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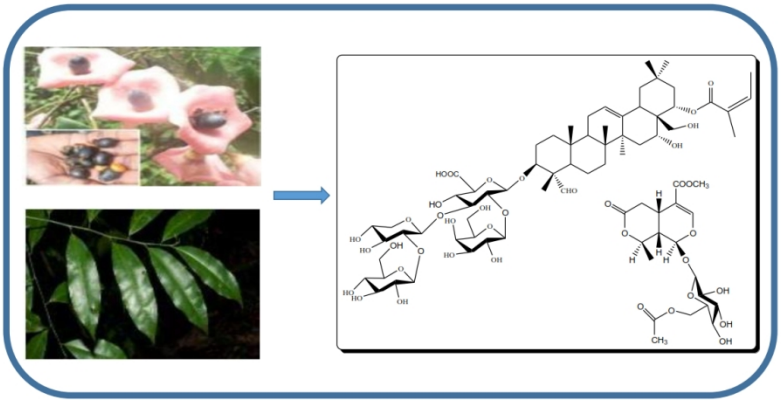

**New oleanane-type glycosides and secoiridoids glucosides from *Aptandra zenkeri***

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**Abstract**

Four new saponins, camelliagenin A and B derivatives, and three new secoiridoid glucosides were isolated from the stem bark of *Aptandra zenkeri* Engl. (Aptandraceae). Their structures were determined based on a combination of 1D- and 2D-NMR experiments techniques and HR-ESI-MS analysis. This is the first report on saponins in genus *Aptandra*.

**Keywords:**

*Aptandra zenkeri* Engl.; Aptandraceae; triterpenoid saponins; secoiridoid glucosides.

## 1. Introduction

The genus *Aptandra* belonging to the Aptandraceae family, is formed by four species, found in south America regions except *Aptandra zenkeri* Engl. present in Africa region (Nickrent et al. 2010). *Aptandra zenkeri* Engl. is a shrub, up to 15 m tall with reddish bark. The fruit are ellipsoid ovoid drupe, subtended by much enlarged, up to 10 cm wide, pink calix. As a folk medicine, this species has usually been used to treat hepatitis and coughing (Aubreville 1959; Burkill 1997; Louis et al. 1948; Neuwinger 2000; Villiers, 1973; List et Horhammer 1972). However, there has been no chemical or biological study reported on this plant. Only phytosterols and tocopherols were mentioned in *Aptandra sprucea* (Wiat et al. 2001). As a part of a continuing study for the discovery of medicinal Ivory Cost species, seven compounds, including four saponins, camelliagenin A and B derivatives, and three secoiridoid glucosides derivatives of kingiside, were isolated from the stem bark of *A. zenkeri*. This paper deals with their isolation and structure elucidation of these compounds.

## 2. Results and Discussion

The aqueous methanol extract obtained from the stem bark of *A. zenkeri* was concentrated under reduced pressure and then dissolved in water and extracted successively with $CHCl_3$ and *n*-BuOH. The *n*-BuOH was fractionated by vacuum-liquid chromatography (VLC) and purified by medium-pressure liquid chromatography on RP-18 and semi-preparative HPLC to yield four undescribed triterpenoid glycosides (**1**-**4**) (Figure 1) and three secoiridoid glucosides (**5**-**7**) (Figure 2). Their structures were established by a detailed analysis of their spectral data mainly by 500 MHz 2D NMR experiments and mass spectrometry. TLC analysis and NMR analysis of COSY, TOCSY, NOESY and HSQC spectra, allowed the full identification of the sugar units as *β*-D-glucopyranosiduronic acid (glcA), *β*-D-xylopyranose (xyl), *β*-D-glucopyranose (glc), and *β*-D-galactopyranose (gal).

Compound **1** was separated as a white, amorphous powder. The molecular formula $C_{58}H_{90}O_{26}$ was deduced from the HR-ESI-MS $[M + Na]^+$ ion at *m*/*z* 1225.5627 (calcd 1255.5618) (Figure S1). The $^1H$ NMR spectrum of **1** (Figure S2) indicated the presence of six singlet methyl groups at $\delta$ 0.93, 0.98, 1.05, 1.07, 1.19, 1.52 (each 3H, s, $H_3$-29, $H_3$-26, $H_3$-25, $H_3$-30, $H_3$-24, $H_3$-27), a methylene and three methines bearing an oxygen function at $\delta_H$ 3.08, 3.28 (each 1H, d, *J*=11.0 Hz, H-28), 3.91 (1H, dd, *J*=11.3, 4.5 Hz, H-3), 4.13 (1H, *br*s, H-16), 5.45 (1H, dd, *J*=12.1, 5.6 Hz, H-22), an olefinic proton at $\delta$ 5.37 (1H, t, *J*=3.6 Hz, H-

12), and an aldehyde signal at $\delta_H$ 9.48 (1H, s, H-23), which were characteristic of a polyhydroxyolean-12-ene triterpene derivative. In the HMBC spectrum (Figure S6), the cross-peaks observed between H-24 and $\delta$ 84.7 (C-3) and $\delta$ 209.3 (C-23) placed a secondary OH at C-3 and an aldehyde group at C-4. The location of the aldehyde group at C-23 was deduced from the chemical shift of C-24 at $\delta_C$ 9.5 characteristic of an axial position, and by comparison of the $^{13}$C NMR spectrum (Figure S3) with that of camelliagenin B (Miyose et al. 2012). In the HMBC spectrum, correlations between H-28 and $\delta_C$ 69.5 (C-16) and 72.4 (C-22) allowed the location of the two secondary OH at C-16 and C-22 and of a primary OH at C-28. Full assignments of the proton and carbon resonances of the aglycone were achieved by analysis of the COSY, HSQC and HMBC spectra (Table S1). The relative configuration of the aglycone of **1** was established from its ROESY spectrum. In the ROESY spectrum (Figure S7), correlations between H-3 and $\delta$ 1.38 (H-5) confirmed the $\alpha$-axial orientation of the two protons. Similarly, the cross-peaks between the protons of the methyl angular groups H-25 and H-24 on one hand and H-26 on the other, confirmed the $\beta$-axial orientation of these three methyl groups. The cross peaks between H-22 and H-30, H-22 and H-18 ($\delta$ 2.56), as well as those between H-16 and H-28, suggested that H-22 and H-16 are both $\beta$-oriented, which means that 22-OH and 16-OH group are both $\alpha$-orientations. The H-3 correlated with H-23 at $\delta$ 9.91, indicating that the glycosidic chain group at C-3 is $\beta$-configured. The triterpene skeleton of **1** was identified as camelliagenin B (3$\beta$,16$\alpha$,22$\alpha$,28-tetrahydroxy,23-aldehyde-olean-12-ene) (Table S1) (Myose et al. 2012). In addition, the signals of angeloyl (ang) group at $\delta_H$ 1.92 (3H, s, ang-5), 1.99 (3H, d, $J$=7.2 Hz, ang-4), and 6.09 (1H, q, $J$=7.2 Hz, ang-3) were observed. The downfield chemical shift of H-22 ($\delta$ 5.45) of **1** and its correlation with C-1 ($\delta$ 168.3) of angeloyl moiety in the HMBC experiment, established that angeloyl esterified C-22 of the aglycone. The aglycone of **1** was thus 22-*O*-angeloyl-camelliagenin B. Furthermore, the presence of four sugar moieties in **1** was evidenced by the $^1$H-NMR spectrum which displayed four anomeric protons at $\delta$ 4.47, 4.64, 4.95, and 5.00, giving correlations with four anomeric carbons at $\delta$ 103.3, 104.7, 101.7, and 100.6, respectively in the HSQC spectrum (Figure S5). A glucuronic acid was identified starting from the anomeric proton at $\delta_H$ 4.47 (d, $J$=7.3 Hz), and characterized by a five spin system possessing large coupling constants ($J$=7.3 Hz) and by a carbonyl (C-6) resonating at $\delta_C$ 172.1 coupled with H-5 ($\delta$ 3.82, d, $J$=9.6 Hz) of the same sugar in the HMBC. The $^{13}$C-NMR signals of the glucuronic acid of **1** were fully determined in the HSQC experiments and revealed it to be substituted at positions C-2 ($\delta$ 76.7) and C-3 ($\delta$ 82.4) as summarized in Table S2. A $\beta$-D-galactopyranose (gal) whose anomeric proton resonated at $\delta$ 4.95 was characterized

by the large coupling constants $J_{H\text{-}2,H\text{-}1}$ and $J_{H\text{-}2,H\text{-}3}$ ($\geq$ 8.1 Hz) and the small coupling constant between H-3 and H-4 ($J_{H\text{-}3,H\text{-}4}$ = 3.3 Hz) as summarized in Table S2 (Agrawal 1992). The third sugar, with an anomeric proton resonating at $\delta$ 5.00 (d, $J$=6.9 Hz), was a pentose identified as $\beta$-D-xylopyranose (xyl) and was found to be substituted in the C-2 position ($\delta$ 82.6) (Table S2). The last sugar unit was identified as terminal $\beta$-D-glucopyranose (glc), starting from its anomeric proton signal at $\delta$ 4.64 (d, $J$=7.1 Hz). The rOe interactions observed in the ROESY spectrum between H-1, H-3 and H-5 of each sugar unit confirmed the $\alpha$-axial orientation of these protons and the $\beta$-anomeric configuration. Complete assignments of the proton and carbon resonances of each sugar (Table S2) were achieved by analysis of COSY (Figure S4), TOCSY (Figure S8), and HSQC (Figure S5) experiments. The position of the sugar components was determined on the basis of the HMBC experiment (Figure S6), which showed long-range correlations between the following proton and carbon pairs: glcA-H-1 and $\delta$ 84.7 (C-3 of the aglycone), indicating that the glycosidic chain was located at C-3 of the aglycone, gal-H-1 and $\delta$ 76.7 (glcA-C-2), xyl-H-1 and $\delta$ 82.4 (glcA-C-3), and glc-H-1 and $\delta$ 82.6 (xyl-C-2). Thus, the structure of **1** was elucidated to be 3-*O*-$\beta$-D-glucopyranosyl-(1→2)-$\beta$-D-xylopyranosyl-(1→3)-[$\beta$-D-galactopyranosyl)-(1→2)]-$\beta$-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B.

Compound **2** was separated as a white, amorphous powder. The HR-ESI-MS peak at *m/z* 1195.5522 $[M + Na]^+$ (Figure S9) indicated the molecular formula of **2** to be $C_{57}H_{88}O_{25}$ (calcd 1195.5522), suggesting one methylene bearing an oxygen (-$CH_2OH$) less than that of **1**. The $^1$H- and $^{13}$C-NMR data of **2** were superimposable on those of **1** except for the sugar moiety (Tables S1 and S2). These data suggested that **2** is a 22-angeloyl-camelliagenin B derivative as **1**, which was further confirmed by COSY, HSQC, HMBC and ROESY experiments on **2** (Figures S12, S13, S14 and S15 respectively). The 1D- and 2D-NMR data of **2** confirmed the presence, as in **1**, of one $\beta$-D-glucopyranosiduronic acid (glcA), one $\beta$-D-galactopyranose (gal), and one $\beta$-D-xylopyranose (xyl) (Table S2). Further analysis indicated that the glucose sugar unit at C-2 of the xylose moiety in **1** was replaced by a $\beta$-D-xylopyranose (xyl') in **2** (Table S2). In addition, the xyl' was assigned to C-2 of xyl from the HMBC correlation between the xyl'-H-1 ($\delta$ 4.53, d, $J$=7.6 Hz) and xyl-C-2 ($\delta$ 83.7).

In a similar fashion, the linkage of gal at C-2 of glcA, of xyl at C-3 of glcA, and of glcA at C-3 of the aglycone were indicated by the correlations between xyl-H-1 ($\delta$ 4.92, d, $J$=7.4 Hz) and glcA-C-2 ($\delta$ 76.4), gal-H-1 ($\delta$ 4.99, d, $J$=7.3 Hz) and glcA-C-3 ($\delta$ 82.5), and glcA-H-1 ($\delta$ 4.45, d, $J$=7.4 Hz) and C-3 of the aglycone ($\delta$ 84.9), respectively. Consequently, the structure

of **2** was concluded to be 3-*O*-*β*-D-xylopyranosyl-(1→2)-*β*-D-xylopyranosyl-(1→3)-[*β*-D-galactopyranosyl)-(1→2)]-*β*-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin B

Compound **3**, separated as a white, amorphous powder, was assigned a molecular formula of $C_{58}H_{92}O_{25}$ according to the HR-ESI-MS peack at *m/z* 1211.5834 $[M+Na]^+$ (calc 1211.5825) (Figure S16). The 2D NMR analysis showed that compounds **1** and **3** differed only in the aglycone part at C-23 position (Table S1). The aldehyde function signal ($\delta_H$ 9.48; $\delta_C$ 209.3) in **1** was replaced by an angular methyl group at $\delta_H$ 1.12/$\delta_C$ 27.0 ($CH_3$-23) in **3**. This was confirmed by a HMBC correlation between $\delta_H$ 0.91 (s) ($H_3$-24)/$\delta_C$ 27.0 (C-23), and the reverse one, between $\delta_H$ 1.12 (s)($H_3$-23)/$\delta_C$ 15.6 (C-24) (Figure S21). The triterpene skeleton of **3** was thus determined as the known camelliagenin A (3*β*,16*α*,22*α*,28-tetrahydroxy-olean-12-ene) (Table S1) (Myose et al. 2012). The downfield chemical shift of H-22 ($\delta$ 5.46) of **3** and its correlation with C-1 ($\delta$ 168.3) of angeloyl moiety in the HMBC experiment, established that angeloyl esterified the hydroxyl at C-22 of the aglycone. The sequence and the attachment of the tetrasaccharide chain in **3** were confirmed as in **1** by an HMBC experiment (Figure S21). Thus, the structure of **3** was elucidated as 3-*O*-*β*-D-glucopyranosyl-(1→2)-*β*-D-xylopyranosyl-(1→3)-[*β*-D-galactopyranosyl)-(1→2)]-*β*-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

Compound **4** exhibited in the HR-ESI-MS (positive-ion mode) a pseudo-molecular ion peak at *m/z* 1181.5732 $[M+Na]^+$ (calcd 1181.5720) (Figure S24) consistent with a molecular formula of $C_{57}H_{90}O_{24}Na$. The NMR signals of compound **4** sugar portion were superimposable to those of **2** (Table S2). The structural analysis also revealed that the NMR signals of the aglycone part of **4** were superimposable to those of **3** (Table S1). Full assignments of the proton and carbon resonances of the aglycone and the sugar parts were achieved by analysis of the COSY, HSQC and HMBC spectra (Table S1). The sequence and the attachment of the tetrasaccharide chain in **4** were confirmed as in **2** and **3** by an HMBC experiment (Figure S29). Thus, the structure of **4** was elucidated as 3-*O*-*β*-D-xylopyranosyl-(1→2)-*β*-D-xylopyranosyl-(1→3)-[*β*-D-galactopyranosyl)-(1→2)]-*β*-D-glucuronopyranosyl-22-*O*-angeloyl-camelliagenin A.

Compound **5**, obtained as colorless amorphous powder, possessed the molecular formula $C_{19}H_{26}O_{12}$ as deduced from its HR-ESI-MS at *m/z* 469.1313 ($[M + Na]^+$ calcd for $C_{19}H_{26}O_{12}Na$ 469.1322) and 487.1418 ($[M + H_2O + Na]^+$ calcd for $C_{19}H_{28}O_{13}Na$ 487.1428) (Figure S32). The $^1H$ NMR spectrum (Figure S33) revealed signals attributed to a trisubstituted olefinic proton at $\delta_H$ 7.50 (s, H-3), an acetal proton at $\delta_H$ 5.80 (d, *J*=6.8, H-1), an

oxymethine at $\delta_H$ 5.21 (dq, *J*=6.6, 4.6 Hz, H-8), an oxymethyl signal at $\delta_H$ 3.70 (s, $H_3$-12), two methines at $\delta_H$ 3.35 (H-5) and 2.24 (H-9), a methylene at $\delta_H$ 2.55 and 2.65 ($H_2$-6), and a secondary methyl at $\delta_H$ 1.00 ($H_3$-10), together with a $\beta$-anomeric proton at $\delta_H$ 4.73 (d, *J*=7.9 Hz, H-1′) and an acetyl group $\delta_H$ 2.03 ($H_3$-2"). The $^{13}C$ NMR spectrum (Figure S34) exhibited signals for a carboxyl carbon at $\delta_C$ 174.4 (C-7), an ester carbon at $\delta_C$ 167.3 (C-11), a methoxy carbon at $\delta_C$ 50.3 (C-12), a trisubstituted double bond at $\delta_C$ 152.7 (C-3), 109.4 (C-4), and an acetal carbon at $\delta_C$ 95.5 (C-1), along with signals for a glycoside moiety and an acetyl group ($\delta_C$ 170.9, C-1″; 20.0, C-2″). These data suggested **5** to be an esterified secoiridoid-type monoterpene glycoside (Tan and Kong 1997; Garcia et al. 1990). The COSY and HSQC experiments (Figures S35 and S36 respectively) allowed assignment of the protons and carbons of a $\beta$-D-glucose unit (glc) starting from the anomeric proton (Table S3). The $\beta$-D-glucose unit possessed two deshielded protons $H_2$-6′ ($\delta_H$ 3.68 and 3.92), which have HMBC correlations with the carbonyl carbon at $\delta_C$ 170.9, confirming the acetylated position of glucose. In the COSY experiment (Figure S35), correlations were observed between H-9/H-1, H-5 and H-8, H-5/H-6, and H-8/H-10. In the HMBC experiment (Figure S37), long-range correlations were observed between the following protons and carbons (H-1 and C-1', C-3, C-5, C-8, C-9, C-10; H-3 and C-4, C-5, C-11; H-5 and C-3, C-6, C-7, C-1; H-8 and C-1, C-5, C-7, C-10 ; H-12/C-11). The above evidence indicated **5** as a derivative of kingiside (Damtoft et al. 1993). The $\alpha$ position of the methyl group (C-10) at C-8 was deduced from the chemical shift value of C-10 signal which appeared at $\delta_C$ 17.9 (17.7 for kingiside against 21.7 for 8-epikingiside) (Damtofi et al. 1993; Xu et al. 2008). The relative configuration of the other stereogenic centers C-1, C-5, and C-9 was established by analyzing coupling constant values, NOESY experiments and comparison with literature data (Damtofi et al. 1993; Garcia et al. 1990; Tan and Kong 1997). Thus, compound **5** was identified as 6'-*O*-acetyl-kingiside.

The positive HR-ESI-MS of compounds **6** and **7** (Figures S38 and S45 respectively) showed the same pseudomolecular ion peak $[M + H_2O + Na]^+$ at *m/z* 527.1733, in accordance with the molecular formula of $C_{22}H_{32}O_{13}$ (calcd for $C_{22}H_{32}O_{13}Na$ 527.1741). The spectral data of **6** and **7** obtained from NMR experiments (Table S3) were similar to those of **5** except for the acyl groups, suggesting that **6** and **7** were kingiside derivatives. The characteristic NMR signals of a tigloyl group at $\delta_H$ 6.91 (dq, *J* = 6.6, 1.2 Hz, H-3"), $\delta_C$ 13.0 (C-4") and 10.8 (C-5") were observed and further assigned by a combination of HSQC (Figures S42 and S49) and HMBC (Figures S43 and S50) experiments (Alabdul Magid et al. 2012). The downfield chemical shift of $H_2$-6' of glc ($\delta_H$ 3.67 and 3.92) of **6** and their correlations with C-1" ($\delta_C$ 167.4) of tigloyl in

the HMBC experiment, established that tigloyl esterified C-6' of the $\beta$-D-glucose unit. Thus, compound **6** was concluded to be 6'-*O*-tiglioyl-kingiside.

Information from 1D and 2D NMR spectra of **7** indicated the presence of signals due to an angeloyl group at $\delta_H$ 6.14 (1H, dq, J = 7.2, 1.4 Hz, H-3″), 2.01 (3H, dd, *J* = 7.2, 1.4 Hz, H-4″), 1.92 (3H, d, *J* = 1.4 Hz, H-5″) and at $\delta_C$ 167.3 (C-1′), 127.9 (C-2″), 138.3 (C-3″), 14.7 (C-4″) and 19.5 (C-5″). These data were in agreement with the corresponding ones reported for angeloyl moiety (Zong et al. 2015). Thus, compound **7** was elucidated as 6'-*O*-angeloyl-kingiside. This is the first report of triterpenoid saponins and iridoid glucosides from *Aptandra* genus and *Aptandraceae* family.

## 3. Experimental procedures

### *3.1. General experimental procedures*

Optical rotations were measured on a Perkin Elmer model 341 polarimeter (589 nm, 20 °C). NMR data were performed in $CD_3OD$ on Bruker Avance 500. HRESIMS data were gained using a Micromass Q-TOF high-resolution mass spectrometer. Mass spectra were recorded in the positive-ion mode in the range *m*/*z* 100−2000, with a mass resolution of 20000 and an acceleration voltage of 0.7 kV. CC was carried out on HP-20 resin (Sigma Aldrich). Flash chromatography was conducted on a Grace Reveleris system equipped with dual UV and ELSD detection using Grace® cartridges (Silica gel or RP-$C_{18}$). HPLC separations were performed on a Dionex apparatus equipped with an ASI-100 autosampler, an Ultimate 3000 pump, a STH 585 column oven, a diode array detector UVD 340S and a Chromeleon software. A prepacked RP-$C_{18}$ column (Phenomenex 250 x 15 mm, Luna 5 µ) was used for semi-preparative HPLC. The eluting mobile phase consisted of $H_2O$ with TFA (0.0025%) and $CH_3CN$ with a flow rate of 5 mL/min and the chromatogram was monitored at 205 and 210 nm. TLC were carried out using silica gel 60 $F_{254}$ pre-coated aluminium plates (0.2 mm, Merck). Spots were visualized through developing agent ($CHCl_3$:MeOH:$H_2O$, 14:6:1) and chromogenic agent (50% aq. $H_2SO_4$) subsequent heating.

### *3.2. Plant material*

The stem bark of *Aptandra zenkeri* Eng. were collected at Adiopodoumé, in August 2016. Its authenticated by National center of floristic of FHB University of Cocody (Ivory Coast). A voucher specimen has been deposited in herbarium of this center (Ake assi 6542).

### *3.3. Extraction and isolation*

Dried and powdered stem bark (800 g) were macerated for 3h with 15 l of 80% aqueous MeOH and further refluxed for 3 h. After cooling, the solution was filtered and concentrated under reduced pressure to give a crude extract (150 g). The MeOH extract was then suspended in $H_2O$ (2 l) and successively partitioned with $CHCl_3$ (3 × 1 l), and *n*-BuOH (3 × 1 l). The aqueous residues was subjected to a Diaion HP-20 open column and eluted with a 100% $H_2O$ and 100% MeOH to provide methanol and aqueous fraction. The *n*-BuOH extract (33 g) was fractionated by silica gel-*vacuum* liquid chromatography (VLC) (235 g, 10 cm × 6 cm) using a step-gradient solvent system $CHCl_3$-MeOH-$H_2O$ from 10:0:0, 9:1:0, 8:2:0, 7:3:0.5 to 6:4:0 to obtain 6 fractions, each 1.5 l [A-F]. A portion of fraction C (3 g) was purified by a flash chromatography over RP18, eluted by a gradient system of $CH_3CN$-$H_2O$ (10% to 50%), in 40 min to afford 40 sub-fractions ($C_1$-$C_{40}$). Fractions $C_{22}$ (131 mg) was purified by semi-prep. HPLC using a gradient from 10- 45% MeCN during 20 min, to yield compounds **5** (R*t* 8.3; 11 mg), **6** (R*t* 16.2; 2 mg), and **7** (R*t* 17.2; 16 mg). A portion of fraction E (1 g) was purified by flash chromatography over RP18, eluted by a gradient system of $CH_3CN$-$H_2O$ (20% to 60%), in 40 min to afford 40 sub-fractions ($E_1$-$E_{40}$). Fractions $E_{25}$ (58 mg) was purified by semi-prep. HPLC using an isocratic elution 45% MeCN during 20 min, to yield compounds **1** (R*t* 11.5 ; 13 mg), **2** (R*t* 12.4; 11 mg), **3** (R*t* 14.8 ; 5 mg), and **4** (R*t* 16.0 ; 6 mg).

### *3.4. Compound 1 : 3-O-β-D-glucopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin B.*

White, amorphous powder ; $[\alpha]^{20}_D$ +8 (*c* 1, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 1225.5627 $[M + Na]^+$ ($C_{58}H_{90}O_{26}Na$ ; calcd for 1225.5618); $^1H$ NMR ($CD_3OD$, 500 MHz) $\delta$: 1.05 (1H, td, *J* = 12.3, 4.5 Hz), 1.74 (1H, dt, *J* = 12.3, 3.2 Hz) (H-1), 1.81 (1H, m), 1.98 (1H, m) (H-2), 3.91 (1H, dd, *J* = 11.3, 4.5 Hz, H-3), 1.38 (1H, m, H-5), 0.94 (1H, m), 1.58 (1H, m) (H-6), 1.28 (1H, m), 1.65 (1H, td, *J* = 13.0, 4.5 Hz) (H-7), 1.83 (1H, m, H-9), 1.97 (2H, m, H-11), 5.37 (1H, t, *J* = 3.6 Hz, H-12), 1.33 (1H, m), 1.74 (1H, brd, *J* = 14.3 Hz) (H-15), 4.13 (1H, brs, H-16), 2.56 (1H, dd, *J* = 14.0, 3.5 Hz, H-18), 1.09 (1H, m), 2.49 (1H, t, *J* = 14.0 Hz, H-19), 1.54 (1H, m), 2.29 (1H, t, *J* = 11.9 Hz) (H-21), 5.45 (1H, dd, *J* = 12.1, 5.6 Hz, H-22), 9.48 (1H, s, H-23), 1.19 (3H, s, H-24), 1.05 (3H, s, H-25), 0.98 (3H, s, H-26), 1.52 (3H, s, H-27), 3.08 (1H, d, *J* = 11 Hz), 3.28 (1H, d, *J* = 11Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.09 (1H, q, *J* = 7.2 Hz, H-3''), 1.99 (3H, d, *J* = 7.2 Hz, H-4''), 1.92 (3H, s, H-5''); $^{13}C$ NMR ($CD_3OD$, 500 MHz) $\delta$: 37.9 (C-1), 24.3 (C-2), 84.7 (C-3), 54.8 (C-4), 47.8 (C-5), 19.8 (C-6), 31.8 (C-7), 39.9 (C-8), 46.5 (C-9), 35.6 (C-10), 23.2 (C-11), 122.8 (C-12), 142.6

(C-13), 41.1 (C-14), 33.8 (C-15), 69.5 (C-16), 43.9 (C-17), 40.4 (C-18), 46.6 (C-19), 31.1 (C-20), 40.7 (C-21), 72.4 (C-22), 209.3 (C-23), 9.5 (C-24), 15.0 (C-25), 15.9 (C-26), 26.4 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); $^{1}$H- and $^{13}$C NMR data for sugar moieties (see Table S2).

### *3.5. Compound 2: 3-O-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin B.*

White, amorphous powder ; $[\alpha]^{20}_{D}$ +6 (*c* 0.81, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 1195.5522 $[M + Na]^+$ ($C_{57}H_{88}O_{25}Na$; calcd for 1195.5512); $^{1}$H NMR ($CD_3OD$, 500 MHz) *δ*: 1.06 (1H, m), 1.74 (1H, dt, *J* = 14.0, 3.5 Hz) (H-1), 1.80 (1H, m), 1.98 (1H, m) (H-2), 3.89 (1H, dd, *J* = 11.5, 4.5 Hz, H-3), 1.38 (1H, brd, *J* = 12.3 Hz, H-5), 0.55 (1H, m), 1.58 (1H, m) (H-6), 1.28 (1H, dt, *J* = 13.1, 3.5 Hz), 1.64 (1H, td, *J* = 13.1, 4.6 Hz) (H-7), 1.81 (1H, m, H-9), 1.97 (2H, m, H-11), 5.37 (1H, t, *J* = 3.6 Hz, H-12), 1.33 (1H, brd, *J* = 14.0 Hz), 1.73 (1H, td, *J* = 14.0, 3.5 Hz) (H-15), 4.13 (1H, brs, H-16), 2.55 (1H, dd, *J* = 14.3, 3.5 Hz, H-18), 1.08 (1H, m), 2.49 (1H, t, *J* = 14.3 Hz, H-19), 1.55 (1H, m), 2.29 (1H, t, *J* = 11.9 Hz) (H-21), 5.46 (1H, dd, *J* = 12.1, 5.5 Hz, H-22), 9.48 (1H, s, H-23), 1.19 (3H, s, H-24), 1.05 (3H, s, H-25), 0.98 (3H, s, H-26), 1.52 (3H, s, H-27), 3.08 (1H, d, *J* = 11.0 Hz), 3.28 (1H, d, *J* = 11.0 Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.08 (1H, q, *J* = 7.3 Hz, H-3''), 1.99 (3H, d, *J* = 7.3 Hz, H-4''), 1.92 (3H, s, H-5''); $^{13}$C NMR ($CD_3OD$, 500 MHz) *δ*: 37.9 (C-1), 24.3 (C-2), 84.9 (C-3), 54.9 (C-4), 47.8 (C-5), 19.8 (C-6), 31.8 (C-7), 39.9 (C-8), 46.5 (C-9), 35.6 (C-10), 23.2 (C-11), 122.8 (C-12), 142.6 (C-13), 41.1 (C-14), 33.8 (C-15), 69.5 (C-16), 43.9 (C-17), 40.4 (C-18), 46.6 (C-19), 31.1 (C-20), 40.7 (C-21), 72.4 (C-22), 209.3 (C-23), 9.4 (C-24), 15.0 (C-25), 15.9 (C-26), 26.4 (C-27), 63.4 (C-28), 32.2 (C-29), 23.8 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); $^{1}$H- and $^{13}$C NMR data for sugar moieties (see Table S2).

