

## *Supplementary Material*

Amphilectene diterpene isonitriles and formamido derivatives from the  
Hainan nudibranch *Phyllidia coelestis*

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S33 - <sup>1</sup>H NMR spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) (CDCl<sub>3</sub>, Bruker 300 MHz).

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S38 - <sup>1</sup>H NMR spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) (CDCl<sub>3</sub>, Bruker 600 MHz).

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S42 - HMBC spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) (CDCl<sub>3</sub>, Bruker 600 MHz, *J*=7Hz).

S43 - <sup>1</sup>H NMR spectrum of 7-formamido amphilecta-10,14-diene (**9**) (CDCl<sub>3</sub>, Bruker 400 MHz).

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S47 - <sup>1</sup>H NMR spectrum of 7-formamido amphilecta-10,14-diene (**9**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz).

S48 - <sup>1</sup>H-<sup>1</sup>H COSY spectrum of 7-formamido amphilecta-10,14-diene (**9**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz).

S49 - HSQC spectrum of 7-formamido amphilecta-10,14-diene (**9**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz).

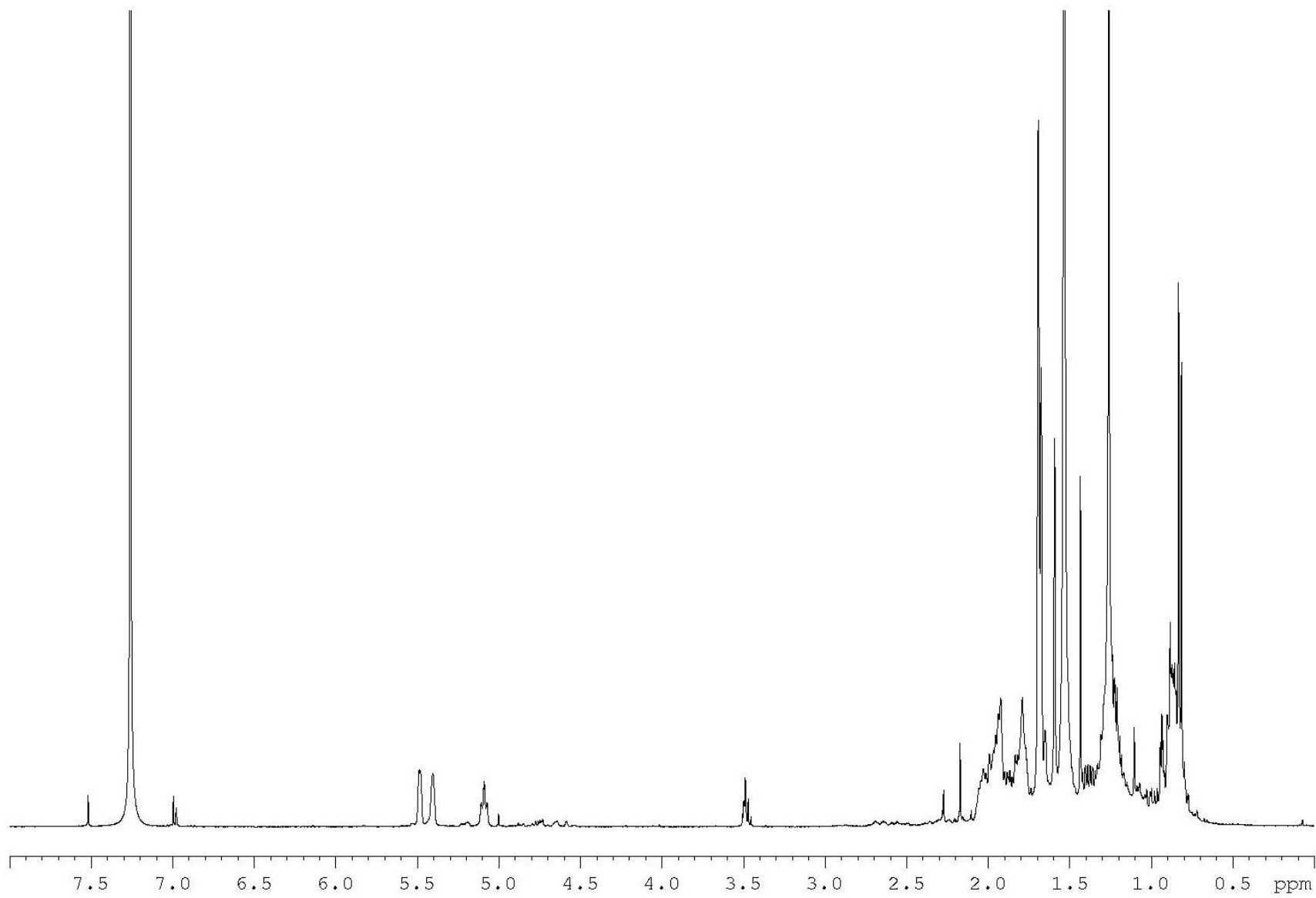
S50 - HMBC spectrum of 7-formamido amphilecta-10,14-diene (**9**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz, *J*=7Hz).

S51 -  $^1\text{H}$  NMR spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

S52 -  $^1\text{H}$ - $^1\text{H}$  COSY spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

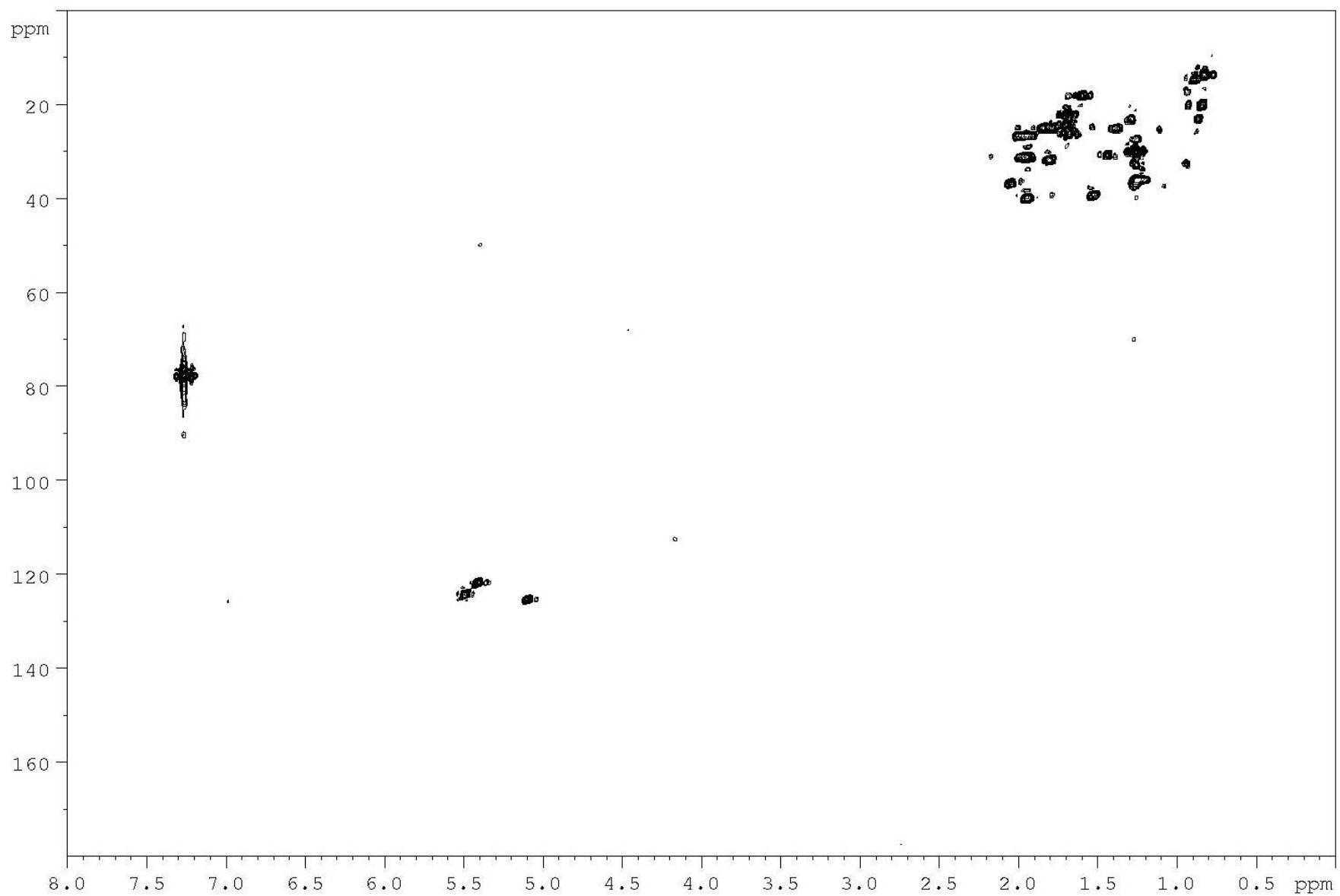
S53 - HSQC spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

S54 - Figure 1. Individuals of *P. coelestis* collected in Hainan (China) in 2002 (a) and 2013 (b).

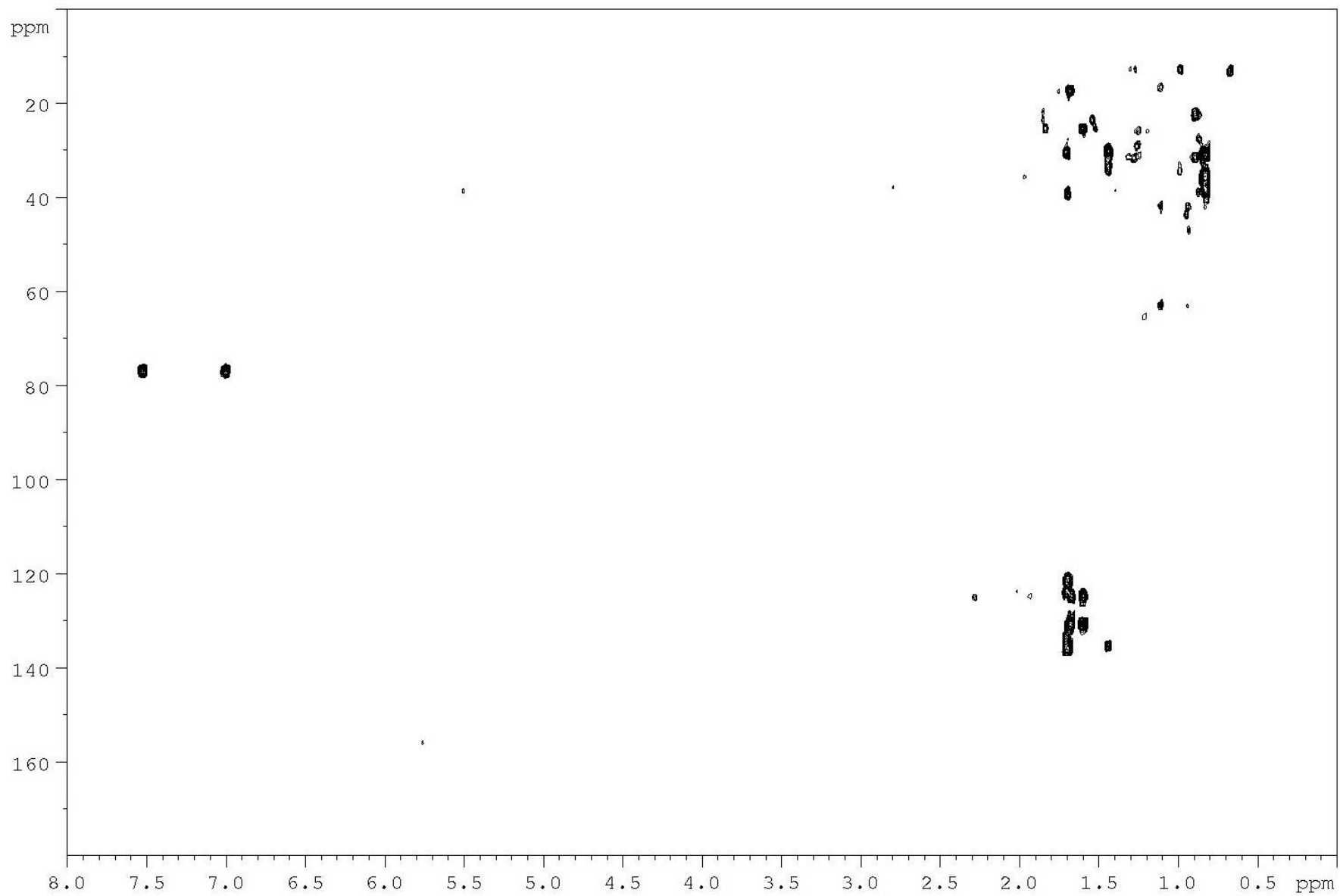


$^1\text{H}$  NMR spectrum of biflora-4,9,15-triene (**1**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



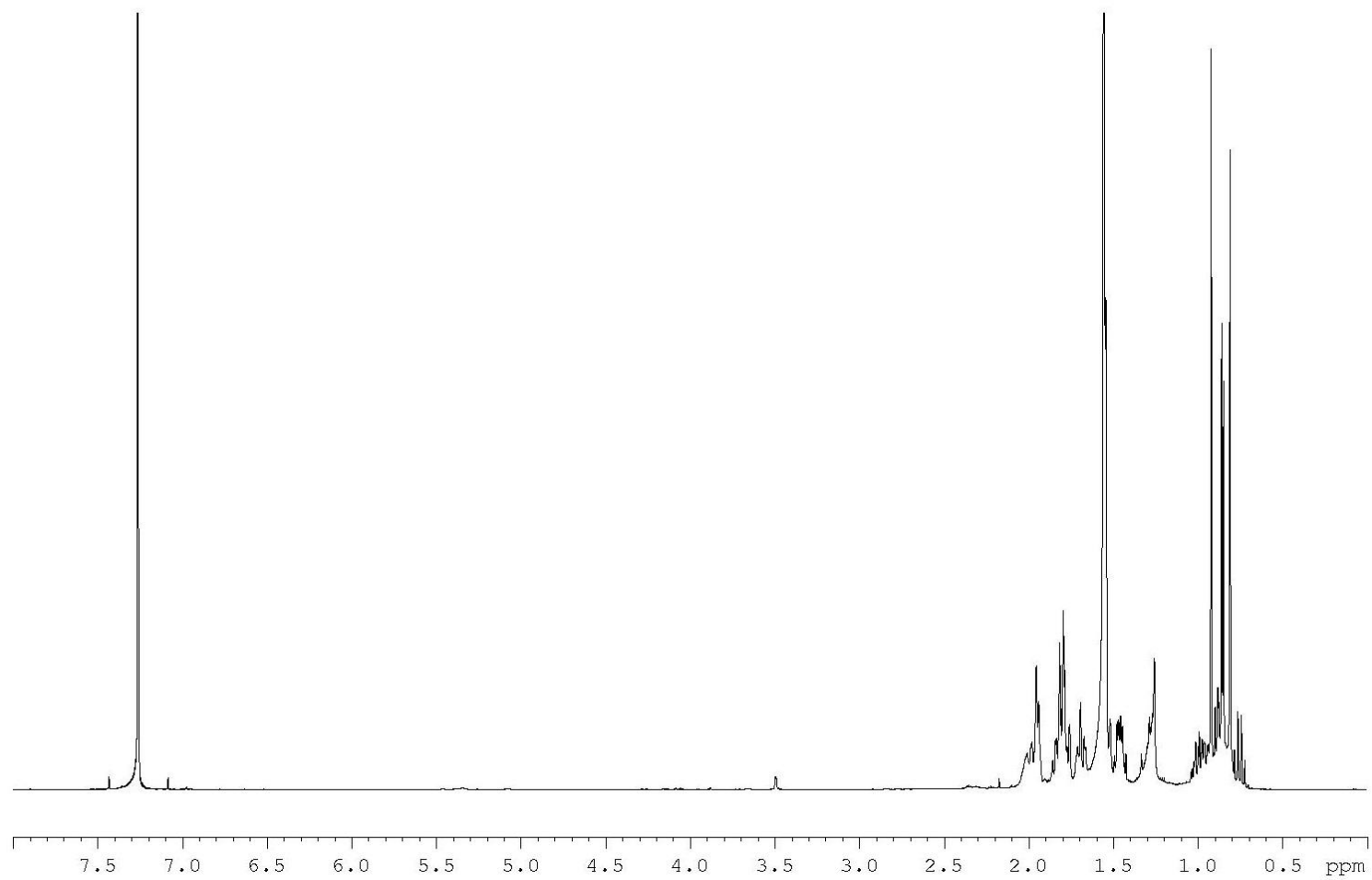


HSQC spectrum of biflora-4,9,15-triene (**1**) (CDCl<sub>3</sub>, Bruker 400 MHz).

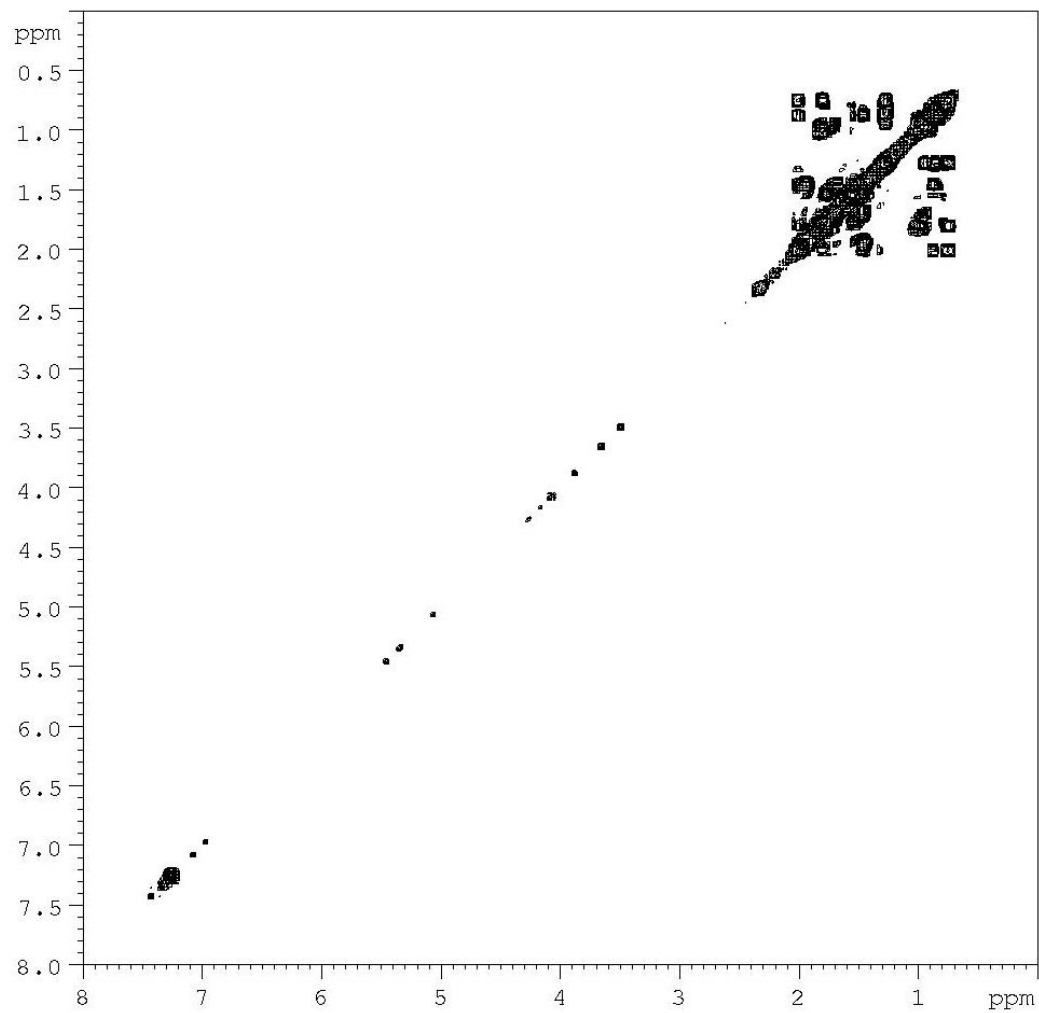


HMBC spectrum of biflora-4,9,15-triene (1) (CDCl<sub>3</sub>, Bruker 400 MHz,  $J=7$ Hz).

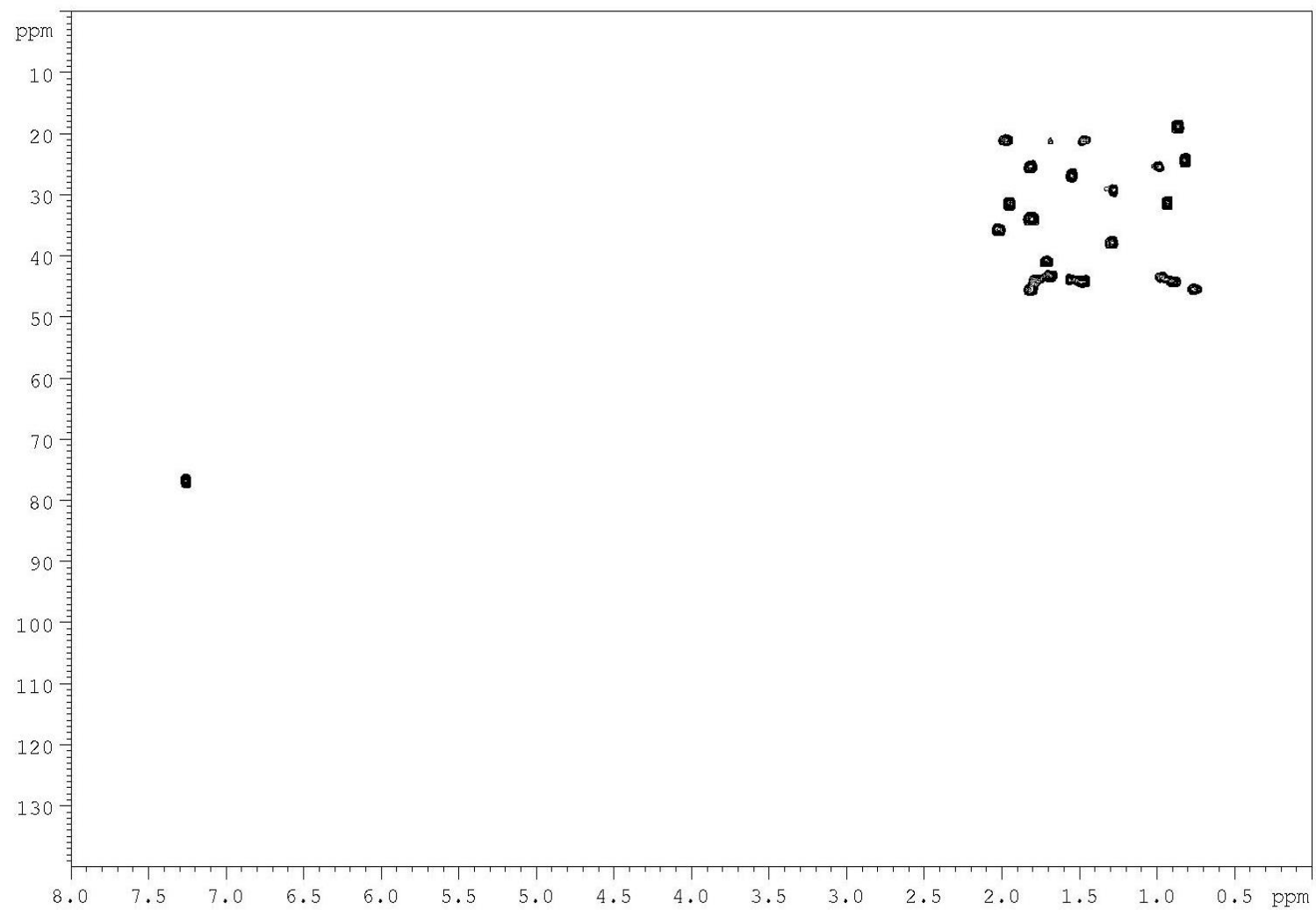




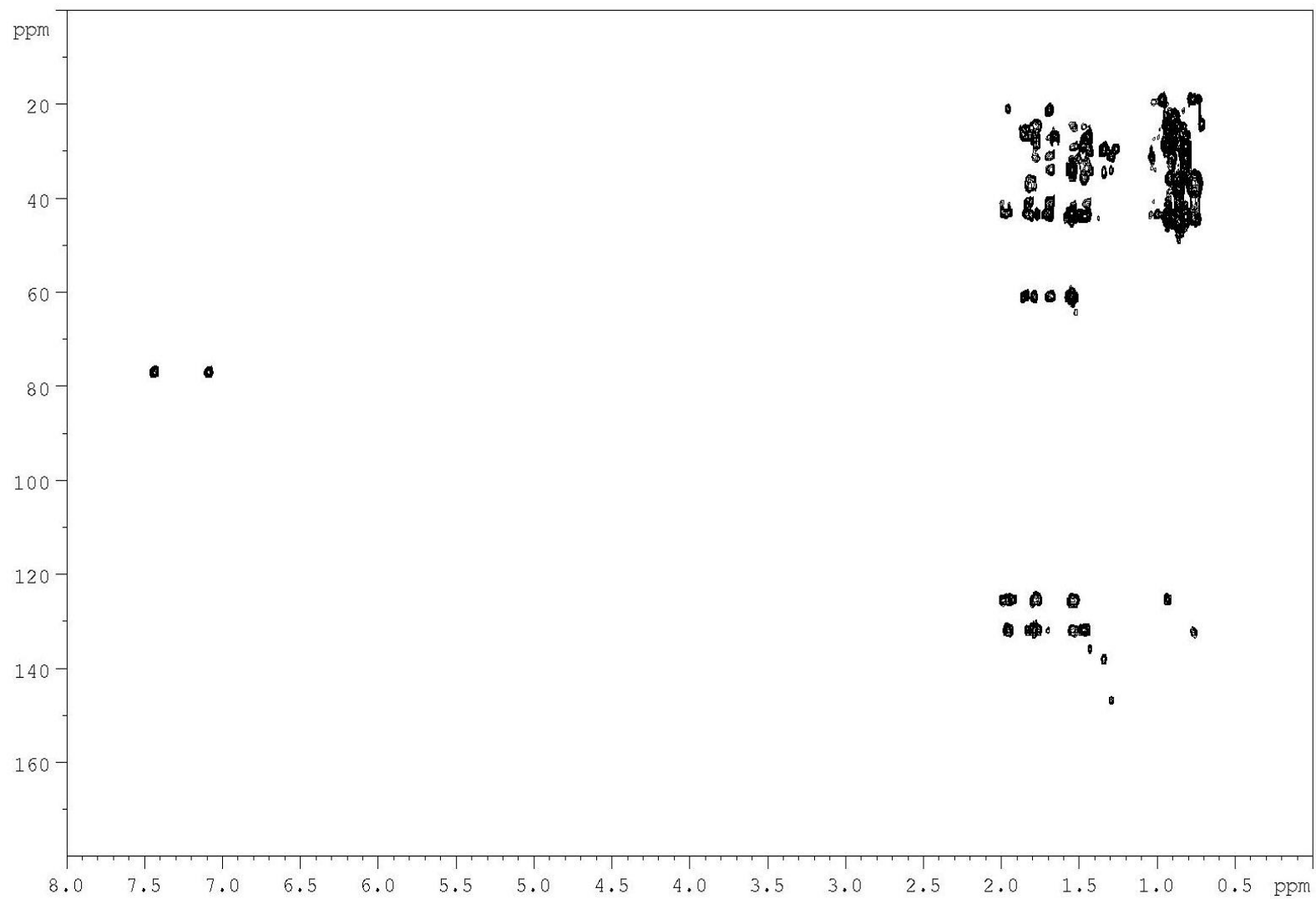
$^1\text{H}$  NMR spectrum of 7-isocyano-11-cycloamphilectene (2) ( $\text{CDCl}_3$ , Bruker 400 MHz).



