Supporting Information

Formal total synthesis of the akummiline alkaloid

(+)‐strictamine

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Contents of Supporting Information

1. General Information………………………………………………………………..S3

2. Experimental Procedures and Compound Characterization ................S4

3. NMR Comparison between Synthetic and Reported Samples.............S18

4. \(^1\)H NMR and \(^{13}\)C NMR Spectra..................................................S20

5. References.........................................................................................S41
1. General Information

All commercially available reagents were used without further purification. All solvents were dried and distilled before use: toluene was distilled from sodium; THF was distilled from sodium/benzophenone ketyl; dichloromethane, acetonitrile and N,N-dimethylformamide were distilled from calcium hydride. Chromatography was conducted by using 200–300 mesh silica gel. All new compounds gave satisfactory spectroscopic analyses (IR, $^1$H NMR, $^{13}$C NMR, HRMS). Infrared (IR) spectra were recorded on a Perkin Elmer Spectrum Two FT-IR spectrometer. NMR spectra were recorded on a 400 MHz NMR or 600 MHz NMR spectrometer. High-resolution mass spectra (HRMS) were recorded on a Bruker BioTOFQ mass spectrometer, by the ESI method. Melting points were determined on a Kofler block (uncorrected). Optical rotation was obtained from Rudolph Research Analytical Autopol VI automatic polarimeter.
2. Experimental Procedures and Compound Characterization

Synthesis of compound S1
To a mixture of compound 16 (35.0 g, 88.7 mmol, 1 equiv), norbornene (16.7 g, 177.4 mmol, 2 equiv), K₂CO₃ (49.1 g, 355.3 mmol, 4 equiv), and PdCl₂ (1.57 g, 8.8 mmol, 10 mmol %) was added 500 mL of DMF (containing 0.5 M H₂O) and 2-(2-bromoethyl)-1,3-dioxolane 17 (64.3 g, 355.3 mmol, 4 equiv). The resulting suspension was stirred at 60 °C for 24 h. After being cooled to room temperature, the reaction mixture was diluted with Et₂O (1000 mL) and washed with water (1000 mL). The aqueous layer was then extracted with Et₂O (2 × 300 mL), and the combined organic extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by silica gel flash column chromatography (PE/EtOAc 4:1) to afford the product S1 (36.4 g, 83%) as a yellow oil. [α]²⁰D = +16.3 (c = 1.138, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s 1H), 7.46 (d, J = 7.6 Hz, 1H), 7.30 – 7.25 (m, 4H), 7.14 – 7.10 (m, 3H), 7.05 (t, J = 7.6 Hz, 1H), 5.13 (d, J = 8.0 Hz, 1H), 5.08 – 4.97 (m, 2H), 4.89 (t, J = 4.0 Hz, 1H), 4.66 – 4.64 (m, 1H), 4.01 – 3.99 (m, 2H), 3.23 (d, J = 6.0 Hz, 2H), 2.81 (t, J = 6.8 Hz, 2H), 2.02 – 1.98 (m, 2H), 1.40 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 172.3, 155.0, 136.5, 135.3, 135.1, 128.5, 128.3, 128.1, 121.1, 119.2, 118.1, 110.4, 105.4, 103.3, 79.6, 66.9, 64.9, 64.9, 54.2, 32.6, 28.2, 27.2, 19.4; IR (neat) 3353, 2971, 1702, 1499, 1164, 743; HRMS (M + Na⁺) calcd for C₂₈H₃₄N₂NaO₆⁺ 517.2309, found 517.2294.

Synthesis of compound 18
(Boc)₂O (15.4 g, 70.8 mmol, 1 equiv) was added dropwise to a stirred solution of
compound S1 (35 g, 70.8 mmol, 1 equiv) and DMAP (8.6 g, 70.8 mmol, 1 equiv) in DCM (350 mL) at room temperature. The reaction was complete in 1 h at the same temperature, before the reaction mixture was diluted with H2O (500 mL) and extracted with DCM (2 × 300 mL). The combined organic extracts were dried over Na2SO4 and concentrated. Purification of the crude product by silica gel flash column chromatography (PE/EtOAc 6:1) afforded compound 18 (35.7 g, 85%) as a yellow oil. 

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\left[\alpha\right]_{D}^{20} = +20.8 \ (c = 1.73, \text{CHCl}_3);\]

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta 8.06\) (d, \(J = 8.0\) Hz, 1H), 7.47 (d, \(J = 8.0\) Hz, 1H), 7.31–7.30 (m, 3H), 7.25–7.18 (m, 4H), 5.25 (d, \(J = 8.4\) Hz, 1H), 5.06 (q, \(J = 12.0\) Hz, 2H), 4.82 (t, \(J = 4.8\) Hz, 1H), 4.70–4.65 (m, 1H), 3.97–3.94 (m, 2H), 3.83–3.81 (m, 2H), 3.25–3.06 (m, 4H), 1.99–1.89 (m, 2H), 1.68 (s, 9H), 1.38 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta 172.2, 155.0, 150.1, 138.2, 135.9, 135.1, 129.6, 128.4, 128.2, 128.0, 123.7, 122.6, 118.1, 115.5, 113.4, 103.6, 83.8, 79.7, 67.1, 64.8, 53.6, 33.6, 28.2, 28.1, 27.3, 21.2; IR (neat) 2976, 1725, 1457, 1366, 1163, 1023, 747; HRMS (M + Na\(^+\)) calcd for C\(_{33}\)H\(_{42}\)N\(_2\)NaO\(_8\)\(^+\) 617.2833, found 617.2811.

