SUPPLEMENTARY MATERIALS FOR

Antimicrobial metabolites from the Indonesian mangrove sediment-derived fungus *Penicillium chrysogenum* sp. ZZ1151

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ABSTRACT

A total of 14 compounds including a novel tetrasubstituted benzene derivative peniprenylphenol A were isolated from a scaled-up culture of the Indonesian mangrove sediment-derived fungus *Penicillium chrysogenum* ZZ1151 in rice medium. Structures of the isolated compounds were determined based on their NMR spectroscopic analyses, HRESIMS data, optical rotation calculations and comparison with the reported data. New peniprenylphenol A (**1**) was found to have antimicrobial activities against human pathogenic methicillin-resistant *Staphylococcus aureus* (MRSA), *Escherichia coli* and *Candida albicans* with MIC values of 6, 13, and 13 μg/mL, respectively. The known compounds of penicimumide (**2**), preparaherquamide (**5**), uridine (**6**), thymine (**7**), 1,2-seco-trypacidin (**8**) communol G (**9**), clavatol (**10**), 4-hydroxybenzeneacetic acid methyl ester (**11**), 2,5-dihydroxyphenylacetic acid methyl ester (**12**), 2-hydroxyphenylacetic acid methyl ester (**13**) and 4-hydroxyphenylethanone (**14**) showed antimicrobial activity against at least one of the three tested pathogens with MIC values of 3−25 μg/mL.

CONTENT

Experimental Section

1. General experimental procedures

Octadecyl-functionalized silica gel (ODS, Cosmosil 75C_{18}–Prep, Nacalai Tesque Inc., Japan) and Sephadex LH-20 (GE Healthcare) were used for column chromatography. HPLC separation was performed on a CXTH LC-3000 preparative HPLC system (Beijing Chuangxin Tongheng Science & Technology Co. Ltd.) using a Fuji-C_{18} CT-30 column (280 × 30 mm, 10 μm) or a 1260 HPLC system (Agilent Technologies) using a Zorbax SB-C_{18} column (250 × 9.4 mm, 5 μm) with a DAD detector. All solvents used for this study were bought from the Shanghai Lingfeng Co. Ltd. (China). NMR spectra were acquired on a JEOL 600 spectrometer (Japan) using standard programs and acquisition parameters. Chemical shifts were expressed in δ (ppm) and referred to the NMR solvent of DMSO-d_6 (δ_C 39.5, δ_H 2.50). Optical rotation values were obtained from an Autopol I polarimeter (Rudolph Research Analytical). UV, ECD, and IR spectra were recorded on a METASH UV-8000 spectrometer (Shanghai METASH Instruments Co. Ltd., China), a JASCO J-815 spectropolarimeter (JASCO Co. Tokyo, Japan), and a Bruker TENSOR II high performance FT-IR spectrometer (Bruker, Germany), respectively. HRESIMS data were obtained from an Agilent 6230 TOF LC/MS spectrometer. Methicillin-resistant *Staphylococcus aureus* (MRSA) ATCC 43300, *Escherichia* coli ATCC 25922, and *Candida albicans* ATCC 10231 were gifts from Drs. Zhongjun Ma, Pinmei Wang, and Bin Wu, respectively. Gentamicin (99.6%), vancomycin (98.0%) and amphotericin B (>95.0%) were purchased from Meilune Biotechnology Co. Ltd. (Dalian, China). Gauze′s agar and rice were purchased from Guangdong Huankai Microbial Science and Technology Co. Ltd. (China) and Yihai Kerry Co. Ltd. (Beijing, China), respectively. Different media were made in the authors′ laboratory, including B solid medium (soluble starch 20.0 g, KNO_3 1.0 g, $MgSO_4 \cdot 7H_2O$ 0.5 g, NaCl 0.5 g, K_2HPO_4 0.5 g, $FeSO_4$ 0.01 g, agar 20.0 g, water 1 L), BY solid medium (soluble starch 20.0 g, KNO3 1.0 g, $MgSO_4 \cdot 7H_2O$ 0.5 g, NaCl 0.5 g, K_2HPO_4 0.5 g, $FeSO_4$ 0.01 g, agar 20.0 g, sea salt 35.0 g, water 1 L), PDA solid medium (potatoes 200.0 g, glucose 20.0 g, agar 20.0 g, boiled into 1 L of water for 15 min), PDAY solid medium (potatoes 200.0 g, glucose 20.0 g, agar 20.0 g, sea salt 35.0 g, boiled into 1 L of water for 15 min), E solid medium (yeast

1.0 g, tryptone 5.0 g, $FeCl_3 \cdot 6H_2O$ 0.17 g, KH_2PO_4 0.12 g, agar 20.0 g, water 1 L), EY solid medium (yeast 1.0 g, tryptone 5.0 g, $FeCl_3 \cdot 6H_2O$ 0.17 g, KH_2PO_4 0.12 g, agar 20.0 g, sea salt 35.0 g, water 1 L), ISP-2 solid medium (yeast extract 4.0 g, malt extract 10.0 g, dextrose 4.0 g, peptone 5.0 g, agar 20.0 g, water 1 L), ISP-2Y solid medium (yeast extract 4.0 g, malt extract 10.0 g, dextrose 4.0 g, peptone 5.0 g, agar 20.0 g, sea salt, 35.0 g, water 1 L), ISP-4 solid medium (soluble starch 10.0 g, K_2HPO_4 1.0 g, $MgSO_4 \cdot 7H_2O$ 1.0 g, NaCl 1 g, $(NH_4)_2SO_4$ 2.0 g, $CaCO_3$ 2.0 g, $FeSO_4$ 1.0 mg, $MnCl_2$ 1.0 mg, $ZnSO_4$ 1.0 mg, agar 20 g, water 1 L), ISP-4Y solid medium (soluble starch 10.0 g, K_2HPO_4 1.0 g, $MgSO_4 \cdot 7H_2O$ 1.0 g, NaCl 1 g, $(NH_4)_2SO_4$ 2.0 g, $CaCO_3$ 2 g, $FeSO_4$ 1.0 mg, $MnCl_2$ 1.0 mg, $ZnSO_4$ 1.0 mg, agar 20.0 g, sea salt, 35.0 g, water 1 L).

2. Isolation and identification of strain ZZ1151

The strain ZZ1151 was isolated from a sediment sample, which was collected from mangrove vegetated tidal flat of Pangkep District South Sulawesi Province, Indonesia. Briefly, sediment sample was air dried at 28 °C for 7 days and the dried sample (1.0 g) was diluted with sterile water to make dilutions of 10^{-2}, 10^{-3}, and 10^{-4} g/mL. Each dilution (200 µL) was transferred to the surface of ten different solid media of B, BY, PDA, PDAY, E, EY, ISP-2, ISP-2Y, ISP-4, and ISP-4Y in Petri dishes following spread plate technique and incubated at 28 °C for 14 days. The single green colored colony of ZZ1151 was picked from the PDA medium plate containing sample with a concentration of 10^{-2} g/mL and then transferred to another PDA medium plate. After an incubation period of 7 days at 28 °C, the single pure colony (ZZ1151) that grew well was transferred onto PDA slant medium and stored at 4 °C for further study.

The strain ZZ1151 was identified by using ITS rDNA sequence analysis conducted by Hangzhou Lizhen Biotechnology Company and its ITS rDNA sequence using nucleotide BLAST (Basic Local Alignment Search Tool) was compared to the GenBank database. The ITS rDNA sequence of strain ZZ1151 has been deposited in the GenBank with accession no. OK605318. The strain (*Penicillium chrysogenum* sp. ZZ1151) was preserved at the Laboratory of Institute of Marine Biology and Pharmacology, Ocean College, Zhoushan Campus, Zhejiang University, China.

3. Scale up culture of strain ZZ1151

For preparing seed broth, pure colony of the strain ZZ1151 from the PDA slant medium was inoculated into a 500 mL Erlenmeyer flask containing 250 mL of liquid potato dextrose broth (PDB) medium and incubated for a period of 4 days in a shaker (180 rpm, 28 °C). The prepared seed broth (5 mL) was inoculated into rice medium (40 g rice with 60 mL 3.5% sea salt solution, g/mL) in 500 mL Erlenmeyer flask and then incubated at 28 °C for 45 days in a static condition. A total of 300 culture flasks were prepared for this study.

4. Extraction and isolation of compounds 1–14

The rice culture in each flask was extracted with EtOAc (300 mL) three times by soaking for 24 h. The combined EtOAc extract solution was dried in *vacuo* to give an extract (94.2 g). This extract was fractionated on a column (160 × 10 cm) of silica gel (500 g) eluting with a mixture of cyclohexane and EtOAc in different ratios (10: 1, 5: 1, 2: 1, 1: 1, 1: 2, 1000 mL each) to give five fractions (Frs. A–E, 1000 mL each).

Fr. A (16.3 g) was fractionated on an ODS (200 g) column (530 × 35 mm) eluting successively with 20%, 30%, 40%, and 50% aqueous solution of MeOH (500 mL each) to give eight subfractions (SFrs. A_1–A_8) with 250 mL eluting solution for each subfraction. Compound **6** (26.3 mg, t_R 19.4 min) was purified from SFr. A_2 by using a Fuji-C_{18} CT-30 column (280 × 30 mm, 10 μm; mobile phase: MeOH/H_2O, 10/90; flow rate: 10 mL/m in; UV detection: 210 nm). By using the same column and mobile phase, SFr. A_3 was separated into SFr. A_{3a} (t_R 23.0 mins) and A_{3b} (t_R 27.2 mins). SFr. A_{3a} was further purified by using an Agilent Zorbax SB-C_{18} column (250 × 9.4 mm, 5 μm; mobile phase: MeOH/H_2O, 8/92; flow rate: 1.0 mL/min; UV detection: 210 nm) to afford compound **7** (4.9 mg; t_R 23.6 mins).

Likewise, Fr. B (27.5 g) was also fractionated by the ODS (200 g) column (530 × 35 mm) eluting with 40% (500 mL), 50% (700 mL), 60% (500 mL), and 70% (500 mL) MeOH. A total of seven subfractions (SFrs. B_1–B_7) was obtained based on result of silica gel TLC and HPLC analyses. Among them, SFrs. B_1 (500 mL), B_2–B_3 (350 mL each), B_4–B_5 (250 mL each), and B_6–B_7 (250 mL each) were from the eluted samples of 40%, 50%, 60%, and 70% MeOH, respectively. SFr. B_1 was repeatedly separated on an ODS (100 g) column (400 × 35

mm) eluting with 40% MeOH (500 mL) to give five subfractions (SFrs. B_{1a}–B_{1e}, 100 mL each). SFr. B_{1d} was further separated on the Fuji-C_{18} CT-30 column (mobile phase: MeOH/H_2O, 45/60; flow rate: 10 mL/min; UV detection: 210 nm) to yield SFrs $B_{1d\text{-}1}$ (t_R 36.4 min) and s and $B_{1d\text{-}2}$ (41.2 min). Compounds **1** (3.3 mg, t_R 31.6 min, ACN/H_2O, 20/80) and **3** (3.5 mg, t_R 25.8 min, MeOH/H_2O, 58/42) were obtained from SFrs $B_{1d\text{-}1}$ and $B_{1d\text{-}2}$, respectively, by purifying on the Agilent Zorbax SB-C_{18} column (flow rate: 1.0 mL/min; UV detection: 210 nm). SFr. B_{1e} was also purified by the Agilent Zorbax SB-C_{18} column (mobile phase: ACN/H_2O, 25/75; flow rate: 1.0 mL/min; UV detection: 210 nm) to afford **14** (3.0 mg, t_R 25.2 mins). By using the Fuji-C_{18} CT-30 column (flow rate: 10 mL/min; UV detection: 210 nm), compound **12** (73.5 mg; t_R 33.5 min, MeOH/H_2O, 40/60) were purified from SFr. B_2, while compounds **11** (19.1 mg, t_R 28.4 min) and **13** (17.1 mg, t_R 33.5 min, MeOH/H_2O, 55/45) were obtained from SFr. B_4.

Similarly, Fr. C (22.1 g) was fractionated on an ODS (200 g) column eluting with 60%, 70%, 80%, and 100% MeOH (500 mL each) to give ten subfractions (SFrs. C_1–C_{10}, 200 mL each). SFr. C_1 was further fractionated by a Sephadex LH-20 (100 g) column eluting with 60% MeOH (700 mL) to give SFrs. C_{1a}–C_{1g} (100 mL each). SFr. C_{1d} was purified by the Fuji-C_{18} CT-30 column (mobile phase: MeOH/H_2O, 65/35; flow rate: 10 mL/min; UV detection: 210 nm) to get compound **10** (11.1 mg, t_R 34.7 min). SFr. C_{1c} was purified by the Agilent Zorbax SB-C_{18} column (mobile phase: ACN/H_2O, 55/45; flow rate: 1.0 mL/min; UV detection: 210 nm) to give compound **8** (2.3 mg, t_R 24.7 min). Whereas SFr. C_7 was further separated by the Fuji-C_{18} CT-30 column (mobile phase: MeOH/H_2O, 77/23; flow rate: 10 mL/min; UV detection: 210 nm) to afford SFrs. C_{7a}–$C_{7c.}$ Purification of SFr. C_{7b} by the Agilent Zorbax SB-C_{18} column (mobile phase: ACN/H_2O, 38/62; flow rate: 1.0 mL/min) to give compound **5** (1.6 mg, t_R 26.7 mins). Finally, SFr. C_6 was fractionated by a Sephadex LH-20 (100 g) column eluting with 65% MeOH (500 mL) to give SFrs. $C_{7a\text{–}7g}$ (50 mL each). SFr. C_{1g} was then purified by the Agilent Zorbax SB-C_{18} column (mobile phase: MeOH/H_2O, 68/32; flow rate: 1.0 mL/min) to yield compound **9** (1.9 mg, t_R 26.5 min).

In the same way, fraction D (19.6 g) was fractionated on an ODS (200 g) column eluting successively with 80%, 90%, and 100% MeOH (600 mL each) to furnish nine

subfractions (SFrs. D_1–D_9, 200 mL each). Compound **4** (6.3 mg, t_R 29.0 min) was obtained from SFr. D_7 through purification by using the Fuji-C_{18} CT-30 column (mobile phase: MeOH/H_2O, 85/15; flow rate: 10 mL/min; UV detection: 210 nm). SFr. D_9 was also separated on the Fuji-C_{18} CT-30 column (mobile phase: MeOH/H_2O, 88/12; flow rate: 10 mL/min; UV detection: 210 nm) to give SFrs. $D_{9a–9c}$. Compound **2** (1.7 mg; t_R 37.9 mins) was purified from SFr. D_{9c} by using the Agilent Zorbax SB-C_{18} column (mobile phase: ACN/H_2O, 75/25; flow rate: 1.0 mL/min; UV detection: 210 nm).

Penicimumide (**2**): Colorless oil; molecular formula $C_{14}H_{27}NO$; $[\alpha]^{20}_D$ –32º; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in $CDCl_3$), see Table S11; HRESIMS *m/z* 226.2169 $[M + H]^+$ (calcd for $C_{14}H_{28}NO$, 226.2171), 248.1989 $[M + Na]^+$ (calcd for $C_{14}H_{27}NNaO$, 248.1990).

