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Synthesis, characterisation and application of enantiomeric isotopomers of Evans' oxazolidinones

Ewan Boyd,[a] Sameer Chavda,[b] Elliot Coulbeck,[b] Gregory S. Coumbarides,[c] Marco Dingjan,[b] Jason Eames,[b,*] Anthony Flinn,[d] Aarti K. Krishnamurthy,[b] Mariam Namutebi,[c] Julian Northen[d] and Yonas Yohannes[c]

[a]*Syngenta, Grangemouth Manufacturing Centre, Earls Road, Grangemouth, Scotland FX3 8XG, UK*
[b]*Department of Chemistry, University of Hull, Cottingham Road, Kingston upon Hull HU6 7RX, UK*
[c]*Department of Chemistry, Queen Mary, University of London, Mile End Road, London E1 4NS, UK*
[d]*Onyx Scientific Limited, Units 97-98, Silverbriar, Sunderland Enterprise Park East, Sunderland SR5 2TQ, UK*

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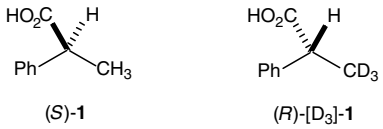
Abstract—The synthesis of a series of enantiomerically pure deuterium-labelled isotopomeric Evans' oxazolidinones is discussed.

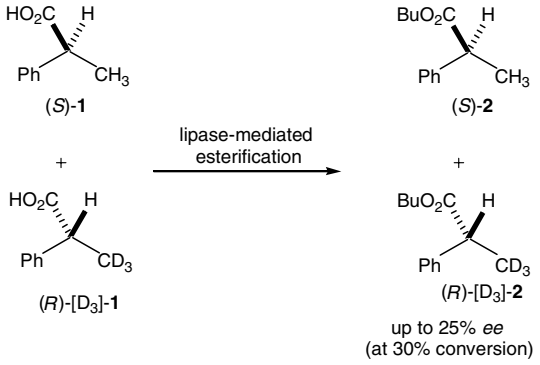
1. Introduction

The synthesis of enantiomerically pure profens,[1] such as ibuprofen[2] and naproxen,[3] is well documented. In particular, the use of quasi-enantiomeric components, such as (*S*)-**1** and (*R*)-[D_3]-**1**,[1] within organic synthesis is developing into an exciting area (Scheme 1).[2] These species are fascinating as they behave as if they were a pair of distinguishable enantiomers. Most importantly, due to their distinguishability the relative composition can easily be measured using standard instrumentation (e.g., NMR spectroscopy, mass spectrometry and HPLC).

Within this field, Reetz[1] has used this particular pair of quasi-enantiomeric 2-phenylpropionic acids, (*S*)-**1** and (*R*)-[D_3]-**1**,[1] as a chiral probe for determining the efficiency of a lipase-mediated esterification (Scheme 2). This kinetic resolution was efficiently monitored in situ by the use of



Scheme 1. Quasi-enantiomeric isotopomers (*S*)-**1** and (*R*)-[D_3]-**1**.



Scheme 2. Kinetic separation of isotopomers (*S*)-**1** and (*R*)-[D_3]-**1**.

mass spectrometry as starting precursors (*S*)-**1** and (*R*)-[D_3]-**1**, and product butyl esters (*S*)-**2** and (*R*)-[D_3]-**2**-d_3 have different molecular masses. The quasi-enantiomeric excess of product **2** was found to increase linearly with conversion; the highest enantiomeric excess (25% ee) was obtained at approximately 30% conversion (Scheme 2). To ensure that there was no secondary kinetic isotope effect, this reaction was monitored additionally using a racemic sample of 2-phenylpropionic acid **1**, which gave a comparable stereoselectivity.

This strategy has recently been used by Harada[3] to measure the stereochemical efficiency of a simple esterification

* Corresponding author. Tel.: +44 1482 466401; fax: +44 1482 466410; e-mail: j.eames@hull.ac.uk

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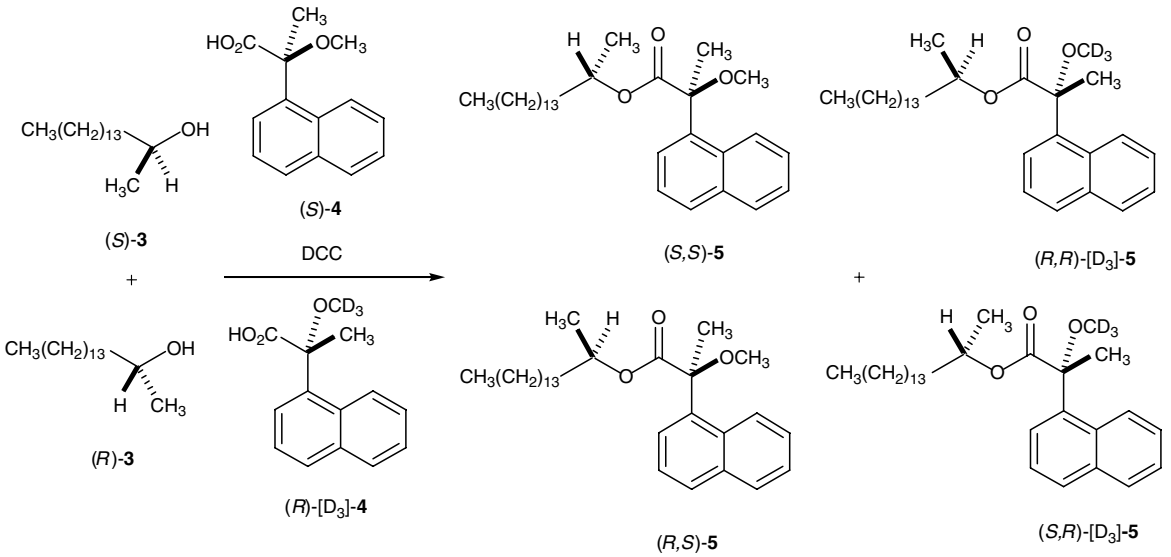


Scheme 3. Kinetic resolution of alcohol **3** using quasi-enantiomeric isotopomers (*S*)-**4** and (*R*)-[D_3]-**4**.

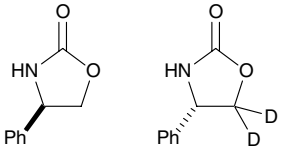
reaction between a racemic alcohol *rac*-**3** {(*S*)-**3** and (*R*)-**3** as shown in Scheme 3} and a quasi-enantiomeric pair of carboxylic acids (*S*)-**4** and (*R*)-[D_3]-**4**, to give the corresponding ester **5**. Harada[3] has shown that the mutual recognition of a scalemic sample of alcohol **3** (of unknown composition) with an equimolar mixture of quasi-enantiomeric carboxylic acids (*S*)-**4** and (*R*)-[D_3]-**4** (mediated by the addition of *racemic* DCC), gave a diastereoisomeric pair of quasi-enantiomers (*S*,*S*)-**5** and (*S*,*R*)-[D_3]-**5**, and (*R*,*S*)-**5** and (*R*,*R*)-[D_3]-**5**, respectively (Scheme 3). The enantiomeric excess of the scalemic alcohol **3** was determined by ^{1}H NMR spectroscopy by comparing the relative amounts of each adduct within each diastereoisomeric pair.

2. Results and discussion

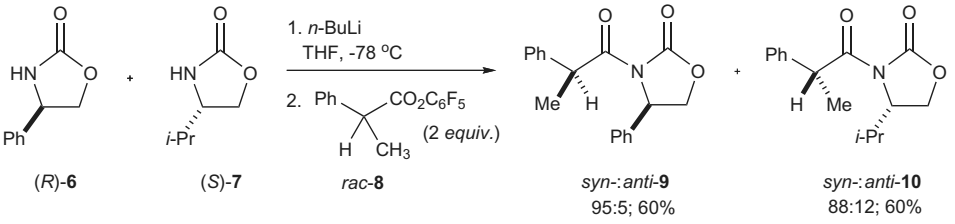
We have recently become interested in the parallel kinetic resolution[4] of profen adducts,[5,6] such as pentafluorophenyl 2-phenylpropionate *rac*-**8** (derived from 2-phenyl propionic acid) using two complementary quasi-enantiomeric Evans' oxazolidinones (*R*)-**6** and (*S*)-**7** to give two separable adducts *syn*-**9** and *syn*-**10**, respectively (Scheme 4). The levels of mutual recognition between these substrates (*R*)-**6** and (*S*)-**8**, and (*S*)-**7** and (*R*)-**8** were shown to be excellent (>76% de).

In an attempt to extend the versatility of this resolution methodology, we were interested in the synthesis of deuterium-labelled quasi-enantiomeric combinations of isotopomers of Evans' oxazolidinones, such as (*R*)-**6** and (*S*)-[D_2]-**6**, and their application as chiral probes for monitoring the efficiency of novel parallel kinetic resolutions (Scheme 5).

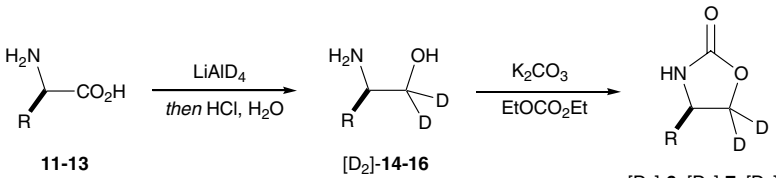
To this aim, we were required to synthesise a series of enantiomerically pure deuterium-labelled oxazolidinones (*S*)-[D_2]-**6**, (*R*)-[D_2]-**7**, (*R*)-[D_2]-**17**, (*S*)-[D_2]-**20** and (*S*)-[D_2]-**21** (Schemes 6 and 7). For synthetic ease, we first chose to incorporate the di-deuterium labels at the *C*(5)-position of the oxazolidinone using Meyers'[7] original lithium aluminium hydride protocol (Scheme 6). These oxazolidinones (*S*)-[D_2]-**6**, (*R*)-[D_2]-**7** and (*R*)-[D_2]-**17** were efficiently synthesised in a good yield by the reduction of the corresponding α-amino acids (*S*)-**11**, (*R*)-**12** and (*R*)-**13** using lithium aluminium deuteride ($LiAlD_4$) {to give the corresponding dideuterio-α-amino alcohols (*S*)-[D_2]-**14**, (*R*)-[D_2]-**15** and (*R*)-[D_2]-**16**}, and cyclisation by the addition of diethylcarbonate in the presence of a sub-stoichiometric amount of



Scheme 5. Quasi-enantiomeric isotopomers (*R*)-**6** and (*S*)-[D_2]-**6**.



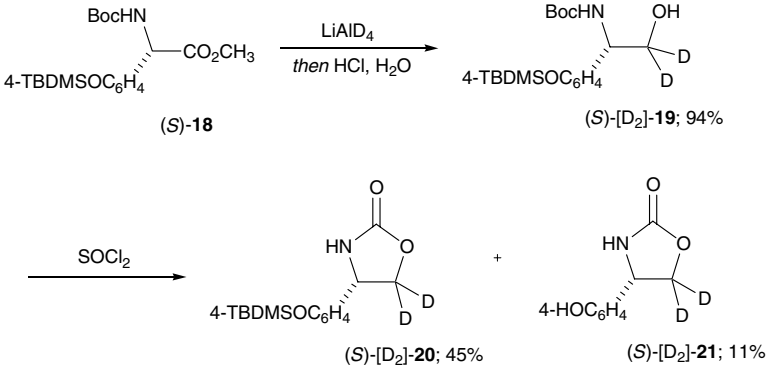
Scheme 4. Parallel kinetic resolution of active ester *rac*-**8**.



11-13 [D2]-14-16 [D2]-6, [D2]-7, [D2]-17

Entry	amino acid	amino alcohol	oxazolidinone
1	(*S*)-**11**; R = Ph	(*S*)-[D$_2$]-**14**; 79%	(*S*)-[D$_2$]-**6**; 40%
2	(*R*)-**12**; R = *i*-Pr	(*R*)-[D$_2$]-**15**; 77%	(*R*)-[D$_2$]-**7**; 57%
3	(*R*)-**13**; R = CH_2Ph	(*R*)-[D$_2$]-**16**; 93%	(*R*)-[D$_2$]-**17**; 40%

Scheme 6. $LiAlD_4$ reduction of α-amino-acids **11**–**13**.



(*S*)-**18** (*S*)-[D$_2$]-**19**; 94% (*S*)-[D$_2$]-**20**; 45% (*S*)-[D$_2$]-**21**; 11%

Scheme 7. Synthesis of oxazolidinones (*S*)-[D$_2$]-**20** and (*S*)-[D$_2$]-**21**.

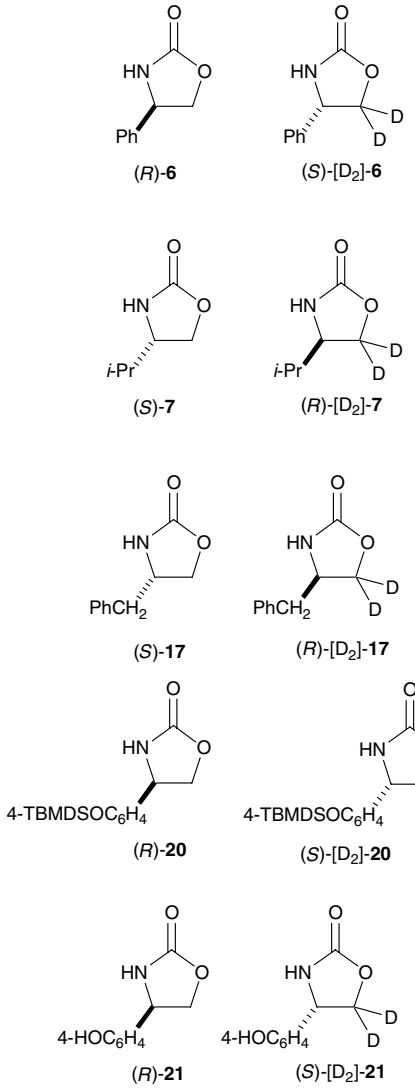
potassium carbonate (Scheme 6). The remaining oxazolidinones (*S*)-[D$_2$]-**20** and (*S*)-[D$_2$]-**21** were efficiently synthesised by the reduction of the protected ester (*S*)-**18** {using lithium aluminium deuteride to give (*S*)-[D$_2$]-**19** in 94% yield}, followed by a thionyl chloride mediated cyclisation using methodology reported by Fox[8] (Scheme 7).

With these deuterium-labelled oxazolidinones (*S*)-[D$_2$]-**6**, (*R*)-[D$_2$]-**7**, (*R*)-[D$_2$]-**17**, (*S*)-[D$_2$]-**20** and (*S*)-[D$_2$]-**21** in hand, we next probed their combination with an equimolar amount of their quasi-enantiomeric partner (*R*)-**6**, (*S*)-**7**, (*S*)-**17**, (*R*)-**20** and (*R*)-**21**, respectively, to give the corresponding quasi-enantiomeric mixtures of (*R*)-**6** and (*S*)-[D$_2$]-**6**, (*S*)-**7** and (*R*)-[D$_2$]-**7**, (*S*)-**17** and (*R*)-[D$_2$]-**17**, (*R*)-**20** and (*S*)-[D$_2$]-**20**, and (*R*)-**21** and (*S*)-[D$_2$]-**21** (Scheme 8). By proton and carbon NMR spectroscopy, these quasi-racemic mixtures (e.g., **A** and [D$_2$]-**B**) were clearly distinguishable (Scheme 9). It is interesting to note, for the CHN group within the *D*-labelled oxazolidinones, [D$_2$]-**B**, there was a noticeable negative isotope shift for both hydrogen, $\mathbf{H}_b$ (~0.010–0.043 ppm), and carbon, $\mathbf{C}_b$ (~0.175–0.183 ppm) as determined by ^1H and ^{13}C NMR spectroscopy, respectively. By mass spectrometry, an approximate equimolar amount of each quasi-enantiomeric isotopomer was present.[9]

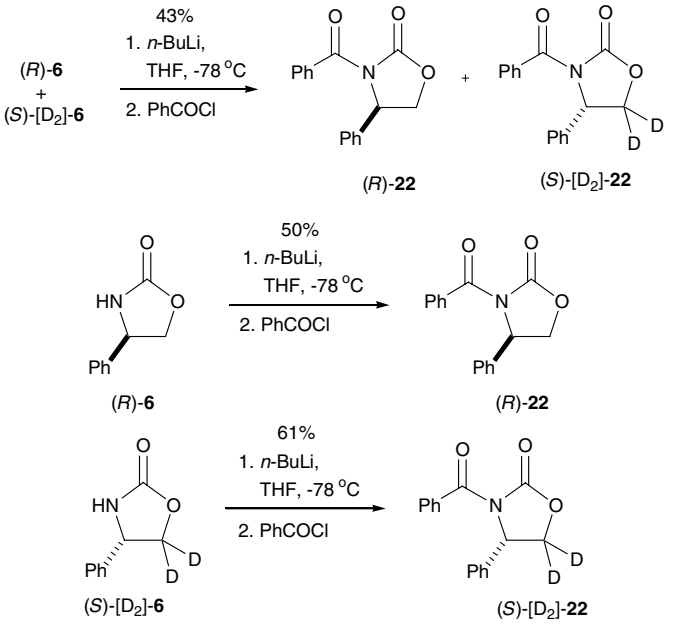
With these oxazolidinones in hand, we first probed the benzoylation of an equimolar mixture of oxazolidinones (*R*)-**6** and (*S*)-[D$_2$]-**6** (Scheme 10). Deprotonation of oxazolidinones (*R*)-**6** and (*S*)-[D$_2$]-**6** with *n*-butyl lithium in THF at −78 °C, followed by addition of benzoyl chloride gave an inseparable equimolar mixture of the quasi-enantiomeric oxazolidinones (*R*)-**22** and (*S*)-[D$_2$]-**22** in good yield (Scheme 10). The relative proportions of each isotopomer (*R*)-**22** and (*S*)-[D$_2$]-**22** were easily confirmed by either mass spectrometry or ^1H NMR spectroscopy. This assignment proved identical to that obtained by pre-mixing an equimolar amount of each individual quasi-enantiomer of (*R*)-**22** and (*S*)-[D$_2$]-**22** (derived from (*R*)-**6** and (*S*)-[D$_2$]-**6**, respectively) (Scheme 10).

