# *Supplementary Materials*

# Antimicrobial Meroterpenoids and Erythritol Derivatives Isolated from the Marine Algal-Derived Endophytic Fungus *Penicillium chrysogenum* XNM-12

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|---|---|---|
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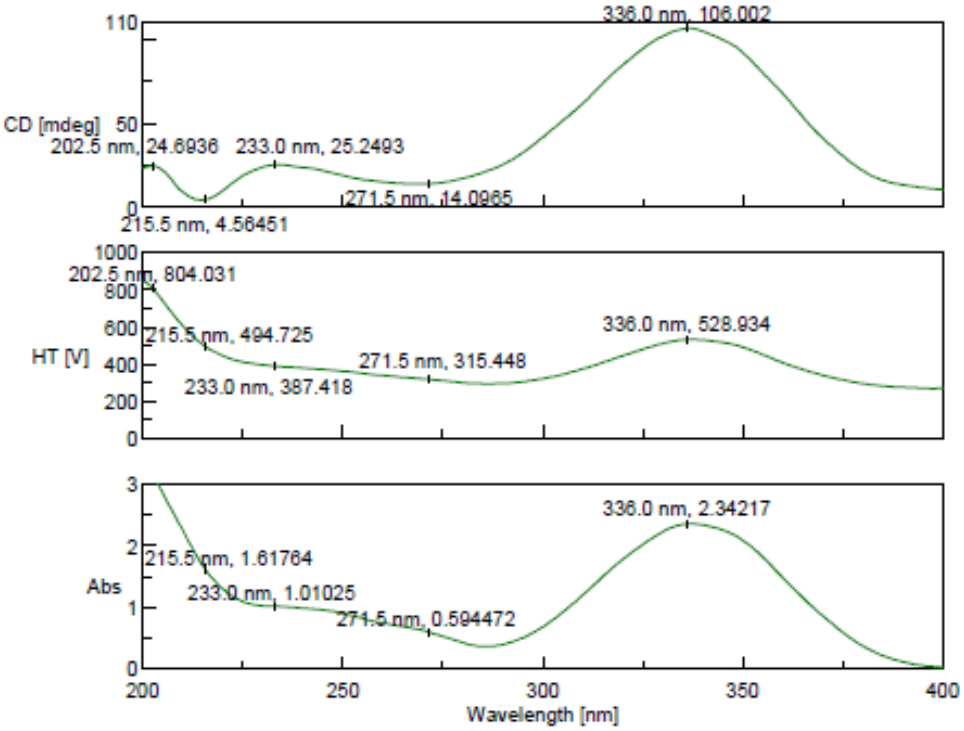
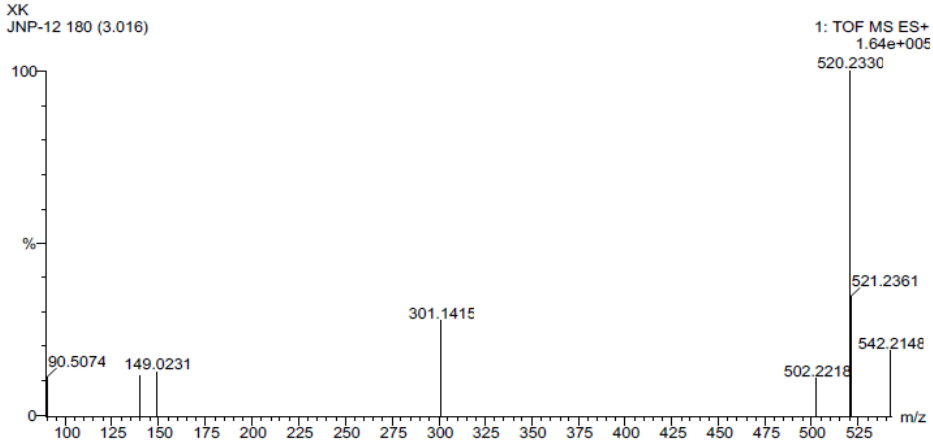



**Figure S1**. The ECD spectrum of **1** in MeOH

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

**Single Mass Analysis**
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
697 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-100 N: 0-10 O: 0-10
XK
JNP-12 180 (3.016)




Minimum: -1.5
Maximum: 1.0 1.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 520.2330 | 520.2335 | -0.5 | -1.0 | 14.5 | 36.3 | n/a | n/a | C30 H34 N O7 |

