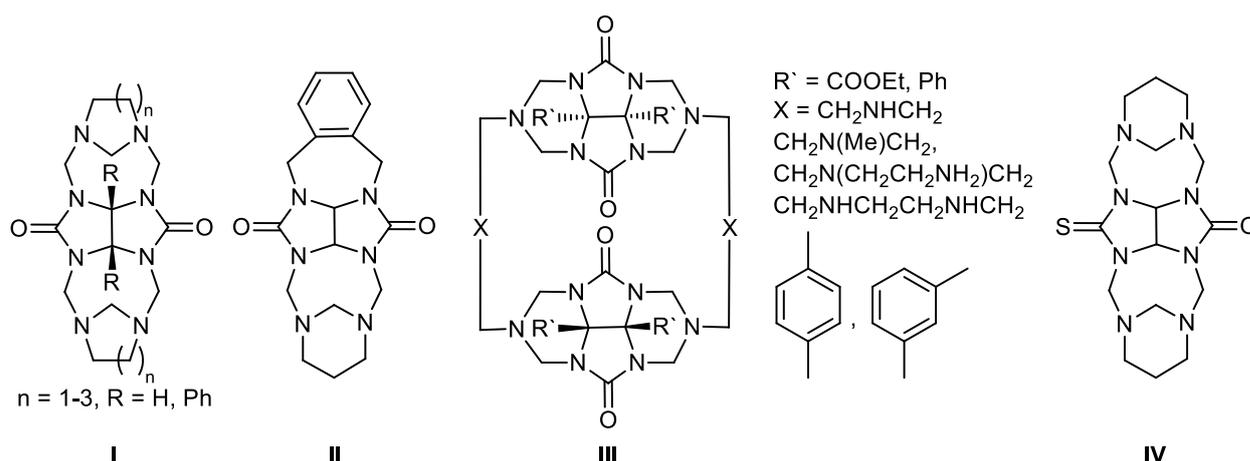


## New cage-fused polyaza polycyclic systems based on thioglycolurils and alkanediamines

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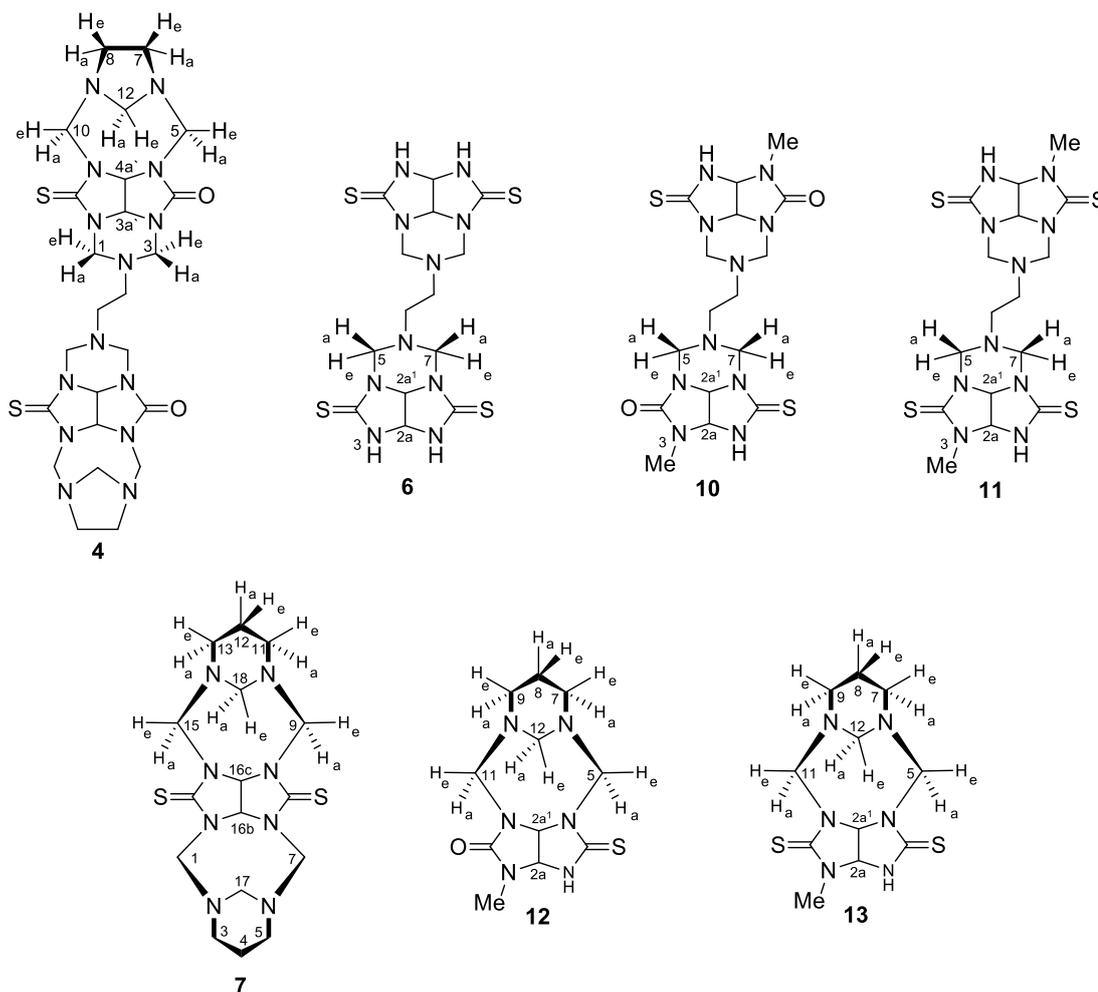
**Figure S1** Known polyheterocyclic systems were synthesized by condensation of glycolurils (semithioglycoluril) with formaldehyde and di(poly)amines.

### General materials and methods

$^1H$  and  $^{13}C$  NMR spectra were recorded using Bruker AM-300 ( $^1H$ , 300.13 MHz;  $^{13}C$ , 75.5 MHz), Bruker DRX500 ( $^1H$ , 500.13;  $^{13}C$ , 125.76 MHz), and Bruker AV600 (2D NMR, 600.13 MHz) spectrometers in DMSO- $d_6$ . Chemical shifts are reported in the  $\delta$  scale relative to Me $_4$ Si as internal standard. Abbreviations for the assignments of hydrogen atoms in NMR data: a: axial; e: equatorial. High resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF II instrument using the electrospray ionization method (ESI). Melting points were determined in a SMP10 instrument (Stuart).

Diamines and paraformaldehyde were purchased from Acros. Monothioglycoluril **1** [S1], dithioglycoluril **5** [S2] and 1-methylthioglycolurils **8,9** [S2] were synthesized according to the literature.

## Synthesis and spectral data of compounds 4,6,7,10-13



**Compound 4** (typical procedure): A suspension of semithioglycoluril **1** (2 eq, 0.50 g, 3.160 mmol), paraformaldehyde (10 eq, 0.48 g, 15.823 mmol), and ethylenediamine **2b** (3 eq, 0.28 g, 4.750 mmol) in MeOH (15 ml) was refluxed for 12 h. The reaction mixture was cooled to room temperature, and the crystals were filtered off and dried in air.

*2,2'-(Ethane-1,2-diyl)bis(4-thioxohexahydro-1H,4H,5H,10H,11H-2,3a,4a,6,9,10a,11a-heptaaza-6,9-methanobenzo[cd]cyclonona[gh]pentalen-11-one)* **4**. Colourless crystals, yield 70%, mp 241–243 °C (H<sub>2</sub>O). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-*d*<sub>6</sub>): 2.53–2.56 (m, 4 H, CH<sub>2</sub> (CH<sub>2</sub>-CH<sub>2</sub>)), 2.67–2.72 (m, 4 H, CH<sub>2</sub> (7a+8a)), 2.80–2.85 (m, 2 H, CH<sub>2</sub> (7e)), 3.12–3.20 (m, 2 H, CH<sub>2</sub> (8e)), 3.89 (d, 2 H, <sup>2</sup>*J* = 11.4 Hz, CH<sub>2</sub> (12a)), 4.21–4.26 (m, 4 H, CH<sub>2</sub> (12e+5a)), 4.35 (d, 2 H, <sup>2</sup>*J* = 13.4 Hz, CH<sub>2</sub> (3a)), 4.37 (d, 2 H, <sup>2</sup>*J* = 14.1 Hz, CH<sub>2</sub> (10a)), 4.49 (d, 2 H, <sup>2</sup>*J* = 13.4 Hz, CH<sub>2</sub> (1a)), 4.61–4.69 (m, 4 H, CH<sub>2</sub> (3e+5e)), 5.26 (d, 2 H, <sup>2</sup>*J* = 13.4 Hz, CH<sub>2</sub> (1e)), 5.39 (d, 2 H, <sup>2</sup>*J* = 14.1 Hz, CH<sub>2</sub> (10e)), 5.60 (d, 2 H, <sup>3</sup>*J* = 7.7 Hz, CH (3a`)), 5.71 (d, 2 H, <sup>3</sup>*J* = 7.7 Hz, CH (4a`)). <sup>13</sup>C NMR, δ, ppm.; (125 MHz, DMSO-*d*<sub>6</sub>): 46.57 (CH<sub>2</sub> (7)); 46.72 (CH<sub>2</sub> (8)); 47.20 (CH<sub>2</sub>-CH<sub>2</sub>); 61.06 (CH<sub>2</sub> (3)); 62.69 (CH<sub>2</sub> (1)); 64.35 (CH<sub>2</sub> (5)); 67.15 (CH<sub>2</sub> (10)); 67.26 (CH (3a`));

72.39 (CH (4a<sup>1</sup>)); 76.86 (CH (12)); 158.19 (C=O); 182.52 (C=S). HRMS, *m/z*: 617.2631 [M+H]<sup>+</sup> (calc. for: C<sub>24</sub>H<sub>36</sub>N<sub>14</sub>O<sub>2</sub>S<sub>2</sub>+H, *m/z*: 617.2631).

**Compounds 6,10,11 (general procedure)**: A suspension of the corresponding glycoluril (2 eq, 0.50 g, 2.660-2.907 mmol), paraformaldehyde (4 eq, 0.16-0.17 g, 5.320-5.814 mmol), and ethylenediamine **2b** (1 eq, 0.080-0.087 g, 1.330-1.453 mmol) in MeOH (15 ml) was refluxed for 12 h. The reaction mixture was cooled to room temperature, and the precipitate of products was filtered off. The filtrate was evaporated under reduced pressure to the solid and recrystallized from DMSO for compound **6**, H<sub>2</sub>O for compound **10** or MeOH for compound **11**.

*6,6''-(Ethane-1,2-diyl)bis(tetrahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4(2H,2a<sup>1</sup>H)-dithione) 6*. Beige powder, yield 17%, mp 244 – 246 °C (DMSO). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-*d*<sub>6</sub>): 2.58 (s, 4 H, CH<sub>2</sub>-CH<sub>2</sub>), 4.45 (d, 4 H, <sup>2</sup>*J* = 13.4 Hz, CH<sub>2</sub>), 5.07 (d, 4 H, <sup>2</sup>*J* = 13.2 Hz, CH<sub>2</sub>), 5.63 (d, 2 H, <sup>3</sup>*J* = 7.9 Hz, CH (2a)), 5.75 (d, 2 H, <sup>3</sup>*J* = 7.9 Hz, CH (2a<sup>1</sup>)), 9.72 (s, 4 H, NH). <sup>13</sup>C NMR, δ, ppm.; (75 MHz, DMSO-*d*<sub>6</sub>): 47.33 (CH<sub>2</sub>-CH<sub>2</sub>); 61.99 (CH<sub>2</sub>); 67.40 (CH (2a)); 74.20 (CH (2a<sup>1</sup>)); 181.60 (C=S). HRMS, *m/z*: 457.0828 [M+H]<sup>+</sup> (calc. for: C<sub>14</sub>H<sub>20</sub>N<sub>10</sub>S<sub>4</sub>+H, *m/z*: 457.0820).

*6,6''-(Ethane-1,2-diyl)bis(3-methyl-1-thioxohexahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]inden-4(2a<sup>1</sup>H)-one) 10*. Red powder, yield 65%, mp 245 – 247 °C (MeOH). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-*d*<sub>6</sub>): 2.30–2.46 (m, 4 H, CH<sub>2</sub>-CH<sub>2</sub>), 2.74 (s, 6 H, Me), 4.24 (d, 2 H, <sup>2</sup>*J* = 13.8 Hz, CH<sub>2</sub>), 4.41 (d, 2 H, <sup>2</sup>*J* = 13.4 Hz, CH<sub>2</sub>), 4.49 (d, 2 H, <sup>2</sup>*J* = 13.7 Hz, CH<sub>2</sub>), 5.00 (d, 2 H, <sup>2</sup>*J* = 13.2 Hz, CH<sub>2</sub>), 5.39 (d, 2 H, <sup>3</sup>*J* = 7.7 Hz, CH (2a)), 5.56 (d, 2 H, <sup>3</sup>*J* = 7.7 Hz, CH (2b)), 9.72 (s, 2 H, NH). <sup>13</sup>C NMR, δ, ppm. (75 MHz, DMSO-*d*<sub>6</sub>): 27.28 (Me); 46.83 (CH<sub>2</sub>-CH<sub>2</sub>); 60.16; 61.31 (CH<sub>2</sub>); 68.53; 68.70 (CH (2a+2a<sup>1</sup>)); 157.61 (C=O); 181.80 (C=S). HRMS, *m/z*: 453.1598 [M+H]<sup>+</sup> (calc. for: C<sub>16</sub>H<sub>24</sub>N<sub>10</sub>O<sub>2</sub>S<sub>2</sub>+H, *m/z*: 453.1592).

