

Supplementary Materials

**Pentaketides and 5-*p*-Hydroxyphenyl-2-pyridone Derivative from
the Culture Extract of a Marine Sponge-Associated Fungus
Hamigera avellanea KUFA0732**

Figure S1. ^1H NMR spectrum of **1** (DMSO-d_6 , 300 MHz).

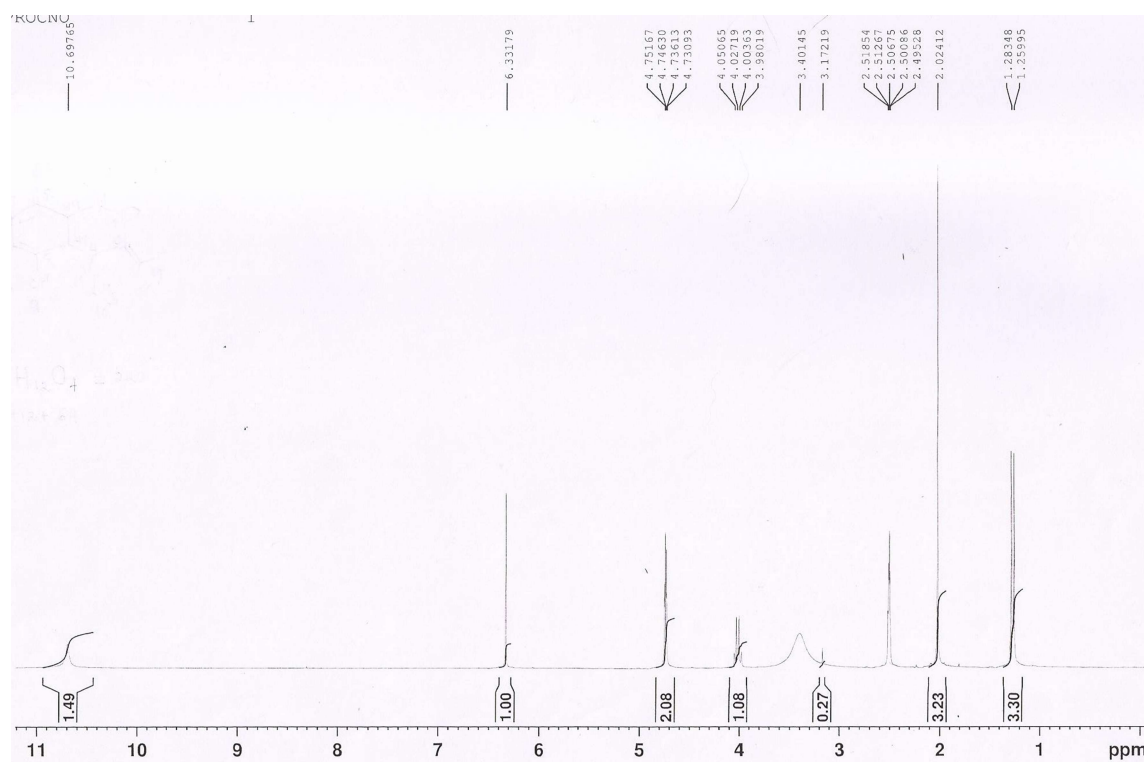


Figure S2. ^{13}C NMR spectrum of **1** (DMSO-d_6 , 75 MHz).

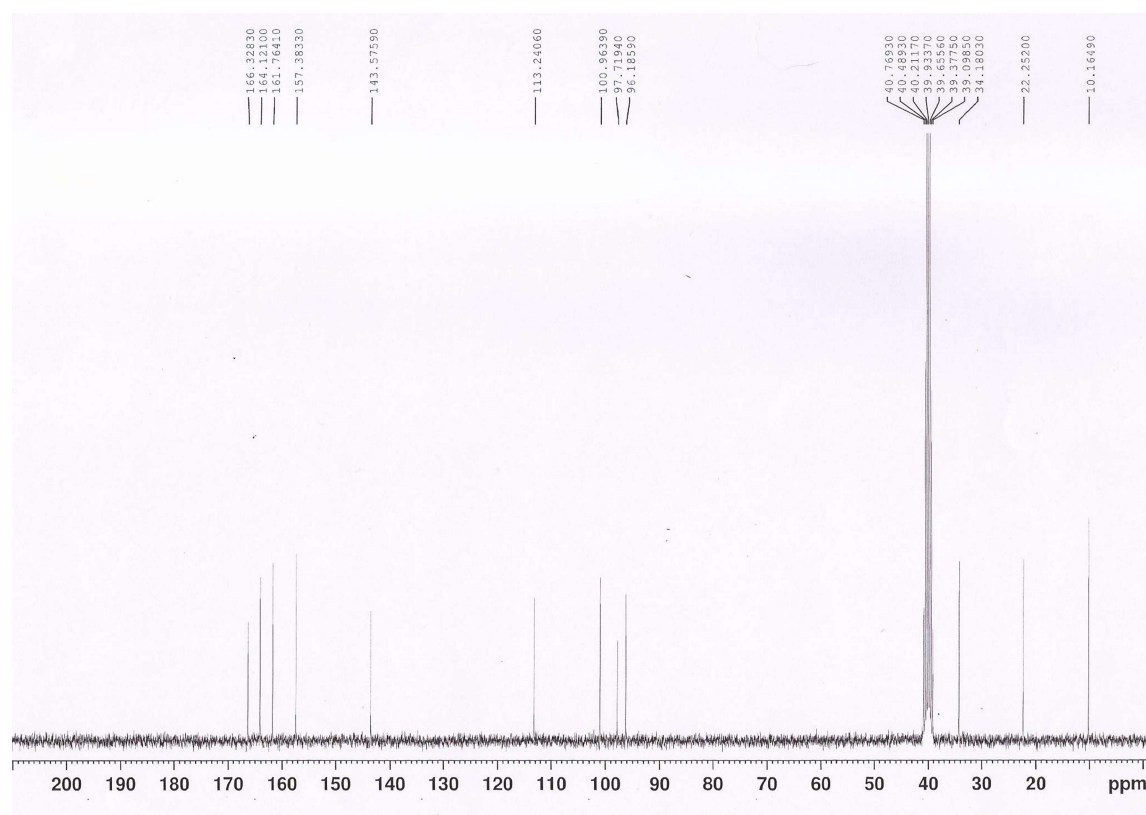


Figure S3. COSY spectrum of **1** (DMSO_{d6}, 300 MHz).

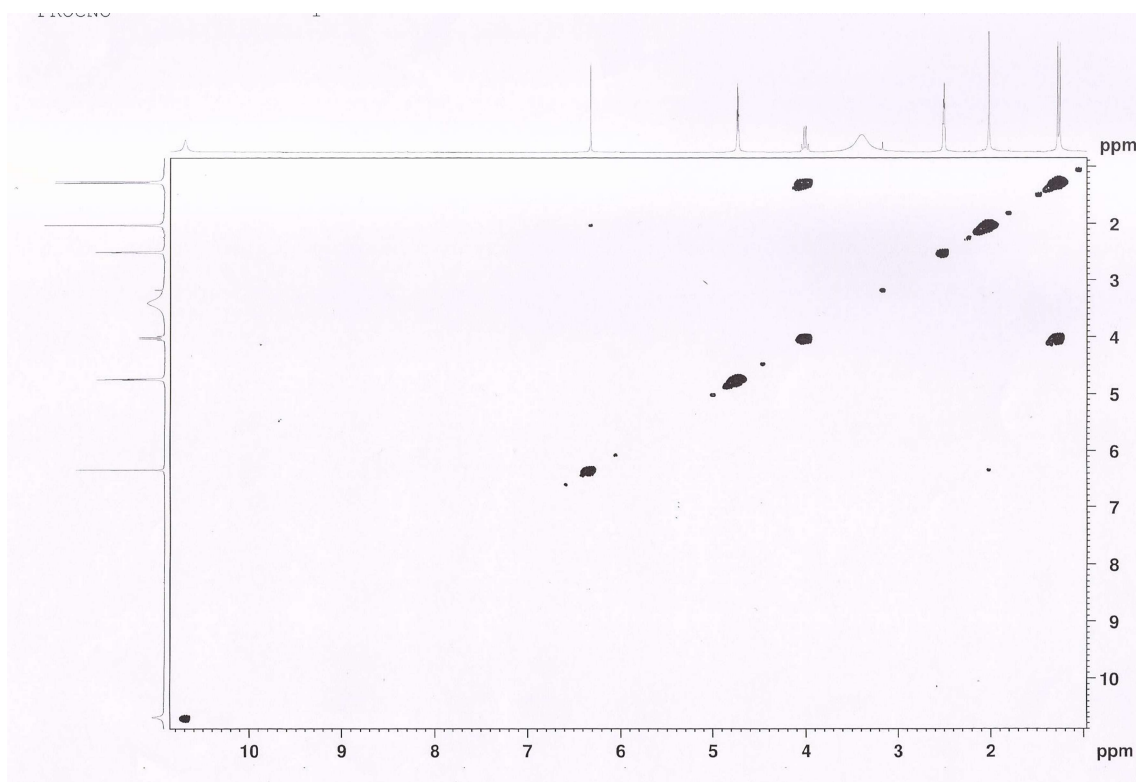


Figure S4. HSQC spectrum of **1** (DMSO_{d6}, 300 MHz).

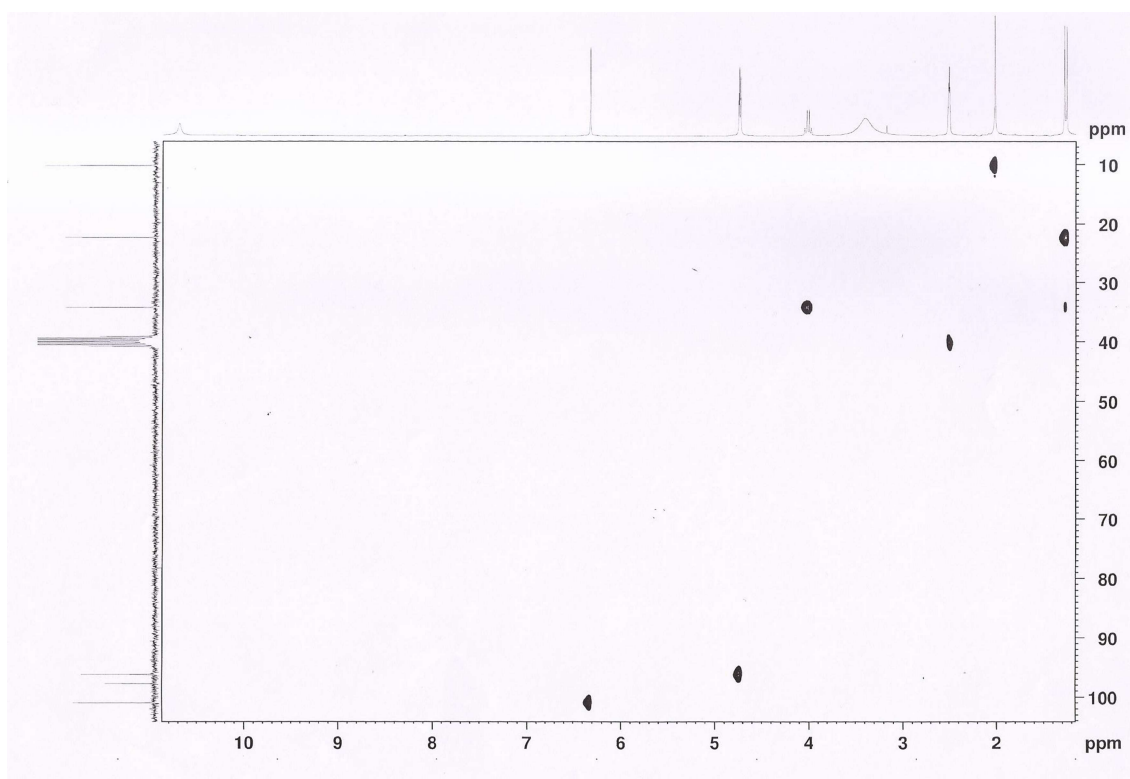


Figure S5. HMBC spectrum of **1** (DMSO_{d6}, 300 MHz).

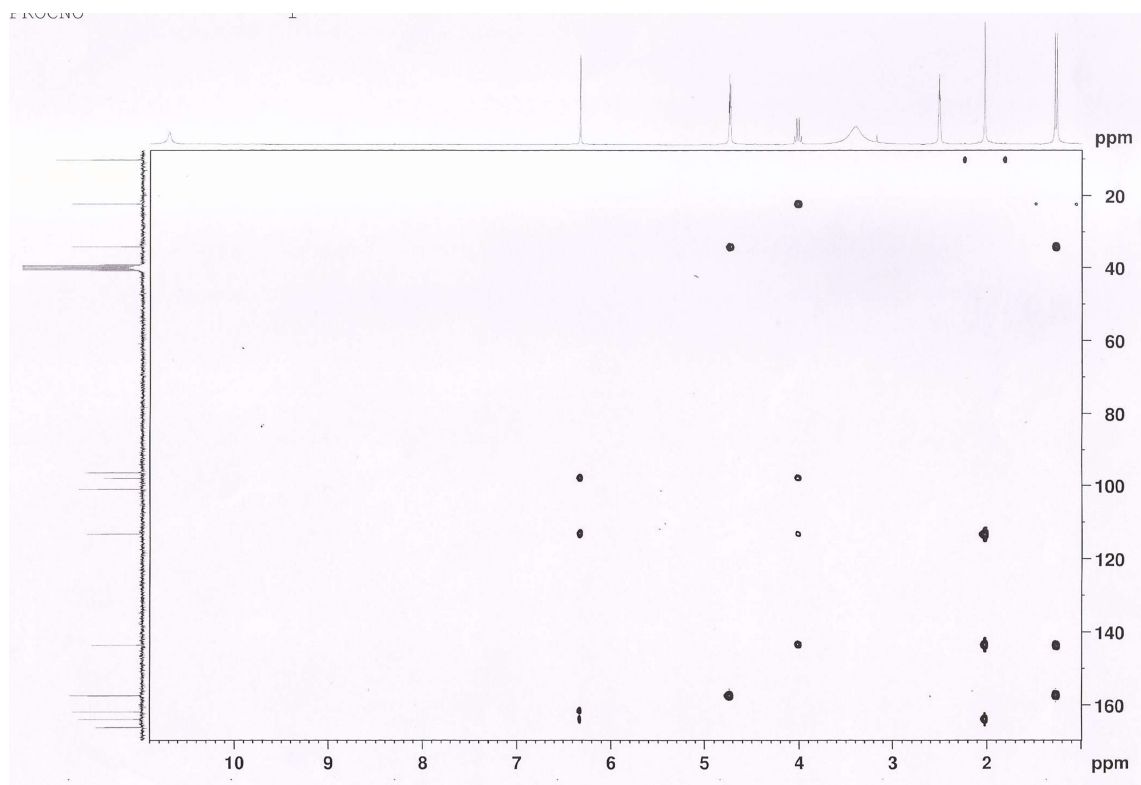


Figure S6. (+)-HRESIMS spectrum of **1**

Elemental Composition Report [MH]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

13 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 12-12 H: 0-150 O: 0-30

Minimum: -1.5

Maximum: 5.0 5.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|------------|
| 221.0814 | 221.0814 | 0.0 | 0.0 | 6.5 | 515.2 | n/a | n/a | C12 H13 O4 |

AK-HSR 39-46
ANAKE-G2-227 237 (1.949)

1: TOF MS ES+
1.44e+007

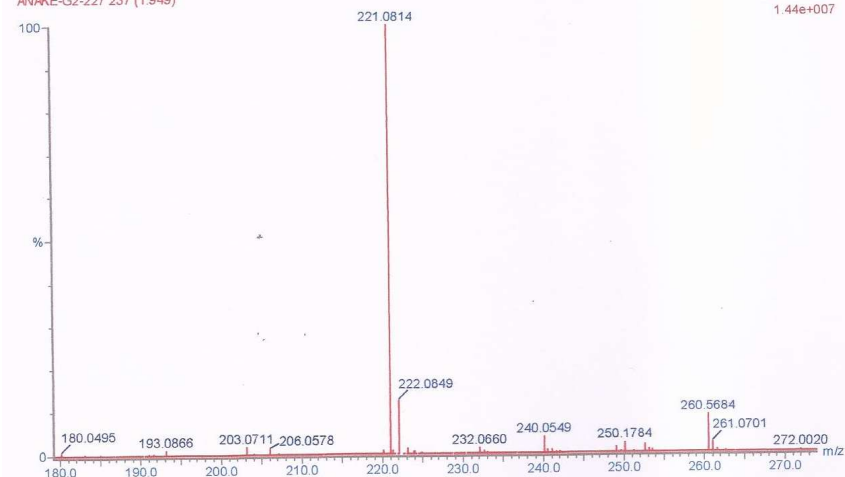


Figure S7. ^1H NMR spectrum of **2** (CDCl_3 , 300 MHz).

