Supporting Information

Structures and Absolute Configurations of Penicillactones

A–C from an Endophytic Microorganism, *Penicillium*

dangeardii Pitt

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S1. Experimental Section

General Experimental Procedures.

Optical rotations and CD spectra were taken on a JASCO P-2000 polarimeter and a JASCO-2000 spectropolarimeter. UV spectra were measured on a JASCO V650 spectrophotometer. IR spectra were recorded on a Nicolet 5700 FT-IR spectrometer by the microscope transmission method. NMR spectra (500 MHz for ^1H , 125 MHz for ^{13}C) were obtained on an INOVA-500 spectrometer. 2D INADEQUATE spectrum was recorded on an Bruker-800 spectrometer. Chemical shifts are given in δ with solvent (acetone- d_6) peaks used as reference. ESI-MS were measured on an Agilent 1100 Series LC/MSD ion trap mass spectrometer. HRESI-MS data were recorded on an Autospec Ultima-TOF mass spectrometer. Preparative HPLC was performed on a Shimadzu LC-6AD instrument with an SPD-10A detector, using a YMC-Pack ODS-A column (2×25cm, 5 μm). SephadexTM LH-20 (Amersham Pharmacia Biotech AB Factory) and ODS (45-70 μm , Merck) were used for column chromatography.

Fungal Material.

The fungal strain of *Penicillium dangeardii* Pitt was isolated from the leaves of *Lysidicie rhodostegia* Hance, collected in June of 2007 at Nanning, Guangxi Province, People's Republic of China. The isolate was identified by Dr. Xianzhi Jiang in Professor X. Liu's culture collection at the Institute of Microbiology, Chinese Academy of Sciences, Beijing (specimen No. 2007-LJJ0021). Plugs of agar supporting mycelial growth were cut and transferred aseptically to a 1000 mL Erlenmeyer flask containing 400 mL of PDA medium (200g of potato and 25 g of commercial sugar in 1000 mL of water). After incubation for 3 days at 28 °C on a rotary shaker at 110 rpm, 20 mL of culture liquid was transferred as seed into each 1000 mL flasks containing culture liquid (400 mL). The cultivation was then kept for 7 days at 28 °C.

Extraction and Isolation.

The filtrate of culture (100 L) was concentrated to 10 L in vacuo at 50 °C. It was adsorbed on macroporous resin. The resin was washed with water then eluted with 95% alcohol. The alcohol fraction collected was concentrated to obtain 63.0 g of a crude material which upon diatomaceous earth column chromatography (ligroine I, Eac, Acet and methanol) gave four fractions. The ethyl acetate extract (30.1 g) was applied to a Sephadex LH-20 column eluted with methanol, to give three fractions (A: 3.5 g; B: 25.1 g, C: 1.3 g). Fraction B (25.1 g) was chromatographed over an ODS column, eluted with a gradient of increasing methanol (5-100%) in water to afford 6 subfractions (B1-B6). Fractions B4 (15.8 g) was purified by RP-HPLC using 50% acetonitrile in water to yield pure compounds **1** (143 mg), **2** (43 mg) and **3** (21 mg).

Compound 1 (penicilactone **A**). White powder, $[\alpha]_{\text{D}}^{20} +54.6^\circ$ (c 0.12, CH_3CN); UV (MeOH) λ_{max} (log ϵ) 212 (0.8), 252 (0.1); IR: 3404.6, 1746.9. ^1H NMR (500 MHz, acetone- d_6) and ^{13}C NMR (125 MHz, acetone- d_6) see Table S1. (+) ESI-MS, m/z 515.2 $[\text{M} + \text{Na}]^+$; (-) ESI-MS, m/z 491.4 $[\text{M}-\text{H}]^-$; $\text{C}_{25}\text{H}_{32}\text{O}_{10}$; HRESIMS m/z 493.20885 $[\text{M} + \text{H}]^+$ ($\text{C}_{25}\text{H}_{33}\text{O}_{10}$, calcd 493.20682), 510.23643 $[\text{M} + \text{NH}_4]^+$ ($\text{C}_{25}\text{H}_{36}\text{NO}_{10}$, calcd 510.23337), 515.1909 $[\text{M} + \text{Na}]^+$ ($\text{C}_{25}\text{H}_{32}\text{NaO}_{10}$, calcd 515.18877).

Structural modification of compounds 1a-1d.

Compound 1a: 10% Pd/C (1 mg) was added to the solution of **1** (2 mg) in MeOH (1 mL). The solution was shaken in hydrogen (2.5 psi) for 12 h. The mixture was filtered to remove the Pd/C and then purified using RP-HPLC (45% CH_3CN in H_2O) to yield compound **1a** (1.5 mg). ^1H NMR (500 MHz, acetone- d_6) and ^{13}C NMR (125 MHz, acetone- d_6) see Table S4.

Compound 1b: 1 mg/mL CrO_3 -AcOH (2 mL) was added to the solution of **1** (10 mg) in

AcOH (3 mL). The solution was stirred for 8 h at 25 °C and then purified using RP-HPLC (60% CH₃CN in H₂O) to yield compound **1b** (8 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S4.

Compound 1c: 10% Pd/C (1 mg) was added to the solution of **1b** (5 mg) in MeOH (2 mL). The solution was shaken with hydrogen (2.5 psi) for 12 hours. The mixture was filtered to remove the Pd/C and then evaporated to remove MeOH. The obtained residue was dissolved in AcOH. The AcOH solution was added 5% Rh/C (2 mg). The solution was then shaken with hydrogen (2.5 psi) for 18 hours at 25 °C and then purified using RP-HPLC (75% CH₃CN in H₂O) to yield compound **1c** (0.7 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S4.

Compound 1d: 1 N NaCO₃ (1 mL) was added to the stirring solution of **1** (5 mg) in H₂O (2 mL) and then the stirring was continued for 12 h at 25 °C. The mixture was lyophilized to remove the water. The dried mixture was then dissolved in DMSO, added CH₃I (2 μL), and stirred for 2 h at 25 °C. The solvent was purified by using RP-HPLC (45% CH₃CN in H₂O) to yield compound **1d** (2.3 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S4.

Measurement of the CD spectrum of In situ formed Rh-complex of **1d**

The method involving in situ complexes of dirhodium tetrakis- (trifluoroacetate) [Rh₂(OCOCF₃)₄] was developed by Snatzke and Gerards and applied to the determination of the absolute stereochemistry of chiral secondary alcohols.^[1] Due to the CD spectrum of the Rh complex of chiral secondary alcohol was measured with the inherent CD spectrum subtracted, the positive Cotton effect (330 nm) in the CD spectrum does not make interference with the inherent Cotton effect.

For CD measurements, **1d** (1 mg) was dissolved in a dry solution of the stock [Rh₂(OCOCF₃)₄] complex (2 mg) in chloroform (5 ml) so that the molar ratio of the stock complex to ligand was around 1:0.6. Then the CD of the prepared Rh-complex solution was measured. By subtracting the inherent CD spectrum of **1d**, the in situ formed Rh-complex of **1d** was obtained (Figure S26).^[1]

Reference: [1] (a) Freleck, J.; Szczepek, W. J. *Tetrahedron: Asymmetry*, **1999**, *10*, 1507-1520. (b) Gerards, M.; Snatzke, G. *Tetrahedron: Asymmetry*, **1990**, *1*, 221-236. (c) Cotton, F. A.; Falvello, L. R.; Gerards, M.; Snatzke, G. *J. Am. Chem. Soc.* **1990**, *112*, 8979-8980.

Discussion on the conformation and NOE correlations of ring B of **1**

The conformation for five-membered ring system is very complicated. In the case of penicillactones, the ring B is multi-constituted with 'big' groups (rings A, C and D). To overcome the steric hindrance, the molecule should exist with minimum energy and one dominant conformation. Therefore, in our study, we minimized the molecular energy with ChemBio 3D to get the most possible dominant conformation (Minimize Energy to Minimum RMS Gradient of 0.100). Fortunately, the resultant conformation and configuration are consistent with the experimental data.

