Supporting Information for:

Stereoselective Aldol Reaction of Glutarimides by Use of Pseudo C₂
Symmetry

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1. General Information

^1H , ^{13}C and ^{19}F NMR spectra were recorded (^1H : 300 MHz; ^{13}C : 75.5 MHz; ^{19}F : 283 MHz) at room temperature with Me_4Si (^1H and ^{13}C) and CFCl_3 (^{19}F) as the internal standards in CDCl_3 . ^{13}C NMR spectra were obtained with complete proton decoupling. Infrared (IR) spectra were obtained with a JASCO A-302 spectrometer. High resolution FAB mass spectra were measured in a positive ion mode.

Anhydrous THF and CH_2Cl_2 were used as received. DMF was freshly distilled from CaH_2 . All other reagents were obtained from commercial sources and used as received. All reactions were carried out under an atmosphere of argon in dried glassware with magnetic stirring.

2. Experimental Procedures and Characterization Data

Diethyl 3-(trifluoromethyl)glutarate:¹

To a stirred solution of LiBr (11.5 g, 132 mmol) in THF (100 mL) at 0 °C were added ethyl diethylphosphonoacetate (19.8 mL, 99.8 mmol) and Et_3N (16.0 mL, 110 mmol), and the mixture was stirred at rt for 10 min. To the resulting solution at 0 °C was added trifluoroacetaldehyde hydrate (12.8 g, 110 mmol), and the whole mixture was stirred for 5 min at that temperature, followed by 1 h at rt. The reaction mixture was quenched with 1 M HCl aq (130 mL) and extracted with Et_2O three times. Concentration at atmospheric pressure after dried over MgSO_4 furnished crude ethyl (*E*)-4,4,4-trifluorobut-2-enoate, which was used for the next step without further purification.

NaH in parafin (4.773 g, 109 mmol, 55 wt%) was at first washed with *n*-hexane, and to its THF solution (50 mL) was slowly added diethyl malonate (16.7 mL, 110 mmol) at 0 °C, and the whole solution was stirred for 30 min at that temperature. Crude ethyl (*E*)-4,4,4-trifluorobut-2-enoate was added to the reaction mixture at 0 °C, which was further stirred for 2 h after warming to rt. The reaction was quenched with 1 M HCl aq (150 mL) and extracted with AcOEt. The organic layer was dried over MgSO_4 and concentrated. The crude diethyl 2-carboethoxy-3-(trifluoromethyl)glutarate was used for the next step without further purification.

To a solution of LiCl (4.07 g, 97.7 mmol) and H_2O (5.16 mL, 286 mmol) in DMSO (86 mL) was added crude diethyl 2-carboethoxy-3-(trifluoromethyl)glutarate and the whole reaction mixture was stirred at 160 °C for 3.5 h. After cooling to rt, the usual

workup furnished a crude mixture that was purified by vacuum distillation to afford 15.1 g (59.0 mmol) of the desired product, diethyl 3-(trifluoromethyl)glutarate.

total yield: 59%, bp: 80.5 °C / 8.3 mmHg, R_f = 0.70 (*n*-hexane/AcOEt, 5:2, v/v). ^1H NMR (300 MHz, CDCl_3): 1.27 (t, J = 7.2 Hz, 6H), 2.51 (dd, J = 16.2 and 4.5 Hz, 2H), 2.67 (dd, J = 16.5 and 5.7 Hz, 2H), 3.29 (m, 1H), 4.15 (q, J = 7.2 Hz, 4H).

3-(Trifluoromethyl)glutaric anhydride:²

To a solution of diethyl 3-(trifluoromethyl)glutarate (12.8 g, 50.0 mmol) in THF (50 mL) and H_2O (50 mL) was added NaOH (9.09 g, 227 mmol) and the reaction mixture was stirred at rt for 12 h. The aqueous layer obtained after extraction with ether was acidified to pH 1 with 6 *M* HCl aq and extracted with AcOEt three times. Concentration after dried over MgSO_4 furnished crude 3-(trifluoromethyl)glutaric acid (9.58 g), which was dissolved in Ac_2O (50 mL) and the mixture was refluxed for 5 h. After concentration, the crude solid was purified by recrystallization from a mixture of AcOEt and *n*-hexane (1:2, v/v) to yield the desired 3-(trifluoromethyl)glutaric anhydride (7.86 g, 43.2 mmol).

total yield: 86%, ^1H NMR (300 MHz, CDCl_3): 2.79–3.10 (m, 5H); ^{13}C NMR (75.5 MHz, CD_3COCD_3) 29.0, 34.4 (q, J = 29.8 Hz), 127.2 (q, J = 277.9 Hz), 206.7; ^{19}F NMR (283 MHz, CDCl_3) –74.86 (d, J = 7.1 Hz).

1,5-Bis[(4*S*)-4-(1-methylethyl)oxazolidin-2-on-3-yl]-3-(trifluoromethyl)pentan-1,5-dione (1):

To a stirred solution of (*S*)-4-(1-methylethyl)-oxazolidin-2-one (1.37 g, 10.5 mmol) in THF (30 mL) at 80 °C was added dropwise a 1.6 *M* solution of *n*-BuLi in *n*-hexane (7.30 mL, 11.5 mmol) and the mixture was stirred for 15 min at that temperature. After a solution of 3-(trifluoromethyl)glutaric anhydride (1.82 g, 10.0 mmol) in THF (10 mL) was added to the reaction mixture and stirred for 15 min, pivaloyl chloride (1.35 mL, 11.0 mmol) was added and stirring was continued at 0 °C for 1 h. A 1.6 *M* solution of *n*-BuLi in *n*-hexane (7.30 mL, 11.5 mmol) was added dropwise to the other flask containing (*S*)-4-(1-methylethyl)oxazolidin-2-one (1.37 g, 10.5 mmol) in THF (30 mL) at –80 °C and after 15 min, this reaction mixture was added to the former solution at –80 °C and the whole was stirred for 1 h at that temperature. The usual workup and purification

by silica gel chromatography (*n*-hexane:AcOEt, 2:3, v/v) afforded 3.12 g (7.39 mmol) of the desired imide **1**.