*6,6''-(Ethane-1,2-diyl)bis(3-methyltetrahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4(2H,2a<sup>1</sup>H)-dithione) 11*. Beige powder, yield 38%, mp 234 – 236 °C (MeOH). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (300 MHz, DMSO-*d*<sub>6</sub>): 2.50–2.53 (s, 4 H, CH<sub>2</sub>-CH<sub>2</sub>), 3.11 (s, 6 H, Me), 4.47–4.60 (m, 4H, CH<sub>2</sub>), 5.00–5.18 (m, 4H, CH<sub>2</sub>), 5.72 (d, 2H, <sup>3</sup>*J* = 8.0 Hz, CH (2a)), 5.79 (d, 2H, <sup>3</sup>*J* = 8.0 Hz, CH (2b)), 9.96 (s, 2H, NH). <sup>13</sup>C NMR, δ, ppm. (75 MHz, DMSO-*d*<sub>6</sub>): 31.70 (Me); 47.57 (CH<sub>2</sub>-CH<sub>2</sub>); 62.48; 63.08 (CH<sub>2</sub>); 72.32 (CH (2a)); 72.94 (CH (2a<sup>1</sup>)); 181.50; 181.82 (C=S). HRMS, *m/z*: 485.1148 [M+H]<sup>+</sup> (calc. for: C<sub>16</sub>H<sub>24</sub>N<sub>10</sub>S<sub>4</sub>+H, *m/z*: 485.1141).

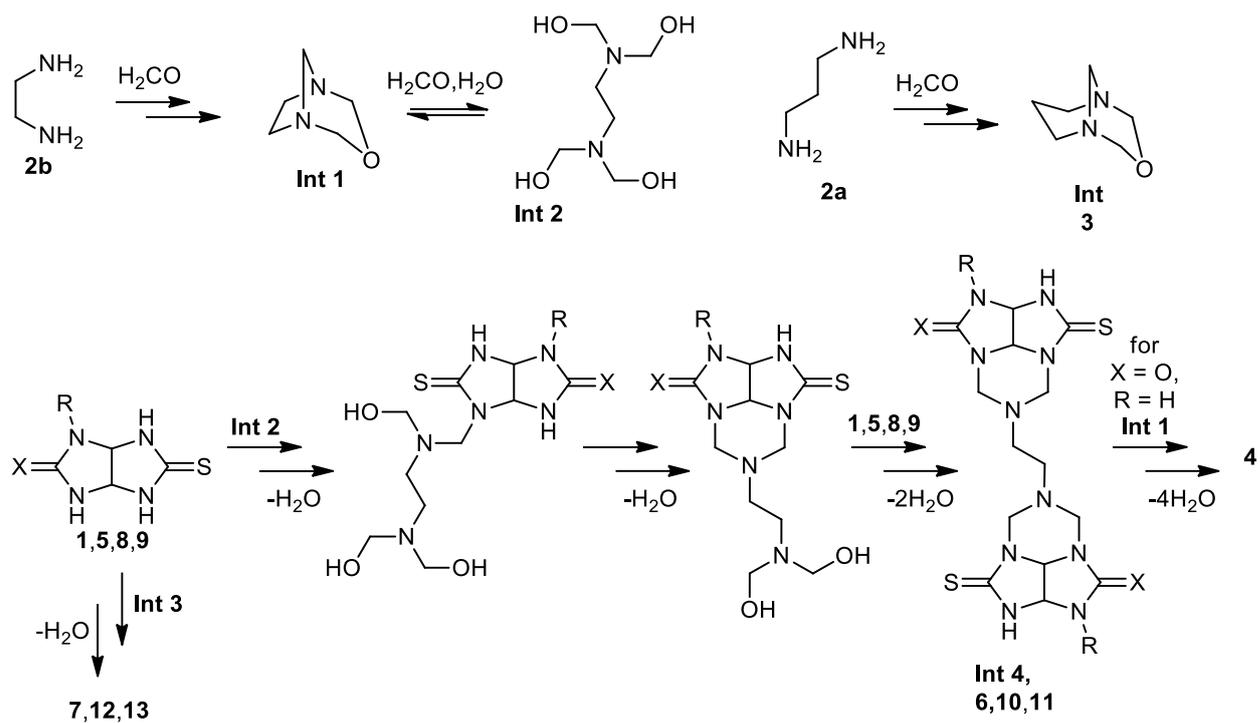
**Compound 7 (typical procedure)**: A suspension of dithioglycoluril **5** (1 eq, 0.50 g, 2.907 mmol), paraformaldehyde (6 eq, 0.52 g, 17.442 mmol), and 1,3-propylenediamine (2 eq, 0.44 g, 5.814 mmol) in MeOH (15 ml) was refluxed for 12 h. The mixture was cooled to room temperature and left overnight; the resulting precipitate was filtered off. The filtrate was evaporated at reduced pressure to the solid and recrystallized from MeOH.

*Perhydro-2,6:10,14-dimethano-2,6,7a,8a,10,14,15a,16a-octaazadicyclodeca[cd,gh]pentalene-8,16-dithione* **7**. Grey powder, yield 79%, mp 228 – 230°C (MeOH, decomp.). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (500 MHz, DMSO-*d*<sub>6</sub>): 0.90 (d, 2 H, <sup>2</sup>*J* = 12.5 Hz, CH<sub>2</sub> (4e+12e)), 1.55–1.67 (m, 2 H, CH<sub>2</sub> (4a+12a)), 2.9–3.05 (m, 4 H, CH<sub>2</sub> (11a+13a+5a+3a)), 3.49–3.56 (m, 4 H, CH<sub>2</sub> (11e+13e+5e+3e)), 4.00–4.14 (m, 4 H, CH<sub>2</sub> (17+18)), 4.31 (d, 4 H, <sup>2</sup>*J* = 14.4 Hz, CH<sub>2</sub> (1a+7a+9a+15a)), 5.76 (d, 4 H, <sup>2</sup>*J* = 14.4 Hz, CH<sub>2</sub> (1e+7e+9e+15e)), 5.89 (s, 2 H, CH-CH). <sup>13</sup>C NMR, δ, ppm. (75 MHz, DMSO-*d*<sub>6</sub>): 21.11 (CH<sub>2</sub> (12+4)); 46.19 (CH<sub>2</sub> (3+5+11+13)); 67.56 (CH<sub>2</sub> (1+7+9+15)); 71.16 (CH<sub>2</sub> (17+18)); 77.70 (CH-CH); 182.13 (C=S). HRMS, *m/z*: 395.1795 [M+H]<sup>+</sup> (calc. for: C<sub>16</sub>H<sub>26</sub>N<sub>8</sub>S<sub>2</sub>+H, *m/z*: 395.1789).

*Compounds 12,13 (general procedure)*: A suspension of the corresponding thioglycoluril **8** or **9** (1 eq, 0.50 g, 2.660-2.907 mmol), paraformaldehyde (3 eq, 0.24-0.26 g, 7.980-8.721 mmol), and propylenediamine **2a** (1 eq, 0.20-0.22 g, 2.660-2.907 mmol) in MeOH (15 ml) was refluxed for 12 h. The reaction mixture was cooled to room temperature and left overnight, the resulting precipitate was filtered off. The filtrate was evaporated at reduced pressure to the solid and recrystallized from water for compound **12** or MeOH for compound **13**.

*3-Methyl-1-thioxohexahydro-5H,7H,11H-2,3,4a,6,10,11a-hexaaza-6,10-methanocyclodeca[cd]pentalen-4(2a<sup>1</sup>H)-one* **12**. White powder, yield 40%, mp 221 – 223 °C (H<sub>2</sub>O). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (500 MHz, DMSO-*d*<sub>6</sub>): 0.88 (d, 1 H, CH<sub>2</sub> (8e), <sup>2</sup>*J* = 12.8 Hz), 1.55–1.58 (m, 1 H, CH<sub>2</sub> (8a)), 2.74 (s, 3 H, Me), 2.90–2.94 (m, 1 H, CH<sub>2</sub> (7a)), 2.96–3.00 (m, 1 H, CH<sub>2</sub> (9a)), 3.04–3.07 (m, 1 H, CH<sub>2</sub> (9e)), 3.17 (d, 1 H, CH<sub>2</sub>, <sup>2</sup>*J* = 5.2 Hz), 3.40–3.43 (m, 1 H, CH<sub>2</sub> (7e)), 3.97 (d, 1 H, <sup>2</sup>*J* = 14.2 Hz, CH<sub>2</sub> (12e)), 4.07–4.10 (m, 2 H, CH<sub>2</sub> (12a+11a)), 4.21 (d, 1 H, <sup>2</sup>*J* = 14.3 Hz, CH<sub>2</sub> (5a)), 4.77 (d, 1 H, <sup>2</sup>*J* = 14.5 Hz, CH<sub>2</sub> (11e)), 5.33 (d, 1 H, <sup>3</sup>*J* = 8.6 Hz, CH (2a)), 5.49 (d, 1 H, <sup>2</sup>*J* = 14.3 Hz, CH<sub>2</sub> (5e)), 5.55 (d, 1 H, <sup>3</sup>*J* = 8.6 Hz, CH (2a<sup>1</sup>)), 9.54 (s, 1 H, NH). <sup>13</sup>C NMR, δ, ppm. (125 MHz, DMSO-*d*<sub>6</sub>): 21.46 (CH<sub>2</sub> (8)); 28.07 (Me); 46.32 (CH<sub>2</sub> (9)); 46.66 (CH<sub>2</sub> (7)); 63.89 (CH<sub>2</sub> (11)); 66.03 (CH<sub>2</sub> (5)); 68.90 (CH (2a)); 70.54 (CH<sub>2</sub> (12)); 74.64 (CH (2a<sup>1</sup>)); 156.99 (C=O); 182.26 (C=S). HRMS, *m/z*: 283.1336 [M+H]<sup>+</sup> (calc. for: C<sub>11</sub>H<sub>18</sub>N<sub>6</sub>OS+H, *m/z*: 283.1339).

*3-Methyltetrahydro-5H,7H,11H-2,3,4a,6,10,11a-hexaaza-6,10-methanocyclodeca[cd]pentalene-1,4(2H,2a<sup>1</sup>H)-dithione* **13**. Beige powder, yield 25%, mp 216 – 218°C (MeOH, decomp.). <sup>1</sup>H NMR, δ, ppm.; *J*/Hz (500 MHz, DMSO-*d*<sub>6</sub>): 0.85 (d, 1 H, <sup>2</sup>*J* = 12.8 Hz, CH<sub>2</sub> (8e)), 1.40–1.45 (m, 1 H, CH<sub>2</sub> (8a)), 2.88–2.97 (m, 2 H, CH<sub>2</sub> (7a+9a)), 3.07 (s, 3 H, Me), 3.37–3.49 (m, 2 H, CH<sub>2</sub> (7e+9e)), 4.04–4.12 (m, 2 H, CH<sub>2</sub> (12e+12a)), 4.20–4.35 (m, 2 H, CH<sub>2</sub> (5a+11a)), 5.46–5.55 (m, 2 H, CH<sub>2</sub> (5e+11e)), 5.63 (d, 1 H, <sup>3</sup>*J* = 8.8 Hz, CH (2a)), 5.82 (d, 1 H, <sup>3</sup>*J* = 8.8 Hz, CH (2a<sup>1</sup>)), 9.81 (s, 1 H, NH). <sup>13</sup>C NMR, δ, ppm.; (75 MHz, DMSO-*d*<sub>6</sub>): 21.34 (CH<sub>2</sub> (8)); 31.84 (Me); 46.36 (CH<sub>2</sub> (7+9)); 66.56; 67.51 (CH<sub>2</sub> (5+11)); 70.80 (CH<sub>2</sub> (12)); 72.63 (CH (2a)); 78.20 (CH (2a<sup>1</sup>)); 180.80; 182.02 (C=S). HRMS, *m/z*: 299.1104 [M+H]<sup>+</sup> (calc. for: C<sub>11</sub>H<sub>18</sub>N<sub>6</sub>S<sub>2</sub>+H, *m/z*: 299.1107).



