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Asymmetric Synthesis of Aminocyclopropanes and *N*-Cyclopropylamino Alcohols Through Direct Amidocyclopropanation of Alkenes Using Chiral Organozinc Carbenoids

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Chiral *N*-(diethoxymethyl)oxazolidinones, prepared from the corresponding oxazolidinones by heating in triethyl orthoformate, can be used as organozinc carbenoid precursors for the direct enantioselective amidocyclopropanation of alkenes. The reaction is successful with a wide range of oxazolidinones and alkenes and proceeds with moderate to excellent yield and stereoselectivity. In most cases the *trans/exo* amidocyclopropane product is favoured, although certain cyclic alkenes such as indene favour the formation of the *endo* cyclopropane. The products can be readily elaborated to produce cyclopropylamino alcohols and amino acids.

Introduction

The aminocyclopropane motif is present in a significant number of biologically active natural products and drugs,[1] and in consequence, a variety of stepwise ionic methods are available for their construction.[2] The elegant variants of the Kulinkovich[3] reaction developed by de Meijere[4] and Szymoniak[5] are particularly noteworthy in this respect. Despite this, there are relatively few direct [2+1] cycloaddition protocols for aminocyclopropane synthesis, and these generally require either addition of an unfunctionalised carbenoid, such as the Simmons–Smith reagent, to an enamine or enamide derivative,[6] or the transition-metal-mediated addition of a diazo ester to an alkene followed by a Curtius or Schmidt reaction.[7] The use of amido- or nitro-substituted diazo compounds and iodonium ylides for cyclopropylamino acid synthesis has also been reported.[8] In conceptual terms, the addition of a suitably functionalised aminocarbenoid to a simple alkene therefore provides a very attractive method. To the best of our knowledge, the addition of a chromium-based Fischer carbenoid possessing a glycine unit by Barluenga provided the first example of this strategy.[9]

Within our own group, we have demonstrated that organozinc carbenoids can be simply generated from carbonyl compounds[10] or their acetal or ketal derivatives,[11] without the necessity of preparing more toxic and/or dangerous *gem* dihalo or diazo precursors, and shown that they are extremely versatile intermediates for the synthesis of highly functionalised cyclopropanes. Furthermore, through selection of simple orthoformates as reagents, it proved possible to develop an inexpensive method for alkoxycyclopropanation.[12]

More recently, we have reported the use of *N*-(diethoxymethyl)amides as suitable precursors for generation of the first examples of amido organozinc carbenoids which undergo cyclopropanation reactions with a wide variety of alkenes to yield the corresponding amidocyclopropanes.[13] We have also reported the use of diphenyloxazolidinone derived carbenoid precursors as suitable reagents for the enantioselective synthesis of aminocyclopropanes.[14] In this paper, we wish to report, in full detail our observations on the scope and limitations of chiral oxazolidinone-derived carbenoid precursors as suitable reagents for constructing aminocyclopropanes, cyclopropylamino alcohols and amidocyclopropane containing peptide motifs.

Results and Discussion

A range of oxazolidinones were synthesised from the corresponding amino acids or amino alcohols as shown in Scheme 1. These oxazolidinones **9**–**21** were converted into the corresponding diethoxymethylamides **22**–**36** by heating in a large excess of triethyl orthoformate under acidic conditions (Scheme 2 and Table 1).[15]

With the carbenoid precursors in hand, we investigated a simple cyclopropanation of cyclohexene using racemic **22** (Scheme 3). A solution of **22** in dichloromethane was added

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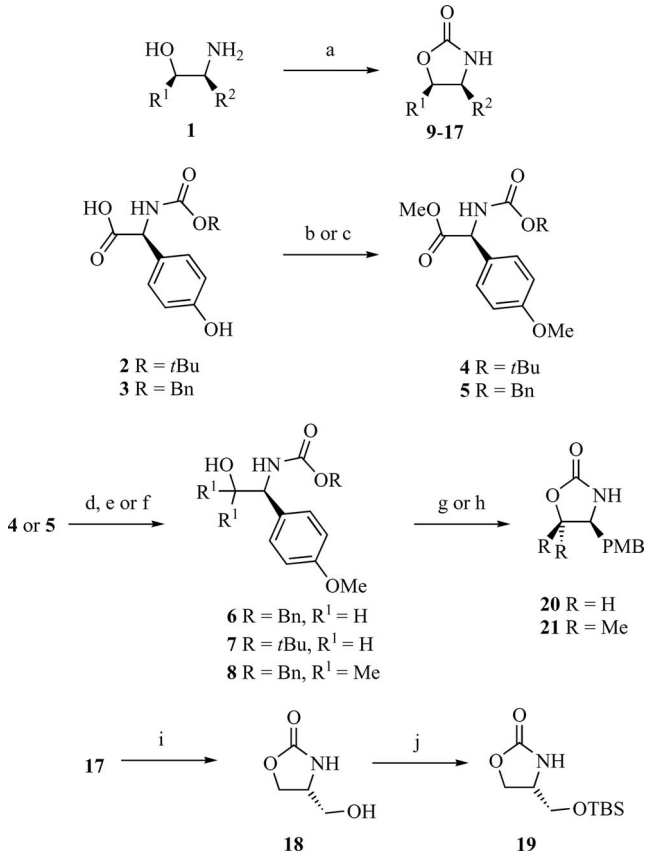
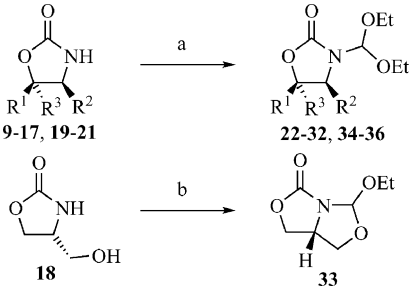


Scheme 1. a. $Cl_3COCOOCCl_3$, Et_3N, CH_2Cl_2 56–100%; b. K_2CO_3, Me_2SO_4, acetone, reflux, 88% (**4**); c. K_2CO_3, MeI, DMF, room temp., 71% (**5**); d. $LiBH_4$, MeOH, Et_2O, 94% (**6**); e. $NaBH_4$, LiCl, THF, 86% (**7**); f. MeMgI, THF, Et_2O, 38% (**8**); g. $SOCl_2$, THF, 90% (**20** from **7**); h. NaH, THF, 98% (**20** from **6**), 70% (**21** from **8**); i. $NaBH_4$, EtOH, 82%; j. TBSCl, imidazole, DMF, 81%.



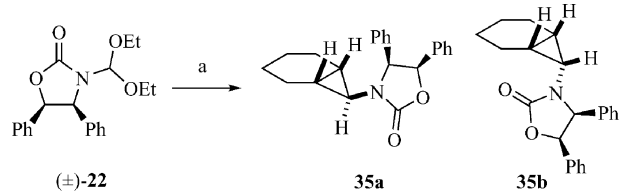
Scheme 2. a. $(EtO)_3CH$, $AlCl_3$, reflux 33–86%; b. $(EtO)_3CH$, TsOH, reflux, 22%.

dropwise by syringe pump to a refluxing mixture of cyclohexene, Zn amalgam, chlorotrimethylsilane and zinc chloride in diethyl ether. Pleasingly, the corresponding amidocyclopropanes **35** were obtained in 58% yield and with good diastereoselectivity (93:7 *exo*:*endo*).

The cyclopropanation of a range of alkenes was then investigated with a selection of chiral oxazolidinone-derived carbenoid precursors. The corresponding amidocyclopropanes **36**–**56** were obtained in moderate to good yield with a wide range of both alkenes and carbenoid precursors (Scheme 4 and Table 2). Pleasingly, either Zn amalgam or a

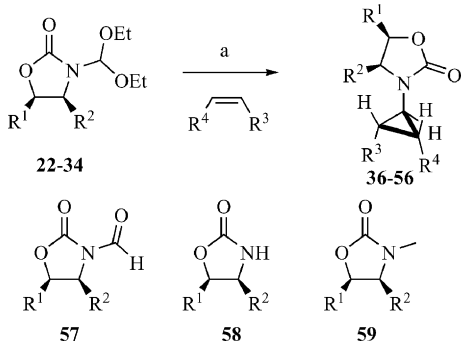
Table 1. Preparation of (diethoxymethyl)oxazolidinone carbenoid precursors.

Oxazolidinone	R^1	R^2	R^3	% Yield	Product
(±)-**9**	Ph	Ph	H	80	(±)-**22**
(+)-**9**	Ph	Ph	H	74	(+)-**22**
(–)-**9**	Ph	Ph	H	68	(–)-**22**
10	H	Bn	H	53	**23**
11	H	*i*Pr	H	55	**24**
12	H	Ph	H	33	**25**
13	H	Et	H	55	**26**
14	H	CH_2*i*Pr	H	63	**27**
15	Ph	Me	H	53	**28**
16	H	CH_2OBn	H	73	**29**
17	H	CO_2Et	H	55	**30**
18	H	CH_2OH	H	22	**31**
19	H	CH_2OTBS	H	60	**32**
20	H	PMB	H	65	**33**
21	Me	PMB	Me	86	**34**



Scheme 3. a. Cyclohexene, Zn(Hg), $ZnCl_2$, Me_3SiCl, Et_2O, reflux, 58%.

combination of Zn dust and CuCl could be used interchangeably as the metal source. Useful functional groups such as silanes, stannanes, esters and protected amines were all tolerated under the reaction conditions. The cyclopropane **44** was obtained in good yield and constitutes a protected form of the aminocyclopropane unit of the antibiotic Belactosin A.[16] In many cases the accurate diastereoselectivity was difficult to determine from crude ^1H NMR spectra due to the presence of side products. However, it should be noted that in almost all cases the amidocyclopropanes could be obtained diastereomerically pure after column chromatography. From the crude ^1H NMR spectra, it was deduced that small quantities of **57**, **58** and **59** were often present. Formamide **57** is most likely formed by hydrolysis of unreacted carbenoid precursor during the work up procedure. Oxazolidinone **58** could be produced by hydrolysis



Scheme 4. a. Alkene, Zn(Hg) or Zn/CuCl, $ZnCl_2$, Me_3SiCl, Et_2O, reflux, 24–83%.

Table 2. Cyclopropanation reactions.

