Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Asymmetric aldol reactions under normal and inverse addition mode of reagents

Saumen Hajra, Aswini Kumar Giri, Ananta Karmakar and Snehardrinarayan Khatua*

Department of Chemistry, Indian Institute of Technology, Kharagpur 721302 (India)

Fax: (+91)-3222-255303; E-mail: shajra@chem.iitkgp.ernet.in

General

All reactions were conducted using oven-dried glassware under an atmosphere of Argon (Ar). Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Flash chromatography was carried out using Spectrochem Silica gel (230-400 mesh) purchased from Spectrochem, India. TLC was performed on aluminium-backed plates coated with Silica gel 60 with F_{254} indicator (Merck).

The ^{1}H NMR spectra were measured with Bruker-200 (200 MHz) and ^{13}C NMR spectra were measured with Bruker-200 (50 MHz) using $CDCl_3$. ^{1}H NMR chemical shifts are expressed in parts per million (δ) downfield to $CHCl_3$ (δ = 7.26); ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the central $CDCl_3$ resonance (δ = 77.0). Coupling constants in ^{1}H NMR are expressed in Hz. Elemental analyses were carried out on a Perkin-Elmer 2400-II. Specific optical rotation values were measured on JASCO P-1020 polarimeter. Melting points were measured in Toshniwal (India) melting point apparatus.

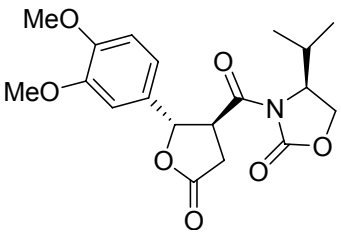
Typical procedure. methods A and B: To a well-stirred solution of the substrate **1** (0.243 g, 1.0 mmol) in CH_2Cl_2 [Method A: 5.7 ml and method B: 2.5 mL] was dropwise added Lewis acid [method A: 0.12 mL of $TiCl_4$, 1.1 mmol and method B: 1.1 mL of Bu_2BOTf (1M) in CH_2Cl_2, 1.1 mmol] at -78 °C under argon atmosphere and the solution allowed to stir for 30 min. To the coloured solution was added *i*-Pr_2NEt (0.21 mL, 1.2 mmol) and allowed to stir for 45 min. at -78 °C. A solution of aldehyde (1.4 mmol) in 0.5 mL of CH_2Cl_2 was dropwise added to the reaction mixture at -78 °C. The resulting

mixture was stirred at -78 °C for 2-3 h and then was gradually raised to -15 °C. The reaction was monitored by TLC and on completion; it was quenched with H_2O and allowed to attain to room temperature. The reaction mixture was extracted with EtOAc (50 mLx3). The combined organic layers was washed with water, dried over Na_2SO_4, filtered through a celite pad and concentrated. ^{1}H NMR analysis of the crude mixture revealed the isomer ratios. Purification by flash column chromatography of the crude using petroleum-ether (60-80) and EtOAc as eluent yielded the major lactone diastereomer **4**.

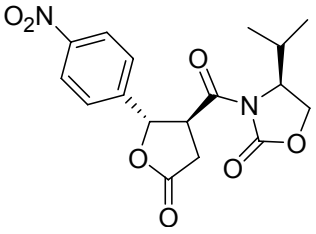
Methods A′ and **B′**: To a well-stirred solution of the substrate **1** (0.243 g, 1.0 mmol) in CH_2Cl_2 [Method **A′**: 12 ml and method B′: 3 ml] was added Lewis acid [method A′: 0.13 mL of $TiCl_4$, 1.2 mmol and method B′: 2.5 mL of Bu_2BOTf (1M) in CH_2Cl_2, 2.5 mmol] dropwise at -78 °C under argon atmosphere and the solution allowed to stir for 30 min. A solution of aldehyde (1.4 mmol) in 0.5 mL of CH_2Cl_2 was added and allowed to stir for additional 15 min. at -78 °C. To the reaction mixture was added *i*-Pr_2NEt (method A′: 0.24 mL, 1.4 mmol and method B′: 0.46 mL, 2.6 mmol) and the resulting mixture was stirred for 2-3 h at -78 °C and then was slowly warmed to -15 °C. The reaction was monitored by TLC and on completion; it was quenched with H_2O and allowed to warm to room temperature. The reaction mixture was extracted with EtOAc (50 mLx3). The combined organic layers was washed with water, dried over Na_2SO_4, filtered through a celite pad and concentrated. ^{1}H NMR analysis of the crude mixture revealed the isomer ratios. Purification by flash column chromatography of the crude using petroleum-ether (60-80) and EtOAc as eluent afforded the major aldol/lactone diastereomer **3/5**.

