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**Table S1**. $^{1}$H and $^{13}$C NMR assignments in pyridine-$d_5$ at 700 and 175 MHz for compounds (**1**; $\alpha$-glucosyl-(2→26)-GAF and $\beta$-glucosyl-(2→26)-GAF**)**. ($\delta$ in ppm, $J$ in Hz).

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**Figure S26.** 2D NMR spectrum ($^{1}$H-$^{1}$H NOESY, 700 MHz, pyridine-$d_5$) of the compound (**3**).

**Table S1**. $^{1}H$ and $^{13}C$ NMR assignments in pyridine-$d_5$ at 700 and 175 MHz for compounds (**1**; $\alpha$-glucosyl-(2→26)-GAF and $\beta$-glucosyl-(2→26)-GAF**)**. ($\delta$ in ppm, $J$ in Hz).

| position | compound **(1)** | position | compound **(1)** |
|---|---|---|---|
| 1 | 37.7 | 1 | 37.7 |
| 2 | 34.2 | 2 | 34.2 |
| 3 | 214.6 | 3 | 214.6 |
| 4 | 46.9 | 4 | 46.9 |
| 5 | 50.7 | 5 | 50.7 |
| 6 | 34.0 | 6 | 34.0 |
| 7 | 199.0 | 7 | 199.0 |
| 8 | 150.2 | 8 | 150.2 |
| 9 | 146.6 | 9 | 146.6 |
| 10 | 39.5 | 10 | 39.5 |
| 11 | 194.9 | 11 | 194.9 |
| 12 | 79.5 | 12 | 79.5 |
| 13 | 48.0 | 13 | 48.0 |
| 14 | 59.1 | 14 | 59.1 |
| 15 | 206.1 | 15 | 206.1 |
| 16 | 38.2 | 16 | 38.2 |
| 17 | 44.9 | 17 | 44.9 |
| 18 | 18.8 | 18 | 18.8 |
| 19 | 12.1 | 19 | 12.1 |
| 20 | 30.0 | 20 | 29.9 |
| 21 | 21.7 | 21 | 21.7 |
| 22 | 48.7 | 22 | 48.8 |
| 23 | 208.2 | 23 | 207.9 |
| 24 | 46.8 | 24 | 46.8 |
| 25 | 35.5 | 25 | 35.5 |
| 26 | 176.2 | 26 | 175.4 |
| 27 | 17.2 | 27 | 17.2 |
| 28 | 20.2 | 28 | 20.2 |
| 29 | 27.2 | 29 | 27.2 |
| 30 | 20.2 | 30 | 20.2 |
| $O\underline{C}OCH_3$ | 170.1 | $O\underline{C}OCH_3$ | 170.1 |
| $OCO\underline{C}H_3$ | 21.7 | $OCO\underline{C}H_3$ | 21.7 |
| $\alpha$-glucose | | $\beta$-glucose | |
| 1' | 91.2 (6.05, d, $J$=3.5 Hz) | 1' | 96.5 (5.38, d, $J$=7.7 Hz) |
| 2' | 75.9 (5.50, dd, $J$=3.5, 9.8 Hz) | 2' | 77.3 (5.65, dd, $J$=7.7, 9.1 Hz) |
| 3' | 72.3 (4.94, m) | 3' | 76.5 (4.27, m) |
| 4' | 72.8 (4.32, m) | 4' | 73.7 (4.63, m) |
| 5' | 73.4 (4.81, m) | 5' | 71.0 (4.33, m) |
| 6' | 62.9 (4.41, m; 4.53, m) | 6' | 62.7 (4.36, m; 4.56, m) |

**Table S2**. $^{1}H$ and $^{13}C$ NMR assignments in pyridine-$d_5$ at 700 and 175 MHz for compounds (**2**; $\alpha$-glucosyl-(2→26)-GAA and $\beta$-glucosyl-(2→26)-GAA**)**. ($\delta$ in ppm, $J$ in Hz).

| position | compound **(2)** | position | compound **(2)** |
|---|---|---|---|
| 1 | 36.0 | 1 | 36.0 |
| 2 | 34.6 | 2 | 34.6 |
| 3 | 216.2 | 3 | 216.2 |
| 4 | 47.0 | 4 | 47.0 |
| 5 | 48.9 | 5 | 48.9 |
| 6 | 29.6 | 6 | 29.6 |
| 7 | 68.7 | 7 | 68.7 |
| 8 | 161.5 | 8 | 161.5 |
| 9 | 139.9 | 9 | 139.9 |
| 10 | 38.3 | 10 | 38.3 |
| 11 | 200.0 | 11 | 200.0 |
| 12 | 52.4 | 12 | 52.4 |
| 13 | 46.7 | 13 | 46.7 |
| 14 | 54.7 | 14 | 54.7 |
| 15 | 72.2 | 15 | 72.2 |
| 16 | 36.9 | 16 | 36.9 |
| 17 | 49.8 | 17 | 49.8 |
| 18 | 19.7 | 18 | 19.7 |
| 19 | 17.5 | 19 | 17.5 |
| 20 | 33.0 | 20 | 32.9 |
| 21 | 20.3 | 21 | 20.3 |
| 22 | 49.8 | 22 | 50.0 |
| 23 | 208.7 | 23 | 208.3 |
| 24 | 47.0 | 24 | 46.9 |
| 25 | 35.4 | 25 | 35.5 |
| 26 | 176.2 | 26 | 175.5 |
| 27 | 17.2 | 27 | 17.3 |
| 28 | 19.6 | 28 | 19.6 |
| 29 | 27.2 | 29 | 27.2 |
| 30 | 20.8 | 30 | 20.8 |
| $\alpha$-glucose | | $\beta$-glucose | |
| 1' | 91.1 (6.04, d, $J$=3.5 Hz) | 1' | 96.5 (5.37, d, $J$=7.7 Hz) |
| 2' | 75.9 (5.48, dd, $J$=3.5, 9.8 Hz) | 2' | 77.2 (5.64, t, $J$=8.4 Hz) |
| 3' | 72.2 (4.94, t, $J$=9.1 Hz) | 3' | 76.4 (4.28, t, $J$=9.1 Hz) |
| 4' | 72.8 (4.30, t, $J$=9.1 Hz) | 4' | 75.2 (4.62, t, $J$=9.1 Hz) |
| 5' | 73.7 (5.80, m) | 5' | 71.1 (4.34, m) |
| 6' | 62.9 (4.42, m; 4.52, dd, $J$=2.8, 11.9 Hz) | 6' | 62.7 (4.56, m; 4.56, dd, $J$=2.1, 11.9 Hz) |

**Table S3**. $^{1}H$ and $^{13}C$ NMR assignments in pyridine-$d_5$ at 700 and 175 MHz for compounds (**3**; $\alpha$-glucosyl-(2→26)-GAG and $\beta$-glucosyl-(2→26)-GAG**)**. ($\delta$ in ppm, $J$ in Hz).

| position | compound **(3)** | position | compound **(3)** |
|---|---|---|---|
| 1 | 35.0 | 1 | 35.0 |
| 2 | 28.1 | 2 | 28.1 |
| 3 | 77.5 | 3 | 77.5 |
| 4 | 39.2 | 4 | 39.2 |
| 5 | 49.7 | 5 | 49.7 |
| 6 | 28.4 | 6 | 28.4 |
| 7 | 66.3 | 7 | 66.3 |
| 8 | 158.8 | 8 | 158.8 |
| 9 | 142.5 | 9 | 142.5 |
| 10 | 38.8 | 10 | 38.8 |
| 11 | 200.8 | 11 | 200.8 |
| 12 | 79.2 | 12 | 79.2 |
| 13 | 52.1 | 13 | 52.1 |
| 14 | 60.0 | 14 | 60.0 |
| 15 | 216.6 | 15 | 216.6 |
| 16 | 38.8 | 16 | 38.8 |
| 17 | 46.6 | 17 | 46.6 |
| 18 | 19.0 | 18 | 19.0 |
| 19 | 12.8 | 19 | 12.8 |
| 20 | 28.8 | 20 | 28.9 |
| 21 | 22.0 | 21 | 21.9 |
| 22 | 48.8 | 22 | 48.9 |
| 23 | 208.6 | 23 | 208.3 |
| 24 | 46.7 | 24 | 46.7 |
| 25 | 35.4 | 25 | 35.5 |
| 26 | 176.3 | 26 | 176.5 |
| 27 | 17.2 | 27 | 17.2 |
| 28 | 23.6 | 28 | 23.6 |
| 29 | 28.7 | 29 | 28.7 |
| 30 | 16.3 | 30 | 16.3 |
| $\alpha$-glucose | | $\beta$-glucose | |
| 1' | 91.1 (6.05, d, $J$=2.8 Hz) | 1' | 96.5 (5.38, d, $J$=8.4 Hz) |
| 2' | 75.9 (5.47, dd, $J$=3.5, 9.8 Hz) | 2' | 77.2 (5.64, t, $J$=8.4 Hz) |
| 3' | 72.2 (4.95, t, $J$=9.8 Hz) | 3' | 76.5 (4.21, t, $J$=9.1 Hz) |
| 4' | 72.7 (4.30, t, $J$=9.1 Hz) | 4' | 75.2 (4.62, t, $J$=9.1 Hz) |
| 5' | 73.7 (4.81, m) | 5' | 71.1 (4.34, m) |
| 6' | 62.9 (4.40, m; 4.56, dd, $J$=2.1, 11.9 Hz) | 6' | 62.7 (4.35, m; 4.52, dd, $J$=2.1, 11.9 Hz) |

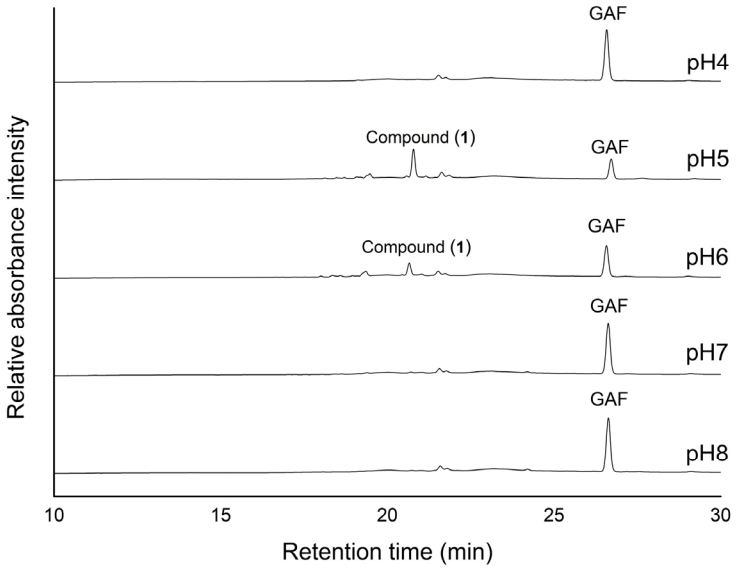



**Figure S1.** High-performance liquid chromatography (HPLC) results of the biotransformation products of ganoderic acid F (GAF) using amylosucrase from *Deinococcus geothermalis* (*Dg*AS) enzyme at different pH levels. The biotransformation condition was 1 mg/mL of GAF, 25 g/mL of *Dg*AS, and 1500 mM of sucrose at 50 mM of acetate buffer (pH 4 and 5), phosphate buffer (pH 6 and 7), or Tris buffer (pH 8) and 40 °C for 24 h. After incubation, the biotransformation products were analyzed using HPLC. The detailed reaction conditions and the HPLC procedure are described in the Materials and Methods section.

