# Supporting Information

# Asymmetric Synthesis of Actinoidic Acid Derivatives

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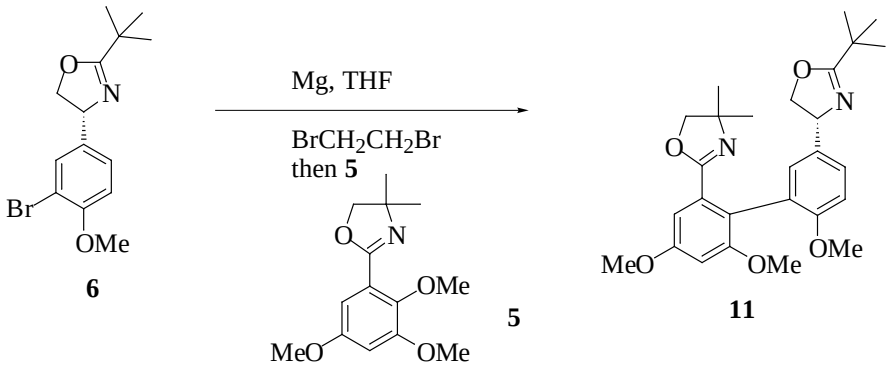
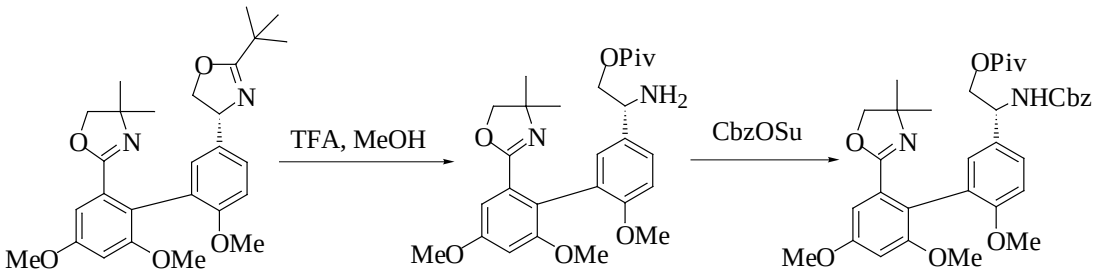


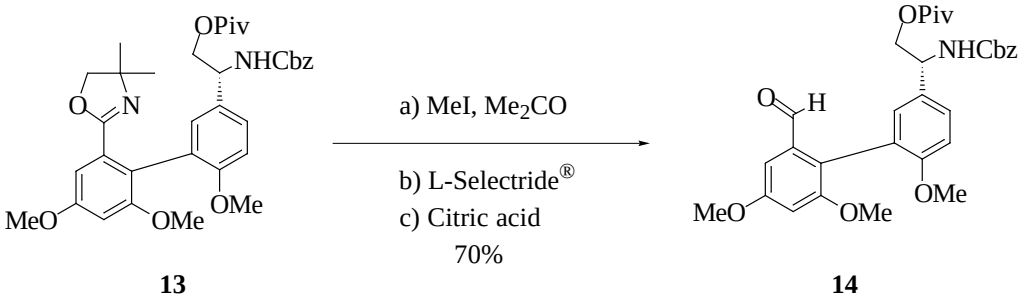

In a two-neck round-bottom flask equipped with a water condenser and a dropping funnel, was placed magnesium (155.0 mg, 6.32 mmol) and flame dried,. A solution of oxazoline **6** (642.0 mg, 2.05 mmol) in anhydrous THF (3 mL) was then introduced and the mixture was heated to 80-90°C. Dibromoethane (455.0 µL, 5.30 mmol) dissolved in anhydrous THF (5 mL) was slowly added via a dropping funnel over 50 min. The reaction mixture was heated to reflux for an additional 30 min before a solution of oxazoline **5** (419 mg, 1.58 mmol) in anhydrous THF (3 mL) was added. After being refluxed for 15 h, the reaction mixture was quenched with aqueous saturated $NH_4Cl$. The aqueous phase was extracted with ether, then $CH_2Cl_2$. The combined organic phases were washed with brine, dried over $Na_2SO_4$, concentrated and the resulting yellow oil was purified by flash chromatography (2/1 Hep/ether, $SiO_2$) to give **11** (640.6 mg; 87%) as a yellow crystalline solid: $[\alpha]_D$ = + 36.5 (*c* 1.0, $CHCl_3$); IR ($CHCl_3$) ν 3697, 2973, 1658, 1602, 1461, 1363, 1270 $cm^{-1}$; $^1H$ NMR ($CDCl_3$, 300 MHz, 2 atropisomers in one to one ratio) δ 1.18 (s, 3H), 1.19 (s, 3H)

