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SuperQuat *N*-acyl-5,5-dimethyloxazolidin-2-ones for the asymmetric synthesis of α-alkyl and β-alkyl aldehydes

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The proclivity of α-branched *N*-2′-benzyl-3′-phenylpropionyl derivatives of (*S*)-4-benzyl-5,5-dimethyl-, (*S*)-4-phenyl-5,5-dimethyl-, (*S*)-4-isopropyl-5,5-dimethyl-, (*S*)-4-benzyl- and (*S*)-4-benzyl-5,5-diphenyl-oxazolidin-2-ones to generate directly 2-benzyl-3-phenylpropionaldehyde upon hydride reduction with DIBAL is investigated. The (*S*)-4-benzyl-5,5-dimethyl-derivative proved optimal for inhibition of endocyclic nucleophilic attack, giving 2-benzyl-3-phenylpropionaldehyde in good yield upon reduction. Application of this methodology for the asymmetric synthesis of chiral aldehydes *via* diastereoselective enolate alkylation of a range of (*S*)-*N*-acyl-4-benzyl-5,5-dimethyloxazolidin-2-ones to afford an array of α-substituted-*N*-acyl-5,5-dimethyloxazolidin-2-ones (85–94% de) and subsequent reduction with DIBAL afforded directly non-racemic α-substituted aldehydes without loss of stereochemical integrity (87–94% ee). The extension of this protocol for the asymmetric synthesis of β-substituted aldehydes is demonstrated, *via* the diastereoselective conjugate addition of a range of organocuprates to (*S*)-*N*-acyl-4-phenyl-5,5-dimethyloxazolidin-2-ones which proceeds with high diastereoselectivity (generally >95% de). Reduction of the conjugate addition products with DIBAL gives non-racemic β-substituted aldehydes in high yields and in high ee (generally >95% ee). This methodology is exemplified by the asymmetric synthesis of (*R*)-3-isopropenylhept-6-enal, which has previously been used in the synthesis of (3*Z*,6*R*)-3-methyl-6-isopropenyl-3,9-decadien-1-yl acetate, a component of the sex pheromones of the California red scale.

Introduction

Homochiral aldehydes are used widely in organic synthesis, with these versatile intermediates being utilised for a range of complex transformations in total synthesis. Synthetically useful homochiral aldehydes may be prepared directly from amino acid or monosaccharide sources, but due to the inherent structural limitations of this approach, the majority of enantiomerically enriched aldehydes are synthesised using chiral auxiliary techniques. Although many versatile chiral auxiliaries have been developed, only a small number allow direct access to aldehydes upon reduction. For instance, Oppolzer *et al.* have demonstrated that certain *N*-acylsultams **1** can be reduced with DIBAL to afford the corresponding aldehydes in excellent yield and in high ee,[1] and Myers' pseudoephedrine auxiliary has also been successfully used for the synthesis of some non-racemic α-substituted aldehydes *via* reduction of *N*-acyl-derivatives **2** with lithium triethoxyaluminium hydride.[2] Similarly, an α-substituted *N*-acyl-2-phenylimino-2-oxazolidine **3** can be cleanly reduced with DIBAL to afford the corresponding homochiral aldehyde in good yield (Fig. 1).[3]

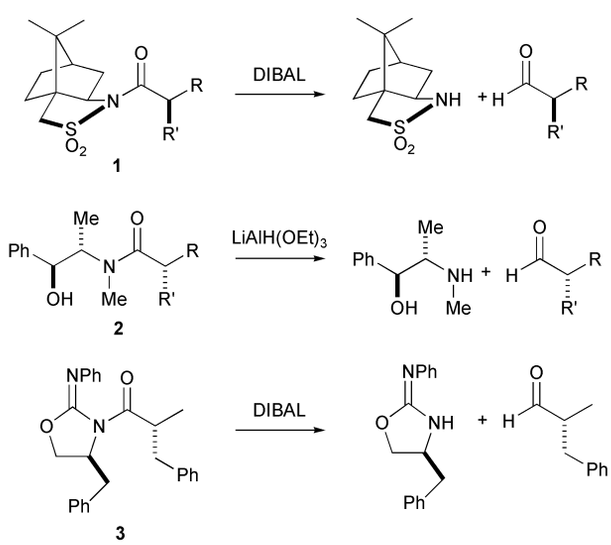

Fig. 1 Direct reduction of *N*-acyl auxiliaries to aldehydes.

Perhaps the most frequently used family of chiral auxiliaries in synthesis are the oxazolidin-2-ones, introduced initially by Evans[4] and developed further within this group[5] and by others.[6] Oxazolidin-2-ones exhibit high levels of stereocontrol in a number of diastereoselective reactions including enolate alkylations,[7] conjugate additions[8] and aldol reactions,[9] although direct conversion of *N*-acyloxazolidin-2-ones to the corresponding aldehydes is complicated by competing endo- and exocyclic cleavage pathways. A variety of approaches have been utilised to circumvent this problem, with the most popular involving reduction to the homochiral alcohol followed by chemoselective oxidation to the desired aldehyde.[10] An alternative approach involves transamidation of the *N*-acyloxazolidin-2-one to the corresponding Weinreb amide with *N*,*O*-dimethylhydroxylamine and trimethylaluminium,[11] with subsequent DIBAL reduction giving the corresponding aldehyde. Another less commonly used technique involves conversion of the *N*-acyloxazolidin-2-one to the thioester, followed by reduction with triethylsilane and palladium on carbon.[12] Although *N*-acyl-derivatives of the related thiazolidine-2-thione auxiliaries furnish the aldehyde directly upon DIBAL reduction, the application of this methodology appears to be limited (Fig. 2).[13]

There is therefore no current general methodology available for the direct reduction of *N*-acyloxazolidinones to the corresponding homochiral aldehydes.[14] Previous investigations from this laboratory have shown that DIBAL reduction of achiral *N*-acyl-5,5-dimethyloxazolidinones generate stable, tetrahedral carbinol species which may be fragmented upon treatment with base to the aldehyde, or in a tandem protocol with a lithiated phosphonate reagent to the α,β-unsaturated ester.[15] This,

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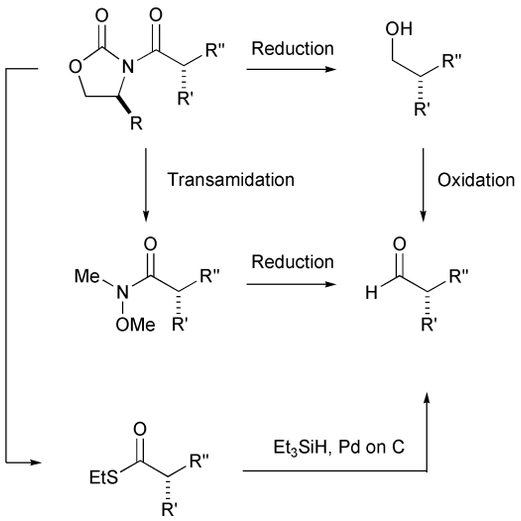


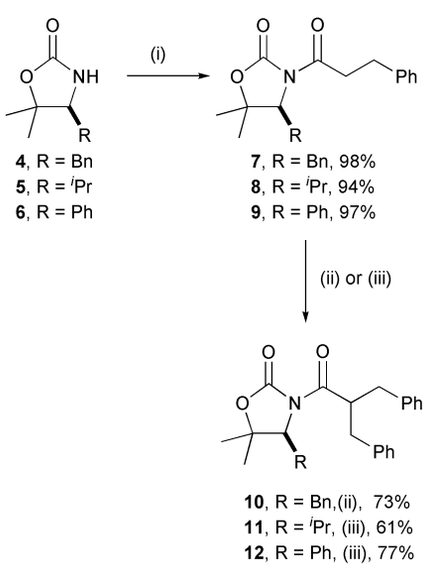
Fig. 2 Methodology for the conversion of *N*-acyloxazolidinones to aldehydes.

combined with the ability of homochiral SuperQuat auxiliaries to control the stereoselectivity of alkylation reactions of attached enolate fragments,[16] and conjugate addition reactions to attached enones,[17] suggested a direct stereoselective synthesis of homochiral α-substituted and β-substituted aldehydes. The realisation of this strategy is described herein, part of which has been communicated previously.[18]

Results and discussion

Asymmetric synthesis of α-alkyl substituted aldehydes

Initial investigations concentrated upon establishing conditions for the direct reduction of homochiral *N*-acyl SuperQuat 5,5-dimethyloxazolidinones to the corresponding α-substituted aldehydes, employing a sterically demanding *N*-acyl side chain as a model system to evaluate the efficiency of this methodology. (*S*)-4-Benzyl-, (*S*)-4-isopropyl- and (*S*)-4-phenyl-5,5-dimethyloxazolidinones **4**–**6** respectively were therefore treated with *n*-BuLi and hydrocinnamoyl chloride, to afford *N*-hydrocinnamoyl oxazolidinones **7**–**9** in 94–98% yield. Subsequent deprotonation with LHMDS and alkylation with BnBr gave the desired *N*-2′-benzyl-3′-phenylpropionyl oxazolidinones **10**–**12** in 61–77% yields (Scheme 1).

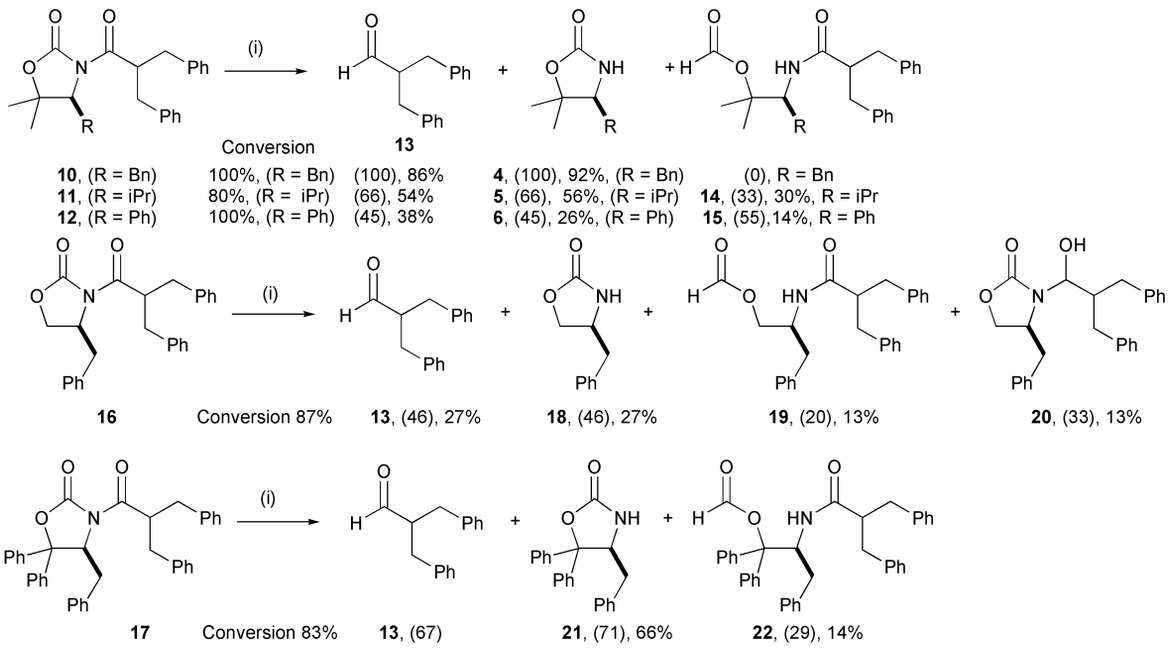


Scheme 1 *Reagents and conditions:* (i). *n*-BuLi, THF, −78 °C then hydrocinnamoyl chloride, −78 °C to rt; (ii). LHMDS, THF, −78 °C then BnBr, −78 °C to 0 °C; (iii) LHMDS, THF, 0 °C then BnBr, 0 °C.

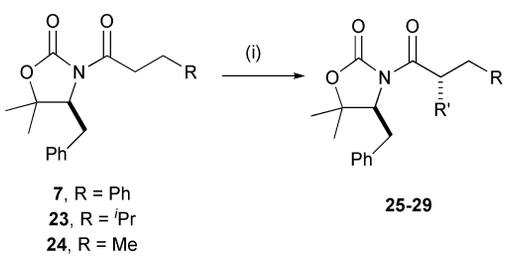
With model compounds **10**–**12** in hand, their behaviour upon reduction was probed *via* treatment with two equivalents of DIBAL in DCM at −78 °C. Reduction of (*S*)-4-benzyl-*N*-acyloxazolidinone **10** proceeded to complete conversion, and gave selectively the desired aldehyde **13** in 86% isolated yield and returned auxiliary **4** in 92% yield upon purification. In contrast, reduction of the (*S*)-4-isopropyl- and (*S*)-4-phenyl-*N*-acyloxazolidinones **11** and **12** furnished a mixture of products, giving aldehyde **13** and the formate esters **14** and **15** (arising from endocyclic cleavage of the *N*-acyloxazolidinone) respectively, plus the parent oxazolidinone auxiliary in each case (Scheme 2). Reduction of the 4-isopropyl-derivative **11** gave, at 80% conversion, a 66 : 66 : 33 ratio of **13** : **5** : **14**,[19] with purification by chromatography giving **13** in 54% yield, oxazolidinone **5** in 56% yield and formate ester **14** in 30% yield. Reduction of the 4-phenyl-derivative **12** gave, at 100% conversion, a 45 : 45 : 55 ratio of **13** : **6** : **15**, furnishing **13** in 38% yield, oxazolidinone **6** in 26% yield and (*S*)-formate ester **14** in 14% isolated yield after purification. The propensity of the related *N*-acyl derivatives of (*S*)-4-benzyloxazolidinone **18** and (*S*)-4-benzyl-5,5-diphenyloxazolidinone **21** to yield aldehyde **13** upon reduction with DIBAL was next investigated. Following standard procedures, (*S*)-4-benzyl-*N*-2′-benzyl-3′-phenylpropionyloxazolidinone **16** and (*S*)-4-benzyl-*N*-2′-benzyl-3′-phenylpropionyl-5,5-diphenyloxazolidinone **17** were prepared in high yield, with DIBAL reduction (under identical conditions to the SuperQuat derivative **10**) giving a complex mixture of products in each case. Reduction of the Evans' (*S*)-4-benzyl-*N*-acyloxazolidinone **16** gave, at 87% conversion, a 46 : 46 : 20 : 33 ratio of **13** : **18** : **19** : **20**, which on purification afforded aldehyde **13** in 27% yield, (*S*)-4-benzyloxazolidin-2-one **18** in 27% yield, formate ester **19** in 13% yield and (*S*)-*N*-1′-hydroxyalkyloxazolidin-2-one **20** (as a single diastereoisomer of unknown absolute configuration at C-1′) in 13% yield.[20] Reduction of the (*S*)-4-benzyl-*N*-acyl-5,5-diphenyloxazolidinone **17** gave, at 83% conversion, a 67 : 71 : 29 ratio of **13** : **21** : **22**, which on purification afforded aldehyde **13**,[21] 5,5-diphenyloxazolidinone **21** in 66% yield and formate ester **22** in 12% yield.

Having demonstrated that (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one **4** was the auxiliary of choice for direct and efficient reduction of α-branched *N*-acyloxazolidinones to their corresponding aldehydes for a model system, the generality of this methodology for the asymmetric synthesis of α-alkyl substituted aldehydes was studied. SuperQuat auxiliary **4** was therefore *N*-acylated with 4-methylvaleryl chloride and butyryl chloride, giving *N*-acyloxazolidinones **23** and **24** in 92% and 78% yield respectively. Subsequent deprotonation of *N*-acyloxazolidinones **7**, **23** and **24** with LHMDS, and alkylation of the lithium enolate of **7** with methyl iodide, allyl bromide and 4-bromo-2-methyl-2-butene, and alkylation of the lithium enolate of **23** and **24** with benzyl bromide gave *N*-acyl-2′-alkyloxazolidin-2-ones **25**–**29** in 85–94% de.[22] In each case the configuration of the major diastereoisomer was assigned in accordance with the standard model for deprotonation/alkylation of *N*-acyloxazolidinones.[23] Attempts to purify the mixture of diastereoisomers **25**–**29** to homogeneity *via* repeated chromatography were unsuccessful, with ^{1}H NMR spectroscopic analysis indicating no evidence of any enhancement in diastereoisomeric purity (Scheme 3).

Treatment of the diastereoisomeric mixtures **25**–**29** (85–94% de) with DIBAL in DCM at −78 °C afforded, in each case, a mixture of (*S*)-4-benzyl-5,5-dimethyloxazolidin-2-one **4** and the enantiomerically enriched aldehydes **30**–**34** as the sole reaction products. Purification to homogeneity was readily achieved *via* chromatography, giving oxazolidinone **4** in 81–98% yield and the required aldehydes **30**–**34** in 74–95% isolated yield. The ees of aldehydes **30**–**34** were determined by immediate reduction of the purified aldehydes with $LiAlH_4$ to the respective alcohols,[24] which were derivatised *via* treatment with

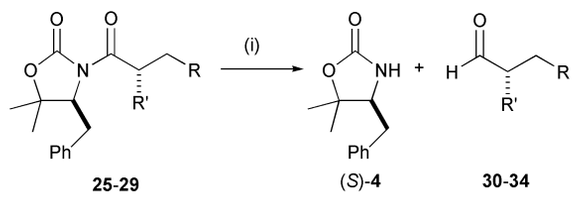


Scheme 2 *Reagents and conditions:* (i). DIBAL, DCM, −78 °C then $NH_4Cl_{(aq)}$. Numbers in brackets refer to the product ratios derived from ^1H NMR spectroscopic analysis of the crude reaction mixture.



