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Supporting Information

General. All operations were performed under an argon atmosphere. Tetrahydrofuran(THF) was distilled from benzophenone ketyl. ^1H NMR (500 MHz) and ^{13}C NMR (125 MHz) spectra were recorded on a Bruker AM500 spectrometer in CDCl_3 solutions using CHCl_3 (^1H , δ 7.24) and CDCl_3 (^{13}C , δ 77.0) as internal standards. IR spectra were recorded on a Horiba FT 300-S spectrophotometer. High-resolution mass spectra were obtained with a JMS-SX102A mass spectrometer at ionization energy of 70eV. Silica-gel column chromatography was carried out with Merck Kieselgel 60 Art.7734. Preparative TLC was performed on a silica-gel (Wakogel B-5F).

Pentacarbonyl[(1-methoxy)alkylidene]tungsten(0) and pentacarbonyl[1-methoxy-2-methyl-1-propylidene]molybdenum(0) were prepared according to the procedure of Harvey's.¹ These complexes are known in the literatures.^{2,3}

General Procedure for the Reaction of Propargyl Metallic Species with TsNCO

To a THF solution (5 mL) of an alkyne (0.90 - 1.2 mmol) was added dropwise a 1.56 M hexane solution (0.40-0.53 mL, 0.62 - 0.83 mmol) of *n*-butyllithium at -78°C . After the mixture was stirred for 30 min at this temperature, a THF solution (2 mL) of a tungsten or a molybdenum carbene complex (0.30 mmol) was slowly added to the mixture. The yellow or red color of the carbene complex changed to pale yellow within a few min. After the mixture was stirred for 1 h at -78°C , a THF solution (4 mL) of tosyl isocyanate (2.0 mmol) was added and the mixture was stirred overnight at -78°C . Then trifluoroacetic acid (0.50 mL) was added at -78°C and the mixture was warmed up to rt. After the mixture was stirred overnight at rt, triethylamine (1.0 mL) was added at 0°C . Then pH 7 phosphate buffer was added and the organic layer was extracted three times with ethyl acetate and dried over MgSO_4 . After removal of the solvent, the residue was dissolved in 10 mL of dichloromethane and a 1.0 M hexane solution of ethylaluminum dichloride (2.0 mL, 2 mmol) was added dropwise at -78°C . After the mixture was stirred at this temperature for 3 h, 10% aqueous Rochelle salt solution was added carefully to the reaction mixture. The aqueous layer was extracted three times with ethyl acetate and the combined extracts were dried over MgSO_4 . After

removal of the solvent, the residue was purified using preparative TLC(hexane: ethyl acetate = 6: 4), yielding the corresponding *N*-cyclized product **3**.

As shown in Scheme 1, when the residue was purified by preparative TLC (hexane: ethyl acetate = 4: 1) without the treatment with ethylaluminum dichloride, a mixture of *O*-cyclized product **2a** and *N*-cyclized product **3a** was obtained.

N-Tosyl-2-imino-5-(1-methyl)ethyl-5-methoxy-3-phenylfuran(**2a**)

yield 69% (using the tungsten complex), 92% (using the molybdenum complex)

IR(neat) 3086, 2970, 1650, 1325, 1184 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.82 (3H, d, $J = 6.9$ Hz), 0.91 (3H, d, $J = 6.9$ Hz), 2.14 (1H, sept, $J = 6.9$ Hz), 2.39 (3H, s), 3.04 (3H, s), 6.98 (1H, s), 7.27 (2H, d, $J = 8.2$ Hz), 7.37-7.39 (3H, m), 7.78-7.80 (2H, m), 7.92 (2H, d, $J = 8.2$ Hz).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 16.5, 17.1, 21.5, 35.7, 51.6, 118.8, 127.9, 128.0, 128.2, 128.6, 129.1, 130.1, 138.2, 139.0, 142.0, 143.4, 166.0.

HRMS Found: m/z 385.1349

Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}$: 385.1352.