### *3.6. Compound 3: 3-O-β-D-glucopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin A.*

White, amorphous powder ; $[\alpha]^{20}_{D}$ -5 (*c* 0.12, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 1211.5834 $[M + Na]^+$ ($C_{58}H_{92}O_{25}Na$; calcd for 1211.5825); $^{1}$H NMR ($CD_3OD$, 500 MHz) *δ*: 1.01 (1H, m), 1.65 (1H, dt, *J* = 12.2, 3.5 Hz) (H-1), 1.74 (1H, m), 1.94 (1H, m) (H-2), 3.22 (1H, dd, *J* = 11.8, 4.0 Hz, H-3), 0.81 (1H, brd, *J* = 11.7 Hz, H-5), 1.44 (1H, m), 1.61 (1H, m) (H-6), 1.37 (1H, m), 1.64 (1H, m) (H-7), 1.69 (1H, m, H-9), 1.94 (2H, m, H-11), 5.36 (1H, t, *J* = 3.3 Hz, H-12), 1.33 (1H, brd, *J* = 13.0 Hz), 1.78 (1H, dd, *J* = 13.0, 4.2 Hz) (H-15), 4.13

(1H, brs, H-16), 2.55 (1H, dd, *J* = 12.7, 3.4 Hz, H-18), 1.06 (1H, m), 2.49 (1H, t, *J* = 13.1 Hz, H-19), 1.58 (1H, m), 2.29 (1H, t, *J* = 12.9 Hz) (H-21), 5.46 (1H, dd, *J* = 12.1, 5.7 Hz, H-22), 1.12 (3H, s, H-23), 0.91 (3H, s, H-24), 1.01 (3H, s, H-25), 0.97 (3H, s, H-26), 1.50 (3H, s, H-27), 3.08 (1H, d, *J* = 11.0 Hz), 3.29 (1H, d, *J* = 11.0 Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.09 (1H, q, *J* = 7.4 Hz, H-3''), 1.99 (3H, d, *J* = 7.4 Hz, H-4''), 1.92 (3H, s, H-5''); $^{13}$C NMR ($CD_3OD$, 500 MHz) *δ*: 38.6 (C-1), 25.7 (C-2), 90.4 (C-3), 39.0 (C-4), 55.7 (C-5), 17.9 (C-6), 32.6 (C-7), 39.6 (C-8), 46.6 (C-9), 36.4 (C-10), 23.3 (C-11), 123.1 (C-12), 142.6 (C-13), 41.1 (C-14), 33.9 (C-15), 69.6 (C-16), 43.9 (C-17), 40.7 (C-18), 47.1 (C-19), 31.1 (C-20), 40.7 (C-21), 72.5 (C-22), 27.0 (C-23), 15.6 (C-24), 14.8 (C-25), 15.9 (C-26), 26.3 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.6 (C-3''), 14.5 (C-4''), 19.5 (C-5''); $^{1}$H- and $^{13}$C NMR data for sugar moieties (see Table S2).

### *3.7. Compound 4 : 3-O-β-D-xylopyranosyl-(1→2)-β-D-xylopyranosyl-(1→3)-[β-D-galactopyranosyl)-(1→2)]-β-D-glucuronopyranosyl-22-O-angeloyl-camelliagenin A.*

White, amorphous powder; $[\alpha]^{20}_{D}$ -3 (*c* 0.26, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 1181.5732 $[M + Na]^+$ ($C_{57}H_{90}O_{24}Na$ ; calcd for 1181.5720); $^{1}$H NMR ($CD_3OD$, 500 MHz) *δ*: 1.05 (1H, m), 1.65 (1H, dt, *J* = 13.5, 3.5 Hz) (H-1), 1.77 (1H, m), 1.95 (1H, m) (H-2), 3.21 (1H, dd, *J* = 11.2, 4.0 Hz, H-3), 0.81 (1H, brd, *J* = 11.4 Hz, H-5), 1.45 (1H, m), 1.58 (1H, m) (H-6), 1.37 (1H, m), 1.64 (1H, m) (H-7), 1.69 (1H, m, H-9), 1.94 (2H, m, H-11), 5.36 (1H, t, *J* = 3.6 Hz, H-12), 1.33 (1H, brd, *J* = 13.7 Hz), 1.78 (1H, dd, *J* = 13.7, 4.0 Hz) (H-15), 4.13 (1H, brs, H-16), 2.56 (1H, dd, *J* = 12.5, 3.6 Hz, H-18), 1.06 (1H, m), 2.48 (1H, t, *J* = 14.1 Hz, H-19), 1.59 (1H, m), 2.29 (1H, t, *J* = 12.2 Hz) (H-21), 5.46 (1H, dd, *J* = 12.2, 5.7 Hz, H-22), 1.11 (3H, s, H-23), 0.91 (3H, s, H-24), 1.01 (3H, s, H-25), 0.97 (3H, s, H-26), 1.50 (3H, s, H-27), 3.07 (1H, d, *J* = 11.1 Hz), 3.29 (1H, d, *J* = 11.1 Hz) (H-28), 0.93 (3H, s, H-29), 1.07 (3H, s, H-30), 6.08 (1H, q, *J* = 7.4 Hz, H-3''), 1.99 (3H, d, *J* = 7.4 Hz, H-4''), 1.92 (3H, s, H-5''); $^{13}$C NMR ($CD_3OD$, 500 MHz) *δ*: 38.6 (C-1), 25.6 (C-2), 90.7 (C-3), 39.1 (C-4), 55.7 (C-5), 17.9 (C-6), 32.6 (C-7), 39.6 (C-8), 46.6 (C-9), 36.4 (C-10), 23.2 (C-11), 123.2 (C-12), 142.5 (C-13), 41.1 (C-14), 33.9 (C-15), 69.6 (C-16), 43.9 (C-17), 40.4 (C-18), 47.1 (C-19), 31.1 (C-20), 40.7 (C-21), 72.5 (C-22), 27.0 (C-23), 15.5 (C-24), 14.8 (C-25), 15.9 (C-26), 26.3 (C-27), 63.4 (C-28), 32.2 (C-29), 23.9 (C-30), 168.3 (C-1''), 128.6 (C-2''), 136.7 (C-3''), 14.5 (C-4''), 19.5 (C-5''); $^{1}$H- and $^{13}$C NMR data for sugar moieties (see Table S2).

### *3.8. Compound 5: 6'-O-acetyl-kingiside.*

Colorless, amorphous powder ; $[\alpha]^{20}_{D}$ -101 (*c* 1, $CH_3OH$); HRESIMS (positive-ion mode): *m/z* 469.1313 $[M + Na]^+$ ($C_{19}H_{26}O_{12}Na$ ; calcd for 469.1322) and *m/z* 487.1418 $[M + H_2O + Na]^+$ $C_{19}H_{28}O_{13}Na$ ; calcd for 487.1428); $^1H$ NMR ($CD_3OD$, 500 MHz) $\delta$: 5.80 (1H, d, *J* = 6.8 Hz, H-1), 7.50 (1H, s, H-3), 3.35 (1H, m, H-5), 2.55 (1H, dd, *J* = 15.9, 7.0 Hz), 2.65 (1H, dd, *J* = 15.9, 6.1 Hz) (H-6), 5.21 (1H, dq, *J* = 6.6, 4.6 Hz, H-8), 2.24 (1H, dt, *J* = 6.8, 5.0 Hz, H-9), 1.00 (3H, d, *J* = 6.6 Hz, H-10), 3.0 (3H, s, 12-$OCH_3$), 4.73 (1H, d, *J* = 7.9 Hz, H-1'), 3.23 (1H, dd, *J* = 9.2, 7.9 Hz, H-2'), 3.40 (1H, t, *J* = 9.5 Hz, H-3'), 3.30 (1H, t, *J* = 9.7 Hz, H-4'), 3.33 (1H, m, H-5'), 3.68 (1H, dd, *J* = 11.8, 4.5 Hz), 3.92 (1H, dd, *J* = 11.8, 2.0 Hz) (H-6'), 2.03 (3H, s, H-2''); $^{13}C$ NMR ($CD_3OD$, 125 MHz) $\delta$: 95.5 (C-1), 152.7 (C-3), 109.4 (C-4), 28.6 (C-5), 34.5 (C-6), 174.4 (C-7), 69.2 (C-8), 42.8 (C-9), 17.9 (C-10), 167.3 (C-11), 50.3 (C-12-$OCH_3$), 99.0 (C-1'), 73.4 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 170.9 (C-1''), 20.0 (C-2'').

### *3.9. Compound 6: 6'-O-tiglioyl-kingiside.*

Colorless, amorphous powder ; $[\alpha]^{20}_{D}$ -78 (*c* 1, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 527.1733 $[M + Na]^+$ ($C_{22}H_{32}O_{13}Na$ ; calcd for 527.1741); $^1H$ NMR ($CD_3OD$, 500 MHz) $\delta$: 5.85 (1H, d, *J* = 6.7 Hz, H-1), 7.49 (1H, s, H-3), 3.38 (1H, m, H-5), 2.52 (1H, dd, *J* = 15.9, 6.9 Hz), 2.63 (1H, dd, *J* = 15.9, 6.7 Hz) (H-6), 5.27 (1H, dq, *J* = 6.5, 4.5 Hz, H-8), 2.30 (1H, dt, *J* = 6.8, 4.5 Hz, H-9), 1.42 (3H, d, *J* = 6.5 Hz, H-10), 3.70 (3H, s, 12-$OCH_3$), 4.74 (1H, d, *J* = 7.9 Hz, H-1'), 3.20 (1H, dd, *J* = 9.1, 7.9 Hz, H-2'), 3.38 (1H, t, *J* = 9.5 Hz, H-3'), 3.27 (1H, t, *J* = 9.7 Hz, H-4'), 3.35 (1H, m, H-5'), 3.67 (1H, dd, *J* = 11.9, 4.9 Hz), 3.92 (1H, dd, *J* = 11.9, 2.1 Hz) (H-6'), 6.91 (1H, dq, *J* = 6.6, 1.2 Hz, H-3''), 1.42 (3H, dd, *J* = 6.6, 1.2 Hz, H-4''), 1.84 (3H, d, *J* = 1.2 Hz, H-5'') ; $^{13}C$ NMR ($CD_3OD$, 125 MHz) $\delta$: 95.2 (C-1), 152.7 (C-3), 109.4 (C-4), 28.7 (C-5), 34.5 (C-6), 174.5 (C-7), 69.0 (C-8), 42.9 (C-9), 17.9 (C-10), 167.2 (C-11), 50.3 (C-12-$OCH_3$), 98.7 (C-1'), 73.3 (C-2'), 77.0 (C-3'), 70.1 (C-4'), 76.5 (C-5'), 61.4 (C-6'), 167.4 (C-1''), 128.5 (C-2''), 137.8 (C-3''), 13.0 (C-4''), 10.8 (C-5'').

### *3.10. Compound 7: 6'-O-angeloyl-kingiside.*

Colorless, amorphous powder ; $[\alpha]^{20}_{D}$ -90 (*c* 0.26, $CH_3OH$); HRESIMS (positive-ion mode) *m/z* 527.1733 $[M + Na]^+$ ($C_{22}H_{32}O_{13}Na$ ; calcd for 527.1741) $^1H$ NMR ($CD_3OD$, 500 MHz) $\delta$: 5.85 (1H, d, *J* = 6.4 Hz, H-1), 7.48 (1H, s, H-3), 3.40 (1H, m, H-5), 2.54 (1H, dd, *J* = 15.9, 6.9 Hz), 2.60 (1H, dd, *J* = 15.9, 6.4 Hz) (H-6), 5.32 (1H, dq, *J* = 6.9, 4.5 Hz, H-8), 2.30 (1H, dt, *J* = 6.9, 4.9 Hz, H-9), 1.44 (3H, d, *J* = 6.5 Hz, H-10), 3.70 (3H, s, 12-$OCH_3$), 4.75 (1H, d, *J* = 7.9 Hz, H-1'), 3.22 (1H, dd, *J* = 9.3, 7.9 Hz, H-2'), 3.38 (1H, t, *J* = 9.5 Hz, H-3'), 3.28 (1H, t,

$J$ = 9.7 Hz, H-4'), 3.33 (1H, m, H-5'), 3.67 (1H, dd, $J$ = 11.9, 5.9 Hz), 3.90 (1H, dd, $J$ = 11.9, 2.1 Hz) (H-6'), 6.14 (1H, dq, $J$ = 7.2, 1.4 Hz, H-3''), 2.01 (3H, dd, $J$ = 7.2, 1.4 Hz, H-4''), 1.92 (3H, d, $J$ = 1.4 Hz, H-5'') ; $^{13}$C NMR ($CD_3OD$, 125 MHz) $\delta$: 95.2 (C-1), 152.7 (C-3), 109.3 (C-4), 28.4 (C-5), 34.4 (C-6), 174.4 (C-7), 68.4 (C-8), 42.8 (C-9), 18.0 (C-10), 167.1 (C-11), 50.9 (C-12-$OCH_3$), 99.0 (C-1'), 73.4 (C-2'), 76.9 (C-3'), 70.2 (C-4'), 77.1 (C-5'), 61.5 (C-6'), 167.3 (C-1''), 127.9 (C-2''), 138.3 (C-3''), 14.7 (C-4''), 19.5 ( (C-5'').

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**Disclosure statement**

The authors have declared no conflict of interest.

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**Appendix A. Supplementary Material**

Supplementary data associated with this article can be found in the online version.

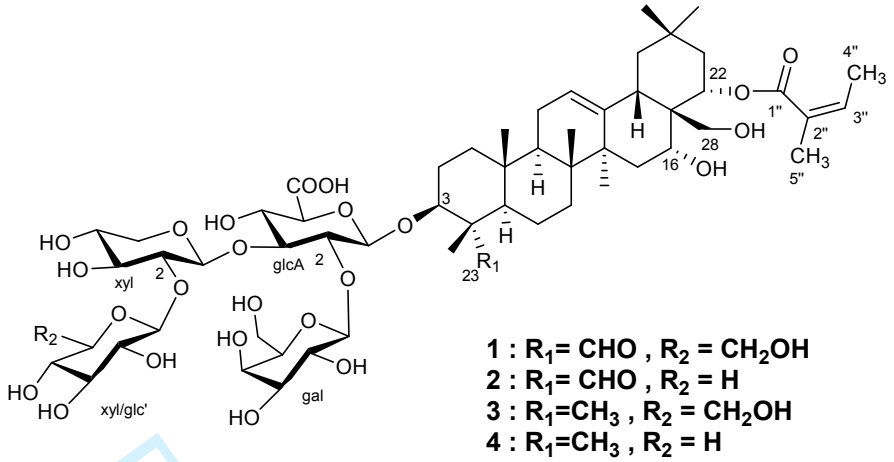


**Figure 1.** The structures of triterpenoid glycosides (**1**-**4**) isolated from the stem bark of *Aptandra zenkeri* Engl.

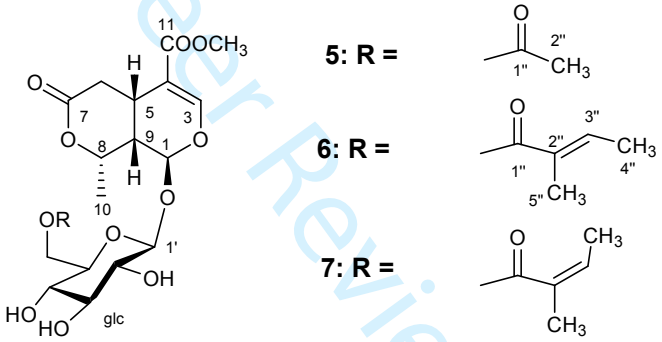


**Figure 2.** The structures of secoiridoid glucosides (**5**-**7**) isolated from the stem bark of *Aptandra zenkeri* Engl.

**SUPPLEMENTARY MATERIAL**

# New oleanane-type glycosides and secoiridoids glucosides from *Aptandra zenkeri*

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**Abstract:** Four new saponins, camelliagenin A and B derivatives, and three new secoiridoid glucosides were isolated from the stem bark of *Aptandra zenkeri* Engl. (Aptandraceae). Their structures were determined based on a combination of 1D- and 2D-NMR experiments techniques and HR-ESI-MS analysis. This is the first report on saponins in genus *Aptandra*.

**Keywords:** *Aptandra zenkeri* Engl.; Aptandraceae; triterpenoid saponins; secoiridoid glucosides

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**List of Supplementary Material**

**Table S1.** $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) data of the aglycone moieties of compounds **1 - 4** ($CD_3OD$)

| | **1** | | **2** | | **3** | | **4** | |
|---|---|---|---|---|---|---|---|---|
| | $\delta_H$ (*m, J* Hz) | $\delta_C$ | $\delta_H$ (*m, J* Hz) | $\delta_C$ | $\delta_H$ (*m,* J Hz) | $\delta_C$ | $\delta_H$ (*m, J* Hz) | $\delta_C$ |
| **1** | 1.05, td (12.3, 4.5) | 37.9 | 1.06, m | 37.9 | 1.01, m | 38.6 | 1.05, m | 38.6 |
| | 1.74, dt (12.3, 3.2) | | 1.74, dt (14.0, 3.5) | | 1.65, dt (12.2, 3.5) | | 1.65, dt (13.5, 3.5) | |
| **2** | 1.81, m | 24.3 | 1.80, m | 24.3 | 1.74, m | 25.7 | 1.77, m | 25.6 |
| | 1.98, m | | 1.98, m | | 1.94, m | | 1.95, m | |
| **3** | 3.91, dd (11.3, 4.5) | 84.7 | 3.89, dd (11.5, 4.5) | 84.9 | 3.22, dd (11.8, 4.0) | 90.4 | 3.21, dd (11.2, 4.0) | 90.7 |
| **4** | | 54.8 | | 54.9 | | 39.0 | | 39.1 |
| **5** | 1.38, m | 47.8 | 1.38, brd (12.3) | 47.8 | 0.81, brd (11.7) | 55.7 | 0.81, brd (11.4) | 55.7 |
| **6** | 0.94, m | 19.8 | 0.55, m | 19.8 | 1.44, m | 17.9 | 1.45, m | 17.9 |
| | 1.58, m | | 1.58, m | | 1.61, m | | 1.58, m | |
| **7** | 1.28, m | 31.8 | 1.28, dt (13.1, 3.5) | 31.8 | 1.37, m | 32.6 | 1.37, m | 32.6 |
| | 1.65, td (13.0, 4.5) | | 1.64, td (13.1, 4.6) | | 1.64, m | | 1.64, m | |
| **8** | | 39.9 | | 39.9 | | 39.6 | | 39.6 |
| **9** | 1.83, m | 46.5 | 1.81, m | 46.5 | 1.69, m | 46.6 | 1.69, m | 46.6 |
| **10** | | 35.6 | | 35.6 | | 36.4 | | 36.4 |
| **11** | 1.97, m | 23.2 | 1.97, m | 23.2 | 1.94, m | 23.3 | 1.94, m | 23.2 |
| **12** | 5.37, t (3.6) | 122.8 | 5.37, t (3.6) | 122.8 | 5.36, t (3.3) | 123.1 | 5.36, t (3.6) | 123.2 |
| **13** | | 142.6 | | 142.6 | | 142.6 | | 142.5 |
| **14** | | 41.1 | | 41.1 | | 41.1 | | 41.1 |
| **15** | 1.33, m | 33.8 | 1.33, brd (14.0) | 33.8 | 1.33, brd (13.0) | 33.9 | 1.33, brd (13.7) | 33.9 |
| | 1.74, brd (14.3) | | 1.73, td (14.0, 3.5) | | 1.78, dd (13.0, 4.2) | | 1.78, dd (13.7, 4.0) | |
| **16** | 4.13, brs | 69.5 | 4.13, brs | 69.5 | 4.13, brs | 69.6 | 4.13, brs | 69.6 |
| **17** | | 43.9 | | 43.9 | | 43.9 | | 43.9 |
| **18** | 2.56, dd (14.0, 3.5) | 40.4 | 2.55, dd (14.3, 3.5) | 40.4 | 2.55, dd (12.7, 3.4) | 40.7 | 2.56, dd (12.5, 3.6) | 40.4 |
| **19** | 1.09, m | 46.6 | 1.08, m | 46.6 | 1.06, m | 47.1 | 1.06, m | 47.1 |
| | 2.49, t (14.0) | | 2.49, t (14.3) | | 2.49, t (13.1) | | 2.48, t (14.1) | |
| **20** | | 31.1 | | 31.1 | | 31.1 | | 31.1 |
| **21** | 1.54, m | 40.7 | 1.55, m | 40.7 | 1.58, m | 40.7 | 1.59, m | 40.7 |
| | 2.29, t (11.9) | | 2.29, t (11.9) | | 2.29, t (12.9) | | 2.29, t (12.2) | |
| **22** | 5.45, dd (12.1, 5.6) | 72.4 | 5.46, dd (12.1, 5.5) | 72.4 | 5.46, dd (12.1, 5.7) | 72.5 | 5.46, dd (12.2, 5.7) | 72.5 |
| **23** | 9.48, s | 209.3 | 9.48, s | 209.3 | 1.12, s | 27.0 | 1.11, s | 27.0 |
| **24** | 1.19, s | 9.5 | 1.19, s | 9.4 | 0.91, s | 15.6 | 0.91, s | 15.5 |
| **25** | 1.05, s | 15.0 | 1.05, s | 15.0 | 1.01, s | 14.8 | 1.01, s | 14.8 |
| **26** | 0.98, s | 15.9 | 0.98, s | 15.9 | 0.97, s | 15.9 | 0.97, s | 15.9 |
| **27** | 1.52, s | 26.4 | 1.52, s | 26.4 | 1.50, s | 26.3 | 1.50, s | 26.3 |
| **28** | 3.08, d (11.0) | 63.4 | 3.08, d (11.0) | 63.4 | 3.08, d (11.0) | 63.4 | 3.07, d (11.1) | 63.4 |
| | 3.28, d (11.0) | | 3.28, d (11.0) | | 3.29, d (11.0) | | 3.29, d (11.1) | |
| **29** | 0.93, s | 32.2 | 0.93, s | 32.2 | 0.93, s | 32.2 | 0.93, s | 32.2 |
| **30** | 1.07, s | 23.9 | 1.07, s | 23.8 | 1.07, s | 23.9 | 1.07, s | 23.9 |
| **$C_{22}$ Angeloyl** | | | | | | | | |
| **1** | | 168.3 | | 168.3 | | 168.3 | | 168.3 |
| **2** | | 128.6 | | 128.6 | | 128.6 | | 128.6 |
| **3** | 6.09, q (7.2) | 136.7 | 6.08, q (7.3) | 136.7 | 6.09, q (7.4) | 136.6 | 6.08, q (7.4) | 136.7 |
| **4** | 1.99, d (7.2) | 14.5 | 1.99, d (7.3) | 14.5 | 1.99, d (7.4) | 14.5 | 1.99, d (7.4) | 14.5 |
| **5** | 1.92, s | 19.5 | 1.92, s | 19.5 | 1.92, s | 19.5 | 1.92, s | 19.5 |

**Table S2** $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR data of the sugar moieties of compounds **1 - 4** ($CD_3OD$).

| | **1** | | **2** | | **3** | | **4** | |
|---|---|---|---|---|---|---|---|---|
| | $\delta_H$, *m* (*J* Hz) | $\delta_C$ | $\delta_H$, *m* (*J* Hz) | $\delta_C$ | $\delta_H$, *m* (*J* Hz) | $\delta_C$ | $\delta_H$, *m* (*J* Hz) | $\delta_C$ |
| **glcA (at C-3)** | | | | | | | | |
| **1** | 4.47, d (7.3) | 103.3 | 4.45, d (7.4) | 103.4 | 4.52, d (7.8) | 104.5 | 4.53, d (7.5) | 105.6 |
| **2** | 3.84, t (8.3) | 76.7 | 3.71, dd (8.0, 7.4) | 76.4 | 3.97, dd (8.8, 7.8) | 77.5 | 3.92, t (8.2) | 77.4 |
| **3** | 3.78, t (8.3) | 82.4 | 3.72, t (8.0) | 82.5 | 3.83, t (9.0) | 82.7 | 3.79, t (82) | 82.5 |
| **4** | 3.62, t (8.5) | 69.6 | 3.58, t (8.5) | 69.6 | 3.61, t (9.0) | 70.3 | 3.61, t (8.5) | 70.0 |
| **5** | 3.82, d (9.6) | 75.0 | 3.82, d (9.5) | 75.0 | 3.73, d (9.1) | 75.3 | 3.78, d (9.5) | 75.2 |
| **6** | | 172.1 | | 172.2 | | 172.4 | | 172.2 |
| **gal (at glcA-C-2)** | | | | | | | | |
| **1** | 4.95, [a] | 101.7 | 4.99, d (7.3) | 101.4 | 4.98, d (7.4) | 101.9 | 5.07, d (7.3) | 101.5 |
| **2** | 3.52, t (8.1) | 72.1 | 3.48, t (8.5) | 72.0 | 3.61, t (8.1) | 72.2 | 3.54, t (8.1) | 72.1 |
| **3** | 3.54, dd (8.1, 3.3) | 73.5 | 3.52, dd (8.5, 3.6) | 73.7 | 3.55, dd (8.1, 3.2) | 73.3 | 3.53, dd (8.1, 2.5) | 74.7 |
| **4** | 3.84, t (3.3) | 69.3 | 3.83, t (3.6) | 69.6 | 3.87, t (3.2) | 68.7 | 3.83, t (2.6) | 69.1 |
| **5** | 3.63, m | 75.2 | 3.64, brt (6.2) | 75.1 | 3.66, m | 75.3 | 3.58, m | 74.7 |
| **6** | 3.75, dd (11.1, 5.3) | 61.0 | 3.73, dd (11.5, 5.3) | 61.1 | 3.69, [a] | 61.0 | 3.65, dd (11.4, 4.7) | 61.4 |
| | 3.80, dd (11.1, 3.0) | | 3.80, dd (11.5, 2.8) | | 3.76, dd (11.4, 2.8) | | 3.80, dd (11.4, 3.0) | |
| **Xyl (at glcA-C-3)** | | | | | | | | |
| **1** | 5.00, d (6.9) | 100.6 | 4.92, d (7.4) | 100.7 | 5.00, d (7.1) | 100.8 | 4.99, d (7.4) | 100.7 |
| **2** | 3.53, dd (8.5, 6.9) | 82.6 | 3.41, dd (8.5, 7.4) | 83.7 | 3.54, dd (8.3, 7.1) | 82.7 | 3.44, dd (8.3, 7.4) | 83.7 |
| **3** | 3.65, t (8.5) | 75.8 | 3.60, t (8.5) | 76.1 | 3.66, t (8.3) | 76.0 | 3.62, t (8.3) | 76.1 |
| **4** | 3.60, m | 69.5 | 3.59, m | 69.5 | 3.59, m | 69.4 | 3.58, m | 69.6 |
| **5** | 3.19, dd (11.5, 8.5) | 65.2 | 3.28, [a] | 65.2 | 3.30, [a] | 65.3 | 3.28, dm (11.4) | 65.4 |
| | 3.96, dd (11.5, 5.1) | | 3.92, dd (11.2, 4.7) | | 4.02, dd (11.5, 5.7) | | 3.94, dd (11.4, 4.5) | |
| **glc′/xyl′ (at xyl-C-2)** | | | | | | | | |
| **1** | 4.64, d (7.1) | 104.7 | 4.53, d (7.6) | 106.6 | 4.69, d (7.3) | 104.6 | 4.56, d (7.2) | 106.0 |
| **2** | 3.31, dd (8.8, 7.1) | 74.5 | 3.30, dd (9.0, 7.6) | 74.8 | 3.33, [a] | 74.3 | 3.31, [a] | 73.4 |
| **3** | 3.41, t (8.8) | 76.7 | 3.35, t (9.0) | 76.5 | 3.42, t (8.0) | 76.7 | 3.35, t (9.0) | 76.6 |
| **4** | 3.37 (8.8) | 70.3 | 3.54, m | 69.6 | 3.37, t (8.5) | 70.2 | 3.37, m | 69.6 |
| **5** | 3.33, m | 77.0 | 3.20, dd (11.2, 10.7) | 65.9 | 3.35, m | 77.0 | 3.21, t (11.2) | 65.9 |
| | | | 3.97, dd (11.5, 5.4) | | | | 3.99, dd (11.2, 5.4) | |
| **6** | 3.76, dd (11.2, 5.9) | 61.5 | | | 3.78, dd (11.0, 5.2) | 61.5 | | |
| | 3.91, dm (11.2) | | | | 3.91, dm (11.0) | | | |

[a] overlapped signals

**Table S3.** $^{1}H$ (500 MHz) and $^{13}C$ (125 MHz) NMR spectroscopic data of compounds **5-7** ($CD_3OD$).

| position | 5 | | 6 | | 7 | |
|---|---|---|---|---|---|---|
| | $\delta_H$ m (*J* in Hz) | $\delta_C$ | $\delta_H$ m (*J* in Hz) | $\delta_C$ | $\delta_H$ m (*J* in Hz) | $\delta_C$ |
| 1 | 5.80, d (6.8) | 95.5 | 5.85, d (6.7) | 95.2 | 5.85, d (6.4) | 95.2 |
| 3 | 7.50, s | 152.7 | 7.49, s | 152.7 | 7.48, s | 152.7 |
| 4 | | 109.4 | | 109.4 | | 109.3 |
| 5 | 3.35, m | 28.6 | 3.38, m | 28.7 | 3.40, m | 28.4 |
| 6 | 2.55, dd (15.9, 7.0) | 34.5 | 2.52, dd (15.9, 6.9) | 34.5 | 2.54, dd (15.9, 6.9) | 34.4 |
| | 2.65, dd (15.9, 6.1) | | 2.63, dd (15.9, 6.7) | | 2.60, dd (15.9, 6.4) | |
| 7 | | 174.4 | | 174.5 | | 174.4 |
| 8 | 5.21, dq (6.6, 4.6) | 69.2 | 5.27, dq (6.5, 4.5) | 69.0 | 5.32, dq (6.9, 4.5) | 68.4 |
| 9 | 2.24, dt (6.8, 5.0) | 42.8 | 2.30, dt (6.8, 4.5) | 42.9 | 2.30, dt (6.9, 4.9) | 42.8 |
| 10 | 1.00, d (6.6) | 17.9 | 1.42, d (6.5) | 17.9 | 1.44, d (6.5) | 18.0 |
| 11 | | 167.3 | | 167.2 | | 167.1 |
| 12 ($OCH_3$) | 3.70, s | 50.3 | 3.70, s | 50.3 | 3.70, s | 50.9 |
| ***β*-D-glc** | | | | | | |
| 1' | 4.73, d (7.9) | 99.0 | 4.74, d (7.9) | 98.7 | 4.75, d (7.9) | 99.0 |
| 2' | 3.23, dd (9.2, 7.9) | 73.4 | 3.20, dd (9.1, 7.9) | 73.3 | 3.22, dd (9.3, 7.9) | 73.4 |
| 3' | 3.40, t (9.5) | 76.9 | 3.38, t (9.5) | 77.0 | 3.38, t (9.5) | 76.9 |
| 4' | 3.30, t (9.7) | 70.2 | 3.27, t (9.7) | 70.1 | 3.28, t (9.7) | 70.2 |
| 5' | 3.33, m | 77.1 | 3.35, m | 76.5 | 3.33, m | 77.1 |
| 6' | 3.68, dd (11.8, 4.5) | 61.5 | 3.67, dd (11.9, 4.9) | 61.4 | 3.67, dd (11.9, 5.9) | 61.5 |
| | 3.92, dd (11.8, 2.0) | | 3.92, dd (11.9, 2.1) | | 3.90, dd (11.9, 2.1) | |
| 1" | | 170.9 | | 167.4 | | 167.3 |
| 2" | 2.03, s | 20.0 | | 128.5 | | 127.9 |
| 3" | | | 6.91, dq (6.6, 1.2) | 137.8 | 6.14, dq (7.2, 1.4) | 138.3 |
| 4" | | | 1.42, dd (6.6, 1.2) | 13.0 | 2.01, dd (7.2, 1.4) | 14.7 |
| 5" | | | 1.84, d (1.2) | 10.8 | 1.92, d (1.4) | 19.5 |