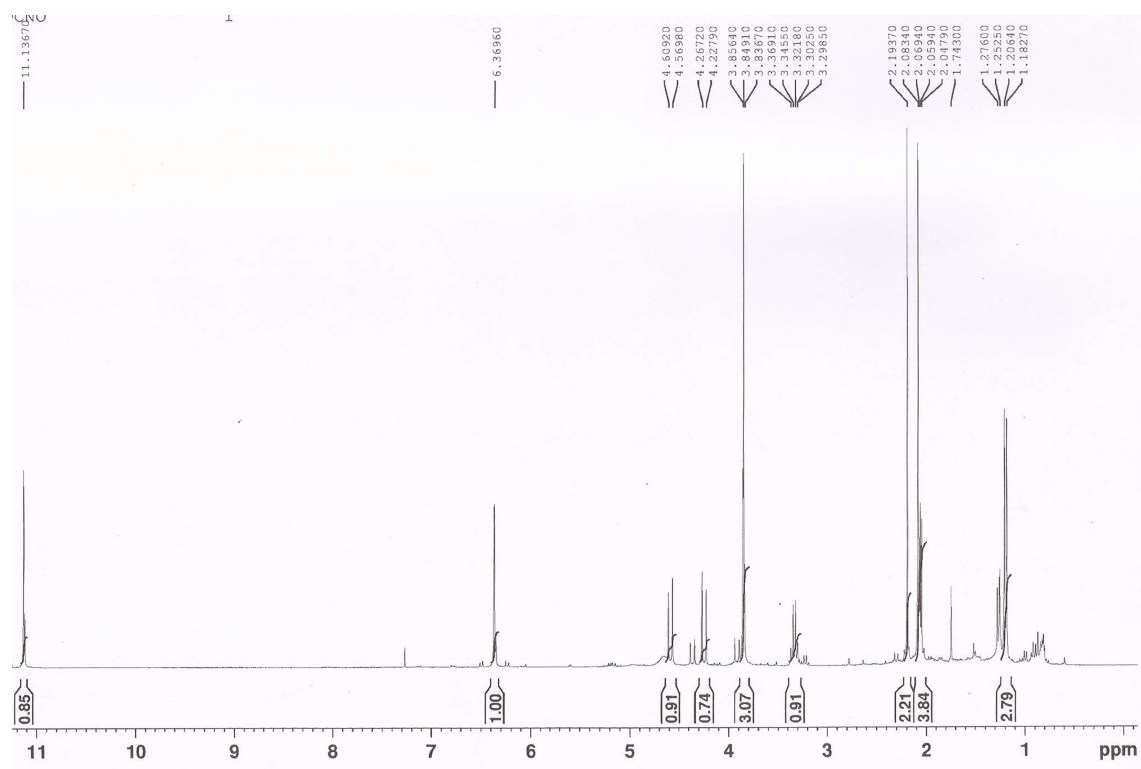


Figure S8. ^{13}C NMR spectrum of **2** (CDCl_3 , 75 MHz).

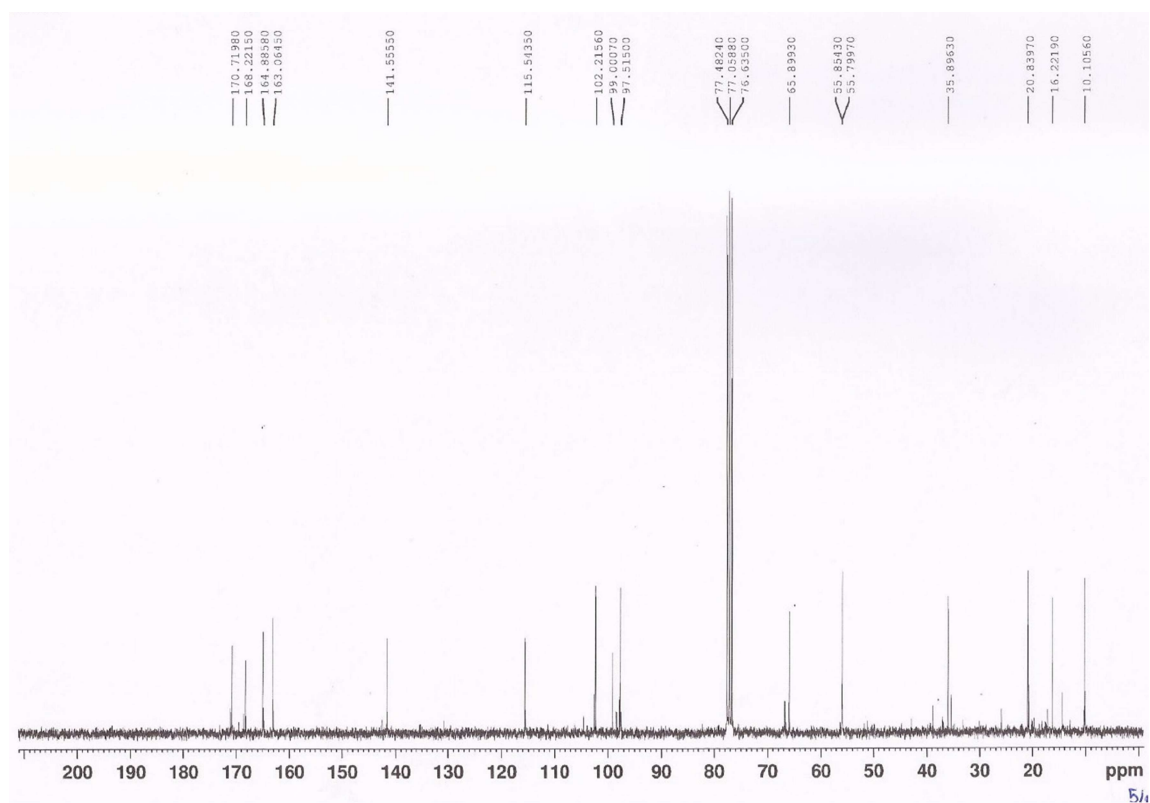


Figure S9. COSY spectrum of **2** (CDCl₃, 300 MHz).

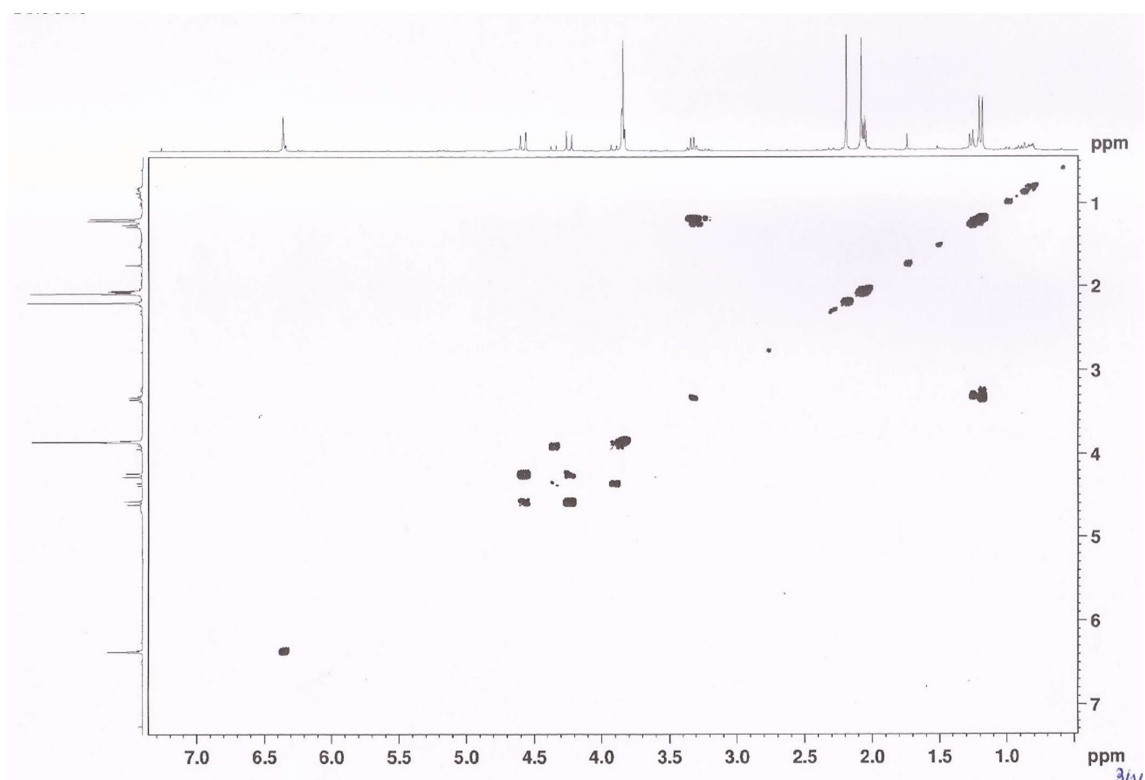


Figure S10. HSQC spectrum of **2** (CDCl₃, 300 MHz).

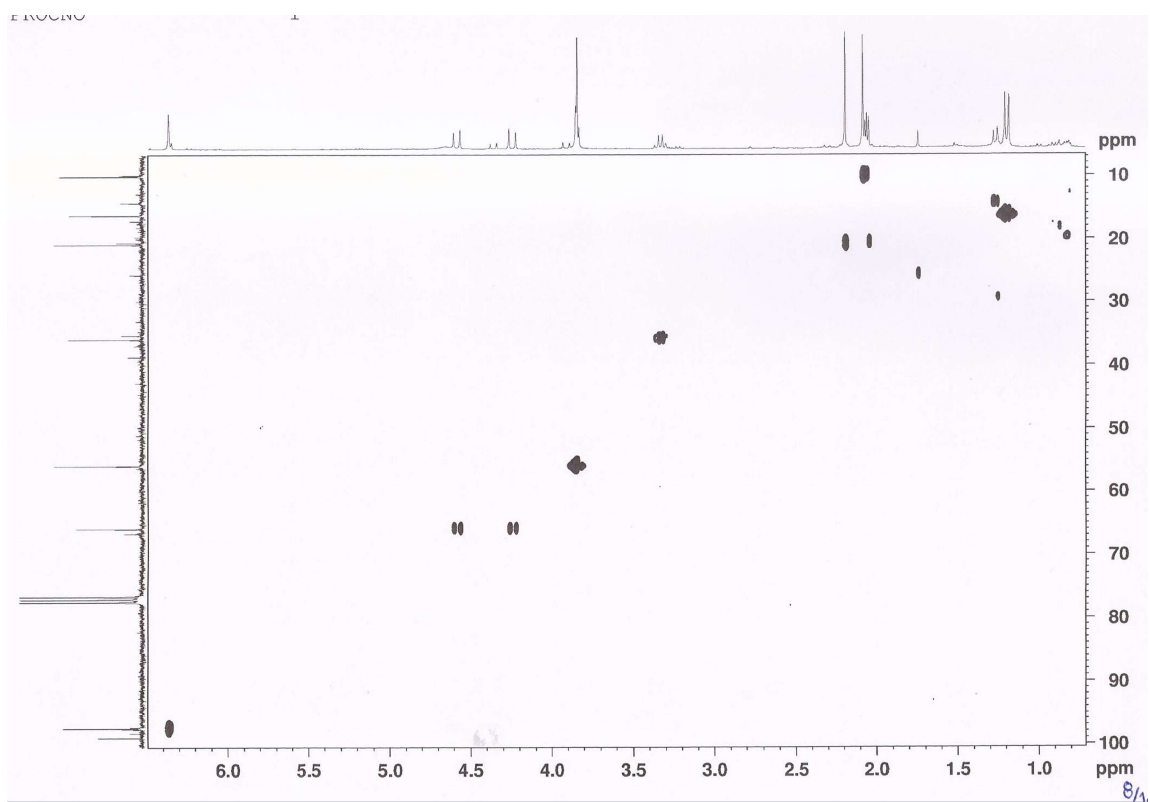


Figure S11. HMBC spectrum of **2** (CDCl₃, 300 MHz).

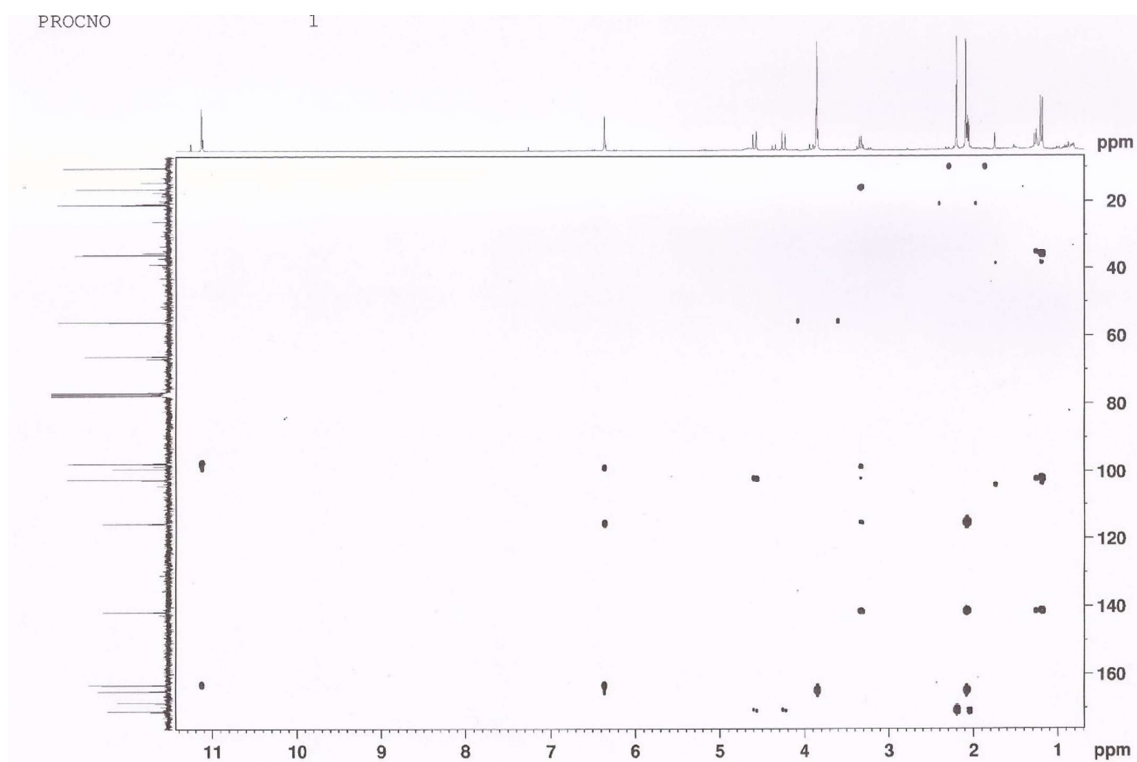


Figure S12. ROESY spectrum of **2** (CDCl₃, 300 MHz).