H-8 simultaneously showed NOE correlations with H-7b and H-9b. Meanwhile, H-7" simultaneously showed NOE correlations with H-7a and H-9a. (Figure 3 in manuscript). H-7" and H-8 have been proved to be in anti orientation based on their coupling constant (*J* = 9.0 Hz). Therefore, conclusion can be drew that H-8, H-7b and H-9b resided on the same face of ring B and H-7a and H-9a were on the opposite face of ring B. We noticed that both H-9a and H-9b are within NOE distance of H-8, and H-8 might also be with NOE distance of H-4 with an opposite configuration of C-5. However, no NOE correlations between H8 and H-9a and between H-4 and H-8 were discovered. Therefore, after the determination of the absolute configuration of C-5 to be S based on relative configuration, more structural modifications were carried out to avoid wrong conclusion. In our study, ring A was oxidized to succinic anhydride. According to the CD of succinic anhydride, C-5 was also

determined to be S. The configuration determined using two methods is consistent, which proves the configuration of C-5 to be S.

We did not carry out the conformational search. Therefore, the parameters such as minima, relative energy and force field have not been studied.

Compound 2 (penicillactone **B**). White powder; $[\alpha]_D^{20} +49.7^\circ$ (*c* 0.13, CH₃CN); UV (MeOH) $\lambda_{\max}$ (log ϵ) 206 (1.4), 242 (0.6); IR: 3444.3, 1819.6, 1763.5, 1669.1. ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S2. HRESIMS *m/z* 533.2030 [M + H]⁺ (C₂₇H₃₃O₁₁, calcd 533.20174), 550.2301 [M + NH₄]⁺ (C₂₇H₃₆NO₁₁, calcd 550.22829), 555.1853 [M + Na]⁺ (C₂₇H₃₂NaO₁₁, calcd 555.1837).

Compound 2a: Iodomethane (CH₃I, 3 μ L) was added to the solution of **2** (5 mg) in DMSO (2 mL). The solution was stirred for 2 h at 25 °C and then purified using RP-HPLC (50% CH₃CN in H₂O) to yield compound **2a** (3.2 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S5.

Compound 2b: 1 mL of 4-nitrobenzyl bormide (1 mg/mL DMF) was added to the stirred solution of **2** (5 mg) in DMF (1 mL). The solution was stirred for 4 h at 25 °C and then purified using RP-HPLC (60% CH₃CN in H₂O) to yield compound **2b** (2.3 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S5.

compound 2c: 10% Pd/C (2 mg) was added to the solution of **2a** (3 mg) in MeOH (1 mL). The solution was shaken with hydrogen (2.5 psi) for 12 hours. The mixture was filtered to remove the Pd/C and then purified using RP-HPLC (45% CH₃CN in H₂O) to yield compound **2c** (1.5 mg). ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S5.

Structural modification of compound 2.

Scheme 1. Compound **2**, reacted with a) MeI, b) NBB, and c) Pd/C to yield **2a**, **2b**, and **2c**, respectively.

Measurement of the CD spectrum of In situ formed Rh-complex of **2a**

For CD measurements, **2a** (1 mg) was dissolved in a dry solution of the stock [Rh₂(OCOCF₃)₄] complex (2 mg) in chloroform (5 ml) so that the molar ratio of the stock complex to ligand was around 1:0.6. Then the CD of the prepared Rh-complex solution was measured. By subtracting the inherent CD spectrum of **2a**, the in situ formed Rh-complex of **2a** was obtained (Figure S56).

Compound 3 (penicillactone **C**). White powder; $[\alpha]_D^{20} +28.4^\circ$ (*c* 0.1, CH₃CN); UV (MeOH) $\lambda_{\max}$ (log ϵ) 206 (0.9), 246 (0.3); IR: 3448.6, 1818.7, 1751.4, 1665.0. ¹H NMR (500 MHz, acetone-*d*₆) and ¹³C NMR (125 MHz, acetone-*d*₆) see Table S3. HRESIMS *m/z* 587.2109 [M + Na]⁺ (C₂₈H₃₆NaO₁₂,

calcd 587.2099).

Determination of the structure of penicillactone **C** (**3**)

The structural assignment of penicillactone **C** (**3**) was confirmed as an acyclic ester for spin system **II** at C2''-C7'' instead of a lactone (ring **D**), as observed in **2**. Except for the C2''-C7'' unit, all chemical shifts in the other positions were similar. The planar structure of **3** was proposed and verified by combining extensive 1D and 2D NMR, IR, and MS spectral data. For the threo vic-diols at C6'' and C7'', the method employing Mo₂(OAc)₄ developed by Snatzke and Frelek is the most practical, simple, and reliable approach for assigning the configuration.^[1] The CD spectrum exhibited a negative cotton effect at 310 nm (Figure S65), indicating the presence of a torsional angle in the HO-C-C-OH at C6''-OH and C7''-OH, and the absolute configurations of C6'' and C7'' were both *S* (Figure S65), which were consistent with the configurations of C6'' and C7'' in **2**. Therefore, the stereochemistry of penicillactone **C** was determined to be 5*R*, 6*S*, 8*S*, 5'*S*, 6''*S*, and 7''*S* based on its highly similar carbon skeleton and biogenesis.

Measurement of the CD spectrum of **3** in DMSO of dimolybdenum tetracetate

Compound **3** (1.2 mg, *ca.* 0.002 M) was dissolved in a stock solution of the dimolybdenum tetracetate (5 mg, *ca.* 0.002 M) in DMSO (1 ml) so that the molar ratio of the stock complex to ligand was about 1:1. The first CD spectrum was recorded immediately after mixing and its time evolution was monitored until stationary (about 30 min after mixing). Then, the inherent CD of compound **3** was subtracted to afford CD spectrum (Figure S65).^[1]

Reference: [1] (a) Górecki, M.; Jablon'ska, E.; Kruszewska, A.; Suszczyn'ska, A.; Urban'czyk-Lipkowska, Z.; Gerards, M.; et al. *J. Org. Chem.* **2007**, *72*, 2906–2916. (b) Górecki, M.; Kamin'ska, A.; Rus'kowska, P.; Suszczyn'ska, A.; Frelek, J. *Polish. J. Chem.* **2006**, *80*, 523–534. (c) Frelek, J.; Klimek, A.; Ruskowska, P. *Curr. Org. Chem.* **2003**, *7*, 1081–1104. (d) Di Bari, L.; Pescitelli, G.; Pratelli, C.; Pini, D.; Salvadori, P. *J. Org. Chem.* **2001**, *66*, 4819–4825. (e) Politi, M.; De Tommasi, N.; Pescitelli, G.; Di Bari, L.; Morelli, I.; Braca, A. *J. Nat. Prod.* **2002**, *65*, 1742–1745.

Proposed biogenetic pathways of **1–3**

Natural products with the maleic anhydride structure can be classified as nonadrines, tautomycin and tautomycetin, chaetomelic anhydrides, and other compounds according to whether the products contain the core structure of nonadrines, the presence of a nine-membered ring with an affixed maleic anhydride.^[1] From the present reports, natural products with maleic anhydride structure were all produced by microorganisms.^[1] Structurally, we consider that reported natural products, rubratoxin B,^[2] isolated from *Penicillium rubrum* and belonging to nonadrine-type anhydride, might be the precursor of **1–3**. A Cope rearrangement of rubratoxin B produced compound **2**. From **2**, compound **1** and **3** was produced via a series of steps (Figure 1).

Figure 1. Proposed biogenetic pathways of **1-3**

References: [1] X. Chen, Y. Zheng, Y. Shen, *Chem. Rev.* **2007**, *107*, 1777–1830.

[2] G. Büchi, K. M. Snader, J. D. White, J. Zanos Gougoutas, S. Singh, *J. Am. Chem. Soc.* **1970**, *92*, 6638–6641

Bioactivity assay against the release of β -glucuronidase

Nature products with anhydride structure have special biological activities, such as antibiotic activities and enzymatic inhibition.^[1] Some of the compounds are strong inhibitors of protein phosphatase, Ras farnesyl transferase and squalene synthase, and inositol monophosphatase. Different from reported anhydrides^[1], penicillactones B and C bearing the core structure of anhydride, showed inhibition of the release of β -glucuronidase from polymorphonuclear leukocytes. Therefore, this is the first report on the inhibition of the release of β -glucuronidase from polymorphonuclear leukocytes by anhydride type compounds. Excessive accumulation of β -glucuronides in body could induce the occurrence of inflammation, cancer and related diseases. Therefore, therapeutic potentials of the penicillactones are antiinflammation, anticancer and etc.

