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Probing the parallel kinetic resolution of 1-phenylethanol using *quasi*-enantiomeric oxazolidinone adducts

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Abstract—The parallel kinetic resolution of racemic 1-phenylethanol using an equimolar combination of *quasi*-enantiomeric oxazolidinones is discussed. The levels of diastereoselectivity were high leading to separable *quasi*-enantiomeric esters in good yield.

1. Introduction

Over the last decade, the kinetic resolution of secondary alcohols by enantioselective alkyl and arylcarbonyl transfer, involving stoichiometric and sub-stoichiometric chiral mediators, has attracted significant attention.[1] Within this area, there have been three distinct approaches; those that utilise either enzymes,[2] chemical resolution[3] and/or thermodynamic separation.[4] In an attempt to improve the levels of stereoselection and chemical yield, a variety of elegant strategies have been developed.[5–9] One particular strategy that holds promise is the parallel kinetic resolution of secondary alcohols, which has attracted significant attention.[10] However, the lack of reports within this field is primarily due to the difficulty in obtaining the required complementary *quasi*-enantiomeric components for efficient parallel kinetic resolution.[8,11] Within this area, Vedejs et al.[10,12] have elegantly shown the parallel resolution of 1-(1′-naphthyl) ethanol *rac*-**3** using a pair of doubly differentiated *quasi*-enantiomeric pyridinium chlorides (*R*)-**1** and (*S*,*S*)-**2** to give two differential carbonates (*S*)-**4** and (*S*,*R*)-**5** in excellent yield with high levels of stereocontrol (Scheme 1).

From this study,[10] it is evident that the (*S*)-enantiomer of 1-(1′-naphthyl) ethanol **3** was selectivity derivatised by pyridinium chloride (*R*)-**1** [to give carbonate (*S*)-**4**], whereas the remaining enantiomer (*R*)-**3** was selectively derivatised using the complementary *quasi*-enantiomeric pyridinium chloride (*S*,*S*)-**2** to give the corresponding carbonate (*S*,*R*)-**5** (Scheme 1). The levels of molecular recognition between these complementary components, (*R*)-**1** and (*S*)-**3**, and (*S*,*S*)-**2** and (*R*)-**3**, were sufficiently high enough to allow efficient separation of their enantiomers.[10]

As a result of this report,[10] we have been interested[13,14] over the last few years in the parallel kinetic resolution of racemic Evans-based oxazolidinones, such as *rac*-**8**, using two *quasi*-enantiomeric profen active esters (*R*)-**6** and (*S*)-**7**, to give two diastereoisomerically pure *syn*-adducts (*R*,*S*)-**9** and (*S*,*R*)-**10** in good yield with excellent levels of diastereoselection (Scheme 2). We were originally interested in these *quasi*-enantiomeric adducts, (*R*,*S*)-**9** and (*S*,*R*)-**10**, as potential alkyl-carbonyl transfer reagents for the resolution of secondary alcohols. To this aim, we herein report our study into the use of *quasi*-enantiomeric Evans' oxazolidinones as complementary *diastereoselective* alkyl-carbonyl transfer components for the parallel kinetic resolution of racemic 1-phenylethanol **12**.

Within this area, Evans et al.[15] has demonstrated the kinetic resolution of 1-phenylethanol *rac*-**12** using a benzoylated oxazolidinone, such as (*S*)-**11** (in the presence of magnesium dibromide and *N*-methyl-piperidine), to give the corresponding 1-phenylethyl benzoate (*R*)-**13** in excellent yield (>90%) with good levels of enantioselectivity (72% ee) (Scheme 3). The levels of stereocontrol were improved (to 85% ee) by the use of a more sterically demanding oxazolidinone (*S*)-**14** (Scheme 3). Recently, Davies and co-workers[16] has extended this methodology

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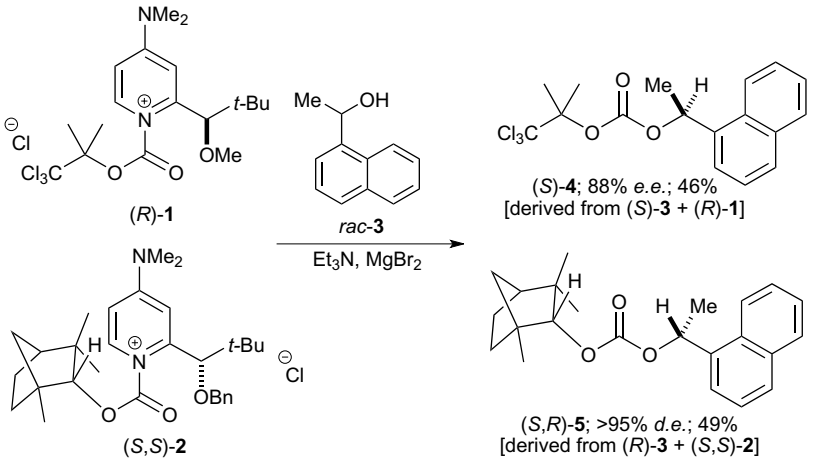
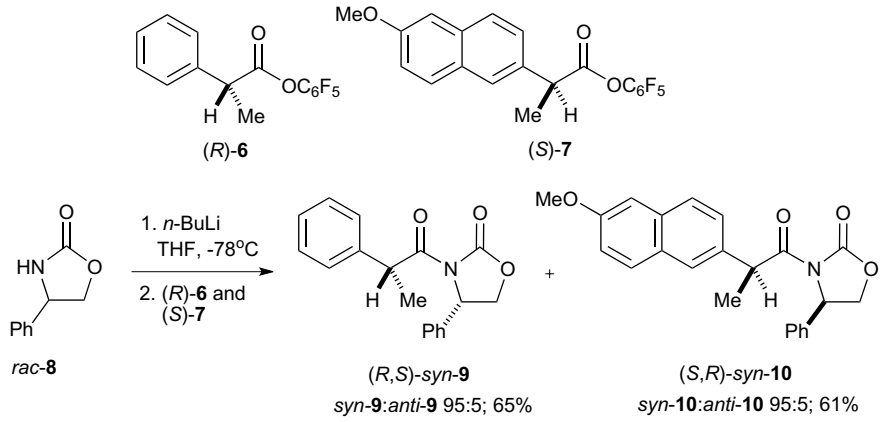
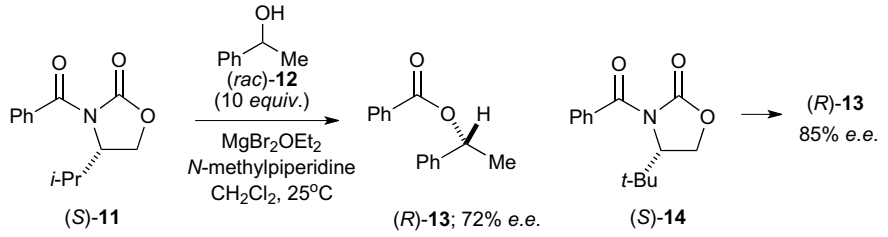


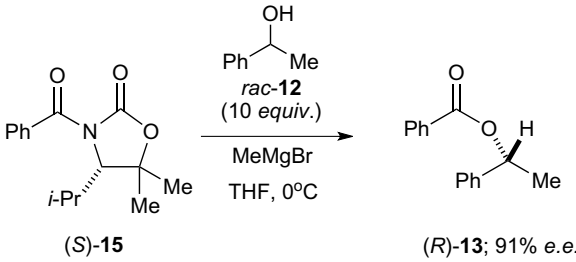
Scheme 1. Parallel kinetic resolution of alcohol (*rac*)-**3** using (*R*)-**1** and (*S*,*S*)-**2**.



Scheme 2. Parallel kinetic resolution of oxazolidinone (*rac*)-**8** using (*R*)-**6** and (*S*)-**7**.



Scheme 3. Kinetic resolution of alcohol (*rac*)-**12** using oxazolidinones (*S*)-**11** and (*S*)-**14**.



Scheme 4. Kinetic resolution of alcohol (*rac*)-**12** using oxazolidinone (*S*)-**15**.

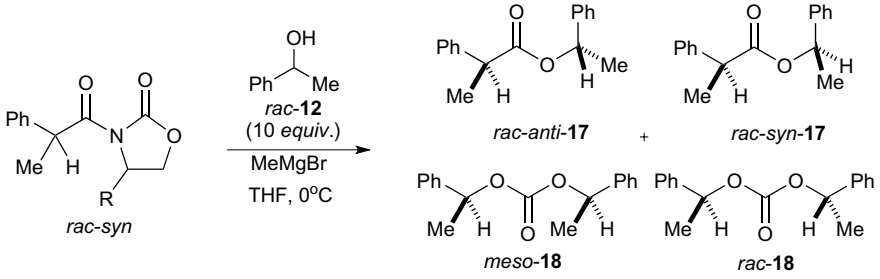
through the use of a designer oxazolidinone, SuperQuat (*S*)-**15**, to give the required 1-phenylethyl benzoate (*R*)-**13** with a higher level of enantiocontrol (91% ee[16] vs 72% ee[15]) as shown in Scheme 4, which was shown to be comparable to that derived from the more expensive and less available oxazolidinone adduct (*S*)-**14** (Scheme 3). Within both these studies,[15,16] the relative enantiomeric recognition was identical; the (*S*)-enantiomer of the oxazolidinone recognised the (*R*)-enantiomer of 1-phenylethanol **12** (and vice versa) to give ester (*R*)-**13** (Scheme 4). Yamada has also probed this particular reaction-type using oxazolidin-2-thiones.[17]

