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Parallel kinetic resolution of active esters using designer oxazolidin-2-ones derived from phenylglycine

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ABSTRACT

The parallel kinetic resolution of racemic pentafluorophenyl 2-phenylpropionate using an equimolar combination of *quasi*-enantiomeric oxazolidin-2-ones is discussed. The levels of diastereoselectivity were excellent (>90% de) leading to separable *quasi*-enantiomeric oxazolidin-2-one adducts in good yield. This methodology was subsequently used to resolve a series of 2-aryl propionic and butanoic acids.

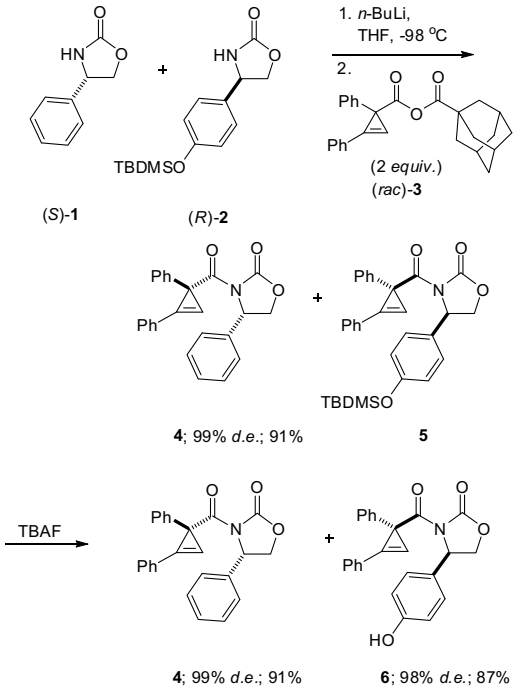
1. Introduction

Over the last decade, there has been a steady increase in the number of reports regarding the use of parallel kinetic resolutions as a strategy for the separation of enantiomers.[1,2] In particular, Fox[3] has elegantly demonstrated the resolution of racemic mixed anhydrides (e.g., *rac*-**3**) using of a pair of *quasi*-enantiomeric Evans' oxazolidin-2-ones (*S*)-**1** and (*R*)-**2** to give the corresponding oxazolidin-2-one adducts **4** and **5** with near perfect levels of stereocontrol (Scheme 1). These adducts were efficiently separated[3] using Vedejs' post-modification strategy[4]—by treatment of a near equimolar mixture of **4** and **5** with TBAF to give the more separable adducts **4** and **6** (Scheme 1).

Using a related approach, we have recently reported[5] the complementary parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** using a pair of *quasi*-enantiomeric Evans' oxazolidin-2-ones (*R*)-**1** and (*S*)-**7** to give the oxazolidin-2-one adducts (*S*,*R*)-*syn*-**9** (in 60% yield) and (*R*,*S*)-*syn*-**10** (in 60% yield) with >90% and 76% diastereoisomeric excesses, respectively (Scheme 2). From this preliminary study, it was evident that a better surrogate oxazolidin-2-one [(*S*)-**7**] for the (*S*)-enantiomer of oxazolidin-2-one **1** was needed to allow more efficient complementary stereocontrol (Scheme 2).[5]

2. Results and discussion

We now report an extension of our study[5,6] using a combination of designer oxazolidin-2-ones (*S*)-**2**, (*S*)-**11**, (*S*)-**12**, (*S*)-**13** and (*S*)-**14** (based on the parent phenylglycine derived oxazolidin-2-one **1**) and discuss their use as complementary *quasi*-enantiomeric oxazolidin-2-ones for the parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** (Scheme 3). For this study, the synthesis and application of the majority of these designer oxazolidin-2-ones have been reported.[3,7–9]



Scheme 1. Parallel kinetic resolution of anhydride (*rac*)-**3** using *quasi*-enantiomeric oxazolidin-2-ones (*S*)-**1** and (*R*)-**2**.

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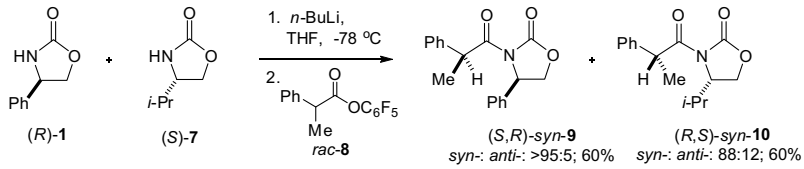
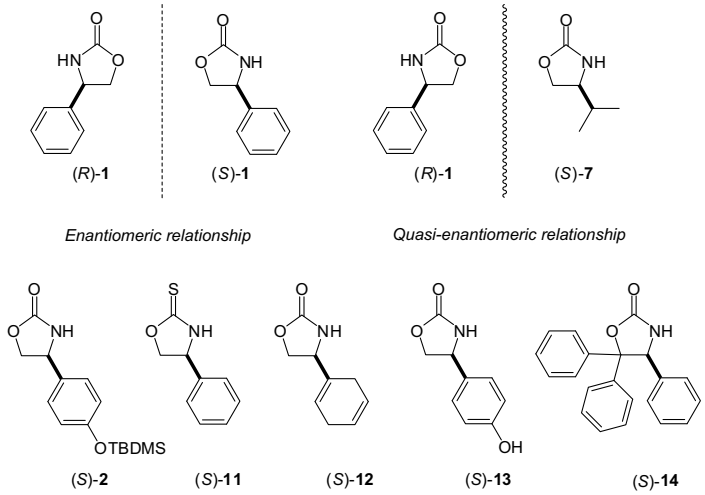


Scheme 2. Parallel kinetic resolution of active ester (*rac*)-**8** using *quasi*-enantiomeric oxazolidin-2-ones (*R*)-**1** and (*S*)-**7**.



Scheme 3. Potential *quasi*-enantiomeric oxazolidin-2-one surrogates for (*S*)-**1**.

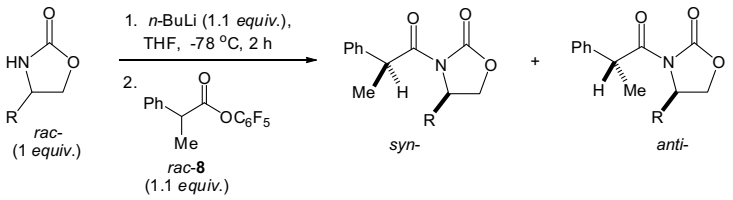
In an attempt to probe the complementarity of these designer oxazolidin-2-ones, we first screened their mutual kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** (Scheme 4). Deprotonation of the oxazolidin-2-ones *rac*-**1**, *rac*-**11**, *rac*-**12**, *rac*-**13**, *rac*-**2** and *rac*-**14** in THF at −78 °C, followed by the addition of pentafluorophenyl 2-phenylpropionate *rac*-**8**, gave after 2 h at −78 °C,[10] the corresponding adducts *rac*-*syn*-**9**, *rac*-*syn*-**15**, *rac*-*syn*-**16**, *rac*-*syn*-**17**, *rac*-*syn*-**18** and *rac*-*syn*-**19**, respectively in good yield with excellent levels of diastereoisomeric control (Scheme 4). These oxazolidin-2-ones appeared to behave similarly to the parent oxazolidin-2-one *rac*-**1** with the exception of Seebach's oxazolidin-2-one *rac*-**14** (Scheme 4: Entry 6). This particular oxazolidin-2-one was less diastereoselective favouring the formation of *syn*-adduct **19** in 53% yield with 78% de which was presumably due to its larger sterically demanding nature[7,11] and associated effects (Scheme 4). By comparison, the phenolic oxazolidin-2-one (*S*)-**13** appeared to be less nucleophilic, requiring a longer reaction time (12 h) for completion.

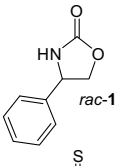
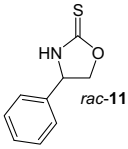
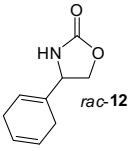
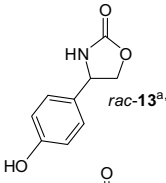
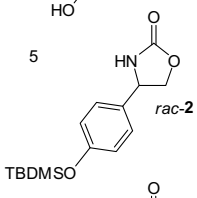
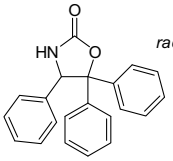
We first investigated the parallel kinetic resolution of pentafluorophenyl 2-phenyl propionate *rac*-**8** using a *quasi*-enantiomeric combination of oxazolidin-2-thione (*R*)-**11** and oxazolidin-2-one (*S*)-**1** (Scheme 5). Deprotonation of an equimolar combination of (*R*)-**11** and (*S*)-**1** with *n*-BuLi in THF at −78 °C, followed by the addition of active ester *rac*-**8**, gave a separable mixture of the corresponding adducts (*S*,*R*)-*syn*-**15** (in 55% yield) and (*R*,*S*)-*syn*-**9** (in 59% yield) with 96% and 92% diastereoisomeric excesses, respectively (Scheme 5). These adducts were easily separable by column chromatography due to their difference in polarity (C═S bond versus C═O bond) {ΔR_F [light petroleum ether (bp 40–60 °C): diethyl ether (1:1)] = 0.22}.

With this information in hand, we next probed the parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** using six pairs of *quasi*-enantiomeric oxazolidin-2-one combinations (*R*)-**1** and (*S*)-**14**, (*R*)-**2** and (*S*)-**14**, (*R*)-**13** and (*S*)-**14**, (*R*)-**1** and (*S*)-**2**, (*R*)-**13** and (*S*)-**1**, and (*R*)-**2** and (*S*)-**13** (Scheme 6). These parallel kinetic resolutions proceeded efficiently to give the adducts (*S*,*R*)-*syn*-**9** and (*R*,*S*)-*syn*-**19** (in 53% and 50% yields with >96% and 96% des, respectively), (*S*,*R*)-*syn*-**18** and (*R*,*S*)-*syn*-**19** (in 81% and 73% yields with >96% and 90% des, respectively), (*S*,*R*)-*syn*-**17** and (*R*,*S*)-*syn*-**19** (in 46% and 58% yields with >94% and 84% des, respectively), (*S*,*R*)-*syn*-**9** and (*R*,*S*)-*syn*-**18** (in 68% and 68% yields with >96% and 96% des, respectively), (*S*,*R*)-*syn*-**17** and (*R*,*S*)-*syn*-**9** (in 56% and 82% yields with 90% and 86% des, respectively), and (*S*,*R*)-*syn*-**18** and (*R*,*S*)-*syn*-**17** (in 61% and 49% yields with 96% and 96% des, respectively) (Scheme 6). The majority of these parallel kinetic resolutions proceeded efficiently leading to the complementary oxazolidin-2-one adducts with excellent levels of diastereocontrol.[12] The best combination of oxazolidin-2-ones was found to be (*R*)-**1** and (*S*)-**2** as they appeared to react at a near-equal and opposite rate, leading to optimum enantiomeric separation.[13] By comparison, the more sterically demanding oxazolidin-2-one **14** appeared to react slightly slower with pentafluorophenyl 2-phenylpropionate **8** than oxazolidin-2-ones **1** and **2**.

Whereas, phenolic oxazolidin-2-one **13** appeared to be less nucleophilic than the structurally related oxazolidin-2-ones **1**, **2** and **14** and required a significantly longer reaction time at an elevated temperature (12 h at rt) for completion.[13] These processes appear to proceed via a sequential kinetic resolution; the faster reacting enantiomer (e.g., **1**, **2** and **14**) gave lower levels of diastereocontrol (related to their mutual kinetic resolution) and the slower reacting enantiomer **13** gave improved diastereoselection.[14]

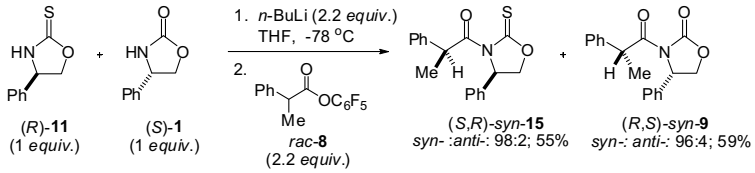
In an attempt to improve chromatographic separation, we chose to perform an in situ de-silylation of oxazolidin-2-one adduct (*R*,*S*)-*syn*-**18** [in the presence of (*S*,*R*)-*syn*-**9** (formed in Scheme 6)] using TBAF in THF (Scheme 7). Treatment of this crude mixture [derived the parallel kinetic resolution of *rac*-**8** using oxazolidin-2-ones (*R*)-**1** and (*S*)-**2**] with TBAF in THF for 3 h at rt, gave a separable mixture of oxazolidin-2-ones (*S*,*R*)-*syn*-**9** and (*R*,*S*)-*syn*-**17** in 58% and 53% yields (Scheme 7).



Entry	Oxazolidin-2-one	Product	D.e.	Yield
1	 rac-**1**	rac-*syn*-**9**:rac-*anti*-**9** >97: <3	>94%[5]	70%[5]
2	 rac-**11**	rac-*syn*-**15**:rac-*anti*-**15** 98: 2	96%	55%
3	 rac-**12**	rac-*syn*-**16**:rac-*anti*-**16** 97: 3	94%	63%
4	 rac-**13**[a,b]	rac-*syn*-**17**:rac-*anti*-**17** 96: 4	92%	50%
5	 rac-**2**	rac-*syn*-**18**:rac-*anti*-**18** >97: <3	>94%	67%
6	 rac-**14**	rac-*syn*-**19**:rac-*anti*-**19** 89: 11	78%	53%

[a] 2.2 *equiv.* of *n*-BuLi used; [b] -78 °C→ RT, 12 h.