yield (from glutaric anhydride): 74%, white solid, mp.: 105–110 °C, R_f = 0.58 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = 91.1 (*c* 0.97, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.88 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 7.2 Hz, 3H), 2.28–2.45 (m, 2H), 3.07 (dd, *J* = 18.0 and 7.5 Hz, 1H), 3.10 (dd, *J* = 18.3 and 7.5 Hz, 1H), 3.38 (dd, *J* = 18.0 and 5.1 Hz, 1H), 3.39 (dd, *J* = 18.0 and 7.5 Hz, 1H), 3.53–3.70 (m, 1H), 4.24 (dd, *J* = 9.3 and 3.3 Hz, 1H), 4.31 (t, *J* = 8.7 Hz, 1H), 4.32 (t, *J* = 9.0 Hz, 1H), 4.39–4.45 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) 14.3, 17.6, 17.7, 28.1, 28.1, 34.2, 34.7 (q, *J* = 27.9 Hz), 58.4, 58.5, 63.4, 63.6, 127.1, (q, *J* = 279.9 Hz), 153.9, 153.9, 169.5, 169.6; ¹⁹F NMR (283 MHz, CDCl₃) –73.15 (d, *J* = 9.3 Hz); IR (CH₂Cl₂): 661, 680, 799, 864, 1020, 1093, 1167, 1210, 1370, 1381, 1706, 1783, 2963 cm^{–1}; Anal. Calcd for C₁₈H₂₅F₃N₂O₆: C, 51.18; H, 5.97; N, 6.63. Found: C, 51.21; H, 5.91; N, 6.58.

General procedure for the boron aldol reaction of the lactones **2** and **6** with aromatic aldehydes in the presence of *i*-Pr₂EtN

(4*S*,5*R*,6*R*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-phenyl-4-(trifluoromethyl)tetrahydropyran-2-one (**2a**):

To a CH₂Cl₂ solution (4 mL) of imide **1** (0.169 g, 0.40 mmol) were added dropwise a 1.0 *M* solution of *n*-Bu₂BOTf in CH₂Cl₂ (1.60 mL, 1.60 mmol) and *i*-Pr₂EtN (286 μL, 1.64 mmol) at 0 °C and the mixture was stirred for 30 min at that temperature. After cooling to –80 °C, benzaldehyde (52.8 μL, 0.52 mmol) was added and the whole was stirred for 30 min at that temperature then for additional 1.5 h at 0 °C. After quenched with a mixture of pH 7 phosphate buffer (3 mL), MeOH (3 mL) and 30% H₂O₂ (3 mL), the mixture was stirred at rt for 1 h. The aqueous solution was extracted with CH₂Cl₂ three times, dried over MgSO₄ and concentrated to furnish a crude solid **4a**. **4a** was then dissolved in THF (4 mL) where Et₃N (55.5 μL) was added at rt and stirring was continued for 14 h at that temperature. The reaction was quenched with 1 *M* HCl aq (3 mL), and the usual workup followed by recrystallization from a mixture solvent of AcOEt and MeOH (3:1, v/v) yielded the desired lactone **2a** (0.128 g, 0.320 mmol).

yield (2 steps): 80%, white solid, mp.: 218–222 °C, R_f = 0.42 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = –24.5 (*c* 1.11, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.06 (d, *J* = 6.9 Hz,

3H), 0.71 (d, $J = 6.9$ Hz, 3H), 1.77 (sepd, $J = 7.2$ and 3.0 Hz, 1H), 2.80 (dd, $J = 17.7$ and 8.4 Hz, 1H), 3.03 (dd, $J = 17.4$ and 9.3 Hz, 1H), 3.31–3.47 (m, 1H), 3.98 (dd, $J = 9.0$ and 2.7 Hz, 1H), 4.07 (t, $J = 9.0$ Hz, 1H), 4.24 (dt, $J = 8.4$ and 2.7 Hz, 1H), 5.20 (t, $J = 9.6$ Hz, 1H), 5.33 (d, $J = 10.2$ Hz, 1H), 7.35–7.45 (m, 5H); ^{13}C NMR (75.5 MHz, CDCl_3) 13.6, 17.7, 27.4 (q, $J = 2.5$ Hz), 28.2, 40.2 (q, $J = 28.5$ Hz), 42.0 (q, $J = 1.2$ Hz), 58.5, 62.9, 81.7, 125.9 (q, $J = 279.1$ Hz), 128.1, 128.8, 130.0, 134.0, 152.7, 167.7, 170.3; ^{19}F NMR (283 MHz, CDCl_3) -73.50 (d, $J = 10.1$ Hz); IR (CH_2Cl_2) 799, 863, 1021, 1095, 1175, 1222, 1200, 1272, 1258, 1370, 1381, 1767, 1785, 2963 cm^{-1} ; Anal. Calcd for $\text{C}_{19}\text{H}_{20}\text{F}_3\text{NO}_5$: C, 57.14; H, 5.05; N, 3.51. Found: C, 56.90; H, 4.97; N, 3.52.

(4*S*,5*R*,6*R*)-6-(4-Methoxyphenyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (2b):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.148 g (0.344 mmol) of the desired lactone **2b**.

yield (2 steps): 86%, white solid, mp.: 171–173 °C, $R_f = 0.55$ (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25} = -43.8$ (c 0.95, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 0.12 (d, $J = 6.9$ Hz, 3H), 0.72 (d, $J = 6.9$ Hz, 3H), 1.78 (sepd, $J = 6.9$ and 3.3 Hz, 1H), 2.85 (dd, $J =$

17.4 and 5.1 Hz, 1H), 3.06 (dd, $J = 17.4$ and 9.3 Hz, 1H), 3.34–3.50 (m, 1H), 3.78 (s, 3H), 4.05 (dd, $J = 9.3$ and 2.7 Hz, 1H), 4.13 (t, $J = 8.7$ Hz, 1H), 4.30 (dt, $J = 8.1$ and 2.7 Hz, 1H), 5.17 (t, $J = 9.9$ Hz, 1H), 5.28 (d, $J = 10.2$ Hz, 1H), 6.80–6.91 (m, 2H), 7.28–7.38 (m, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) 13.4, 17.5, 27.2 (q, $J = 2.5$ Hz), 28.2, 39.9 (q, $J = 28.5$ Hz), 41.9, 55.1, 58.3, 62.8, 81.1, 114.0, 125.9 (q, $J = 279.2$ Hz), 126.0, 129.4, 152.7, 160.7, 168.0, 170.2; ^{19}F NMR (283 MHz, CDCl_3) -73.51 (d, $J = 9.3$ Hz); IR (CH_2Cl_2): 548, 564, 702, 774, 980, 1023, 1031, 1062, 1102, 1122, 1176, 1202, 1226, 1260, 1301, 1325, 1375, 1387, 1406, 1466, 1488, 1518, 1613, 1695, 1768, 1783, 2360, 2988, 3056 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{22}\text{F}_3\text{NO}_6$: C, 55.94; H, 5.16; N, 3.26. Found: C, 55.95; H, 5.25; N, 3.26.

