Asymmetric alkylations using SuperQuat auxiliaries—an investigation into the synthesis and stability of enolates derived from 5,5-disubstituted oxazolidin-2-ones

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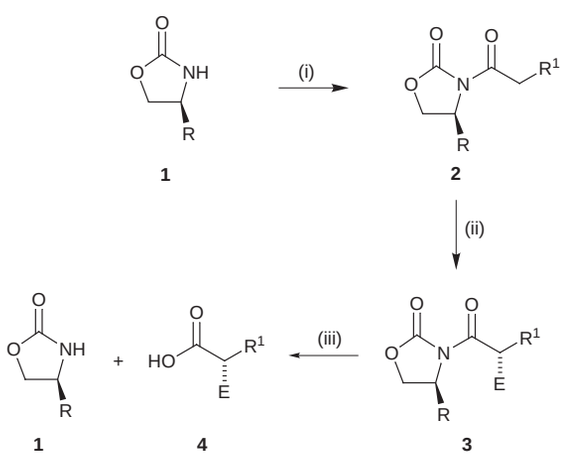
Studies on the alkylation of enolates derived from a range of *N*-acyl-5,5-dimethyloxazolidin-2-ones and *N*-acyl-5,5-diphenyloxazolidin-2-ones reveal that high yields and high diastereoselectivities are best obtained when homochiral 4-isopropyl-5,5-dimethyloxazolidin-2-one is employed as a chiral auxiliary.

Introduction

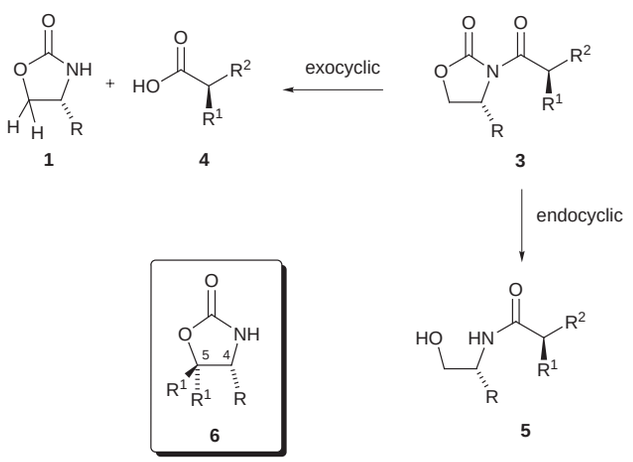
The role of chiral auxiliaries in asymmetric synthesis for the preparation of homochiral molecules is now firmly established in organic synthesis.[1] Perhaps the most versatile and widely used of these chiral auxiliaries is that devised by Evans *et al.* which is based on the use of chiral oxazolidin-2-ones **1** to control facial selectivity during enolate alkylation of enolates of *N*-acyl fragments.[2] This methodology has had enormous impact within the synthetic community since homochiral α-substituted carboxylic acids arising from this methodology are easily transformed into a large number of synthetically useful homochiral fragments.[3] The general strategy employed when using Evans' auxiliary for asymmetric synthesis involves derivatisation of the chiral auxiliary **1** with an acid chloride to afford an acyl fragment **2**, followed by enolate formation and alkylation with an electrophile to afford a major diastereoisomeric product **3** containing a new stereogenic centre in high de. Purification of the major diastereoisomer **3** to homogeneity, followed by nucleophilic cleavage, affords the desired homochiral product **4** whilst regenerating the chiral auxiliary **1** for further use (Scheme 1).[4] Other developments within this area have seen the



Scheme 1 *Reagents and conditions*: (i) *n*-BuLi, R^1CH_2COCl; (ii) LDA, electrophile; (iii) LiOH.

extension of this methodology to the stereoselective control of a wide range of chemistry including aldol reactions, 1,4-conjugate additions, hydroxylation, halogenation, Diels–Alder reactions, ene reactions, cyclopropanations, α-amino acid synthesis and iterative propionate homologation.[5]

Whilst the impact of Evans' auxiliary **1** has been far reaching, there are practical problems associated with its use in synthesis, particularly on a large scale. The yields obtained for alkylation of enolates derived from *N*-acyl fragments **2** are not quantitative, affording α-substituted products **3** in 70–92% yield for activated electrophiles.[6] More importantly these enolate alkylations often occur with incomplete stereochemical control, affording oily mixtures of diastereoisomers which must be separated by chromatography affording diminished yields of the desired diastereoisomer **3**. Major isolation problems may also occur during nucleophilic cleavage of **3** to the parent auxiliary **1** and homochiral fragment **4**, since sterically hindered α-substituted acyl fragments are cleaved *via* a competing endocyclic cleavage to afford *N*-acyl-amino alcohols **5** (Scheme 2).[7] This



Scheme 2

competing endocyclic pathway is particularly troublesome since it results in a decreased yield of the desired homochiral acid **4**, and a complex mixture of compounds which must be separated. While this endocyclic cleavage problem may be overcome by deploying the more nucleophilic species LiOOH for hydrolysis,[7] the use of this reagent on a large scale is clearly undesirable.

As part of a continuing program into the development of robust chiral auxiliaries for use on a large scale, and in order to address fully these troublesome cleavage problems, we have recently reported on the development of a new class of chiral auxiliary, the 5,5-substituted SuperQuats as exemplified by the 5,5-dimethyl derivative **6** (R^1 = Me). These auxiliaries provide superior performance to many of the *N*-acyl chiral auxiliaries currently in common usage. Since our initial communication in this area, a number of publications have appeared which

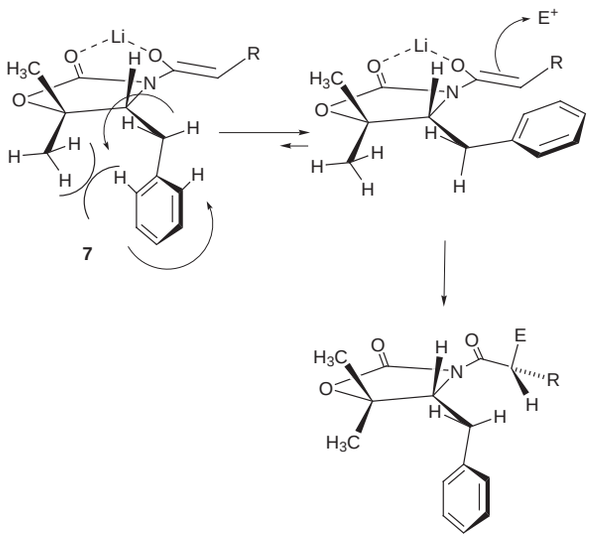


Fig. 1 Steric interaction between the benzyl group and the *syn* 5-C methyl group results in rotation around the 4-C-benzyl bond directing the benzyl group beneath the plane of the enolate. This conformation effectively blocks the bottom face of the enolate from electrophilic attack.

propose the use of 5,5-diphenyloxazolidin-2-ones **6** (R^1 = Ph) for asymmetric synthesis.[8,9] At the inception of our work into the design of SuperQuat auxiliaries, we also considered using this class of oxazolidin-2-one as a chiral auxiliary, however our results in this area clearly indicated that alkylation of enolates derived from 5,5-dimethyloxazolidin-2-ones were more effective than alkylation of enolates derived from the corresponding 5,5-diphenyloxazolidin-2-ones. We now describe herein the direct comparison of the performance of enolates derived from different classes of 5,5-substituted oxazolidin-2-one, which clearly reveal that 4-isopropyl-5,5-dimethyl SuperQuat is the auxiliary of choice for asymmetric enolate alkylations. Part of this work has been previously communicated.[10,11]

Results and discussion

Synthetic rationale behind the design of SuperQuat auxiliaries

In order to address the problems associated with Evans' auxiliary **1**, we proposed a range of new oxazolidin-2-ones, the SuperQuats **6**, containing geminal substituents at the 5-C position. There were two fundamental reasons behind this structural design. Firstly, it was proposed that the diastereoselectivity obtained during alkylation of enolate fragments of *N*-acyl SuperQuats **7** would be improved relative to the des obtained using enolates derived from Evans' auxiliary, because the presence of geminal dialkyl groups at 5-C would serve to direct the conformation of the stereocontrolling group at 4-C close to the point of enolate alkylation at 2′-C. It was reasoned that this conformation would provide more steric hindrance in the transition state of the enolate reactions and would result in increased stereofacial bias towards any incoming electrophile.[12] We reasoned that this structural design would result in improved alkylation diastereoselectivities as illustrated for the enolate **7** of the phenylalanine derived SuperQuat as shown in Fig. 1. Our second design criterion was based on the geminal 5-C substituents of the SuperQuat auxiliary conferring superior cleavage properties to the corresponding α-substituted *N*-acyl fragment **8**, since the presence of 5-C-dialkyl groups would serve to protect the oxazolidin-2-one carbonyl from nucleophilic attack by sterically blocking the Burgi–Dunitz angle of trajectory at 2-C. As a result, any competing endocyclic cleavage pathway should be completely suppressed, and only the products of the desired exocyclic cleavage pathway would be produced (Fig. 2).

Our initial attention was therefore directed towards developing a versatile synthesis of a range of SuperQuat auxiliaries **6** derived from glycine, alanine, phenylglycine and valine, each containing either methyl or phenyl groups at their 5-C position.

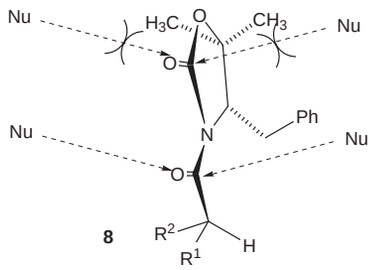
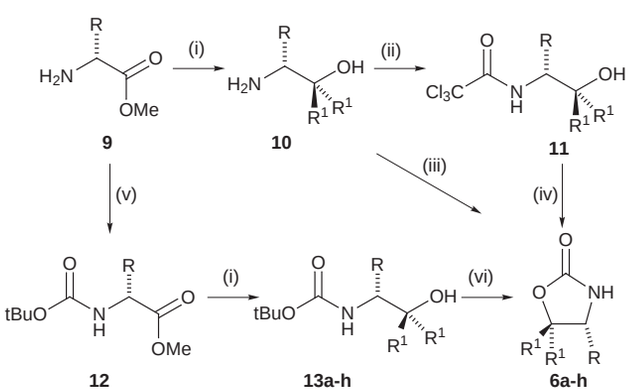


Fig. 2 Steric interactions between the geminal 5-C dimethyl groups and the incoming nucleophile block attack at the carbonyl of the oxazolidin-2-one.

Synthesis of SuperQuat auxiliaries

Three routes were developed for the synthesis of SuperQuat auxiliaries **6a**–**h** starting from the corresponding parent α-amino acid methyl ester **9**. The first two approaches were used in the initial phases of these studies and involved the addition of excess Grignard reagent to the parent α-amino acid methyl ester **9** to afford the corresponding tertiary alcohol **10**, which was then transformed directly to the corresponding SuperQuat auxiliary **6** *via* treatment with 1,1′-carbonyldiimidazole (CDI). Alternatively **10** could be treated with trichloroacetyl chloride to afford trichloroacetamide **11** which readily underwent base promoted cyclisation to afford the desired chiral auxiliary **6** (Scheme 3).[10]



Scheme 3 *Reagents and conditions*: (i) 4 equiv. R^1MgBr, THF; (ii) CCl_3COCl, pyridine; (iii) CDI, CH_2Cl_2; (iv) K_2CO_3, EtOH; (v) Boc_2O, K_2CO_3; (vi) *t*-BuOK, THF.

Scale up of these synthetic routes proved capricious however since the absolute yields of SuperQuat auxiliary **6** obtained were sensitive to the nature of the functionality of both the starting α-amino acid methyl ester **9**, and the Grignard reagent deployed. As a result, these routes were superseded by a versatile protocol which enabled syntheses of all of the SuperQuats **6a**–**h** used in this study to be carried out on a multigram scale in good yield (Table 1). Treatment of the methyl esters of *N*-Boc α-amino acids **12** with excess Grignard reagent afforded *N*-Boc-protected amino alcohols **13a**–**h**, which were then subjected to base catalysed cyclisation with KO^{t}Bu to afford SuperQuat auxiliaries **6a**–**h**. It is interesting to note that the *N*-Boc protecting group of **12** serves three functions during this synthetic protocol. Firstly it acts as a suitable *N*-protecting group decreasing the polarity of the parent amino alcohol **10**, thus facilitating its isolation from magnesium salts contained within the crude reaction mixture. Secondly the presence of the acidic carbamate proton results in an anion α to the stereogenic centre of **12** disfavouring racemisation by excess Grignard

Table 1 Preparation of SuperQuats **6** from *N*-protected α-amino acid esters **12**

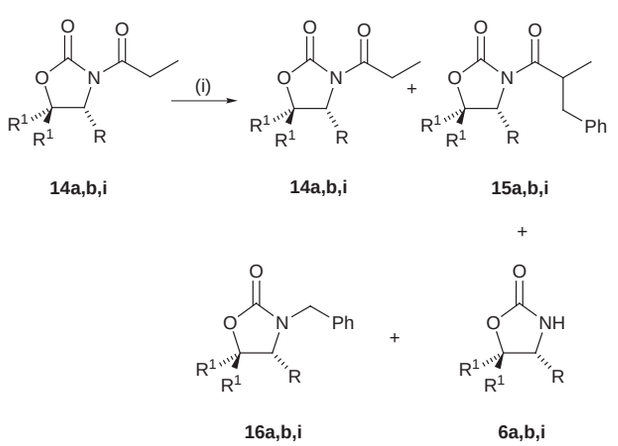
SuperQuat **6**	R	R^1	Overall yield (%) from **12**[a]	Mp (°C)	$[\alpha]_D^{23}$ ($CHCl_3$)
a	H	Me	40	78–82	—
b	H	Ph	46	196–197	—
c	Me	Me	57	64	−2.85 (*c* 4)
d	Me	Ph	47	>220	+288.4 (*c* 0.5)
e	Ph	Me	63	149	−77.6 (*c* 0.5)
f	Ph	Ph	66	>230	+218.1 (*c* 1)
g	^{i}Pr	Me	63	87	−24.2 (*c* 1)
h	^{i}Pr	Ph	55	>220	+315.6 (*c* 0.5)

[a] Overall yields based on the two step transformation of **12**→**13** and **13**→**6**, where alcohol **13** was isolated for characterisation before subsequent use. In each case the crude ^{1}H NMR spectrum indicated that both transformations were essentially quantitative and clean.

reagent. Finally the *N*-Boc protecting group of **13** is deployed as a sacrificial carbonyl equivalent during formation of the oxazolidin-2-one ring system of **6**.[11]

Initial alkylation studies using achiral *N*-acyl oxazolidin-2-ones

Preliminary alkylation studies carried out on *N*-acyl compounds derived from Evans' auxiliary **1** revealed that the primary decomposition pathway of enolates derived from oxazolidin-2-one chiral auxiliaries involved fragmentation of the enolate to afford the parent oxazolidin-2-one, presumably *via* a ketene decomposition pathway or *via* a Claisen condensation type process. We were concerned that introduction of functional groups at the 5-C position of the oxazolidin-2-one would have an adverse effect on the reactivity of the corresponding *N*-acyl enolates and as a result we carried out model studies on the stability of enolates of *N*-acyl fragments derived from the three achiral oxazolidin-2-ones **6a**,**b** and **6i** (R, R^1 = H). *N*-Propionyl oxazolidin-2-ones **14a**,**b**,**i** were prepared *via* treatment of the parent oxazolidin-2-ones **6a**,**b**,**i** with *n*-BuLi at −78 °C in THF, followed by addition of propionyl chloride. Compounds **14a**,**b**,**i** were subjected to alkylation conditions known to cause small amounts of enolate decomposition for the simplest unsubstituted *N*-propionyl SuperQuat **14i**. Therefore, *N*-acyl fragments **14a,b,i** were deprotonated with 1.1 equiv. of LHMDS in THF at −78 °C for 30 minutes, followed by addition of 3 equiv. of benzyl bromide at −78 °C and the reaction mixture stirred for 2 hours. The reaction mixture was warmed to room temperature, stirred for 24 hours and after aqueous work-up afforded varying mixtures of starting material **14a**,**b**,**i**, the desired α-benzylated product **15a**,**b**,**i**, and products resulting from enolate decomposition; the SuperQuats **6a,b,i** and *N*-benzyl SuperQuats **16a**,**b**,**i** (Scheme 4).

