

Isolated compounds from *Turpinia formosana* Nakai induce ossification

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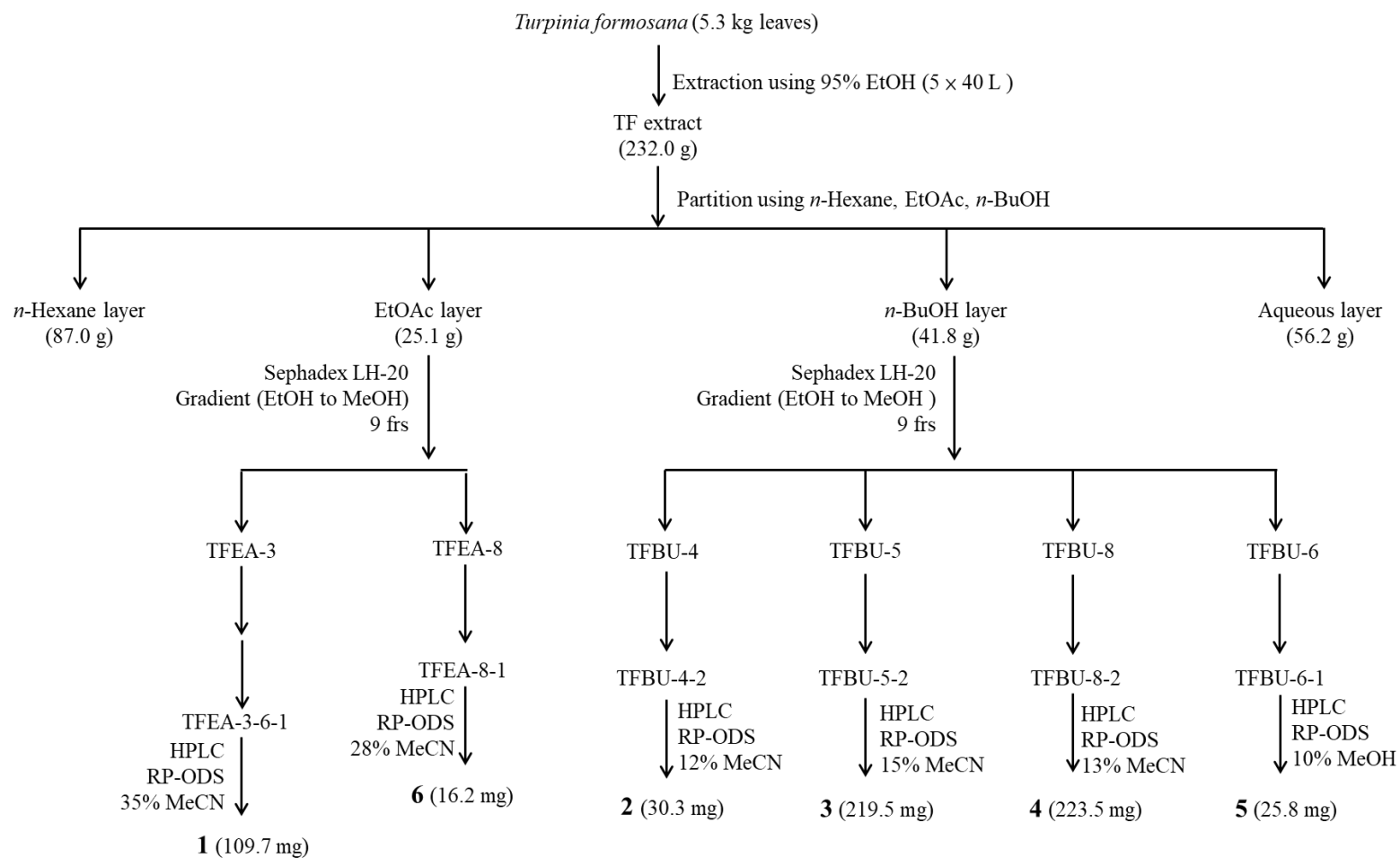


Chart S1. Isolation and purification of compounds from *Turpinia formosana*.

Scheme S1. Spectral data of isolated compounds

3,3'-Di-O-methylellagic acid-4-O- α -L-arabinofuranoside (**1**). Yellow powder, UV (MeOH)

$\lambda_{\max}$ (log ϵ): 367 (4.13), 246 (4.74), 211 (5.15). ESI-MS (negative) m/z 461.1 [M – H][–]

¹H-NMR (500 MHz, DMSO-*d*₆)

δ : 7.70 (1H, *s*, H-5), 7.45 (1H, *s*, H-5'), 5.63 (1H, *brs*, H-1''), 4.23 (1H, *d*, *J*= 3.9 Hz, H-2''), 4.07 (3H, *s*, 3'- OCH₃), 4.03 (3H, *s*, 3- OCH₃), 3.97 (1H, *m*, H-4''), 3.87 (1H, *m*, H-3''), 3.62 (1H, *m*, H-5''), 3.50 (1H, *m*, H-5'')

¹³C-NMR (125 MHz, DMSO-*d*₆)

δ : 158.4 (C-7), 158.2 (C-7'), 152.9 (C-4'), 150.7 (C-4), 141.9 (C-3), 141.4 (C-2), 140.8 (C-2'), 140.2 (C-3'), 113.8 (C-1), 112.5 (C-6'), 111.7 (C-5'), 111.6 (C-5), 111.6 (C-6), 110.8 (C-1'), 107.5 (C-1''), 86.1 (C-4''), 82.1 (C-2''), 76.6 (C-3''), 61.4 (3- OCH₃), 61.0 (3'- OCH₃), 60.9 (C-5'')

Gentistic acid 5-O- β -D-(6'-O-galloyl) glucopyranoside (**2**). Brown powder, UV (MeOH) $\lambda_{\max}$

(log ϵ): 209 (5.09). ESI-MS (negative) m/z 467.2 [M – H][–]

¹H-NMR (500 MHz, methanol-*d*₄)

δ : 7.77 (1H, *d*, *J*= 3.1 Hz, H-6), 7.30 (2H, *s*, H-galloyl), 7.06 (1H, *dd*, *J*= 3.1, 8.9 Hz, H-4), 6.72 (1H, *d*, *J*= 8.9 Hz, H-3), 4.90 (1H, *d*, *J*= 7.6 Hz, H-1'), 4.75 (1H, *d*, *J*= 11.9 Hz, H-6'), 4.10 (1H, *dd*, *J*=8.6, 11.9 Hz, H-6'), 3.86 (1H, *t*, *J*=8.6 Hz, H-5'), 3.51 (1H, *t*, *J*=9.3 Hz, H-3'), 3.46 (1H, *t*, *J*=9.3 Hz, H-2'), 3.34 (1H, *d*, *J*=6.6 Hz, H-4')

¹³C-NMR (125 MHz, methanol-*d*₄)

δ : 176.0 (1-COOH), 168.7 (COO⁻), 158.0 (C-2), 151.3 (C-5), 146.6(C-3'', 5''), 139.8 (C-4''), 124.2 (C-4), 121.1 (C-1''), 119.7 (C-1), 117.9 (C-3), 117.3 (C-6), 110.2 (C-2'', 6''), 103.2 (C-1'), 77.7 (C-3'), 75.9 (C-5'), 74.9 (C-2'), 71.9 (C-4'), 66.0 (C-6')

Strictinin (**3**). Brown powder, UV (MeOH) $\lambda_{\max}$ (log ϵ): 272 (4.50), 211 (5.30). ESI-MS (negative) m/z 633.1 $[M - H]^-$

¹H-NMR (500 MHz, acetone-*d*₆)

δ : 7.17 (2H, *s*, H-galloyl), 6.69 (1H, *s*), 6.58 (1H, *s*), 5.70 (1H, *d*, $J = 8.1$ Hz, H-1), 5.18 (1H, *dd*, $J = 13.3, 6.3$ Hz, H-6), 4.87 (1H, *t*, $J = 9.7$ Hz, H-4), 4.08 (1H, *dd*, $J = 9.7, 6.3$ Hz, H-5), 3.80 (1H, *t*, $J = 9.7$ Hz, H-3), 3.74 (1H, *d*, $J = 13.3$ Hz, H-6), 3.68 (1H, *t*, $J = 8.7$ Hz, H-2)

Casuarinin (**4**). Cameo brown powder, UV (MeOH) $\lambda_{\max}$ (log ϵ): 210 (5.45). ESI-MS (negative) m/z 935.0 $[M - H]^-$

¹H-NMR (500 MHz, acetone-*d*₆)

δ : 7.10 (2H, *s*, H-galloyl), 6.48, 6.54, 6.76 (each 1H, *s*, H-HHDP), 5.62 (1H, *dd*, $J = 8.8, 3.0$ Hz, H-1), 5.40 (1H, *d*, $J = 5.0$ Hz, H-4), 5.39 (1H, *brs*, H-3), 5.32 (1H, *m*, H-5), 4.78 (1H, *dd*, $J = 13.5, 3.0$ Hz, H-6), 4.68 (1H, *dd*, $J = 5.0, 1.5$ Hz, H-2), 4.06 (1H, *d*, $J = 13.5$ Hz, H-6)

¹³C-NMR (125 MHz, acetone-*d*₆)

δ : 169.7, 168.8, 168.6, 164.0 (-COO⁻), 165.7 (galloyl-COO⁻), 138.6, 136.6, 135.5, 134.6 (HHDP C-5), 146.3, 145.7, 145.2, 145.1, 144.7, 144.5, 143.9, 143.6 (HHDP C-4,6), 145.9 (galloyl-3,5), 139.1 (galloyl-4), 121.2 (galloyl-1), 110.1 (galloyl-2,6), 116.9, 108.3, 107.0, 105.3 (HHDP C-3), 127.7, 127.2, 125.1, 120.9 (HHDP C-2), 116.3, 116.0, 115.9, 115.2 (HHDP C-1), 76.7 (C-2), 74.3 (C-4), 71.2 (C-5), 69.9 (C-3), 67.7 (C-1), 64.6 (C-6)

Casuariin (5). Light brown powder, UV (MeOH) $\lambda_{\max}$ (log ϵ): 209 (5.30). ESI-MS (negative) m/z 783.1 $[M - H]^-$

^1H -NMR (500 MHz, acetone- d_6)

δ : 6.73, 6.52, 6.38 (each 1H, s, H-HHDP), 5.44 (1H, *t*, J = 2.5 Hz, H-3), 5.32 (1H, *d*, J = 5.0 Hz, H-1), 5.05 (1H, *dd*, J = 8.5, 2.5 Hz, H-4), 4.64 (2H, *m*), 4.08 (1H, *dd*, J =8.5, 2.5 Hz, H-5), 3.83 (1H, *d*, J =12.5 Hz)

^{13}C -NMR (125 MHz, acetone- d_6)

δ : 170.2, 169.6, 168.7, 165.5 (-COO $^-$), 146.0, 145.7, 145.1, 145.0 (HHDP C-4, 4'), 144.3, 144.2, 143.6, 143.5 (C-6, 6'), 138.7, 136.5, 135.6, 134.8 (C-5, 5'), 127.3, 127.0, 125.1, 119.8 (C-2, 2'), 116.9, 116.3, 116.1, 115.9 (C-1,1'), 114.9, 108.5, 106.9, 105.1 (C-3, 3'), 76.9, 76.8 (C-4), 70.6 (C-3), 68.1 (C-5), 68.0, 67.0 (C-1)

(-)-Epicatechin-3-*O*- β -D-allopyranoside (6). Light yellow powder, UV (MeOH) $\lambda_{\max}$ (log ϵ): 280 (3.68), 217 (4.32). ESI-MS (negative) m/z 451.1 $[M - H]^-$

^1H -NMR (500 MHz, DMSO- d_6)

