

## 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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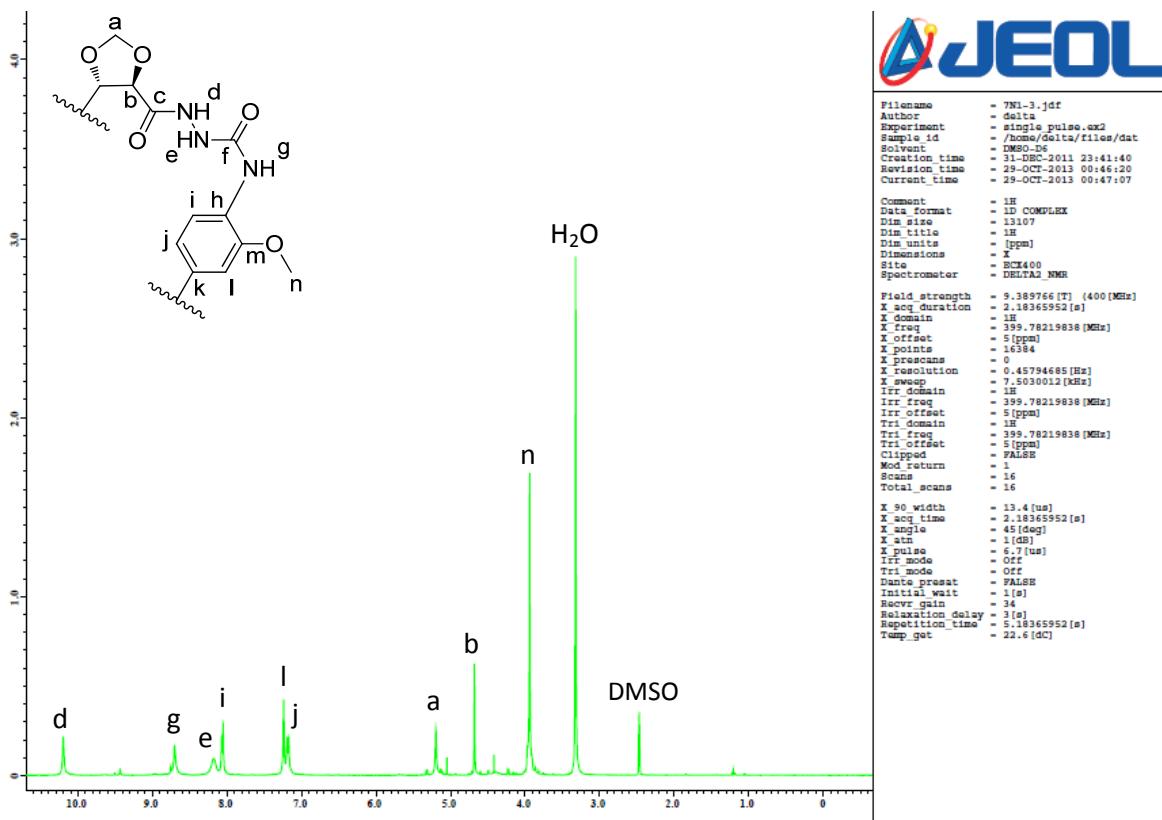
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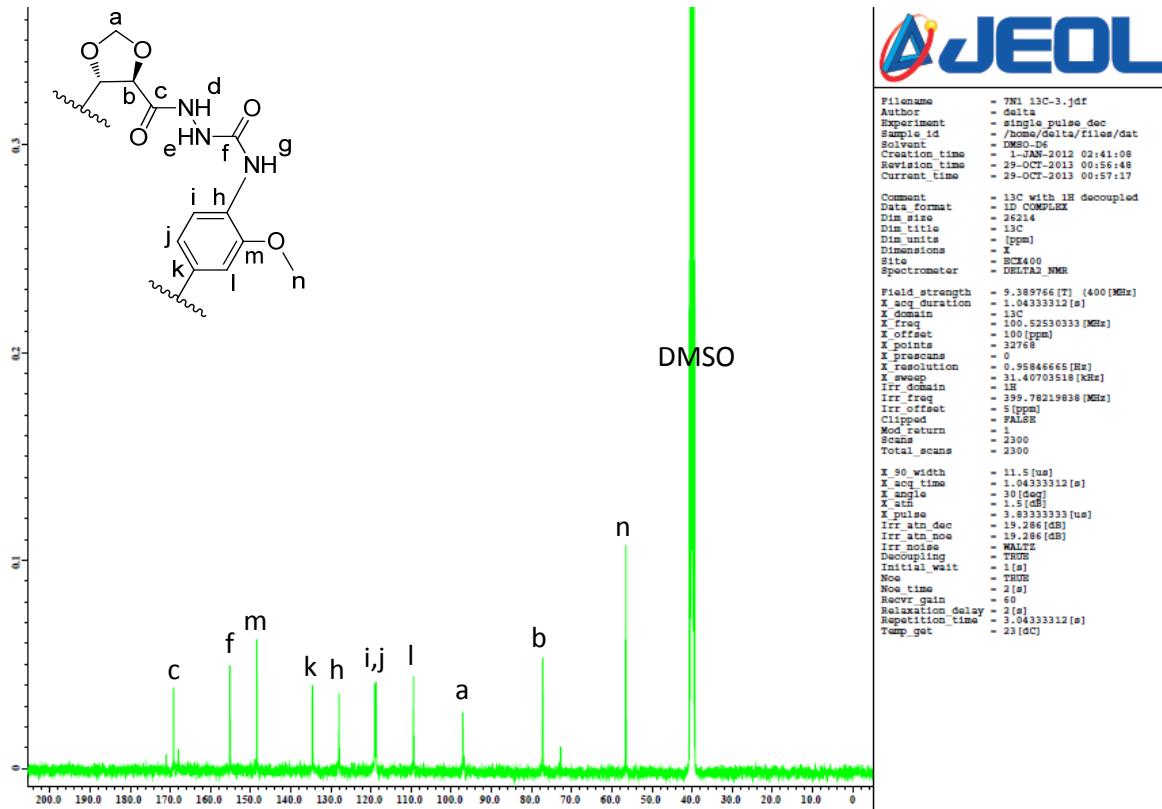
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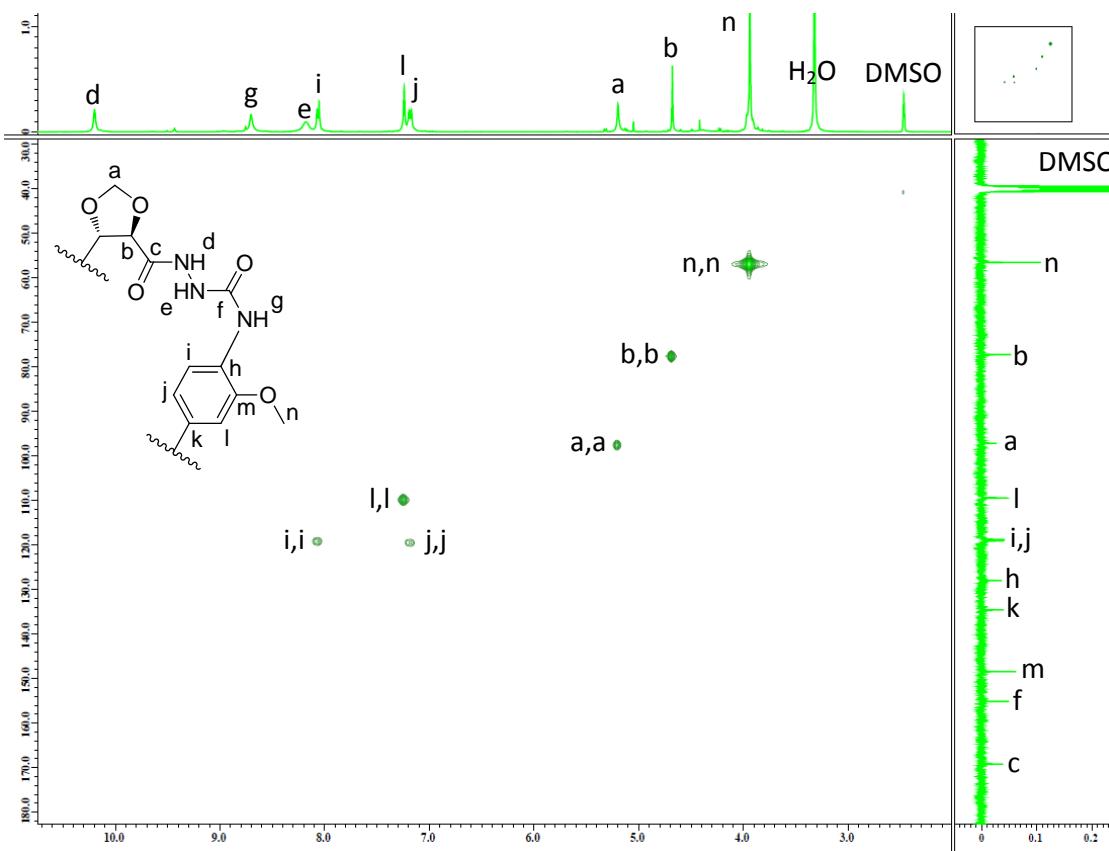
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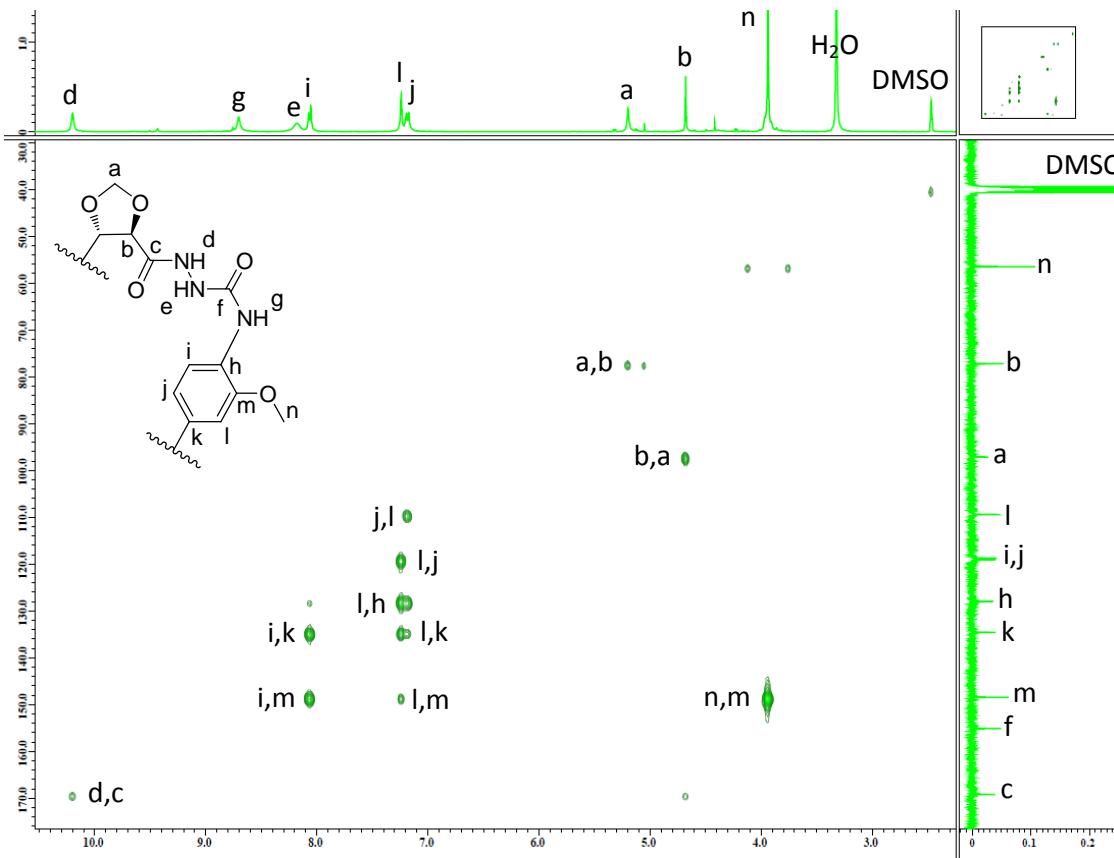
**Figure 1.** <sup>1</sup>H NMR spectrum of macrocycle (**9**) (400 MHz, DMSO-*d*<sub>6</sub>).



**Figure 2.** <sup>13</sup>C NMR spectrum of macrocycle (**9**) (100 MHz, DMSO-*d*<sub>6</sub>).



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



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

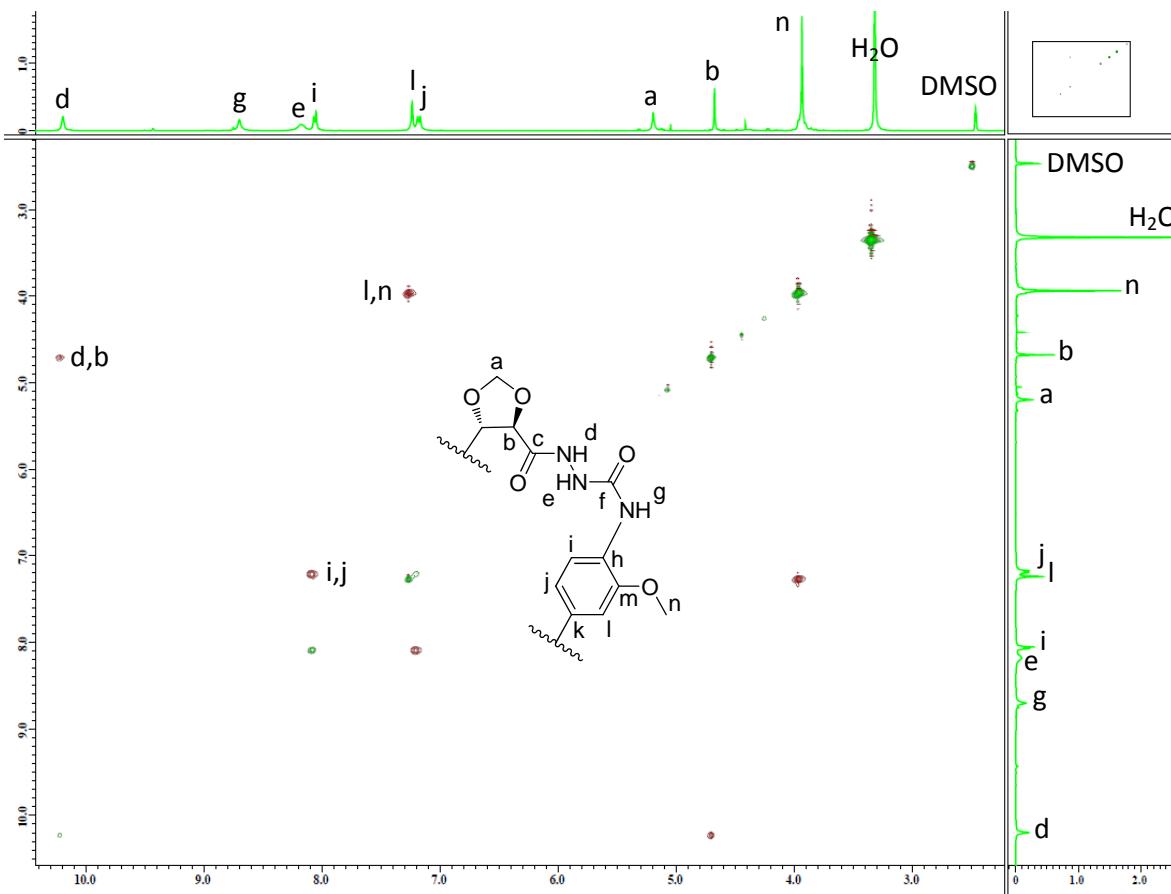


Figure 5. 2D ROESY NMR spectrum of macrocycle (9) (DMSO-*d*<sub>6</sub>).

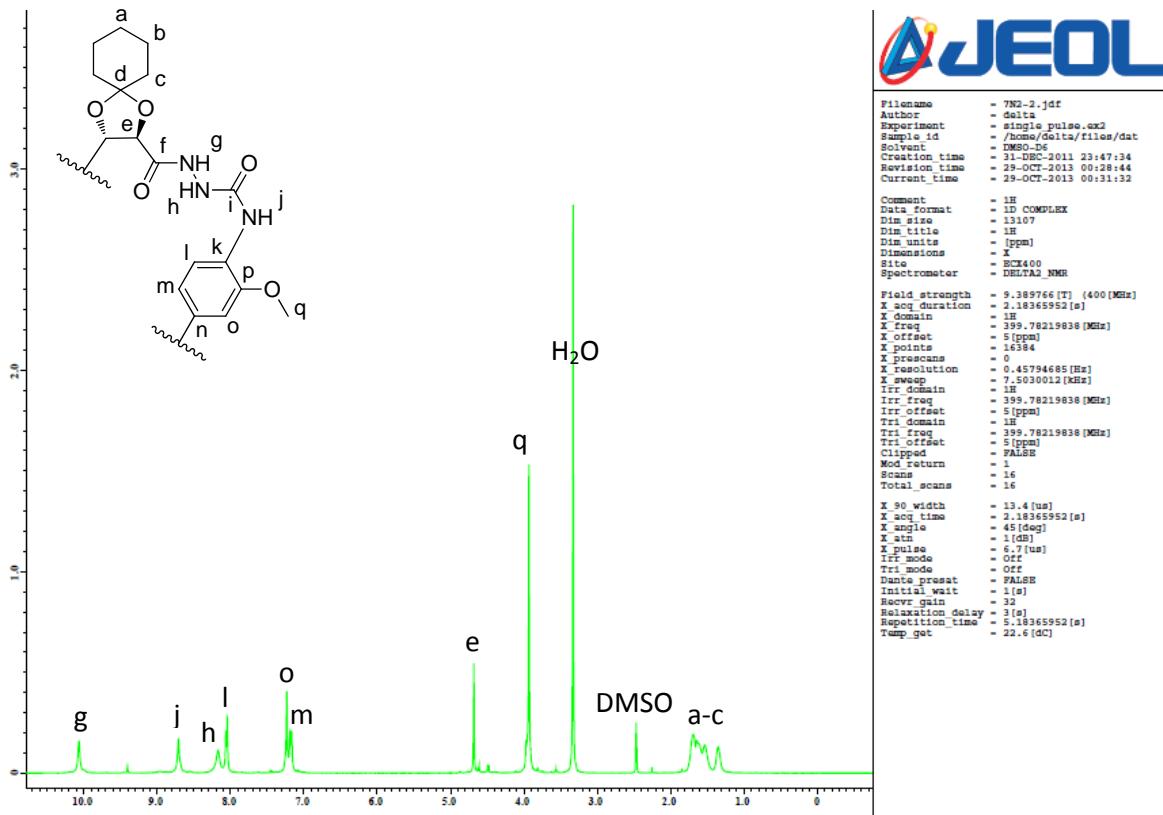


Figure 6. <sup>1</sup>H NMR spectrum of macrocycle (10) (400 MHz, DMSO-*d*<sub>6</sub>).

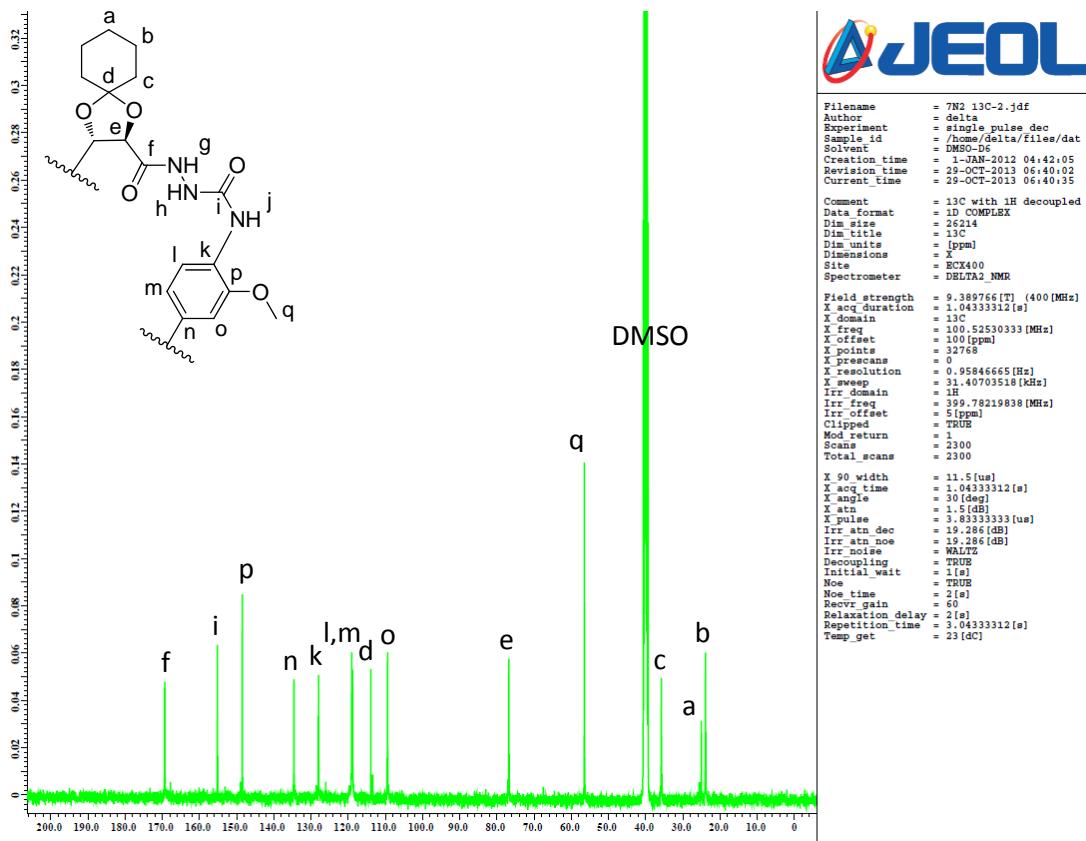


Figure 7.  $^{13}\text{C}$  NMR spectrum of macrocycle (**10**) (100 MHz,  $\text{DMSO}-d_6$ ).

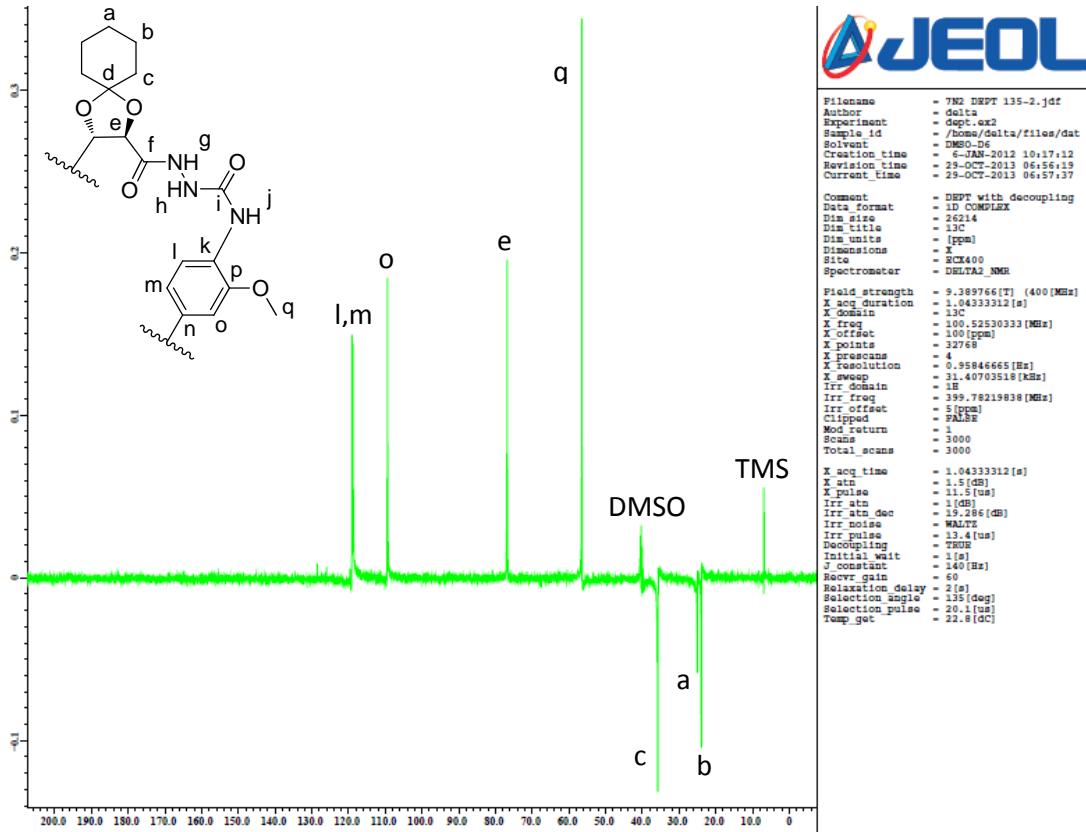
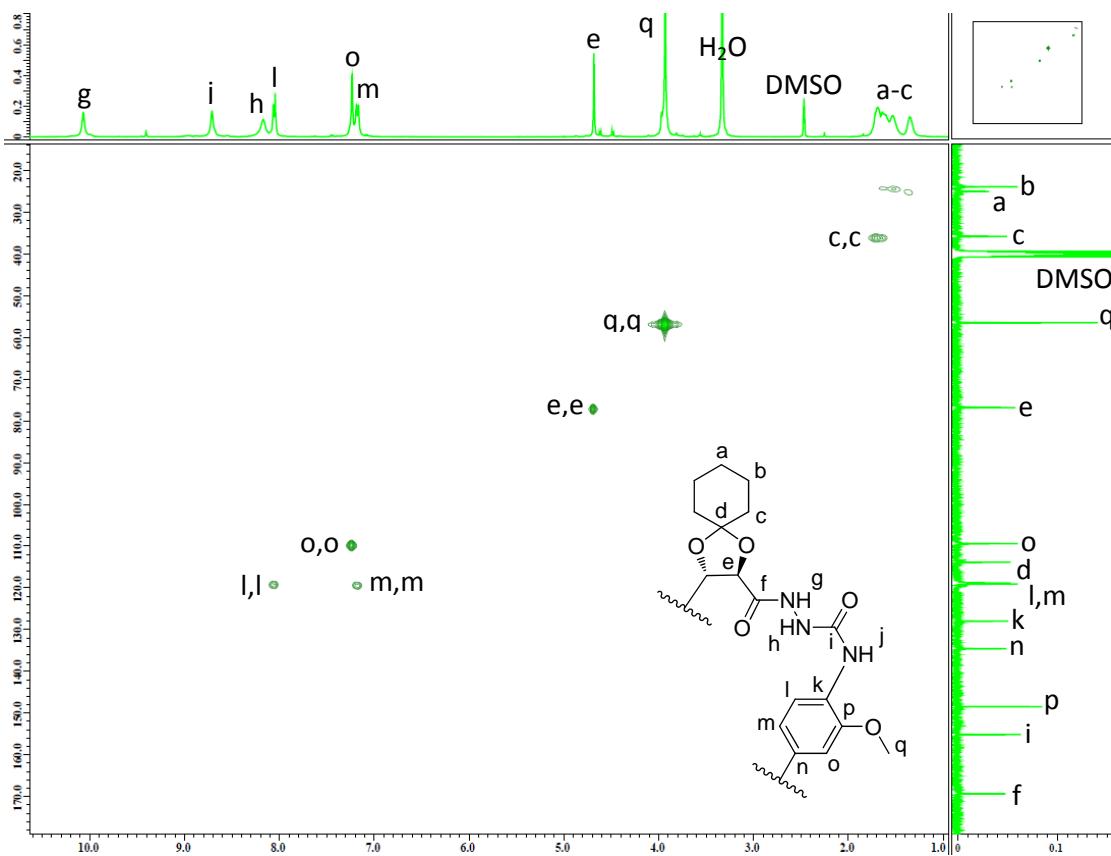
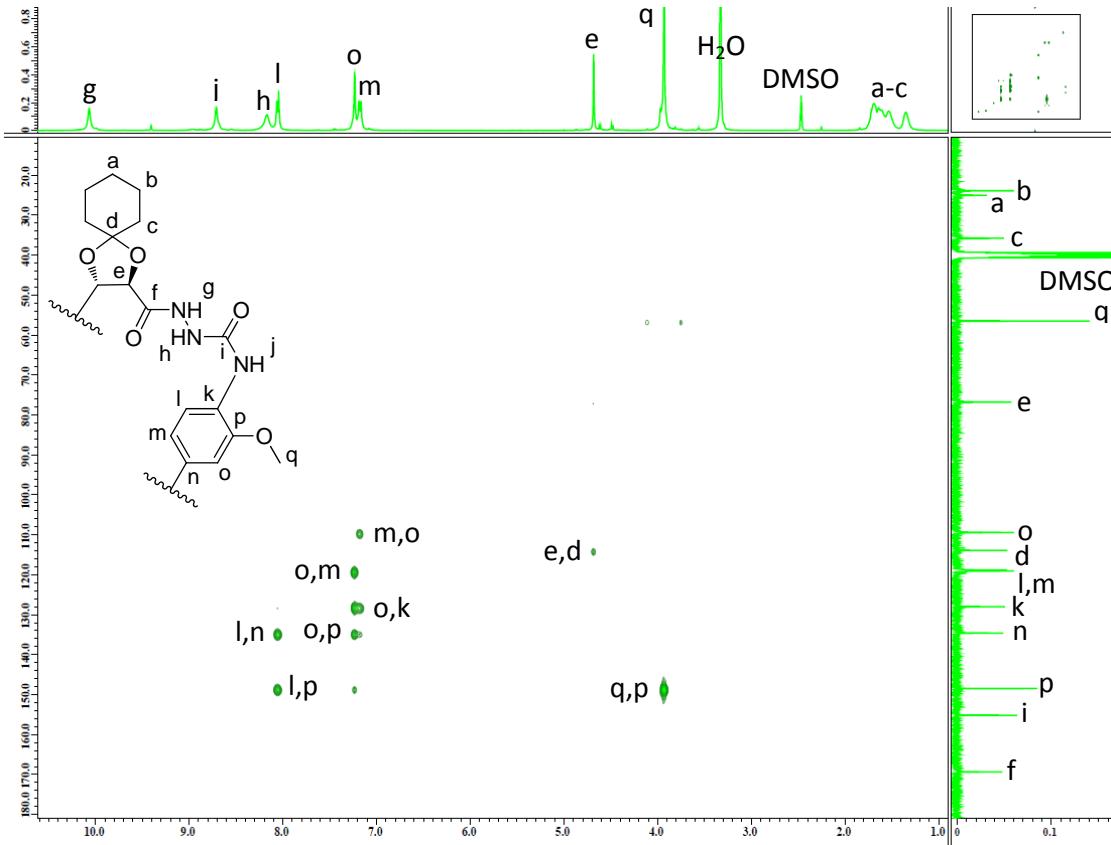
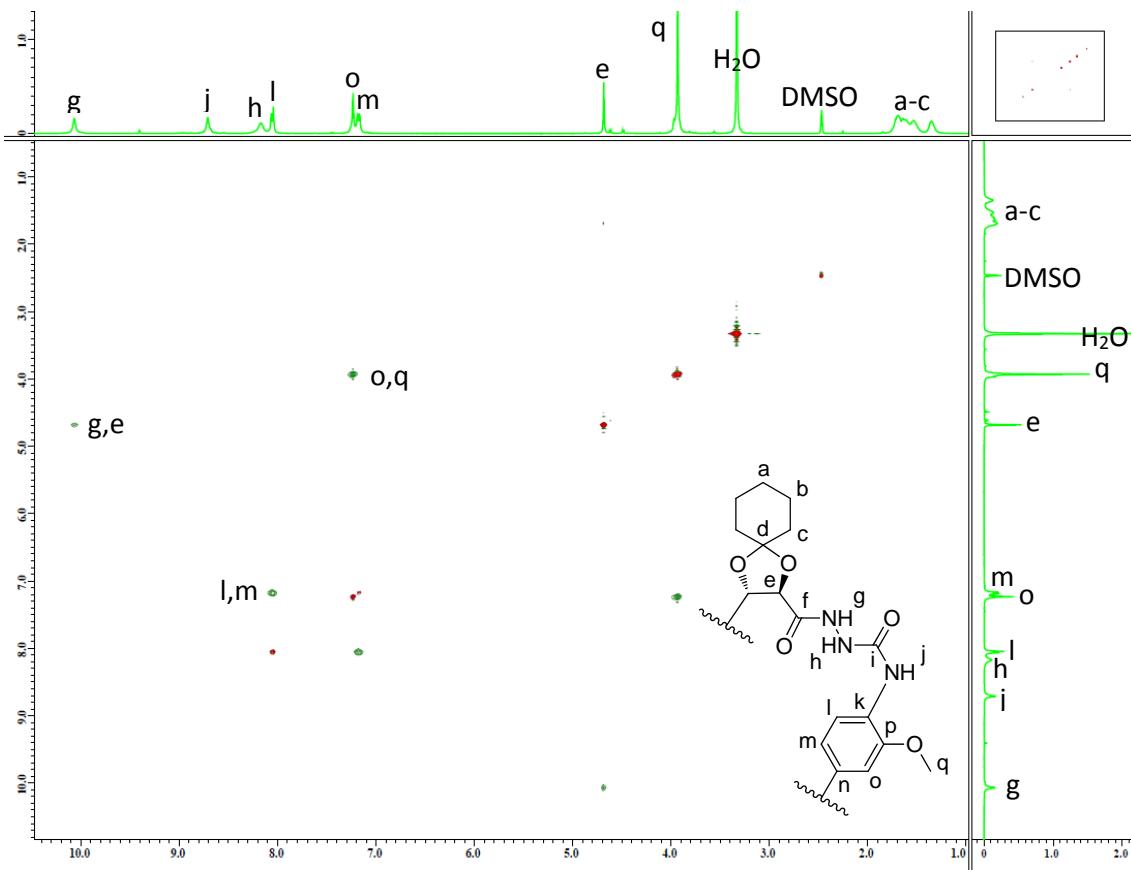
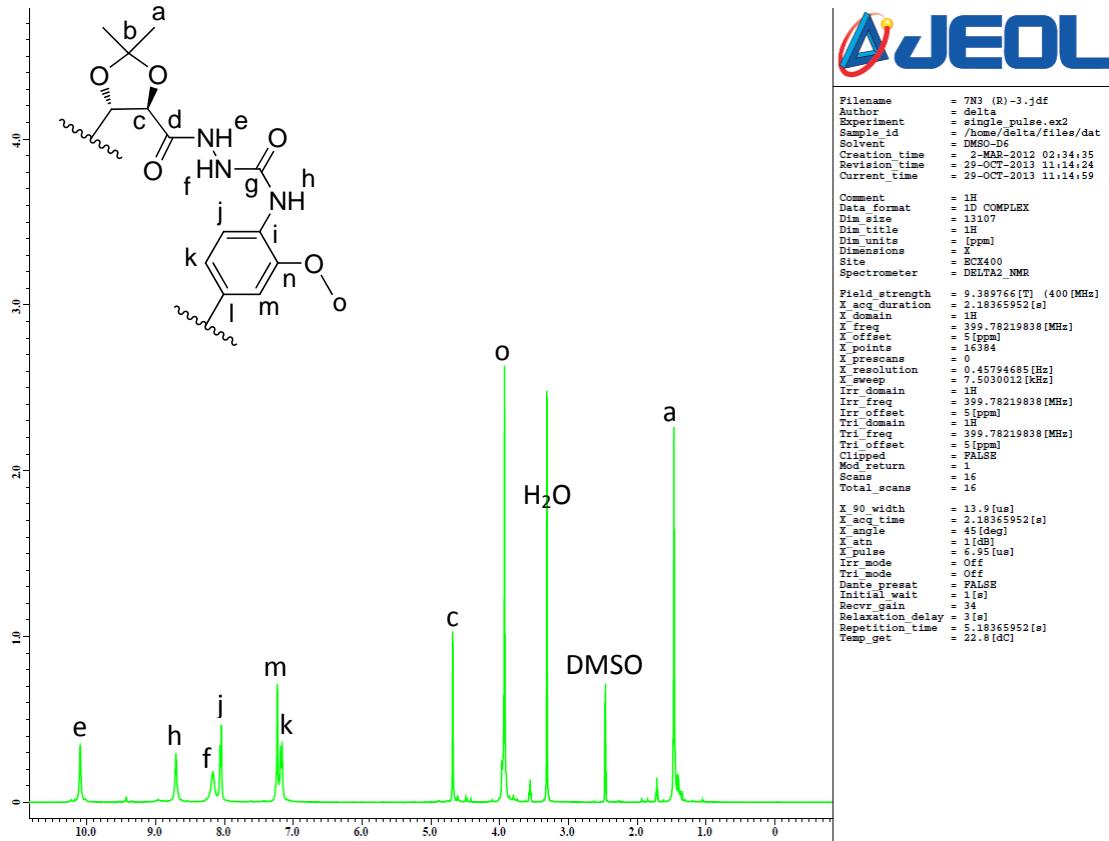


