

# **Total synthesis of desoxycyclomarin C and the cyclomarazines A and B**

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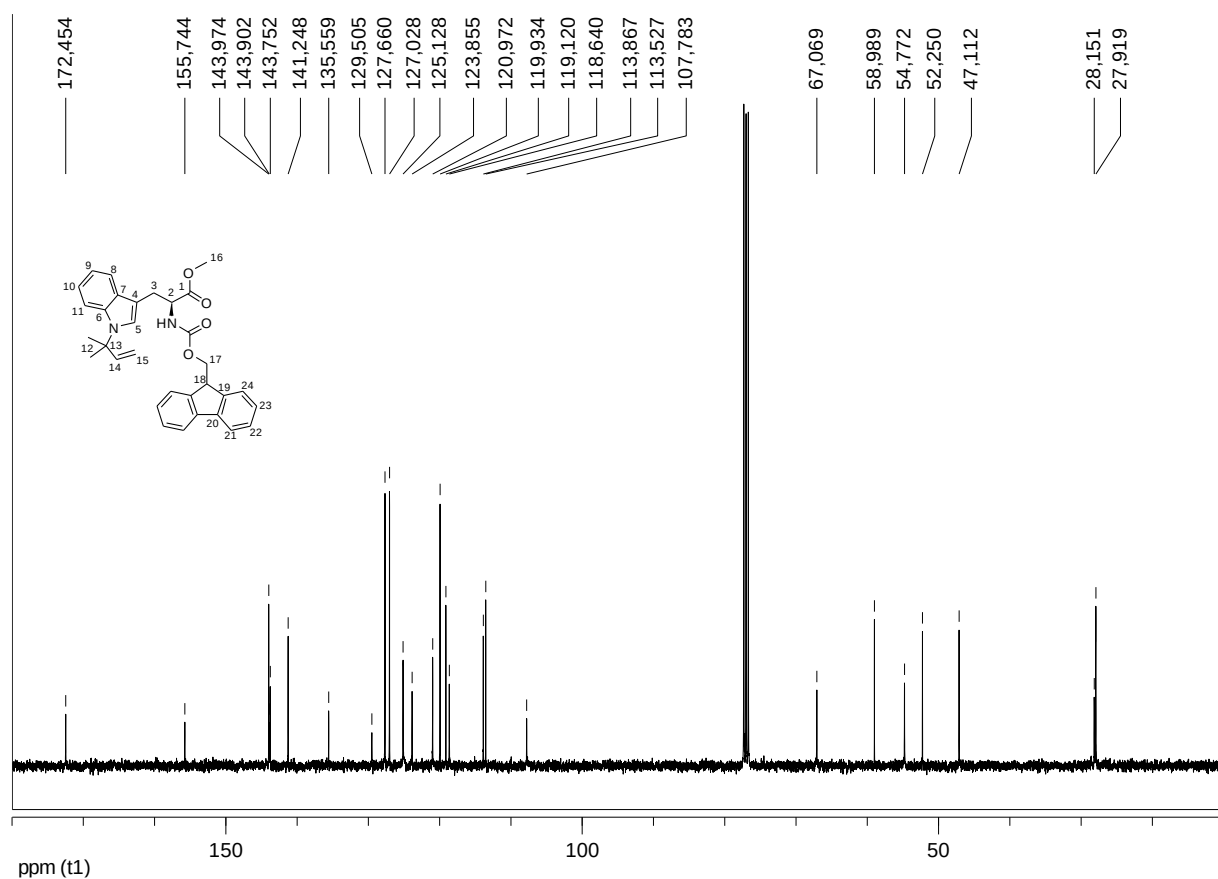
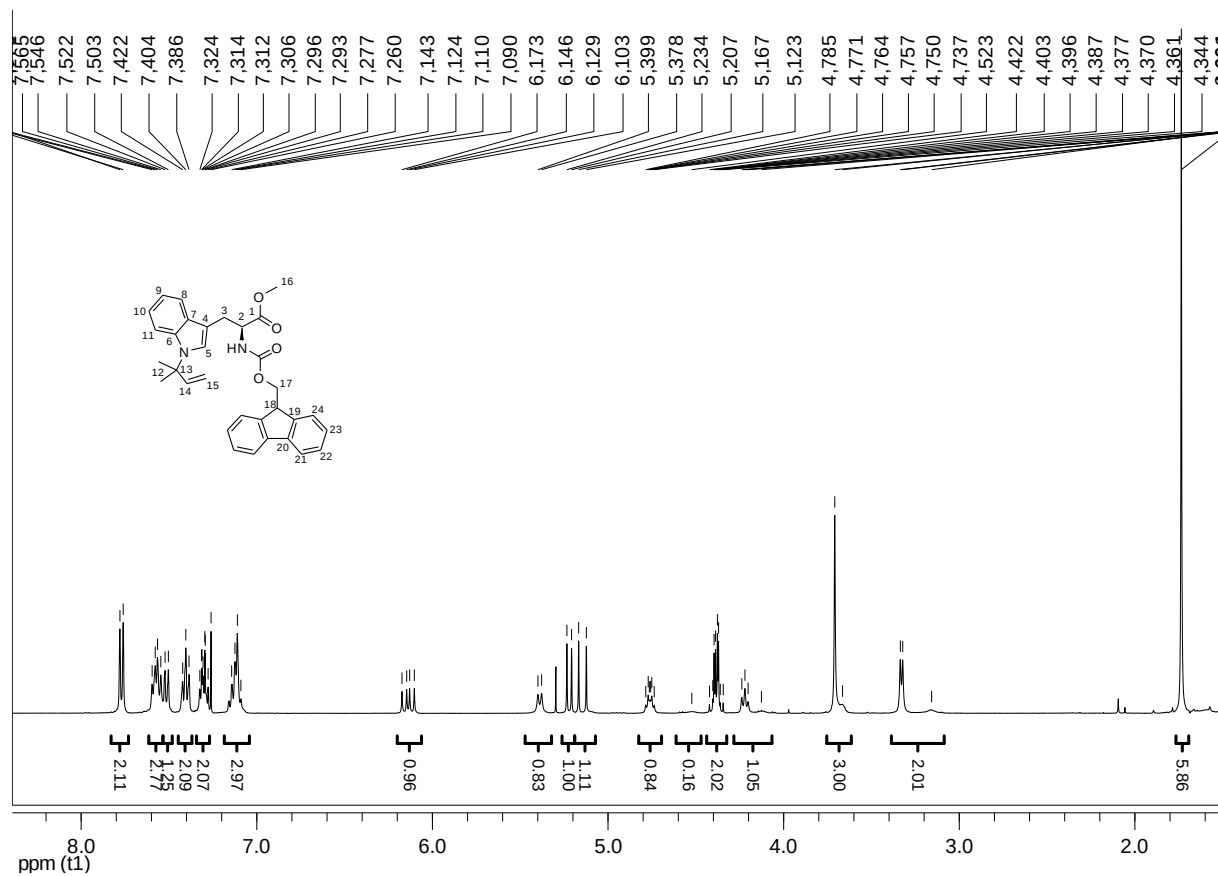
## **Supporting Information**