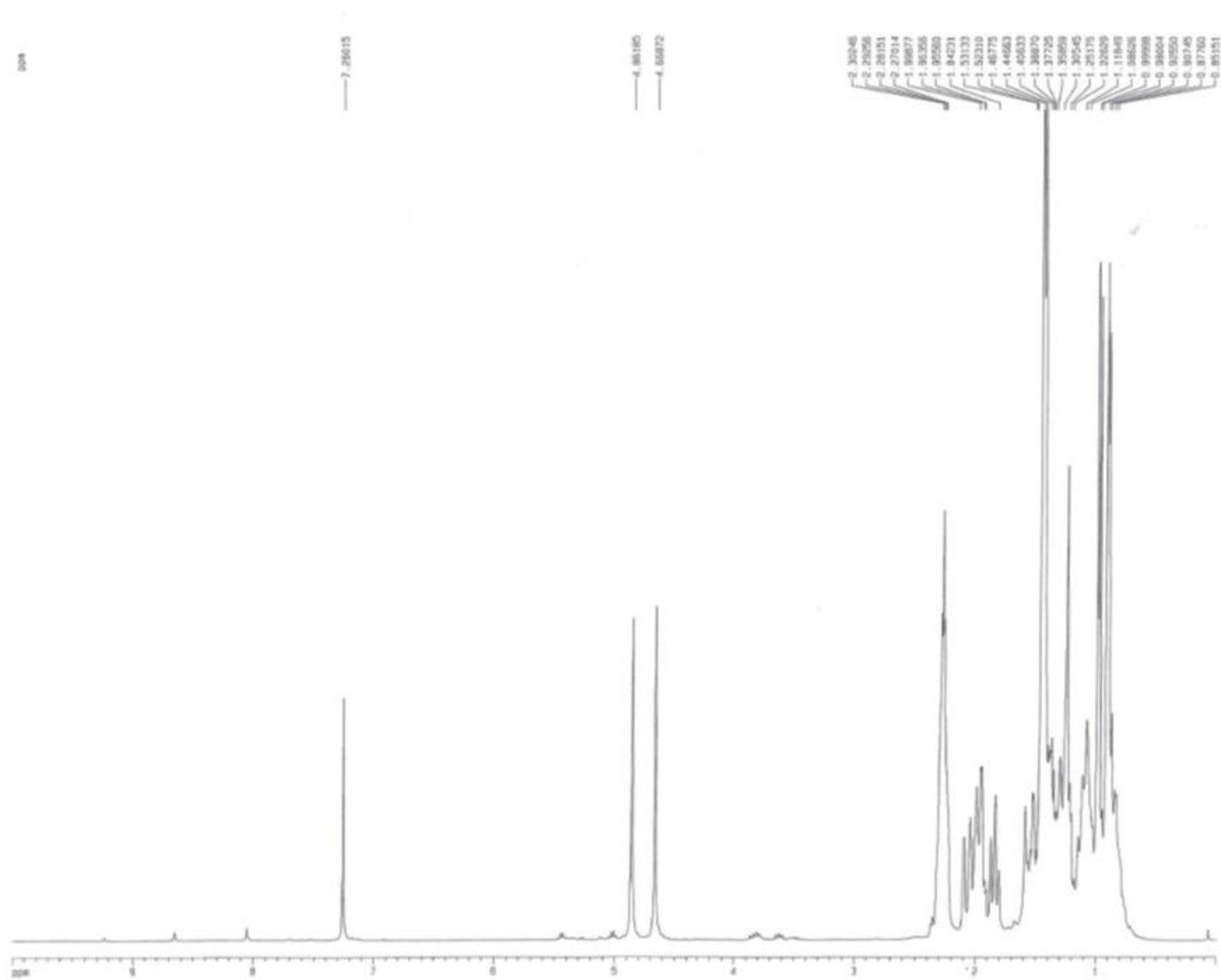
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyano-11-cycloamphilectene (**2**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



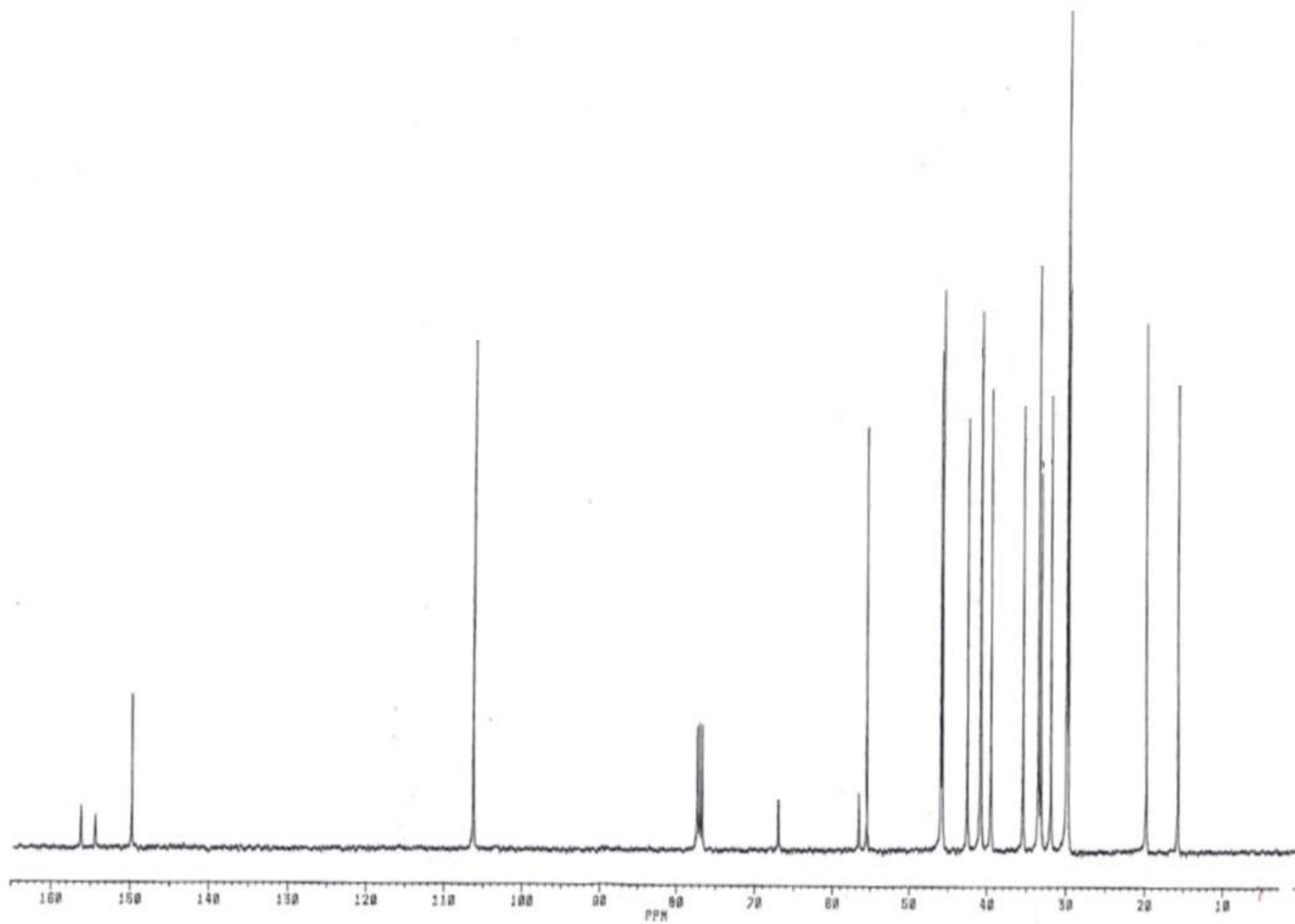
HSQC spectrum of 7-isocyano-11-cycloamphilectene (**2**) (CDCl<sub>3</sub>, Bruker 400 MHz).



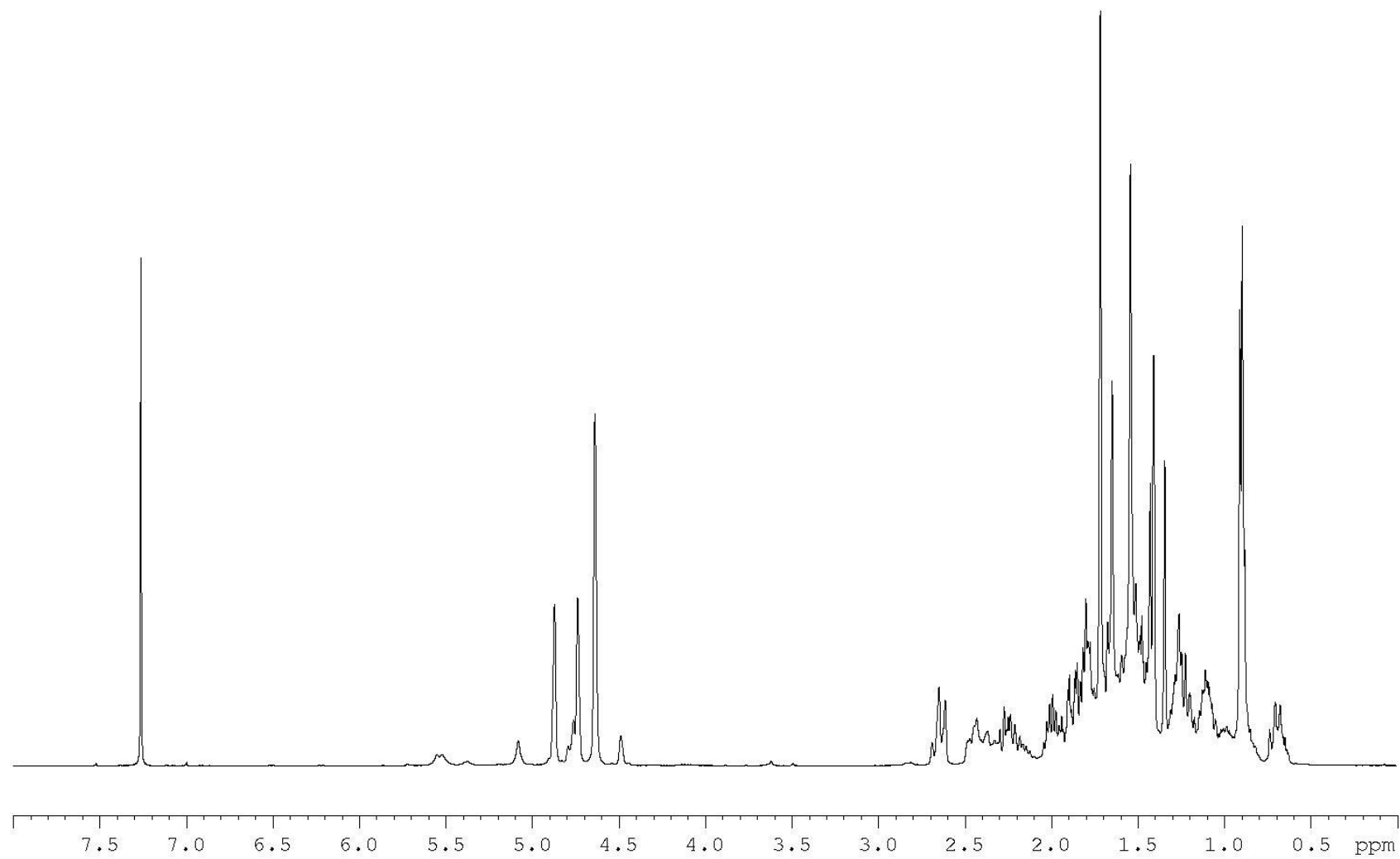
HMBC spectrum of 7-isocyano-11-cycloamphilectene (**2**) ( $\text{CDCl}_3$ , Bruker 400 MHz,  $J=7\text{Hz}$ )



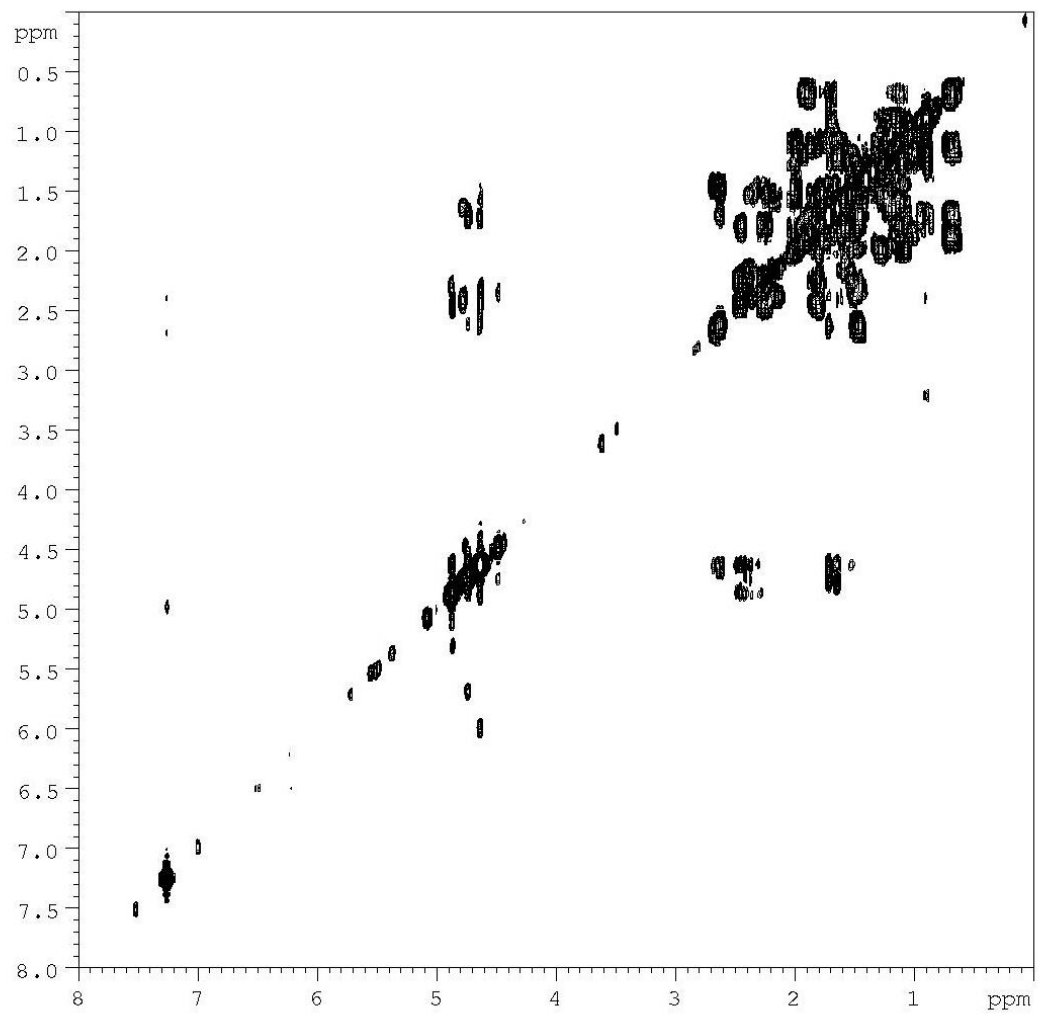
$^1\text{H}$  NMR spectrum of 8,15-diisocyno-11(20)-amphilectene (**3**) ( $\text{CDCl}_3$ , Bruker 300 MHz).



$^{13}\text{C}$  NMR spectrum of 8,15-diisocyano-11(20)-amphilectene (**3**) ( $\text{CDCl}_3$ , Bruker 300 MHz).

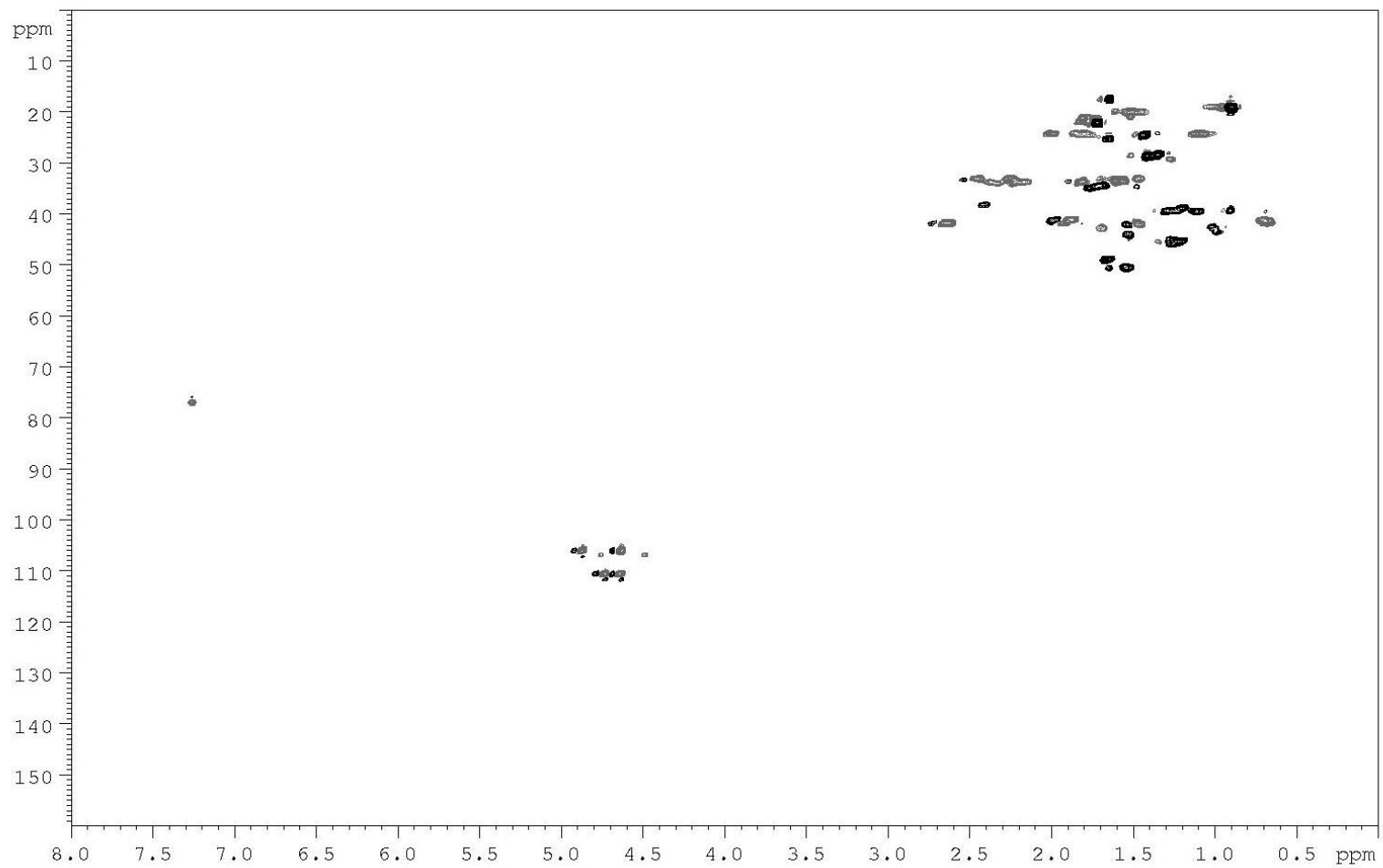


$^1\text{H}$  NMR spectrum of 7-isocyanoamphilecta-11(20),15-diene (**4**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

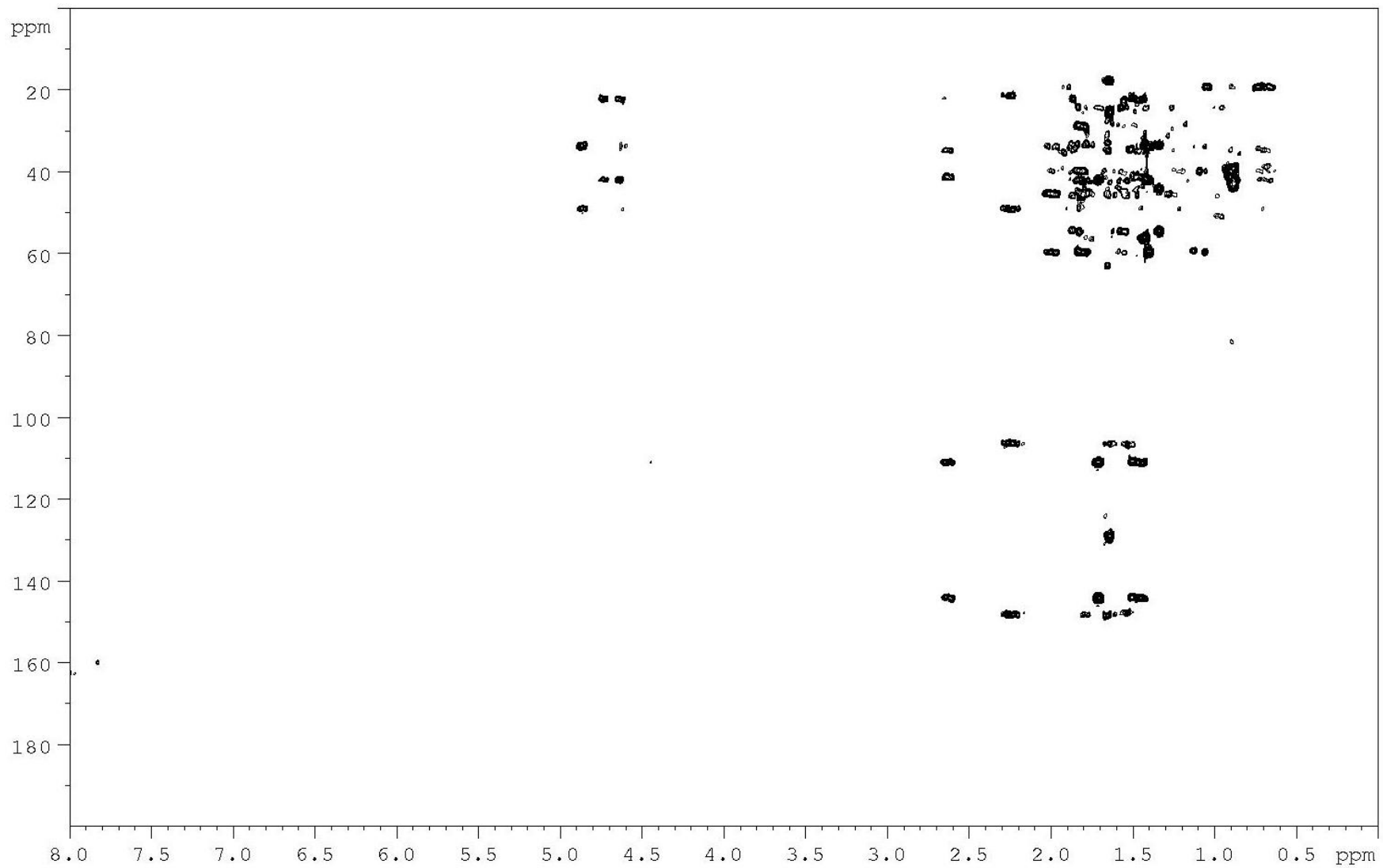


$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyanoamphilecta-11(20),15-diene (**4**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