(4*S*,5*R*,6*R*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-[4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)tetrahydropyran-2-one (2c):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.148 g (0.316 mmol) of the desired lactone **2c**.

yield (2 steps): 79%, white solid, mp.: 138–141 °C, $R_f = 0.63$ (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25} = -26.8$ (c 0.93, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 0.067 (d, $J = 6.9$ Hz, 3H), 0.73 (d, $J = 7.2$ Hz, 3H), 1.77 (sepd, $J = 6.9$ and 3.0 Hz, 1H), 2.88 (dd, $J = 17.7$

and 5.1 Hz, 1H), 3.10 (dd, $J = 17.7$ and 9.3 Hz, 1H), 3.37–3.55 (m, 1H), 4.05 (dd, $J = 9.3$ and 2.7 Hz, 1H), 4.14 (t, $J = 9.0$ Hz, 1H), 4.30 (dt, $J = 7.8$ and 2.7 Hz, 1H), 5.19 (t, $J = 9.9$ Hz, 1H), 5.40 (d, $J = 10.2$ Hz, 1H), 7.57 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H); ^{13}C NMR (75.5 MHz, CDCl_3) 13.3, 17.5, 27.3 (q, $J = 3.1$ Hz), 28.2, 40.1 (q, $J = 28.5$ Hz), 42.1, 58.5, 62.9, 80.6, 123.6 (q, $J = 271.7$ Hz), 125.7 (q, $J = 3.8$ Hz), 125.8 (q, $J = 279.1$ Hz), 128.6, 132.1 (q, $J = 32.3$ Hz), 137.9, 152.7, 167.3, 169.8; ^{19}F NMR (283 MHz, CDCl_3) -73.54 (d, $J = 9.0$ Hz), -64.29 (s); IR (CH_2Cl_2): 738, 1020, 1040, 1067, 1103, 1131, 1173, 1200, 1223, 1266, 1301, 1326, 1387, 1405, 1425, 1694, 1784, 2360 cm^{-1} ; Anal. Calcd for $\text{C}_{20}\text{H}_{19}\text{F}_6\text{NO}_5$: C, 51.40; H, 4.10; N, 3.00. Found: C, 51.26; H, 4.19; N, 2.98.

(4S,5R,6R)-6-Furyl-5-[[[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (2d):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.131 g (0.336 mmol) of the desired lactone **2d**.
yield (2 steps): 84%, white solid, mp.: 151–154 °C, $R_f = 0.57$ (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25} = +19.8$ (c 0.81, CHCl_3); ^1H NMR (300 MHz, CDCl_3): 0.55 (d, $J = 6.9$ Hz, 3H), 0.80 (d, $J = 6.9$ Hz, 3H), 2.03 (sepd, $J = 6.9$ and 3.6 Hz, 1H), 2.80 (dd, $J = 17.7$ and 7.5 Hz, 1H), 3.01 (dd, $J = 17.4$ and 7.8 Hz, 1H), 3.31–3.49 (m, 1H), 4.17 (dd, $J = 9.0$ and 2.7 Hz, 1H), 4.25 (dd, $J = 9.3$ and 7.8 Hz, 1H), 4.39 (ddd, $J = 7.8$, 3.6 and 2.7 Hz, 1H), 5.28 (t, $J = 9.3$ Hz, 1H), 5.52 (d, $J = 9.9$ Hz, 1H), 6.38 (dd, $J = 3.3$ and 1.8 Hz, 1H), 6.62 (d, $J = 3.3$ Hz, 1H), 7.44 (dd, $J = 1.8$ and 0.9 Hz, 1H); ^{13}C NMR (75.5 MHz, CDCl_3) 14.4, 17.5, 27.3 (q, $J = 3.2$ Hz), 28.5, 39.5, 39.9 (q, $J = 28.5$ Hz), 58.7, 63.4, 74.2, 110.8, 111.1, 125.7 (q, $J = 279.1$ Hz), 143.9, 147.5, 152.9, 166.9, 169.9; ^{19}F NMR (283 MHz, CDCl_3) -73.19 (d, $J = 6.8$ Hz); IR (CH_2Cl_2): 525, 741, 767, 801, 1017, 1065, 1103, 1122, 1176, 1194, 1199, 1281, 1387, 1697, 1785 cm^{-1} ; HRMS (FAB) m/z : calcd. for $\text{C}_{17}\text{H}_{19}\text{F}_3\text{NO}_6$ $[\text{M} + \text{H}]^+$ 390.1164; found 390.1172.

(4S,5R,6R)-6-(1-Methylethyl)-5-[[[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (2e):

Isobutyraldehyde (47.2 μL , 0.52 mmol) and TiCl_4 (0.057 mL, 0.52 mmol) were added and the same chromatographic purification (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.101

g (0.276 mmol) of the desired lactone **2e**.

yield (2 steps): 69%, white solid, mp.: 107–110 °C, R_f = 0.61 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +3.5 (*c* 0.86, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.89 (d, *J* = 7.2 Hz, 3H), 0.95 (d, *J* = 7.2 Hz, 3H), 1.06 (d, *J* = 6.6 Hz, 3H), 1.09 (d, *J* = 6.9 Hz, 3H),

1.74 (sepd, *J* = 6.9 and 2.1 Hz, 1H), 2.30 (sepd, *J* = 7.2 and 3.6 Hz, 1H), 2.69 (dd, *J* = 17.4 and 6.6 Hz, 1H), 2.94 (dd, *J* = 17.4 and 8.4 Hz, 1H), 3.13–3.29 (m, 1H), 4.23–4.32 (m, 2H), 4.38 (dd, *J* = 9.9 and 1.8 Hz, 1H), 4.49 (dt, *J* = 7.2 and 3.6 Hz, 1H), 4.75 (t, *J* = 9.0 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) 14.3, 14.4, 17.5, 19.6, 27.2 (q, *J* = 2.5 Hz), 28.4, 29.9, 38.7, 40.4 (q, *J* = 28.5 Hz), 58.6, 63.1, 83.5, 125.8 (q, *J* = 279.2 Hz), 153.0, 168.0, 171.0; ¹⁹F NMR (283 MHz, CDCl₃) –73.16 (d, *J* = 8.8 Hz); IR (CH₂Cl₂): 740, 1022, 1059, 1082, 1109, 1122, 1140, 1179, 1201, 1227, 1301, 1376, 1387, 1694, 1761, 1786 cm^{–1}; Anal. Calcd for C₁₆H₂₂F₃NO₅: C, 52.60; H, 6.07; N, 3.83. Found: C, 52.72; H, 6.04; N, 3.97.