Figure 8. DEPT 135 spectrum of macrocycle (**10**) ( $\text{DMSO}-d_6$ ).

**Figure 9.** 2D HMQC spectrum of macrocycle (**10**) (DMSO-*d*<sub>6</sub>).**Figure 10.** 2D HMBC spectrum of macrocycle (**10**) (DMSO-*d*<sub>6</sub>).



**Figure 11.** 2D ROESY NMR spectrum of macrocycle (**10**) ( $\text{DMSO}-d_6$ ).



**Figure 12.** <sup>1</sup>H NMR spectrum of macrocycle (**11**) (400 MHz,  $\text{DMSO}-d_6$ ).

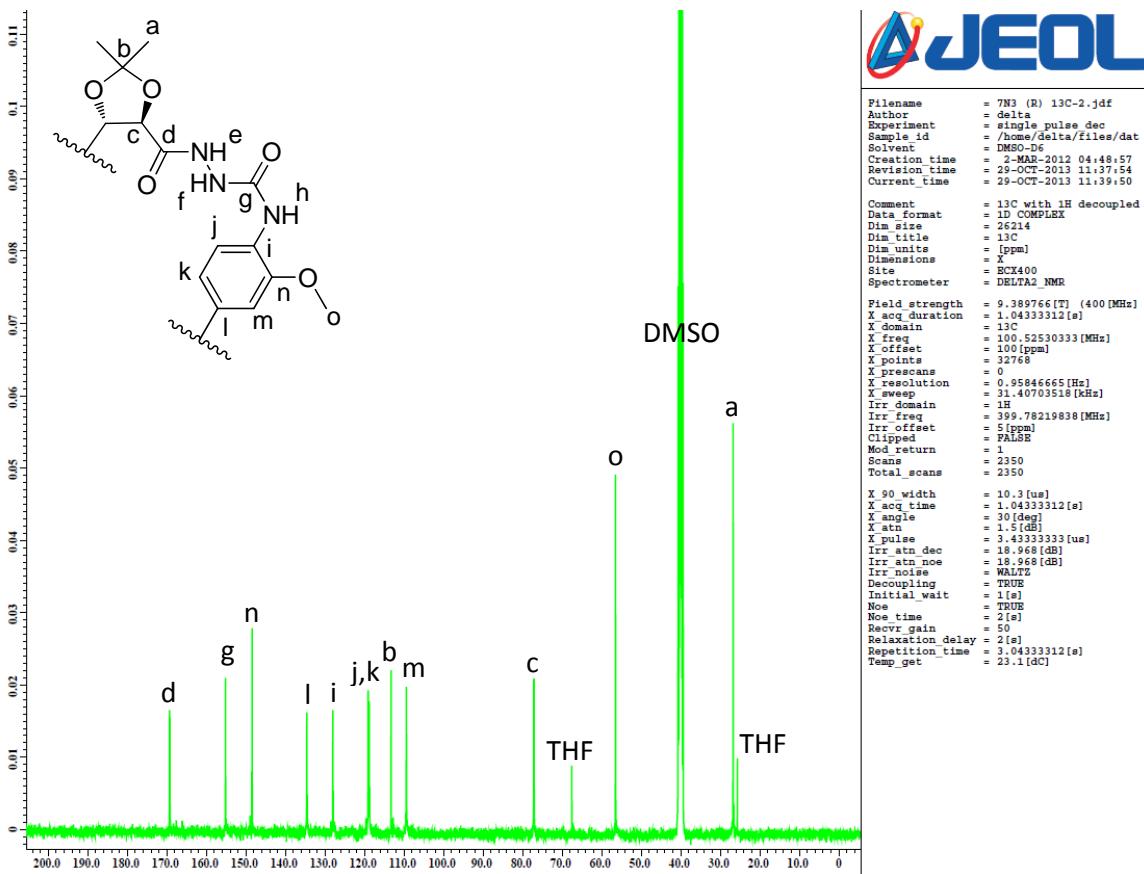


Figure 13. <sup>13</sup>C NMR spectrum of macrocycle (11) (100 MHz, DMSO-*d*<sub>6</sub>).

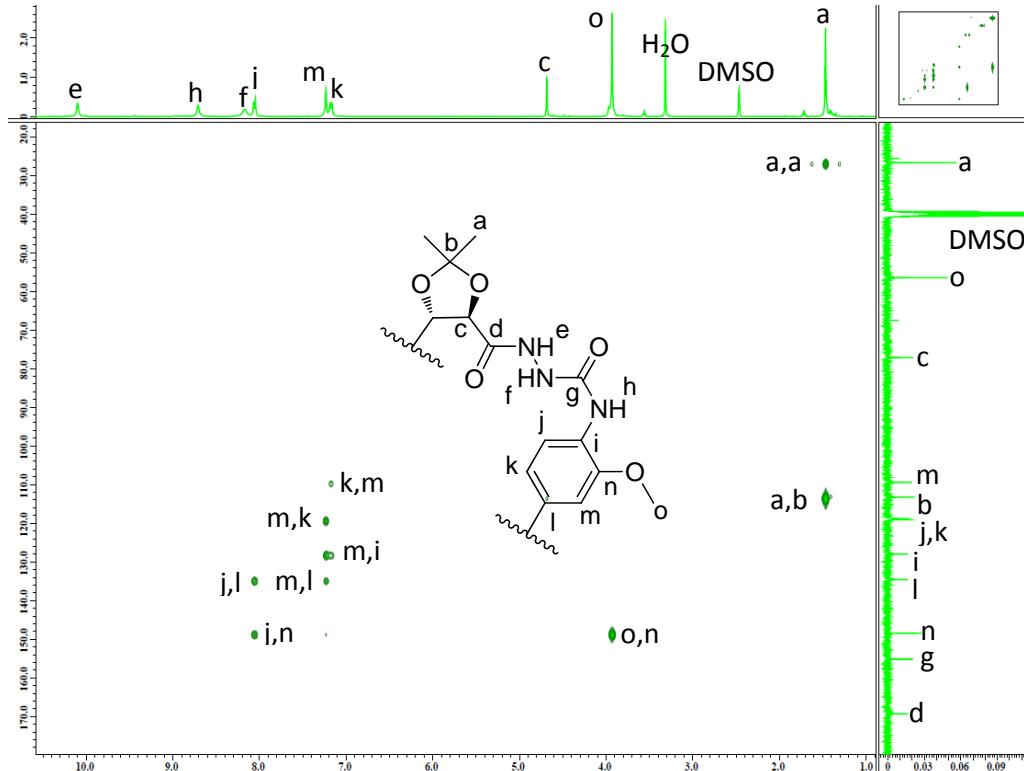
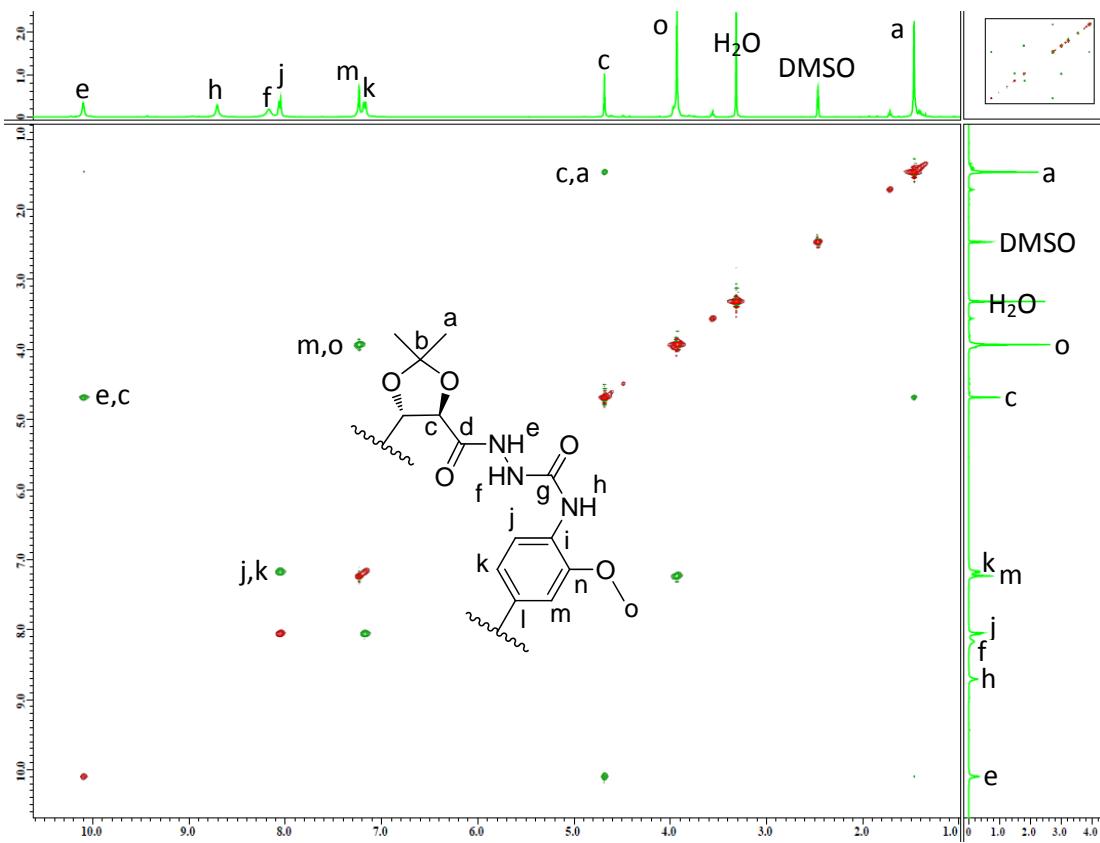
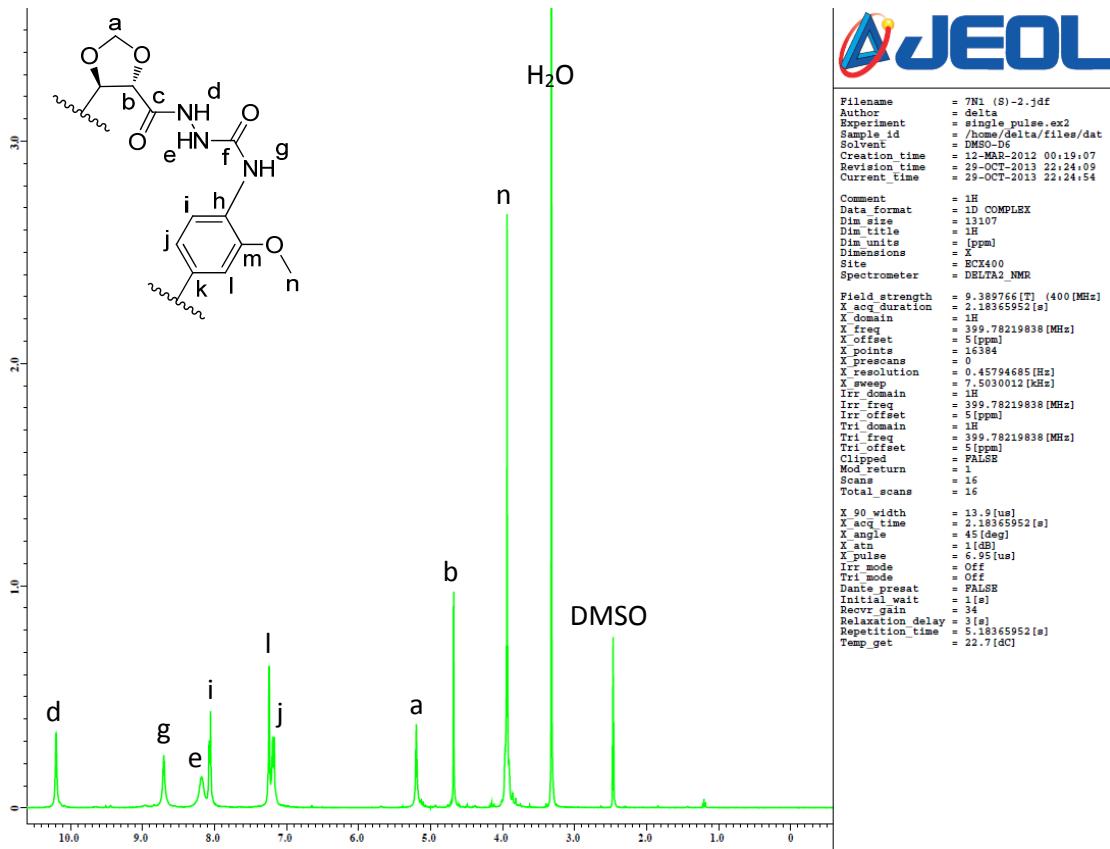


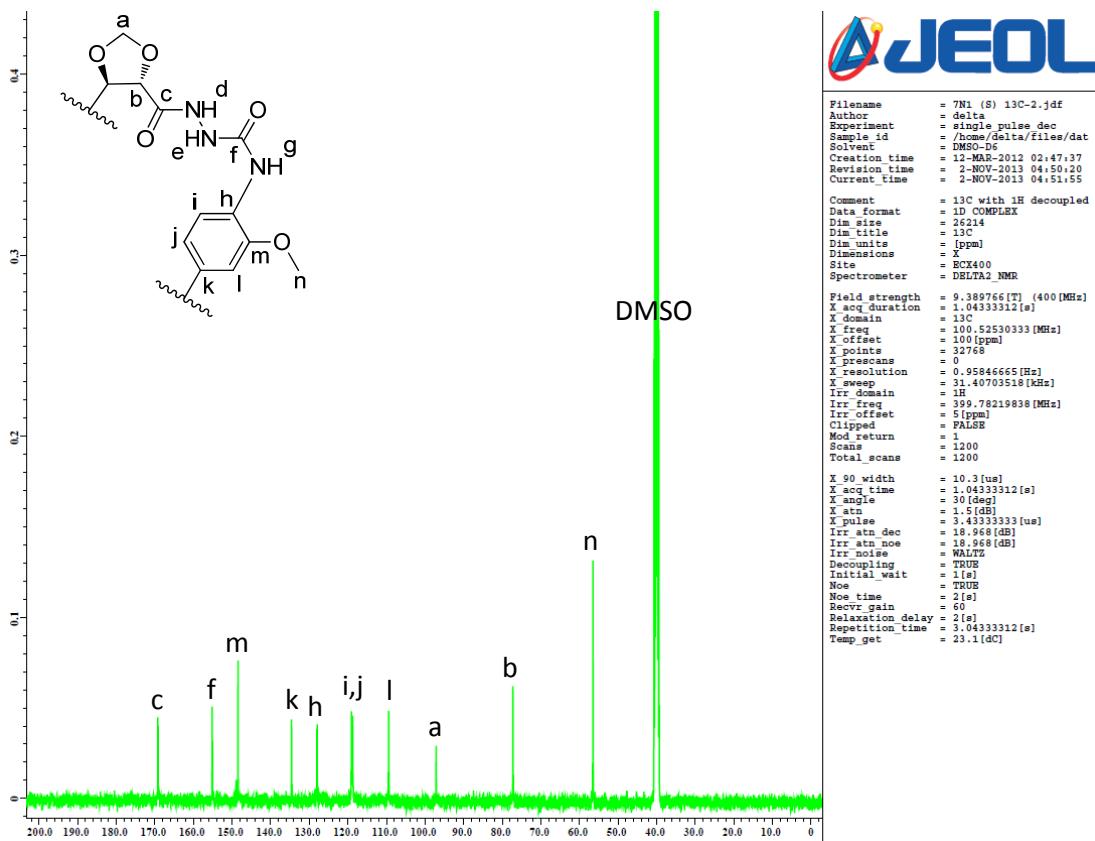
Figure 14. 2D HMBC spectrum of macrocycle (11) (DMSO-*d*<sub>6</sub>).



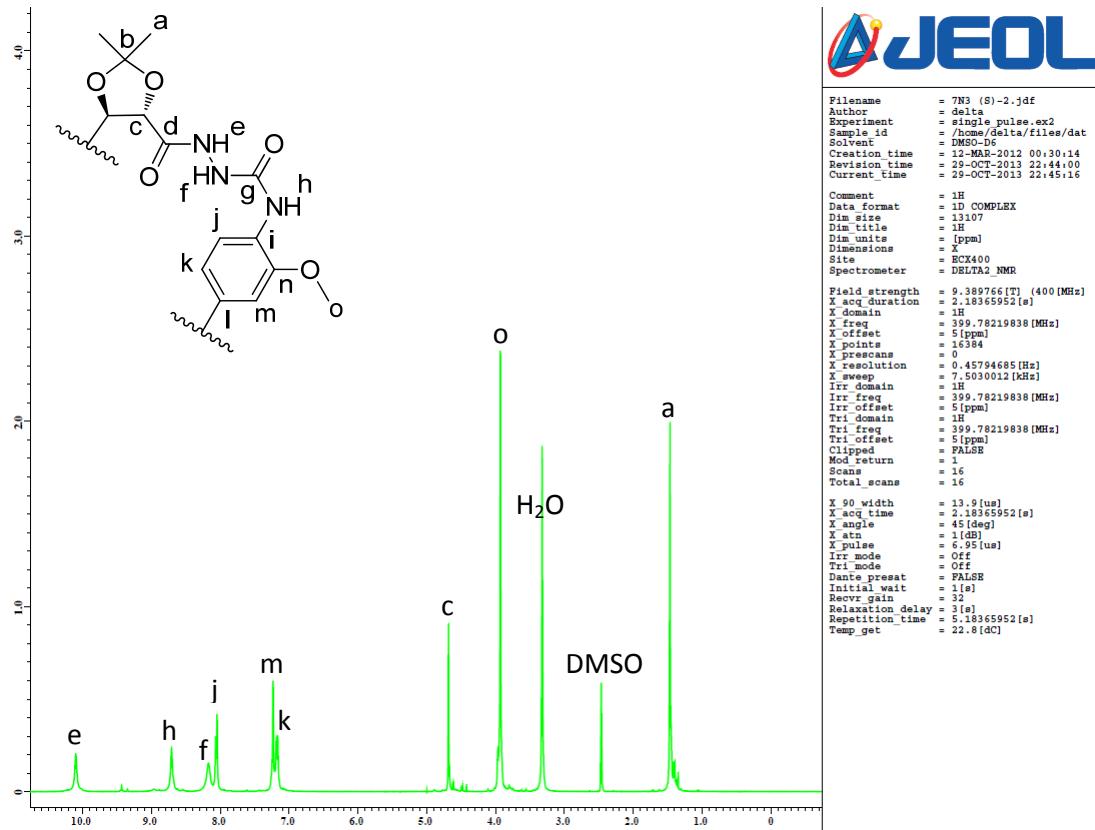
**Figure 15.** 2D ROESY NMR spectrum of macrocycle (**11**) (DMSO-*d*<sub>6</sub>).



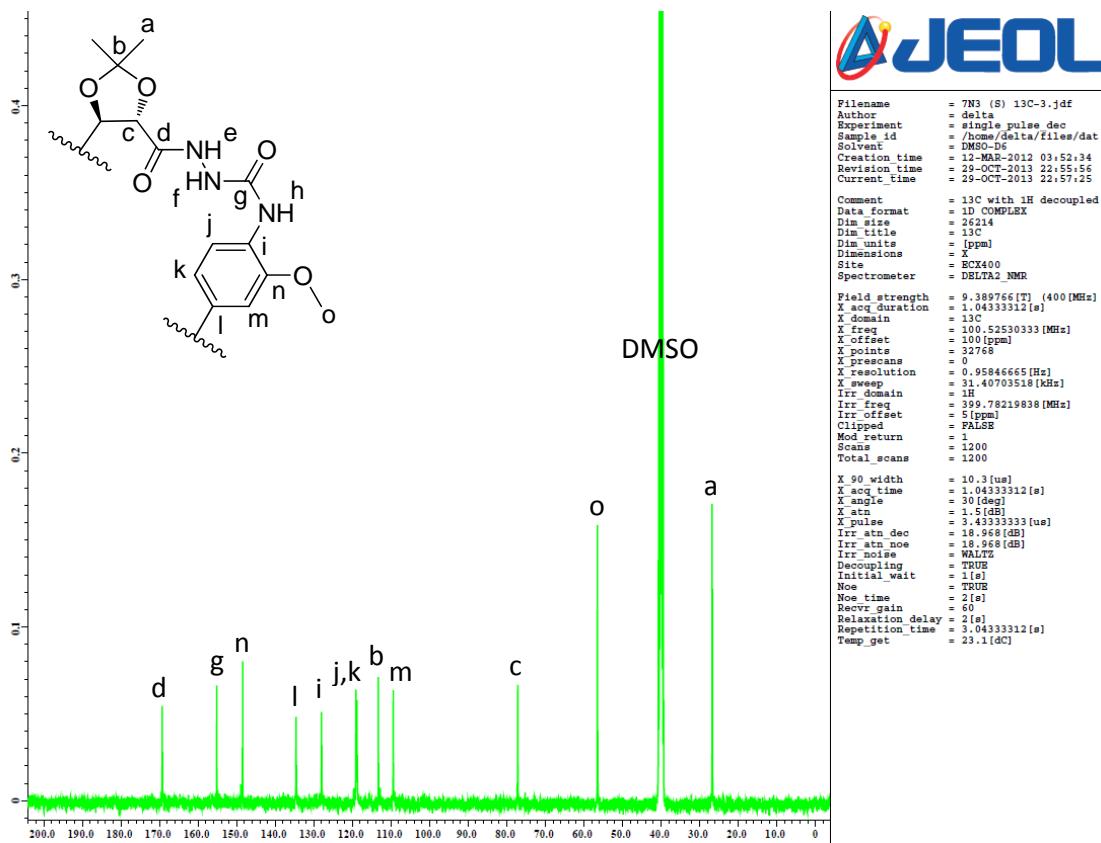
**Figure 16.**  $^1\text{H}$  NMR spectrum of macrocycle (**12**) (400 MHz,  $\text{DMSO}-d_6$ ).



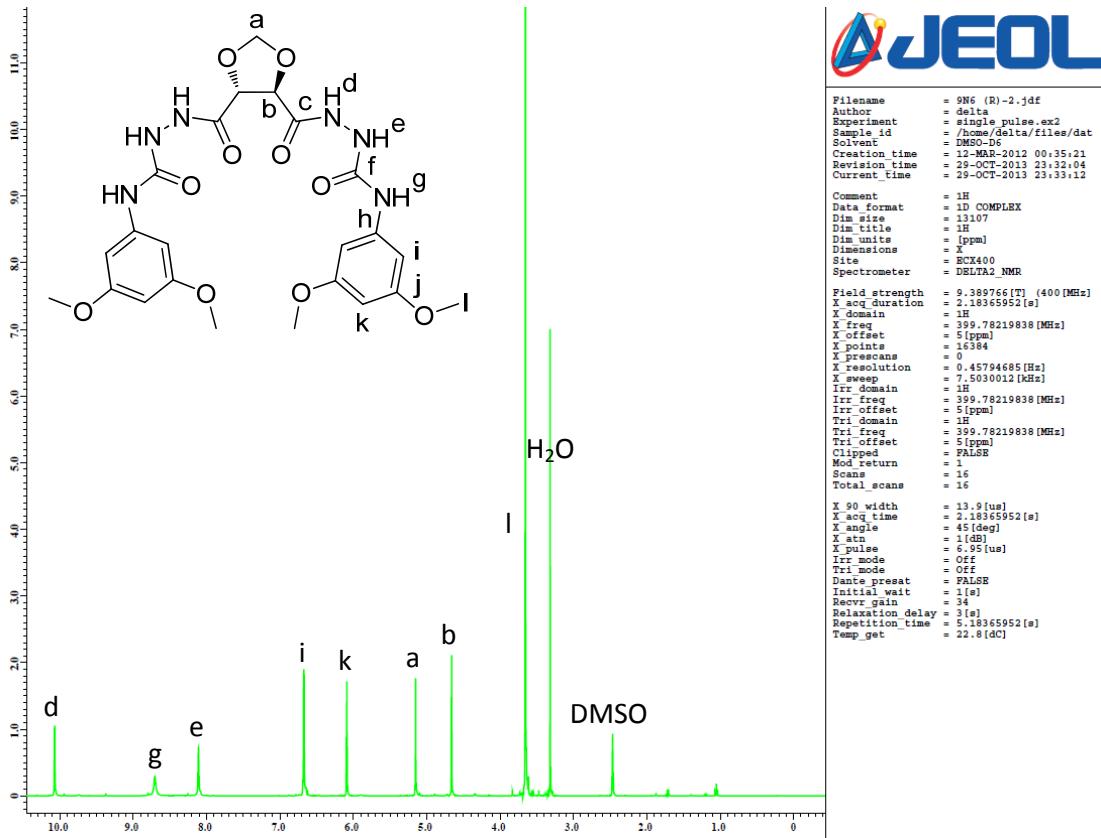
**Figure 17.**  $^{13}\text{C}$  NMR spectrum of macrocycle (**12**) (100 MHz,  $\text{DMSO}-d_6$ ).