We next studied the parallel kinetic resolution of a series of structurally related racemic pentafluorophenate esters (*rac*)-**27**–**30** using an equimolar combination of quasi-enantiomeric oxazolidinones (*R*)-**6** and (*S*)-[D$_2$]-**6** (Scheme 11 and 12). These active esters *rac*-**27**–**30** were efficiently synthesised in a good yield by the sequential addition of *N*,*N*′-dicyclohexylcarbimide (DCC) and pentafluorophenol (C_6F_5OH) to a stirred solution of the corresponding carboxylic acids *rac*-**23**-**26** in dichloromethane (Scheme 11).

Deprotonation of the equimolar combination of oxazolidinones, (*R*)-**6** and (*S*)-[D$_2$]-**6**, with *n*-butyl lithium at −78 °C in THF, followed by the addition of pentafluorophenyl active esters *rac*-**27**–**30** in THF, gave a pair of separable diastereoisomeric adducts, *syn*-**31**-**34** and *syn*-[D$_2$]-**31**–**34**

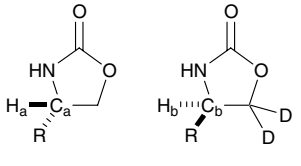


Scheme 8. Quasi-enantiomeric isotopomers oxazolidinones **6**, **7**, **17**, **20** and **21**.



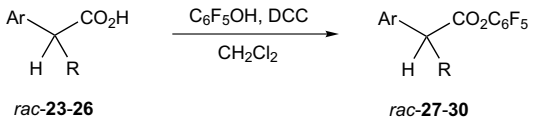
Scheme 10. Benzoylation of isotopomeric oxazolidinones **6**.

(*syn*-**A** and *syn*-[D_2]-**B**), and *anti*-**31-34** and *anti*-[D_2]-**31**–**34** (*anti*-**A** and *anti*-[D_2]-**A**), respectively (Scheme 12). The levels of mutual diastereoselectivity (*syn*- to *anti*-) were excellent, ranging from 95:5 (Scheme 12: entry 3) to >98:2 (Scheme 12: entry 2). Each pair of diastereoisomeric adducts (e.g., for oxazolidinones *syn*-**32** and *syn*-[D_2]-**32**, and *anti*-**32** and *anti*-[D_2]-**32**—see Scheme 12: entry 2) contain a near equimolar amount of two both isotopomers; for *syn*-**32** and *syn*-[D_2]-**32**; ratio 50:50 (±2%), and *anti*-**32** and *anti*-[D_2]-**32**; ratio 50:50 (±2%). The levels of diastereocontrol (90–96% de) and relative isotopomeric composition were determined by ^{1}H NMR spectroscopy. This relative composition was verified through a combination of column chromatography and mass spectrometry to determine the relative diastereoselectivity and isotopic composition,



Entry	*quasi*-enantiomeric oxazolidinones **A** and **B**	isotope shifts $\Delta\delta(H_a - H_b)$ ppm	isotope shifts $\Delta\delta(C_a - C_b)$ ppm
1	(*R*)-**12** + (*S*)-[D_2]-**6**; R = Ph	0.0119 ppm	0.175 ppm
2	(*S*)-**7** + (*R*)-[D_2]-**7**; R = *i*-Pr	0.0120 ppm	0.191 ppm
3	(*S*)-**17** + (*R*)-[D_2]-**17**; R = $PhCH_2$	0.0430 ppm	0.183 ppm
4	(*R*)-**20** + (*S*)-[D_2]-**20**; R = 4-$TBDMSOC_6H_4$	0.0100 ppm	0.175 ppm
5	(*R*)-**21** + (*S*)-[D_2]-**21**; R = 4-HOC_6H_4	0.0138 ppm	0.183 ppm

Scheme 9. Isotope shifts for oxazolidinones **6**, **7**, **17**, **20** and **21**.



rac-**23**-**26** *rac*-**27**-**30**

Entry	Carboxylic acids	Ar	R	Active esters	Yield
1	**23** (=**1**)	Ph	CH_3	*rac*-**27** (=**8**)	92%
2	**24**	Ph	CH_2CH_3	*rac*-**28**	72%
3	**25**	4-$CH_3C_6H_4$-	CH_3	*rac*-**29**	65%
4	**26**	4-*i*-BuC_6H_4-	CH_3	*rac*-**30**	75%

Scheme 11. Synthesis of active esters (*rac*)-**27**–**30**.

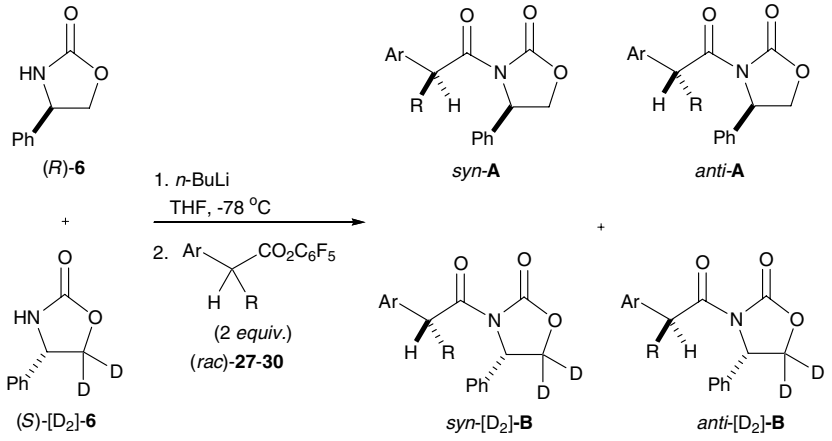
respectively. In order to ensure that there was no secondary kinetic isotope effect, these processes were repeated using a related mutual kinetic resolution protocol, which gave near identical levels of diastereoselectivity (Scheme 13).

With this information in hand, we next probed the mutual kinetic separation of an equimolar mixture of quasi-enantiomeric isotopomers (*R*)-**6** and (*S*)-[D_2]-**6** using a combination of quasi-enantiomeric pentafluorophenyl active esters (*R*)-**28** and (*S*)-**35** (Scheme 14). Deprotonation of the equimolar mixture of oxazolidinones, (*R*)-**6** and (*S*)-[D_2]-**6**, with *n*-butyl lithium at −78 °C in THF, followed by the addition of the active esters (*R*)-**28** and (*S*)-**35** in THF, gave a separable mixture of *syn*-oxazolidinones (*S*,*R*)-*syn*-**36** and (*R*,*S*)-*syn*-[D_2]-**32** in 87% and 77%, respectively (Scheme 14). The relative levels of mutual recognition were determined by ^{1}H NMR spectroscopy of the crude reaction mixture, and were shown to be excellent for both oxazolidinone components; for (*R*)-**6**, the mutual recognition was 96:4 [(*S*,*R*)-*syn*-**36**: (*R*,*R*)-*anti*-**32**] and for its quasi-enantiomeric component, (*S*)-[D_2]-**6**, was 98:2 {(*R*,*S*)-*syn*-[D_2]-**32**: (*S*,*S*)-*anti*-[D_2]-**36**}. It is interesting to note that oxazolidinone (*R*)-**6** mutually recognised the active ester (*S*)-**35** {to give [(*S*,*R*)-*syn*-**36**]} and its complementary quasi-enantiomeric *D*-labelled oxazolidinone (*S*)-[D_2]-**6**, recognised the related active ester (*R*)-**28** {to give (*R*,*S*)-*syn*-[D_2]-**32**} in a near equal fashion.

3. Conclusion

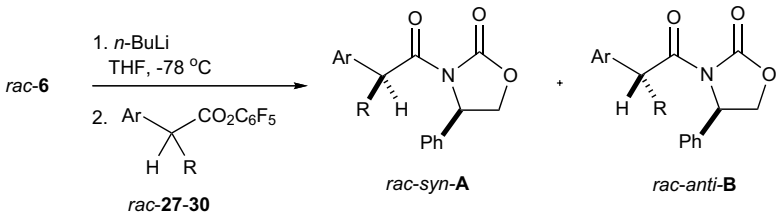
In conclusion, we have reported the synthesis of a series of enantiomerically pure *C*(5)-di-deuterium-labelled oxazolidinones (*S*)-[D_2]-**6**, (*R*)-[D_2]-**7**, (*R*)-[D_2]-**17**, (*S*)-[D_2]-**20** and (*S*)-[D_2]-**21** in a good yield. We have also shown that these oxazolidinones {e.g., (*S*)-[D_2]-**6**} can be combined with their non-labelled enantiomer [e.g., (*R*)-**6**] to give a quasi-racemic mixture (*R*)-**6** and (*S*)-[D_2]-**6**. This combination of quasi-enantiomeric oxazolidinone isotopomers has additionally been shown to be a versatile chiral probe for the discovery of novel parallel kinetic resolutions involving Evans' based oxazolidinones.

The nearest analogy to this work is that of Vedejs[10] with the parallel kinetic resolution of [^{12}C/^{13}C]-differentially labelled substrates. In recent years, the use of quasi-enantiomeric isotopomers as chiral probes for monitoring the



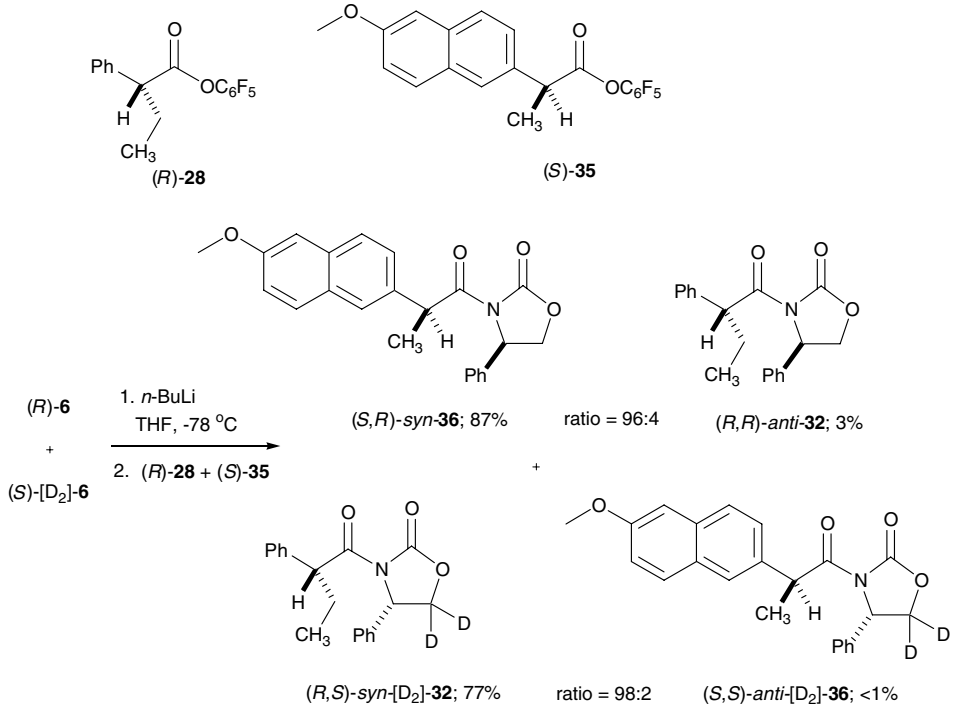
Entry	Active ester	Ar	R	Oxazolidinones **A**	Oxazolidinones **B**	*syn*-**A**: *syn*-[D_2]-**B**	*anti*-**A**: *anti*-[D_2]-**A**
1	**27** (=**8**)	Ph	CH_3	*syn*-**31**:*anti*-**31**; 97:3	*syn*-[D_2]-**31**:*anti*-[D_2]-**31**; 97:3	52:48 (±2%); 70%	50:50 (±2%); 3%
2	**28**	Ph	CH_2CH_3	*syn*-**32**:*anti*-**32**; >98:2	*syn*-[D_2]-**32**:*anti*-[D_2]-**32**; >98:2	50:50 (±2%); 87%	50:50 (±2%); 1%
3	**29**	4-$CH_3C_6H_4$-	CH_3	*syn*-**33**:*anti*-**33**; 95:5	*syn*-[D_2]-**33**:*anti*-[D_2]-**33**; 95:5	50:50 (±2%); 69%	51:49 (±2%); 2%
4	**30**	4-*i*-BuC_6H_4-	CH_3	*syn*-**34**:*anti*-**34**; 97:3	*syn*-[D_2]-**34**:*anti*-[D_2]-**34**; 97:3	50:50 (±2%); 79%	52:48 (±2%); 2%

Scheme 12. Parallel kinetic resolution of active esters (*rac*)-**27**–**30** using quasi-enantiomeric isotopomers (*R*)-**6** and (*S*)-[D_2]-**6**.



Entry	Active ester	Ar	R	Oxazolidinones	*syn*-**A**	*anti*-**A**
1	**27**	Ph	CH_3	*syn*-**31**:*anti*-**31**; 97:3	70%	2%
2	**28**	Ph	CH_2CH_3	*syn*-**32**:*anti*-**32**; >98:2	69%	1%
3	**29**	4-$CH_3C_6H_4$-	CH_3	*syn*-**33**:*anti*-**33**; 95:5	56%	2%
4	**30**	4-*i*-BuC_6H_4-	CH_3	*syn*-**34**:*anti*-**34**; 96:4	56%	1%

Scheme 13. Mutual kinetic resolution of active esters (*rac*)-**27**–**30** using *rac*-**6**.



Scheme 14. Mutual kinetic separation of quasi-enantiomeric isotopomers (*R*)-**6** and (*S*)-[D_2]-**6** using two quasi-enantiomeric active esters (*R*)-**28** and (*S*)-**35**.

stereochemical outcome of other related processes has become increasingly popular.[11] Within our laboratory, we are currently studying these applications, which 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 250 MHz and 400 MHz Fourier transform spectrometers 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[12] were measured using an automatic AA-10 Optical Activity

Ltd polarimeter. The levels of *D*-incorporation were determined by a combination of mass, proton and carbon NMR spectra. All isotopically labelled derivatives have been given an L superscript and unlabelled derivatives a U superscript.

4.2. Dideuterio-phenylglycinol (*S*)-[D_2]-14

Lithium aluminium deuteride (5.31 g, 126.6 mmol) was slowly added to THF (150 ml). The resulting solution was cooled to 0 °C using an ice bath. L-Phenylglycine (*S*)-**11** (12.23 g, 80.9 mmol) was then slowly added 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 ether (3 × 150 ml) and the organic filtrates were dried over $MgSO_4$, and concentrated under reduced pressure to give dideuterio phenylglycinol (*S*)-[D_2]-**14** (8.89 g, 79%) as a white powder; mp = 77–79 °C (unlabelled lit.[13] 76.5–78.5 °C); $[\alpha]_D^{20} = +33.0$ (*c* 0.9, 1 M HCl); lit.[14] $[\alpha]_D^{20} = +32$ (*c* 0.75, 1 M HCl); ν_{max} ($CHCl_3$)/cm^{-1} 3270 (NH), 3042 (OH), 2255 (CD) and 2134 (CD); δ_H (400 MHz; $CDCl_3$) 7.35–7.24 (5H, m, 5 × CH; Ph), 4.00 (1H, s, CHN) and 2.90–2.40 (3H, br s, OH and 2 × NH); δ_C (100 MHz; $CDCl_3$) 142.4 (*i*-C; Ph), 128.5,[2] 127.4[1] and 126.4[2] (5 × CH; Ph), 67.2 (1C, quintet, $^1J_{C,D} = 22.1$ Hz, CD_2) and 57.1 (CHN) (found MH^+, 140.1039; $C_8H_{10}D_2NO$ requires 140.1039).

