

## Supplementary Material

### Synthesis of tetramethoxy-(tetra-hydrazinecarboxamide) cyclophanes with unexpected conformation and investigation of their solution-phase recognition of chiral carboxylic guests using time-of-flight and tandem mass spectrometry

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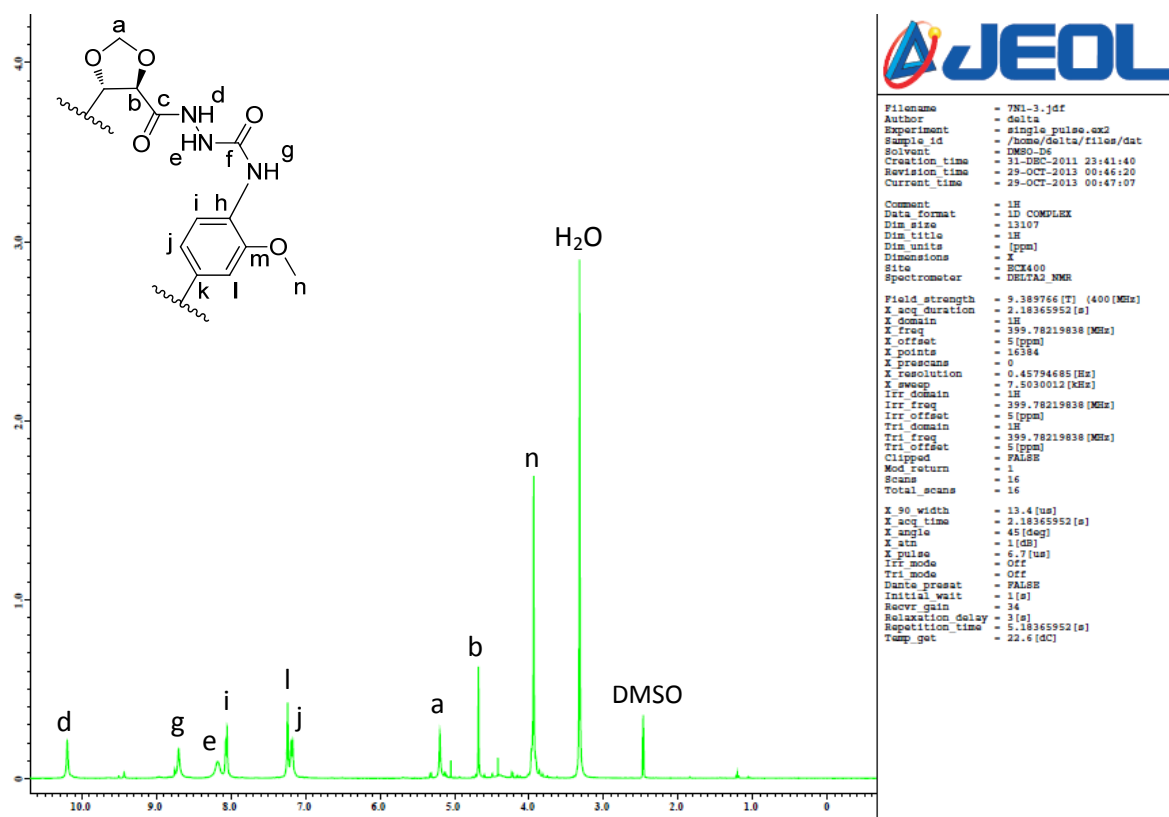


Figure 1.  $^1\text{H}$  NMR spectrum of macrocycle (9) (400 MHz,  $\text{DMSO-}d_6$ ).

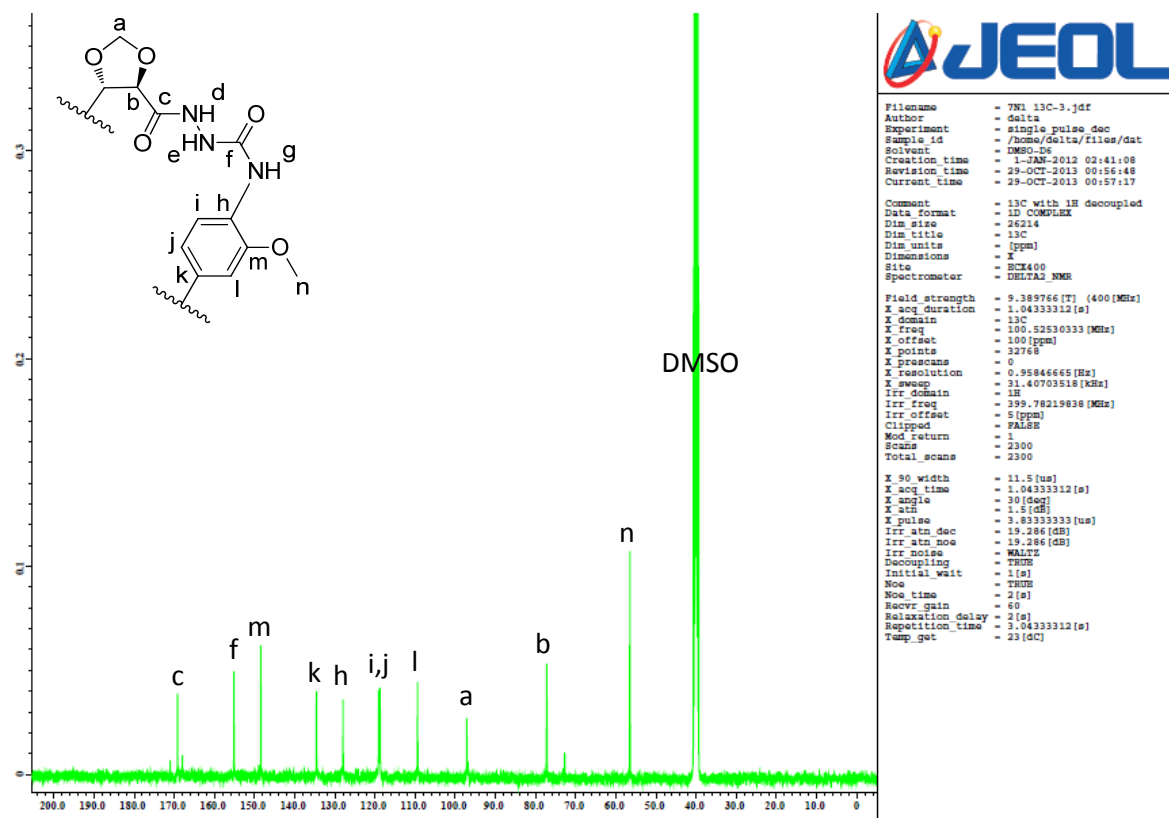


Figure 2.  $^{13}\text{C}$  NMR spectrum of macrocycle (9) (100 MHz,  $\text{DMSO-}d_6$ ).

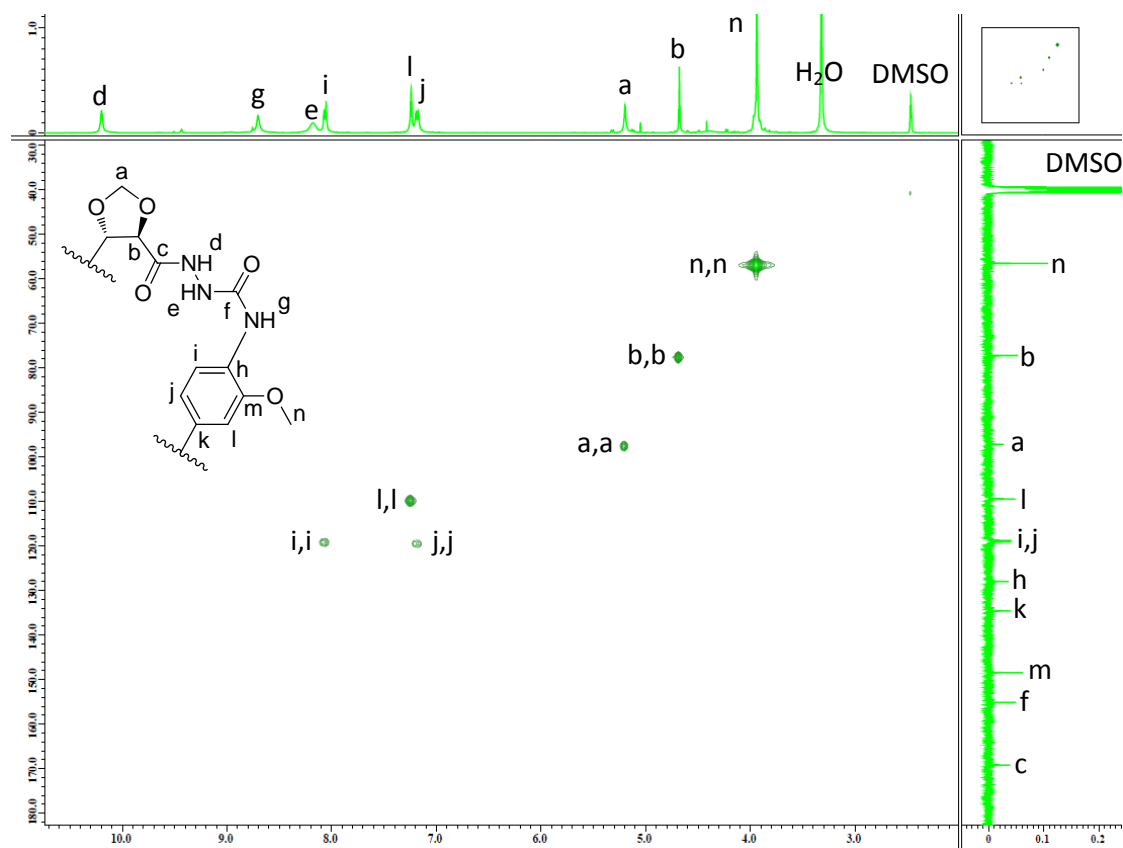


Figure 3. 2D HMQC spectrum of macrocycle (9) (DMSO- $d_6$ ).

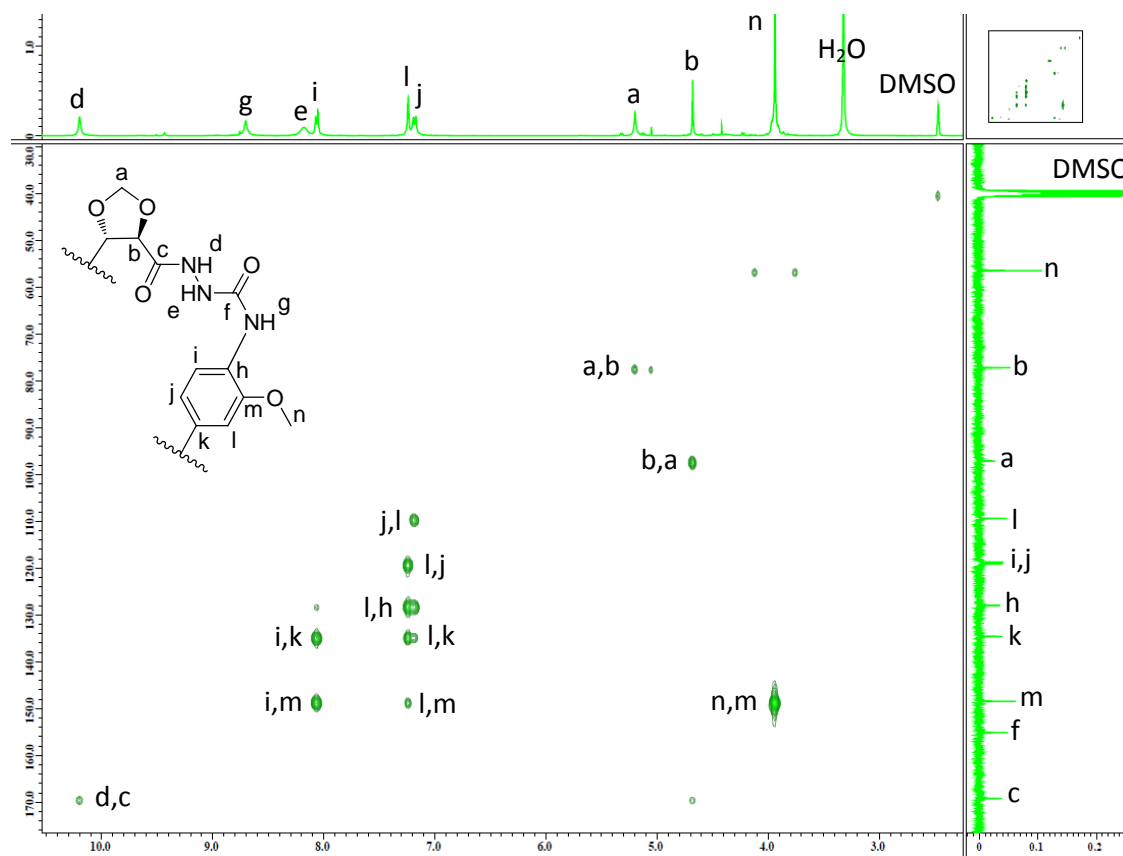


Figure 4. 2D HMBC spectrum of macrocycle (9) (DMSO- $d_6$ ).

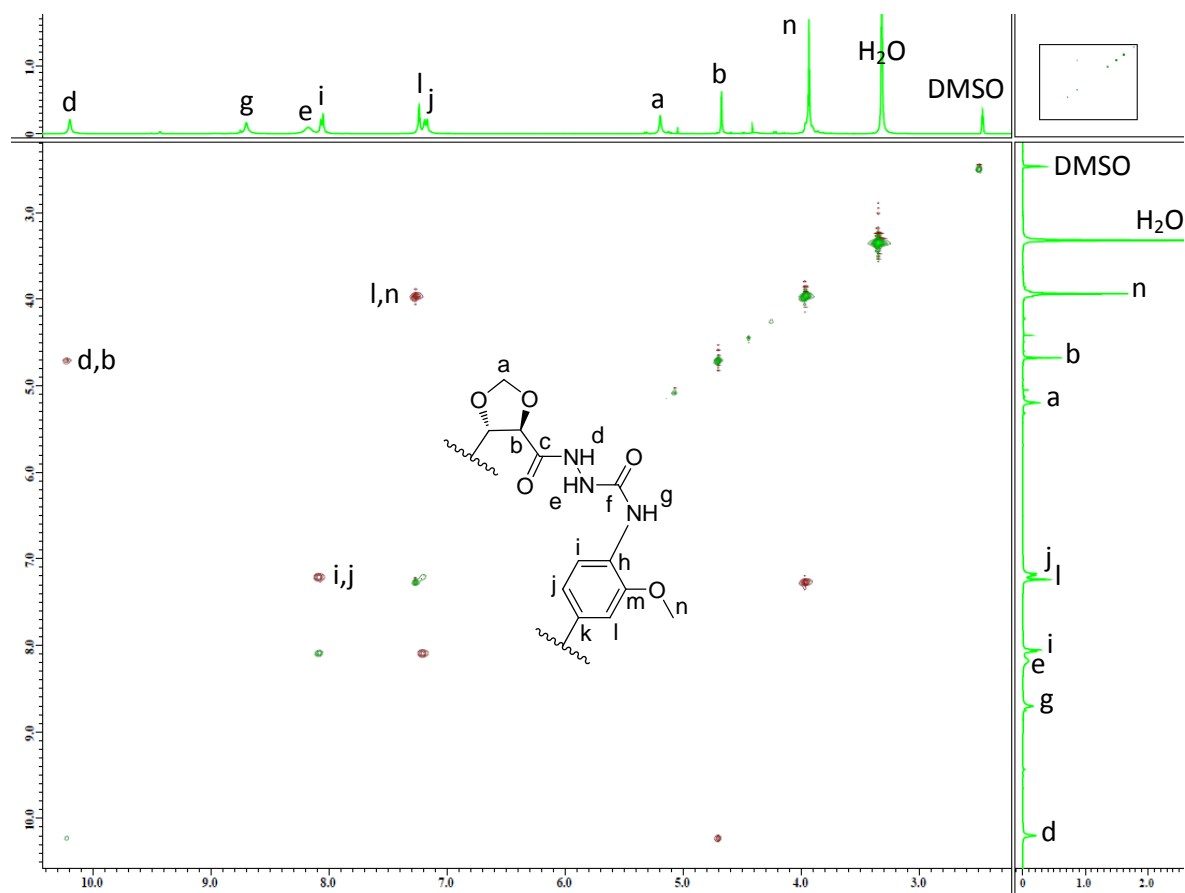


Figure 5. 2D ROESY NMR spectrum of macrocycle (9) (DMSO- $d_6$ ).

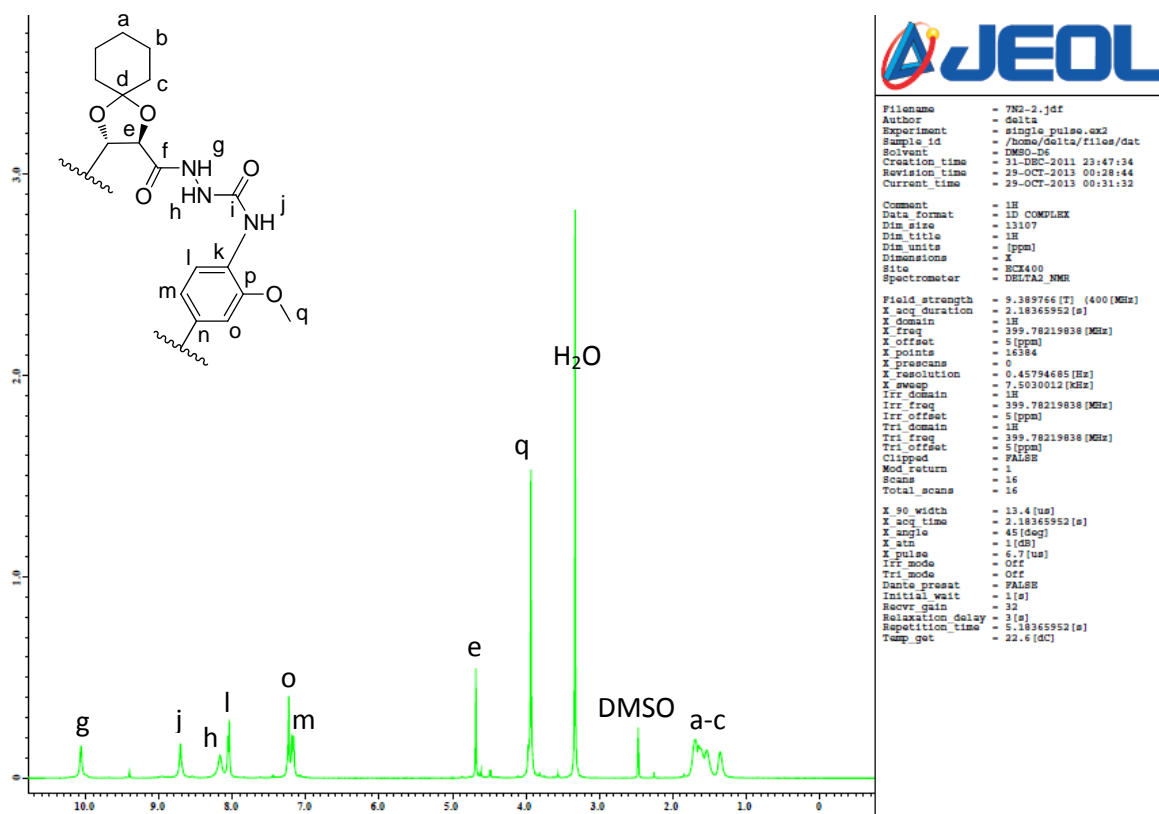


Figure 6.  $^1\text{H}$  NMR spectrum of macrocycle (10) (400 MHz, DMSO- $d_6$ ).



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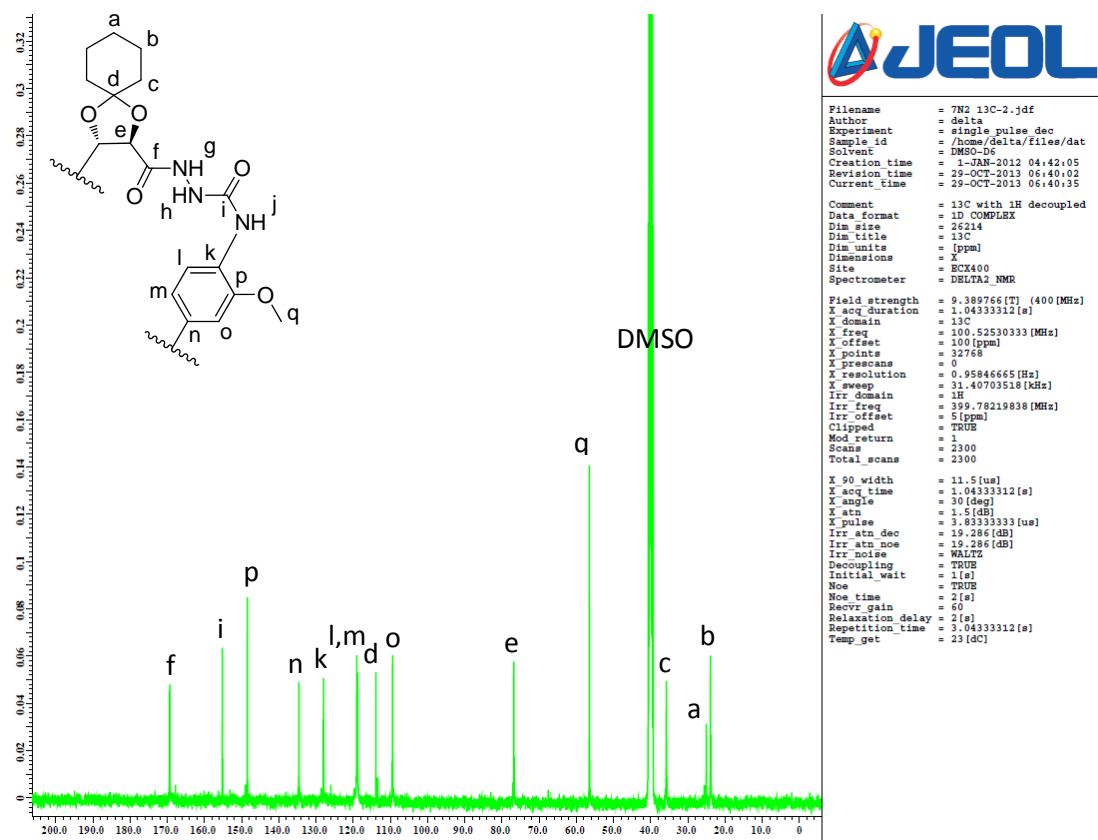


Figure 7.  $^{13}\text{C}$  NMR spectrum of macrocycle (10) (100 MHz,  $\text{DMSO}-d_6$ ).

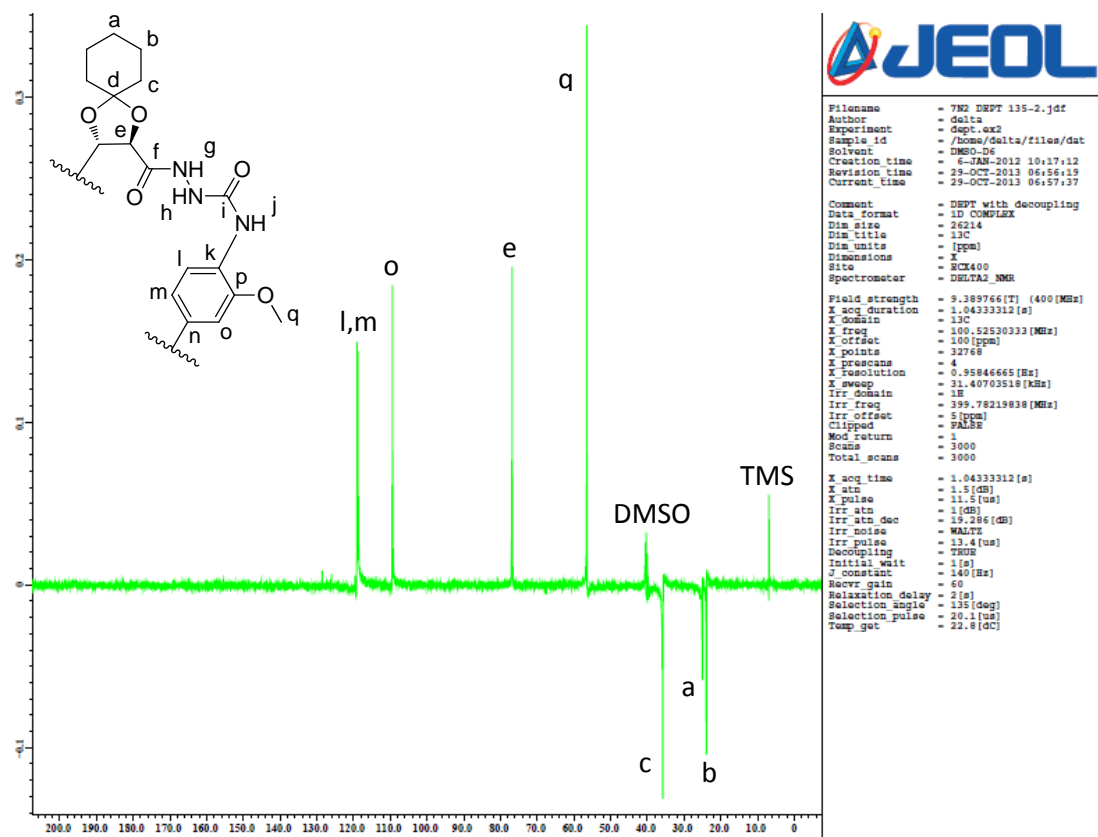
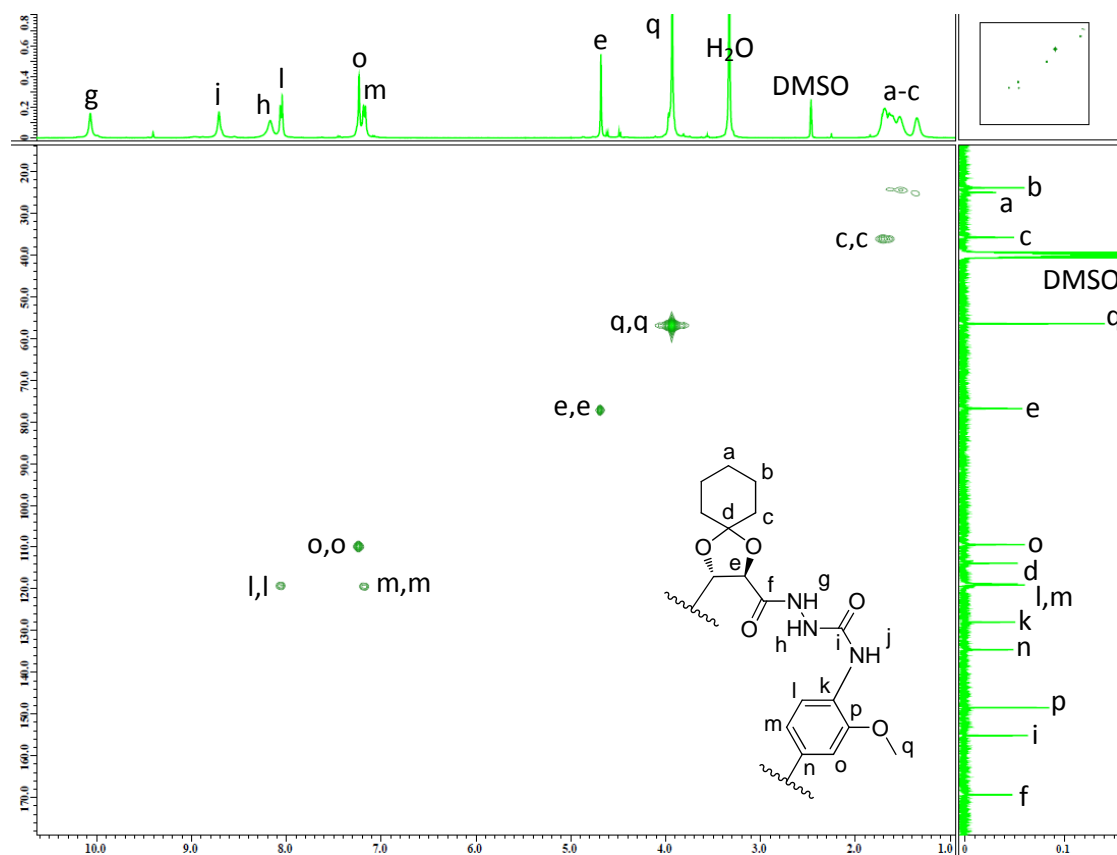
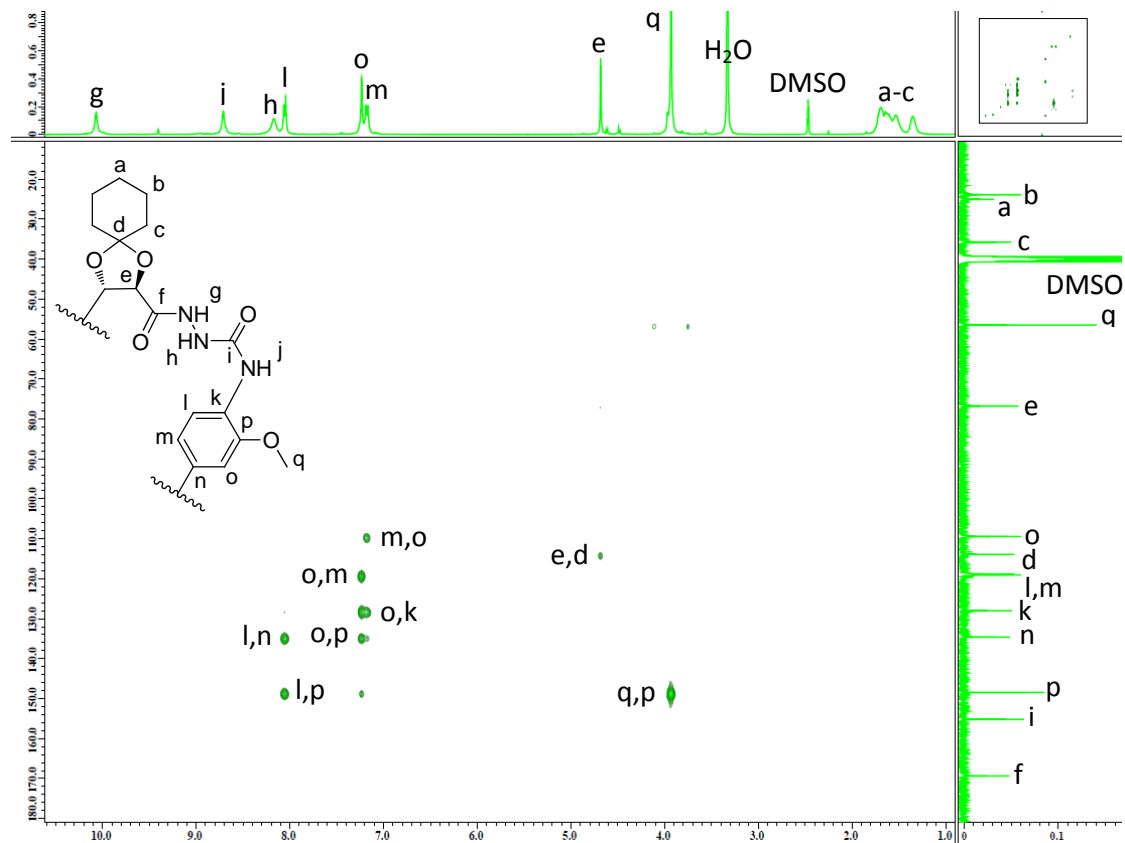


Figure 8. DEPT 135 spectrum of macrocycle (10) ( $\text{DMSO}-d_6$ ).