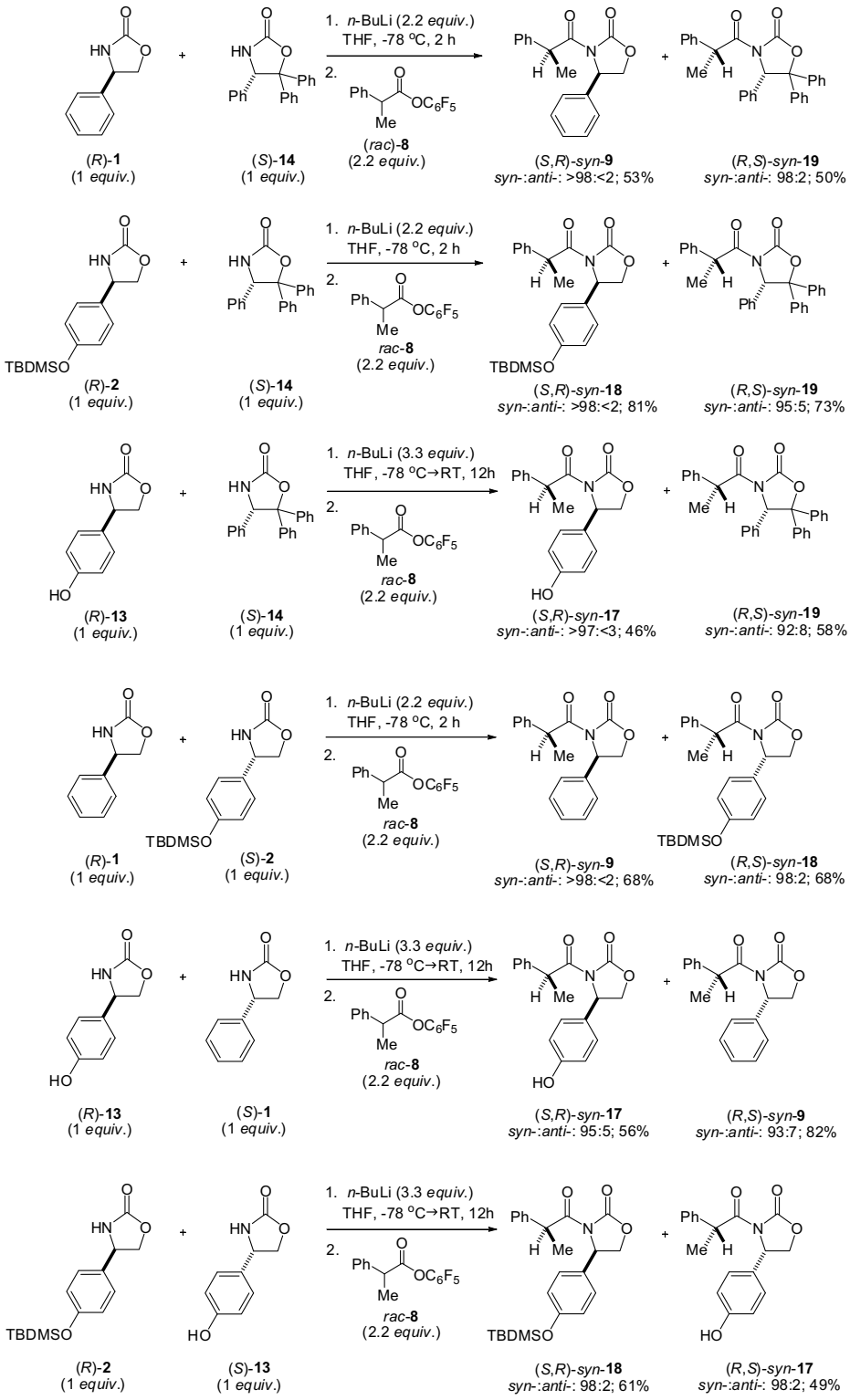
Scheme 4. Mutual kinetic resolution of active ester (*rac*)-**8** using oxazolidin-2-ones (*rac*)-**1**, (*rac*)-**2**, (*rac*)-**11**, (*rac*)-**12**, (*rac*)-**13** and (*rac*)-**14**.



Scheme 5. Parallel kinetic resolution of active ester (*rac*)-**8** using a *quasi*-enantiomeric oxazolidin-2-ones (*R*)-**11** and (*S*)-**1**.

Under our standard reaction conditions, it appears that the best combination was the Fox's and Evans' oxazolidin-2-ones (*R*)-**1** and (*S*)-**2**, respectively (Scheme 6). They appeared to behave as near-perfect *quasi*-enantiomeric partners reacting with *rac*-**1** in an equal and opposite stereochemical sense with similar reaction rates.[13] By comparison, the related oxazolidin-2-ones (*R*)-**13** and (*S*)-**14** reacted at different rates (to Evans' oxazolidin-2-one **1**) and these resolution processes appear to have some sequential resolution character with improved diastereoselection (Scheme 6).

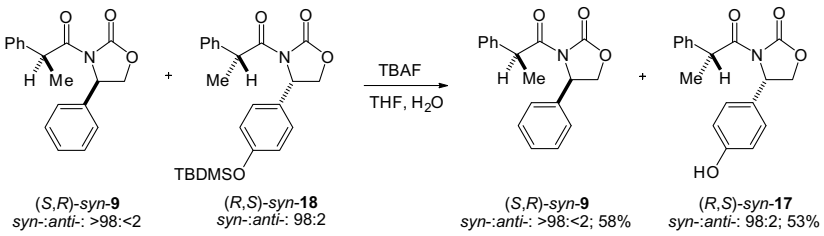
With this information in hand, we next investigated the parallel kinetic resolution of a variety of pentafluorophenyl 2-aryl substituted carboxylic acids[15] *rac*-**20**, *rac*-**21**, *rac*-**22** and *rac*-**23** using a combination of Evans' and Fox's oxazolidin-2-ones (*R*)-**1** and (*S*)-**2** (Scheme 8). Treatment of an equimolar combination of oxazoli-



Scheme 6. Parallel kinetic resolution of active ester (*rac*)-**8** using *quasi*-enantiomeric oxazolidin-2-ones **1**, **2**, **13** and **14**.

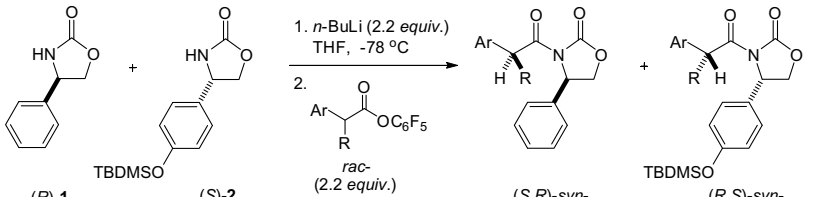
din-2-ones (*R*)-**1** and (*S*)-**2** with *n*-BuLi in THF at −78 °C, followed by the addition of active esters *rac*-**20**, *rac*-**21**, *rac*-**22** and *rac*-**23**, gave the corresponding oxazolidin-2-one adducts (*S*,*R*)-*syn*-**24** and (*R*,*S*)-*syn*-**28** (in 71% and 62% yields with >96% and >96% des, respectively), (*S*,*R*)-*syn*-**25** and (*R*,*S*)-*syn*-**29** (in 69% and 72% yields with 94% and 94% des, respectively), (*S*,*R*)-*syn*-**26** and (*R*,*S*)-*syn*-**30** (in 50% and 53% yields with 94% and 94% des, respectively) and (*S*,*R*)-*syn*-**27** and (*R*,*S*)-*syn*-**31** (in 70% and 72% yields with >96% and >96% des, respectively) (Scheme 8). These reactions proceeded efficiently leading to the required separable oxazolidin-2-one adducts in good yield (~60% yield) with high diastereoselectivity (~94% de) (Scheme 8).

Hydrolysis of a pair of *quasi*-enantiomeric adducts [e.g., (*S*,*R*)-*syn*-**9** and (*R*,*S*)-*syn*-**17**] using LiOH monohydrate/hydrogen



(*S*,*R*)-*syn*-**9** *syn*-:*anti*-: >98:<2 (*R*,*S*)-*syn*-**18** *syn*-:*anti*-: 98:2 (*S*,*R*)-*syn*-**9** *syn*-:*anti*-: >98:<2; 58% (*R*,*S*)-*syn*-**17** *syn*-:*anti*-: 98:2; 53%

Scheme 7. Post-modification of oxazolidin-2-one adduct (*R*,*S*)- *syn*-**18** to give (*R*,*S*)-*syn*-**17**.



(*R*)-**1** (1 *equiv*.) (*S*)-**2** (1 *equiv*.) (*S*,*R*)-*syn*- (*R*,*S*)-*syn*-

Active ester	Ar	R	Oxazolidin-2-oneadducts derived from (*R*)-**1**	D.e.	Yield	Oxazolidin-2-one adducts derived from (*S*)-**2**	D.e.	Yield
rac-**8**	Ph	Me	(*S*,*R*)-*syn*-**9**: (*R*,*R*)-*anti*-**9** >98:<2	96%	68%	(*R*,*S*)-*syn*-**18**: (*S*,*S*)-*anti*-**18** 98:2	96%	68%
rac-**20**	Ph	Et	(*S*,*R*)-*syn*-**24**: (*R*,*R*)-*anti*-**24** >98:<2	96%	71%	(*R*,*S*)-*syn*-**28**: (*S*,*S*)-*anti*-**28** >98:<2	96%	62%
rac-**21**	4-MeC_6H_4-	Me	(*S*,*R*)-*syn*-**25**: (*R*,*R*)-*anti*-**25** 97:3	94%	69%	(*R*,*S*)-*syn*-**29**: (*S*,*S*)-*anti*-**29** 97:3	94%	72%
rac-**22**	4-ClC_6H_4-	Me	(*S*,*R*)-*syn*-**26**: (*R*,*R*)-*anti*-**26** 97:3	94%	50%	(*R*,*S*)-*syn*-**30**: (*S*,*S*)-*anti*-**30** 97:3	94%	53%
rac-**23**	4-*i*-BuC_6H_4-	Me	(*S*,*R*)-*syn*-**27**: (*R*,*R*)-*anti*-**27** >98:<2	96%	70%	(*R*,*S*)-*syn*-**31**: (*S*,*S*)-*anti*-**31** >98:<2	96%	72%

Scheme 8. Parallel kinetic resolution of active esters **8** and **20**-**23** using oxazolidin-2-ones (*R*)-**1** and (*S*)-**2**.

peroxide proceeded efficiently, leading to the enantiomerically pure 2-phenylpropionic acids (*S*)- and (*R*)-**32** in 92% and 90% yield (Scheme 9). In addition, hydrolysis of the remaining complementary designer oxazolidin-2-ones (*R*,*S*)-*syn*-**18** and (*R*,*S*)-*syn*-**19** gave the required enantiomerically pure 2-phenylpropionic acid (*R*)-**32** in 90% and 58% yields, respectively (Scheme 9).[16]

3. Conclusion

In conclusion, we have reported the efficient parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** using combinations of oxazolidin-2-ones **1**, **2**, **13** and **14**. The levels of diastereocontrol were found to be excellent, favouring the formation of the corresponding *syn*-oxazolidin-2-one adducts **9**, **18**, **17** and **19** in good yields with excellent levels of diastereoselectivity. The preferred combination of *quasi*-enantiomeric oxazolidin-2-ones for the parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-**8** was found to be the oxazolidin-2-ones (*R*)-**1** and (*S*)-**2**. These oxazolidin-2-ones were shown to be efficient *quasi*-enantiomers for the parallel kinetic resolution and separation of a variety of 2-aryl propionic and butanoic acids.

