

## SUPPORTING INFORMATION

### **Synthesis of the Pentasaccharide Moiety of Starfish Asterosaponin Luidiaquinoside and its Conformational Analysis**

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### **Solution conformational Studies:**

NMR data were acquired on Bruker Avance-III HD 500 MHz NMR spectrometer and Agilent-DD2 700 MHz NMR spectrometer at 300 °K and 298 °K respectively in suitable solvents. Resonance assignments were carried out using Two-Dimensional  $^1\text{H}$ - $^1\text{H}$  COSY,  $^1\text{TOCSY}$ ,<sup>2</sup> ROESY<sup>3</sup> and indirect detection experiments like  $^1\text{H}$ - $^{13}\text{C}$  HSQC, HMBC. All NMR data were processed using TopSpin3.2. Proton spectra were acquired with 16 to 32 transients with 16K points zero filled to 32k data points. 2D  $^1\text{H}$ - $^1\text{H}$  TOCSY and ROESY were acquired with 2k complex data points in F2 and 128 to 256 in F1 dimension with a relaxation delay of 2 s between transients was used for all experiments. The 2D TOCSY NMR data were acquired with a spin-lock time of 80 ms. 2D ROESY NMR data were acquired with a mixing time of 200 ms. Water suppression was carried out using presaturation and excitation sculpting techniques. Data were processed using standard apodizing functions prior to Fourier transformation. 2D  $^1\text{H}$ - $^{13}\text{C}$  HSQC NMR data were acquired, with  $^{13}\text{C}$  decoupling during the acquisition period, over an F2 frequency width of 12 ppm into 2k complex data points. 16 to 32 transients were accumulated for each of 128 t1 increments over an F1 frequency width of 200 ppm centered at 100 ppm. Phase sensitive data were acquired in a sensitivity-improved manner using an echo-anti-echo acquisition mode. 2D  $^1\text{H}$ - $^{13}\text{C}$  HMBC NMR data were acquired over an F2 frequency width of 12 ppm into 2k complex data points. 32 to 64 transients were accumulated for each of 128 t1 increments over an F1 frequency width of 200 ppm centered at 100 ppm.

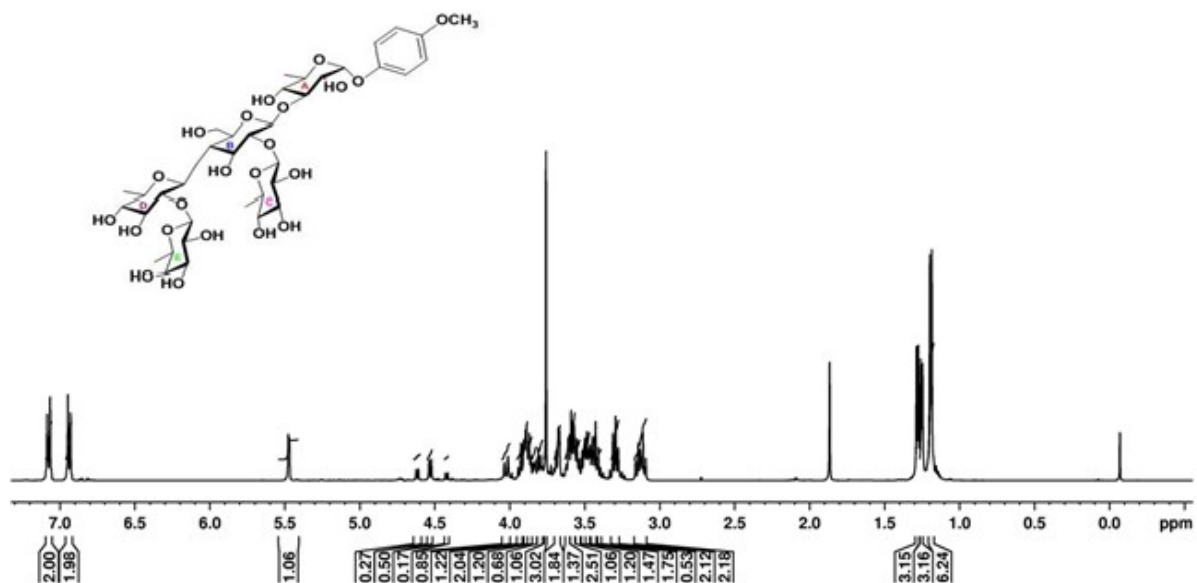


Figure 1: <sup>1</sup>H spectrum of compound 1 (500 MHz, D<sub>2</sub>O, 300 K)

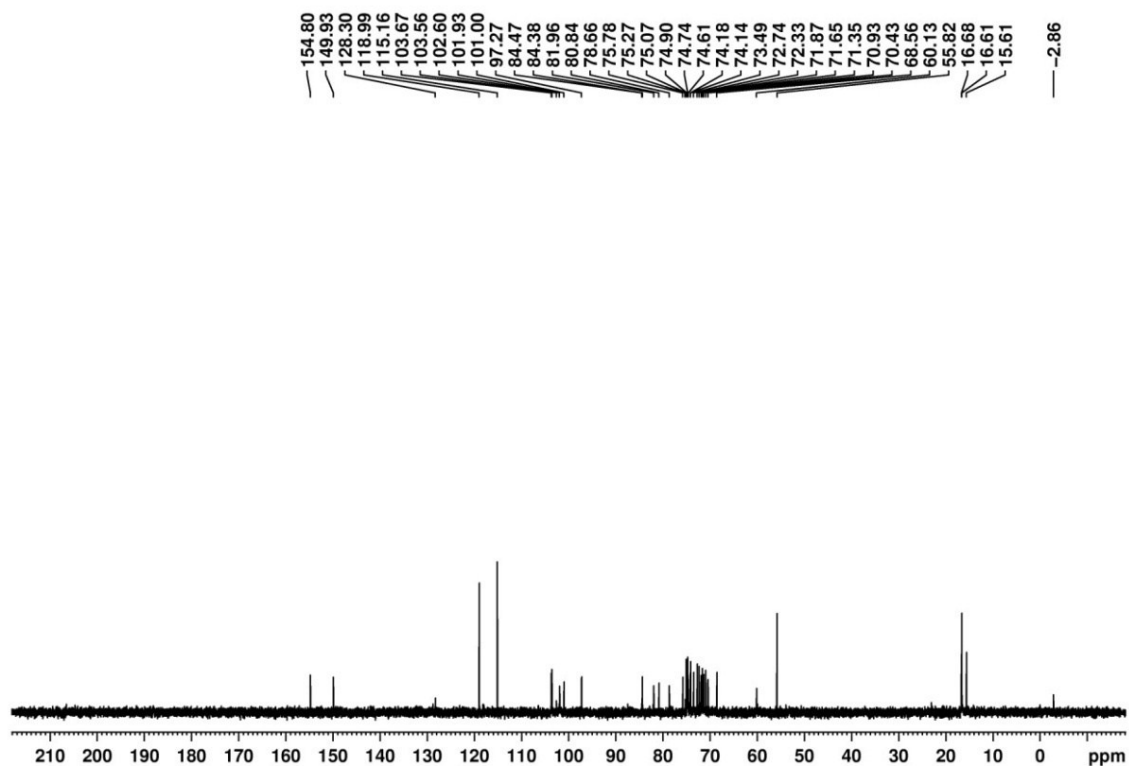


Figure 2: <sup>13</sup>C spectrum of compound 1 (125 MHz, D<sub>2</sub>O, 300K)

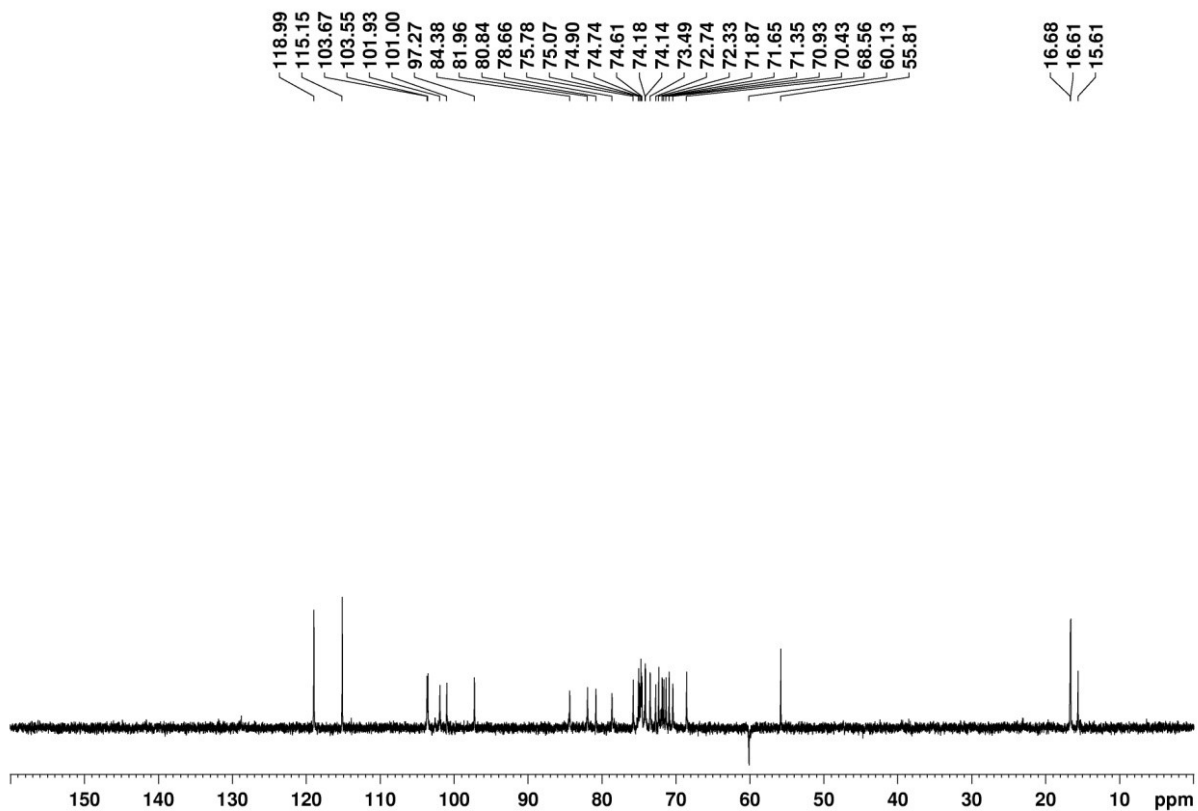


Figure 3:  $^{13}\text{CDEPT-135}^\circ$  Spectrum of compound 1 (125 MHz,  $\text{D}_2\text{O}$ , 300K)

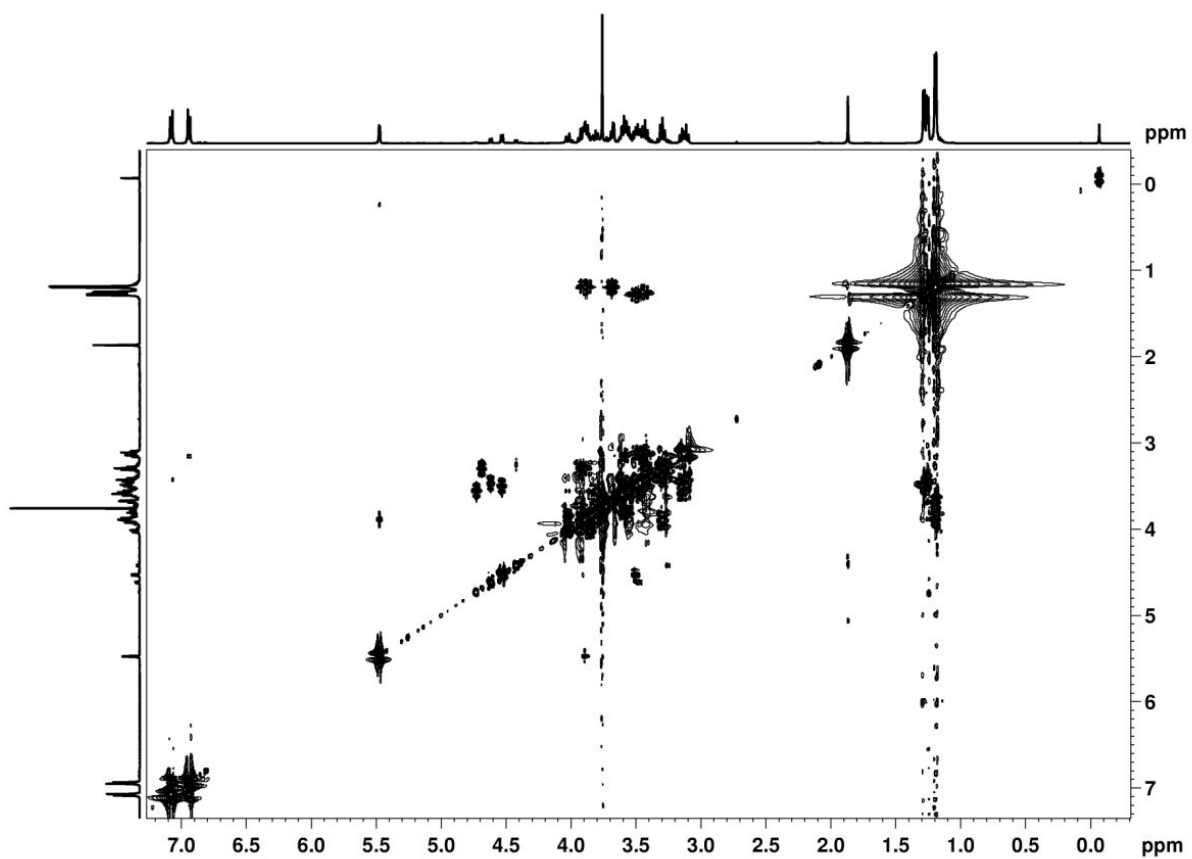
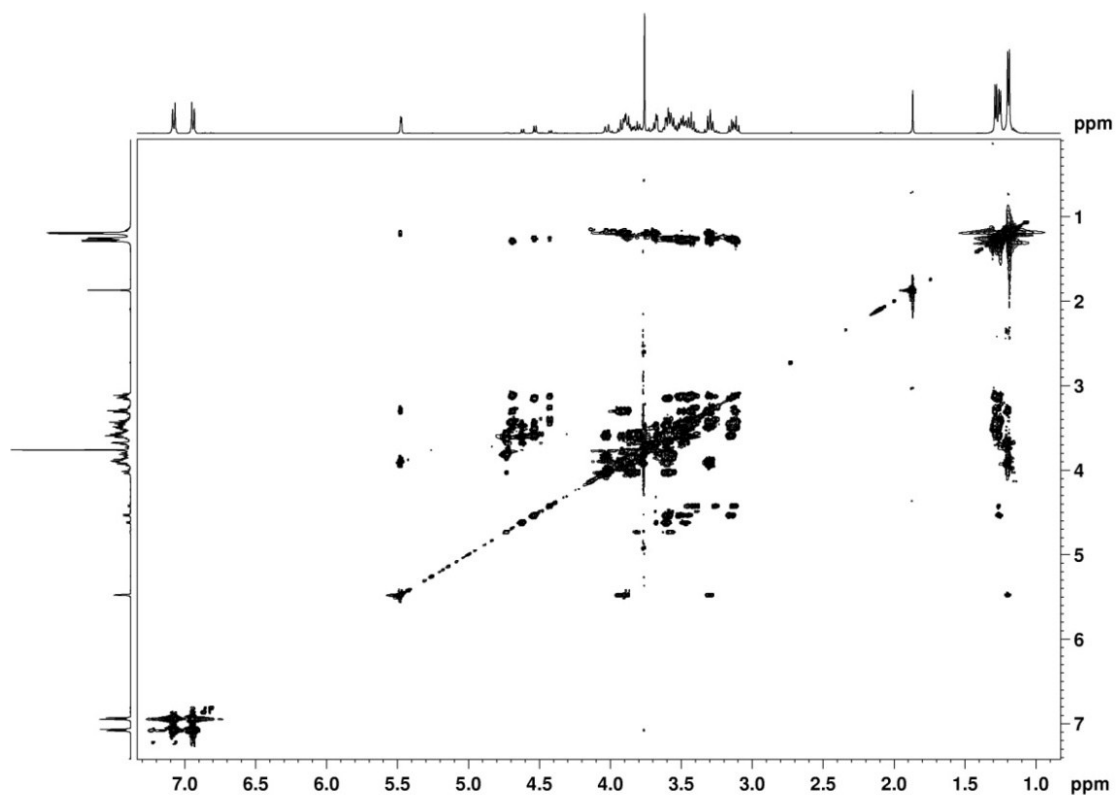
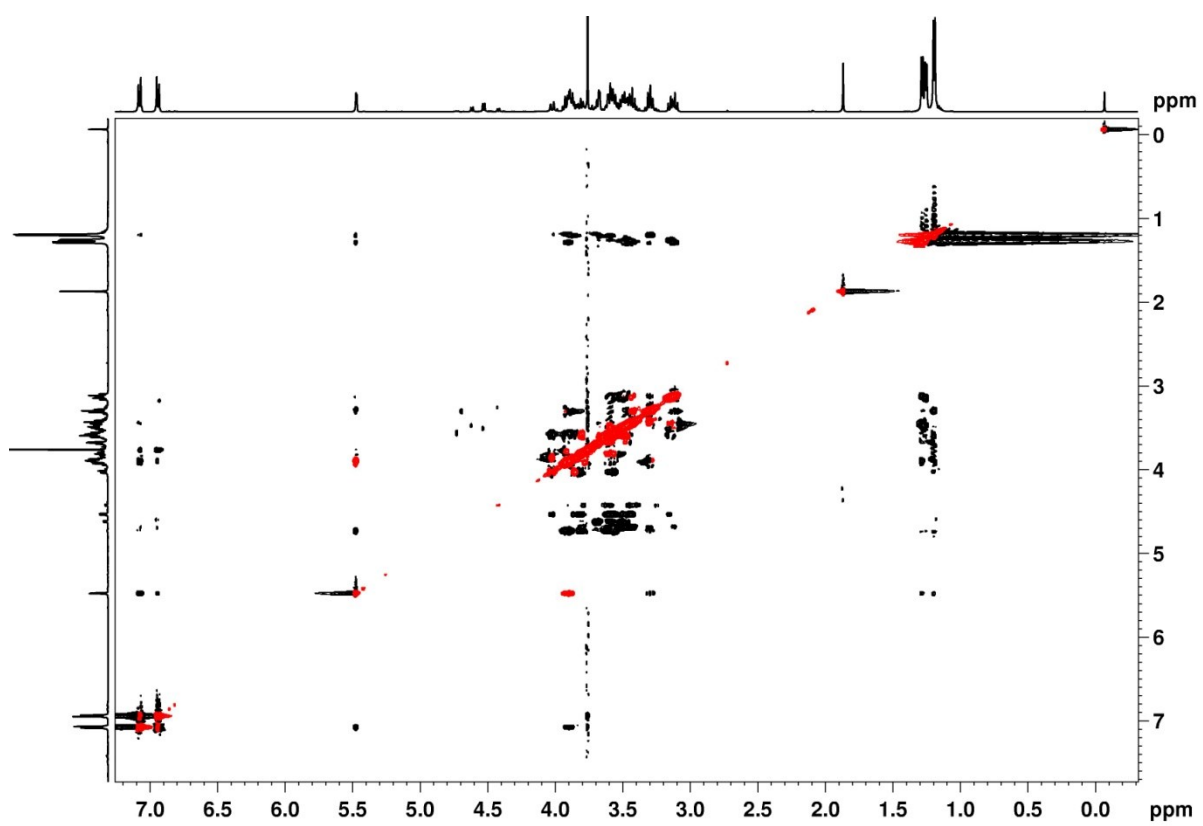


Figure 4: 2D-COSY Spectrum of compound 1 (500 MHz,  $\text{D}_2\text{O}$ , 300K)