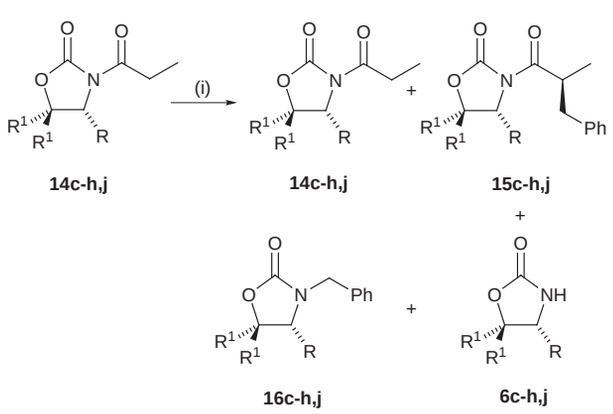


Scheme 4 *Reagents and conditions*: (i) LHMDS, THF, −78 °C, 30 min; 3 equiv. BnBr, 2 h, −78 °C; rt, 24 h.

Examination of the trend in chemoselectivities described in Table 2 revealed that introduction of substituents at 5-C of the oxazolidin-2-one ring had clearly decreased enolate stability/reactivity towards enolate alkylation. Under these conditions the enolate fragment derived from the completely unfunctionalised oxazolidin-2-one **6i** cleanly afforded the desired α-benzylated fragment **15i** in 93% yield with only 7% decomposition to *N*-benzyl-SuperQuat **16i**. The enolate of SuperQuat **6a**, where the two 5-C hydrogens of the parent oxazolidin-2-one had been replaced with two methyl groups, resulted in an *N*-acyl compound **14a** whose enolate afforded alkylated material **15a** in 79% yield with only small amounts of the decomposition products SuperQuat **6a** (6%) and *N*-benzyl-SuperQuat **16a** (11%) being observed. In contrast, the enolate derived from the corresponding 5,5-diphenyloxazolidin-2-one **6b** was not only unstable (31% yield of the parent SuperQuat **6b** and 29% yield of *N*-benzyl-SuperQuat **16b**) but relatively unreactive to electrophilic substitution (11% yield of starting material **14b**), affording the desired α-benzylated product **15b** in a derisory 29% yield. These results indicated that useful yields of alkylated products were only likely to be obtained using lithium enolates derived from the 5,5-dimethyl-SuperQuat auxiliary, rather than the corresponding 5,5-diphenyl-SuperQuat analogue.

Probing diastereoselectivities using enolates of 5,5-dimethyl and 5,5-diphenyl SuperQuats

Our attention then turned to probing what effect changing the stereocontrolling substituent at 4-C of the oxazolidin-2-one would have on both the diastereoselectivity and yield of alkylation of *N*-acyl SuperQuat enolates. *N*-Acylated SuperQuats **14c**–**h**,**j** were prepared as described (*n*-BuLi, propionyl chloride, THF, −78 °C), and deprotonated and benzylated under the standard control conditions described (Scheme 5, Table 3).



Scheme 5 *Reagents and conditions*: (i) LHMDS, THF, −78 °C, 30 min; 3 equiv. BnBr, 2 h, −78 °C; rt, 24 h.

Once again examination of the trend in selectivities observed in Table 3 clearly reveals that alkylation of the enolates of 5,5-diphenyl-*N*-acyl SuperQuats **14d**,**f**,**h** resulted in much lower yields of the desired α-benzylated products than enolates of the corresponding *N*-acyl-5,5-dimethyl-SuperQuats **14c**,**e**,**g**. The best yielding alanine derived (4*R*)-*N*-acyl-5,5-diphenyl-4-methyl-SuperQuat **14d** afforded the desired benzylated product **15d** in only 40% yield and 65% de.

These results are consistent with the enolate alkylation studies recently detailed by Gibson *et al.* who described the use of 5,5-diphenyl-SuperQuat and related 5,5-diaryl-SuperQuats as chiral auxiliaries for asymmetric synthesis.[8] They reported that the enolate of *N*-propionyl-SuperQuat **14h** was benzylated to afford **15h** in >95% de and isolated in a low 46% yield (LDA, THF, 0 °C, BnBr), but with no mention of any products arising from enolate decomposition. In our hands, the results obtained for this auxiliary are comparable, however in practice separation of the alkylated product **15h** from acyl starting

Table 2

Oxazolidin-2-one	R	R^1	Yield (%) starting material	Yield (%) benzylated material	Yield (%) SuperQuat	Yield (%) *N*-benzyl SuperQuat[a]
6i[b]	H	H	**14i** (0)	**15i** (93)	**6i** (0)	**16i** (7)
6a	H	Me	**14a** (4)	**15a** (79)	**6a** (6)	**16a** (11)
6b	H	Ph	**14b** (11)	**15b** (29)	**6b** (31)	**16b** (29)

[a] Authentic samples of *N*-benzyl-SuperQuats **16a**,**b**,**i** were prepared in all cases *via* deprotonation of the parent SuperQuat **6a**,**b**,**i** with *n*-BuLi, and treatment with benzyl bromide in THF at −78 °C. [b] Oxazolidin-2-one **6i** was purchased from the Aldrich Chemical Company.

Table 3 Diastereoselectivities and yields obtained for benzylation of the enolates of *N*-acylated SuperQuats **14c**–**h**,**j**

Reactant	R	R^1	Yield (%) starting material[a]	Alkylated product		Yield (%) SuperQuat	Yield (%) *N*-benzyl SuperQuat
				Yield (%)	de (%)[b]		
14c	Me	Me	**14c** (10)	**15c** (69)	81	**6c** (11)	**16c** (10)
14d	Me	Ph	**14d** (19)	**15d** (40)	65	**6d** (16)	**16d** (25)
14e	Ph	Me	**14e** (8)	**15e** (70)	70	**6e** (5)	**16e** (17)
14f	Ph	Ph	**14f** (49)	**15f** (0)	—	**6f** (8)	**16f** (43)
14g	^{i}Pr	Me	**14g** (20)	**15g** (71)	>95	**6g** (0)	**16g** (9)
14h	^{i}Pr	Ph	**14h** (52)	**15h** (35)	>95	**6h** (4)	**16h** (9)
14j	^{i}Pr	H	**14j** (14)	**15j** (55)	>95	**6j** (18)	**16j** (13)

[a] All product ratios were determined by integration of the relevant signals in the 500 MHz ^{1}H NMR spectra. [b] All diastereomeric ratios were determined by integration of the relevant signals in the 500 MHz ^{1}H NMR spectra corresponding to the benzylic protons of the major and minor diastereoisomers. [c] *N*-Propionyl SuperQuat **14j** was prepared *via* acylation of Evans' auxiliary [(4*R*)-(+)-4-isopropyl-oxazolidin-2-one] purchased from the Aldrich Chemical Company.

material **14h** by silica gel chromatography was not possible. Seebach *et al.* subsequently reported that the lithium enolate of **14h** was very unreactive towards alkylation, affording the *N*-benzyloxazolidin-2-one **16h** as the major product when benzyl bromide was employed as an electrophile for alkylation.[9]

Examination of the diastereoselectivities observed when changing the stereocontrolling group at 4-C of the 5,5-dimethyl-SuperQuats clearly revealed that increasing the effective steric bulk at this position leads to a dramatic increase in the diastereoselectivity of enolate benzylation (**14c**, R = Me, de = 81%; **14e**, R = Ph, de = 70%; **14g**, R = ^{i}Pr, de = >95%), whilst the overall yield of isolated benzylated product remained relatively constant (Scheme 5, Table 3).

Molecular modelling on SuperQuat enolates

We were intrigued as to why the introduction of steric bulk at the 5-C position of the oxazolidin-2-one ring had such an adverse effect on enolate reactivity. We therefore carried out molecular modelling studies in order to determine whether subtle conformational differences between the enolates **17** and **18**, of *N*-propionyl-5,5-dimethyl-4-isopropyl-SuperQuat **14g** and *N*-propionyl-4,5,5-triphenyl-SuperQuat **14f** respectively could be responsible for the observed differences in enolate reactivities. Examination of the conformation of enolate **17** clearly revealed a transition state in accordance with the original mechanism proposed for Evans' auxiliary, involving formation of a (*Z*)-enolate; coordination of the exocyclic and endocyclic carbonyl to the lithium counterion; and approach of the electrophile from the opposing face to the 4-C stereodirecting group. Furthermore the relative orientation of the stereodirecting isopropyl group to the 5-C geminal methyl groups was consistent with our original model for this system, where steric interactions direct the *pro*-(*R*)-isopropyl methyl away from the *gem*-dimethyl group, effectively shielding the *pro-(R)* face of the enolate.

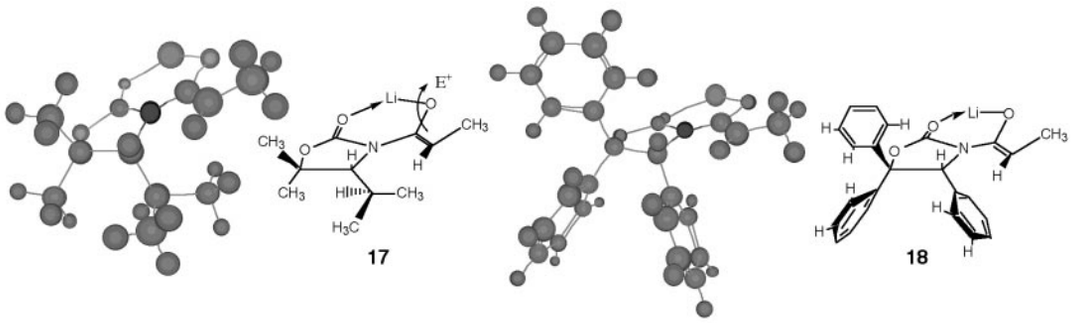
In contrast to **17** the enolate **18** reveals a propeller like conformation where steric interactions between the stereodirecting 4-C-phenyl group and the *syn*-5-C phenyl group result in both phenyl groups adopting a parallel orientation (Fig. 3). This conformation results in the *pro*-(*R*)-5-C-phenyl group adopting an edge-on conformation orthogonal to the *pro*-(*S*)-5-C-phenyl group with one of the *ortho*-aromatic ring protons being directed over the plane of the oxazolidin-2-one ring. This conformation results in both faces of enolate **18** being sterically hindered and accounts for the observed decreases in both diastereoselectivity and enolate reactivity observed for the enolates of these 5,5-diphenyl-SuperQuat systems. These conformational analyses are supported by the recently reported X-ray crystallographic structures of *N*-acyl-oxazolidin-2-ones derived from 5,5-diphenyl-SuperQuat.[9]

Optimisation of alkylation conditions for *N*-acyl-SuperQuat 14g

Having determined that alkylation of the lithium enolate of valine derived *N*-acyl-SuperQuat **14g** afforded the best diastereoselectivities (>95% de), we developed a new set of alkylation conditions which optimised the yield of benzylated product **15g**. After much investigation[13] we found that the lithium enolate of **14g** could be benzylated in THF at −78 °C with 5 equivalents of BnBr to afford **15g** in 93% isolated yield with less than 3% decomposition product. Furthermore, benzylation using these conditions *at 0 °C* afforded **15g** in an isolated 92% yield, with less than 5% decomposition product. These conditions contrast favourably with those recently reported by Seebach *et al.* who reported that the lithium enolate of *N*-acyl-5,5-diphenyl-SuperQuat **14h** was completely unreactive towards alkylation, and could only be benzylated in 81% yield, 96% de, when the corresponding *zinc enolate* was deployed.

Cleavage of α-benzylated-*N*-acyl-SuperQuat 15g

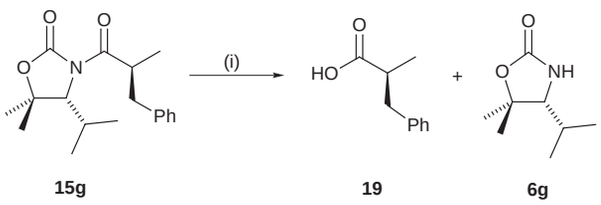
In order to confirm the efficacy of the 5-C-dimethyl substituents of the SuperQuat auxiliary for completely suppressing any endocyclic cleavage pathway, we needed to demonstrate that homochiral α-benzylated-*N*-propionyl SuperQuat **15g** could be cleaved *via* alkaline hydrolysis to afford homochiral α-substituted acid **19**, and homochiral SuperQuat **6g** (Scheme 6). Gratifyingly, treatment of **15g** with LiOH (2 equiv.) in THF–H_2O (3:1) afforded the desired carboxylic acid fragment **19** {$[\alpha]_D^{23}$ = +26.5 (*c* 1.0 in $CHCl_3$) {lit.,[14] $[\alpha]_D^{23}$ = +25.5 (*c* 1.0 in $CHCl_3$)}, and homochiral SuperQuat **6g** {$[\alpha]_D^{23}$ −23.9 (*c* 1 in $CHCl_3$)} in quantitative yield. No products from the endocyclic cleavage



Minimised structure of the enolate **17** of *N*-propionyl-5,5-dimethyl-4-isopropyl-SuperQuat **14g**

Minimised structure of the enolate **18** of *N*-propionyl-4,5,5-triphenyl-SuperQuat **14f**

Fig. 3



Scheme 6 *Reagents and conditions*: (i) LiOH, THF, H_2O.

pathway were observed in the ^{1}H NMR spectra of the crude reaction product, whilst ^{1}H NMR experiments with the chiral shift reagent tris{3-[heptafluoropropyl(hydroxy)methylene]-(+)-camphorato}europium(III) indicated no loss of stereochemical integrity at the stereogenic centre of **19** (≥95% ee). The positive sign of rotation for homochiral acid **19** served to confirm the absolute stereochemistry of the α-centre formed during alkylation of the enolate of **14g** (*vide infra*).