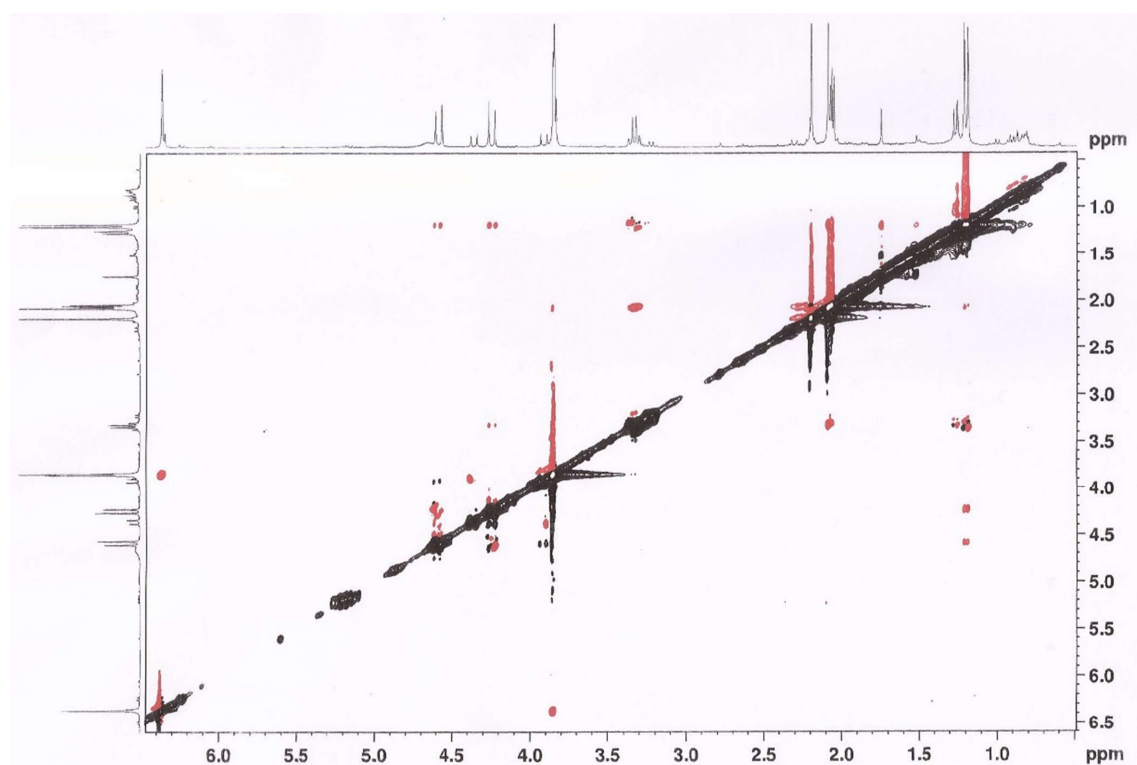


Figure S13. (+)-HRESIMS spectrum of 2.

Elemental Composition Report [MH]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

20 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 15-15 H: 0-150 O: 0-30

Minimum:

-1.5

Maximum:

5.0 5.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|------------|
| 311.1133 | 311.1131 | 0.2 | 0.6 | 6.5 | 592.6 | n/a | n/a | C15 H19 O7 |

Elemental Composition Report [MNa]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

41 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 15-15 H: 0-150 O: 0-30 Na: 0-1

Minimum:

-1.5

Maximum:

5.0 5.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|------|------|-----|-------|------|---------|---------------|
| 333.0948 | 333.0950 | -0.2 | -0.6 | 6.5 | 602.1 | n/a | n/a | C15 H18 O7 Na |

AKHSR 62-79
ANAKE-G2-228 235 (1.936)

1: TOF MS ES+
1.25e+007



Figure S14. ^1H NMR spectrum of **3** (CDCl_3 , 300 MHz).

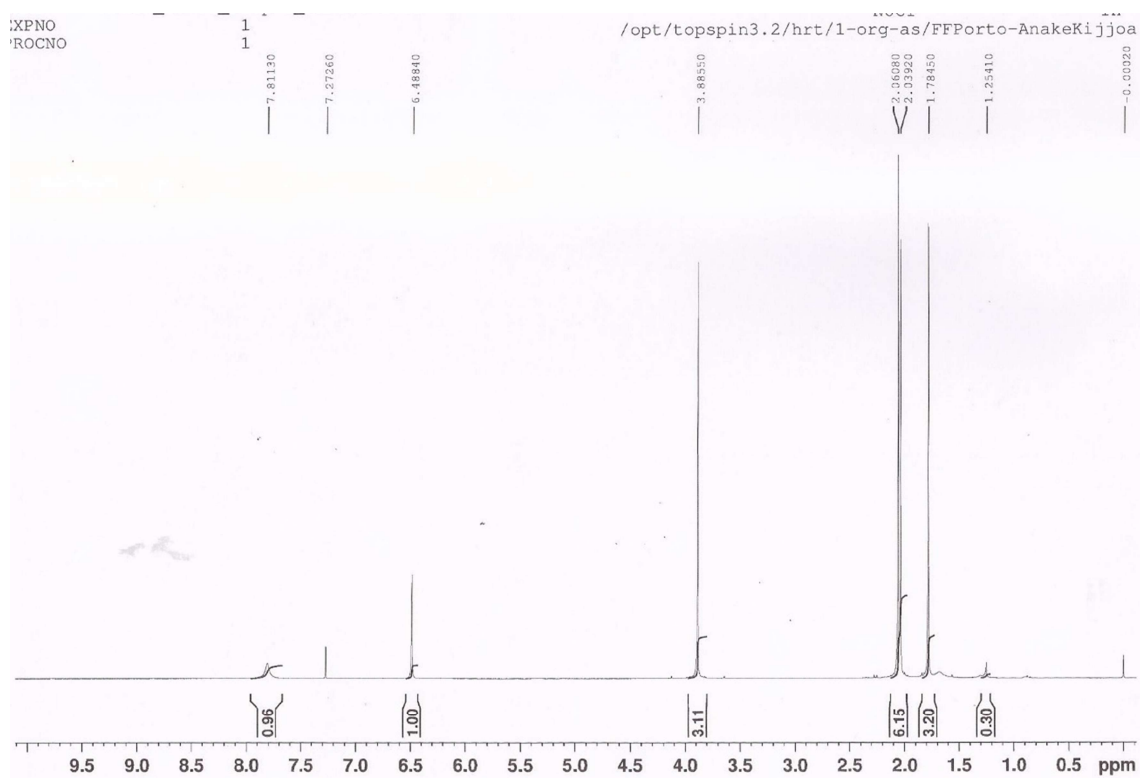


Figure S15. ^{13}C NMR spectrum of **3** (CDCl_3 , 75 MHz).

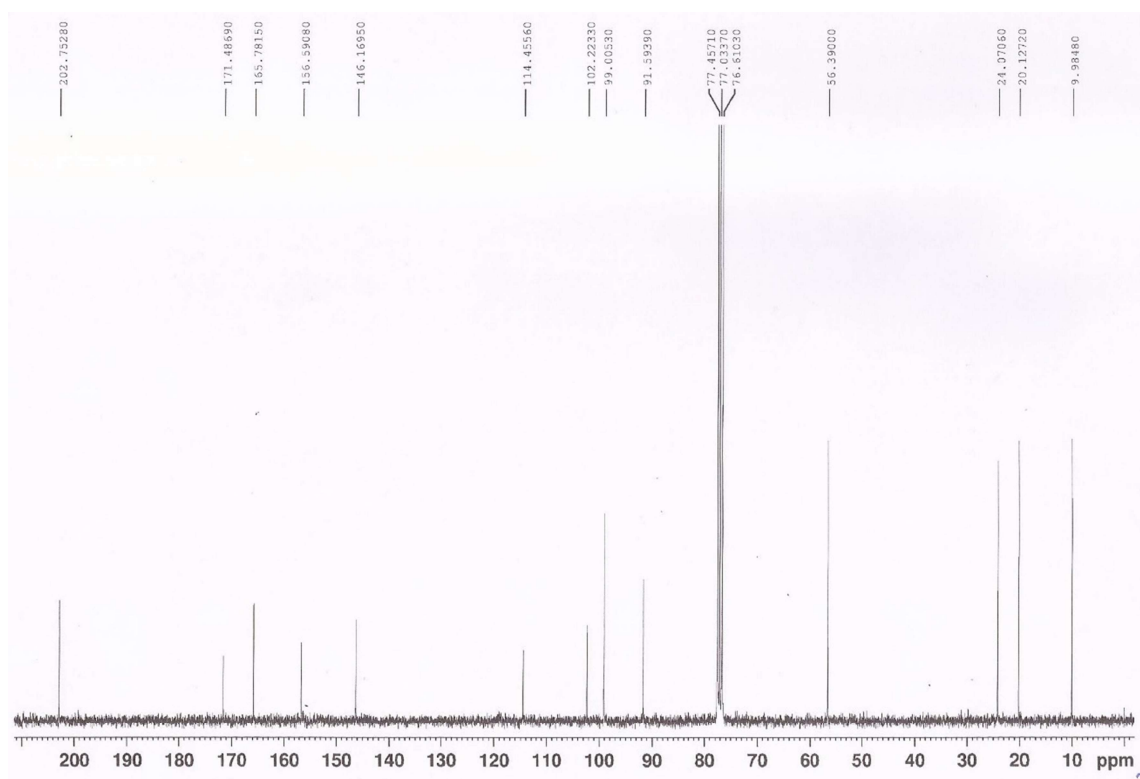


Figure S16. COSY spectrum of **3** (CDCl₃, 300 MHz).

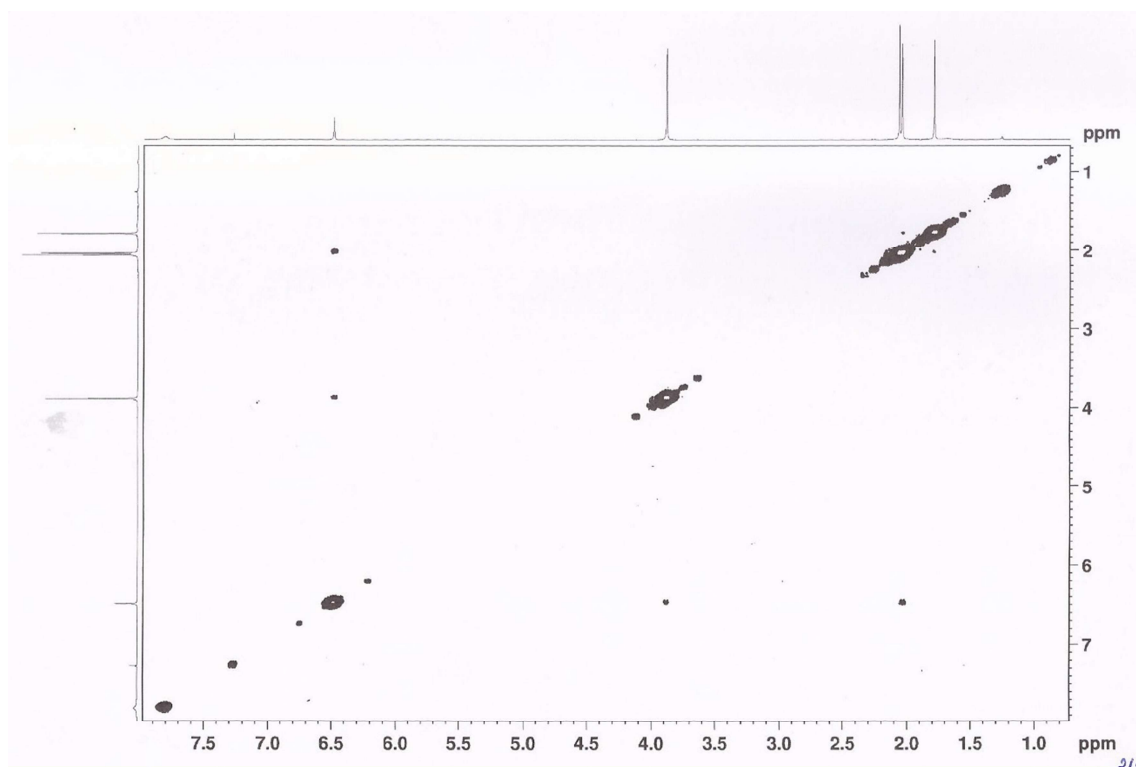


Figure S17. HSQC spectrum of **3** (CDCl₃, 300 MHz).

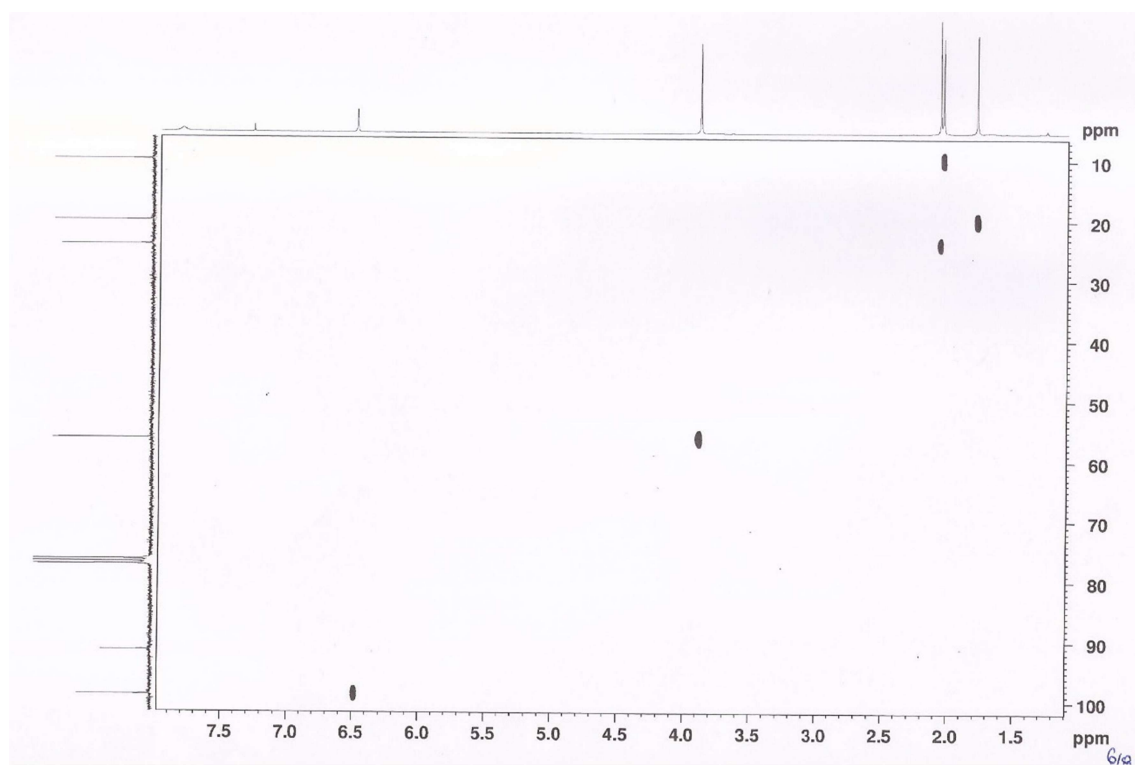


Figure S18. HMBC spectrum of **3** (CDCl₃, 300 MHz).

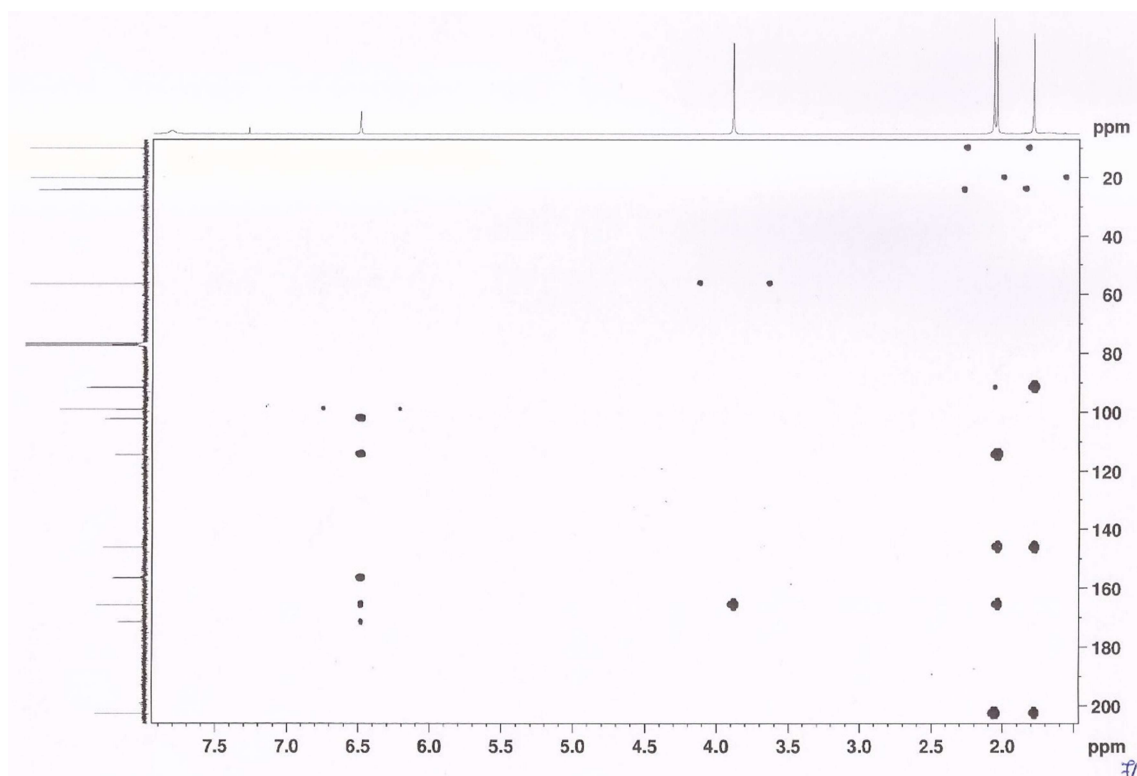


Figure S19. ¹H NMR spectrum of **4a** (CDCl₃, 300 MHz).

