Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information

Characterization Data

for

A remarkable temperature effect in the desymmetrisation of bridged *meso*-tricyclic succinic anhydrides with chiral oxazolidin-2-ones

Narendra R. Chaubey and Sunil K. Ghosh*

Bio-Organic Division, Bhabha Atomic Research Centre, Mumbai 400085, INDIA

E-mail: ghsunil@barc.gov.in

Table of Contents

1. General Experimental

All reactions were performed in oven-dried (120 ºC) or flame-dried glass apparatus under dry N_2 or argon atmosphere. Tetrahydrofuran (THF) was dried from sodium/benzophenone while *t*-BuOH was dried from CaH_2 followed by storage over 4 Å molecular sieves. *n*-BuLi (1.5 M in hexane) was purchased from Aldrich. Anhydride **3a** was made from meso-2,3-Dimethyl succinic acid following the reported procedure[1]. Anhydrides **2a**, **4a**, **2c** and **2e** were purchased from Aldrich and their saturated counterparts **2b**, **4b**, **2d** and **2f** were prepared following the reported procedure[2]. Oxazolidin-2-ones **1a**[3], **1b**[4], **1c**[5] and **1d**[6] were prepared following literature procedures. Solvent removal was carried out using a rotary evaporator connected to a dry ice condenser. TLC (0.5 mm) was carried out using home made silica plates with fluorescence indicator. Column chromatography was performed on silca gel (230-400 mesh). The ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker 200/300/500 MHz spectrometers. The spectra were referenced to residual chloroform (δ 7.25 ppm., ^{1}H; δ 77.00 ppm, ^{13}C). The IR spectra were recorded with a JASCO FT IR spectrophotometer in NaCl cells or in KBr discs. Peaks are reported in cm^{-1}. Melting points (mp) were determined on a Fischer John's melting point apparatus and were uncorrected. Optical rotations were measured with a JASCO DIP-360 polarimeter. Elemental analyses (C, H) were carried out at Analytical Facility of Indian Institute of Technology (IIT), Hydrometallurgy Section and Bio-Organic Division BARC, Mumbai, India.

2. General Procedures

General Procedure-I: Desymmetrisation of anhydride 2a with oxazolidin-2-one 1a at –78 ºC.

n-Butyl lithium (720 µL, 1.6 M in hexane, 1.15 mmol) was added slowly to a suspension of oxazolidin-2-one **1a** (369 mg, 1 mmol) in dry THF (2.5 mL) at 0 ºC to –10 ˚C under argon atmosphere. After 10 minutes, the reaction mixture was cooled to –78 ºC. Dry DMPU (1.2 mL) was added to the reaction mixture followed by a solution of the anhydride **2a** (197 mg, 1.2 mmol) in dry THF (2.5 mL). After 15 minutes at –78 ºC, the reaction mixture was acidified with 5% citric acid solution, brought to room temperature and extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was esterified with ethereal diazomethane, concentrated under reduced pressure and purified by

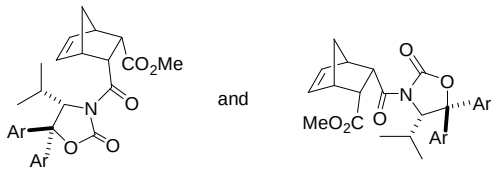
column chromatography to give a mixture of methyl esters **5a** and **6a** (**5a**:**6a** = 50/50) (416 mg, 76%) as a solid.

General Procedure-II: Desymmetrisation of anhydride 2a with oxazolidin-2-one 1a at 28 ºC.

n-Butyl lithium (720 µL, 1.6 M in hexane, 1.15 mmol) was added slowly to a suspension of oxazolidin-2-one **1a** (369 mg, 1 mmol) in dry THF (2.5 mL) at 0 ºC to –10 ˚C under argon atmosphere. After 10 minutes, the reaction mixture was brought to 28 ºC. Dry DMPU (1.2 mL) was added to the reaction mixture followed by a solution of the anhydride **2a** (197 mg, 1.2 mmol) in dry THF (2.5 mL). After 15 minutes at 28 ºC, the reaction mixture was acidified with 5% citric acid solution and extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was esterified with ethereal diazomethane, concentrated under reduced pressure and purified by column chromatography to give a mixture of methyl esters **5a** and **6a** (**5a**:**6a** = 90/10) (482 mg, 88%) as a solid.

3. Characterization data of products

Desymmetrisation of anhydride 2a with 1a



Ar = 2-MeO-5-Me-C_6H_3-;**5a** Ar = 2-MeO-5-Me-C_6H_3-; **6a**

Data for **5a**: mp 149-151 ºC; R_f = 0.5 (85:15 hexane/ethyl acetate); $[\alpha]^{25}_D$ –172.31 (*c* 0.65, MeOH); IR ($CHCl_3$ film) 3020, 2967, 2837, 1771, 1735, 1698, 1502 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.74 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.98 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.25-1.42 (m, 2 H, CHC*H*$_2$CH), 1.62-1.75 (m, 1 H, CH$_3$C*H*CH$_3$), 2.29 (s, 3 H, ArC*H*$_3$), 2.35 (s, 3 H, ArC*H*$_3$), 2.83 (s, broad, 1 H, C*H*CHCON), 3.14 (s, broad, 1 H, C*H*CHCOOMe), 3.37 (dd, *J* = 3.3, 9.9 Hz, 1 H, C*H*CON), 3.46 (s, 3 H, ArOC*H*$_3$), 3.49 (s, 3 H, ArOC*H*$_3$), 3.58 (s, 3 H, COOC*H*$_3$), 4.21 (dd, *J* = 3.3, 9.8 Hz, 1 H, C*H*COOMe), 5.66 (d, *J* = 1.5 Hz, 1 H, C*H*N), 5.97 (dd, *J* = 2.9, 5.5 Hz, 1 H, C=C*H*), 6.37 (dd, *J* = 2.9, 5.5 Hz, 1 H, C*H*=C), 6.61 (d, *J* = 8.3 Hz, 1

H, Ar), 6.71 (d, *J* = 8.3 Hz, 1 H, Ar), 7.01 (d, *J* = 1.5 Hz, 1 H, Ar), 7.05 (d, *J* = 1.6 Hz, 1 H, Ar), 7.19 (s, 1 H, Ar), 7.70 (d, *J* = 1.9 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.3, 20.2, 20.3, 21.7, 29.4, 45.6, 46.5, 47.4, 48.0, 48.9, 50.8, 54.8, 55.4, 62.1, 88.7, 110.5, 113.5, 125.8, 126.5, 127.5, 128.2, 128.3, 128.5, 128.7, 129.9, 133.9, 134.9, 152.2, 153.2, 156.0, 171.4, 172.7; Anal. Calcd for $C_{32}H_{37}NO_7$ (547.64): C, 70.18; H, 6.81; N, 2.56. Found: C, 69.88; H, 6.73; N, 2.78.

Data for **6a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.72 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.93 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.40-1.50 (m, 2 H, CHC*H*$_2$CH), 1.65-1.73 (m, 1 H, CH$_3$C*H*CH$_3$), 2.28 (s, 3 H, ArC*H*$_3$), 2.35 (s, 3 H, ArC*H*$_3$), 3.13 (s, broad, 1 H, C*H*CHCON), 3.21 (dd, *J* = 3.3, 9.8 Hz, 1 H, C*H*CON), 3.35-3.40 (m, 1 H, C*H*CHCOOMe), 3.40 (s, 3 H, COOC*H*$_3$), 3.46 (s, 6 H, 2 × ArOC*H*$_3$), 4.38 (dd, *J* = 3.3, 9.8 Hz, 1 H, C*H*COOMe), 5.74 (d, *J* = 1.6 Hz, 1 H, C*H*N), 6.14 (dd, *J* = 2.9, 5.5 Hz, 1 H, C=C*H*), 6.4 (dd, *J* = 2.9, 5.5 Hz, 1 H, C*H*=C), 6.62 (d, *J* = 8.3 Hz, 1 H, Ar), 6.68 (d, *J* = 8.3 Hz, 1 H, Ar), 6.97-7.06 (m, 2 H, Ar), 7.24 (d, *J* = 1.6 Hz, 1 H, Ar), 7.68 (d, *J* = 1.9 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.0, 20.7, 20.8, 22.9, 30.0, 46.0, 47.8, 48.3, 48.6, 48.9, 51.1, 55.4, 56.2, 61.9, 88.6, 111.1, 113.9, 127.0, 128.0, 128.1, 128.7, 128.9 (2 C), 129.0, 129.9, 133.9, 136.2, 152.7, 153.3, 156.4, 171.9, 172.9.

Desymmetrisation of anhydride 2b with 1a

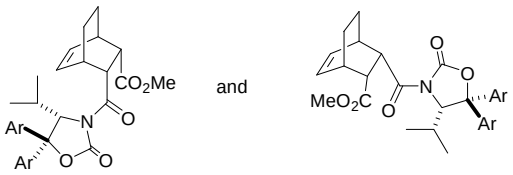
Ar = 2-MeO-5-Me-C$_6$H$_3$-; **5b** Ar = 2-MeO-5-Me-C$_6$H$_3$-; **6b**

Data for **5b**: mp 185-186 ºC; R_f = 0.47 (90:10 hexane/ethyl acetate); $[\alpha]^D_{24}$ –129.55 (*c* 0.88, MeOH); IR (chloroform film) 2962, 2836, 1772, 1736, 1696, 1503, 1464, 1374, 1253, 1199 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.79 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 1.05 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.13-1.58 (m, 5 H, 2 × CH$_2$, CH), 1.65-1.82 (m, 1 H, CH$_3$C*H*CH$_3$), 1.93-2.15 (m, 1 H, CH), 2.28 (s, 3 H, ArC*H*$_3$), 2.26-2.38 (m, 1 H, C*H*CHCON), 2.40 (s, 3 H, ArC*H*$_3$), 2.52-2.61 (m, 1 H, C*H*CHCOOMe), 2.90-3.01 (m, 1 H, C*H*CON), 3.52 (s, 6 H, ArOC*H*$_3$), 3.64 (s, 3 H, COOC*H*$_3$), 4.22 (dd, *J* = 4.5, 12.2 Hz, 1 H, C*H*COOMe), 5.81 (d, *J* = 1.7 Hz, 1 H, NC*H*), 6.67 (d, *J* = 8.3 Hz, 1 H, Ar), 6.72 (d, *J* = 8.3 Hz, 1 H, Ar), 7.01-7.10 (m, 2 H, Ar), 7.29 (d, *J* = 3.2 Hz, 1 H, Ar), 7.74 (d, *J* = 2.0 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.7, 20.5 (2 C), 22.0,

22.9, 24.4, 29.6, 39.4, 40.4, 46.0, 47.2, 50.8, 55.1, 55.7, 62.0, 88.7, 110.7, 113.7, 126.0, 126.9, 127.5, 128.5, 128.6 (2 C), 128.7, 128.9, 129.9, 152.4, 153.0, 156.2, 172.0, 173.1; Anal. Calcd for $C_{32}H_{39}NO_7$ (549.65): C, 69.92; H, 7.15; N, 2.55. Found: C, 69.56; H, 7.35; N, 2.69.