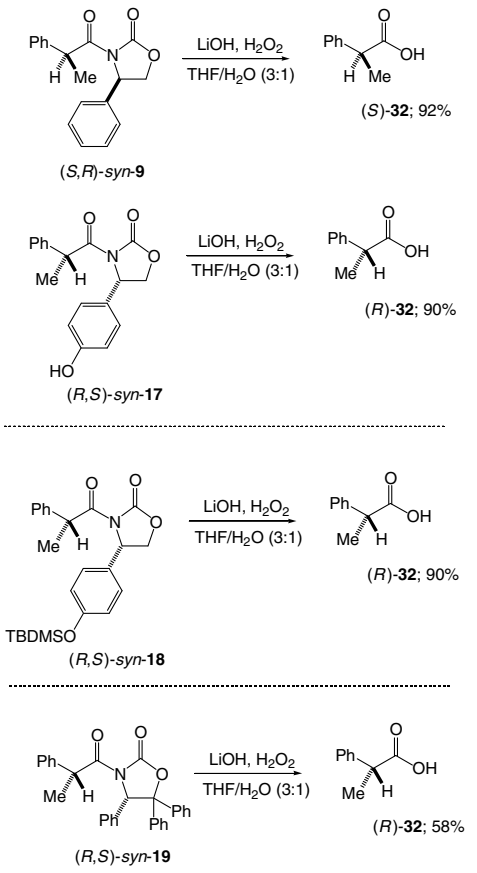
4. Experimental

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 rotations were measured using an automatic AA-10 Optical Activity Ltd polarimeter. The active esters, pentafluorophenyl 2-phenylpropionate *rac*-**8**, pentafluorophenyl phenylbutanoate *rac*-**20**, pentafluorophenyl 2-(4-methylphenyl)propionate *rac*-**21**, pentafluorophenyl 2-(4-chlorophenyl)propionate *rac*-**22** and pentafluorophenyl 2-(4-isobutylphenyl)propionate *rac*-**23** have been reported elsewhere.[15]

4.2. 4-Phenyl-oxazolidin-2-thione *rac*-11[8,9]

Carbon disulfide (1.74 g, 22.92 mmol) was added to a stirred solution of *rac*-phenylglycinol (1.50 g, 10.94 mmol) and aqueous $NaHCO_3$ (20 mL, 1 M) at room temperature. The resulting solution was stirred at 100 °C for 15 min. After being cooled to room temperature, the reaction mixture was extracted with dichloromethane (3 × 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to give the oxazolidin-2-thione *rac*-**11** (1.35 g, 69%) as a white powder; R_F [diethyl ether] 0.78; mp 158–162 °C; ν_{max} ($CHCl_3$)



Scheme 9. Synthesis of 2-phenylpropionic acids (*S*)- and (*R*)-**32**.

cm^{-1} 1709 (C=S); δ_H (400 MHz; $CDCl_3$) 8.17 (1H, s, NH), 7.42–7.34 (3H, m, 3 × CH; Ph), 7.30–7.27 (2H, m, 2 × CH; Ph), 5.13 (1H, dd, *J* 8.9 and 6.9, C*H*$_A$H$_B$O), 4.95 (1H, t, *J* 8.9, CHN) and 4.38 (1H, dd, *J* 8.9 and 6.9, CH$_A$*H*$_B$O); δ_C (100 MHz; $CDCl_3$) 189.7 (NC=S), 137.7 (*i*-C; Ph), 129.3[2], 129.1[1] and 126.1[2] (5 × CH; Ar), 77.5 (CH_2O) and 60.1 (CHN) (Found MH$^+$, 180.0481; $C_9H_{10}NOS$ requires 180.0478).

4.3. 2,5-Dihydrophenylglycinol

Lithium aluminium hydride (1.85 g, 49.5 mmol) was slowly added to THF (100 mL). The resulting solution was cooled to 0 °C using an ice-bath. *rac*-2,5-Dihydrophenylglycine (5.02 g, 32.76 mmol) was then slowly added for over 5 min. The ice-bath was then removed, and the resulting solution was refluxed for 16 h. The reaction mixture was then cooled to 10 °C, and diluted with diethyl ether (50 mL). The reaction was sequentially quenched with water (5 mL), sodium hydroxide (15%, 5 mL) and water (15 mL). The resulting solution was stirred for 30 min and the white precipitate was filtered. The filter cake was washed with diethyl ether (3 × 150 mL) and the organic filtrates were dried over $MgSO_4$, and concentrated under reduced pressure to give *rac*-2,5-dihydrophenylglycinol (3.32 g, 73%) as a colourless oil; ν_{max} ($CHCl_3$) cm^{-1} 3355 (NH), 3030 (NH) and 2881 (OH); δ_H (400 MHz; $CDCl_3$) 5.75–5.60 (3H, m, 3 × CH=), 3.63 (1H, dd, *J* 10.6 and 4.2, C*H*$_A$H$_B$O), 3.43 (1H, dd, *J* 10.6 and 7.2, CH$_A$*H*$_B$O), 3.31 (1H, dd, *J* 7.2 and 4.2, CHN), 2.70–2.50 (5H, m, 2 × CH_2 and OH) and 2.41 (2H, br s, NH_2); δ_C (100 MHz; $CDCl_3$) 135.2 (R_2C=), 124.0, 123.7 and 120.0 (3 × CH=), 64.8 (CH_2O), 58.1 (CHN), 26.3 and 26.1 (2 × CH_2); *m*/*z* 140.1 (100%, MH$^+$).

4.4. 4-(2,5-Dihydrophenyl)-oxazolidin-2-one *rac*-12

Anhydrous potassium carbonate (0.31 g, 2.23 mmol) was added to a solution of *rac*-2,5-dihydrophenylglycinol (3.10 g, 22.3 mmol) and diethylcarbonate (5.55 g, 5.69 mL, 46.99 mmol). The resulting mixture was subjected to short-path distillation for 4 h, at 135 °C, to give the by-product (ethanol), which was collected in the receiver flask. The reaction was quenched with water and extracted with dichloromethane (2 × 50 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to give the crude oxazolidin-2-one *rac*-**12**. This residue was re-crystallised from a mixture of hot light petroleum ether (bp 40–60 °C):ethyl acetate: (1:2) to give 4-(2,5-dihydrophenyl)-oxazolidin-2-one *rac*-**12** (2.43 g, 66%) as a white solid;R_F [diethyl ether] 0.44; mp 74–78 °C; ν_{max} ($CHCl_3$) cm^{-1} 1750 (C=O); δ_H (400 MHz; $CDCl_3$) 5.86 (1H, br s, NH), 5.75–5.60 (3H, br s, 3 × CH=), 4.47 (1H, t, *J* 8.6, C*H*$_A$H$_B$O), 4.33 (1H, dd, *J* 8.6 and 6.1, CH$_A$*H*$_B$O), 4.08 (1H, dd, *J* 8.6 and 6.1, CHN), 2.72–2.56 (4H, m, 2 × CH_2); δ_C (100 MHz; $CDCl_3$) 159.8 (C=O), 132.3 (R_2C=), 123.9, 123.1 and 122.9 (3 × CH=), 68.9 (CH_2O), 57.8 (CHN), 26.3 and 23.9 (2 × CH_2) (Found MH$^+$, 166.0683; $C_9H_{12}NO_2$ requires 166.0683).

4.5. 4-(4-*tert*-Butyldimethylsilyoxyphenyl)-oxazolidin-2-one *rac*-2 and 4-(4-hydroxyphenyl)-oxazolidin-2-one *rac*-13

Using Fox's protocol,[3] thionyl chloride (10.4 g, 6.3 mL, 87.1 mmol) was added to the *rac*-*N*-*tert*-butoxycarbonyl-(4-*tert*-butyldimethylsilyoxyphenyl)-glycinol (4.00 g, 10.9 mmol). The resulting solution was stirred for 12 h. The remaining thionyl chloride was removed through distillation, and the residual thionyl chloride was removed under reduced pressure. The resulting residue was dissolved in ethyl acetate (20 mL) and sequentially washed with water, $NaHCO_3$ (saturated) and brine, dried over $MgSO_4$ and concentrated under reduced pressure. Dichloromethane (50 mL) was added, and the insoluble 4-(4-hydroxyphenyl)-oxazolidin-2-one *rac*-**13** (0.29 g, 15%) was removed through filtration; white powder; mp 141–143 °C; R_F [diethyl ether] 0.05; R_F [EtOAc] 0.70; ν_{max} (ethanol) cm^{-1} 2974 (NH) and 1751 (C=O); δ_H (400 MHz; $CDCl_3$) 9.47 (1H, s, OH), 8.03 (1H, s, NH), 7.12 (2H, dt, *J* 8.5 and 2.4, 2 × CH; Ar), 6.75 (2H, dt, *J* 8.5 and 2.4, 2 × CH; Ar), 4.80 (1H, dd, *J* 8.4 and 6.8, CHN), 4.58 (1H, t, *J* 8.4, C*H*$_A$H$_B$O) and 3.93 (1H, dd, *J* 8.4 and 6.8, CH$_A$*H*$_B$O); δ_C (100 MHz; $CDCl_3$) 158.9 (C=O), 157.2 (*i*-CO; Ar), 131.0 (*i*-C; Ar), 127.4[2] and 115.4[2] (4 × CH; Ar), 71.6 (CH_2O) and 54.8 (CHN) (Found MNH_4^+, 197.0923; $C_9H_{13}N_2O_3$ requires 197.0921). The filtrate was concentrated under reduced pressure, and re-crystallised in hot ethyl acetate to give the 4-[4-(*tert*-butyldimethylsilyloxy)phenyl]-oxazolidin-2-one *rac*-**2** (1.56 g, 49%) as a white crystalline solid; mp 110–112 °C; R_F [diethyl ether] 0.42; R_F [EtOAc] 0.80; ν_{max} (ethanol) cm^{-1} 2974 (NH) and 1750 (CO); δ_H (400 MHz; $CDCl_3$) 8.13 (1H, s, NH), 7.27 (2H, br d, *J* 8.4, 2 × CH; Ar), 6.91 (2H, br d, *J* 8.4, 2 × CH; Ar), 4.91 (1H, dd, 8.4 and 6.7, CHN), 4.67 (1H, t, *J* 8.4, C*H*$_A$H$_B$O), 4.01 (1H, dd, *J* 8.4 and 6.7, CH$_A$*H*$_B$O), 0.99 (9H, s, 3 × CH_3C; *t*-Bu) and 0.22 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 158.9 (C=O), 154.9 (*i*-CO; Ar), 133.8 (*i*-C; Ar), 127.5[2] and 120.1[2] (4 × CH; Ar), 71.5 (CH_2O), 54.7 (CHN), 25.6[3] (3 × CH_3C; *t*-Bu), 17.9 (CH_3C; *t*-Bu) and −4.5[2] (2 × CH_3Si) (Found MNa^+, 316.1342; $C_{15}H_{23}NO_3SiNa$ requires 316.1339).

4.6. 4,5,5-Triphenyl-oxazolidin-2-one *rac*-14

Synthesised by mixing an equimolar amount of its (*S*)- and (*R*)-**14** enantiomers; characterisation data: R_F [diethyl ether] 0.50; mp 219–220 °C; ν_{max} ($CHCl_3$) cm^{-1} 1763 (C=O); δ_H (400 MHz; $CDCl_3$) 7.62 (2H, dt, *J* 7.2 and 2.2, 2 × CH; Ph), 7.39–7.26 (3H, m, 3 × CH; Ph), 7.09–6.98 (5H, m, 5 × CH; Ph), 6.95 (5H, br s, 5 × CH; Ph),

5.54 (1H, s, CHN) and 5.53 (1H, br s, NH); δ_C (100 MHz; $CDCl_3$) 158.0 (C=O), 142.8, 138.8 and 137.1 (3 × *i*-C; 3 × Ph), 128.6[2], 128.5[1], 128.4[1], 128.3[2], 127.8[2], 127.5[2], 127.3[1], 126.5[2] and 126.2[2] (15 × CH; 3 × Ph), 90.7 (CPh_2O) and 65.8 (CHN) (Found MNH_4^+, 333.1598; $C_{21}H_{21}N_2O_2$ requires 333.1598).

4.7. 4-Phenyl-oxazolidin-2-thione (*R*)-11[8,9]

In the same way as for the oxazolidin-2-thione *rac*-**11**,[8] (*R*)-phenylglycinol (1.59 g, 11.5 mol) and carbon disulfide (1.90 g, 24.9 mmol) in aqueous $NaHCO_3$ (20 mL, 1 M) gave the oxazolidin-2-thione (*R*)-**11** (1.26 g, 65%) as a white powder; R_F [diethyl ether] 0.78; mp 120–121 °C (lit.[9] 120–121 °C); $[\alpha]_D^{25} = -80.3$ (*c* 0.3, $CHCl_3$), lit.[8] $[\alpha]_D^{25} = -79.3$ (*c* 0.21, $CHCl_3$); lit.[9] for (*S*)-**11** $[\alpha]_D^{25} = +82.7$ (*c* 0.21, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1} 1709 (C=S); δ_H (400 MHz; $CDCl_3$) 8.17 (1H, s, NH), 7.42–7.34 (3H, m, 3 × CH; Ph), 7.30–7.27 (2H, m, 2 × CH; Ph), 5.13 (1H, dd, *J* 8.9 and 6.9, CH_AH_BO), 4.95 (1H, t, *J* 8.9, CHN) and 4.38 (1H, dd, *J* 8.9 and 6.9, CH_AH_BO); δ_C (100 MHz; $CDCl_3$) 189.7 (NC=S), 137.7 (*i*-C; Ph), 129.3[2], 129.1[1] and 126.1[2] (5 × CH; Ar), 77.5 (CH_2O) and 60.1 (CHN) (Found MH^+, 180.0478; C_9H_9NOS requires 180.0481).

4.8. 4-Phenyl-oxazolidin-2-one (*S*)-1

In the same way as for the oxazolidin-2-one *rac*-**12**, (*S*)-phenylglycinol (8.47 g, 61.8 mmol), potassium carbonate (0.85 g, 6.1 mmol) and diethylcarbonate (15.32 g, 15.71 mL, 129.8 mmol) gave the (*S*)-oxazolidin-2-one **1** (5.70 g, 57%) as a white powder. This was recrystallised from a mixture of hot light petroleum ether (bp 40–60 °C)/ethyl acetate: (1:2) to give 4-phenyl-oxazolidin-2-one (*S*)-**1** as white crystals; mp 130–133 °C, (lit.[17] 131–133 °C); R_F [ethyl acetate/ethanol (9:1)] 0.71; $[\alpha]_D^{22} = +47.8$ (*c* 0.8, $CHCl_3$) {for (*S*)-; lit.[17] $[\alpha]_D^{20} = +49.5$ (*c* 2.1, $CHCl_3$)}; ν_{max} ($CHCl_3$) cm^{-1} 3262 (NH) and 1736 (C=O); δ_H (400 MHz; $CDCl_3$) 7.41–7.31 (5H, m, 5 × CH; Ph), 5.69 (1H, s, NH), 4.93 (1H, dd, *J* 8.6 and 6.9, CHN), 4.72 (1H, t, *J* 8.6, CH_AH_BO) and 4.17 (1H, dd, *J* 8.6 and 6.9, CH_AH_BO); δ_C (100 MHz; $CDCl_3$) 159.4 (C=O), 139.3 (*i*-C; Ph), 129.2,[2] 128.9[1] and 126.0[2] (5 × CH; Ph), 72.5 (CH_2O) and 56.3 (CHN) (Found MNH_4^+, 181.0970; $C_9H_9NO_2$ requires 181.0972).