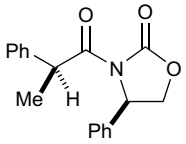
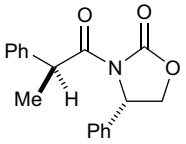
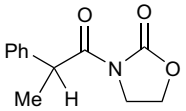
2. Results and discussion

For our study, we first probed the mutual kinetic resolution of a series of 2-phenylpropionated oxazolidinones *rac-syn*-**9**, *rac-anti*-**9** and *rac*-**16** with 1-phenylethanol *rac*-**12** (10 equiv) to determine the potential levels of complementary recognition (Scheme 5). For a comparable study to Evans'[15] and Davies',[16] we chose to add the oxazolidinones *rac-syn*-**9**, *rac-anti*-**9** and *rac*-**16** to a stirred solution of magnesium 1-phenylethoxide bromide and 1-phenylethanol (ratio 1:9) in THF at 0 °C (Scheme 5). After stirring for 12 h, this gave the corresponding 1-phenylethyl 2-phenylpropionate **17** in moderate yield (41–59%) with good levels of diastereoselectivity, favouring the formation of the *anti*-diastereoisomer in 68%, 24% and 0% de, respectively (Scheme 5). The levels of stereocontrol were determined by ^{1}H NMR spectroscopy (400 MHz) by integration of the corresponding methyl doublets in *anti*- and *syn*-**17**.[18]

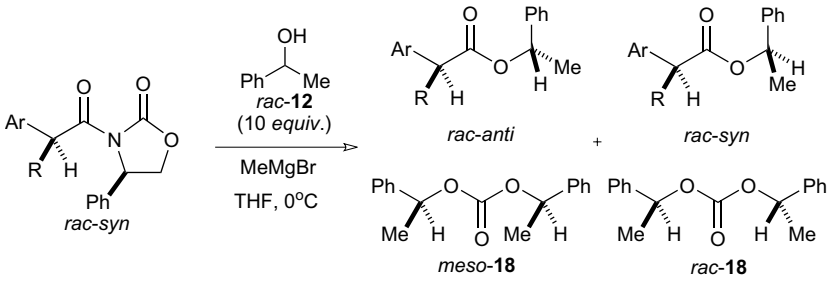
Interestingly, the formation of 1-phenylethyl-2-phenylpropionate **17** must have occurred via *exo*-cleavage of the corresponding oxazolidinone and the levels of stereoselection appear to be governed by the relative stereogenicity of the oxazolidinone framework (Scheme 5). For the simplest oxazolidinone *rac*-**16** [formed by addition of lithiated oxazolidin-2-one to a solution of a pentafluorophenyl 2-phenylpropionate *rac*-**6** in 61% yield] gave no level of enantiomer selection for racemic 1-phenylethanol **12** (Scheme 5, entry 3). However, when using the diastereoisomeric oxazolidinones *rac-syn*- and *rac-anti*-**9**, these gave improved levels of diastereocontrol for ester **17** in favour of the *anti*-diastereoisomer (Scheme 5: entries 1 and 2). Interestingly, *syn*-oxazolidinone **9** gave higher levels of enantiomer selection for racemic 1-phenylethanol **12** than its related oxazolidinone *anti*-**9** (68% de vs 24% de) (Scheme 5: entry 1 vs entry 2). Evidently, the stereo-directing phenyl group at the *C*(4)-position within the oxazolidinone ring in *rac-syn*- and *rac-anti*-**9** appears to be less dominant than their adjacent 2-phenylpropionyl motif as both these diastereoisomers favoured the formation of *anti*-ester **17** (Scheme 5). In contrast to Evans[15] and Davies,[16] it appears that this enantiomeric recognition process is dependent on both the structural nature of the parent oxazolidinone and the carbonyl-transferring motif.

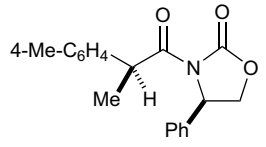
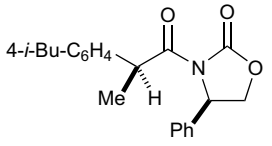
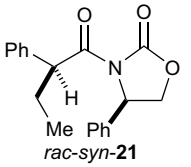
The formation of the carbonates *meso*- and *rac*-**18** must have occurred via *endo*-cleavage[19] of the oxazolidinone ring (Scheme 5). The levels of stereocontrol and yield were found to be dependent on the structural nature of the oxazolidinone adduct. However, in all cases, *meso*-carbonate **18** was found to be the major diastereoisomer (from 14% to 40% de) (Scheme 5). The absence of



Entry	Oxazolidinone	*rac*-ester-**17** *anti*-:*syn*-	D.e	carbonate **18** *meso*-: *rac*-	D.e
1	 *rac-syn*-**9**	84:16; 55%	68%	65:35; 14%	30%
2	 *rac-anti*-**9**	62:38; 41%	24%	57:43; 4%	14%
3	 *rac*-**16**	50:50; 59%	0%	70:30; <1%	40%

Scheme 5. Mutual kinetic resolution of alcohol (*rac*)-**12** using oxazoldinones (*rac*)-**9** and **16**.

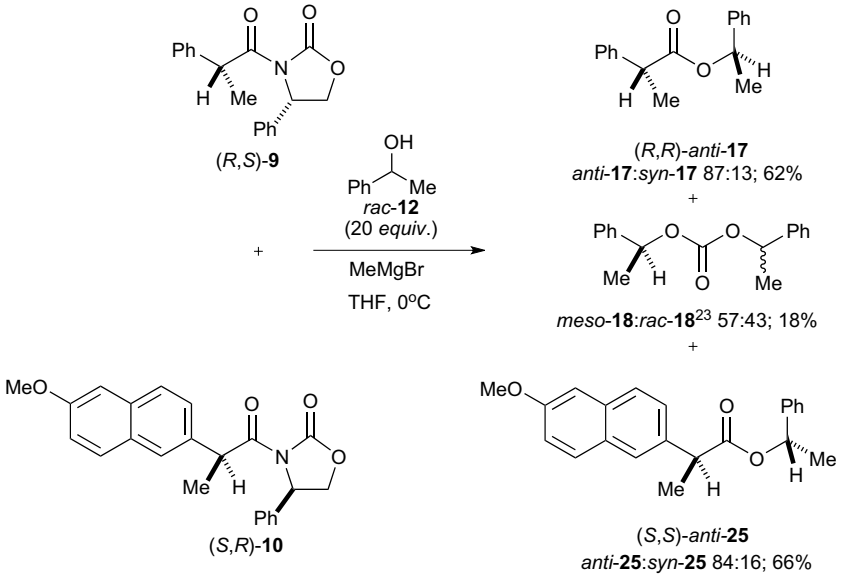


Entry	Oxazolidinone	*rac*-Ester *anti*-: *syn*-	De	Carbonate **18** *meso*-: *rac*-	De
1	 *rac-syn*-**19**	*rac*-**22**; 53% 83:17	66%	64:34; 12%	30%
2	 *rac-syn*-**20**	*rac*-**23**; 54% 85:15	70%	63:37; 21%	26%
3	 *rac-syn*-**21**	*rac*-**24**; 35% 88:12	76%	62:38; 19%	24%

Scheme 6. Mutual kinetic resolution of alcohol (*rac*)-**12** using oxazolidinones **19**–**21**.

carbonate formation from Evans' and Davies' studies was presumably due to the promoted *exo*-cleavage.[20] Davies has also demonstrated that his designer SuperQuat oxazolidinones sterically disfavours *endo*-cleavage.[16,21]

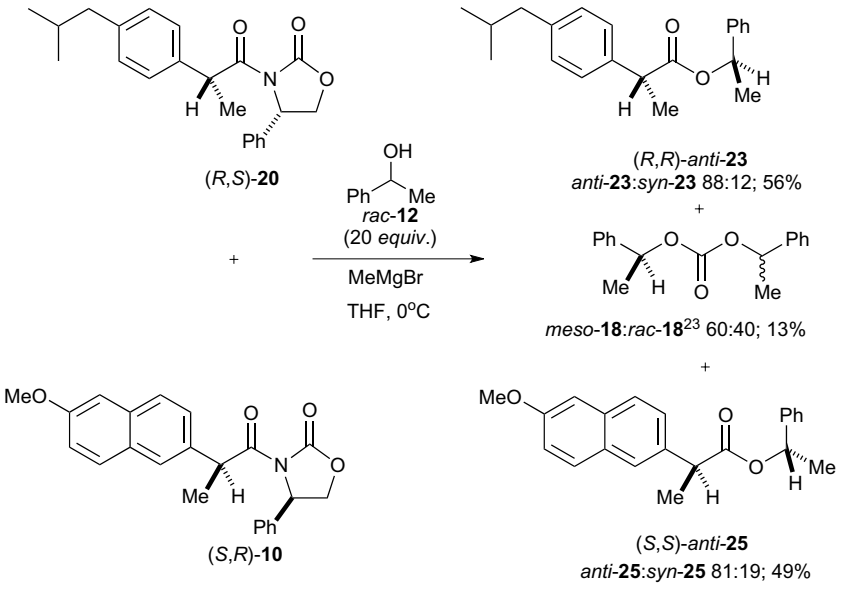
With this information in hand, we next investigated the mutual kinetic resolution of racemic 1-phenylethanol **12** using a series of structurally related *syn*-diastereoisomeric oxazolidinones *rac-syn*-**19**–**21** (Scheme 6). The addition of