**Figure 9.** 2D HMQC spectrum of macrocycle (**10**) (DMSO- $d_6$ ).



**Figure 10.** 2D HMBC spectrum of macrocycle (**10**) (DMSO- $d_6$ ).

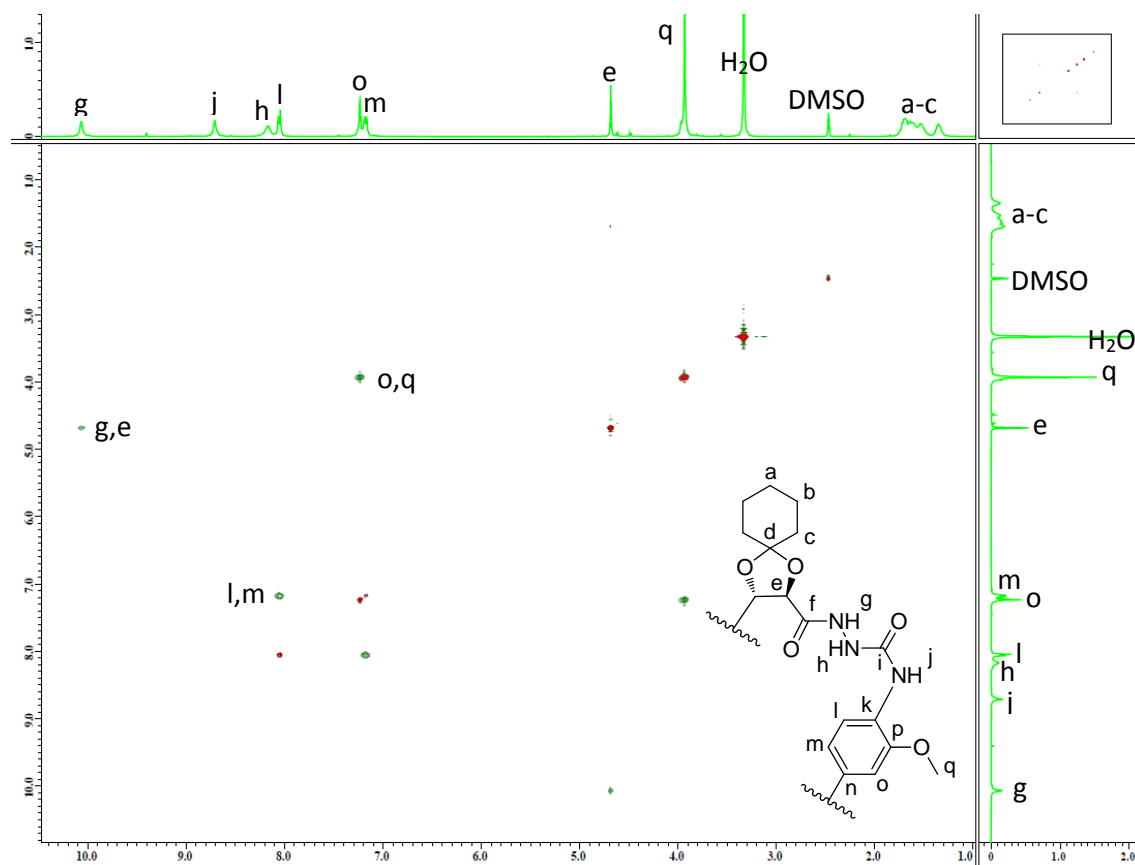


Figure 11. 2D ROESY NMR spectrum of macrocycle (10) (DMSO- $d_6$ ).

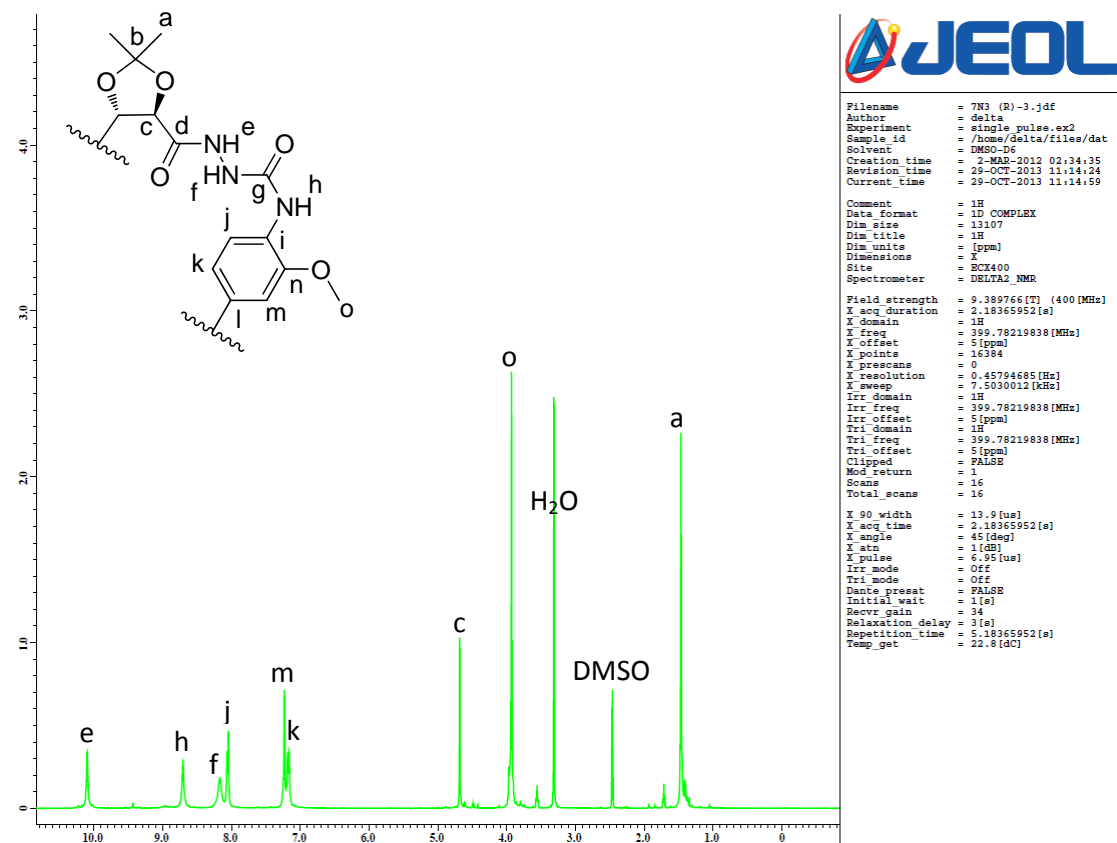


Figure 12.  $^1\text{H}$  NMR spectrum of macrocycle (11) (400 MHz, DMSO- $d_6$ ).

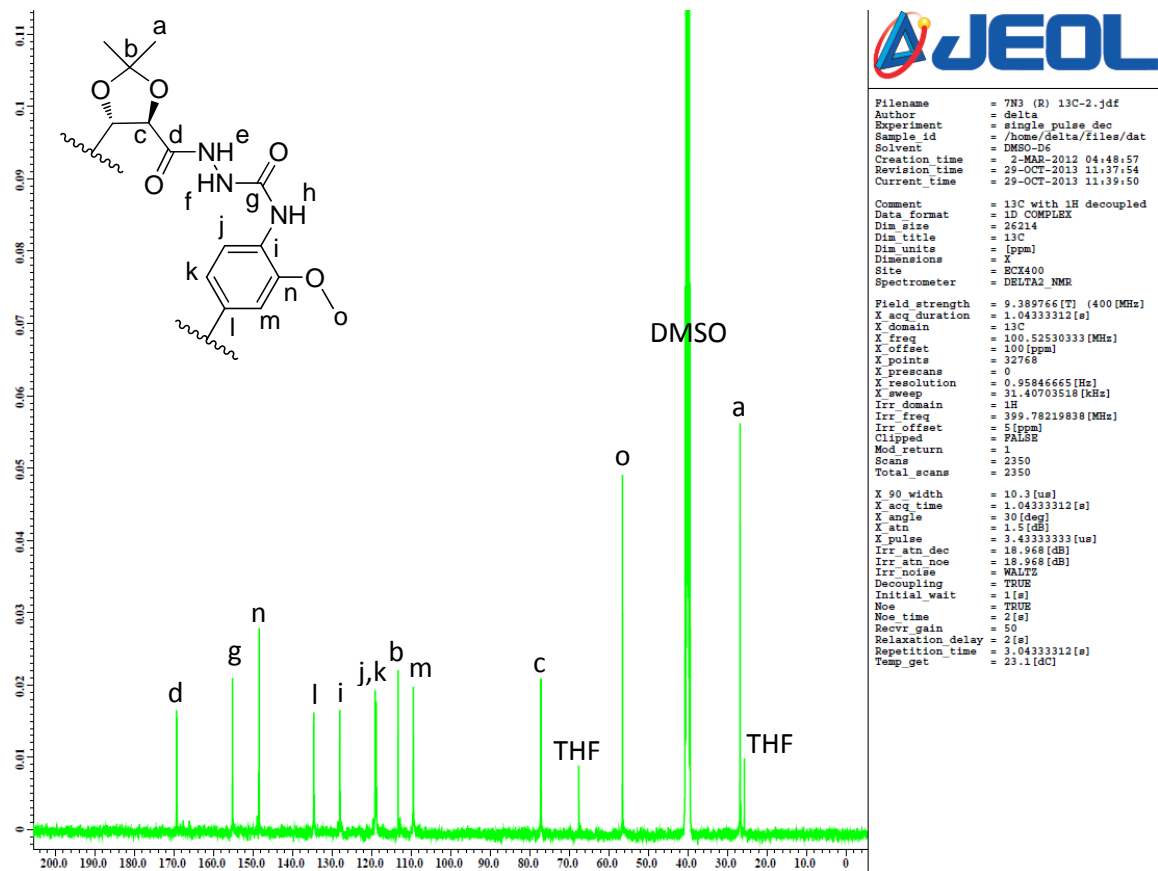


Figure 13.  $^{13}\text{C}$  NMR spectrum of macrocycle (**11**) (100 MHz,  $\text{DMSO}-d_6$ ).

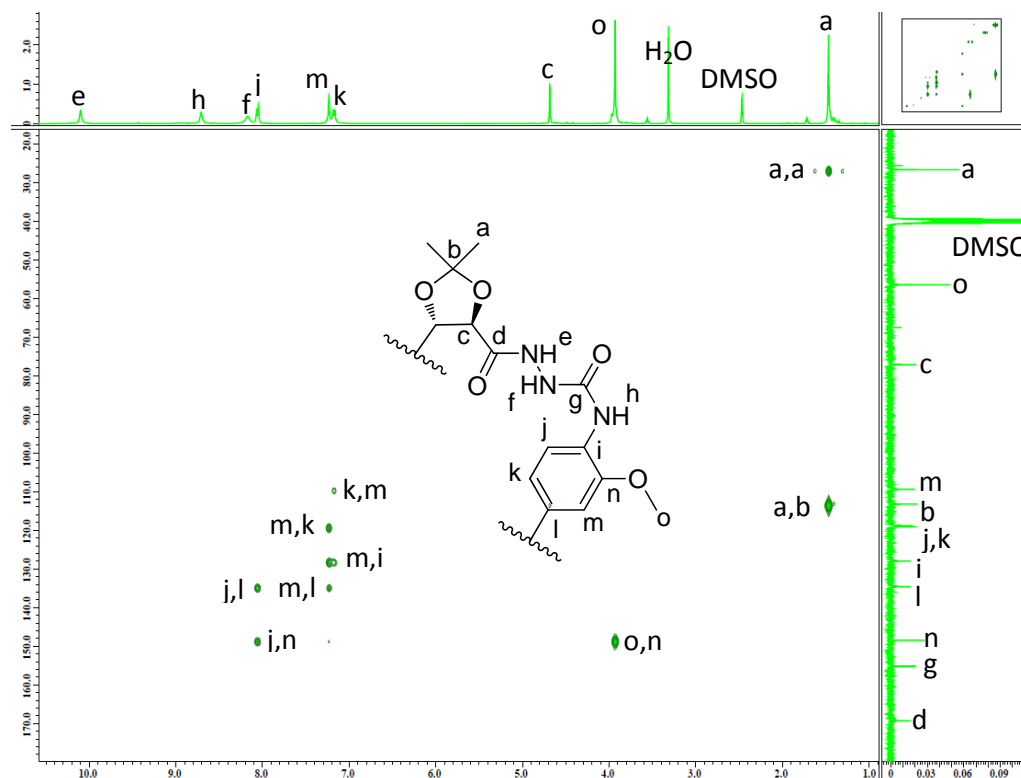


Figure 14. 2D HMBC spectrum of macrocycle (**11**) ( $\text{DMSO}-d_6$ ).

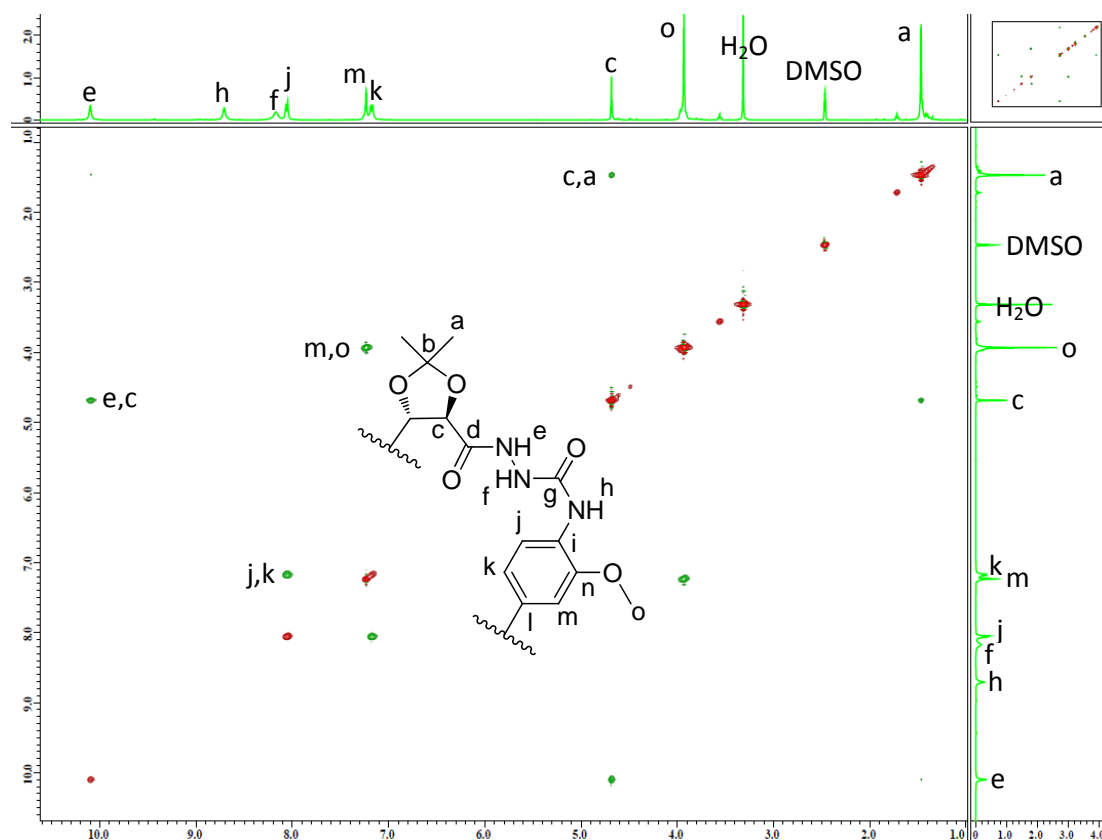


Figure 15. 2D ROESY NMR spectrum of macrocycle (11) (DMSO- $d_6$ ).

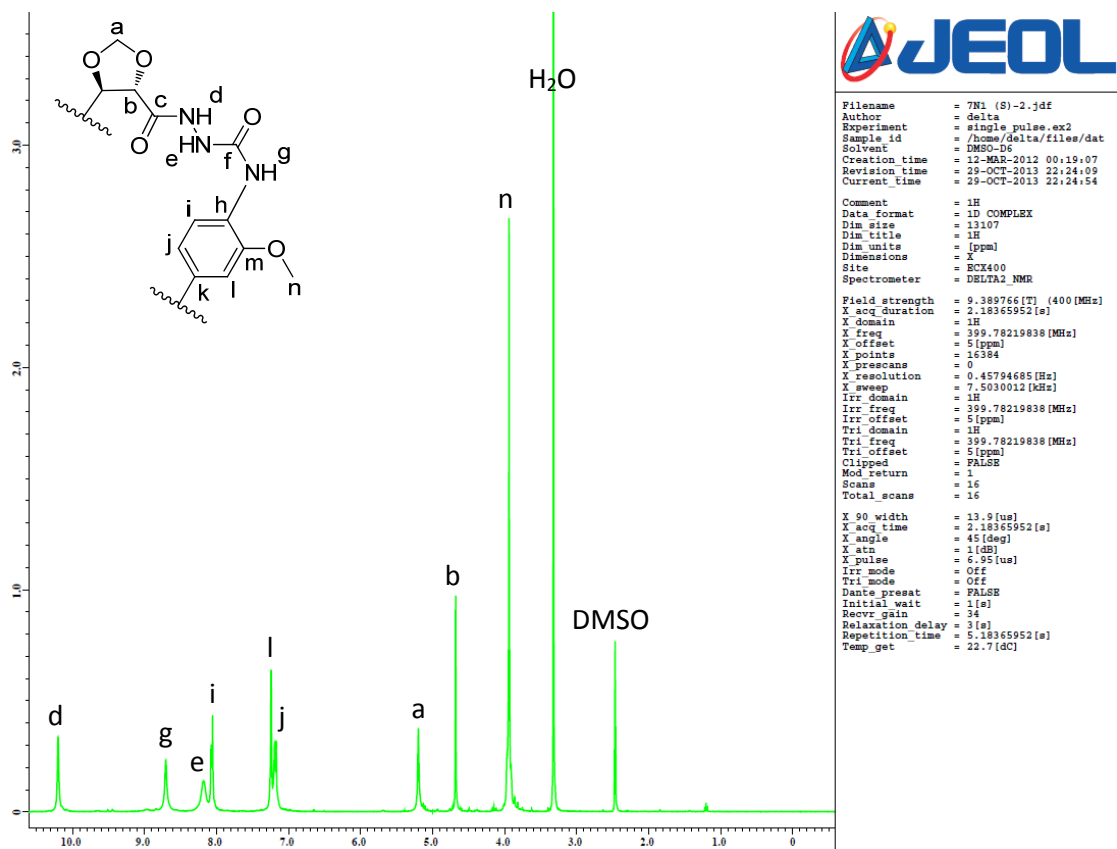
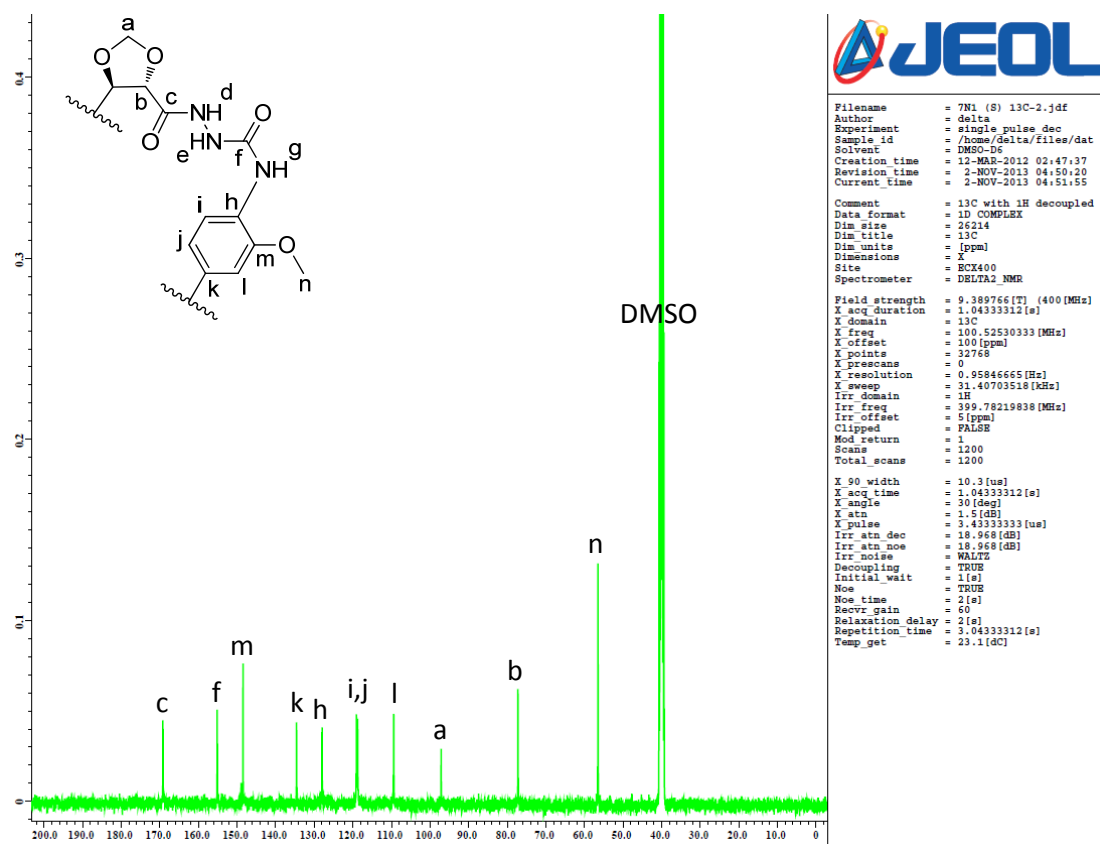
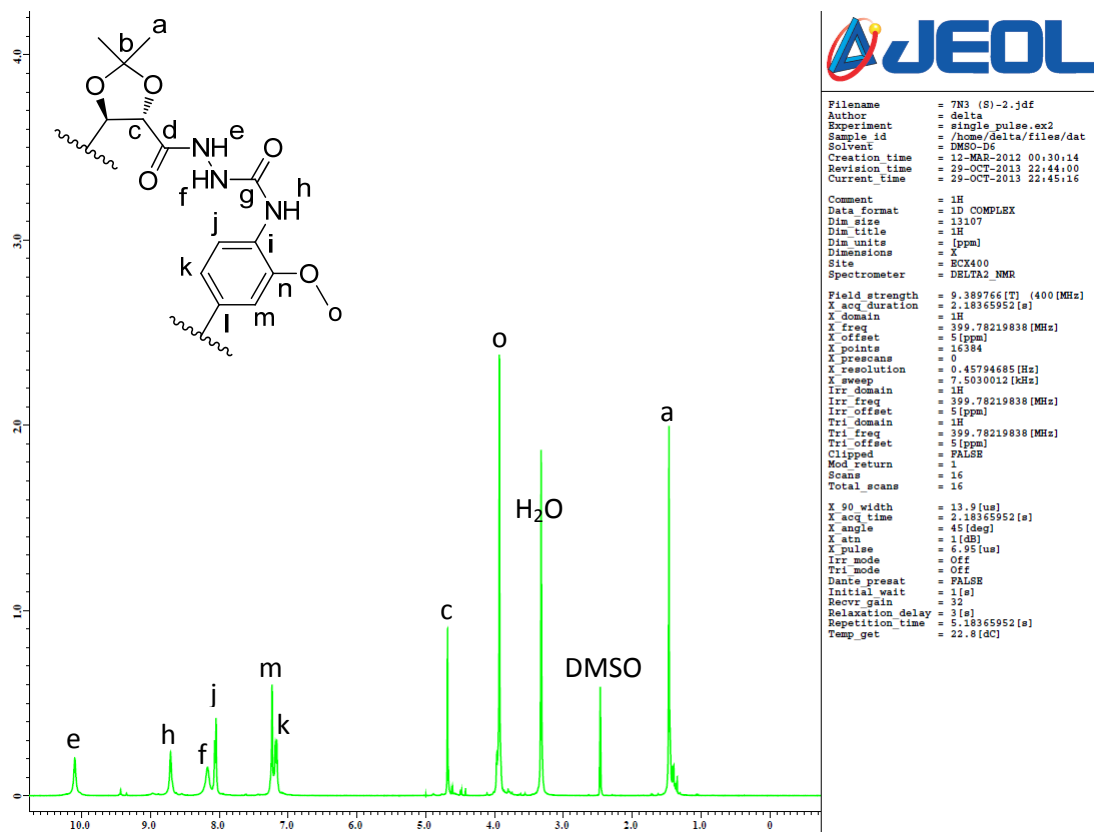


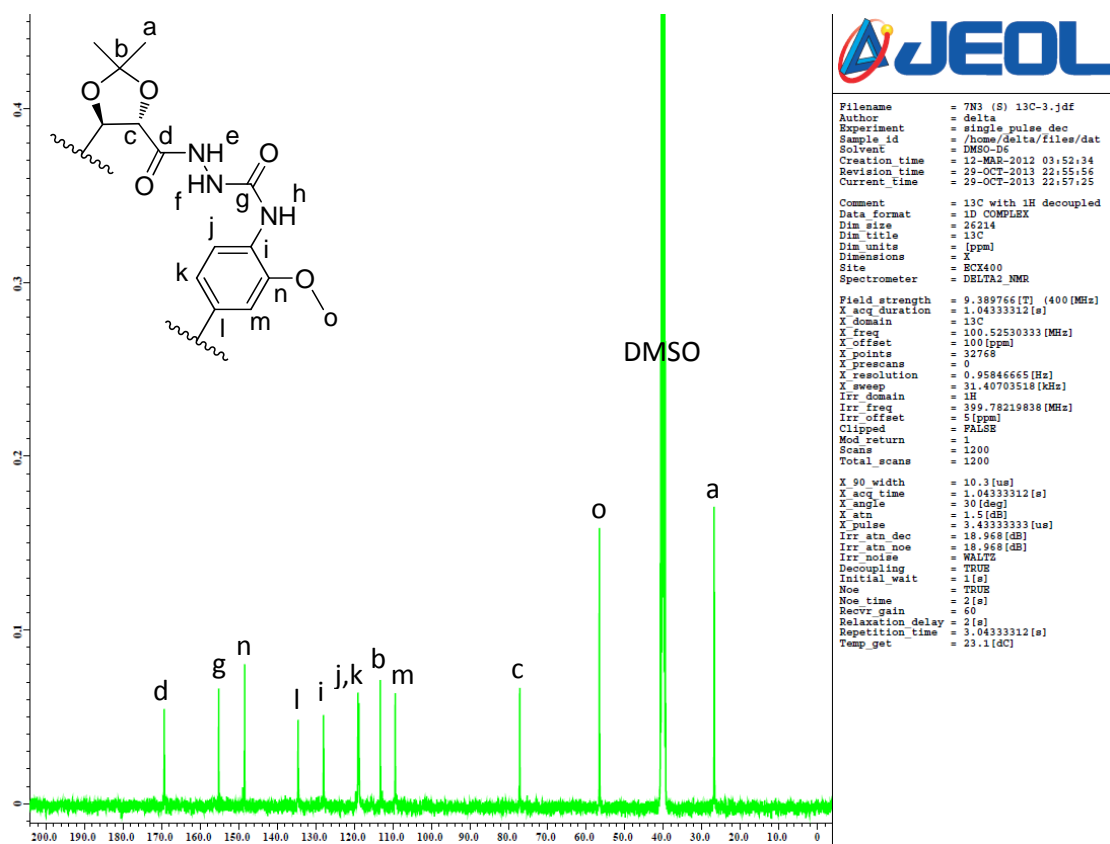
Figure 16.  $^1\text{H}$  NMR spectrum of macrocycle (12) (400 MHz, DMSO- $d_6$ ).



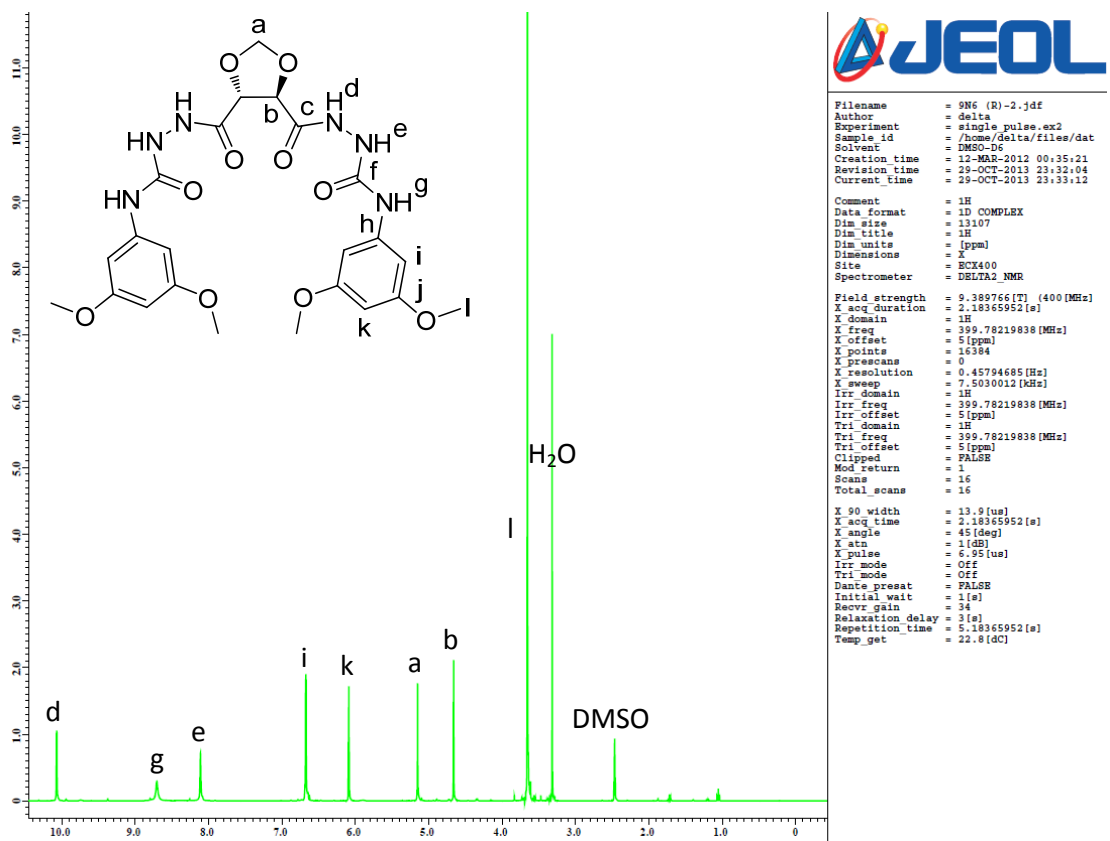
**Figure 17.**  $^{13}\text{C}$  NMR spectrum of macrocycle (**12**) (100 MHz,  $\text{DMSO-}d_6$ ).