δ : 9.19, 8.95, 8.69, 8.66 (each 1H, s, 5, 7, 3', 4'-OH), 6.89 (1H, *d*, J =2.0 Hz, H-2'), 6.68 (1H, *dd*, J =8.2, 2.0 Hz, H-6'), 6.60 (1H, *d*, J =8.2 Hz, H-5'), 5.88 (1H, *d*, J = 2.3 Hz, H-6), 5.74 (1H, *d*, J = 2.3 Hz, H-8), 5.13 (1H, *d*, J = 3.1 Hz, H-2), 4.75 (1H, *d*, J = 3.5 Hz, 3''-OH), 4.57 (2H, *dd*, J = 10.0, 6.9 Hz, 2'', 4''-OH), 4.51 (1H, *d*, J = 7.5 Hz, H-1''), 4.35 (1H, *t*, J = 5.7 Hz, 6''-OH), 4.22 (1H, *m*, H-3), 3.79 (1H, *dd*, J =6.1, 3.0 Hz, H-3''), 3.65 (1H, *m*, H-6''), 3.49 (1H, *m*, H-5''), 3.40 (1H, *m*, H-6''), 3.25 (1H, *m*, H-4''), 3.11 (1H, *m*, H-2''), 2.68 (1H, *dd*, J = 16.0, 5.0 Hz, H-4), 2.33 (1H, *dd*, J = 16.0, 7.8 Hz, H-4)

¹³C-NMR (125 MHz, DMSO-*d*₆)

δ: 156.6 (C-7), 156.2 (C-5), 155.1 (C-8a), 144.4 (C-4'), 144.2 (C-3'), 129.6 (C-1'), 118.6 (C-6'), 115.3 (C-2'), 114.7 (C-5'), 99.6 (C-1''), 98.5 (C-4a), 95.2 (C-8), 94.0 (C-6), 76.7 (C-2), 74.4 (C-5''), 72.4 (C-3), 71.5 (C-3''), 70.6 (C-2''), 67.7 (C-4''), 61.7 (C-6''), 23.0 (C-4

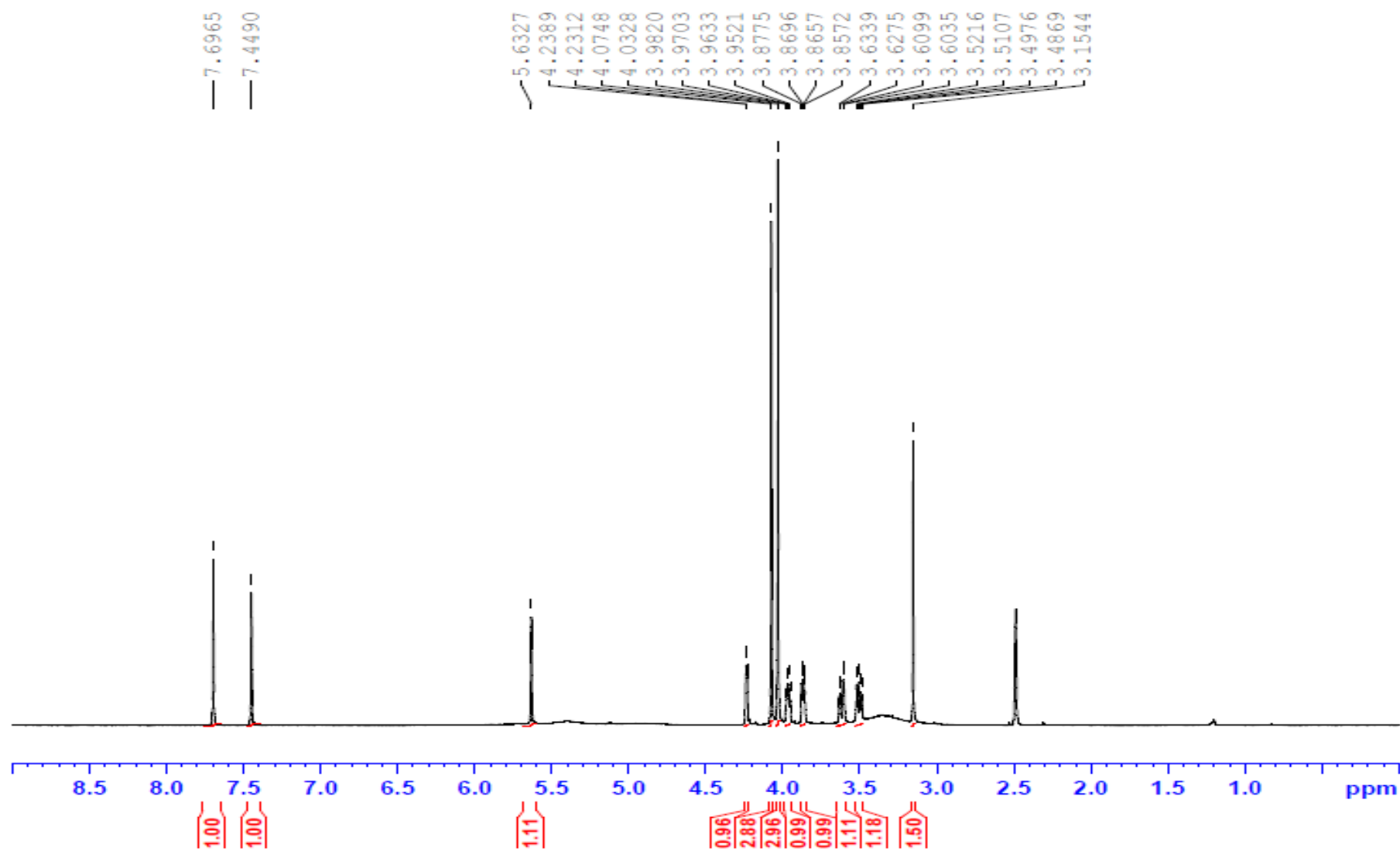


Figure S 1A. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) spectrum of **1**