Data for **6b**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.69 (d, J = 6.7 Hz, 3 H, CH_3CHCH$_3$), 1.01 (d, J = 7.2 Hz, 3 H, CH$_3$CHCH_3), 1.40-2.05 (m, 7 H, 3 × CH_2, CH), 2.32 (s, 3 H, ArCH_3), 2.35 (s, 3 H, ArCH_3), 2.48-2.91 (m, 1 H, CHCHCON), 2.78-2.92 (m, 2 H, CHCHCOOMe, CHCON1), 3.44 (s, 3 H, COOCH_3), 3.48 (s, 6 H, ArOCH_3), 4.06 (dd, J = 4.1, 11.4 Hz, 1 H, CHCOOMe), 5.82 (d, J = 1.3 Hz, 1 H, NCH), 6.61 (d, J = 8.3 Hz, 1 H, Ar), 6.69 (d, J = 8.3 Hz, 1 H, Ar), 6.98-7.05 (m, 2 H, Ar), 7.29 (d, J = 1.8 Hz, 1 H, Ar), 7.68 (d, J = 1.9 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.9, 20.7, 20.9, 22.9, 23.5, 24.7, 29.9, 39.8, 39.9, 41.5, 46.6, 47.0, 50.9, 55.3, 56.2, 62.1, 88.7, 111.0, 113.9, 127.0, 128.0 (2 C), 128.6, 128.9, 129.0 (2 C), 129.9, 152.7, 153.1, 156.4, 172.1, 172.9.

Desymmetrisation of anhydride 2c with 1a



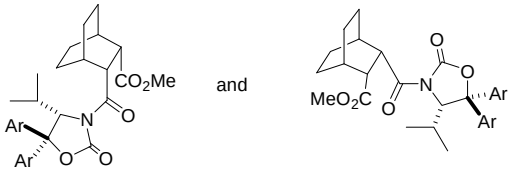
Ar = 2-MeO-5-Me-C_6H_3-; **5c** Ar = 2-MeO-5-Me-C_6H_3-;**6c**

Data for **5c**: mp 181-183 ºC; R_f = 0.16 (90:10 hexane/ethyl acetate); $[\alpha]^D_{23}$ –154.62 (*c* 0.52, MeOH); IR (chloroform film) 3024, 2949, 2870, 2836, 1774, 1739, 1702, 1502 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.73 (d, J = 6.6 Hz, 3 H, CH_3CHCH$_3$), 0.96 (d, J = 7.0 Hz, 3 H, CH$_3$CHCH_3), 1.06-1.31 (m, 3 H, CH_2CH), 1.42-1.53 (m, 2 H, CHCHCON, CH), 1.60-1.74 (m, 1 H, CH$_3$CHCH$_3$), 2.28 (s, 3 H, ArCH_3), 2.35 (s, 3 H, ArCH_3), 2.93-3.01 (m, 2 H, CHCON, CHCHCOOMe), 3.45 (s, 3 H, ArOCH_3), 3.49 (s, 3 H, ArOCH_3), 3.56 (s, 3 H, COOCH_3), 4.22 (dd, J = 1.2, 10.3 Hz, 1 H, CHCOOMe), 5.65 (s, 1 H, CHN), 5.97 (t, J = 7.2 Hz, 1 H, CH=CH), 6.46 (t, J = 7.2 Hz, 1 H, CH=CH), 6.61 (d, J = 8.3 Hz, 1 H, Ar), 6.70 (d, J = 8.3 Hz, 1 H Ar), 7.03 (d, J = 8.1 Hz, 2 H, Ar), 7.19 (s, 1 H, Ar), 7.70 (s, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.8, 20.6, 20.7, 22.2, 24.2, 24.7, 29.6, 31.9, 33.7, 46.4, 47.5, 51.4, 55.3, 55.9, 62.5, 89.1, 110.8, 113.9, 126.2, 126.8, 127.9, 128.6, 128.8 (2 C), 129.0, 130.2, 130.9, 133.4, 152.6, 153.7, 156.4,

172.3, 173.8; Anal. Calcd for $C_{33}H_{39}NO_7$ (561.67): C, 70.57; H, 7.00; N, 2.49. Found: C, 70.46; H, 6.99; N, 2.56.

Data for **6c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.72 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.93 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.19-1.82 (m, 5 H, 2 × C*H*$_2$, CH$_3$C*H*CH$_3$), 2.28 (s, 3 H, ArC*H*$_3$), 2.35 (s, 3 H, ArC*H*$_3$), 2.83-3.02 (m, 3 H, C*H*C*H*CON, C*H*CHCOOMe), 3.37 (s, 3 H, COOC*H*$_3$), 3.47 (s, 3 H, ArOC*H*$_3$), 3.48 (s, 3 H, ArOC*H*$_3$), 4.30 (dd, *J* = 1.9, 10.2 Hz, 1 H, C*H*COOMe), 5.75 (d, *J* = 1.2 Hz, 1 H, NC*H*), 6.18 (t, *J* = 7.2 Hz, 1 H, C*H*=CH), 6.47 (t, *J* = 7.2 Hz, 1 H, CH=C*H*), 6.61 (d, *J* = 8.3 Hz, 1 H, Ar), 6.68 (d, *J* = 8.3 Hz, 1 H, Ar), 6.98-7.04 (m, 2 H, Ar), 7.26 (s, 1 H, Ar), 7.68 (d, *J* = 1.7 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.0, 20.7, 20.8, 22.8, 24.5, 24.8, 30.2, 31.9, 34.6, 47.1 (2 C), 51.1, 55.3, 56.2, 61.6, 88.5, 111.1, 113.9, 126.8, 127.8, 128.0, 128.8 (2 C), 128.9, 129.0, 129.9, 130.8, 133.8, 152.7, 153.1, 156.4, 172.4, 173.5.

Desymmetrisation of anhydride 2d with 1a

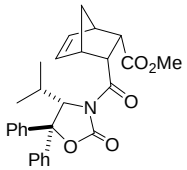


Ar = 2-MeO-5-Me-C$_6$H$_3$-;**5d** Ar = 2-MeO-5-Me-C$_6$H$_3$-; **6d**

Data for **5d**: mp 172-173 ºC; R_f = 0.59 (90:10 hexane/ethyl acetate); $[\alpha]^D_{25}$ –137.19 (*c* 0.605, MeOH); IR (chloroform film) 3019, 2947, 2362, 1771, 1733, 1696, 1503 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.76 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 1.01 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.09-1.50 (m, 8 H, 4 × CH$_2$), 1.64-1.79 (m, 1 H, CH$_3$C*H*CH$_3$), 2.04-2.18 (m, 2 H, C*H*CHCON, C*H*CHCOOMe), 2.22 (s, 3 H, ArC*H*$_3$), 2.36 (s, 3 H, ArC*H*$_3$), 2.75 (d, broad, *J* = 11 Hz, 1 H, CHC*H*CON), 3.47 (s, 3 H, ArOC*H*$_3$), 3.48 (s, 3 H, ArOC*H*$_3$), 3.60 (s, 3 H, COOC*H*$_3$), 4.39 (dd, *J* = 1.9, 11.0 Hz, 1 H, C*H*COOMe), 5.74 (d, *J* = 1.7 Hz, 1 H, NC*H*), 6.62 (d, *J* = 8.3 Hz, 1 H, Ar), 6.67 (d, *J* = 8.3 Hz, 1 H, Ar), 6.96-7.06 (m, 2 H, Ar), 7.22 (d, *J* = 1.7 Hz, 1 H, Ar), 7.70 (d, *J* = 2.0 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.9, 20.5 (2 C), 20.9, 21.0, 22.2, 25.0, 25.6 (2 C), 27.5, 29.5, 42.7, 43.4, 51.2, 55.1, 55.7, 62.3, 88.6, 110.7, 113.7, 126.0, 126.8, 127.5, 128.5, 128.7 (2 C), 129.0, 130.0, 152.5, 153.4, 156.1, 173.3, 174.1; Anal. Calcd for $C_{33}H_{41}NO_7$ (563.68): C, 70.32; H, 7.33; N, 2.48. Found: C, 69.99; H, 7.67; N, 2.12.

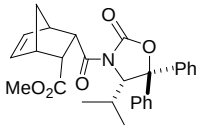
Data for **6d**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.67 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.99 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.20-1.80 (m, 9 H, 4 × CH$_2$, CH$_3$C*H*CH$_3$), 2.00-2.20 (m, 2 H, C*H*CHCON, C*H*CHCOOMe), 2.31 (s, 3 H, ArC*H*$_3$), 2.34 (s, 3 H, ArC*H*$_3$), 2.66 (d, broad, *J* = 10.9 Hz, 1 H, CHC*H*CON), 3.43 (s, 3 H, COOC*H*$_3$), 3.49 (s, 3 H, ArOC*H*$_3$), 3.51 (s, 3 H, ArOC*H*$_3$), 4.27 (dd, *J* = 3.1, 10.9 Hz, 1 H, C*H*COOMe), 5.84 (d, *J* = 1.3 Hz, 1 H, NC*H*), 6.61 (d, *J* = 8.3 Hz, 1 H, Ar), 6.69 (d, *J* = 8.3 Hz, 1 H, Ar), 6.97-7.05 (m, 2 H, Ar), 7.33 (d, *J* = 1.8 Hz, 1 H, Ar), 7.69 (d, *J* = 2.0 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.8, 20.7, 20.9, 21.3, 21.4, 22.7, 25.2, 25.9, 26.1, 28.3, 30.1, 42.8, 44.0, 51.1, 55.2, 56.2, 61.8, 88.6, 110.9, 114.0, 126.7, 127.7, 127.8, 128.6 (2 C), 129.0, 129.1, 130.1, 152.6, 152.8, 156.5, 173.6, 174.0.