N-Tosyl-4-(1-methyl)ethyl-4-methoxy-2-phenyl-2-butene-4-lactam(**3a**)

yield 18% (using the tungsten complex), trace(using the molybdenum complex); 79% (using the molybdenum complex. with EtAlCl_2 treatment)

IR(neat) 2931, 1730, 1597, 1362, 1171 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.77 (3H, d, $J = 6.9$ Hz), 1.19 (3H, d, $J = 6.9$ Hz), 2.40 (3H, s), 3.11 (3H, s), 3.15 (1H, sept, $J = 6.9$ Hz), 7.00 (1H, s), 7.31 (2H, d, $J = 8.3$ Hz), 7.35-7.37 (3H, m), 7.72-7.74 (2H, m), 8.07 (2H, d, $J = 8.3$ Hz).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 17.3, 18.4, 21.6, 34.6, 52.3, 102.4, 127.4, 128.6, 128.8, 129.1, 129.2, 130.0, 135.9, 137.7, 139.9, 145.0, 166.0.

Anal Found: C, 65.40; H, 6.01; N, 3.68; S, 8.38%

Calcd for $\text{C}_{21}\text{H}_{23}\text{NO}_4\text{S}$: C, 65.42; H, 6.01; N, 3.63; S, 8.32%.

N-Tosyl-4-(1-methyl)ethyl-2-hexyl-4-methoxy-2-butene-4-lactam

yield 83%

IR(neat) 2931, 2858, 1728, 1468, 1174 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.67 (3H, d, $J = 6.9$ Hz), 0.82 (3H, t, $J = 6.8$ Hz), 1.08 (3H, d, $J = 6.9$ Hz), 1.22-1.28 (6H, m), 1.46 (2H, quint, $J = 7.4$ Hz), 2.20 (2H, tt, $J = 1.4$, 7.4 Hz), 2.38 (3H, s), 3.00 (3H, s), 3.03 (1H, sept, $J = 6.9$ Hz), 6.43 (1H, t, $J = 1.4$ Hz), 7.28 (2H, d, $J = 8.3$ Hz), 8.00 (2H, d, $J = 8.3$ Hz).

^{13}C -NMR(CDCl_3): 13.9, 17.2, 18.4, 21.6, 22.4, 25.0, 27.3, 28.7, 31.3, 34.2, 52.0, 103.4, 128.6, 129.2, 136.2, 139.5, 141.5, 144.8, 168.0.

HRMS Found: m/z 393.1995

Calcd for $\text{C}_{21}\text{H}_{31}\text{NO}_4\text{S}$: 393.1975.

N-Tosyl-4-methoxy-2,4-diphenyl-2-butene-4-lactam

yield 80%

IR(neat) 3072, 2937, 1732, 1373, 1174 cm^{-1} .

^1H -NMR(CDCl_3): 2.35 (3H, s), 3.50 (3H, s), 6.91 (1H, s), 7.12 (2H, d, $J = 8.2$ Hz), 7.31-7.38 (6H, m), 7.44-7.45 (2H, m), 7.49 (2H, d, $J = 8.3$ Hz), 7.78-7.80 (2H, m).

^{13}C -NMR(CDCl_3): 21.5, 51.8, 96.3, 126.5, 127.5, 128.4, 128.7, 128.8, 128.8, 128.9, 130.0, 134.7, 135.6, 135.8, 143.8, 144.8, 166.9.

HRMS Found: m/z 419.1168

Calcd for $\text{C}_{24}\text{H}_{21}\text{NO}_4\text{S}$: 419.1192.

N-Tosyl-2-hexyl-4-methoxy-4-phenyl-2-butene-4-lactam

yield 87%

IR(neat) 2952, 2925, 1734, 1597, 1450, 1373 cm^{-1} .