(4*S*,5*R*,6*R*)-5-{[(4*S*)-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl}-6-[(*E*)-prop-1-en-1-yl]-4-(trifluoromethyl)tetrahydropyran-2-one (2f):

1.0 *M* solution of *n*-Bu₂BOTf in CH₂Cl₂ (0.88 mL, 0.88 mmol) and *i*-Pr₂EtN (160 μL, 0.92 mmol) were employed for the formation of enolate, and the same chromatographic purification (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.0872 g (0.240 mmol) of the desired lactone **2f**.

yield (2 steps): 60%, colorless oil, R_f = 0.61 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = –5.7 (*c* 1.00, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.85 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 3H), 1.72 (dd, *J* = 6.6 and 1.8 Hz, 3H), 2.24 (sepd, *J* = 6.9 and 3.6 Hz, 1H), 2.73 (dd, *J* = 17.4 and 5.7 Hz, 1H), 2.93 (dd, *J* = 17.1 and 9.0 Hz, 1H), 3.29–3.49 (m, 1H), 4.25 (dd, *J* = 9.3 and 3.3 Hz, 1H), 4.29 (t, *J* = 9.3 Hz, 1H), 4.45 (dt, *J* = 7.5 and 3.3 Hz, 1H), 4.73–4.81 (m, 2H), 5.65 (ddq, *J* = 16.5, 7.8 and 1.5 Hz, 1H), 5.88 (dq, *J* = 15.3 and 6.6 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) 14.5, 17.8, 17.8, 27.2 (q, *J* = 2.5 Hz), 28.5, 39.4 (q, *J* = 28.6 Hz), 41.0, 59.0, 63.4, 80.6, 125.0, 126.0 (q, *J* = 278.5 Hz), 134.9, 153.3, 167.7, 170.4; ¹⁹F NMR (283 MHz, CDCl₃) –73.7 (d, *J* = 9.1 Hz); IR (neat) 736, 754, 774, 929, 972, 1021, 1058, 1101, 1121, 1144, 1176, 1205, 1224, 1240, 1260, 1271, 1302, 1375, 1388, 1409, 1465, 1487, 1698, 1784, 2859, 2877, 2925, 2969 cm^{–1}; HRMS (EI) *m/z*: calcd. for C₁₆H₂₀F₃NO₅ [M]⁺ 363.1294; found 363.1268.

General procedure for the boron aldol reactions of the lactone **3 and **7** with aromatic aldehydes in the presence of Et₃N**

(4*R*,5*S*,6*S*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-phenyl-4-(trifluoromethyl)tetrahydropyran-2-one (3a**):**

A 1.0 *M* solution of *n*-Bu₂BOTf in CH₂Cl₂ (1.20 mL, 1.20 mmol) and Et₃N (172 μ L, 1.24 mmol) were stirred for 1 h at 0 °C where a solution of the imide **1** (0.169 g, 0.40 mmol) in CH₂Cl₂ (4 mL) was added, and the reaction was continued for 2 h at that temperature. After cooling to –80 °C, Et₃N (13.5 μ L, 0.100 mmol) was added and the whole was stirred for 30 min at that temperature. Benzaldehyde (52.8 μ L, 0.52 mmol) was introduced and the reaction mixture was stirred for 30 min at that temperature then for 4.5 h at 0 °C, which was then quenched with pH 7 buffer (3 mL), MeOH (3 mL) and 30% H₂O₂ (3 mL), stirred at rt for 1 h, and extracted with CH₂Cl₂ three times. Concentration after dried over MgSO₄ furnished crude oil which was treated with THF (4 mL) and Et₃N (55.5 μ L) at rt and stirred for 14 h at that temperature. The reaction was quenched with 1 *M* HCl aq (3 mL) and extracted with AcOEt three times. Concentration after dried over MgSO₄ furnished crude oil that was purified by silica gel chromatography to afford the desired lactone **3a** (0.123 g, 0.308 mmol).

yield (2 steps): 77%, white solid, mp.: 170–171 °C, *R*_f = 0.64 (*n*-hexane:AcOEt, 1:1, v/v); [α]_D²⁵ = +141.4 (*c* 0.88, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.75 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 7.2 Hz, 3H), 2.20 (sepd, *J* = 6.6 and 4.2 Hz, 1H), 2.91 (dd, *J* = 17.4 and 4.5 Hz, 1H), 3.09 (dd, *J* = 17.7 and 6.6 Hz, 1H), 3.37 (t, *J* = 8.4 Hz, 1H), 3.52–3.68 (m, 1H), 3.85 (ddd, *J* = 6.0, 4.2 and 2.1 Hz, 1H), 3.93 (dd, *J* = 9.0 and 2.1 Hz, 1H), 5.00 (t, *J* = 9.9 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 7.33–7.41 (m, 5H); ¹³C NMR (75.5 MHz, CDCl₃) 14.6, 17.5, 27.1 (q, *J* = 2.5 Hz), 28.6, 38.8 (q, *J* = 28.5 Hz), 43.5, 59.0, 63.4, 80.7, 125.9 (q, *J* = 278.5 Hz), 127.0, 128.4, 129.6, 134.2, 152.5, 167.9, 169.9; ¹⁹F NMR (283 MHz, CDCl₃) –73.81 (d, *J* = 10.1 Hz); IR (CH₂Cl₂) 702, 740, 1024, 1041, 1054, 1102, 1122, 1140, 1178, 1201, 1224, 1277, 1300, 1325, 1376, 1386, 1413, 1459, 1485, 1696, 1770, 1783, 2970 cm^{–1}; Anal. Calcd for C₁₉H₂₀F₃NO₅: C, 57.14; H, 5.05; N, 3.51. Found: C, 57.50; H, 5.07; N, 3.50.

(4*R*,5*S*,6*S*)-6-(4-Methoxyphenyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (3b**):**

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1,

v/v) furnished 0.132 g (0.308 mmol) of the desired lactone **3b**.

yield (2 steps): 77%, white solid, mp.: 223–224 °C, R_f = 0.56 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +172.8 (*c* 0.90, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.76 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 2.20 (sepd, *J* = 6.9 and 4.2 Hz, 1H), 2.89 (dd, *J* = 17.7 and 4.5 Hz, 1H), 3.07 (dd, *J* = 17.7 and 9.9 Hz, 1H), 3.47 (t, *J* = 8.4 Hz, 1H), 3.49–3.65 (m, 1H), 3.81 (s, 3H), 3.89 (ddd, *J* =