**Synthesis of compound 15**

To a solution of 18 (20.0 g, 33.6 mmol, 1 equiv) in THF (800 mL) was added 1.2 N HCl (480 mL), and the mixture was stirred at 40 °C for 24 h. After the reaction was quenched by saturated aqueous NaHCO\(_3\), the aqueous layer was extracted with EtOAc (2 × 200 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), filtrated and concentrated under reduced pressure to afforded crude aldehyde which was used without further purification. To a solution of the crude aldehyde in dry THF (200 mL) under argon was added \(N\)-bromosuccinimide (6.0 g, 33.6 mmol, 1 equiv) and pyridinium \(p\)-toluenesulfonate (8.4 g, 33.6 mmol, 1 equiv). The resulting brown solution was stirred at 0 °C for 1 h. The mixture was then treated with a 10% NaHCO\(_3\)
aqueous solution and a 10% Na₂S₂O₄ aqueous solution. The organic layer was dried over Na₂SO₄ and concentrated. The residue was quickly purified by flash chromatography to afford product 19 (15.0 g, 71% for two steps). Due to the limited stability, this aldehyde was used immediately in the next step. To a stirred solution of compound 19 and tin (II) chloride dihydrate (15.1 g, 67.2 mmol, 2 equiv) in DCM (400 mL) at –10 °C was treated with dizao-acetic acid ethyl ester 20 (4.6 g, 40.3 mmol, 1.2 equiv). The reaction was complete in 2 h, then diluted with H₂O (500 mL) and extracted with DCM (2 × 300 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated. The crude product was subjected to silica gel flash column chromatography (PE/EtOAc 15:1) to afford bromide 15 (12.5 g, 74%) as a yellow oil. [α] D = −82.0 (c = 1.00, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.63 (brs, 1H), 7.38 – 7.32 (m, 6H), 7.27 – 7.23 (m, 1H), 7.07 (t, J = 7.2 Hz, 1H), 5.19 – 5.06 (m, 2H), 4.20 (q, J = 7.2 Hz, 2H), 3.85 – 3.81 (m, 1H), 3.60 – 3.53 (m, 1H), 3.34 – 3.30 (m, 3H), 3.17 (dd, J = 12.8, 7.2 Hz, 1H), 3.06 – 2.99 (m, 1H), 2.63 – 2.57 (m, 1H), 2.40 (brs 1H), 1.57 (s, 9H), 1.31 – 1.27 (m, 12H); ¹³C NMR (150 MHz, CDCl₃) δ 202.5, 170.9, 167.2, 151.5, 150.7, 141.7, 135.0, 130.2, 128.6, 128.5, 128.4, 126.9, 122.7, 90.3, 82.3, 67.2, 61.1, 59.1, 49.4, 39.6, 30.9, 28.3, 28.0, 14.1; IR (neat) 2978, 1718, 1477, 1367, 1256, 1149; HRMS (M + Na⁺) calcd for C₃₅H₄₃BrN₂NaO₉⁺ 737.2044, found 737.2014.

Synthesis of compound 21
To a solution of compound 15 (10.0 g, 14.0 mmol, 1 equiv) in dry THF (300 mL) was added N,N’-dimethylthelyenediamine (492 mg, 5.6 mmol, 0.4 equiv), CuCN (250 mg, 2.8 mmol, 0.2 equiv) and Cs₂CO₃ (9.0 g, 28.0 mmol, 2 equiv) in a round bottom flask under nitrogen. The mixture was stirred at refluxing temperature for 3 h, before it was cooled to room temperature, and diluted with ethyl acetate. The mixture was filtered,
and the resulting filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel flash column chromatography (PE/EtOAc 20:1) gave the cyclized product 21 (5.4 g, 61%) as a white solid. m.p. 124 – 126 °C; \([\alpha]^{20}_D = -81.6\) (c = 1.09, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 12.79 (s, 1H), 7.83 (brs, 1H), 7.53 (d, \(J = 7.2\) Hz, 1H), 7.38 – 7.31 (m, 5H), 7.19 (t, \(J = 7.2\) Hz, 1H), 6.97 (t, \(J = 7.2\) Hz, 1H), 5.13 (s, 2H), 4.39 – 4.25 (m, 2H), 3.97 – 3.93 (m, 1H), 3.69 – 3.64 (m, 1H), 3.28 (dd, \(J = 13.2\), 7.6 Hz, 1H), 2.82 (brs, 1H), 2.40 (d, \(J = 18.8\) Hz, 1H), 2.17 – 2.11 (m, 2H), 1.60 (s, 9H), 1.43 (t, \(J = 7.2\) Hz, 3H), 1.25 (brs, 9H); \(^1^3\)C NMR (150 MHz, CDCl₃) \(\delta\) 174.0, 172.7, 171.8, 151.8, 151.0, 142.4, 135.3, 132.1, 128.5, 128.3, 128.1, 124.8, 122.3, 117.3, 99.5, 90.1, 81.7, 80.4, 66.8, 60.8, 60.0, 54.8, 37.6, 28.2, 27.9, 27.8, 26.3, 14.3; IR (neat) 2976, 1717, 1367, 1232, 1156, 754; HRMS (M + Na⁺) calcd for C₃₅H₄₂N₂NaO₉⁺ 657.2782, found 657.2760.