^1H -NMR(CDCl_3): 0.83 (3H, t, $J = 6.9$ Hz), 1.21-1.32 (6H, m), 1.45-1.54 (2H, m), 2.27 (2H, tq, $J = 1.5, 6.9$ Hz), 2.35 (3H, s), 3.39 (3H, s), 6.37 (1H, t, $J = 1.5$ Hz), 7.11 (2H, d, $J = 8.2$ Hz), 7.25-7.36 (5H, m), 7.45 (2H, d, $J = 8.2$ Hz).

^{13}C -NMR(CDCl_3): 13.9, 21.5, 22.4, 24.8, 17.2, 18.8, 31.3, 51.5, 97.3, 126.3, 128.3, 128.5, 128.6, 128.9, 135.9, 136.1, 138.7, 144.0, 144.6, 168.4.

HRMS Found: m/z 427.1812

Calcd for $\text{C}_{24}\text{H}_{29}\text{NO}_4\text{S}$: 427.1819.

TOTAL SYNTHESIS OF PI-091

1-Iodo-2-methyl-1-octene(7)

To a 1,2-dichloroethane solution (10 mL) of zirconocene dichloride (0.57 g, 2.2 mmol) was added a 2 M hexane solution of trimethylaluminum (5 mL, 10 mmol) at 0 °C. To this solution, a 1,2-dichloroethane solution (4 mL) of 1-octyne (0.56 g, 5.1 mmol) was added dropwise at 0 °C. After the solution was stirred for 15 h at 0 °C, a THF solution (10 mL) of iodine (0.80 g, 3.1 mmol) was added at -35 °C and the mixture was slowly warmed up to rt over 3 h. Then the reaction mixture was poured

carefully into 2M HCl (30 mL). The aqueous layer was extracted three times with pentane and the combined extracts were dried over MgSO₄. After removal of the solvent, the crude product was purified by silica gel chromatography (pentane), yielding 1.0 g of 1-iodo-2-methyl-1-octene (78%).

IR(neat) 2954, 2927, 1460, 1271, 1142 cm⁻¹.

¹H-NMR(CDCl₃): 0.86 (3H, t, *J* = 6.9 Hz), 1.22-1.30 (6H, m), 1.40 (2H, quint, *J* = Hz), 1.80 (3H, s), 2.17 (2H, t, *J* = 7.4 Hz), 5.83 (1H, s).

¹³C-NMR(CDCl₃): 14.1, 22.6, 23.8, 27.7, 28.7, 31.6, 40.0, 74.3, 148.3.

HRMS Found: *m/z* 252.0349

Calcd for C₉H₁₇I: 252.0375.

4-Methyl-1-trimethylsilyl-3-decen-1-yne(8)

To a piperidine solution (10 mL) of 2-methyl-1-iodo-1-octene (9.2 g, 0.036 mol) was added bis(acetonitrile)dichloro palladium(II) (0.63g, 2.4 mmol), a piperidine solution (5 mL) of trimethylsilylacetylene (3.6 g, 0.036 mmol) and copper iodide (0.69 g, 3.6 mmol) at rt. The reaction mixture was warmed up to 40 °C for 4 h. After the mixture was cooled to rt, the reaction was quenched by saturated aqueous ammonium chloride. The aqueous layer was extracted three times with pentane and the combined extracts were dried over MgSO₄. After removal of solvent, the crude product was purified by silica gel chromatography (pentane), yielding 6.3 g of 4-methyl-1-trimethylsilyl-3-decen-1-yne(82 %).

IR(neat) 2958, 2929, 2858, 2133, 1462, 1250, 845 cm⁻¹.

¹H-NMR(CDCl₃): 0.17 (9H, s), 0.86 (3H, t, *J* = 6.9 Hz), 1.21-1.31 (6H, m), 1.38 (2H, quint, *J* = 7.6 Hz), 1.87 (3H, s), 2.04 (2H, t, *J* = 7.6 Hz), 5.28 (1H, s).