1.27 (s, 9H), 3.58 (d, *J* = 1 Hz, 1H), 3.60 (d, *J* = 1 Hz, 1H), 3.68, 3.69 (s, 3H), 3.72 (s, 3H), 3.86 (s, 3H), 4.03, 4.06 (dd, *J* = 7.8, 8.0 Hz, 1H), 4.51, 4.55 (dd, *J* = 2.0, 8.3 Hz, 1H), 5.10 (m, 1H), 6.60 (d, *J* = 2.4 Hz, 1H), 6.86, 6.87 (d, *J* = 7.7 Hz, 1H), 6.86, 6.88 (d, *J* = 2.4 Hz, 1H), 6.91, 6.92 (d, *J* = 2.3 Hz, 1H), 7.13, 7.16 (dd, *J* = 2.3, 7.7 Hz, 1H); $^{13}$C NMR ($CDCl_3$, 75 MHz, 2 atropisomers in one to one ratio) δ 28.0/ 28.1, 29.7, 33.4, 55.5, 55.9, 56.0, 67.1, 68.7/69.2, 74.9/75.1, 79.3/79.4, 101.4, 104.8/104.9, 110.6/110.9, 120.5, 126.1/126.5, 126.3, 129.4/129.8, 130.8, 134.2/134.3, 156.9/157.1, 158.3, 159.7, 163.4/163.6, 174.7; MS (CI) *m/z* 467 $[M+H]^+$; Anal. Calcd. for $C_{27}H_{34}N_2O_5$: C, 69.50; H 7.34; N 6.00. Found: C, 69.05; H, 7.64; N 5.94.



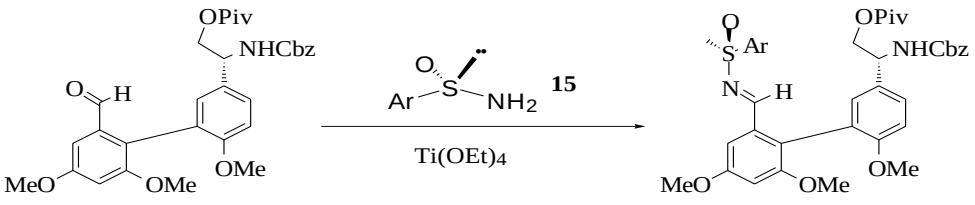

**11** **12** **13**

To a solution of **11** (666.0 mg, 1.43 mmol) in anhydrous methanol (2.3 mL) was added TFA (438 μL, 5.72 mmol, 4 eq) dropwise via a syringe. The mixture was stirred at room temperature, under an argon atmosphere for 2 h and was concentrated in vacuo to give crude amino ester **12** which was directly engaged in the following reaction. To the solution of the so obtained crude amino ester in dioxane and saturated aqueous $NaHCO_3$ was added CbZOSu (712 mg, 2.86 mmol, 2 eq). After being stirred at room temperature for 2 h, the reaction mixture was diluted with saturated aqueous $NH_4Cl$ and extracted with EtOAc. The organic phase was washed with brine, dried over $Na_2SO_4$, concentrated and the resulting solid was purified by flash chromatography (2/3 EtOAc/Hep, $SiO_2$) to afford **13** as a white crystalline solid (680 mg; 77%)**:** Rf = 0.29 (3/2 EtOAc/Hep); m.p. 54°C; $[\alpha]_D$ -20.0 (*c* +7.5, $CHCl_3$); IR ($CHCl_3$) ν 3440, 2971, 1724, 1601, 1505, 1463, 1266 $cm^{-1}$; $^1$H NMR (250 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 7.33 (s, 5H), 7.22 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.05 (d, *J* = 1.8 Hz, 1H), 6.90 (d, *J* = 2.2 Hz, 1H), 6.84 (d, *J* = 8.5 Hz, 1H), 6.61 (d, *J* = 2.2 Hz, 1H), 5.23 (d, *J* = 7.8 Hz, 1H), 5.01-5.15 (m, 3H), 4.19-4.33 (m, 2H), 3.87 (s, 3H), 3.73 (s, 3H), 3.69 (s, 3H), 3.59 (d, *J* = 8.0 Hz, 1H), 3.53 (d, *J* = 8.0 Hz, 1H), 1.16 (s, 15H); $^{13}$C NMR (75 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 178.5, 163.3, 159.8, 158.3, 157.4, 155.8, 136.5, 130.8, 129.8, 129.7, 129.6, 128.6, 128.2, 127.0, 126.6, 120.2, 110.8, 110.8, 101.5, 101.4, 67.2, 66.9, 66.7, 66.5, 56.0, 55.7, 53.9, 38.9, 31.0, 28.1, 28.0, 27.2; MS (CI): *m/z* 618; Anal. Calcd for $C_{35}H_{42}N_2O_8$: C, 67.94; H, 6.84; N, 4.52.