(8*R*,9*S*)-Dihydroisoflavipucine (**3**): Colorless crystal; molecular formula $C_{12}H_{17}NO_4$; $[\alpha]^{20}_D$ +136.9º; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table S11;

Peniciherquamide A (**4**): Colorless oil; molecular formula $C_{27}H_{33}N_3O_4$; $[\alpha]^{20}_D$ +85.85º; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) NMR data (in $CDCl_3$), see Table S12.

Preparaherquamide (**5**): Colorless oil; molecular formula $C_{22}H_{27}N_3O$; $[\alpha]^{20}_D$ +116.38º; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in $CDCl_3$), see Table S12.

Uridine (**6**): Colorless crystal; molecular formula $C_9H_{12}N_2O_6$; $[\alpha]^{20}_D$ +60º; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table S13.

Thymine (**7**): Bright yellow needle crystal; molecular formula $C_5H_6N_2O_2$; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table 13.

1,2-Seco-trypacidin (**8**): White amorphous powder; molecular formula $C_{18}H_{18}O_7$; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table S14.

Communol G (**9**): Yellow amorphous powder; molecular formula $C_{11}H_{14}O_4$; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table S14.

Clavatol (**10**): Colorless oil; molecular formula $C_{10}H_{12}O_3$; ^{13}C NMR (150 MHz) and ^1H NMR (600 MHz) data (in DMSO-d_6), see Table S14.

4-Hydroxybenzeneacetic acid methyl ester (**11**): Colorless oil; molecular formula

$C_9H_{10}O_3$; ^{13}C NMR data (150 MHz, in DMSO-d_6), see Table S15, ^1H NMR data (600 MHz, in DMSO-d_6), see Table S16.

2,5-Dihydroxyphenylacetic acid methyl ester (**12**): Pale yellow oil; molecular formula $C_9H_{10}O_4$; ^{13}C NMR data (150 MHz, in DMSO-d_6), see Table S15, ^1H NMR data (600 MHz, in DMSO-d_6), see Table S16.

2-Hydroxyphenylacetic acid methyl ester (**13**): White amorphous powder; molecular formula $C_9H_{10}O_3$; ^{13}C NMR data (150 MHz, in DMSO-d_6), see Table S15, ^1H NMR data (600 MHz, in DMSO-d_6), see Table S16.

4-Hydroxyphenylethanone (**14**): Colorless needle crystal; molecular formula $C_8H_8O_2$; ^{13}C NMR data (150 MHz, in DMSO-d_6), see Table S15, ^1H NMR data (600 MHz, in DMSO-d_6), see Table S16.

5. Optical rotation (OR) calculations

Monte Carlo conformational searches were carried out by means of the Spartan′s 10 software using Merck Molecular Force Field (MMFF). The conformers with Boltzmann-population of over 5% were chosen for optical rotation (OR) calculations, and then the conformers were initially optimized at B3LYP/6-31+g (d, p) level in MeOH using the Conductor-like Polarizable Continuum Model (CPCM). The theoretical calculation of OR was conducted in MeOH using Time-dependent Density Functional Theory (TD-DFT) at the B3LYP/6-311+g (d, p) level for all conformers of the tested compound.

6. ECD calculations

Monte Carlo conformational searches were carried out by means of the Spartan′s 10 software using Merck Molecular Force Field (MMFF). The conformers with Boltzmann-population of over 5% were chosen for ECD calculations and then the conformers were initially optimized at B3LYP/6-31+g (d, p) level in MeOH using the CPCM polarizable conductor calculation model. The theoretical calculation of ECD was conducted in MeOH using Time-dependent Density functional theory (TD-DFT) at the B3LYP/6-311+g (d, p) level for all conformers of compound **1**. Rotatory strengths for a total of 30 excited states were calculated. ECD spectra were generated using the program SpecDis 1.6

(University of Würzburg, Würzburg, Germany) and GraphPad Prism 5 (University of California San Diego, USA) from dipole-length rotational strengths by applying Gaussian band shapes with sigma = 0.3 eV.

7. Antimicrobial activity assay

The micro-broth dilution method as described in the previous study (Ye et al. 2016) was applied to determine the antimicrobial activities of tested compounds against the growth of methicillin-resistant *Staphylococcus aureus (*MRSA), *Escherichia coli*, and *Candida albicans*. Vancomycin, gentamicin, and amphotericin B were used as positive controls.

Figure S_1. Colony of *Penicillium chrysogenum* sp. ZZ1151 cultured in PDA medium

Figure S_2. ITS rDNA sequence of *Penicillium chrysogenum* sp. ZZ1151

TTCGGGTTGATCGGCAAGCGCCGGCCGGGCCTACAGAGCGGGTGACAAAGCCCC
ATACGCTCGAGGACCGGACGCGGTGCCGCCGCTGCCTTTCGGGCCCGTCCCCCG
GGATCGGAGGACGGGGCCCAACACACAAGCCGTGCTTGAGGGCAGCAATGACG
CTCGGACAGGCATGCCCCCCGGAATACCAGGGGGCGCAATGTGCGTTCAAAGAC
TCGATGATTCACTGAATTTGCAATTCACATTACGTATCGCATTTCGCTGCGTTCTTC
ATCGATGCCGGAACCAAGAGATCCGTTGTTGAAAGTTTTAAATAATTTATATTTTC
ACTCAGACTACAATCTTCAGACAGAGTTCGAGGGTGTCTTCGGCGGGCGCGGGC
CCGGGGGGCGTAAGCCCCCCGGCGGCCAGTTAAGGCGGGCCCGCCGAAGCAACA
AGGTAAAATAAACACGGGTGGGAGGTTGGACCCAGAGGGCCCTCACTCGGTAAT
GATCCTTCCGCAGG (503 bp)

Figure S_3**.** Key HMBC correlations of **1** (A) and the experimental ECD spectrum of **1** and the calculated ECD curves of the model molecules of 8*S*-**1** and 8*R*-**1** at the b3lyp/6-311+g (d, p) level (B)

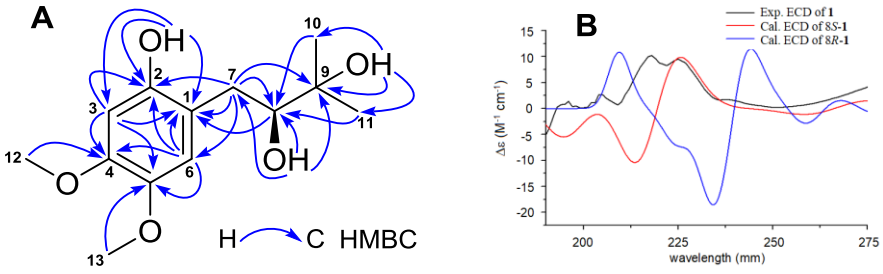


Table S_1. Sequences producing significant alignments of strain ZZ1151

Accession	Description	Max score	Total score	Query coverage	E-value	Identity (%)
MK267450.1	*Penicillium chrysogenum* isolate E20401_ITS small subunit ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal transcribed spacer 2, complete sequence; and large subunit ribosomal RNA gene, partial sequence	929	929	100%	0	100
MK178856.1	*Penicillium chrysogenum* isolate Seq_MEL-07 small subunit ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal transcribed spacer 2, complete sequence; and large subunit ribosomal RNA gene, partial sequence	929	929	100%	0	100
MH865997.1	*Penicillium chrysogenum* strain CBS 132216 small subunit ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal transcribed spacer 2, complete sequence; and large subunit ribosomal RNA gene, partial sequence	929	929	100%	0	100
MF077262.1	*Penicillium chrysogenum* strain F-98 small subunit ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal transcribed spacer 2, complete sequence; and large subunit ribosomal RNA gene, partial sequence	929	929	100%	0	100
MF077261.1	*Penicillium chrysogenum* strain F-94 small subunit ribosomal RNA gene, partial sequence; internal transcribed spacer 1, 5.8S ribosomal RNA gene, and internal transcribed spacer 2, complete sequence; and large subunit ribosomal RNA gene, partial sequence	929	929	100%	0	100

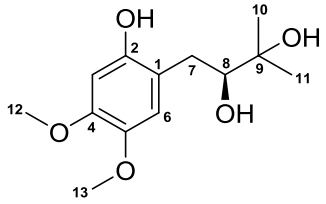


Table S_2. ^{13}C NMR (150 MHz) and ^{1}H NMR (600 MHz) data of peniprenlphenol A (**1**, in DMSO-d_6)

No.	δ_C, type	δ_H, *J* in Hz	H → C
1	118.0, C	–	–
2	149.4, C	–	–
3	101.2, CH	6.42, s	C_1, C_2, C_4, C_5
4	147.6, C	–	–
5	141.4, C	–	–
6	116.1, CH	6.71, s	C_1, C_2, C_4, C_5, C_7
7	31.8, CH_2	2.77, dd (14.2, 2.2); 2.30, dd (14.2, 10.1)	C_1, C_2, C_6, C_8, C_9
8	78.4, CH	3.35, m	C_1, C_7, C_9, C_{10}, C_{11}
9	71.7, C	–	–
10	26.2[a], CH_3	1.09[a], s	C_8, C_9, C_{11}
11	24.6[a], CH_3	1.08[a], s	C_8, C_9, C_{10}
12	55.5, CH_3	3.67, s	C_4
13	56.4, CH_3	3.65, s	C_5
OH-2	–	8.88, s	C_1, C_2, C_3
OH-8	–	4.86, d (5.6)	C_7, C_8, C_9
OH-9	–	4.22, s	C_8, C_9, C_{10}, C_{11}

[a] The data with the same label in each column may be interchanged.

Table S_3. Gibbs free energies[a] and equilibrium populations[b] of low-energy conformers of 8*R*-**1**

Conformers	In MeOH	
	E	Optical rotation (OR)
8*R*-**1a**	-883.5912487	-43.92
8*R*-**1b**	-883.5877371	-108.94
8*R*-**1c**	-883.5876964	4.44
8*R*-**1d**	-883.5875648	57.56
8*R*-**1e**	-883.5850352	-64.79
Average		–42.46

[a] B3LYP/6-31+G (d, p), in kcal/mol; [b] from Δ*G* values at 298.15K.

Table S_4. Cartesian coordinates for the low-energy reoptimized MMFF conformers of **8*R*-1** at B3LYP/6-311+G (d, p) level of theory in MeOH

8*R*-**1a**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	2.0425	-0.6361	-1.5862
2	6	0	1.4036	-1.8063	-2.0105
3	6	0	0.0504	-1.9879	-1.6800
4	6	0	-0.6188	-1.0302	-0.9027
5	6	0	0.0200	0.1416	-0.4722
6	6	0	1.3604	0.3143	-0.8232
7	8	0	0.9157	2.0141	1.8315
8	6	0	-0.3214	1.2672	1.7806
9	6	0	-0.7671	1.1687	0.3141
10	6	0	-2.5786	1.1046	2.9669
11	6	0	-1.3377	1.9664	2.7255
12	8	0	2.0281	-2.8034	-2.7121
13	6	0	-0.5247	-3.6137	-3.3016
14	8	0	-0.7303	-3.0705	-2.0018
15	6	0	3.4209	-2.6640	-2.9616
16	8	0	2.0835	1.4101	-0.4418
17	6	0	-1.7349	3.3649	2.2440
18	8	0	-0.6561	2.1270	3.9874
19	1	0	3.0827	-0.4331	-1.8169
20	1	0	-1.6625	-1.2092	-0.6518
21	1	0	1.0309	2.2040	2.7894
22	1	0	-0.0872	0.2724	2.1810
23	1	0	-1.8302	0.9116	0.2557
24	1	0	-0.6534	2.1363	-0.1916
25	1	0	-3.1769	0.9755	2.0605
26	1	0	-2.2962	0.1145	3.3421
27	1	0	-3.2198	1.5523	3.7351
28	1	0	-1.4585	-4.0954	-3.6085
29	1	0	-0.2924	-2.8450	-4.0470
30	1	0	0.2465	-4.3889	-3.2740
31	1	0	3.9875	-2.6017	-2.0267
32	1	0	3.6210	-1.8028	-3.6074
33	1	0	3.7553	-3.5605	-3.4925
34	1	0	1.6869	1.7712	0.3829
35	1	0	-2.2844	3.3313	1.2983
36	1	0	-0.8543	4.0035	2.1142
37	1	0	-2.3681	3.8651	2.9862
38	1	0	-1.2824	2.5316	4.6146

8*R*-**1b**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	2.0224	-1.7474	-0.7403
2	6	0	1.1223	-2.3834	-1.5951
3	6	0	-0.1550	-1.8511	-1.7925
4	6	0	-0.4856	-0.6276	-1.1991
5	6	0	0.4194	0.0434	-0.3576
6	6	0	1.6660	-0.5505	-0.1239
7	8	0	1.0528	1.2575	2.4205
8	6	0	-0.2260	1.3114	1.7484
9	6	0	0.0247	1.3809	0.2347
10	6	0	-2.4866	2.4934	1.8976
11	6	0	-1.0202	2.5120	2.3335
12	8	0	1.5291	-3.5441	-2.1998
13	6	0	-1.3067	-3.8002	-2.4094
14	8	0	-1.1321	-2.3955	-2.5834
15	6	0	2.1136	-3.2423	-3.4686
16	8	0	2.6002	0.0072	0.7022
17	6	0	-0.3774	3.8648	2.0135
18	8	0	-0.9814	2.3488	3.7669
19	1	0	3.0016	-2.1790	-0.5568
20	1	0	-1.4674	-0.2038	-1.3992
21	1	0	0.8245	1.4096	3.3646
22	1	0	-0.7422	0.3792	2.0117
23	1	0	-0.8703	1.7401	-0.2844
24	1	0	0.8244	2.0972	0.0064
25	1	0	-2.6023	2.6605	0.8230
26	1	0	-2.9554	1.5367	2.1541
27	1	0	-3.0587	3.2662	2.4240
28	1	0	-2.3487	-4.0349	-2.6486
29	1	0	-0.6773	-4.3525	-3.1126
30	1	0	-1.1234	-4.1242	-1.3785
31	1	0	1.3944	-2.7510	-4.1333
32	1	0	2.4106	-4.1877	-3.9323
33	1	0	3.0112	-2.6246	-3.3539
34	1	0	2.1326	0.5574	1.3702
35	1	0	-0.3897	4.0800	0.9406
36	1	0	0.6592	3.9035	2.3659
37	1	0	-0.9053	4.6763	2.5279
38	1	0	-1.4971	3.0742	4.1633
8*R*-**1c**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	2.0007	-0.5031	-1.8861