**Figure 18.**  $^1\text{H}$  NMR spectrum of macrocycle (**13**) (400 MHz,  $\text{DMSO-}d_6$ ).



**Figure 19.**  $^{13}\text{C}$  NMR spectrum of macrocycle (**13**) (100 MHz,  $\text{DMSO-}d_6$ ).



**Figure 20.**  $^1\text{H}$  NMR spectrum of compound (**14**) (400 MHz,  $\text{DMSO-}d_6$ ).

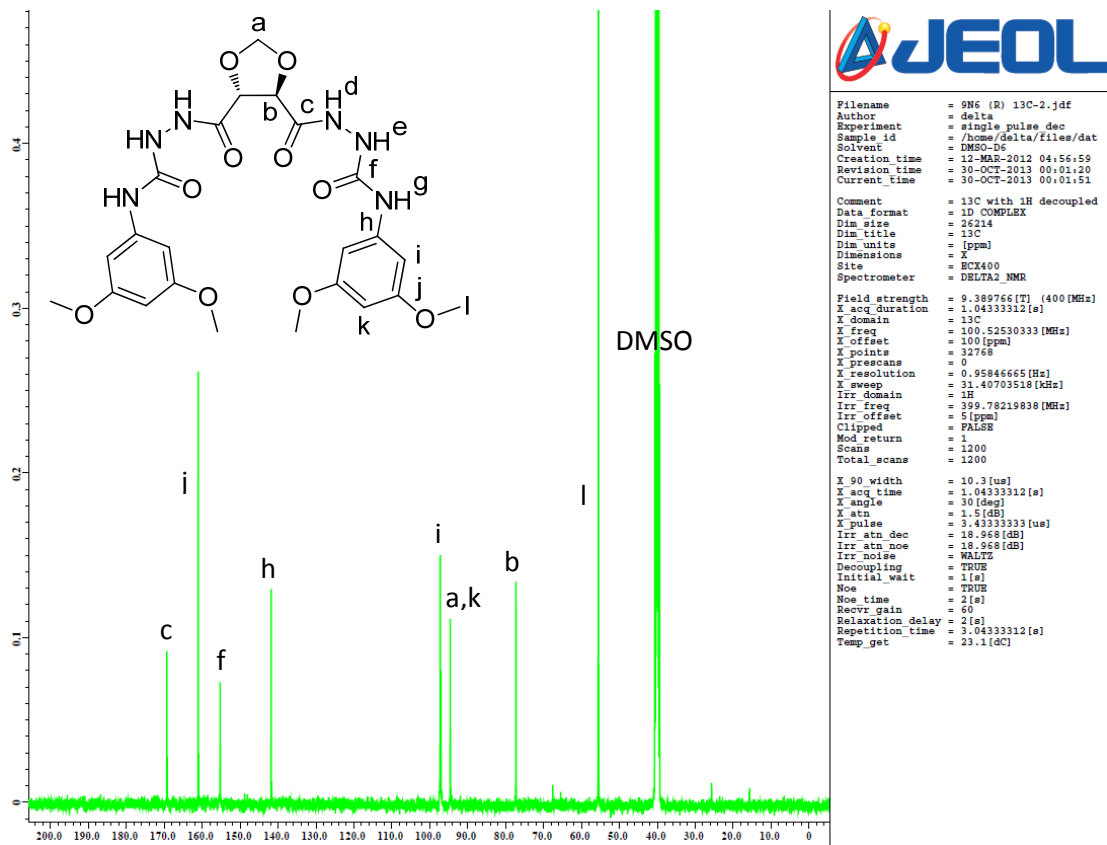


Figure 21.  $^{13}\text{C}$  NMR spectrum of compound (14) (100 MHz,  $\text{DMSO}-d_6$ ).

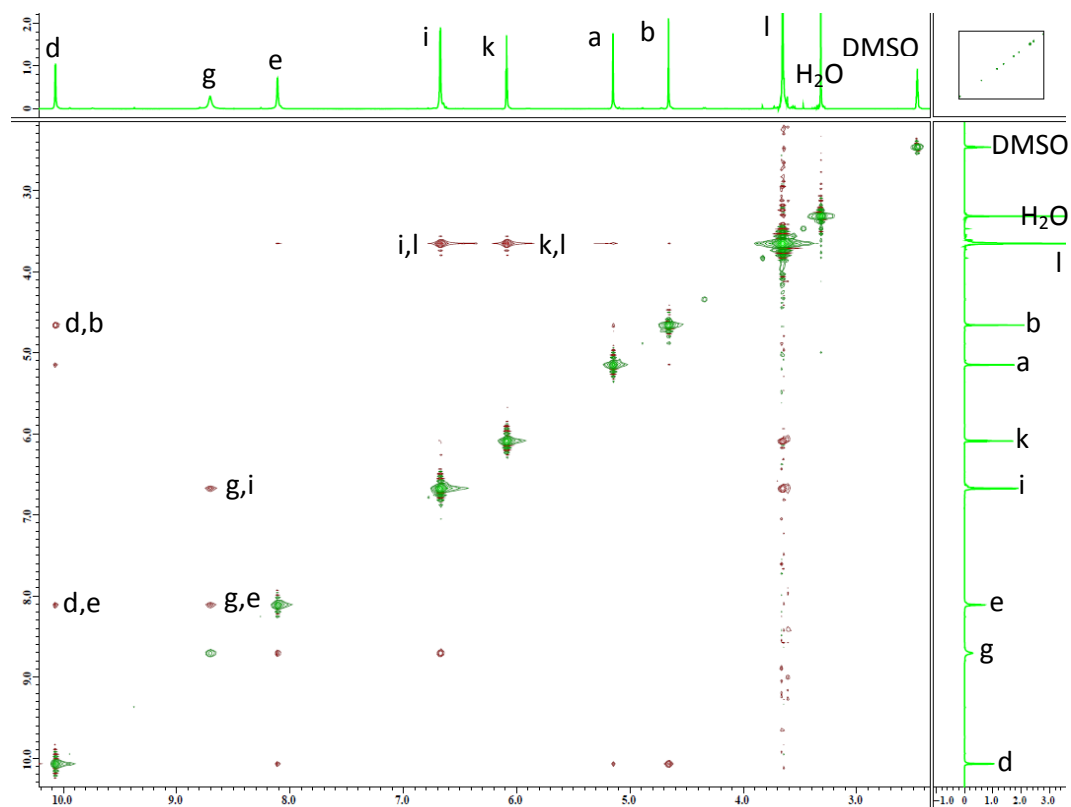


Figure 22. 2D ROESY NMR spectrum of compound (14) ( $\text{DMSO}-d_6$ ).

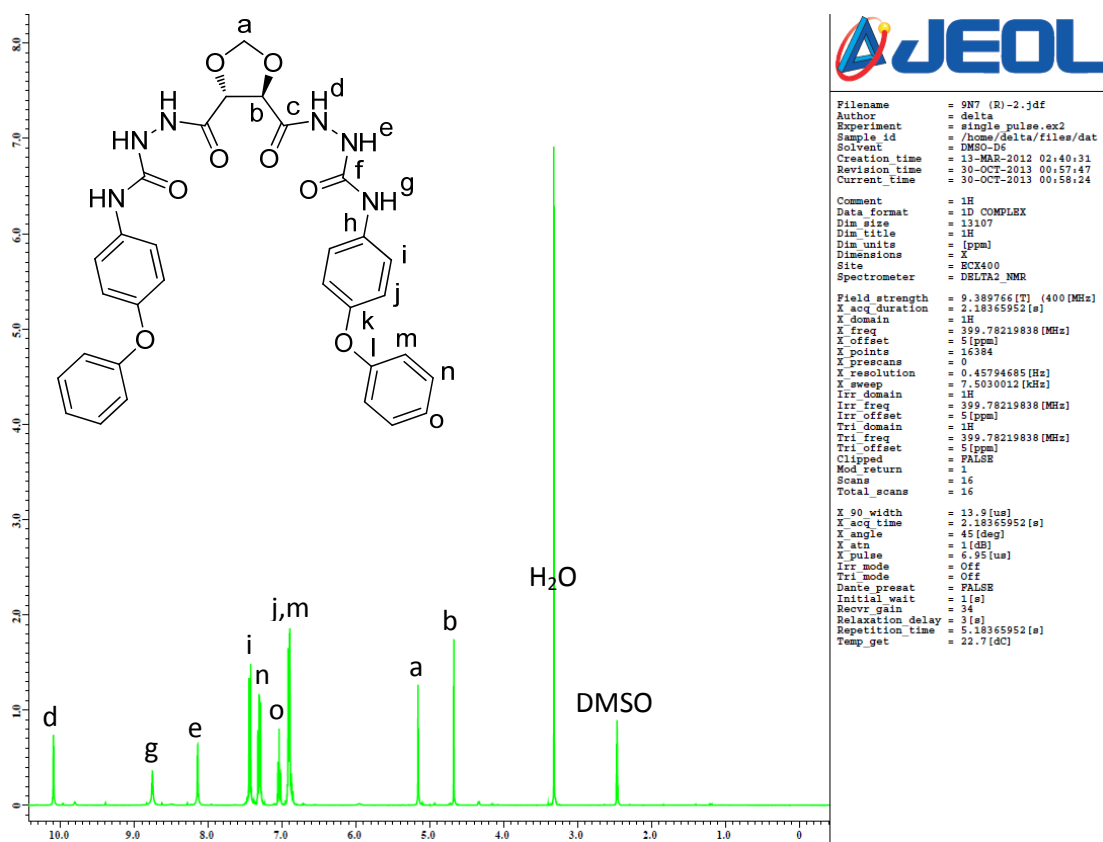


Figure 23.  $^1\text{H}$  NMR spectrum of compound (15) (400 MHz,  $\text{DMSO}-d_6$ ).

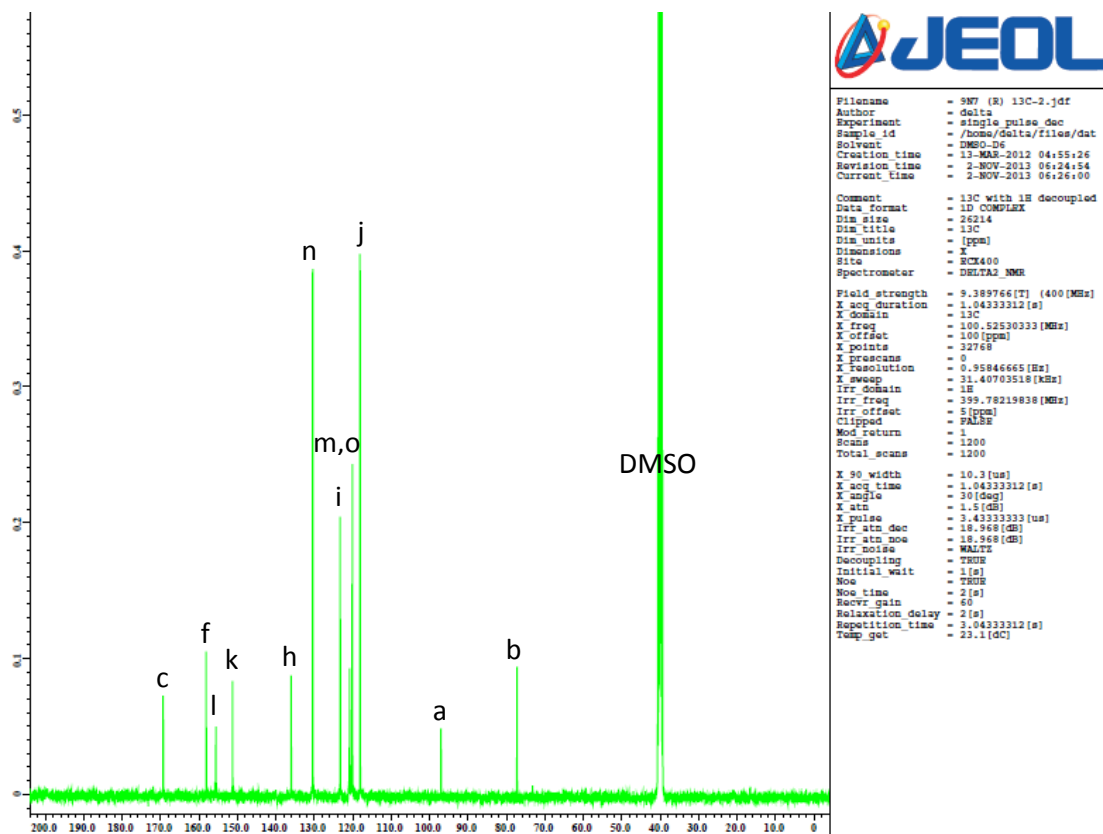


Figure 24.  $^{13}\text{C}$  NMR spectrum of compound (15) (100 MHz,  $\text{DMSO}-d_6$ ).



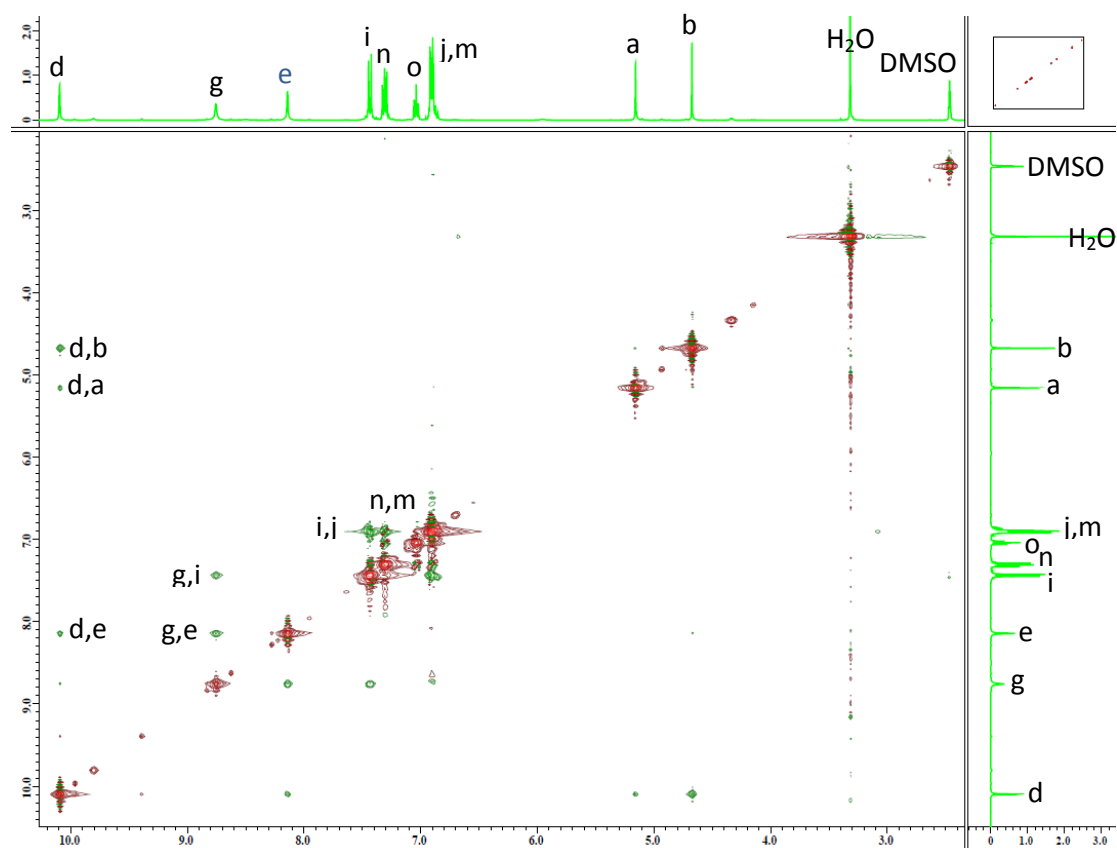


Figure 25. 2D ROESY NMR spectrum of compound (15) (DMSO- $d_6$ ).

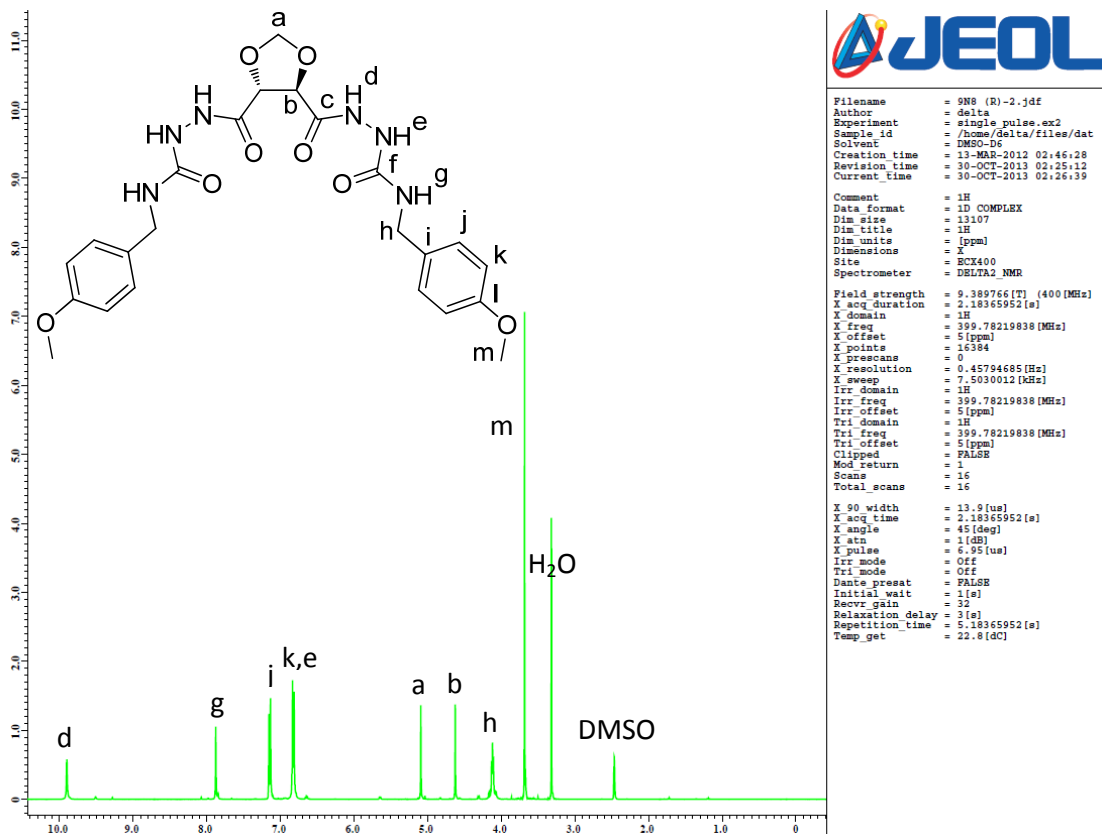
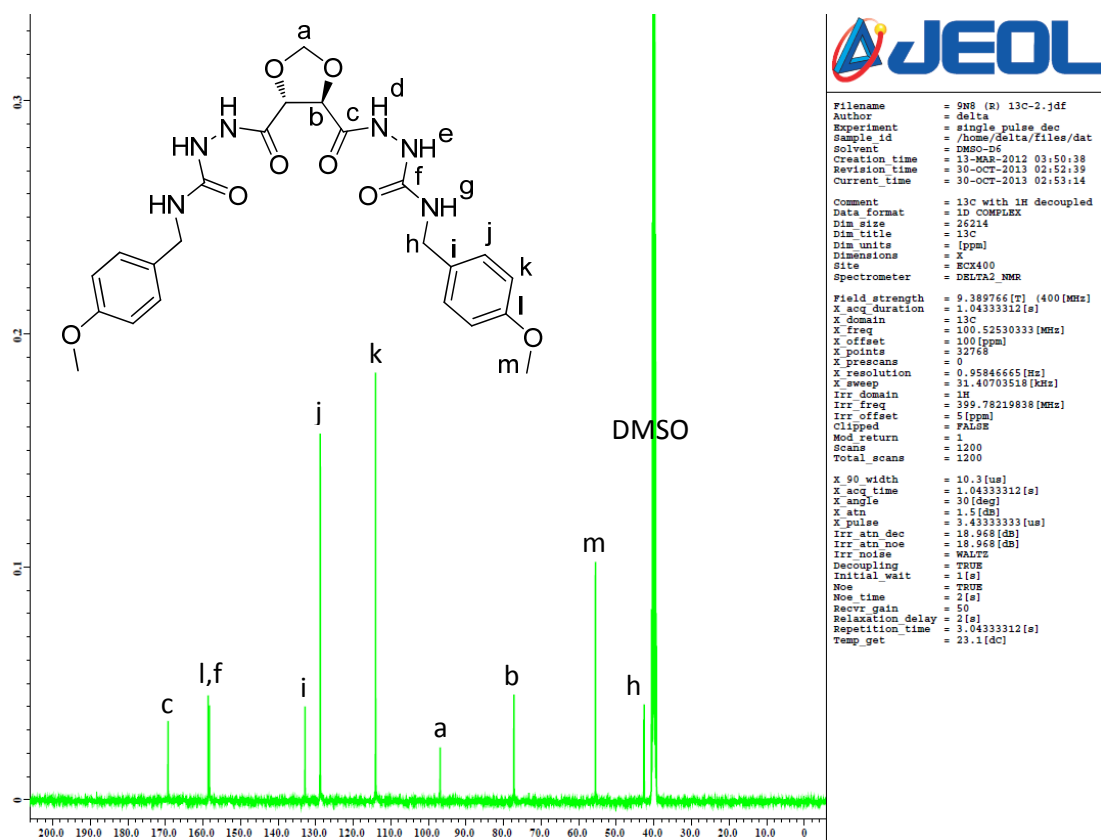
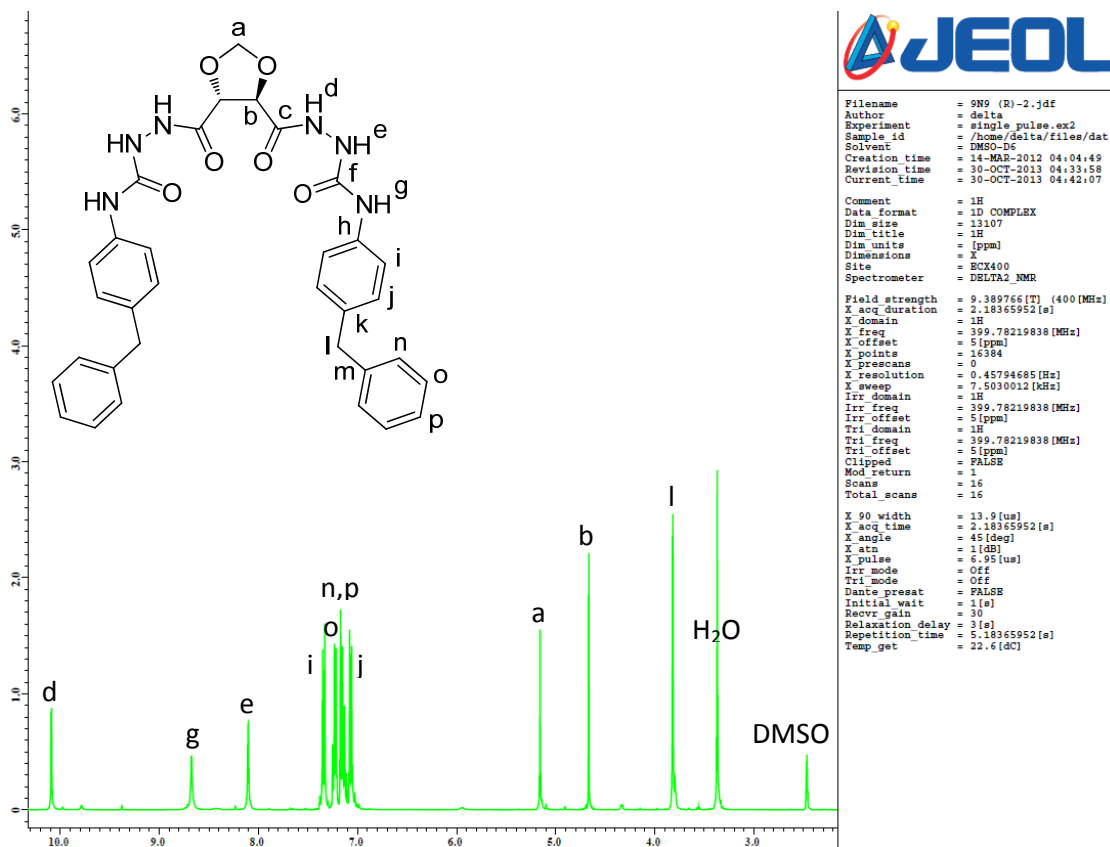


Figure 26.  $^1\text{H}$  NMR spectrum of compound (16) (400 MHz, DMSO- $d_6$ ).



**Figure 27.**  $^{13}\text{C}$  NMR spectrum of compound (16) (100 MHz,  $\text{DMSO-}d_6$ ).



**Figure 28.**  $^1\text{H}$  NMR spectrum of compound (17) (400 MHz,  $\text{DMSO-}d_6$ ).

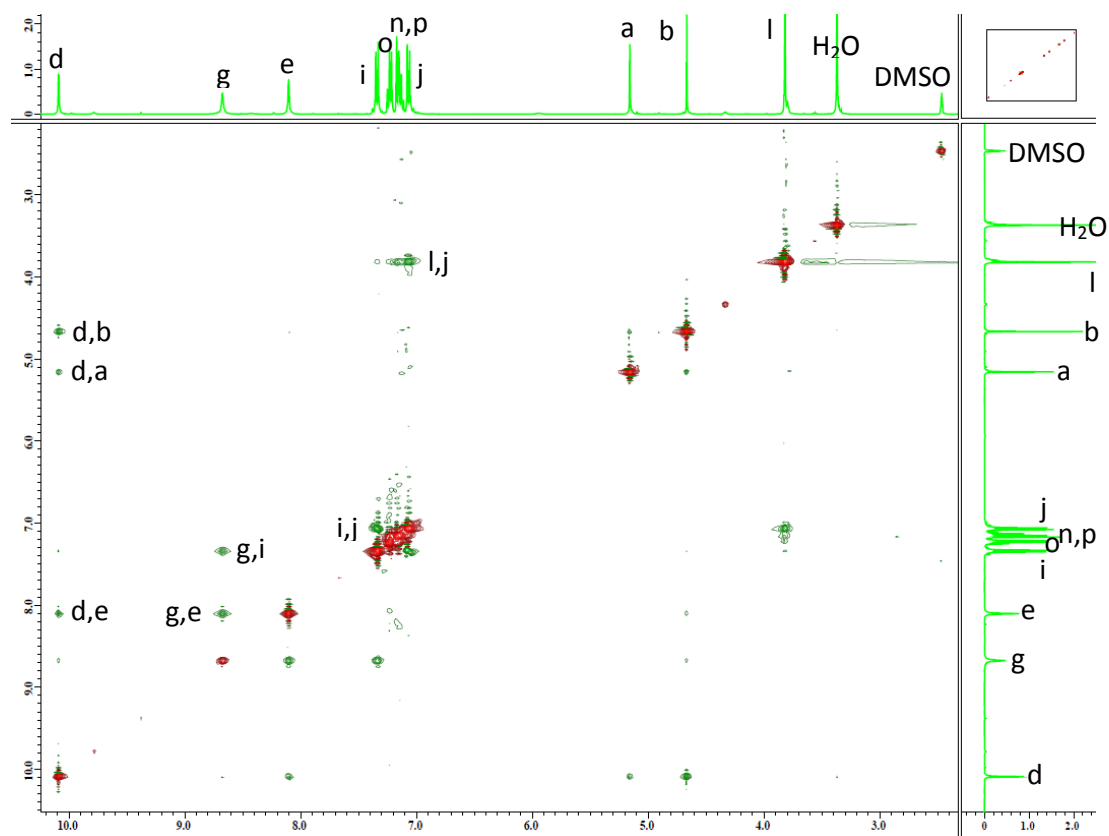


Figure 29. 2D ROESY NMR spectrum of compound (17) ( $\text{DMSO-}d_6$ ).

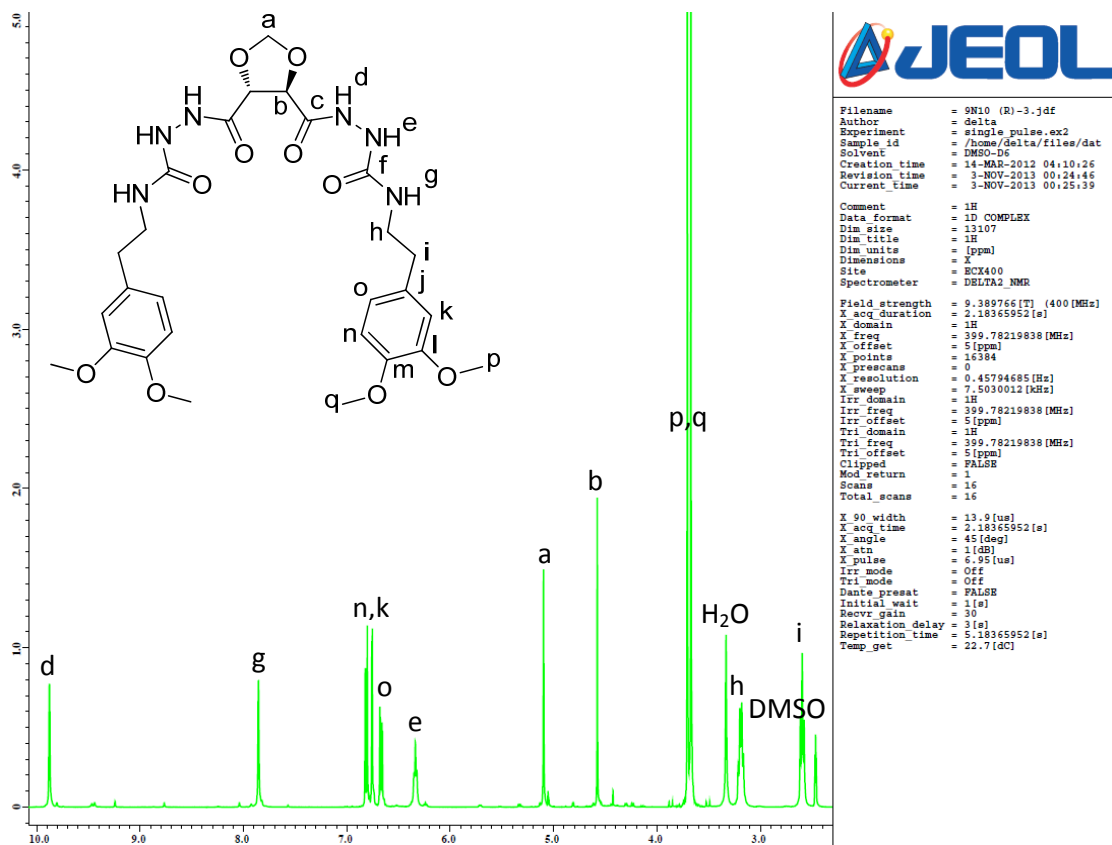


Figure 30.  $^1\text{H}$  NMR spectrum of compound (18) (400 MHz,  $\text{DMSO-}d_6$ ).