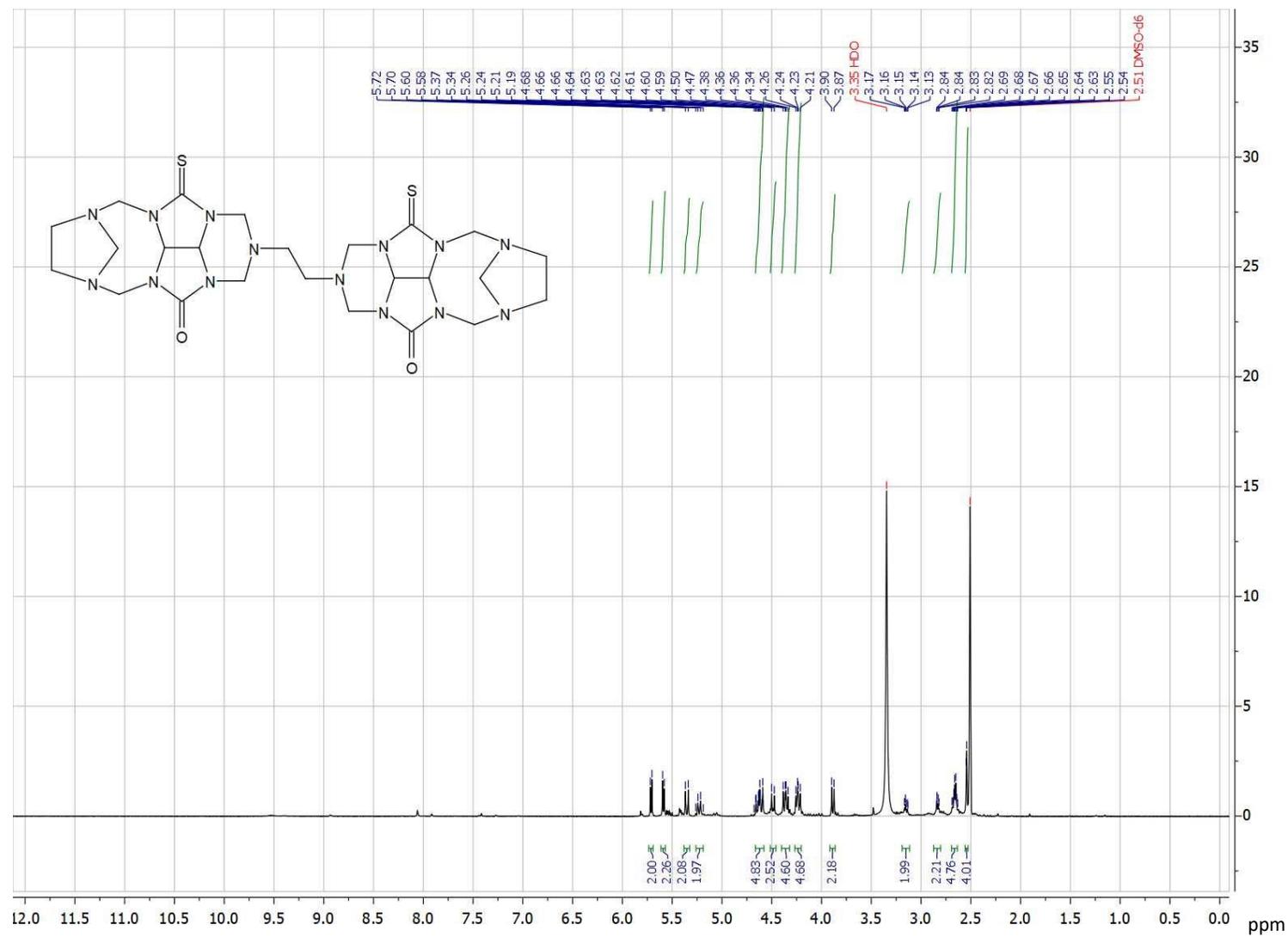
**Scheme S1** Proposed mechanism for formation of new polyheterocycles **4,6,7,10-13**.

## References

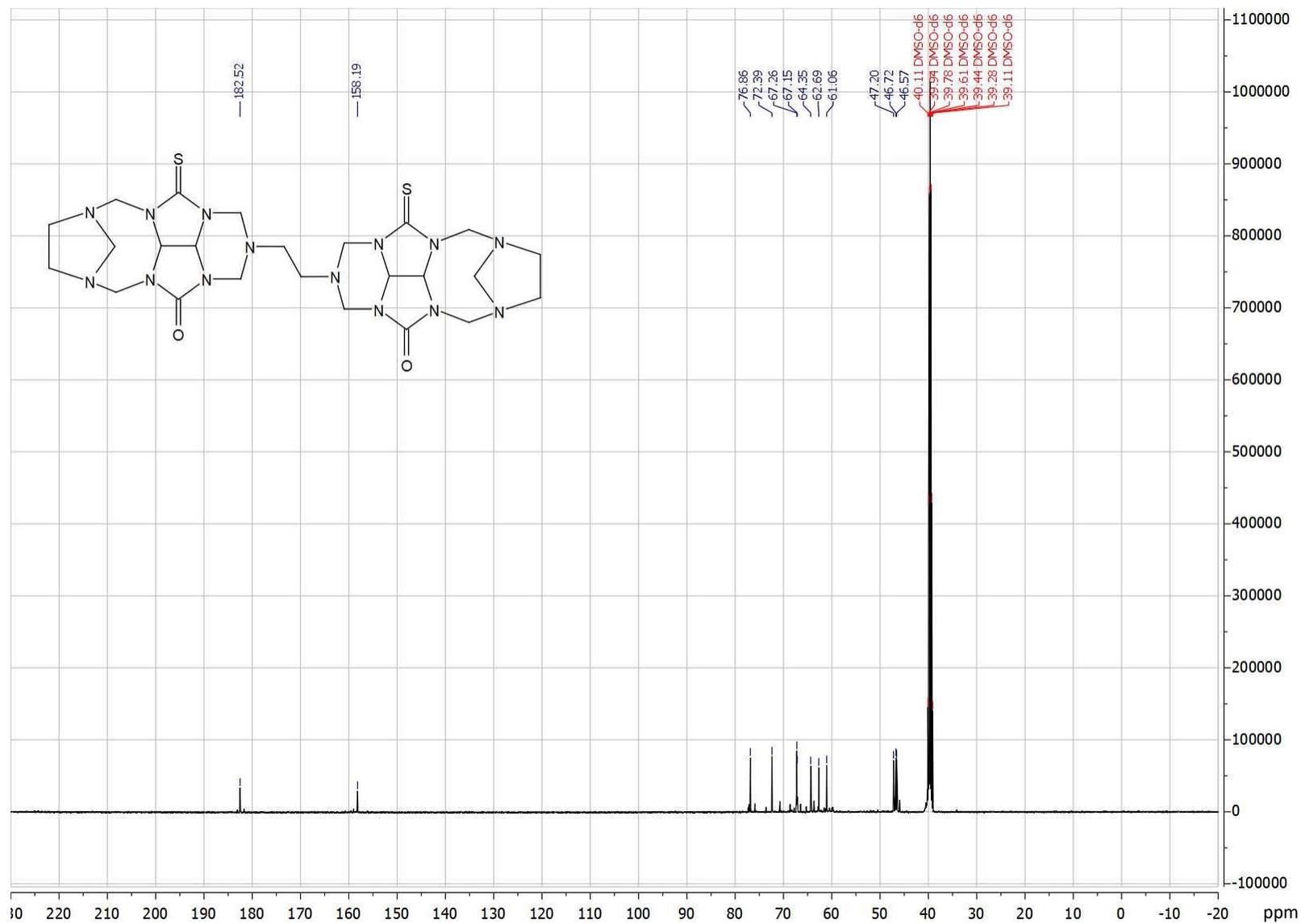
- [S1] V.V. Baranov, E. L. Yatsenko, E. K. Melnikova, Yu. V. Nelyubina and A. N. Kravchenko, *Chem. Heterocycl. Compd.*, 2019, **55**, 160 (*Khim. Geterotsikl. Soedin.*, 2019, **55**, 160).
- [S2] V. V. Baranov, Yu. V. Nelyubina, A. N. Kravchenko, N. G. Kolotyrykina and K. A. Biriukova, *Tetrahedron Lett.*, 2015, **56**, 6085.

## NMR spectra of synthesized polyheterocycles

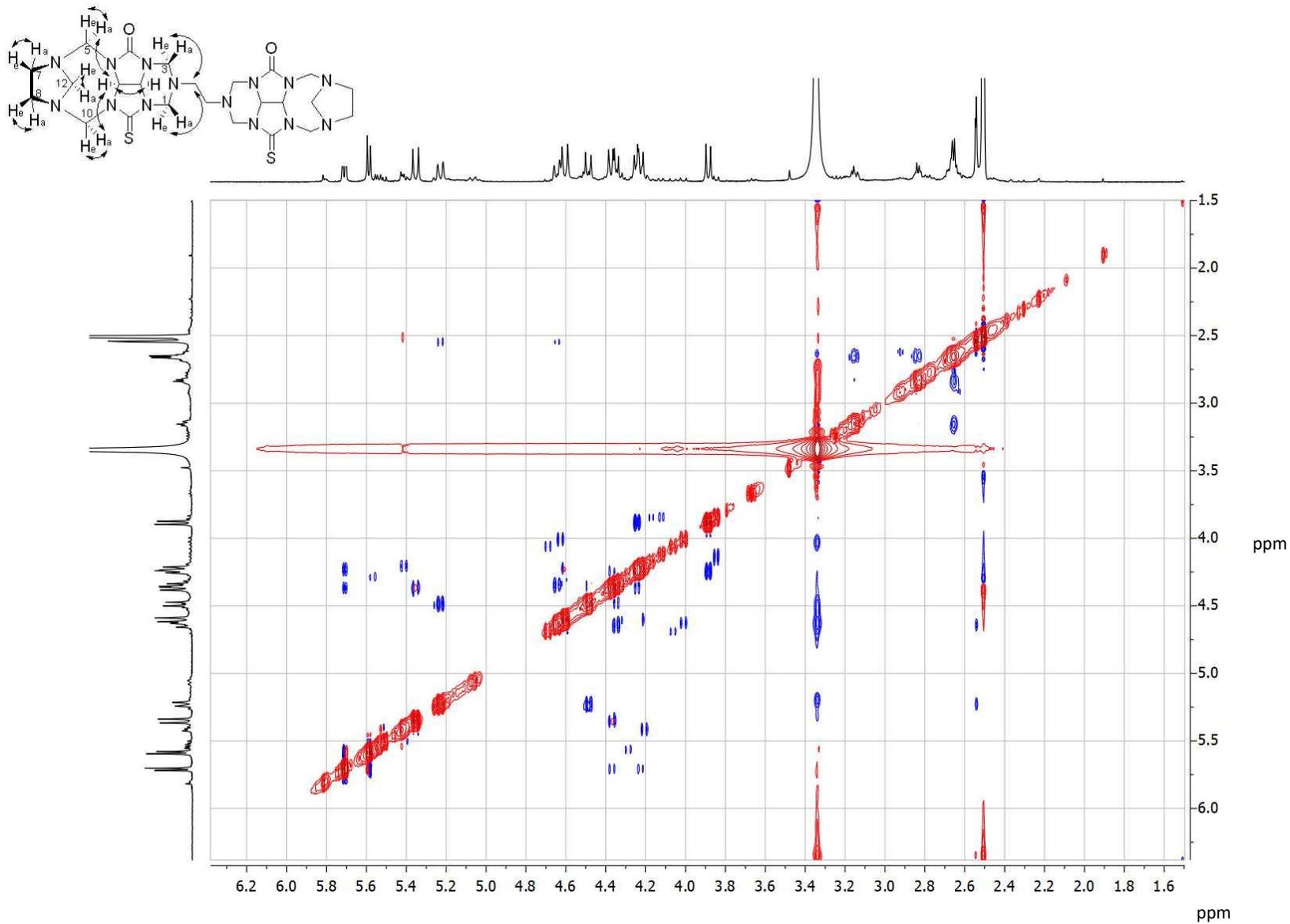
$^1\text{H}$  NMR spectrum of 2,2'-(ethane-1,2-diyl)bis(4-thioxohexahydro-1*H*,4*H*,5*H*,10*H*,11*H*-2,3*a*,4*a*,6,9,10*a*,11*a*-heptaaza-6,9-methanobenzo-*[cd]*cyclonona[*gh*]pentalen-11-one), **4**