2	6	0	1.2851	-1.6283	-2.2941
3	6	0	-0.0465	-1.7934	-1.9027
4	6	0	-0.6278	-0.8604	-1.0370
5	6	0	0.0852	0.2692	-0.5974
6	6	0	1.4070	0.4251	-1.0339
7	8	0	1.1991	1.9867	1.7300
8	6	0	-0.0679	1.2905	1.7257
9	6	0	-0.6110	1.2818	0.2891
10	6	0	-2.2505	1.1555	3.0477
11	6	0	-0.9919	1.9792	2.7680
12	8	0	1.9266	-2.5344	-3.0976
13	6	0	-0.8187	-3.1512	-3.6496
14	8	0	-0.8537	-2.8419	-2.2575
15	6	0	2.5151	-3.5571	-2.2913
16	8	0	2.1866	1.4798	-0.6514
17	6	0	-1.3592	3.4151	2.3824
18	8	0	-0.2258	2.0473	3.9892
19	1	0	3.0262	-0.3586	-2.2123
20	1	0	-1.6588	-1.0150	-0.7263
21	1	0	1.3843	2.1242	2.6857
22	1	0	0.1507	0.2687	2.0619
23	1	0	-1.6844	1.0639	0.2891
24	1	0	-0.4947	2.2693	-0.1757
25	1	0	-2.9106	1.0979	2.1777
26	1	0	-1.9872	0.1367	3.3537
27	1	0	-2.8214	1.5872	3.8780
28	1	0	-0.6705	-2.2642	-4.2762
29	1	0	-0.0545	-3.9066	-3.8528
30	1	0	-1.7876	-3.5854	-3.9154
31	1	0	1.7554	-4.1052	-1.7233
32	1	0	3.2713	-3.1423	-1.6156
33	1	0	3.0120	-4.2652	-2.9611
34	1	0	1.8615	1.8069	0.2173
35	1	0	-1.9679	3.4518	1.4737
36	1	0	-0.4624	4.0248	2.2272
37	1	0	-1.9230	3.9007	3.1876
38	1	0	-0.7908	2.4502	4.6730

8*R*-**1d**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	2.1044	-0.6896	0.5240
2	6	0	1.6058	-1.9285	0.1085
3	6	0	0.2238	-2.1564	0.1991
4	6	0	-0.6295	-1.1379	0.6491

5	6	0	-0.1363	0.1147	1.0470
6	6	0	1.2447	0.3125	0.9821
7	8	0	-0.0224	3.2286	0.9134
8	6	0	-1.2421	2.4689	0.8039
9	6	0	-1.1034	1.1459	1.5764
10	6	0	-3.0509	1.7353	-0.8446
11	6	0	-1.6984	2.4292	-0.6807
12	8	0	2.3842	-2.9314	-0.4055
13	6	0	0.2153	-4.5202	0.1810
14	8	0	-0.4368	-3.3029	-0.1670
15	6	0	3.7730	-2.6734	-0.5670
16	8	0	1.8445	1.4822	1.3553
17	6	0	-0.6698	1.8488	-1.6549
18	8	0	-1.8635	3.8176	-1.0544
19	1	0	3.1638	-0.4584	0.4948
20	1	0	-1.6967	-1.3465	0.6959
21	1	0	-0.1936	4.0253	0.3648
22	1	0	-1.9806	3.0679	1.3551
23	1	0	-0.7841	1.3733	2.6031
24	1	0	-2.0997	0.6967	1.6751
25	1	0	-2.9943	0.6675	-0.6145
26	1	0	-3.8043	2.1934	-0.1940
27	1	0	-3.4236	1.8433	-1.8698
28	1	0	0.7630	-4.4496	1.1275
29	1	0	-0.5586	-5.2841	0.3065
30	1	0	0.8680	-4.8493	-0.6327
31	1	0	4.2574	-2.5038	0.4001
32	1	0	3.9440	-1.8356	-1.2511
33	1	0	4.2273	-3.5634	-1.0132
34	1	0	1.1784	2.2051	1.3295
35	1	0	-0.5635	0.7669	-1.5569
36	1	0	0.3127	2.3146	-1.5235
37	1	0	-0.9634	2.0526	-2.6919
38	1	0	-2.1949	3.8404	-1.9704

	8*R*-**1e**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	-0.8511	2.0452	-1.7329
2	6	0	-1.9786	2.1232	-0.9142
3	6	0	-2.0008	1.4155	0.2912
4	6	0	-0.8701	0.7128	0.7187
5	6	0	0.2820	0.6578	-0.0806
6	6	0	0.2647	1.3200	-1.3136
7	8	0	2.3916	-1.2741	-1.5597

8	6	0	1.6555	-1.4642	-0.3315
9	6	0	1.4908	-0.1201	0.4021
10	6	0	1.6043	-3.0539	1.6738
11	6	0	2.4155	-2.5498	0.4800
12	8	0	-3.0154	2.8685	-1.4100
13	6	0	-4.0245	0.4068	0.6557
14	8	0	-3.0978	1.3954	1.1118
15	6	0	-3.5636	3.7841	-0.4623
16	8	0	1.3679	1.2386	-2.1189
17	6	0	3.8059	-2.0932	0.9315
18	8	0	2.6110	-3.6759	-0.3956
19	1	0	-0.8599	2.5624	-2.6874
20	1	0	-0.9025	0.1992	1.6769
21	1	0	2.0521	-0.4450	-1.9574
22	1	0	0.6800	-1.8699	-0.6288
23	1	0	1.3816	-0.2760	1.4806
24	1	0	2.3825	0.5063	0.2718
25	1	0	1.4690	-2.2864	2.4410
26	1	0	0.6158	-3.4011	1.3522
27	1	0	2.0954	-3.9165	2.1394
28	1	0	-4.8691	0.3960	1.3511
29	1	0	-4.4103	0.6478	-0.3405
30	1	0	-3.5710	-0.5907	0.6578
31	1	0	-4.3947	3.3220	0.0777
32	1	0	-3.9668	4.6348	-1.0205
33	1	0	-2.8116	4.1710	0.2350
34	1	0	1.2449	1.8482	-2.8690
35	1	0	3.7536	-1.2635	1.6431
36	1	0	4.4179	-1.7814	0.0779
37	1	0	4.3470	-2.9185	1.4089
38	1	0	2.8590	-3.2754	-1.2555

Table S_5. Gibbs free energies[a] and equilibrium populations[b] of low-energy conformers of 8*S*-**1**

Conformers	In MeOH	
	E	Optical rotation (OR)
8*S*-**1a**	-883.5912460	43.96
8*S*-**1b**	-883.5875578	-57.58
8*S*-**1c**	-883.5854281	-37.80
8*S*-**1d**	-883.5850318	64.78
8*S*-**1e**	-883.5892776	67.98
Average		44.66

[a] B3LYP/6-31+G (d, p), in kcal/mol; [b] from Δ*G* values at 298.15K.

Table S_6. Cartesian coordinates for the low-energy reoptimized MMFF conformers of 8*S*-**1** at B3LYP/6-311+G (d, p) level of theory in MeOH

8*S*-**1a**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.0468	2.1994	-1.0769
2	6	0	2.2675	1.9877	-0.4268
3	6	0	2.3307	1.0063	0.5762
4	6	0	1.1989	0.2326	0.8761
5	6	0	-0.0248	0.4393	0.2233
6	6	0	-0.0748	1.4299	-0.7596
7	8	0	-2.3674	-0.6552	-1.4885
8	6	0	-1.6618	-1.382	-0.4567
9	6	0	-1.2291	-0.3844	0.6281
10	6	0	-3.845	-2.0052	0.7509
11	6	0	-2.5911	-2.5236	0.0405
12	8	0	3.4184	2.6669	-0.7279
13	6	0	4.2799	1.7362	1.7036
14	8	0	3.4384	0.6579	1.3088
15	6	0	3.378	3.5901	-1.8084
16	8	0	-1.2109	1.7026	-1.4694
17	6	0	-1.8435	-3.5241	0.9241
18	8	0	-3.0295	-3.2194	-1.1456
19	1	0	0.9311	2.948	-1.8531
20	1	0	1.2864	-0.5295	1.6479
21	1	0	-2.7764	-1.3653	-2.0319
22	1	0	-0.7849	-1.8233	-0.9477
23	1	0	-2.0456	0.3103	0.864
24	1	0	-0.9928	-0.9122	1.5582
25	1	0	-3.6018	-1.4837	1.6816
26	1	0	-4.4117	-1.3242	0.1064
27	1	0	-4.5232	-2.8318	0.9929
28	1	0	3.7165	2.6476	1.9328
29	1	0	4.7967	1.4322	2.6195
30	1	0	5.0459	1.9206	0.9448
31	1	0	4.3832	4.0053	-1.9292
32	1	0	2.7003	4.422	-1.5904
33	1	0	3.1099	3.0925	-2.7462
34	1	0	-1.7677	0.8916	-1.4866
35	1	0	-1.5181	-3.0807	1.8694
36	1	0	-0.9639	-3.9196	0.4036
37	1	0	-2.4771	-4.3882	1.1556
38	1	0	-3.5874	-3.9666	-0.8632

8*S*-**1b**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.9072	0.6529	-1.0560
2	6	0	2.1333	1.3172	0.1538
3	6	0	1.5334	0.8092	1.3167
4	6	0	0.6885	-0.3083	1.2422
5	6	0	0.4413	-0.9657	0.0268
6	6	0	1.0730	-0.4670	-1.1145
7	8	0	-1.4376	-2.0949	-2.1917
8	6	0	-1.7382	-2.1562	-0.7836
9	6	0	-0.4315	-2.1974	0.0271
10	6	0	-2.4202	0.3523	-0.7899
11	6	0	-2.8077	-1.0853	-0.4331
12	8	0	2.8902	2.4526	0.2717
13	6	0	2.9370	1.7950	2.9433
14	8	0	1.6395	1.3327	2.5814
15	6	0	3.4360	3.0094	-0.9172
16	8	0	0.9223	-1.0291	-2.3507
17	6	0	-3.2540	-1.1793	1.0261
18	8	0	-3.9449	-1.4111	-1.2671
19	1	0	2.3557	0.9857	-1.9860
20	1	0	0.2319	-0.6679	2.1625
21	1	0	-2.3213	-2.0344	-2.6166
22	1	0	-2.2091	-3.1407	-0.6534
23	1	0	-0.6743	-2.4739	1.0609
24	1	0	0.1903	-3.0190	-0.3551
25	1	0	-1.6554	0.7575	-0.1249
26	1	0	-2.0662	0.4261	-1.8237
27	1	0	-3.2919	1.0145	-0.7221
28	1	0	3.0250	1.7109	4.0312
29	1	0	3.7380	1.1914	2.5019
30	1	0	3.0497	2.8528	2.6889
31	1	0	3.9786	3.9186	-0.6404
32	1	0	2.6467	3.2955	-1.6201
33	1	0	4.1532	2.3239	-1.3803
34	1	0	0.0945	-1.5596	-2.3616
35	1	0	-2.4517	-0.9082	1.7184
36	1	0	-3.5930	-2.1938	1.2645
37	1	0	-4.1067	-0.5176	1.2173
38	1	0	-4.6616	-0.7888	-1.0469
8*S*-**1c**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z

1	6	0	-0.7959	2.4198	1.1711
2	6	0	0.5159	2.8735	1.0401
3	6	0	1.5524	1.9640	0.8180
4	6	0	1.2508	0.6079	0.6510
5	6	0	-0.0701	0.1327	0.7553
6	6	0	-1.0831	1.0647	1.0153
7	8	0	-2.5448	-1.5159	-0.2443
8	6	0	-1.1603	-1.7205	-0.6136
9	6	0	-0.3203	-1.3591	0.6267
10	6	0	0.4333	-3.5618	-1.4519
11	6	0	-1.0090	-3.1910	-1.0989
12	8	0	0.7393	4.2201	1.1607
13	6	0	3.3519	3.1594	1.7212
14	8	0	2.8778	2.2881	0.6958
15	6	0	0.7234	4.8264	-0.1331
16	8	0	-2.3991	0.7179	1.1279
17	6	0	-1.9143	-3.4514	-2.3123
18	8	0	-1.4646	-4.0416	-0.0347
19	1	0	-1.5990	3.1220	1.3738
20	1	0	2.0698	-0.0826	0.4604
21	1	0	-2.8056	-2.3555	0.1955
22	1	0	-0.9358	-1.0373	-1.4416
23	1	0	-0.8143	-1.6992	1.5461
24	1	0	0.6508	-1.8611	0.5960
25	1	0	0.8644	-2.8557	-2.1686
26	1	0	1.0725	-3.6054	-0.5649
27	1	0	0.4787	-4.5651	-1.8921
28	1	0	3.2553	4.2030	1.4090
29	1	0	2.8547	2.9902	2.6833
30	1	0	4.4184	2.9559	1.8599
31	1	0	0.9035	5.8976	-0.0017
32	1	0	-0.2527	4.7039	-0.6158
33	1	0	1.5179	4.4261	-0.7723
34	1	0	-2.5503	-0.1133	0.6277
35	1	0	-1.6517	-2.8019	-3.1537
36	1	0	-2.9705	-3.2958	-2.0667
37	1	0	-1.8331	-4.4935	-2.6429
38	1	0	-1.3562	-4.9654	-0.3256

	8*S*-**1d**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.5267	2.3455	-0.2789
2	6	0	0.7118	2.8678	0.7265
3	6	0	-0.4172	2.1516	1.1350

4	6	0	-0.7802	0.9711	0.4795
5	6	0	0.0130	0.4561	-0.5572
6	6	0	1.1741	1.1528	-0.9113
7	8	0	1.6627	-2.1004	-1.6123
8	6	0	0.4644	-2.0309	-0.8088
9	6	0	-0.3981	-0.8316	-1.2444
10	6	0	-0.7441	-3.6904	-2.3582
11	6	0	-0.2402	-3.4097	-0.9394
12	8	0	1.1379	4.0481	1.2757
13	6	0	-0.6662	2.1699	3.4117
14	8	0	-1.2244	2.5730	2.1587
15	6	0	0.1076	5.0292	1.3884
16	8	0	1.9762	0.6378	-1.8929
17	6	0	-1.3726	-3.5794	0.0736
18	8	0	0.7416	-4.4190	-0.6389
19	1	0	2.4251	2.8868	-0.5591
20	1	0	-1.6824	0.4518	0.7948
21	1	0	1.9783	-1.1780	-1.7145
22	1	0	0.8070	-1.9109	0.2270
23	1	0	-0.3366	-0.6818	-2.3299
24	1	0	-1.4550	-1.0102	-1.0198
25	1	0	-1.5342	-2.9951	-2.6574
26	1	0	0.0702	-3.6269	-3.0884
27	1	0	-1.1407	-4.7098	-2.4323
28	1	0	-0.5721	1.0797	3.4700
29	1	0	0.3037	2.6461	3.5907
30	1	0	-1.3514	2.4931	4.2011
31	1	0	0.5811	6.0139	1.3244
32	1	0	-0.3783	4.9614	2.3657
33	1	0	-0.6297	4.9623	0.5801
34	1	0	2.6628	1.2961	-2.1039
35	1	0	-2.2114	-2.9051	-0.1205
36	1	0	-1.0115	-3.3997	1.0927
37	1	0	-1.7534	-4.6074	0.0605
38	1	0	1.5558	-4.1078	-1.0880

	8*S*-**1e**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.5154	2.0458	-0.3905
2	6	0	1.6532	1.8973	0.9880
3	6	0	1.3273	0.6892	1.6179
4	6	0	0.9004	-0.3844	0.8268
5	6	0	0.7610	-0.2580	-0.5728