In our study, compounds **1-3** were assessed for their inhibitory activities against the release of β -glucuronidase in rat PMNs induced by PAF in vitro. Ginkgolide B (purity >90%; Sigma–Aldrich; St. Louis, MO, USA) was used as a positive control. Briefly, each test sample was dissolved in DMSO at a concentration of 0.1 M and diluted with RPMI-1640 to 10^{-3} – 10^{-5} M. The test samples (2.5 μ L) were incubated with a suspension of rat PMNs (245 μ L) at a density of 2.5×10^6 cells mL^{-1} at 37 °C for 15 min, and 1×10^{-3} M cytochalasin B (2.5 μ L) was added for another 5 min. After addition of PAF (2.5 μ L), the mixture was incubated for another 5 min. Subsequently, the mixture was put in an ice-bath to terminate the reaction. After centrifugation at 1000 rpm for 5 min, the supernatant was obtained. The supernatant (25 μ L) and 2.5 mM phenolphthalein-glucuronic acid (25 μ L) were incubated with 0.1 M HOAc buffer (100 μ L, pH 4.6) at 37 °C for 18 h. The reaction was terminated by the addition of 0.3 M NaOH (150 μ L). The absorbance was read at 550 nm, and the inhibitory ratio (IR) was calculated as $\text{IR}(\%) = (A_{\text{PAF}} - A_t) / (A_{\text{PAF}} - A_c) \times 100\%$, where A_{PAF} , A_t , and A_c refer to the average absorbance of three wells of PAF, test compounds, and control groups, respectively. The compounds (IR > 50% at 10 μ M) were tested at three concentrations (0.1, 1, 10 μ M) and each concentration of the compounds was

tested in three parallel wells. A dose-response curve was plotted for each compound, and the IC₅₀ value was calculated as the concentration of test compound resulting in 50% reduction of optical density compared with the control.^[2]

References: [1] X. Chen, Y. Zheng, Y. Shen, *Chem. Rev.* **2007**, *107*, 1777–1830.

[2] (a) Kang, J.; Chen, R.Y.; Yu, D.Q. *Planta Med.* **2006**, *72*, 52-59. b) Nawaz, H.R.; Malik, A.; Khan, P.M.; Shujaat, S.; Rahman, A.U. *Chem. Pharm Bull.* **2000**, *48*, 1771-1773.

Table S1. NMR (500 MHz for ^1H , 125 MHz for ^{13}C , 200 MHz for 2D INADEQUATE) spectral data of compound **1** (in acetone- d_6)

position	δ_{C}	δ_{H} (J in Hz)	Carbon multiplicity	^1H - ^1H COSY	Key HMBC Correlations	2D INADEQUATE correlations	Key NOE correlations
1	180.2		C			C5	
3	96.8	5.85(d,6.0)	CH	H4	C1/C5/C4	C4	H4a
4	40.5	H4a: 3.06(dd,13.0,6.0), H4b: 1.82(d,13.0)	CH ₂	H3	C1/C5/C6/C9	C3	H4a: H3/H9b H4b:H4a
5	54.8		C			C1/C6	
6	59.0		C			C5/C6a/C3'	
6a	172.4		C			C6	
7	40.9	H7a: 2.74(dd,13.0,10.0), H7b: 2.29(dd,13.0,8.5)	CH ₂	H8	C5/C6a/C8/C9/C7''/C3'	C8	H7a:H7b/H6''/H7'' H7b:H8/H6''
8	39.6	2.92(m)	CH	H7/H9/H7''	C5/C6/C6''	C7/C9/C7''	H7b/H6''/H9b
9	38.2	2.59(m),2.21(m)	CH ₂	H8	C1/C4/C6/C7/C8/C7''	C8	H9a-H7'' H9b-H8/H4a
2'	172.4		C			C3'	
3'	134.6		C			C2'/C6/C4'	
4'	154.1	7.73(brs)	CH	H5'	C2'/C6	C3'/C5'	H8
5'	81.8	5.16(brt,5.0)	CH	H6'/H4'	C2'/C3'/C7'	C4'/C6'	
6'	33.7	1.92(m),1.68(m)	CH ₂	H5'/H7'	C4'/C8'	C5'/C7'	

7'	25.4	1.47(m)	CH ₂	H6'/H8'		C6'/C8'	
8'	29.6	1.39(m)	CH ₂	H7'/H9'		C7'/C9'	
9'	32.3	1.34(m)	CH ₂	overlap		C8'/	
						C10'	
10'	23.2	1.34(m)	CH ₂	overlap		C9'	
11'	14.3	0.90(t,6.5)	CH ₃	H10'	C9'		
2''	164.3					C3''	
3''	121.0	5.92(d,10.0)	CH	H4''	C4''/C5''	C2''/C4''	
4''	147.3	7.09(dd,10.0,6.0)	CH	H3''/H5''	C2''/C6''	C3''/C5''	
5''	27.0	2.78(m),2.38(m)	CH ₂	H4''/H6''	C3''/C4''/C7''	C4''/C6''	
6''	78.9	4.55(brd,12.0)	CH	H5''/H7''	C2''/C4''/C7''/C8	C5''/C7''	H7a/9a/H7''/H5''a/H5''b
7''	75.4	3.69(d,9.0)	CH	H6''/H8	C5''/C7''/C8	C6''/C8	H5''b/H6''/H7a/H9a

Table S2. NMR (500 MHz for ^1H , 125 MHz for ^{13}C) spectral data of compound **2** (in acetone- d_6)

position	δ_{C}	δ_{H} (J in Hz)	Carbon multiplicity	^1H - ^1H COSY	Key HMBC Correlations	Key NOE correlations
1	175.9					
3	167.0					
4	102.6					
4a	157.1	7.74(s)	CH		C3/C5	H9a
5	58.9					
6	60.7					
6a	172.2					
7	38.3	2.54(2H,d,8.5)	CH ₂	H8	C5/C6a/C8/C9/C7''/C3'	
8	38.8	3.14(m)	CH	H7/H9/H7''	C5/C6/C6''	H7''/H6''/ H7/H9a/H4'
9	35.7	2.76(dd,14.5,10.8), 2.32(dd,14.5,5.0)	CH ₂	H8	C1/C4/C6/C7/C8/C7''	
2'	171.8					
3'	134.6					
4'	151.9	7.66(brs)	CH	H5'	C2'/C6	H7/H8/9a
5'	81.5	4.99(m)	CH	H4'/H6'	C2'/C3'/C7'	

6'	32.8	1.84(m),1.64(m)	CH ₂	H5'/H7'	C4'/C8'	
7'	24.8	1.39(m)	CH ₂	H6'		
8'	28.9	1.33(m)	CH ₂	overlap		
9'	31.8	1.28(m)	CH ₂	overlap		
10'	22.6	1.28(m)	CH ₂	overlap		
11'	14.3	0.87(t,6.5)	CH ₃	overlap	C9'	
2"	163.7					
3"	120.5	5.91(dd,10.0,2.5)	CH	H4"	C4"/C5"	
4"	146.9	7.08(m)	CH	H3"/H5"	C2"/C6"	
5"	26.4	2.82(m),2.39(ddd; 18.5,6.0,5.0)	CH ₂	H4"/H6"	C3"/C4"/C7"	
6"	78.3	4.58(brdd,10.0,2.5)	CH	H5"/H7"	C2"/C4"/C7"/C8	H7/H8/H7"/H5"a/H5"b
7"	74.8	3.83(brd,10.0)	CH	H6"/H8	C5"/C7"/C8	H8/H5"b/H5"b/H6"/H7/H9b
6a-OCH ₃	52.3	3.58(s)	CH ₃		C6	

