

## **Supporting Information**

# **Architectural Chemistry: Synthesis of Topologically Diverse Macromulticycles by Sequential Multiple Multicomponent Macrocyclizations**

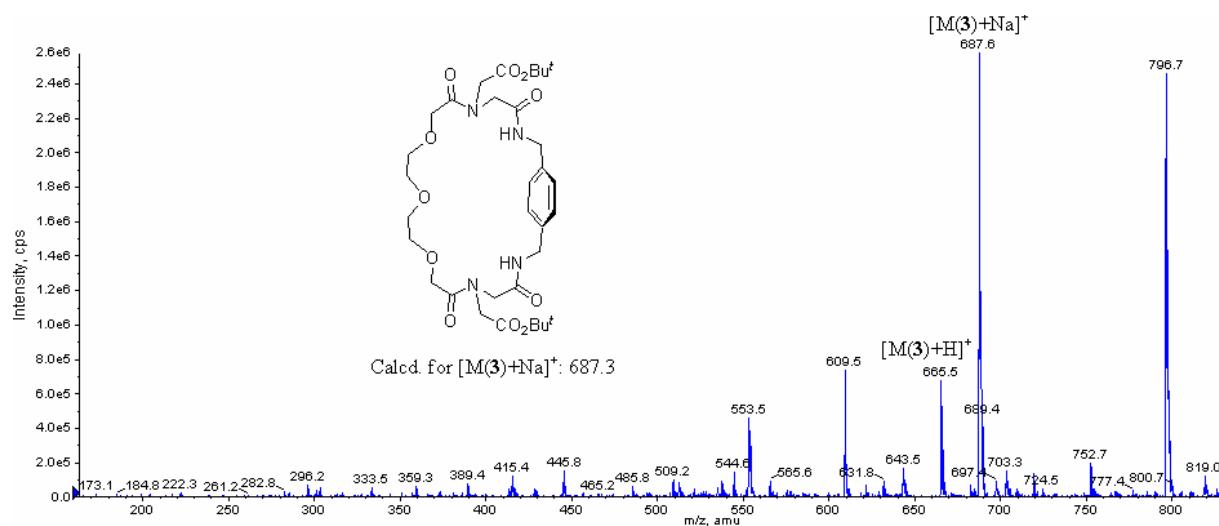
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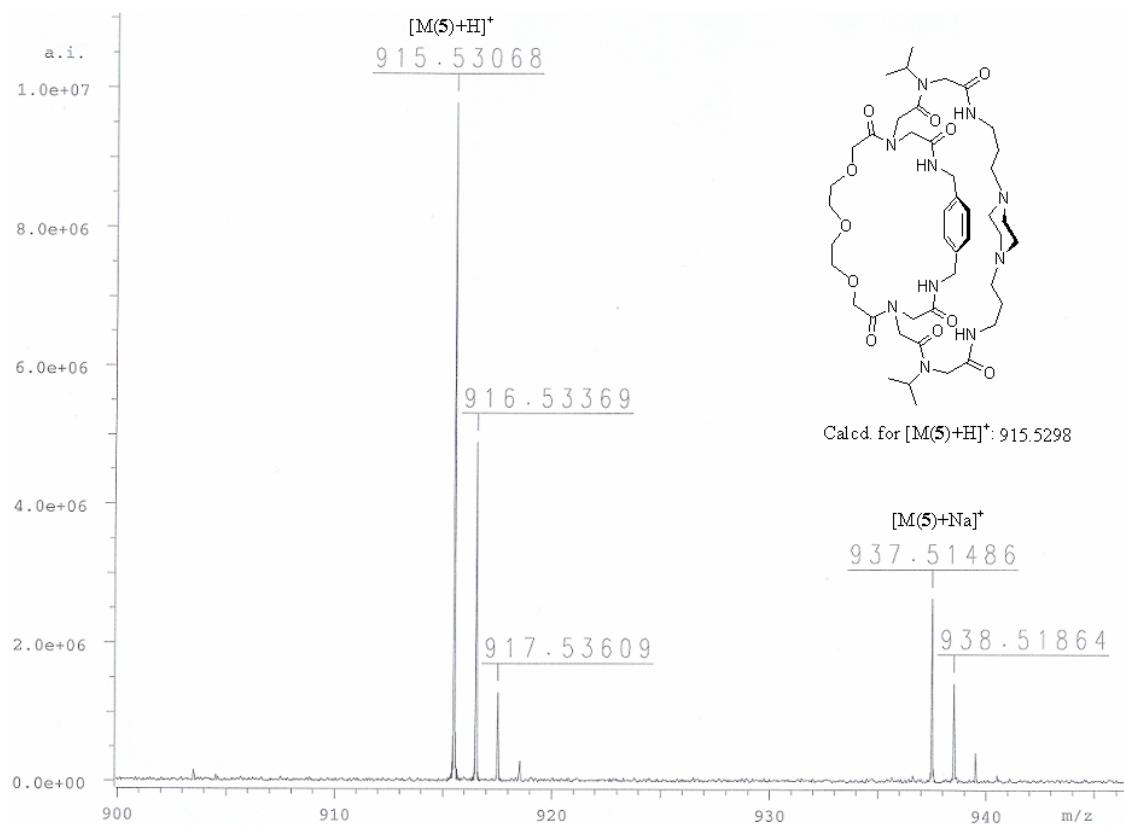
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10400, Cuba.*

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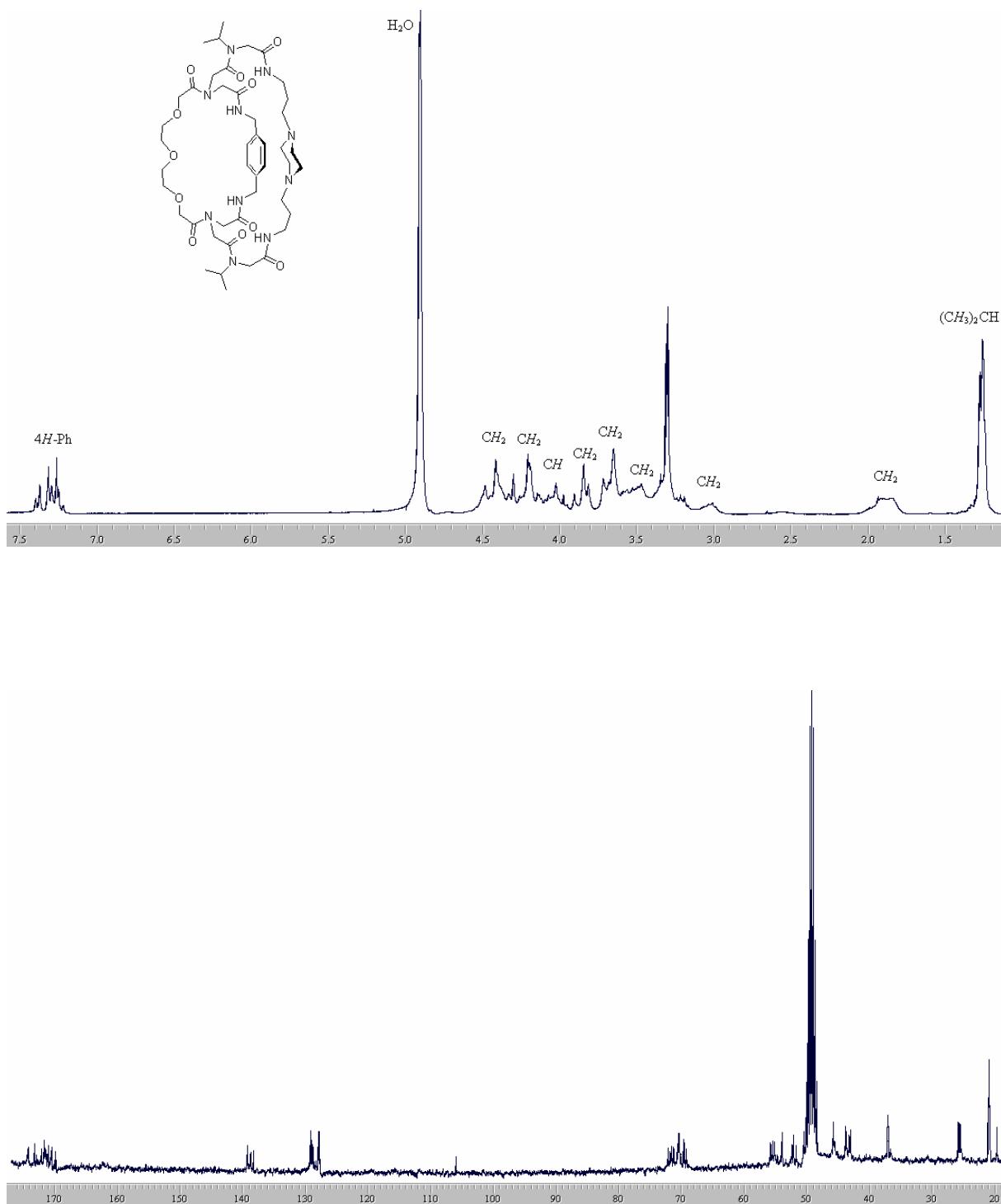
- S2 – S7 MS and NMR spectra of macrobicycles (cryptands) and intermediate macrocycle precursors.
- S8 – S13 Selected MS and NMR spectra of steroid-based clam-shaped macrobicycles.
- S14 – S18 Selected MS and NMR spectra of igloo-shaped macrotetracycles and intermediate precursor macrocycles.
- S19 RP-HPLC analysis of the chiral cryptands **9** and **13**.