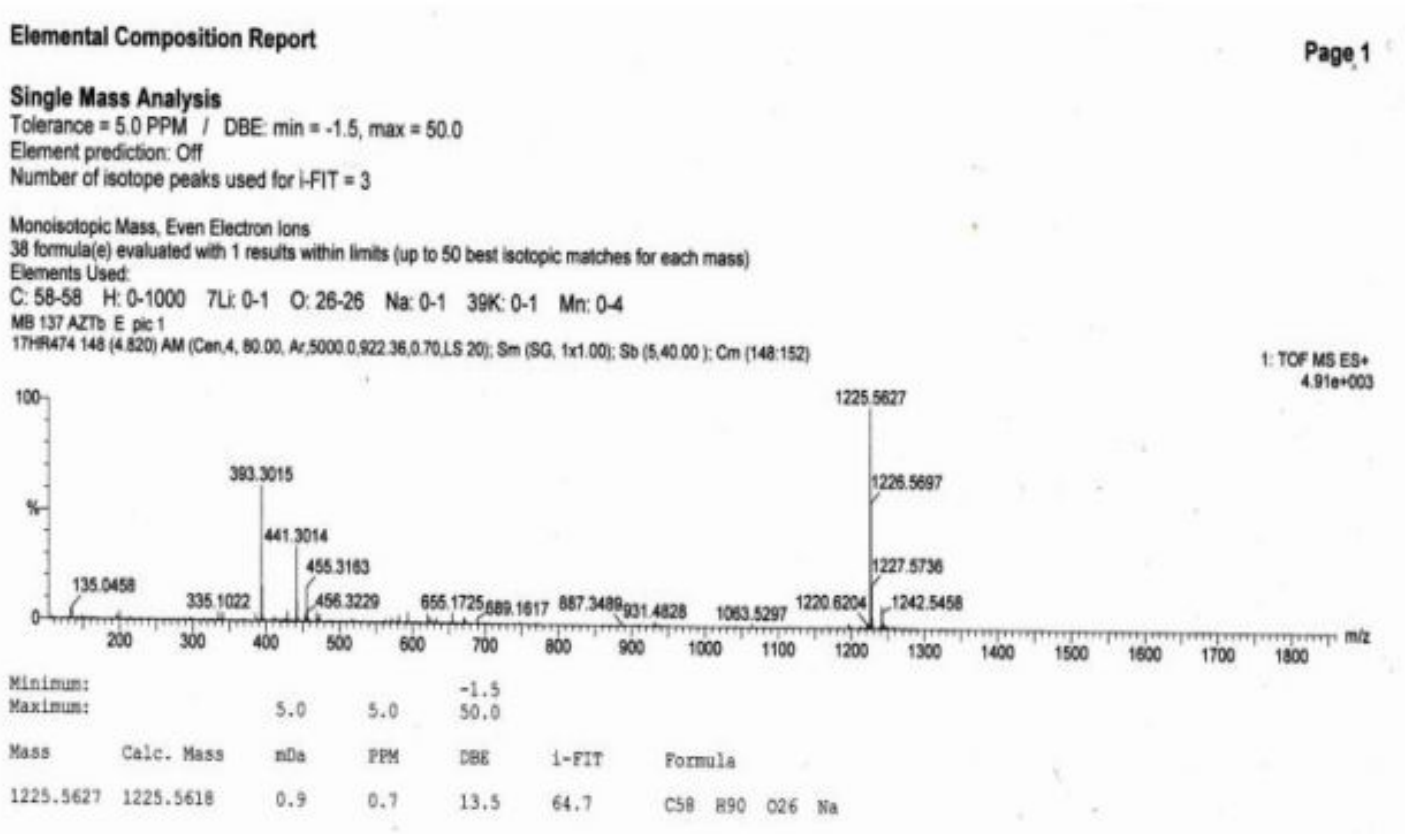



**Figure S1.** The HRESIMS of **1**

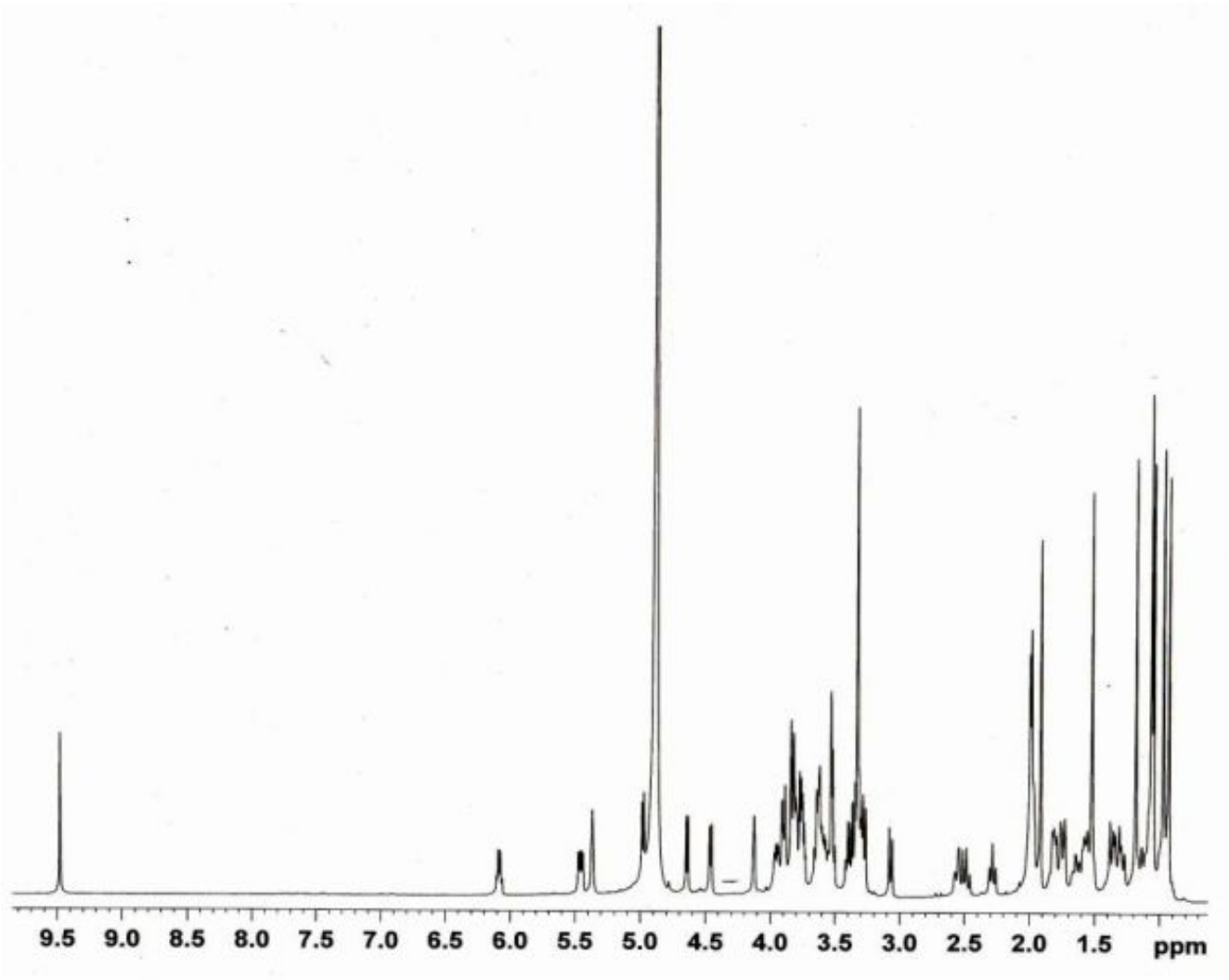



**Figure S2.** The $^{1}$H-NMR spectrum of **1** in $CD_3OD$

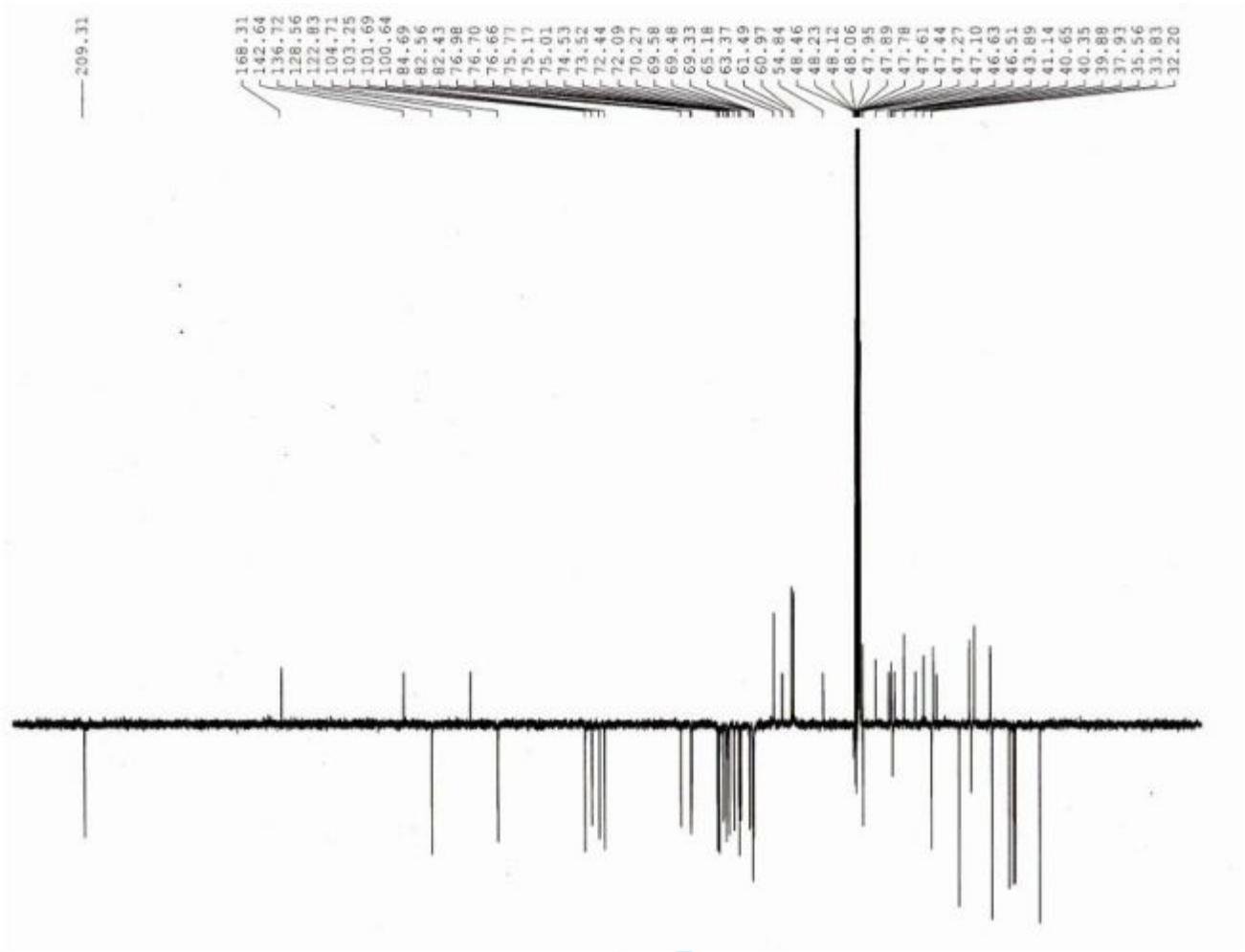



**Figure S3.** The DEPT spectrum of **1** in $CD_3OD$

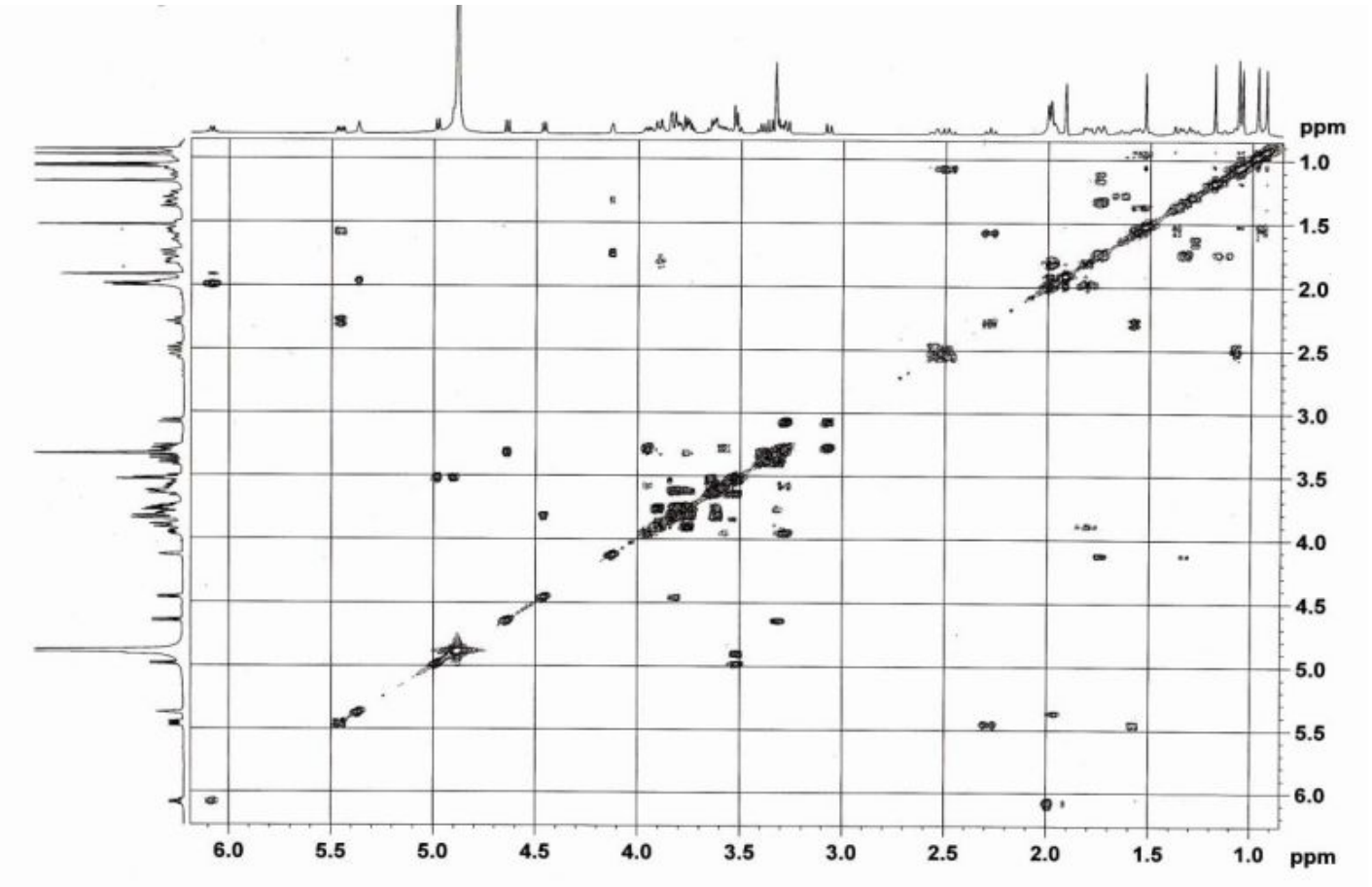



**Figure S4.** The $^{1}H$-$^{1}H$ COSY spectrum of **1** in $CD_3OD$

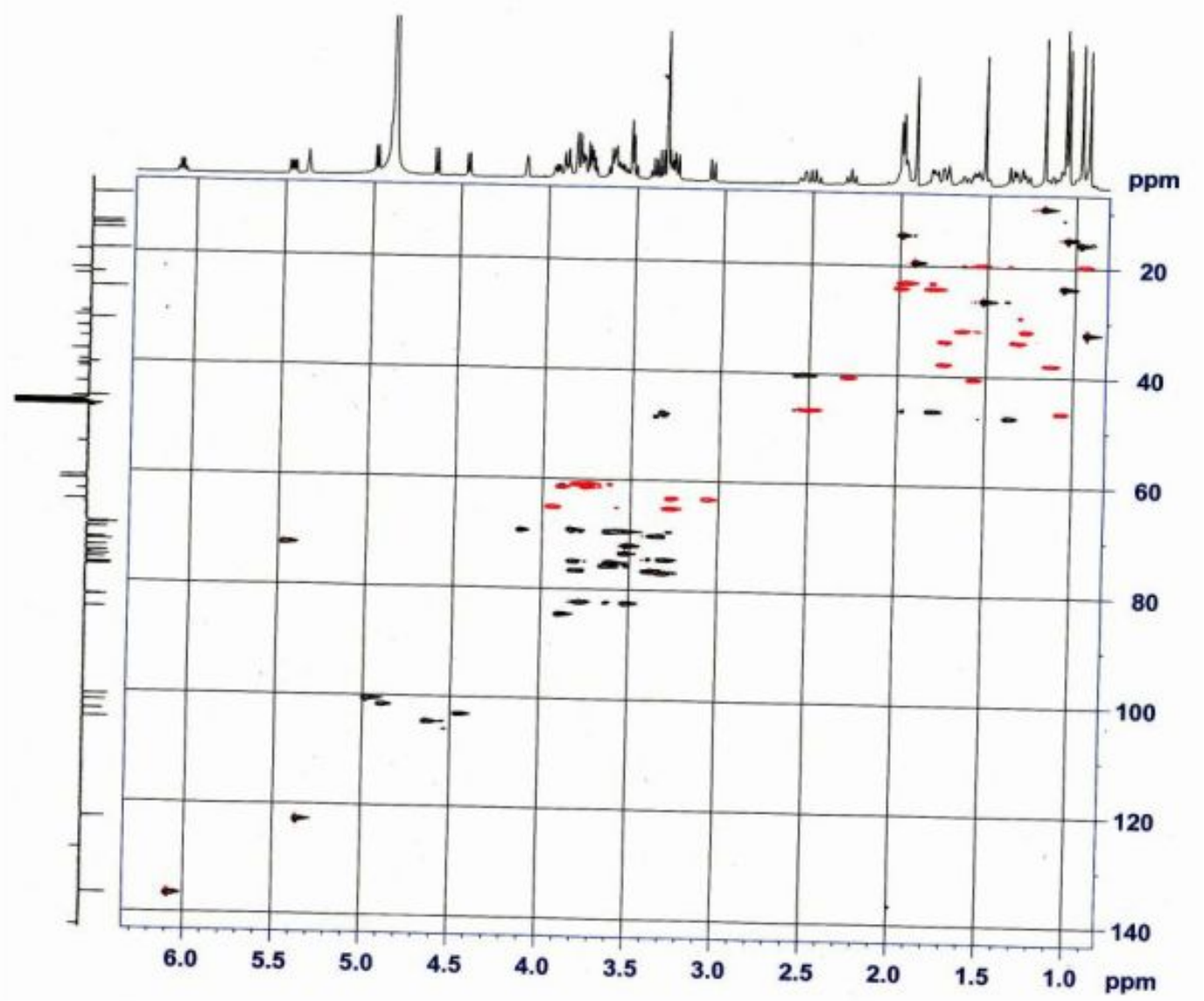



**Figure S5.** The HSQC spectrum of **1** in $CD_3OD$

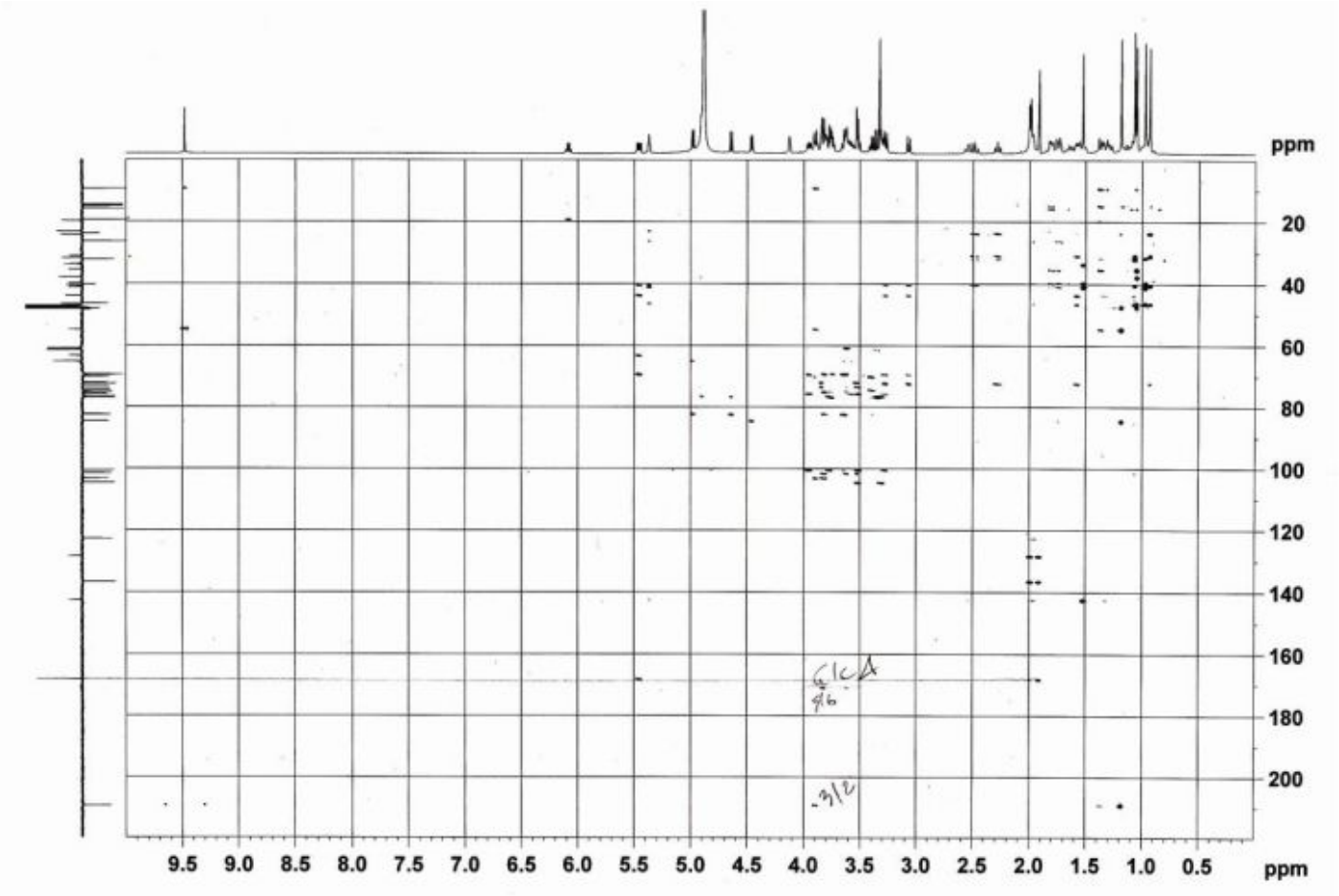



**Figure S6.** The HMBC spectrum of **1** in $CD_3OD$

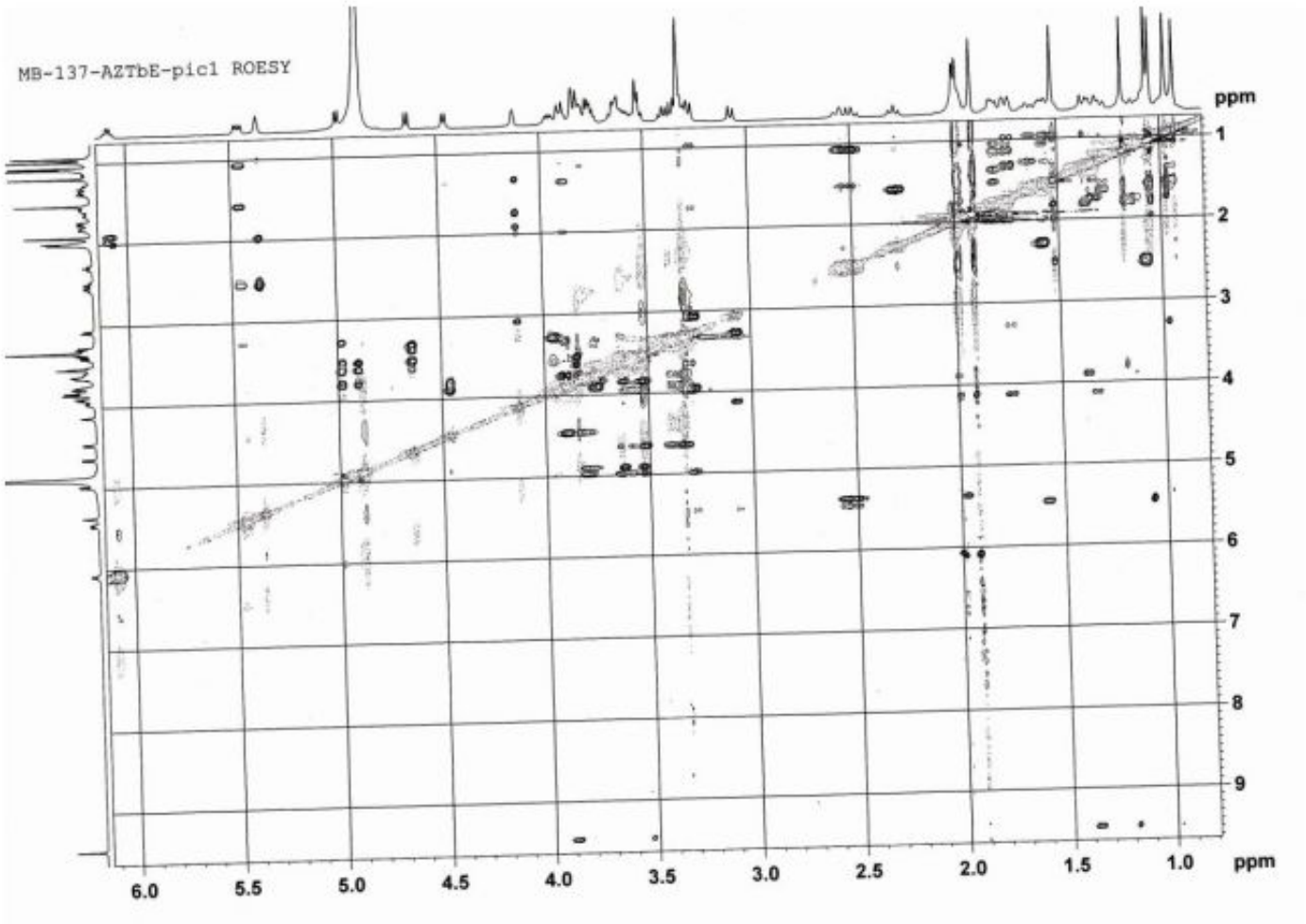



**Figure S7.** The $^{1}H$-$^{1}H$ ROESY spectrum of **1** in $CD_3OD$

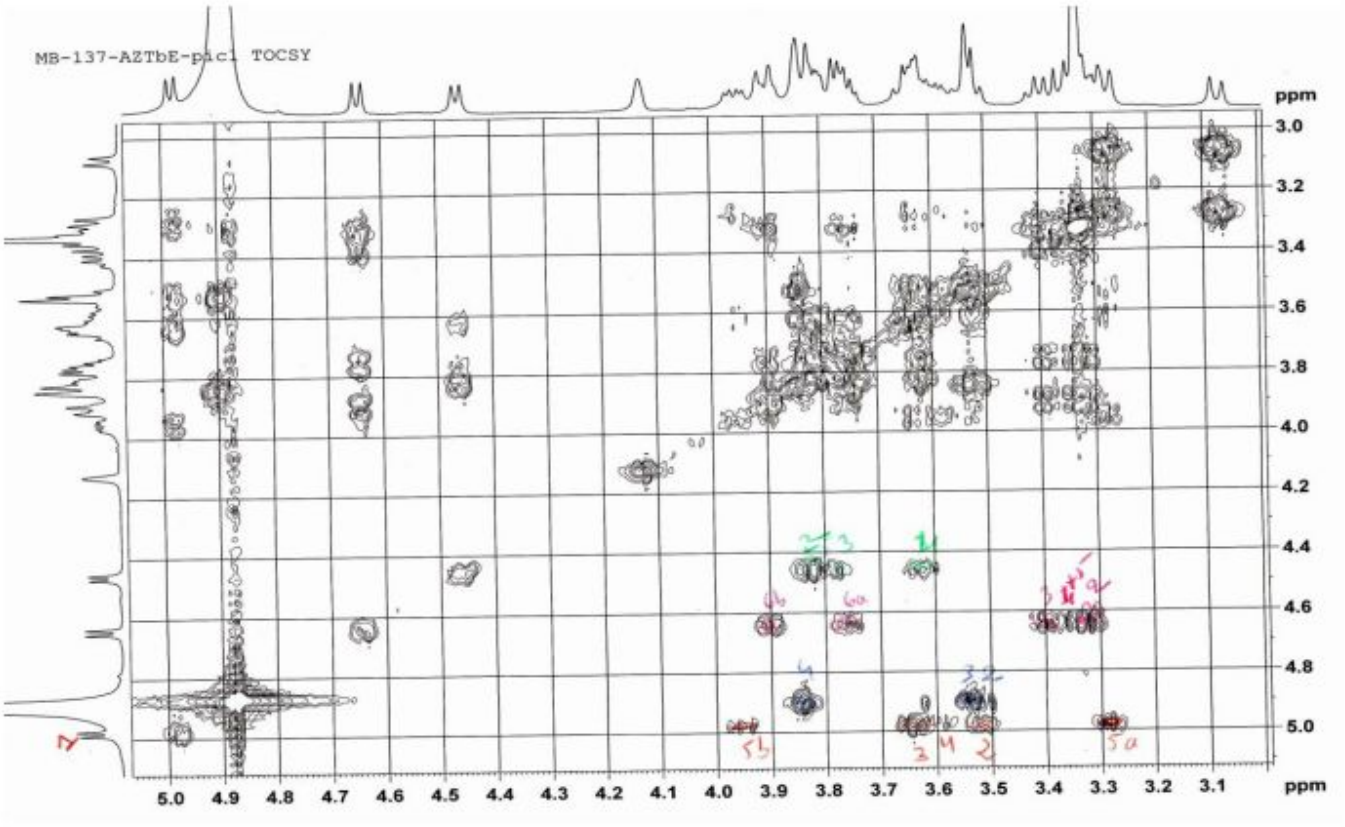



**Figure S8.** The $^{1}H$-$^{1}H$ TOCSY spectrum of **1** in $CD_3OD$

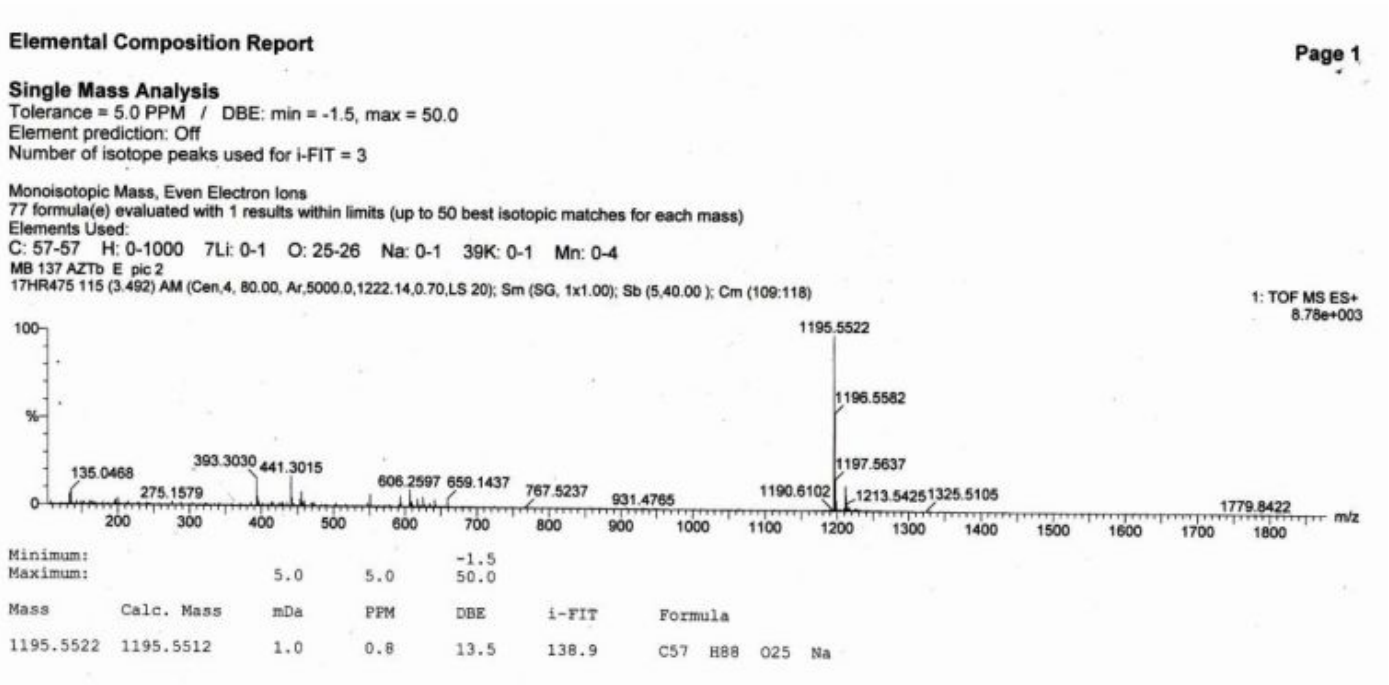



**Figure S9.** The HRESIMS of **2**

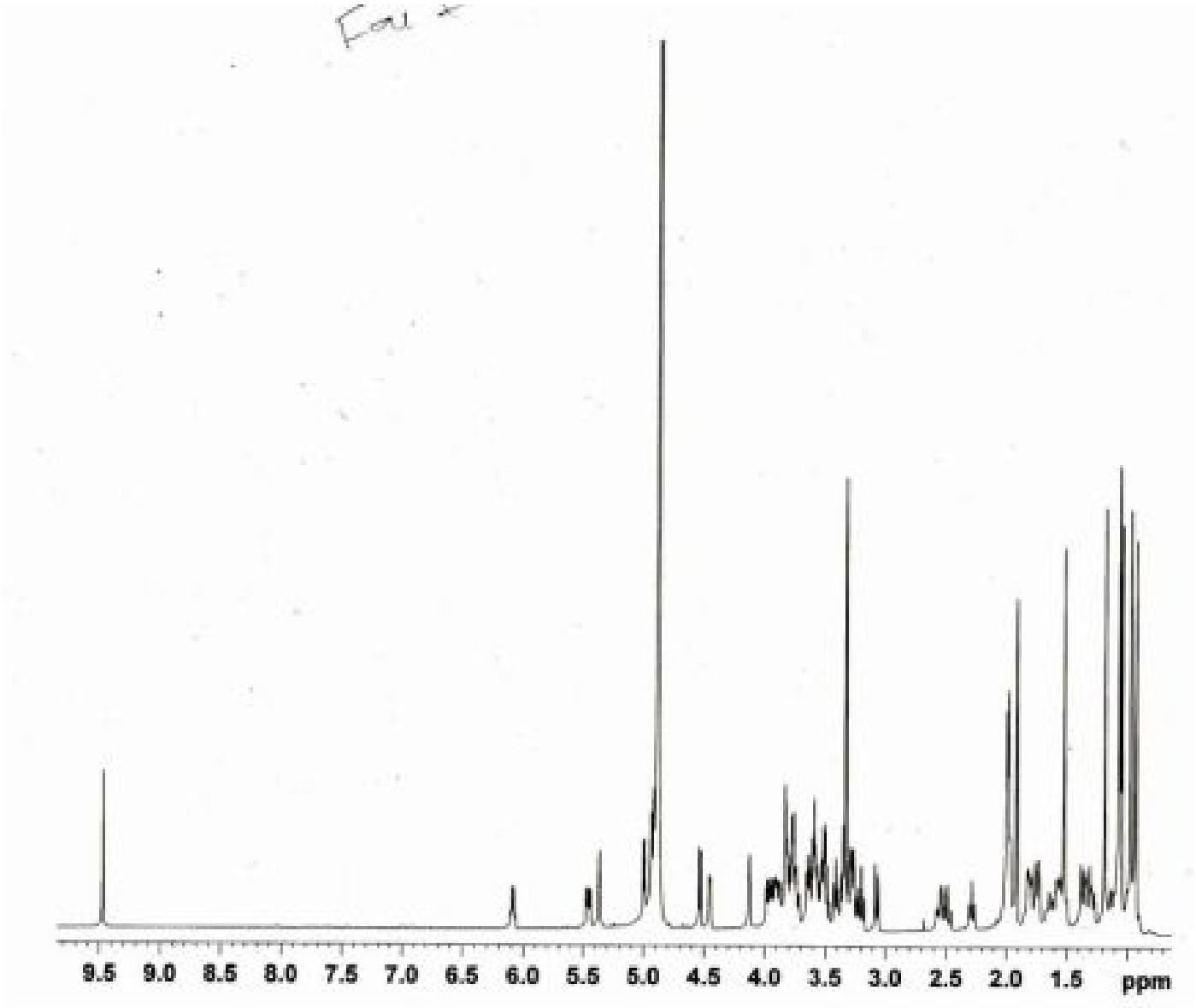