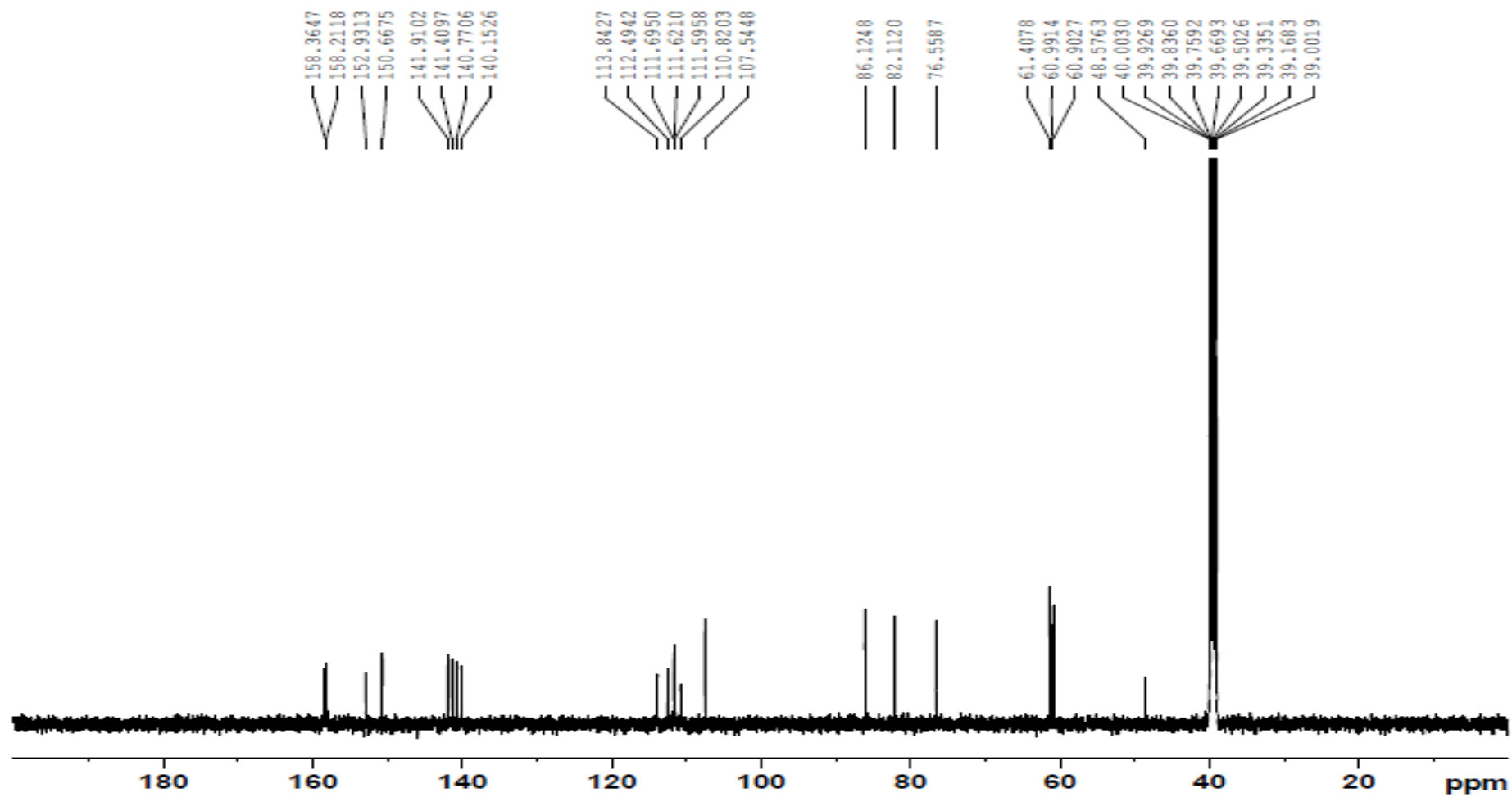


Figure S 1B. ¹³C NMR (DMSO-*d*₆, 125 MHz) spectrum of **1**

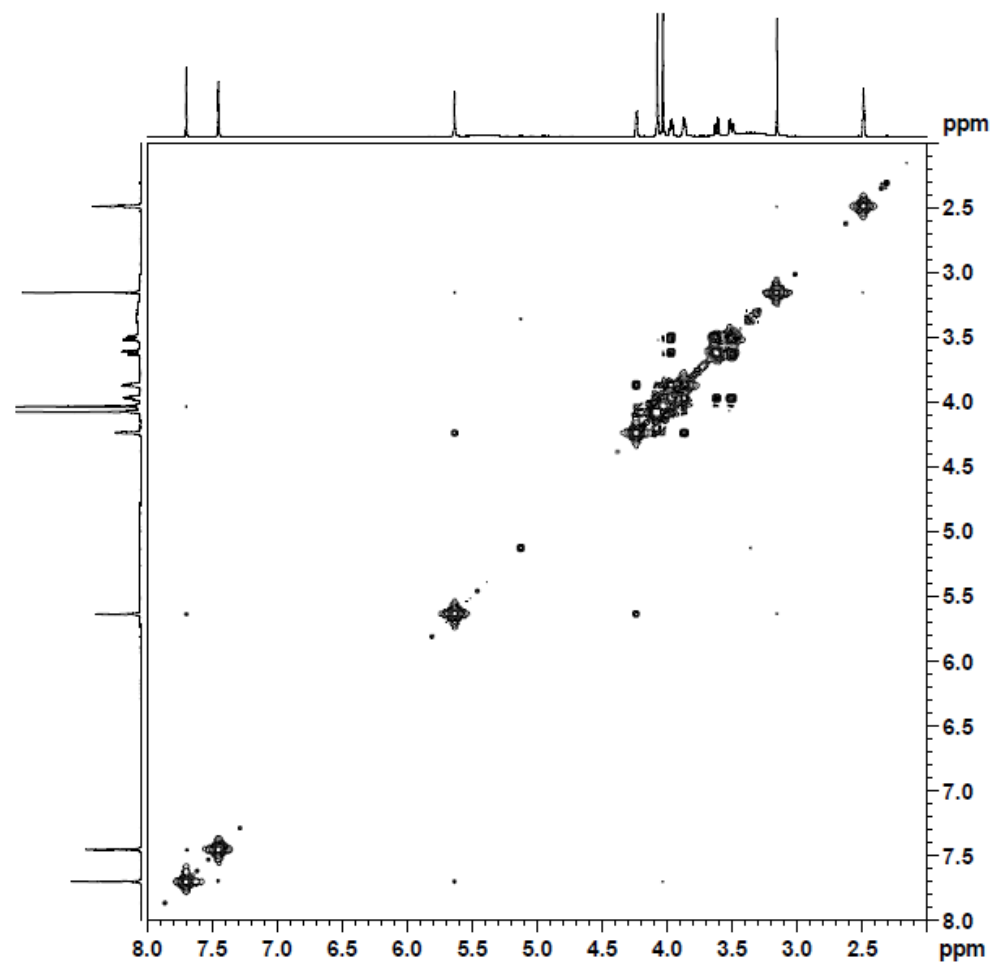


Figure S 1C. ^1H - ^1H COSY spectrum of **1**

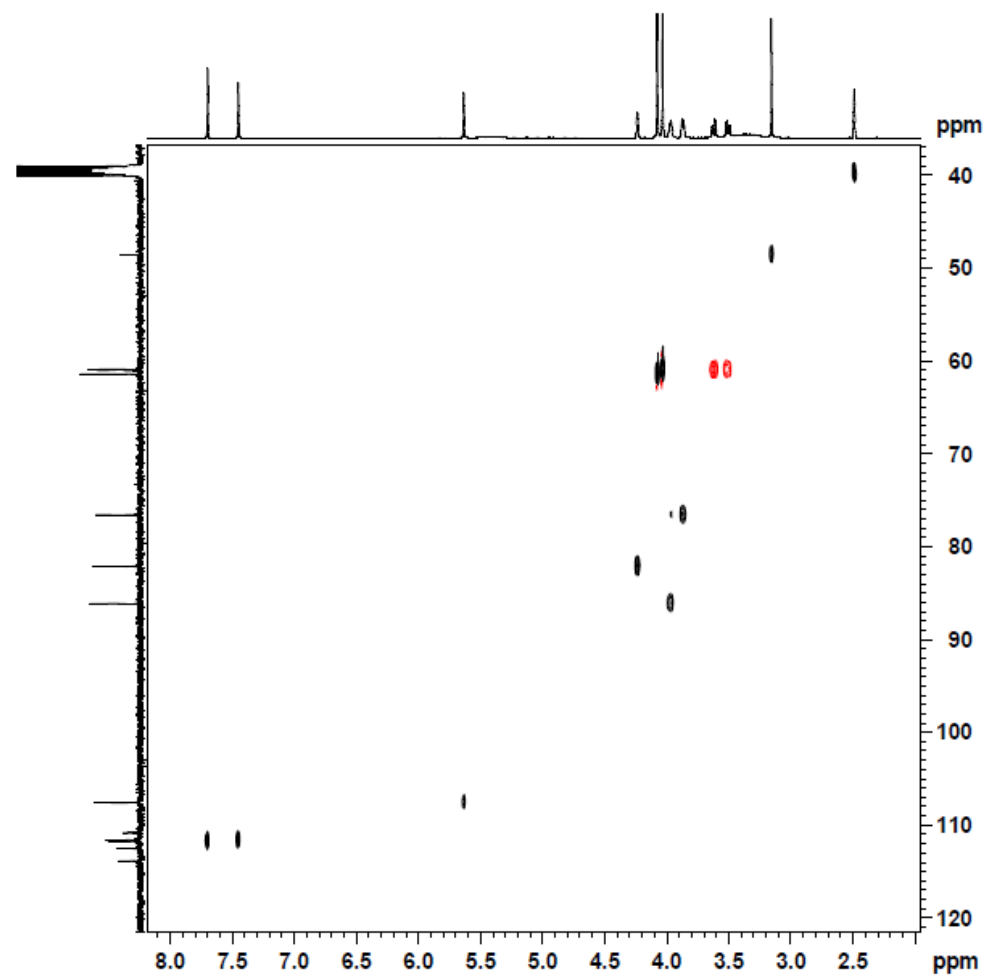


Figure S 1D. HSQC spectrum of **1**

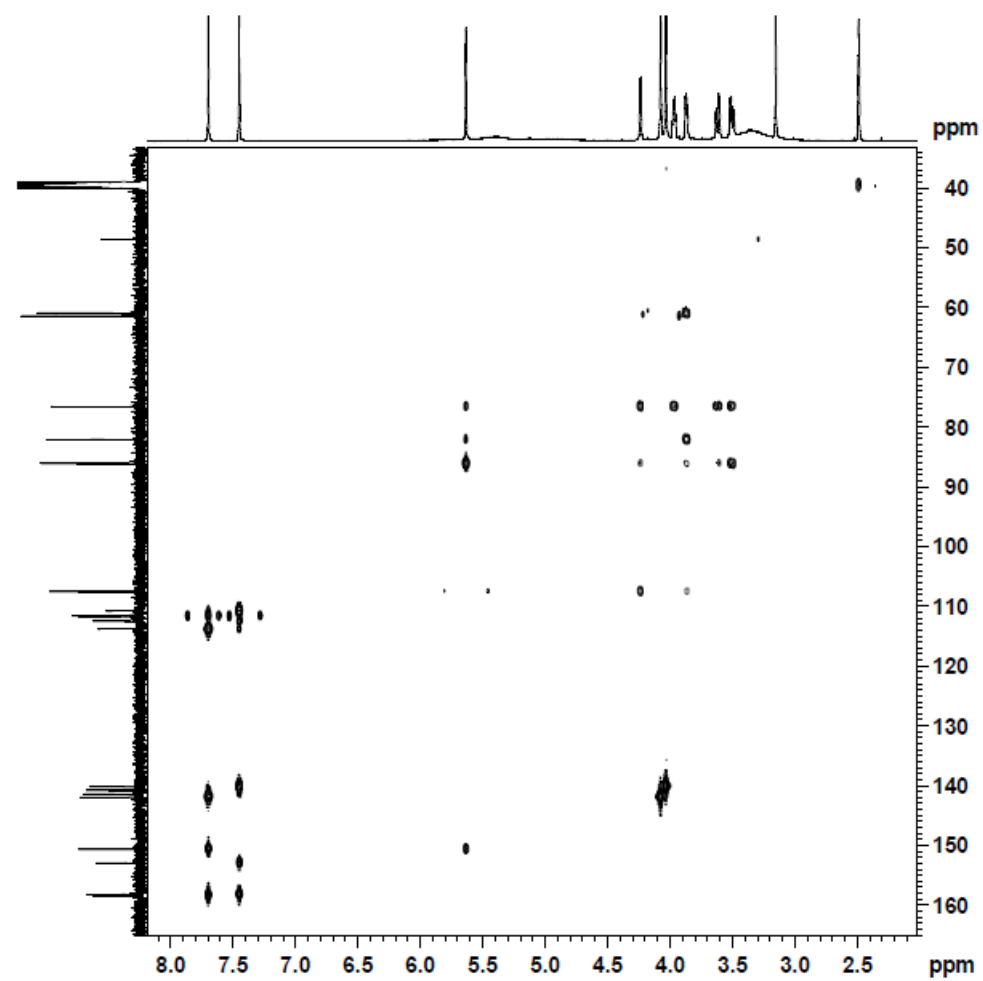


Figure S 1E. HMBC spectrum of **1**

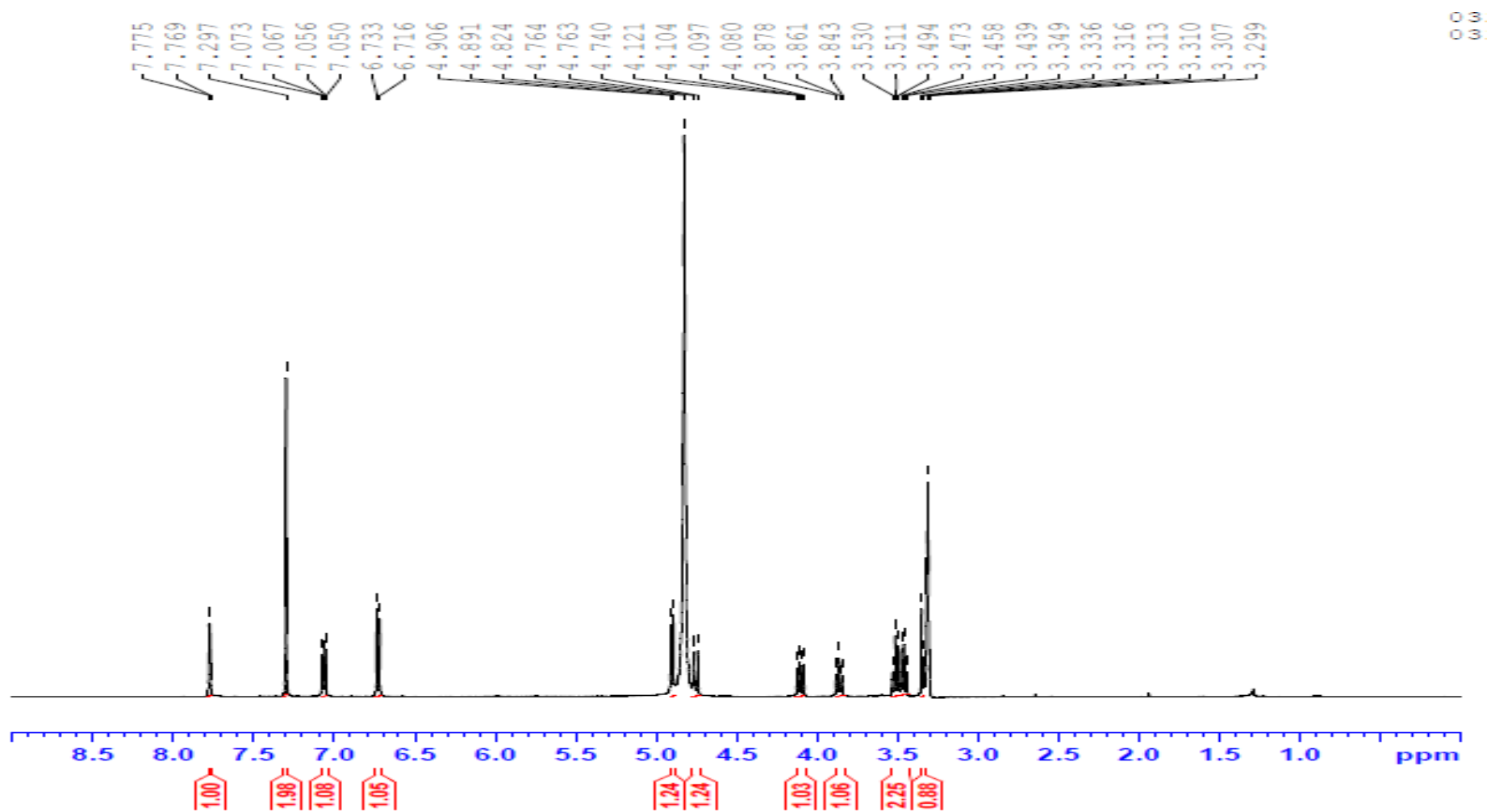


Figure S 2A. ¹H NMR (Methanol-*d*₄, 500 MHz) spectrum of **2**