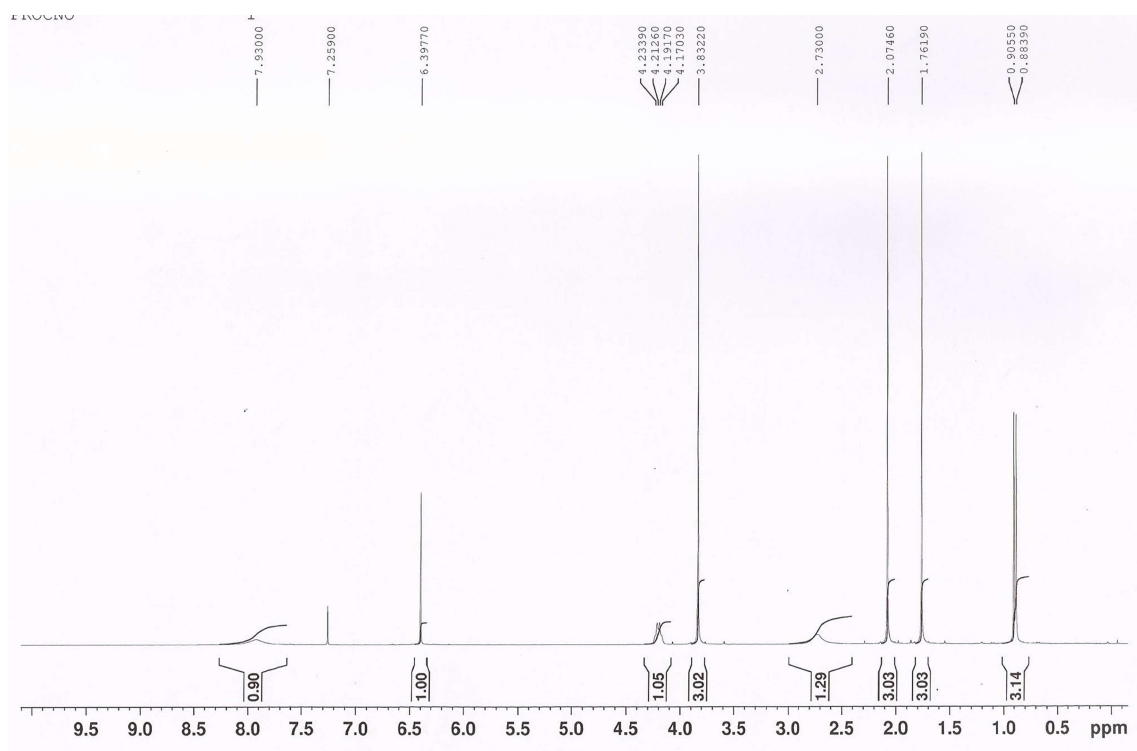


Figure S20. ^{13}C NMR spectrum of **4a** (CDCl_3 , 75 MHz).

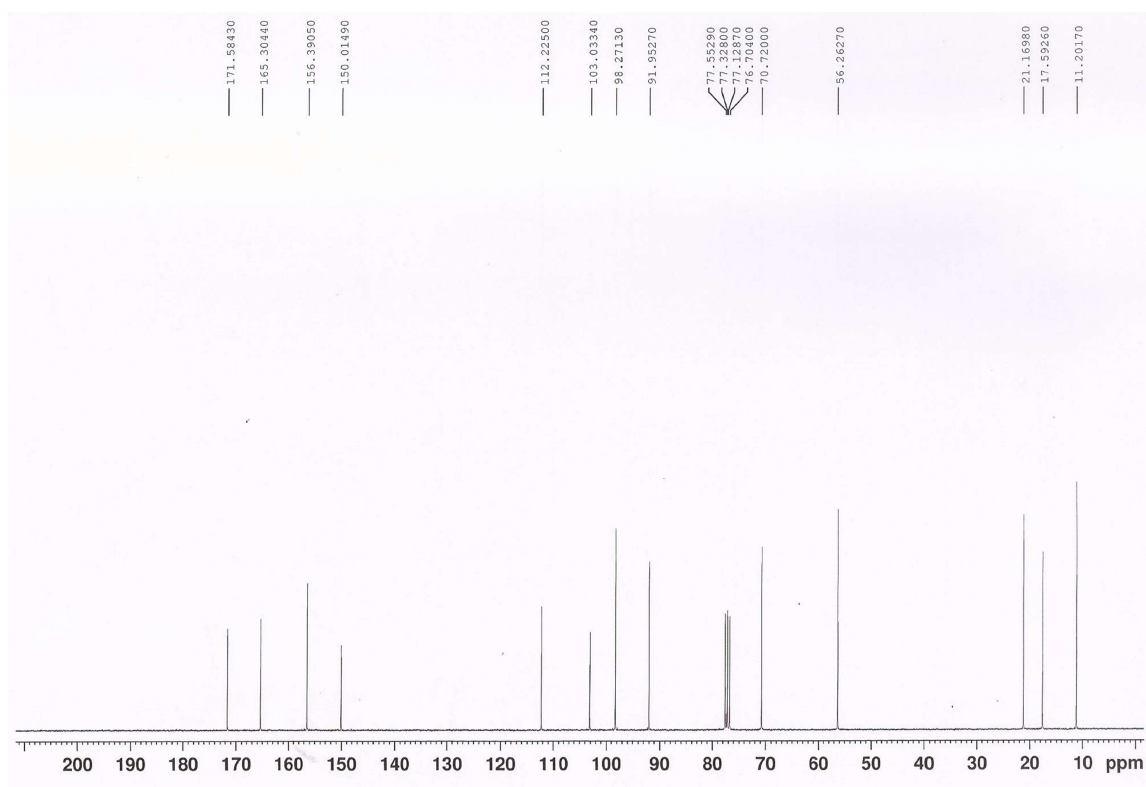


Figure S21. COSY spectrum of **4a** (CDCl_3 , 300 MHz).

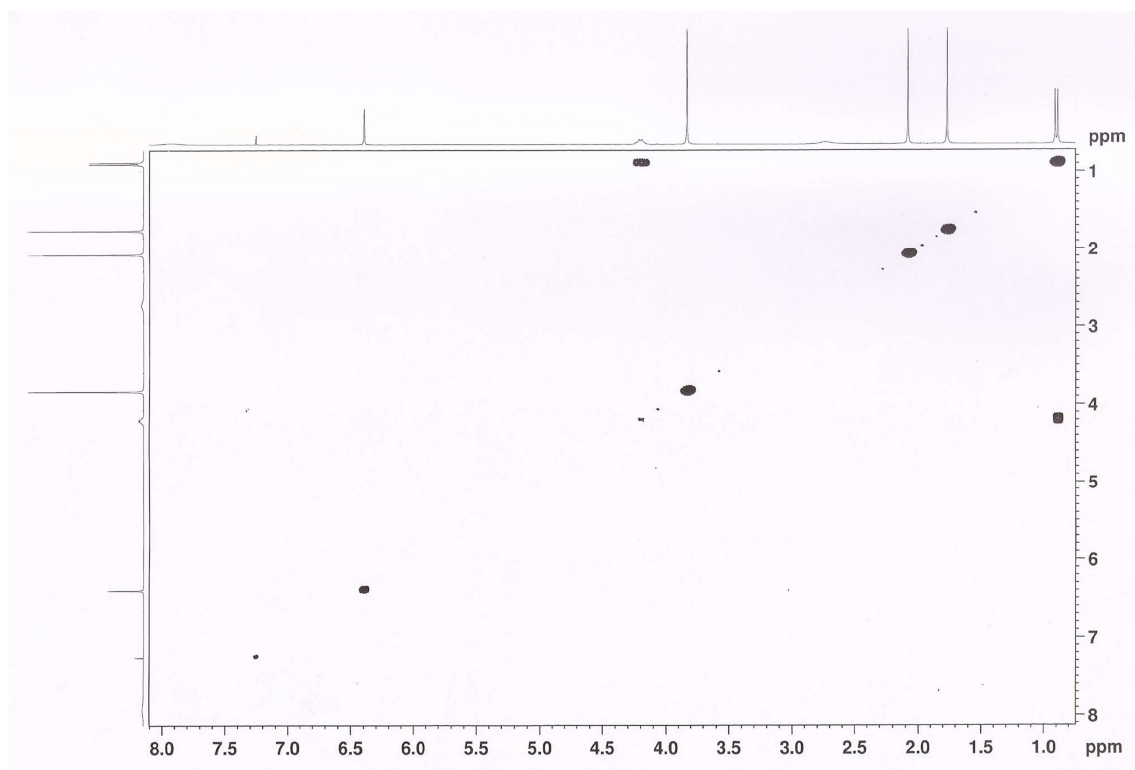


Figure S22. HSQC spectrum of **4a** (CDCl₃, 300 MHz).

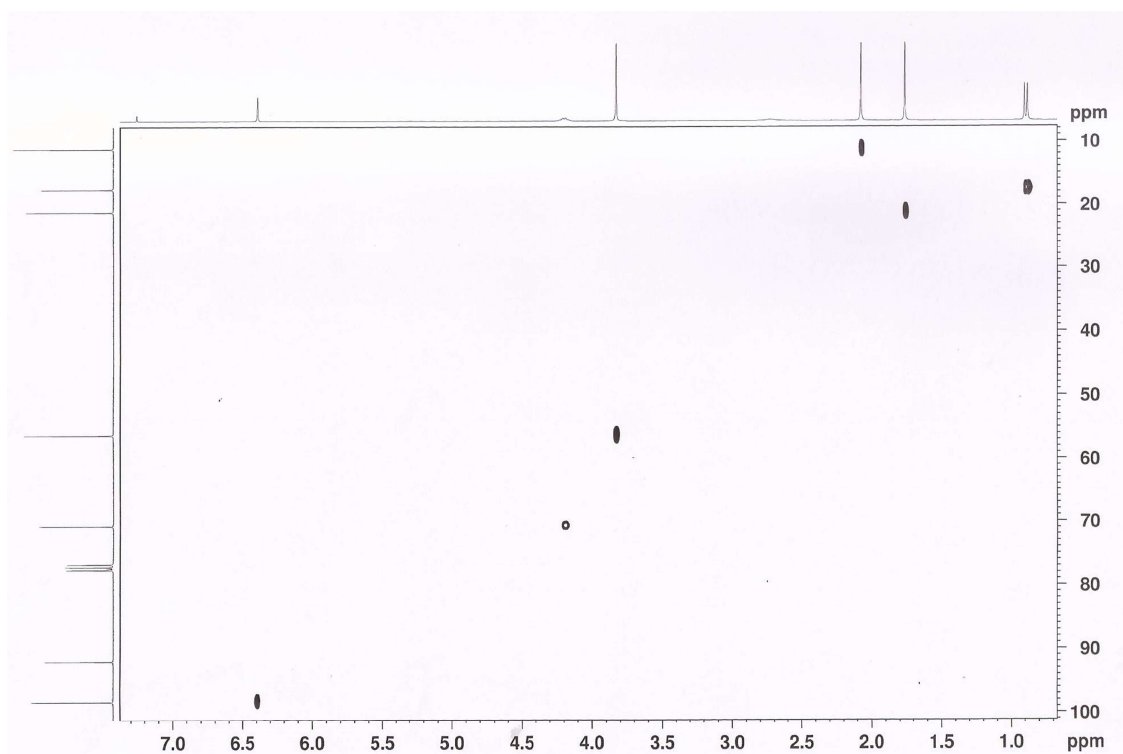


Figure S23. HMBC spectrum of **4a** (CDCl₃, 300 MHz).

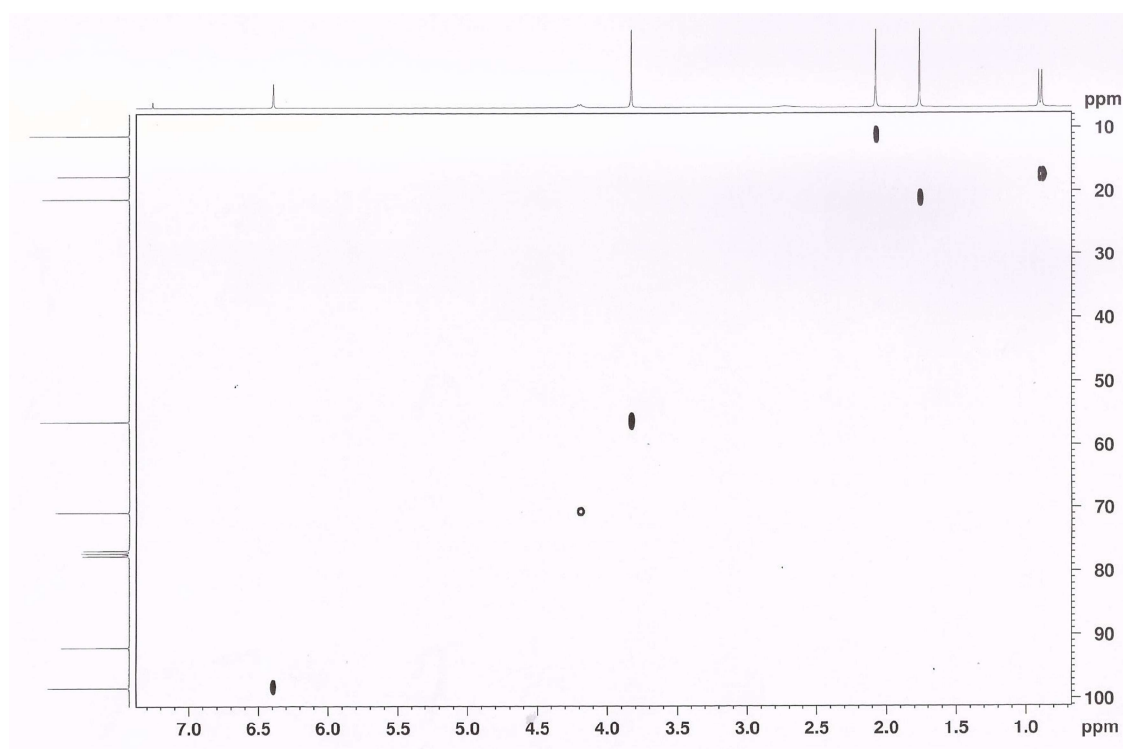


Figure S24. ^1H NMR spectrum of **4b** (CDCl_3 , 300 MHz).

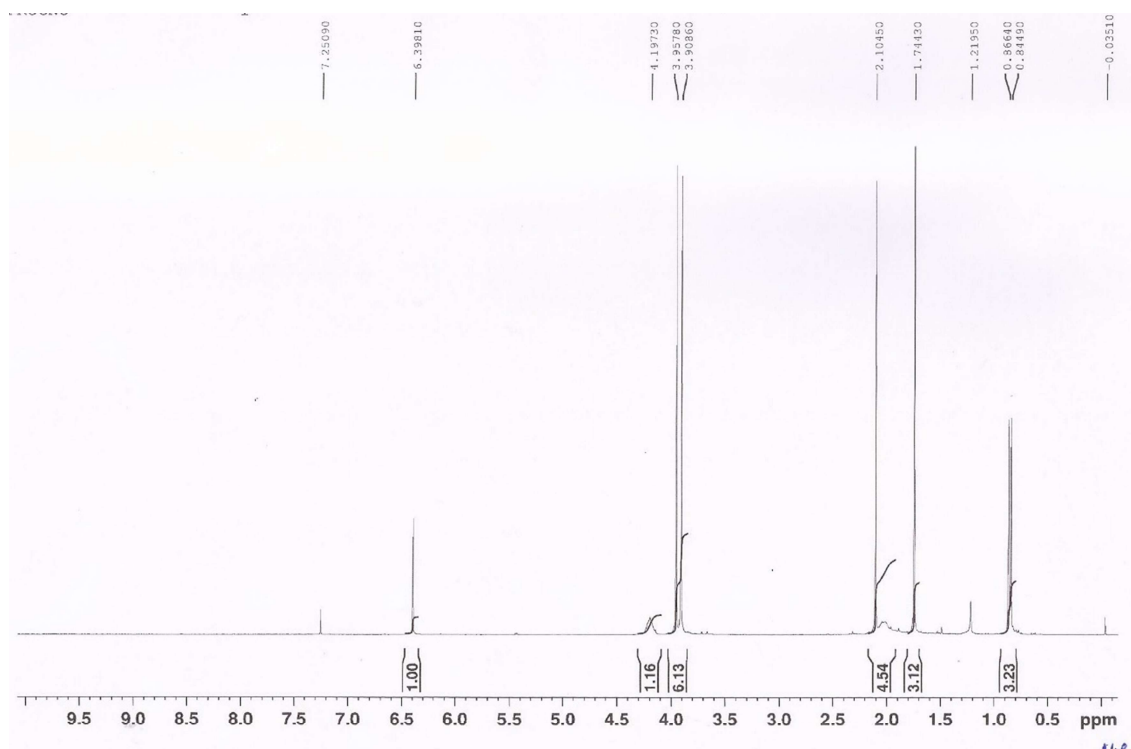


Figure S25. ^{13}C NMR spectrum of **4b** (CDCl_3 , 75 MHz).