Conclusions

Studies on a range of enolates derived from unsubstituted, 5,5-dimethyl and 5,5-diphenyl oxazolidin-2-ones reveal that very high diastereoselectivities and yields are only obtained when homochiral 5,5-dimethyl-4-isopropyloxazolidin-2-one **6g** is employed as a chiral auxiliary. The geminal dimethyl groups at 5-C of the oxazolidin-2-one ring completely suppress any endocyclic cleavage pathway enabling simple alkaline cleavage of **15g** with LiOH to afford homochiral α-substituted carboxylic acid **19** in excellent yield.

Experimental

Melting points (mp) were obtained using a Griffin Gallenkamp melting point apparatus and are uncorrected. Optical rotations ($[\alpha]_D^{25}$) values are given in 10^{-1} deg cm^2 g^{-1} and were measured with a Perkin-Elmer 241 polarimeter with a thermally jacketed 1 dm cell at approximately 20 °C. Concentrations (*c*) are given in g 100 ml^{-1}. Infrared (IR) spectra were recorded on a Perkin-Elmer 1750 Fourier Transform spectrometer and only characteristic absorptions are reported in wavenumbers (cm^{-1}). Proton magnetic resonance spectra (^{1}H NMR) were recorded in $CDCl_3$ (unless otherwise stated) at 200 MHz on a Varian Gemini 200 spectrometer, at 400 MHz on a Bruker AC400 and at 500 MHz on a Bruker AM500 spectrometer and are referenced to the residual solvent peak. The following abbreviations were used: s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet and br, broad. Coupling constants (*J*) were recorded in hertz to the nearest 0.5 Hz. Carbon magnetic resonance spectra (^{13}C NMR) were recorded at 50.3 MHz on a Varian Gemini 200 spectrometer, at 100.6 MHz on a Bruker AC400 spectrometer and at 125.7 MHz on a Bruker AMX500 spectrometer using DEPT editing. Diastereomeric excesses were determined by peak integration of the crude reaction products' ^{1}H NMR spectrum. Low resolution mass spectra (*m*/*z*) were recorded on a VG Masslab 20-250, a VG Autospec, a Trio 1 GCMS, a VG BIO Q or an APCI Platform spectrometer. Microanalyses were performed by Mr R. Prior of the Dyson Perrins Analytical Service and at the analytical service of the Inorganic Chemistry Laboratories, University of Oxford. Column chromatography was performed on silica gel (Kieselgel 60). Anhydrous THF and diethyl ether were obtained by distillation from sodium–benzophenone ketyl under nitrogen. Benzyl bromide was fractionally distilled under vacuum before use from Na_2CO_3. *n*-Butyllithium was used as a solution in hexanes (approx. 1.4 M) and titrated before use. Lithium bis-(trimethylsilyl)amide was used as supplied (Aldrich) as a solution in THF (1 M). Unless otherwise stated all other reagents were used as supplied. Petrol refers to petroleum ether boiling in the range indicated. Ether refers to diethyl ether.

General method for the synthesis of α-amino acid methyl ester hydrochlorides

Thionyl chloride (1.5 equiv.) was carefully added dropwise to a stirred suspension of the α-amino acid (1 equiv.) in methanol (2 cm^3 mmol^{-1}) at 0 °C. The reaction was allowed to warm to room temperature and stirred for 24 hours, after which the solvent was removed *in vacuo* to give the α-amino acid methyl ester hydrochloride in quantitative yield. The products had essentially identical ^{1}H NMR spectra and specific rotations to those in the literature.

General method for the synthesis of *N*-Boc-α-amino acid methyl esters

Solid sodium hydrogen carbonate (3.0 equiv.) was added in one portion to a stirred solution of the α-amino acid methyl ester hydrochloride (1 equiv.) in ethanol (sufficient to dissolve the amino acid methyl ester) at 0 °C, immediately followed by addition of solid Boc_2O (1.05 equiv.) in one portion. The reaction was allowed to warm to room temperature and stirred for 48 h, after which the reaction was filtered through Celite, washed with diethyl ether and evaporated. The crude material was redissolved in diethyl ether, filtered through Celite with the ether washings and evaporated to afford the desired *N*-Boc-α-amino acid methyl ester. The products had essentially identical spectroscopic data to those in the literature.

General procedure for the preparation of the dimethyl substituted *N*-Boc amino alcohols

Method A. The *N*-Boc-α-amino acid methyl ester (1 equiv.) was dissolved in freshly distilled THF (20 cm^3 mmol^{-1}) and cooled to 0 °C. Methylmagnesium bromide (3.0 M solution in ether, 4 equiv.) was added dropwise under nitrogen (**CARE!** Initial addition results in evolution of methane) over 30 min

and the reaction left to stir at room temperature for 30 h. The reaction was cooled to 0 °C, cautiously quenched with saturated NH_4Cl (aq.) and extracted with ethyl acetate (×3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated to give the *N*-Boc amino alcohol.

Method B. Magnesium turnings (4 equiv.) were stirred in dry ether (5 cm^3 20 $mmol^{-1}$ Mg) under dry conditions and a small volume of methyl iodide (4 equiv.) added dropwise with gentle heating to initiate the formation of the Grignard reagent. Once an exothermic reaction had commenced, ether (10 cm^3 20 $mmol^{-1}$ Mg) was added to the residual methyl iodide and this addition was continued at a rate as to sustain the reaction at gentle reflux. Once addition was complete, the reaction was left to cool to room temperature, and the *N*-Boc-α-amino acid methyl ester (1 equiv.) in ether (5 cm^3 20 $mmol^{-1}$ Mg) added dropwise over 15 min. The reaction was left to stir for 48 h, then quenched with NH_4Cl (aq.) and extracted with ether (×3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated to give the desired dimethyl substituted alcohol.

***N*-Boc-3-amino-2-methylpropan-2-ol**[15] **13a.** The desired amino alcohol **13a** was obtained from *N*-Boc-glycine methyl ester **9** (R = H) (15.0 g, 0.087 mol) by Method B as a clear oil (9.45 g, 57%) after high vacuum distillation, bp 100 °C/1 mm Hg; ν_{max} (Nujol)/cm^{-1} 3366, 1694; δ_H(200 MHz) 1.21 (6 H, s, 2-Me and 1-H_3), 1.45 [9 H, s, (CH_3)$_3$], 2.51 (1 H, br, O*H*), 3.12 (1 H, d, *J* 6.3, 3-H_2), 5.04 (1 H, br, N*H*); δ_C(50 MHz) 26.7 (2-Me and 1-C), 28.2 [(*C*H_3)$_3$], 51.1 (3-C), 70.8 [(CH$_3$)$_3$*C*O], 79.3 (2-C), 157.2 (C=O); *m*/*z* (APCI) 245 (6%), 190 (5, MH^+), 189 (5), 134 (82), 116 (100).

(3*R*)-*N*-Boc-3-amino-2-methylbutan-2-ol 13c. The desired amino alcohol **13c** was obtained from *N*-Boc-D-alanine methyl ester **12** (R = Me) (3.00 g, 0.015 mol) by Method B as a waxy solid (2.66 g, 87%), mp 32 °C; $[\alpha]_D^{25}$ = +1.75 [*c* 1.6 in $CHCl_3$; lit.,[16] +1.6 (*c* 1.6 in $CHCl_3$)]; ν_{max} (KBr)/cm^{-1} 3435, 1694; δ_H(400 MHz) 1.05 (3 H, d, *J* 6.8, 4-H_3), 1.10 (3 H, s, CH_3), 1.15 (3 H, s, CH_3), 1.37 [9 H, s, (CH_3)$_3$C], 2.37 (1 H, br, O*H*), 3.51 (1 H, m, 3-H_1), 4.69 (1 H, m, N*H*); δ_C(50 MHz) 16.7 (4-C), 26.1 (*C*H_3), 27.9 (*C*H_3), 28.9 [(*C*H_3)$_3$C], 55.1 (3-C), 73.5 (2-C), 79.9 [(CH$_3$)$_3$*C*], 156.9 (C=O); *m*/*z* (APCI) 226 (4%, M^+ + Na), 159 (5), 148 (12, $M^+ - C_4H_7$), 130 (75, $M^+ - C_4H_9O$), 104 (100, $M^+ - C_5H_7O_2$).

(1*R*)-*N*-Boc-1-amino-2-methyl-1-phenylpropan-2-ol 13e. The desired amino alcohol **13e** was obtained from *N*-Boc-D-phenylglycine methyl ester **12** (R = Ph) (2.00 g, 7.55 mmol) by Method A as a fluffy white solid after recrystallisation from petrol (bp 40–60 °C)–ether (1.43 g, 75%), mp 123 °C; $[\alpha]_D^{25}$ = −29.5 (*c* 1 in $CHCl_3$) (Found: C, 67.9; H, 8.9; N, 5.2. $C_{15}H_{23}NO_3$ requires C, 67.90; H, 8.7; N, 5.3%); ν_{max} (Nujol)/cm^{-1} 3473, 3396, 1667; δ_H(200 MHz) 1.06 (3 H, s, CH_3), 1.34 (3 H, s, CH_3), 1.40 [9 H, s, (CH_3)$_3$], 4.53 (1 H, br d, *J* 9.5, 1-H_1), 5.57 (1 H, br d, *J* 9.5, N*H*), 7.24–7.39 (5 H, m, ArC*H*); δ_C(50 MHz) 27.4 (*C*H$_3$), 27.5 (*C*H$_3$), 28.2 [(*C*H$_3$)$_3$C], 62.8 (1-C), 72.7 (2-C), 79.5 [(CH$_3$)$_3$*C*], 127.6 (Ar*C*H), 128.0 (Ar*C*H), 128.3 (Ar*C*H), 140.1 (ArC_{ipso}), 156.2 (C=O); *m*/*z* (APCI) 288 (8%), 266 (8, MH^+), 221 (10), 210 (15), 166 (100), 149 (27), 148 (32), 106 (11).

(3*R*)-*N*-Boc-3-amino-2,4-dimethylpentan-2-ol 13g. *N*-Boc-D-valine methyl ester **12** (R = i-Pr) (4.00 g, 0.017 mol) was treated with methylmagnesium bromide (Method B) to yield the desired amino alcohol **13g** (3.45 g, 88%) as a white waxy solid, mp 45–47 °C; $[\alpha]_D^{25}$ +8.7 (*c* 1 in $CHCl_3$) (Found: C, 62.4; H, 10.9; N, 5.9. $C_{12}H_{25}NO_3$ requires C, 62.30; H, 10.9; N, 6.1%); ν_{max}(film)/cm^{-1} 3445, 1694; δ_H(400 MHz) 0.90 (3 H, d, *J* 6.8, CH_3CH), 0.94 (3 H, d, *J* 6.8, CH_3CH), 1.22 (3 H, s, CH_3), 1.25 (3 H, s, CH_3), 1.44 [9 H, s, (CH_3)$_3$C], 2.09 (1 H, m, 4-H_1), 3.38 (1 H, dd, *J* 2.6 and 10.1, 3-H_1), 4.85 (1 H, br, *J* 10.1, N*H*); δ_C(100 MHz) 16.8 (*C*H$_3$), 22.3 (*C*H$_3$), 27.0 (*C*H$_3$), 28.1 (*C*H$_3$), 28.4 [(*C*H$_3$)$_3$C], 29.0 (4-C), 61.7 (3-C), 73.7 (2-C), 79.1 [(CH$_3$)$_3$*C*], 156.9 (C=O); *m*/*z* (APCI) 232 (4%, MH^+), 187 (3), 176 (20, $M^+ - C_4H_7$), 158 (100, $M^+ - C_4H_9O$), 132 (64), 114 (63).

General procedure for the preparation of the diphenyl substituted *N*-Boc amino alcohols

Magnesium turnings (4 equiv.) were stirred in dry THF (5 cm^3 20 $mmol^{-1}$ Mg) under dry conditions and a small volume of bromobenzene (4 equiv.) added dropwise with gentle heating to initiate the formation of the Grignard reagent. Once an exothermic reaction had commenced, THF (10 cm^3 20 $mmol^{-1}$ Mg) was added to the residual bromobenzene and this added dropwise at a rate as to sustain the reaction at gentle reflux. Once addition was complete, the reaction was left to cool to room temperature, and the *N*-Boc-α-amino acid methyl ester (1 equiv.) in THF (5 cm^3 20 $mmol^{-1}$ Mg) added dropwise over 15 min. The reaction was left to stir for 48 h, then quenched with NH_4Cl(aq) and extracted with ether (×3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated to give the desired diphenyl substituted alcohol.

***N*-Boc-2-amino-1,1-diphenylethanol 13b.** The desired amino alcohol **13b** was obtained from *N*-Boc-glycine methyl ester **12** (R = H) (2.50 g, 14.4 mmol) using the above method, followed by recrystallisation from hexane–dichloromethane as a white powder (2.90 g, 64%), mp 100–102 °C (Found: C, 72.9; H, 7.7; N, 4.1. $C_{19}H_{23}NO_3$ requires C, 72.8; H, 7.40; N, 4.5%); ν_{max}(KBr)/cm^{-1} 3370, 1678; δ_H(400 MHz) 1.39 [9 H, s, (CH_3)$_3$C], 3.48 (1 H, br, O*H*), 3.95 (2 H, d, *J* 6.5, 2-H_2), 7.28–7.48 (10 H, m, ArC*H*); δ_C(50 MHz) 28.2 [(*C*H$_3$)$_3$C], 50.3 (2-C), 78.4 [(CH$_3$)$_3$*C*], 80.0 (1-C), 126.4 (Ar*C*H), 127.4 (Ar*C*H), 128.5 (Ar*C*H), 135.3 (ArC_{ipso}), 145.0 (C=O); *m*/*z* (APCI) 269 (4%), 251 (2), 240 (20, $M^+ - C_4H_9O$), 214 (32, $M^+ - C_5H_7O_2$), 196 (100).