**Figure S10.** The $^{1}$H-NMR spectrum of **2** in $CD_3OD$

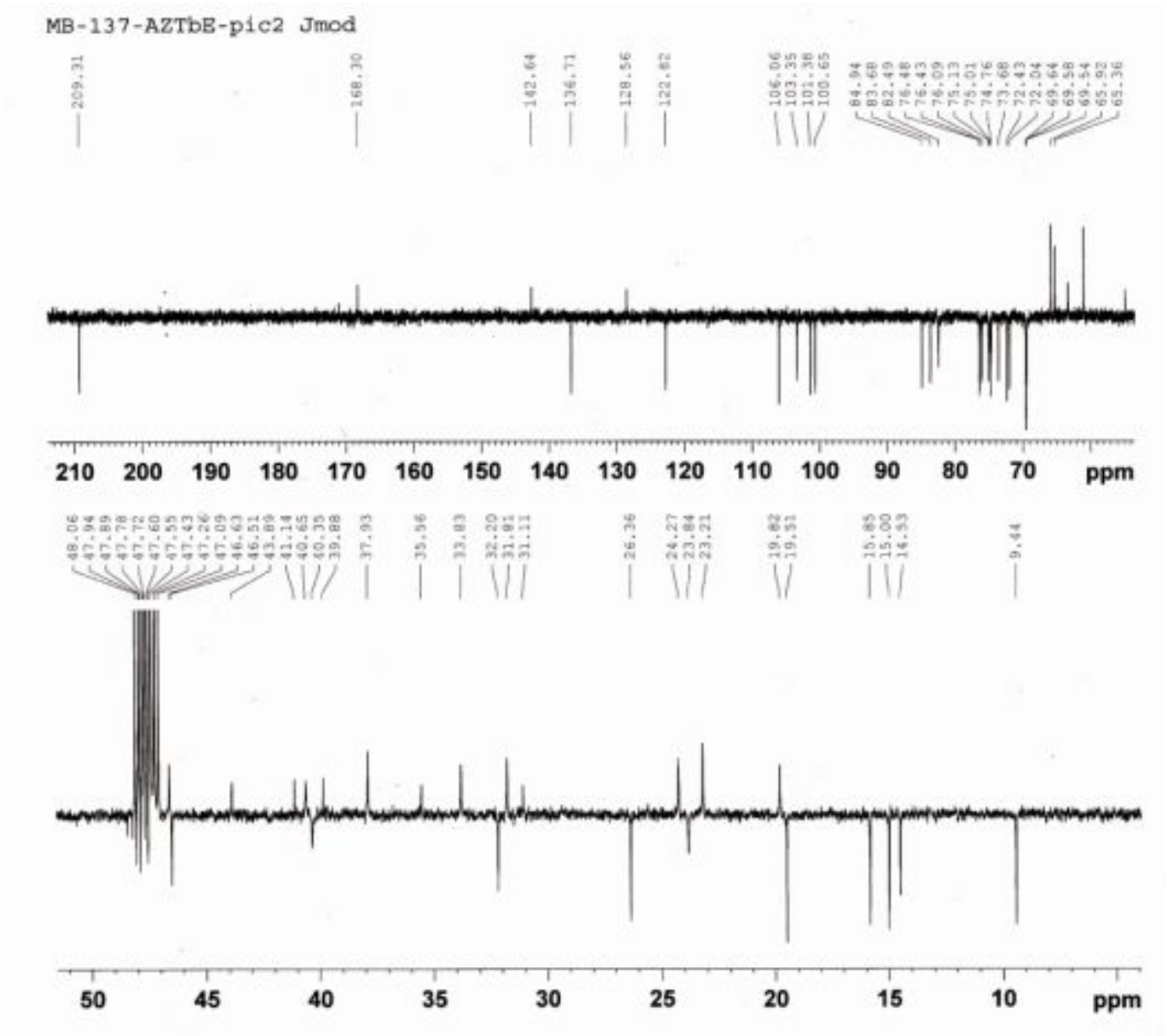



**Figure S11.** The *J*-mod spectrum of **2** in $CD_3OD$

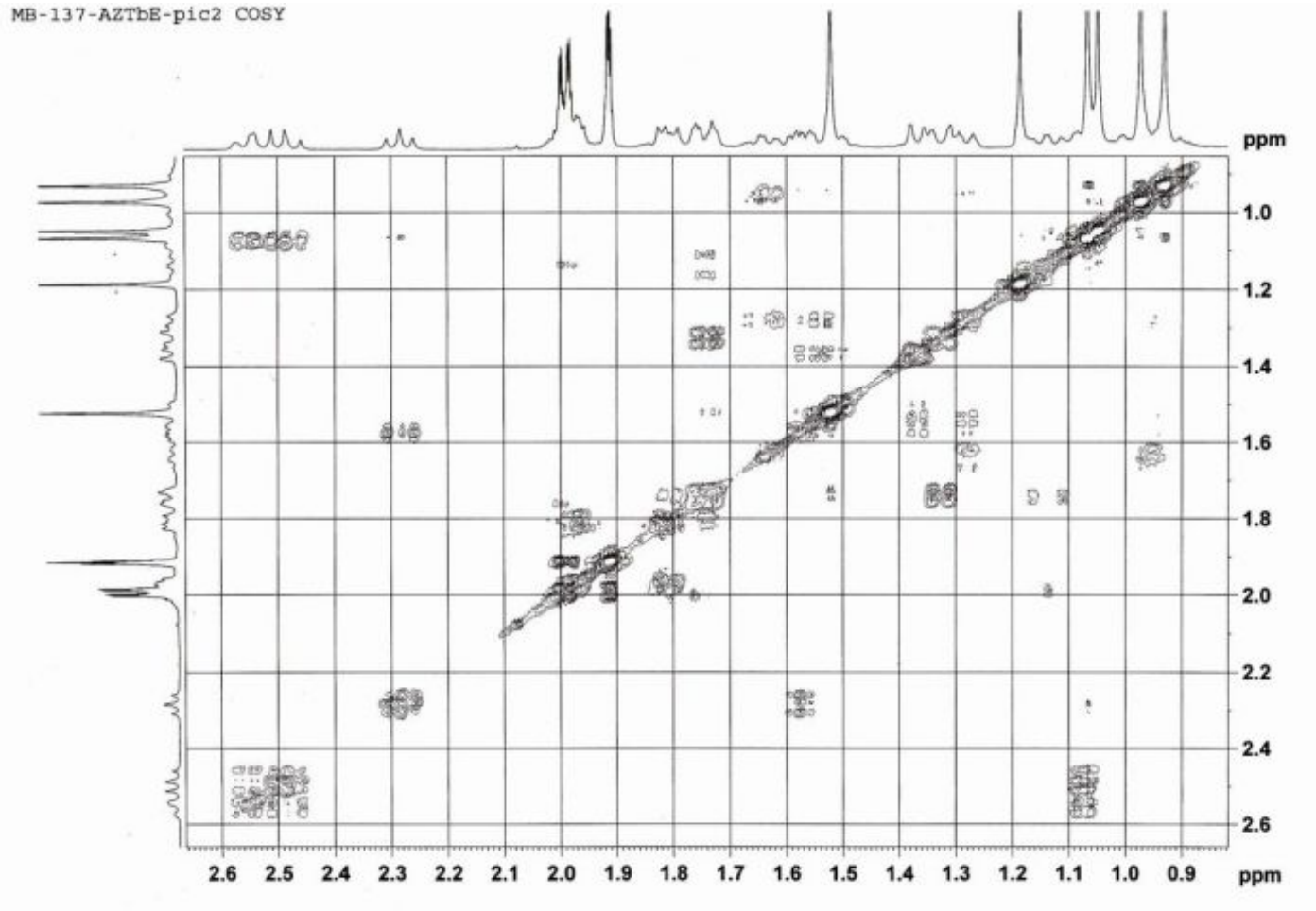



**Figure S12.** The $^{1}H$-$^{1}H$ COSY spectrum of **2** in $CD_3OD$

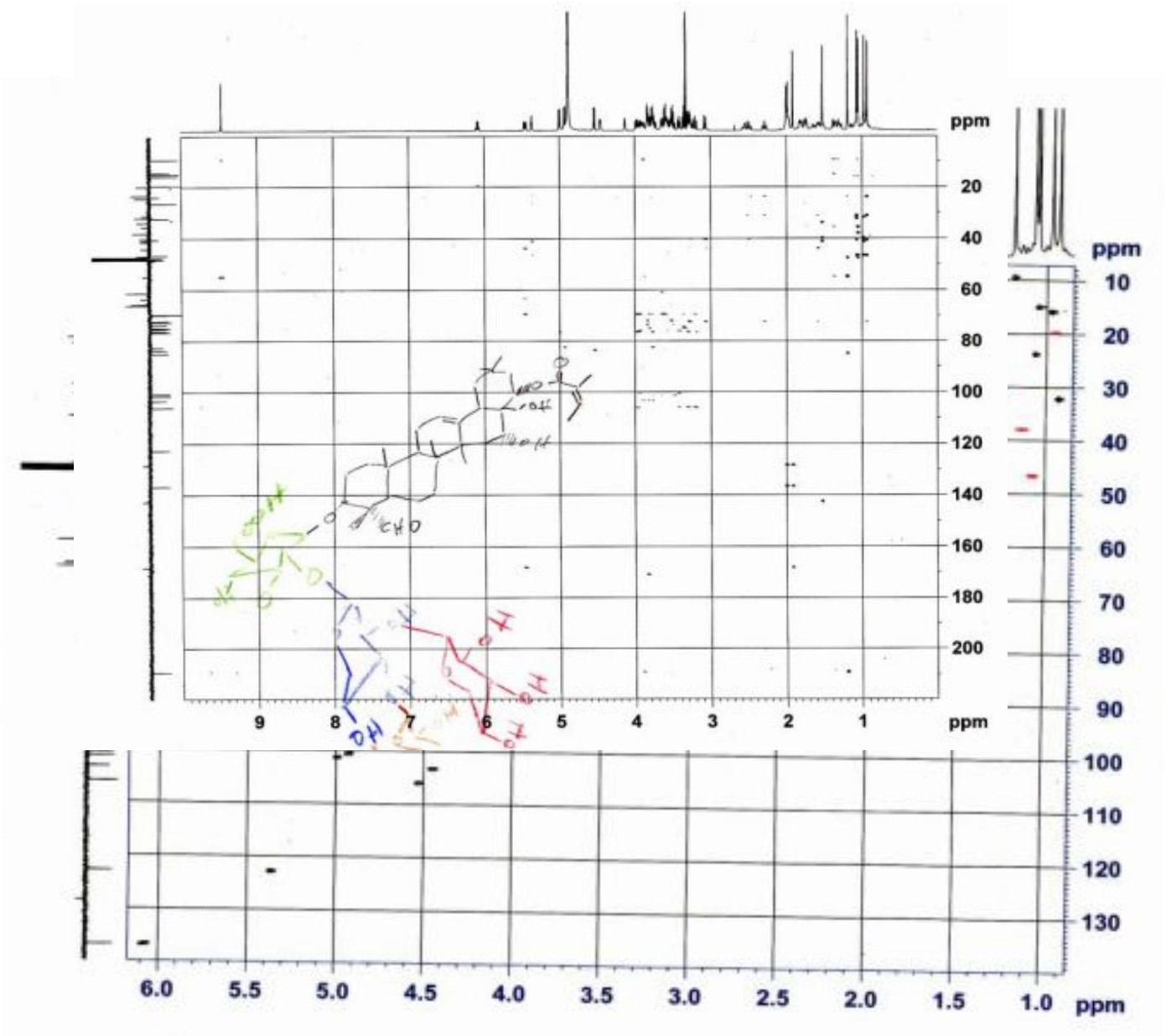



**Figure S13.** The HSQC spectrum of **2** in $CD_3OD$

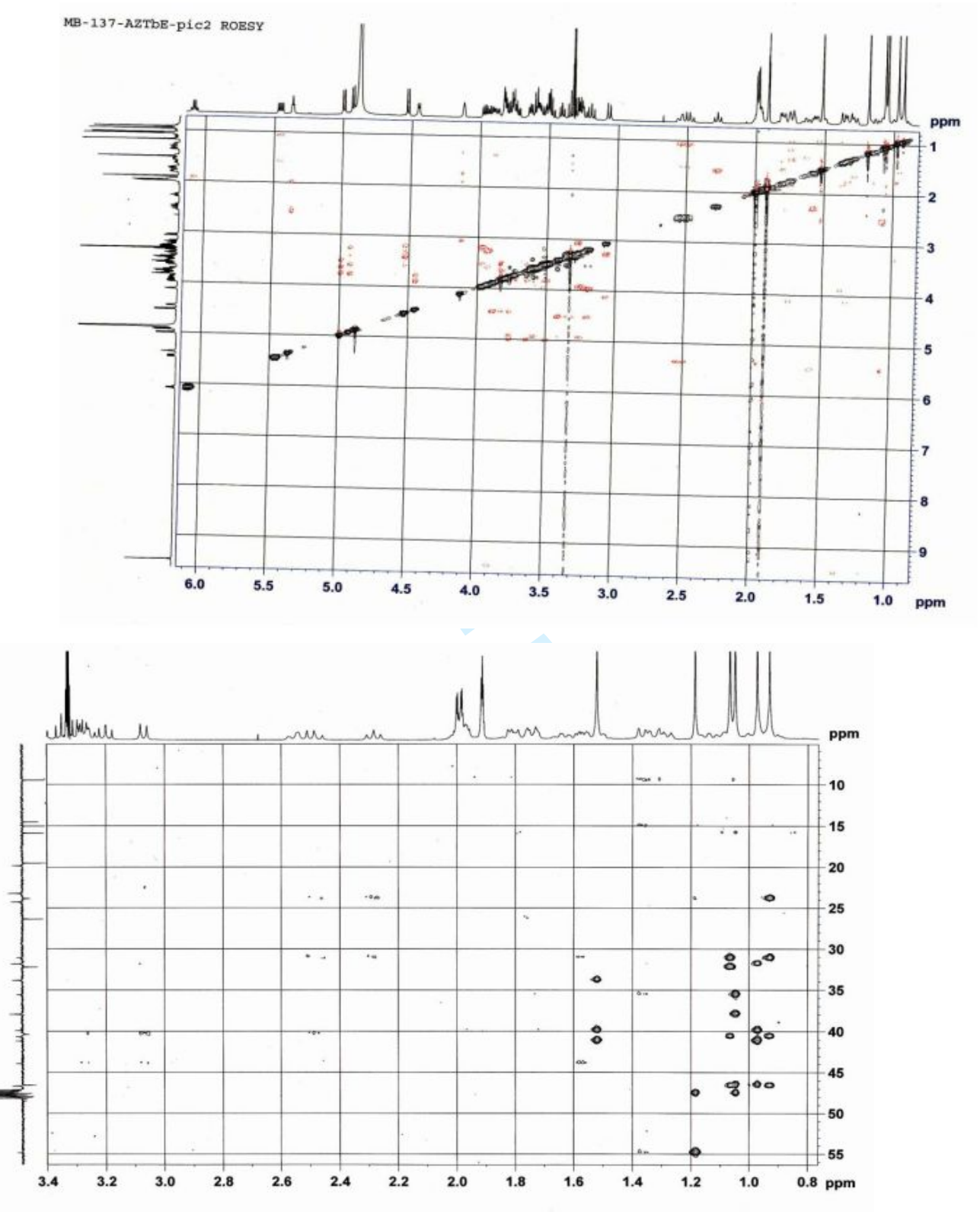


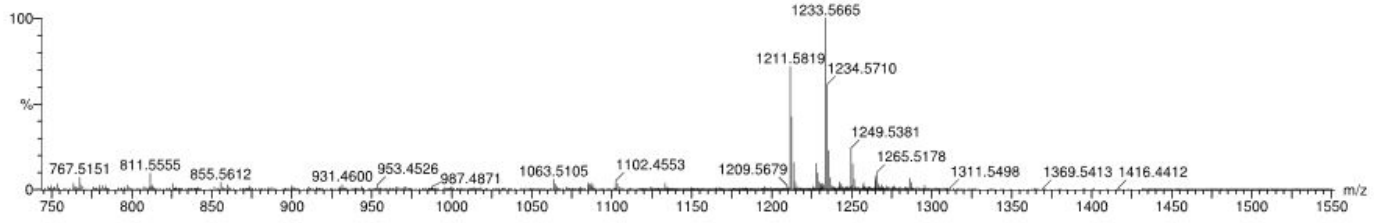

**Figure S14.** The HMBC spectrum of **2** in $CD_3OD$

**Elemental Composition Report** Page 1

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 58-58 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1
MB.137.AZTb E pic 3
18HR08 251 (8.155) AM (Cen,4, 80.00, Ar,5000.0,472.67,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00 ); Cm (237:268)

1: TOF MS ES+
6.15e+003




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 5.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 1211.5819 | 1211.5825 | -0.6 | -0.5 | 12.5 | 25.5 | C58 H92 O25 Na |

