# Supplementary Information

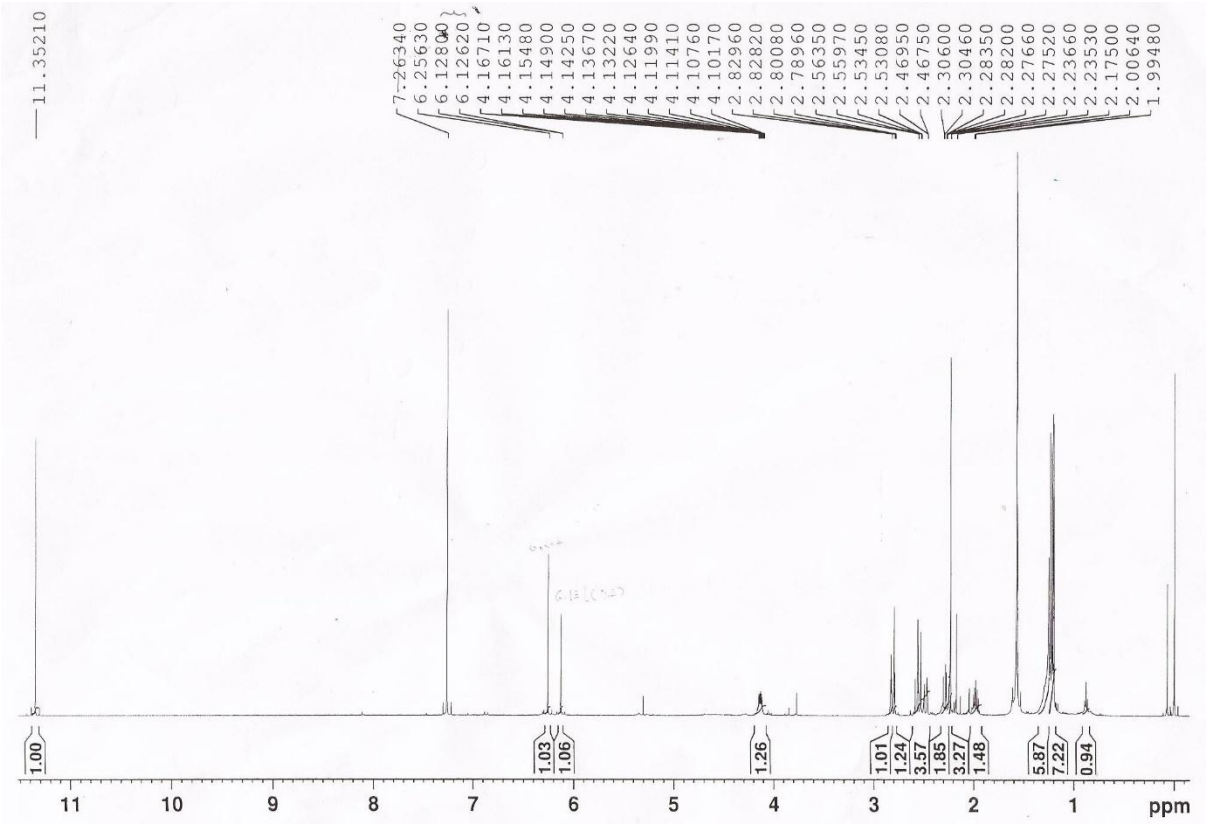


**Figure S1.** $^{1}$H NMR spectrum of compound **1** ($CDCl_3$, 500.13 MHz).

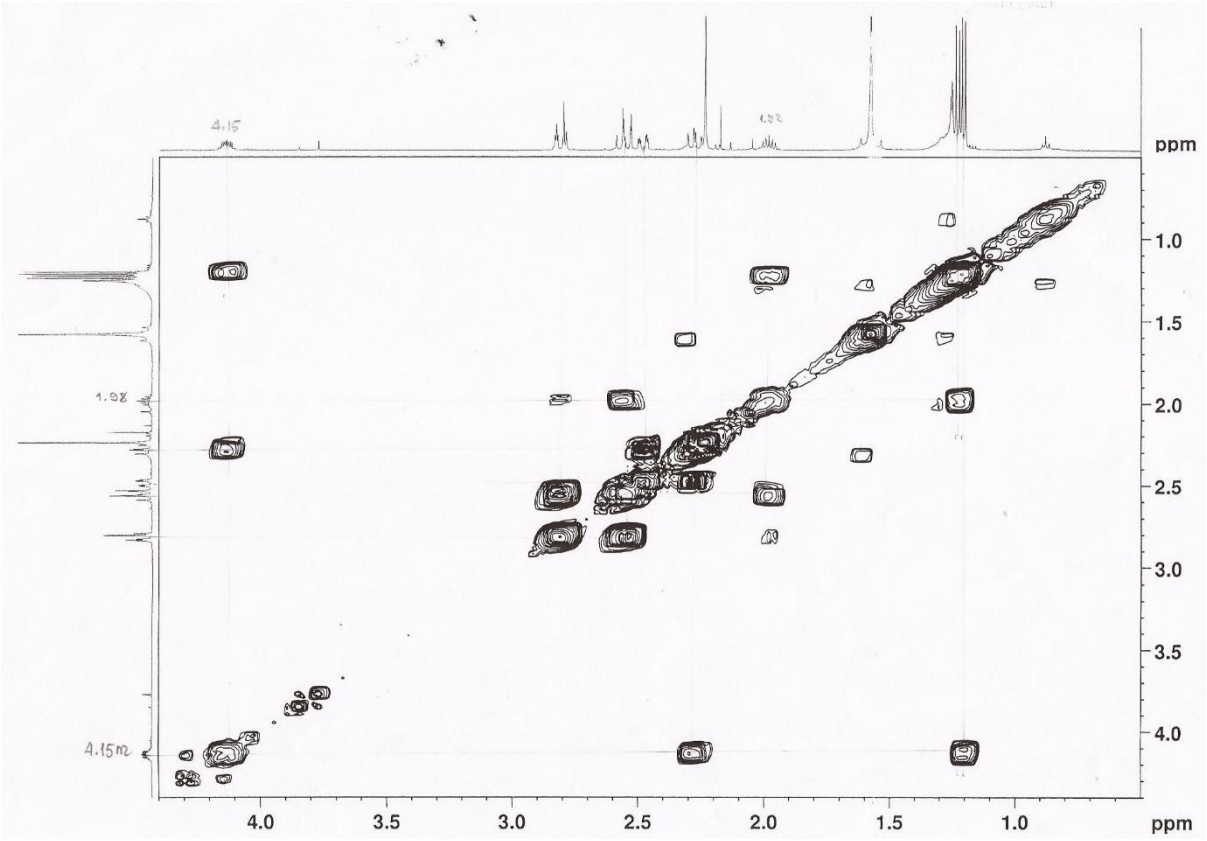


**Figure S2.** COSY spectrum of compound **1** ($CDCl_3$, 500.13 MHz).

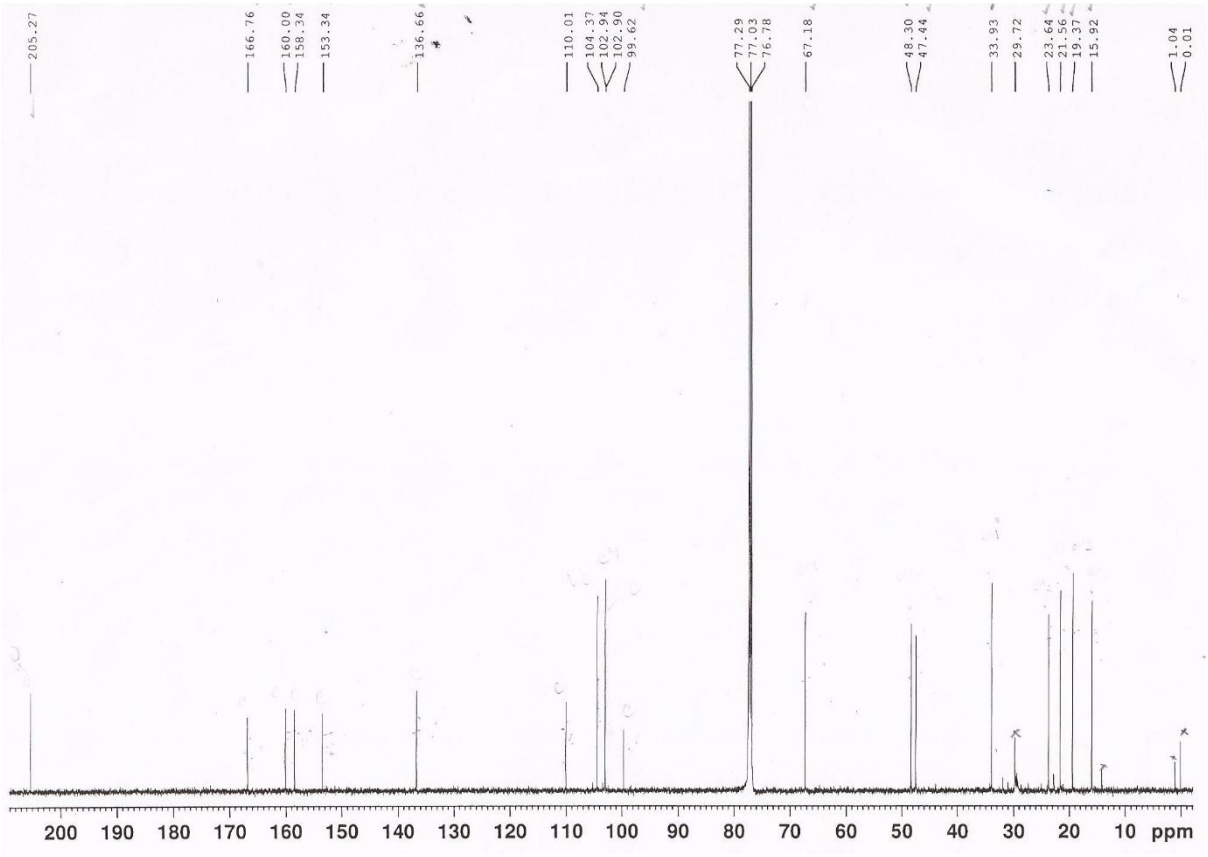


**Figure S3.** $^{13}C$ NMR spectrum of compound **1** ($CDCl_3$, 125.8 MHz).

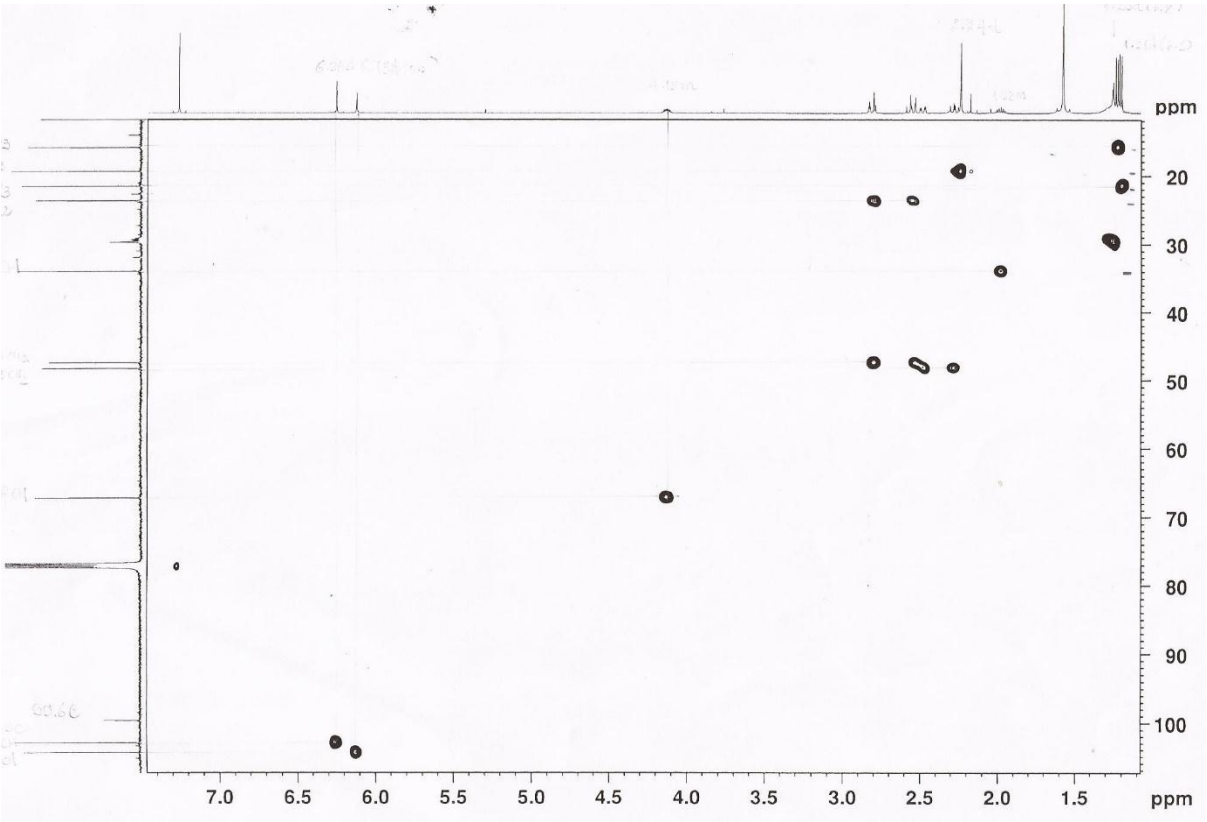