	R	R'	d.e.	Yield (%)
25	Ph	Me	85%	75
26	Ph	$CH_2CH{=}CH_2$	86%	71
27	Ph	$CH_2CH{=}CMe_2$	94%	80
28	^{i}Pr	Bn	91%	98
29	Me	Bn	94%	94

Scheme 3 *Reagents and conditions*: (i). LHMDS, THF, −78 °C then alkyl halide, −78 °C to 0 °C.



	d.e.	R	R'		e.e.	Yield (%)
25	85%	Ph	Me	**30**	87%	87
26	86%	Ph	$CH_2CH{=}CH_2$	**31**	87%	76
27	94%	Ph	$CH_2CH{=}CMe_2$	**32**	94%	74
28	91%	^{i}Pr	Bn	**33**	91%	95
29	94%	Me	Bn	**34**	94%	95

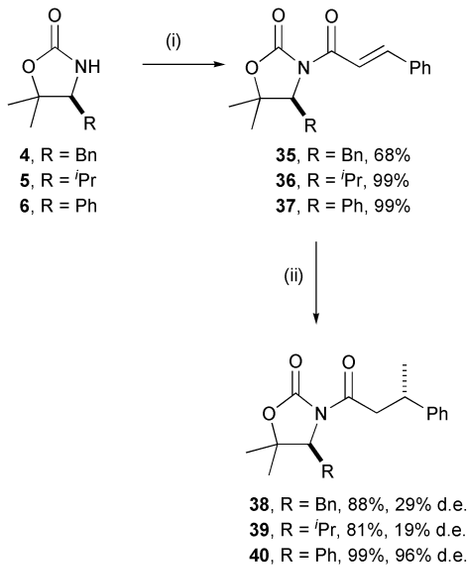
Scheme 4 *Reagents and conditions*: (i). DIBAL, DCM, −78 °C then $NH_4Cl_{(aq)}$.

(*R*)-Mosher's acid chloride and the ^{19}F NMR spectra of the resulting Mosher's esters compared with those prepared from authentic racemic alcohols.[25] Within experimental error, the ees of the alcohols corresponds to the des of the starting *N*-acyloxazolidinones **25**–**29**, indicating that no racemisation had occurred at the stereogenic centres of aldehydes **30**–**34** under the reductive conditions of the reaction (Scheme 4).

Having demonstrated that diastereoselective alkylation of SuperQuat oxazolidinone enolates followed by DIBAL reduction allows the direct synthesis of enantiomerically enriched α-substituted aldehydes, the extension of this methodology for the asymmetric synthesis of β-substituted aldehydes *via* diastereoselective conjugate addition and DIBAL reduction was investigated.[26]

Asymmetric synthesis of β-substituted aldehydes

The diastereoselective conjugate addition of organocuprates and other nucleophilic reagents to homochiral α,β-unsaturated compounds has been widely used in asymmetric synthesis.[27] Initial studies on the application of organocuprate methodology for the asymmetric synthesis of β-substituted aldehydes were directed towards determining which SuperQuat auxiliary **4**–**6** would be best suited to this approach. *N*-Acylation of the lithium anions of (*S*)-4-benzyl-, (*S*)-4-isopropyl- and (*S*)-4-phenyl-5,5-dimethyloxazolidinones **4**–**6** with cinnamoyl chloride afforded (*S*)-*N*-cinnamoyl-4-alkyl-5,5-dimethyloxazolidin-2-ones **35**–**37** in good yields, which were each subjected to BF_3 promoted conjugate addition of an organocuprate derived from $CuBr{\cdot}SMe_2$ complex and methylmagnesium bromide. While conjugate addition to (*S*)-4-phenyl-*N*-cinnamoyloxazolidinone **37** gave the known (4*S*,3′*S*)-*N*-[(3-methyl)-dihydrocinnamoyl]-4-phenyl-5,5-dimethyloxazolidin-2-one **40** in >96% de,[17] addition to the (*S*)-4-benzyl- and (*S*)-4-isopropyl-derived substrates **35** and **36** proceeded with much lower levels of diastereoselectivity, giving (4*S*,3′*S*)-*N*-[(3-methyl)dihydrocinnamoyl]-4-benzyl-5,5-dimethyloxazolidin-2-one **38** in 29% de and (4*S*,3′*S*)-*N*-[(3-methyl)dihydrocinnamoyl]-4-isopropyl-5,5-dimethyloxazolidin-2-one **39** in 19% de. In the 4-phenyl case, purification by chromatography gave (4*S*,3′*S*)-**40** in 99% yield and in >96% de, while in the 4-isopropyl case [combined yield of diastereoisomers 81%] repeated purification yielded a homogenous sample of the major diastereoisomer (4*S*,3′*S*)-**39** in 16% isolated yield. However, the diastereoisomers of the 4-benzyl-derivative (4*S*,3′*S*)-**38** proved inseparable (29% de) by repeated chromatography (88% isolated yield), and so were taken on to the reduction stage as a mixture (Scheme 5). Although there is no conclusive explanation for the remarkable disparity in stereodirecting capability shown by the SuperQuat oxazolidinones in organocuprate conjugate addition reactions,

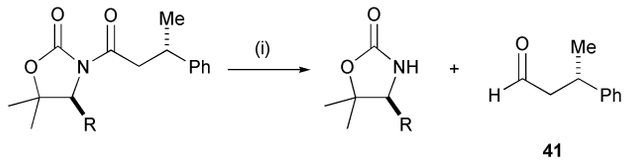


Scheme 5 *Reagents and conditions:* (i). *n*-BuLi, THF, −78 °C then cinnamoyl chloride, THF, −78 °C to rt; (ii) MeMgBr, CuBr·SMe_2, BF_3·Et_2O, THF–SMe_2 (*v* : *v* 1 : 2), −40 °C.

this selectivity parallels related work by Hruby, who showed that organometallic conjugate addition to Evans' (*S*)-4-phenyloxazolidin-2-one derivatives proceeded with much higher levels of diastereoselectivity than addition to the (*S*)-4-benzyloxazolidin-2-one derivatives.[28]

Reduction of (4*S*,3′*S*)-4-phenyl-**40** (>96% de) with DIBAL in DCM at −78 °C afforded (*S*)-3-phenylbutanal **41** in 88% yield, whose specific rotation {$[a]_D^{25}$ +33.8 (*c* 0.5, Et_2O); lit.[29] $[a]_D^{25}$ +38.0 (*c* 0.2, Et_2O), lit.[30] $[a]_D^{25}$ +37.1 (*c* 0.2, Et_2O)} confirmed the sense of asymmetric induction at C(3) in the conjugate addition reaction. Similarly, treatment of the 4-Bn and 4-^{i}Pr derivatives **38** and **39** (>98% de and 29% de respectively) gave aldehyde **41** (71% and 76% yield respectively) and the parent oxazolidinone as the only reaction products upon treatment with DIBAL (Scheme 6).

While reduction of each *N*-acyl-5,5-dimethyloxazolidinone **38**–**40** furnished selectively the aldehyde upon treatment with DIBAL, (*S*)-4-phenyl-5,5-dimethyloxazolidin-2-one **4** was chosen as the auxiliary of choice for the asymmetric synthesis of β-substituted aldehydes due to the high level of diastereoselectivity noted upon conjugate addition to *N*-acyl derivative **37**. Further investigations were directed toward establishing the generality of this protocol, with the BF_3 promoted conjugate addition of a range of organocuprates to (*S*)-*N*-cinnamoyl-4-phenyl-5,5-dimethyloxazolidin-2-one **37** or the known (*S*)-*N*-crotonyl-4-phenyl-5,5-dimethyloxazolidin-2-



Scheme 6 *Reagents and conditions*: (i). DIBAL, DCM, −78 °C then $NH_4Cl_{(aq)}$.

one **42** affording the desired conjugate addition products **43**–**47** in >91% de. With the exception of *N*-acyloxazolidinone **47**, purification of each of the major diastereoisomers to homogeneity *via* chromatography was possible, giving β-substituted oxazolidinone derivatives **43**–**47** in >58% yield, with subsequent treatment of **43**–**47** with DIBAL affording the desired β-substituted aldehydes **48**–**52** in 72–90% yield. The ees of aldehydes **41** and **48**–**52** were determined as >91% ee,[31] consistent with no loss of stereochemical integrity of the β-centre upon production of the aldehyde (Scheme 7).

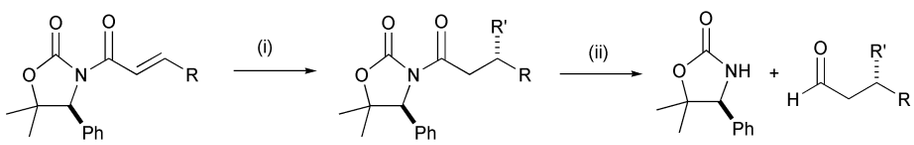
The utility of this methodology was further exemplified by the synthesis of (*R*)-3-isopropenylhept-6-enal **55**, which has previously been used in the synthesis of (3*Z*,6*R*)-3-methyl-6-isopropenyl-3,9-decadien-1-yl acetate **56**, a component of the sex pheromones of the California red scale. Conjugate addition of the isopropenyl-derived organocuprate to the readily prepared *N*-acyloxazolidinone **53** gave β-isopropenyl substituted oxazolidinone **54** in 63% yield and >95% de after purification, which on reduction with DIBAL gave the desired aldehyde **55** {$[a]_D^{25}$ +8.6 (*c* 1.2, $CHCl_3$), lit.[32] $[a]_D$ +9.0 (*c* 1.4, $CHCl_3$)} in 84% yield and in >95% ee (Scheme 8).[31]

In conclusion, we have demonstrated that both α-substituted and β-substituted aldehydes may be selectively prepared by direct reduction of *N*-acyl-5,5-dimethyloxazolidin-2-ones with DIBAL in DCM with no loss of stereochemical integrity. The further application of this methodology for complex natural product synthesis[33] is currently under way within this laboratory.

Experimental

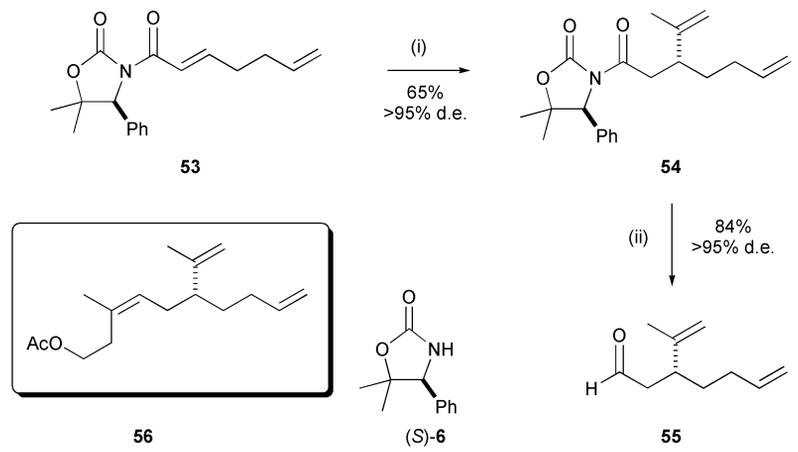
General experimental

All reactions were carried out under nitrogen or argon using standard vacuum line techniques, using glassware that was flame dried and cooled under nitrogen. THF and Et_2O were distilled from sodium–benzophenone ketyl; DCM was distilled from calcium hydride prior to use. *n*-Butyllithium was used as a



	R	R'	d.e.	Yield (%)		e.e.	Yield (%)
40	Ph	Me	>96%	99	**41**	>95%	88
43	Ph	$CH_2CH{=}CH_2$	>95%	97	**48**	>95%	88
44	Ph	$CHMe_2$	>95%	60	**49**	>95%	72
45	Ph	Bn	>95%	58	**50**	>95%	96
46	Me	Ph	97%	70	**51**	>95%	84
47	Me	Bn	91%	83	**52**	91%	90

Scheme 7 *Reagents and conditions:* (i). R′MgX, Me_2S·CuBr, BF_3, Me_2S : THF (*v* : *v* 1 : 2), −40 °C; (ii). DIBAL, DCM −78 °C then $NH_4Cl_{(aq)}$.



53 54 56 (*S*)-6 55

Scheme 8 *Reagents and conditions*: (i). CH_2=C(Me)MgBr, Me_2S·CuBr, BF_3·Et_2O, Me_2S–THF, −40 °C; (ii). DIBAL, DCM, −78 °C then $NH_4Cl_{(aq)}$.

solution in hexanes and was titrated against diphenylacetic acid prior to use. LHMDS was used as supplied (Aldrich) as a 1 M solution in THF. DIBAL was used as supplied (Aldrich) as a 1 M solution in hexanes. $LiAlH_4$ was used as supplied (Aldrich) as a 1 M solution in THF. CuBr·SMe_2 was recrystallised from SMe_2 and pentane immediately prior to use. Grignard reagents were used as solutions in THF and titrated against menthol and phenanthroline. All other reagents were used as supplied without further purification. Flash column chromatography was performed on silica gel (Kieselgel 60). TLC was performed on Merck aluminium sheets coated with 0.2 mm silica gel 60 F_{254}. Plates were visualised either by UV light (254 nm), iodine, ammonium molybdate (7% solution in ethanol) or potassium permanganate (1% in 2% aqueous acetic acid, containing 7% potassium carbonate). Infra red spectra were recorded as thin films or KBr discs using a Perkin-Elmer PARAGON 1000 FT-IR spectrometer. Selected peaks are reported in cm^{-1}. ^1H NMR spectra were recorded on Varian Gemini 200 (200 MHz), Bruker DPX-200 (200 MHz), Bruker DPX-400 (400 MHz), Bruker DQX-400 (400 MHz) or Bruker AM-500 (500 MHz) spectrometers. Chemical shifts (δ_H) are reported in parts per million (ppm) and are referenced to the residual solvent peak. Coupling constants (J) are measured in Hertz. Two dimensional COSY spectra were recorded on the Bruker DPX-200 (200 MHz), the Bruker DQX-400 (400 MHz) or the Bruker DPX-400 (400 MHz) spectrometers. ^{13}C spectra were recorded at 50.31 MHz on the Varian Gemini 200 or the Bruker DPX-200 spectrometers, at 100.62 MHz on the Bruker DQX-400 or the Bruker DPX-400 spectrometers and at 125.77 MHz on the Bruker AM-500 spectrometer. Low resolution mass spectra (m/z) were recorded on either a VG Masslab 20–250 instrument (CI, NH_3) or Platform instrument (APCI). MALDI spectra were recorded on a Micromass MALDI TOF SPEC 2E spectrometer. Major peaks are listed with intensities quoted as percentages of the base peak. Accurate mass measurements were recorded on a VG Autospec and a Waters 2790-Micromass LCT electrospray ionisation mass spectrometer operating at a resolution of 5000 full width half height. Positive ion spectra were calibrated relative to PEG with tetraoctylammonium bromide as the internal lock mass. Negative ion spectra were calibrated relative to poly-DL-alanine with leucine enkephalin as the internal lock mass. Optical rotations were recorded on a Perkin-Elmer 241 polarimeter, using a path length of 10 cm, in spectroscopic grade solvents (Aldrich), with concentrations (c) given in g/100 cm^3, solvent and temperature as recorded. Elemental analyses were obtained by Mrs A. Douglas of the Inorganic Chemistry Analytical Department using an Elementar Vario EL combustion elemental analyser. Melting points were recorded on a Gallenkamp Hot Stage apparatus and are uncorrected.

Representative Procedure 1

n-BuLi (1.1 eq) was added to a stirred solution of the oxazolidin-2-one (1.0 eq) in THF at −78 °C. After 15 minutes, the acid chloride (1.3 eq) was added dropwise and stirred at −78 °C for 15 minutes before being warmed to rt. After 2 hours, the reaction mixture was quenched with saturated aqueous NH_4Cl solution and acetic acid, extracted with EtOAc, washed sequentially with saturated aqueous $NaHCO_3$ and brine and dried. The organic extracts were concentrated *in vacuo* and purified by either flash column chromatography on silica gel or recrystallisation.

Representative Procedure 2a and 2b

LHMDS (1.5 eq) was added to a stirred solution of *N*-acyloxazolidin-2-one (1.0 eq) in THF (a) at 0 °C or (b) at −78 °C. After 30 minutes, the alkyl halide (3.0 eq) was added *via* syringe to the resultant enolate and the reaction mixture stirred at 0 °C for 5 hours before the addition of saturated aqueous NH_4Cl solution, and the solution extracted with EtOAc, washed with brine and dried. The organic extracts were concentrated *in vacuo* and purified by flash column chromatography on silica gel.

Representative Procedure 3

DIBAL (2.0 eq) was added dropwise to a stirred solution of *N*-acyloxazolidin-2-one (1.0 eq) in CH_2Cl_2 at −78 °C. The reaction was quenched at −78 °C after 20 minutes with saturated aqueous NH_4Cl solution, warmed to rt and stirred for a further 20 minutes. The resultant mixture was filtered through Celite® (eluent: CH_2Cl_2), dried, and concentrated *in vacuo*.