¹³C-NMR(CDCl₃): 0.1, 14.1, 19.4, 22.6, 27.5, 28.9, 31.7, 38.7, 96.3, 103.6, 104.7, 154.6.

HRMS Found: *m/z* 207.1601

Calcd for C₁₃H₂₃Si: 207.1569 (M⁺- CH₃).

4-Methyl-3-decen-1-yne(6)

To a dichloromethane (40 mL) solution of 4-methyl-1-trimethylsilyl-3-decen-1-yne (4.8 g, 22 mmol) was added a 1.0M THF solution of tetrabutylammonium fluoride(21 mL, 21 mmol) at 0 °C. After the mixture was stirred for 2 h at 0 °C, the reaction was quenched with pH 7 phosphate buffer. The aqueous layer was extracted three times with pentane and the combined extracts were dried over Na₂SO₄. After the

evaporation of the solvent, the residue was purified by silica gel chromatography (pentane), yielding 3.0 g of 4-methyl-3-decen-1-yne(93%).

IR(neat) 3311, 2956, 2929, 2856, 2100, 1462 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.86 (3H, t, $J = 6.9$ Hz), 1.23-1.28 (6H, m), 1.39 (2H, quint, $J = 7.5$ Hz), 1.87 (3H, s), 2.05 (2H, t, $J = 7.5$ Hz), 2.96 (1H, s), 5.24 (1H, s).

$^{13}\text{C-NMR}(\text{CDCl}_3)$:14.1, 19.2, 22.6, 27.4, 28.9, 31.7, 38.6, 79.3, 81.9, 103.6, 154.5.

HRMS Found: m/z 150.1413

Calcd for $\text{C}_{11}\text{H}_{18}$: 150.1409.

N-Tosyl-4-(1-methyl)ethyl-4-methoxy-2-[(*E*)-(2-methyl)-1-octenyl]-2-butene-4-lactam(**5**)

To a THF solution (5 mL) of 4-methyl-3-decen-1-yne (184 mg, 1.2 mmol) was added a hexane solution of *n*-butyllithium (0.65 mL, 1.65 M, 1.1 mmol) at -78°C . After the mixture was stirred for 30 min, a THF solution (7.5 mL) of pentacarbonyl[1-methoxy-2-methylpropylidene]molybdenum(0) (249 mg, 0.77 mmol) was added slowly. After the reaction mixture was stirred for 40 min, tosyl isocyanate (511 mg, 2.6 mmol) in THF(3 mL) was added. The color of the reaction mixture changed from pale yellow to wine red. The reaction mixture was stirred overnight at -78°C and then trifluoroacetic acid (1.0 mL) was added. The mixture was warmed up to rt and was further stirred for 3 h. Again it was cooled to 0°C , and 1.5 mL of triethylamine was added and then pH 7 phosphate buffer was added. The aqueous layer was extracted three times with ethyl acetate, and the combined extracts were dried over MgSO_4 . After evaporation of the solvent, the crude product was dissolved in dichloromethane (10 mL) and a 1 M hexane solution of ethylaluminum dichloride (3.0 mL, 3.0 mmol) was added at -78°C . After the mixture was stirred for 1.5 h, 10% aqueous Rochelle salt was carefully added to the reaction mixture. The aqueous layer was extracted three times with ethyl acetate, and the combined extracts were dried over MgSO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane: ethyl acetate = 3: 1), yielding 292 mg (87%) of *N*-tosyl-4-(1-methyl)ethyl-4-methoxy-2-[(*E*)-(2-methyl)-1-octenyl]-2-butene-4-lactam .

IR(neat) 2918, 2891, 1724, 1458, 1178 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.72 (3H, d, $J = 6.9$ Hz), 0.84 (3H, d, $J = 6.9$ Hz), 1.13 (3H, d, $J = 6.9$ Hz), 1.24-1.39 (6H, m), 1.42 (2H, quint, $J = 7.5$ Hz), 1.80 (3H, s), 2.12

(2H quint, $J = 7.5$ Hz), 2.40 (3H, s), 3.06 (3H, s), 3.10 (1H, sept, $J = 6.9$ Hz), 5.90 (1H, s), 6.47 (1H, s), 7.29 (2H, d, $J = 8.1$ Hz), 8.04 (2H, d, $J = 8.1$ Hz).