**Figure S4.** HSQC spectrum of compound **1** ($CDCl_3$, 500.13 MHz).

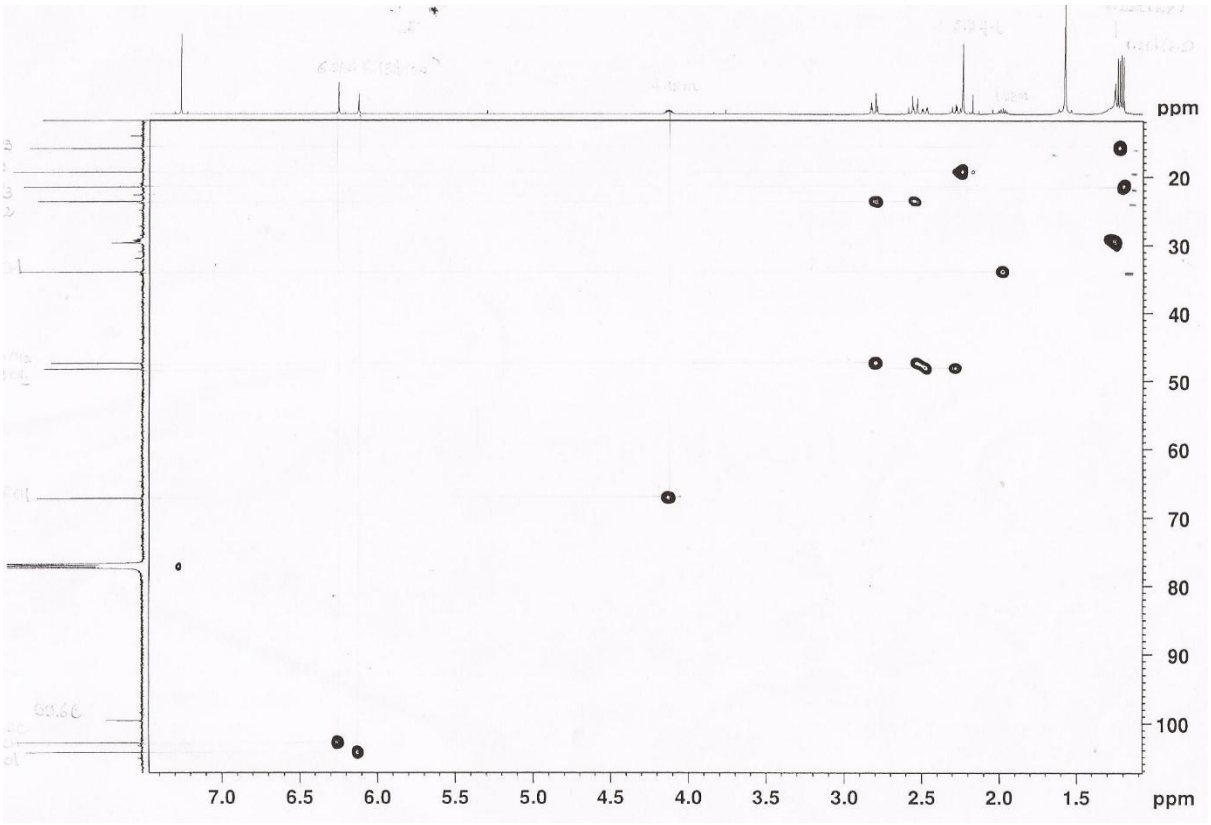


**Figure S5.** HMBC spectrum of compound **1** ($CDCl_3$, 500.13 MHz).

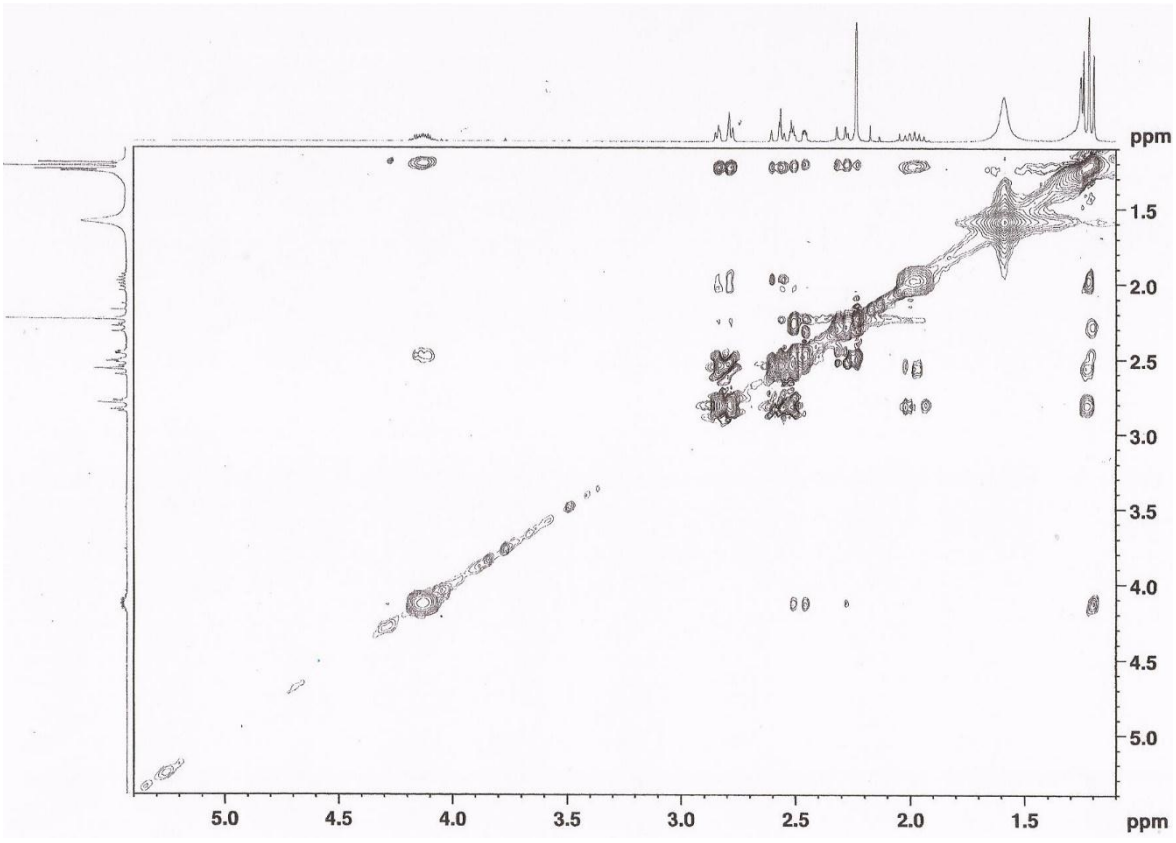


**Figure S6.** NOESY spectrum of compound **1** ($CDCl_3$, 500.13 MHz).

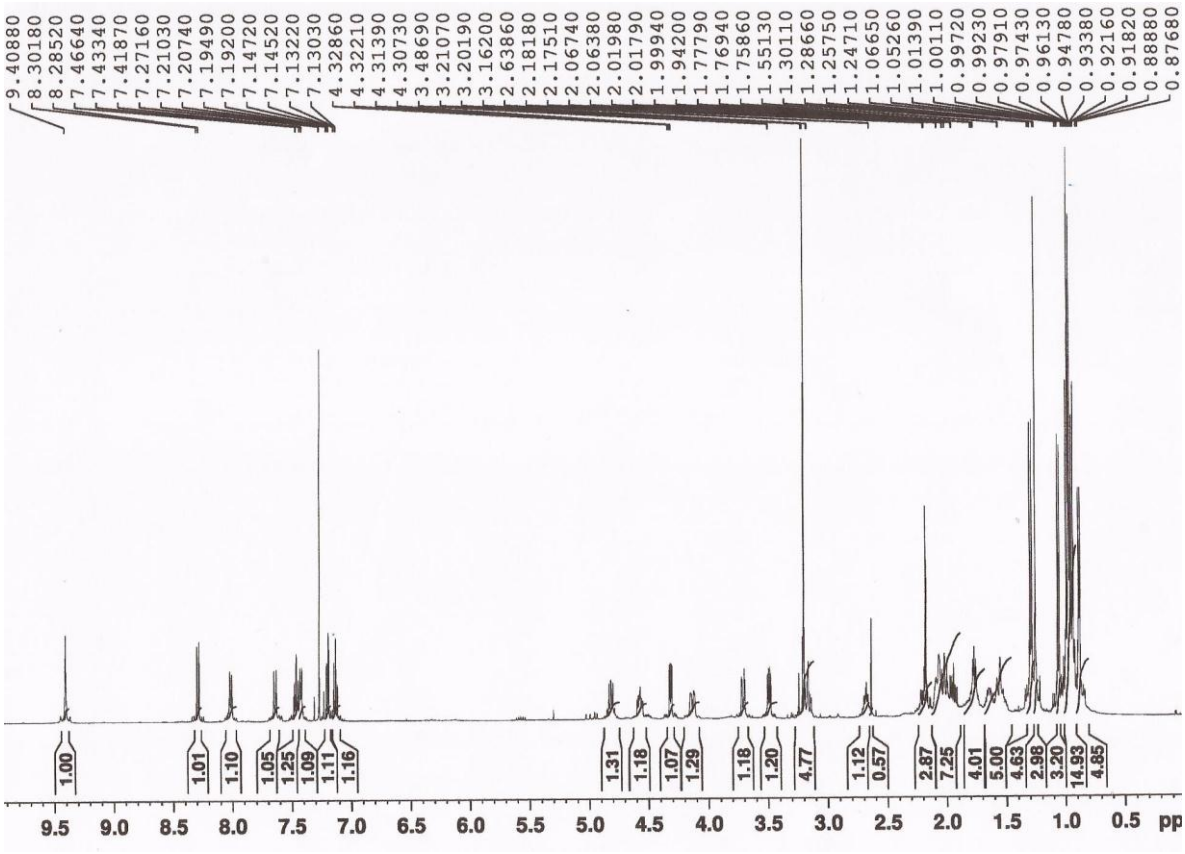


**Figure S7.** $^{1}$H NMR spectrum of compound **2** ($CDCl_3$, 500.13 MHz).

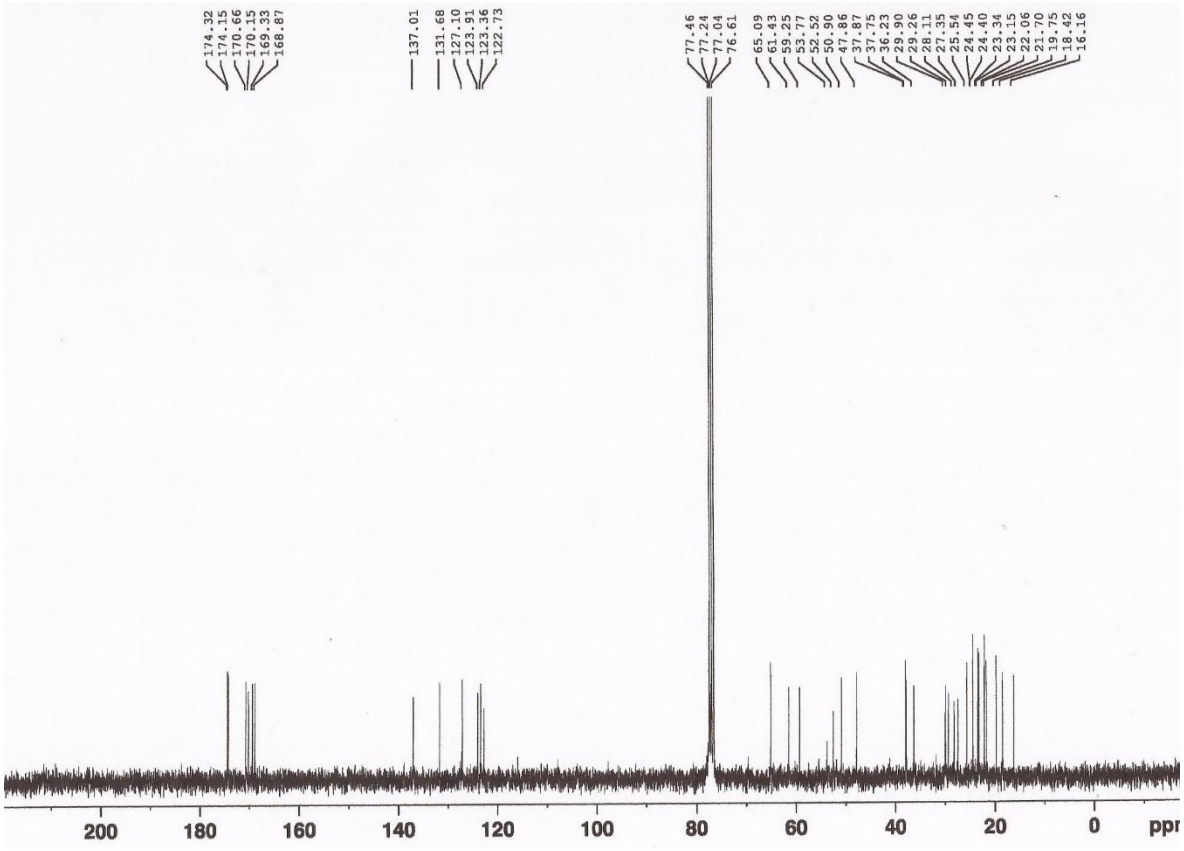