**Figure S2**. The HR-ESI-MS data of **1**

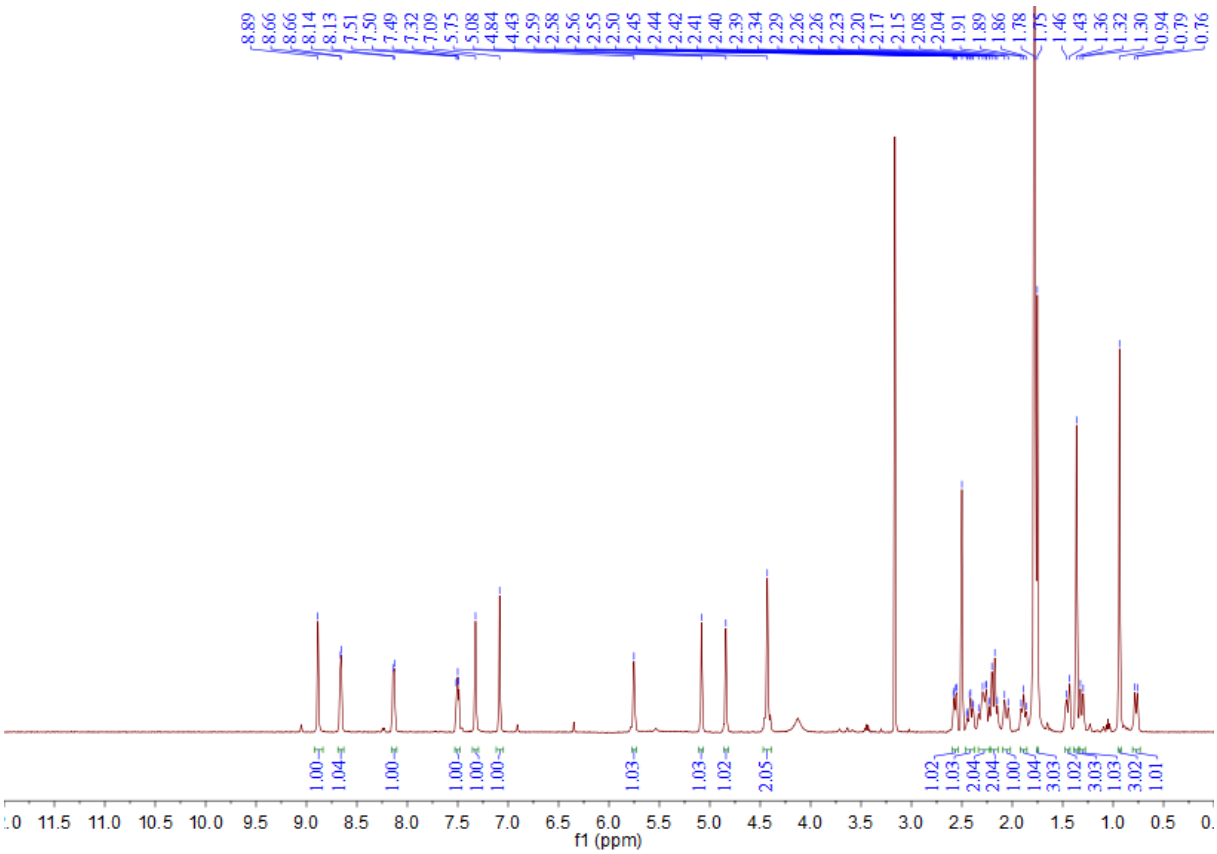



**Figure S3**. The $^{1}$H NMR spectrum (500 MHz) of **1** in DMSO-$d_6$

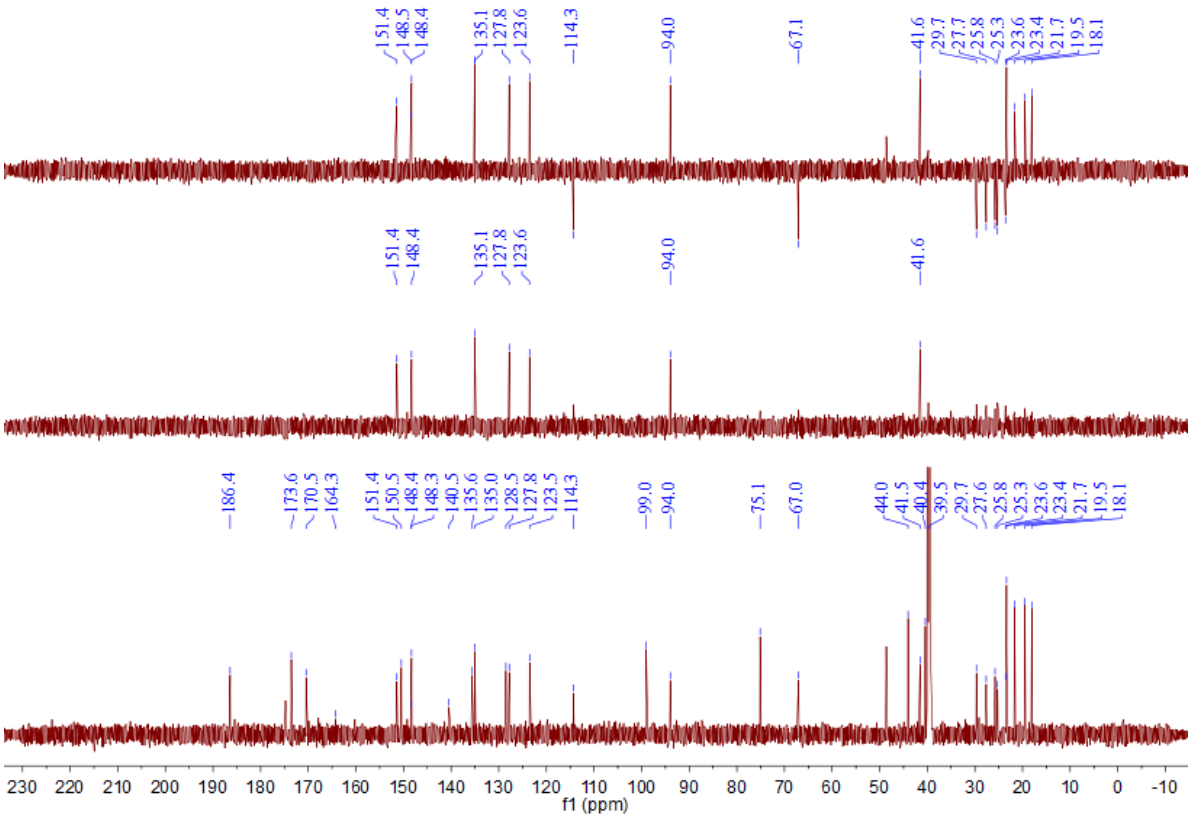



**Figure S4**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **1** in DMSO-$d_6$

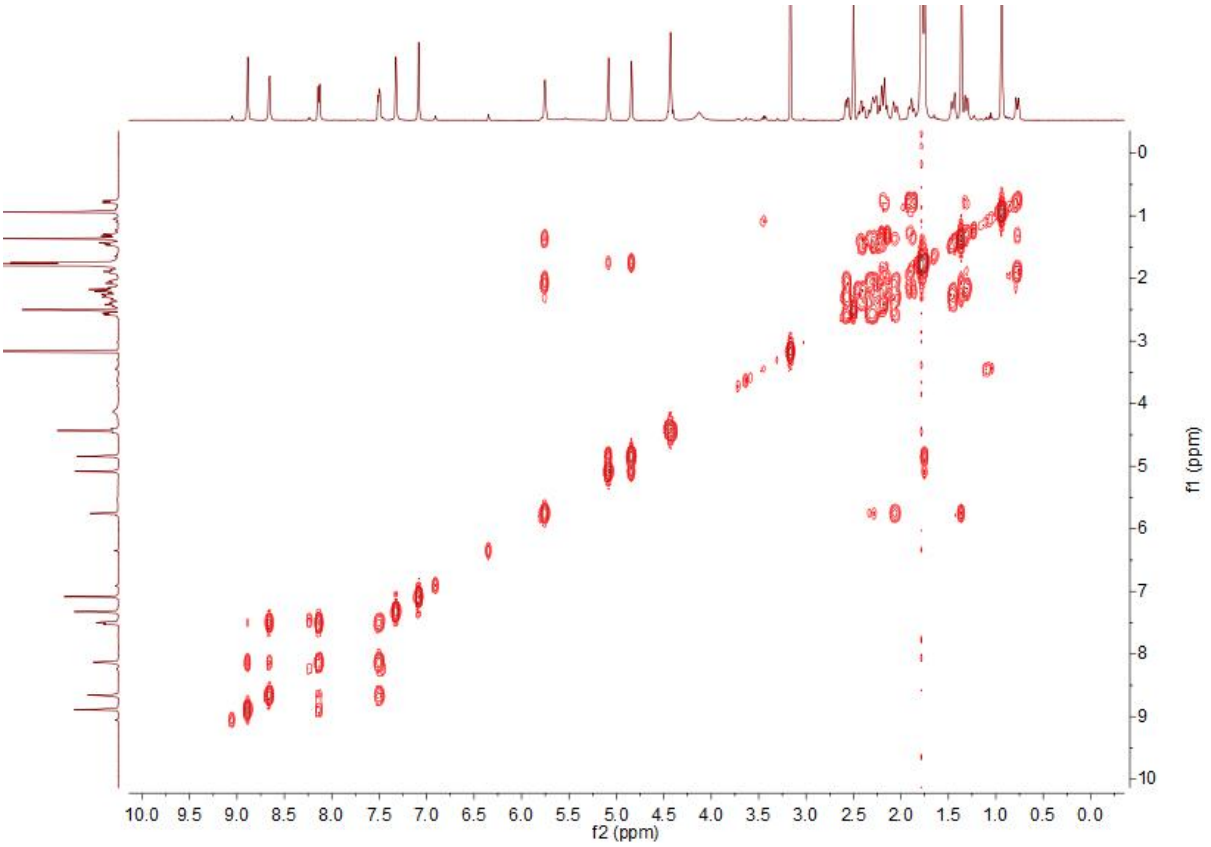



**Figure S5**. The $^{1}$H-$^{1}$HCOSY spectrum (500 MHz) of **1** in DMSO-$d_6$

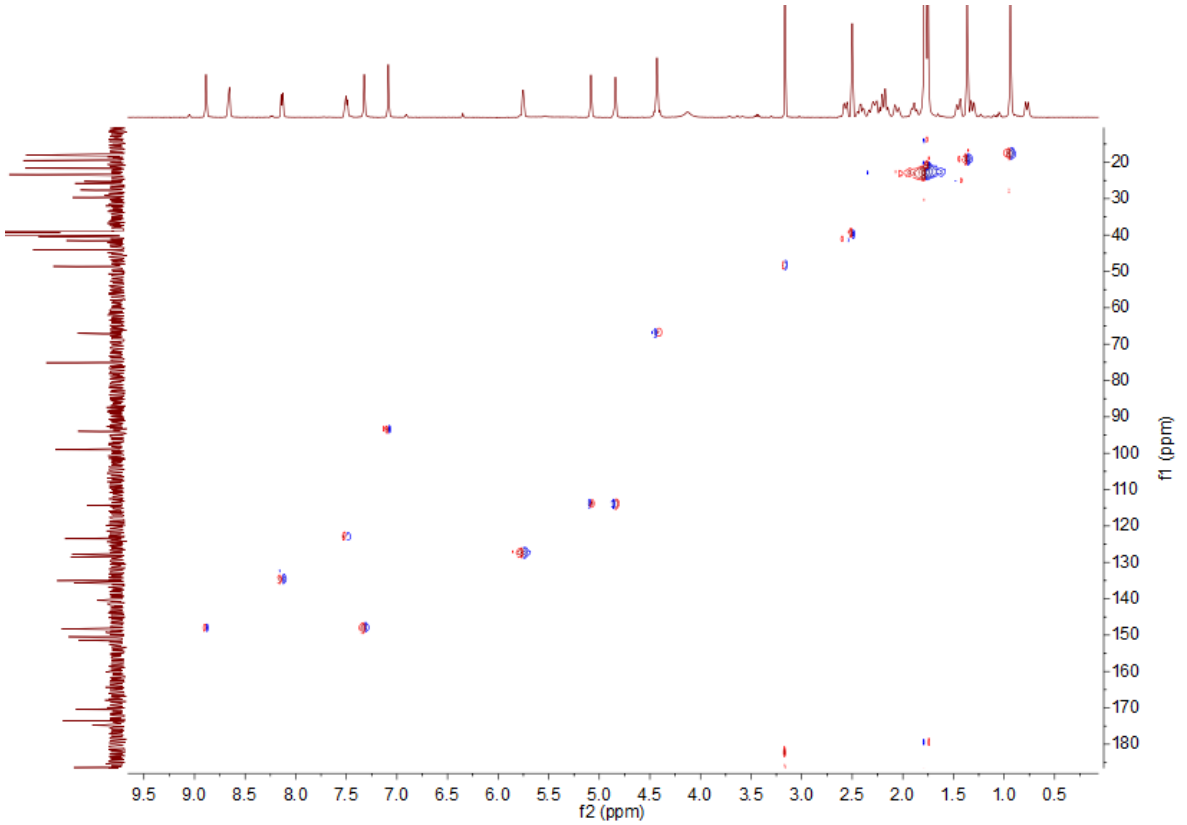



**Figure S6**. The HSQC spectrum (500 MHz) of **1** in DMSO-$d_6$

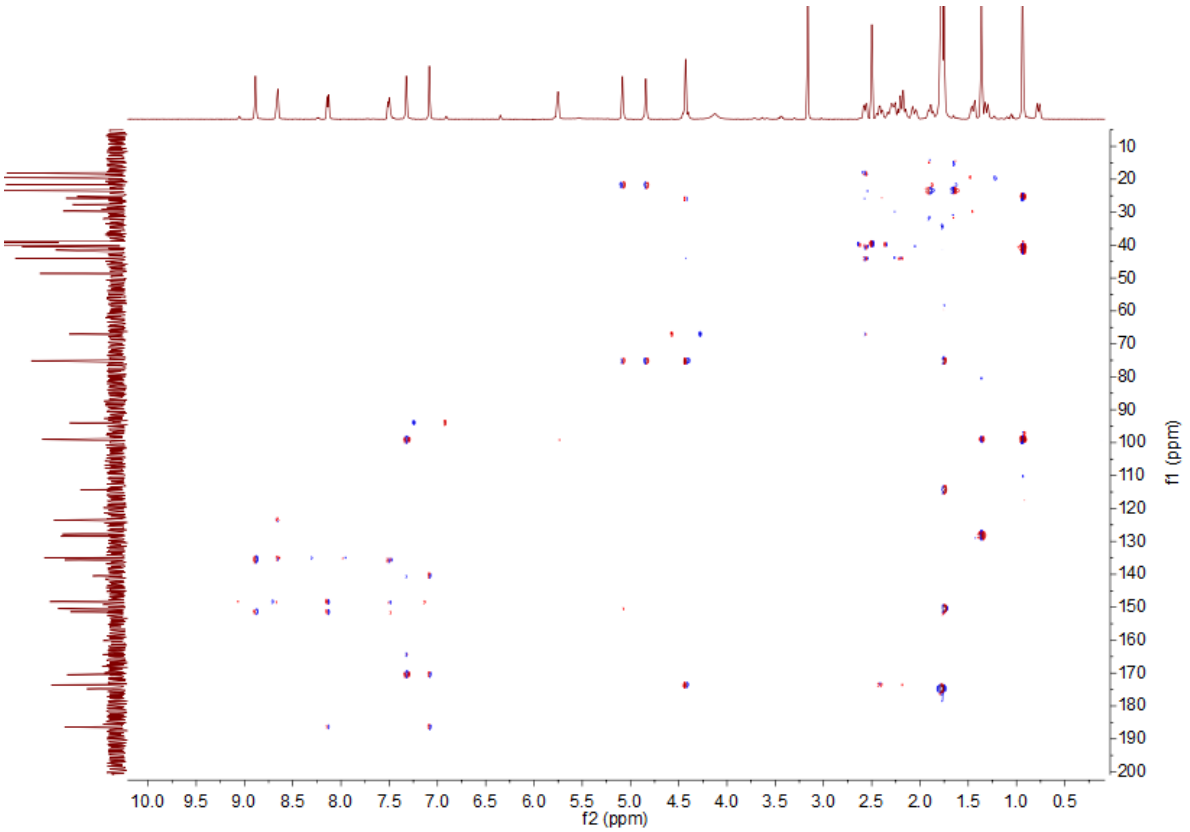



**Figure S7**. The HMBC spectrum (500 MHz) of **1** in DMSO-$d_6$

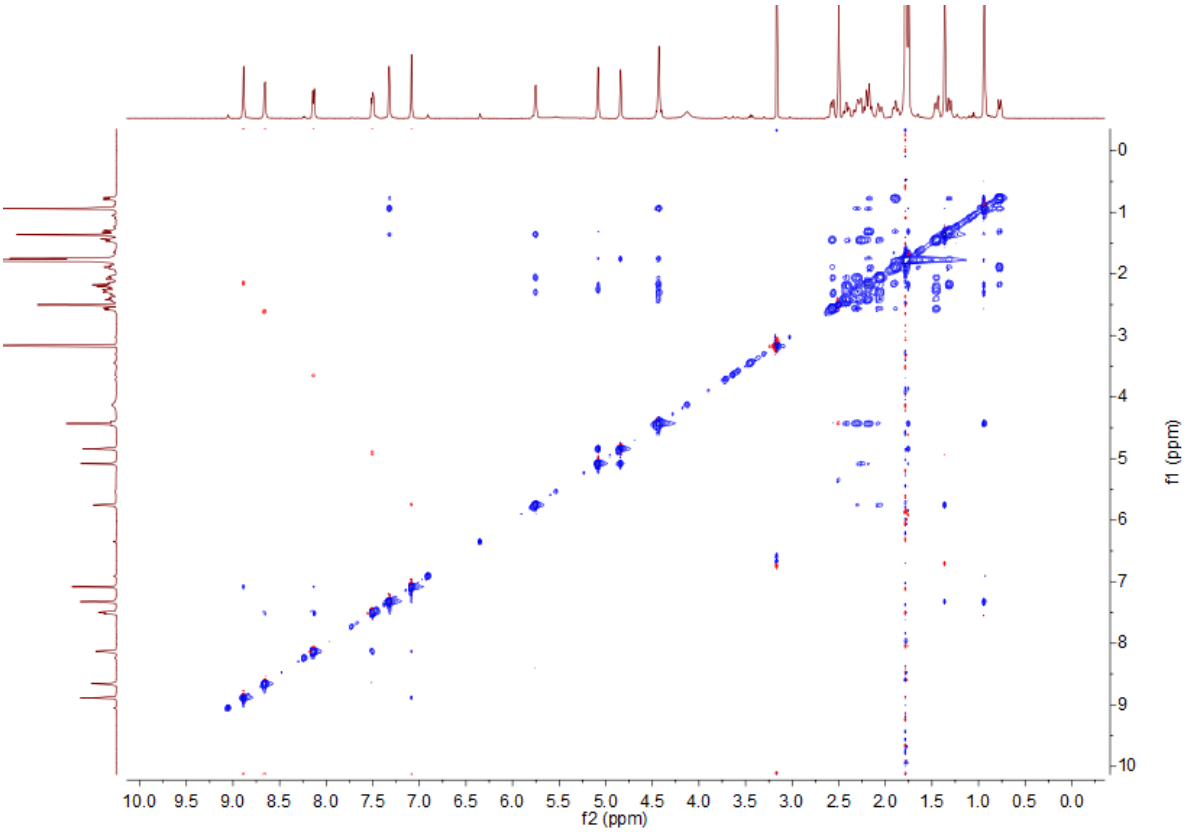
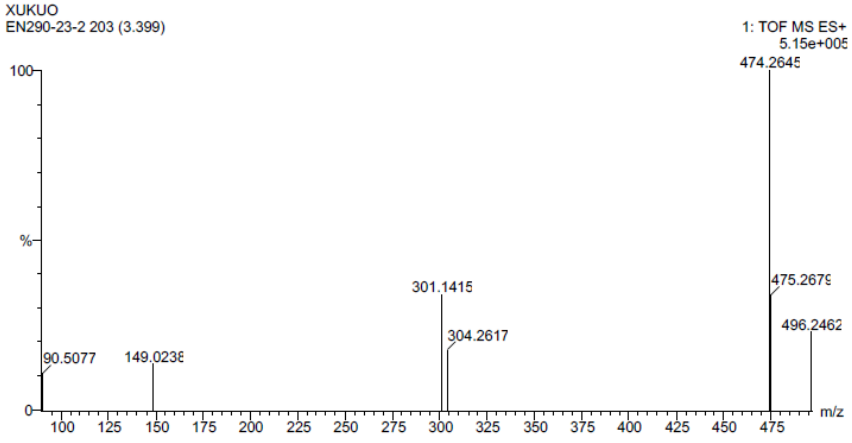



**Figure S8**. The NOESY spectrum (500 MHz) of **1** in DMSO-$d_6$

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

**Single Mass Analysis**
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
360 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-5 O: 0-10
XUKUO
EN290-23-2 203 (3.399)




Minimum: -1.5
Maximum: 1.0 1.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 474.2645 | 474.2644 | 0.1 | 0.2 | 13.5 | 38.7 | n/a | n/a | C30 H36 N O4 |