(2*R*)-*N*-Boc-2-amino-1,1-diphenylpropanol 13d. The desired amino alcohol **13d** was obtained from *N*-Boc-D-alanine methyl ester **9** (R = Me) (1.00 g, 4.92 mmol) using the above method, followed by recrystallisation from petrol (bp 40–60 °C)–ether as a white powder (1.03 g, 64%), mp 151–152 °C; $[\alpha]_D^{25}$ = +46.5 (*c* 0.2 in $CHCl_3$) (Found: C, 73.3; H, 7.7; N, 4.2. $C_{20}H_{25}NO_3$ requires C, 73.4; H, 7.70; N, 4.3%); ν_{max}(KBr)/cm^{-1} 3406, 1673; δ_H(400 MHz) 1.09 (3 H, d, *J* 6.6, 3-H_3), 1.35 [9 H, s, (CH_3)$_3$C], 2.85 (1 H, br, O*H*), 4.75 (1 H, m, 2-H_1), 4.82 (1 H, m, N*H*), 7.17–7.23 (2H, m, Ar*CH*), 7.27–7.33 (4H, m, Ar*CH*), 7.44 (2 H, d, *J* 7.3, Ar*CH*), 7.50 (2 H, d, *J* 7.3, Ar*CH*); δ_C(50 MHz) 16.3 (3-C), 28.2 [(*C*H$_3$)$_3$C], 51.9 (2-C), 79.4 [(CH$_3$)$_3$*C*], 80.9 (1-C), 125.8 (Ar*C*H), 126.2 (Ar*C*H), 127.1 (Ar*C*H), 128.4 (Ar*C*H), 128.5 (Ar*C*H), 145.3 (ArC_{ipso}), 145.4 (ArC_{ipso}), 155.9 (C=O); *m*/*z* (APCI) 283 (6%), 265 (3), 255 (5), 254 (32, $M^+ - C_4H_9O$), 228 (15, $M^+ - C_5H_7O_2$), 211 (22), 210 (100).

(2*R*)-*N*-Boc-2-amino-1,1,2-triphenylethanol 13f. The desired amino alcohol **13f** was obtained from *N*-Boc-D-phenylglycine methyl ester **9** (R = Ph) (1.00 g, 3.77 mmol) using the above method, followed by recrystallisation from petrol (bp 40–60 °C)–ether as a white powder (1.20 g, 82%), mp 197 °C; $[\alpha]_D^{25}$ = +215.2 (*c* 0.5 in $CHCl_3$) (Found: C, 77.15; H, 7.3; N, 3.40. $C_{25}H_{27}NO_3$ requires C, 77.1; H, 7.0; N, 3.60%); ν_{max}(KBr)/cm^{-1} 3455, 3415, 1670; δ_H(400 MHz) 1.34 [9 H, s, (CH_3)$_3$C], 2.67 (1 H, br, O*H*), 5.61 (1 H, m, 2-H_1), 5.75 (1 H, m, N*H*), 7.00–7.03 (2 H, m, ArC*H*), 7.08–7.18 (8 H, m, ArC*H*), 7.25–7.29 (1 H, m, ArC*H*), 7.36 (2 H, t, *J* 7.6, ArC*H*), 7.60 (2 H, d, *J* 7.6, ArC*H*); δ_C(100 MHz) 28.2 [(*C*H$_3$)$_3$], 60.2 (2-C), 79.6 (1-C), 81.1 [(CH$_3$)$_3$*C*], 125.5 (Ar*C*H), 126.3 (Ar*C*H), 126.8 (Ar*C*H), 127.2 (Ar*C*H), 127.3 (Ar*C*H), 127.8 (Ar*C*H), 127.9 (Ar*C*H), 128.3

(Ar*C*H), 128.5 (Ar*C*H), 138.3 (ArC_{ipso}), 144.2 (ArC_{ipso}), 144.5 (ArC_{ipso}), 155.2 (C=O); *m*/*z* (APCI) 500 (4%), 448 (15), 412 (3, M^+ + Na), 345 (56), 316 (13), 272 (100, $M^+ - C_5H_{11}NO_2$).

(2*R*)-*N*-Boc-2-amino-1,1-diphenyl-3-methylbutanol 13h. The desired amino alcohol **13h** was obtained from *N*-Boc-D-valine methyl ester **9** (R = i-Pr) (4.00 g, 0.017 mol) using the above method, followed by recrystallisation from petrol (bp 40–60 °C)–ethyl acetate as a crystalline solid (4.48 g, 74%), mp 188–190 °C; $[\alpha]_D^{25}$ = +68.8 (*c* 1 in $CHCl_3$) (Found: C, 74.3; H, 8.1; N, 3.8. $C_{22}H_{29}NO_3$ requires C, 74.3; H, 8.2; N, 3.9%); ν_{max}(film)/cm^{-1} 3428, 1680; δ_H(400 MHz) 0.89 (3 H, d, *J* 6.9, CH_3), 0.91 (3 H, d, *J* 6.9, CH_3), 1.34 [9 H, s, (CH_3)$_3$C], 1.81 (1 H, dsept, *J* 2.0 and 6.9, 3-H_1), 2.67 (1 H, br, O*H*), 4.61 (1 H, dd, *J* 10.2 and 2.0, 2-H_1), 5.04 (1 H, d, *J* 10.2, N*H*), 7.15–7.35 (6 H, m, ArC*H*), 7.46 (2 H, d, *J* 7.4, ArC*H*), 7.51 (2 H, d, *J* 7.7, ArC*H*); δ_C(100 MHz) 17.4 (*C*H$_3$), 22.7 (*C*H$_3$), 28.7 [(*C*H$_3$)$_3$C], 28.8 (3-C), 59.0 (2-C), 79.0 [(CH$_3$)$_3$*C*], 82.4 (1-C), 125.3 (Ar*C*H), 125.7 (Ar*C*H), 126.7 (Ar*C*H), 128.2 (Ar*C*H), 128.3 (Ar*C*H), 145.6 (ArC_{ipso}), 146.3 (ArC_{ipso}), 156.3 (C=O); *m*/*z* (APCI) 311 (5%), 282 (12, $M^+ - C_4H_9O$), 256 (15, $M^+ - C_5H_7O_2$), 239 (22), 238 (100, $M^+ - C_5H_9O_3$), 221 (18), 196 (6), 150 (42).

General procedure for the preparation of the oxazolidinones

Potassium *tert*-butoxide (1.1 equiv.) was added in one portion to a stirred solution of the *N*-Boc amino alcohol (1 equiv.) in freshly distilled THF (5 cm^3 mmol^{-1}) at 0 °C. After 30 min, the solvent was evaporated, and the residue taken up in ethyl acetate and washed with brine. The organic layer was dried ($MgSO_4$) and evaporated to give crude product which was recrystallised to yield the desired oxazolidin-2-one.

5,5-Dimethyloxazolidin-2-one 6a. The glycine derived amino alcohol **13a** (5.00 g, 26.4 mmol) was cyclised by the described procedure and recrystallised from ethyl acetate–petrol (bp 60–80 °C) to give the dimethylglycine SuperQuat **6a** (2.15 g, 71%) as off white crystals, mp 78–82 °C (lit.,[17] 79–82 °C); ν_{max}(film)/cm^{-1} 3265, 1763; δ_H(200 MHz) 1.49 (6 H, s, 2 × 5-Me), 3.38 (2 H, s, 4-H_2), 5.90 (1 H, br, N*H*); δ_C(50 MHz) 27.1 (2 × 5-Me), 52.7 (4-C), 81.1 (5-C), 160.4 (2-C); *m*/*z* (APCI) 231 (5%, M_2H^+), 138 (6, M^+ + Na), 122 (5, M^+ + Li), 117 (8), 116 (100, MH^+).

5,5-Diphenyloxazolidin-2-one 6b. The glycine derived amino alcohol **13b** (2.00 g, 6.38 mol) was cyclised by the described procedure and recrystallised from hot ethyl acetate to give the diphenylglycine SuperQuat **6b** (1.10 g, 72%), mp 196–197 °C (Found: C, 75.30; H, 5.3; N, 5.8. $C_{15}H_{13}NO_2$ requires C, 75.30; H, 5.5; N, 5.9%); ν_{max}(KBr)/cm^{-1} 3260, 1740; δ_H(400 MHz) 4.21 (2 H, s, 4-H_2), 5.96 (1 H, br, N*H*), 7.29–7.43 (10 H, m, ArC*H*); δ_C(50 MHz) 53.4 (4-C), 86.5 (5-C), 125.5 (Ar*C*H), 128.2 (Ar*C*H), 128.6 (Ar*C*H), 142.4 (ArC_{ipso}), 158.8 (2-C); *m*/*z* (APCI) 251 (5%), 241 (6), 240 (MH^+, 52), 197 (25), 196 (100, $MH^+ - CO_2$).

(4*R*)-4,5,5-Trimethyloxazolidin-2-one 6c. The desired SuperQuat **6c** was obtained from the alanine derived amino alcohol **13c** (2.431 g, 12.0 mmol) by the above method as a white crystalline solid after recrystallisation from petrol (bp 60–80 °C)–ether (1.015 g, 66%), mp 64 °C (lit.,[18] 61 °C); $[\alpha]_D^{25}$ = −2.85 (*c* 4 in $CHCl_3$) [lit.,[18] −2.6 (*c* 4 in $CHCl_3$)]; ν_{max}(KBr)/cm^{-1} 3274, 1733; δ_H(400 MHz) 1.15 (3 H, d, *J* 6.5, 4-Me), 1.30 (3 H, s, 5-Me), 1.42 (3 H, s, 5-Me), 3.62 (1 H, q, *J* 6.5, 4-H_1), 6.45 (1 H, br, N*H*); δ_C(100 MHz) 16.1 (*C*H$_3$), 21.4 (*C*H$_3$), 27.1 (*C*H$_3$), 57.1 (4-C), 83.5 (5-C), 159.2 (2-C); *m*/*z* (APCI) 281 (5%, M_2^+ + Na), 259 (8, M_2^+ + H), 210 (6), 152 (33, M^+ + Na), 130 (100, MH^+).

(4*R*)-5,5-Diphenyl-4-methyloxazolidin-2-one 6d. The desired SuperQuat **6d** was obtained from the alanine derived amino alcohol **13d** (0.500 g, 1.53 mmol) by the above method as a crystalline solid after recrystallisation from petrol (bp 60–80 °C)–ethyl acetate (0.283 g, 73%), mp >220 °C; $[\alpha]_D^{25}$ = +288.4 (*c* 0.5 in $CHCl_3$) (Found: C, 75.8; H, 5.95; N, 5.5. $C_{16}H_{15}NO_2$ requires C, 75.9; H, 6.0; N, 5.5%); ν_{max}(KBr)/cm^{-1} 3264, 1744, 1723; δ_H(400 MHz) 1.01 (3 H, d, *J* 6.5, 4-Me), 4.68 (1 H, q, *J* 6.5, 4-H_1), 5.32 (1 H, br, N*H*), 7.26–7.42 (8 H, m, ArC*H*), 7.51 (2 H, m, ArC*H*); δ_C(100 MHz) 19.3 (4-Me), 56.2 (4-C), 89.4 (5-C), 126.0 (Ar*C*H), 126.2 (Ar*C*H), 127.8 (Ar*C*H), 128.1 (Ar*C*H), 128.3 (Ar*C*H), 128.5 (Ar*C*H), 139.2 (ArC_{ipso}), 142.4 (ArC_{ipso}), 157.9 (2-C); *m*/*z* (APCI$^+$) 254 (42%, MH^+), 210 (100), 104 (32).

(4*R*)-5,5-Dimethyl-4-phenyloxazolidin-2-one 6e. The desired SuperQuat **6e** was obtained from the phenylglycine amino alcohol **13e** (93.8 g, 0.345 mol) by the above method as a crystalline solid after recrystallisation from ethyl acetate–petrol (bp 40–60 °C) (55.16 g, 84%), mp 149 °C; $[\alpha]_D^{25}$ = −77.6 (*c* 0.5 in $CHCl_3$) (Found: C, 69.3; H, 7.05; N, 7.4. $C_{11}H_{13}NO_2$ requires C, 69.1; H, 6.85; N, 7.3%); ν_{max}($CHCl_3$)/cm^{-1} 1753; δ_H(200 MHz) 0.93 (3 H, s, 5-Me), 1.61 (3 H, s, 5-Me), 4.66 (1 H, s, 4-H_1), 6.25 (1 H, s, N*H*), 7.44–7.25 (5H, m, ArC*H*); δ_C(125 MHz) 23.5 (5-Me), 28.0 (5-Me), 65.9 (4-C), 84.6 (5-C), 126.7 (Ar*C*H), 128.72 (Ar*C*H), 128.9 (Ar*C*H), 137.2 (ArC_{ipso}), 159.8 (2-C); *m*/*z* (CI$^+$) 210 (5%), 209 (48), 193 (12), 192 (100, MH^+), 148 (10).

(4*R*)-4,5,5-Triphenyloxazolidin-2-one 6f. The desired SuperQuat **6f** was obtained from the phenylglycine derived amino alcohol **13f** (0.250 g, 0.642 mmol) by the above method as a white solid after recrystallisation from petrol (bp 60–80 °C)–ethyl acetate (0.164 g, 81%), mp >230 °C (lit.,[19] 246.5–247.2 °C); $[\alpha]_D^{25}$ = +218.1 (*c* 1 in $CHCl_3$) [lit.,[19] +218.15 (*c* 1 in $CHCl_3$)]; ν_{max}(KBr)/cm^{-1} 3274, 1755, 1727; δ_H(400 MHz) 5.51 (1 H, br, N*H*), 5.67 (1 H, s, 4-H_1), 7.08 (5 H, s, ArC*H*), 7.12–7.14 (2 H, m, ArC*H*), 7.18–7.21 (3 H, ArC*H*), 7.42 (1 H, t, *J* 7.5, ArC*H*), 7.49 (2 H, t, *J* 7.5, ArC*H*), 7.73 (2 H, d, *J* 7.5, ArC*H*); δ_C(100 MHz) 65.8 (4-C), 90.7 (5-C), 126.2 (Ar*C*H), 126.5 (Ar*C*H), 127.3 (Ar*C*H), 127.5 (Ar*C*H), 127.8 (Ar*C*H), 128.3 (Ar*C*H), 128.5 (Ar*C*H), 128.6 (Ar*C*H), 137.1 (ArC_{ipso}), 138.8 (ArC_{ipso}), 142.8 (ArC_{ipso}), 157.9 (2-C); *m*/*z* (APCI$^+$) 374 (11%), 327 (4), 316 (4, MH^+), 273 (18), 272 (100, $MH^+ - CO_2$), 270 (28).