4.9. 4-[4-(*tert*-Butyldimethylsilyloxy)phenyl]-oxazolidin-2-one (*S*)-2 and 4-(4-Hydroxyphenyl)-oxazolidin-2-one (*S*)-13

In the same way as for the oxazolidin-2-one *rac*-**2**, thionyl chloride (12.9 g, 7.9 mL, 0.108 mmol) and (*S*)-*N*-*tert*-butoxycarbonyl-(4-*tert*-butyldimethylsilyoxyphenyl)-glycinol (5.00 g, 13.6 mmol) gave the 4-(4-hydroxyphenyl)-oxazolidin-2-one (*S*)-**13** (0.34 g, 14%) as a white powder; mp 201–204 °C; R_F [diethyl ether] 0.42; $[\alpha]_D^{20} = +41.4$ (*c* 1.7, ethanol); ν_{max} (ethanol) cm^{-1} 2974 (NH) and 1751 (C=O); δ_H (400 MHz; $CDCl_3$) 9.47 (1H, s, OH), 8.03 (1H, s, NH), 7.12 (2H, dt, *J* 8.5 and 2.4, 2 × CH; Ar), 6.75 (2H, dt, *J* 8.5 and 2.4, 2 × CH; Ar), 4.80 (1H, dd, *J* 8.4 and 6.8, CHN), 4.58 (1H, t, *J* 8.4, CH_AH_BO) and 3.93 (1H, dd, *J* 8.4 and 6.8, CH_AH_BO); δ_C (100 MHz; $CDCl_3$) 158.9 (C=O), 157.2 (*i*-CO; Ar), 131.0 (*i*-C; Ar), 127.4[2] and 115.4[2] (4 × CH; Ar), 71.6 (CH_2O) and 54.8 (CHN) (Found MNH_4^+, 197.0923; $C_9H_{13}N_2O_3$ requires 197.0921); *m*/*z* 179 (20%, M^+), 149 (20, M^+-CH_2O), 120 (100, ArCH=CH_2^+), 107 (25, $ArCH_2^+$) and 94 (15, $PhOH^+$); and 4-[4-(*tert*-butyldimethylsilyloxy)phenyl]-oxazolidin-2-one (*S*)-**2** (1.99 g, 50%) as a white crystalline solid; mp 130–132 °C; R_F [diethyl ether] 0.71; $[\alpha]_D^{20} = +36.3$ (*c* 2.0, ethanol); ν_{max} (ethanol) cm^{-1} 2974 (NH) and 1750 (C=O); δ_H (400 MHz; $CDCl_3$) 8.13 (1H, s, NH), 7.27 (2H, br d, *J* 8.4, 2 × CH; Ar), 6.91 (2H, br d, *J* 8.4, 2 × CH; Ar), 4.91 (1H, dd, *J* 8.4 and 6.7, CHN), 4.67 (1H, t, *J* 8.4, CH_AH_BO), 4.01 (1H, dd, *J* 8.4 and 6.7, CH_AH_BO), 0.99 (9H, s, 3 × CH_3C; *t*-Bu) and 0.22 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 158.9 (C=O), 154.9 (*i*-CO; Ar), 133.8 (*i*-C; Ar), 127.5[2] and 120.1[2] (4 × CH; Ar), 71.5 (CH_2O), 54.7 (CHN), 25.6[3] (3 × CH_3C; *t*-Bu), 17.9 (CH_3C; *t*-Bu) and −4.5[2] (2 × CH_3Si) (Found MNa^+, 316.1342; $C_{15}H_{23}NO_3SiNa$ requires 316.1339); *m*/*z* 293 (10%, M^+), 236 (ArCH=NH^+) and 119 (100, $OC_6H_4CH{=}NH^+$).

4.10. 4-[4-(*tert*-Butyldimethylsilyloxy)phenyl]-oxazolidin-2-one (*R*)-2 and 4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*)-13

In the same way as for the oxazolidin-2-one *rac*-**2**, thionyl chloride (12.9 g, 7.9 mL, 0.108 mmol) and (*R*)-*N*-*tert*-butoxycarbonyl-(4-*tert*-butyldimethylsilyoxyphenyl)-glycinol (5.00 g, 13.6 mmol) gave the 4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*)-**13** (0.38 g, 16%) as a white powder; R_F [diethyl ether] 0.42; mp 201–204 °C; $[\alpha]_D^{20} = -39.4$ (*c* 0.7, EtOH) (Found MNH_4^+, 197.0919; $C_9H_{13}N_2O_3$ requires 197.0921) (Found M^+, 179.0574; $C_9H_9NO_3$ requires 179.0577). This compound was spectroscopically identical to its above (*S*)-enantiomer; and 4-[4-(*tert*-butyldimethylsilyloxy)-phenyl]-oxazolidin-2-one (*R*)-**2** (1.79 g, 45%) as a white crystalline solid; R_F [diethyl ether] 0.71; mp 130–132 °C; $[\alpha]_D^{20} = -34.8$ (*c* 1.7, ethanol); $[\alpha]_D^{20} = -37.2$ (*c* 1.28, DMSO) {lit.[3] $[\alpha]_D^{20} = -37.6$ (*c* 1.05, THF)} (Found M^+, 293.1445; $C_{15}H_{23}NO_3Si$ requires 293.1442); *m*/*z* 293 (10%, M^+), 236 (ArCH=NH^+) and 119 (100, $OC_6H_4CH{=}NH^+$). This compound was spectroscopically identical to its above (*S*)-enantiomer.

4.11. 4,5,5-Triphenyl-oxazolidin-2-one (*S*)-14

Available from Aldrich Chemical Limited and Onyx Scientific Limited; characterisation data: white powder; R_F [diethyl ether] 0.50; mp 232–234 °C; $[\alpha]_D^{20} = -213.3$ (*c* 0.5, EtOH); ν_{max} ($CHCl_3$) cm^{-1} 1763 (C=O); δ_H (400 MHz; $CDCl_3$) 7.62 (2H, dt, *J* 7.2 and 2.2, 2 × CH; Ph), 7.39–7.26 (3H, m, 3 × CH; Ph), 7.09–6.98 (5H, m, 5 × CH; Ph), 6.95 (5H, br s, 5 × CH; Ph), 5.54 (1H, s, CHN) and 5.53 (1H, br s, NH); δ_C (100 MHz; $CDCl_3$) 158.0 (C=O), 142.8, 138.8 and 137.1 (3 × *i*-C; 3 × Ph), 128.6[2], 128.5[1], 128.4[1], 128.3[2], 127.8[2], 127.5[2], 127.3[1], 126.5[2] and 126.2[2] (15 × CH; 3 × Ph), 90.7 (CPh_2O) and 65.8 (CHN) (Found MNH_4^+, 333.1598; $C_{21}H_{21}N_2O_2$ requires 333.1598); *m*/*z* 315 (5%, M^+), 256 (10, $PhCHCPh_2^+$), 183 (100, $Ph_2C{=}OH^+$), 105 (90, $PhCH{=}NH^+$) and 77 (80, Ph^+).

5. Mutual kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8

5.1. (2*RS*,4*SR*)-3-(2-Phenylpropionyl)-4-phenyl-oxazolidin-2-thione *rac*-*syn*-15

n-BuLi (0.37 mL, 2.5 M in hexane, 0.92 mmol) was added to a stirred solution of 4-phenyl-oxazolidin-2-thione *rac*-**11** (0.15 g, 0.84 mmol) in THF at −78 °C. After stirring for 1 h, a solution of pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.29 g, 0.92 mmol) in THF (1 mL) was added. The resulting mixture was stirred for 2 h at −78 °C. The reaction was quenched with water (10 mL). The organic layer was extracted with diethyl ether (2 × 10 mL), dried (over $MgSO_4$) and evaporated under reduced pressure to give a mixture of diastereoisomeric oxazolidin-2-ones **15** [ratio 98:2: *syn*-:*anti*-]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidin-2-thione (*RS*,*SR*)-*syn*-**15** (0.143 g, 55%) as a white solid;R_F [light petroleum ether (bp 40–60 °C)/diethyl ether: (1:1)] 0.67; mp 118–119 °C; ν_{max} ($CHCl_3$) cm^{-1} 1700 (C=S); δ_H (400 MHz; $CDCl_3$) 7.20–7.08 (6H, m, 6 × CH; Ph^A and Ph^B), 6.94 (2H, dt, *J* 6.9 and 1.8, 2 × CH; Ph^A), 6.88 (2H, dt, *J* 7.0 and 1.8, 2 × CH; Ph^B), 5.98 (1H, q, *J* 6.9, $PhCHCH_3$),

5.61 (1H, dd, *J* 9.2 and 6.1, CHN), 4.68 (1H, t, *J* 9.2, C*H*$_A$H$_B$O), 4.20 (1H, dd, *J* 9.2 and 6.1, CH$_A$*H*$_B$O) and 1.35 (3H, d, *J* 6.9, PhCHC*H*$_3$), δ_C (100 MHz; $CDCl_3$) 185.2 (C=S), 174.8 (C=O), 139.1 and 136.9 (2 × *i*-C; 2 × Ph), 128.8,[2] 128.7,[1] 128.5,[2] 128.3,[2] 127.1[1] and 126.4[2] (10 × CH; 2 × Ph), 73.6 (CH_2O), 62.6 (CHN), 43.9 (Ph*C*HCH$_3$) and 18.7 (PhCH*C*H$_3$) (Found MH$^+$, 312.1054; $C_{18}H_{17}NO_2S$ requires 312.1053).

5.2. (2*RS*,4*SR*)-3-(2-Phenylpropionyl)-4-(2,5-dihydrophenyl)-oxazolidin-2-one *rac-syn*-16

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.40 mL, 2.5 M in hexane, 0.99 mmol), oxazolidin-2-one *rac*-**12** (0.15 g, 0.90 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.31 g, 0.99 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones **16** [ratio 97:3: (*syn*-:*anti*-)]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidin-2-one (*RS*,*SR*)-*syn*-**16** (0.17 g, 63%) as a viscous colourless oil; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.68; ν_{max} ($CHCl_3$) cm^{-1} 1775 (C=O) and 1705 (C=O); δ_H (400 MHz; $CDCl_3$) 7.41–7.17 (5H, m, 5 × CH; Ph), 5.60 (1H, m, CH=), 5.50 (1H, m, CH=), 5.43 (1H, m, CH=), 5.10 (1H, q, *J* 7.0, PhC*H*CH$_3$), 4.89 (1H, dd, *J* 8.8 and 3.8, CHN), 4.39 (1H, t, *J* 8.8, C*H*$_A$H$_B$O), 3.96 (1H, dd, *J* 8.8 and 3.8, CH$_A$*H*$_B$O), 2.66–2.50 (2H, m, 2 × CH), 2.45–2.31 (1H, m, CH), 2.02–1.91 (1H, m, CH) and 1.43 (3H, d, *J* 7.0, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 153.1 (OC=O), 140.0 (*i*-C; Ph), 130.5 (R_2C=), 128.5,[2] 128.1[2] and 127.0[1] (5 × CH; Ph), 123.6, 122.9 and 122.8 (3 × CH=), 66.6 (CH_2O), 58.7 (CHN), 43.4 (Ph*C*HCH$_3$), 26.1 and 23.6 (2 × CH_2) and 18.6 (PhCH*C*H$_3$) (Found M$^+$, 295.1201; $C_{18}H_{19}NO_3$ requires 295.1201); (Found MNH_4^+, 315.1702; $C_{18}H_{23}N_2O_3$ requires 315.1703).

5.3. (2*RS*,4*SR*)-3-(2-Phenylpropionyl)-4-(4-hydroxyphenyl)-oxazolidin-2-one *rac-syn*-17

In the same way[10] as for oxazolidin-2-one **15**, *n*-butyl lithium (0.64 mL, 2.5 M in hexane, 1.61 mmol), oxazolidin-2-one *rac*-**13** (0.132 g, 0.73 mmol) [derived from pre-mixing an equimolar amount of (*R*)- and (*S*)-**13**] and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.25 g, 0.80 mmol) at −78 °C, then allowed to warm to rt for over 12 h, gave a mixture of two diastereoisomeric oxazolidin-2-ones **17** [ratio 96:4: *syn*-:*anti*-]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidin-2-one (*RS*,*SR*)-*syn*-**17** (0.107 g, 50%) as a colourless crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.12; mp 150–152 °C; ν_{max} (ethanol) cm^{-1} 1783 (C=O) and 1756 (C=O); δ_H (400 MHz; $CDCl_3$) 7.16–7.11 (3H, m, 3 × CH; Ph), 7.04–6.99 (2H, m, 2 × CH; Ph), 6.73 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 6.55 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 5.95 (1H, s, OH), 5.32 (1H, dd, *J* 9.0 and 5.0, CHN), 5.01 (1H, q, *J* 7.0, PhC*H*CH$_3$), 4.54 (1H, t, *J* 9.0, C*H*$_A$H$_B$O), 4.00 (1H, dd, *J* 9.0 and 5.0, CH$_A$*H*$_B$O) and 1.33 (3H, d, *J* 7.0, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 155.7 (*i*-CO; Ar), 153.1 (OC=O), 139.8 (*i*-C; Ph), 130.4 (*i*-C; Ar), 128.5[2], 128.1[2] and 127.1[1] (5 × CH; Ph), 127.5[2] and 115.6[2] (4 × CH; Ar), 69.7 (CH_2O), 57.4 (CHN), 43.9 (Ph*C*HCH$_3$) and 18.6 (PhCH*C*H$_3$) (Found MNH_4^+, 329.1493; $C_{18}H_{21}N_2O_4$ requires 329.1493); *m*/*z* 311 (20%, M$^+$), 132 (100, Ph(CH$_3$)C=C=O$^+$) and 105 (40, PhCHCH$_3^+$).