**Figure S9**. The HR-ESI-MS data of **2**

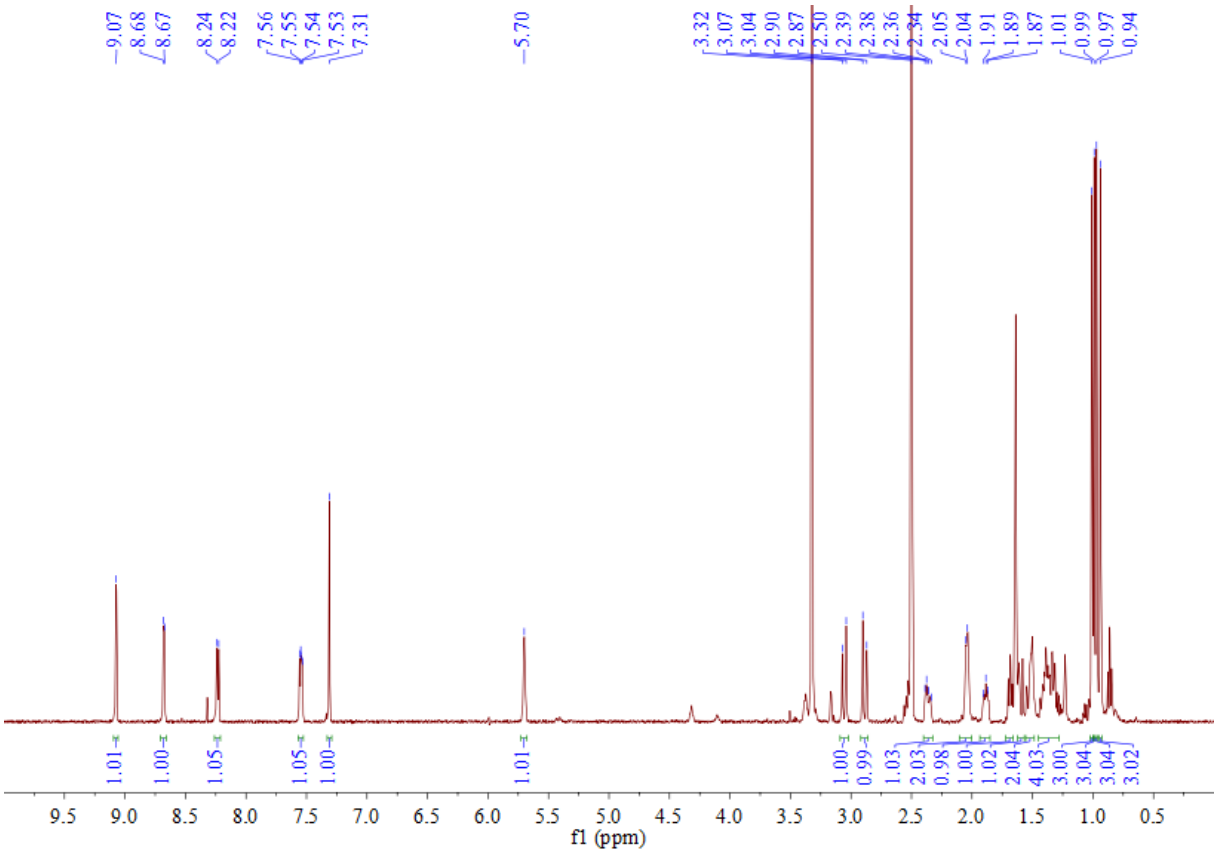



**Figure S10**. The $^{1}$H NMR spectrum (500 MHz) of **2** in DMSO-$d_6$

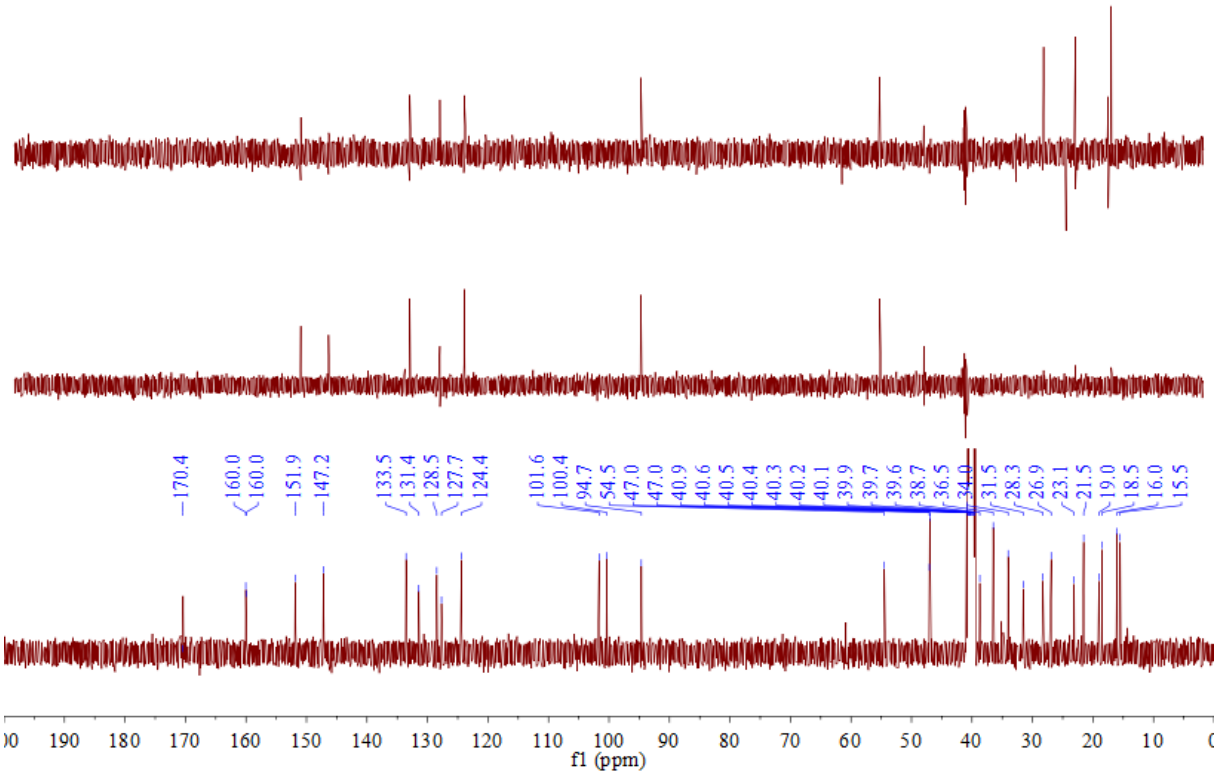
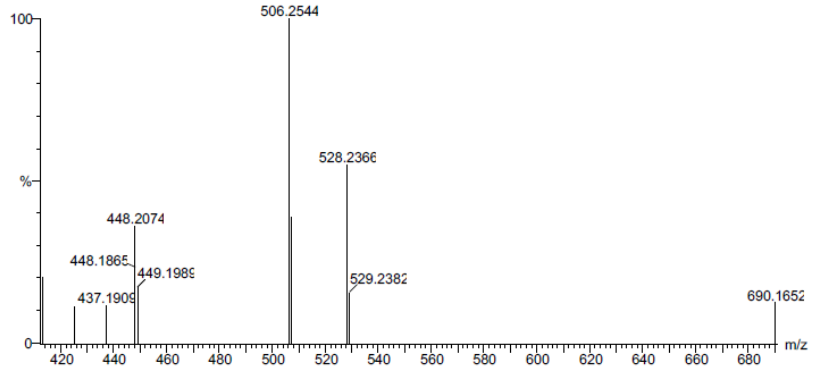



**Figure S11**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **2** in DMSO-$d_6$

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

**Single Mass Analysis**
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
386 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-100 H: 0-100 N: 0-5 O: 0-10
XUKUO
EN290-10 197 (3.302) 1: TOF MS ES+ 1.68e+004




| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Minimum: | | -1.5 | | | | | | |
| Maximum: | | 1.0 | 1.0 | 50.0 | | | | |
| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
| 506.2544 | 506.2543 | 0.1 | 0.2 | 13.5 | 28.8 | n/a | n/a | C30 H36 N O6 |