Representative Procedure 4

$LiAlH_4$ (2.0 eq) was added to a stirred solution of aldehyde (1.0 eq) in THF at 0 °C. After 10 minutes the reaction was quenched with ice and EtOAc and stirred for a further 3 hours at rt. The resultant mixture was filtered through Celite®, dried and concentrated *in vacuo*. The crude reaction mixture was purified by flash column chromatography on silica gel to furnish the desired alcohol.

Representative Procedure 5

RMgHal (3.0 eq) was added to a stirred solution of freshly recrystallised CuBr·SMe_2 (1.5 eq) in SMe_2 and THF ($v : v$ 1 : 2) at −40 °C. After 10 minutes, BF_3·Et_2O (1.5 eq) was added dropwise *via* syringe. The resultant mixture was stirred for 10 minutes before addition of *N*-acyl-5,5-dimethyloxazolidin-2-one (1.0 eq) *via* cannula as a solution in THF. After 20 hours, saturated aqueous NH_4Cl was added and the solvents evaporated. EtOAc and water ($v : v$ 3 : 1) was added to the solid residue

and the resultant suspension filtered through glass wool before the organic layer was washed sequentially with 10% NH_4OH (x 2), water and brine. The resultant solution was dried, concentrated *in vacuo* and purified by flash column chromatography on silica gel to give the desired product.

Preparation of (*S*)-3-(3′-phenylpropionyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 7

Following Representative Procedure 1, *n*-BuLi (1.3 M, 1.1 mL, 1.48 mmol), (*S*)-4 (300 mg, 1.46 mmol) and hydrocinnamoyl chloride (0.24 mL, 1.60 mmol) in THF (40 mL) furnished **7** (481 mg, 98%) as a pale yellow oil after flash column chromatography; R_f 0.24 [5 : 1 hexane : Et_2O]; $C_{21}H_{23}NO_3$ requires C, 74.75, H, 6.9, N, 4.15%; found C, 75.0, H, 6.6, N, 4.15%; $[\alpha]_D^{22}$ −27.8 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.33 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.37 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.86 [1H, dd, J 14.4, 9.5, $CHCH_AH_BPh$], 2.93–2.99 [2H, m, CH_2CH_2Ph], 3.13 [1H,dd, J 14.4, 3.9, $CHCH_AH_BPh$], 3.22–3.29 [2H, m, CH_2CH_2Ph], 4.51 [1H, dd, J 9.5, 3.9, $CHCH_2Ph$], 7.19–7.33 [10H, m, PhH]; ν_{max} ($CHCl_3$) 1774 [C=O exocyclic], 1698 [C=O endocyclic]; δ_C (125 MHz, $CDCl_3$) 22.2, 28.4 [$C(CH_3)_2$], 30.4, 35.2 [C(4)CH_2Ph and CH_2CH_2Ph], 37.2 [CH_2CH_2Ph], 63.5 [C(4)H], 82.3 [$C(CH_3)_2$], 126.5, 127.0, 128.5, 128.7, 128.9, 129.3 [*p/m/o-Ph*], 137.2, 140.7 [*i-Ph*], 152.9 [C=O endocyclic], 173.0 [C=O exocyclic]; *m/z* (CI^+, NH_3), 338 (100%, MH^+).

Preparation of (*S*)-3-(3′-phenylpropionyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one 8

Following Representative Procedure 1, *n*-BuLi (10.50 mL, 21.0 mmol), (*S*)-**5** (3.00 g, 19.1 mmol) and hydrocinnamoyl chloride (3.69 mL, 24.84 mmol) in THF (75 mL) furnished **8** (5.19 g, 94%) as a pale yellow oil after flash column chromatography; R_f 0.16 [5 : 1 40–60 °C petrol : Et_2O]; $C_{17}H_{23}NO_3$ requires C, 70.6, H, 8.0, N, 4.8%; found C, 70.5, H, 8.3, N, 4.65%; $[\alpha]_D^{25}$ +33.6 (c = 1.3, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.91 [3H, d, J 6.9, $CH(CH_3)_A(CH_3)_B$], 0.99 [3H, d, J 7.0, $CH(CH_3)_A(CH_3)_B$], 1.32 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.49 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.05–2.16 [1H, m, $CH(CH_3)_2$] 2.95–3.08 [2H, m, CH_2CH_2Ph], 3.22–3.39 [2H, m, CH_2CH_2Ph], 4.14 [1H, d, J 6.5, $CHCH(CH_3)_2$], 7.17–7.31 [5H, m, PhH]; ν_{max} ($CHCl_3$) 1774 [C=O exocyclic], 1699 [C=O endocyclic]; δ_C (125 MHz, $CDCl_3$) 17.0, 21.4 [$CH(CH_3)_2$], 28.7 [$C(CH_3)_2$], 29.5 [C(4)CH], 30.7 [CH_2CH_2Ph], 36.9 [CH_2CH_2Ph], 66.3 [C(4)H], 82.8 [$C(CH_3)_2$], 126.2, 128.4, 128.5 [*p/m/o-Ph*], 140.5 [*i-Ph*], 153.5 [C=O endocyclic], 173.0 [C=O exocyclic]; *m/z* (CI^+, NH_3), 290 (100%, MH^+).

Preparation of (*S*)-3-(3′-phenylpropionyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 9

Following Representative Procedure 1, *n*-BuLi (1.15 mL, 2.9 mmol), (*S*)-**5** (500 mg, 2.6 mmol) and hydrocinnamoyl chloride (0.5 mL, 3.41 mmol) in THF (20 mL) furnished **9** (793 mg, 94%) as a white solid after recrystallisation; mp 148–150 °C [hexane–Et_2O] $[\alpha]_D^{25}$ +35.9 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.99 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.58 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.88–3.01 [2H, m, CH_2CH_2Ph], 3.31–3.35 [2H, m, CH_2CH_2Ph], 5.06 [1H, s, C(4)H], 7.01–7.53 [10H, m, PhH]; ν_{max} ($CHCl_3$) 1780 [C=O exocyclic], 1703 [C=O endocyclic]; δ_C (125 MHz, $CDCl_3$) 23.7, 28.9 [$C(CH_3)_2$], 30.3 [CH_2CH_2Ph], 37.3 [CH_2CH_2Ph], 66.9 [C(4)H], 81.5 [$C(CH_3)_2$], 126.2, 128.4, 128.5, 128.9 [*p/m/o-Ph*], 136.3, 140.7 [*i-Ph*], 153.2 [C=O endocyclic], 172.2 [C=O exocyclic]; HRMS $C_{20}H_{22}NO_3$ [MH^+] requires 324.1595; found 324.1604.

Preparation of (*S*)-3-(2′-benzyl-3′-phenylpropionyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 10

Following Representative Procedure 2b, LHMDS (4.49 mL, 4.49 mmol), **7** (1.00 g, 2.99 mmol) and benzyl bromide (1.10 mL, 8.97 mmol) in THF (40 mL) furnished **10** (0.93 g, 73%) as a white solid by flash column chromatography; R_f 0.29 [7 : 1 hexane : Et_2O]; mp 84–86 °C [hexane–Et_2O]; $[\alpha]_D^{22}$ +38.9 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.84 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.18 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.50 [1H, dd, J 14.6, 9.9, $CHCH_AH_BPh$], 2.73 [1H, dd, J 14.6, 3.4, $CHCH_AH_BPh$], 2.83–3.11 [4H, m, $CH(CH_2Ph)_2$], 4.25 [1H, dd, J 9.9, 3.4, $CHCH_2Ph$], 4.74–4.82 [1H, m, $CH(CH_2Ph)_2$], 7.16–7.32 [15H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 22.0, 27.6 [$C(CH_3)_2$], 34.9 [$CHCH_2Ph$], 38.6, 39.0 [$CH(CH_2Ph)_2$], 45.8 [$CHCH_2Ph$], 63.3 [$CH(CH_2Ph)_2$], 81.7 [$C(CH_3)_2$], 126.4, 126.6 [*p-Ph*], 128.4, 128.6, 129.0, 129.1, 129.3 [*m/o-Ph*], 137.1, 138.7, 138.9 [*i-Ph*], 152.1 [C=O endocyclic], 175.5 [C=O exocyclic]; ν_{max} (KBr) 1781 [C=O exocyclic], 1696 [C=O endocyclic]; *m/z* APCI+ 206 [90%, SQH^+], 428 [100%, MH^+]; HRMS $C_{28}H_{30}NO_3$ [MH^+] requires 428.2221; found 428.2236.

Preparation of (*S*)-3-(2′-benzyl-3′-phenylpropionyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one 11

Following Representative Procedure 2a, LHMDS (2.10 mL, 2.07 mmol), **8** (0.40 g, 1.38 mmol) and benzyl bromide (0.49 mL, 4.15 mmol) in THF (10 mL) furnished **11** (0.32 g, 61%) as a white solid after flash column chromatography; R_f 0.3 [5 : 1 hexane : Et_2O]; mp 80–81 °C [hexane–Et_2O]; $[\alpha]_D^{22}$ +37.5 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.52 [3H, d, J 6.8, $CH(CH_3)_A(CH_3)_B$], 0.70 [3H, s, $C(CH_3)_A(CH_3)_B$], 0.71 [3H, d, J 6.8, $CH(CH_3)_A(CH_3)_B$], 1.32 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.84–2.18 [1H, m, $CH(CH_3)_2$], 2.83–3.12 [4H, m, $CH(CH_2Ph)_2$], 3.87 [1H, d, J 2.8, $CHCH(CH_3)_2$], 4.85–4.93 [1H, m, $CH(CH_2Ph)_2$], 7.11–7.35 [10H, m, PhH]; δ_C (50 MHz, $CDCl_3$) 16.7, 21.6 [$CH(CH_3)_2$], 21.6 [$CH(CH_3)_2$], 28.1, 29.8 [$C(CH_3)_2$], 39.3, 40.0 [$CH(CH_2Ph)_2$], 45.8 [$CHCH(CH_3)_2$], 66.7 [$CH(CH_2Ph)_2$], 82.7 [$C(CH_3)_2$], 126.8, 126.9 [*p-Ph*], 128.9, 129.6, 129.8 [*m/o-Ph*], 139.1, 139.4 [*i-Ph*], 153.6 [C=O endocyclic], 176.1 [C=O exocyclic]; ν_{max} (KBr) 1771 [C=O exocyclic], 1695 [C=O endocyclic]; *m/z* APCI+ 336 [60%, $MH^+ - CO_2$], 380 [50%, MH^+], 402 [100%, MNa^+]; HRMS $C_{24}H_{30}NO_3$ [MH^+] requires 380.2221; found 380.2238.

Preparation of (*S*)-3-(2′-benzyl-3-phenyl-propionyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 12

Following Representative Procedure 2a, LHMDS (0.93 mL, 0.93 mmol), **9** (200 mg, 0.62 mmol) and benzyl bromide (0.24 mL, 1.86 mmol) in THF (10 mL) furnished **12** (200 mg, 77%) as a white solid after flash column chromatography; R_f 0.23 [5 : 1 hexane : Et_2O]; mp 148–150 °C [hexane–Et_2O]; $[\alpha]_D^{22}$ +43.2 (c = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.79 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.06 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.79–3.05 [4H, m, $CH(CH_2Ph)_2$], 4.74 [1H, s, $CHPh$], 4.86–4.93 [1H, m, $CH(CH_2Ph)_2$], 7.16–7.30 [15H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 23.9, 28.6 [$C(CH_3)_2$], 39.2, 39.8 [$CH(CH_2Ph)_2$], 46.4 [$CHPh$], 67.3 [$CH(CH_2Ph)_2$], 82.3 [$C(CH_3)_2$], 126.5, 126.7, 126.9 [*p-Ph*], 128.6, 128.9, 129.2, 129.6, 129.7 [*m/o-Ph*], 136.5, 139.1, 139.4 [*i-Ph*], 153.1 [C=O endocyclic], 175.6 [C=O exocyclic]; ν_{max} (KBr) 1777 [C=O endocyclic], 1703 [C=O exocyclic]; *m/z* APCI+ 414 [95%, MH^+], 436 [100%, MNa^+]; HRMS $C_{27}H_{30}NO_3$ [MH^+] requires 416.2221; found 416.2234.

Preparation of 2-benzyl-3-phenylpropionaldehyde 13[34] from (*S*)-10

Following Representative Procedure 3, DIBAL (0.70 mL, 0.70 mmol) and (*S*)-**10** (150 mg, 0.35 mmol) in CH_2Cl_2 (5 mL) furnished **13** (68 mg, 86%) as a clear, colourless oil and (*S*)-**4** as a white solid (66 mg, 92%) after flash column chromatography. Data for **13**; R_f 0.33 [7 : 1 hexane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 2.74–2.82 [2H, m, $CH(CH_2Ph)_A(CH_2Ph)_B$], 2.99–3.06 [3H, m, $CH(CH_2Ph)_A(CH_2Ph)_B$ and $CH(CH_2Ph)_2$], 7.17–7.34 [10H, m, PhH], 9.75 [1H, s, CHO].

Preparation of 2-benzyl-3-phenylpropionaldehyde 13 and (*S*)-2-(2′-benzyl-3′-phenylpropionylamino)-1,1-dimethyl-2-isopropylethyl formate 14 from (*S*)-11

Following Representative Procedure 3, DIBAL (1.10 mL, 0.80 mmol) and (*S*)-**11** (150 mg, 0.40 mmol) in CH_2Cl_2 (5 mL) furnished **13** (48 mg, 54%) as a clear oil, (*S*)-**14** (46 mg, 30%) as a white solid and (*S*)-**5**[35] (35 mg, 56%) as a white solid after flash column chromatography. Data for (*S*)-**14**; R_f 0.3 [1 : 1 hexane : Et_2O]; m.p 86–87 °C [hexane–Et_2O]; $[a]_D^{22}$ −4.3 (*c* = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.42 [3H, d, *J* 6.8, $CH(CH_3)_A(CH_3)_B$], 0.53 [3H, d, *J* 6.9, $CH(CH_3)_A(CH_3)_B$], 0.86 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.39 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.89–1.95 [1H, m, $CH(CH_3)_2$], 2.75–2.82 [1H, m, $CH(CH_2Ph)_2$], 2.85–2.92 [2H, m, $CH(CH_2Ph)_A(CH_2Ph)_B$], 2.98–3.04 [2H, m, $CH(CH_2Ph)_A(CH_2Ph)_B$], 3.63 [1H, dd, *J* 10.3, 2.3, $CHCH(CH_3)_2$], 5.48 [1H, d, *J* 10.3, NH], 7.13–7.30 [10H, m, PhH], 7.81 [1H, s, OCHO]; δ_C (100 MHz, $CDCl_3$) 16.2, 22.0 [$CH(CH_3)_2$], 23.9, 24.8 [$C(CH_3)_2$], 27.4 [$CH(CH_3)_2$], 39.1, 39.4 [$CH(CH_2Ph)_2$], 52.8 [$CH(CH_2Ph)_2$], 59.7 [$CHCH(CH_3)_2$], 85.5 [$C(CH_3)_2$], 126.4 [*p-Ph*], 128.4, 128.5, 128.6, 129.0, 129.1 [*m/o-Ph*], 139.4, 139.5 [*i-Ph*], 160.2 [OCHO], 173.5 [C=O]; ν_{max} (KBr) 1726 [C=O formate ester], 1666 [C=O amide]; *m/z* APCI+ 336 [100%, $MH^+ - HCO_2H$], 404 [10%, MNa^+]; HRMS $C_{24}H_{32}NO_3$ [MH^+] requires 382.2377; found 382.2370.

Preparation of 2-benzyl-3-phenylpropionaldehyde 13, (*S*)-2-(2′-benzyl-3′-phenylpropionylamino)-1,1-dimethyl-2-phenylethyl formate 15 from (*S*)-12

Following Representative Procedure 3, DIBAL (0.96 mL, 0.68 mmol) and (*S*)-**12** (140 mg, 0.34 mmol) in CH_2Cl_2 (5 mL) furnished **13** (30 mg, 38%) as a clear oil, (*S*)-**15** (19 mg, 14%) as a white solid and (*S*)-**6** (38 mg, 26%) as a cream solid after flash column chromatography. Data for (*S*)-**15**; R_f 0.39 [1 : 1 hexane : Et_2O]; mp 78–81 °C [hexane–Et_2O]; $[a]_D^{22}$ −25.0 (*c* = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.01 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.17 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.60–2.78 [1H, m, $CH(CH_2Ph)_2$], 2.83–3.06 [4H, m, $CH(CH_2Ph)_2$], 4.72 [1H, d, *J* 9.2, CHPh], 6.12 [1H, d, *J* 9.2, NH], 6.91–7.28 [15H, m, PhH], 7.80 [1H, s, OCHO]; δ_C (100 MHz, $CDCl_3$) 23.6, 24.8 [$C(CH_3)_2$], 39.2, 39.4 [$CH(CH_2Ph)_2$], 53.0 [$CH(CH_2Ph)_2$], 60.6 [CHPh], 84.5 [$C(CH_3)_2$], 126.2, 126.4, 127.4 [*p-Ph*], 128.1, 128.3, 128.5, 128.6, 129.1 [*m/o-Ph*], 137.8, 139.1, 139.5 [*i-Ph*], 160.2 [OCHO], 172.8 [C=O]; ν_{max} (film) 1723 [C=O formate ester], 1670 [C=O amide]; *m/z* APCI+ 370 [100%, $MH^+ - HCO_2H$], 416 [75%, MH^+], 439 [80%, MNa^+]; HRMS $C_{27}H_{30}NO_3$ [MH^+] requires 416.2221; found 416.2234.

