Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Biomimetic Total Syntheses of Spirobacillenes A and B

Hongzhi Yang,[§] Juan Feng,[§] and Yefeng Tang*

The Comprehensive AIDS Research Center, Department of Pharmacology & Pharmaceutical Sciences, School of Medicine, Tsinghua University, Beijing 100084, China

E-mail: yefengtang@tsinghua.edu.cn

[§]These authors contributed equally to this work.

Table of Contents

General Information:

Experimental details

Unless otherwise mentioned, all reactions were carried out under a nitrogen atmosphere and an hydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent purification was conducted according to Purification of Laboratory Chemicals (Peerrin, D. D.; Armarego, W. L. and Perrins, D. R., Pergamon Press: Oxford, 1980). Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials.

Reactions were monitored by Thin Layer Chromatography on plates (GF254) supplied by Yantai Chemicals (China) using UV light as visualizing agent and an ethanolic solution of phosphomolybdic acid and cerium sulfate, and heat as developing agents. If not specially mentioned, flash column chromatography uses silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

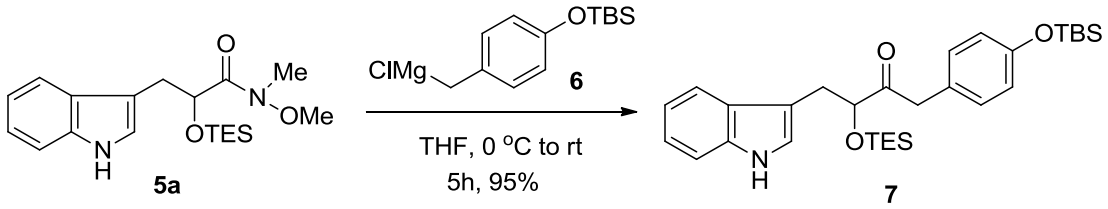
NMR spectra were recorded on Bruker AV400 instrument. TMS was used as internal standard for ^{1}H NMR (0 ppm), and solvent signal was used as reference for ^{13}C NMR (CDCl3, 77.160ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br= broad, td = triple doublet, qd= quarter doublet, m = multiplet.

Infrared (IR) spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker ESI-Q/TOF MS , Low-resolution mass spectral analyses were performed with a Waters AQUITY UPLCTM/MS.

Part 1: Experimental Details and Characteristic Data

Synthesis of compound 5a: To a solution of Weinreb amide **5** (1.50 g, 6.04 mmol, 1.0 equiv.) in CH_2Cl_2 (50 mL) was added imidazole (1.65 g, 24.16 mmol, 4.0 equiv.) and then a solution of TESCl (2.30 mL, 12.08 mmol, 2.0 equiv.) dropwise at room temperature. After stirring for 30 min, the solution was quenched by addition of H_2O (5 mL). The organic layer was then separated, and the aqueous layer was extracted with CH_2Cl_2 (50 mL x 3). The combined organic extracts were washed with 0.2N HCl aq. (20 mL x 2) and sat. aq. $NaHCO_3$ (100 mL x 1), dried over Na_2SO_4, filtered, and evaporated under reduced pressure. Purification by flash chromatography on silica gel (PE/EtOAc = 3:1) provided compound **6**[1] (1.75 g, 80%) as white solid.

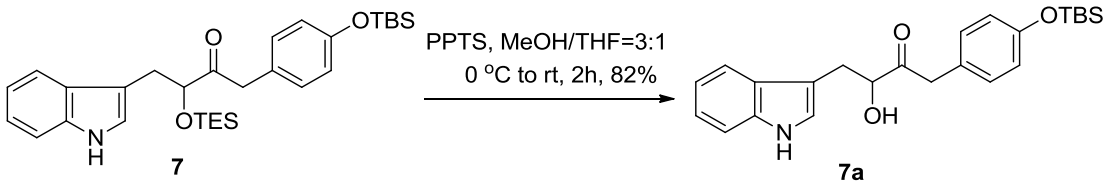
Characteristic data of 5a: R_f = 0.36 (silica gel, PE/EtOAc = 3:1); IR ν_{max} (film): 2876, 1654, 1457, 1086, 1009, 988, 706 cm^{-1}; ^1H NMR (400 MHz , $CDCl_3$) δ 8.53 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H), 7.36 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.8, 7.1 Hz, 1H), 7.11 (t, *J* = 7.5, 7.3 Hz, 1H), 7.06 (s, 1H), 4.88 (t, *J* = 7.2, 5.9 Hz, 1H), 3.41 (s, 3H), 3.30 (dd, *J* = 14.0, 5.9 Hz, 1H), 3.14 (s, 3H), 3.06 (dd, *J* = 14.0, 7.2 Hz, 1H), 0.85 (t, *J* = 15.8, 7.9 Hz, 9H), 0.51 (q, *J* = 15.4, 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.4, 136.3, 127.7, 123.8, 121.7, 119.1, 118.6, 111.4, 111.1, 69.5, 61.2, 32.6, 31.1, 6.7, 4.6 ppm; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{19}H_{30}N_2O_3Si$ 385.1918, found 385.1918.



Synthesis of compound 7: Amide **5a** (0.38 g, 1.05 mmol, 1.0 equiv.) was dissolved in THF (4.0 mL) in a dry flask with a stir bar, and then the solution was cooled to 0℃. A solution of (4-(tert-butyldimethylsilyloxy)benzyl) magnesium chloride **7**[2] (1.48 g, 5.25 mmol, 5.0 equiv.) was then added slowly over 5 min and the mixture was warmed to rt. It was then stirred 5 h until the starting material had been consumed. A saturated aqueous ammonium chloride solution (1.5 mL) was slowly added to the reaction mixture, and the resulting slurry was partitioned between CH_2Cl_2 (30 mL) and half-saturated aqueous ammonium chloride solution (50 mL). The layers were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic phases were dried over sodium sulfate, filtered, and evaporated. Purification of the residue by flash chromatography on silica gel (EtOAc/petroleum ether = 12:1) afforded ketone **8**[1] as faint yellow oil (0.53 g, 95%).

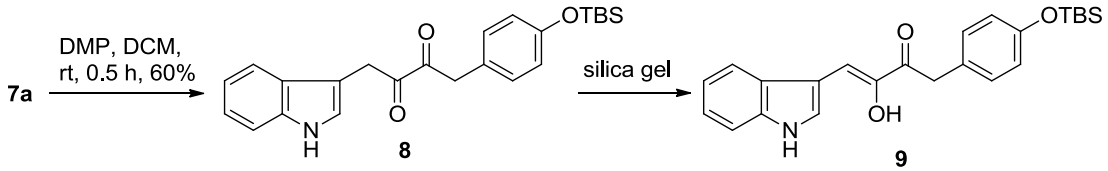
Characteristic data of 7: R_f = 0.62 (silica gel, PE/EtOAc = 2:1); IR ν_{max} (film): 2360, 1713, 1506, 1249, 908, 835 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.62 (d, *J* = 7.7 Hz, 1H),

7.34 (d, *J* =7.9 Hz, 1H), 7.20 (t, *J* = 7.7, 7.2 Hz, 1H), 7.13 (t, *J* = 7.4, 7.2 Hz, 1H), 6.96 (s, 1H), 6.86 (d, *J* = 8.0 Hz, 2H), 6.75 (d, *J* = 8.1 Hz, 2H), 4.51 (t, *J* = 5.7 Hz, 1H), 3.70 (d, *J* = 16.5 Hz, 1H), 3.58 (d, *J* = 16.6 Hz, 1H), 3.12 (d, *J* = 5.7 Hz, 1H), 1.00 (s, 9H), 0.90 (t, *J* = 7.9 Hz, 9H), 0.52 (q, *J* = 7.8 Hz, 6H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 154.5, 136.2, 130.8, 127.8, 126.7, 123.4, 122.1, 120.1, 119.5, 119.2, 111.2, 110.8, 78.6, 44.4, 31.6, 25.8, 18.3, 18.1, 6.8, 4.7, -4.3 ppm; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{30}H_{45}NO_3Si_2$ 546.2830, found 546.2831.



Synthesis of compound 7a: Ketone **7** (0.17 g, 0.32 mmol, 1.0 equiv.) was dissolved in MeOH (3 mL) and THF (1 mL). To the solution was added PPTS (2.4 mg, 0.01 mmol, 0.03 equiv.) at 0 ℃. The reaction mixture was allowed to warm to r.t. and stirred for 2 h, at which time it was quenched with sat. $NaHCO_3$, and extracted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated to dryness in vacuo. The crude product was purified by flash silica gel column chromatography eluting with EtOAc/petroleum ether (1:5 then 1:3) to give compound **7a**[3] (0.11 g, 82%) as a faint yellow oil.

Characteristic data of 7a: R_f = 0.15 (silica gel, PE/EtOAc = 3.5:1); IR ν_{max} (film): 3412, 2916, 2361, 1710, 1510, 1472, 1457 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.7, 7.2 Hz, 1H), 7.14 (t, *J* = 7.4, 7.2 Hz, 1H), 7.05 (s, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 8.0 Hz, 2H), 4.60 (dd, *J* = 6.6, 4.8 Hz, 1H), 3.72 (d, *J* = 16.0 Hz, 1H), 3.67 (d, *J* = 16.0 Hz, 1H), 3.31 (dd, *J* = 10.5, 4.8 Hz, 2H), 3.13 (dd, *J* = 15.0, 6.6 Hz, 1H), 0.98 (s, 9 H), 0.19 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 155.0, 136.3, 130.6, 127.6, 125.9, 123.1, 122.4, 120.4, 119.9, 118.9, 111.4, 110.6, 76.1, 45.0, 30.0, 25.8, 18.3, -4.3 ppm; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{24}H_{31}NO_3Si$ 432.1965, found 432.1966.

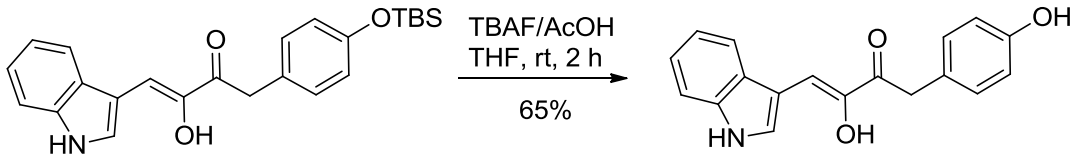


Synthesis of compound 8 and 9: Compound **7a** (0.17 g, 0.422 mmol, 1.0 equiv.) was dissolved in CH_2Cl_2 (5.0 mL). To the stirring solution was added Dess-Martin periodinane (0.36 g, 0.845 mmol, 2.0 equiv.). The reaction was stirred for 0.5 h and then diluted with water and extraction with CH_2Cl_2 (3 x 5 mL), dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude was purified by flash column chromatography on silica gel using a gradient mixture of EtOAc/petroleum ether (1:4) to afford **8** as yellow oil (0.10 g, 60%), which was gradually tautomerized into **9** after long-standing in the hood.
Note: when the purification was made by preparative TLC, **9** was obtained as the major isomer.

Characteristic data of 8: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.32 (d, *J* = 8.1 Hz, 1H), 7.21 (t, *J* = 7.1, 7.1 Hz, 1H), 7.14 (t, *J* = 7.6, 7.2 Hz,1H), 6.97 (s, 1H), 6.92 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 8.4 Hz, 2H), 4.16 (s, 2H), 3.92 (s, 2H), 1.01 (s, 9H), 0.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 196.3, 154.9, 136.2, 130.9, 127.2, 124.7, 124.1, 122.5,

120.3, 112.0, 118.8, 111.4, 105.8, 42.5, 33.3, 25.8, 18.3 ppm

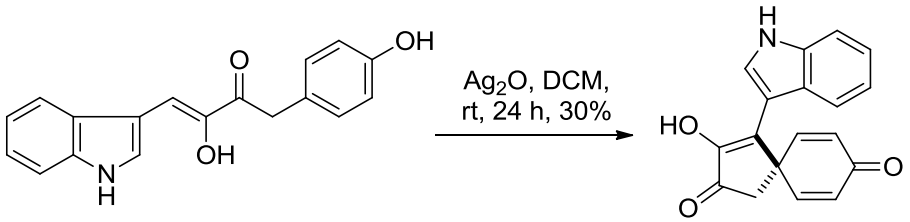
Characteristic data of 9: R_f = 0.28 (silica gel, PE/EtOAc = 4:1); IR ν_{max} (film): 2359, 1706, 1609, 1509, 1361, 1254, 1232, 912 cm^{-1}; ^1H NMR (400 MHz , $CDCl_3$) δ 8.53 (s, 1H), 8.07 (s, 1H), 7.76 (d, *J* = 7.2 Hz, 1H), 7.40 (d, *J* = 7.6 Hz, 1H), 7.14 (m, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 7.04 (s, 1H), 6.80 (d, *J* = 8.0 Hz, 2H), 4.09 (s, 2H), 0.96 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.8, 154.8, 144.9, 135.8, 130.3, 128.9, 127.6, 126.9, 123.0, 120.8, 120.4, 118.3, 111.7, 110.9, 108.1, 41.2, 25.8, 18.3, 1.1, -4.3 ppm; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{24}H_{29}NO_3Si$ 430.1809, found 430.1808.



9 pre-spirobacillene A (**3**)

Synthesis of pre-spirobacillene A (3): At 0°C a solution of synthetic **9** (23 mg, 0.056 mmol) in THF (1 mL) was treated with an aliquot (3 drops) of a solution prepared by addition of glacial AcOH (3 drops) to TBAF (1.0 M in THF, 0.5 mL). The reaction mixture was stirred for 2 h and then partitioned between ether and water (10 mL each). The organic phase was washed with water and brine (10 mL each), dried over Na_2SO_4, filtered, and concentrated. Flash chromatography (CH_2Cl_2/Acetone = 20:1) gave pre-spirobacillene **A**[4] (10.7 mg, 65%) as a yellow solid.

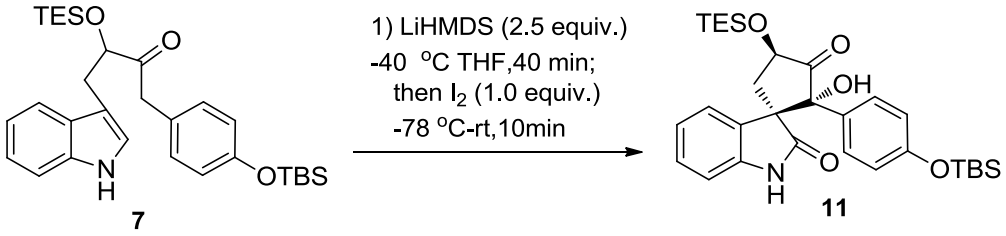
Characteristic data of pre-spirobacillene A (3): R_f = 0.32 (silica gel, CH_2Cl_2/Acetone = 5:1); IR ν_{max} (film): 2359, 2340, 1607, 1513, 1357, 1230, 1171, 1128 cm^{-1}; ^1H NMR (400 MHz , CD_3CN)) δ 9.78 (s, 1H), 8.06 (d, *J* = 2.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.27 (m, 1H), 7.24 (m, 1H), 7.20 (d, *J* = 8.4 Hz, 2H), 6.94 (s, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 4.16 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 195.0, 156.8, 145.7, 137.0, 131.5, 129.9, 127.9, 123.5, 121.3, 119.4, 118.3, 116.3, 112.8, 111.1, 108.8, 41.5 ppm; HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{15}NO_3$ 294.1125, found 294.1127.



pre-spirobacillene A (3) **spirobacillene A (1)**

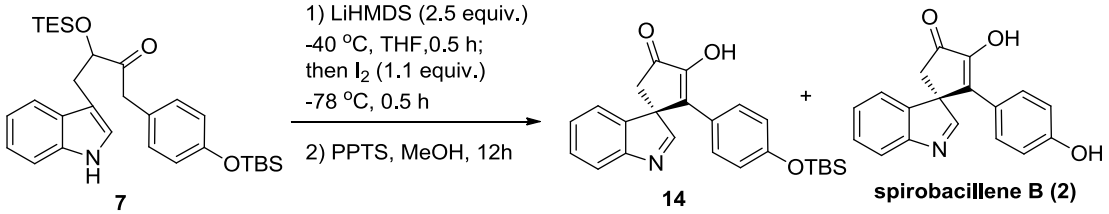
Synthesis of spirobacillene A (1): To a solution of pre-spirobacillene A (0.19 g, 0.648 mmol, 1.0 equiv.) in CH_2Cl_2 (30 mL) was added Ag_2O (3.0, 12.96 mmol, 20.0 equiv.) in one portion. The reaction mixture was kept stirring in a flask which was covered by aluminum foiland protected with N_2. The reaction was stopped after 24 h, and the mixture was filtered through celite and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography on silica gel using a gradient mixture of CH_2Cl_2/Acetone (20:1, 15:1, 10:1) to afford spirobacillene A as yellow solid (57 mg, 30%) and recoveried substantial material pre-spirobacillene A (76 mg, 40%).

Characteristic spirobacillene A (1): R_f = 0.14 (silica gel, CH_2Cl_2/Acetone = 20:1); IR νmax (film): 2924, 2857, 2249, 1649, 1627, 1368, 1038, 918 cm-1; ^{1}H NMR (400 MHz, CD_3CN)) δ 9.63 (s, 1H), 7.98 (d, *J* = 7.9 Hz, 1H), 7.46 (m, 2H), 7.24 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1H), 7.16 (ddd, *J* = 7.9, 7.2, 1.2 Hz, 1H), 7.06 (d, *J* = 9.8 Hz, 2H), 6.34 (d, *J* = 9.8 Hz, 2H), 2.76 (s, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 197.6, 185.1, 154.3, 148.2, 137.0, 136.4, 129.2, 126.1, 125.3, 122.7, 122.5, 120.2, 111.8, 109.2, 47.0, 42.2 ppm; HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{13}NO_3$ 292.0968, found 292.0966.



Synthesis of compound 11: To a solution of **7** (40.0 mg, 0.076 mmol) in dry THF (2 mL) was added LiHMDS (0.19 mL, 1 M in THF, 0.19 mmol) slowly at -40℃. After being stirred at this temperature for 40 min, a solution of iodine (19.3 mg, 0.076 mmol) in THF (0.5 mL) was added dropwise at -78℃. The solution was maintained at this temperature for 10 min and then warmed to room temperature，stirred for 20 min and then quenched with saturated $Na_2S_2O_3$ solution (2 mL) and it was extracted with EtOAc. The organic phase was washed with brine, dried over Na_2SO_4, filtered, and evaporated to dryness in vacuo. The crude product was purified by preparative TLC, **11** (24 mg, 58%) was obtained.

Characteristic data of compound 11: ^{1}H NMR (400 MHz , $CDCl_3$) δ 8.63 (s, 1H), 7.16 (d, *J* = 8.6 Hz, 2H), 7.13 (dd, *J* = 7.8, 7.5 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 2H), 6.69 (dd, *J* = 7.8, 7.7 Hz, 1H), 5.77 (d, *J* = 7.5 Hz, 1H), 5.03 (dd, *J* = 9.3, 9.0 Hz, 1H), 2.64 (dd, *J* = 13.8, 9.0 Hz, 1H), 2.20 (dd, *J* = 13.8, 9.3 Hz, 1H), 1.04 (t, *J* = 7.9 Hz, 9H), 0.99 (s, 9H), 0.75 (m, 6H), 0.20 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 217.2, 180.8, 155.9, 141.7, 131.9, 129.1, 128.7, 127.5, 126.0, 121.9, 110.0, 83.6, 69.8, 58.8, 37.7, 29.8, 25.8, 18.4, 6.8, 5.0, 1.2, -4.3, -4.3 ppm; HRMS (ESI) m/z $[M+Na]^+$calcd for $C_{30}H_{43}NO_5Si_2$ 576.2572, found 576.2558.