**Figure S12**. The HR-ESI-MS data of **3**

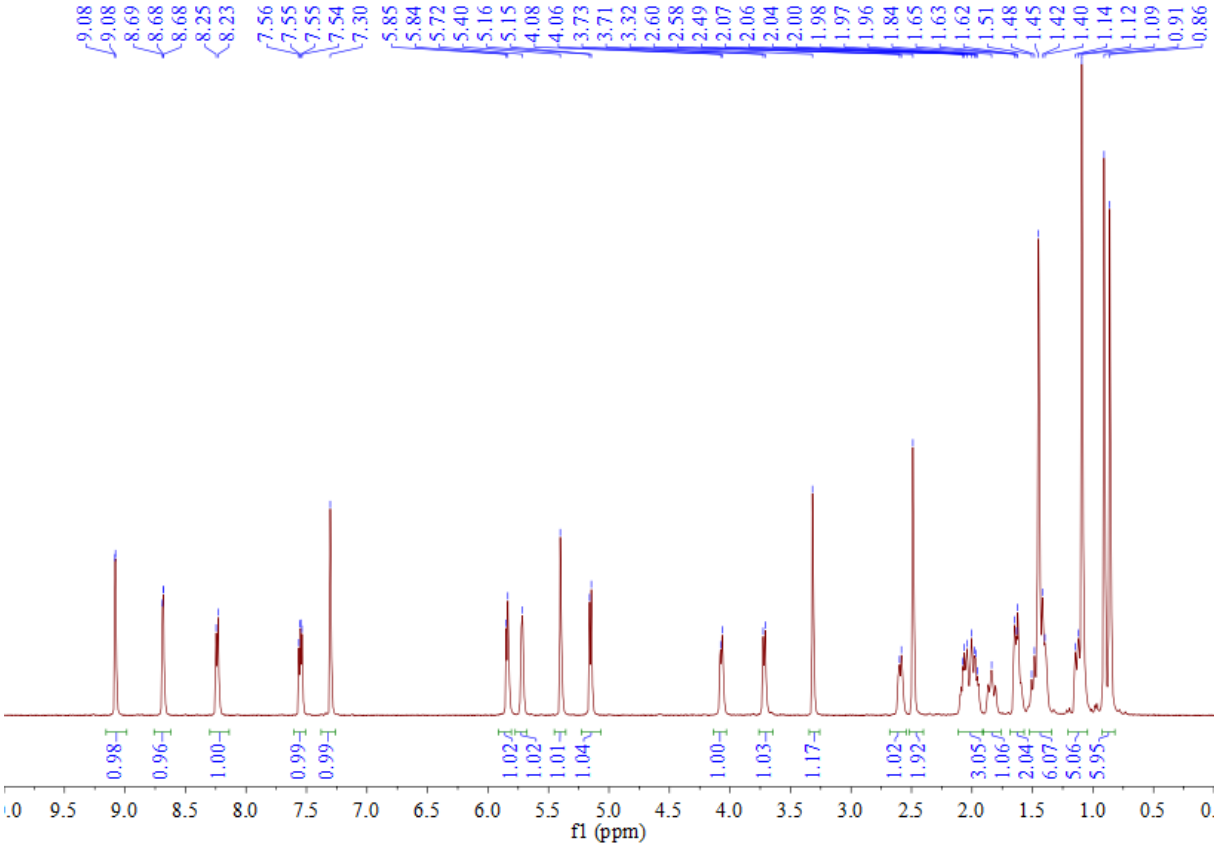



**Figure S13**. The $^{1}$H NMR spectrum (500 MHz) of **3** in DMSO-$d_6$

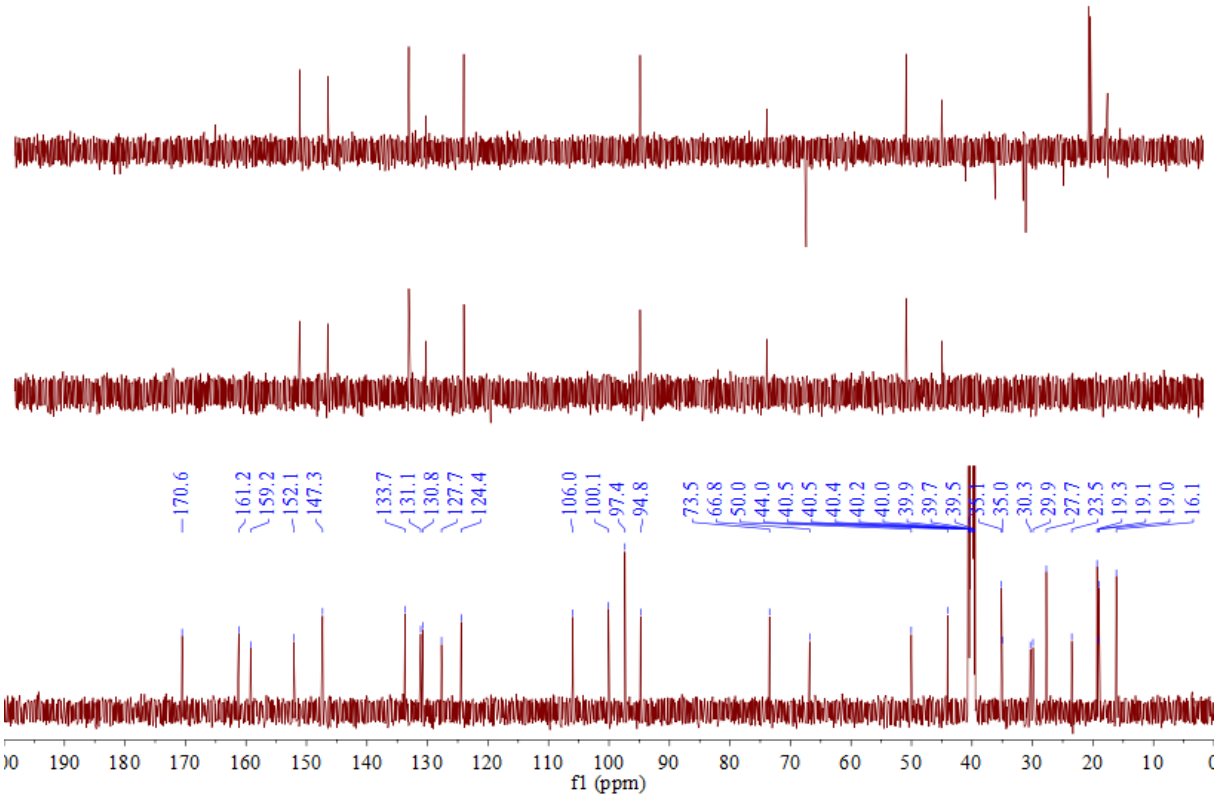



**Figure S14**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **3** in DMSO-$d_6$

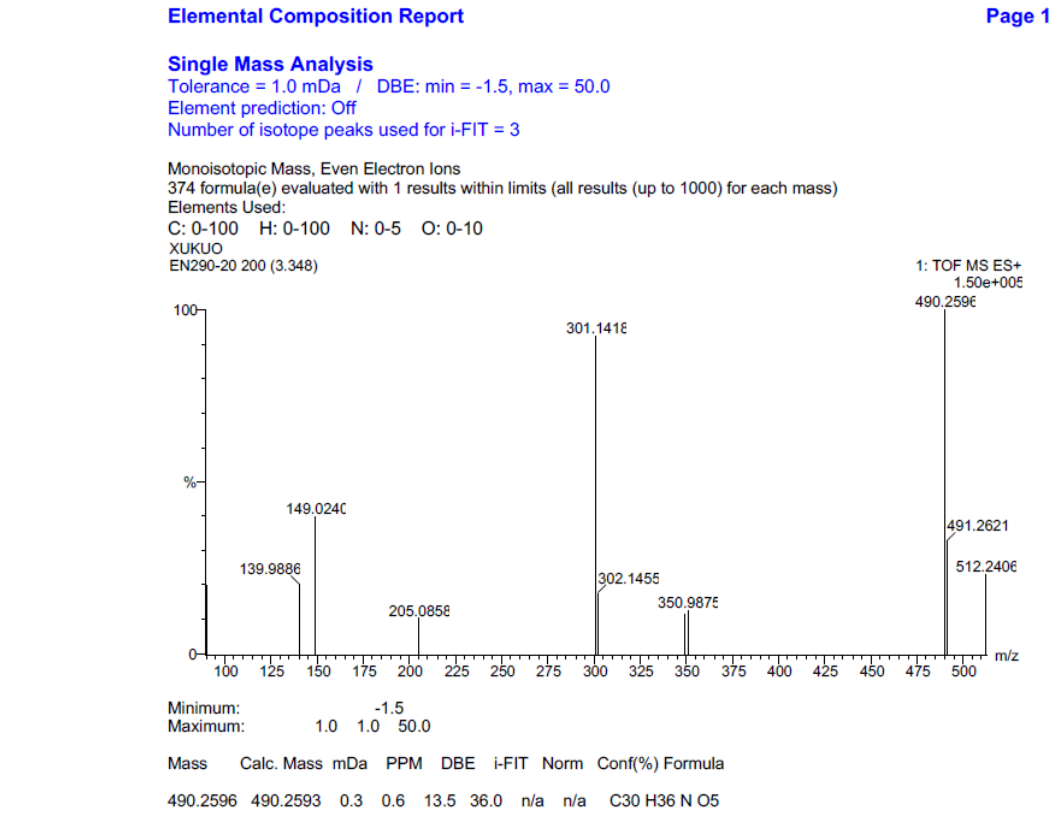



**Figure S15**. The HR-ESI-MS data of **4**

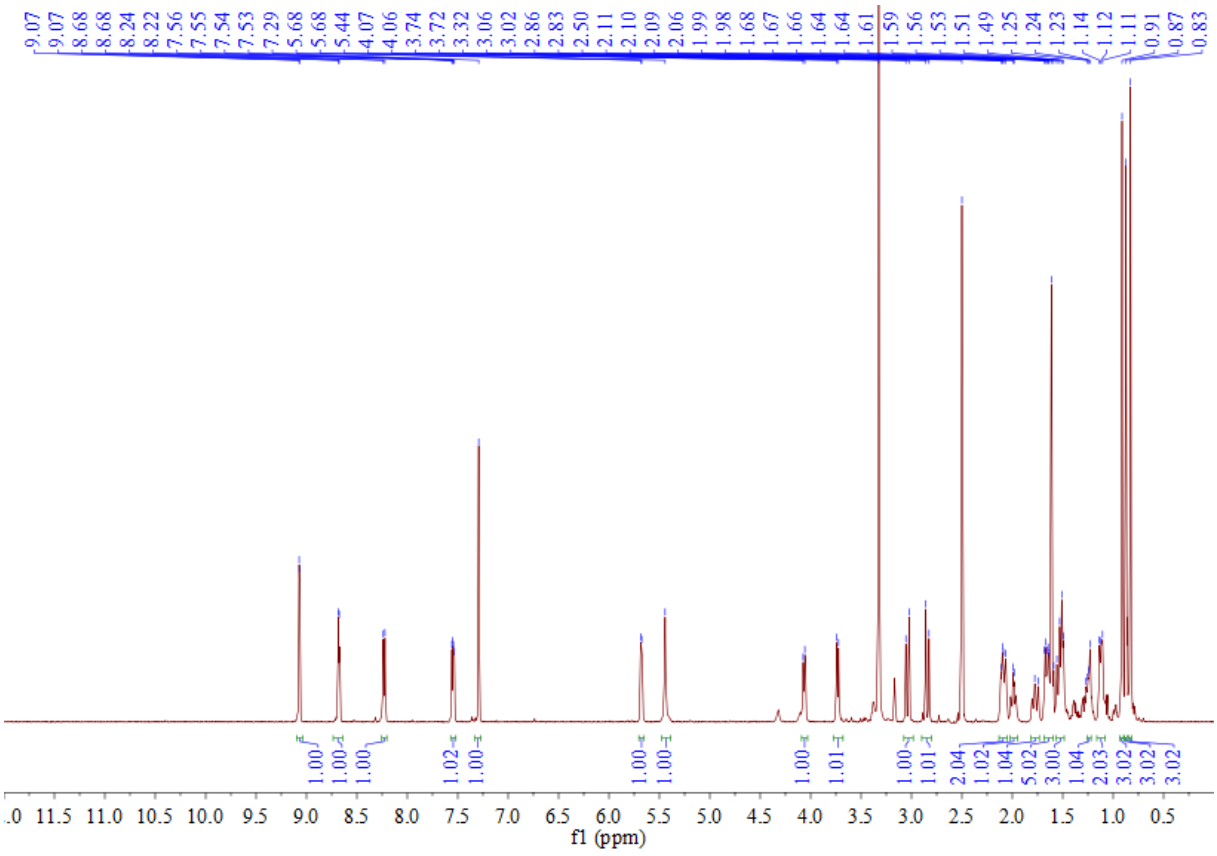



**Figure S16**. The $^{1}$H NMR spectrum (500 MHz) of **4** in DMSO-$d_6$

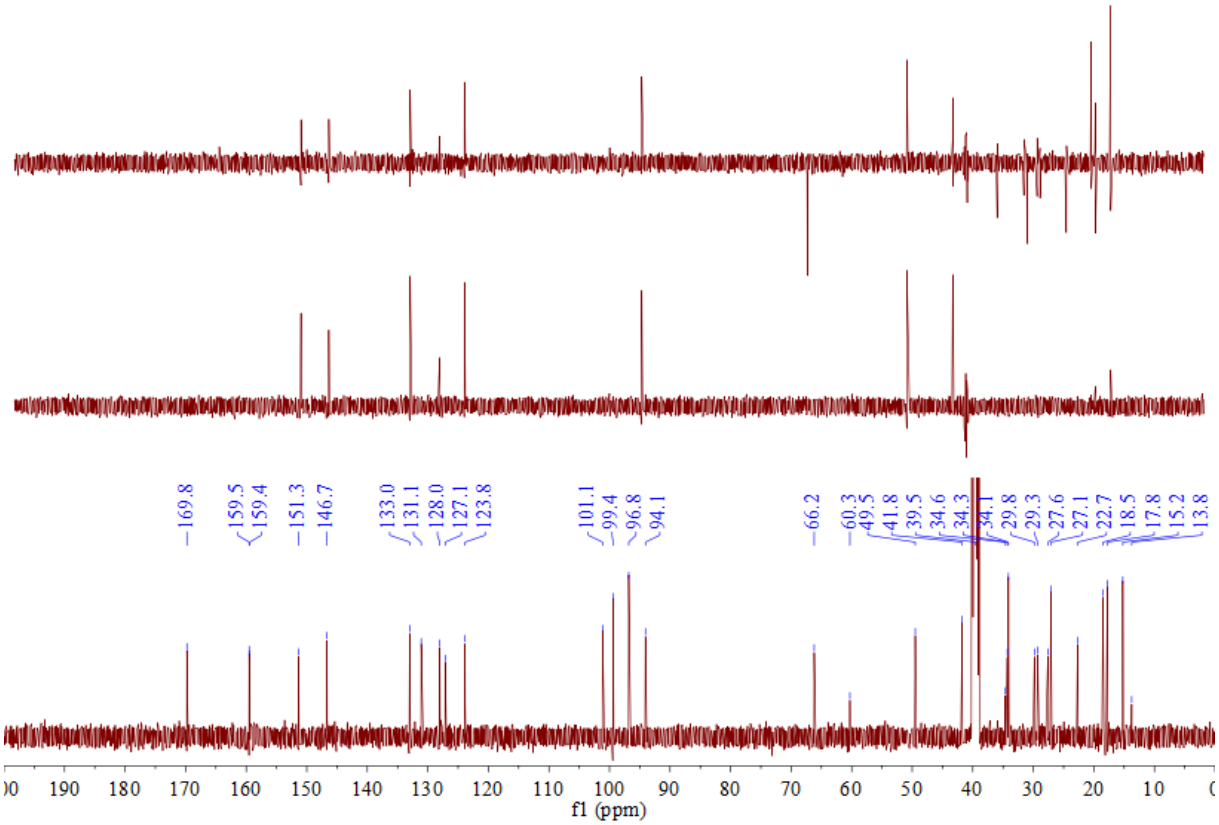



**Figure S17**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **4** in DMSO-$d_6$

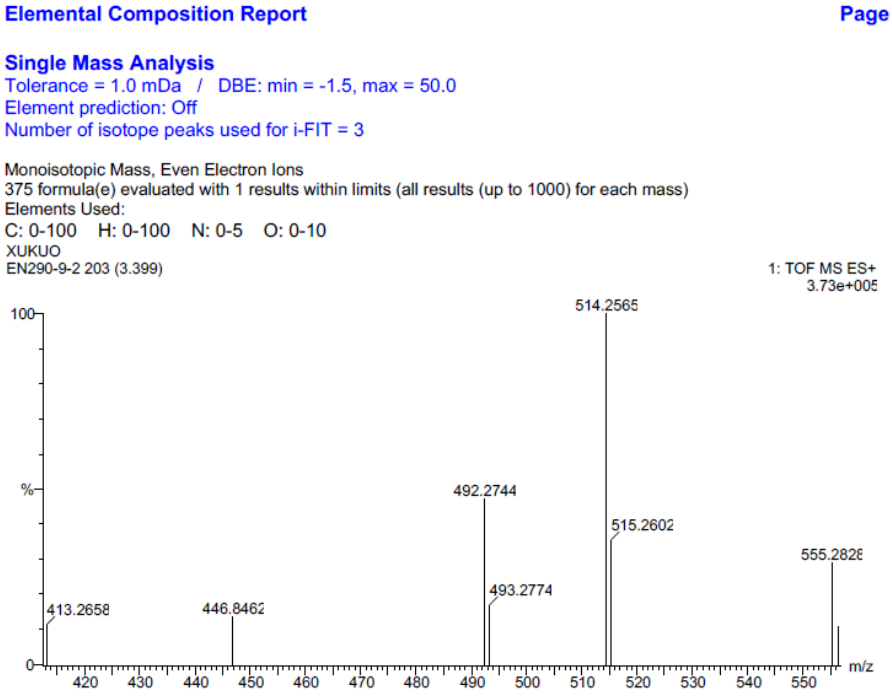