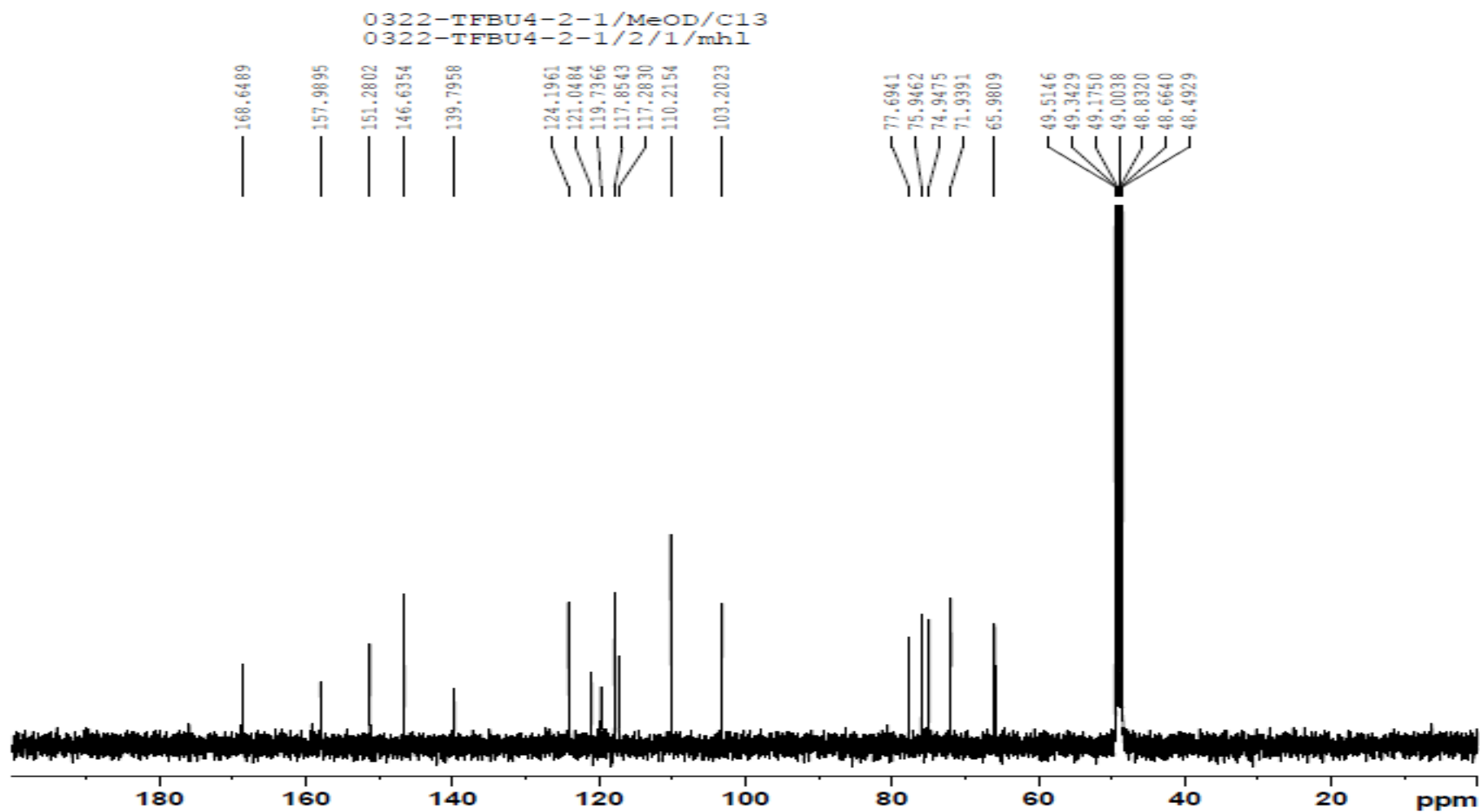


Figure S 2B. ^{13}C NMR (Methanol- d_4 , 125 MHz) spectrum of **2**

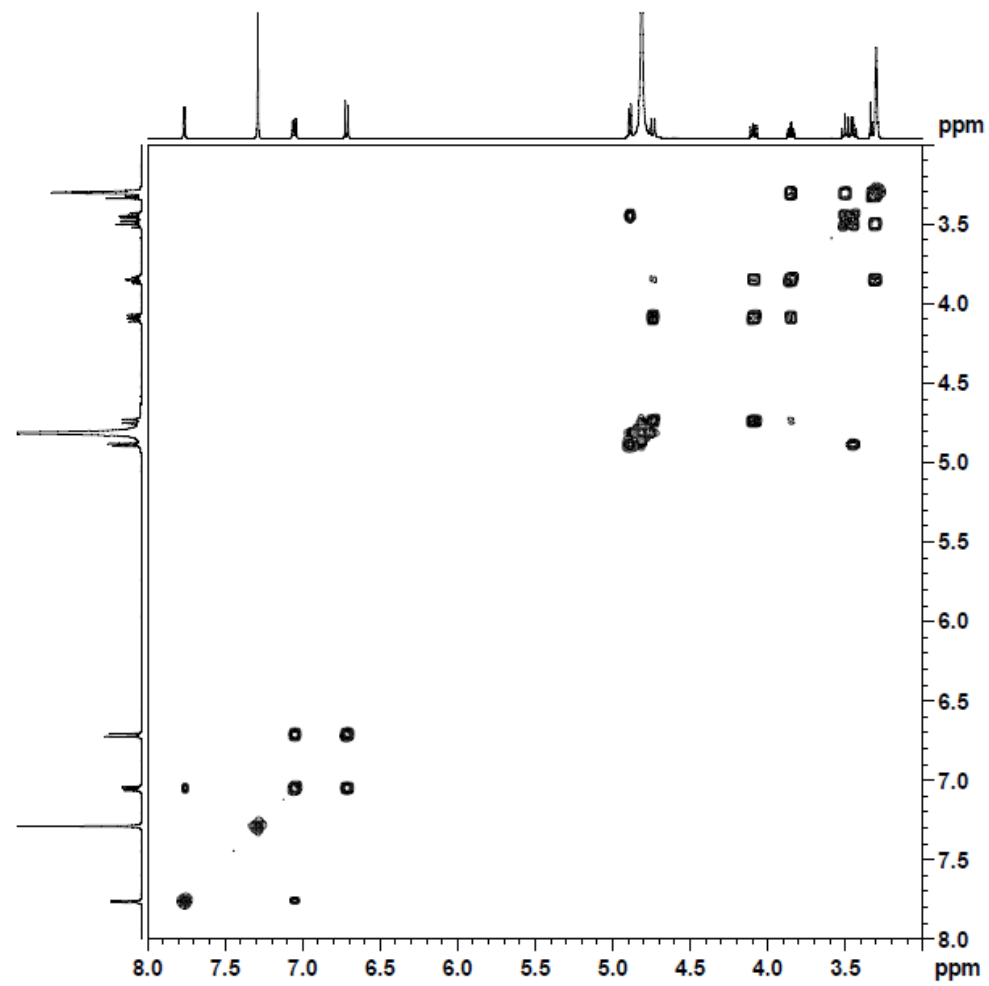


Figure S 2C. ^1H - ^1H COSY spectrum of **2**

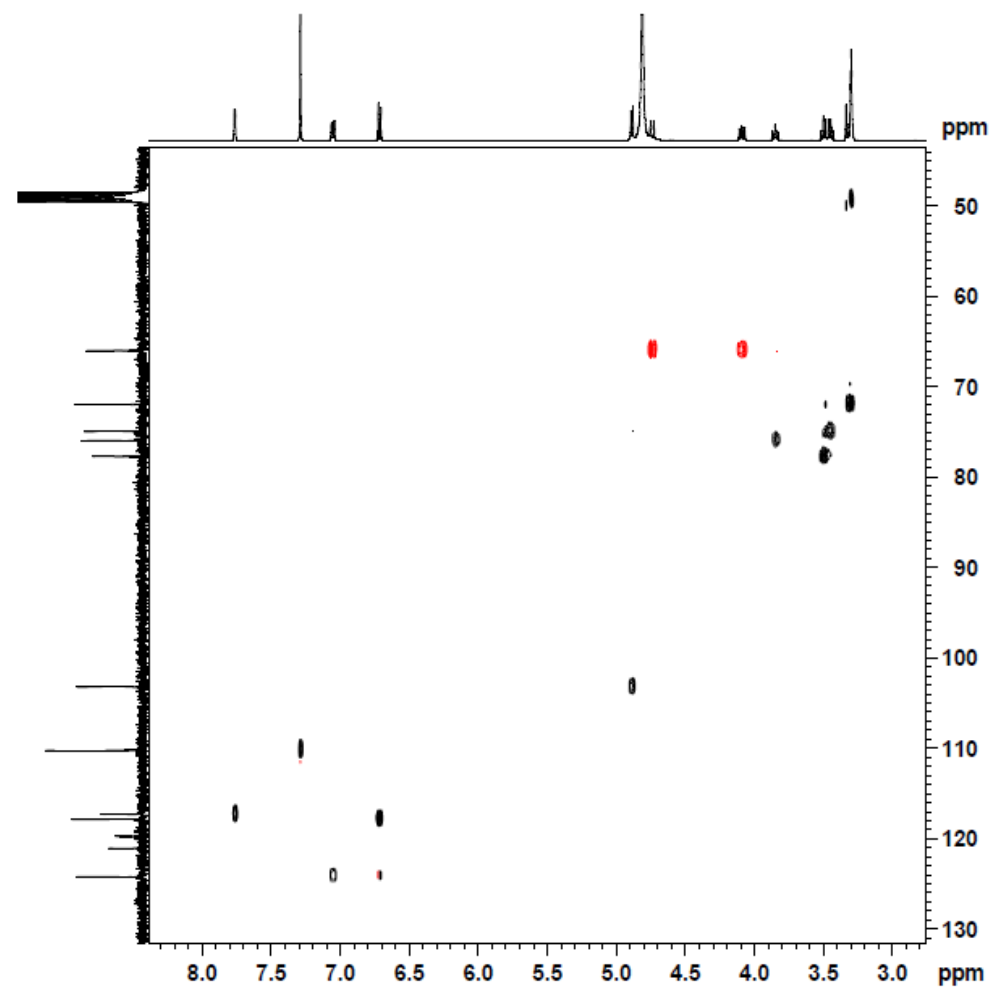


Figure S 2D. HSQC spectrum of **2**

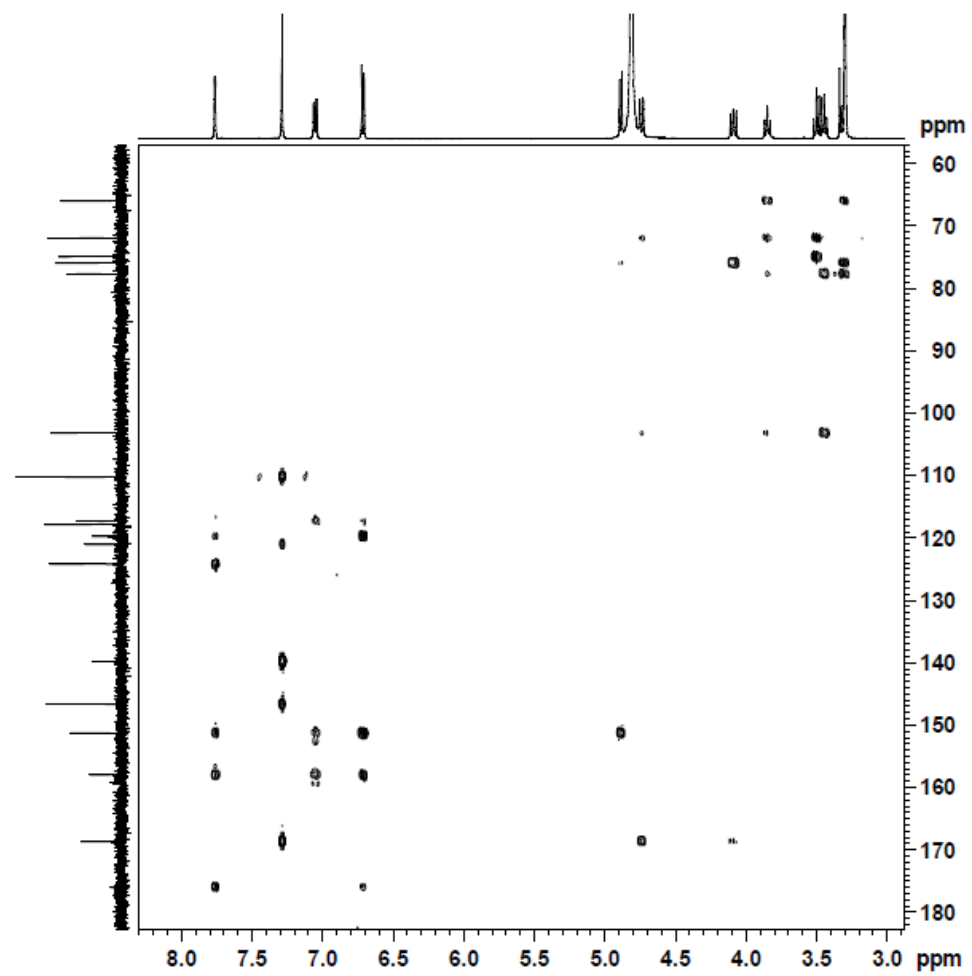


Figure S 2E. HMBC spectrum of **2**

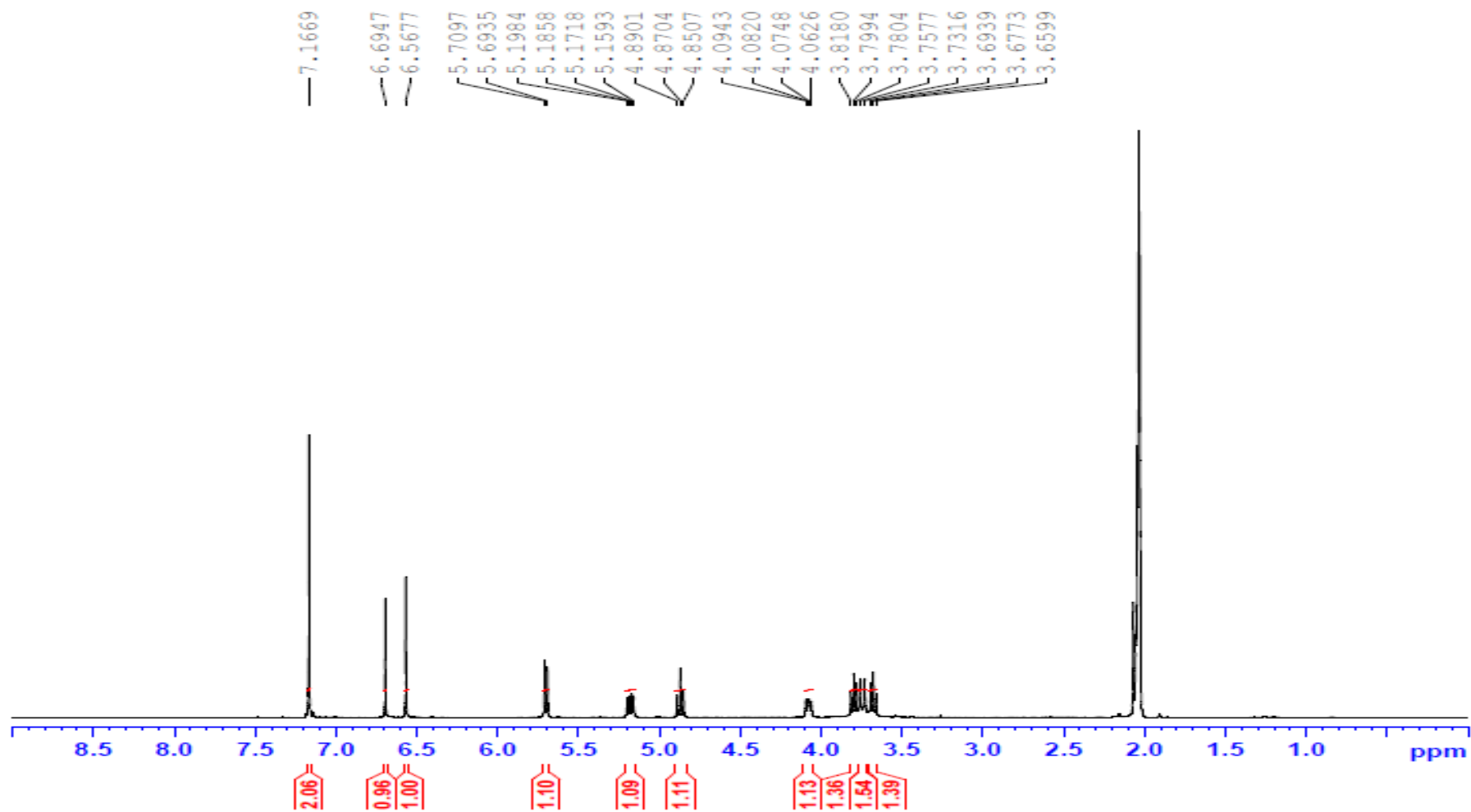