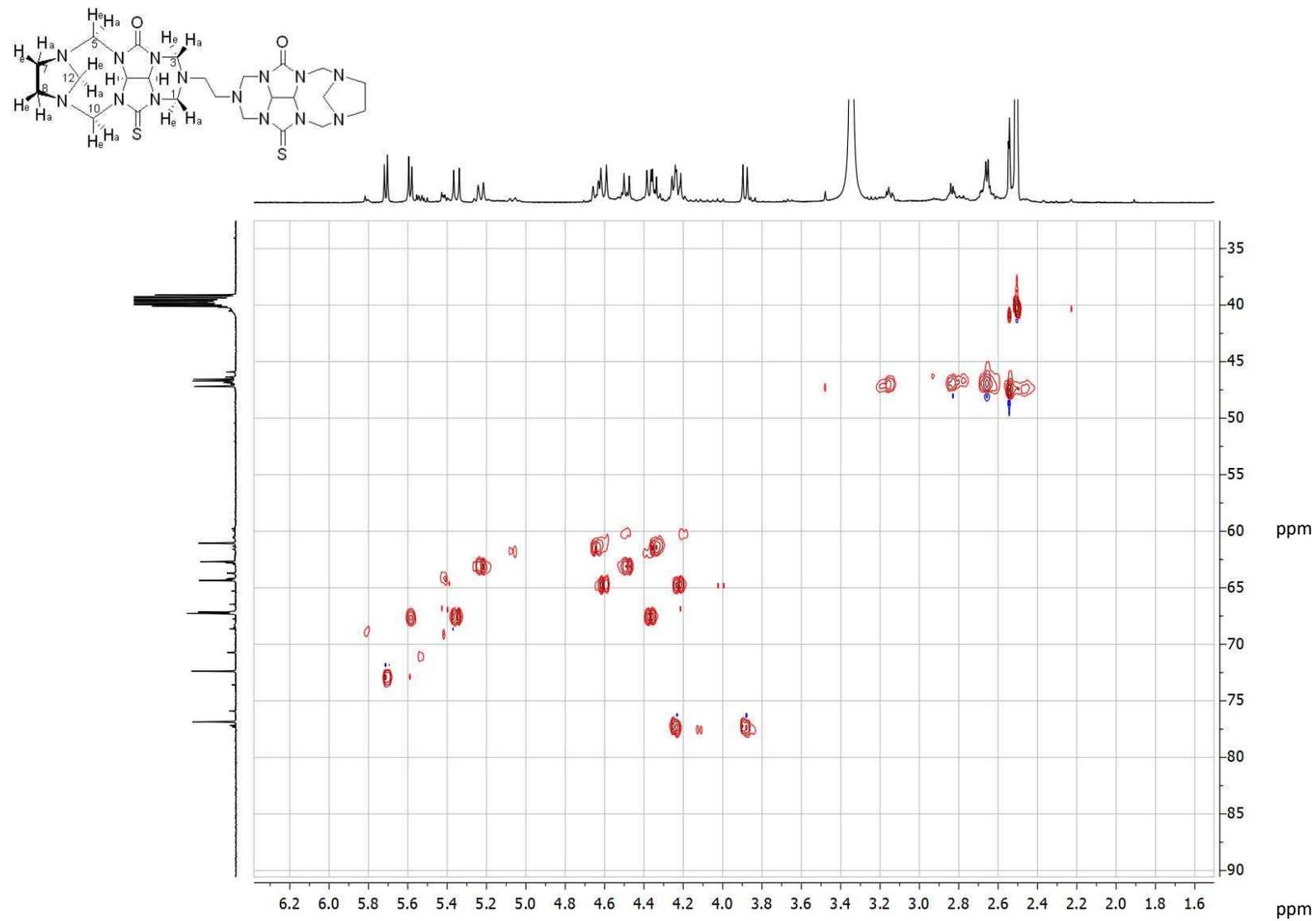
$^{13}\text{C}$  NMR spectrum of 2,2'-(ethane-1,2-diyl)bis(4-thioxohexahydro-1*H*,4*H*,5*H*,10*H*,11*H*-2,3*a*,4*a*,6,9,10*a*,11*a*-heptaaza-6,9-methanobenzo-*[cd]*cyclonona[*gh*]pentalen-11-one), **4**



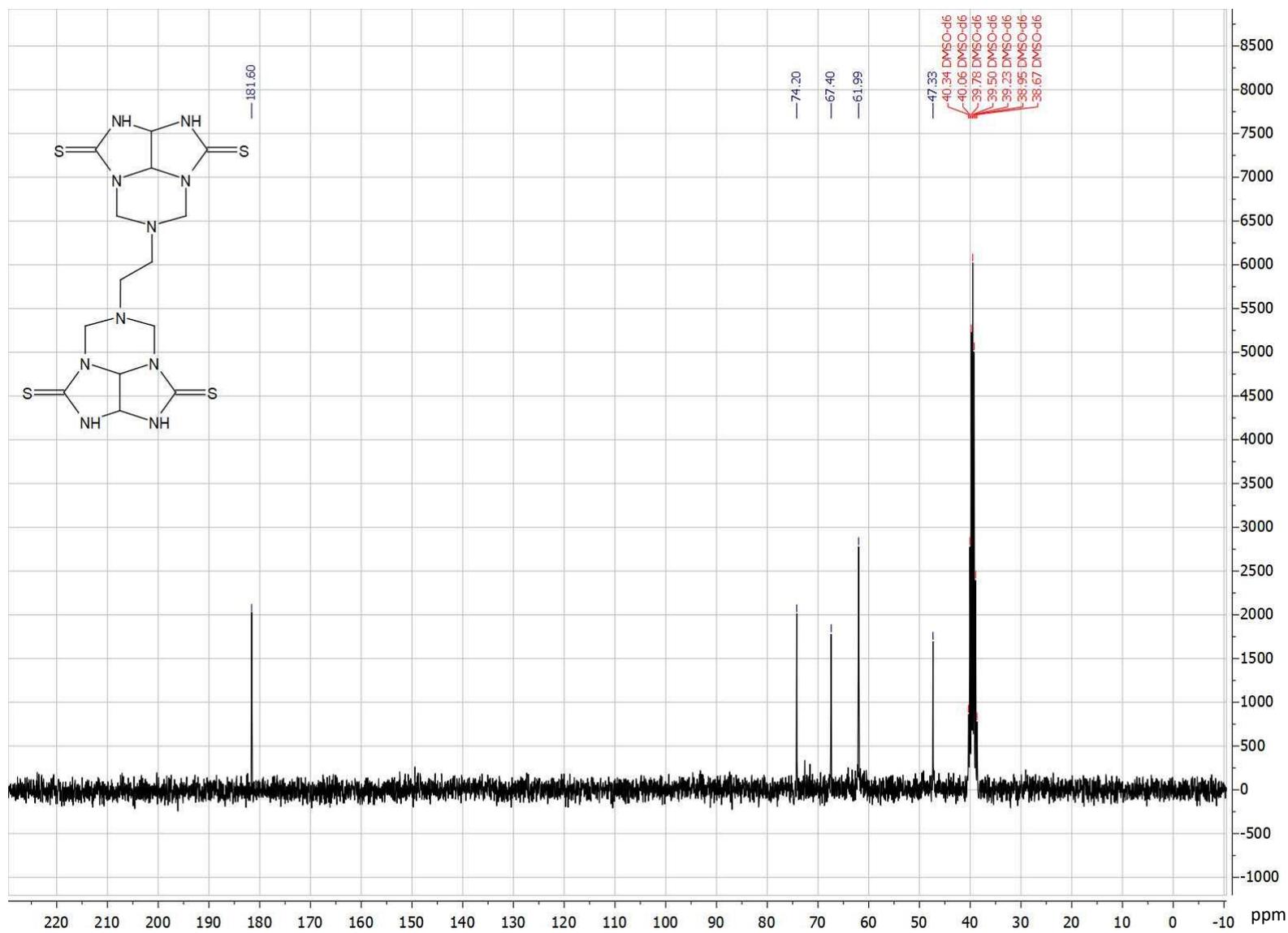
NOESY spectrum of 2,2'-(ethane-1,2-diyl)bis(4-thioxohexahydro-1*H*,4*H*,5*H*,10*H*,11*H*-2,3*a*,4*a*,6,9,10*a*,11*a*-heptaaza-6,9-methanobenzo-*[cd]*cyclonona[*gh*]pentalen-11-one), **4**



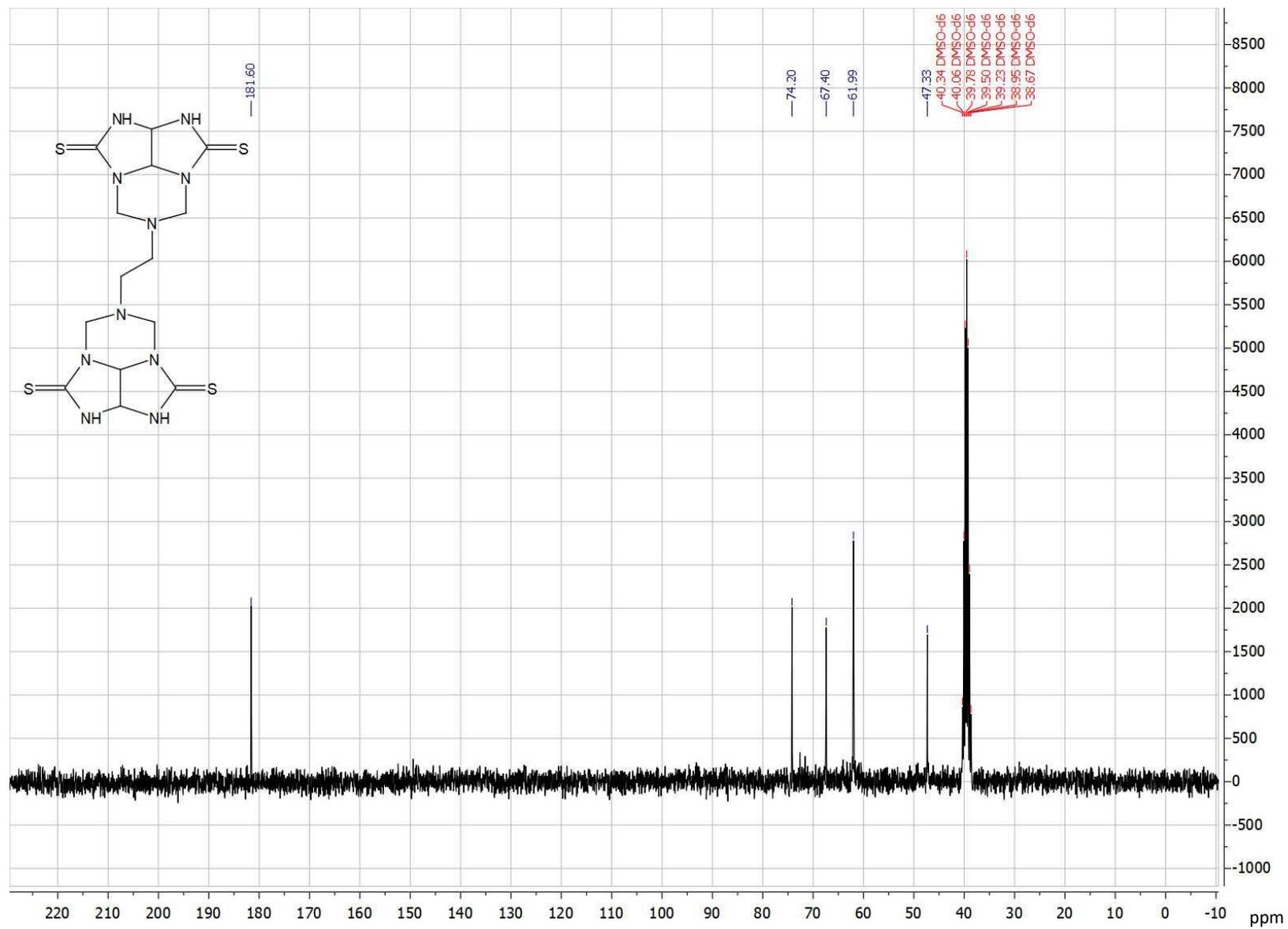
HSQC spectrum of 2,2'-(ethane-1,2-diyl)bis(4-thioxohexahydro-1*H*,4*H*,5*H*,10*H*,11*H*-2,3*a*,4*a*,6,9,10*a*,11*a*-heptaaza-6,9-methanobenzo-*[cd]*cyclonona[*gh*]pentalen-11-one), **4**