7.5, 3.9 and 1.8 Hz, 1H), 3.96 (dd, *J* = 9.0 and 2.1 Hz, 1H), 4.99 (t, *J* = 9.9 Hz, 1H), 5.16 (d, *J* = 10.2 Hz, 1H), 6.87–6.92 (m, 2H), 7.25–7.30 (m, 2H); ¹³C NMR (75.5 MHz, CD₃COCD₃) 15.0, 17.7, 28.0 (q, *J* = 2.4 Hz), 30.5, 39.7 (q, *J* = 27.9 Hz), 44.6, 55.7, 60.0, 64.6, 80.8, 114.7, 127.7 (q, *J* = 277.9 Hz), 127.9, 129.3, 153.8, 161.5, 168.8, 171.0; ¹⁹F NMR (283 MHz, CDCl₃) –73.74 (d, *J* = 9.3 Hz); IR (CH₂Cl₂): 544, 621, 635, 655, 831, 849, 863, 896, 928, 977, 1032, 1057, 1101, 1123, 1176, 1201, 1223, 1300, 1386, 1420, 1442, 1465, 1485, 1517, 1586, 1613, 1696, 1768, 1784, 2841, 2878, 2938, 2971, 3009 cm^{–1}. Anal. Calcd for C₂₀H₂₂F₃NO₆: C, 55.94; H, 5.16; N, 3.26. Found: C, 55.56; H, 4.86; N, 3.24.

(4R,5S,6S)-5-[[[(4S)-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-[4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)tetrahydropyran-2-one (3c):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.140 g (0.300 mmol) of the desired lactone **3c**.

yield (2 steps): 75%, white solid, mp: 141–144 °C, R_f = 0.74 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +163.2 (*c* 0.93, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.76 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 2.21 (sepd, *J* = 6.9 and 3.9 Hz, 1H), 2.92 (dd, *J* =

17.7 and 4.8 Hz, 1H), 3.10 (dd, *J* = 17.7 and 9.9 Hz, 1H), 3.42 (t, *J* = 8.7 Hz, 1H), 3.52–3.69 (m, 1H), 3.92 (ddd, *J* = 8.1, 4.2 and 2.4 Hz, 1H), 3.98 (dd, *J* = 9.0 and 2.4 Hz, 1H), 5.04 (t, *J* = 9.9 Hz, 1H), 5.30 (d, *J* = 10.2 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H); ¹³C NMR (75.5 MHz, CDCl₃) 14.3, 17.5, 27.2 (q, *J* = 2.5 Hz), 28.5, 39.2 (q, *J* = 28.5 Hz), 43.4, 58.9, 63.3, 79.9, 123.5 (q, *J* = 271.7 Hz), 125.4 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 264.8 Hz), 127.6, 131.8 (q, *J* = 33.5 Hz), 138.3, 152.5, 167.5, 169.6; ¹⁹F NMR (283 MHz, CDCl₃) –73.72 (d, *J* = 9.0 Hz), –64.04 (s); IR (CH₂Cl₂): 605, 660, 750, 775, 836, 854, 881, 897, 928, 977, 1019, 1050, 1067, 1101, 1129, 1175, 1200, 1224, 1326, 1301, 1326, 1376, 1386, 1412, 1423, 1467, 1487, 1623, 1696, 1785, 2880, 2941 cm^{–1}; HRMS (FAB) *m/z*: calcd. for C₂₀H₂₀F₆NO₅ [M + H]⁺ 468.1246; found 468.1234.

(4R,5S,6S)-6-Furyl-5-[[[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (3d):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.934 g (0.240 mmol) of the desired lactone **3d**.

yield (2 steps): 60%, yellow oil, R_f = 0.54 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +177.5 (*c* 0.41, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.81 (d, *J* = 6.9 Hz, 3H), 0.87 (d, *J* = 7.2 Hz, 3H), 2.27 (sepd, *J* = 6.9 and 3.6 Hz, 1H), 2.83 (dd, *J* = 17.4 and 6.0 Hz, 1H), 3.01 (dd, *J* = 17.4 and 9.0 Hz, 1H), 3.46–3.62 (m, 1H), 3.93 (t, *J* = 9.0 Hz, 1H), 4.13 (t, *J* = 7.5 Hz, 1H), 4.11–4.16 (m, 1H), 5.21 (t, *J* = 8.7 Hz, 1H), 5.42 (d, *J* = 9.9 Hz, 1H), 6.40 (dd, *J* = 3.3 and 1.8 Hz, 1H), 6.50 (dd, *J* = 3.3 and 0.3 Hz, 1H), 7.46 (dd, *J* = 1.8 and 0.9 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) 14.4, 17.8, 27.3 (q, *J* = 2.5 Hz), 28.5, 39.3 (q, *J* = 28.5 Hz), 40.6 (q, *J* = 1.3 Hz), 59.2, 63.5, 74.1, 110.8, 110.9, 125.8 (q, *J* = 279.2 Hz), 143.9, 147.6, 152.8, 167.0, 169.8; ¹⁹F NMR (283 MHz, CDCl₃) –73.40 (d, *J* = 9.3 Hz); IR (neat): 598, 701, 739, 930, 976, 1015, 1058, 1102, 1122, 1143, 1153, 1177, 1199, 1226, 1281, 1301, 1325, 1377, 1387, 1466, 1486, 1506, 1697, 1784, 2934, 2968 cm^{–1}; HRMS (EI) *m/z*: calcd. for C₁₇H₁₈F₃NO₆ [M]⁺ 389.1086; found 389.1054.

3-Methyl-1,5-bis[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]pentan-1,5-dione (5a):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 1.84 g (5.00 mmol) of the desired imide **5a** from 3-methylglutaric anhydride (1.28 g, 10.0 mmol).

yield (from the glutaric anhydride): 50%, white solid, mp.: 138–143 °C, R_f = 0.52 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +101.4 (*c* 0.84, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.88 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 6H), 1.08 (d, *J* = 6.6 Hz, 3H), 2.62 (oct, *J* = 6.6 Hz, 1H), 2.29–2.45 (m, 2H), 2.86 (dd, *J* = 16.5 and 6.9 Hz, 1H), 2.88 (dd, *J* = 15.9 and 6.3 Hz, 1H), 2.99 (dd, *J* = 15.9 and 6.9 Hz, 1H), 3.03 (dd, *J* = 16.5 and 6.6 Hz, 1H), 4.20 (dd, *J* = 9.0 and 3.0 Hz, 2H), 4.28 (t, *J* = 8.7 Hz, 1H), 4.30 (t, *J* = 8.7 Hz, 1H), 4.39–4.45 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) 14.4, 14.5, 17.8, 17.8, 20.1, 26.1, 28.2, 28.2, 41.4, 41.8, 58.2, 58.3, 63.2, 63.2, 153.9, 154.0, 171.7, 171.7; IR (CH₂Cl₂): 1023, 1191, 1217, 1303, 1374, 1388, 1701, 1780 cm^{–1}; Anal. Calcd for C₁₈H₂₈N₂O₆: C, 58.68; H, 7.66; N, 7.60. Found: C, 58.52; H, 7.68; N, 7.60.