**13** **14**

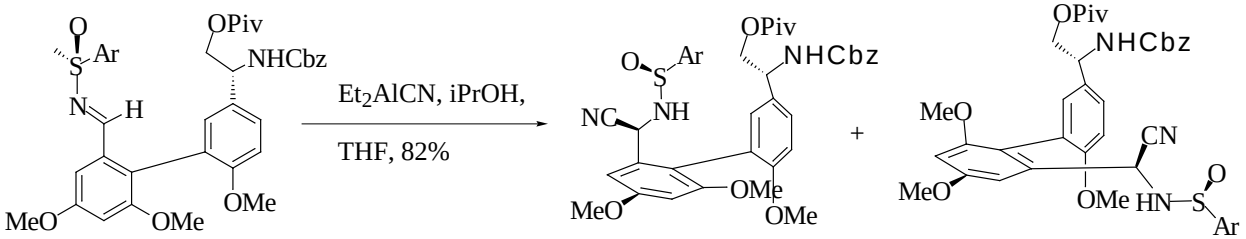
To a solution of **13** (743 mg, 1.20 mmol) in acetone (10 mL) was added MeI (226 µL, 3.60 mmol, 3 eq). The mixture was stirred at 40°C under an argon atmosphere for 15 h until the disappearance of the starting material. The mixture was concentrated in vacuo to give a yellow crystalline solid, which was filtered, washed with pentane, then dried in vacuo. To the solution of the so obtained oxazolinium salt in anhydrous $CH_2Cl_2$ was added, at 0°C, L-Selectride® (2.40 mL, 1 M in hexane, 2.40 mmol, 2 eq). The mixture was stirred at 0°C, under an argon atmosphere for 5 min, then a saturated aqueous solution of citric acid and a small amount of silica gel were added. The reaction mixture was vigourosly stirred for 5 h at 0°C and was brought back to room temperature. The mixture was extracted with $CH_2Cl_2$. The combined organic extracts were dried over $Na_2SO_4$ and concentrated. Flash chromatography (3/2 Hep/EtOAc, $SiO_2$) afforded **14** as a pinkish crystalline solid (594 mg, 90%): Rf = 0.37 (2/3 EtOAc/Hep); m.p. 50°C; $[\alpha]_D$ -3.7 (*c* 1.4, $CHCl_3$); IR ($CHCl_3$) ν 3025, 1718, 1681, 1606, 1512, 1475, 1340 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 9.58 (s, 1H), 7.28-7.38 (m, 6H), 7.17 (dd, *J* = 2.9, 2.9 Hz, 1H), 7.11 (d, *J* = 2.2 Hz, 1H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.77 (d, *J* = 2.2 Hz, 1H), 5.28 (br s, 1H), 5.00-5.15 (m, 1H), 5.14 (d, *J* = 12.2 Hz, 1H), 5.07 (d, *J* = 12.2 Hz, 1H), 4.34 (dd, *J* = 5.2, 11.5 Hz, 1H), 4.27 (dd, *J* = 6.5, 11.5 Hz, 1H), 3.90 (s, 3H), 3.72 (s, 3H), 3.70 (s, 3H), 1.16 (s, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 192.3, 178.5, 160.3, 158.4, 157.1, 155.8, 136.3, 135.7, 131.1, 130.3, 128.6, 128.2, 127.8, 124.2, 122.3, 110.9, 105.1, 100.6, 67.0, 66.2, 53.0, 55.7, 55.7, 38.9, 29.8, 27.1; MS (CI): *m/z* 550.