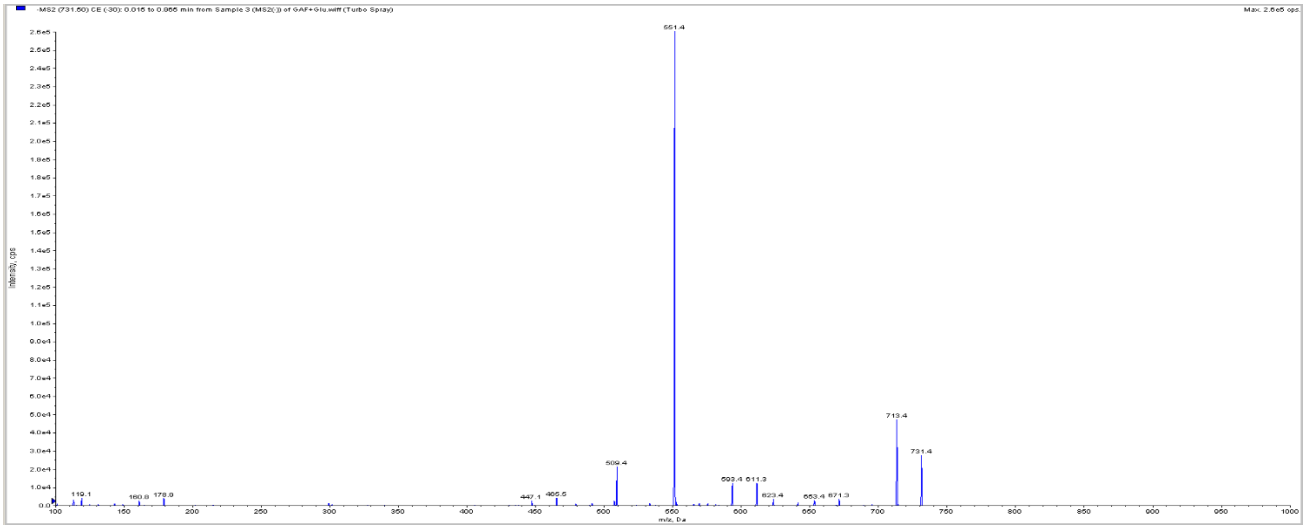



**Figure S2.** The mass-mass analysis of compound (**1**) at the negative mode. A significant signal at m/z 731.4 showed the corresponding m/z signal of molecular weight 732 of GAF-glucoside (570+180-18) at the negative mode.