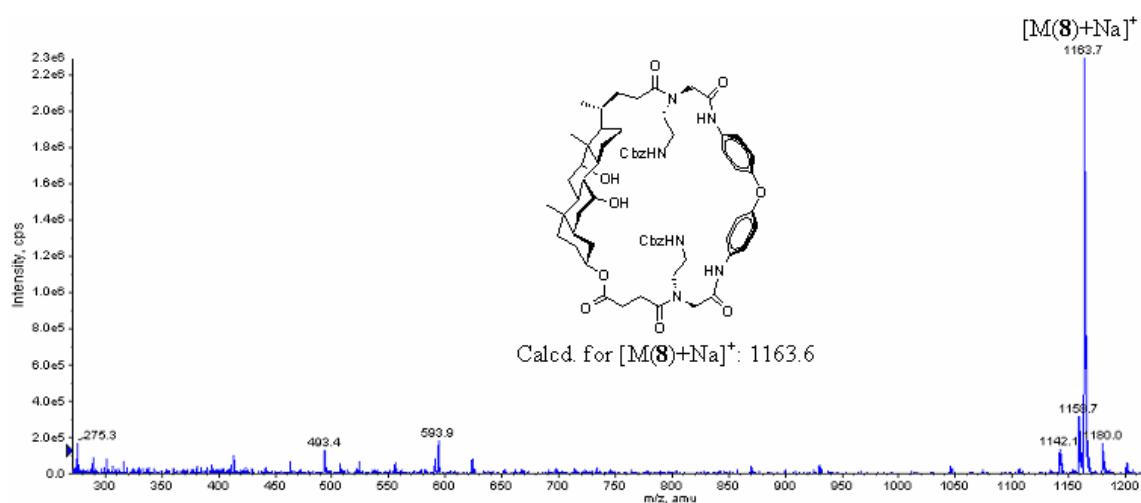
**Figure 1.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intemediate **3**.



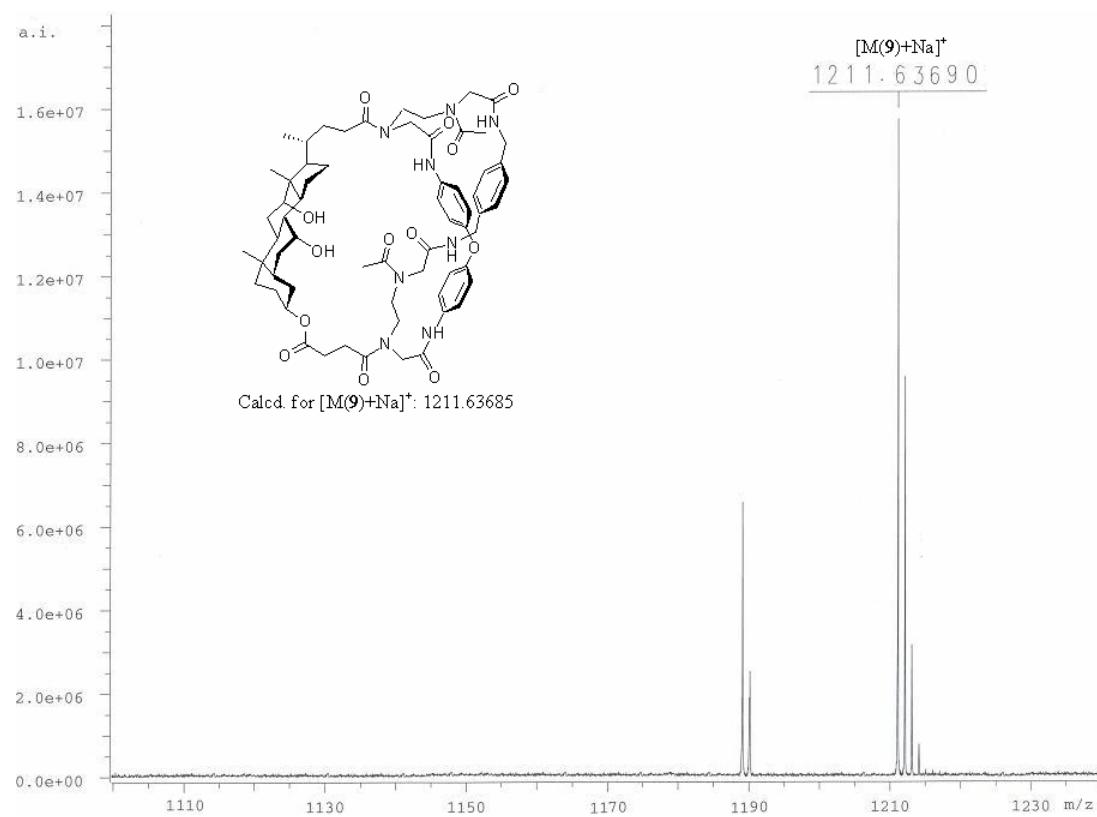
**Figure 2.** HR-MS (ESI-FT-ICR) spectrum of cryptand **5**.



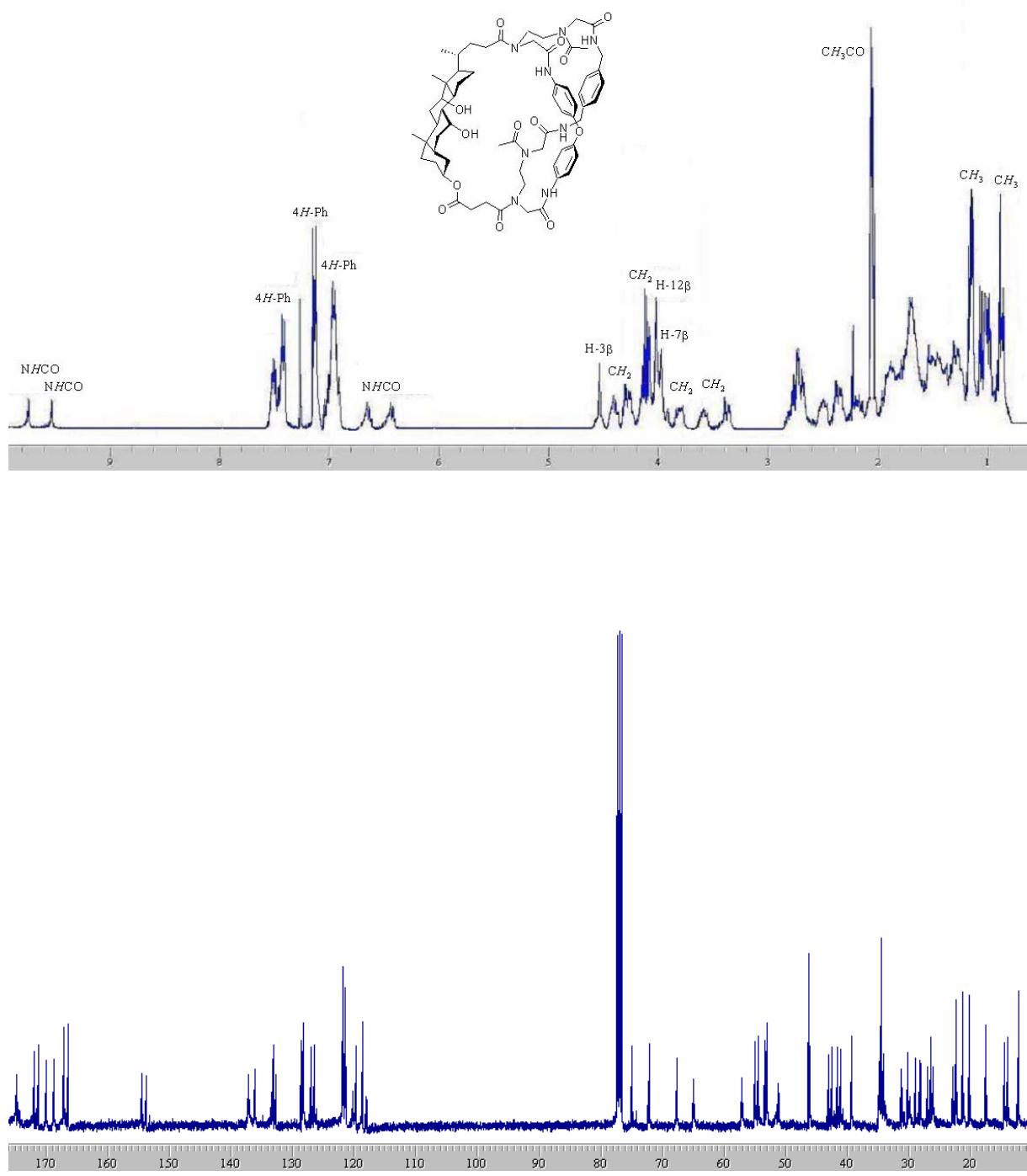
**Figure 3.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of cryptand **5** in  $\text{CD}_3\text{OD}$ .



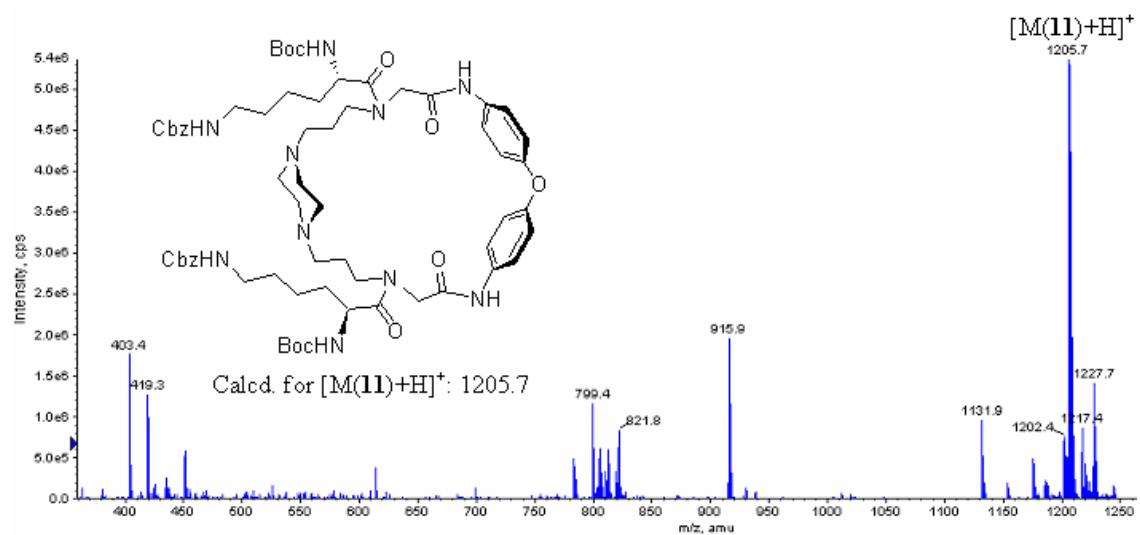
**Figure 4.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intemediate **8**.