Figure S 3A. ¹H NMR (acetone-*d*₆, 500 MHz) spectrum of **3**

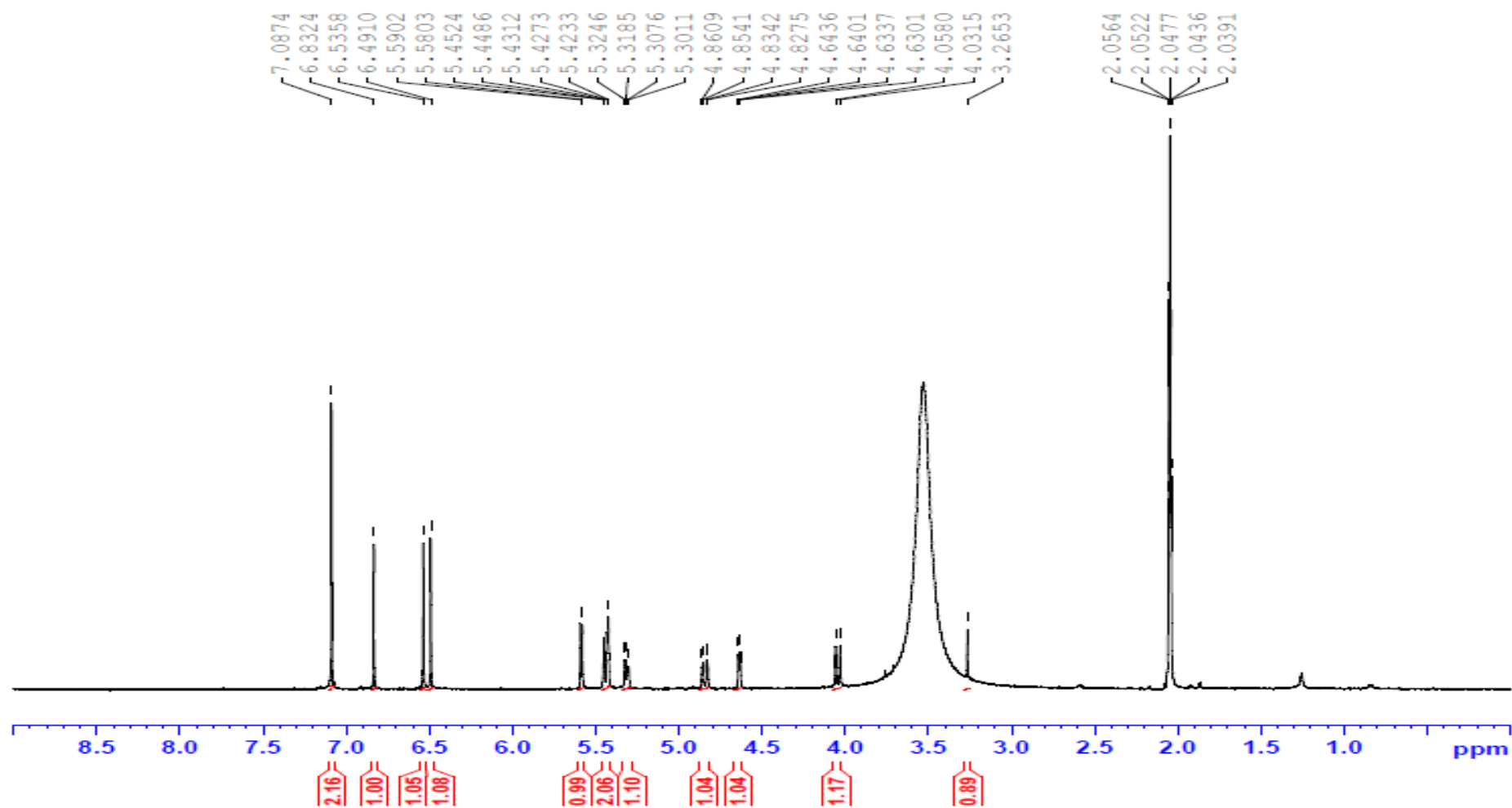


Figure S 4A. ¹H NMR (acetone-*d*₆, 500 MHz) spectrum of 4

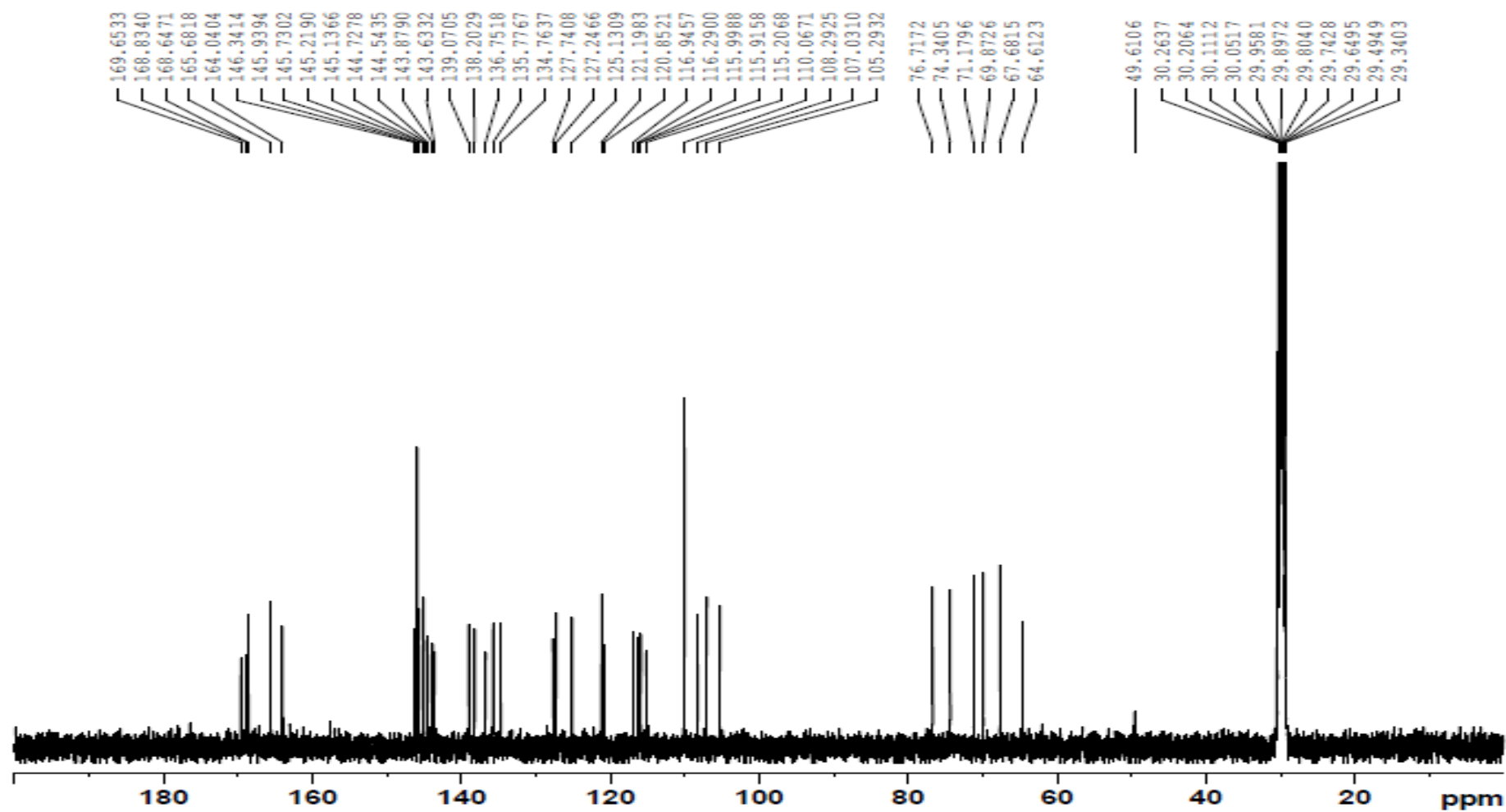


Figure S 4B. ¹³C NMR (acetone-*d*₆, 125 MHz) spectrum of 4

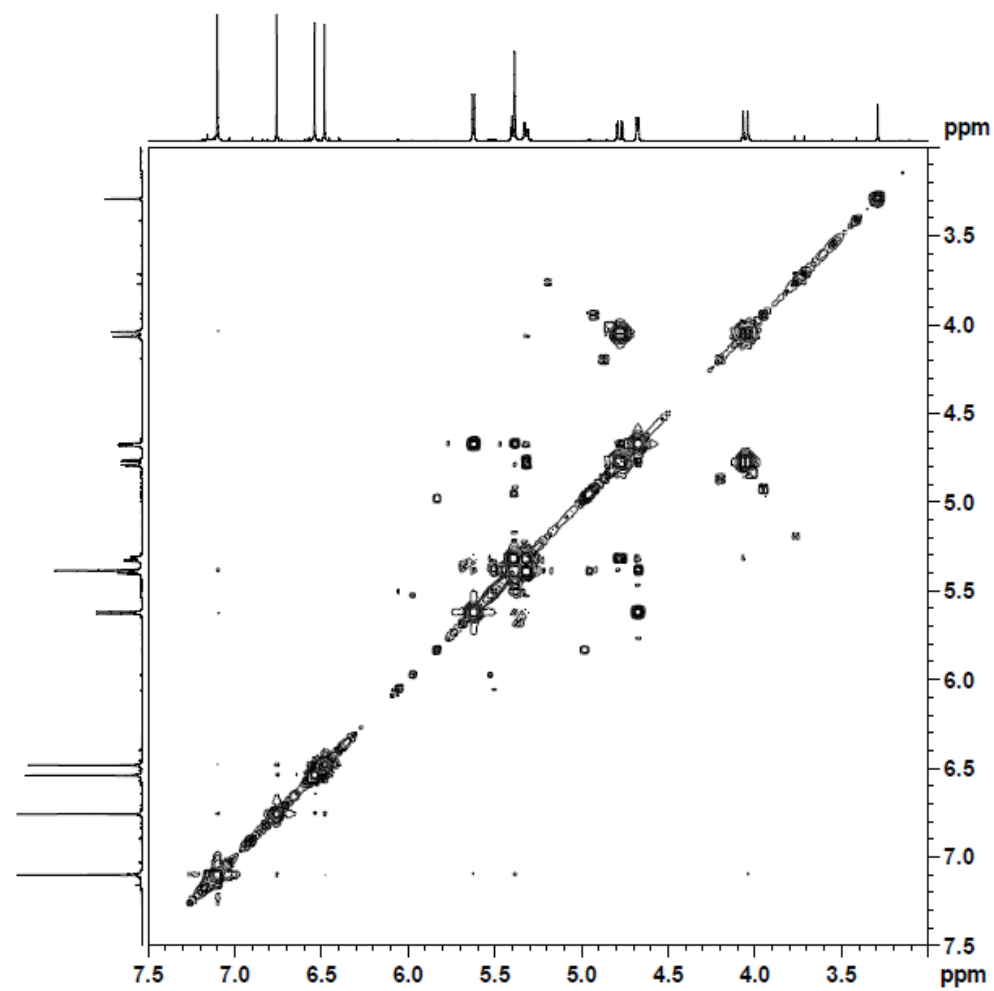


Figure S 4C. ^1H - ^1H COSY spectrum of 4

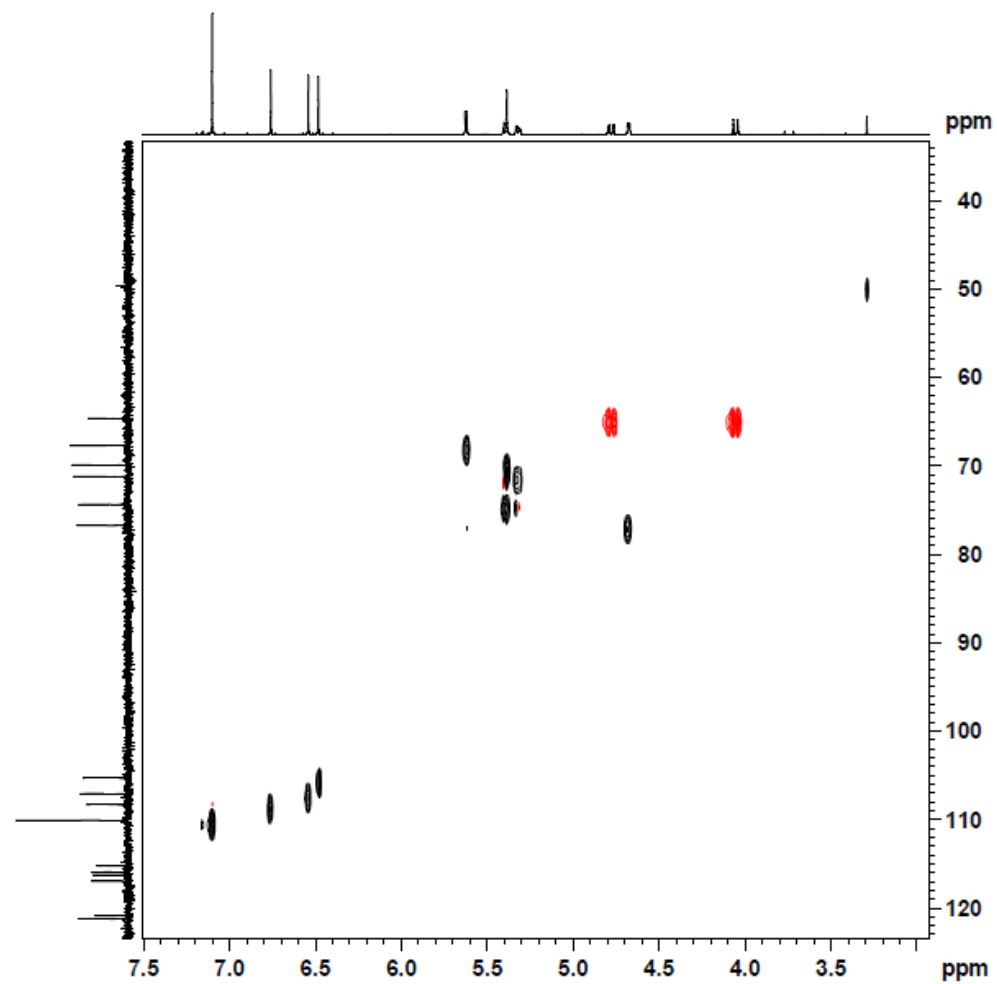


Figure S 4D. HSQC spectrum of **4**

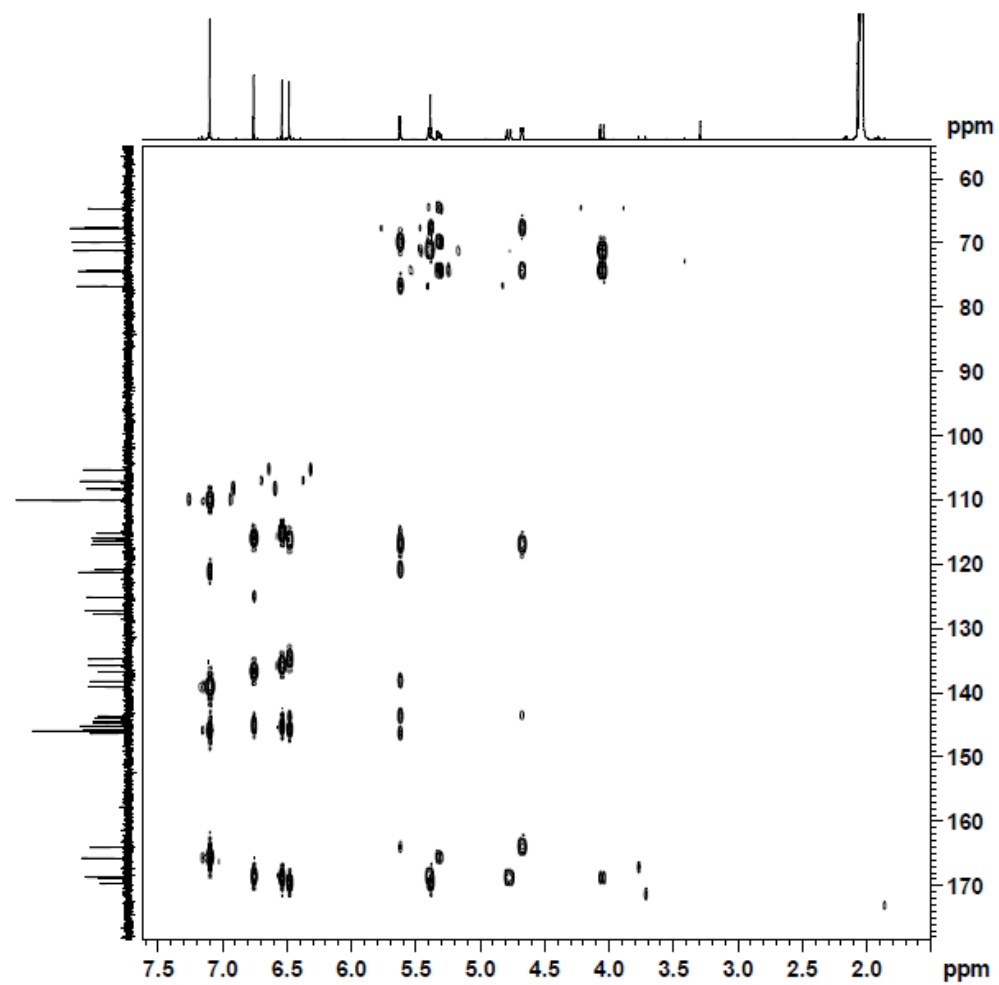