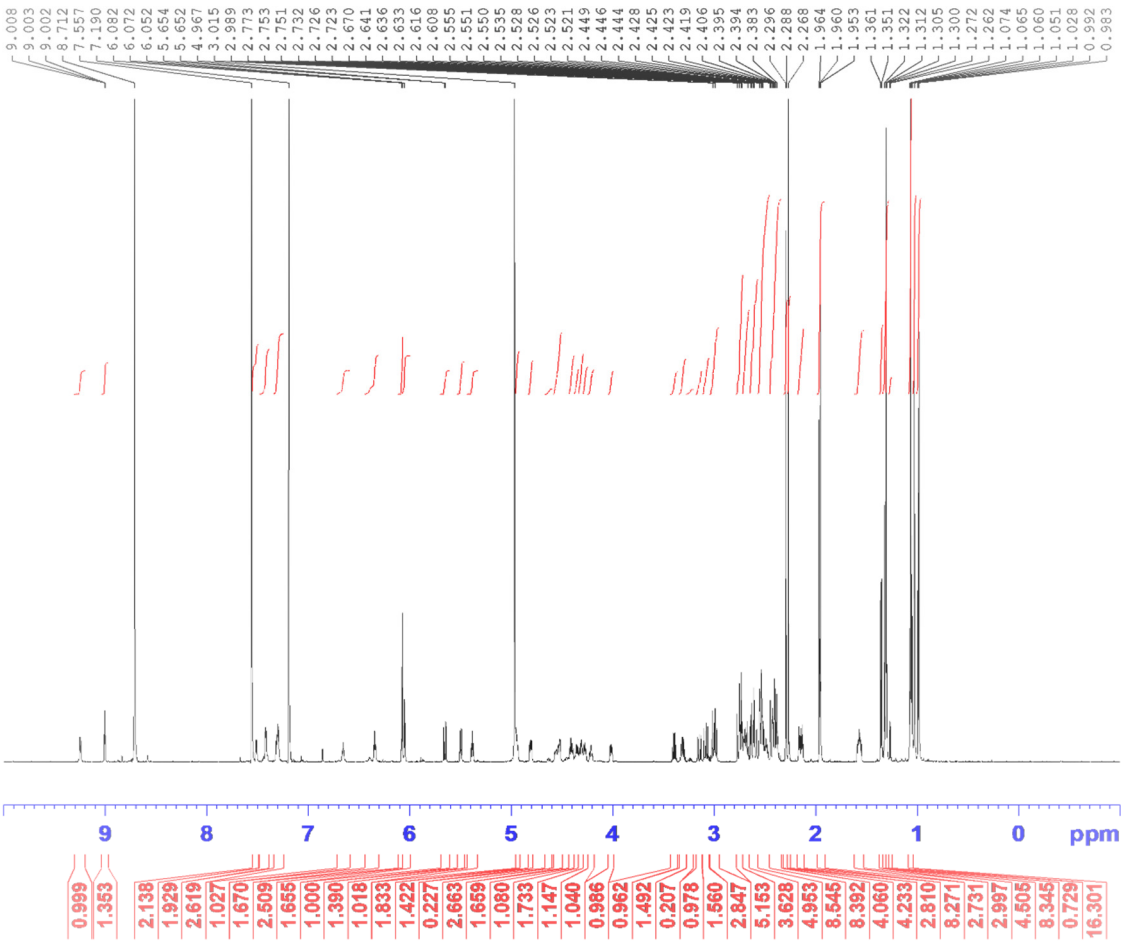



**Figure S3.** 1D NMR spectrum ($^1$H-NMR, 700 MHz, pyridine-$d_5$) of the compound (**1**).

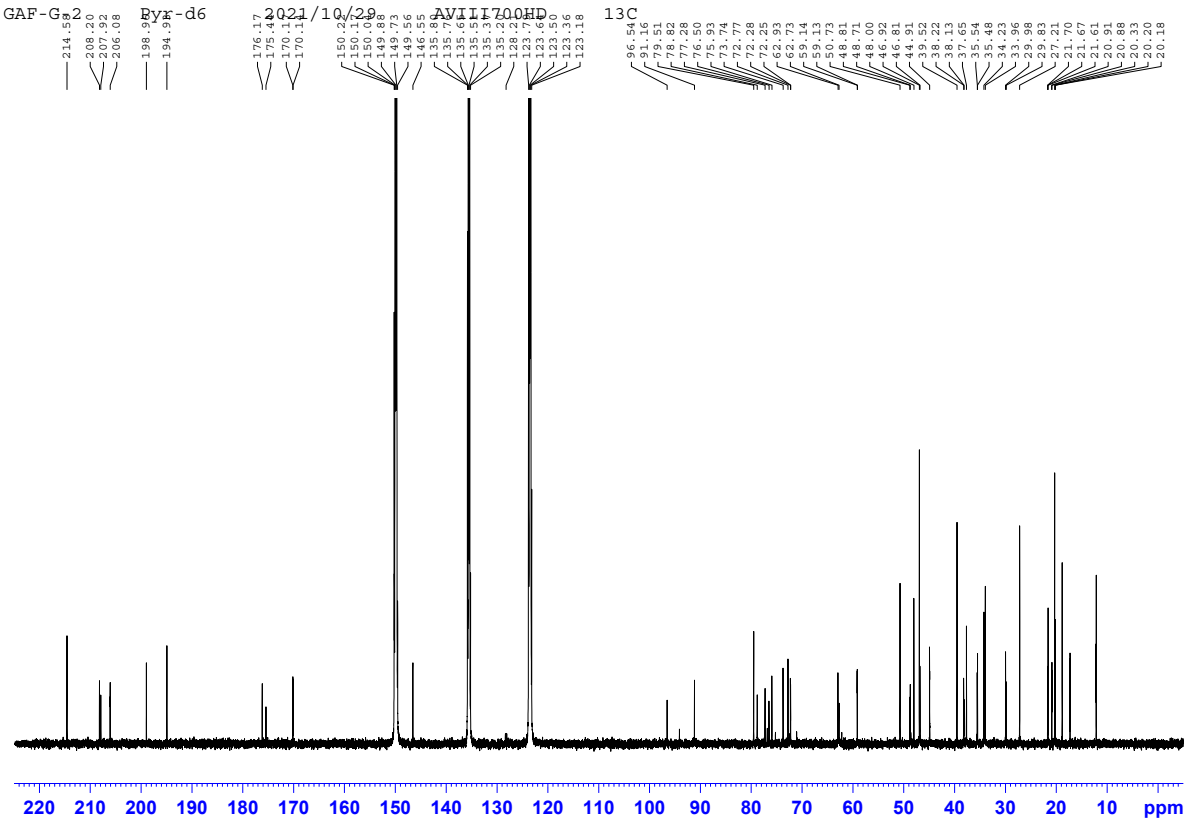



**Figure S4.** 1D NMR spectrum ($^{13}$C-NMR, 175 MHz, pyridine-$d_5$) of the compound (**1**).

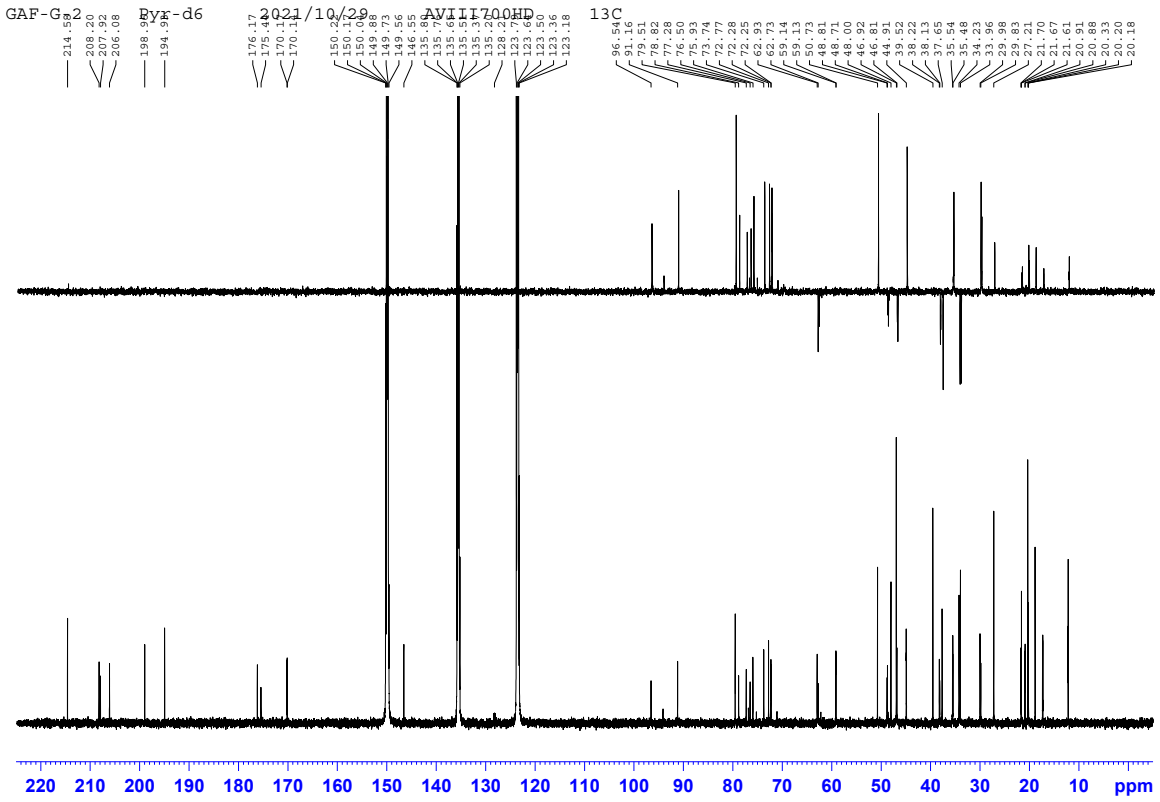



**Figure S5.** 1D NMR spectrum (DEPT-135, 175 MHz, pyridine-$d_5$) of the compound (**1**).

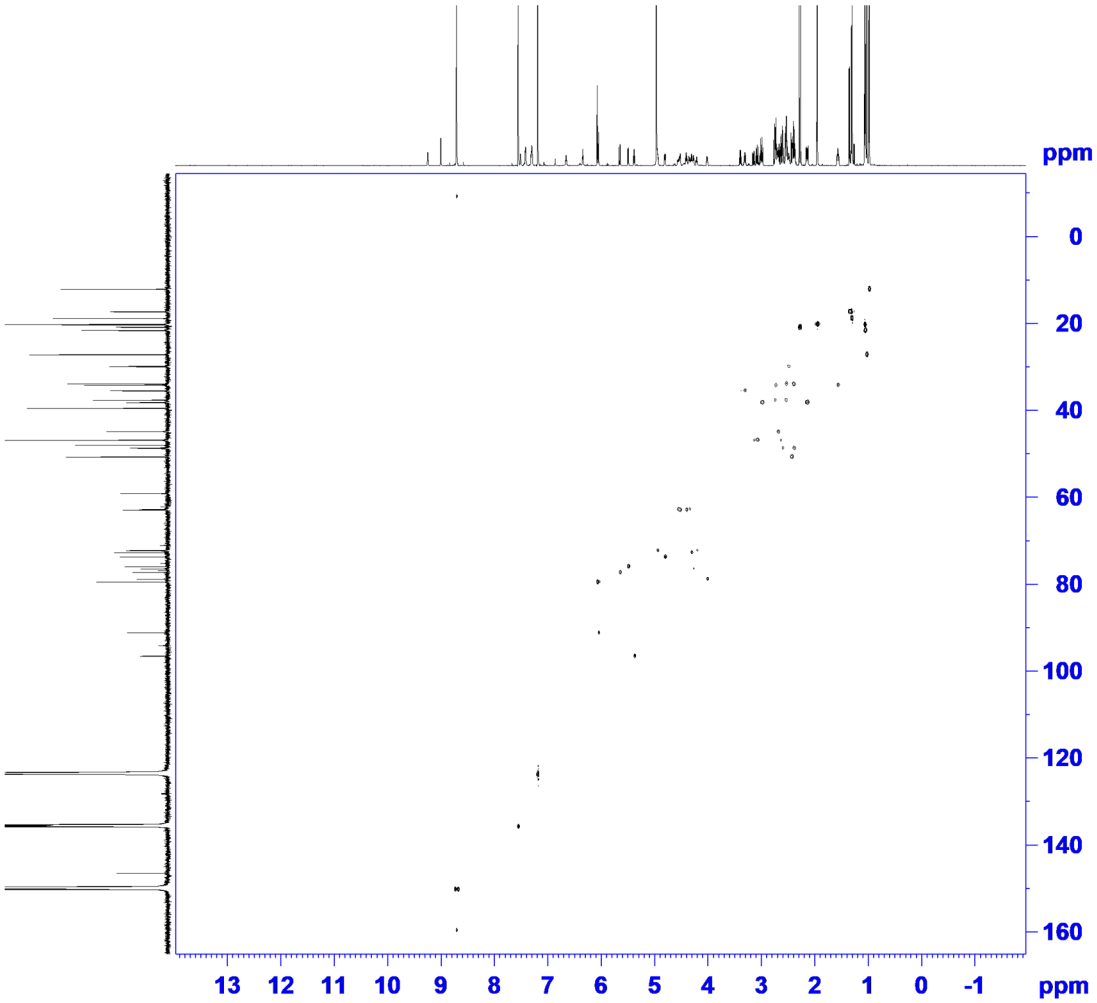



**Figure S6.** 2D NMR spectrum ($^{1}H$-$^{13}C$ HSQC, 700 MHz, pyridine-$d_5$) of the compound (**1**).

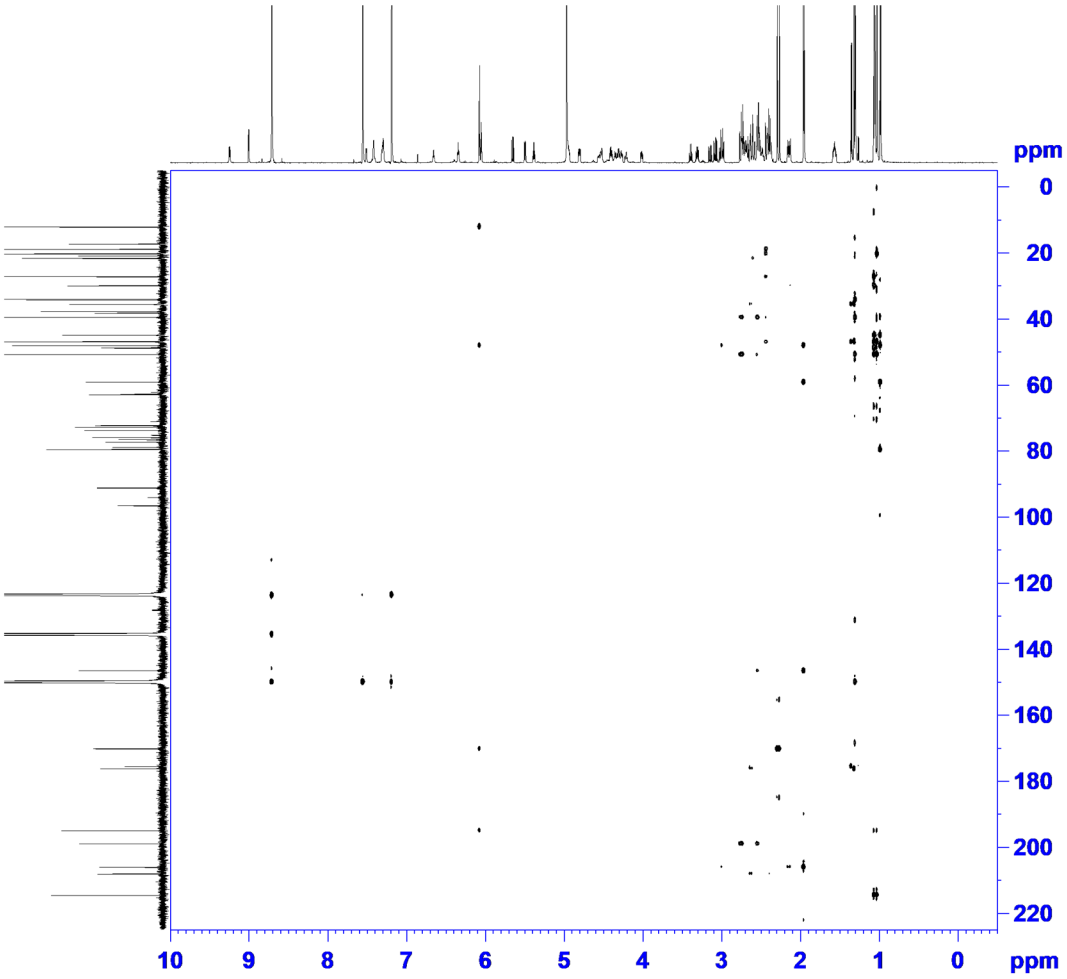



**Figure S7.** 2D NMR spectrum ($^{1}$H-$^{13}$C HMBC, 700 MHz, pyridine-$d_5$) of the compound (**1**).

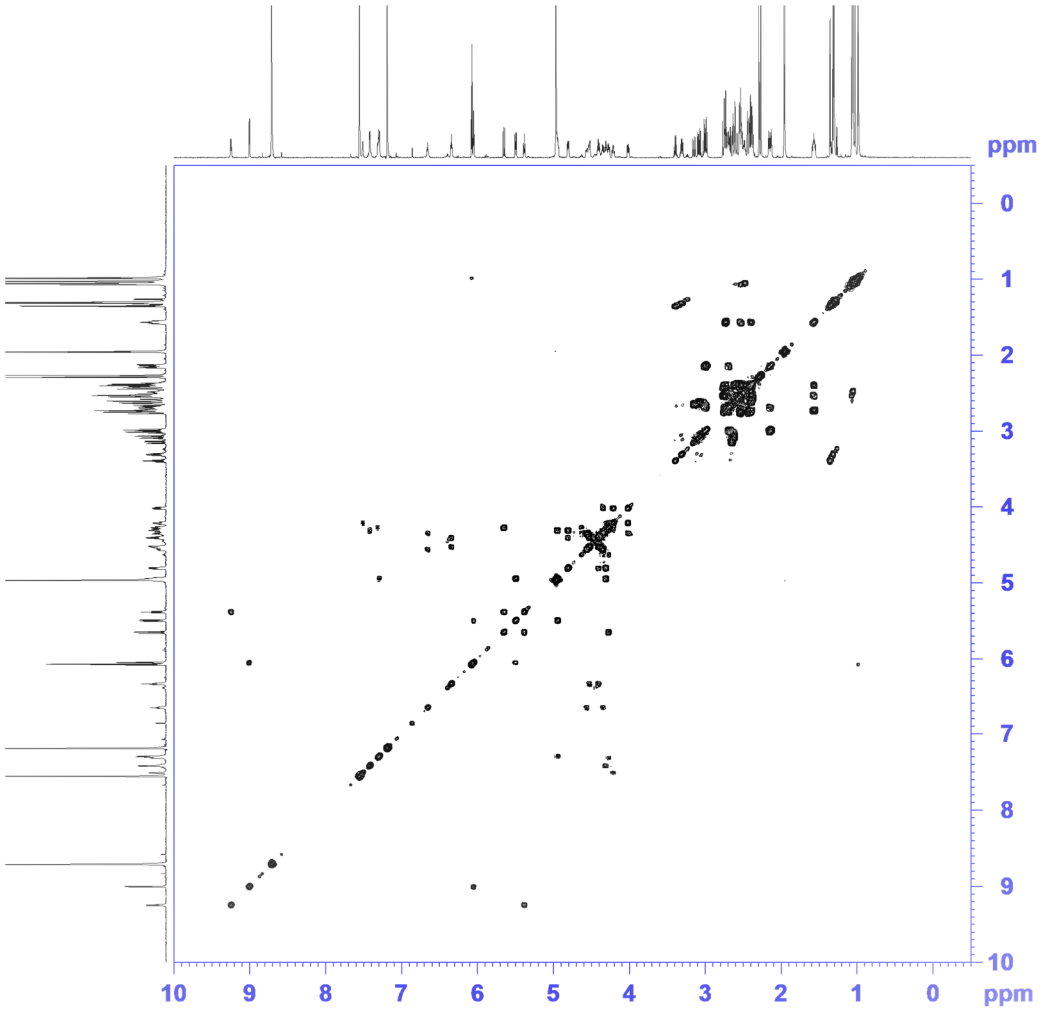



**Figure S8.** 2D NMR spectrum ($^{1}$H-$^{1}$H COSY, 700 MHz, pyridine-$d_5$) of the compound (**1**).

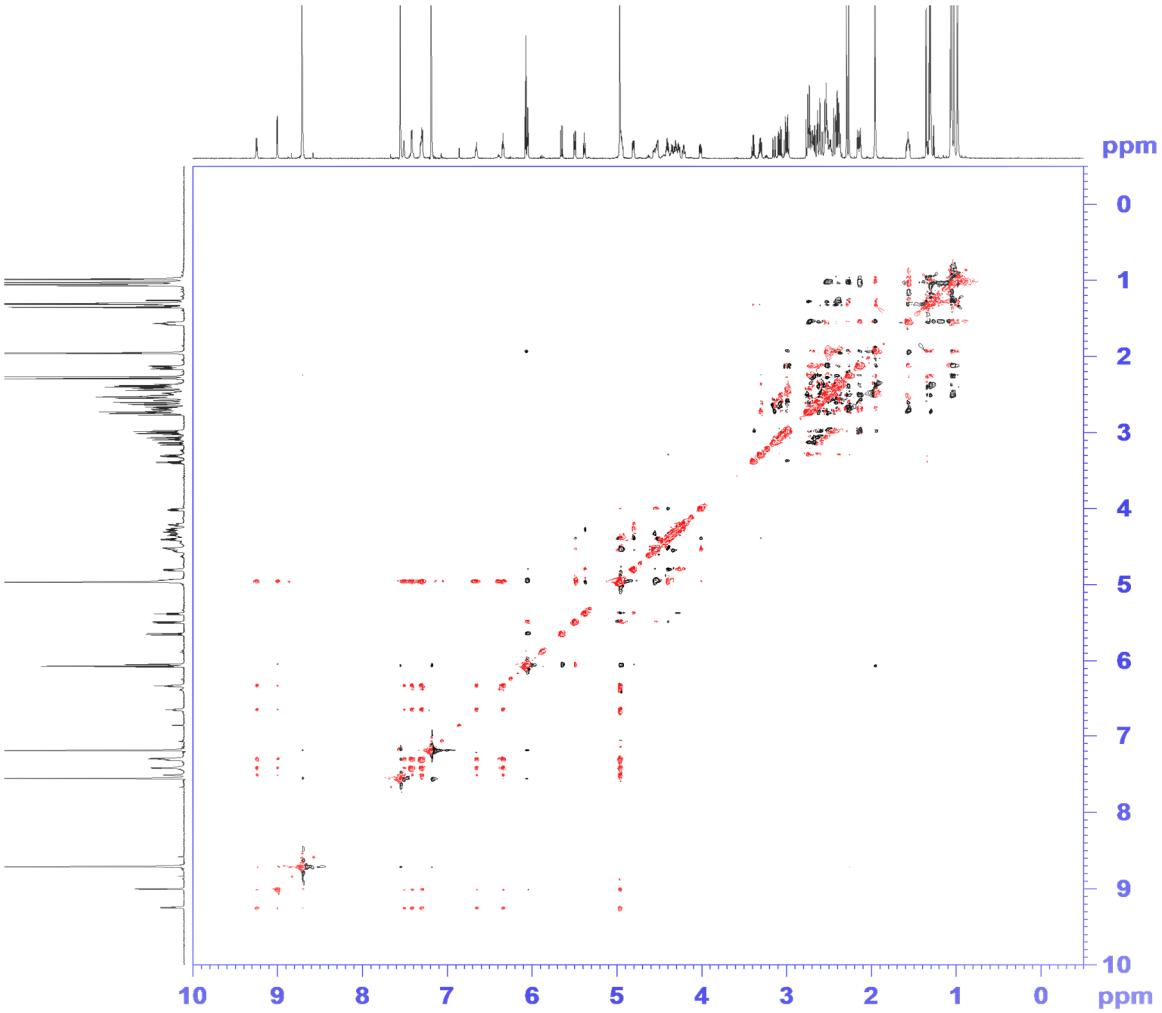
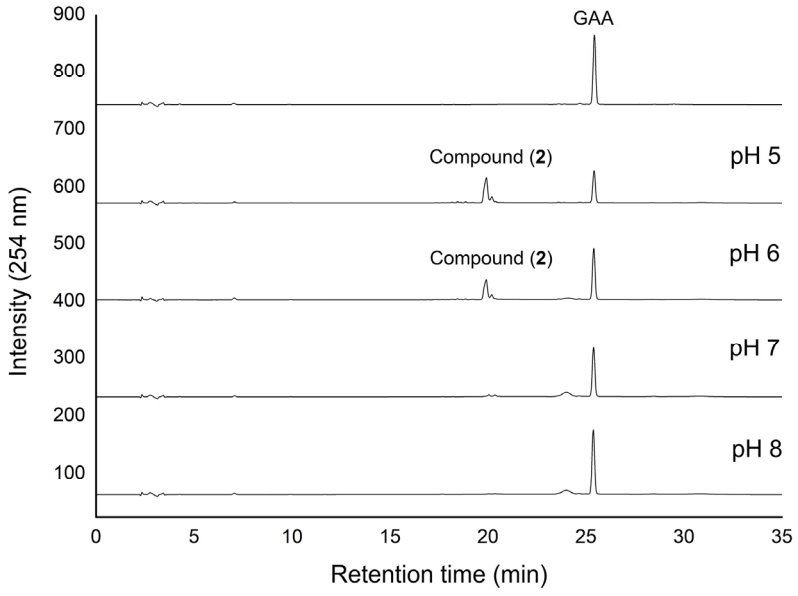