4.3. 4-Phenyl-5,5-dideuterio-oxazolidinone (*S*)-[D_2]-6

Anhydrous potassium carbonate (0.88 g, 6.3 mmol) was added to a solution of dideuteriophenylglycinol (*S*)-[D_2]-**14** (8.49 g, 61 mmol) and diethyl carbonate (15.32 g, 15.8 ml, 129.8 mol). 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 crude oxazolidinone (*S*)-[D_2]-**6**. This residue was recrystallised from a mixture of hot petroleum ether (40–60 °C)/ethyl acetate (1:2) to give 4-phenyl-5,5-dideuterio-oxazolidinone (*S*)-[D_2]-**6** (4.02 g, 40%) as white crystals; mp = 124–127 °C (unlabelled (*S*)-; lit.[15] 132–133 °C); R_f [ethyl acetate/ethanol (9:1)] 0.71; $[\alpha]_D^{20} = +48.4$ (*c* 1.01, $CHCl_3$), unlabelled (*S*)-; lit.[15] $[\alpha]_D^{20} = +49.5$ (*c* 2.1,$CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 3270 (NH), 2256 (CD), 2140 (CD) and 1748 (C=O); δ_H (400 MHz; $CDCl_3$) 7.37–7.25 (5H, m, 5 × CH; Ph), 5.95–5.84 (1H, br s, NH) and 4.97 (1H, s, CHN); δ_C (100 MHz; $CDCl_3$) 159.7 (C=O), 139.6 (*i*-C; Ph), 129.2,[2] 128.9[1] and 126.1[2] (5 × CH; Ph), 71.9 (1C, quintet, $^1J_{C,D} = 23.3$ Hz CD_2) and 56.2 (CHN) (found MNH_4^+, 183.1097; $C_9H_{11}D_2N_2O_2$ requires MNH_4^+, 183.1097).

4.4. Equimolar mixture of 4-phenyl-5,5-dideuterio-oxazolidinone (*S*)-[D_2]-6 and 4-phenyl-oxazolidinone (*R*)-6

An equimolar mixture of each adduct (~10 mg) was added to dichloromethane (5 ml). The solution was evaporated to give the above equimolar mixture of quasi-enantiomeric isotopomers.

Melting point: (*S*)-[D_2]-**6**; (*R*)-**6** = 121-124 °C {for *rac*-**6** = 130–132 °C; lit.[16] 137–139 °C}.

δ_H (400 MHz; $CDCl_3$) 7.41-7.31 (10H, m, 10 × CH; Ph^U and Ph^L), 6.43 (2H, s, NH^U and NH^L), 4.94 (1H, dd, *J* 8.6 and 6.9, CHN^U), 4.93 (1H, s, CHN^L), 4.72 (1H, t, *J* 8.6, $CH_AH_BO^U$) and 4.17 (1H, dd, *J* 8.6 and 6.9, $CH_AH_BO^U$); δ_C (100 MHz; $CDCl_3$) 159.9 (2 × $C{=}O^U$ and $C{=}O^L$), 139.4 (2 × *i*-C; Ph^U and Ph^L), 129.1,[4] 128.7[2] and 125.9[4] (10 × CH; Ph), 72.6 (CH_2O^U), 72.1 (1C, quintet, $^1J_{C,D} = 23.8$, CD_2O^L), 56.3 (CHN^U) and 56.1 (CHN^L). By mass spectrometry, this mixture of oxazolidinones (*S*)-[D_2]-**6** and (*R*)-**6** gave a 52:48 ratio of (*S*)-[D_2]-**6**:(*R*)-**6**; for (*S*)-[D_2]-**6**; found MNH_4^+, 183.1097; $C_9H_{11}D_2N_2O_2$ requires MNH_4^+, 183.1097, and for (*R*)-**6**; found MNH_4^+, 181.0970; $C_9H_{13}N_2O_2$ requires MNH_4^+, 181.0972; and IR spectroscopy, ν_{max} (CH_2Cl_2)/cm^{-1} 2305 (br, C–D) and 1760 (C=O); {$[\alpha]_D^{20} = \sim 0.0$ (*c* 1.0, DMSO)}.

Isotopic shifts by NMR spectroscopy. Proton NMR spectroscopy: negative isotope shift at 4.93 ppm (CHN) is 0.0119 ppm (4.78 Hz at 400 MHz). Carbon NMR spectroscopy shifts: (a) negative isotopic shift at 72.6 ppm (CH_2O) was 0.4278 ppm (43 Hz at 100.6 MHz); (b) negative isotopic shift at 56.3 ppm (CHN) was 0.175 ppm (17.6 Hz at 100.6 MHz).

4.5. Dideuteriovalinol (*R*)-[D_2]-15

In the same way as amino alcohol (*S*)-[D_2]-**14**, D-valine (*R*)-**12** (10.5 g, 89.5 mmol) and lithium aluminium deuteride (5.09 g, 121.3 mol) in THF (150 ml) gave (*R*)-dideuteriovalinol (*R*)-[D_2]-**15** (7.20 g, 77%) as a white powder; mp = 29–31 °C (unlabelled lit.[17] 39–40 °C); $[\alpha]_D^{20} = -13.4$ (*c* 2.4, $CHCl_3$)]; [lit.[17] unlabelled $[\alpha]_D^{20} = -14.0$ (*c* 9.9, ethanol)]; ν_{max} ($CHCl_3$)/cm^{-1} 3375 (NH), 3054 (NH), 2965 (OH), 2305 (CD) and 2256 (CD); δ_H (400 MHz; $CDCl_3$) 3.10–2.70 (3H, m, OH and NH_2), 2.50 (1H, br d, *J* 6.2, CHN), 1.54 (1H, broad septet, *J* ~ 6.7, $CH(CH_3)_2$), 0.86 (3H, d, *J* 6.8, $^ACH_3CH^BCH_3$) and 0.84 (3H, d, *J* 6.8, $^ACH_3CH^BCH_3$); δ_C (100 MHz; $CDCl_3$) 63.7 (1C, quintet, $^1J_{C,D} = 23.1$, CD_2O), 58.1 (CHN), 30.8 ($CH(CH_3)_2$), 19.1 (CH_3) and 18.3 (CH_3); *m*/*z* 105.9 (100%, M^+).

4.6. 4-Isopropyl-5,5-dideuterio-oxazolidinone (*R*)-[D_2]-7

In the same way as oxazolidinone (*S*)-[D_2]-**6**, dideuteriovalinol (*R*)-[D_2]-**15** (6.99 g, 66.47 mmol), potassium carbonate (0.92 g, 6.64 mmol) and diethylcarbonate (16.49 g, 16.91 ml, 139.66 mmol) gave dideuteriooxazolidinone (*R*)-[D_2]-**7** (4.93 g, 57%) as a white powder. This was recrystallised from a mixture of hot petroleum ether (40–60 °C)/ethyl acetate (ratio: 1:2) to give white crystal; mp = 60–

62 °C (unlabelled (*S*)-; lit.[18] 70–72 °C); R_f [ethyl acetate/ethanol (9:1)] 0.66; $[\alpha]_D^{20} = +16.6$ (*c* 5.2, $CHCl_3$); (unlabelled (*S*)- lit.[19] $[\alpha]_D^{20} = -16.5$ (*c* 6.0, ethanol)); ν_{max} ($CHCl_3$)/cm^{-1} 3265 (NH), 2306 (CD), 2254 (CD) and 1752 (C=O); δ_H (400 MHz; $CDCl_3$) 7.10–6.90 (1H, br s, NH), 3.45 (1H, d, *J* 6.7, CHN), 1.69 (1H, m, $CH(CH_3)_2$), 0.87 (3H, d, *J* 6.8, $^{A}CH_3CH^{B}CH_3$) and 0.82 (3H, d, *J* 6.8, $^{A}CH_3CH^{B}CH_3$); δ_C (100 MHz; $CDCl_3$) 166 (OC=O), 67.8 (1C, quintet, $^1J_{C,D} = 24.4$, CD_2O), 58.1 (CHN), 32.5 ($CH(CH_3)_2$), 17.8 (CH_3) and 17.5 (CH_3) (found MH^+, 132.0990; $C_6H_{10}D_2NO_2$ requires 132.0988).

4.7. Equimolar mixture of 4-isopropyl-5,5-dideuterio-oxazolidinone (*R*)-[D_2]-7 and 4-isopropyl-oxazolidinone (*S*)-7

An equimolar mixture of each adduct (~10 mg) was added to dichloromethane (5 ml). The solution was evaporated to give the above equimolar mixture of quasi-enantiomeric isotopomers.

Melting point: (*R*)-[D_2]-**7**; (*S*)-**7** = 77–78 °C; {*rac*-**7** = 73–75 °C; lit.[20] 75 °C}.

δ_H (400 MHz; $CDCl_3$) 7.20–7.05 (2H, br s, NH^U and NH^L), 4.37 (1H, t, *J* 8.8, $CH_AH_BO^U$), 4.02 (1H, dd, *J* 8.8 and 6.4, $CH_AH_BO^U$), 3.55 (1H, br, CHN^U), 3.52 (1H, d, *J* 7.8, CHN^L), 1.65 (2H, br octet, $J \sim 6.7$, $CH(CH_3)_2^U$ and $CH(CH_3)_2^L$), 0.89 (6H, d, *J* 6.8, $^{A}CH_3CH^{B}CH_3^U$ and $^{A}CH_3$-$CH^{B}CH_3^U$) and 0.82 (6H, d, *J* 6.8, $^{A}CH_3CH^{B}CH_3^U$ and $^{A}CH_3CH^{B}CH_3^U$); δ_C (100 MHz; $CDCl_3$) 160.6 (OC=O^U and OC=O^L), 68.5 (CH_2O^L), 67.8 (1C, quintet, $^1J_{C,D} = 23.1$, CD_2O^L), 58.3 (CHN^U), 58.1 (CHN^L), 32.6 ($CH(CH_3)_2^U$), 32.5 ($CH(CH_3)_2^L$), 17.8 (CH_3^U and CH_3^L) and 17.6 (CH_3^U and CH_3^L). By mass spectrometry, this mixture of oxazolidinones (*R*)-[D_2]-**7** and (*S*)-**7** gave a 49:51 ratio of (*R*)-[D_2]-**7**:(*S*)-**7**; for (*R*)-[D_2]-**7**; found MNH_4^+, 149.1255; $C_6H_{13}D_2N_2O_2$ requires MNH_4^+, 149.1254, and for (*R*)-**7**; found MNH_4^+, 147.1129; $C_9H_{15}N_2O_2$ requires MNH_4^+, 147.1128; and IR spectroscopy, ν_{max} (CH_2Cl_2)/cm^{-1} 2305 (C–D) and 2253 (C–D) and 1752 (C=O); {$[\alpha]_D^{20} = +0.4$ (*c* 20.0, $CHCl_3$)}.

Isotopic shifts by NMR spectroscopy. Proton NMR spectroscopy shifts: negative isotope shift at 3.55 ppm (CHN) is 0.012 ppm (4.86 Hz at 400 MHz). Carbon NMR spectroscopy shifts: (a) negative isotopic shift at 68.5 ppm (CH_2O) was 0.649 ppm (65.3 Hz at 100.6 MHz); (b) negative isotopic shift at 58.3 ppm (CHN) was 0.191 ppm (19.2 Hz at 100.6 MHz); (c) negative isotopic shift at 32.5 ppm ($CH_2(CH_3)_2$) was 0.053 ppm (5.4 Hz at 100.6 MHz).

4.8. Dideuterio-phenylalaninol (*R*)-[D_2]-16

In the same way as amino alcohol (*S*)-[D_2]-**14**, D-phenylalanine (*R*)-**13** (9.50 g, 57.5 mmol) and lithium aluminium deuteride (3.66 g, 87.2 mmol) in THF (150 ml) gave dideuterio-phenylalaninol (*R*)-[D_2]-**16** (8.19 g, 93%) as a white powder; mp = 82–85 °C (lit.[21] 88–90 °C); $[\alpha]_D^{20} = +26.4$ (*c* 1, 1 M HCl); lit.[14] $[\alpha]_D^{20} = +23.0$ (*c* 1.2, HCl/H_2O); ν_{max} ($CHCl_3$)/cm^{-1} 3361 (NH and OH), 2920 (NH and OH); 2853 (NH and OH), 2411 (CD) and 2305.2 (CD); δ_H (400 MHz; $CDCl_3$) 7.38–7.17 (5H, m, 5 × CH; Ph), 3.10 (1H, dd, *J* 8.6 and 5.2, CHN), 2.78 (1H, dd, *J* 13.4 and 5.2, CH_AH_BPh), 2.51 (1H, dd, *J* 13.4 and 8.6, CH_AH_BPh) and 2.34–1.98 (3H, br s, OH and 2 × NH); δ_C (100 MHz; $CDCl_3$) 138.6 (*i*-C; Ph), 129.1,[2] 128.5[2] and 126.3[1] (5 × CH; Ph), 65.3 (1C, quintet, $^1J_{C,D} = 21.5$ Hz, CD_2O), 53.9 (CHN) and 40.7 (CH_2Ph); *m*/*z* 153.9 (100%, M^+).

4.9. 4-Benzyl-5,5-dideuterio-oxazolidinone (*R*)-[D_2]-17

In the same way as oxazolidinone (*S*)-[D_2]-**6**, dideuterio-phenylglycinol (*R*)-[D_2]-**16** (8.41 g, 54.8 mmol), potassium carbonate (0.82 g, 6.0 mmol) and diethylcarbonate (13.79 g, 14.15 ml, 0.12 mol) gave (*R*)-dideuterio-oxazolidinone (*R*)-[D_2]-**17** (3.88 g, 40%) as a white powder. This was recrystallised from a mixture of hot petroleum ether (40–60 °C)/ethyl acetate (1:2) to give white crystal; mp = 70–73 °C (lit.[22] 87–88.5 °C unlabelled); R_f [ethyl acetate/ethanol (9:1)] 0.71; $[\alpha]_D^{20} = +53.7$ (*c* 1.03, $CHCl_3$); (unlabelled lit.[23] $[\alpha]_D^{20} = -62.0$ (*c* 1.0, $CHCl_3$)); ν_{max} ($CHCl_3$)/cm^{-1} 3272 (NH), 2305 (CD), 2255 (CD) and 1755 (C=O); δ_H (400 MHz; $CDCl_3$) 7.34–7.23 (3H, m, 3 × CH; Ph), 7.18–7.06 (2H, m, 2 × CH; Ph), 5.47 (1H, br s, NH), 4.07 (1H, t, *J* 7.0, CHN) and 2.87 (2H, d, *J* 7.0, CH_2Ph); δ_C (100 MHz; $CDCl_3$) 159.4 (C=O), 135.9 (*i*-C; Ph), 129.1,[2] 128.9[2] and 127.3[1] (5 × CH; Ph), 69.5 (1C, quintet, $^1J_{C,D} = 22.6$ Hz, CD_2O), 53.6 (CHN) and 41.4 (CH_2Ph) (found MNa^+, 202.0806; $C_{10}H_9D_2NO_2Na$ requires 202.0808).

4.10. Equimolar mixture of 4-benzyl-5,5-dideuterio-oxazolidinone (*R*)-[D_2]-17 and 4-benzyl-oxazolidinone (*R*)-17

The solution was evaporated to give the above equimolar mixture of quasi-enantiomeric isotopomers. Melting point: (*R*)-[D_2]-**17**; (*S*)-**17** = 53–65 °C; {(*rac*)-**17** = 65–67 °C; lit.[24] 72–74 °C}. δ_H (400 MHz; $CDCl_3$) 7.34–7.23 (6H, m, 6 × CH; Ph^U and Ph^L), 7.18–7.06 (4H, m, 4 × CH; Ph^U and Ph^L), 5.47 (2H, br s, NH^U and NH^L), 4.45 (1H, dd, *J* 8.4 and 8.1, $CH_AH_BO^U$), 4.15 (1H, dd, *J* 8.4 and 5.7, $CH_AH_BO^U$), and 4.12–4.05 (1H, m, CHN^U), 4.10 (1H, t, *J* 7.1, CHN^L) and 2.87 (4H, d, *J* 7.0, CH_2Ph^U and CH_2Ph^L); δ_C (100 MHz; $CDCl_3$) 159.9 (C=O^U and C=O^L), 135.9 (2 × *i*-C; Ph^U and Ph^L), 130.0,[4] 128.9[4] and 127.3[2] (10 × CH; Ph^U and Ph^L), 69.6 (1C, CH_2O^U), 69.5 (1C, quintet, $^1J_{C,D} = 22.4$ Hz, CD_2O^L), 53.7 (CHN^U), 53.6 (CHN^L), 41.4 (CH_2Ph^U) and 41.3 (CH_2Ph^L). By mass spectrometry, this mixture of oxazolidinones (*R*)-[D_2]-**17** and (*S*)-**17** gave a 48:52 ratio of (*R*)-[D_2]-**12**:(*S*)-**12**; for (*R*)-[D_2]-**12**; found MNH_4^+, 197.1254; $C_{10}H_{13}D_2N_2O_2$ requires MNH_4^+, 197.1254, and for (*S*)-**12**; found MNH_4^+, 195.1128; $C_{10}H_{15}N_2O_2$ requires MNH_4^+, 195.1128; and IR spectroscopy, ν_{max} (CH_2Cl_2)/cm^{-1} 2358 (CD), 2341 (CD) and 1755 (C=O); {$[\alpha]_D^{20} = \sim 0.0$ (*c* 1.0, DMSO)}.