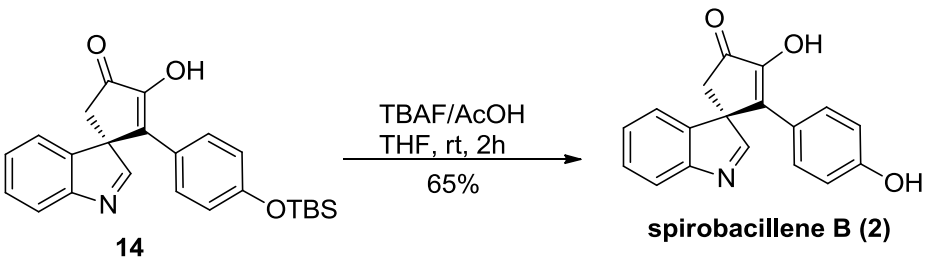


Synthesis of compound 14 and spirobacillene B (2): To a solution of **7** (0.12 g, 0.23 mmol) in dry THF (9 mL) was added LiHMDS (0.58 mL, 1 M in THF, 0.58 mmol) slowly at -40°C with N_2 protection. After being stirred at this temperature for 30 min, the reaction mixture was cooled down to -78 °C, and a solution of iodine (59 mg, 0.23 mmol) in THF (0.5 mL) was added dropwise. The solution was maintained at this temperature for 10 min and then warmed to room temperature over 0.5 h. Then a solution of PPTS[3] (8.80 mg, 0.034 mmol) in MeOH（27 mL）was added, The solution was maintained at room temperature for 12 h and then quenched with saturated $NaHCO_3$ (5 mL) and it was extracted with EtOAc. The organic phase was washed with

brine, dried over Na_2SO_4, filtered, and evaporated to dryness in vacuo. The crude product was purified by flash silica gel column chromatography eluting with CH_2Cl_2/Acetone (2:1) to give compound **14** (25 mg, 27%) and spirobacillene **B** as yellow solid (7.0 mg, 10%).

Characteristic data of compound 14: R_f = 0.32 (silica gel, CH_2Cl_2/Acetone = 2:1); IR νmax (film): 3675, 2359, 2342, 1653, 1558, 838, 701 cm-1; ^{1}H NMR (400 MHz , CD_3CN)) δ 8.27 (s, 1H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.45 (ddd, *J* = 7.5 Hz, 1H), 7.30 (ddd, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 2.94 (d, *J* = 19.0 Hz, 1H), 2.56 (d, *J* = 19.0 Hz, 1H), 0.95 (s, 9H), 0.16 (s, 6H); ^{13}C NMR (100 MHz, CD_3CN) δ 198.7, 193.8, 177.1, 156.9, 150.4, 142.4, 135.5, 129.3, 128.9, 127.7, 126.2, 122.3, 121.8, 120.1, 61.6, 38.4, 25.2, 18.2, -5.0 ppm; HRMS (ESI) m/z $[M+H]^+$calcd for $C_{24}H_{27}NO_3Si$ 406.1833, found 406.1835.

Characteristic data of spirobacillene B (**2**): R_f = 0.15 (silica gel, CH_2Cl_2/Acetone = 2:1); IR νmax (film): 2925, 1700, 1604, 1385, 1268, 840, 835, 733 cm-1; ^{1}H NMR (400 MHz, CD_3CN) δ 8.27 (s, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.45 (ddd, *J* = 7.8, 6.6, 1.6 Hz, 1H), 7.31 (ddd, *J* = 7.5, 6.6, 1.6 Hz, 1H), 7.10 (d, *J* = 8.7 Hz, 2H), 6.66 (d, *J* = 8.8 Hz, 2H), 2.93 (d, *J* = 18.8 Hz, 1H), 2.56 (d, *J* = 18.8 Hz, 1H); ^{13}C NMR (150 MHz, CD_3CN) δ 198.5, 177.1, 158.0, 155.3, 149.8, 142.4, 135.7, 129.4, 128.8, 127.4, 124.5, 122.1, 121.7, 115.4, 61.4, 38.2 ppm; HRMS (ESI) m/z $[M+H]^+$calcd for $C_{18}H_{13}NO_3$ 292.0968, found 292.0966.



Synthesis of spirobacillene B (2): To a solution of synthetic compound **14** (21.1 mg, 0.055 mmol) in THF (1 mL) was treated with an aliquot (3 drops) of a solution prepared by addition of glacial AcOH (3 drops) to TBAF (1.0 M in THF, 0.5 mL). The reaction mixture was stirred for 10 min and then partitioned between ether and water (10 mL each). The organic phase was washed with water and brine (10 mL each), dried over Na2SO4, filtered, and concentrated. The crude product was purified by flash silica gel column chromatography eluting with CH_2Cl_2/Acetone (2:1) to give spirobacillene **B**[4] (10.4 mg, 65%).

.

Chiral separation of racemic spirobacillene B (**2**)

In the original isolation paper, both spirobacillene A (**1**) and B (**2**) were reported as optically active substances ($[\alpha]_D^{25}$ = 4.4 (c 0.10, CH_3CN) for **1** and $[\alpha]_D^{25}$ = 6.5 (c 0.05, CH_3CN) for **2**). However, spirobacillene A (**1**) does not possess a stereocenter at all. We think that the optical rotation reported for **1** should be attributed to the instrument noise or to small amounts of other chiral compounds present in the sample.

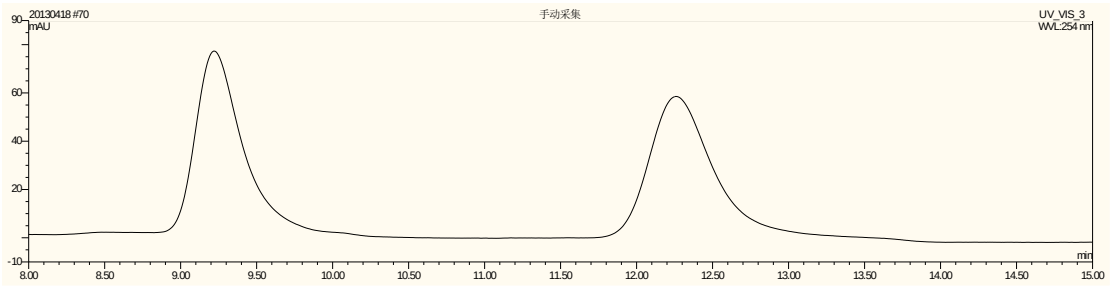
Spirobacillene B (**2**) is a chiral compound. However, the reported optical rotation for **2** was measured at a low concentration and the value is very small, making it quite suspicious. We assume that spirobacillene B (**2**) may exist as a racemic substance in the nature. In order to clarify

that if the naturally occurring spirobacillene B is a racemic or enantiopure compound, we separated the two entiomers of spirobacillene B by chrial HPLC. It turned out that, the rotation values of (+)-**2** and (-)-**2** are $[\alpha]_D^{25}$ = 16.6 (c 1.0, CH_3CN) and $[\alpha]_D^{25}$ = -14.4 (c 1.0, CH_3CN), respectively. This data, if not confirm, at least supports our assumption that the naturally occurring **2** is a racemic or partially racemic substance.

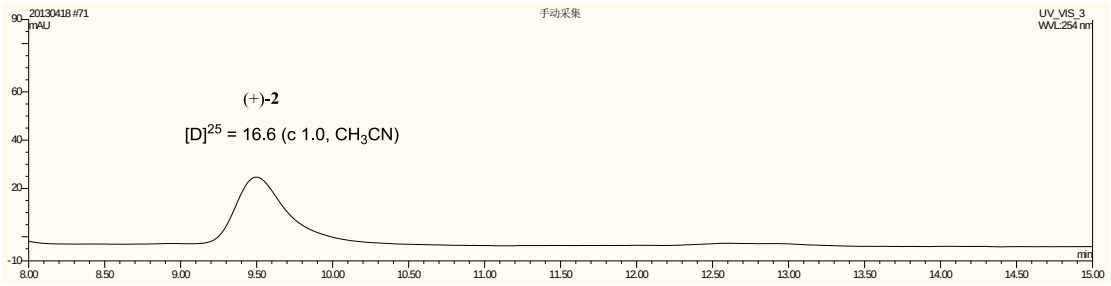
Chiral separation of racemic spirobacillene B (**2**)

HPLC profiles of separation of **2** on chiral column (phenomenex p/No 00G-4456-E0, Desc: Lux 3 μ Cellulose-2, Size:250*4.60 mm; Detector: 356 nm; Solvent: MeOH: H_2O = 70:30; Temperature: 25 ^oC)

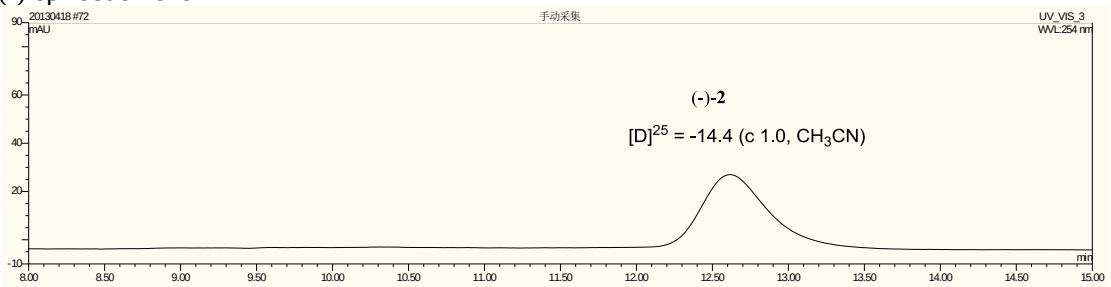
(±)-spirobacillene B



(+)-spirobacillene B



(-)-spirobacillene B



References

[1] Christiansen, M. A.; Butler, A. W.; Hill, A. R.; Andrus, M. B. *Synlett*. **2009**, 653-657.

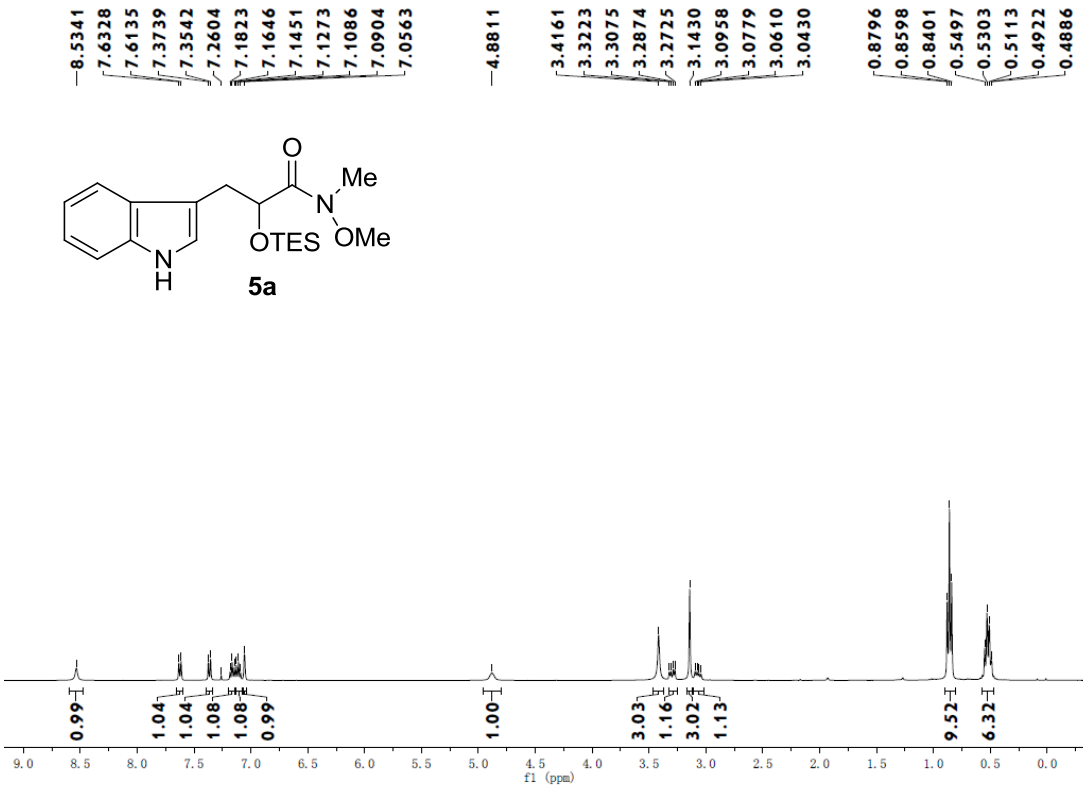
[2] (a) Adamczyk, M.; Johnson, D. D.; Mattingly, P. G.; Pan, Y.; Reddy, R. E. *Org. Prep. Proced. Int*. **2001**, *33*, 477-485. (b) Balskus, E. P.; Walsh, C. T. *J. Am. Chem. Soc.* **2008**, *130*, 15260-15261.

[3] Shimada, K.; Kaburagi, Y.; Fukuyama, T. *J. Am. Soc. Chem.* **2003**, *125*, 4048-4049.

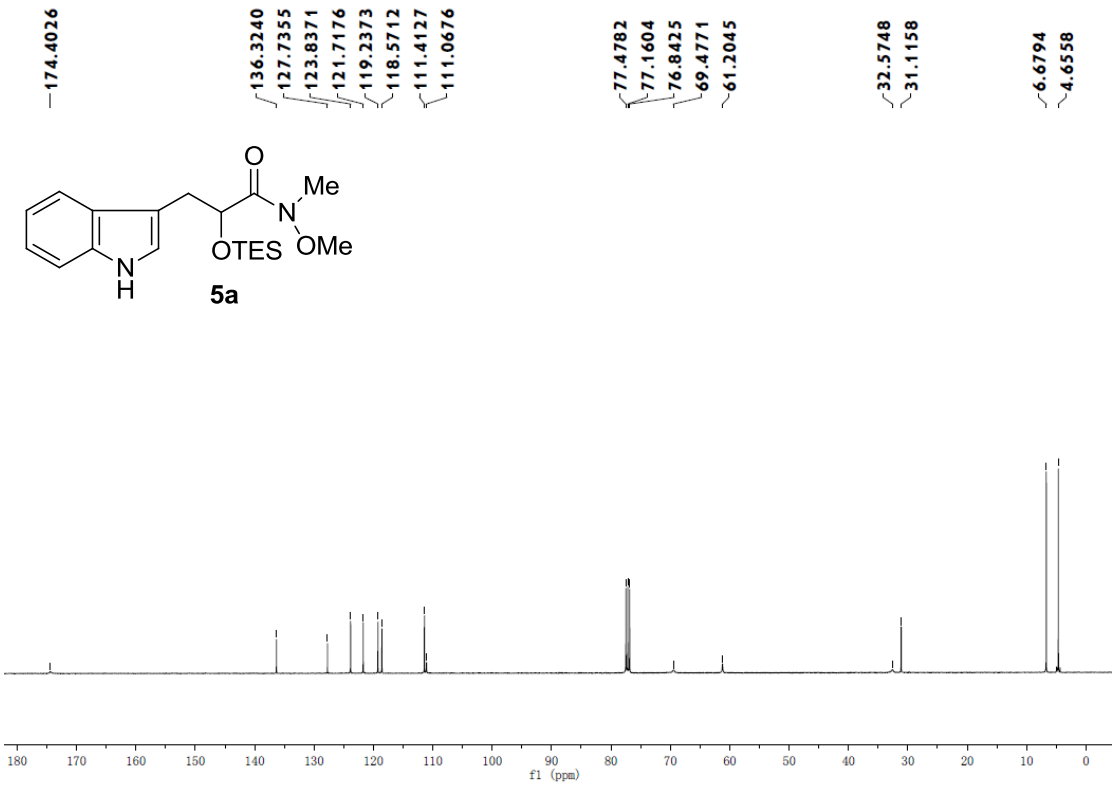
[4] Smith, A. B., III; Condon, S. M.; Mccauley, J. A.; Leazer, J. L., Jr.; Leahy, J. W.; Maleczka, R. E. *J. Am. Chem. Soc.* **1997**, *119*, 962-973.

Part 2: NMR Spectra

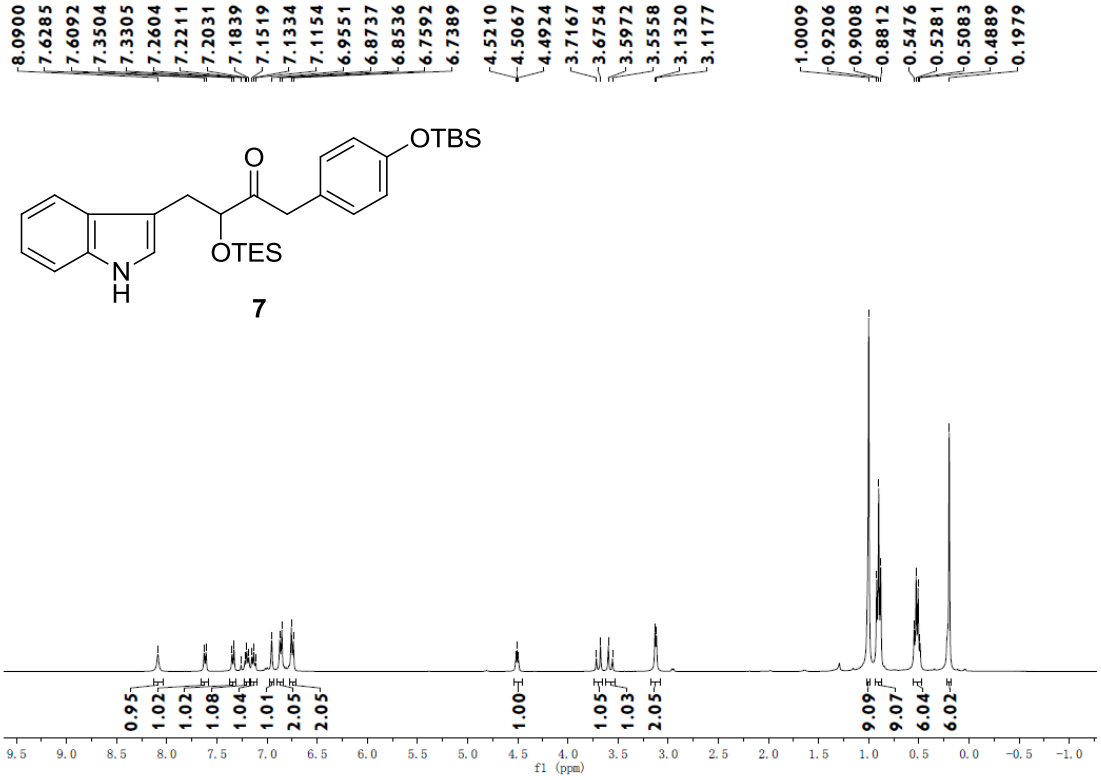
^{1}H-NMR Spectrum for **5a** ($CDCl_3$, 400 MHz)



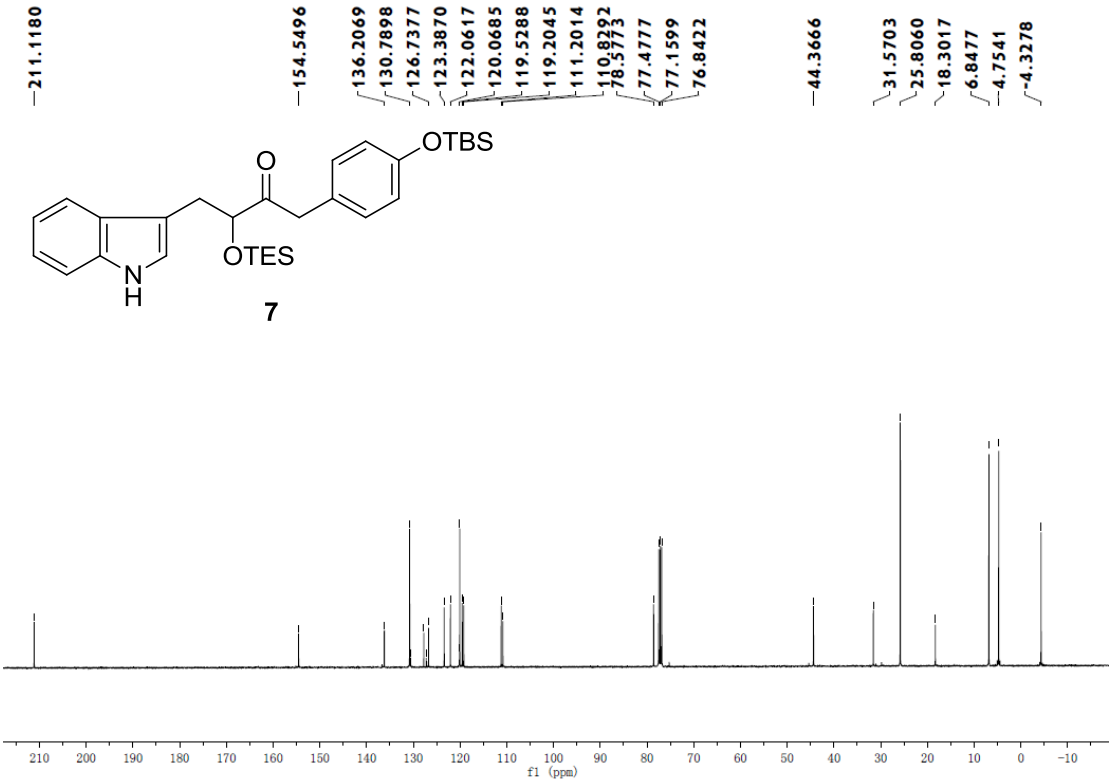
^{13}C-NMR Spectrum for **5a** ($CDCl_3$, 101 MHz)