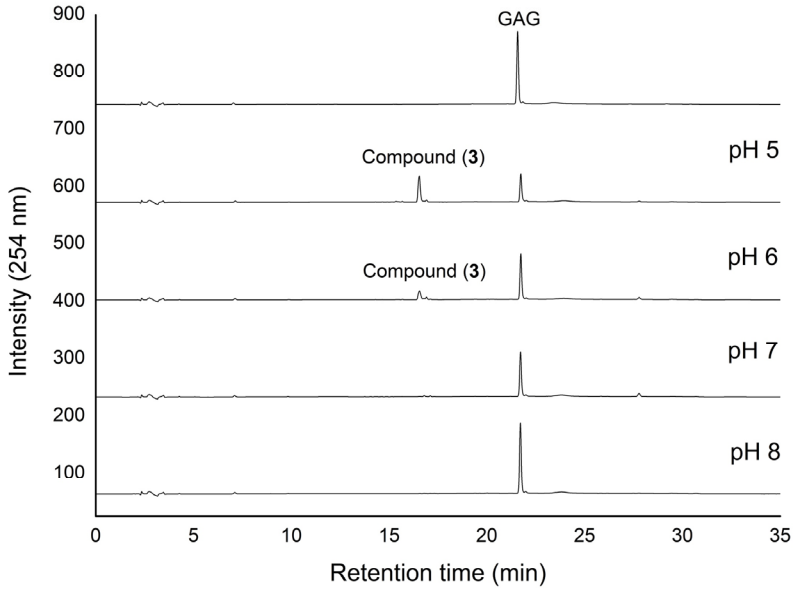



**Figure S9.** 2D NMR spectrum ($^{1}$H-$^{1}$H NOESY, 700 MHz, pyridine-$d_5$) of the compound (**1**).




(**a**)




(**b**)

**Figure S10.** HPLC results of the biotransformation products of GAA (a) and GAG) (b) using *Dg*AS enzyme at different pH levels. The detailed reaction conditions and the HPLC procedure are the same as in Figure 2 and described in the Materials and Methods section.

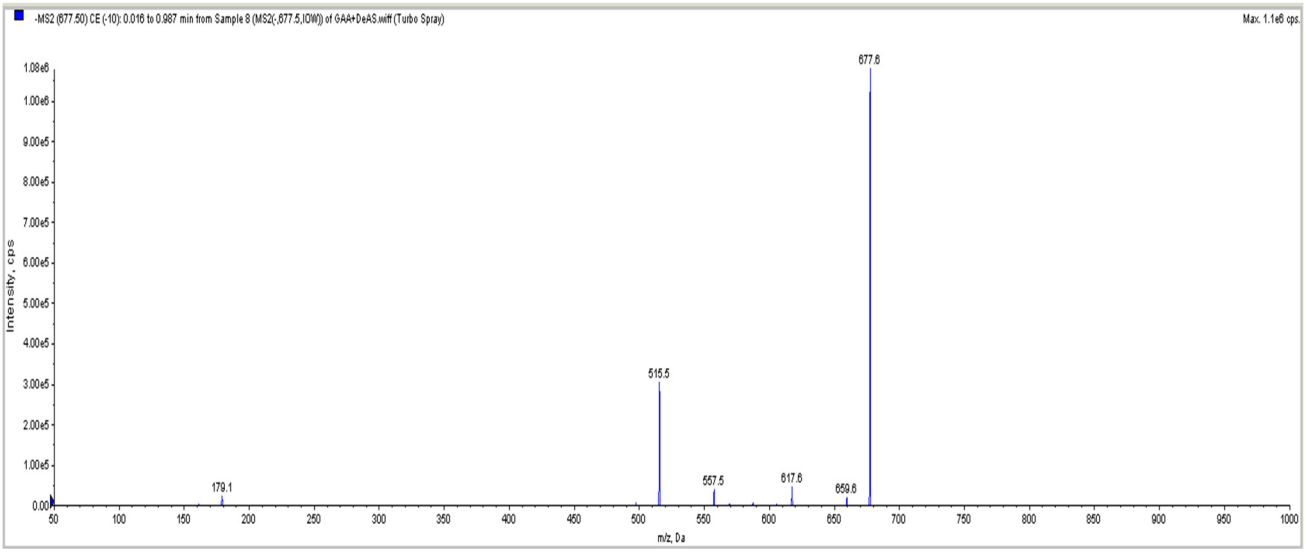



**Figure S11.** The mass-mass analysis of compound (**2**) at the negative mode. A significant signal at m/z 677.6 showed the corresponding m/z signal of molecular weight 678 of GAA-glucoside (516+180-18) at the negative mode.

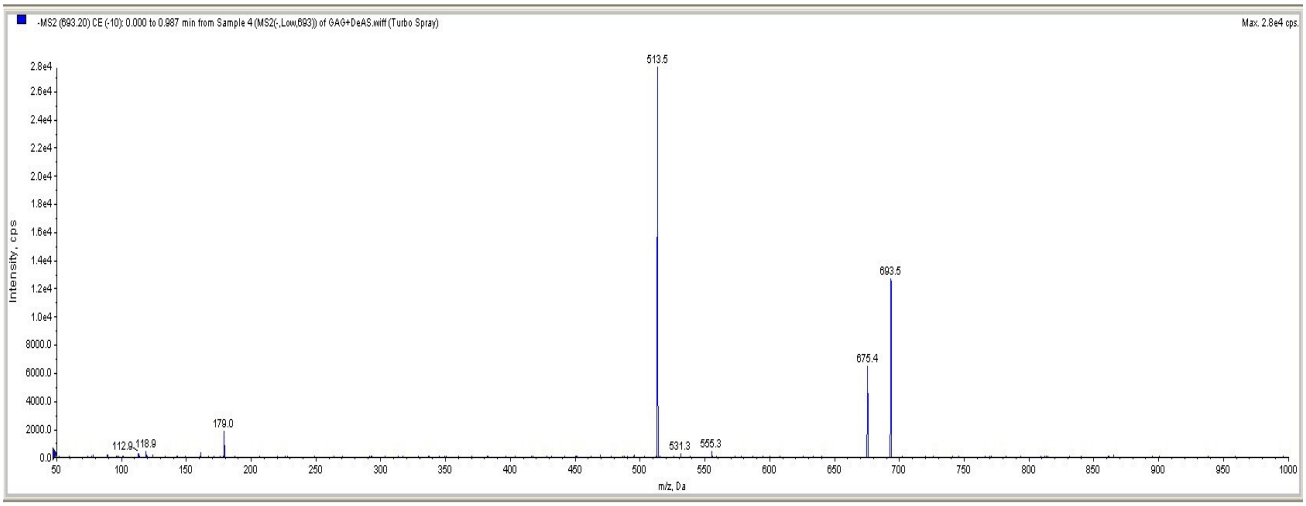



**Figure S12.** The mass-mass analysis of compound (**3**) at the negative mode. A significant signal at m/z 693.5 showed the corresponding m/z signal of molecular weight 694 of GAG-glucoside (532+180-18) at the negative mode.

