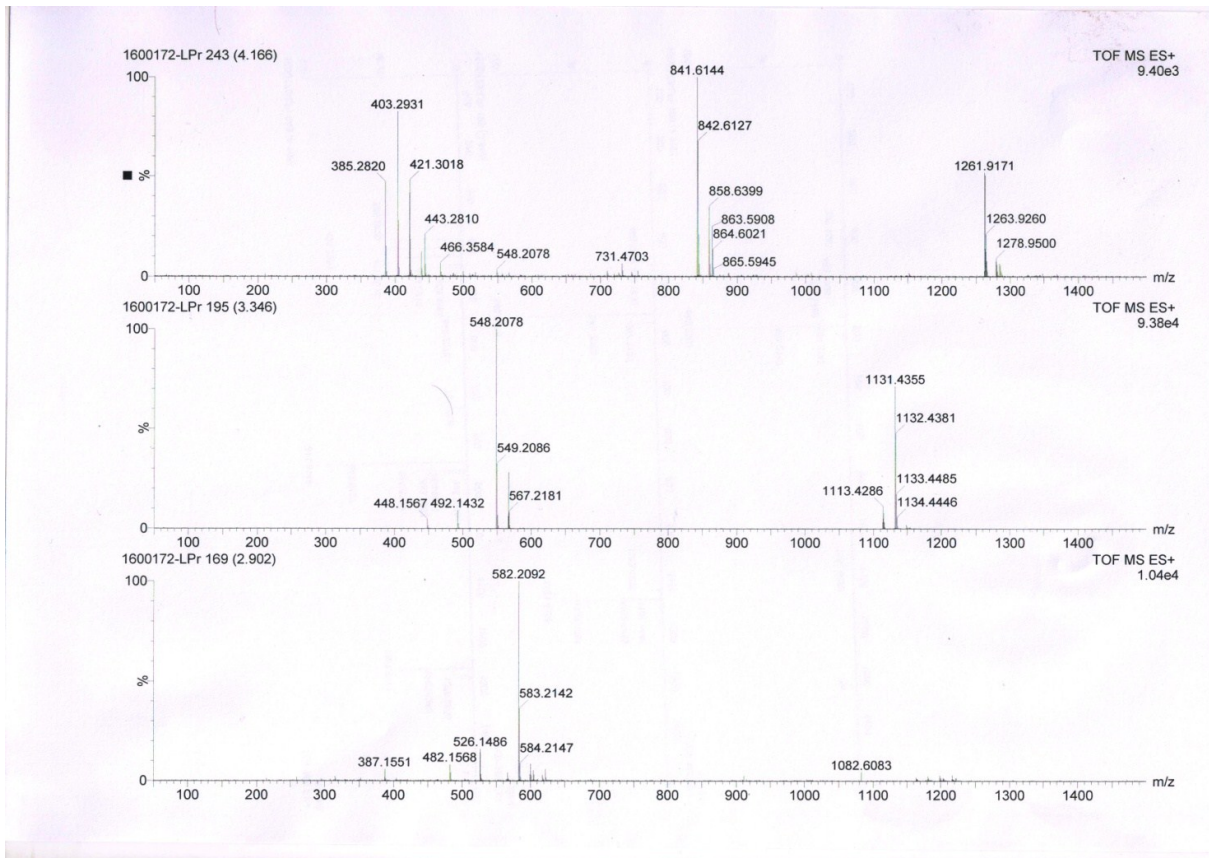
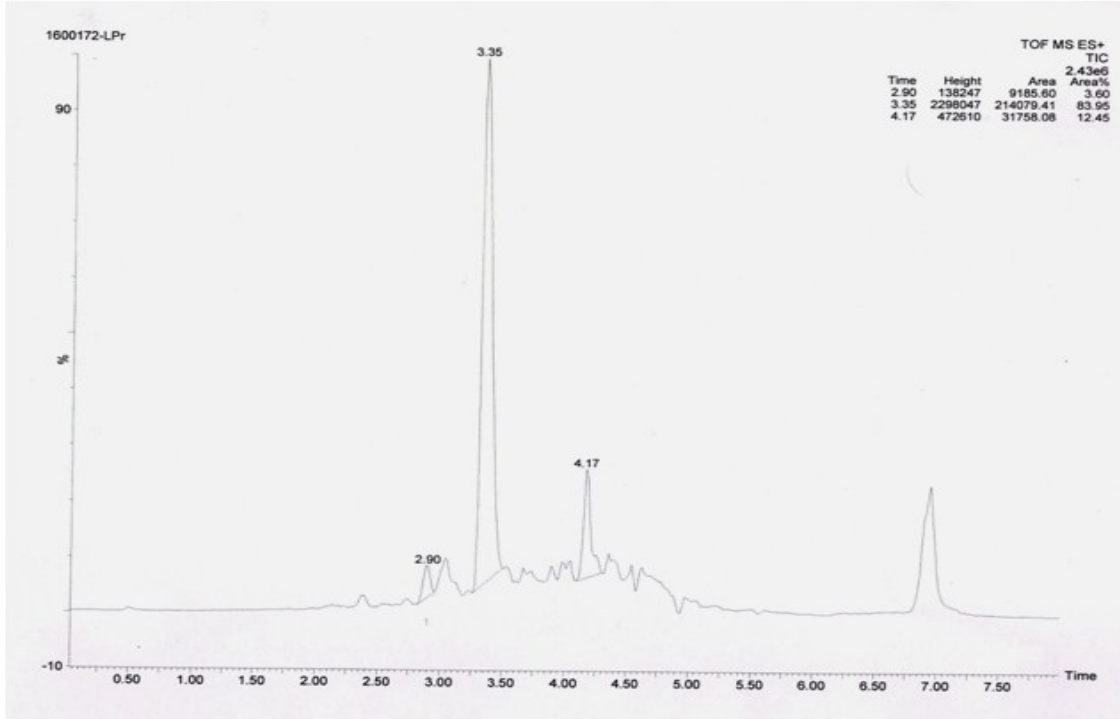
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of Ligated product **4d**



