

## Total Syntheses of Huperserratin A and B

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## Supporting Information

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## 1 General Information

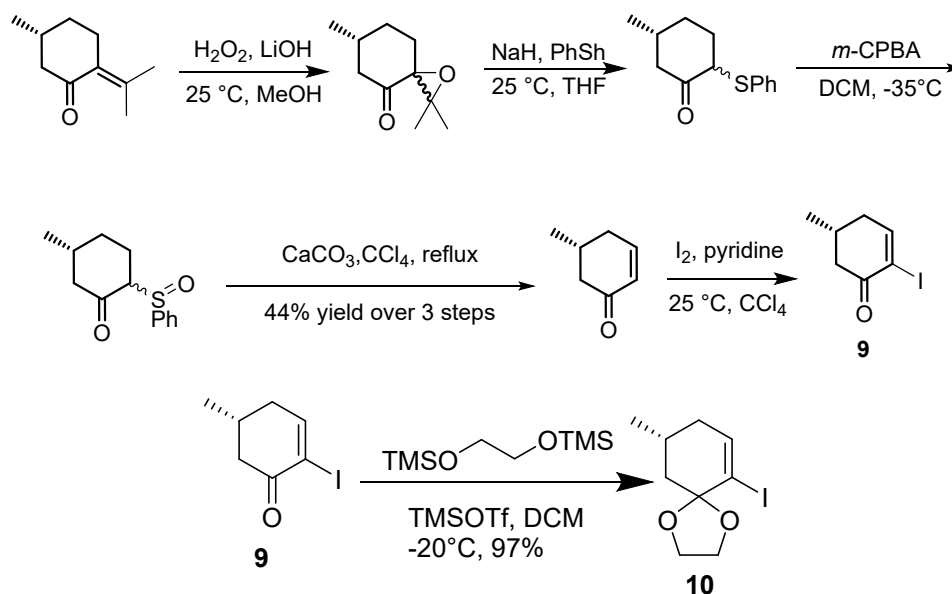
All air and water sensitive reactions were carried out under argon atmosphere with dry solvents under anhydrous conditions, unless otherwise noted. All the chemicals were purchased commercially and used without further purification. Tetrahydrofuran and dichloromethane were distilled according to standard procedures. Reactions that required heating were set up in an oil bath. Reactions were monitored by thin-layer chromatography (TLC) carried out on 0.25 mm Tsingdao silica gel plates (60F-254) that were analyzed by an ethanolic solution of phosphomolybdic acid and heat as developing agents. If not specially mentioned, flash column chromatography used silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were acquired on Bruker Avance III 400, 500 and 600 NMR spectrometers. Chemical shifts were given in parts per million (ppm) with reference to residual solvent signals [ $^1\text{H}$  NMR:  $\text{CDCl}_3$  (7.26),  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  (77.16);  $^1\text{H}$  NMR:,  $^{13}\text{C}$  NMR:]. Peak multiplicities were recorded as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad singlet. Infrared (IR) spectra were recorded on a BRUKER Tensor-27 Fourier-Transform Infrared spectrometer. High resolution mass spectral (HRMS) data were obtained at the mass spectrometry service operated at Agilent 6540 Q-TOF spectrometer and a Shimadzu UPLC-IT-TOF spectrometer for electrospray ionization (ESI) and were reported as (m/z). X-ray diffraction was conducted using Bruker APEX DUO diffractometer with graphite-monochromated  $\text{CuK}\alpha$  radiation. Optical rotations were measured on a Jasco P-1020 polarimeter. Melting points were measured on a WRX-5A melting point apparatus.

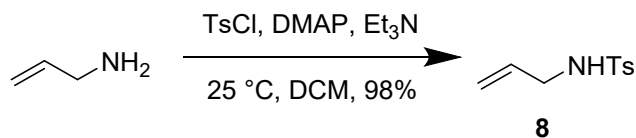
## 2 Experiment data:

### Preparation of compound 9:

Synthesis of compound **9** was implemented exactly as reported<sup>1,2</sup>.

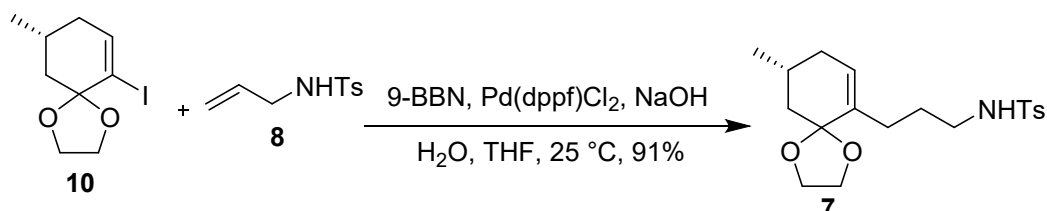


Enone **9** (280 mg, 1.2 mmol, 1.0 equiv) was dissolved in DCM (10 mL) and cooled down to -20 °C. 1,2-Bis(trimethylsilyloxy)ethane (0.34 mL, 1.4 mmol, 1.2equiv) and TMSOTf (0.01 mL, 0.06 mmol, 0.05 equiv) was added to the mixture dropwise. The reaction was left stirring for 10 h at -20 °C and quenched with Et<sub>3</sub>N (1 mL). The mixture was concentrated *in vacuo* and directly subjected to flash column chromatography (petroleum ether/ethyl acetate = 200:1) to afford the desired product **10** (322 mg, 97% yield) as a colorless oil. The analytical data matches what was previously reported<sup>3</sup>. R<sub>f</sub> = 0.20 (petroleum ether/ethyl acetate = 200:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.62 (dd, *J* = 5.7, 2.2 Hz, 1H), 4.24 - 4.16 (m, 2H), 4.03 - 3.92 (m, 2H), 2.15 - 2.08 (m, 1H), 2.00 - 1.96 (m, 2H), 1.75 (ddd, *J* = 17.4, 10.4, 2.2 Hz, 1H), 1.58 (t, *J* = 13.0 Hz, 1H), 0.96 (d, *J* = 6.5 Hz, 3H) ppm. <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 144.1, 106.8, 103.2, 66.0, 65.3, 42.6, 37.6, 27.4, 21.1 ppm. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>9</sub>H<sub>14</sub>IO<sub>2</sub> 281.0033; Found 281.0035.