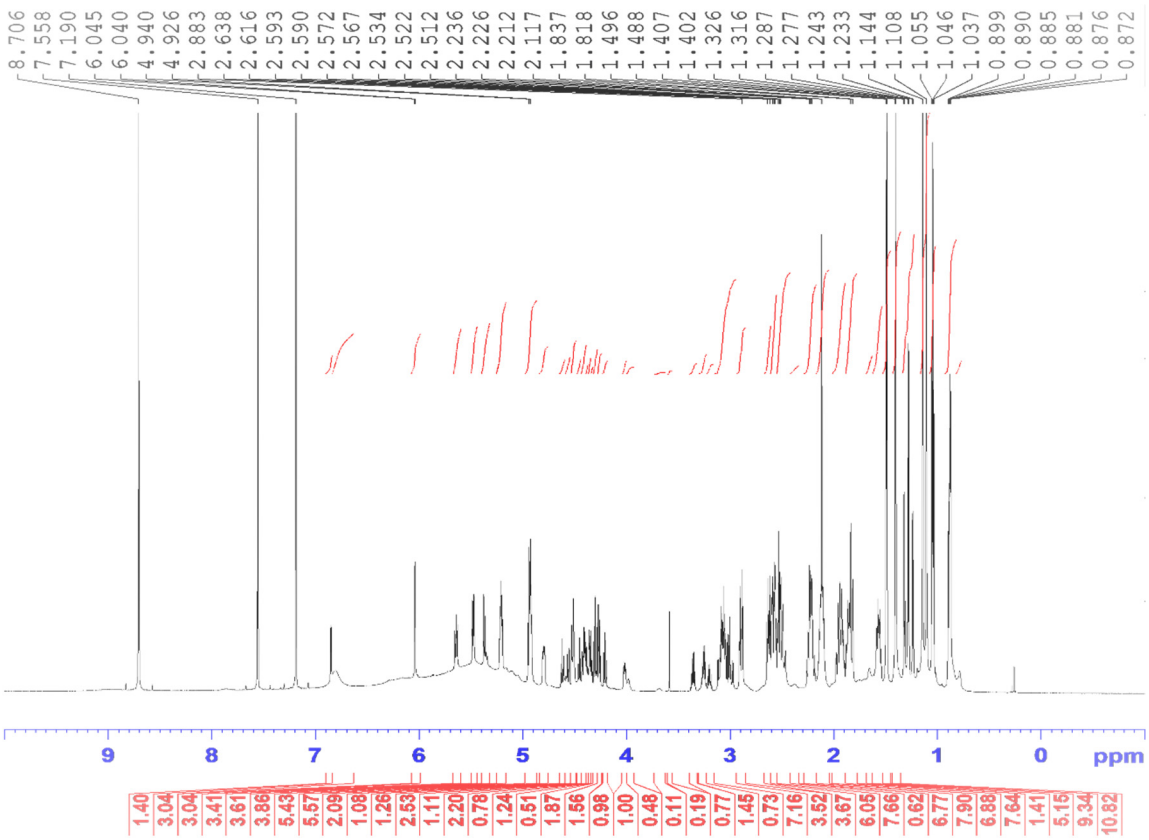



**Figure S13.** 1D NMR spectrum ($^1$H-NMR, 700 MHz, pyridine-$d_5$) of the compound (**2**).

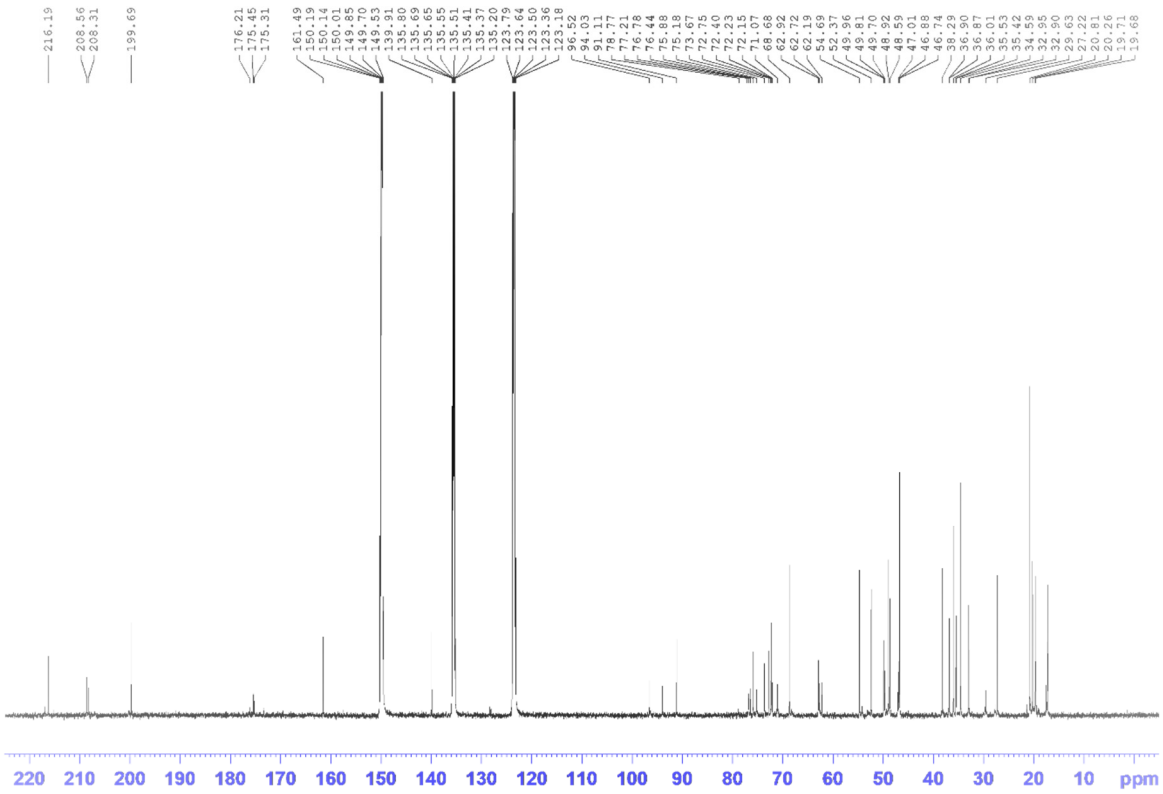



**Figure S14.** 1D NMR spectrum ($^{13}$C-NMR, 175 MHz, pyridine-$d_5$) of the compound (**2**).

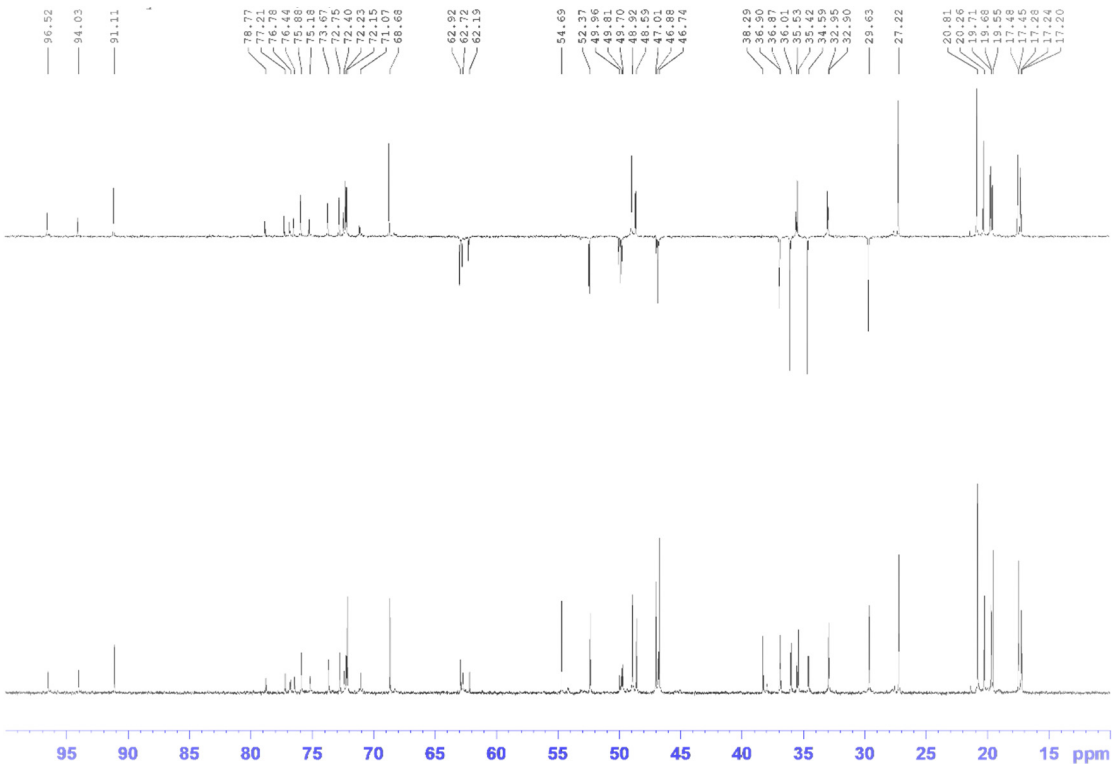



**Figure S15.** 1D NMR spectrum (DEPT-135, 175 MHz, pyridine-$d_5$) of the compound (**2**).

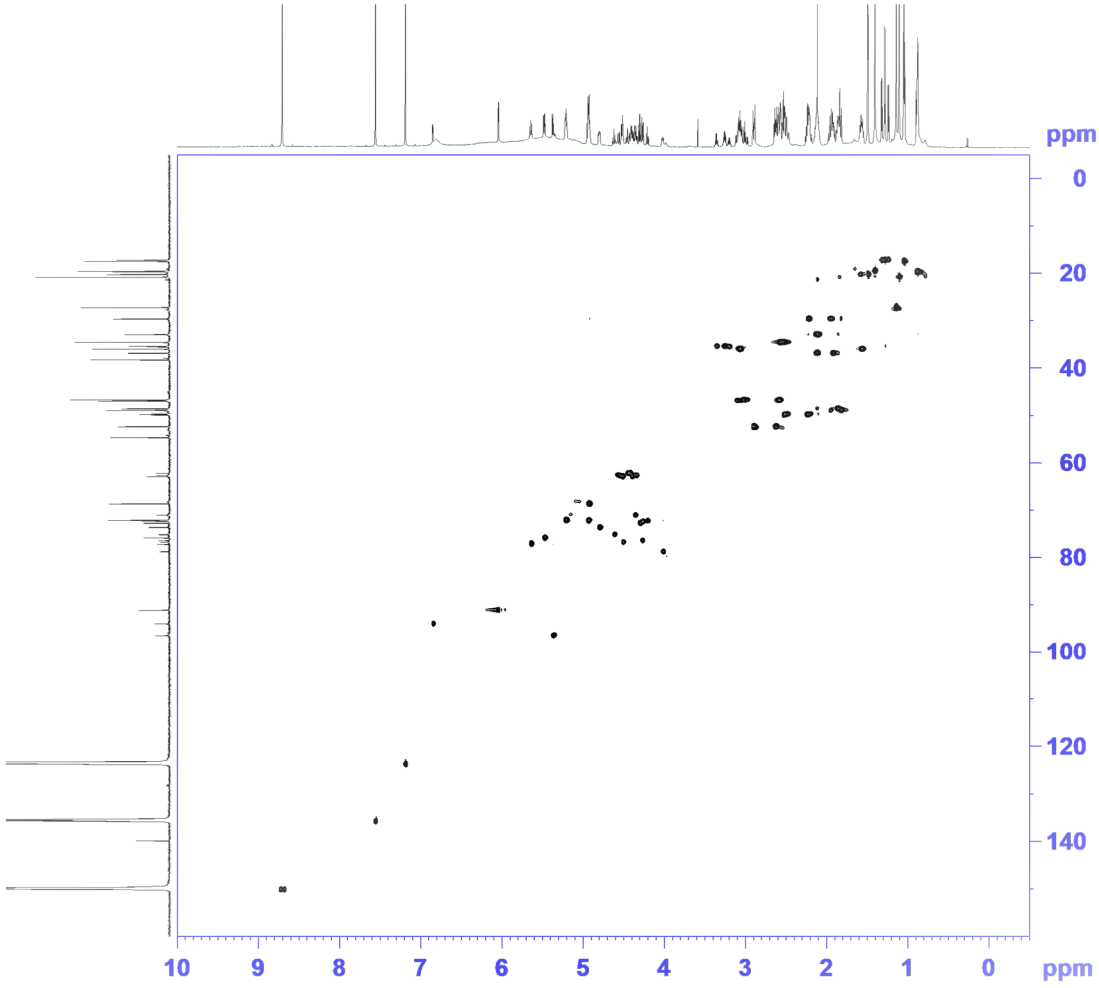