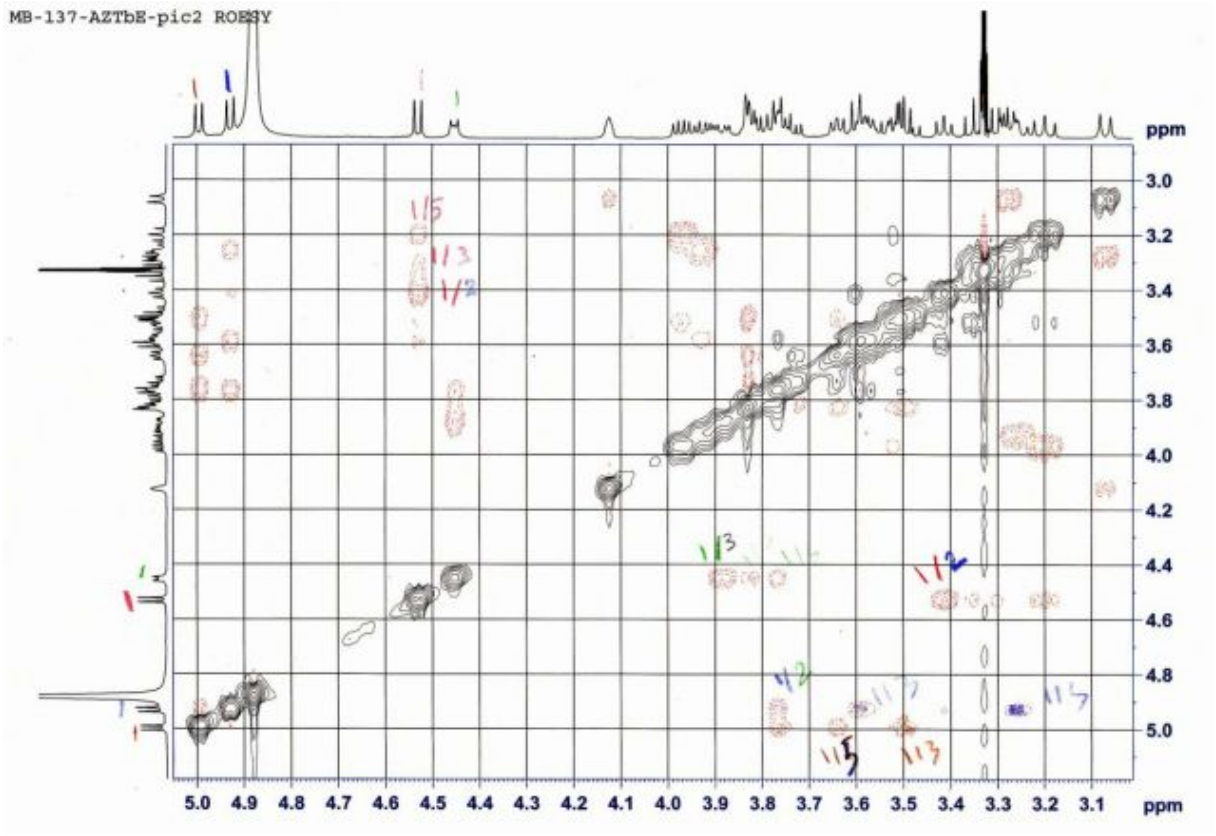



**Figure S15.** The $^{1}$H-$^{1}$H ROESY spectrum of **2** in $CD_3OD$

**Figure S16.** The HRESIMS of **3**

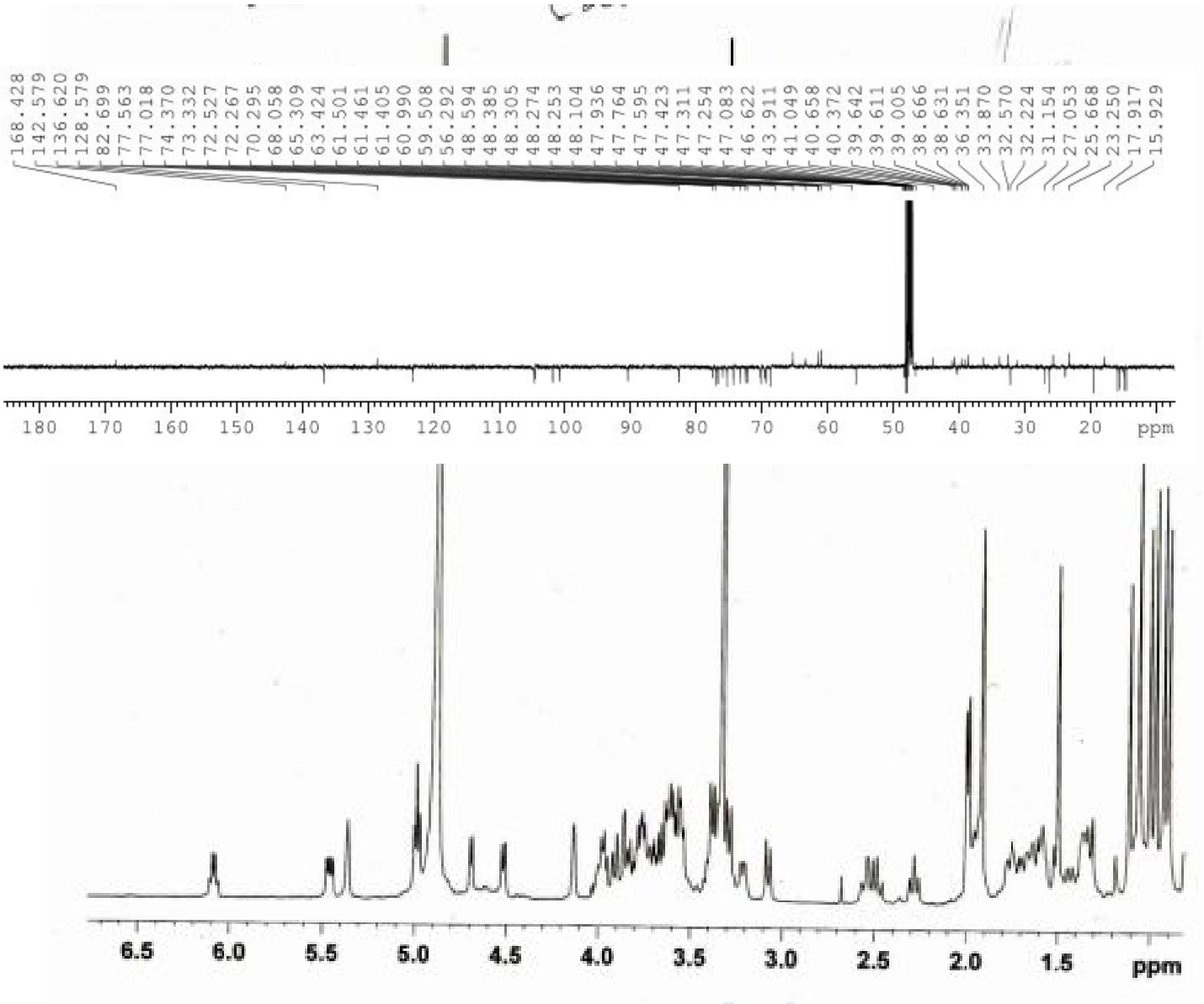



**Figure S17.** The $^{1}$H-NMR spectrum of **3** in $CD_3OD$

**Figure S18.** The *J*-mod spectrum of **3** in $CD_3OD$

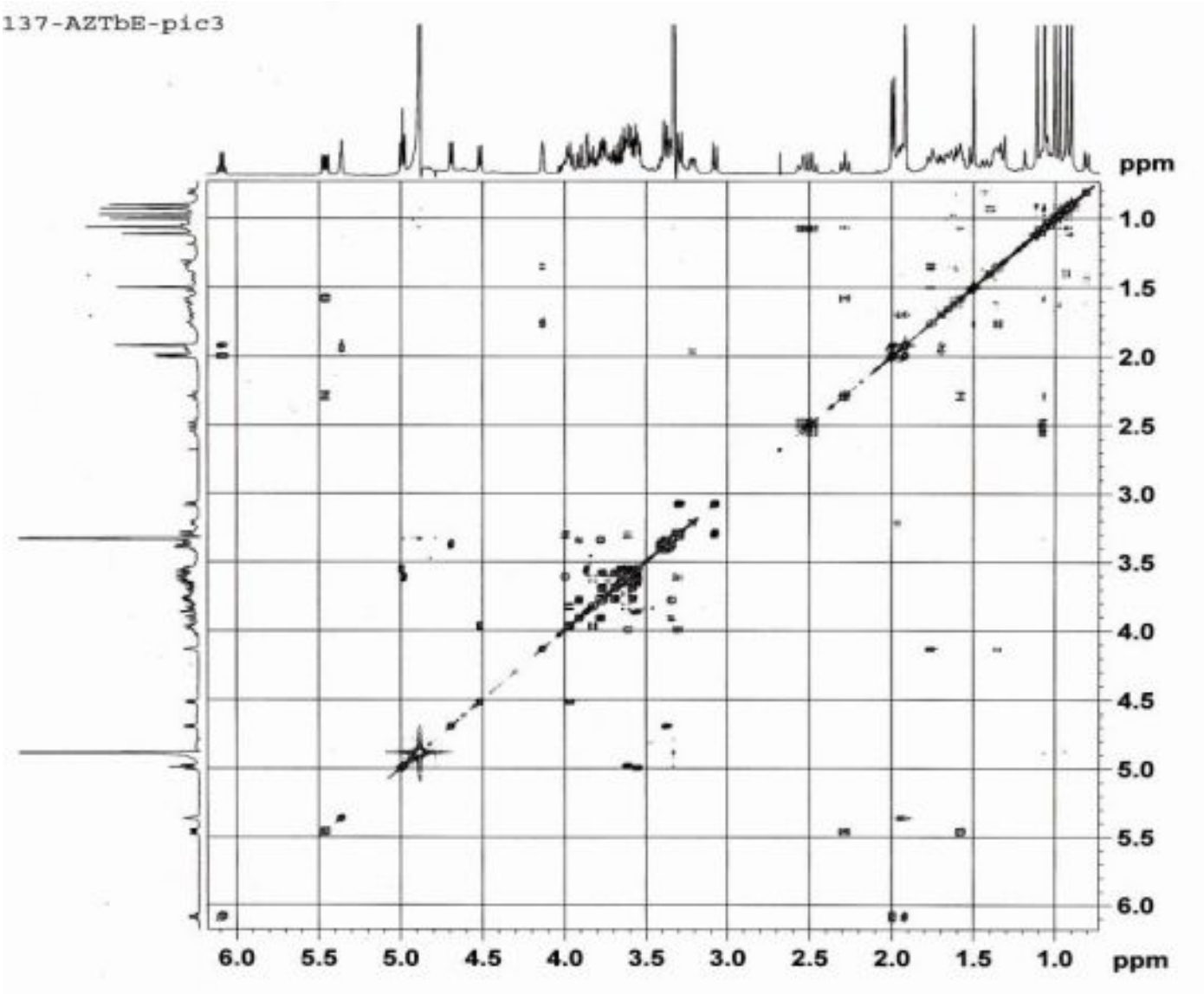



**Figure S19.** The $^{1}H$-$^{1}H$ COSY spectrum of **3** in $CD_3OD$

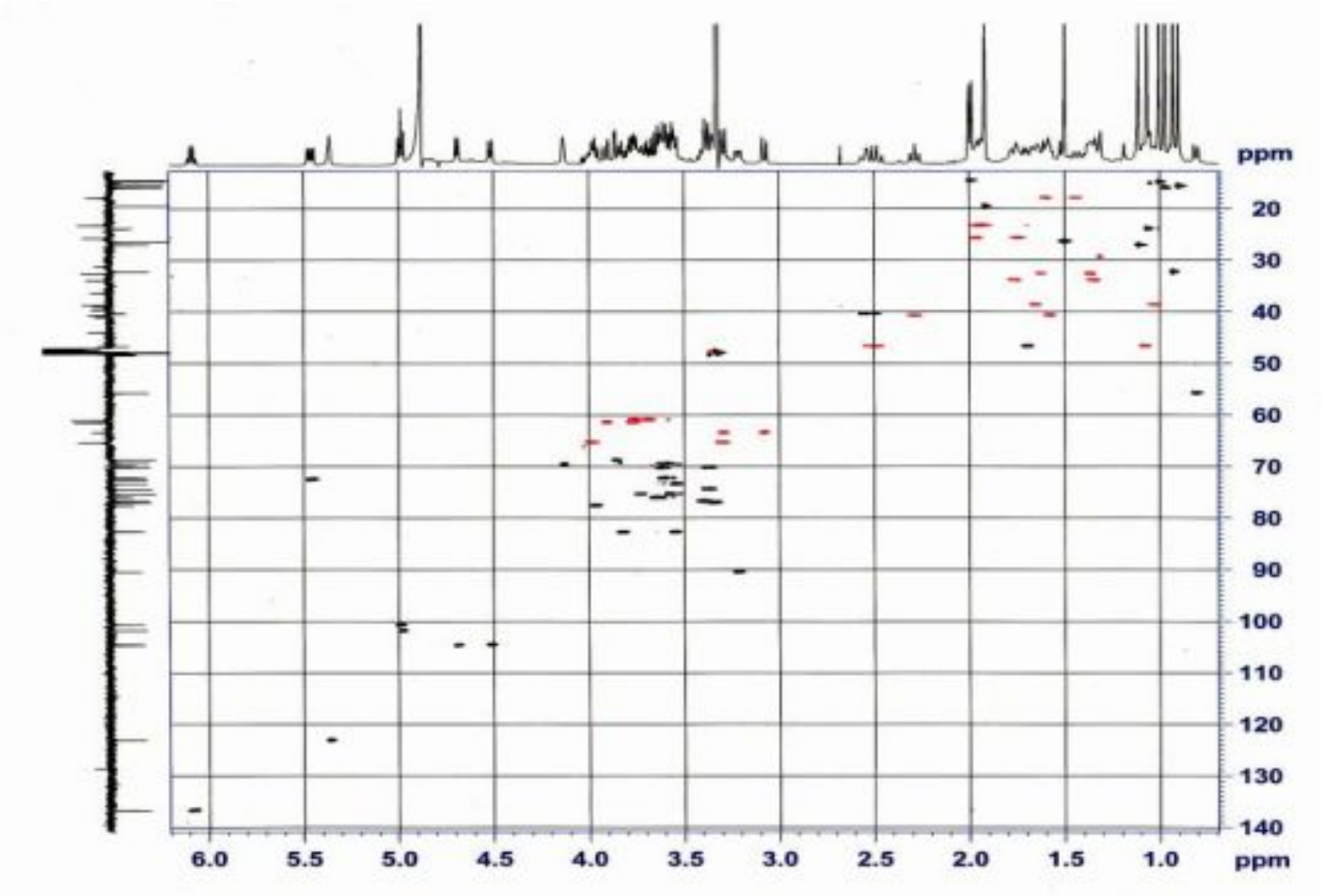



**Figure S20.** The HSQC spectrum of **3** in $CD_3OD$

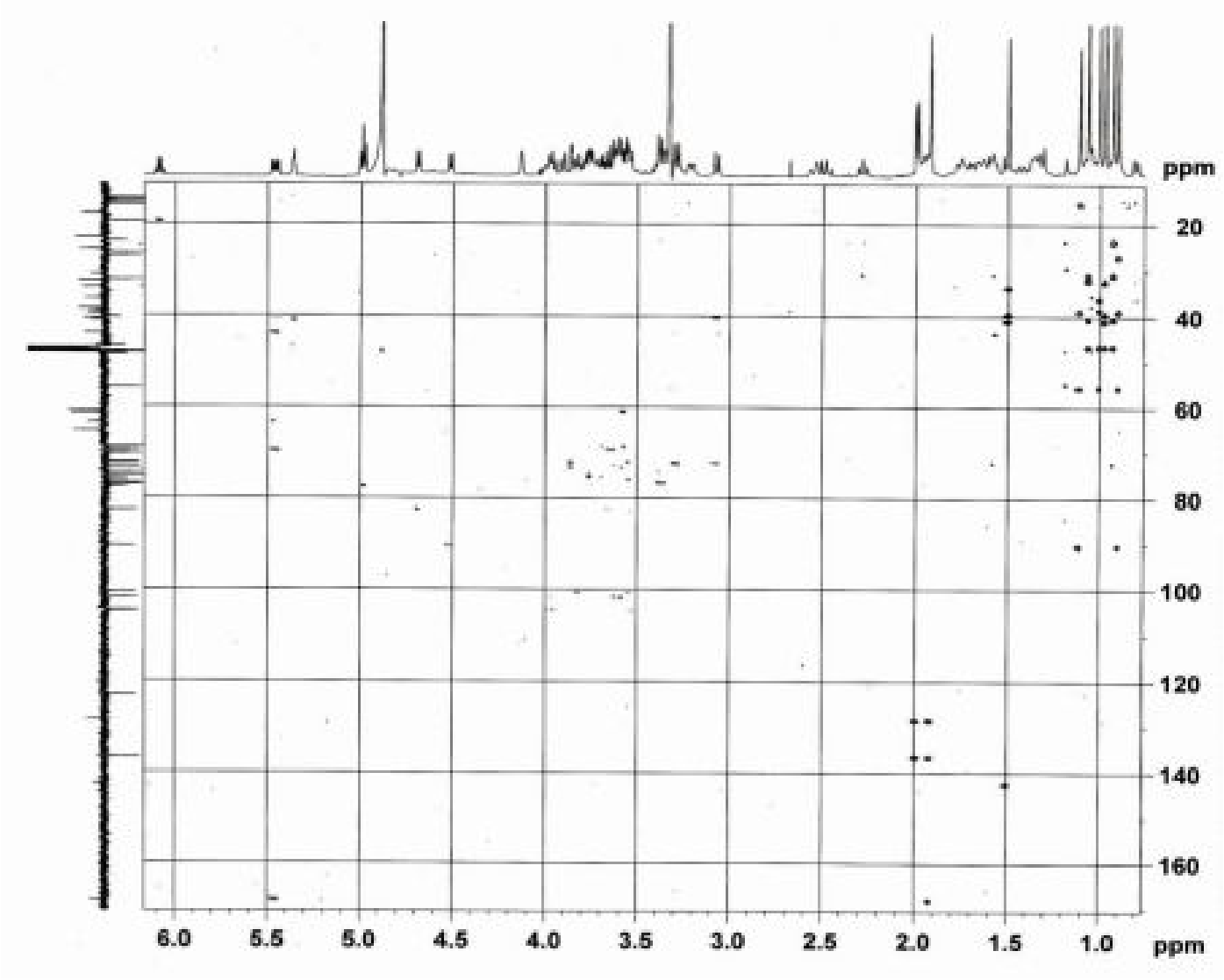



**Figure S21.** The HMBC spectrum of **3** in $CD_3OD$

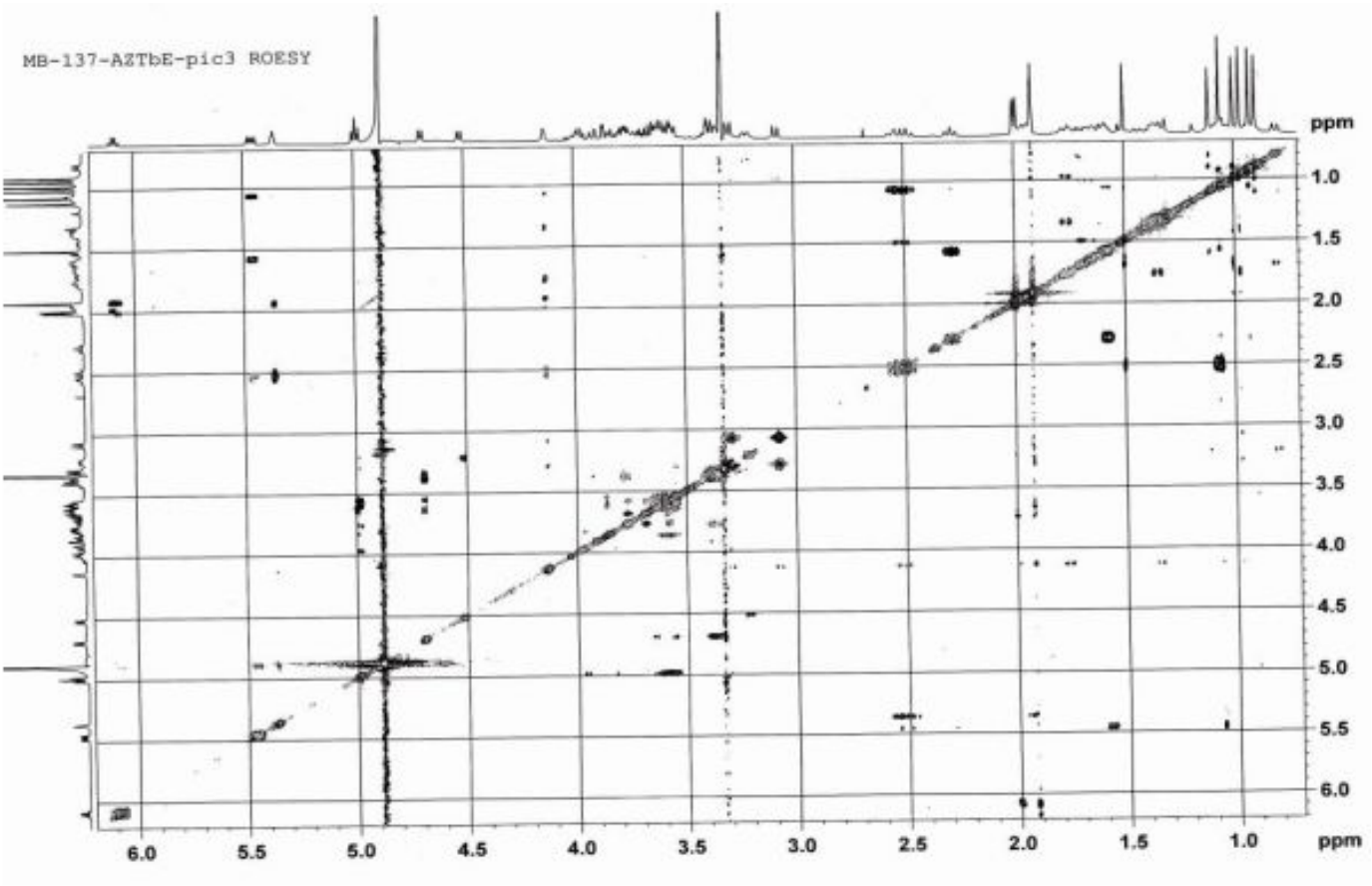



**Figure S22.** The $^{1}H$-$^{1}H$ ROESY spectrum of **3** in $CD_3OD$

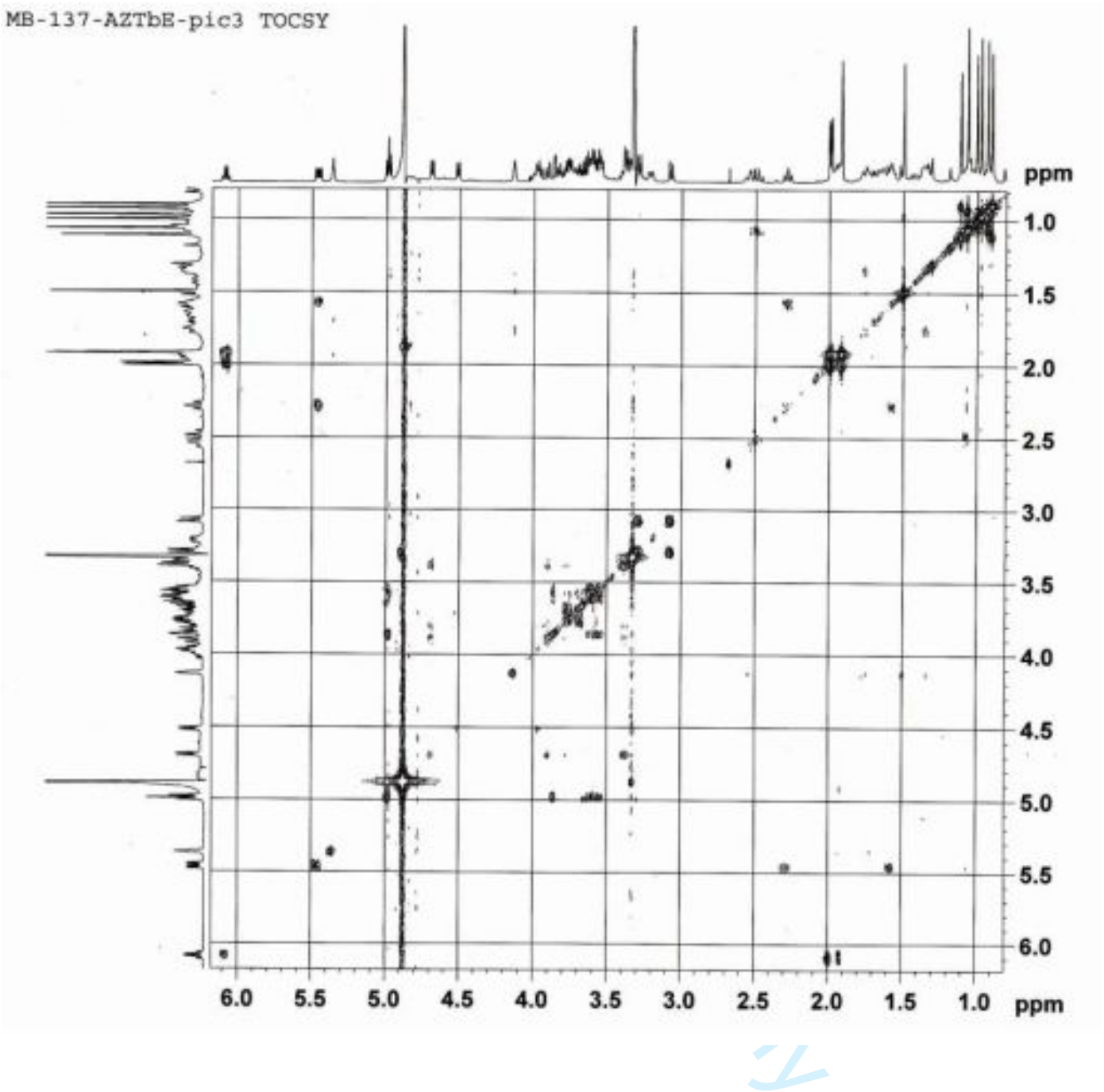
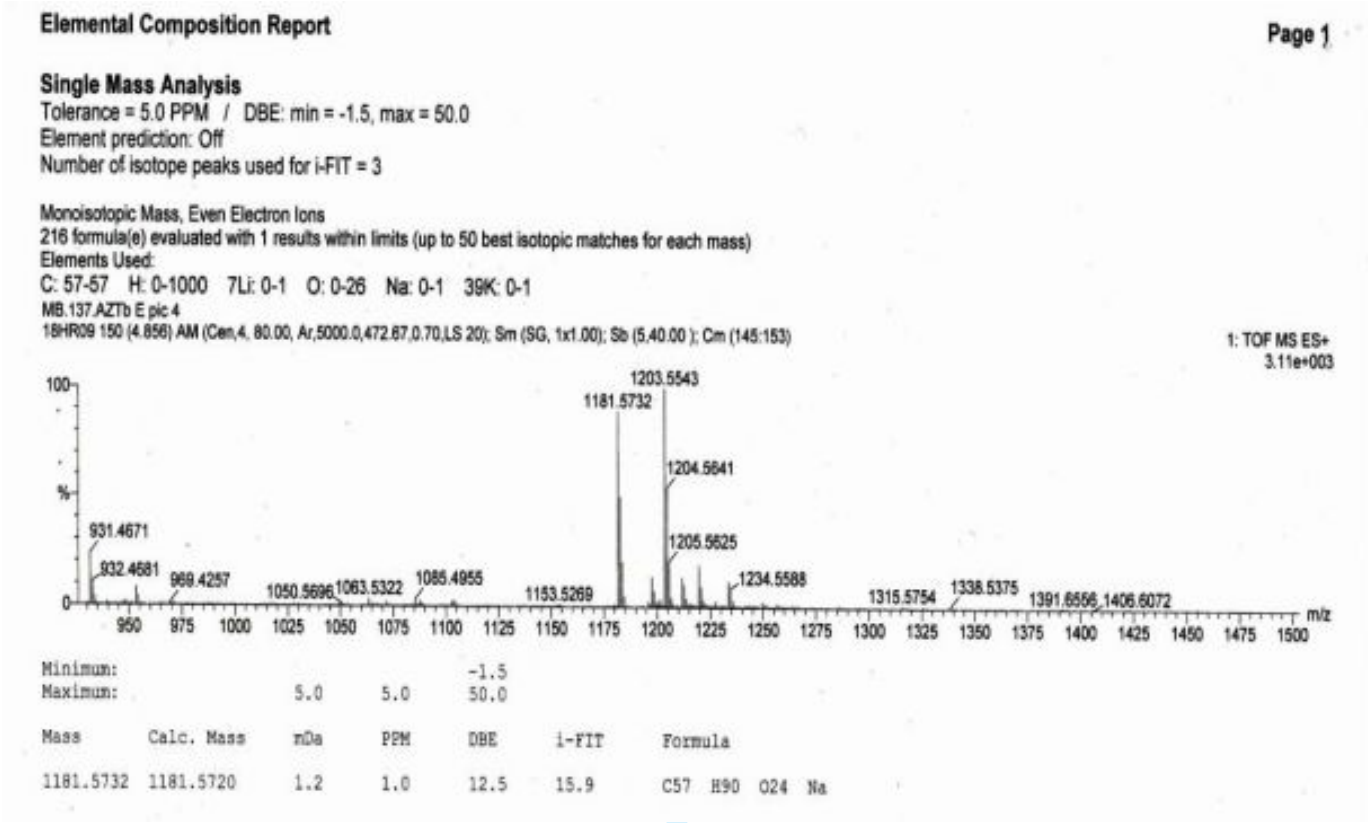



**Figure S23.** The $^{1}H$-$^{1}H$ TOCSY spectrum of **3** in $CD_3OD$



**Elemental Composition Report** Page 1

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 57-57 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1
MB.137.AZTb E pic 4
18HR09 150 (4.856) AM (Cen,4, 80.00, Ar,5000.0,472.67,0.70,LS 20); Sm (SG, 1x1.00); Sb (5.40,00 ); Cm (145:153)



| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 5.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 1181.5732 | 1181.5720 | 1.2 | 1.0 | 12.5 | 15.9 | C57 H90 O24 Na |