^{13}C -NMR(CDCl_3): 14.0, 17.4, 18.5, 19.6, 21.6, 22.5, 27.7, 29.0, 31.6, 34.5, 41.1, 52.2, 103.6, 111.9, 128.8, 129.2, 135.4, 136.1, 137.5, 144.9, 149.4, 168.1.

HRMS Found: m/z 433.2267

Calcd for $\text{C}_{24}\text{H}_{35}\text{NO}_4\text{S}$: 433.2287.

N-Tosyl-4-(1-methyl)ethyl-4-methoxy-2-[(1*S*, 2*S*)-1,2-dihydroxy-2-methyloctyl]-2-butene-4-lactam(4)

This dihydroxylation reaction was carried out according to Sharpless' procedure.⁴

AD-mix α (1.1 g) was dissolved in *t*-butyl alcohol and water (3 mL each) and methanesulfonamide (90 mg, 0.92 mmol) was added at 0 °C. A *t*-butyl alcohol and water (4: 1) solution (5 mL) of *N*-tosyl-4-(1-methyl)ethyl-4-methoxy-2-[(*E*)-(2-methyl)-1-octenyl]-2-butene-4-lactam (191 mg, 0.44 mmol) was added at 0 °C. The reaction mixture was stirred for 8 h at 0 °C and then a small amount of Na_2SO_3 was added, followed by the addition of pH 7 phosphate buffer. The organic layer was extracted three times with ethyl acetate and the combined extracts were dried over Na_2SO_4 . The solvent was removed under reduced pressure and the residue was purified by preparative TLC (hexane: ethyl acetate = 9: 4), yielding **4a** (less polar isomer) 76 mg (38%) and **4b** (more polar isomer) 78 mg (39%). The optical purities of **4a** and **4b** were determined to be 91% ee and 93% ee by using chiral shift reagents, $\text{Eu}(\text{hfc})_3$ and $\text{Pr}(\text{hfc})_3$ respectively.

4a

IR(KBr) 3525(br), 2931, 1732, 1371, 1174 cm^{-1} .

^1H -NMR(CDCl_3): 0.69 (3H, d, $J = 6.9$ Hz), 0.85 (3H, t, $J = 6.8$ Hz), 1.01 (3H, s), 1.11 (3H, d, $J = 6.9$ Hz), 1.24-1.34 (8H, m), 1.47-1.51 (2H, m), 2.41 (3H, s), 2.81 (1H, s), 3.06 (3H, s), 3.07 (1H, sept, $J = 6.9$ Hz), 3.16 (1H, d, $J = 7.0$ Hz), 4.27 (1H, d, $J = 7.0$ Hz), 6.78 (1H, s), 7.30 (2H, d, $J = 8.3$ Hz), 8.00 (2H, d, $J = 8.3$ Hz).

^{13}C -NMR(CDCl_3): 14.0, 17.3, 18.4, 21.7, 22.6, 23.6, 29.7, 31.7, 34.4, 38.8, 52.5, 72.3, 74.0, 104.0, 128.6, 129.4, 140.5, 144.5, 145.2, 168.2.

HRMS Found: m/z 382.1337

Calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_6\text{S}$: 382.1325 (M - C_6H_{13}).