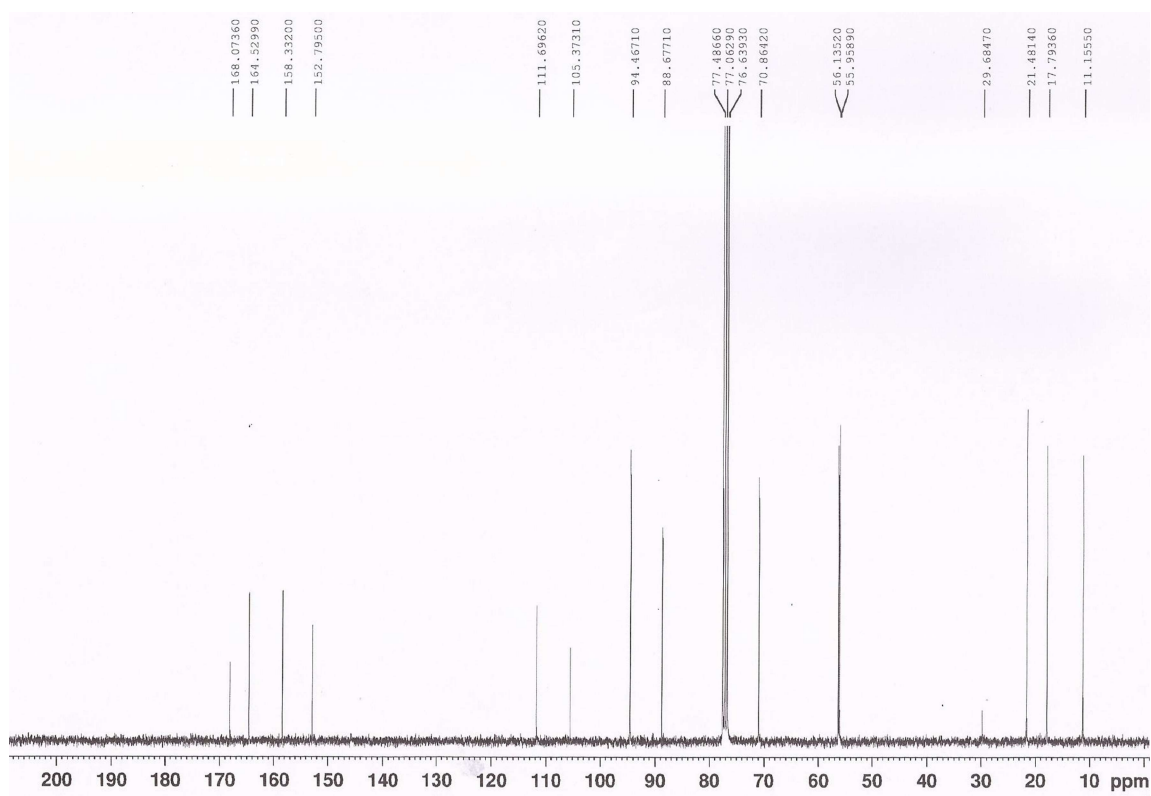


Figure S26. COSY spectrum of **4b** (CDCl₃, 300 MHz).

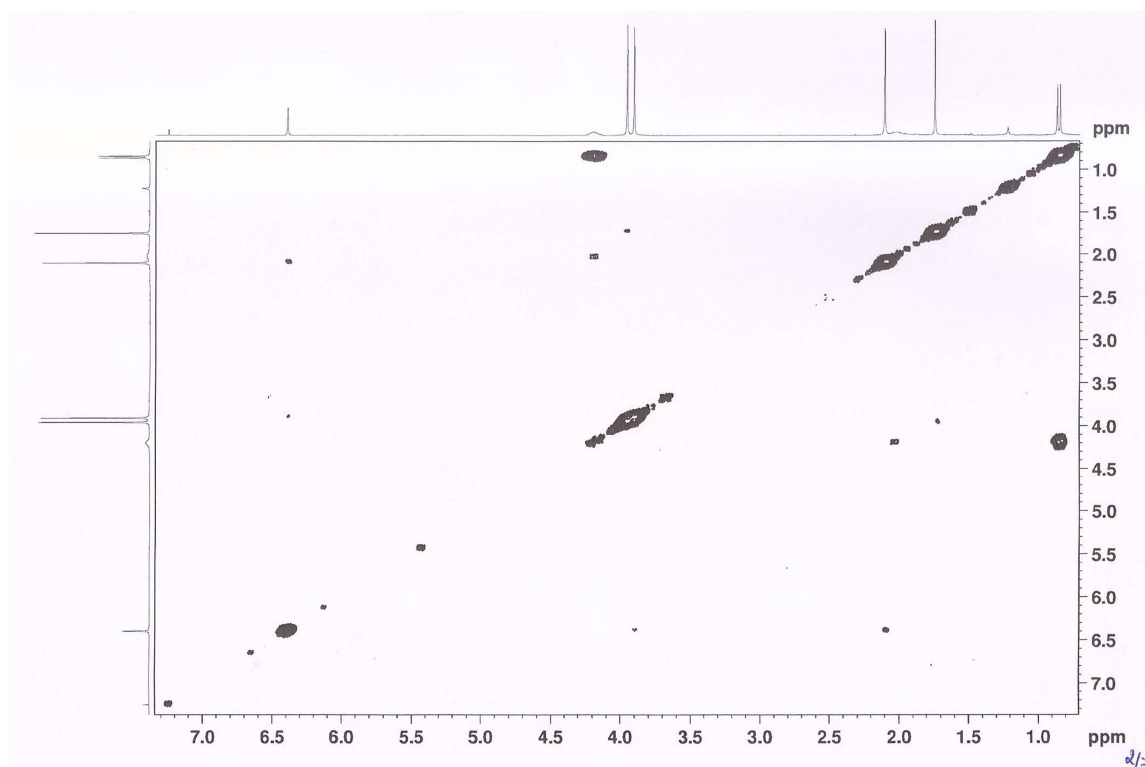


Figure S27. HSQC spectrum of **4b** (CDCl₃, 300 MHz).

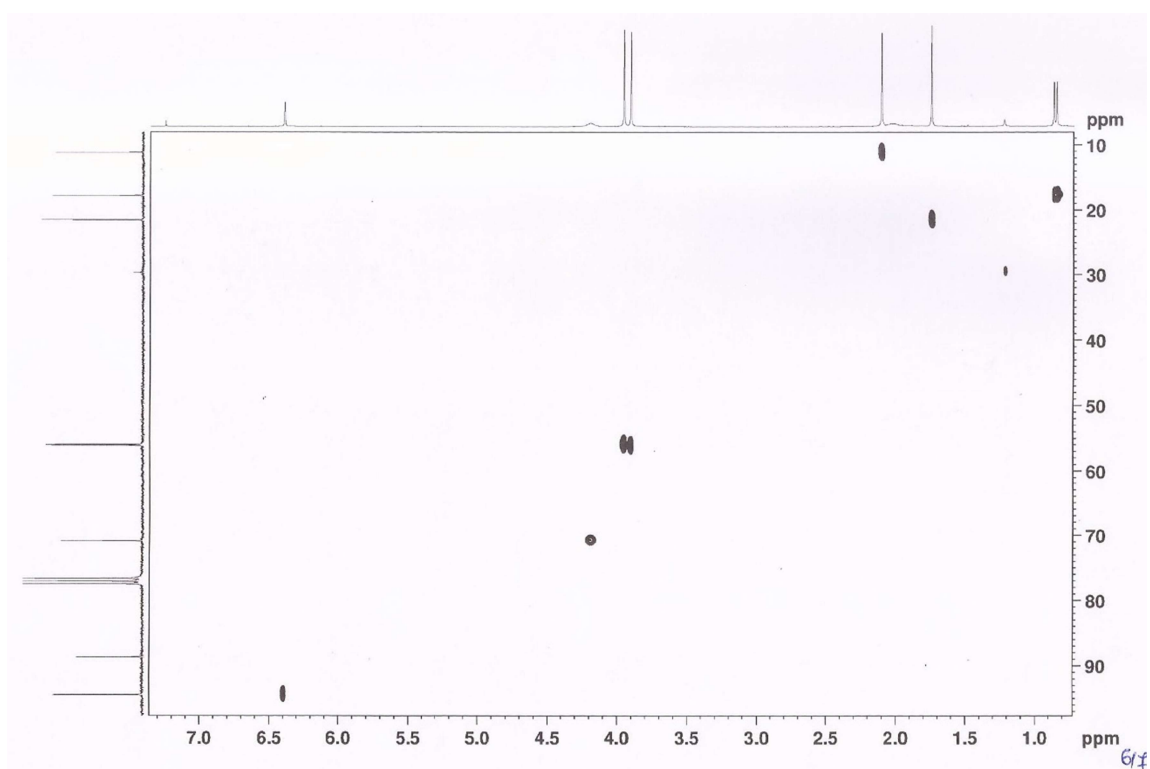


Figure S28. HMBC spectrum of **4b** (CDCl₃, 300 MHz).

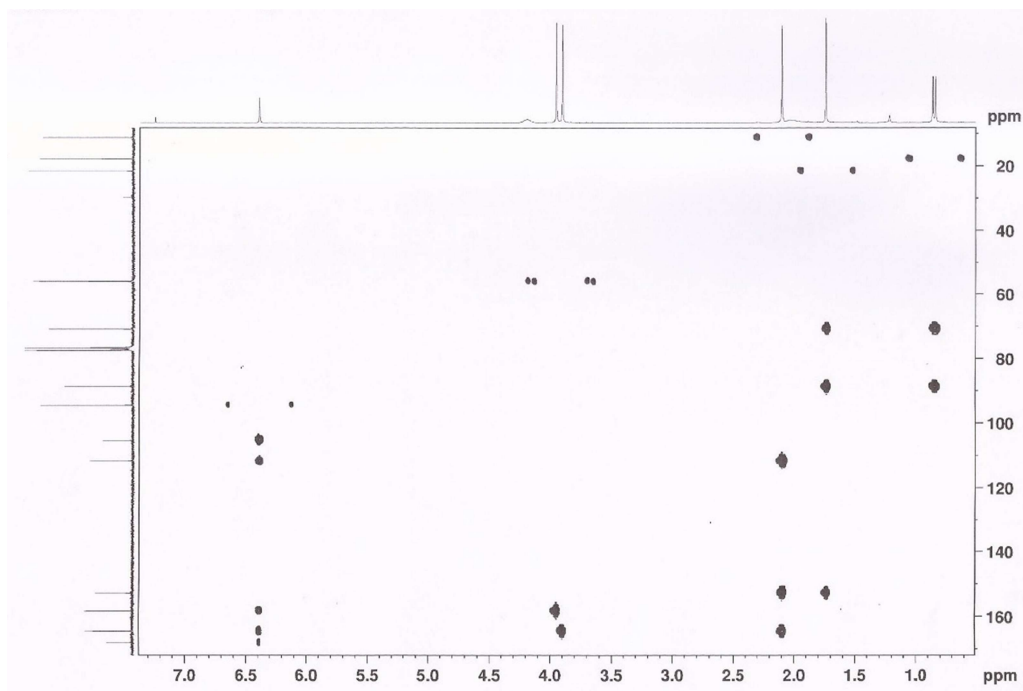


Figure S29. (+)-HRESIMS of **4b**

Elemental Composition Report [MH]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

17 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 14-14 H: 0-150 O: 0-30

Minimum:

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|------------|
| 267.1233 | 267.1232 | 0.1 | 0.4 | 5.5 | 845.2 | n/a | n/a | C14 H19 O5 |

Elemental Composition Report [MNa]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

36 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 14-14 H: 0-150 O: 0-30 Na: 0-1

Minimum:

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|---------------|
| 289.1053 | 289.1052 | 0.1 | 0.3 | 5.5 | 662.1 | n/a | n/a | C14 H18 O5 Na |

AKHSR 150-166/35-59 Prep 1
ANAKE-G2-234 191 (1.577)

1: TOF MS ES+
3.62e+007

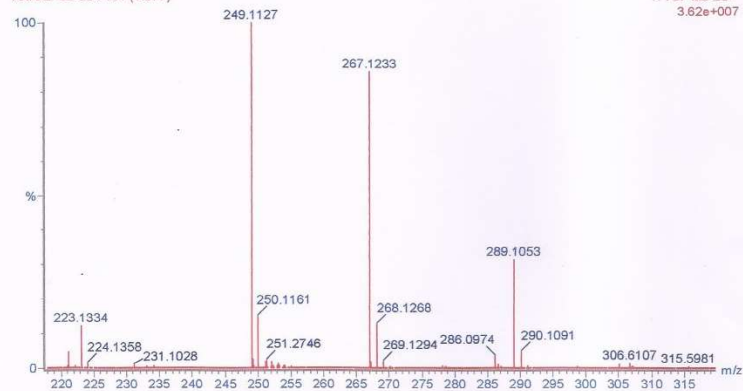


Figure S30. ^1H NMR spectrum of **5** (CDCl_3 , 300 MHz).

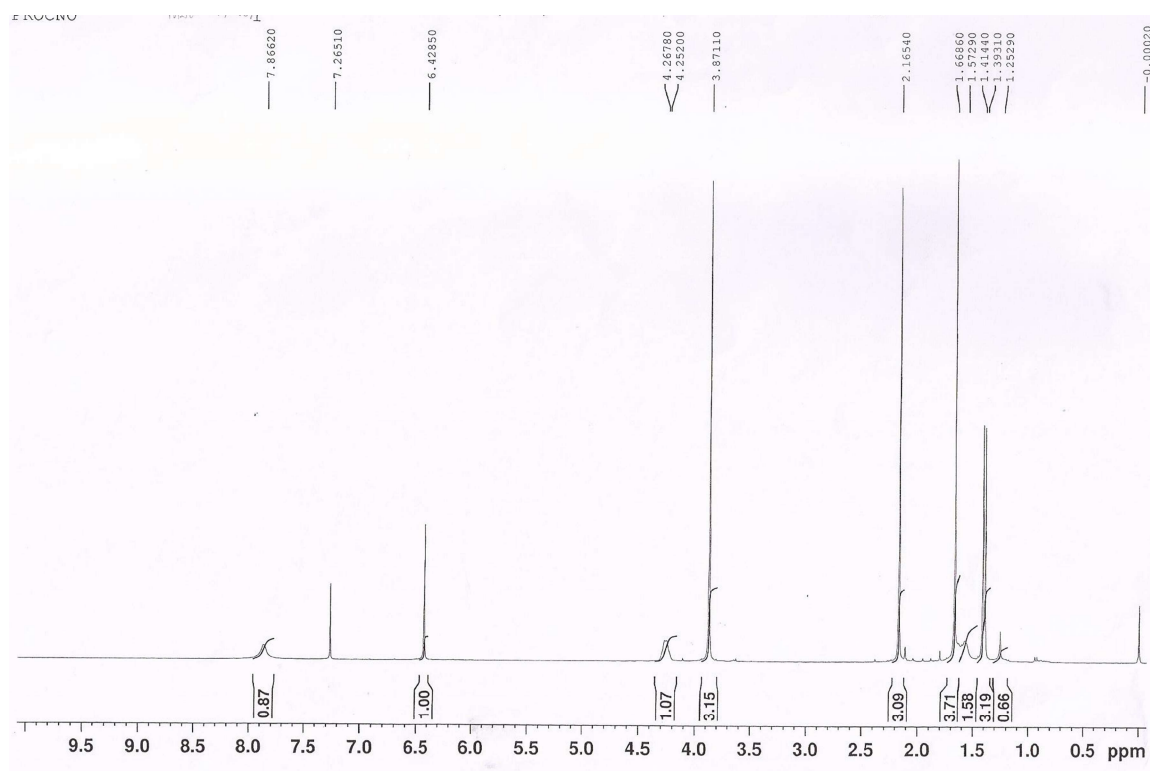


Figure S31. ^{13}C NMR spectrum of **5** (CDCl_3 , 75 MHz).