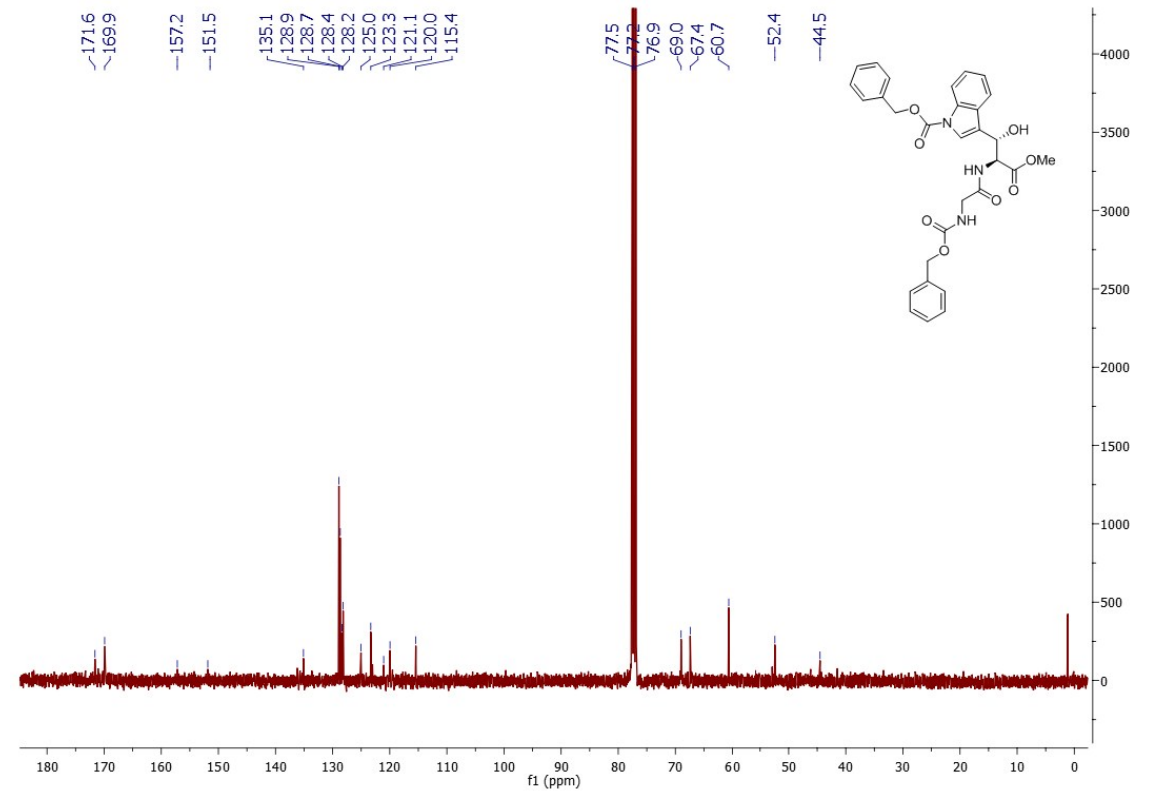
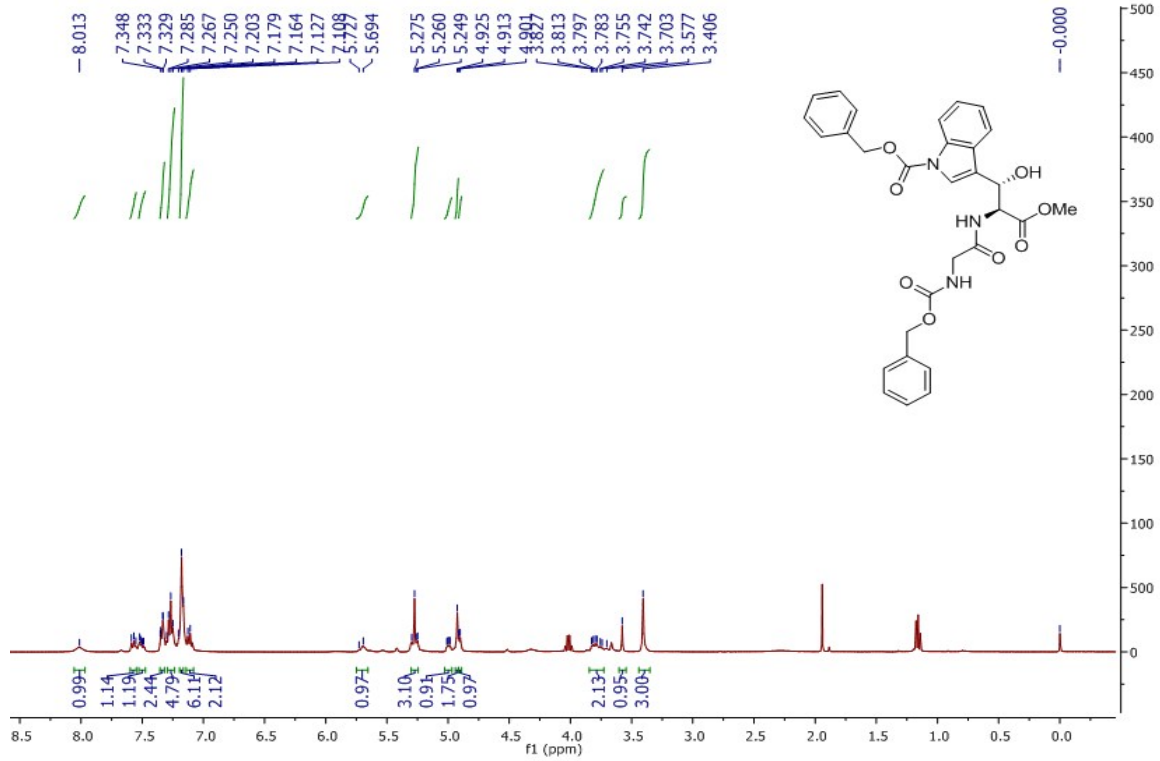
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of Ligated product **4e**