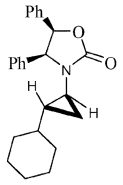
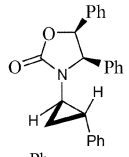
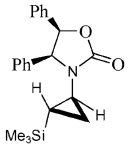
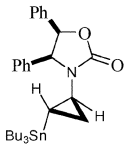
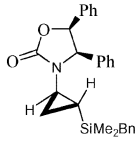
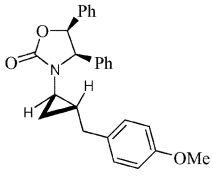
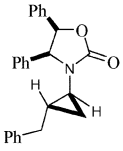
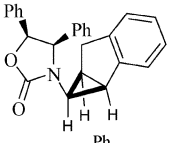
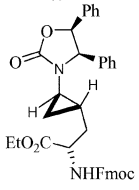
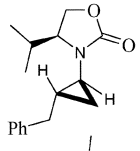
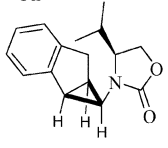
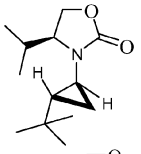
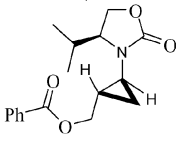
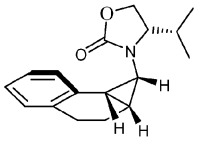
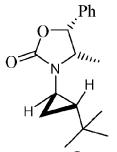
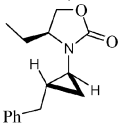
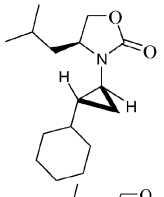
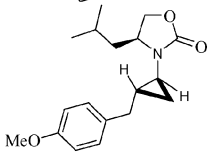
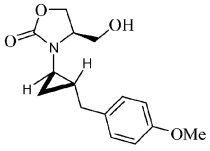
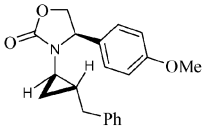
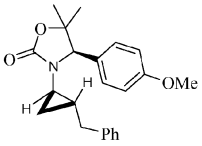
Product(s)		Yield	*dr*[a]
	**36**	74 %[f]	88:8[c]
	**37**	54 %[f]	56:28[d]:6[c]:6[d]
	**38**	59 %[f]	–[b]
	**39**	24 %[f]	–[b]
	**40**	42 %[f]	–[b]
	**41**	63 %[f]	87:9[c]
	**42**	83 %[f]	84:12[c]
	**43**	76 %[f]	–[b]
	**44**	70 %[f]	–[b]
	**45**	42 %[g] 30 %[g,h]	>90:10
	**46**	40 %[g]	>90:10

Table 2. *(Continued)*.

Product(s)		Yield	*dr*[a]
	**47**	29 %[g]	>90:10
	**48**	13 %[g]	82:14[e]
	**49**	40 %[g]	59:37[c]
	**50**	20 %[g]	–[b]
	**51**	44 %[g]	92:4[e]
	**52**	47 %[f]	>90:10
	**53**	44 %[f]	–[b]
	**54**	23 %[g]	–[b]
	**55**	29 %[g]	82:14[c]
	**56**	36 %[g]	–[b]

[a] Any diastereoisomers not observed by ^{1}H NMR were considered to be <2%. [b] No other diastereoisomers were observed/isolated. [c] The minor diastereoisomer was a *trans*/*exo* cyclopropane. [d] The minor diastereoisomer was a *cis*/*endo* cyclopropane. [e] The stereochemistry of the minor diastereoisomer was not determined. [f] Zn(Hg) was used. [g] Zn/CuCl was used. [h] Reaction carried out as a one-pot procedure from the oxazolidinone **11** and triethyl orthoformate.

of unreacted carbenoid precursor or the organozinc carbenoid intermediate. *N*-methyl compound **59** may be derived from protonation of the intermediate organozinc carbenoid, presumably by traces of HCl present in the reaction mixture, and subsequent reduction with zinc. The absolute and/or relative stereochemistry of the cyclopropanes **40** and **43** was confirmed by X-ray diffraction.[17] The geometry of all the cyclopropanes (*cis*/*trans*, *exo*/*endo*) was determined on the basis of the ^{1}H-^{1}H coupling constants, but the relative stereochemistry between the oxazolidinone chiral centres and the cyclopropane ring was assigned by analogy with the X-ray crystal structures obtained for **40** and **43**.

Notably, we were also able to carry out a direct "one-pot" carbenoid-generation cyclopropanation reaction to give **45** by dropwise addition of a solution of triethyl orthoformate and oxazolidinone **11** to a refluxing mixture of alkene, zinc dust, copper(I) chloride, zinc chloride and chlorotrimethylsilane. Although the cyclopropane **45** was only obtained in a moderate 30% yield, this approach compares favourably with the two-step route (23% yield over two steps).

In most cases, a strong preference for the formation of one of the two possible diastereoisomers of *trans*-cyclopropane was observed. The observed diastereoselectivity is to a large extent independent of the carbenoid precursor used – similar levels of diastereoselectivity were obtained when allyl benzene was cyclopropanated with a range of oxazolidinones (**42**, **51**, and **55**), although very hindered systems gave higher selectivity (**45** and **56**). In general, the nature of the alkene had a larger effect on the diastereoselectivity. Indene yielded predominantly the *endo*-cyclopropanes **43** and **46** in accordance with our findings with achiral carbenoid precursors.[13] The cyclopropanes derived from styrene (**37**) and dihydronaphthalene (**49**) were obtained with lower selectivity, although it is notable that the diastereoselectivity obtained is higher than with the corresponding achiral pyrrolidinone and oxazolidinone carbenoid precursors.[13] Overall, the stereochemical preferences of these reactions are in accordance with the quadrant model we have introduced to rationalise cyclopropanation reactions involving achiral amidoorganozinc carbenoids (Figure 1). Thus, coordination of the oxazolidinone carbonyl to the zinc atom present in the carbenoid prevents rotation about the N–C bond and forces the alkene to approach the carbenoid from the opposite face to the bulky R group. In the case where R^2 = H (monosubstituted alkenes), the alkene substituent R^1 prefers to occupy the unhindered quadrant A (**i**). When $R^2 \neq$ H, the situation is more finely balanced and the R^2 group is either placed in the hindered quadrant B where there is a steric clash with the oxazolidine ring (giving the *exo* cyclopropane) (**i**), or the reaction proceeds via transition state (**ii**) in which the groups occupy quadrants C and D in which there is moderate steric hindrance due to the presence of the oxazolidinone carbonyl and the zinc atom (giving the *endo* cyclopropanes). The minor products were different in each case, depending on both the alkene and the oxazolidinone. In the case of styrene, all four possible diastereoisomeric cyclopropanes were observed. The major isomer being the expected *trans* cyclopropane from our transition-state model, and the other major component being the *cis* cyclopropane formed via transition state (**ii**). We have previously noted that styrene displays a greater tendency towards the formation of a *cis* cyclopropane than other monosubstituted alkenes.[13] With most other alkenes, the minor products observed were usually the other possible *trans* isomer formed via transition state (**iii**) where the alkene approaches the carbenoid on the same face as the oxazolidinone substituent. As expected, increasing the steric bulk on the oxazolidinone ring leads to a greater stereoselectivity (e.g. **55** and **56**). We would expect that transition state (**iii**) would become more unfavourable with greater steric bulk at R, and transition state (**i**) would be relatively unaffected.

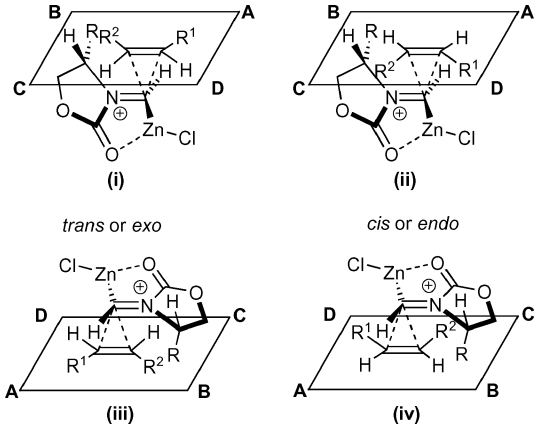
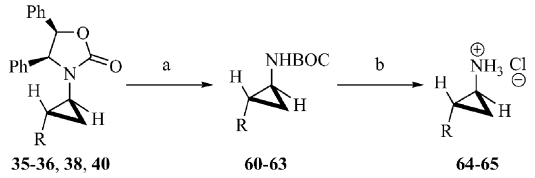


Figure 1. The proposed quadrant model explaining the approach of the alkene to the organozinc carbenoid.

The diphenyloxazolidinone ring could be successfully removed by hydrogenolysis to leave the aminocyclopropanes, which were isolated as their BOC derivatives (Scheme 5, **60**–**63**). This deprotection protocol was considerably more effective when the hydrogenation was carried out in the presence of BOC_2O, rather than as a two-step procedure. Deprotection of cyclopropane **37** was unsuccessful due to concomitant hydrogenolysis of the benzylic cyclopropane ring. Unfortunately, amino-acid containing cyclopropane **44** also failed to undergo successful hydrogenolysis. In this case, the cleavage of the oxazolidinone ring was very slow, and a mixture of partially deprotected products was obtained. The ^{1}H NMR spectrum suggested that partial deprotection of the Fmoc group had also occurred under the reaction conditions. As illustrated in Scheme 5, the BOC aminocyclopropane derivatives **60** and **61** could easily be deprotected to give the corresponding cyclopropylamines as their hydrochloride salts (Table 3).

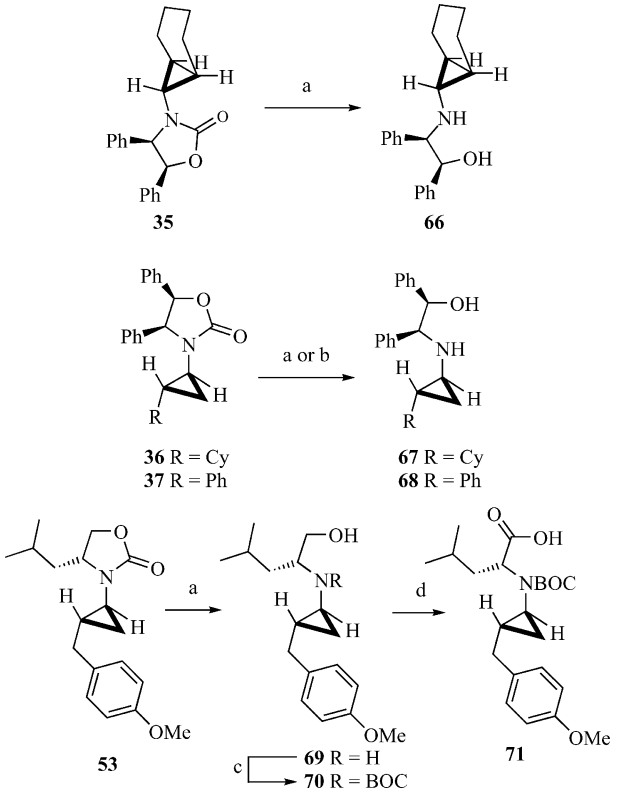
The oxazolidinone-substituted cyclopropanes **35**–**56** are potentially versatile intermediates for accessing cyclopropyl-containing amino alcohols and amino acids. With this end in mind, a procedure for the base-mediated ring opening of the oxazolidinones was investigated (Scheme 6). The amino alcohols **66**–**69** were obtained in moderate to good yield and amino alcohol **69** was successfully protected and oxidised to the amino acid derivative **71** (Scheme 6).