3-(1-Methylethyl)-1,5-bis[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]pentan-1,5-dione (5b):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 1.57 g (3.96 mmol) of the desired imide **5b** from 3-isopropylglutaric anhydride (1.21 g, 7.76 mmol).

yield (from the glutaric anhydride): 51%, white solid,

mp.: 105–106 °C, R_f = 0.70 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +103.2 (*c* 0.95, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.87 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 7.2 Hz, 3H), 0.90 (d, *J* = 7.2 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 3H), 0.93 (d, *J* = 6.9 Hz, 6H), 1.82 (sextd, *J* = 6.9 and 3.9 Hz, 1H), 2.36 (sextd, *J* = 6.9 and 3.9 Hz, 2H), 2.47–2.57 (m, 1H), 2.69 (dd, *J* = 15.6 and 8.4 Hz, 1H), 2.92 (dd, *J* = 17.1 and 7.2 Hz, 1H), 2.98 (dd, *J* = 16.8 and 5.4 Hz, 1H), 3.15 (dd, *J* = 15.6 and 4.5 Hz, 1H), 4.19 (dd, *J* = 8.7 and 2.7 Hz, 2H), 4.28 (dd, *J* = 16.5 and 8.4 Hz, 2H), 4.35–4.41 (m, 2H); ¹³C NMR (75.5 MHz, CDCl₃) 14.59, 14.64, 17.96, 17.98, 18.9, 19.0, 28.35, 28.44, 31.1, 36.0, 36.9, 37.2, 58.5, 58.7, 63.25, 63.31, 154.08, 154.14, 172.7, 172.8; IR (CH₂Cl₂): 702, 774, 972, 996, 1021, 1060, 1099, 1122, 1143, 1204, 1236, 1267, 1300, 1343, 1382, 1434, 1466, 1487, 1697, 1782, 2876, 2937, 3059 cm⁻¹; Anal. Calcd for C₂₀H₃₂N₂O₆: C, 60.59; H, 8.14; N, 7.07. Found: C, 60.91; H, 8.52; N, 6.86.

1,5-Bis[(4S)-4-(1-methylethyl)oxazolidin-2-on-3-yl]-3-phenylpentan-1,5-dione (5c):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 3.19 g (7.41 mmol) of the desired imide **5c** from 3-phenylglutaric anhydride (2.43 g, 12.8 mmol).

yield (from the glutaric anhydride): 62%, white solid,

mp.: 122–124 °C, R_f = 0.50 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +91.3 (*c* 0.85, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.62 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.84 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 2.12 (sextd, *J* = 6.9 and 3.9 Hz, 1H), 2.28 (sextd, *J* = 6.9 and 3.9 Hz, 1H), 3.18 (dd, *J* = 16.5 and 6.6 Hz, 1H), 3.20 (dd, *J* = 16.5 and 6.3 Hz, 1H), 3.46 (dd, *J* = 16.8 and 7.8 Hz, 1H), 3.53 (dd, *J* = 16.5 and 7.8 Hz, 1H), 3.85 (quint, *J* = 7.2 Hz, 1H), 4.09–4.37 (m, 6H), 7.14–7.31 (m, 6H); ¹³C NMR (75.5 MHz, CDCl₃) 14.1, 14.4, 17.5, 17.7, 28.0, 28.2, 37.1, 40.7, 41.2, 58.1, 58.2, 63.1, 63.2, 126.5, 127.4, 128.2, 142.6, 153.7, 153.8, 170.8, 171.0; IR (CH₂Cl₂): 702, 735, 970, 998, 1019, 1060, 1074, 1106, 1121, 1142, 1177, 1207, 1284, 1301, 1342, 1373, 1389, 1484, 1704, 1775, 2875, 2937, 2964 cm⁻¹; Anal. Calcd for C₂₃H₃₀N₂O₆: C, 64.17; H, 7.02; N, 7.07.

6.51. Found: C, 64.18; H, 7.22; N, 6.26.

3-[(*tert*-Butyldimethylsilyl)oxy]-1,5-bis[(4*S*)-4-(1-methylethyl)oxazolidin-2-on-3-yl]pentan-1,5-dione (5d**):**

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 1.01 g (2.09 mmol) of the desired imide **5d** from 3-[(*tert*-butyldimethylsilyl)oxy]glutaric anhydride (1.00 g, 4.09 mmol).

yield (from the glutaric anhydride): 51%, white solid, mp.: 95–96 °C, R_f = 0.70 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = +89.2 (*c* 0.70, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.09 (s, 3H), 0.10 (s, 3H), 0.85 (s, 9H), 0.87 (d, *J* = 6.9 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.91 (d, *J* = 6.9 Hz, 6H), 2.30–2.45 (m, 2H), 3.04 (dd, *J* = 15.9 and 6.3 Hz, 1H), 3.21 (d, *J* = 6.0 Hz, 2H), 3.41 (dd, *J* = 16.2 and 6.0 Hz, 1H), 4.18–4.30 (m, 4H), 4.37–4.42 (m, 2H), 4.73 (quint, *J* = 6.0 Hz, 1H); ¹³C NMR (75.5 MHz, CDCl₃) –5.0, –4.9, 14.5, 14.6, 17.9, 17.97, 18.0, 25.7, 28.2, 28.4, 43.0, 43.2, 58.45, 58.54, 63.2, 63.3, 65.1, 154.0, 170.4, 170.5; IR (CH₂Cl₂): 717, 779, 813, 838, 972, 1020, 1064, 1099, 1119, 1142, 1183, 1208, 1247, 1301, 1315, 1337, 1364, 1387, 1465, 1487, 1703, 1782, 2856, 2930, 2963 cm^{–1}; Anal. Calcd for C₂₃H₄₀N₂O₇Si: C, 57.00; H, 8.32; N, 5.78. Found: C, 57.07; H, 8.76; N, 5.61.