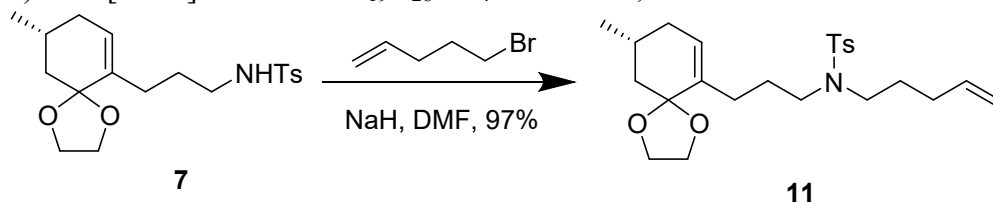


Allylamine (610 mg, 10.7 mmol, 1 equiv) was dissolved in dichloromethane (20 mL). Et<sub>3</sub>N (2.23 ml, 16 mmol, 1.5 equiv) and DMAP (390mg, 3.2 mmol, 0.3 equiv) were added. Then a solution of tosyl chloride (2 g, 10.7 mmol, 1 equiv) in dichloromethane (10 mL) was added dropwise. The solution was stirred for 1 h at 25 °C, before water (20 mL) was added. After phase separation, the organic layer was extracted three times with dichloromethane (20 mL each). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (petroleum

ether/ethyl acetate = 9:1) to afford the desired product **8** (2.21g, 98% yield) as a white solid. The analytical data matches what was previously reported<sup>4</sup>.  $R_f = 0.23$  (petroleum ether/ethyl acetate = 9:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.75 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 2H), 5.70 (m, 1H), 5.26 - 4.98 (m, 2H), 3.56 (d,  $J = 5.9$  Hz, 2H), 2.41 (s, 3H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 137.0, 133.0, 129.7, 127.2, 117.6, 45.7, 21.5 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{Na}]^+$  Calcd for  $\text{C}_{10}\text{H}_{13}\text{NO}_2\text{SNa}$  234.0559; Found 234.0561.

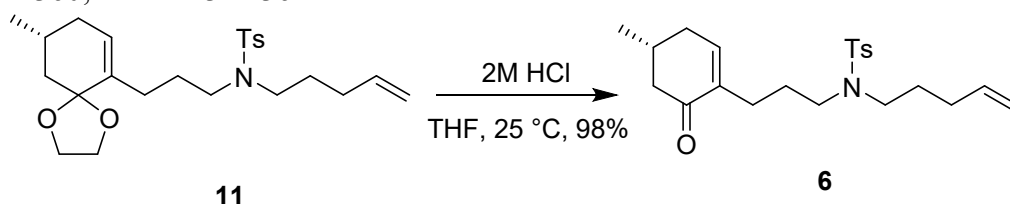


To a solution of **8** (253 mg, 1.2 mmol, 1.2 equiv) in 10 mL THF was added 9-BBN (0.5 M in THF, 2.6 mL, 1.3 mmol, 1.3 equiv) at 25 °C. The resulting mixture was stirred for 2 h. In a separate flask, **10** (280 mg, 1 mmol, 1.0 equiv) was dissolved in 15 mL THF, then 1.26 mL 15% (wt%) aq. NaOH was added. The resulting mixture was degassed by bubbling  $\text{N}_2$ .  $\text{Pd}(\text{dppf})_2\text{Cl}_2$  (73mg, 0.1 equiv) was charged to the flask in one portion. The above solution was added over 20 min at rt. The orange solution was stirred at 25 °C for 30 min at rt before being diluted with sat. aq.  $\text{NH}_4\text{Cl}$ . The layers were separated and the aqueous layer was extracted repeatedly with  $\text{Et}_2\text{O}$ . The combined organic layers were washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 8:2) to afford the desired product **7** (332 mg, 91% yield) as a colorless oil.  $R_f = 0.21$  (petroleum ether/ethyl acetate = 8:2).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 2H), 5.60 (d,  $J = 3.4$  Hz, 1H), 4.94 (t,  $J = 6.2$  Hz, 1H), 4.10 - 3.98 (m, 2H), 3.98 - 3.88 (m, 2H), 2.93 (q,  $J = 6.5$  Hz, 2H), 2.42 (s, 3H), 2.09 - 1.99 (m, 2H), 1.87 - 1.78 (m, 2H), 1.67 - 1.59 (m, 3H), 1.34 - 1.19 (m, 2H), 0.94 (d,  $J = 6.5$  Hz, 3H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.1, 137.1, 135.7, 129.6, 129.5, 127.1, 108.4, 65.4, 64.3, 42.5, 42.0, 33.9, 28.1, 27.5, 25.7, 21.5 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{19}\text{H}_{28}\text{NO}_4\text{S}$  366.1734; Found 366.1733.

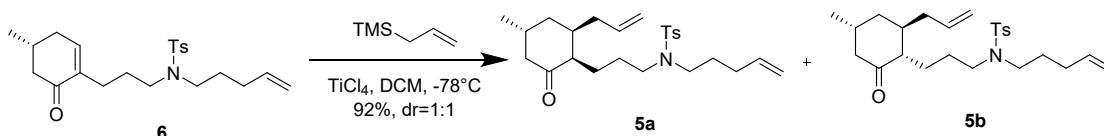


To a suspension of sodium hydride (60%, 80mg, 2mmol, 3 equiv) in 10 ml DMF at 0 °C under argon was added to **7** (240 mg, 0.66 mmol, 1 equiv). After stirring for 15 min, 5-bromo-1-pentene (0.12ml, 1mmol, 1.5 equiv) was added dropwise to the resulting mixture at 0°C. The ice bath was removed and the reaction mixture was stirred at 25 °C for 4 h. The reaction mixture was quenched with the addition of water and extracted with diethyl ether three times. The combined organic layers were washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was

concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 9:1) to afford the desired product **11** (276 mg, 97% yield) as a colorless oil.  $R_f = 0.22$  (petroleum ether/ethyl acetate = 9:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.67 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 5.81 - 5.71 (m, 1H), 5.63 (d,  $J = 3.2$  Hz, 1H), 5.05 - 4.91 (m, 2H), 4.06 - 3.89 (m, 4H), 3.10 (t,  $J = 6.7$  Hz, 4H), 2.41 (s, 3H), 2.14 - 1.98 (m, 5H), 1.82 (d,  $J = 13.3$  Hz, 1H), 1.71 - 1.57 (m, 6H), 1.31 (t,  $J = 12.9$  Hz, 1H), 0.95 (d,  $J = 6.6$  Hz, 3H) ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.9, 137.6, 137.1, 136.6, 129.6, 128.6, 127.2, 115.2, 108.3, 65.5, 64.4, 48.3, 47.7, 42.3, 34.0, 30.9, 27.8, 27.6, 27.5, 26.3, 21.5, 21.5 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{24}\text{H}_{36}\text{NO}_4\text{S}$  434.2360; Found 434.2362.



A solution of compound **11** (500 mg, 1.15 mmol) in THF (20 mL) was treated with HCl (10 mL of a 2 M aqueous solution). The resulting mixture was stirred at 25 °C for 2 h then treated with  $\text{NaHCO}_3$  (20 mL of a saturated aqueous solution) and extracted with diethyl ether. The combined organic phases were washed with brine then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 9:1) to afford the desired product **6** (440 mg, 98% yield) as a colorless oil.  $R_f = 0.21$  (petroleum ether/ethyl acetate = 9:1).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 8.0$  Hz, 2H), 7.29 (d,  $J = 8.0$  Hz, 2H), 6.72 (d,  $J = 3.2$  Hz, 1H), 5.76 (m, 1H), 5.05 - 4.93 (m, 2H), 3.09 (m, 4H), 2.52 - 2.41 (m, 2H), 2.42 (s, 3H), 2.24 - 2.12 (m, 4H), 2.09 - 2.00 (m, 4H), 1.66 - 1.57 (m, 3H), 1.05 (d,  $J = 6.3$  Hz, 3H). ppm.  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  199.6, 145.3, 143.0, 138.3, 137.5, 136.8, 129.6, 127.1, 115.3, 48.1, 47.9, 46.6, 34.3, 30.8, 30.6, 27.8, 27.6, 26.7, 21.5, 21.2 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{22}\text{H}_{32}\text{NO}_3\text{S}$  390.2097; Found 390.2099.