Synthesis of compound S2

A mixture of compound 21 (5.0 g, 7.8 mmol) and Pd/C (10% Pd, 250 mg) in EtOH (200 mL) was stirred at room temperature under 1.0 atm pressure of H₂ for 2 h. The mixture was then filtered through a pad of Celite and the obtained filtrate was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (DCM/MeOH 10:1) to afford S2 (4.1 g, 95%) as a white solid. m.p. 112 – 114 °C; \([\alpha]^{20}_D = -100.6\) (c = 1.55, CHCl₃); \(^1\)H NMR (400 MHz, CDCl₃) \(\delta\) 12.81 (s, 1H), 9.28 (brs, 1H), 7.80 (brs, 1H), 7.55 (d, \(J = 7.2\) Hz, 1H), 7.20 (t, \(J = 7.2\) Hz, 1H), 6.99 (t, \(J = 7.2\) Hz, 1H), 4.41 – 4.26 (m, 2H), 3.89 (t, \(J = 8.8\) Hz, 1H), 3.70 – 3.66 (m, 1H), 3.32 (dd, \(J = 12.8\), 7.2 Hz, 1H), 2.78 (brs, 1H), 2.40 (d, \(J = 18.0\) Hz, 1H), 2.22 – 2.13 (m, 2H), 1.59 (s, 9H), 1.45 (t, \(J = 7.2\) Hz, 3H), 1.34 (brs, 9H); \(^1^3\)C NMR (150 MHz, CDCl₃) \(\delta\) 179.1, 173.7, 171.8, 151.9, 142.3, 132.1, 128.5, 124.9, 123.0, 117.9, 99.5, 90.0, 81.7, 80.7, 60.9, 59.9, 55.1, 37.5, 28.2, 27.7, 26.3, 14.3; IR
(neat) 2966, 1717, 1367, 1310, 1234, 1156, 755; HRMS (M + Na\(^+\)) calcd for C\(_{28}H_{36}N_2NaO_9\) \(^+\) 567.2313, found 567.2294.

**Synthesis of compound 14**

A solution of compound S\(_2\) (2.0 g, 3.7 mmol, 1 equiv) and 2,2’-dithiopyridene-1-1’-(bis)-N-oxide (1.1 g, 4.4 mmol, 1.2 equiv) in dry DCM (200 mL) under nitrogen was cooled to 0 °C and shielded from light. Tributylphosphine (0.9 g, 4.4 mmol, 1.2 equiv) was added. After the mixture was stirred for 1 h at room temperature, t-BuSH (1.6 g, 18.5 mmol, 5 equiv) was added, and the reaction was exposed to hv (Hg light) and stirred for another 1.5 h. The reaction mixture was concentrated under reduced pressure. Subjection of the crude material to silica gel flash column chromatography (PE/EtOAc 20:1) afforded the decarboxylated 14 (1.6 g, 87%) as a white solid. m.p. 139 – 141 °C; \([\alpha]\)\(^{20}\) \(_D\) = −104.8 (c = 1.26, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 12.89 (s, 1H), 7.70 (brs, 1H), 7.52 (d, \(J\) = 7.2 Hz, 1H), 7.18 (t, \(J\) = 7.2 Hz, 1H), 6.96 (t, \(J\) = 7.2 Hz, 1H), 4.43 – 4.27 (m, 2H), 3.63 – 3.61 (m, 1H), 3.50 (t, \(J\) = 9.6 Hz, 1H), 3.01 – 2.94 (m, 1H), 2.88 (dd, \(J\) = 12.8, 6.4 Hz, 1H), 2.77 – 2.68 (m, 1H), 2.42 – 2.35 (m, 1H), 2.17 – 2.08 (m, 1H), 1.95 (td, \(J\) = 13.2, 4.8 Hz, 1H), 1.58 (s, 9H), 1.46 (t, \(J\) = 7.6 Hz, 3H), 1.42 (s, 9H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\) 173.8, 172.2, 152.9, 151.3, 142.4, 133.1, 128.1, 124.7, 122.4, 117.6, 99.9, 89.2, 81.4, 79.8, 60.7, 56.0, 46.7, 32.9, 28.4, 28.3, 27.8, 26.5, 14.3; IR (neat) 2963, 1707, 1475, 1381, 1366, 1238, 1169, 754; HRMS (M + Na\(^+\)) calcd for C\(_{27}H_{36}N_2NaO_7\) \(^+\) 523.2414, found 523.2398.