**Figure S8.** $^{13}$C NMR spectrum of compound **2** ($CDCl_3$, 125.8 MHz).

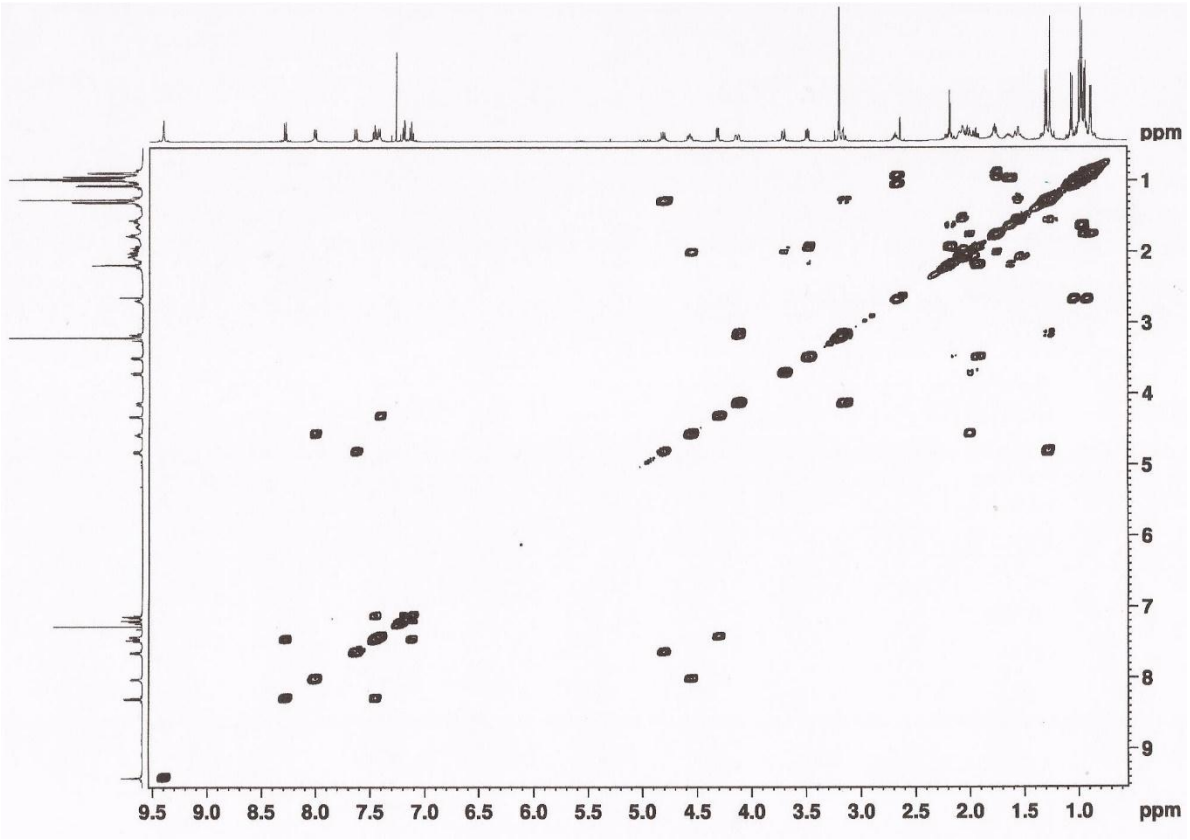


**Figure S9.** COSY spectrum of compound **2** ($CDCl_3$, 500.13 MHz).

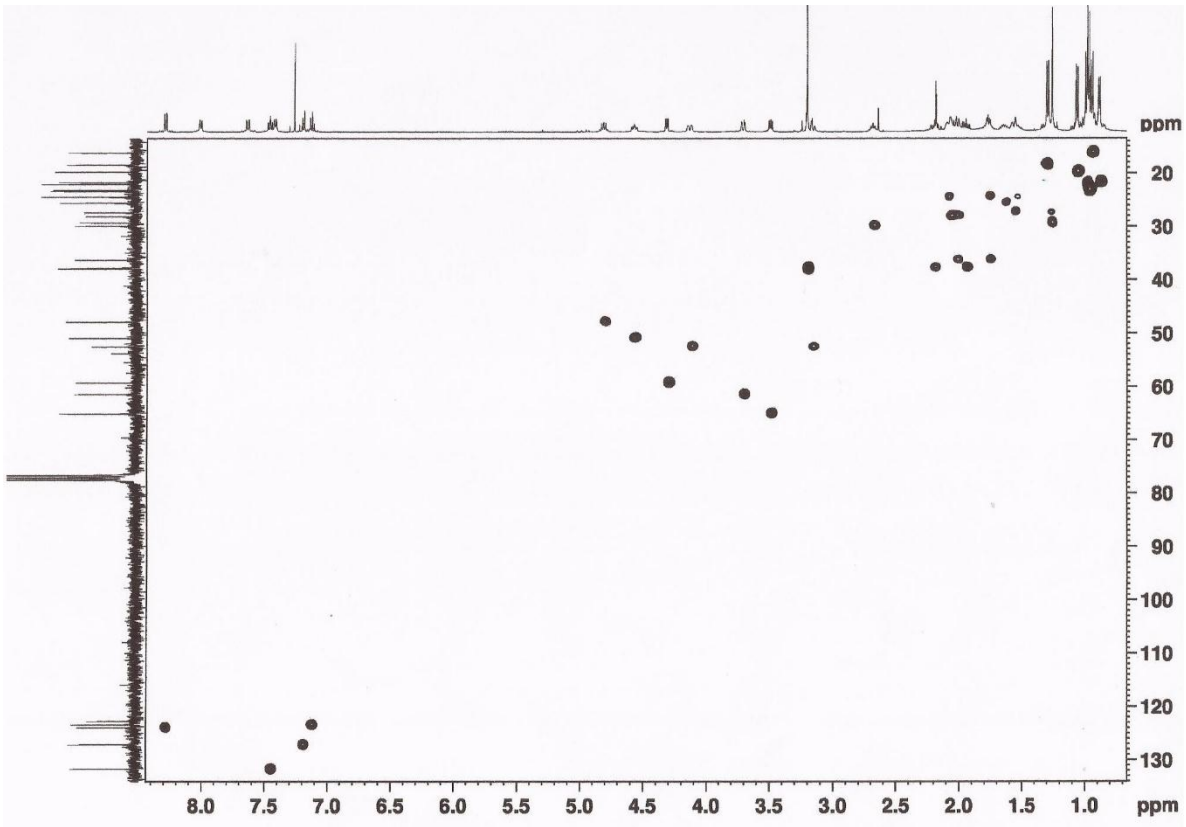


**Figure S10.** HSQC spectrum of compound **2** ($CDCl_3$, 500.13 MHz).

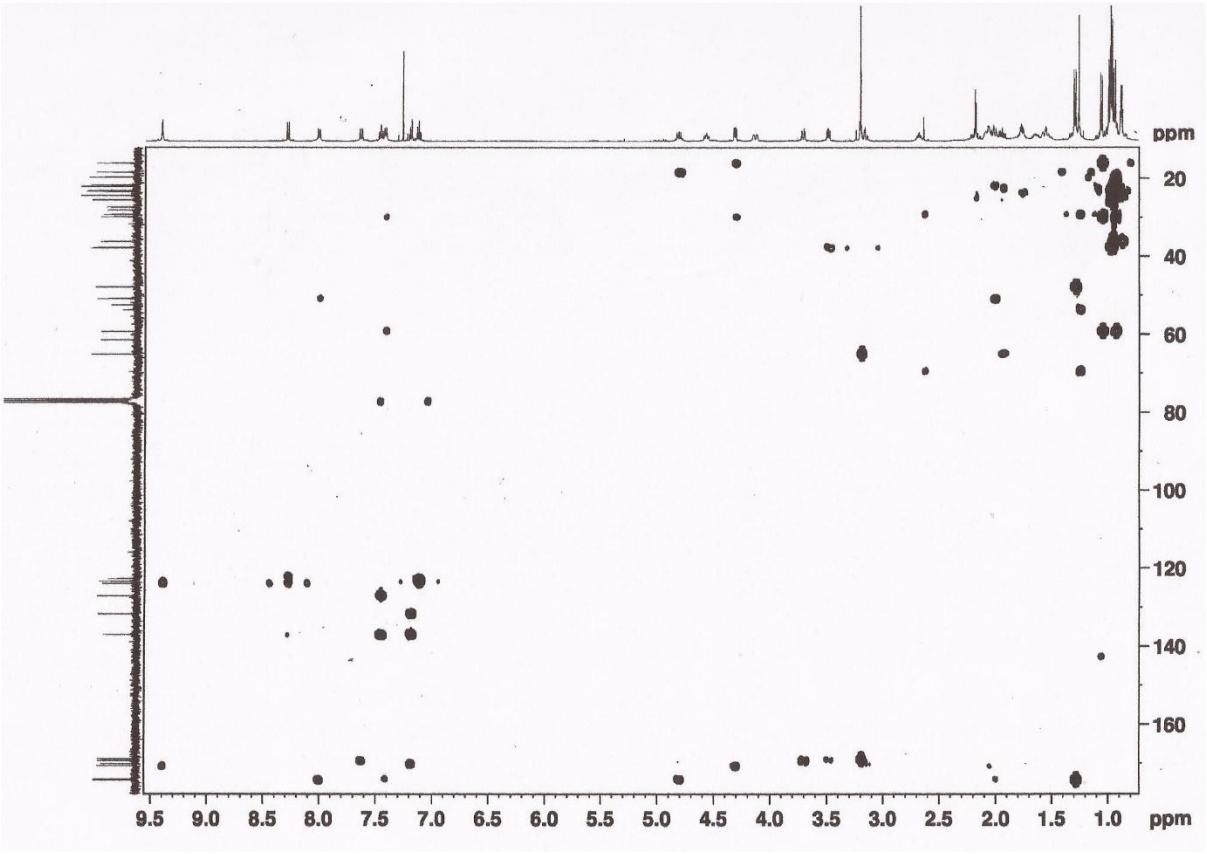


**Figure S11.** HMBC spectrum of compound **2** ($CDCl_3$, 500.13 MHz).

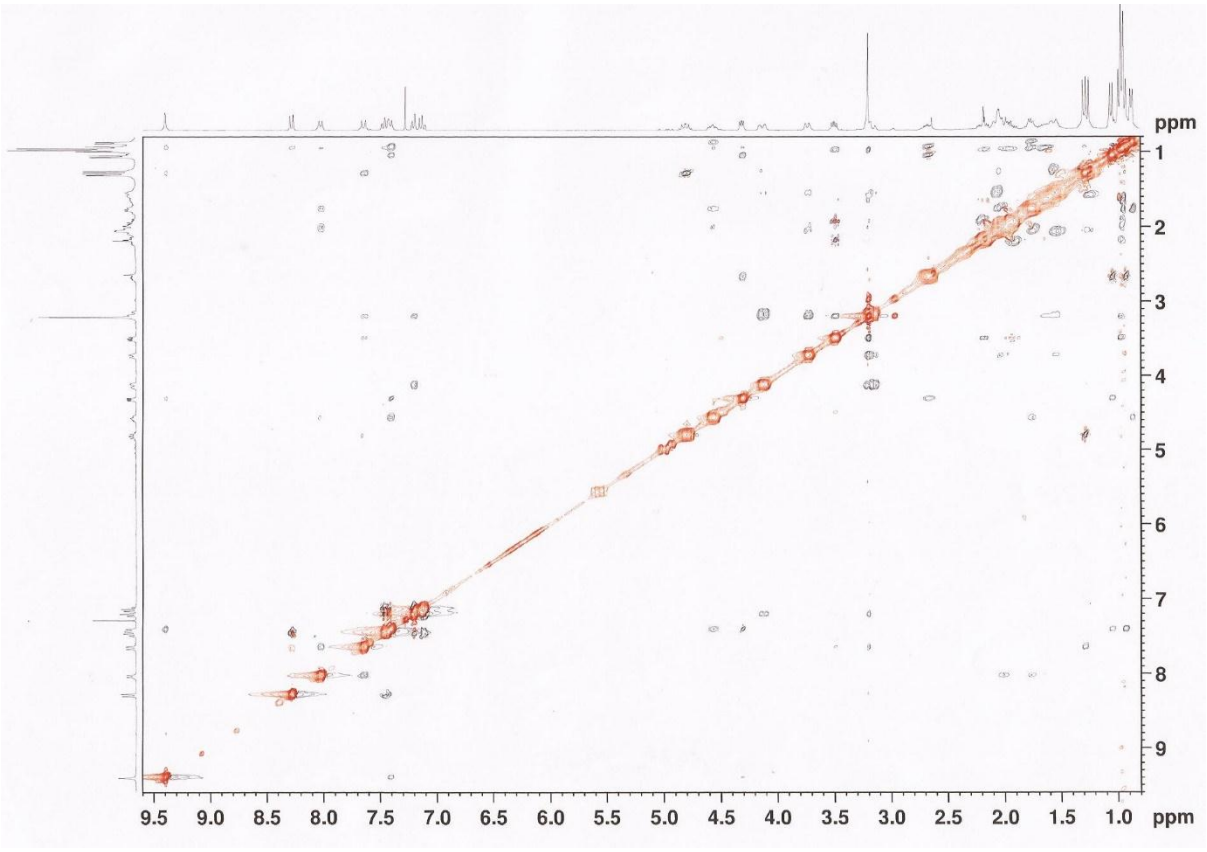