6	6	0	1.0767	0.9735	-1.1607
7	8	0	-0.8707	-0.4537	-3.2333
8	6	0	-0.9925	-1.3927	-2.1478
9	6	0	0.3347	-1.4681	-1.3727
10	6	0	-2.4385	0.3036	-0.8102
11	6	0	-2.3069	-1.1167	-1.3666
12	8	0	2.0507	2.9984	1.7060
13	6	0	1.0208	-0.5121	3.6562
14	8	0	1.4643	0.6557	2.9803
15	6	0	3.4445	2.9126	2.0015
16	8	0	0.9875	1.2007	-2.5039
17	6	0	-2.5477	-2.1526	-0.2683
18	8	0	-3.3589	-1.2616	-2.3494
19	1	0	1.7480	2.9951	-0.8632
20	1	0	0.6708	-1.3424	1.2826
21	1	0	-1.7642	-0.4476	-3.6412
22	1	0	-1.1090	-2.3648	-2.6472
23	1	0	0.3016	-2.3472	-0.7168
24	1	0	1.1453	-1.6693	-2.0871
25	1	0	-1.7783	0.4836	0.0402
26	1	0	-2.2367	1.0553	-1.5808
27	1	0	-3.4640	0.4903	-0.4687
28	1	0	1.1389	-0.3420	4.7307
29	1	0	-0.0402	-0.7040	3.4645
30	1	0	1.6349	-1.3779	3.3878
31	1	0	3.7383	3.8431	2.4965
32	1	0	4.0398	2.8151	1.0865
33	1	0	3.6612	2.0855	2.6853
34	1	0	0.3712	0.5464	-2.9013
35	1	0	-1.8090	-2.0780	0.5349
36	1	0	-2.5163	-3.1684	-0.6782
37	1	0	-3.5437	-2.0299	0.1726
38	1	0	-4.2103	-1.1197	-1.8975

Table S_7. Gibbs free energies[a] and equilibrium populations[b] of low-energy conformers of 8*S*-**1**

Conformers	In MeOH	
	G	*P* (%)
8*S*-**1a**	-883.5912492	11.65%
8*S*-**1b**	-883.5876904	0.27%
8*S*-**1c**	-883.5875641	0.23%
8*S*-**1d**	-883.5931479	87.19%
8*S*-**1e**	-883.5885329	0.65%

[a] B3LYP/6-31+g (d, p), in kcal/mol; [b] from G values at 298.15K.

Table S_8. Cartesian coordinates for the low-energy reoptimized MMFF conformers of 8*S*-**1** at B3LYP/6-31+g (d, p) level of theory in MeOH

8*S*-**1a**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	-1.97673	-1.39946	0.143896
2	6	0	-2.81003	-0.30081	-0.09321
3	6	0	-2.25613	0.98795	-0.01977
4	6	0	-0.88707	1.151788	0.241078
5	6	0	-0.04823	0.05264	0.474781
6	6	0	-0.61811	-1.22076	0.414373
7	8	0	2.469687	-1.60123	-0.26046
8	6	0	2.359877	-0.16026	-0.30903
9	6	0	1.409053	0.290444	0.809954
10	6	0	4.469659	0.158635	1.126411
11	6	0	3.795098	0.428778	-0.2218
12	8	0	-4.13636	-0.4074	-0.4188
13	6	0	-4.24124	2.240766	0.286336
14	8	0	-2.91629	2.173434	-0.23022
15	6	0	-4.67271	-1.71312	-0.58864
16	8	0	0.110837	-2.36088	0.608689
17	6	0	3.81959	1.923049	-0.54919
18	8	0	4.565275	-0.25953	-1.22982
19	1	0	-2.34593	-2.41874	0.110883
20	1	0	-0.48735	2.163343	0.276001
21	1	0	3.226846	-1.79476	-0.85721
22	1	0	1.936344	0.074759	-1.29396
23	1	0	1.628935	-0.24267	1.743872
24	1	0	1.548002	1.356185	1.021265
25	1	0	3.959939	0.67004	1.948708
26	1	0	4.498589	-0.91417	1.346308
27	1	0	5.512717	0.495713	1.112417
28	1	0	-4.96114	1.899456	-0.46313
29	1	0	-4.35406	1.692291	1.228175
30	1	0	-4.46112	3.293116	0.492247
31	1	0	-5.72176	-1.60651	-0.88147
32	1	0	-4.64674	-2.27488	0.350751
33	1	0	-4.15801	-2.25269	-1.39059
34	1	0	1.047783	-2.17328	0.374388
35	1	0	3.29281	2.520755	0.200195
36	1	0	3.36585	2.113059	-1.52843
37	1	0	4.850309	2.290752	-0.6122
38	1	0	5.464596	0.115074	-1.22453
8*S*-**1b**			Standard Orientation (Ångstroms)		

No.	Atom	Type	X	Y	Z
1	6	0	1.934029	-1.54228	-0.35653
2	6	0	2.797883	-0.48198	-0.08389
3	6	0	2.320338	0.83157	-0.08834
4	6	0	0.955782	1.064638	-0.29184
5	6	0	0.065434	0.006417	-0.54668
6	6	0	0.579711	-1.2963	-0.56975
7	8	0	-2.49306	-1.5728	0.20636
8	6	0	-2.32451	-0.14062	0.307722
9	6	0	-1.39142	0.318508	-0.82268
10	6	0	-4.46454	0.314545	-1.04367
11	6	0	-3.73707	0.506545	0.290365
12	8	0	4.113109	-0.77886	0.161458
13	6	0	4.299337	1.982303	-0.58901
14	8	0	3.075309	1.951141	0.142778
15	6	0	4.316148	-0.92812	1.568035
16	8	0	-0.20576	-2.39142	-0.79387
17	6	0	-3.69177	1.986979	0.67352
18	8	0	-4.50126	-0.18925	1.297798
19	1	0	2.308697	-2.56103	-0.38164
20	1	0	0.597723	2.091714	-0.27202
21	1	0	-3.23835	-1.76195	0.819172
22	1	0	-1.86167	0.037948	1.286774
23	1	0	-1.66321	-0.16403	-1.77034
24	1	0	-1.49124	1.397137	-0.98442
25	1	0	-3.96093	0.836504	-1.86308
26	1	0	-4.54374	-0.7472	-1.30186
27	1	0	-5.49213	0.691431	-0.98271
28	1	0	4.556623	3.032841	-0.75667
29	1	0	5.106489	1.537457	-0.00032
30	1	0	4.217737	1.500969	-1.57032
31	1	0	4.084871	-0.00208	2.106005
32	1	0	5.373595	-1.15737	1.730028
33	1	0	3.724392	-1.75924	1.967356
34	1	0	-1.12405	-2.17704	-0.51451
35	1	0	-3.16708	2.592437	-0.07089
36	1	0	-3.1987	2.121867	1.642877
37	1	0	-4.70455	2.391036	0.78579
38	1	0	-5.38727	0.214745	1.331143
	8*S*-**1c**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	-1.56846	-1.45813	-0.04923
2	6	0	-2.40806	-0.35791	0.152899

3	6	0	-1.95131	0.91098	-0.2362
4	6	0	-0.66106	1.062582	-0.76587
5	6	0	0.193611	-0.03554	-0.95082
6	6	0	-0.28986	-1.295	-0.58949
7	8	0	2.878197	-1.56946	-0.54219
8	6	0	2.795488	-0.1453	-0.74654
9	6	0	1.547055	0.190176	-1.58017
10	6	0	2.041846	0.194142	1.718092
11	6	0	3.01702	0.587514	0.605432
12	8	0	-3.64703	-0.43895	0.731013
13	6	0	-4.02322	2.034822	-0.41382
14	8	0	-2.63368	2.095261	-0.1077
15	6	0	-4.07872	-1.71238	1.19313
16	8	0	0.441789	-2.43973	-0.7354
17	6	0	3.057019	2.10611	0.43244
18	8	0	4.325232	0.15672	1.049928
19	1	0	-1.86999	-2.46626	0.214416
20	1	0	-0.33643	2.062895	-1.04644
21	1	0	3.674001	-1.67846	0.023288
22	1	0	3.659812	0.083593	-1.38583
23	1	0	1.62526	1.231738	-1.91651
24	1	0	1.567694	-0.41399	-2.49794
25	1	0	1.038133	0.591263	1.55562
26	1	0	1.978883	-0.89365	1.828567
27	1	0	2.387959	0.575642	2.68645
28	1	0	-4.24706	1.326768	-1.21966
29	1	0	-4.60246	1.80942	0.486156
30	1	0	-4.32839	3.028615	-0.75676
31	1	0	-3.40662	-2.10355	1.963957
32	1	0	-4.18609	-2.4175	0.362503
33	1	0	-5.06566	-1.58433	1.64815
34	1	0	1.395257	-2.20499	-0.78693
35	1	0	2.085965	2.51017	0.132051
36	1	0	3.801933	2.392506	-0.31851
37	1	0	3.356451	2.597717	1.365291
38	1	0	4.527144	0.629246	1.877766

8*S*-**1d**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.992072	-1.67249	-0.33134
2	6	0	2.867408	-0.60553	-0.13791
3	6	0	2.410999	0.719148	-0.18764
4	6	0	1.045605	0.951846	-0.3953
5	6	0	0.140926	-0.11555	-0.57154

6	6	0	0.637972	-1.42428	-0.52569
7	8	0	-2.41183	-1.6109	0.344305
8	6	0	-2.23567	-0.17653	0.333623
9	6	0	-1.31939	0.191026	-0.84333
10	6	0	-4.39862	0.180921	-1.01059
11	6	0	-3.64577	0.474904	0.290371
12	8	0	4.197964	-0.90307	0.028488
13	6	0	2.964621	3.035947	-0.28687
14	8	0	3.356259	1.696787	-0.02065
15	6	0	4.54443	-0.84362	1.411588
16	8	0	-0.16535	-2.51958	-0.67055
17	6	0	-3.58775	1.980965	0.553063
18	8	0	-4.39311	-0.13322	1.364537
19	1	0	2.362372	-2.69274	-0.31949
20	1	0	0.660601	1.965775	-0.43174
21	1	0	-3.14399	-1.75062	0.985349
22	1	0	-1.75541	0.07362	1.288356
23	1	0	-1.61295	-0.35541	-1.74882
24	1	0	-1.41306	1.25591	-1.08116
25	1	0	-3.9076	0.632255	-1.87819
26	1	0	-4.48781	-0.89759	-1.18112
27	1	0	-5.42306	0.56811	-0.96189
28	1	0	3.855438	3.666692	-0.20902
29	1	0	2.569729	3.142157	-1.30276
30	1	0	2.243015	3.387985	0.457398
31	1	0	4.4858	0.178969	1.798117
32	1	0	5.580801	-1.18063	1.510545
33	1	0	3.914296	-1.51229	2.009131
34	1	0	-1.07144	-2.28105	-0.37232
35	1	0	-3.0768	2.52259	-0.24792
36	1	0	-3.07442	2.190457	1.498171
37	1	0	-4.59686	2.397462	0.653188
38	1	0	-5.28117	0.267632	1.37451

8*S*-**1e**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.998539	-1.40549	0.012716
2	6	0	2.832617	-0.28188	-0.00261
3	6	0	2.257008	0.974878	-0.24836
4	6	0	0.885918	1.073122	-0.53388
5	6	0	0.047392	-0.05256	-0.53176
6	6	0	0.628458	-1.2866	-0.23471
7	8	0	-2.52604	-1.61715	0.33075
8	6	0	-2.35765	-0.17961	0.298842

9	6	0	-1.41763	0.123176	-0.88398
10	6	0	-3.72999	1.987674	0.067536
11	6	0	-3.7706	0.462833	0.191262
12	8	0	4.186884	-0.3402	0.193573
13	6	0	3.998729	2.349977	0.594339
14	8	0	2.90637	2.183124	-0.30199
15	6	0	4.787751	-1.62601	0.280141
16	8	0	-0.08791	-2.44862	-0.17698
17	6	0	-4.63105	0.071787	1.402133
18	8	0	-4.40181	-0.08604	-0.97678
19	1	0	2.380357	-2.40009	0.216634
20	1	0	0.479432	2.056955	-0.76144
21	1	0	-3.2537	-1.78983	-0.3075
22	1	0	-1.89119	0.118619	1.245614
23	1	0	-1.64093	-0.53017	-1.73746
24	1	0	-1.55748	1.148667	-1.23732
25	1	0	-3.14282	2.439506	0.873242
26	1	0	-3.32125	2.308328	-0.89547
27	1	0	-4.74254	2.406679	0.107018
28	1	0	3.816647	1.882024	1.568095
29	1	0	4.925695	1.986956	0.140995
30	1	0	4.121654	3.423958	0.766687
31	1	0	4.456874	-2.15415	1.180249
32	1	0	5.869769	-1.48305	0.359618
33	1	0	4.596814	-2.21683	-0.62188
34	1	0	-1.02383	-2.23073	0.026133
35	1	0	-4.18552	0.421891	2.338866
36	1	0	-4.76841	-1.01327	1.46412
37	1	0	-5.63781	0.497794	1.318883
38	1	0	-5.27875	0.330116	-1.06374

Table S_9. Gibbs free energies[a] and equilibrium populations[b] of low-energy conformers of 8*R*-**1**

Conformers	In MeOH	
	G	*P* (%)
8*R*-**1a**	-883.5888321	0.01%
8*R*-**1b**	-883.5979622	98.71%
8*R*-**1c**	-883.5834777	0.00%
8*R*-**1d**	-883.5850388	0.00%
8*R*-**1e**	-883.5938641	1.28%

[a] B3LYP/6-31+g (d, p), in kcal/mol; [b] from G values at 298.15K.