Preparation of (*S*)-3-(2′-benzyl-3′-phenylpropionyl)-4-benzyloxazolidin-2-one 16

Following Representative Procedure 2b, LHMDS (2.43 mL, 2.43 mmol), (*S*)-3-(3-phenylpropionyl)-4-benzyloxazolidin-2-one (500 mg, 1.62 mmol) and benzyl bromide (0.58 mL, 4.86 mmol) in THF (25 mL) furnished (*S*)-**16** (520 mg, 80%) as a white solid after flash column chromatography; R_f 0.1 [5 : 1 40–60 °C petrol : Et_2O]; mp 98–99 °C [hexane–Et_2O]; $[a]_D^{22}$ +94.2 (*c* = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.43–2.49 [1H, m, $CH_2CHCH_AH_BPh$], 2.84–2.97 [4H, m, $CH(CH_2Ph)_A(CH_AH_B-Ph)_B$ and $CH_2CHCH_AH_BPh$], 3.00–3.19 [1H, m, $CH(CH_2Ph)_A(CH_AH_BPh)_B$], 3.77–3.81 [1H, m, $CH_AH_BCHCH_2Ph$], 3.93–3.95 [1H, m, $CH_AH_BCHCH_2Ph$], 4.40–4.46 [1H, m, CH_2CHCH_2Ph], 4.46–4.71 [1H, m, $CH(CH_2Ph)_2$], 6.97–7.34 [15H, m, PhH]; δ_C (50 MHz, $CDCl_3$) 38.0, 38.6, 39.2 [$CH(CH_2Ph)_2$ and CH_2CHCH_2Ph], 46.7 [$CH(CH_2Ph)_2$], 55.5 [CH_2CHCH_2Ph], 66.1 [CH_2CHCH_2Ph], 126.9, 127.7 [*p-Ph*], 128.8, 128.9, 129.3, 129.6, 129.8 [*m/o-Ph*], 135.6, 139.3, 139.4 [*i-Ph*], 153.3 [C=O endocyclic], 175.8 [C=O exocyclic]; ν_{max} (KBr) 1770 [C=O endocyclic], 1689 [C=O exocyclic]; *m/z* APCI+ 356 [30%, $MH^+ - CO_2$], 374 [100%, $MH^+ - CO$], 400 [100%, MH^+]; HRMS $C_{26}H_{26}NO_3$ [MH^+] requires 400.1908; found 400.1921.

Preparation of (*S*)-3-(2′-benzyl-3′-phenylpropionyl)-4-benzyl-5,5-diphenyloxazolidin-2-one 17

n-BuLi (0.4 mL, 0.64 mmol) was added to a stirred solution of (*S*)-4-benzyl-5,5-diphenyloxazolidin-2-one (200 mg, 0.61 mmol) in anhydrous THF (20 mL) at 0 °C. After stirring for 5 minutes, hydrocinnamoyl chloride (0.11 mL, 0.73 mmol) was added dropwise *via* syringe and the reaction mixture allowed to warm to ambient temperature. After 20 hours the reaction mixture was quenched with saturated aqueous ammonium chloride solution, extracted with diethyl ether, washed sequentially with 1 M hydrochloric acid, 1 M sodium hydroxide and brine, dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash column chromatography on silica afforded (*S*)-3-(3′-phenylpropionyl)-4-benzyl-5,5-diphenyloxazolidin-2-one (267 mg, 0.58 mmol, 95%) as a pale yellow oil; R_f 0.38 [3 : 1 30–40 °C petroleum ether : Et_2O]; $[a]_D^{24}$ −214.17 (*c* 1.2, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.556 [4H, m, $CHCH_2Ph$ & $CH(CH_AH_BPh)(CH_CH_DPh)$], 2.867 [1H, dd, *J* 13.9, 8.6, $CH(CH_AH_BPh)(CH_CH_DPh)$], 3.090 [1H, dd, *J* 14.5, 6.9, $CH(CH_AH_BPh)(CH_CH_DPh)$], 4.427–4.500 [1H, m, $CH(CH_2Ph)_2$], 5.520 [1H, dd, *J* 4.7, 7.7, $CHCH_2Ph$], 6.586–6.606 [2H, m, PhH], 6.927–6.969 [2H, m, PhH], 6.987–7.129 [8H, m, PhH], 7.174–7.435 [13H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 30.2, 37.0 [CH_2CH_2Ph], 36.6 [$CHCH_2Ph$], 61.9 [$CHCH_2Ph$], 88.5 [CPh_2], 125.9, 126.2, 126.4, 126.5 [*p-Ph*], 128.2, 128.3, 128.4, 128.4, 128.8, 128.9, 129.0 [*m/o-Ph*], 136.2, 137.5, 140.3, 141.4 [*i-Ph*], 152.0 [C=O endocyclic], 171.6 [C=O exocyclic]; ν_{max} (film) 1783, 1699 [C=O]; HRMS $C_{31}H_{28}NO_3$ [MH^+] requires 462.2064, found 462.2090; *m/z* ES + 484 [95%, MNa^+].

LHMDS (0.65 mL, 0.65 mmol) was added dropwise to a stirred solution of (*S*)-3-(3′-phenylpropionyl)-4-benzyl-5,5-diphenyloxazolidin-2-one (200 mg, 0.43 mmol) in anhydrous THF (10 mL) at −78 °C. After stirring for 30 minutes, benzyl bromide (0.15 mL, 1.30 mmol) was added dropwise *via* syringe and the resultant mixture was warmed to 0 °C. After stirring for 5 hours the reaction mixture was quenched with saturated aqueous ammonium chloride solution, extracted with ethyl acetate, washed with brine, dried and concentrated *in vacuo*. Purification by flash column chromatography afforded **17** (124 mg, 52%) as a pale yellow oil and returned (*S*)-3-(3′-phenylpropionyl)-4-benzyl-5,5-diphenyloxazolidin-2-one (59 mg, 30%); R_f 0.40 [5 : 1 30–40 °C petroleum ether : Et_2O]; $[a]_D^{24}$ −119.9 (*c* 1.95, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.56 [4H, m, $CHCH_2Ph$ & $CH(CH_AH_BPh)(CH_CH_DPh)$], 2.87 [1H, dd, *J* 13.9, 8.6, $CH(CH_AH_BPh)(CH_CH_DPh)$], 3.090 [1H, dd, *J* 14.5, 6.9, $CH(CH_AH_BPh)(CH_CH_DPh)$], 4.43–4.50 [1H, m, $CH(CH_2Ph)_2$], 5.52 [1H, dd, *J* 4.7, 7.7, $CHCH_2Ph$], 6.59–6.61 [2H, m, PhH], 6.93–6.97 [2H, m, PhH], 6.99–7.13 [8H, m, PhH], 7.17–7.44 [13H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 36.1 [$CHCH_2Ph$], 37.2, 38.0 [$CH(CH_2Ph)_2$], 46.1 [$CH(CH_2Ph)_2$], 62.1 [$CHCH_2Ph$], 88.1 [CPh_2], 125.7, 126.2, 126.3, 126.4, 126.5 [*p-Ph*], 128.0, 128.1, 128.2, 128.4, 128.6, 128.8, 128.9, 129.3 [*m/o-Ph*], 136.1, 137.4, 138.5, 128.9, 141.2 [*i-Ph*], 151.7 [C=O endocyclic], 174.4 [C=O exocyclic]; ν_{max} (KBr) 1783, 1700 [C=O]; HRMS $C_{38}H_{34}NO_3$ [MH^+] requires 552.2534, found 552.2534; *m/z* CI+ 460 [40%, $MH^+ - CH_2Ph$], 508 [100%, $MH^+ - CO_2$], 552 [85%, MH^+].

Preparation of 2-benzyl-3-phenylpropionaldehyde 13, (*S*)-2-(2′-benzyl-3′-phenylpropionylamino)-2-benzylethyl formate 19, (*S*)-3-(2′-benzyl-1′-hydroxy-3′-phenylpropyl)-4-benzyloxazolidin-2-one 20 from (*S*)-16

Following Representative Procedure 3, DIBAL (1.00 mL, 1.00 mmol) and (*S*)-**16** (200 mg, 0.50 mmol) in CH_2Cl_2 (8 mL) furnished **13** (32 mg, 27%) as a clear colourless oil, **20** (26 mg, 13%) as a white solid, (*S*)-**19** (26 mg, 13%) as a white solid and **18** (25 mg, 27%) as a white solid and returned unreacted (*S*)-**16** (40 mg, 20%) after flash column chromatography.

Data for **20**: R_f 0.1 [1 : 1 hexane : Et_2O]; mp 87–90 °C [hexane–Et_2O]; $[\alpha]_D^{25}$ +32.4 (c = 0.25, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.53 [1H, dd, J 14.0, 6.5, CH(C$H_A$$H_B$Ph)($CH_2$Ph)], 2.613 [1H, dd, J 13.8, 10.8, CH(CH_2Ph)(C$H_C$$H_D$Ph)], 2.66–2.78 [3H, m, CH($CH_A$$H_B$Ph)($CH_C$$H_D$Ph) and O$H$], 3.15–3.21 [1H, m, C$H$($CH_2$Ph)$_2$], 3.36 [1H, app. t, J 8.3, C$H_A$$H_B$CHCH$_2$Ph], 3.40–3.50 [2H, m, CHCH_2Ph], 3.57–3.64 [1H, m, CH_2CHCH_2Ph], 3.77 [1H, dd, J 8.7, 4.1, $CH_A$$H_B$CHCH$_2$Ph], 5.27 [1H, dd, J 8.8, 5.3, CH(OH)], 6.99–7.36 [15H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 36.2, 36.5, 40.1 [CH(CH_2Ph)$_2$ and CH_2CHCH_2Ph], 44.64 [CH(CH_2Ph)$_2$], 55.3 [$CH_2$$CHCH_2$Ph], 66.7 [$CH_2CHCH_2$Ph], 81.8 [$C$H(OH)], 126.2, 127 [*i-Ph*], 128.5, 128.7, 128.9, 128.9, 129.6 [*m/o-Ph*], 136.2, 139.5, 140.2 [*p-Ph*], 157.9 [C=O]; ν_{max} (KBr) 1730 [C=O]; *m/z* CI+ 178 [100%, auxH$^+$], 384 [10%, MH$^+$ − H_2O].

Data for **19**: R_f 0.23 [1 : 1 hexane : Et_2O]; mp 92–97 °C [hexane–Et_2O]; $[\alpha]_D^{22}$ −3.1 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.40 [1H, dd, J 13.7, 8.3, CH_2CHC$H_A$$H_B$Ph], 2.46–2.52 [1H, m, C$H$($CH_2$Ph)$_2$], 2.57 [1H, dd, J 13.7, 5.4, CH_2CHC$H_A$$H_B$Ph], 2.78–2.84 [2H, m, CH(C$H_A$$H_B$Ph)(C$H_C$$H_D$Ph)], 2.96–3.04 [2H, m, CH($CH_A$$H_B$Ph)($CH_C$$H_D$Ph)], 3.62 [1H, dd, J 11.4, 4.3, C$H_A$$H_BCHCH_2$Ph], 3.81 [1H, dd, J 11.4, 5.4, $CH_A$$H_B$CH-$CH_2$Ph], 4.25–4.33 [1H, m, CH_2CHCH_2Ph], 5.04 [1H, d, J 8.6, NH], 6.85–7.36 [15H, m, PhH], 7.73 [1H, s, CHO]; δ_C (100 MHz, $CDCl_3$) 37.1, 37.4 [CH(CH_2Ph)$_2$ and CH_2CHCH_2Ph], 48.3 [CH(CH_2Ph)$_2$], 53.1 [$CH_2$$CHCH_2$Ph], 63.5 [$CH_2$CH-$CH_2$Ph], 126.3, 126.5, 126.7 [*p-Ph*], 128.2, 128.4, 128.5, 128., 128.9, 129.1 [*m/o-Ph*], 136.4, 139.5, 139.5 [*i-Ph*], 160.6 [C=O formate ester], 173.3 [C=O amide]; ν_{max} (KBr) 1725 [C=O formate ester], 1637 [C=O amide]; *m/z* APCI+ 402 [100%, MH$^+$], 424 [20%, MNa$^+$]; HRMS $C_{26}H_{28}NO_3$ [MH$^+$] requires 402.2064; found 402.2064.

Preparation of (*S*)-2-(2′-benzyl-3′-phenylpropionylamino)-2-benzyl-1,1-diphenylethyl formate 22

Following Representative Procedure 3, DIBAL (0.44 mL, 0.44 mmol) and (*S*)-**17** (120 mg, 0.22 mmol) in CH_2Cl_2 (5 mL) furnished **13** contaminated with unidentified products (52 mg), (*S*)-**22** (15 mg, 14%) and **21** (48 mg, 66%) as a white solid after flash column chromatography. Data for **22**: R_f 0.09 [5 : 1 30–40 °C petroleum ether : Et_2O; double eluted]; $[\alpha]_D^{24}$ −59.2 (c 0.60, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 2.14 [1H, dd, J 14.3, 10.1, CHC$H_A$$H_B$Ph], 2.20–2.26 [1H, m, C$H$($CH_2$Ph)$_2$], 2.32 [1H, dd, J 13.8, 5.4, CH(C$H_A$$H_B$Ph)($CH_2$Ph)], 2.42 [1H, dd, J 13.8, 8.8, CH($CH_A$$H_B$Ph)($CH_2$Ph)], 2.52 [1H, dd, J 13.6, 4.8, CH(CH_2-Ph)(C$H_C$$H_D$Ph)], 2.67 [1H, dd, J 13.6, 9.5, CH(CH_2Ph)(CH_C-H_DPh)], 3.02 [1H, dd, J 14.3, 3.5, CHC$H_A$$H_B$Ph], 5.28 [1H, s, N$H$], 5.80–5.86 [1H, m, C$HCH_2$Ph], 6.88 [2H, d, J 6.8, PhH], 6.99–7.41 [23H, m, PhH], 7.88 [1H, s, CHO]; δ_C (100 MHz, $CDCl_3$) 37.1, 37.4, 38.0 [CHCH$_2$Ph, CH(CH_2Ph)$_2$ and CH(CH$_2$Ph)$_2$], 52.5 [CHCH$_2$Ph], 90.0 [CPh$_2$], 126.0, 126.2, 126.6, 126.6, 128.0 [*i-Ph*], 127.7, 128.0, 128.2, 128.3, 128.4, 128.9, 129.0, 129.3 [*m/o-Ph*], 137.1, 139.4, 139.5, 139.7 [*p-Ph*], 173.8 [CHO], 175.0 [C=O amide]; ν_{max} (film) 1724, 1683 [C=O]; HRMS $C_{38}H_{35}NO_3Na$ [MNa$^+$] requires 576.2510, found 576.2516; *m/z* ES+ 508 [70%, MH$^+$ − CO_2], 576 [100%, MNa$^+$].

Preparation of (*S*)-3-(4′-methylpentanoyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 23

Following Representative Procedure 1, *n*-BuLi (1.10 mL, 2.68 mmol), (*S*)-**4** (500 mg, 2.46 mmol) and 4-methylvaleryl chloride (prepared by treatment of 4-methylvaleric acid (1.59 g, 9.76 mmol) with oxalyl chloride (4.26 mL, 48.8 mmol) and DMF (cat.) in hexane (10 mL)) in THF (20 mL) furnished **23** (580 mg, 78%) as a clear colourless oil after flash column chromatography; R_f 0.28 [5 : 1 30–40 °C petrol : Et_2O]; $[\alpha]_D^{22}$ −37.7 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.93 [6H, d, J 6.4, CH(CH_3)$_2$], 1.36 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.38 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.48–1.64 [3H, m, CH_2CH(CH_3)$_2$], 2.85–2.94 [3H, m, CHC$H_A$$H_B$Ph and $CH_2$$CH_2$CH($CH_3$)$_2$], 3.14 [1H, dd, J 14.3, 3.9, CHC$H_A$$H_B$Ph], 4.51 [1H, dd, J 9.5, 3.9, CHCH_2Ph], 7.22–7.33 [5H, m, PhH]; δ_C (50 MHz, $CDCl_3$) 22.7 [CH(CH_3)$_2$], 22.8 [CH(CH_3)$_2$], 28.1, 29.0 [C(CH_3)$_2$], 33.6 [CH_2CH(CH_3)$_2$], 34.2 [$CH_2$$CH_2$CH($CH_3$)$_2$], 35.8 [CH$CH_2$Ph], 63.9 [$CH$$CH_2$Ph], 82.5 [$C$($CH_3$)$_2$], 127.2 [*p-Ph*], 129.1, 129.5 [*m/o-Ph*], 137.5 [*i-Ph*], 153.1 [C=O endocyclic], 174.2 [C=O exocyclic]; ν_{max} (film) 1778 [C=O endocyclic], 1699 [C=O exocyclic]; *m/z* APCI+ 260 [10%, MH$^+$ − CO_2], 304 [35%, MH$^+$], 326 [15%, MNa$^+$]; HRMS $C_{18}H_{26}N0_3$ [MH$^+$] requires 304.1908; found 304.1903.