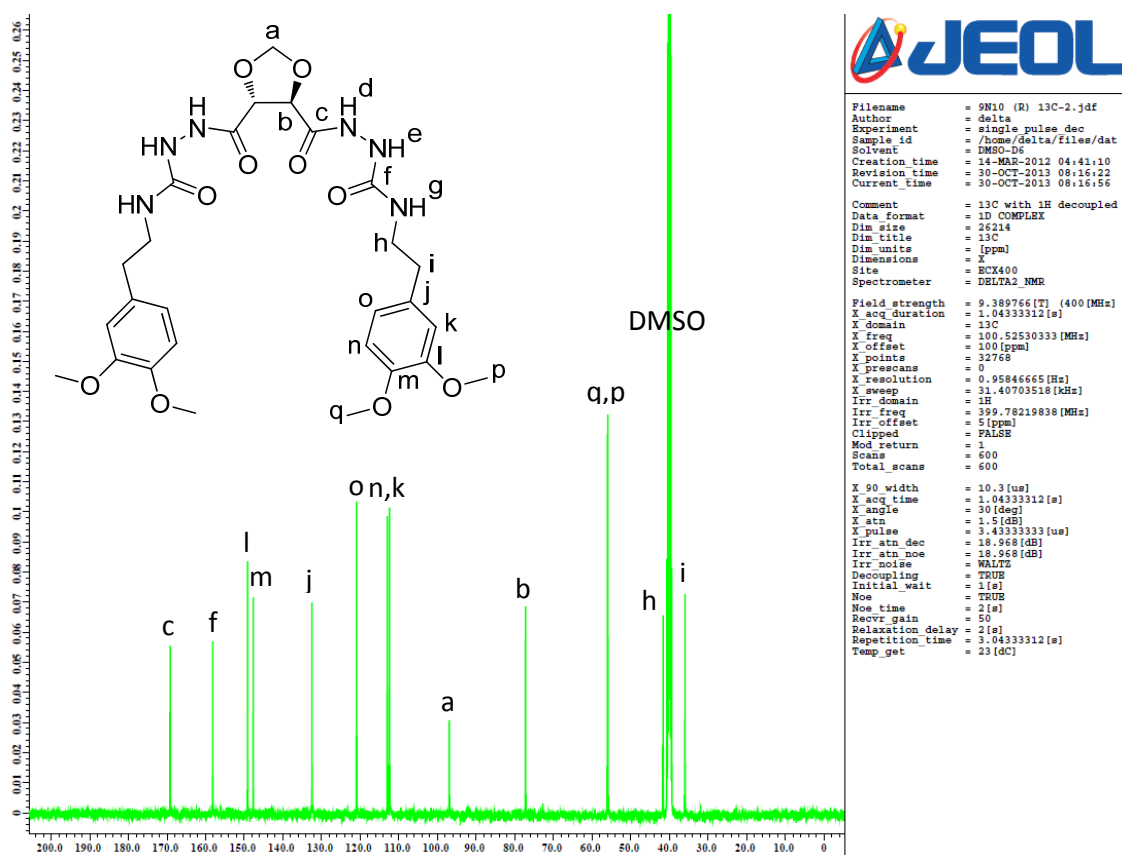


Figure 31.  $^{13}\text{C}$  NMR spectrum of compound (18) (100 MHz,  $\text{DMSO-}d_6$ ).

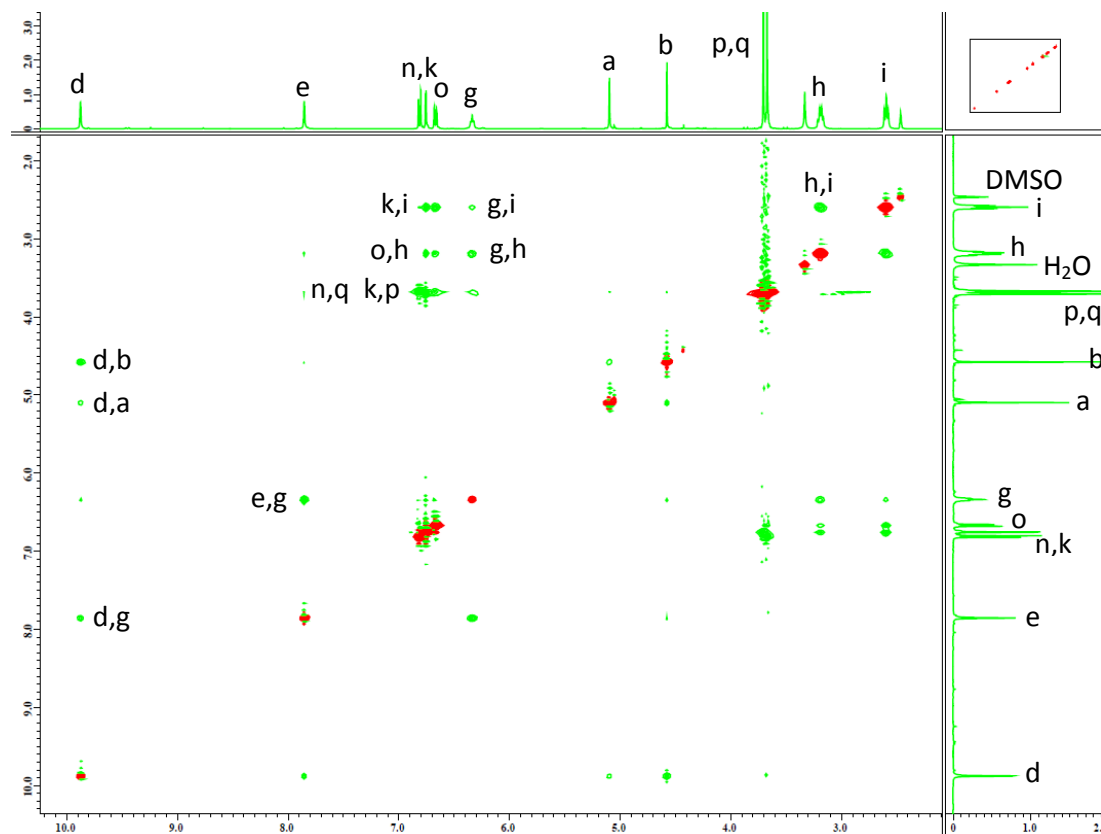


Figure 32. 2D ROESY NMR spectrum of compound (18) ( $\text{DMSO-}d_6$ ).

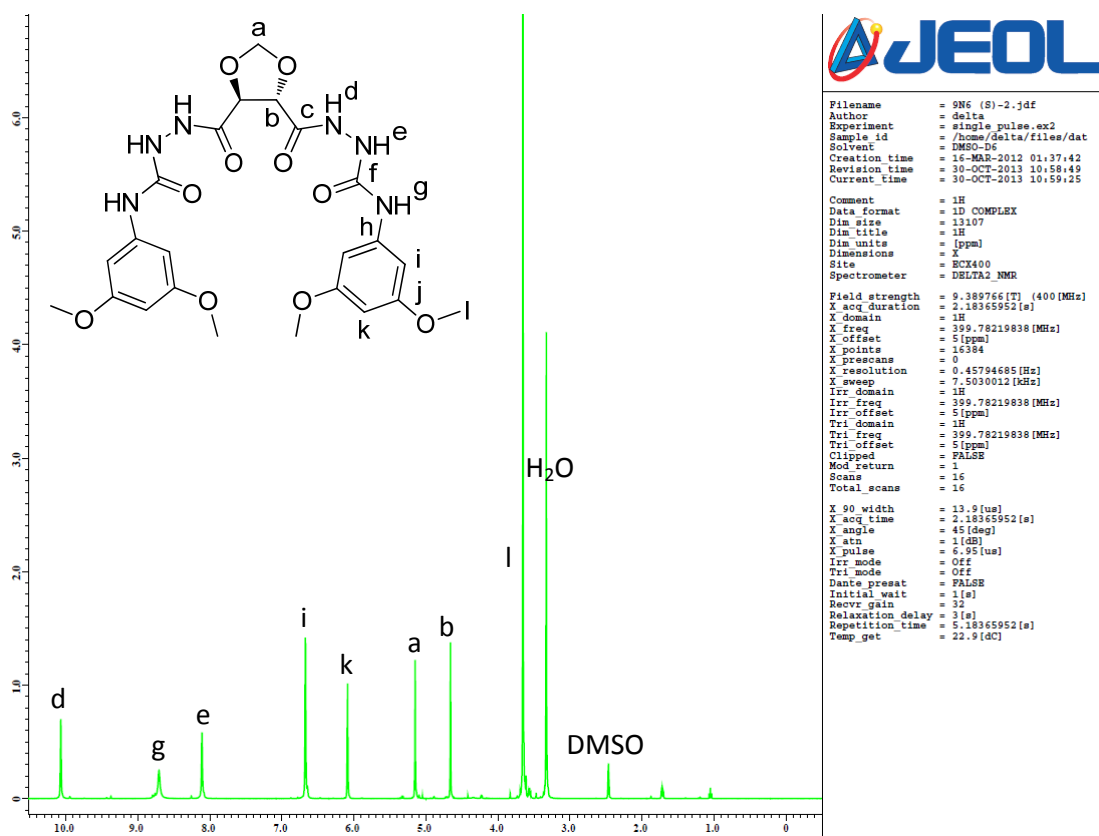


Figure 33. <sup>1</sup>H NMR spectrum of compound (19) (400 MHz, DMSO-*d*<sub>6</sub>).

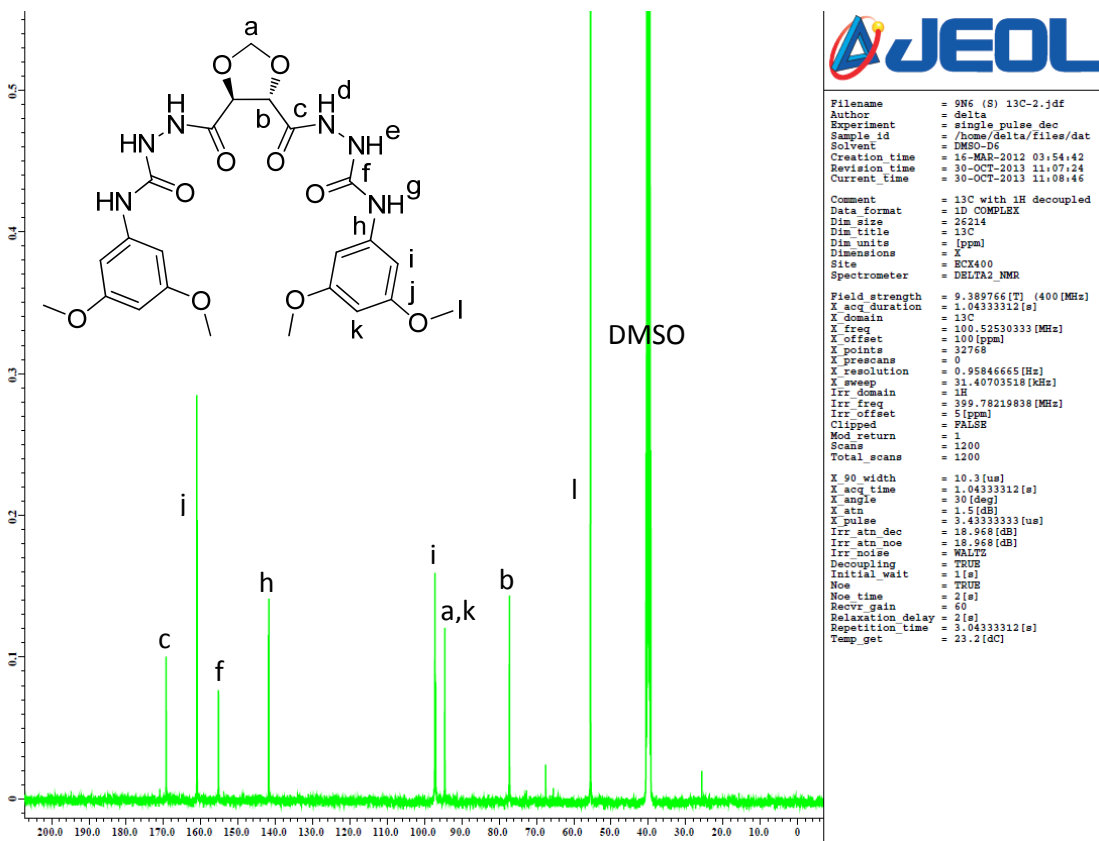


Figure 34. <sup>13</sup>C NMR spectrum of compound (19) (100 MHz, DMSO-*d*<sub>6</sub>).

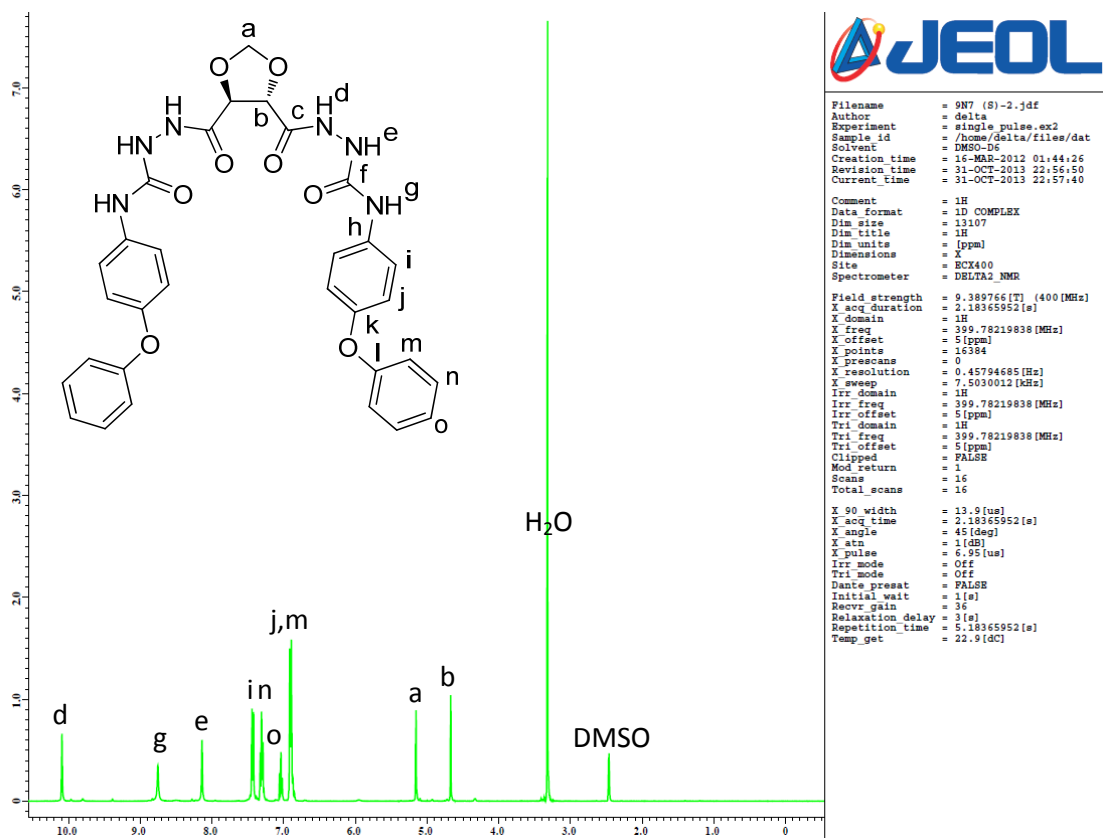


Figure 35.  $^1\text{H}$  NMR spectrum of compound (20) (400 MHz,  $\text{DMSO}-d_6$ ).

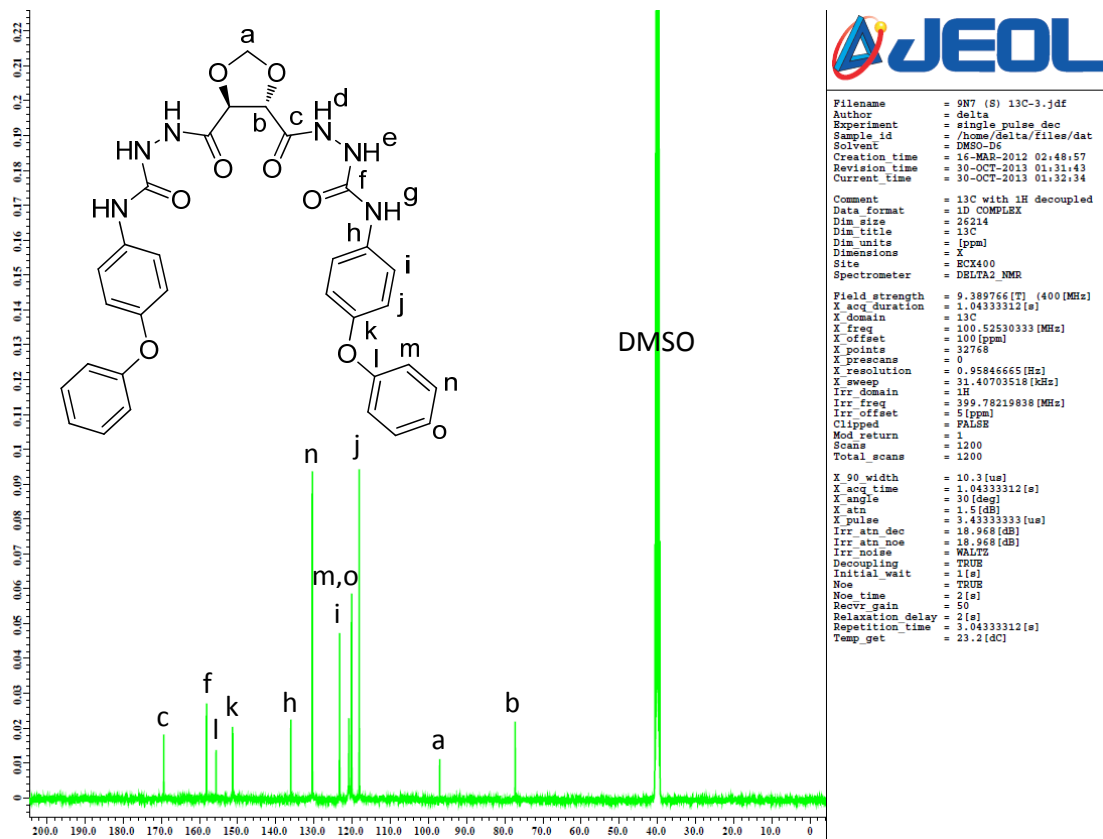


Figure 36.  $^{13}\text{C}$  NMR spectrum of compound (20) (100 MHz,  $\text{DMSO}-d_6$ ).

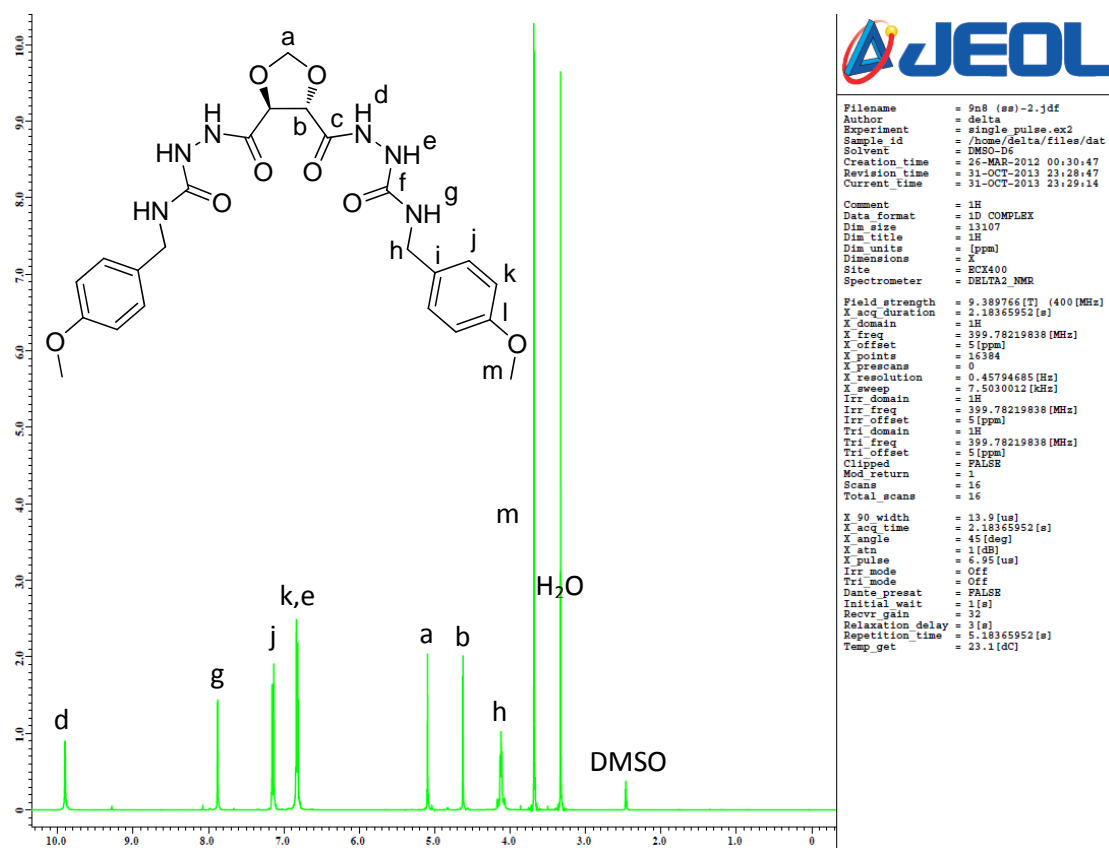


Figure 37.  $^1\text{H}$  NMR spectrum of compound (21) (400 MHz,  $\text{DMSO}-d_6$ ).

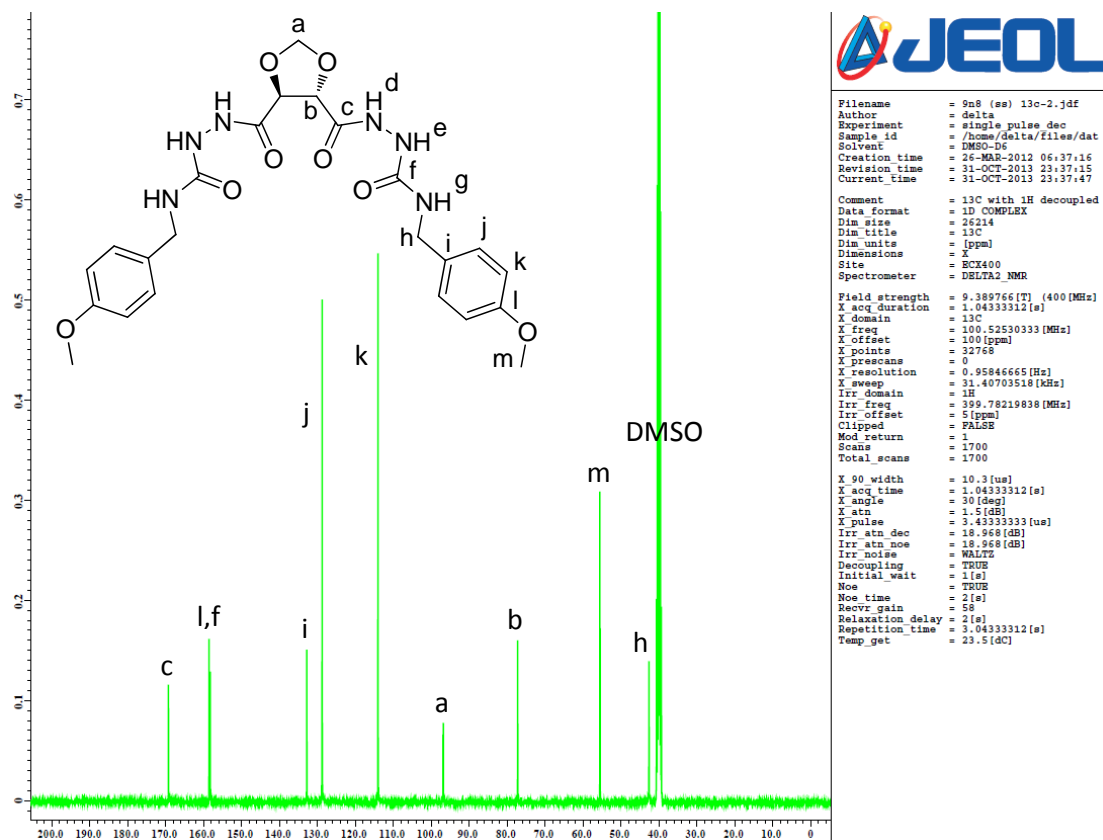
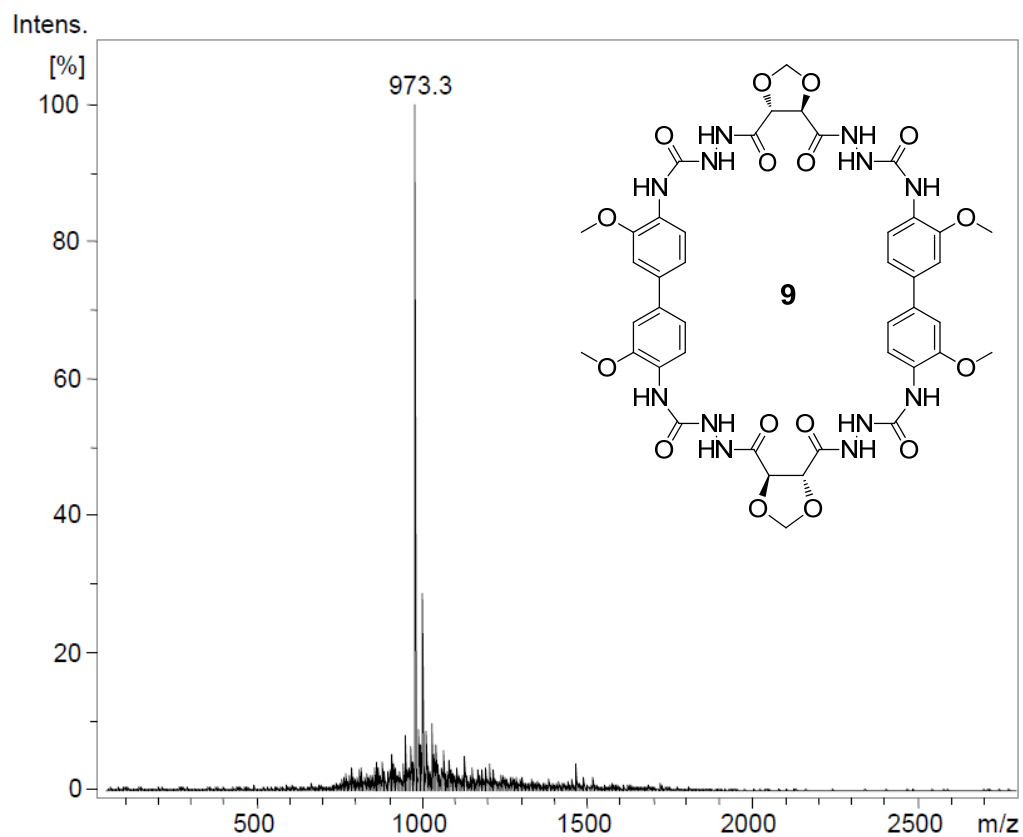
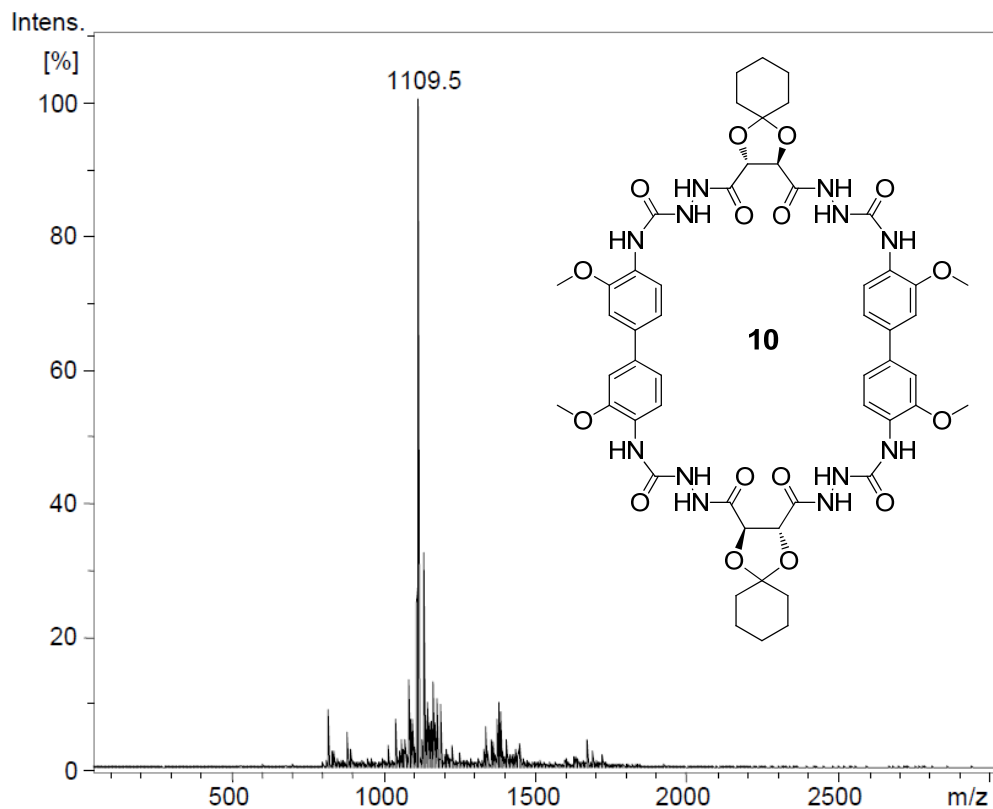


Figure 38.  $^{13}\text{C}$  NMR spectrum of compound (21) (100 MHz,  $\text{DMSO}-d_6$ ).