**Figure S18**. The HR-ESI-MS data of **5**

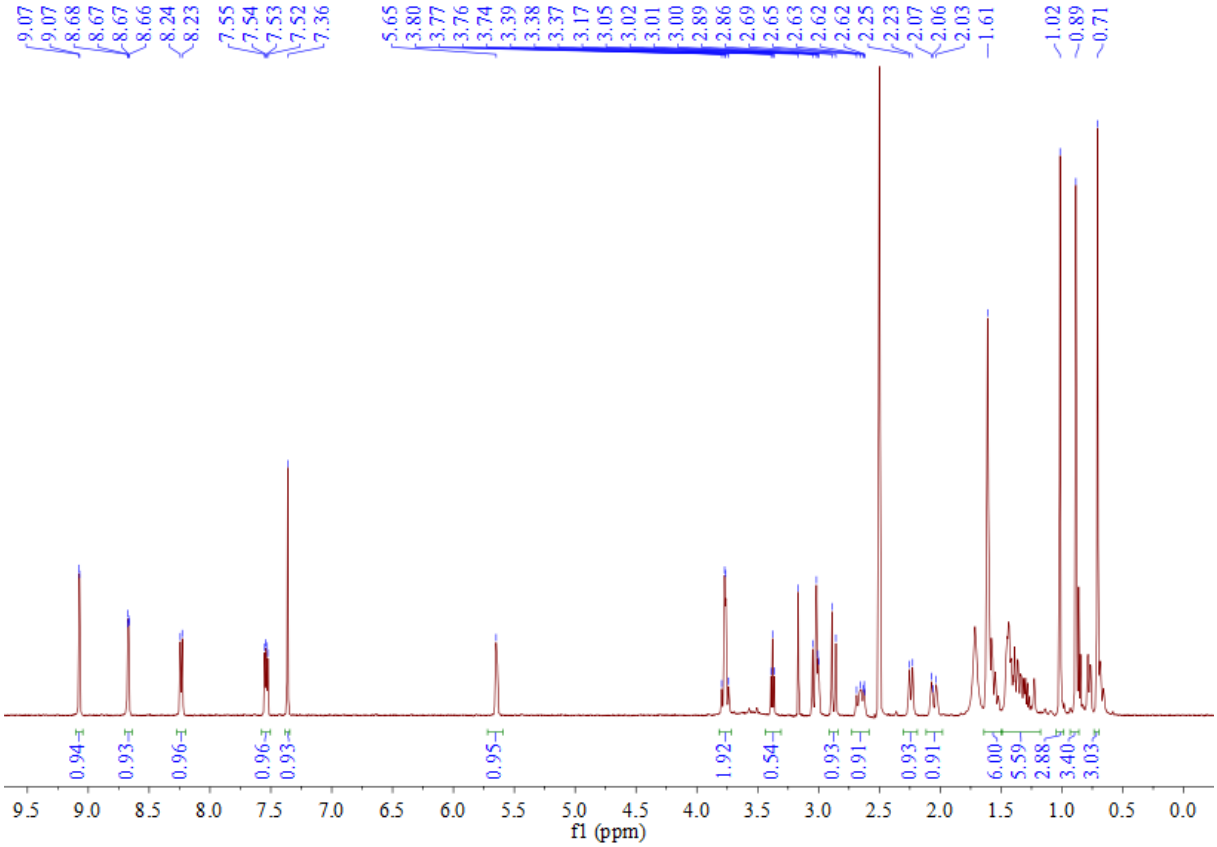



**Figure S19**. The $^{1}$H NMR spectrum (500 MHz) of **5** in DMSO-$d_6$

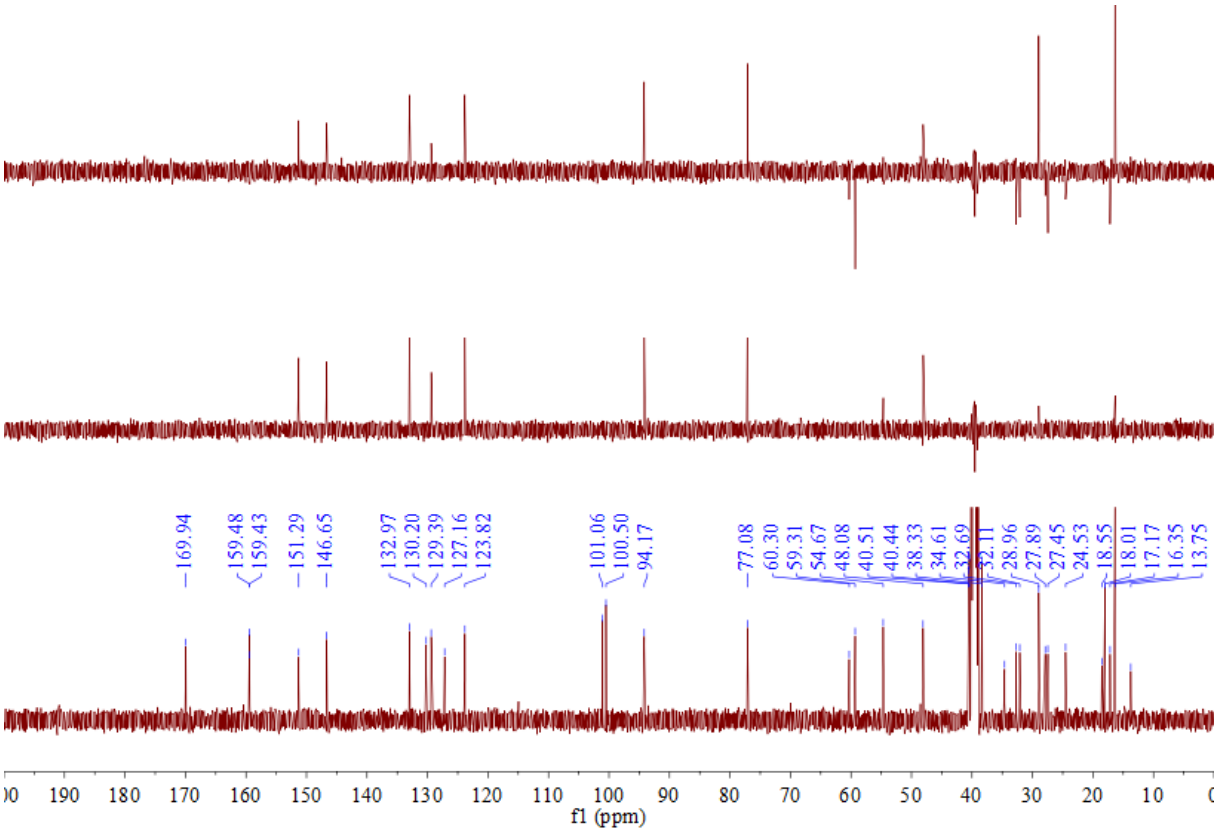


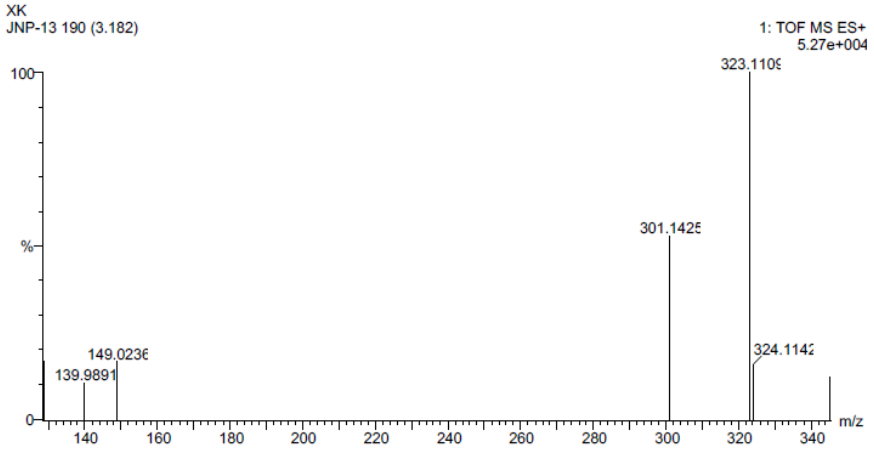

**Figure S20**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **5** in DMSO-$d_6$

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

**Single Mass Analysis**
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
83 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-100 O: 0-10 Na: 0-1

XK
JNP-13 190 (3.182)