Scheme 5. a. H_2, $Pd(OH)_2/C$, THF, BOC_2O, 72–95%; b. HCl, *i*PrOH, 74%.

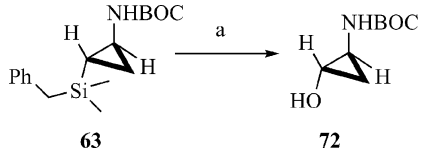
Table 3. Deprotection of diphenyloxazolidinones.

Cyclopropane	Product	Step 1	Product	Step 2
35	**60**	93%	**64**	74%
36	**61**	72%	**65**	74%
38	**62**	80%	–	–
40	**63**	95%	–	–



Scheme 6. a. LiOH, H_2O, EtOH, reflux, 84% (**66**), 74% (**67**), 67% (**69**); b. $KOSiMe_3$, THF, 60 °C 70% (**68**); c. BOC_2O, CH_2Cl_2, 80%; d. RuO_2, $NaIO_4$, CCl_4, MeCN, H_2O, 65%.

Silylcyclopropane **63** was also successfully oxidised under Tamao–Fleming conditions to yield the rigid β-amino alcohol scaffold present in the cyclopropane **72** (Scheme 7).



Scheme 7. Bu_4NF, THF, then $KHCO_3$, H_2O_2, MeOH, 88%.

Conclusions

In summary, diethoxymethyl derivatives can be easily prepared from a wide range of readily accessible chiral oxazolidinones. These compounds can be successfully employed as organozinc carbenoid precursors in stereoselective amidocyclopropanation reactions with a wide range of alkenes to give the corresponding amidocyclopropanes. Diphenyloxazolidinone derivatives can be readily deprotected to give the free aminocyclopropanes as BOC derivatives or hydrochloride salts. By base-mediated opening of the oxazolidinone ring, chiral cyclopropylamino alcohols can be obtained, which can also be oxidised to the corresponding amino acids after protection of the secondary amine. A highly unusual 2-amino-1-hydroxycyclopropane was also prepared by oxidation of a readily accessible 2-amino-1-silylcyclopropane.

Experimental Section

General: All reactions were carried out in oven-dried glassware under nitrogen unless otherwise indicated. Diethyl ether, tetrahydrofuran, toluene and dichloromethane were used following purification from an anhydrous engineering zeolite drying apparatus. Methanol and ethanol were distilled from magnesium turnings and iodine. Anhydrous dimethylformamide was obtained from the Aldrich chemical company or by distillation from calcium hydride. Triethylamine was distilled from potassium hydroxide before use. Chlorotrimethylsilane was distilled from calcium hydride immediately prior to use. Styrene, indene, and 1,2-dihydronaphthalene were distilled before use. PE stands for petroleum ether with the boiling range given. All other chemicals were used as supplied unless otherwise indicated. Column chromatography was carried out using BDH (40–60 μm) silica gel and analytical thin-layer chromatography was carried out using Merck Kieselgel aluminium-backed plates coated with silica gel. Components were visualised using combinations of ultra-violet lights, iodine, ceric ammonium molybdate, phosphomolybdic acid and potassium permanganate. Melting points were determined using a Reichert hot-stage apparatus and are uncorrected. Optical rotations were measured using a Perkin–Elmer 241 or Perkin–Elmer 343 polarimeter (sodium D-line, 529 nm) and $[a]_D^T$ values are given in 10^{-1} deg cm^2 g^{-1}, concentration (*c*) in g per 100 mL. Infrared (IR) spectra were recorded with a Perkin–Elmer 1605 Fourier transform spectrometer or a Perkin–Elmer spectrum 100 FT-IR spectrometer as thin films. ^{1}H NMR spectra were recorded at 300 MHz with a Bruker AMX300 spectrometer, at 400 MHz with a Bruker AMX400 or Avance 400 spectrometer, at 500 MHz with a Bruker Avance 500 spectrometer, or at 600 MHz with a Bruker Avance 600 spectrometer in the stated solvent using residual protic solvent $CHCl_3$ (δ = 7.26 ppm, s), DMSO (δ = 2.56 ppm, qn) or D_2O (4.79, s) as the internal standard. Chemical shifts are quoted in ppm using the following abbreviations: s for singlet, d for doublet, t for triplet, q for quartet, qn for quintet, m for multiplet, br. for broad or a combinations of these. The coupling constants (*J*) are measured in Hertz. ^{13}C NMR spectra were recorded at 75 MHz with a Bruker AMX300 spectrometer, at 100 MHz with a Bruker AMX400 or Avance 400 spectrometer, at 125 MHz with a Bruker Avance 500 spectrometer or at 150 MHz with a Bruker Avance 600 spectrometer in the stated solvent using the central reference of $CHCl_3$ (δ = 77.0 ppm, t), DMSO (δ = 39.52 ppm, septet) as the internal standard. Chemical

shifts are reported to the nearest 0.1 ppm. Mass spectra and elemental analysis were performed at the Department of Chemistry, University College London.

Methyl (*R*)-2-(*tert*-Butoxycarbonyl)amino-2-(4-methoxyphenyl)acetate (4):[18] Anhydrous potassium carbonate (3.1 g, 22.45 mmol) and dimethyl sulfate (1.77 mL, 18.7 mmol) were added successively to a solution of (*R*)-*N*-(*tert*-butoxycarbonyl)-4-hydroxyphenylglycine (2.0 g, 7.48 mmol) in acetone (50 mL) under nitrogen. The reaction mixture was heated at reflux for 4 h and then cooled to room temperature, filtered, and concentrated in vacuo. The residue was dissolved in EtOAc (150 mL) and the organic extract was then washed with an aqueous $NaHCO_3$ solution (5%, 50 mL) and brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (PE/EtOAc, 3:1) to give **4** (1.95 g, 6.6 mmol, 88%) as a white solid; m.p. 82–83 °C (ref.[18] 66–67 °C). $[\alpha]_D^{25}$ = –145.6 (*c* = 1.14, $CHCl_3$) ref.[18] $[\alpha]_D^{25}$ = –95.3 (*c* = 1.2, $CHCl_3$). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3365 (br., NH), 2955 (m), 1746 (s), 1714 (s), 1611 (w), 1514 (s), 1367 (w), 1249 (m), 1166 (s), 1055 (m), 1031 (m) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 1.42 [s, 9 H, $C(CH_3)_3$], 3.71 (s, 3 H, OCH_3), 3.79 (s, 3 H, OCH_3), 5.22–5.27 (m, 1 H, CHN), 5.48 (br. s, 1 H, NH), 6.87 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.27 (d, *J* = 8.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.3, 52.6, 55.3, 57.0, 80.1, 114.3, 128.4, 129.0, 154.8, 159.7, 171.9 ppm. MS (CI^+): *m*/*z* (%) = 296 (21) [M + H], 240 (52), 207 (53), 180 (100), 136 (94), 121 (22). HMRS: [M + H], found 296.14985. $C_{15}H_{22}NO_5$ calcd. 296.14979.

(*R*)-Methyl 2-(Benzyloxycarbonyl)-2-(4-methoxyphenyl)acetate (5):[19] Prepared according to the literature procedure.[20] When the procedure used for the preparation of the ester **4** was employed, racemisation occurred. White solid (71%); m.p. 62–65 °C (EtOAc/PE), ref.[19] 54–56 °C (Et_2O/PE). $[\alpha]_D^{23}$ = –113.8 (*c* = 1.07, $CHCl_3$), ref.[19], (*S*)-enantiomer, $[\alpha]_D^{20}$ = +106.9 (*c* = 0.58, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3267, 3035, 1746, 1608, 1512, 1455, 1410, 1351, 1293, 1217 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 3.72 (s, 3 H, OMe), 3.79 (s, 3 H, OMe), 5.07 (d, *J* = 12.4 Hz, 1 H, C*H*HPh), 5.11 (d, *J* = 12.4 Hz, 1 H, CH*H*Ph), 5.33 (d, *J* = 7.1 Hz, 1 H, C*H*N), 5.83 (br. d, *J* = 7.1 Hz, 1 H, NH), 6.88 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.29 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.29–7.36 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 52.7, 55.2, 57.3, 67.0, 114.3, 128.1, 128.4, 128.5, 128.6, 128.8, 136.1, 155.3, 159.7, 171.5 ppm. MS: (EI): *m*/*z* (%) = 329 (4) [M^+], 270 (50), 226 (67), 194 (69), 162 (100). HRMS: [M^+], found 329.12670, $C_{18}H_{19}NO_5$ calcd. 329.12632.

(*R*)-Benzyl 2-Hydroxy-1-(4-methoxyphenyl)ethylcarbamate (6):[21] Lithium borohydride (256 mg, 10.8 mmol) was added portionwise to a solution of **5** (2.40 g, 7.31 mmol) in anhydrous ether (30 mL) and methanol (0.44 mL), and the resulting solution was stirred for 15 min at room temperature. Saturated aqueous ammonium chloride solution (20 mL) was added and the resulting suspension stirred for 10 min. The aqueous mixture was extracted with ethyl acetate (2 × 40 mL) and the combined organic layers washed with brine, dried with $MgSO_4$ and then concentrated to give the alcohol as a white solid (2.08 g, 6.87 mmol, 94%) which was used without further purification; m.p. 116–117 °C (EtOAc), ref.[21] 111–112 °C ($CHCl_3$). $[\alpha]_D^{20}$ = –28.9 (*c* = 0.98, $CHCl_3$); ref.[21], (*S*)-enantiomer, $[\alpha]_D^{25}$ = +45.2 (*c* = 0.5, 95% EtOH). IR (film): $\tilde{\nu}_{max}$ = 3333, 2957, 1697, 1697, 1612, 1455, 1343, 1247, 1179 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.31 (br. s, 1 H, OH), 3.79 (s, 3 H, OMe), 3.79–3.84 (m, 2 H, CH_2OH), 4.76–4.81 (m, 1 H, CHN), 5.07 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 5.11 (d, *J* = 12.1 Hz, 1 H, C*H*HPh), 5.50 (br. s, 1 H, NH), 6.88 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.21 (d, *J* = 8.6 Hz, 2 H, Ar-H), 7.29–7.38 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.3, 56.6, 66.5, 67.0, 114.2, 127.7, 128.2, 128.5, 131.1, 136.2, 156.4, 159.2 ppm. MS (EI): *m*/*z* (%) = 302 (12) [M^+], 270 (54), 223 (23), 194 (100), 176 (36), 135 (34). HRMS: [M + H], found 302.13957, $C_{17}H_{20}NO_5$ calcd. 302.13923.