Isotopic shifts by NMR spectroscopy. Proton NMR spectroscopy shifts: negative isotope shift at 4.10 ppm (CHN) is 0.0043 ppm (1.64 Hz at 400 MHz). Carbon NMR spectroscopy shifts: (a) negative isotopic shift at 69.6 ppm (CH_2O) was 0.067 ppm (67.4 Hz at 100.6 MHz); (b) negative isotopic shift at 53.7 ppm (CHN) was 0.183 ppm (18.4 Hz at

100.6 MHz); (c) negative isotopic shift at 41.4 ppm (CH_2Ph) was 0.045 ppm (4.6 Hz at 100.6 MHz).

4.11. *N*-*tert*-Butoxycarbonyl-(4-*tert*-butyldimethylsilyoxyphenyl)-dideuterioglycinol (*S*)-[D_2]-19

Lithium aluminium deuteride (1.53 g, 36.5 mmol) was slowly added to a stirred solution of ester (*S*)-**18** (5.01 g, 12.8 mmol) {$[\alpha]_D^{20} = +68.7$ (*c* 12.7, CH_2Cl_2)} in ether (50 ml) at 0 °C. The resulting solution was stirred for 3 h. Ammonium chloride (50 ml) was slowly added, and the resulting solution was extracted with ether (3 × 100 ml). The combined organic layers were dried (over $MgSO_4$) and evaporated under reduced pressure to give the dideuterio-alcohol (*S*)-[D_2]-**19** (4.46 g, 94%) as an oil; $[\alpha]_D^{20} = +20.0$ (*c* 38.5, CH_2Cl_2) [unlabelled (*S*)-**19** $[\alpha]_D^{20} = +25.9$ (*c* 31.5, CH_2Cl_2)]; ν_{max} ($CHCl_3$)/cm^{-1} 2305 (CD) and 1694 (C=O) (NH); δ_H (400 MHz; $CDCl_3$) 7.04 (2H, dd, *J* 8.6 and 2.9, 2 × CH; Ar), 6.72 (2H, dd, *J* 8.6 and 2.9, 2 × CH; Ar), 5.20 (1H, br s, NH), 4.59 (1H, br s, OH), 3.60 (1H, br s, CHN), 1.39–1.34 (9H, br s, *t*-BuO), 0.89 (9H, s, *t*-BuSi), 0.10 (6H, s, 2 × CH_3Si); δ_C (100 MHz; $CDCl_3$) 156.3 (*i*-CO; Ar), 155.0 (C=O), 132.0 (*i*-C; Ar), 127.6 (2 × CH; Ar); 120.4 (2 × CH; Ar), 79.9 (CO; *t*-BuO), 65.5 (1C, multiplet, CD_2O), 56.1 (CHN), 28.3 (3 × Me; *t*-BuO), 25.6 (3 × Me; *t*-BuSi) and −4.5 (2 × Me, $SiMe_2$) (found MH^+, 370.2381; $C_{19}H_{32}D_2NO_4$ requires 370.2381; unlabelled—found MH^+, 368.2251; $C_{19}H_{33}NO_4Si$ requires 368.2252).

4.12. 4-(4-*tert*-Butyldimethylsilyoxyphenyl)-5,5-dideuterio-oxazolidin-2-one (*S*)-[D_2]-20 and 4-(4-hydroxyphenyl)-5,5-dideuterio-oxazolidin-2-one (*S*)-[D_2]-21

Thionyl chloride (11.4 g, 7.0 ml, 95.9 mmol) was added to dideuterio-glycinol (*S*)-[D_2]-**19** (4.36 g, 11.8 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 oxazolidinone (*S*)-[D_2]-**21** (0.21 g, 11%) was removed through filtration. The filtrate was concentrated under reduced pressure, and recrystallised in hot ethyl acetate to give oxazolidinone (*S*)-[D_2]-**20** (1.52 g, 45%) as a white powder; mp = 132–133 °C {for (*R*)-: 132–135 °C; lit.[8] (*R*)-unlabelled 142–142.5 °C}; $[\alpha]_D^{20} = +34.4$ (*c* 3.1, DMSO), {for (*R*)-: $[\alpha]_D^{20} = -37.2$ (*c* 1.28, DMSO); lit.[8] (*R*)-unlabelled $[\alpha]_D^{20} = -37.6$ (*c* 1.05, THF)}; ν_{max} ($CHCl_3$)/cm^{-1} 2264 (CD), 2221 (CD) and 1750 (C=O); δ_H (400 MHz; $CDCl_3$) 7.15 (2H, dt, *J* 8.4 and 4.8, 2 × CH; Ar), 6.79 (2H, dt, *J* 8.4 and 4.8, 2 × CH; Ar), 5.90 (1H, br s, NH), 4.83 (1H, s, CHN), 0.93 (9H, s, 3 × CH_3; *t*-Bu) and 0.15 (6H, s, 2 × CH_3; $SiCH_3$); δ_C (100 MHz; $CDCl_3$) 159.7 (C=O), 156.1 (*i*-CO; Ar), 131.8 (*i*-C; Ar), 127.2[2] and 120.6[2] (2 × CH; Ar), 72.0 (1C, quintet, $^1J_{C,D} = 23.1$ Hz, CD_2O), 55.8 (CHN), 25.6 (3 × CH_3; *t*-Bu) and −4.4 (2 × CH_3; 2 × $SiCH_3$) (found M^+, 295.1562; $C_{15}H_{21}D_2NO_3Si^+$ requires 295.1567) (unlabelled (*S*)-**20**: found MNa^+, 316.1342; $C_{15}H_{23}NO_3SiNa$ requires 316.1339); and oxazolidinone (*S*)-[D_2]-**21** (0.21 g, 11%) as a white powder; mp= 193–195 °C {(*R*)-unlabelled: 190–192 °C}; $[\alpha]_D^{20} = +21.6$ (*c* 2.2, DMSO); {(*R*)-unlabelled: $[\alpha]_D^{20} = -36.6$ (*c* 3.2, DMSO)}; ν_{max} ($CHCl_3$)/cm^{-1} 3600–3200 (OH), 2255 (CD), 2221 (CD) and 1754 (C=O); δ_H (400 MHz; [d_6]-DMSO) 9.41 (1H, s, OH), 7.96 (1H, s, NH), 7.05 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar), 6.88 (2H, dt, *J* 8.5 and 2.5, 2 × CH; Ar), 4.77 (1H, s, CHN); δ_C (100 MHz; [d_6]-DMSO) 158.6 (OC=O), 157.7 (*i*-CO; Ar), 131.0 (*i*-C; Ar), 127.3[2] and 115.3[2] (4 × CH; Ar), 70.9 (1C, quintet, $^1J_{C,D} = 23.8$Hz, CD_2O) and 54. (CHN) (found MH^+, 199.1045; $C_9H_8D_2NO_3$ requires 199.1046) (unlabelled (*S*)-**21**: found MNH_4^+, 197.0919; $C_9H_{13}N_2O_3$ requires 197.0921; and unlabelled (*R*)-**21**: found M^+, 179.0578; $C_9H_9NO_3$ requires 179.0577).

4.13. Equimolar mixture of 4-(4-*tert*-butyldimethylsilyoxyphenyl)-5,5-dideuterio-oxazolidin-2-one (*S*)-[D_2]-20 and 4-(4-*tert*-butyldimethylsilyoxyphenyl)-oxazolidin-2-one (*R*)-20

The solution was evaporated to give the above equimolar mixture of quasi-enantiomeric isotopomers. Melting point: (*S*)-[D_2]-**20**; (*R*)-**20** = 110–112 °C. δ_H (400 MHz; $CDCl_3$) 7.12 (4H, dt, *J* 8.4 and 4.8, 4 × CH; Ar^U and Ar^L), 6.76 (4H, dt, *J* 8.4 and 4.8, 4 × CH; Ar^U and Ar^L), 6.30 (2H, br s, NH^U and NH^U), 4.82 (1H, t, *J* 8.6, CHN^U), 4.81 (1H, s, CHN^L), 4.60 (1H, t, *J* 8.6, $CH_AH_BO^U$), 4.07 (1H, dd, *J* 8.6 and 7.4, $CH_AH_BO^L$), 0.92 (18H, s, 3 × CH_3; *t*-Bu^U and *t*-Bu^L) and 0.13 (12H, s, 2 × CH_3; $SiCH_3^U$ and $SiCH_3^L$); δ_C (100 MHz; $CDCl_3$) 160.2 (C=O^U and C=O^L), 156.2 (*i*-CO; Ar^U and Ar^L), 132.3 (*i*-C; Ar^U), 132.2 (*i*-C; Ar^L), 127.4[4] and 120.6[4] (8 × CH; Ar^U and Ar^L), 72.9 (1H, s, CH_2O^U), 72.2 (1C, quintet, $^1J_{C,\ D} = 20.7$ Hz, CD_2O^L), 56.1 (CHN^U), 55.9 (CHN^L), 25.8 (6 × CH_3; *t*-Bu^U and *t*-Bu^L) and −4.3 (4 × CH_3; 4 × $SiCH_3^U$ and $SiCH_3^L$) (found $M^UNH_4^+$, 311.1786; $C_{15}H_{27}N_2O_3Si$ requires 311.1785; and found $M^LNH_4^+$, 313.1910; $C_{15}H_{25}D_2N_2O_3Si$ requires 313.1911); ν_{max} (DMSO)/cm^{-1} 2265 (CD), 2221 (CD) and 1755 (C=O); {$[\alpha]_D^{20} = \sim 0.0$ (*c* 1.7, DMSO)}. Isotopic shifts by NMR spectroscopy. Proton NMR spectroscopy shifts: negative isotope shift at 4.81 ppm (CHN) is 0.0105 ppm (4.20 Hz at 400 MHz). Carbon NMR spectroscopy shifts: (a) negative isotopic shift at 132.2 ppm (*i*-C; Ar) was 0.0115 ppm (1.2 Hz at 100.6 MHz); (b) negative isotopic shift at 72.6 ppm (CH_2O) was 0.634 ppm (63.7 Hz at 100.6 MHz); (c) negative isotopic shift at 55.9 ppm (CHN) was 0.175 ppm (17.5 Hz at 100.6 MHz).

4.14. Equimolar mixture of 4-(4-hydroxyphenyl)-5,5-dideuterio-oxazolidin-2-one (*S*)-[D_2]-21 and 4-(4-hydroxyphenyl)-oxazolidin-2-one (*R*)-21

The solution was evaporated to give the above equimolar mixture of quasi-enantiomeric isotopomers. Melting point: (*S*)-[D_2]-**21**; (*R*)-**21** = 140-145 °C. δ_H (400 MHz; [d_6]-DMSO) 9.55 (2H, s, OH^U and OH^L), 8.09 (2H, s, NH^U and NH^L), 7.17 (4H, dt, *J* 8.4 and 4.8, 4 × CH; Ar^U and Ar^L), 6.80 (4H, dt, *J* 8.4 and 4.8, 4 × CH; Ar^U and Ar^L), 4.85 (1H, br t, *J* 8.2 ~ 7.3, CHN^U), 4.80 (1H, s, CHN^L), 4.63 (1H, t, *J* 8.4, $CH_AH_BO^U$) and 3.98 (1H, dd, *J* 8.4 and 6.6, $CH_AH_BO^U$); δ_C (100 MHz; [d_6]-DMSO) 158.9

(OC=O^{U} and C=O^{L}), 157.2 (*i*-CO; Ar^{L} and Ar^{U}), 131.0 (*i*-C; Ar, Ar^{L} and Ar^{U}), 127.4[4] and 115.5[4] (8 × CH; Ar^{L} and Ar^{U}), 71.6 (CH_2O^{U}) and 70.9 (1C, quintet, $^{1}J_{C,D} = 21.5$ Hz, CD_2O^{L}), 54.8 (CHN^{U}) and 54.6 (CHN^{L}). (found M^{U+}, 179.0574; $C_9H_9NO_3$ requires 179.0577; and found M^{L+}, 181.0700; $C_9H_7D_2NO_3$ requires 181.0702); ν_{max} (DMSO)/cm^{-1} 2265 (CD), 2221 (CD) and 1752 (C=O); {$[\alpha]_D^{20} = \sim 0.0$ (*c* 0.45, DMSO)}. Proton NMR spectroscopy shifts: negative isotope shift at 4.85 ppm (CHN) is 0.0138 ppm (5.52 Hz at 400 MHz). Carbon NMR spectroscopy shifts: (a) negative isotopic shift at 71.6 ppm (CH_2O) was 0.680 ppm (68.4 Hz at 100.6 MHz); (c) negative isotopic shift at 55.8 ppm (CHN) was 0.183 ppm (18.4 Hz at 100.6 MHz).

4.15. 4-Phenyl-5,5-dideuterio-3-benzoyl oxazolidin-2-one (*S*)-[D$_2$]-22 and 4-phenyl-3-benzoyl-oxazolidin-2-one (*R*)-22

n-BuLi (0.55 ml, 2.5 M in hexane, 1.36 mmol) was added to a stirred solution of oxazolidinone (*R*)-**6** (0.1 g, 0.62 mmol) and (*S*)-[D$_2$]-**6** (0.1 g, 0.62 mmol) in THF at −78 °C. After stirring for 1 h, a solution of benzoyl chloride (0.21 g, 1.48 mmol) in THF (5 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. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (1:1) to give an inseparable mixture of oxazolidinones (*R*)-**22** and (*S*)-[D$_2$]-**22** (0.142 g, 43%) as a white solid; R_f [diethyl ether/petroleum ether (1:1)] 0.69; mp = 175–176 °C (unlabelled (*rac*)-**22**; mp = 174–176 °C); $[\alpha]_D^{20} = \sim 0.0$ (*c* 1.0, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2410 (CD), 2305 (CD), 1768 (C=O) and 1695 (C=O); δ_H (400 MHz; $CDCl_3$) 7.64 (4H, dd, *J* 8.2 and 2.1, 4 × CH; *C*(2)–PhCO^{U} and *C*(2)–PhCO^{L}); 7.47 (2H, tt, *J* 7.5 and 1.2, 2 × CH; *C*(4)–PhCO^{U} and *C*(4)–PhCO^{U}), 7.38–7.27 (14H, m, 14 × CH; Ph^{U}, Ph^{L}, PhCO^{U} and PhCO^{L}), 5.57 (1H, dd, *J* 8.8 and 7.3, CHN^{U}), 5.56 (1H, s, CHN^{L}), 4.71 (2H, t, *J* 8.8, $CH_AH_BO^{U}$), 4.26 (1H, t, *J* 8.8 and 7.2, $CH_AH_BO^{U}$); δ_C (100 MHz; $CDCl_3$) 169.2 (NC=O^{U} and NC=O^{L}), 153.6 (OC=O^{U} and OC=O^{L}), 137.6 (*i*-C; Ph^{U} and Ph^{L}), 132.8 (*i*-C; Ph), 132.7,[1] 129.3,[2] 129.2,[2] 128.9,[1] 127.9[2] and 126.3[2] (20 × CH; 2 × Ph^{U} and 2 × Ph^{L}), 69.8 (CH_2O^{U}), 69.2 (1C, quintet, $^{1}J_{C,D} = 23.0$ Hz, CD_2O^{L}), 58.7 (CHN^{U}) and 58.6 (CHN^{L}).

Isotopic shifts by NMR spectroscopy. Proton NMR shifts: negative Isotopic shift at 5.57 ppm was 0.0110 ppm (4.4 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 69.8 ppm (CD_2O) was 0.5276 ppm (53.0 Hz at 100.6 MHz); (b) negative isotopic shift at 58.7 ppm (CHN) was 0.1759 ppm (17.6 Hz at 100.6 MHz). (found $M^{U}NH_4^{+}$, 285.1235; $C_{16}H_{17}N_2O_3^{+}$ requires 285.1234; and found $M^{L}NH_4^{+}$, 287.1360; $C_{16}H_{15}D_2N_2O_3^{+}$ requires 287.1359).