Table S3. NMR (500 MHz for ^1H , 125 MHz for ^{13}C) spectral data for compound **3** (in acetone- d_6)

position	δ_{C}	δ_{H} (J in Hz)	Carbon multiplicity	^1H - ^1H COSY	Key HMBC Correlations	Key NOE correlations
1	176.8					
3	167.8					
4	102.3					
4a	158.9	7.77(s)	CH		C3/C5	H9a
5	59.5					
6	61.3					
6a	172.8					
7	39.1	2.52(d,8.5)	CH ₂	H8	C5/C6a/C8/C9/C7''/C3'	
8	40.0	3.01(m)	CH	H7/H9/H7''	C5/C6/C6''	H7''/H6''/ H7/H9a/H4'
9	35.9	2.71(dd,14.0,10.8), 2.24(dd,14.0,5.0)	CH ₂	H8	C1/C4/C6/C7/C8/C7''	
2'	172.4					
3'	135.4					
4'	152.3	7.65(hrs)	CH	H5'	C2'/C6	H7/H8/9a
5'	81.9	4.97(m)	CH	H4'/H6'	C2'/C3'/C7'	

6'	33.4	1.84(m),1.64(m)	CH ₂	H5'/H7'	C4'/C8'
7'	25.3	1.40(m)	CH ₂	H6'	
8'	29.5	1.33(m)	CH ₂	overlap	
9'	32.4	1.27(m)	CH ₂	overlap	
10'	23.3	1.27(m)	CH ₂	overlap	
11'	14.3	0.87(t,6.5)	CH ₃	H10'	C9'
2''	167.3				
3''	120.9	5.87(brd,11.5)	CH	H4''	C4''/C5''
4''	148.6	6.50(m)	CH	H3''/H5''	C2''/C6''
5''	35.0	2.91(m)	CH ₂	H4''/H6''	C3''/C4''/C7''
6''	76.9	3.68(brd,9.5)	CH	H5''/H7''	C2''/C4''/C7''/C8
7''	71.7	3.68(brd,9.5)	CH	H6''/H8	C5''/C7''/C8
6a-OCH ₃	52.8	3.66(s)	CH ₃		C6
2'' a-OCH ₃	52.8	3.58(s)	CH ₃		C2''

Table S4. ¹H NMR (500 MHz) and ¹³C NMR(125 MHz) spectral data for compounds **1a-1d** (in acetone-*d*₆).

position	1a		1b		1c		1d	
	δ_C	δ_H	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	181.1		176.3		174.4		175.2	
2								
3	96.6	5.85	174.8		173.8		205.7	9.68(s)
4	39.5	2.87	51.3	3.21 (d,11), 2.53 (d, 11)	51.3	3.05 (d,11), 2.71(d, 11)	48.2	2.90 (brs)
5	58.5		60.7		59.0		60.3	
6	56.1		56.8		56.8		56.8	
7	39.5	2.58	38.9	2.66(m),2.49(m)	38.8	2.76(m),2.39(m)	38.5	2.76(m),2.39(m)
8	38.3	2.87	38.6	2.96(m)	37.6	2.88(m)	37.6	2.90(overlap)
9	39.5	2.36	37.5	2.65(m),2.35(m)	37.6	2.63(m),2.34(m)	37.5	2.63(m),2.34(m)
2'	172.3		172.9		172.1		172.5	
3'	134.5		129.0		25.6	2.88(m),1.64(m)	133.3	
4'	154.0	7.72	157.5	7.73 (brs)	26.2	1.82(m)	152.7	7.75 (brs)
5'	81.9	5.19	83.5	5.19(t,5.0)	80.9	5.20(m)	82.0	5.17(t,5.0)
6'	33.7	1.94,1.67	32.6	1.85(m),1.64(m)	33.8	1.85(m),1.64(m)	33.8	1.85(m),1.64(m)
7'	25.3	1.43	24.4	1.43(m)	25.4	1.43(m)	25.4	1.43(m)

8'	29.6	1.37	31.3	1.36(m)	30.7	1.36(m)	30.3	1.36(m)
9'	32.4	1.32	32.5	1.29(m)	31.2	1.29(m)	32.2	1.29(m)
10'	19.2	1.32	23.2	1.29(m)	23.2	1.29(m)	23.2	1.29(m)
11'	14.3	0.91	14.5	0.95(t;5.5)	13.4	0.78(t;5.5)	14.3	0.87(t;5.5)
2''	171.5		162.7		161.7		164.1	
3''	23.2	2.20	121.9	5.81(d;10.5)	25.2	2.23(2H, m)	121.1	5.89(d;10.5)
4''	25.5	2.07,1.67	145.7	6.85(t;7.5)	24.3	1.87(m),1.63(m)	147.3	7.06(t;7.5)
5''	29.6	2.56,2.36	27.7	2.55(m),2.33(m)	27.7	2.35(m),2.27(m)	27.7	2.55(m),2.33(m)
6''	80.5	4.41	80.7	5.02(m)	79.2	4.79(m)	79.2	4.48(br.d;13.0)
7''	76.1	3.58	208.8		208.1		76.1	3.67(br.d;9.0)
6a-OCH ₃							52.7	3.56(s)
1-OCH ₃							52.6	3.55 (s)

Note: The splitting modes of the ¹H NMR data of **1a** were not assigned. Probably the trace Pd-C residue during the catalytic hydrogenation caused the paramagnetic effect to make the ¹H NMR peaks broad. The quality of ¹³C NMR spectrum showed that compound **1a** is pure enough to carry out the further experiments.

Table S5. ^1H NMR (500 MHz) and ^{13}C NMR(125 MHz) spectral data for compounds **2a-2c** (in acetone- d_6).

position	2a		2b		2c	
	δ_{C}	δ_{H} (J in Hz)	δ_{C}	δ_{H} (J in Hz)	δ_{C}	δ_{H} (J in Hz)
1	176.0		175.3		176.0	
3	166.4		166.7		166.8	
4	104.2		106.3		104.5	
4a	161.3	7.65(s)	164.4	7.68(s)	161.6	7.64(s)
5	59.1		59.7		59.4	
6	60.9		60.8		61.3	
6a	171.9		172.7		172.7	
7	38.4	2.47(m)	39.0	2.49(d;8.5)	38.9	2.51(m)
8	38.4	3.05(m)	39.8	3.14(m)	38.8	3.09(m)
9	35.8	2.60(m),2.29(m)	38.7	2.73(m),2.35(m)	36.0	2.64(m),2.31(m)
2'	171.9		172.4		172.2	
3'	134.6		134.8		135.0	
4'	152.3	7.38(br.s)	152.6	7.47(br.s)	152.7	7.37(s)
5'	81.7	5.11(m)	81.9	4.60(m)	82.1	5.11(m)
6'	33.2	1.87(m),1.66(m)	33.5	1.84(m),1.64(m)	33.5	1.89(m),1.63(m)
7'	25.2	1.41(m)	25.3	1.39(m)	25.2	1.37(m)
8'	29.7	1.34(m)	29.3	1.33(m)	29.5	1.34(m)

9'	32.4	1.29(m)	32.3	1.28(m)	32.4	1.29(m)
10'	23.2	1.29(m)	23.1	1.28(m)	23.2	1.29(m)
11'	13.9	0.83(t;6.5)	14.3	0.86(t;6.5)	14.3	0.83(t;6.5)
2"	166.4		164.4		172.2	
3"	120.7	5.87(dd;10.0,2.5)	121.0	5.93(dd;10.0,2.5)	29.4	2.23 (2H, m)
4"	147.0	7.03(m)	147.5	7.09(m)	25.4	1.87,1.63(m)
5"	26.9	2.80(m),2.38(m)	26.9	2.82(m),2.39(m)	19.2	2.55(m),2.33(m)
6"	78.5	4.53(br.dd;10.0,2.5)	79.0	4.57(br.dd;10.0,2.5)	80.6	4.41(br.dd;10.0,2.5)
7"	74.9	3.76 (br.d;10.0)	75.6	3.68(br.d;10.0)	76.0	3.70(br.d;10.0)
6a-OCH ₃	52.7	3.54(s)	53.1	3.58(s)	53.0	3.56(s)
4a-OCH ₃	63.1	3.93(s)			64.2	3.92(s)
4a-NBB						
1'''			77.5	5.43(dd;17.0,12.5)		
2'''			143.1			
3'''			130.5	7.81(d;10)		
4'''			124.8	8.33(d;10)		
5'''			152.6			
6'''			124.8	8.33(d;10)		
7'''			130.5	7.81(d;10)		