### **Content**

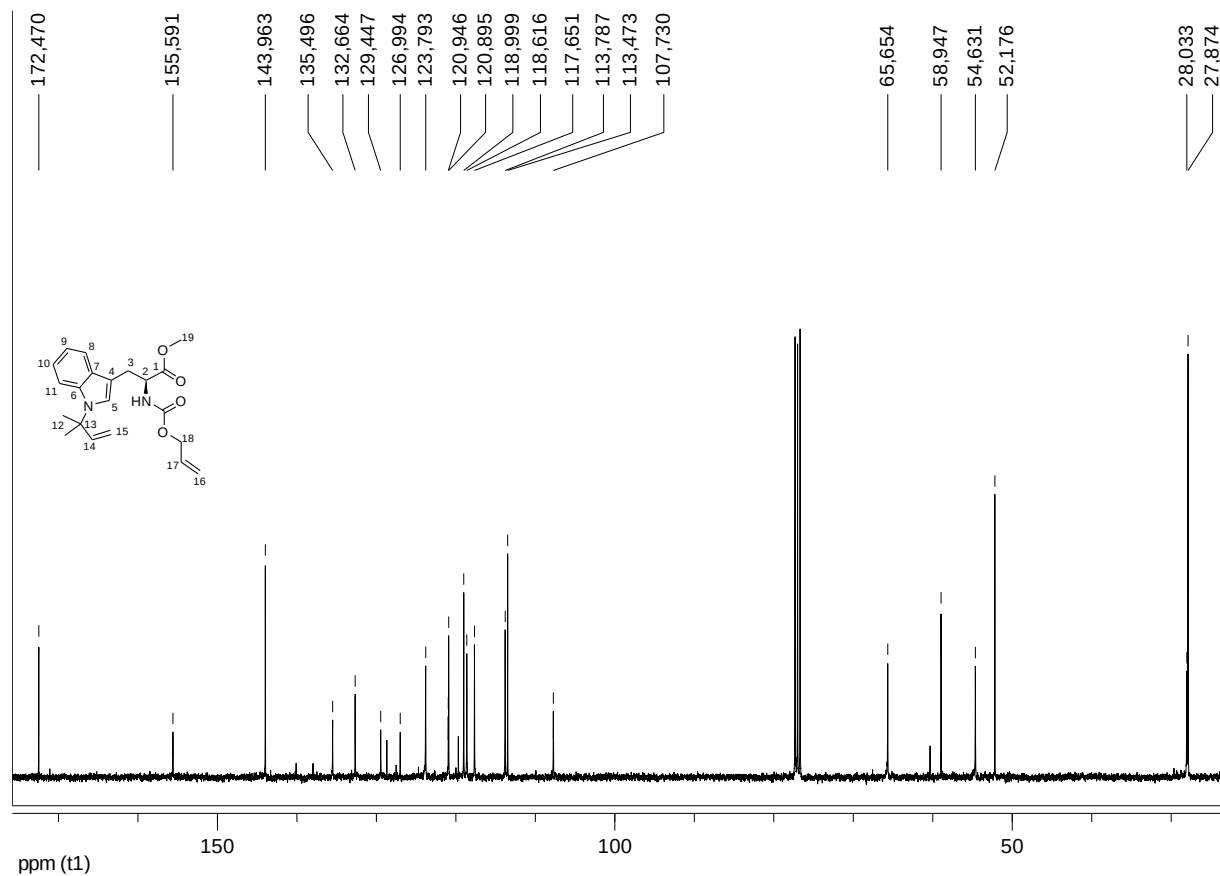
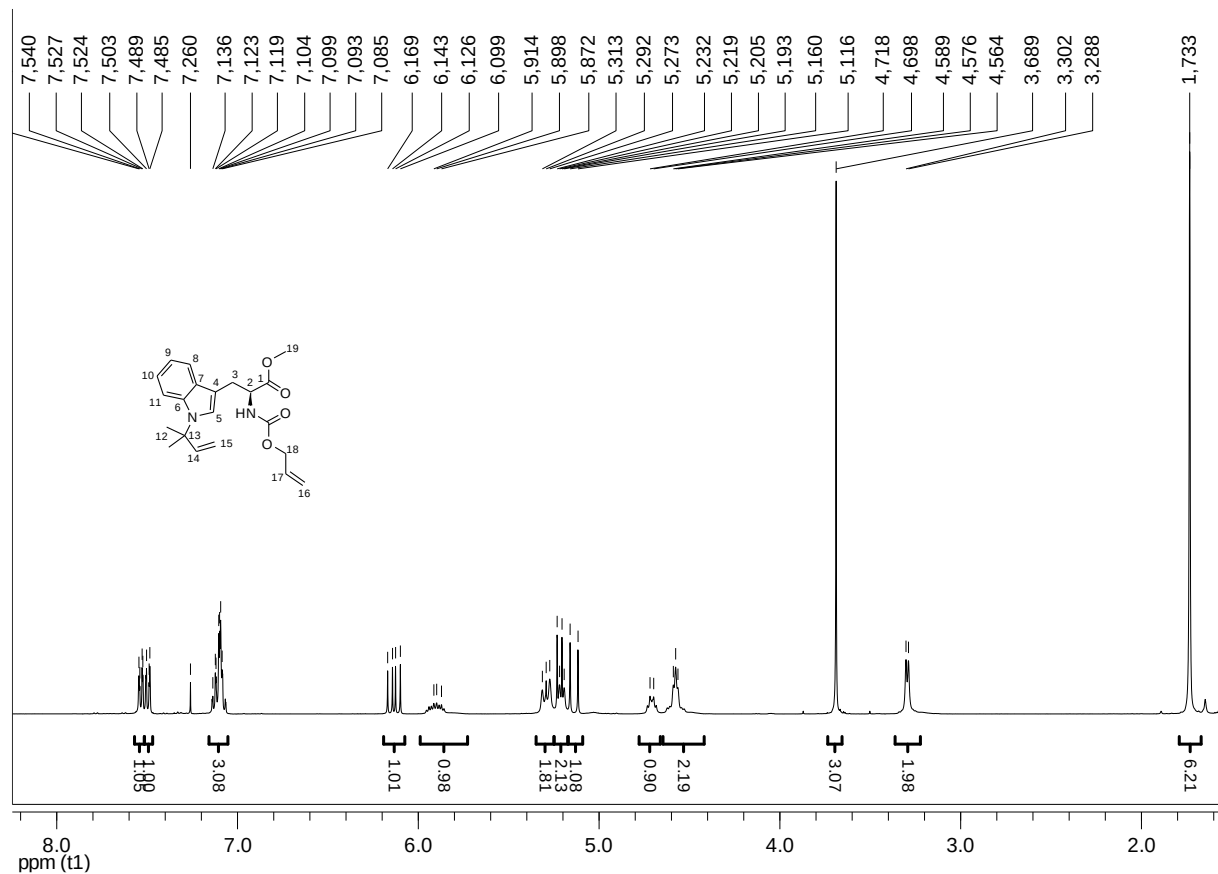
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| Copies of the NMR-Spectra ..... | 2 |
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# Copies of the NMR-Spectra

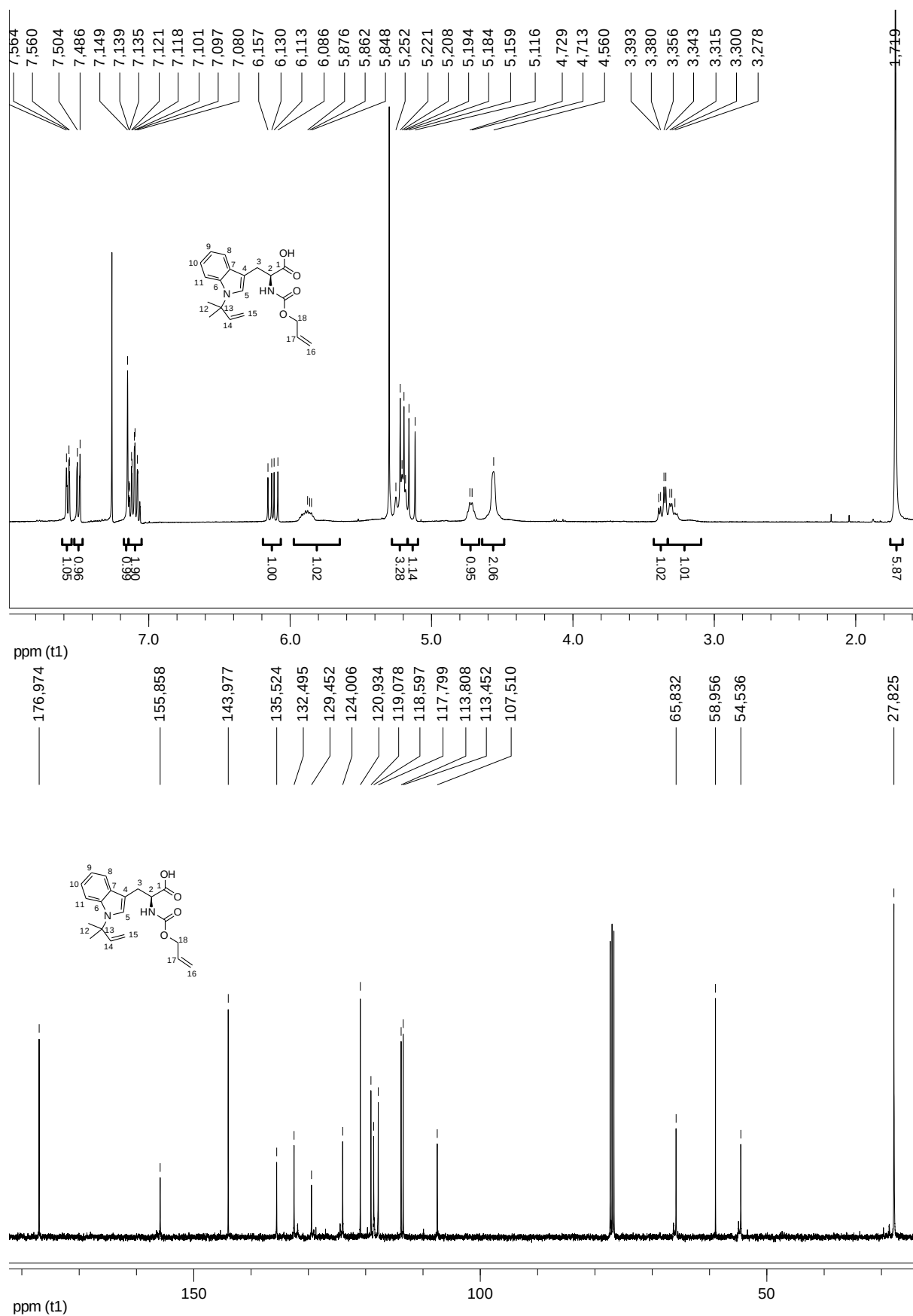
(S)-N-Fmoc-N'-tert-prenyl-tryptophan methyl ester (2)