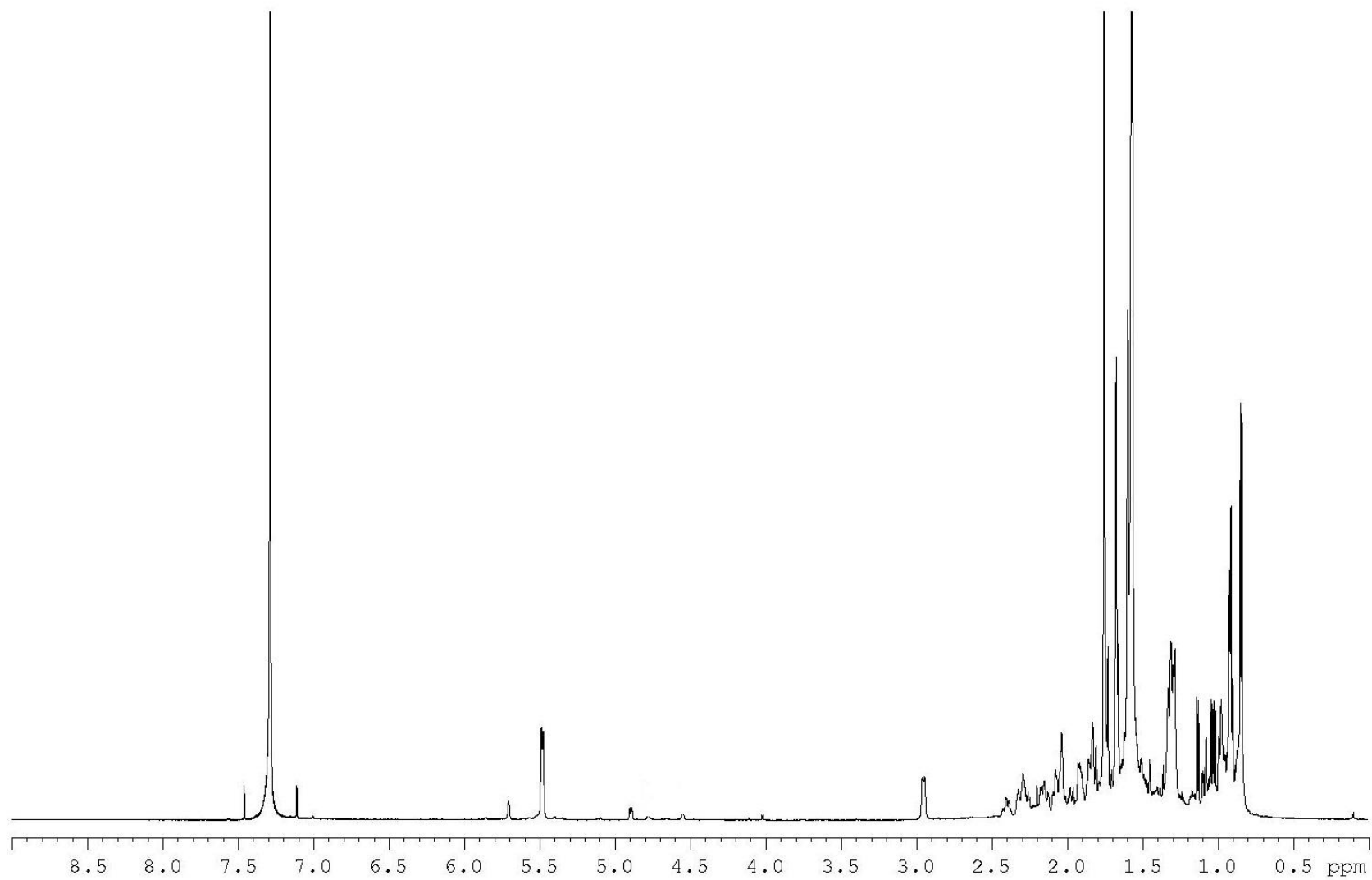




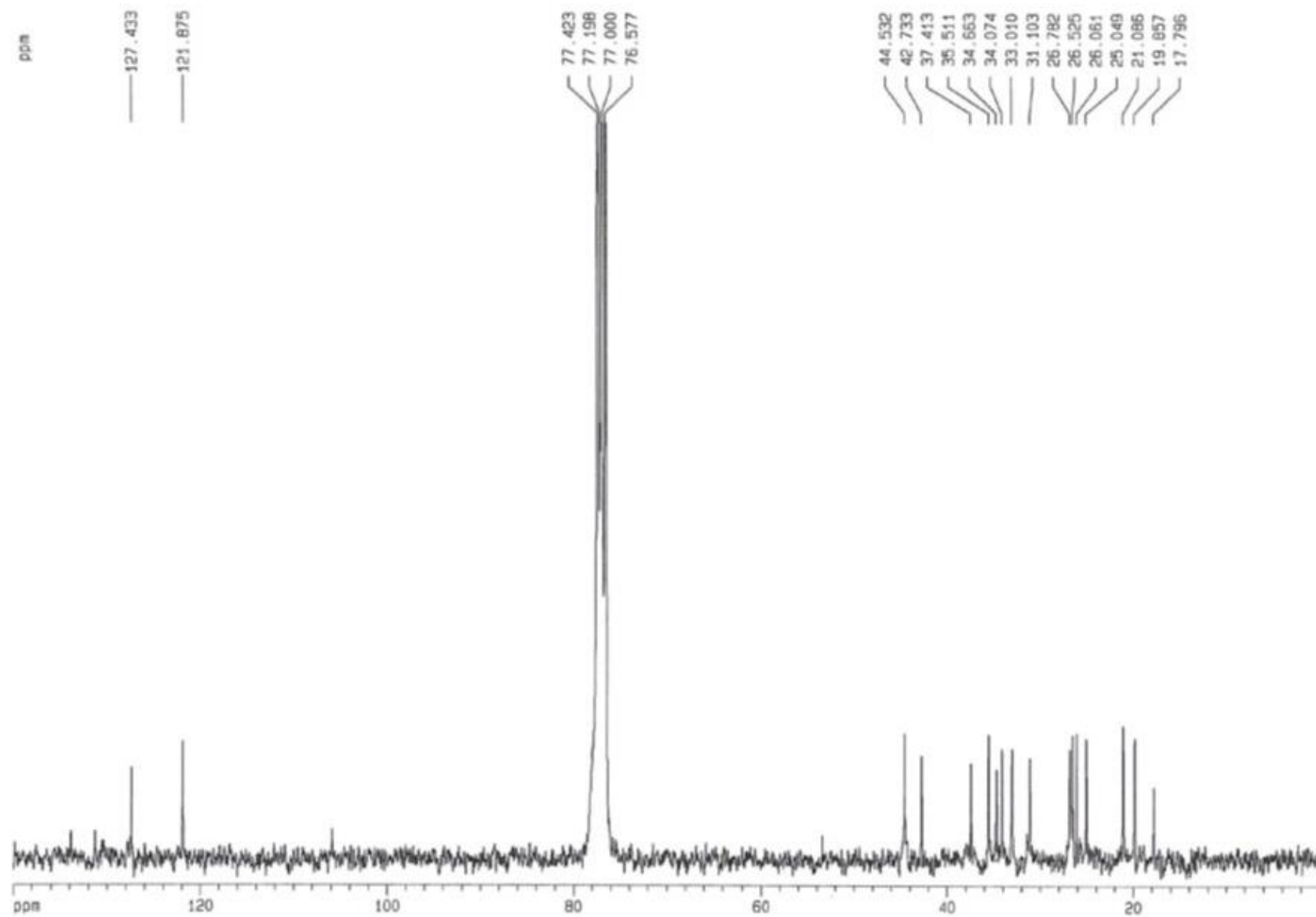
HSQC spectrum of 7-isocyanoamphilecta-11(20),15-diene (**4**) (CDCl<sub>3</sub>, Bruker 400 MHz).



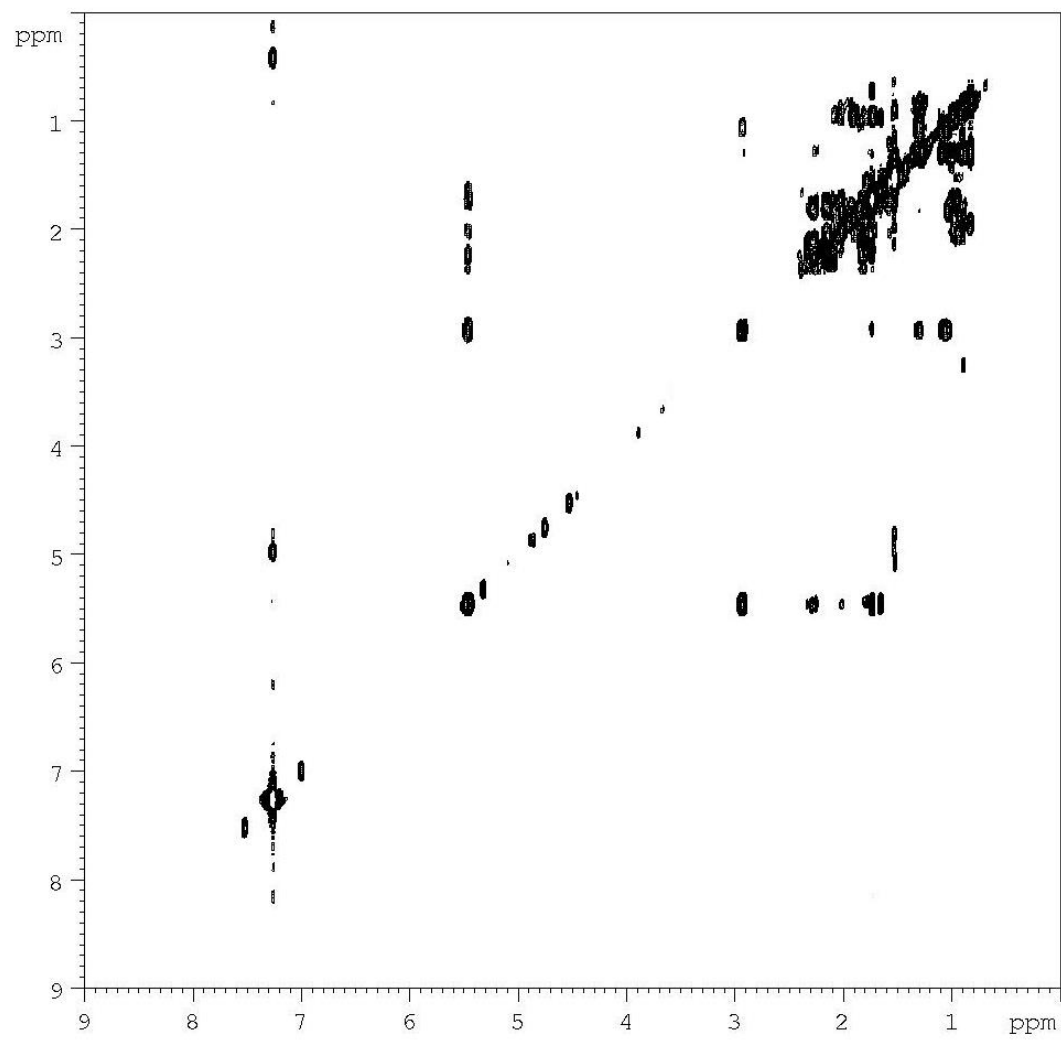
HMBC spectrum of 7-isocyanoamphilecta-11(20),15-diene (**4**) ( $\text{CDCl}_3$ , Bruker 400 MHz,  $J=7\text{Hz}$ ).



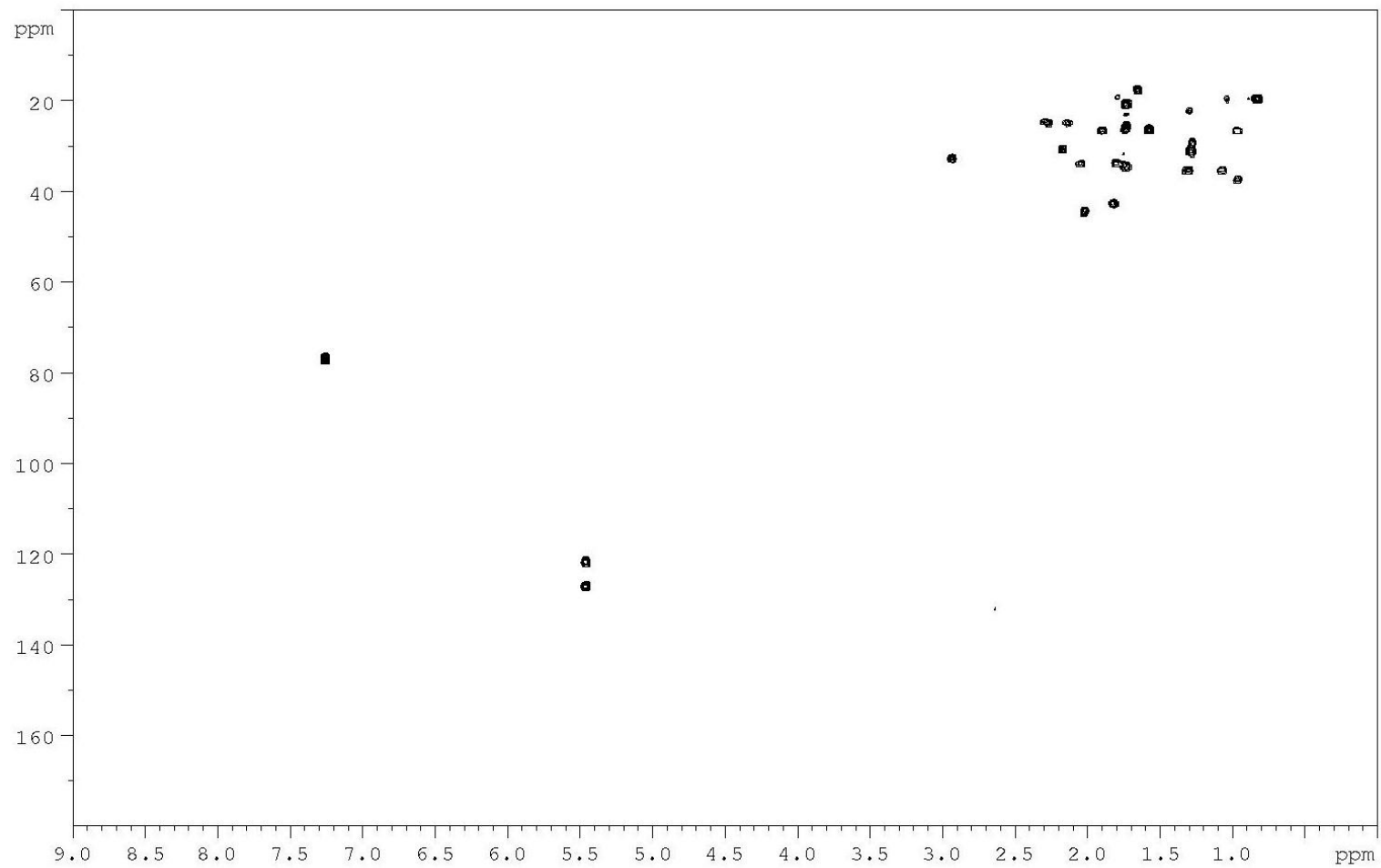
$^1\text{H}$  NMR spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



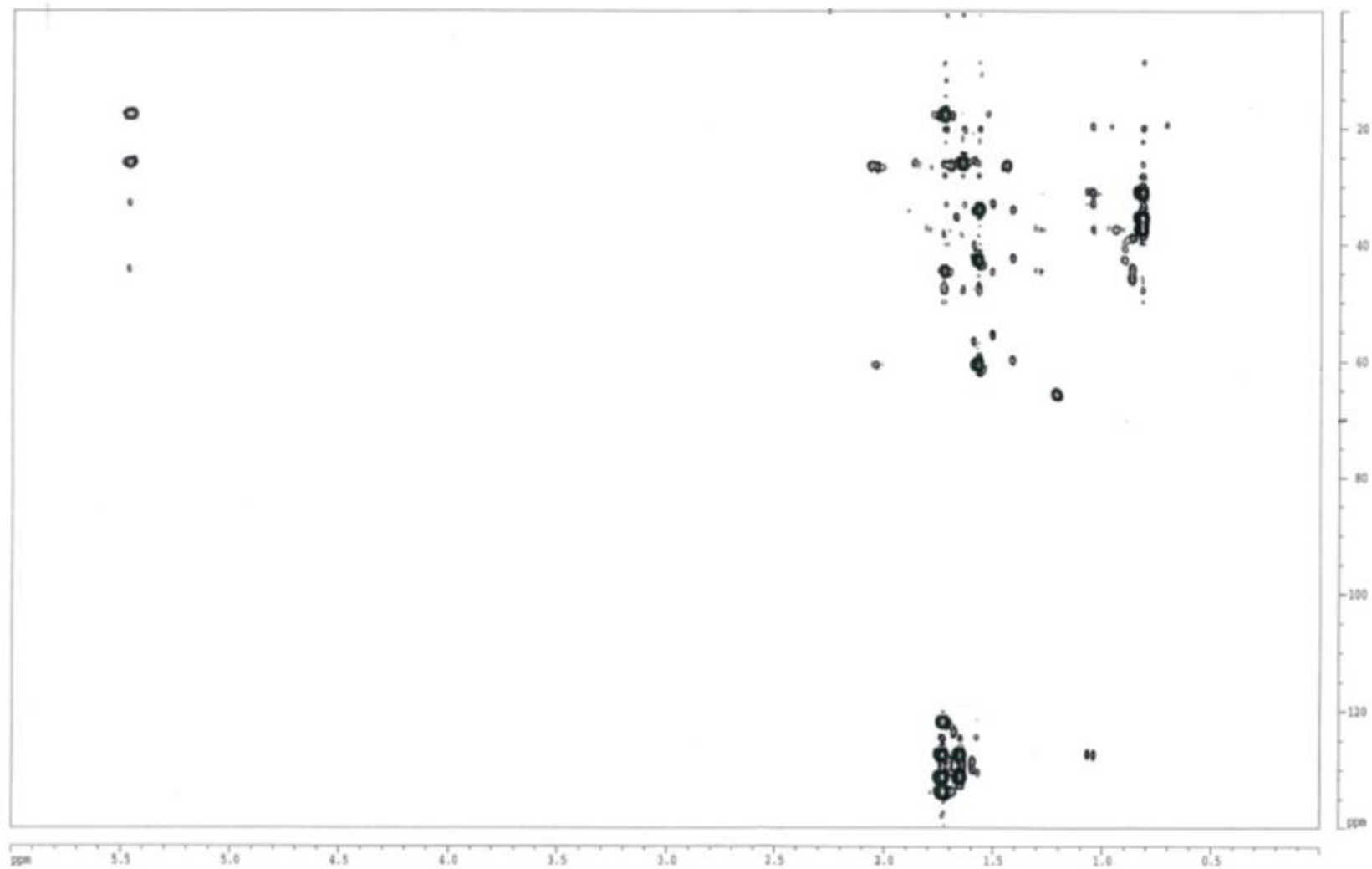
<sup>13</sup>C NMR spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) (CDCl<sub>3</sub>, Bruker 300 MHz).



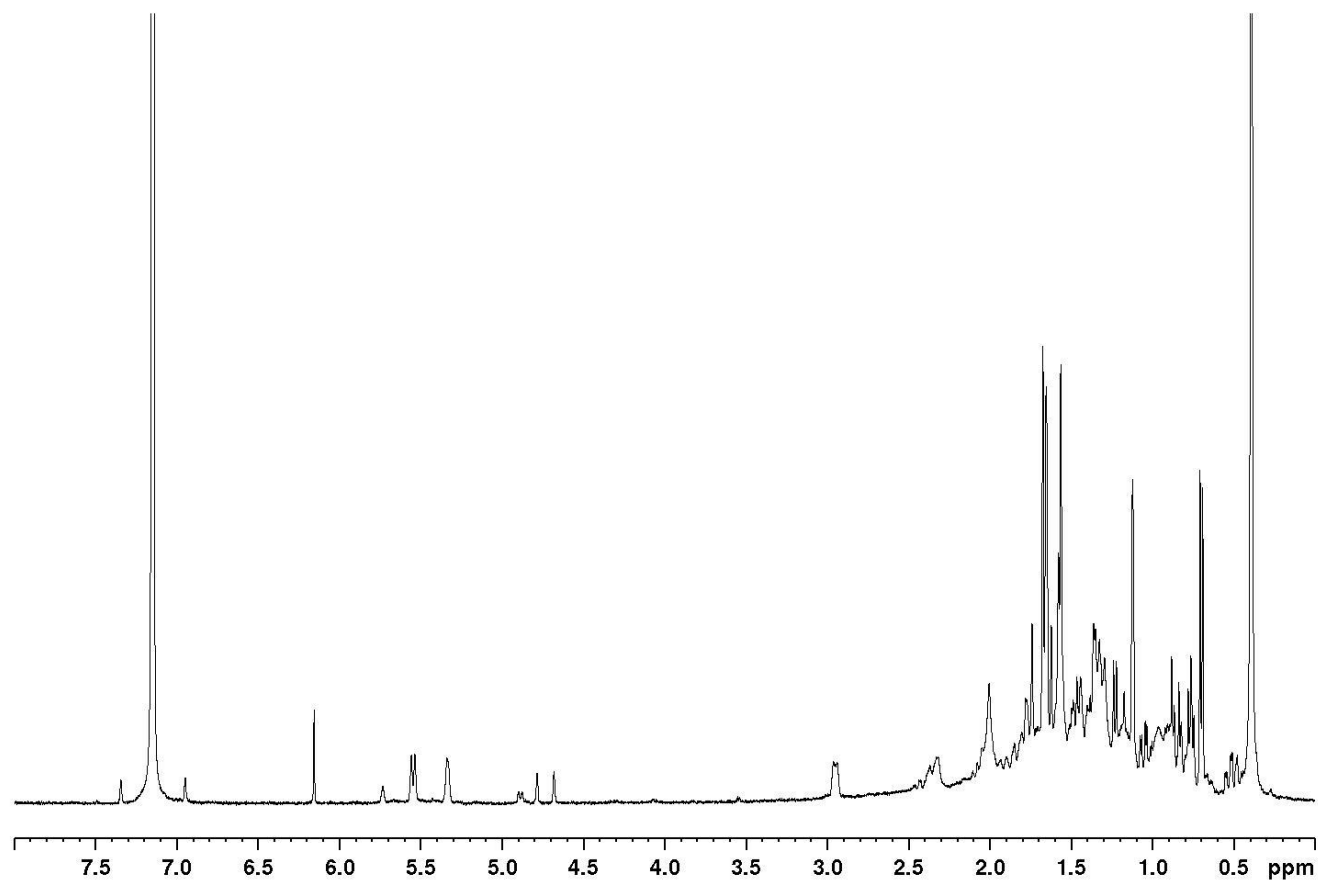
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



HSQC spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) (CDCl<sub>3</sub>, Bruker 400 MHz).