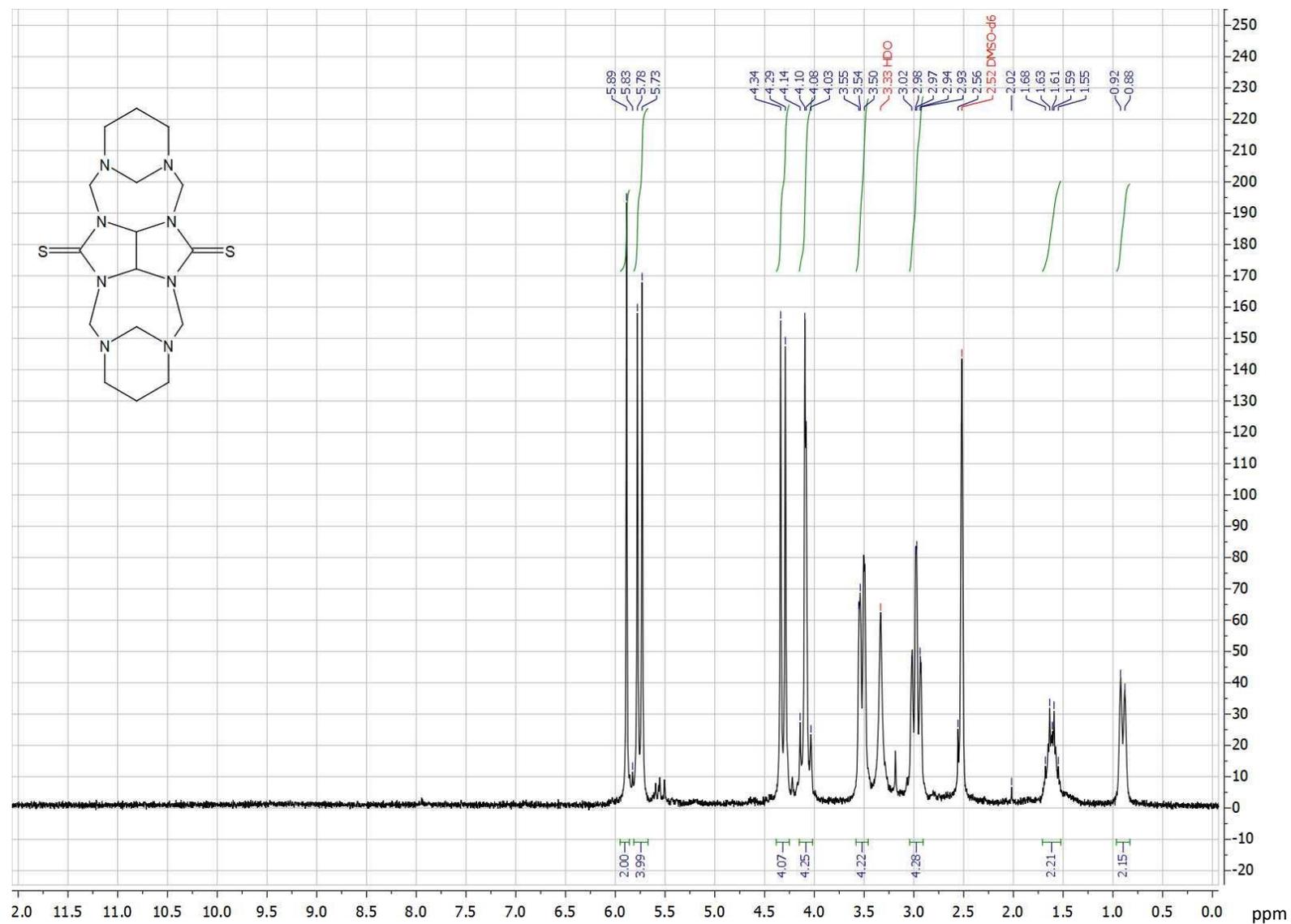
<sup>1</sup>H NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(tetrahydro-5H-2,3,4a,6,7a-pentaazacyclopena[cd]indene-1,4(2H,2a<sup>1</sup>H)-dithione), **6**



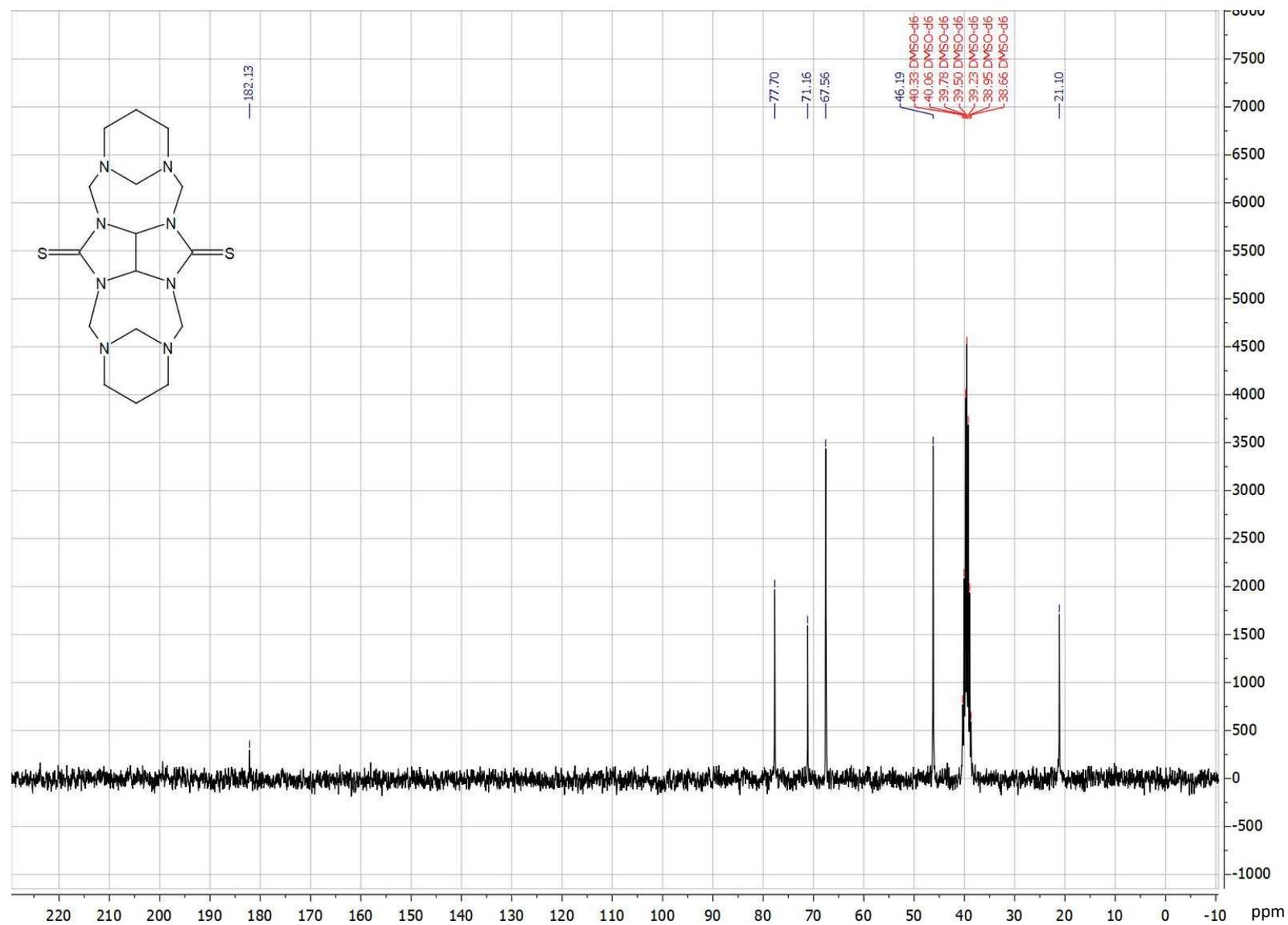
$^{13}\text{C}$  NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(tetrahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4(2H,2a1H)-dithione), **6**



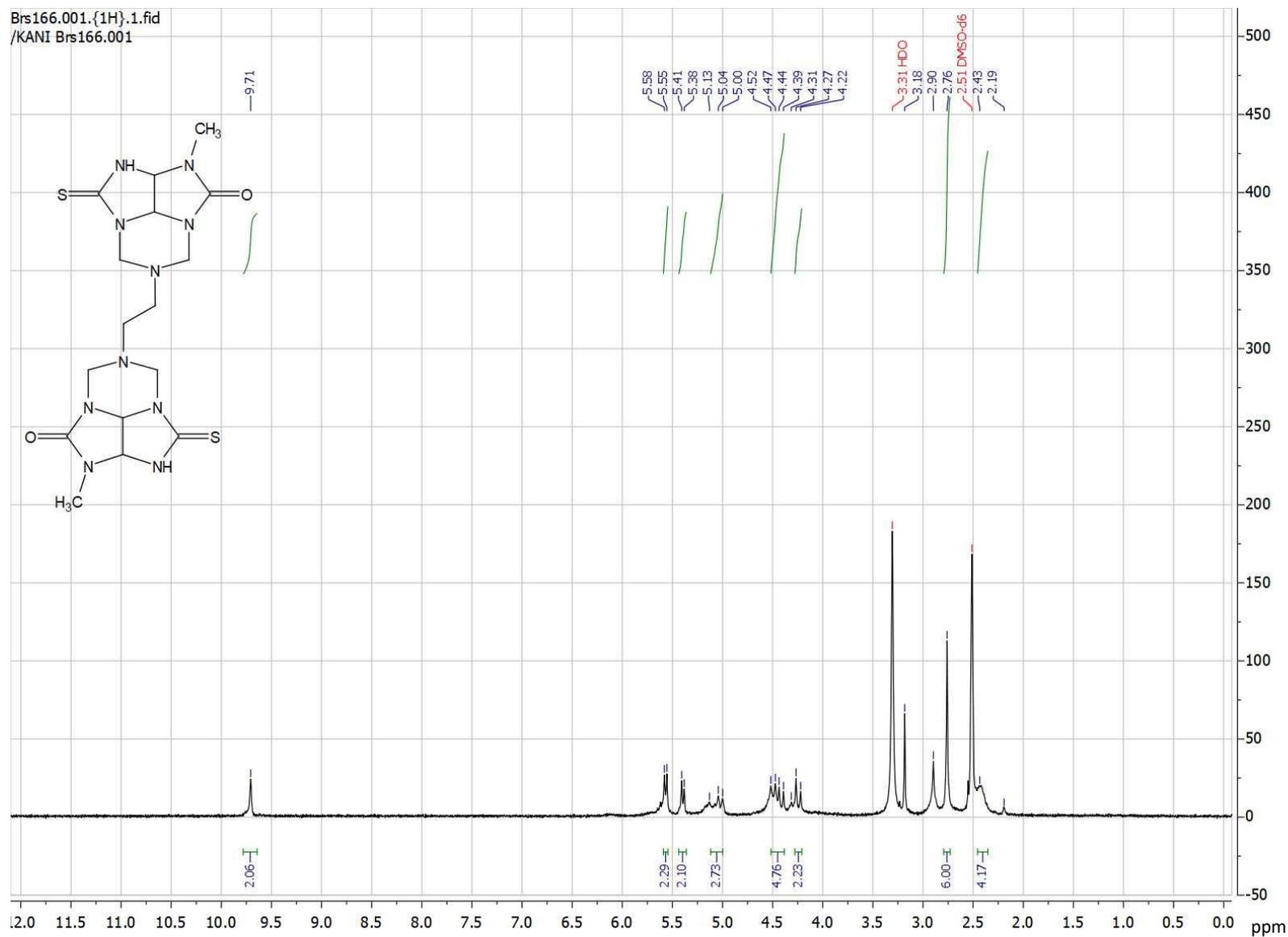
<sup>1</sup>H NMR spectrum of perhydro-2,6:10,14-dimethano-2,6,7a,8a,10,14,15a,16a-octaazadicyclodeca[*cd,gh*]pentalene-8,16-dithione, **7**



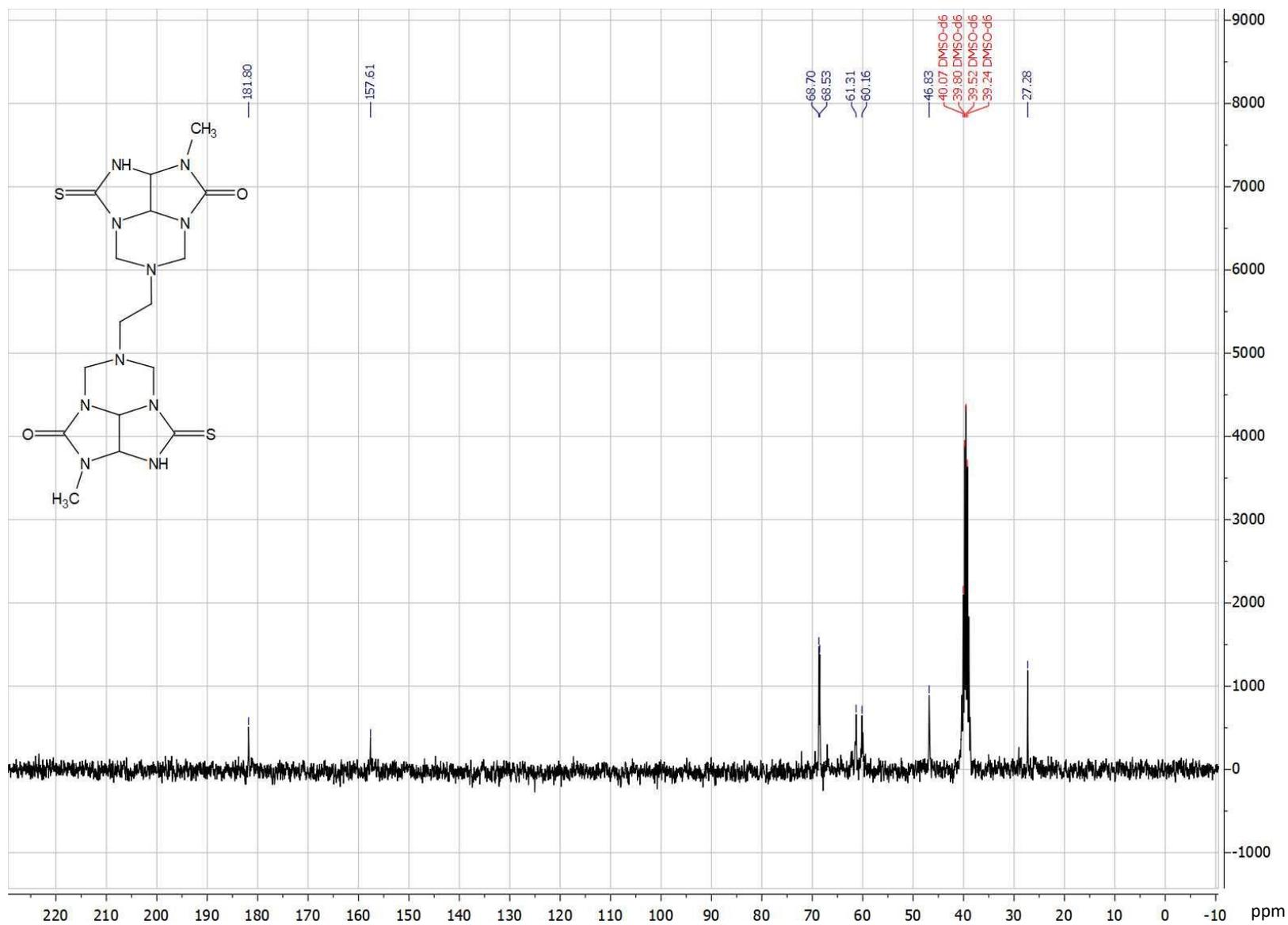
$^{13}\text{C}$  NMR spectrum of perhydro-2,6:10,14-dimethano-2,6,7a,8a,10,14,15a,16a-octaazadicyclodeca[*cd,gh*]pentalene-8,16-dithione **7**