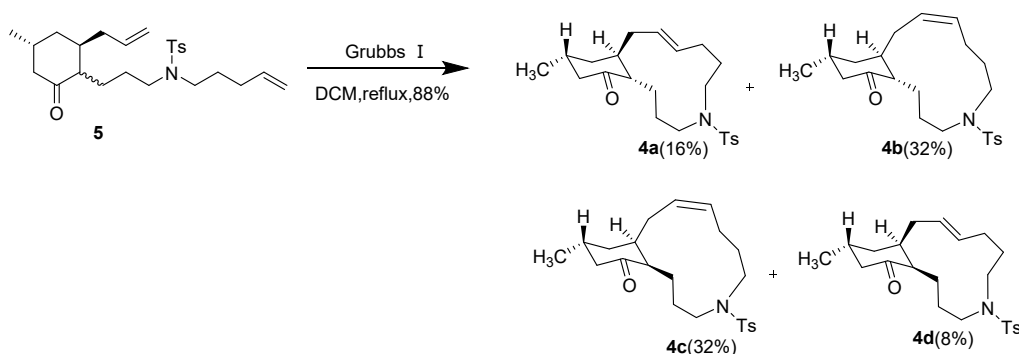


$\text{TiCl}_4$  (74  $\mu\text{L}$ , 0.67 mmol, 2 equiv) was added dropwise to a cooled ( $-78$  °C) solution of **6** (130 mg, 0.33 mmol, 1 equiv) and allyltrimethylsilane (132  $\mu\text{L}$ , 0.84 mmol, 2.5 equiv) in DCM (90 mL) under an argon atmosphere. The reaction was stirred for 20 min at  $-78$  °C and then water was added. The resulting slurry was allowed to gradually warm (2 h) to 25 °C and extracted with DCM. The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The mixture of diastereomers **5** could not be purified by silica gel flash chromatography. The crude residue **5** was used in the subsequent step without further purification.  $R_f = 0.20$  (petroleum ether/ethyl acetate = 9:1).

The mixture was isolated for characterization purposes by purifying a small amount of crude by HPLC (Waters X-Bridge C18, MeCN/ H<sub>2</sub>O = 72/28, flow rate = 0.8 mL/min, I= 254 nm)

**5a** (tR =15.2 min, 46% yield) : Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.79 - 5.66 (m, 2H), 5.07 - 4.93 (m, 4H), 3.16 - 3.02 (m, 4H), 2.41 (s, 3H), 2.28 (dd, *J* = 12.7, 3.3 Hz, 1H), 2.13 - 2.07 (m, 4H), 2.05 - 1.98 (m, 3H), 1.91 - 1.87 (m, 1H), 1.62 - 1.58 (m, 5H), 1.50 - 1.43 (m, 3H), 0.96 (d, *J* = 6.4 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 214.1, 143.1, 137.5, 136.9, 136.0, 129.6, 127.1, 117.0, 115.3, 54.0, 48.1, 47.8, 47.1, 39.2, 38.1, 34.0, 30.8, 29.4, 27.8, 27.2, 26.3, 21.5, 21.4 ppm. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>38</sub>NO<sub>3</sub>S 432.2567; Found 432.2573.

**5b** (tR =16.7 min, 46% yield): Colorless oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.79 - 5.71 (m, 1H), 5.68 - 5.59 (m, 1H), 5.02 - 4.95 (m, 4H), 3.10 - 3.05 (m, 4H), 2.47 - 2.43 (m, 1H), 2.40 (s, 3H), 2.35 (ddd, *J* = 12.5, 4.1, 1.9 Hz, 1H), 2.20 - 2.15 (m, 1H), 2.05 - 1.93 (m, 5H), 1.90-1.85(m, 1H), 1.65 - 1.58 (m, 4H), 1.53 - 1.48 (m, 1H), 1.44 - 1.38 (m, 2H), 1.17 - 1.10 (m, 1H), 0.98 (d, *J* = 6.2 Hz, 3H) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 212.2, 143.0, 137.5, 136.9, 136.5, 129.6, 127.1, 116.4, 115.3, 53.4, 50.2, 48.3, 47.8, 40.3, 36.6, 31.9, 30.8, 29.7, 27.8, 26.9, 23.5, 22.2, 21.5 ppm. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>25</sub>H<sub>38</sub>NO<sub>3</sub>S 432.2567; Found 432.2570.



The mixture of diastereomers **5** (820 mg, 1.9 mmol, 1.0 equiv) was dissolved in DCM (800 mL). Grubbs I (160 mg, 0.19 mmol, 0.1 equiv) was added to the mixture. The reaction refluxed for 24 h. The mixture was concentrated *in vacuo*. The mixture was isolated for characterization purposes by purifying a small amount of crude by HPLC (Waters XBridge C18, MeCN/ H<sub>2</sub>O = 60/40, flow rate = 0.8 mL/min, I= 254 nm). R<sub>f</sub> = 0.15 (petroleum ether/ethyl acetate = 9:1).

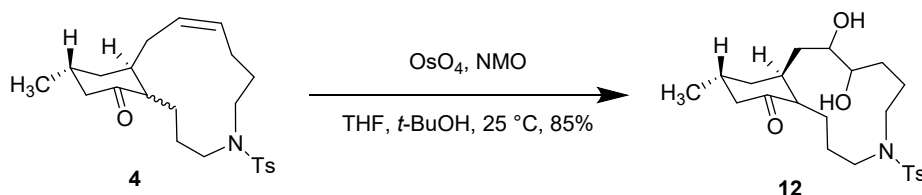
**4a** (tR =28.8 min, 16% yield) : Colorless oil. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 7.66 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 5.46 - 5.35 (m, 2H), 3.23 - 3.12 (m, 2H), 2.86 - 2.80 (m, 1H), 2.71 - 2.64 (m, 1H), 2.38 (s, 3H), 2.32 - 2.28 (m, 1H), 2.16 - 2.12 (m, 1H), 2.10 - 1.93 (m, 4H), 1.82 - 1.76 (m, 3H), 1.73 - 1.53 (m, 4H), 1.45 - 1.36 (m, 2H), 1.33 - 1.23 (m, 2H), 0.89 (d, *J* = 6.3 Hz, 3H).ppm. <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 214.1, 143.1, 137.5, 136.9, 136.0, 129.6, 127.1, 117.0, 115.3, 54.0, 48.1, 47.8, 47.1, 39.2, 38.1, 34.0, 30.8, 29.4, 27.8, 27.2, 26.3, 21.5, 21.4 ppm. HRMS (ESI-TOF) *m/z*: [M+H]<sup>+</sup> Calcd for C<sub>23</sub>H<sub>34</sub>NO<sub>3</sub>S 404.2254; Found 404.2255.