Figure S1. ESIMS and HRESIMS of penicillactone A (1)

MS Formula Results: + Scan (7.303 min) (200903121.d)

m/z		Ion	Formula	Abundance							
493.20885		(M+H)+	C25 H33 O10	962582							
Best		Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
✓		C18 H36 O15	C18 H37 O15	69.19		493.2127	7.84	51.86	72.86	99.43	1
✓		C25 H32 O10	C25 H33 O10	91.72		493.20682	-4.09	83.6	98.89	99.36	10
m/z		Ion	Formula	Abundance							
510.23643		(M+NH4)+	C25 H36 N O10	2117656.5							
Best		Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
✓		C25 H32 O10	C25 H36 N O10	77.31		510.23337	-6.14	67.92	88.02	83.24	10
m/z		Ion	Formula	Abundance							
515.1909		(M+Na)+	C25 H32 Na O10	1051975.3							
Best		Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
✓		C18 H36 O15	C18 H36 Na O15	69.36		515.19464	7.63	55.41	67.81	99.12	1
✓		C25 H32 O10	C25 H32 Na O10	91.23		515.18877	-4.31	82.83	99.01	98.7	10

Figure S2. ^1H NMR spectrum of penicillactone **A** (**1**)

Figure S3. ^{13}C NMR spectrum of penicillactone A (**1**)

The figure displays a 2D ^{13}C - ^{13}C NMR spectrum of compound **1**. The chemical structure of **1** is shown in the top left corner, with carbon atoms labeled from 1 to 11'. The spectrum features a 1D ^{13}C NMR spectrum along the top and left axes, with the chemical shift in ppm indicated on the right (ranging from 10 to 360 ppm) and bottom (ranging from 210 to 10 ppm). The 2D plot shows diagonal peaks representing the 1D spectrum and off-diagonal cross-peaks indicating carbon-carbon correlations. These cross-peaks are color-coded: green for C1-C6, red for C7-C11, and blue for C1'-C6'. Specific correlations are labeled with carbon numbers (e.g., C1, C2', C3'', C4', C5', C6'') and connected by lines to their corresponding peaks in the 2D plot.

Figure S5. ^1H - ^1H COSY spectrum of penicillactone A (1)

Figure S6. HSQC spectrum of penicillactone **A** (**1**)

INOVA-500 gHSQC 435-4 IN CD3COCD3 09.04.15 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Sample #5, Operator: walkup
File: ghsqc_01
INOVA-500 "IMM-501"

Relax. delay 1.301 sec
Acq. time 0.199 sec
Width 4632.3 Hz
2D Width 25133.5 Hz
8 repetitions
2 x 128 increments
OBSERVE H1, 499.7733210 MHz
DECOUPLE C13, 125.6793772 MHz
Power 33 dB
on during acquisition
off during delay
W40_cold modulated
DATA PROCESSING
Gauss apodization 0.055 sec
F1 DATA PROCESSING
Gauss apodization 0.002 sec
FT size 4096 x 2048
Total time 53 min, 46 sec

Figure S7. HMBC spectrum of penicillactone A (1)

INOVA-501 gHMBC 435-4 IN C03C0C03 09.04.15 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Sample #5, Operator: walkup
File: Ghmhc_01
INOVA-500 "HM-501"
Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 4632.3 Hz
2D Width 30155.9 Hz
32 repetitions
160 increments
OBSERVE H1, 499.7733209 MHz
DATA PROCESSING
Sine bell 0.045 sec
F1 DATA PROCESSING
Sine bell 0.003 sec
FT size 2048 x 2048
Total time 1 hr, 44 min, 5 sec

Figure S8. Spin decoupling allows the rapid identification of coupled partner (H3-H4) by removing couplings to the irradiated spin.

Figure S9. Homonuclear spin decoupling allows the rapid identification of coupled partner of (H6"-H7"-H8) by removing couplings to the irradiated spin.

Figure S10. NOE spectrum of penicillactone A (1)

Figure S11. HRESIMS spectrum of compound **1a**.

MS Formula Results: - Scan (5.105 min) Sub (201004232.d)

m/z	Ion	Formula	Abundance
493.2068	(M-H) ⁻	C ₂₅ H ₃₃ O ₁₀	44981.2

Best	Formula (M)	Ion Formula	Calc m/z	Score	✓	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☒	C ₂₅ H ₃₄ O ₁₀	C ₂₅ H ₃₃ O ₁₀	493.2079	96.79			494.2141	494.2152	2.17	2.17	99.34	97.18	95.05	493.2068	9
☐	C ₂₆ H ₃₀ N ₄ O ₆	C ₂₆ H ₂₉ N ₄ O ₆	493.2093	86.13			494.2141	494.2165	4.86	4.86	93.06	95.06	77.5	493.2068	14
☐	C ₂₀ H ₃₄ N ₂ O ₁₂	C ₂₀ H ₃₃ N ₂ O ₁₂	493.2039	81.63			494.2141	494.2112	-5.98	5.98	92.21	96.06	68.06	493.2068	5
☐	C ₃₃ H ₂₆ N ₄ O	C ₃₃ H ₂₅ N ₄ O	493.2034	66.62			494.2141	494.2107	-7.02	7.02	55.81	95.17	58.83	493.2068	23

Figure S12. ^1H NMR spectrum of compound **1a**.

Figure S13. ^{13}C NMR spectrum of compound **1a**.

Figure S14. HSQC spectrum of compound **1a**.

Figure S15. HMBC spectrum of compound **1a**.

Figure S16. HRESIMS spectrum of compound **1b**.

m/z	Ion	Formula	Abundance
493.20885	(M+H) ⁺	C ₂₅ H ₃₃ O ₁₀	962582

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☐	C ₁₈ H ₃₆ O ₁₅	C ₁₈ H ₃₇ O ₁₅	69.19		493.2127	7.84	51.86	72.86	99.43	1
☒	C ₂₅ H ₃₂ O ₁₀	C ₂₅ H ₃₃ O ₁₀	91.72		493.20682	-4.09	83.6	98.89	99.36	10

m/z	Ion	Formula	Abundance
510.23643	(M+NH ₄) ⁺	C ₂₅ H ₃₆ N O ₁₀	2117656.5

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☒	C ₂₅ H ₃₂ O ₁₀	C ₂₅ H ₃₆ N O ₁₀	77.31		510.23337	-6.14	67.92	88.02	83.24	10

m/z	Ion	Formula	Abundance
515.1909	(M+Na) ⁺	C ₂₅ H ₃₂ Na O ₁₀	1051975.3

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☐	C ₁₈ H ₃₆ O ₁₅	C ₁₈ H ₃₆ Na O ₁₅	69.36		515.19464	7.63	55.41	67.81	99.12	1
☒	C ₂₅ H ₃₂ O ₁₀	C ₂₅ H ₃₂ Na O ₁₀	91.23		515.18877	-4.31	82.83	99.01	98.7	10

Chemical structure of compound **1b** is shown above the spectrum. The structure is a complex polycyclic molecule featuring a cyclohexane ring, a carboxylic acid group, a lactone, and a furan ring. The spectrum displays the following peaks and integrations:

Chemical Shift (ppm)	Integration
7.73	1.00
6.88	1.19
5.87	1.14
5.17	1.00
5.16	1.31
3.44	1.24
3.42	1.18
3.28	1.17
3.17	1.11
3.06	0.98
3.02	1.55
2.99	1.56
2.97	2.01
2.96	0.86
2.95	1.32
2.89	1.59
2.88	19.89
2.85	5.50
2.85	
2.77	
2.69	
2.61	
2.59	
2.55	
2.53	
2.52	
2.48	
2.34	
2.31	
2.21	
2.19	
2.13	
2.04	
1.95	
1.94	
1.94	
1.93	
1.93	
1.92	
1.92	
1.91	
1.79	
1.75	
1.74	
1.73	
1.72	
1.58	
1.57	
1.56	
1.35	
1.33	
1.32	
1.30	
1.29	
1.24	
1.23	
1.21	
1.21	
1.19	
1.18	
1.17	
1.16	
1.09	
0.95	
0.82	
0.81	
0.79	
0.79	
0.77	
0.76	
0.75	
0.74	
0.00	
-0.05	

Figure S18. ^{13}C NMR spectrum of compound **1b**.