**14** **16**

A solution of sulfinamide **15**[1] (217 mg, 1.39 mmol, 1.5 eq), aldehyde **14** (512 mg, 0.93 mmol, 1 eq), titanium (IV) ethoxide (975 µL, 4.65 mmol, 5 eq) in anhydrous $CH_2Cl_2$ (50 mL),was refluxed for 4 h under an argon atmosphere. The reaction mixture was cooled down to 0°C and

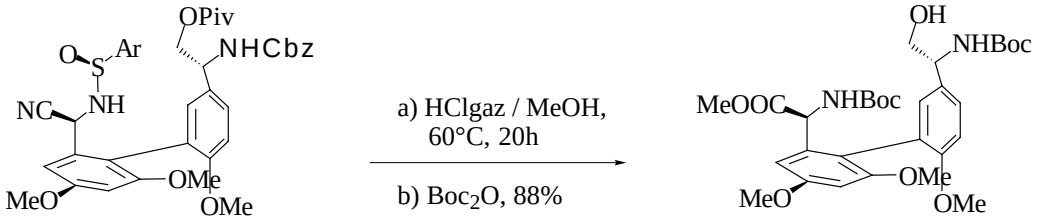
quenched by addition of $H_2O$. The turbid solution was filtered through celite and the filter cake was washed with $CH_2Cl_2$. The phases were separated, the aqueous phase was extracted with $CH_2Cl_2$ and the combined organic portions were washed by brine, dried over $Na_2SO_4$ and concentrated in vacuo. The resulting crude product was purified by flash chromatography (2/1 Hep/EtOAc, $SiO_2$) to afford **16** (white solid, 416 mg; 65%) as a non separable mixture of 2 atropisomers: Rf = 0.42 (3/2 Hep/EtOAc); m.p. 58°C; $[\alpha]_D$ +88.0 (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) ν 3690, 3442, 3022, 3015, 2400, 1724, 1608, 1505, 1479, 1399, 1323, 1288, 1265, 1573 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 8.40, 8.38 (s, 1H), 7.57 (d, *J* = 6.5 Hz, 1H), 7.53 (d, *J* = 6.5 Hz, 1H), 7.31 (m, 1H), 7.30 (br s, 5H), 7.25, 7.21 (d, *J* = 2.5 Hz, 1H), 7.12, 7.06 (d, *J* = 2.3 Hz, 1H), 6.95 (d, *J* = 8.6 Hz, 1H), 6.66, 6.67 (d, *J* = 2.5 Hz, 1H), 5.25 (br s, 1H), 5.06-5.17 (m, 3H), 4.32 (dd, *J* = 11.3, 5.7 Hz, 1H), 4.28 (dd, *J* = 11.3, 4.9 Hz, 1H), 3.87, 3.86 (s, 3H), 3.72, 3.69 (s, 3H), 3.68, 3.60 (s, 3H), 2.49, 2.48 (s, 3H), 1.16 (s, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$, 2 atropisomers in one to one ratio) δ 178.5, 160.6, 160.4, 160.0, 158.3, 157.0, 155.8, 148.0, 142.0, 136.3, 133.8, 131.2, 130.2, 129.8, 129.7, 128.5, 128.1, 127.9, 125.0, 124.8, 111.36, 103.3, 103.2, 102.0, 101.9, 66.9, 66.1, 55.9, 55.7, 55.6, 53.8, 38.8, 27.1, 21.44; . MS (CI): *m/z* 547; Anal. Calcd for $C_{38}H_{42}N_2O_8S$: C, 66.45; H, 6.16; N, 4.07. Found: C, 66.74; H, 6.31; N, 4.01.




**16** **17** **18**

In a round-bottom flask was dissolved the sulfinimine **16** (56.0 mg, 0.08 mmol) in anhydrous THF (3.0 mL) and cooled to -78°C. In a separate round-bottom flask were introduced THF (6.0 mL), $Et_2AlCN$ (3.32 mL, 0.40 mmol, 5 eq) and anhydrous $^i$PrOH (169 µL, 0.26 mmol, 3.3 eq). The solution was stirred for 15 min at room temperature, under an argon atmosphere and added via a syringe to the sulfinimine solution at -78°C. After 15 min, the reaction mixture was brought to room temperature, stirred overnight. The reaction mixture was recooled to -78°C and quenched by addition of aqueous $NaHCO_3$. The suspension was diluted with EtOAc, filtered trough celite. The filter cake was washed with EtOAc. The filtrate was diluted with $H_2O$ and extracted with EtOAc. The combined organic layers were dried over $Na_2SO_4$, concentrated to give the crude product which was purified by flash chromatography (3/2 Hep/EtOAc, $SiO_2$) to give 2 separable atropisomeres **17** and **18**, as 2 white solids (1/1, 53 mg, 91% yield). Compound **17:** Rf = 0.20 (3/2 Hep/EtOAc); m.p. 66°C; $[\alpha]_D$ +47.5 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 3440, 3343, 3022, 3015,