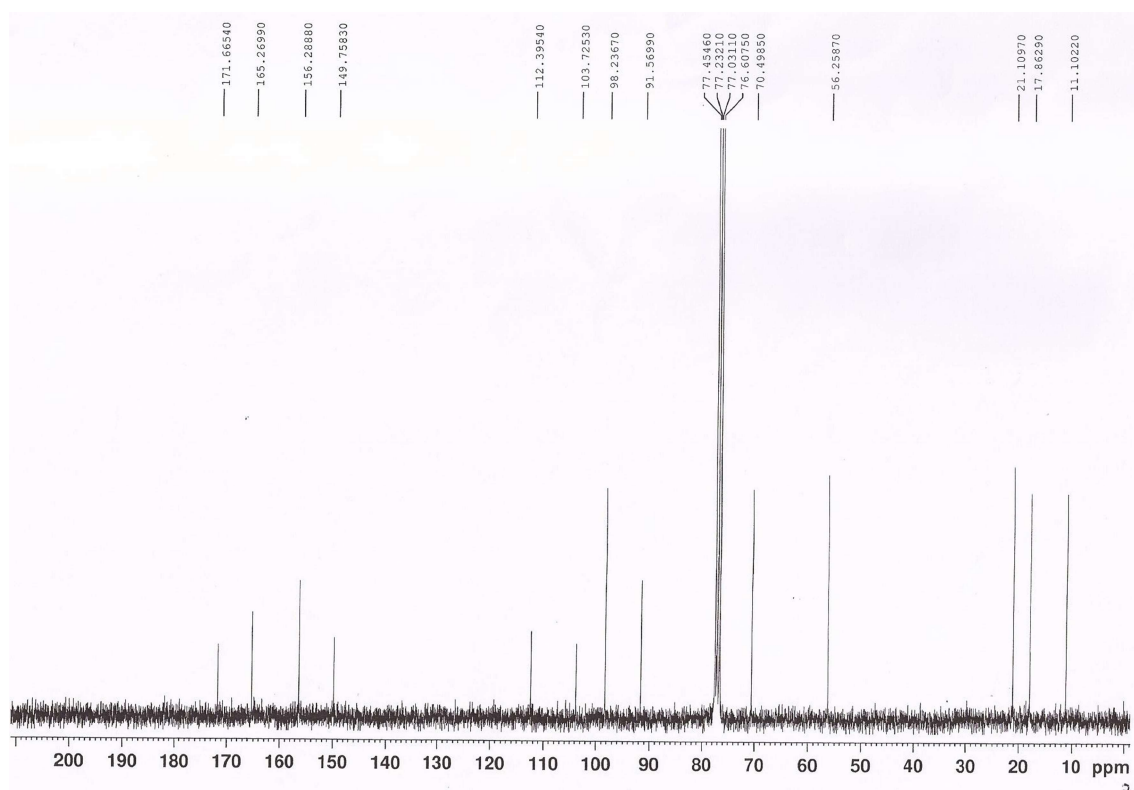


Figure S32. COSY spectrum of **5** (CDCl₃, 300 MHz).

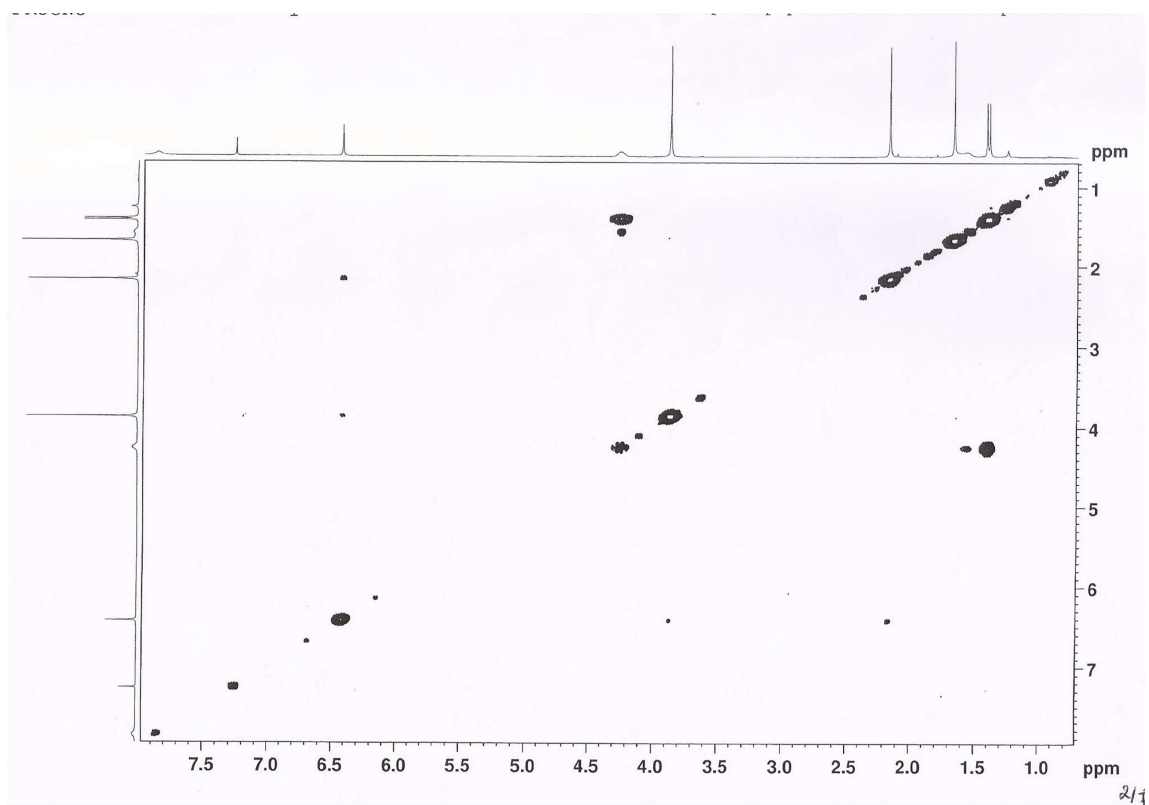


Figure S33. HSQC spectrum of **5** (CDCl₃, 300 MHz).

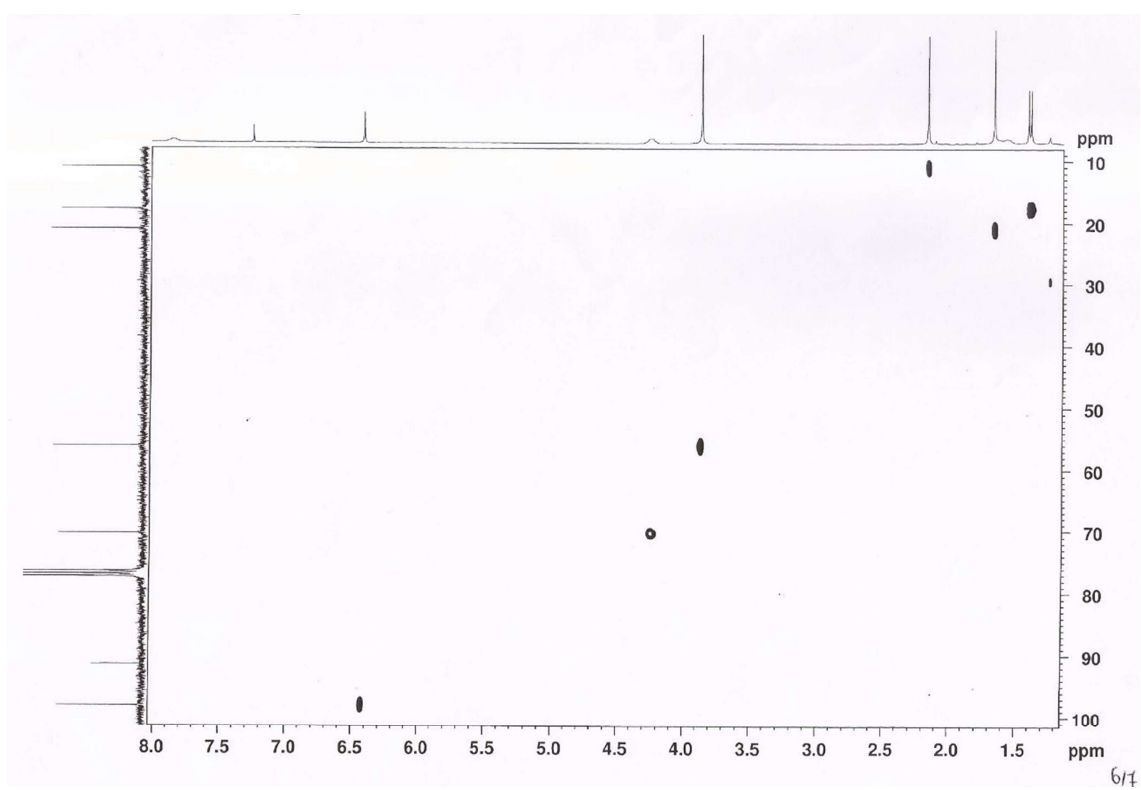


Figure S34. HMBC spectrum of **5** (CDCl₃, 300 MHz).

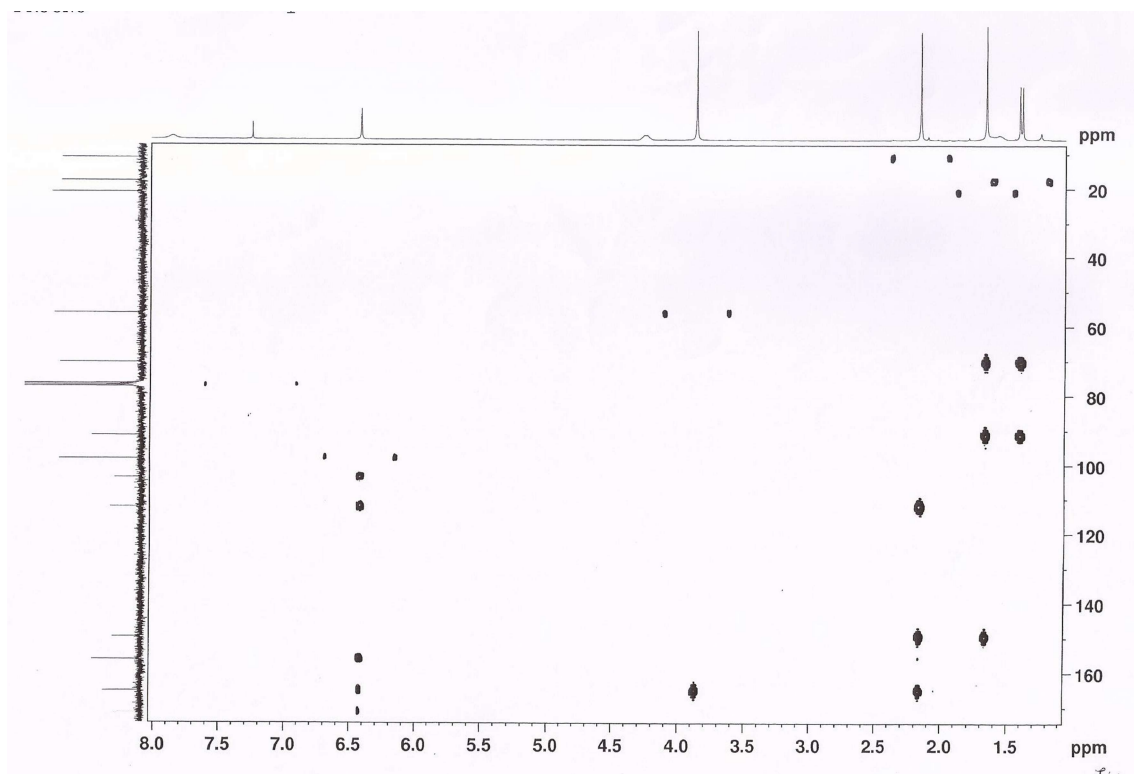


Figure S35. (+)-HRESIMS of **5**.

Elemental Composition Report [MH]⁺

Single Mass Analysis:

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

16 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 13-13 H: 0-150 O: 0-30

Minimum:

-1.5

Maximum:

5.0

5.0

100.0

Mass

Calc. Mass

mDa

PPM

DBE

i-FIT

Norm

Conf(%)

Formula

253.1077

253.1076

0.1

0.4

5.5

832.1

n/a

n/a

C₁₃ H₁₇ O₅

AKHSR 117-149

ANAKE-G2-233 193 (1.599)

1: TOF MS ES+
4.14e+007



Figure S36. ^1H NMR spectrum of **6** (DMSO-d_6 , 300 MHz).

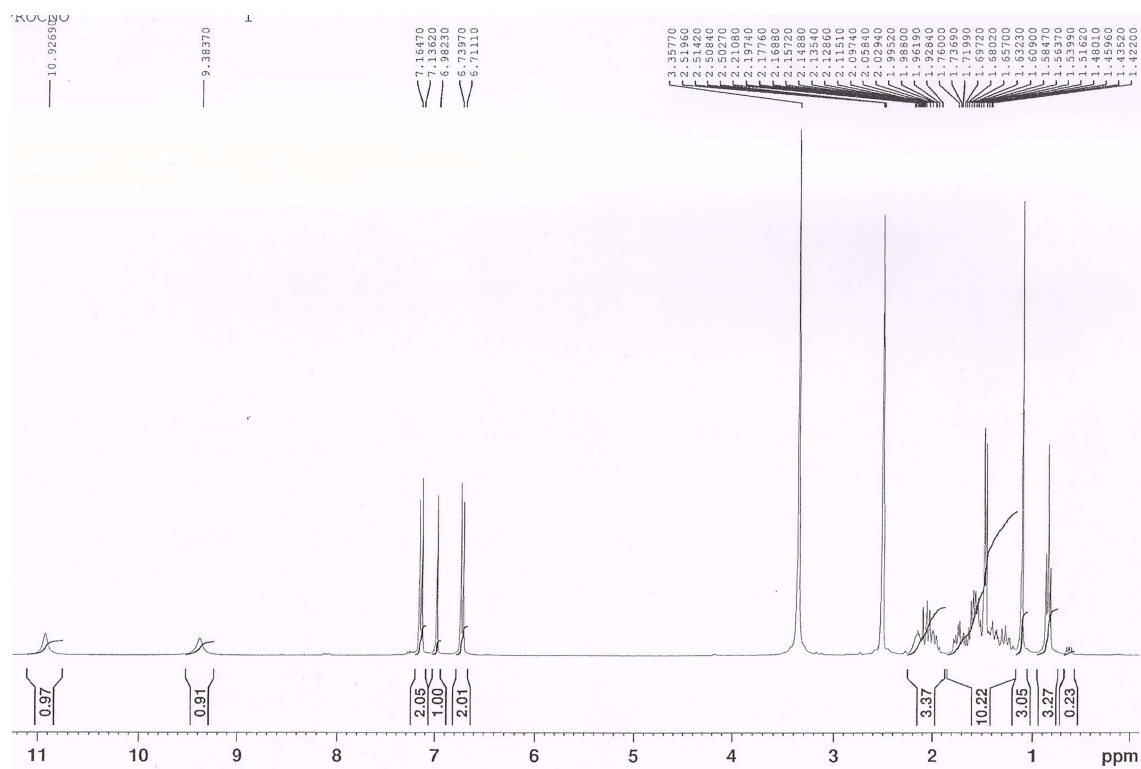


Figure S37. ^{13}C NMR spectrum of **6** (DMSO-d_6 , 75 MHz).