Table S_{10}. Cartesian coordinates for the low-energy reoptimized MMFF conformers of 8*R*-**1a** at B3LYP/6-31+g (d, p) level of theory in MeOH

8*R*-**1a**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.940462	-1.514846	-0.290507
2	6	0	2.788247	-0.410569	-0.199719
3	6	0	2.276778	0.840333	0.156746
4	6	0	0.926751	0.950309	0.510186
5	6	0	0.062693	-0.157935	0.452499
6	6	0	0.590668	-1.382616	0.025924
7	8	0	-2.52068	-1.47076	-0.658489
8	6	0	-2.359036	-0.077848	-0.30829
9	6	0	-1.382625	0.011396	0.874157
10	6	0	-3.735916	2.043908	0.107401
11	6	0	-3.76695	0.520844	-0.038268
12	8	0	4.113593	-0.597174	-0.49448
13	6	0	3.926459	2.216083	-0.800543
14	8	0	2.994379	2.002752	0.256775
15	6	0	4.820251	-0.965505	0.692018
16	8	0	-0.171177	-2.510102	-0.092739
17	6	0	-4.459745	-0.114321	1.170165
18	8	0	-4.576652	0.193515	-1.186823
19	1	0	2.329488	-2.479362	-0.602788
20	1	0	0.554139	1.921104	0.830459
21	1	0	-3.364634	-1.508594	-1.159876
22	1	0	-1.934451	0.405612	-1.197468
23	1	0	-1.484886	0.976017	1.382583
24	1	0	-1.60738	-0.759463	1.622538
25	1	0	-3.220331	2.363349	1.017585
26	1	0	-3.239413	2.508005	-0.752225
27	1	0	-4.753705	2.450438	0.131337
28	1	0	4.061178	3.296958	-0.907881
29	1	0	4.899899	1.789752	-0.542767
30	1	0	3.568366	1.831443	-1.762231
31	1	0	4.470886	-1.929763	1.077216
32	1	0	4.735444	-0.192382	1.46384
33	1	0	5.877989	-1.068434	0.431747
34	1	0	-1.104916	-2.242025	-0.244099
35	1	0	-3.93432	0.104592	2.104811
36	1	0	-4.535503	-1.201714	1.059666
37	1	0	-5.488044	0.254446	1.263088
38	1	0	-4.313732	0.778777	-1.920101
8*R*-**1b**			Standard Orientation (Ångstroms)		

No.	Atom	Type	X	Y	Z
1	6	0	2.082611	-1.47752	0.090899
2	6	0	2.904391	-0.3584	-0.05997
3	6	0	2.346763	0.929615	0.057302
4	6	0	0.979014	1.070652	0.3328
5	6	0	0.14807	-0.05327	0.489866
6	6	0	0.721823	-1.32029	0.350208
7	8	0	-2.3488	-1.65529	-0.40227
8	6	0	-2.25558	-0.21491	-0.32481
9	6	0	-1.3145	0.14822	0.833808
10	6	0	-3.73818	1.865505	-0.38428
11	6	0	-3.69807	0.348112	-0.19435
12	8	0	4.251177	-0.41311	-0.32472
13	6	0	2.699197	3.295446	0.011283
14	8	0	3.217014	1.979288	-0.10816
15	6	0	4.846132	-1.69925	-0.42411
16	8	0	-0.0071	-2.47141	0.461505
17	6	0	-4.37746	-0.0513	1.118897
18	8	0	-4.4535	-0.25297	-1.26682
19	1	0	2.465079	-2.48821	0.003968
20	1	0	0.538194	2.056309	0.438518
21	1	0	-3.09771	-1.80606	-1.02123
22	1	0	-1.83039	0.109871	-1.28313
23	1	0	-1.4617	1.191855	1.131799
24	1	0	-1.53689	-0.46081	1.719505
25	1	0	-3.22516	2.398363	0.421263
26	1	0	-3.27884	2.149389	-1.33785
27	1	0	-4.77294	2.225523	-0.42308
28	1	0	3.524776	3.995661	-0.14869
29	1	0	1.942931	3.493887	-0.75517
30	1	0	2.302483	3.474593	1.015953
31	1	0	4.753557	-2.25226	0.516369
32	1	0	5.913241	-1.55913	-0.62232
33	1	0	4.425228	-2.26563	-1.26133
34	1	0	-0.93828	-2.27314	0.213991
35	1	0	-3.8779	0.387723	1.987848
36	1	0	-4.39634	-1.14001	1.239576
37	1	0	-5.42392	0.275143	1.129028
38	1	0	-5.36104	0.099155	-1.22651

8*R*-**1c**			Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	-1.54717	-1.48619	-0.502
2	6	0	-2.40149	-0.39959	-0.31313

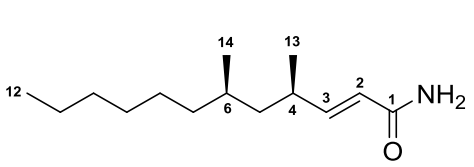
3	6	0	-1.96995	0.713872	0.411405
4	6	0	-0.70695	0.686548	1.014395
5	6	0	0.16617	-0.40523	0.846479
6	6	0	-0.27756	-1.48422	0.072321
7	8	0	2.897163	-1.67004	0.021098
8	6	0	2.775341	-0.39928	0.689337
9	6	0	1.501689	-0.38364	1.552035
10	6	0	3.005256	2.121387	0.34178
11	6	0	3.00733	0.748688	-0.33135
12	8	0	-3.64936	-0.46191	-0.87574
13	6	0	-3.43488	2.331641	-0.46745
14	8	0	-2.697	1.849064	0.652589
15	6	0	-4.55662	-1.08099	0.038946
16	8	0	0.480721	-2.59682	-0.15442
17	6	0	2.06644	0.735657	-1.53909
18	8	0	4.33544	0.514447	-0.85653
19	1	0	-1.87122	-2.34055	-1.08903
20	1	0	-0.40588	1.541332	1.616843
21	1	0	3.70773	-1.57097	-0.52484
22	1	0	3.619904	-0.38486	1.392497
23	1	0	1.517528	-1.26119	2.213262
24	1	0	1.547529	0.484688	2.221322
25	1	0	2.018106	2.38515	0.731916
26	1	0	3.726124	2.151057	1.166661
27	1	0	3.312548	2.902559	-0.36312
28	1	0	-2.91414	2.167007	-1.41752
29	1	0	-4.43571	1.891053	-0.48388
30	1	0	-3.55584	3.412142	-0.34142
31	1	0	-4.61525	-0.52507	0.981418
32	1	0	-4.27857	-2.12372	0.227076
33	1	0	-5.54978	-1.07339	-0.41998
34	1	0	1.427203	-2.37429	-0.00906
35	1	0	1.049522	1.037328	-1.28154
36	1	0	2.034143	-0.25249	-2.01025
37	1	0	2.422903	1.426642	-2.31266
38	1	0	4.541809	1.237787	-1.4757

	8*R*-**1d**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.952629	-1.64259	-0.25319
2	6	0	2.797078	-0.53815	-0.13216
3	6	0	2.263455	0.692977	0.260567
4	6	0	0.916108	0.796484	0.619905
5	6	0	0.066267	-0.31698	0.536153

6	6	0	0.602854	-1.5269	0.080877
7	8	0	-2.66511	-1.47816	-0.71341
8	6	0	-2.32385	-0.13562	-0.30446
9	6	0	-1.39317	-0.17464	0.922053
10	6	0	-3.46565	2.119545	0.098032
11	6	0	-3.66507	0.612948	-0.06916
12	8	0	4.105506	-0.75756	-0.47258
13	6	0	3.128965	2.429479	-0.95652
14	8	0	3.021362	1.831687	0.337714
15	6	0	5.036213	-0.24692	0.481482
16	8	0	-0.22615	-2.60828	-0.04346
17	6	0	-4.46749	0.045249	1.10528
18	8	0	-4.46789	0.428064	-1.24999
19	1	0	2.367609	-2.58365	-0.60091
20	1	0	0.534707	1.758566	0.954616
21	1	0	-1.84213	-2.00528	-0.63837
22	1	0	-1.81739	0.318364	-1.16578
23	1	0	-1.49603	0.738448	1.518011
24	1	0	-1.66008	-1.00608	1.586827
25	1	0	-2.93047	2.370563	1.018063
26	1	0	-2.90967	2.533673	-0.75075
27	1	0	-4.43113	2.638718	0.114397
28	1	0	2.142256	2.695307	-1.35225
29	1	0	3.710469	3.35022	-0.85093
30	1	0	3.657092	1.775077	-1.65814
31	1	0	4.656084	-0.2924	1.508494
32	1	0	5.329799	0.773348	0.219373
33	1	0	5.934471	-0.87031	0.432596
34	1	0	0.318948	-3.3901	-0.24599
35	1	0	-3.95124	0.185384	2.059882
36	1	0	-4.66577	-1.0238	0.970565
37	1	0	-5.44811	0.530677	1.173302
38	1	0	-4.33125	-0.51208	-1.4924

	8*R*-**1e**		Standard Orientation (Ångstroms)		
No.	Atom	Type	X	Y	Z
1	6	0	1.668262	-1.53514	-0.04385
2	6	0	2.498763	-0.42996	0.152348
3	6	0	2.038141	0.850695	-0.2057
4	6	0	0.754442	0.997348	-0.75029
5	6	0	-0.09453	-0.11077	-0.93621
6	6	0	0.389176	-1.37201	-0.57648
7	8	0	-2.77899	-1.65826	-0.53722
8	6	0	-2.69895	-0.23367	-0.73628

9	6	0	-1.45005	0.106887	-1.56794
10	6	0	-2.9622	2.013023	0.451385
11	6	0	-2.92341	0.493762	0.618097
12	8	0	3.765326	-0.49262	0.679741
13	6	0	2.521855	3.184022	-0.41595
14	8	0	2.909713	1.888454	0.015613
15	6	0	4.271309	-1.77713	1.014802
16	8	0	-0.34059	-2.51742	-0.72586
17	6	0	-1.95059	0.09541	1.731285
18	8	0	-4.23288	0.062713	1.057307
19	1	0	1.981805	-2.54138	0.210977
20	1	0	0.392303	1.978128	-1.04129
21	1	0	-3.57669	-1.77263	0.024511
22	1	0	-3.56285	-0.00421	-1.3758
23	1	0	-1.46597	-0.49817	-2.48523
24	1	0	-1.53393	1.147476	-1.90589
25	1	0	-1.9901	2.418079	0.155814
26	1	0	-3.7046	2.302881	-0.30077
27	1	0	-3.26447	2.500815	1.385331
28	1	0	2.347821	3.206597	-1.49676
29	1	0	1.643415	3.535919	0.134749
30	1	0	3.346103	3.870094	-0.19831
31	1	0	3.673255	-2.24348	1.804581
32	1	0	5.286377	-1.6456	1.401923
33	1	0	4.334257	-2.42092	0.131236
34	1	0	-1.29476	-2.28655	-0.77649
35	1	0	-0.9461	0.491718	1.57182
36	1	0	-1.88937	-0.99279	1.838346
37	1	0	-2.29782	0.474273	2.700322
38	1	0	-4.43268	0.521971	1.893034



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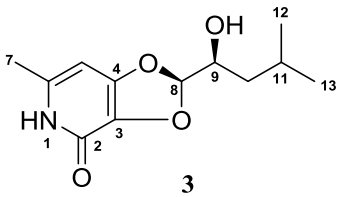
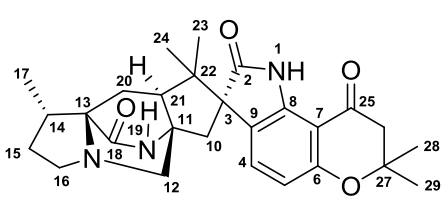


3

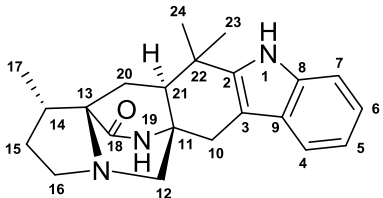
Table S_{11}. ^{13}C NMR (150 MHz) and ^{1}H NMR (600 MHz) data of penicimumide (**2**) and (8*R*,9*S*)-dihydroisoflavipucine (**3**)

No.	**2**[a]		**3**[b]	
	δ_C, type	δ_H, *J* in Hz	δ_C, type	δ_H, *J* in Hz
1	168.6, C	–	–	11.50, br s
2	121.0, CH	5.76, d (15.5)	154.1, C	–
3	152.1, CH	6.68, dd (15.5, 8.6)	130.5, C	–
4	34.2, CH	2.40, m	152.8, C	–
5	44.0, CH_2	1.33, m; 1.07, m	91.8, CH	6.00, s
6	30.4, CH	1.37, m	141.4, C	–
7	37.5, CH_2	1.21[c], m; 1.06, m	18.5, CH_3	2.13, s
8	26.9, CH_2	1.22[c], m	113.3, CH	5.98, d (2.9)
9	29.7, CH_2	1.21[c], m	68.1, CH	3.70, m
10	32.0, CH_2	1.23[c], m	39.3, CH_2	1.38, ddd (13.8, 10.3, 4.1); 1.19, ddd (13.8, 10.3, 3.0)
11	22.7, CH_2	1.26, m	23.7, CH	1.79, m
12	14.2, CH_3	0.86, t (6.6)	21.4, CH_3	0.85, d (6.6)
13	20.6, CH_3	1.02, d (6.3)	23.5, CH_3	0.90, d (6.6)
14	19.5, CH_3	0.82, d (6.3)		
OH-9	–	–	–	5.20, d (6.6)

[a,b] The data were recorded in $CDCl_3$ and DMSO-d_6, respectively; [c] The data were overlapped.



4

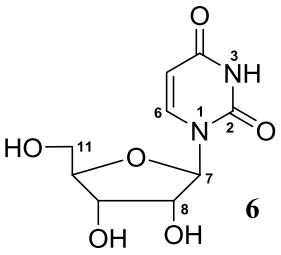


5

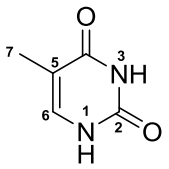
Table S_{12}. ^{13}C NMR (150 MHz) and ^{1}H NMR (600 MHz) data of peniciherquamide A (**4**) and preparaherquamide (**5**)

No.	**4**[a]		**5**[b]	
	δ_C, type	δ_H, *J* in Hz	δ_C, type	δ_H, *J* in Hz
NH-1	–	9.30, s	–	8.15, s
2	183.4, C	–	141.3, C	–
3	60.9, C	–	103.3, C	–
4	132.3, CH	7.24, d (8.3)	117.3, CH	7.29, d (8.0)
5	109.6, CH	6.52, d (8.3)	118.1, CH	6.92, t (8.0)
6	159.2, C	–	120.5, CH	7.01, t (8.0_
7	105.0, C	–	110.7, CH	7.26, d (8.0)
8	142.9, C	–	136.4, C	–
9	121.7, C	–	126.5, C	–
10	39.6, CH_2	2.22, d (14.9); 1.92, d (14.9)	29.3[c], CH_2	2.76, d (15.6); 2.72, d (15.6)
11	61.8, C	–	55.6, C	–
12	60.4, CH_2	3.64, d (10.8); 2.61, d (10.8)	59.6, CH_2	3.27, d (10.0); 2.06, d (10.0)
13	68.1, C	–	64.4, C	–
14	39.9, CH	1.93, m	40.0, CH	1.93, m
15	30.2, CH_2	2.04, m; 1.82, m	30.2[c], CH_2	2.01, m; 1.83, m
16	52.9, CH_2	3.19, m; 2.37, m	53.4, CH_2	3.08[e], m; 2.13, m
17	13.1, CH_3	1.40, d (7.3)	13.1, CH_3	1.31, d (7.0)
18	173.7, C	–	172.7, C	–
NH-19	–	–	–	10.83, s
20	27.5, CH_2	2.07, dd (12.3, 10.8); 1.41, m	29.0[c], CH_2	1.99, dd (13.6, 11.2); 1.58, d (11.2)
21	53.3, CH	3.07, t (10.8)	46.1, CH	3.08[e], m
22	46.4, C	–	33.8, C	–
23	20.8[c], CH_3	1.09[c], s	23.6[d], CH_3	1.30[c], s
24	24.0[c], CH_3	0.85[c], s	30.1[d], CH_3	1.28[c], s
25	193.7, C	–		
26	48.8, CH_2	2.73, d (16.2); 2.69, d (16.2)		
27	79.5, C	–		
28	26.7[d], CH_3	1.47[d], s		
29	26.8[d], CH_3	1.50[d], s		

[a,b] The data were recorded in $CDCl_3$ and DMSO-d_6, respectively; [c,d] The data with the same label in each column may be interchanged; [e] The data were overlapped.