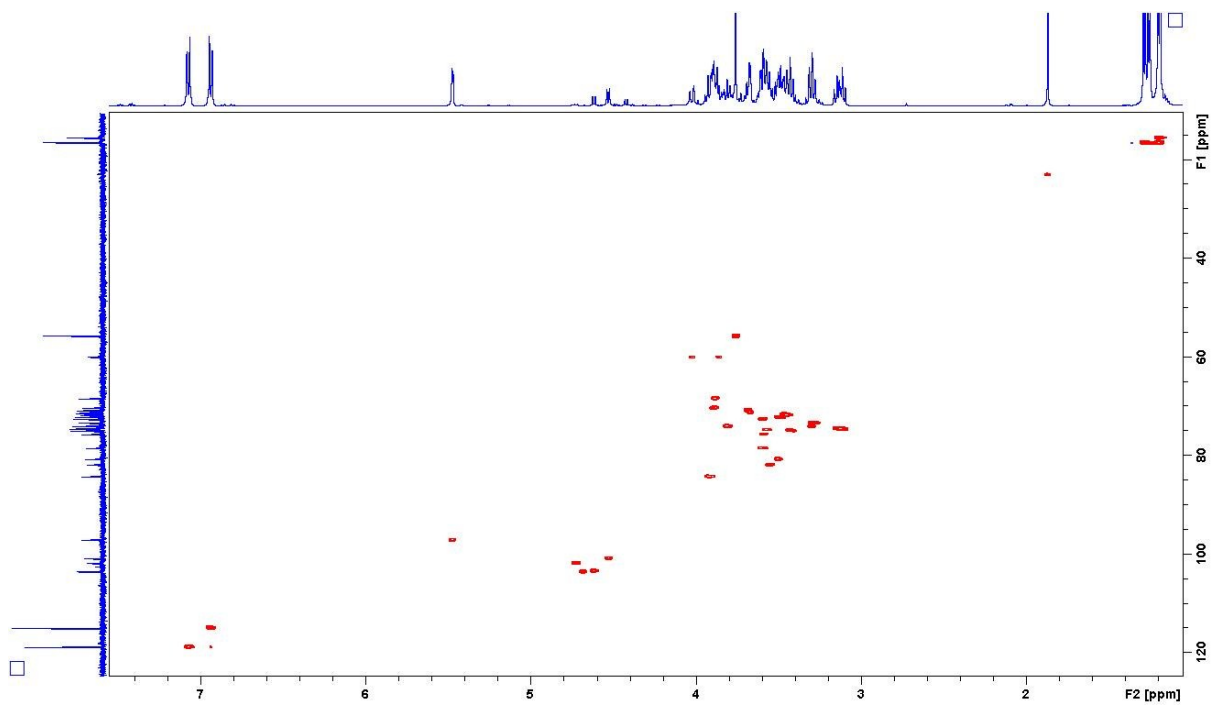


**Figure 5:** 2D-TOCSY spectrum of compound 1 (500 MHz, D<sub>2</sub>O, 300K)

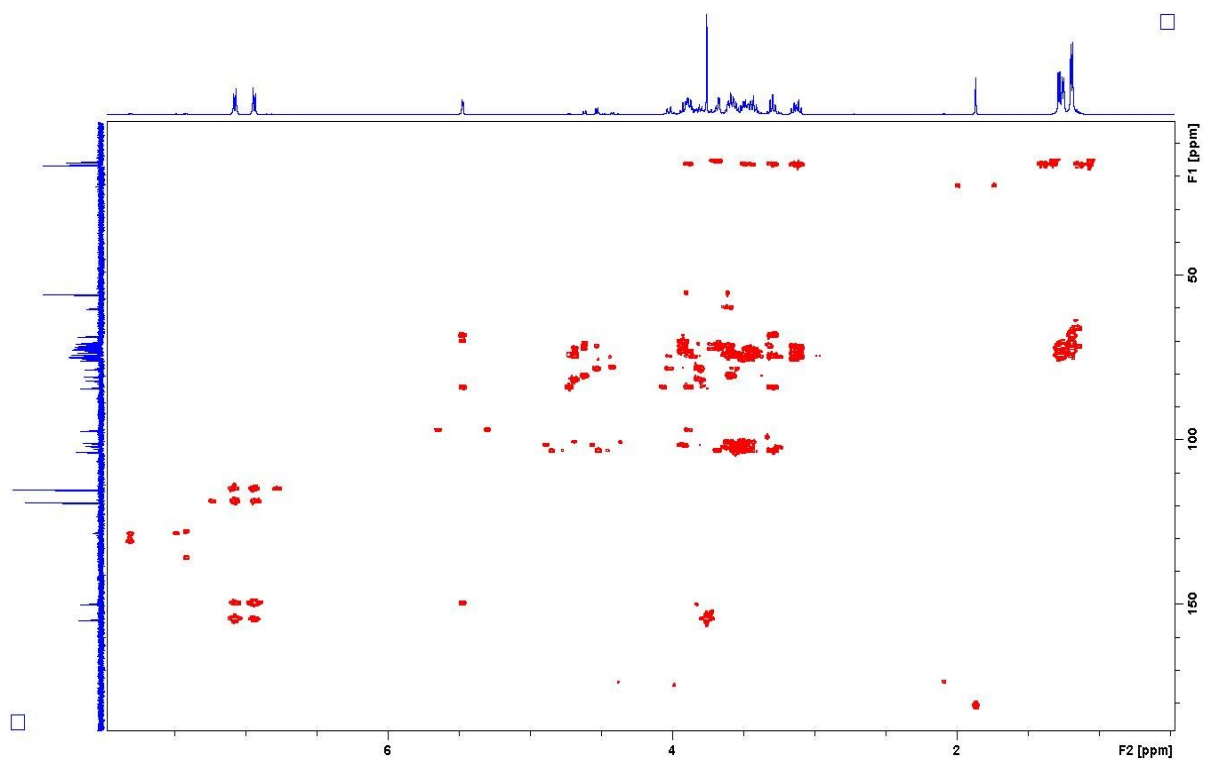


**Figure 6:** 2D-ROESY spectrum of compound 1 (500 MHz, D<sub>2</sub>O, 300K)

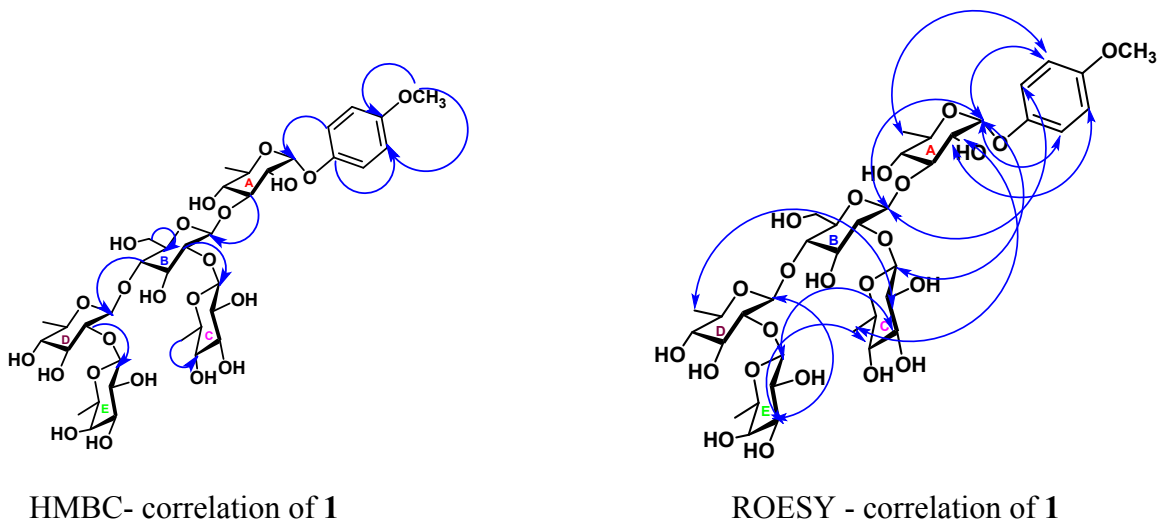




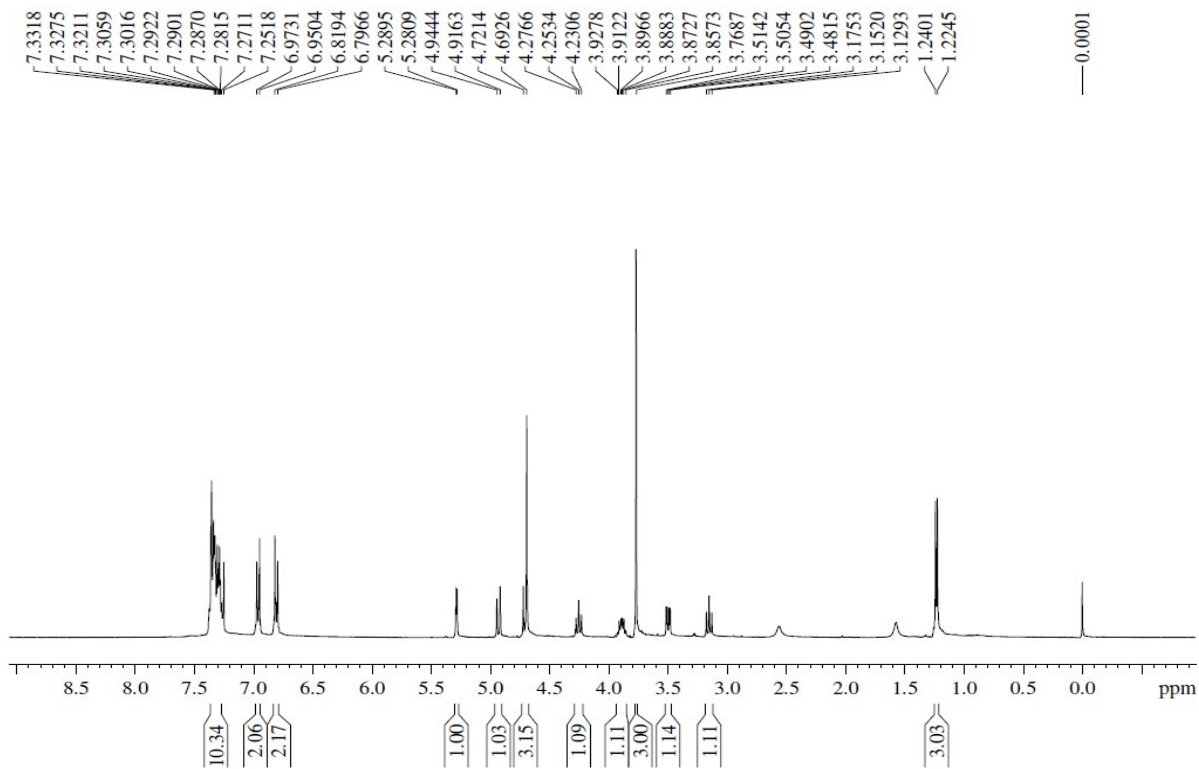
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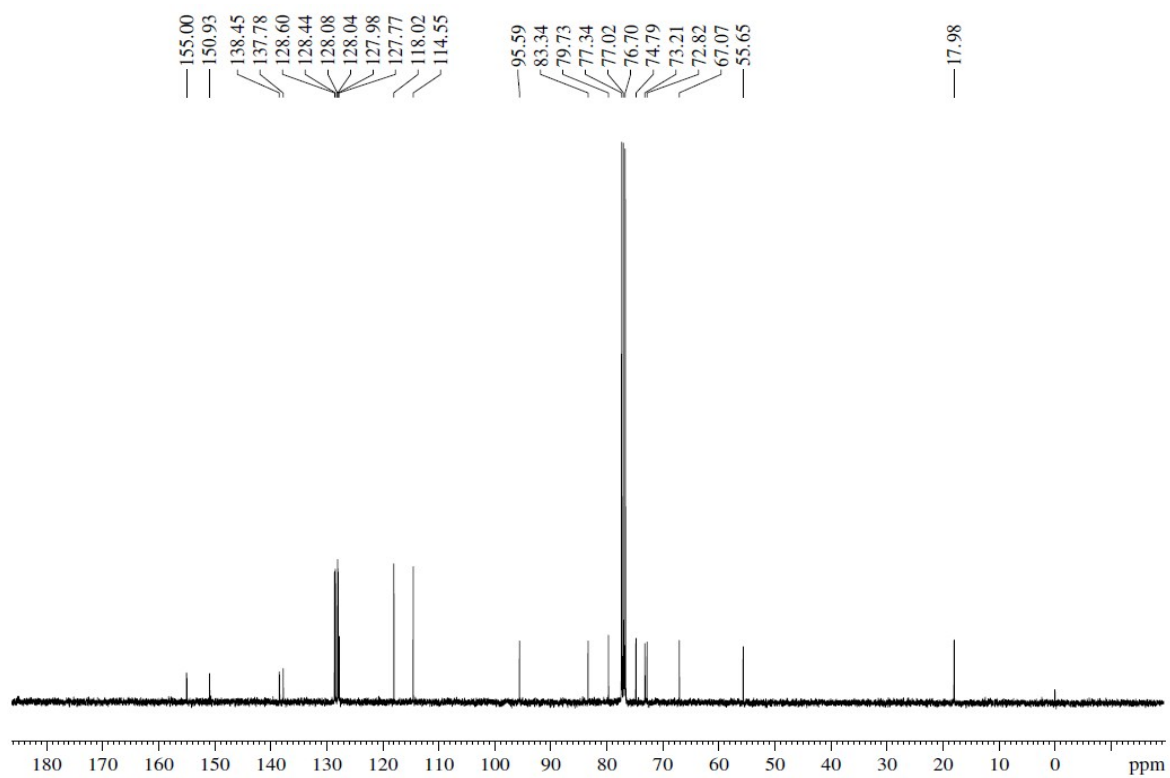
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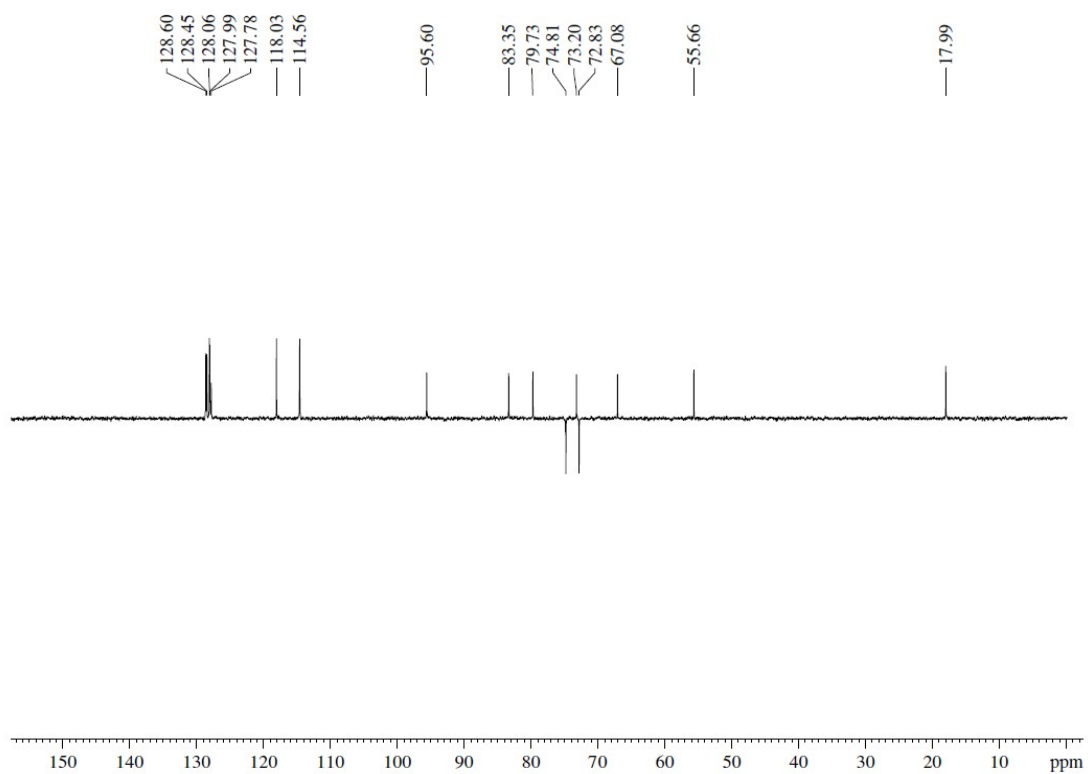
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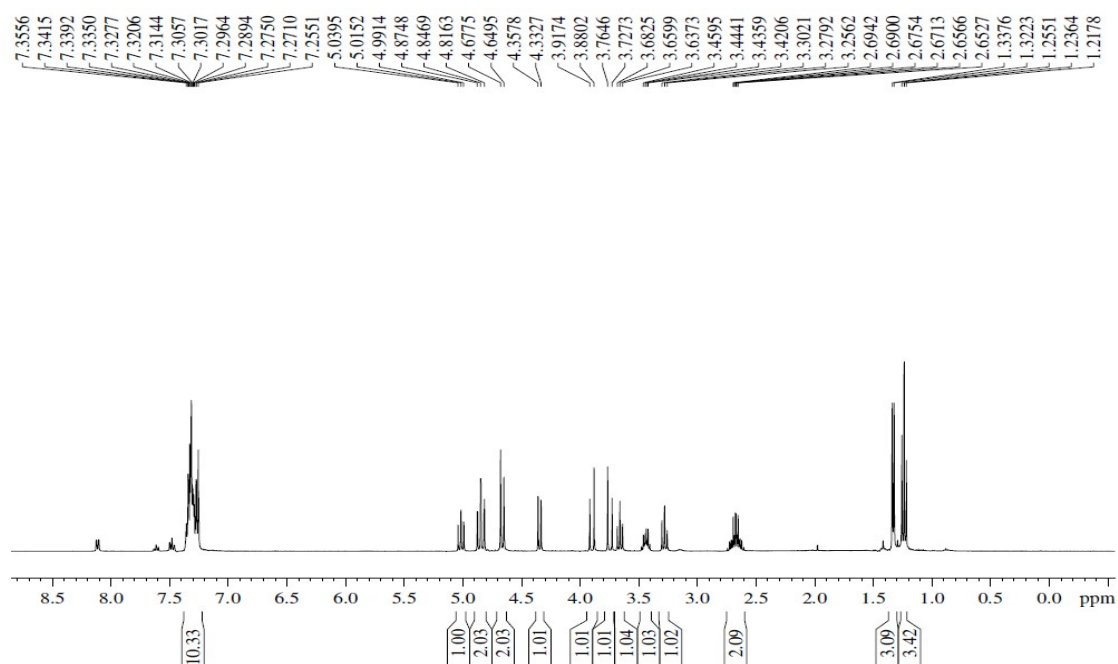
**Figure 10:**  $^1\text{H}$  spectrum of compound **2** (400 MHz,  $\text{CDCl}_3$ , 300 K)



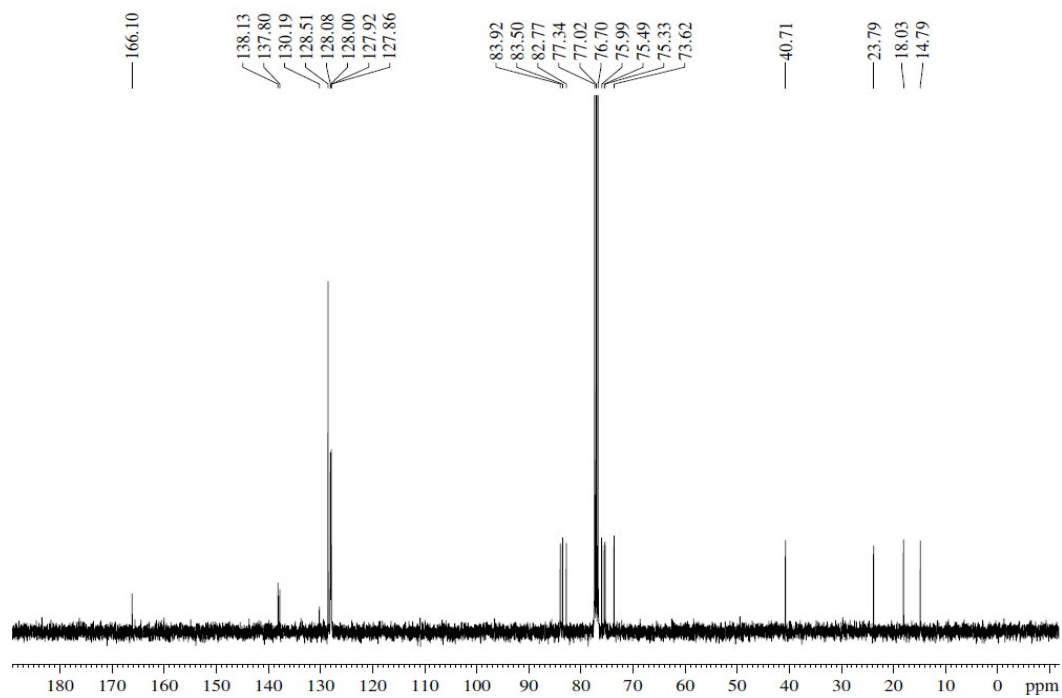
**Figure 11:**  $^{13}\text{C}$  spectrum of compound **2** (100 MHz,  $\text{CDCl}_3$ , 300 K)



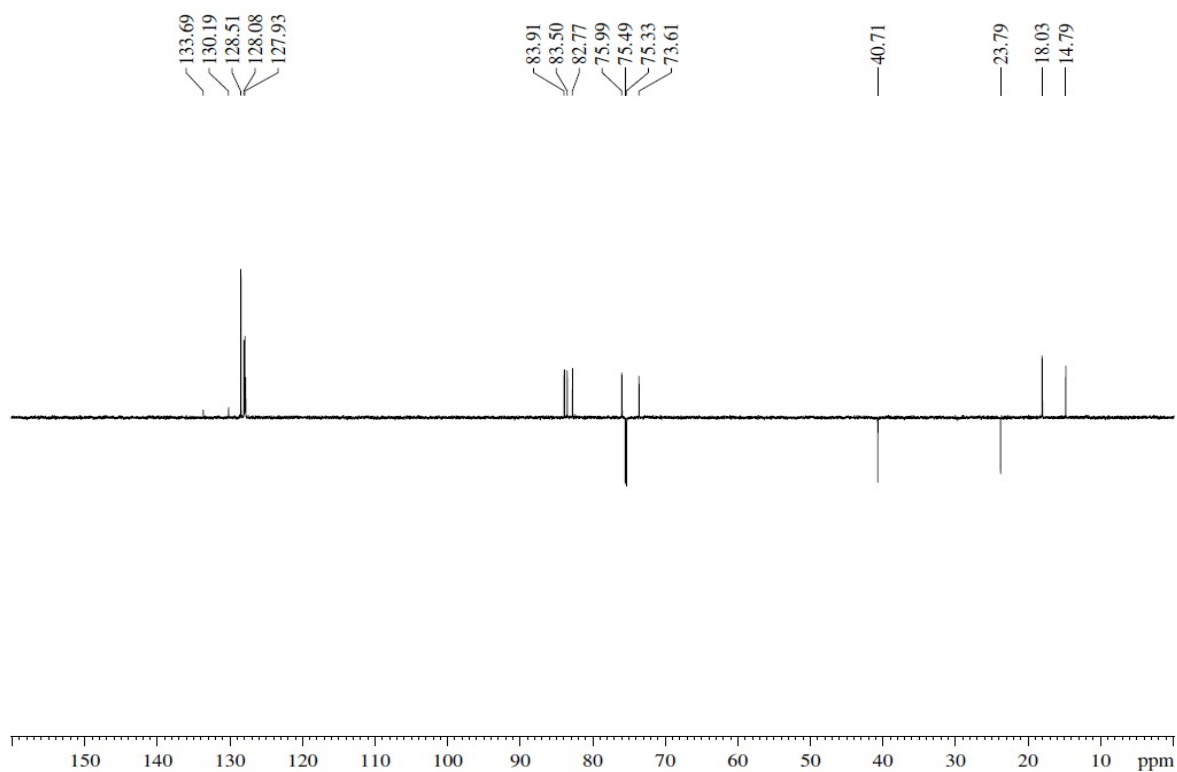
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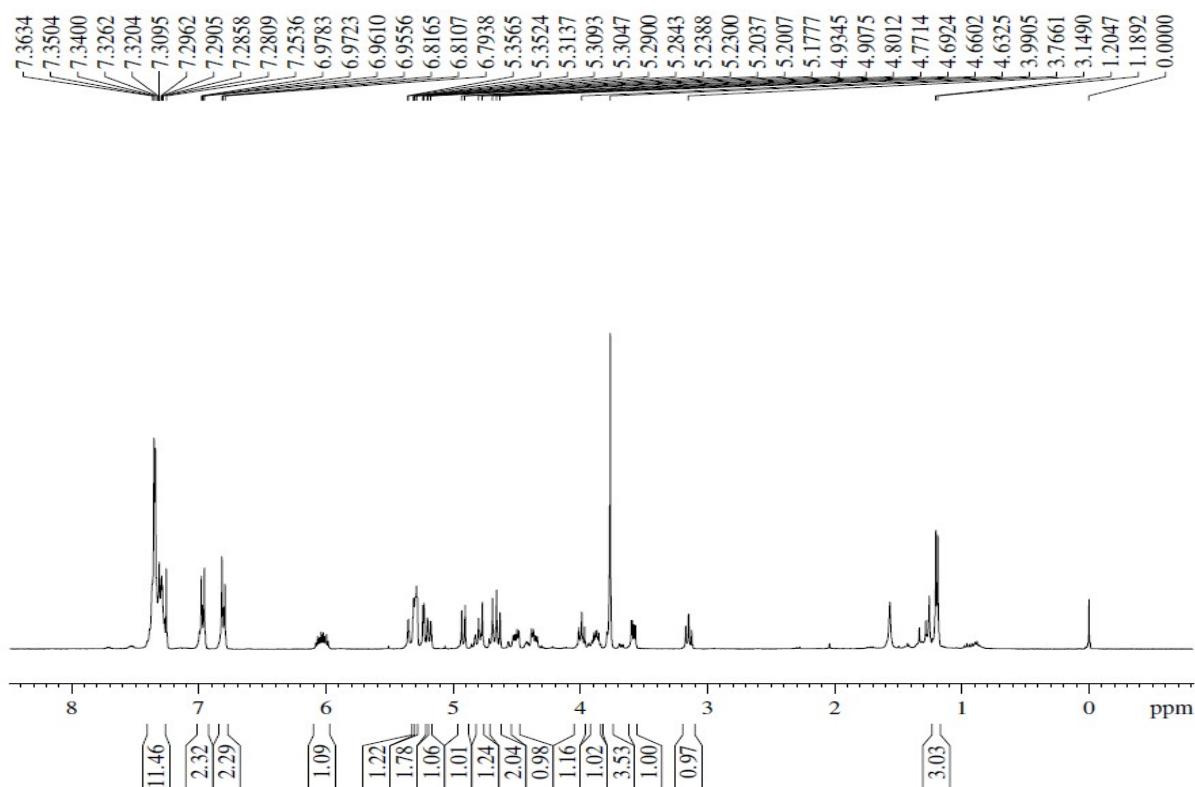
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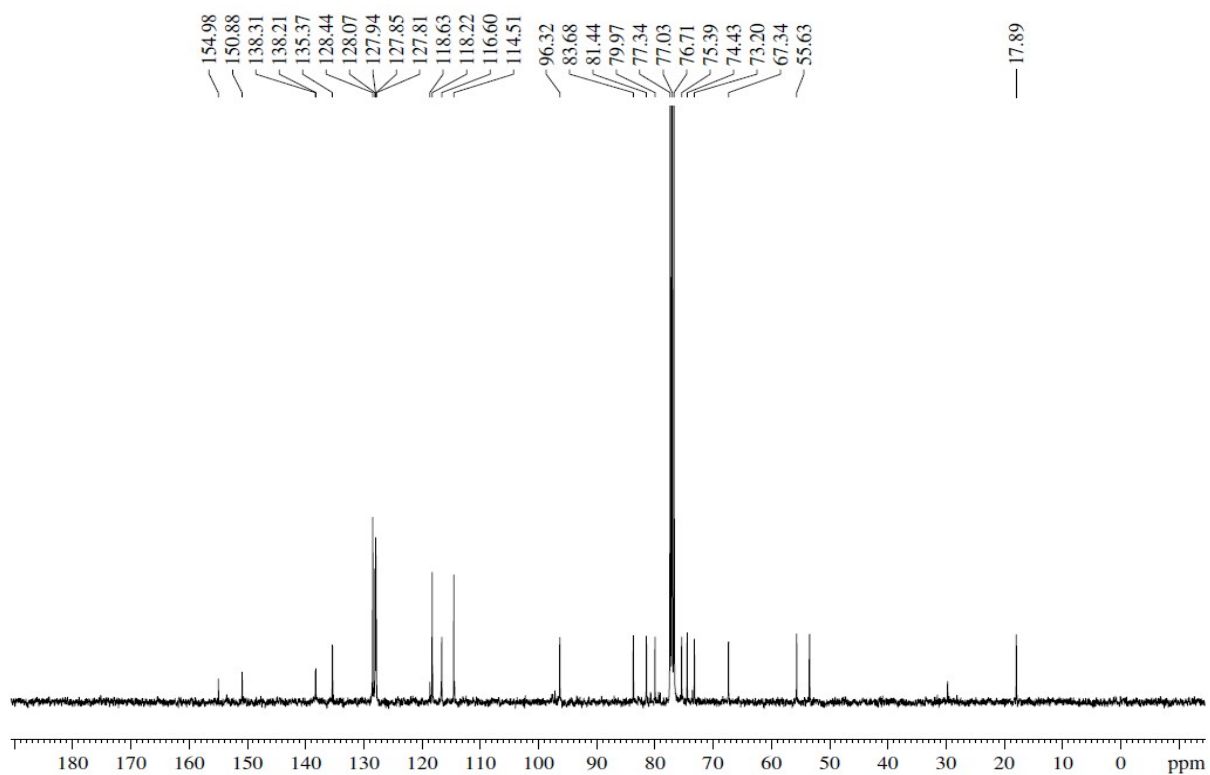
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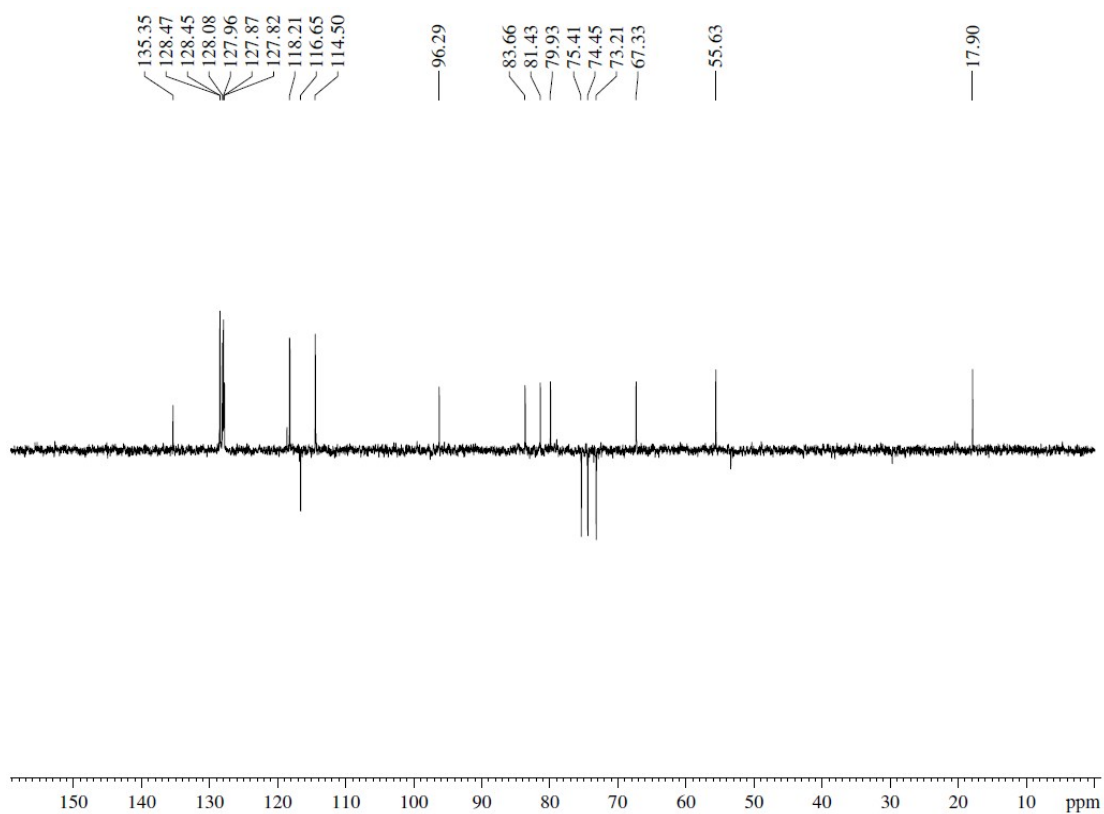
**Figure 15:**  $^{13}\text{CDEPT-135}^\circ$  spectrum of compound **5** (100 MHz,  $\text{CDCl}_3$ , 300 K)