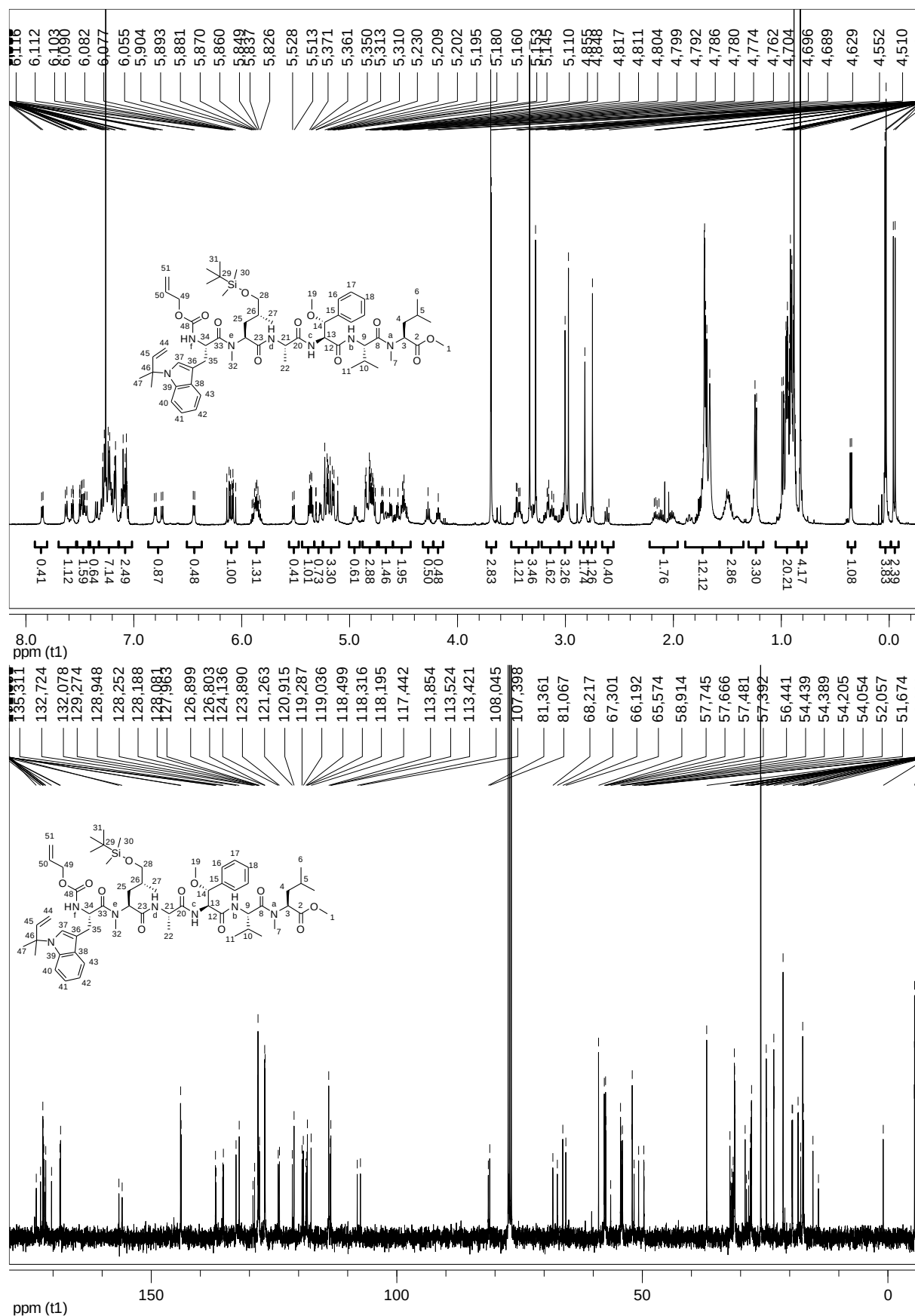
**(S)-N-Alloc-N'-tert-prenyl-tryptophan methyl ester (3)**



**(S)-N-Alloc-N'-tert-prenyl-tryptophan (4)**



***N*-Alloc-(*S*)-[*N'*-(*tert*-prenyl)-tryptophanyl]-*N*-methyl-(2*S*,4*R*)-[5-(*tert*-butyldimethylsilyl)oxy-leucyl]-(*S*)-alanyl-(2*S*,3*R*)-(3-methoxyphenylalanyl)-(*S*)-valyl-(*S*)-*N*-methyl-leucine methyl ester (6)**



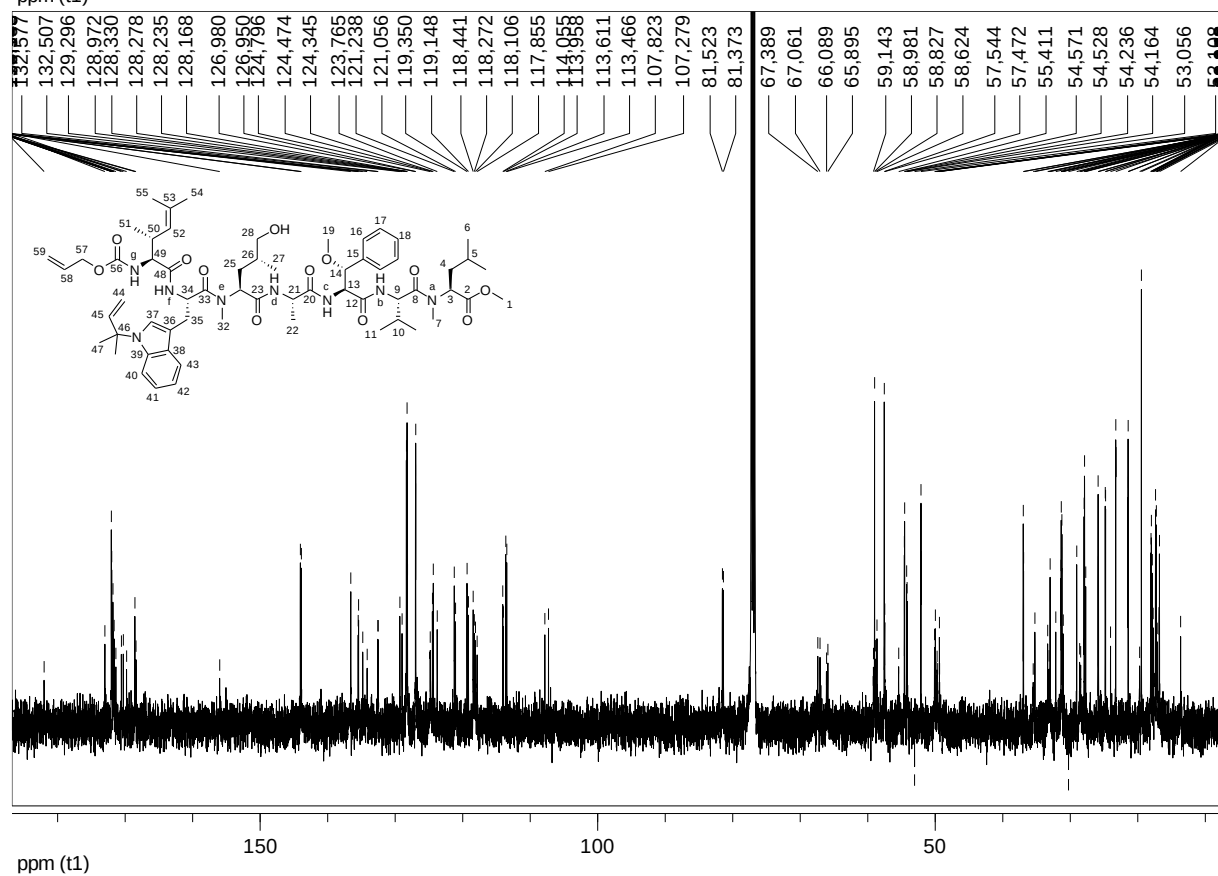
[illegible]