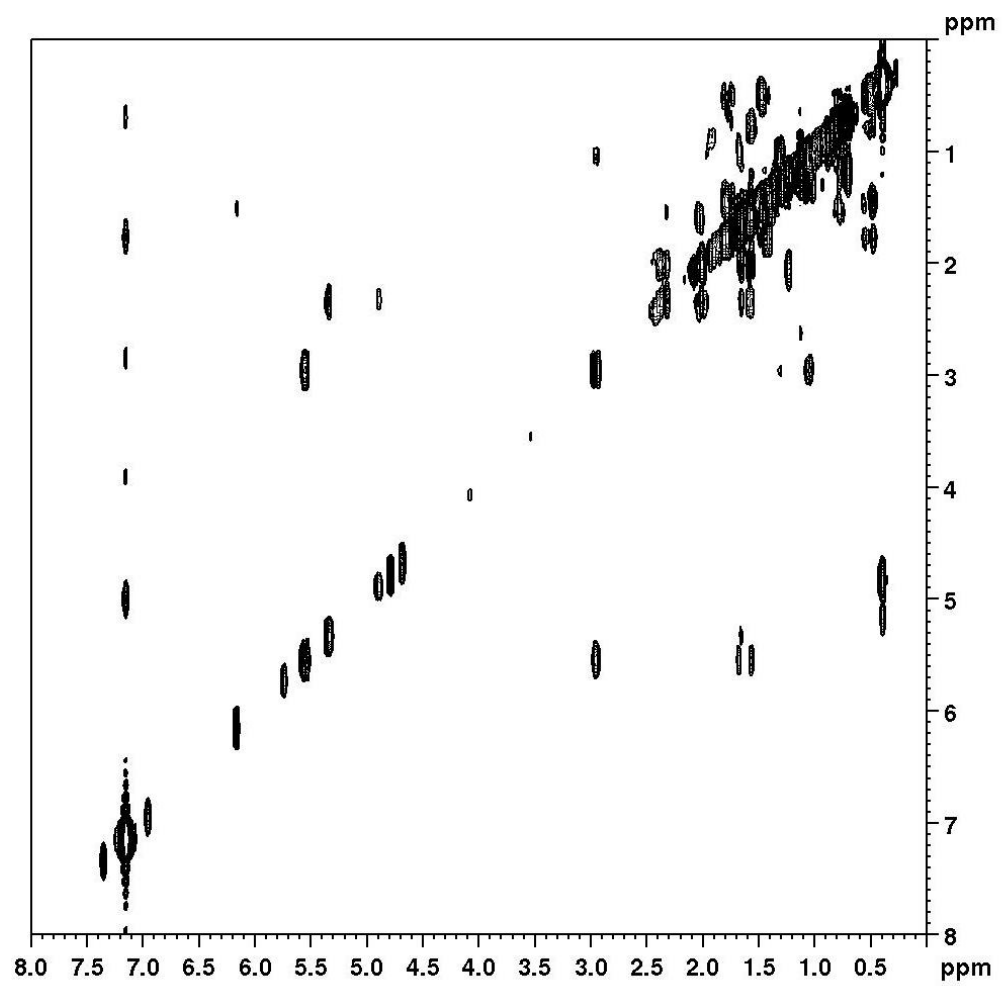


HMBC spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) ( $\text{CDCl}_3$ , Bruker 500 MHz,  $J=7\text{Hz}$ ).

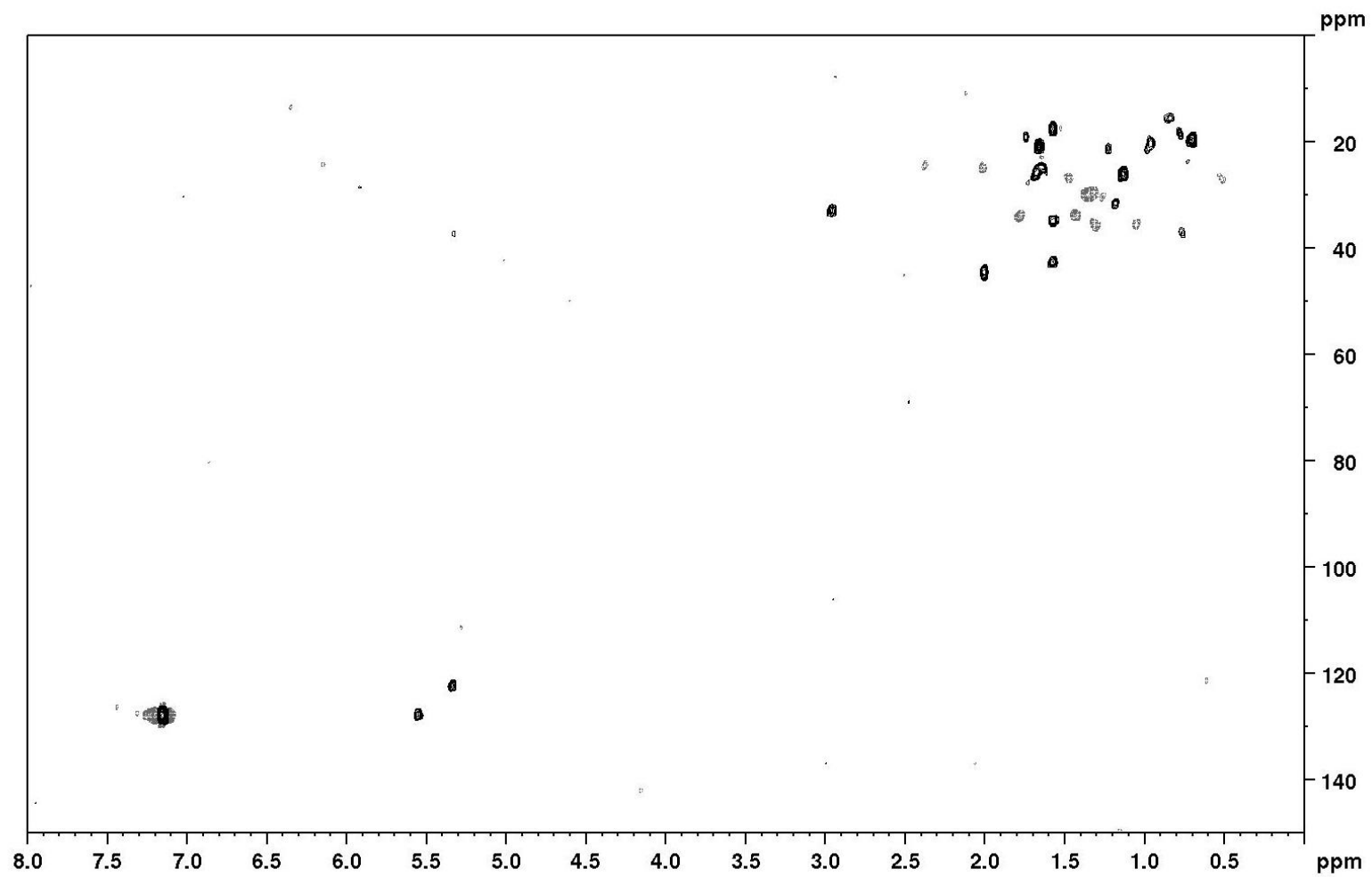


<sup>1</sup>H NMR spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz).

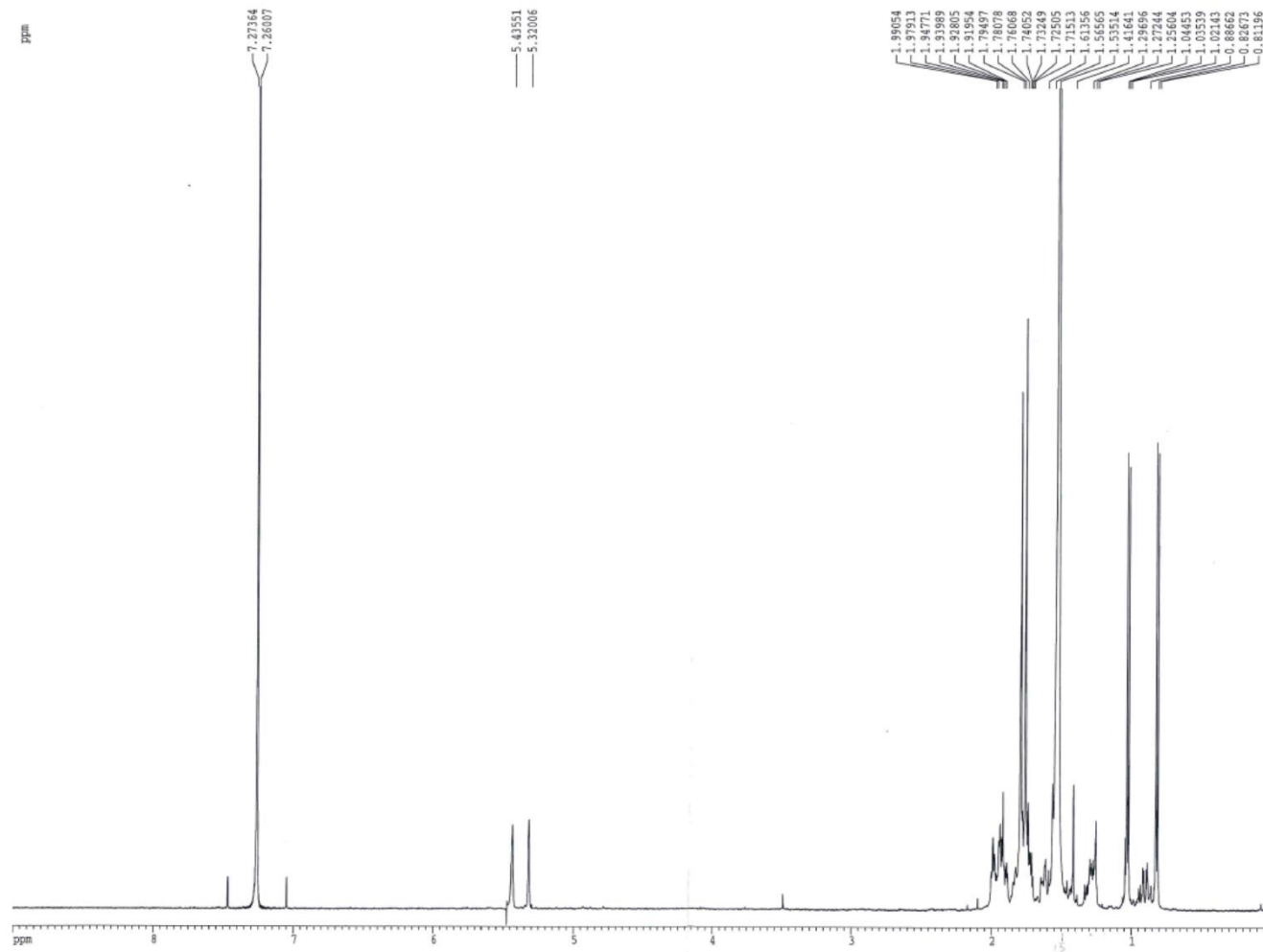




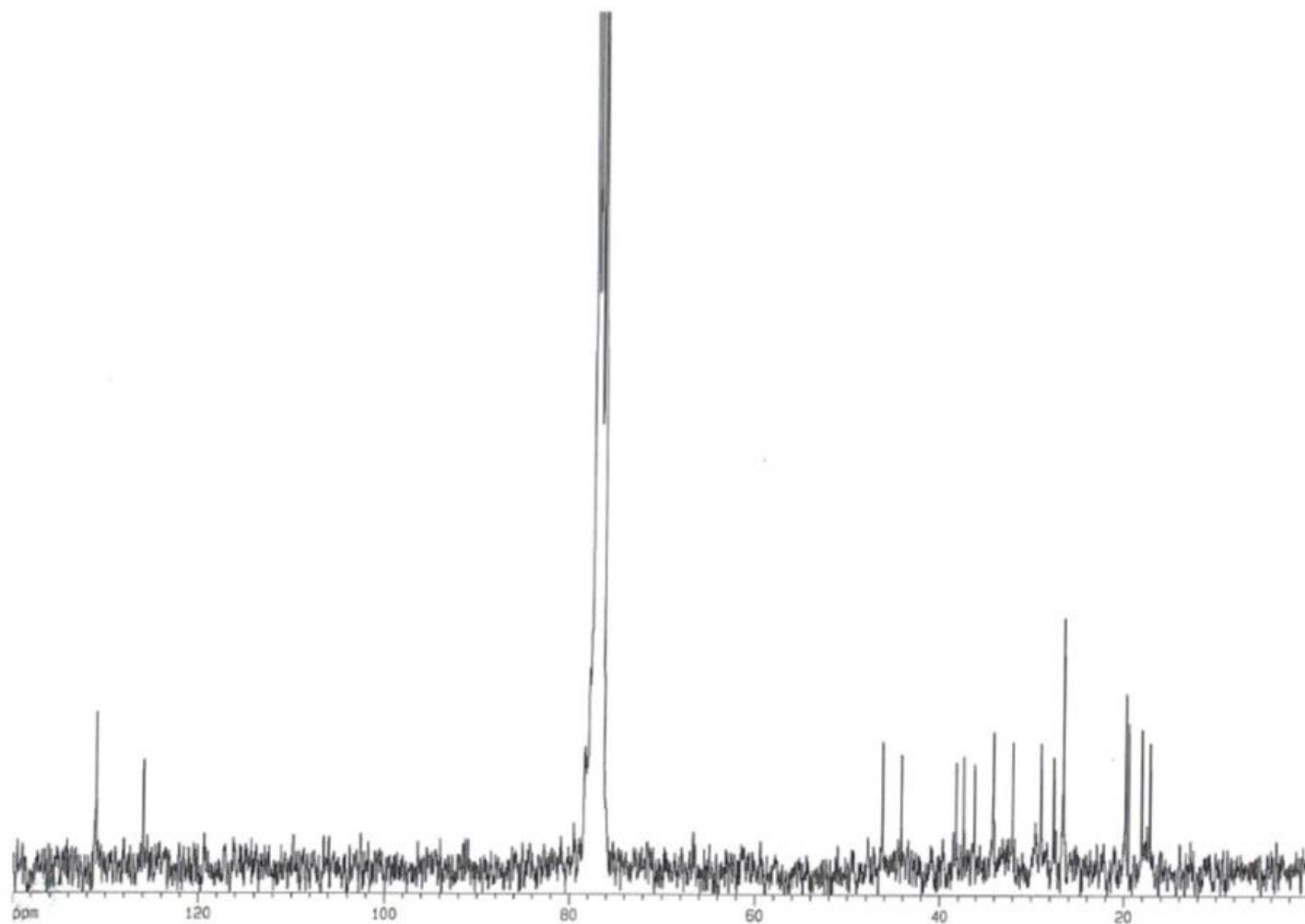
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) ( $\text{C}_6\text{D}_6$ , Bruker 400 MHz).



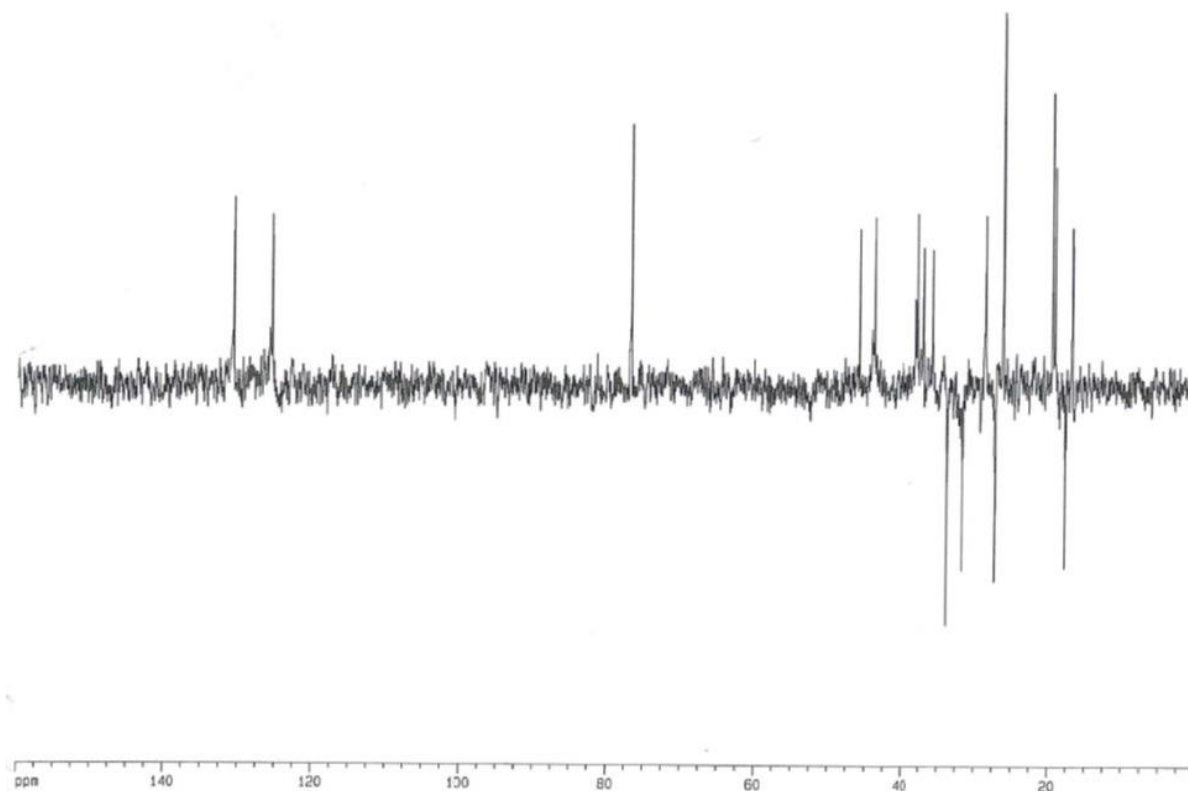
HSQC spectrum of 7-isocyanoamphilecta-10,14-diene (**5**) ( $C_6D_6$ , Bruker 400 MHz).



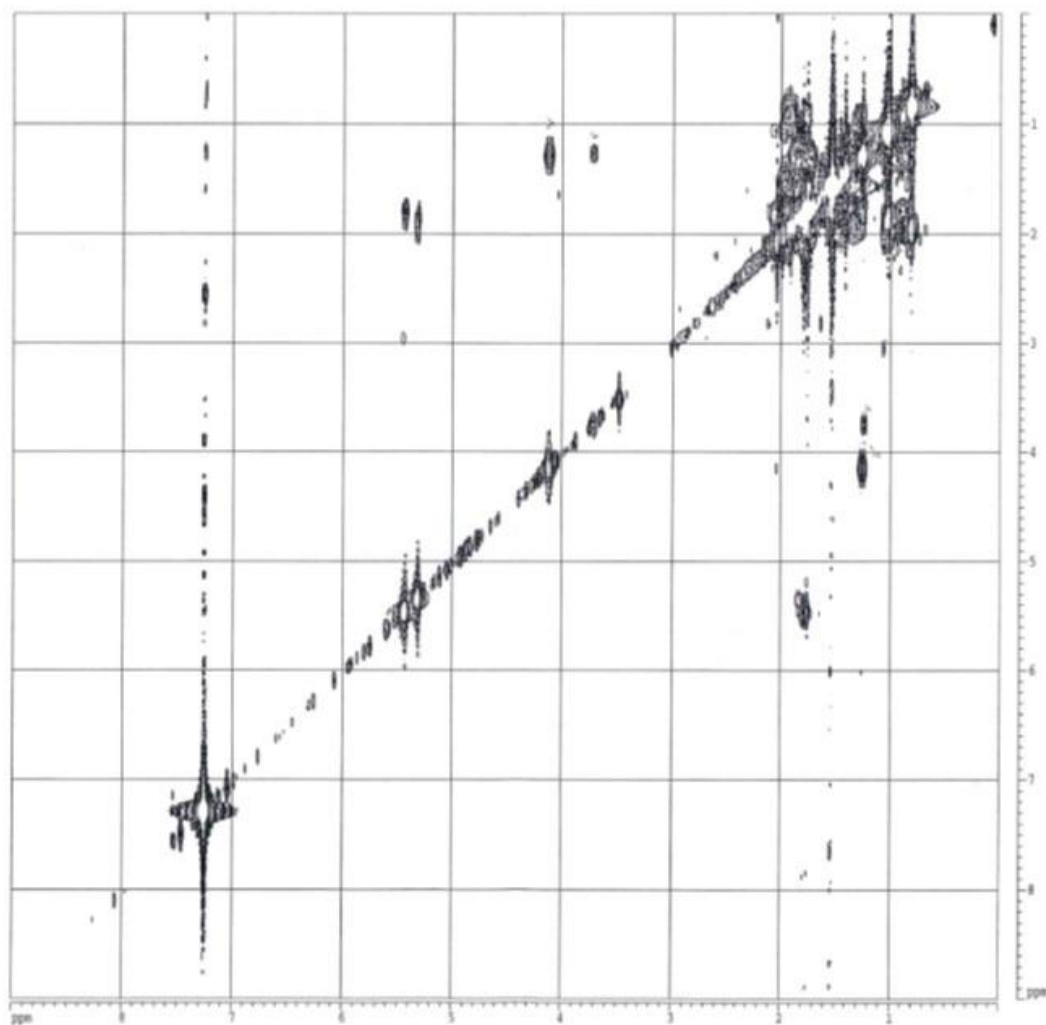
$^1\text{H}$  NMR spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 500 MHz).



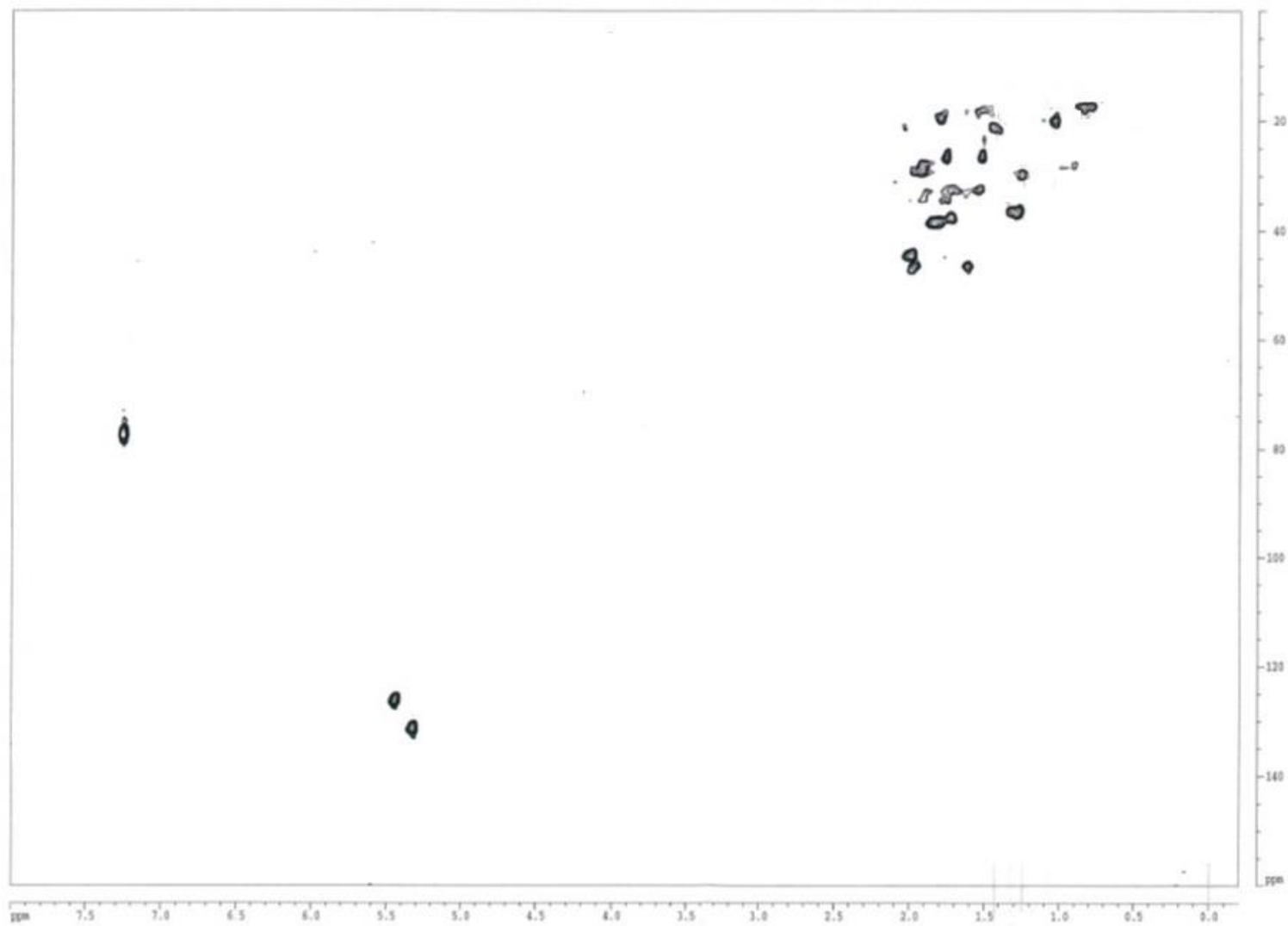
$^{13}\text{C}$  NMR spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 300 MHz).