**4b** (tR =31.8 min, 32% yield) : Colorless oil. <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ

7.64 (d,  $J = 8.0$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 5.52 (m, 2H), 3.18 - 3.10 (m, 1H), 3.02 - 2.95 (m, 1H), 2.81 - 2.74 (m, 2H), 2.57 (dd,  $J = 13.0, 5.9$  Hz, 1H), 2.38 (s, 3H), 2.43 - 2.32 (m, 3H), 2.09 - 2.02 (m, 3H), 1.98 - 1.88 (m, 2H), 1.83 - 1.77 (m, 2H), 1.71 - 1.63 (m, 1H), 1.60 - 1.46 (m, 3H), 1.27 - 1.21 (m, 2H), 0.82 (d,  $J = 7.1$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  212.2, 143.1, 134.8, 131.6, 129.8, 127.1, 126.0, 53.6, 50.5, 48.7, 47.6, 37.6, 36.4, 30.0, 29.9, 29.3, 26.4, 22.9, 21.0, 20.8, 18.7 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{34}\text{NO}_3\text{S}$  404.2254; Found 404.2250.

**4c** (tR =33.5 min, 32% yield) : Colorless needles (from MeOH). **m.p.** 120 - 125 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.63 (d,  $J = 8.0$  Hz, 2H), 7.40 (d,  $J = 8.0$  Hz, 2H), 5.50 - 5.45(m,1H), 5.38 - 5.32(m, 1H), 3.49 - 3.43(m, 1H), 3.18 - 3.13 (m, 1H), 2.66 - 2.59 (m, 1H), 2.58 - 2.53 (m, 2H), 2.40 - 2.38 (m, 1H), 2.38 (s, 3H), 2.29 - 2.19 (m, 2H), 2.14 - 2.10 (m, 1H), 2.06 - 2.01 (m, 2H), 1.96 - 1.83 (m, 3H), 1.73 - 1.66 (m, 1H), 1.49 - 1.40 (m, 3H), 1.34 - 1.21 (m, 3H), 0.96 (d,  $J = 6.4$  Hz, 3H). ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  211.9, 143.2, 134.7, 129.8, 129.4, 129.2, 127.2, 51.8, 51.0, 49.4, 48.4, 39.0, 36.8, 29.9, 29.4, 25.0, 24.4, 22.5, 21.7, 21.4, 21.0. ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{34}\text{NO}_3\text{S}$  404.2254; Found 404.2255.

**4d** (tR =35.4 min, 8% yield) : Colorless needles (from MeOH). **m.p.** 117 - 120 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO-}d_6$ )  $\delta$  7.63 (d,  $J = 8.0$  Hz, 2H), 7.43 (d,  $J = 8.0$  Hz, 2H), 5.55 - 5.32 (m, 2H), 3.13 - 3.02 (m, 2H), 2.71 - 2.65 (m, 1H), 2.59 - 2.55 (m, 1H), 2.40 (s, 3H), 2.36 - 2.28 (m, 1H), 2.24 (dd,  $J = 13.5, 3.4$  Hz, 1H), 2.14 - 2.00 (m, 2H), 1.93 - 1.85 (m, 3H), 1.74 - 1.71 (m, 6H), 1.57 - 1.50 (m, 1H), 1.42 - 1.33 (m, 1H), 1.24 - 1.11 (m,2H), 0.94 (d,  $J = 6.3$  Hz, 3H). ppm.  $^{13}\text{C}$  NMR (125 MHz,  $\text{DMSO-}d_6$ )  $\delta$  212.4, 143.6, 134.3, 131.9, 130.3, 130.2, 127.9, 53.3, 50.7, 49.8, 48.5, 41.7, 36.9, 34.9, 31.4, 30.4, 27.9, 23.7, 23.0, 22.5, 21.4 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{34}\text{NO}_3\text{S}$  404.2254; Found 404.2254.

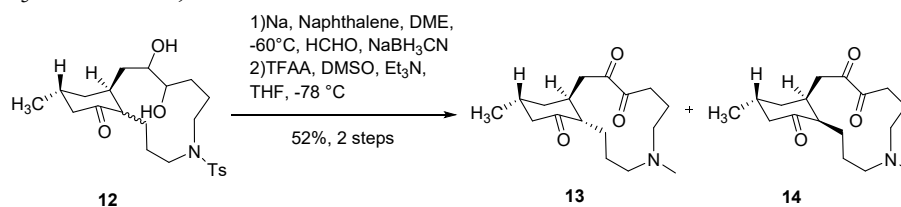


To a solution of **4** (260 mg, 0.65 mmol, 1.0 equiv) in THF and BuOH at r.t was added  $\text{OsO}_4$  (180  $\mu\text{L}$ , 0.01 mmol, 0.02 equiv, 0.07M in *t*-BuOH) and NMO (150 mg, 1.3 mmol, 2.0 equiv), the reaction was stirred for 4 h at 25 °C. The reaction mixture was poured onto  $\text{Na}_2\text{SO}_3$  and extracted with EtOAc. The combined organic phases were washed with brine then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The mixture was isolated for characterization purposes by purifying a small amount of crude by HPLC (Waters XBridge C18, MeOH/  $\text{H}_2\text{O}$  = 60/40, flow rate = 0.8 mL/min, I= 254 nm).  $R_f = 0.20$  (petroleum ether/ethyl acetate = 9:1).  $R_f = 0.2$  (dichloromethane/ methanol = 9:1).

**12a** (tR =7.8 min) : Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.64 (d,  $J = 8.0$  Hz, 2H), 7.30 (d,  $J = 8.0$  Hz, 2H), 3.64 (d,  $J = 9.7$  Hz, 1H), 3.60 - 3.50 (m, 2H), 3.50 - 3.41 (m, 2H), 2.68 - 2.56 (m, 3H), 2.42 (s, 3H), 2.34 - 2.30 (m, 2H), 2.15 - 2.06 (m, 1H), 2.02 - 1.99 (m, 2H), 1.97 - 1.93 (m, 1H), 1.86 - 1.78 (m, 2H), 1.75 - 1.64 (m,

2H), 1.61 - 1.51 (m, 2H), 1.49 - 1.42 (m, 3H), 1.25 - 1.22 (m, 2H), 1.01 (d,  $J = 6.9$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  213.8, 143.4, 135.3, 129.7, 127.3, 74.0, 72.1, 52.7, 51.0, 50.6, 46.1, 35.6, 35.5, 33.8, 30.1, 28.9, 26.8, 22.6, 21.5, 20.8, 20.4. ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{36}\text{NO}_5\text{S}$  438.2309; Found 438.2305.