4.16. 4-Phenyl-3-benzoyl-oxazolidin-2-one (*R*)-22

In the same way as oxazolidinone **22**, *n*-BuLi (0.56 ml, 2.5 M in hexane, 1.4 mmol), oxazolidinone (*R*)-**6** (0.21 g, 1.28 mmol) and benzoyl chloride (0.22 g, 1.54 mmol) in THF (5 ml), gave oxazolidinone (*R*)-**22** (0.17 g, 50%) as a white powder; R_f [diethyl ether/petroleum ether (1:1)] 0.69; mp = 180–183 °C; {lit.[25] 187–188 °C} $[\alpha]_D^{20} = -91.8$ (*c* 0.73, $CHCl_3$) {lit.[25] −75.9 (*c* 0.94, ethyl acetate)}; ν_{max} ($CHCl_3$)/cm^{-1} 1769 (C=O) and 1697 (C=O); δ_H (400 MHz; $CDCl_3$) 7.64 (2H, dd, *J* 8.2 and 2.1, 2 × CH; *C*(2)–PhCO); 7.48 (1H, tt, *J* 7.5 and 1.2, 1 × CH; *C*(4)–PhCO), 7.38–7.26 (7H, m, 7 × CH; Ph and PhCO), 5.57 (1H, dd, *J* 8.8 and 7.2, CHN), 4.71 (1H, t, *J* 8.8, CH_AH_BO), 4.25 (1H, t, *J* 8.8 and 7.2, CH_AH_BO), δ_C (100 MHz; $CDCl_3$) 169.2 (NC=O), 153.8 (OC=O), 137.6 (*i*-C; Ph), 132.8 (*i*-C; Ph), 132.7,[1] 129.3,[2] 129.2,[2] 128.9,[1] 127.9[2] and 126.3[2] (10 × CH; 2 × Ph), 69.8 (CH_2O) and 58.7 (CHN) (found MNH_4^{+}, 285.1236; $C_{16}H_{17}N_2O_3^{+}$ requires 285.1234).

4.17. 4-Phenyl-5,5-dideuterio-3-benzoyl oxazolidin-2-one (*S*)-[D$_2$]-22

In the same way as oxazolidinone **22**, *n*-BuLi (0.56 ml, 2.5 M in hexane, 1.4 mmol), oxazolidinone (*S*)-[D$_2$]-**6** (0.21 g, 1.28 mmol) and benzoyl chloride (0.22 g, 1.54 mmol) in THF (5 ml), gave the oxazolidinone (*S*)-[D$_2$]-**22** (0.21 g, 61%) as a white solid; R_f [diethyl ether/petroleum ether (1:1)] 0.69; mp = 180–182 °C {lit.[25] unlabelled 187–188 °C}; $[\alpha]_D^{20} = +77.7$ (*c* 0.4, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2410 (CD), 2305 (CD), 1786 (C=O) and 1692 (C=O); δ_H (400 MHz; $CDCl_3$) 7.64 (2H, dd, *J* 8.2 and 1.2, 2 × CH; *C*(2)–PhCO); 7.48 (1H, tt, *J* 7.5 and 1.2, 1 × CH; *C*(4)–PhCO), 7.42–7.24 (7H, m, 7 × CH; Ph and PhCO) and 5.57 (1H, s, CHN); δ_C (100 MHz; $CDCl_3$) 169.2 (NC=O), 153.6 (OC=O), 137.6 (*i*-C; Ph), 132.8 (*i*-C; Ph), 132.7,[1] 129.3,[2] 129.2,[2] 128.9,[1] 127.9[2] and 126.3[2] (10 × CH; 2 × Ph), 69.8 (1C, quintet, $^{1}J_{C,D} = 23.0$ Hz; CD_2O) and 58.5 (CHN) (found MNH_4^{+}, 287.1364; $C_{16}H_{15}D_2N_2O_3^{+}$ requires 287.1359).

4.18. (±)-Pentafluorophenyl 2-phenylpropionate *rac*-27

2-Phenylpropionic acid *rac*-**23** (5.00 g, 33.32 mmol) was added to a stirred solution of *N*,*N*′-dicyclohexylcarbodiimide (DCC) (7.58 g, 36.73 mmol) in dichloromethane (20 ml) and stirred for 10 min. A solution of pentafluorophenol (6.15 g, 33.43 mmol) in dichloromethane (20 ml) was slowly added, and the resulting solution was stirred for 12 h. The resulting precipitate (*N*,*N*′-dicyclohexylurea) was filtered off (using suction filtration). Water (30 ml) was added and the solution was extracted with dichloromethane (3 × 50 ml) and dried (over $MgSO_4$). The combined organic layers were evaporated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel eluting with light petroleum (40–60 °C)/diethyl ether (9:1) to give pentafluorophenyl 2-phenylpropionate *rac*-**27** (9.71 g, 92%) as a white needle-like solid; R_f [light petroleum (40–60 °C)/diethyl ether (9:1)] 0.63; mp 27–28 °C; ν_{max} (film)/cm^{-1} 1784 (C=O); δ_H (270 MHz; $CDCl_3$) 7.41–7.28 (5H, m, 5 × CH; Ph), 4.07 (1H, q, *J* 7.2, CH_3CH) and 1.64 (3H, d, *J* 7.2, CH_3CH); δ_C (100 MHz; $CDCl_3$) 170.6 (OC=O), 141.1 (142.40 and 139.90, 2C, ddt, $^{1}J_{C,F} = 251.3$ Hz, $^{2}J_{C,F} = 12.2$ Hz and $^{3}J_{C,F} = 3.8$ Hz, C(2)–F), 139.4 (140.70 and 138.18, 1C, dtt, $^{1}J_{C,F} = 253.2$ Hz, $^{2}J_{C,F} = 13.4$ Hz and

$^3J_{C,F} = 4.2$ Hz, C(4)–F), 138.7 (*i*-C; Ph), 137.8 (139.05 and 136.58, 2C, dtdd, $^1J_{C,F} = 249.1$ Hz, $^2J_{C,F} = 14.5$ Hz, $^3J_{C,F} = 5.7$ Hz and $^4J_{C,F} = 3.1$ Hz, C(3)–F), 128.9, 127.8 and 127.5 (3 × CH; Ar, × CH; Ph), 125.2 (1C, tdt, $^2J_{C,F} = 14.2$ Hz, $^4J_{C,F} = 4.2$ Hz and $^3J_{C,F} = 2.0$ Hz, *i*-CO; OC_6F_5), 45.1 (PhCH) and 18.5 (CH_3CH); δ_F (378 MHz; $CDCl_3$) −152.6 (2F, d, $^3J_{F,F}$ 20.9, F_{ortho}), −157.9 (1F, t, $^3J_{F,F}$ 20.9, F_{para}) and −162.3 (2F, t, $^3J_{F,F}$ 20.9, F_{meta}) (found M^+, 316.0514. $C_{15}H_9F_5O_2$ requires M^+, 316.0517).

4.19. (±)-Pentafluorophenyl 2-phenylbutyrate *rac*-28

In the same way as the active ester *rac*-**27**, 2-phenylbutyric acid *rac*-**24** (5.0 g, 30.4 mmol), DCC (6.91 g, 33.4 mmol) and pentafluorophenol (5.6 g, 30.4 mmol) in dichloromethane (40 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/diethyl ether (9:1) gave, pentafluorophenyl 2-phenylbutyrate *rac*-**28** (7.2 g, 72%) as a white needle-like solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.70; mp 41–43 °C; ν_{max} ($CHCl_3$)/cm^{-1} 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.41–7.27 (5H, m, 5 × CH; Ph), 3.83 (1H, t, *J* 7.7, CHO), 2.25 (1H, ddq, 13.7, 7.7 and 7.5, $CH_AH_BCH_3$), 1.95 (1H, ddq, 13.7, 7.7 and 7.5, $CH_AH_BCH_3$), 1.01 (3H, t, *J* 7.5, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.1 (OC=O), 141.2 (142.43 and 139.93, 2C, ddtd, $^1J_{C,F} = 251.3$ Hz, $^2J_{C,F} = 11.9$ Hz, $^3J_{C,F} = 3.4$ Hz and $^4J_{C,F} = 3.4$ Hz, C(2)–F), 139.5 (140.72 and 138.24, 1C, dtt, $^1J_{C,F} = 252.8$ Hz, $^2J_{C,F} = 13.9$ Hz and $^3J_{C,F} = 3.8$ Hz, C(4)–F), 137.9 (139.14 and 136.60, 2C, dtdd, $^1J_{C,F} = 254.3$ Hz, $^2J_{C,F} = 14.2$ Hz, $^3J_{C,F} = 4.9$ Hz and $^4J_{C,F} = 2.6$ Hz, C(3)–F), 137.3 (*i*-C; Ph), 128.3, 127.9 and 127.8 (3 × CH; Ph), 125.2 (1C, tdt, $^2J_{C,F} = 14.2$ Hz, $^4J_{C,F} = 4.4$ Hz and $^3J_{C,F} = 2.2$ Hz, *i*-CO; OC_6F_5), 52.8 (PhCH), 26.7 (CH_2) and 11.9 (CH_3); δ_F (378 MHz; $CDCl_3$) −152.4 (2F, d, $^3J_{F,F}$ 17.1, F_{ortho}), −157.9 (1F, t, $^3J_{F,F}$ 21.9, F_{para}) and −162.3 (2F, dd, $^3J_{F,F}$ 21.9 and 17.1, F_{meta}) (found M, 330.0677; $C_{16}H_{11}F_5O_2$ requires 330.0674).

4.20. (+)-Pentafluorophenyl 2-phenylbutyrate (*R*)-28

In the same way as the active ester *rac*-**27**, (+)-2-phenylbutyric acid (*S*)-**24**, DCC (6.91 g, 33.4 mmol) and pentafluorophenol (5.6 g, 30.4 mmol) gave, pentafluorophenyl-2-phenylbutyrate (*R*)-**28** (7.58 g, 76%) as an oil; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.78; $[\alpha]_D^{20} = +69.5$ (*c* 5.3, $CHCl_3$) {for (*S*)-**28**; $[\alpha]_D^{20} = -77.4$ (*c* 34.8, $CHCl_3$)}; ν_{max} ($CHCl_3$)/cm^{-1} 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.41–7.27 (5H, m, 5 × CH; Ph), 3.83 (1H, t, *J* 7.7, CHO), 2.25 (1H, ddq, 13.7, 7.7 and 7.5, $CH_AH_BCH_3$), 1.95 (1H, ddq, 13.7, 7.7 and 7.5, $CH_AH_BCH_3$), 1.01 (3H, t, *J* 7.5, CH_2CH_3); δ_C (100 MHz; $CDCl_3$) 170.1 (OC=O), 141.2 (142.43 and 139.93, 2C, dddt, $^1J_{C,F} = 251.3$ Hz, $^2J_{C,F} = 11.9$ Hz, $^3J_{C,F} = 3.4$ Hz and $^4J_{C,F} = 3.4$ Hz, C(2)–F), 139.5 (140.72 and 138.24, 1C, dtt, $^1J_{C,F} = 252.8$ Hz, $^2J_{C,F} = 13.9$ Hz and $^3J_{C,F} = 3.8$ Hz, C(4)–F), 137.9 (139.14 and 136.60, 2C, dtdd, $^1J_{C,F} = 254.3$ Hz, $^2J_{C,F} = 14.2$ Hz, $^3J_{C,F} = 4.9$ Hz and $^4J_{C,F} = 2.6$ Hz, C(3)–F), 137.3 (*i*-C; Ph), 128.3, 127.9 and 127.8 (3 × CH; Ph), 125.2 (1C, tdt, $^2J_{C,F} = 14.2$ Hz, $^4J_{C,F} = 4.4$ Hz and $^3J_{C,F} = 2.2$ Hz, *i*-CO; OC_6F_5), 52.8 (PhCH), 26.7 (CH_2) and 11.9 (CH_3); δ_F (378 MHz; $CDCl_3$) −152.4 (2F, d, $^3J_{F,F}$ 17.1, F_{ortho}), −157.9 (1F, t, $^3J_{F,F}$ 21.9, F_{para}) and −162.3 (2F, dd, $^3J_{F,F}$ 21.9 and 17.1, F_{meta}) (found M, 330.0677; $C_{16}H_{11}F_5O_2$ requires 330.0674).

4.21. (±)-Pentafluorophenyl 2-tolylpropionate *rac*-29

In the same way as the active ester *rac*-**27**, 2-tolylpropionic acid *rac*-**25** (2.19 g, 13.3 mmol), DCC (3.04 g, 14.7 mmol) and pentafluorophenol (2.51 g, 13.6 mmol) in dichloromethane (20 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/diethyl ether (9:1) gave, pentafluorophenyl 2-tolylpropionate *rac*-**29** (2.85 g, 65%) as an oil; R_f [light petroleum (40–60 °C)/diethyl ether (9:1)] 0.65; ν_{max} (film)/cm^{-1} 1785 (C=O); δ_H (270 MHz; $CDCl_3$) 7.24 (2H, d, *J* 8.2, 2 × CH; Ar), 7.18 (2H, d, *J* 8.2, 2 × CH; Ar), 4.03 (1H, q, *J* 7.2, CH_3CH), 2.34 (3H, s, CH_3; Ar) and 1.62 (3H, d, *J* 7.2, CH_3CH); δ_C (100 MHz; $CDCl_3$) 170.6 (OC=O), 141.1 (142.51 and 139.89, 2C, ddt, $^1J_{C,F} = 251.6$ Hz, $^2J_{C,F} = 11.9$ Hz and $^3J_{C,F} = 4.6$ Hz, C(2)–F), 139.4 (140.63 and 138.12, 1C, dtt, $^1J_{C,F} = 252.8$ Hz, $^2J_{C,F} = 13.4$ Hz and $^3J_{C,F} = 3.8$ Hz, C(4)–F), 137.8 (139.07 and 136.56, 2C, dtdd, $^1J_{C,F} = 252.8$ Hz, $^2J_{C,F} = 12.1$ Hz, $^3J_{C,F} = 5.3$ Hz and $^4J_{C,F} = 3.1$ Hz, C(3)–F), 137.4 and 135.8 (2 × *i*-C; Ar), 129.5 and 127.2 (2 × CH; Ar), 125.2 (1C, tdt, $^2J_{C,F} = 14.3$ Hz, $^4J_{C,F} = 4.6$ Hz and $^3J_{C,F} = 2.3$ Hz, *i*-CO; OC_6F_5), 44.6 (PhCH), 20.8 (CH_3; Ar) and 18.4 (CH_3CH) (found M^+, 330.0671; $C_{16}H_{11}F_5O_2$ requires 330.0674).

4.22. (±)-Pentafluorophenyl 2-(4-*iso*butylphenyl)propionate *rac*-30

In the same way as the active ester (*rac*)-**27**, 2-(4-*iso*butylphenyl)propionic acid *rac*-**26** (5 g, 24.3 mmol), DCC (5.50 g, 26.7 mmol) and pentafluorophenol (4.65 g, 25.5 mmol) in dichloromethane (100 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/diethyl ether (9:1), pentafluorophenyl 2-(4-*iso*butylphenyl)propionate *rac*-**30** (6.78 g, 75%) as a white needle-like solid; mp = 48–49 °C; R_f [light petroleum (40–60 °C)/ether (9:1)] 0.63; ν_{max} ($CHCl_3$)/cm^{-1} 1782 (CO); δ_H (270 MHz; $CDCl_3$) 7.26 (2H, dt, *J* 8.2 and 2.2, 2 × CH; Ar), 7.14 (2H, dt, *J* 8.2 and 2.2, 2 × CH; Ar), 4.04 (1H, q, *J* 7.2, CHCO), 2.46 (2H, d, *J* 7.2, CH_2CH), 1.92–1.80 (1H, m, $CH(CH_3)_2$), 1.62 (3H, d, *J* 7.2, CH_3CHCO), 0.99 (3H, d, *J* 6.7, $(CH_3)_ACH(CH_3)_B$) and 0.88 (3H, d, *J* 6.7, $(CH_3)_BCH(CH_3)_A$); δ_C (100 MHz; $CDCl_3$) 170.3 (OC=O), 140.8 (*i*-C; Ar), 141.2 (142.92 and 139.42, 2C, ddt, $^1J_{C,F} = 251.3$ Hz, $^2J_{C,F} = 11.9$ Hz and $^3J_{C,F} = 4.2$ Hz, C(2)–F), 138.9 (140.18 and 137.66, 1C, dtt, $^1J_{C,F} = 253.2$ Hz, $^2J_{C,F} = 13.8$ Hz and $^3J_{C,F} = 3.8$ Hz, C(4)–F), 137.3 (138.61 and 136.08, 2C, dtdd, $^1J_{C,F} = 254.7$ Hz, $^2J_{C,F} = 14.5$ Hz, $^3J_{C,F} = 5.3$ and $^4J_{C,F} = 3.0$ Hz, C(3)–F), 135.5 (*i*-C; Ar), 129.1 and 126.7 (2 × CH; Ar), 124.7 (1C, tdt, $^2J_{C,F} = 14.2$ Hz, $^4J_{C,F} = 4.6$ Hz and $^3J_{C,F} = 2.3$ Hz, *i*-CO; OC_6F_5), 44.5 (CH_2; Ar), 44.4 (PhCH), 29.7 ($CHCH_2$), 21.9 ($CH(CH_3)_2$) and 18.0 (CH_3CH) (found M, 372.1144; $C_{19}H_{17}F_5O_2$ requires 372.1143).