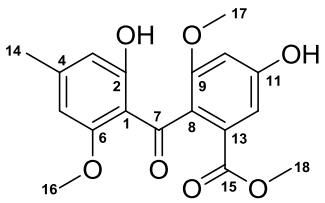
6



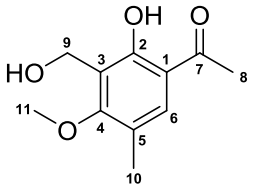
7

Table S_{13}. ^{13}C NMR (150 MHz) and ^{1}H NMR (600 MHz) data of uridine (**6**) and thymine (**7**) (in DMSO-d_6)

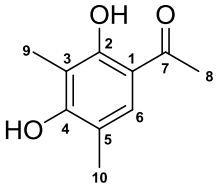
No.	**6**		**7**	
	δ_C, type	δ_H, *J* in Hz	δ_C, type	δ_H, *J* in Hz
1	–	–	–	–
2	150.8, C	–	151.5, C	–
3	–	11.31, s	–	–
4	163.2, C	–	164.9, C	–
5	101.8, CH	5.63, d (8.2)	107.6, C	–
6	140.8, CH	7.87, d (8.2)	137.8, CH	7.25, s
7	87.7, CH	5.77, d (5.3)	11.8, CH_3	1.72, s
8	73.6, CH	4.02, br s		
9	69.9, CH	3.96, br s		
10	84.9, CH	3.83, dd (7.8, 3.6)		
11	60.9, CH_2	3.60, d (12.5); 3.53, d (12.5)		
OH-8	–	5.09, br s		
OH-9	–	5.38, br s		
OH-11	–	5.09, br s		



8



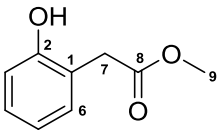
9



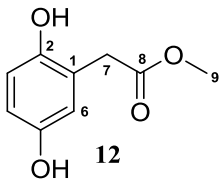
10

Table S_{14}. ^{13}C NMR (150 MHz) and ^{1}H NMR (600 MHz) data of 1,2-seco-trypacidin (**8**), communol G (**9**), and clavatol (**10**) (in DMSO-d_6)

No.	**8**		**9**		**10**	
	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	110.1, C	–	110.8, C	–	112.1, C	–
2	163.3, C	–	161.3, C	–	160.5, C	–
3	103.5, CH	6.69, d (1.9)	116.1, C	–	110.3, C	–
4	147.8, C	–	161.8, C	–	160.7, C	–
5	110.1 CH	6.89, d (1.9)	112.0, C	–	115.9, C	–
6	160.8, C	–	133.0, CH	7.67, s	130.2, CH	7.52, s
7	199.3, C	–	203.3, C	–	201.3, C	–
8	125.8, C	–	26.2, CH_3	2.54, s	26.2, CH_3	2.52, s
9	156.6, C	–	57.3, CH_2	4.47, s	8.1, CH_3	2.01, s
10	103.2, CH	6.26, s	15.9, CH_3	2.14, s	16.2, CH_3	2.13, s
11	158.1, C	–	62.0, CH_3	3.23, s		
12	107.2, C	6.38, s				
13	127.9, C	–				
14	21.9, CH_3	2.26, s				
15	165.7, C	–				
16	52.1, CH_3	3.33, s				
17	55.9, CH_3	3.63, s				
18	55.9, CH_3	3.62, s				
OH-2	–	12.96, s				
OH-11	–	10.05, br s				



11



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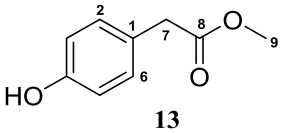

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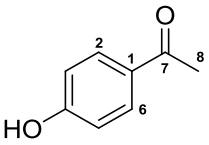


14

Table S_{15}. ^{13}C NMR data of 4-hydroxybenzeneacetic acid methyl ester (**11**), 2,5-dihydroxyphenylacetic acid methyl ester (**12**), 2-hydroxyphenylacetic acid methyl ester (**13**) , and 4-hydroxyphenylethanone (**14**) (150 MHz, in DMSO-d_6)

No.	**11**	**12**	**13**	**14**
1	124.3, C	122.0, C	121.2, C	128.5, C
2	130.2, CH	148.1, C	155.4, C	130.7, CH
3	115.1, CH	115.7, CH	114.8, CH	115.2, CH
4	156.3, C	114.6, CH	128.1, CH	162.2, C
5	115.1, CH	149.9, C	118.8, CH	115.2, CH
6	130.2, CH	117.8, CH	131.1, CH	130.7, CH
7	39.3, CH_2	35.4, CH_2	35.1, CH_2	196.0, C
8	172.0, C	172.1, C	171.7, C	26.2 CH_3
9	51.5, CH_3	51.6, CH_3	51.4, CH_3	

Table S_{16}. ^{1}H NMR data of 4-hydroxybenzeneacetic acid methyl ester (**11**), 2,5-dihydroxyphenylacetic acid methyl ester (**12**), 2-hydroxyphenylacetic acid methyl ester (**13**), and 4-hydroxyphenylethanone (**14**) (600 MHz, in DMSO-d_6, J in Hz)

No.	**11**	**12**	**13**	**14**
2	7.03, d (8.1)	–	–	7.82, d (8.3)
3	6.69, d (8.1)	6.64, d (8.6)	6.79, d (8.0)	6.82, d (8.3)
4	–	6.62, dd (8.6, 2.9)	7.05, td (8.0, 1.8)	–
5	6.69, d (8.1)	–	6.72, t (8.0)	6.82, d (8.3)
6	7.03, d (8.1)	6.58, d (2.9)	7.09, dd (8.0, 1.8)	7.82, d (8.3)
7	3.52, s	3.51, s	3.55, s	–
8	–	–	–	2.46, s
9	3.58, s	3.59, s	3.58, s	–
OH	9.39, br s	8.77, br s; 8,68, br s	9.49, s; 8,68, br s	–

Table S_{17} Antimicrobial activity of compounds **1**–**14** (MIC: μg/mL)

Compounds	*S. aureus* (MRSA)	*E. coli*	*C. albicans*
1	6	13	13
2	NA	13	NA
3	NA	NA	NA
4	NA	NA	NA
5	7	25	25
6	25	13	13
7	25	13	NA
8	7	3	13
9	25	NA	NA
10	25	25	NA
11	25	13	25
12	NA	NA	25
13	13	NA	7
14	25	NA	NA
Vancomycin	0.75	NT	NT
Gentamycin	NT	0.75	NT
Amphotericin B	NT	NT	3.0

NA: No activity at a concentration of 50 μg/mL; NT: No testing.

Figure S_4. ^{1}H NMR spectrum of peniprenylphenol A (**1**, 600 MHz, in DMSO-d_6)

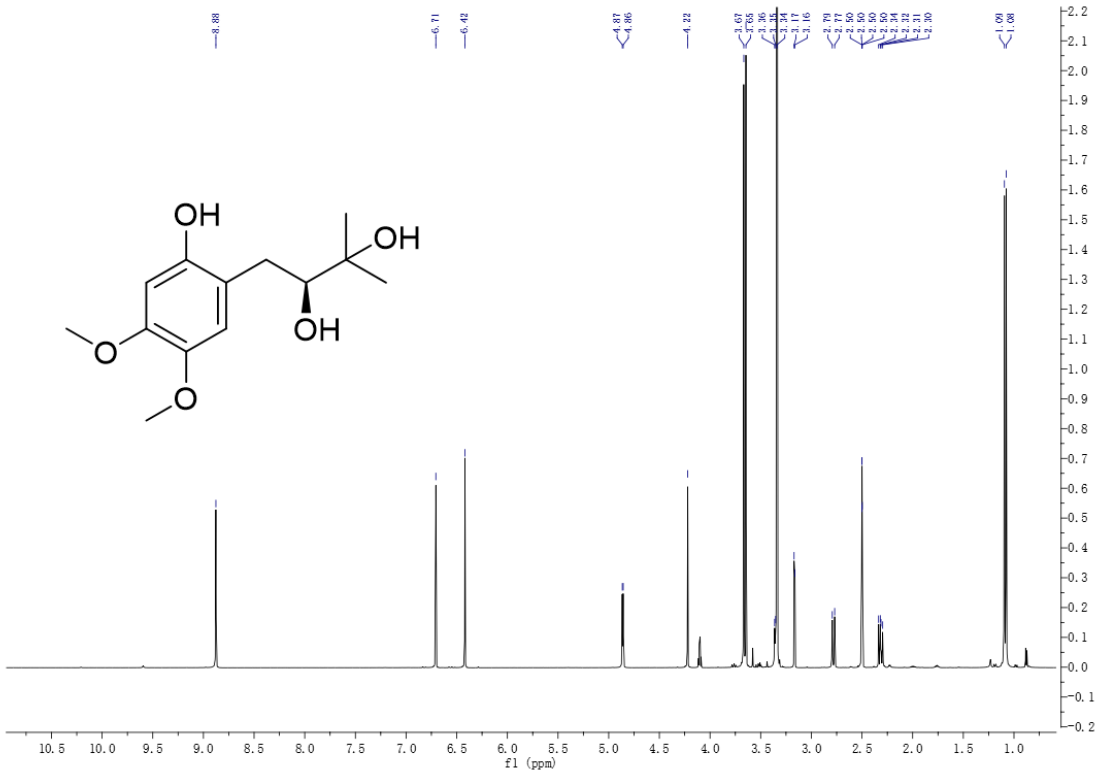


Figure S_5. ^{1}H NMR spectrum of peniprenylphenol A (**1**, 600 MHz, in DMSO-d_6)

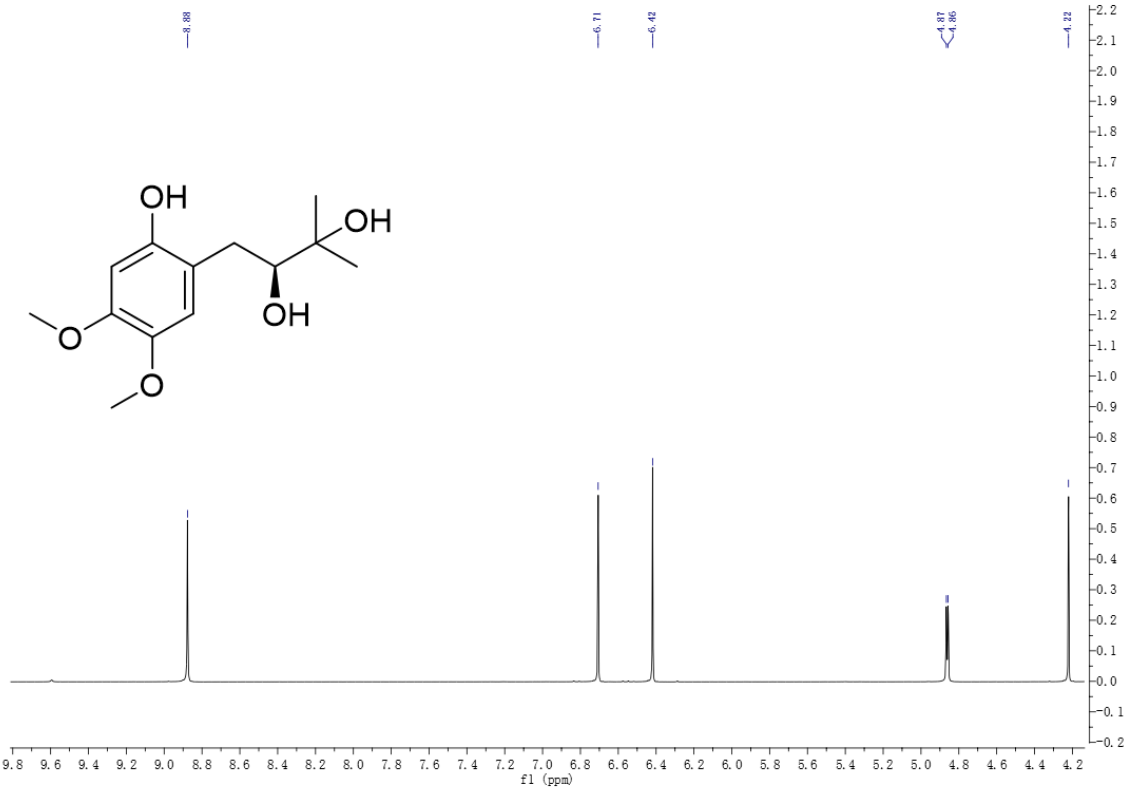


Figure S_6. ^{1}H NMR spectrum of peniprenylphenol A (**1**, 600 MHz, in DMSO-d_6)

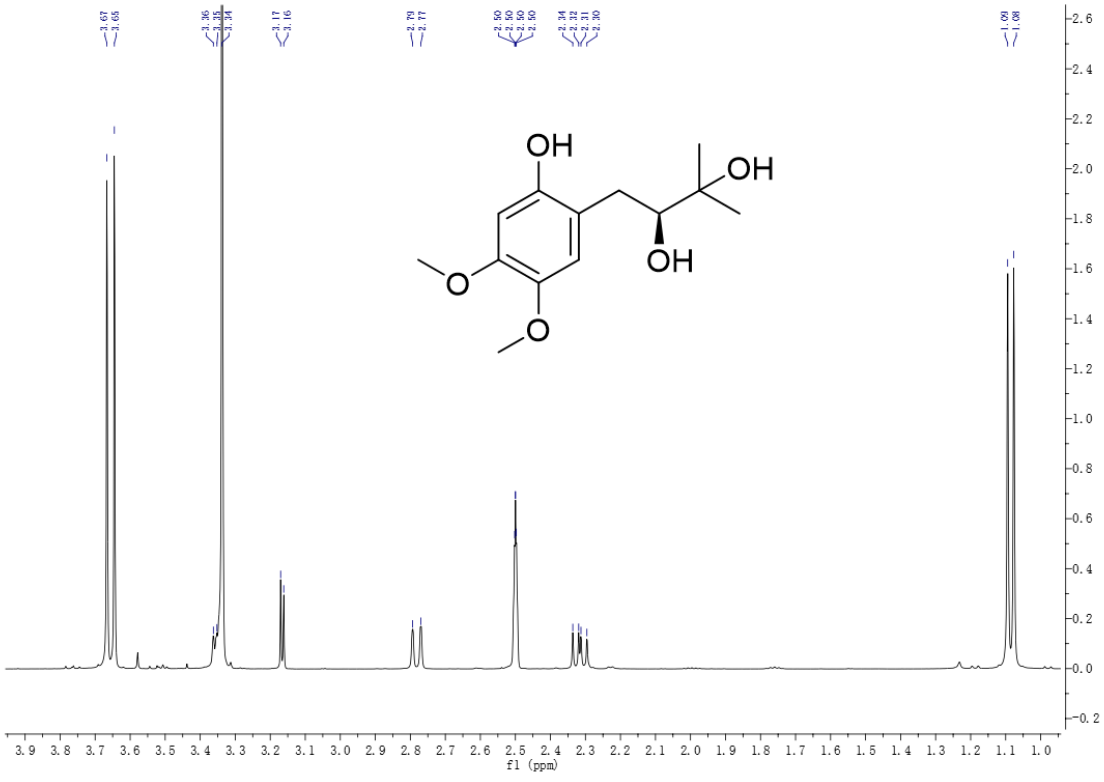


Figure S_7. ^{13}C NMR spectrum of peniprenylphenol A (**1**, 150 MHz, in DMSO-d_6)