Spectroscopic data:

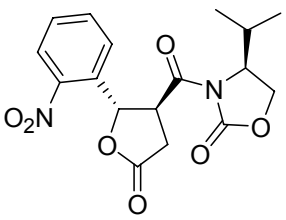
(2'*S*, 3'*S*, 4*S*)-4-Isopropyl-3-[5-oxo-2-(3,4-dimethoxy-phenyl)-tetrahydro-furan-3-carbonyl]-oxazolidin-2-one (4a): 3 h at -78 °C and then 24 h at -15 °C. 65% (method A) and 81% (method B); obtained as a white solid; mp 123-125 °C; $[\alpha]_D^{29}$ +154.04 (c 0.62, CH_3COCH_3); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.92 (dd, *J* = 8.9, 1.8 Hz, 1H), 6.90 (s, 1H), 6.82 (d, *J* = 8.9 Hz, 1H), 5.82 (d, *J* = 7.5 Hz, 1H), 4.55-4.45 (m, 2H), 4.45-4.25 (m, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.24 (dd, *J* = 17.2, 8.9 Hz, 1H), 2.71 (dd, *J* = 17.2, 9.4 Hz, 1H), 2.45-2.25 (m, 1H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H); ^{13}C- NMR (50 MHz, $CDCl_3$): δ 173.6, 170.0, 153.3, 149.4, 149.1, 129.6, 118.5, 111.0, 109.1, 81.4, 63.7, 58.4, 55.8, 55.7, 48.0, 33.1, 28.1, 17.6, 14.5. Anal. Calcd for ($C_{19}H_{23}NO_7$ + 1 H_2O): C, 57.71; H, 6.37; N, 3.54, found: C, 57.31; H, 6.10; N, 3.38.



(2'*S*, 3'*S*, 4*S*)-4-Isopropyl-3-[5-oxo-2-(4-nitro-phenyl)-tetrahydro-furan-3-carbonyl]-oxazolidin-2-one (4b): 3 h at -78 °C; 62% (method A) and 78% (method B); obtained as a gummy liquid. $[\alpha]_D^{29}$ +116.05 (c 0.51, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 5.99 (d, *J* = 7.5 Hz, 1H), 4.60-4.10 (m, 4H), 3.24 (dd, *J* = 17.4, 9.1 Hz, 1H), 2.73 (dd, *J* = 17.4, 9.2 Hz, 1H), 2.55-2.25 (m, 1H), 0.90 (d, *J* = 5.6 Hz, 3H), 0.84 (d, *J* = 5.6 Hz, 3H); ^{13}C- NMR (50 MHz, $CDCl_3$): δ 172.9, 169.4, 153.3, 147.9, 144.7, 126.8 (2C), 123.8 (2C), 79.6, 63.9, 58.5, 48.4, 32.8, 28.2, 17.7, 14.6. Anal. Calcd for ($C_{17}H_{18}N_2O_7$ + 1.5 H_2O): C, 52.44; H, 5.44; N, 7.19, found: C, 52.55; H, 5.17; N, 7.25.

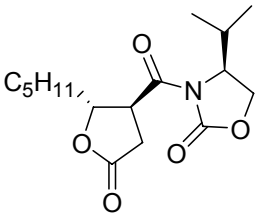


(2'*S*, 3'*S*, 4*S*)-4-Isopropyl-3-[5-oxo-2-(2-nitro-phenyl)-tetrahydro-furan-3-carbonyl]-oxazolidin-2-one (4c): 3 h at -78 °C; 65% (method A) and 70% (method B); obtained as a