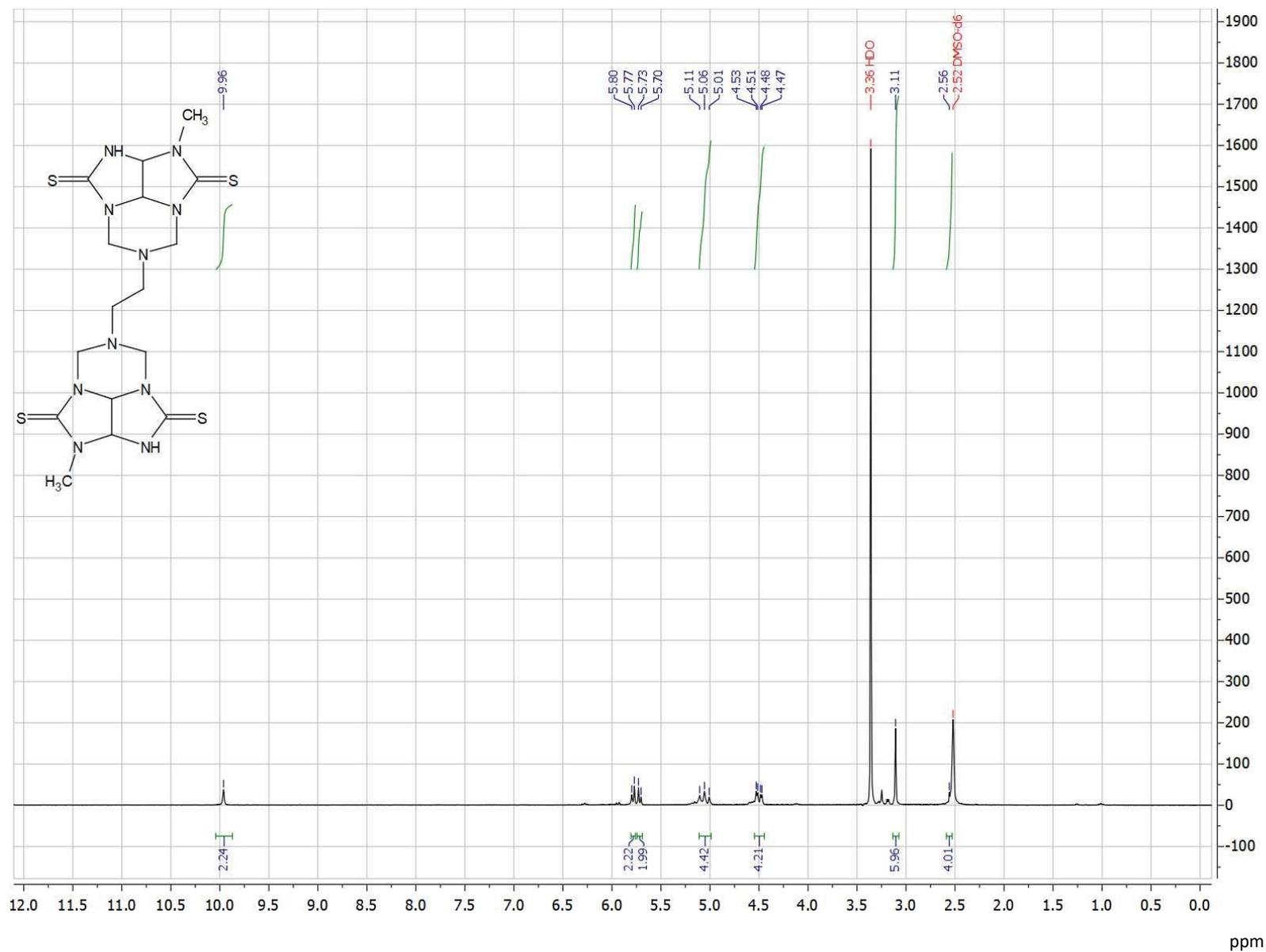
<sup>1</sup>H NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(3-methyl-1-thioxohexahydro-5H-2,3,4a,6,7a-pentazacyclopenta[cd]inden-4(2a<sup>1</sup>H)-one), **10**



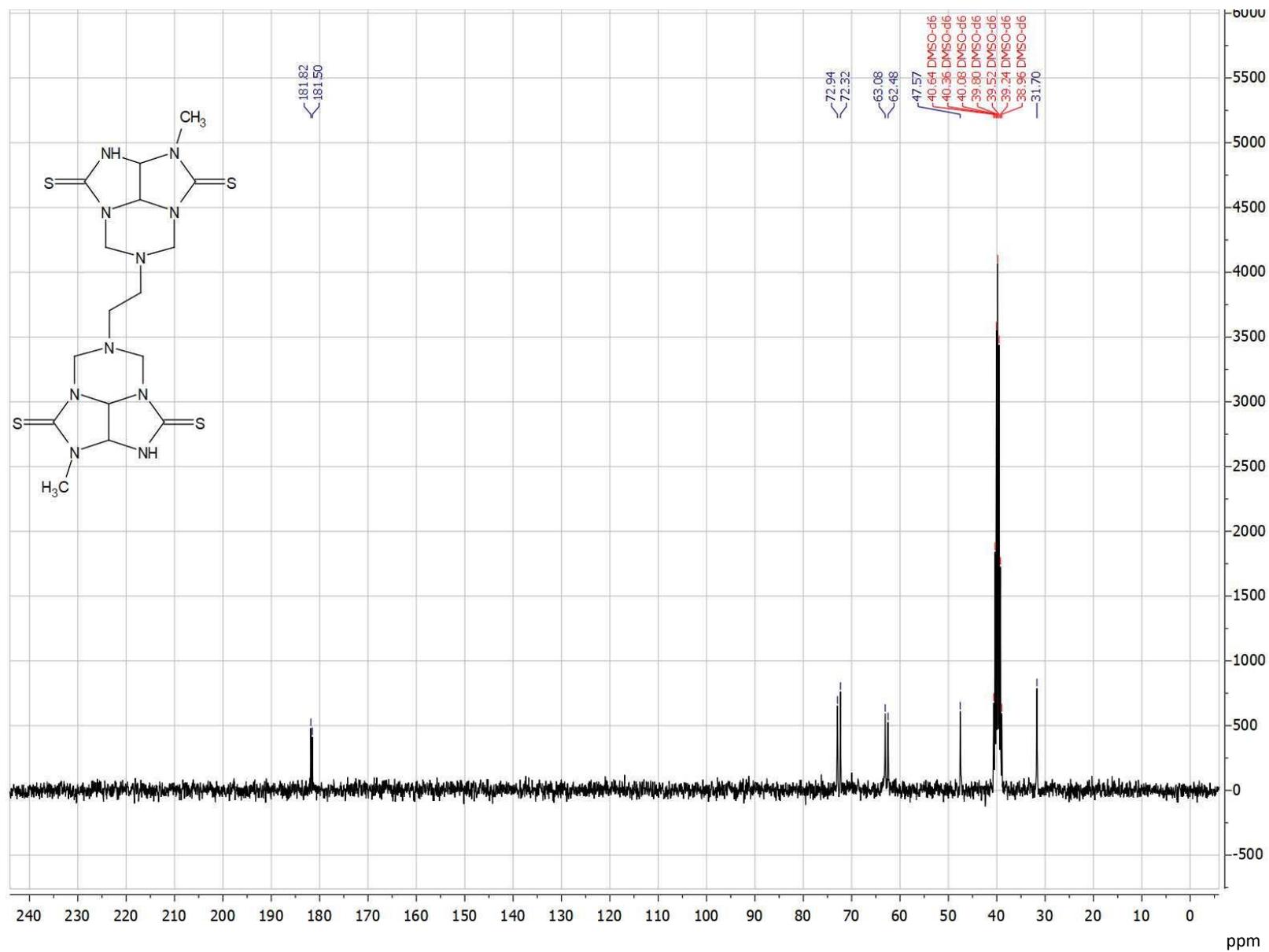
$^{13}\text{C}$  NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(3-methyl-1-thioxohexahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]inden-4(2a<sup>1</sup>H)-one), **10**



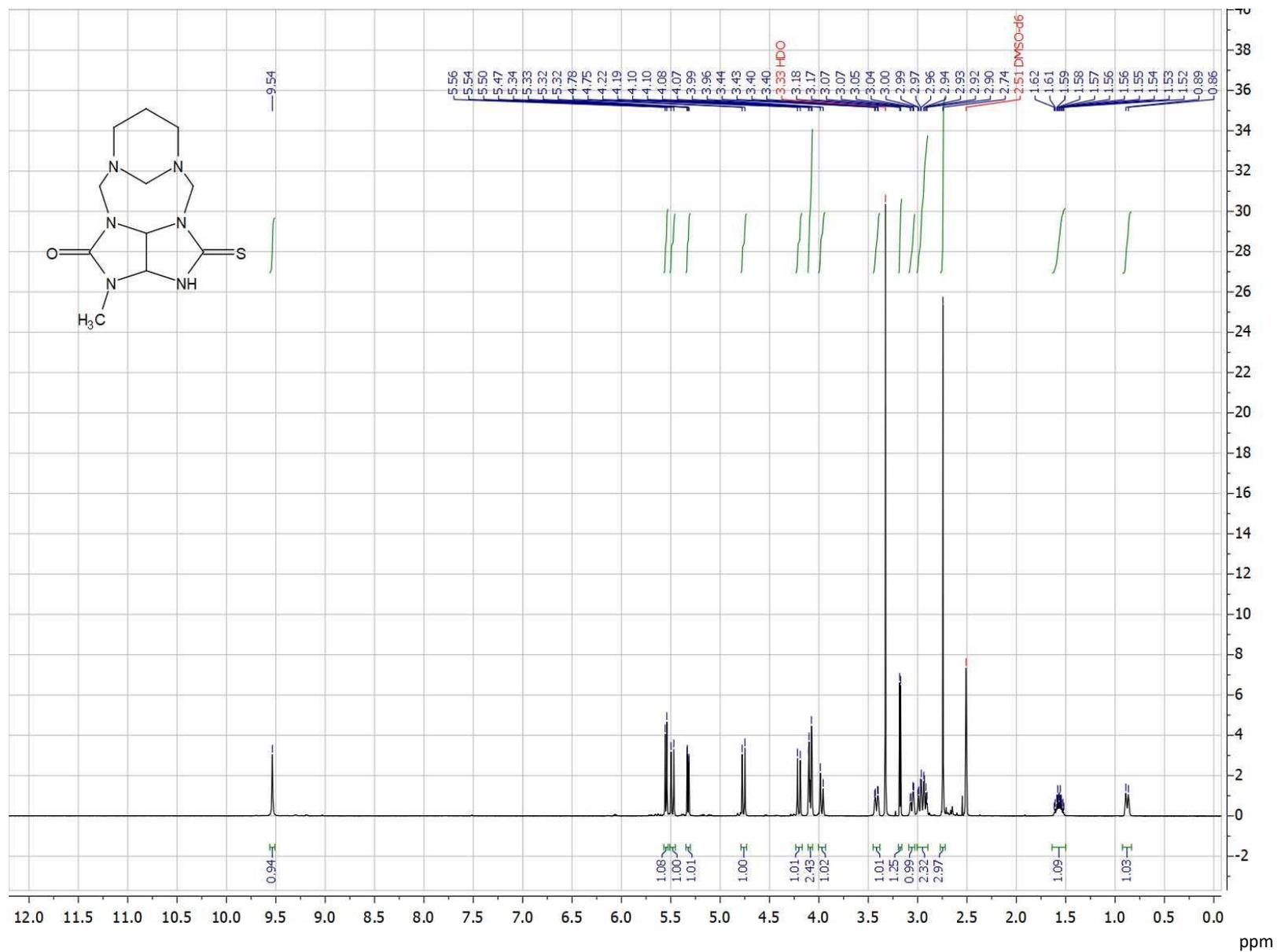
<sup>1</sup>H NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(3-methyltetrahydro-5H-2,3,4a,6,7a-pentaazacyclopenta[cd]indene-1,4(2H,2a<sup>1</sup>H)-dithione), **11**