**<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 1.**

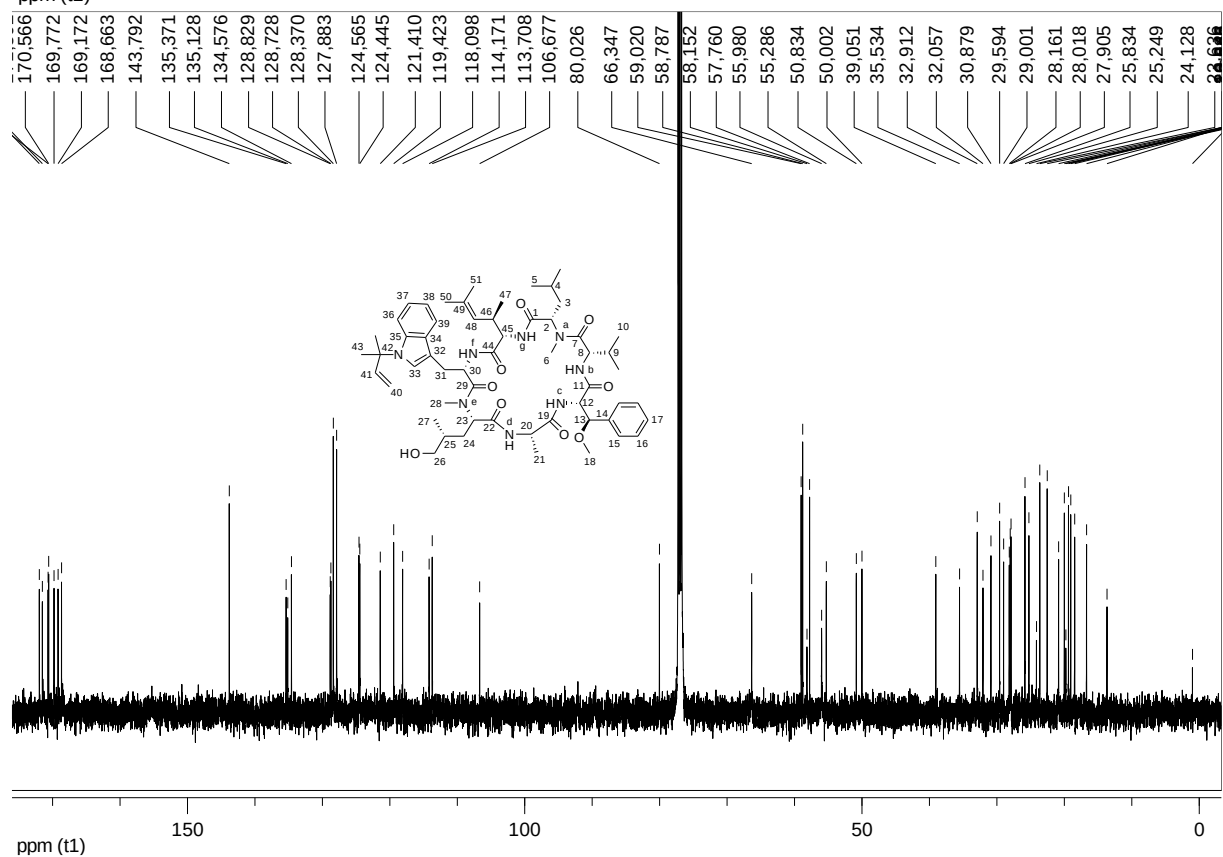
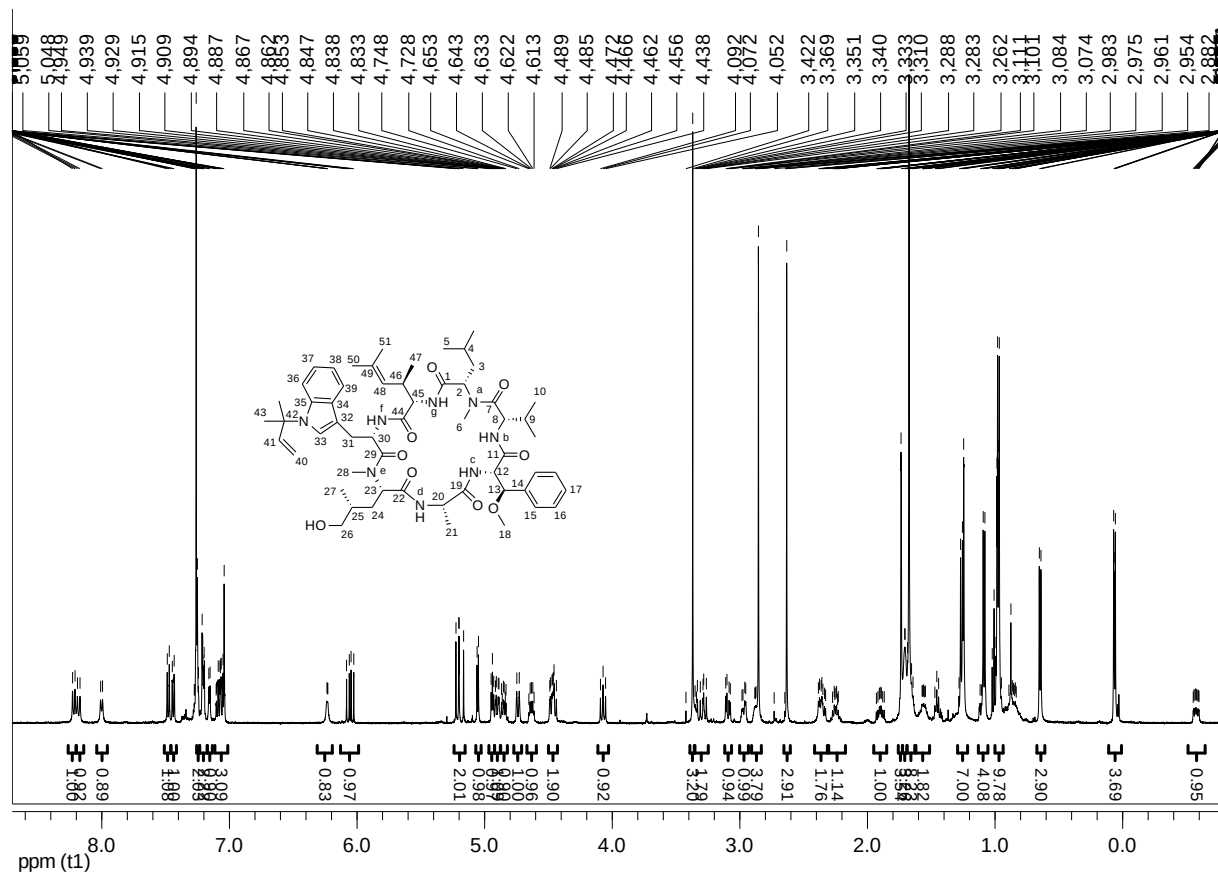
**Chemical structure of compound 1:** A complex molecule featuring a central benzene ring (atoms 10-18) substituted with a 1,3,4-trisubstituted phenyl group (atoms 19-27), a 1,3,4-trisubstituted phenyl group (atoms 28-36), a 1,3,4-trisubstituted phenyl group (atoms 37-45), and a 1,3,4-trisubstituted phenyl group (atoms 46-54). The molecule also contains a 1,3,4-trisubstituted phenyl group (atoms 55-63) and a 1,3,4-trisubstituted phenyl group (atoms 64-72).

**Peak list (ppm):** 8.834, 8.818, 6.670, 6.656, 6.616, 6.103, 6.094, 6.081, 6.068, 6.059, 6.047, 5.902, 5.894, 5.883, 5.366, 5.352, 5.342, 5.331, 5.321, 5.285, 5.262, 5.250, 5.226, 5.204, 5.197, 5.191, 5.179, 5.170, 5.162, 5.138, 5.104, 5.078, 5.063, 5.048, 5.038, 5.035, 5.033, 5.030, 5.022, 5.016, 5.014, 5.012, 5.010, 4.975, 4.956, 4.913, 4.892, 4.846, 4.821, 4.814.

**Integration values:** 0.41, 1.01, 1.52, 2.20, 4.05, 1.63, 0.32, 1.00, 0.90, 2.23, 2.14, 1.46, 1.96, 0.89, 0.90, 2.82, 4.76, 1.94, 4.30, 4.19, 1.02, 5.64, 10.04, 2.48, 2.97, 18.14, 1.32, 0.40.

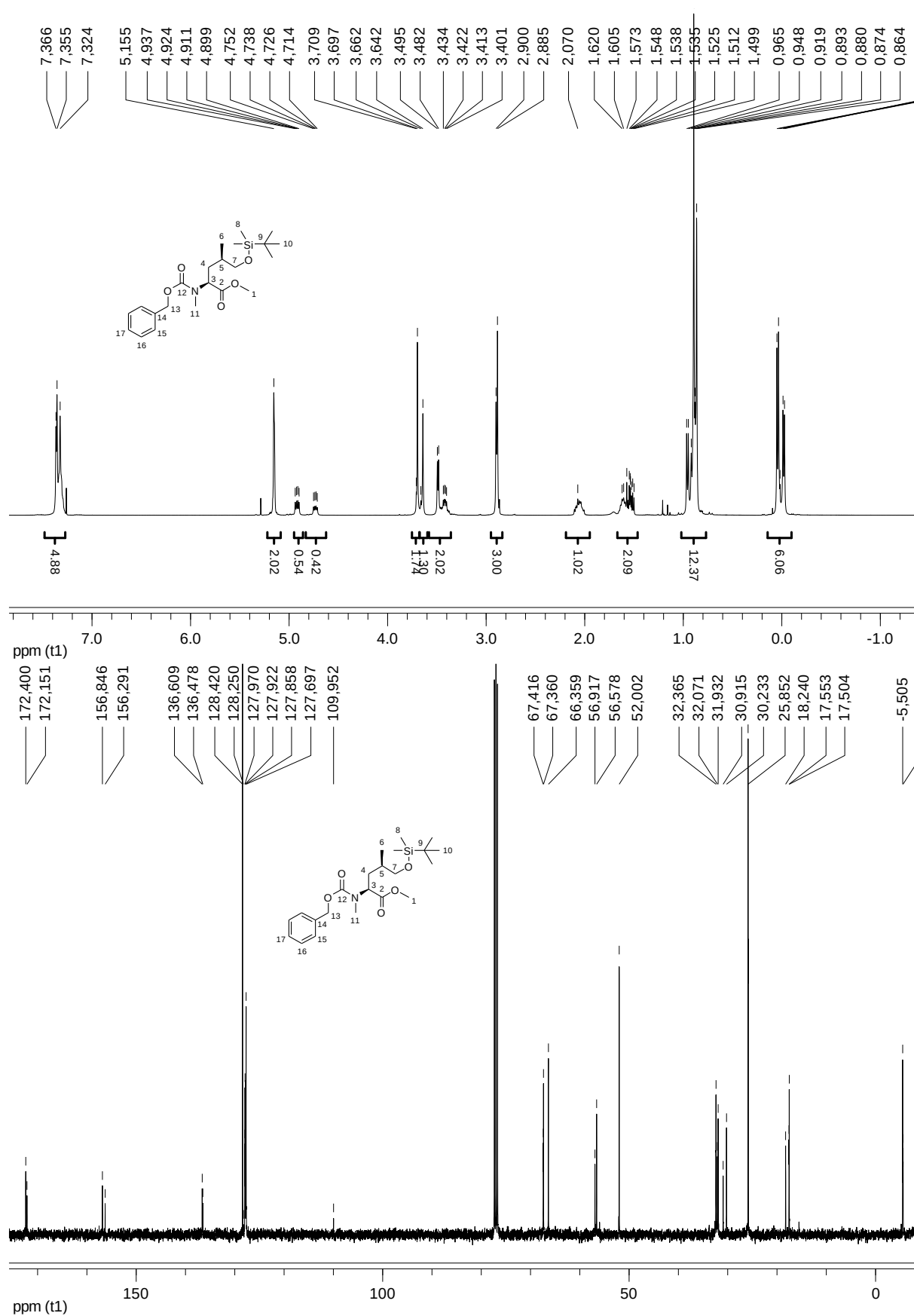


Desoxycyclomarin C (9)