**Figure S16.** 2D NMR spectrum ($^{1}$H-$^{13}$C HSQC, 700 MHz, pyridine-$d_5$) of the compound (**2**).

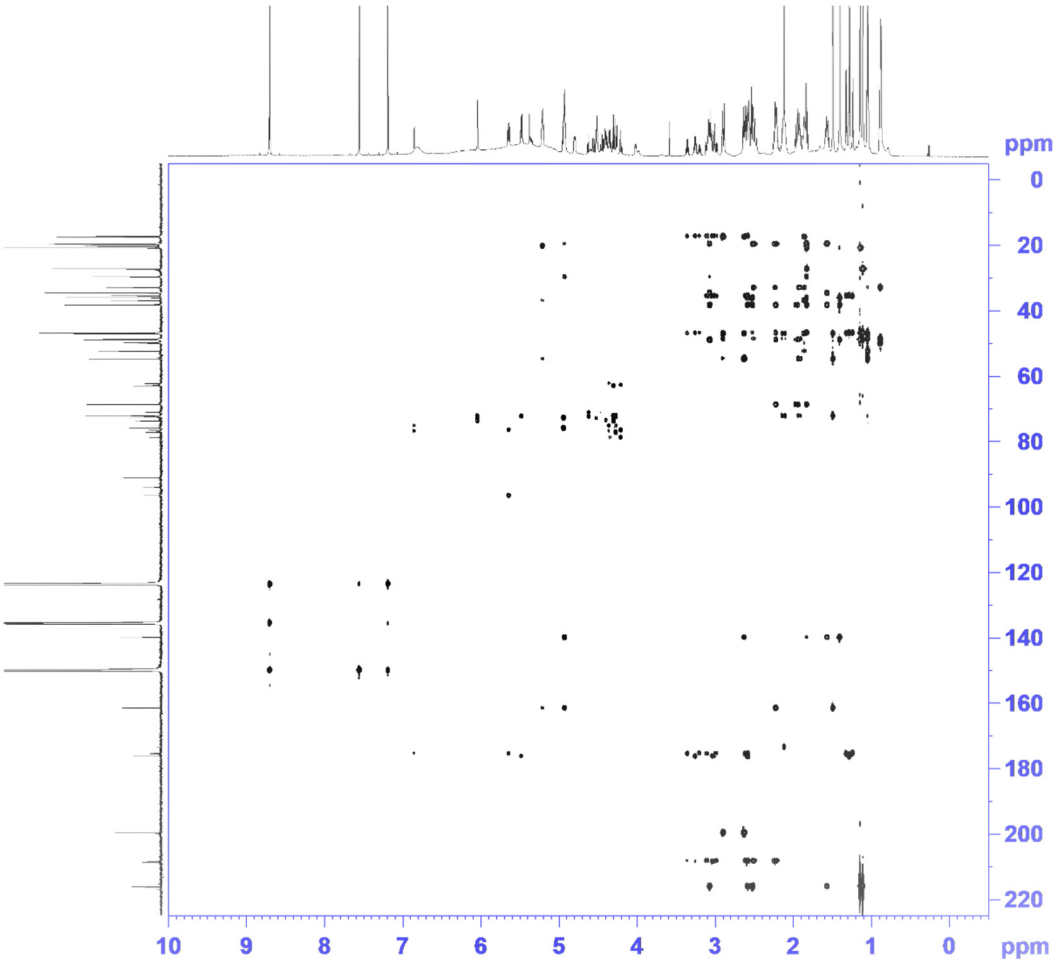



**Figure S17.** 2D NMR spectrum ($^{1}$H-$^{13}$C HMBC, 700 MHz, pyridine-$d_5$) of the compound (**2**).

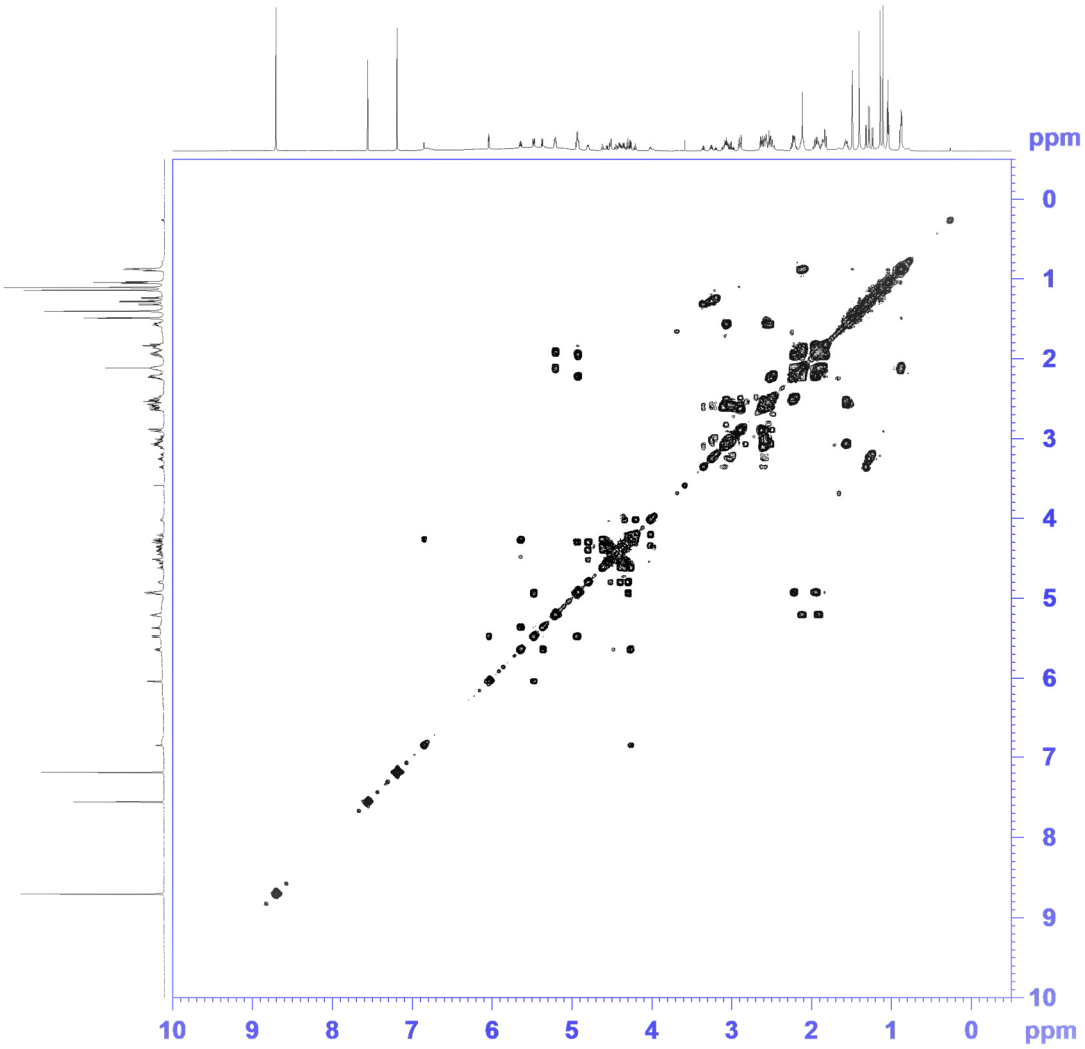



**Figure S18.** 2D NMR spectrum ($^{1}$H-$^{1}$H COSY, 700 MHz, pyridine-$d_5$) of the compound (**2**).

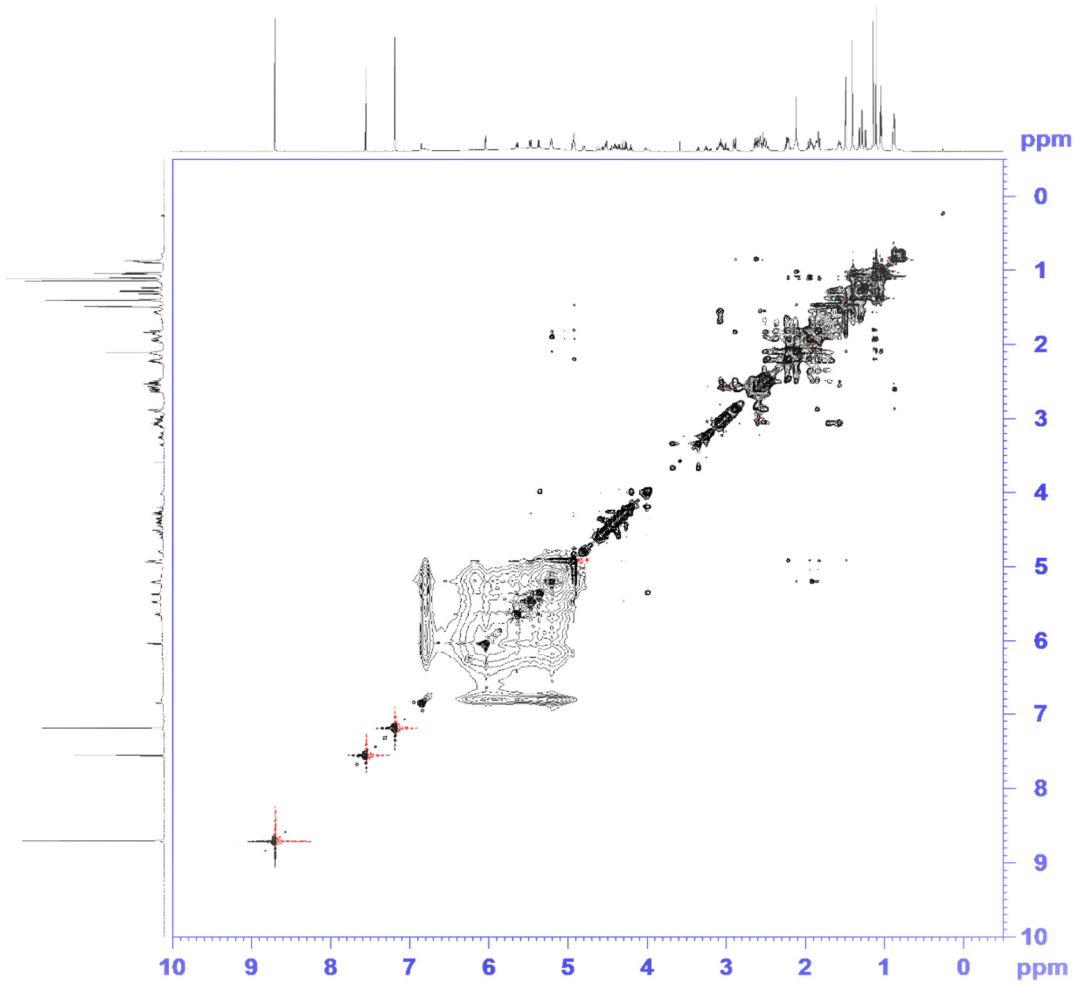



**Figure S19.** 2D NMR spectrum ($^{1}$H-$^{1}$H NOESY, 700 MHz, pyridine-$d_5$) of the compound (**2**).

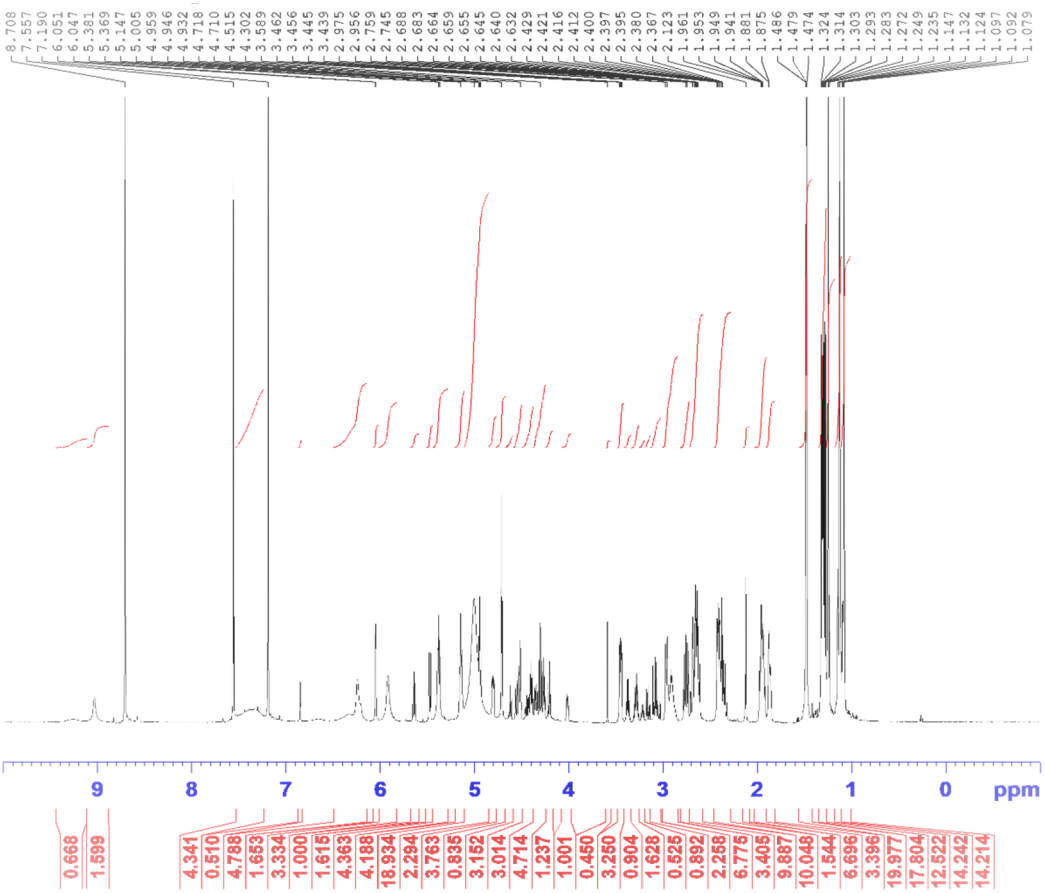