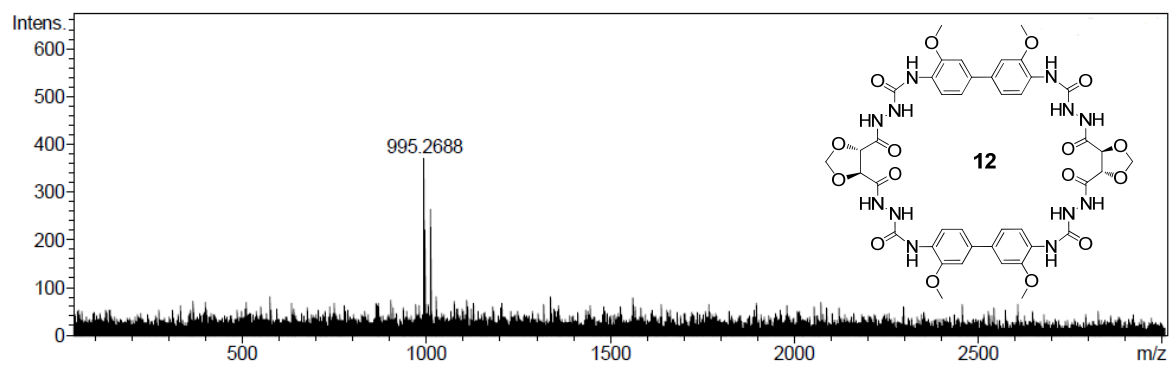


**Figure 39.** ESI-TOF MS of macrocycle (**9**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+H]<sup>+</sup>).

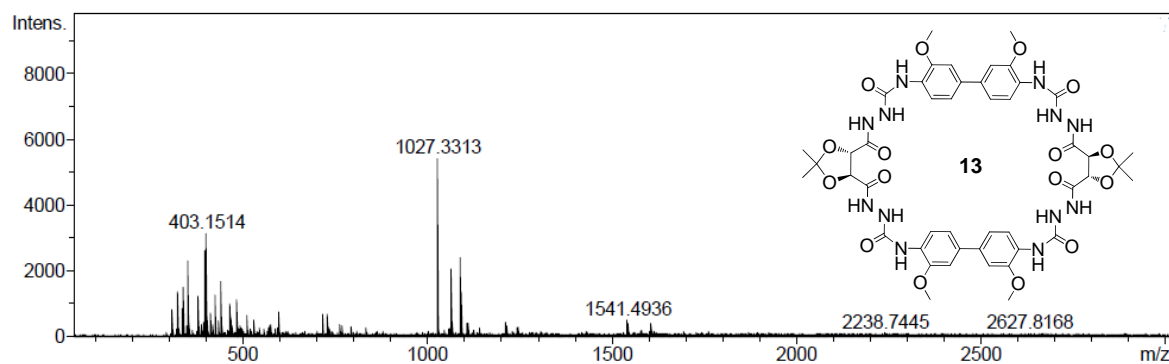


**Figure 40.** ESI-TOF MS of macrocycle (**10**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+H]<sup>+</sup>).

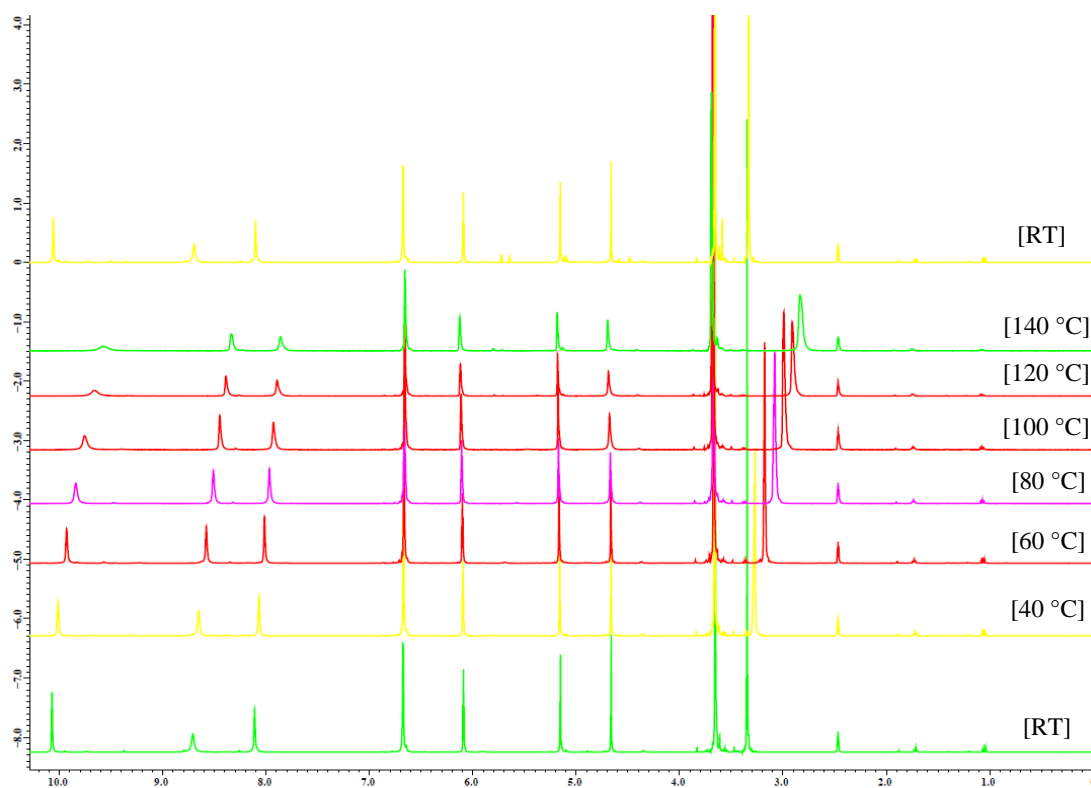




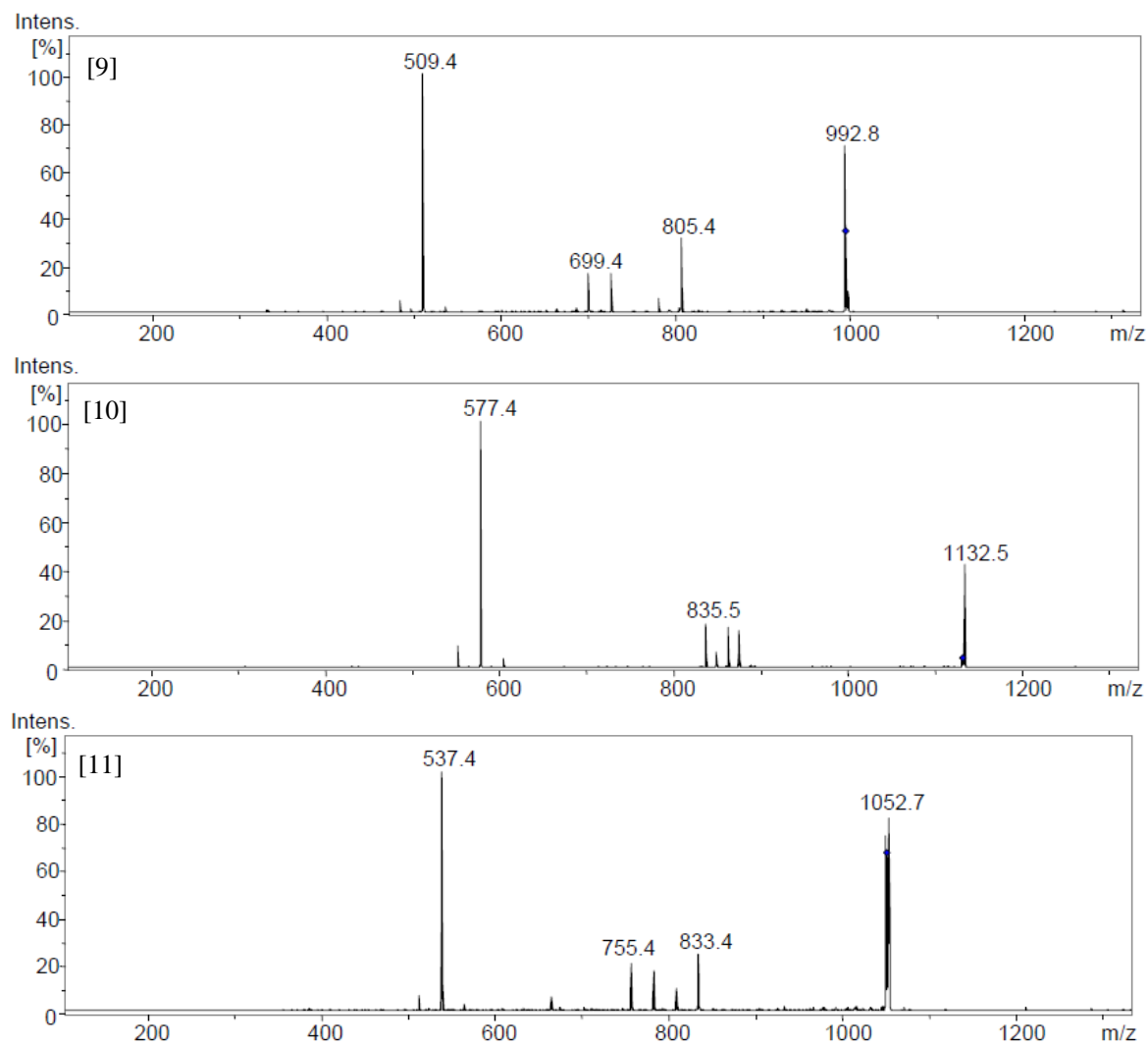
**Figure 41.** ESI-TOF MS of macrocycle (12) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+Na]<sup>+</sup>).



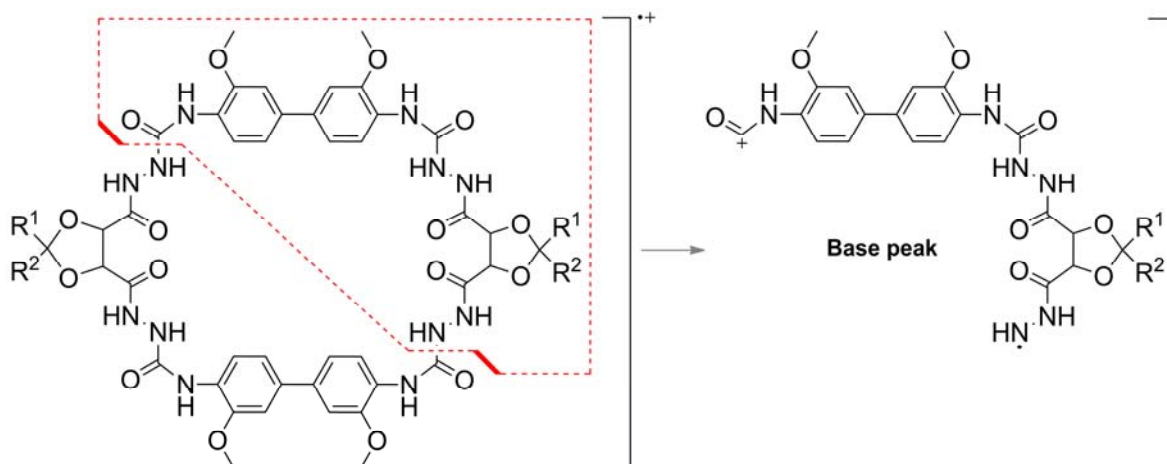
**Figure 42.** ESI-TOF MS of macrocycle (13) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



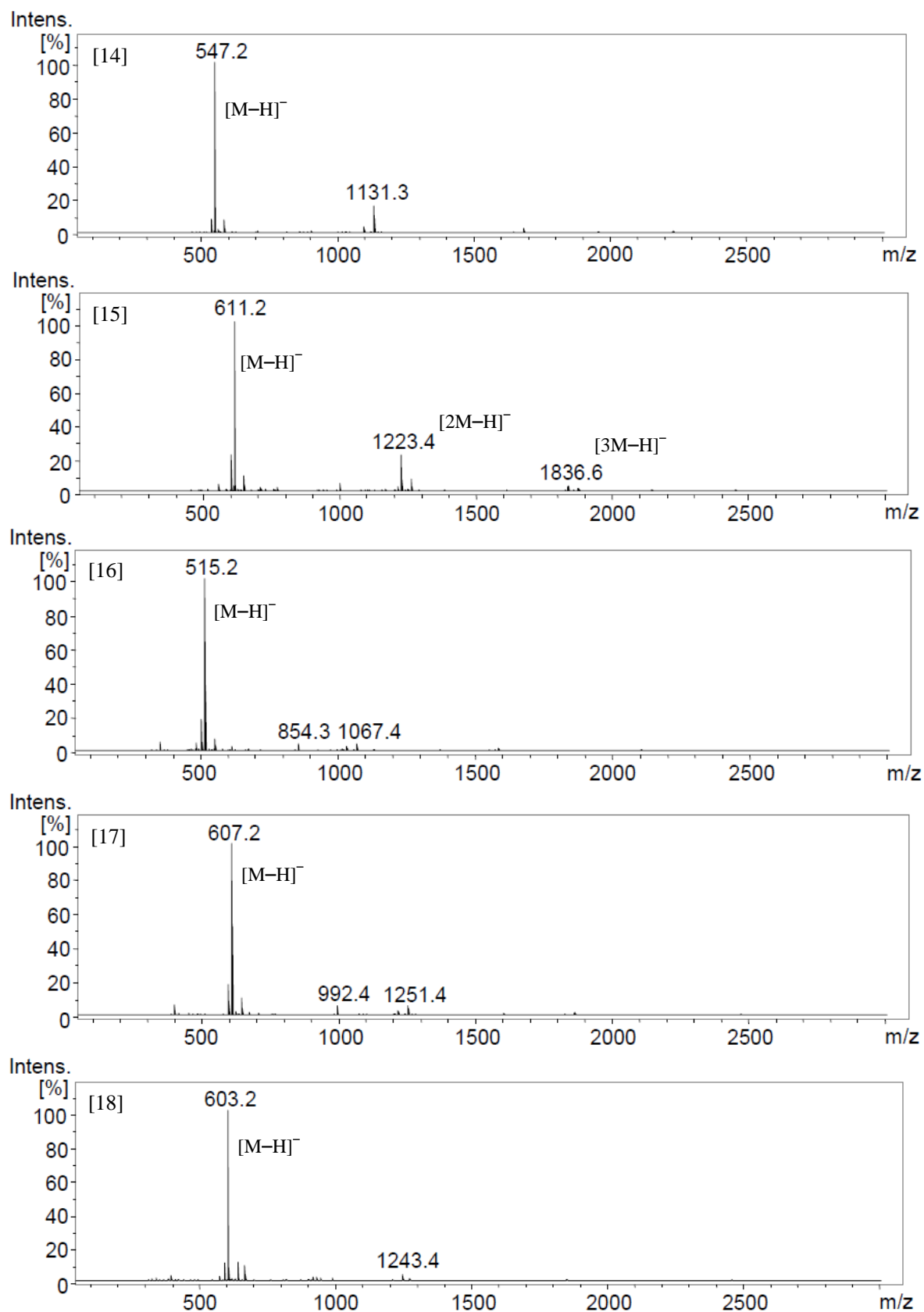
**Figure 43.** Stacked VT-NMR spectra of compound (14) (400 MHz, DMSO-*d*<sub>6</sub>).



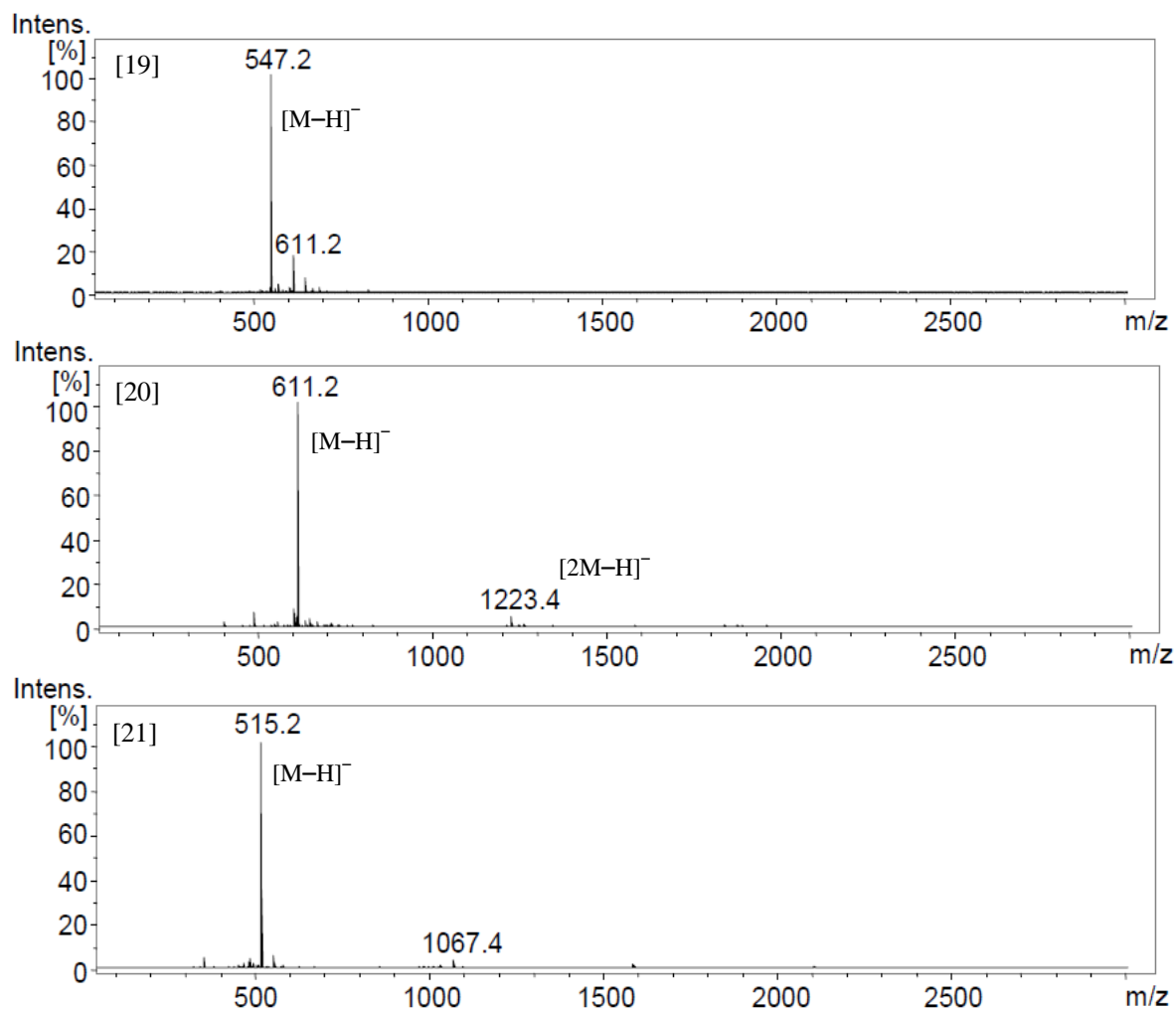
**Figure 44.** ESI-MS/MS of macrocycles (**9-11**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+Na]<sup>+</sup>).



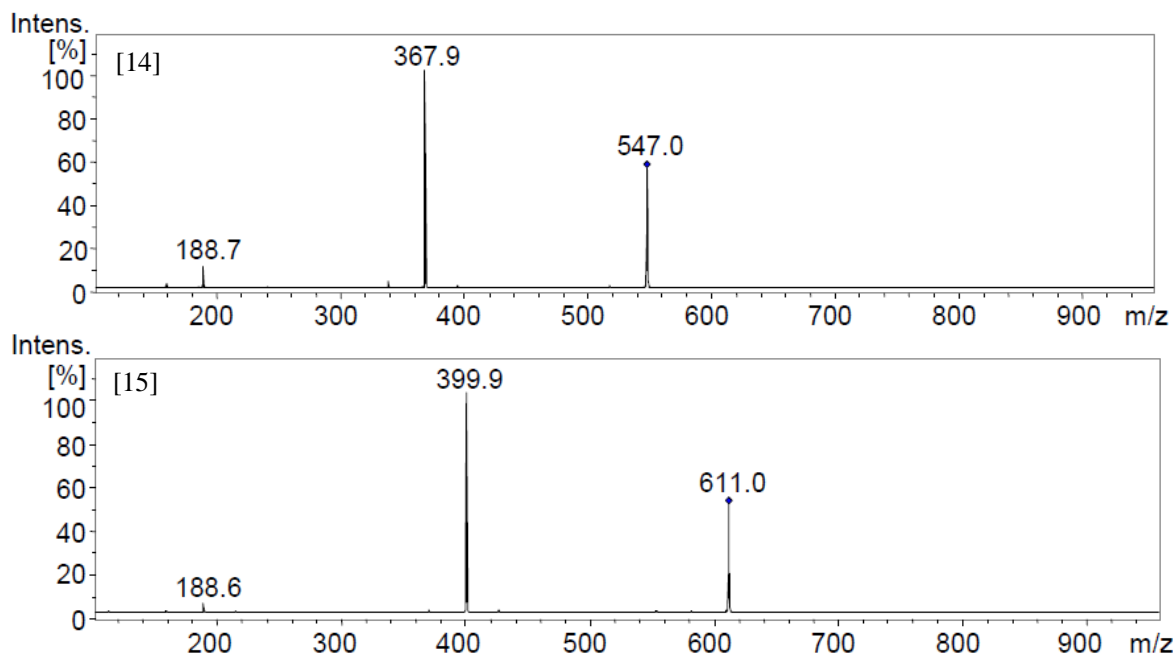
**Figure 45.** Proposed fragmentation mechanism of macrocycles (**9-13**).



**Figure 46.** ESI-TOF MS of compounds (14-18) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



**Figure 47.** ESI-TOF MS of compounds (**19-21**) (DMF/CH<sub>3</sub>CN, negative ion mode,  $[M-H]^-$ ).



**Figure 48.** ESI-MS/MS of compounds (**14** and **15**) (DMF/CH<sub>3</sub>CN, negative ion mode,  $[M-H]^-$ ).

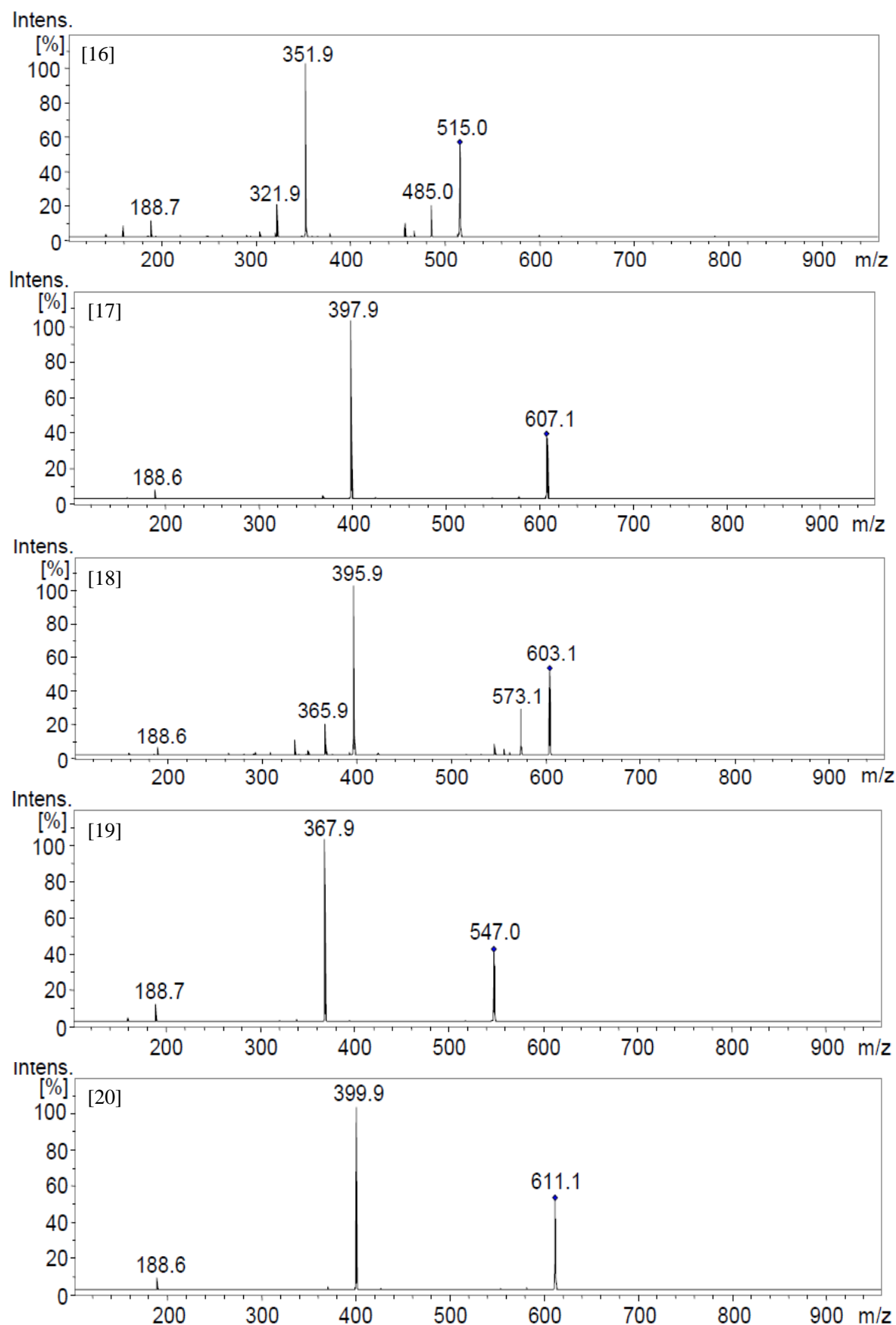


Figure 49. ESI-MS/MS of compounds (16-20) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]).

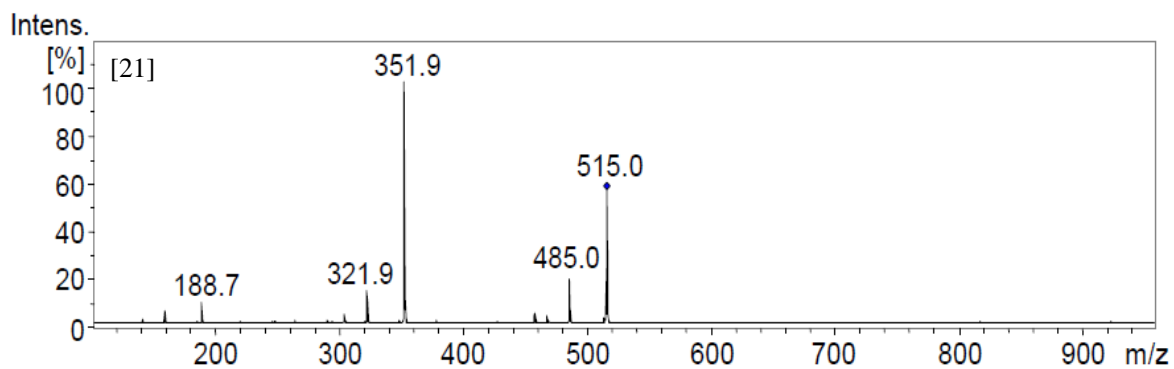


Figure 50. ESI-MS/MS of compounds (21) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).

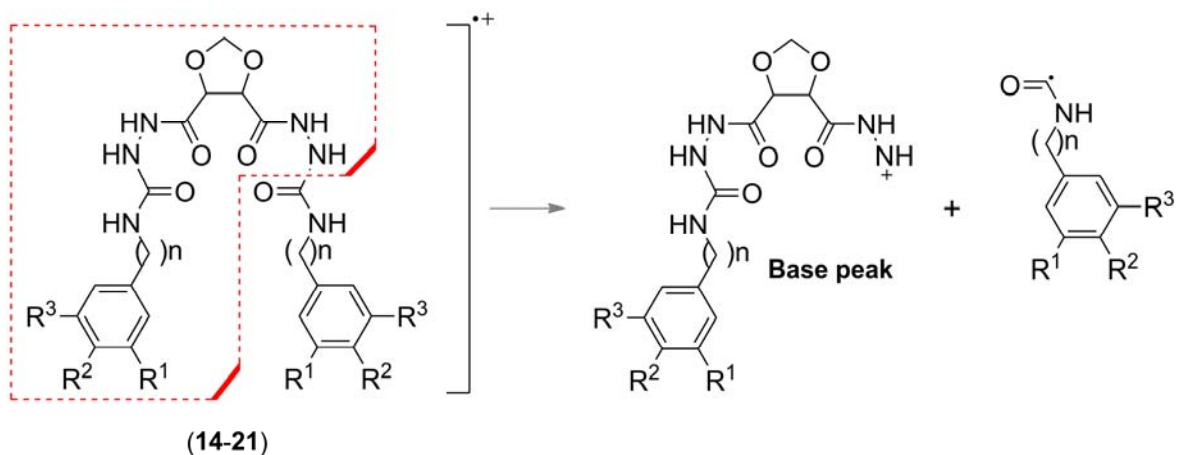


Figure 51. Proposed fragmentation mechanism of compounds (14-21).

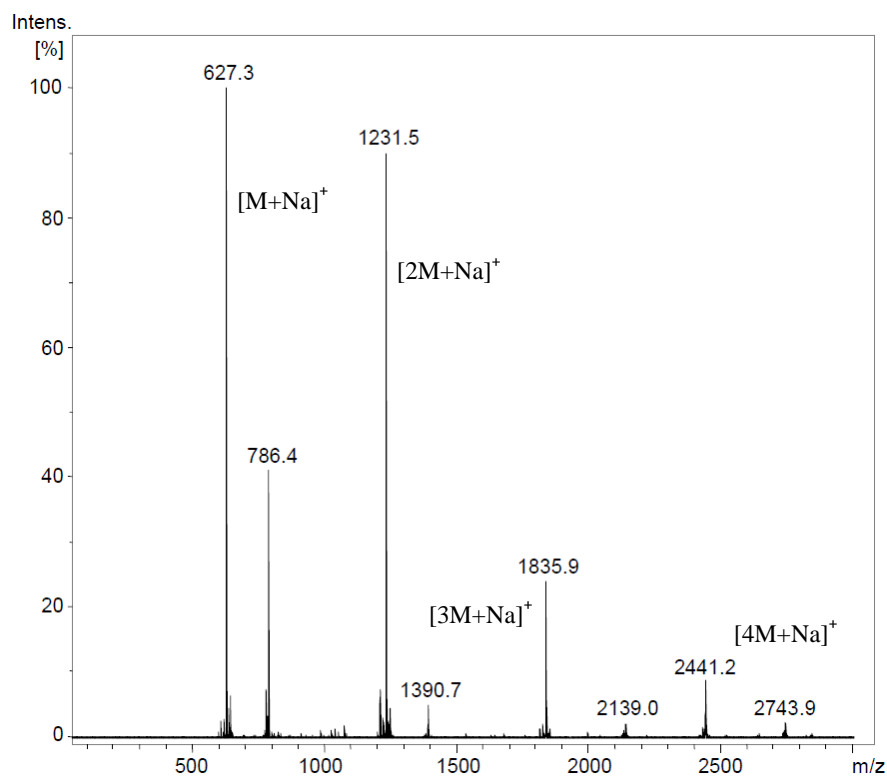


Figure 52. ESI-TOF MS for self-assembled associations of compound (18) (CH<sub>3</sub>CN/DMF).