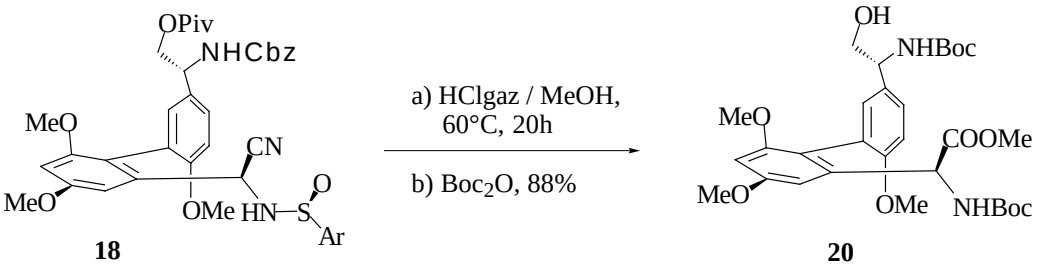
2960, 2840, 2401, 2349, 2245, 1720, 1606, 1508, 1490, 1463, 1223, 1160 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.1 Hz, 3H), 7.28 (br s, 5H), 7.18 (d, J = 1.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 1H), 6.74 (d, *J* = 2.2 Hz, 1H), 6.55 (d, *J* = 2.2 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 1H), 5.10 (m, 3H), 5.00 (d, *J* = 4.0 Hz, 1H), 4.64 (d, *J* = 4.0 Hz, 1H), 4.41 (dd, *J* = 11.0, 6.7 Hz, 1H), 4.34 (dd, *J* = 11.0, 7.3 Hz, 1H), 3.88 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 2.38 (s, 3H), 1.10 (s, 9H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 178.4, 161.1, 158.8, 157.0, 156.2, 142.3, 138.9, 136.9, 134.5, 123.3-130.6, 118.2, 111.1, 103.5, 100.2, 67.1, 65.4, 56.0, 55.8, 55.7, 53.8, 42.2, 38.8, 27.1, 21.5; MS (FAB) *m/z* 720 $[M+Li]^+$; Anal. Calcd for $C_{39}H_{43}N_3O_8S$: C, 65.62; H, 6.07; N, 5.88. Found: C, 65.02; H, 6.01; N, 5.78. Compound **18:** Rf = 0.11 (3/2 Hep/EtOAc); m.p. 68°C; $[\alpha]_D$ +41.5 (*c* 2.8, $CHCl_3$); IR ($CHCl_3$) ν 3682, 3440, 3030, 3013, 2961, 2935, 2399, 2361, 1716, 1606, 1507, 1490, 1463, 1420, 1339 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.20-7.33 (m, 8H), 7.02 (d, J = 1.8 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 2.2 Hz, 1H), 5.30 (br s, 1H), 5.11, (m, 4H), 4.66 (d, *J* = 2.3 Hz, 1H), 4.35 (m, 2H), 3.87 (s, 3H), 3.76 (s, 3H), 3.65 (s, 3H), 2.40 (s, 3H), 1.15 (s, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 178.5, 160.9, 158.8, 156.9, 155.9, 142.3, 139.7, 136.5, 134.4, 123.3-130.9, 119.4, 111.7, 104.1, 100.2, 67.0, 65.9, 56.0, 55.8, 55.7, 53.7, 41.5, 38.9, 27.2, 21.6; MS (FAB) *m/z* 720 $[M+Li]^+$; Anal. Calcd for $C_{39}H_{43}N_3O_8S$: C, 65.62; H, 6.07; N, 5.88. Found: C, 65.52; H, 6.51; N, 5.92.