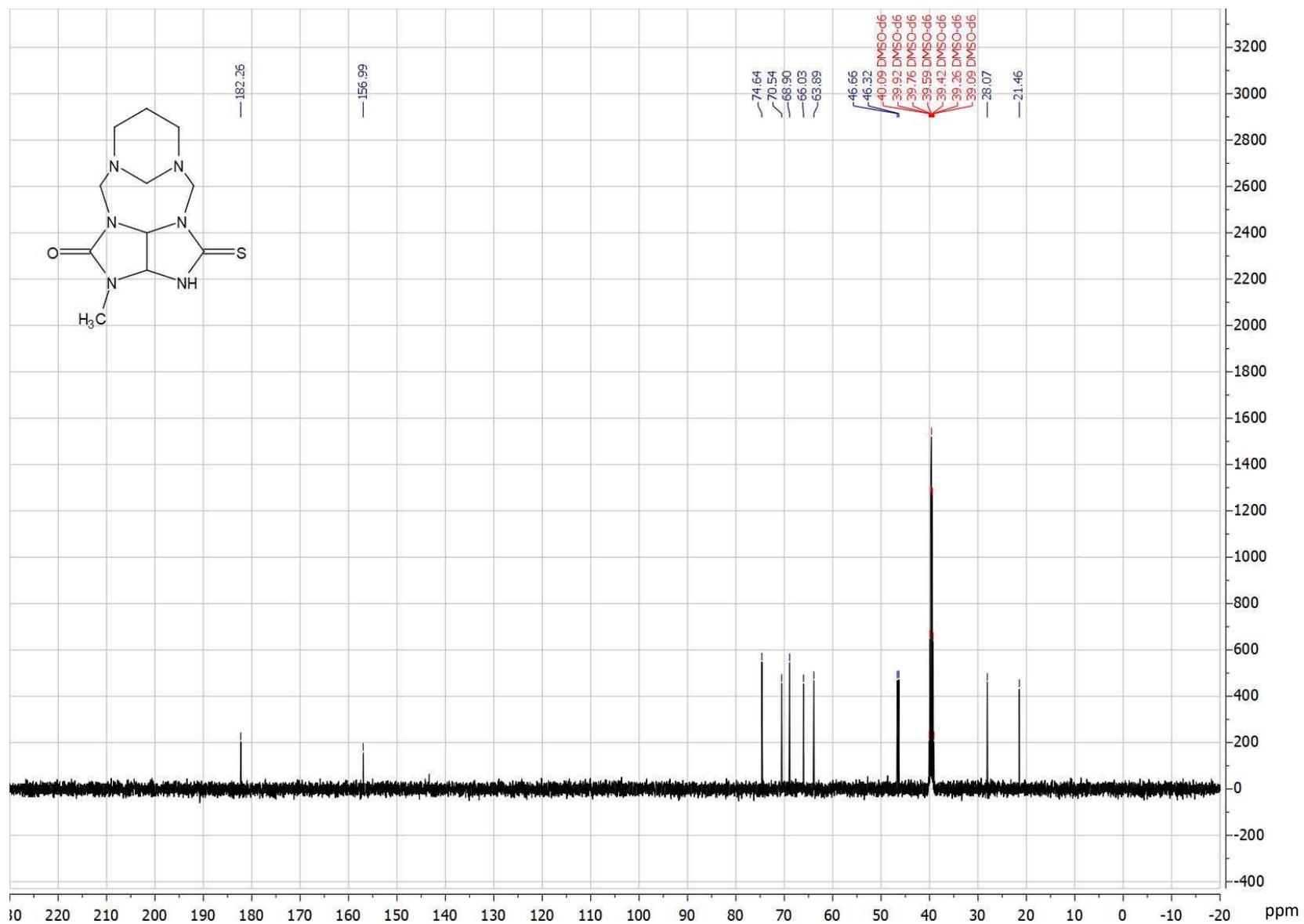
$^{13}\text{C}$  NMR spectrum of 6,6''-(ethane-1,2-diyl)bis(3-methyltetrahydro-5H-2,3,4a,6,7a-pentaazacyclo-penta[cd]indene-1,4(2H,2a<sup>1</sup>H)-dithione), **11**



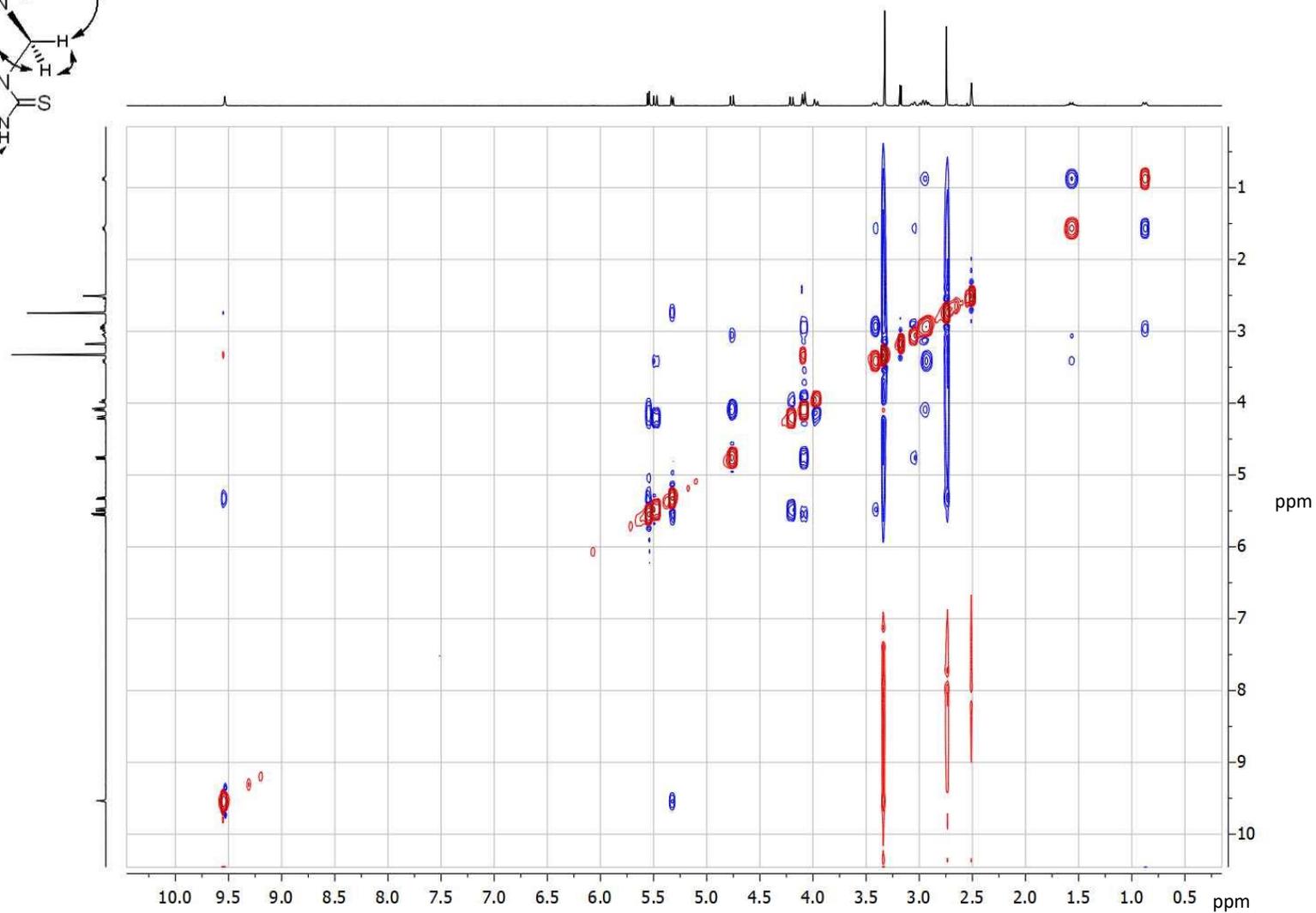
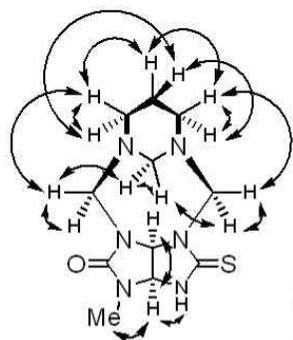
$^1\text{H}$  NMR spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4a,6,10,11a-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2a<sup>1</sup>*H*)-one, **12**



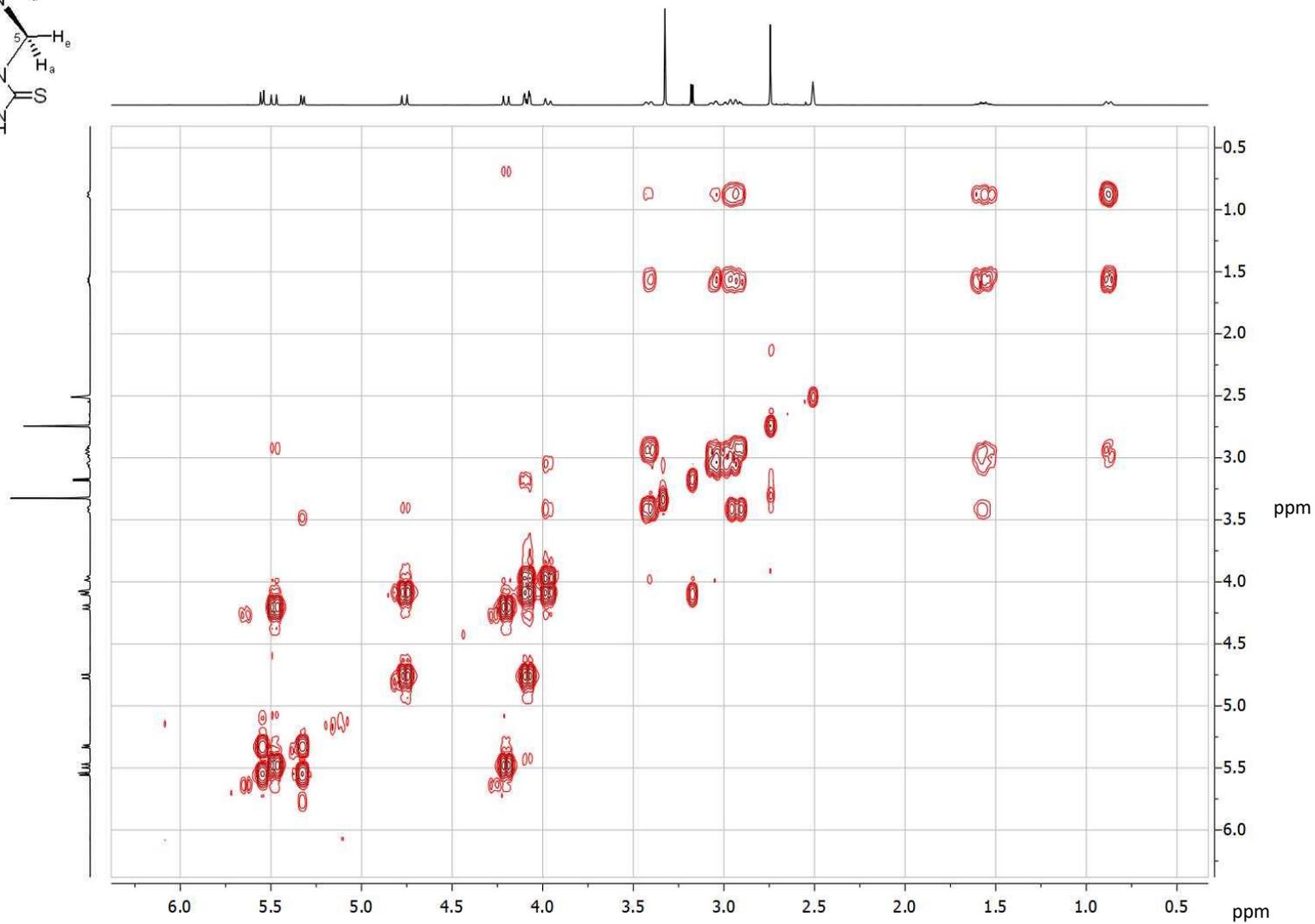
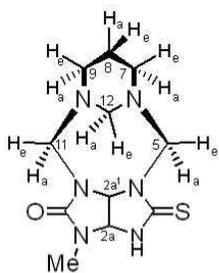
$^{13}\text{C}$  NMR spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4a,6,10,11a-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2a<sup>1</sup>*H*)-one, **12**