(*R*)-2-(*tert*-Butoxycarbonyl)amino-2-(4-methoxyphenyl)ethanol (7):[22] Anhydrous lithium chloride (1.15 g, 27.09 mmol) and sodium borohydride (1.02 g, 27.09 mmol) were added successively to a solution of ester **4** (2.0 g, 6.77 mmol) in dry THF (30 mL) under nitrogen. The reaction mixture was stirred for 4 h and then cooled to 4 °C prior to the addition of saturated NH_4Cl solution (10 mL). The mixture was stirred for 30 min and the precipitate filtered and washed with EtOAc (20 mL). The organic layer was separated and washed with brine (10 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo to give **7** (1.55 g, 5.8 mmol, 86%) as a white solid; m.p. 141–142 °C (EtOAc), ref.[22] 130–132 °C (EtOH/EtOAc). $[\alpha]_D^{25}$ = –38.3 (*c* = 0.6, $CHCl_3$), ref.[22] $[\alpha]_D^{26}$ = –38.1 (*c* = 1.31, $CHCl_3$). IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3372 (br.), 2998 (m), 1682 (s), 1514 (s), 1446 (w), 1245 (m), 1171 (m), 1053 (m), 1031 (m) cm^{-1}. ^1H NMR (500 MHz, 330 K, $CDCl_3$): δ = 1.38 [s, 9 H, $C(CH_3)_3$], 1.91 (br. s, 1 H, OH), 3.78 (s, 3 H, OCH_3), 3.79–3.81 (m, 2 H, CH_2OH), 4.67–4.72 (m, 1 H, CHN), 5.04 (br. s, 1 H, NH), 6.86–6.89 (m, 2 H, Ar-H), 7.18–7.22 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, 330 K, $CDCl_3$): δ = 28.4, 55.3, 56.6, 66.9, 79.9, 114.4, 127.8, 131.8, 156.1, 159.4 ppm. MS (CI^+): *m*/*z* (%) = 268 (41) [M + H], 194 (99), 151 (100), 104 (62). HMRS: [M + H], found 268.15511 $C_{14}H_{22}NO_4$ calcd. 268.15488. $C_{14}H_{21}NO_4$ (267.32): calcd. C 62.90, H 7.92, N 5.24; found C 62.75, H 7.95, N 5.27.

(*R*)-Benzyl 2-Hydroxy-1-(4-methoxyphenyl)-2-methylpropylcarbamate (8): A solution of iodomethane (15.4 mL, 250 mmol) in diethyl ether (70 mL) was added dropwise to a suspension of magnesium turnings (9.12 g, 376 mmol) in diethyl ether (280 mL) under nitrogen. After the addition was completed (vigorous reflux), the reaction mixture was heated under reflux for a further 45 min, and then cooled to room temperature. A solution of ester **5** (20.6 g, 63.1 mmol) in THF (60 mL) was then added dropwise. After the addition was completed, the reaction mixture was heated under reflux for a further 30 min, and then cooled to room temperature. The reaction was quenched by dropwise addition of acetone (50 mL) and then saturated ammonium chloride (50 mL). The layers were separated and the aqueous layer extracted with diethyl ether (2 × 250 mL). The combined organic layers were washed with brine (300 mL), dried ($MgSO_4$) and concentrated. The crude product was purified by column chromatography (7:3 PE:EtOAc) to give the alcohol as a colourless oil which became a white solid on standing in the freezer (8.33 g, 23.66 mmol, 38%); m.p. 58–60 °C $[\alpha]_D^{22}$ = –26.0 (*c* = 2.14, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3423, 3034, 2973, 2837, 1694, 1612, 1586, 1510, 1455, 1376, 1342, 1302, 1280, 1242, 1178, 1144, 1107 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.05 (s, 3 H, Me), 1.35 (s, 3 H, Me), 1.55 (br. s, 1 H, OH), 3.80 (s, 3 H, OMe), 4.52 (br. d, *J* = 8.4 Hz, 1 H, C*H*NH), 5.03 (d, *J* = 12.3 Hz, 1 H, C*H*HPh), 5.09 (d, *J* = 12.3 Hz, 1 H, CH*H*Ph), 5.74 (br. d, *J* = 8.4 Hz, 1 H, NH), 6.87 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.21 (d, *J* = 8.4 Hz, 2 H, Ar-H), 7.29–7.36 (m, 5 H, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 27.7, 53.3, 62.8, 66.9, 72.9, 113.7, 128.2, 128.6, 129.0, 131.6, 136.5, 156.2, 159.1 ppm. MS (EI): *m*/*z* (%) = 352 (58) [M^+], 281 (15), 266 (25), 219 (19), 176 (100), 173 (75). HRMS: M +, found 352.15311, $C_{19}H_{23}NO_4$ calcd. 352.15247.

General Procedure for the Preparation of Oxazolidinones: A solution of triphosgene (2.58 g, 8.68 mmol) in dry dichloromethane (10 mL) was added dropwise over 45 min to a suspension of amino alcohol (24.8 mmol) and triethylamine (7.6 mL, 54.56 mmol) in dry dichloromethane (70 mL) under nitrogen at 4 °C. The reaction mixture was stirred for a further 15 min at 4 °C and then warmed to

room temperature and stirred for 1 h. Saturated aqueous NH_4Cl solution (25 mL) and dichloromethane or ethyl acetate (50 mL) were added to the reaction mixture and after stirring for 20 min, the mixture was transferred into a separating funnel. The aqueous layer was separated and the organic layer washed with water (25 mL). The combined aqueous layers were extracted with dichloromethane (50 mL) and the combined organic extracts were then dried ($MgSO_4$), filtered, and concentrated in vacuo.

***cis*-4,5-Diphenyl-2-oxazolidinone (9):**[23] The crude product was recrystallised twice from EtOAc/isohexane to give **1** [(±)-**1**, 69%; (+)-**1** 82%; (–)-**1** 85%] as a white solid; m.p. (±)-**1** 191–192 °C (EtOAc/isohexane), ref.[23a] 193.5–194.5 °C (EtOAc/hexane), (+)-**1** 232–233 °C (EtOAc), ref.[23b] 232.5–233.5 °C (toluene), (–)-**1** 231–232 °C. $[\alpha]_D^{20}$ = (+)-**1** +66.3 (*c* 0.85, MeOH), ref.[23b] $[\alpha]_D^{20}$ = +60.6 (*c* = 0.86, MeOH), (–)-**1** –59.6 (*c* 0.86, MeOH), ref.[23c] $[\alpha]_D^{27}$ = –58.4 (*c* = 0.91, MeOH). IR (film): $\tilde{\nu}_{max}$ = 3278 (br.), 1752 (s), 1499 (w), 1446 (m), 1393 (w), 1350 (w), 1221 (w), 1071 (w), 1022 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 5.17 (d, *J* = 8.0 Hz, 1 H, C*H*NH), 5.42 (br. s, 1 H, NH), 5.94 (d, *J* = 8.0 Hz, 1 H, C*H*O), 6.90–6.98 (m, 4 H, Ar-H), 7.06–7.11 (m, 6 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 61.4, 82.3, 126.9, 127.9, 128.1, 128.3, 134.4, 136.0, 159.6 ppm.

(*S*)-4-Benzyl-2-oxazolidinone (10):[24] The crude product was recrystallised from EtOAc/hexane to give **2** (75%) as a white solid; m.p. 84–88 °C (PE) ref.[24] 85–87 °C;$[\alpha]_D^{23}$ = –63.1 (*c* = 1.02, $CHCl_3$), ref.[24] $[\alpha]_D^{25}$ = –62 (*c* = 1.0, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3261, 1751 (s), 1738 (s), 1700 (s), 1407, 1247, 1095 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 2.84 (dd, *J* = 13.6, 8.2 Hz, 1 H, C*H*HPh), 2.90 (dd, *J* = 13.6, 5.8 Hz, 1 H, CH*H*Ph), 4.05–4.12 (m, 1 H, C*H*N), 4.16 (dd, *J* = 8.7, 5.6 Hz, 1 H, C*H*HO), 4.49 (t, *J* = 8.3 Hz, 1 H, CH*H*O), 4.99 (br. s, 1 H, NH), 7.16–7.20 (m, 2 H, Ar-H), 7.26–7.30 (m, 1 H, Ar-H), 7.33–7.37 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 41.7, 53.9, 69.8, 127.4, 129.0, 129.2, 136.0, 158.9 ppm.

(*S*)-4-Isopropyl-2-oxazolidinone (11):[25] Yellow solid (89%), used without further purification; m.p. 65–68 °C, ref.[25] 67–70 °C. $[\alpha]_D^{16}$ = +8.92 (*c* = 1.11, $CHCl_3$), ref.[25] $[\alpha]_D^{26}$ = +15.5 (*c* = 5.2, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3300 (w), 2963, 1753 (s), 1240 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (d, *J* = 6.8 Hz, 3 H, CH_3CHCH_3), 0.96 (d, *J* = 6.8 Hz, 3 H, CH_3CHCH_3), 1.73 (octet, *J* = 6.8 Hz, 1 H, $CHMe_2$), 3.53–3.65 (m, 1 H, C*H*NH), 4.10 (dd, *J* = 8.7, 6.3 Hz, 1 H, C*H*HO), 4.44 (t, *J* = 8.7 Hz, 1 H, CH*H*O), 5.98 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6, 18.0, 32.7, 58.3, 68.6, 160.1 ppm. MS (CI^+): *m*/*z* (%) = 130 (100) [M + H], 102 (2), 86 (7). HRMS: [M + H], found 130.08634. $C_6H_{12}O_2N$ calcd. 130.08680.

(*R*)-(–)-4-Phenyl-2-oxazolidinone (12):[23b] White solid (72%), used without further purification; m.p. 129–130 °C, ref.[23b] 132–134 °C (EtOAc/hexane). $[\alpha]_D^{17}$ = –60.4 (*c* = 1.0, $CHCl_3$), ref.[23b] $[\alpha]_D^{20}$ = –57.7 (*c* = 1.083, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 3268 (br.), 2915 (w), 1757 (s), 1399 (w), 1216, 1042 (w), 925 (w), 757 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.15 (dd, *J* = 8.8, 6.9 Hz, 1 H, C*H*HO), 4.69 (t, *J* = 8.6 Hz, 1 H, CH*H*O), 4.93 (dd, *J* = 8.6, 6.9 Hz, 1 H, CHN), 6.32 (br. s, 1 H, NH), 7.22–7.41 (m, 5 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3, 72.5, 126.0, 128.7, 129.1, 139.5, 159.9 ppm. MS (EI): *m*/*z* (%) = 163 (24) [M^+], 133 (73), 104 (100), 91 (30), 77 (32).

(*S*)-4-Ethyloxazolidin-2-one (13):[26] Yellow oil (60%), used without further purification. $[\alpha]_D^{20}$ = –7.24 (*c* = 0.76, $CHCl_3$), ref.[26] $[\alpha]_D^{30}$ = –5.3 (*c* = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 2247 (w), 1749, 1248 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.94 (t, *J* = 7.5 Hz, 3 H, CH_3CH_2), 1.55–1.65 (m, 2 H, CH_2CH_3), 3.76–3.85 (m, 1 H, C*H*NH), 4.02 (dd, *J* = 8.5, 6.1 Hz, 1 H, C*H*HO), 4.48 (t, *J* = 8.5 Hz, 1 H, CH*H*O), 6.28 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 9.3, 28.2, 53.9, 70.0, 160.3 ppm. MS (CI^+): *m*/*z* (%) = 116 (100) [M + H], 99 (4), 86 (8). HRMS: [M + H], found 116.07058. $C_5H_{10}O_2N$ calcd. 116.07115.