Desymmetrisation of anhydride 2a with 1b



7a

and



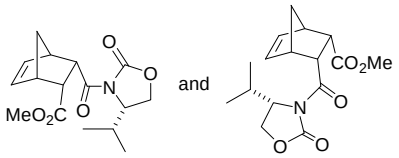
8a

Data for **7a**: mp 176-178 °C; R_f = 0.65 (85:15 hexane/ethyl acetate); $[\alpha]^{27}_{D}$ –129 (*c* 1, MeOH); IR ($CHCl_3$ film) 3021, 2971, 2876, 1778, 1735, 1704, 1450, 1437 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.76 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.88 (d, *J* = 7.0 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.28-1.33 (m, 2 H, CH$_2$), 1.92-2.03 (m, 1 H, CH$_3$C*H*CH$_3$), 2.72 (s, broad, 1 H, C*H*CHCON), 3.10 (s, broad, 1 H, C*H*CHCOOMe), 3.31 (dd, *J* = 3.3, 9.8 Hz, 1 H, C*H*CON), 3.56 (s, 3 H, COOC*H*$_3$), 4.21 (dd, *J* = 3.3, 9.8 Hz, 1 H, C*H*COOMe), 5.27 (d, *J* = 2.9 Hz, 1 H, C*H*N), 5.48 (dd, *J* = 2.9, 5.2 Hz, 1 H, C*H*=CH), 6.31 (dd, *J* = 2.9, 5.3 Hz, 1 H, CH=C*H*), 7.26-7.52 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.8, 21.0, 29.5, 45.6, 46.8, 47.5, 48.2, 48.7, 51.0, 65.2, 89.1, 125.1 (2 C), 125.5 (2 C), 127.6, 128.1 (2 C), 128.3, 128.6 (2 C), 133.4, 135.6, 137.6, 142.4, 153.0, 171.2, 173.0.

Data for **8a**: mp 162-165 °C; R_f = 0.65 (85:15 hexane/ethyl acetate); $[\alpha]^{25}_{D}$ –120 (*c* 1, MeOH); IR ($CHCl_3$ film) 3063, 3021, 2971, 2876, 1776, 1737, 1706, 1450 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.75 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.86 (d, *J* = 7.0 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.38-1.51 (m, 2 H, CH$_2$), 1.91-1.95 (m, 1 H, CH$_3$C*H*CH$_3$), 3.12 (s, broad, 1 H, C*H*CHCON), 3.18 (s, 3 H, COOC*H*$_3$), 3.25 (s, broad, 1 H, C*H*CHCOOMe), 3.33 (dd, *J* = 3.5, 9.8 Hz, 1 H, C*H*CON),

4.20 (dd, *J* = 3.1, 9.7 Hz, 1 H, C*H*COOMe), 5.34 (d, *J* = 3.2 Hz, 1 H, C*H*N), 6.22-6.28 (m, 2 H, CH=CH), 7.25-7.49 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.2, 21.7, 29.7, 45.9, 47.2, 47.9, 48.6, 49.0, 50.7, 64.1, 88.9, 125.6 (2 C), 125.7 (2 C), 127.6, 128.0 (3 C), 128.4 (2 C), 134.6, 135.1, 138.3, 142.3, 152.8, 172.0, 172.2; Anal. Calcd for $C_{28}H_{29}NO_5$ (459.53): C, 73.18; H, 6.36; N, 3.05. Found: C, 73.29; H, 6.35; N, 3.26.

Desymmetrisation of anhydride 2a with 1c

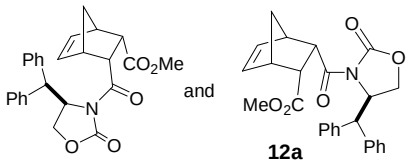


10a **9a**

Data for **10a** (from the mixture; dr = 96/4): mp 64-66 °C; R_f = 0.22 (90:10 hexane/ethyl acetate); $[\alpha]^{27}_D$ +45 (*c* 1, EtOAc); IR ($CHCl_3$ film) 3023, 2968, 1775, 1732, 1702, 1386 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.89 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.90 (d, *J* = 7.2 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.41-1.52 (m, 2 H, CH$_2$), 2.30-2.36 (m, 1 H, CH$_3$C*H*CH$_3$), 3.17-3.23 (m, 2 H, C*H*CHCON, C*H*CHCOOMe), 3.58 (s, 3 H, COOC*H*$_3$), 3.62 (dd, *J* = 3.6, 9.6 Hz, 1 H, C*H*CON), 4.08 (dd, *J* = 2.9, 9.7 Hz, 1 H, C*H*COOMe), 4.15 (dd, *J* = 3.3, 9.0 Hz, 1 H, OC*H*$_A$H$_B$), 4.25 (dd, *J* = 8.5, 8.5 Hz, 1 H, OCH$_A$*H*$_B$) 4.39-4.45 (m, 1 H, C*H*N), 6.07 (dd, *J* = 2.5, 5.5 Hz, 1 H, C*H*=CH), 6.47 (dd, *J* = 2.4, 5.1 Hz, 1 H, CH=C*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.5, 17.6, 28.5, 46.2, 46.4, 48.0, 48.6, 49.3, 51.3, 58.5, 63.3, 132.7, 137.3, 154.4, 172.7, 173.0; Anal. Calcd for $C_{16}H_{21}NO_5$ (307.34): C, 62.53; H, 6.89; N, 4.56. Found: C, 62.43; H, 7.02; N, 4.70.

Data for **9a** (from the mixture): ^{1}H NMR (300 MHz, $CDCl_3$) Recognizable peak at δ 2.44-2.50 (m, 1 H, Me$_2$C*H*). Remaining proton resonances overlapped with protons from **10a**.

Desymmetrisation of anhydride 2a with 1d

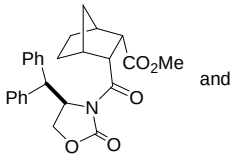


11a **12a**

Data for **11a** (pure diastereoisomer): mp 111-113 °C; R_f = 0.23 (90:10 hexane/ethyl acetate); $[\alpha]^{D}_{23}$ –120 (*c* 1, EtOAc); IR ($CHCl_3$ film) 3026, 1777, 1731, 1699, 1388, 1257 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.36-1.46 (m, 2 H, CH_2), 3.02 (s, broad, 1 H, C*H*CHCON), 3.18 (s, broad, 1 H, C*H*CHCOOMe), 3.56 (s, 3 H, COOCH_3), 3.59 (dd, *J* = 2.8, 9.6 Hz, 1 H, C*H*CON), 3.88 (dd, *J* = 2.9, 9.6 Hz, 1 H, C*H*COOMe), 4.29-4.46 (m, 2 H, OCH_2), 4.73 (d, *J* = 5.8 Hz, 1 H, Ph_2CH), 5.27-5.36 (m, 1 H, C*H*N), 6.01 (dd, *J* = 2.9, 5.5 Hz, 1 H, C*H*=CH), 6.43 (dd, *J* = 2.9, 5.4 Hz, 1 H, CH=C*H*), 7.09-7.37 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.1, 46.3, 48.0, 48.6, 49.6, 51.0, 51.3, 56.3, 64.9, 126.6, 127.3, 128.2 (4 C), 128.5 (2 C), 129.0 (2 C), 132.4, 137.7, 138.2, 139.5, 153.8, 172.3, 172.9; Anal. Calcd for $C_{26}H_{25}NO_5$ (431.48): C, 72.37; H, 5.84; N, 3.25. Found: C, 72.47; H, 5.84; N, 3.35.

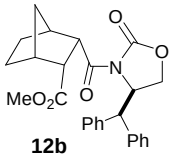
Data for **12a** (from the mixture; dr = 60/40): Recognizable peak at δ 5.08-5.20 (m, 1 H, NCH), 6.26 (dd, *J* = 2.8, 5.4 Hz, 1 H, CH=C*H*), 6.34 (dd, *J* = 2.8, 5.6 Hz, 1 H, CH=C*H*). Remaining proton resonances overlapped with protons from **11a**.

Desymmetrisation of anhydride 2b with 1d



11b

and



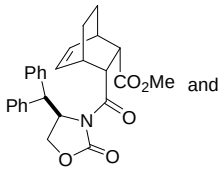
12b

Data for **11b**: mp 169-170 °C; R_f = 0.49 (85:15 hexane/ethyl acetate); $[\alpha]^{D}_{27}$ –153 (*c* 1, EtOAc); IR ($CHCl_3$ film) 3020, 2968, 2363, 2968, 1778, 1731, 1697, 1389 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.37-1.47 (m, 5 H, 2 × CH_2, CH), 1.97-2.06 (m, 1 H, CH), 2.53 (s, broad, 1 H, C*H*CHCON), 2.59 (s, broad, 1 H, C*H*CHCOOMe), 3.29 (dd, *J* = 4.5, 11.4 Hz, 1 H, C*H*CON), 3.53 (dd, *J* = 3.5, 11.6 Hz, 1 H, C*H*COOMe), 3.61 (s, 3 H, COOCH_3), 4.32-4.46 (m, 2 H, OCH_2), 4.79 (d, *J* = 5.3 Hz, 1 H, PhC*H*Ph), 5.29-5.37 (m, 1 H, NC*H*), 7.09-7.35 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.3, 24.4, 39.2, 40.4, 40.7, 46.5, 47.7, 50.7, 51.3, 56.6, 64.9, 126.7, 127.5, 128.2 (2 C), 128.4 (2 C), 128.6 (2 C), 129.1 (2 C), 138.1, 139.6, 153.5, 172.1, 173.5; Anal. Calcd for $C_{26}H_{27}NO_5$ (433.5): C, 72.04; H, 6.28; N, 3.23. Found: C, 72.29; H, 6.30; N, 3.06.

