Supporting Information

Concise Asymmetric Total Synthesis of Catunaregin

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Table of contents

Experimental procedure ............................................................................................................ S1
Syntheses of (S)- and (R)-MTPA esters, and δ values of the Mosher’s esters ...................... S8
1H and 13C NMR spectra of new compounds ........................................................................ S10
General
All reactions involving air- and moisture-sensitive reagents were carried out using standard syringe-
septumcap techniques. Unless otherwise noted, all solvents and reagents were obtained from
commercial suppliers and used without further purification. Routine monitoring of reactions were
carried out Merck silica gel 60 F254 TLC plates. Column chromatography was performed on Kanto
Chemical Silica Gel 60N (spherical, neutral 60–230 µm) with the solvents indicated. Melting points
were taken on a Yanako MP-S3 micro melting point apparatus and are uncorrected. Measurement
of optical rotations was performed with a JASCO P-2200 polarimeter. Infrared spectral
measurements were carried out with a Perkin–Elmer Paragon 1000 FT-IR and a JASCO FT/IR-
4100 spectrometer, and only noteworthy absorptions were listed. 1H and 13C NMR spectra were
measured with a JEOL JNM-ECS400 (400 MHz) or a Burker AV-600 (600 MHz) spectrometer.
Chemical shifts were expressed in ppm using CHCl3 (7.26 ppm) for 1H NMR and CHCl3 (77.0
ppm) for 13C NMR in CDCl3 as an internal standard. HRMS spectra measured on a Micromass LCT
spectrometer.

**tert-Butyl 2-Acetyl-4-oxopentanoate (S1).**

To a stirred suspension of sodium hydride (55% dispersion in mineral oil, 6.58 g, 157 mmol) in
tetrahydrofuran (400 mL) was added dropwise **tert**-butyl acetoacetate (7) (20.0 mL, 19.1 g, 121
mmol) at 0°C. After stirred for 0.5 h at 0°C, to this reaction mixture was added dropwise α-
chloroacetone (12.5 mL, 14.5 g, 157 mmol) at 0 °C, and then stirred for 96 h at room temperature.
The reaction mixture was quenched with 1.0 M HCl aqueous solution (100 mL) at 0 °C, and
extracted with ether (2 × 300 mL). The combined organic layers were washed with brine, and the
washed solution was dried over MgSO4. The dried solution was filtered and the filtrate was
concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–
EtOAc, 7:1) to afford the intermediate S1 (19.5 g, 91.0 mmol, 75%) as a colorless liquid. Those
spectra data were identified for those of previous report.
1-\textit{tert}-Butyl 4-methyl 2-acetyl-2-(2-oxopropyl)succinate (S2).

To a stirred suspension of sodium hydride (55% dispersion in mineral oil, 2.88 g, 65.8 mmol) in tetrahydrofuran (170 mL) was added dropwise S1 (10.9 g, 50.9 mmol) at 0 °C. After stirred for 0.5 h at room temperature, to this mixture was added dropwise methyl bromoacetate (5.30 mL, 8.56 g, 56.0 mmol) at 0 °C, and then stirred for 16 h at room temperature. The reaction mixture was quenched with 1.0 M HCl aqueous solution (80 mL) and extracted with Et$_2$O (2 × 200 mL). The combined organic layers were washed with brine, and the washed solution was dried over MgSO$_4$. The dried solution was filtered and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–EtOAc, 4:1) to afford the intermediate S2 (11.8 g, 41.2 mmol, 81%) as a colorless liquid. Those spectra data were identified for those of previous report.

Methyl 2-(2,5-Dimethylfuran-3-yl)acetate (8).

To a stirred solution of S2 (11.8 g, 41.2 mmol) in CH$_2$Cl$_2$ (140 mL) was added trifluoroacetic acid (24.5 mL, 37.6 g, 330 mmol) at 0 °C. After stirred for 13 h at room temperature, the mixture was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–EtOAc, 9:1) to afford 8 (4.30 g, 25.6 mmol, 62%) as a pale yellow oil. Those spectra data were identified for those of previous report.

2-(2,5-Dimethylfuran-3-yl)acetic acid (9).

To a stirred solution of 8 (2.99 g, 17.8 mmol) in MeOH (35 mL) were added 3.0 M NaOH aqueous solution (12.5 mL) at room temperature. After stirred for 15 min at same temperature, the reaction was acidified by adding 1.0 M HCl aqueous solution, and extracted with CHCl$_3$ (3 × 150 mL). The
combined organic layers were washed with brine, dried over MgSO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by recrystallization (hexane) to afford 9 (2.70 g, 17.5 mmol, 99%) as colorless needles. 