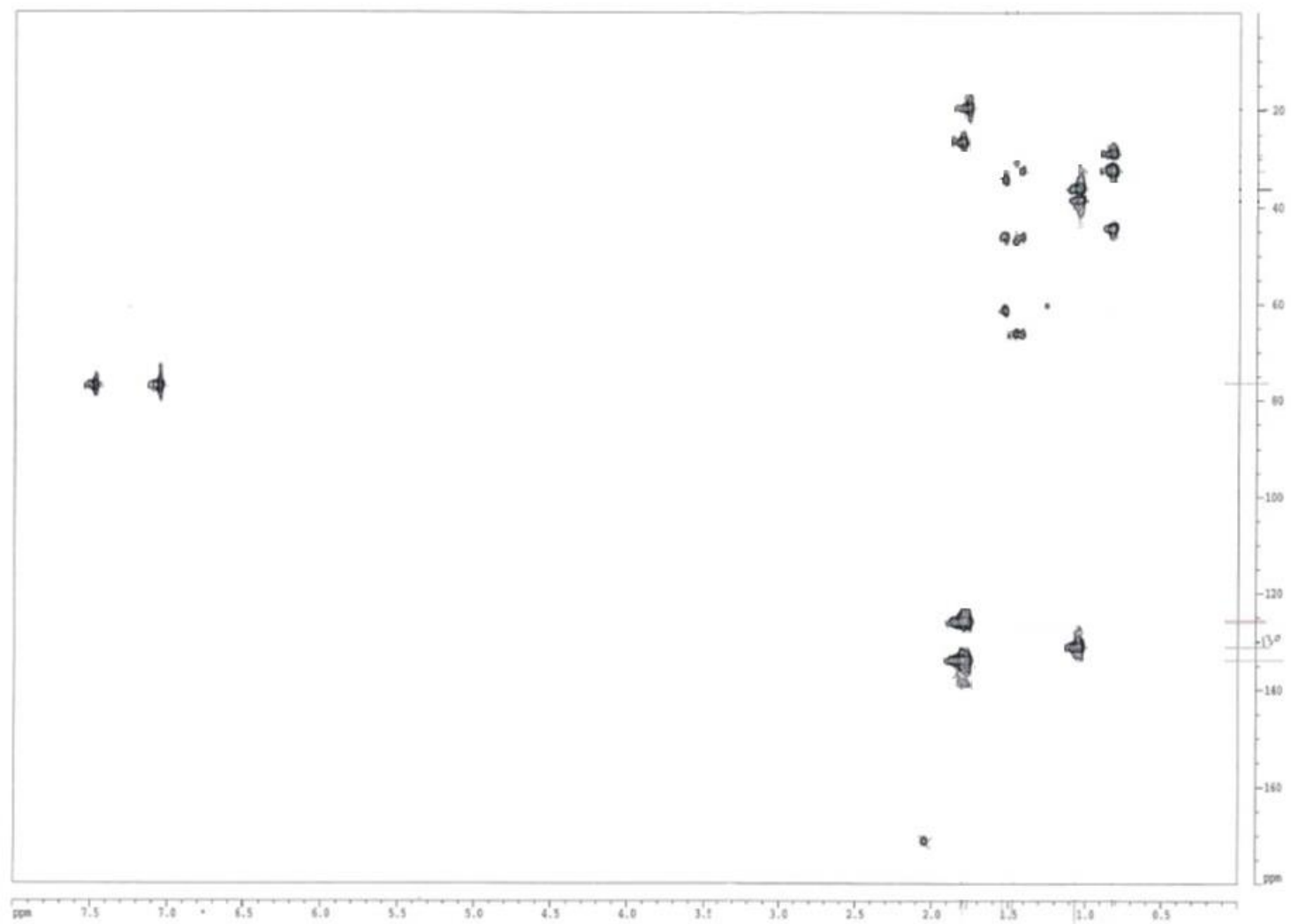
DEPT spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 300 MHz).



$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 500 MHz).

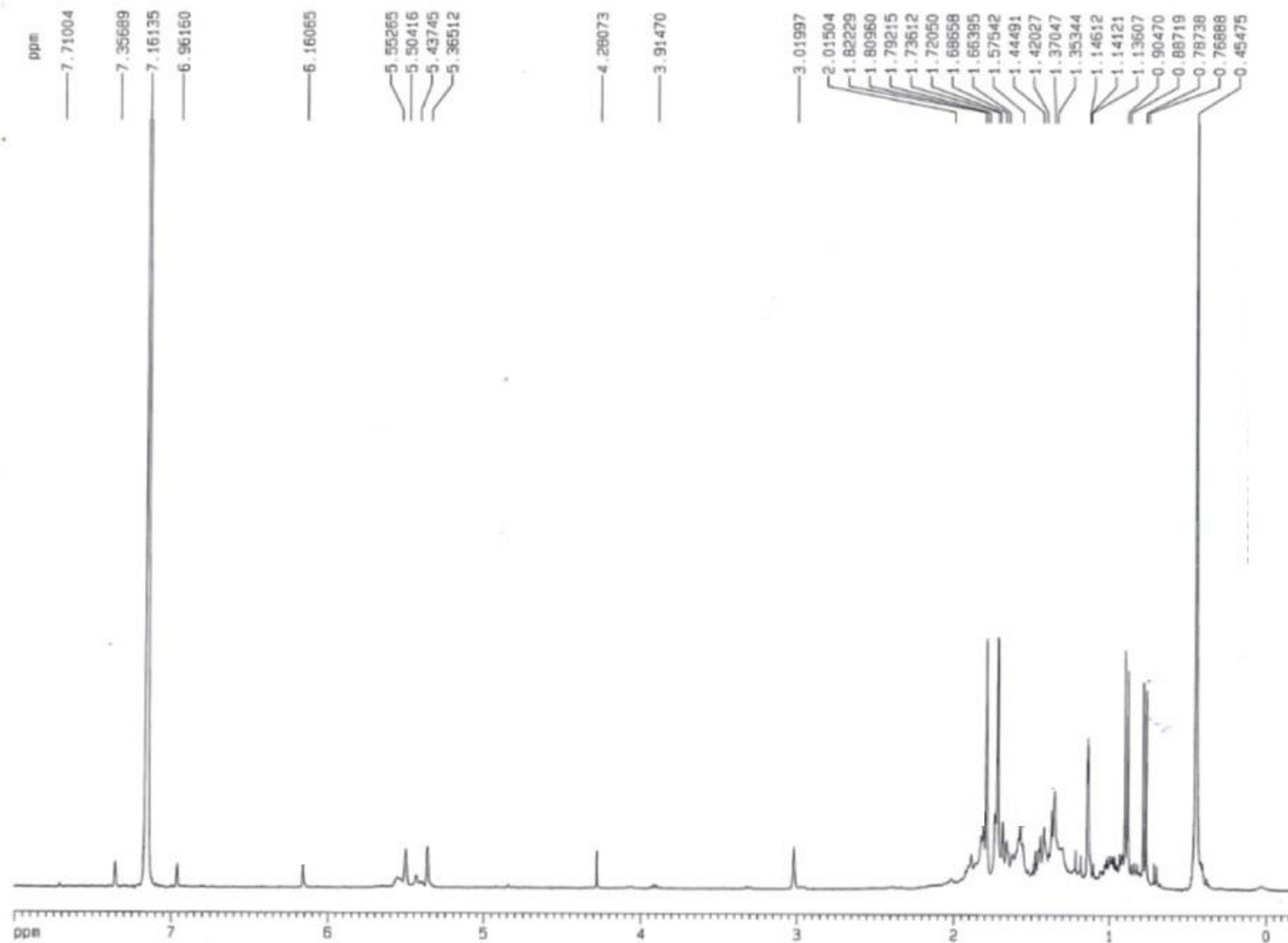


HSQC spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 500 MHz).

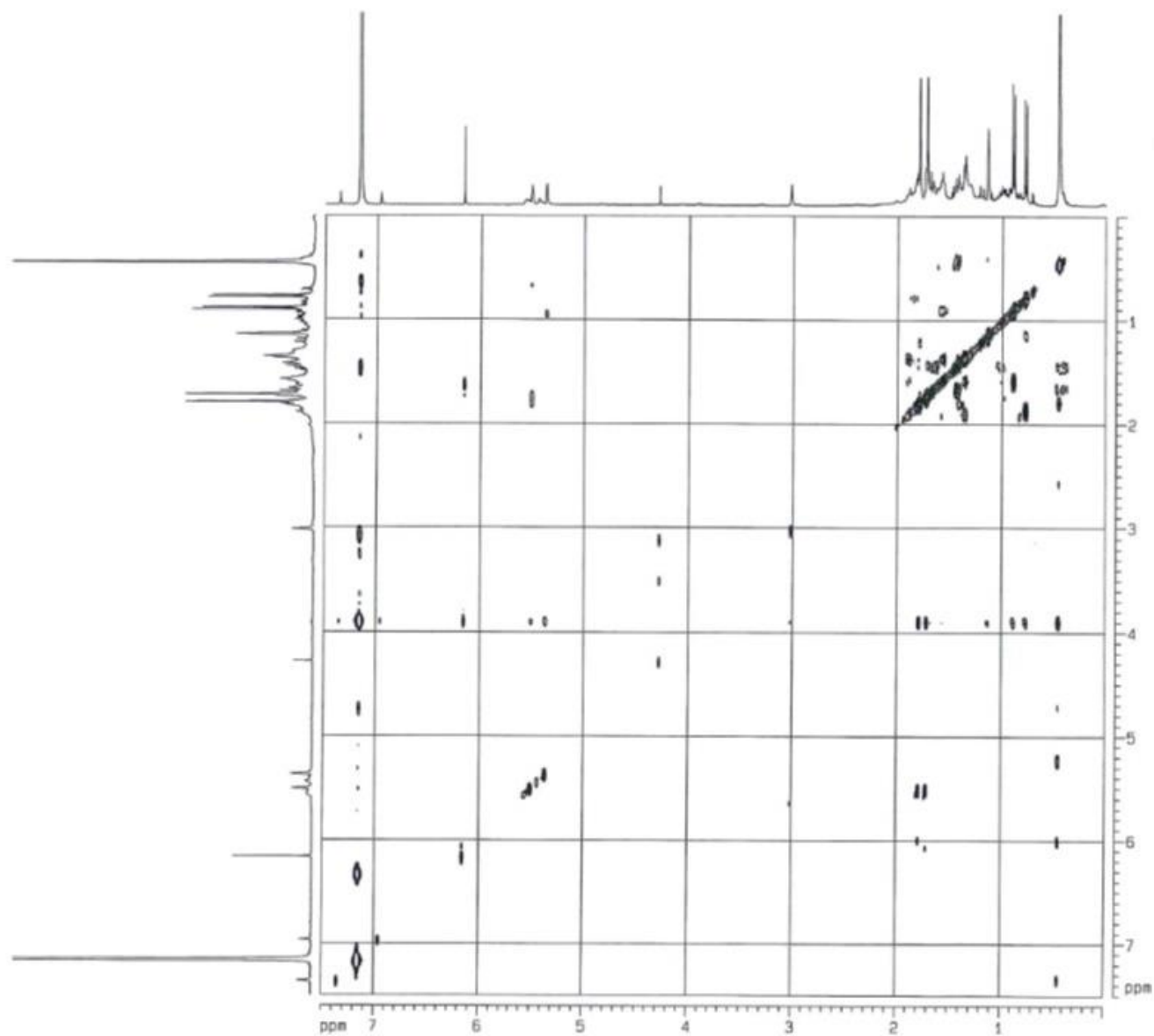


HMBC spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $\text{CDCl}_3$ , Bruker 500 MHz,  $J=7\text{Hz}$ ).

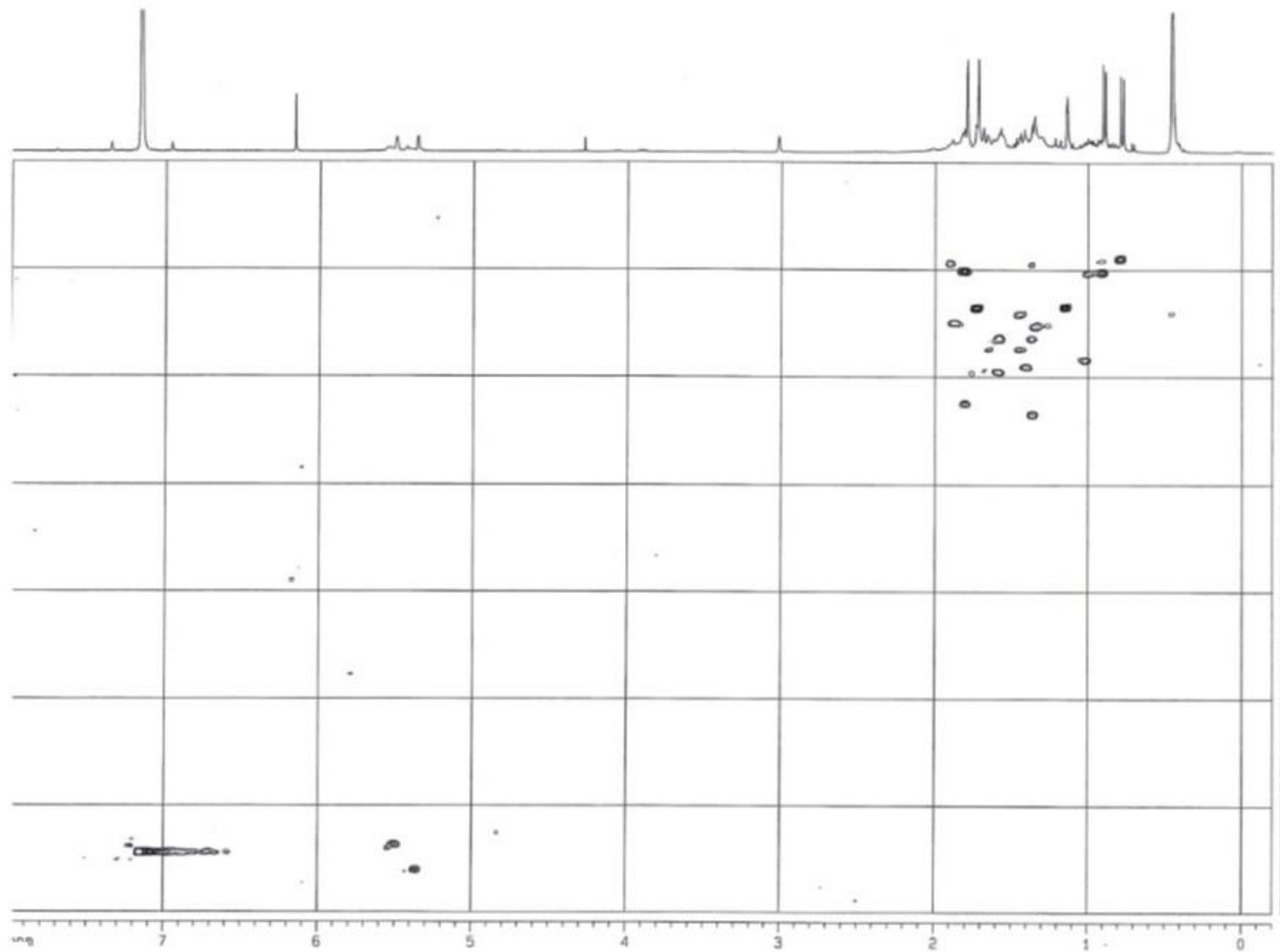




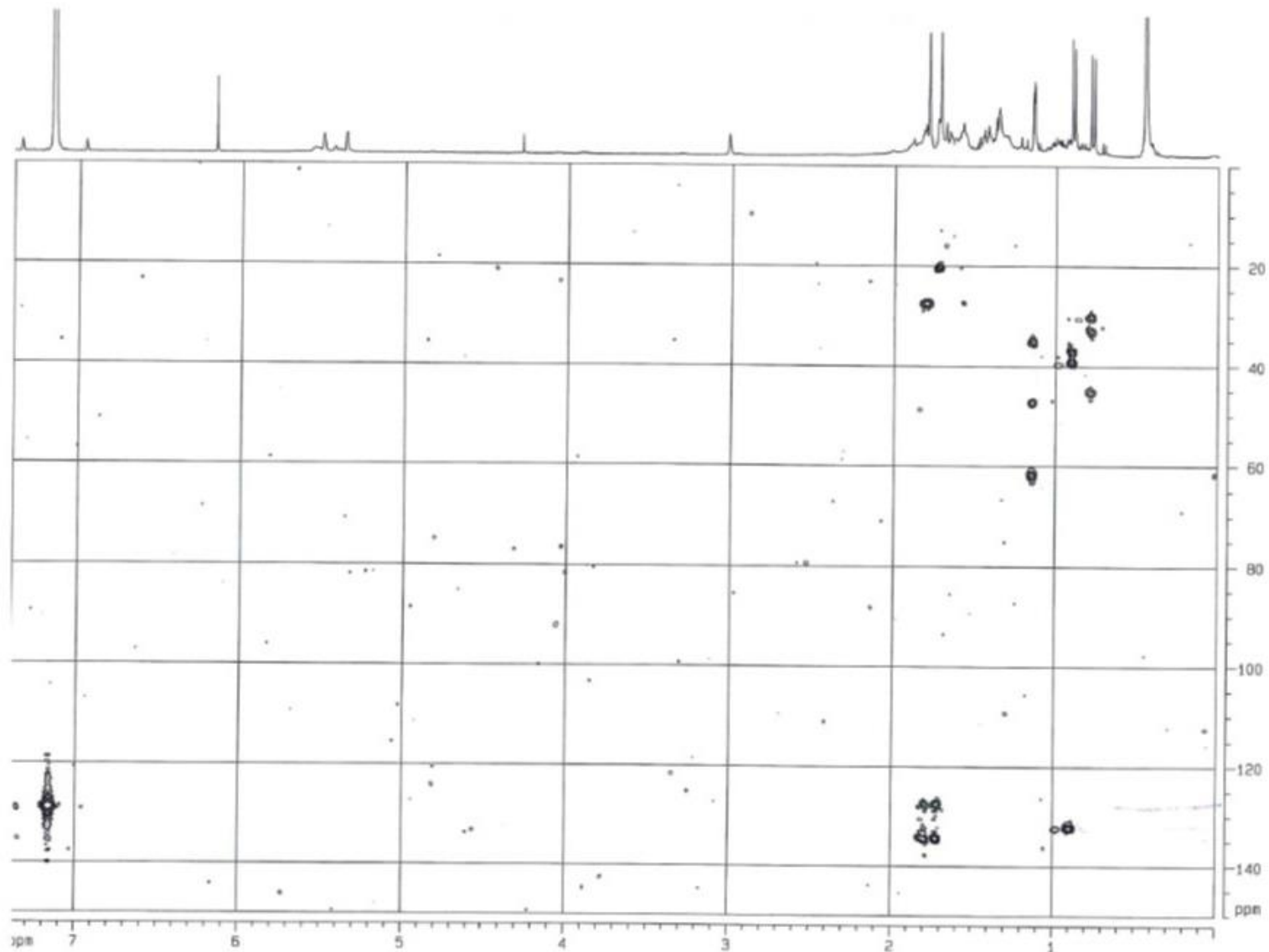
<sup>1</sup>H NMR spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) (C<sub>6</sub>D<sub>6</sub>, Bruker 500 MHz).



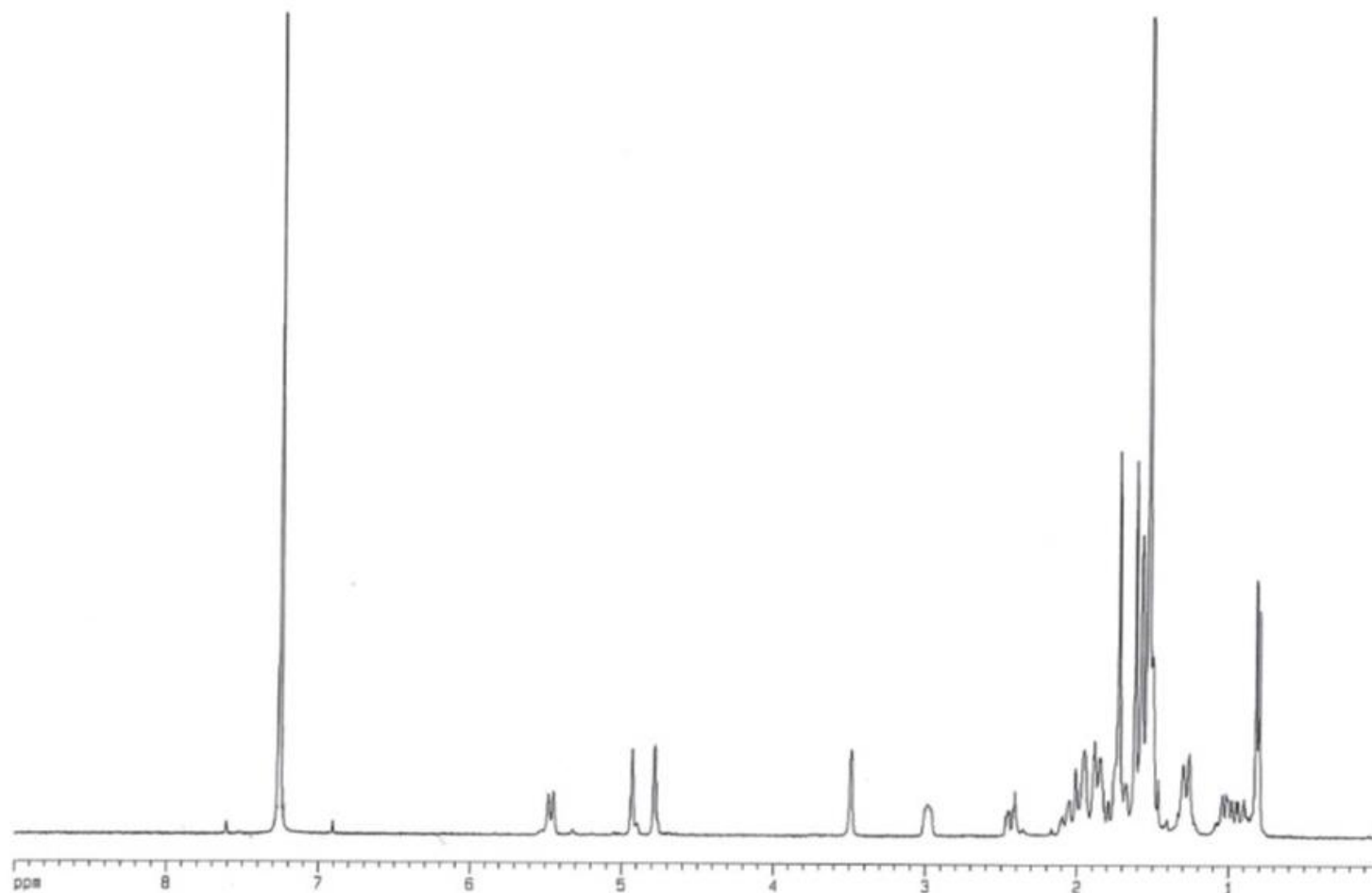
<sup>1</sup>H-<sup>1</sup>H COSY spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) (C<sub>6</sub>D<sub>6</sub>, Bruker 500 MHz).



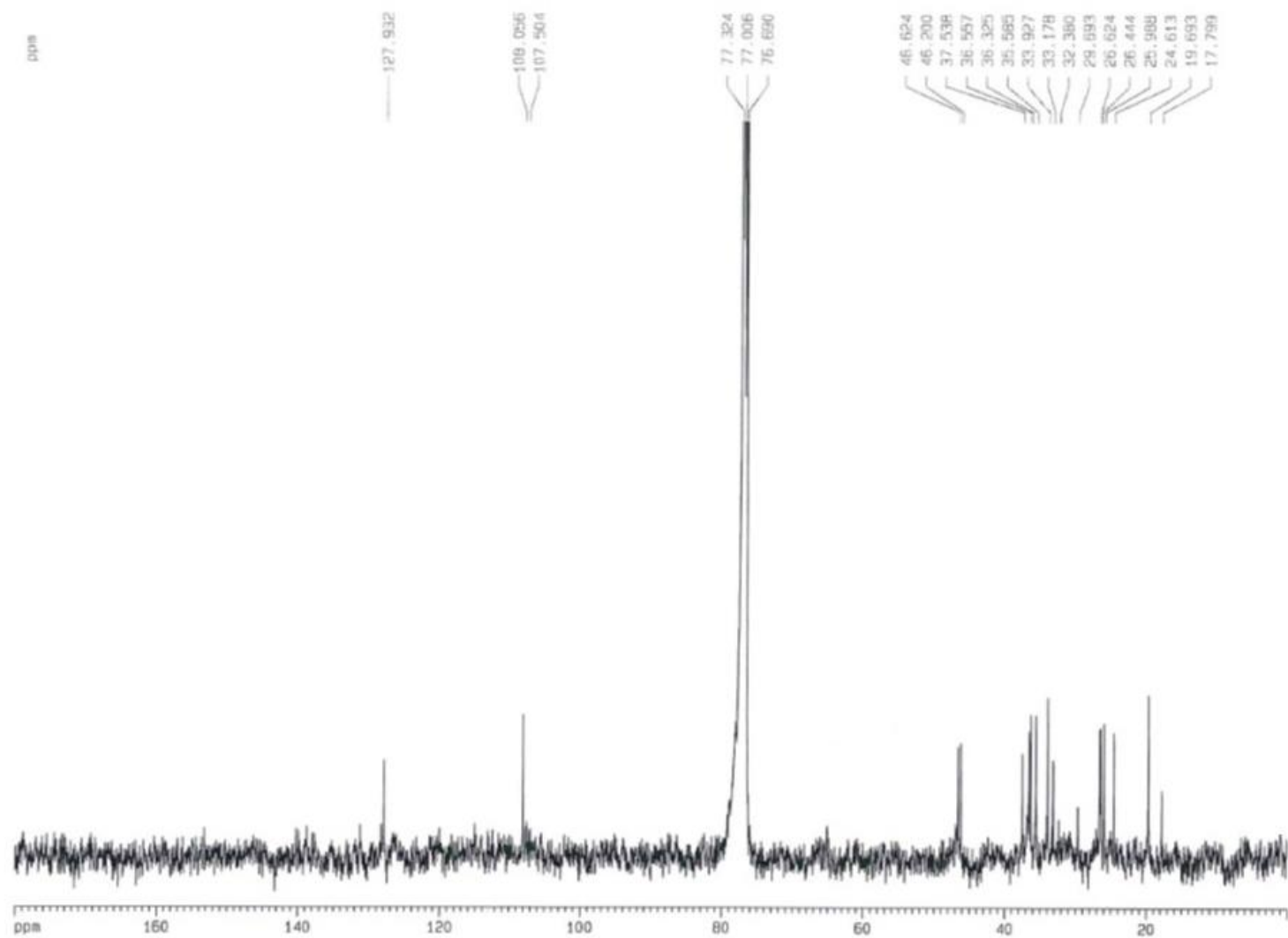
HSQC spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $C_6D_6$ , Bruker 500 MHz).