Figure S19. HRESIMS spectrum of compound **1c**.

MS Formula Results: - Scan (6.603 min) Sub (2013061301.d)

m/z	Ion	Formula	Abundance
491.192	(M-H)-	C25 H31 O10	2228083

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C30 H28 N4 O S	C30 H27 N4 O S	491.1911	99.43		492.1993	492.1984	-1.85	1.85	99.37	98.62	99.88	491.192	19
☐	C26 H28 N4 O6	C26 H27 N4 O6	491.1936	99.39		492.1993	492.2009	3.24	3.24	98.78	99.64	99.64	491.192	15
☒	C25 H32 O10	C25 H31 O10	491.1923	99.19		492.1993	492.1995	0.55	0.55	97.4	99.76	99.99	491.192	10
☐	C29 H32 O5 S	C29 H31 O5 S	491.1898	99.05		492.1993	492.197	-4.55	4.55	98.91	98.76	99.29	491.192	14
☐	C33 H24 N4 O	C33 H23 N4 O	491.1877	98.31		492.1993	492.195	-8.69	8.69	98.59	99.7	97.44	491.192	24

Figure S20. ^1H NMR spectrum of compound **1c**.

Figure S21. ^{13}C NMR spectrum of compound **1c**.

Figure S22. HRESIMS spectrum of compound **1d**.

MS Formula Results: - Scan (6.963 min) Sub (2013061303.d)

m/z	Ion	Formula	Abundance
519.2235	(M-H)-	C27 H35 O10	225147.1

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☒	C27 H36 O10	C27 H35 O10	519.2236	99.52		520.2308	520.2308	0.12	0.12	98.41	99.91	100	519.2235	10
☐	C28 H32 N4 O6	C28 H31 N4 O6	519.2249	99.48		520.2308	520.2322	2.67	2.67	98.68	99.89	99.75	519.2235	15
☐	C32 H32 N4 O S	C32 H31 N4 O S	519.2224	99.42		520.2308	520.2297	-2.15	2.15	99.29	98.75	99.84	519.2235	19
☐	C31 H36 O5 S	C31 H35 O5 S	519.2211	99.27		520.2308	520.2283	-4.7	4.7	99.72	98.81	99.24	519.2235	14
☐	C29 H36 N4 O S2	C29 H35 N4 O S2	519.2258	98.34		520.2308	520.2331	4.32	4.32	97.31	97.56	99.36	519.2235	14
☐	C28 H40 O5 S2	C28 H39 O5 S2	519.2244	98.34		520.2308	520.2317	1.76	1.76	96.35	97.63	99.89	519.2235	9
☐	C24 H40 O10 S	C24 H39 O10 S	519.2269	98.04		520.2308	520.2342	6.58	6.58	96.91	98.43	98.51	519.2235	5

m/z	Ion	Formula	Abundance
565.2297	(M-H)-	C28 H37 O12	448301.8

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C29 H34 N4 O8	C29 H33 N4 O8	565.2304	99.64		566.237	566.2377	1.11	1.11	98.86	99.94	99.96	565.2297	15
☒	C28 H38 O12	C28 H37 O12	565.2291	99.62		566.237	566.2363	-1.23	1.23	98.79	99.96	99.95	565.2297	10
☐	C33 H34 N4 O3 S	C33 H33 N4 O3 S	565.2279	99.32		566.237	566.2352	-3.32	3.32	99	99.13	99.61	565.2297	19
☐	C32 H38 O7 S	C32 H37 O7 S	565.2265	99.15		566.237	566.2338	-5.67	5.67	99.57	99.18	98.88	565.2297	14
☐	C26 H38 N4 O8 S	C26 H37 N4 O8 S	565.2338	98.64		566.237	566.241	7.05	7.05	99.11	98.83	98.28	565.2297	10
☐	C25 H42 O12 S	C25 H41 O12 S	565.2324	98.64		566.237	566.2397	4.71	4.71	97.46	98.9	99.23	565.2297	5
☐	C30 H38 N4 O3 S2	C30 H37 N4 O3 S2	565.2313	98.64		566.237	566.2385	2.62	2.62	97.14	98.19	99.76	565.2297	14
☐	C29 H42 O7 S2	C29 H41 O7 S2	565.2299	98.54		566.237	566.2372	0.28	0.28	96.37	98.25	100	565.2297	9
☐	C38 H34 N2 O S	C38 H33 N2 O S	565.2319	98.54		566.237	566.2392	3.79	3.79	96.27	99.35	99.5	565.2297	23
☐	C34 H34 N2 O6	C34 H33 N2 O6	565.2344	98.29		566.237	566.2417	8.22	8.22	97.94	99.98	97.66	565.2297	19

m/z	Ion	Formula	Abundance
597.2556	(M-H)-	C29 H41 O13	1388847.1

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Mat	Mass Match	m/z	DBE
☐	C34 H38 N4 O4 S	C34 H37 N4 O4 S	597.2541	99.58		598.263	598.2614	-2.69	2.69	99.77	99.01	99.74	597.2556	18
☐	C30 H38 N4 O9	C30 H37 N4 O9	597.2566	99.4		598.263	598.2639	1.5	1.5	98.25	99.76	99.92	597.2556	14
☐	C39 H38 N2 O2 S	C39 H37 N2 O2 S	597.2581	99.2		598.263	598.2654	4.05	4.05	98.81	99.23	99.42	597.2556	22
☐	C33 H42 O8 S	C33 H41 O8 S	597.2528	99.17		598.263	598.26	-4.91	4.91	99.27	99.1	99.16	597.2556	13
☒	C29 H42 O13	C29 H41 O13	597.2553	99.11		598.263	598.2625	-0.71	0.71	97.05	99.83	99.98	597.2556	9
☐	C42 H34 N2 O2	C42 H33 N2 O2	597.2548	98.97		598.263	598.262	-1.57	1.57	96.66	99.85	99.91	597.2556	27
☐	C35 H38 N2 O7	C35 H37 N2 O7	597.2606	98.63		598.263	598.2679	8.24	8.24	99.28	99.83	97.63	597.2556	18
☐	C37 H34 N4 O4	C37 H33 N4 O4	597.2507	98.42		598.263	598.258	-8.31	8.31	98.65	99.8	97.59	597.2556	23
☐	C31 H42 N4 O4 S2	C31 H41 N4 O4 S2	597.2575	98.36		598.263	598.2647	2.93	2.93	96.31	98.14	99.7	597.2556	13
☐	C30 H46 O8 S2	C30 H45 O8 S2	597.2561	98.02		598.263	598.2634	0.72	0.72	94.57	98.24	99.98	597.2556	8

4-Jz

Chemical structure of **1d** is shown above the spectrum. The structure is a complex polycyclic molecule with a central carbon atom bonded to a hydrogen atom, a methyl ester group, a propyl group, and a cyclohexane ring. The cyclohexane ring is further substituted with a carboxylic acid group, a methyl ester group, and a propyl group. The spectrum displays the following chemical shifts (ppm) and integrations:

Chemical Shift (ppm)	Integration
9.68	1.00
7.75, 7.74	1.25
7.07, 7.05, 7.05	1.59
5.89, 5.88, 5.88	1.56
5.35, 5.17, 5.16	1.29
4.74, 4.49, 4.47	1.37
4.12, 4.11	1.59
3.78, 3.67, 3.61, 3.61, 3.49, 3.23	9.87
2.90, 2.77, 2.77, 2.17, 2.16, 2.16, 2.09, 2.00, 2.00	1.30
2.06, 2.06, 2.05, 2.05, 1.57, 1.38, 1.37, 0.90, 0.89	2.40, 0.93, 2.57, 2.80, 2.39, 2.82, 17.14
0.14, 0.00, 0.00	7.49

Figure S24. ^{13}C NMR spectrum of compound **1d**.

Figure S25. CD spectra of compound **1**, **1a**, **1c** and **1-1a**

Figure S26. CD spectrum of in situ formed Rh-complex of **1d**.