R_f = 0.45 (hexane–AcOEt–AcOH = 1:1:0.04); Mp: 52–54 °C (hexane); IR (KBr) 3407, 3104, 2985, 2949, 2924, 2676, 1713, 1586, 1434, 1415, 1229, 1099, 991, 926, 800 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.20 (3H, s), 2.22 (3H, s), 3.34 (2H, s), 5.88 (1H, s); ¹³C NMR (100 MHz, CDCl₃) δ 11.3, 13.4, 30.8, 107.7, 111.4, 147.2, 149.7, 178.2; HRMS (ESI–TOF) calcd for C₈H₁₀O₃Na ([M + Na]+) 177.0528, found 177.0527; Anal. Calcd for C₈H₁₀O₃: C, 62.33; H, 6.54. Found: C, 62.20, 6.51.

(S)-4-Benzyl-3-[2-(2,5-dimethylfuran-3-yl)acetyl]oxazolidin-2-one (11).

To a stirred solution of 9 (1.75 g, 11.4 mmol) and triethylamine (1.75 mL, 1.26 g, 12.6 mmol) in THF (38 mL) under argon was added dropwise pivaloyl chloride (1.54 mL, 1.51 g, 12.5 mmol) at –78 °C, and the reaction mixture was stirred for 0.5 h at 0 °C. To this mixture was added dropwise a solution of lithium (S)-4-benzyl-2-oxooxazolin-3-ide in THF (42 mL), prepared from (S)-4-benzyloxazolidin-2-one (2.22 g, 12.5 mmol) and n-buthyllithium (1.63 M in hexane, 7.69 mL, 12.5 mmol), at –78 °C. After stirred for 1 h at 0 °C, the reaction was quenched with saturated NH₄Cl aqueous solution (50 mL), and extracted with AcOEt (2 × 120 mL). The combined organic layers was washed with brine, dried over MgSO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 4:1) to afford 11 (3.30 g, 10.5 mmol, 93%) as a colorless oil.

R_f = 0.61 (hexane–AcOEt = 2:1); [α]₀²⁵ +56.4 (c 1.00, CHCl₃); IR (neat) 3029, 2981, 2921, 1781, 1701, 1584, 1454, 1390, 1356, 1211, 1197, 1111, 1052, 994, 762, 747, 703 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.23 (3H, s), 2.24 (3H, s), 2.77 (1H, dd, J = 13.3, 9.6 Hz), 3.29 (1H, dd, J = 13.3, 3.2 Hz), 3.94 and 4.01 (2H, ABq, J = 17.0 Hz), 4.18 (1H, A part of ABX, J = 9.2, 3.2 Hz), 4.22 (1H, B part of ABX, J = 9.2, 7.6 Hz), 4.64–4.70 (1H, m), 5.92 (1H, s), 7.16–7.19 (2H, m), 7.24–7.34 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ 11.5, 13.4, 31.9, 37.7, 55.2, 66.1, 107.9, 111.4, 127.3, 128.9 (2C), 129.4 (2C), 135.1, 147.5, 149.6, 153.4, 171.0; HRMS (ESI–TOF) calcd for C₁₈H₁₉NO₄Na ([M + Na]+) 336.1212, found 336.1208.

4-[(1S,2S)-3-((S)-4-Benzyl-2-oxooxazolidin-3-yl)-2-(2,5-dimethylfuran-3-yl)-1-hydroxy-3-oxopropyl]-2-methoxyphenyl 2-nitrobenzenesulfonate (13).
To a stirred solution of 11 (1.31 g, 4.18 mmol) in CH₂Cl₂ (14 mL) were added dropwise N,N-diisopropylethylamine (0.981 mL, 0.728 g, 5.63 mmol), and di-n-butylboryl trifluoromethanesulfonate (1.0 M in CH₂Cl₂, 4.74 mL, 4.74 mmol) at 0 °C. After stirred for 45 min at 0 °C, to this mixture was added dropwise a solution of O-o-Ns-vanillin 12 (1.00 g, 2.96 mmol) in CH₂Cl₂ (10 mL) at −78 °C. After stirred for 2.5 h at −78 °C, the reaction was quenched with MeOH (40 mL) and saturated NH₄Cl aqueous solution (40 mL) at −78 °C, and extracted with CHCl₃ (2 × 200 mL). The combined organic layers were washed with brine, and the washed solution was dried over Na₂SO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford 13 (1.89 g, 2.90 mmol, 98%) as a colorless oil.