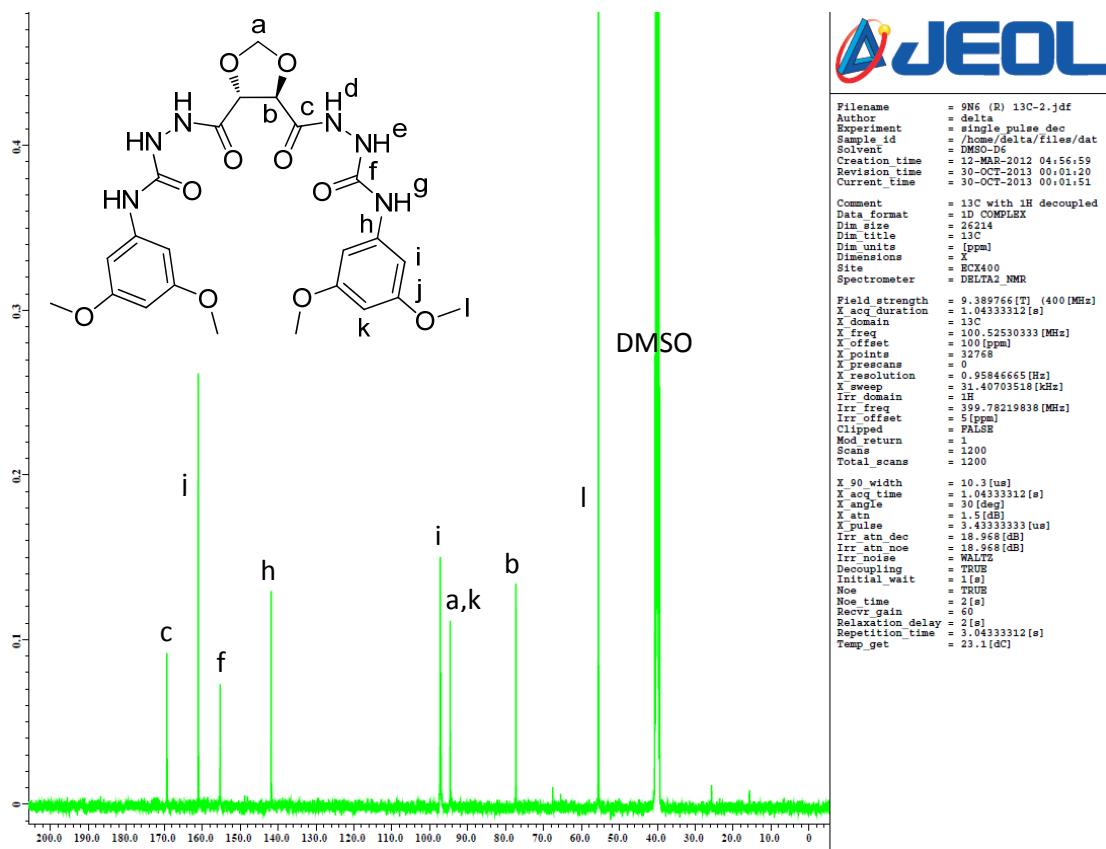
**Figure 18.**  $^1\text{H}$  NMR spectrum of macrocycle (**13**) (400 MHz,  $\text{DMSO}-d_6$ ).



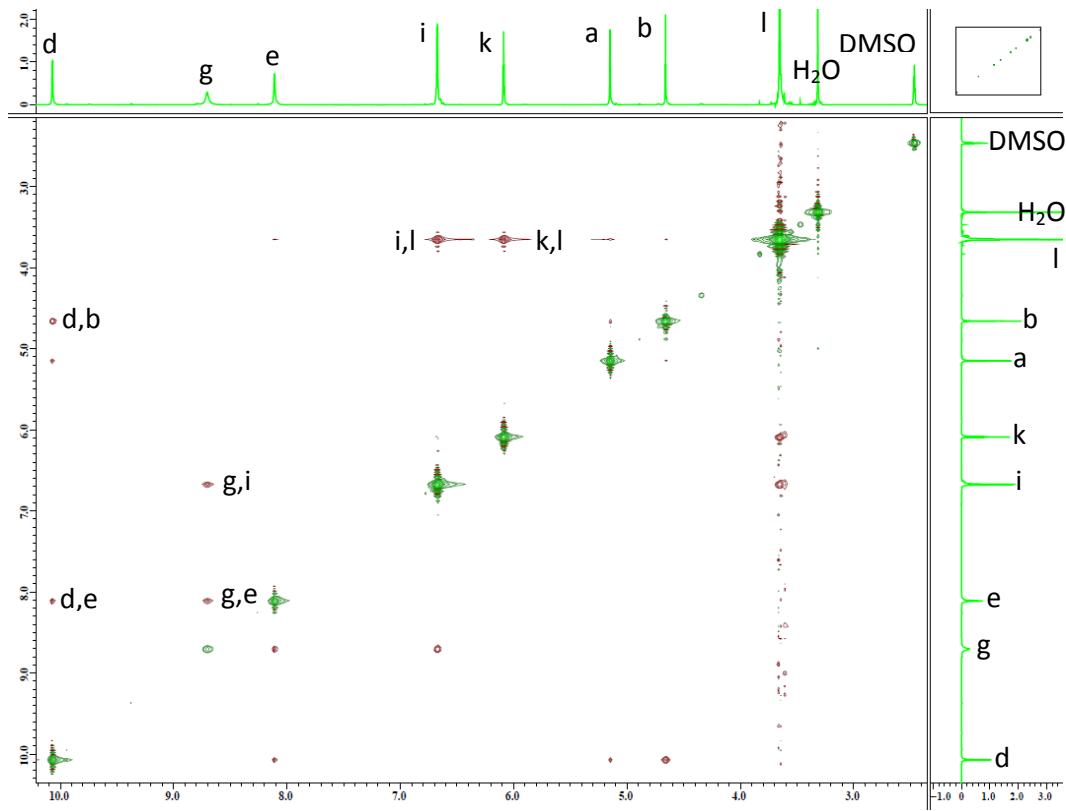
**Figure 19.**  $^{13}\text{C}$  NMR spectrum of macrocycle (**13**) (100 MHz,  $\text{DMSO}-d_6$ ).



**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) ( $\text{DMSO}-d_6$ ).

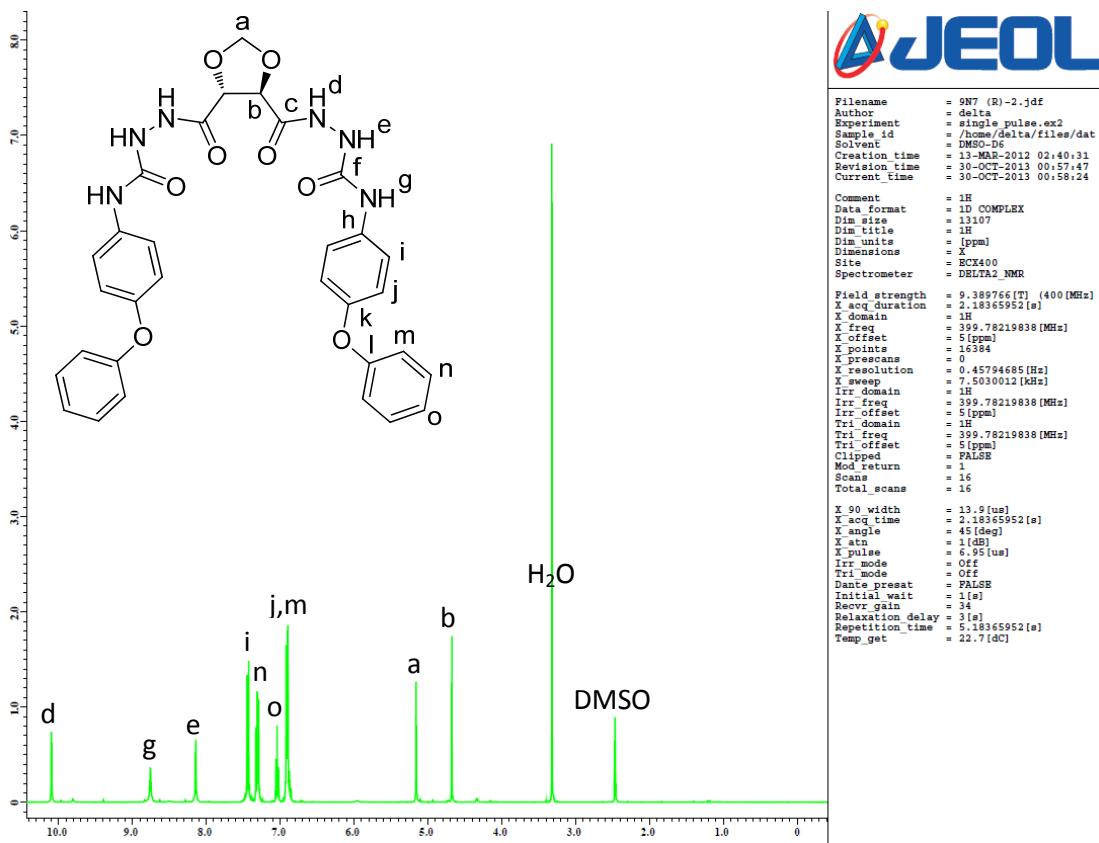


Figure 23.  $^1\text{H}$  NMR spectrum of compound (15) (400 MHz,  $\text{DMSO}-d_6$ ).

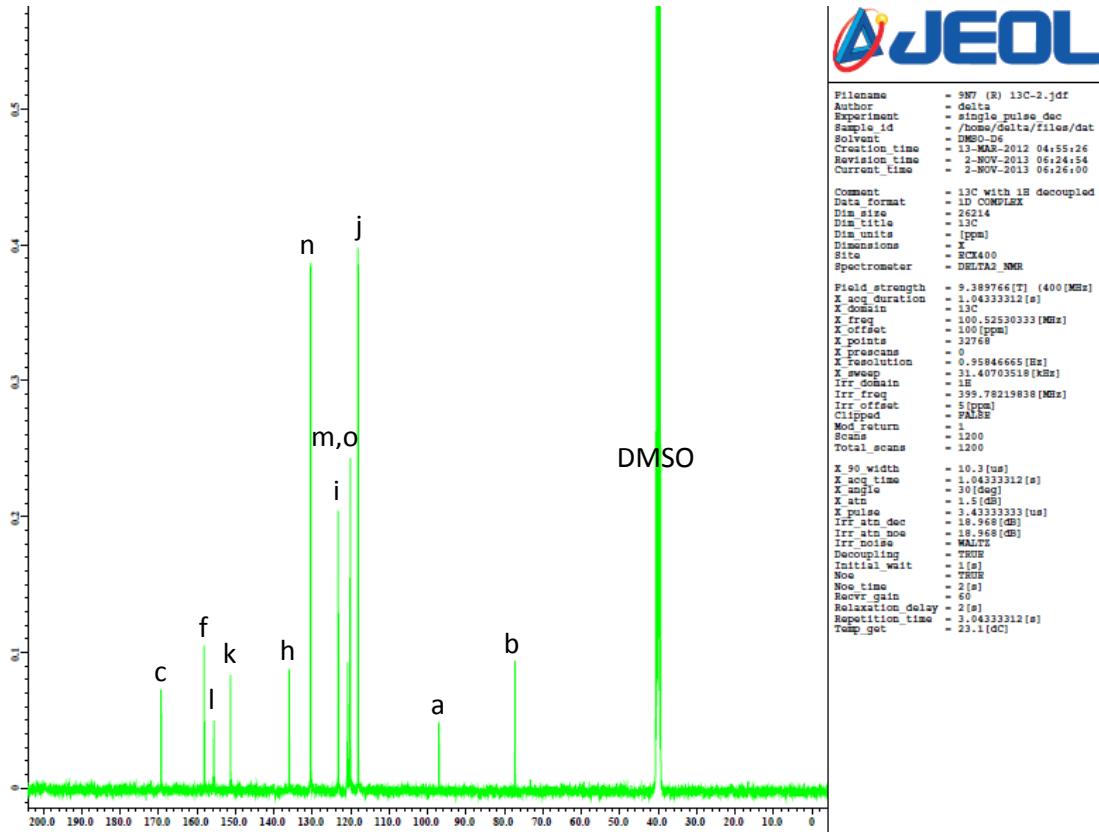
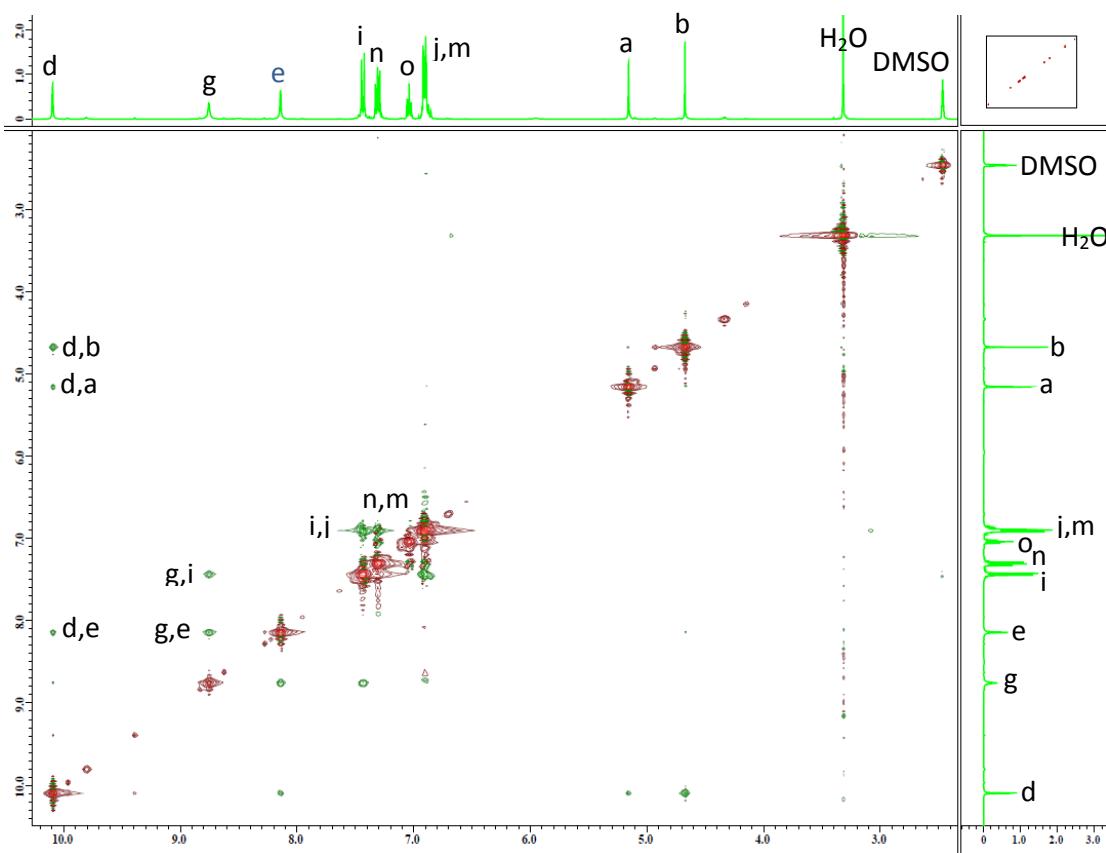
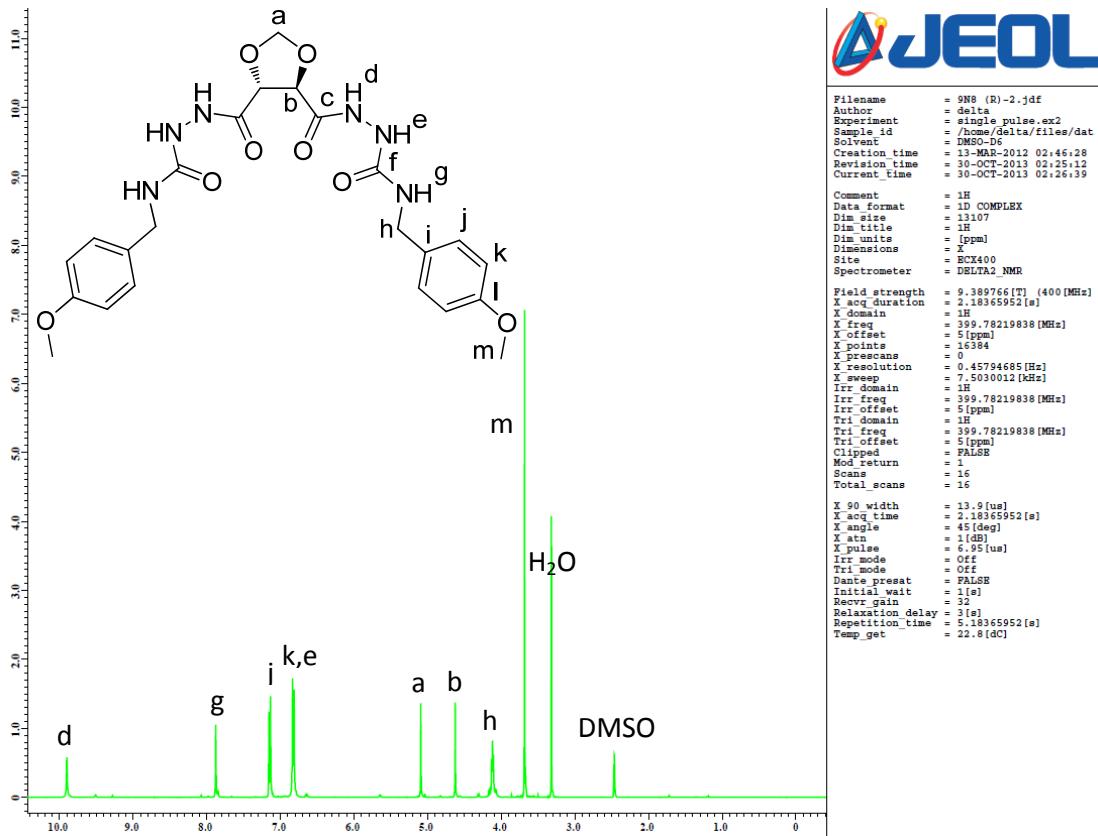


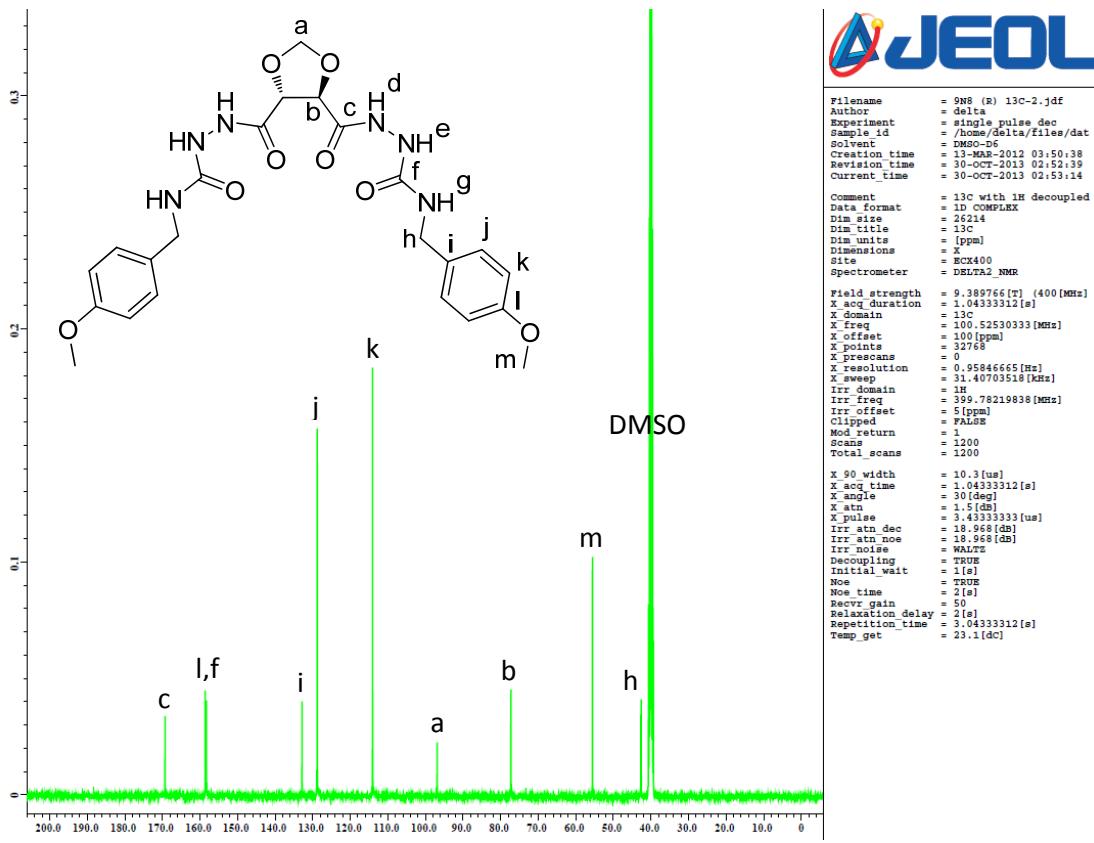
Figure 24.  $^{13}\text{C}$  NMR spectrum of compound (15) (100 MHz,  $\text{DMSO}-d_6$ ).



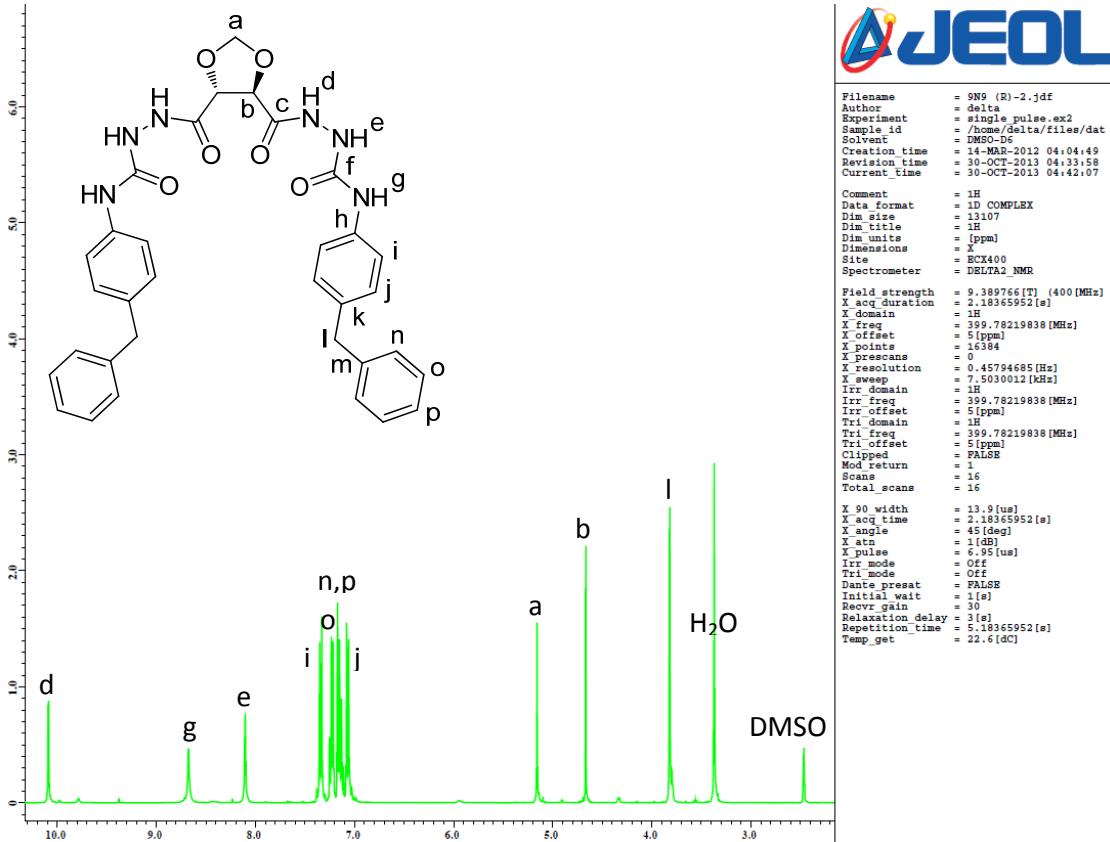
**Figure 25.** 2D ROESY NMR spectrum of compound (**15**) (DMSO-*d*<sub>6</sub>).



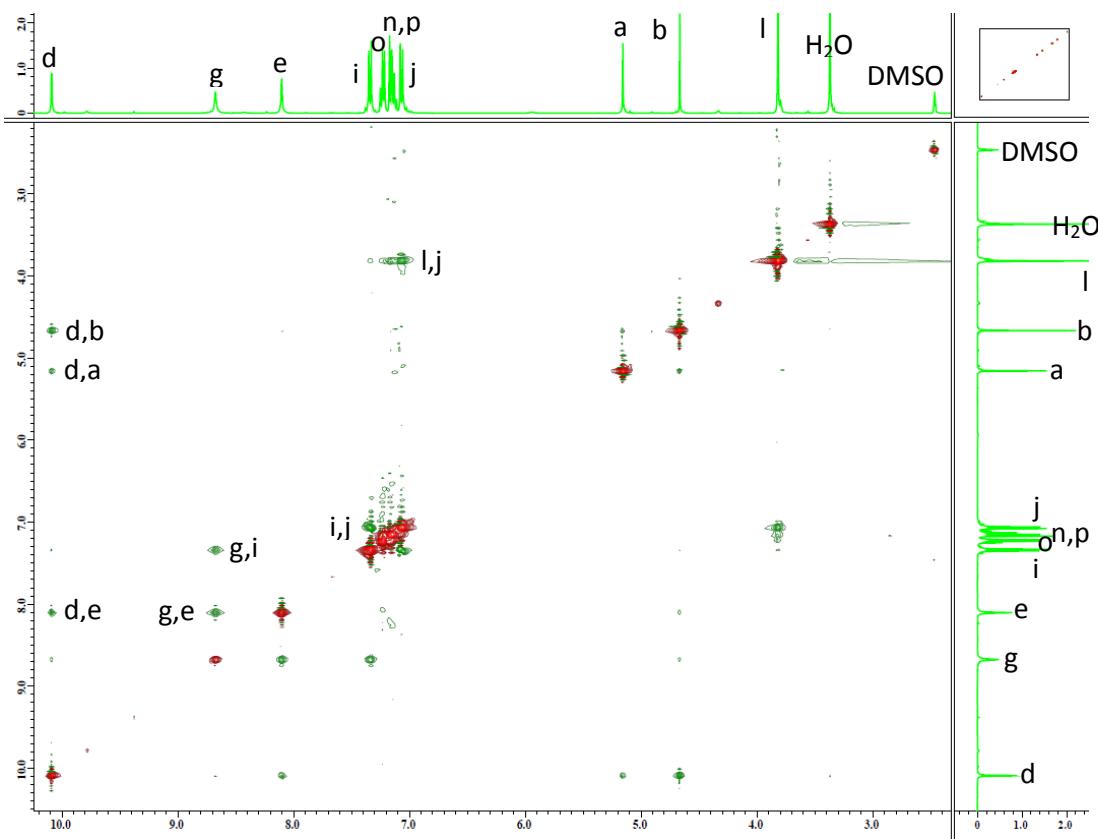
**Figure 26.** <sup>1</sup>H NMR spectrum of compound (**16**) (400 MHz, DMSO-*d*<sub>6</sub>).



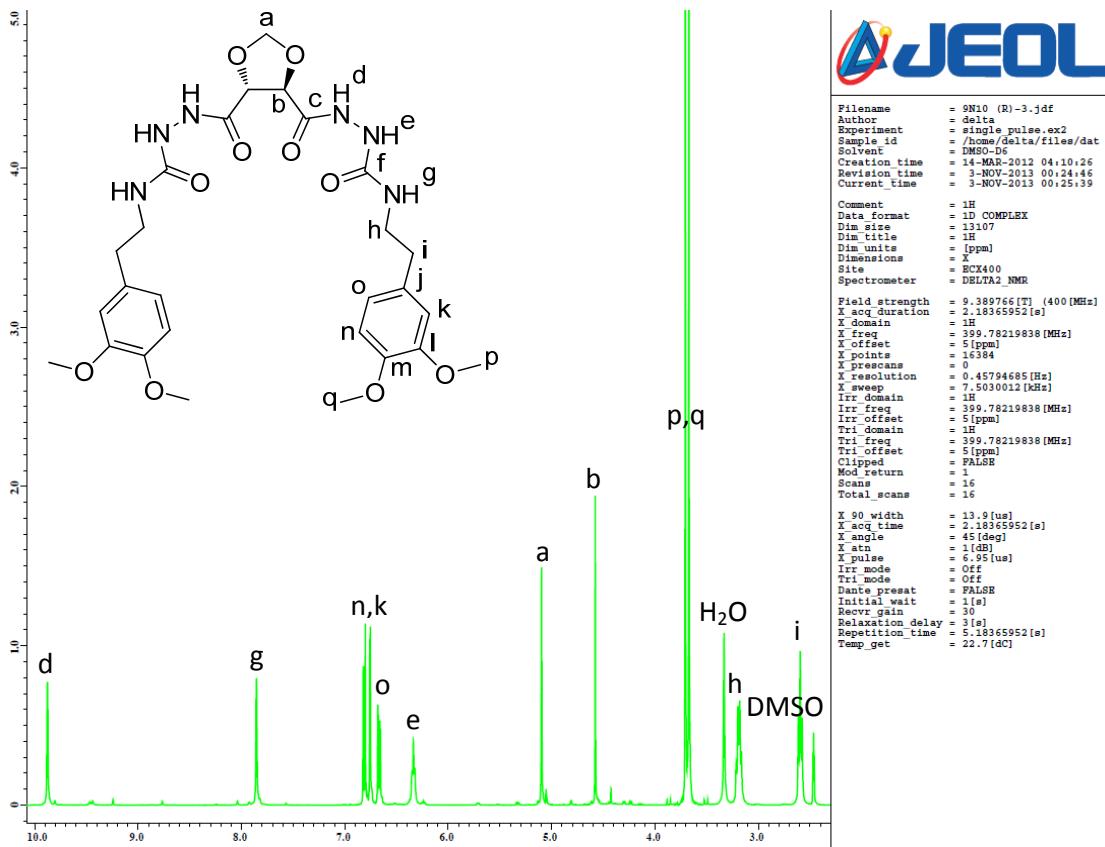
**Figure 27.**  $^{13}\text{C}$  NMR spectrum of compound (**16**) (100 MHz,  $\text{DMSO}-d_6$ ).