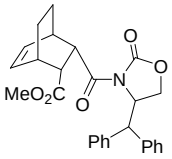
Data for **12b**: ^1H NMR (200 MHz, $CDCl_3$) δ 1.43-1.57 (m, 5 H, 2 × CH_2, CH), 1.92-2.04 (m, 1 H, CH), 2.60 (s, broad, 1 H, C*H*CHCON), 2.67 (s, broad, 1 H, C*H*CHCOOMe), 3.05 (dd, *J* =

3.5, 11.3 Hz, 1 H, C*H*CON), 3.71 (s, 3 H, COOCH_3), 4.21 (dd, *J* = 4.3, 11.3 Hz, 1 H, C*H*COOMe), 4.47 (d, *J* = 5.7 Hz, 2 H, OCH_2), 4.84 (d, *J* = 1.8 Hz, 1 H, PhC*H*Ph), 5.22-5.29 (m, 1 H, NC*H*), 7.03-7.36 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 23.1, 24.8, 39.4, 39.6, 40.8, 46.3, 47.6, 49.1, 50.9, 56.3, 63.7, 126.8, 127.5, 127.9 (2 C), 128.4 (2 C), 128.6 (2 C), 129.3 (2 C), 137.8, 139.7, 152.9, 172.3, 173.1.

Desymmetrisation of anhydride 2c with 1d



11c and

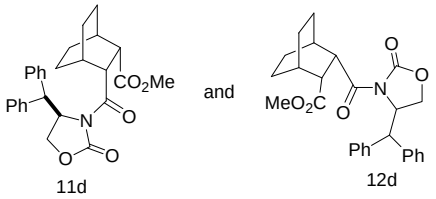


12c

Data for **11c**: mp 195-197 °C; R_f = 0.30 (85:15 hexane/ethyl acetate); $[\alpha]^{D}_{26}$ –94 (*c* 1, EtOAc); IR ($CHCl_3$ film) 3058, 2949, 2869, 1777, 1739, 1702, 1390 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.19-1.43 (m, 2 H, CH_2), 1.50-1.63 (m, 2 H, CH_2), 2.57-2,63 (m, 1 H, C*H*CHCON), 2.94-3.02 (m, 1 H, C*H*CHCOOMe), 3.24 (dd, *J* = 2.3, 10.3 Hz, 1 H, C*H*CON), 3.57 (s, 3 H, COOCH_3), 3.76 (dd, *J* = 1.3, 10.2 Hz, 1 H, C*H*COOMe), 4.29-4.42 (m, 2 H, OCH_2), 4.73 (d, *J* = 6.1 Hz, 1 H, PhC*H*Ph), 5.25-5.33 (m, 1 H, NC*H*), 6.21 (t, *J* = 7.2 Hz, 1 H, C*H*=CH), 6.35 (t, *J* = 7.0 Hz, 1 H, CH=C*H*), 7.10-7.39 (m, 10 H, Ar); ^{13}C NMR (50 MHz, CDCl3) δ 23.9, 24.3, 32.6 (2 C), 46.9, 48.7, 51.0, 51.4, 56.3, 64.9, 126.6, 127.3, 128.2 (4 C), 128.5 (2 C), 128.9 (2 C), 130.7, 134.0, 138.1, 139.4, 153.6, 173.0, 173.2; Anal. Calcd for $C_{27}H_{27}NO_5$ (445.51): C, 72.79; H, 6.11; N, 3.14. Found: C, 72.53; H, 5.87; N, 3.21.

Data for **12c**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.26-1.35 (m, 2 H, CH_2), 1.56-1.66 (m, 2 H, CH_2), 2.81-2.87 (m, 1 H, C*H*CHCON), 3.00-3.08 (m, 1 H, C*H*CHCOOMe), 3.21 (dd, *J* = 1.7, 10.2 Hz, 1 H, C*H*CON), 3.68 (s, 3 H, COOCH_3), 4.17 (dd, *J* = 1.8, 10.3 Hz, 1 H, C*H*COOMe), 4.46 (d, *J* = 5.5 Hz, 2 H, OCH_2), 4.81 (d, *J* = 1.9 Hz, 1 H, PhC*H*Ph), 5.15-5.19 (m, 1 H, NC*H*), 6.26 (t, *J* = 7.3 Hz, 1 H, C*H*=CH), 6.45 (t, *J* = 7.2 Hz, 1 H, CH=C*H*), 7.01-7.05 (m, 2 H, Ar), 7.14-7.36 (m, 8 H, Ar); ^{13}C NMR (50 MHz, CDCl3) δ 24.1, 24.3, 32.1, 33.4, 46.8, 47.9, 49.0, 51.2, 56.7, 63.7, 126.6, 127.2, 127.7 (2 C), 128.2 (2 C), 128.4 (2 C), 129.2 (2 C), 131.3, 132.9, 137.8, 139.9, 153.2, 172.5, 173.5.

Desymmetrisation of anhydride 2d with 1d

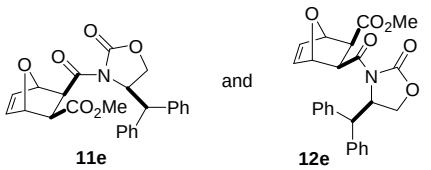


11d 12d

Data for **11d**: mp 221-223 °C; R_f = 0.37 (80:20 hexane/ethyl acetate); $[\alpha]^{D}_{25}$ –125 (*c* 1, CH_2Cl_2); IR ($CHCl_3$ film) 3021, 2947, 2868, 1771, 1724, 1697, 1450, 1389 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.26-1.77 (m, 8 H, 4 × CH_2), 1.83 (s, broad, 1 H, C*H*CHCON), 2.07 (s, broad, 1 H, C*H*CHCOOMe), 3.01 (d, broad, *J* = 10.8 Hz, 1 H, C*H*CON), 3.62 (s, 3 H, COOCH_3), 3.83 (d, broad, *J* = 10.8 Hz, 1 H, C*H*COOMe), 4.37 (d, *J* = 5.4 Hz, 2 H, OCH_2), 4.75 (d, *J* = 5.6 Hz, 1 H, PhC*H*Ph), 5.32 (q, *J* = 5.5, 1 H, NC*H*), 7.11-7.16 (m, 5 H, Ar), 7.22-7.34 (m, 5 H, Ar); ^{13}C NMR (50 MHz, CDCl3) δ 20.9, 21.2, 25.5, 25.7, 26.4, 26.8, 43.0, 43.9, 51.0, 51.3, 56.6, 64.9, 126.8, 127.5, 128.2 (2 C), 128.4 (2 C), 128.6 (2 C), 129.0 (2 C), 138.1, 139.5, 153.3, 173.4, 174.1; Anal. Calcd for $C_{27}H_{29}NO_5$ (447.5): C, 72.46; H, 6.53; N, 3.13. Found: C, 72.01; H, 6.37; N, 3.17.

Data for **12d**: ^1H NMR (500 MHz, $CDCl_3$) δ 1.40-1.69 (m, 8 H, 3 × CH_2, CH), 1.98 (s, broad, 1 H, C*H*CHCON), 1.98-2.08 (m, 1 H, CH), 2.17 (s, broad, 1 H, C*H*CHCOOMe), 2.92 (d, *J* = 11 Hz, 1 H, C*H*CON), 3.72 (s, 3 H, COOCH_3), 4.37-4.41 (m, 1 H, C*H*COOMe), 4.44-4.47 (m, 2 H, OCH_2), 4.81 (s, broad, 1 H, PhC*H*Ph), 5.24-5.27 (m, 1 H, NC*H*), 7.04 (d, broad, *J* = 7 Hz, 2 H, Ar), 7.14 (d, broad, *J* = 8 Hz, 2 H, Ar), 7.26-7.36 (m, 6 H, Ar); ^{13}C NMR (125 MHz, CDCl3) δ 21.3, 21.4, 25.4, 25.7, 25.8, 27.8, 43.1, 44.3, 49.2, 51.2, 56.4, 63.7, 127.0, 127.7, 128.1 (2 C), 128.7 (2 C), 128.8 (2 C), 129.4 (2 C), 138.1, 139.9, 152.9, 173.6, 174.3.

Desymmetrisation of anhydride 2e with 1d



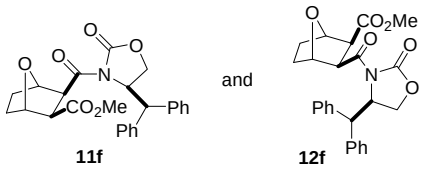
11e **12e**

Data for **11e**: mp 149-150 °C; R_f = 0.34 (70:30 hexane/ethyl acetate); $[\alpha]^{24}_{D}$ –43 (*c* 1, $CHCl_3$); IR ($CHCl_3$ film) 3028, 1776, 1737, 1705, 1390, 1250, 1215 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ

3.00 (d, *J* = 8.5 Hz, 1 H, C*H*CON), 3.45 (d, *J* = 8.5 Hz, 1 H, C*H*COOMe), 3.68 (s, 3 H, COOCH_3), 4.38 (dd, *J* = 2.7, 9.2 Hz, 1 H, CH_AH$_B$O), 4.45 (dd, *J* = 8.7, 8.7 Hz, 1 H, CH$_A$$H_B$O), 4.73 (d, *J* = 6 Hz, 1 H, PhC*H*Ph), 4.94 (s, broad, 1 H, C*H*CHCON), 5.27 (s, broad, 1 H, C*H*CHCOOMe), 5.37-5.40 (m, 1 H, NC*H*), 6.43 (dd, *J* = 1.5, 6.0 Hz, 1 H, C*H*=CH), 6.47 (dd, *J* = 1.5, 5.5 Hz, 1 H, CH=C*H*), 7.14 (d, *J* = 7.5 Hz, 2 H, Ar), 7.21 (d, *J* = 7.5 Hz, 2 H, Ar), 7.24-7.37 (m, 6 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 46.6, 48.7, 51.7, 52.3, 56.6, 65.6, 80.7, 81.0, 127.0, 127.7, 128.5 (4 C), 128.9 (2 C), 129.2 (2 C), 136.8 (2 C), 138.3, 139.6, 154.4, 171.3, 171.7; Anal. Calcd for $C_{25}H_{23}NO_6$ (433.45): C, 69.27; H, 5.35; N, 3.23. Found: C, 69.17; H, 5.14; N, 3.52.