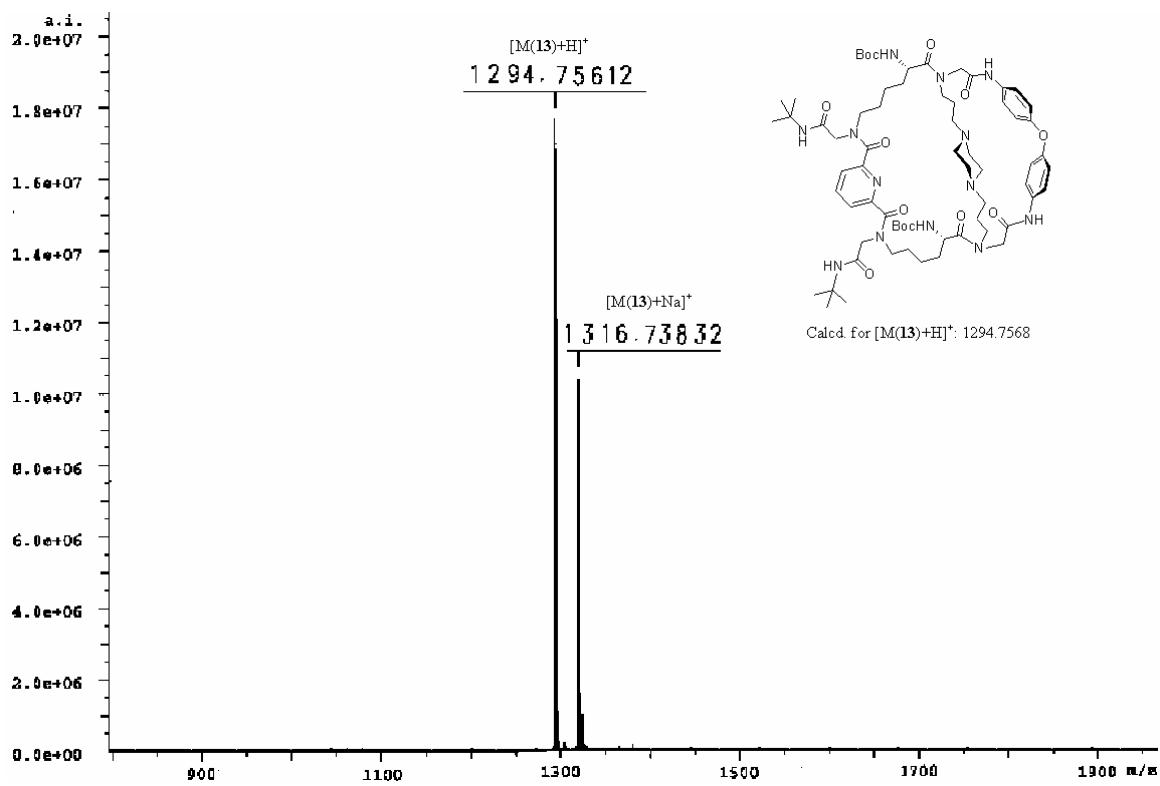
**Figure 5.** HR-MS (ESI-FT-ICR) spectrum of cryptand **9**.



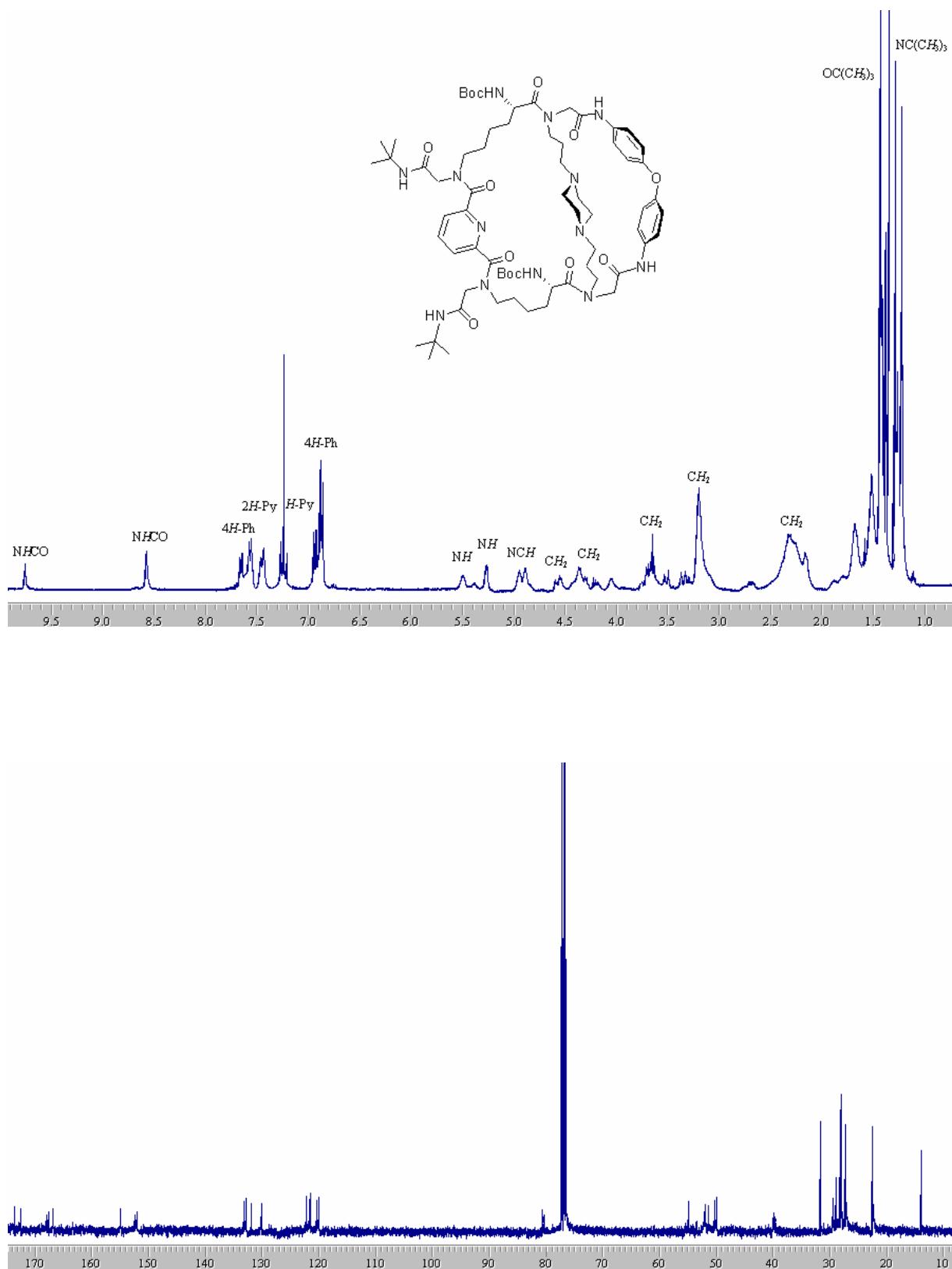
**Figure 6.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of cryptand **9** in  $\text{CDCl}_3$ .



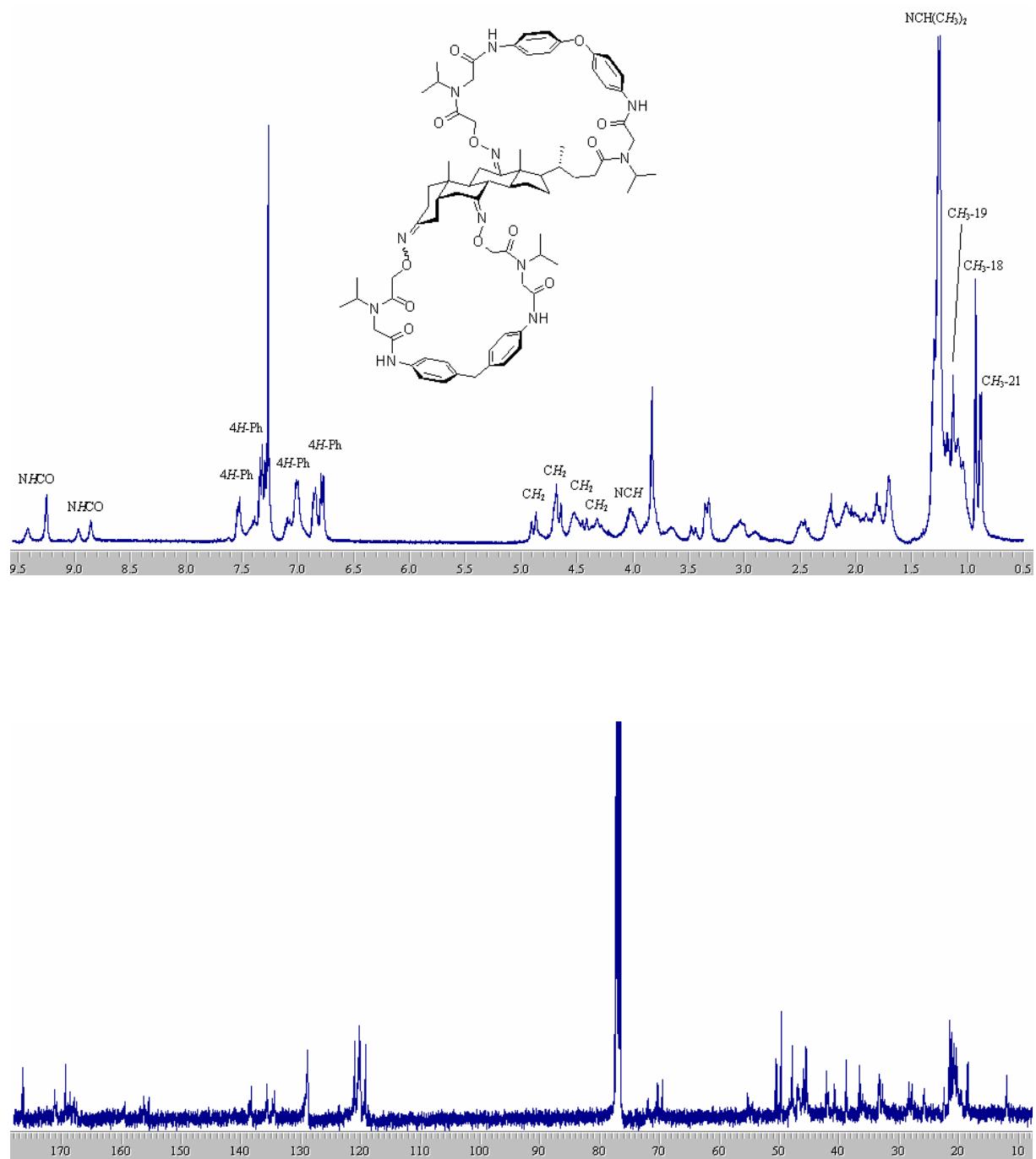
**Figure 7.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intemediate **9**.