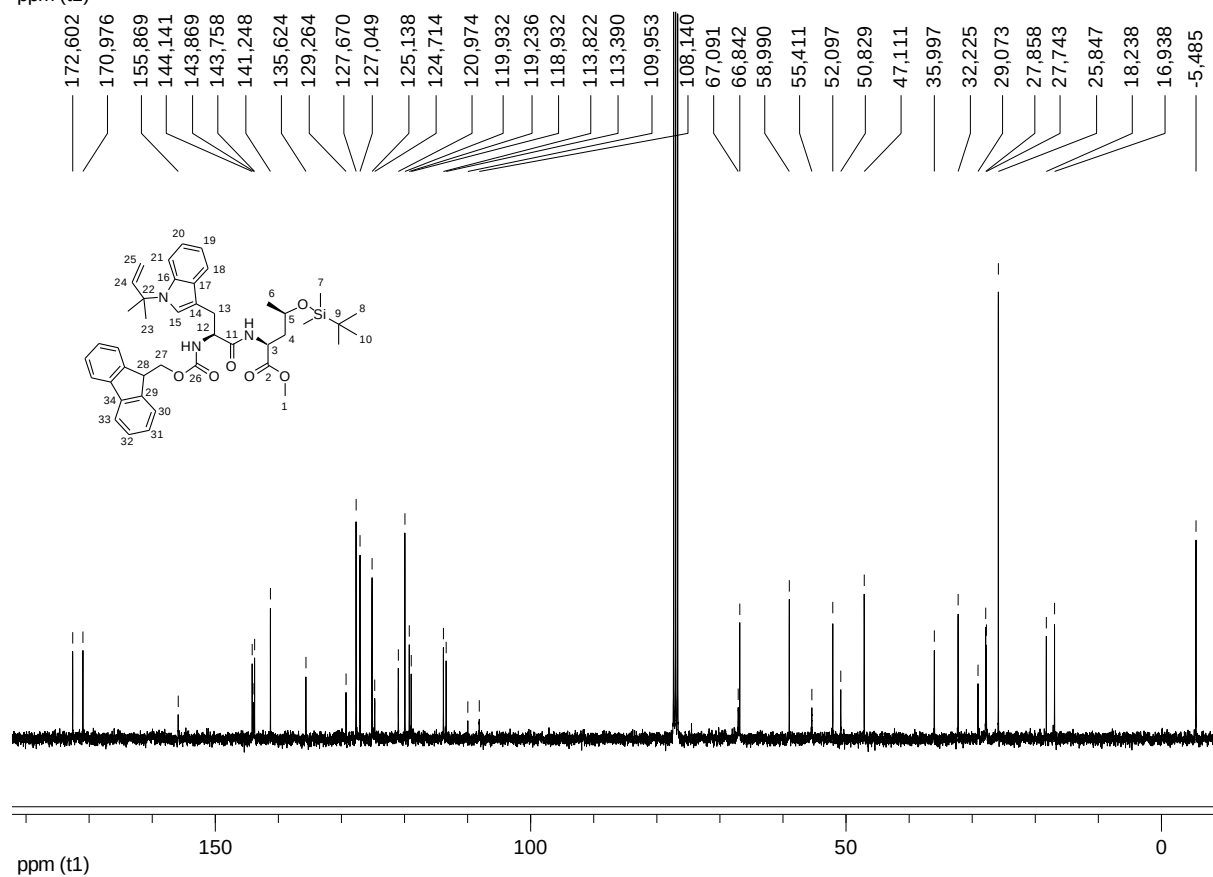
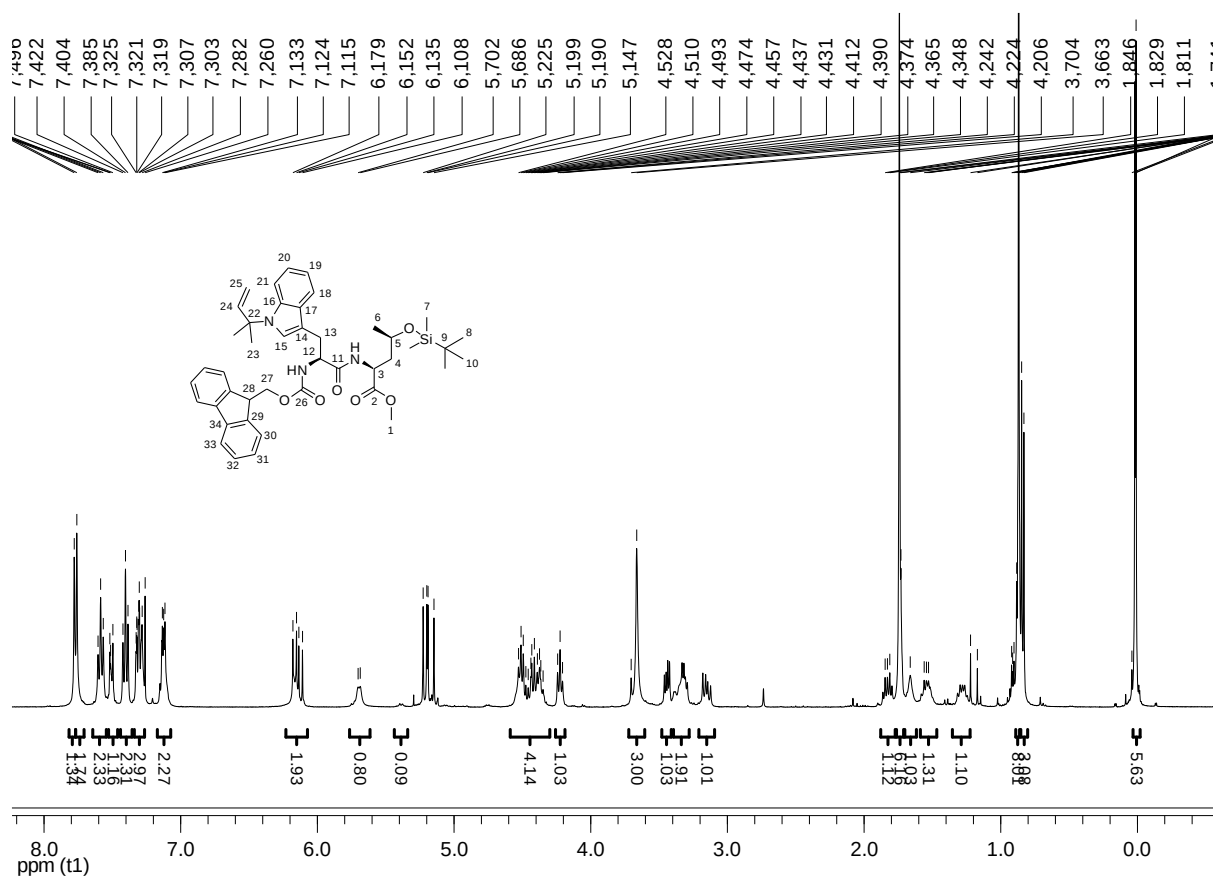




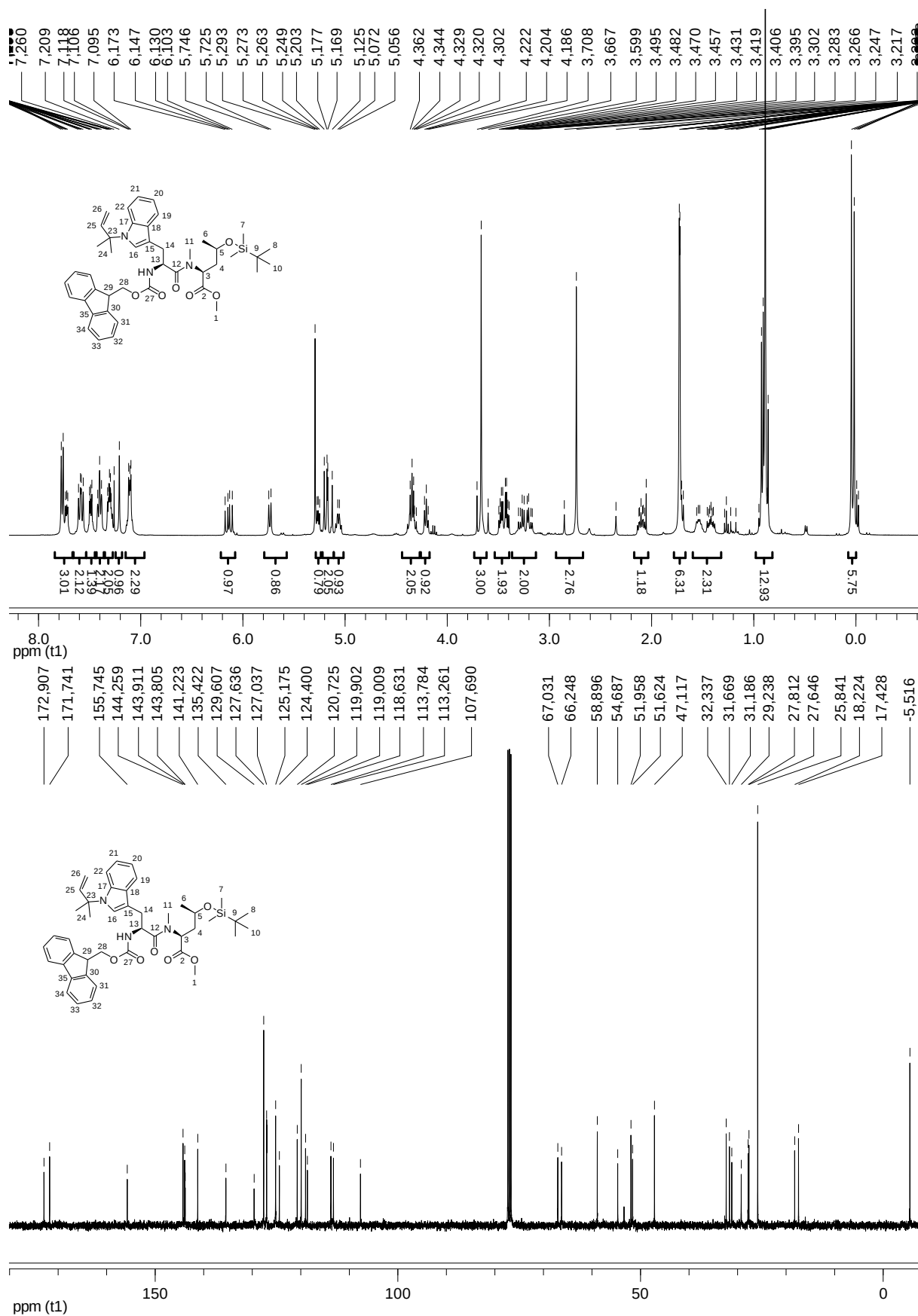
(2S,4R)-5-[(*tert*-butyldimethylsilyl)oxy]-*N*-methyl-leucine methyl ester (11)