Preparation of (*S*)-3-butyryl-4-benzyl-5,5-dimethyloxazolidin-2-one 24

Following Representative Procedure 1, *n*-BuLi (5.37 mL, 10.73 mmol), (*S*)-**4** (2.00 g, 9.76 mmol) and butyryl chloride (1.32 mL, 12.69 mmol) in THF (50 mL) furnished **24** (2.06 g, 77%) as a white solid after flash column chromatography; R_f 0.18 [5 : 1 40–60 °C petrol : Et_2O]; mp 109–110 °C [hexane–Et_2O]; $[\alpha]_D^{22}$ −44.6 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.96 [3H, t, J 7.4, $CH_2$$CH_2CH_3$], 1.35 [3H, s, C($CH_3$)$_A$($CH_3$)$_B$], 1.368 [3H, s, C($CH_3$)$_A$($CH_3$)$_B$], 1.65–1.71 [2H, m, CH_2C$H_2$$CH_3$], 2.85–2.93 [3H, m, C$H_2$$CH_2$$CH_3$ and CHC$H_A$$H_B$Ph], 3.13 [1H, dd, J 14.3, 4.0, CHC$H_A$$H_B$Ph], 4.51 [1H, dd, J 9.5, 4.0, CHCH_2Ph], 7.20–7.32 [5H, m, PhH]; δ_C (50 MHz, $CDCl_3$) 14.1 [$CH_2$$CH_2$$CH_3$], 18.2 [$CH_2$$CH_2$$CH_3$], 22.7, 29.0 [C($CH_3$)$_2$], 35.8 [CH$CH_2$Ph], 38.0 [$CH_2$$CH_2$$CH_3$], 63.9 [$CH$$CH_2$Ph], 82.6 [$C$($CH_3$)$_2$], 127.2 [*p-Ph*], 129.1, 129.5 [*m/o-Ph*], 137.5 [*i-Ph*], 153.1 [C=O endocyclic], 173.9 [C=O exocyclic]; ν_{max} (KBr) 1771 [C=O endocyclic], 1699 [C=O exocyclic]; *m/z* APCI+ 276 [10%, MH$^+$], 298 [5%, MNa$^+$]; HRMS $C_{16}H_{22}NO_3$ [MH$^+$] requires 276.1595; found 276.1594.

Preparation of (2′*S*,4*S*)-3-(2′-methyl-3′-phenylpropionyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 25

Following Representative Procedure 2b, LHMDS (4.45 mL, 4.45 mmol), (*S*)-**7** (1.00 g, 2.97 mmol) and methyl iodide (0.55 mL, 8.91 mmol) in THF (50 mL) furnished **25** (782 mg, 75%, 85% de) as pale yellow solid after flash column chromatography; R_f 0.2 [5 : 1 hexane : Et_2O]; mp 90–91 °C [hexane–Et_2O]; $C_{22}H_{25}NO_3$ requires C, 75.2, H, 7.2, N, 4.0%; found C, 75.0, H, 7.1, N, 3.9%; $[\alpha]_D^{25}$ +34.8 (c = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.03 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.17 [3H, d, J 6.8, CHCH_3], 1.33 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 2.68 [1H, dd, J 13.4, 6.9, CHC$H_A$$H_B$Ph (exocyclic)], 2.88 [1H, dd, J 14.3, 9.0, CHC$H_A$$H_B$Ph (auxiliary)], 3.03 [1H, dd, J 14.3, 4.6, CHC$H_A$$H_B$Ph (auxiliary)], 2.98 [1H, dd, J 13.4, 8.5, CHC$H_A$$H_B$Ph (exocyclic)], 4.15–4.21 [1H, m, CHCH_3], 4.37 [1H, dd, J 9.0, 4.6, CHCH_2Ph], 7.15–7.32 [10H, m, PhH]; δ_C (125 MHz, $CDCl_3$) 17.3 [CHCH$_3$], 22.0, 27.7 [C(CH_3)$_2$], 35.1 [CHCH$_2$Ph], 39.2 [CH(CH_3)], 39.9 [CHCH$_2$Ph], 63.4 (CH_2Ph)], 82.1 [C(CH_3)$_2$], 126.5, 127.0, 128.6, 128.8, 129.3 [*p/m/o-Ph*], 137.7, 138.7, 139.6 [*i-Ph*], 152.6 [C=O endocyclic], 176.9 [C=O exocyclic]; ν_{max} ($CHCl_3$) 1771 [C=O exocyclic], 1697 [C=O endocyclic]; *m/z* (CI$^+$, NH_3) 352 [100%, MH$^+$].

Preparation of (2′*S*,4*S*)-3-(2′-allyl-3′-phenylpropionyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 26

Following Representative Procedure 2b, LHMDS (1.35 mL, 1.35 mmol), (*S*)-**7** (300 mg, 0.90 mmol) and allyl bromide (0.24 mL, 2.70 mmol) in THF (20 mL) furnished **161** (250 mg, 71%, 86% de) as a yellow oil after flash column chromatography; R_f 0.18 [7 : 1 hexane : Et_2O]; $[\alpha]_D^{22}$ +53.4 (c = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.89 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.26 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 2.30–2.37 [1H, m, C$H_A$$H_B$CH=$CH_2$], 2.46–2.53 [1H, m, $CH_A$$H_B$CH=$CH_2$], 2.77–3.06 [4H, m, CHC$H_2$Ph (auxiliary and exocyclic)], 4.32 [1H, dd, J 9.8, 3.5, CHCH_2Ph

(auxiliary)], 4.40–4.48 [1H, m, C*H*CH_2CH=CH_2], 5.02–5.12 [2H, m, CH_2CH=CH_2], 5.77–5.87 [1H, m, CH_2C*H*=CH_2], 7.14–7.32 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 22.1, 27.6 [C(CH_3)$_2$], 35.4, 37.0 [2 × CH_2Ph], 38.3 [CH_2CH=CH_2], 43.7 [CHCH_2CH=CH_2], 63.6 [CHCH_2Ph], 81.9 [C(CH_3)$_2$], 117.3 [CH_2CH=CH_2], 126.3, 126.7 [*p-Ph*], 128.4, 128.6, 128.9, 129.0 [*m*/*o-Ph*], 135.0 [CH_2CH=CH_2], 137.0, 139.0 [*i-Ph*], 152.3 [*C*=O endocyclic], 175.5 [*C*=O exocyclic]; ν_{max} (film) 1773 [C=O endocyclic], 1696 [C=O exocyclic]; *m*/*z* APCI+ 334 [40%, $MH^+ - CO_2$], 378 [80%, MH^+]; HRMS $C_{24}H_{28}NO_3$ [MH^+] requires 378.2064; found 378.2065.

Preparation of (2′*S*,4*S*)-3-(2′-benzyl-5′-methylhex-4′-enoyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 27

Following Representative Procedure 2b, LHMDS (1.12 mL, 1.12 mmol), (*S*)-**7** (250 mg, 0.75 mmol) and 1-bromo-3-methylbut-2-ene (0.26 mL, 2.25 mmol) in THF (15 mL) furnished **27** (241 mg, 80%, 94% de) as pale yellow oil by flash column chromatography; R_f 0.25 [5 : 1 hexane : Et_2O]; $[\alpha]_D^{22}$ +26.4 (*c* = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.89 [3H, s, CH=C(CH_3)$_A$(CH_3)$_B$], 1.26 [3H, s, CH=C(CH_3)$_A$(CH_3)$_B$], 1.61 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.69 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 2.21–2.28 [1H, m, C$H_A$$H_B$CH=C($CH_3$)$_2$], 2.43–2.51 [1H, m, $CH_A$$H_B$CH=C($CH_3$)$_2$], 2.76–3.02 [4H, m, 2 × CHCH_2Ph], 4.31 [1H, dd, *J* 9.7, 3.5, C*H*CH_2Ph (auxiliary)], 4.35–4.43 [1H, dd, *J* 9.7, 3.5, C*H*CH_2Ph (exocyclic)], 5.18–5.22 [1H, m, C*H*=C(CH_3)$_2$], 7.12–7.33 [10H, m, Ph*H*]; δ_C (50 MHz, $CDCl_3$) 18.3, 26.3 [CH=C(CH_3)$_2$], 22.6, 28.1 [C(CH_3)$_2$], 32.0, 35.7 [CHCH_2Ph (auxiliary and exocyclic)], 38.7 [CH_2CH=C(CH_3)$_2$], 44.9 [CHCH_2Ph (exocyclic)], 64.0 [CHCH_2Ph (auxiliary)], 82.2 [C(CH_3)$_2$], 121.2 [CH=C(CH_3)$_2$], 126.7, 127.2 [*p-Ph*], 128.8, 129.1, 129.5 [*m*/*o-Ph*], 134.6 [CH=C(CH_3)$_2$], 137.6, 139.8 [*i-Ph*], 152.7 [*C*=O endocyclic], 176.5 [*C*=O exocyclic]; ν_{max} (film) 1776 [C=O exocyclic], 1695 [C=O endocyclic]; *m*/*z* APCI+ 362 [30%, $MH^+ - CO_2$], 406 [100%, MH^+]; HRMS $C_{26}H_{32}NO_3$ [MH^+] requires 406.2377; found 406.2377.

Preparation of (2′*R*,4*S*)-3-(2′-phenyl-4′-methylpentanoyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 28

Following Representative Procedure 2b, LHMDS (1.50 mL, 1.50 mmol), (*S*)-**23** (300 mg, 0.99 mmol) and benzyl bromide (0.35 mL, 2.97 mmol) in THF (15 mL) furnished **28** (390 mg, 98%, 91% de) as a white solid after flash column chromatography; R_f 0.29 [5 : 1 hexane : Et_2O]; $[\alpha]_D^{22}$ −62.7 (*c* = 1.0, $CHCl_3$); mp 94–96 °C [hexane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.89 [3H, d, *J* 6.6, CH(CH_3)$_A$(CH_3)$_B$], 0.93 [3H, d, *J* 6.6, CH(CH_3)$_A$(CH_3)$_B$], 1.27 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.32 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.27–1.36 [1H, m, C$H_A$$H_B$CH($CH_3$)$_2$], 1.53–1.63 [1H, m, CH_2CH(CH_3)$_2$], 1.75–1.82 [1H, m, $CH_A$$H_B$CH-($CH_3$)$_2$], 2.52 [1H, dd, *J* 14.5, 10.1, C(4)HC$H_A$$H_B$Ph], 2.75 [1H, dd, *J* 13.3, 7.3, C(2′)HC$H_A$$H_B$Ph], 2.83 [1H, dd, *J* 14.5, 2.9, C(4)HC$H_A$$H_B$Ph], 2.97 [1H, dd, *J* 13.3, 8.0, C(2′)HC$H_A$$H_B$Ph], 4.38–4.51 [2H, m, C(4)*H*CH_2Ph and C*H*CH_2(CH_3)$_2$], 7.19–7.42 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 22.2, 22.3 [CH(CH_3)$_2$], 23.1 [C*H*(CH_3)$_2$], 26.3, 28.4 [C(CH_3)$_2$], 34.7 [CH_2CH(CH_3)$_2$], 39.5, 40.9 [C(4)HCH_2Ph and C(2′)HCH_2Ph], 42.2 [C(2′)H], 63.6 [C(4)H], 81.7 [C(CH_3)$_2$], 126.3, 126.7 [*p-Ph*], 128.3, 128.6, 128.8, 129.0, 129.3 [*m*/*o-Ph*], 137.1, 138.9 [*i-Ph*], 152.2 [*C*=O exocyclic], 176.8 [*C*=O endocyclic]; ν_{max} (KBr) 1770 [C=O endocyclic], 1691 [C=O exocyclic]; *m*/*z* APCI+ 350 [20%, $MH^+ - CO_2$], 394 [100%, MH^+], 416 [10%, MNa^+]; HRMS $C_{25}H_{32}NO_3$ [MH^+] requires 394.2377; found 394.2390.

Preparation of (2′*R*,4*S*)-3-(2′-benzylbutyryl)-4-benzyl-5,5-dimethyloxazolidin-2-one 29

Following Representative Procedure 2b, LHMDS (1.64 mL, 1.64 mmol), (*S*)-**24** (0.30 g, 1.09 mmol) and benzyl bromide (0.39 mL, 3.27 mmol) in THF (15 mL) furnished **29** (370 mg, 94%, 94% de) as a clear colourless oil by flash column chromatography; R_f 0.24 [5 : 1 hexane : Et_2O]; $C_{23}H_{27}NO_3$ requires C, 75.6, H, 7.45, N, 3.8%; found C, 75.4, H, 7.5, N, 3.5%; $[\alpha]_D^{22}$ −69.6 (*c* = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.94 [3H, t, *J* 7.4, $CHCH_2C$*H*$_3$] 1.28 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.31 [3H, s, C(CH_3)$_A$(CH_3)$_B$], 1.53–1.63 [1H, m, CHC$H_A$$H_B$$CH_3$], 1.71–1.82 [1H, m, CHC$H_A$$H_B$$CH_3$], 2.55 [1H, dd, *J* 14.6, 10.0, CHCH_A-H_BPh (auxiliary)], 2.76 [1H, dd, *J* 13.4, 7.1, CHC$H_A$$H_B$Ph (exocyclic)], 2.84 [1H, dd, *J* 14.6, 3.2, CHC$H_A$$H_B$Ph (auxiliary)], 3.00 [1H, dd, *J* 13.4, 8.2, CHC$H_A$$H_B$Ph (exocyclic)], 4.20–4.27 [1H, m, C*H*$CH_2$$CH_3$], 4.48 [1H, dd, *J* 10.0, 3.2, C*H*CH_2Ph (auxiliary)], 7.16–7.31 [10H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 11.7 [CHCH_2CH_3], 22.2, 28.5 [C(CH_3)$_2$], 25.1 [CHC$H_2$$CH_3$], 34.8, 38.6 [CHC$H_2$Ph (auxiliary and exocyclic)], 45.8 [C*H*CH_2-CH_3], 63.6 [C*H*CH_2Ph (auxiliary)], 81.7 [C(CH_3)$_2$], 126.3, 126.7 [*p-Ph*], 128.3, 128.6, 129.0, 129.3 [*m*/*o-Ph*], 137.1, 139.1 [*i-Ph*], 152.3 [*C*=O endocyclic], 176.5 [*C*=O exocyclic]; ν_{max} (film) 1777 [C=O endocyclic], 1695 [C=O exocyclic]; *m*/*z* APCI+ 366 [100%, MH^+], 388 [10%, MNa^+].

Preparation of (*S*)-2-methyl-3-phenylpropionaldehyde 30[36]

Following Representative Procedure 3, DIBAL (1.15 mL, 1.15 mmol) and **25** (200 mg, 0.56 mmol) in CH_2Cl_2 (5 mL) furnished **30** (74 mg, 87%, 87% ee) as a clear, colourless oil and (*S*)-**4** (115 mg, 98%) as a white solid after flash column chromatography. Data for **30**; R_f 0.27 [10 : 1 40–60 °C petrol : Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.10 [3H, d, *J* 6.9, CHCH_3], 2.59–2.74 [2H, m, C*H*C$H_A$$H_B$Ph], 3.11 [1H, dd, *J* 13.3, 5.6, CHC$H_A$$H_B$Ph], 7.15–7.33 [5H, m, Ph*H*], 9.74 [1H, d, *J* 1.5, C*H*O]; $[\alpha]_D^{22}$ −1.1 (*c* = 1.0, $CHCl_3$), {lit.[36] $[\alpha]_D^{23}$ −4.42 (*c* = 0.4, MeOH)}.

Following Representative Procedure 4, $LiAlH_4$ (0.07 mL, 0.07 mmol) and **30** (20 mg, 0.14 mmol) in THF (2 mL) furnished (*S*)-2-methyl-3-phenylpropan-1-ol[37] (17 mg, 79%) as a clear colourless oil after flash column chromatography; R_f 0.22 [2 : 1 30–40 °C petrol : Et_2O]; δ_H (200 MHz, $CDCl_3$) 0.93 [3H, d, *J* 6.7, CHCH_3], 1.45 [1H, s, O*H*], 1.91–2.04 [1H, m, C*H*CH_2Ph], 2.44 [1H, dd, *J* 13.4, 7.9, CHC$H_A$$H_B$Ph], 2.77 [1H, dd, *J* 13.4, 6.3, CHC$H_A$$H_B$Ph], 3.44–3.60 [2H, m, C$H_2$OH], 7.17–7.34 [5H, m, Ph*H*]; $[\alpha]_D^{18}$ −14.0 (*c* = 0.25, $CHCl_3$), {lit.[37a] $[\alpha]_D^{20}$ −11.1 (*c* = 0.83, $CHCl_3$); lit.[37b] $[\alpha]_D^{20}$ −10.1 (*c* = 0.8, $CHCl_3$)}.

Preparation of (*S*)-2-allyl-3-phenylpropionaldehyde 31[38]

Following Representative Procedure 3, DIBAL (1.07 mL, 1.07 mmol) and **26** (200 mg, 0.53 mmol) in CH_2Cl_2 (5 mL) furnished **31** (70 mg, 76%, 87% ee) as a clear, colourless oil and (*S*)-**4** (88 mg, 0.43 mmol, 81%) as a white solid after flash column chromatography; R_f 0.26 [10 : 1 hexane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 2.26–2.33 [1H, m, C$H_A$$H_B$CH=$CH_2$], 2.37–2.44 [1H, m, $CH_A$$H_B$CH=$CH_2$], 2.72–3.04 [2H, m, C*H*C$H_A$$H_B$Ph], 3.47–3.52 [1H, m, CHC$H_A$$H_B$Ph], 5.06–5.13 [2H, m, CH_2CH=CH_2], 5.72–5.83 [1H, m, CH_2C*H*=CH_2], 7.17–7.36 [5H, m, Ph*H*], 9.72 [1H, d, *J* 1.8, C*H*O]; $[\alpha]_D^{22}$ −28.4 (*c* = 1, $CHCl_3$).