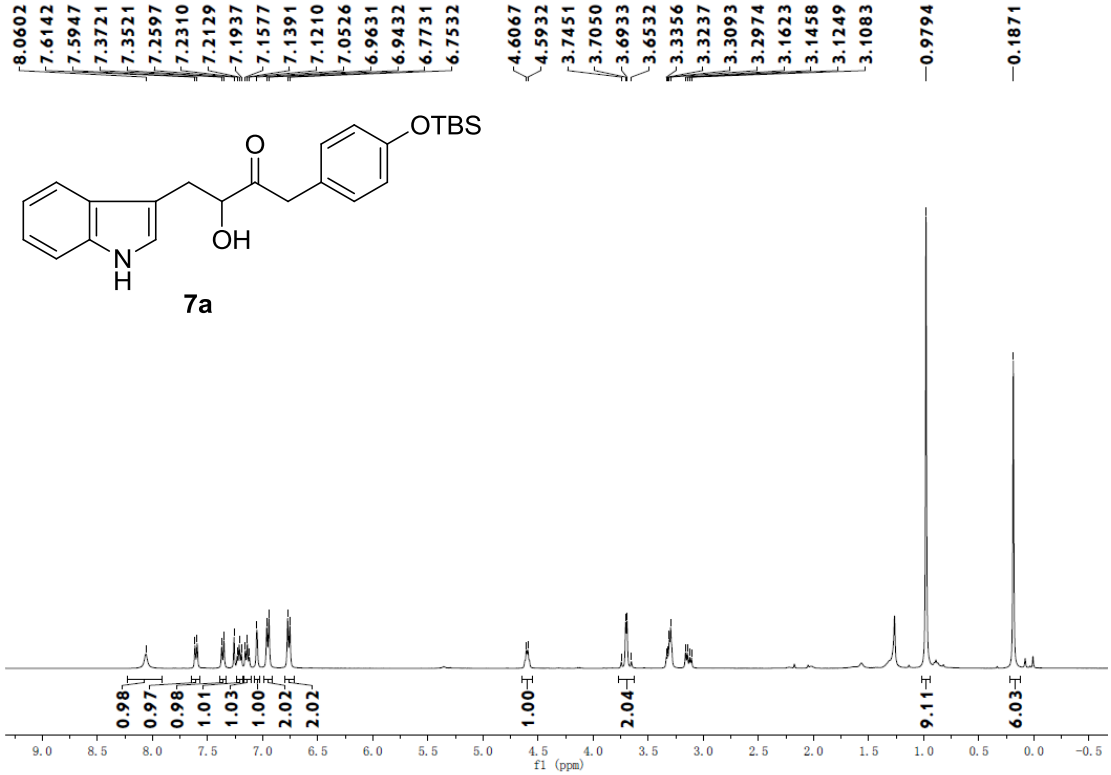
^{1}H-NMR Spectrum for **7** ($CDCl_3$, 400 MHz)



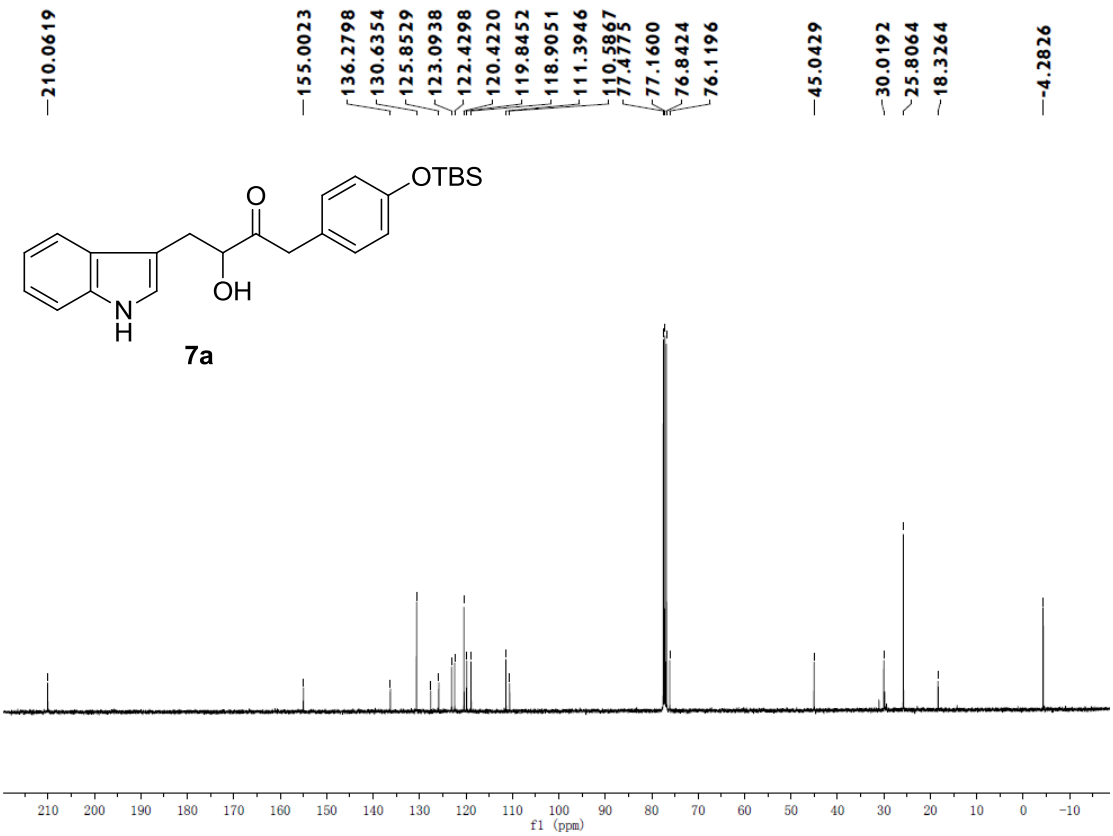
^{13}C-NMR Spectrum for **7** ($CDCl_3$, 101 MHz)



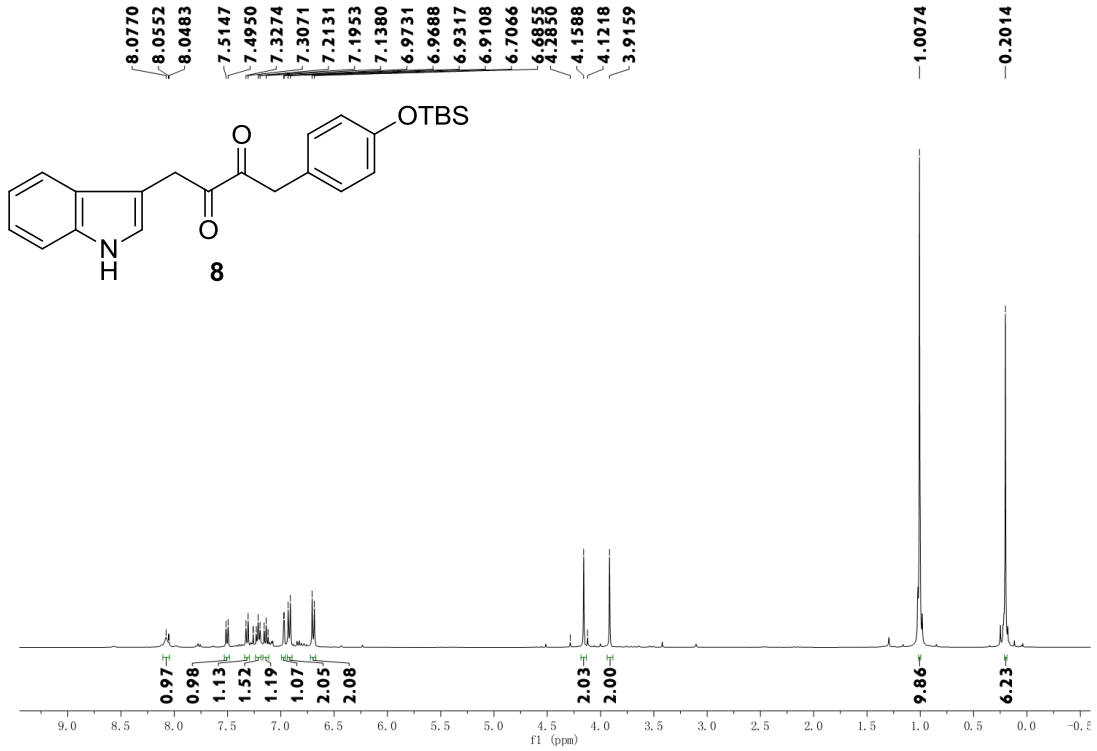
^{1}H-NMR Spectrum for **7a** ($CDCl_3$, 400 MHz)



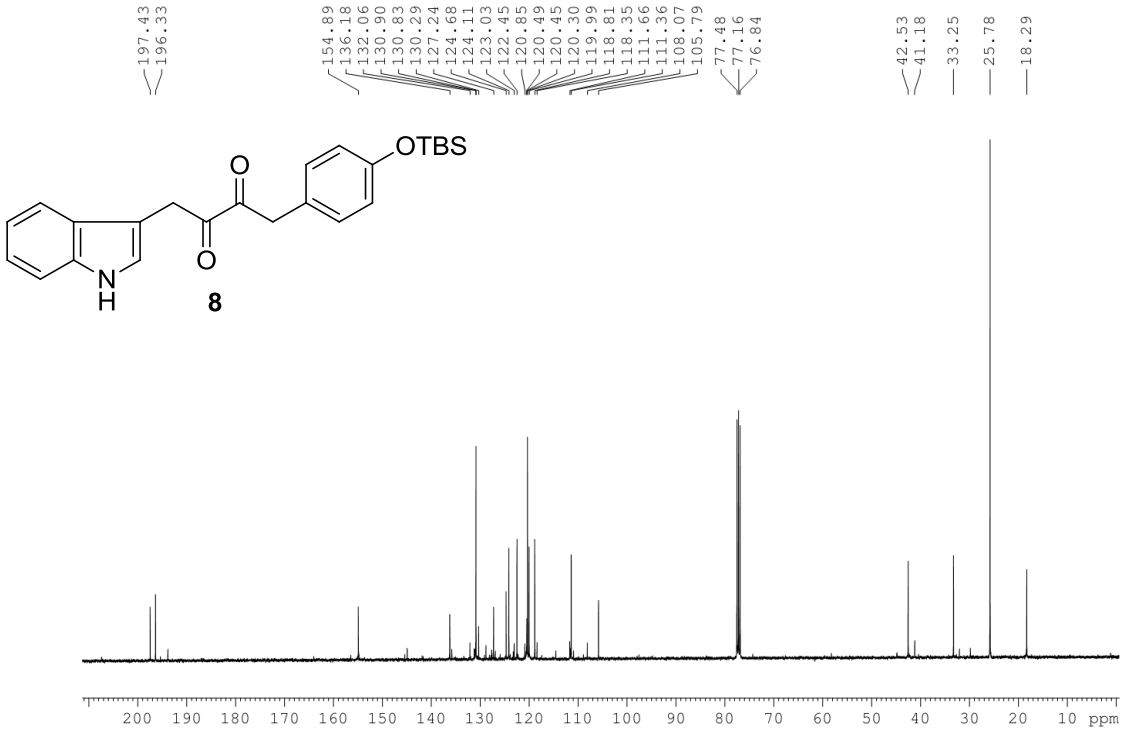
^{13}C-NMR Spectrum for **7a** ($CDCl_3$, 101 MHz)



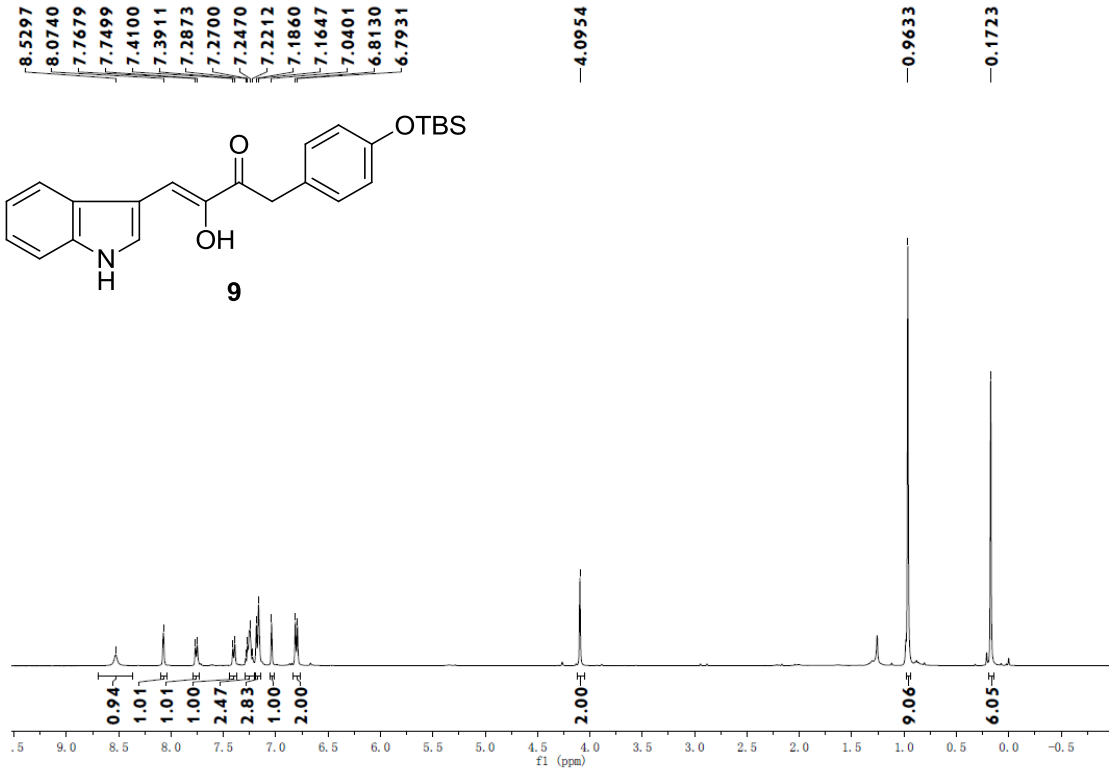
^{1}H-NMR Spectrum for **8** ($CDCl_3$, 400 MHz)



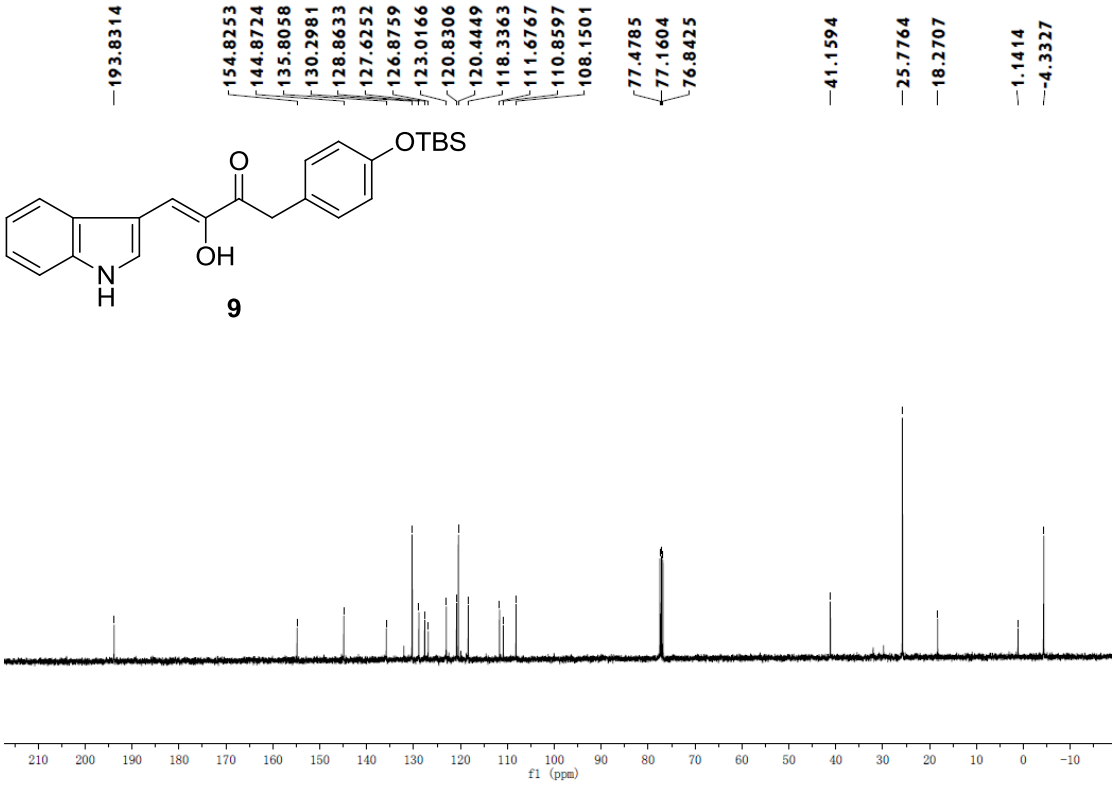
^{13}C-NMR Spectrum for **8** ($CDCl_3$, 101 MHz)



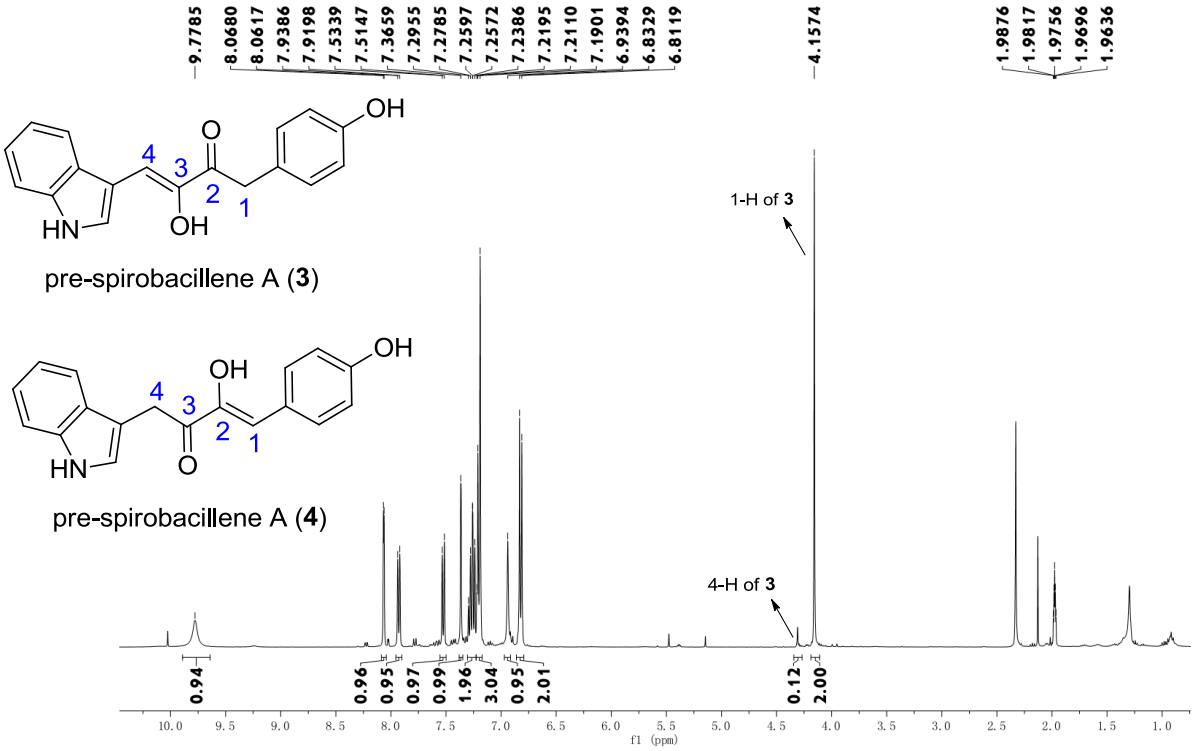
^{1}H-NMR Spectrum for **9** ($CDCl_3$, 400 MHz)