**Synthesis of compound S3**

To a solution of compound 14 (2.0 g, 4.0 mmol, 1 equiv) in anhydrous DCM (100 mL)
at −78 °C was added DIPEA (2.1 g, 16.0 mmol, 4 equiv). After stirred for 10 min, Tf₂O (2.2 g, 8.0 mmol, 2 equiv) was added. The resulting reaction was stirred for 2 h, before saturated NaHCO₃ solution was added. The mixture was extracted with DCM (2 × 100 mL), and the combined organic layers were dried over Na₂SO₄ and evaporated to dryness. The crude product was purified by silica gel flash column chromatography (PE/EtOAc 20:1) to give product S₃ (2.4 g, 95%) as a white solid. m.p. 78 – 80 °C; [α]²⁰D = −79.0 (c = 0.72, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.68 (brs, 1H), 7.23 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 6.98 (t, J = 7.2 Hz, 1H), 4.33 – 4.15 (m, 2H), 3.85 (d, J = 13.2 Hz, 1H), 3.55 (t, J = 9.2 Hz, 1H), 3.02 – 2.85 (m, 3H), 2.46 – 2.40 (m, 1H), 2.37 – 2.29 (m, 1H), 2.02 (td, J = 13.6, 5.6 Hz, 1H), 1.58 (s, 9H), 1.42 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 163.8, 148.2, 142.3, 129.3, 124.4, 123.1, 119.7, 118.0, 116.5, 86.8, 81.9, 80.5, 61.9, 58.1, 46.4, 32.5, 28.4, 28.2, 27.7, 26.8, 26.3, 13.8; IR (neat) 2966, 1713, 1424, 1386, 1212, 1140, 884, 755; HRMS (M + Na⁺) calcd for C₂₈H₃₅F₃N₂NaO₉S⁺ 655.1907, found 655.1887.

Synthesis of compound 22

To a solution of compound S₃ (2.0 g, 3.1 mmol, 1 equiv) in THF (100 mL) in a round bottom flask was added Pd(PPh₃)₄ (183 mg, 0.16 mmol, 0.05 equiv), TEA (3.1 g, 31.0 mmol, 10 equiv) and HCO₂H (1.4 g, 31.0 mmol, 10 equiv). The mixture was stirred under reflux for 24 h, and then cooled to room temperature. After being diluted with EtOAc, the mixture was filtered, and filtrate was concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (PE/EtOAc 20:1) to give the desired enoate 22 (1.7 g, 86%) as a white solid. m.p. 89 – 91 °C; [α]²⁰D = −89.8 (c = 0.69, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.66 (brs, 1H), 7.59 (d, J = 7.2 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 7.01 – 6.99 (m, 1H), 6.96 (t, J = 7.2 Hz, 1H), 4.19 – 4.14 (m, 2H), 3.75 (d, J = 12.4 Hz, 1H), 3.50 (t, J = 9.6 Hz, 1H), 1.58 (s, 9H), 1.42 (s, 9H), 1.25 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 163.8, 148.2, 142.3, 129.3, 124.4, 123.1, 119.7, 118.0, 116.5, 86.8, 81.9, 80.5, 61.9, 58.1, 46.4, 32.5, 28.4, 28.2, 27.7, 26.8, 26.3, 13.8; IR (neat) 2966, 1713, 1424, 1386, 1212, 1140, 884, 755; HRMS (M + Na⁺) calcd for C₂₈H₃₅F₃N₂NaO₉S⁺ 655.1907, found 655.1887.
3.07 – 2.93 (m, 2H), 2.54 – 2.47 (m, 1H), 2.34 – 2.26 (m, 1H), 2.16 – 2.08 (m, 1H), 1.75 (td, \(J = 13.6, 5.2\) Hz, 1H), 1.57 (s, 9H), 1.42 (s, 9H), 1.27 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 166.0, 153.1, 151.5, 142.6, 139.5, 131.6, 131.5, 128.2, 125.2, 123.0, 117.8, 88.7, 81.1, 79.7, 60.4, 56.8, 46.2, 32.7, 28.4, 28.3, 27.5, 24.1, 14.1; IR (neat) 2976, 1707, 1476, 1383, 1162, 772; HRMS (M + Na\(^+\)) calcd for C\(_{27}\)H\(_{36}\)N\(_2\)NaO\(_6\)^{+} 507.2465, found 507.2450.