Figure S27. IR spectrum of penicillactone A (1)

Figure S28. ESIMS and HRESIMS of penicillactone B (2)

MS Formula Results: + Scan (7.866 min) Sub (200905053.d)

m/z		Ion	Formula	Abundance
	533.203	(M+H)+	C27 H33 O11	322696.3

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☐	C20 H36 O16	C20 H37 O16	66.96		533.20761	8.7	42.26	82.63	97.54	3
☒	C27 H32 O11	C27 H33 O11	95.8		533.20174	-2.34	93.94	96.84	98.27	12

m/z		Ion	Formula	Abundance
	550.2301	(M+NH4)+	C27 H36 N O11	1088419.4

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☐	C20 H36 O16	C20 H40 N O16	66.23		550.23416	7.67	52.42	77.31	80.56	3
☒	C27 H32 O11	C27 H36 N O11	89.01		550.22829	-3.36	88.33	99.25	78.08	12

m/z		Ion	Formula	Abundance
	555.18527	(M+Na)+	C27 H32 Na O11	706727.8

Best	Formula (M)	Ion Formula	Score	Cr	Calc m/z	Diff (ppm)	Mass Ma	Abund M	Spacing	DBE
☐	C20 H36 O16	C20 H36 Na O16	69.26		555.18956	8.07	49.31	78.24	98.39	3
☒	C27 H32 O11	C27 H32 Na O11	95.23		555.18368	-2.96	90.91	99.39	98.88	12

Figure S29. Accurate masses, molecular formulas of **2** and fragment ions by HRESI-MS² in negative mode.

Peak List

<i>m/z</i>	Abund	Formula	Ion
165.0183	1591		
239.1272	1880		
361.1646	1644		
405.156	2308	C ₂₁ H ₂₅ O ₈	M* ⁻
487.2032	717		

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Figure S30. ^1H NMR spectrum of penicillactone **B** (**2**)

Figure S31. ^{13}C NMR spectrum of penicillactone **B** (**2**)

Figure 32. ^1H - ^1H COSY spectrum of penicillactone **B** (2)

Figure S33. HSQC spectrum of penicillactone B (2)

INOVA-500 gHSQC 468-2 IN CD3COCD3 09.03.16 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Operator: walkup
File: HSQCCD3C0CD30316-468-2
INOVA-500 "INM-501"

Relax. delay 1.301 sec
Acq. time 0.198 sec
Width 4033.9 Hz
2D width 26516.4 Hz
4 repetitions
2 x 128 increments
OBSERVE H1, 499.7733196 MHz
DECOUPLE C13, 125.6818298 MHz
Power 33 dB
on during acquisition
off during delay
W40 cold modulated
DATA PROCESSING
Gauss apodization 0.051 sec
F1 DATA PROCESSING
Gauss apodization 0.002 sec
FT size 4096 x 2048
Total time 27 min, 18 sec

Figure S34. HMBC spectrum of penicillactone **B** (2)

INOVA-500 gHMBC 468-2 IN CD3COCD3 09.03.16 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Operator: walkup
File: HMBCCD3CDCD30316-468-2
INOVA-500 "1HM-501"

Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 4015.9 Hz
2D Width 28518.4 Hz
32 repetitions
160 increments
OBSERVE H1, 499.7733228 MHz
DATA PROCESSING
Sine bell 0.031 sec
F1 DATA PROCESSING
Sine bell 0.003 sec
FT size 2048 x 2048
Total time 1 hr, 44 min, 7 sec

Figure S35. NOESY spectrum of penicillactone **B** (2)

INOVA-501 NOESY 468-2 IN CD3COCD3 09.04.20 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Sample #3, Operator: walkup
File: Noesy 01
INOVA-500 "INM-501"

Relax. delay 1.200 sec
Mixing 0.800 sec
Acq. time 0.185 sec
Width 6220.4 Hz
2D Width 6220.4 Hz
4 repetitions
2 x 200 increments
OBSERVE H1, 499.7733203 MHz
DATA PROCESSING
Gauss apodization 0.044 sec
F1 DATA PROCESSING
Gauss apodization 0.017 sec
F1 size 4096 x 4096
Total time 59 min, 46 sec

Figure S36. NOE spectrum of penicillactone **B** (2).

Figure S37. UV spectrum of penicillactone B (2)

Figure S38. IR spectrum of penicillactone **B** (2)

Figure S39. HRESIMS spectrum of 2a.

MS Formula Results: + Scan (7.297 min) Sub (201005183.d)

m/z	Ion	Formula	Abundance
567.2446	(M+H) ⁺	C ₂₉ H ₃₅ N ₄ O ₈	146681.2

Best	Formula (M)	Ion Formula	Calc m/z	Score	▼	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☒	C ₂₉ H ₃₄ N ₄ O ₈	C ₂₉ H ₃₅ N ₄ O ₈	567.2449	97.07			566.2373	566.2377	0.66	0.66	92.85	97.32	99.48	567.2446	15
☐	C ₂₈ H ₃₈ O ₁₂	C ₂₈ H ₃₉ O ₁₂	567.2436	97.07			566.2373	566.2363	-1.69	1.69	99	95.6	96.64	567.2446	10
☐	C ₁₇ H ₃₈ N ₆ O ₁₅	C ₁₇ H ₃₉ N ₆ O ₁₅	567.2468	81.62			566.2373	566.2395	3.91	3.91	65.37	97.8	83.27	567.2446	2
☐	C ₂₄ H ₃₄ N ₆ O ₁₀	C ₂₄ H ₃₅ N ₆ O ₁₀	567.2409	80.34			566.2373	566.2336	-6.45	6.45	98.32	97.96	60.75	567.2446	11
☐	C ₂₃ H ₃₈ N ₂ O ₁₄	C ₂₃ H ₃₉ N ₂ O ₁₄	567.2396	68.55			566.2373	566.2323	-8.8	8.8	93.62	96.43	39.58	567.2446	6
☐	C ₃₄ H ₃₄ N ₂ O ₆	C ₃₄ H ₃₅ N ₂ O ₆	567.249	67.08			566.2373	566.2417	7.77	7.77	73.49	96.46	48.55	567.2446	19
☐	C ₂₁ H ₄₂ O ₁₇	C ₂₁ H ₄₃ O ₁₇	567.2495	64.91			566.2373	566.2422	8.68	8.68	80.28	95.16	40.56	567.2446	1

m/z	Ion	Formula	Abundance
589.2263	(M+Na) ⁺	C ₂₈ H ₃₈ NaO ₁₂	160207.5

Best	Formula (M)	Ion Formula	Calc m/z	Score	▼	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☒	C ₂₈ H ₃₈ O ₁₂	C ₂₈ H ₃₈ NaO ₁₂	589.2255	97.55			566.2371	566.2363	-1.39	1.39	95.4	99.61	97.81	589.2263	10
☐	C ₂₉ H ₃₄ N ₄ O ₈	C ₂₉ H ₃₄ N ₄ NaO ₈	589.2269	95.74			566.2371	566.2377	0.96	0.96	86.96	99.84	98.96	589.2263	15
☐	C ₁₇ H ₃₈ N ₆ O ₁₅	C ₁₇ H ₃₈ N ₆ NaO ₁₅	589.2287	83.04			566.2371	566.2395	4.21	4.21	72.52	98.41	81.67	589.2263	2
☐	C ₂₄ H ₃₄ N ₆ O ₁₀	C ₂₄ H ₃₄ N ₆ NaO ₁₀	589.2229	82.55			566.2371	566.2336	-6.16	6.16	98.01	99.34	64.89	589.2263	11
☐	C ₂₃ H ₃₈ N ₂ O ₁₄	C ₂₃ H ₃₈ N ₂ NaO ₁₄	589.2215	72.05			566.2371	566.2323	-8.5	8.5	96.25	99.5	43.8	589.2263	6
☐	C ₂₁ H ₄₂ O ₁₇	C ₂₁ H ₄₂ NaO ₁₇	589.2314	67.1			566.2371	566.2422	8.98	8.98	85.85	99.15	39.83	589.2263	1
☐	C ₃₄ H ₃₄ N ₂ O ₆	C ₃₄ H ₃₄ N ₂ NaO ₆	589.2309	64.98			566.2371	566.2417	8.07	8.07	64.9	99.89	47.57	589.2263	19

Figure S40. ^1H NMR spectrum of **2a**.