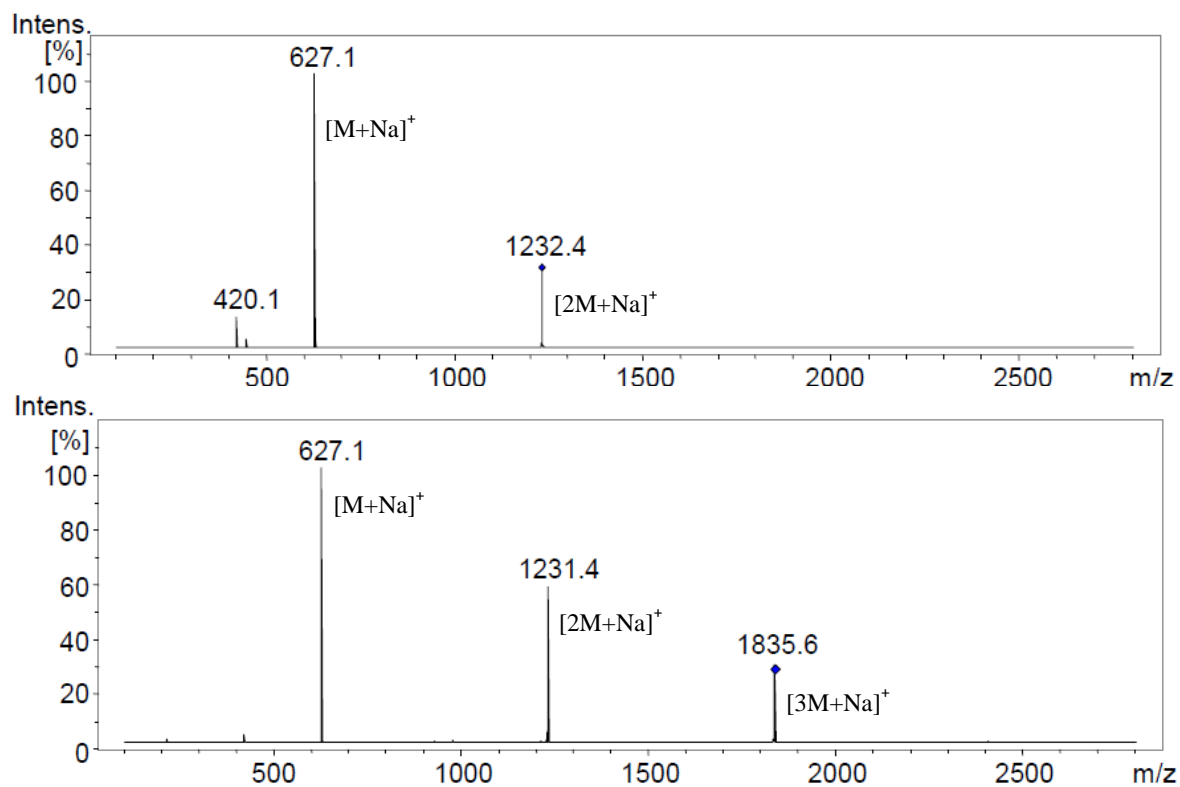


Figure 53. ESI-MS/MS of  $m/z$  1231.5 and 1835.9 (DMF/CH<sub>3</sub>CN, positive ion mode,  $[M+Na]^+$ ).

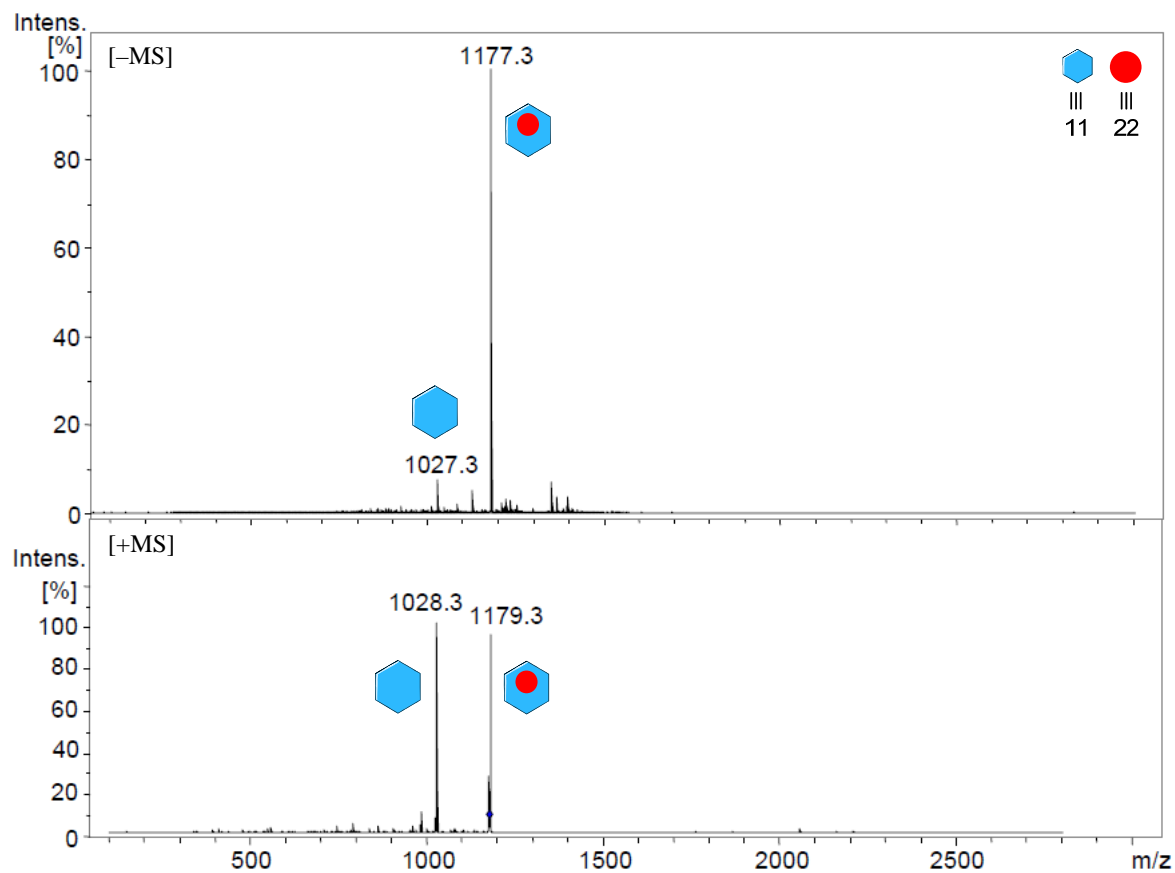


Figure 54. ESI-TOF MS and ESI-MS/MS of Ht/Gt complex 11/22 (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).

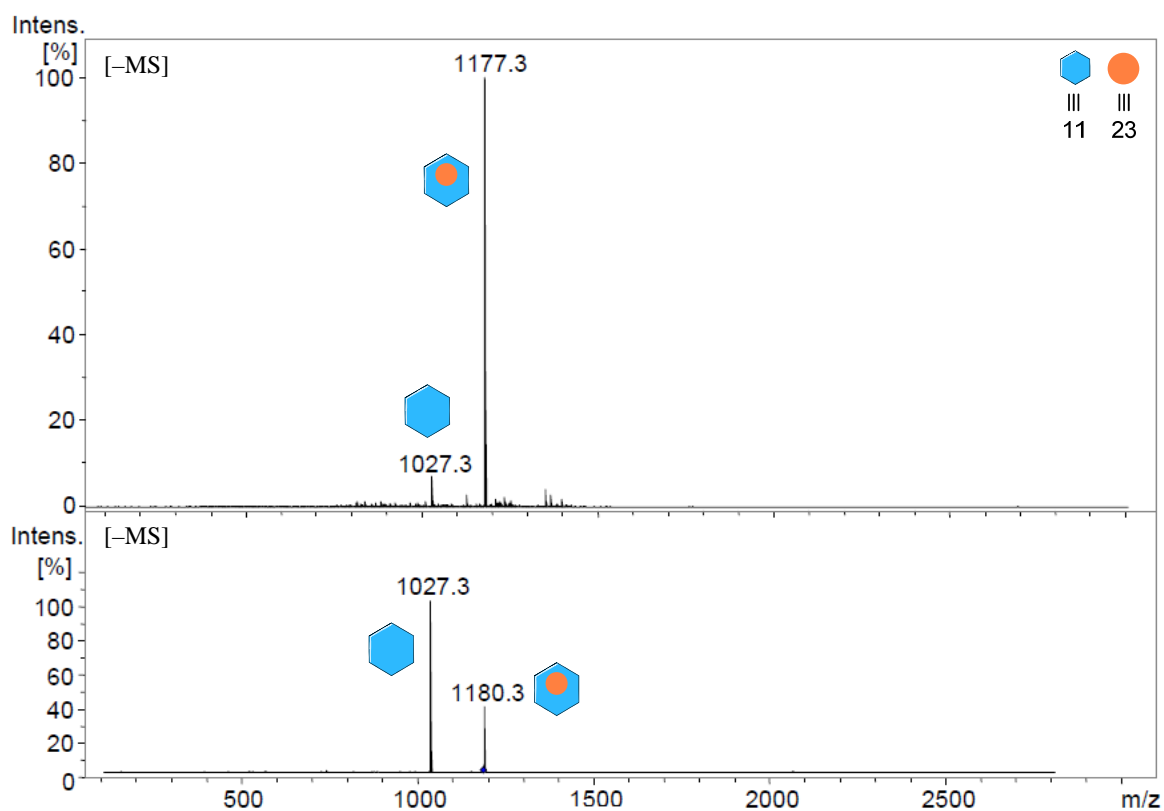


Figure 55. ESI-TOF MS and ESI-MS/MS of Ht/Gt complex 11/23 (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).

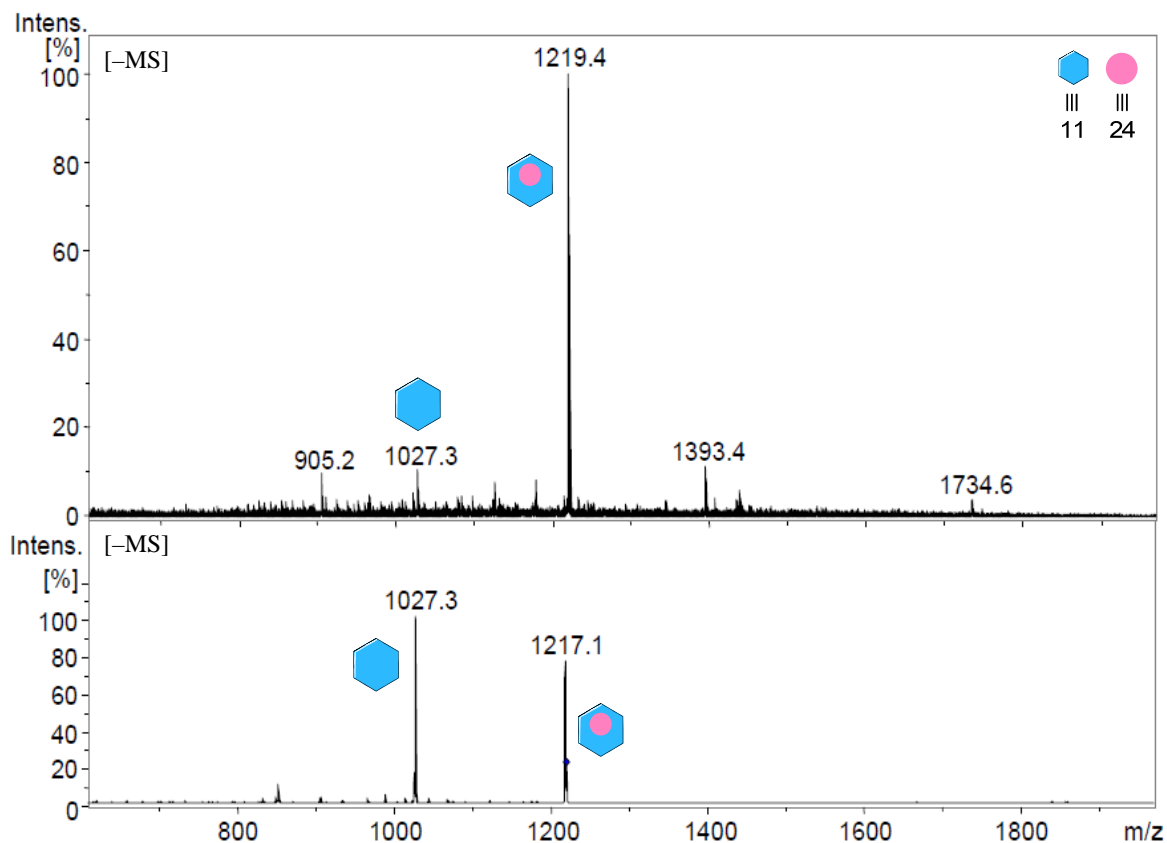
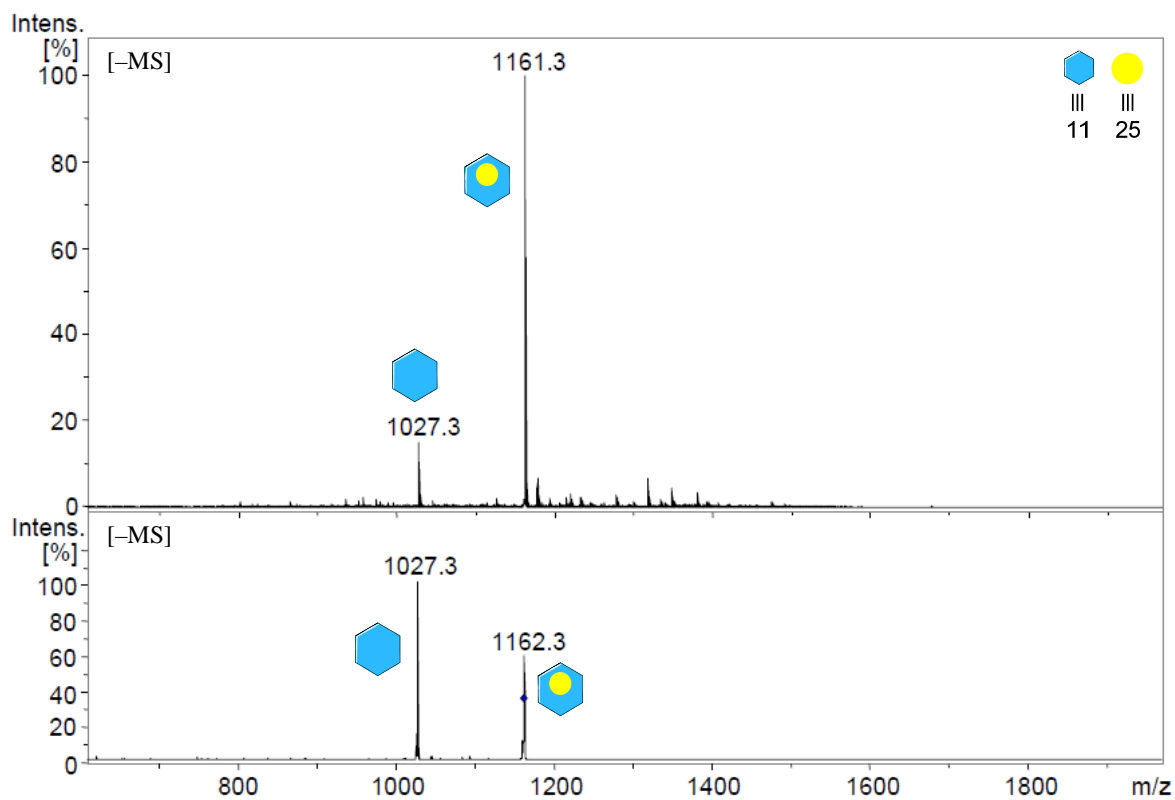
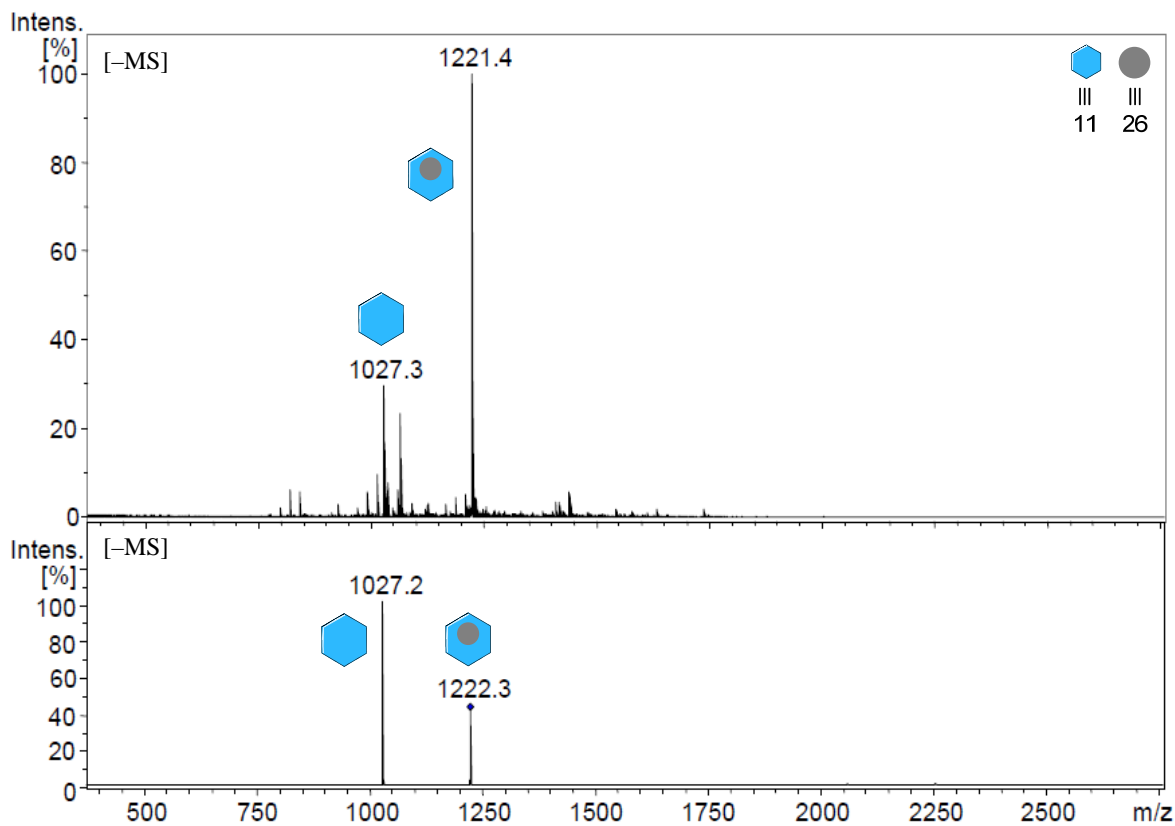


Figure 56. ESI-TOF MS and ESI-MS/MS of Ht/Gt complex 11/24 (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).

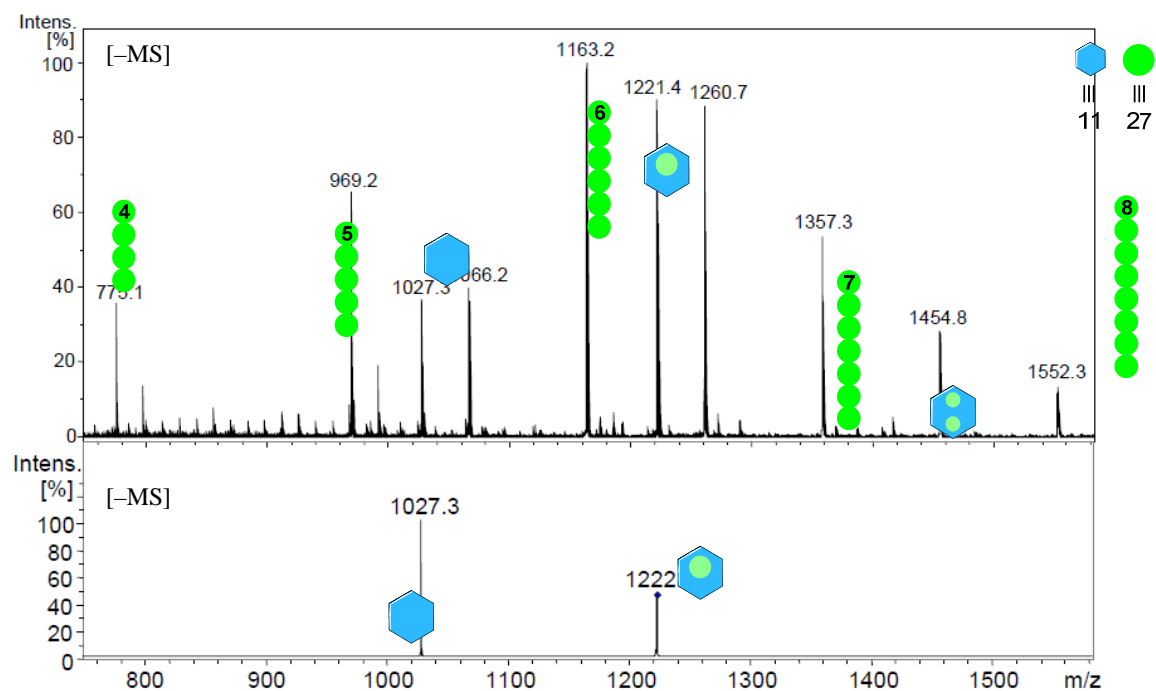




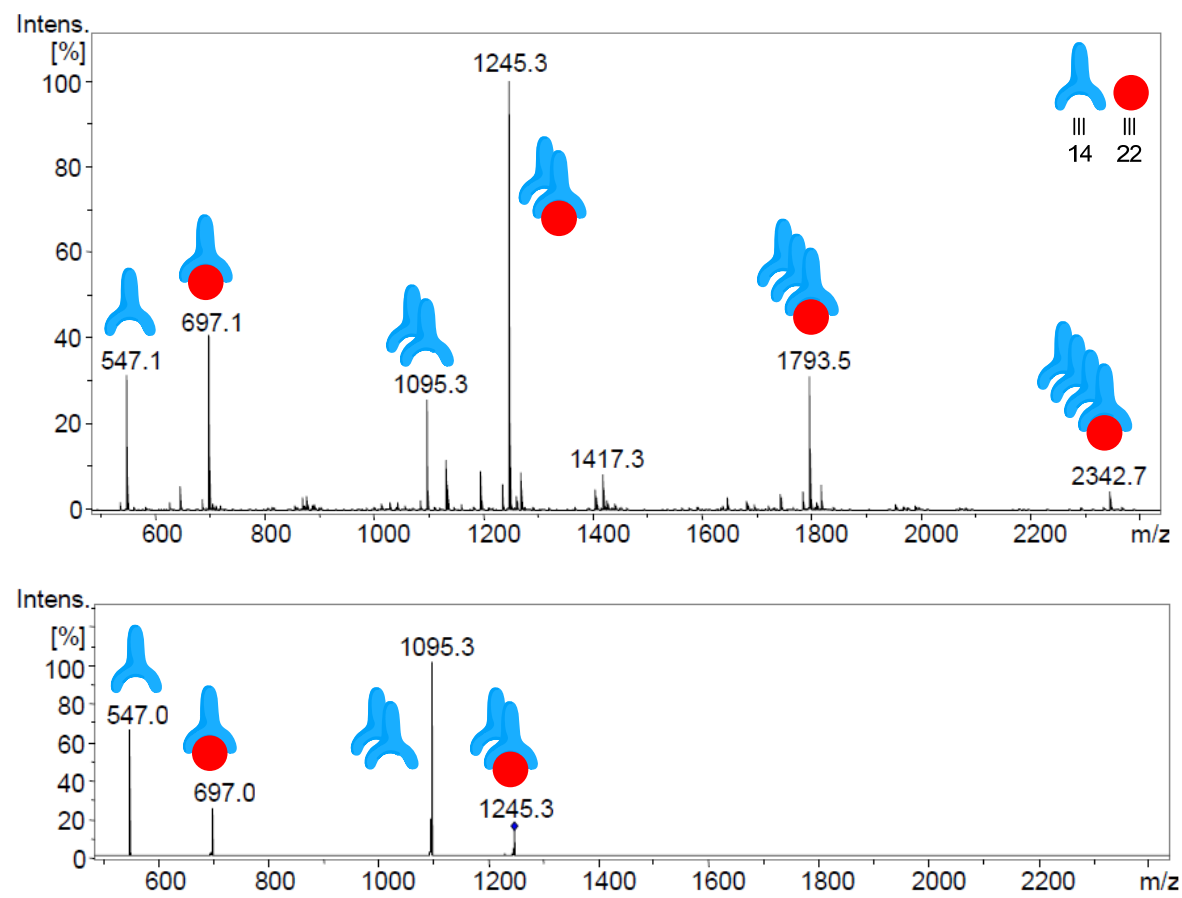
**Figure 57.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



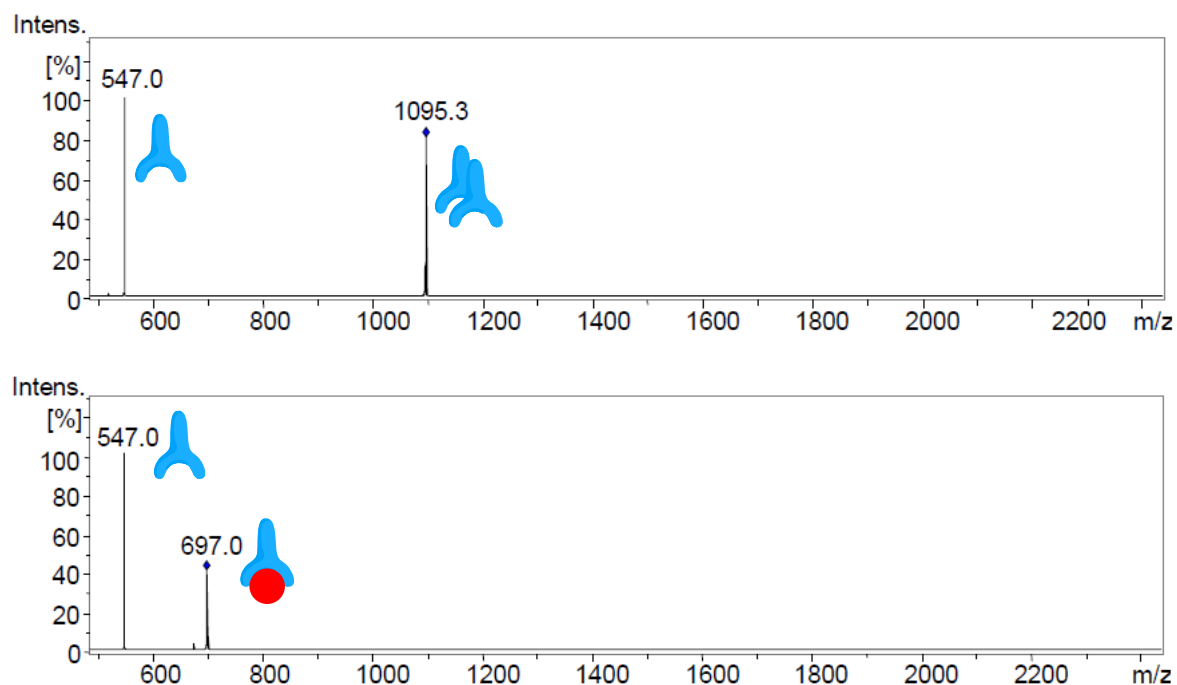
**Figure 58.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



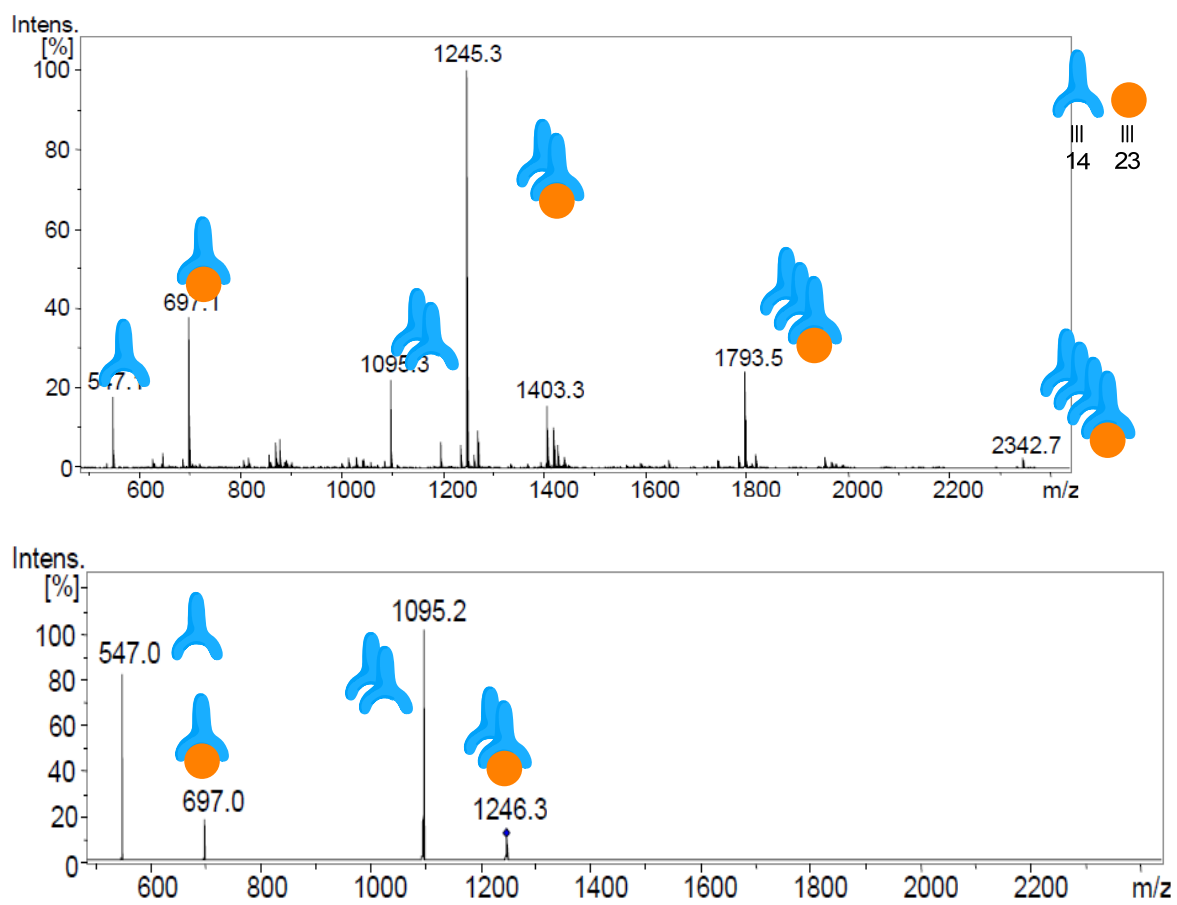
**Figure 59.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



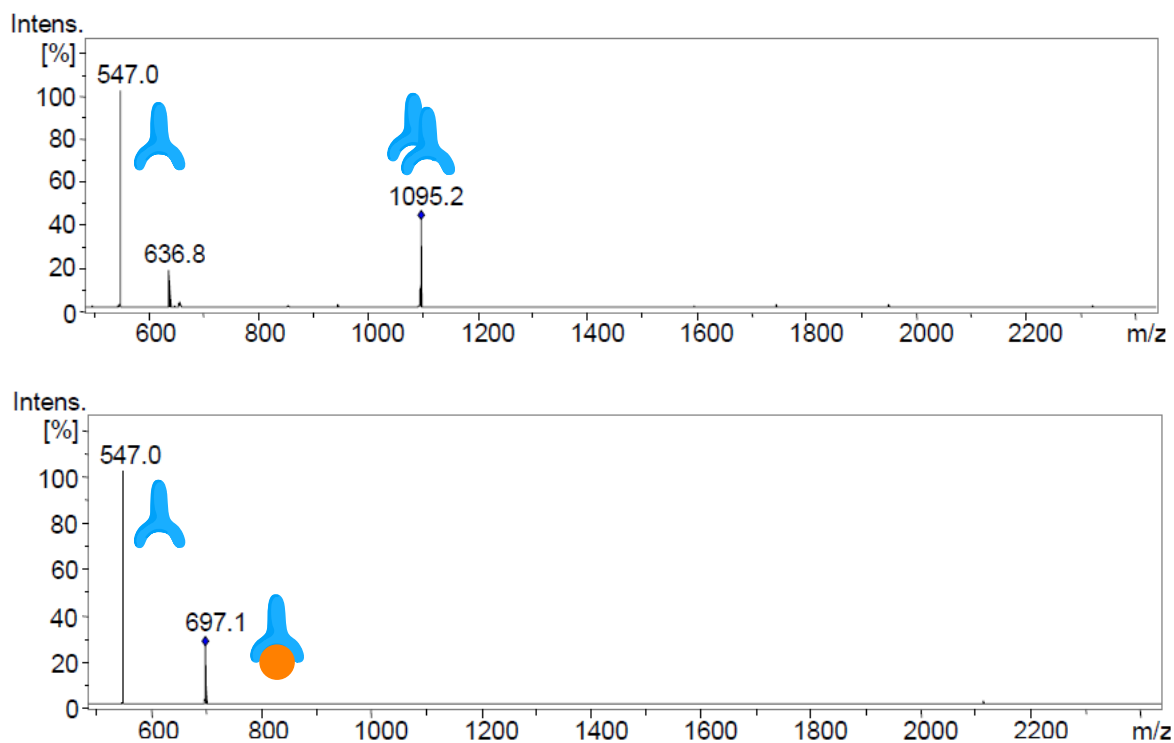
**Figure 60.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/22**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 1245.3.