**Synthesis of compound 23**

To a solution of compound 22 (2.0 g, 4.1 mmol, 1 equiv) in EtOAc (100 mL) was added conc. HCl (100 mL) at 0 °C. After being stirred for 3 h at the same temperature, the mixture was neutralized with saturated NaHCO\(_3\) solution. The layers were separated and the aqueous phase was extracted with EtOAc (3 × 200 mL). The combined organic phases were dried over Na\(_2\)SO\(_4\) and concentrated, the crude product were used without further purification. To a solution of crude amine in THF (200 mL) was added a 10\% Na\(_2\)CO\(_3\) aqueous solution (200 mL) and Boc\(_2\)O (1.3 g, 6.2 mmol, 1.5 equiv) at 25 °C. The resulting mixture was stirred at refluxing temperature for 3 h, then diluted with EtOAc (200 mL) and water (200 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 × 200 mL). The combined organic layers were dried over Na\(_2\)SO\(_4\), concentrated under reduced pressure. Purification of the crude material by silica gel flash column chromatography (PE/EtOAc 15:1) provided 23 (1.4 g, 86\% for 2 steps) as a white solid. m.p. 124 – 126 °C; [\(\alpha\)]\(_{20}^{D}\) = −273.4 (c = 1.13, CHCl\(_3\)); \(^1\)H NMR (400 MHz, CDCl\(_3\), some signals exist as a pair due to the presence of amide rotamers) \(\delta\) 7.44 (d, \(J = 7.6\) Hz, 1H), 6.98 – 6.94 (m, 2H), 6.66 – 6.60 (m, 1H), 6.53 – 6.49 (m, 1H), 5.48/4.85 (s, 1H), 4.10 (q, \(J = 7.2\) Hz, 2H), 3.57 – 3.52/3.47 – 3.44 (m, 1H), 3.09 – 2.95 (m, 2H), 2.80/2.61 (dd, \(J = 13.2, 4.8\) Hz, 1H), 2.51 – 2.43 (m, 1H), 2.15 – 1.98 (m, 2H), 1.60/1.54 (dd, \(J = 13.2, 4.8\) Hz, 1H), 1.33 (s, 9H), 1.20 (t, \(J = 7.2\) Hz, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), some signals exist
as a pair due to the presence of amide rotamers) δ 165.9/165.8, 153.8/153.0, 149.5/148.8, 139.9/139.3, 133.4/133.3, 130.4/130.1, 128.4/128.3, 126.0/125.8, 119.2/118.7, 109.9/109.7, 87.3/86.7, 80.2/79.4, 60.3/60.2, 57.1/56.0, 46.3, 33.5/32.8, 28.7, 28.3/28.1, 27.2/26.8, 24.1/24.0, 14.1; IR (neat) 2976, 1709, 1679, 1388, 1259, 1161, 745; HRMS (M + Na⁺) calcd for C₂₂H₂₈N₂NaO₄⁺ 407.1931, found 407.1941.

**Synthesis of compound 24**

To a stirred solution of compound 23 (2.0 g, 5.2 mmol, 1 equiv) and NaBH₃CN (1.3 g, 20.8 mmol, 4 equiv) in dry THF (200 mL) was added slowly a solution of TiCl₄ (5.9 g, 31.2 mmol, 6 equiv) in DCM (40 mL) at –40 °C. The reaction was stirred at the same temperature for 4 h before it was quenched by addition of saturated NaHCO₃ solution. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 100 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (PE/EtOAc 4:1) to give the product 24 (1.9 g, 95%) as a colorless oil. [α]²⁰_D = −77.8 (c = 0.54, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.42 (d, J = 7.6 Hz, 1H), 7.14 (dd, J = 4.8, 2.8 Hz, 1H), 6.99 (td, J = 7.6, 1.2 Hz, 1H), 6.66 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 7.6 Hz, 1H), 4.59 (brs, 1H), 4.12 (q, J = 7.2 Hz, 2H), 4.00 (brs, 1H), 3.59 (brs, 1H), 3.25 – 3.19 (m, 1H), 3.11 – 3.04 (m, 1H), 2.72 – 2.65 (m, 1H), 2.56 – 2.49 (m, 1H), 2.25 – 2.11 (m, 2H), 1.91 – 1.84 (m, 2H), 1.41 (s, 9H), 1.24 (t, J = 7.2 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 166.6, 155.7, 150.1, 141.8, 132.9, 131.5, 127.7, 126.0, 118.4, 109.5, 78.8, 64.6, 60.0, 48.0, 37.4, 36.8, 28.3, 23.6, 21.5, 14.0; IR (neat) 3357, 2929, 1709, 1511, 1249, 1169, 1065; HRMS (M + Na⁺) calcd for C₂₂H₃₀N₂NaO₄⁺ 409.2097, found 409.2088.
Synthesis of compound S4

To a solution of 24 (1.5 g, 3.8 mmol, 1 equiv) in DCM (150 mL) was added TsCl (1.48 g, 7.8 mmol, 2 equiv) and DMAP (950 mg, 7.8 mmol, 2 equiv) at room temperature. The reaction mixture was stirred overnight under reflux and concentrated under reduced pressure. Purification of the residue by silica gel flash chromatography (PE/EtOAc 10:1) yielded S4 (2.1 g, 98%) as a pale yellow oil. $[\alpha]^{20}_D = -42.2 \ (c = 0.60, \text{CHCl}_3)$; $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 7.73 – 7.70 (m, 3H), 7.39 (d, $J = 7.8$ Hz, 1H), 7.25 – 7.23 (m, 3H), 7.20 (t, $J = 7.8$ Hz, 1H), 6.95 (t, $J = 7.8$ Hz, 1H), 4.24 – 4.15 (m, 2H), 4.13 – 4.11 (m, 1H), 3.97 (s, 1H), $^1$H NMR (600 MHz, CDCl$_3$) $\delta$ 166.8, 155.3, 144.0, 143.9, 139.3, 137.2, 135.1, 130.5, 129.7, 128.3, 126.9, 127.1, 124.1, 115.6, 79.0, 66.6, 60.6, 49.2, 37.9, 36.6, 28.3, 26.8, 26.2, 22.4, 21.4, 14.1; IR (neat) 3402, 2975, 1709, 1509, 1258, 1166, 757; HRMS (M + Na$^+$) calcd for C$_{29}$H$_{36}$N$_2$NaO$_6$S$^+$ 563.2186, found 563.2169.