Following Representative Procedure 4, $LiAlH_4$ (0.03 mL, 0.03 mmol) and **31** (10 mg, 0.05 mmol) in THF (2 mL) furnished (*S*)-2-allyl-3-phenylpropan-1-ol[39] (10 mg, 100%) as a clear colourless oil after flash column chromatography; R_f 0.26 [2 : 1 30–40 °C petrol : Et_2O]; δ_H (200 MHz, $CDCl_3$) 1.44 [1H, s, O*H*], 1.87–2.01 [1H, m, C*H*CH_2Ph], 2.16 [2H, t, *J* 7.0, CH_2CH=CH_2], 2.64–2.68 [2H, m, CH_2Ph], 3.50–3.61 [2H, m, CH_2OH], 5.05–5.14 [2H, m, CH=CH_2], 5.76–5.97 [1H, m, C*H*=CH_2], 7.19–7.35 [5H, m, Ph*H*]; $[\alpha]_D^{20}$ −13.3 (*c* = 0.55, $CHCl_3$).

Preparation of (*S*)-2-benzyl-5-methyl-hex-4-enal 32

Following Representative Procedure 3, DIBAL (1.00 mL, 1.00 mmol) and **27** (200 mg, 0.50 mmol) in CH_2Cl_2 (5 mL) furnished **32** (75 mg, 74%, 94% ee) as a clear, colourless oil and (*S*)-**4**

(87 mg, 85%) as a white solid after flash column chromatography; Data for **32**; R_f 0.26 [12 : 1 hexane : Et_2O]; $[\alpha]_D^{23}$ −54.8 (c = 1.0, $CHCl_3$); ν_{max} (film) 1732 [C=O]; δ_H (400 MHz, $CDCl_3$) 1.58 [3H, s, CH=C(CH_3)$_A$(CH$_3$)$_B$], 1.71 [3H, s, CH=C(CH$_3$)$_A$-(CH_3)$_B$], 2.18–2.35 [2H, m, CH_2CH=C(CH$_3$)$_2$], 2.64–2.78 [2H, m, CHCH_AH$_B$Ph], 2.97–3.03 [1H, m, CHCH$_A$$H_B$Ph], 5.08–5.13 [1H, m, C$H$=C(CH$_3$)$_2$], 7.16–7.41 [5H, m, Ph$H$], 9.70 [1H, d, J 2.0, CHO]; δ_C (100 MHz, $CDCl_3$) 17.8, 25.8 [CH=C(CH_3)$_2$], 27.2 [CH_2CH=C(CH$_3$)$_2$], 34.4 [CHCH$_2$Ph], 53.8 [CHCH$_2$Ph], 120.1 [CH=C(CH$_3$)$_2$], 126.3 [p-Ph], 129.0, 129.3 [m/o-Ph], 134.4 [i-Ph], 139.0 [CH=C(CH$_3$)$_2$], 204.6 [CHO]; m/z CI+ (NH$_3$) 203 [10%, MH$^+$], 220 [100%, MNH$_3^+$]; HRMS $C_{14}H_{18}O$ [MH$^+$] requires 202.1353; found 202.1356.

Following Representative Procedure 4, $LiAlH_4$ (0.03 mL, 0.03 mmol) and **32** (10 mg, 0.05 mmol) in THF (2 mL) furnished (*S*)-2-benzyl-5-methylhex-4-en-1-ol[40] (9 mg, 0.04 mmol, 80%) as a clear colourless oil; R_f 0.21 [2 : 1 hexane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.61 [3H, s, CH=C(CH_3)$_A$(CH$_3$)$_B$], 1.72 [3H, s, CH=C(CH$_3$)$_A$(CH_3)$_B$], 1.83–1.93 [1H, m, CHCH$_2$Ph], 2.02–2.19 [2H, m, CHCH_2Ph], 2.59–2.69 [2H, m, CH_2CH=C(CH$_3$)$_2$], 3.48–3.58 [2H, m, CH_2OH], 5.17–5.21 [1H, m, CH=C(CH$_3$)$_2$], 7.18–7.31 [5H, m, PhH]; $[\alpha]_D^{23}$ −30.2 (c = 0.5, $CHCl_3$), {lit.[40] *ent*- $[\alpha]_D^{24}$ +27.0 (c = 1, $CHCl_3$)}.

Preparation of (*R*)-2-benzyl-4-methylpentanal 33

Following Representative Procedure 3, DIBAL (1.02 mL, 1.02 mmol) and **28** (200 mg, 0.51 mmol) in CH_2Cl_2 (5 mL) furnished **33** (93 mg, 95%, 91% ee) as a clear colourless and (*S*)-**4** (94 mg, 90%) as a white solid after flash column chromatography; Data for **33**; R_f 0.28 [12 : 1 hexane : Et_2O]; $[\alpha]_D^{25}$ +1.1 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.88 [3H, d, J 6.5, CH(CH_3)$_A$(CH$_3$)$_B$], 0.90 [3H, d, J 6.4, CH(CH$_3$)$_A$(CH_3)$_B$], 1.24–1.31 [1H, m, CH_AH$_B$-CH(CH$_3$)$_2$], 1.58–1.70 [2H, m, CH$_A$$H_B$CH(CH$_3$)$_2$ and CH$_2$CH-(CH$_3$)$_2$], 2.68–2.93 [1H, m CHCH_AH$_B$Ph], 2.94–2.99 [1H, m, CHCH$_A$$H_B$Ph], 7.14–7.32 [5H, m, PhH], 9.65 [1H, d, J 2.8, CHO]; δ_C (100 MHz, $CDCl_3$) 22.9, 22.2 [CH(CH_3)$_2$], 25.7 [CH(CH$_3$)$_2$], 35.6 [CH_2CH(CH$_3$)$_2$], 37.9 [CHCH$_2$Ph], 51.5 [CHCH$_2$Ph], 126.4 [p-Ph], 128.6, 128.9 [m/o-Ph], 138.7 [i-Ph], 204.9 [CHO]; ν_{max} (film) 1707 [C=O]; m/z EI+ 91 [100%, CH$_2$Ph$^+$], 190 [15%, M$^+$]; HRMS $C_{13}H_{18}O$ [M$^+$] requires 190.1353; found 190.1354.

Following Representative Procedure 4, $LiAlH_4$ (0.13 mL, 0.13 mmol) and **33** (50 mg, 0.26 mmol) in THF (5 mL) furnished (*R*)-2-benzyl-4-methylpentan-1-ol (44 mg, 89%) as a clear colourless oil; R_f 0.19 [2 : 1 hexane : Et_2O]; $[\alpha]_D^{18}$ +2.2 (c = 1.75, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.86 [3H, d, J 9.9, CH(CH_3)$_A$(CH$_3$)$_B$], 0.89 [3H, d, J 9.8, CH(CH$_3$)$_A$(CH_3)$_B$], 0.91–1.20 [2H, m, CH_AH$_B$CH(CH$_3$)$_2$ and OH], 1.24–1.33 [1H, m, CH$_A$$H_B$CH(CH$_3$)$_2$], 1.64–1.76 [1H, m, C$H$(CH$_3$)$_2$], 1.84–1.94 [1H, m, C$HCH_2$Ph], 2.64 [2H, app. d, J 7.2, CHCH_2Ph], 3.51 [2H, app. d, J 5.0, CH_2OH], 7.19–7.22 [3H, m, PhH], 7.27–7.31 [2H, m, PhH]; δ_C (50 MHz, $CDCl_3$) 22.6, 22.7 [CH(CH_3)$_2$], 25.1 [CH(CH$_3$)$_2$], 37.7 [CHCH$_2$Ph], 40.0, 40.3 [CHCH$_2$Ph and CH$_2$CH(CH$_3$)$_2$], 64.9 [CH$_2$OH], 126.0 [p-Ph], 128.4, 129.4 [m/o-Ph], 141.0 [i-Ph]; ν_{max} (film) 3349.9 [O–H]; m/z CI+ (NH$_3$) 210 [100%, MNH$_4^+$]; HRMS $C_{13}H_{24}NO$ [MNH$_4^+$] requires 210.1851, found 210.1856.

Preparation of (*R*)-2-benzylbutanal 34[41]

Following Representative Procedure 3, DIBAL (1.09 mL, 1.09 mmol) and **29** (200 mg, 0.55 mmol) in CH_2Cl_2 (5 mL) furnished **34** (85 mg, 95%, 94% ee) as a clear colourless oil and (*S*)-**4** (92 mg, 0.45 mmol, 82%) as a white solid after flash column chromatography; R_f 0.27 [12 : 1 hexane : Et_2O]; $[\alpha]_D^{22}$ +4.5 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.95 [3H, t, J 7.5, CHCH$_2$CH_3], 1.52–1.74 [2H, m, CHCH_2CH$_3$], 2.54–2.61 [1H, m, CHCH$_2$-CH$_3$], 2.73 [1H, dd, J 14.1, 7.1, CHCH_AH$_B$Ph], 3.00 [1H, dd, J 14.1, 7.4, CHCH$_A$$H_B$Ph], 7.17–7.37 [5H, m, PhH], 9.68 [1H, d, J 2.4, CHO];

Following Representative Procedure 4, $LiAlH_4$ (0.06 mL, 0.06 mmol) and **34** (20 mg, 0.12 mmol) in THF (5 mL) furnished (*R*)-2-benzylbutan-1-ol[42] (18 mg, 91%) as a clear colourless oil; R_f 0.18 [2 : 1 hexane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.95 [3H, t, J 3.4, CHCH$_2$CH_3], 1.29–1.50 [3H, m, CHCH_2CH$_3$ and OH], 1.71–1.77 [1H, m, CHCH$_2$CH$_3$], 2.65 [2H, app. d, J 7.0, CHCH_2Ph], 3.55 [2H, d, J 5.2, CH_2OH], 7.19–7.31 [5H, m, PhH]; $[\alpha]_D^{18}$ −8.0 (c = 0.55, $CHCl_3$), {lit.[42] $[\alpha]_D^{23}$ −5.0 (c = 1.0, CH_2Cl_2)}.

Preparation of (4*S*,2′*E*)-3-(3′-phenylacryloyl)-4-benzyl-5,5-dimethyloxazolidin-2-one 35

Following Representative Procedure 1, *n*-BuLi (2.20 mL, 5.37 mmol), (*S*)-**4** (1.00 g, 4.89 mmol) and cinnamoyl chloride (1.06 g, 6.36 mmol) in THF (60 mL) furnished **35** (1.11 g, 68%) as an orange oil after flash column chromatography; R_f 0.24 [3 : 1 hexane : Et_2O]; $[\alpha]_D^{23}$ −64.9 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.40 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.42 [3H, s, C(CH$_3$)$_A$-(CH_3)$_B$], 2.94 [1H, dd, J 14.4, 9.7, CHCH_AH$_B$Ph], 3.28 [1H, dd, J 14.4, 3.6, CHCH$_A$$H_B$Ph], 4.64 [1H, dd, J 9.7, 3.6, CHCH$_2$Ph], 7.19–7.43 [8H, m, PhH], 7.59–7.66 [2H, m, PhH], 7.82–7.96 [2H, m, CH=CH]; δ_C (50 MHz, $CDCl_3$) 22.3, 8.6 [C(CH_3)$_2$], 35.3 [CH_2Ph], 63.9 [CHCH$_2$Ph], 82.3 [C(CH$_3$)$_2$], 117.3 [CH=CHPh], 126.8, 130.6 [p-Ph], 128.0, 128.6, 128.9, 129.1 [m/o-Ph], 134.6, 137.1 [i-Ph], 146.1 [CH=CHPh], 152.7 [C=O endocyclic], 165.5 [C=O exocyclic]; ν_{max} (film) 1770 [C=O endocyclic], 1682 [C=O exocyclic]; m/z APCI+ 336 [100%, MH$^+$]; HRMS $C_{21}H_{21}NO_3$ [MH$^+$] requires 336.1595, found 336.1610.

Preparation of (4*S*,2′*E*)-3-(3′-phenylacryloyl)-4-isopropyl-5,5-dimethyloxazolidin-2-one 36

Following Representative Procedure 1, *n*-BuLi (2.90 mL, 7.01 mmol), (*S*)-**5** (1.00 g, 6.37 mmol) and cinnamoyl chloride (1.38 g, 8.28 mmol) in THF (40 mL) furnished **36** (1.81 g, 99%) as a white solid after flash column chromatography; R_f 0.18 [5 : 1 40–60 °C petrol : Et_2O]; mp 71–73 °C [hexane–Et_2O]; $C_{17}H_{21}$-NO_3 requires C. 71.0, H. 7.4, N, 4.9%, found C, 71.05, H, 7.5, N, 4.8%; $[\alpha]_D^{23}$ −108.7 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.00 [3H, d, J 6.8, CH(CH_3)$_A$(CH$_3$)$_B$], 1.08 [3H, d, J 7.0, CH(CH$_3$)$_A$(CH_3)$_B$], 1.43 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.55 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.17–2.25 [1H, m, CH(CH$_3$)$_2$], 4.31 [1H, d, J 3.4, CHCH(CH$_3$)$_2$], 7.39–7.45 [3H, m, PhH], 7.61–7.66 [2H, m, PhH], 7.84–8.02 [2H, m, CH=CH]; δ_C (50 MHz, $CDCl_3$) 17.1, 21.4 [CH(CH_3)$_2$], 21.5, 29.7 [C(CH_3)$_2$], 28.8 [CH(CH$_3$)$_2$], 66.5 [CHCH(CH$_3$)$_2$], 82.8 [C(CH$_3$)$_2$], 117.2 [p-Ph], 128.6, 128.8 [m/o-Ph], 130.5 [CH=CHPh], 134.6 [i-Ph], 146.2 [CH=CHPh], 153.6 [C=O endocyclic], 165.9 [C=O exocyclic]; ν_{max} (KBr) 1774 [C=O endocyclic], 1680 [C=O exocyclic]; m/z APCI+ 288 [100%, MH$^+$].

Preparation of (4*S*,2′*E*)-3-(3′-phenylacryloyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 37[17]

Following Representative Procedure 1, *n*-BuLi (11.5 mL, 28.79 mmol), (*S*)-**6** (5.00 g, 26.18 mmol) and cinnamoyl chloride (5.70 g, 34.03 mmol) in THF (250 mL) furnished **37** (8.38 g, 99%) as a white solid after flash column chromatography; R_f 0.14 [3 : 1 hexane : Et_2O]; mp 147–150 °C [hexane–EtOAc] {lit.[5] 149 °C [40–60 °C petrol–EtOAc]}; δ_H (400 MHz, $CDCl_3$) 1.04 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.66 [3H, s, C(CH$_3$)$_A$CH_3)$_B$], 5.23 [1H, s, CHPh], 7.21–7.43 [8H, m, PhH], 7.55–7.64 [2H, m, PhH], 7.80 [1H, d, J 15.7, CH=CHPh], 8.05 [1H, d, J 15.7, CH=CHPh]; $[\alpha]_D^{23}$ −27.0 (c = 1.0, $CHCl_3$) {lit.[17] *ent*-$[\alpha]_D^{26}$ +26.0 (c = 1.0, $CHCl_3$)}.

Preparation of (3′*S*,4*S*)- and (3′*R*,4*S*)-4-benzyl-3-(3′-phenylbutyryl)-5,5-dimethyloxazolidin-2-one 38

Following Representative Procedure 5, CuBr·SMe_2 (185 mg, 0.90 mmol), MeMgBr (0.60 mL, 1.80 mmol), BF_3·Et_2O

(0.11 mL, 0.90 mmol) and **35** (200 mg, 0.60 mmol) in SMe_2 (4 mL) and THF (8 mL, 4 mL) furnished an inseparable mixture of (3′*S*,4*S*)- and (3′*R*,4*S*)-**38** (186 mg, 88%, 29% de) as a white solid after flash column chromatography; R_f 0.21 [5 : 1 hexane : Et_2O, double eluted]; mp 85–88 °C [hexane–Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.13 [3H, s, $C(CH_3)_A(CH_3)_B$ (minor)], 1.30–1.33 [15H, m, $C(CH_3)_A(CH_3)_B$ (minor), $C(CH_3)_2$ (major) and $CHCH_3$ (major and minor)], 2.68 [1H, dd, *J* 14.5, 9.8, $CHCH_AH_BPh$ (major)], 2.82 [1H, dd, *J* 14.4, 9.6, $CHCH_AH_BPh$ (minor)], 2.98 [1H, dd, *J* 14.5, 3.5, $CHCH_AH_BPh$ (major)], 3.04–3.17 [3H, m, $CHCH_AH_BPh$ (minor), $CHCH_3$ (minor) and $CH_AH_BCHCH_3$ (major)], 3.33–3.51 [4H, m, $CHCH_3$ (major), CH_2CHCH_3 (minor) and $CH_AH_BCHCH_3$ (major)], 4.40 [1H, dd, *J* 9.5, 4.0, $CHCH_2Ph$ (minor)], 4.47 [1H, dd, *J* 9.8, 3.5, $CHCH_2Ph$ (major)], 7.17–7.33 [20H, m, Ph*H* (major and minor)]; δ_C (100 MHz, $CDCl_3$) 22.0, 22.2, 22.3 [$C(CH_3)_2$ (major and minor)], 28.1 [$CHCH_3$ (minor)], 28.5 [$CHCH_3$ (major)], 34.9 [$CHCH_3$ (major)], 35.3 [$CHCH_3$ (minor)], 36.2 [$CHCH_2$-Ph (major)], 36.4 [$CHCH_2Ph$ (minor)], 42.9 [CH_2CHCH_3 (minor)], 43.3 [CH_2CHCH_3 (major)], 63.4, 63.3 [$CHCH_2Ph$ (major and minor)], 82.0, 82.1 [$C(CH_3)_2$ (major and minor)], 126.3, 126.4 [*p-Ph* (major and minor)], 126.7, 127.0, 128.4, 128.5, 128.6, 128.9, 129.0 [*m*/*o-Ph* (major and minor)], 136.9 [*i-Ph* (major and minor)], 145.5, 145.6 [C=O endocyclic (major and minor)], 172.3, 172.1 [C=O exocyclic (major and minor)]; ν_{max} (KBr) 1784 [C=O endocyclic], 1698 [C=O exocyclic]; *m*/*z* APCI+ 352 [50%, MH^+]; HRMS $C_{22}H_{26}NO_3$ [MH^+] requires 352.1908, found 352.1906.