$[\alpha]^{27}_{\text{D}} -9.71^\circ$ (c, 0.79, CH_2Cl_2)

4b

IR(neat) 3512(br), 2931, 1732, 1371, 1174 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.76 (3H, d, $J = 7.0$ Hz), 0.85 (3H, t, $J = 6.9$ Hz), 1.02 (3H, s), 1.12 (3H, d, $J = 7.0$ Hz), 1.22-1.34 (8H, m), 1.49 (2H, quint, $J = 8.1$ Hz), 2.41 (3H, s), 2.58 (1H, s), 3.00 (3H, s), 3.03 (1H, d, $J = 6.7$ Hz), 3.08 (1H, sept, $J = 6.9$ Hz), 4.30 (1H, d, $J = 6.7$ Hz), 6.80 (1H, s), 7.31 (2H, d, $J = 8.3$ Hz), 8.01 (2H, d, $J = 8.3$ Hz).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 14.0, 17.4, 18.4, 21.7, 22.5, 23.6, 29.7, 31.7, 34.6, 38.8, 52.5, 72.0, 74.1, 104.2, 128.7, 129.3, 140.6, 144.4, 145.2, 168.2.

HRMS Found: m/z 382.1295

Calcd for $\text{C}_{18}\text{H}_{24}\text{NO}_6\text{S}$: 382.1325.

$[\alpha]^{26}_{\text{D}} +23.1^\circ$ (c, 0.81, CH_2Cl_2)

4-(1-Methyl)ethyl-4-methoxy-2-[(1*S*,2*S*)-1,2-dihydroxy-2-methyloctyl]-2-butene-4-lactam(**9a**)

To a methanol solution (6 mL) of **4a** (51 mg, 0.11 mmol) was added a 0.1M THF solution of samarium diiodide (6.5 mL, 0.65 mmol) dropwise at -78°C . The reaction mixture was quenched with 4% aqueous sodium carbonate containing a small amount of sodium sulfite. The aqueous layer was extracted three times with ethyl acetate, and the combined extracts were dried over MgSO_4 . After removal of the solvent, the residue was purified using preparative TLC (hexane: ethyl acetate = 1: 1), giving 29 mg of **9a** (85%).

IR(neat) 3248(br), 2958, 2924, 1693, 1385, 1124 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.85 (3H, d, $J = 6.9$ Hz), 0.92 (3H, d, $J = 6.9$ Hz), 0.94 (3H, d, $J = 6.9$ Hz), 1.07 (3H, s), 1.22-1.37 (8H, m), 1.54 (2H, t, $J = 7.9$ Hz), 2.04 (1H, sept, $J = 6.9$ Hz), 3.15 (3H, s), 3.63 (1H, d, $J = 7.9$ Hz), 4.10 (1H, s), 4.25 (1H, d, $J = 7.9$ Hz), 6.42 (1H, s), 6.60 (1H, s).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 14.1, 17.1, 17.4, 22.6, 23.2, 23.8, 29.8, 31.8, 35.3, 38.5, 50.7, 73.4, 73.6, 94.8, 140.1, 145.7, 172.6.

HRMS Found: m/z 313.0425

Calcd for $\text{C}_{17}\text{H}_{31}\text{NO}_4$: 313.2254.

$[\alpha]^{30}_{\text{D}} +10.6^\circ$ (c, 0.48, MeOH)

4-(1-Methyl)ethyl-4-methoxy-2-[(1*S*,2*S*)-1,2-dihydroxy-2-methyloctyl]-2-butene-4-lactam(**9b**)

9b was prepared by the same procedure for the synthesis of **9a**.

IR(neat) 3249(br), 2956, 2924, 1695, 1377, 1126 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.85 (3H, t, $J = 6.9$ Hz), 0.94 (3H, d, $J = 6.9$ Hz), 0.95 (3H, d, $J = 6.9$ Hz), 1.09 (3H, s), 1.22-1.38 (8H, m), 1.53 (2H, t, $J = 7.9$ Hz), 2.04 (1H, sept, $J = 6.9$ Hz), 3.11(3H, s), 3.74 (1H, d, $J = 7.9$ Hz), 3.98 (1H, s), 4.26 (1H, d, $J = 7.9$ Hz), 6.58 (1H, s), 6.61 (1H, s).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 14.0, 17.1, 17.3, 22.6, 23.0, 23.7, 29.8, 31.8, 35.2, 38.5, 50.7, 73.5, 73.6, 95.0, 140.3, 145.6, 172.7.