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R_f = 0.26 \text{ (hexane–AcOEt = 2:1);} \quad \left[\alpha\right]_D^{25} = +4.7 \text{ (c 1.00, CHCl}_3\text{);} \quad \text{IR (neat) 3502, 3088, 2921, 2850, 1774, 1690, 1604, 1545, 1501, 1385, 1364, 1272, 1199, 1111, 1031, 864, 852, 760 cm}^{-1}; \quad \text{¹H NMR (400 MHz, CDCl}_3\text{)}  \delta 2.04 (3H, s), 2.26 (3H, s), 2.67 (1H, dd, J = 13.6, 9.2 Hz), 2.90–3.06 (1H, br s), 3.09 (1H, dd, J = 13.6, 3.2 Hz), 3.49 (3H, s), 4.02–4.12 (2H, m), 4.53–4.60 (1H, m), 5.15 (1H, d, J = 6.8 Hz), 5.18 (1H, d, J = 6.8 Hz), 6.13 (1H, s), 6.84–6.91 (2H, m); 7.01–7.08 (2H, m); 7.11 (1H, d, J = 8.4 Hz), 7.22–7.29 (3H, m); 7.68–7.75 (1H, m); 7.76–7.85 (2H, m); 8.00–8.05 (1H, m); \text{¹³C NMR (100 MHz, CDCl}_3\text{)}  \delta 11.3, 13.5, 37.3, 47.6, 54.7, 55.5, 56.8, 74.2, 106.4, 111.3, 112.1, 119.2, 123.7, 124.5, 127.3, 128.8 (2C), 129.4 (2C), 129.9, 131.6, 131.8, 134.6, 134.9, 137.7, 141.5, 148.3, 150.1, 150.2, 151.2, 152.7, 172.7; \quad \text{HRMS (ESI–TOF) calcd for C}_{32}H_{30}N_2O_1SNa ([M + Na]^+) 673.1468, found 673.1465.}

4-[(1S,2S)-3-((S)-4-Benzyl-2-oxooxazolidin-3-yl)-2-(2,5-dimethylfuran-3-yl)-3-oxo-1-(triethylsilyloxy)propyl]-2-methoxyphenyl 2-nitrobenzenesulfonate (S3).

To a stirred solution of 13 (500 mg, 0.768 mmol) in CH₂Cl₂ (4 mL) were added dropwise 1,8-diazabicyclo[5.4.0]undec-7-ene (0.689 mL, 703 mg, 4.62 mmol), and triethylsilyl
trifluoromethanesulfonate (0.434 mL, 508 mg, 1.92 mmol) at –78 °C under argon, and the mixture was stirred for 20 h at –50 °C. The reaction was quenched with saturated NH₄Cl aqueous solution (5 mL), and extracted with CHCl₃ (3 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford S₃ (527 mg, 0.689 mmol, 90%) as a colorless gum.

Rₐ = 0.45 (hexane–AcOEt–Et₂O = 2:1:1); [α]D²⁵ +10.9 (c 1.00, CHCl₃); IR (neat) 3028, 2955, 2914, 2877, 1732, 1604, 1548, 1500, 1464, 1417, 1387, 1282, 1266, 1200, 1148, 1111, 1007, 866, 851, 761, 741, 591 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.34 (6H, q, J = 7.9 Hz), 0.71 (9H, t, J = 7.9 Hz), 2.21 (3H, s), 2.25 (3H, s), 2.65 (1H, dd, J = 13.5, 8.9 Hz), 3.06 (1H, dd, J = 13.5, 3.0 Hz), 3.50 (3H, s), 3.92–4.03 (2H, m), 4.36–4.42 (1H, m), 5.00 (1H, d, J = 8.2 Hz), 5.25 (1H, d, J = 8.2 Hz), 6.20 (1H, s), 6.88 (1H, dd, J = 8.2, 1.8 Hz), 6.99 (1H, d, J = 1.4 Hz), 7.01–7.11 (3H, m), 7.20–7.30 (3H, m), 7.67–7.75 (1H, m), 7.77–7.84 (2H, m), 8.01 (1H, d, J = 8.2 Hz); ¹³C NMR (100 MHz, CDCl₃) δ 4.5 (3C), 6.4 (3C), 11.6, 13.5, 37.3, 49.0, 54.9, 55.6, 65.6, 75.9, 106.7, 111.3, 114.4, 119.4, 123.4, 124.4, 127.2, 128.7 (2C), 129.4 (2C), 129.8, 131.5, 131.7, 134.87, 134.89, 137.4, 144.0, 148.4, 149.2, 149.3, 151.1, 152.9, 171.5; HRMS (ESI–TOF) calcd for C₃₈H₄₄N₂O₄SiNa ([M + Na]+) 787.2333, found 787.2331.