Data for **12e** (from the mixture): ^{1}H NMR (300 MHz, $CDCl_3$) Recognizable peak at δ 3.78 (s, 3 H, CO_2Me). Remaining proton resonances merged with protons from **11e**.

Desymmetrisation of anhydride 2f with 1d

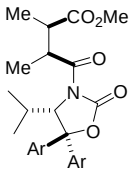


11f **12f**

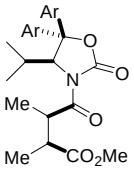
Data for **11f**: mp 152 °C; R_f = 0.46 (70:30 hexane/ethyl acetate); $[\alpha]^D_{25}$ –80 (*c* 0.5, CH_3Cl); IR ($CHCl_3$ film) 2952, 1777, 1737, 1705, 1383, 1210 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.50-1.59 (m, 2 H, CH_2), 1.72-1.83 (m, 2 H, CH_2), 3.14 (d, *J* = 9.5 Hz, 1 H, C*H*CON), 3.65 (d, *J* = 9.0 Hz, 1 H, C*H*COOMe), 3.65 (s, 3 H, COOCH_3), 4.38 (dd, *J* = 3, 9 Hz, 1 H, CH_AH$_B$O), 4.44 (dd, *J* = 8.7, 8.7 Hz, 1 H, CH$_A$$H_B$O), 4.61 (d, *J* = 4.5 Hz, 1 H, CH$_2$C*H*CHCON), 4.73 ((d, *J* = 6.0 Hz, 1 H, PhC*H*Ph), 4.92 (d, *J* = 4.5 Hz, 1 H, CH$_2$C*H*CHCOOMe), 5.33-5.36 (m, 1 H, NC*H*), 7.13 (d, *J* = 7.0 Hz, 2 H, Ar), 7.19-7.37 (m, 8 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 28.8, 29.0, 51.4, 51.7, 52.1, 53.7, 56.5, 65.5, 78.7 (2 C), 127.0, 127.7, 128.4 (2 C), 128.5 (2 C), 128.9 (2 C), 129.3 (2 C), 138.2, 139.6, 154.2, 170.8, 171.7; Anal. Calcd for $C_{25}H_{25}NO_6$ (435.47): C, 68.95; H, 5.79; N, 3.22. Found: C, 68.96; H, 5.92; N, 3.30.

Data for **12f** (from the mixture): ^{1}H NMR (300 MHz, $CDCl_3$) Recognizable peak at δ 3.68 (s, 3 H, CO_2Me). Remaining proton resonances merged with protons from **11f**.

Desymmetrisation of anhydride 3a with 1a



and

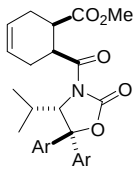


Ar = 2-MeO-5-Me-C_6H_3-; **13** Ar = 2-MeO-5-Me-C_6H_3-;**14**

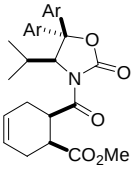
Data for **13** (from the mixture): mp 147-149 ºC; R_f = 0.40 (90:10 hexane/ethyl acetate); IR ($CHCl_3$ film) 3019, 2972, 1774, 1732, 1692, 1503 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 0.74 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.96 (d, *J* = 6.9 Hz, 3 H, C*H*$_3$CHCON), 0.97 (d, *J* = 7.2 Hz, 3 H, C*H*$_3$CHCOOMe), 1.27 (d, *J* = 6.9 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.60-1.76 (m, 1 H, CH$_3$C*H*CH$_3$), 2.24 (s, 3 H, ArC*H*$_3$), 2.37 (s, 3 H, ArC*H*$_3$), 2.79-2.88 (m, 1 H, CH$_3$C*H*CON), 3.48 (s, 3 H, ArOC*H*$_3$), 3.49 (s, 3 H, ArOC*H*$_3$), 3.63 (s, 3 H, COOC*H*$_3$), 3.80-3.88 (m, 1 H, CH$_3$C*H*COOMe), 5.80 (d, *J* = 2.1 Hz, 1 H, NC*H*), 6.64 (d, *J* = 8.4 Hz, 1 H, Ar), 6.70 (d, *J* = 8.1 Hz, 1 H, Ar), 6.98-7.08 (m, 2 H, Ar), 7.24 (d, *J* = 1.8 Hz, 1 H, Ar), 7.72 (d, *J* = 2.1 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.5, 15.9, 17.1, 20.5 (2 C), 22.4, 29.8, 40.8, 42.5, 51.5, 55.4, 55.9, 61.8, 88.9, 111.0, 113.9, 126.2, 127.0, 127.7, 128.8 (3 C), 129.1, 130.1, 152.6, 152.7, 156.3, 175.1, 175.2; Anal. Calcd for $C_{29}H_{37}NO_7$ (511.61): C, 68.08; H, 7.29; N, 2.74. Found: C, 67.89; H, 7.03; N, 2.67.

Data for **14** (from the mixture): ^1H NMR (300 MHz, $CDCl_3$) Recognizable peak at δ 5.78 (d, *J* = 2.1 Hz, 1 H, NC*H*). Remaining proton resonances overlapped with protons from **13**.

Desymmetrisation of anhydride 4a with 1a



and



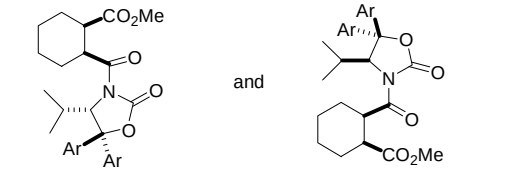
Ar = 2-MeO-5-Me-C_6H_3-; **15a** Ar = 2-MeO-5-Me-C_6H_3-**16a**

Data for **15a**: mp 137 ºC; R_f = 0.37 (90/10 hexane/ethyl acetate); $[\alpha]^{24}_D$ –174 (*c* 1, MeOH); IR ($CHCl_3$ film) 3026, 2964, 2837, 1771, 1735, 1699, 1503 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.70 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.87 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.61-1.75 (m, 1 H, CH$_3$C*H*CH$_3$), 2.28 (s, 3 H, ArC*H*$_3$), 2.35 (s, 3 H, ArC*H*$_3$), 2.34-2.51 (m, 1 H, CHCON), 2.34-2.51-2.84 (m, 4 H, C*H*$_2$CHCOOMe, C*H*$_2$*CH*CON), 3.44 (s, 3 H, ArOC*H*$_3$), 3.45 (s, 3 H,

ArOCH_3), 3.49 (s, 3 H, COOMe), 4.08-4.16 (m, 1 H, CH_2CHCOOMe), 5.62-5.79 (m, 2 H, *CH*=*CH*), 5.81 (d, *J* = 1.6 Hz, 1 H, NCH), 6.61 (d, *J* = 8.2 Hz, 1 H, Ar), 6.68 (d, *J* = 8.3 Hz, 1 H, Ar), 6.99-7.08 (m, 2 H, Ar), 7.30 (d, *J* = 1.6 Hz, 1 H, Ar), 7.69 (d, *J* = 1.9 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.8, 20.6, 20.7, 22.2, 25.7, 27.4, 30.0, 37.9, 39.0, 51.3, 55.4, 56.0, 61.1, 88.7, 111.0, 113.9, 123.4, 125.9, 126.5, 127.3, 128.0, 128.9 (2 C), 129.0 (2 C), 130.0, 152.6, 152.8, 156.3, 173.8 (2 C); Anal. Calcd for $C_{31}H_{37}NO_7$ (535.63): C, 69.51; H, 6.96; N, 2.62. Found: C, 69.57; H, 7.03; N, 2.57.

Data for **16a**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.78 (d, *J* = 6.7 Hz, 3 H, CH_3CHCH_3), 0.98 (d, *J* = 7.0 Hz, 3 H, CH_3CHCH_3), 1.66-1.76 (m, 1 H, CH_3CHCH_3), 1.85-2.13 (m, 2 H, CH_2CHCON), 2.22 (s, 3 H, ArCH_3), 2.36 (s, 3 H, ArCH_3), 2.43-2.82 (m, 2 H, $CH_2CHCOOMe$), 3.00-3.10 (m, 1 H, CH_2CHCON), 3.47 (s, 3 H, ArOCH_3), 3.48 (s, 3 H, ArOCH_3), 3.66 (s, 3 H, COOMe), 4.00-4.16 (m, 1 H, CH_2CHCOOMe), 5.41-5.47 (m, 1 H, C*H*=CH), 5.69-5.73 (m, 1 H, CH=C*H*), 5.74 (d, *J* = 1.6 Hz, 1 H, NC*H*), 6.63 (d, *J* = 8.3 Hz, 1 H, Ar), 6.69 (d, *J* = 8.3 Hz, 1 H, Ar), 6.99-7.11 (m, 3 H, Ar), 7.69 (d, *J* = 1.72 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.0, 20.7 (2 C), 22.2, 25.8, 26.3, 29.8, 37.7, 40.0, 51.5, 53.3, 55.4, 56.1, 62.7, 89.3, 111.2, 114.0, 123.7, 125.5, 126.9, 127.6, 128.5, 128.7, 129.2 (2 C), 130.1, 152.9, 153.5, 156.3, 173.5, 173.8.