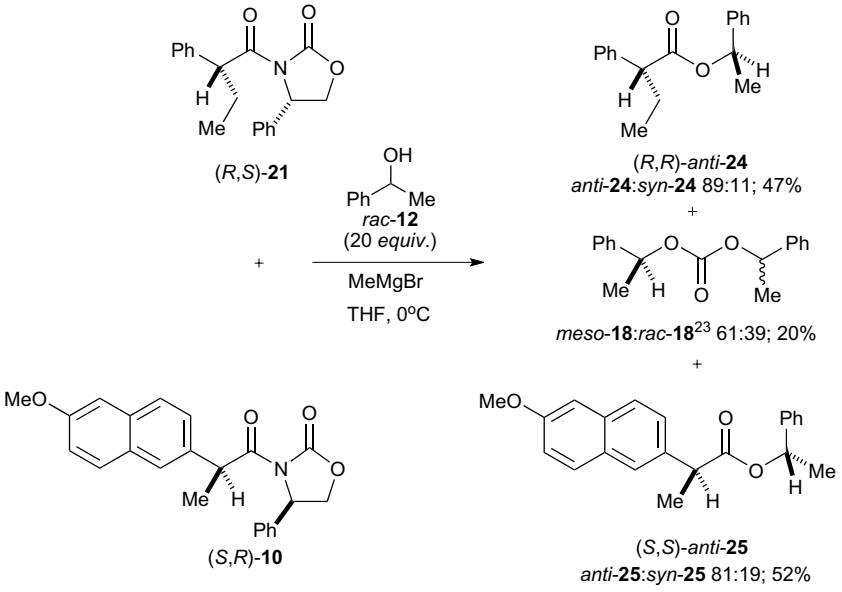
Scheme 7. Parallel kinetic resolution of alcohol (*rac*)-**12** using oxazolidinones **9** and **10**.

methyl magnesium bromide (1 equiv) to a stirred solution of 1-phenylethanol *rac*-**12** (10 equiv), followed by the addition of oxazolidinones *rac-syn*-**19**–**21** in THF at 0 °C, gave a racemic mixture of diastereoisomeric esters *rac-anti*- and *rac-syn*-**22**–**24** and carbonates *meso*- and *rac*-**18** in moderate to good yields (Scheme 6). For 2-(4-methylphenyl)- and 2-(4-isobutylphenyl)propionyl oxazolidinones *rac*-**19** and *rac*-**20**, these favoured the formation of the esters *rac-anti*-**22** and *rac-anti*-**23** in 53% and 54% yields, respectively, with near identical levels of diastereoselection (66% and 70% de) to its closely related parent oxazolidinone *rac-syn*-**9** (Scheme 6, entries 1 and 2 vs Scheme 5, entry 1). Whereas the use of a more structurally demanding 2-phenylbutyryl motif in oxazolidinone *rac-syn*-**21** gave a slight improvement in enantiomer selection favouring formation of the ester *anti*-**24** with 76% de in lower yield (35%) (Scheme 6, entry 3).

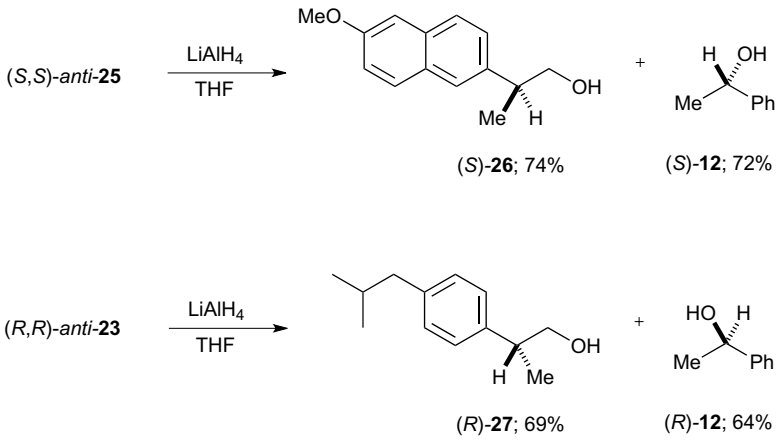
We next turned our attention to probing the parallel kinetic resolution of 2-phenylethanol *rac*-**12** using three combinations of enantiomerically pure *quasi*-enantiomeric oxazolidinones (Schemes 7–9). For this study, we chose to use a more polar naproxen-derived oxazolidinone (*S*,*R*)-*syn*-**10** as our complementary component due to its known separability from related profen-derived adducts (as shown in Scheme 7).[13,14,22] We chose to screen three structurally related parallel kinetic resolutions, by the addition of an equimolar combination of (*R*,*S*)-*syn*-**9** and (*S*,*R*)-*syn*-**10**,



Scheme 8. Parallel kinetic resolution of alcohol (*rac*)-**12** using oxazolidinones **10** and **20**.[23]



Scheme 9. Parallel kinetic resolution of alcohol (*rac*)-**12** using oxazolidinones **10** and **21**.



Scheme 10. Synthesis of alcohols (*S*)-**26** and (*R*)-**27**, and 1-phenylethanol (*S*)-and (*R*)-**12**.

(*R*,*S*)-*syn*-**20** and (*S*,*R*)-*syn*-**10**, and (*R*,*S*)-*syn*-**21** and (*S*,*R*)-*syn*-**10** to a stirred solution of preformed racemic magnesium 2-phenylethoxide bromide and 2-phenylethanol *rac*-**12** (ratio 1:9) in THF at 0 °C (Schemes 7–9).

These parallel resolutions proceeded efficiently giving three pairs of diastereoisomeric esters, *anti*- and *syn*-**17** (87:13; 62%) and *anti*- and *syn*-**25** (84:16; 66%) (in Scheme 7), *anti*- and *syn*-**23** (88:12; 56%) and *anti*- and *syn*-**25** (81:19; 49%) (in Scheme 8), and *anti*- and *syn*-**24** (89:11; 47%) and *anti*- and *syn*-**25** (81:19; 52%), respectively (Scheme 9), in good yield, with good to excellent levels of diastereocontrol (68–78% de). These levels of complementary stereocontrol were near identical to their corresponding mutual kinetic resolution. The complementary esters **17**, **23** and **24** were efficiently separated from the more polar naproxen-derived ester **25**, by flash column chromatography on silica gel, eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (9:1) ($\Delta R_F = 0.25$) (Schemes 7–9). The remaining byproduct, oxazolidinone *rac*-**8**, was recovered in ~40% yield.[24]

Access to the (*S*)-enantiomer of 1-phenylethanol **12** was achieved by $LiAlH_4$ reduction of ester (*S*,*S*)-*anti*-**25**, to give 1-phenylethanol (*S*)-**12** and 2-(6-methoxy-2-naphthyl)propanol (*S*)-**26** in 72% and 74% yields, respectively (Scheme 10). $LiAlH_4$ reduction of the complementary ester (*R*,*R*)-*anti*-**23** gave an inseparable mixture of 2-(4-isobutylphenyl)propanol (*R*)-**27** and 1-phenylethanol (*R*)-**12** in 69% and 64% yields.[25]

3. Conclusion

In conclusion, we have reported a diastereoselective parallel kinetic resolution approach for the resolution of 2-phenylethanol *rac*-**12**, using an equimolar combination of *quasi*-enantiomeric oxazolidinones [e.g., (*R*,*S*)-**9** and (*S*,*R*)-**10**]. The levels of diastereocontrol were found to be excellent and predictably favoured the formation of the corresponding *anti*-diastereoisomeric ester (*R*,*S*)-**17**. We are currently exploring the scope and limitation of this diastereoselective alkyl-carbonyl transfer reaction and competing carbonate formation, and this will be reported in due course.

4. Experimental

4.1. General

All solvents were distilled before use. All reactions were carried out under nitrogen using oven-dried glassware. Flash column chromatography was carried out using Merck Kieselgel 60 (230–400 mesh). Thin layer chromatography (TLC) was carried out on commercially available pre-coated plates (Merck Kieselgel $60F_{254}$ silica). Proton and carbon NMR spectra were recorded on a Bruker 400 MHz Fourier transform spectrometer using an internal deuterium lock. Chemical shifts are quoted in parts per million downfield from tetramethylsilane. Carbon NMR spectra were recorded with broad proton decoupling. Infrared spectra were recorded on a Shimadzu 8300 FTIR spectrometer. Optical rotation was measured using an automatic AA-10 Optical Activity Ltd polarimeter. For all the mutual and parallel kinetic resolutions reported, the yields are based on the amount of oxazolidinone present.