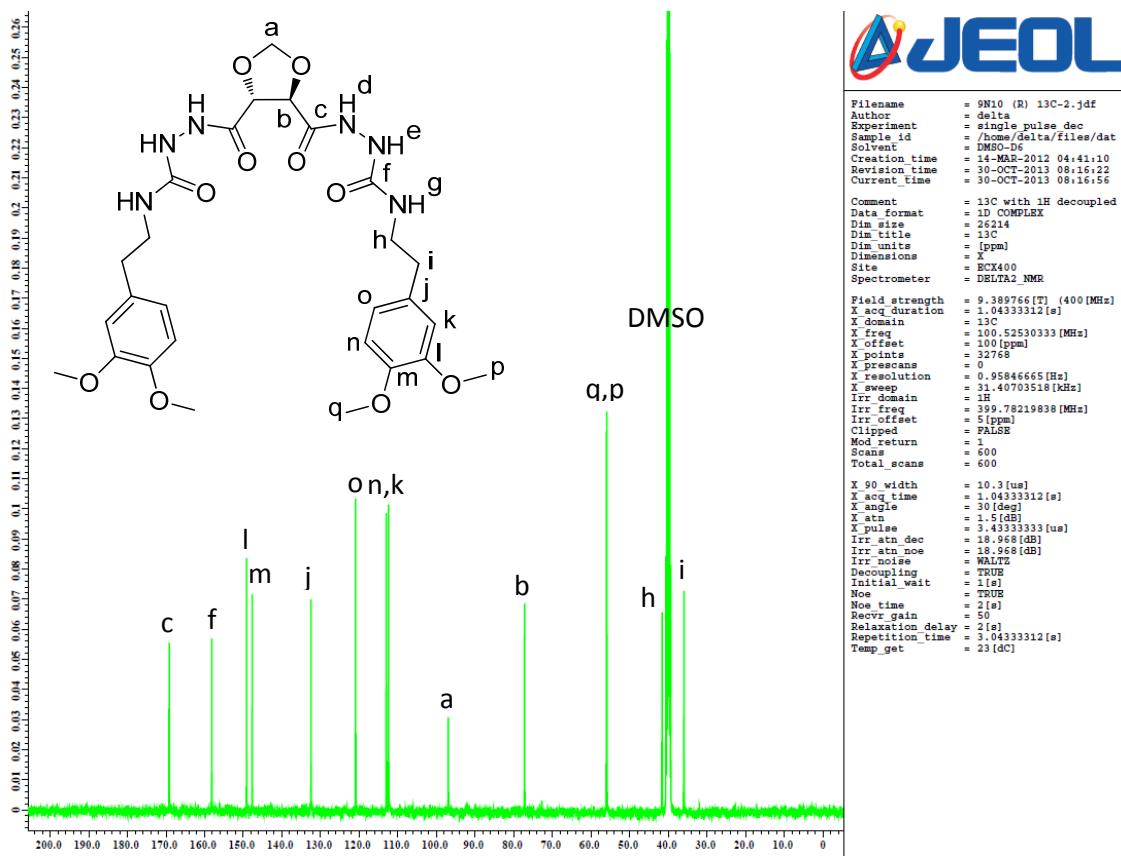
**Figure 28.**  $^1\text{H}$  NMR spectrum of compound (**17**) (400 MHz,  $\text{DMSO}-d_6$ ).



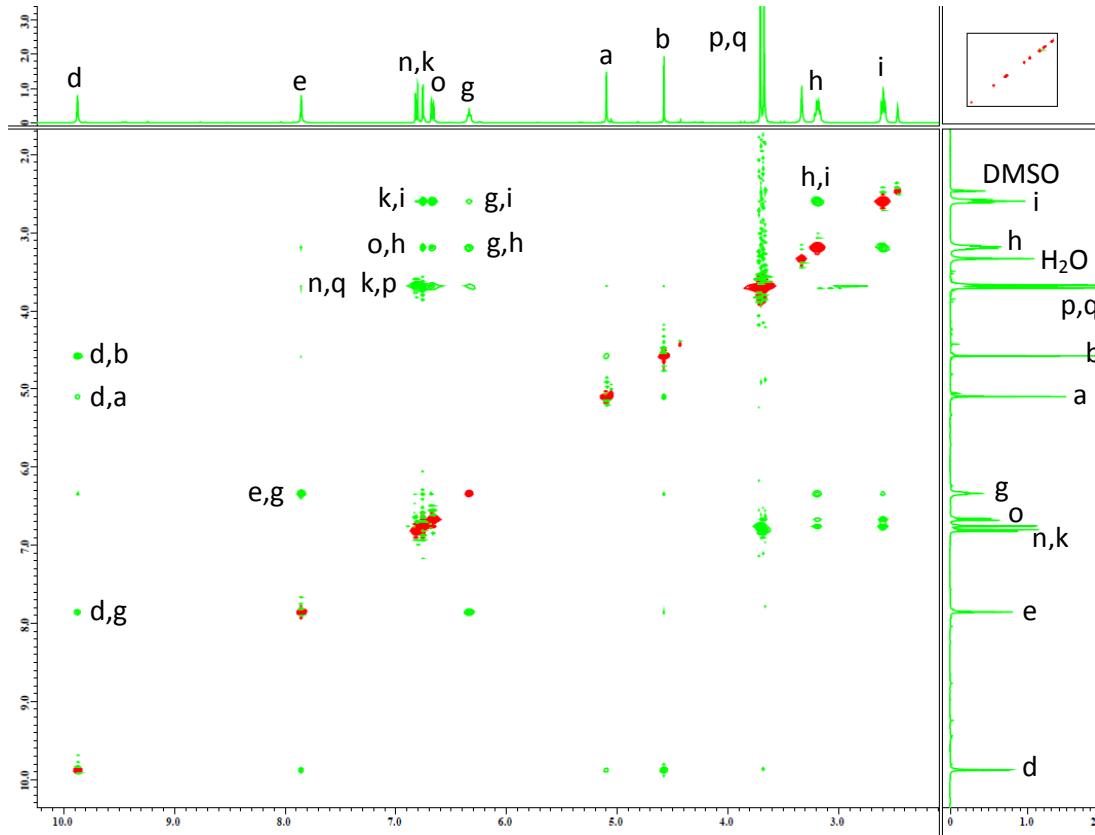
**Figure 29.** 2D ROESY NMR spectrum of compound (17) (DMSO-*d*<sub>6</sub>).



**Figure 30.** <sup>1</sup>H NMR spectrum of compound (18) (400 MHz, DMSO-*d*<sub>6</sub>).



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



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

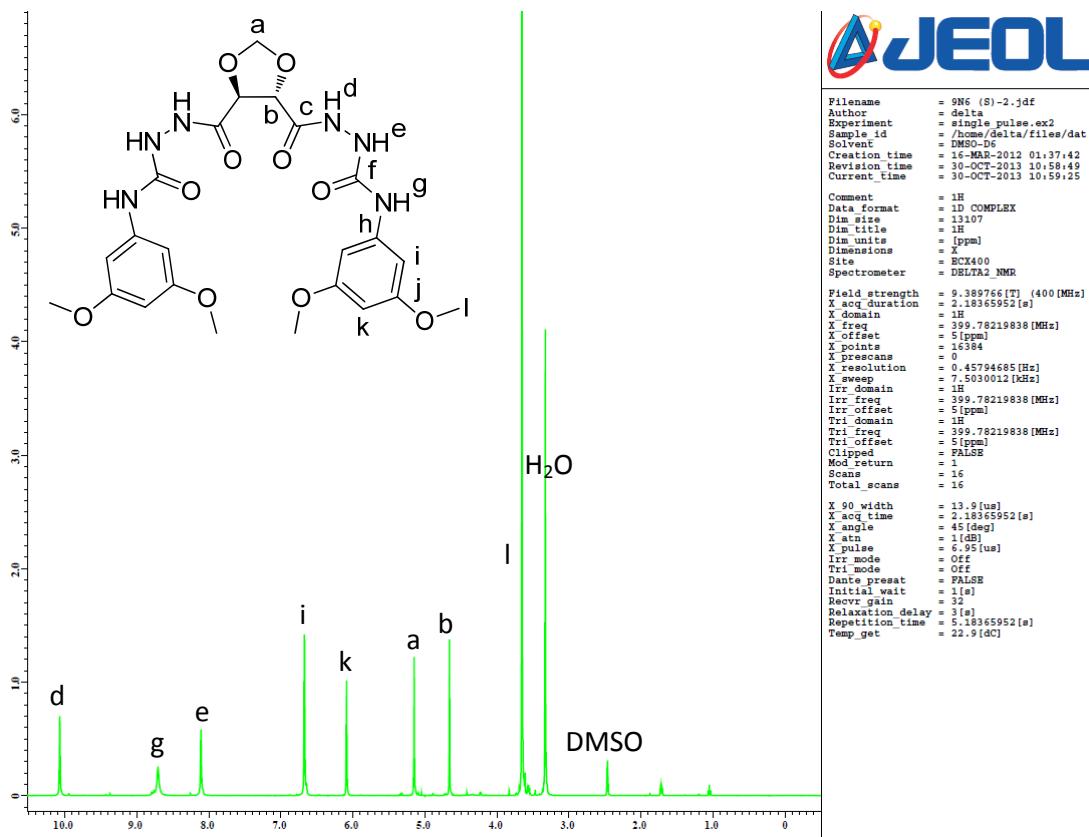


Figure 33.  $^1\text{H}$  NMR spectrum of compound (19) (400 MHz,  $\text{DMSO}-d_6$ ).

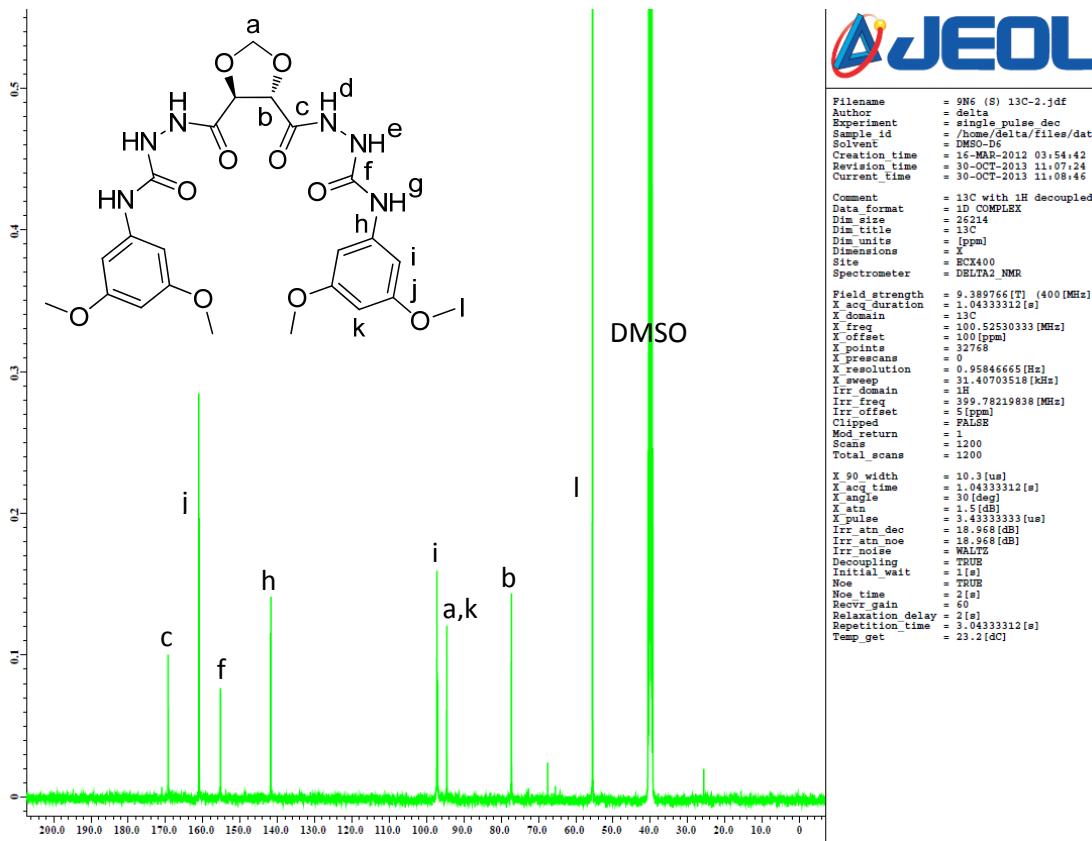
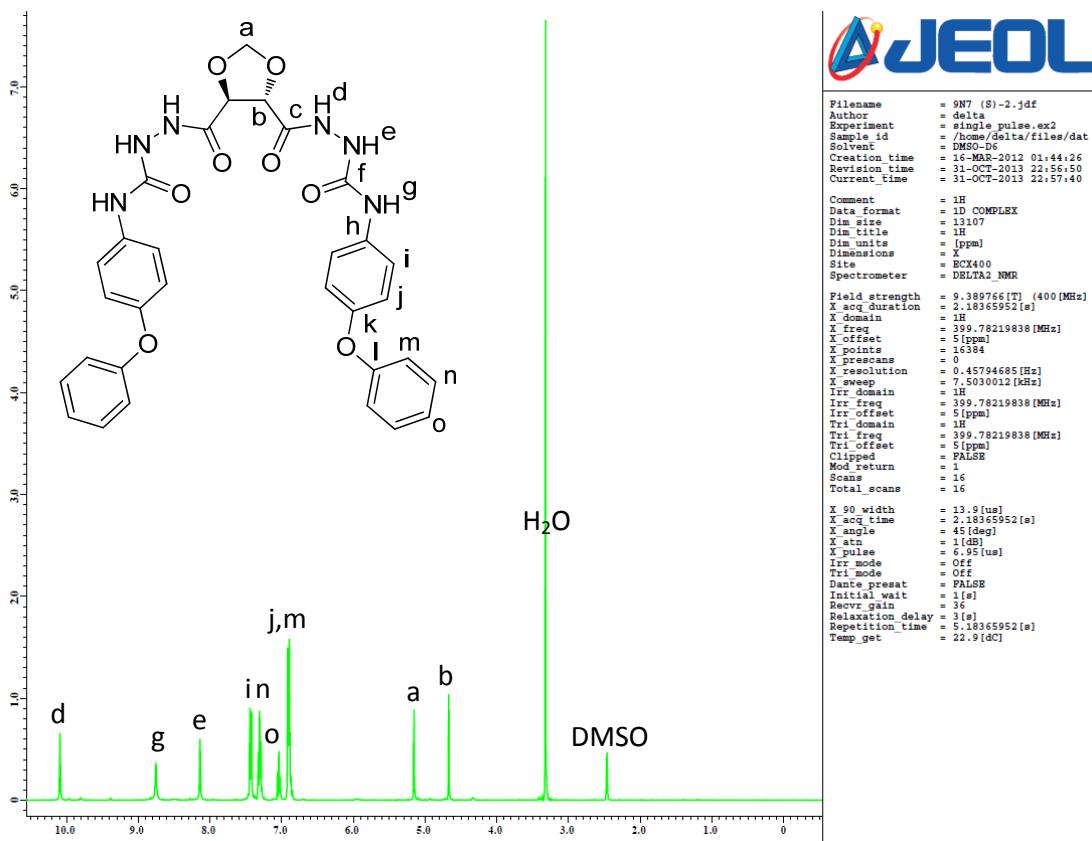
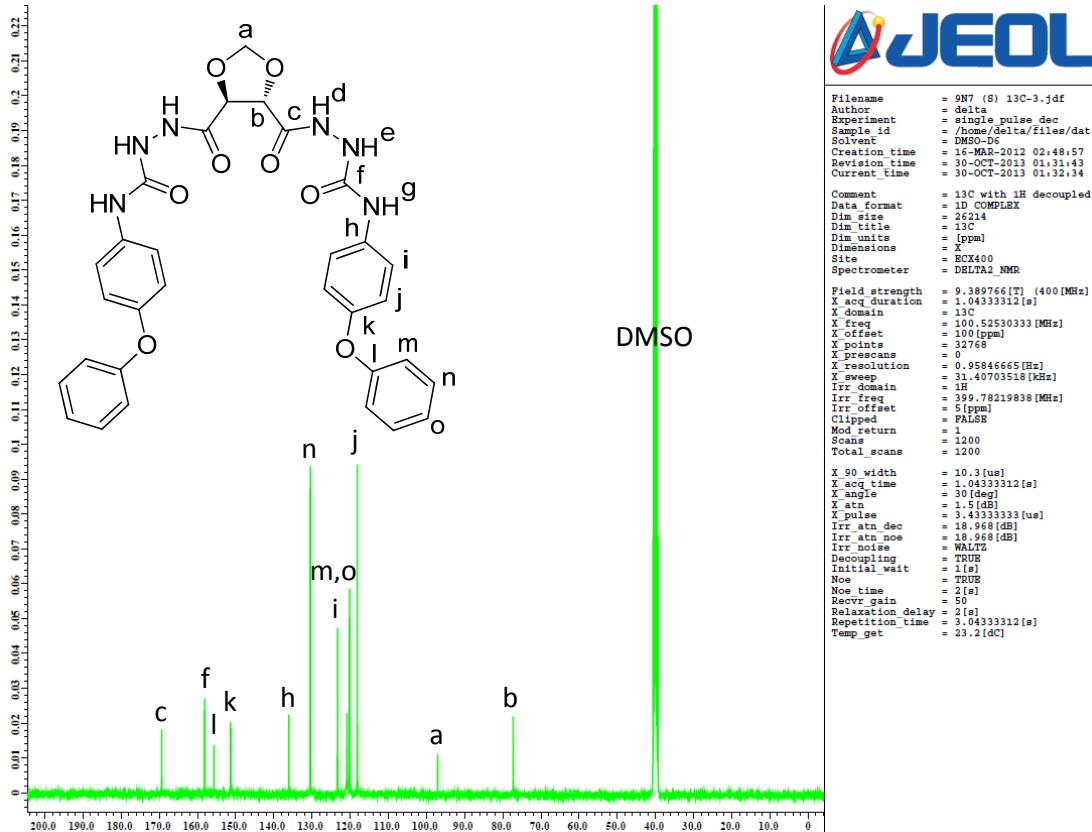


Figure 34.  $^{13}\text{C}$  NMR spectrum of compound (19) (100 MHz,  $\text{DMSO}-d_6$ ).



**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,  $\text{DMSO}-d_6$ ).

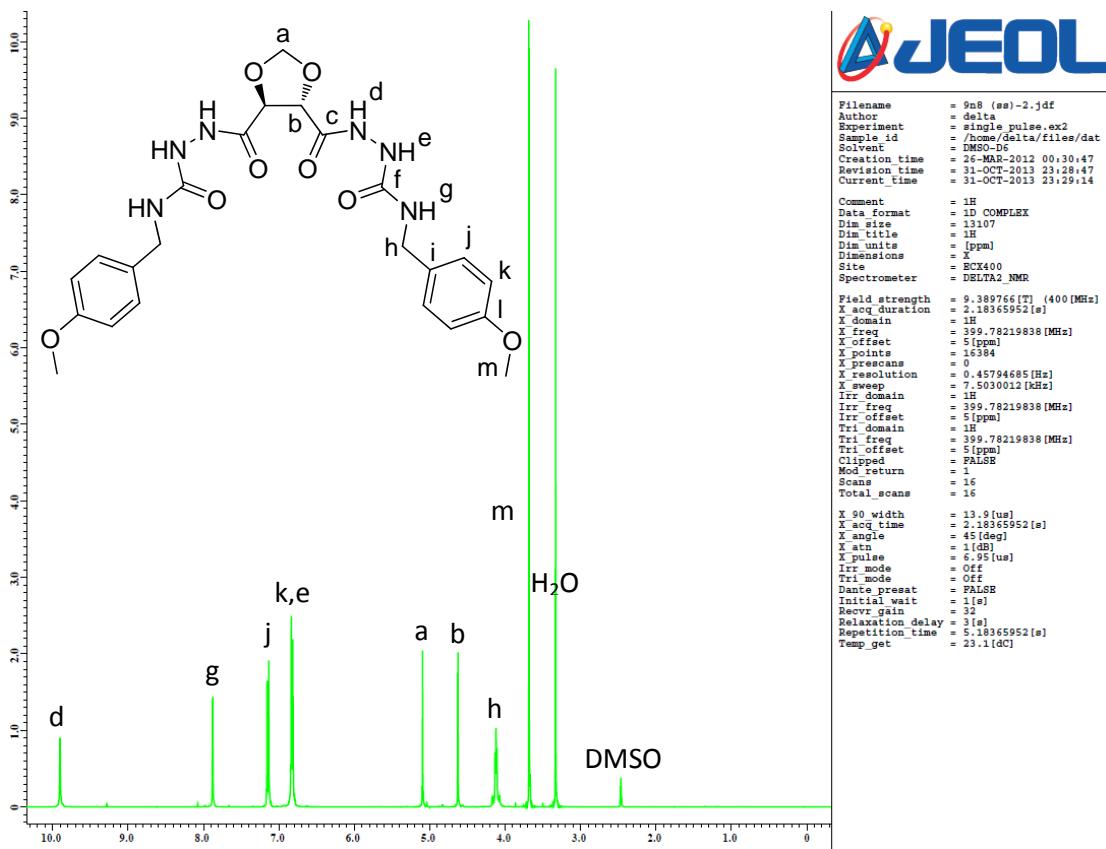


Figure 37.  $^1\text{H}$  NMR spectrum of compound (21) (400 MHz,  $\text{DMSO}-d_6$ ).

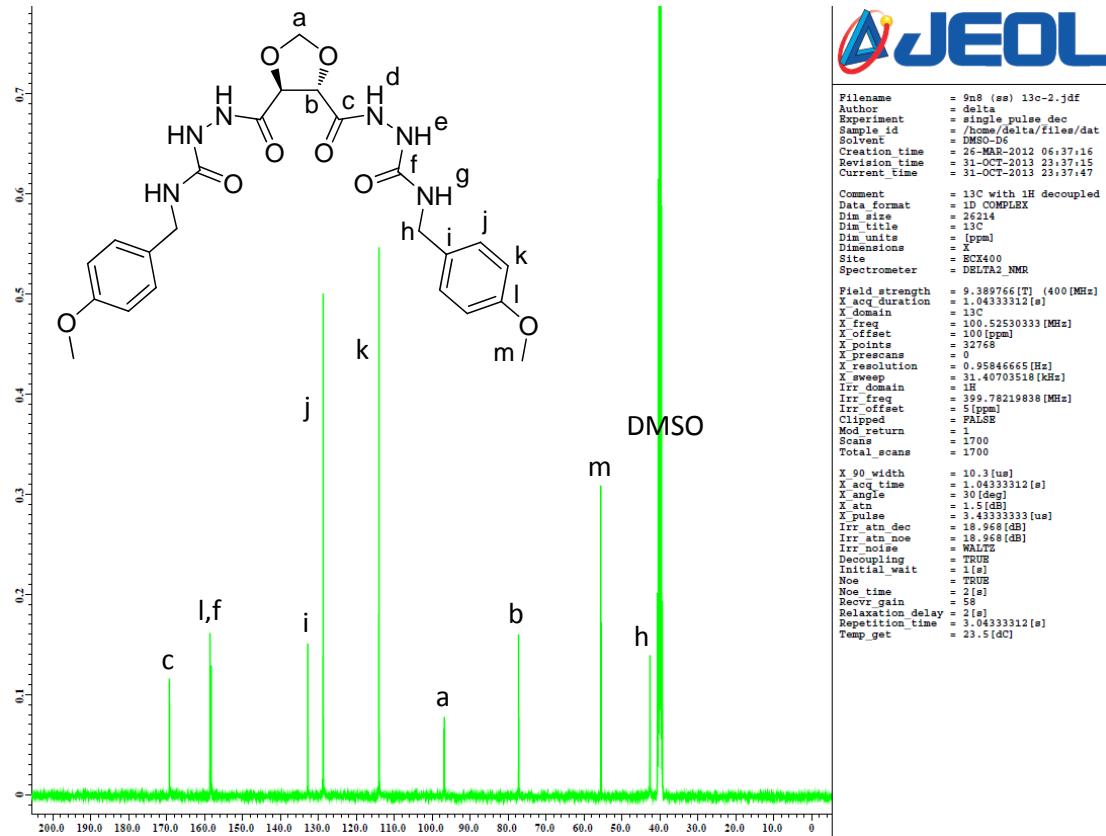
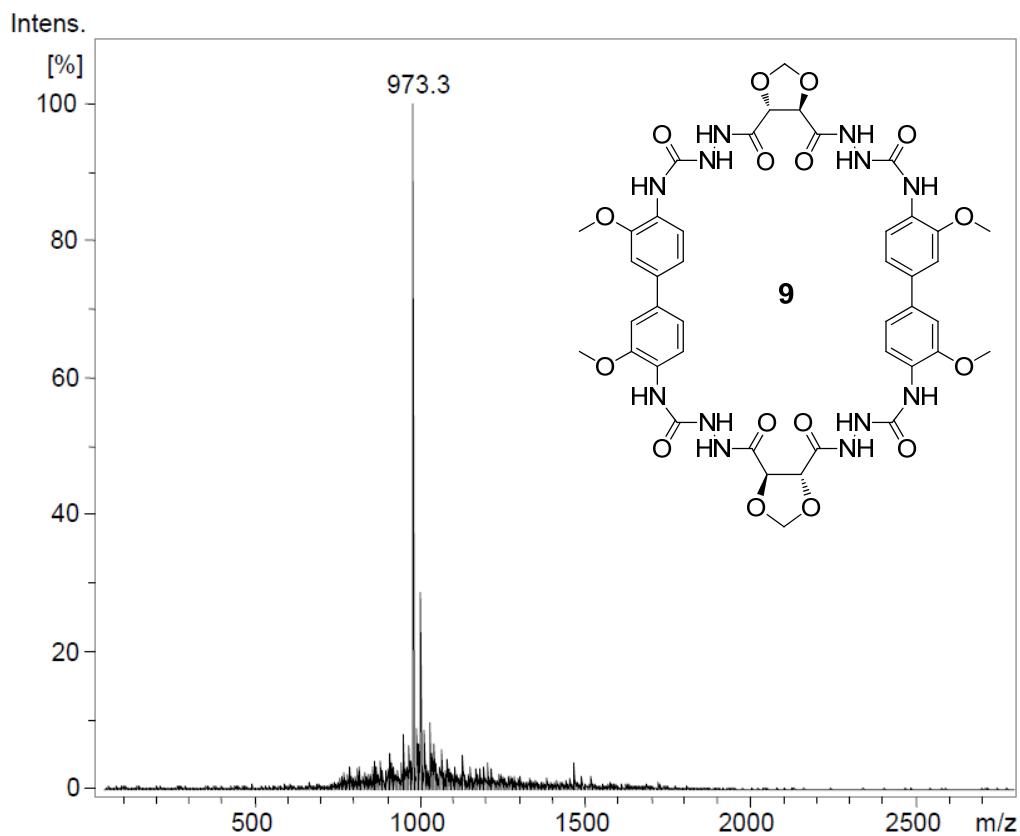
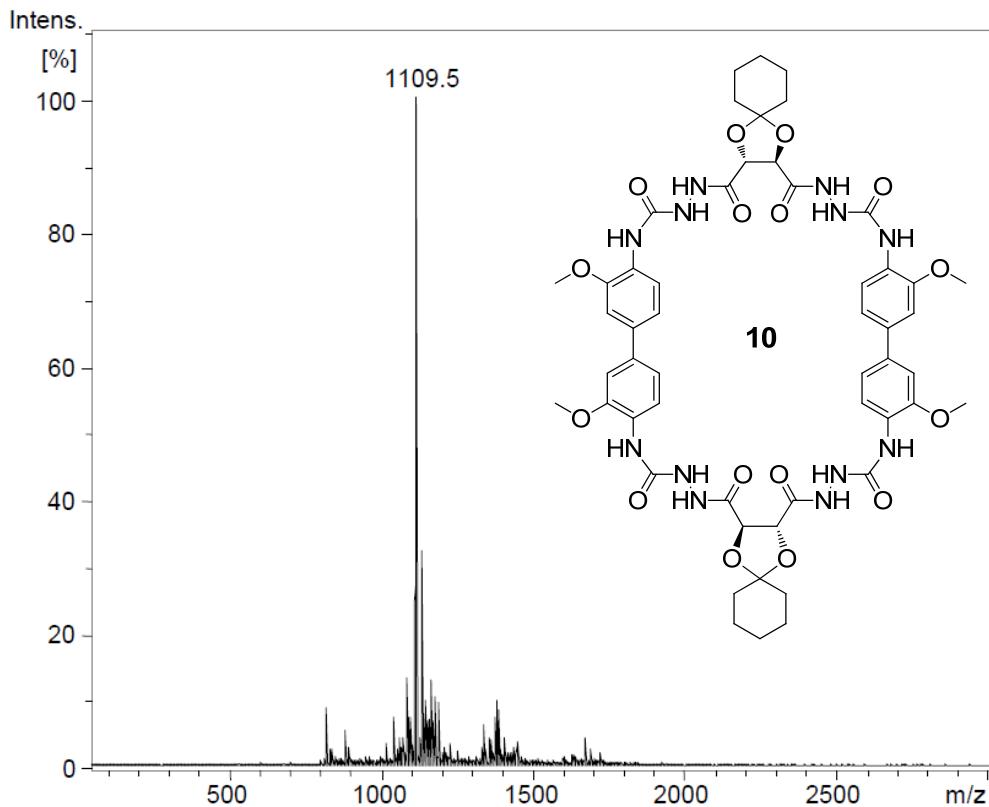


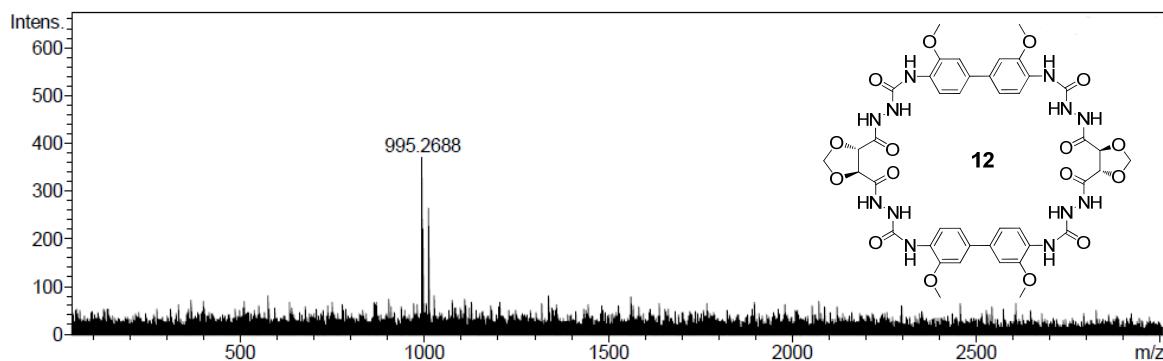
Figure 38.  $^{13}\text{C}$  NMR spectrum of compound (21) (100 MHz,  $\text{DMSO}-d_6$ ).