Desymmetrisation of anhydride 4b with 1a



Ar = 2-MeO-5-Me-C_6H_3-;**15b** Ar = 2-MeO-5-Me-C_6H_3-; **16b**

Data for **15b**: mp 127-128 °C; R_f = 0.14 (90:10 hexane/ethyl acetate); $[\alpha]^{25}_D$ –164 (*c* 0.5, ethyl acetate); IR ($CHCl_3$ film) 2932, 2859, 1775, 1733, 1699, 1502, 1200 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.70 (d, *J* = 6.6 Hz, 3 H, CH_3CHCH_3), 0.93 (d, *J* = 7.0 Hz, 3 H, CH_3CHCH_3), 1.25-2.25 (m, 9 H, 4 × CH_2-*c*-hex, CH_3CHCH_3), 2.28 (s, 3 H, ArCH_3), 2.34 (s, 3 H, ArCH_3), 2.40-2.50 (m, 1 H, CHCON), 3.39 (s, 3 H, COOCH_3), 3.45 (s, 6 H, 2 × ArOCH_3), 4.03-4.14 (m, 1 H, CHCOOMe), 5.82 (d, *J* = 1.4 Hz, 1 H, NC*H*), 6.61 (d, *J* = 8.3 Hz, 1 H, Ar), 6.67 (d, *J* = 8.3 Hz, 1 H, Ar), 6.99-7.05 (m, 2 H, Ar), 7.30 (d, *J* = 1.5 Hz, 1 H, Ar), 7.69 (d, *J* = 1.8 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.7, 20.5, 20.7, 21.9, 22.4, 24.5, 24.9, 27.9, 29.8, 39.9, 42.4, 51.0,

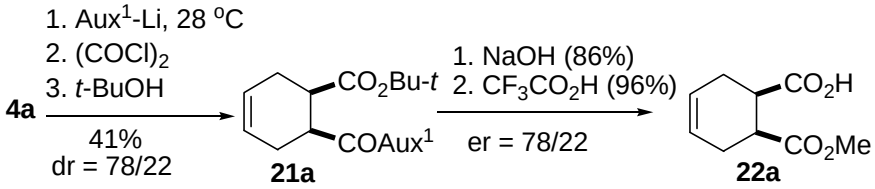
55.2, 55.9, 60.9, 88.5, 110.9, 113.8, 126.5, 127.3, 127.8, 128.7 (3 C), 128.9, 129.9, 152.5, 152.6, 156.3, 173.9, 174.2; Anal. Calcd for $C_{31}H_{39}NO_7$ (537.64): C, 69.25; H, 7.31; N, 2.61. Found: C, 68.93; H, 7.22; N, 2.68.

Data for **16b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, *J* = 7.0 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.98 (d, *J* = 7.5 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.25-1.29 (m, 3 H, C*H*$_2$-*c*-hex., C*H*-*c*-hex), 1.39-1.46 (m, 2 H, C*H*$_2$-*c*-hex), 1.69-1.72 (m, 1 H, CH$_3$C*H*CH$_3$), 1.78-1.81 (m, 1 H, C*H*-*c*-hex), 1.94-1.96 (m, 1 H, C*H*-*c*-hex), 2.18-2.23 (m, 1 H, C*H*-*c*-hex), 2.24 (s, 3 H, ArC*H*$_3$), 2.37 (s, 3 H, ArC*H*$_3$), 2.65-2.69 (m, 1 H, C*H*CON), 3.47 (s, 3 H, ArOC*H*$_3$), 3.48 (s, 3 H, ArOC*H*$_3$), 3.65 (s, 3 H, COOCH$_3$), 4.18-4.22 (m, 1 H, C*H*COOMe), 5.71 (d, *J* = 1.5 Hz, 1 H, NC*H*), 6.63 (d, *J* = 8.0 Hz, 1 H, Ar), 6.69 (d, *J* = 8.0 Hz, 1 H, Ar), 6.99-7.05 (m, 2 H, Ar), 7.18 (s, 1 H, Ar), 7.71 (d, *J* = 1.5 Hz, 1 H, Ar); ^{13}C NMR (125 MHz, $CDCl_3$) δ 15.9, 20.6, 20.7, 22.0, 22.3, 24.4, 25.5, 26.8, 29.7, 39.4, 42.9, 51.5, 55.4, 56.0, 62.4, 110.7, 113.9, 126.5, 127.1 (2 C), 128.2, 128.8 (2 C), 129.0 (2 C), 130.0 (2 C), 152.7, 156.3, 174.3, 174.4.

4. Determination of absolute configuration of products

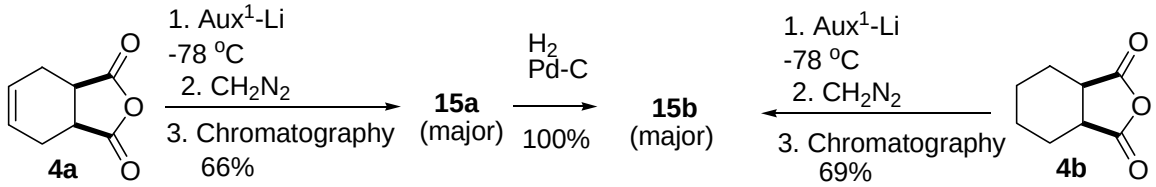
a. General Details

The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **4a** with oxazolidin-2-one **1a** were determined by converting them to known hemi ester **22a**. For this, the anhydride opening product (dr = 78/22) obtained from anhydride **4a** was converted to the corresponding *t*-Bu ester **21a** from which the oxazolidin-2-one **1a** was removed by alkaline hydrolysis and the resulting acid was converted to methyl ester by diazomethane treatment. The resulting diester was subsequently treated with TFA leading to hemi ester **22a** {$[\alpha]_D^{26}$ +8.6 (*c* 1.28, EtOH); *lit.*[7] $[\alpha]_D^{25}$ +18 (*c* 2.1, EtOH) for sample of 98% ee}. The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **3a** with oxazolidin-2-one **1a** were tentatively assigned in analogy with the anhydride **4a** openings with oxazolidinone **1a**.



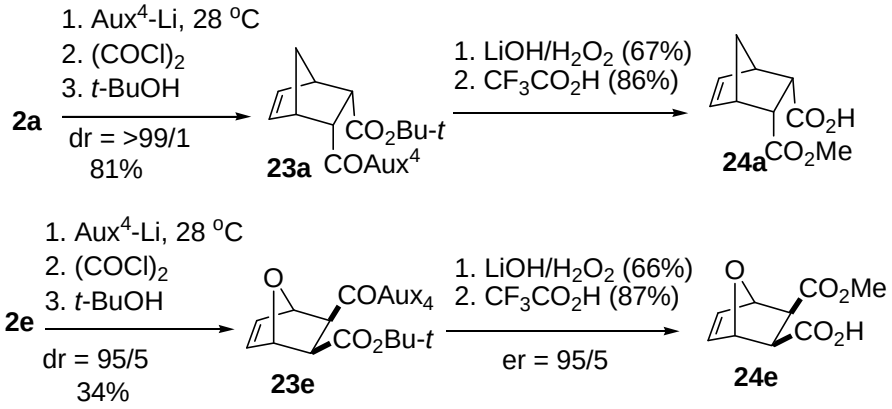
Scheme 1

The absolute configuration of the products from the desymmetrisation reaction of anhydrides **4b** with oxazolidin-2-one **1a** was determined by saturating the double bonds by catalytic hydrogenation of the major methyl ester **15a**, obtained from the desymmetrisation of **4a** leading to **15b** indicating that major diastereoisomer **15a** stereochemically corresponds to the major diastereoisomer **15b** (Scheme 2).



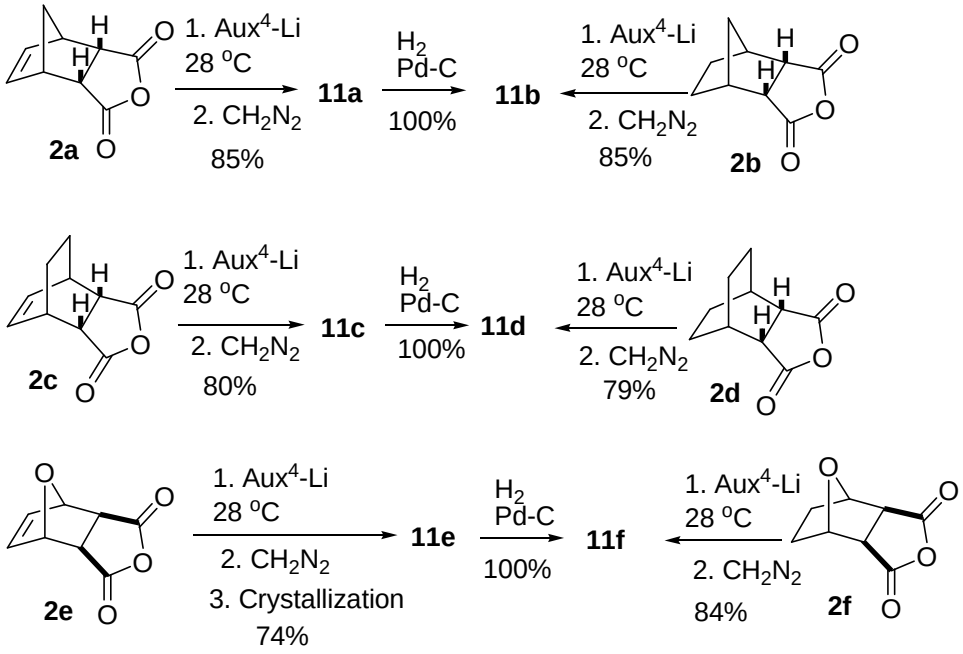
Scheme 2

The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **2a** and **2e** with oxazolidin-2-one **1d** were determined by converting them to known hemi esters **24a** and **24e**, respectively. For this, the anhydride opening product (dr = >99/1) obtained from anhydride **2a** was converted to the corresponding *t*-Bu ester **23a** from which the auxazolidin-2-one **2d** was removed by $LiOH/H_2O_2$ hydrolysis and the resulting acid was converted to methyl ester by diazomethane treatment. The resulting diester was subsequently treated with TFA leading to hemi ester **24a** {$[\alpha]_D^{23}$ –6.7 (*c* 1.5, CCl_4); *lit.*[1] $[\alpha]_D^{25}$ +6.8 (*c* 1.5, CCl_4) for the *ent*-**24a** for sample of 95% ee} (Scheme 3). In an analogous way, the anhydride opening product (dr = 95/5) obtained from anhydride **2e** was converted to the corresponding *t*-Bu ester **23e** and then to the known hemi ester **24e** {$[\alpha]_D^{24}$ +10.9 (*c* 0.6, MeOH); *lit.*[1] $[\alpha]_D^{25}$ –10.3 (*c* 1.5, MeOH) for the *ent*-**24e** for sample of 95% ee}. The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **2c** with oxazolidin-2-one **1d** were not determined but were tentatively assigned in analogy with the anhydride **2a** openings.