**17** **19**

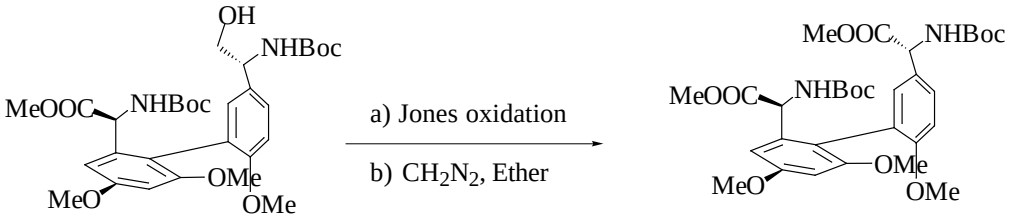
Compound **17** (25.0 mg, 0.035 mmol, 1 eq) was dissolved in anhydrous methanol saturated with gazeous hydrochloride (7.0 mL). After being stirred for 20 h at 60°C, the reaction mixture was concentrated to give a crude product which was immediately converted into the *N*-Boc derivative by treatment with di-tert butyl dicarbonate under standard conditions. Purification by preparative silica plate (3/2 EtOAc/Hep) afforded **19** as a white solid (18 mg, 88%): Rf = 0.25 (3/2 EtOAc/Hep); m.p. 82°C; $[\alpha]_D$ +34.0 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 3687, 3440, 3029, 3015, 2928, 2855, 2401, 1739, 1705, 1605, 1505, 1209, 1202, 1160 $cm^{-1}$; $^1H$ NMR (250 MHz, $CDCl_3$) δ 7.36 (dd, *J* = 1.8, 8.5 Hz, 1H), 7.08 (d, *J* = 1.8 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 6.45 (d, *J* = 2.0 Hz, 1H), 5.72 (m, 1H), 5.60 (d, *J* = 8.9 Hz, 1H), 5.15 (d, *J* = 8.9 Hz, 1H), 4.82 (m, 1H), 3.98 (m, 2H), 3.84 (s, 3H), 3.77 (s, 3H), 3.70 (s, 3H), 3.59 (s, 3H), 1.45 (s, 9H), 1.41 (s, 9H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 172.1, 160.6, 157.6, 155.8, 154.8, 137.8, 124.8-130.8,

*m/z* 591; Anal. Calcd for $C_{30}H_{42}N_2O_{10}$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.38; H, 7.29; N, 4.34. HRMS (FAB) calcd for $[C_{30}H_{42}N_2O_{10}+H]^+$: 591.29177, found: 591.29398. CD (acetonitrile) $[\theta]_{260}$ -0.70, $[\theta]_{235}$ -3.65, $[\theta]_{225}$ 0, $[\theta]_{212}$ +10.00, $[\theta]_{201}$ 0.




**18** **20**

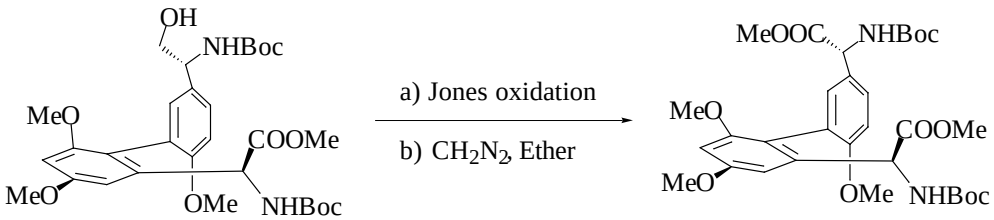
Following the same protocole as described above, compound **18** was transformed into **20** with similar efficiency**:** Rf = 0.25 (3/2 EtOAc/Hep); m.p. 71°C; $[\alpha]_D$ +19.0 (*c* 1.5, $CHCl_3$); IR ($CHCl_3$) ν 3685, 3618, 3349, 3026, 3015, 2977, 2400, 1747, 1706, 1604, 1506, 1424, 1228, 1205, 1045, 928 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 6.91 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 6.44 (d, *J* = 2.0 Hz, 1H), 5.38 (m, 1H), 5.19 (d, *J* = 7.3 Hz, 1H), 5.12 (d, *J* = 7.3 Hz, 1H), 4.77 (m, 1H), 3.60-3.80 (m, 2H), 3.82 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 1.41 (s, 9H), 1.33 (s, 9H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 172.1, 160.4, 158.9, 157.0, 155.8, 154.7, 136.8, 124.8-132.1, 120.3, 111.2, 103.8, 99.0, 80.1, 79.7, 66.2, 56.0, 55.8, 55.5, 55.3, 52.6, 28.4; MS (CI): *m/z* 591; Anal. Calcd for $C_{30}H_{42}N_2O_{10}$: C, 61.00; H, 7.17; N, 4.74. Found: C, 60.79; H, 7.24; N, 4.54. CD (acetonitrile) $[\theta]_{260}$ +0.3, $[\theta]_{228}$ +6.6, $[\theta]_{219}$ 0, $[\theta]_{204}$ -14.1, $[\theta]_{198}$ 0.