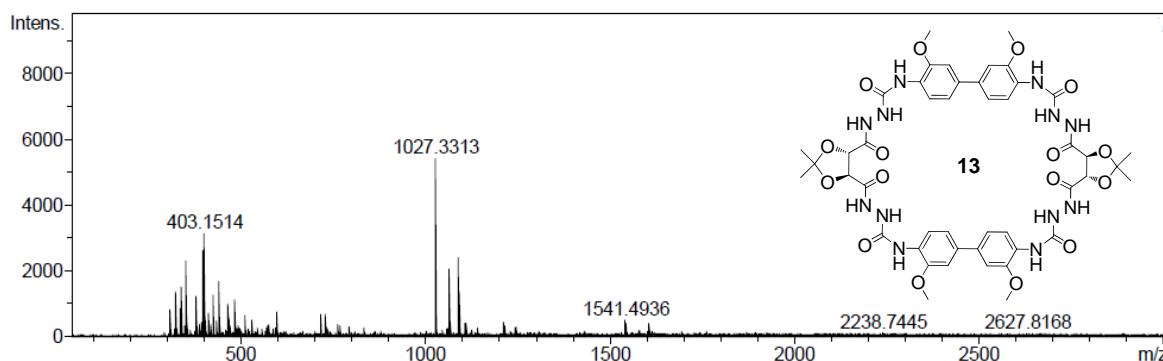
**Figure 39.** ESI-TOF MS of macrocycle (**9**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+H]<sup>+</sup>).



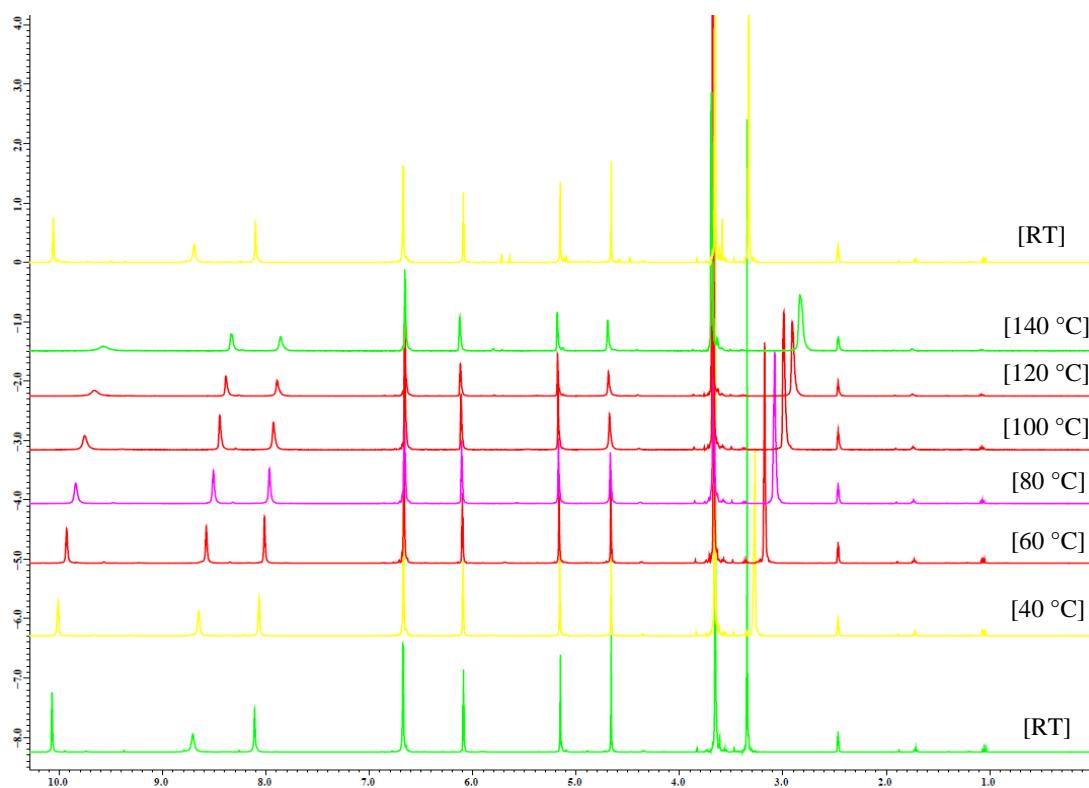
**Figure 40.** ESI-TOF MS of macrocycle (**10**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+H]<sup>+</sup>).



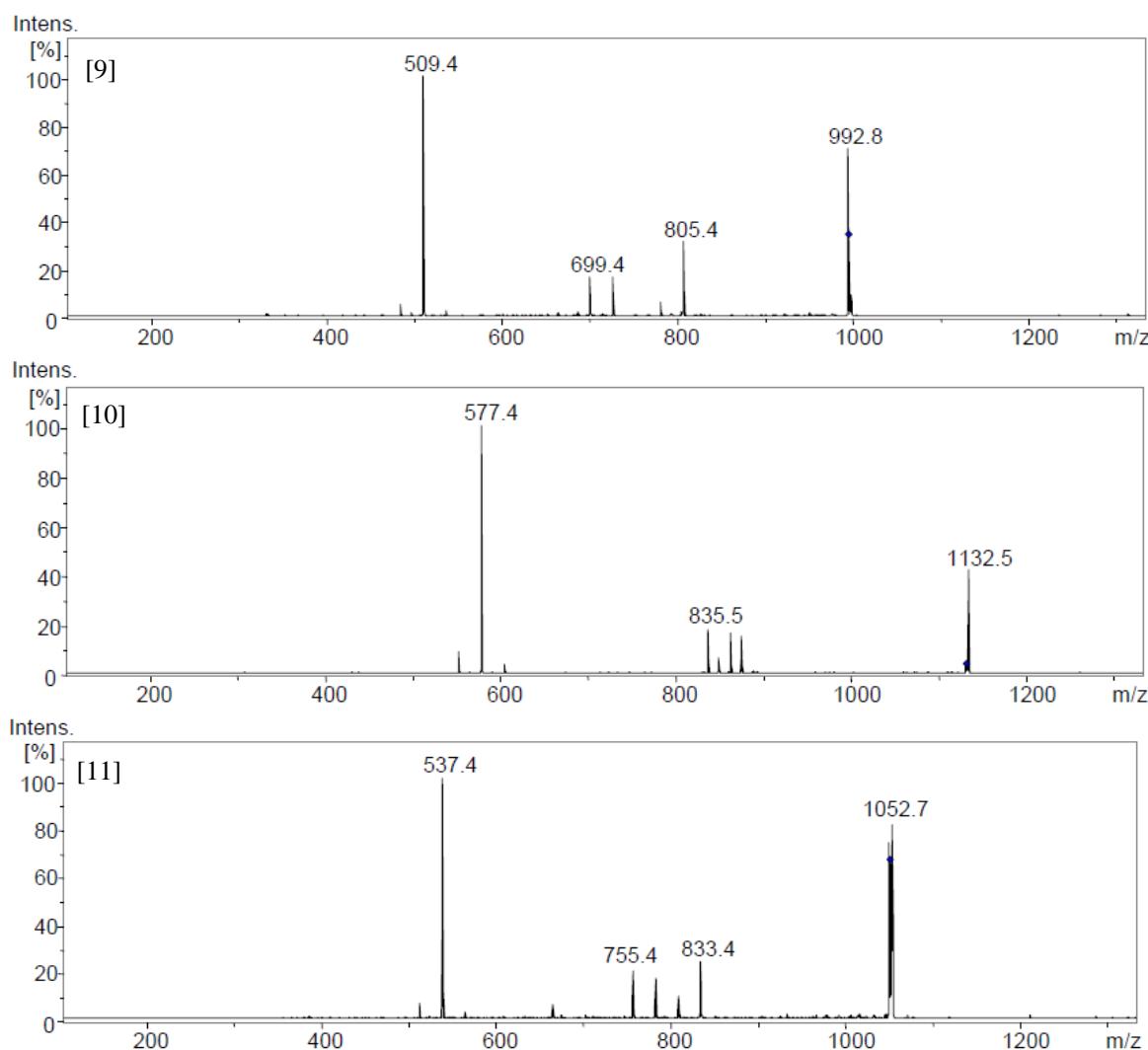
**Figure 41.** ESI-TOF MS of macrocycle (**12**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+Na]<sup>+</sup>).



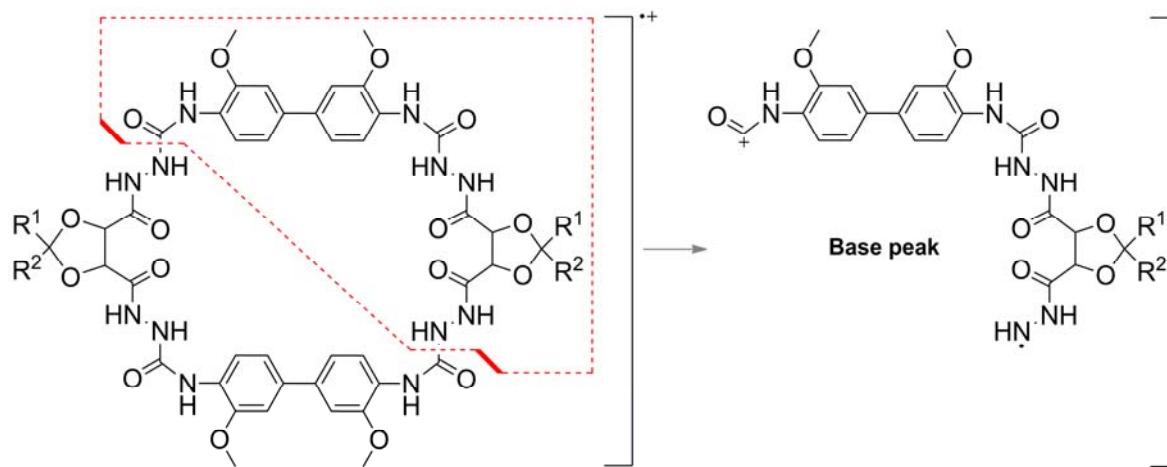
**Figure 42.** ESI-TOF MS of macrocycle (**13**) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



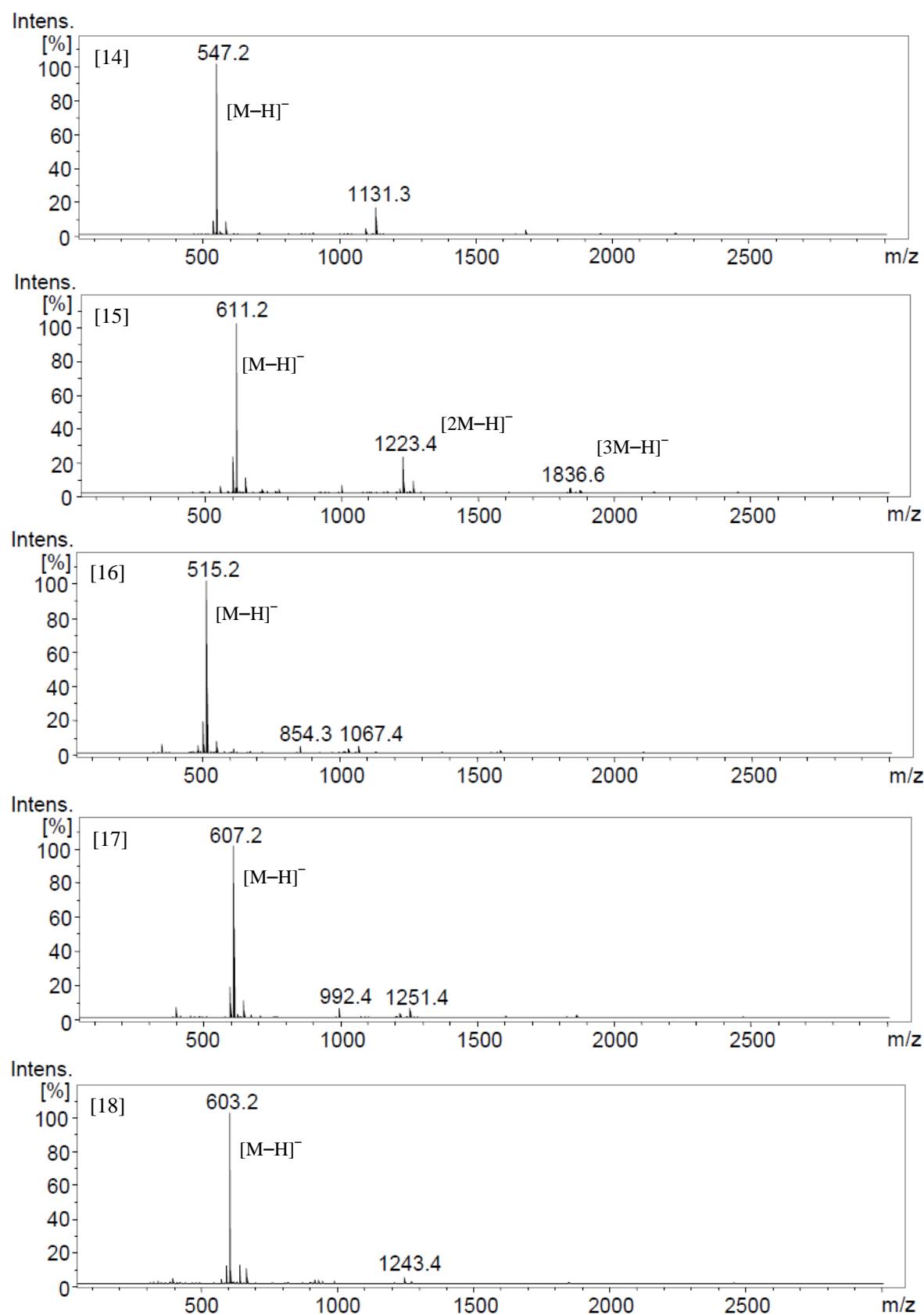
**Figure 43.** Stacked VT-NMR spectra of compound (**14**) (400 MHz, DMSO-*d*<sub>6</sub>).



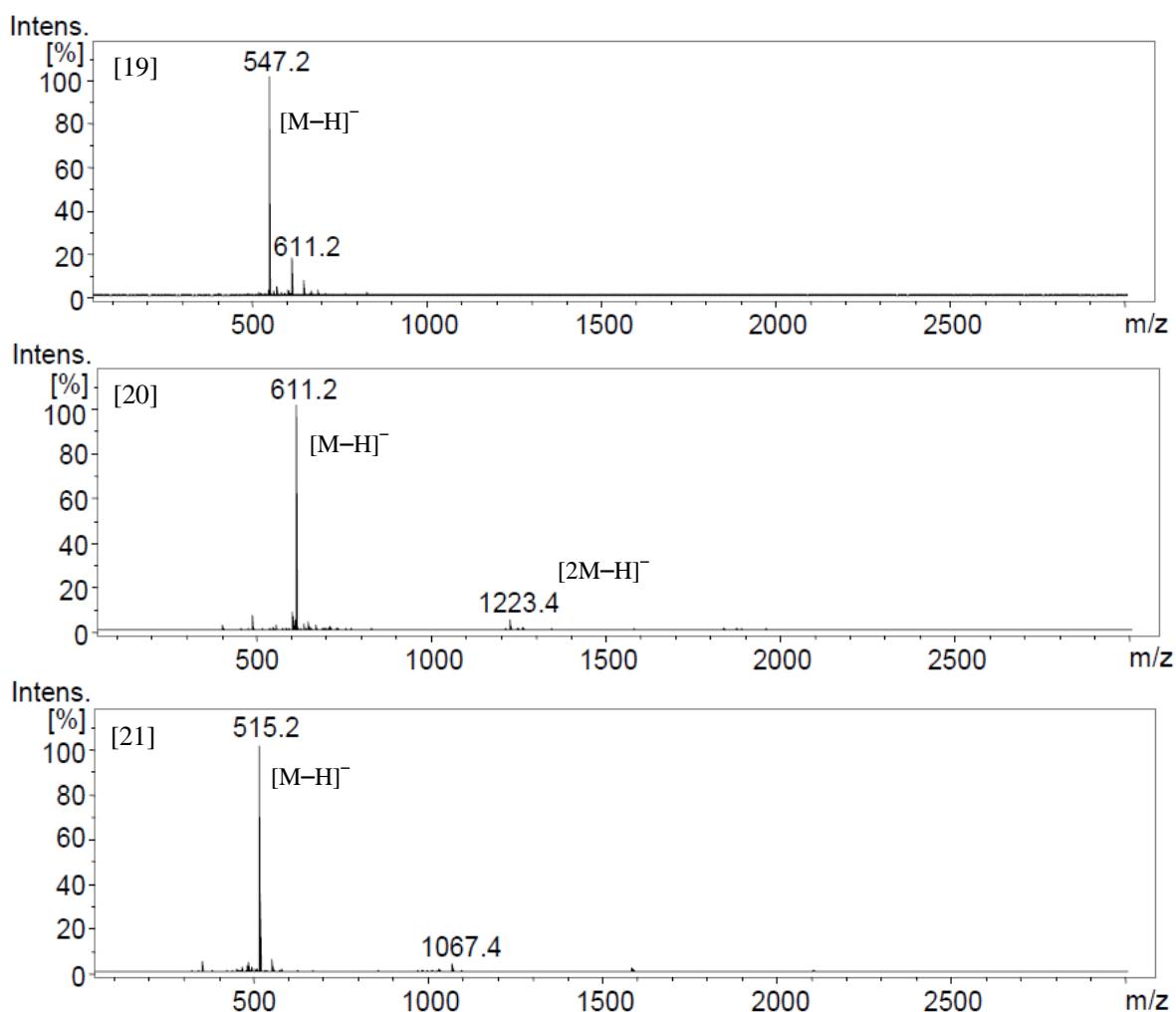
**Figure 44.** ESI-MS/MS of macrocycles (**9-11**) (DMF/CH<sub>3</sub>CN, positive ion mode, [M+Na]<sup>+</sup>).



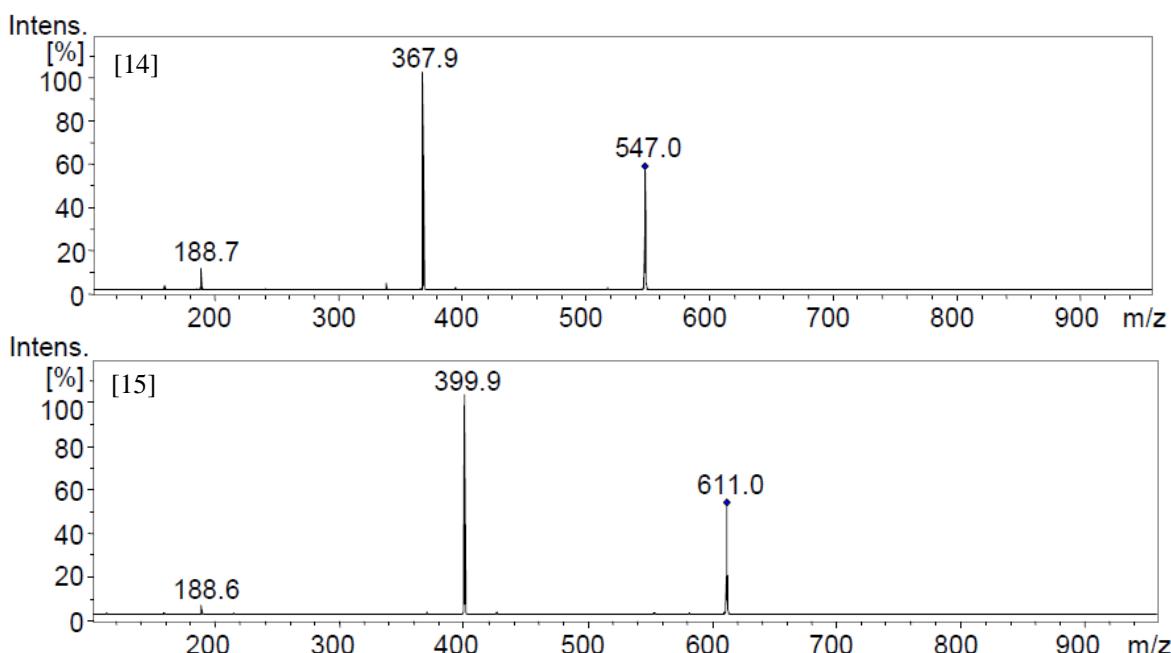
**Figure 45.** Proposed fragmentation mechanism of macrocycles (**9-13**).



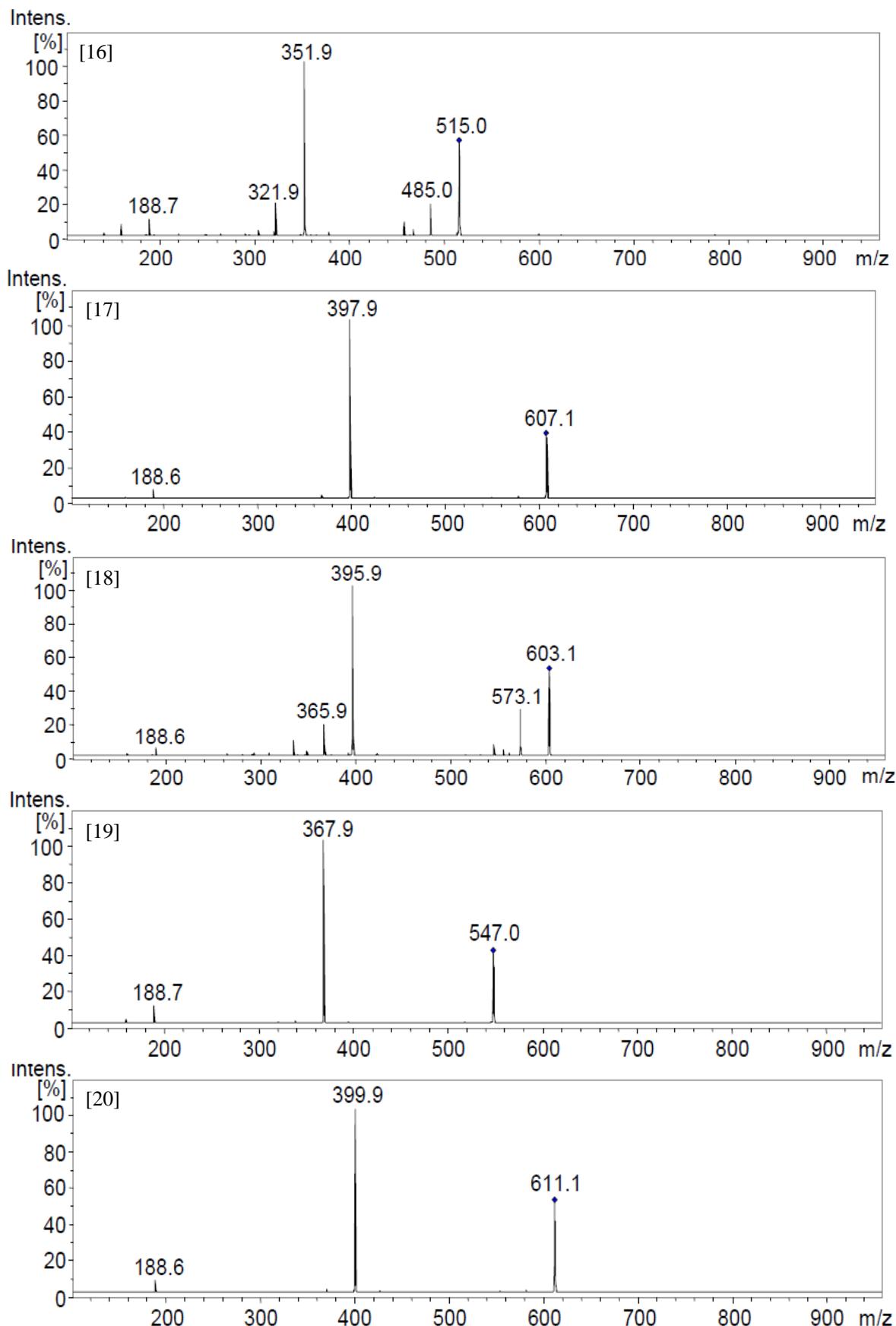
**Figure 46.** ESI-TOF MS of compounds (**14-18**) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



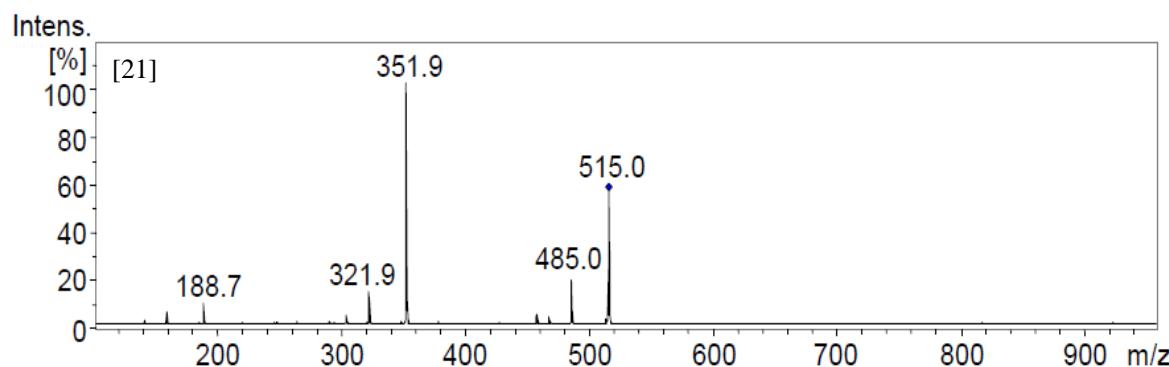
**Figure 47.** ESI-TOF MS of compounds (**19-21**) (DMF/CH<sub>3</sub>CN, negative ion mode,  $[M-H]^-$ ).



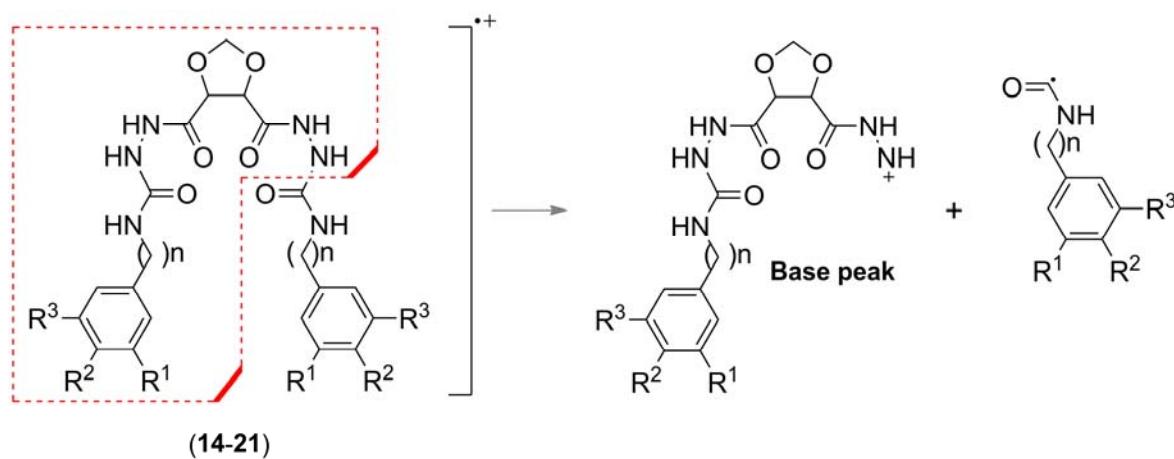
**Figure 48.** ESI-MS/MS of compounds (**14** and **15**) (DMF/CH<sub>3</sub>CN, negative ion mode,  $[M-H]^-$ ).