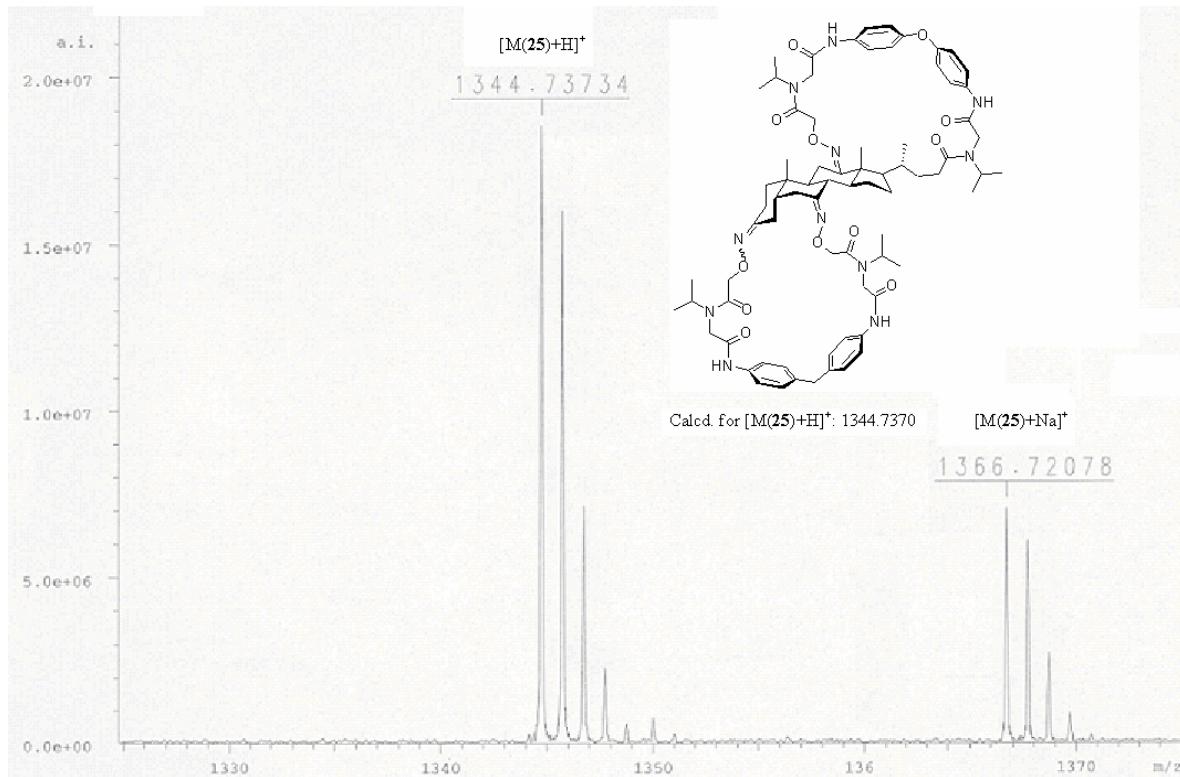
**Figure 8.** HR-MS (ESI-FT-ICR) spectrum of cryptand **13**.



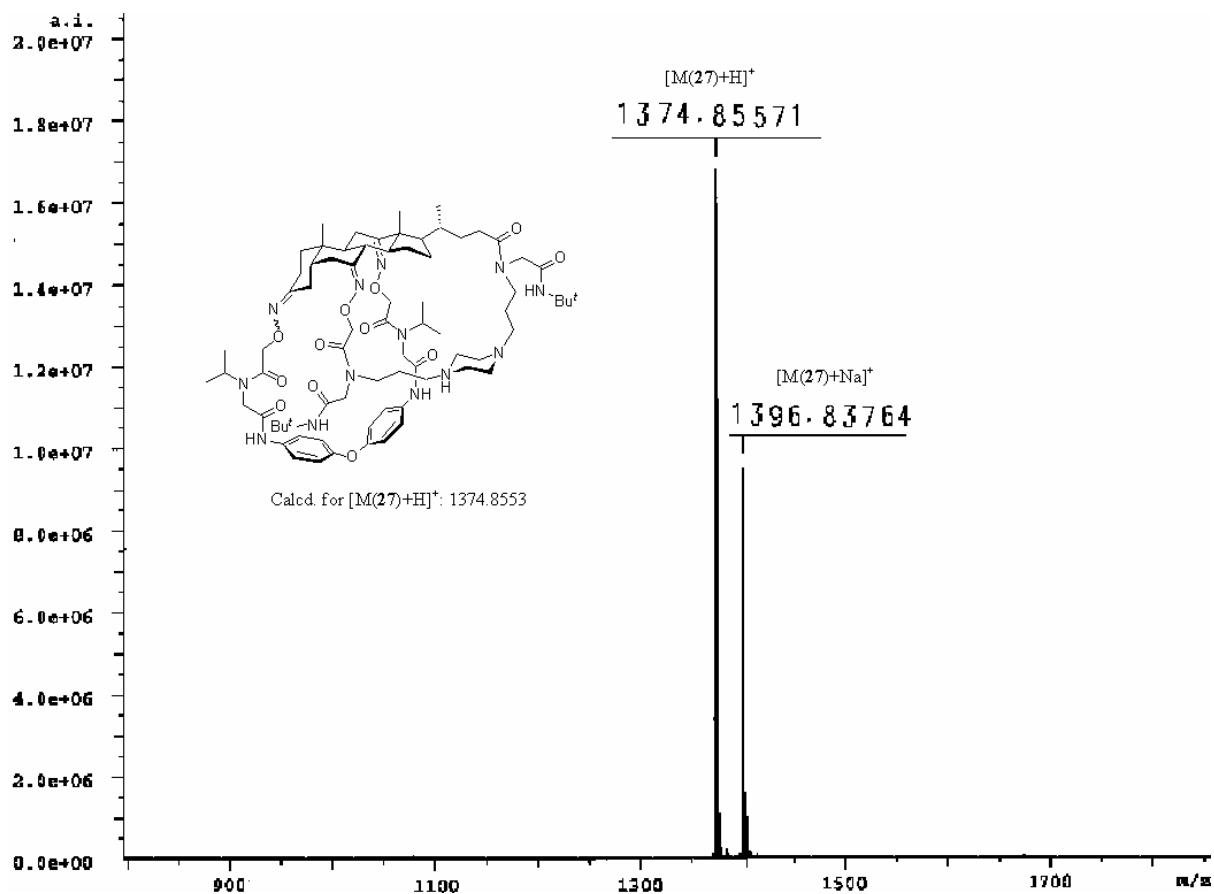
**Figure 9.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of cryptand **13** in  $\text{CDCl}_3$ .