LC-MS data of ligated product **4e**

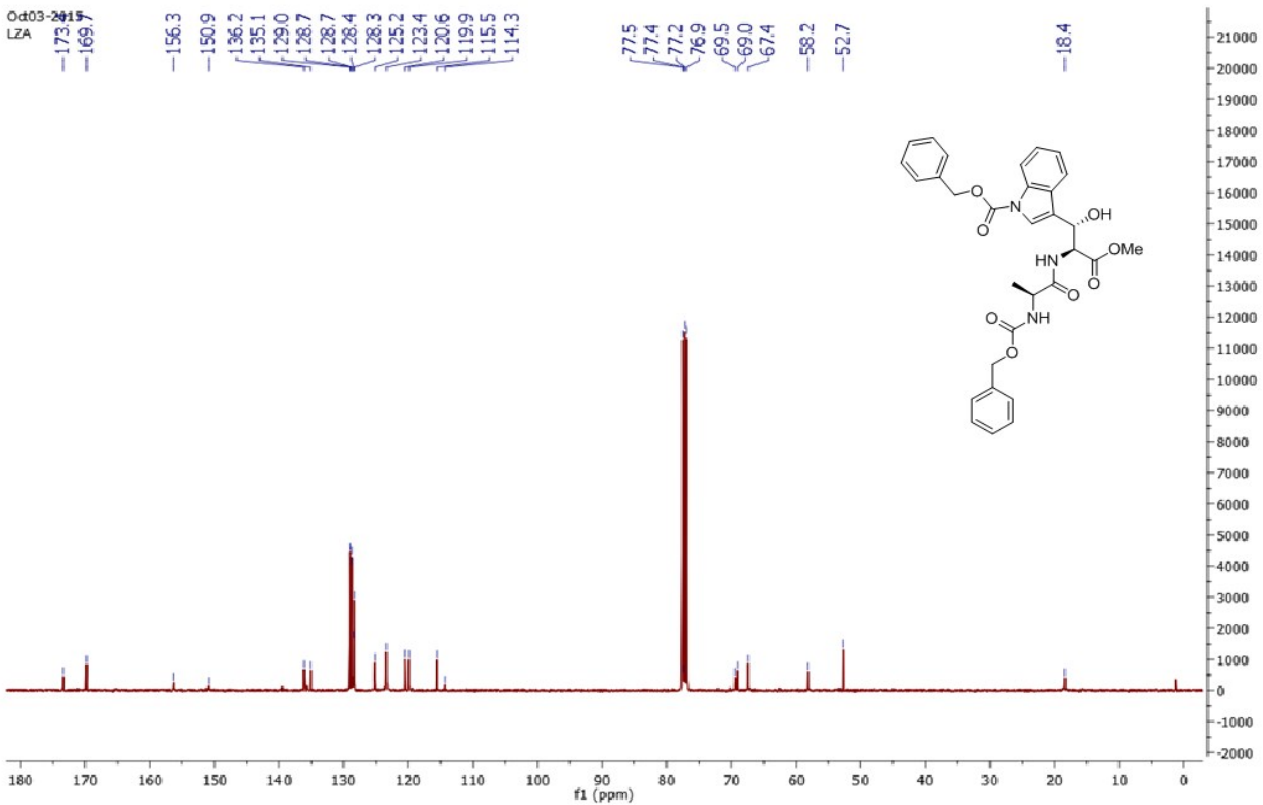
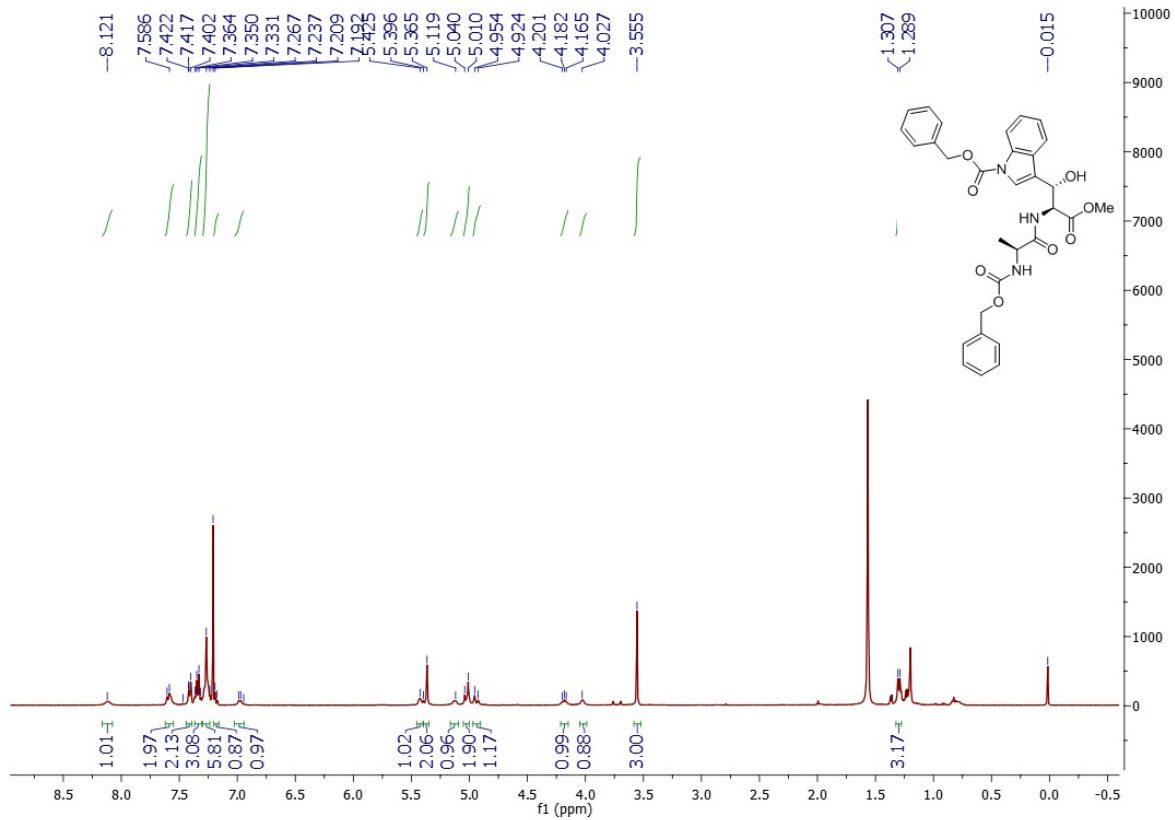


$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ) of Ligated product **4f**