Minimum: -1.5
Maximum: 1.0 1.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 323.1109 | 323.1107 | 0.2 | 0.6 | 4.5 | 29.7 | n/a | n/a | C14 H20 O7 Na |

**Figure S21**. The HR-ESI-MS data of **6**

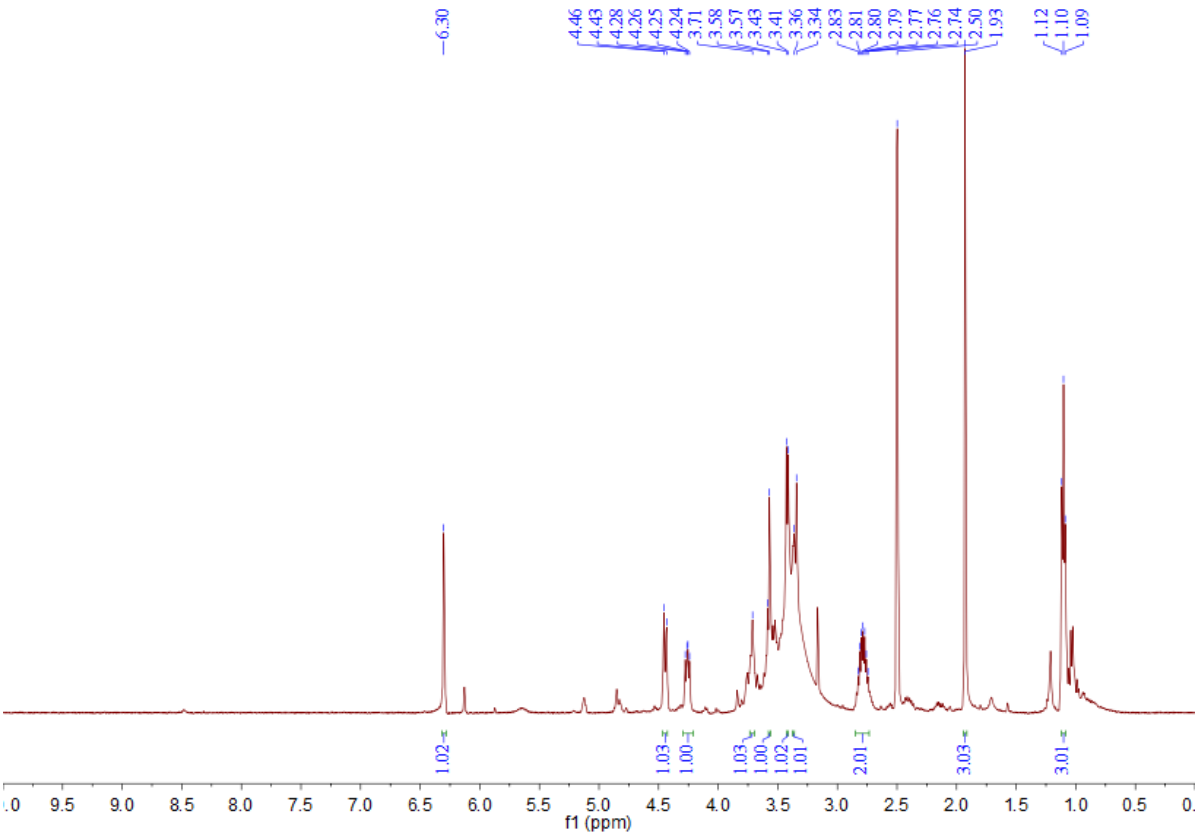



**Figure S22**. The $^{1}$H NMR spectrum (500 MHz) of **6** in DMSO-$d_6$

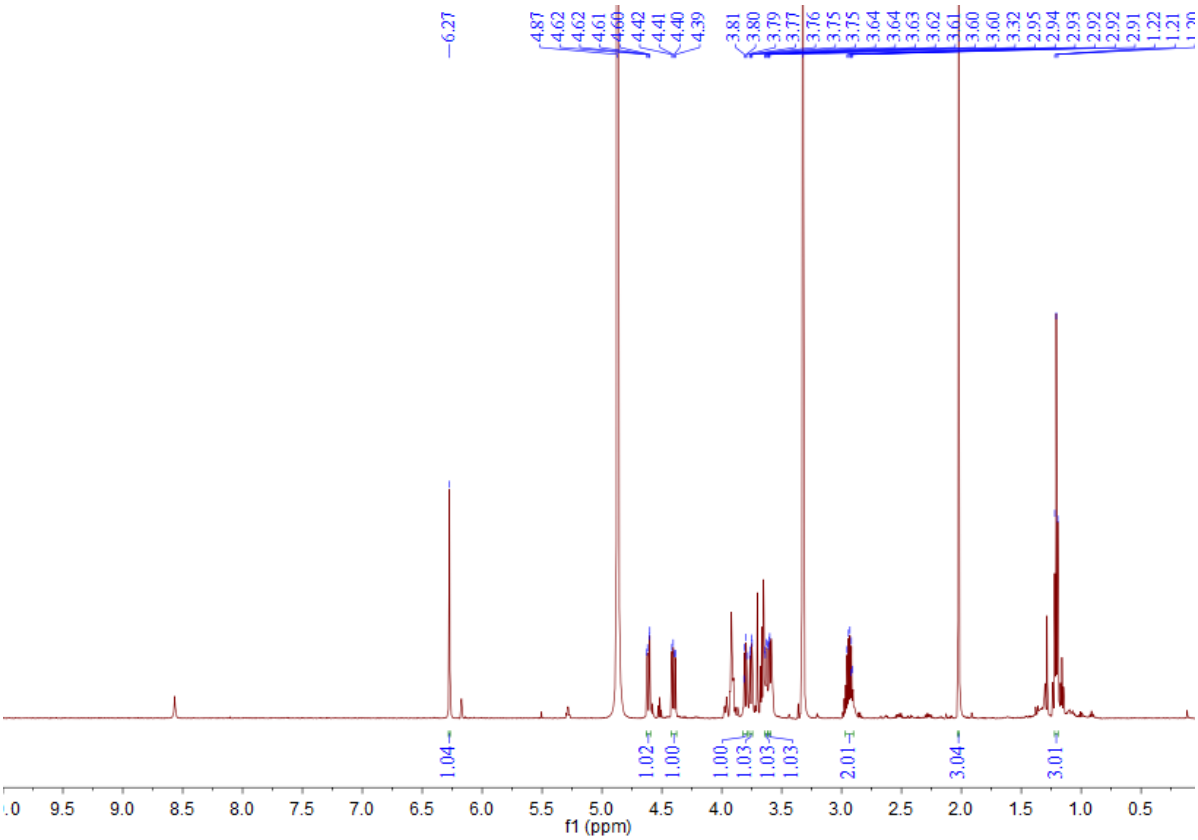



**Figure S23**. The $^{1}$H NMR spectrum (500 MHz) of **6** in MeOH-$d_4$

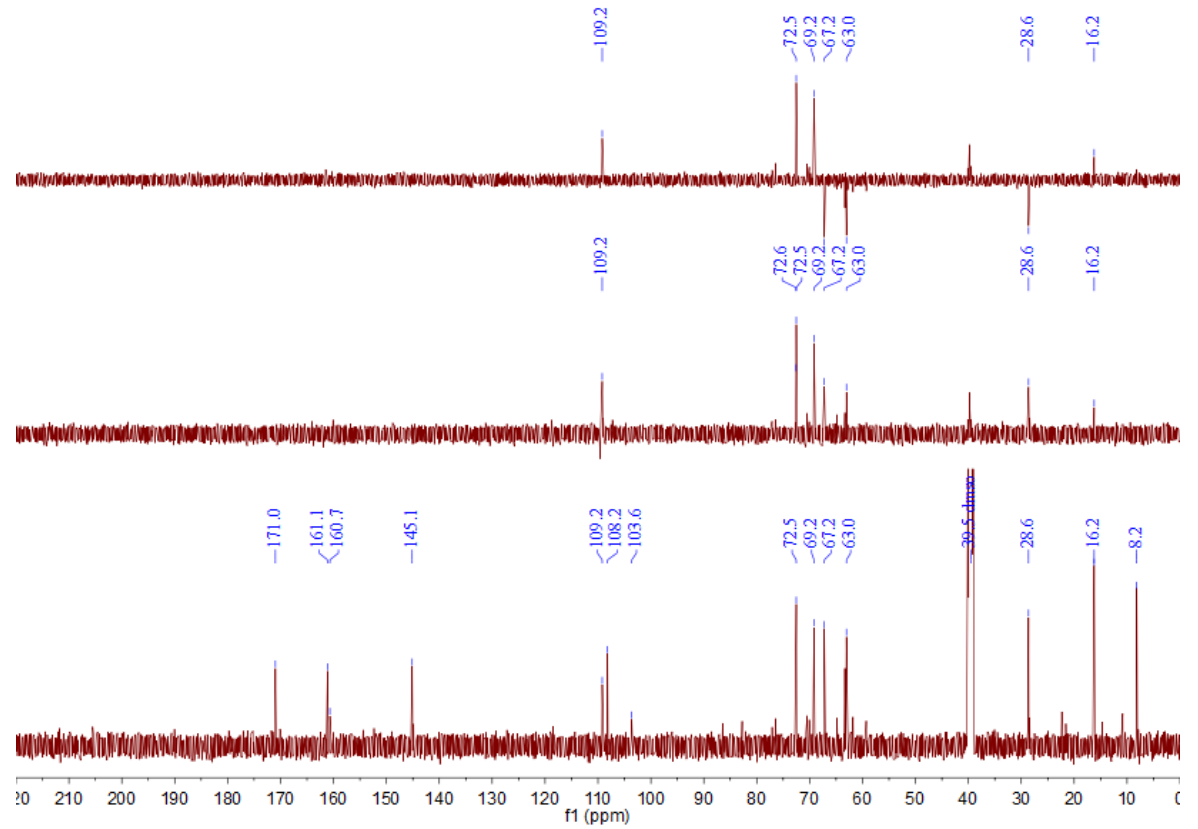



**Figure S24**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **6** in DMSO-$d_6$

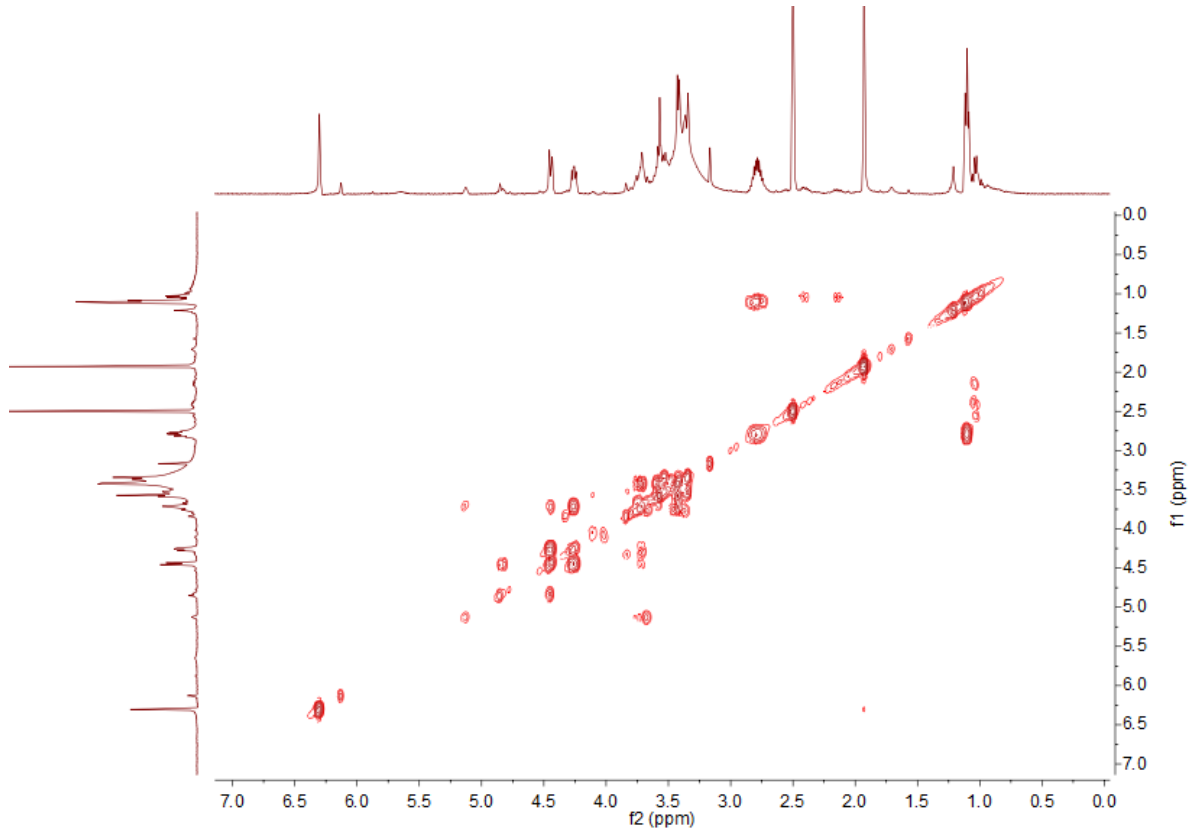



**Figure S25**. The $^{1}$H-$^{1}$H COSY spectrum (500 MHz) of **6** in DMSO-$d_6$

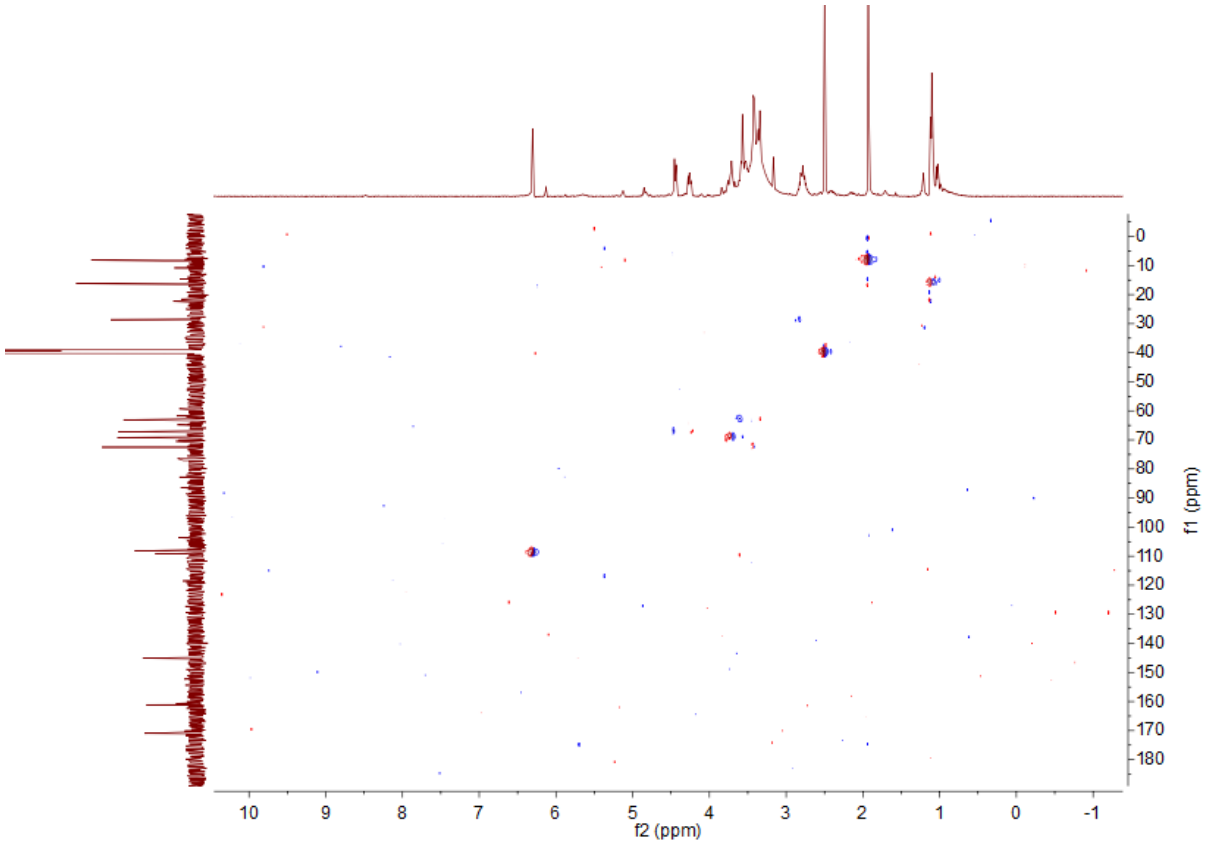



**Figure S26**. The HSQC spectrum (500 MHz) of **6** in DMSO-$d_6$

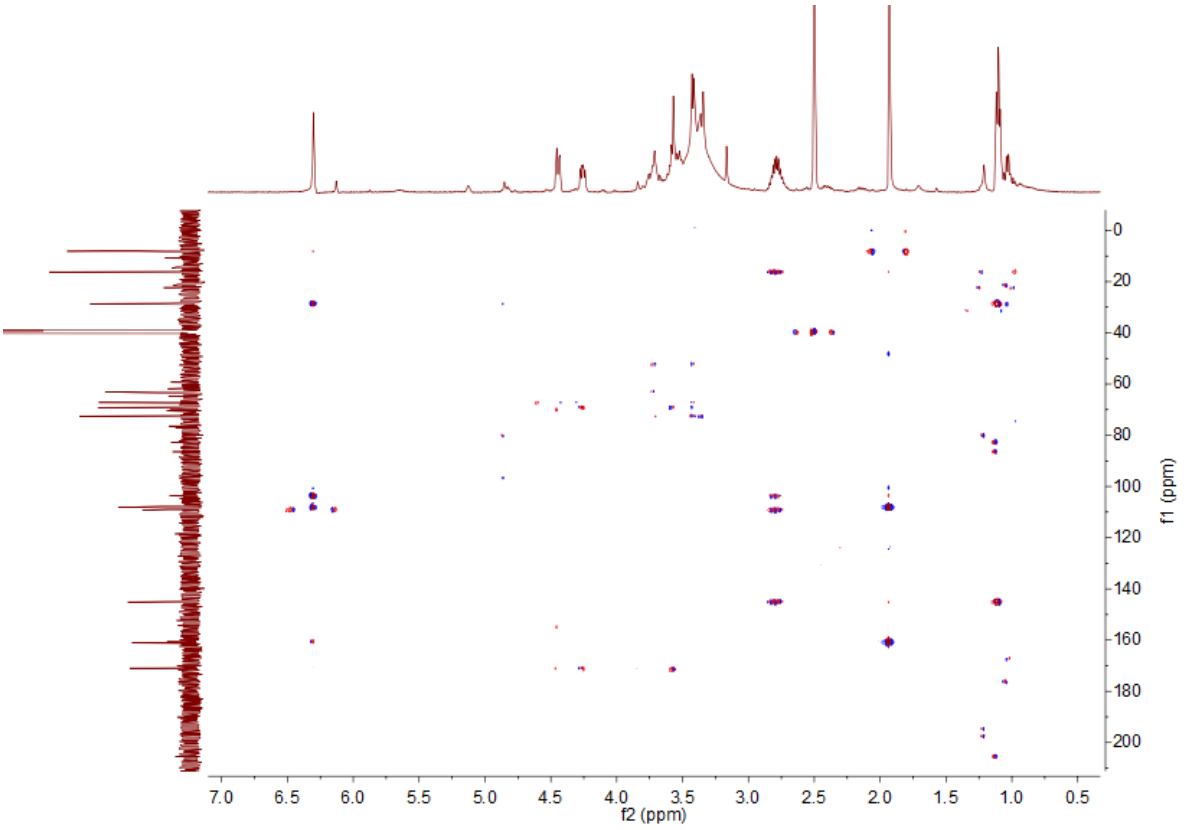



**Figure S27**. The HMBC spectrum (500 MHz) of **6** in DMSO-$d_6$

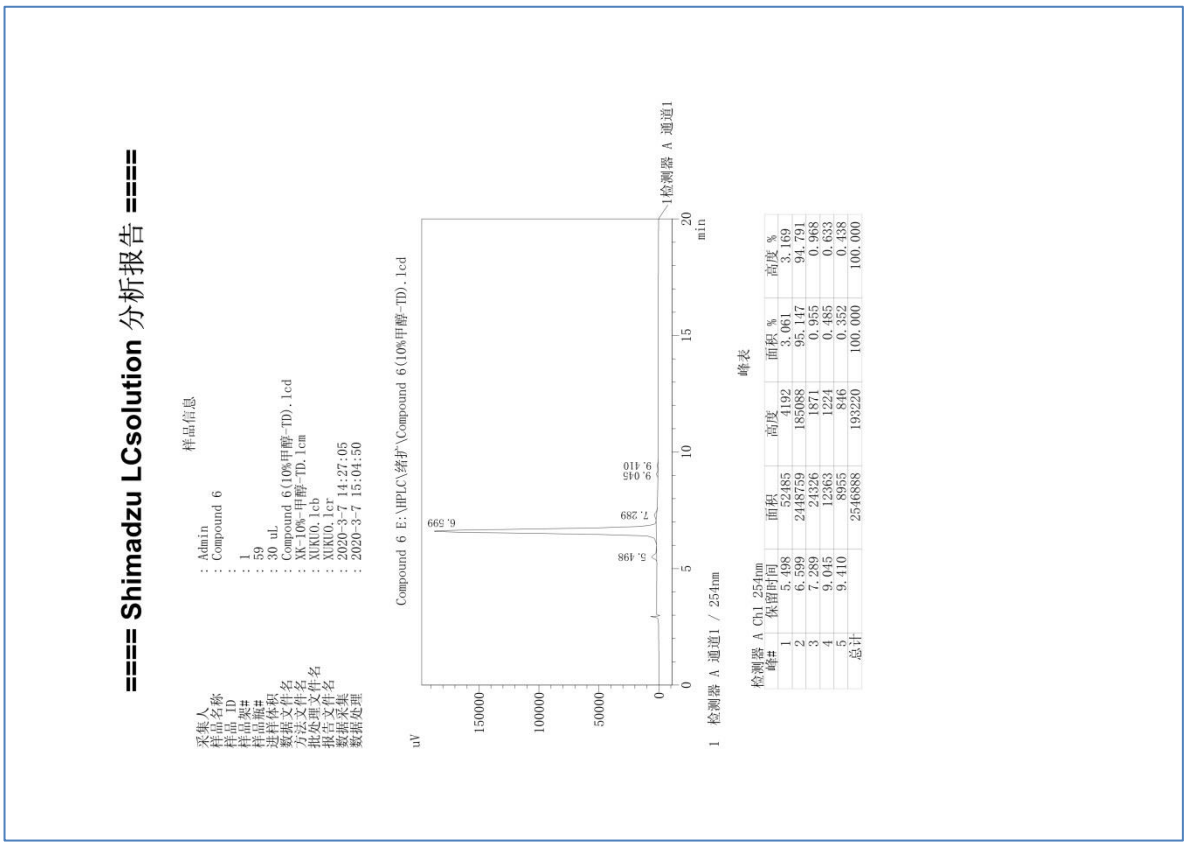
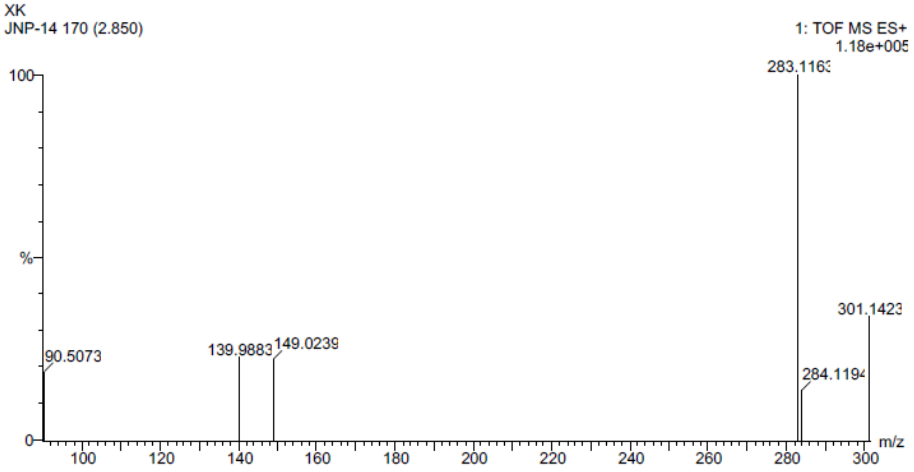



**Figure S28**. The HPLC spectrum of **6** (254nm, 10-100%MeOH, 20 min)

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

**Single Mass Analysis**
Tolerance = 1.0 mDa / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
72 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-50 H: 0-100 O: 0-10 Na: 0-1
XK
JNP-14 170 (2.850)




Minimum: -1.5
Maximum: 1.0 1.0 50.0

| Mass | Calc. Mass | mDa | PPM | DBE | i-FIT | Norm | Conf(%) | Formula |
|---|---|---|---|---|---|---|---|---|
| 283.1163 | 283.1158 | 0.5 | 1.8 | 2.5 | 32.3 | n/a | n/a | C12 H20 O6 Na |