4.23. (+)-Pentafluorophenyl-2-(6-methoxy-naphthalene-2-yl)propionate (*S*)-35

In the same way as the active ester *rac*-**27**, (*S*)-(+)-6-methoxy-(2-naphthyl)propionic acid (5.0 g, 21.7 mmol), DCC (4.93 g, 23.9 mmol) and pentafluorophenol (4.0 g, 21.7 mmol) gave, pentafluorophenyl-2-(6-methoxy-naphthalene-2-yl)propionate (*S*)-**35** (7.24 g, 84%) as a white powder; mp = 78–80 °C; R_f [light petroleum (40–60 °C)/ether (1:1)] 0.65; $[\alpha]_D^{20} = +93.6$ (*c* 5.6, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 1781 (C=O); δ_H (250 MHz; $CDCl_3$) 7.76–7.13 (6H, m, 6 × CH; Ar), 4.38 (1H, q, *J* 7.2, C*H*CH_3) 3.91 (3H, s, CH_3) and 1.71 (3H, d, *J* 7.2, CH_3CH); δ_C (100 MHz; $CDCl_3$) 170.7 (C=O), 157.9 (*i*-CO; Ar), 141.0 (142.32 and 139.82.67, 2C, ddt, $^1J_{C,F} = 249.8$ Hz, $^2J_{C,F} = 12.2$ Hz and $^3J_{C,F} = 4.6$ Hz, C(2)–F), 139.3 (140.63 and 138.11, 1C, dtt, $^1J_{C,F} = 252.1$ Hz, $^2J_{C,F} = 13.0$ Hz and $^3J_{C,F} = 4.5$ Hz, C(4)–F), 137.8 (139.04 and 136.54, 2C, dtdd, $^1J_{C,F} = 250.6$ Hz, $^2J_{C,F} = 13.8$ Hz, $^3J_{C,F} = 5.3$ and $^4J_{C,F} = 3.0$ Hz, C(3)–F), 133.9, 133.7 and 128.9 (3 × *i*-C; Ar), 129.3, 127.5, 126.2, 125.7, 119.3 and 105.6 (6 × CH; Ar), 125.2 (1C, m, *i*-CO; OC_6F_5), 55.3 (OCH_3), 45.9 (Ar*C*H) and 18.5 (CH*C*H_3); δ_F (378 MHz; $CDCl_3$) −152.5 (2F, d, $^3J_{F,F}$ 17.0, F_{ortho}), −157.9 (1F, t, $^3J_{F,F}$ 21.6, F_{para}) and −162.3 (2F, dd, $^3J_{F,F}$ 21.6 and 17.0, F_{meta}) (found M^+, 396.0783; $C_{20}H_{13}F_5O_3^+$ requires 396.0779).

4.24. Synthesis of (4*RS*,2*RS*)-3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *anti*-31 and (4*RS*,2*RS*)-3-(2-phenylpropionyl)-4-phenyl-oxazolidin-2-one *syn*-31

n-BuLi (4.86 ml, 3 M in hexane, 14.6 mmol) was added to a stirred solution of oxazolidinone *rac*-**6** (2 g, 12.2 mmol) in THF at −78 °C. After stirring for 1 h, a solution of pentafluorophenyl 2-phenylpropionate (*rac*)-**27** (4.99 g, 15.8 mmol) in THF (5.0 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 separable mixture of two pairs of diastereoisomers (ratio: *syn*-:*anti*-97:3) of oxazolidinones *syn*-**31** and *anti*-**31**. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (1:1) to give oxazolidinone *anti*-**31** (71 mg, ~2%) as white needle-like crystals; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.40; mp 106–108 °C; ν_{max} ($CHCl_3$); cm^{-1} 1780 (C=O) and 1700 (C=O); δ_H (270 MHz; $CDCl_3$) 7.39–7.26 (10H, m, 10 × CH; 2 × Ph), 5.32 (1H, dd, *J* 8.8 and 3.2, CHN), 5.11 (1H, q, *J* 7.2, PhCH), 4.55 (1H, t, *J* 8.8, C$H_A$$H_B$O), 4.21 (1H, dd, *J* 8.8 and 3.2, CH_AH_BO) and 1.40 (3H, d, *J* 7.2, CH_3CH); δ_C (62.9 MHz; $CDCl_3$) 174.1 (NC=O), 152.9 (OC=O), 140.2 (*i*-C; Ph_A), 139.4 (*i*-C; Ph_B), 129.3, 128.7, 128.6, 128.2, 127.3 and 125.8 (6 × CH; Ph_A and Ph_B), 69.7 (CH_2O), 58.1 (CHN), 43.2 (PhCH) and 19.4 (CH_3) (found MH^+, 296.1282; $C_{18}H_{18}NO_3^+$ requires 296.1287); and oxazolidinone *syn*-**31** (2.51 g, 70%) as a white solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.30; mp 124–125 °C; ν_{max} ($CHCl_3$)/cm^{-1} 1780 (C=O) and 1705 (C=O); δ_H (270 MHz; $CDCl_3$) 7.29–7.21 (10H, m, 10 × CH; 2 × Ph), 5.45 (1H, dd, *J* 9.0 and 5.1, CHN), 5.09 (1H, q, *J* 6.9, PhCH), 4.63 (1H, t, *J* 9.0, C$H_A$$H_B$O), 4.08 (1H, dd, *J* 9.0 and 5.1, CH_AH_BO) and 1.39 (3H, d, *J* 6.9, CH_3CH); δ_C (62.9 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, 128.7, 128.5, 128.2, 127.1 and 125.9 (6 × CH; Ph_A and Ph_B), 69.6 (CH_2O), 57.9 (CHN), 43.9 (PhCH) and 18.6 (CH_3) (found MH^+, 296.1286; $C_{15}H_{18}NO_3^+$ requires 296.1287).

4.25. Synthesis of (4*RR*,2*SS*)-4-phenyl-3-[2′-phenylbutyryl]oxazolidin-2-one *anti*-32 and (4*RR*,2*RR*)-4-phenyl-3-[2′-phenylbutyryl]oxazolidin-2-one *syn*-32

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (1.34 ml, 2.5 M in hexanes, 3.37 mmol), oxazolidinone (*rac*)-**6** (0.4 g, 3.06 mmol) and pentafluorophenyl 2-phenylbutyrate (*rac*)-**28** (1.01 g, 3.06 mmol) in THF (5 ml), gave a separable pair of diastereoisomers (ratio: *syn*-:*anti*->98:2). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give the oxazolidinone *anti*-**32** (~9 mg, 1%) as a viscous oil; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.55; ν_{max} ($CHCl_3$)/cm^{-1} 1780 (C=O) and 1703 (C=O); δ_H (250 MHz; $CDCl_3$) 7.44–7.21 (10H, m, 10 × CH; 2 × Ph), 5.34 (1H, dd, *J* 8.7 and 3.4, CHN), 4.96 (1H, t, *J* 7.7, PhCH), 4.54 (1H, br t, *J* 8.7, C$H_A$$H_B$O), 4.20 (1H, dd, *J* 8.7 and 3.4, CH_AH_BO), 2.01 (1H, ddq, *J* 13.6, 7.7 and 7.3, C$H_A$$H_B$$CH_3$), 1.74 (1H, ddq, *J* 13.6, 7.7 and 7.3, $CH_AH_B$$CH_3$) and 0.76 (3H, t, *J* 7.4, C$H_3$$CH_2$); δ_C (62.9 MHz; $CDCl_3$) 173.7 (NC=O), 153.4 (OC=O), 139.5 (*i*-C; Ph), 138.6 (*i*-C; Ph), 129.1, 128.8, 128.7, 128.5, 127.3 and 125.8 (6 × CH; Ph_A and Ph_B), 69.4 (CH_2O), 58.1 (CHN), 50.4 (PhCH), 27.7 (CH_2Ph) and 12.0 (CH_3) (found MH^+, 310.1430; $C_{19}H_{20}NO_3$ requires 310.1443) and oxazolidinone *syn*-**32** (0.63 g, 69%) as a viscous oil; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.35; ν_{max} (film)/cm^{-1} 1780 (C=O) and 1700 (C=O); δ_H (250 MHz; $CDCl_3$) 7.26–6.87 (10H, m, 10 × CH; 2 × Ph), 5.46 (1H, dd, *J* 8.9 and 5.0, CHN), 4.90 (1H, t, *J* 7.5, CHCO), 4.63 (1H, t, *J* 8.9, C$H_A$$H_B$O), 4.07 (1H, dd, *J* 8.9 and 5.0, CH_AH_BO), 1.95 (1H, ddq, 13.6, 7.5 and 7.3, C$H_A$$H_B$$CH_3$), 1.65 (1H, ddq, 13.6, 7.5 and 7.3, $CH_AH_B$$CH_3$) and 0.87 (3H, t, *J* 7.4, CH_3CH_2); δ_C (62.9 MHz; $CDCl_3$) 173.2 (NC=O), 153.2 (OC=O), 138.4 (*i*-C; Ph_A), 138.1 (*i*-C; Ph_B), 128.9,[2] 128.8,[2] 128.4,[1] 128.3,[2] 127.2[1] and 125.7[2] (6 × CH; Ph_A and Ph_B), 69.6 (CH_2O), 57.8 (CHN), 51.2 (PhCH), 26.3 (CH_2Ph) and 12.0 (CH_3) (found MH^+, 310.1437; $C_{19}H_{20}NO_3$ requires 310.1443).

4.26. Synthesis of (4*RR*,2*RR*)-3-[2′-(4-methylphenyl)propionyl]-4-phenyl-oxazolidin-2-one *anti*-33 and (4*RR*,2*SS*)-3-[2′-(4-methylphenyl)propionyl]-4-phenyl-oxazolidin-2-one *syn*-33

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.71 ml, 2 M in hexane, 1.42 mmol), oxazolidinone *rac*-**6** (0.2 g, 1.22 mmol) and pentafluorophenyl 2-(4-methylphenyl)propionate *rac*-**29** (0.46 g, 1.39 mmol) in THF (5 ml), gave a separable pair of diastereoisomers (ratio: *syn*-**33**:*anti*-**33** => 95:5). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give oxazolidinone *anti*-**33** (8 mg, ~2%) as an oil; R_f [light petroleum

(40–60 °C)/diethyl ether (1:1)] 0.50; ν_{max} ($CHCl_3$)/cm^{-1} 1779 (C=O) and 1703 (C=O); δ_H (270 MHz; $CDCl_3$) 7.35–7.23 (5H, m, 5 × CH; Ph), 7.18 (2H, dt, *J* 8.0 and 2.0, 2 × CH; Ar), 7.05 (2H, br d, *J* 8.0, 2× CH; Ar), 5.33 (1H, dd, *J* 8.9 and 2.9, CHN), 5.08 (1H, q, *J* 7.1, ArCH), 4.54 (1H, t, *J* 8.9, CH_AH$_B$O), 4.20 (1H, dd *J* 8.9 and 3.2, CH$_A$$H_B$O), 2.33 (3H, s, CH_3; Ar) and 1.39 (3H, d, *J* 7.1, CH_3CHAr); δ_C (100.6 MHz; $CDCl_3$) 174.2 (NC=O), 153.2 (OC=O), 140.6 (*i*-C; Ar), 139.4 (*i*-C; Ar), 137.2 (*i*-C; Ar), 136.9 (*i*-C; Ph), 129.3 and 128.0 (2 × CH; Ar), 128.8, 128.5 and 125.8 (3 × CH; Ph), 69.7 (CH_2O), 58.1 (CHN), 42.8 (ArCH), 21.0 (CH_3; Ar) and 19.4 (*C*H_3CH) (found MNH_4^+, 327.1700; $C_{19}H_{23}N_2O_3^+$ requires 327.1709); and oxazolidinone *syn*-**33** (0.24 g, 62%) as a white solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.30; mp 102–104 °C [(*S*,*R*)-**33**; mp 107–109 °C]; ν_{max} ($CHCl_3$)/cm^{-1} 1780 (C=O) and 1700 (C=O); δ_H (270 MHz; $CDCl_3$) 7.28–7.15 (3H, m, 3 × CH; Ph and/or Ar), 7.10–6.90 (6H, m, 6 × CH, Ph and Ar), 5.44 (1H, dd, *J* 8.9 and 5.0, CHN), 5.05 (1H, q, *J* 6.9; ArCH), 4.63 (1H, t, *J* 8.9, CH_AH$_B$O), 4.07 (1H, dd, *J* 8.9 and 5.2, CH$_A$$H_B$O), 2.32 (3H, s, CH_3; Ar) and 1.34 (3H, d, *J* 6.9, CH_3CH); δ_C (100.6 MHz; $CDCl_3$) 173.8 (NC=O), 153.1 (OC=O), 138.7 (*i*-C; Ar), 136.9 (*i*-C; Ar), 136.5 (*i*-C; Ph), 129.3 and 127.3 (2 × CH; Ar), 129.2, 128.7 and 125.9 (3 × CH; Ph), 69.6 (CH_2O), 57.9 (CHN), 43.4 (ArCH), 22.6 (CH_3; Ar) and 19.4 (*C*H_3CH) (found MNH_4^+, 327.1701; $C_{19}H_{23}N_2O_3^+$ requires 327.1709).

4.27. Synthesis of (4*RR*,2*RR*)-3-[2′-(4-isobutylphenyl)propionyl]-4-phenyl-oxazolidin-2-one *anti*-34 and (4*RR*,2*SS*)-3-[2′-(4-isobutylphenyl)propionyl]-4-phenyl-oxazolidin-2-one *syn*-34

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.73 ml, 2 M in hexane, 1.46 mmol), oxazolidinone (*rac*)-**6** (0.21 g, 1.2 mmol) and pentafluorophenyl 2-(4-*iso*butylphenyl)propionate (*rac*)-**30** (0.53 g, 1.42 mmol) in THF (5 ml), gave a separable pair of diastereoisomers (ratio: *syn*-**34**:*anti*-**34** = 96:4). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give oxazolidinone *anti*-**34** (47 mg, ~1%) as an oil; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.62; mp 150–154 °C; [for (*R*,*R*)-*anti*-**34**; mp = 155–158 °C]; ν_{max} ($CHCl_3$)/cm^{-1} 1780 (C=O) and 1701 (C=O); δ_H (270 MHz; $CDCl_3$) 7.39–7.23 (7H, m, 7 × CH; Ar and Ph), 7.07 (2H, dt, *J* 8.2 and 1.9, 2 × CH, Ar), 5.33 (1H, dd, *J* 8.4 and 3.2, CHN), 5.10 (1H, q, *J* 7.1, ArCH), 4.55 (1H, t, *J* 8.9, CH_AH$_B$O), 4.20 (1H, dd *J* 8.9 and 3.2, CH$_A$$H_B$O), 2.42 (2H, d, *J* 7.2, CH_2), 1.88–1.78 (1H, m, C*H* (CH_3)$_2$), 1.39 (3H, d, *J* 7.1, CH_3CHAr) and 0.89 (6H, d, *J* 6.7, 2 × CH_3, CH_3^ACHCH_3^B); δ_C (100.6 MHz; $CDCl_3$) 173.9 (NC=O), 153.2 (OC=O), 140.6 (*i*-C; Ar), 138.3 (*i*-C; Ar), 137.0 (*i*-C; Ph), 129.3 and 128.0 (2 × CH; Ar), 128.8, 128.5 and 125.8 (3 × CH; Ph), 69.6 (CH_2O), 57.8 (CHN), 45.1 (*C*H(CH_3)$_2$), 43.3 (ArCH), 30.2 (CH_2), 22.4 (2C, s, *C*H_3^ACH*C*H_3^B) and 18.5 (*C*$H_3$$CH_2$) (found MH^+, 352.1913; $C_{22}H_{26}NO_3$ requires 352.1907); and oxazolidinone *syn*-**34** (0.24 g, 56%) as a white solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.43; mp 69–71 °C [for (*S*,*R*)-*syn*-**34**; mp = 97–99 °C]; ν_{max} ($CHCl_3$)/cm^{-1} 1779 (C=O) and 1705 (C=O); δ_H (270 MHz; $CDCl_3$) 7.28–7.15 (3H, m, 3 × CH; Ph and/or Ar), 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, ArCH), 4.63 (1H, t, *J* 9.0, CH_AH$_B$O), 4.06 (1H, dd, *J* 9.0 and 5.2, CH$_A$$H_B$O), 2.43 (2H, d, *J* 7.4, CH_2), 1.89–1.79 (1H, m, C*H*(CH_3)$_2$), 1.38 (3H, d, *J* 6.9, CH_3CH) and 0.90 (6H, d, *J* 6.7, 2 × CH_3, CH_3^ACHCH_3^B); δ_C (100.6 MHz; $CDCl_3$) 174.3 (NC=O), 153.3 (OC=O), 140.7 (*i*-C; Ar), 139.4 (*i*-C; Ar), 137.4 (*i*-C; Ph), 129.3 and 127.0 (2 × CH; Ar), 129.2, 128.7 and 125.8 (3 × CH; Ph), 69.7 (CH_2O), 58.1 (CHN), 45.1 (*C*H(CH_3)$_2$), 42.7 (ArCH), 30.2 (CH_2), 22.4 (2C, s, CH_3^ACH*C*H_3^B) and 19.4 (*C*$H_3$$CH_2$) (found MH^+, 352.1909; $C_{22}H_{26}NO_3$ requires 352.1907).