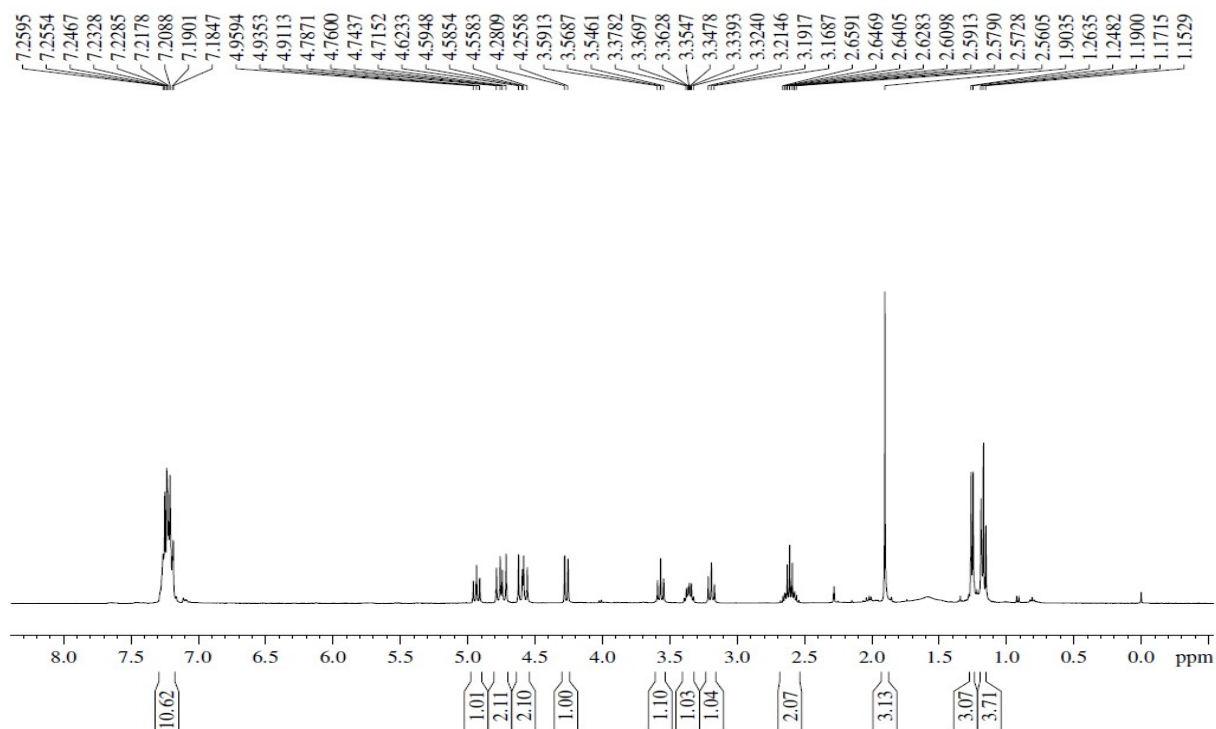
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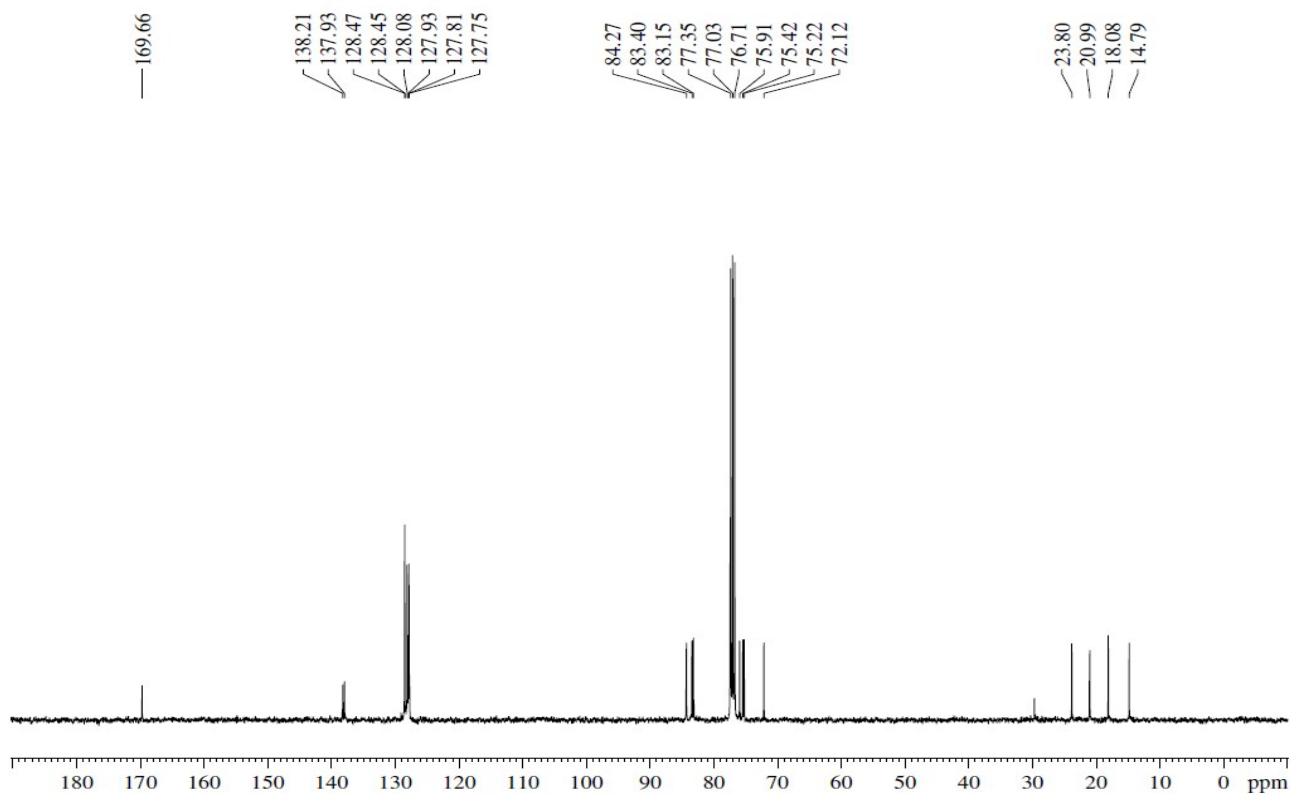
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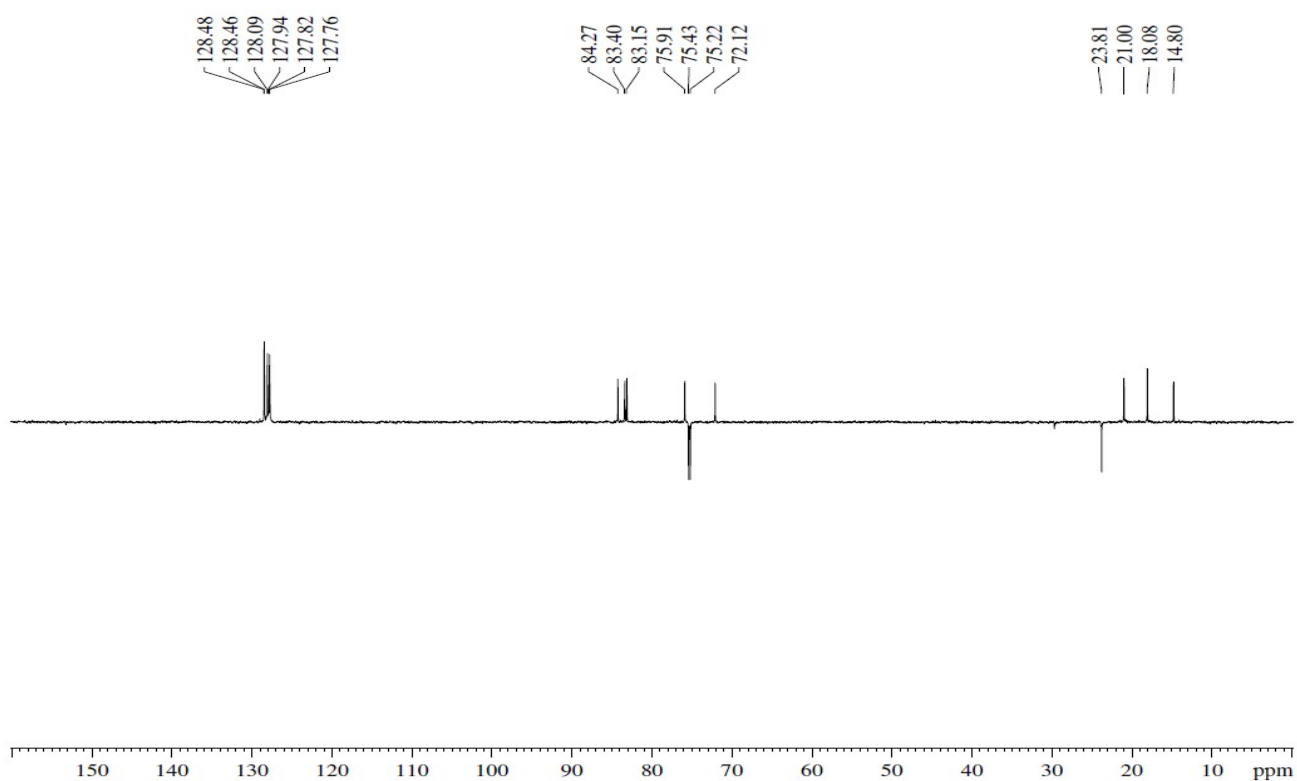
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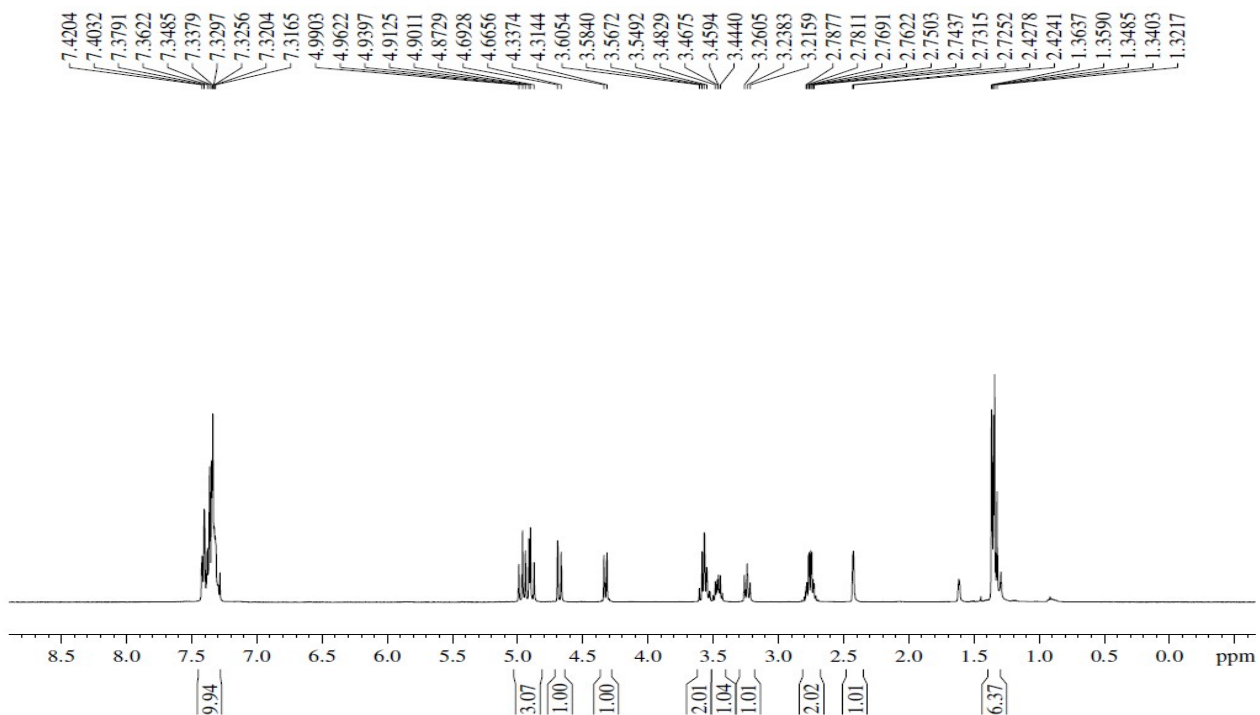
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**Figure 20:**  $^{13}\text{C}$  spectrum of compound **10** (100 MHz,  $\text{CDCl}_3$ , 300 K)