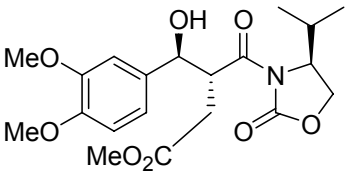
gummy liquid. $[\alpha]_D^{26}$ = - 19.3 (c 1, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.19 (d, *J* = 9.2 Hz, 1H), 7.71 (dt, *J* = 14.7, 7.8 Hz, 2H), 7.52 (t, *J* = 7.09 Hz, 1H), 6.64 (d, *J* = 6.4 Hz, 1H), 5.53-5.41 (m, 1H), 4.35-4.00 (m, 3H), 3.02 (dd, *J* = 17.1, 7.8 Hz, 1H), 2.85 (dd, *J* = 17.1, 3.3 Hz, 1H), 1.85-1.50 (m, 1H), 0.69 (d, *J* = 6.8 Hz, 3H), 0.19 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 174.1, 170.6, 153.1, 146.6, 133.9, 131.2, 129.5, 128.8, 125.2, 78, 62.9, 58.3, 42.6, 34.3, 28.2, 17.8, 13.7. Anal. Calcd for $C_{17}H_{18}N_2O_7$: C, 56.35; H, 5.01; N, 7.73; found: C, 56.65; H, 4.99, N, 7.75.

(2'*R*, 3'*S*, 4*S*)-4-Isopropyl-3-(5-oxo-2-pentyl-tetrahydro-furan-3-carbonyl)-oxazolidin-2-one (4d): 2 h at -78 °C then 15 h at -15 °C; 60% (method A) and 80% (method B); obtained as a

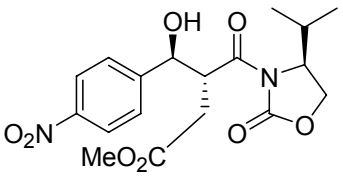


gummy liquid. $[\alpha]_D^{29}$ +106.93 (c 0.50, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 4.79 (dd, *J* = 6.3, 6.1 Hz, 1H), 4.55-4.40 (m, 1H), 4.40-4.05 (m, 3H) 3.04 (dd, *J* = 17.6, 9.4 Hz, 1H), 2.66 (dd, *J* = 17.6, 7.1 Hz, 1H), 2.50-2.20 (m, 1H), 1.80-1.50 (m, 2H), 1.50-1.10 (m, 6H), 1.00-0.60 (m, 3H), 0.94 (d, *J* = 6.8 Hz, 3H), 0.87 (d, *J* = 6.8 Hz, 3H); ^{13}C- NMR (50 MHz, $CDCl_3$): δ 174.1, 170.8, 153.5, 81.3, 63.6, 58.5, 44.8, 34.9, 32.6, 31.2, 28.1, 24.8, 22.2, 17.7, 14.5, 13.7. Anal. Calcd for $C_{16}H_{25}NO_5$: C, 61.72; H, 8.09; N, 4.50, found: C, 61.68; H, 8.46; N, 4.31.

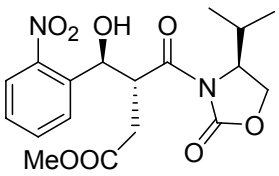
(3*R*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(3,4-dimethoxy-phenyl)-butyric acid methyl ester (3a): 2.5 h. at -78 °C; 76% (method A') and 92% (method B'); obtained as a white solid; mp 125-127 °C; $[\alpha]_D^{29}$ - 11.60 (c 0.53, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 6.99 (d, *J* = 1.7 Hz, 1H), 6.91 (dd, *J* = 8.2, 1.7 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 4.90-4.70 (m, 1H), 4.61 (d, *J* = 8.5 Hz, 1H), 4.55-4.40 (m, 1H), 4.33 (t, *J* = 8.1 Hz, 1H), 4.21 (dd, *J* = 8.1, 2.4 Hz, 1H), 3.89 (s, 3H), 3.85 (s, 3H), 3.57 (s, 3H), 2.89 (dd, *J* = 17.2, 11.2 Hz, 1H), 2.40-2.20 (m, 1H,), 2.22 (dd, *J* = 17.2, 3.7 Hz, 1H), 0.89 (d, *J* = 7.1 Hz, 3H), 0.78 (d, *J* = 7.1 Hz, 3H); ^{13}C- NMR (50 MHz, $CDCl_3$): δ 174.7, 172.1, 154.9, 149.3, 148.9, 134.2, 118.8, 111.1, 109.3, 76.1, 63.6, 59.1, 55.9, 55.8, 51.7, 45.0, 34.2, 28.8, 17.8, 14.6.. Anal. Calcd for $C_{20}H_{27}NO_8$: C, 58.67; H, 6.65; N, 3.42, found: C, 58.87; H, 6.71; N, 3.49.