**12b** (tR = 8.6 min): Colorless oil.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.65 (d,  $J = 7.9$  Hz, 2H), 7.31 (d,  $J = 7.9$  Hz, 2H), 3.83 - 3.77 (m, 1H), 3.69 (d,  $J = 8.0$  Hz, 1H), 3.60 - 3.49 (m, 1H), 3.30 - 3.22 (m, 1H), 2.70 - 2.61 (m, 1H), 2.53 - 2.43 (m, 2H), 2.42 (s, 3H), 2.38 - 2.34 (m, 1H), 2.21 - 2.12 (m, 5H), 2.03 - 1.91 (m, 4H), 1.80 - 1.73 (m, 2H), 1.68 - 1.64 (m, 1H), 1.62 - 1.52 (m, 2H), 1.46 - 1.42 (m, 1H), 1.31 - 1.25 (m, 2H), 0.88 (d,  $J = 7.2$  Hz, 3H). ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  212.1, 143.4, 134.4, 129.7, 127.5, 74.1, 72.8, 53.8, 51.4, 49.4, 48.0, 39.2, 37.6, 32.2, 29.6, 25.3, 24.5, 22.9, 22.1, 21.5, 19.0 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{23}\text{H}_{36}\text{NO}_5\text{S}$  438.2309; Found 438.2305.



To a cooled ( $-60$  °C) solution of p-toluenesulfonamide **12** (44 mg, 0.1 mmol, 1.0 equiv) in 1,2-dimethoxy-ethane (5 mL) was slowly added sodium naphthalenide (0.4 ml, 0.2 mmol, 2 equiv, 0.5M in DME), previously prepared from naphthalene (516 mg, 4.0 mmol) and sodium (71 mg, 3.0 mmol) in 1,2-dimethoxyethane (6 mL). Then the reaction was quenched by the addition of acetonitrile - acetic acid (4 mL, V:V=10:1), Then the cooling bath was removed and the solution was allowed to warm to rt in 2 minutes, and added formaldehyde (86mg, 1mmol, 10.0 equiv, 35% wt. solution in water), followed by  $\text{NaBH}_3\text{CN}$  (20 mg, 0.3 mmol, 3.0 equiv). The mixture was stirred at rt for 4 h, and then aqueous  $\text{NaHCO}_3$  (10 mL) was added, and the mixture was extracted with  $\text{CHCl}_3$  (10 mL  $\times$  3). The combined organic phases were washed with brine then dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The residue was purified by silica gel column chromatography (dichloromethane/ methanol = 4:1) to give diols. To a solution of DMSO (64  $\mu\text{L}$ , 0.9 mmol, 9.0 equiv) in dry THF (5 mL) was added TFAA (85  $\mu\text{L}$ , 0.6 mmol, 6.0 equiv) at  $-78$  °C. and the mixture was stirred at that temperature for 30 min. To this solution was added a solution of diols in THF (3 mL) over 15 min, and stirring was continued at  $-78$  °C for an additional 30 min.  $\text{Et}_3\text{N}$  (250  $\mu\text{L}$ , 1.8 mmol, 18.0 equiv) was slowly added, and the mixture was warmed to  $25$  °C in the course of 2 h, The mixture was poured into ethyl acetate (10 mL), and the resulting mixture was washed with water. The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (petroleum ether/ethyl acetate = 9:1) to afford the desired product **13** (8.2 mg, 28% yield) and **14** (7.0 mg, 24% yield)

Data for **13**

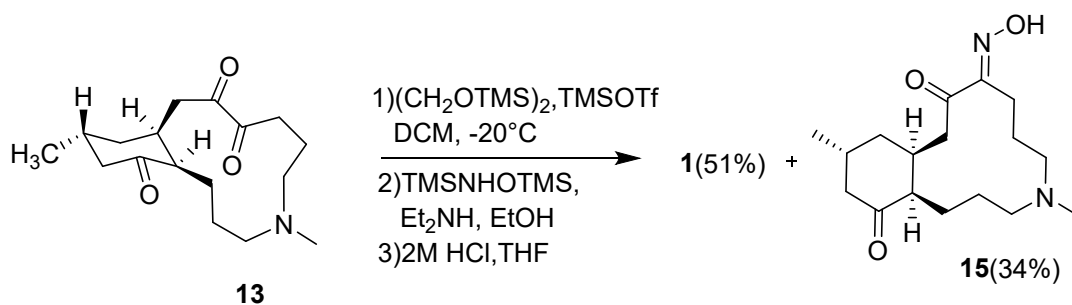
$R_f = 0.25$  (petroleum ether/ethyl acetate = 9:1). Colorless oil.  $^1\text{H}$  NMR (500 MHz,



Pyridine-*d*5)  $\delta$  3.68 - 3.58 (m, 1H), 3.26 (dt,  $J = 12.0, 5.9$  Hz, 1H), 2.99 - 2.88 (m, 1H), 2.70 (dd,  $J = 14.1, 5.9$  Hz, 1H), 2.56 - 2.53 (m, 1H), 2.45 (td,  $J = 12.0, 4.5$  Hz, 1H), 2.24 - 2.15 (m, 2H), 2.14 - 2.11 (m, 1H), 2.01 (dd,  $J = 14.1, 4.5$  Hz, 2H), 1.98 - 1.89 (m, 2H), 1.82 (dt,  $J = 12.3, 3.7$  Hz, 1H), 1.72 (s, 3H), 1.76 - 1.70 (m, 1H), 1.61 - 1.57 (m, 1H), 1.50 - 1.48 (m, 1H), 1.46 - 1.39 (m, 2H), 1.31 (dt,  $J = 13.4, 4.5$  Hz, 1H), 1.25 - 1.18 (m, 1H), 0.87 (d,  $J = 7.0$  Hz, 3H). ppm.  $^{13}\text{C}$  NMR (125 MHz, Pyridine-*d*5)  $\delta$  213.0, 197.5, 196.5, 59.0, 54.5, 48.9, 44.8, 37.0, 36.6, 34.5, 32.6, 32.0, 30.1, 25.3, 22.9, 20.2, 19.6 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{28}\text{NO}_3$  294.2064; Found 294.2064.

#### Data for **14**

$R_f = 0.21$  (petroleum ether/ethyl acetate = 9:1). Colorless oil.  $^1\text{H}$  NMR (500 MHz, Pyridine-*d*5)  $\delta$  2.62 - 2.49 (m, 2H), 2.28 - 2.22 (m, 3H), 2.20 - 2.09 (m, 3H), 1.95 - 1.84 (m, 2H), 1.78 - 1.76 (m, 1H), 1.68 (s, 3H), 1.61 - 1.51 (m, 1H), 1.48 (ddd,  $J = 13.5, 5.9, 3.8$  Hz, 1H), 1.39 - 1.13 (m, 6H), 0.94 - 0.83 (m, 2H), 0.81 (d,  $J = 7.2$  Hz, 3H). ppm.  $^{13}\text{C}$  NMR (125 MHz, Pyridine-*d*5)  $\delta$  211.4, 198.1, 196.9, 58.5, 54.9, 48.1, 48.1, 37.4, 37.0, 36.0, 32.1, 30.6, 30.0, 25.4, 24.4, 21.0, 18.8 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{28}\text{NO}_3$  294.2064; Found 294.2065.