4.2. Synthesis of 3-(2-phenylpropionyl)-oxazolidin-2-one *rac*-16

n-BuLi (0.96 ml, 2.5 M in hexanes, 2.40 mmol) was added to a stirred solution of oxazolidin-2-one (0.19 g, 2.18 mmol) in THF (10 ml) at −78 °C. After stirring for 1 h, a solution of pentafluorophenyl 2-phenylpropionate *rac*-**6** (0.69 g, 2.18 mmol) in THF (10 ml) was added. The resulting mixture was stirred for 2 h at −78 °C. The reaction was quenched with water (25 ml). The organic layer was extracted with dichloromethane (3 × 25 ml), washed with brine (25 ml), dried over $MgSO_4$ and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1), to give 3-(2-phenylpropionyl)-oxazolidin-2-one *rac*-**16** (0.29 g, 61%) as a colourless liquid; R_F [light petroleum (bp 40–60 °C)–diethyl

ether (1:1)] 0.14; ν_{max} ($CHCl_3$) cm^{-1} 1772 (NC=O) and 1700 (OC=O); δ_H (400 MHz; $CDCl_3$) 7.37 (2H, dt, *J* 7.1 and 1.5, 2 × CH; Ph), 7.31 (2H, br ddd, *J* 7.1, 1.5 and 1.0, 2 × CH; Ph), 7.27–7.22 (1H, br tt, *J* 7.1 and 1.5, CH; Ph), 5.11 (1H, q, *J* 7.0, C*H*CH_3), 4.42–4.25 (2H, m, CH_2O), 4.11–4.02 (1H, ABq, CH_AH_BN), 3.97–3.89 (1H, ABq, CH_AH_BN) and 1.50 (3H, d, *J* 7.0, CH_3); δ_C (100 MHz; $CDCl_3$) 174.4 (NC=O), 152.9 (OC=O), 140.2 (*i*-C; Ph), 128.4[2], 129.0[2] and 127.0[1] (5 × CH; Ph), 61.6 (CH_2O), 42.7 (CH_2N), 42.6 (*C*HCH_3) and 19.2 (CH_3) (Found M^+, 219.0888; $C_{12}H_{13}NO_3$ requires 219.0890); *m*/*z* 219 (3%, M^+), 132 (10, $PhCH_3C{=}C{=}O^+$), 105 (55, $PhCH_3CH^+$), 104 (50, $PhCHCH_2^+$), 77 (95, $C_6H_5^+$) and 43 (100, $NHCO^+$).

4.3. 1-Phenylethyl-2-phenylpropionate *rac-anti*-17 [derived from the mutual kinetic resolution of 1-phenylethanol *rac*-12 and 3-(2-phenylpropionyl)-oxazolidin-2-one *rac*-16]

Methyl magnesium bromide (0.37 ml, 3 M in diethyl ether, 1.00 mmol) was added to a stirred solution of 1-phenylethanol *rac*-**12** (1.23 g, 10.00 mmol) in THF (6 ml) at 0 °C. After stirring for 10 min, a solution of oxazolidinone adduct *rac*-**16** (0.22 g, 1.00 mmol) in THF (6 ml) was added. The resulting solution was stirred for 12 h at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (10 ml). The organic layer was extracted with dichloromethane (3 × 25 ml), washed with water (25 ml), dried (over $MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1) to give an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl 2-phenylpropionates *rac-anti*- and *rac-syn*-**17** (0.15 g, 59%; *syn*-:*anti*- 50:50), and di-(1-phenylethyl) carbonates *meso*- and *rac*-**18** (~2 mg, 0.7%; *meso*-:*rac*- 70:30) as an oil.

Characterisation data for:

4.3.1. 1-Phenylethyl-2-phenylpropionate *rac-anti*-17. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.80; ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 7.30–7.14 (8H, m, 8 × CH; 2 × Ph), 7.05–7.00 (2H, m, 2 × CH; 2 × Ph), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.68 (1H, q, *J* 7.2, PhC*H*CH_3), 1.43 (3H, d, *J* 7.2, $PhCHCH_3$) and 1.42 (3H, d, *J* 6.6, $PhCHCH_3O$); δ_C (100 MHz; $CDCl_3$) 173.5 (C=O), 141.6 (*i*-C; Ph^A), 140.4 (*i*-C; Ph^B), 128.5,[2] 128.3,[2] 127.6.,[2] 127.5,[1] 127.0[1] and 125.6[2] (10 × CH; Ph^A and Ph^B), 72.4 (PhCHO), 45.7 (PhCH), 22.3 ($PhCHCH_3O$) and 18.3 ($PhCHCH_3$) (Found MNH_4^+, 272.1647; $C_{17}H_{22}NO_2$ requires 272.1645); *m*/*z* 254 (10%, M^+) and 105 (100, $PhCHCH_3^+$).

4.3.2. 1-Phenylethyl-2-phenylpropionate *rac-syn*-17. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.78; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.28–7.13 (10H, m, 10 × CH; Ph^A and Ph^B), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.66 (1H, q, *J* 7.2, PhC*H*CH_3), 1.41 (3H, d, *J* 7.2, $PhCHCH_3$) and 1.35 (3H, d, *J* 6.6, $PhCHCH_3O$); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 141.6 (*i*-C; Ph^A), 140.5 (*i*-C; Ph^B), 128.5,[2] 128.4,[2] 127.8,[1] 127.5,[2] 127.0[1] and 126.0[2] (10 × CH; Ph^A and Ph^B), 72.5 (PhCHO), 45.6 (PhCH), 22.0 ($PhCHCH_3O$) and 18.3 ($PhCHCH_3$) (Found MNH_4^+, 272.1648; $C_{17}H_{22}NO_2$ requires 272.1645); *m*/*z* 254 (5%, M^+), 105 (100, $PhCHCH_3^+$) and 77 (10, $C_6H_5^+$).

4.3.3. Di-(1-phenylethyl)-carbonate *meso*-18.[26] Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.75; ν_{max} ($CHCl_3$); cm^{-1} 1751 (C=O); δ_H (400 MHz; $CDCl_3$) 7.39–7.23 (10H, m, 10 × CH; Ph^A and Ph^B), 5.69 (2H, q, *J* 6.8, 2 × PhC*H*CH_3) and 1.59 (6H, d, *J* 6.8, 2 × PhC*H*CH_3); δ_C (100 MHz; $CDCl_3$) 153.9 (C=O), 141.2 (2 × *i*-C; 2 × Ph), 128.5 (4 × CH; 2 × Ph), 128.1 (2 × CH; 2 × Ph), 126.1 (4 × CH; 2 × Ph), 76.4 (2 × Ph*C*HCH_3) and 22.4 (2 × $PhCHCH_3$) (Found MNH_4^+, 288.1593; $C_{17}H_{22}NO_4$ requires 288.1594); *m*/*z* 269 (1%, M^+-H), 165 (15, $M^+-PhCHCH_3$), 121 (30, $PhCHCH_3O^+$), 105 (100, $PhCHCH_3^+$) and 77 (40, $C_6H_5^+$).

4.3.4. Di-(1-phenylethyl)-carbonate *rac*-18.[27] Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.75; ν_{max} ($CHCl_3$); cm^{-1} 1742 (C=O); δ_H (400 MHz; $CDCl_3$) 7.38–7.26 (10H, m, 10 × CH; Ph^A and Ph^B), 5.66 (2H, q, *J* 6.8, 2 × PhC*H*CH_3) and 1.53 (6H, d, *J* 6.8, 2 × $PhCHCH_3$); δ_C (100 MHz; $CDCl_3$) 153.8 (C=O), 141.1 (2 × *i*-C; 2 × Ph), 128.5 (4 × CH; 2 × Ph), 128.0 (2 × CH; 2 × Ph), 126.0 (4 × CH; 2 × Ph), 76.3 (2 × Ph*C*HCH_3) and 22.2 (2 × $PhCHCH_3$) (Found MNH_4^+, 288.1593; $C_{17}H_{22}NO_4$ requires 288.1594); *m*/*z* 269 (1%, $M-H^+$), 165 (10, $M^+-PhCHCH_3$), 121 (25, $PhCHCH_3O^+$), 105 (100, $PhCHCH_3^+$) and 77 (75, $C_6H_5^+$).

4.4. Mutual kinetic resolution of 1-phenylethanol *rac*-12 with 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *rac-anti*-9

In the same way as above, methyl magnesium bromide (0.26 ml, 3 M in diethyl ether, 0.78 mmol), 1-phenylethanol *rac*-**12** (0.95 g, 7.79 mmol) and 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *rac-anti*-**9** (0.23 g, 0.78 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1→7:3) an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl-2-phenylpropionates *rac-anti*- and *rac-syn*-**17** (81 mg, 41%; *anti*-:*syn*- 62:38) and di-(1-phenylethyl) carbonates *meso*- and *rac*-**18** (9 mg, 4%; *meso*-:*rac*- 57:43), which were spectroscopically identical to that previously obtained.

4.5. Mutual kinetic resolution of 1-phenylethanol *rac*-12 with 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *rac-syn*-9

In the same way as above, methyl magnesium bromide (0.23 ml, 3 M in diethyl ether, 0.68 mmol), 1-phenylethanol *rac*-**12** (0.83 g, 6.77 mmol) and 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *rac-syn*-**9** (0.2 g, 0.68 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1→7:3) an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl-2-phenylpropionates *rac-anti*- and *rac-syn*-**17** (95 mg, 55%; *anti*-:*syn*- 84:16) and di-(1-phenylethyl) carbonates *meso*- and *rac*-**18** (25 mg, 14%; *meso*-:*rac*- 65:35), which were spectroscopically identical to that previously obtained.

4.6. Mutual kinetic resolution of 1-phenylethanol *rac*-12 with 4-phenyl-[3-(4-methylphenyl)-2-propyl]-oxazolidin-2-one *rac-syn*-19

In the same way as above, methyl magnesium bromide (0.52 ml, 3 M in diethyl ether, 1.55 mmol), 1-phenylethanol *rac*-**12** (1.90 g, 15.52 mmol) and 4-phenyl-[3-(4-methylphenyl)-2-propyl]-oxazolidin-2-one *rac-syn*-**19** (0.48 g, 1.55 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1) an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl-2-(4-methylphenyl)propionates *rac-anti*- and *rac-syn*-**22** (0.21 g, 53%; *anti*-:*syn*- 83:17) and di-(1-phenylethyl)carbonate *meso*- and *rac*-**18** (49 mg, 12%; *meso*-:*rac*- 64:36).