**19** **3**

A solution of alcohol **19** (17.0 mg, 0.028 mmol) in acetone (250.0 µL) was cooled to 0°C. To this solution was added 21.6 µL (0.056 mmol) of Jone's reagent (1 g of $CrO_3$ in 2.91 mL of $H_2O$ and 0.84 mL of $H_2SO_4$). The reaction mixture was stirred under an argon atmosphere at -20°C for 15 h, quenched with $H_2O$ and the aqueous phase was extracted with dichloromethane. The combined organic extracts were washed with brine, dried over $Na_2SO_4$, concentrated in vacuo to give the crude acid which was converted to the ester by treatment with a solution of $CH_2N_2$ in ether. Purification on a preparative silica plate (3/2 EtOAc/Hep) afforded desired compound **3** (14 mg, 80% global yield) and epimerized compound in a 7/1 ratio. Compound **3:** Rf = 0.36 (1/1

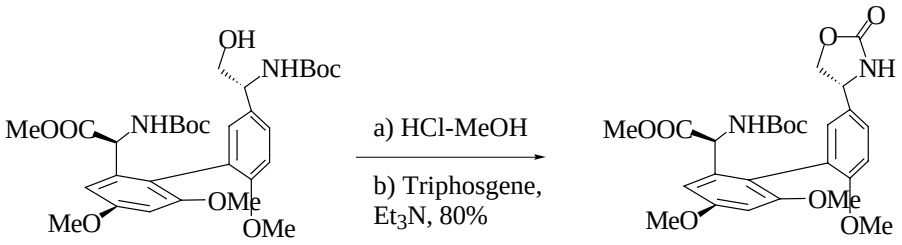
EtOAc/Hep); $[\alpha]_D$ +20.5 (*c* 3.0, $CHCl_3$); IR ($CHCl_3$) ν 3023, 2955, 2839, 2359, 1743, 1706, 1605, 1505, 1464, 1437, 1368, 1343, 1228, 1203, 1161, 1058 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.39 (br d, *J* = 8.4 Hz, 1H), 7.04 (br s, 1H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.49 (br s, 1H), 6.46 (br s, 1H), 6.20 (d, *J* = 7.6 Hz, 1H), 5.48 (d, *J* = 9.0 Hz, 1H), 5.27 (d, *J* = 7.6 Hz, 1H), 5.17 (d, *J* = 9.0 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 3.68 (s, 3H), 3.66 (s, 3H), 3.59 (s, 3H), 1.45 (s, 9H), 1.44 (s, 9H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 172.4, 172.2, 160.0, 158.9, 158.3, 155.7, 154.9, 137.9, 127.9-131.8, 111.3, 119.8, 103.3, 98.4, 80.3, 79.9, 56.0, 55.9, 55.5, 54.8, 52.7, 52.4, 28.6; MS (EI): *m/z* 619; HRMS (FAB) calcd for $[C_{31}H_{42}N_2O_{11}+H]^+$: 619.28669, found: 619.28612. Epimer of compound **21:** Rf = 0.37 (1/1 EtOAc/Hep); $[\alpha]_D$ +23.0 (*c* 2.3, $CHCl_3$); IR ($CHCl_3$) ν 3617, 3030, 3011, 2400, 2283, 1711, 1603, 1508, 1437, 1240, 1190 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 2.0, 8.7 Hz, 1H), 7.74 (d, *J* = 2.0 Hz, 1H), 7.03 (d, *J* = 8.7 Hz, 1H), 6.56 (d, *J* = 2.3 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 1H), 5.30 (br s, 1H), 5.05 (d, *J* = 7 Hz, 1H), 3.88 (s, 3H), 3.86 (s, 6H), 3.67 (s, 3H), 3.59 (s, 3H), 1.40 (s, 9H), 1.32 (s, 9H); $^{13}C$ NMR (62.5 MHz, $CDCl_3$) δ 171.2, 160.6, 158.9, 155.2, 155.0, 154.9, 137.2, 126.7-131.8, 119.2, 110.7, 104.2, 99.2, 80.5, 80.0, 56.0, 55.9, 55.6, 54.9, 52.7, 52.5, 28.6, 28.4; MS (ESI): 619, 641 $[M+Na]^+$; HRMS (FAB) calcd for $[C_{31}H_{42}N_2O_{11}+H]^+$: 619.28669, found: 619.28619.