(4*S*,5*R*,6*R*)-4-Methyl-5-[(4*S*)-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl}-6-phenyltetrahydropyran-2-one (6a**):**

Purification of the crude materials by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.0995 g (0.288 mmol) of the desired lactone **6a**.

yield (2 steps): 77%, white solid, mp.: 156–158 °C, R_f = 0.37 (*n*-hexane:AcOEt, 1:1, v/v); $[\alpha]_D^{25}$ = –12.6 (*c* 0.91, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.04 (d, *J* = 6.9 Hz, 3H), 0.71 (d, *J* = 7.2 Hz, 3H), 1.08 (d, *J* = 6.6 Hz, 3H), 1.81 (sepd, *J* = 6.9 and 3.3 Hz, 1H), 2.43 (dd, *J* = 17.1 and 10.2 Hz, 1H), 2.50–2.65 (m, 1H), 2.94 (dd, *J* = 17.1 and 5.7 Hz, 1H), 4.04 (dd, *J* = 9.3 and 2.7 Hz, 1H), 4.15 (t, *J* = 9.0 Hz, 1H), 4.36 (dt, *J* = 8.1 and 3.0 Hz, 1H), 4.67 (t, *J* = 10.2 Hz, 1H), 5.72 (d, *J* = 10.2 Hz, 1H), 7.31–7.40 (m, 5H); ¹³C NMR (75.5 MHz, CDCl₃) 13.3, 17.6, 19.2, 27.8, 31.8, 36.9, 49.4, 58.1, 62.5, 83.9, 127.7, 128.6, 129.2, 136.1, 153.2, 169.6, 171.7; IR (CH₂Cl₂) 701, 738, 1027, 1037, 1061, 1076, 1095, 1121, 1143, 1154, 1181, 1203, 1225, 1246, 1266, 1300, 1332, 1364, 1386, 1457, 1489, 1692, 1742, 1780, 2967

cm⁻¹; Anal. Calcd for C₁₉H₂₃NO₅: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.94; H, 6.81; N, 4.01.

(4*S*,5*R*,6*R*)-4-(1-Methylethyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-6-phenyltetrahydropyran-2-one (6b):

Purification of the crude materials by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.136 g (0.364 mmol) of the desired lactone **6b**.

yield (2 steps): 91%, white solid, mp.: 117–119 °C, *R*_f = 0.31 (*n*-hexane:AcOEt, 2:1, v/v); [α]_D²⁵ = +6.2 (*c* 0.26, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.44 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.9 Hz, 3H), 0.96 (d, *J* = 6.6 Hz, 3H), 1.73 (sexd, *J* = 6.9 and 3.3 Hz, 1H), 1.82 (sexd, *J* = 6.9 and 3.3 Hz, 1H), 2.51–2.66 (m, 2H), 2.83 (dd, *J* = 15.9 and 7.5 Hz, 1H), 4.02 (dd, *J* = 9.3 and 2.7 Hz, 1H), 4.12 (dd, *J* = 9.0 and 8.4 Hz, 1H), 4.31 (dt, *J* = 8.1 and 2.7 Hz, 1H), 4.81 (t, *J* = 9.3 Hz, 1H), 5.22 (d, *J* = 9.9 Hz, 1H), 7.30–7.42 (m, 5H); ¹³C NMR (75.5 MHz, CDCl₃) 13.4, 16.8, 17.9, 20.2, 28.0, 29.8, 30.9, 41.9, 46.4, 58.5, 62.6, 83.1, 128.0, 128.6, 129.4, 135.6, 153.0, 171.6, 172.6; IR (CH₂Cl₂): 700, 739, 1007, 1027, 1061, 1096, 1121, 1142, 1201, 1224, 1247, 1303, 1338, 1385, 1464, 1690, 1747, 1779, 2877 cm⁻¹; HRMS (FAB) *m/z*: calcd. for C₂₁H₂₈NO₅ [M + H]⁺ 374.1967; found 374.1974.

(4*S*,5*R*,6*R*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4,6-diphenyltetrahydropyran-2-one (6c):

Purification of the crude materials by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.122 g (0.300 mmol) of the desired lactone **6c**.

yield (2 steps): 75%, white solid, mp.: 157–159 °C, *R*_f = 0.47 (*n*-hexane:AcOEt, 2:1, v/v); [α]_D²⁵ = +36.2 (*c* 0.59, CHCl₃); ¹H NMR (300 MHz, CDCl₃): 0.18 (d, *J* = 6.9 Hz, 3H), 0.59 (d, *J* = 6.9 Hz, 3H), 1.77 (sexd, *J* = 6.9 and 3.3 Hz, 1H), 3.00 (dd, *J* = 18.3 and 12.0 Hz, 1H), 3.13 (dd, *J* = 18.3 and 6.0 Hz, 1H), 3.43 (t, *J* = 5.7 Hz, 1H), 3.62 (dt, *J* = 11.7 and 6.0 Hz, 1H), 3.77–3.83 (m, 2H), 5.14 (t, *J* = 10.8 Hz, 1H), 5.60 (d, *J* = 10.5 Hz, 1H), 7.26–7.46 (m, 10H); ¹³C NMR (75.5 MHz, CDCl₃) 14.1, 17.5, 28.5, 36.5, 43.8, 49.3, 58.3, 63.0, 84.3, 127.4, 127.8, 127.9, 128.6, 128.9, 129.3, 136.1, 139.0, 152.7, 169.1, 170.8; IR (CH₂Cl₂): 700, 739, 772, 1024, 1071, 1099, 1120, 1142, 1172, 1203, 1243, 1277, 1298, 1327, 1341, 1385, 1458, 1482, 1692, 1741, 1781, 2927, 2965 cm⁻¹; HRMS (FAB) *m/z*: calcd. for

C₂₄H₂₆NO₅ [M + H]⁺ 408.1811; found 408.1835.

(4*R*,5*S*,6*S*)-4-Methyl-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-phenyltetrahydropyran-2-one (6a):

Purification of the crude material by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.104 g (0.300 mmol) of the desired lactone **7a**.

yield (2 steps): 83%, white solid, mp.: 195–198 °C, *R*_f = 0.53 (*n*-hexane:AcOEt, 1:1, v/v); [α]_D²⁵ = +99.9 (*c* 0.64, CHCl₃); ¹H

NMR (300 MHz, CDCl₃): 0.81 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 7.2 Hz, 3H), 1.12 (d, *J* = 6.3 Hz, 3H), 2.24 (sepd, *J* = 7.2 and 3.9 Hz, 1H), 2.44 (dd, *J* = 17.4 and 9.9 Hz, 1H), 2.57–2.72 (m, 1H), 2.96 (dd, *J* = 17.4 and 6.3 Hz, 1H), 3.55 (t, *J* = 8.7 Hz, 1H), 3.95–4.00 (m, 2H), 4.44 (t, *J* = 10.2 Hz, 1H), 5.33 (d, *J* = 10.4 Hz, 1H), 7.27–7.36 (m, 5H); ¹³C NMR (75.5 MHz, CDCl₃) 14.9, 17.7, 19.3, 28.8, 31.0, 36.7, 50.5, 58.9, 63.4, 83.3, 126.8, 128.3, 128.9, 136.4, 153.1, 169.6, 171.7; IR (CH₂Cl₂): 701, 738, 976, 1026, 1042, 1057, 1075, 1095, 1121, 1143, 1203, 1225, 1243, 1266, 1300, 1315, 1333, 1340, 1365, 1387, 1457, 1486, 1693, 1740, 1779, 2966 cm⁻¹; Anal. Calcd for C₁₉H₂₃NO₅: C, 66.07; H, 6.71; N, 4.06. Found: C, 65.71; H, 6.45; N, 3.96.