HRMS Found: m/z 298.1991

Calcd for $\text{C}_{17}\text{H}_{31}\text{NO}_4$: 298.2019 (M - CH_3).

$[\alpha]^{29}_{\text{D}} -7.6^\circ$ (c, 0.34, CH_2Cl_2)

4-(1-Methyl)ethyl-4-methoxy-2-[(2S)-2-hydroxy-2-methyloctanoyl]-2-butene-4-lactam(**10a**, **PI-091**)

To a dichloromethane-DMSO solution (1.5 mL each) of **9a** (24 mg, 0.080 mmol) was added a total amount of 0.4 mL of triethylamine and 270 mg (1.7 mmol) of $\text{SO}_3 \cdot \text{pyridine}$ in several portions over 10 h (until the starting material disappeared). The reaction was quenched with pH 7 phosphate buffer. The organic layer was extracted three times with ethyl acetate and the combined extracts were dried over MgSO_4 . After removal of the solvent, the residue was purified by preparative TLC (hexane: ethyl acetate = 7: 3), yielding **10a** 21mg (85%).

IR(neat) 3245(br), 2935, 1705, 1462, 1092 cm^{-1} .

$^1\text{H-NMR}(\text{CDCl}_3)$: 0.83(3H, t, $J = 6.8$ Hz), 0.94(3H, d, $J = 6.9$ Hz), 0.98 (3H, d, $J = 6.9$ Hz), 1.21-1.32(8H, m), 1.34 (3H, s), 1.61-1.69(1H, m), 1.76-1.82 (1H, m), 2.08 (1H, sept, $J = 6.9$ Hz), 3.14 (3H, s), 5.67 (1H, s), 6.74 (1H, s), 7.54 (1H, d, $J = 1.9$ Hz).

$^{13}\text{C-NMR}(\text{CDCl}_3)$: 14.0, 16.9, 17.1, 22.5, 23.3, 23.4, 29.6, 31.7, 35.2, 38.6, 51.1, 78.6, 94.6, 139.5, 158.0, 170.1, 198.6.

HRMS Found: m/z 311.2115

Calcd for $\text{C}_{17}\text{H}_{29}\text{NO}_4$: 311.2098.

$[\alpha]^{27}_{\text{D}} -31.1^\circ$ (c, 0.36, CHCl_3)

4-(1-Methyl)ethyl-4-methoxy-2-[(2S)-2-hydroxy-2-methyloctanoyl]-2-butene-4-lactam(**10b**, **PI-091**)

10b was prepared by the same procedure for the synthesis of **10a**.

IR(neat) 3238(br), 2935, 1722, 1464, 1093 cm^{-1} .

^1H -NMR(CDCl_3): 0.83(3H, t, $J = 6.8$ Hz), 0.94(3H, d, $J = 6.9$ Hz), 0.98 (3H, d, $J = 6.9$ Hz), 1.21-1.28(8H, m), 1.34 (3H, s), 1.59-1.65(1H, m), 1.71-1.79 (1H, m), 2.09 (1H, sept, $J = 6.9$ Hz), 3.15 (3H, s), 5.71 (1H, s), 6.80 (1H, s), 7.55 (1H, d, $J = 2.0$ Hz).

^{13}C -NMR(CDCl_3): 14.0, 16.9, 17.1, 22.5, 23.3(2 peaks), 29.6, 31.7, 35.3, 38.6, 51.2, 78.6, 94.6, 139.5, 158.2, 170.1, 198.6.

HRMS Found: m/z 311.2076

Calcd for $\text{C}_{17}\text{H}_{29}\text{NO}_4$: 311.2098.

$[\alpha]^{26}_{\text{D}}$ -28.7° (c, 0.46, CHCl_3)

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