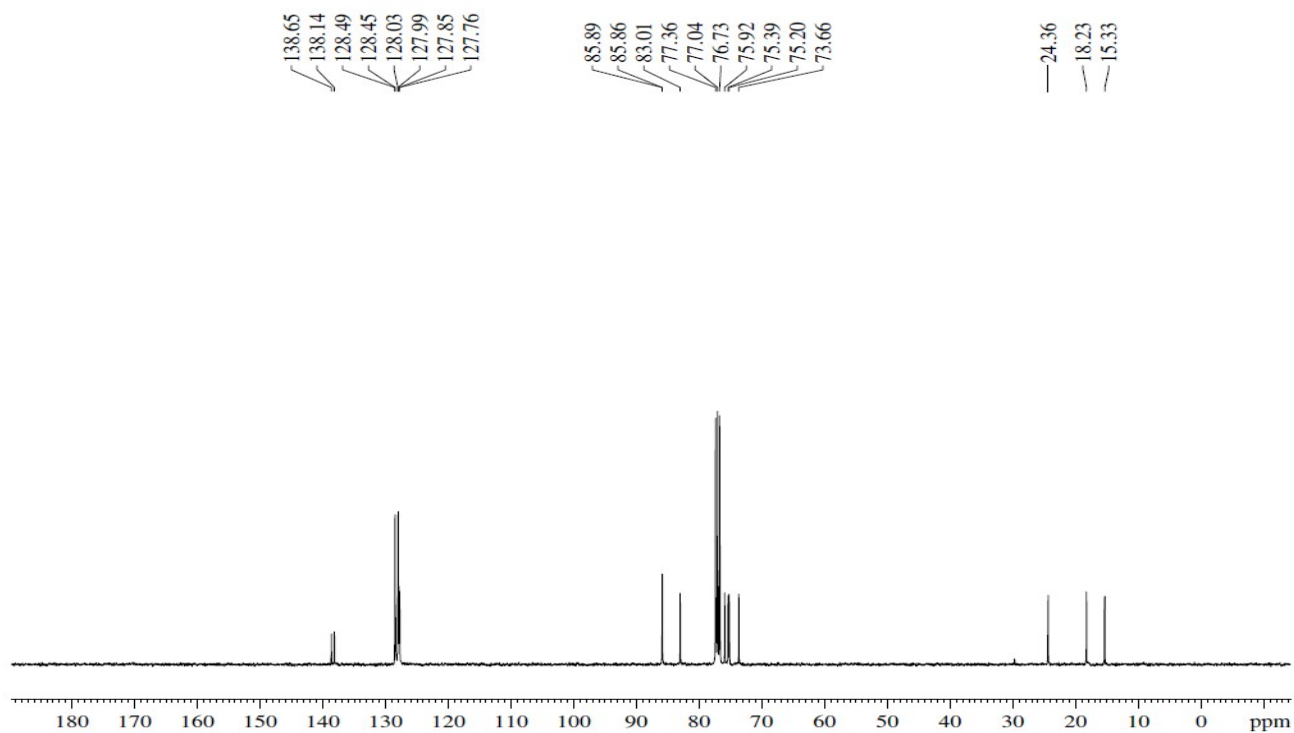


**Figure21:**  $^{13}\text{CDEPT-135}^\circ$  Spectrum of compound **10** (100 MHz,  $\text{CDCl}_3$ , 300 K)

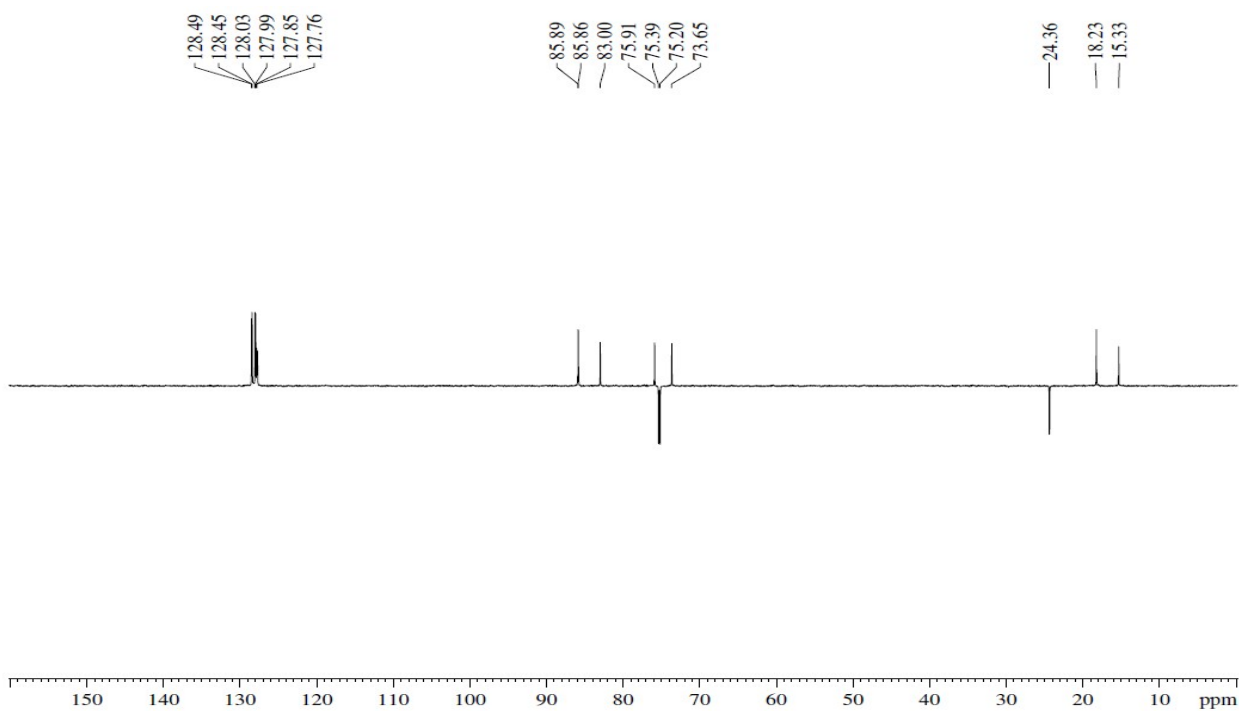


**Figure22:**  $^1\text{H}$  spectrum of compound **11** (400 MHz,  $\text{CDCl}_3$ , 300 K)

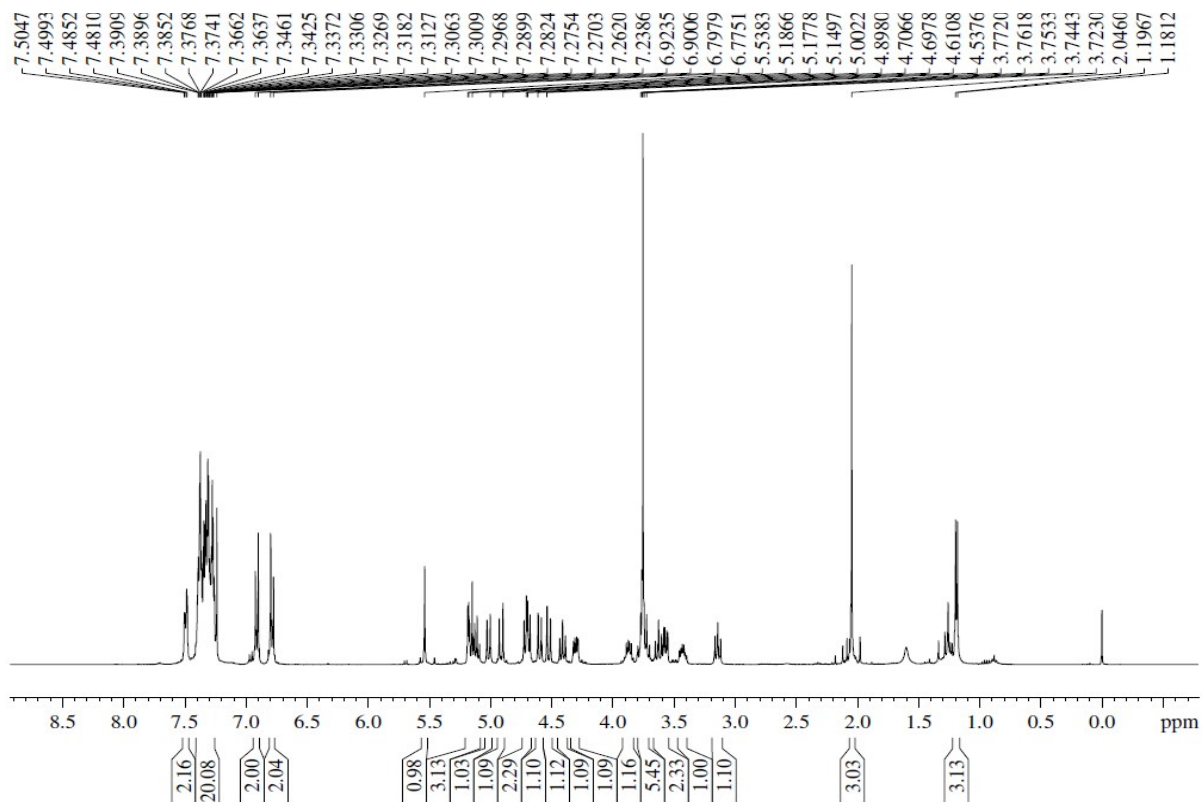




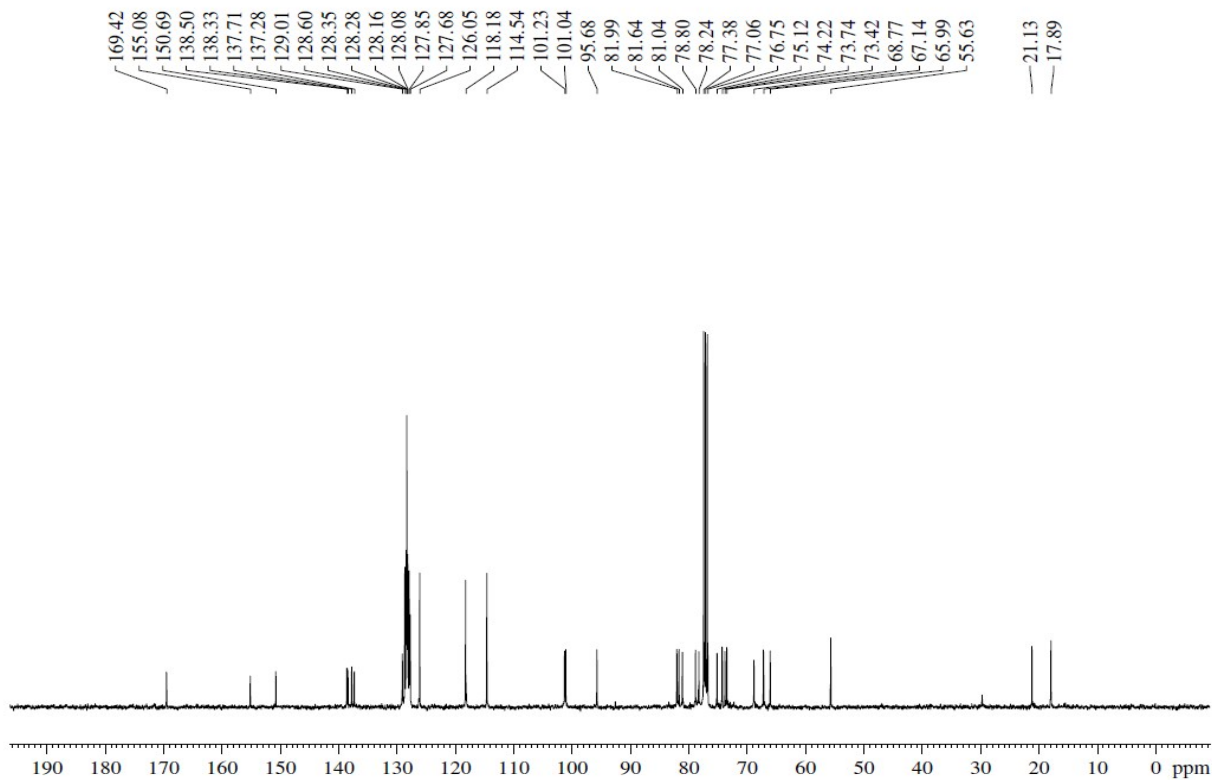
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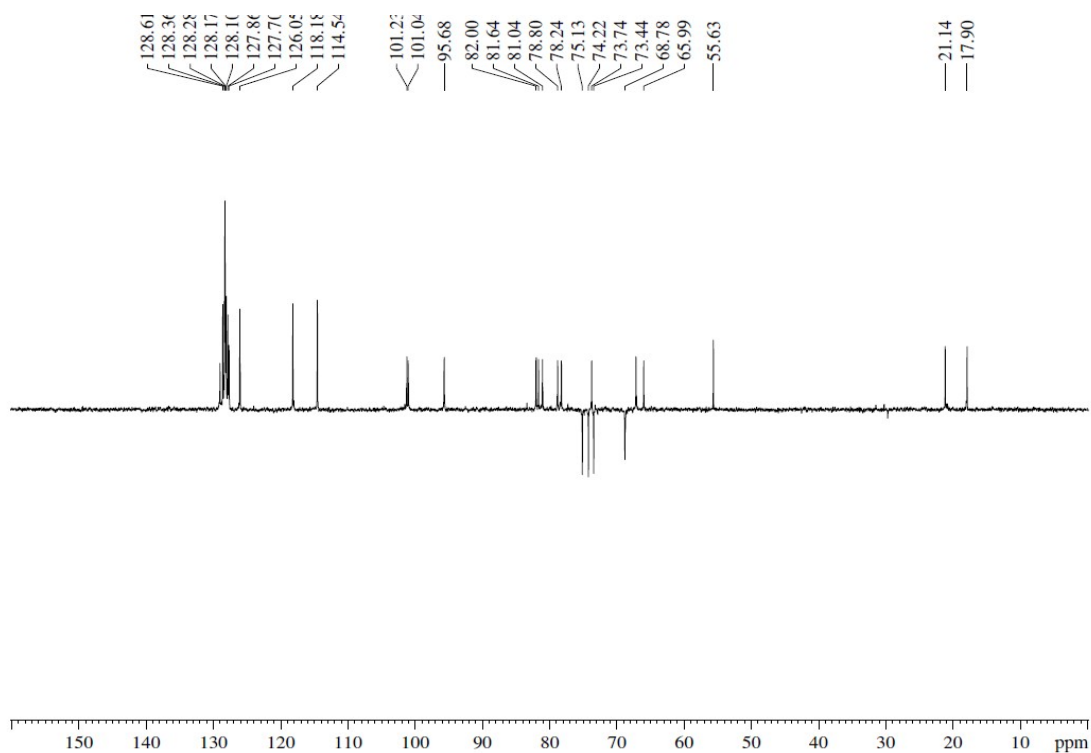
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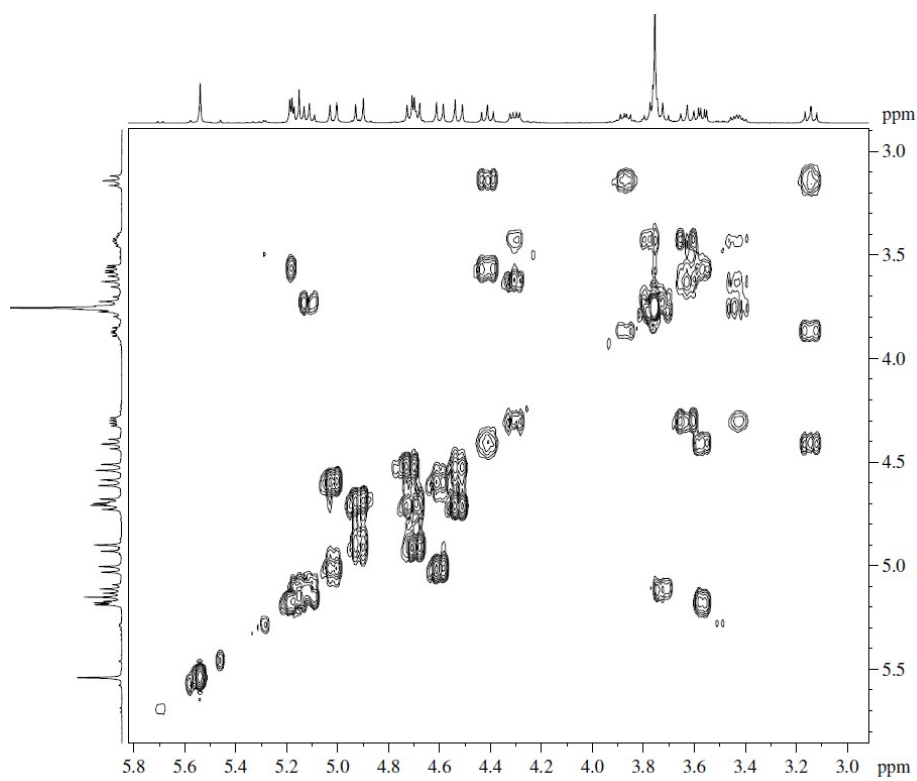
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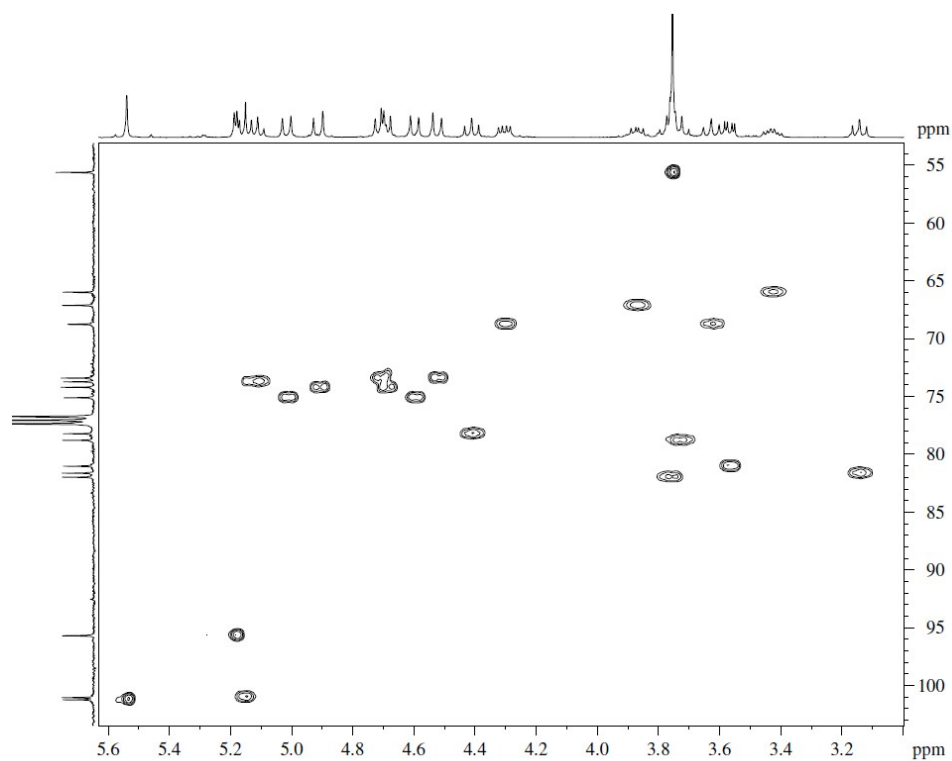
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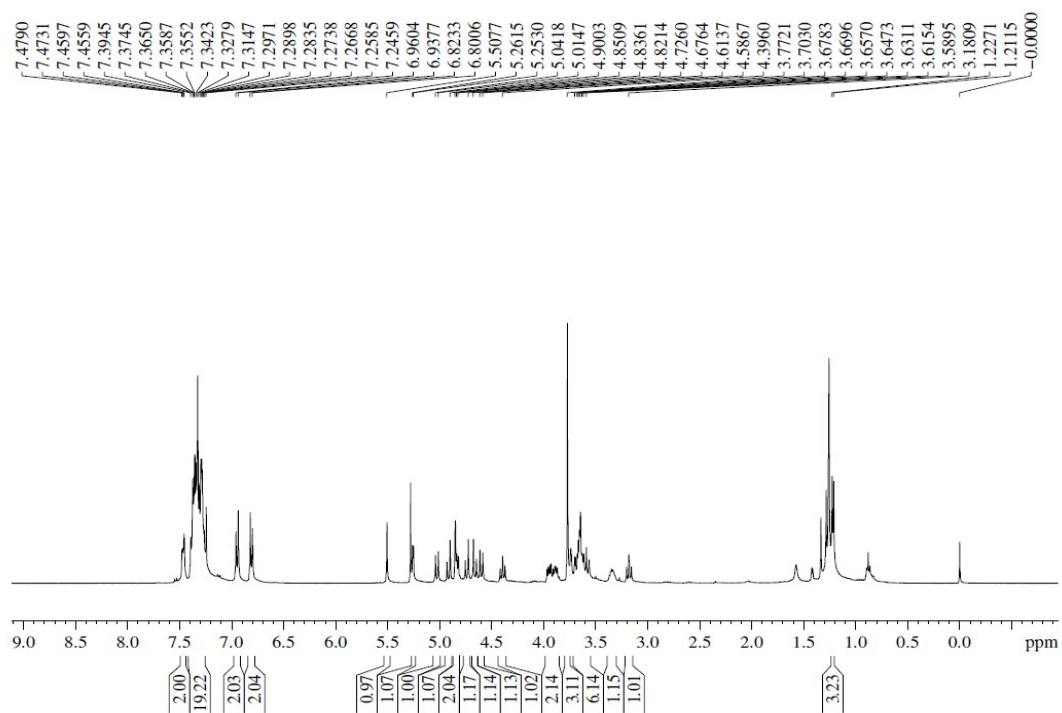
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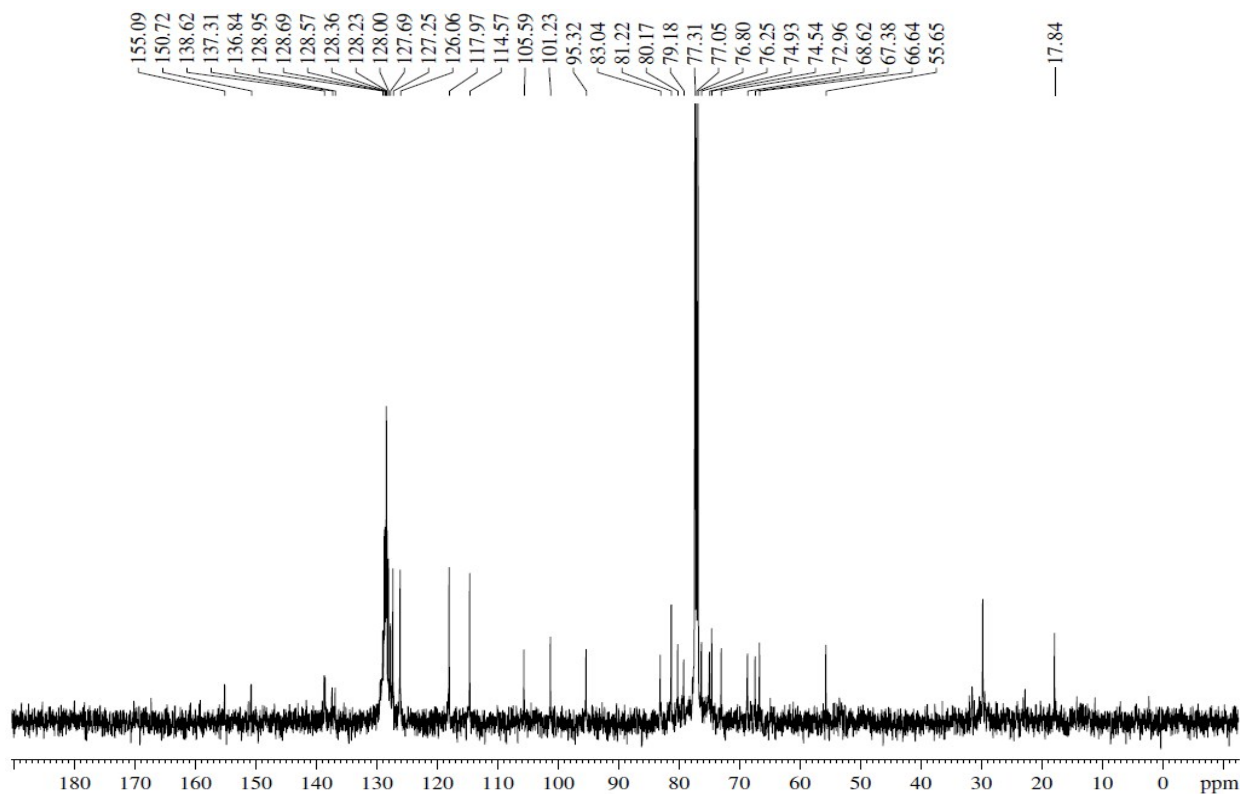
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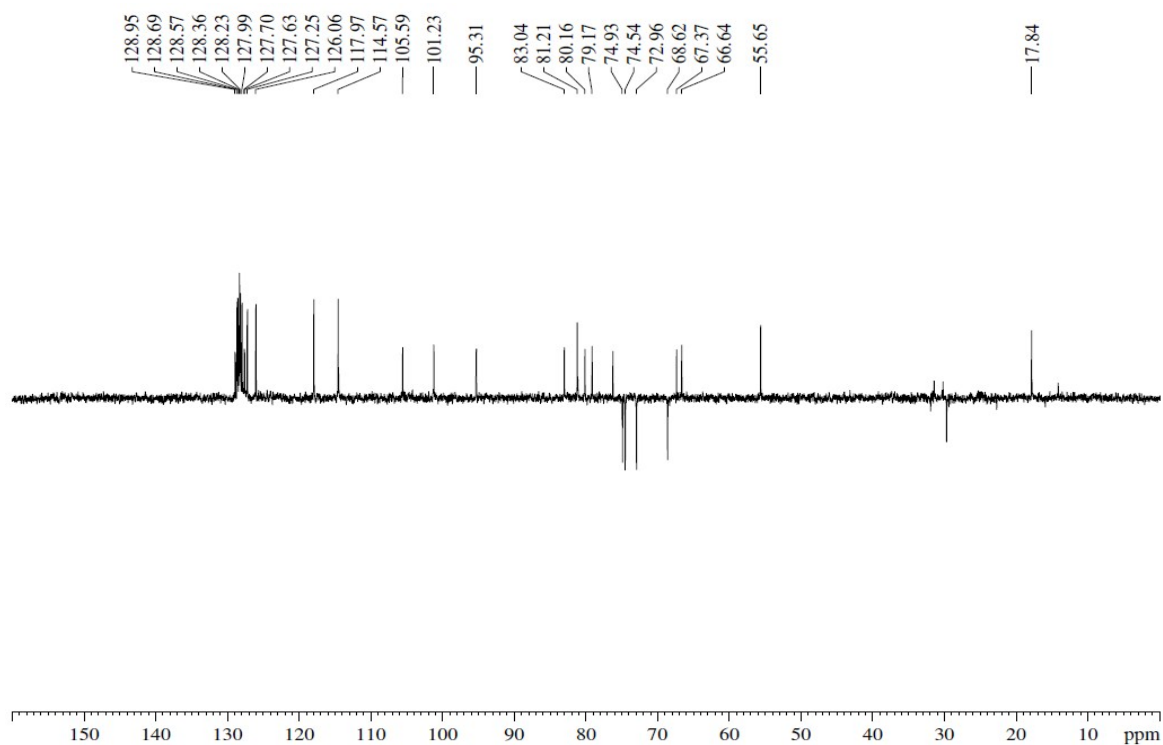
**Figure 29:** 2D- HSQC spectrum (selected regions) of compound **12** (400 MHz, CDCl<sub>3</sub>, 300 K)



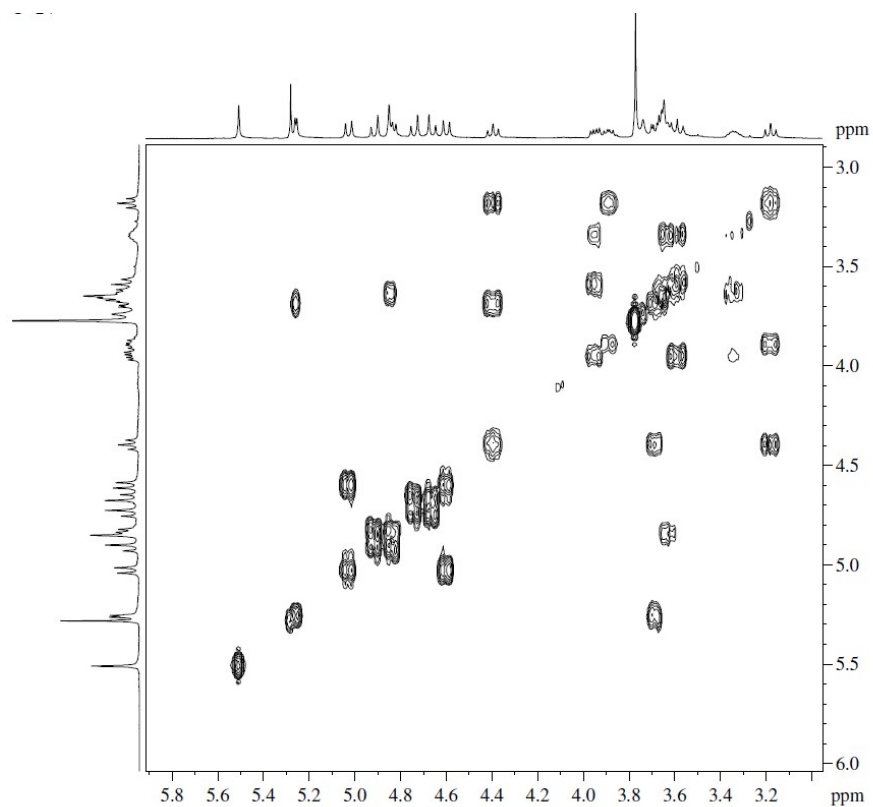
**Figure30:** <sup>1</sup>H spectrum of compound **13** (400 MHz, CDCl<sub>3</sub>, 300 K)



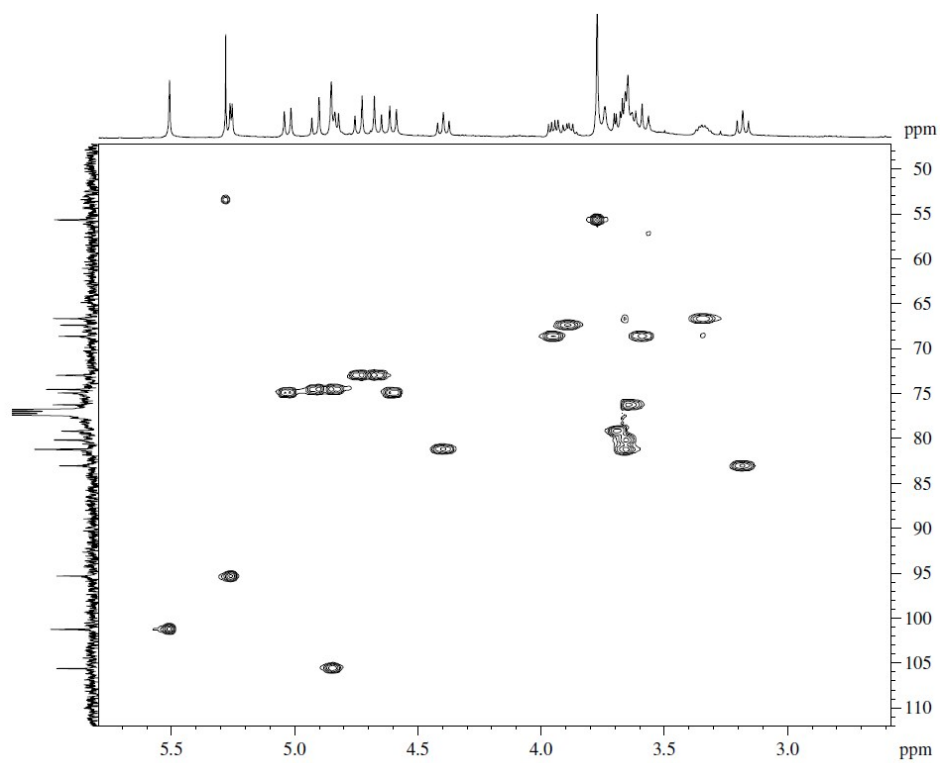
**Figure 31:**  $^{13}\text{C}$  Spectrum of compound **13** (100 MHz,  $\text{CDCl}_3$ , 300 K)