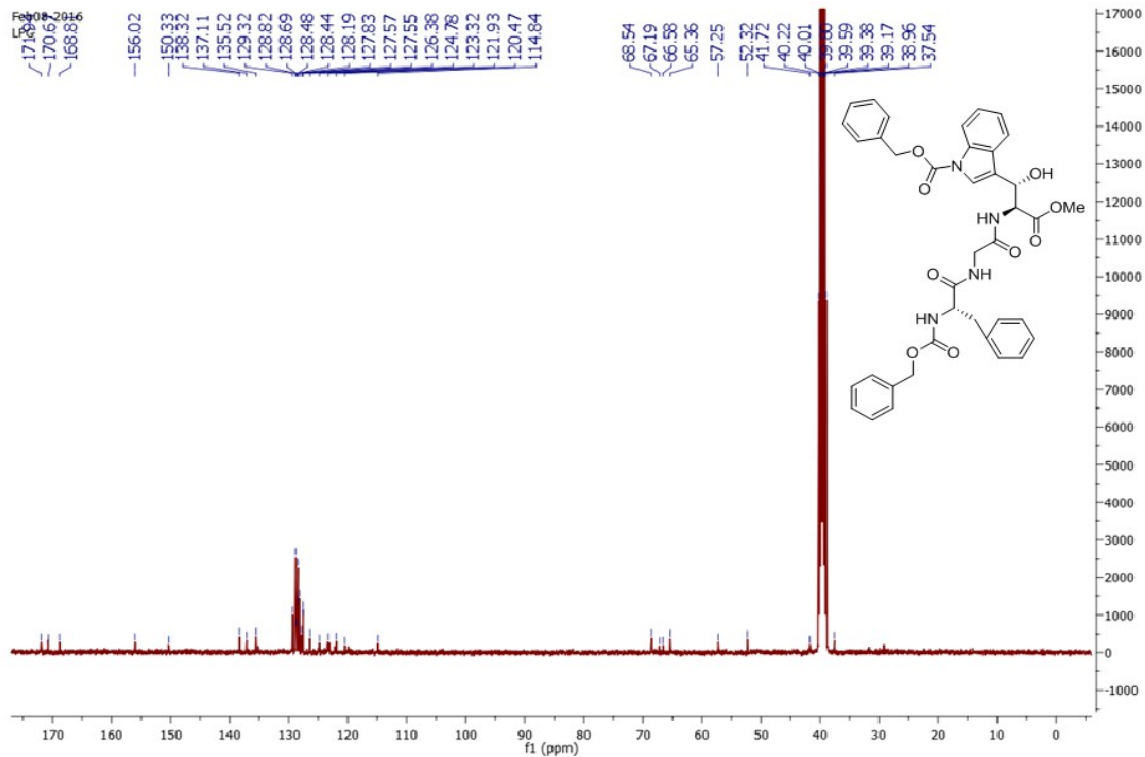
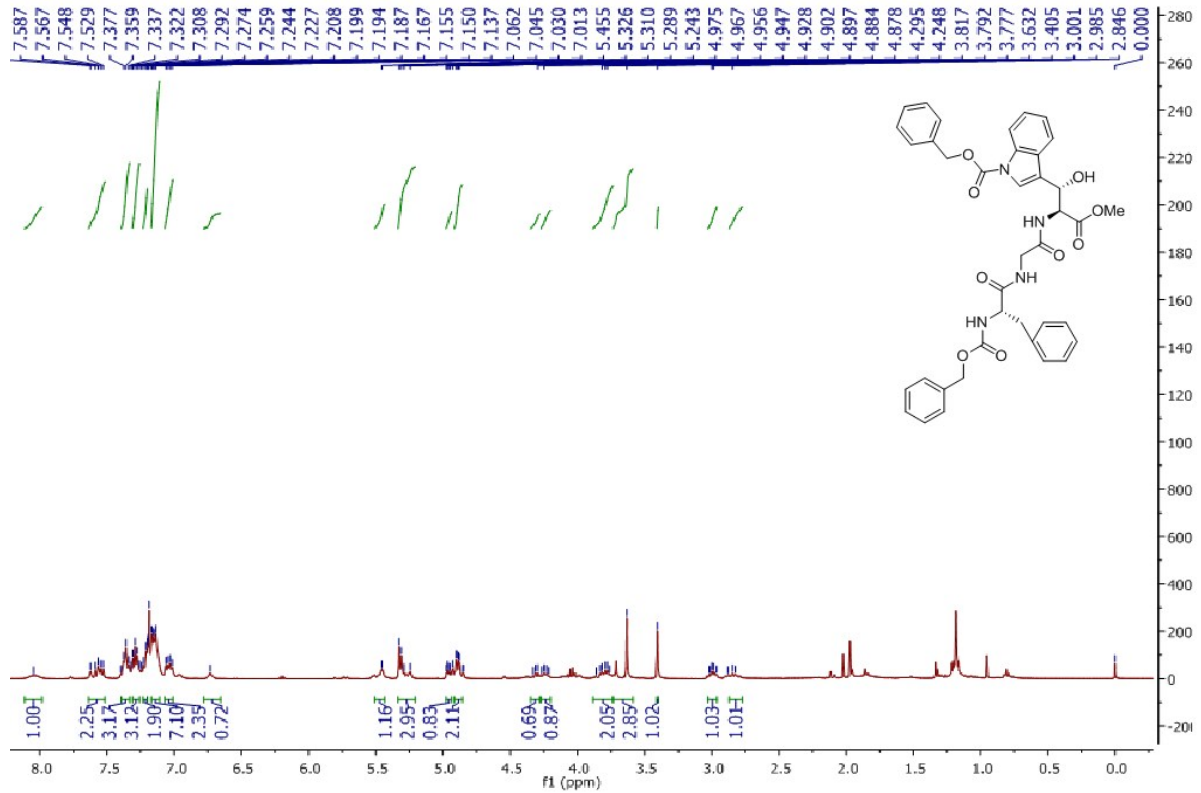