4-[(1S,2R)-2-(2,5-dimethylfuran-3-yl)-3-hydroxy-1-(triethylsilyloxy)propyl]-2-methoxyphenyl 2-nitrobenzenesulfonate (15).

To a stirred suspension of lithium chloride (108 mg, 2.54 mmol) in THF (5 mL) were added sodium borohydride (95.9 mg, 2.54 mmol) at room temperature, and the mixture was stirred for 0.5 h at 40 °C. To this mixture was added dropwise a solution of S₄ (194 mg, 0.254 mmol) in THF (2.5 mL) at 40 °C, and the mixture was stirred for 25 h at 50 °C. The reaction was quenched with saturated NH₄Cl aqueous solution (5 mL), and extracted with CHCl₃ (3 × 20 mL). The combined organic layers were washed with brine, dried over Na₂SO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford 15 (117 mg, 0.198 mmol, 78%) as colorless oil.

Rₐ = 0.50 (hexane–AcOEt = 1:2); [α]D²⁵ –27.0 (c 0.3, CHCl₃); IR (neat) 3582, 3419, 3098, 2955, 2914, 2877, 1732, 1604, 1548, 1500, 1464, 1417, 1387, 1282, 1266, 1200, 1148, 1111, 1007, 866, 851, 761, 741, 591 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 0.41–0.55 (6H, m), 0.82–0.87 (9H, m),
1.72 (3H, s), 1.79 (1H, br s), 2.18 (3H, s), 2.77 (1H, ddd, $J = 7.3$, 7.3, 3.7 Hz), 3.38 (3H, s), 3.70 (1H, dd, $J = 10.5$, 7.3 Hz), 3.84 (1H, dd, $J = 10.5$, 7.3 Hz), 4.93 (1H, d, $J = 3.7$ Hz), 5.77 (1H, s), 6.55 (1H, d, $J = 1.8$ Hz), 6.69 (1H, dd, $J = 8.2$, 1.8 Hz), 7.07 (1H, dd, $J = 8.2$ Hz), 7.65–7.70 (1H, m), 7.78–7.97 (1H, m); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 4.65 (3C), 6.67 (3C), 10.9, 13.4, 46.9, 55.3, 63.7, 74.9, 106.8, 111.3, 115.1, 118.4, 123.3, 124.6, 130.0, 131.6 (2C), 134.7, 137.1, 144.2, 148.0, 148.5, 148.8, 150.7; HRMS (ESI–TOF) calcd for C$_{28}$H$_{37}$NO$_9$SSiNa ([M + Na]$^+$) 614.1856, found 614.1860.

4-[(1R,3S,3aR,6S,7aR)-1,6-Dimethylhexahydro-1H-1,6-epoxyfuro[3,4-c]pyran-3-yl]-2-methoxyphenyl 2-nitrobenzenesulfonate (16).

To a stirred solution of 15 (74.0 mg, 0.125 mmol) in THF (1 mL) was added concentrated H$_2$SO$_4$ (0.200 mL) at room temperature under argon, and the mixture was stirred for 8 h at the same temperature. The reaction was carefully poured into saturated NaHCO$_3$ aqueous solution, and extracted with CHCl$_3$ (3 × 30 mL). The combined organic layers were washed with brine, dried over MgSO$_4$. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 1:3) to afford 16 (37.0 mg, 0.0775 mmol, 62%) as a colorless oil, and diol 14 (2.2 mg, 0.00461 mmol, 4%) as a colorless oil.