5.4. (2*RS*,4*SR*)-3-(2-Phenylpropionyl)-4-[4-(*tert*-butyldimethylsilyloxy)phenyl]-oxazolidin-2-one *rac-syn*-18

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.48 mL, 2.5 M in hexane, 1.21 mmol), oxazolidin-2-one *rac*-**2** (0.32 g, 1.10 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.38 g, 1.21 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones **18** [ratio >97:3: *syn*-:*anti*-]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidin-2-one (*RS*,*SR*)-*syn*-**18** (0.31 g, 67%) as a white crystalline solid; mp 120–121 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.51; ν_{max} ($CHCl_3$) cm^{-1} 1774 (C=O) and 1711 (C=O); δ_H (400 MHz; $CDCl_3$) 7.41–7.17 (5H, m, 5 × CH; Ph), 7.19 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 6.84 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 5.29 (1H, dd, *J* 8.6 and 3.1, CHN), 5.10 (1H, q, *J* 7.0, PhC*H*CH$_3$), 4.52 (1H, t, *J* 8.6, C*H*$_A$H$_B$O), 4.22 (1H, dd, *J* 8.6 and 3.1, CH$_A$*H*$_B$O), 1.41 (3H, d, *J* 7.0, PhCHC*H*$_3$), 0.98 (9H, s, 3 × CH_3C; *t*-Bu) and 0.20 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 174.5 (NC=O), 155.9 (*i*-C; Ar), 153.3 (OC=O), 140.2 (*i*-C; Ph), 131.9 (*i*-C; Ar), 128.6[2], 128.2[2] and 127.2[1] (5 × CH; Ph), 127.3[2] and 120.6[2] (4 × CH; Ar), 69.9 (CH_2O), 57.6 (CHN), 43.2 (Ph*C*HCH$_3$), 25.6[3] (3 × *C*H$_3$C; *t*-Bu), 19.4 (PhCH*C*H$_3$), 18.1 (CH$_3$*C*; *t*-Bu) and -4.4[2] (2 × CH_3Si); (Found MNa$^+$, 448.1912; $C_{24}H_{31}NO_4SiNa$ requires 448.1915); *m*/*z* 425 (15%, M$^+$), 132 (60, Ph(CH$_3$)C=C=O$^+$) and 105 (100, PhCHCH$_3^+$).

5.5. (2*RS*,4*SR*)-3-(2-Phenylpropionyl)-4,5,5-triphenyl-oxazolidin-2-one *rac-syn*-19

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.48 mL, 2.5 M in hexane, 1.21 mmol), oxazolidin-2-one *rac*-**14** (0.34 g, 1.10 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.38 g, 1.21 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones **19** [ratio 89:11: *syn*-:*anti*-]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidin-2-one (*RS*,*SR*)-*syn*-**19** (0.26 g, 53%) as a white powder; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.69; mp = 160–165 °C; ν_{max} ($CHCl_3$) cm^{-1} 1780 (C=O) and 1704 (C=O); δ_H (400 MHz; $CDCl_3$) 7.63 (2H, br d, *J* 7.7, 2 × CH; Ph), 7.46–7.36 (4H, m, 4 × CH; Ph), 7.19 (2H, dd, *J* 5.0, and 2.0, 2 × CH; Ph), 7.11–7.07 (2H, m, 2 × CH; Ph), 7.01–6.86 (8H, m, 8 × CH; Ph), 6.65 (2H, br d, *J* 7.7, 2 × CH; Ph), 6.25 (1H, s, CHN), 4.98 (1H, q, *J* 7.0, PhC*H*CH$_3$) and 1.35 (3H, d, *J* 7.0, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.2 (NC=O), 152.0 (OC=O), 141.8, 138.0 and 135.0 (3 × *i*-C; 3 × Ph-oxazolidin-2-one), 139.5 (*i*-C; Ph), 128.9[2], 128.8[1], 128.4[2], 128.3[2], 127.9[3], 127.6[2], 127.5[1], 127.4[2], 127.0[1], 126.2[2] and 126.1[2] (20 × CH; 4 × Ph), 88.5 (CPh_2O), 66.0 (CHN), 44.0 (Ph*C*HCH$_3$) and 19.0 (PhCH*C*H$_3$) (Found M$^+$, 447.1835; $C_{30}H_{25}NO_3$ requires 447.1829); *m*/*z* 447 (10%, M$^+$), 315 (5, M−Ph(CH$_3$)C=C=O$^+$), 256 (15, PhCHCPh$_2^+$), 183 (20, Ph$_2$C=OH$^+$), 105 (100, PhCH=NH$^+$) and 77 (20, Ph$^+$).

6. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8

6.1. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-thione (*R*)-11 and oxazolidin-2-one (*S*)-1

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.71 mL, 2.5 M in hexane, 1.78 mmol), 4-phenyl-oxazolidin-2-thione (*R*)-**11** (0.145 g, 0.81 mmol), 4-phenyl-oxazolidin-2-one (*S*)-**1** (0.130 g, 0.81 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.56 g, 1.78 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-thiones **15** [ratio 98:2: *syn*-:*anti*-] and two diastereoisomeric oxazolidin-2-ones **9** [ratio 96:4: *syn*-:*anti*-]. The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the

oxazolidin-2-thione (*S*,*R*)-*syn*-**15** (0.14 g, 55%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether: (1:1)] 0.67; mp 84–86 °C; $[\alpha]_D^{25} = -58.3$ (*c* 4.0, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1} 1707 (C=S) and 1702 (C=O); δ_H (400 MHz; $CDCl_3$) 7.20–7.08 (6H, m, 6 × CH; Ph^A and Ph^B), 6.94 (2H, dt, *J* 6.9 and 1.8, 2 × CH; Ph^A), 6.88 (2H, dt, *J* 7.0 and 1.8, 2 × CH; Ph^B), 5.98 (1H, q, *J* 6.9, PhC*H*CH_3), 5.61 (1H, dd, *J* 9.2 and 6.1, CHN), 4.68 (1H, t, *J* 9.2, CH_AH_BO), 4.20 (1H, dd, *J* 9.2 and 6.1, CH_AH_BO) and 1.35 (3H, d, *J* 6.9, PhCHCH_3), δ_C (100 MHz; $CDCl_3$) 185.2 (C=S), 174.8 (C=O), 139.1 and 136.9 (2 × *i*-C; 2 × Ph), 128.8,[2] 128.7,[1] 128.5,[2] 128.3,[2] 127.1[1] and 126.4[2] (10 × CH; 2 × Ph), 73.6 (CH_2O), 62.6 (CHN), 43.9 (PhCHCH_3) and 18.7 (PhCHCH_3) (Found MH^+, 312.1054; $C_{18}H_{17}NO_2S$ requires 312.1053); and the oxazolidin-2-one (*R*,*S*)-*syn*-**9** (0.14 g, 59%) as a white solid; mp 124–126 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.45; $[\alpha]_D^{23} = -91.9$ (*c* 4.9, $CHCl_3$) {for (*S*,*R*)-*syn*-**9**, lit.[19] $[\alpha]_D^{20} = +88.5$ (*c* 4.0, $CHCl_3$)}; ν_{max} ($CHCl_3$)/cm^{-1}1778 (C=O) and 1701 (C=O); δ_H (400 MHz; $CDCl_3$) 7.29–7.21 (10H, m, 10 × CH; 2 × Ph), 5.45 (1H, dd *J* 9.0 and 5.1, CHN), 5.09 (1H, q, *J* 6.9, PhC*H*CH_3), 4.63 (1H, t, *J* 9.0, CH_AH_BO), 4.08 (1H, dd, *J* 9.0 and 5.1, CH_AH_BO) and 1.39 (3H, d, *J* 6.9, PhCHCH_3); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 153.2 (C=O), 139.9 and 138.3 (2 × *i*-C; 2 × Ph), 128.9,[2] 128.5,[3] 128.2,[2] 127.1[1] and 125.9[2] (10 × CH; 2 × Ph), 69.6 (CH_2O), 57.9 (NCH), 43.9 (PhCHCH_3) and 18.6 (PhCHCH_3) (Found MH^+, 296.1286; $C_{18}H_{18}NO_3$ requires 296.1287).

6.2. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-14

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.54 mL, 2.5 M in hexane, 1.34 mmol), 4-phenyl-oxazolidin-2-one (*R*)-**1** (0.10 g, 0.61 mmol), 4,5,5-triphenyl-oxazolidin-2-one (*S*)-**14** (0.19 g, 0.62 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.42 g, 1.34 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**9** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**19** (ratio 98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the (2*S*,4*R*)-3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**9** (96 mg, 53%) as a white solid; mp 140–142 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.39; ν_{max} ($CHCl_3$) cm^{-1}1778 (C=O) and 1701 (C=O); $[\alpha]_D^{20} = +92.5$ (*c* 4.9, $CHCl_3$); {lit.[19] $[\alpha]_D^{20} = +88.5$ (*c* 4.0, $CHCl_3$)}; δ_H (400 MHz; $CDCl_3$) 7.29–7.21 (10H, m, 10 × CH; 2 × Ph), 5.45 (1H, dd *J* 9.0 and 5.1, CHN), 5.09 (1H, q, *J* 6.9, PhC*H*CH_3), 4.63 (1H, t, *J* 9.0, CH_AH_BO), 4.08 (1H, dd, *J* 9.0 and 5.1, CH_AH_BO) and 1.39 (3H, d, *J* 6.9, PhCHCH_3); δ_C (100 MHz; $CDCl_3$) 173.7 (NC=O), 153.2 (OC=O), 139.9 (*i*-C; Ph^A), 138.3 (*i*-C; Ph^B), 128.9,[2] 128.5,[3] 128.2,[2] 127.1[1] and 125.9[2] (10 × CH; 2 × Ph), 69.6 (CH_2O), 57.9 (CHN), 43.9 (PhCHCH_3) and 18.6 (PhCHCH_3) (Found MH^+, 296.1286; $C_{15}H_{18}NO_3^+$ requires 296.1287); and (2*R*,4*S*)-3-(2-phenylpropionyl)-4,5,5-triphenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**19** (0.14 g, 50%) as a white powder; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.69; mp 154–156 °C; $[\alpha]_D^{20} = -255.1$ (*c* 3.4, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1} 1780 (C=O) and 1704 (C=O); δ_H (400 MHz; $CDCl_3$) 7.63 (2H, br d, *J* 7.7, 2 × CH; Ph), 7.46–7.36 (4H, m, 4 × CH; Ph), 7.19 (2H, br dd, *J* 5.0, and 2.0, 2 × CH; Ph), 7.11–7.07 (2H, m, 2 × CH; Ph), 7.01–6.86 (8H, m, 8 × CH; Ph), 6.65 (2H, br d, *J* 7.7, 2 × CH; Ph), 6.25 (1H, s, CHN), 4.98 (1H, q, *J* 7.0, PhC*H*CH_3) and 1.35 (3H, d, *J* 7.0, PhCHCH_3); δ_C (100 MHz; $CDCl_3$) 173.2 (NC=O), 152.0 (OC=O), 141.8, 138.0 and 135.0 (3 × *i*-C; 3 × Ph-oxazolidin-2-one), 139.5 (*i*-C; Ph), 128.9[2], 128.8[1], 128.4[2], 128.3[2], 127.9[3], 127.6[2], 127.5[1], 127.4[2], 127.0[1], 126.2[2] and 126.1[2] (20 × CH; 4 × Ph), 88.5 (CPh_2O), 66.0 (CHN), 44.0 (PhCHCH_3) and 19.0 (PhCHCH_3) (Found MNa^+, 448.1912; $C_{24}H_{31}NO_4SiNa$ requires 448.1915); *m*/*z* 447 (10%, M^+), 315 (5, $M^+ - Ph(CH_3)C{=}C{=}O$), 256 (15, $PhCHCPh_2^+$), 183 (20, $Ph_2C{=}OH^+$), 105 (100, $PhCH{=}NH^+$) and 77 (20, Ph^+).