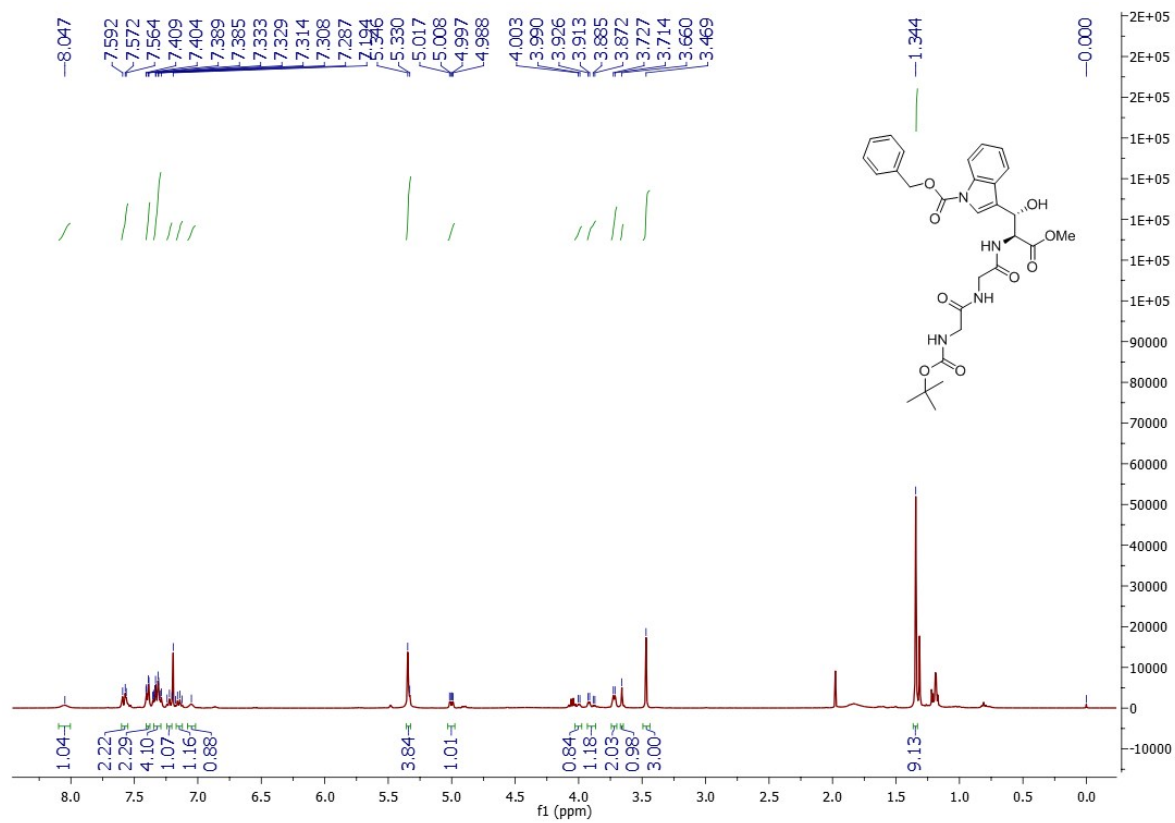
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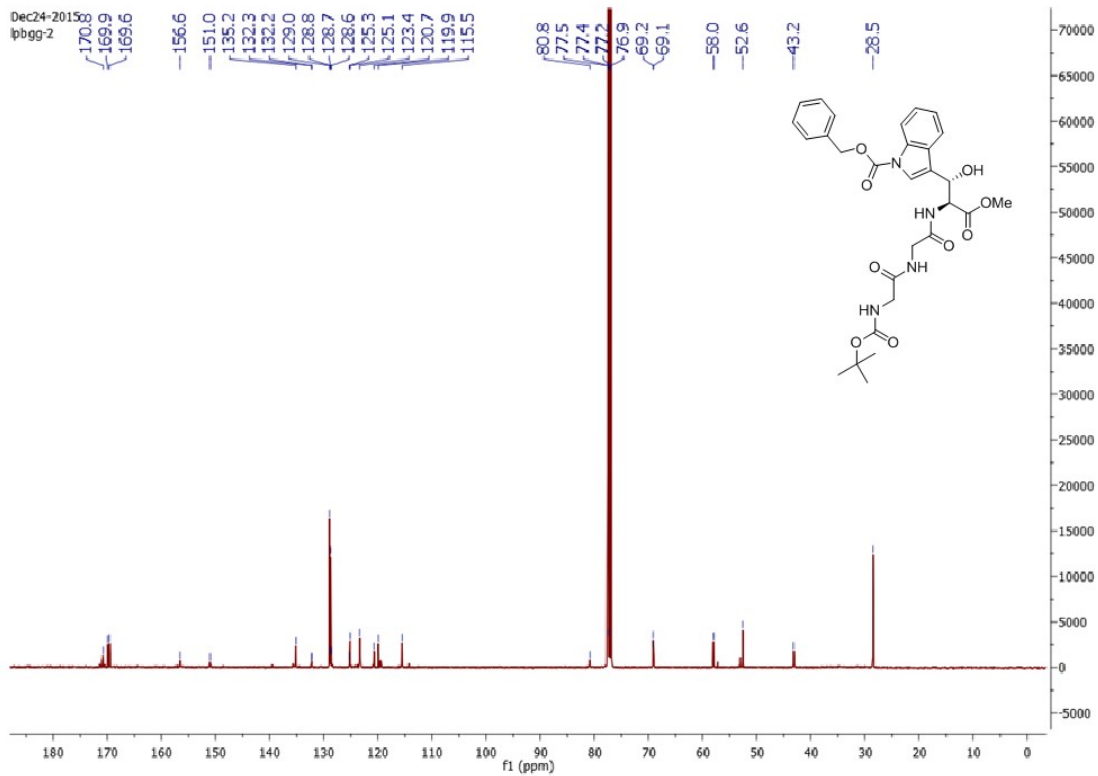