Data of 16

$R_f = 0.57$ (hexane–AcOEt = 1:9); [α]$_D^{25}$ +33.3 (c 0.55, CHCl$_3$); IR (neat) 3502, 3096, 2985, 2936, 2879, 2360, 2341, 1732, 1604, 1546, 1505, 1465, 1453, 1385, 1274, 1200, 1166, 1112, 1059, 1032, 942, 896, 852, 758, 592 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.48 (3H, s), 1.60 (3H, s), 1.88 (1H, dd, $J = 12.4$, 4.1 Hz), 2.26 (1H, d, $J = 12.4$ Hz), 2.45–2.50 (1H, m), 2.68 (1H, dd, $J = 10.1$, 3.7 Hz), 3.57 (3H, s), 3.75–3.78 (2H, m), 4.98 (1H, d, $J = 3.7$ Hz), 6.82–6.86 (2H, m), 7.15 (1H, d, $J = 8.7$ Hz), 7.68–7.74 (1H, m), 7.79–7.84 (1H, m), 7.85–7.88 (1H, m), 8.03 (1H, d, $J = 7.8$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 22.5, 24.7, 33.2, 45.5, 48.0, 55.6, 63.0, 84.6, 106.1, 110.2, 115.5, 117.8, 124.3, 124.7, 130.2, 131.6, 131.9, 134.8, 137.5, 143.5, 148.4, 151.5; HRMS (ESI–TOF) calcd for C$_{22}$H$_{23}$NO$_9$SSNa ([M + Na]$^+$) 500.0991, found 500.0994.

Data of diol 14

$R_f = 0.56$ (hexane–AcOEt = 1:19); [α]$_D^{25}$ −20.2 (c 0.27, CHCl$_3$); IR (neat) 3558, 3399, 3099, 3008, 2921, 1717, 1604, 1546, 1502, 1465, 1419, 1384, 1271, 1199, 1175, 1110, 1059, 1031, 864, 853, 864.
765 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.52–1.70 (1H, br s), 1.87 (3H, s), 2.23 (3H, s), 2.34–2.42 (1H, br s), 2.80–2.86 (1H, m), 3.49 (3H, s), 3.72–3.76 (2H, m), 4.92 (1H, d, \(J = 5.0\) Hz), 5.95 (1H, s), 6.74 (1H, s), 6.80 (1H, dd, \(J = 8.7, 1.4\) Hz), 7.13 (1H, d, \(J = 8.2\) Hz), 7.71 (1H, ddd, \(J = 8.2, 7.8, 1.4\) Hz), 7.81 (1H, ddd, \(J = 8.2, 7.8, 1.4\) Hz), 7.86 (1H, ddd, \(J = 8.2, 1.4\) Hz), 8.02 (1H, d, \(J = 8.2, 1.4\) Hz); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 11.2, 13.5, 46.3, 55.9, 64.0, 74.4, 106.0, 111.0, 114.8, 118.6, 123.7, 124.7, 130.2, 131.6, 131.8, 134.8, 137.5, 143.4, 148.4, 148.5, 150.1, 151.2; HRMS (ESI–TOF) calcd for C\(_{22}\)H\(_{23}\)NO\(_9\)SNa ([M + Na]\(^{+}\)) 500.0991, found 500.0987.

4-[(1\(R\),3\(S\),3\(a\)\(R\),6\(S\),7\(a\)\(R\))-1,6-dimethylhexahydro-1\(H\)-1,6-epoxyfuro[3,4-c]pyran-3-yl]-2-methoxyphenol [catunaregin (1)].

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\begin{align*}
\text{Me} & \quad \text{O} & \quad \text{Me} & \quad \text{O–Ns} \\
\text{O–Me} & \quad \text{O} & \quad \text{O} \\
\text{H} & & & \quad \text{H} \\
\end{align*}
\]

\[\text{Me} \quad \text{O} & \quad \text{Me} & \quad \text{O} \\
\text{O–Me} & \quad \text{O} & \quad \text{O} \\
\text{H} & & & \quad \text{H} \\
\]

To a stirred solution of 16 (37.0 mg, 0.0775 mmol) and cesium carbonate (126 mg, 0.387 mmol) in CH\(_3\)CN (1 mL) was added dropwise thiophenol (23.8 \(\mu\)L, 25.6 mg, 0.0232 mmol) at 0 °C, and the mixture was stirred for 2 h at room temperature. The reaction was quenched with saturated NH\(_4\)Cl aqueous solution, and the mixture was extracted with AcOEt (2 × 30 mL). The combined organic layers were washed with brine, dried over MgSO\(_4\). The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 1:9) to afford 1 (22.6 mg, 0.0773 mmol, 100%) as a colorless oil.