6.3. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-2 and oxazolidin-2-one (*S*)-14

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.36 mL, 2.5 M in hexane, 0.902 mmol), 4-4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*R*)-**2** (0.12 g, 0.41 mmol), 4,5,5-triphenyl-oxazolidin-2-one (*S*)-**14** (0.13 g, 0.41 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.28 g, 0.902 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**18** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**19** (ratio 95:5: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the (2*S*,4*R*)-3-(2-phenylpropionyl)-4-[4-(*tert*-butyldimethylsilyloxy)-phenyl]-oxazolidin-2-one (*S*,*R*)-*syn*-**18** (0.141 g, 81%) as a cream crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.51; mp 96–98°C; $[\alpha]_D^{20} = +89.1$ (*c* 4.2, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1} 1779 (NC=O) and 1706 (OC=O); δ_H (400 MHz; $CDCl_3$) 7.14–7.10 (3H, m, 3 × CH; Ph), 7.01–6.96 (2H, m, 2 × CH; Ph), 6.74 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar), 6.59 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar), 5.31 (1H, dd, *J* 9.0 and 5.0, CHN), 4.99 (1H, q, *J* 7.0, PhC*H*CH_3), 4.49 (1H, t, *J* 9.0, CH_AH_BO), 3.98 (1H, dd, *J* 9.0 and 5.0, CH_AH_BO), 1.30 (3H, d, *J* 7.0, PhCHCH_3), 0.89 (9H, s, 3 × CH_3C; *t*-Bu) and 0.10 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 173.5 (NC=O), 155.7 (*i*-CO; Ar), 153.0 (OC=O), 139.8 (*i*-C; Ph), 130.9 (*i*-C; Ar), 128.4[2], 128.0[2] and 126.9[1] (5 × CH; Ph), 127.2[2] and 120.2[2] (4 × CH; Ar), 69.6 (CH_2O), 57.2 (CHN), 43.7 (PhCHCH_3), 25.5[3] (3 × CH_3C; *t*-Bu), 18.5 (PhCHCH_3), 18.1 (CH_3C; *t*-Bu), −4.5 ($CH_3^ASiCH_3^B$) and −4.6 ($CH_3^ASiCH_3^B$) (Found MH^+, 426.2096; $C_{24}H_{32}NO_4Si$ requires 426.2095); *m*/*z* 425 (20%, M^+), 132 (70, $Ph(CH_3)C{=}C{=}O^+$) and 105 (100, $PhCHCH_3^+$); and (2*R*,4*S*)-3-(2-phenylpropionyl)-4,5,5-triphenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**19** (0.14 g, 73%); R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.69, which was spectroscopically identical to that reported previously.

6.4. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-13 and oxazolidin-2-one (*S*)-14

In the same way[10] as for oxazolidin-2-one **15**, *n*-butyl lithium (0.74 mL, 2.5 M in hexane, 1.85 mmol), 4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*)-**13** (0.10 g, 0.55 mmol), 4,5,5-triphenyl-oxazolidin-2-one (*S*)-**14** (0.175 g, 0.55 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.41 g, 1.28 mmol) at −78 °C, then allowed to warm to rt over 12 h, gave a mixture of two diastereoisomeric oxazolidin-2-one (*S*,*R*)-**17** (ratio >97:3: *syn*-:*anti*-) and oxazolidin-2-one (*R*,*S*)-**19** (ratio 92:8: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give the (2*S*,4*R*)-3-(2-phenylpropionyl)-4-(4-hydroxyphenyl)-oxazolidin-2-one (*S*,*R*)-*syn*-**17** (78 mg, 46%) as a colourless crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.12; mp 135–137 °C; $[\alpha]_D^{20} = +81.2$ (*c* 1.3, $CHCl_3$); $[\alpha]_D^{20} = +77.2$ (*c* 1.3, ethanol); ν_{max} (ethanol) cm^{-1} 1783 (NC=O) and 1756 (OC=O); δ_H (400 MHz; $CDCl_3$) 7.16–7.11 (3H, m, 3 × CH; Ph), 7.04–6.99 (2H, m, 2 × CH; Ph), 6.73 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 6.55 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 5.95 (1H, s, OH), 5.32 (1H, dd, *J* 9.0 and 5.0, CHN), 5.01 (1H, q, *J* 7.0, PhC*H*CH_3), 4.54 (1H, t, *J* 9.0, CH_AH_BO), 4.00 (1H, dd, *J* 9.0 and 5.0, CH_AH_BO) and 1.33 (3H, d, *J* 7.0, PhCHCH_3); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 155.7 (*i*-CO; Ar),

153.1 (OC=O), 139.8 (*i*-C; Ph), 130.4 (*i*-C; Ar), 128.5[2], 128.1[2] and 127.1[1] (5 × CH; Ph), 127.5[2] and 115.6[2] (4 × CH; Ar), 69.7 (CH_2O), 57.4 (CHN), 43.9 (PhCHCH$_3$) and 18.6 (PhCHCH$_3$) (Found MNH_4^+, 329.1493; $C_{18}H_{21}N_2O_2$ requires 329.1496); *m*/*z* 311 (20%, M^+), 132 (100, Ph(CH_3)C=C=O$^+$) and 105 (40, PhCHCH$_3^+$); and (2*R*,4*S*)-3-(2-phenylpropionyl)-4,5,5-triphenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**19** (0.142 g, 58%); R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.51, which was spectroscopically identical to that reported previously.

6.5. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.53 mL, 2.5 M in hexane, 1.34 mmol), 4 phenyl-oxazolidin-2-one (*R*)-**1** (0.10 g, 0.61 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*S*)-**2** (0.18 g, 0.61 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.42 g, 1.34 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**9** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**18** (ratio 98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-4-phenyl-3-(2-phenyl-propionyl)oxazolidin-2-one (*S*,*R*)-*syn*-**9** (0.12 g, 68%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.39, which was spectroscopically identical to that reported previously; and (2*R*,4*S*)-3-(2-phenylpropionyl)-4-[4-(*tert*-butyldimethylsilyloxy)phenyl]-oxazolidin-2-one (*R*,*S*)-*syn*-**18** (0.19 g, 68%) as a white crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.51; mp 96–98 °C; $[\alpha]_D^{20} = -95.2$ (*c* 2.0, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1} 1779 (NC=O) and 1706 (OC=O); δ_H (400 MHz; $CDCl_3$) 7.14–7.10 (3H, m, 3 × CH; Ph), 7.01–6.96 (2H, m, 2 × CH; Ph), 6.74 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar), 6.59 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar), 5.31 (1H, dd, *J* 9.0 and 5.0, CHN), 4.99 (1H, q, *J* 7.0, PhC*H*CH$_3$), 4.49 (1H, t, *J* 9.0, CH_AH$_B$O), 3.98 (1H, dd, *J* 9.0 and 5.0, CH$_A$*H*$_B$O), 1.30 (3H, d, *J* 7.0, PhCHC*H*$_3$), 0.89 (9H, s, 3 × CH_3C; *t*-Bu) and 0.10 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 173.5 (NC=O), 155.7 (*i*-C; Ar), 153.0 (OC=O), 139.8 (*i*-C; Ph), 130.9 (*i*-C; Ar), 128.4[2], 128.0[2] and 126.9[1] (5 × CH; Ph), 127.2[2] and 120.2[2] (4 × CH; Ar), 69.6 (CH_2O), 57.2 (CHN), 43.7 (PhCHCH$_3$), 25.5[3] (3 × *C*H$_3$C; *t*-Bu), 18.5 (PhCHC*H*$_3$), 18.1 (CH$_3$*C*; *t*-Bu), −4.5 (*C*H$_3^A$SiCH$_3^B$) and −4.6 (CH$_3^A$SiC*H*$_3^B$); (Found MNa^+, 448.1912; $C_{24}H_{31}NO_4SiNa$ requires 448.1915); *m*/*z* 425 (10%, M^+), 132 (60, Ph(CH_3)C=C=O$^+$) and 105 (100, PhCHCH$_3^+$).

6.6. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2 (involving a TBAF purification step)

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.53 mL, 2.5 M in hexane, 1.34 mmol), 4 phenyl-oxazolidin-2-one (*R*)-**1** (0.10 g, 0.61 mmol), 4-(*tert*-butyldimethylsilyloxy)-phenyl-oxazolidin-2-one (*S*)-**2** (0.18 g, 0.61 mmol), pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.42 g, 1.34 mmol), followed by the addition of TBAF (1.82 mL, 1 M in THF, 1.83 mmol) after 2 h, and stirring the resulting solution at rt for 2 h, gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**9** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**18** (ratio 98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-4-phenyl-3-(2-phenyl-propionyl)oxazolidin-2-one (*S*,*R*)-*syn*-**9** (0.10 g, 58%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.39, which was spectroscopically identical to that reported previously; and (2*R*,4*S*)-3-(2-phenylpropionyl)-4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*,*S*)-*syn*-**17** (0.10 g, 53%) as a white crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.12, which was spectroscopically identical to that reported previously.

6.7. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-13 and oxazolidin-2-one (*S*)-1

In the same way[10] as for oxazolidin-2-one **15**, *n*-butyl lithium (0.81 mL, 2.5 M in hexane, 2.02 mmol), 4-hydroxyphenyl-oxazolidin-2-one (*R*)-**13** (0.11 g, 0.61 mmol), 4-phenyl-oxazolidin-2-one (*S*)-**1** (0.10 g, 0.61 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.446 g, 1.41 mmol) at −78 °C, then allowed to warm to rt over 12 h, gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**17** (ratio 95:5: *syn*-:*anti*-) and (*R*,*S*)-**9** (ratio 93:7: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-(2-phenylpropionyl)-4-(4-hydroxyphenyl)-oxazolidin-2-one (*S*,*R*)-*syn*-**17** (0.106 g, 56%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.12, which was spectroscopically identical to that reported previously; and (2*R*,4*S*)-3-(2-phenyl-propionyl)-4-phenyl-oxazolidin-2-one (*R*,*S*)-*syn*-**9** (0.148 g, 82%) as a white solid; mp 124–126 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.39; $[\alpha]_D^{23} = -91.9$ (*c* 4.9, $CHCl_3$) {lit.[19] (*S*,*R*)-*syn*-**9**; $[\alpha]_D^{20} = +88.5$ (*c* 4.0, $CHCl_3$)}; ν_{max} ($CHCl_3$) cm^{-1}1778 (C=O) and 1701 (C=O); δ_H (400 MHz; $CDCl_3$) 7.29–7.21 (10H, m, 10 × CH; 2 × Ph), 5.45 (1H, dd *J* 9.0 and 5.1, CHN), 5.09 (1H, q, *J* 6.9, PhC*H*CH$_3$), 4.63 (1H, t, *J* 9.0, CH_AH$_B$O), 4.08 (1H, dd, *J* 9.0 and 5.1, CH$_A$*H*$_B$O) and 1.39 (3H, d, *J* 6.9, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.7 (C=O), 153.2 (C=O), 139.9 and 138.3 (2 × *i*-C; 2 × Ph), 128.9,[2] 128.5,[3] 128.2,[2] 127.1[1] and 125.9[2] (10 × CH; 2 × Ph), 69.6 (CH_2O), 57.9 (CHN), 43.9 (PhCHCH$_3$) and 18.6 (PhCHCH$_3$) (Found MH^+, 296.1286; $C_{18}H_{18}NO_3$ requires 296.1287).

6.8. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-8 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-2 and oxazolidin-2-one (*S*)-13

In the same way[10] as for oxazolidin-2-one **15**, *n*-butyl lithium (0.45 mL, 2.5 M in hexane, 1.12 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*R*)-**2** (0.10 g, 0.34 mmol), 4-hydroxyphenyl-oxazolidin-2-one (*S*)-**13** (61 mg, 0.34 mmol) and pentafluorophenyl 2-phenylpropionate *rac*-**8** (0.23 g, 0.78 mmol) at −78 °C, then allowed to warm to rt over 12 h, gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**18** (ratio 98:2: *syn*-:*anti*-) and (*R*,*S*)-**17** (ratio 98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-(2-phenylpropionyl)-4-[4-(*tert*-butyldimethylsilyloxy)-phenyl]-oxazolidin-2-one (*S*,*R*)-*syn*-**18** (88 mg, 61%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.51, which was spectroscopically identical to that reported previously; and (2*R*,4*S*)-3-(2-phenylpropionyl)-4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*,*S*)-*syn*-**17** (51 mg, 49%) as a colourless crystalline solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.12; mp 135–137 °C; $[\alpha]_D^{20} = -78.6$ (*c* 2.5, $CHCl_3$); {(*S*,*R*)-**17**; $[\alpha]_D^{20} = +81.2$ (*c* 1.3, $CHCl_3$)}; ν_{max} (ethanol) cm^{-1} 1783 (C=O) and 1756 (C=O); δ_H (400 MHz; $CDCl_3$) 7.16–7.11 (3H, m, 3 × CH; Ph), 7.04–6.99 (2H, m, 2 × CH; Ph), 6.73 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 6.55 (2H, dt, *J* 8.6 and 2.4, 2 × CH; Ar), 5.95 (1H, br s, OH), 5.32 (1H, dd, *J* 9.0 and 5.0, CHN), 5.01 (1H, q, *J* 7.0, PhC*H*CH$_3$), 4.54 (1H, t, *J* 9.0, CH_AH$_B$O), 4.00 (1H, dd, *J* 9.0 and 5.0, CH$_A$*H*$_B$O) and 1.33 (3H, d, *J* 7.0, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 155.7 (*i*-CO; Ar), 153.1 (OC=O), 139.8 (*i*-C; Ph),

130.4 (*i*-C; Ar), 128.5[2], 128.1[2] and 127.1[1] (5 × CH; Ph), 127.5[2] and 115.6[2] (4 × CH; Ar), 69.7 (CH_2O), 57.4 (CHN), 43.9 (PhCHCH$_3$) and 18.6 (PhCHCH_3) (Found MNH_4^+, 329.1493; $C_{18}H_{21}N_2O_2$ requires 329.1493).