**Figure S12.** NOESY spectrum of compound **2** ($CDCl_3$, 500.13 MHz).

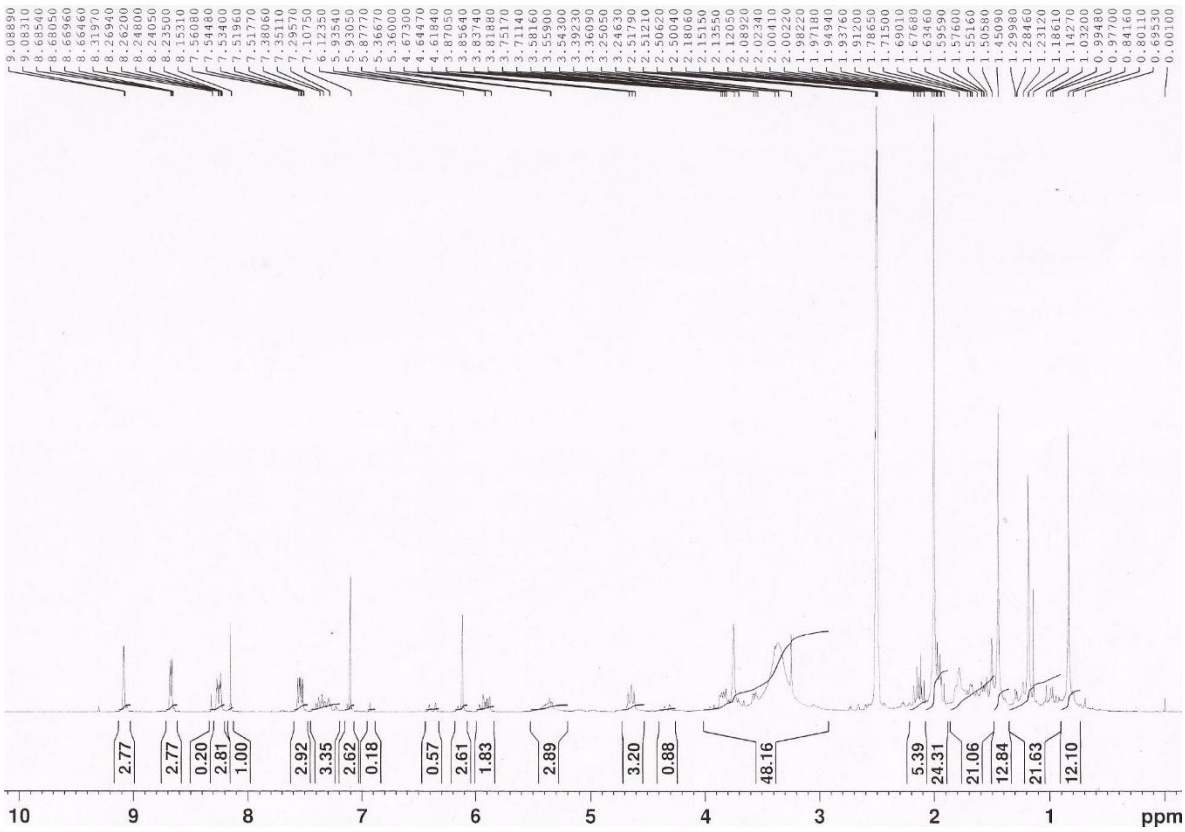


**Figure S13.** $^{1}$H NMR spectrum of compound **3** (DMSO, 300.13 MHz).

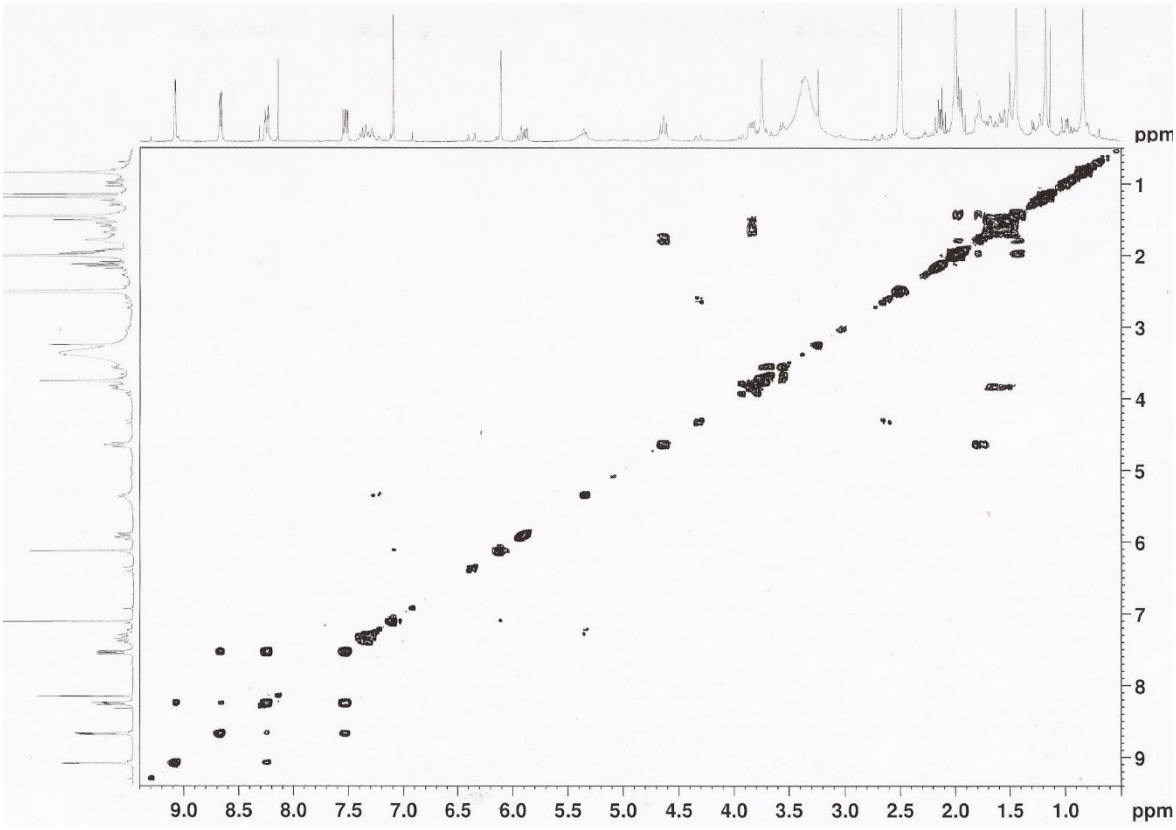


**Figure S14.** COSY spectrum of compound **3** (DMSO, 300.13 MHz).

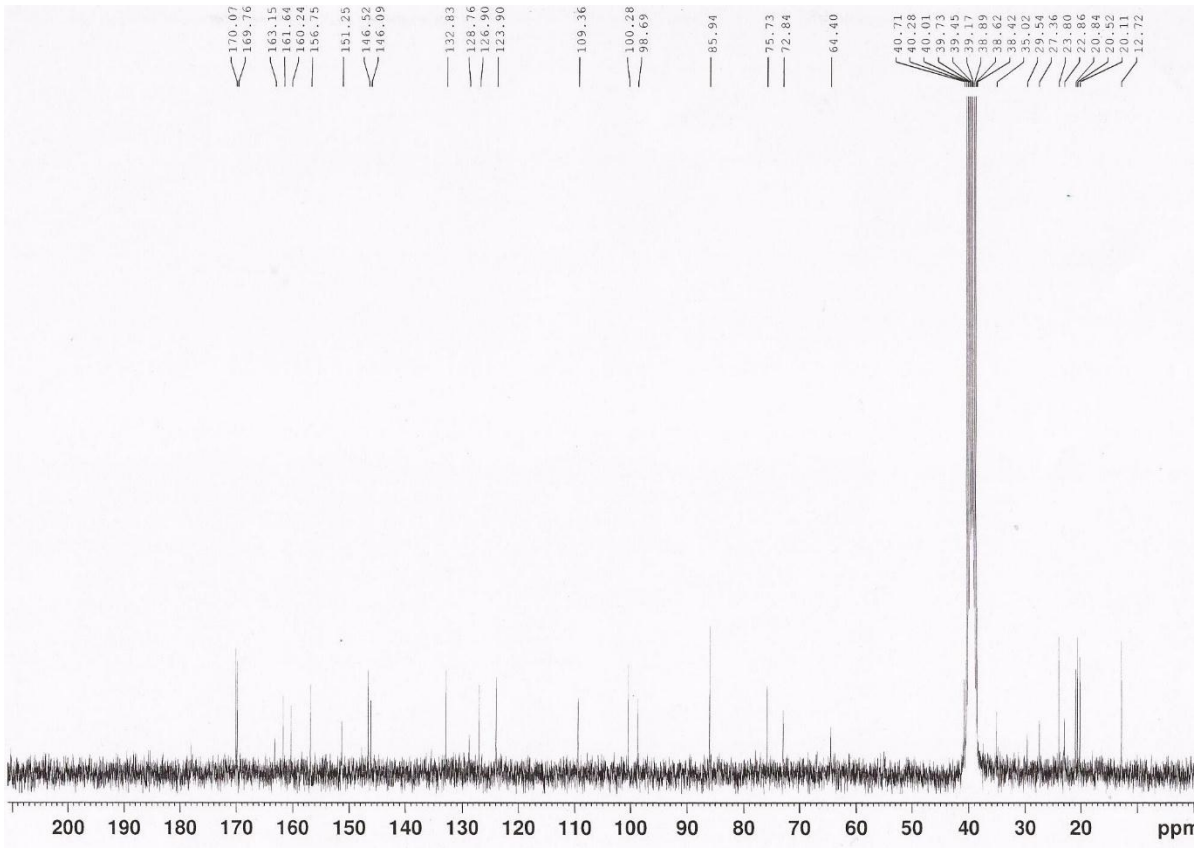