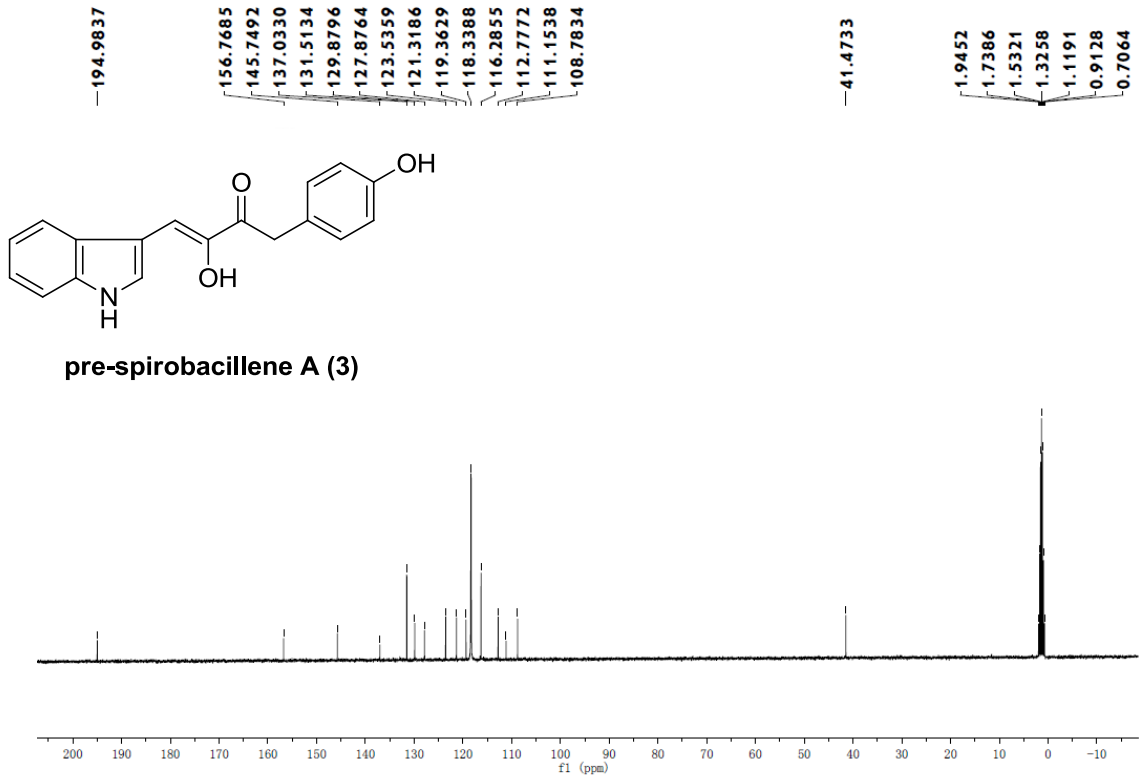
^{13}C-NMR Spectrum for **9** ($CDCl_3$, 101 MHz)



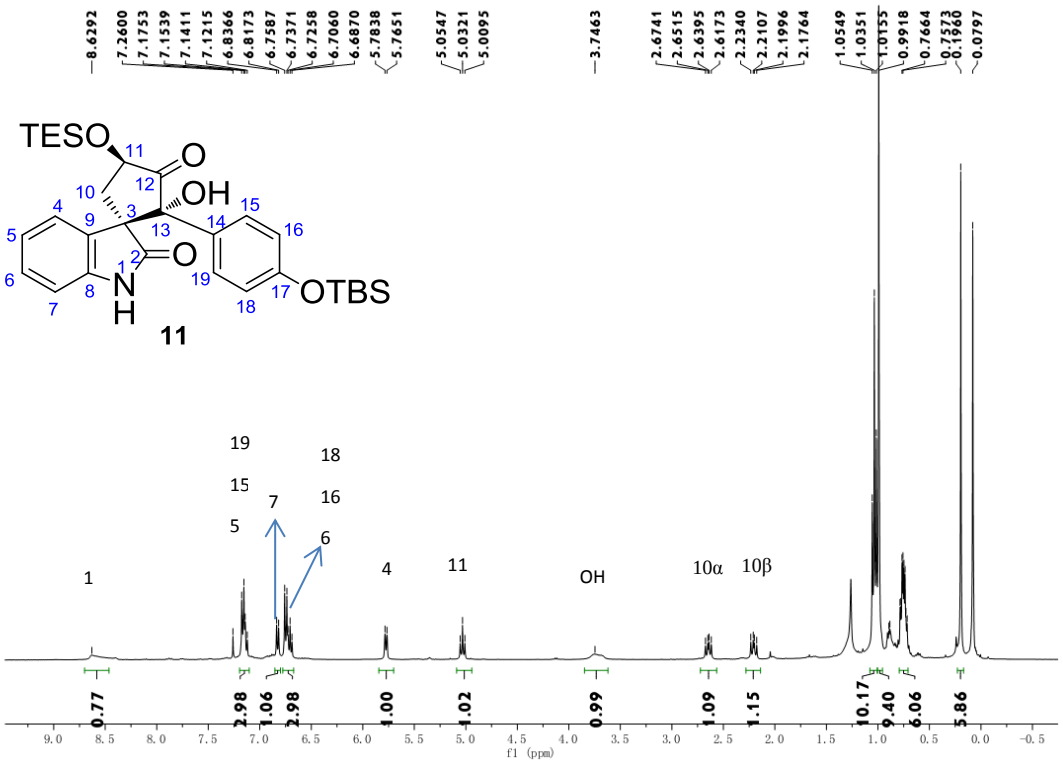
^{1}H-NMR Spectrum for pre-spirobacillene A and B (16:1) ($CDCl_3$, 400 MHz)



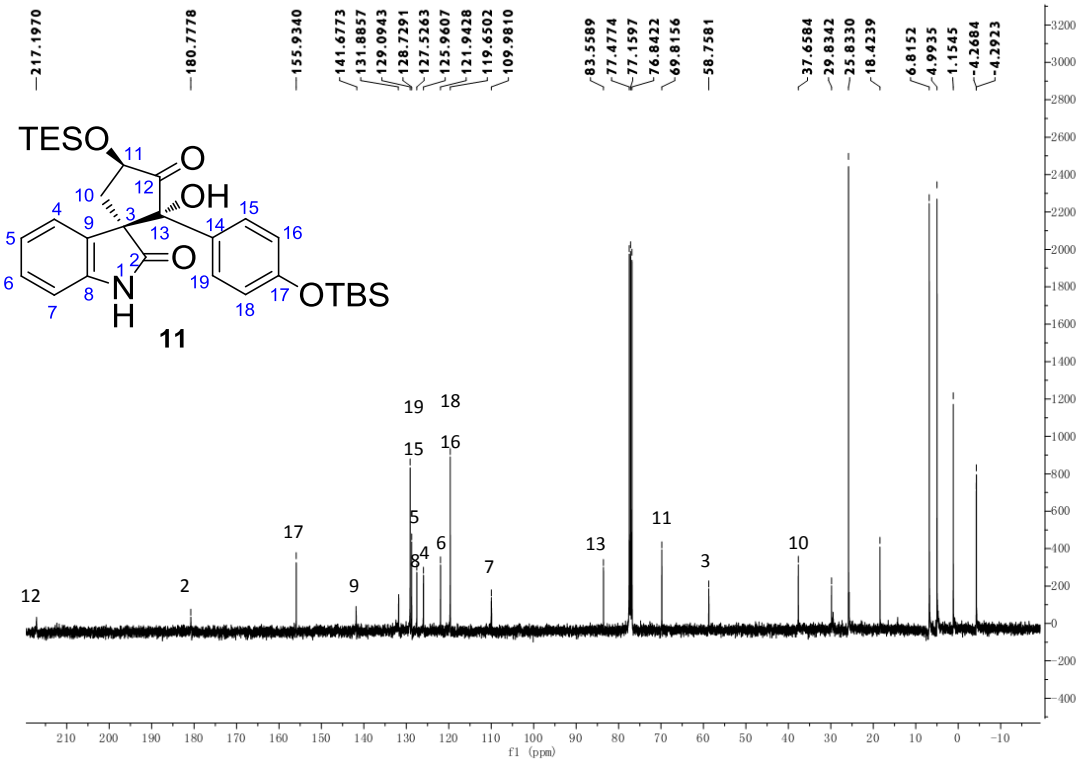
^{13}C-NMR Spectrum for pre-spirobacillene A **(3)** ($CDCl_3$, 101 MHz)



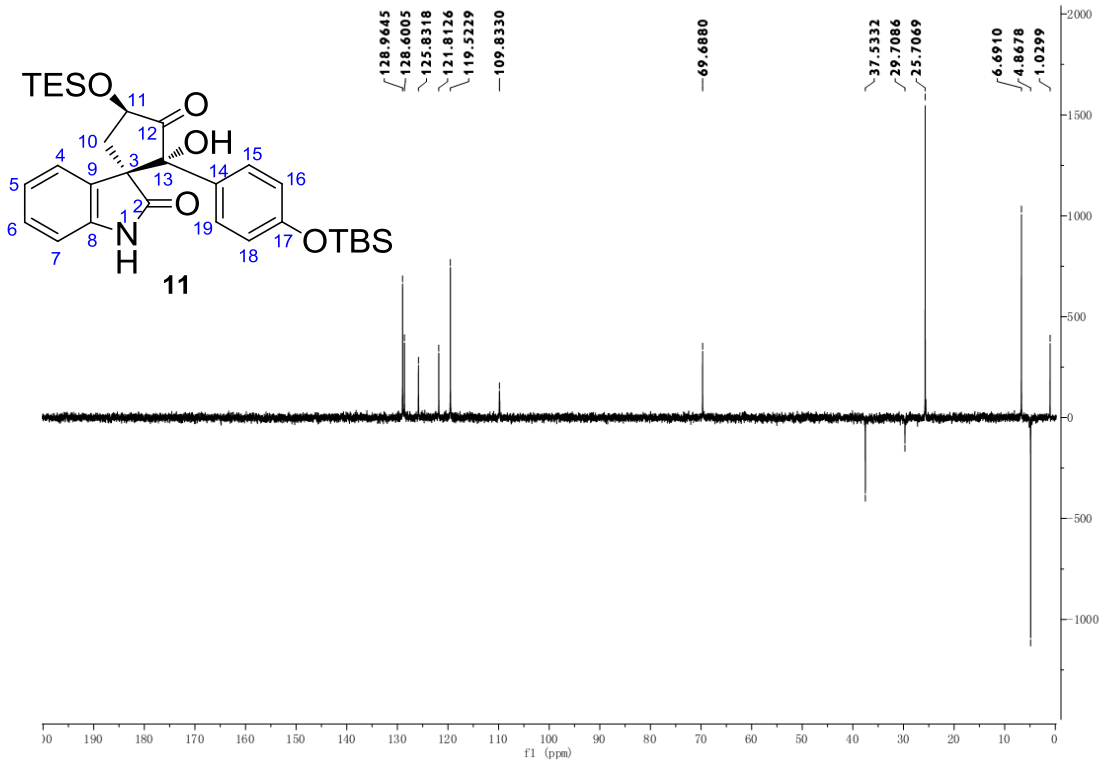
^{1}H-NMR Spectrum for compound **11** ($CDCl_3$, 400 MHz)



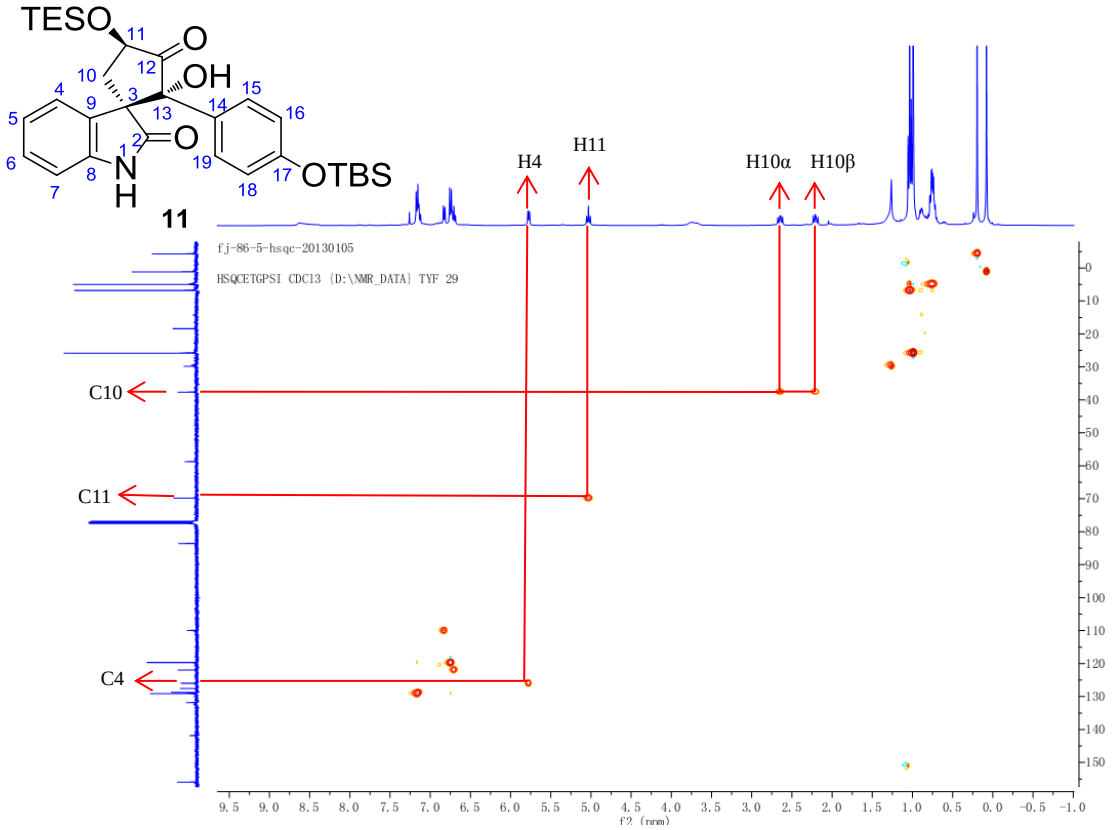
^{13}C-NMR Spectrum for compound **11** ($CDCl_3$, 101 MHz)



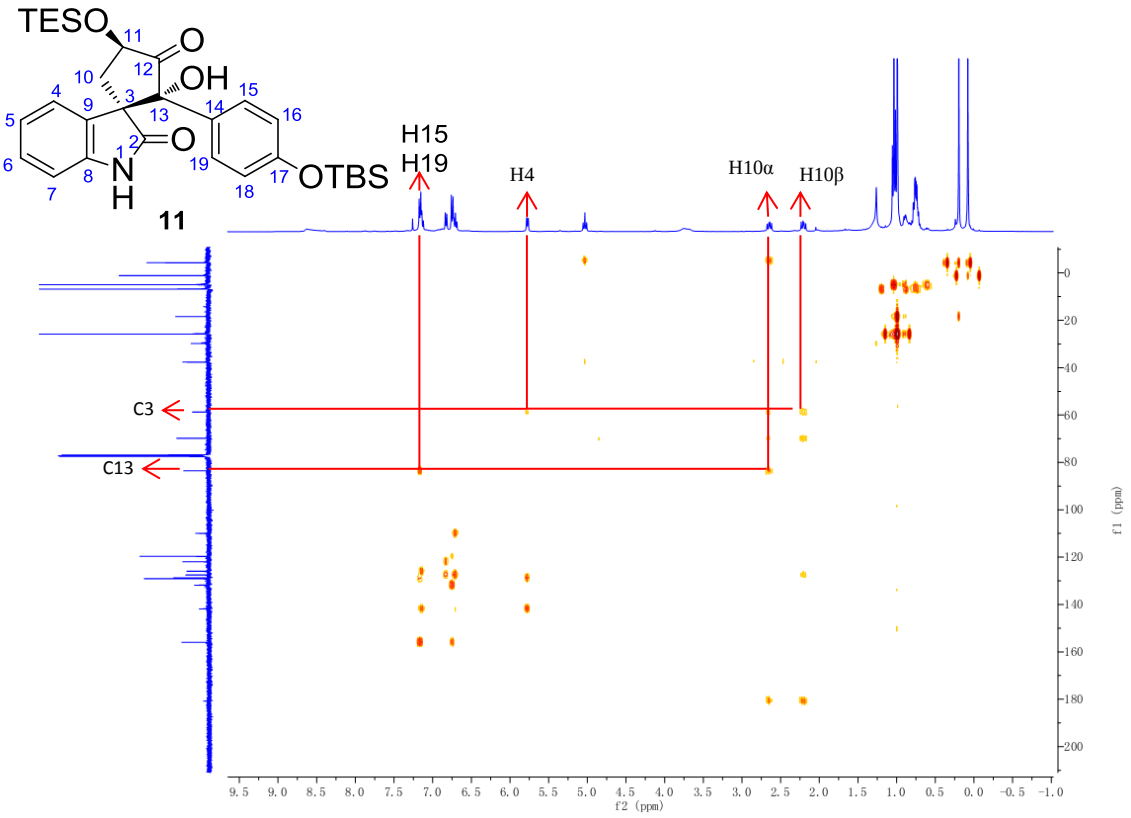
DEPT Spectrum for compound **11** ($CDCl_3$, 101 MHz)



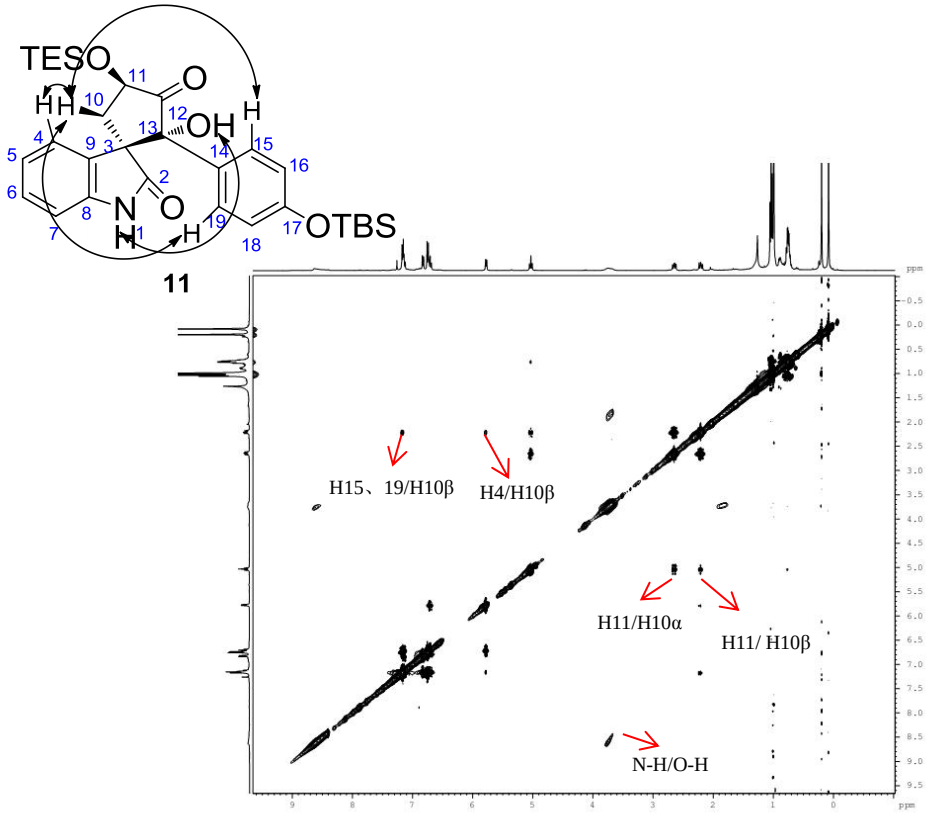
HSQC Spectrum for compound **11** ($CDCl_3$, 400 MHz)