**Figure S29**. The HR-ESI-MS data of **7**

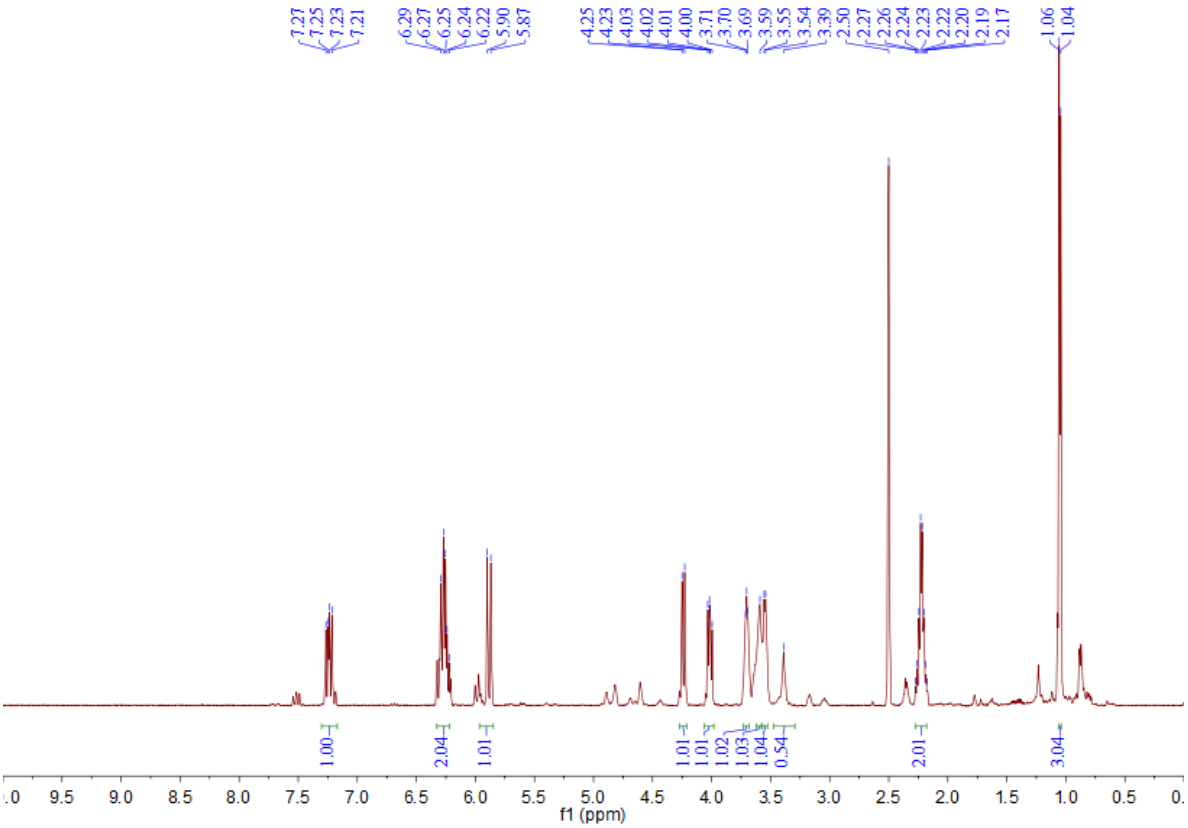



**Figure S30**. The $^{1}$H NMR spectrum (500 MHz) of **7** in DMSO-$d_6$

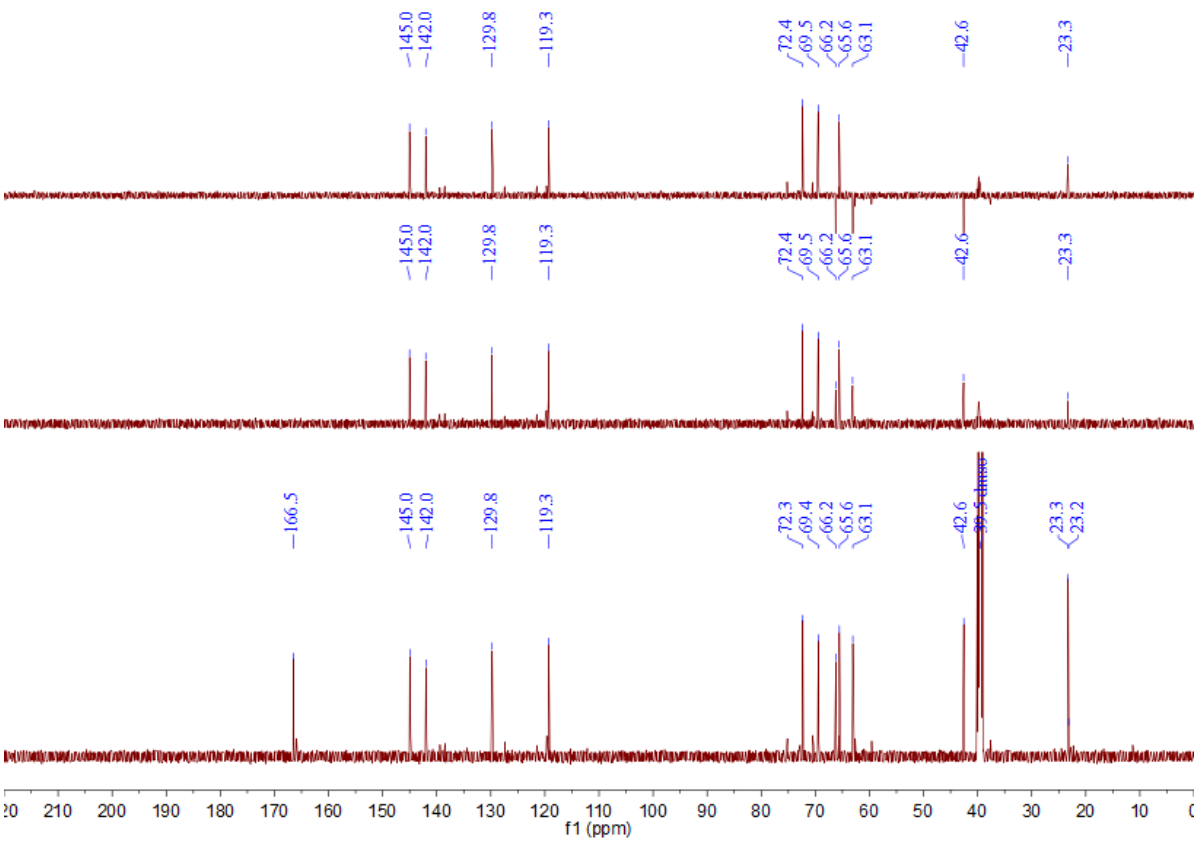



**Figure S31**. The $^{13}$C NMR and DEPT spectrum (125 MHz) of **7** in DMSO-$d_6$

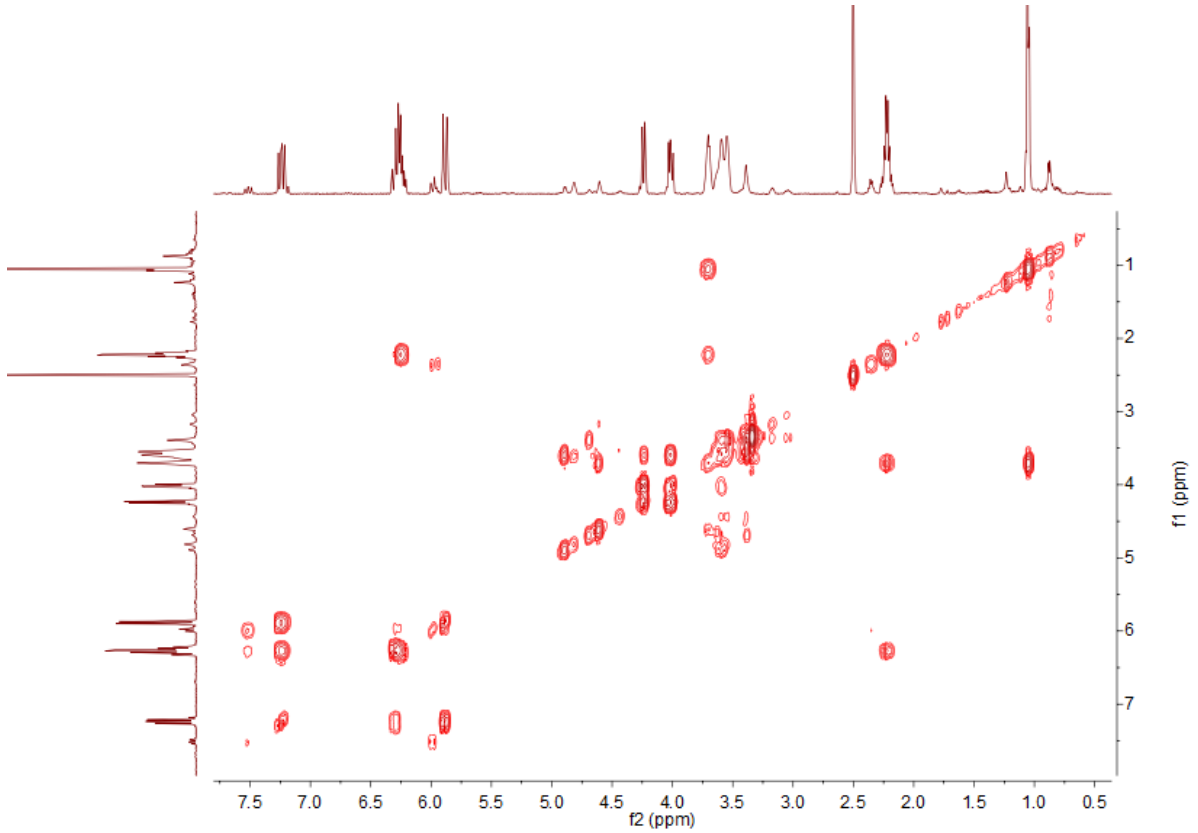



**Figure S32**. The $^{1}$H-$^{1}$H COSY spectrum (500 MHz) of **7** in DMSO-$d_6$

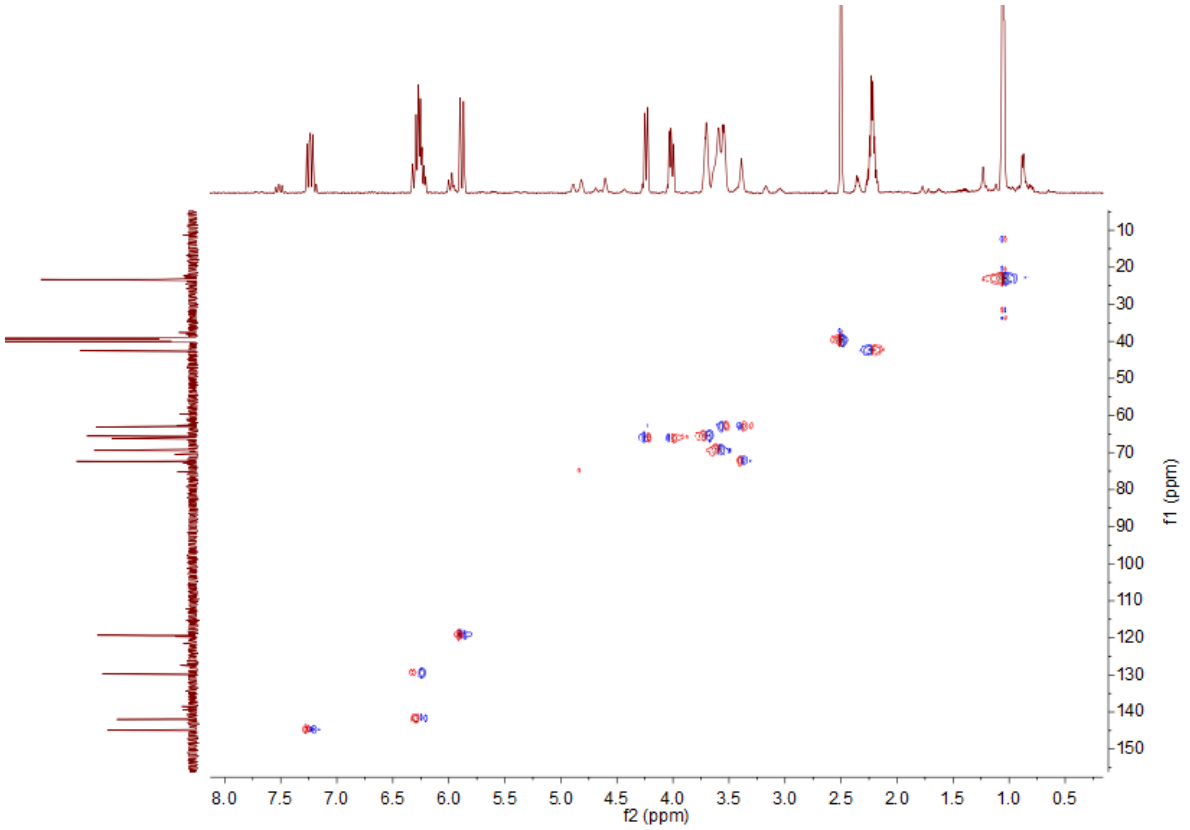



**Figure S33**. The HSQC spectrum (500 MHz) of **7** in DMSO-$d_6$

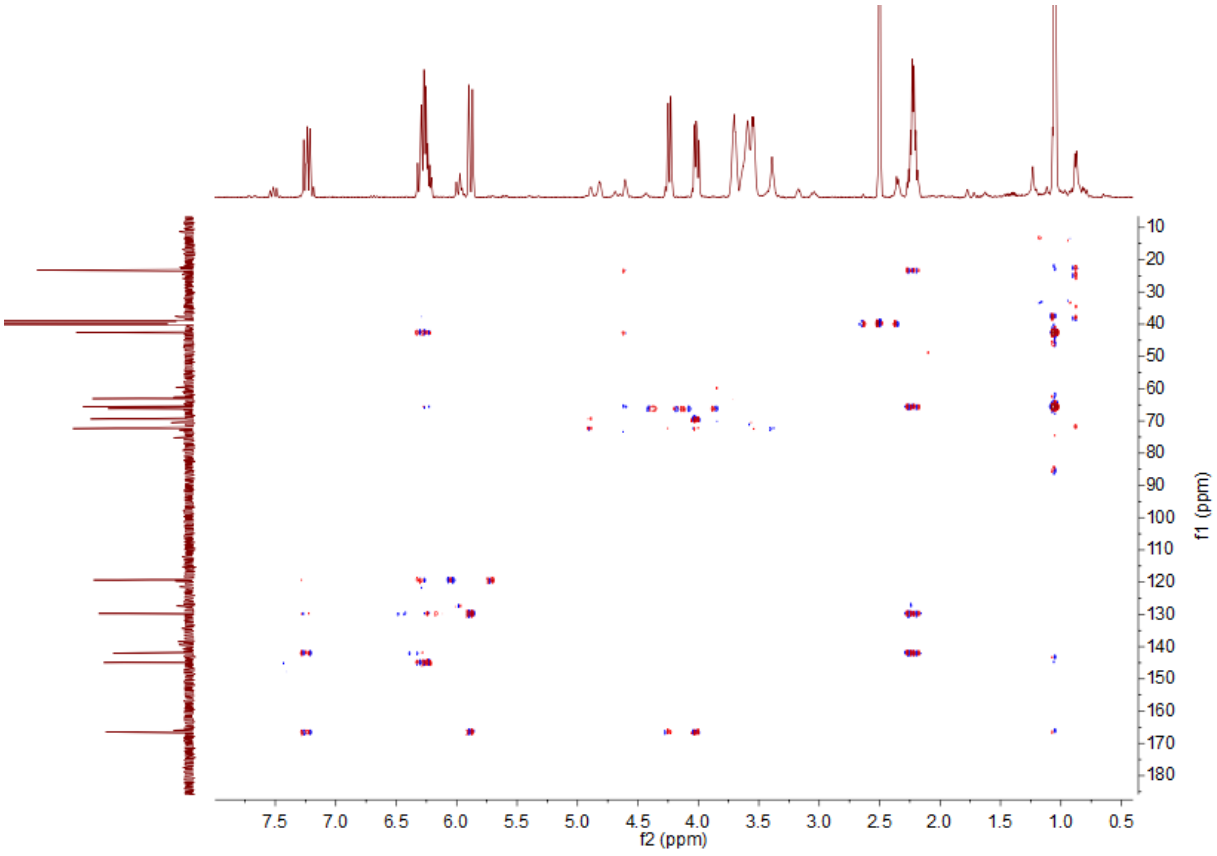



**Figure S34**. The HMBC spectrum (500 MHz) of **7** in DMSO-$d_6$

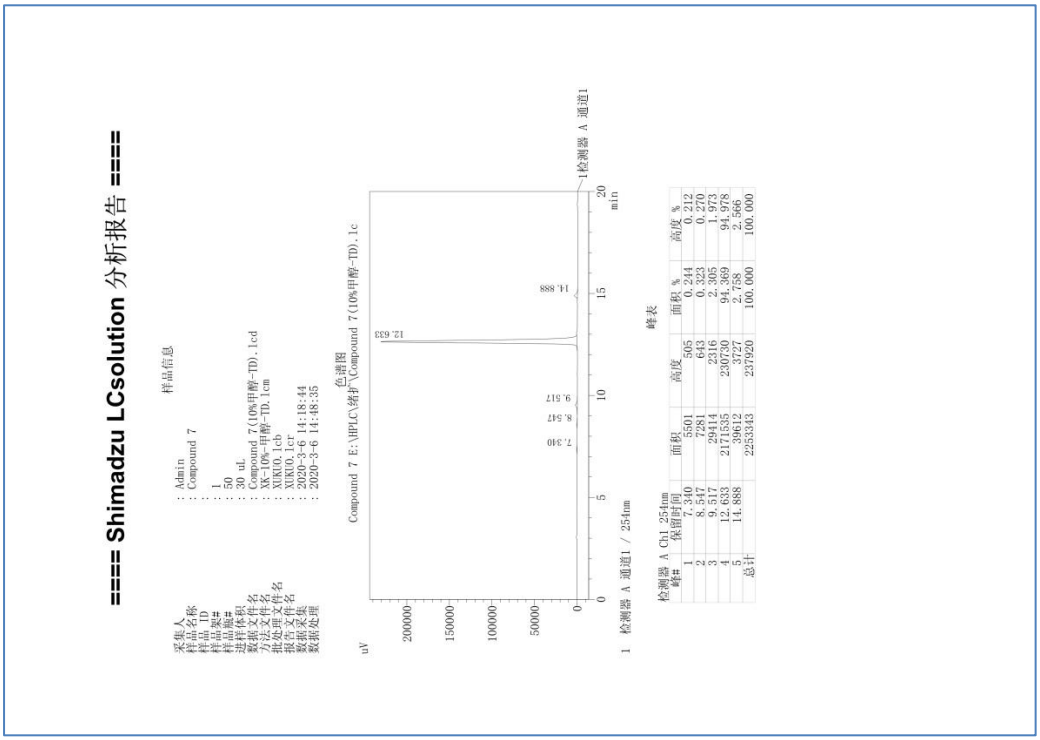



**Figure S35**. The HPLC spectrum of **7** (254nm, 10-100%MeOH, 20 min)

## Theoretical calculations of compound 1

The theoretical calculations of ECD and NMR were carried on the Yinfo Cloud Platform (http://cloud.yinfotek.com). Conformational analysis of **1** was performed using Confab with systematic search algorithm at MMFF94 force field with RMSD threshold of 0.5 Å and energy window of 7 kcal/mol [1]. The energies of all dominative conformers were provided in Table S1. At first, conformers were optimized at PM6 and HF/6-31G(d) theory levels, consecutively. Room-temperature equilibrium populations were calculated according to Boltzmann distribution law, based on which dominative conformers were saved with the values over 1%. The chosen conformers were further optimized at B3LYP/6-31G(d) in gas phase. Vibrational frequency analysis confirmed the stable structures. Finally, the ECD calculations were executed in methanol with IEFPCM model using Time-dependent Density functional theory (TD-DFT) at the B3LYP/6-311G(d,p) level. Rotatory strengths for 50 excited states were calculated. The ECD spectrum of **1** was simulated by overlapping Gaussian functions ($\sigma$ and UV-shift values were set 0.35 eV and –30 nm, respectively) [2]. As a result, the experimental ECD spectrum of **1** was matched well with the calculated spectrum of (7*E*, 12*S*, 16*S*, 17*R*, 20*R*, and 21*R*)-isomer.