Synthesis of compound S5

A solution of S4 (500 mg, 0.93 mmol, 1 equiv), AIBN (30 mg, 0.19 mmol, 0.2 equiv) and NBS (247 mg, 1.4 mmol, 1.5 equiv) in dry CCl$_4$ (100 mL) was reflux under N$_2$ for 2.5 h. After evaporation under reduced pressure, the residue was subjected to silica gel flash chromatography (PE/EtOAc 20:1) to give S5 (372 mg, 65%) as a yellow oil. $[\alpha]^{20}_D = +21.0 \ (c = 0.58, \text{CHCl}_3)$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.76 (d, $J = 8.4$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 8.4$ Hz, 2H), 7.25
- 7.20 (m, 2H), 6.96 (t, $J = 8.0$ Hz, 1H), 4.79 – 4.77 (m, 1H), 4.51 (dd, $J = 10.4$, 4.8 Hz, 1H), 4.31 – 4.20 (m, 2H), 3.95 (brs, 1H), 2.97 – 2.81 (m, 2H), 2.62 (dt, $J = 14.8$, 4.0 Hz, 1H), 2.40 (s, 3H), 2.34 – 2.27 (m, 2H), 1.42 (s, 9H), 1.32 (t, $J = 7.2$ Hz, 3H), 0.56 – 0.50 (m, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) $\delta$ 165.9, 155.2, 144.3, 140.6, 139.1, 135.9, 135.3, 131.6, 129.9, 128.7, 126.9, 125.4, 124.4, 115.8, 79.1, 63.4, 61.4, 49.5, 40.7, 38.4, 36.6, 34.7, 28.4, 25.1, 21.5, 14.0; IR (neat) 3402, 2976, 1712, 1506, 1364, 1246, 1167, 771; HRMS (M + Na$^+$) calcd for C$_{29}$H$_{35}$BrN$_2$NaO$_6$S$^+$ 641.1291, found 641.1272.

**Synthesis of 13**

A solution of compound S5 (500 mg, 0.81 mmol, 1 equiv) and DBU (246 mg, 1.6 mmol, 2 equiv) in PhMe (50 mL) was stirred at 50 °C for 2 h. After quenching the reaction with saturated NH$_4$Cl solution, the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over Na$_2$SO$_4$ and concentrated under reduced pressure. Purification of the residue through silica gel flash chromatography (PE/EtOAc 10:1) furnished compound 13 (426 mg, 98%) as a colorless oil. [\(\alpha\)]$^2_0$ = $-23.0$ (c = 0.59, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.72 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.20 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 6.0$ Hz, 1H), 6.97 (t, $J = 7.6$ Hz, 1H), 6.26 (dd, $J = 9.6$, 3.6 Hz, 1H), 6.05 – 6.02 (m, 1H), 4.93 (s, 1H), 4.23 – 4.15 (m, 2H), 4.07 (brs, 1H), 2.92 – 2.87 (m, 2H), 2.62 – 2.54 (m, 1H), 2.37 (s, 3H), 1.44 (s, 9H), 1.28 (t, $J = 7.2$ Hz, 3H), 0.39 – 0.32 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.8, 155.3, 144.2, 139.1, 137.5, 134.5, 133.3, 132.5, 129.7, 128.2, 128.0, 127.1, 125.4, 124.5, 122.5, 115.5, 79.1, 67.2, 60.7, 48.5, 40.5, 37.0, 28.4, 21.5, 14.1; IR (neat) 3402, 2977, 1704, 1511, 1358, 1257, 1166, 756; HRMS (M + Na$^+$) calcd for C$_{29}$H$_{34}$N$_2$NaO$_6$S$^+$ 561.2029, found 561.2014.
Synthesis of 25
To a solution of compound 13 (500 mg, 0.93 mmol, 1 equiv) in DMF (50 mL) was added Cs₂CO₃ (246 mg, 1.8 mmol, 2 equiv). The reaction mixture was stirred at room temperature for 30 min, before it was diluted with EtOAc (200 mL) and water (200 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 × 50 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The crude product was purified by silica gel flash column chromatography (PE/EtOAc 15:1) to give the cyclized product 25 (455 mg, 91%) as a white foam. [α]²⁰_D = +82.9 (c = 0.44, CHCl₃); ¹H NMR (400 MHz, CDCl₃, some signals exist as a pair due to the presence of amide rotamers) δ 7.81/7.74 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.17 (t, J = 7.6 Hz, 1H), 7.09 (brs, 1H), 6.98 – 6.96 (m, 1H), 5.58/5.44 (brs, 1H), 4.20 – 4.18/4.02 – 3.98 (m, 3H), 3.20 – 3.15 (m, 1H), 3.06 – 2.94 (m, 2H), 2.66 – 2.61 (m, 1H), 2.37 – 2.35 (m, 4H), 1.68 – 1.65 (m, 1H), 1.57/1.48 (s, 9H), 1.16 (t, J = 7.2 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃, some signals exist as a pair due to the presence of amide rotamers) δ 165.5, 155.0/154.6, 144.6/144.3, 142.8, 139.6/139.1, 133.1, 131.3, 129.7, 129.2/129.1, 128.4/128.2, 127.8, 126.1/126.0, 123.4/123.2, 114.2, 80.4/80.1, 69.6/69.3, 60.2, 47.6/46.8, 44.3, 39.0/37.9, 31.0/30.5, 28.7/28.5/28.3, 21.5, 14.0; IR (neat) 2975, 1714, 1691, 1591, 1439, 1282, 1124, 749; HRMS (M + Na⁺) calcd for C₂₉H₃₄N₂NaO₆S⁺ 561.2029, found 561.2017.