**Figure S15.** $^{13}$C NMR spectrum of compound **3** (DMSO, 75.47 MHz).

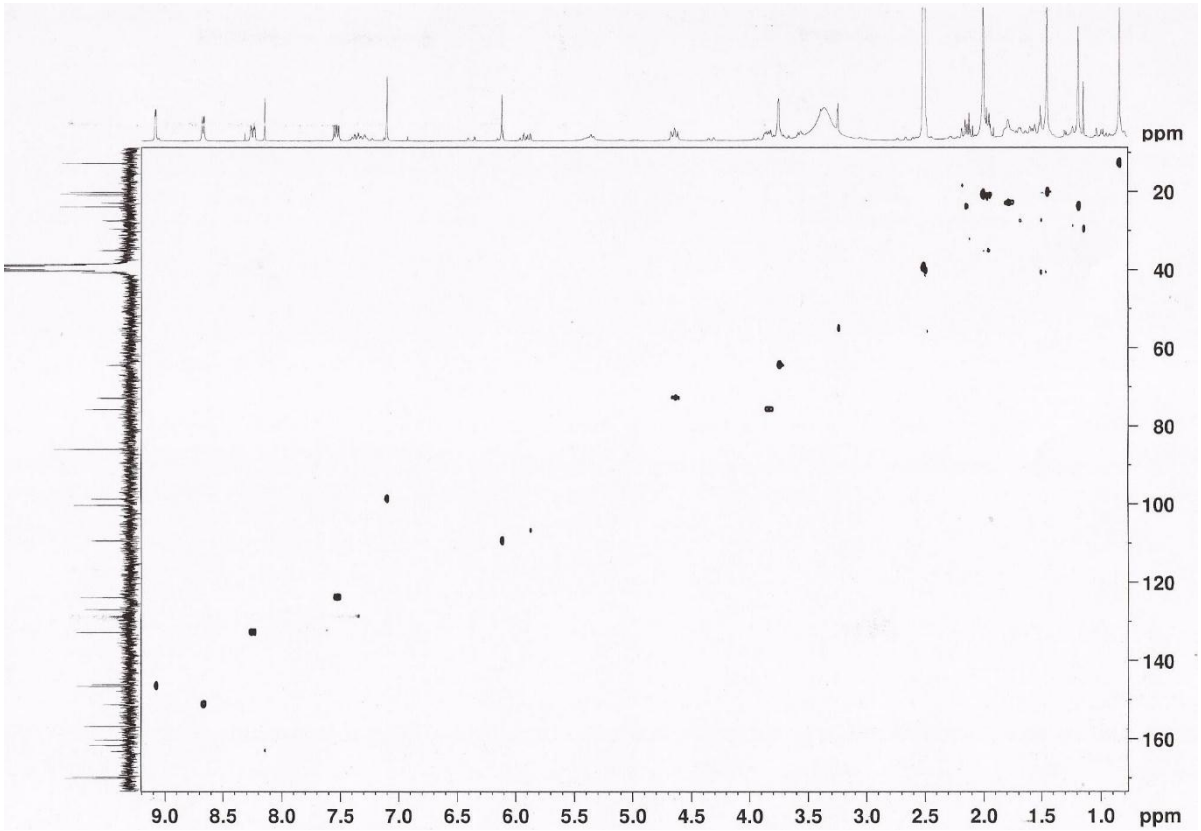


**Figure S16.** HSQC spectrum of compound **3** (DMSO, 300.13 MHz).

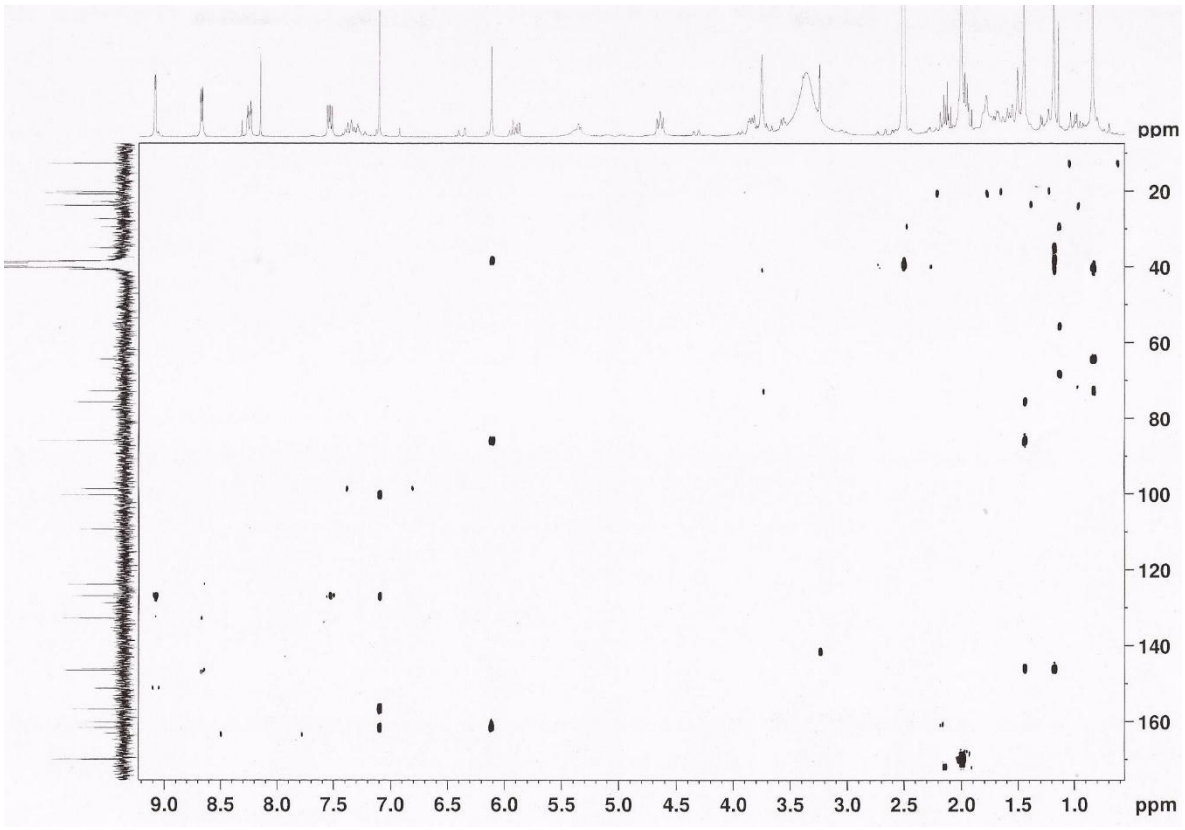


**Figure S17.** HMBC spectrum of compound **3** (DMSO, 300.13 MHz).

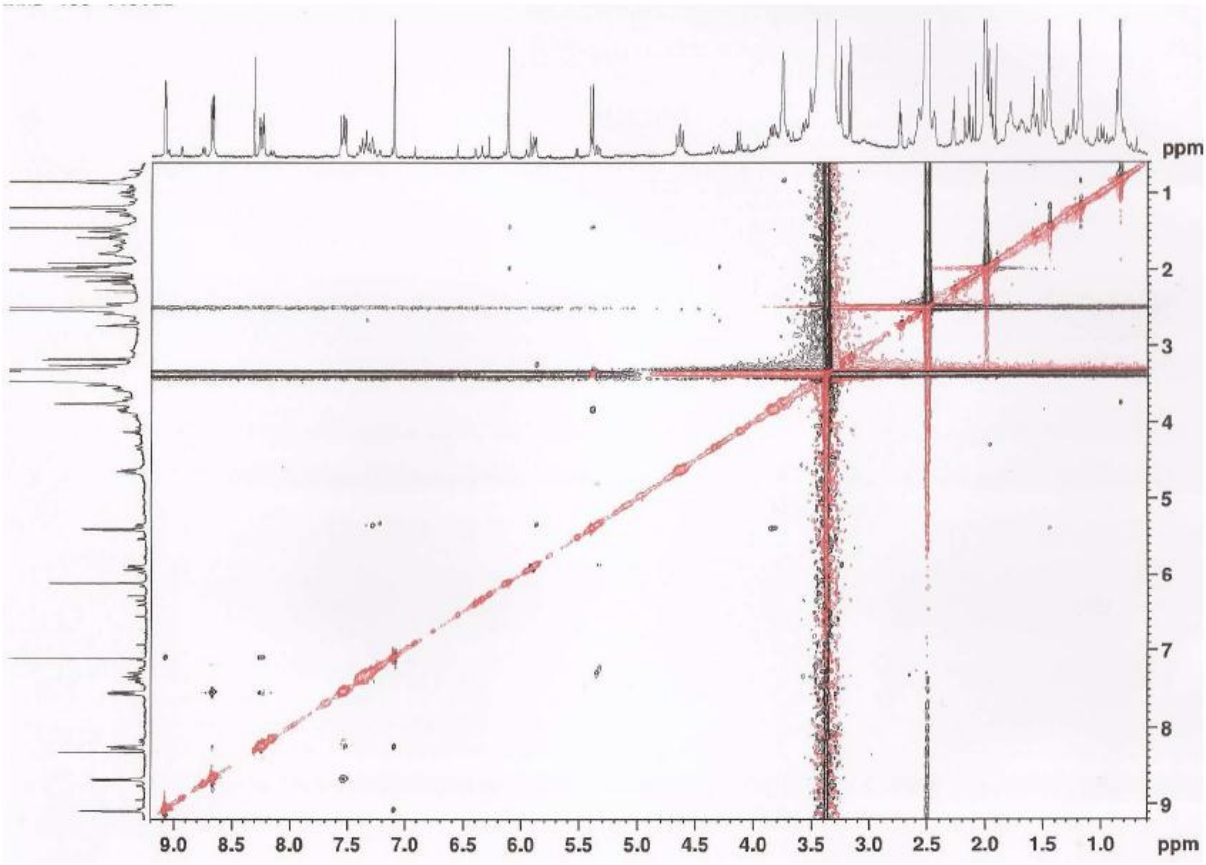


**Figure S18.** NOESY spectrum of compound **3** (DMSO, 300.13 MHz).

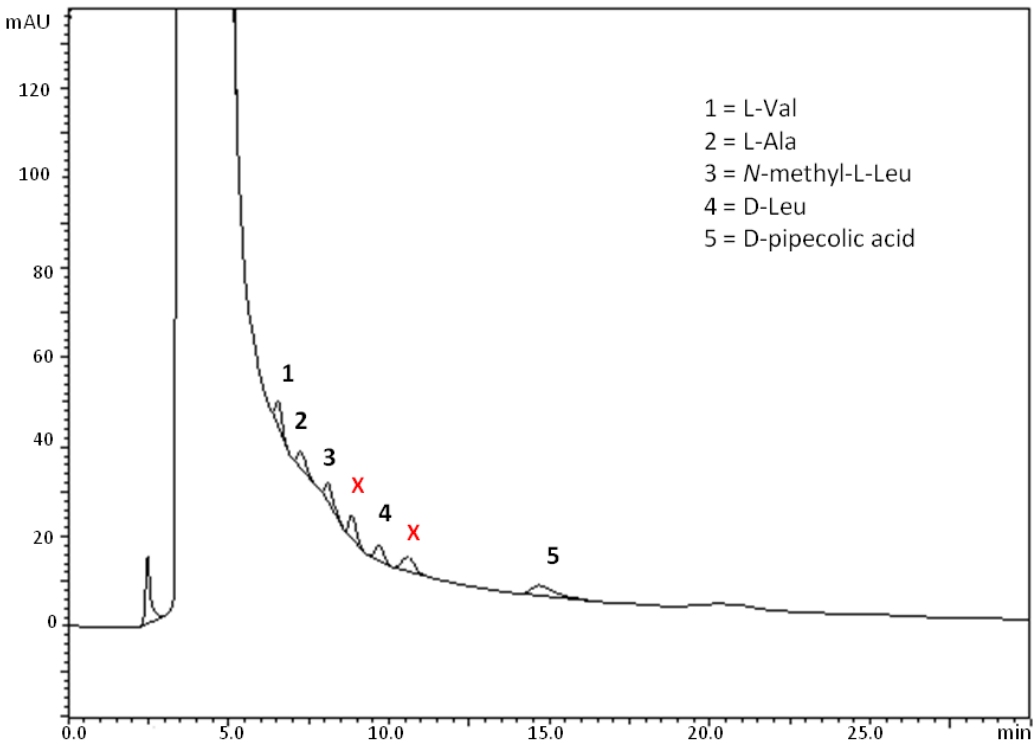