(*S*)-4-Isobutyloxazolidin-2-one (14):[27] Yellow oil (99%), used without further purification. $[\alpha]_D^{16}$ = –11.6 (*c* = 1.0, $CHCl_3$) ref.[27] (*R*)-isomer, $[\alpha]_D^{22}$ = +11.9 (*c* = 1.17, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3336 (s, br), 2980, 2871, 1750 (s), 1408 (w), 1235 (w), 1028 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 4.1 Hz, 3 H, CH_3CHCH_3), 0.94 (d, *J* = 4.1 Hz, 3 H, CH_3CHCH_3), 1.34–1.44 (m, 1 H, $CHMe_2$), 1.50–1.71 (m, 2 H, CH_2CHMe_2), 3.89–4.00 (m, 2 H, C*H*NH, C*H*HO), 4.49 (t, *J* = 7.4 Hz, 1 H, CH*H*O), 6.21 (br. s, 1 H, NH) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.1, 22.9, 25.1, 44.4, 51.0, 70.7, 159.9 ppm. MS (EI): *m*/*z* (%) = 143 (23) [M^+], 130 (5), 86 (100). HRMS: M^+, found 143.09423. $C_7H_{13}O_2N$ calcd. 143.09462.

(4*S*,5*R*)-4-Methyl-5-phenyl-2-oxazolidinone (15):[28] Pale yellow solid (100%). A small sample was purified by column chromatography (EtOAc/PE, 1:1); m.p. 116–119 °C (PE) ref.[28] 116–117 °C. $[\alpha]_D^{23}$ = –163.8 (*c* = 1.02, $CHCl_3$), ref.[28] $[\alpha]_D^{20}$ = –170.0 (*c* = 1.20, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3269, 1719 (s), 1383, 1353, 1238 cm^{-1}. ^1H NMR (600 MHz, $CDCl_3$): δ = 1.07 (d, *J* = 6.6 Hz, 3 H, CH_3), 4.19–4.25 (m, 1 H, C*H*CH_3), 5.19 (br. s, 1 H, NH), 5.74 (d, *J* = 8.0 Hz, 1 H, CHO), 7.32 (d, *J* = 7.3 Hz, 2 H, Ar-H), 7.35–7.39 (m, 1 H, Ar-H), 7.42 (t, *J* = 7.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$): δ = 17.6, 52.3, 81.0, 125.9, 128.6, 134.8, 158.9 ppm.

(±)-4-(Benzyloxymethyl)-2-oxazolidinone (16): The crude product was purified by flash column chromatography (PE 40–60 °C/EtOAc, 3:2 to 7:3) to give a yellow oil (56%). IR (film): $\tilde{\nu}_{max}$ = 3320 (br., NH), 2906 (w), 2864 (w), 1752 (s), 1410 (m), 1232 (m), 1096 (s), 1056 (s), 1036 (s) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.43 (d, *J* = 5.7 Hz, 2 H, CH_2OCH_2Ph), 3.93–4.02 (m, 1 H, CHNCO), 4.11 (dd, *J* = 8.7, 5.1 Hz, 1 H, C*H*HOCO), 4.39 (t, *J* = 8.7 Hz, 1 H, CH*H*OCO), 4.50 (s, 2 H, CH_2Ph), 6.46 (br. s, 1 H, NH), 7.24–7.35 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 51.8, 62.2, 71.4, 73.4, 127.6, 127.8, 127.6, 137.3, 159.9 ppm. MS (EI): *m*/*z* (%) = 208 (4) [M + H], 146 (100). HMRS: [M + H], found 208.09751. $C_{11}H_{14}NO_3$ calcd. 208.09682.

(*S*)-Ethyl-2-oxazolidinone-4-carboxylate (17): White solid (79%), used without further purification; m.p. 69–71 °C (EtOAc/hexane). $[\alpha]_D^{22}$ = –24.0 (*c* = 1.0, CH_2Cl_2). IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 3270 (br., NH), 1745 (s), 1402 (m), 1379 (m), 1214 (s), 1131 (m), 1019 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 1.30 (t, *J* = 7.2 Hz, 3 H, CH_3), 4.26 (q, *J* = 7.2 Hz, 2 H, CH_2CH_3), 4.37 (dd, *J* = 9.6, 4.6 Hz, 1 H, C*H*HOCO), 4.52 (dd, *J* = 9.0, 4.6 Hz, 1 H, CHNCO), 4.60 (dd, *J* = 9.6, 9.0 Hz, 1 H, CH*H*OCO), 5.58 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.9, 53.7, 62.2, 66.6, 159.1, 170.1 ppm. MS (FAB): *m*/*z* = 160 (M + H, 100). HMRS: [M + H], found 160.06086. $C_6H_{10}NO_4$ calcd. 160.06098.

(*R*)-4-(Hydroxymethyl)oxazolidin-2-one (18):[29] Sodium borohydride (0.45 g, 11.74 mmol) was added portionwise to a solution of ester **17** (1.78 g, 11.18 mmol) in absolute ethanol (22 mL) under nitrogen at 4 °C. The reaction mixture was stirred for a further 10 min at 4 °C and then warmed to room temperature and stirred for 2 h. The reaction was quenched carefully with saturated aqueous NH_4Cl solution (1.8 mL) and, after stirring for 30 min, the mixture was filtered through Celite. The solvents were removed in vacuo and the crude product was purified by flash column chromatography (EtOAc/MeOH, 9:1 then 8.5:1.5) to give the alcohol as a white solid (0.99 g, 8.45 mmol, 76%); m.p. 77–81 °C, ref.[29] 96–99 °C ($CHCl_3$). $[\alpha]_D^{20}$ = +29.2 (*c* = 1.0, MeOH); ref.[29]

$[a]_D^{25}$ = +32.25 (*c* = 1.044, MeOH). IR (film): $\tilde{\nu}_{max}$ = 3276 (br., s), 1732 (s), 1418, 1259, 1037, 939 cm^{-1}. ^1H NMR (400 MHz, D_2O): δ = 3.58 (dd, *J* = 12.0, 4.4 Hz, 1 H, C*H*HOH), 3.67 (dd, *J* = 12.0, 3.7 Hz, 1 H, CH*H*OH), 4.03–4.09 (m, 1 H, *CH*CH_2O), 4.29 (dd, *J* = 9.0, 5.1 Hz, 1 H, C*H*HO), 4.56 (t, *J* = 9.0 Hz, 1 H, CH*H*O) ppm. ^{13}C NMR (75 MHz, D_2O): δ = 53.8, 62.6, 68.1, 159.9 ppm. MS (EI): *m*/*z* (%) = 118 (45) [M + H], 106 (12), 97 (25), 91 (7), 86 (100). HRMS: $[M]^+$, found 117.04312. $C_4H_7O_3N$ calcd. 117.04259.

(*S*)-4-[(*tert*-Butyldimethylsilyloxy)methyl]-2-oxazolidinone (19):[27] *tert*-Butyldimethylsilyl chloride (1.23 g, 8.17 mmol) and imidazole (1.11 g, 16.35 mmol) were added successively to a solution of alcohol **18** (0.87 g, 7.43 mmol) in dry DMF (10 mL) under nitrogen at 4 °C. The reaction mixture was stirred for a further 30 min at 4 °C and then warmed to room temperature and stirred for 44 h. The reaction was quenched with saturated aqueous $NaHCO_3$ solution (40 mL) and the aqueous layer was extracted with EtOAc (3 × 40 mL). The combined organic extracts were dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (PE 40–60 °C/EtOAc, 1:1) to give **19** (1.39 g, 6.01 mmol, 81%) as a white solid; m.p. 76–79 °C (ref.[27] 59–60 °C). $[a]_D^{19}$ = +34.6 (*c* = 1.44, $CHCl_3$); ref.[27] $[a]_D^{21}$ = +13.4 (*c* = 1.45, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3300 (br., NH), 2926 (w), 2864 (w), 1751 (s), 1414 (w), 1252 (w), 1136 (w), 1043 (m), 941 (w), 839 (m), 779 (m) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.04 (s, 6 H, 2 × CH_3Si), 0.86 [s, 9 H, $C(CH_3)_3$], 3.59 (d, *J* = 5.5 Hz, 2 H, $CH_2OTBDMS$), 3.87–3.93 (m, 1 H, CHN), 4.14 (dd, *J* = 8.8, 4.9 Hz, 1 H, C*H*HO), 4.42 (t, *J* = 8.8 Hz, 1 H, CH*H*O), 5.69 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.5, 18.1, 25.7, 53.6, 64.8, 67.0, 73.4, 159.6 ppm. MS (EI): *m*/*z* (%) = 232 (15) [M + H], 216 (62), 174 (82), 131 (100), 101 (93), 75 (92). HMRS: [M + H], found 232.13671. $C_{10}H_{22}NO_3Si$ calcd. 232.13635; C 51.94, H 9.47, N 6.03; $C_{10}H_{21}NO_3Si$ calcd. C 51.91, H 9.15, N 6.05; found C 51.94, H 9.47, N 6.03.

(*R*)-4-(4-Methoxyphenyl)oxazolidin-2-one (20). Method A:[30] Thionyl chloride (0.92 mL, 12.57 mmol) was added dropwise to a solution of alcohol **7** (0.42 g, 1.57 mmol) in dry THF (10.5 mL) under nitrogen at 4 °C. The reaction mixture was stirred for a further 10 min at 4 °C and then warmed to room temperature and stirred for 3 h. The reaction mixture was then concentrated in vacuo and the crude product purified by flash column chromatography (EtOAc/PE 30–40 °C 7:3) to give the oxazolidinone **20** (0.27 g, 1.4 mmol, 90%) as a white solid.