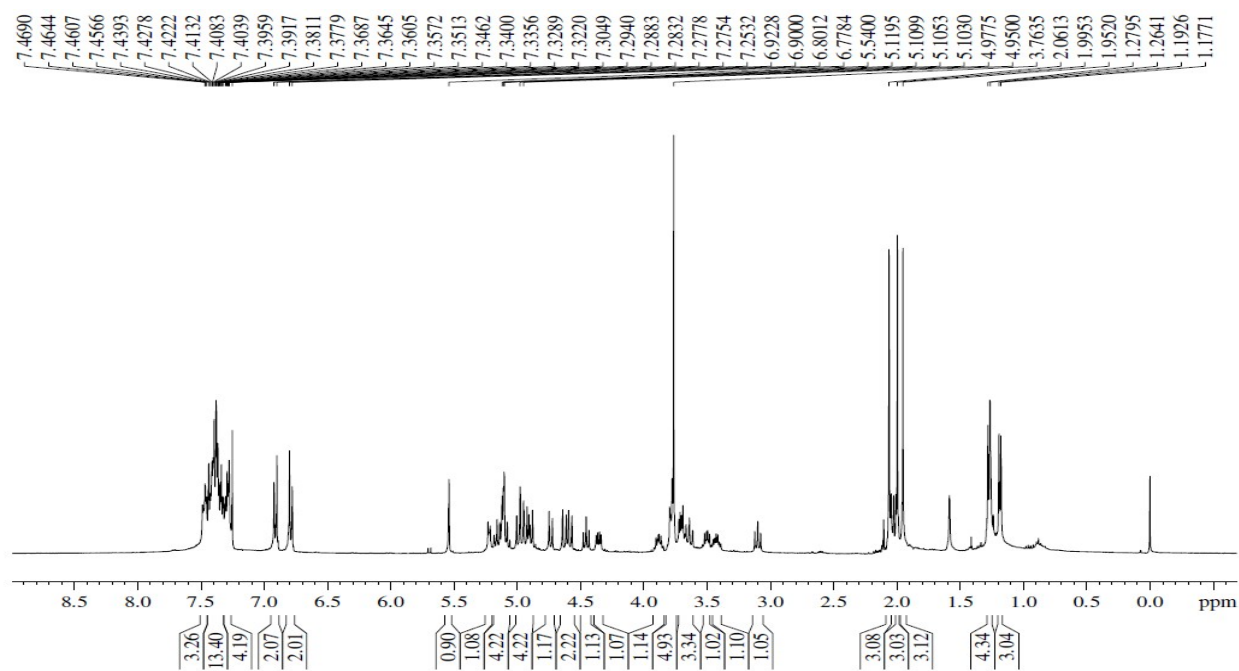
**Figure 32:**  $^{13}\text{C}$  DEPT-135° spectrum of compound **13** (100 MHz,  $\text{CDCl}_3$ , 300 K)



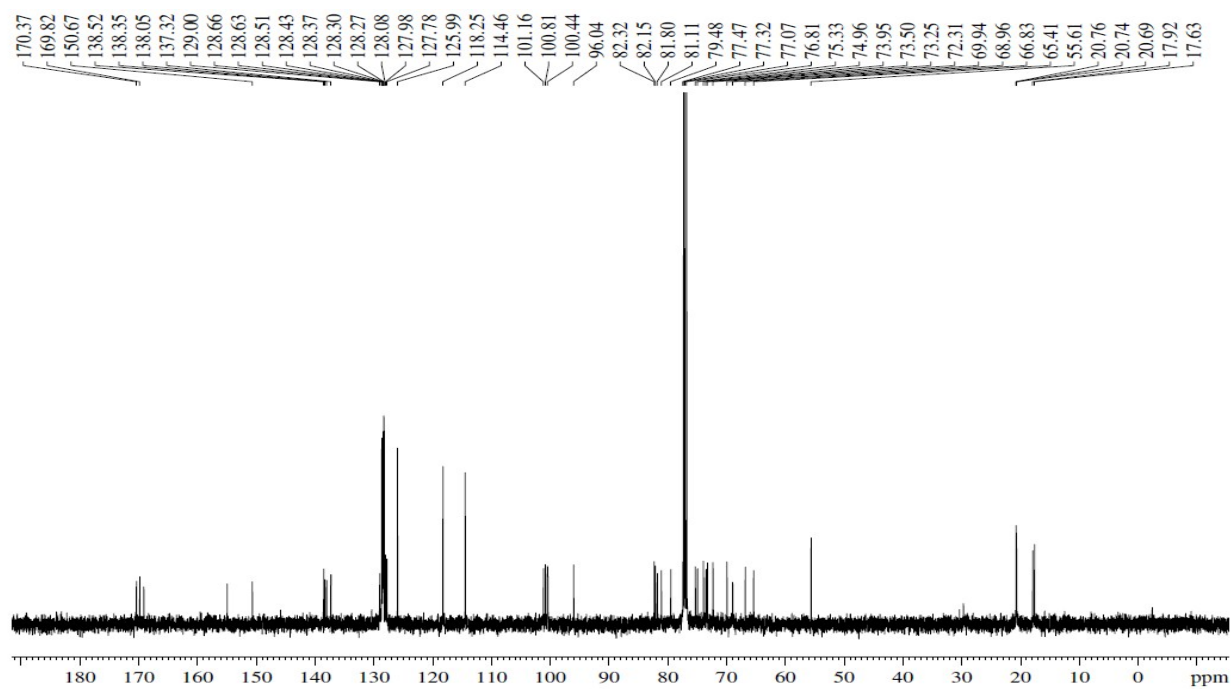
**Figure 33:** 2D-COSY spectrum (selected regions) of compound **13** (400 MHz, CDCl<sub>3</sub>, 300 K)



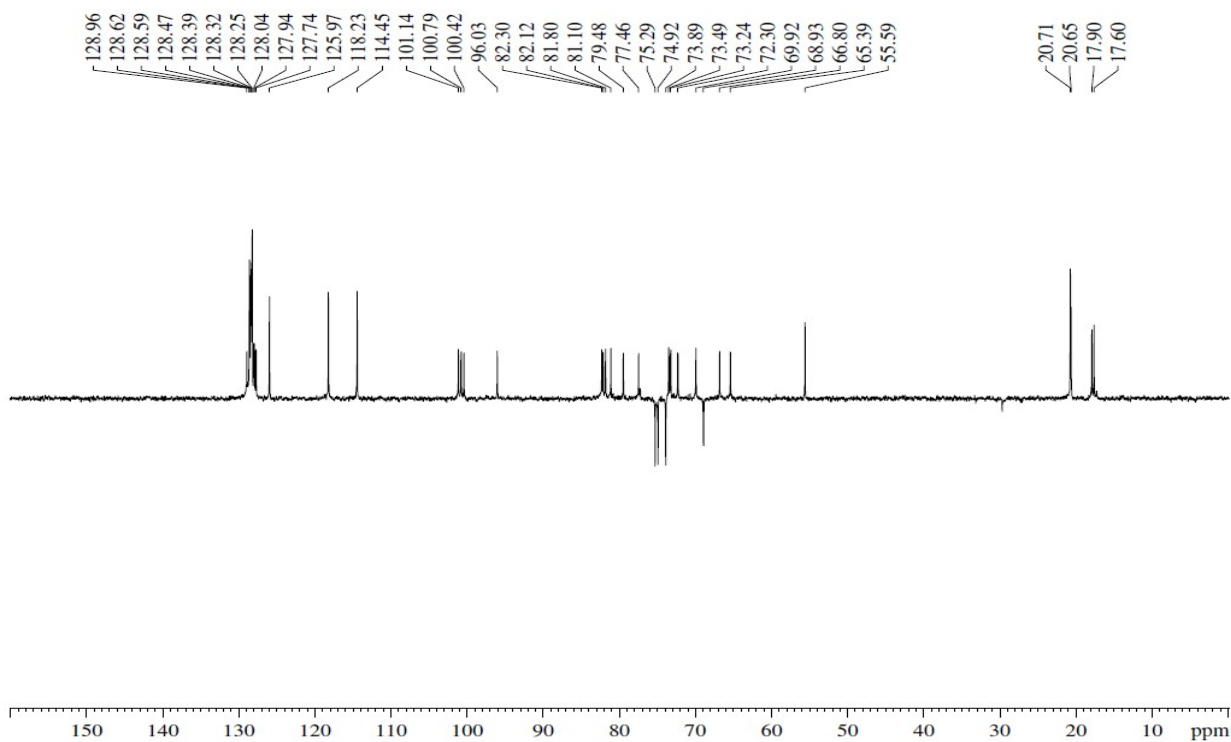
**Figure 34:** 2D- HSQC spectrum (selected regions) of compound **13** (400 MHz, CDCl<sub>3</sub>, 300 K)



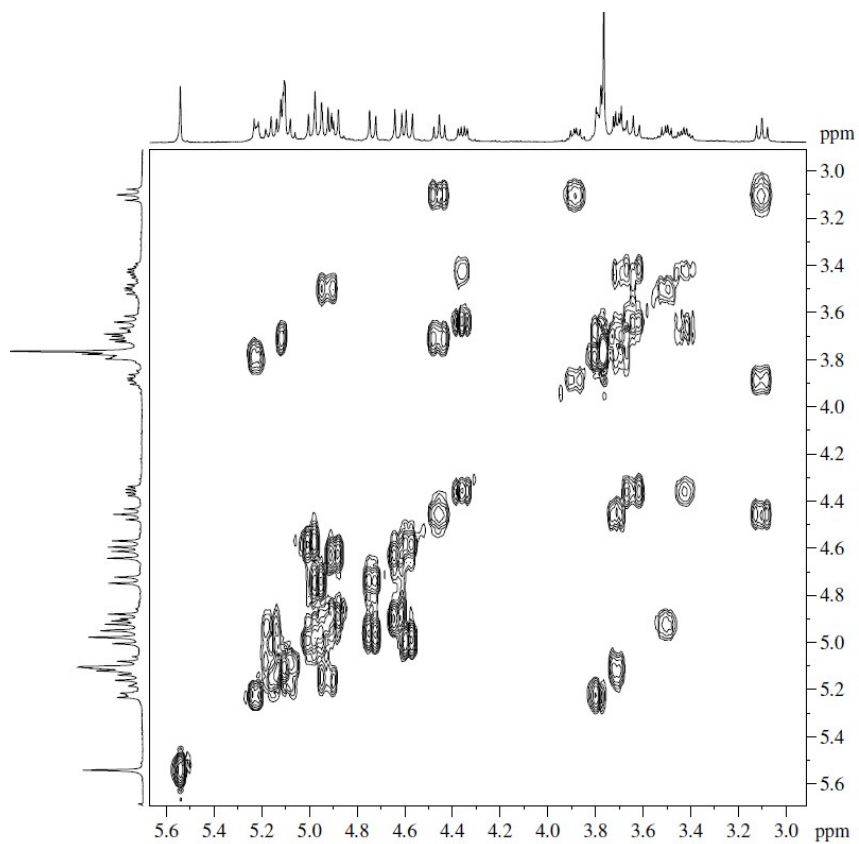
**Figure 35:**  $^1\text{H}$  spectrum of compound **14** (400 MHz,  $\text{CDCl}_3$ , 300 K)



**Figure 36:**  $^{13}\text{C}$  spectrum of compound **14** (100 MHz,  $\text{CDCl}_3$ , 300 K)

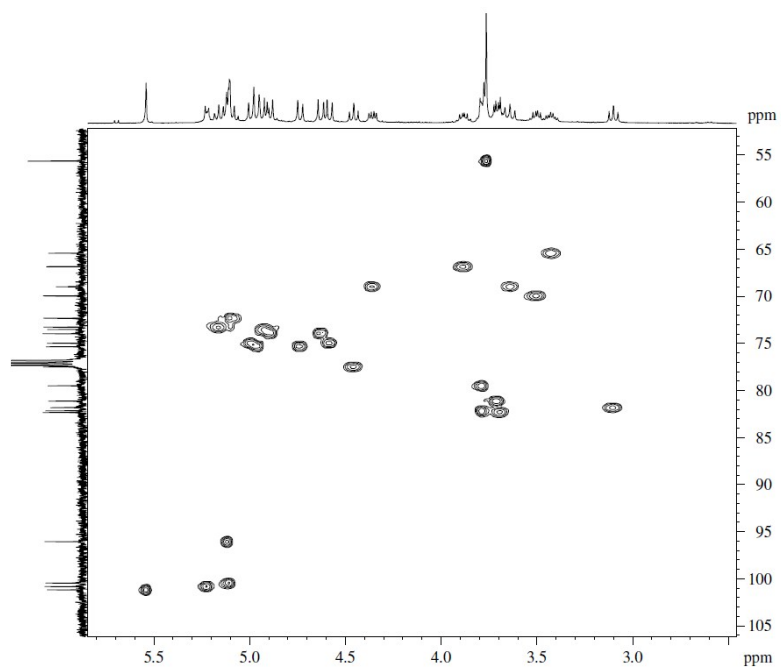


**Figure 37:**  $^{13}\text{CDEPT-135}^\circ$  Spectrum of compound **14** (100 MHz,  $\text{CDCl}_3$ , 300 K)

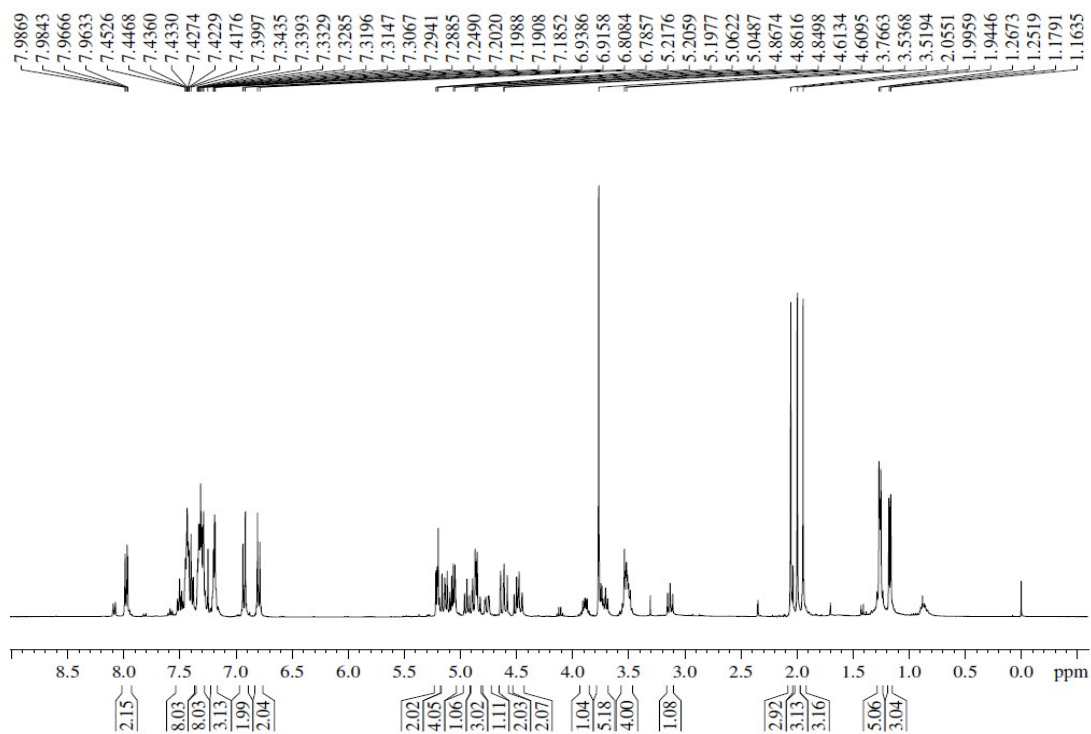


**Figure 38:** 2D- HSQC spectrum (selected regions) of compound **14** (400 MHz,  $\text{CDCl}_3$ , 300 K)

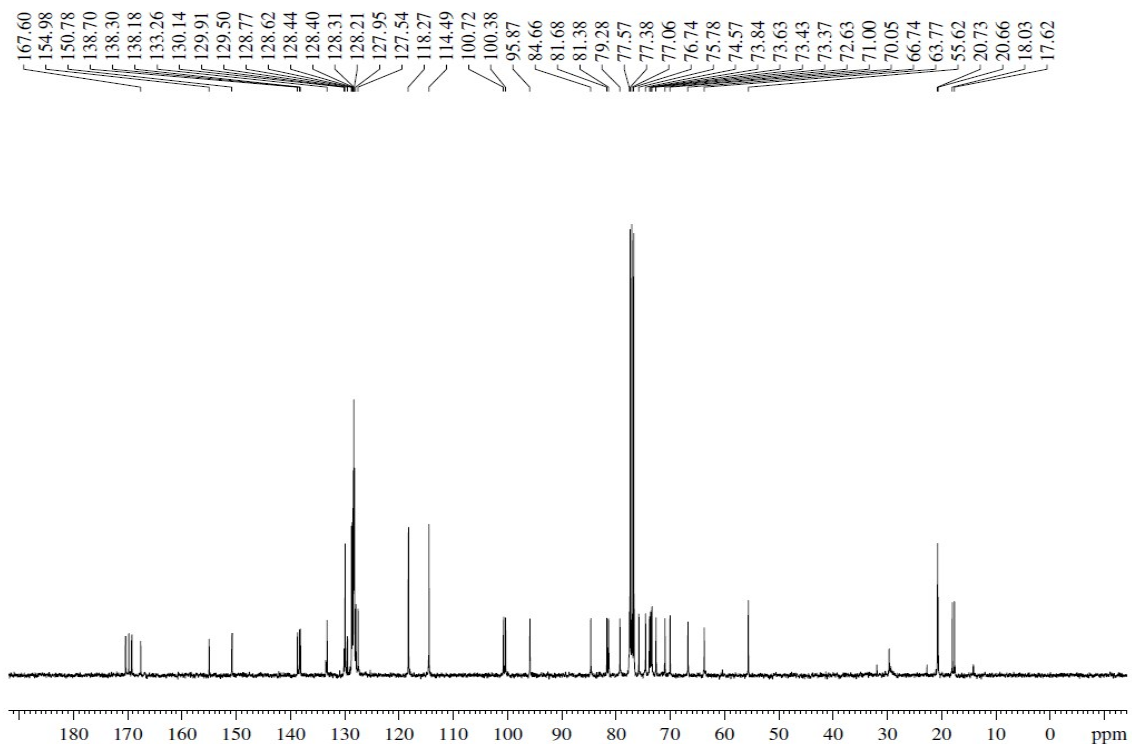




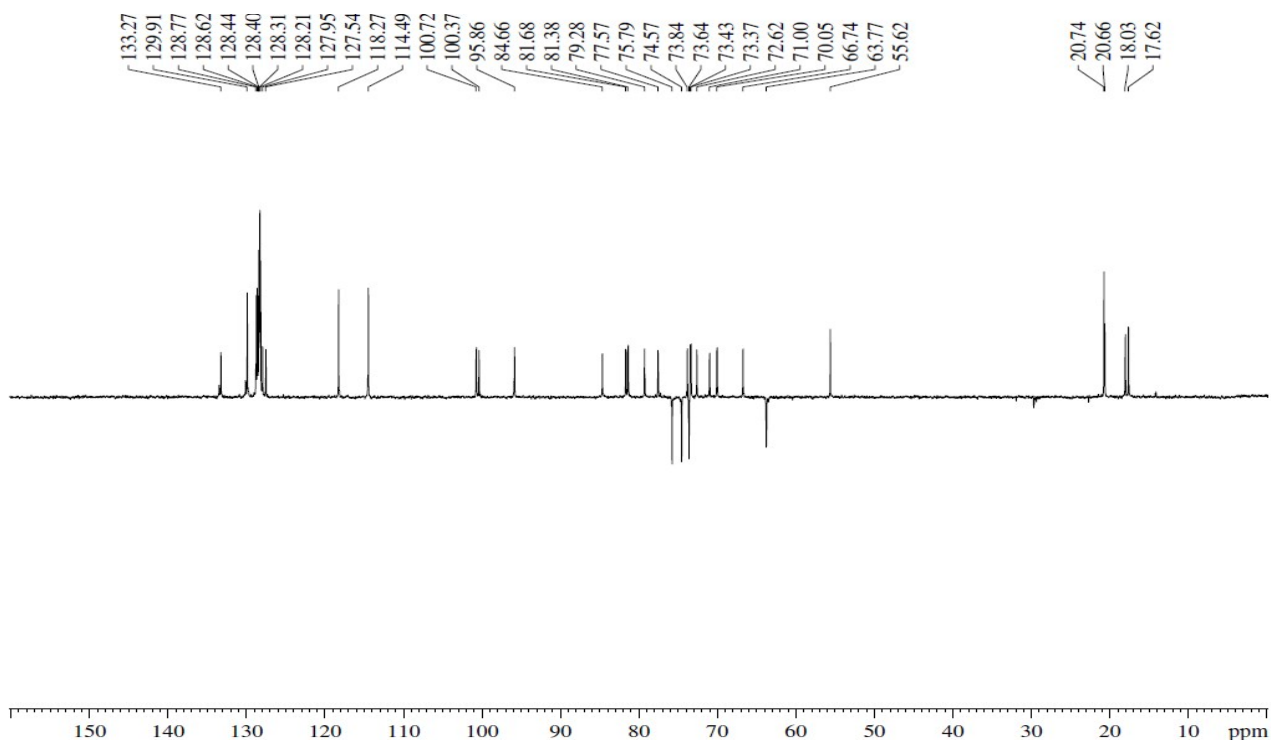
**Figure 39:** 2D-HSQC spectrum (selected regions) of compound **14** (400 MHz, CDCl<sub>3</sub>, 300 K)



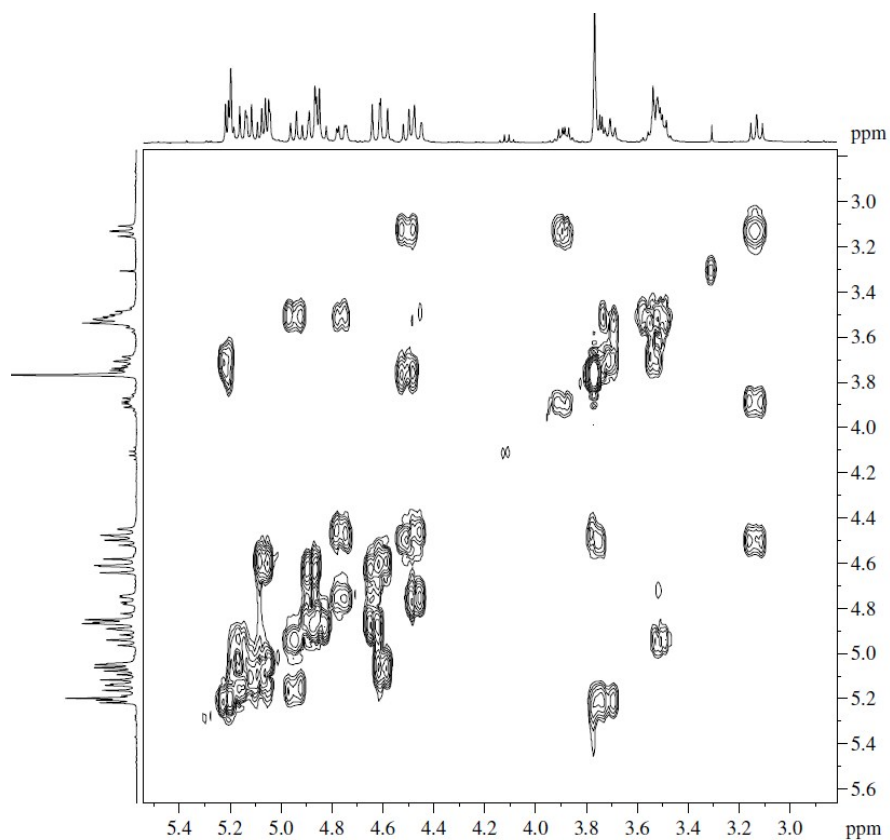
**Figure 40:** <sup>1</sup>H spectrum of compound **15** (400 MHz, CDCl<sub>3</sub>, 300 K)