Figure S41. ^{13}C NMR spectrum of **2a**.

Figure 42. ^1H - ^1H COSY spectrum of compound **2a**.

Figure 43. HSQC spectrum of compound **2a**.

Figure 44. HMBC spectrum of compound **2a**.

Figure S45. HRESIMS spectrum of **2b**.

MS Formula Results: + Scan (8.316 min) Sub (201005262.d)

m/z	Ion	Formula	Abundance
733.1868	(M+H) ⁺	C35 H42 Br O12	47913.6

	Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
+	✓	C35 H41 Br O12	C35 H42 Br O12	733.1854	96.76		732.1796	732.1781	-1.95	1.95	98.63	98.65	94.68	733.1868	15
+	□	C28 H45 Br O17	C28 H46 Br O17	733.1913	76.23		732.1796	732.184	5.97	5.97	84.72	98.66	59.92	733.1868	6
+	□	C40 H46 Br2 O3	C40 H47 Br2 O3	733.1886	67.83		732.1798	732.1814	2.21	2.21	0	98.42	93.23	733.1868	17

m/z	Ion	Formula	Abundance
755.1698	(M+Na) ⁺	C35 H41 Br Na O...	146812

	Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
+	✓	C35 H41 Br O12	C35 H41 Br Na O...	755.1674	92.09		732.1806	732.1781	-3.41	3.41	97.17	99.76	85.19	755.1698	15
+	□	C28 H45 Br O17	C28 H45 Br Na O...	755.1732	85.73		732.1807	732.184	4.52	4.52	91.29	99.7	75.41	755.1698	6
+	□	C40 H46 Br2 O3	C40 H46 Br2 Na...	755.1706	70.95		732.1808	732.1814	0.77	0.77	0	99.63	99.19	755.1698	17

Figure S46. ^1H NMR spectrum of compound **2b**.

Figure S47. ^{13}C NMR spectrum of compound **2b**.

Figure S48. HMBC spectrum of compound 2b.

INOVA-501 gHMBC 468-2-YS IN CD3COCD3 2010.01.18 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Sample #6, Operator: walkup
File: Ghmbc_01
INOVA-500 "IMM-501"

Relax. delay 1.000 sec
Mixing 0.080 sec
Acq. time 0.128 sec
Width 4798.5 Hz
2D Width 30154.5 Hz
32 repetitions
256 increments
OBSERVE H1, 499.7687565 MHz
DATA PROCESSING
Sine bell 0.055 sec
F1 DATA PROCESSING
Sine bell 0.004 sec
FT size 2048 x 2048
Total time 2 hr, 46 min, 21 sec

Figure S49. HRESIMS spectrum of 2c.

MS Formula Results: - Scan (6.860 min) Sub (201004231.d)

m/z		Ion	Formula	Abundance
533.2037		(M+H)+	C27 H33 O11	97170.7

Best	Formula (M)	Ion Formula	Calc m/z	Score	Cross S	Mass	Calc Mass	Diff (ppm)	Abs Diff (ppm)	Abund Match	Spacing Match	Mass Match	m/z	DBE
☒	C27 H34 O11	C27 H33 O11	533.2028	97.41		534.211	534.2101	-1.58	1.58	96.43	99.07	97.17	533.2037	11
☐	C28 H30 N4 O7	C28 H29 N4 O7	533.2042	95.83		534.211	534.2114	0.91	0.91	87.88	98.92	99.05	533.2037	16
☐	C22 H34 N2 O13	C22 H33 N2 O13	533.1988	69.77		534.211	534.2061	-9.12	9.12	97.12	99.48	38.51	533.2037	7
☐	C33 H30 N2 O5	C33 H29 N2 O5	533.2082	62.87		534.211	534.2155	8.45	8.45	64.44	98.58	44.07	533.2037	20

Figure S50. ^1H NMR spectrum of **2c**.

Figure S51. ^{13}C NMR spectrum of **2c**.

Figure S52. ^1H - ^1H COSY spectrum of compound **2c**.

Figure S53. HSQC spectrum of compound **2c**.

Figure S54. HMBC spectrum of compound **2c**.

Figure S55. CD spectra of **2**, **2c** and **2-2c**.

Figure S56. CD spectrum of in situ formed Rh-complex of **2a**..

Figure S57. HRESIMS spectrum of penicillactone **C** (**3**).

MS Formula Results: + Scan (8.247 min) (200902191.d)

m/z	Ion	Formula	Abundance
587.2109	(M+Na)+	C28 H36 Na O12	305733.7

Best	Formula (M)	Ion Formula	Score	Cross Score	Calc m/z	Diff (ppm)	Mass Match	Abund Match	Spacing Match
☐	☐	C21 H40 O17	66.52		587.2158	8.7	42.28	81.65	96.83
☒	☒	C28 H36 O12	97.11		587.2099	-1.71	96.71	98.84	95.81

Figure S58. ^1H NMR spectrum of Penicillactone **C** (**3**).

Figure S59. ^{13}C NMR spectrum of penicillactone C (**3**).

Figure S60. ^1H - ^1H COSY spectrum of penicillactone C (**3**).

INDVA-500 GPCSY-NMR 471-1 IN CD3COCD3

Solvent: acetone
Temp: 25.0 C / 298.1 K
File: 0502
INDVA-500 "NMR500"

Relax. delay 1.000 sec
Acq. time 0.188 sec
Width 5500.9 Hz
2D Width 5500.9 Hz
Single scan
256 increments
OBSERVE H1: 500.0872446 MHz
DATA PROCESSING
Sg. sine bell 0.093 sec
F1 DATA PROCESSING
Sg. sine bell 0.047 sec
FT size 2048 x 2048
Total time 5 min, 32 sec

Figure S61. HSQC spectrum of penicillactone **C** (**3**).

INOVA-500 HSQC-NMR 471-1 IN CD3COCD3 CH,CH3

Solvent: acetone
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: 0503
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Acq. time 0.186 sec
Width 5500.9 Hz
2D Width 21378.9 Hz
16 repetitions
2 x 90 increments
OBSERVE H1, 500.0372446 MHz
DECOUPLE C13, 125.7564387 MHz
Power 30 dB
on during acquisition
off during delay
GARP-1 modulated
DATA PROCESSING
Gauss apodization 0.086 sec
F1 DATA PROCESSING
Gauss apodization 0.008 sec
FT size 2048 x 2048
Total time 1 hr, 53 sec

Figure S62. HMBC spectrum of penicillactone **C** (**3**).

INOVA-500 HMBC-NMR 471-1 IN CD3COCD3

Solvent: acetone
Temp. 25.0 C / 298.1 K
User: 1-14-87
File: 0504
INOVA-500 "NMR500"

Relax. delay 1.000 sec
Acq. time 0.186 sec
Width 5500.9 Hz
2D Width 25781.5 Hz
80 repetitions
200 increments
OBSERVE H1: 500.0872446 MHz
DATA PROCESSING
Sine bell 0.078 sec
F1 DATA PROCESSING
Sine bell 0.004 sec
FT size 2048 x 2048
Total time 5 hr, 39 min, 49 sec

Figure S63. NOESY spectrum of penicillactone C (**3**).

INOVA-501 NOESY 473-1 IN CD3COCD3 09.04.20 cold probe

Solvent: acetone
Temp. 25.0 C / 298.1 K
Sample #2, Operator: walkup
File: Noesy_01
INOVA-500 "INM-501"

Relax. delay 1.200 sec
Mixing 0.800 sec
Acq. time 0.177 sec
Width 5786.2 Hz
2D Width 5786.2 Hz
4 repetitions
2 x 200 increments
OBSERVE H1, 499.7733235 MHz
DATA PROCESSING
Gauss apodization 0.045 sec
F1 DATA PROCESSING
Gauss apodization 0.016 sec
FT size 4096 x 4096
Total time 1 hr, 8 sec

Figure S64. NOE spectrum of penicilactone **C** (**3**).

Figure S65. Circular dichroism spectrum of **3** in DMSO of dimolybdenum tetracetate (the inherent CD of **3** was subtracted).

Figure S66. UV spectrum of penicillactone C (3).

Figure S67. IR spectrum of penicillactone C (3)