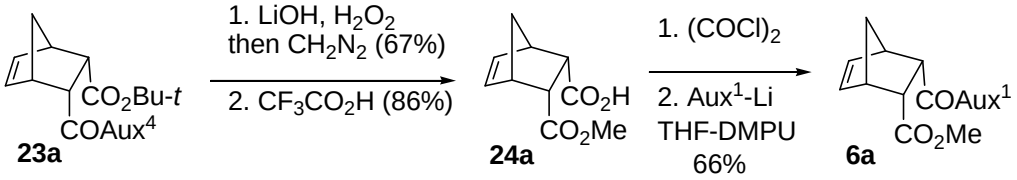
Scheme 3

The absolute configuration of the products from the desymmetrisation reaction of anhydrides **2b** with oxazolidin-2-one **1d** was determined by saturating the double bonds by catalytic hydrogenation of the methyl esters **11a**, obtained from the desymmetrisation of **2a** leading to **11b** indicating that major diastereoisomer **11a** stereochemically corresponds to the major diastereoisomer **11b** (Scheme 4). Similarly, the anhydride opening products **11c** obtained from anhydride **2c** was hydrogenated to give the saturated esters **11d** where **11c** stereochemically corresponded to **11d**. In an analogous way, the anhydride opening products (dr = 95/5) **11e**/**12e** obtained from anhydride **2e** was crystallized to get pure **11e** which was hydrogenated to give the saturated esters **11f**.



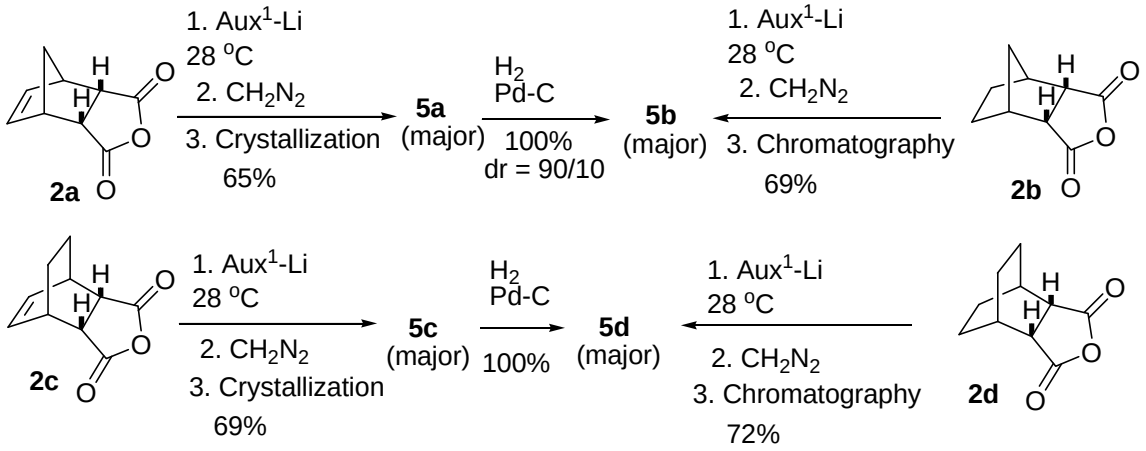
Scheme 4

To compare the facial selectivity of anhydride opening between oxazolidin-2-ones **1a** and **1d**, the hemi ester **24a** as obtained from the desymmetrisation of anhydride **2a** with oxazolidin-2-one **1d** (Scheme 3) at 28 °C was converted to its acid chloride and then reacted with the lithium salt of oxazolidin-2-one **1a** leading to diastereoisomer **6a** (Scheme 5). This confirmed that oxazolidin-2-ones **1a** and **1d** preferred for the same facial selectivity 28 °C.



Scheme 5

The absolute configuration of the products from the desymmetrisation reaction of anhydrides **2b** with oxazolidin-2-one **1a** was determined by saturating the double bonds by catalytic hydrogenation of pure methyl ester **5a**, obtained from the desymmetrisation of **2a** followed by crystallization, leading to **5b** indicating that major diastereoisomer **5a** stereochemically corresponds to the major diastereoisomer **5b** (Scheme 6). Similarly, the anhydride opening product, pure methyl ester **5c**, obtained from desymmetrisation of anhydride **2c** followed by crystallization, was hydrogenated to give the saturated esters **5d** thus **5c** stereochemically corresponded to **5d**.



Scheme 6

The absolute configuration of the desymmetrisation products obtained from the reaction of anhydride **2a** with oxazolidin-2-one **1b** (methyl esters **7a/8a)** were not determined but were tentatively assigned in analogy with the anhydride **2a** openings with oxazolidin-2-one **1a**. The absolute configuration of the desymmetrisation products obtained from the reaction of anhydride

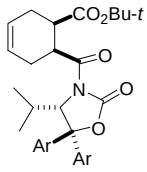
2a with oxazolidin-2-one **1c** (methyl esters **9a/10a)** were not determined but were tentatively assigned on the basis our earlier studies.[3,8]

The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **2c** with oxazolidin-2-one **1a** (methyl esters **5c/6c)** were not determined but were tentatively assigned in analogy with the anhydride **2a** openings with oxazolidinone **1a**.

The absolute configuration of the desymmetrisation products obtained from the reaction of anhydrides **2d** with oxazolidin-2-one **1a** (methyl esters **5d/6d)** were not determined but were tentatively assigned in analogy with the anhydride **2a** openings with oxazolidinone **1a** and saturation experiment as depicted in Scheme 6.

b. Experimental and characterization data

Preparation of *t*-butyl ester 21a from the desymmetrisation product of anhydride 4a with oxazolidin-2-one 1a at 28 °C

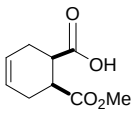


Ar = 2-MeO-5-Me-C_6H_3-; **21a**

n-Butyl lithium (720 µL, 1.6 M in hexane, 1.15 mmol) was added slowly to a suspension of oxazolidin-2-one **1a** (370 mg, 1 mmol) in dry THF (2.5 mL) at 0 ºC to –10 ˚C under argon atmosphere. After 10 minutes, the reaction mixture was brought to 28 ºC. Dry DMPU (1.2 mL) was added to the reaction mixture followed by a solution of the anhydride **4a** (183 mg, 1.2 mmol) in dry THF (2.5 mL). After 15 minutes at 28 ºC, the reaction mixture was acidified with 5% citric acid solution and extracted with ethyl acetate. The extract was washed with water, dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in dry dichloromethane (5 mL) and dry DMF (10 µL) was added under argon atmosphere. The solution was cooled in an ice-bath and oxalyl chloride (305 µL, 3.5 mmol) was added slowly. After 2 h at room temperature, the reaction mixture was concentrated under reduced pressure followed by high vacuum (0.1 Torr). The residue was dissolved in dry dichloromethane (2.5 mL), cooled on ice-water bath and a solution of DMAP (183 mg, 1.5 mmol) in dry *t*-butanol (2.5 mL) was added into it. The mixture was stirred overnight at room temperature and evaporated under reduced pressure. The residue was purified by column chromatography to give the *t*-butyl ester **21a** (236 mg, 41%); R_f = 0.41 (90:10, hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.69 (d, *J* = 6.7 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.87 (d, *J* = 7.1 Hz, 3 H, CH$_3$CHC*H*$_3$), 1.27 (s, 9 H, OC[C*H*$_3$]$_3$), 1.67-1.77 (m, 1 H, CH$_3$C*H*CH$_3$), 2.28-2.41 (m, 1 H, C*H*CON), 2.28 (s, 3 H, ArC*H*$_3$), 2.35 (s, 3 H, ArC*H*$_3$), 2.59-2.82 (m, 4 H, C*H*$_2$CHCHC*H*$_2$), 3.47 (s, 3 H, ArOC*H*$_3$), 3.48 (s, 3 H, ArOC*H*$_3$), 4.07-4.17 (m, 1 H, C*H*COO^{t}Bu), 5.59-5.78 (m, 2 H, C*H*=C*H*), 5.84 (d, *J* = 1.3 Hz, NC*H*), 6.62 (d, *J* = 8.3 Hz, 1 H, Ar), 6.68 (d, *J* = 8.3 Hz, 1 H, Ar), 6.98-7.11 (m, 2 H, Ar), 7.36 (d, *J* = 1.8 Hz, 1 H, Ar), 7.70 (d, *J* = 1.8 Hz, 1 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.6, 20.5,

20.7, 22.1, 25.8, 27.7 (3 C), 27.8, 30.1, 38.1, 40.1, 55.2, 56.0, 61.1, 79.6, 88.4, 111.1, 114.0, 123.2, 126.4, 126.8, 127.4, 128.1, 128.8 (2 C), 128.9 (3 C), 129.9, 152.6, 156.3, 172.3, 173.6.