Figure S 4E. HMBC spectrum of **4**

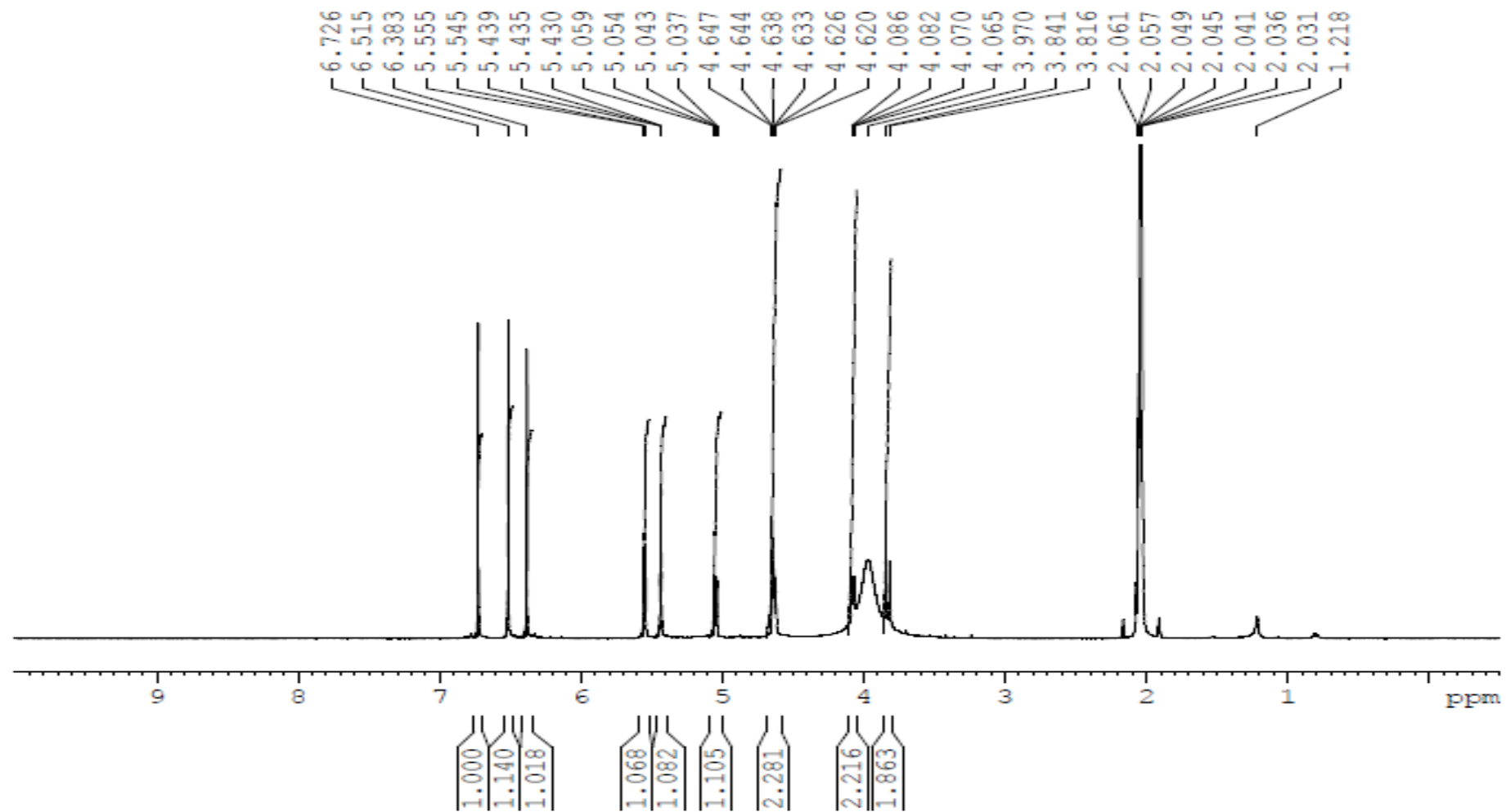


Figure S 5A. ¹H NMR (acetone-*d*₆, 500 MHz) spectrum of **5**

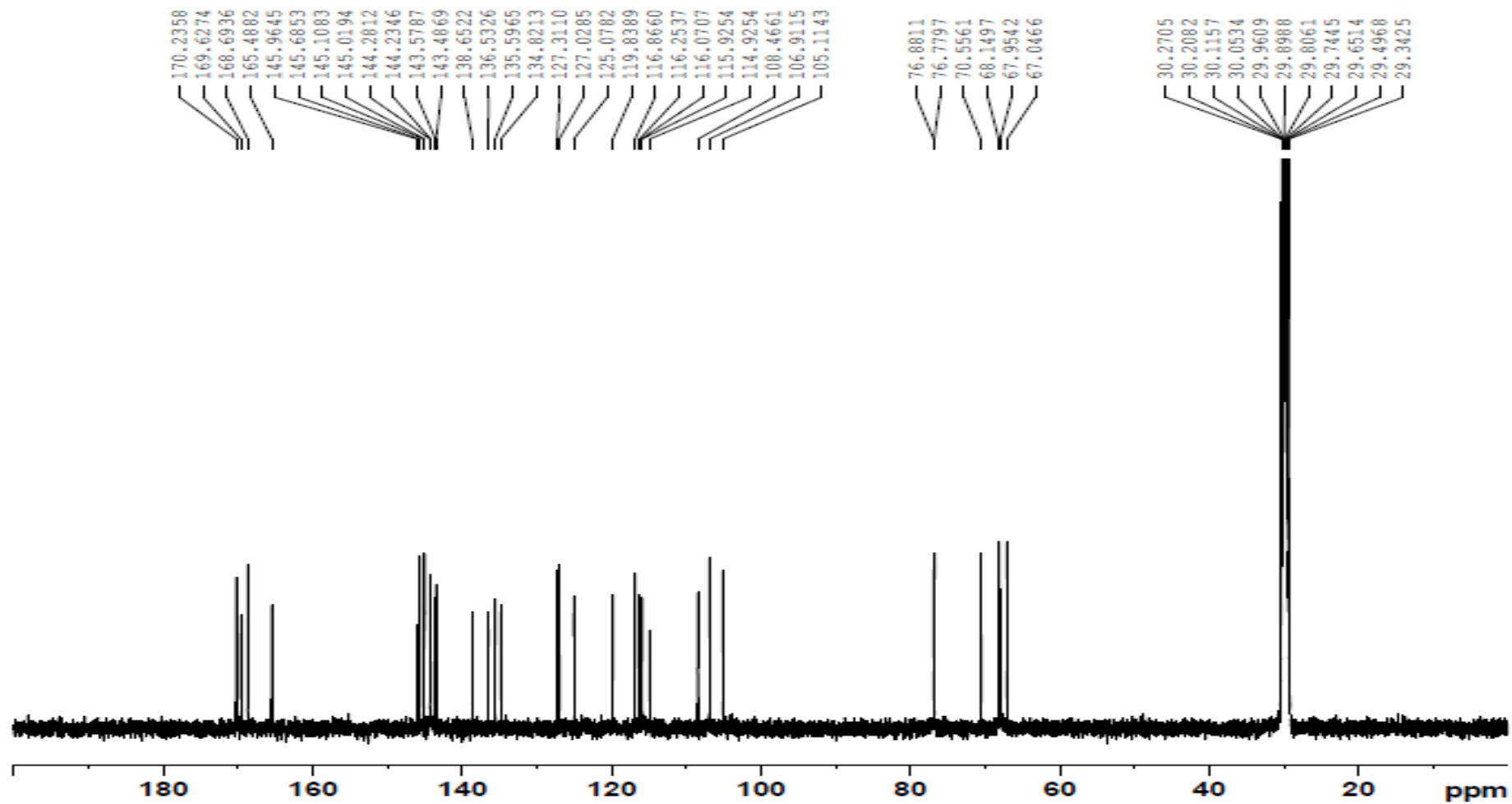


Figure S 5B. ¹³C NMR (acetone-*d*₆, 125 MHz) spectrum of compound **5**

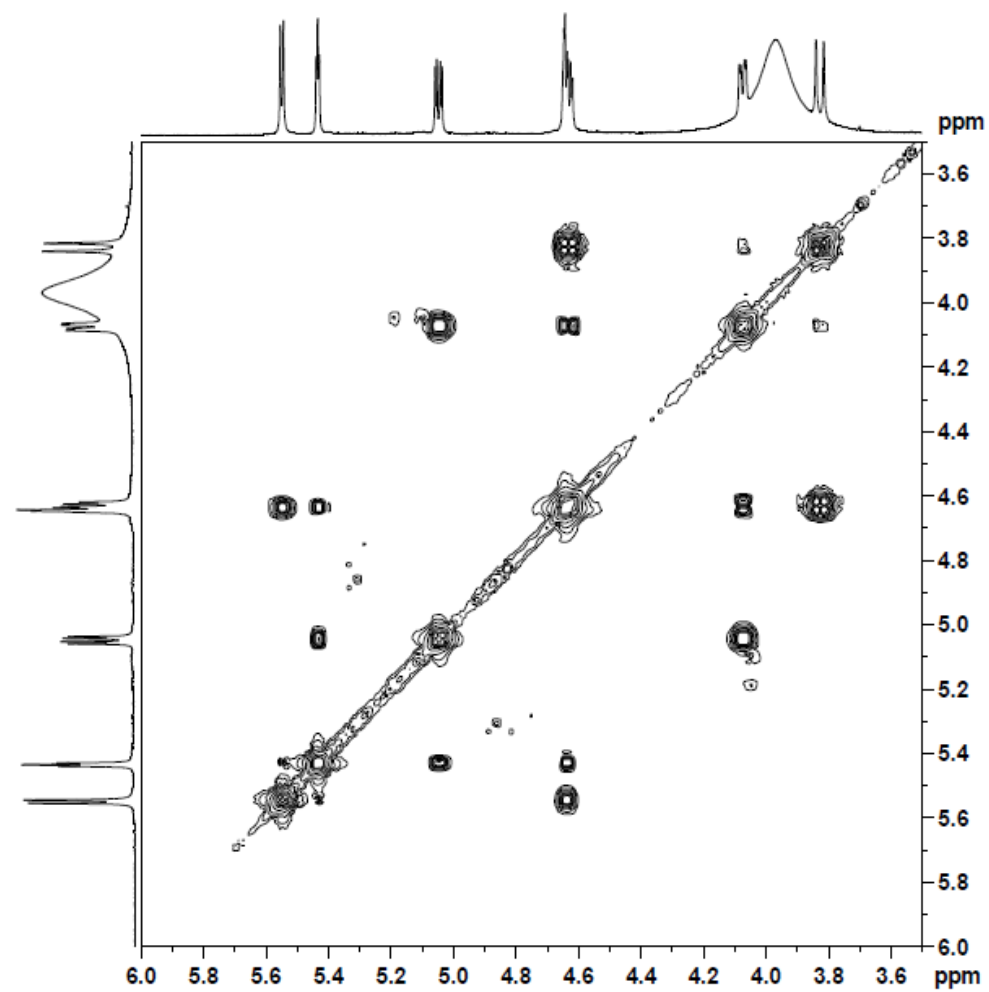


Figure S 5C. ^1H - ^1H COSY spectrum of **5**

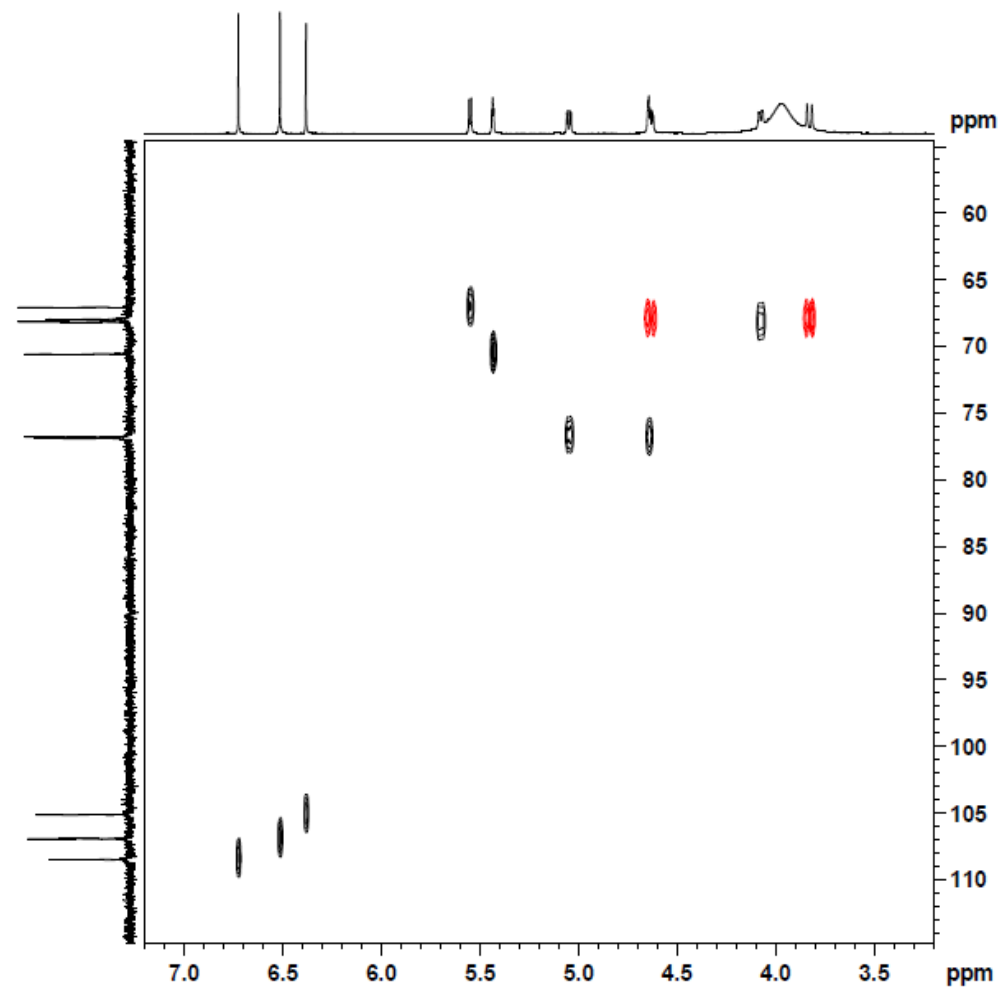


Figure S 5D. HSQC spectrum of **5**