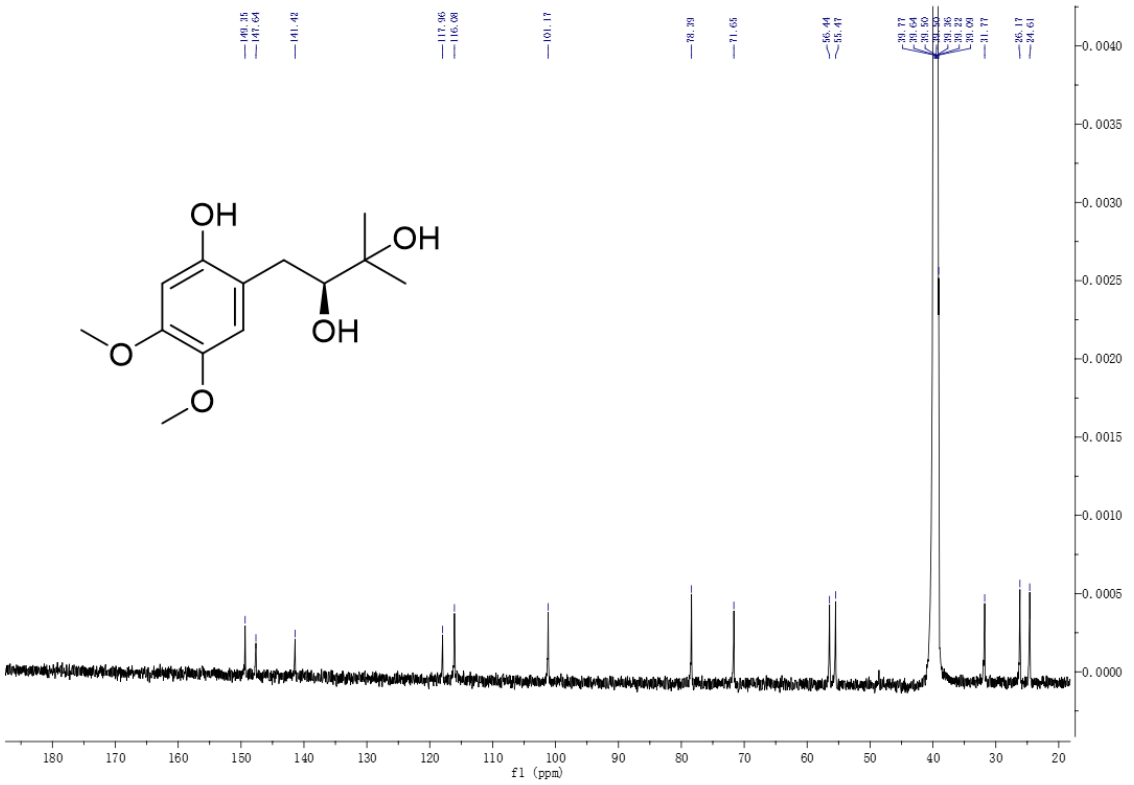


Figure S_8. ^{13}C NMR spectrum of peniprenylphenol A (**1**, 150 MHz, in DMSO-d_6)

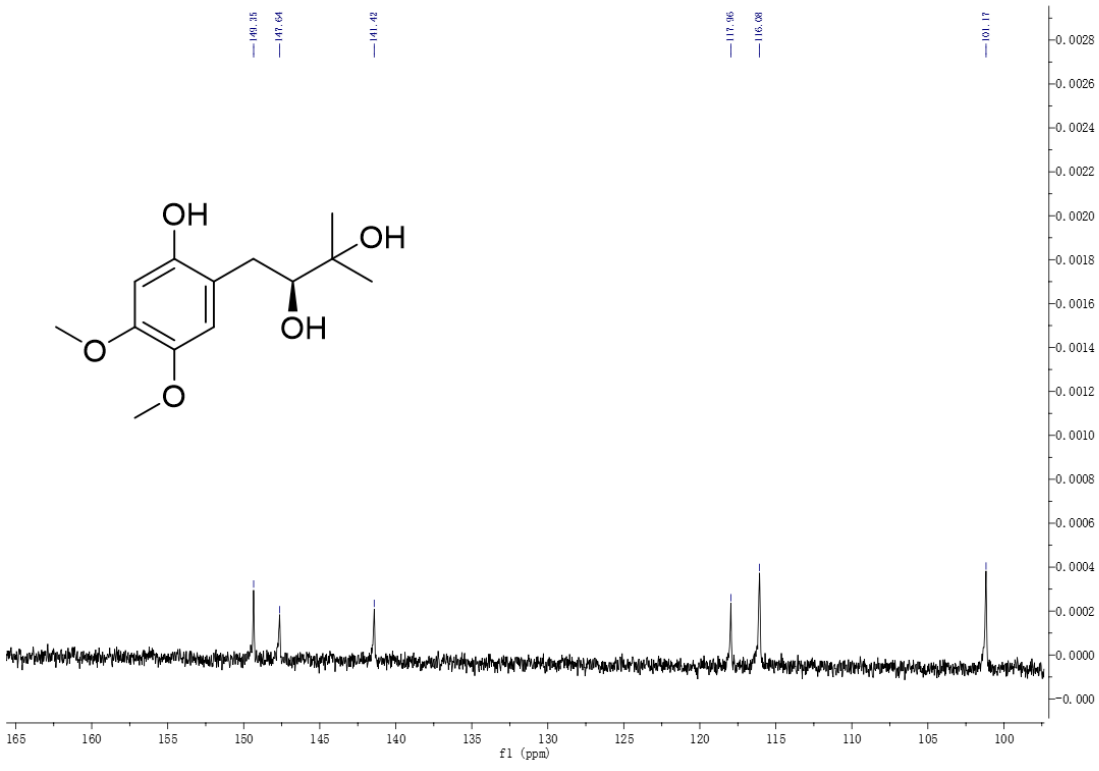


Figure S_9. ^{13}C NMR spectrum of peniprenylphenol A (**1**, 150 MHz, in DMSO-d_6)