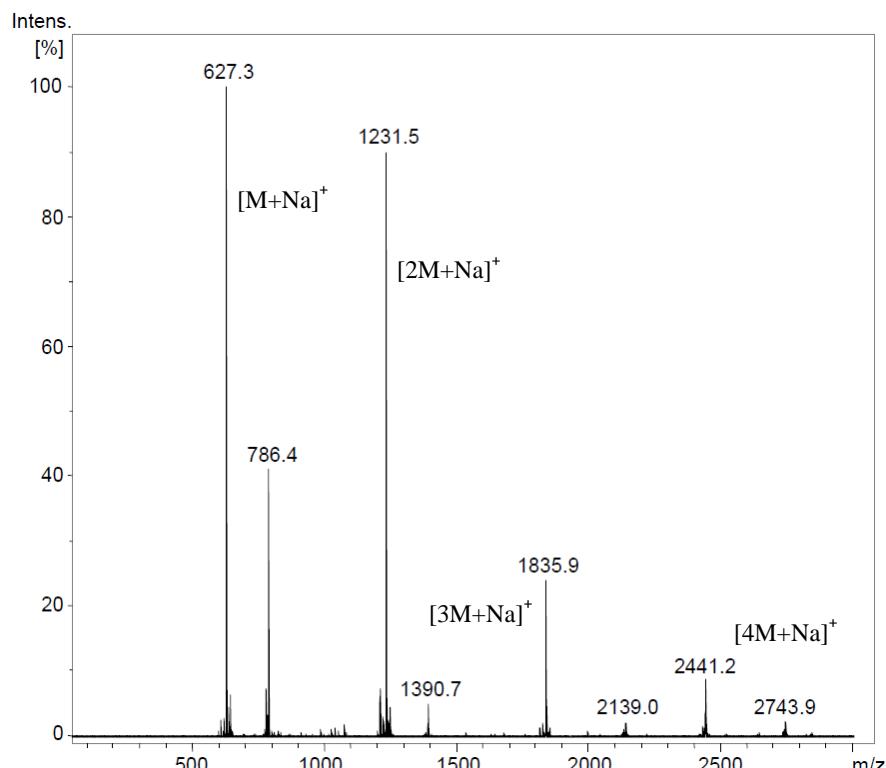
**Figure 49.** ESI-MS/MS of compounds (**16-20**) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



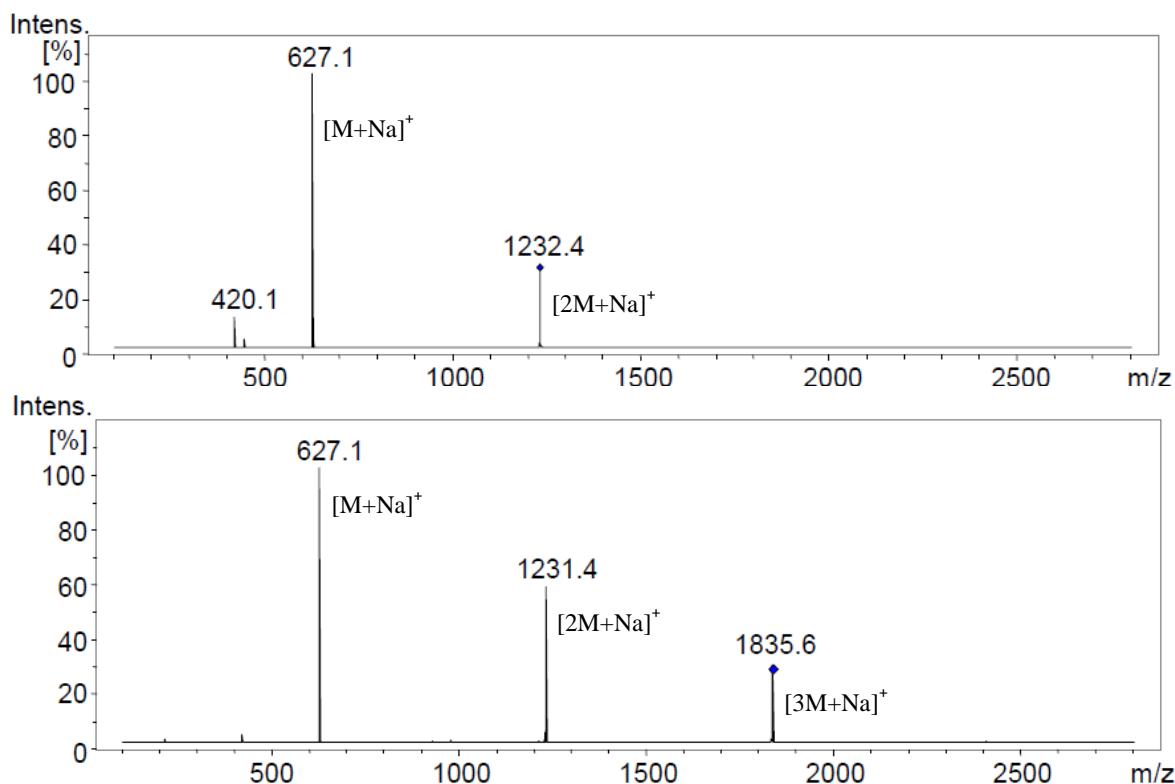
**Figure 50.** ESI-MS/MS of compounds (21) (DMF/CH<sub>3</sub>CN, negative ion mode, [M-H]<sup>-</sup>).



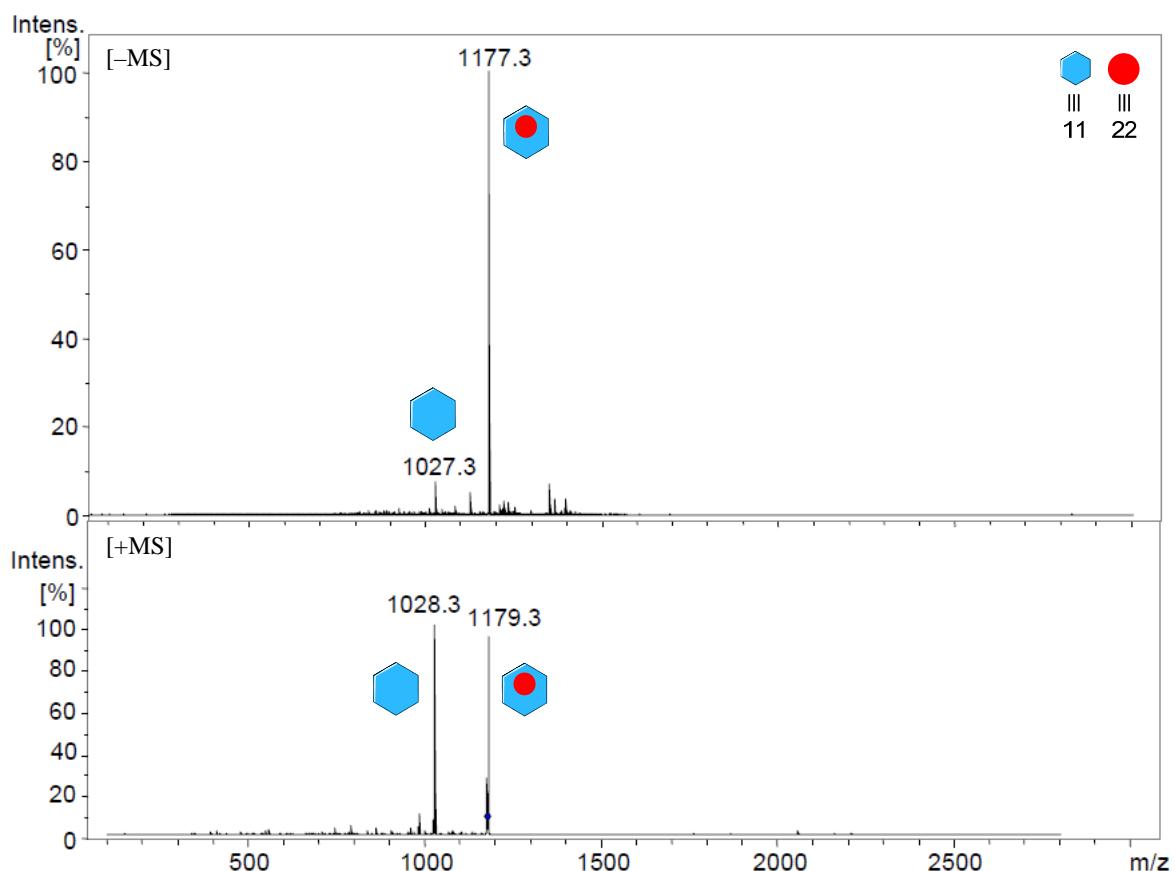
**Figure 51.** Proposed fragmentation mechanism of compounds (14-21).



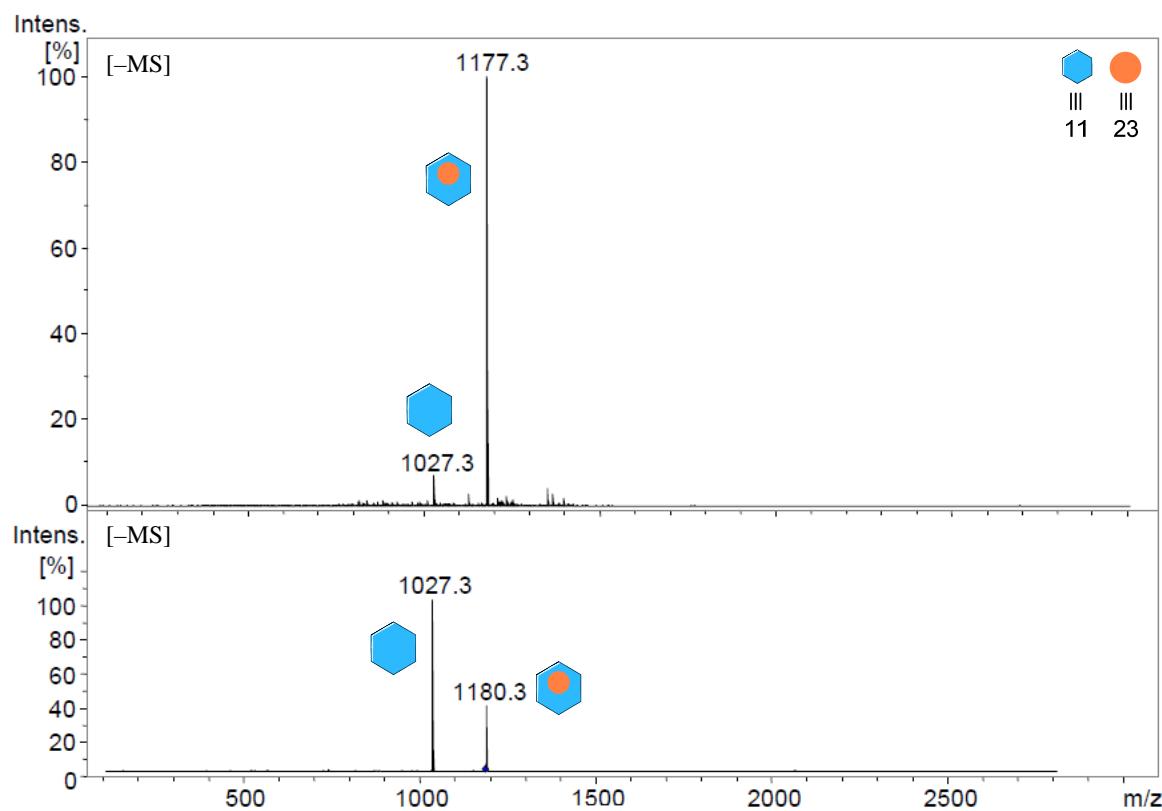
**Figure 52.** ESI-TOF MS for self-assembled associations of compound (18) (CH<sub>3</sub>CN/DMF).



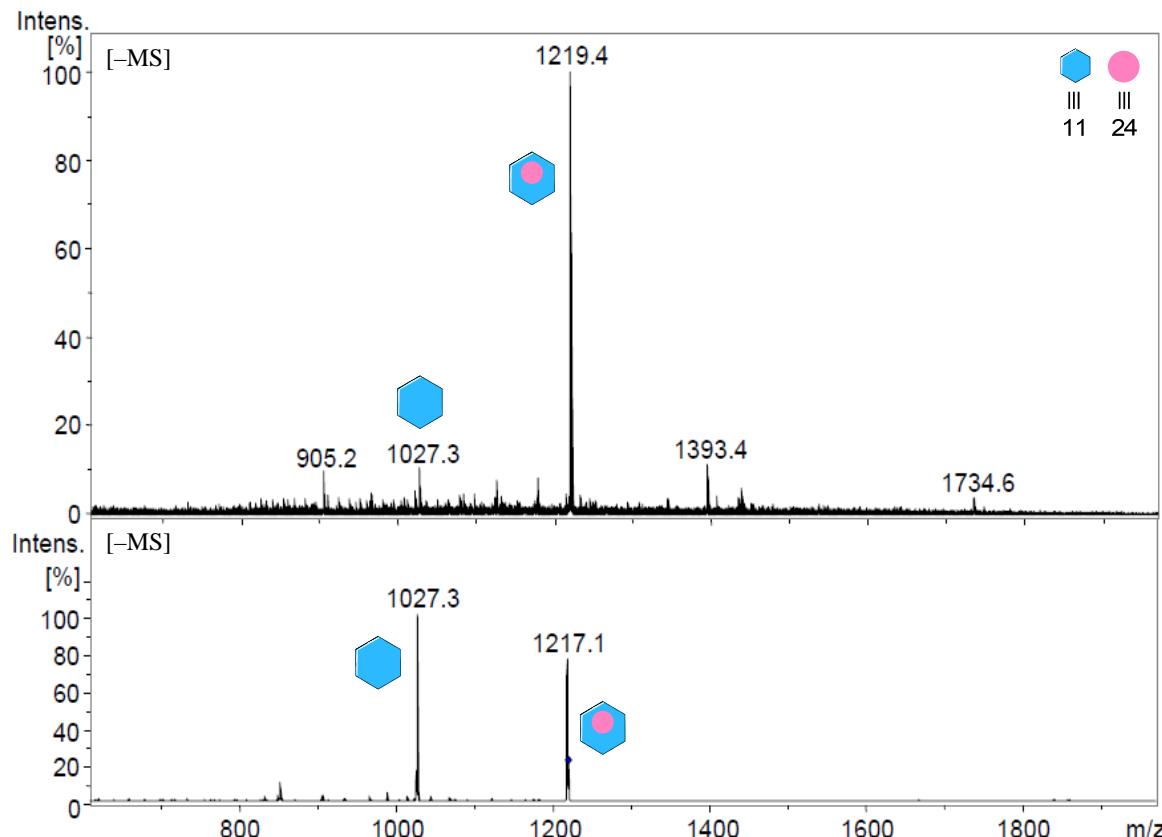
**Figure 53.** ESI-MS/MS of  $m/z$  1231.5 and 1835.9 (DMF/CH<sub>3</sub>CN, positive ion mode, [M+Na]<sup>+</sup>).



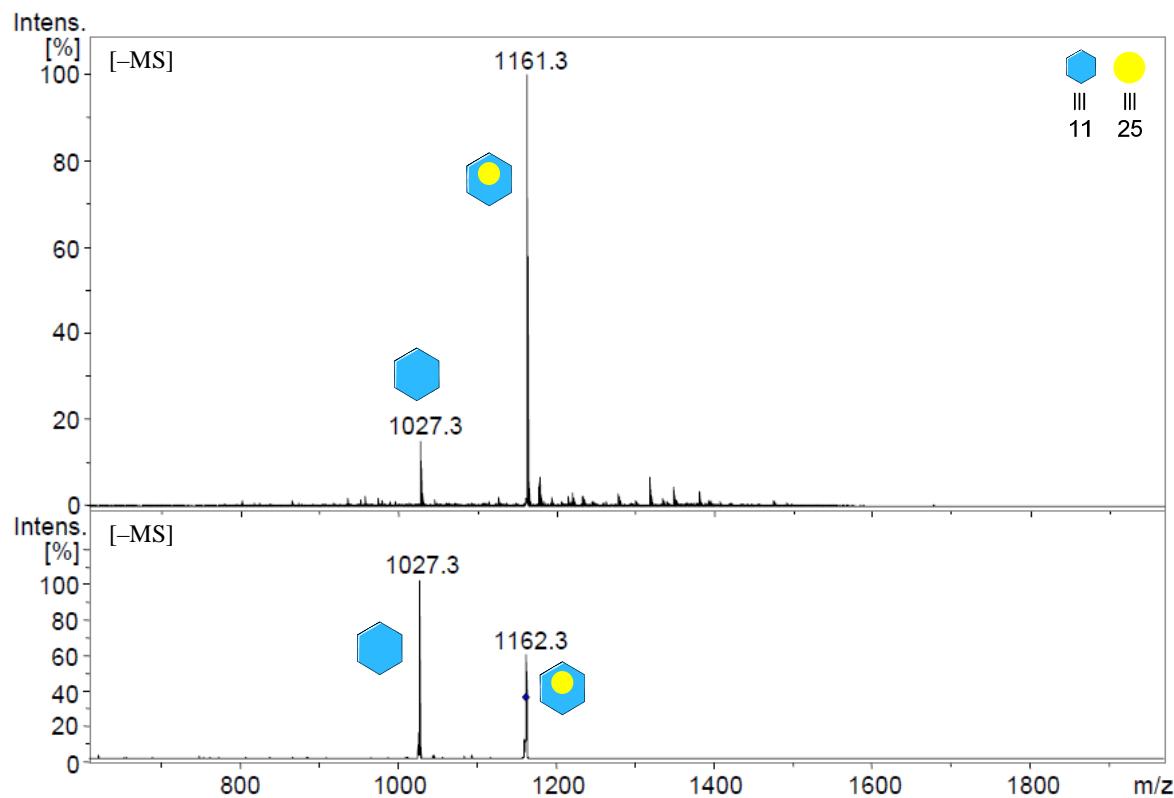
**Figure 54.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/22** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



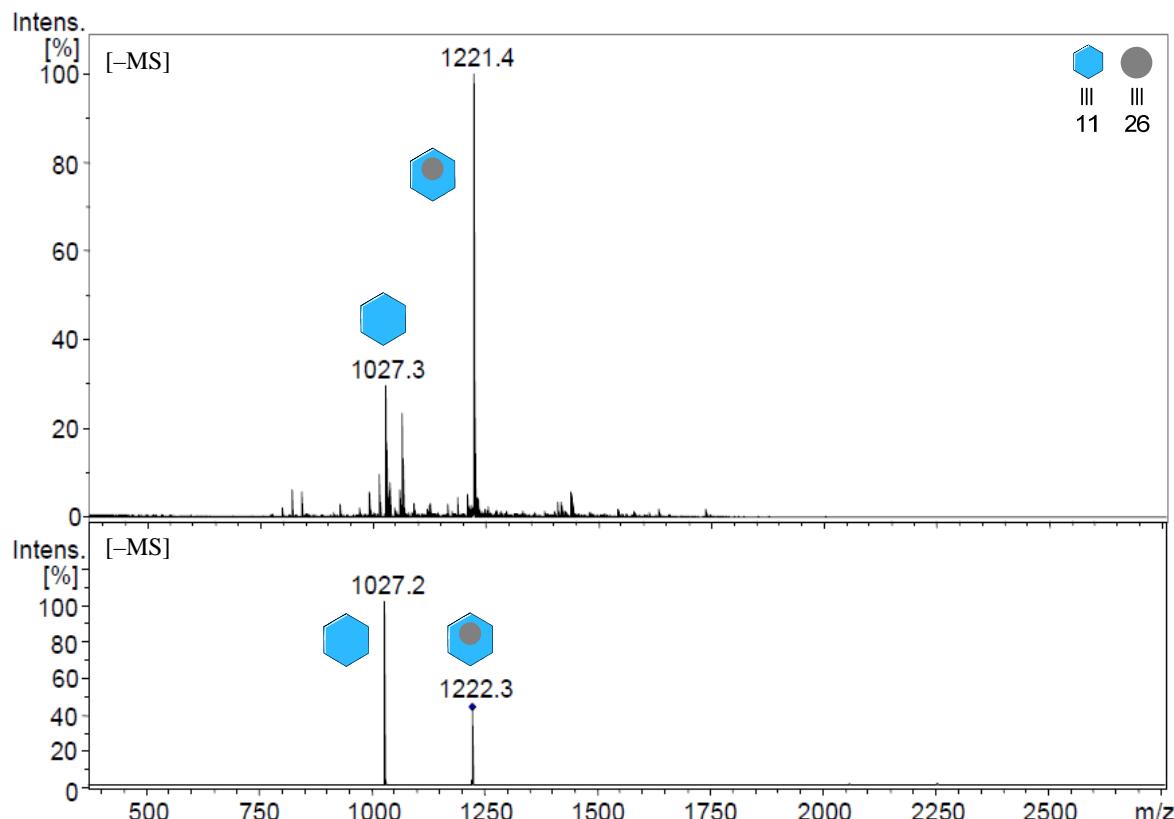
**Figure 55.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/23** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



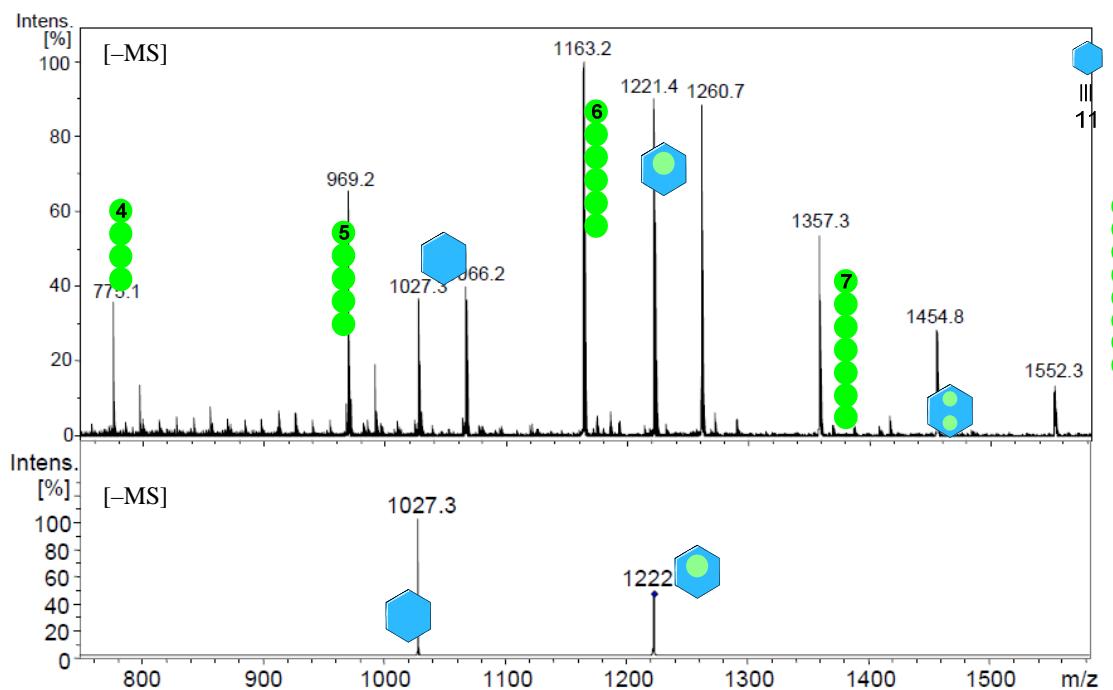
**Figure 56.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/24** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



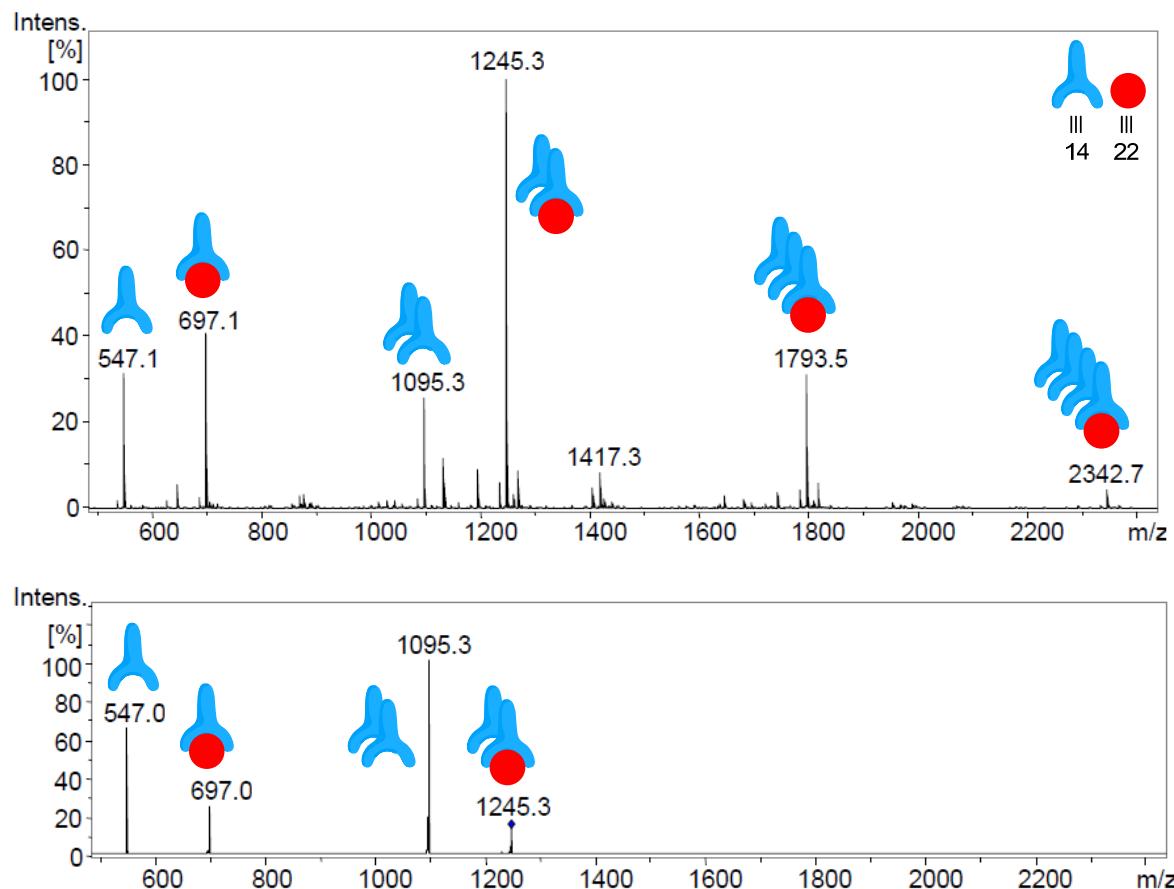
**Figure 57.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



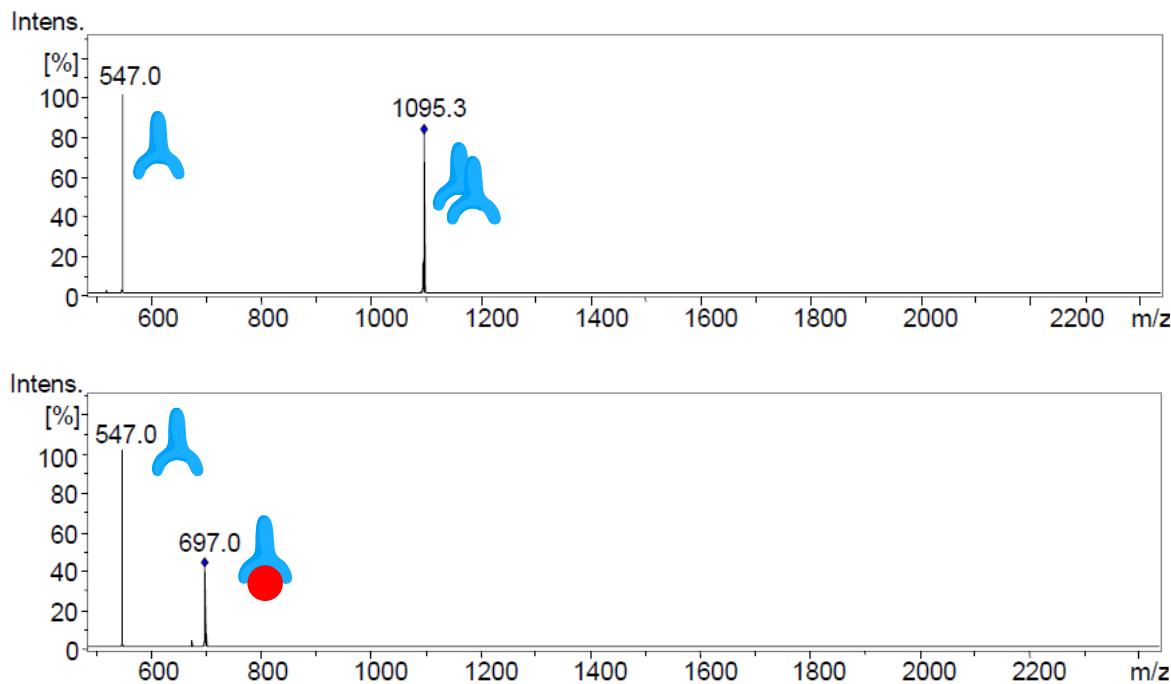
**Figure 58.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



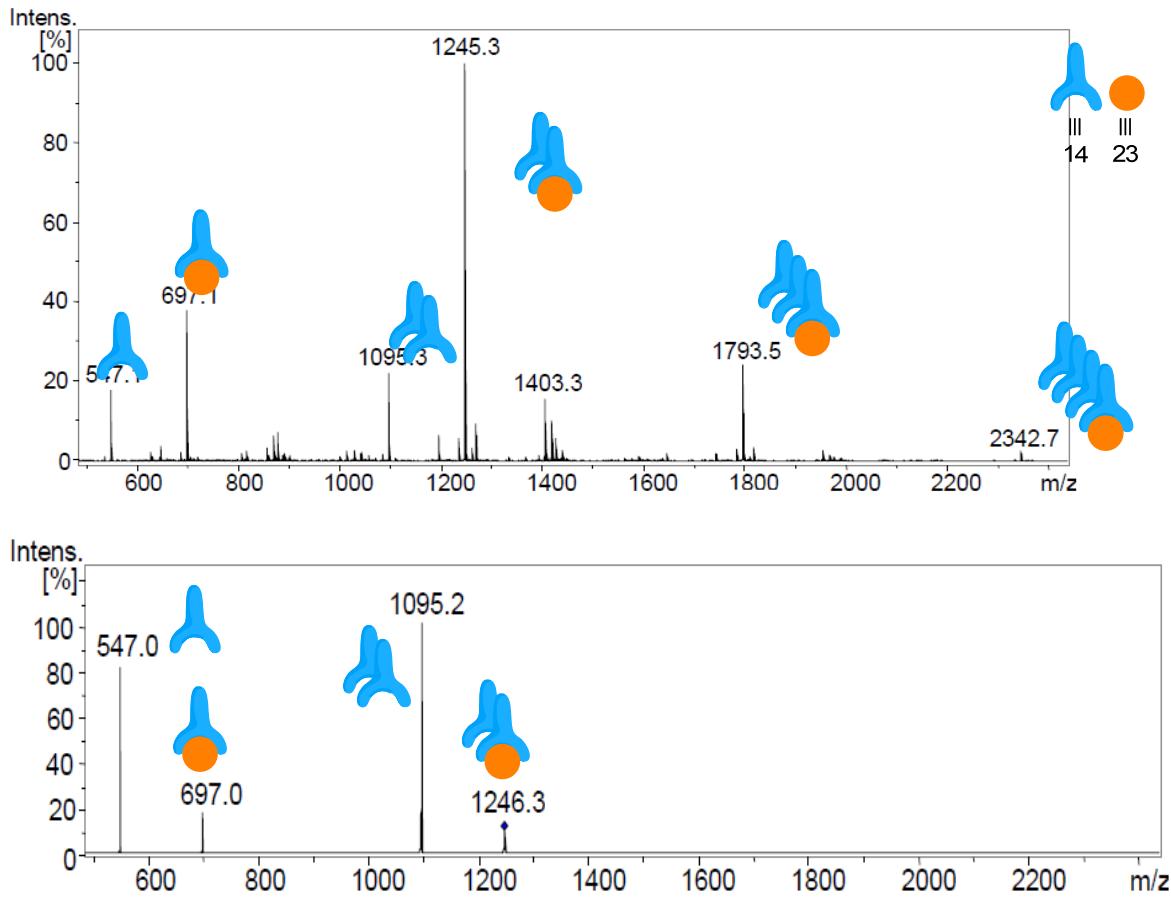
**Figure 59.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **11/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O).