Characterisation data for:

4.6.1. 1-Phenylethyl-2-(4-methylphenyl)propionate *rac-anti*-22. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.79; ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 7.20–7.12 (3H, m, 3 × CH; Ph), 7.08–7.00 (6H, m, 3 × CH; Ar and Ph), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.64 (1H, q, *J* 7.2, ArC*H*CH_3), 2.25 (3H, s, CH_3; Ar), 1.41 (3H, d, *J* 6.6, PhCHC*H*$_3$O) and 1.40 (3H, d, *J* 7.2, ArCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 141.7 (*i*-C; Ar), 137.4 (*i*-C; Ph), 136.6 (*i*-CCH_3; Ar), 129.2,[2] and 125.7[2] (4 × CH; Ar), 128.3,[2] 127.5,[1] and 127.4[2] (5 × CH; Ph), 72.4 (Ph*C*HCH$_3$O), 45.3 (Ar*C*HCH$_3$), 22.3 (PhCH*C*H$_3$O), 21.0 (CH_3; Ar) and 18.4 (ArCH*C*H$_3$) (Found MNH_4^+, 286.1804; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268 (5%, M^+), 119 (100, $ArCHCH_3^+$) and 105 (60, $PhCHCH_3^+$).

4.6.2. 1-Phenylethyl-2-(4-methylphenyl)propionate *rac-syn*-22. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.79; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.38–7.27 (5H, m, 5 × CH; Ph), 7.22 (2H, br d, *J* 8.2, 2 × CH; Ar), 7.15 (2H, br d, *J* 8.2, 2 × CH; Ar), 5.87 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.72 (1H, q, *J* 7.1, ArC*H*CH_3), 2.34 (3H, s, CH_3; Ar), 1.48 (3H, d, *J* 7.1, ArCHC*H*$_3$) and 1.44 (3H, d, *J* 6.6, PhCHC*H*$_3$O); δ_C (100 MHz; $CDCl_3$) 173.9 (C=O), 141.7 (*i*-C; Ar), 137.5 (*i*-C; Ph), 136.6 (*i*-CCH_3; Ar), 129.2,[2] and 126.0[2] (4 × CH; Ar), 128.4,[2] 127.8,[1] and 127.3[2] (5 × CH; Ph), 72.4 (Ph*C*HCH$_3$O), 45.2 (Ar*C*HCH$_3$), 22.0 (PhCH*C*H$_3$O), 21.0 (CH_3; Ar) and 18.5 (ArCH*C*H$_3$) (Found MNH_4^+, 286.1801; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268 (7%, M^+), 119 (100, $ArCHCH_3^+$) and 105 (70, $PhCHCH_3^+$).

4.7. Mutual kinetic resolution of 1-phenylethanol *rac*-12 with 4-phenyl-3-[2-(4-isopropyl)phenylpropionyl]-oxazolidin-2-one *rac-syn*-20

In the same way as above, methyl magnesium bromide (0.52 ml, 3 M in diethyl ether, 1.52 mmol), 1-phenylethanol *rac*-**12** (1.91 g, 15.65 mmol) and 4-phenyl-[3-(4-isopropylphenyl)-2-propyl]-oxazolidin-2-one *rac-syn*-**20** (0.55 g, 1.52 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1) an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl-2-(4-isopropylphenyl)-propionates *rac-anti*- and *rac-syn*-**23** (0.21 g, 54%; *anti*-:*syn*- 85:15) and di-(1-phenylethyl)-carbonate *meso*- and *rac*-**18** (88 mg, 21%; *meso*-:*rac*- 63:37).

Characterisation data for:

4.7.1. 1-Phenylethyl-2-(4-isopropylphenyl)propionate *rac-anti*-23. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.85; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.21–7.17 (3H, m, 3 × CH; Ph), 7.11 (2H, br d, *J* 8.1, 2 × CH; Ar), 7.08–7.05 (2H, m, Ph), 7.05 (2H, br d, *J* 8.1, 2 × CH; Ar), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.65 (1H, q, *J* 7.2, ArC*H*CH_3), 2.37 (2H, d, *J* 7.1, CH_2Ar), 1.77 (1H, triple septet (appears as a nonet), *J* 7.1 and 6.6, C*H*$(CH_3)_2$), 1.42 (3H, d, *J* 6.6, PhCHC*H*$_3$O), 1.41 (3H, d, *J* 7.1, ArCHC*H*$_3$) and 0.82 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 141.7 (*i*-C; Ar), 140.4 (*i*-C; Ph), 137.6 (*i*-*C*CH_2; Ar), 129.2,[2] and 125.6[2] (4 × CH; Ar), 128.2,[2] 127.5,[1] and 127.3[2] (5 × CH; Ph), 72.3 (Ph*C*HCH$_3$O), 45.3 (Ar*C*HCH$_3$), 45.0 (*C*H$_2$Ar) 30.2 (*C*H$(CH_3)_2$), 22.3[3] (3 C, CH(*C*H$_3$)$_2$ and PhCH*C*H$_3$O) and 18.2 (ArCH*C*H$_3$) (Found MNH_4^+, 328.2273; $C_{21}H_{30}NO_2$ requires 328.2271); *m*/*z* 310 (5%, M^+), 161 (100, $ArCHCH_3^+$) and 105 (80, $PhCHCH_3^+$).

4.7.2. 1-Phenylethyl-2-(4-isopropylphenyl)propionate *rac-syn*-23. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.84; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.27–7.19 (5H, m, 5 × CH; Ph), 7.14 (2H, dt, *J* 8.1 and 1.8, 2 × CH; Ar), 7.02 (2H, dt, *J* 8.1 and 1.8, 2 × CH; Ar), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.64 (1H, q, *J* 7.2, ArC*H*CH_3), 2.38 (2H, d, *J* 7.1, CH_2Ar), 1.78 (1H, triple septet (appears as a nonet), *J* 7.1 and 6.6, C*H*$(CH_3)_2$), 1.40 (3H, d, *J* 7.2, ArCHC*H*$_3$), 1.34 (3H, d, *J* 6.6, PhCH*C*H$_3$O) and 0.83 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$); δ_C (100 MHz; $CDCl_3$) 174.0 (C=O), 141.7 (*i*-C; Ar), 140.4 (*i*-C; Ph), 137.6 (*i*-*C*CH_2; Ar), 129.2,[2] and 125.9[2] (4 × CH; Ar), 128.4,[2] 127.7,[1] and 127.2[2] (5 × CH; Ph), 72.4 (Ph*C*HCH$_3$O), 45.2 (Ar*C*HCH$_3$), 45.0 (*C*H$_2$Ar) 30.2 (*C*H$(CH_3)_2$), 22.3[2] (CH(*C*H$_3$)$_2$), 22.0 (PhCH*C*H$_3$O) and 18.3 (ArCH*C*H$_3$) (Found MNH_4^+, 328.2271; $C_{21}H_{30}NO_2$ requires 328.2271); *m*/*z* 310 (5%, M^+), 161 (100, $ArCHCH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.8. Mutual kinetic resolution of 1-phenylethanol *rac*-12 with 4-phenyl-3-(2-phenylbutyryl)-oxazolidin-2-one *rac-syn*-21

In the same way as above, methyl magnesium bromide (0.34 ml, 3 M in diethyl ether, 1.03 mmol), *rac*-1-phenylethanol **12** (1.26 g, 10.31 mmol) and 4-phenyl-3-(2-phenylbutyryl)-oxazolidin-2-one *rac-syn*-**21** (0.32 g, 1.03 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1→7:3) an inseparable mixture[25] of two pairs of diastereoisomeric 1-phenylethyl-2-phenylbutyrates *rac-anti*- and *rac-syn*-**24** (98 mg, 35%; *anti*-:*syn*- 88:12) and di-(1-phenylethyl)carbonate *meso*- and *rac*-**18** (53 mg, 19%; *meso*-:*rac*- 62:38).

Characterisation data for:

4.8.1. 1-Phenylethyl-2-phenylbutyrate[28] *rac-anti*-24. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.79; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.30–7.14 (8H, m, 8 × CH; Ph^A and Ph^B), 7.05–7.00 (2H, m, 2 × CH; Ph^A or Ph^B), 5.88 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.51 (1H, t, *J* 7.6, PhC*H*CH_2CH_3), 2.13 (1H, ddq, *J* 13.7, 7.6 and 7.5, C*H*$_A$H$_B$$CH_3$), 1.82 (1H, ddq, *J* 13.7, 7.6 and 7.5, CH$_A$*H*$_B$$CH_3$), 1.51 (3H, d, *J* 6.6, PhCHC*H*$_3$O) and 0.90 (3H, t, *J* 7.5, C*H*$_3$$CH_2$); δ_C (100 MHz; $CDCl_3$) 172.8 (C=O), 141.5 (*i*-C; PhCHCH$_3$O), 138.8 (*i*-C; PhCHCH_3), 128.3,[2] 128.1,[2] 127.9,[2] 127.4,[1] 126.9[1] and 125.9[2] (10 × CH; Ph^A and Ph^B), 72.2 (Ph*C*HCH$_3$O), 53.5 (Ph*C*HCH$_3$), 26.4 (CH_3*C*H_2), 22.2 (PhCH*C*H$_3$O) and 12.0 (*C*H$_3$$CH_2$) (Found MNH_4^+, 286.1805; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268 (5%, M^+), 119 (30, $PhCHCH_2CH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.8.2. 1-Phenylethyl-2-phenylbutyrate *rac-syn*-24. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.75; ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.38–7.23 (10H, m, 10 × CH; Ph^A and Ph^B), 5.88 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.51 (1H, t, *J* 7.5, PhC*H*CH_2CH_3), 2.11 (1H, ddq, *J* 13.5, 7.5 and 7.5, C*H*$_A$H$_B$$CH_3$), 1.80 (1H, ddq, *J* 13.5, 7.5 and 7.5, CH$_A$*H*$_B$$CH_3$), 1.44 (3H, d, *J* 6.6, PhCHC*H*$_3$O) and 0.87 (3H, t, *J* 7.5, C*H*$_3$$CH_2$); δ_C (100 MHz; $CDCl_3$) 173.3 (C=O), 141.7 (*i*-C; PhCHCH$_3$O), 139.1 (*i*-C; PhCHCH_3), 128.5,[2] 128.4,[2] 127.9,[2] 127.7,[1] 127.1[1] and 126.0[2] (10 × CH; Ph^A and Ph^B), 72.5 (Ph*C*HCH$_3$O), 53.6 (Ph*C*HCH$_2$CH$_3$), 26.6 (CH_3*C*H_2), 21.9 (PhCH*C*H$_3$O) and 12.1 (*C*H$_3$$CH_2$) (Found MNH_4^+, 286.1805; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268 (5%, M^+), 119 (50, $PhCHCH_2CH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.9. Parallel kinetic resolution of 1-phenylethanol *rac*-12 using 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-9 and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-10