**Figure S24.** The HRESIMS of **4**

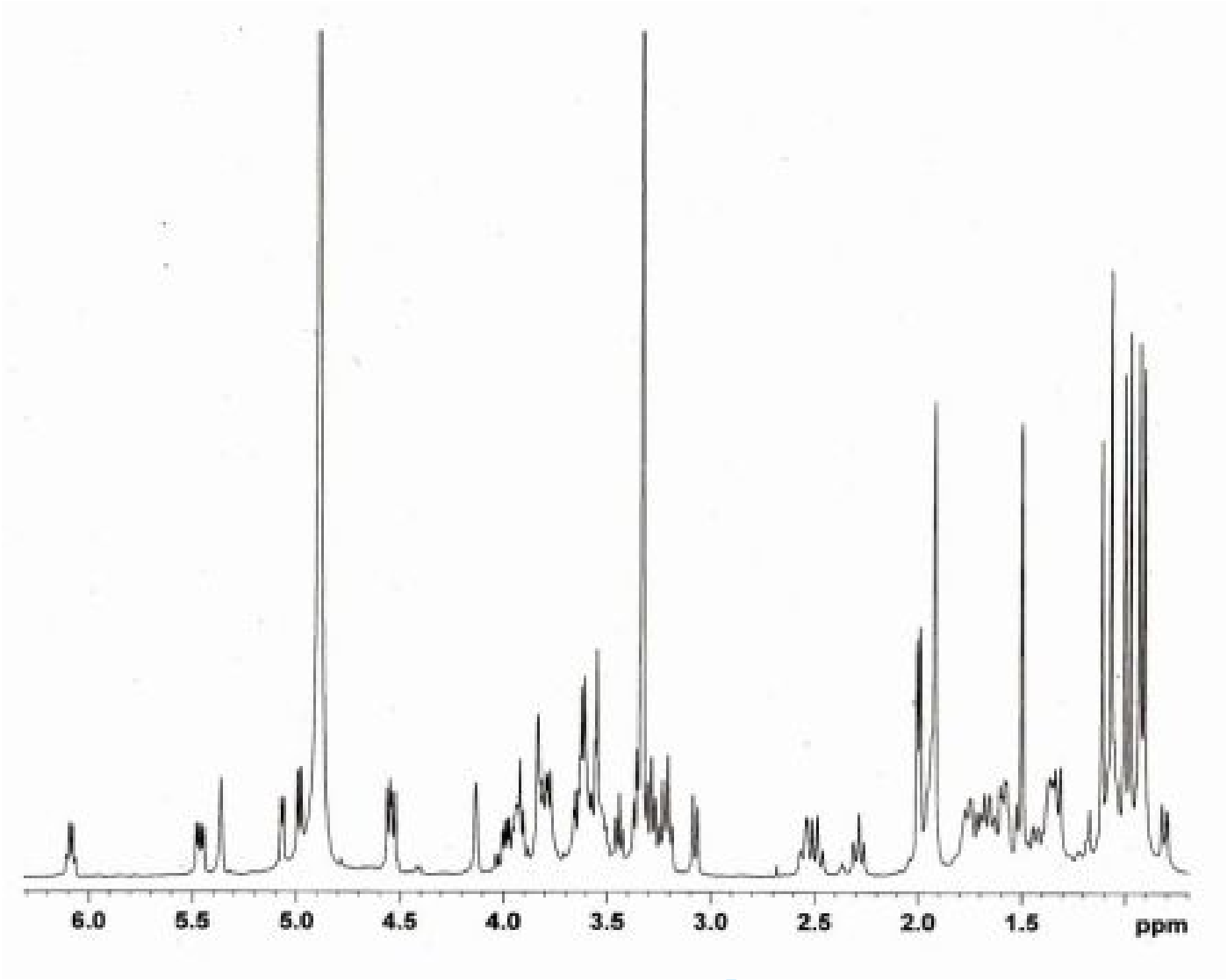



**Figure S25.** The $^{1}$H-NMR spectrum of **4** in $CD_3OD$

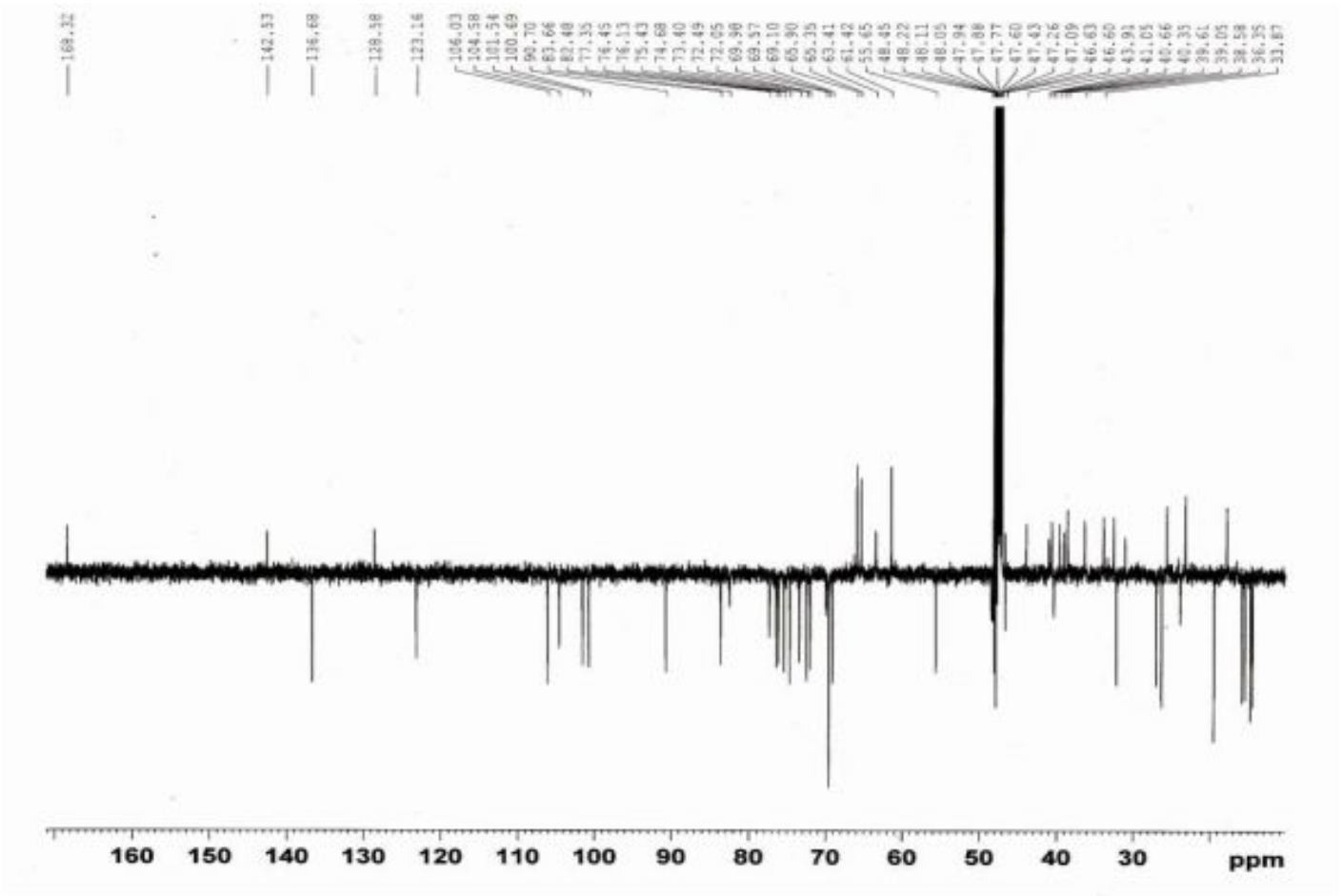



**Figure S26.** The *J*-mod spectrum of **4** in $CD_3OD$

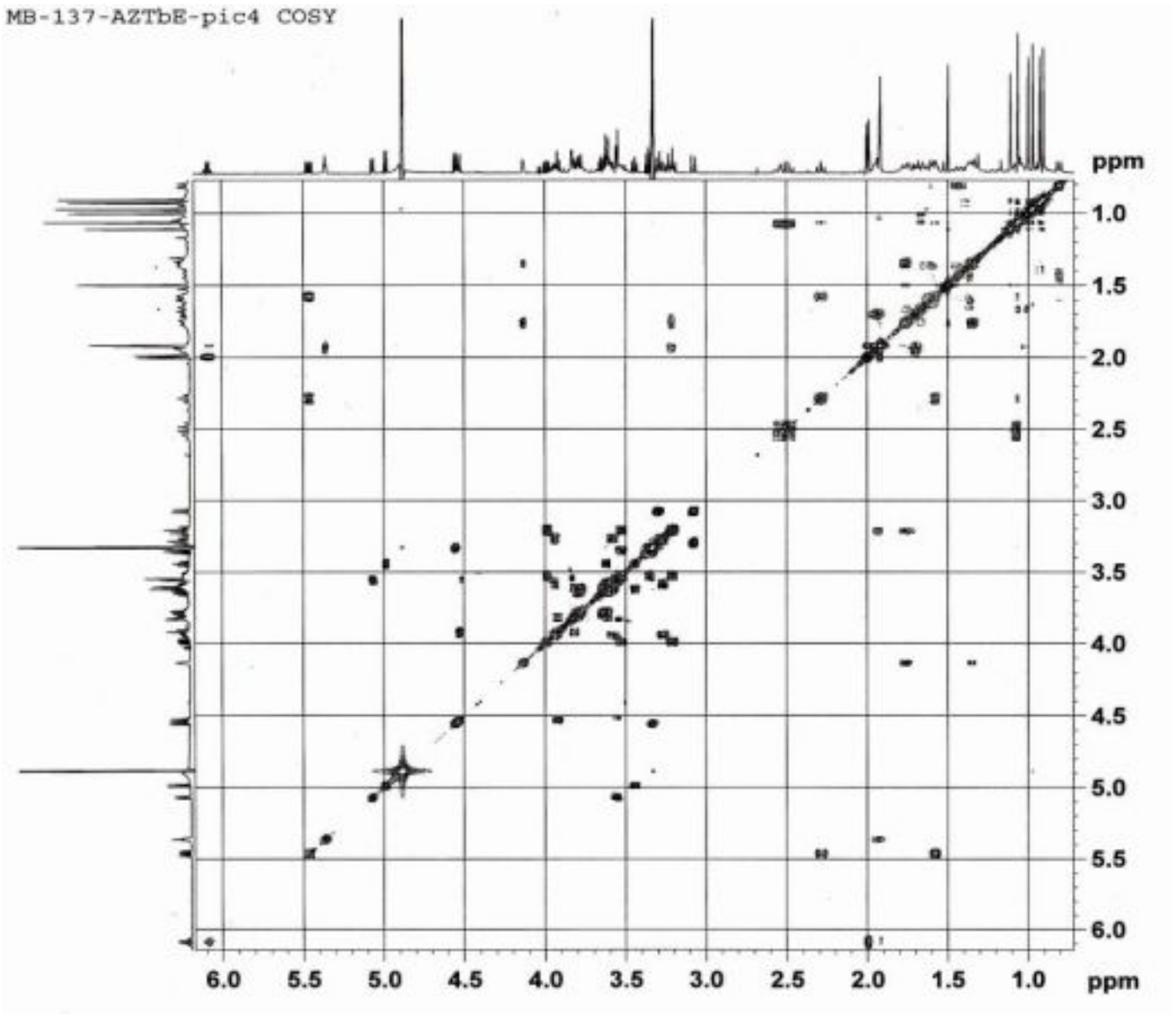



**Figure S27.** The $^{1}H$-$^{1}H$ COSY spectrum of **4** in $CD_3OD$

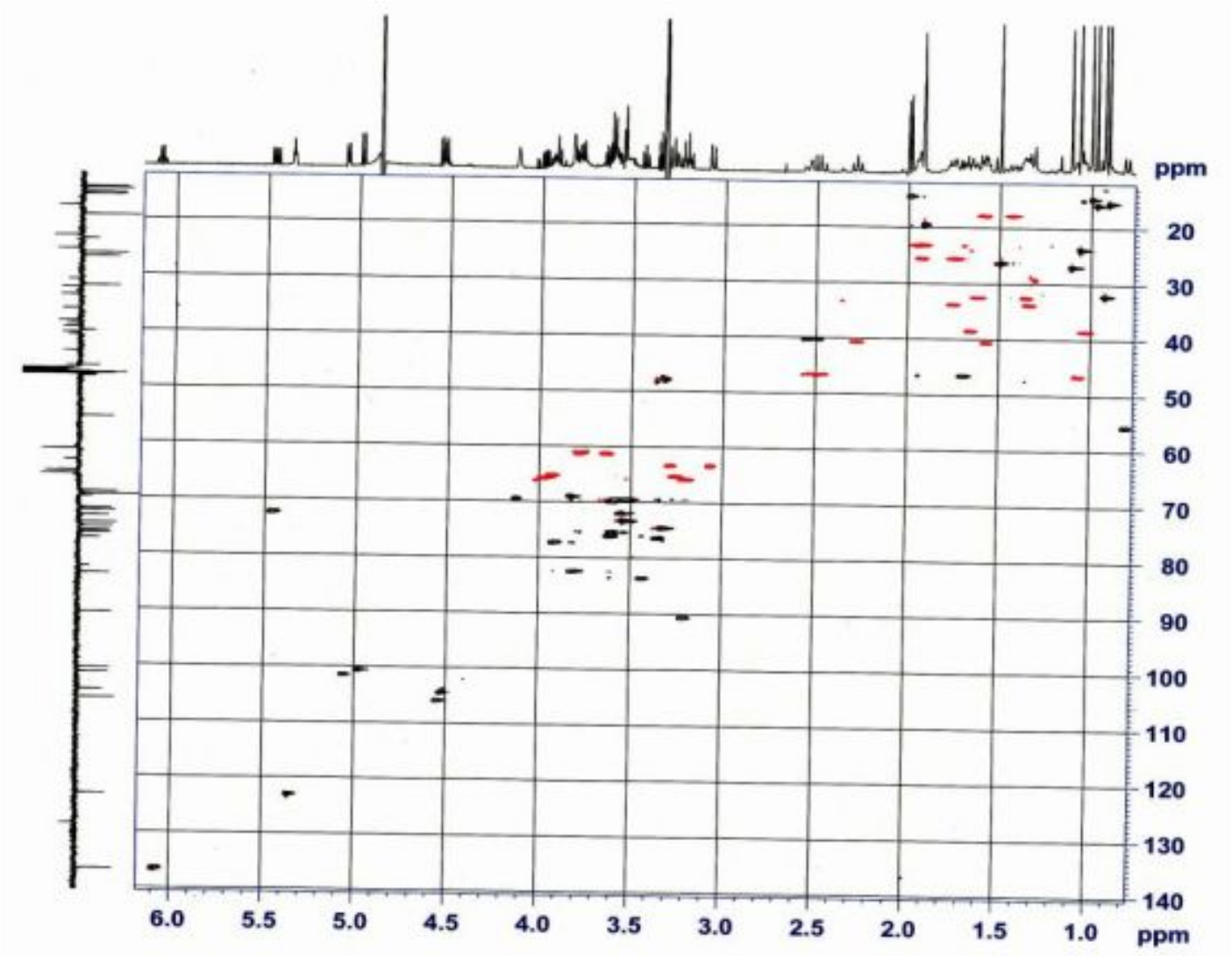



**Figure S28.** The HSQC spectrum of **4** in $CD_3OD$

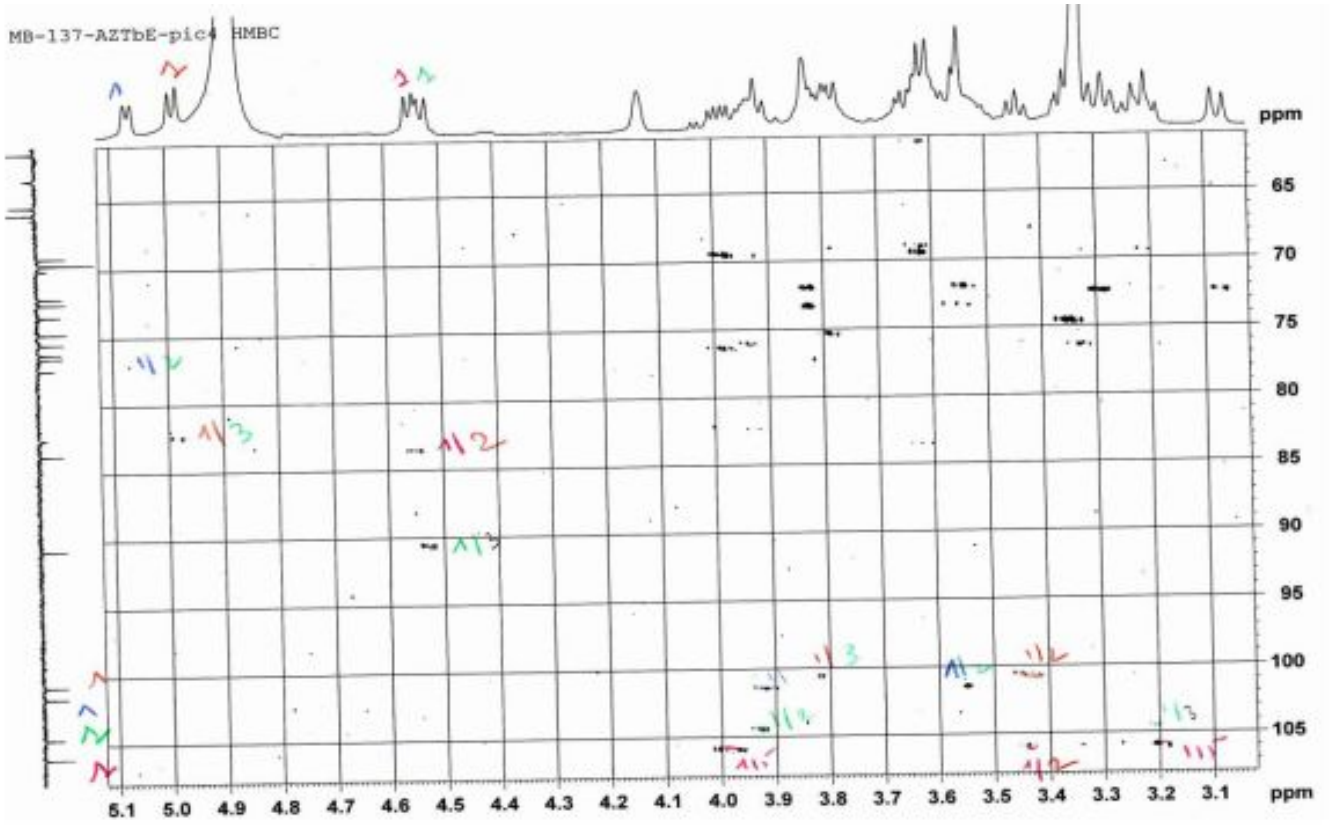



**Figure S29.** The HMBC spectrum of **4** in $CD_3OD$

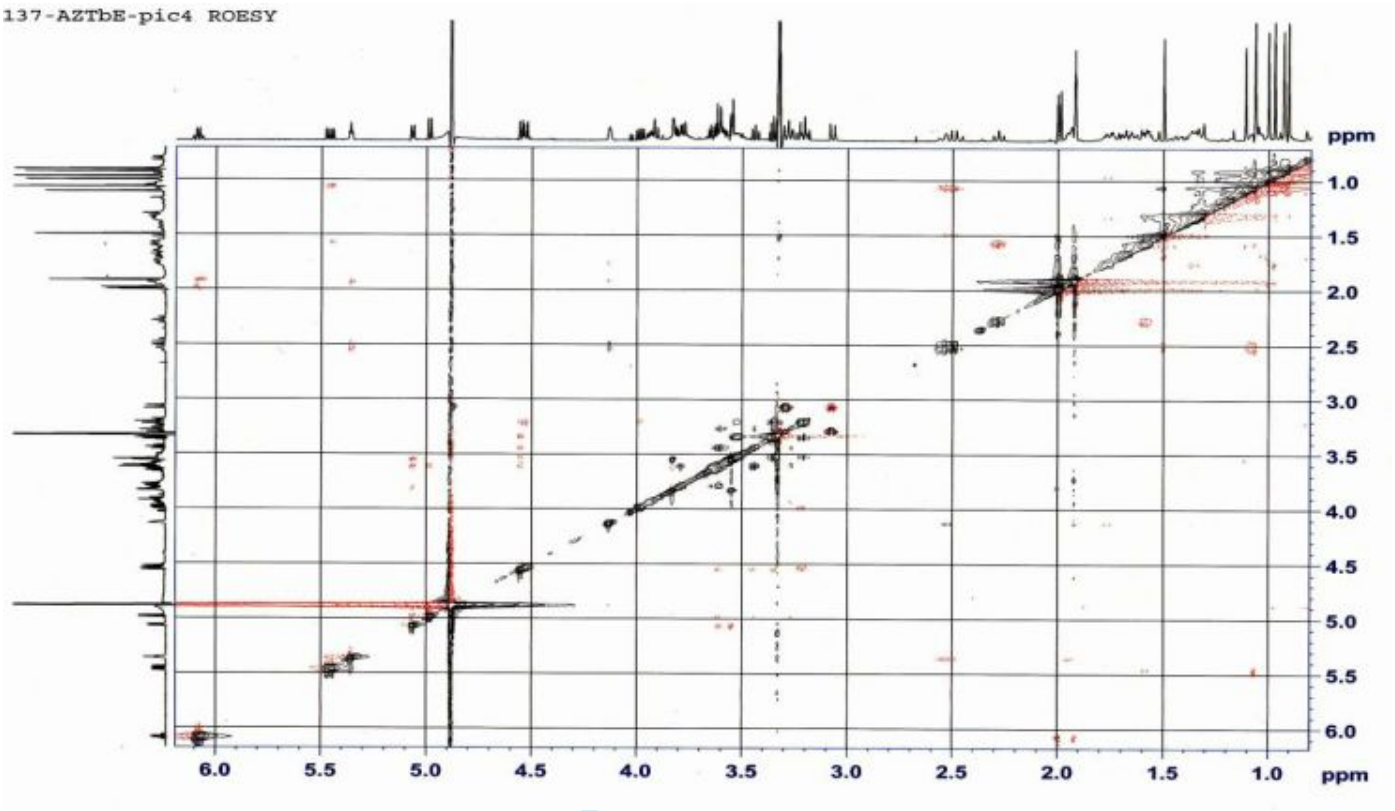



**Figure S30.** The $^{1}$H-$^{1}$H ROESY spectrum of **4** in $CD_3OD$

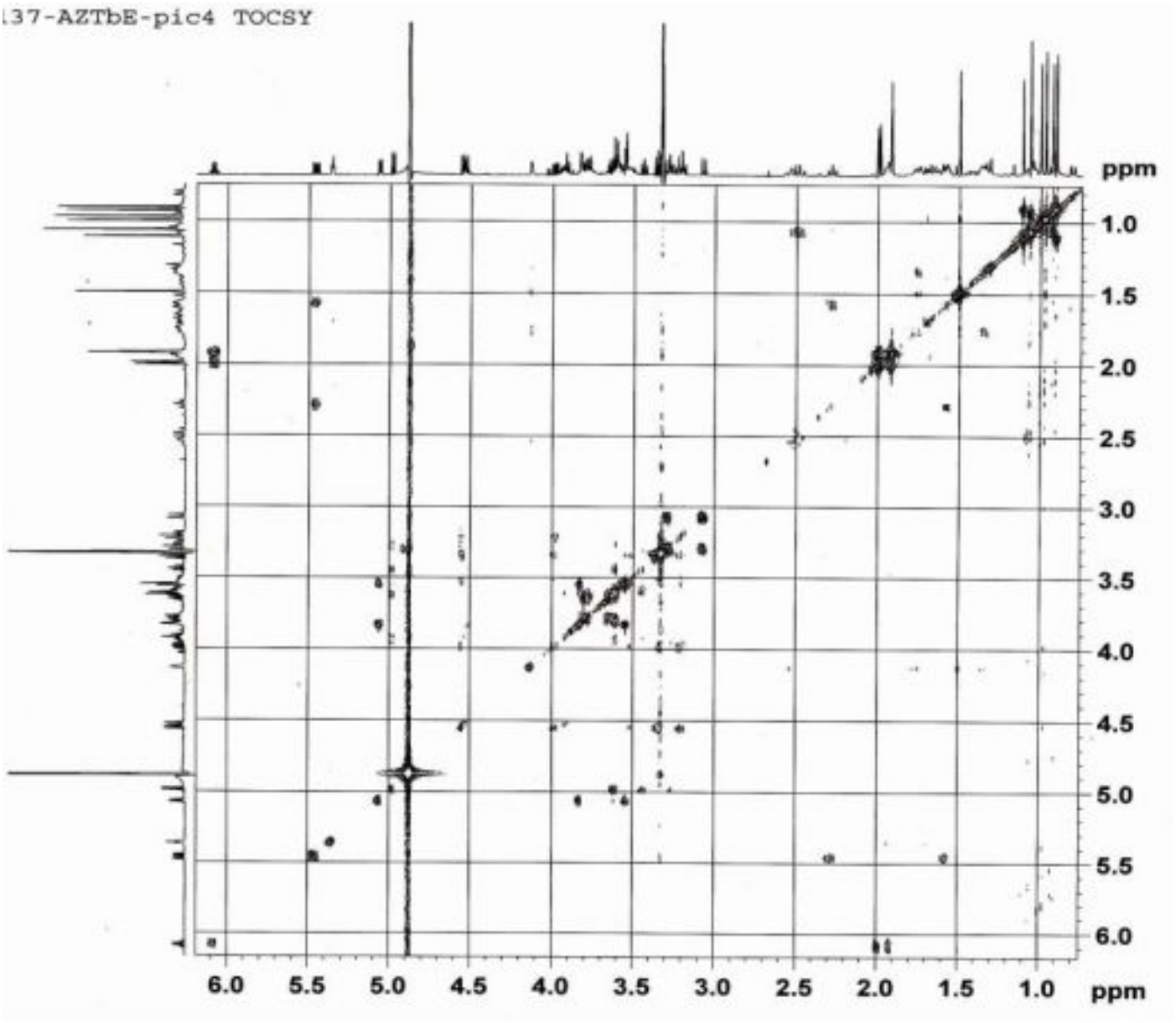



**Figure S31.** The $^{1}H$-$^{1}H$ TOCSY spectrum of **4** in $CD_3OD$

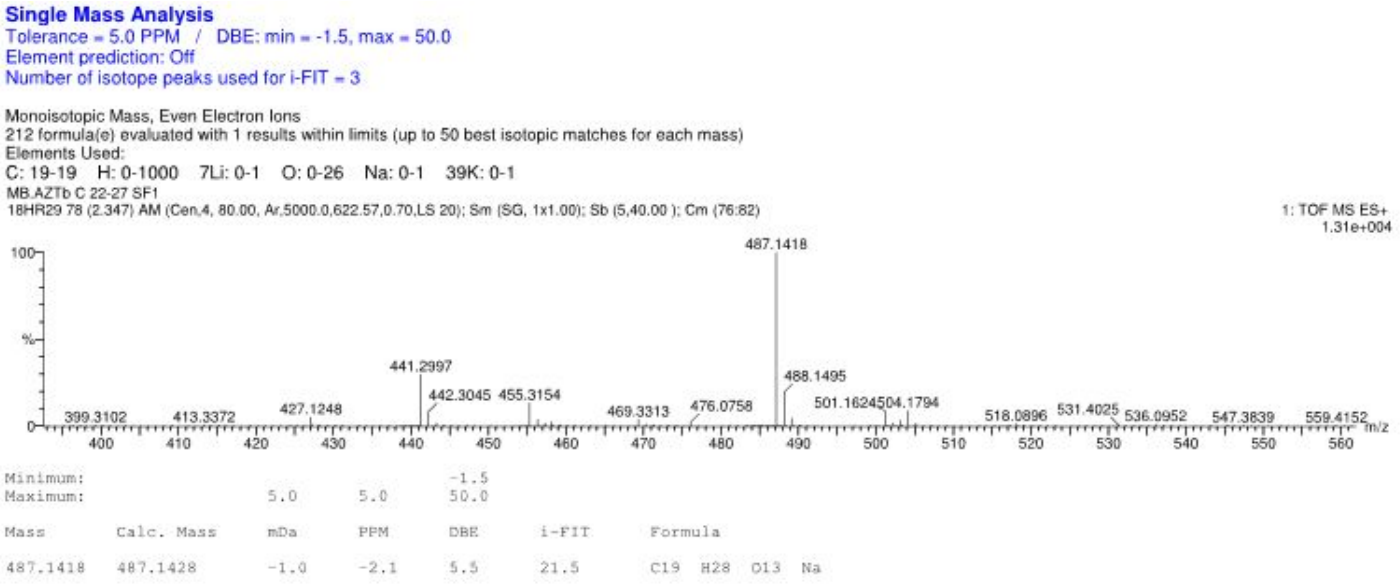



**Figure S32.** The HRESIMS of **5**

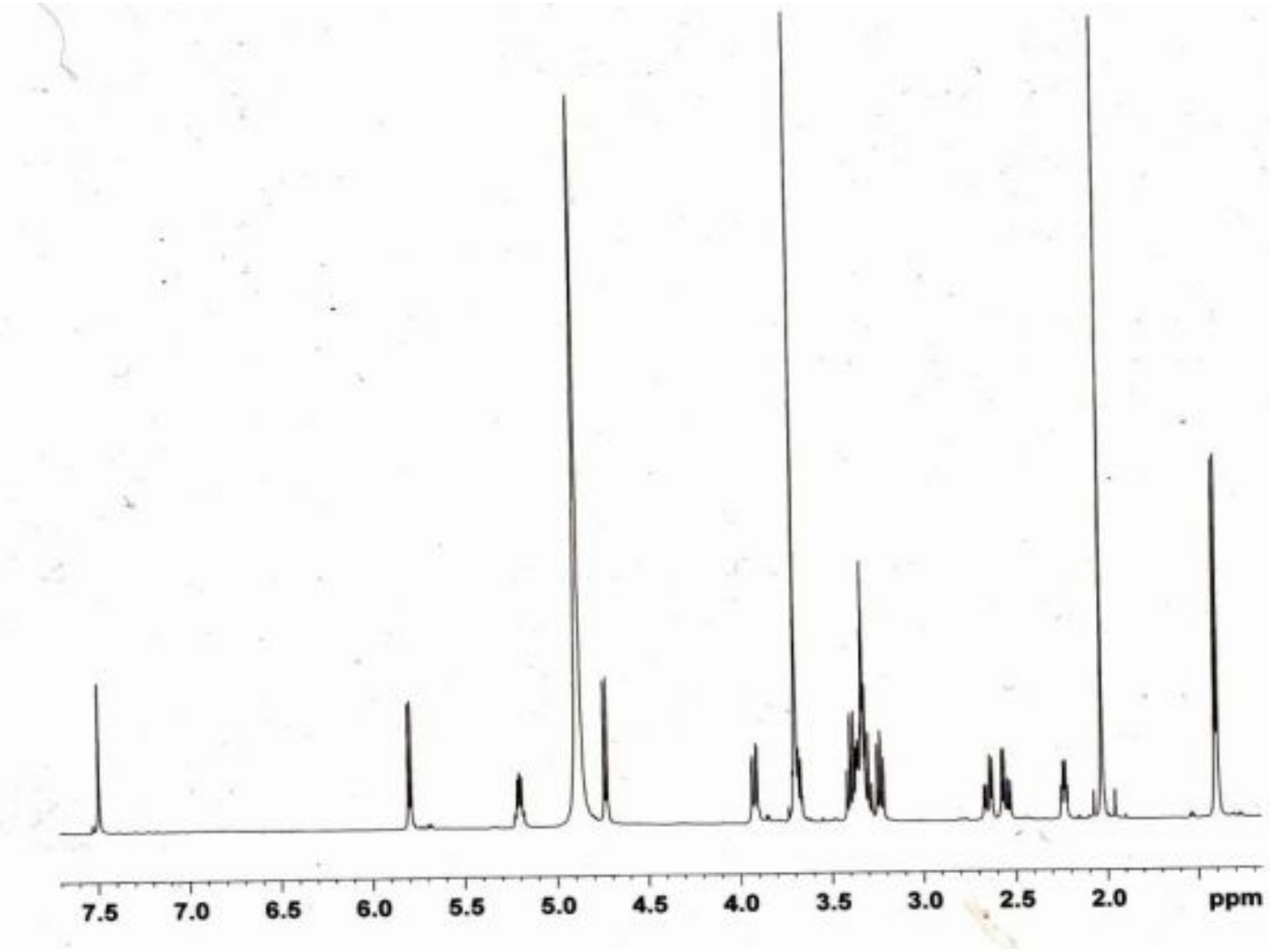