Preparation of (3′*S*,4*S*)- and (3′*R*,4*S*)-4-isopropyl-3-(3′-phenylbutyryl)-5,5-dimethyloxazolidin-2-one 39

Following Representative Procedure 5, CuBr·SMe_2 (321 mg, 1.56 mmol), MeMgBr (1.04 mL, 3.12 mmol), $BF_3{\cdot}Et_2O$ (0.19 mL, 1.56 mmol) and **36** (300 mg, 1.04 mmol) in SMe_2 (3 mL) and THF (6 mL) furnished (3′*S*,4*S*)-**39** (50 mg, >98% de, 16%) as a white solid. Further elution gave fractions consisting of a 5 : 4 mixture of (3′*S*,4*S*)- and (3′*R*,4*S*)-**39** (190 mg, 60%) as a clear colourless oil and a 3 : 14 mixture of (3′*S*,4*S*)- and (3′*R*,4*S*)- (17 mg, 0.06 mmol, 5%) as a clear colourless oil after repeated flash column chromatography.

Data for major diastereoisomer (3′*S*,4*S*)-**39**: R_f 0.3 [5 : 1 hexane : Et_2O; double eluted]; mp 52°–53 °C [hexane/–$_2$O]; $[\alpha]_D^{25}$ +58.0 (*c* = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.93 [3H, d, *J* 6.8, $CH(CH_3)_A(CH_3)_B$], 0.96 [3H, d, *J* 7.0, $CH(CH_3)_A(CH_3)_B$], 1.10 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.34 [3H, d, *J* 6.9, $CHCH_3$], 1.45 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.05–2.12 [1H, m, $CH(CH_3)_2$], 3.12 [1H, dd, *J* 15.5, 6.3, $CH_AH_BCHCH_3$], 3.36–3.45 [1H, m, $CHCH_3$], 3.50 [1H, dd, *J* 15.5, 8.3, $CH_AH_BCHCH_3$], 4.02 [1H, d, *J* 3.3, $CHCH(CH_3)_2$], 7.15–7.19 [1H, m, Ph*H*], 7.24–7.30 [4H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 17.0, 21.3 [$CH(CH_3)_2$], 21.3 [$CHCH_3$], 22.5, 29.5 [$C(CH_3)_2$], 28.3 [$CH(CH_3)_2$], 36.5 [$CHCH_3$], 42.5 [CH_2CHCH_3], 66.2 [$CHCH(CH_3)_2$], 82.7 [$C(CH_3)_2$], 125.2 [*p-Ph*], 127.0, 128.5 [*m*/*o-Ph*], 145.6 [*i-Ph*], 153.6 [C=O endocyclic], 172.3 [C=O exocyclic]; ν_{max} (KBr) 1772 [C=O endocyclic], 1700 [C=O exocyclic]; *m*/*z* APCI+ 304 [5%, MH^+]; HRMS $C_{18}H_{26}NO_3$ [MH^+] requires 304.1908, found 304.1908.

Data for minor diastereoisomer (3′*R*,4*S*)-**39**: R_f 0.25 [5 : 1 hexane : Et_2O; double eluted]; δ_H (400 MHz, $CDCl_3$) 0.75 [3H, d, *J* 6.7, $CH(CH_3)_A(CH_3)_B$], 0.82 [3H, d, *J* 7.0, $CH(CH_3)_A(CH_3)_B$], 1.34 [3H, d, *J* 7.0, $CHCH_3$], 1.36 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.48 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.99–2.07 [1H, m, $CH(CH_3)_2$], 3.05 [1H, dd, *J* 15.7, 7.2, $CH_AH_BCHCH_3$], 3.37–3.46 [1H, m, $CHCH_3$], 3.55 [1H, dd, *J* 15.7, 7.6, $CH_AH_BCHCH_3$], 4.12 [1H, d, *J* 3.1, $CHCH(CH_3)_2$], 7.15–7.41 [5H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 16.7, 22.2 [$CH(CH_3)_2$], 21.3, 29.5 [$C(CH_3)_2$], 28.3 [$CH(CH_3)_2$], 28.8 [$CHCH_3$], 36.4 [$CHCH_3$], 42.9 [CH_2CHCH_3], 66.1 [$CHCH(CH_3)_2$], 82.6 [$C(CH_3)_2$], 125.3 [*p-Ph*], 127.0, 128.4 [*m*/*o-Ph*], 145.6 [*i-Ph*], 153.5 [C=O endocyclic], 172.4 [C=O exocyclic]; ν_{max} (KBr) 1771 [C=O endocyclic], 1698 [C=O exocyclic]; *m*/*z* APCI+ 260 [15%, MH^+-CO_2], 304 [10%, MH^+]; HRMS $C_{18}H_{26}NO_3$ [MH^+] requires 304.1908, found 304.1914.

Preparation of (3′*S*,4*S*)-4-phenyl-3-(3′-phenylbutyryl)-5,5-dimethyloxazolidin-2-one 40 [17]

Following Representative Procedure 5, CuBr·SMe_2 (481 mg, 2.34 mmol), MeMgBr (1.56 mL, 4.67 mmol), $BF_3{\cdot}Et_2O$ (0.30 mL, 2.34 mmol) and **37** (500 mg, 1.56 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished **40** (518 mg, 1.54 mmol, 99%) as a white solid after flash column chromatography; R_f 0.18 [5 : 1 hexane : Et_2O]; mp 111–113 °C [hexane–Et_2O], {lit.[17] mp 112 °C [hexane–Et_2O]}; δ_H (400 MHz, $CDCl_3$) 1.00 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.33 [3H, d, *J* 7.0, $CHCH_3$], 1.46 [3H, s, $C(CH_3)_A(CH_3)_B$], 3.18 [1H, dd, *J* 16.2, 6.5, $CH_AH_BCHCH_3$], 3.40–3.43 [1H, m, $CHCH_3$], 3.59 [1H, dd, *J* 16.2, 8.3, $CH_AH_BCHCH_3$], 4.99 [1H, s, $CHPh$], 7.14–7.45 [10H, m, Ph*H*]; $[\alpha]_D^{23}$ +66.5 (*c* = 1.0, $CHCl_3$).

Preparation of (*S*)-3-phenylbutanal 41 [30] from 40

Following Representative Procedure 3, DIBAL (0.89 mL, 0.89 mmol) and (3′*S*,4*S*)-**40** (150 mg, 0.45 mmol) in CH_2Cl_2 (5 mL) furnished (*S*)-**41** (58 mg, 88%, >95% ee) as a clear, colourless oil and (*S*)-**6** (64 mg, 0.33 mmol, 75%) as a white solid after flash column chromatography; R_f 0.31 [6 : 1 pentane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.33 [3H, d, *J* 7.0, $CHCH_3$], 2.67 [1H, ddd, *J* 16.7, 7.7, 2.0, $CH_AH_BCHCH_3$], 2.77 [1H, ddd, *J* 16.7, 6.8, 2.0, $CH_AH_BCHCH_3$], 3.33–3.42 [1H, m, $CHCH_3$], 7.20–7.34 [5H, m, Ph*H*], 9.72 [1H, t, *J* 2.0, CHO]; $[\alpha]_D^{25}$ +33.8 (*c* = 0.5, Et_2O), lit.[29] $[\alpha]_D^{25}$ +38.0 (c 0.2, Et_2O), lit.[30] $[\alpha]_D^{25}$ +37.1 (*c* = 0.2, Et_2O)}.

Following Representative Procedure 4, $LiAlH_4$ (0.03 mL, 0.03 mmol) and (*S*)-**41** (10 mg, 0.06 mmol) in THF (2 mL) furnished (*S*)-3-phenylbutan-1-ol[43] (9 mg, 0.06 mmol, 99%) as a clear colourless oil; R_f 0.25 [1 : 1 pentane : Et_2O]; δ_H (200 MHz, $CDCl_3$) 1.36 [3H, d, *J* 7.0, $CHCH_3$], 1.88–1.98 [2H, m, CH_2CHCH_3], 2.91–3.02 [1H, m, $CHCH_3$], 3.59–3.67 [2H, m, CH_2OH], 7.23–7.43 [5H, m, Ph*H*]; $[\alpha]_D^{25}$ +28.9 (*c* = 0.45, $CHCl_3$), {lit.[43a] $[\alpha]_D^{25}$ +29.0 (*c* = 1.4, $CHCl_3$), lit.[43b] $[\alpha]_D^{25}$ +25.5 (*c* = 1.52, $CHCl_3$)}.

Preparation of 3-phenylbutanal 41 from 38

Following Representative Procedure 3, DIBAL (0.28 mL, 0.28 mmol) and (3′*S*,4*S*):(3′*S*,4*S*)-**38** (50 mg, 29% de, 0.14 mmol) in CH_2Cl_2 (5 mL) furnished **41** (15 mg, 76%) as a clear, colourless oil and (*S*)-**4** (23 mg, 80%) as a white solid after flash column chromatography.

Preparation of (*S*)-3-phenylbutanal 41 from 39

Following Representative Procedure 3, DIBAL (0.92 mL, 0.92 mmol) and **39** (70 mg, >98% de, 0.23 mmol) in CH_2Cl_2 (5 mL) furnished (*S*)-**41** (24 mg, 71%) as a clear, colourless oil and (*S*)-**5** (27 mg, 75%) as a white solid after flash column chromatography; R_f 0.31 [6 : 1 pentane : Et_2O]; $[\alpha]_D^{25}$ +34.2 (*c* = 1.0, Et_2O).

Preparation of (*S*)-3-(3′-methylacryloyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 42 [17]

Following Representative Procedure 1, *n*-BuLi (3.5 mL, 8.64 mmol), (*S*)-**6** (1.5 g, 7.85 mmol) and crotonyl chloride (0.98 mL, 10.21 mmol) in THF (30 mL) furnished **42** (1.83 g, 91%) as a white solid after flash column chromatography; R_f 0.22 [2 : 1 hexane : Et_2O]; mp 96–99 °C [hexane–Et_2O] {lit.[17] 104 °C [40–60 °C petrol–EtOAc]}; δ_H (400 MHz, $CDCl_3$) 1.00 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.62 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.95 [3H, dd, *J* 6.9, 1.6, $CH{=}CHCH_3$], 5.13 [1H, s, $CHPh$], 7.05–7.17 [3H, m,

432PhH and CH=CH], 7.30–7.39 [4H, m, PhH]; $[\alpha]_D^{23}$ +79.1 (c = 1.0, $CHCl_3$) {lit.[17] *ent*-$[\alpha]_D^{24}$ −82.6 (c = 1.0, $CHCl_3$).

Preparation of (3′*S*,4*S*)-3-(3′-phenylhex-5-enyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 43

Following Representative Procedure 5, CuBr·SMe_2 (481 mg, 2.34 mmol), CH_2=$CHCH_2MgBr$ (2.34 mL, 4.67 mmol), BF_3·Et_2O (0.30 mL, 2.34 mmol) and **37** (500 mg, 1.56 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished **43** (551 mg, 97%, >95% de) as a white solid after flash column chromatography; R_f 0.16 [5 : 1 hexane : Et_2O]; mp 85–89 °C [hexane/Et_2O]; $[\alpha]_D^{23}$ +91.6 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.94 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.35 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.33–2.46 [2H, m, CH_2CH=CH_2], 3.16 [1H, dd, J 16.4, 5.3, CH_AH_BCHPh], 3.25–3.32 [1H, m, CH_2CHPh], 3.62 [1H, dd, J 16.4, 9.4, CH_AH_B-CHPh], 4.89 [1H, s, C(4)HPh], 4.93–5.00 [2H, m, CH_2CH=CH_2], 5.58–5.69 [1H, m, CH_2CH=CH_2], 7.07–7.37 [10H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 23.5, 28.6 [$C(CH_3)_2$], 40.7 [CH_2-CH=CH_2], 41.0 [CH_2CHPh], 41.6 [CH_2CHPh], 66.9 [$CHPh$ (auxiliary)], 82.3 [$C(CH_3)_2$], 116.9 [CH_2CH=CH_2], 126.6, 127.7 [*p-Ph*], 128.4, 128.5, 128.6, 129.51 [*m*/*o-Ph*], 136.2, 136.0 [*i-Ph*], 143.6 [CH_2CH=CH_2], 153.2 [C=O endocyclic], 171.7 [C=O exocyclic]; ν_{max} (KBr) 1770 [C=O endocyclic], 1702 [C=O exocyclic]; *m*/*z* APCI+ 364 [50%, MH^+]; HRMS $C_{23}H_{26}NO_3$ [MH^+] requires 364.1908, found 364.1905.

Preparation of (3′*R*,4*S*)-3-(4′-methyl-3′-phenylpentanoyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 44

Following Representative Procedure 5, CuBr·SMe_2 (480 mg, 2.34 mmol), $Me_2CHMgBr$ (2.34 mL, 4.67 mmol), BF_3·Et_2O (0.30 mL, 2.34 mmol) and **37** (500 mg, 1.56 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished **44** (340 mg, 60%, >95% de) as a white solid after flash column chromatography; R_f 0.2 [5 : 1 hexane : Et_2O; double eluted]; mp 122–124 °C [hexane/Et_2O]; $[\alpha]_D^{23}$ +108.7 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.74 [3H, d, J 6.7, $CH(CH_3)_A(CH_3)_B$], 0.92 [3H, s, $C(CH_3)_A(CH_3)_B$], 0.96 [3H, d, J 6.7, $CH(CH_3)_A(CH_3)_B$], 1.26 [3H, s, $C(CH_3)_A$-$(CH_3)_B$], 1.83–1.92 [1H, m, $CH(CH_3)_2$], 2.92–2.97 [1H, m, $CHCH(CH_3)_2$], 3.12 [1H, dd, J 16.0, 4.5, CH_AH_BCHPh], 3.79 [1H, dd, J 16.0, 10.9, CH_AH_BCHPh], 4.80 [1H, s, $CHPh$ (auxiliary)], 7.03–7.35 [10H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 20.5, 20.7 [$CH(CH_3)_2$], 23.5, 28.4 [$C(CH_3)_2$], 33.4 [$CH(CH_3)_2$], 38.5 [CH_2CHPh], 49.1 [$CHCH(CH_3)_2$], 66.9 [$CHPh$ (auxiliary)], 82.2 [$C(CH_3)_2$], 126.3 [*p-Ph*], 128.1, 128.4, 128.5, 128.7 [*m*/*o-Ph*], 136.2, 142.9 [*i-Ph*], 153.3 [C=O endocyclic], 172.3 [C=O exocyclic]; ν_{max} (KBr) 1771 [C=O endocyclic], 1698 [C=O exocyclic]; *m*/*z* APCI+ 366 [5%, MH^+]; HRMS $C_{23}H_{28}NO_3$ [MH^+] requires 366.2064, found 366.2060.

Preparation of (3′*S*,4*S*)-3-(3′,4′-diphenylbutyryl)-4-phenyl-5,5-dimethyloxazolidin-2-one 45

Following Representative Procedure 5, CuBr·SMe_2 (480 mg, 2.34 mmol), $PhCH_2MgCl$ (3.34 mL, 4.67 mmol), BF_3·Et_2O (0.30 mL, 2.34 mmol) and **37** (500 mg, 1.56 mmol) in SMe_2 (10 mL) and THF (30 mL) **45** (374 mg, 58%, >95% de) as a white solid after flash column chromatography; R_f 0.13 [5 : 1 hexane : Et_2O]; mp 94–96 °C [hexane–Et_2O]; $C_{27}H_{27}NO_3$ requires C, 78.4, H, 6.6, N, 3.4%, found C, 78.3, H, 6.6, N, 3.3%; $[\alpha]_D^{23}$ +47.0 (c = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.93 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.32 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.88–2.98 [2H, m, $CHCH_2Ph$], 3.07 [1H, dd, J 16.3, 5.1, CH_AH_BCHPh], 3.46–3.53 [1H, m, $CHCH_2Ph$], 3.77 [1H, dd, J 16.3, 9.9, CH_AH_B-CHPh], 4.86 [1H, s, $CHPh$ (auxiliary)], 7.03–7.38 [15H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 23.4, 28.5 [$C(CH_3)_2$], 40.3 [$CHCH_2Ph$], 43.2 [CH_2CHPh], 43.9 [$CHCH_2Ph$], 66.9 [$CHPh$ (auxiliary)], 82.3 [$C(CH_3)_2$], 126.1, 126.5 [*p-Ph*], 127.7, 128.1, 128.5, 128.8, 129.2, 129.5 [*m*/*o-Ph*], 136.2, 139.5, 143.3 [*i-Ph*], 153.2 [C=O endocyclic], 171.7 [C=O exocyclic]; ν_{max} (KBr) 1773 [C=O endocyclic], 1710 [C=O exocyclic]; *m*/*z* APCI+ 414 [10%, MH^+].