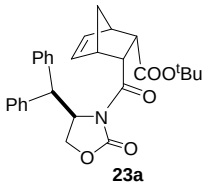
Preparation of hemiester 22a from 21a



22a

To a solution of this *t*-butyl ester **21a** (190 mg, 0.33 mmol) in THF (2 mL), aq. NaOH solution (0.6 mL, 1.1 M) was added. Methanol was added dropwise to obtain a homogeneous solution and the resulting solution was stirred at room temperature for 18 h. After evaporating the solvent the residue was acidified with aq. sodium bisulphate solution and extracted with ethyl acetate. Ethyl acetate was evaporated and the residue was treated with diazomethane to obtain methyl ester. The resulting suspension was filtered and the filtrate was evaporated to give crude diester. Crude product was purified by column chromatography to give pure diester (68 mg, 86%); R_f = 0.48 (90:10, hexane/ethyl acetate); [^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 1.27 (s, 9 H, OC[C*H*$_3$]$_3$), 2.06-2.55 (m, 4 H, C*H*$_2$CHCHC*H*$_2$), 2.90-3.02 (m, 2 H, CH$_2$C*H*CH*H*CH$_2$), 3.67 (s, 3 H, COOC*H*$_3$), 5.60-5.71 (m, 2 H, C*H*=C*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.6, 26.1, 27.9 (3 C), 39.9, 40.6, 51.4, 80.6, 124.9, 125.3, 172.1, 173.7.] Trifluoroacetic acid (1 mL) was added to a stirred solution of the diester (68 mg, 0.28 mmol) in dry dichloromethane (1 mL) at 0 ºC. After 2 h at 0 ºC, the reaction mixture was concentrated under reduced pressure and the residue was purified by column chromatography to give hemiester **22a** (50 mg, 96%); $[\alpha]_D^{26}$ = +8.6 (*c* 1.28, EtOH); *lit.*[7] $[\alpha]_D^{25}$ = +18 (*c* 2.1, EtOH; 98% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.32-2.64 (m, 4 H, C*H*$_2$CHCHC*H*$_2$), 3.01-3.12 (m, 2 H, CH$_2$C*H*CH*H*CH$_2$), 3.69 (s, 3 H, COOC*H*$_3$), 5.61-5.74 (m, 2 H, C*H*=C*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.6, 25.8, 39.5, 39.6, 51.8, 125.0, 125.1, 173.6, 179.3.

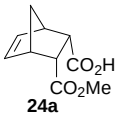
Preparation of *t*-butyl ester 23a from the desymmetrisation product of anhydride 2a with oxazolidin-2-one 1d at 28 °C



23a

Following the procedure described for the preparation of *t*-butyl ester **21a**, oxazolidinone **1d** (253 mg, 1 mmol) and anhydride **2a** (197 mg, 1.2 mmol) gave *t*-butyl ester **23a** (385 mg, 81 %); R_f = 0.5 (90:10, hexane/ethyl acetate) ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33-1.43 (m, 2 H, CHC*H*$_2$CH), 1.36 (s, 9 H, OC[C*H*$_3$]$_3$), 3.02 (bs, 1 H, C*H*CHCON), 3.12 (bs, 1 H, C*H*CHCOO^{t}Bu), 3.54 (dd, *J* = 3.7, 9.6 Hz, 1 H, C*H*CON), 3.72 (dd, *J* = 2.9, 9.6 Hz, 1 H, C*H*COO^{t}Bu), 4.26-4.39 (m, 2 H, OC*H*$_2$), 4.71 (d, *J* = 5.9 Hz, 1 H, Ph$_2$C*H*), 5.27-5.36 (m, 1 H, C*H*N), 5.96 (dd, *J* = 2.9, 5.5 Hz, 1 H, C*H*=CH), 6.50 (dd, *J* = 2.9, 5.5 Hz, 1 H, CH=C*H*), 7.09-7.38 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.7 (3 C), 46.1, 46.8, 48.0, 49.0, 50.9, 51.4, 56.5, 65.1, 80.1, 126.6, 127.3, 128.2 (4 C), 128.5 (2 C), 129.0 (2 C), 131.7, 138.1, 138.4, 139.6, 153.8, 171.8, 172.6; Anal. Calcd for $C_{29}H_{31}NO_5$ (473.56): C, 73.55; H, 6.60; N, 2.96. Found: C, 73.25; H, 6.56; N, 2.85.

Preparation of hemiester 24a from 23a

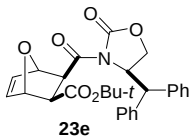


24a

Hydrogen peroxide (200 μL, 30% w/v) was added to a stirred and degassed solution of t-butyl ester **23a** (113 mg, 0.24 mmol) in THF (3.5 mL) and water (1.5 mL) at 0 ˚C. After few minutes lithium hydroxide (20 mg, 0.48 mmol) was added and the mixture was allowed to attain room temperature. After 24 h at room temperature the mixture was quenched with aq. sodium sulphite solution, acidified with aq. sodium bisulphate solution and extracted with ethyl acetate. The solvent was evaporated and residue was treated with diazomethane to get diester. The compound was purified by column chromatography to give pure diester (40 mg, 67%); [R_f = 0.56 (90:10, hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.25-1.49 (m, 2 H, CHC*H*$_2$CH), 1.39 (s, 9

H, OC[C*H*$_3$]$_3$), 3.12 (bs, 2 H, C*H*CHCOO^{t}Bu, C*H*CHCOOMe), 3.21 (dd, *J* = 2.7, 10.0 Hz, 1 H, C*H*COO^{t}Bu), 3.25 (dd, *J* = 3.1, 10.0 Hz, 1 H, C*H*COOMe), 3.60 (s, 3 H, COOC*H*$_3$), 6.16 (dd, *J* = 3.0, 5.5 Hz, 1 H, C*H*=CH), 6.35 (dd, *J* = 3.0, 5.5 Hz, 1 H, CH=C*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.0 (3 C), 46.1, 46.7, 48.2, 48.6, 49.3, 51.2, 80.3, 134.1, 135.4, 171.4, 173.0.] Following the similar procedure described for preparaton of hemi ester **22a**, this diester (48 mg, 0.19 mmol) gave **24a** (32 mg, 86%). $[\alpha]_D^{22}$ = –6.67 (*c* 1.5, CCl_4); *lit.*[7] *ent*-**24a**, $[\alpha]_D^{25}$ = +6.8 (*c* 1.5, CCl_4; 95% ee); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.33 (d, *J* = 8.6 Hz, 1 H, CHC*H*$_A$H$_B$CH), 1.49 (d, *J* = 8.6 Hz, 1 H, CHCH$_A$*H*$_B$CH), 3.16 (bs, 1 H, C*H*CHCOOH), 3.19 (bs, 1 H, C*H*CHCOOMe), 3.27 (dd, *J* = 3.0, 10.1 Hz, 1 H, C*H*COOH), 3.34 (dd, *J* = 2.9, 10.1 Hz, 1 H, C*H*COOMe), 3.59 (s, 3 H, COOC*H*$_3$), 6.21 (dd, *J* = 2.8, 5.4 Hz, 1 H, C*H*=CH), 6.32 (dd, *J* = 2.9, 5.4 Hz, 1 H, C*H*=CH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 46.1, 46.5, 48.1, 48.3, 48.8, 51.4, 134.4, 135.5, 172.9 (2 C).

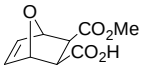
Preparation of *t*-butyl ester 23e from the desymmetrisation product of anhydride 2e with oxazolidin-2-one 1d at 28 °C



23e

Following the procedure described for the preparation of *tert*-butyl ester **21a**, oxazolidinone **1d** (177 mg, 0.7 mmol) and anhydride **2e** (139 mg, 0.84 mmol) gave *tert*-butyl ester **23e** (115 mg, 34%); R_f = 0.24 (80:20, hexane/ethyl acetate); IR ($CHCl_3$ film) 3027, 2978, 2925, 2853, 1779, 1726, 1391, 1368 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.42 (s, 9 H, OC[C*H*$_3$]$_3$), 2.96 (d, *J* = 8.5 Hz, 1 H, C*H*CON), 3.27 (d, *J* = 8.6 Hz, 1 H, C*H*COO^{t}Bu), 4.30-4.44 (m, 2 H, OC*H*$_2$), 4.69 (d, *J* = 6.6 Hz, 1 H, Ph$_2$C*H*), 5.03 (bs, 1 H, C*H*CHCON), 5.12 (bs, 1 H, C*H*CHCOO^{t}Bu), 5.36-5.45 (m, 1 H, NC*H*), 6.38-6.48 (m, 2 H, C*H*=C*H*), 7.14-7.35 (m, 10 H, Ar); ^{13}C NMR (50 MHz, $CDCl_3$) δ 27.8 (3 C), 46.5, 50.0, 52.1, 56.6, 65.6, 80.2, 81.3 (2 C), 126.9, 127.6, 128.4 (2 C), 128.5 (2 C), 128.8 (2 C), 129.1 (2 C), 136.5, 137.0, 138.4, 139.7, 154.1, 170.4, 171.6.

Preparation of hemiester 24e from 23e



24e

Following the procedure described for the preparation of diester from *tert*-butyl ester **23a**, compound **23e** (100 mg, 0.21 mmol) gave the diester (35 mg, 66%); [R_f = 0.22 (80:20, hexane/ethyl acetate); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.43 (s, 9 H, OC[CH_3]$_3$), 2.72 (s, 2 H, C*H*COO^{t}Bu, C*H*COOMe), 3.69 (s, 3 H, COOCH_3), 5.21 (d, *J* = 7.8 Hz, 2 H, C*H*CHCOO^{t}Bu, C*H*CHCOOMe), 6.44-6.51 (m, 2 H, C*H*=C*H*); ^{13}C NMR (50 MHz, $CDCl_3$) δ 28.0 (3 C), 46.7, 47.9, 51.9, 80.3, 80.6, 81.3, 136.5, 136.7, 170.3, 172.0.] Following the similar procedure described for the preparation of hemiester **22a**, this diester (21 mg, 0.08 mmol) gave hemiester **24e** (14 mg, 87%); $[\alpha]_D^{24}$ = 10.9 (*c* 0.64, MeOH); *lit.*[7] for *ent*-**24e**, $[\alpha]_D^{25}$ = –10.3 (*c* 1.5, MeOH; 92% ee)^{1}H NMR (200 MHz, $CDCl_3$) δ 2.82-2.91 (m, 2 H, C*H*COOH, C*H*COOMe), 3.71 (s, 3 H, COOCH_3), 5.27-5.32 (m, 2 H, C*H*CHCOOH, C*H*CHCOOMe), 6.44-6.51 (m, 2 H, C*H*=C*H*).

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