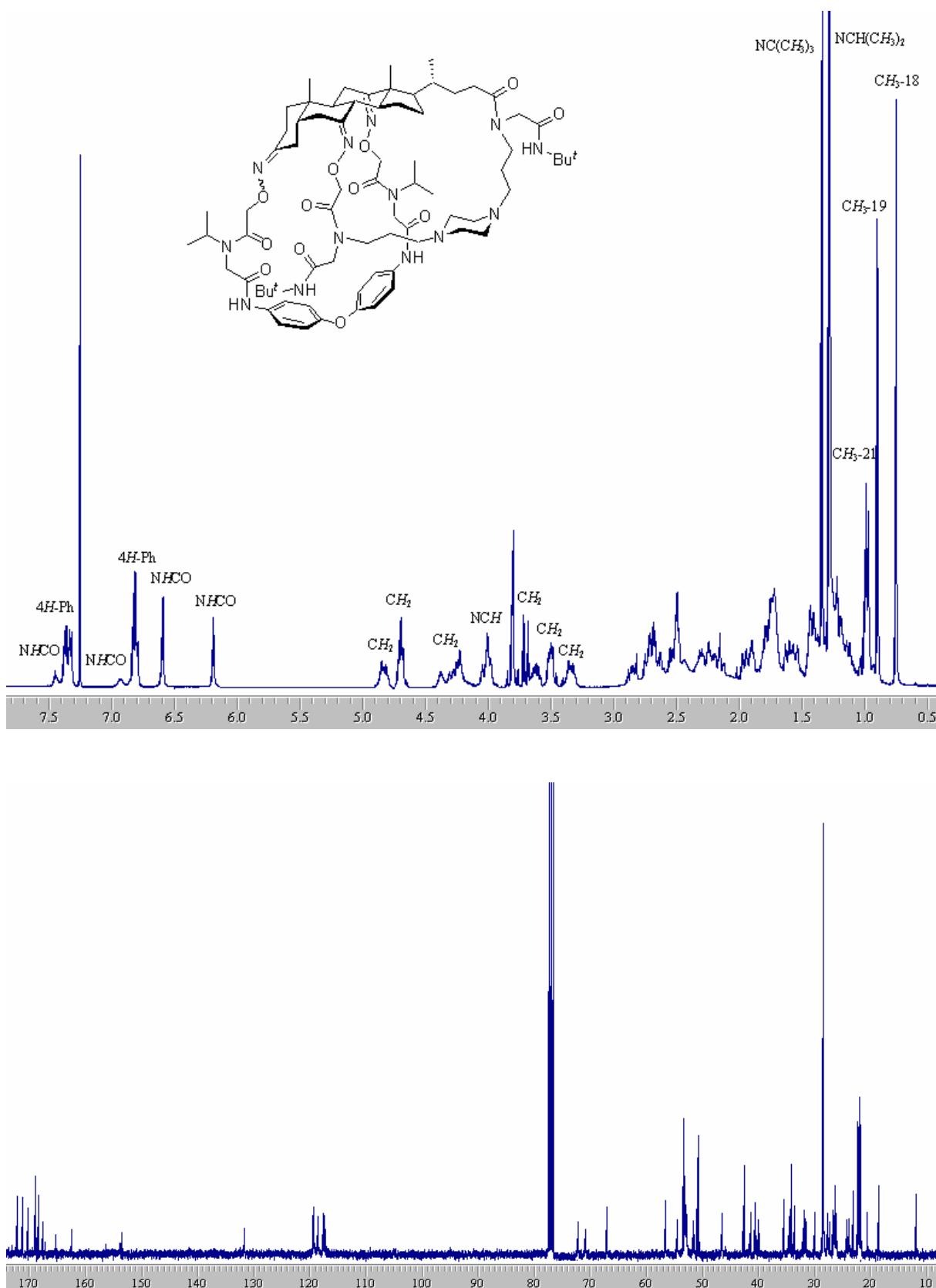
**Figure 10.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the steroid-based clam **25** in CDCl<sub>3</sub>.



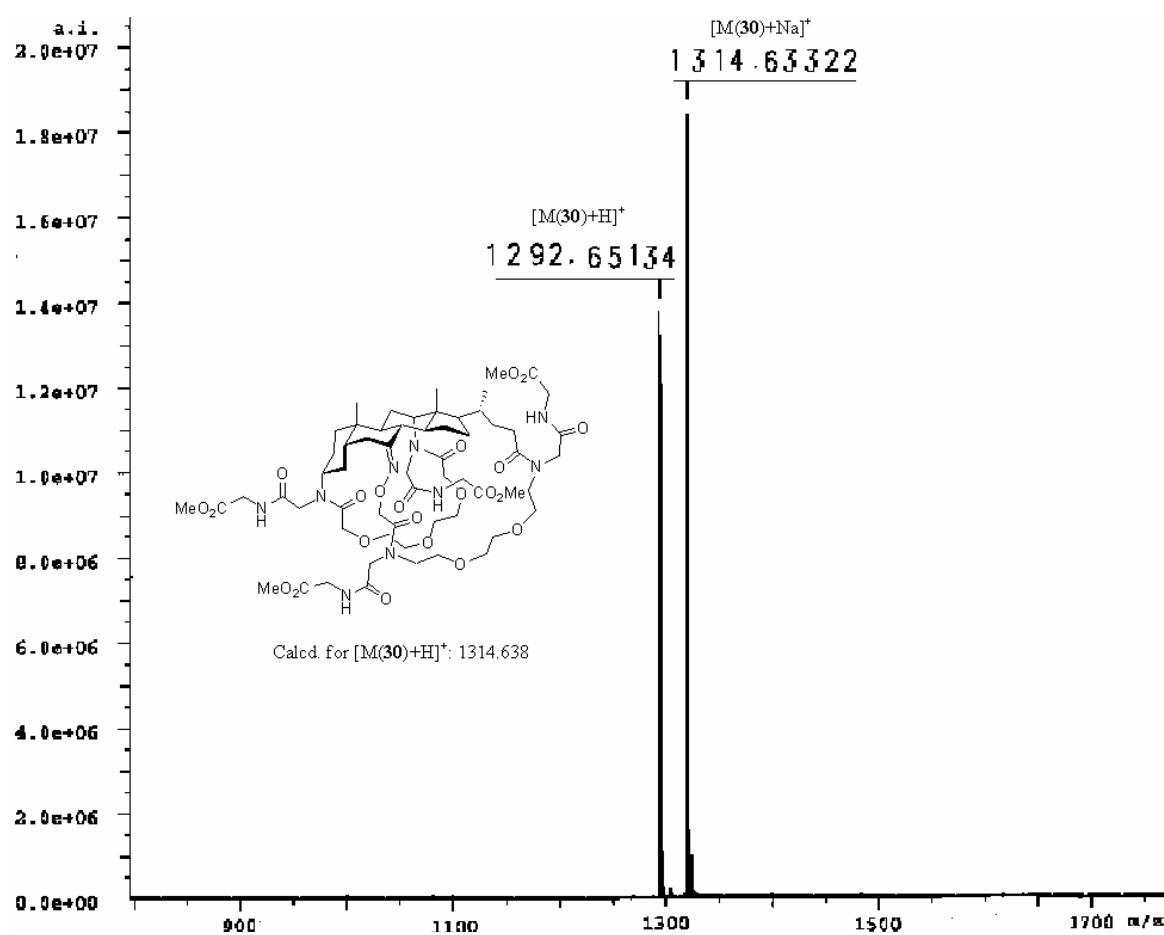
**Figure 11.** HR-MS (ESI-FT-ICR) spectrum of the steroid-based "clam" **25**.



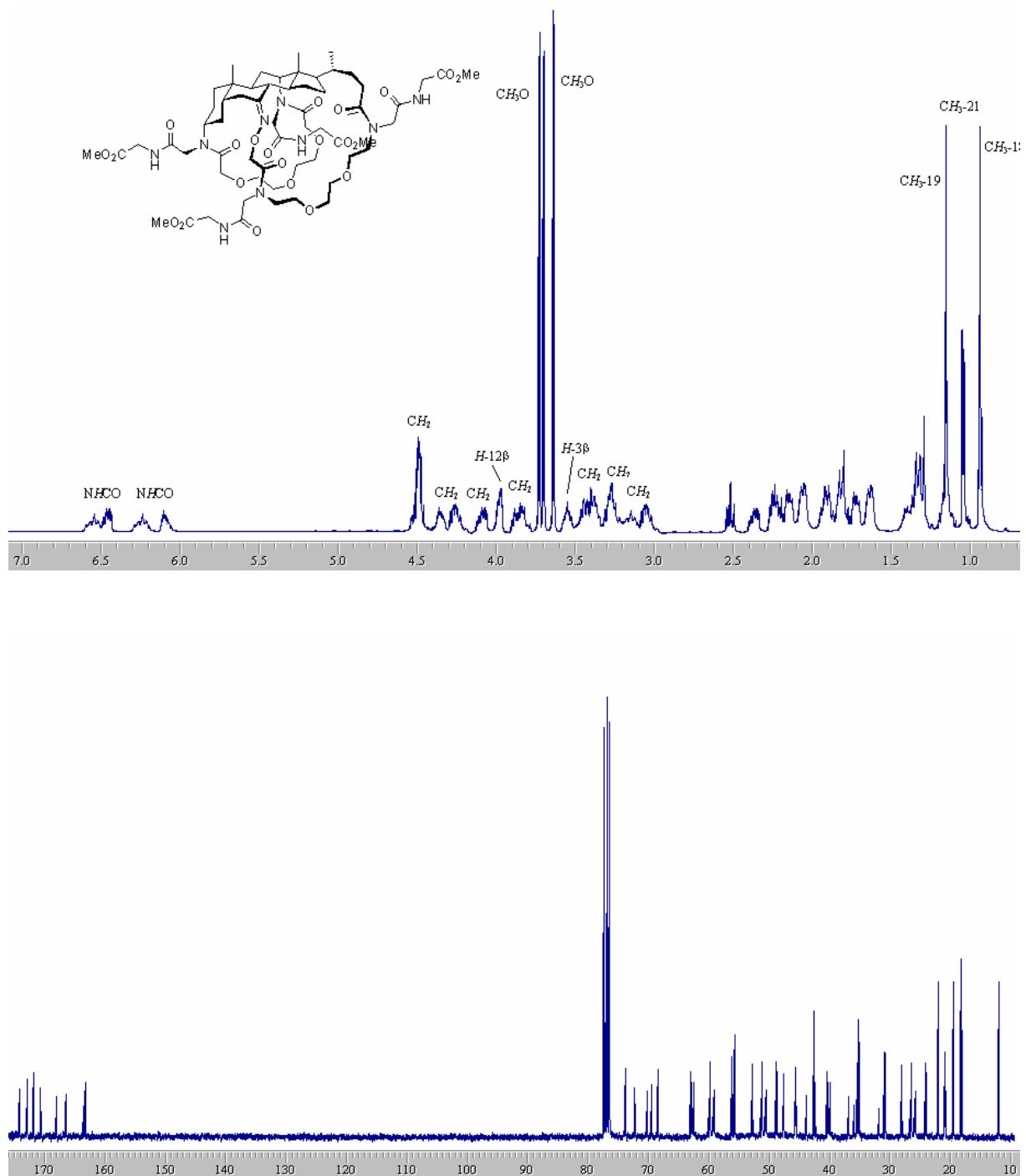
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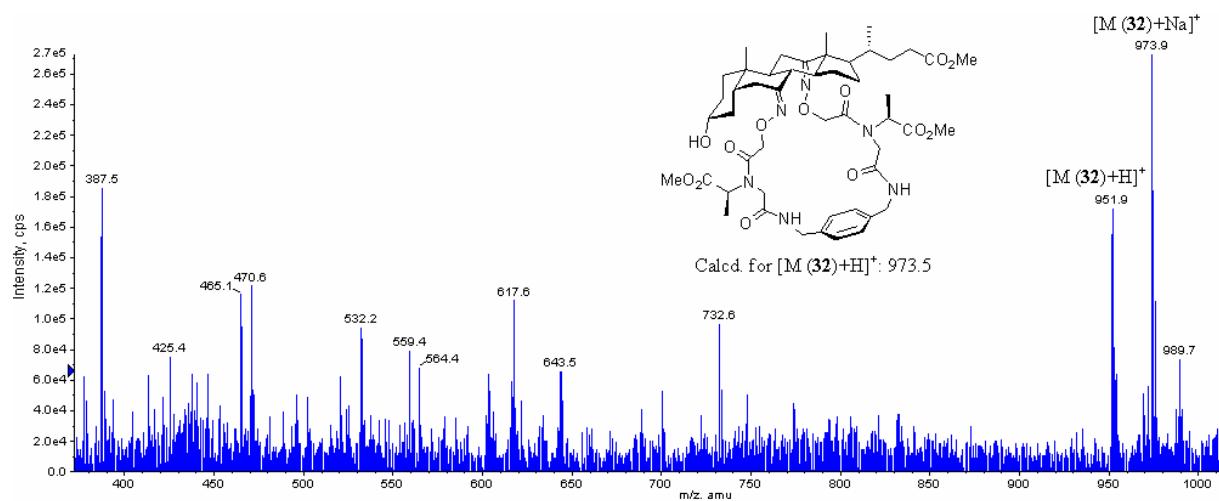
**Figure 13.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the steroid-based "clam" **27** in CDCl<sub>3</sub>.