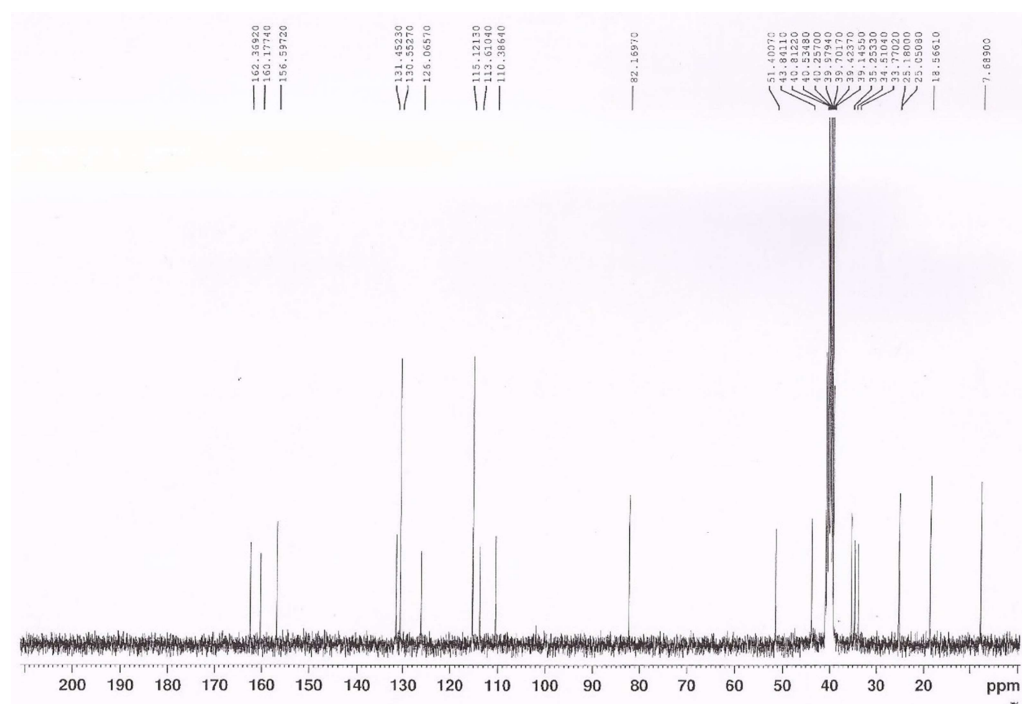


Figure S38. COSY spectrum of **6** (DMSO_{d6}, 300 MHz).

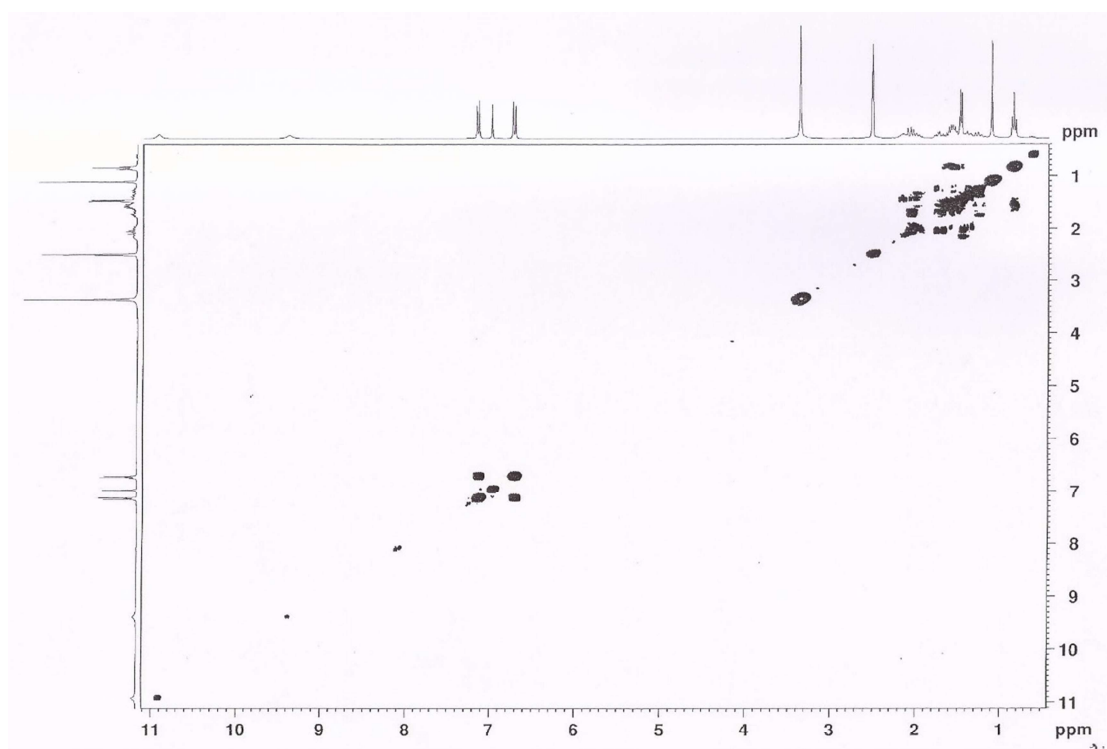


Figure S39. HSQC spectrum of **6** (DMSO_{d6}, 300 MHz).

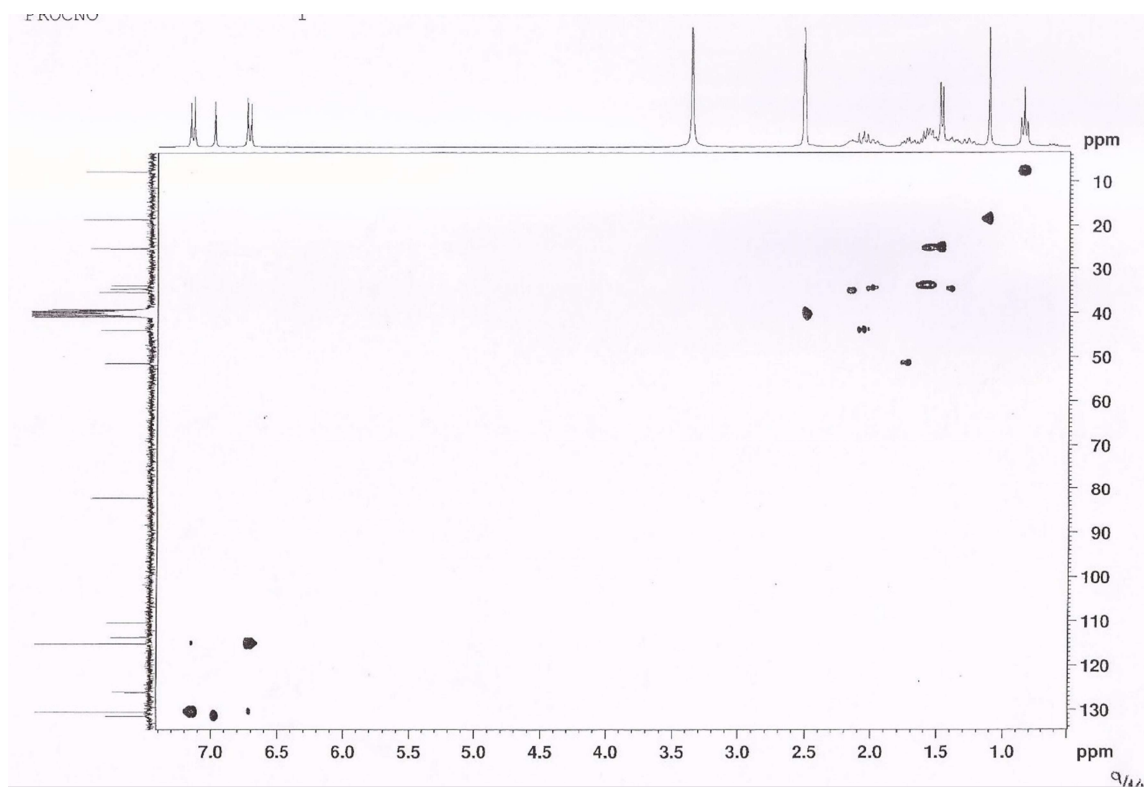


Figure S40. HMBC spectrum of **6** (DMSO_d₆, 300 MHz).

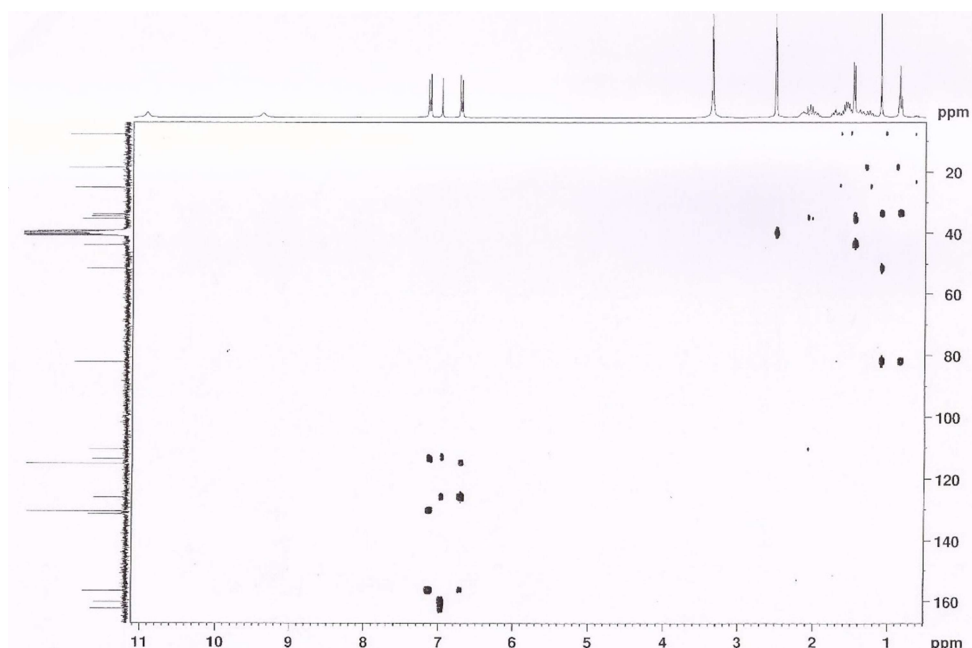


Figure S41. (+)-HRESIMS of **6**.

Match for C₂₁H₂₅NO₃ (No match for C₂₁H₂₆O₃)

Elemental Composition Report [MH]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

372 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 18-25 H: 0-150 N: 0-30 O: 0-30

Minimum: -1.5

Maximum: 5.0 5.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|--|
| 340.1913 | 340.1913 | 0.0 | 0.0 | 9.5 | 991.8 | n/a | n/a | C ₂₁ H ₂₆ N O ₃ |

Elemental Composition Report [MNa]⁺

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

592 formula(e) evaluated with 1 results within limits (up to 100 closest results for each mass)

Elements Used:

C: 21-21 H: 0-150 N: 0-30 O: 0-30 Na: 0-1

Minimum: -1.5

Maximum: 5.0 5.0 100.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|----------|------------|-----|-----|-----|-------|------|---------|---|
| 362.1734 | 362.1732 | 0.2 | 0.6 | 9.5 | 901.3 | n/a | n/a | C ₂₁ H ₂₅ N O ₃ Na |

AKHSR 326-349/33-25
ANAKE-G2-235 250 (2.108)

1: TOF MS ES+
3.80e+007

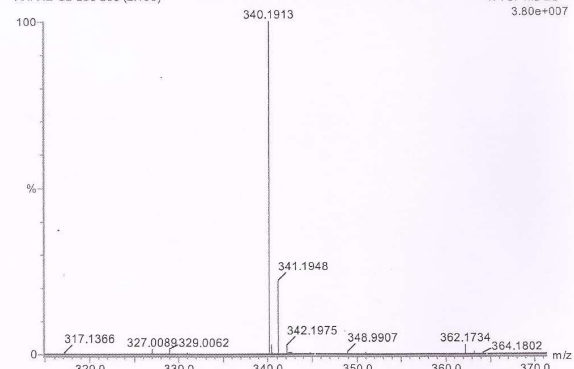


Figure S42. ^1H NMR spectrum of **7** (CDCl_3 , 300 MHz).

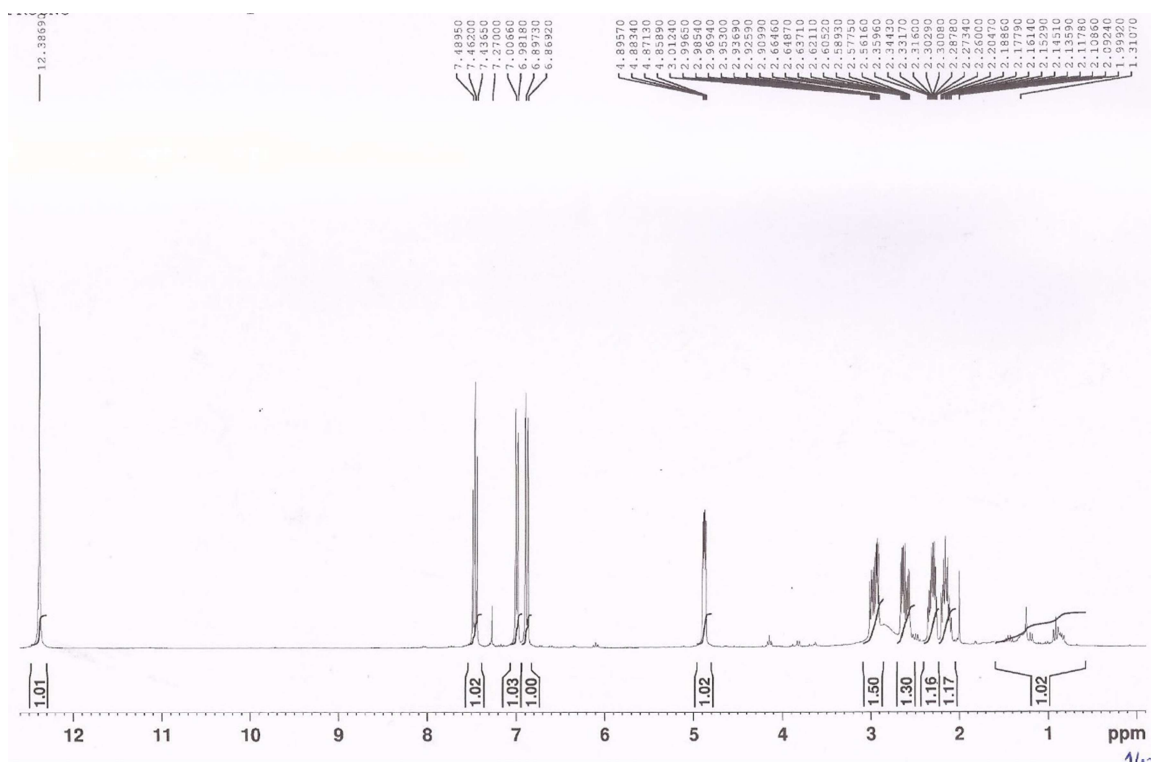


Figure S43. ^{13}C NMR spectrum of **7** (CDCl_3 , 75 MHz).

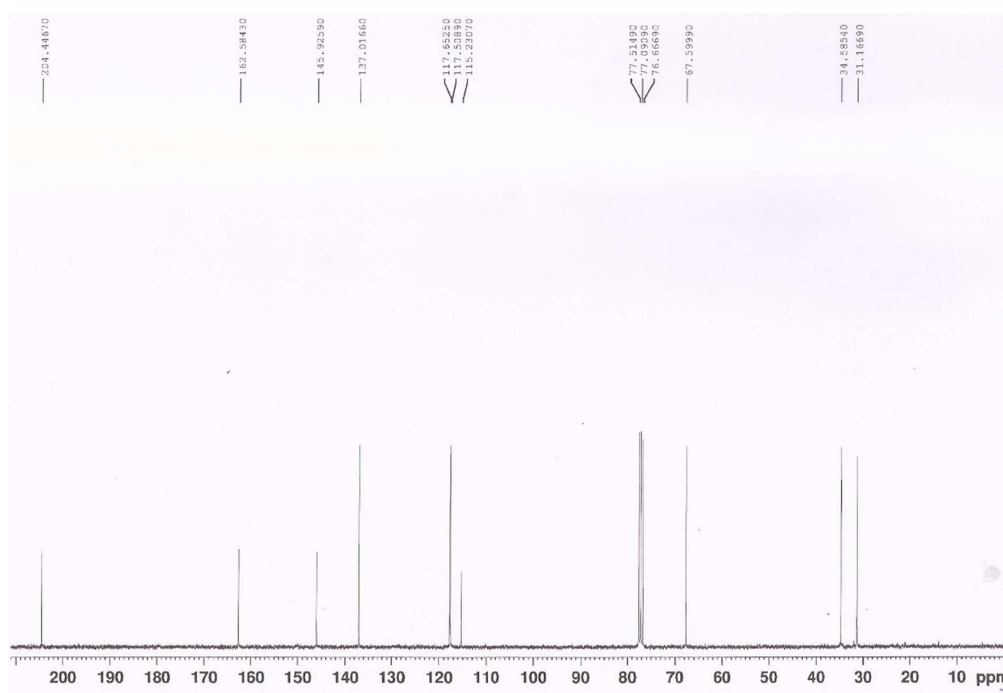


Figure S44. COSY spectrum of **7** (CDCl₃, 300 MHz).