Methyl magnesium bromide (1.65 ml, 3 M in diethyl ether, 4.94 mmol) was added to a stirred solution of 1-phenylethanol *rac*-**12** (6.04 g, 49.35 mmol) in THF (20 ml) at 0 °C. After stirring for 10 min, a mixed solution of 3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**9** (0.73 g, 2.47 mmol) and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**10** (0.93 g, 2.47 mmol) in THF (40 ml) was added. The resulting mixture was stirred overnight at room temperature. The reaction was quenched with saturated aqueous NH_4Cl (30 ml). The organic layer was extracted with dichloromethane (3 × 50 ml), washed with water (50 ml), dried (over $MgSO_4$) and evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)–diethyl ether (9:1–0:1) to give two pairs of inseparable diastereoisomers[25] (*R*,*R*)-*anti*- and (*S*,*S*)-*syn*-**17** (0.39 g, 62%) (ratio: *anti*-:*syn*- 87:13) and *meso*- and *rac*-**18** (0.24 g, 18%) (ratio: *syn*-:*anti*- 57:43), and (*S*,*S*)-*anti*- and (*R*,*R*)-*syn*-**25** (0.55 g, 66%) (ratio: *anti*-:*syn*- 84:16).

Characterisation data for:[29]

4.9.1. 1-Phenylethyl-2-phenylpropionate[30] (*R*,*R*)-*anti*-17. Transparent solid; mp 81–83 °C; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.80; $[\alpha]_D^{20} = +10.5$ (*c* 3.0, $CHCl_3$) {lit.;[30] $[\alpha]_D^{20} = +9.9$ (*c* 0.87, $CHCl_3$)}; ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 7.30–7.14 (8H, m, 8 × CH; Ph^A and Ph^B), 7.05–7.00 (2H, m, 2 × CH; Ph^A or Ph^B), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.68 (1H, q, *J* 7.2, PhC*H*CH_3), 1.43 (3H, d, *J* 7.2, PhCHC*H*$_3$) and 1.42 (3H, d, *J* 6.6, PhCHC*H*$_3$O); δ_C (100 MHz; $CDCl_3$) 173.5 (C=O), 141.6 (*i*-C; PhCHCH$_3$O), 140.4 (*i*-C; PhCHCH_3), 128.5,[2] 128.3,[2] 127.6.,[2] 127.5,[1] 127.0,[1] and 125.6,[2] (10 × CH; Ph^A and Ph^B), 72.4 (Ph*C*HCH$_3$O), 45.7 (Ph*C*HCH$_3$), 22.3 (PhCH*C*H$_3$O) and 18.3 (PhCH*C*H$_3$) (Found MNH_4^+, 272.1648; $C_{17}H_{22}NO_2$ requires 272.1645); *m*/*z* 254 (10%, M^+) and 105 (100, $PhCHCH_3^+$).

4.9.2. 1-Phenylethyl-2-phenylpropionate (*R*,*S*)-*syn*-17. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.78; $[\alpha]_D^{20} = -60.4$ (*c* 1.9, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.28–7.13 (10H, m, 10 × CH; Ph^A and Ph^B), 5.78 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.66 (1H, q, *J* 7.2, PhC*H*CH_3), 1.41 (3H, d, *J* 7.2, PhCHC*H*$_3$) and 1.35 (3H, d, *J* 6.6, PhCHC*H*$_3$O); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 141.6 (*i*-C; Ph^A), 140.5 (*i*-C; Ph^B), 128.5,[2] 128.4,[2] 127.8,[1] 127.5,[2] 127.0[1] and 126.0[2] (10 × CH; Ph^A and Ph^B), 72.5 (Ph*C*HCH$_3$O), 45.6 (Ph*C*HCH$_3$), 22.0 (PhCH*C*H$_3$O) and 18.3 (PhCH*C*H$_3$) (Found MNH_4^+, 272.1647; $C_{17}H_{22}NO_2$ requires 272.1645); *m*/*z* 254 (5%, M^+), 105 (100, $PhCHCH_3^+$) and 77 (10, Ph^+).

4.9.3. 1-Phenylethyl-2-(6-methoxy-naphthalene-2-yl)propionate (*S*,*S*)-*anti*-25. White solid; mp 94–96 °C; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.62; $[\alpha]_D^{20} = +26.6$ (*c* 3.2, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.66 (1H, d, *J* 8.4, CH; Ar), 7.63 (1H, d, *J* 8.4, CH; Ar), 7.55 (1H, br s, CH; Ar), 7.33 (1H, dd, *J* 8.3 and 1.8, CH; Ar), 7.19–7.08 (7 H, m, 7 × CH; Ar and Ph), 5.86 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.90 (3H, s, OCH_3; Ar), 3.88 (1H, q, *J* 7.2, ArC*H*CH_3), 1.56 (3H, d, *J* 7.2, ArCHC*H*$_3$) and 1.50 (3H, d, *J* 6.6, PhCHC*H*$_3$O); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 147.5 (*i*-CO; Ar), 141.6 (*i*-C; Ph), 135.6 (*i*-C; Ar), 133.6 and 128.9 (2 × *i*-C; Ar), 129.3,[1] 127.0,[1] 126.4,[1] 126.0,[1] 118.8[1] and 105.5[1] (6 × CH; Ar), 128.2,[2] 127.5[1] and 125.7[2] (5 × CH; Ph), 72.5 (Ph*C*HCH$_3$O), 55.3 (OCH_3), 45.6 (Ar*C*HCH$_3$), 22.3 (PhCH*C*H$_3$O) and 18.4 (ArCH*C*H$_3$) (Found MNH_4^+, 352.1907; $C_{22}H_{26}NO_3$ requires 352.1907); *m*/*z* 334 (20%, M^+), 185 (100, $ArCHCH_3^+$) and 105 (60, $PhCHCH_3^+$).

4.9.4. 1-Phenylethyl-2-(6-methoxy-naphthalene-2-yl)propionate (*S*,*R*)-*syn*-25. White solid; mp 73–75 °C; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.61; $[\alpha]_D^{20} = +8.75$ (*c* 1.64, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1730 (C=O); δ_H (400 MHz; $CDCl_3$) 7.68 (2H, dd, *J* 8.4 and 2.0, 2 × CH; Ar), 7.66 (1H, br s, CH; Ar), 7.40 (1H, dd, *J* 8.4 and 1.8, CH; Ar), 7.33–7.25 (5H, 5 × CH; Ph), 7.12 (1H, dd, *J* 8.4 and 1.8, CH; Ar), 7.10 (1H, br s, CH; Ar),

5.85 (1H, q, *J* 6.6, PhC*H*CH$_3$O), 3.90 (3H, s, OCH$_3$; Ar), 3.85 (1H, q, *J* 7.2, ArC*H*CH$_3$), 1.54 (3H, d, *J* 7.2, ArCHC*H*$_3$) and 1.40 (3H, d, *J* 6.6, PhCHC*H*$_3$O); δ_C (100 MHz; $CDCl_3$) 173.9 (C=O), 157.6 (*i*-CO; Ar), 141.6 (*i*-C; Ph), 135.7 (*i*-C; Ar), 133.6 and 128.9 (2 × *i*-C; Ar), 129.3, 127.0, 126.3, 125.9, 118.9 and 105.5 (6 × CH; Ar and Ph), 128.4,[2] 127.8,[1] and 126.0[2] (5 × CH; Ph), 72.6 (Ph*C*HCH$_3$O), 55.3 (OCH$_3$), 45.6 (Ar*C*HCH$_3$), 22.0 (PhCHC*H*$_3$O) and 18.5 (ArCH*C*H$_3$) (Found MNH_4^+, 352.1905; $C_{22}H_{26}NO_3$ requires 352.1907); *m*/*z* 334 (20%, M^+), 185 (100, $ArCHCH_3^+$) and 105 (50, $PhCHCH_3^+$).