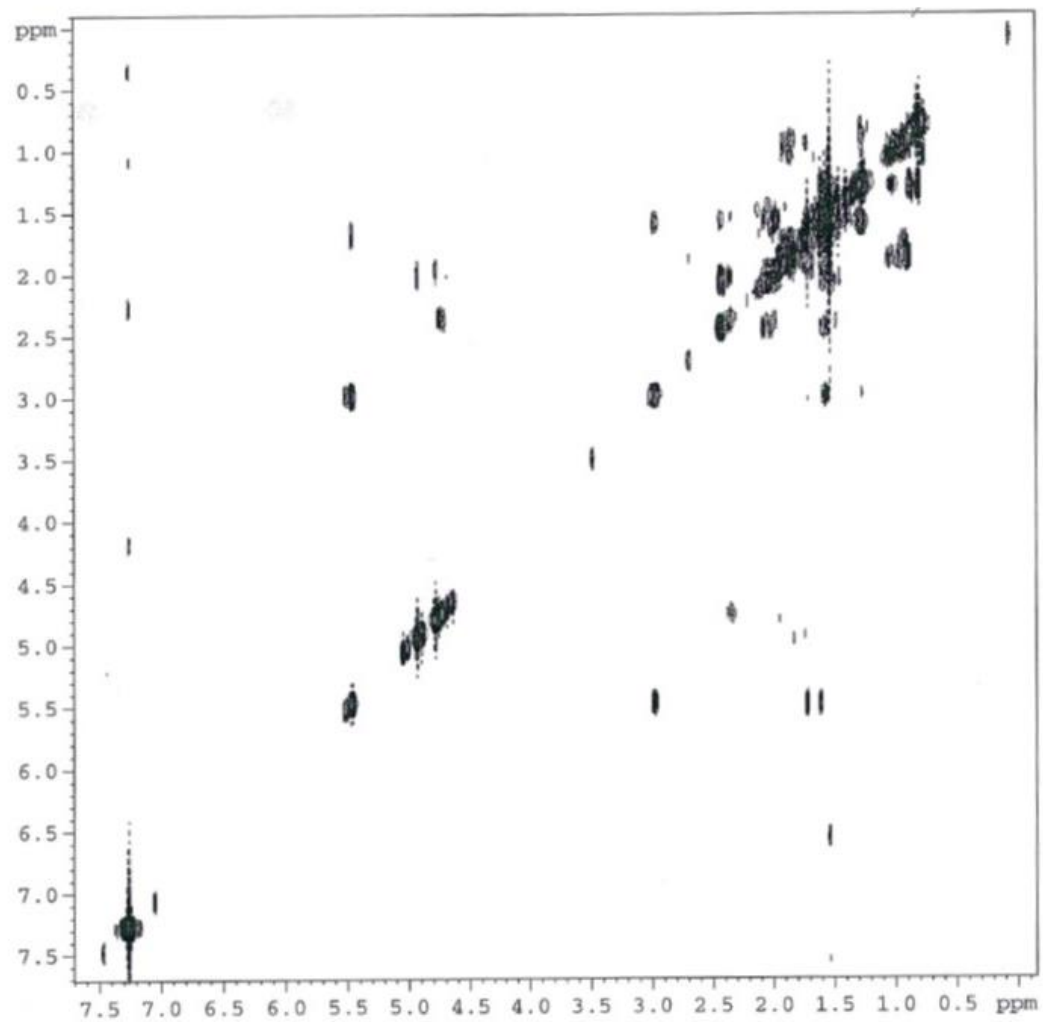
HMBC spectrum of 7-isocyanoamphilecta-1,14-diene (**6**) ( $C_6D_6$ , 500 MHz,  $J=7$ Hz).



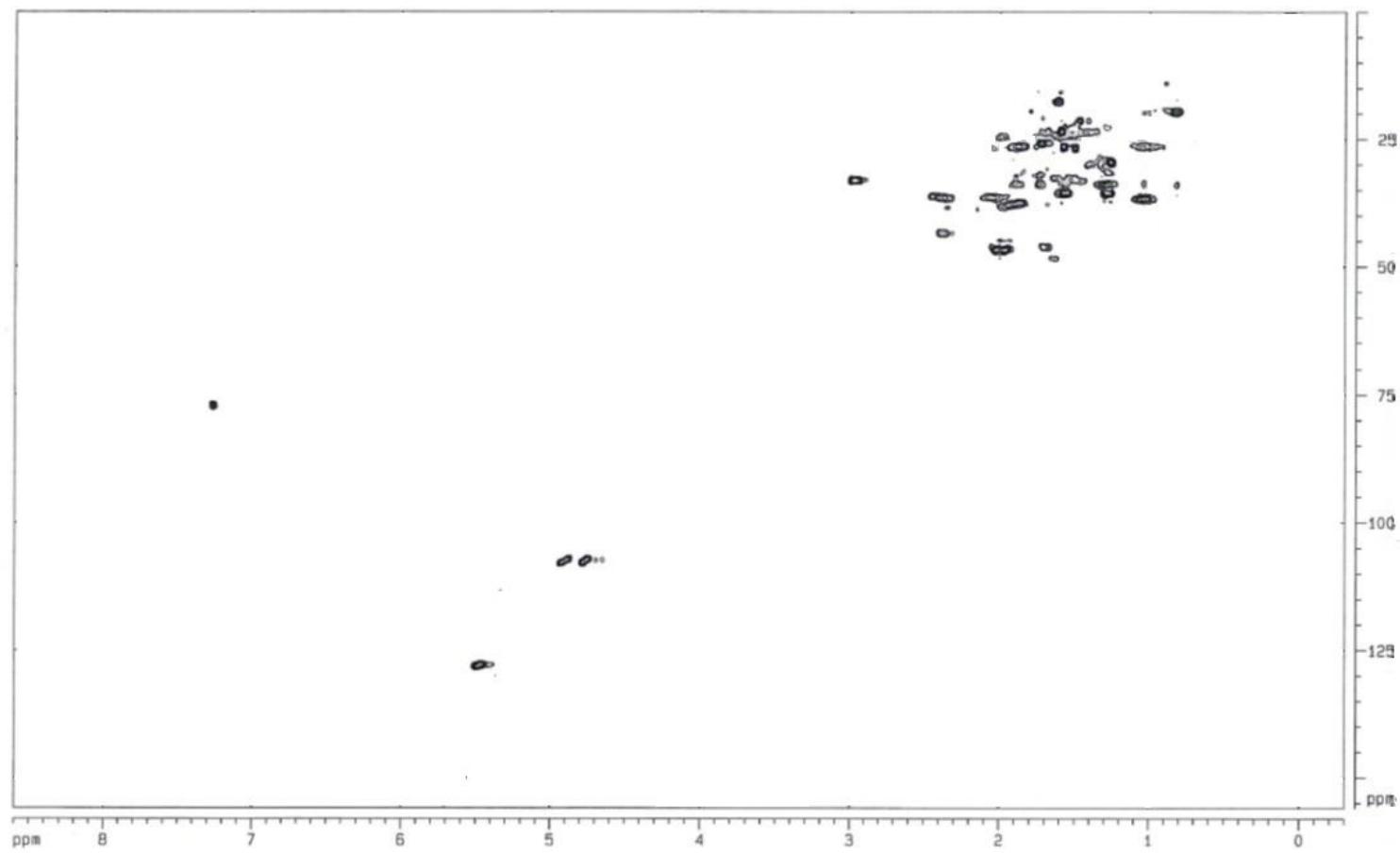
<sup>1</sup>H NMR spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) (CDCl<sub>3</sub>, Bruker 300 MHz).



$^{13}\text{C}$  NMR spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) ( $\text{CDCl}_3$ , Bruker 300 MHz).

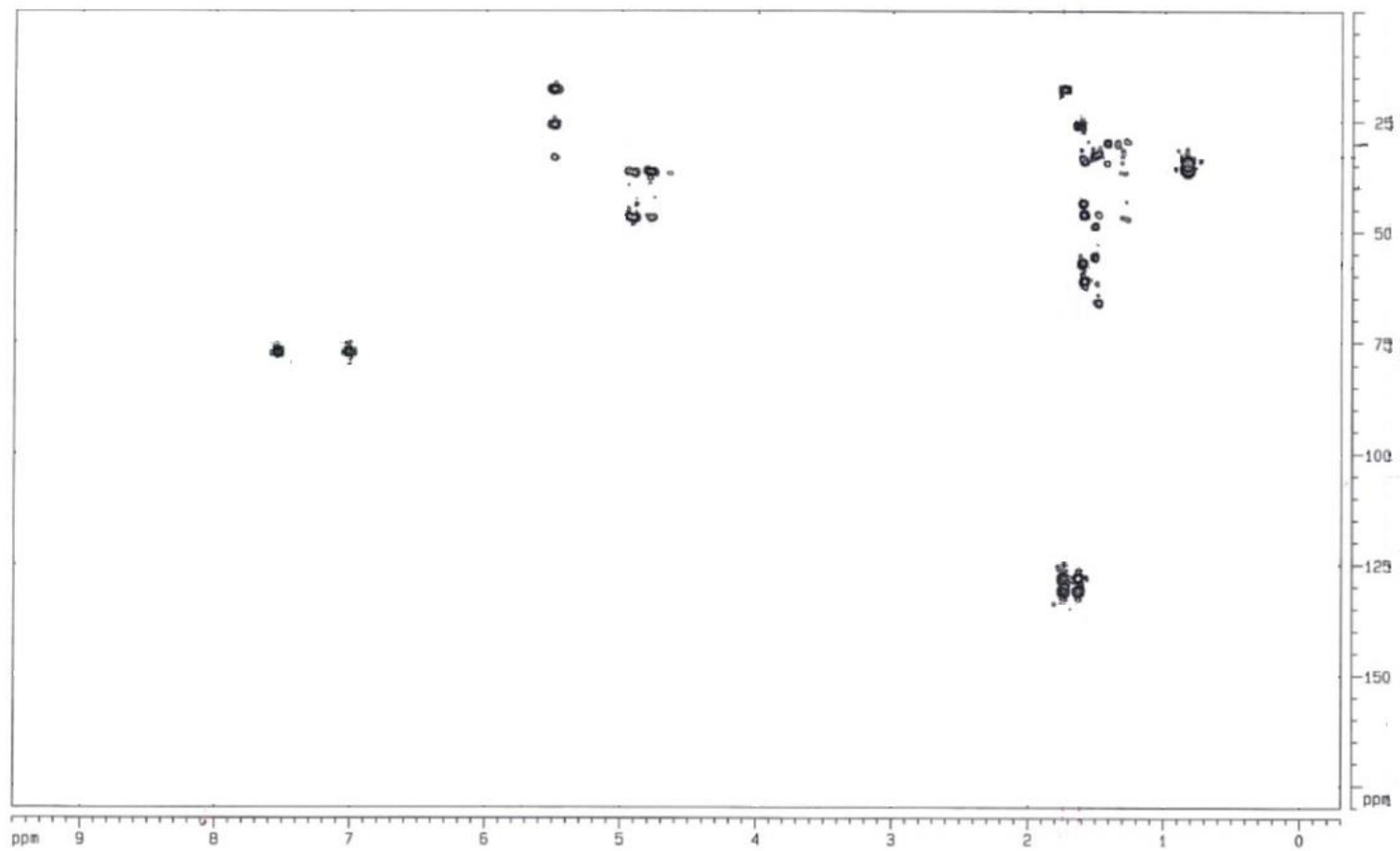


$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) ( $\text{CDCl}_3$ , Bruker 500 MHz).

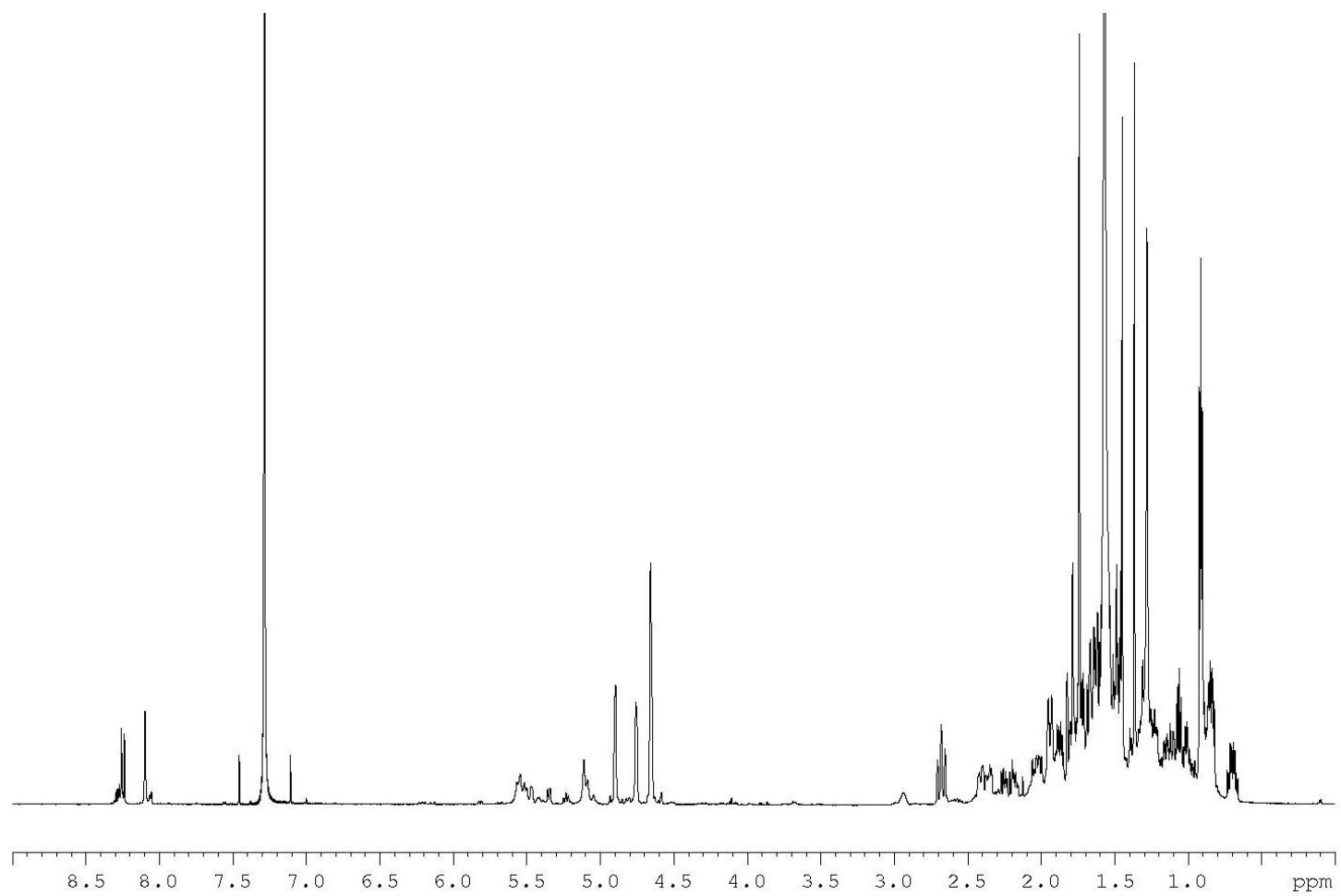


HSQC spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) ( $\text{CDCl}_3$ , Bruker 500 MHz).

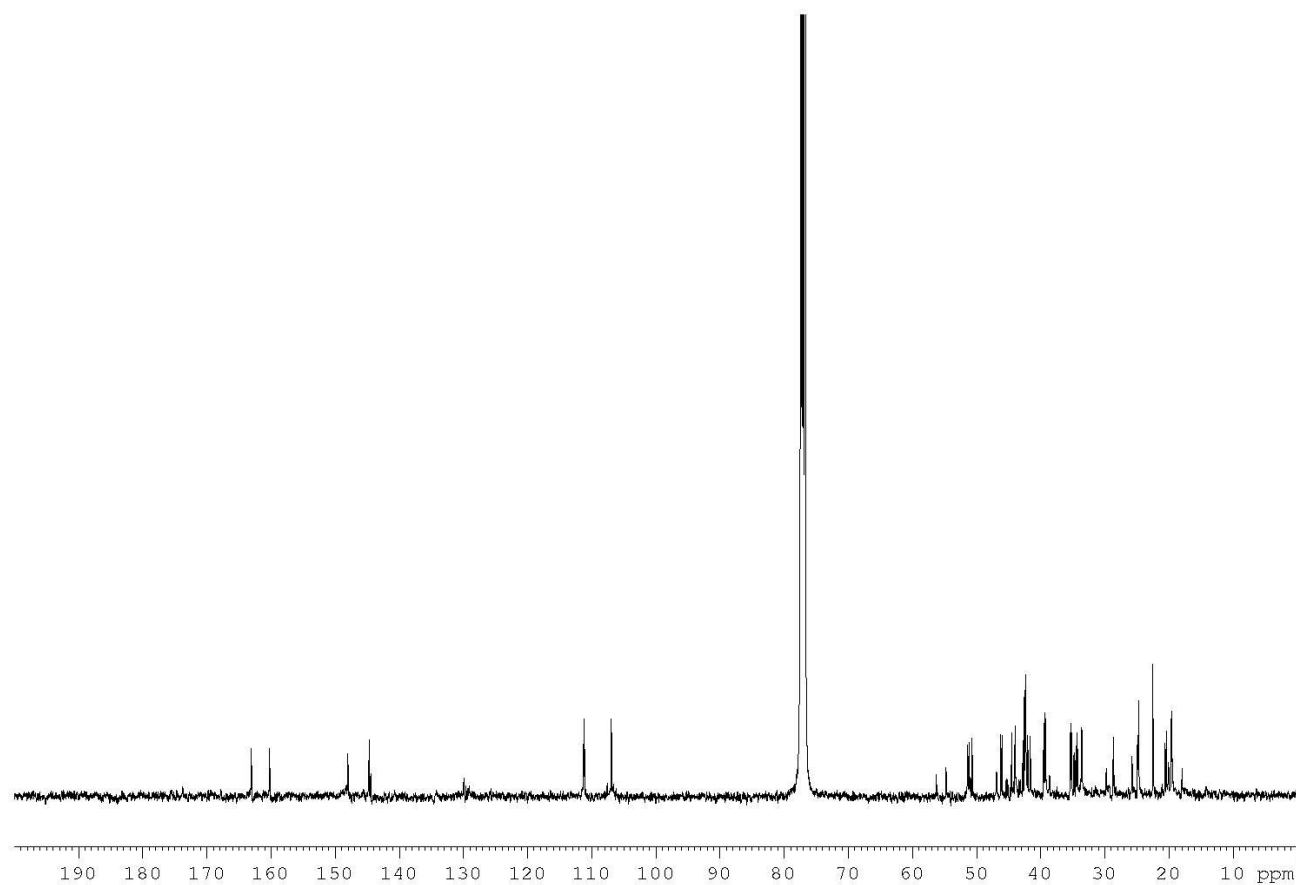




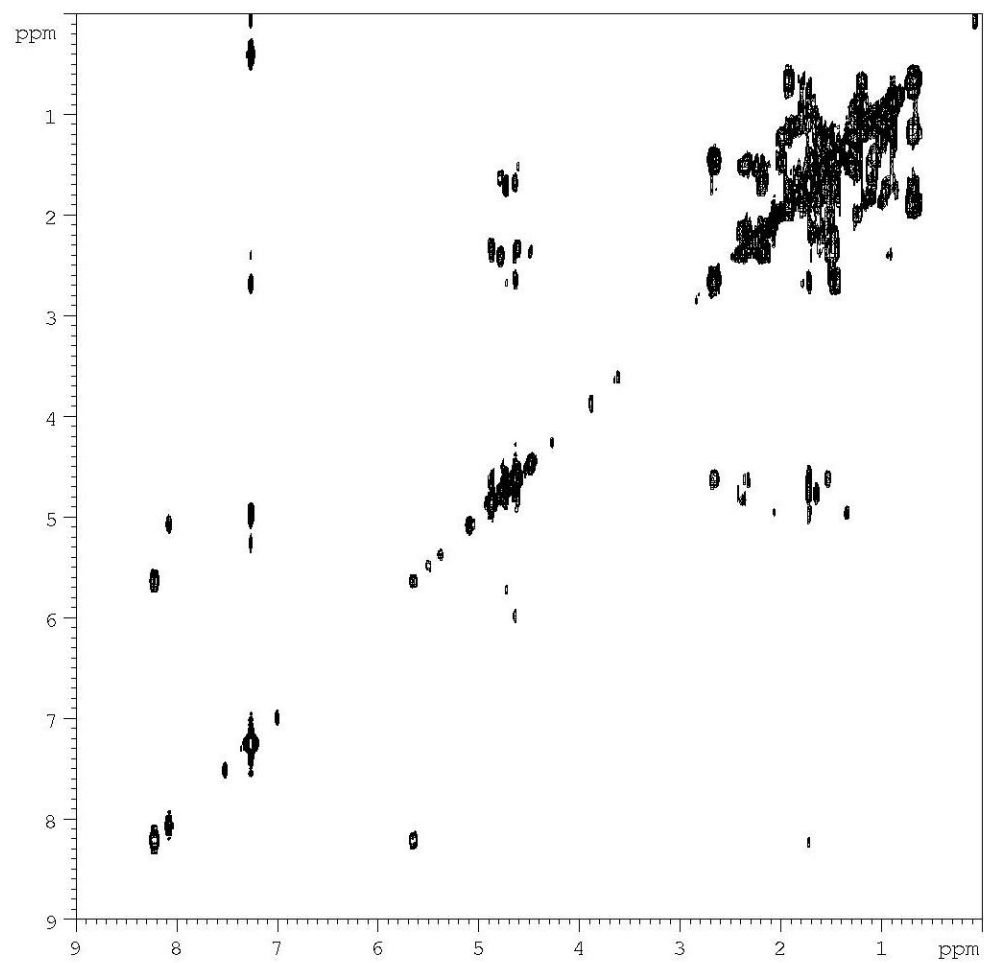
HMBC spectrum of 7-isocyanoamphilecta-11(20),14-diene (**7**) ( $\text{CDCl}_3$ , Bruker 500 MHz,  $J=7\text{Hz}$ ).