(4*R*)-5,5-Dimethyl-4-isopropyloxazolidin-2-one 6g. The desired SuperQuat **6g** was obtained from the valine derived amino alcohol **13g** (3.04 g, 0.013 mol) by the above method as white needles after recrystallisation from petrol (bp 40–60 °C)–ethyl acetate (1.46 g, 72%), mp 87 °C; $[\alpha]_D^{25}$ = −24.2 (*c* 1 in $CHCl_3$) (Found: C, 61.3; H, 9.6; N, 8.80. $C_8H_{15}NO_2$ requires C, 61.1; H, 9.6; N, 8.9%); ν_{max}(KBr)/cm^{-1} 3247, 1739; δ_H(400 MHz) 0.92 [3 H, d, *J* 6.6, (CH_3)$_2$CH], 0.99 [3 H, d, *J* 6.6, (CH_3)$_2$CH], 1.39 (3 H, s, 5-Me), 1.49 (3 H, s, 5-Me), 1.82 [1 H, dsept, *J* 8.6 and 6.6, C*H*(CH$_3$)$_2$], 3.19 (1 H, d, *J* 8.6, 4-H_1), 6.31 (1 H, br, N*H*); δ_C(50 MHz) 19.8 (*C*H$_3$), 21.1 (*C*H$_3$), 21.1 (*C*H$_3$), 28.3 (*C*H$_3$), 28.5 [(CH$_3$)$_2$*C*H], 68.5 (4-C), 83.9 (5-C), 159.9 (2-C); *m*/*z* (APCI$^+$) 315 (4%, M_2H^+), 180 (4), 159 (11), 158 (100, MH^+).

(4*R*)-5,5-Diphenyl-4-isopropyloxazolidin-2-one 6h. The desired SuperQuat **6h** was obtained from the valine derived amino alcohol **13h** (3.043 g, 8.56 mmol) by the above method as white needles after recrystallisation from ethyl acetate (1.785 g, 74%), mp >220 °C (lit.,[19] 252.9–253.5 °C); $[\alpha]_D^{25}$ = +315.6 (*c* 0.5 in $CHCl_3$) [lit.,[19] +270.78 (*c* 1 in $CHCl_3$)]; ν_{max}(KBr)/cm^{-1} 3293, 1766, 1745; δ_H(200 MHz) 0.69 (3 H, d, *J* 6.8, CH_3CH), 0.90 (3 H, d, *J* 6.8, CH_3CH), 1.85 [1 H, dsept, *J* 3.5 and 6.8, (CH$_3$)$_2$C*H*], 4.36 (1 H, d, *J* 3.5, 4-H_1), 6.32 (1 H, br, N*H*), 7.25–7.43 (8 H, m, ArC*H*), 7.55 (2 H, dd, *J* 6.6 and 1.0, ArC*H*); δ_C(100 MHz) 18.3 (*C*H$_3$), 23.5 (*C*H$_3$), 32.3 [(CH$_3$)$_2$*C*H], 68.5 (4-C), 92.1 (5-C), 128.4 (Ar*C*H), 129.00 (Ar*C*H), 130.4 (Ar*C*H), 130.8 (Ar*C*H), 131.3 (Ar*C*H), 141.8 (ArC_{ipso}), 146.6

(ArC_{ipso}), 161.3 (2-C); *m/z* (APCI$^+$) 282 (27%, MH^+), 239 (18), 238 (100, $MH^+ - CO_2$), 236 (21), 196 (20).

General procedure for the *N*-benzylation of the oxazolidinones

n-Butyllithium (1.1 equiv.) was added dropwise *via* syringe to a stirred solution of the oxazolidin-2-one (1 equiv.) in THF (10 cm^3 $mmol^{-1}$) at −78 °C under a nitrogen atmosphere and the mixture allowed to stir for 15 min. Benzyl bromide (3 equiv.) was added at −78 °C and the reaction stirred at this temperature for 30 min, then allowed to warm to room temperature over 24 h. Saturated NH_4Cl (aq.) was added and the reaction extracted with ethyl acetate (×3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated to yield the desired *N*-benzyl oxazolidinone.

***N*-Benzyl-5,5-dimethyloxazolidin-2-one 16a.** Reaction of the oxazolidinone **6a** (0.200 g, 1.17 mmol) as described above, followed by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C), 1:4] gave the title compound **16a** (0.239 g, 100%) as a clear oil (Found: MH^+, 206.1177. $C_{12}H_{16}NO_2$ requires *m/z* 206.1181); ν_{max}(film)/cm^{-1} 1732; δ_H(400 MHz) 1.42 (6 H, s, 2 × 5-Me), 3.14 (2 H, s, 4-H_2), 4.44 (2 H, s, CH_2Ph), 7.28–7.35 (5 H, m, ArC*H*); δ_C(100 MHz) 27.2 (2 × 5-Me), 48.0 (4-C), 55.9 (*C*H_2Ph), 77.5 (5-C), 128.1 (ArC*H*), 128.2 (ArC*H*), 129.0 (ArC*H*), 136.2 (ArC_{ipso}), 157.9 (2-C); *m/z* (APCI) 228 (4%, M^+ + Na), 207 (42), 206 (100, MH^+), 162 (2), 122 (9).

***N*-Benzyl-5,5-diphenyloxazolidin-2-one 16b.** Reaction of the oxazolidinone **6b** (0.250 g, 1.04 mmol) as described above, followed by crystallisation from ethyl acetate–petrol (bp 40–60 °C) gave the title compound **16b** (0.339 g, 99%) as a white powder, mp 156 °C (Found: C, 80.1; H, 6.1; N, 4.2. $C_{22}H_{19}NO_2$ requires C, 80.2; H, 5.8; N, 4.25%); ν_{max}(KBr)/cm^{-1} 1747, 1437; δ_H(400 MHz) 3.98 (2 H, s, PhCH_2), 4.49 (2 H, s, 4-H_2), 7.18–7.20 (2 H, m, ArC*H*), 7.26–7.38 (13 H, m, ArC*H*); δ_C(100 MHz) 48.2 (4-C), 56.5 (Ph*C*H_2), 83.3 (5-C), 125.4 (Ar*C*H), 127.9 (Ar*C*H), 128.1 (Ar*C*H), 128.6 (Ar*C*H), 128.8 (Ar*C*H), 135.4 (ArC_{ipso}), 142.4 (2 × ArC_{ipso}), 157.1 (2-C); *m/z* (APCI) 330 (100%, MH^+), 286 (31, $MH^+ - CO_2$).

(4*R*)-*N*-Benzyl-4,5,5-trimethyloxazolidin-2-one 16c. Reaction of the oxazolidinone **6c** (0.150 g, 1.16 mmol) as described above, followed by purification by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C), 1:5] gave the title compound **16c** (0.227 g, 89%) as a clear oil; $[a]_D^{25}$ = +36.8 (*c* 1 in $CHCl_3$) (Found: MH^+, 220.1332. $C_{13}H_{18}NO_2$ requires *m/z* 220.1338); ν_{max}(film)/cm^{-1} 1743; δ_H(400 MHz) 1.09 (3 H, d, *J* 6.6, 4-Me), 1.30 (3 H, s, 5-Me), 1.35 (3 H, s, 5-Me), 3.29 (1 H, q, *J* 6.6, 4-H_1), 4.04 (1 H, d, *J* 15.3, CH_2Ph), 4.80 (1 H, d, *J* 15.3, CH_2Ph), 7.29–7.39 (5 H, m, ArC*H*); δ_C(50 MHz) 13.2 (4-Me), 21.5 (5-Me), 26.8 (5-Me), 45.5 (*C*H_2Ph), 58.9 (4-C), 80.7 (5-C), 127.9 (Ar*C*H), 128.1 (Ar*C*H), 128.9 (Ar*C*H), 136.5 (ArC_{ipso}), 157.8 (2-C); *m/z* (APCI) 242 (12%, M^+ + Na), 221 (18), 220 (100, MH^+).

(4*R*)-*N*-Benzyl-5,5-diphenyl-4-methyloxazolidin-2-one 16d. Reaction of the oxazolidinone **6d** (0.300 g, 1.18 mmol) as described above, followed by crystallisation from ethyl acetate–petrol (bp 40–60 °C) gave the title compound **16d** (0.324 g, 80%) as white needles, mp 157–158 °C; $[a]_D^{25}$ = +211.8 (*c* 1 in $CHCl_3$) (Found: C, 80.2; H, 6.00; N, 4.0. $C_{23}H_{21}NO_2$ requires C, 80.4; H, 6.2; N, 4.1%); ν_{max}(KBr)/cm^{-1} 1745; δ_H(400 MHz) 0.92 (3 H, d, *J* 6.5, 4-Me), 4.05 (1 H, d, *J* 15.3, PhCH_2), 4.33 (1 H, q, *J* 6.5, 4-H_1), 4.90 (1 H, d, *J* 15.3, PhCH_2), 7.14 (2 H, m, ArC*H*), 7.23–7.39 (13 H, m, ArC*H*); δ_C(100 MHz) 15.6 (4-Me), 45.9 (4-C), 57.9 (Ph*C*H_2), 87.0 (5-C), 126.0 (ArC*H*), 126.3 (ArC*H*), 127.8 (ArC*H*), 127.9 (ArC*H*), 128.0 (ArC*H*), 128.1 (ArC*H*), 128.3 (ArC*H*), 128.4 (ArC*H*), 128.7 (ArC*H*), 135.6 (ArC_{ipso}), 139.4 (ArC_{ipso}), 142.3 (ArC_{ipso}), 156.9 (2-C); *m/z* (APCI) 366 (5%, M^+ + Na), 345 (28), 344 (100, MH^+), 300 (10, $MH^+ - CO_2$), 122 (6).

(4*R*)-*N*-Benzyl-5,5-dimethyl-4-phenyloxazolidin-2-one 16e. Reaction of the oxazolidinone **6e** (0.500 g, 1.97 mmol) as described above, followed by crystallisation from hot petrol (bp 40–60 °C)–ether gave the title compound **16e** (0.497 g, 90%) as needles, mp 117–118 °C; $[a]_D^{25}$ = −108.0 (*c* 1 in $CHCl_3$) (Found: C, 76.75; H, 6.7; N, 4.95. $C_{18}H_{19}NO_2$ requires C, 76.8; H, 6.8; N, 5.0%); ν_{max}(KBr)/cm^{-1} 1728; δ_H(400 MHz) 0.94 (3 H, s, 5-Me), 1.44 (3 H, s, 5-Me), 3.68 (1 H, d, *J* 14.8, PhCH_2), 4.13 (1 H, s, 4-H_1), 5.00 (1 H, d, *J* 14.8, PhCH_2), 7.11–7.14 (4 H, m, ArC*H*), 7.29–7.32 (3 H, m, ArC*H*), 7.39–7.44 (3 H, m, ArC*H*); δ_C(50 MHz) 23.8 (5-Me), 28.5 (5-Me), 46.2 (*C*H_2), 68.1 (4-C), 81.3 (5-C), 127.8 (Ar*C*H), 128.1 (Ar*C*H), 128.7 (Ar*C*H), 128.9 (Ar*C*H), 129.1 (Ar*C*H), 135.2 (ArC_{ipso}), 135.9 (ArC_{ipso}), 158.1 (2-C); *m/z* (APCI) 304 (5%, M^+ + Na), 283 (23), 282 (100, MH^+), 238 (4, $MH^+ - CO_2$).

(4*R*)-*N*-Benzyl-4,5,5-triphenyloxazolidin-2-one 16f. The title compound **16f** was obtained after attempted alkylation of the propionyl SuperQuat **14f** (0.100 g, 0.269 mmol) using the procedure described subsequently, and isolated by column chromatography as a white solid (0.044 g, 40%), mp 161 °C; $[a]_D^{25}$ = +102.0 (*c* 0.5 in $CHCl_3$) (Found: C, 82.9; H, 5.6; N, 3.3. $C_{28}H_{23}NO_2$ requires C, 82.9; H, 5.7; N, 3.45%); ν_{max}(KBr)/cm^{-1} 1740; δ_H(200 MHz) 3.61 (1 H, d, *J* 15.8, CH_2Ph), 4.98 (1 H, d, *J* 15.8, CH_2Ph), 5.18 (1 H, s, 4-H_1), 6.89–7.50 (20 H, m, ArC*H*); δ_C(50 MHz) 46.3 (*C*H_2Ph), 68.0 (4-C), 88.1 (5-C), 126.2 (Ar*C*H), 126.7 (Ar*C*H), 127.4 (Ar*C*H), 127.7 (Ar*C*H), 127.9 (Ar*C*H), 128.1 (Ar*C*H), 128.5 (Ar*C*H), 128.7 (Ar*C*H), 128.8 (Ar*C*H), 134.9 (ArC_{ipso}), 135.5 (ArC_{ipso}), 139.2 (ArC_{ipso}), 143.3 (ArC_{ipso}), 157.4 (2-C); *m/z* (APCI) 812 (20%, $(MH)_2^+$), 810 (12), 407 (25), 406 (100, MH^+), 362 (30, $MH^+ - CO_2$), 343 (30), 238 (50).

(4*R*)-*N*-Benzyl-5,5-dimethyl-4-isopropyloxazolidin-2-one 16g. Reaction of the oxazolidinone **6g** (0.300 g, 1.908 mmol) as described above, followed by crystallisation from dichloromethane–petrol (bp 60–80 °C) gave the title compound **16g** (0.384 g, 81%) as a highly crystalline solid, mp 113 °C; $[a]_D^{25}$ = +74.3 (*c* 1 in $CHCl_3$) (Found: MH^+, 248.1659. $C_{15}H_{22}NO_2$ requires *m/z* 248.1651); ν_{max}(KBr)/cm^{-1} 1737; δ_H(500 MHz) 1.03 [3 H, d, *J* 7.1, $(CH_3)_2$CH], 1.10 [3 H, d, *J* 7.1, $(CH_3)_2$CH], 1.24 (3 H, s, 5-Me), 1.42 (3 H, s, 5-Me), 2.02 [1 H, dsept, *J* 2.2 and 7.1, $(CH_3)_2$C*H*], 3.30 (1 H, d, *J* 2.2, 4-H_1), 4.02 (1 H, d, *J* 15.2, PhCH_2), 5.10 (1 H, d, *J* 15.2, PhCH_2), 7.28–7.39 (5 H, m, ArC*H*); δ_C(50 MHz) 16.8 [(*C*H_3)$_2$CH], 21.3 (5-Me), 22.0 [(*C*H_3)$_2$CH], 28.8 [$(CH_3)_2$*C*H], 29.3 (5-Me), 47.5 (Ph*C*H_2), 66.6 (4-C), 81.3 (5-C), 128.1 (Ar*C*H), 128.6 (Ar*C*H), 128.9 (Ar*C*H), 136.3 (ArC_{ipso}), 158.3 (2-C); *m/z* (APCI) 495 (12%, M_2H^+), 249 (bp 40), 248 (100, MH^+), 122 (13).