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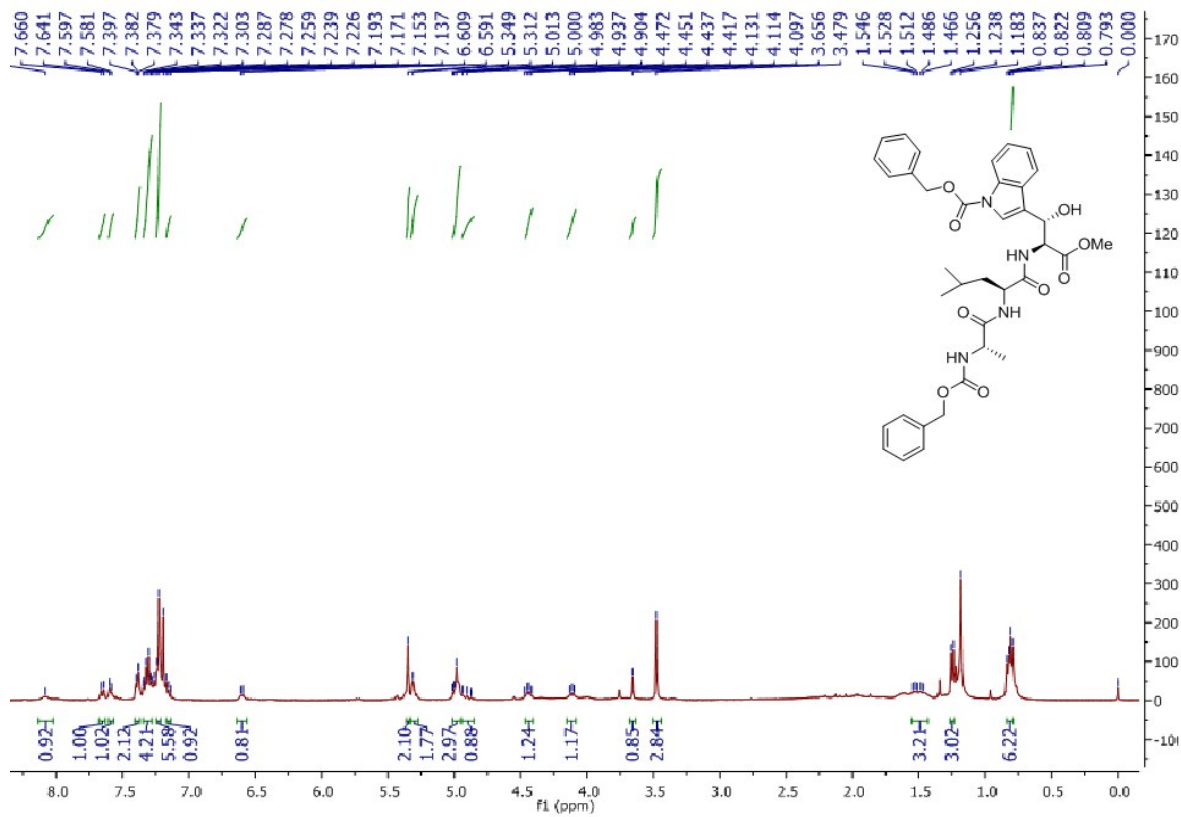


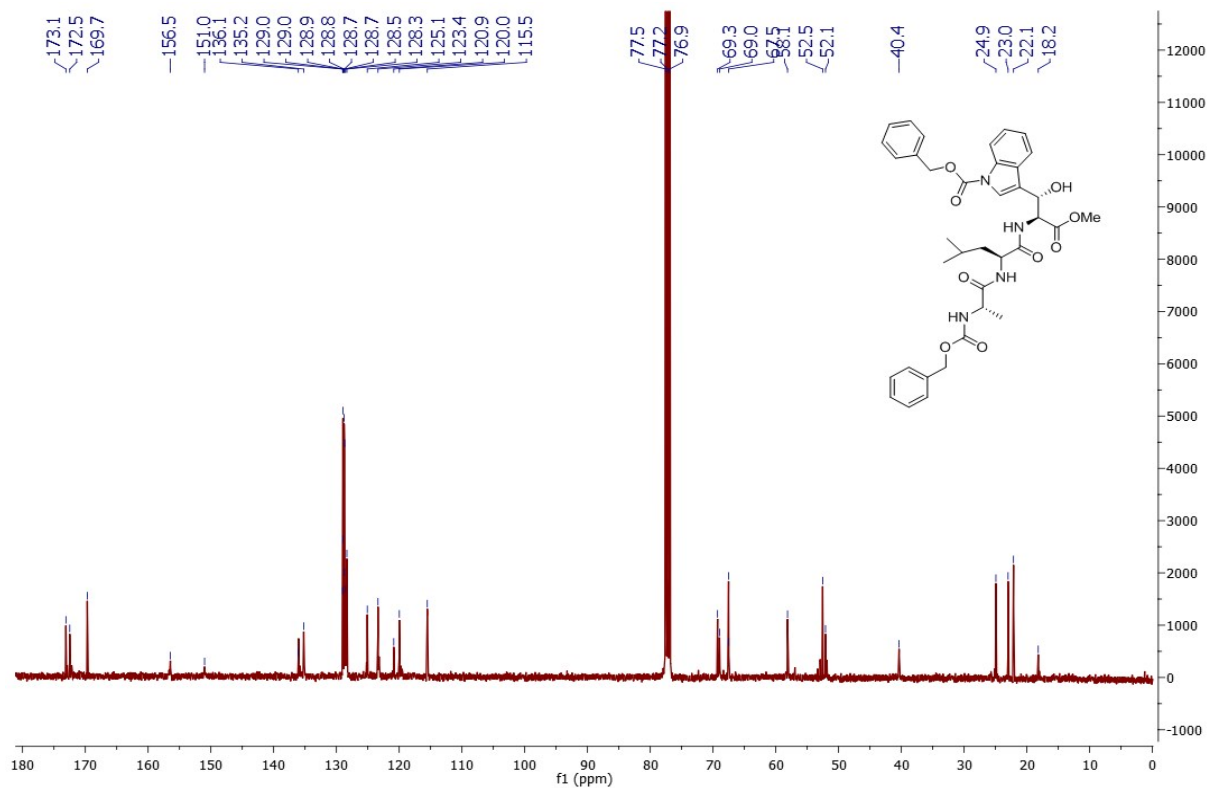
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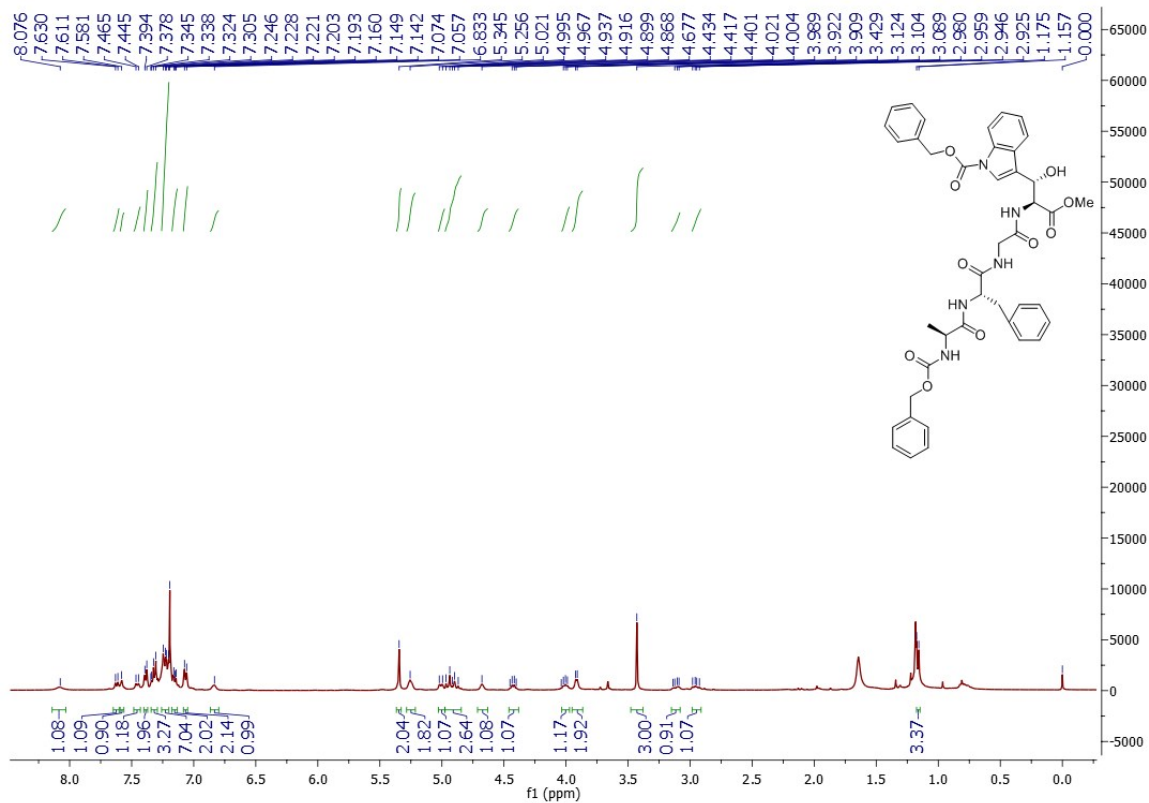