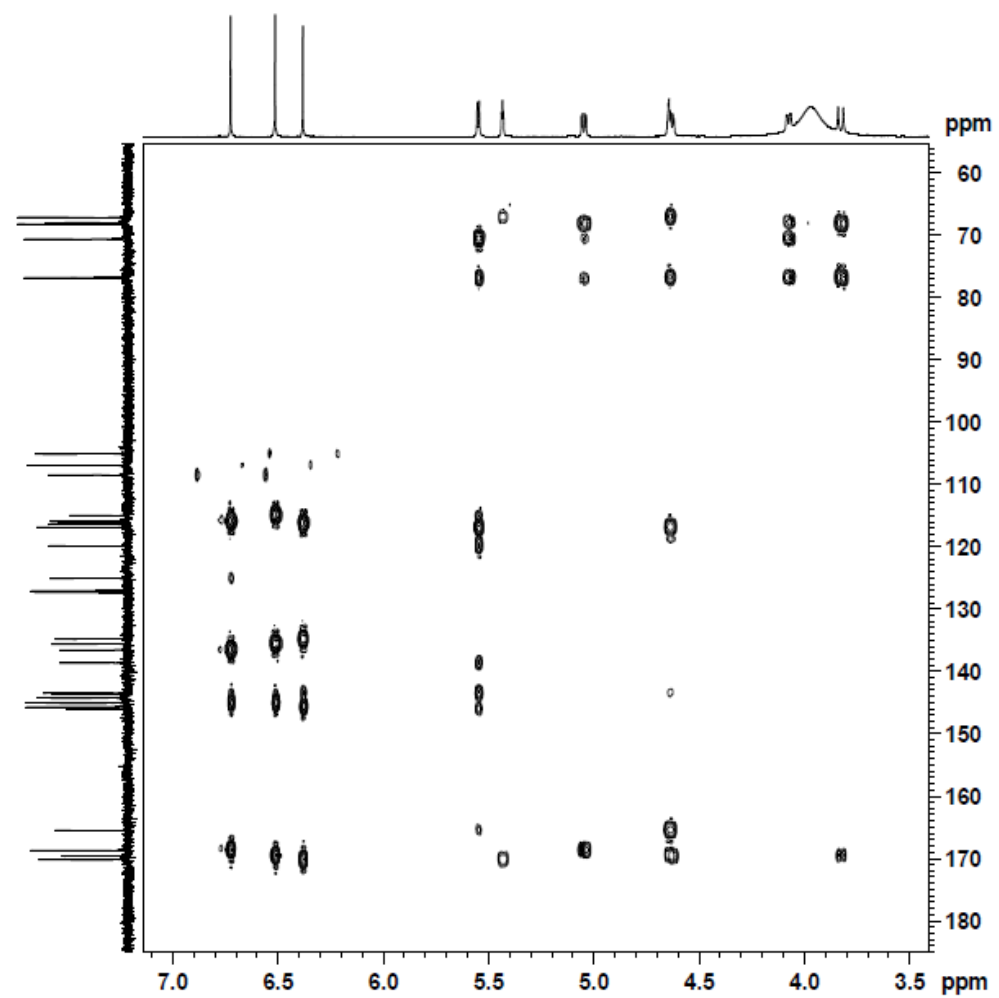


Figure S 5E. HMBC spectrum of **5**

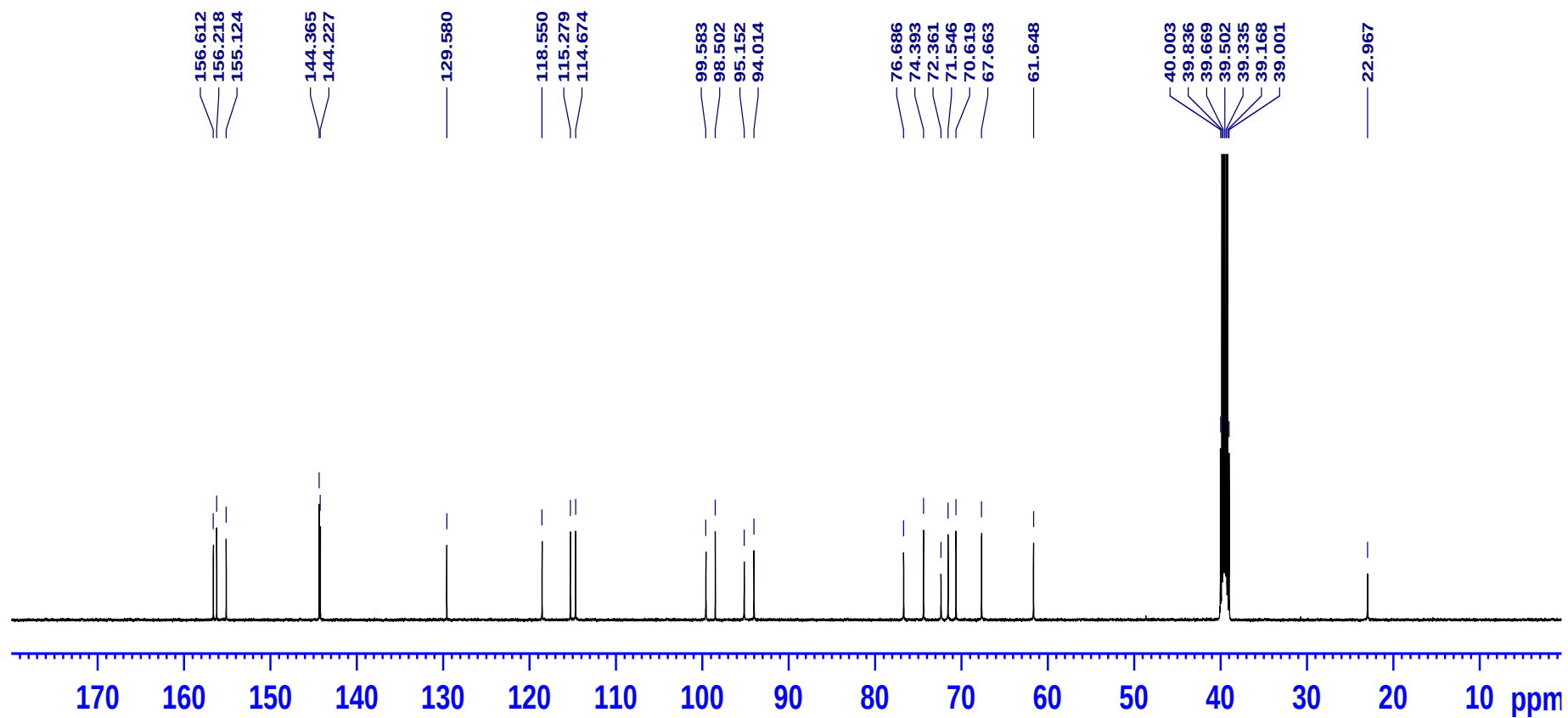


Figure S 6B. ¹³C NMR (DMSO-*d*₆, 125 MHz) spectrum of **6**

COSY DMSO 1-8

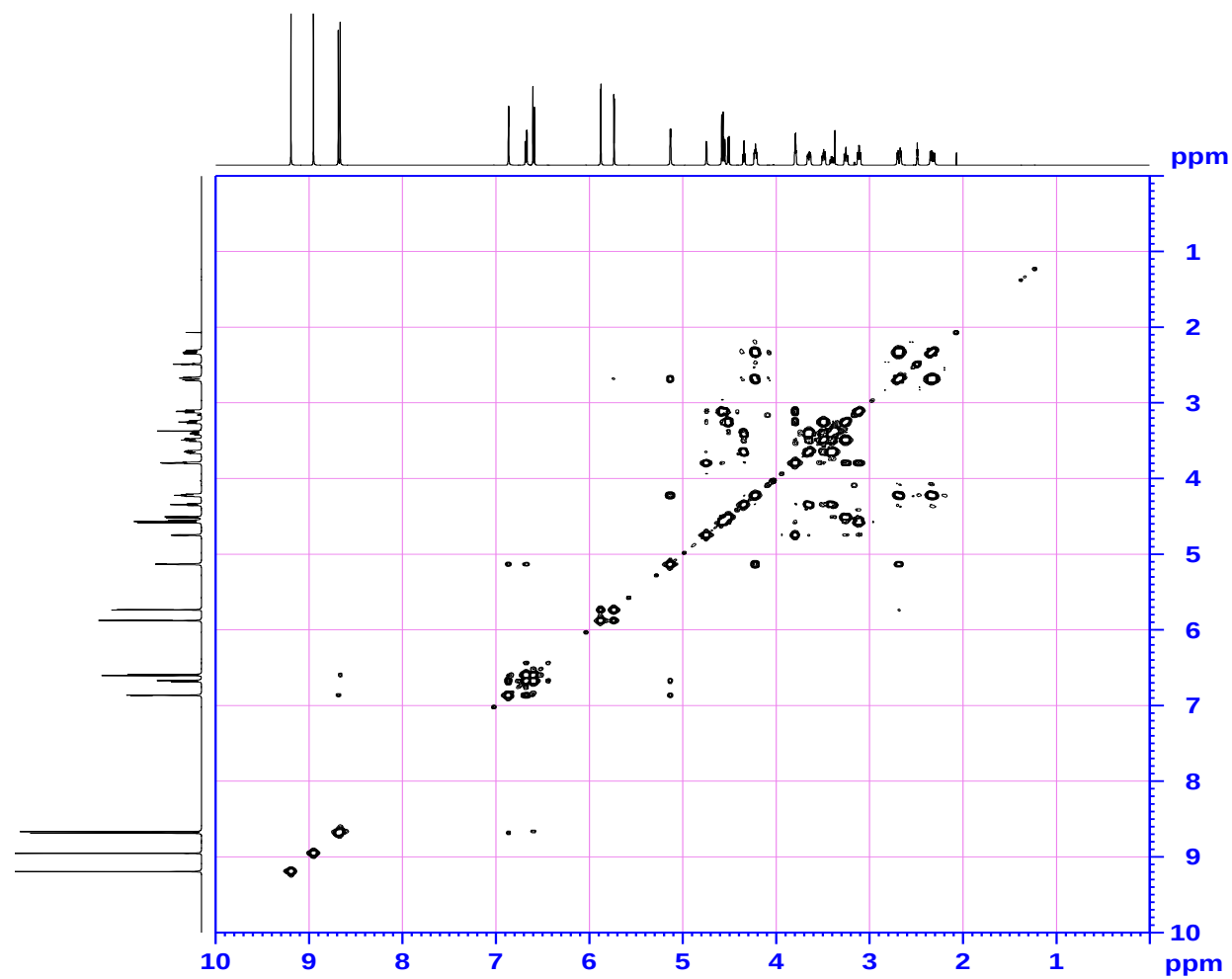


Figure S 6C. ^1H - ^1H COSY spectrum of 6

[illegible]

Figure S 6D. HSQC spectrum of **6**

2D NMR Spectrum of Compound 12f

Acquisition Parameters:

- NAME: 12f
- EXPNO: 1
- PROCNO: 1
- DATE_: 20120204
- Time: 12.42
- INSTRUM: spect
- PROBHD: 5 mm CPYHD 1H
- PULPROG: zgpg30
- TD: 65536
- SOLVENT: DMSO
- NS: 24
- DS: 4
- SWH: 12.000 MHz
- F2: 299.624 MHz
- F1: 125.761 MHz
- RG: 655
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- RG3: 655
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- RG255: 655
- RG256: 655
- RG257: 655
- RG258: 655
- RG259: 655
- RG260: 655
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Figure S 6E. HMBC spectrum of **6**