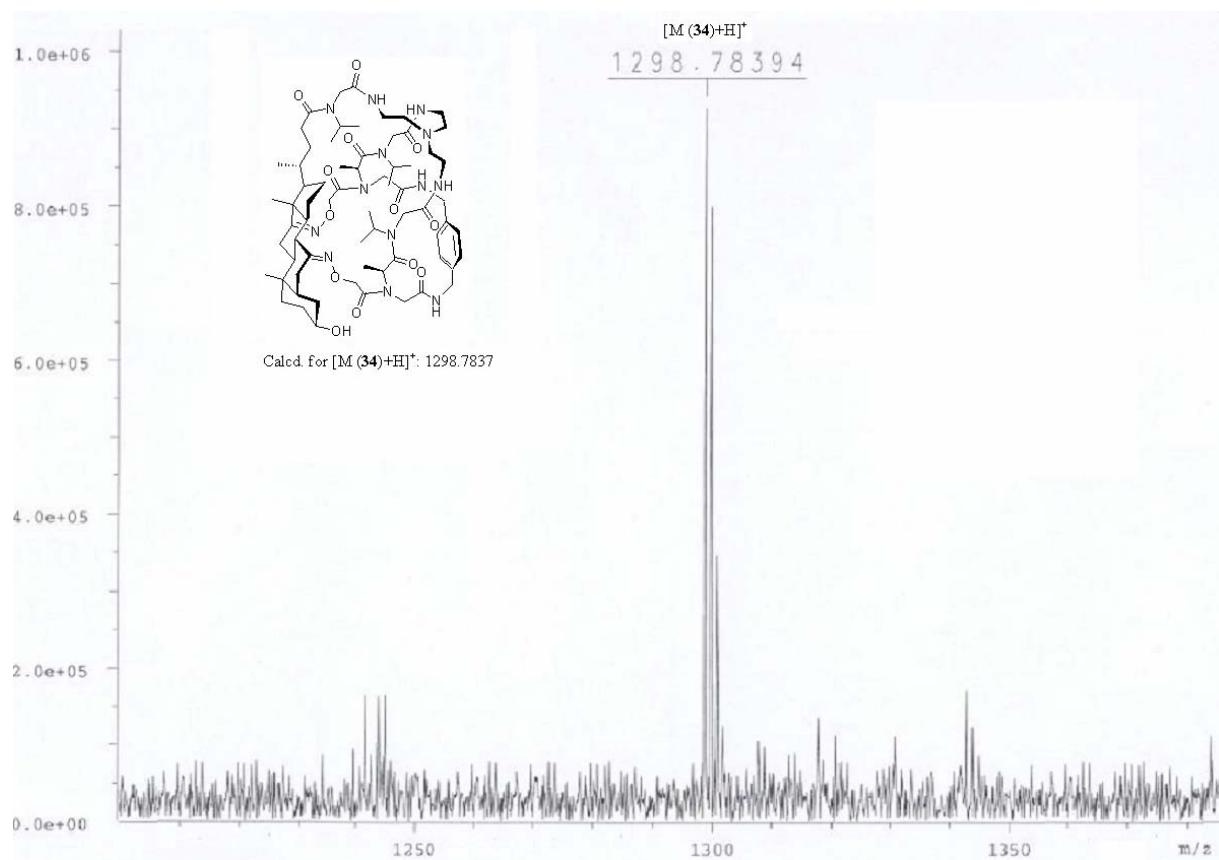
**Figure 14.** HR-MS (ESI-FT-ICR) spectrum of the steroid-based "clam" **30**.



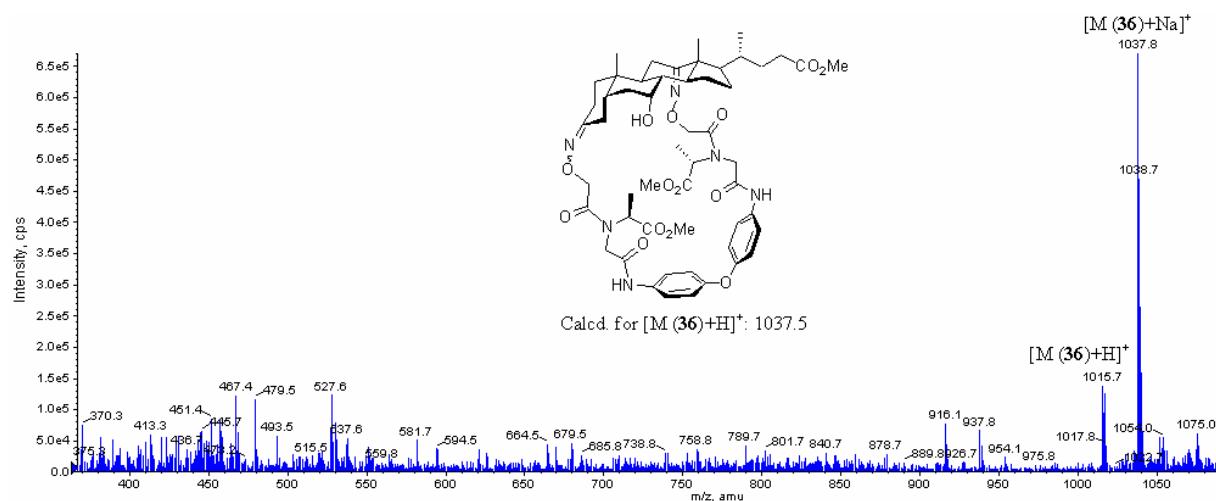
**Figure 15.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of the steroid-based "clam" **30** in  $\text{CDCl}_3$ .



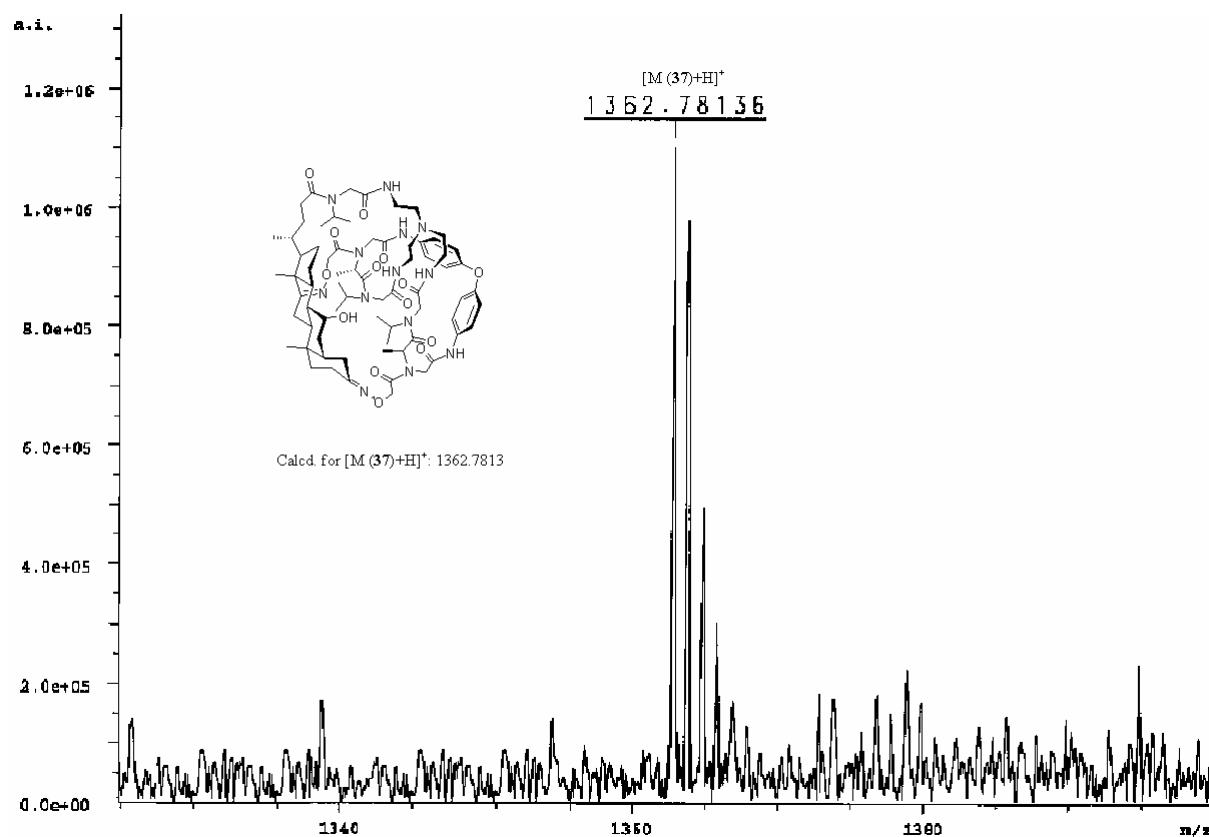
**Figure 16.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intemediate **32**.