4.28. Parallel kinetic resolution of pentafluorophenyl 2-phenylpropionate *rac*-27 using a quasi-enantiomeric combination of oxazolidinones (*R*)-6 and (*S*)-[D$_2$]-6

n-BuLi (0.50 ml, 2.5 M in hexanes, 1.23 mmol) was added to a stirred solution of oxazolidinone (*R*)-**6** (99 mg, 0.60 mmol) and (*S*)-[D_2]-**6** (0.10 g, 0.60 mmol) in THF at −78 °C. After stirring for 1 h, a solution of pentafluorophenyl 2-phenyl-propionate (*rac*)-**27** (0.46 mg, 1.45 mmol) in THF (5.0 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 separable mixture of two pairs of diastereoisomers (ratio: *syn*-:*anti*- > 97:3) of oxazolidinones *syn*-**31** and *syn*-[D_2]-**31**, and *anti*-**31** and *anti*-[D_2]-**31**. The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (1:1) to give oxazolidinones *anti*-**31** and *anti*-[D_2]-**31** (11 mg, ~3%) [ratio 50:50 (±2%)] as a white solid; R_f [light petroleum/diethyl ether (1:1)] 0.62; mp = 94–96 °C; $[\alpha]_D^{20} = -0.5$ (*c* 0.1, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2364 (CD), 1780 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.35–7.15 (20H, m, 20 × CH, Ar^U, Ar^L, Ph^U and Ph^L), 5.27 (1H, dd, *J* 9.1 and 3.3, C*H*NCH_2^U), 5.26 (1H, s, CHNCD_2^L), 5.08 (2H, q, *J* 6.9, ArC*H*CH_3^U and ArC*H*CH_3^L), 4.89 (1H, t, *J* 8.9, CH_AH$_B$O^U), 3.97 (1H, dd, *J* 8.9 and 3.3, CH$_A$$H_B$O^U) and 1.34 (6H, d, *J* 6.9, ArCHCH_3^U and ArCHCH_3^L); δ_C (100 MHz; $CDCl_3$) 174.0 (NC=O^U and NC=O^L), 153.47 (OC=O^U and OC=O^L), 140.1 (*i*-C; Ph^U and Ph^L), 139.3 (2 × *i*-C; Ph^U and Ph^L), 129.2,[4] 128.7,[2] 128.5,[4] 128.1,[4] 127.2[2] and 125.7,[4] (20 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.7 (CH_2O^U), 58.0 (CHN^U), 57.9 (CHN^L), 43.2 (PhCH^U and PhCH^L), 19.3 (CH*C*H_3^U and CH*C*H_3^L) (found $M^UNH_4^+$, 313.1548; $C_{18}H_{21}NO_3$ requires 313.1547) and (found $M^UNH_4^+$, 315.1670; $C_{18}H_{29}D_2NO_3$ requires 325.1670). By mass spectrometry, found *anti*-**31**: *anti*-[D_2]-**31** ratio: 52:48. Proton NMR shift: negative isotopic shift at 5.27 ppm (CHN) was 0.0098 ppm (3.94 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 57.9 ppm (CHN) was 0.1757 ppm (17.6 Hz at 100.6 MHz); and *syn*-**31**:*syn*-[D_2]-**31** [ratio 52:48 (±2%)] (0.24 g, 70%); R_f [light petroleum/diethyl ether (1:1)] 0.43; mp = 106–108 °C; $[\alpha]_D^{20} = +1.8$ (*c* 4.6, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2360 (CD), 1780 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.25–7.09 (12H, m, 6 × CH,

Ph^U and Ph^L), 7.03–7.00 (4H, m, 2 × CH, Ar^U, Ar^L, Ph^U and Ph^L), 6.86–6.83 (4H, m, 2 × CH, Ar^U and Ar^L), 5.36 (1H, dd, *J* 9.1 and 5.1, C*H*NCH_2^U), 5.36 (1H, s, CHNCD_2^L), 5.02 (2H, q, *J* 7.0, ArC*H*CH_3^U and ArC*H*CH_3^L), 4.54 (1H, t, *J* 9.1, CH_AH_BO^U), 3.97 (1H, dd, *J* 9.1 and 5.1, CH_A H_BO^U) and 1.30 (6H, d, *J* 7.0, ArCHCH_3^U and ArCHCH_3^L); δ_C (100 MHz; $CDCl_3$) 173.5 (NC=O^U and NC=O^L), 153.0 (OC=O^U) and 152.9 (OC=O^L), 139.7 (*i*-C; Ph^U and Ph^L), 139.1 (2 × *i*-C; Ph^U and Ph^L), 128.7,[4] 128.4,[6] 128.0[4] 127.0[2] and 125.7[4] (20 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.4 (CH_2O^U), 68.8 (1C, quintet, *J* 22.6, CD_2O^L), 57.6 (CHN^U), 57.5 (CHN^L), 43.7 (PhCH^U and PhCH^L), 18.5 (CH*C*H_3^U and CH*C*H_3^L) (found $M^UNH_4^+$, 313.1543; $C_{18}H_{21}NO_3$ requires 313.1547 and found $M^LNH_4^+$, 315.1673; $C_{18}H_{29}D_2NO_3$ requires 325.1672). By mass spectrometry, found *syn*-**31**: *syn*-[D_2]-**31** ratio: 54:46. (By EI, found M^{U+}, 295.1199; $C_{18}H_{17}NO_3$ requires 295.15203 and found M^{L+}, 297.1325; $C_{18}H_{15}D_2NO_3$ requires 297.1332). Proton NMR shift: negative isotopic shift at 5.35 ppm (CHN) was 0.0098 ppm (3.92 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 153.0 ppm (*i*-C; Ph) was 0.011 ppm (1.15 Hz at 100.6 MHz); (b) negative isotopic shift at 69.4 ppm (CH_2O) was 0.645 ppm (64.9 Hz at 100.6 MHz); (c) negative isotopic shift at 57.5 ppm (CHN) was 0.1726 ppm (17.4 Hz at 100.6 MHz).

4.29. Parallel kinetic resolution of pentafluorophenyl 2-phenylbutyrate *rac*-28 using a quasi-enantiomeric combination of oxazolidinones (*R*)-6 and (*S*)-[D_2]-6

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.43 ml, 3 M in hexane, 1.3 mmol), oxazolidinone (*R*)-**6** (0.103 g, 0.63 mmol), oxazolidinone (*S*)-[D_2]-**6** (0.104 g, 0.63 mmol) and pentafluorophenyl 2-phenylbutyrate (*rac*)-**28** (0.45 g, 1.38 mmol) in THF (10 ml), gave a separable mixture of two pairs of diastereoisomers (ratio: *syn*-**32** and *syn*-[D_2]-**32**: *anti*-**32** and *anti*-[D_2]-**32** => 98:2). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give oxazolidinone *anti*-**32** and *anti*-[D_2]-**32** (<5 mg, 1%) [ratio 50:50 (±2%)] as a white solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.55; mp = 110–112 °C; $[\alpha]_D^{20} = \sim 0.0$ (*c* 0.9, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2306 (CD), 1781 (C=O) and 1701 (C=O); δ_H (400 MHz; $CDCl_3$) 7.45–7.15 (20H, m, 10 × CH, Ph^U and Ph^L), 5.36 (1H, dd, *J* 8.8 and 3.4, C*H*NCH_2^U), 5.34 (1H, s, CHNCD_2^L), 4.95 (2H, t, *J* 7.7, PhC*H*CH_2^U and PhC*H*CH_2^L), 4.57 (1H, t, *J* 8.8, CH_AH_BO^U), 4.21 (1H, dd, *J* 8.8 and 3.4, CH_AH_BO^U), 1.94 (2H, ddq, 13.6, 7.7 and 7.3, CH_AH_BCH_3^U and CH_AH_BCH_3^L), 1.64 (2H, 13.6, 7.7 and 7.3, CH_AH_BCH_3^U and CH_AH_BCH_3^L) and 0.78 (6H, t, *J* 7.5, CH_3CH_2^U and CH_3CH_2^L); δ_C (100 MHz; $CDCl_3$) 173.8 (NC=O^U and NC=O^L), 153.4 (OC=O^U and OC=O^L), 139.4 (*i*-C; Ph^U and Ph^L), 138.6 (2 × *i*-C; Ar^U and Ar^L), 129.3,[4] 128.9,[4] 128.8,[2] 128.6,[4] 127.4[2] and 125.9[4] (20 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.6 (CH_2O^U), 69.2 (1C, quintet, $^1J_{CD} = 22.9$ Hz, CD_2O^L), 58.2 (CHN^U), 57.9 (CHN^L), 50.4 ($ArCH^U$ and $ArCH^L$), 27.7 ($CH_3CH_2^U$ and $CH_3CH_2^L$) and 14.0 ($CH_3CH_2^U$ and $CH_3CH_2^L$); For *anti*-**32**; found MNH_4^+, 327.1700; $C_{19}H_{23}N_2O_3^+$ requires 327.1709, and *anti*-[D_2]-**32**; found MNH_4^+, 329.1831; $C_{19}H_{21}D_2N_2O_3^+$ requires 329.1834; isotopic shifts by NMR spectroscopy. By mass spectrometry, found *anti*-**32**: *anti*-[D_2]-**32** ratio: 51:49. Proton NMR shift: negative isotopic shift at 5.34 ppm (CHN) was 0.0103 ppm (4.10 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 69.6 ppm (CH_2O) was 0.410 ppm (41 Hz at 100.6 MHz); (b) negative isotopic shift at 58.2 ppm (CHN) was 0.168 ppm (16.91 Hz at 100.6 MHz); and the oxazolidinones *syn*-**32** and *syn*-[D_2]-**32** (0.34 g, 87%) [ratio 50:50 (±2%)] as a white solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.35; mp 69–72 °C; $[\alpha]_D^{20} = +1.1$ (*c* 6, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2310 (CD), 1780 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.28–7.15 (12H, m, 6 × CH, Ph^U and Ph^L), 7.10–7.08 (4H, m, 2 × CH, Ph^U and Ph^L), 6.90–6.85 (4H, m, 2 × CH, Ph^U and Ph^L), 5.48 (1H, dd, *J* 9.1 and 5.0, C*H*NCH_2^U), 5.46 (1H, s, CHNCD_2^L), 4.91 (2H, t, *J* 7.5, PhC*H*CH_2^U and PhC*H*CH_2^L), 4.63 (1H, t, *J* 9.0, CH_AH_BO^U), 3.97 (1H, dd, *J* 9.0 and 5.0, CH_AH_BO^U) and 1.95 (2H, ddq, 13.6, 7.5 and 7.3, CH_AH_BCH_3^U and CH_AH_BCH_3^L), 1.65 (2H, ddq, 13.6, 7.5 and 7.3, CH_AH_BCH_3^U and CH_AH_BCH_3^L) and 0.87 (6H, t, *J* 7.3, CH_3CH_2^U and CH_3CH_2^L); δ_C (100 MHz; $CDCl_3$) 172.8 (NC=O^U and NC=O^L), 153.0 (OC=O^U and OC=O^L), 138.2 (*i*-C; Ph^U), 138.1 (*i*-C; Ph^L), 137.9 (2 × *i*-C; Ar^U and Ar^L), 128.6,[4] 128.5,[4] 128.2,[4] 128.1,[2] 126.9[2] and 125.5[4] (20 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.3 (CH_2O^U), 68.7 (1C, quintet, $^1J_{CD} = 23.8$ Hz, CD_2O^L), 57.4 (CHN^U), 57.3 (CHN^L), 51.0 ($ArCH^U$ and $ArCH^L$), 26.0 ($CH_3CH_2^U$ and $CH_3CH_2^L$) and 18.3 ($CH_3CH_2^U$ and $CH_3CH_2^L$); For *syn*-**32**; found MH^+, 310.1436; $C_{19}H_{20}NO_3^+$ requires 310.1438; and *syn*-[D_2]-**32** found MH^+, 312.1563; $C_{19}H_{18}D_2NO_3^+$ requires 312.1563. By mass spectrometry, found *syn*-**32**: *syn*-[D_2]-**32** ratio: 52:48.

Isotopic shifts by NMR spectroscopy. Proton NMR shift: negative isotopic shift at 5.46 ppm (CHN) was 0.00985 ppm (3.94 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 138.1 ppm (*i*-C; Ph) was 0.0306 ppm (3.07 Hz at 100.6 MHz); (b) negative isotopic shift at 69.3 ppm (CH_2O) was 0.649 ppm (65.3 Hz at 100.6 MHz); (c) negative isotopic shift at 57.4 ppm (CHN) was 0.091 ppm (9.22 Hz at 100.6 MHz).

4.30. Parallel kinetic resolution of pentafluorophenyl 2-(4-methylphenyl)propionate *rac*-29 using a quasi-enantiomeric combination of oxazolidinones (*R*)-6 and (*S*)-[D_2]-6

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.43 ml, 3 M in hexane, 1.3 mmol), oxazolidinone (*R*)-**6** (0.104 g, 0.63 mmol), oxazolidinone (*S*)-[D_2]-**6** (0.104 g, 0.63 mmol) and pentafluorophenyl 2-(4-methylphenyl)propionate (*rac*)-**29** (0.51 g, 1.54 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/ether (7:3) a separable mixture of two pairs of diastereoisomers (ratio: *syn*-**33** and *syn*-[D_2]-**33**: *anti*-**33** and *anti*-[D_2]-**33** = 96:4). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give oxazolidinone *anti*-**33** and *anti*-[D_2]-**33** [ratio 51:49 (±2%)] (8 mg, ~2%) as a white solid; R_f [light petroleum/diethyl ether (1:1)] 0.50; mp = 80–82 °C; $[\alpha]_D^{20} =$

−0.5 (*c* 0.2, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2315 (CD), 1780 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.35–7.23 (10H, m, 5 × CH, Ph^U and Ph^L), 7.17 (4H, d, *J* 7.8, 4 × CH; Ar^U and Ar^L), 7.06 (4H, d, *J* 7.8, 4 × CH; Ar^U and Ar^L), 5.25 (1H, dd, *J* 8.9 and 3.2, $CHNCH_2^U$), 5.24 (1H, s, $CHNCD_2^L$), 5.02 (2H, q, *J* 6.9, $ArCHCH_3^U$ and $ArCHCH_3^L$), 4.48 (1H, t, *J* 8.9, $CH_AH_BO^U$), 4.15 (1H, dd, *J* 8.9 and 3.2, $CH_AH_BO^U$) and 2.25 (6H, s, $ArCH_3^U$ and $ArCH_3^L$) and 1.32 (6H, d, *J* 6.9, $ArCHCH_3^U$ and $ArCHCH_3^L$); δ_C (100 MHz; $CDCl_3$) 174.2 ($NC{=}O^U$ and $NC{=}O^L$), 153.3 ($OC{=}O^U$ and $OC{=}O^L$), 138.3 (2 × *i*-C; Ph^U and Ph^L), 137.1 (2 × *i*-C; Ar^U and Ar^L), 136.9 (2 × *i*-C; Ar^U and Ar^L), 129.3,[4] 129.2,[4] 128.7,[2] 128.0[4] and 125.8[4] (18 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.8 (CH_2O^U), 58.0 (CHN^U), 57.9 (CHN^L), 42.7 ($ArCH^U$ and $ArCH^L$), 19.3 ($ArCH_3^U$ and $ArCH_3^L$) and 14.1 (CH_3CH^U and CH_3CH^L); (found $M^UNH_4^+$, 327.1703; $C_{19}H_{23}N_2O_3$ requires 327.1700 and found $M^LNH_4^+$, 329.1830; $C_{19}H_{23}N_2O_3$ requires 327.1829). By mass spectrometry, found *anti*-**33**: *anti*-[D_2]-**33** ratio: 53:47. Proton NMR shift: negative isotopic shift at 5.25 ppm (CHN) was 0.0101 ppm (4.08 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 57.9 ppm (CHN) was 0.168 ppm (16.9 Hz at 100.6 MHz); and *syn*-**33**:*syn*-[D_2]-**33** [ratio 50:50 (±2%)] (0.27 g, 69%); R_f [light petroleum/diethyl ether (1:1)] 0.30; mp = 74–76 °C; $[\alpha]_D^{20} = +1.3$ (*c* 9.0, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2355 (CD), 1780 (C=O) and 1700 (C=O); δ_H (400 MHz; $CDCl_3$) 7.30–7.20 (6H, m, 6 × CH, Ph^U and Ph^L), 7.10–6.95 (12H, m, 12 × CH, Ph^U, Ph^L, Ar^U and Ar^L), 5.46 (1H, dd, *J* 9.0 and 5.2, $CHNCH_2^U$), 5.45 (1H, s, $CHNCD_2^L$), 5.09 (2H, q, *J* 6.9, $ArCHCH_3^U$ and $ArCHCH_3^L$), 4.61 (1, t, *J* 8.9, $CH_AH_BO^U$), 4.05 (1H, dd, *J* 8.9 and 5.2, $CH_AH_BO^U$) and 2.34 (6H, s, $ArCH_3^U$ and $ArCH_3^L$) and 1.30 (6H, d, *J* 6.9, $ArCHCH_3^U$ and $ArCHCH_3^L$); δ_C (100 MHz; $CDCl_3$) 173.6 ($NC{=}O^U$ and $NC{=}O^L$), 152.9 ($OC{=}O^U$ and $OC{=}O^L$), 138.2 (*i*-C; Ph^U), 138.1 (*i*-C; Ph^L), 136.7 (2 × *i*-C; Ar^U and Ph^L), 136.6 (2 × *i*-C; Ar^U and Ar^L), 129.9,[4] 128.6,[4] 128.2,[2] 127.8[4] and 125.7[4] (18 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.3 (CH_2O^U), 68.7 (1C, quintet, $^1J_{CD} = 24.5$ Hz, CD_2O^L), 57.5 (CHN^U), 57.4 (CHN^L), 43.0 ($ArCH^U$ and $ArCH^L$), 20.9 ($ArCH_3^U$ and $ArCH_3^L$) and 18.5 (CH_3CH^U and CH_3CH^L); (found M^{U+}, 309.1360; $C_{19}H_{19}NO_3$ requires 309.1359 and found M^{L+}, 311.1485; $C_{19}H_{17}D_2NO_3$ requires 311.1485). By mass spectrometry, found *syn*-**33**: *syn*-[D_2]-**33** ratio: 51:49. Proton NMR shift: negative isotopic shift at 5.45 ppm (CHN) was 0.0098 ppm (3.92 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 138.1 ppm (*i*-C; Ph) was 0.0306 ppm (3.07 Hz at 100.6 MHz); (b) negative isotopic shift at 69.3 ppm (CH_2O) was 0.641 ppm (64.5 Hz at 100.6 MHz); (c) negative isotopic shift at 57.5 ppm (CHN) was 0.168 ppm (16.9 Hz at 100.6 MHz).