**20** **21**

Following the same protocole as described above, compound **20** was transformed into **21** with similar efficiency**.** Partial epimerization was also observed. Compound **21**: Rf = 0.40 (1/1 EtOAc/Hep); $[\alpha]_D$ +10.0 (*c* 3.0, $CHCl_3$); IR ($CHCl_3$) ν 3447, 2986, 2930, 2852, 2364, 1742, 1710, 1604, 1491, 1465, 1438, 1368, 1342, 1266, 1161 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 2.0, 8.6 Hz, 1H), 7.15 (d, *J* = 2.0 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 6.51 (br s, 1H), 6.50 (br s, 1H), 5.50 (d, 1H), 5.30 (br s, 1H), 5.20 (br s, 1H), 4.92 (d, 1H), 3.83 (s, 3H), 3.73 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 3.62 (s, 3H), 1.45 (s, 9H), 1.41 (s, 9H); $^{13}C$ NMR (50 MHz, $CDCl_3$) δ 172.1, 158.3, 160.6, 158.7, 154.7, 138.0, 128.4-131.2, 117.4, 111.1, 102.7, 99.1, 80.3, 79.9, 57.2, 56.0, 55.7, 55.6, 55.0, 52.6, 28.4; MS (EI): *m/z* 619; MS (ESI) 619, 641.2 $[M+Na]^+$; HRMS (FAB) calcd for $[C_{31}H_{42}N_2O_{11}+H]^+$: 619.28669, found: 619.28463. Epimer of **21:** Rf = 0.46 (1/1 EtOAc/Hep); $[\alpha]_D$ +24.0 (*c* 2.0, $CHCl_3$); IR ($CHCl_3$) ν 3610, 3028, 3011, 2405, 2284, 1712, 1604, 1439, 1195 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) δ 8.08 (dd, *J* = 8.6, 2.0Hz, 1H), 7.90 (d, *J* = 2.0 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.52 (d, *J* = 2.2 Hz, 1H), 6.49

(d, *J* = 2.2 Hz, 1H), 5.35 (bs, 1H), 5.15 (bs, 1H), 4.95 (bs, 1H), 3.88 (s, 3H), 3.84 (s, 3H), 3.78 (s, 3H), 3.68 (s, 3H), 3.62 (s, 3H), 1.42 (s, 9H), 1.40 (s, 9H); $^{13}$C NMR (62.5 MHz, $CDCl_3$) δ 171.5, 160.8, 160.2, 158.4, 134.5, 122.7-131.6, 116.9, 110.4, 102.7, 99.0, 80.7, 79.9, 56.0, 55.9, 55.6, 55.0, 52.6, 51.9, 28.4; MS (EI): *m/z* 619; MS (ESI) 619, 641.2 $[M+Na]^+$, 657.1 $[M+K]^+$; HRMS (FAB) calcd for $[C_{31}H_{42}N_2O_{11}]^+$: 618.27886, found: 618.28174.




**19** **4**

To a solution of compound **19** (7 mg, 0.012 mmol) in methanol (250 µL) was added HCl at 0°C. The mixture was brought back to room temperature and stirred for 3 h. The reaction mixture was concentrated to give a crystalline solid, which was dissolved in anhydrous $CH_2Cl_2$ (400 µL) and cooled to -78°C, triphosgene (2.5 mg, 0.006 mmol) and triethylamine (4 µL, 0.024 mmol, 2 eq) were added. After being stirred at -78°C under an argon atmosphere for 6h, the reaction mixture was quenched with aqueous saturated $NaHCO_3$. The aqueous phase was extracted with $CH_2Cl_2$. The combined organic phase was washed with brine, dried over $Na_2SO_4$, concentrated. The crude product was purified on a preparative silica plate (3/2 EtOAc/Hep) to afford oxazolidinone **4** (4 mg, 80%) as a white opaque oil **:** Rf = 0.25 (3/2 EtOAc/Hep); $[\alpha]_D$ +24.0 (*c* 0.9, $CHCl_3$); IR ($CHCl_3$) ν 3684, 3621, 3463, 3018, 2977, 2920, 2896, 2400, 2248, 1750, 1708, 1602, 1580, 1477, 1334, 1223, 1046, 929 $cm^{-1}$; $^1$H NMR (300 MHz, $CDCl_3$) δ 7.65 (br s, 1H), 7.17 (br d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.69 (s, 1H), 6.53 (s, 1H), 6.11 (m, 2H), 4.88 (m, 1H), 4.67 (m, 2H), 4.22 (m, 1H), 3.85 (s, 3H), 3.78 (s, 3H), 3.72 (s, 3H), 3.63 (s, 3H); $^{13}$C NMR (62.5 MHz, $CDCl_3$) δ 167.8, 164.3, 162.3, 160.0, 152.0, 134.9, 125.9-129.4, 120.1, 111.2, 103.9, 100.1, 84.3, 60.4, 55.9, 55.7, 52.8; MS (CI): *m/z* 417.

(1) Davis, F. A.; Zhang, Y.; Andemichael, Y.; Fang, T.; Fanelli, D. L.; Zhang, H. *J. Org. Chem.* **1999**, *64*, 1403.