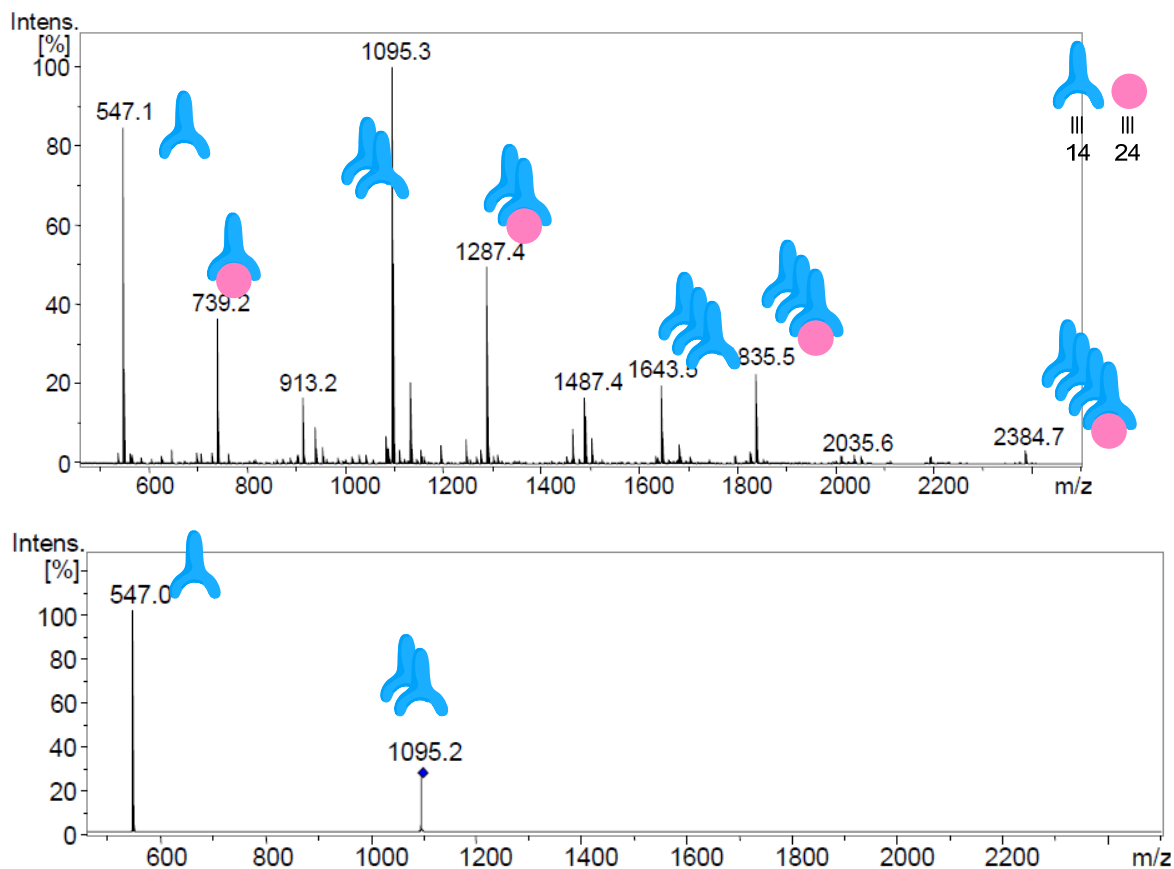
**Figure 61.** ESI-MS/MS of Ht/Gt complex **14/22** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1095.3 and 697.1).



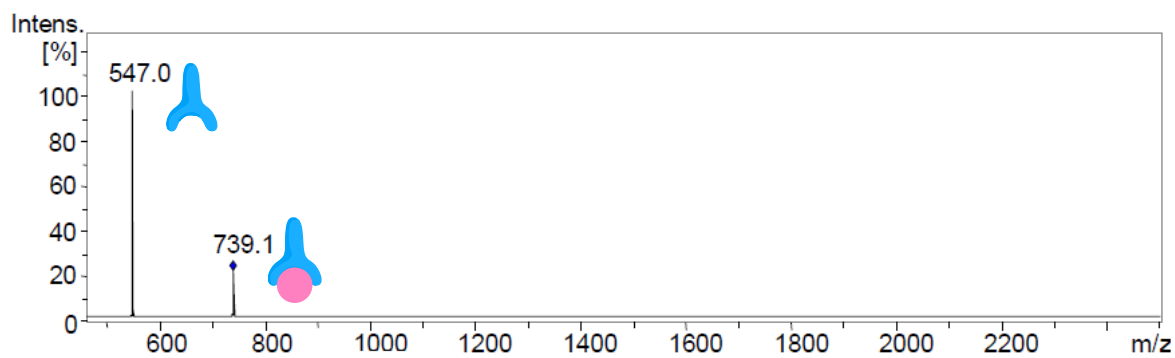
**Figure 62.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/23**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1245.3.



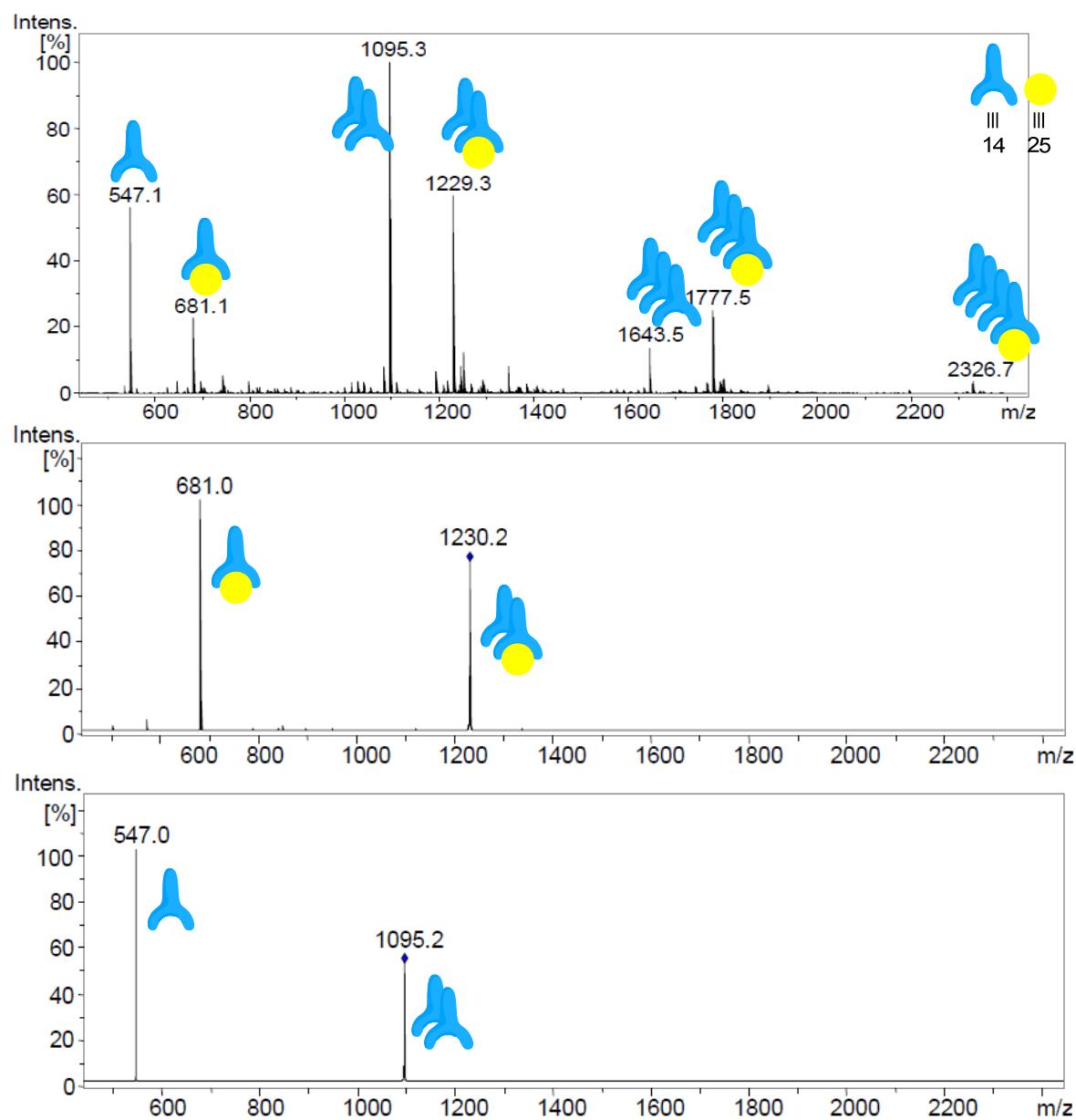
**Figure 63.** ESI-MS/MS of Ht/Gt complex **14/23** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 1095.3 and 697.1).



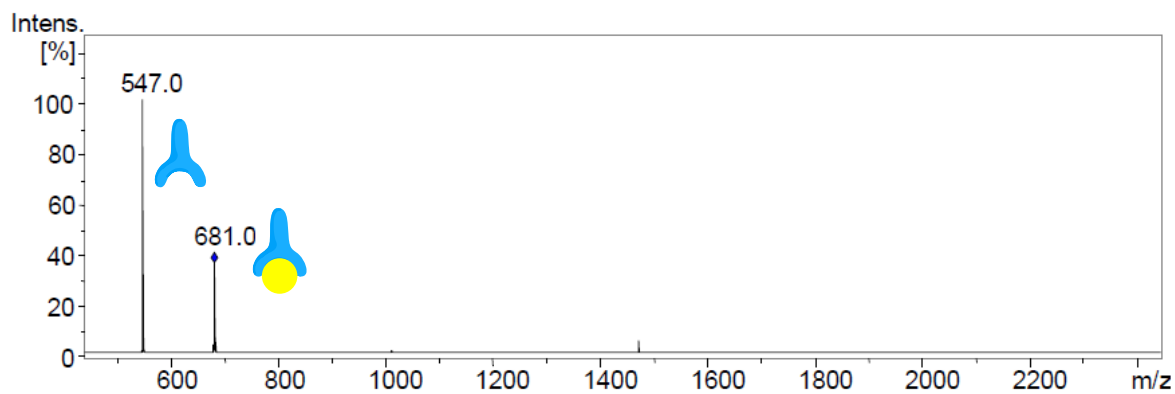
**Figure 64.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/24**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 1095.3.



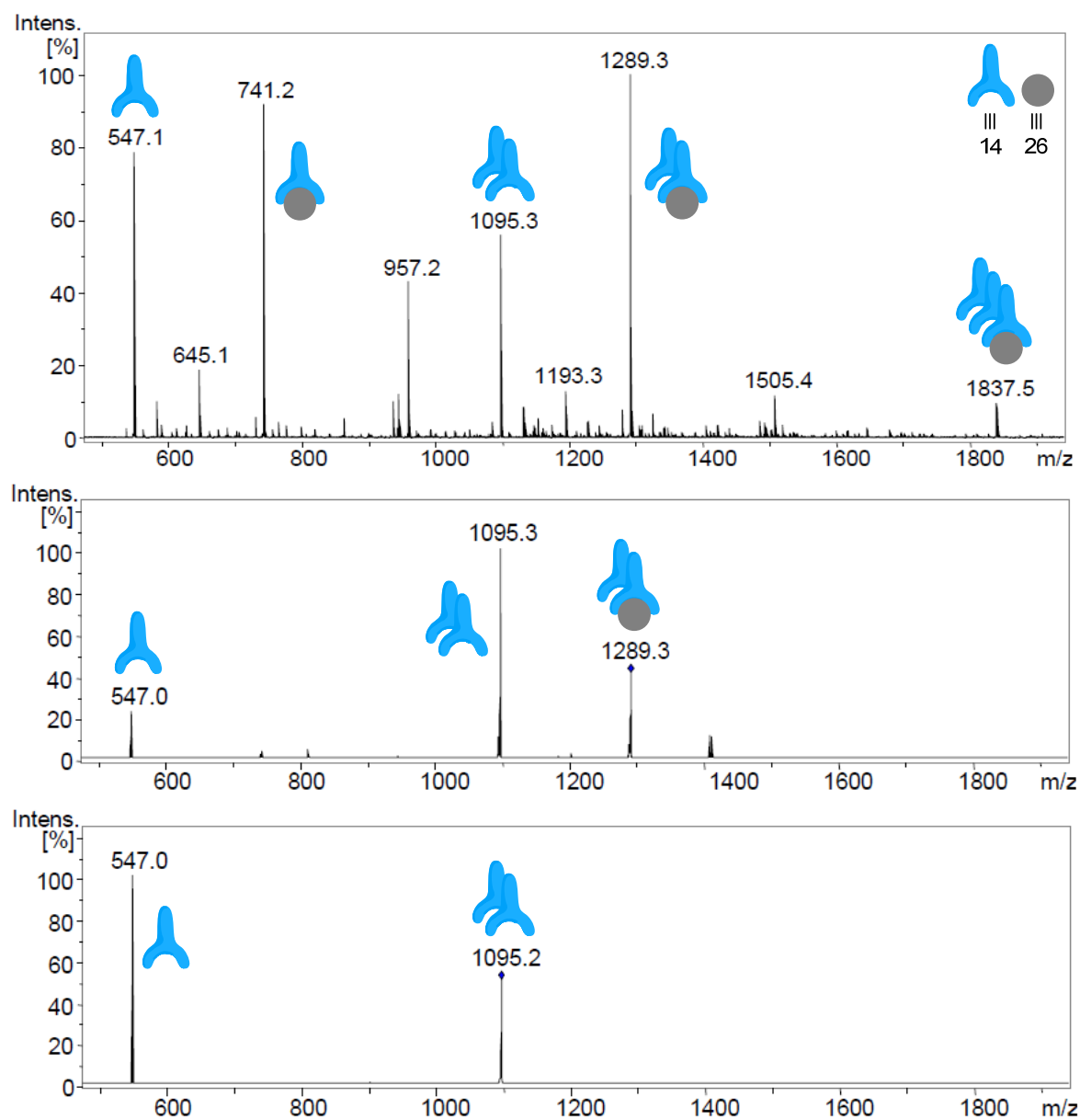
**Figure 65.** ESI-MS/MS of Ht/Gt complex **14/24** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 739.2).



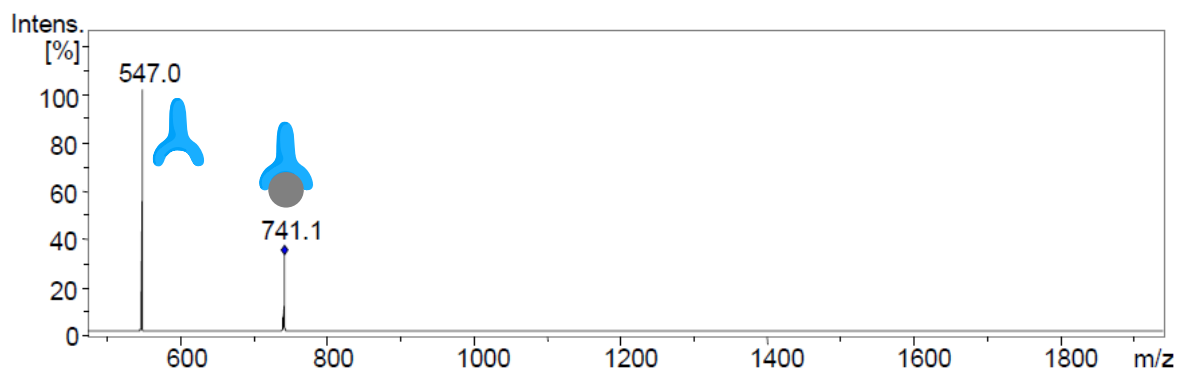
**Figure 66.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 1229.3 and 1095.3).



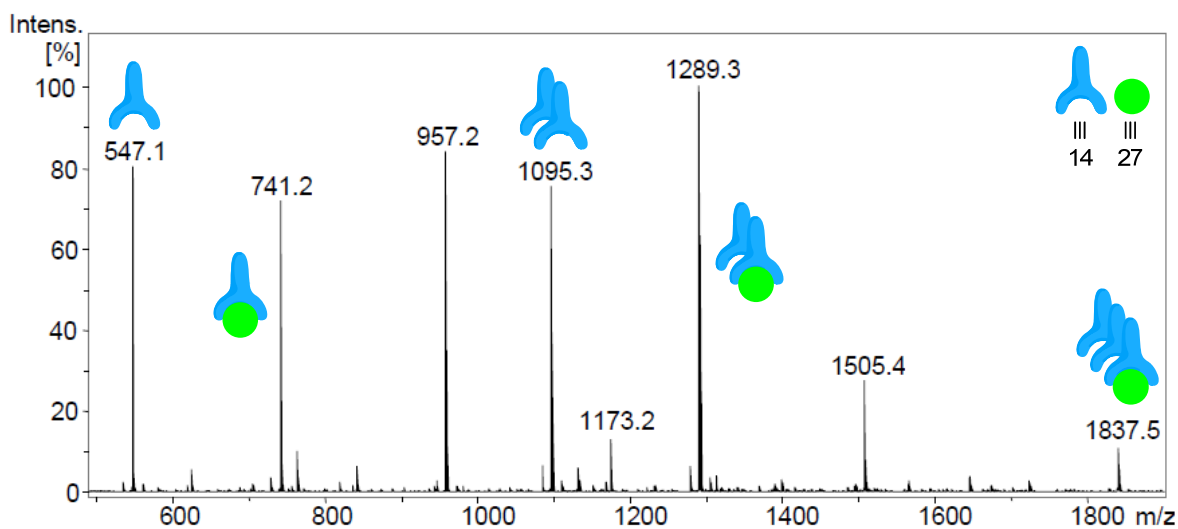
**Figure 67.** ESI-MS/MS of Ht/Gt complex **14/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  681.1).



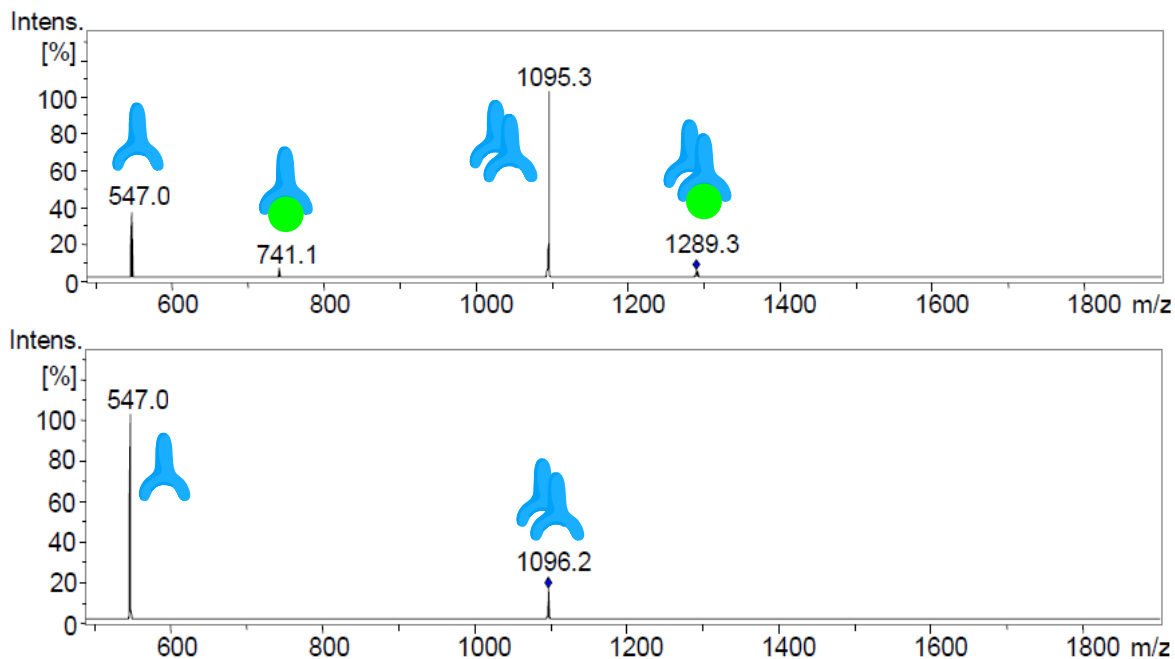
**Figure 68.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative mode,  $m/z$  1289.3 and 1095.3).



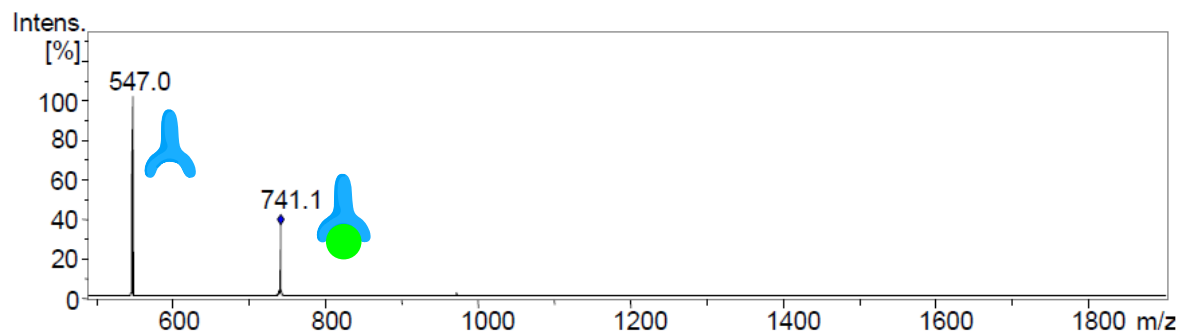
**Figure 69.** ESI-MS/MS of Ht/Gt complex **14/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  741.2).



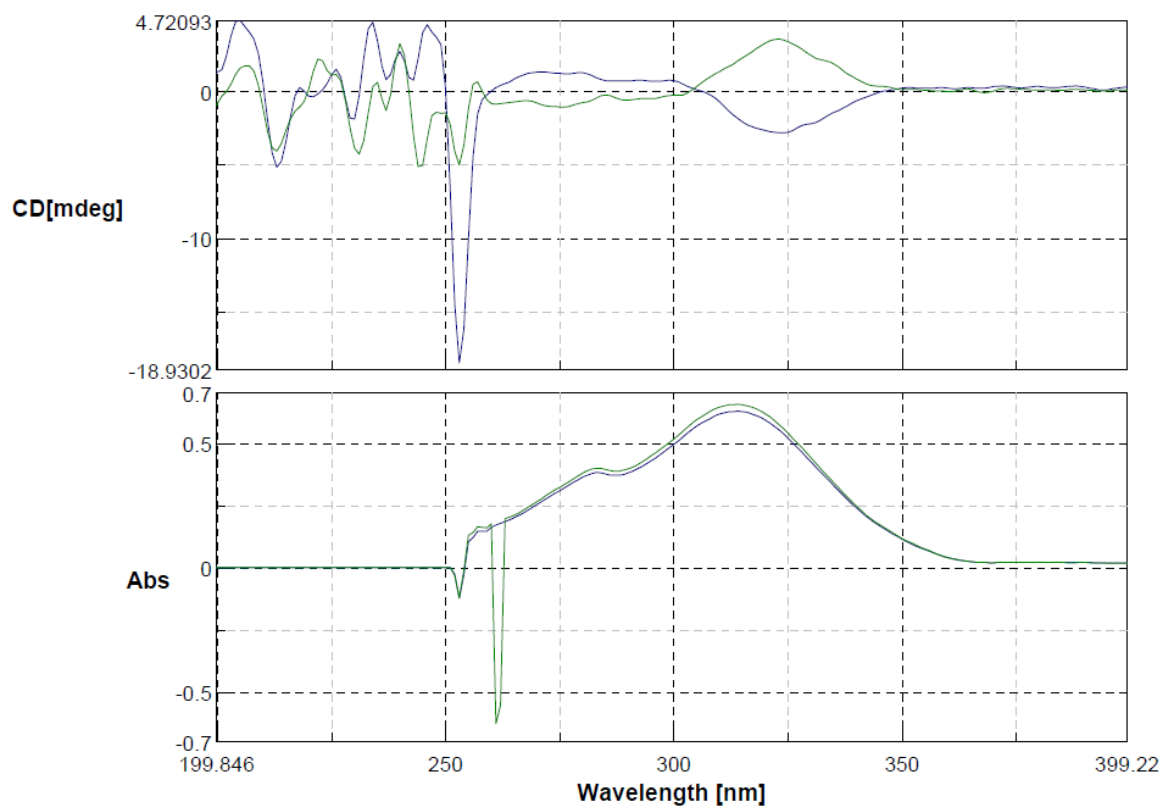
**Figure 70.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode).



**Figure 71.** ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1289.3 and 1095.3).



**Figure 72.** ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, *m/z* 741.2).



**Figure 73.** CD spectra of macrocycles (**9**, blue) and (**12**, green), DMSO.



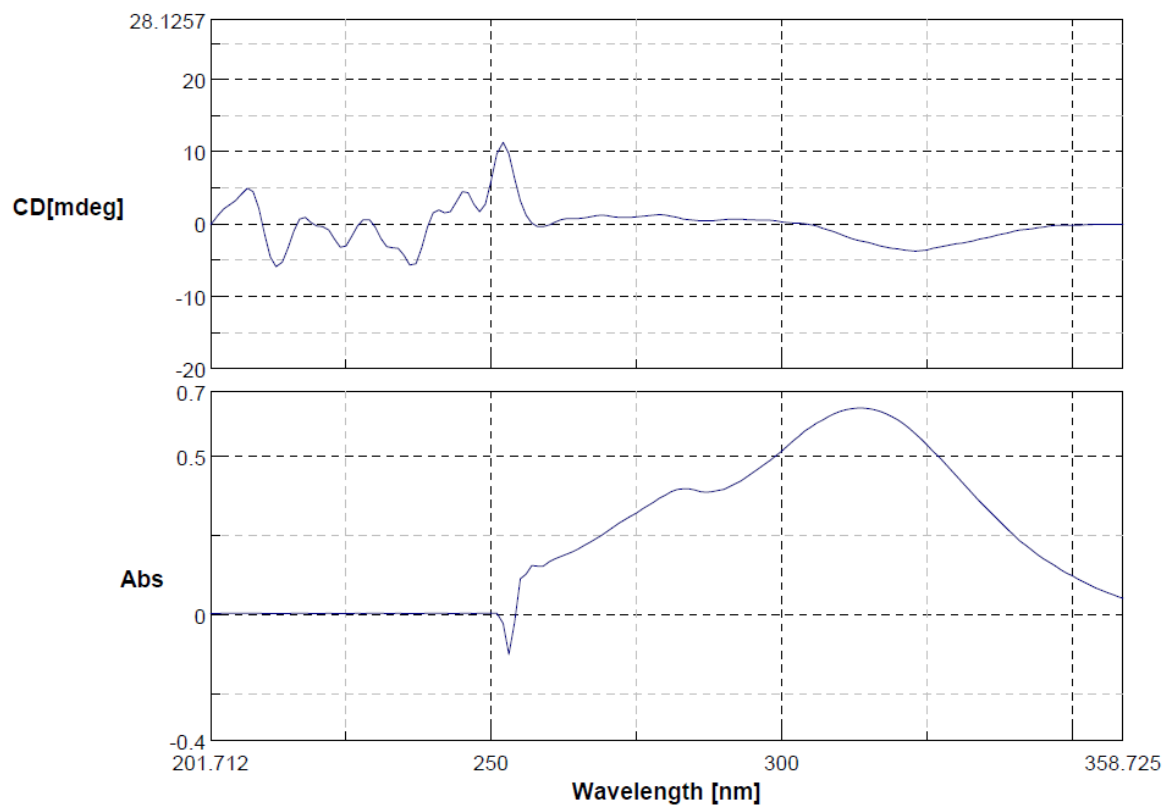


Figure 74. CD spectrum of macrocycles (10), DMSO.