The above optimized conformations were further conducted into $^{13}$C-NMR calculations, which were carried out using the Gauge-Including Atomic Orbitals (GIAO) method at mPW1PW91/6-311+G(2d,p) level in DMSO simulated by the IEFPCM model [3]. Finally, the TMS-corrected NMR chemical shift values were averaged based on Boltzmann distribution and fitted to the experimental values by linear regression. As a result, the TMS-corrected computed $^{13}$C-NMR chemical shift of compound **1** was fitted to the experimental values by Ordinary Least Squares (OLS) Linear Regression method in order to remove systematic error that results from the conformational search and random error from experimental conditions (Table S2). Relatively higher $R^2$ and lower CMAD and CLAD values were shown in both $^{13}$C-NMR Linear Regression for (7*E*, 12*S*, 16*S*, 17*R*, 20*R*, and 21*R*)-isomer, which further supported the data of the ECD calculation.

**Table S1.** The selected conformers of **1** with Boltzmann distribution over 1%.

| Conformers | Energy (kcal/mol) | Population (%) |
|---|---|---|
| 1 | 108.64 | 29.29 |
| 2 | 108.69 | 26.92 |
| 3 | 108.91 | 18.57 |
| 4 | 108.92 | 18.26 |
| 5 | 110.23 | 2.00 |
| 6 | 110.31 | 1.75 |
| 7 | 110.44 | 1.40 |
| 8 | 110.47 | 1.33 |

**Table S2.** Experimental and calculated $^{13}$C-NMR chemical shifts of **1**.

| Position | Experimental | Calculated | Fitted | Residue |
|---|---|---|---|---|
| 1 | 148.3 | 157.6497721 | 148.3272 | -0.0272 |
| 2 | 128.5 | 139.5167951 | 130.8624 | -2.36239 |
| 3 | 135 | 142.8913135 | 134.1126 | 0.887439 |
| 4 | 123.5 | 129.0017913 | 120.7348 | 2.765164 |
| 5 | 151.4 | 160.7459463 | 151.3093 | 0.090709 |
| 6 | 186.4 | 193.7836939 | 183.1297 | 3.270327 |
| 7 | 94 | 98.3128387 | 91.1767 | 2.823299 |
| 8 | 170.5 | 179.9479279 | 169.8037 | 0.696277 |
| 9 | 140.5 | 141.3593472 | 136.637 | 3.86296 |
| 10 | 164.3 | 172.2550605 | 162.3943 | 1.905679 |
| 11 | 148.4 | 169.691203 | 149.925 | -1.5249 |
| 12 | 99 | 106.2241465 | 98.7965 | 0.203505 |
| 13 | 135.6 | 137.8683478 | 131.275 | 4.32532 |
| 14 | 127.8 | 141.0855288 | 132.373 | -4.5733 |
| 15 | 23.6 | 31.06219489 | 26.40409 | -2.80409 |
| 16 | 41.5 | 44.55883742 | 39.40341 | 2.096587 |
| 17 | 40.4 | 49.48447924 | 44.14756 | -3.74756 |
| 18 | 25.3 | 29.42959099 | 24.83164 | 0.468355 |
| 19 | 27.6 | 30.48711538 | 25.8502 | 1.749798 |
| 20 | 75.1 | 88.64159996 | 79.86183 | -4.76183 |
| 21 | 44 | 53.25734315 | 47.7814 | -3.7814 |
| 22 | 25.8 | 30.98632834 | 26.33102 | -0.53102 |
| 23 | 29.7 | 34.43590228 | 29.65348 | 0.046515 |
| 24 | 173.6 | 183.4828274 | 173.2084 | 0.39163 |
| 25 | 67 | 74.17570582 | 67.92897 | -0.92897 |
| 26 | 19.5 | 21.48233474 | 17.17723 | 2.322773 |
| 27 | 18.1 | 21.29209459 | 16.994 | 1.106004 |
| 28 | 150.5 | 159.124968 | 149.748 | 0.751958 |

| | | | | |
|---|---|---|---|---|
| 29 | 114.3 | 124.6640714 | 116.557 | -2.25695 |
| 30 | 21.7 | 22.50753193 | 18.16465 | 3.535352 |

## References:


1. Noel M OBoyle, Tim V, ermeersch, Christopher J Flynn, Anita R Maguire Maguire, and Geoffey R Hutchison. Confab-systematic generation of diverse low-energy conformers. *Journal of Cheminformatics*, 2011, 3, 3–8.
2. Stephens, P. J.; Harada, N. ECD cotton effect approximated by the Gaussian curve and other methods. *Chirality* 2010, 22, 229–233.
3. Michael W. Lodewyk, Matthew R. Siebert, and Dean J. Tantillo. Computational Prediction of 1H and 13C Chemical Shifts: A Useful Tool for Natural Product, Mechanistic, and Synthetic Organic Chemistry. *Chem. Rev.*, 2012, 112, 1839–1862.

## Antimicrobial assay

**Antifungal bioassay:** The isolated compounds were tested in vitro for the antifungal activity against five pathogenic fungi: *Alternaria alternata* (*A. alternata*), *Botrytis cinerea* (*B. cinerea*), *Fusarium oxysporum* (*F. oxysporum*), *Penicillium digitatum* (*P. digitatum*), and *Valsa mali* (*V. mali*). All of these phytopathogenic fungi tested were purchased from Qingdao Agricultural University (Qingdao, People's Republic of China). Antifungal activity was assessed by the microbroth dilution method in 96-well flat-microtiter plates using potato dextrose (PD) medium. The test compounds were made up to 2 mg/mL in DMSO. The commercial fungicide prochloraz was used as a positive control. The solution of equal concentration of DMSO was used as a negative control. The fungi were incubated in the PD medium for 18−36 h at 28 ± 0.5 ℃ at 150 rpm, and spore concentrations of different microorganism were diluted to approximately $1 \times 10^6$ colony-forming units/mL (CFU/mL) with PD medium. Test compounds (10 μL) were added to 96-well microplates, and 90 μL of PD medium was added. Serial dilutions were made in the 96-well round-bottom sterile plates in triplicate in 50 μL of PD medium, and then 50 μL of the fungal suspension was added. In flat-microtiter plates, tested compounds, fungal suspension, and sterile water were added to make up final concentrations of the compounds in the range of 1−64 μg/mL. Each measurement consisted of three replicates. Cultures then grew in the dark at 28 ± 0.5 ℃ for 48 h. Minimum inhibitory concentrations (MICs) were inspected as the lowest concentrations in which no fungal growth could be observed.

**Antibacterial bioassay:** The isolated compounds were tested in vitro for the antibacterial activity against four pathogenetic bacteria: *Escherichia coli* (*E. coli*), *Micrococcus luteus* (*M. luteus*), *Pseudomonas aeruginosa* (*P. aeruginosa*), and *Ralstonia solanacearum* (*R. solanacearum*). Antibacterial activity was assessed by the microbroth dilution method in 96-well flat-microtiter plates using a beef protein liquid (BP) medium. Antibacterial activity was assessed according to the same procedure as antifungal bioassay. Chloromycetin was used as a positive control, and the solution of equal concentration of DMSO was used as a negative control. Cultures were grown for 24 h at 37 ± 0.5 ℃ in the dark without shaking, in a moist chamber.

**Table S3.** $^{1}H$, $^{13}C$ NMR COSY and HMBC data of compound **1** in DMSO-$d_6$.

| Position | $\delta_H$ (mult, *J* in Hz) | $\delta_C$, type | COSY | HMBC |
|---|---|---|---|---|
| 2 | 8.89 (s) | 148.3, CH | | 4, 7, |
| 3 | | 128.5, C | | |
| 4 | 8.14 (d, 8.0) | 135.0, CH | 5 | 2, 6, 7 |
| 5 | 7.50 (m) | 123.5, CH | 4, 6 | 3 |
| 6 | 8.66 (d, 4.5) | 151.4, CH | 5 | 4 |
| 7 | | 186.4, C | | |
| 9 | | 164.3, C | | |
| 10 | | 140.5, C | | |
| 11 | | 170.5, C | | |
| 12 | 7.09 (s) | 94.0, CH | | 3, 10 |
| 14 | | 99.0, C | | |
| 15 | 7.32 (s) | 148.4, CH | | 9, 11, 16, 20 |
| 16 | | 135.6, C | | |
| 17 | 5.75 (s) | 127.8, CH | 18 | 14, 19, 30 |
| 18a | 2.29 (overlap) | 23.6, $CH_2$ | 17, 19 | 16, 20, 24 |
| 18b | 2.06 (d, 18.0) | | | |
| 19 | 2.57 (dd, 5.0, 12.0) | 41.5, CH | 18 | 14, 17, 21, 25, 29 |
| 20 | | 40.4, C | | |
| 21a | 1.89 (t, 12.5) | 25.3, $CH_2$ | 22 | 14, 19, 23, 31 |
| 21b | 0.77 (d, 12.5) | | | |
| 22a | 2.18 (t, 14.0) | 27.6, $CH_2$ | 21 | 20, 24, 32 |
| 22b | 1.31 (d, 14.0) | | | |
| 23 | | 75.1, C | | |
| 24 | | 44.0, C | | |
| 25a | 2.27 (overlap) | 25.8, $CH_2$ | 26 | 19, 23, 27, 29 |
| 25b | 1.45 (d, 15.5) | | | |
| 26a | 2.42 (dt, 14.0, 5.0) | 29.7, $CH_2$ | 25 | 24 |
| 26b | 2.20 (overlap) | | | |
| 27 | | 173.6, C | | |
| 29 | 4.43 (s) | 67.0, $CH_2$ | | 19, 23, 25 |
| 30 | 1.36 (s) | 19.5, $CH_3$ | | 14, 17 |
| 31 | 0.94 (s) | 18.1, $CH_3$ | | 14, 19, 20 |
| 32 | | 150.5, C | | |
| 33a | 5.08 (s) | 114.3, $CH_2$ | | 23, 34 |
| 33b | 4.84 (s) | | | |
| 34 | 1.75 (s) | 21.7, $CH_3$ | | 23, 33 |

**Table S4.** $^{1}H$, $^{13}C$ NMR COSY and HMBC data of compound **6** in DMSO-$d_6$.

| Position | $\delta_H$ (mult, *J* in Hz) | $\delta_C$, type | COSY | HMBC |
|---|---|---|---|---|
| 1a | 4.44 (d, 11.0) | 67.2, $CH_2$ | 2 | 3, 7′ |
| 1b | 4.26 (dd, 11.0, 7.0) | | | |
| 2 | 3.71 (m) | 69.2, CH | 1, 3 | 4 |
| 3 | 3.42 (overlap) | 72.5, CH | 2, 4 | 1 |
| 4a | 3.58 (m) | 63.0, $CH_2$ | 3 | 2 |
| 4b | 3.36 (overlap) | | | |
| 1′ | | 103.6, C | | |
| 2′ | | 161.1, C | | |
| 3′ | | 108.2, C | | |
| 4′ | | 160.7, C | | |
| 5′ | 6.30 (s) | 109.2, CH | | 1′, 3′, 9′ |
| 6′ | | 145.1, C | | |
| 7′ | | 171.0, C | | |
| 8′ | 1.93 (s) | 8.2, $CH_3$ | | 2′, 4′ |
| 9′ | 2.78 (m) | 28.6, $CH_2$ | 10′ | 1′, 5′ |
| 10′ | 1.10 (t, 7.5) | 16.2, $CH_3$ | 9′ | 6′ |

**Table S5.** $^{1}H$, $^{13}C$ NMR COSY and HMBC data of compound **7** in DMSO-$d_6$.

| Position | $\delta_H$ (mult, *J* in Hz) | $\delta_C$, type | COSY | HMBC |
|---|---|---|---|---|
| 1a | 4.24 (d, 11.0) | 66.2, $CH_2$ | 2 | 3, 1′ |
| 1b | 4.01 (dd, 11.0, 7.5) | | | |
| 2 | 3.59 (m) | 69.4, CH | 1, 3 | 4 |
| 3 | 3.38 (overlap) | 72.3, CH | 2, 4 | 1 |
| 4a | 3.55 (m) | 63.1, $CH_2$ | 3 | 2 |
| 4b | 3.39 (overlap) | | | |
| 1′ | | 166.5, C | | |
| 2′ | 5.88 (d, 15.5) | 119.3, CH | 3′ | 4′ |
| 3′ | 7.24 (dd, 15.5, 10.0) | 145.0, CH | 2′, 4′ | 1′, 5′ |
| 4′ | 6.27 (overlap) | 129.8, CH | 3′, 5′ | 2′, 6′ |
| 5′ | 6.25 (overlap) | 142.0, CH | 4′, 6′ | 3′, 7′ |
| 6′ | 2.22 (m) | 42.6, $CH_2$ | 5′, 7′ | 4′, 8′ |
| 7′ | 3.70 (m) | 65.6, CH | 6′, 8′ | 5′ |
| 8′ | 1.05 (d, 6.0) | 23.3, $CH_3$ | 7′ | 6′ |

**Table S6.** The experimental and reported specific rotations of compounds **2**−**5**.

| Compounds | Experimental specific rotations/$[\alpha]_D^{25}$ | Reported specific rotations/$[\alpha]_D^{25}$ | Ref. |
|---|---|---|---|
| **2** | +71 °(*c* 0.1, $CH_2Cl_2$) | +58 °(*c* 0.1, $CH_2Cl_2$) | [1] |
| **3** | +149 °(*c* 0.1, $CH_2Cl_2$) | +124 °(*c* 0.2, $CH_2Cl_2$) | [2] |
| **4** | +137 °(*c* 0.1, $CH_2Cl_2$) | +167 °(*c* 0.2, $CH_2Cl_2$) | [1] |
| **5** | +85 °(*c* 0.2, $CH_2Cl_2$) | +104 °(*c* 0.1, $CH_2Cl_2$) | [3] |

## References


[1] Li, C.; Gloer, J.B.; Wicklow, D.T.; Dowd, P.F. Antiinsectan decaturin and oxalicine analogues from *Penicillium thiersii*. *J. Nat. Prod.* **2005**, *68*, 319–322.

[2] Zhang, Y.; Li, C.; Swenson, D.C.; Gloer, J.B.; Wicklow, D.T.; Dowd, P.F. Novel antiinsectan oxalicine alkaloids from two undescribed fungicolous *Penicillium* spp. *Org. Lett.* **2003**, *5*, 773–776.

[3] Wang, P.L.; Li, D.Y.; Xie, L.R.; Wu, X.; Hua, H.M.; Li, Z.L. Novel decaturin alkaloids from the marine-derived fungus *Penicillium oxalicum*. *Nat. Prod. Commun.* **2013**, *8*, 1397–1398.