***N*-Fmoc-*N'*-(*tert*-prenyl)-(2*S*)-tryptophanyl-(2*S*,4*R*)-5-[(*tert*-butyldimethylsilyl)oxy]-leucine methyl ester (12a)**

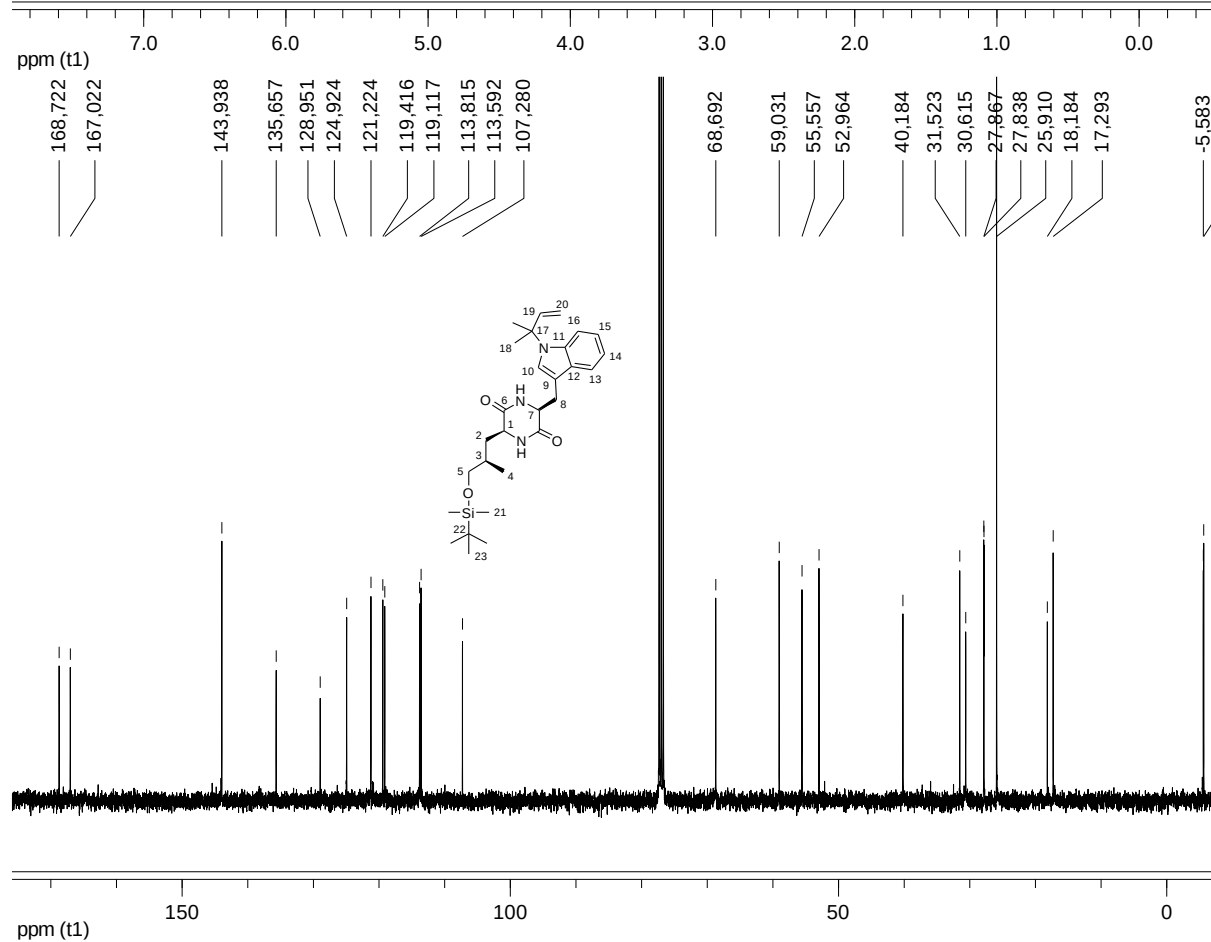


***N*-Fmoc-*N'*-(*tert*-prenyl)-(2*S*)-tryptophanyl-(2*S*,4*R*)-5-[(*tert*-butyldimethylsilyl)oxy]-*N*-methyleucine methyl ester (12b)**

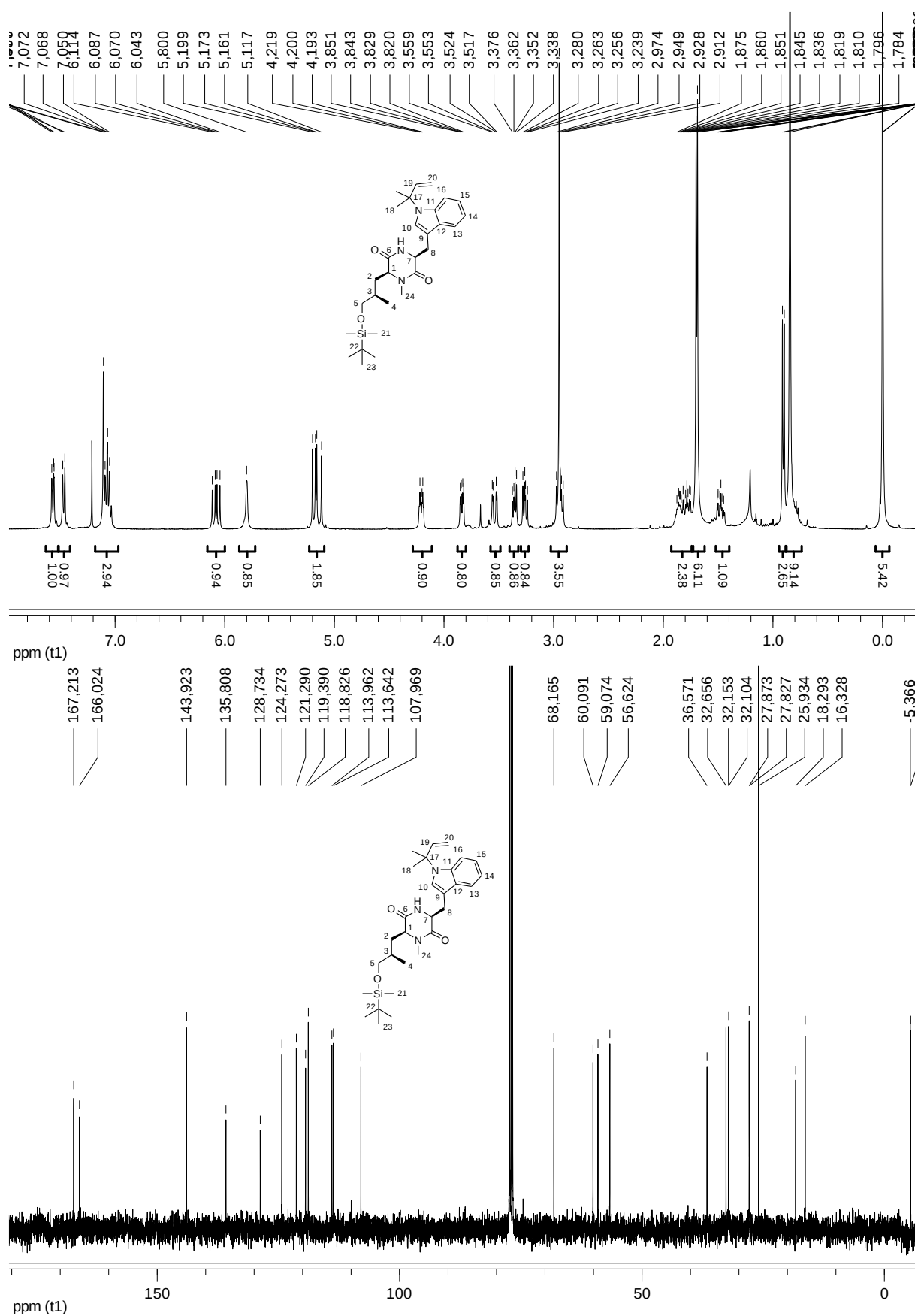


<sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>) of compound 10. The spectrum displays peaks corresponding to the structure shown in the inset, which is labeled with atom numbers 1 through 23. The chemical shift ranges from 0.97 to 7.49 ppm. Integration values are provided below the baseline for each major peak group.