\(R_f = 0.67\) (hexane–AcOEt = 1:9); \([\alpha]_{D}^{25} +38.5\) (c 0.350, MeOH); \([\alpha]_{D}^{24} +40.3\) (c 0.405, CHCl\(_3\)); IR (neat) 3408, 2984, 2937, 2879, 1608, 1603, 1517, 1460, 1450, 1432, 1385, 1331, 1270, 1238, 1195, 1170, 1113, 1057, 1032, 942, 847, 819, 794, 762 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.49 (3H, s), 1.60 (3H, s), 1.88 (1H, dd, \(J = 12.3, 3.7\) Hz), 2.26 (1H, d, \(J = 12.3\) Hz), 2.46–2.52 (1H, m), 2.71 (1H, dd, \(J = 10.1, 3.7\) Hz), 3.73–3.78 (2H, m), 3.91 (3H, s), 4.95 (1H, d, \(J = 4.1\) Hz), 5.60 (1H, s), 6.77–6.83 (2H, m), 6.86–6.90 (1H, m); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 22.6, 24.8, 33.3, 45.7, 47.8, 55.9, 62.9, 85.3, 105.9, 108.6, 114.4, 115.3, 118.8, 134.4, 145.2, 146.5; HRMS (ESI–TOF) calcd for C\(_{16}\)H\(_{20}\)O\(_5\)Na ([M + Na]\(^{+}\)) 315.1208, found 315.1201.
Syntheses of (S)- and (R)-MTPA esters, and Δδ values of the Mosher’s esters.

(S)-(1S,2S)-3-[(S)-4-Benzyl-2-oxooxazolidin-3-yl]-2-(2,5-dimethylfuran-3-yl)-1-[3-methoxy-4-(2-nitrophenylsulfonoyloxy)phenyl]-3-oxopropyl 3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate (S4a).

To a stirred solution of 13 (50.0 mg, 0.0768 mmol) in CH$_2$Cl$_2$ (1 mL) was added pyridine (31.0 μL, 30.4 mg, 0.384 mmol), and (R)-(−)-α-methoxy-α-trifluoromethylphenylacetyl chloride (28.8 μL, 38.8 mg, 0.154 mmol) in 0 °C. After stirred for 5 h at room temperature, the reaction was quenched with saturated NH$_4$Cl aqueous solution (3 mL), and extracted with CHCl$_3$ (3 × 10 mL). The combined organic layers were washed with brine, dried over Na$_2$SO$_4$. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford S4a (51.4 mg, 59.3 mmol, 77%) as colorless amorphous solid.

R$_f$ = 0.56 (hexane–AcOEt = 1:1); [α]$_D^{20}$ –12.5 (c 0.34, CHCl$_3$); IR (neat) 3430, 3027, 2950, 2922, 2849, 1774, 1752, 1696, 1638, 1606, 1546, 1502, 1452, 1389, 1362, 1271, 1255, 1201, 1182, 1113, 1022, 999, 863, 851, 760, 717 cm$^{-1}$; $^1$H NMR (600 MHz, CDCl$_3$) δ 1.93 (3H, s), 2.25 (3H, s), 2.68 (1H, dd, $J$ = 13.6, 8.3 Hz), 2.95 (1H, dd, $J$ = 13.6, 3.4 Hz), 3.26 (3H, m), 3.54 (3H, s), 4.02 (1H, A part of ABX, $J$ = 9.0, 3.6 Hz), 4.08 (1H, B part of ABX, $J$ = 9.0, 8.4 Hz), 4.46–4.52 (1H, m), 5.65 (1H, d, $J$ = 10.0 Hz), 6.10 (1H, s), 6.49 (1H, d, $J$ = 10.0 Hz), 6.92–6.97 (2H, m), 7.02 (1H, d, $J$ = 1.9 Hz), 7.07 (1H, dd, $J$ = 8.4, 1.8 Hz), 7.14–7.19 (3H, m), 7.20–7.23 (3H, m), 7.27–7.29 (2H, m), 7.35–7.39 (1H, m), 7.72–7.79 (2H, m), 7.80–7.84 (1H, m), 8.09 (1H, d, $J$ = 7.9 Hz); $^{13}$C NMR (150 MHz, CDCl$_3$) δ 11.2, 13.6, 37.1, 45.1, 54.5, 55.3, 55.7, 65.7, 77.04, 84.3 (q, $J$ = 27.5 Hz), 105.8, 112.56, 112.64, 120.5, 123.2 (q, $J$ = 288.7 Hz), 124.3, 124.4, 126.9 (2C), 127.3, 128.2 (2C), 128.7 (2C), 129.36, 129.42 (2C), 129.9, 131.5, 131.8, 132.0, 134.4, 135.0, 137.7, 138.4, 148.4, 149.9, 150.1, 151.6, 152.9, 165.5, 170.1; HRMS (ESI–TOF) calcd for C$_{42}$H$_{37}$F$_3$N$_2$O$_{13}$SNa ([M + Na$^+$]) 889.1866, found 889.1856.