(3*R*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(4-nitro-phenyl)-butyric acid methyl ester (3b): 2.5 h at -78 °C; 67% (method A') and 88% (method B'); obtained as a white solid; mp 103-105 °C. $[\alpha]_D^{29}$ +1.69 (c 0.5, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.22 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 4.95-4.70 (m, 2H), 4.55-4.25 (m, 1H), 4.32 (t, *J* = 8.6 Hz, 1H), 4.19 (dd, *J* = 8.6, 2.3 Hz, 1H), 3.61 (s, 3H), 2.96 (dd, J = 17.3, 10.3 Hz, 1H), 2.38 (dd, *J* = 17.3, 4.2 Hz, 1H), 2.30-2.00 (m, 1H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H); ^{13}C-NMR (50 MHz, $CDCl_3$): δ 173.8, 171.6, 154.5, 148.6, 147.5, 127.2 (2C), 123.5 (2C), 74.4, 63.5, 58.8, 52.0, 44.3, 33.7, 28.6, 17.6, 14.5. Anal. Calcd for $C_{18}H_{22}N_2O_8$: C, 54.82; H, 5.62; N, 7.10, found: C, 54.54; H, 5.91; N, 6.95.

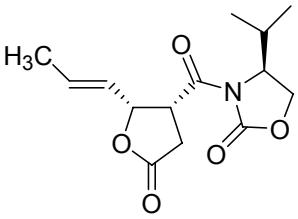


(3*R*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(2-nitro-phenyl)-butyric acid methyl ester (3c): 3 h at -78 °C; 62% (method A′) and 74% (method B′); obtained



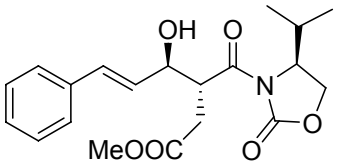
as a gummy liquid. $[\alpha]_D^{26}$ = - 20.8 (c 1.48, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.00 (d, *J* = 8.1 Hz, 1H), 7.80 (d, *J* = 7.8 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.24 (q, *J* = 6.2 Hz, 1H), 5.56 (t, *J* = 6.8 Hz, 1H), 5.00-4.80 (m, 1H), 4.40 (m, 1H), 4.29 (t, *J* = 8.1, 1H), 4.15 (dd, *J* = 8.1, 2.1 Hz, 1H), 3.93 (d, *J* = 8.6 Hz, 1H), 3.59 (s, 3H), 3.15 (dd, *J* = 17.3, 11.8 Hz, 1H), 2.44 (dd, *J* = 17.3, 3.7 Hz, 1H), 2.35-2.10 (m, 1H), 0.80 (d, *J* = 7.0 Hz, 3H), 0.65 (d, *J* = 7.0 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 174.3, 172.0, 154.4, 148, 137, 133.6, 128.7, 128.0, 124.7, 70.1, 63.5, 59, 51.8, 43.2, 34.6, 28.7, 17.5, 14.6. Anal. Calcd for ($C_{18}H_{22}N_2O_8$ + $1H_2O$): C, 52.42; H, 5.87; N, 6.79; found: C, 52.54; H, 6.01; N, 6.88.

(2'*R*, 3'*R*, 4*S*)-4-Isopropyl-3-(5-oxo-2-prop-1-enyl-tetrahydro-furan-3-carbonyl)-oxazolidin-2-one (5e): 6 h at -78 °C, 56% (method A') and 66% (method B'); obtained as a gummy liquid.



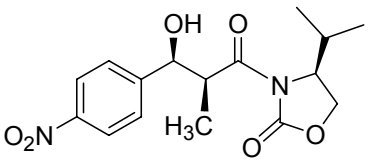
$[\alpha]_D^{26}$ +168.70 (c 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.00-5.70 (m, 1H), 5.50-5.30 (m, 2H), 4.63 (q, *J* = 8.6 Hz, 1H), 4.50-4.10 (m, 3H), 3.23 (dd, *J* = 17.9, 8.8 Hz, 1H), 2.55 (dd, *J* = 17.9, 9.0 Hz, 1H), 2.40-2.18 (m, 1H), 1.65 (d, *J* = 6.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (50 MHz, $CDCl_3$): δ 174.8, 168.7, 153.6, 133.5, 124.4, 80.4, 63.8, 58.8, 43.9, 30.3, 28.5, 17.7, 14.4. Anal. Calcd for $C_{14}H_{19}NO_5$: C, 59.78; H, 6.81; N, 4.98, found: C, 60.08; H, 7.01; N, 4.92.