Method B: Sodium hydride (60% in mineral oil, 125 mg, 3.1 mmol) was added portionwise to a solution of benzyl carbamate **6** (602 mg, 2 mmol) in THF (10 mL) under nitrogen at room temperature. After stirring for 30 min, water (10 mL) was added and the reaction mixture extracted with ethyl acetate (3 × 20 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (PE 40–60 °C/EtOAc, 1:1) to give the oxazolidinone **20** as a white solid (379 mg, 1.96 mmol, 98%); m.p. 149–151 °C, ref.[30] racemic, 111 °C. $[a]_D^{22}$ = –34.0 (*c* = 0.5, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3372 (br.), 1684 (s), 1517 (m), 1367 (w), 1245 (m), 1172 (m), 1053 (m), 1032 (m), 668 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 3.81 (s, 3 H, OCH_3), 4.16 (dd, *J* = 8.5, 7.0 Hz, 1 H, C*H*HO), 4.70 (t, *J* = 8.5 Hz, 1 H, CH*H*O), 4.91 (dd, *J* = 8.5, 7.2 Hz, 1 H, CHN), 5.46 (br. s, 1 H, NH), 6.89–6.95 (m, 2 H, Ar-H), 7.24–7.30 (m, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 55.4, 56.0, 72.7, 114.5, 127.4, 131.2, 159.3, 160.0 ppm. MS (EI): *m*/*z* (%) = 193 (49) $[M^+]$, 163 (22), 135 (100), 121 (18), 77 (15). HRMS: M^+, found 193.07398. $C_{10}H_{11}NO_3$ calcd. 193.07389; $C_{10}H_{11}NO_3$ (193.20): calcd. C 62.17, H 5.74, N 7.25; found C 62.06, H 5.84, N 7.16.

(*R*)-4-(4-Methoxyphenyl)-5,5-dimethyloxazolidin-2-one (21): Sodium hydride (60% in mineral oil, 704 mg, 17.6 mmol) was added portionwise to a solution of benzyl carbamate **8** (5.93 g, 16.9 mmol) in THF (70 mL) under nitrogen at room temperature. After stirring for 60 min, water (70 mL) was added and the reaction mixture extracted with ethyl acetate (3 × 50 mL). The combined organic layers were washed with brine (70 mL), dried ($MgSO_4$) and concentrated. The residue was purified by flash column chromatography (PE 40–60 °C/EtOAc, 1:1) to give the oxazolidinone **21** as a white solid (2.09 g, 11.8 mmol, 70%); m.p. 145–147 °C. $[a]_D^{20}$ = –55.6 (*c* = 0.79, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3280, 2980, 1746, 1613, 1515, 1464, 1374, 1294, 1251 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.93 (s, 3 H, CH_3), 1.58 (s, 3 H, CH_3), 3.80 (s, 3 H, CH_3O), 4.59 (s, 1 H, CH), 5.87 (br. s, 1 H, NH), 6.90 (d, *J* = 8.7 Hz, 2 H, Ar-*H*), 7.18 (d, *J* = 8.7 Hz, 2 H, Ar-*H*) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.6, 28.0, 55.3, 65.5, 84.7, 114.1, 127.6, 128.7, 158.9, 159.8 ppm. MS (EI): *m*/*z* (%) = (%)177 (50) [M – CO_2], 151 (22), 107 (87), 91 (100). HRMS: [M – CO_2], found 177.04984, $C_{11}H_{15}NO$ calcd. 177.11536.

General Procedure for the Preparation of Carbenoid Precursors: A mixture of oxazolidinone (20.9 mmol), aluminium chloride (0.41 g, 3.1 mmol) and triethyl orthoformate (103 mL, 0.63 mol) was heated at 155 °C for 24 h. The reaction mixture was cooled to room temperature and then quenched with saturated aqueous $NaHCO_3$ solution (50 mL). The aqueous phase was extracted with diethyl ether (200 mL, then 100 mL) and the combined organic extracts were washed with brine (50 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography to give the diethoxymethlamide. The *N*-(diethoxymethyl)amides are sometimes unstable in chloroform solution, so it is preferable to record NMR spectra in $[D_6]$DMSO and optical rotations in CH_2Cl_2.

(±)-3-(Diethoxymethyl)-4,5-diphenyl-2-oxazolidinone (±)-(22): White solid (80%) which can readily be recrystallised from hexane; m.p. (±)-**22** 93.5–94.5 °C (hexane), (+)-**22** 93–95 °C (hexane), (–)-**22** 92.5–94.5 °C (hexane); (+)-**22** $[a]_D^{20}$ = +6.0 (*c* = 0.55, CH_2Cl_2), (–)-**22** $[a]_D^{26}$ = –4.5 (*c* = 1.12, CH_2Cl_2). IR (film): $\tilde{\nu}_{max}$ = 2979 (m), 1735 (s), 1455 (m), 1414 (m), 1385 (m), 1161 (m), 1102 (s), 1066 (s), 1037 (m), 1025 (m) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.72 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.30 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 3.24 (dq, *J* = 9.2, 7.1 Hz, 1 H, C*H*HCH_3), 3.47 (dq, *J* = 9.2, 7.1 Hz, 1 H, CH*H*CH_3), 3.66 (dq, *J* = 9.2, 7.1 Hz, 1 H, C*H*HCH_3), 3.75 (dq, *J* = 9.2, 7.1 Hz, 1 H, CH*H*CH_3), 5.25 (d, *J* = 8.2 Hz, 1 H, CHN), 5.87 (s, 1 H, OCHO), 5.91 (d, *J* = 8.2 Hz, 1 H, CHO), 6.93–7.12 (m, 10 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.0, 14.9, 60.5, 62.6, 62.7, 81.5, 102.0, 126.0, 127.6, 127.7, 127.8, 134.2, 136.4, 157.4 ppm. ^1H NMR (400 MHz, DMSO): δ = 0.65 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 1.19 (t, *J* = 7.1 Hz, 3 H, CH_2CH_3), 3.20 (dq, *J* = 9.3, 7.1 Hz, 1 H, C*H*HCH_3), 3.41 (dq, *J* = 9.3, 7.1 Hz, 1 H, CH*H*CH_3), 3.58–3.66 (m, 2 H, CH_2CH_3), 5.35 (d, *J* = 8.1 Hz, 1 H, CHN), 5.77 (s, 1 H, OCHO), 6.03 (d, *J* = 8.1 Hz, 1 H, CHO), 6.90–7.12 (m, 10 H, H_{arom}) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 14.0, 14.8, 59.4, 61.6, 61.9, 80.3, 101.6, 126.0, 127.2, 127.3, 127.5, 127.6, 134.7, 136.9, 156.5 ppm. MS (FAB): *m*/*z* (%) = 364 (100) [M + Na], 296 (14), 262 (46), 180 (5). HMRS: [M + Na], found 364.15313. $C_{20}H_{23}NNaO_4$ calcd. 364.15247; $C_{20}H_{23}NO_4$ (341.41): calcd. C 70.36, H 6.79, N 4.10; found C 70.32, H 6.80, N 4.10.

(*S*)-4-Benzyl-3-(diethoxymethyl)-2-oxazolidinone (23): Pale yellow oil (53%). $[a]_D^{20}$ = +51.5 (*c* = 1.22, DCM). IR (film): $\tilde{\nu}_{max}$ = 2978 (w), 1753 (s), 1404, 1233, 1058 (s) cm^{-1}. ^1H NMR (400 MHz, DMSO): δ = 1.20 (t, *J* = 7.0 Hz, 3 H, CH_2CH_3), 1.21 (t, *J* = 7.0 Hz,

CH_2CH_3), 2.78 (dd, J = 13.6, 8.6 Hz, 1 H, C*H*HPh), 3.25 (dd, J = 13.6, 2.6 Hz, 1 H, CH*H*Ph), 3.52–3.71 (m, 4 H, 2 × CH_2CH$_3$), 4.00–4.05 (m, 1 H, C*H*HO), 4.17–4.22 (m, 2 H, CH*H*O, C*H*CH$_2$Ph), 5.74 [br. s, 1 H, CH(OEt)$_2$], 7.23–7.28 (m, 3 H, Ar-H), 7.32 (t, J = 7.6 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (150 MHz, DMSO): δ = 15.2, 15.3, 52.7, 62.4, 62.4, 67.2, 102.5, 127.1, 129.0, 129.7, 136.9, 157.1 ppm. MS (FAB): m/z (%) = 302 (74) [M + Na], 234 (100), 200 (23), 176 (21), 154 (25). HRMS: [M + Na], found 302.13687. $C_{15}H_{21}O_4NNa$ calcd. 302.13682.

(*S*)-3-(Diethoxymethyl)-4-isopropyl-2-oxazolidinone (24): Colourless oil (55%). $[\alpha]_D^{19}$ = +35.9 (c = 1.18, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3493, 2976, 2878, 1755 (s), 1634 (s), 1487, 1414, 1234, 1063 (s) cm^{-1}. ^{1}H NMR (500 MHz, DMSO): δ = 0.86 (d, J = 7.0 Hz, 3 H, CH_3CHCH$_3$), 0.89 (d, J = 7.0 Hz, 3 H, CH$_3$CHCH_3), 1.19 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$), 1.22 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$), 2.16–2.24 (m, 1 H, CHMe$_2$), 3.52–3.73 (m, 4 H, 2 × OCH_2CH$_3$), 3.97 (ddd, J = 9.0, 4.8, 3.3 Hz, 1 H, C*H*CH$_2$O) 4.20 (dd, J = 9.0, 4.8 Hz, 1 H, C*H*HO), 4.31 (t, J = 9.0 Hz, 1 H, CH*H*O), 5.71 [s, 1 H, CH(OEt)$_2$] ppm. ^{13}C NMR (125 MHz, DMSO): δ = 14.1, 14.7, 14.7, 17.6, 29.0, 55.8, 61.9, 62.2, 63.1, 102.1, 157.1 ppm. MS (EI): m/z (%) = 254 (100) [M + Na], 186 (68), 184 (10), 172 (79). HRMS: [M + Na], found 254.13712. $C_{11}H_{21}O_4NNa$ calcd. 254.13712.

(*R*)-(–)-3-(Diethoxymethyl)-4-phenyl-2-oxazolidinone (25): Colourless oil (33%). $[\alpha]_D^{17}$ = –49.9 (c = 1.8, CH_2Cl_2). IR (film): $\tilde{\nu}_{max}$ = 2978, 2903 (w), 1761 (s), 1458, 1402, 1216, 1066 (s), 765 (w), 707 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.65 (t, J = 7.1 Hz, 3 H, CH_3), 1.21 (t, J = 7.1 Hz, 3 H, CH_3), 3.10 (dq, J = 9.2, 7.1 Hz, 1 H, C*H*HCH$_3$), 3.32 (dq, J = 9.2, 7.1 Hz, 1 H, CH*H*CH$_3$), 3.66 (dq, J = 9.4, 7.1 Hz, 1 H, C*H*HCH$_3$), 4.19 (dq, J = 9.4, 7.1 Hz, 1 H, CH*H*CH$_3$), 4.19 (dd, J = 8.9, 5.9 Hz, 1 H, C*H*HO), 4.60 (t, J = 8.9 Hz, 1 H, CH*H*O), 5.00 (dd, J = 8.9, 5.9 Hz, 1 H, CHPh), 5.71 [s, 1 H, CH(OEt)$_2$], 7.24–7.36 (m, 5 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.8, 14.7, 55.4, 61.8, 62.8, 70.9, 102.5, 126.9, 128.2, 128.5, 140.1, 157.9 ppm. MS (EI): m/z (%) = 265 (14) [M$^+$], 220 (86), 192 (77), 148 (62), 121 (71), 103 (100), 91 (38), 77 (53) [Ph$^+$], 75 (92). HMRS: [M]$^+$, found 265.12982. $C_{14}H_{19}NO_4$ calcd. 265.13086.