(4*R*)-*N*-Benzyl-5,5-diphenyl-4-isopropyloxazolidin-2-one 16h. Reaction of the oxazolidinone **6h** (0.300 g, 1.07 mmol) as described above, followed by crystallisation from dichloromethane–petrol (bp 60–80 °C) gave the title compound **16h** (0.247 g, 62%) as white needles, mp 135 °C; $[a]_D^{25}$ = +200.0 (*c* 1 in $CHCl_3$) (Found: C, 81.0; H, 6.7; N, 3.7. $C_{25}H_{25}NO_2$ requires C, 80.8; H, 6.8; N, 3.8%); ν_{max}(KBr)/cm^{-1} 1737; δ_H(400 MHz) 0.79 [3 H, d, *J* 6.7, $(CH_3)_2$CH], 1.05 [3 H, d, *J* 7.4, $(CH_3)_2$CH], 1.90 (1 H, m, $(CH_3)_2$C*H*], 4.07 (1 H, d, *J* 15.2, CH_2Ph), 4.10 (1 H, d, *J* 1.6, 4-H_1), 5.09 (1 H, d, *J* 15.2, CH_2Ph), 6.80 (2 H, d, *J* 7.5, ArC*H*), 7.13 (2 H, t, *J* 7.5, ArC*H*), 7.20–7.31 (7 H, m, ArC*H*), 7.37–7.44 (4 H, m, ArC*H*); δ_C(50 MHz) 16.4 (*C*H_3), 22.6 (*C*H_3), 29.8 [$(CH_3)_2$*C*H], 48.3 (*C*H_2Ph), 66.4 (4-C), 88.1 (5-C), 125.4 (Ar*C*H), 126.1 (Ar*C*H), 127.7 (Ar*C*H), 127.9 (Ar*C*H), 128.1 (Ar*C*H), 128.4 (Ar*C*H), 128.7 (Ar*C*H), 135.4 (ArC_{ipso}), 139.2 (ArC_{ipso}), 144.4 (ArC_{ipso}), 157.6 (2-C); *m/z* (APCI) 743 (18%,

M_2H^+), 394 (4, M^+ + Na), 373 (21), 372 (100, MH^+), 328 (4, $MH^+ - CO_2$).

***N*-Benzyloxazolidin-2-one 16i.** Reaction of the oxazolidinone **6i** (0.500 g, 5.74 mmol) as described above, followed by chromatography on silica gel eluting with petrol (bp 40–60 °C)–ethyl acetate (7:3 respectively) gave the title compound **16i** (0.233 g, 23%) as a crystalline solid, mp 76–77 °C (Found: C, 67.6; H, 6.1; N, 7.85. $C_{10}H_{11}NO_2$ requires C, 67.8; H, 6.3; N, 7.9%); ν_{max}(KBr)/cm^{-1} 1740; δ_H(400 MHz) 3.43 (2 H, t, *J* 8.0, 4-H_2), 4.31 (2 H, t, *J* 8.0, 5-H_2), 4.44 (2 H, s, CH_2Ph), 7.29–7.39 (5 H, m, ArC*H*); δ_C(50 MHz) 43.9 (4-C), 48.3 (*C*H_2Ph), 61.8 (5-C), 128.2 (Ar*C*H), 128.3 (Ar*C*H), 129.0 (Ar*C*H), 136.0 (ArC_{ipso}), 158.8 (2-C); *m*/*z* (APCI) 179 (20%), 178 (100, MH^+), 122 (4), 100 (11).

(4*R*)-*N*-Benzyl-4-isopropyloxazolidin-2-one 16j. Reaction of the oxazolidinone **6j** (0.200 g, 1.55 mmol) as described above, followed by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C), 1:4] gave the title compound **16j** (0.292 g, 86%) as an oil; $[a]_D^{25}$ = +24.6 (*c* 1 in $CHCl_3$) (Found: MH^+, 220.1331. $C_{13}H_{18}NO_2$ requires *m*/*z* 220.1338); ν_{max}(film)/cm^{-1} 1732; δ_H(400 MHz) 0.82 [3 H, d, *J* 6.9, (CH_3)$_2$CH], 0.86 [3 H, d, *J* 6.9, (CH_3)$_2$CH], 2.07 [1 H, m, (CH$_3$)$_2$C*H*], 3.55 (1 H, ddd, *J* 9.0, 5.8 and 3.5, 4-H_1), 3.97 (1 H, d, *J* 15.2, CH_2Ph), 4.07 (1 H, dd, *J* 9.0 and 5.8, 5-H_1), 4.18 (1 H, t, *J* 9.0, 5-H_1), 4.88 (1 H, d, *J* 15.2, CH_2Ph); δ_C(100 MHz) 14.1 (*C*H$_3$), 17.6 (*C*H$_3$), 27.1 [(CH$_3$)$_2$*C*H], 45.9 (*C*H$_2$Ph), 58.1 (4-C), 62.7 (5-C), 127.9 (Ar*C*H), 128.1 (Ar*C*H), 128.8 (Ar*C*H), 135.8 (ArC_{ipso}), 158.7 (2-C); *m*/*z* (APCI) 242 (3%, M^+ + Na), 221 (30), 220 (100, MH^+), 142 (4), 122 (4).

General procedure for the acylation of the oxazolidin-2-ones

n-Butyllithium (1.1 equiv.) was added dropwise *via* syringe to a stirred solution of the oxazolidin-2-one (1 equiv.) in THF (10 cm^3 mmol^{-1}) at −78 °C under a nitrogen atmosphere and the mixture allowed to stir for 15 min. Propionyl chloride (1.3 equiv.) was added at −78 °C and the reaction stirred at this temperature for 30 min, then allowed to warm to room temperature over 2 h. Saturated NH_4Cl (aq.) was added and the reaction extracted with ethyl acetate (×3). The combined organic extracts were washed with $NaHCO_3$ (aq.), brine, dried ($MgSO_4$) and evaporated to give the *N*-acylated oxazolidinone.

***N*-Propionyl-5,5-dimethyloxazolidin-2-one 14a.** Reaction of the oxazolidin-2-one **6a** (0.500 g, 4.34 mmol) under the reaction conditions described above, followed by crystallisation from ether–petrol (bp 40–60 °C) gave the title compound **14a** (0.499 g, 67%) as colourless needles, mp 48 °C (Found: C, 55.9; H, 7.8; N, 8.0. $C_8H_{13}NO_3$ requires C, 56.1; H, 7.65; N, 8.2%); ν_{max}(film)/cm^{-1} 1765, 1695; δ_H(200 MHz) 1.14 (3 H, t, *J* 7.4, CH_3CH$_2$), 1.48 (6 H, s, 2 × 5-Me), 2.91 (2 H, q, *J* 7.4, CH$_3$*C*H$_2$), 3.72 (2 H, s, 4-H_2); δ_C(50 MHz) 8.1 (*C*H$_3$CH$_2$), 27.2 (2 × 5-Me), 28.9 (CH$_3$*C*H$_2$), 54.3 (4-C), 78.6 (5-C), 152.9 (2-C), 174.9 (C=O$_{acyl}$); *m*/*z* (CI) 189 (100%, MH^+ + NH_3), 172 (60, MH^+), 133 (12), 116 (5), 72 (9).

***N*-Propionyl-5,5-diphenyloxazolidin-2-one 14b.** Reaction of oxazolidin-2-one **6b** (0.300 g, 1.25 mmol) under the reaction conditions described above, followed by column chromatography on silica gel eluting with petrol [bp 40–60 °C]–ethyl acetate (4:1 respectively) gave the title compound **14b** (0.267 g, 72%) as a white solid, mp 82–83 °C (Found: MH^+, 296.1292. $C_{18}H_{18}NO_3$ requires *m*/*z* 296.1287); ν_{max}(film)/cm^{-1} 1786, 1707; δ_H(400 MHz) 1.16 (3 H, t, *J* 7.4, CH_3CH$_2$), 2.94 (2 H, q, *J* 7.4, CH$_3$CH_2), 4.62 (2 H, s, 4-H_2), 7.32–7.43 (10 H, m, ArC*H*); δ_C(100 MHz) 8.1 (*C*H$_3$), 28.9 (CH$_3$*C*H$_2$), 54.9 (4-C), 83.8 (5-C), 125.3 (Ar*C*H), 128.5 (Ar*C*H), 128.8 (Ar*C*H), 141.4 (ArC_{ipso}), 152.2 (2-C), 174.1 (C=O$_{acyl}$); *m*/*z* (CI) 296 (24%, MH^+), 253 (25), 252 (100, $MH^+ - CO_2$), 196 (6), 183 (30), 165 (6), 124 (4), 105 (11).

(4*R*)-*N*-Propionyl-4,5,5-trimethyloxazolidin-2-one 14c. Reaction of the oxazolidin-2-one **6c** (0.350 g, 2.71 mmol) under the reaction conditions described above, followed by crystallisation from hot petrol (bp 60–80 °C) gave the title compound **14c** (0.272 g, 54%) as a white solid, mp 84 °C (lit.,[18] 82 °C); $[a]_D^{25}$ = −57.8 (*c* 0.9 in $CHCl_3$) [lit.,[18] −51 (*c* 0.9 in $CHCl_3$)]; ν_{max}(film)/cm^{-1} 1760, 1698; δ_H(400 MHz) 1.16 (3 H, t, *J* 7.3, CH$_2$CH_3), 1.27 (3 H, d, *J* 6.6, 4-Me), 1.40 (3 H, s, 5-Me), 1.42 (3 H, s, 5-Me), 2.92 (2 H, m, CH_2CH$_3$), 4.17 (1 H, q, *J* 6.6, 4-H_1); δ_C(100 MHz) 8.3 (*C*H$_3$CH$_2$), 14.7 (4-Me), 21.5 (5-Me), 27.8 (5-Me), 29.3 (*C*H$_2$), 58.8 (4-C), 81.4 (5-C), 152.8 (2-C), 174.4 (C=O$_{acyl}$); *m*/*z* (APCI) 279 (4%), 208 (6, M^+ + Na), 186 (6, MH^+), 142 (6, $MH^+ - CO_2$), 131 (9), 130 (100, $M^+ - C_3H_4O$).

(4*R*)-*N*-Propionyl-5,5-diphenyl-4-methyloxazolidin-2-one 14d. Reaction of the oxazolidin-2-one **6d** (0.300 g, 1.18 mmol) under the reaction conditions described above, followed by crystallisation from petrol (bp 60–80 °C) gave the title compound **14d** (0.269 g, 74%) as a crystalline solid, mp 101 °C; $[a]_D^{25}$ = +299.1 (*c* 1 in $CHCl_3$) (Found: C, 73.8; H, 6.2; N, 4.5. $C_{19}H_{19}NO_3$ requires C, 73.8; H, 6.2; N, 4.5%); ν_{max}(film)/cm^{-1} 1790, 1705; δ_H(400 MHz) 1.04 (3 H, d, *J* 6.5, 4-Me), 1.12 (3 H, t, *J* 7.4, CH_3CH$_2$), 2.79 (1 H, dq, *J* 17.9 and 7.4, CH$_3$CH_2), 2.94 (1 H, dq, *J* 17.9 and 7.4, CH$_3$CH_2), 5.38 (1 H, q, *J* 6.5, (4-H_1), 7.28–7.41 (8 H, m, ArC*H*), 7.50 (2 H, d, *J* 7.0, ArC*H*); δ_C(100 MHz) 8.2 (*C*H$_3$CH$_2$), 16.4 (4-Me), 29.1 (CH$_3$*C*H$_2$), 57.1 (4-C), 88.0 (5-C), 125.7 (Ar*C*H), 126.0 (Ar*C*H), 128.0 (Ar*C*H), 128.4 (Ar*C*H), 128.7 (Ar*C*H), 128.8 (Ar*C*H), 138.4 (ArC_{ipso}), 141.3 (ArC_{ipso}), 152.1 (2-C), 173.7 (C=O$_{acyl}$); *m*/*z* (APCI) 332 (6%, M^+ + Na), 310 (5, MH^+), 266 (28, $MH^+ - CO_2$), 210 (100).

(4*R*)-*N*-Propionyl-5,5-dimethyl-4-phenyloxazolidin-2-one 14e. Reaction of the oxazolidin-2-one **6e** (0.250 g, 1.31 mmol) under the reaction conditions described above, followed by crystallisation from cold petrol (bp 40–60 °C) gave the title compound **14e** (0.302 g, 93%) as a white solid, mp 60 °C; $[a]_D^{25}$ = −47.8 (*c* 1 in $CHCl_3$) (Found: MH^+, 248.1290. $C_{14}H_{18}NO_3$ requires *m*/*z* 248.1287); ν_{max}(film)/cm^{-1} 1777, 1702; δ_H(200 MHz) 1.01 (3 H, s, 5-Me), 1.12 (3 H, t, *J* 8.8, CH_3CH$_2$), 1.61 (3 H, s, 5-Me), 3.00 (2 H, q, *J* 8.8, CH$_3$CH_2), 5.08 (1 H, s, 4-H_1), 7.10–7.16 (2 H, m, ArC*H*), 7.32–7.42 (3 H, m, ArC*H*); δ_C(50 MHz) 8.1 (*C*H$_3$CH$_2$), 23.6 (5-Me), 28.9 (5-Me), 29.3 (CH$_3$*C*H$_2$), 67.0 (4-C), 82.5 (5-C), 126.5 (Ar*C*H), 128.8 (Ar*C*H), 129.1 (Ar*C*H), 136.7 (ArC_{ipso}), 153.9 (2-C), 174.1 (C=O$_{acyl}$); *m*/*z* (CI) 265 (20%, MH^+ + NH_3), 248 (100, MH^+), 209 (8), 203 (16), 192 (20).

(4*R*)-*N*-Propionyl-4,5,5-triphenyloxazolidin-2-one 14f. Reaction of the oxazolidin-2-one **6f** (0.200 g, 0.634 mmol) under the reaction conditions described above, followed by purification by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C), 1:5] and crystallisation from ether–petrol (bp 60–80 °C) gave the title compound **14f** (0.179 g, 76%) as a white solid, mp 48 °C; $[a]_D^{25}$ = +257.2 (*c* 1 in $CHCl_3$) (Found: C, 77.3; H, 5.8; N, 3.65. $C_{24}H_{21}NO_3$ requires C, 77.6; H, 5.70; N, 3.8%); ν_{max}(film)/cm^{-1} 1790, 1694; δ_H(400 MHz) 1.08 (3 H, t, *J* 7.5, CH_3CH$_2$), 2.94 (2 H, m, CH$_3$CH_2), 6.22 (1 H, s, 4-H_1), 7.00–7.16 (10 H, m, ArC*H*), 7.37–7.47 (3 H, m, ArC*H*), 7.65 (2 H, d, *J* 7.2, ArC*H*); δ_C(50 MHz) 7.9 (*C*H$_3$CH$_2$), 29.2 (*C*H$_2$), 66.0 (4-C), 89.1 (5-C), 126.2 (Ar*C*H), 126.4 (Ar*C*H), 127.7 (Ar*C*H), 127.9 (Ar*C*H), 128.5 (Ar*C*H), 129.2 (Ar*C*H), 136.1 (ArC_{ipso}), 138.3 (ArC_{ipso}), 142.1 (ArC_{ipso}), 153.1 (2-C), 173.6 (C=O$_{acyl}$); *m*/*z* (APCI) 394 (5%, M^+ + Na), 372 (6, MH^+), 328 (22, $MH^+ - CO_2$), 316 (18), 272 (100).