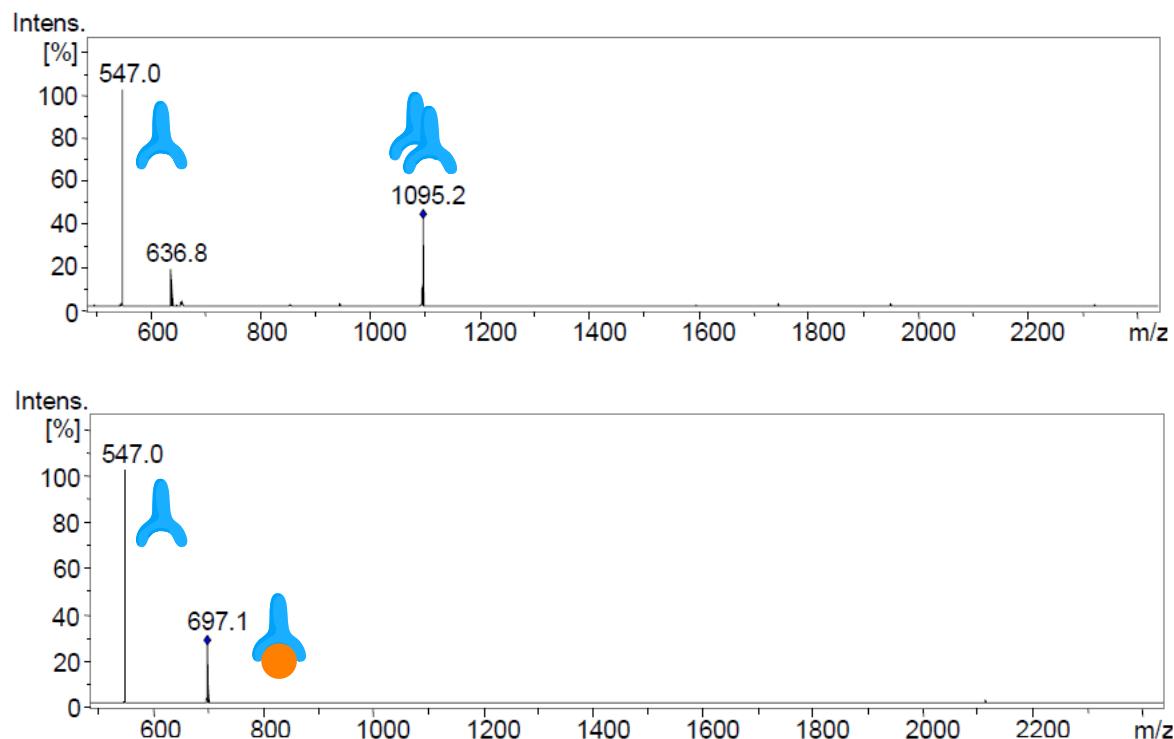
**Figure 60.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/22**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode, m/z 1245.3.



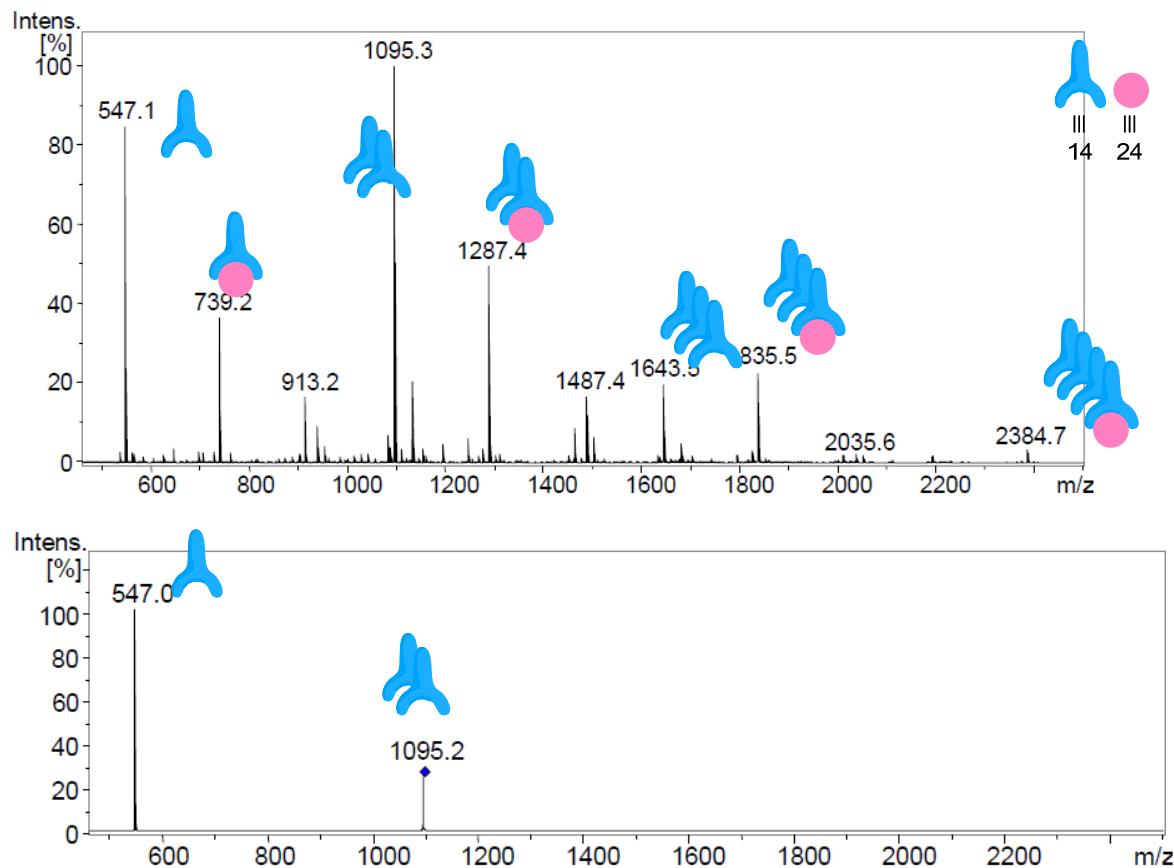
**Figure 61.** ESI-MS/MS of Ht/Gt complex **14/22** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1095.3 and 697.1).



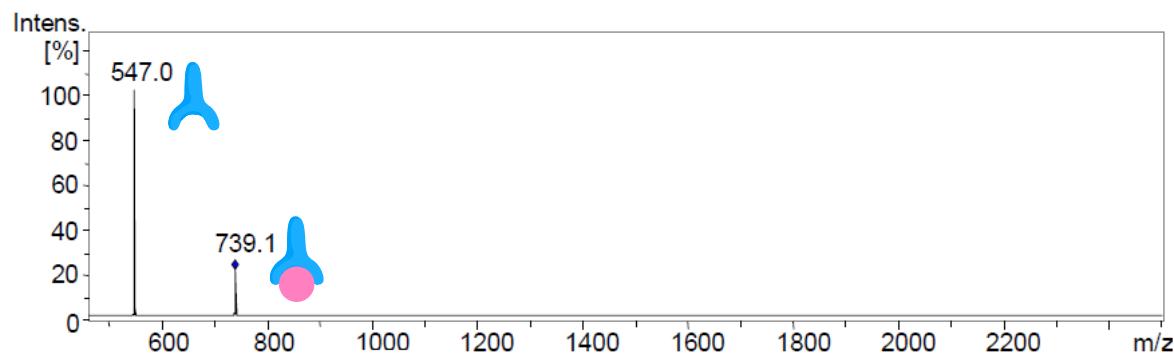
**Figure 62.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/23**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1245.3.



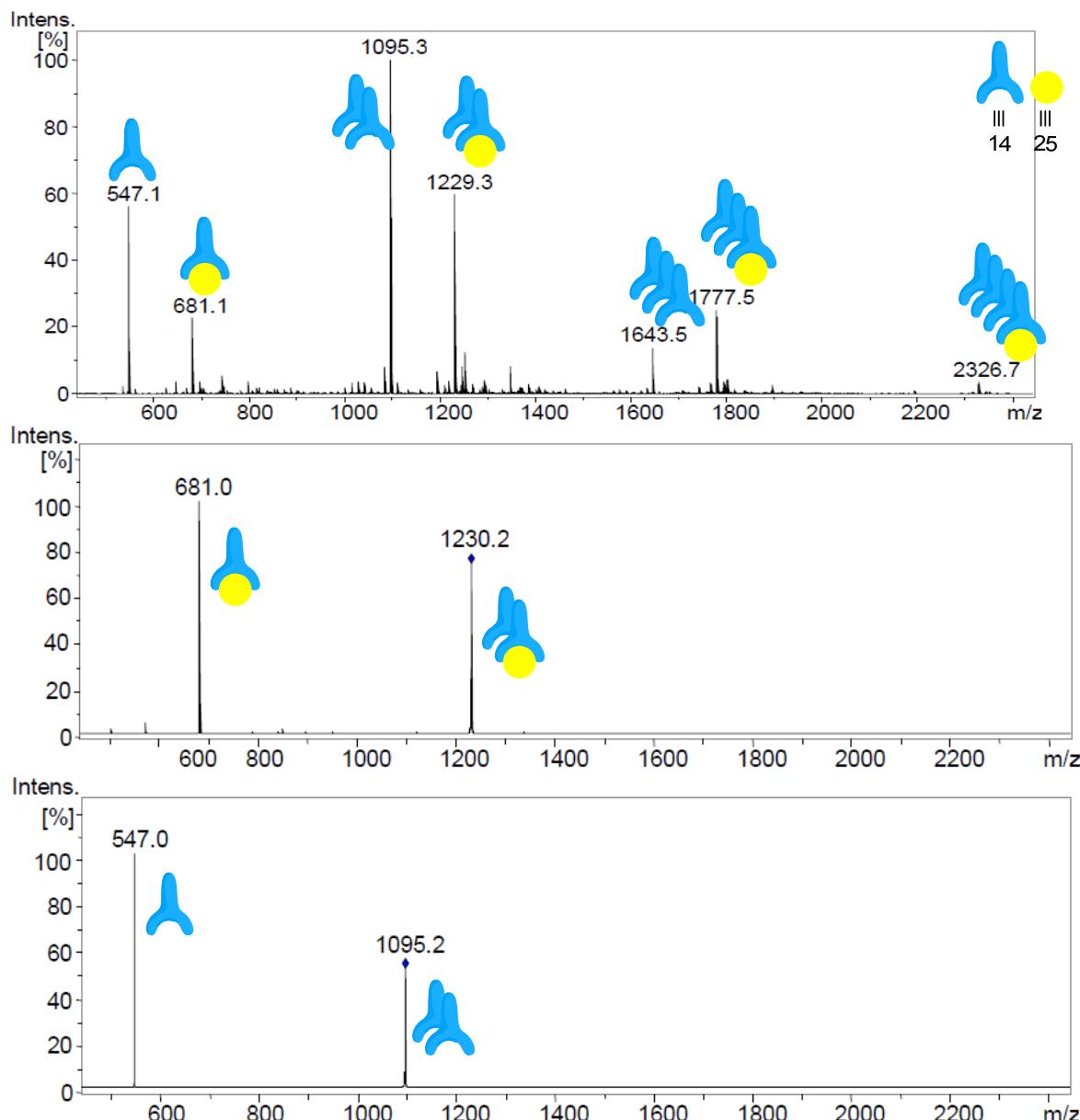
**Figure 63.** ESI-MS/MS of Ht/Gt complex **14/23** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1095.3 and 697.1).



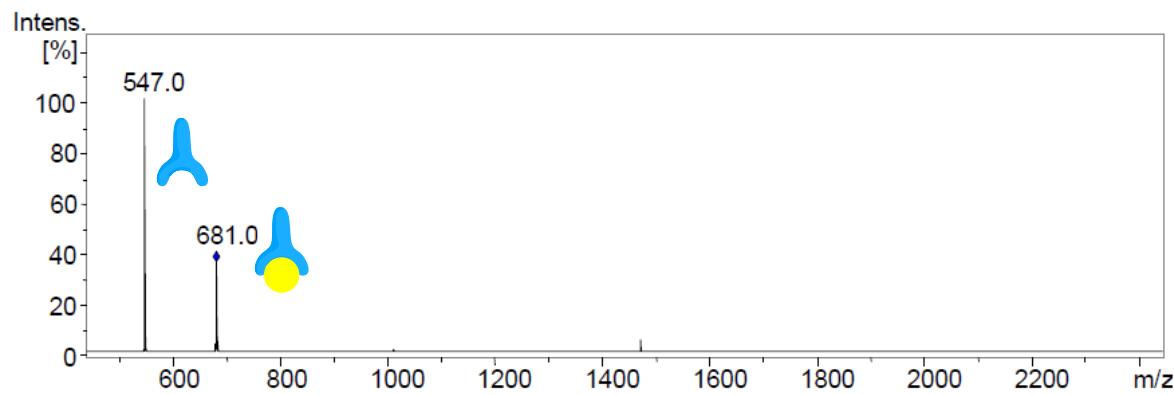
**Figure 64.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/24**, DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1095.3.



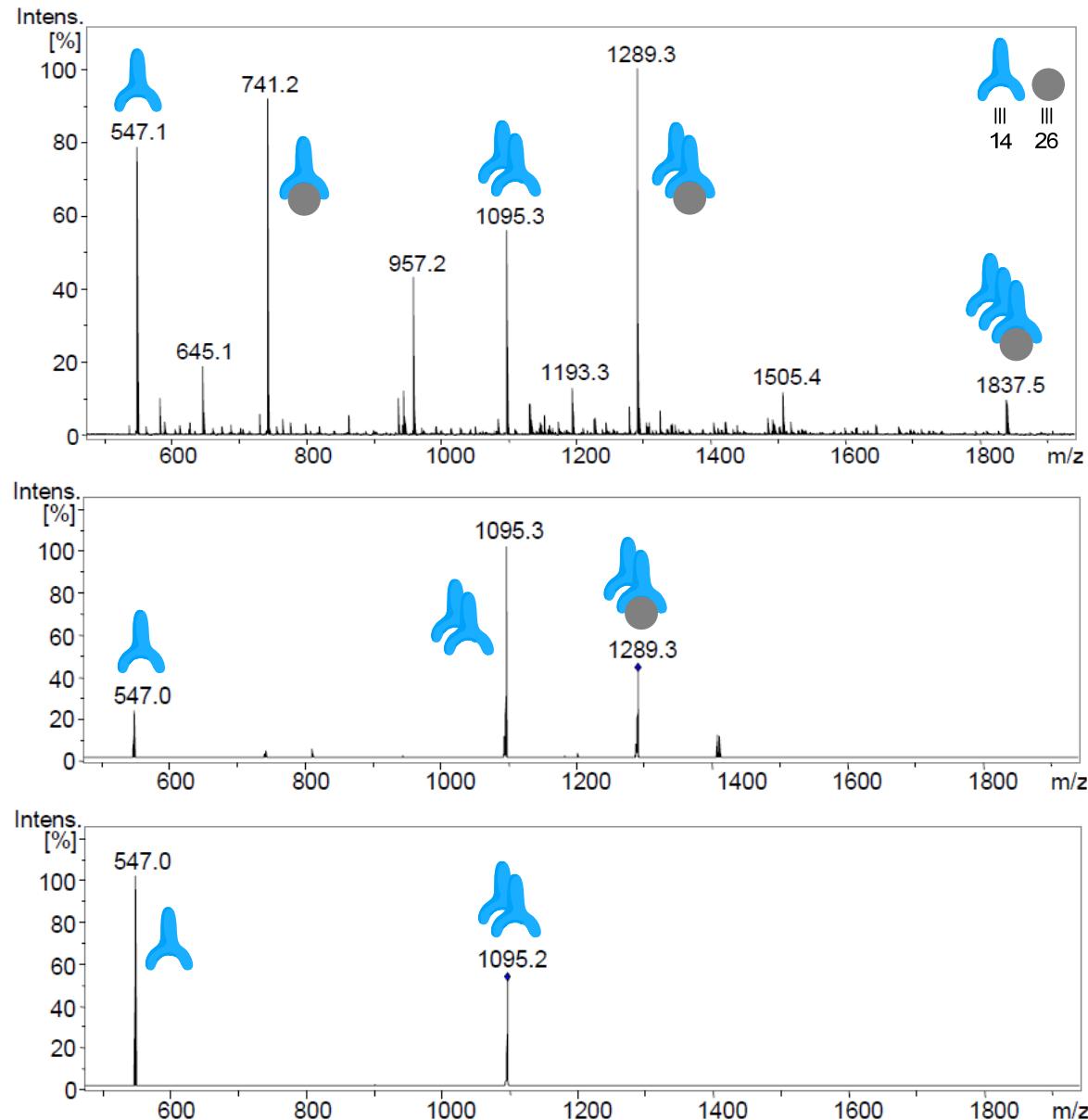
**Figure 65.** ESI-MS/MS of Ht/Gt complex **14/24** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  739.2).



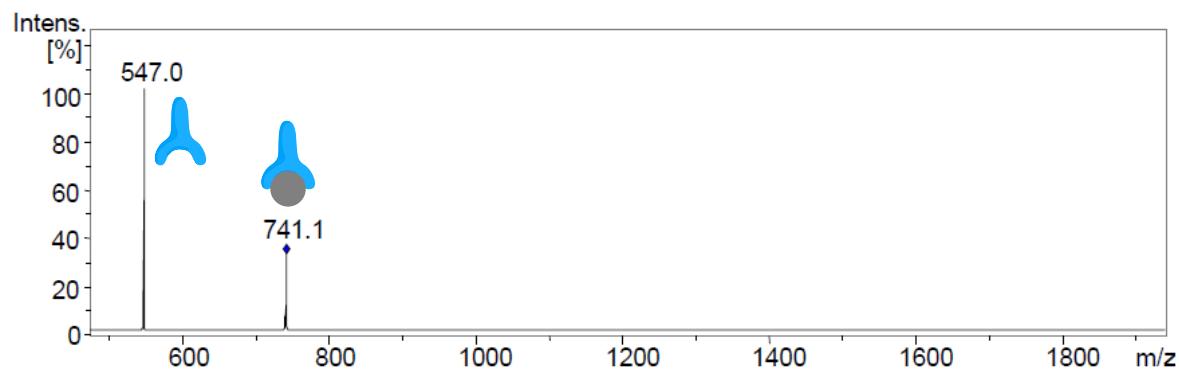
**Figure 66.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1229.3 and 1095.3).



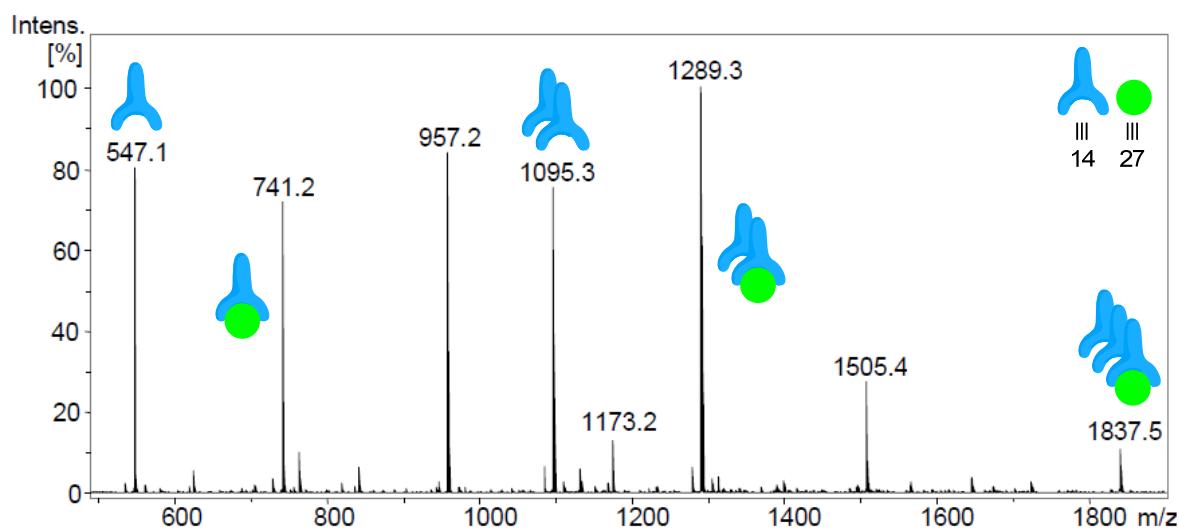
**Figure 67.** ESI-MS/MS of Ht/Gt complex **14/25** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  681.1).



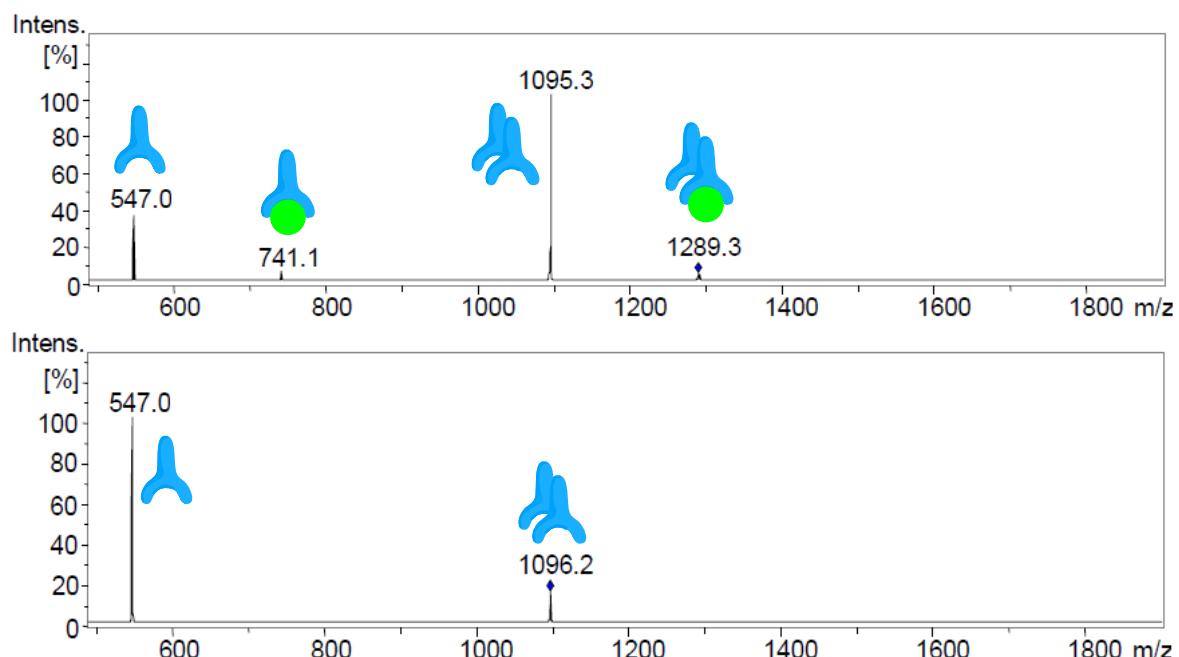
**Figure 68.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative mode,  $m/z$  1289.3 and 1095.3).



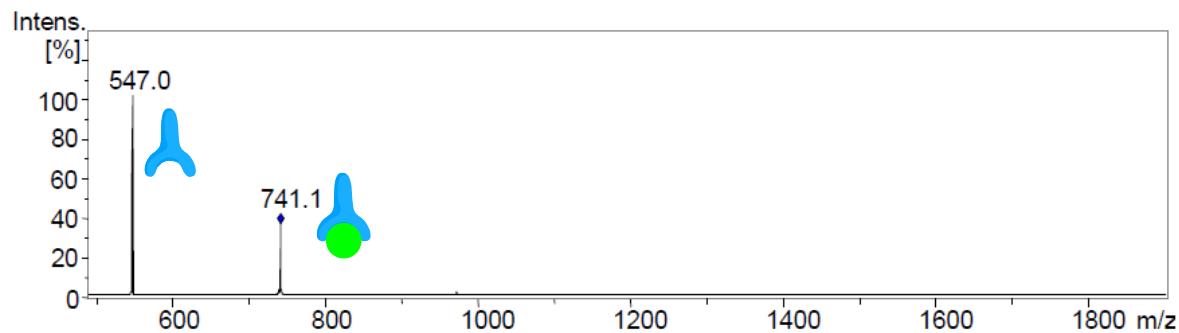
**Figure 69.** ESI-MS/MS of Ht/Gt complex **14/26** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  741.2).



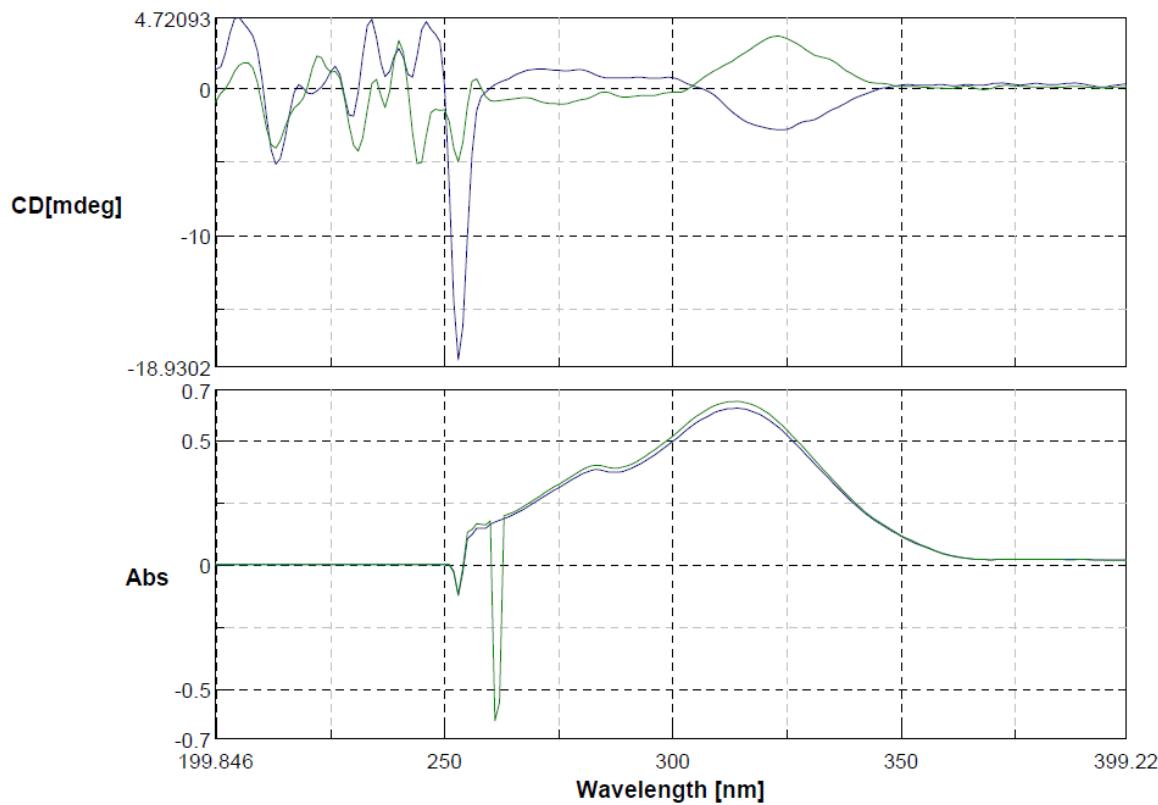
**Figure 70.** ESI-TOF MS and ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode).



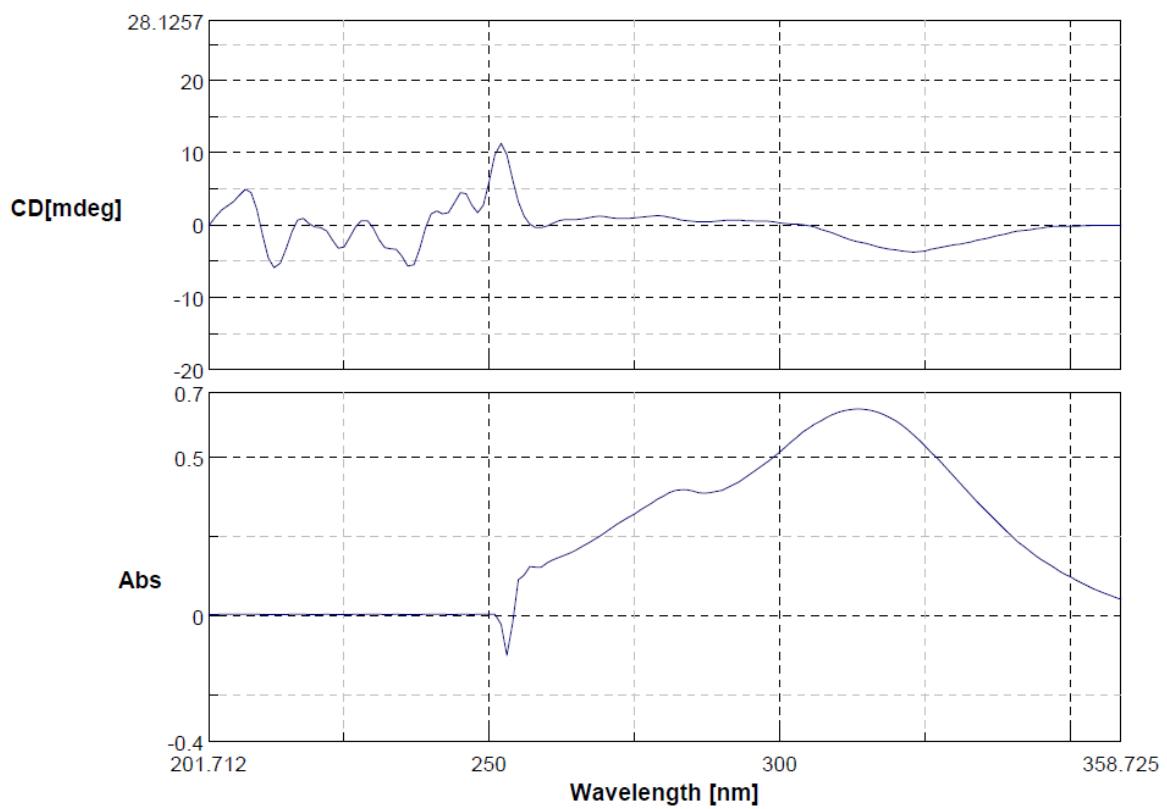
**Figure 71.** ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  1289.3 and 1095.3).