Synthesis of S6
To a solution of compound 25 (250 mg, 0.46 mmol, 1 equiv) in dry MeOH (25 mL)
under N₂ was added NaOMe (248 mg, 4.6 mmol, 10 equiv). The reaction mixture was stirred at 60 °C for 12 h, cooled to room temperature and quenched with saturated NH₄Cl solution. The aqueous layer was extracted with EtOAc (2 × 50 mL), and the combined organic layers were dried over Na₂SO₄ and concentrated to dryness. The residue was purified by silica gel flash chromatography (PE/EtOAc 15:1) to give S₆ (219 mg, 90%) as a white foam. [α]₂⁰₀D = +83.0 (c = 0.48, CHCl₃); ¹H NMR (400 MHz, CDCl₃, some signals exist as a pair due to the presence of amide rotamers) δ 7.81/7.74 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.11 (brs, 1H), 6.99 – 6.97 (m, 1H), 5.58/5.44 (brs, 1H), 4.21 – 4.18/4.02 – 3.99 (m, 1H), 3.56 (m, 3H), 3.21 – 3.16 (m, 1H), 3.04 – 2.94 (m, 2H), 2.66 – 2.59 (m, 1H), 2.37 – 2.35 (m, 4H), 1.67 – 1.64 (m, 1H), 1.57/1.48 (s, 9H); ¹³C NMR (150 MHz, CDCl₃, some signals exist as a pair due to the presence of amide rotamers) δ 165.8, 155.0/154.5, 144.7/144.3, 142.8, 140.1/139.6, 133.1, 131.3/131.2, 129.7, 129.0/128.8, 128.4/128.2, 127.8, 126.0/125.9, 123.5/123.2, 114.2, 80.4/80.2, 69.6/69.3, 51.2, 47.6/46.8, 44.3, 38.9/37.9, 30.9/30.5, 28.7/28.5/28.3, 26.8, 21.5; IR (neat) 2976, 1714, 1691, 1390, 1283, 1162, 745; HRMS (M + Na⁺) calced for C₂₈H₃₂N₂NaO₆S⁺ 547.1873, found 547.1873.

Synthesis of S₇

To a solution of S₆ (100 mg, 0.19 mmol, 1 equiv) in dry THF/HMPA (20:1 10 mL) was added SmI₂ (0.1 M in THF, 19 mL, 1.9 mmol, 10 equiv) at room temperature. The reaction mixture was stirred for 5 h and then quenched by saturated NH₄Cl solution. After the aqueous layer was extracted with EtOAc (2 ×10 mL), the combined organic layers were dried over Na₂SO₄, and evaporated off. The residue was subjected to silica gel flash chromatography (PE/EtOAc 10:1) to give S₇ (53 mg, 75%) as a white foam.[α]₂⁰₀D = +125.2 (c = 0.40, CHCl₃); ¹H NMR (400 MHz, CDCl₃, some
signals exist as a pair due to the presence of amide rotamers) $\delta$ 7.42 (d, $J = 7.2$ Hz, 1H), 7.07 – 7.03 (m, 2H), 6.79 (t, $J = 7.2$ Hz, 1H), 6.70 (d, $J = 7.2$ Hz, 1H), 4.77/4.60 (brs, 1H), 4.11/4.00 (dd, $J = 13.6$, 4.8 Hz, 1H), 3.89 (brs, 1H), 3.59 (s, 3H), 3.52 (dd, $J = 10.8$, 3.6 Hz, 1H), 3.08 – 2.96 (m, 1H), 2.81 – 2.67 (m, 2H), 2.36 – 2.28 (m, 1H), 1.96 – 1.86 (m, 1H), 1.46 (s, 9H); $^{13}$C NMR (150 MHz, CDCl$_3$, some signals exist as a pair due to the presence of amide rotamers) $\delta$ 166.3, 155.4/155.0, 151.1, 139.1/138.6, 131.7, 129.7/129.5, 127.9, 126.1/126.0, 119.8/119.6, 110.9, 80.0/79.9, 67.5/67.3, 51.1, 48.2, 47.2, 44.5, 39.8/39.2, 31.0/30.7, 29.1/28.8, 28.5/28.4; IR (neat) 3345, 2976, 1676, 1321, 1364, 1243, 1165, 1059, 746; HRMS (M + H$^+$) calcd for C$_{21}$H$_{27}$N$_2$O$_4^+$ 371.1965, found 371.1965.