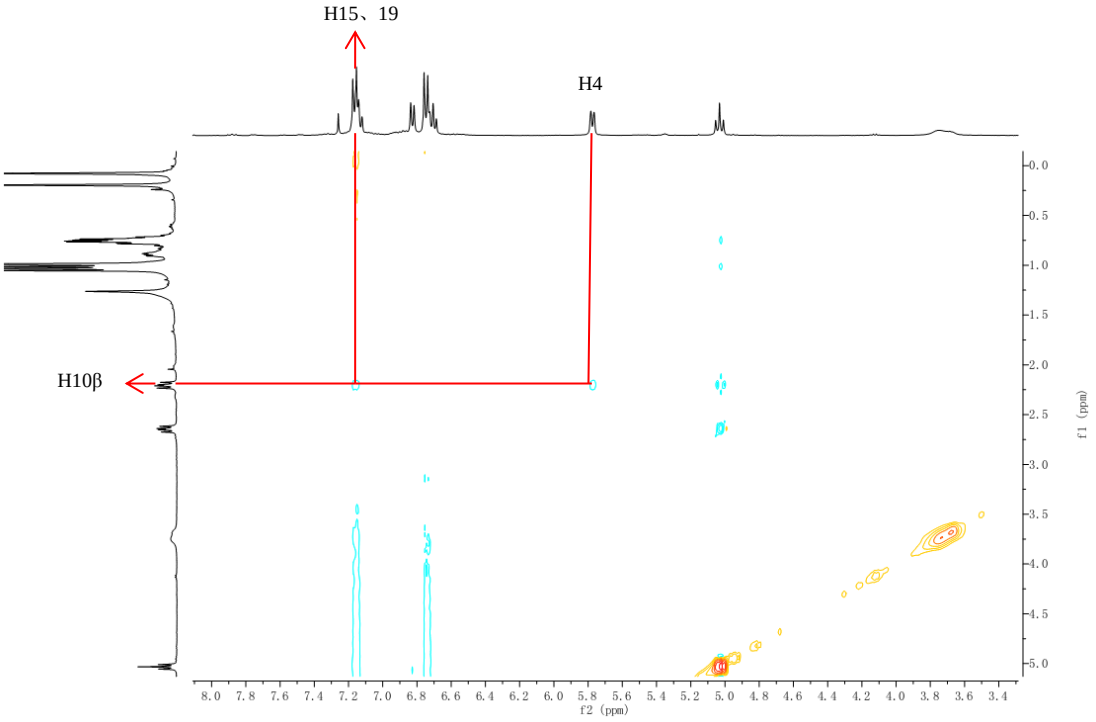


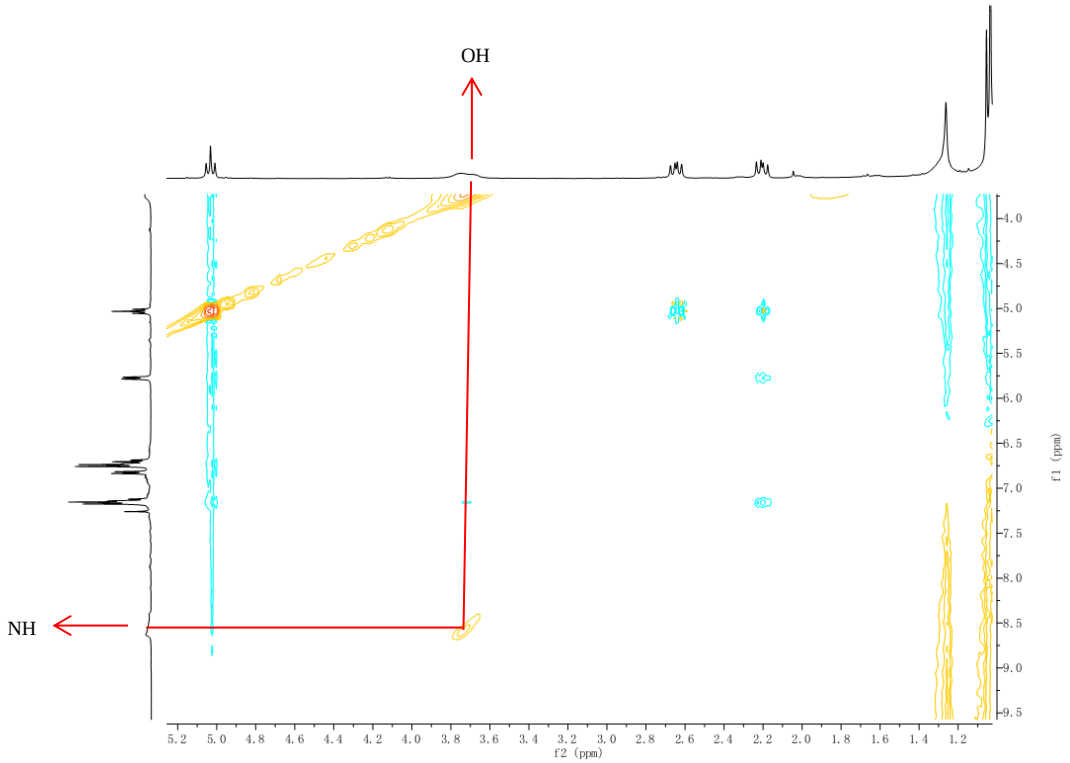
HMBC Spectrum for compound **11** ($CDCl_3$, 400 MHz)



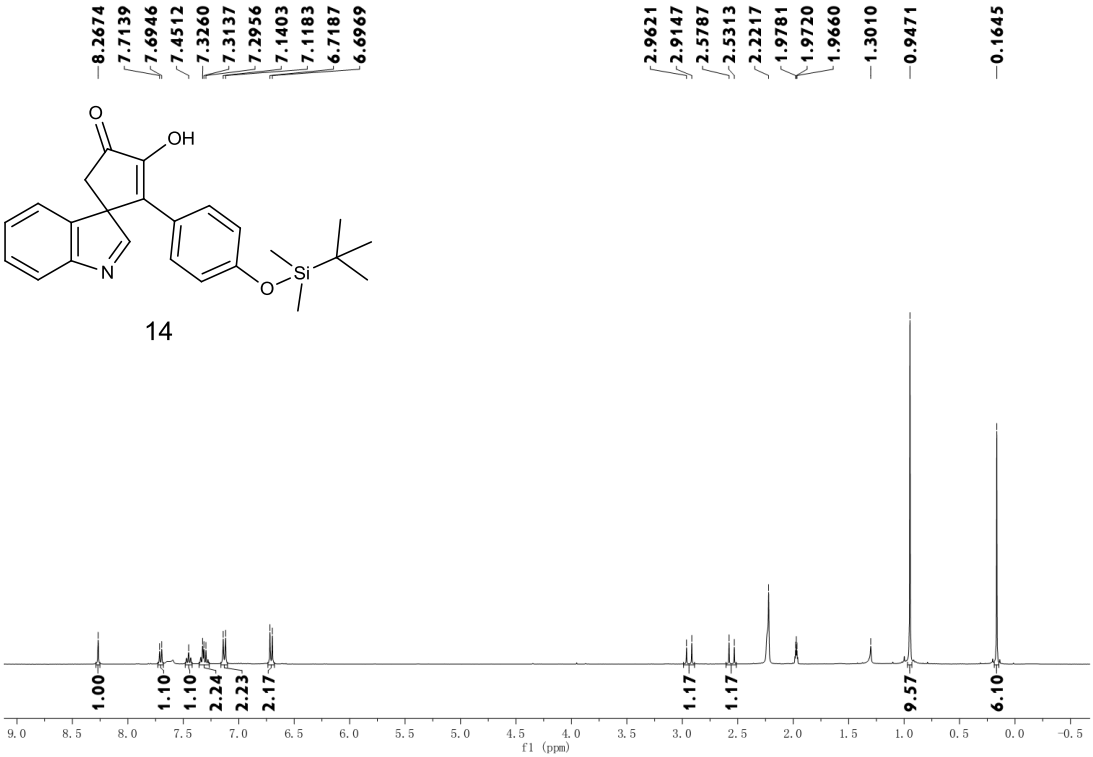
NOESY Spectrum for compound **11** ($CDCl_3$, 400 MHz)



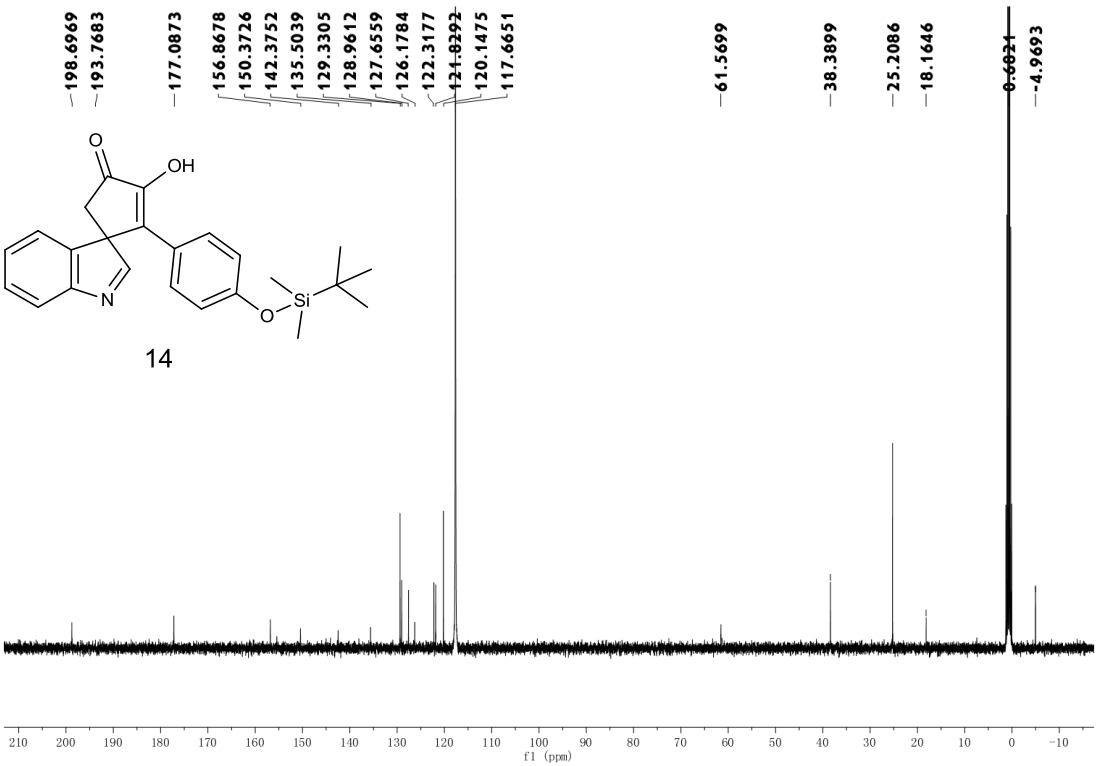

H15、19
H4
H10β
f2 (ppm)
f1 (ppm)


OH
NH
f2 (ppm)
f1 (ppm)

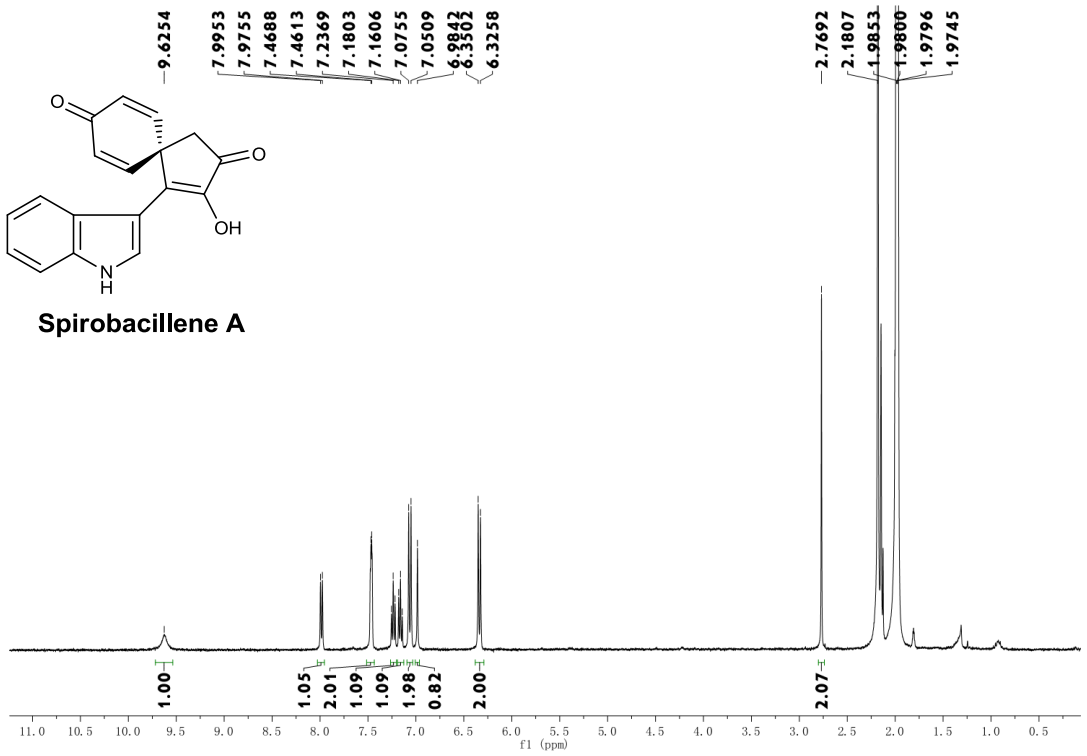
^{1}H-NMR Spectrum for compound **14** (CD_3CN, 400 MHz)



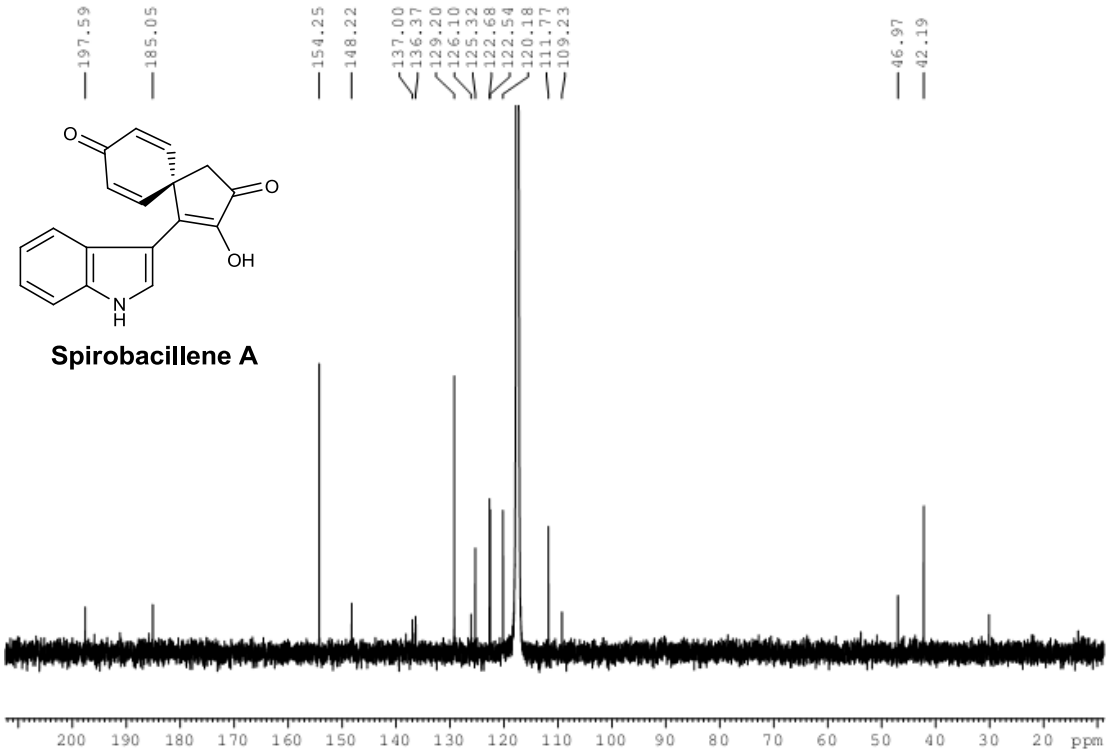
^{13}C-NMR Spectrum for compound **14** (CD_3CN, 101 MHz)



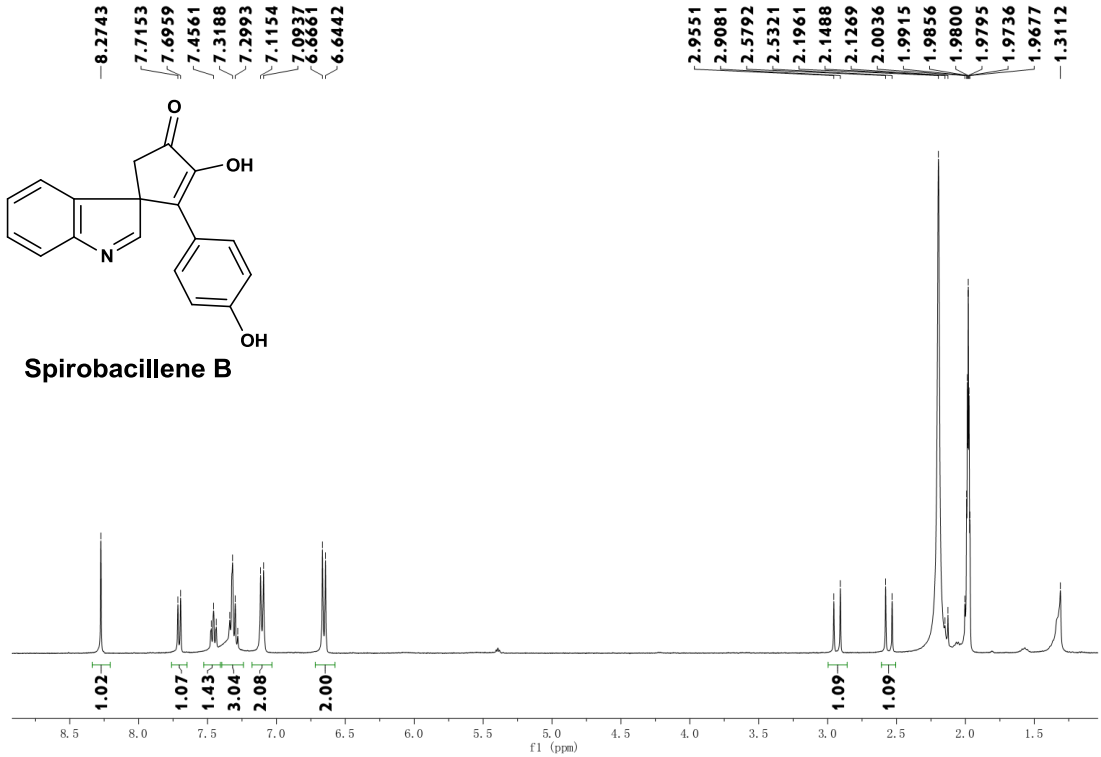
^{1}H-NMR Spectrum for Spirobacillene A **(1)** (CD_3CN, 400 MHz)



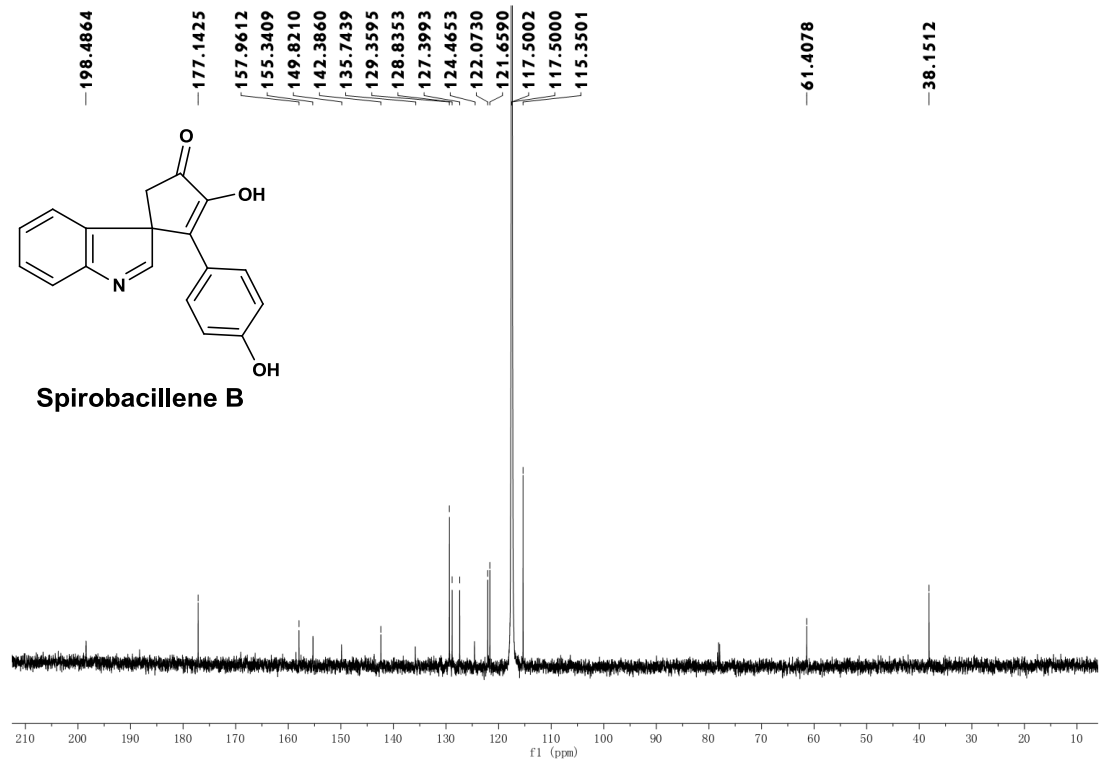
^{13}C-NMR Spectrum for spirobacillene A **(1)** (CD_3CN, 101 MHz)