(*S*)-3-(Diethoxymethyl)-4-ethyloxazolidin-2-one (26): Pale yellow oil (55%). $[\alpha]_D^{19}$ = +27.7 (c = 1.18, EtOAc). IR (film): $\tilde{\nu}_{max}$ = 2976 (s), 1757 (s), 1412 (s), 1223, 1063 (s) cm^{-1}. ^{1}H NMR (500 MHz, DMSO): δ = 0.87 (d, J = 7.5 Hz, 3 H, CH_3CH$_2$), 1.19 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$O), 1.21 (t, J = 7.0 Hz, 3 H, CH_3CH$_2$O), 1.53–1.64 (m, 1 H, C*H*HCH$_3$), 1.82–1.91 (m, 1 H, CH*H*CH$_3$) 3.52–3.69 (m, 4 H, 2 × OCH_2CH$_3$), 3.93–3.99 (m, 1 H, C*H*CH$_2$O), 4.06 (dd, J = 8.6, 6.0 Hz, 1 H, C*H*HO), 4.44 (t, J = 8.6 Hz, 1 H, CH*H*O), 5.70 [s, 1 H, CH(OEt)$_2$] ppm. ^{13C} NMR (125 MHz, DMSO): δ = 8.1, 14.7, 25.8, 52.4, 61.8, 62.0, 67.0, 102.0, 157.0 ppm. MS (EI): m/z (%) = 240 (100) [M + Na], 172 (30). HRMS: [M + Na], found 240.12164. $C_{10}H_{19}O_4NNa$ calcd. 240.12063.

(*S*)-3-(Diethoxymethyl)-4-isobutyloxazolidin-2-one (27): Yellow oil (63%). $[\alpha]_D^{5}$ = +38.1 (c = 1.05, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 2960 (s), 1743 (s), 1533 (w), 1470, 1410 (s), 1248 (s), 1067 (s), 899 (w) cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ = 0.91 (d, J = 6.6 Hz, 3 H, CH_3CHCH$_3$), 0.93 (d, J = 6.6 Hz, 3 H, CH$_3$CHCH_3), 1.20 (q, J = 7.1 Hz, 6 H, 2 × CH_3CH$_2$), 1.37–1.46 (m, 1 H, C*H*HCHMe$_2$), 1.56–1.69 (m, 1 H, CHMe$_2$), 1.82–1.90 (m, 1 H, CH*H*CHMe$_2$), 3.50–3.69 (m, 4 H, 2 × CH_2CH$_3$), 3.97–4.06 (m, 2 H, C*H*HO, C*H*CH$_2$O), 4.48–4.52 (m, 1 H, CH*H*O), 5.70 [s, 1 H, CH(OEt)$_2$] ppm. ^{13}C NMR (75 MHz, DMSO): δ = 14.6, 21.5, 23.4, 24.1, 42.2, 50.3, 61.4, 61.9, 68.0, 101.9, 156.9 ppm. MS (FAB): m/z (%) = 268 (100) [M + Na], 166 (56). HRMS: [M + Na], found 268.15269. $C_{12}H_{23}O_4NNa$ calcd. 268.15247.

(4*S*,5*R*)-3-(Diethoxymethyl)-4-methyl-5-phenyloxazolidin-2-one (28): Pale yellow oil (53%). $[\alpha]_D^{20}$ = –38.0 (c = 1.02, DCM). IR (film): $\tilde{\nu}_{max}$ = 2979 (w), 1750 (s), 1386, 1244, 1223, 1059 (s) cm^{-1}. ^{1}H NMR (600 MHz, DMSO): δ = 0.74 (d, J = 6.4 Hz, 3 H, CH_3), 1.24 (t, J = 7.1 Hz, 3 H, CH_2CH_3), 1.37 (t, J = 7.1 Hz, CH_2CH_3), 3.51 (dq, J = 9.6, 7.1 Hz, 1 H, C*H*HCH$_3$), 3.57–3.67 (m, 3 H, CH*H*CH$_3$, CH_2CH$_3$), 4.31–4.36 (m, 1 H, C*H*CH$_3$), 5.73–5.75 [m, 2 H, CHPh, CH(OEt)$_2$], 7.31–7.33 (m, 2 H, Ar-H), 7.35–7.39 (m, 1 H, Ar-H), 7.41–7.45 (m, 2 H, Ar H) ppm. ^{13}C NMR (150 MHz, DMSO): δ = 15.2, 15.2, 16.7, 51.7, 62.2, 62.5, 79.0, 102.3, 126.7, 128.8, 128.9, 135.8, 156.6 ppm. MS (FAB): m/z (%) = 302 (100) [M + Na], 234 (77), 200 (31), 190 (27), 176 (18). HRMS: [M + Na], found 302.13635. $C_{15}H_{21}NNaO_4$ calcd. 302.13682.

(±)-4-(Benzyloxymethyl)-3-(diethoxymethyl)-2-oxazolidinone (29): Colourless oil (73%). IR (film): $\tilde{\nu}_{max}$ = 2978 (m), 1759 (s), 1414 (m), 1242 (m), 1220 (m), 1063 (s) cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ = 1.07 (t, J = 7.0 Hz, 3 H, CH$_2$CH_3), 1.13 (t, J = 7.0 Hz, 3 H, CH$_2$CH_3), 3.43–3.57 (m, 4 H, CH_2CH$_3$), 3.58 (d, J = 4.2 Hz, 2 H, CH_2OCH$_2$Ph), 4.08 (qd, J = 8.6, 4.5 Hz, 1 H, CHNCO), 4.19 (dd, J = 8.6, 4.8 Hz, 1 H, C*H*HOCO), 4.38 (t, J = 8.6 Hz, 1 H, CH*H*OCO), 4.47 (d, J = 12.1 Hz, 1 H, C*H*HPh), 4.51 (d, J = 12.1 Hz, 1 H, CH*H*Ph), 5.64 [s, 1 H, CH(OEt)$_2$], 7.25–7.37 (m, 5 H, Ar-H) ppm. ^{13}C NMR (100 MHz, DMSO): δ = 14.6, 14.7, 50.8, 61.7, 62.0, 65.8, 69.6, 72.5, 101.6, 127.6, 128.3, 138.1, 156.9 ppm. MS (EI): m/z (%) = 309 (6) [M$^+$], 280 (42), 264 (59), 190 (32), 157 (51), 128 (52), 103 (100), 91 (98), 77 (30). HMRS: [M]$^+$, found 309.15778. $C_{16}H_{23}NO_5$ calcd. 309.15707.

(*S*)-Ethyl 3-(Diethoxymethyl)-2-oxazolidinone-4-carboxylate (30): Yellow oil (55%). $[\alpha]_D^{20}$ = –22.4 (c = 1.02, CH_2Cl_2). IR (film): $\tilde{\nu}_{max}$ = 2981 (m), 2955 (w), 2905 (w), 1770 (s), 1751 (s), 1405 (m), 1375 (m), 1066 (s), 1025 (m) cm^{-1}. ^{1}H NMR (500 MHz, DMSO): δ = 1.05 (t, J = 7.0 Hz, 3 H, CHOCH$_2$CH_3), 1.13 (t, J = 7.0 Hz, 3 H, CHOCH$_2$CH_3), 1.21 (t, J = 7.0 Hz, 3 H, COOCH$_2$CH_3), 3.45–3.59 (m, 4 H, 2 × CHOCH_2CH$_3$), 4.07–4.17 (m, 2 H, COOCH_2CH$_3$), 4.20 (dd, J = 9.0, 3.7 Hz, 1 H, C*H*HOCON), 4.42 (dd, J = 9.0, 3.7 Hz, CHNCO), 4.53 (t, J = 9.0 Hz, 1 H, CH*H*OCON), 5.65 [s, 1 H, CH(OEt)$_2$] ppm. ^{13}C NMR (125 MHz, DMSO): δ = 13.8, 14.4, 14.7, 52.7, 61.1, 61.1, 62.2, 65.8, 100.8, 156.1, 170.6 ppm. MS (EI): m/z (%) = 261 (49) [M$^+$], 216 (90), 188 (100), 160 (95). HMRS: [M]$^+$, found 261.12092. $C_{11}H_{19}NO_6$ calcd. 261.12069.

(7a*R*)-5-Ethoxy-dihydro-1*H*-oxazolo[3,4-*c*]oxazol-3(5*H*)-one (31): *p*-Toluenesulfonic acid monohydrate (163 mg, 0.85 mmol) was added to a solution of the alcohol **18** (650 mg, 5.55 mmol) in triethyl orthoformate (11 mL). The reaction mixture was heated at reflux (150 °C) for 6 h. The triethyl orthoformate was evaporated and the resulting mixture purified by column chromatography (EtOAc/PE, 1:1) to give the orthoester as an unstable pale yellow liquid (205 mg, 22%). $[\alpha]_D^{20}$ = +61.85 (c = 1.24, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 2925 (w), 1732 (s), 1410, 1242, 1033 cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ = 1.19 (t, J = 7.1 Hz, 3 H, CH_3CH$_2$), *3*.62 (q, J = 7.1 Hz, 2 H, CH_2CH$_3$), 3.76 (br. t, J = 7.8 Hz, 1 H, C*H*HOCH), 4.26 (dd, J = 8.3, 7.1 Hz, 1 H, CH*H*OCH), 4.31–4.41 (m, 2 H, C*H*HOCO, CHNCO), 4.63 (dd, J = 9.1, 7.5 Hz, 1 H, CH*H*OCO), 6.02 (s, 1 H, EtOCHN) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 14.6, 54.8, 60.4, 67.7, 69.8, 107.1, 159.5 ppm. MS (CI$^+$): m/z (%) = 174 (28) [M + H], 146 (30), 128 (100), 118 (93), 100 (17). HRMS: [M + H], found 174.07685. $C_7H_{12}O_4N$ calcd. 174.07663.

(*S*)-4-[(*tert*-Butyldimethylsilyloxy)methyl]-3-(diethoxymethyl)-2-oxazolidinone (32): Colourless oil (60%). IR (film): $\tilde{\nu}_{max}$ = 2977, 2954, 2929, 2858, 1758 (s), 1408, 1250, 1099 (s), 1065 (s), 854, 837, 773 cm^{-1}. ^{1}H NMR (400 MHz, DMSO): δ = 0.02 (s, 3 H, CH_3Si), 0.04 (s, 3 H, CH_3Si), 0.84 [s, 9 H, C(CH$_3$)$_3$], 1.12 (t, J = 7.3 Hz, 3

H, CH_2CH_3), 1.13 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 3.46–3.60 (m, 4 H, 2 × CH_2CH_3), 3.67 (dd, J = 10.4, 2.9 Hz, 1 H, CHHOTBDMS), 3.71 (dd, J = 10.4, 4.5 Hz, 1 H, CHHOTBDMS), 3.98 (dtd, J = 8.5, 4.5, 2.9 Hz, 1 H, $CHCH_2O$), 4.11 (dd, J = 8.5, 4.5 Hz, 1 H, CHHO), 4.35 (t, J = 8.5 Hz, 1 H, CHHO), 5.64 [s, 1 H, $CH(OEt)_2$] ppm. ^{13}C NMR (100 MHz, DMSO): δ = –5.6, –5.5, 14.7, 17.8, 25.6, 52.3, 61.6, 61.8, 62.8, 65.5, 101.6, 156.9 ppm.