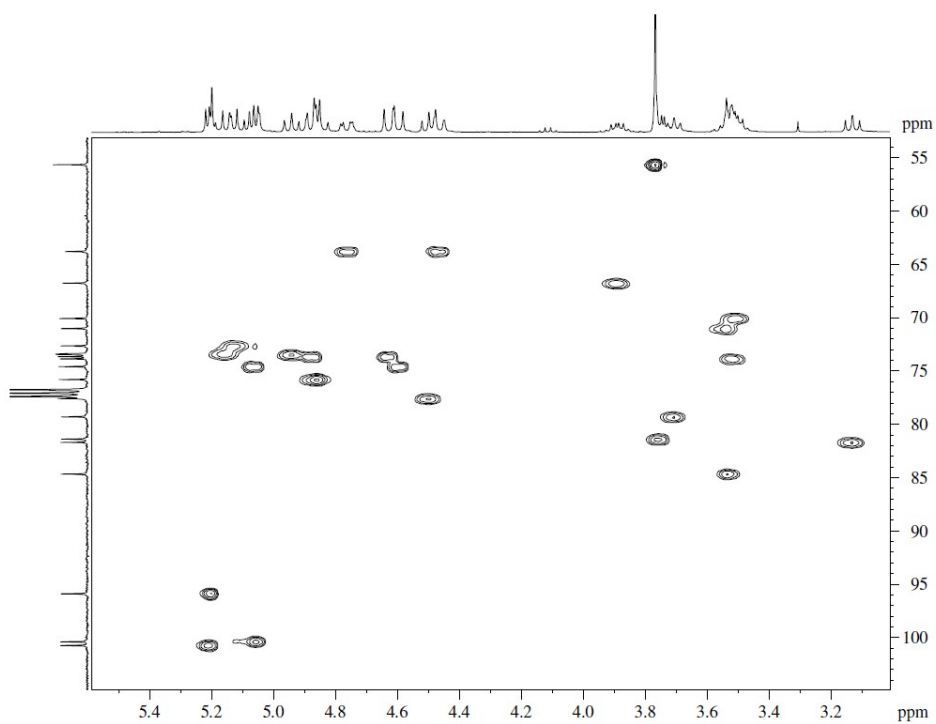
**Figure 41:**  $^{13}\text{C}$  Spectrum of compound **15** (100 MHz,  $\text{CDCl}_3$ , 300 K)



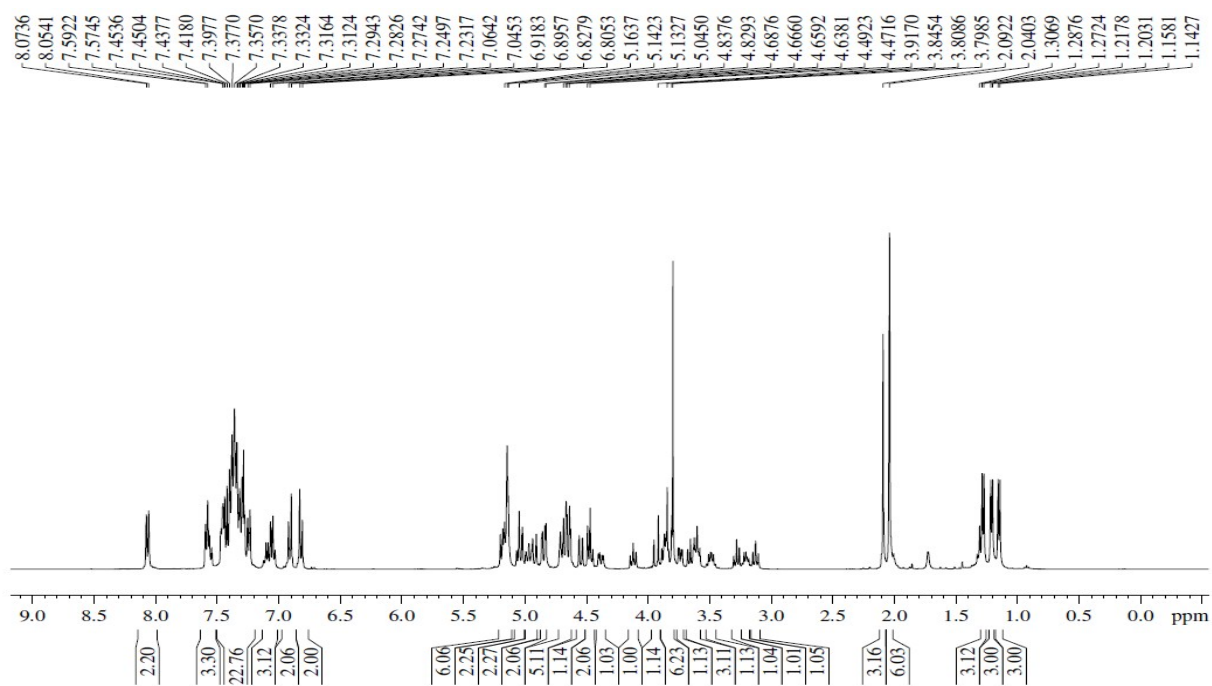
**Figure 42:**  $^{13}\text{C}$  DEPT-135 Spectrum of compound **15** (100 MHz,  $\text{CDCl}_3$ , 300 K)



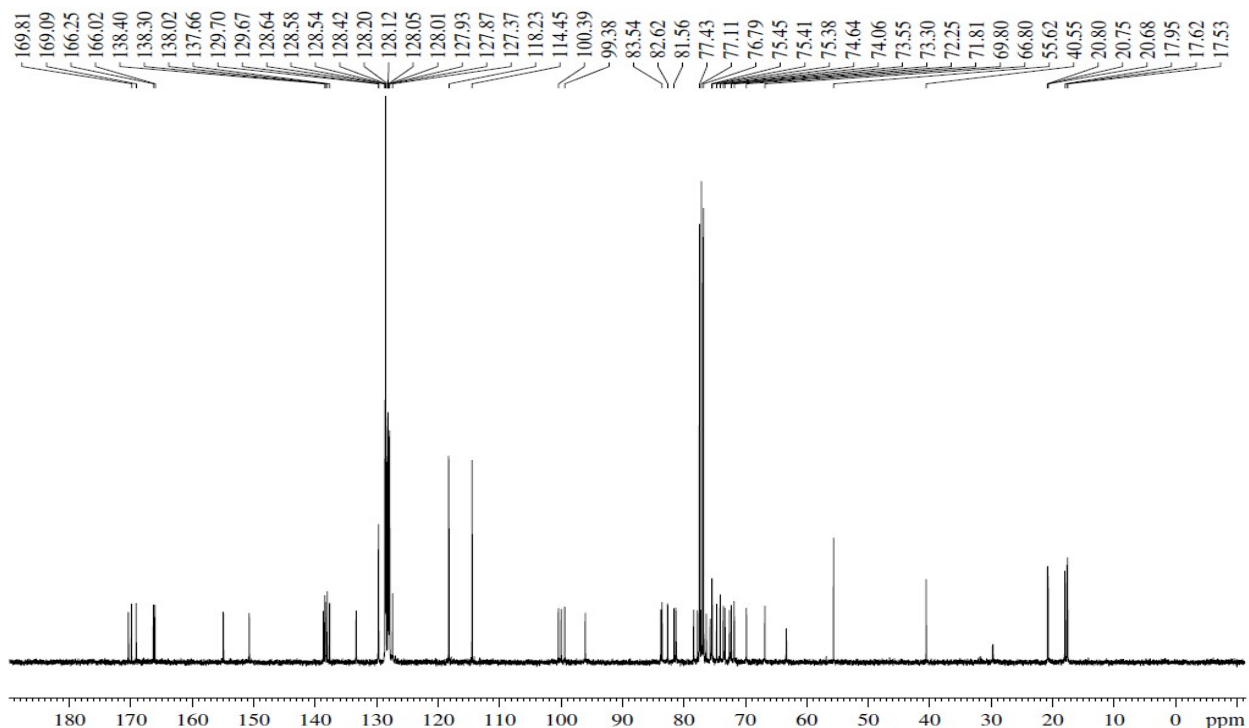
**Figure 43:** 2D- COSY spectrum (selected regions) of compound **15** (400 MHz, CDCl<sub>3</sub>, 300 K)



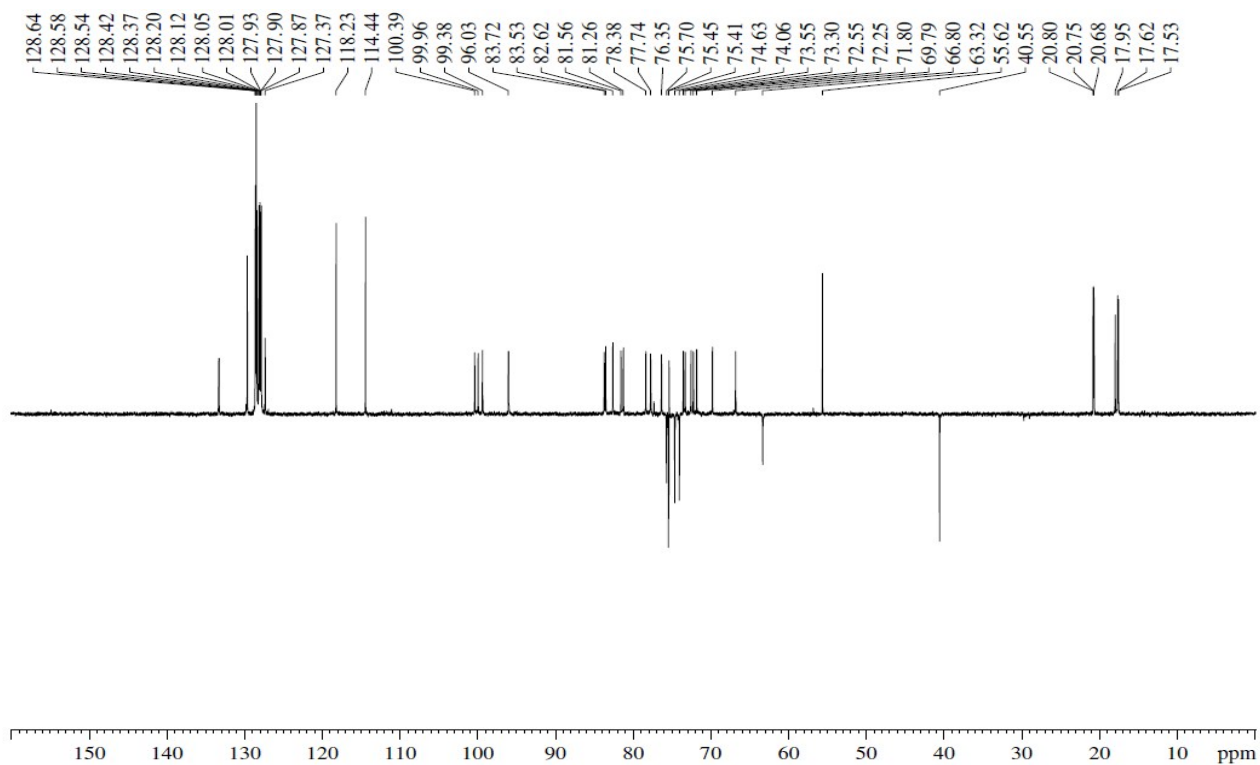
**Figure44:** 2D- HSQC spectrum (selected regions) of compound **15** (400 MHz, CDCl<sub>3</sub>, 300 K)



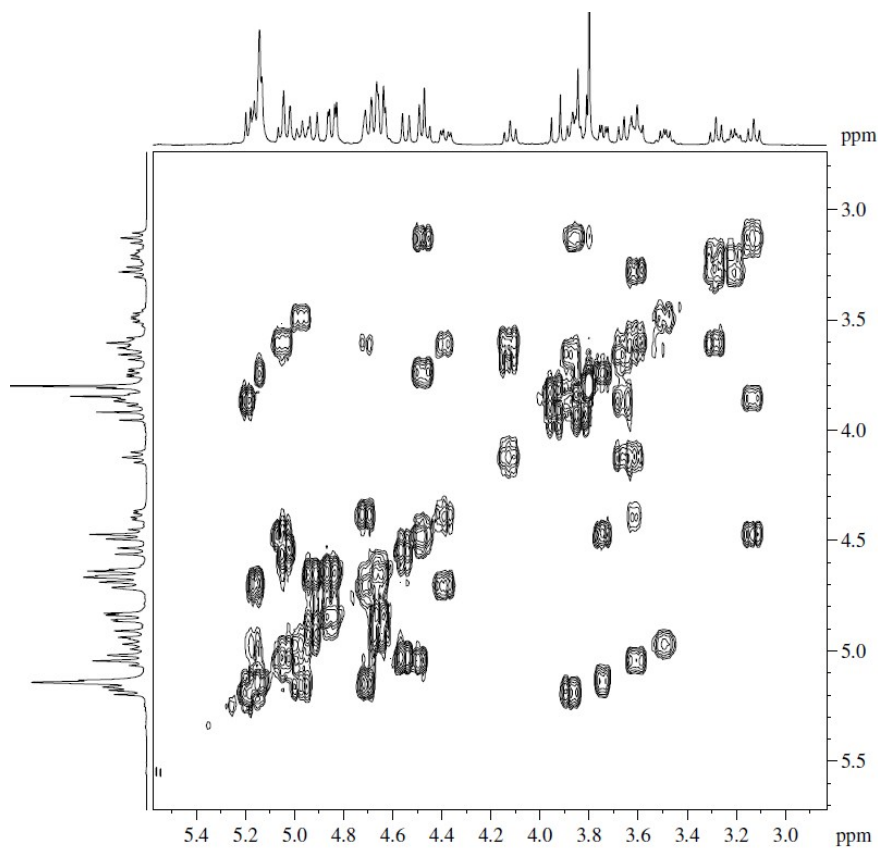
**Figure 45:**  $^1\text{H}$  spectrum of compound **16** (400 MHz,  $\text{CDCl}_3$ , 300 K)



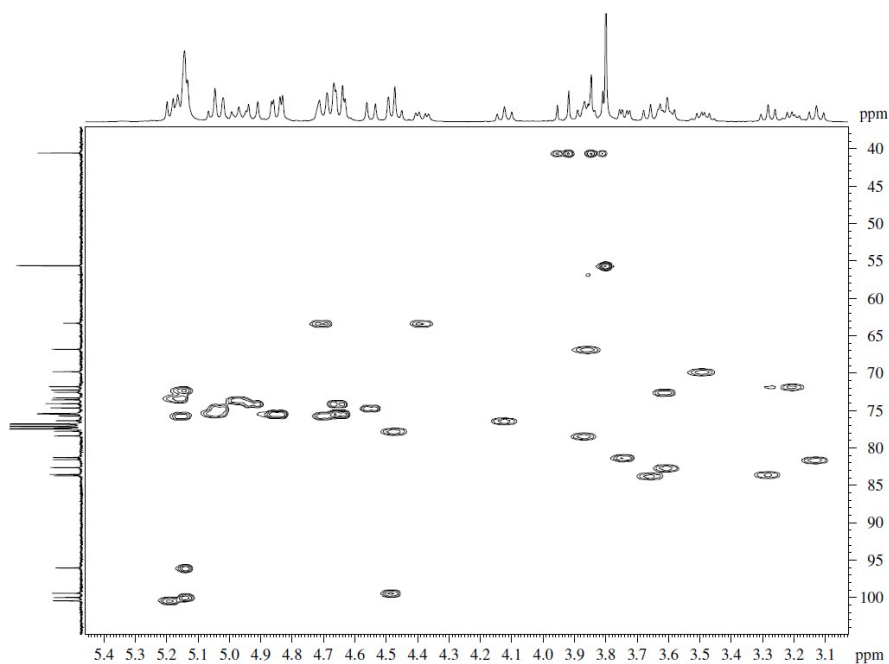
**Figure 46:**  $^{13}\text{C}$  spectrum of compound **16** (100 MHz,  $\text{CDCl}_3$ , 300 K)



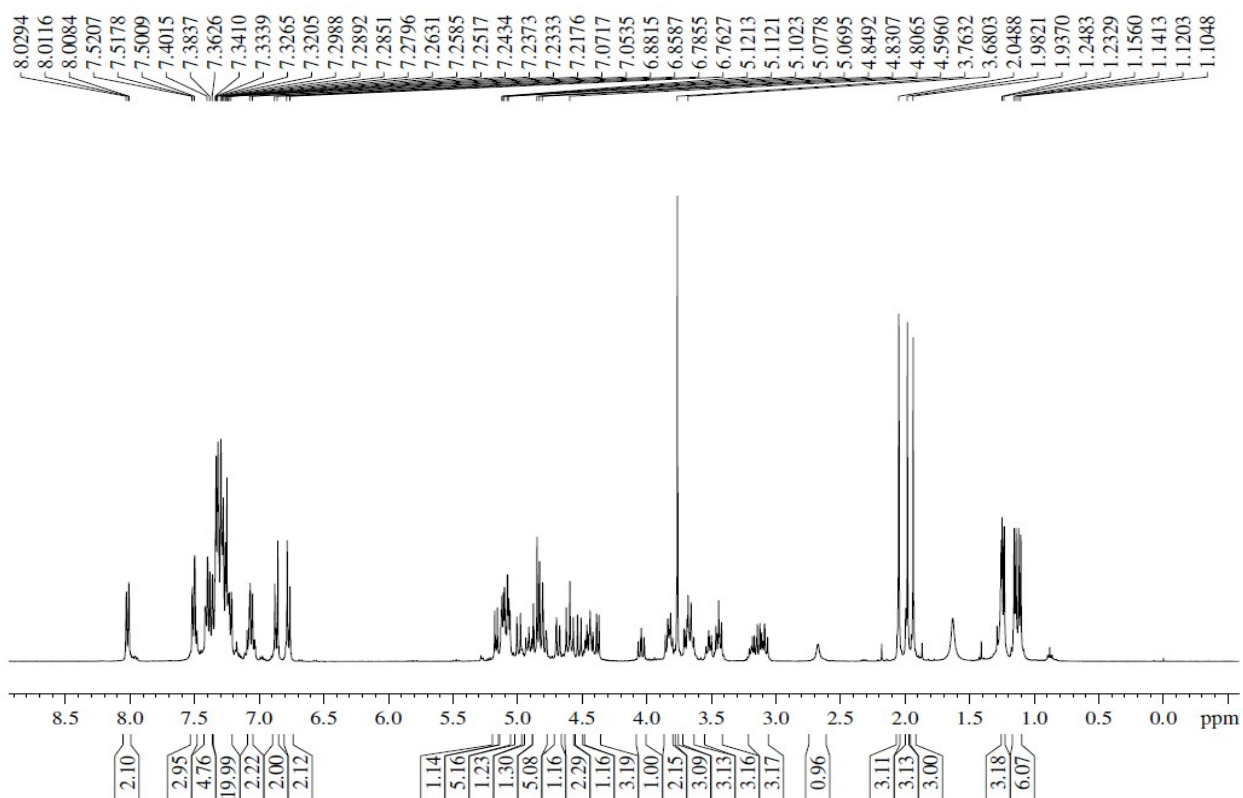
**Figure 47:**  $^{13}\text{CDEPT-135}^\circ$  Spectrum of compound **16** (100 MHz,  $\text{CDCl}_3$ , 300 K)



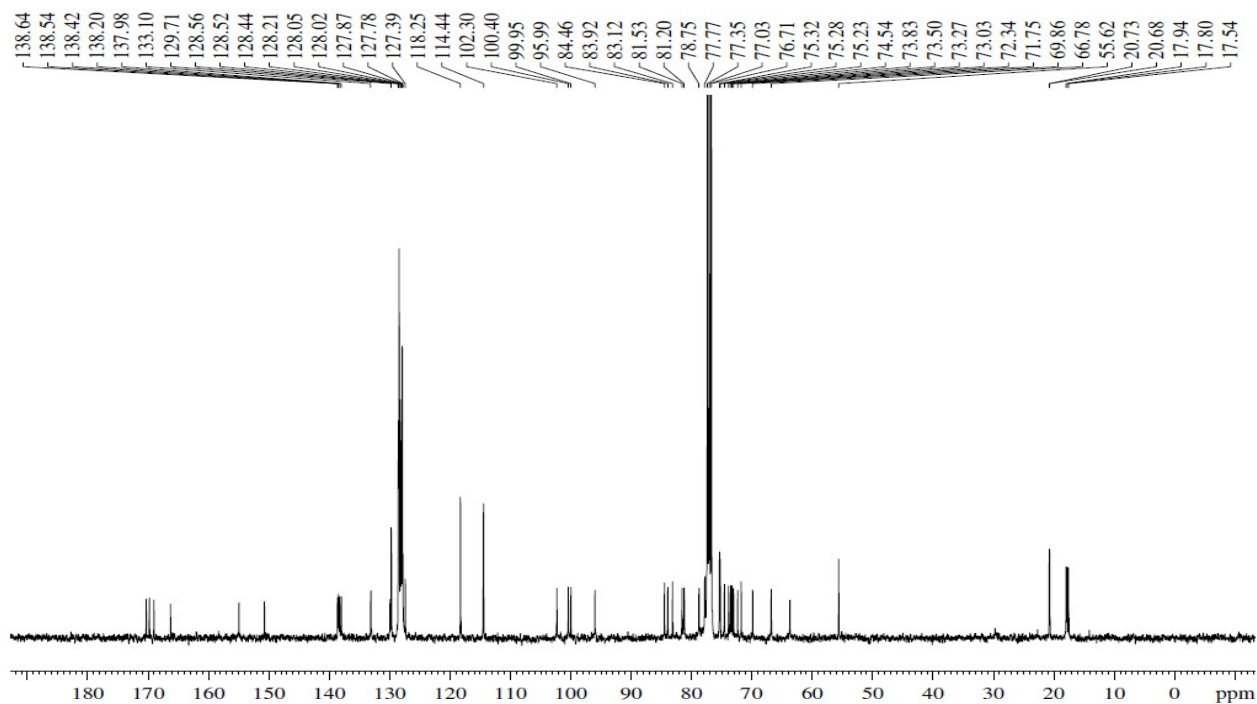
**Figure48:** 2D- COSY spectrum (selected regions) of compound **16** (400 MHz,  $\text{CDCl}_3$ , 300 K)



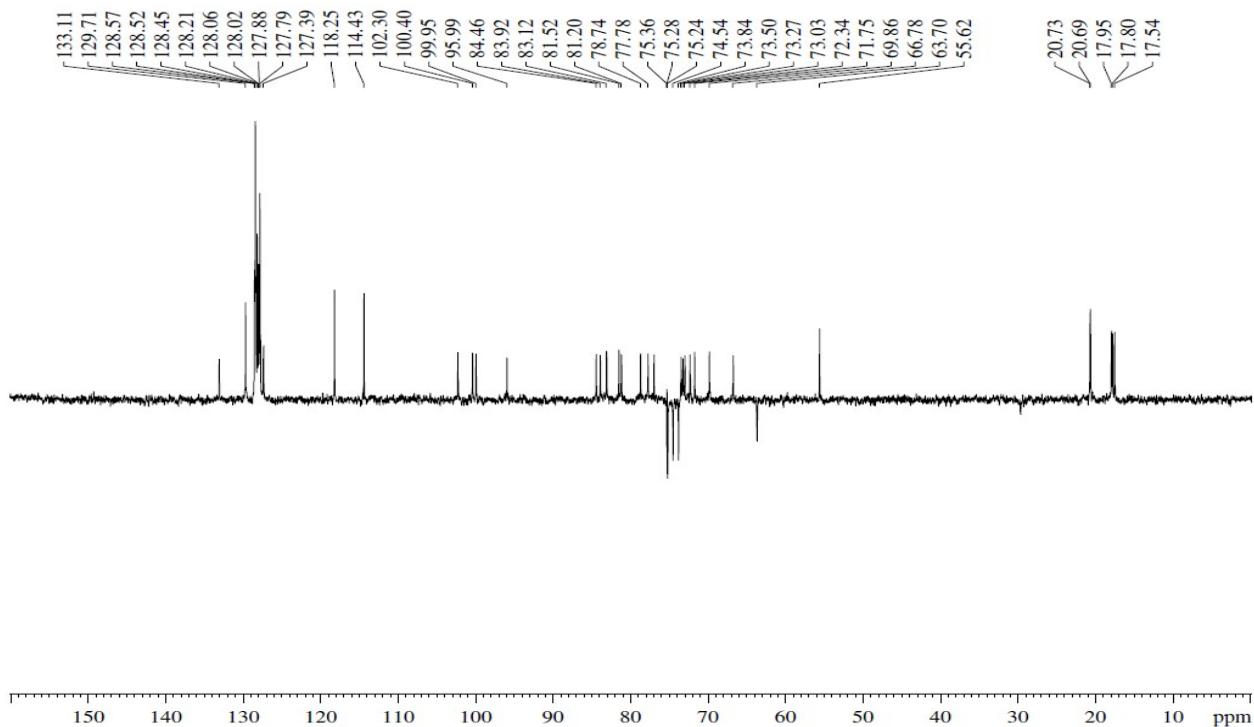
**Figure49:** 2D- HSQC spectrum (selected regions) of compound **16** (400 MHz, CDCl<sub>3</sub>, 300 K)