4.31. Parallel kinetic resolution of pentafluorophenyl 2-(4-isobutylphenyl)propionate *rac*-20 using a quasi-enantiomeric combination of oxazolidinones (*R*)-6 and (*S*)-[D_2]-6

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.43 ml, 3 M in hexane, 1.3 mmol), oxazolidinone (*R*)-**6** (0.102 g, 0.62 mmol), oxazolidinone (*S*)-[D_2]-**6** (0.103 g, 0.62 mmol) and pentafluorophenyl 2-(4-isobutylphenyl)propionate (*rac*)-**20** (0.57 mg, 1.52 mmol) in THF (5 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/ether (7:3) a separable mixture of two pairs of diastereoisomers (ratio: *syn*-**34** and *syn*-[D_2]-**34**: *anti*-**34** and *anti*-[D_2]-**34** = 97:3). The residue was purified by flash column chromatography on silica gel eluting with light petroleum (bp 40–60 °C)/diethyl ether (7:3) to give oxazolidinone *anti*-**34** and *anti*-[D_2]-**34** ([ratio 52:48 (±2%)]) (8 mg, ~2%) as a white solid; R_f [light petroleum/diethyl ether (1:1)] 0.62; mp = 103–105 °C; $[\alpha]_D^{20} = -0.8$ (*c* 0.3, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2365 (CD), 1778 (C=O) and 1701 (C=O); δ_H (400 MHz; $CDCl_3$) 7.34–7.16 (14H, m, 7 × CH, Ar^U, Ar^L, Ph^U and Ph^L), 7.01 (4H, dt, *J* 8.2 and 1.8, 2 × CH, Ar^U and Ar^L), 5.26 (1H, dd, *J* 8.7 and 3.3, $CHNCH_2^U$), 5.25 (1H, s, $CHNCD_2^L$), 5.04 (2H, q, *J* 6.9, $ArCHCH_3^U$ and $Ar_YCHCH_3^L$), 4.49 (1H, t, *J* 8.7, $CH_AH_BO^U$), 4.14 (1H, dd, *J* 8.7 and 3.3, $CH_AH_BO^U$) and 2.36 (4H, dd, *J* 8.3 and 1.8, $ArCH_2^U$ and $ArCH_2^L$), 1.79–1.72 (2H, m, $CH(CH_3)_2^U$ and $CH(CH_3)_2^L$), 1.41 (6H, d, *J* 6.9, $ArCHCH_3^U$ and $ArCHCH_3^L$) and 0.85–0.75 (12H, d, *J* 6.9, $CH(CH_3)_2^U$ and $CH(CH_3)_2^L$); δ_C (100 MHz; $CDCl_3$) 174.4 ($NC{=}O^U$ and $NC{=}O^L$), 153.3 ($OC{=}O^U$ and $OC{=}O^L$), 140.8 (2 × *i*-C; Ar^U and Ar^L), 139.5 (*i*-C; Ph^U), 139.4 (*i*-C; Ph^L), 137.4 (2 × *i*-C; Ar^U and Ar^L), 129.4,[4] 129.3,[4] 128.7,[2] 127.9[4] and 125.9[4] (18 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.7 (CH_2O^U), 58.1 (CHN^U), 58.0 (CHN^L), 45.2 ($CH(CH_3)_2^U$ and $CH(CH_3)_2^L$), 42.8 ($ArCH^U$ and $ArCH^L$), 30.2 (CH_2^U and CH_2^L), 22.4 ($CH^ACH_3^BCH_3^L$ and $CH^ACH_3^BCH_3^L$) and 19.5 (CH_3CH^U and CH_3CH^L); (found $M^UNH_4^+$, 369.2171; $C_{22}H_{29}N_2O_3$ requires 369.2173 and found $M^LNH_4^+$, 371.2296; $C_{22}H_{27}D_2N_2O_3$ requires 371.2298). By mass spectrometry, found *anti*-**31**: *anti*-[D_2]-**31** ratio: 54:46. Proton NMR shift: negative isotopic shift at 5.27 ppm (CHN) was 0.00965 ppm (3.86 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 139.4 ppm (*i*-C; Ph) was 0.0344 ppm (3.44 Hz at 100.6 MHz); (b) negative isotopic shift at 58.1 ppm (CHN) was 0.172 ppm (17.3 Hz at 100.6 MHz); and *syn*-**34**:*syn*-[D_2]-**34** [ratio 50:50 (±2%)] (0.35 g, 79%) as a white solid; R_f [light petroleum/diethyl ether (1:1)] 0.43; mp = 71–73 °C; $[\alpha]_D^{20} = +1.1$ (*c* 2.0, $CHCl_3$); ν_{max}($CHCl_3$)/cm^{-1} 2361 (CD), 1781 (C=O) and 1703 (C=O); δ_H (400 MHz; $CDCl_3$) 7.28–7.16 (6H, m, 3 × CH, Ph^U and Ph^L), 6.97–6.88 (8H, m, 4 × CH, Ar^U, Ar^L, Ph^U and Ph^L), 6.82 (4H, dt, *J* 7.1 and 1.5, 2 × CH, Ar^L and Ar^U), 5.36 (1H, dd, *J* 8.9 and 5.1, $CHNCH_2$), 5.35 (1H, s, $CHNCD_2$), 5.02 (2H, q, *J* 7.0, Ar^LCHCH_3 and Ar^UCHCH_3), 4.52 (1H, t, *J* 8.9, CH_AH_BO), 3.96 (1H, dd, *J* 8.9 and 5.1, CH_AH_BO) and 2.36 (4H, dd, *J* 7.1 and 2.2, Ar^UCH_2 and Ar^LCH_2), 1.89–1.82 (2H, m, $CH(CH_3)_2^U$ and $CH(CH_3)_2^L$), 1.30 (6H, d, *J* 7.0, $ArCHCH_3^U$ and $ArCHCH_3^L$) and 0.95 (6H, *J* 6.7, $CH^ACH_3^BCH_3^U$ and $CH^ACH_3^BCH_3^L$) and 0.93 (6H, *J* 6.7, $CH^ACH_3^BCH_3^U$ and $CH^ACH_3^BCH_3^L$); δ_C (100 MHz; $CDCl_3$) 173.7 ($NC{=}O^U$ and $NC{=}O^L$), 153.0 ($OC{=}O^U$ and $OC{=}O^L$), 140.3 (2 × *i*-C; Ar^U and Ar^L), 138.2 (*i*-C; Ph^U), 138.1 (*i*-C; Ph^L), 136.8 (2 × *i*-C; Ar^U and Ar^L), 129.0,[4] 128.6,[4] 128.3,[2] 127.7[4] and 125.6[4] (18 × CH; Ar^U, Ar^L, Ph^U and Ph^L), 69.3 (CH_2O^U), 68.7 (1C, quintet, $^1J_{CD} = 22.9$ Hz, CD_2O^L), 57.5 (CHN^U), 57.3 (CHN^L), 44.8 ($CH(CH_3)_2^U$ and $CH(CH_3)_2^L$), 43.1 ($ArCH^U$ and $ArCH^L$), 30.0 (CH_2^U and CH_2^L), 22.3 (2 × $CH^ACH_3^BCH_3^L$), 22.1 (2×

$CH^{A}CH_3^{B}CH_3^{L}$) and 18.3 (CH_3CH^{U} and CH_3CH^{L}); (found $M^{U}NH_4^+$, 369.2169; $C_{22}H_{29}N_2O_3$ requires 369.2173 and found $M^{L}NH_4^+$, 371.2296; $C_{22}H_{27}D_2N_2O_3$ requires 371.2298). By mass spectrometry, found *syn*-**34**: *syn*-[D_2]-**34** ratio: 52:48. Proton NMR shift: negative isotopic shift at 5.45 ppm (CHN) was 0.00975 ppm (3.90 Hz at 400 MHz). Carbon NMR shifts: (a) negative isotopic shift at 138.2 ppm (*i*-C; Ph) was 0.0382 ppm (3.84 Hz at 100.6 MHz); (b) negative isotopic shift at 69.3 ppm (CH_2O) was 0.404 ppm (40.7 Hz at 100.6 MHz); (c) negative isotopic shift at 57.4 ppm (CHN) was 0.084 ppm (8.45 Hz at 100.6 MHz).

4.32. Parallel kinetic resolution of equimolar amount of 4-phenyl-oxazolidinone (*R*)-6 and 4-phenyl-5,5-dideuterio-oxazolidinone (*S*)-[D_2]-6 using pentafluorophenyl 2-phenylbutyrate acid (*R*)-28 and pentafluorophenyl (6-methoxy-2-napthyl)-2-phenylpropionate (*S*)-35

In the same way as oxazolidinone *syn*-**31**, *n*-BuLi (0.43 ml, 3 M in hexane, 1.3 mmol), oxazolidinone (*R*)-**6** (0.103 g, 0.63 mmol), oxazolidinone (*S*)-[D_2]-**6** (0.104 g, 0.63 mmol), pentafluorophenyl 2-phenylbutyrate (*R*)-**28** (0.25 g, 0.76 mmol) and pentafluorophenyl (6-methoxy-2-napthyl)-2-phenylpropionate (*S*)-**35** (0.3 g, 0.75 mmol) in THF (10 ml), gave after purification by flash column chromatography on silica gel eluting with light petroleum ether/ether (7:3) a separable mixture of oxazolidinone (*S*,*R*)-*syn*-**36** (0.205 g, 87%) (ratio = (*S*,*R*)-*syn*-**36**: (*R*,*R*)-*anti*-**32**; 96:4), (*R*,*R*)-*anti*-**32** (6 mg, ~3%) and (*R*,*S*)-*syn*-[D_2]-**32** (150 mg, 77%) (ratio = (*R*,*S*)-*syn*-[D_2]-**32**: (*S*,*S*)-*anti*-[D_2]-**32**; >98:2).

4.33. Characterisation for: (4*R*)-phenyl-3-(2*R*-phenylbutyryl)-oxazolidin-2-one *anti*-32

White solid; R_f [light petroleum (40–60 °C)/diethyl ether (1:1)] 0.55; mp = 145–149 °C; $[\alpha]_D^{20} = -160.0$ (*c* 0.74, $CHCl_3$); ν_{max} ($CHCl_3$)/cm^{-1} 2359 (CD), 1780 (C=O), 1703 (C=O) and 1600 (Ph); δ_H (250 MHz; $CDCl_3$) 7.44–7.21 (10H, m, 10 × CH; 2 × Ph), 5.28 (1H, dd, *J* 8.7 and 3.4, CHN), 4.88 (1H, t, *J* 7.5, PhCH), 4.49 (1H, br t, *J* 8.7, CH_AH_BO), 4.20 (1H, dd, *J* 8.7 and 3.4, CH_AH_BO), 1.95 (1H, double quintet, *J* 13.5 and 7.5, $CH_AH_BCH_3$), 1.65 (1H, double quintet, *J* 13.5 and 7.5, $CH_AH_BCH_3$) and 0.73 (3H, t, *J* 7.5, CH_3CH_2); δ_C (62.9 MHz; $CDCl_3$) 173.7 (NC=O), 153.4 (OC=O), 139.5 (*i*-C; Ph), 138.6 (*i*-C; Ph), 129.1, 128.8, 128.7, 128.5, 127.3 and 125.8 (6 × CH; Ph_A and Ph_B), 69.4 (CH_2O), 58.1 (CHN), 50.4 (PhCH), 27.7 (CH_2Ph) and 12.0 (CH_3) (found MH^+, 310.1430; $C_{19}H_{20}NO_3$ requires 310.1443).

4.34. (4*S*)-Phenyl-3-(2*R*-phenylbutyryl)-5,5-dideuterio-oxazolidin-2-one *syn*-[D_2]-32

White solid; R_f [light petroleum/diethyl ether (1:1)] 0.35; mp 58–60 °C; $[\alpha]_D^{20} = -54.2$ (*c* 4.6, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 7.19–7.01 (6H, m, 6× CH; Ph_A and Ph_B), 7.03 (2H, m, 2 × CH, Ph_A), 6.81 (2H, dt, *J* 6.9 and 1.5, 2 × CH, Ph_B), 5.35 (1H, s, CHPh), 4.81 (1H, t, *J* 7.4, CHCO), 1.94 (1H, dq, *J* 13.7 and 7.4, $CH_AH_BCH_3$), 1.71 (1H, dq, *J* 13.7 and 7.4, $CH_AH_BCH_3$) and 0.87 (3H, t, *J* 7.4, CH_3CH_2); δ_C (100 MHz; $CDCl_3$) 173.0 (NC=O), 153.1 (OC=O), 138.1 and 137.9 (2 × *i*-C; 2 × Ph), 128.7,[2] 128.6,[2] 128.3,[3] 127.0[1] and 125.6[2] (10 × CH; 2 × Ph), 68.7 (1C, quintet, $^1J_{C,D} = 22.9$ Hz, CD_2O), 57.4 (CHN), 51.0 (PhCH), 26.1 (CH_2) and 11.9 (CH_3) (found MNH_4^+, 329.1835; $C_{19}H_{21}D_2N_2O_3$ requires 329.1832).

4.35. (4*R*,2*S*)-3-[2-(6-Methoxynaphthyl)propionyl]-4-phenyl-oxazolidin-2-one *syn*-36

White solid; R_f [light petroleum/diethyl ether (1:1)] 0.17; mp 110–115 °C; $[\alpha]_D^{20} = +166.2$ (*c* 1.5, $CHCl_3$); δ_H (400 MHz; $CDCl_3$) 7.65 (1H, d, *J* 8.6, CH; Ar), 7.55 (1H, d, *J* 8.6, CH; Ar), 7.35 (1H, s, CH; Ar), 7.31–7.22 (2H, m, 2 × CH; Ph), 7.18–7.11 (4H, m, 1 × CH; Ar, and 3 × CH; Ph), 6.95 (2H, d, *J* 7.3, 2 × CH; Ar), 5.44 (1H, dd, *J* 8.9 and 5.3, CHN), 5.22 (1H, q, *J* 6.9, CHCO), 4.58 (1H, t, *J* 8.9, CH_AH_BO), 4.03 (1H, dd, *J* 8.9 and 5.3, CH_AH_BO), 3.92 (3H, s, CH_3O) and 1.48 (3H, d, *J* 6.9, CH_3CH); δ_C (100.6 MHz; $CDCl_3$) 173.5 (NC=O), 157.5 (OC=O), 152.9 (*i*-CO; Ar), 138.2, 135.0, 133.6 and 128.6 (4 × *i*-C; Ar), 129.3, 128.7 and 128.3 (3 × CH; Ph), 127.1, 126.9, 126.3, 125.8, 118.8 and 105.4 (6 × CH; Ar), 69.4 (CH_2O), 57.7 (CHN), 55.1 (OCH_3), 43.7 (ArCH) and 18.6 (CH_3) (found MH^+, 376.1553; $C_{23}H_{22}NO_4$ requires 376.1549).

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