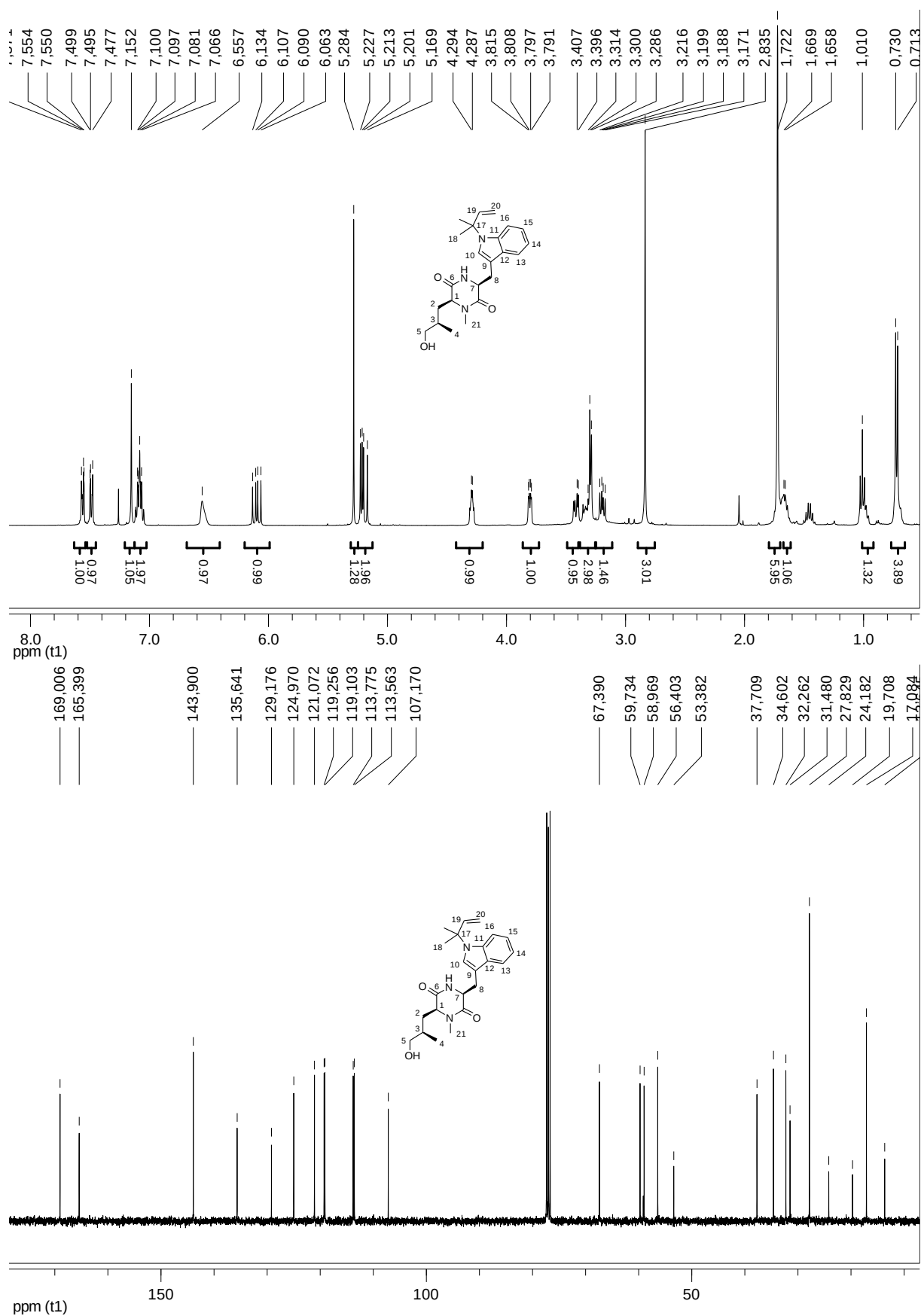
| Chemical Shift (ppm)                                          | Integration |
|---------------------------------------------------------------|-------------|
| 7.493, 7.488                                                  | 0.97        |
| 7.171, 7.123, 7.119, 7.111, 7.105, 7.099, 7.092, 7.088        | 1.00        |
| 6.780, 6.149, 6.122, 6.105, 6.078                             | 2.06        |
| 5.235, 5.209, 5.166, 4.295, 4.285, 4.277, 4.073, 4.046        | 0.92        |
| 3.449, 3.441, 3.432, 3.423, 3.416, 3.395, 3.386, 3.346, 3.325 | 1.90        |
| 3.000, 3.271, 3.252, 3.235, 3.216                             | 1.92        |
| 1.745, 1.730, 1.715, 1.705, 1.696, 1.680, 1.671               | 0.93        |
| 0.97, 1.00                                                    | 0.95        |
| 0.92                                                          | 3.96        |
| 0.94                                                          | 6.94        |
| 1.11                                                          | 1.11        |
| 2.75                                                          | 9.64        |
| 5.92                                                          | 2.75        |



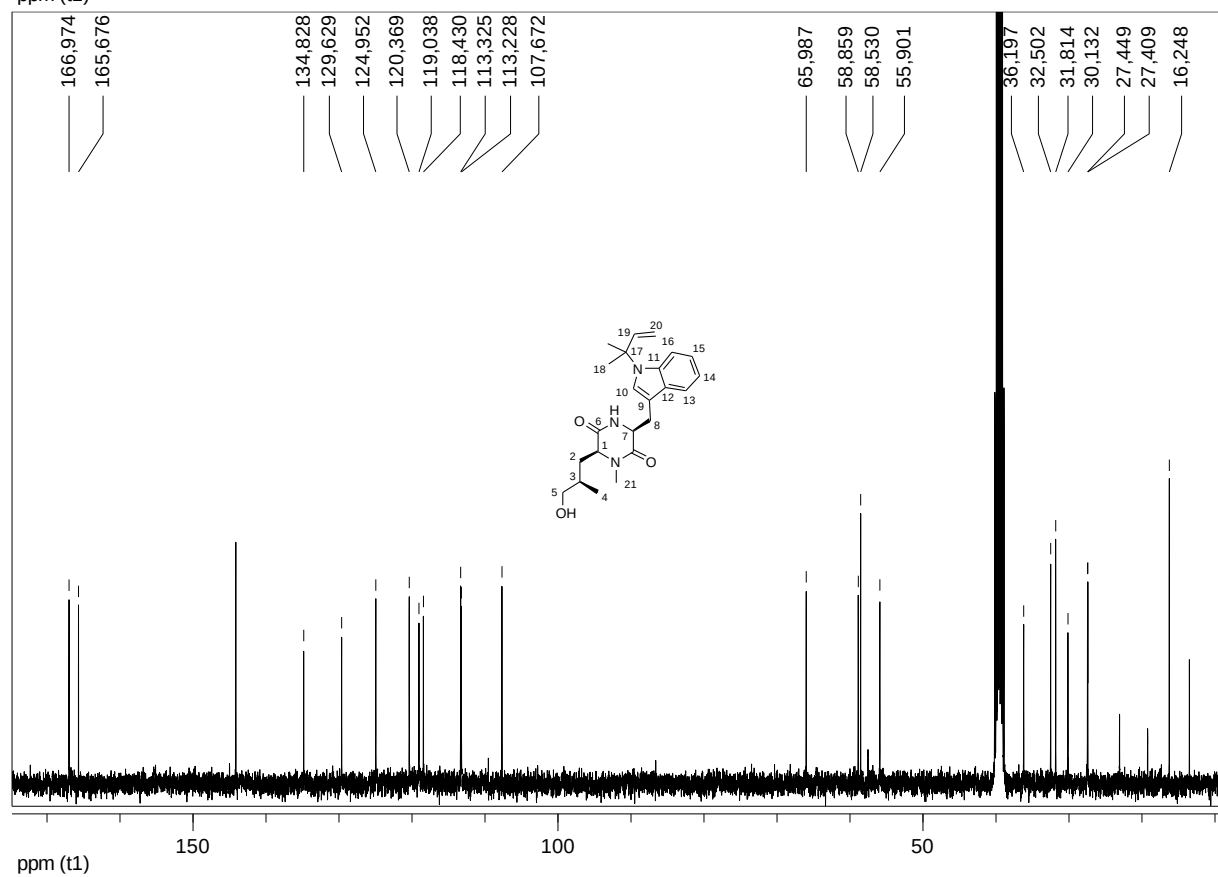
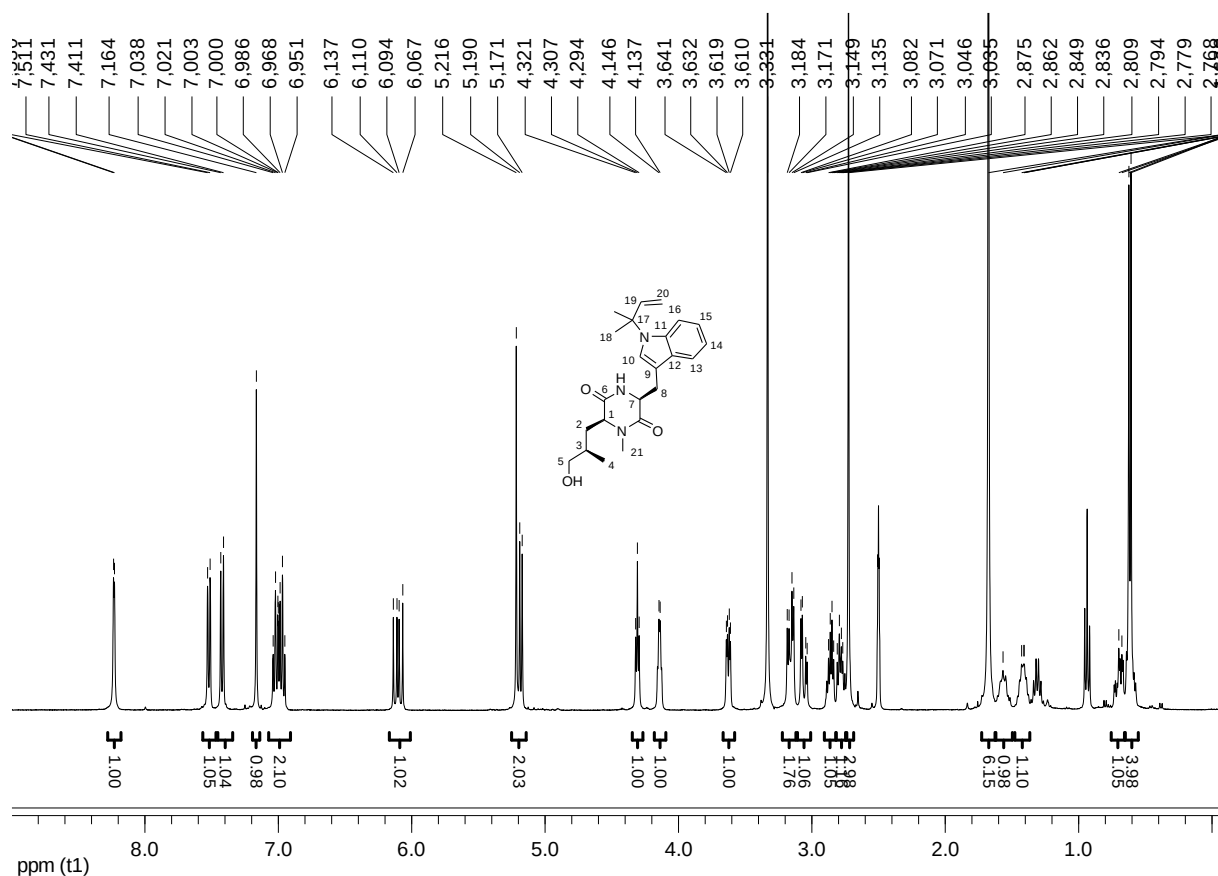
***O*-(*tert*-butyldimethylsilyl)-cyclomarazine A (14b)**