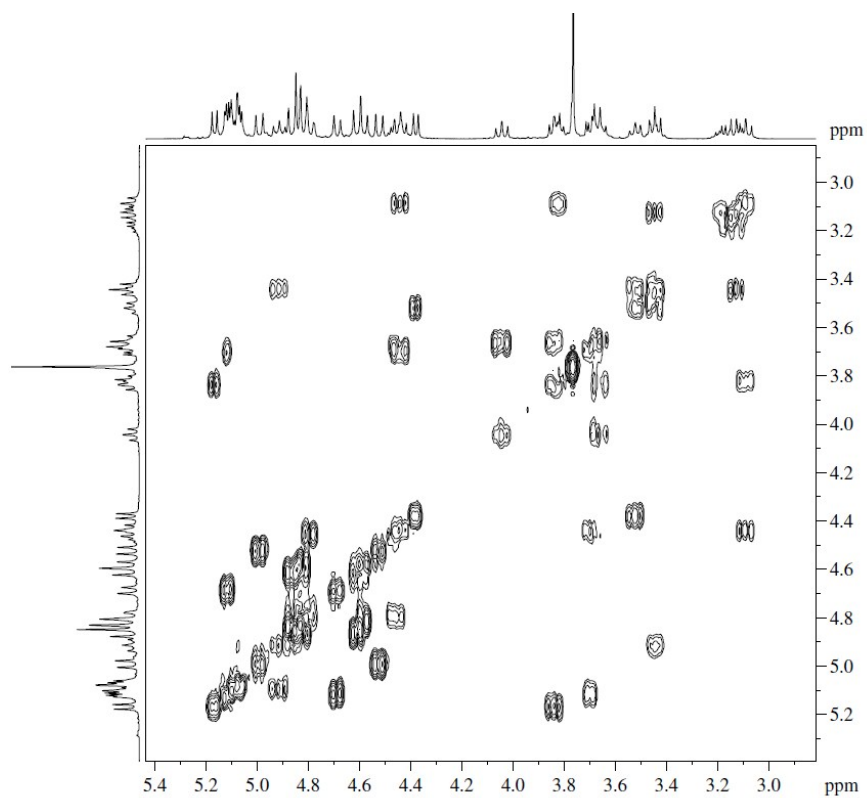
**Figure50:** <sup>1</sup>H spectrum of compound **17** (400 MHz, CDCl<sub>3</sub>, 300 K)



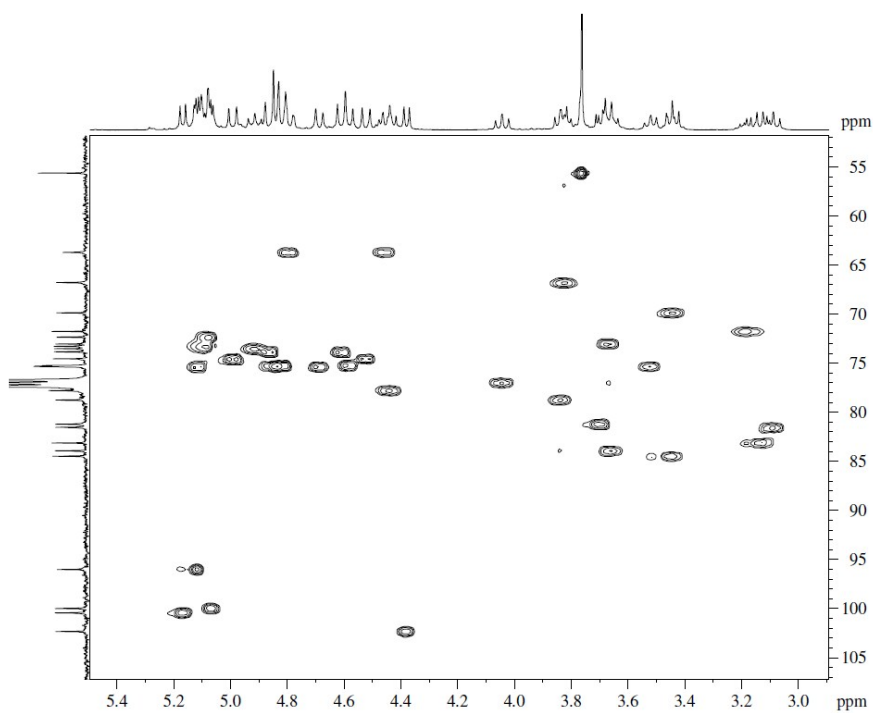
**Figure 51:**  $^{13}\text{C}$  Spectrum of compound **17** (100 MHz,  $\text{CDCl}_3$ , 300 K)



**Figure 52:**  $^{13}\text{C}$  DEPT-135 Spectrum of compound **17** (100 MHz,  $\text{CDCl}_3$ , 300 K)

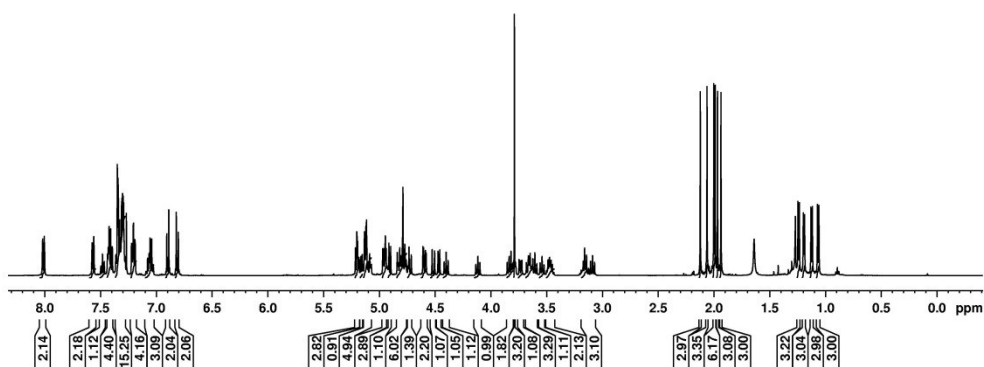


**Figure53:** 2D- COSY spectrum (selected regions) of compound **17** (400 MHz, CDCl<sub>3</sub>, 300 K)

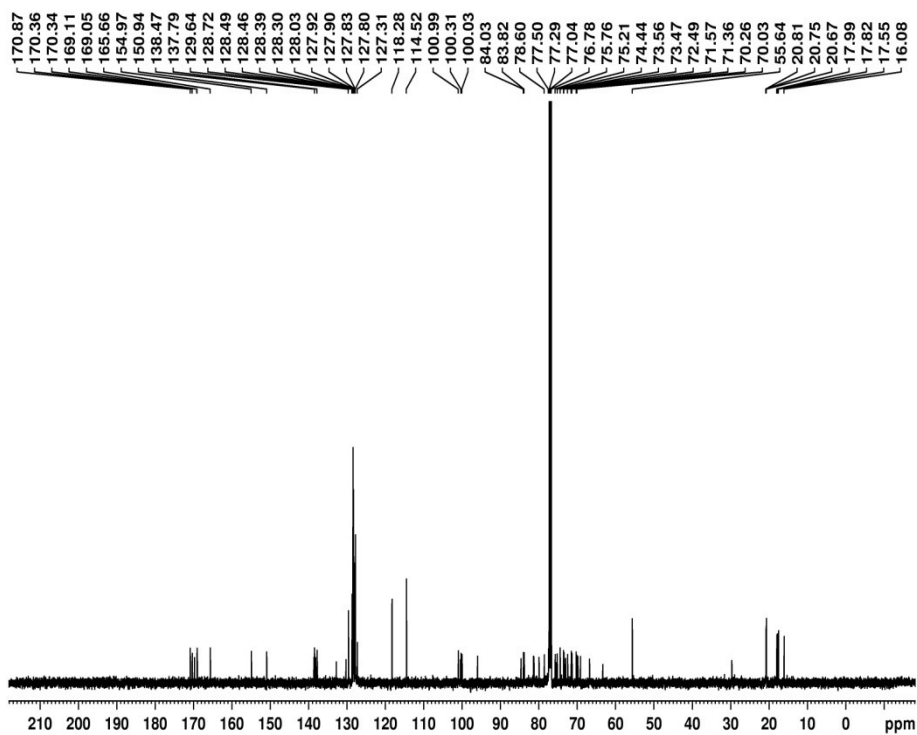


**Figure54:** 2D- HSQC spectrum (selected regions) of compound **17** (400 MHz, CDCl<sub>3</sub>, 300 K)

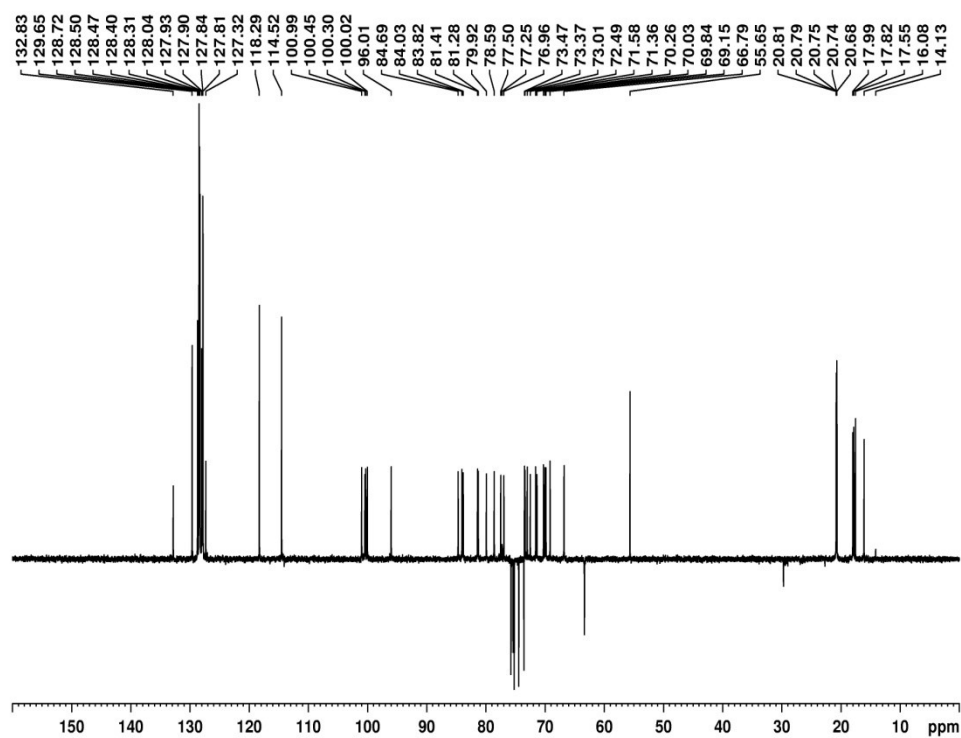




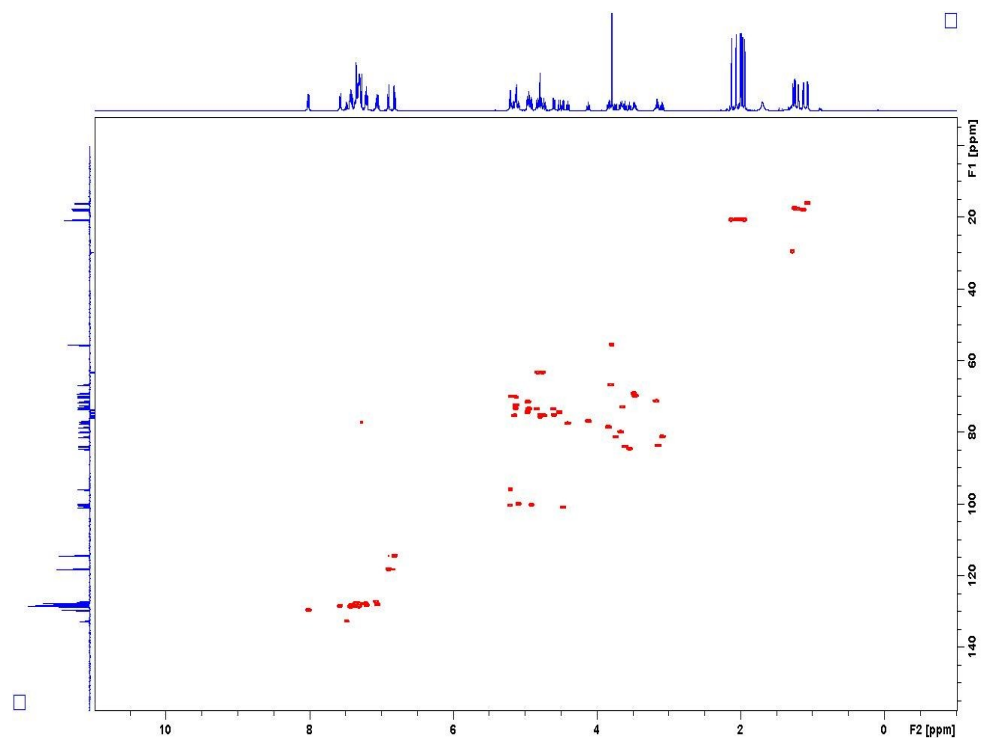
**Figure 55:**  $^1\text{H}$  spectrum of compound **18** (500 MHz,  $\text{CDCl}_3$ , 300 K)



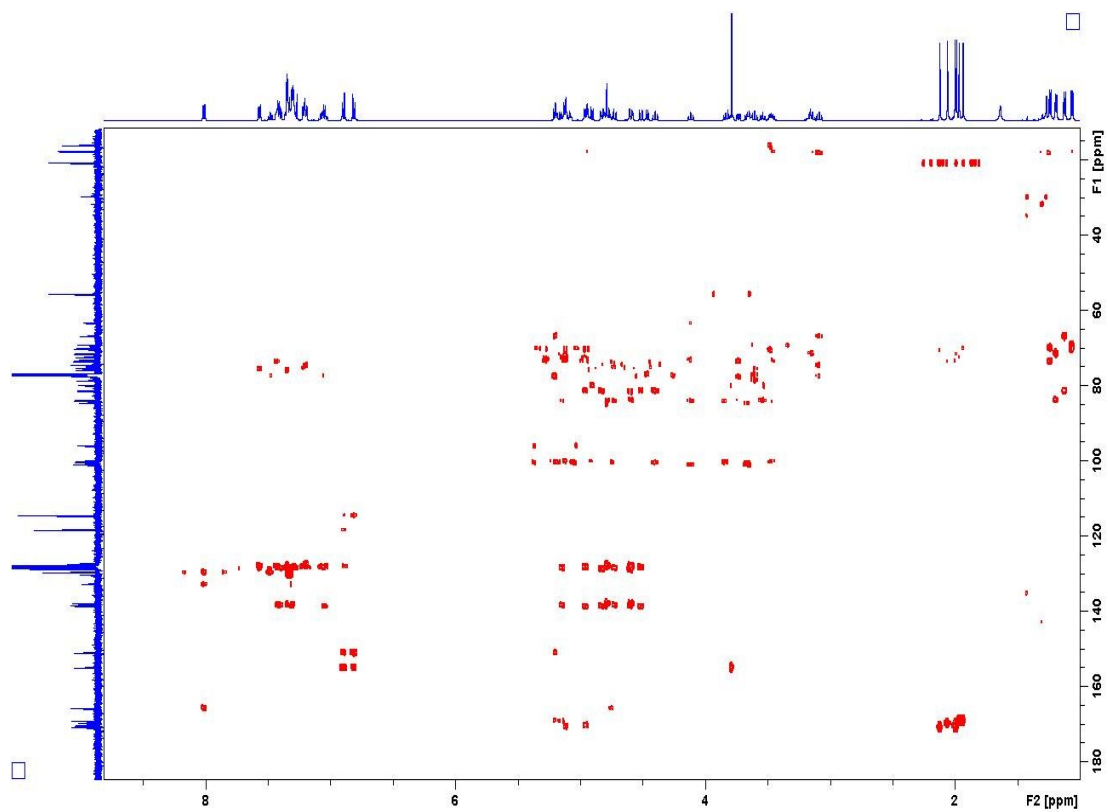
**Figure 56:**  $^{13}\text{C}$  spectrum of compound **18** (125 MHz,  $\text{CDCl}_3$ , 300 K)



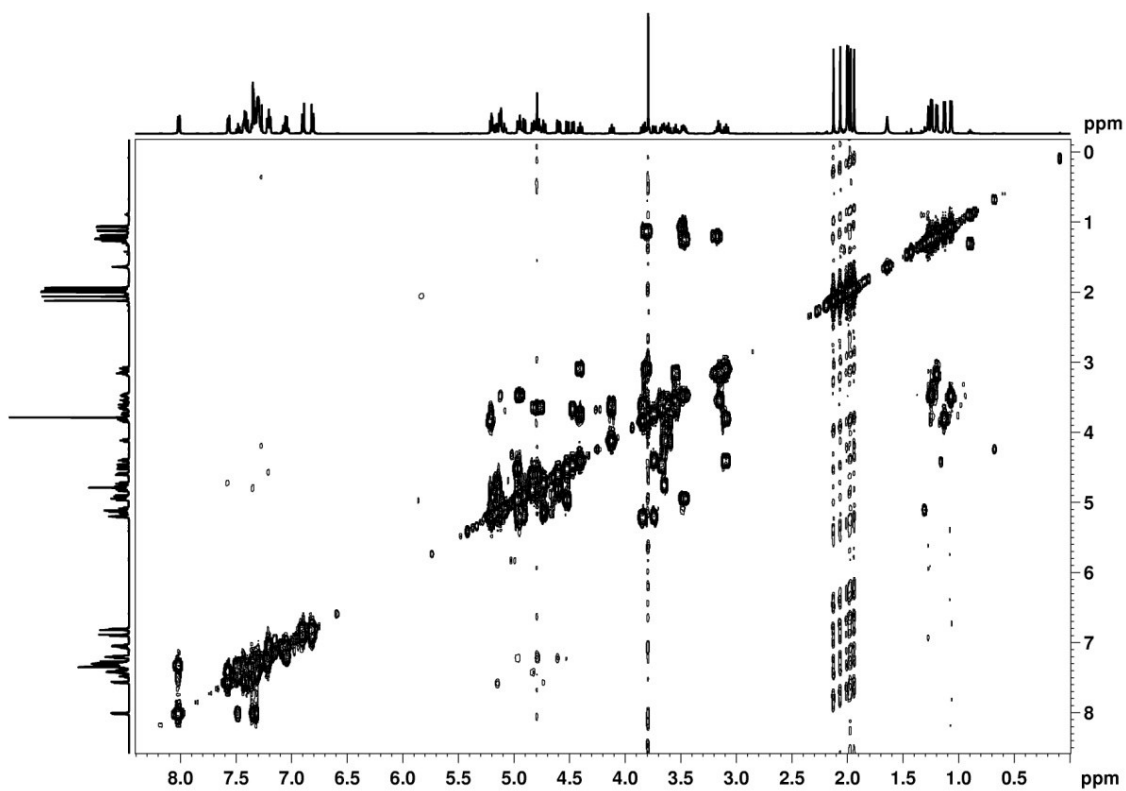
**Figure 57:**  $^{13}\text{C}$  Dept- $135^\circ$  spectrum of compound **18** (125 MHz,  $\text{CDCl}_3$ , 300 K)



**Figure 58:** 2D-HSQC Spectrum of compound **18** (500 MHz,  $\text{CDCl}_3$ , 300 K)



**Figure 59:** 2D- HMBC spectrum of compound **18** (500 MHz, CDCl<sub>3</sub>, 300 K)



**Figure 60:** 2D- COSY spectrum of compound **18** (500 MHz, CDCl<sub>3</sub>, 300 K)

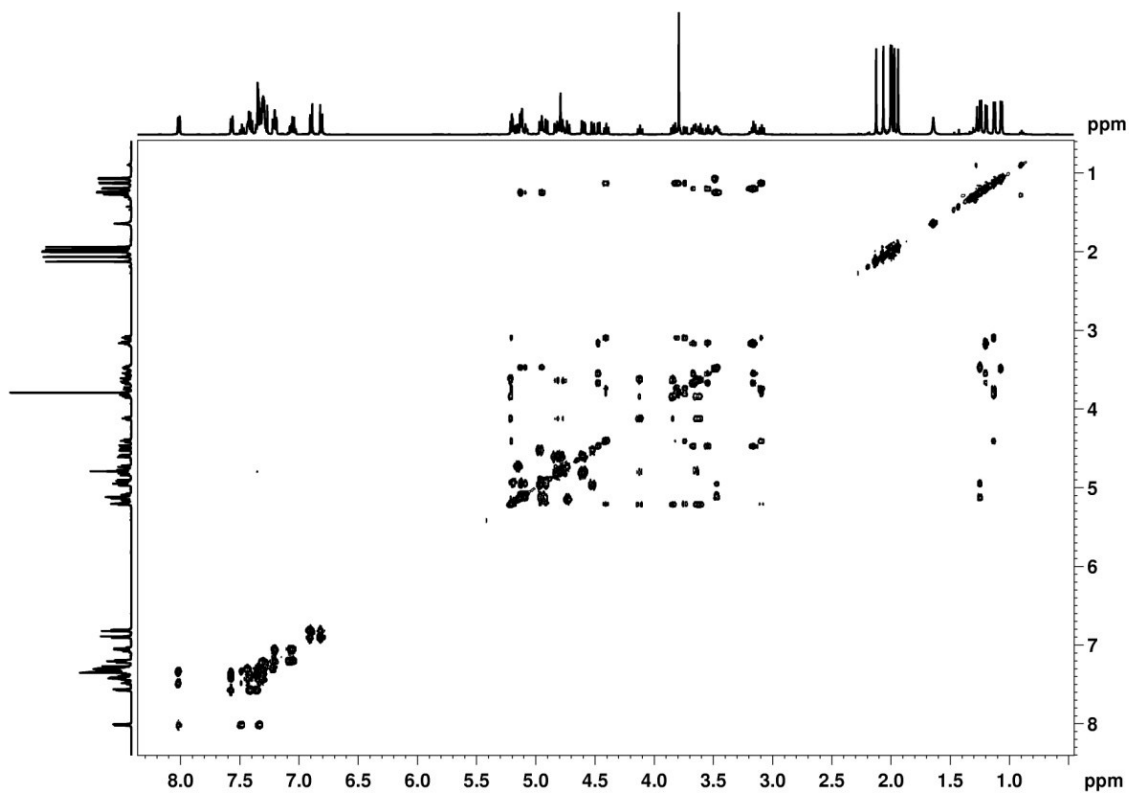


Figure 61: 2D -TOCSY spectrum of compound **18** (500 MHz, CDCl<sub>3</sub>, 300 K)