Preparation of (3′*R*,4*S*)-3-(3′-phenylbutyryl)-4-phenyl-5,5-dimethyloxazolidin-2-one 46[17]

Following Representative Procedure 5, CuBr·SMe_2 (596 mg, 2.90 mmol), PhMgBr (8.8 mL, 5.79 mmol), BF_3·Et_2O (0.37 mL, 2.90 mmol) and **42** (500 mg, 1.93 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished (3′*R*,4*S*)-**46** (453 mg, 70%, 97% de) as a white solid after flash column chromatography; R_f 0.15 [5 : 1 hexane : Et_2O, double eluted]; mp 117–118 °C [hexane–Et_2O], {lit.[17] mp 114 °C [pentane–EtOAc]}; δ_H (400 MHz, $CDCl_3$) 0.95 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.28 [3H, s, $CHCH_3$], 1.59 [3H, s, $C(CH_3)_A(CH_3)_B$], 3.20 [1H, dd, J 15.7, 7.8, $CH_AH_BCHCH_3$], 3.32–3.38 [1H, m, $CHCH_3$], 3.51 [1H, dd, J 15.7, 6.8, CH_AH_B-$CHCH_3$], 5.04 [1H, s, $CHPh$], 7.19–7.30 [10H, m, PhH]; $[\alpha]_D^{23}$ +25.0 (c = 1.0, $CHCl_3$) {lit.[17] *ent*-$[\alpha]_D^{28}$ −28.8 (c = 1.0, $CHCl_3$)}.

Preparation of (3′*S*,4*S*)-4-phenyl-3-(3′-methyl-4-phenylbutyryl)-5,5-dimethyloxazolidin-2-one 47

Following Representative Procedure 5, CuBr·SMe_2 (596 mg, 2.90 mmol), $PhCH_2MgBr$ (3.15 mL, 5.79 mmol), BF_3·Et_2O (0.37 mL, 2.90 mmol) and **42** (500 mg, 1.93 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished **47** (561 mg, 83%, 91% de) as a white solid after flash column chromatography; R_f 0.2 [5 : 1 hexane : Et_2O, double eluted]; mp 130–131 °C [hexane–Et_2O]; $[\alpha]_D^{25}$ +41.0 (c = 0.5, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.88 [3H, d, J 6.6, $CHCH_3$], 0.99 [3H, s, $C(CH_3)_A(CH_3)_B$], 1.58 [3H, s, $C(CH_3)_A(CH_3)_B$], 2.33–2.39 [1H, m, $CHCH_3$], 2.46 [1H, dd, J 13.2, 8.2, $CHCH_AH_BPh$], 2.68 [1H, dd, J 13.2, 5.9, $CHCH_A$-H_BPh], 2.87 [1H, dd, J 16.2, 8.1, $CH_AH_BCHCH_3$], 3.01 [1H, dd, J 16.2, 5.5, $CH_AH_BCHCH_3$], 5.08 [1H, s, $CHPh$], 7.12–7.39 [10H, m, PhH]; δ_C (100 MHz, $CDCl_3$) 19.2 [$CHCH_3$], 23.7, 29.0 [$C(CH_3)_2$], 31.6 [$CHCH_3$], 43.0, 42.1 [$CHCH_2Ph$ and CH_2-$CHCH_3$], 67.0 [$CHPh$], 82.3 [$C(CH_3)_2$], 125.9, 128.6 [*p-Ph*], 128.2, 128.9, 129.3 [*m*/*o-Ph*], 136.4, 140.3 [*i-Ph*], 153.2 [C=O endocyclic], 172.4 [C=O exocyclic]; ν_{max} (KBr) 1774 [C=O endocyclic], 1701 [C=O exocyclic]; *m*/*z* APCI+ 352 [5%, MH^+]; HRMS $C_{22}H_{26}NO_3$ [MH^+] requires 352.1908, found 352.1921.

Preparation of (*S*)-3-phenylhex-5-enal 48[44]

Following Representative Procedure 3, DIBAL (0.83 mL, 0.83 mmol) and **43** (150 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) furnished **48** (63 mg, >95% ee, 88%) as a clear, colourless oil and (*S*)-**6** (77 mg, 98%) as a white solid after flash column chromatography; R_f 0.18 [12 : 1 pentane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 2.31–2.47 [2H, m, CH_2CH=CH_2], 2.70–2.83 [2H, m, CH_2-$CHPh$], 3.31 [1H, app. quin., J 7.3, $CHPh$], 4.97–5.05 [2H, m, CH=CH_2], 5.62–5.72 [1H, m, CH=CH_2], 7.10–7.34 [5H, m, PhH], 9.69 [1H, t, J 1.9, CHO]; $[\alpha]_D^{25}$ +14.4 (c = 0.5, $CHCl_3$), {lit.[44b] *ent*-$[\alpha]_D^{20}$ −13.4 (c = 0.98, C_6H_6; 82% ee).

Preparation of (*R*)-4-methyl-3-phenylpentanal 49[45]

Following Representative Procedure 3, DIBAL (0.82 mL, 0.82 mmol) and **44** (150 mg, 0.41 mmol) in CH_2Cl_2 (5 mL) furnished **49** (52 mg, >95% ee, 72%) as a pale yellow oil and (*S*)-**6** (52 mg, 66%) as a white solid after flash column chromatography; R_f 0.24 [12 : 1 pentane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.78 [3H, d, J 6.7, $CH(CH_3)_A(CH_3)_B$], 0.96 [3H, d, J 6.7, $CH(CH_3)_A(CH_3)_B$], 1.84–1.92 [1H, m, $CH(CH_3)_2$], 2.72–2.85 [2H, m, CH_2CHPh], 2.94–2.99 [1H, m, $CHPh$], 7.15–7.32 [5H, m, PhH], 9.61 [1H, t, J 2.2, CHO]; $[\alpha]_D^{23}$ −8.4 (c = 0.5, $CHCl_3$).

Preparation of (*S*)-3,4-diphenylbutanal 50[46]

Following Representative Procedure 3, DIBAL (0.48 mL, 0.48 mmol) and **45** (100 mg, 0.24 mmol) in CH_2Cl_2 (5 mL) furnished **50** (52 mg, >95% ee, 96%) as a clear, colourless oil and (*S*)-**6**

(39 mg, 84%) as a white solid after flash column chromatography; R_f 0.15 [12 : 1 pentane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 2.71–2.84 [2H, m, CH_2Ph], 2.89 [1H, dd, *J* 13.5, 7.9, C$H_A$$H_B$CHPh], 2.97 [1H, dd, *J* 13.5, 7.1, CH$_A$$H_B$CHPh], 3.46–3.54 [1H, m, C*H*Ph], 7.00–7.08 [2H, m, Ph*H*], 7.16–7.49 [8H, m, Ph*H*], 9.60 [1H, s, C*H*O]; $[\alpha]_D^{23}$ −6.6 (*c* = 0.5, $CHCl_3$), {lit.[46] $[\alpha]_D^{23}$ −8.4 (*c* = 0.5, $CHCl_3$)}.

Preparation of (*R*)-3-phenylbutanal 51

Following Representative Procedure 3, DIBAL (0.89 mL, 0.89 mmol) and **46** (150 mg, 0.45 mmol) in CH_2Cl_2 (5 mL) furnished **51** (55 mg, >95% ee, 84%) as a clear, colourless oil and (*S*)-**6** (83 mg, 98%) as a white solid after flash column chromatography; (*R*)-**51**: R_f 0.15 [12 : 1 pentane : Et_2O]; $[\alpha]_D^{25}$ −34.6 (*c* = 0.5, Et_2O), {lit.[29] $[\alpha]_D^{25}$ −38.0 (*c* = 0.2, Et_2O), lit.[30] $[\alpha]_D^{25}$ −38.5 (*c* = 0.2, Et_2O)}.

Preparation of (*S*)-3-methyl-4-phenylbutanal 52[47]

Following Representative Procedure 3, DIBAL (0.86 mL, 0.86 mmol) and **47** (150 mg, 0.43 mmol) in CH_2Cl_2 (5 mL) furnished **52** (62 mg, 90%, 91% ee) as a clear, colourless oil and (*S*)-**6** (75 mg, 92%) as a white solid after flash column chromatography; R_f 0.21 [12 : 1 pentane : Et_2O]; δ_H (400 MHz, $CDCl_3$) 0.99 [3H, d, *J* 6.6, CHCH_3], 2.25 [1H, ddd, *J* 15.6, 7.4, 2.4, C$H_A$$H_B$CHCH$_3$], 2.34–2.47 [2H, m, C*H*CH$_3$ and CH$_A$$H_B$-CHCH$_3$], 2.54–2.64 [2H, m, C$H_2$Ph], 7.16–7.32 [5H, m, Ph*H*], 9.72 [1H, t, *J* 2.0, C*H*O]; $[\alpha]_D^{23}$ −8.4 (*c* = 0.5, $CHCl_3$; 91% ee).

Preparation of (*S*)-3-(hepta-2′,6′-dienoyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 53

Following Representative Procedure 1, *n*-BuLi (1.15 mL, 2.88 mmol), (*S*)-**6** (500 mg, 2.62 mmol) and hepta-2,6-dienoyl chloride (3.4 mmol; prepared from hepta-2,6-dienoic acid (429 mg, 3.40 mmol), oxalyl chloride (1.49 mL, 17.02 mmol) and DMF (cat.) in hexane) furnished **53** (571 mg, 77%) as a pale yellow oil after flash column chromatography; R_f 0.32 [1 : 1 pentane : Et_2O]; $[\alpha]_D^{24}$ +64.8 (*c* = 0.4, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 1.00 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.62 [3H, s, C(CH$_3$)$_A$(CH_3)$_B$], 2.21–2.26 [2H, m, CH$_2$CH_2CH=CH$_2$], 2.35–2.40 [2H, m, CH_2CH$_2$CH=CH$_2$], 4.98–5.08 [2H, m, CH$_2$CH$_2$CH=CH_2], 5.13 [1H, s, C*H*Ph], 5.76–5.86 [1H, m, CH$_2$CH$_2$C*H*=CH$_2$], 7.05–7.39 [7H, m, Ph*H* and CO.C*H*=C*H*]; δ_C (100 MHz, $CDCl_3$) 23.7, 29.0 [C(*C*H$_3$)$_2$], 31.9, 32.0 [*C*H$_2$*C*H$_2$CH=CH$_2$], 67.2 [*C*HPh], 82.3 [*C*(CH$_3$)$_2$], 115.6 [CH$_2$CH$_2$CH=*C*H$_2$], 120.8 [CH$_2$CH$_2$*C*H=CH$_2$], 128.5 [*p-Ph*], 128.8 [*m*/*o-Ph*], 136.4 [*i-Ph*], 137.0 [CH=*C*HCH$_2$CH$_2$CH=CH$_2$], 150.8 [*C*H=CHCH$_2$CH$_2$CH=CH$_2$], 153.2 [*C*=O endocyclic], 164.8 [*C*=O exocyclic]; ν_{max} (film) 1771 [C=O endocyclic], 1694 [C=O exocyclic]; *m*/*z* APCI+ 256 [30%, $MH^+ - CO_2$], 300 [50%, MH^+]; HRMS $C_{18}H_{22}NO_3$ [MH^+] requires 300.1594, found 300.1605.

Preparation of (3′*R*,4*S*)-3-(3-isopropenylhept-6-enoyl)-4-phenyl-5,5-dimethyloxazolidin-2-one 54

Following Representative Procedure 5, CuBr·SMe_2 (436 mg, 2.12 mmol), (C(CH$_3$)=CH$_2$)MgCl (8.98 mL, 4.49 mmol), BF_3·Et_2O (0.27 mL, 2.12 mmol) and **53** (400 mg, 1.41 mmol) in SMe_2 (10 mL) and THF (30 mL) furnished **54** (287 mg, 63%) as a pale yellow oil after flash column chromatography; R_f 0.3 [5 : 1 pentane : Et_2O, double eluted]; $[\alpha]_D^{24}$ +74.2 (*c* = 1.0, $CHCl_3$); δ_H (400 MHz, $CDCl_3$) 0.99 [3H, s, C(CH_3)$_A$(CH$_3$)$_B$], 1.42–1.51 [2H, m, CH_2CH$_2$CH=CH$_2$], 1.60 [3H, s, C(CH$_3$)$_A$-(CH_3)$_B$], 1.66 [3H, s, CH(C(CH_3)=CH$_2$)], 1.89–2.06 [2H, m, CH$_2$CH_2CH=CH$_2$], 2.65–2.72 [1H, m, C*H*(C(CH$_3$)=CH$_2$)], 3.01–3.12 [2H, m, CH_2CH(C(CH$_3$)=CH$_2$)], 4.72–4.75 [2H, m, CH(C(CH$_3$)=CH_2)], 4.92–5.01 [2H, m, CH$_2$CH$_2$CH=CH_2], 5.05 [1H, s, C*H*Ph], 5.72–5.82 [1H, m, CH$_2$CH$_2$C*H*=CH$_2$], 7.11–7.15 [2H, m, Ph*H*], 7.30–7.39 [3H, m, Ph*H*]; δ_C (100 MHz, $CDCl_3$) 18.6, 23.6 [C(*C*H$_3$)$_2$], 29.0 [CH(C(*C*H$_3$)=CH$_2$)], 31.3, 32.0 [*C*H$_2$*C*H$_2$CH=CH$_2$], 40.0 [*C*H$_2$CH(C(CH$_3$)=CH$_2$], 42.8 [*C*H(C(CH$_3$)=CH$_2$], 67.0 [*C*HPh], 82.3 [*C*(CH$_3$)$_2$], 112.4, 114.6 [CH$_2$CH$_2$CH=*C*H$_2$ and CH(C(CH$_3$)=*C*H$_2$)], 128.7, 128.8 [*m*/*o-Ph*], 136.3 [*i-Ph*], 138.4 [*p-Ph*], 146.0 [CH(*C*(CH$_3$)=CH$_2$)], 153.1 [*C*=O endocyclic], 171.8 [*C*=O exocyclic]; ν_{max} (film) 1778 [C=O endocyclic], 1715 [C=O exocyclic]; *m*/*z* APCI+ 342 [100%, MH^+]; HRMS $C_{21}H_{28}NO_3$ [MH^+] requires 342.2064, found 342.2067.

Preparation of (*R*)-3-isopropenylhept-6-enal 55[32]

Following Representative Procedure 3, DIBAL (1.26 mL, 1.26 mmol), **54** (215 mg, 0.63 mmol) in CH_2Cl_2 (10 mL) furnished **55** (80 mg, >95% ee, 84%) as a pale, yellow oil and (*S*)-**6** (93 mg, 77%) as a white solid after flash column chromatography; R_f 0.38 [6 : 1 30–40 °C petrol : Et_2O]; δ_H (400 MHz, $CDCl_3$) 1.46–1.62 [2H, m, CH_2CH$_2$CH=CH$_2$], 1.67 [3H, s, CH(C(CH_3)=CH$_2$)], 1.93–2.09 [2H, m, CH$_2$CH_2CH=CH$_2$], 2.39–2.50 [2H, m, CH_2CHO], 2.51–2.75 [1H, m, C*H*(C(CH$_3$)=CH$_2$)], 4.80–4.84 [2H, m, CH(C(CH$_3$)=CH_2)], 4.94–5.05 [2H, m, CH$_2$CH$_2$CH=CH_2], 5.75–5.85 [1H, m, CH$_2$CH$_2$C*H*=CH$_2$], 9.68 [1H, t, *J* 2.5, C*H*O]; $[\alpha]_D^{25}$ +8.6 (*c* = 1.15, $CHCl_3$), {lit.[32] $[\alpha]_D$ +9.0 (*c* = 1.4, $CHCl_3$)}.

Following Representative Procedure 4, $LiAlH_4$ (0.05 mL, 0.05 mmol), **55**(10 mg, 0.05 mmol) in THF (2 mL) furnished (*R*)-3-isopropenylhept-6-en-1-ol (6 mg, 60%) as a pale, yellow oil; δ_H (400 MHz, $CDCl_3$) 1.36–1.50 [2H, m, CH_2CH$_2$CH=CH$_2$], 1.57 [1H, br s, O*H*], 1.59–1.64 [2H, m, CH_2CH$_2$OH], 1.63 [3H, s, CH(C(CH_3)=CH$_2$)], 1.89–2.05 [2H, m, CH$_2$CH_2CH=CH$_2$], 2.21–2.28 [1H, m, C*H*(C(CH$_3$)=CH$_2$)], 3.55–3.65 [2H, m, CH$_2$CH_2OH], 4.76–4.79 [2H, m, CH(C(CH$_3$)=CH_2)], 4.92–5.02 [2H, m, CH$_2$CH$_2$CH=CH_2], 5.75–5.85 [1H, m, CH$_2$CH$_2$C*H*=CH$_2$]; $[\alpha]_D^{25}$ −5.6 (*c* = 0.25, $CHCl_3$), {lit.[32] $[\alpha]_D$ −5.0 (*c* = 1.5, $CHCl_3$)}.

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