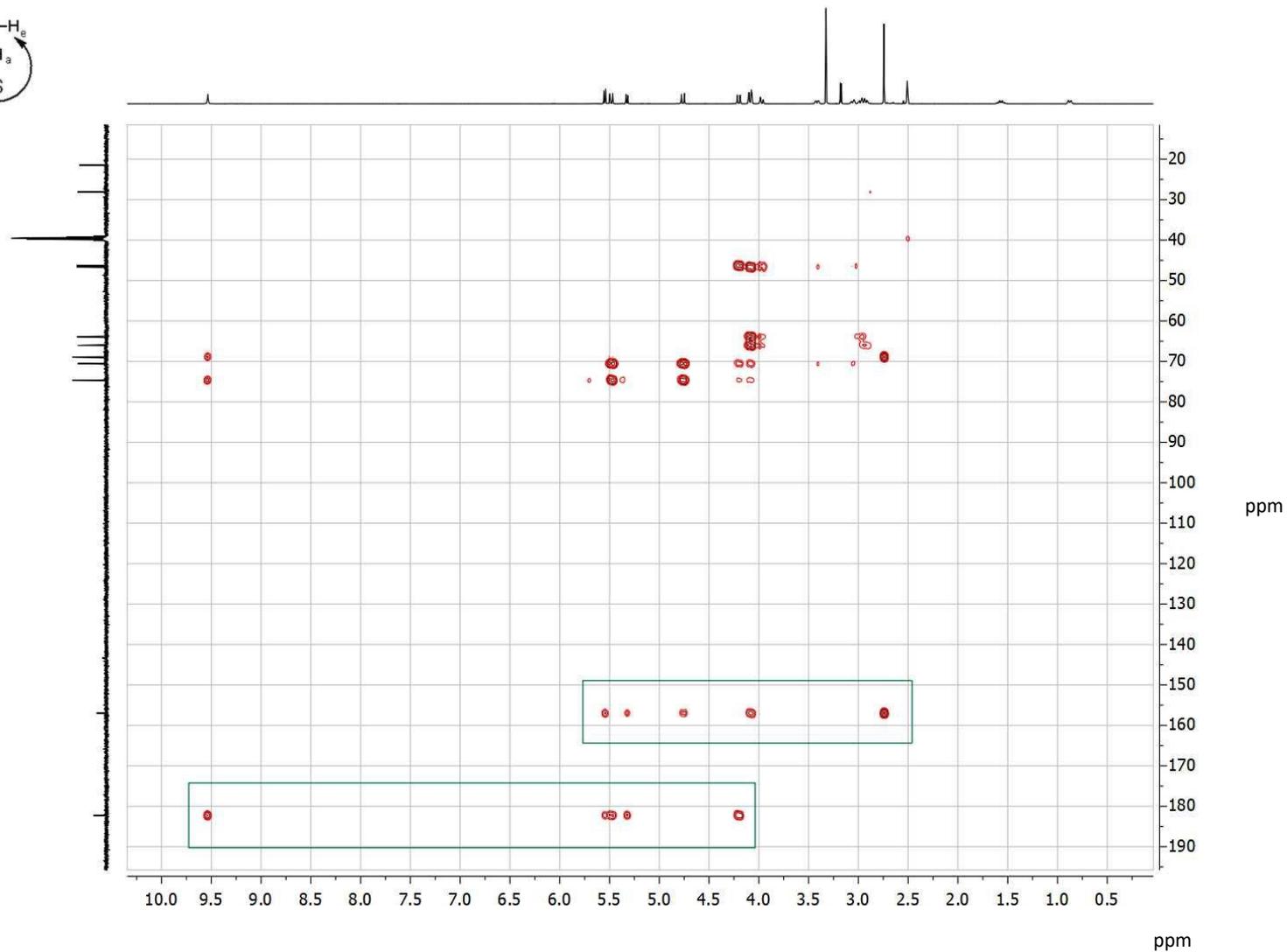
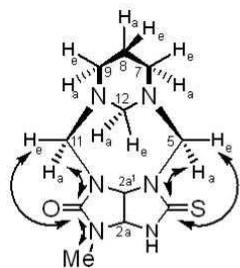
NOESY spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4*a*,6,10,11*a*-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2*a*<sup>1</sup>*H*)-one **12**



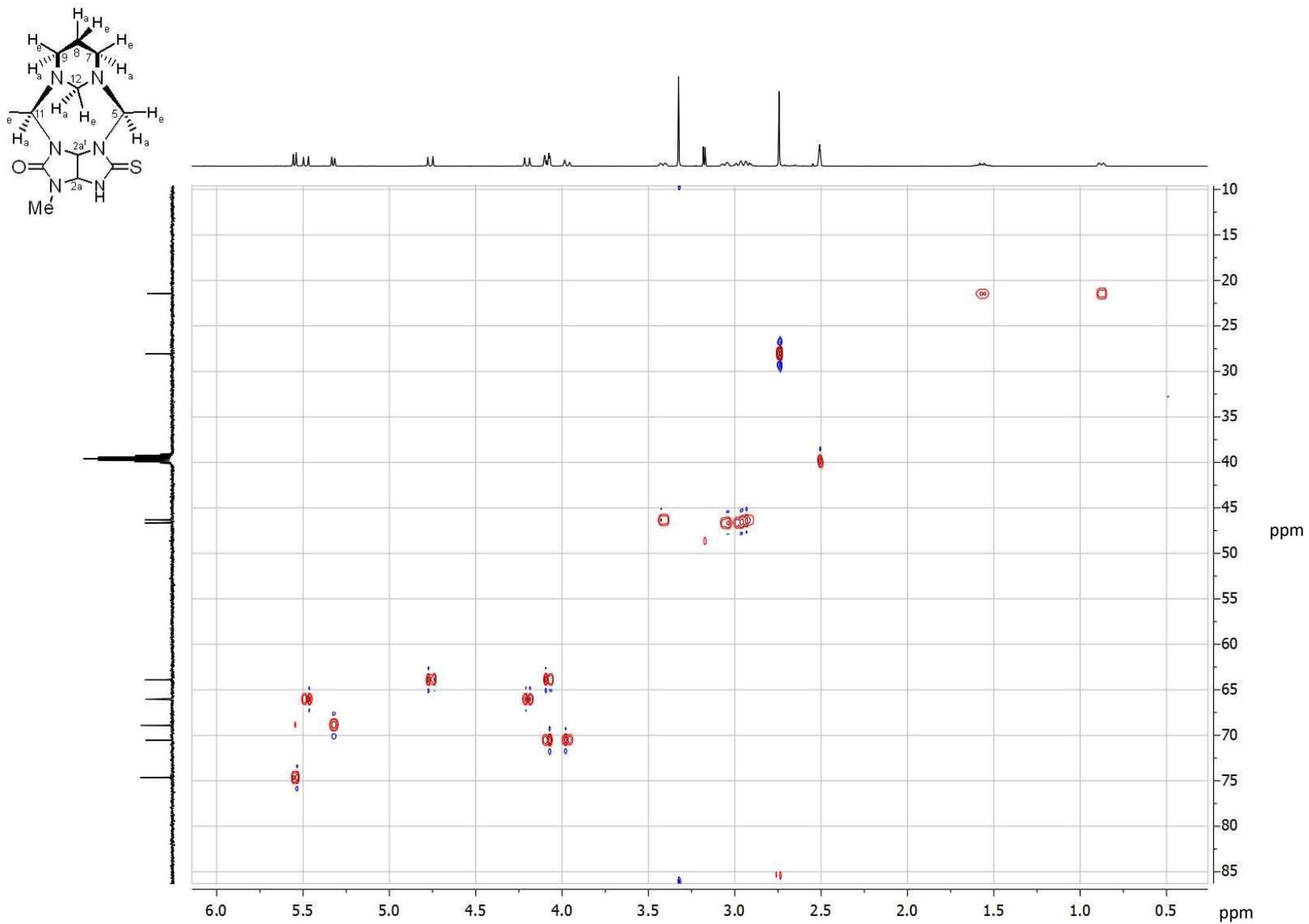
COSY spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4*a*,6,10,11*a*-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2*a*<sup>1</sup>*H*)-one, **12**



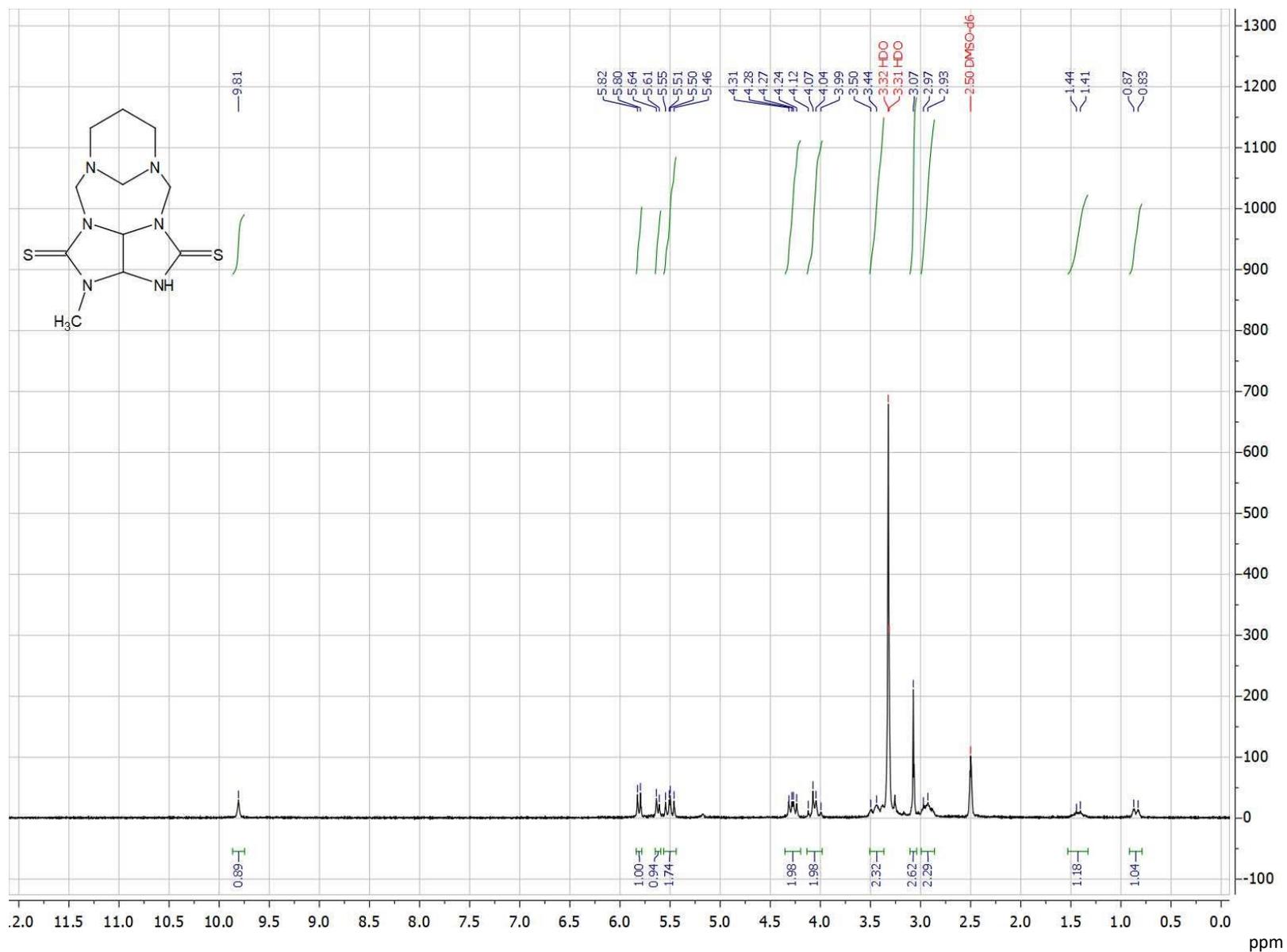
HMBC spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4*a*,6,10,11*a*-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2*a*<sup>1</sup>*H*)-one, **12**



HSQC spectrum of 3-methyl-1-thioxohexahydro-5*H*,7*H*,11*H*-2,3,4*a*,6,10,11*a*-hexaaza-6,10-methanocyclodeca[*cd*]pentalen-4(2*a*<sup>1</sup>*H*)-one, **12**



<sup>1</sup>H NMR spectrum of 3-methyltetrahydro-5*H*,7*H*,11*H*-2,3,4a,6,10,11a-hexaaza-6,10-methanocyclodeca[*cd*]pentalene-1,4(2*H*,2a<sup>1</sup>*H*)-dithione, **13**



$^{13}\text{C}$  NMR spectrum of 3-methyltetrahydro-5*H*,7*H*,11*H*-2,3,4*a*,6,10,11*a*-hexaaza-6,10-methanocyclodeca[*cd*]pentalene-1,4(2*H*,2*a*<sup>1</sup>*H*)-dithione, **13**