**Figure S20.** 1D NMR spectrum ($^1$H-NMR, 700 MHz, pyridine-$d_5$) of the compound (**3**).

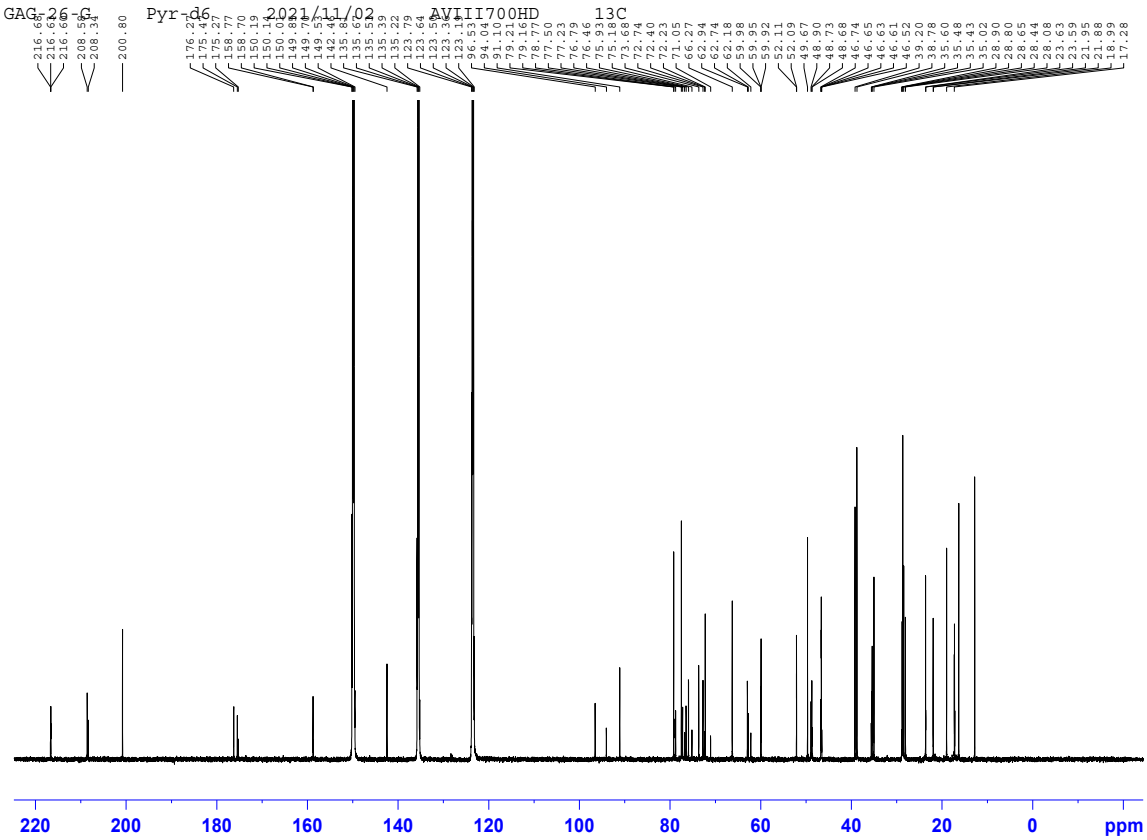



**Figure S21.** 1D NMR spectrum ($^{13}$C-NMR, 175 MHz, pyridine-$d_5$) of the compound (**3**).

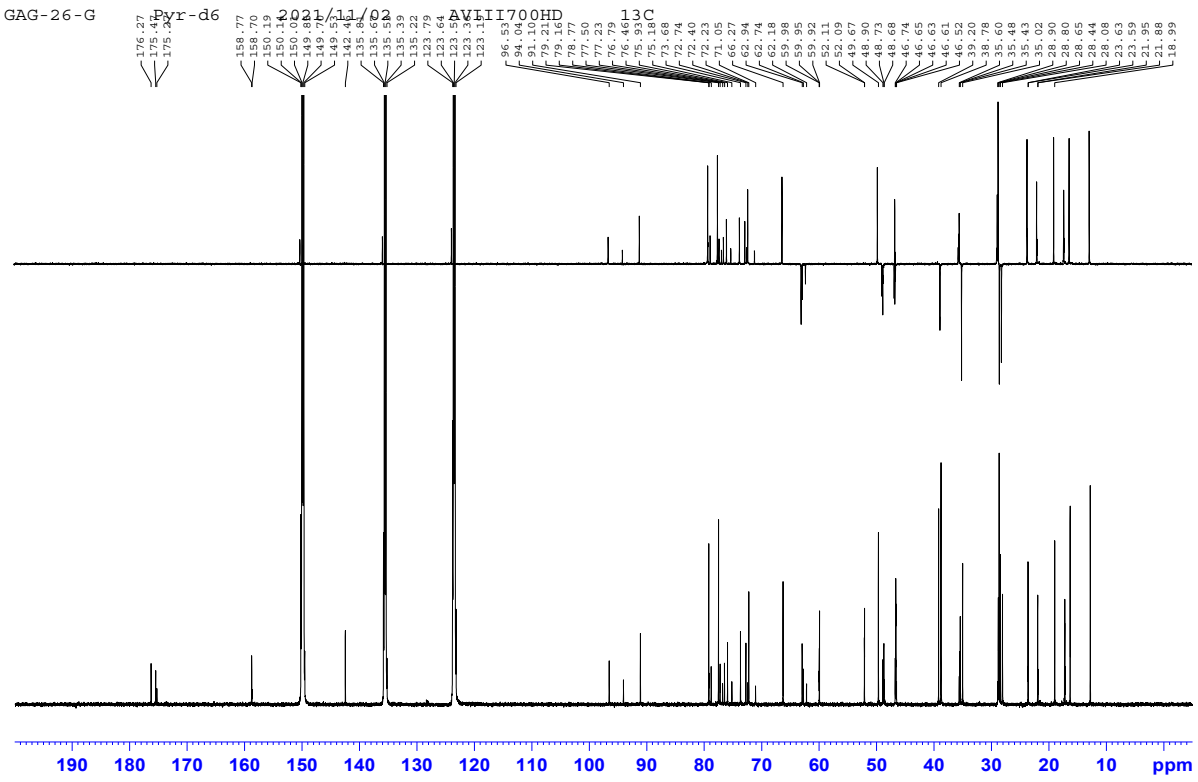



**Figure S22.** 1D NMR spectrum (DEPT-135, 175 MHz, pyridine-$d_5$) of the compound (**3**).

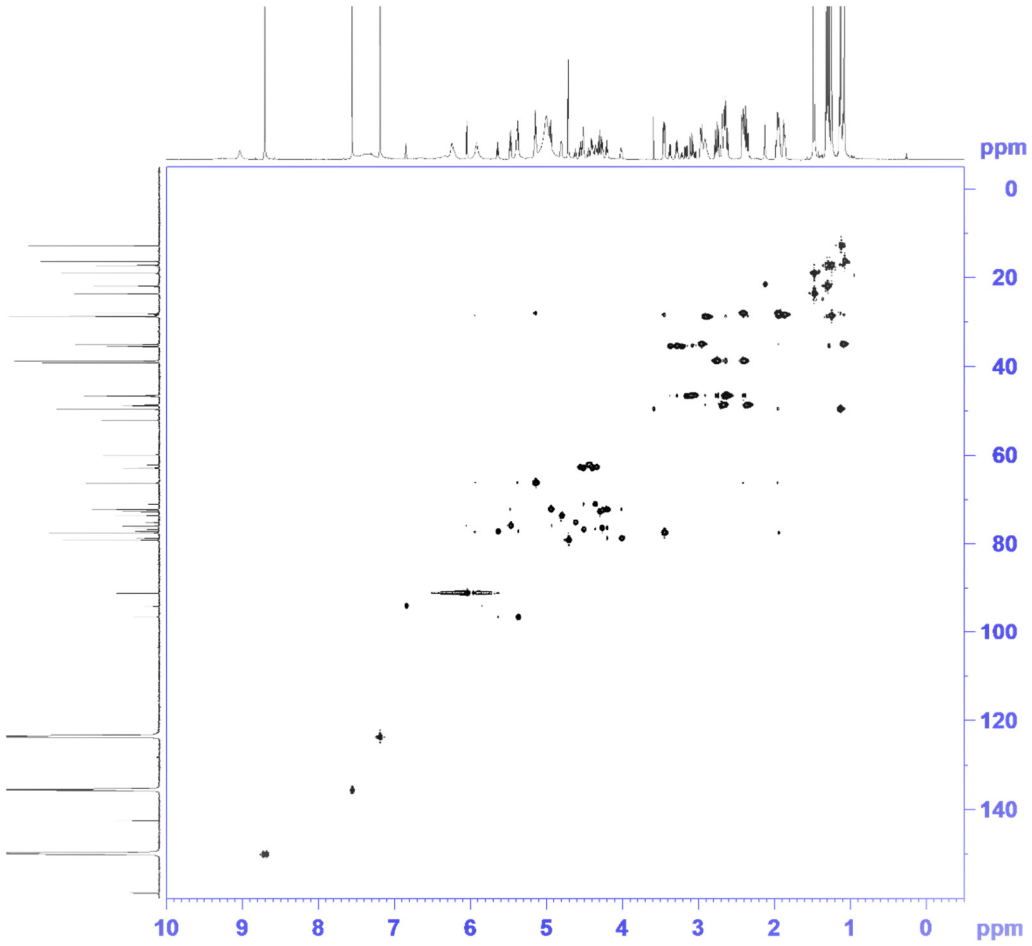