**Figure S33.** The $^{1}$H-NMR spectrum of **5** in $CD_3OD$

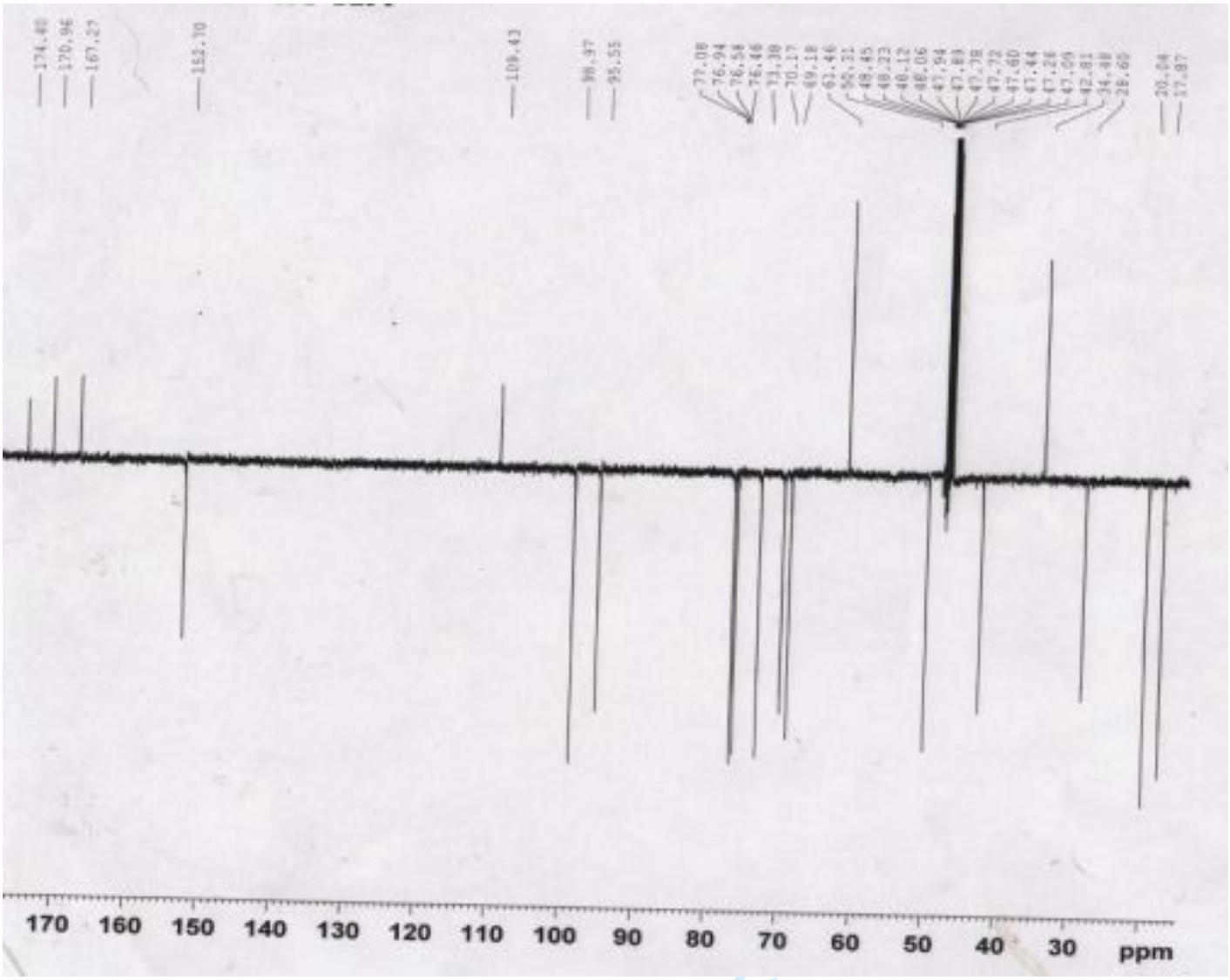



**Figure S34.** The DEPT spectrum of **5** in $CD_3OD$

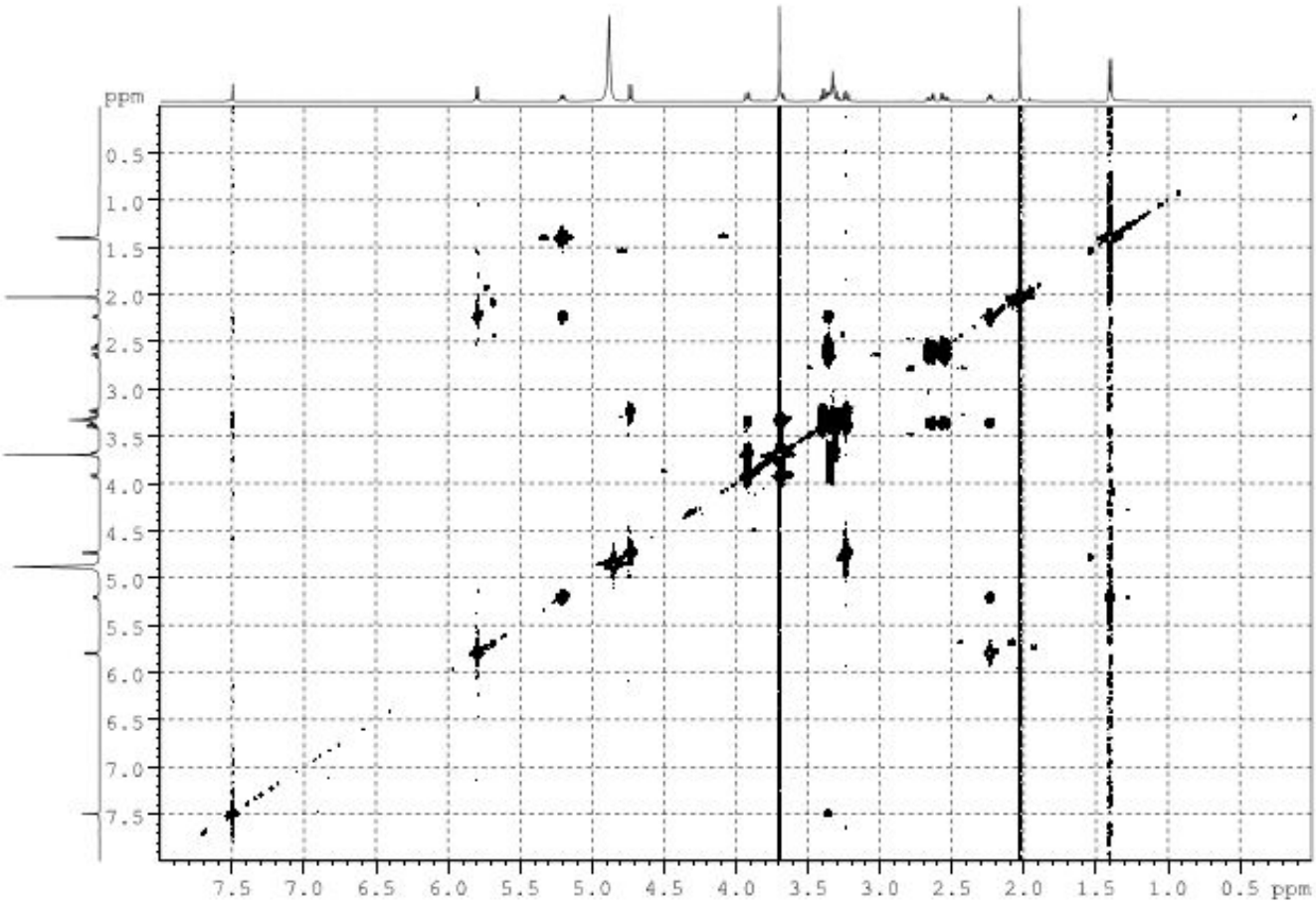



**Figure S35.** The $^{1}H$-$^{1}H$ COSY spectrum of **5** in $CD_3OD$

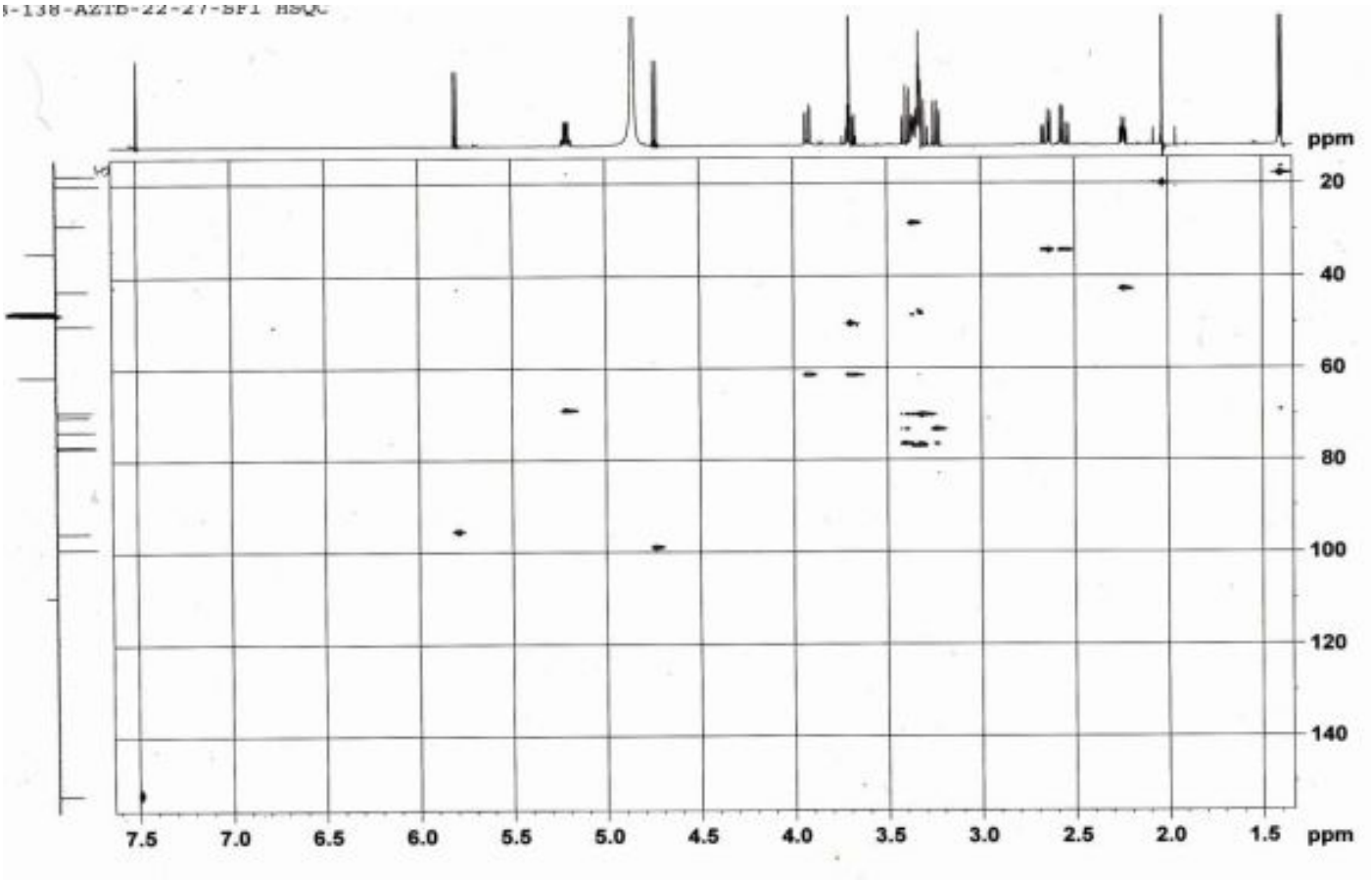



**Figure S36.** The HSQC spectrum of **5** in $CD_3OD$

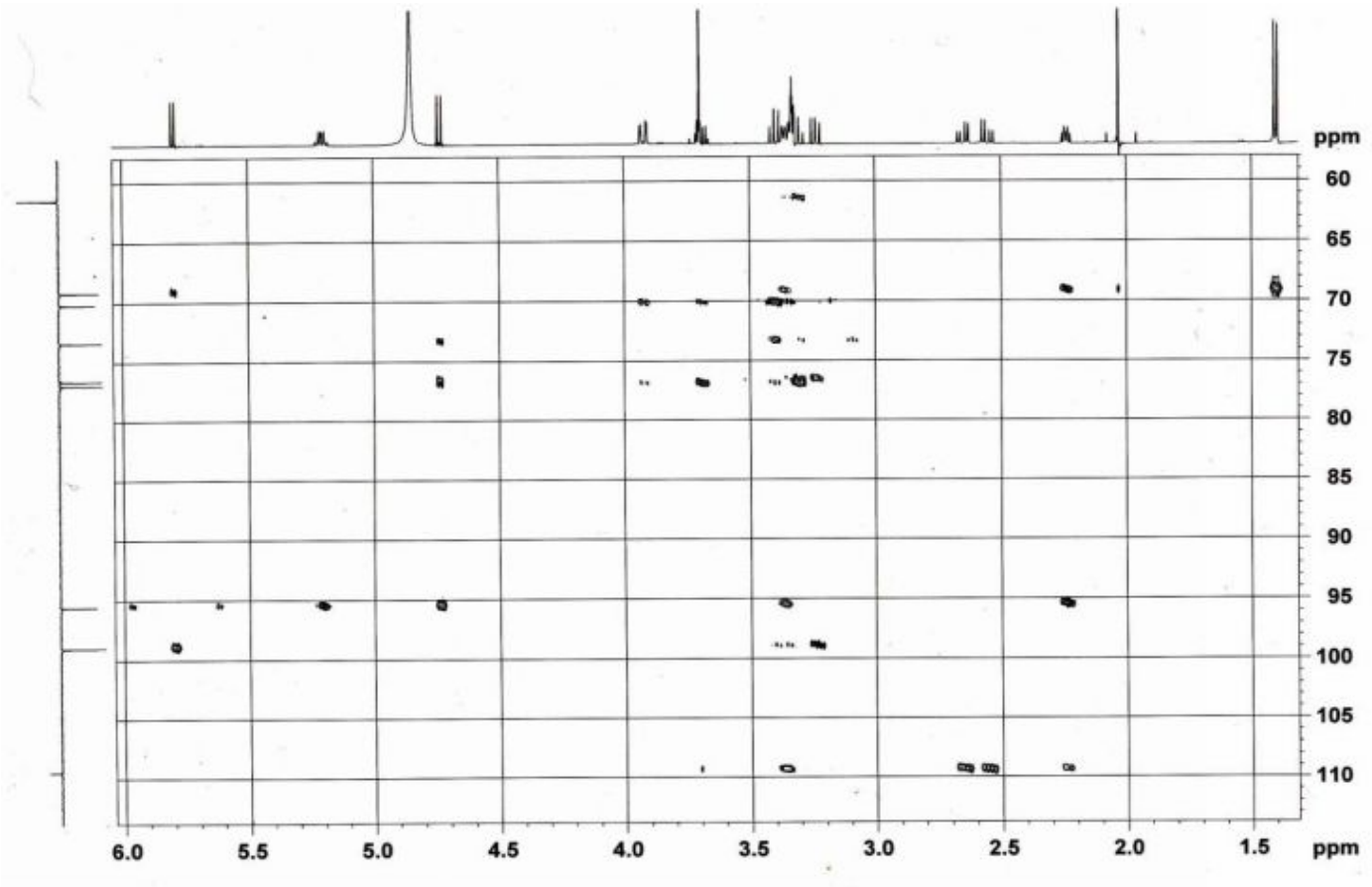


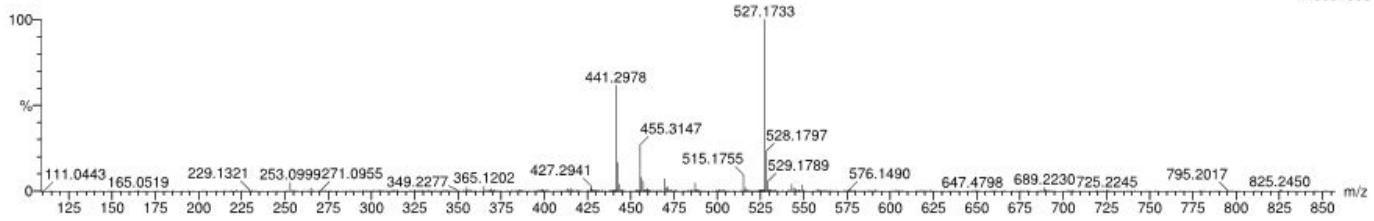

**Figure S37.** The HMBC spectrum of **5** in $CD_3OD$

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 22-22 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1
MB.AZTb C 22-27 SF10`
18HR30 45 (1.342) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00 ); Cm (36:50)

1: TOF MS ES+
7.39e+003




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 5.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 527.1733 | 527.1741 | -0.8 | -1.5 | 6.5 | 9.2 | C22 H32 O13 Na |