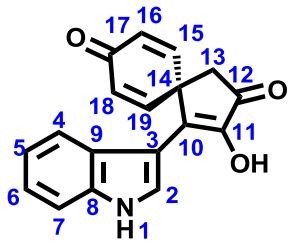
^{1}H-NMR Spectrum for Spirobacillene B **(2)** (CD_3CN, 400 MHz)



^{13}C-NMR Spectrum for spirobacillene B **(2)** (CD_3CN, 150 MHz)



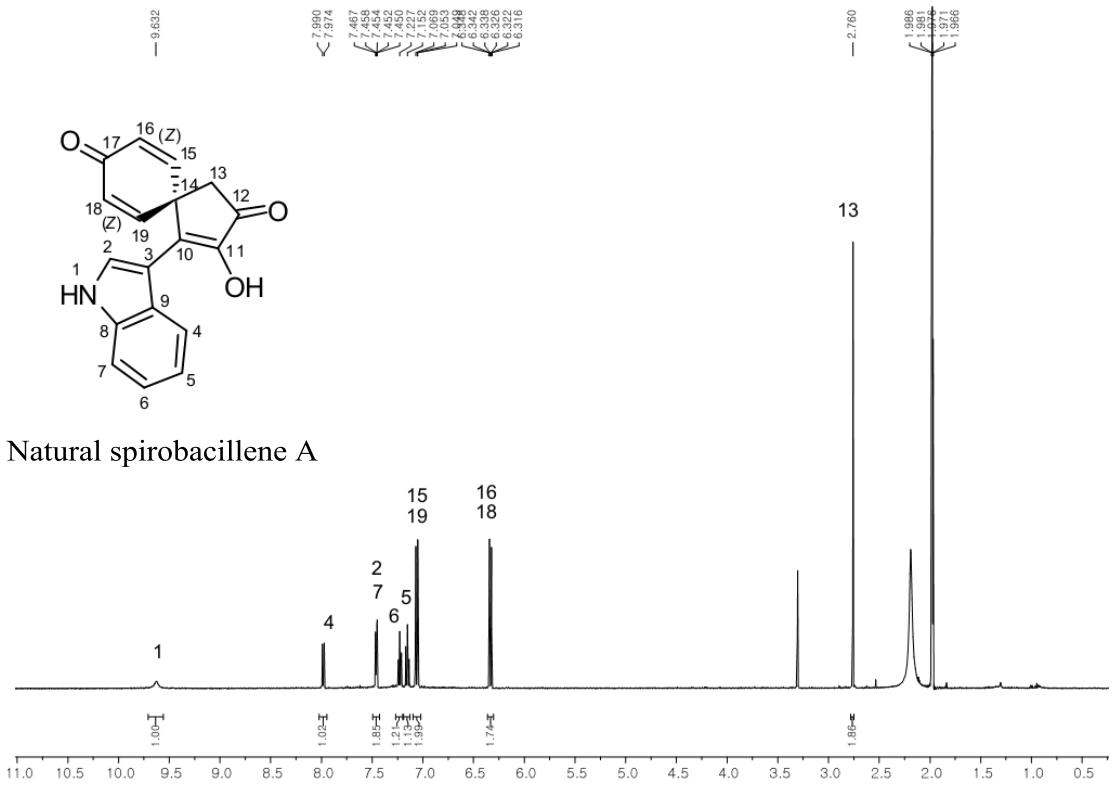
Comparison of NMR spectrum of synthetic spirobacillene A (CD_3CN, 400 MHz) with that of natural spirobacillene A (CD_3CN, 500 MHz)



Spirobacillene A

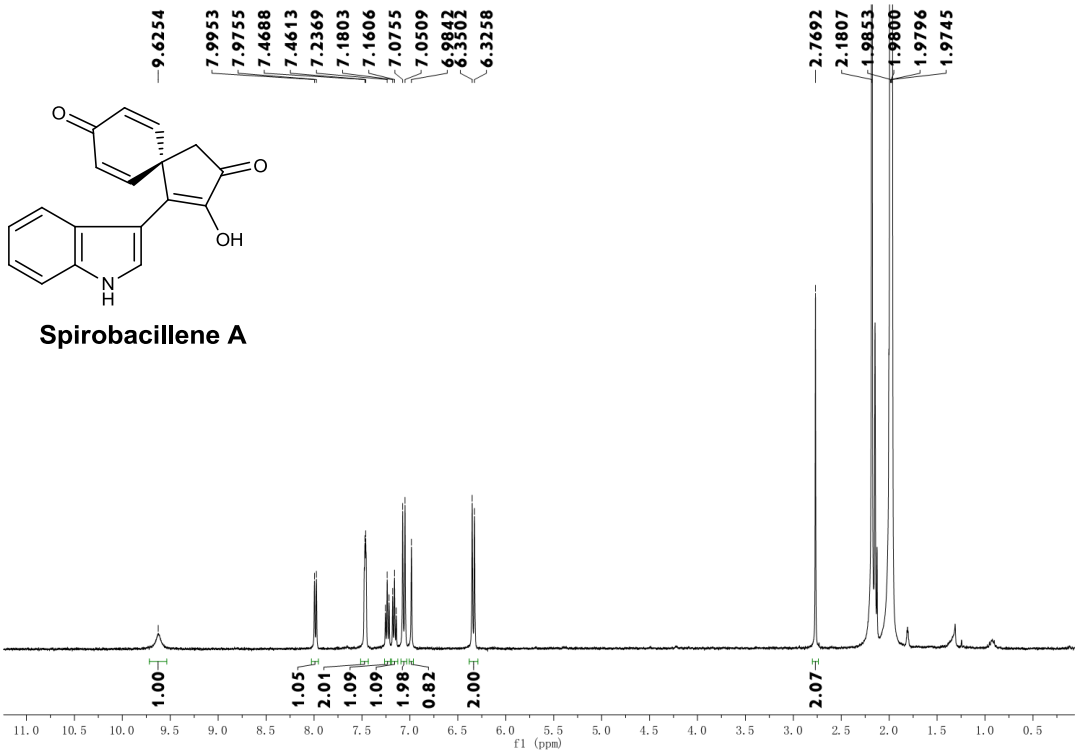
position	^{1}H NMR (δ in ppm, J in Hz)		^{13}C NMR (δ in ppm)	
	Natural	Synthetic	Natural	Synthetic
1	9.63 br s	9.63 br s		
2	7.46 m[c]	7.47 m[c]	125.3	125.3
3			109.2	109.2
4	7.98 d (8.0)	7.98 d (7.9)	122.5	122.5
5	7.16 ddd (8.0, 7.0, 1.2)	7.16 ddd (7.9, 7.2, 1.2)	120.1	120.2
6	7.23 ddd (8.0, 7.0, 1.2)	7.24 ddd (7.9, 7.2, 1.2)	122.7	122.7
7	7.46 m[c]	7.47 mc	111.7	111.8
8			136.3	136.4
9			126.0	126.1
10			137.0	137.0
11			148.2	148.2
12			197.6	197.6
13	2.76 s	2.77 s	42.1	42.2
14			47.0	47.0
15	7.06 d (10.0)	7.06 d (9.8)	154.2	154.3
16	6.33 d (10.0)	6.34 d (9.8)	129.1	129.2
17			185.0	185.1
18	6.33 d (10.0)	6.34 d (9.8)	129.1	129.2
19	7.06 d (10.0)	7.06 d (9.8)	154.2	154.3

^{1}H NMR spectrum (CD_3CN, 500 MHz)



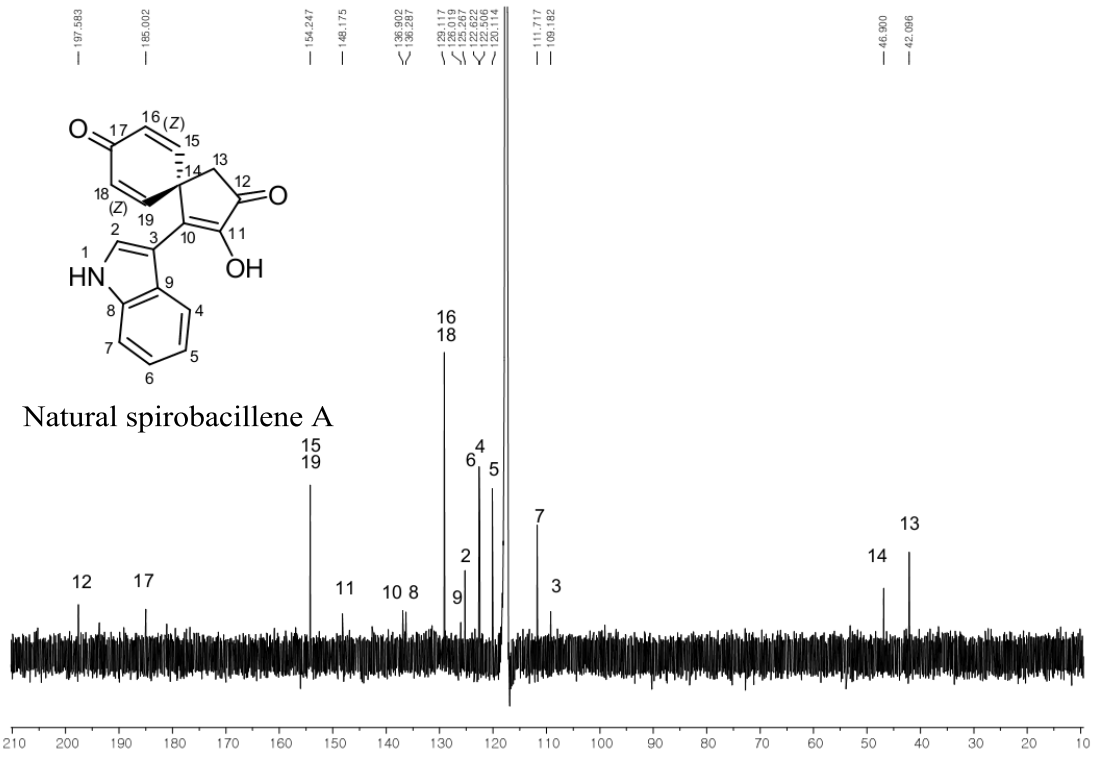
Natural spirobacillene A

^{1}H NMR spectrum (CD_3CN, 400 MHz)

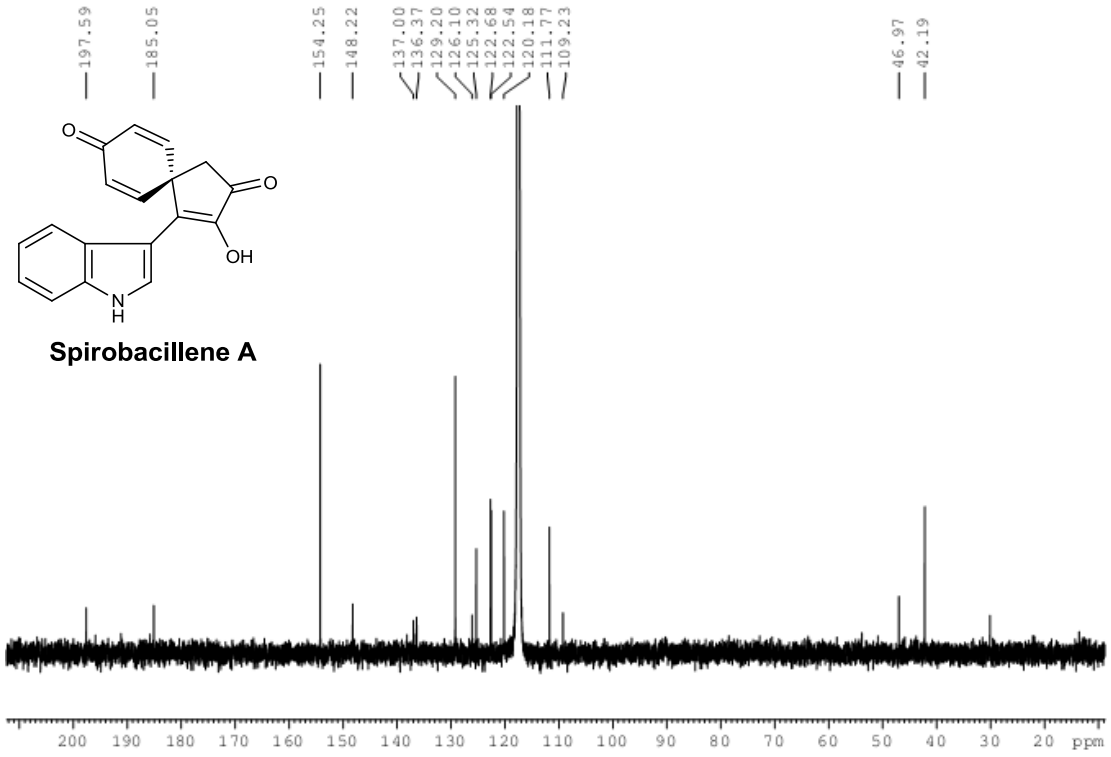


Spirobacillene A

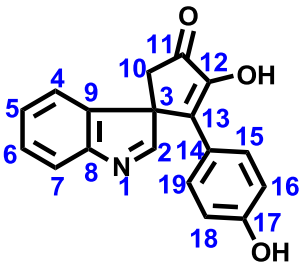
^{13}C NMR spectrum (CD_3CN, 125 MHz)



^{13}C NMR spectrum (CD_3CN, 101 MHz)



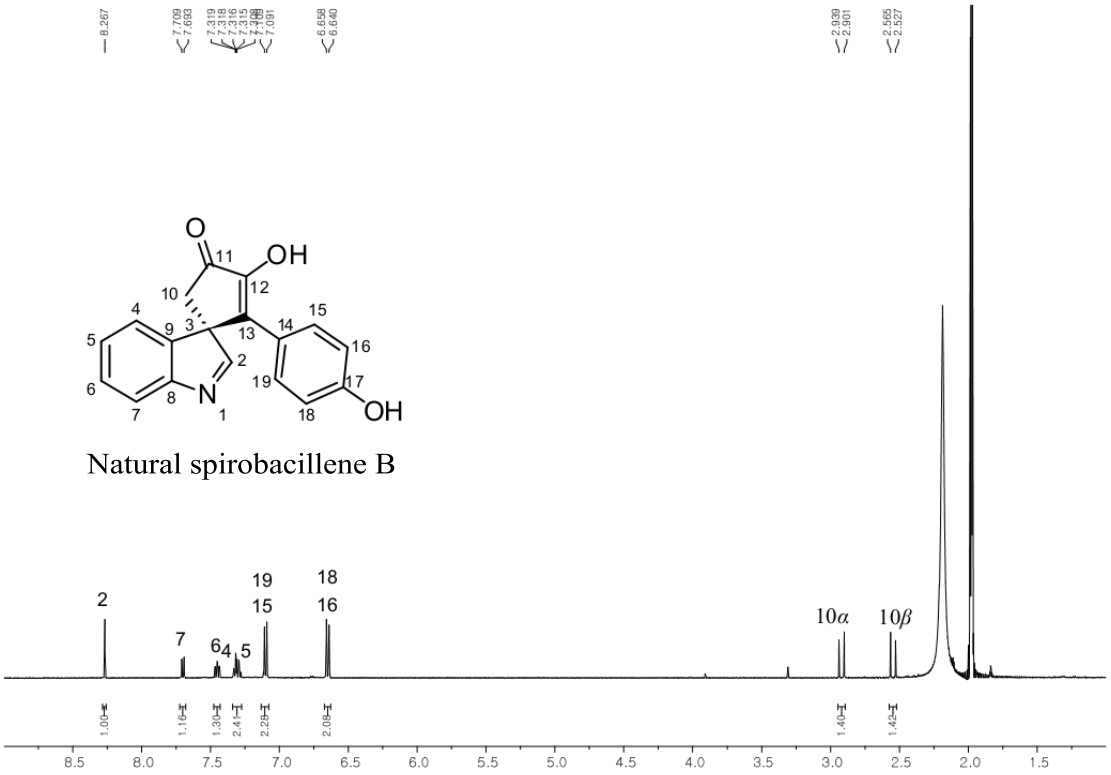
Comparison of NMR spectrum of synthetic spirobacillene B (CD_3CN, 400 MHz for H-NMR, 150 MHz for C-NMR) with that of natural spirobacillene A (CD_3CN, 500 MHz)



Spirobacillene B

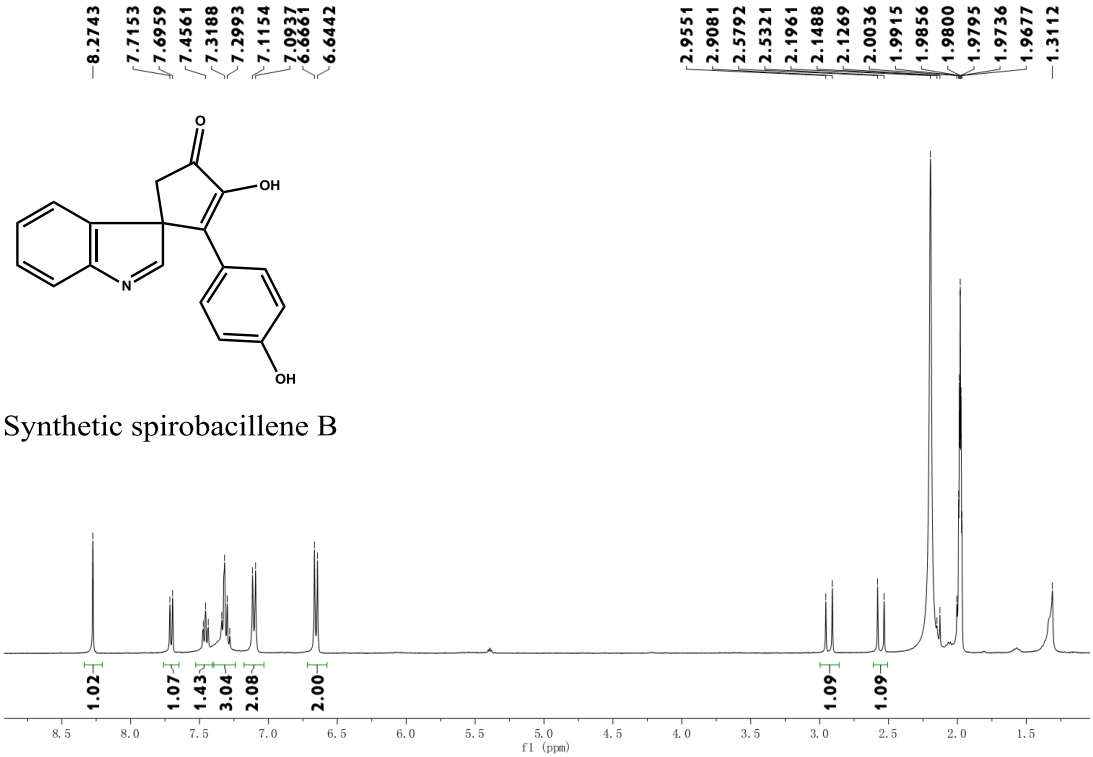
position	^{1}H NMR (δ in ppm, J in Hz)		^{13}C NMR (δ in ppm)	
	Natural	Synthetic	Natural	Synthetic
1				
2	8.27 s	8.27 s	177.2	177.1
3			61.4	61.4
4	7.32 d (7.5)	7.32 d (7.5)	122.1	122.1
5	7.30 ddd (7.5, 6.5, 1.5)	7.31 ddd (7.5, 6.6, 1.6)	127.4	127.4
6	7.45 ddd (8.0, 6.5, 1.5)	7.45 ddd (7.8, 6.6, 1.6)	128.9	128.8
7	7.70 d (8.0)	7.71 d (7.8)	121.7	121.7
8			155.3	155.3
9			142.4	142.4
10α	2.92 d (19.0)	2.93 d (18.8)	38.2	38.2
10β	2.55 d (19.0)	2.56 d (18.8)		
11			199.0	198.5
12			150.0	149.8
13			135.8	135.7
14			124.6	124.5
15	7.10 d (9.0)	7.10 d (8.7)	129.4	129.4
16	6.65 d (9.0)	6.66 d (8.8)	115.4	115.4
17			158.0	158.0
18	6.65 d (9.0)	6.66 d (8.8)	115.4	115.4
19	7.10 d (9.0)	7.10 d (8.7)	129.4	129.4