**Figure S19.** Chromatogram of the acidic hydrolysate of compound **2**. Chromatographic conditions: column, Chirobiotic T; mobile phase, MeOH:$H_2O$:$CH_3CO_2H$ (70:30:0.02 v/v/v); flow rate, 0.5 mL/min; detection, 210 nm.

**Table S1.** Chiral HPLC analysis of the acidic hydrolysate of compound **2** *.

| | **Retain Time (min)** |
|---|---|
| L-valine | 6.60 |
| D-valine | 8.32 |
| L-alanine | 7.16 |
| D-alanine | 9.36 |
| L-leucine | 6.78 |
| D-leucine | 9.67 |
| L-pipecolic acid | 8.68 |
| D-pipecolic acid | 14.67 |
| *N*-methyl-L-leucine | 8.09 |
| Acidic hydrolysate of **2** | 6.59, 7.20, 8.09, 8.83, 9.67, 10.57, 14.69 |
| Acidic hydrolysate of **2** + DL-valine (coinjection) | 6.61, 7.31, 8.30, 8.10, 8.84, 9.70, 10.50, 14.95 |
| Acidic hydrolysate of **2** + DL-alanine (coinjection) | 6.59, 7.19, 8.04, 8.81, 9.37, 9.70, 10.50, 14.90 |
| Acidic hydrolysate of **2** + DL-leucine | 6.60, 6.76, 7.26, 8.04, 8.83, 9.67, 10.54, 15.02 |
| Acidic hydrolysate of **2** + DL-pipecolic acid (coinjection) | 6.58, 7.20, 8.09, 8.64, 8.84, 9.77, 10.64, 14.64 |
| Acidic hydrolysate of **2** + *N*-methyl-L-leucine (coinjection) | 6.59, 7.20, 8.09, 8.83, 9.67, 10.57, 14.69 |

* Chromatographic conditions: column, Chirobiotic T; mobile phase, methanol:water:acetic acid (70:30:0.02 v/v/v); flow rate, 0.5 mL/min; detection, 210 nm.