(3*R*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(cinnamyl)-butyric acid methyl ester (3f): 3 h at -78 °C; 41% (method A′) and 49% (method B′); obtained as a



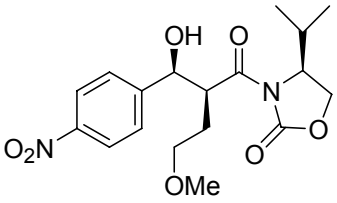
gummy liquid. $[\alpha]_D^{26}$ = +30.5 (c 1.48, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 7.45-7.15 (m, 5H), 6.62 (d, *J* = 16.0 Hz, 1H), 6.23 (dd, *J* = 16.0, 6.3 Hz, 1H), 4.70- 4.20 (m, 3H), 4.33 (t, *J* = 8.7 Hz 1H), 4.20 (dd, *J* = 8.7, 2.4 Hz, 1H), 3.61 (s, 3H), 2.98 (dd, *J* = 17.2 10.8 Hz, 1H), 2.58 (dd, *J* = 17.2, 3.9 Hz, 1H), 2.45-2.15 (m, 1H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.68 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 174.2, 172.2, 154.8, 136, 132.4, 128.7, 128.2 (2C), 128, 126.6 (2C), 74.1, 63.7, 59.1, 51.9, 44.2, 33.7, 28.8, 17.8, 14.7. Anal. Calcd for $C_{20}H_{25}NO_6$: C, 63.99; H, 6.71; N, 3.73; found: C, 64.13; H, 6.63; N, 3.86.

(2'*S*, 3'*S*, 4*S*)-3-[3-(4-nitro-phenyl)-3-hydroxy-2-methyl-propionyl]-4-isopropyl-2-oxazolidinone (7a): 2 h at -78 °C; 66% (method A), 52% (method B), 71% (method A') and 58%



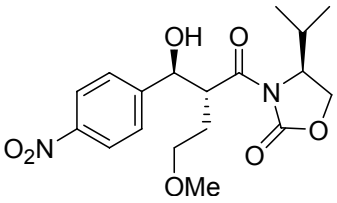
(method B'); obtained as a gummy liquid. $[\alpha]_D^{25}$ +92.70 (c 1, CH_3OH); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.21 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 5.23 (m, 1H), 4.50 (m, 1H), 4.40-4.15 (m, 2H), 4.15-4.00 (m, 1H), 3.65 (br S, 1H), 2.45-2.20 (m, 1H), 1.12 (d, *J* = 7.0 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H). ^{13}C-NMR (50 MHz, $CDCl_3$): δ 174.8, 153.7, 149.1, 146.9, 126.9 (2C), 123.1 (2C), 72.9, 63.3, 60.1, 44.9, 28.2, 17.5, 14.4, 10.0. Anal. Calcd for $C_{16}H_{20}N_2O_6$: C, 57.14; H, 5.99; N, 8.33, found: C, 57.42; H, 6.23; N, 8.17.

(3*S*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(4-nitro-phenyl)-1-methoxy-butane (7b). 3 h at -78 °C; <5% (method A) and 74% (method B); yellowish gummy



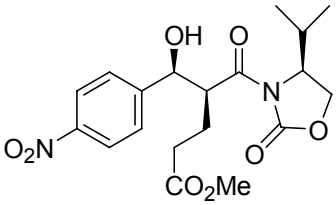
liquid; $[\alpha]_D^{25}$ +141.53 (c 0.5, CH_3OH); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 5.08 (d, *J* = 4.9 Hz, 1H), 4.50-4.25 (m, 2H), 4.16 (dd, *J* = 9.2, 2.9 Hz, 1H), 4.06 (t, *J* = 9.2 Hz, 1H), 3.71 (br S, 1H), 3.39 (t, *J* = 6.2 Hz, 2H), 3.23 (s, 3H), 2.50-2.05 (m, 2H), 1.80-1.60 (m, 1H), 0.88 (t, *J* = 7.2 Hz, 6H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ 174.5, 153.7, 148.8, 147.3, 127.3 (2C), 123.3 (2C), 73.0, 70.7, 63.1, 58.6 (2C), 48.0, 28.2, 27.4, 17.9, 14.4. Anal. Calcd for $C_{18}H_{24}N_2O_7$: C, 56.83; H, 6.36; N, 7.36, found: C, 57.09; H, 6.61; N, 7.37.