^{1}H NMR spectrum (CD_3CN, 500 MHz)



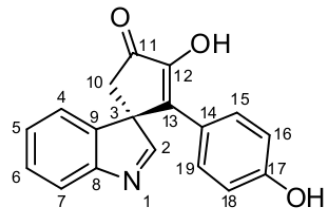
Natural spirobacillene B

^{1}H NMR spectrum (CD_3CN, 400 MHz)



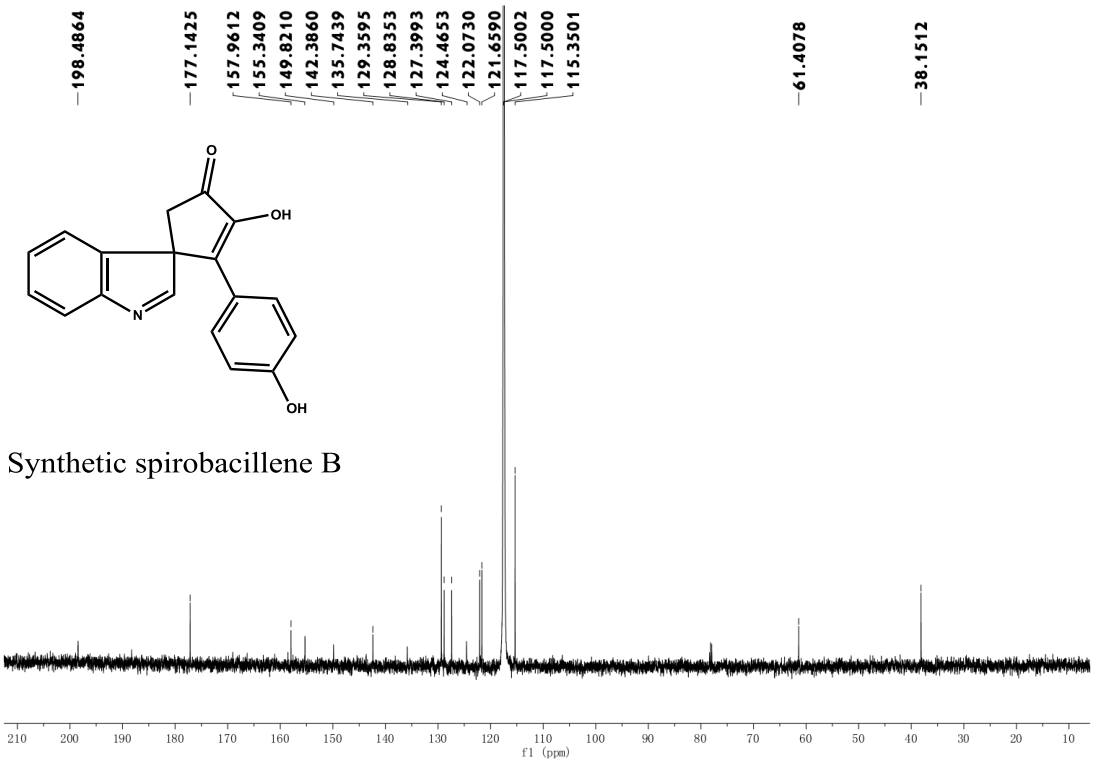
Synthetic spirobacillene B

^{1}H NMR spectrum (CD_3CN, 500 MHz)



Natural spirobacillene B

^{13}C NMR spectrum (CD_3CN, 150 MHz)



Synthetic spirobacillene B

Part 3: X-ray Crystallographic Studies for Compound 14

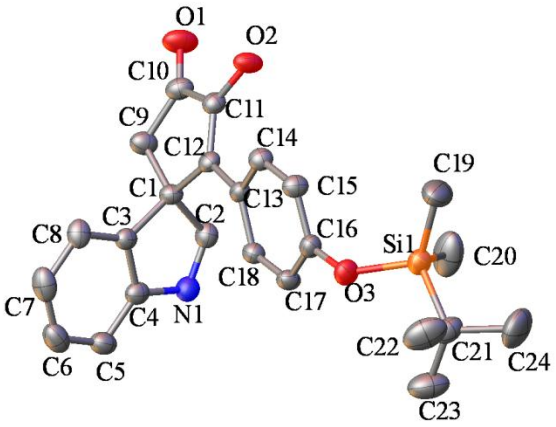


Figure 1.X-ray structure of Compound 14

Table 1. Crystal data and structure refinement for sa 2478.

Identification code	sa2478
Empirical formula	C24 H27 N O3 Si
Formula weight	405.56
Temperature	173(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, P2(1)2(1)2(1)
Unit cell dimensions	a = 11.284(3) A alpha = 90 deg.
	b = 14.658(3) A beta = 90 deg.
	c = 27.222(7) A gamma = 90 deg.
Volume	4502.4(18) A^3
Z, Calculated density	8, 1.197 Mg/m^3
Absorption coefficient	0.128 mm^-1
F(000)	1728
Crystal size	0.48 x 0.28 x 0.09 mm
Theta range for data collection	1.95 to 27.47 deg.
Limiting indices	-14<=h<=14, -18<=k<=18, -35<=l<=35
Reflections collected / unique	44582 / 5686 [R(int) = 0.0670]
Completeness to theta = 27.47	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6035
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5686 / 0 / 535
Goodness-of-fit on F^2	1.274
Final R indices [I>2sigma(I)]	R1 = 0.0575, wR2 = 0.1275
R indices (all data)	R1 = 0.0594, wR2 = 0.1284
Absolute structure parameter	-10(10)
Largest diff. peak and hole	0.284 and -0.278 e.A^-3

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for sa2478.
U(eq) is defined as one third of the trace of the orthogonalizedUij tensor.

	x	y	z	U(eq)
Si(1)	2556(1)	5678(1)	4831(1)	38(1)
Si(2)	6942(1)	3526(1)	5432(1)	29(1)
O(1)	-630(3)	2267(2)	2117(1)	49(1)
O(2)	536(3)	2557(2)	3053(1)	37(1)
O(3)	3287(2)	5591(2)	4303(1)	34(1)
O(4)	10797(3)	7807(2)	7847(1)	48(1)
O(5)	9661(3)	7500(2)	6899(1)	41(1)
O(6)	6554(2)	4453(2)	5747(1)	35(1)
N(1)	597(3)	5929(2)	1973(1)	32(1)
N(2)	9394(3)	4203(2)	8038(1)	33(1)
C(1)	1018(3)	4374(2)	2145(1)	28(1)
C(2)	199(3)	5195(2)	2167(1)	32(1)
C(3)	2067(3)	4823(2)	1901(1)	27(1)
C(4)	1771(3)	5727(2)	1804(1)	31(1)
C(5)	2544(4)	6320(3)	1576(1)	38(1)
C(6)	3650(4)	5988(3)	1444(2)	45(1)
C(7)	3948(3)	5095(3)	1533(1)	44(1)
C(8)	3170(3)	4490(3)	1765(1)	34(1)
C(9)	421(4)	3615(3)	1828(1)	36(1)
C(10)	47(3)	2897(2)	2192(1)	33(1)
C(11)	646(3)	3102(2)	2663(1)	28(1)
C(12)	1213(3)	3916(2)	2643(1)	26(1)
C(13)	1850(3)	4350(2)	3050(1)	25(1)
C(14)	2273(3)	3821(2)	3444(1)	30(1)
C(15)	2768(3)	4235(2)	3857(1)	32(1)
C(16)	2838(3)	5182(2)	3889(1)	30(1)
C(17)	2469(3)	5714(2)	3496(1)	31(1)
C(18)	1980(3)	5301(2)	3082(1)	28(1)
C(19)	2739(6)	4626(3)	5210(2)	71(2)
C(20)	960(4)	5843(5)	4681(2)	79(2)
C(21)	3222(4)	6692(3)	5144(1)	42(1)
C(22)	4520(5)	6514(4)	5274(2)	72(2)
C(23)	3144(5)	7522(3)	4805(2)	66(1)
C(24)	2516(6)	6898(4)	5616(2)	81(2)
C(25)	9052(3)	5760(2)	7837(1)	26(1)
C(26)	9846(3)	4920(2)	7841(1)	30(1)
C(27)	7962(3)	5346(2)	8071(1)	27(1)

C(28)	8211(3)	4435(2)	8183(1)	30(1)
C(29)	7392(4)	3865(3)	8391(1)	44(1)
C(30)	6285(4)	4224(4)	8497(2)	52(1)
C(31)	6035(4)	5135(3)	8401(1)	46(1)
C(32)	6865(3)	5703(3)	8183(1)	35(1)
C(33)	9632(3)	6532(3)	8146(1)	34(1)
C(34)	10088(3)	7198(2)	7772(1)	33(1)
C(35)	9516(3)	6982(2)	7302(1)	29(1)
C(36)	8908(3)	6187(2)	7324(1)	26(1)
C(37)	8257(3)	5736(2)	6926(1)	25(1)
C(38)	7900(3)	6218(2)	6504(1)	33(1)
C(39)	7341(3)	5785(2)	6120(1)	35(1)
C(40)	7118(3)	4852(2)	6140(1)	28(1)
C(41)	7432(3)	4365(2)	6554(1)	29(1)
C(42)	8000(3)	4802(2)	6941(1)	27(1)
C(43)	8441(4)	3134(3)	5628(2)	41(1)
C(44)	5778(4)	2660(3)	5547(2)	48(1)
C(45)	6977(4)	3890(3)	4770(1)	39(1)
C(46)	7917(6)	4624(4)	4713(2)	85(2)
C(47)	7295(5)	3084(4)	4438(2)	63(1)
C(48)	5789(5)	4261(4)	4610(2)	65(1)

Table 3.Bond lengths [A] and angles [deg] for sa2478.

Si(1)-O(3)	1.662(3)
Si(1)-C(20)	1.862(5)
Si(1)-C(19)	1.867(5)
Si(1)-C(21)	1.871(4)
Si(2)-O(6)	1.664(3)
Si(2)-C(44)	1.853(4)
Si(2)-C(43)	1.865(4)
Si(2)-C(45)	1.880(4)
O(1)-C(10)	1.217(4)
O(2)-C(11)	1.334(4)
O(2)-H(2)	0.8400
O(3)-C(16)	1.374(4)
O(4)-C(34)	1.216(4)
O(5)-C(35)	1.344(4)
O(5)-H(5)	0.8400
O(6)-C(40)	1.377(4)
N(1)-C(2)	1.281(5)
N(1)-C(4)	1.433(5)

N(2)-C(26)	1.286(4)
N(2)-C(28)	1.433(5)
C(1)-C(3)	1.508(5)
C(1)-C(2)	1.519(5)
C(1)-C(12)	1.528(4)
C(1)-C(9)	1.560(5)
C(2)-H(2A)	0.9500
C(3)-C(8)	1.387(5)
C(3)-C(4)	1.392(5)
C(4)-C(5)	1.379(5)
C(5)-C(6)	1.387(6)
C(5)-H(5A)	0.9500
C(6)-C(7)	1.372(6)
C(6)-H(6)	0.9500
C(7)-C(8)	1.398(5)
C(7)-H(7)	0.9500
C(8)-H(8)	0.9500
C(9)-C(10)	1.507(5)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.478(5)
C(11)-C(12)	1.356(5)
C(12)-C(13)	1.467(4)
C(13)-C(18)	1.404(4)
C(13)-C(14)	1.405(4)
C(14)-C(15)	1.395(5)
C(14)-H(14)	0.9500
C(15)-C(16)	1.393(5)
C(15)-H(15)	0.9500
C(16)-C(17)	1.387(5)
C(17)-C(18)	1.395(5)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-H(19A)	0.9800
C(19)-H(19B)	0.9800
C(19)-H(19C)	0.9800
C(20)-H(20A)	0.9800
C(20)-H(20B)	0.9800
C(20)-H(20C)	0.9800
C(21)-C(22)	1.530(6)
C(21)-C(23)	1.531(6)
C(21)-C(24)	1.541(6)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800

C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(27)	1.512(5)
C(25)-C(26)	1.522(5)
C(25)-C(36)	1.539(4)
C(25)-C(33)	1.554(5)
C(26)-H(26)	0.9500
C(27)-C(32)	1.378(5)
C(27)-C(28)	1.398(5)
C(28)-C(29)	1.368(5)
C(29)-C(30)	1.386(6)
C(29)-H(29)	0.9500
C(30)-C(31)	1.391(7)
C(30)-H(30)	0.9500
C(31)-C(32)	1.387(6)
C(31)-H(31)	0.9500
C(32)-H(32)	0.9500
C(33)-C(34)	1.501(5)
C(33)-H(33A)	0.9900
C(33)-H(33B)	0.9900
C(34)-C(35)	1.468(5)
C(35)-C(36)	1.354(5)
C(36)-C(37)	1.467(4)
C(37)-C(42)	1.400(4)
C(37)-C(38)	1.407(4)
C(38)-C(39)	1.375(5)
C(38)-H(38)	0.9500
C(39)-C(40)	1.391(5)
C(39)-H(39)	0.9500
C(40)-C(41)	1.380(5)
C(41)-C(42)	1.390(4)
C(41)-H(41)	0.9500
C(42)-H(42)	0.9500
C(43)-H(43A)	0.9800
C(43)-H(43B)	0.9800
C(43)-H(43C)	0.9800
C(44)-H(44A)	0.9800
C(44)-H(44B)	0.9800
C(44)-H(44C)	0.9800

C(45)-C(48)	1.511(6)
C(45)-C(46)	1.517(7)
C(45)-C(47)	1.531(6)
C(46)-H(46A)	0.9800
C(46)-H(46B)	0.9800
C(46)-H(46C)	0.9800
C(47)-H(47A)	0.9800
C(47)-H(47B)	0.9800
C(47)-H(47C)	0.9800
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800

O(3)-Si(1)-C(20)	107.5(2)
O(3)-Si(1)-C(19)	111.12(19)
C(20)-Si(1)-C(19)	109.6(3)
O(3)-Si(1)-C(21)	104.77(17)
C(20)-Si(1)-C(21)	112.6(2)
C(19)-Si(1)-C(21)	111.1(2)
O(6)-Si(2)-C(44)	106.62(17)
O(6)-Si(2)-C(43)	110.08(16)
C(44)-Si(2)-C(43)	112.6(2)
O(6)-Si(2)-C(45)	105.47(15)
C(44)-Si(2)-C(45)	111.84(19)
C(43)-Si(2)-C(45)	109.97(19)
C(11)-O(2)-H(2)	109.5
C(16)-O(3)-Si(1)	124.0(2)
C(35)-O(5)-H(5)	109.5
C(40)-O(6)-Si(2)	128.7(2)
C(2)-N(1)-C(4)	106.4(3)
C(26)-N(2)-C(28)	106.9(3)
C(3)-C(1)-C(2)	98.7(3)
C(3)-C(1)-C(12)	118.0(3)
C(2)-C(1)-C(12)	113.5(3)
C(3)-C(1)-C(9)	114.0(3)
C(2)-C(1)-C(9)	108.9(3)
C(12)-C(1)-C(9)	103.8(3)
N(1)-C(2)-C(1)	115.8(3)
N(1)-C(2)-H(2A)	122.1
C(1)-C(2)-H(2A)	122.1
C(8)-C(3)-C(4)	120.0(3)
C(8)-C(3)-C(1)	132.0(3)
C(4)-C(3)-C(1)	108.1(3)
C(5)-C(4)-C(3)	122.2(3)

C(5)-C(4)-N(1)	126.8(3)
C(3)-C(4)-N(1)	111.0(3)
C(4)-C(5)-C(6)	117.7(4)
C(4)-C(5)-H(5A)	121.1
C(6)-C(5)-H(5A)	121.1
C(7)-C(6)-C(5)	120.6(4)
C(7)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(6)-C(7)-C(8)	122.1(4)
C(6)-C(7)-H(7)	119.0
C(8)-C(7)-H(7)	119.0
C(3)-C(8)-C(7)	117.4(4)
C(3)-C(8)-H(8)	121.3
C(7)-C(8)-H(8)	121.3
C(10)-C(9)-C(1)	104.8(3)
C(10)-C(9)-H(9A)	110.8
C(1)-C(9)-H(9A)	110.8
C(10)-C(9)-H(9B)	110.8
C(1)-C(9)-H(9B)	110.8
H(9A)-C(9)-H(9B)	108.9
O(1)-C(10)-C(11)	126.0(4)
O(1)-C(10)-C(9)	126.5(3)
C(11)-C(10)-C(9)	107.5(3)
O(2)-C(11)-C(12)	127.1(3)
O(2)-C(11)-C(10)	121.7(3)
C(12)-C(11)-C(10)	111.0(3)
C(11)-C(12)-C(13)	125.6(3)
C(11)-C(12)-C(1)	110.8(3)
C(13)-C(12)-C(1)	123.4(3)
C(18)-C(13)-C(14)	117.7(3)
C(18)-C(13)-C(12)	121.8(3)
C(14)-C(13)-C(12)	120.3(3)
C(15)-C(14)-C(13)	120.8(3)
C(15)-C(14)-H(14)	119.6
C(13)-C(14)-H(14)	119.6
C(16)-C(15)-C(14)	120.4(3)
C(16)-C(15)-H(15)	119.8
C(14)-C(15)-H(15)	119.8
O(3)-C(16)-C(17)	119.8(3)
O(3)-C(16)-C(15)	120.5(3)
C(17)-C(16)-C(15)	119.7(3)
C(16)-C(17)-C(18)	119.9(3)
C(16)-C(17)-H(17)	120.1
C(18)-C(17)-H(17)	120.1

C(17)-C(18)-C(13)	121.4(3)
C(17)-C(18)-H(18)	119.3
C(13)-C(18)-H(18)	119.3
Si(1)-C(19)-H(19A)	109.5
Si(1)-C(19)-H(19B)	109.5
H(19A)-C(19)-H(19B)	109.5
Si(1)-C(19)-H(19C)	109.5
H(19A)-C(19)-H(19C)	109.5
H(19B)-C(19)-H(19C)	109.5
Si(1)-C(20)-H(20A)	109.5
Si(1)-C(20)-H(20B)	109.5
H(20A)-C(20)-H(20B)	109.5
Si(1)-C(20)-H(20C)	109.5
H(20A)-C(20)-H(20C)	109.5
H(20B)-C(20)-H(20C)	109.5
C(22)-C(21)-C(23)	109.3(4)
C(22)-C(21)-C(24)	109.6(4)
C(23)-C(21)-C(24)	108.5(4)
C(22)-C(21)-Si(1)	110.8(3)
C(23)-C(21)-Si(1)	109.5(3)
C(24)-C(21)-Si(1)	109.1(3)
C(21)-C(22)-H(22A)	109.5
C(21)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(21)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(21)-C(23)-H(23A)	109.5
C(21)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(21)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(21)-C(24)-H(24A)	109.5
C(21)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(21)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(27)-C(25)-C(26)	98.7(3)
C(27)-C(25)-C(36)	117.3(3)
C(26)-C(25)-C(36)	113.4(3)
C(27)-C(25)-C(33)	114.0(3)
C(26)-C(25)-C(33)	109.8(3)