(4*R*,5*S*,6*S*)-4-(1-Methylethyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-6-phenyltetrahydropyran-2-one (7b):

Purification of the crude materials by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.133 g (0.356 mmol) of the desired lactone **7b**.

yield (2 steps): 89%, white solid, mp.: 139–142 °C, *R*_f = 0.38 (*n*-hexane:AcOEt, 2:1, v/v); [α]_D²⁵ = +254.4 (*c* 0.28 CHCl₃); ¹H

NMR (300 MHz, CDCl₃): 0.75 (d, *J* = 6.9 Hz, 3H), 0.83 (d, *J* = 6.9 Hz, 3H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.98 (d, *J* = 6.9 Hz, 3H), 1.79 (sexd, *J* = 6.6 and 4.5 Hz, 1H), 2.18 (sexd, *J* = 6.9 and 3.0 Hz, 1H), 2.56 (dd, *J* = 16.8 and 5.1 Hz, 1H), 2.70–2.79 (m, 1H), 2.90 (dd, *J* = 16.5 and 9.0 Hz, 1H), 3.33 (t, *J* = 9.0 Hz, 1H), 3.85–3.91 (m, 2H), 4.57 (t, *J* = 9.9 Hz, 1H), 5.18 (d, *J* = 9.9 Hz, 1H), 7.30–7.37 (m, 5H); ¹³C NMR (75.5 MHz, CDCl₃) 14.8, 17.66, 17.71, 19.1, 28.9, 30.8, 31.3, 40.5, 47.3, 59.0, 63.3, 82.4, 126.9, 128.3, 129.0, 135.8, 152.8, 171.6, 172.2; IR (CH₂Cl₂): 701, 737, 1028, 1048, 1095, 1121, 1143, 1169, 1200, 1224, 1249, 1266, 1300, 1337, 1363, 1386, 1456, 1464, 1485, 1694, 1746, 1777, 2876, 2922, 2930, 2964 cm⁻¹; HRMS (FAB) *m/z*: calcd. for C₂₁H₂₈NO₅ [M + H]⁺ 374.1967; found 374.1919.

(4*R*,5*S*,6*S*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4,6-diphenyltetrahydropyran-2-one (7c):

Purification of the crude materials by silica gel chromatography (*n*-hexane:AcOEt, 2:1, v/v) furnished 0.135 g (0.332 mmol) of the desired lactone **7c**.

yield (2 steps): 83%, white solid, mp.: 169–170 °C, R_f = 0.47 (*n*-hexane:AcOEt, 2:1, v/v); $[\alpha]_D^{25}$ = +118.0 (*c* 0.58, CHCl₃); ¹H

NMR (300 MHz, CDCl₃): 0.16 (d, *J* = 6.9 Hz, 3H), 0.56 (d, *J* = 7.2 Hz, 3H), 1.70 (sexd, *J* = 6.9 and 4.2 Hz, 1H), 2.91 (dd, *J* = 18.6 and 12.0 Hz, 1H), 3.14 (dd, *J* = 18.3 and 6.3 Hz, 1H), 3.47 (dd, *J* = 9.0 and 8.4 Hz, 1H), 3.74 (dt, *J* = 11.4 and 6.0 Hz, 1H), 3.47 (dd, *J* = 9.0 and 8.4 Hz, 1H), 3.80 (dd, *J* = 9.3 and 2.1 Hz, 1H), 3.88 (ddd, *J* = 7.8, 4.2 and 2.4 Hz, 1H), 5.14 (t, *J* = 10.5 Hz, 1H), 5.46 (d, *J* = 10.2 Hz, 1H), 7.19–7.38 (m, 10H); ¹³C NMR (75.5 MHz, CDCl₃) 14.2, 17.4, 28.6, 37.5, 42.8, 49.5, 58.5, 63.1, 84.2, 126.9, 127.5, 127.8, 128.4, 129.0, 129.2, 136.2, 139.5, 152.6, 169.1, 170.6; IR (CH₂Cl₂): 701, 739, 1027, 1038, 1063, 1101, 1169, 1205, 1244, 1266, 1300, 1323, 1386, 1694, 1743, 1781, 2967 cm⁻¹; HRMS (FAB) *m/z*: calcd. for C₂₄H₂₆NO₅ [M + H]⁺ 408.1811; found 408.1769.

3. References

1. Shinohara, N.; Haga, J.; Yamazaki, T.; Kitazume, T.; Nakamura, S. *J. Org. Chem.* **1995**, *60*, 4363–4374.
2. Gootjes, J.; Nauta, W. T. *Recl. Trav. Chim. Pays-Bas* **1965**, *84*, 1183–1199.

4. NMR Spectra

(4*S*,5*R*,6*R*)-6-Furyl-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4-(trifluoromethyl)tetrahydropyran-2-one (2d):

(4*S*,5*R*,6*R*)-5-[(4*S*)-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-[(*E*)-prop-1-en-1-yl]-4-(trifluoromethyl)tetrahydropyran-2-one (2f):

(4*R*,5*S*,6*S*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-6-[4-(trifluoromethyl)phenyl]-4-(trifluoromethyl)tetrahydropyran-2-one (3c):

(4*R*,5*S*,6*S*)-6-Furyl-5-{[(4*S*)-4-(1-methylethyl)oxazolidin-2-on-3-yl]carbonyl}-4-(trifluoromethyl)tetrahydropyran-2-one (3d):

(4*S*,5*R*,6*R*)-4-(1-Methylethyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-6-phenyltetrahydropyran-2-one (6b):

(4*S*,5*R*,6*R*)-5-{[(4*S*)-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl}-4,6-diphenyltetrahydropyran-2-one (6c):

(4*R*,5*S*,6*S*)-4-(1-Methylethyl)-5-[[*(4S)*-4-(1-methylethyl)oxazolidin-2-on-3-yl]-carbonyl]-6-phenyltetrahydropyran-2-one (7b):

(4*R*,5*S*,6*S*)-5-[[*(4S)*-4-(1-Methylethyl)oxazolidin-2-on-3-yl]carbonyl]-4,6-diphenyltetrahydropyran-2-one (7c):