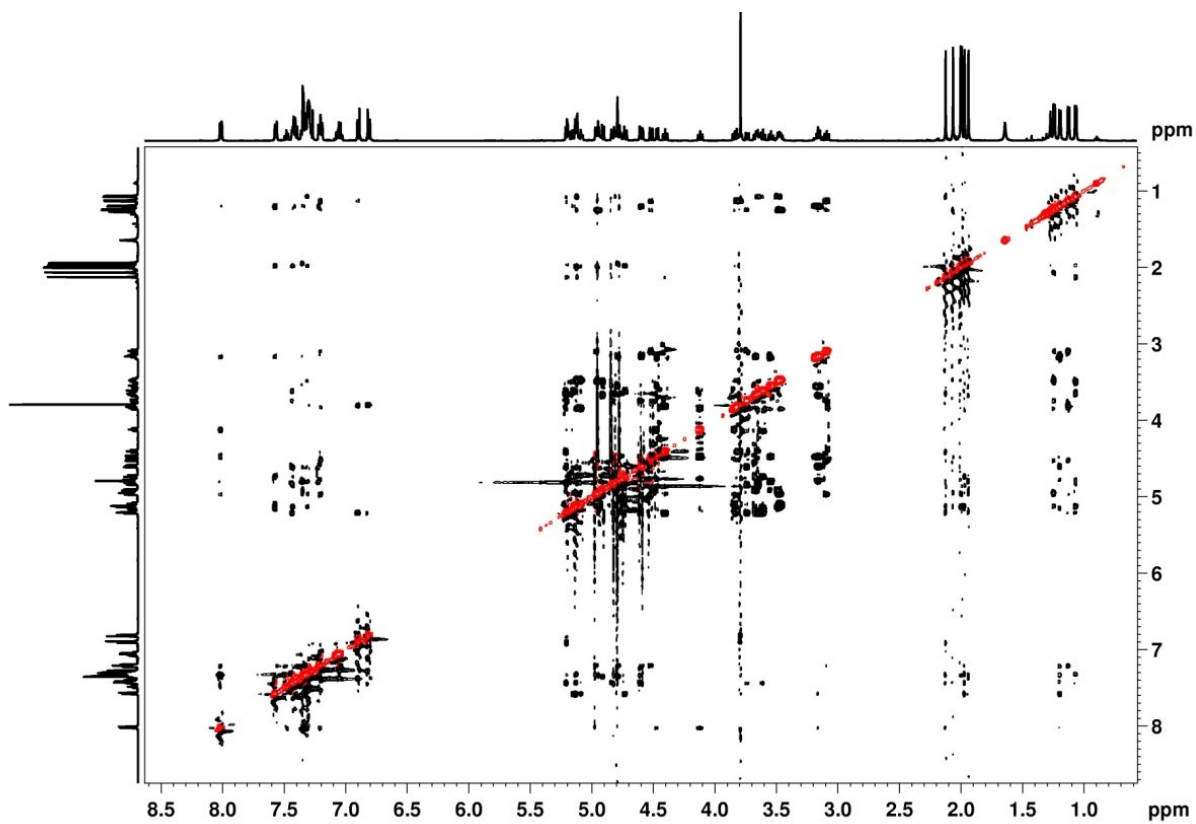
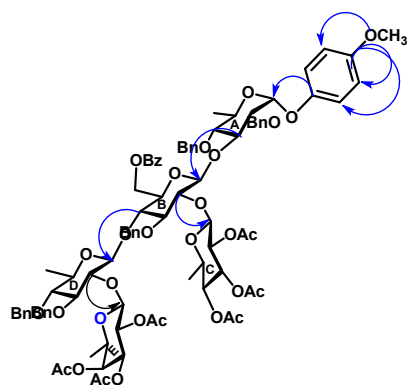
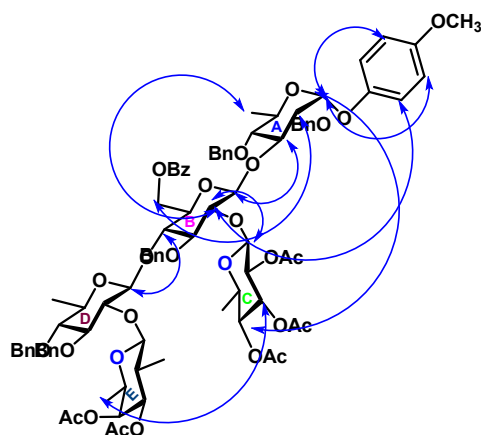


Figure 62: 2D-ROESY spectrum of compound **18** (500 MHz, CDCl<sub>3</sub>, 300 K)



HMBC- correlation of **18**



ROESY correlations of **18**

**Figure 63:** HMBC and ROESY- correlation of compound **18**

**Table S1:**  $^1\text{H}$  and  $\text{C}^{13}$  NMR chemical shifts ( $\delta$  in ppm) and coupling constants ( $J$  in Hz) for compound **1** (500 MHz, 300K,  $\text{D}_2\text{O}$ )

Ring Protons	A	B	C	D	E
<b>C<sub>1</sub>H</b>	5.47 (H-1 <sub>A</sub> , <i>d</i> , $^3J_{\text{C1H-C2H}} = 3.6$ )	4.73 (H-1 <sub>B</sub> , <i>d</i> , $^3J_{\text{C1H-C2H}} = 8.3$ )	4.68 (H-1 <sub>C</sub> , <i>d</i> , $^3J_{\text{C1H-C2H}} = 7.4$ )	4.61 (H-1 <sub>D</sub> , <i>d</i> , $^3J_{\text{C1H-C2H}} = 7.8$ )	4.53 (H-1 <sub>E</sub> , <i>d</i> , $^3J_{\text{C1H-C2H}} = 7.9$ )
<b>C<sub>2</sub>H</b>	3.90, (H-2 <sub>A</sub> , <i>dd</i> , $^3J_{\text{C2H-C3H}} = 3.6, 9.1$ )	3.55, (H-2 <sub>B</sub> , <i>dd</i> , $^3J_{\text{C2H-C3H}} = 8.1, 7.5$ )	3.29, (H-2 <sub>C</sub> , <i>m</i> )	3.46 (H-2 <sub>D</sub> , <i>m</i> )	3.50 (H-2 <sub>E</sub> , <i>dd</i> , $^3J_{\text{C2H-C3H}} = 7.9, 8.1$ )
<b>C<sub>3</sub>H</b>	3.28 (H-3 <sub>A</sub> , <i>t</i> , $^3J_{\text{C3H-C4H}} = 8.9$ )	3.80 (H-3 <sub>B</sub> , <i>dd</i> , $^3J_{\text{C3H-C4H}} = 8.1, 5.3$ )	3.42, (H-3 <sub>C</sub> , <i>m</i> )	3.60 (H-3 <sub>D</sub> , <i>dd</i> , $^3J_{\text{C3H-C4H}} = 9.7, 3.8$ )	3.59 (H-3 <sub>E</sub> , <i>m</i> )
<b>C<sub>4</sub>H</b>	3.89 (H-4 <sub>A</sub> , <i>m</i> )	3.61 (H-4 <sub>B</sub> , <i>m</i> )	3.11, (H-4 <sub>C</sub> , <i>dd</i> , $^3J_{\text{C4H-C5H}} = 6.1, 4.5$ )	3.47 (H-4 <sub>D</sub> , <i>dd</i> , $^3J_{\text{C4H-C5H}} = 6.1, 3.8$ )	3.14 (H-4 <sub>E</sub> , <i>t</i> , 9.27)
<b>C<sub>5</sub>H</b>	3.89 (H-5 <sub>A</sub> , <i>m</i> )	3.57 (H-5 <sub>B</sub> , <i>m</i> )	3.49, (H-5 <sub>C</sub> , <i>dd</i> , $^3J_{\text{C5H-CH3}} = 6.3, 4.6$ )	3.68 (H-5 <sub>D</sub> , <i>dd</i> , $^3J_{\text{C5H-CH3}} = 6.1, 6.5$ )	3.44 (H-5 <sub>E</sub> , <i>m</i> )
<b>CH<sub>3</sub></b>	1.18 (3H, <i>d</i> , $^3J_{\text{C5H-CH3}} = 6.7$ )	-	1.28 (3H, <i>d</i> , $^3J_{\text{C5H-CH3}} = 6.3$ )	1.19 (3H, <i>d</i> , $^3J_{\text{C5H-CH3}} = 6.5$ )	1.25 (3H, <i>d</i> , $^3J_{\text{C5H-CH3}} = 6.4$ )
<b>Carbons</b>	C-1 <sub>A</sub> =97.27, C-2 <sub>A</sub> =84.36, C-3 <sub>A</sub> =73.43 C-4 <sub>A</sub> =68.57 C-5 <sub>A</sub> =70.91 Me-C=16.60	C-1 <sub>B</sub> =101.92, C-2 <sub>B</sub> =81.93, C-3 <sub>B</sub> =74.15 C-4 <sub>B</sub> =72.73 C-5 <sub>B</sub> =74.83 CH <sub>2</sub> -C=60.09	C-1 <sub>C</sub> =103.69, C-2 <sub>C</sub> =74.11, C-3 <sub>C</sub> =74.98 C-4 <sub>C</sub> =74.74 C-5 <sub>C</sub> =72.25 Me-C=16.62	C-1 <sub>D</sub> =103.49, C-2 <sub>D</sub> =71.65, C-3 <sub>D</sub> =74.98 C-4 <sub>D</sub> =73.43 C-5 <sub>D</sub> =68.57 Me-C=16.54	C-1 <sub>E</sub> =100.93, C-2 <sub>E</sub> =80.78, C-3 <sub>E</sub> =72.73 C-4 <sub>E</sub> =74.74 C-5 <sub>E</sub> =71.77 Me-C=16.64
<b>Others:-</b> H1 = 3.75, sH3, H3' = 7.07 d, $J = 8.9$ H4, H4' = 6.94, d, $J = 8.9$ ; Carbons: C1=55.82, C2=154.80, C3, C3'=118.97 C4, C4'=115.11, C5=149.9; B-CH <sub>2</sub> <sup>a</sup> = 3.85 (1H, <i>dd</i> , $^3J_{\text{C5H-CH}} = 13.7, 9.1$ ); B-CH <sub>2</sub> <sup>b</sup> = 4.01 (1H, <i>dd</i> , $^3J_{\text{C5H-CH3}} = 13.7, 7.8$ )					

**Table S2:**  $^1\text{H}$  and  $\text{C}^{13}$  NMR chemical shifts ( $\delta$  in ppm) and coupling constants ( $J$  in Hz) for compound **18** (500 MHz, 300K,  $\text{CDCl}_3$ )

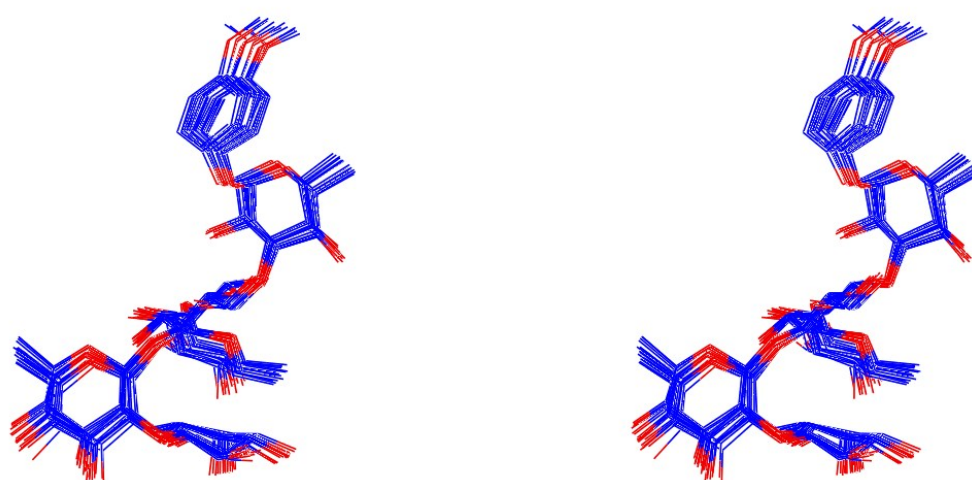
Ring Proton	A	B	C	D	E
<b>C<sub>1</sub>H</b>	5.20 (H-1 <sub>A</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=3.6$ )	5.21 (H-1 <sub>B</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=8.2$ )	5.08 (H-1 <sub>C</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=8.2$ )	4.46 (H-1 <sub>D</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=7.7$ )	4.90 (H-1 <sub>E</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=8.1$ )
<b>C<sub>2</sub>H</b>	3.73 (H-2 <sub>A</sub> , <i>d</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=3.6$ , 9.4)	3.84 (H-2 <sub>B</sub> , <i>dd</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=$ 8.2,9.2)	5.12 (H-2 <sub>C</sub> , <i>m</i> )	3.67 (H-2 <sub>D</sub> , <i>dd</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=7.7$ , 9.0)	5.18 (H-2 <sub>E</sub> , <i>dd</i> , $^3J_{\text{C}_{1\text{H}}-\text{C}_{2\text{H}}}=$ 6.4,8.1)
<b>C<sub>3</sub>H</b>	4.41 (H-3 <sub>A</sub> , <i>t</i> , $^3J_{\text{C}_{3\text{H}}-\text{C}_{4\text{H}}}=9.4$ )	3.61 (H-3 <sub>B</sub> , <i>t</i> , $^3J_{\text{C}_{3\text{H}}-\text{C}_{4\text{H}}}=9.2$ )	5.12 (H-3 <sub>C</sub> , <i>m</i> )	3.54 (H-3 <sub>D</sub> , <i>t</i> , $^3J_{\text{C}_{3\text{H}}-\text{C}_{4\text{H}}}=9.0$ )	4.95 (H-3 <sub>E</sub> , <i>dd</i> , $^3J_{\text{C}_{3\text{H}}-\text{C}_{4\text{H}}}=6.4$ , 9.1)
<b>C<sub>4</sub>H</b>	3.09 (H-4 <sub>A</sub> , <i>dd</i> , $^3J_{\text{C}_{4\text{H}}-\text{C}_{5\text{H}}}=$ 3.6,9.4)	4.12 (H-4 <sub>B</sub> , <i>t</i> , $^3J_{\text{C}_{4\text{H}}-\text{C}_{5\text{H}}}=9.2$ )	4.94 (H-4 <sub>C</sub> , <i>m</i> )	3.15 (H-4 <sub>D</sub> , <i>t</i> , $^3J_{\text{C}_{4\text{H}}-\text{C}_{5\text{H}}}=9.0$ )	5.12 (H-4 <sub>E</sub> , <i>m</i> )
<b>C<sub>5</sub>H</b>	3.80 (H-5 <sub>A</sub> , <i>m</i> )	3.65 (H-5 <sub>B</sub> , <i>m</i> )	3.47 (H-5 <sub>C</sub> , <i>t</i> , $^3J_{\text{C}_{5\text{H}}-\text{CH}_3}=$ 8.62)	3.17 (H-5 <sub>D</sub> , <i>m</i> )	3.48 (H-5 <sub>E</sub> , <i>m</i> )
<b>CH<sub>3</sub></b>	1.12 (3H, <i>d</i> , $^3J_{\text{C}_{5\text{H}}-\text{CH}_3}=6.2$ )	-	1.24 (3H, <i>d</i> , $^3J_{\text{C}_{5\text{H}}-\text{CH}}=$ 6.0)	1.19 (3H, <i>d</i> , $^3J_{\text{C}_{5\text{H}}-\text{CH}_3}=6.6$ )	1.06, (3H, <i>d</i> , $^3J_{\text{C}_{5\text{H}}-\text{CH}_3}=$ 6.3)
<b>Carbons</b>	C-1 <sub>A</sub> = 96.01, C-2 <sub>A</sub> = 81.41, C-3 <sub>A</sub> = 77.40 C-4 <sub>A</sub> = 81.28 C-5 <sub>A</sub> = 78.59 Me-C = 17.99	C-1 <sub>B</sub> = 100.47, C-2 <sub>B</sub> = 78.58, C-3 <sub>B</sub> = 84.06 C-4 <sub>B</sub> = 76.96 C-5 <sub>B</sub> = 79.73 CH <sub>2</sub> -C = 63.75	C-1 <sub>C</sub> = 100.02 C-2 <sub>C</sub> = 72.41, C-3 <sub>C</sub> = 73.36 C-4 <sub>C</sub> = 73.50 C-5 <sub>C</sub> = 69.80 Me-C = 17.56	C-1 <sub>D</sub> = 101.30, C-2 <sub>D</sub> = 79.92, C-3 <sub>D</sub> = 84.69 C-4 <sub>D</sub> = 71.36 C-5 <sub>D</sub> = 83.85 Me-C = 17.78	C-1 <sub>E</sub> = 100.30, C-2 <sub>E</sub> = 70.03, C-3 <sub>E</sub> = 71.55 C-4 <sub>E</sub> = 70.26 C-5 <sub>E</sub> = 69.16 Me-C = 16.08
<b>Others:-</b> H1= 3.79, <i>s</i> , CH <sub>2</sub> , 4.82 (1H <sub>a</sub> , <i>m</i> ), 4.75, (1H <sub>b</sub> , <i>m</i> ) H <sub>3</sub> ,H <sub>3'</sub> = 6.89 <i>d</i> , $J=8.89$ , H <sub>4</sub> ,H <sub>4'</sub> = 6.80, <i>d</i> , $J=8.89$ : Carbons : C1= 55.64, C2 = 155.00, C3,C3' = 118.29, C4,C4' = 114.55, C5 = 150.93					

### Molecular Dynamics Study:-

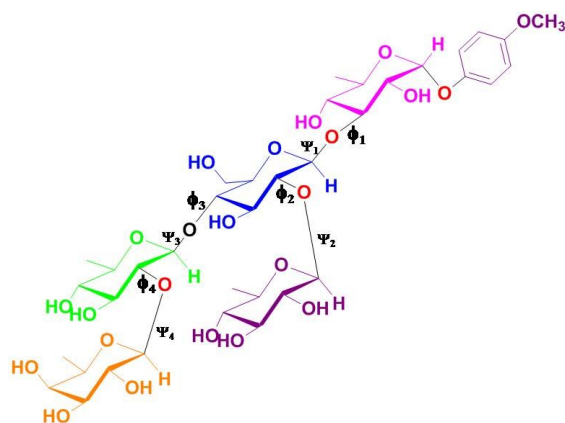
Energy minimization and molecular dynamics (MD) calculations were performed on Discovery studio 3.0 version, using CHARMM<sup>4</sup> force field with default parameters throughout the simulation. Distance restraints used in the simulated molecular dynamics were calculated from the volume integrals of the cross peaks in the ROESY spectra using two-spin approximation with a reference distance of 1.80 Å for the geminal protons. Force constant of 10 K cal/Å, 5 K cal/Å and 30 K cal/Å were used for distance, torsional and H-bonding restraints respectively. Minimization was done with steepest descent algorithm followed by conjugate gradient methods for maximum 1000 iterations each. The molecules were initially equilibrated for 5 pS and then subjected to 1nS production run. Starting from 50 K, they were heated to 300 K in five steps increasing the temperature 50 K at each step. 20 structures were stored from the production run and are again energy minimized with the above mentioned protocol.

**Table S3:** Distance constraints used in the MD calculation for compound **1**, derived from ROESY experiment in D<sub>2</sub>O (500 MHz, 300K)

Residue	Atom	Residue	Atom	Upper bond	Lower bond
A	CH3	Ar	H-3	5.9	4.8
A	H-1	Ar	H-3	3.58	2.93
A	CH3	A	H-1	4.42	3.61
A	CH3	A	H-2	3.08	2.52
A	H-1	A	H-3	3.62	2.99
A	H-2	Ar	H3-H3'	3.66	2.99
A	H-2	Ar	H4-H4'	4.28	3.50
A	H-1	B	H-1	3.45	2.82
A	H-2	C	CH3	3.89	3.18
A	H-1	C	CH3	4.29	3.51
B	H-1	A	H-5	2.70	2.21
B	H-1	Ar	H3-H3'	5.43	4.44
B	H-1	B	H-3	3.15	2.58
B	H-1	D	H-3	2.35	1.92
C	H-1	C	H-2	3.40	2.78
C	H-1	C	H-3	3.78	3.09
C	H-1	C	H-4	4.26	3.49
C	H-4	E	CH3	3.08	2.52
C	H-3	E	H-1	3.27	2.67
C	H-5	E	H-4	2.59	2.12
D	CH3	D	H-5	3.33	2.72
D	H-1	D	H-5	3.23	2.64
D	H-1	E	H-3	3.65	2.99
E	H-1	E	H-3	2.78	2.28
E	H-1	E	H-4	4.25	3.48



**Figure 64:-**Stereoview of the 20 superimposed least energy conformations of compound**1**



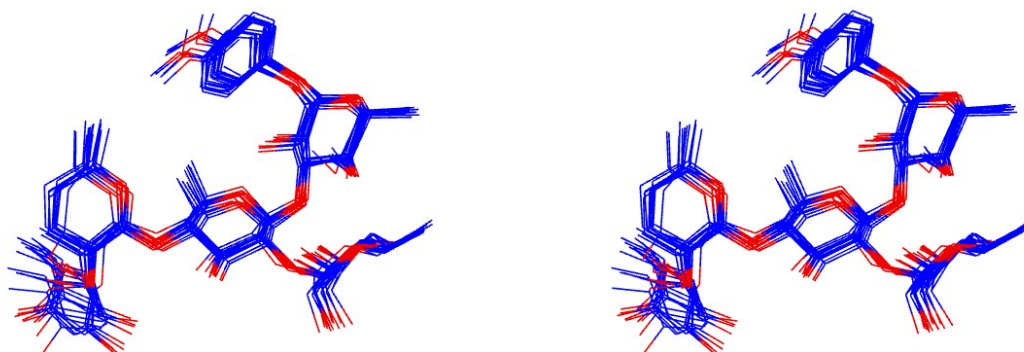
**TableS4:** Torsional angle  $\phi$  and  $\Psi$  of glycosidic linkage of compound **1**

Dihedral angle	Residue	$\theta$
$\phi_1$	H3-C3-O-H1	$36\pm 5$
$\Psi_1$	C3-O-C1-H1	$20\pm 5$
$\phi_2$	H2-C2-O-C1	$5.20\pm 2$
$\Psi_2$	C2-O-C1-H1	$58\pm 10$
$\phi_3$	H4-C4-O-C1	$-69\pm 10$
$\Psi_3$	C4-O-C1-H1	$20\pm 5$
$\phi_4$	H2-C2-O-C1	$-138\pm 10$
$\Psi_4$	C2-O-C1-H1	$57\pm 5$

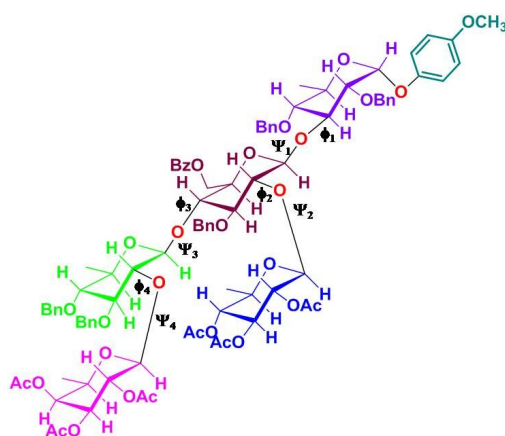
**Table S5:** Distance constraints used in MD calculation for compound **18** derived from ROESY experiment in  $\text{CDCl}_3$  (500 MHz, 300K)

Residue	Atom	Residue	Atom	Upper bond	Lower bond
A	H-1	Ar	H-3	4.1	3.38
A	H-2	A	H-1	3.65	2.99
A	H-4	A	H-2	3.78	3.09
A	H-2	B	CH2	3.24	2.61
A	H-3	B	H-1	3.79	3.10
B	H-2	Ar	H4-4'	3.63	2.97
B	H-5	B	H-1	3.21	2.63
B	H-2	C	H-1	3.94	3.23
B	H-4	D	H-1	3.82	3.12
C	CH3	C	H-4	3.83	3.13
C	CH3	C	H-5	3.62	2.96
C	H-5	C	H-1	3.73	3.05
C	H-4	A	H-1	3.56	2.91
D	CH3	D	H-4	3.35	2.74
D	H-1	D	H-3	3.94	3.22
D	H-4	D	H-1	3.59	2.94
D	H-2	E	H-1	3.67	3.03
E	CH3	E	H-5	3.57	2.92
E	H-5	E	H-1	2.78	2.27





**Figure 65:** Stereoview of the 15 superimposed least energy conformations of compound **18**, protecting group (Bn, Bz, Ac,) remove for the clarity



**Table S6:** Torsional angle  $\phi$  and  $\Psi$  of glycosidic linkage of compound **18**

Dihedral angle	Residue	$\theta$
$\phi_1$	H3-C3-O-H1	$20 \pm 5$
$\Psi_1$	C3-O-C1-H1	$154 \pm 10$
$\phi_2$	H2-C2-O-C1	$-106 \pm 5$
$\Psi_2$	C2-O-C1-H1	$178 \pm 15$
$\phi_3$	H4-C4-O-C1	$45 \pm 5$
$\Psi_3$	C4-O-C1-H1	$100 \pm 5$
$\phi_4$	H2-C2-O-C1	$-162 \pm 10$
$\Psi_4$	C2-O-C1-H1	$59 \pm 5$

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