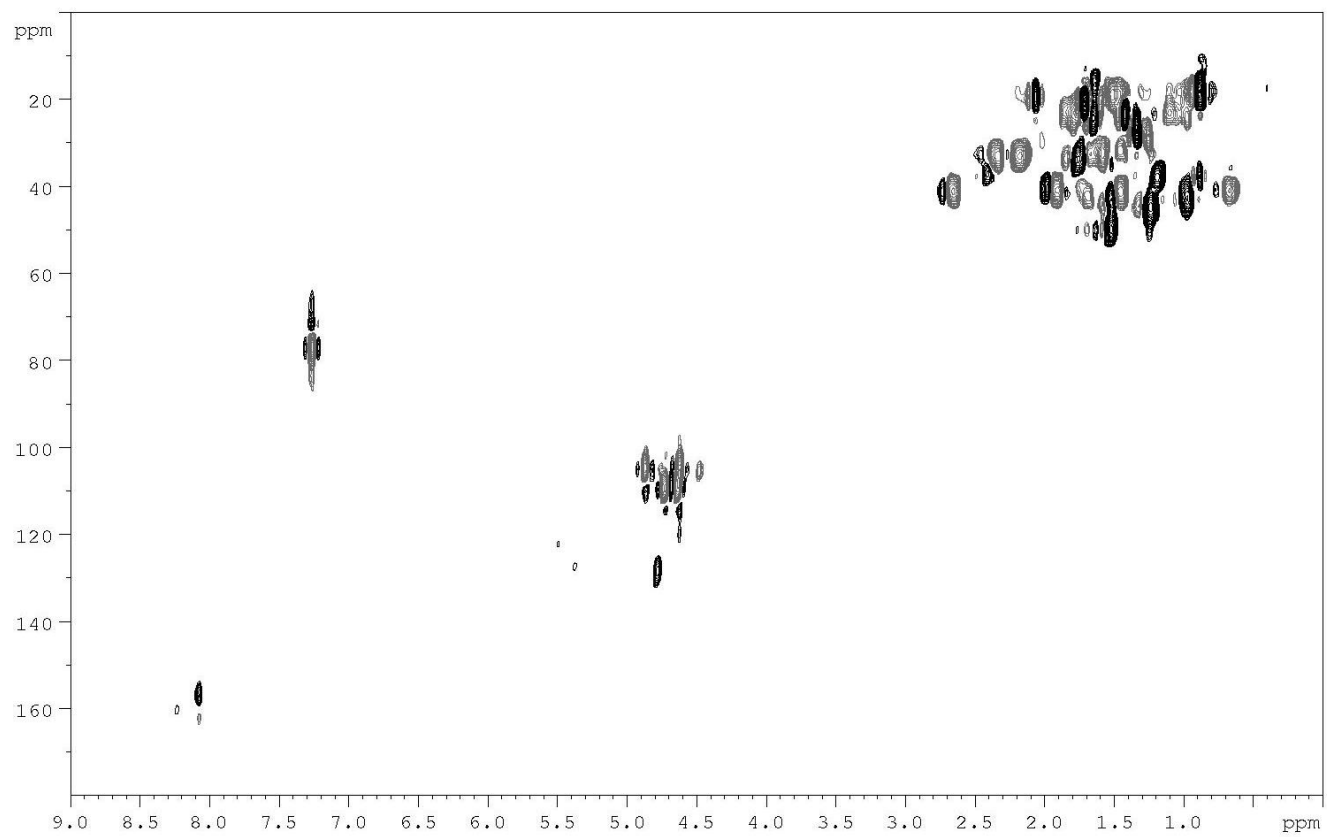
<sup>1</sup>H NMR spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) (CDCl<sub>3</sub>, Bruker 600 MHz).



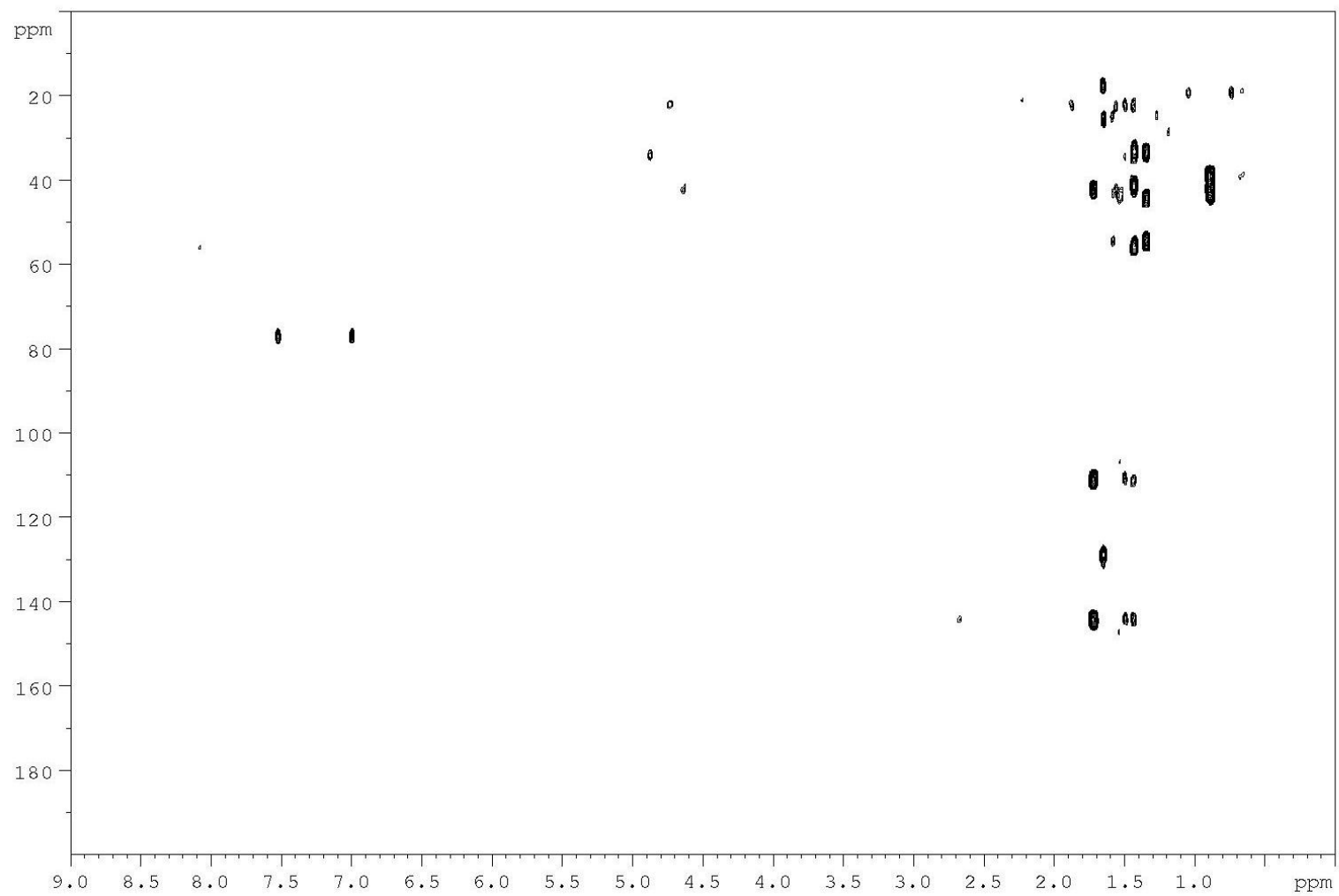
$^{13}\text{C}$  NMR spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



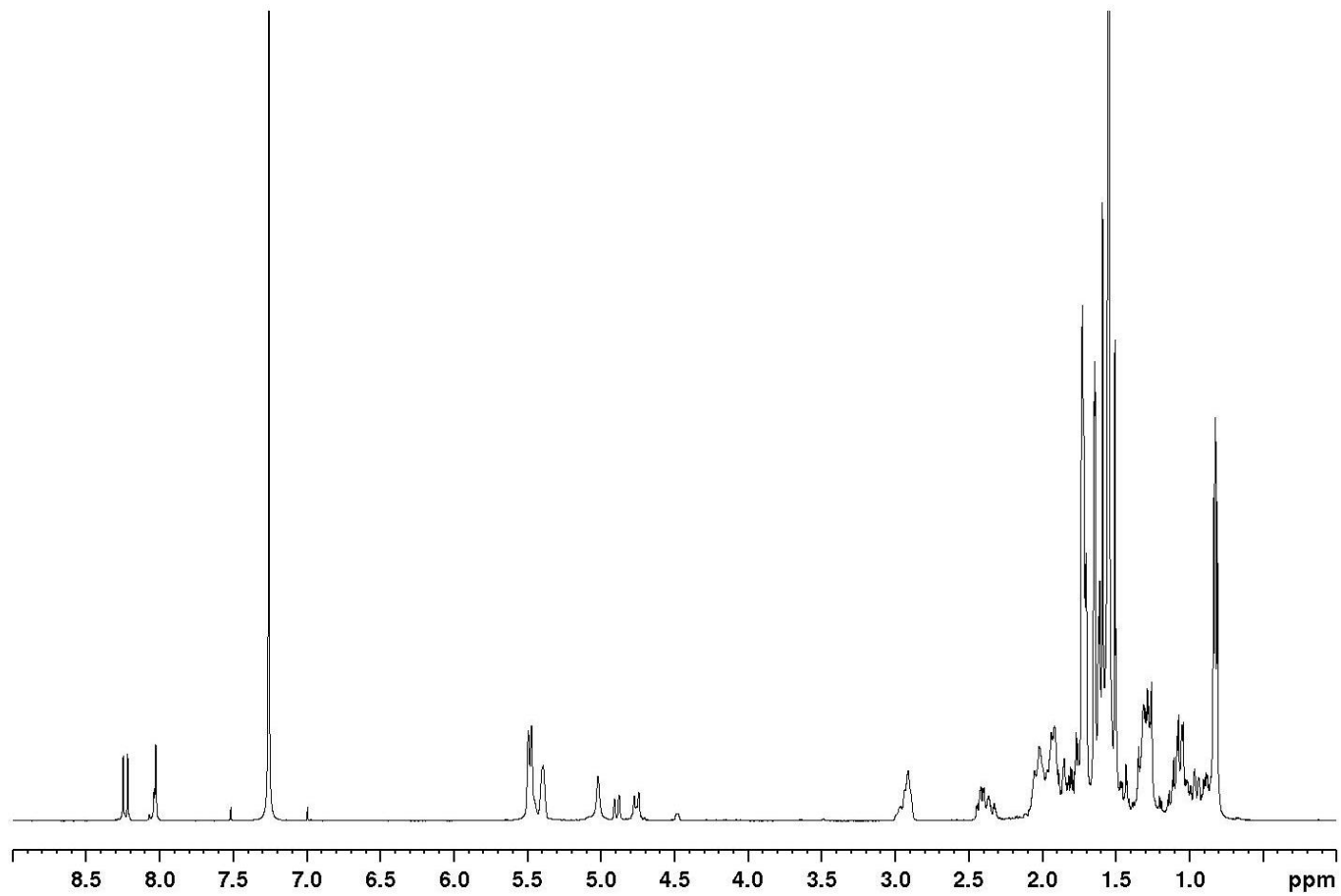
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) ( $\text{CDCl}_3$ , Bruker 600 MHz).



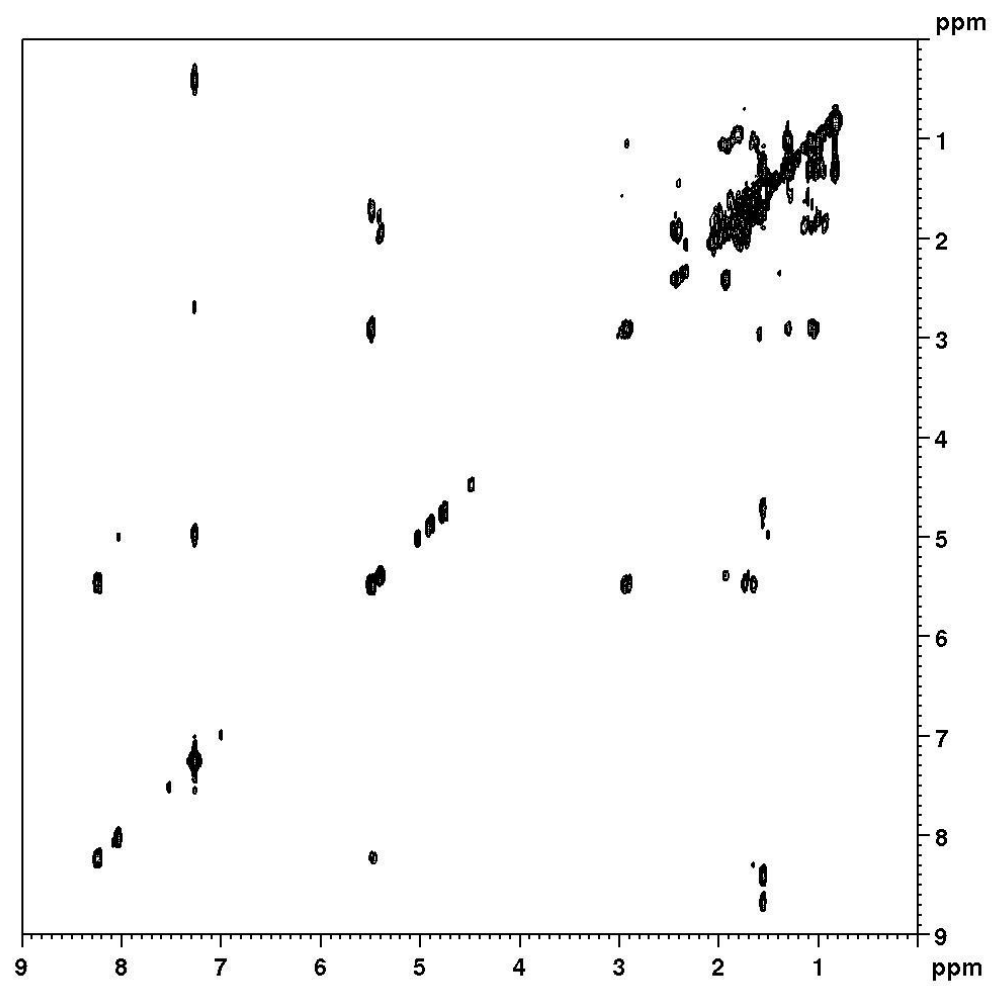
HSQC spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) (CDCl<sub>3</sub>, Bruker 600 MHz).



HMBC spectrum of 7-formamidoamphilecta-11(20),15-diene (**8**) (CDCl<sub>3</sub>, Bruker 600 MHz, *J*=7Hz).

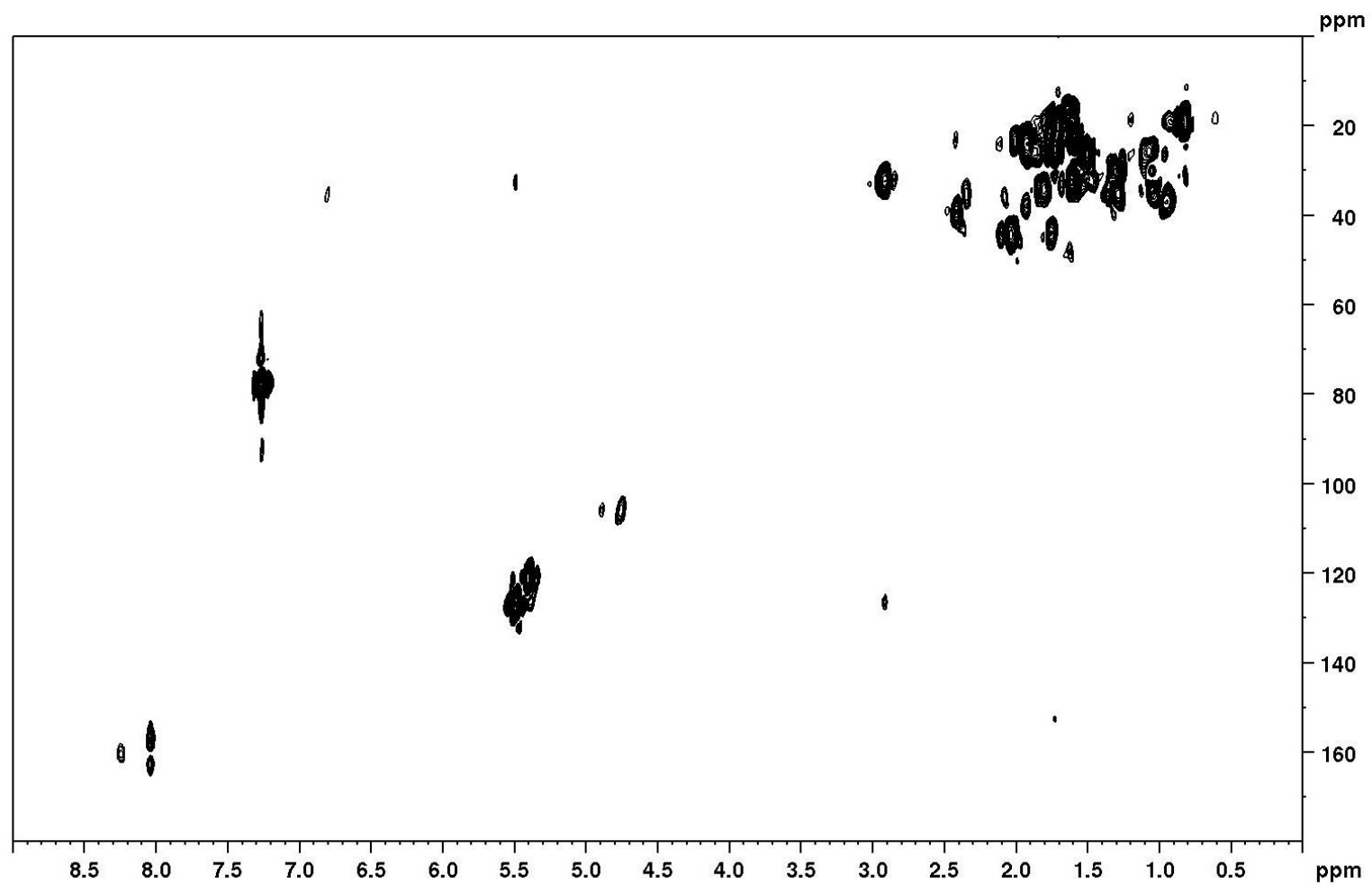


$^1\text{H}$  NMR spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

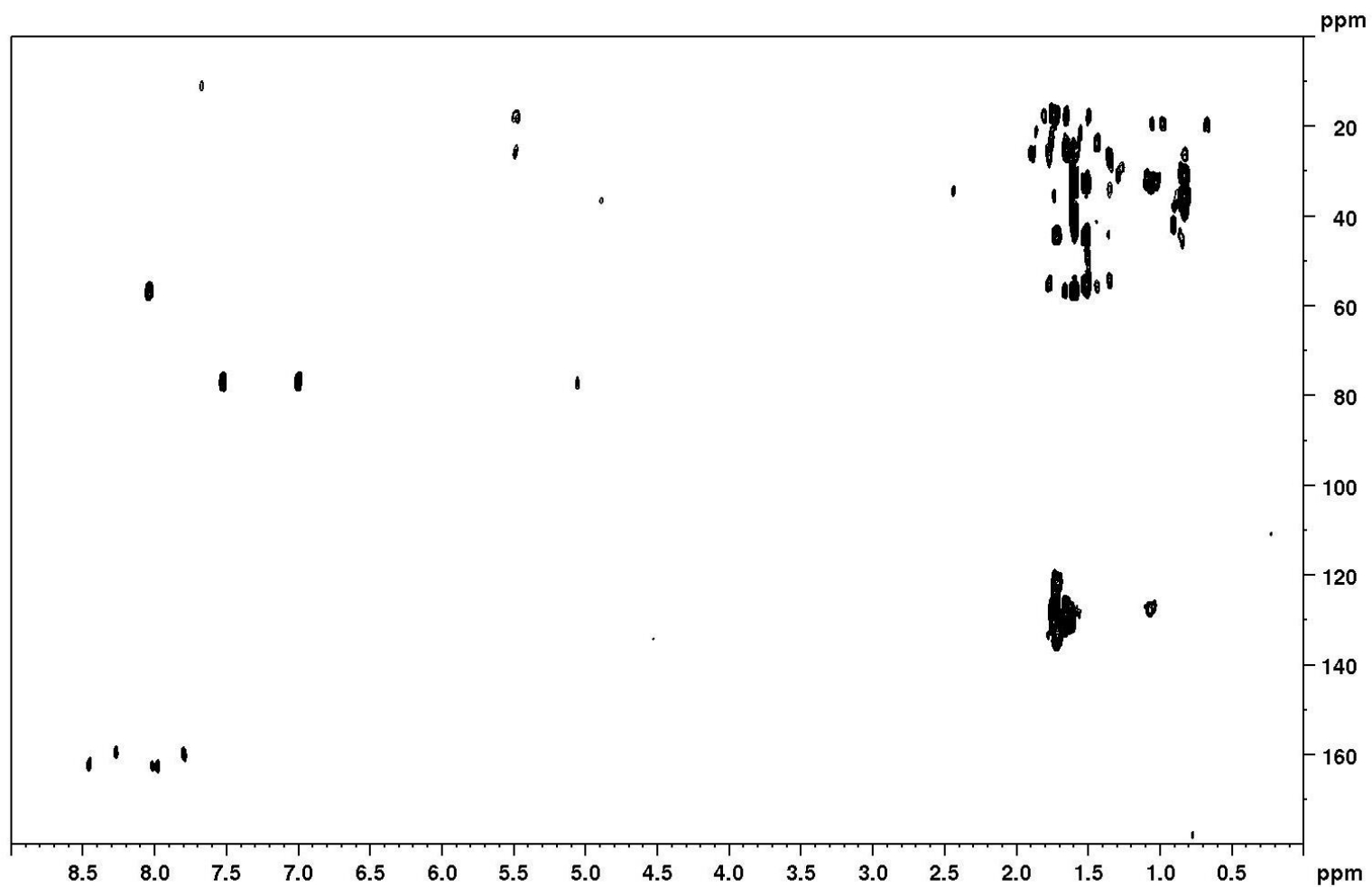


$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $\text{CDCl}_3$ , Bruker 400 MHz).

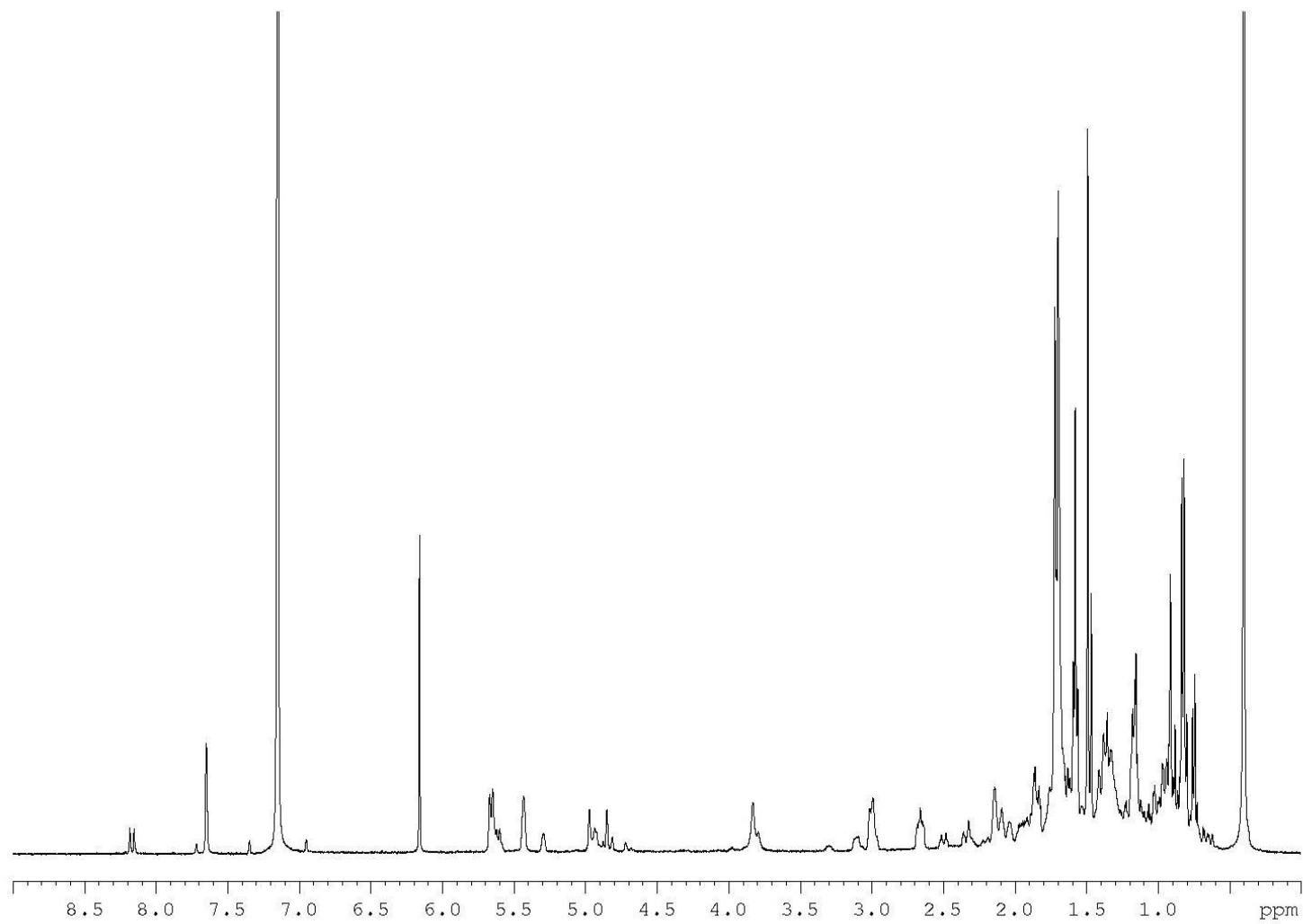




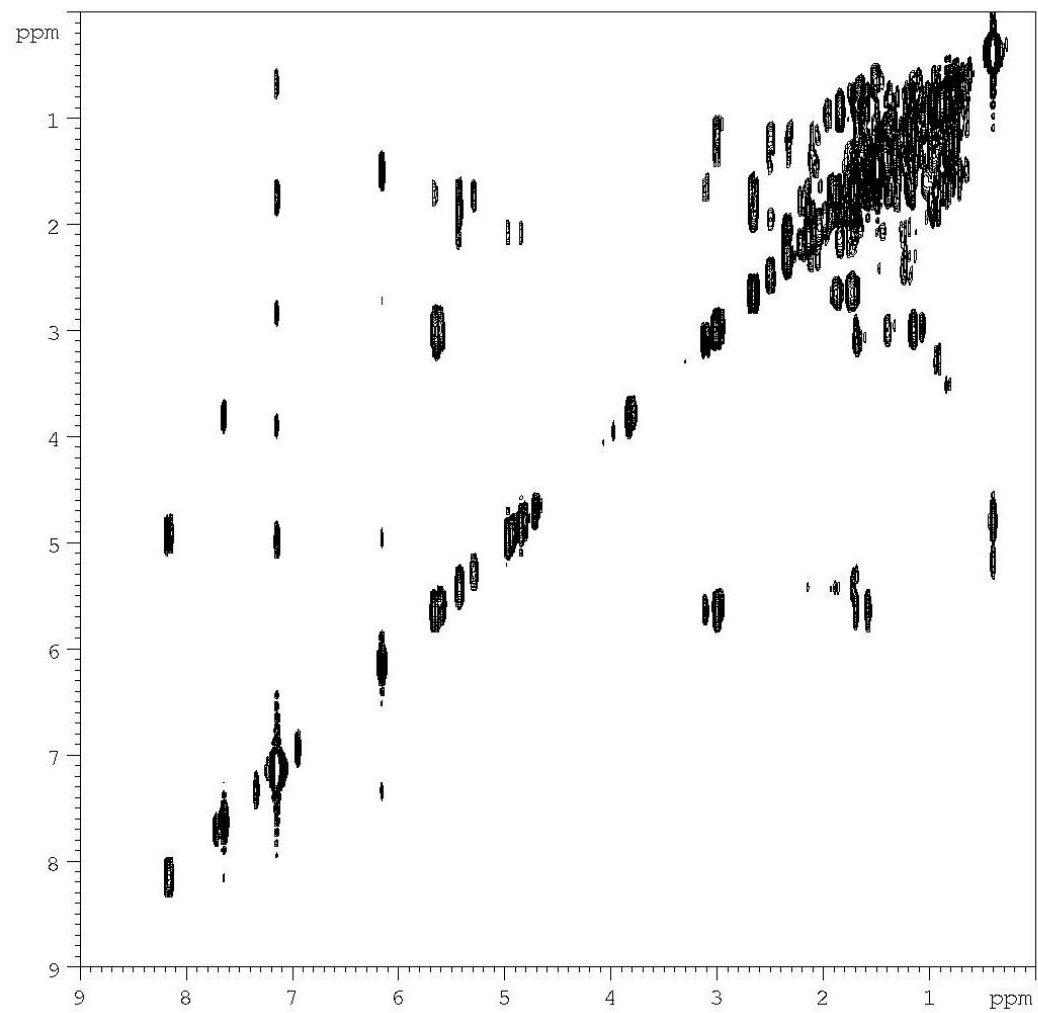
HSQC spectrum of 7-formamido amphilecta-10,14-diene (**9**) (CDCl<sub>3</sub>, Bruker 400 MHz).