Triketone **13** (440 mg, 1.5 mmol, 1.0 equiv) was dissolved in DCM (10 mL) and cooled down to  $-20^\circ\text{C}$ . 1,2-Bis(trimethylsilyloxy)ethane (0.88 mL, 3.6 mmol, 2.4 equiv) and TMSOTf (27  $\mu\text{L}$ , 0.15 mmol, 0.1 equiv) was added to the mixture dropwise. The reaction was left stirring for 10 h at  $-20^\circ\text{C}$  and quenched with  $\text{Et}_3\text{N}$  (1 mL). The mixture was concentrated *in vacuo* and dissolved in EtOH (10 mL), then  $\text{Et}_2\text{NH}$  (1.5 mL, 15.0 mmol, 10.0 equiv) and TMSNHOTMS (265 mg, 1.5 mmol, 1.0 equiv) was added. The mixture was stirred at  $25^\circ\text{C}$  for 4 h and concentrated *in vacuo*. The residue was added THF (10 mL) and 2M HCl (10 mL). The reaction was left stirring for 1 h at  $25^\circ\text{C}$  and then adjusted to basic pH with saturated aqueous  $\text{NaHCO}_3$  solution. The resulting mixture was extracted with EtOAc. The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (dichloromethane/ acetone = 8:2) to afford the desired product **1** (235 mg, 51% yield) and **15** (157.0 mg, 34% yield)

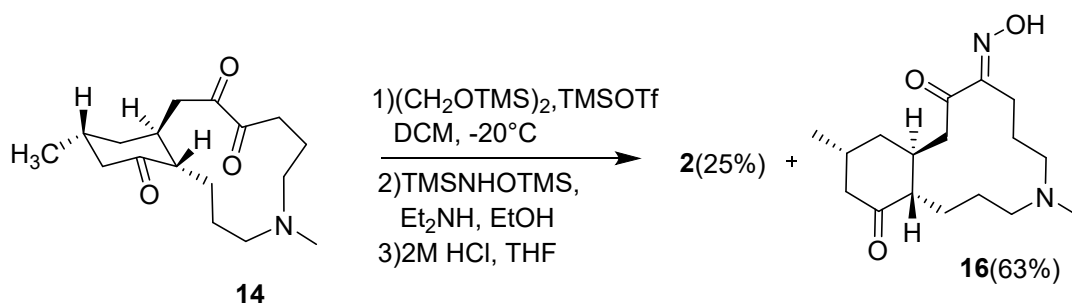
#### Data for **1**

$R_f = 0.2$  (dichloromethane/ acetone = 8:2). Colorless oil.  $^1\text{H}$  NMR (600 MHz, Pyridine-*d*5)  $\delta$  3.31 - 3.30 (m, 2H), 3.25 (t,  $J = 12.1$  Hz, 1H), 2.67 (dd,  $J = 13.8, 6.0$  Hz, 1H), 2.62 (m, 1H), 2.56 (dd,  $J = 13.1, 3.5$  Hz, 1H), 2.54 (m, 1H), 2.29 - 2.23 (m, 2H), 2.20 (m, 1H), 2.15 - 2.12 (m, 3H), 2.02 (s, 3H), 1.97 (dd,  $J = 13.7, 5.5$  Hz, 1H),

1.92 (ddd,  $J = 14.0, 9.7, 4.6$  Hz, 1H), 1.84 (ddd,  $J = 14.6, 10.0, 5.1$  Hz, 1H), 1.64 - 1.62 (m, 2H), 1.44 (dt,  $J = 13.6, 4.5$  Hz, 1H), 1.33 (m, 1H), 1.29 - 1.19 (m, 1H), 0.92 (d,  $J = 7.0$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Pyridine- $d_5$ )  $\delta$  214.2, 199.7, 159.3, 58.7, 56.4, 52.9, 46.0, 41.3, 36.6, 36.0, 34.0, 30.8, 26.8, 24.1, 24.0, 22.0, 21.5 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}_3$  309.2173; Found 309.2177.

#### Data for **15**

$R_f = 0.3$  (dichloromethane/ acetone = 8:2). Colorless oil.  $^1\text{H}$  NMR (600 MHz, Pyridine- $d_5$ )  $\delta$  3.72 (dd,  $J = 16.3, 10.9$  Hz, 1H), 3.16 - 3.07 (m, 1H), 2.93 - 2.86 (m, 2H), 2.65 - 2.58 (m, 2H), 2.47 - 2.41 (m, 2H), 2.25 (dd,  $J = 16.4, 3.3$  Hz, 1H), 2.08 - 2.05 (m, 1H), 2.05 - 1.97 (m, 2H), 1.94 (s, 3H), 1.89 - 1.79 (m, 2H), 1.75 - 1.71 (m, 1H), 1.70 - 1.64 (m, 1H), 1.48 - 1.41 (m, 1H), 1.37 - 1.25 (m, 4H), 0.85 (d,  $J = 6.5$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Pyridine- $d_5$ )  $\delta$  213.5, 198.7, 160.1, 58.8, 56.5, 50.8, 46.6, 40.3, 39.4, 37.0, 34.0, 30.9, 24.0, 23.9, 22.1, 21.3, 21.2 ppm. HRMS (ESI-TOF)  $m/z$ :  $[\text{M}+\text{H}]^+$  Calcd for  $\text{C}_{17}\text{H}_{29}\text{N}_2\text{O}_3$  309.2173; Found 309.2175.



Triketone **14** (290 mg, 1.0 mmol, 1.0 equiv) was dissolved in DCM (10 mL) and cooled down to  $-20^\circ\text{C}$ . 1,2-Bis(trimethylsilyloxy)ethane (0.59 mL, 2.4 mmol, 2.4 equiv) and TMSOTf (9  $\mu\text{L}$ , 0.1 mmol, 0.1 equiv) was added to the mixture dropwise. The reaction was left stirring for 10 h at  $-20^\circ\text{C}$  and quenched with  $\text{Et}_3\text{N}$  (1 mL). The mixture was concentrated *in vacuo* and dissolved in EtOH (10 mL), then  $\text{Et}_2\text{NH}$  (1.0 mL, 10.0 mmol, 10.0 equiv) and TMSNHOTMS (175 mg, 1.0 mmol, 1.0 equiv) was added. The mixture was stirred at  $25^\circ\text{C}$  for 4 h and concentrated *in vacuo*. The residue was added THF (10 mL) and 2M HCl (10 mL). The reaction was left stirring for 1 h at  $25^\circ\text{C}$  and then adjusted to basic pH with saturated aqueous  $\text{NaHCO}_3$  solution. The resulting mixture was extracted with EtOAc. The combined organic phases were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . The dried solution was concentrated *in vacuo*. The crude product was purified by silica gel flash chromatography (dichloromethane/ acetone = 8:2) to afford the desired product **2** (77 mg, 25% yield) and **16** (194 mg, 63% yield)