(4*R*)-*N*-Propionyl-5,5-dimethyl-4-isopropyloxazolidin-2-one 14g. Reaction of the oxazolidin-2-one **6g** (0.300 g, 1.91 mmol)

under the reaction conditions described above, followed by crystallisation from hot petrol (bp 60–80 °C) gave the title compound **14g** (0.299 g, 73%) as a crystalline solid, mp 62 °C; $[\alpha]_D^{25} = -37.0$ (*c* 1 in $CHCl_3$) (Found: C, 62.1; H, 8.80; N, 6.3. $C_{11}H_{19}NO_3$ requires C, 61.9; H, 8.9; N, 6.6%); ν_{max}(film)/cm^{-1} 1773, 1702; δ_H(400 MHz) 0.94 [3 H, d, *J* 6.9, $(CH_3)_2CH$], 1.03 [3 H, d, *J* 6.9, $(CH_3)_2C$], 1.18 (3 H, t, *J* 7.4, CH_3CH_2), 1.37 (3 H, s, 5-Me), 1.50 (3 H, s, 5-Me), 2.14 [1 H, dsept, *J* 3.4 and 6.9, $(CH_3)_2CH$], 2.89 (1 H, dq, *J* 17.5 and 7.4, CH_2CH_3), 3.00 (1 H, dq, *J* 17.5 and 7.4, CH_2CH_3), 4.14 (1 H, d, *J* 3.4, 4-H_1); δ_C(100 MHz) 8.7 (CH_3CH_2), 17.0 (CH_3), 21.4 (CH_3), 21.5 (5-Me), 28.8 (CH_2CH_3), 29.1 [$CH(CH_3)_2$], 29.5 (5-Me), 66.2 (4-C), 82.8 (5-C), 153.6 (2-C), 174.6 (C=O_{acyl}); *m*/*z* (APCI) 428 [12%, $(MH)_2^+$], 384 [5, $(MH)_2^+ - CO_2$], 270 (13), 214 (33, MH^+), 158 (100).

(4*R*)-*N*-Propionyl-5,5-diphenyl-4-isopropyloxazolidin-2-one 14h. Reaction of the oxazolidin-2-one **6h** (0.300 g, 1.07 mmol) under the reaction conditions described above, followed by crystallisation from hot petrol (bp 60–80 °C)–ethyl acetate gave the title compound **14h** (0.242 g, 64%) as a white solid, mp 106 °C; $[\alpha]_D^{25} = +199.3$ (*c* 1 in $CHCl_3$) (Found: C, 74.70; H, 6.7; N, 4.0. $C_{21}H_{23}NO_3$ requires C, 74.75; H, 6.9; N, 4.15%); ν_{max}(film)/cm^{-1} 1774, 1710; δ_H(400 MHz) 0.77 [3 H, d, *J* 6.8, $(CH_3)_2CH$], 0.88 [3 H, d, *J* 6.8, $(CH_3)_2CH$], 1.10 (3 H, t, *J* 7.4, CH_3CH_2), 1.97 [1 H, dsept, *J* 3.4 and 6.8 $(CH_3)_2CH$], 2.74 (1 H, dq, *J* 17.3 and 7.4, CH_2CH_3), 2.94 (1 H, dq, *J* 17.3 and 7.4, CH_2CH_3), 5.38 (1 H, d, *J* 3.4, 4-H_1), 7.26–7.42 (8 H, m, ArC*H*), 7.48 (2 H, d, *J* 7.2, ArC*H*); δ_C(50 MHz) 8.5 (CH_3CH_2), 16.2 (CH_3CH), 21.7 (CH_3CH), 28.1 (CH_3CH_2), 29.8 [$(CH_3)_2CH$], 64.4 (4-C), 89.4 (5-C), 125.8 (Ar*C*H), 125.9 (Ar*C*H), 126.1 (Ar*C*H), 128.1 (Ar*C*H), 128.6 (Ar*C*H), 128.8 (Ar*C*H), 129.1 (Ar*C*H), 138.4 (ArC_{ipso}), 142.6 (ArC_{ipso}), 153.3 (2-C), 174.3 (C=O_{acyl}); *m*/*z* (APCI) 472 [4%, $(MH)_2^+$], 416 (6), 394 (4), 360 (20, M^+ + Na), 350 (12), 338 (23, MH^+), 294 (85, $MH^+ - CO_2$), 238 (100).

***N*-Propionyloxazolidin-2-one 14i.** Reaction of oxazolidin-2-one **6i** (2.0 g, 0.023 mol) under the reaction conditions described above, followed by crystallisation from hot petrol (bp 40–60 °C)–ethyl acetate gave the title compound **14i** (1.92 g, 58%) as needles, mp 81–82 °C (Found: C, 50.3; H, 6.40; N, 9.7. $C_6H_9NO_3$ requires C, 50.35; H, 6.3; N, 9.8%); ν_{max}(KBr)/cm^{-1} 1768, 1698; δ_H(400 MHz) 1.22 (3 H, t, *J* 7.4, CH_3CH_2), 2.98 (2 H, q, *J* 7.4, CH_3CH_2), 4.07 (2 H, t, *J* 8.1, 4-H_2), 4.46 (2 H, t, *J* 8.1, 5-H_2); δ_C(50 MHz) 8.1 (CH_3), 28.6 (CH_3CH_2), 42.4 (4-C), 62.1 (5-C), 153.9 (2-C), 174.5 (C=O_{acyl}); *m*/*z* (APCI) 166 (52%, M^+ + Na), 153 (54), 144 (26, MH^+), 118 (100), 100 (56).

***N*-Propionyl-4-isopropyloxazolidin-2-one 14j.** Reaction of the oxazolidin-2-one **6j** (0.300 g, 2.32 mmol) under the reaction conditions described above, followed by silica gel chromatography (ethyl acetate–petrol, 1:9) gave the title compound **14j** (0.402 g, 94%) as an oil; $[\alpha]_D^{25} = -92.8$ (*c* 1 in $CHCl_3$); ν_{max}(film)/cm^{-1} 1781, 1704; δ_H(400 MHz) 0.86 [3 H, d, *J* 7.0, $(CH_3)_2CH$], 0.90 [3 H, d, *J* 7.0, $(CH_3)_2CH$], 1.15 (3 H, t, *J* 7.3, CH_3CH_2), 2.36 [1 H, dsept, *J* 3.5 and 7.0, $(CH_3)_2CH$], 2.83–3.00 (2 H, m, CH_3CH_2), 4.20 (1 H, dd, *J* 3.5 and 8.7, 5-H_1), 4.26 (1 H, t, *J* 8.7, 5-H_1), 4.42 (1 H, dt, *J* 8.7 and 3.5, 4-H_1); δ_C(50 MHz) 8.0 (CH_3CH_2), 14.2 [$(CH_3)_2CH$], 17.5 [$(CH_3)_2CH$], 28.1 [$(CH_3)_2CH$], 28.8 (CH_3CH_2), 58.1 (4-C), 63.2 (5-C), 154.3 (2-C), 174.0 (C=O_{acyl}); *m*/*z* (CI) 203 (100%, MH^+ + NH_3), 186 (52, MH^+), 147 (10).

General procedure for the benzylation of the *N*-propionyloxazolidin-2-ones

Lithium bis(trimethylsilyl)amide (1.1 equiv.) was added dropwise *via* syringe to a stirred solution of the *N*-propionyloxazolidin-2-one (1 equiv.) in THF (15 cm^3 mmol^{-1}) at −78 °C under a nitrogen atmosphere and the mixture allowed to stir for 30 min. Benzyl bromide (3 equiv.) was added at −78 °C and the reaction stirred at this temperature for 2 h, then allowed to warm to room temperature over a further 22 h. Saturated NH_4Cl (aq.) was added and the reaction extracted with ethyl acetate (×3). The combined organic extracts were washed with brine, dried ($MgSO_4$) and evaporated.

***N*-(2-Methyl-1-oxo-3-phenylpropyl)-5,5-dimethyloxazolidin-2-one 15a.** Benzylation of the corresponding *N*-propionyl auxiliary **14a** (0.100 g, 0.584 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15a** was isolated by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C); 1:9 respectively] as an oil (0.120 g, 79%) (Found: MH^+, 262.1448. $C_{15}H_{20}NO_3$ requires *m*/*z* 262.1443); ν_{max}($CHCl_3$)/cm^{-1} 1703, 1783; δ_H(200 MHz) 1.16 (3 H, d, *J* 6.7, CH_3CH), 1.28 (3 H, s, 5-Me), 1.41 (3 H, s, 5-Me), 2.64 (1 H, dd, *J* 5.6 and 13.3, PhCH_2), 3.03 (1 H, dd, *J* 7.2 and 13.3, PhCH_2), 3.56 (1 H, d, *J* 11.0, 4-H_1), 3.65 (1 H, d, *J* 11.0, 4-H_1), 4.12 (1 H, m, COC*H*), 7.12–7.28 (5 H, m, ArC*H*); δ_C(50 MHz) 16.7 (CH_3CH), 26.9 (5-Me), 27.0 (5-Me), 39.3 (CO*C*H), 40.0 (PhCH_2), 54.4 (4-C), 78.3 (5-C), 126.3 (Ar*C*H), 128.1 (Ar*C*H), 128.3 (Ar*C*H), 139.2 (Ar*C*), 152.3 (2-C), 176.8 (C=O_{acyl}); *m*/*z* (CI) 279 (43%, MH^+ + NH_3), 262 (100, MH^+), 218 (6), 133 (5), 118 (13).

***N*-(2-Methyl-1-oxo-3-phenylpropyl)-5,5-diphenyloxazolidin-2-one 15b.** Benzylation of the corresponding *N*-propionyl auxiliary **14b** (0.100 g, 0.339 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15b** was isolated by column chromatography [ethyl acetate–petrol (bp 40–60 °C); 1:9 respectively] on silica gel as an oil (0.039 g, 30%) (Found: MH^+, 386.1767. $C_{25}H_{24}NO_3$ requires *m*/*z* 386.1756); ν_{max}(film)/cm^{-1} 1782, 1699; δ_H(400 MHz) 1.15 (3 H, *J* 6.8, CH_3CH), 2.64 (1 H, dd, *J* 13.4 and 6.7, PhCH_2), 3.04 (1 H, dd, *J* 13.4 and 7.9, PhCH_2), 4.10 (1 H, m, COC*H*), 4.55 (2 H, m, 4-H_2), 7.13–7.23 (5 H, m, ArC*H*), 7.30–7.41 (10 H, m, ArC*H*); δ_C(50 MHz) 16.4 (CH_3CH), 39.4 (CO*C*H), 39.6 (CH_2Ph), 55.1 (4-C), 83.7 (5-C), 125.5 (ArC*H*), 125.6 (ArC*H*), 128.5 (ArC*H*), 128.8 (ArC*H*), 129.0 (ArC*H*), 129.3 (ArC*H*), 135.3 (ArC_{ipso}), 139.2 (ArC_{ipso}), 141.6 (ArC_{ipso}), 152.2 (2-C), 176.9 (C=O_{acyl}); *m*/*z* (APCI) 386 (14%, MH^+), 343 (26), 342 (100, $MH^+ - CO_2$), 252 (20), 221 (6), 195 (8), 180 (19), 91 (15).

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-4,5,5-trimethyloxazolidin-2-one 15c. Benzylation of the corresponding *N*-propionyl auxiliary **14c** (0.100 g, 0.540 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15c** was obtained in a diastereomeric excess of 81%, and isolated by column chromatography [ethyl acetate–petrol (bp 60–80 °C); 1:9 respectively] on silica gel as an oil (0.066 g, 44%) in >95% de (^{1}H NMR); $[\alpha]_D^{25} = +4.3$ (*c* 1 in $CHCl_3$) (Found: C, 69.5; H, 8.0; N, 5.1. $C_{16}H_{21}NO_3$ requires C, 69.8; H, 7.7; N, 5.1%); ν_{max}(film)/cm^{-1} 1770, 1698; δ_H(400 MHz) 1.09 (3 H, d, *J* 6.5, CH_3CH), 1.16 (3 H, d, *J* 6.8, 4-Me), 1.34 (3 H, s, 5-Me), 1.42 (3 H, s, 5-Me), 2.65 (1 H, dd, *J* 13.3 and 7.9, PhCH_2), 3.07 (1 H, dd, *J* 13.3 and 7.1, PhCH_2), 4.10–4.18 (2 H, m, 4-H_1 and COC*H*), 7.17–7.29 (5 H, m, ArC*H*); δ_C(50 MHz) 14.2 (CH_3CH), 16.4 (4-Me), 21.4 (5-Me), 27.6 (5-Me), 39.4 (CO*C*H), 39.9 (PhCH_2), 58.9 (4-C), 81.2 (5-C), 126.5 (Ar*C*H), 129.5 (Ar*C*H), 139.4 (ArC_{ipso}), 152.7 (2-C), 177.3 (C=O_{acyl}); *m*/*z* (APCI) 298 (5%, M^+ + Na), 277 (9), 276 (72, MH^+), 232 (15, $MH^+ - CO_2$), 130 (100).

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-5,5-diphenyl-4-methyloxazolidin-2-one 15d. Benzylation of the corresponding *N*-propionyl auxiliary **14d** (0.100 g, 0.323 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15d** was obtained in a diastereomeric excess of 65%, and isolated by column chromatography [ethyl acetate–petrol (bp 60–80 °C); 1 : 4 respectively] on silica gel as an oil (0.051 g, 40%) in 68% de (by ^{1}H NMR); $[\alpha]_D^{25}$ = +249.6 (*c* 0.5 in $CHCl_3$) (Found: MH^+, 400.1924. $C_{26}H_{26}NO_3$ requires *m*/*z* 400.1913); ν_{max}(film)/cm^{-1} 1783, 1699; δ_H(400 MHz) *major diastereomer*: 0.93 [3 H, d, *J* 6.5, C*H*$_3$CH(CO)], 1.06 (3 H, d, *J* 6.5, 4-Me), 2.67 (1 H, dd, *J* 13.4 and 8.2, PhC*H*$_2$), 3.15 (1 H, dd, *J* 13.4 and 6.7, PhC*H*$_2$), 4.07 (1 H, m, COC*H*), 5.41 (1 H, q, *J* 6.5, 4-H$_1$), 7.28–7.44 (13 H, m, ArC*H*), 7.53 (2 H, d, *J* 7.4, ArC*H*); *minor diastereomer*: 0.93 [3 H, d, *J* 6.5, C*H*$_3$CH(CO)], 1.22 (3 H, d, *J* 6.8, 4-Me), 2.59 (1 H, m, CHC*H*$_2$), 2.94 (1 H, m, CHC*H*$_2$), 4.02 (1 H, m, C*H*CH$_2$), 5.38 (1 H, m, 4-H$_1$), 7.28–7.44 (13 H, m, ArC*H*), 7.53 (2 H, d, *J* 7.4, ArC*H*); δ_C(100 MHz) *mixture of diastereomers*: 16.3 (*C*H$_3$), 16.4 (*C*H$_3$), 29.7 (*C*H$_3$), 39.2 (CO*C*H$_{major}$), 39.5 (CH$_2$), 39.3 (CO*C*H$_{minor}$), 57.2 (4-C$_{minor}$), 57.1 (4-C$_{major}$), 87.8 (5-C), 125.8 (Ar*C*H), 126.0 (Ar*C*H), 126.3 (Ar*C*H), 128.0 (Ar*C*H), 128.2 (Ar*C*H), 128.4 (Ar*C*H), 128.8 (Ar*C*H), 129.2 (Ar*C*H), 138.3 (Ar*C*H), 139.1 (Ar*C*$_{ipso}$), 141.2 (Ar*C*$_{ipso}$), 151.7 (2-C), 176.2 (C=O$_{acyl}$); *m*/*z* (APCI) 438 (M^+ + K, 2%), 422 (8, M^+ + Na), 400 (8, MH^+), 356 (100, $MH^+ - CO_2$), 210 (67).