**Synthesis of 26**

To a solution of S7 (80 mg, 0.22 mmol, 1 equiv) in dry DCM (10 mL) was added PhIO (238 mg, 1.1 mmol, 5 equiv) and the reaction mixture was stirred at room temperature. After 2 h, the mixture was filtered, and the obtained filtrate was concentrated under reduced pressure. Purification of the crude product by silica gel flash column chromatography (PE/EtOAc 8:1) gave imine 26 (67 mg, 85%) as a colorless oil. [$\alpha$]$^D_{20} = -64.2$ (c = 0.26, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$, some signals exist as a pair due to the presence of amide rotamers) $\delta$ 7.91 (d, $J = 7.6$ Hz, 1H), 7.66 (d, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.27 – 7.24 (m, 1H), 7.07 (brs, 1H), 5.52/5.39 (brs, 1H), 4.15 – 4.12/3.99 – 3.97 (m, 1H), 3.78 (s, 3H), 3.24 – 3.21 (m, 1H), 2.91 – 2.81 (m, 3H), 1.48 (s, 9H), 1.42 – 1.34 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$, some signals exist as a pair due to the presence of amide rotamers) $\delta$ 181.5, 165.5, 155.7, 154.2, 140.6/140.2, 139.3, 129.9, 128.6, 126.2, 125.9, 121.1, 80.7, 54.8, 51.8, 50.4, 38.0, 37.2/37.0, 34.8/34.5, 28.3; IR (neat) 3345, 2976, 1676, 1321, 1364, 1243, 1165, 1059, 746; HRMS (M + H$^+$) calcd for C$_{21}$H$_{24}$N$_2$O$_4^+$ 369.1809, found 369.1810.
Synthesis of 12

To a solution of 26 (50 mg, 0.14 mmol, 1 equiv) in DCM (5 mL) was added TFA (0.5 mL) at room temperature. After stirring at room temperature for 1.5 h, the mixture was concentrated in vacuo. The resulting crude amine was directly dissolved in CH$_3$CN (5 mL) followed by addition of Cs$_2$CO$_3$ (221 mg, 0.68 mmol, 5 equiv), (Z)-1-bromo-2-iodobut-2-ene 27 (105 mg, 0.41 mmol, 3 equiv) and 4 Å molecular sieves (50 mg) at room temperature. After stirring in dark at rt for 24 h, the mixture was diluted with water and extracted with EtOAc (2 × 5 mL). The combined organic layers were dried over Na$_2$SO$_4$, concentrated under reduced pressure. The residue was purified by silica gel flash chromatography (PE/EtOAc 15:1 to 5:1) to give 12 (51 mg, 85%) as a yellow oil. [$\alpha$]$^D_{20}$ = $-98.0$ (c = 0.24, CHCl$_3$); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.23 (t, J = 7.6 Hz, 1H), 7.05 (t, J = 3.6 Hz, 1H), 5.89 (q, J = 6.4 Hz, 1H), 3.95 (d, J = 6.4 Hz, 1H), 3.75 (s, 3H), 3.38 (d, J = 14.0 Hz, 1H), 3.22 (d, J = 14.0 Hz, 1H), 3.09 – 3.02 (m, 1H), 2.95 – 2.89 (m, 1H), 2.81 – 2.74 (m, 1H), 2.70 – 2.63 (m, 2H), 1.79 (d, J = 6.4 Hz, 1H), 1.57 (td, J = 12.8, 4.4 Hz, 1H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 183.0, 165.7, 155.9, 141.1, 140.0, 132.9, 129.7, 128.3, 126.2, 125.4, 120.7, 108.4, 65.0, 55.2, 54.7, 51.6, 43.1, 35.8, 33.8, 21.7; IR (neat) 2947, 1714, 1630, 1597, 1435, 1259, 1090, 774; HRMS (M + H$^+$) calcd for C$_{20}$H$_{22}$IN$_2$O$_2$ $^+$ 449.0720, found 449.0720.
3. NMR Comparison between Synthetic and Reported Samples

**Table 1.** $^1$H NMR data comparison between our synthetic and the previously reported (Zhu’s\cite{2}, Fujii/Ohno’s\cite{3} and Gaich’s\cite{4}) compounds.

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<th>$^1$H NMR (400 MHz, CDCl$_3$)</th>
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Table 2. $^{13}$C NMR data comparison between our synthetic and the previously reported (Zhu’s[2], Fujii/Ohno’s[3] and Gaich’s[4]) compounds.

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4. $^1$H NMR and $^{13}$C NMR Spectra

$^1$H and $^{13}$C NMR Spectra of compound S1
$^1$H and $^{13}$C NMR Spectra of compound 18
$^1$H and $^{13}$C NMR Spectra of compound 15
$^1$H and $^{13}$C NMR Spectra of compound 21
$^1$H and $^{13}$C NMR Spectra of compound S2
$^1$H and $^{13}$C NMR Spectra of compound 14
$^1$H and $^{13}$C NMR Spectra of compound S3
$^1$H and $^{13}$C NMR Spectra of compound 22
$^1$H and $^{13}$C NMR Spectra of compound 23
$^1$H and $^{13}$C NMR Spectra of compound 24
$^1$H and $^{13}$C NMR Spectra of compound S4
$^1$H and $^{13}$C NMR Spectra of compound S5
DEPT and gCOSY Spectra of compound S5
gHMQC and gHMBC Spectra of compound S5
NOEDS Spectra of compound S5
$^1$H and $^{13}$C NMR Spectra of compound 13
$^1$H and $^{13}$C NMR Spectra of compound 25
$^1$H and $^{13}$C NMR Spectra of compound S6
$^1$H and $^{13}$C NMR Spectra of compound S7
$^1$H and $^{13}$C NMR Spectra of compound 26
$^1$H and $^{13}$C NMR Spectra of compound 12
5. Reference:


(4) (a) R. Eckermann, M. Breunig and T. Gaich, *Chem. Commun.*, 2016, **52**, 11363;