7. Parallel kinetic resolution of active esters *rac*-20–23 using a *quasi*-enantiomeric combination of oxazolidin-2-ones (*R*)-1 and (*S*)-2

7.1. Parallel kinetic resolution of pentafluorophenyl 2-phenylbutanoate *rac*-20 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.59 mL, 2.5 M in hexane, 1.496 mmol), 4-phenyl-oxazolidin-2-one (*R*)-**1** (0.11 g, 0.68 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*S*)-**2** (0.20 g, 0.68 mmol) and pentafluorophenyl 2-phenylbutanoate *rac*-**20** (0.49 g, 1.49 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**24** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**28** (ratio >98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-(2-phenylbutanoyl)-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**24** (0.15 g, 71%) as a white solid; mp 82–84 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.40; $[\alpha]_D^{20} = +77.4$ (*c* 4.0, $CHCl_3$); ν_{max} (CH_2Cl_2) cm^{-1} 1772 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.17–7.09 (6H, m, 6 × CH; Ph), 7.04–7.02 (2H, m, 2 × CH; Ph), 6.81–6.79 (2H, m, 2 × CH; Ph), 5.38 (1H, dd, *J* 8.8 and 5.0, CHN), 4.82 (1H, t, *J* 7.5, PhC*H*Et), 4.55 (1H, t, *J* 8.8, CH_AH_BO), 3.98 (1H, dd, *J* 8.8 and 5.0, CH$_A$*H*$_B$O), 2.01–1.90 (1H, ddq, *J* 13.5, 7.3 and 7.5, CH_AH_BCH$_3$), 1.68–1.57 (1H, ddq, *J* 13.5, 7.3 and 7.5, CH$_A$*H*$_B$CH$_3$) and 0.84 (3H, t, *J* 7.5, C*H*$_3$CH$_2$); δ_C (100 MHz; $CDCl_3$) 173.0 (NC=O), 153.1 (OC=O), 138.2 (*i*-C; Ph^A), 138.0 (*i*-CC; Ph^B), 128.8[2], 128.7[2], 128.4[1], 128.3[2], 127.1[1] and 125.6[2] (10 × CH; Ph^A and Ph^B), 69.4 (CH_2O), 57.7 (CHN), 51.1 (PhCH), 26.2 (*C*H$_2$CH$_3$) and 11.9 (CH$_2$*C*H$_3$) (Found MH^+, 310.1437; $C_{19}H_{20}NO_3$ requires 310.1443); and (2*R*,3*S*)-3-(2-phenylbutanoyl)-4-[4-(*tert*-butyldimethylsilanyloxy)phenyl]-oxazolidin-2-one (*R*,*S*)-*syn*-**28** (0.18 g, 62%) as a colourless oil; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.69; $[\alpha]_D^{20} = -89.4$ (*c* 4.4, $CHCl_3$); ν_{max} (CH_2Cl_2) cm^{-1} 1778 (C=O) and 1709 (C=O); δ_H (400 MHz; $CDCl_3$) 7.19–7.15 (3H, m, 3 × CH; Ph), 7.07–7.04 (2H, m, 2 × CH; Ph), 6.75 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar), 6.61 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar), 5.37 (1H, dd, *J* 8.9 and 5.0, CHN), 4.84 (1H, t, *J* 7.5, PhCH), 4.56 (1H, t, *J* 8.9, CH_AH_BO), 4.03 (1H, dd, *J* 8.9 and 5.0, CH$_A$*H*$_B$O), 2.00 (1H, dquint, *J* 13.8 and 7.3, CH_AH_BCH$_3$), 1.66 (1H, dquint, *J* 13.8 and 7.3, CH$_A$C*H*$_B$CH$_3$), 0.94 (9H, s, 3 × CH$_3$; *t*-Bu), 0.83 (3H, t, *J* 7.3, C*H*$_3$CH$_2$), 0.15 (6H, s, 2 × SiCH$_3$); δ_C (100 MHz; $CDCl_3$) 173.0 (NC=O), 155.7 (OC=O), 153.1 (*i*-CO; Ar), 138.1 (*i*-C; Ph) 130.9 (*i*-C; Ar), 128.6,[2] 128.3,[2] 127.1,[2] 127.0[1] and 120.2[2] (9 × CH; Phand Ar), 69.6 (CH_2O), 57.3 (CHN), 51.1 (PhCH), 26.2 (*C*H$_2$CH$_3$), 25.6[3] (3 × CH$_3$; *t*-Bu), 18.1 (CH$_3$*C*; *t*-Bu), 11.9 (CH$_2$*C*H$_3$) and −4.5[2] (2 × SiCH$_3$) (Found MNH_4^+, 447.2218; $C_{25}H_{37}N_2O_4Si$ requires 447.2217).

7.2. Parallel kinetic resolution of pentafluorophenyl 2-(4-methylphenyl)propionate *rac*-21 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.59 mL, 2.5 M in hexane, 1.496 mmol), 4-phenyl-oxazolidin-2-one (*R*)-**1** (0.11 g, 0.68 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*S*)-**2** (0.20 g, 0.68 mmol) and pentafluorophenyl 2-(4-methylphenyl)propionate *rac*-**21** (0.49 g, 1.496 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**25** (ratio 97:3: *syn*-:*anti*-) and (*R*,*S*)-**29** (ratio 97:3: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-[(4-methylphenyl)propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**25** (0.14 g, 69%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.39; mp 105–110 °C {for (*R*,*S*)-*syn*-**25**; mp 105–110 °C}; ν_{max} ($CHCl_3$) cm^{-1} 1780 (C=O) and 1700 (C=O); $[\alpha]_D^{20} = +121.6$ (*c* 0.6, $CHCl_3$) {for (*R*,*S*)-*syn*-**25**; $[\alpha]_D^{20} = -116.5$ (*c* 0.8, $CHCl_3$)}; δ_H (400 MHz, $CDCl_3$) 7.21–7.12 (3H, m, 3 × CH; Ph), 6.96 (2H, br d, *J* 8.2, 2 × CH; Ar), 6.90 (2H, br d, *J* 8.2, 2 × CH; Ar), 6.86 (2H, d, *J* 6.9, 2 × CH; Ph), 5.36 (1H, dd, *J* 9.1 and 5.1, CHN), 5.01 (1H, q, *J* 6.9, ArC*H*CH$_3$), 4.54 (1H, t, *J* 9.1, CH_AH_BO), 3.99 (1H, dd, *J* 9.1 and 5.1, CH$_A$*H*$_B$O), 2.24 (3H, s, CH$_3$; Ar) and 1.32 (3H, d, *J* 6.9, ArCHC*H*$_3$); δ_C (100 MHz, $CDCl_3$) 173.5 (NC=O), 154.9 (OC=O), 138.4 (*i*-CMe; Ar), 136.8 (*i*-C; Ar), 136.4 (*i*-C; Ph), 129.1[2], 128.6[2], 128.4[1], 127.6[2] and 125.7[2] (9 × CH; Ph and Ar), 69.6 (CH_2O), 57.8 (CHN), 43.2 (ArC*H*CH$_3$), 21.0 (CH$_3$; Ar) and 18.7 (ArCH*C*H$_3$) (Found MNH_4^+, 327.1701; $C_{19}H_{23}N_2O_3^+$ requires 327.1709); and (2*R*,4*S*)-3-[2-(4-methylphenyl)propionyl]-4-[4-(*tert*-butyldimethylsiloxyloxy)phenyl]-oxazolidin-2-one (*R*,*S*)-*syn*-**29** (0.21 g, 72%) as a colourless oil; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.62; $[\alpha]_D^{20} = -120.3$ (*c* 6.0, $CHCl_3$); ν_{max} (CH_2Cl_2) cm^{-1} 1773 (C=O) and 1704 (C=O); δ_H (400 MHz; $CDCl_3$) 6.98 (2H, br d, *J* 8.0, 2 × CH; Ar^A), 6.91 (2H, dt, *J* 8.0 and 1.8, 2 × CH; Ar^A), 6.79 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar^B), 6.63 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar^B), 5.35 (1H, dd, *J* 8.9 and 4.9, CHN), 4.99 (1H, q, *J* 6.9, ArC*H*CH$_3$), 4.56 (1H, t, *J* 8.9, CH_AH_BO), 4.05 (1H, dd, *J* 8.9 and 4.9, CH$_A$*H*$_B$O), 2.27 (3H, s, CH$_3$; Ar^A), 1.33 (3H, d, *J* 6.9, ArCHC*H*$_3$), 0.94 (9H, s, 3 × CH$_3$; *t*-Bu) and 0.15 (6H, s, 2 × SiCH$_3$); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 155.8 (OC=O), 153.1 (*i*-CO; Ar^B), 136.9, 136.6 and 130.9 (3 × *i*-C; Ar^A and Ar^B), 129.1, 128.0, 127.4 and 120.2 (4 × CH; Ar^{A}and Ar^B), 69.7 (CH_2O), 57.3 (CHN), 43.4 (ArCHCH$_3$), 25.6[3] (3 × CH$_3$; *t*-Bu), 21.0 (CH$_3$; Ar^A), 18.7 (ArCHCH$_3$), 18.2 (CH$_3$*C*; *t*-Bu) and −4.5[2] (2 × SiCH$_3$) (Found MNH_4^+, 457.2513; $C_{25}H_{37}N_2O_4Si$ requires 457.2517).

7.3. Parallel kinetic resolution of pentafluorophenyl 2-(4-chlorophenyl)propionate *rac*-22 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.59 mL, 2.5 M in hexane, 1.496 mmol), 4-phenyl-oxazolidin-2-one (*R*)-**1** (0.11 g, 0.68 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*S*)-**2** (0.20 g, 0.68 mmol) and pentafluorophenyl 2-(4-chlorophenyl)propionate *rac*-**22** (0.52 g, 1.496 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**26** (ratio 97:3: *syn*-:*anti*-) and (*R*,*S*)-**30** (ratio 97:3: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-[(4-chlorophenyl)propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**26** (0.11 g, 50%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.27; mp 142–145 °C {for (*R*,*S*)-*syn*-**26**; mp 142–144 °C}; ν_{max} ($CHCl_3$) cm^{-1} 1782 (C=O) and 1700 (C=O); $[\alpha]_D^{20} = +144.4$ (*c* 1.6, $CHCl_3$) {for (*R*,*S*)-*syn*-**26**; $[\alpha]_D^{20} = -142.4$ (*c* 1.5, $CHCl_3$)}; δ_H (400 MHz, $CDCl_3$) 7.32–7.22 (3H, m, 3 × CH; Ph), 7.18 (2H, dt, *J* 8.5 and 2.2, 2 × CH; Ar), 7.01 (2H, dt, *J* 8.5 and 2.2, 2 × CH; Ar), 6.95 (2H, dt, *J* 6.8 and 1.5, 2 × CH; Ph), 5.45 (1H, dd, *J* 9.0 and 4.8, CHN), 5.06 (1H, q, *J* 6.8, ArC*H*CH$_3$), 4.65 (1H, t, *J* 9.0, CH_AH_BO), 4.13 (1H, dd, *J* 9.0 and 4.8, CH$_A$*H*$_B$O) and 1.37 (3H, d, *J* 6.8, ArCHC*H*$_3$); δ_C (100 MHz, $CDCl_3$) 173.8 (NC=O), 152.8 (OC=O), 138.2 (*i*-CC; Ar), 133.2 (*i*-C; Ar), 132.8 (*i*-CCl; Ar), 129.7[2], 128.8[2], 128.6[3] and 125.6[2] (9 × CH; 2 × Ar), 69.4 (CH_2O), 57.9 (CHN), 43.8

(ArCHCH$_3$) and 18.9 (ArCHCH$_3$) (Found M(^{35}Cl)$^+$ 329.0815; $C_{18}H_{16}ClNO_3^+$ requires 329.0813); and (2*R*,4*S*)-3-[(4-chlorophenyl)propionyl]-4-[4-(*tert*-butyldimethylsilyloxy)phenyl]-oxazolidin-2-one (*R*,*S*)-*syn*-**30** (0.16 g, 53%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.44; mp 103–107 °C; $[\alpha]_D^{20} = -130.8$ (*c* 4.2, $CHCl_3$); ν_{max} (CH_2Cl_2) cm^{-1} 1781 (C=O) and 1712 (C=O); δ_H (400 MHz; $CDCl_3$) 7.13 (2H, dt, *J* 8.6 and 2.5, 2 × CH; Ar^A), 6.95 (2H, dt, *J* 8.6 and 2.5, 2 × CH; Ar^A), 6.80 (2H, dt, *J* 8.6 and 2.9, 2 × CH; Ar^B), 6.65 (2H, dt, *J* 8.6 and 2.9, 2 × CH; Ar^B), 5.35 (1H, dd, *J* 9.0 and 4.8, CHN), 5.00 (1H, q, *J* 6.9, ArC*H*CH$_3$), 4.57 (1H, t, *J* 9.0, C*H*$_A$H$_B$O), 4.07 (1H, dd, *J* 9.0 and 4.8, CH$_A$*H*$_B$O), 1.32 (3H, d, *J* 6.9, ArCHC*H*$_3$), 0.94 (9H, s, 3 × CH$_3$; *t*-Bu) and 0.15 (6H, s, 2 × SiCH$_3$); δ_C (100 MHz; $CDCl_3$) 173.2 (NC=O), 155.9 (OC=O), 153.0 (*i*-CO; Ar^B), 138.4 (*i*-CCl; Ar), 132.9 and 130.8 (2 × *i*-C; Ar^A and Ar^B), 129.5, 128.6, 127.3 and 120.4 (4 × CH; Ar^A and Ar^B), 69.7 (CH_2O), 57.3 (CHN), 43.2 (ArCHCH$_3$), 25.6[3] (3 × CH$_3$; *t*-Bu), 18.5 (ArCHCH$_3$), 18.2 (CH$_3$C; *t*-Bu) and −4.6[2] (2 × SiCH$_3$) (Found M(^{35}Cl)$^+$, 459.1620; $C_{24}H_{30}ClNO_4Si$ requires 459.1620).