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-5,5-dimethyl-4-phenyloxazolidin-2-one 15e. Benzylation of the corresponding *N*-propionyl auxiliary **14e** (0.100 g, 0.404 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15e** was obtained in a diastereomeric excess of 70%, and isolated by chromatography on silica gel [ethyl acetate–petrol (bp 60–80 °C); 3 : 7 respectively] as an oil (0.075 g, 55%) in 87% de (by ^{1}H NMR); $[\alpha]_D^{25}$ = −12.6 (*c* 1 in $CHCl_3$) (Found: MH^+, 338.1753. $C_{21}H_{24}NO_3$ requires *m*/*z* 338.1756); ν_{max}($CHCl_3$)/cm^{-1} 1704, 1773; δ_H(200 MHz) *major diastereomer*: 0.97 (3 H, s, 5-Me), 1.16 (3 H, d, *J* 6.7, C*H*$_3$CH), 1.61 (3 H, s, 5-Me), 2.51 (1 H, dd, *J* 8.1 and 13.3, PhC*H*$_2$), 3.14 (1 H, dd, *J* 6.7 and 13.3, PhC*H*$_2$), 4.23 (1 H, m, COC*H*), 5.09 (1 H, s, 4-H$_1$), 6.96–7.35 (10 H, m, ArC*H*); *minor diastereomer*: 0.95 (3 H, s, 5-Me), 1.19 (3 H, d, *J* 6.8, C*H*$_3$CH), 1.35 (3 H, s, 5-Me), 2.69 (1 H, dd, *J* 7.1 and 13.5, PhC*H*$_2$), 3.02 (1 H, dd, *J* 8.2 and 13.5, PhC*H*$_2$), 4.27 (1 H, m, COC*H*), 4.94 (1 H, s, 4-H$_1$), 7.10–7.41 (10H, m, ArC*H*); δ_C(125 MHz) *major diastereomer*: 16.5 (*C*H$_3$CH), 23.8 (5-Me), 29.0 (5-Me), 39.6 (Ph*C*H$_2$ and CH$_3$*C*H), 67.1 (4-C), 82.1 (5-C), 126.2 (Ar*C*H), 128.3 (Ar*C*H), 128.8 (Ar*C*H), 129.2 (Ar*C*H), 136.1 (Ar*C*$_{ipso}$), 139.1 (Ar*C*$_{ipso}$), 156.0 (2-C), 177.0 (C=O$_{acyl}$); *minor diastereomer*: 17.0 (*C*H$_3$CH), 23.5 (5-Me), 28.5 (5-Me), 39.5 (Ph*C*H$_2$), 39.7 (CO*C*H), 67.0 (4-C), 82.3 (5-C), 126.4 (Ar*C*H), 126.5 (Ar*C*H), 128.6 (Ar*C*H), 128.8 (Ar*C*H), 129.1 (Ar*C*H), 129.4 (Ar*C*H), 136.7 (Ar*C*$_{ipso}$), 139.6 (Ar*C*$_{ipso}$), 153.2 (2-C), 176.5 (C=O$_{acyl}$); *m*/*z* (APCI) 360 (4%, M^+ + Na), 339 (14), 338 (100, MH^+), 294 (5), 282 (10), 192 (41), 148 (4), 122 (6).

Attempted alkylation of (4*R*)-*N*-propionyl-4,5,5-triphenyloxazolidin-2-one 14f. Benzylation of the corresponding *N*-propionyl auxiliary **14f** (0.100 g, 0.269 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. Only the acyl SuperQuat **14f** and *N*-benzyl-SuperQuat **16f** were obtained in a 54 : 46 ratio respectively.

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-5,5-dimethyl-4-isopropyloxazolidin-2-one 15g. Benzylation of the corresponding *N*-propionyl auxiliary **14g** (0.100 g, 0.469 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15g** was obtained in a diastereomeric excess of >95%, and isolated by silica gel chromatography [ethyl acetate–petrol (bp 40–60 °C); 1 : 9 respectively] as an oil (0.049 g, 34%) in >95% de (by ^{1}H NMR); $[\alpha]_D^{25}$ = +8.0 (*c* 1 in $CHCl_3$) (Found: C, 71.3; H, 8.5; N, 4.6. $C_{18}H_{25}NO_3$ requires C, 71.3; H, 8.3; N, 4.6%); ν_{max}(film)/cm^{-1} 1772, 1700; δ_H(400 MHz) 0.75 [3 H, d, *J* 6.9, (C*H*$_3$)$_2$CH], 0.84 [3 H, d, *J* 6.9, (C*H*$_3$)$_2$CH], 1.15 (3 H, d, *J* 6.7, C*H*$_3$CH), 1.38 (3 H, s, 5-Me), 1.49 (3 H, s, 5-Me), 2.03 [1 H, dsept, *J* 3.1 and 6.9, (CH$_3$)$_2$C*H*], 2.64 (1 H, dd, *J* 13.3 and 3.1, PhC*H*$_2$), 3.19 (1 H, dd, *J* 13.3 and 7.2, PhC*H*$_2$), 4.15 (1 H, d, *J* 3.1, 4-H$_1$), 4.22 (1 H, m, COC*H*), 7.26–7.32 (5 H, m, ArC*H*); δ_C(50 MHz) 16.5 [(*C*H$_3$)$_2$CH and 5-Me], 21.2 [(*C*H$_3$)$_2$CH and 5-Me], 28.7 (*C*H$_3$CH), 29.4 [(CH$_3$)$_2$*C*H], 39.3 (CO*C*H), 40.0 (Ph*C*H$_2$), 66.1 (4-C), 82.6 (5-C), 126.5 (Ar*C*H), 128.5 (Ar*C*H), 129.5 (Ar*C*H), 139.5 (Ar*C*$_{ipso}$), 153.6 (2-C), 177.3 (C=O$_{acyl}$); *m*/*z* (APCI) 304 (100%, MH^+), 260 (9, $MH^+ - CO_2$), 158 (63), 122 (15).

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-5,5-diphenyl-4-isopropyloxazolidin-2-one 15h. Benzylation of the corresponding *N*-propionyl auxiliary **14h** (0.100 g, 0.295 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15h** was obtained in a diastereomeric excess of >95%, and obtained as an inseparable mixture (0.052 g) of acyl compound **14h** and the desired product **15h** (58 : 42 respectively) after silica gel chromatography [ethyl acetate–petrol (bp 60–80 °C); 1 : 9 respectively]. The compound was thus characterised as fully as possible from data obtained from the reaction mixture (Found: MH^+, 428.2230. $C_{28}H_{30}NO_3$ requires *m*/*z* 428.2226); ν_{max}(film)/cm^{-1} 1784, 1705; δ_H(400 MHz) 0.60 (3 H, d, *J* 6.7, C*H*$_3$CH), 0.72 [3 H, d, *J* 7.0, (C*H*$_3$)$_2$CH], 0.85 [3 H, d, *J* 6.7, (C*H*$_3$)$_2$CH], 1.90 [1 H, m, (CH$_3$)$_2$C*H*], 2.61 (1 H, dd, *J* 13.3 and 7.9, PhC*H*$_2$), 3.17 (1 H, dd, *J* 13.3 and 7.2, PhC*H*$_2$), 4.04 (1 H, m, COC*H*), 5.40 (1 H, d, *J* 3.3, 4-H$_1$), 7.14–7.50 (15 H, m, ArC*H*); δ_C(100 MHz) 16.1 [(*C*H$_3$)$_2$CH], 21.5 [(*C*H$_3$)$_2$CH], 29.6 (*C*H$_3$CH), 29.9 [(CH$_3$)$_2$*C*H], 39.1 (CO*C*H), 39.8 (Ph*C*H$_2$), 64.4 (4-C), 89.2 (5-C), 125.6–129.2 (Ar*C*H), 138.1 (Ar*C*$_{ipso}$), 139.2 (Ar*C*$_{ipso}$), 142.3 (Ar*C*$_{ipso}$), 152.8 (2-C), 176.2 (C=O$_{acyl}$); *m*/*z* (CI) 428 (90%, MH^+), 384 (40, $MH^+ - CO_2$).

***N*-(2-Methyl-1-oxo-3-phenylpropyl)oxazolidin-2-one 15i.** Benzylation of the corresponding *N*-propionyl auxiliary **14i** (0.250 g, 1.75 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15i** was isolated as an oil by column chromatography [ethyl acetate–petrol (bp 60–80 °C); 1 : 4 respectively] on silica gel (0.311 g, 76%) (Found: MH^+, 234.1125. $C_{13}H_{16}NO_3$ requires *m*/*z* 234.1130); ν_{max}(film)/cm^{-1} 1771, 1704; δ_H(400 MHz) 1.18 (3 H, d, *J* 6.7, C*H*$_3$CH), 2.65 (1 H, dd, *J* 13.3 and 7.9, PhC*H*$_2$), 3.07 (1 H, dd, *J* 13.3 and 7.0, PhC*H*$_2$), 3.89–4.03 (2 H, m, 4-H$_2$), 4.09 (1 H, m, CH$_3$C*H*), 4.29 (1 H, td, *J* 9.0 and 7.2, 5-H$_1$), 4.37 (1 H, td, *J* 9.0 and 6.6, 5-H$_1$), 7.19–7.30 (5 H, m, ArC*H*); δ_C(100 MHz) 16.5 (*C*H$_3$), 39.2 (CO*C*H), 39.6 (Ph*C*H$_2$), 42.7 (4-C), 61.9 (5-C), 126.5 (Ar*C*H), 128.5 (Ar*C*H), 129.4 (Ar*C*H), 139.1 (Ar*C*$_{ipso}$), 153.5 (2-C), 178.9 (C=O$_{acyl}$); *m*/*z* (APCI) 256 (18%, M^+ + Na), 234 (25, MH^+), 208 (30), 190 (42), 147 (64), 119 (100).

(4*R*)-*N*-[(2*S*)-2-Methyl-1-oxo-3-phenylpropyl]-4-isopropyl-oxazolidin-2-one 15j. Benzylation of the corresponding *N*-propionyl auxiliary **14j** (0.100 g, 0.540 mmol) according to the above procedure provided the crude reaction product, the composition of which was determined by ^{1}H NMR spectroscopy. The benzylated product **15j** was obtained in a diastereomeric

excess of >95%, and isolated by column chromatography [ethyl acetate–petrol (bp 60–80 °C), 1.5:9 respectively] on silica gel as an oil (0.083 g, 56%); $[a]_D^{25} = -9.9$ (*c* 1 in $CHCl_3$) (Found: MH^+, 276.1605. $C_{16}H_{22}NO_3$ requires *m*/*z* 276.1600); ν_{max}(film)/cm^{-1} 1779, 1699; δ_H(400 MHz) 0.60 [3 H, d, *J* 7.0, $(CH_3)_2CH$], 0.84 [3 H, d, *J* 7.0, $(CH_3)_2CH$], 1.16 (3 H, d, *J* 6.7, CH_3CH), 2.16 [1 H, dsept, *J* 3.6 and 7.0, $(CH_3)_2CH$], 2.63 (1 H, dd, *J* 13.2 and 7.6, $PhCH_2$), 3.13 (1 H, dd, *J* 13.2 and 7.4, $PhCH_2$), 4.12–4.20 (2 H, m, 5-H_1 and COC*H*), 4.25 (1 H, t, *J* 8.6, 5-H_1), 4.44 (1 H, dt, *J* 8.6 and 3.6, 4-H_1), 7.16–7.29 (5 H, m, ArC*H*); δ_C(50 MHz) 14.1 [$(CH_3)_2CH$], 16.4 (CH_3CH), 17.8 [$(CH_3)_2CH$], 28.1 [$(CH_3)_2CH$], 39.4 (CO*C*H), 40.0 ($PhCH_2$), 58.4 (4-C), 63.0 (5-C), 126.5 (Ar*C*H), 128.5 (Ar*C*H), 129.4 (Ar*C*H), 139.4 (ArC_{ipso}), 154.0 (2-C), 176.8 ($C{=}O_{acyl}$); *m*/*z* (APCI) 366 (4%), 276 (55, MH^+), 263 (14), 223 (3), 147 (22), 130 (100), 119 (13).

(2*S*)-2-Methyl-3-phenylpropanoic acid 19

Lithium hydroxide monohydrate (0.021 g, 0.51 mmol) was added to a vigorously stirred solution of (4*R*)-*N*-[(2*S*)-2-methyl-1-oxo-3-phenylpropyl]-5,5-dimethyl-4-isopropyloxazolidin-2-one **15g** (0.071 g, 0.234 mmol) in a THF–water mixture (3:1; 4 cm^3) and left to stir for 24 h at room temperature. The mixture was evaporated, sodium hydrogen carbonate (10 cm^3) added and extracted with ether (3 × 10 cm^3). The combined organic extracts were dried ($MgSO_4$) and evaporated to afford recovered SuperQuat **6g** [0.036 g, 98%; $[a]_D^{25} = -23.9$ (*c* 1 in $CHCl_3$)]. The aqueous extracts were acidified (1 M HCl), extracted with CH_2Cl_2 (3 × 15 cm^3), dried ($MgSO_4$), and evaporated to give the crude product which was distilled on a Kugelrohr apparatus to provide the desired acid **19** as an oil (0.037 g, 96%); $[a]_D^{25} = +26.5$ (*c* 1 in $CHCl_3$) [lit.,[14] +25.5 (*c* 1 in $CHCl_3$)]; δ_H(200 MHz) 1.20 (3 H, d, *J* 6.5, 2-Me), 2.62–2.85 (2 H, m, 2-H_1 and 3-H_1), 3.09 (1 H, dd, *J* 12.6 and 5.8, 3-H_1).

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