(3*R*, 4*S*, 4'*S*)-4-Hydroxy-3-(4-isopropyl-2-oxazolidinone-3-carbonyl)-4-(4-nitro-phenyl)-1-methoxy-butane (8b). 3 h at -78 °C; 70% (method A') and 64% (method B'); yellowish gummy

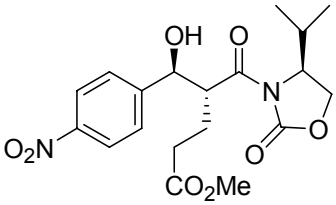


liquid; $[\alpha]_D^{26}$ -10.56 (c 1, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 8.7 Hz, 2H), 4.96 (d, *J* = 5.1 Hz, 1H), 4.80-4.60 (m, 1H), 4.40-4.25 (m, 1H), 4.25-4.00 (m, 2H), 3.60-3.35 (m, 2H), 3.23 (s, 3H), 2.40-2.15 (m, 1H), 2.10-1.70 (m, 1H), 1.81 (dd, *J* = 14.2, 3.9 Hz, 1H), 0.75 (d, *J* = 7.0 Hz, 3H), 0.39 (d, *J* = 6.9 Hz, 3H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ 175.9, 154.0, 149.7, 147.4, 127.0 (2C), 123.5 (2C), 75.1, 70.7, 63.2, 58.5 (2C), 45.7, 30.8, 28.8, 17.6, 14.2. Anal. Calcd for $C_{18}H_{24}N_2O_7$: C, 56.83; H, 6.36; N, 7.36, found: C, 56.91; H, 6.52; N, 7.44.

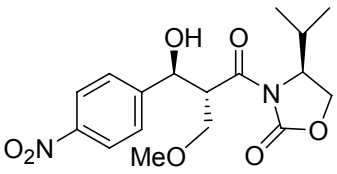
(4*S*, 5*S*, 4'*S*)-5-Hydroxy-4-(4-isopropyl-2-oxazolidinone-3-carbonyl)-5-(4-nitro-phenyl)-pentanoic acid methyl ester (7c). 3 h at -78 °C; <5% (method A) and 40% (method B); yellowish gummy liquid; $[\alpha]_D^{26}$ +66.10 (c 0.5, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.60 (d, *J* = 8.8 Hz, 2H), 5.11 (d, *J* = 4.2 Hz, 1H), 4.50-4.30 (m, 2H), 4.30-4.00 (m, 2H), 3.60 (s, 3H), 3.30 (br S, 1H), 2.45-2.00 (m, 4H), 2.00-1.75 (m, 1H), 0.89 (d, *J* = 7.3 Hz, 6H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ 174.2, 173.0, 153.6, 148.3, 147.3, 127.0 (2C), 123.4 (2C), 72.6, 63.2, 58.6, 51.6, 48.5, 31.2, 28.2, 24.6, 17.8, 14.4. Anal. Calcd for ($C_{19}H_{24}N_2O_8$ + 1 H_2O): C, 53.52; H, 6.15; N, 6.57, found: C, 53.75; H, 6.22; N, 6.45.



(4*R*, 5*S*, 4'*S*)-5-Hydroxy-4-(4-isopropyl-2-oxazolidinone-3-carbonyl)-5-(4-nitro-phenyl)-pentanoic acid methyl ester (8c). 3 h at -78 °C; 36% (method A') and <5% (method B'); yellowish gummy liquid; $[\alpha]_D^{26}$ +11.39 (c 1, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.56 (d, *J* = 8.6 Hz, 2H), 4.92 (br t, *J* = 5.3 Hz, 1H), 4.60-4.45 (m, 1H), 4.45-4.30 (m, 1H), 4.30-4.00 (m, 2H), 3.62 (br d, *J* = 5.4 Hz, 1H), 3.62 (s, 3H), 2.35 (t, *J* = 7.3 Hz, 2H), 2.15-2.00 (m, 2H), 2.00-1.75 (m, 1H), 0.82 (d, *J* = 8.3 Hz, 3H), 0.45 (d, *J* = 8.3 Hz, 3H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ 175.0, 172.9, 154.0, 149.4, 147.5, 127.1 (2C), 123.7 (2C), 74.7, 63.3, 58.7, 51.7, 47.2, 31.5, 28.4, 25.0, 17.7, 14.1. Anal. Calcd for $C_{19}H_{24}N_2O_8$: C, 55.88; H, 5.92; N, 6.86, found: C, 55.62; H, 6.13; N, 6.35.