4.9.5. Di-(1-phenylethyl)-carbonate (*R*,*R*)-18. White needle-like crystals; mp 48–50 °C; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.75; $[\alpha]_D^{20} = +116.6$ (*c* 0.8, $CHCl_3$); ν_{max} ($CHCl_3$); cm^{-1} 1742.5 (C=O); δ_H (400 MHz; $CDCl_3$) 7.38–7.26 (10H, m, 10 × CH; Ph^A and Ph^B), 5.66 (2H, q, *J* 6.8, 2 × PhC*H*CH$_3$) and 1.53 (6H, d, *J* 6.8, 2 PhC*H*C*H*$_3$); δ_C (100 MHz; $CDCl_3$) 153.8 (C=O), 141.1 (2 × *i*-C; Ph), 128.5[4], 128.0[2], 126.0[4] (10 × CH; 2 × Ph), 76.3 (2 × Ph*C*HCH$_3$) and 22.2 (2 × PhCH*C*H$_3$) (Found MNH_4^+, 288.1596; $C_{17}H_{22}NO_4$ requires 288.1594); *m*/*z* 269 (1%, M^+-H), 165 (10, $M^+-PhCHCH_3$), 121 (25, $PhCH_3C{=}OH^+$), 105 [100, $PhCHCH_3^+$) and 77 (75, Ph^+).

4.10. Parallel kinetic resolution of 1-phenylethanol *rac*-12 using 3-[2-(4-isopropylphenyl)propionyl]-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-20 and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-10

In the same way as above, methyl magnesium bromide (0.59 ml, 3 M in diethyl ether, 1.76 mmol), 1-phenylethanol *rac*-**12** (2.15 g, 17.59 mmol), 3-[2-(4-isopropylphenyl)propionyl]-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**20** (0.309, 0.88 mmol) and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**10** (0.331 g, 0.88 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1→7:3) two pairs of inseparable diastereoisomers[25] (*R*,*R*)-*anti*- and (*R*,*S*)-*syn*-**23** (154 mg, 56%) (ratio: *anti*-:*syn*- 88:12) and *meso*- and *rac*-**18** (60 mg, 13%) (ratio: *anti*-:*syn*- 60:40), and (*S*,*S*)-*anti* and (*S*,*R*)-*syn*-**25** (137 mg, 49%) (ratio; *anti*-:*syn*- 81:19).

Characterisation data for:[29]

4.10.1. 1-Phenylethyl-2-(4-isopropylphenyl)propionate (*R*,*R*)-*anti*-23. Oil R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.85; $[\alpha]_D^{20} = -14.2$ (*c* 11.4, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.21–7.17 (3H, m, 3 × CH; Ph), 7.11 (2H, br d, *J* 8.1, 2 × CH; Ar), 7.08–7.05 (2H, m, 2 × CH; Ph), 7.05 (2H, br d, *J* 8.1, 2 × CH; Ar), 5.78 (1H, q, *J* 6.6, PhCHO), 3.65 (1H, q, *J* 7.2, ArCH), 2.37 (2H, d, *J* 7.1, CH$_2$Ar), 1.77 (1H, triple septet, *J* 7.1 and 6.6, C*H*(CH$_3$)$_2$), 1.42 (3H, d, *J* 6.6, PhCHC*H*$_3$O), 1.41 (3H, d, *J* 7.1, ArC*H*$_3$CH) and 0.82 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 141.7 (*i*-C; PhCHCH$_3$O), 140.4 (*i*-C; ArCHCH$_3$), 137.6 (*i*-*C*CH$_2$; Ar), 129.2,[2] and 125.6[2] (4 × CH; Ar), 128.2,[2] 127.5,[1] and 127.3[2] (5 × CH; Ph), 72.3 (PhCH$_3$*C*HO), 45.3 (Ar*C*HCH$_3$), 45.0 (CH$_2$Ar), 30.2 (*C*H(CH$_3$)$_2$), 22.3[3] (3 C, CH(*C*H$_3$)$_2$ and OCH*C*H$_3$) and 18.2 (ArCH*C*H$_3$) (Found MNH_4^+, 328.2273; $C_{21}H_{30}N_1O_2$ requires 328.2271); *m*/*z* 310 (5%, M^+), 161 (100, $ArCHCH_3^+$) and 105 (80, $PhCHCH_3^+$).

4.10.2. 1-Phenylethyl-2-(4-isopropylphenyl)propionate (*S*,*R*)-*anti*-23. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.84; $[\alpha]_D^{20} = +29.4$ (*c* 0.65, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.27–7.19 (5H, m, 5 × CH; Ph), 7.14 (2H, dt, *J* 8.1 and 1.8, 2 × CH; Ar), 7.02 (2H, dt, *J* 8.1 and 1.8, 2 × CH; Ar), 5.78 (1H, q, *J* 6.6, PhC*H*CH$_3$O), 3.64 (1H, q, *J* 7.2, ArC*H*CH$_3$), 2.38 (2H, d, *J* 7.1, CH$_2$Ar), 1.78 [1H, triple septet, *J* 7.1 and 6.6, C*H*(CH$_3$)$_2$], 1.40 (3H, d, *J* 7.2, ArCHC*H*$_3$), 1.34 (3H, d, *J* 6.6, ArCHC*H*$_3$O) and 0.83 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$); δ_C (100 MHz; $CDCl_3$) 174.0 (C=O), 141.7 (*i*-C; PhCHCH$_3$O), 140.4 (*i*-C; ArCHCH$_3$), 137.6 (*i*-*C*CH$_2$; Ar), 129.2,[2] and 125.9[2] (4 × CH; Ar), 128.4,[2] 127.7,[1] and 127.2[2] (5 × CH; Ph), 72.4 (Ph*C*HCH$_3$O), 45.2 (Ar*C*HCH$_3$), 45.0 (CH$_2$Ar) 30.2 [*C*H(CH$_3$)$_2$], 22.3[2] (CH(*C*H$_3$)$_2$), 22.0 (PhCH*C*H$_3$O) and 18.3 (ArCH*C*H$_3$) (Found MNH_4^+, 328.2271; $C_{21}H_{30}N_1O_2$ requires 328.2271); *m*/*z* 310 (5%, M^+), 161 (80, $ArCHCH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.11. Parallel kinetic resolution of *rac*-1-phenylethanol 12 using 3-(2-phenylbutyryl)-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-21 and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-10

In the same way as above, methyl magnesium bromide (0.23 ml, 3 M in diethyl ether, 0.69 mmol), 1-phenylethanol *rac*-**12** (0.75 g, 6.14 mmol), 3-(2-phenylbutyryl)-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**21** (0.11 g, 0.35 mmol) and 3-[2-(6-methoxy-naphthalen-2-yl)-propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**10** (0.13 g, 0.35 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether–diethyl ether (9:1→0:1), two pairs of inseparable diastereoisomers[25] (*R*,*R*)-*anti*- and (*S*,*S*)-*syn*-**24** (44 mg, 47%) (ratio: *anti*-:*syn*- 89:11) and *meso*- and *rac*-**18** (36 mg, 20%) (ratio: *syn*-:*anti*- 61:39), and (*S*,*S*)-*anti*- and (*R*,*R*)-*syn*-**25** (60 mg, 52%) (ratio: *anti*-:*syn*- 81:19).

Characterisation data for:[29]

4.11.1. 1-Phenylethyl-2-phenylbutyrate[30–32] (*S*,*S*)-*anti*-24. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.79; $[\alpha]_D^{20} = -12.9$ (*c* 6.2, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.30–7.14 (8H, m, 8 × CH; 2 × Ph), 7.05–7.00 (2H, m, 2 × CH; 2 × Ph), 5.88 (1H, q, *J* 6.6, PhC*H*CH$_3$O), 3.51 (1H, t, *J* 7.6, PhC*H*CH$_3$), 2.13 (1H, ddq, *J* 13.7, 7.6 and 7.5, C*H*$_A$H$_B$CH$_3$), 1.82 (1H, ddq, *J* 13.7, 7.6 and 7.5, CH$_A$*H*$_B$CH$_3$), 1.51 (3H, d, *J* 6.6, PhCHC*H*$_3$O) and 0.90 (3H, t, *J* 7.5, C*H*$_3$CH$_2$); δ_C (100 MHz; $CDCl_3$) 172.8 (C=O), 141.5 (*i*-C; Ph^A), 138.8 (*i*-C; Ph^B), 128.3,[2] 128.1,[2] 127.9,[2] 127.4,[1] 126.9[1] and 125.9[2] (10 × CH; Ph^A and Ph^B), 72.2 (Ph*C*HCH$_3$O), 53.5 (Ph*C*HCH$_3$), 26.4 (CH$_3$*C*H$_2$), 22.2 (PhCHC*H*$_3$O) and 12.0 (*C*H$_3$CH$_2$) (Found MNH_4^+, 286.1805; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268

(5%, M^+), 119 (30, $PhCHCH_2CH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.11.2. 1-Phenylethyl-2-phenylbutyrate[31] (*R*,*S*)-*syn*-24. Oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.75; $[\alpha]_D^{20} = +56.4$ (*c* 1.95, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1723 (C=O); δ_H (400 MHz; $CDCl_3$) 7.38–7.23 (10H, m, 10 × CH; Ph^A and Ph^B), 5.88 (1H, q, *J* 6.6, PhC*H*CH_3O), 3.51 (1H, t, *J* 7.5, PhC*H*CH_3), 2.11 (1H, ddq, *J* 13.5, 7.5 and 7.5, C$H_AH_B$$CH_3$), 1.80 (1H, ddq, *J* 13.5, 7.5 and 7.5, $CH_AH_B$$CH_3$), 1.44 (3H, d, *J* 6.6, PhCHCH_3O) and 0.87 (3H, t, *J* 7.5, CH_3CH_2); δ_C (100 MHz; $CDCl_3$) 173.3 (C=O), 141.7 (*i*-C; Ph^A), 139.1 (*i*-C; Ph^B), 128.5,[2] 128.4,[2] 127.9,[2] 127.7,[1] 127.1[1] and 126.0[2] (10 × CH; Ph^A and Ph^B), 72.5 (Ph*C*HCH$_3$O), 53.6 (Ph*C*HCH$_3$), 26.6 (CH_3*C*H$_2$), 21.9 (PhCH*C*H$_3$O) and 12.1 (*C*H$_3$CH$_2$) (Found MNH_4^+, 286.1805; $C_{18}H_{24}NO_2$ requires 286.1802); *m*/*z* 268 (5%, M^+), 119 (50, $PhCHCH_2CH_3^+$) and 105 (100, $PhCHCH_3^+$).