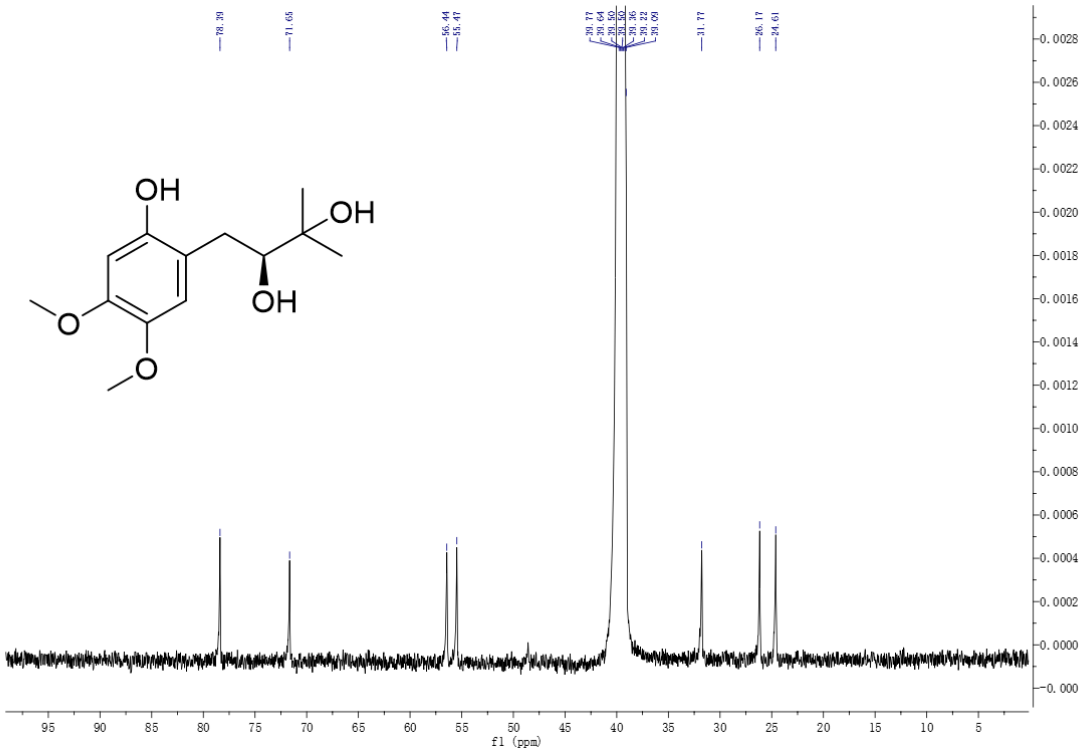


Figure S_{10}. HMQC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

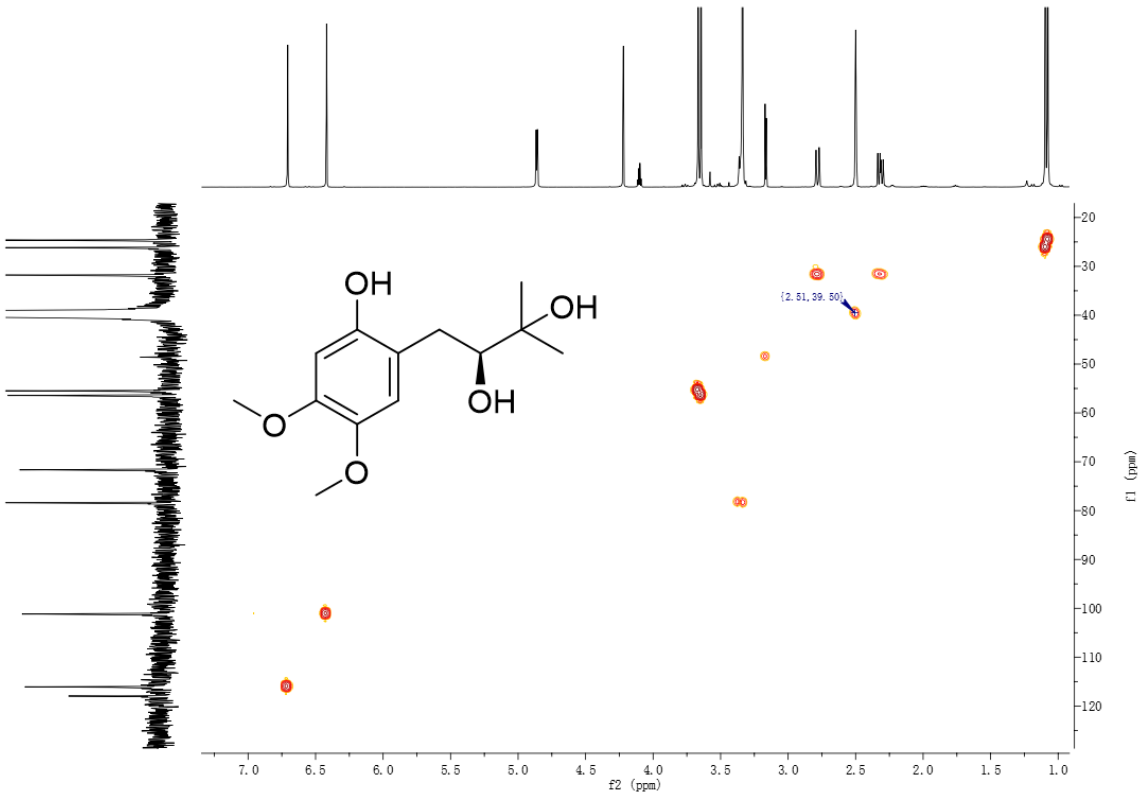


Figure S_{11}. HMQC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

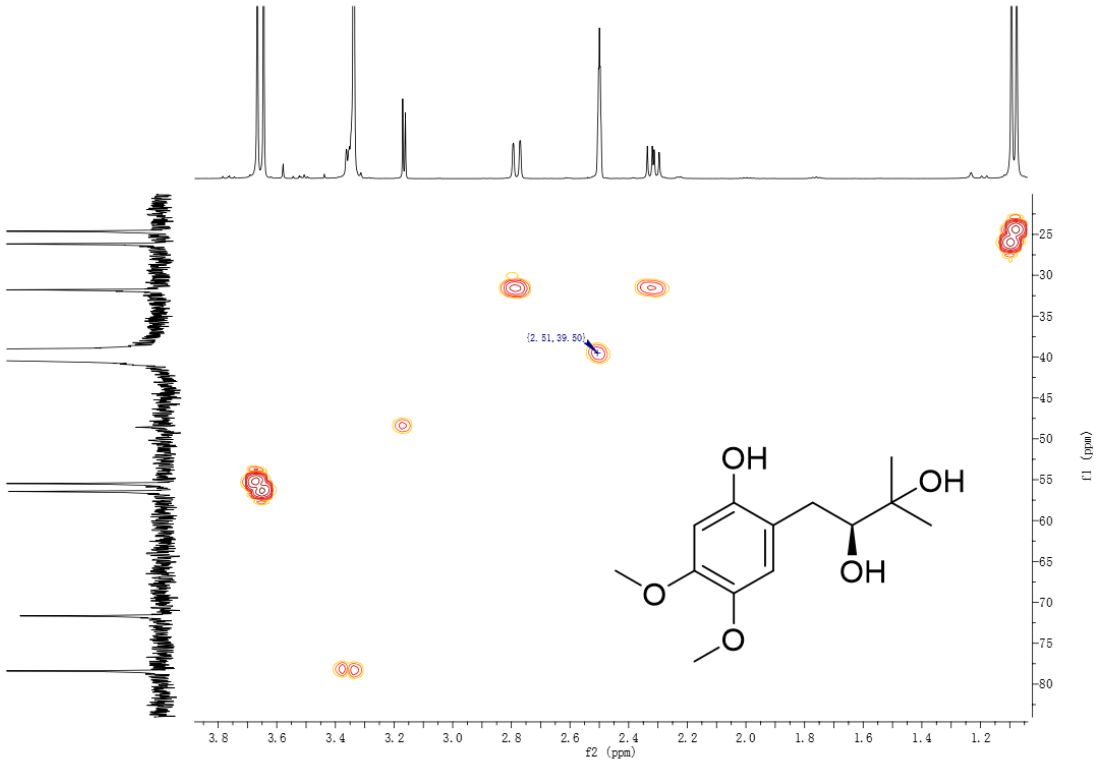


Figure S_{12}. HMBC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

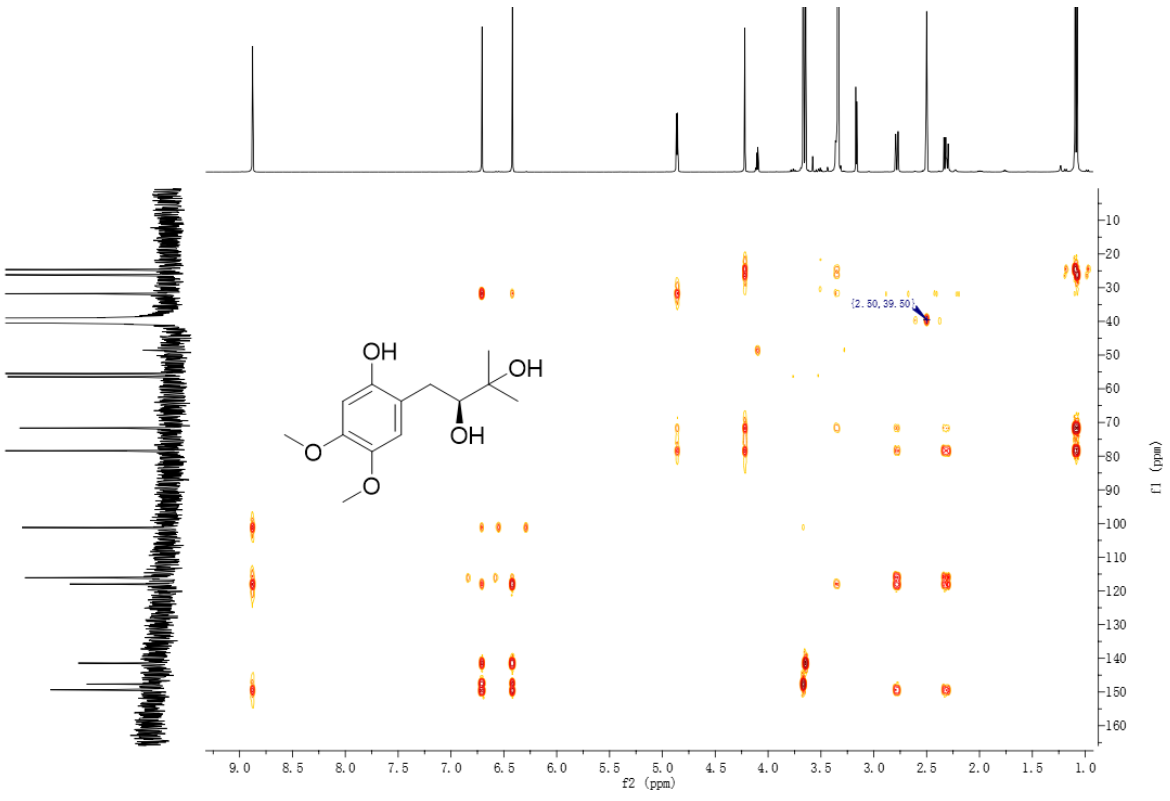


Figure S_{13}. HMBC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

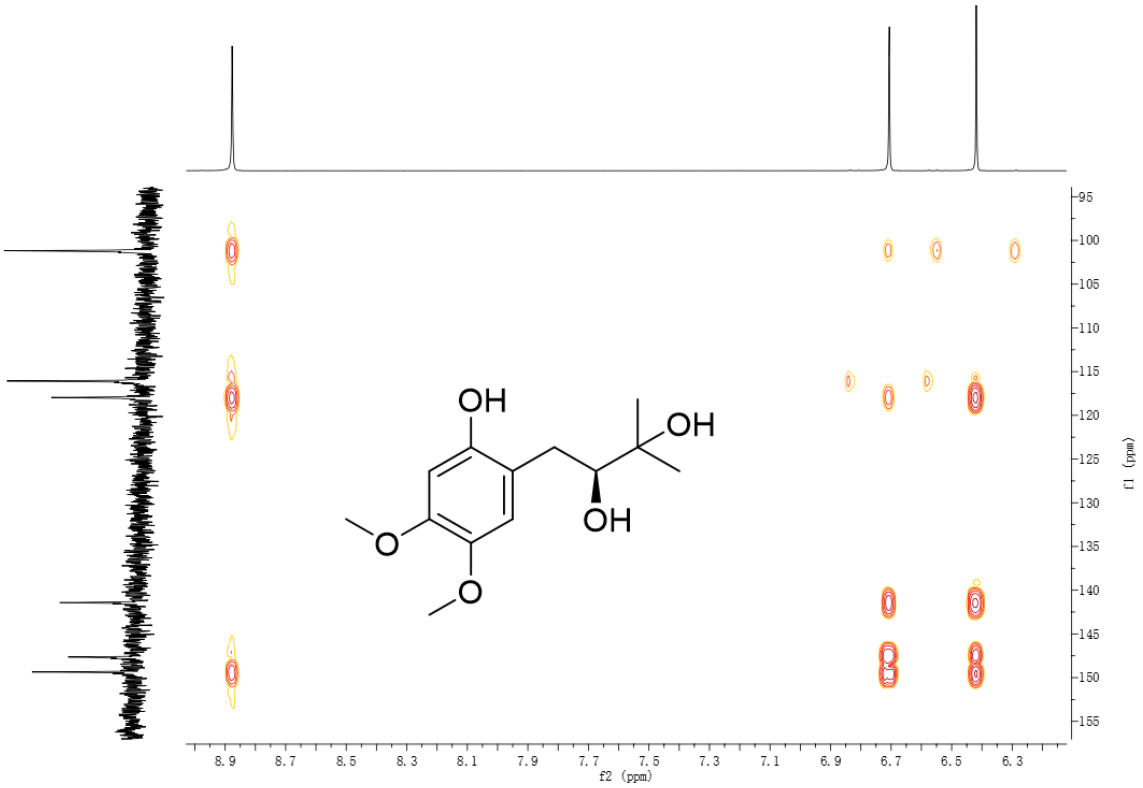


Figure S_{14}. HMBC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

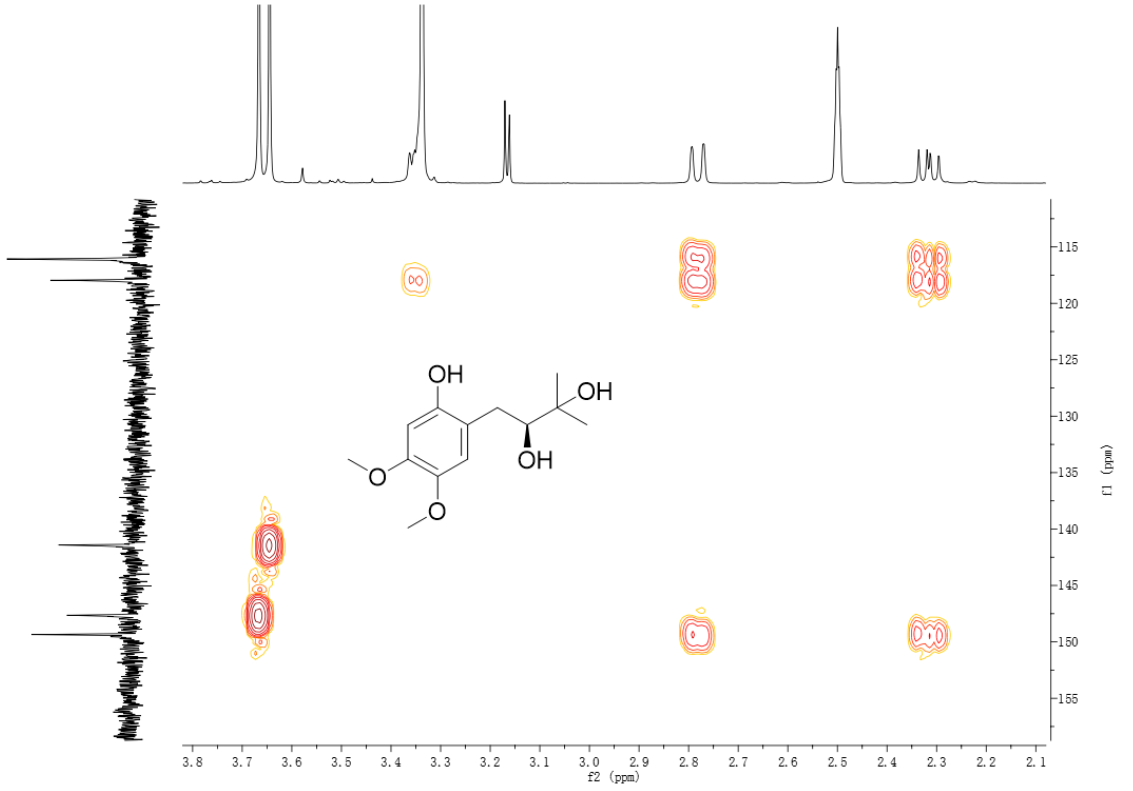


Figure S_{15}. HMBC spectrum of peniprenylphenol A (**1**, in DMSO-d_6)

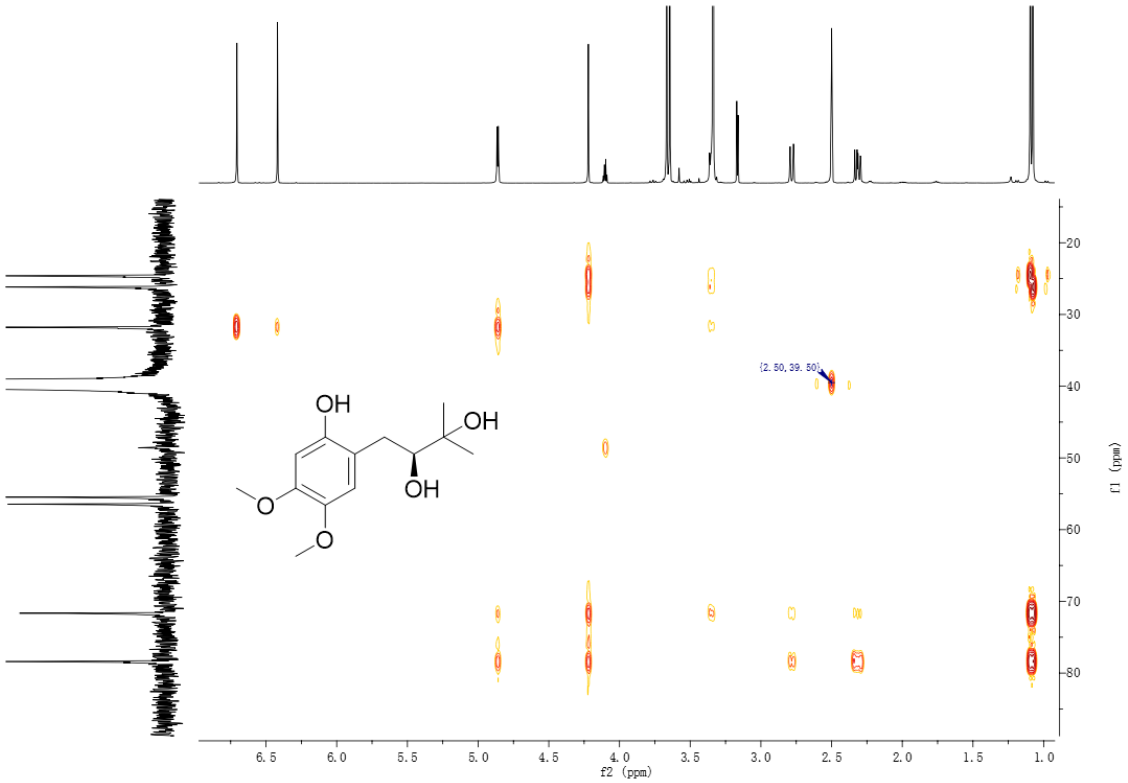
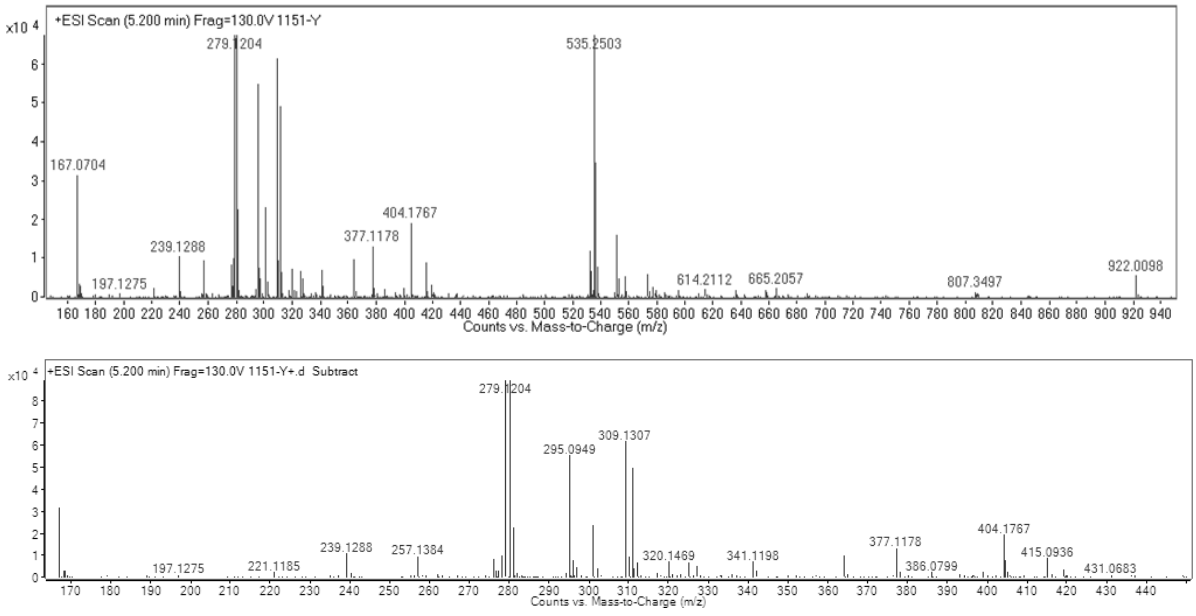


Figure S_{16}. HRESIMS spectrum of peniprenylphenol A (**1**)



$[M + H]^+$: *m/z* 257.1384 (calcd for $C_{13}H_{21}O_5$, 257.1389), $[M + Na]^+$: *m/z* 279.1204 $[M + Na]^+$ (calcd for $C_{13}H_{20}NaO_5$, 279.1208), $[M + K]^+$: *m/z* 295.0949 (calcd for $C_{13}H_{20}KO_5$, 295.0948), $[2M + Na]^+$: *m/z* 535.2503 (calcd for $C_{26}H_{40}NaO_{10}$, 535.2519),

Figure S_{17}. UV spectrum of peniprenylphenol A (**1**)

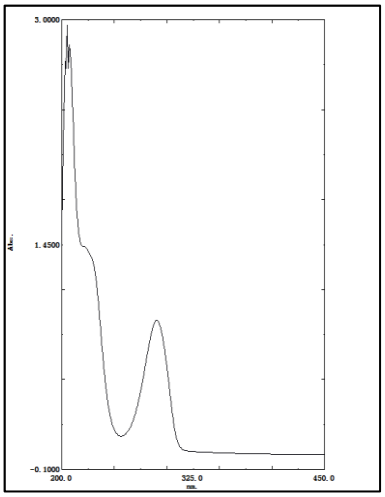


Figure S_{18}. IR spectrum of peniprenylphenol A (**1**)