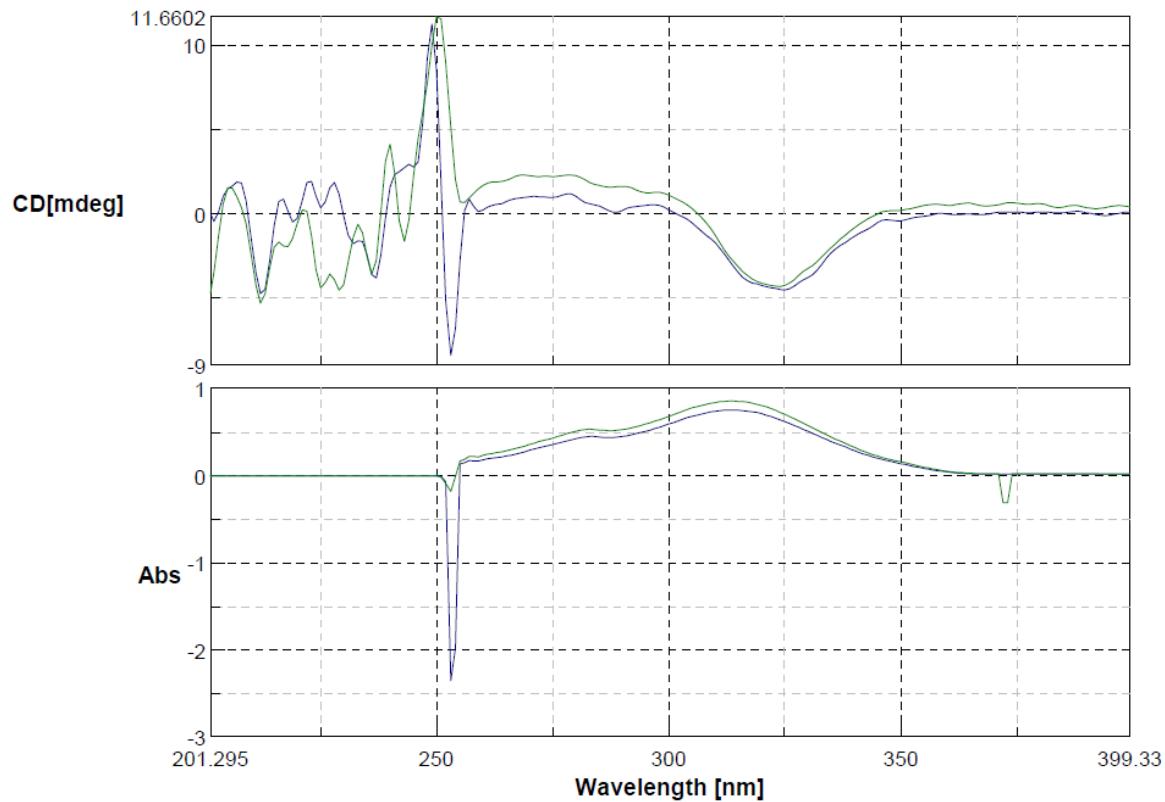
**Figure 72.** ESI-MS/MS of Ht/Gt complex **14/27** (DMF/CH<sub>3</sub>CN/H<sub>2</sub>O, negative ion mode,  $m/z$  741.2).



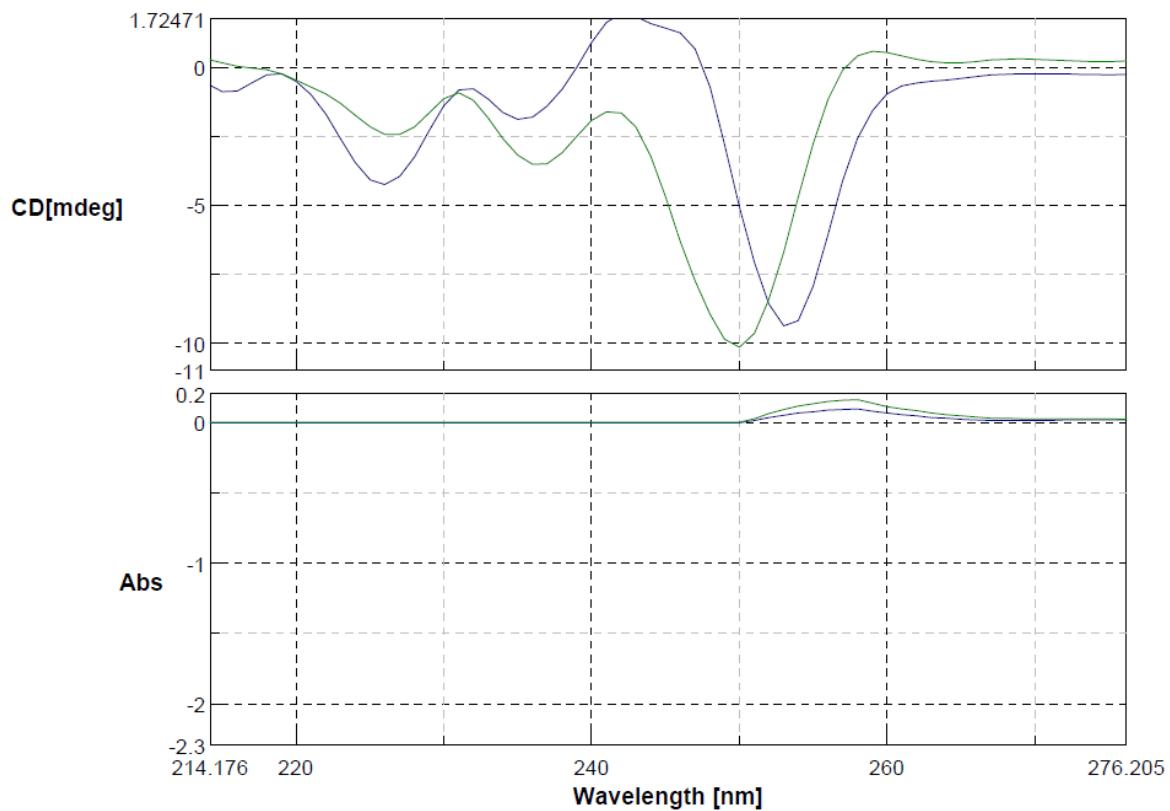
**Figure 73.** CD spectra of macrocycles (**9**, blue) and (**12**, green), DMSO.



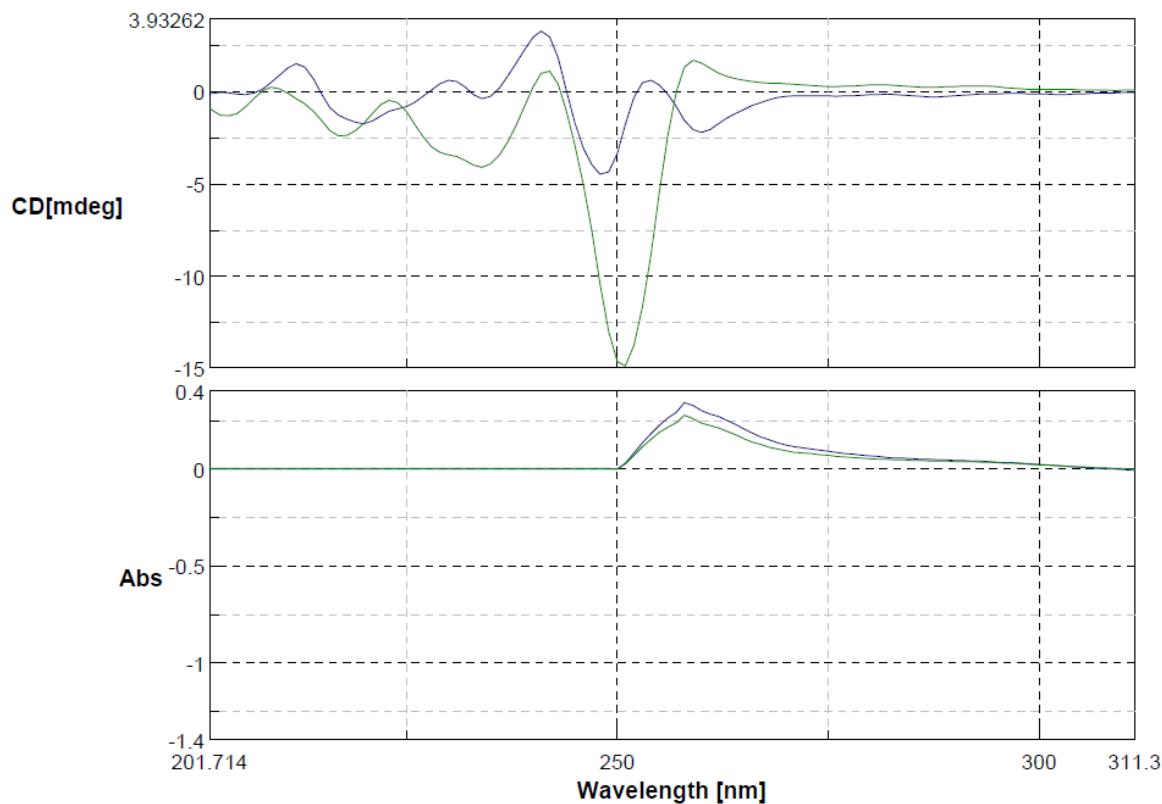
**Figure 74.** CD spectrum of macrocycles (**10**), DMSO.



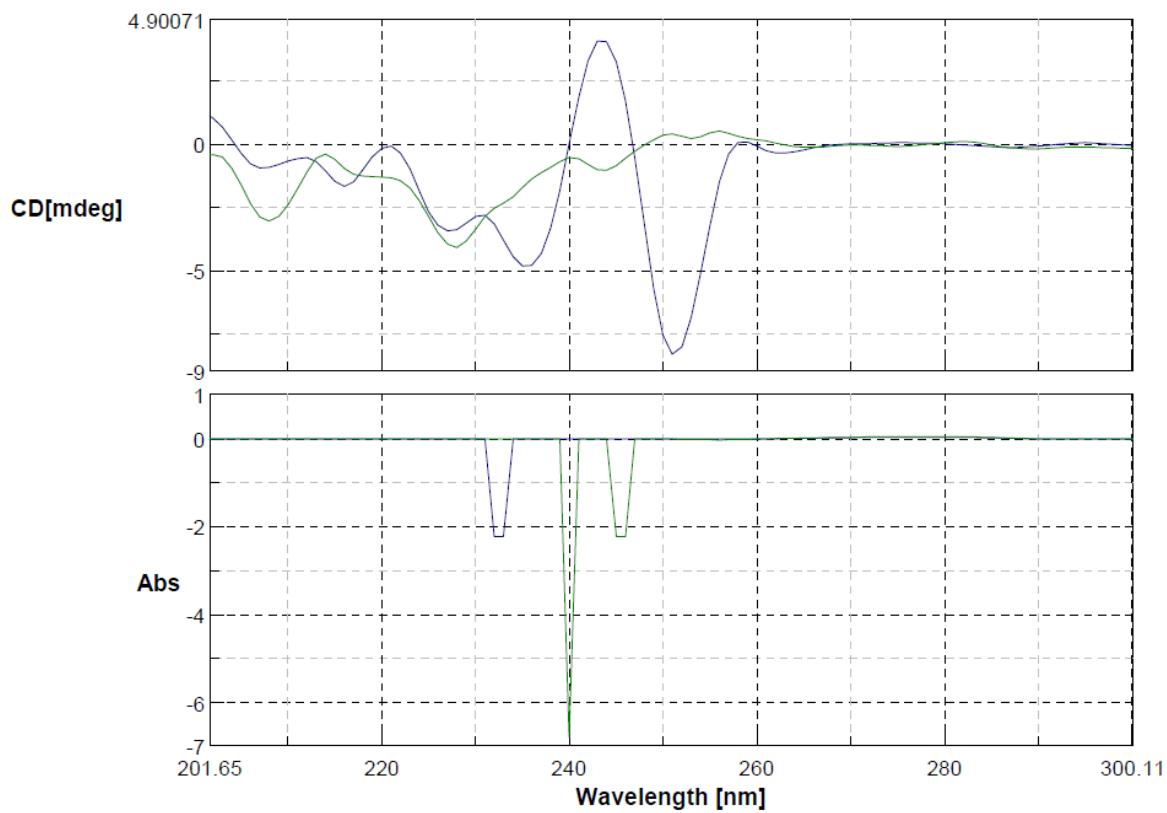
**Figure 75.** CD spectra of macrocycles (**11**, blue) and (**13**, green), DMSO.



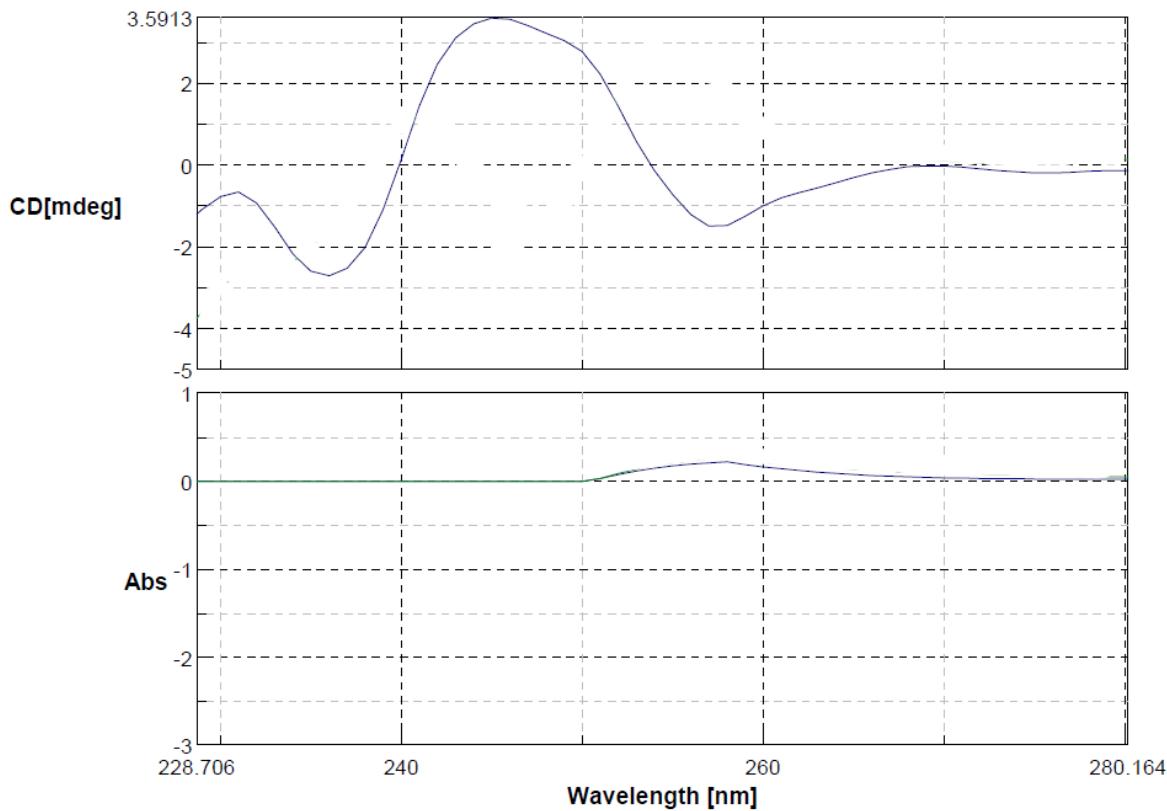
**Figure 76.** CD spectra of compounds (**14**, blue) and (**19**, green), DMSO.



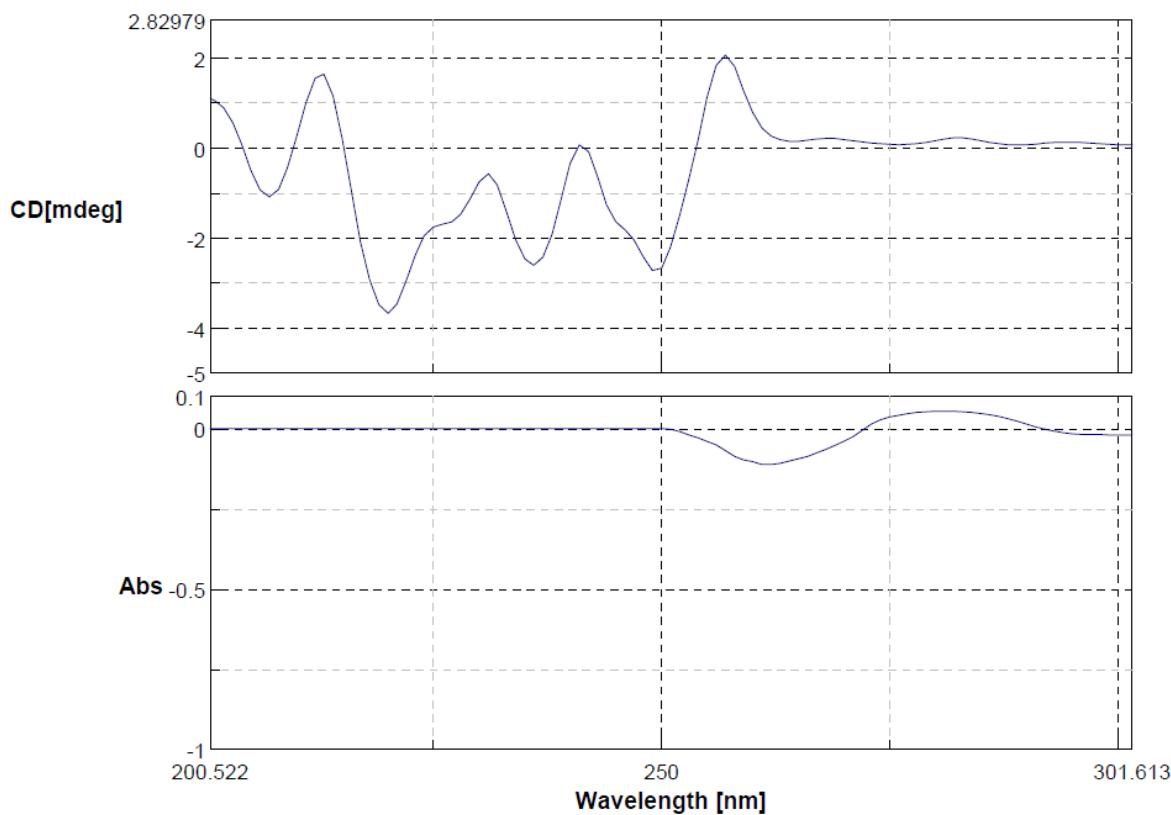
**Figure 77.** CD spectra of compounds (**15**, blue) and (**20**, green), DMSO.



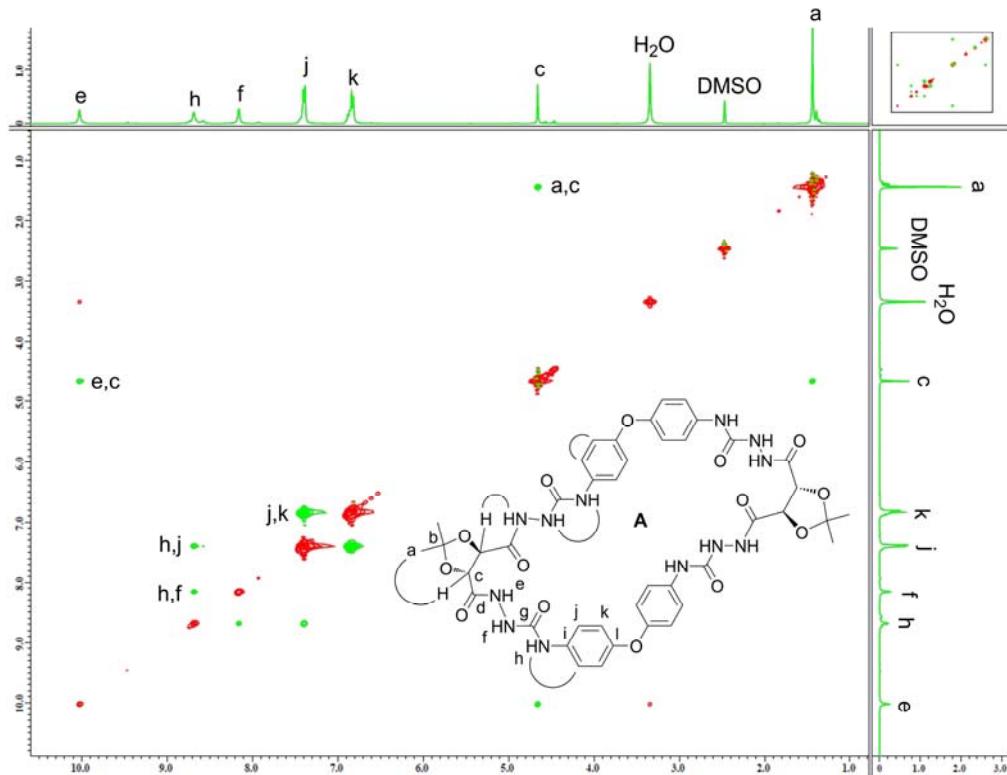
**Figure 78.** CD spectra of compounds **(16**, blue) and **(21**, green), DMSO.



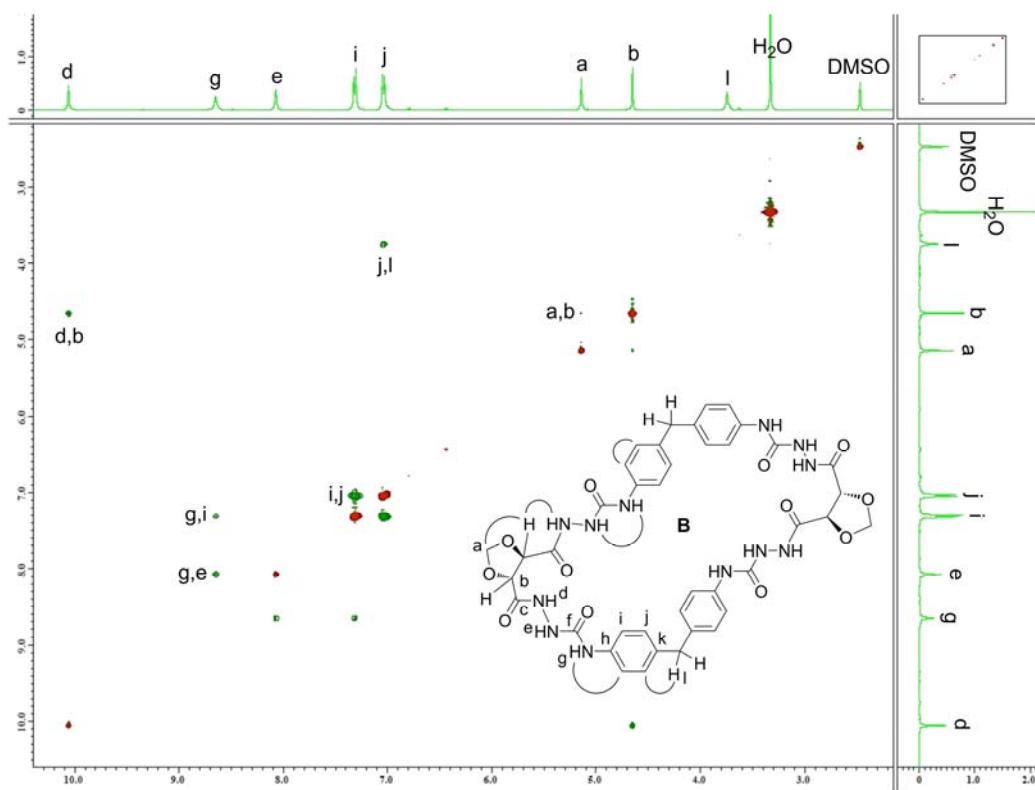
**Figure 79.** CD spectrum of compound **(17)**, DMSO.



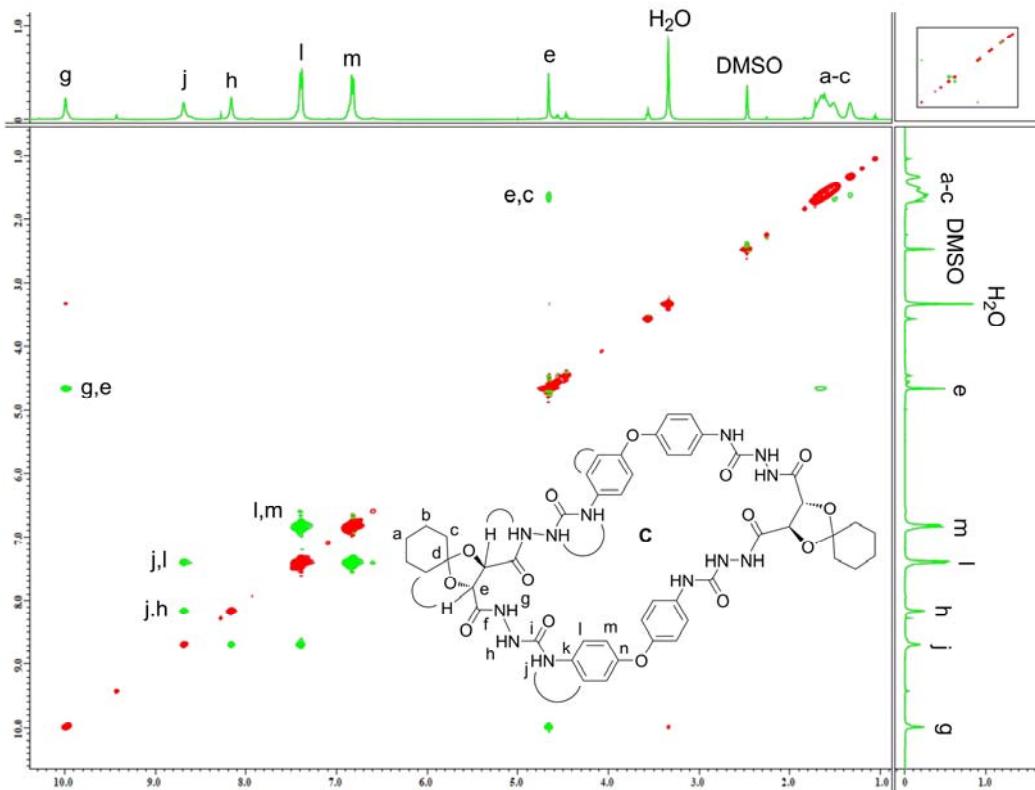
**Figure 80.** CD spectrum of compound (**18**), DMSO.



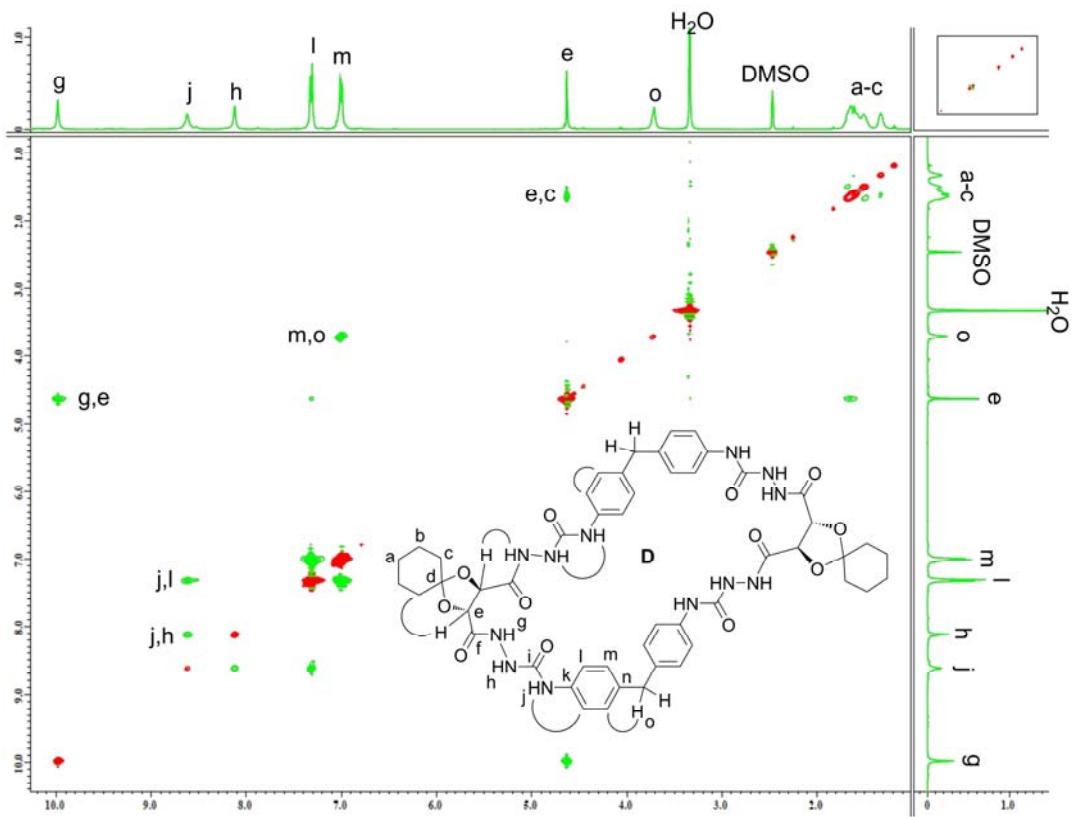
**Figure 81.** 2D ROESY NMR spectrum of macrocycle (**A**) showing *syn/anti* orientation of the NH moieties, (DMSO-*d*<sub>6</sub>).



**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, ( $\text{DMSO}-d_6$ ).