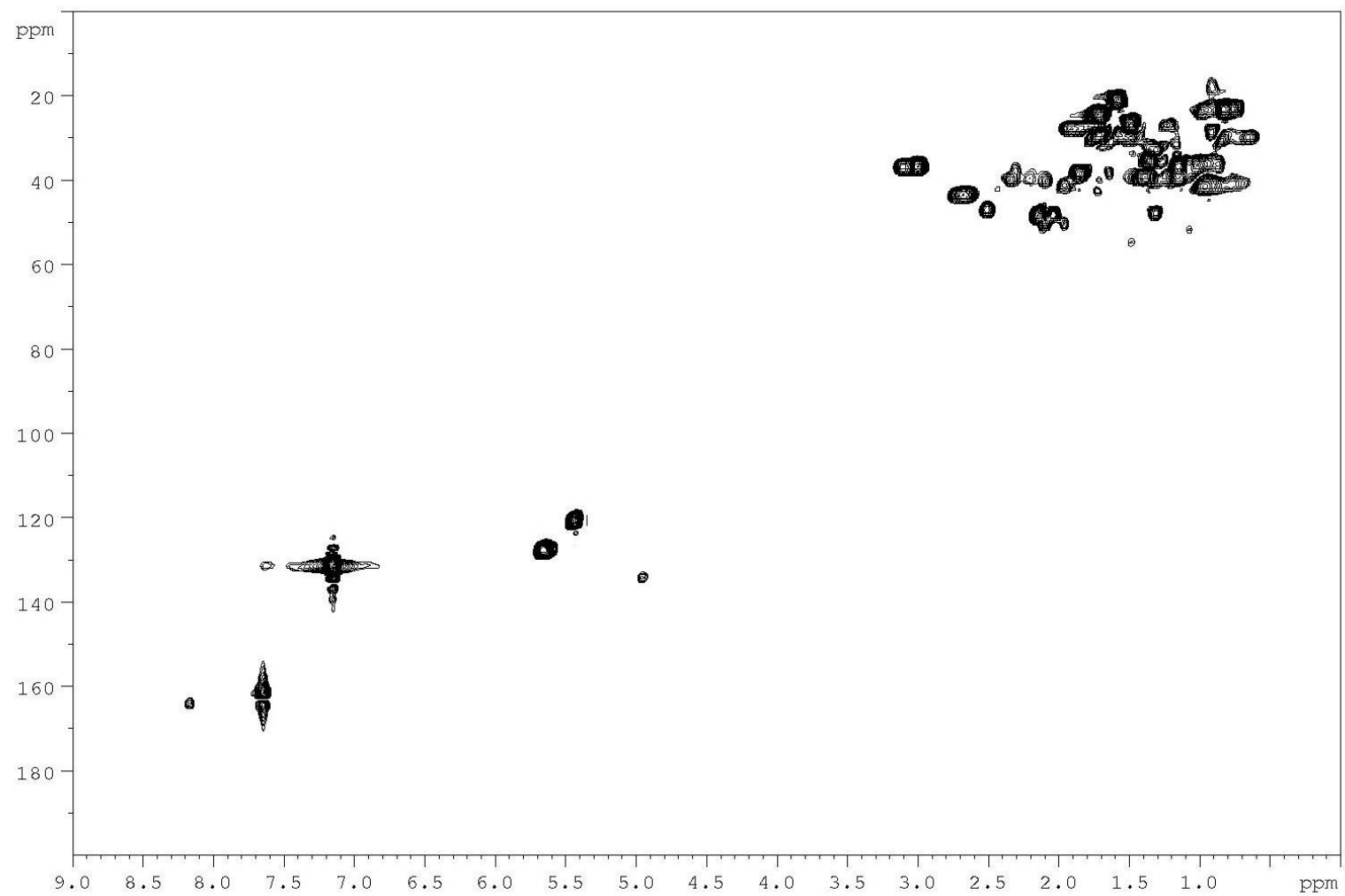
HMBC spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $\text{CDCl}_3$ , Bruker 400 MHz,  $J=7\text{ Hz}$ ).



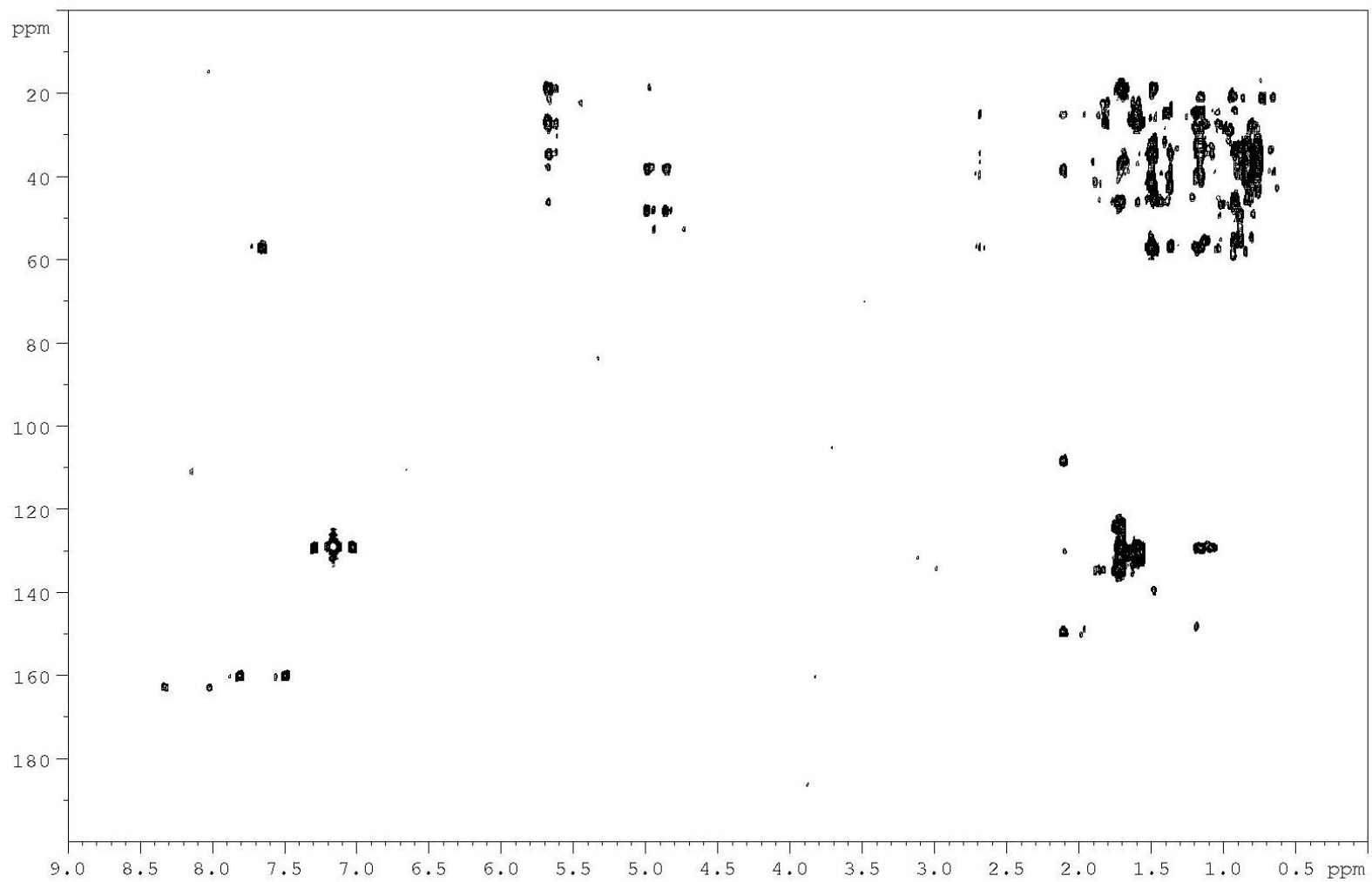
<sup>1</sup>H NMR spectrum of 7-formamido amphilecta-10,14-diene (**9**) (C<sub>6</sub>D<sub>6</sub>, Bruker 400 MHz).



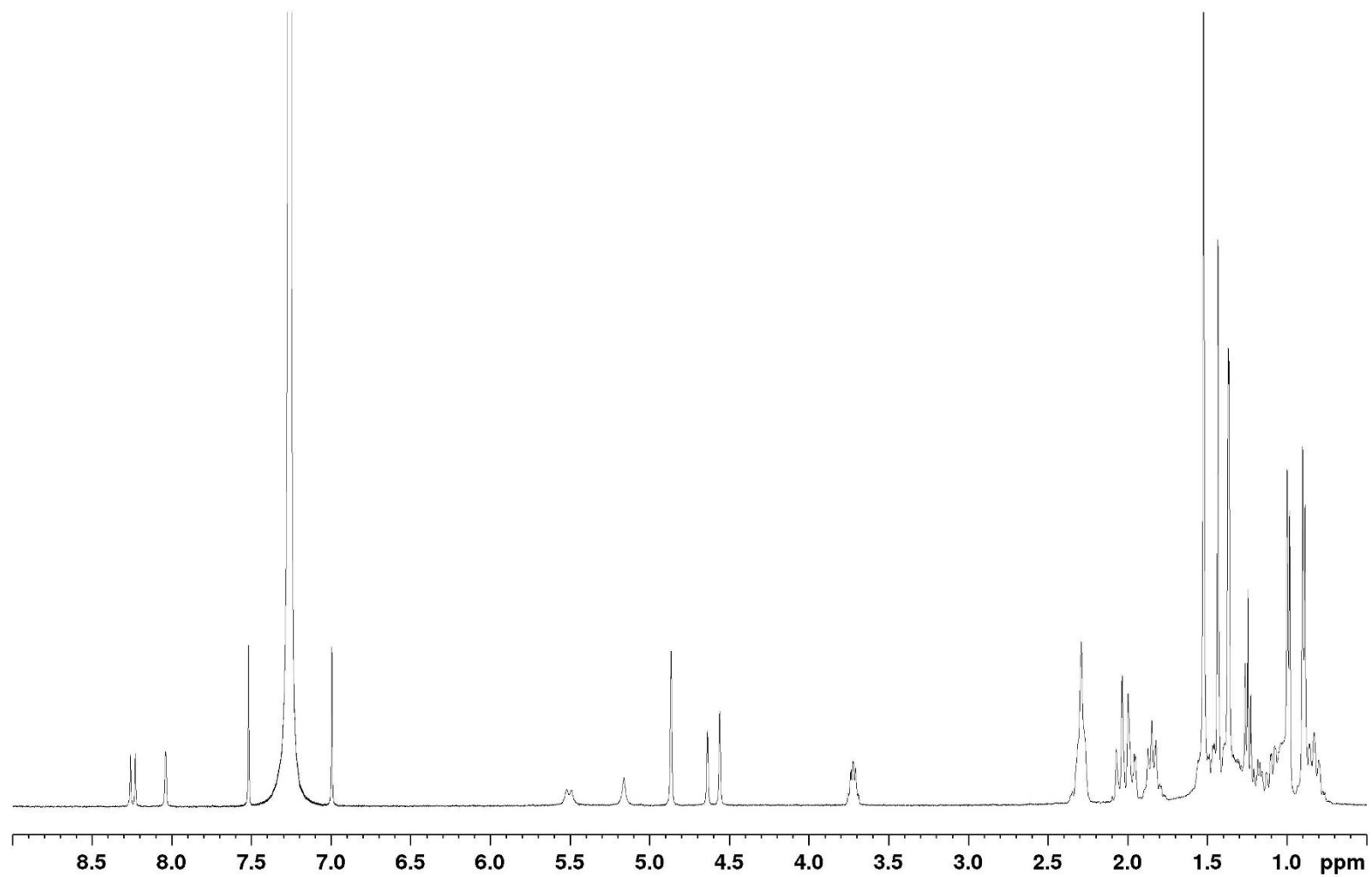
$^1\text{H}$ - $^1\text{H}$  COSY spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $\text{C}_6\text{D}_6$ , Bruker 400 MHz).



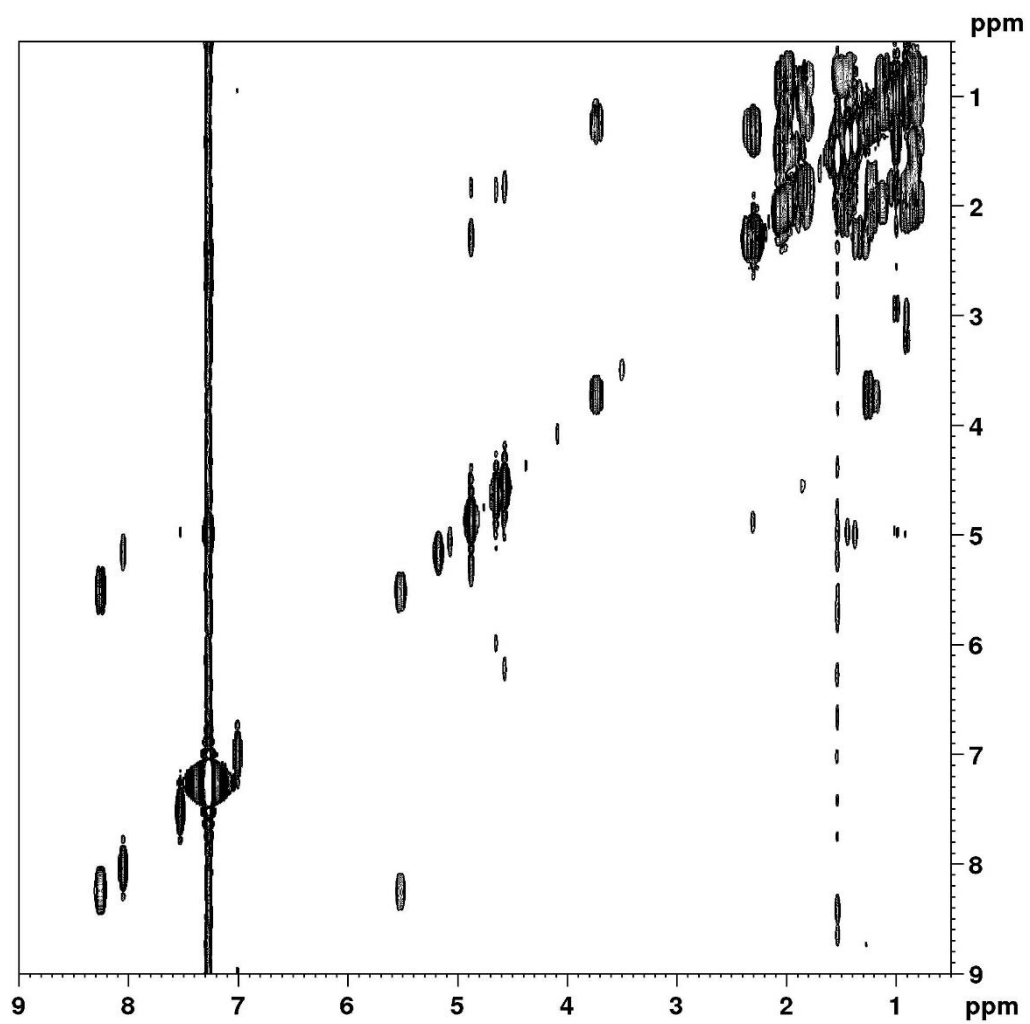
HSQC spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $C_6D_6$ , Bruker 400 MHz).



HMBC spectrum of 7-formamido amphilecta-10,14-diene (**9**) ( $C_6D_6$ , Bruker 400 MHz,  $J=7$ Hz).

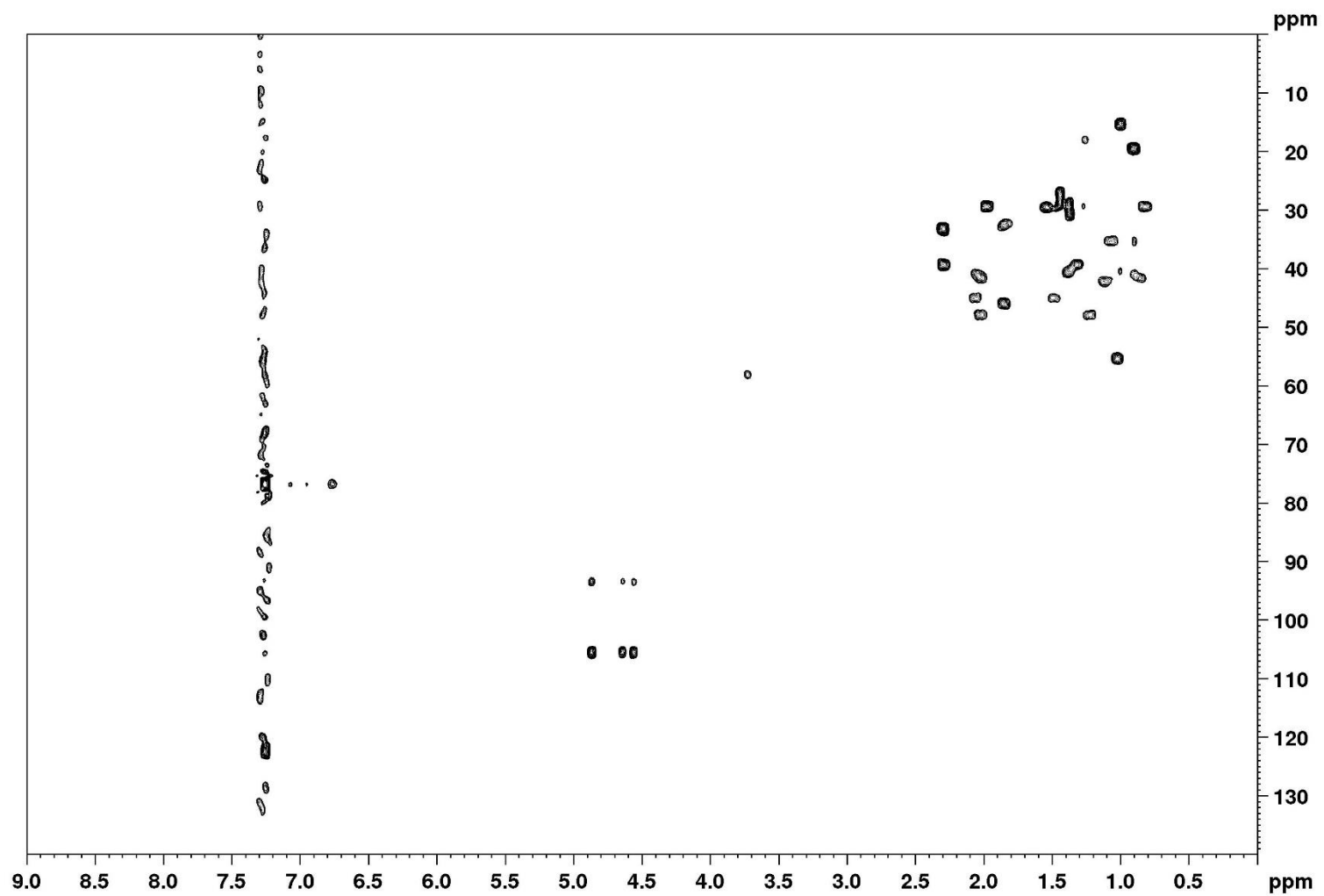


<sup>1</sup>H NMR spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) (CDCl<sub>3</sub>, Bruker 400 MHz).

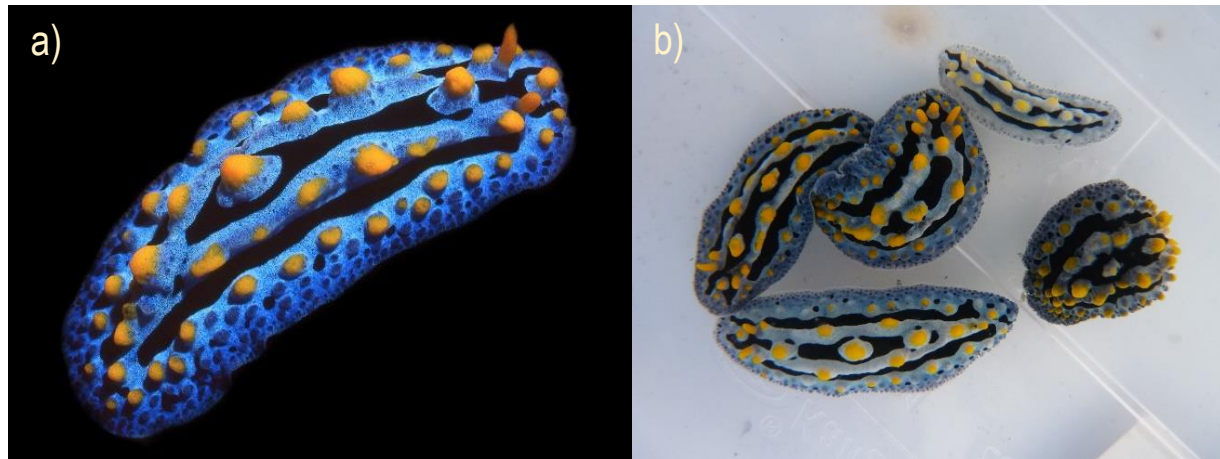


<sup>1</sup>H-<sup>1</sup>H COSY spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) (CDCl<sub>3</sub>, Bruker 400 MHz).





HSQC spectrum of 8-isocyano-15-formamido-11(20)-amphilectene (**10**) ( $\text{CDCl}_3$ , Bruker 400 MHz).



**Figure 1.** Individuals of *P. coelestis* collected in Hainan (China) in 2002 (a) and 2013 (b).