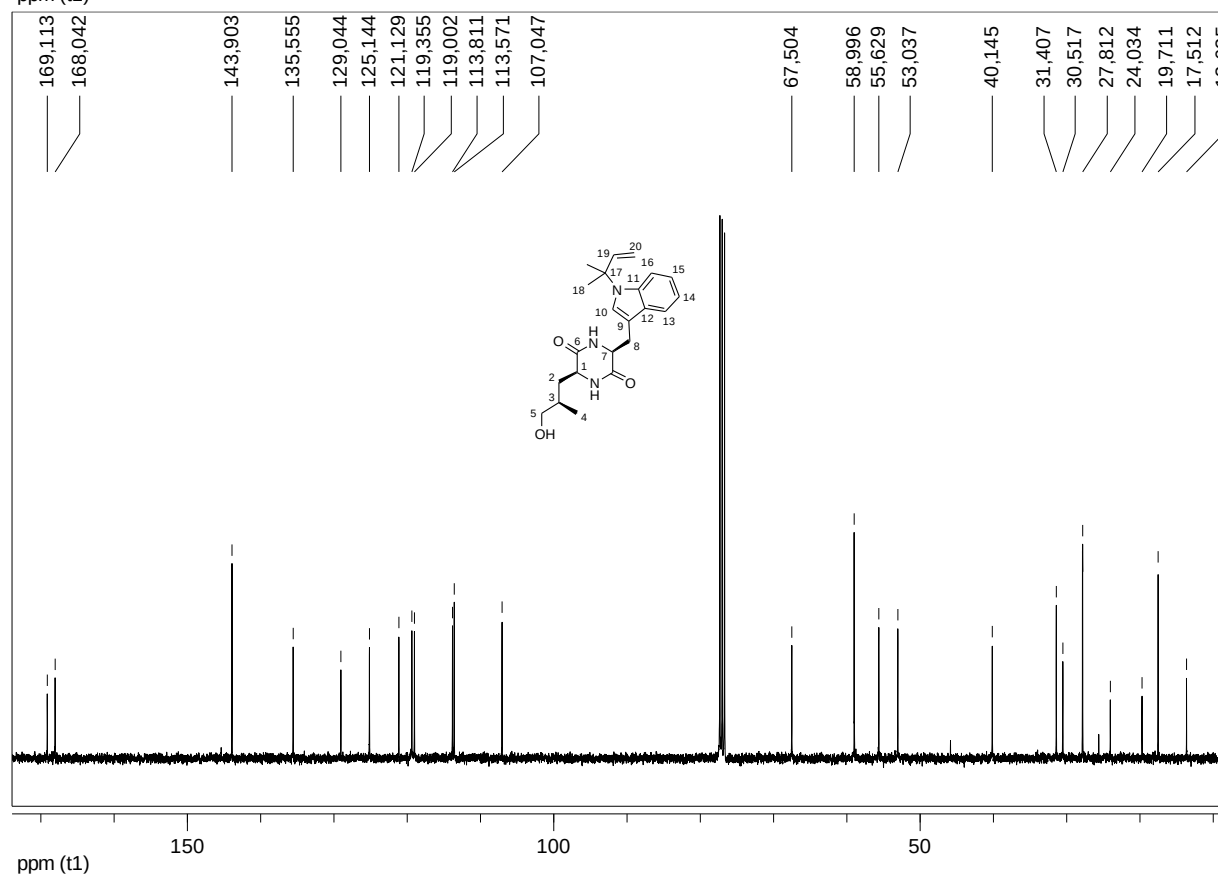
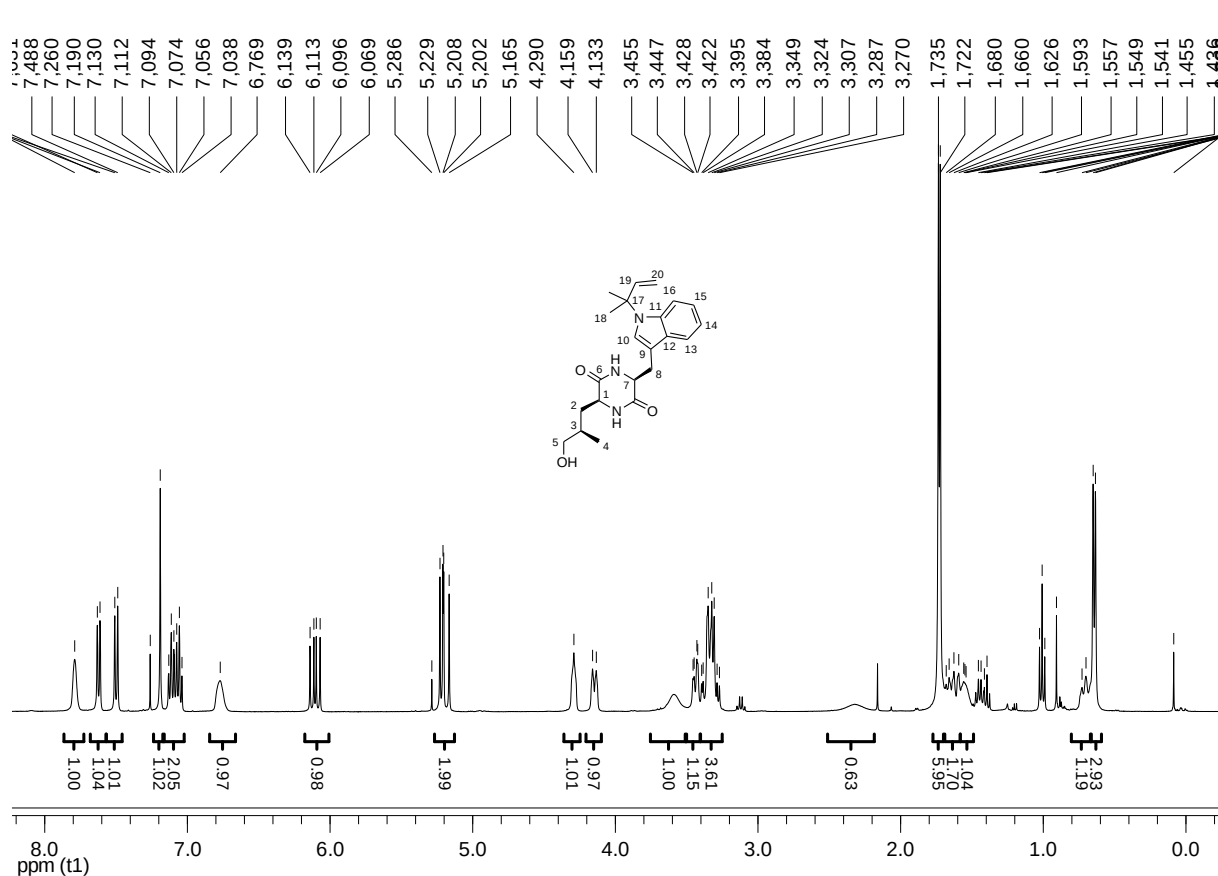
**Cyclomarazine A (CDCl<sub>3</sub>)**



**Cyclomarazine A (DMSO-d6)**



**Cyclomarazine B** (CDCl<sub>3</sub>)





**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

Chemical structure of compound **1** is shown above the spectra. The structure is numbered 1 through 20.

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