4.12. $LiAlH_4$ reduction of ester (*S*,*S*)-*anti*-25

$LiAlH_4$ (52 mg, 1.37 mmol) was added to a stirred solution of ester (*S*,*S*)-*anti*-**25** (0.229 g, 0.69 mmol) in THF (5 ml) at 0 °C. The resulting solution was stirred for 4 h. Water (25 ml) was added, and the resulting solution extracted with dichloromethane (3 × 25 ml). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography eluting with light petroleum ether (bp 40–60 °C)–diethyl ether (7:3→1:1) to give 1-phenylethanol (*S*)-**12** (60 mg, 72%) as an oil; R_F [light petroleum ether (bp 40–60 °C)–diethyl ether (1:1)] 0.33; $[\alpha]_D^{20} = -43.0$ (*c* 11.4, $CHCl_3$) {lit.[33] $[\alpha]_D^{20} = -45.5$ (*c* 5.0, methanol); ν_{max} ($CHCl_3$)/cm^{-1} 3019 (OH); δ_H (400 MHz; $CDCl_3$) 7.38–7.24 (5H, m, 5 × CH; Ph), 4.88 (1H, qd, *J* 6.4 and 1.9, CH_3C*H*), 2.04 (1H, d, *J* 1.9, OH) and 1.49 (3H, d, *J* 6.4, CH_3CH); δ_C (100 MHz; $CDCl_3$) 145.8 (*i*-C; Ph), 128.5[2], 127.4[1] and 125.3[2] (5 × CH; Ph), 70.3 (CH_3*C*H) and 25.1 (CH_3CH); and 2-(6-methoxy-2-naphthyl)propanol (*S*)-**26** (0.11 g, 74%) as an oil; R_F [light petroleum ether (bp 40–60 °C)–diethyl ether (1:1)] 0.20; $[\alpha]_D^{20} = -17.7$ (*c* 22.0, $CHCl_3$); lit.[34] $[\alpha]_D^{20} = -17.5$ (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3019 (OH); δ_H (400 MHz; $CDCl_3$) 7.64 (1H, d, *J* 8.4, CH; Ar), 7.62 (1H, d, *J* 8.4, CH; Ar), 7.53 (1H, br s, CH; Ar), 7.27 (1H, dd, *J* 8.6 and 1.8, CH; Ar), 7.09–7.03 (2H, m, 2 × CH; Ar), 3.83 (3H, s, CH_3O), 3.70 (2H, ABq, CH_2OH), 3.01 (1H, ddq (appears as a sextet with *J* 6.9), CH_3C*H*), 1.29 (1H, br s, OH) and 1.28 (3H, d, *J* 7.2, CH_3CH); δ_C (100 MHz; $CDCl_3$) 157.4 (*i*-CO; Ar), 138.6, 133.5 and 129.0 (3 × *i*-C; Ar), 129.1, 127.2, 126.2, 125.9, 118.9 and 105.6 (6 × CH; Ar), 68.6 (CH_3O), 55.3 (CH_2OH), 42.3 (CH_3*C*H) and 17.6 (*C*H$_3$CH).

4.13. $LiAlH_4$ reduction of ester (*R*,*R*)-*anti*-23

$LiAlH_4$ (61 mg, 1.61 mmol) was added to a stirred solution of ester (*R*,*R*)-*anti*-**23** (0.25 g, 0.81 mmol) in THF (5 ml) at 0 °C. The resulting solution was stirred for 4 h. Water (25 ml) was added, and the resulting solution was extracted with dichloromethane (3 × 25 ml). The combined organic layers were dried over $MgSO_4$, filtered, and evaporated under reduced pressure. The residue was purified by column chromatography eluting with light petroleum ether (bp 40–60 °C)–diethyl ether (7:3→1:1) to give an inseparable mixture (~0.169 g) of 1-phenylethanol (*R*)-**12** (63 mg, 64%) and 2-(4-isopropylphenyl)propanol (*R*)-**27** (0.106 mg, 69%). The relative amount of (*R*)-**12** and (*R*)-**27** was determined by ^1H NMR spectroscopy.

Characterisation data for 2-(4-isopropylphenyl)propanol (*R*)-**27** [derived from $NaBH_4$ reduction of (4*R*,2*R*)-4-isopropyl-3-[2-(4-isopropylphenyl)propionyl]-oxazolidin-2-one[35]; colourless oil; R_F [light petroleum (bp 40–60 °C)–diethyl ether (1:1)] 0.44; $[\alpha]_D^{20} = +18.5$ (*c* 1.6, $CHCl_3$); {lit.[36] (*S*)-**27**; 89% ee; $[\alpha]_D^{20} = -13.0$ (*c* 1.0, $CHCl_3$)}; ν_{max} ($CHCl_3$)/cm^{-1} 3019 (OH); δ_H (400 MHz; $CDCl_3$) 7.16 (2H, dd, *J* 8.3 and 2.0, 2 × CH; Ar), 7.12 (2H, dd, *J* 8.3 and 2.0, 2 × CH; Ar), 3.71 (1H, dd, *J* 6.9 and 1.0, CH_AH_BOH), 3.69 (1H, br d, *J* 6.9, CH_AH_BOH), 2.94 (1H, ddq (appears as a sextet, *J* 6.9), ArC*H*CH_3), 2.46 (2H, d, *J* 7.2, CH_2Ar), 1.86 (1H, m, (appears as a nonet, *J* 6.6), $(CH_3)_2$C*H*), 1.57 (1H, s, OH), 1.28 (3H, d, *J* 6.9, ArCHCH_3) and 0.91 (2 × 3 H, d, *J* 6.6, $(CH_3)_2$CH); δ_C (100 MHz; $CDCl_3$) 140.7 (*i*-C; Ar), 140.1 (*i*-C; Ar), 129.4[2] and 127.2[2] (4 × CH; Ar), 68.8 (CH_2OH), 45.0 (Ar*C*HCH$_3$), 42.0 (CH_2Ar), 30.2 (CH_3*C*HCH$_3$), 22.4[2] (*C*H$_3$CH*C*H$_3$) and 17.6 (ArCH*C*H$_3$).

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18. For *rac-anti*-**17**, the methyl doublets appear at 1.43 ppm (3H, d, $J = 7.2$ Hz, PhC*H*CH_3O) and 1.42 ppm (3H, d, $J = 6.6$ Hz, PhC*H*CH_3). Whereas, for *rac-syn*-**17**, the methyl doublets appear at 1.41 ppm (3H, d, $J = 7.2$ Hz, PhC*H*CH_3O) and 1.35 ppm (3H, d, $J = 6.6$ Hz, PhC*H*CH_3).
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20. Increasing the sterically demanding nature of the oxazolidinone ring at the *C*(4)-position has been shown to increase the relative rate of benzoyl transfer; for additional information, see Ref. 15. From our study, increasing the sterically demanding nature of the oxazolidinone [at *C*(4) position] and the phenylacetyl transfer group [at the *C*(2) position] appears to disfavour *exo*-cleavage (and promote competitive *endo*-cleavage).
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22. For active esters; R_F (light petroleum ether (40–60 °C)–diethyl ether 9:1) = 0.69 [for (*R*)-**6**] and 0.50 [for (*S*)-**7**]. For oxazolidinone adducts; R_F (light petroleum ether (40–60 °C)–diethyl ether 7:3) = 0.36 [for (*R*,*S*)-**20**], 0.33 [for (*R*,*S*)-**9**] and 0.24 [for (*S*,*R*)-**10**].
23. For a perfect PKR, the enantiomeric excesses of the chiral carbonates were assumed to be zero due to equal and opposite complementary reactions occurring with two *quasi*-enantiomeric oxazolidinone adducts; this is also the case for an MKR. However, a kinetic resolution between oxazolidinone (*S*,*R*)-**10** and 1-phenylethanol *rac*-**12** gave the corresponding diastereoisomeric esters (*S*,*S*)-*anti*- and (*S*,*R*)-*syn*-**25** in 38% yield (ratio *anti*-:*syn*- 90:10) with 80% de and the carbonates *meso*- and (*R*,*R*)-**18** in 26% yield (ratio *meso*-:(*R*,*R*)- 65:35) with 30% de and ~6% ee (for (*R*,*R*)-**18**). The specific rotation for this stereoisomeric mixture [*meso*-:(*R*,*R*)- 65:35] was $[\alpha]_D^{20} = +2.4$. The specific rotation of (*R*,*R*)-**18**); $[\alpha]_D^{20} = +116.6$ (*c* 0.8, $CHCl_3$).
24. The oxazolidinone *rac*-**8** can be recycled through a PKR using the active esters (*R*)-**6** and (*S*)-**7** (see Scheme 2). For additional information, see Refs. 14,35.
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