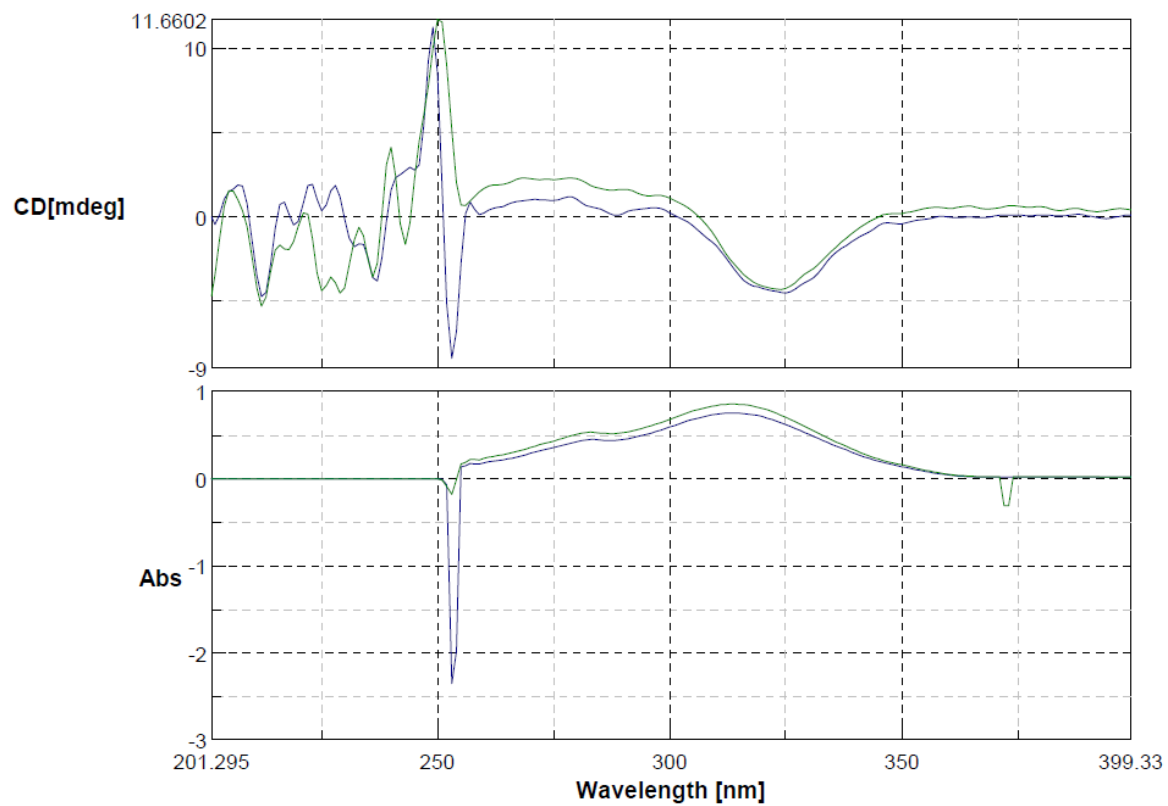
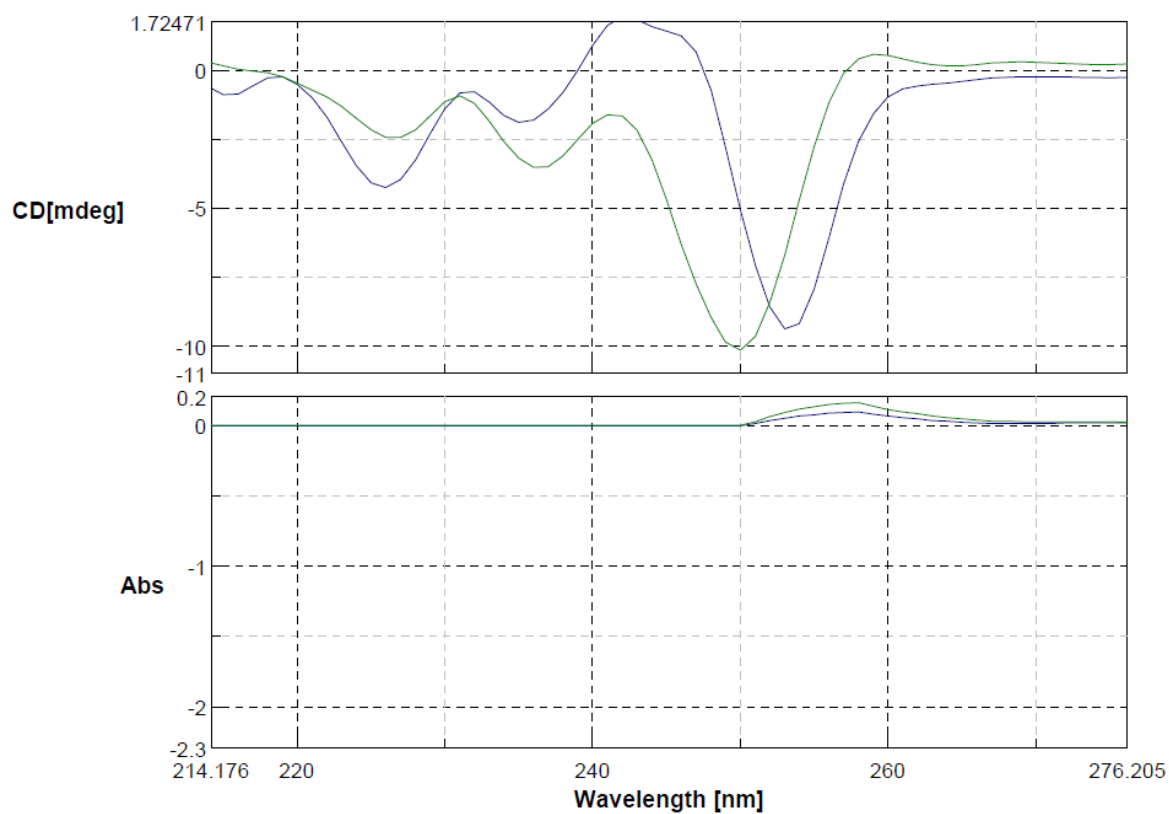
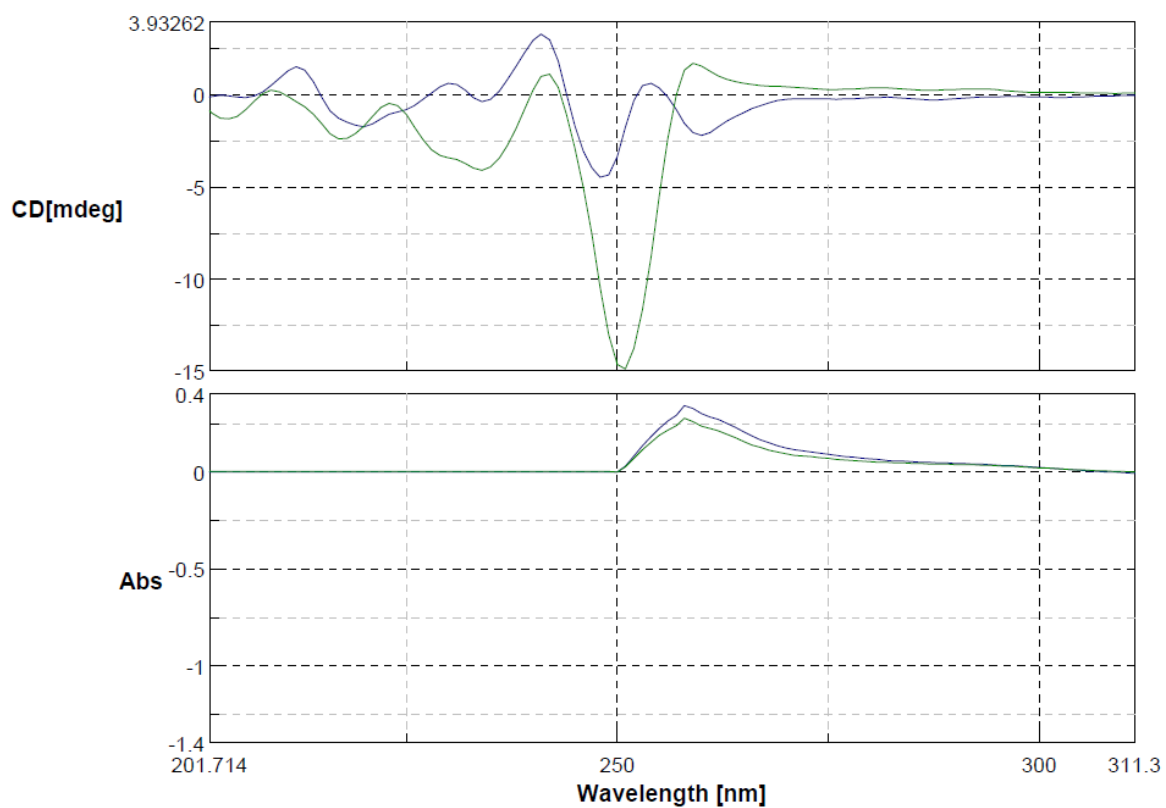


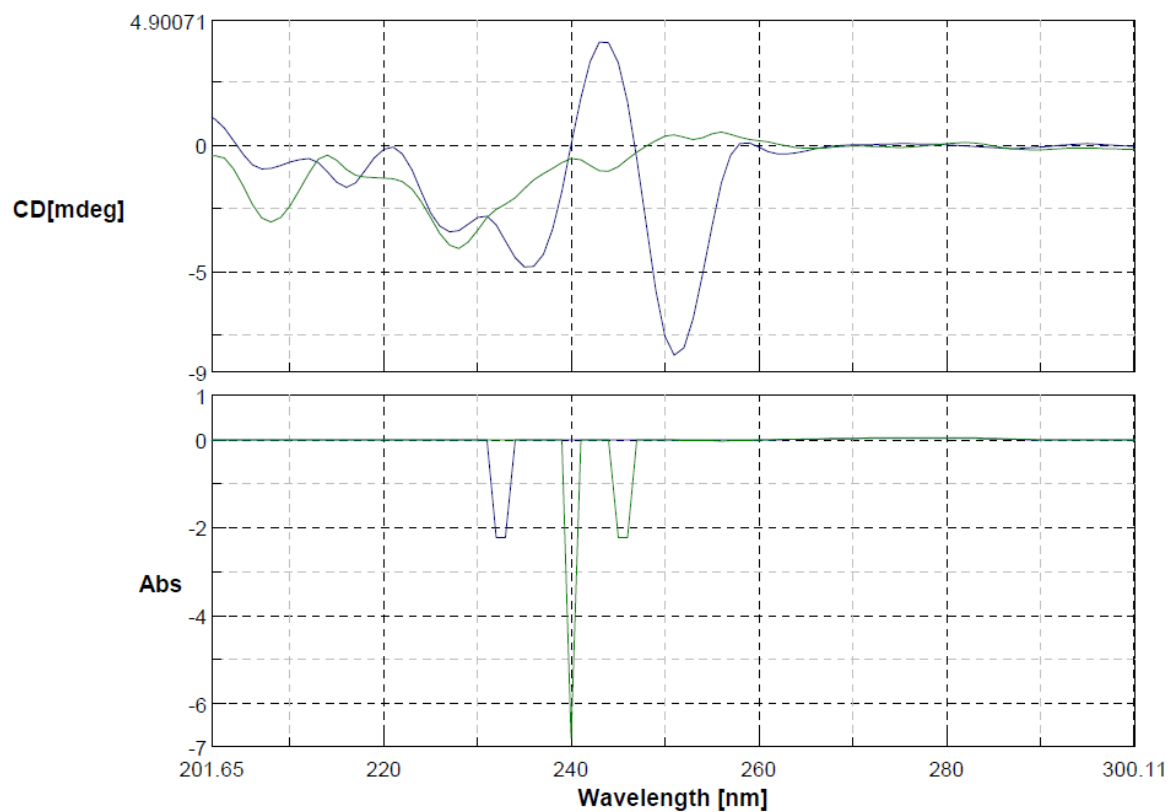
Figure 75. CD spectra of macrocycles (11, blue) and (13, green), DMSO.



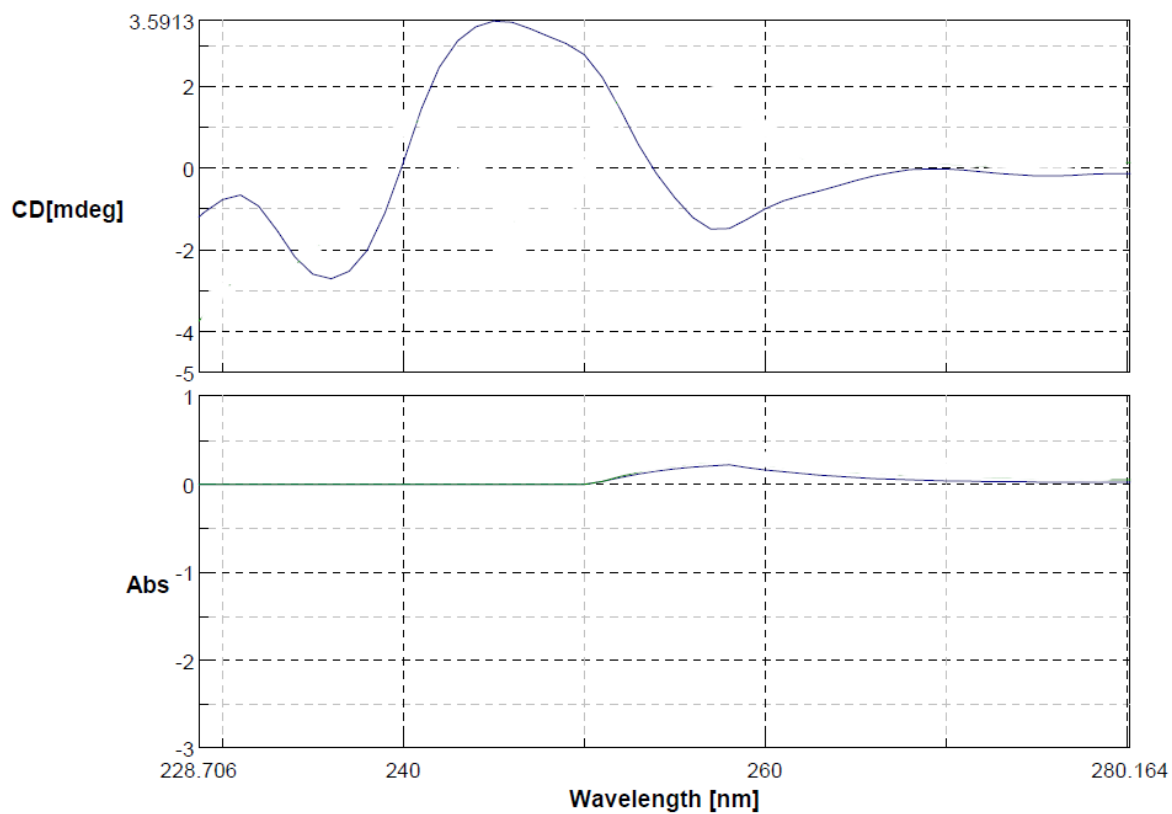
**Figure 76.** CD spectra of compounds (**14**, blue) and (**19**, green), DMSO.



**Figure 77.** CD spectra of compounds (**15**, blue) and (**20**, green), DMSO.



**Figure 78.** CD spectra of compounds (**16**, blue) and (**21**, green), DMSO.



**Figure 79.** CD spectrum of compound (**17**), DMSO.

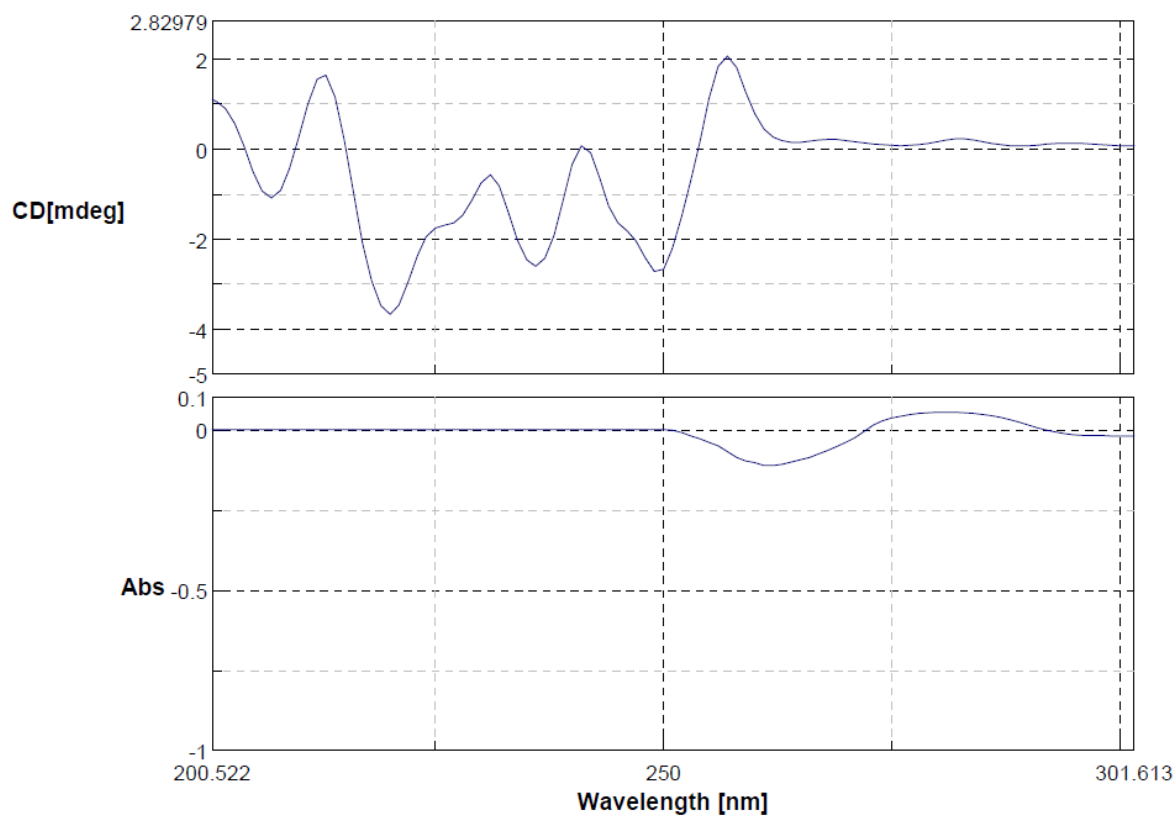


Figure 80. CD spectrum of compound (18), DMSO.

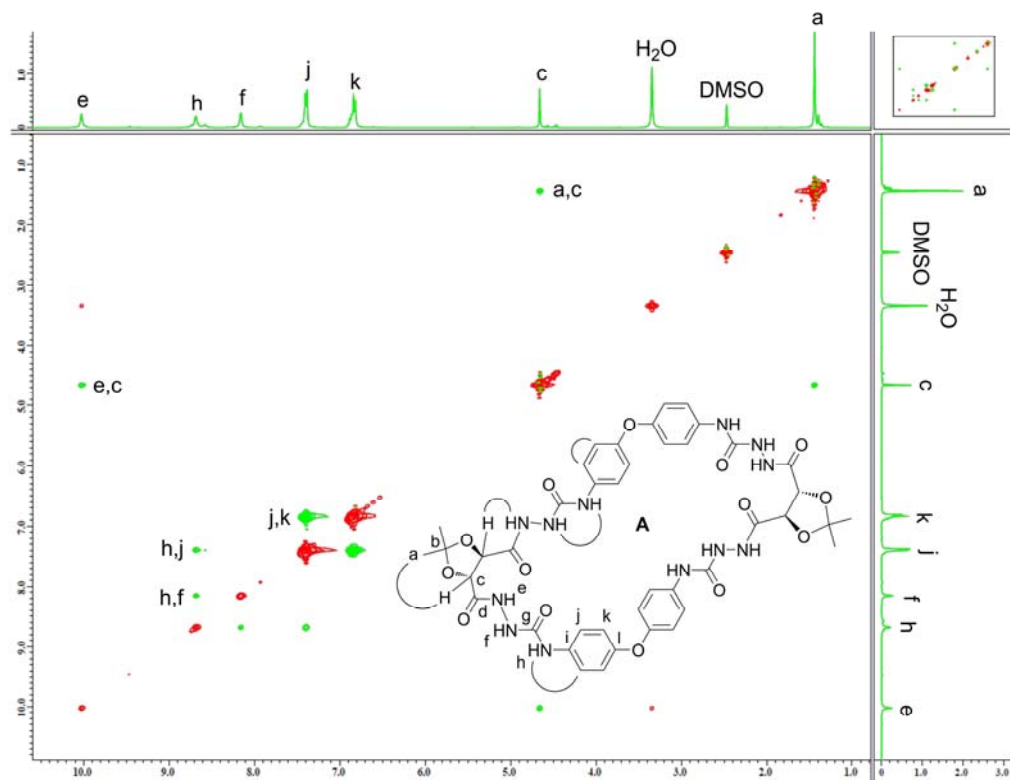
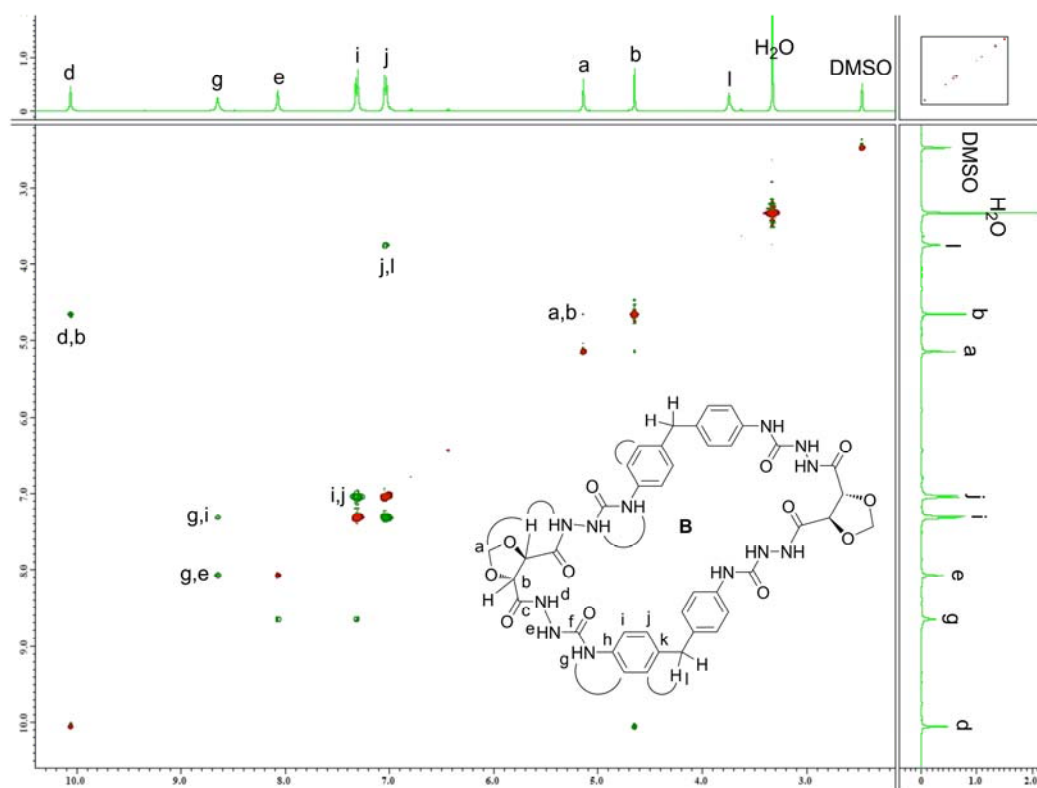
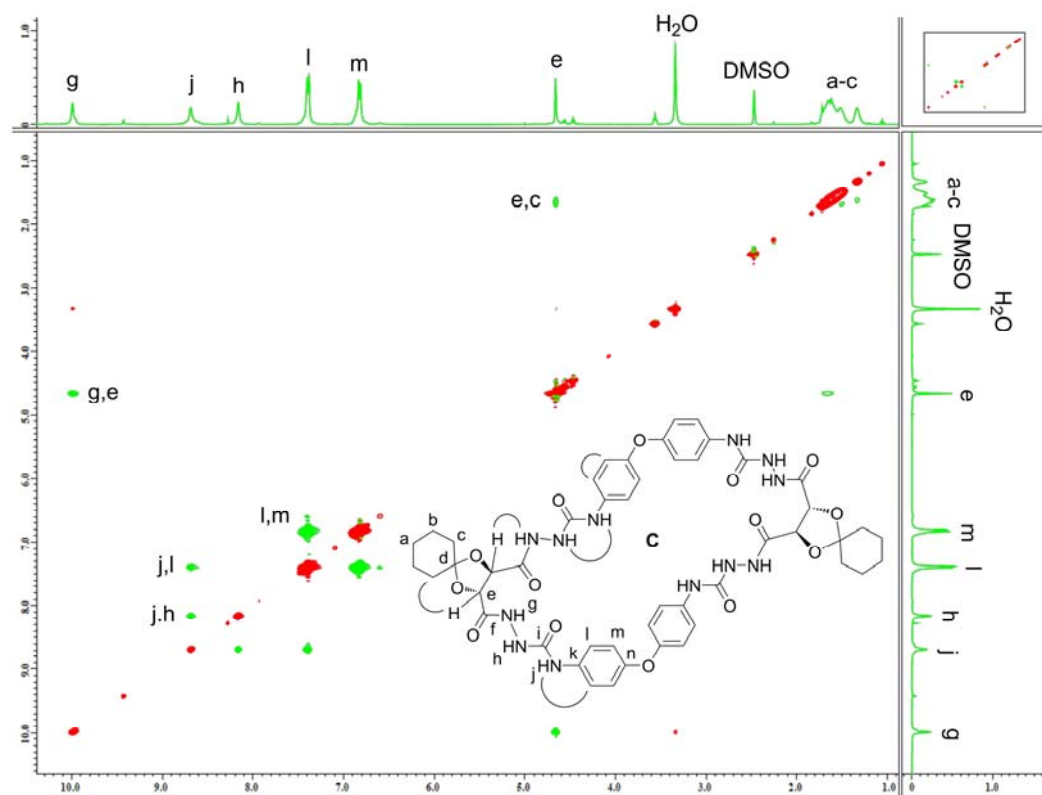


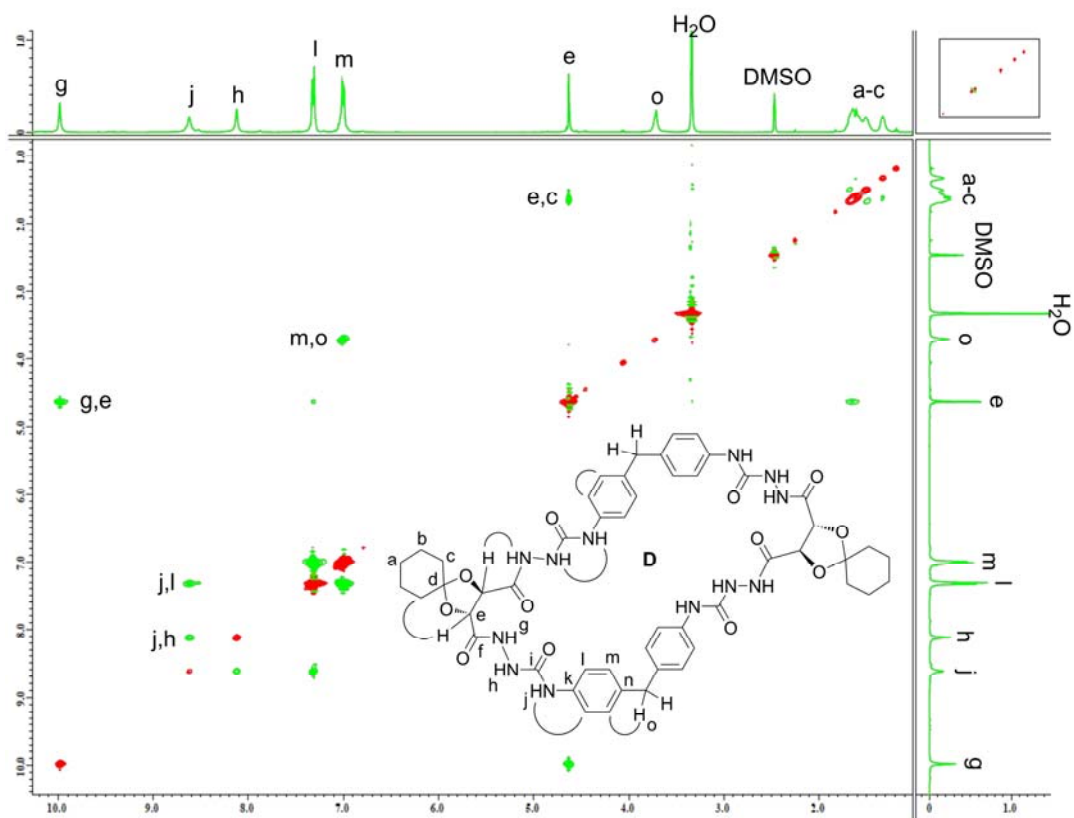
Figure 81. 2D ROESY NMR spectrum of macrocycle (A) showing *syn/anti* orientation of the NH moieties, (DMSO- $d_6$ ).



**Figure 82.** 2D ROESY NMR spectrum of macrocycle (**B**) showing *syn/anti* orientation of the NH moieties, (DMSO- $d_6$ ).



**Figure 83.** 2D ROESY NMR spectrum of macrocycle (**C**) showing *syn/anti* orientation of the NH moieties, (DMSO- $d_6$ ).



**Figure 84.** 2D ROESY NMR spectrum of macrocycle (**D**) showing *syn/anti* orientation of the NH moieties, (DMSO- $d_6$ ).