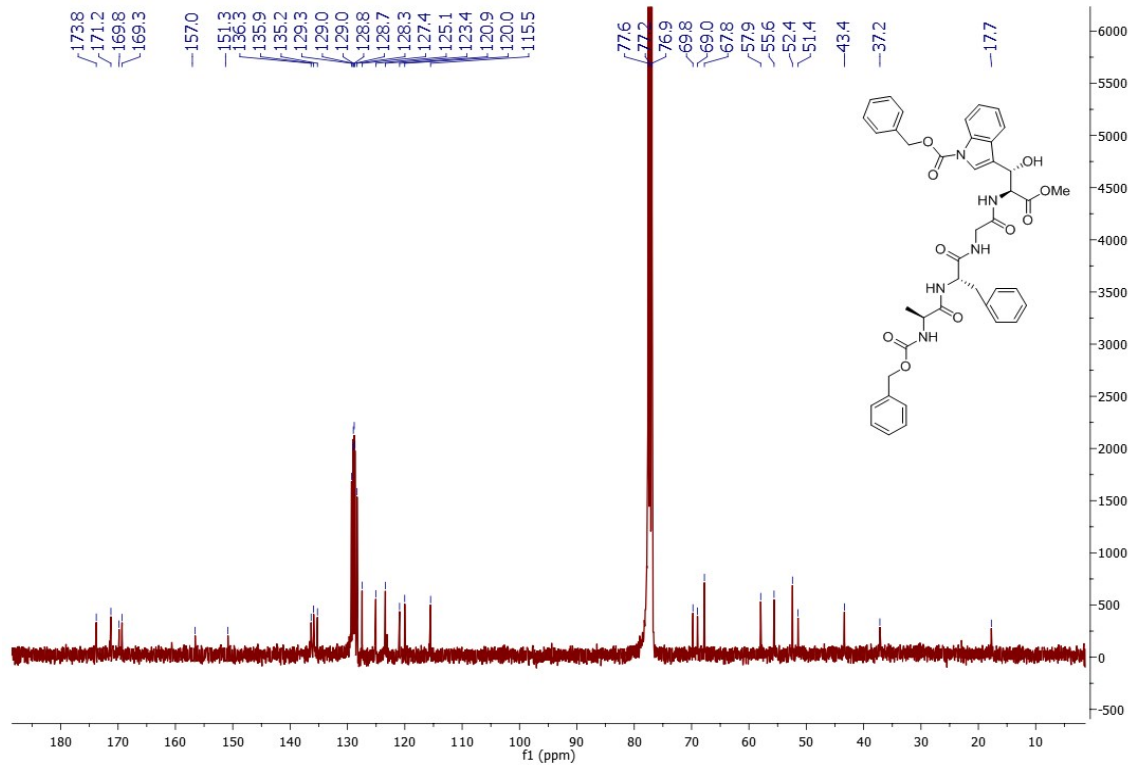
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of Ligated product **4j**