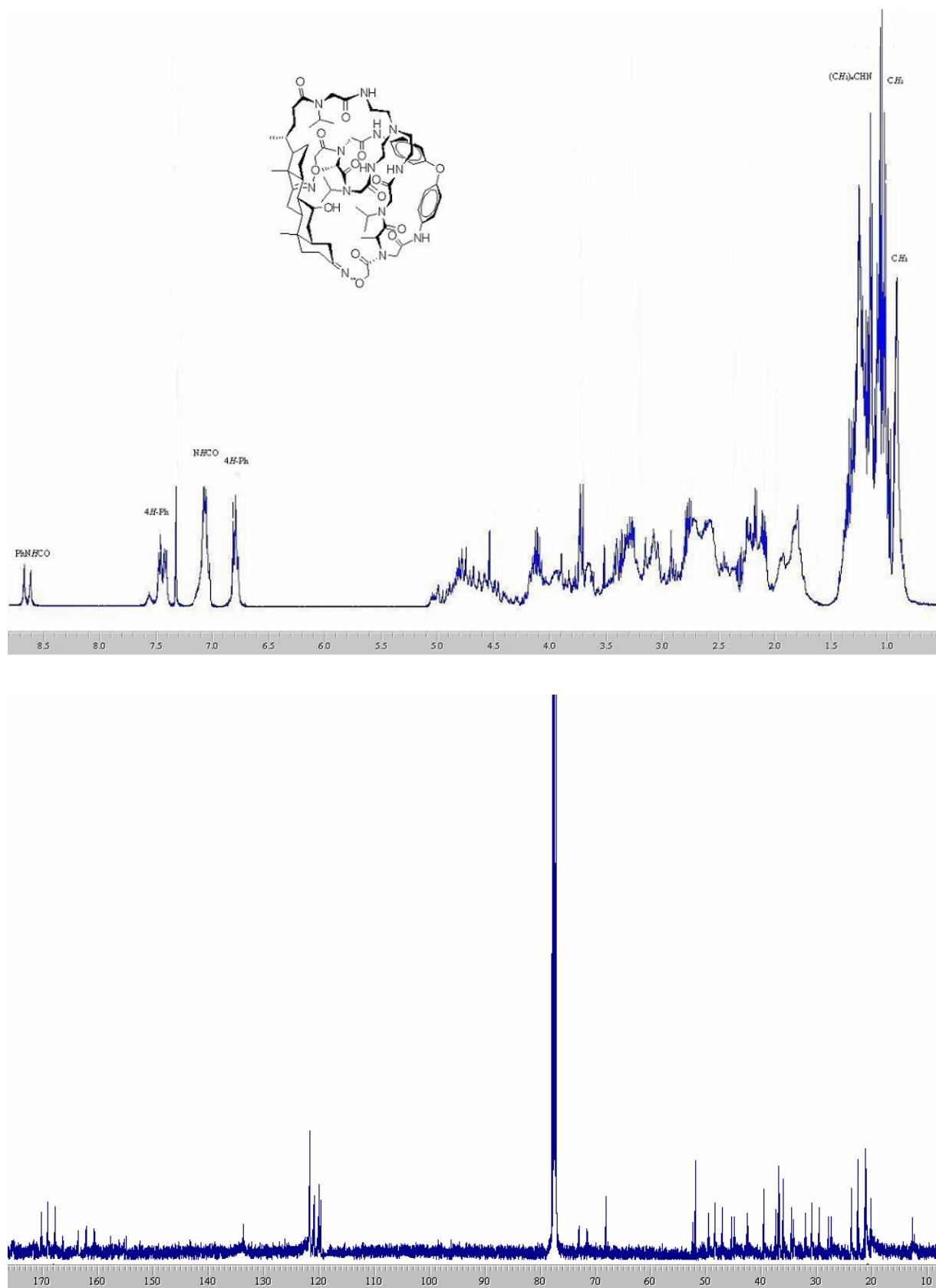
**Figure 17.** HR-MS (ESI-FT-ICR) spectrum of macrotetracycle "igloo" **34**.



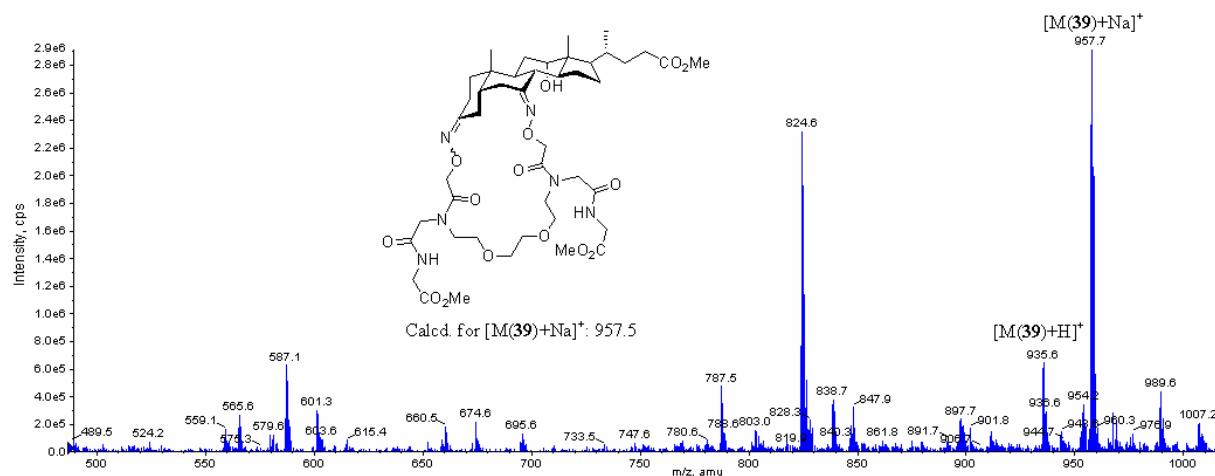
**Figure 18.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intemediate **36**.



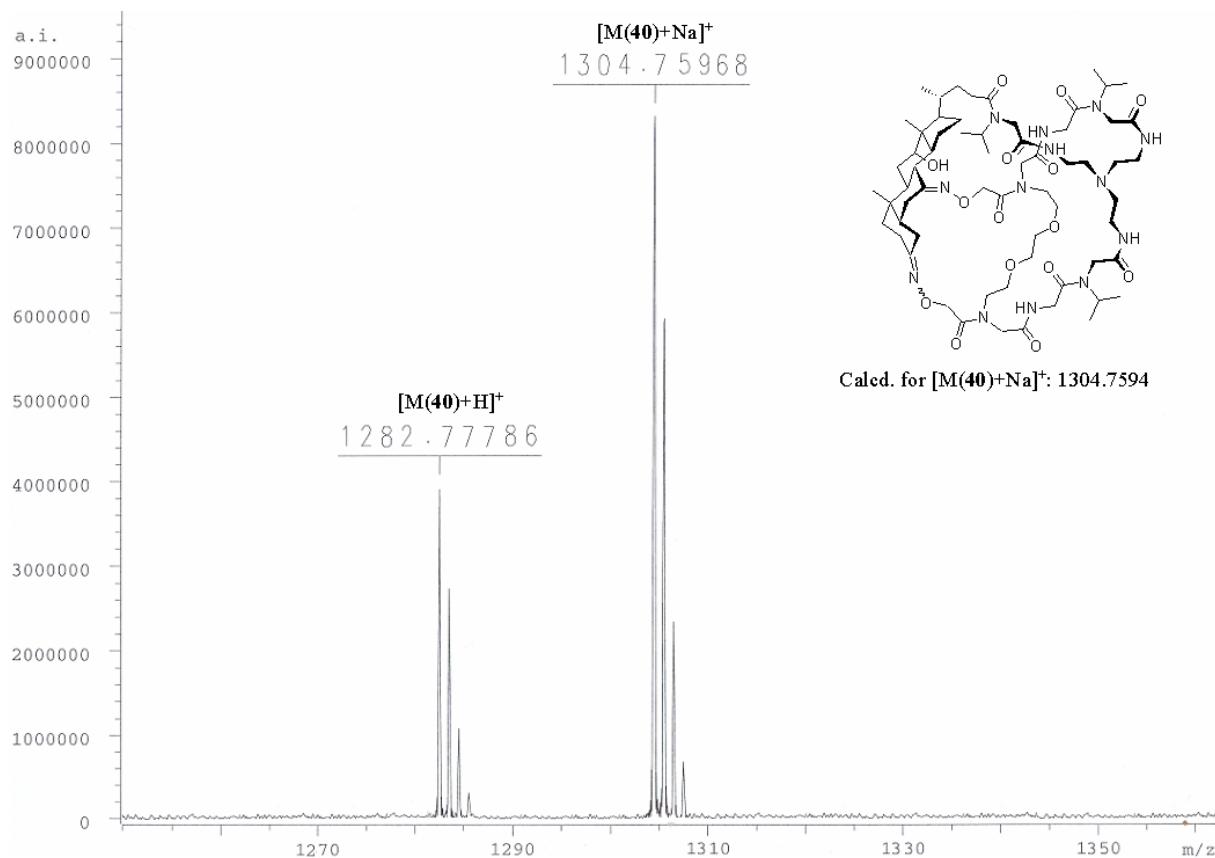
**Figure 19.** HR-MS (ESI-FT-ICR) spectrum of macrotetracycle **37**.