#### Data for **2**

$R_f = 0.21$  (dichloromethane/ acetone = 8:2). Colorless oil.  $^1\text{H}$  NMR (600 MHz, Pyridine- $d_5$ )  $\delta$  3.25 (m, 1H), 3.21 (t,  $J = 11.8$  Hz, 1H), 2.89 (m, 1H), 2.78 (dd,  $J = 12.6, 3.1$  Hz, 1H), 2.60 - 2.53 (m, 1H), 2.53 - 2.49 (m, 1H), 2.46 (dd,  $J = 14.2, 5.7$  Hz, 1H), 2.42 - 2.35 (m, 1H), 2.24 - 2.22 (m, 1H), 2.18 (m, 2H), 2.11 (dd,  $J = 14.2, 7.0$  Hz, 1H), 2.02 (m, 1H), 1.98 (s, 3H), 1.97 - 1.93 (m, 1H), 1.90 - 1.81 (m, 1H), 1.77 - 1.63 (m, 4H), 1.55 - 1.51 (m, 1H), 1.41 - 1.36 (m, 1H), 0.88 (d,  $J = 7.2$  Hz, 3H) ppm.  $^{13}\text{C}$  NMR (150 MHz, Pyridine- $d_5$ )  $\delta$  213.4, 199.6, 160.0, 58.3, 54.5, 54.2, 48.1, 42.1,

39.0, 36.8, 34.3, 30.2, 29.5, 27.8, 25.3, 22.6, 20.9 ppm. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub> 309.2173; Found 309.2172.

**Data for 16**

*R<sub>f</sub>* = 0.22 (dichloromethane/ acetone = 8:2). Colorless oil. <sup>1</sup>H NMR (600 MHz, Pyridine-*d*<sub>5</sub>) δ 3.79 (dd, *J* = 17.1, 4.6 Hz, 1H), 2.97 - 2.90 (m, 2H), 2.89 - 2.84 (m, 1H), 2.68 - 2.64 (m, 1H), 2.61 (dd, *J* = 13.1, 5.6 Hz, 1H), 2.51 (d, *J* = 18.9 Hz, 1H), 2.45 (t, *J* = 10.5 Hz, 1H), 2.35 (td, *J* = 11.9, 4.1 Hz, 1H), 2.28 - 2.22 (m 3H), 2.21 - 2.17 (m, 1H), 2.17 - 2.12 (m, 1H), 1.91 (s, 3H), 1.87 - 1.80 (m, 2H), 1.73 - 1.71 (m, 1H), 1.66 - 1.56 (m, 1H), 1.56 - 1.51 (m, 2H), 1.49 - 1.41 (m, 1H), 0.87 (d, *J* = 7.1 Hz, 3H) ppm. <sup>13</sup>C NMR (150 MHz, Pyridine-*d*<sub>5</sub>) δ 212.7, 198.8, 160.6, 59.5, 56.3, 50.1, 48.7, 39.8, 39.0, 38.2, 36.7, 30.9, 24.7, 23.7, 22.4, 21.9, 19.7 ppm. HRMS (ESI-TOF) m/z: [M+H]<sup>+</sup> Calcd for C<sub>17</sub>H<sub>29</sub>N<sub>2</sub>O<sub>3</sub> 309.2173; Found 309.2170.

**Table S1:** NMR comparison of natural and synthetic huperserratin A (**1**).

	<sup>1</sup> H-NMR [ppm, mult, <i>J</i> (Hz)]		<sup>13</sup> C-NMR	
	isolation	synthetic	isolation	synthetic
1a	2.25, m	2.27, m	58.6	58.7
1b	2.13, m	2.13, m		
2a	2.12, m	2.11, m	24.0	24.0
2b	1.64, m	1.63, m		
3a	3.29, overlap	3.31, overlap	36.0	36.0
3b	2.60, m	2.62, m		
4			199.6	199.7
5			159.3	159.3
6a	3.23, t (12.9)	3.25, t (12.1)	26.8	26.8
6b	2.54, dd (12.9, 3.4)	2.56, dd (13.1, 3.5)		
7	3.28, overlap	3.30, overlap	34.1	34.0
8a	1.93, ddd (14.0, 9.8, 4.8)	1.92, ddd (14.0, 9.7, 4.6)	36.7	36.6
8b	1.44, dt (14.0, 4.2)	1.44, dt (13.6, 4.5)		
9a	2.27, m	2.29, m	56.5	56.4
9b	2.15, m	2.15, m		
10a	1.33, m	1.33, m	24.1	24.1
10b	1.24, m	1.25, m		
11a	1.82, ddd (14.6, 10.1, 5.2)	1.84, ddd (14.6, 10.0, 5.1)	22.0	22.0
11b	1.61, m	1.62, m		
12	2.52, m	2.54, m	53.0	52.9
13			214.0	214.2
14a	2.65, dd (13.8, 6.0)	2.67, dd (13.8, 6.0)	46.1	46.0
14b	1.96, dd (13.8, 5.9)	1.97, dd (13.7, 5.5)		
15	2.20, m	2.20, m	30.8	30.8
16	0.92, d, (7.0)	0.92, d, (7.0)	21.4	21.5
N-CH <sub>3</sub>	2.02, s	2.02, s	41.3	41.3

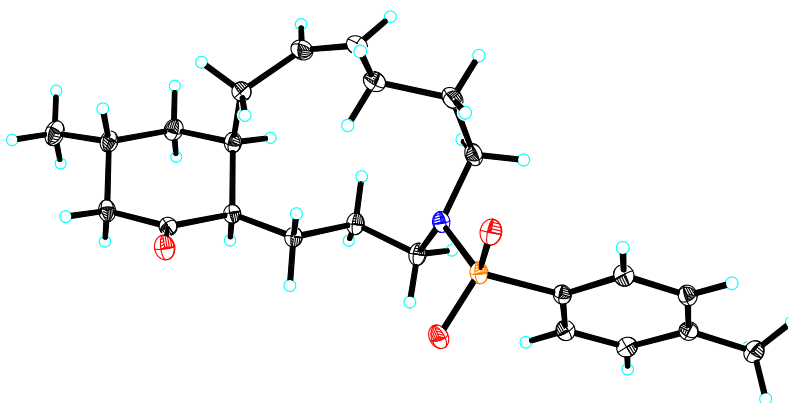
**Table S2:** NMR comparison of natural and synthetic hyperserratines B (2).