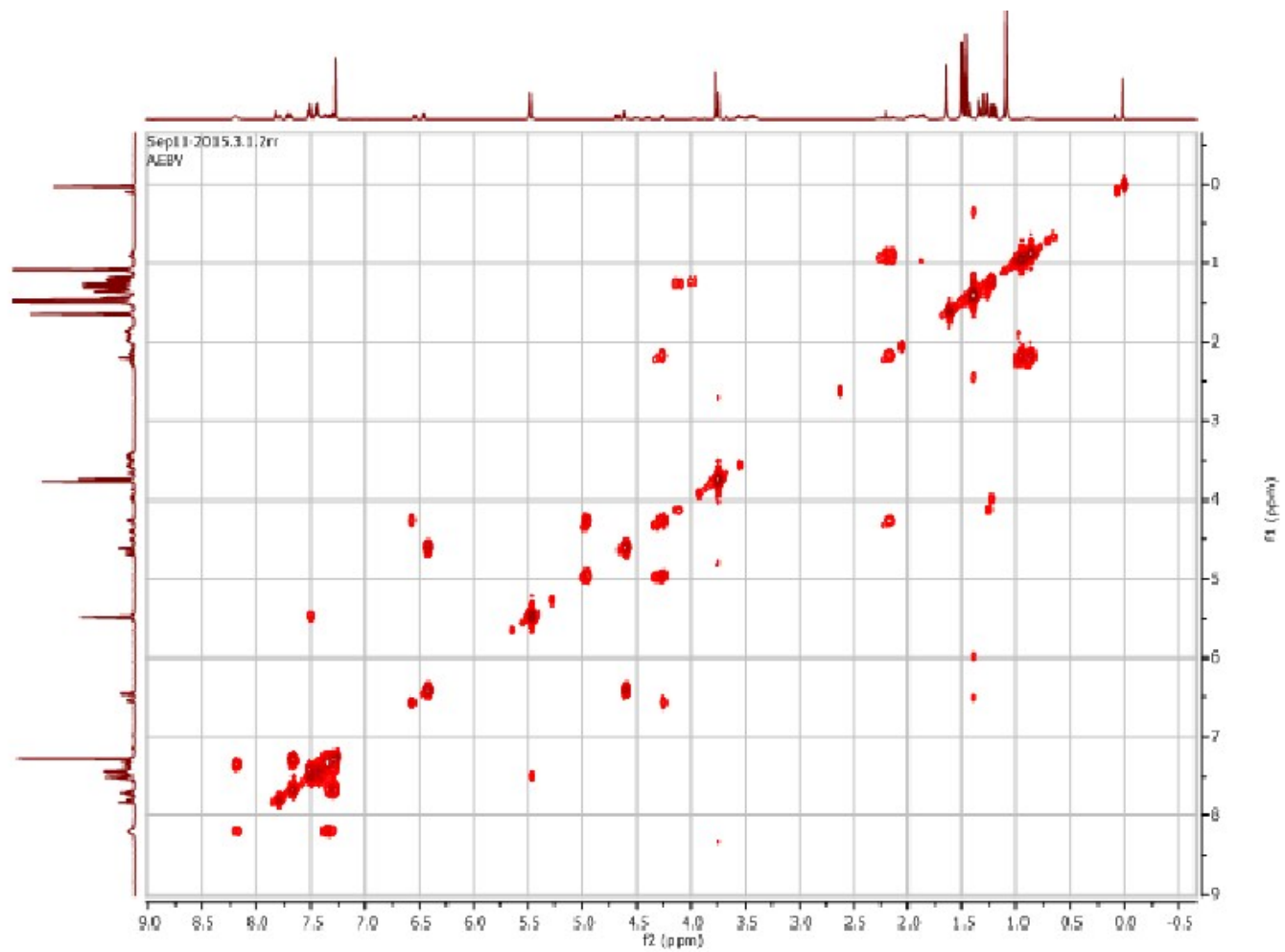


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) of Ligated product 4k**

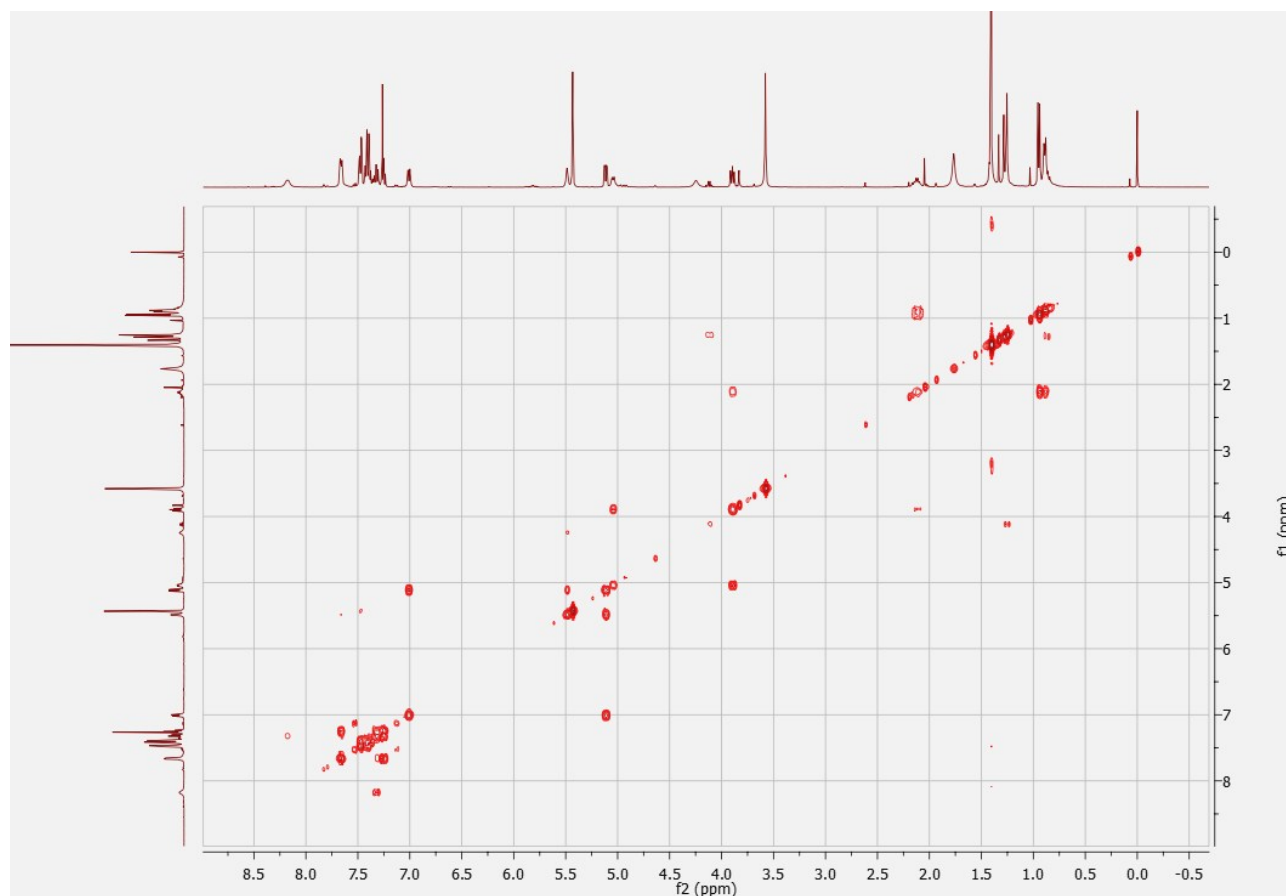




2D NMR (COSY) of precursor of ligation reaction N<sub>3</sub>-Trp(Cbz)(O-Val-Boc)-OMe **3c**



2D NMR (COSY) of Ligated peptide Boc-Val-Trp(OH)(Cbz)-OMe **4c**



2D NMR (HMBC) of Ligated peptide Boc-Val-Trp(OH)(Cbz)-OMe **4c**