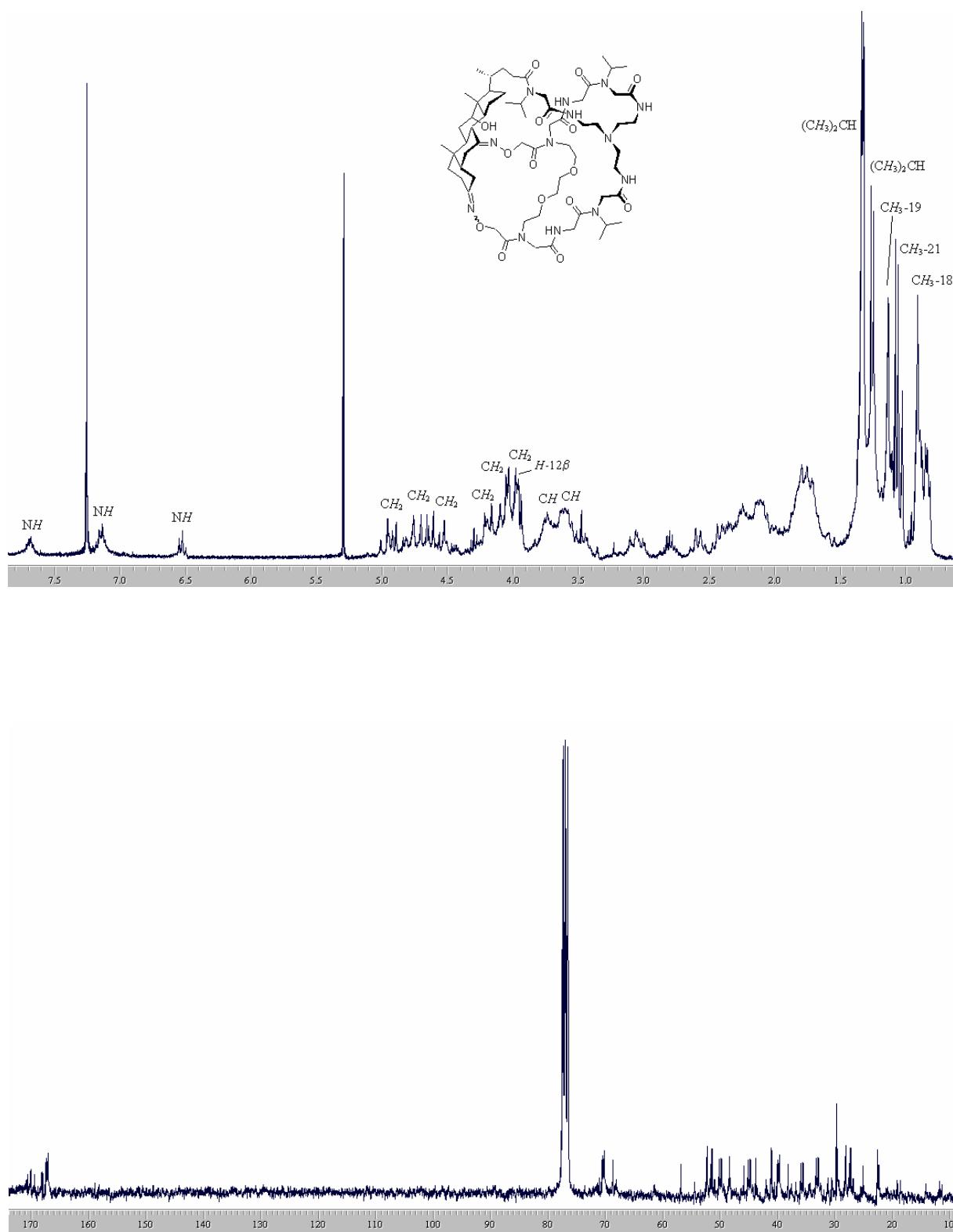
**Figure 20.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of macrotetracycle **35** in  $\text{CDCl}_3$ .



**Figure 21.** ESI-MS spectrum (ion positive mode) of the crude macrocyclic intermediate **39**.

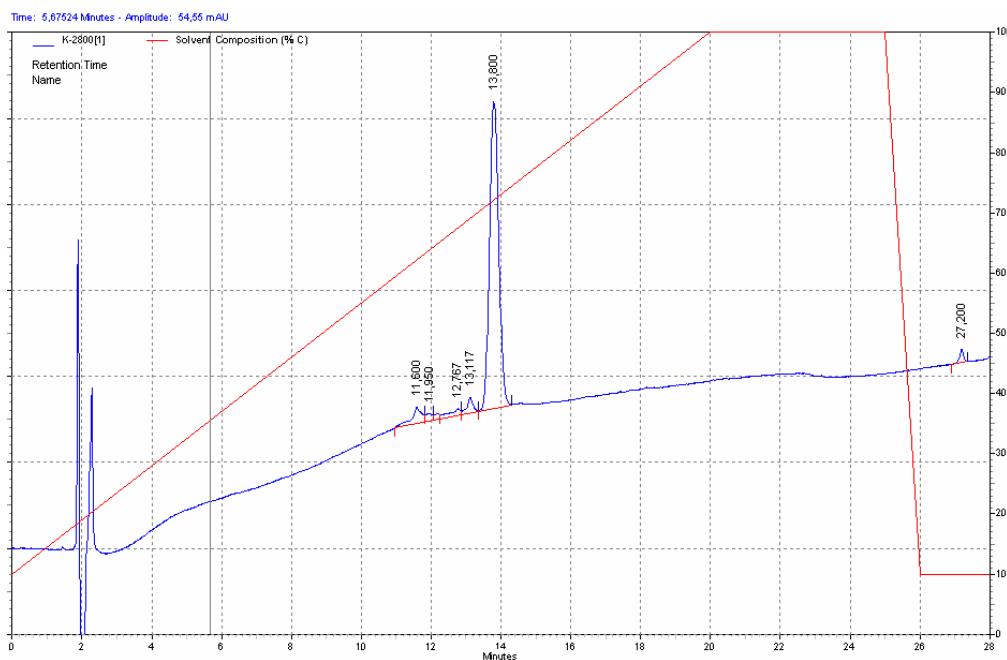


**Figure 22.** HR-MS (ESI-FT-ICR) spectrum of macrotetracycle **40**.

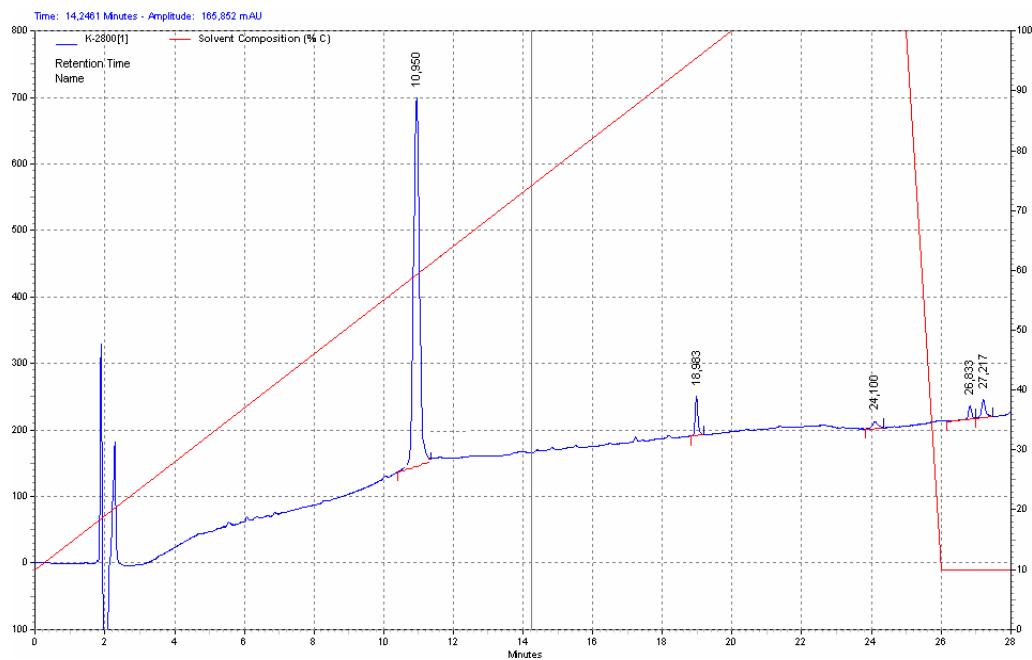


**Figure 23.** <sup>1</sup>H and <sup>13</sup>C NMR spectra of macrotetracycle **40** in  $\text{CDCl}_3$ .

Analytic RP-HPLC, column: ODS-A 120 5 $\mu$ m 4.6x159mm + VS (SNr.176), conditions: CH<sub>3</sub>CN: H<sub>2</sub>O gradient CH<sub>3</sub>CN10%>in20min>100%(5min), detection: 210 nm



**Figure 24.** RP-HPLC analysis of cryptand **9**.



**Figure 25.** RP-HPLC analysis of cryptand **13**.