**Figure S38.** The HRESIMS of **6**

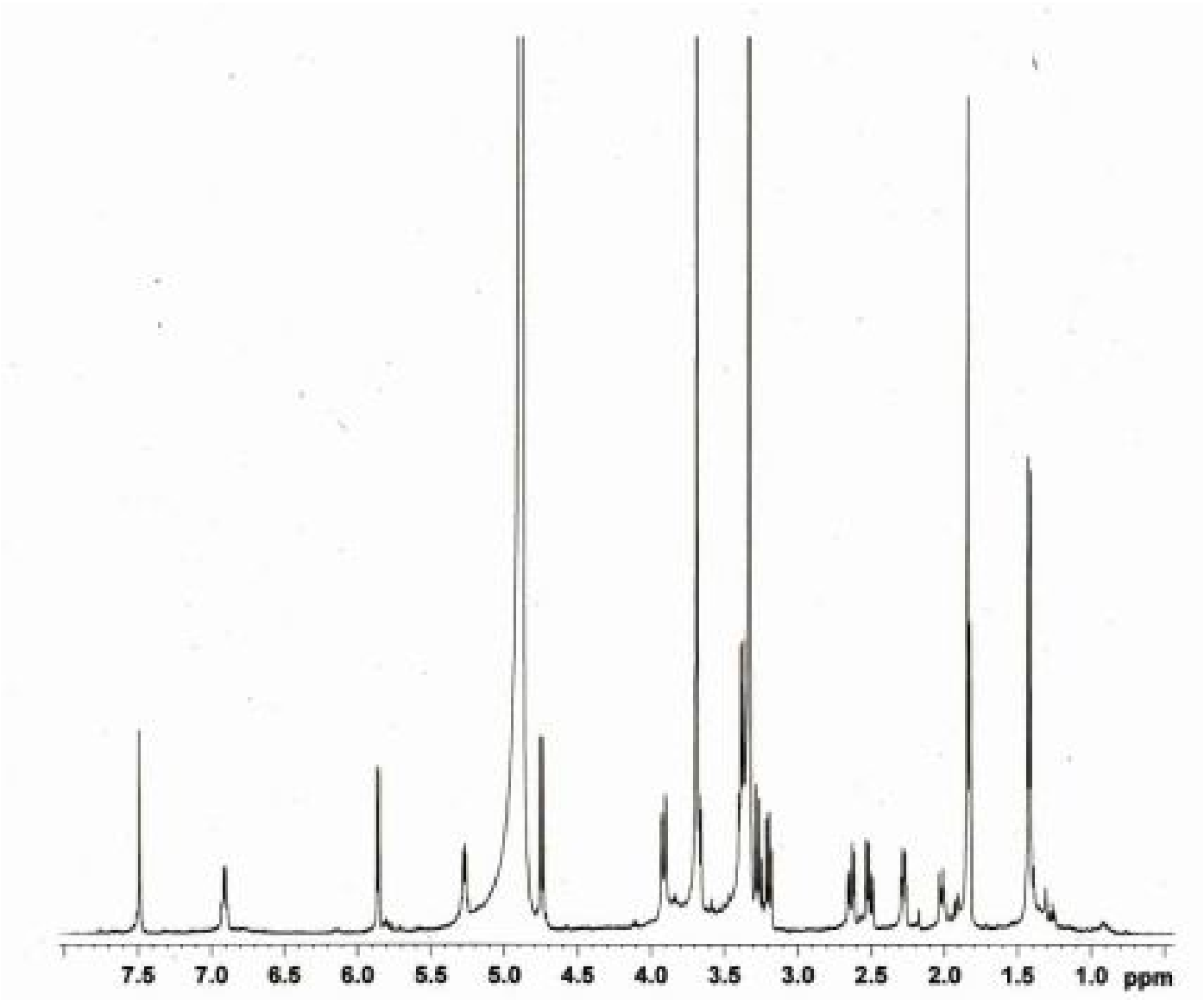



**Figure S39.** The $^{1}$H-NMR spectrum of **6** in $CD_3OD$

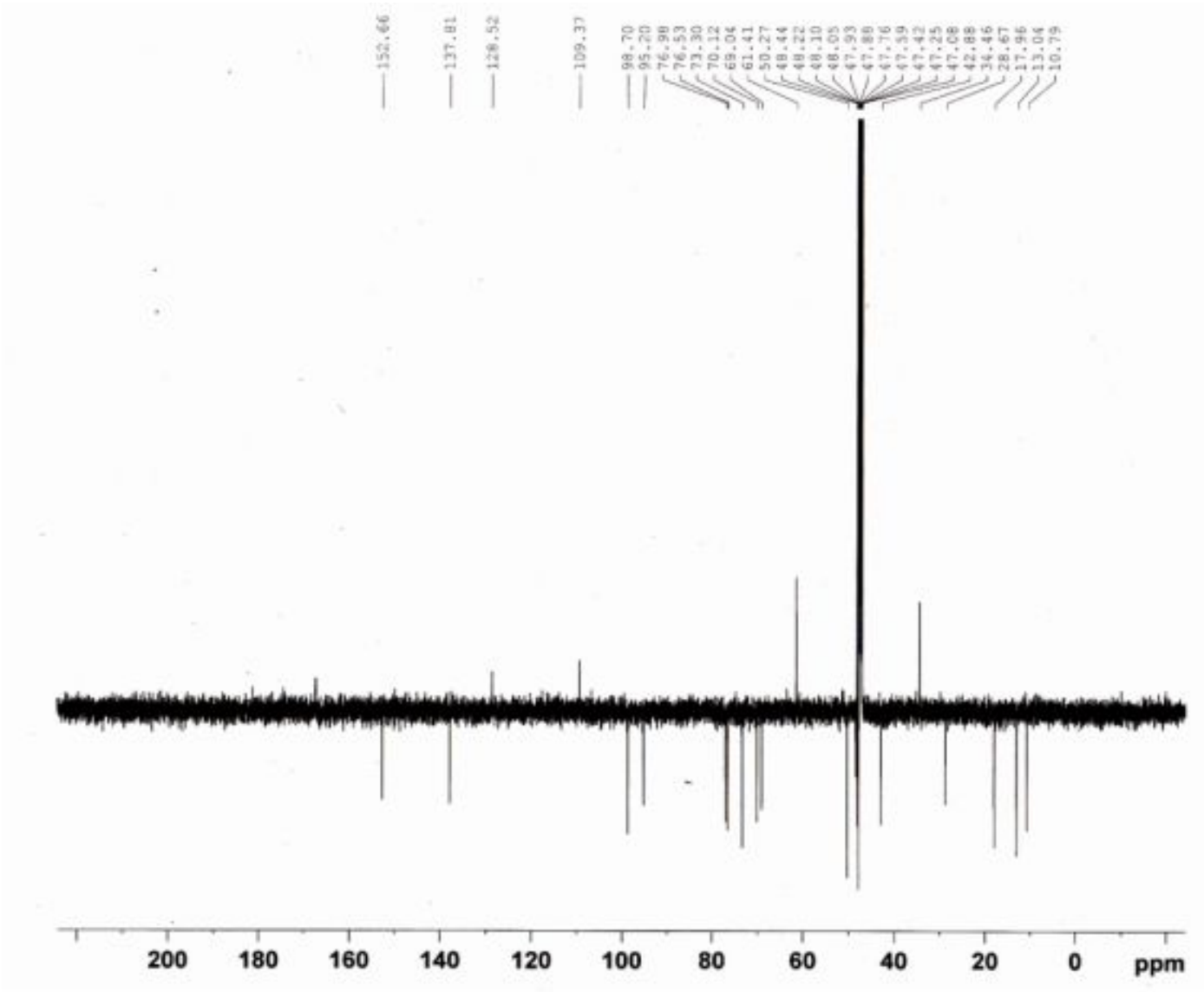



**Figure S40.** The DEPTQ spectrum of **6** in $CD_3OD$

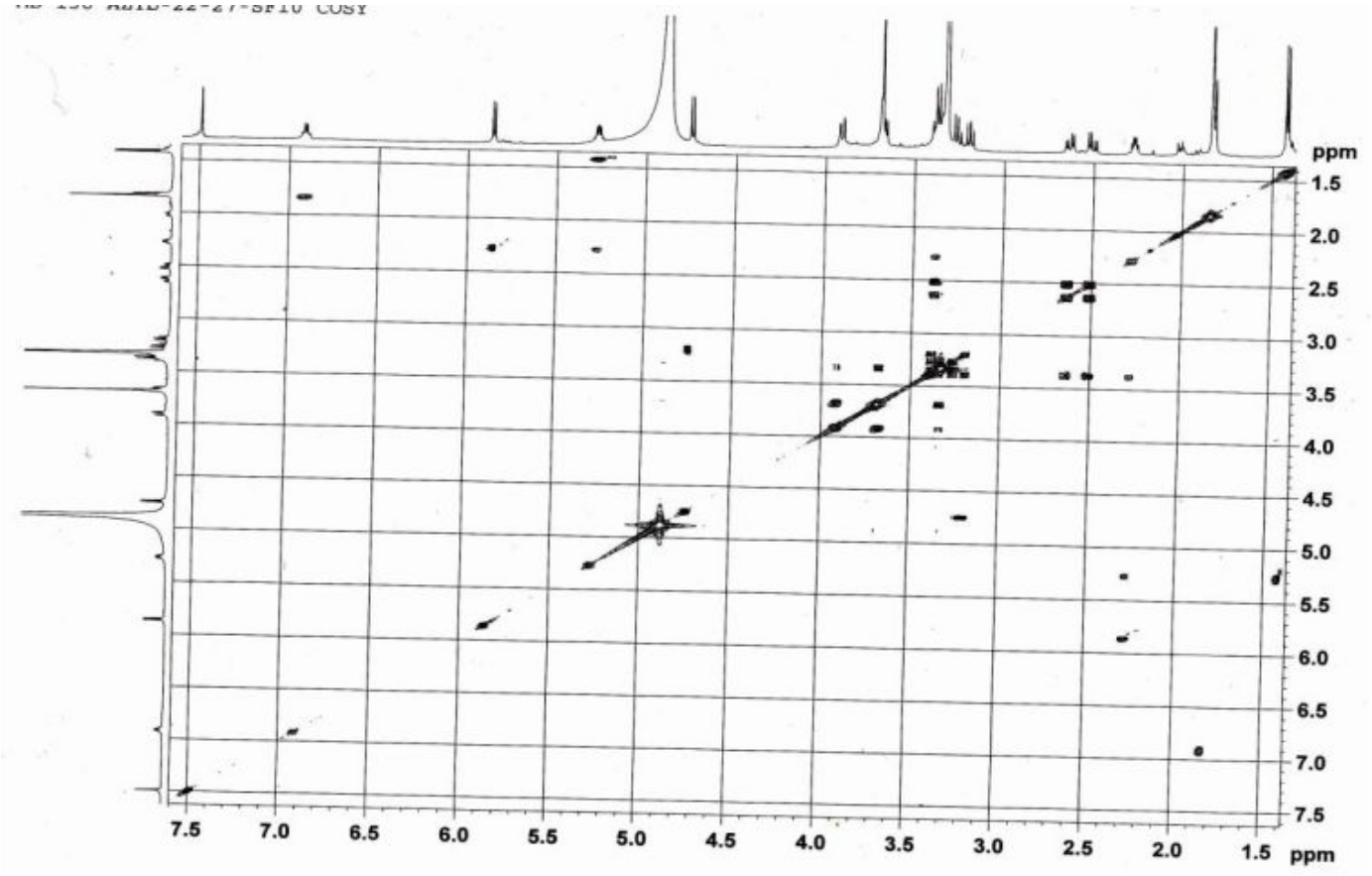



**Figure S41.** The $^{1}$H-$^{1}$H COSY spectrum of **6** in $CD_3OD$

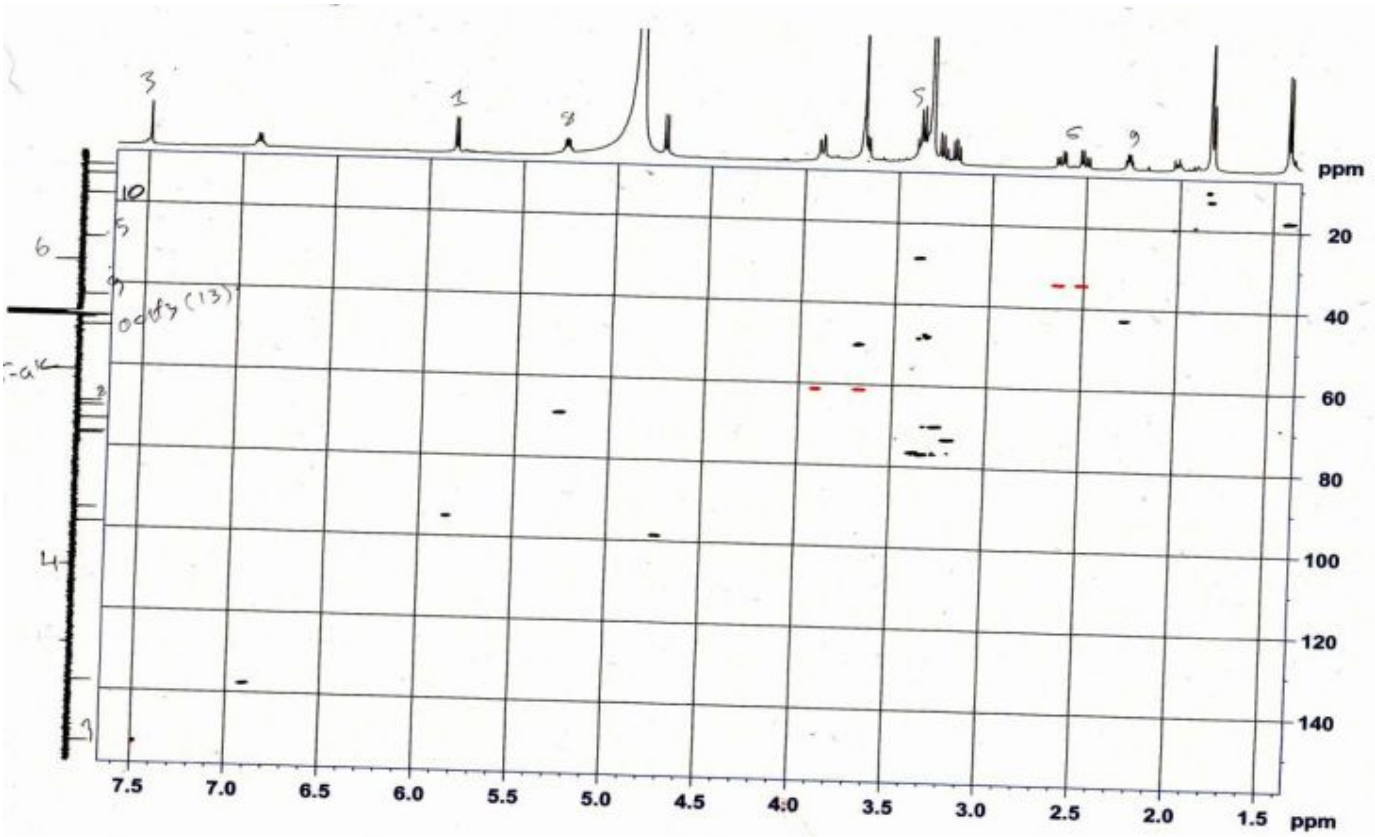



**Figure S42.** The HSQC spectrum of **6** in $CD_3OD$

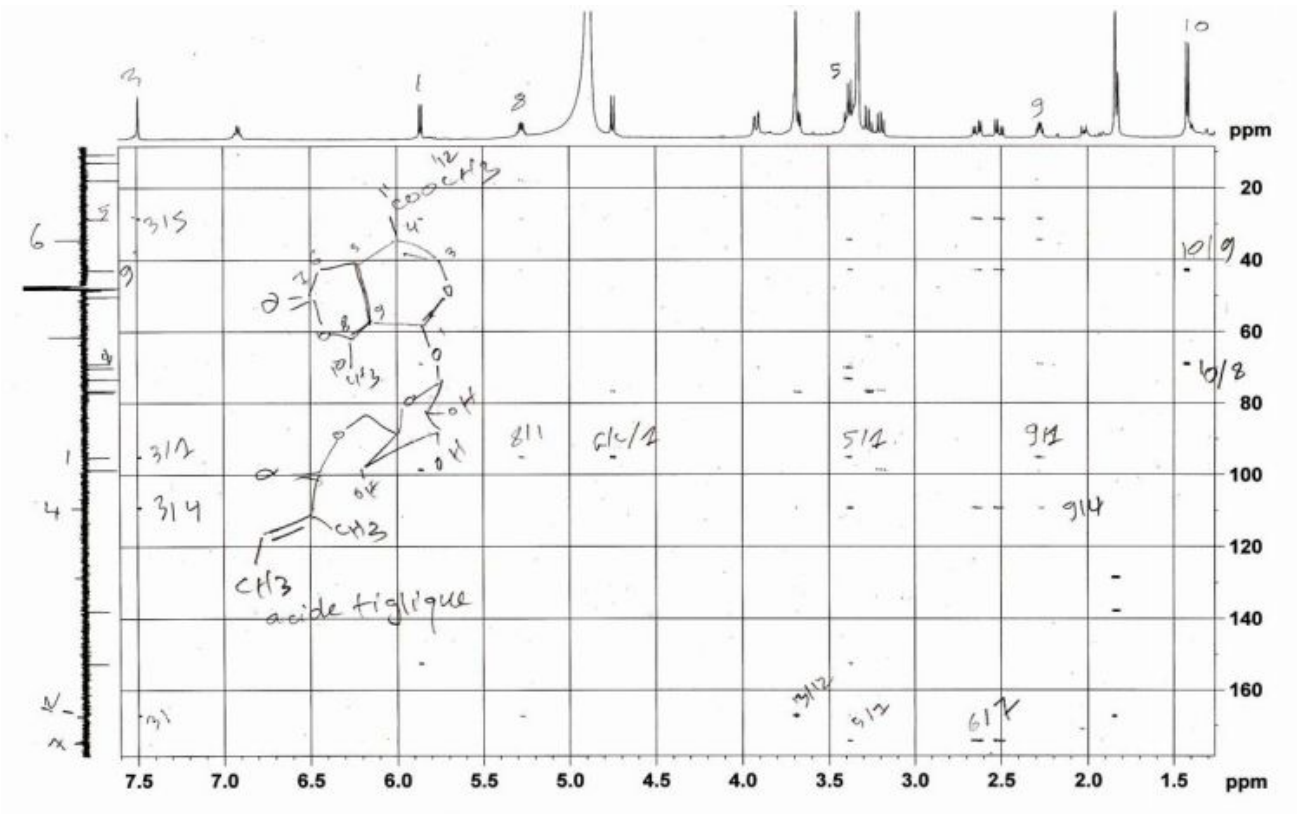



**Figure S43.** The HMBC spectrum of **6** in $CD_3OD$

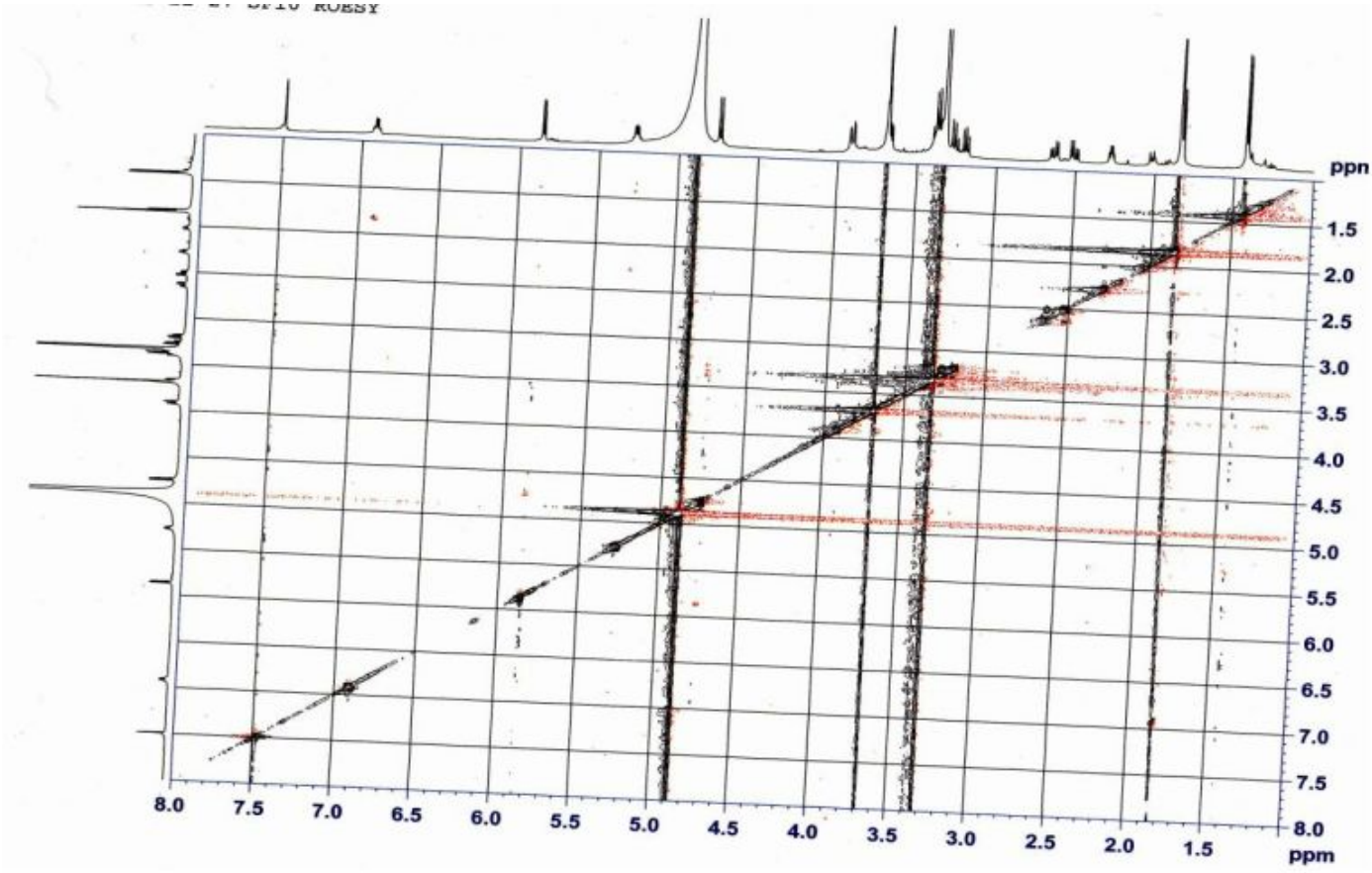


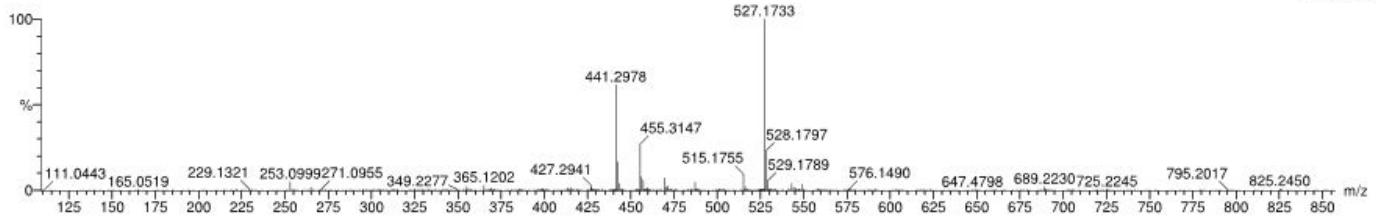

**Figure S44.** The $^{1}$H-$^{1}$H ROESY spectrum of **6** in $CD_3OD$

**Elemental Composition Report** **Page 1**

**Single Mass Analysis**
Tolerance = 5.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
216 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 22-22 H: 0-1000 7Li: 0-1 O: 0-26 Na: 0-1 39K: 0-1
MB.AZTb C 22-27 SF10`
18HR30 45 (1.342) AM (Cen,4, 80.00, Ar,5000.0,622.57,0.70,LS 20); Sm (SG, 1x1.00); Sb (5,40.00 ); Cm (36:50)

1: TOF MS ES+
7.39e+003




| | | | | | | |
|---|---|---|---|---|---|---|
| Minimum: | | | | -1.5 | | |
| Maximum: | | 5.0 | 5.0 | 50.0 | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Formula |
| 527.1733 | 527.1741 | -0.8 | -1.5 | 6.5 | 9.2 | C22 H32 O13 Na |

**Figure S45.** The HRESIMS of **7**

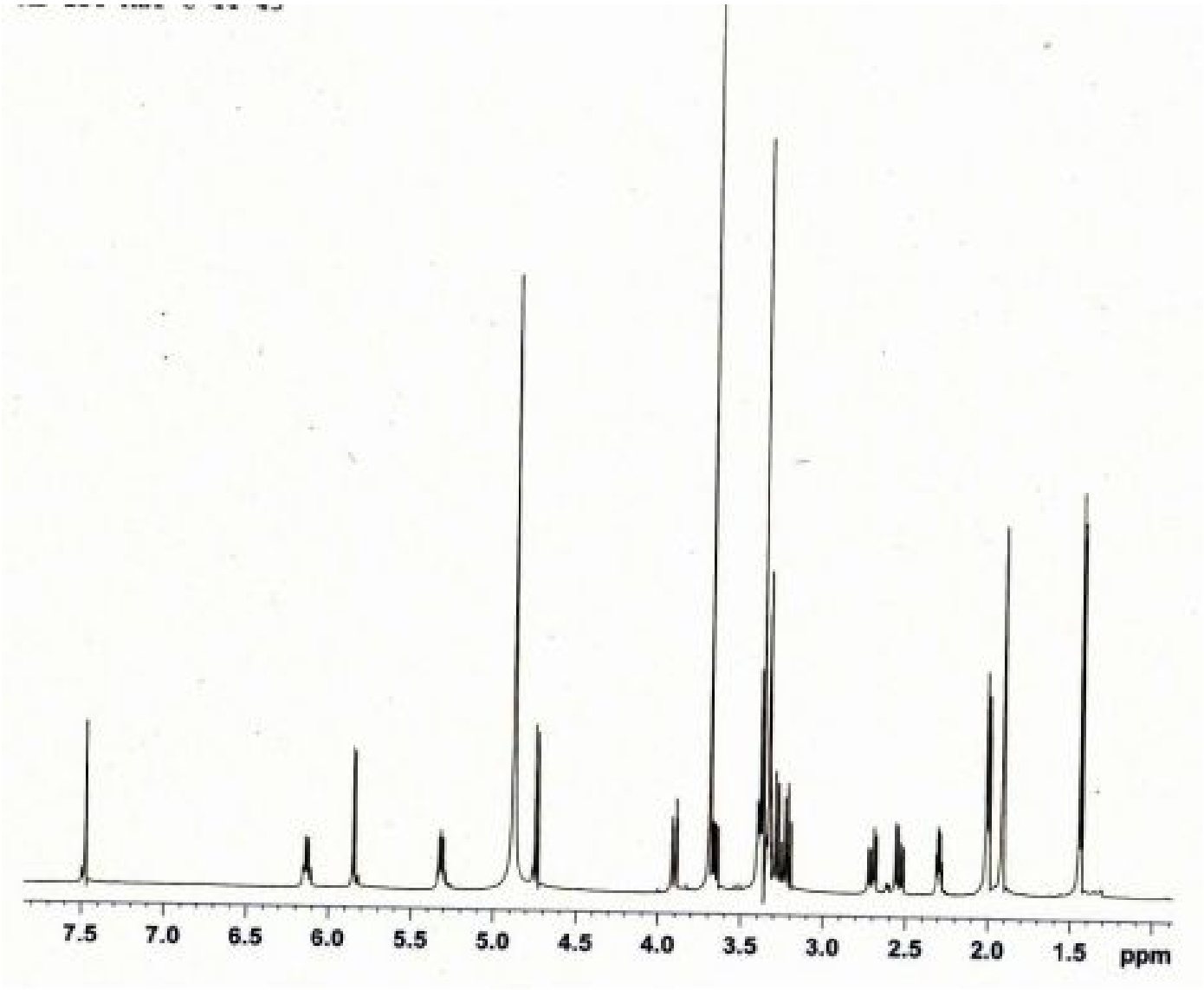



**Figure S46.** The $^{1}$H-NMR spectrum of **7** in $CD_3OD$

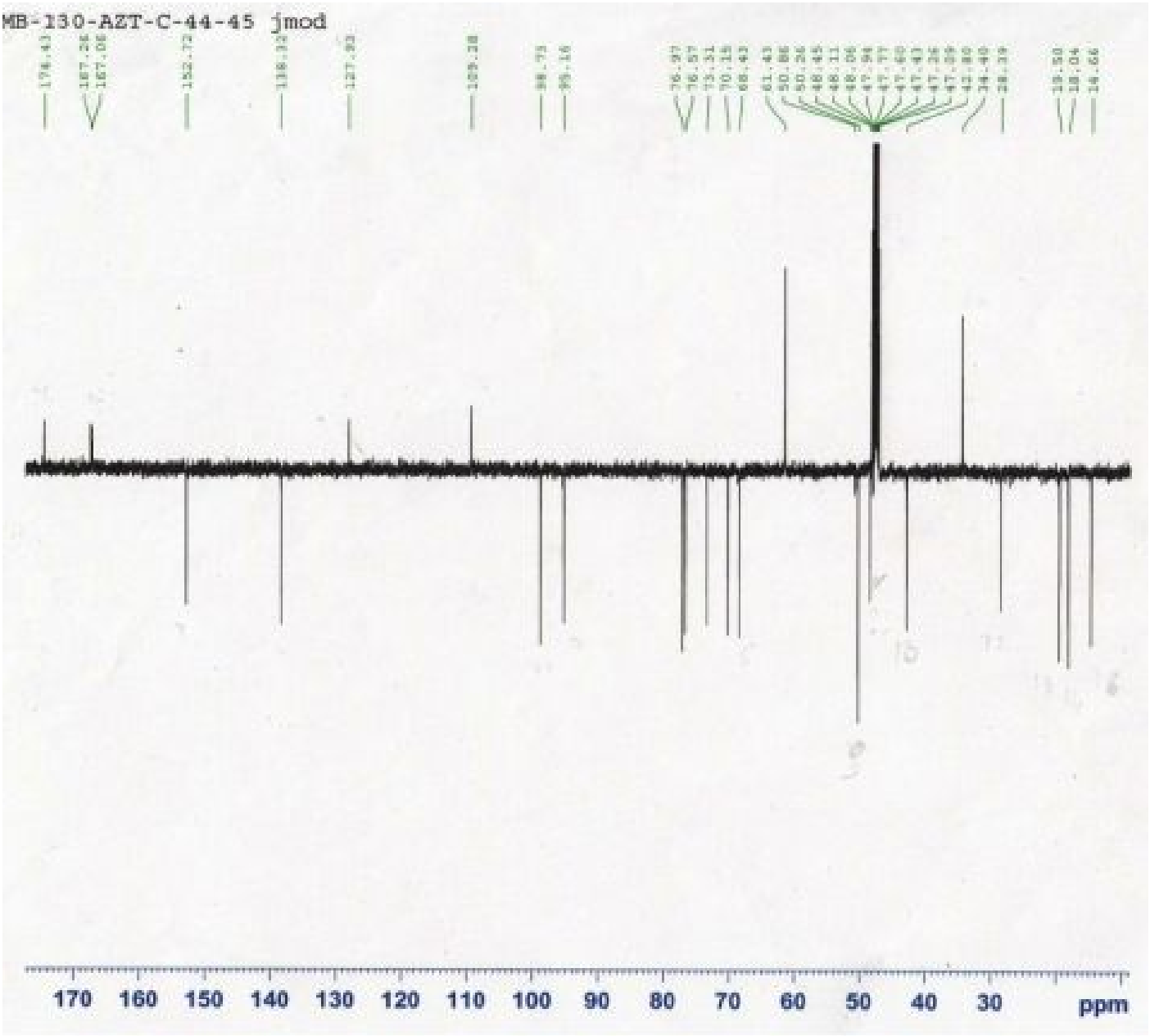



**Figure S47.** The *J-mod* spectrum of **7** in $CD_3OD$

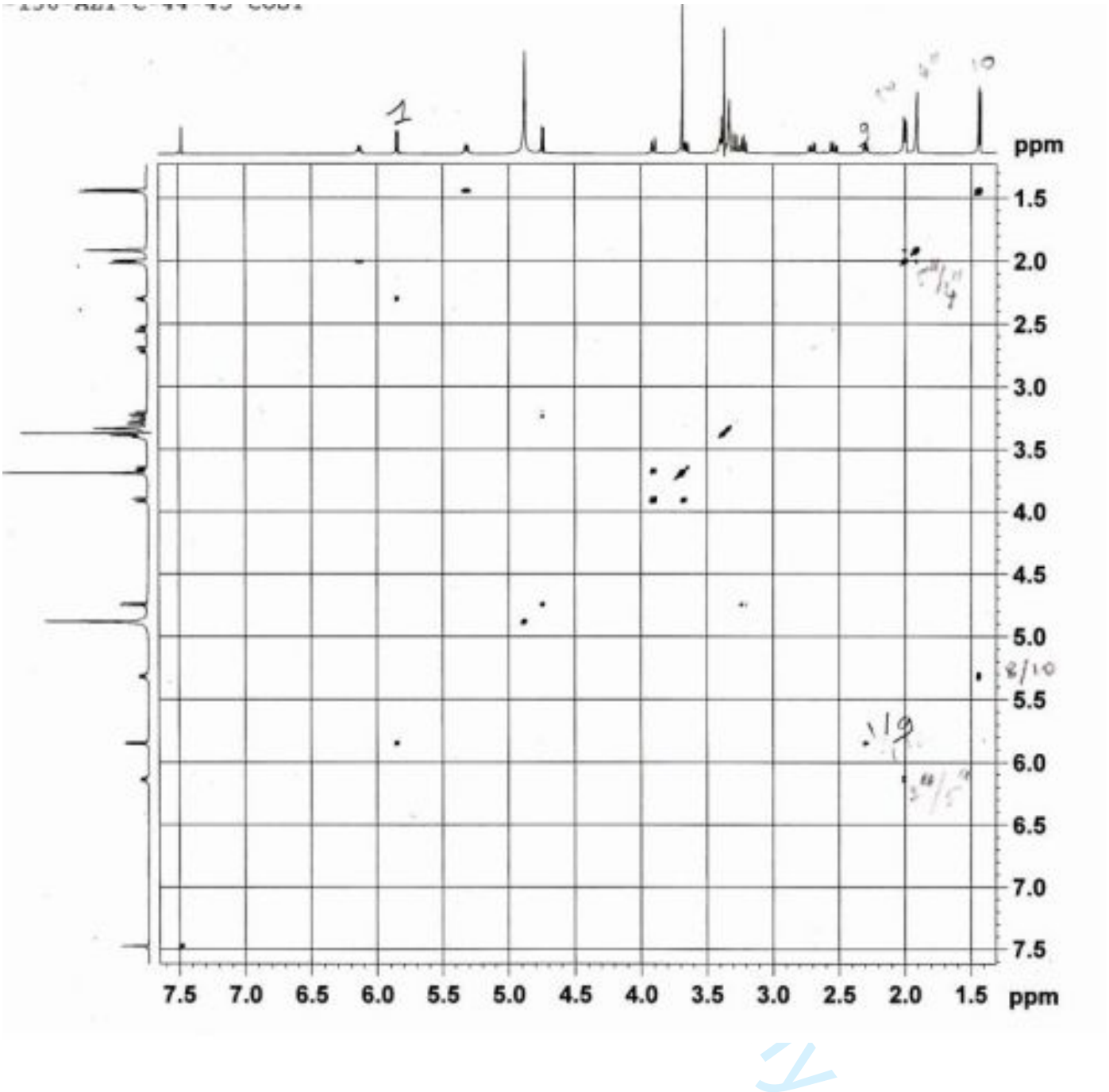



**Figure S48.** The $^{1}H$-$^{1}H$ COSY spectrum of **7** in $CD_3OD$

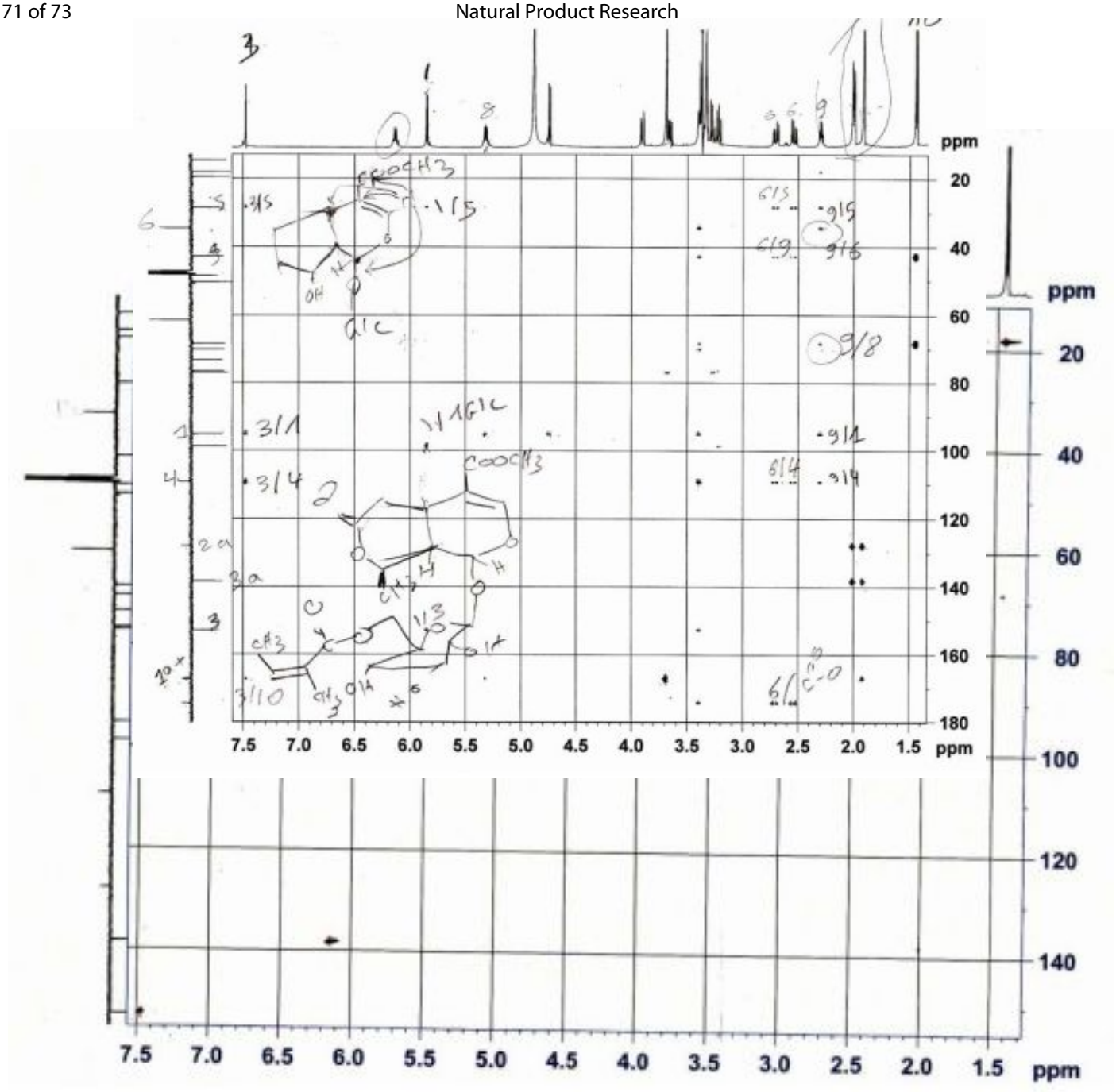



**Figure S49.** The HSQC spectrum of **7** in $CD_3OD$

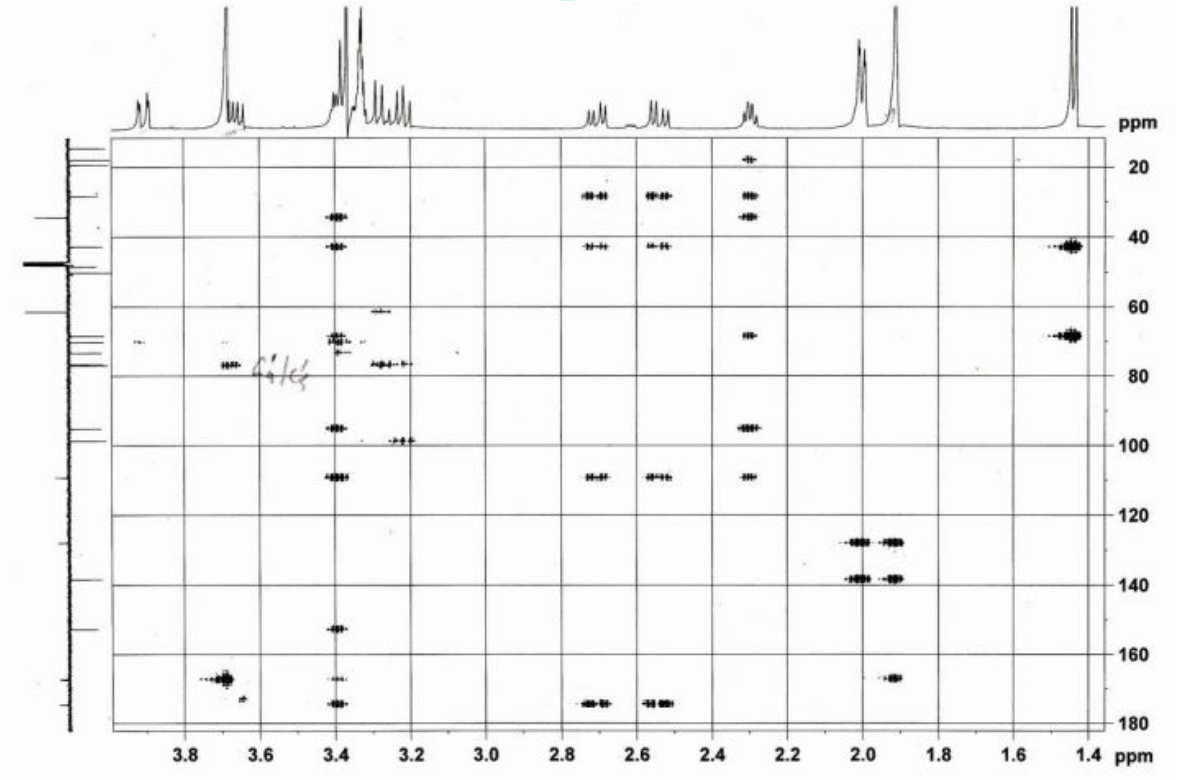



**Figure S50.** The HMBC spectrum of **7** in $CD_3OD$

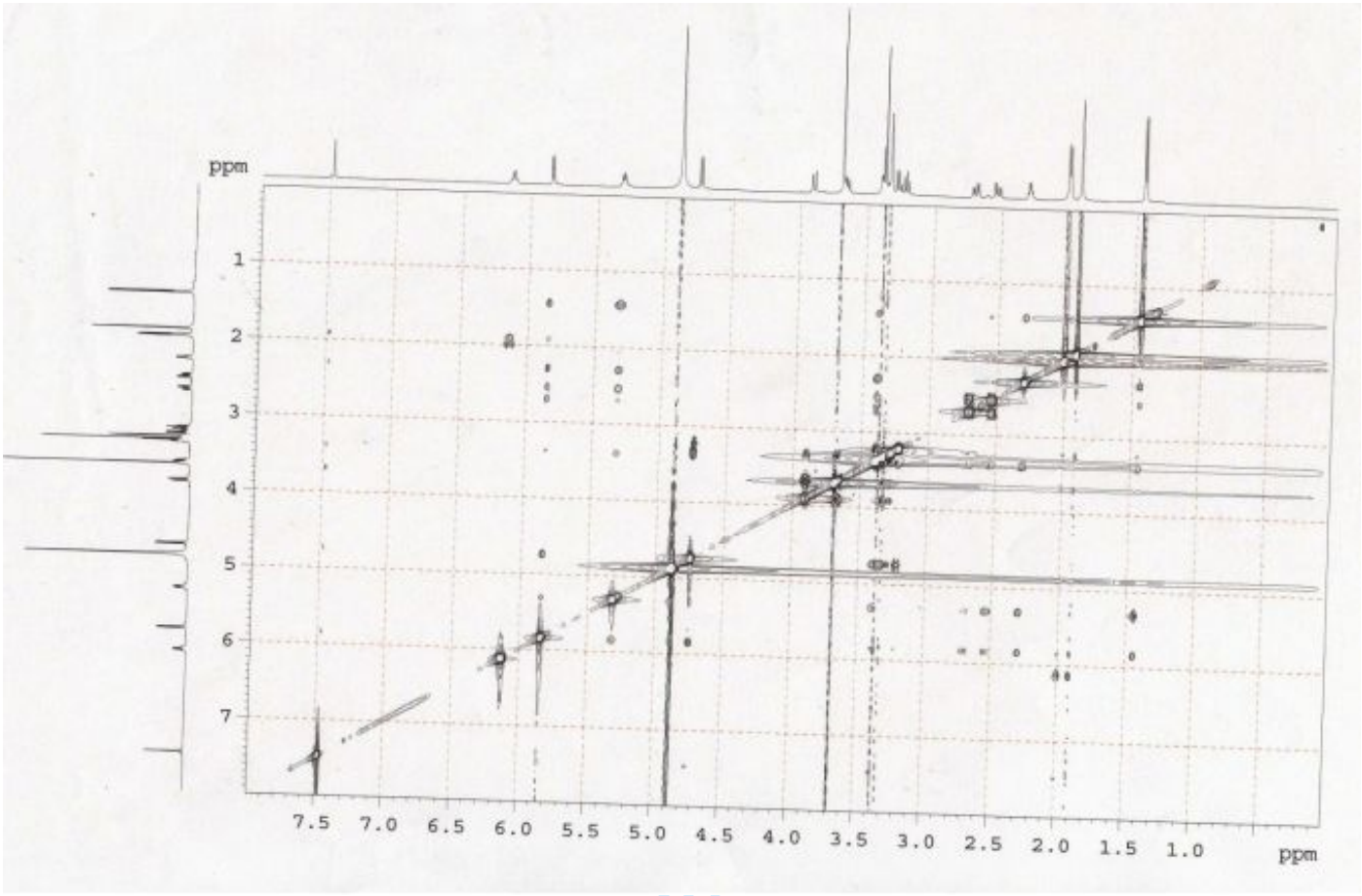



**Figure S51.** The $^{1}H$-$^{1}H$ NOESY spectrum of **7** in $CD_3OD$