**Figure S23.** 2D NMR spectrum ($^{1}$H-$^{13}$C HSQC, 700 MHz, pyridine-$d_5$) of the compound (**3**).

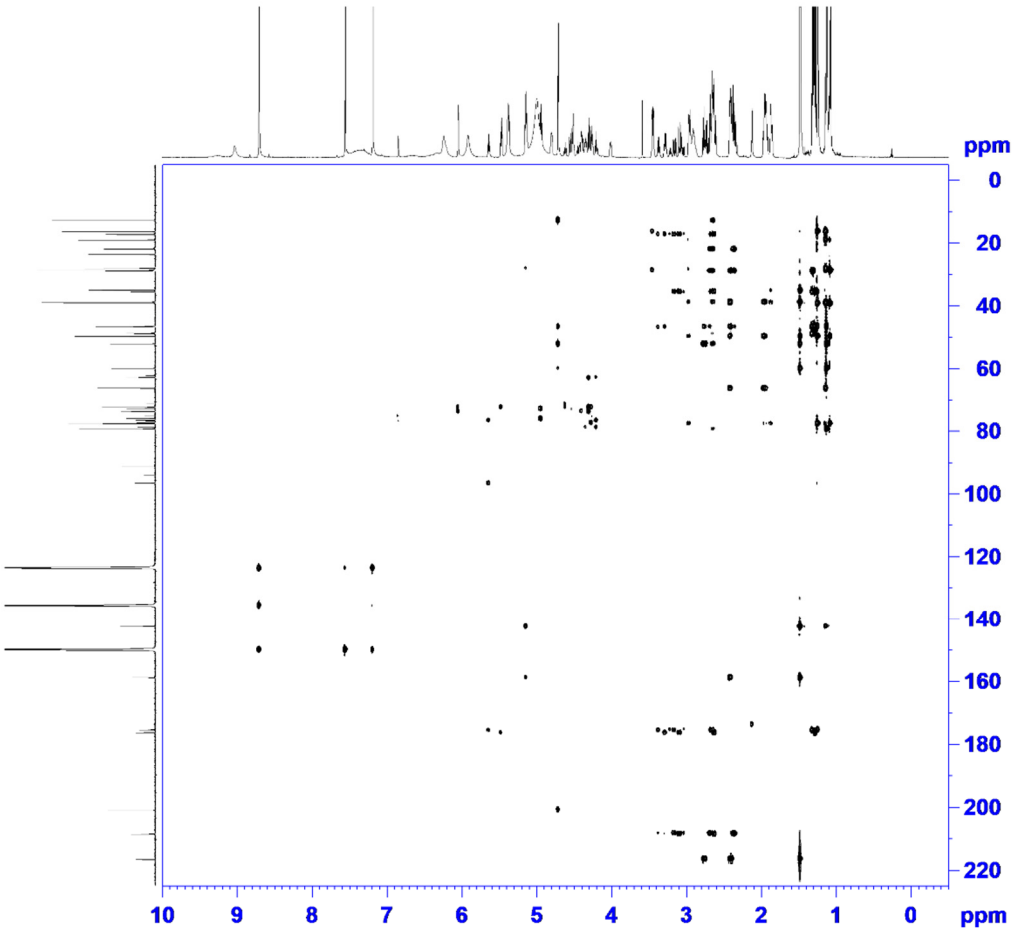



**Figure S24.** 2D NMR spectrum ($^{1}$H-$^{13}$C HMBC, 700 MHz, pyridine-$d_5$) of the compound (**3**).

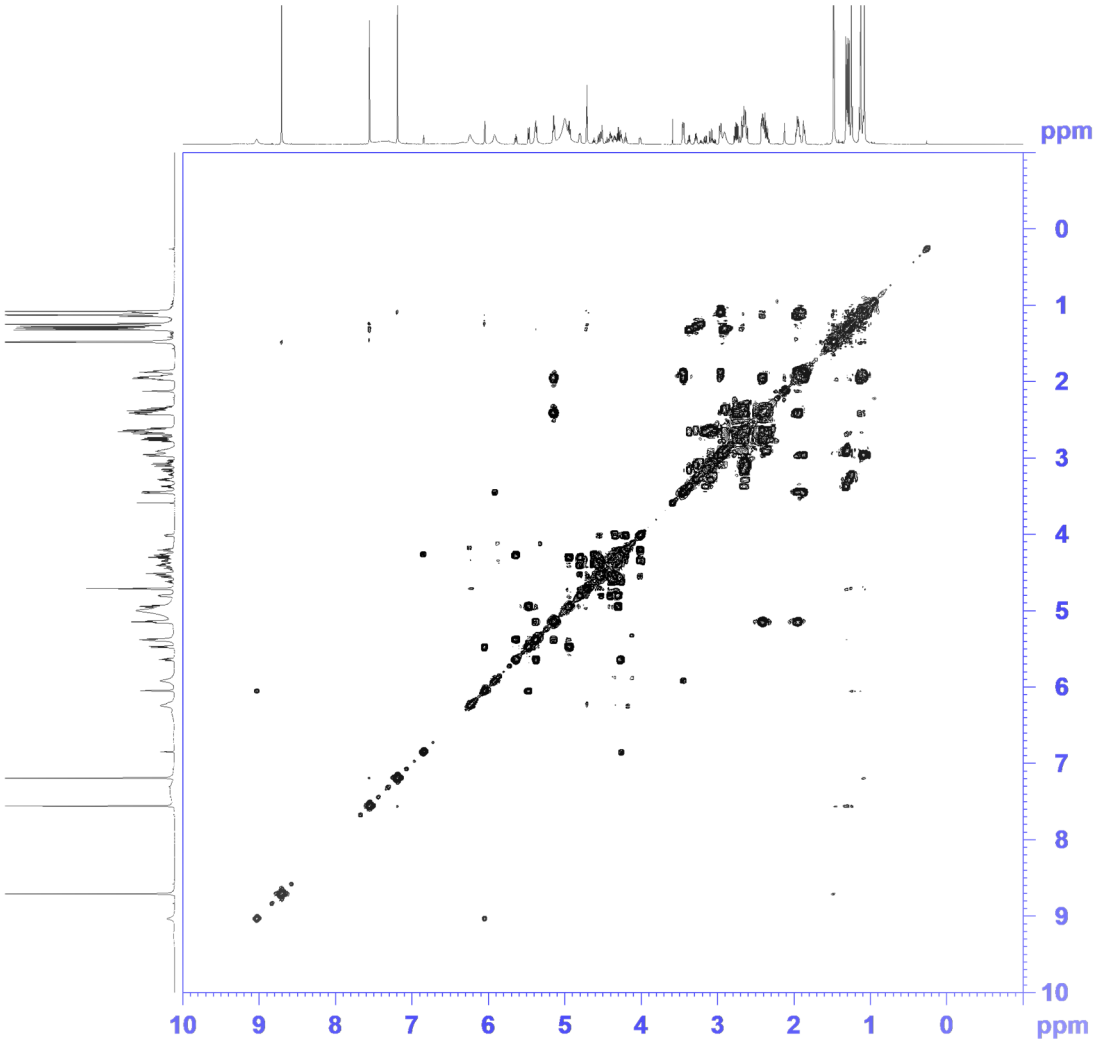



**Figure S25.** 2D NMR spectrum ($^{1}$H-$^{1}$H COSY, 700 MHz, pyridine-$d_5$) of the compound (**3**).

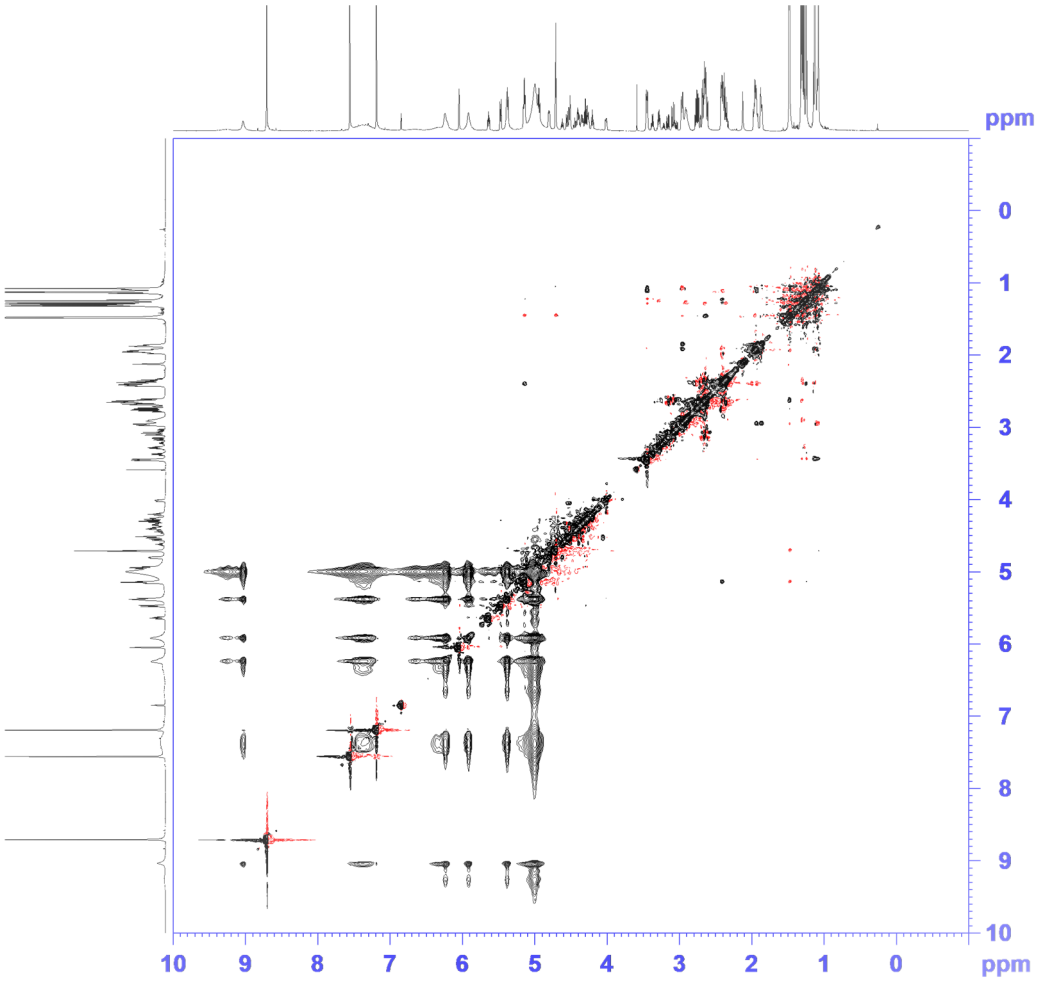



**Figure S26.** 2D NMR spectrum ($^{1}$H-$^{1}$H NOESY, 700 MHz, pyridine-$d_5$) of the compound (**3**).