(R)-(1S,2S)-3-[(S)-4-benzyl-2-oxooxazolidin-3-yl]-2-(2,5-dimethylfuran-3-yl)-1-(3-methoxy-4-((2-nitrophenyl)sulfonoyloxy)phenyl)-3-oxopropyl 3,3,3-Trifluoro-2-methoxy-2-phenylpropanoate (S4b).

To a stirred solution of 13 (50.0 mg, 0.0768 mmol) in CH$_2$Cl$_2$ (1 mL) was added pyridine (31.0 μL, S8
30.4 mg, 0.384 mmol), and (S)-(+)–α-methoxy-α-trifluoromethylphenylacetyl chloride (28.8 μL, 38.8 mg, 0.154 mmol) in 0 °C. After stirred for 5 h at room temperature, the reaction was quenched with saturated NH₄Cl aqueous solution (3 mL), and extracted with CHCl₃ (3 × 10 mL). The combined organic layers were washed with brine, dried over Na₂SO₄. The dried solution was filtered, and the filtrate was concentrated in vacuo. The resulting residue was purified by column chromatography (hexane–AcOEt, 2:1) to afford S4b (61.9x mg, 71.4 mmol, 93%) as colorless amorphous solid.

Rf = 0.63 (hexane–AcOEt = 1:1); [α]D²⁰ +16.8 (c 0.62, CHCl₃); IR (neat) 3432, 3026, 2950, 2923, 2850, 1775, 1753, 1696, 1637, 1606, 1546, 1502, 1452, 1389, 1365, 1270, 1255, 1202, 1182, 1113, 1030, 1000, 864, 851, 760 cm⁻¹; ¹H NMR (600 MHz, CDCl₃) δ 2.18 (3H, s), 2.28 (3H, s), 2.69 (1H, dd, J = 13.6, 8.3 Hz), 2.98 (1H, dd, J = 13.6, 3.2 Hz), 3.26 (3H, m), 3.41 (3H, s), 4.00 (1H, A part of ABX, J = 9.1, 3.0 Hz), 4.05 (1H, B part of ABX, J = 9.1, 8.3 Hz), 4.46–4.51 (1H, m), 5.66 (1H, d, J = 10.2 Hz), 6.20 (1H, s), 6.34 (1H, d, J = 10.2 Hz), 6.82 (1H, d, J = 1.9 Hz), 6.94–6.99 (3H, m), 7.06–7.12 (3H, m), 7.21–7.27 (5H, m), 7.33–7.37 (1H, m), 7.73–7.77 (2H, m), 7.80–7.84 (1H, m), 8.08–8.11 (1H, m); ¹³C NMR (150 MHz, CDCl₃) δ 11.5, 13.6, 37.1, 45.3, 54.5, 55.1, 55.5, 65.7, 77.9, 84.5 (q, J = 27.5 Hz), 105.7, 112.0, 113.4, 120.7, 123.2 (q, J = 288.7 Hz), 124.1, 124.4, 127.1 (2C), 127.3, 128.2 (2C), 128.8 (2C), 129.4 (2C), 129.5, 129.9, 131.6, 131.81, 131.84, 134.5, 134.9, 137.5, 138.3, 148.4, 150.1, 150.3, 151.4, 152.8, 165.3, 170.1; HRMS (ESI–TOF) calcd for C₄₂H₃₇F₃N₂O₁₃SNa ([M + Na⁺]⁺) 889.1866, found 889.1863.

S3a: (S)-MTPA ester (from (R)-MTPACl)
S3b: (R)-MTPA ester (from (S)-MTPACl)
S10
(+)-catunaregin (1)
S4b: R = (R)-MTPA from (S)-MTPACl