	<sup>1</sup> H-NMR [ppm, mult, <i>J</i> (Hz)]		<sup>13</sup> C-NMR	
	isolation	synthetic	isolation	synthetic
1a	2.48, m	2.50, m	54.6	54.5
1b	2.00, m	2.01, m		
2a	1.93, m	1.95, m	22.7	22.6
2b	1.84, m	1.86, m		
3a	3.22, m	3.25, m	34.3	34.3
3b	2.87, m	2.89, m		
4			199.7	199.6
5			160.0	160.0
6a	3.19, t (12.7)	3.21, t (11.8)	30.2	30.2
6b	2.76, dd (12.7, 3.0)	2.78, dd (12.6, 3.1)		
7	2.54, m	2.57, m	36.9	36.8
8a	1.67, m	1.68, m	39.1	39.0
8b	1.67, m	1.68, m		
9a	2.16, m	2.18, m	58.3	58.3
9b	2.16, m	2.18, m		
10a	1.50, m	1.53, m	25.3	25.3
10b	1.36, m	1.38, m		
11a	1.71, m	1.73, m	27.9	27.8
11b	1.67, m	1.68, m		
12	2.37, m	2.39, m	54.2	54.2
13			213.4	213.4
14a	2.44, dd (14.1, 5.6)	2.46, dd (14.2, 5.7)	48.1	48.1
14b	2.09, dd (14.1, 7.1)	2.11, dd (14.2, 7.0)		
15	2.20, m	2.22, m	29.5	29.5
16	0.87, d (6.9)	0.88, d (7.2)	21.0	20.9
N-CH <sub>3</sub>	1.97, s	1.98, s	42.1	42.1

### 3 Crystallographic Data of 4c and 4d

#### Crystal data for compound 4c

$C_{23}H_{33}NO_3S$ ,  $M = 403.56$ ,  $a = 13.2454(4)$  Å,  $b = 5.4741(2)$  Å,  $c = 15.2485(5)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 103.7940(10)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1073.73(6)$  Å<sup>3</sup>,  $T = 100.(2)$  K, space group  $P1211$ ,  $Z = 2$ ,  $\mu(\text{Cu K}\alpha) = 1.517$  mm<sup>-1</sup>, 17550 reflections measured, 4177 independent reflections ( $R_{int} = 0.0553$ ). The final  $R_I$  values were 0.0329 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0849 ( $I > 2\sigma(I)$ ). The final  $R_I$  values were 0.0334 (all data). The final  $wR(F^2)$  values were 0.0854 (all data). The goodness of fit on  $F^2$  was 1.044. Flack parameter = 0.114(8).



Displacement ellipsoids are drawn at the 30% probability level.

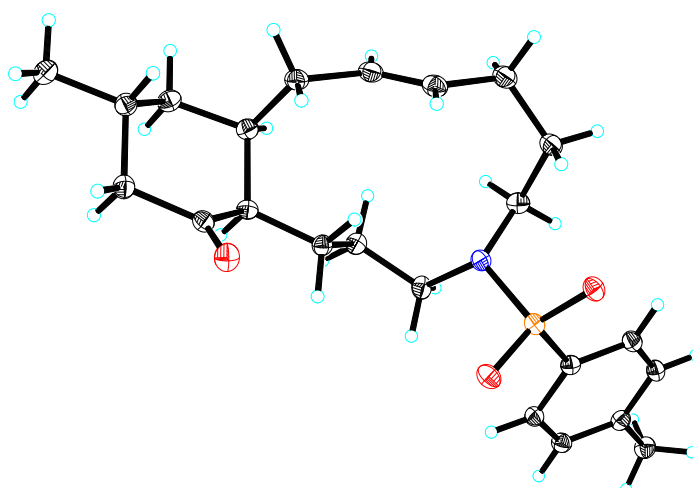
Table 1. Crystal data and structure refinement for 4c.

Identification code	global	
Empirical formula	C23 H33 N O3 S	
Formula weight	403.56	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	$a = 13.2454(4)$ Å	$\alpha = 90^\circ$ .
	$b = 5.4741(2)$ Å	$\beta = 103.7940(10)^\circ$ .
	$c = 15.2485(5)$ Å	$\gamma = 90^\circ$ .
Volume	$1073.73(6)$ Å <sup>3</sup>	
Z	2	

Density (calculated)	1.248 Mg/m <sup>3</sup>
Absorption coefficient	1.517 mm <sup>-1</sup>
F(000)	436
Crystal size	0.520 x 0.300 x 0.150 mm <sup>3</sup>
Theta range for data collection	2.98 to 72.31°.
Index ranges	-16<=h<=16, -6<=k<=6, -17<=l<=18
Reflections collected	17550
Independent reflections	4177 [R(int) = 0.0553]
Completeness to theta = 72.31°	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.80 and 0.36
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4177 / 1 / 255
Goodness-of-fit on F <sup>2</sup>	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0329, wR2 = 0.0849
R indices (all data)	R1 = 0.0334, wR2 = 0.0854
Absolute structure parameter	0.114(8)
Largest diff. peak and hole	0.341 and -0.308 e.Å <sup>-3</sup>

### Crystal data for 4d

C<sub>23</sub>H<sub>33</sub>NO<sub>3</sub>S,  $M = 403.56$ ,  $a = 5.34400(10)$  Å,  $b = 11.7296(3)$  Å,  $c = 34.6594(8)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 90^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 2172.55(9)$  Å<sup>3</sup>,  $T = 100.(2)$  K, space group  $P212121$ ,  $Z = 4$ ,  $\mu(\text{Cu K}\alpha) = 1.499$  mm<sup>-1</sup>, 17780 reflections measured, 4129 independent reflections ( $R_{int} = 0.1310$ ). The final  $R_I$  values were 0.0343 ( $I > 2\sigma(I)$ ). The final  $wR(F^2)$  values were 0.0767 ( $I > 2\sigma(I)$ ). The final  $R_I$  values were 0.0702 (all data). The final  $wR(F^2)$  values were 0.0809 (all data). The goodness of fit on  $F^2$  was 1.065. Flack parameter = 0.027(12).



Displacement ellipsoids are drawn at the 30% probability level.

Table 1. Crystal data and structure refinement for **4d**.

Identification code	global	
Empirical formula	C <sub>23</sub> H <sub>33</sub> N O <sub>3</sub> S	
Formula weight	403.56	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Orthorhombic	
Space group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	
Unit cell dimensions	a = 5.34400(10) Å	α = 90°.
	b = 11.7296(3) Å	β = 90°.
	c = 34.6594(8) Å	γ = 90°.
Volume	2172.55(9) Å <sup>3</sup>	
Z	4	
Density (calculated)	1.234 Mg/m <sup>3</sup>	
Absorption coefficient	1.499 mm <sup>-1</sup>	
F(000)	872	
Crystal size	0.370 x 0.050 x 0.050 mm <sup>3</sup>	
Theta range for data collection	2.55 to 69.93°.	
Index ranges	-5 ≤ h ≤ 6, -13 ≤ k ≤ 14, -41 ≤ l ≤ 42	
Reflections collected	17780	
Independent reflections	4129 [R(int) = 0.1310]	
Completeness to theta = 69.93°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.93 and 0.57	

Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	4129 / 0 / 255
Goodness-of-fit on F <sup>2</sup>	1.065
Final R indices [I>2sigma(I)]	R1 = 0.0343, wR2 = 0.0767
R indices (all data)	R1 = 0.0702, wR2 = 0.0809
Absolute structure parameter	0.027(12)
Largest diff. peak and hole	0.249 and -0.291 e.Å <sup>-3</sup>



#### 4 Reference

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# 5 <sup>1</sup>H and <sup>13</sup>C NMR Spectra