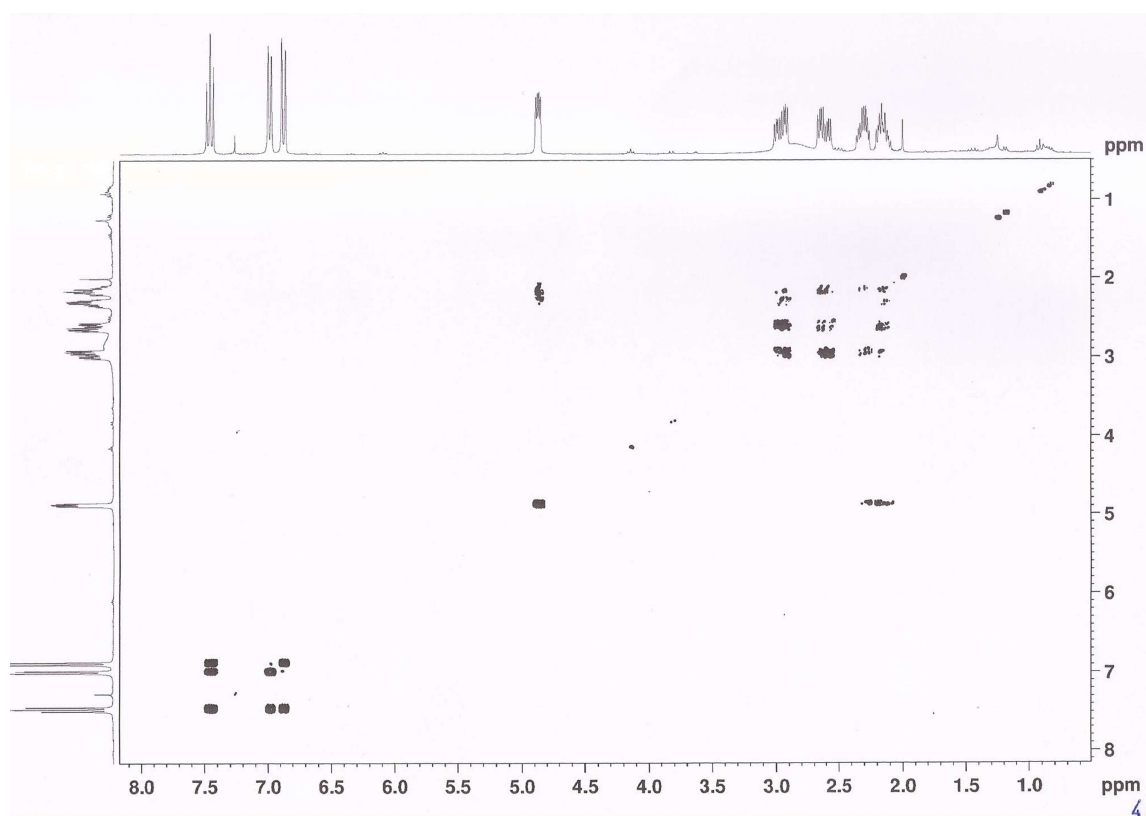


Figure S45. HSQC spectrum of **7** (CDCl₃, 300 MHz).

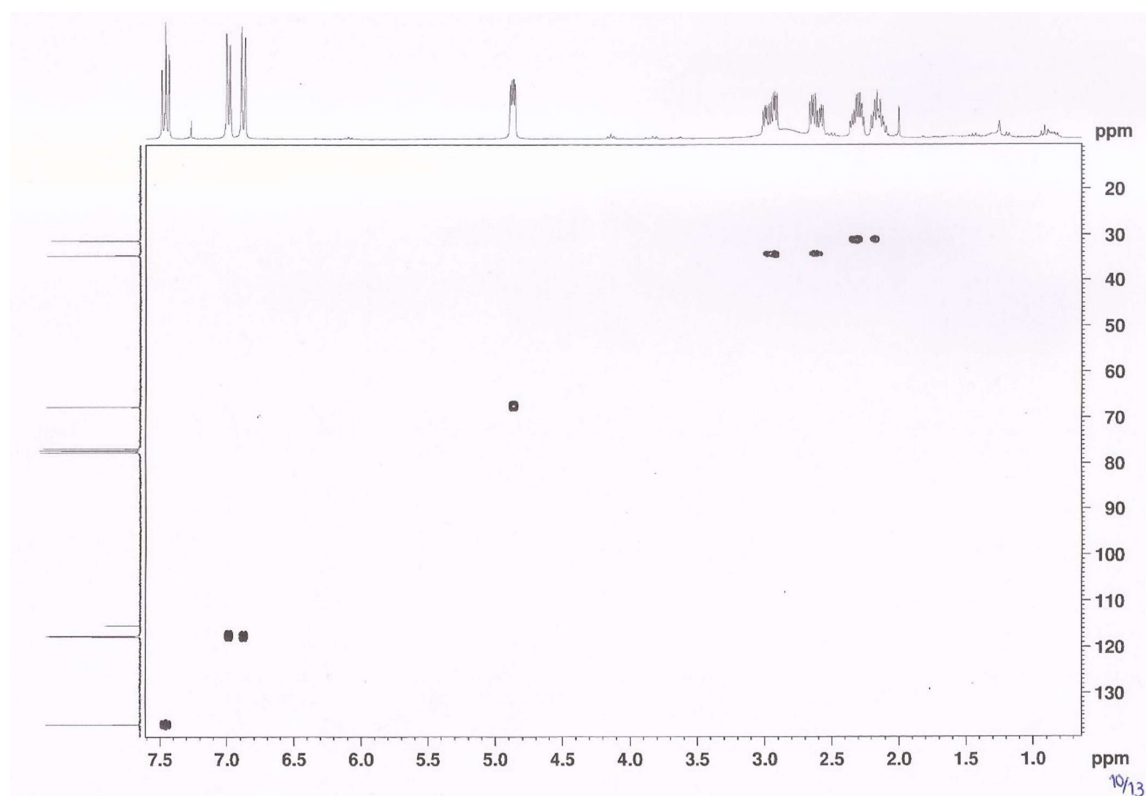


Figure S46. HMBC spectrum of **7** (CDCl₃, 300 MHz).

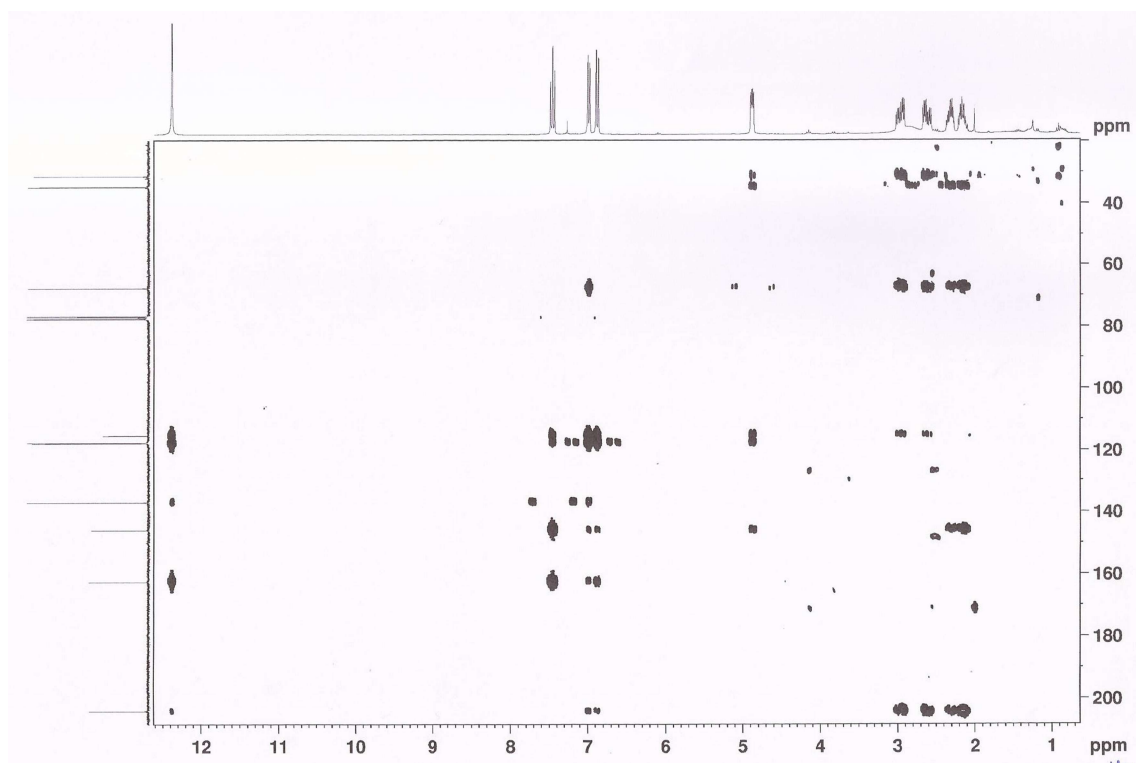


Table S1. ¹H and ¹³C NMR data (CDCl₃, 300 and 75 MHz), COSY and HMBC for **3**.

| Position | δ _C , type | δ _H , (J in Hz) | COSY | HMBC |
|----------|-----------------------|----------------------------|---------------------------|-------------------------|
| 1 | 171.5, CO | | | |
| 3 | 91.6, C | | | |
| 3a | 146.2, C | | | |
| 4 | 114.5 C | | | |
| 5 | 165.8, C | | | |
| 6 | 99.0, CH | 6.49, s | H ₃ -11, OMe-5 | C-1, 4, 5, 7, 7a |
| 7 | 156.6, C | | | |
| 7a | 102.2, C | | | |
| 8 | 202.8, CO | | | |
| 9 | 24.1 CH ₃ | 2.06, s | | C-8 |
| 10 | 20.1, CH ₃ | 1.78, s | | C-3, 3 ^a , 8 |
| 11 | 10.0, CH ₃ | 2.04, s | H-6 | C-3a, 4, 5 |
| OMe-5 | 56.4, CH ₃ | 3.89, s | H-6 | C-5 |
| OH-7 | 7.81, brs | | | |

Table S2. ^1H and ^{13}C NMR (300 and 75 MHz, CDCl_3), COSY and HMBC of **4a**.

| Position | δ_{C} , type | δ_{H} , (J in Hz) | COSY | HMBC |
|----------|----------------------------|---------------------------------|-------------------|----------------|
| 1 | 171.6, CO | | | |
| 3 | 92.0, C | | | |
| 3a | 150.0, C | | | |
| 4 | 112.2, C | | | |
| 5 | 165.3, C | | | |
| 6 | 98.3, CH | 6.40, s | | 1, 4, 5, 7, 7a |
| 7 | 156.4, C | | | |
| 7a | 103.0, C | | | |
| 8 | 70.7, CH | 4.20, m | H ₃ -9 | |
| 9 | 17.6, CH ₃ | 0.89, d (6.5) | H-8 | C-3, 8 |
| 10 | 21.2, CH ₃ | 1.76, s | | C-3, 3a, 8 |
| 11 | 11.2, CH ₃ | 2.07, s | | C-3a, 4, 5 |
| OMe-5 | 56.3 OCH ₃ , | 3.83, s | | C-5 |
| OH-7 | - | 7.93, br | | |
| OH-8 | | 2.73, br | | |

Table S3. Comparison of ^1H and ^{13}C NMR data of **4a** (300 and 75 MHz, CDCl_3) with those of (*R*)-7-hydroxy-3-((*R*)-1-hydroxyethyl)-5-methoxy-3,4-dimethylisobenzofuran-1(3*H*)-one (400 and 100 MHz, CDCl_3) and (*R*)-7-hydroxy-3-((*S*)-1-hydroxyethyl)-5-methoxy-3,4-dimethylisobenzofuran-1(3*H*)-one (500 and 125 MHz, CDCl_3)

| | 4a | | (<i>R</i>)-7-hydroxy-3-((<i>R</i>)-1-hydroxyethyl)-5-methoxy-3,4-dimethylisobenzofuran-1(3 <i>H</i>)-one | | (<i>R</i>)-7-hydroxy-3-((<i>S</i>)-1-hydroxyethyl)-5-methoxy-3,4-dimethylisobenzofuran-1(3 <i>H</i>)-one | |
|----------|----------------------------|---------------------------------|---|---------------------------------|---|---------------------------------|
| Position | δ_{C} , type | δ_{H} , (J in Hz) | δ_{C} , type | δ_{H} , (J in Hz) | δ_{C} , type | δ_{H} , (J in Hz) |
| 1 | 171.6, CO | | 171.7, CO | | 171.5, CO | |
| 3 | 92.0, C | | 92.1, C | | 91.3, C | |
| 3a | 150.0, C | | 150.1, C | | 149.9 | |
| 4 | 112.2, C | | 112.5, C | | 112.2, C | |
| 5 | 165.3, C | | 165.6, C | | 165.4, C | |
| 6 | 98.3, CH | 6.40, s | 98.5, CH | 6.41, s | 98.2, CH | 6.43, s |
| 7 | 156.4, C | | 156.8, C | | 156.5, C | |
| 7a | 103.0, C | | 103.3, C | | 103.0, C | |
| 8 | 70.7, CH | 4.20, m | 71.2, C | 4.19, q (6.5) | 70.9, CH | 4.22, m |
| 9 | 17.6, CH ₃ | 0.89, d (6.5) | 18.1, CH ₃ | 0.91 d (6.5) | 17.5, CH ₃ | 0.93, d (6.8) |
| 10 | 21.2, CH ₃ | 1.76, s | 21.5, CH ₃ | 1.78, s | 21.3, CH ₃ | 1.81, s |
| 11 | 11.2, CH ₃ | 2.07, s | 11.4, CH ₃ | 2.09, s | 11.2, CH ₃ | 2.11, s |
| OMe-5 | 56.3, CH ₃ | 3.83, s | 56.5, CH ₃ | 3.85, s | 56.3, CH ₃ | 3.88, s |

| | | | | | | |
|------|---|----------|---|-------|---|----------------|
| OH-7 | - | 7.93, br | - | 7.84, | - | 7.88 |
| OH-8 | | 2.73, br | | | | 1.97, d (10.3) |

Table S4. ^1H and ^{13}C NMR data (DMSO- d_6 , 300 and 75 MHz), COSY and HMBC for 7.

| Position | δ_{C} , type | δ_{H} , (J in Hz) | COSY | HMBC |
|----------|----------------------------|--|--------|-------------------------|
| 1 | 204.4, CO | | | |
| 2 | 34.6, CH ₂ | 2.96, ddd (17.9, 8.1, 4.8) 2.61, ddd (17.9, 8.3, 4.8) | H-3 | C-1, 3, 4, 8a |
| 3 | 31.2, CH ₂ | 2.16, m 2.32, m | H-2, 4 | C-1, 2, 4, 4a |
| 4 | 67.6, CH | 4.88, dd (7.3, 3.7) | H-3 | C-2, 3, 4a, 5, 8a |
| 4a | 145.9, C | | | |
| 5 | 117.5, CH | 6.99, d (7.4) | H-6 | C-1, 4, 4a, 6, 7, 8, 8a |
| 6 | 137.0, CH | 7.46, dd (8.3, 7.4) | H-5, 7 | C-4a, 5, 7, 8, 8a |
| 7 | 117.7, CH | 6.88, d (8.3) | H6- | C-4, 4a, 5, 8, 8a |
| 8 | 162.6, C | | | |
| 8a | 115.2, C | | | |
| OH-8 | - | 12.39, s | | C-6, 7, 8, 8a |