(2*S*, 3*S*, 4'*S*)-3-Hydroxy-2-(4-isopropyl-2-oxazolidinone-3-carbonyl)-3-(4-nitro-phenyl)-1-methoxy-propane (8d). 3 h at -78 °C; 40% (method A') and <5% (method B'); yellowish gummy



liquid; $[\alpha]_D^{26}$ +8.53 (c 0.5, $CHCl_3$); ^{1}H-NMR (200 MHz, $CDCl_3$): δ 8.20 (d, *J* = 8.6 Hz, 2H), 7.59 (d, *J* = 8.6 Hz, 2H), 5.08 (d, *J* = 5.9 Hz, 1H), 4.90-4.70 (m, 1H), 4.50-4.35 (m, 1H), 4.35-4.10 (m, 2H), 3.75-3.45 (m, 2H), 3.26 (s, 3H), 2.20-1.95 (m, 1H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.49 (d, *J* = 6.9 Hz, 3H). ^{13}C- NMR (50 MHz, $CDCl_3$): δ 173.4, 153.6, 149.0, 147.3, 126.8 (2C), 123.5 (2C), 72.0, 71.1, 63.0, 59.0, 58.5, 48.6, 28.2, 17.5, 13.9. Anal. Calcd for $C_{17}H_{22}N_2O_7$: C, 55.73; H, 6.05; N, 7.65, found: C, 56.04; H, 6.21; N, 7.66.

Single crystal data collection and refinements:

Data of **3a** were collected on Bruker-Nonius Mach3 CAD4 X-ray diffractometer that uses graphite monochromated Mo Kα radiation (λ=0.71073 Å) by ω-scan method. The structure was solved by Direct methods using the programme SHELXS-97 [G. M. Sheldrick, (1990) "SHELXS-97 Program for Crystal Structure Determination", *Acta Crystallogr.,* **A46**, 467- 473.] and refined by least square methods on F^2 using SHELXL-97.[G. Sheldrick, (1997) "SHELXL-97-A Program for Crystal Structure Refinement", Universität Göttingen, Göttingen, Germany.] Non-hydrogen atoms were refined anisotropically and hydrogen atoms on C-atoms were fixed at calculated positions and refined using a riding model. Hydrogen atom on O atom of hydroxyl group was located in difference Fourier maps and refined isotropically. For the O—H one DFIX restrains [$d_{O\text{-}H}$ = 0.95(2)Å] is applied .

Table S1: X-Ray data for compound 3a

Empirical formula	$C_{20}H_{27}N_1O_8$
Formula weight	409.43
Temperature, K	173(2)
Wavelength (Å)	0.71073
Crystal system, Space group	Monoclinic, P 2_1
Unit cell dimensions	
a (Å)	8.632(2)
b (Å)	10.071(3)
c (Å)	12.195(2)
α (°)	90
β(°)	95.043(10)
γ(°)	90
V (Å^3)	1056.2(4)
Z	2
$D_{calc.}$ (Mg/m^3)	1.287
Absorp. coeff. (mm^{-1})	0.100
F(000)	436
Crystal size (mm)	0.20 x 0.20 x 0.10
θ Range (°)	1.68 to 24.96
Reflections collected	2102
Independent reflections	1967[R(int) = 0.02]
Absorption correction	None
Data / restraints / parameters	1967 / 2 / 271
Goodness-of-fit on F^2	1.024
R1, wR2 Final [I>2σ(I)]	0.0496, 0.1100
R1, wR2 (all data)	0.0931, 0.1271
Absolute structure parameter	2(2)
Diffractometer	CAD4-MACH3