C(36)-C(25)-C(33)	103.8(3)
N(2)-C(26)-C(25)	115.5(3)
N(2)-C(26)-H(26)	122.2
C(25)-C(26)-H(26)	122.2
C(32)-C(27)-C(28)	119.6(3)
C(32)-C(27)-C(25)	132.2(3)
C(28)-C(27)-C(25)	108.1(3)
C(29)-C(28)-C(27)	122.6(4)
C(29)-C(28)-N(2)	126.7(3)
C(27)-C(28)-N(2)	110.7(3)
C(28)-C(29)-C(30)	117.6(4)
C(28)-C(29)-H(29)	121.2
C(30)-C(29)-H(29)	121.2
C(29)-C(30)-C(31)	120.5(4)
C(29)-C(30)-H(30)	119.7
C(31)-C(30)-H(30)	119.7
C(32)-C(31)-C(30)	121.4(4)
C(32)-C(31)-H(31)	119.3
C(30)-C(31)-H(31)	119.3
C(27)-C(32)-C(31)	118.3(4)
C(27)-C(32)-H(32)	120.9
C(31)-C(32)-H(32)	120.9
C(34)-C(33)-C(25)	104.6(3)
C(34)-C(33)-H(33A)	110.8
C(25)-C(33)-H(33A)	110.8
C(34)-C(33)-H(33B)	110.8
C(25)-C(33)-H(33B)	110.8
H(33A)-C(33)-H(33B)	108.9
O(4)-C(34)-C(35)	126.5(3)
O(4)-C(34)-C(33)	126.1(3)
C(35)-C(34)-C(33)	107.5(3)
O(5)-C(35)-C(36)	125.8(3)
O(5)-C(35)-C(34)	122.4(3)
C(36)-C(35)-C(34)	111.6(3)
C(35)-C(36)-C(37)	127.5(3)
C(35)-C(36)-C(25)	109.8(3)
C(37)-C(36)-C(25)	122.7(3)
C(42)-C(37)-C(38)	117.1(3)
C(42)-C(37)-C(36)	121.5(3)
C(38)-C(37)-C(36)	121.3(3)
C(39)-C(38)-C(37)	121.3(3)
C(39)-C(38)-H(38)	119.3
C(37)-C(38)-H(38)	119.3
C(38)-C(39)-C(40)	120.4(3)

C(38)-C(39)-H(39)	119.8
C(40)-C(39)-H(39)	119.8
O(6)-C(40)-C(41)	122.2(3)
O(6)-C(40)-C(39)	118.1(3)
C(41)-C(40)-C(39)	119.6(3)
C(40)-C(41)-C(42)	119.9(3)
C(40)-C(41)-H(41)	120.1
C(42)-C(41)-H(41)	120.1
C(41)-C(42)-C(37)	121.6(3)
C(41)-C(42)-H(42)	119.2
C(37)-C(42)-H(42)	119.2
Si(2)-C(43)-H(43A)	109.5
Si(2)-C(43)-H(43B)	109.5
H(43A)-C(43)-H(43B)	109.5
Si(2)-C(43)-H(43C)	109.5
H(43A)-C(43)-H(43C)	109.5
H(43B)-C(43)-H(43C)	109.5
Si(2)-C(44)-H(44A)	109.5
Si(2)-C(44)-H(44B)	109.5
H(44A)-C(44)-H(44B)	109.5
Si(2)-C(44)-H(44C)	109.5
H(44A)-C(44)-H(44C)	109.5
H(44B)-C(44)-H(44C)	109.5
C(48)-C(45)-C(46)	109.6(4)
C(48)-C(45)-C(47)	108.3(4)
C(46)-C(45)-C(47)	108.8(4)
C(48)-C(45)-Si(2)	111.1(3)
C(46)-C(45)-Si(2)	108.3(3)
C(47)-C(45)-Si(2)	110.6(3)
C(45)-C(46)-H(46A)	109.5
C(45)-C(46)-H(46B)	109.5
H(46A)-C(46)-H(46B)	109.5
C(45)-C(46)-H(46C)	109.5
H(46A)-C(46)-H(46C)	109.5
H(46B)-C(46)-H(46C)	109.5
C(45)-C(47)-H(47A)	109.5
C(45)-C(47)-H(47B)	109.5
H(47A)-C(47)-H(47B)	109.5
C(45)-C(47)-H(47C)	109.5
H(47A)-C(47)-H(47C)	109.5
H(47B)-C(47)-H(47C)	109.5
C(45)-C(48)-H(48A)	109.5
C(45)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5

C(45)-C(48)-H(48C)	109.5
H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4.Anisotropic displacement parameters (A^2 x 10^3) for sa2478.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

U11	U22	U33	U23	U13	U12
Si(1)	44(1)	38(1)	32(1)	-6(1)	3(1)	-4(1)
Si(2)	30(1)	29(1)	26(1)	-2(1)	-2(1)	-2(1)
O(1)	62(2)	38(2)	47(2)	1(1)	-17(2)	-20(2)
O(2)	52(2)	28(1)	31(1)	3(1)	-9(1)	-13(1)
O(3)	38(1)	38(1)	26(1)	-6(1)	-4(1)	-5(1)
O(4)	58(2)	36(1)	50(2)	3(1)	-17(2)	-17(1)
O(5)	61(2)	29(1)	33(1)	5(1)	-4(1)	-16(1)
O(6)	39(1)	36(1)	30(1)	-9(1)	-7(1)	6(1)
N(1)	35(2)	33(2)	29(1)	1(1)	-2(1)	4(1)
N(2)	41(2)	30(2)	29(1)	2(1)	-2(1)	6(1)
C(1)	30(2)	23(2)	30(2)	1(1)	-3(1)	-2(2)
C(2)	31(2)	35(2)	29(2)	-1(1)	-1(1)	3(2)
C(3)	32(2)	26(2)	22(1)	0(1)	-3(1)	-2(1)
C(4)	38(2)	29(2)	25(2)	-1(1)	-5(1)	-2(2)
C(5)	48(2)	32(2)	35(2)	2(1)	0(2)	-8(2)
C(6)	43(2)	57(3)	35(2)	0(2)	2(2)	-16(2)
C(7)	26(2)	71(3)	34(2)	-3(2)	-1(2)	-2(2)
C(8)	31(2)	45(2)	26(2)	1(2)	-5(1)	7(2)
C(9)	42(2)	33(2)	33(2)	2(2)	-7(2)	-8(2)
C(10)	32(2)	27(2)	41(2)	-1(2)	-8(2)	-1(2)
C(11)	32(2)	25(2)	28(2)	0(1)	-3(1)	3(2)
C(12)	27(2)	22(2)	28(2)	-1(1)	-1(1)	4(1)
C(13)	25(2)	25(2)	26(1)	-4(1)	2(1)	-3(1)
C(14)	31(2)	28(2)	31(2)	1(1)	-3(1)	2(2)
C(15)	35(2)	30(2)	31(2)	2(1)	-7(1)	-1(2)
C(16)	33(2)	31(2)	27(2)	-4(1)	1(1)	-3(2)
C(17)	38(2)	26(2)	30(2)	0(1)	0(1)	-8(2)
C(18)	31(2)	26(2)	29(2)	2(1)	1(1)	-1(2)
C(19)	121(5)	42(2)	48(3)	7(2)	22(3)	-6(3)
C(20)	41(3)	115(5)	80(4)	-36(4)	8(2)	-5(3)
C(21)	57(3)	35(2)	34(2)	-6(2)	-10(2)	5(2)

C(22)	71(3)	55(3)	89(4)	-17(3)	-34(3)	-3(3)
C(23)	87(4)	38(2)	73(3)	3(2)	-22(3)	-6(3)
C(24)	117(5)	78(4)	48(3)	-29(3)	7(3)	4(4)
C(25)	26(2)	24(2)	27(2)	1(1)	-3(1)	-1(1)
C(26)	30(2)	33(2)	28(2)	3(1)	-1(1)	3(2)
C(27)	30(2)	32(2)	20(1)	-1(1)	-2(1)	0(2)
C(28)	33(2)	31(2)	27(2)	-1(1)	-1(1)	-3(2)
C(29)	60(3)	40(2)	31(2)	6(2)	-1(2)	-15(2)
C(30)	47(2)	72(3)	36(2)	4(2)	0(2)	-27(2)
C(31)	31(2)	79(3)	29(2)	-3(2)	-3(2)	-1(2)
C(32)	32(2)	47(2)	26(2)	-6(2)	-4(1)	4(2)
C(33)	37(2)	32(2)	33(2)	-2(2)	-9(2)	-1(2)
C(34)	37(2)	25(2)	36(2)	-3(1)	-5(2)	0(2)
C(35)	34(2)	22(2)	32(2)	-3(1)	-1(2)	-1(2)
C(36)	26(2)	23(2)	28(2)	0(1)	2(1)	4(1)
C(37)	24(2)	24(2)	26(2)	0(1)	2(1)	0(1)
C(38)	40(2)	25(2)	34(2)	1(1)	-5(2)	-2(2)
C(39)	44(2)	32(2)	28(2)	7(1)	-6(2)	3(2)
C(40)	27(2)	34(2)	24(2)	-8(1)	2(1)	-1(2)
C(41)	36(2)	24(2)	26(2)	-2(1)	2(1)	-4(2)
C(42)	31(2)	25(2)	26(2)	0(1)	-1(1)	-1(2)
C(43)	42(2)	43(2)	38(2)	-3(2)	-3(2)	7(2)
C(44)	44(2)	42(2)	57(3)	4(2)	-2(2)	-11(2)
C(45)	48(2)	39(2)	29(2)	-4(2)	-1(2)	3(2)
C(46)	115(5)	96(4)	43(3)	19(3)	11(3)	-48(4)
C(47)	81(4)	76(3)	31(2)	-12(2)	-5(2)	28(3)
C(48)	82(3)	73(3)	38(2)	0(2)	-8(2)	31(3)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for sa2478.

	x	y	z	U(eq)
H(2)	162	2084	2973	55
H(5)	10028	7979	6974	61
H(2A)	-561	5166	2317	38
H(5A)	2328	6935	1512	46
H(6)	4206	6381	1290	54
H(7)	4707	4882	1435	52
H(8)	3389	3875	1827	41
H(9A)	-274	3860	1649	43
H(9B)	989	3361	1587	43
H(14)	2220	3175	3428	36

H(15)	3060	3868	4119	38
H(17)	2549	6358	3510	37
H(18)	1730	5671	2815	34
H(19A)	3584	4519	5271	106
H(19B)	2405	4102	5034	106
H(19C)	2325	4703	5524	106
H(20A)	667	5313	4499	118
H(20B)	866	6393	4481	118
H(20C)	506	5911	4986	118
H(22A)	4978	6425	4972	107
H(22B)	4577	5966	5479	107
H(22C)	4838	7038	5455	107
H(23A)	2317	7618	4707	99
H(23B)	3628	7416	4511	99
H(23C)	3435	8063	4978	99
H(24A)	2564	6375	5839	122
H(24B)	1684	7013	5531	122
H(24C)	2848	7439	5777	122
H(26)	10623	4926	7706	36
H(29)	7575	3245	8459	52
H(30)	5692	3844	8637	62
H(31)	5280	5374	8487	55
H(32)	6682	6322	8112	42
H(33A)	9041	6824	8364	41
H(33B)	10288	6290	8349	41
H(38)	8047	6855	6484	39
H(39)	7107	6125	5840	41
H(41)	7261	3731	6574	34
H(42)	8219	4459	7223	33
H(43A)	8407	2917	5968	61
H(43B)	9002	3643	5605	61
H(43C)	8704	2637	5413	61
H(44A)	5002	2912	5460	71
H(44B)	5781	2492	5896	71
H(44C)	5936	2117	5348	71
H(46A)	8695	4370	4796	127
H(46B)	7737	5134	4933	127
H(46C)	7924	4841	4372	127
H(47A)	6682	2613	4466	94
H(47B)	8061	2830	4540	94
H(47C)	7347	3292	4097	94
H(48A)	5562	4770	4823	97
H(48B)	5191	3778	4632	97
H(48C)	5843	4475	4269	97

Table 6.Torsion angles [deg] for sa2478.

C(20)-Si(1)-O(3)-C(16)	-35.0(4)
C(19)-Si(1)-O(3)-C(16)	84.9(4)
C(21)-Si(1)-O(3)-C(16)	-155.0(3)
C(44)-Si(2)-O(6)-C(40)	114.4(3)
C(43)-Si(2)-O(6)-C(40)	-8.0(3)
C(45)-Si(2)-O(6)-C(40)	-126.6(3)
C(4)-N(1)-C(2)-C(1)	-2.2(4)
C(3)-C(1)-C(2)-N(1)	2.6(4)
C(12)-C(1)-C(2)-N(1)	128.3(3)
C(9)-C(1)-C(2)-N(1)	-116.5(3)
C(2)-C(1)-C(3)-C(8)	179.2(3)
C(12)-C(1)-C(3)-C(8)	56.7(5)
C(9)-C(1)-C(3)-C(8)	-65.5(5)
C(2)-C(1)-C(3)-C(4)	-1.9(3)
C(12)-C(1)-C(3)-C(4)	-124.4(3)
C(9)-C(1)-C(3)-C(4)	113.4(3)
C(8)-C(3)-C(4)-C(5)	-0.3(5)
C(1)-C(3)-C(4)-C(5)	-179.3(3)
C(8)-C(3)-C(4)-N(1)	180.0(3)
C(1)-C(3)-C(4)-N(1)	0.9(4)
C(2)-N(1)-C(4)-C(5)	-179.0(3)
C(2)-N(1)-C(4)-C(3)	0.7(4)
C(3)-C(4)-C(5)-C(6)	-0.1(5)
N(1)-C(4)-C(5)-C(6)	179.6(3)
C(4)-C(5)-C(6)-C(7)	0.7(6)
C(5)-C(6)-C(7)-C(8)	-0.9(6)
C(4)-C(3)-C(8)-C(7)	0.2(5)
C(1)-C(3)-C(8)-C(7)	178.9(3)
C(6)-C(7)-C(8)-C(3)	0.4(5)
C(3)-C(1)-C(9)-C(10)	143.6(3)
C(2)-C(1)-C(9)-C(10)	-107.4(3)
C(12)-C(1)-C(9)-C(10)	13.9(4)
C(1)-C(9)-C(10)-O(1)	166.1(4)
C(1)-C(9)-C(10)-C(11)	-13.4(4)
O(1)-C(10)-C(11)-O(2)	3.8(6)
C(9)-C(10)-C(11)-O(2)	-176.6(3)
O(1)-C(10)-C(11)-C(12)	-171.8(4)
C(9)-C(10)-C(11)-C(12)	7.8(4)
O(2)-C(11)-C(12)-C(13)	1.7(6)
C(10)-C(11)-C(12)-C(13)	177.0(3)
O(2)-C(11)-C(12)-C(1)	-173.7(3)

C(10)-C(11)-C(12)-C(1)	1.7(4)
C(3)-C(1)-C(12)-C(11)	-137.2(3)
C(2)-C(1)-C(12)-C(11)	108.2(3)
C(9)-C(1)-C(12)-C(11)	-9.9(4)
C(3)-C(1)-C(12)-C(13)	47.4(4)
C(2)-C(1)-C(12)-C(13)	-67.3(4)
C(9)-C(1)-C(12)-C(13)	174.6(3)
C(11)-C(12)-C(13)-C(18)	-152.8(3)
C(1)-C(12)-C(13)-C(18)	22.0(5)
C(11)-C(12)-C(13)-C(14)	22.3(5)
C(1)-C(12)-C(13)-C(14)	-162.9(3)
C(18)-C(13)-C(14)-C(15)	2.1(5)
C(12)-C(13)-C(14)-C(15)	-173.2(3)
C(13)-C(14)-C(15)-C(16)	0.8(5)
Si(1)-O(3)-C(16)-C(17)	105.8(3)
Si(1)-O(3)-C(16)-C(15)	-75.2(4)
C(14)-C(15)-C(16)-O(3)	177.7(3)
C(14)-C(15)-C(16)-C(17)	-3.3(6)
O(3)-C(16)-C(17)-C(18)	-178.0(3)
C(15)-C(16)-C(17)-C(18)	2.9(5)
C(16)-C(17)-C(18)-C(13)	0.0(5)
C(14)-C(13)-C(18)-C(17)	-2.5(5)
C(12)-C(13)-C(18)-C(17)	172.8(3)
O(3)-Si(1)-C(21)-C(22)	-65.2(4)
C(20)-Si(1)-C(21)-C(22)	178.2(4)
C(19)-Si(1)-C(21)-C(22)	54.8(4)
O(3)-Si(1)-C(21)-C(23)	55.4(4)
C(20)-Si(1)-C(21)-C(23)	-61.2(4)
C(19)-Si(1)-C(21)-C(23)	175.4(4)
O(3)-Si(1)-C(21)-C(24)	174.0(3)
C(20)-Si(1)-C(21)-C(24)	57.4(4)
C(19)-Si(1)-C(21)-C(24)	-66.0(4)
C(28)-N(2)-C(26)-C(25)	2.0(4)
C(27)-C(25)-C(26)-N(2)	-2.1(4)
C(36)-C(25)-C(26)-N(2)	-127.0(3)
C(33)-C(25)-C(26)-N(2)	117.4(3)
C(26)-C(25)-C(27)-C(32)	-179.2(3)
C(36)-C(25)-C(27)-C(32)	-57.1(5)
C(33)-C(25)-C(27)-C(32)	64.5(5)
C(26)-C(25)-C(27)-C(28)	1.3(3)
C(36)-C(25)-C(27)-C(28)	123.5(3)
C(33)-C(25)-C(27)-C(28)	-115.0(3)
C(32)-C(27)-C(28)-C(29)	1.8(5)
C(25)-C(27)-C(28)-C(29)	-178.6(3)

C(32)-C(27)-C(28)-N(2)	-179.9(3)
C(25)-C(27)-C(28)-N(2)	-0.4(4)
C(26)-N(2)-C(28)-C(29)	177.2(4)
C(26)-N(2)-C(28)-C(27)	-1.0(4)
C(27)-C(28)-C(29)-C(30)	-1.1(5)
N(2)-C(28)-C(29)-C(30)	-179.1(3)
C(28)-C(29)-C(30)-C(31)	-0.8(6)
C(29)-C(30)-C(31)-C(32)	2.1(6)
C(28)-C(27)-C(32)-C(31)	-0.6(5)
C(25)-C(27)-C(32)-C(31)	-180.0(3)
C(30)-C(31)-C(32)-C(27)	-1.3(5)
C(27)-C(25)-C(33)-C(34)	-144.8(3)
C(26)-C(25)-C(33)-C(34)	105.5(3)
C(36)-C(25)-C(33)-C(34)	-16.0(4)
C(25)-C(33)-C(34)-O(4)	-164.7(4)
C(25)-C(33)-C(34)-C(35)	15.7(4)
O(4)-C(34)-C(35)-O(5)	-5.0(6)
C(33)-C(34)-C(35)-O(5)	174.5(3)
O(4)-C(34)-C(35)-C(36)	171.2(4)
C(33)-C(34)-C(35)-C(36)	-9.3(4)
O(5)-C(35)-C(36)-C(37)	-1.8(6)
C(34)-C(35)-C(36)-C(37)	-177.9(3)
O(5)-C(35)-C(36)-C(25)	174.4(3)
C(34)-C(35)-C(36)-C(25)	-1.6(4)
C(27)-C(25)-C(36)-C(35)	138.0(3)
C(26)-C(25)-C(36)-C(35)	-107.8(3)
C(33)-C(25)-C(36)-C(35)	11.3(4)
C(27)-C(25)-C(36)-C(37)	-45.5(4)
C(26)-C(25)-C(36)-C(37)	68.7(4)
C(33)-C(25)-C(36)-C(37)	-172.2(3)
C(35)-C(36)-C(37)-C(42)	158.6(3)
C(25)-C(36)-C(37)-C(42)	-17.2(5)
C(35)-C(36)-C(37)-C(38)	-19.2(5)
C(25)-C(36)-C(37)-C(38)	164.9(3)
C(42)-C(37)-C(38)-C(39)	-1.2(5)
C(36)-C(37)-C(38)-C(39)	176.8(3)
C(37)-C(38)-C(39)-C(40)	-0.1(6)
Si(2)-O(6)-C(40)-C(41)	-52.2(4)
Si(2)-O(6)-C(40)-C(39)	129.7(3)
C(38)-C(39)-C(40)-O(6)	179.8(3)
C(38)-C(39)-C(40)-C(41)	1.7(6)
O(6)-C(40)-C(41)-C(42)	-180.0(3)
C(39)-C(40)-C(41)-C(42)	-1.9(5)
C(40)-C(41)-C(42)-C(37)	0.5(5)

C(38)-C(37)-C(42)-C(41)	0.9(5)
C(36)-C(37)-C(42)-C(41)	-177.0(3)
O(6)-Si(2)-C(45)-C(48)	-58.2(3)
C(44)-Si(2)-C(45)-C(48)	57.3(4)
C(43)-Si(2)-C(45)-C(48)	-176.9(3)
O(6)-Si(2)-C(45)-C(46)	62.3(4)
C(44)-Si(2)-C(45)-C(46)	177.8(4)
C(43)-Si(2)-C(45)-C(46)	-56.4(4)
O(6)-Si(2)-C(45)-C(47)	-178.5(3)
C(44)-Si(2)-C(45)-C(47)	-63.0(4)
C(43)-Si(2)-C(45)-C(47)	62.8(4)

Symmetry transformations used to generate equivalent atoms:

Table 7.Hydrogen bonds for sa2478 [A and deg.].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)