7.4. Parallel kinetic resolution of pentafluorophenyl 2-(4-isobutylphenyl)propionate *rac*-23 using a *quasi*-enantiomeric combination of oxazolidin-2-one (*R*)-1 and oxazolidin-2-one (*S*)-2

In the same way as for oxazolidin-2-one **15**, *n*-butyl lithium (0.59 mL, 2.5 M in hexane, 1.496 mmol), 4-phenyl-oxazolidin-2-one (*R*)-**1** (0.11 g, 0.68 mmol), 4-(*tert*-butyldimethylsilyloxy)phenyl-oxazolidin-2-one (*S*)-**2** (0.20 g, 0.68 mmol) and pentafluorophenyl 2-(4-isobutylphenyl)propionate *rac*-**23** (0.56 g, 1.496 mmol) gave a mixture of two diastereoisomeric oxazolidin-2-ones (*S*,*R*)-**27** (ratio >98:2: *syn*-:*anti*-) and (*R*,*S*)-**31** (ratio >98:2: *syn*-:*anti*-). The crude residue was purified by flash chromatography on silica gel eluting with light petroleum ether (bp 40–60 °C)/diethyl ether (7:3) to give (2*S*,4*R*)-3-[(4-isobutylphenyl)propionyl]-4-phenyl-oxazolidin-2-one (*S*,*R*)-*syn*-**27** (0.167 g, 70%) as a white solid; mp 86–88 °C; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.41; $[\alpha]_D^{25} = +118.7$ (*c* 6.0, $CHCl_3$) {for (*R*,*S*)-*syn*-**27**; lit.[18] $[\alpha]_D^{25} = -114.6$ (*c* 4.2, $CHCl_3$); ν_{max} ($CHCl_3$) cm^{-1}1779 (C=O) and 1705 (C=O); δ_H (400 MHz; $CDCl_3$) 7.28–7.15 (3H, m, 3 × CH; Ph), 7.00 (4H, m, 4 × CH, Ph and Ar), 6.90 (2H, dt, *J* 7.9 and 1.9, 2 × CH; Ar), 5.44 (1H, dd *J* 9.2 and 5.2, CHN), 5.09 (1H, q, *J* 6.9, ArC*H*CH$_3$), 4.63 (1H, t, *J* 9.0, C*H*$_A$H$_B$O), 4.06 (1H, dd, *J* 9.0 and 5.2, CH$_A$*H*$_B$O), 2.43 (2H, d, *J* 7.4, CH_2Ar), 1.89–1.79 (1H, nonet, *J* 6.8, (CH$_3$)$_2$C*H*), 1.38 (3H, d, *J* 6.9, ArCHC*H*$_3$), 0.90 (3H, d, *J* 6.6, C*H*$_3^A$CHCH$_3^B$) and 0.89 (3H, d, *J* 6.6, CH$_3^A$CHC*H*$_3^B$); δ_C (100.6 MHz; $CDCl_3$) 174.3 (NC=O), 153.3 (OC=O), 140.7 (*i*-C; Ar), 139.4 (*i*-C; Ar), 137.4 (*i*-C; Ph), 129.3[2] and 127.9[2] (4 × CH; Ar), 128.8,[2] 128.5[1] and 125.8[2] (5 × CH; Ph), 69.7 (CH_2O), 58.1 (CHN), 45.1 (*C*H(CH$_3$)$_2$), 42.7 (ArCHCH$_3$), 30.2 (*C*H$_2$Ar), 22.4[2] ((CH$_3$)$_2$CH) and 19.4 (*C*H$_3$CH$_2$) (Found MH$^+$, 352.1909; $C_{22}H_{26}NO_3$ requires 352.1907); *m*/*z* 351.1 (10% M$^+$), 188.1 (10, Ar(CH$_3$)C=C=O$^+$), 161.1 (10, Ar$^+$CHCH$_3$), 145.1 (100, ArCH$_2^+$) and 77.1 (10, Ph$^+$) (Found MNH_4^+, 369.2171; $C_{22}H_{29}N_2O_3$ requires 369.2173); and (2*R*,4*S*)-3-[(4-isobutylphenyl)propionyl]-4-[4-(*tert*-butyldimethylsilyloxy)-phenyl]-oxazolidin-2-one (*R*,*S*)-*syn*-**31** (0.23 g, 72%) as a white solid; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:1)] 0.65; mp 68–70 °C; $[\alpha]_D^{20} = -129.6$ (*c* 3.4, $CHCl_3$); ν_{max} (CH_2Cl_2) cm^{-1} 1780 (C=O) and 1707 (C=O); δ_H (400 MHz; $CDCl_3$) 6.96 (4H, br s, 4 × CH; Ar^A), 6.74 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar^B), 6.61 (2H, dt, *J* 8.4 and 2.4, 2 × CH; Ar^B), 5.37 (1H, dd, *J* 8.8 and 5.1, CHN), 5.05 (1H, q, *J* 6.9, ArC*H*CH$_3$), 4.56 (1H, t, *J* 8.8, C*H*$_A$H$_B$O), 4.03 (1H, dd, *J* 8.8 and 5.1, CH$_A$*H*$_B$O), 2.40 (2H, d, *J* 6.8, CH_2Ar), 1.82 (1H, nonet, *J* 6.8, (CH$_3$)$_2$C*H*), 1.35 (3H, d, *J* 7.1, ArCHC*H*$_3$), 0.95 (9H, s, 3 × CH$_3$; *t*-Bu), 0.87 (3H, d, *J* 6.8, C*H*$_3^A$CHCH$_3^B$), 0.86 (3H, d, *J* 6.8, CH$_3^A$CHC*H*$_3^B$) and 0.15 (6H, s, 2 × SiCH$_3$); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O), 155.7 (OC=O), 153.1 (*i*-CO; Ar), 140.4, 136.9 and 130.9 (3 × *i*-C; Ar^A and Ar^B), 129.1, 127.8, 127.2 and 120.2 (4 × CH; Ar$_A$and Ar$_B$), 69.6 (CH_2O), 57.2 (CHN), 45.0 (CH_2Ar), 43.3 (ArCHCH$_3$), 30.2 ((CH$_3$)$_2$CH), 25.6[3] (3 × CH$_3$; *t*-Bu), 22.4 and 22.3 (2 × CH$_3$; *i*-Bu), 18.4 (ArCHCH$_3$), 18.1 (CH$_3$C; *t*-Bu) and −4.5[2] (2 × SiCH$_3$) (Found MNH_4^+, 499.2980; $C_{28}H_{43}N_2O_4Si$ requires 499.2987).

7.5. (+)-2-Phenylpropionic acid (*S*)-32 hydrolysis of oxazolidin-2-one adduct (*S*,*R*)-*syn*-9

Lithium hydroxide monohydrate (71 mg, 1.71 mmol) was slowly added to a stirred solution of oxazolidin-2-one (*R*,*S*)-*syn*-**9** (0.15 g, 0.57 mmol) and hydrogen peroxide (58 mg, 0.48 mL, 1.71 mmol, 40%/w) in THF/water (3:1; 4 mL). The reaction mixture was stirred at room temperature for 12 h. The reaction was quenched with water (10 mL) and extracted with dichloromethane (3 × 10 mL). The combined organic layers were dried over $MgSO_4$ and evaporated under reduced pressure to give the recovered oxazolidin-2-one (*R*)-**1** (80 mg, 87%) as a white solid; $[\alpha]_D^{20} = -48.3$ (*c* 2.0, $CHCl_3$), {for (*S*)-; lit.[17] $[\alpha]_D^{20} = +49.5$ (*c* 2.1, $CHCl_3$)}; and 2-phenylpropionic acid (+)-(*S*)-**32** (78 mg, 92%) as colourless oil; R_F [light petroleum ether (bp 40–60 °C)/diethyl ether (1:9)] 0.5; $[\alpha]_D^{20} = +71.7$ (*c* 1.0, $CHCl_3$), {lit.[17] $[\alpha]_D^{22} = +71.2$ (*c* 0.66, $CHCl_3$)}; ν_{max} ($CHCl_3$) cm^{-1} 1706 (C=O); δ_H (400 MHz; $CDCl_3$) 7.45–6.98 (5H, m, 5 × CH; Ph), 3.75 (1H, q, *J* 7.2, PhC*H*CH$_3$) and 1.5 (3H, d, *J* 7.2, PhCHC*H*$_3$); δ_C (100 MHz; $CDCl_3$) 180.4 (C=O), 139.7 (*i*-C; Ph), 128.7,[2] 127.6[2] and 127.4[1] (5 × CH; Ph), 45.3 (PhC*H*CH$_3$) and 18.1 (PhCHC*H*$_3$) (Found MH$^+$ 151.0753. $C_9H_{11}NO_2^+$ requires 151.0759).

7.6. Hydrolysis of oxazolidin-2-one adduct (*R*,*S*)-*syn*-17

In the same way as above, lithium hydroxide monohydrate (60 mg, 1.43 mmol), hydrogen peroxide (48 mg, 0.40 mL, 1.43 mmol, 40%/w) and oxazolidin-2-one (*R*,*S*)-*syn*-**17** (0.11 g, 0.36 mmol) in THF/water (3:1; 4 mL) gave after an acidic extraction, 2-phenylpropionic acid (−)-(*R*)-**32** (48 mg, 90%) as a colourless oil; $[\alpha]_D^{20} = -69.5$ (*c* 1.0, $CHCl_3$) {lit.[19] $[\alpha]_D^{22} = -71.2$ (*c* 0.66, $CHCl_3$)}, which was spectroscopically identical to that reported previously.

7.7. Hydrolysis of oxazolidin-2-one adduct (*R*,*S*)-*syn*-18

In the same way as above, lithium hydroxide monohydrate (53 mg, 1.24 mmol), hydrogen peroxide (42 mg, 0.35 mL, 1.24 mmol, 40%/w) and oxazolidin-2-one (*R*,*S*)-*syn*-**18** (0.132 g, 0.31 mmol) in THF/water (3:1; 4 mL) gave after an acidic extraction, 2-phenylpropionic acid (−)-(*R*)-**32** (41 mg, 90%) as a colourless oil; $[\alpha]_D^{20} = -71.4$ (*c* 0.7, $CHCl_3$) {lit.[19] $[\alpha]_D^{22} = -71.2$ (*c* 0.66, $CHCl_3$)}, which was spectroscopically identical to that reported previously.

7.8. Hydrolysis of oxazolidin-2-one adduct (*R*,*S*)-*syn*-19

In the same way as above, lithium hydroxide monohydrate (13 mg, 0.30 mmol), hydrogen peroxide (10 mg, 80 μL, 0.30 mmol, 40%/w) and oxazolidin-2-one (*R*,*S*)-*syn*-**19** (67 mg, 0.15 mmol) in THF/water (3:1; 4 mL) gave after an acidic extraction, (−)-2-phenylpropionic acid (*R*)-**32** (13 mg, 58%) as a colourless oil; $[\alpha]_D^{20} = -71.8$ (*c* 2.0, $CHCl_3$) {lit.[19] $[\alpha]_D^{22} = -71.2$ (*c* 0.66, $CHCl_3$)}, which was spectroscopically identical to that reported previously.

For the hydrolysis of oxazolidin-2-one adduct (*S*,*R*)-*syn*-**24** see Ref. 19.

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12. These levels of diastereocontrol correspond to an approximate selectivity factor, *s*, ranging from 11.5 (84% de) to 49 (96 de).
13. The addition of two (*R*)-enantiomeric lithiated oxazolidin-2-ones (1 equiv each) to pentafluorophenyl 2-(4-isobutylphenyl)propionate (*S*)-**23** (1 equiv) in THF and stirring the resulting solution at −78 °C for 2 h, gave the corresponding (*S*,*R*)-*syn*-adducts which qualitatively revealed their relative rates of addition (assuming they have similar basicity). For oxazolidin-2-one combinations; (*R*)-**1**:(*R*)-**14**, (*R*)-**2**:(*R*)-**14**, (*R*)-**1**:(*R*)-**2**, (*R*)-**1**:(*R*)-**13**, (*R*)-**14**:(*R*)-**13**, and (*R*)-**2**:(*R*)-**13**, gave their corresponding (*S*,*R*)-*syn*-adducts in a relative proportion of 70:30, 70:30, 52:48, 100:0, 100:0 and 100:0, respectively.
14. The levels of diastereoselection were found to be dependent on the structural nature of the complementary oxazolidin-2-one. For example, for a sterically demanding oxazolidin-2-one, like (*S*)-**14**, the levels of diastereocontrol were higher for the parallel kinetic resolution of (*rac*)-**8** using a complementary oxazolidin-2-one, such as either (*R*)-**1**, (*R*)-**2** or (*R*)-**13**, than its corresponding mutual kinetic resolution [in the presence of (*R*)-**14**]. For additional information, see: Coulbeck, E.; Eames, J. Unpublished results.
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