(*R*)-3-(Diethoxymethyl)-4-(4-methoxyphenyl)oxazolidin-2-one (33): Colourless oil (65%). $[\alpha]_D^{22}$ = –57.6 (c = 0.92, CH_2Cl_2). IR (film): $\tilde{\nu}_{max}$ = 2978, 2935, 2910, 1757, 1662, 1516, 1248 cm^{-1}. ^{1}H NMR (500 MHz, DMSO): δ = 0.68 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 1.14 (t, J = 7.0 Hz, 3 H, CH_3CH_2), 3.11 (dq, J = 9.3, 7.1 Hz, 1 H, $CHHCH_3$), 3.27–3.34 (m, 1 H, $CHHCH_3$), 3.48–3.59 (m, 2 H, CH_2CH_3), 3.72 (s, 3 H, OCH_3), 4.63 (dd, J = 8.8, 6.5 Hz, 1 H, CHHO), 4.63 (t, J = 8.8 Hz, 1 H, CHHO), 4.95 (dd, J = 8.8, 6.5 Hz, 1 H, CH_2CHN), 5.61 (s, 1 H, OCHO), 6.89 (d, J = 8.4 Hz, 2 H, Ar-H), 7.27 (d, J = 8.4 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, DMSO): δ = 14.0, 14.7, 54.6, 55.1, 61.1, 61.9, 70.5, 102.1, 113.6, 128.4, 132.0, 157.2, 158.9 ppm. MS (EI): m/z (%) = 295 (59) [M$^+$], 250 (100) [[M – C_2H_5O]$^+$], 194 (22), 162 (37), 134 (78), 103 (89), 75 (94). HRMS: [M]$^+$, found 295.14199. $C_{15}H_{21}NO_5$ calcd. 295.14197.

(*R*)-3-(Diethoxymethyl)-4-(4-methoxyphenyl)-5,5-dimethyloxazolidin-2-one (34): Colourless oil (86%). $[\alpha]_D^{20}$ = –60.7 (c = 0.56, CH_2Cl_2). IR (film): $\tilde{\nu}_{max}$ = 2979, 1753, 1614, 1515, 1392, 1291, 1249, 1178 cm^{-1}. ^{1}H NMR (500 MHz, DMSO): δ = 0.71 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 0.83 (s, 3 H, CH_3C), 1.14 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 1.45 (s, 3 H, CH_3C), 3.23 (dq, J = 9.2, 7.1 Hz, 1 H, $CHHCH_3$), 3.39 (dq, J = 9.2, 7.1 Hz, 1 H, $CHHCH_3$), 3.57 (dq, J = 9.4, 7.1 Hz, 2 H, 2 × $CHHCH_3$), 3.73 (s, 3 H, CH_3O), 4.58 (s, 1 H, ArCHN), 5.68 [s, 1 H, $CH(OEt)_2$], 6.89 (d, J = 8.7 Hz, 2 H, Ar-H), 7.14 (d, J = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, DMSO): δ = 14.1, 14.7, 23.2, 28.1, 55.0, 61.8, 61.9, 63.1, 82.3, 101.6, 113.3, 128.3, 129.9, 156.2, 158.8 ppm. MS: (EI): m/z (%) = 323 (10) [M + Na], 278 (11), 249 (7), 234 (14), 163 (39), 135 (19), 134 (10). HRMS: [M + Na], found 323.17353, $C_{17}H_{25}NO_5Na$ calcd. 323.17326.

General Procedure for Cyclopropanation Reactions: A solution of carbenoid precursor (1.25 mmol) in dry dichloromethane or ether (1.5 mL) was added by a motorised syringe pump over 6 h to a vigorously stirred mixture of zinc amalgam (0.82 g, 12.5 mmol) [or zinc dust (0.82 g, 12.5 mmol, 12.5 equiv.) and copper(I) chloride (82 mg, 0.83 mmol)], zinc chloride (1 M solution in diethyl ether, 1.25 mL, 1.25 mmol), chlorotrimethylsilane (0.79 mL, 6.25 mmol) and alkene (1.0 mmol) in dry diethyl ether (5.5 mL) under nitrogen at reflux. The mixture was stirred for 16 h and then cooled to room temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and after stirring for 20 min, the mixture was filtered and the separated zinc washed with dichloromethane (10 mL). The organic solvents were removed in vacuo and the aqueous layer was extracted with diethyl ether, dichloromethane, or ethyl acetate (3 × 10 mL).[31] The combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated to give the crude cyclopropane which was purified by column chromatography.

Procedure for One-Pot Cyclopropanation Reaction: Chlorotrimethylsilane (2.4 mL, 15.0 mmol) was added to a suspension of zinc (1.32 g, 20.1 mmol), CuCl (132 mg, 1.33 mmol) in diethyl ether (1 mL) and zinc chloride (1 M solution in Et_2O, 2.7 mL, 2.7 mmol). A solution of allylbenzene (160 mg, 1.35 mmol) in diethyl ether (2 mL) was added dropwise to the reaction mixture which was then heated to reflux. A solution of oxazolidinone **11** (349 mg, 2.71 mmol) in triethyl orthoformate (2.24 mL, 13.5 mmol) and CH_2Cl_2 (2 mL) was added dropwise by a motorised syringe pump (0.25 mL/h) to the reaction which was then heated under reflux overnight. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution (10 mL) and after stirring for 20 min, the mixture was filtered and the separated zinc washed with diethyl ether (10 mL). The aqueous layer was extracted with diethyl ether (3 × 10 mL) and the combined organic extracts were washed with brine (10 mL), dried ($MgSO_4$), filtered and concentrated to give the crude cyclopropane which was purified by column chromatography.

(±)-3-(Bicyclo[4.1.0]hept-7-yl)-4,5-diphenyl-2-oxazolidinone (35): White solid; **35a**: m.p. 154–156 °C. IR (film): $\tilde{\nu}_{max}$ = 3035 (w), 2929 (m), 2855 (w), 1755 (s), 1499 (w), 1455 (m), 1404 (m), 1218 (w), 1197 (w), 1121 (w), 1080 (w), 1026 (w) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): **35a**: δ = 0.86–1.06 (m, 2 H), 1.07–1.24 (m, 4 H), 1.48 (dddd, J = 10.0, 7.1, 3.4, 2.2 Hz, 1 H), 1.68–1.95 (m, 3 H), 2.10 (t, J = 3.4 Hz, 1 H, CHN), 4.86 (d, J = 8.0 Hz, 1 H, CHNCO), 5.75 (d, J = 8.0 Hz, 1 H, CHOCO), 6.89–6.93 (m, 2 H, Ar-H), 6.97–7.01 (m, 2 H, Ar-H), 7.05–7.14 (m, 6 H, Ar-H); **35b**: δ = 0.85 (dddd, J = 11.6, 9.5, 7.3, 2.1 Hz, 1 H), 1.15–2.11 (m, 9 H), 2.30 (t, J = 7.4 Hz, 1 H, CHN), 4.98 (d, J = 7.4 Hz, 1 H, CHNCO), 5.84 (d, J = 7.4 Hz, 1 H, CHOCO), 6.89–7.16 (m, 10 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): **35a**: δ = 17.5, 20.0, 21.0, 21.1, 22.0, 22.2, 36.1, 66.3, 79.5, 125.9, 127.7, 127.8, 128.1, 128.2, 134.6, 158.1; **35b**: δ = 12.3, 13.7, 18.7, 20.3, 22.3, 32.3, 67.0, 79.9, 126.0, 127.8, 127.9, 128.3, 128.4, 134.1, 159.6 ppm. MS (CI$^+$): m/z (%) = 334 (100) [M + H], 290 (100), 256 (16), 208 (12), 130 (11), 91 (6). HMRS: [M + H], found 334.18079. $C_{22}H_{24}NO_2$ calcd. 334.18069. $C_{22}H_{23}NO_2$ (333.43): calcd. C 79.25, H 6.95, N 4.20; found C 79.13, H 6.98, N 4.24.

(±)-(4*S*,5*R*)-3-[(1*S*,2*S*)-2-Cyclohexylcyclopropyl]-4,5-diphenyloxazolidin-2-one (36a) and (±)-(4*S*,5*R*)-3-[(1*R*,2*R*)-2-Cyclohexylcyclopropyl]-4,5-diphenyloxazolidin-2-one (36b): Fraction 1: mixture of **36a** and **36b** (33 mg) as a white solid; Fraction 2: **36a** as a white solid; **36a**: m.p. 146–148 °C. IR (film): $\tilde{\nu}_{max}$ = 2924 (s), 2851 (m), 1751 (s), 1456 (m), 1406 (s), 1265 (s), 1196 (m), 1078 (m), 1026 (m) cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): **36a**: δ = 0.28–0.37 (m, 1 H, CHCHCHN), 0.67–0.73 (m, 1 H, CHHCHN), 0.73–0.81 (m, 2 H, CHCHN, CHHCHN), 0.88–0.97 (m, 2 H, cy-H), 0.99–1.15 (m, 4 H, cy-H), 1.39–1.52 (m, 2 H, cy-H), 1.55–1.66 (m, 2 H, cy-H), 2.17 (dt, J = 6.7, 3.5 Hz, 1 H, CHN), 4.82 (d, J = 8.0 Hz, 1 H, CHNCO), 5.73 (d, J = 8.0 Hz, 1 H, CHOCO), 6.86–6.90 (m, 2 H, Ar-H), 6.95–6.99 (m, 2 H, Ar-H), 7.01–7.11 (m, 6 H, Ar-H) ppm; **36b**: δ = 0.36 (ddd, J = 7.2, 6.4, 5.5 Hz, 1 H, CHHCHN), 0.53–0.62 (m, 1 H, CHCHN), 0.67 (ddd, J = 9.2, 5.5, 3.6 Hz, 1 H, CHHCHN), 0.94–1.33 (m, 6 H, H-cy), 1.54–1.76 (m, 4 H, H-cy), 1.94–2.02 (m, 1 H, H-cy), 2.18 (dt, J = 7.2, 3.6 Hz, 1 H, CHN), 4.80 (d, J = 7.9 Hz, 1 H, CHNCO), 5.70 (d, J = 7.9 Hz, 1 H, CHOCO), 6.85–7.14 (m, 10 H, Ar-H); **36a**: ^{13}C NMR (125 MHz, $CDCl_3$): δ = 13.6, 25.7, 25.8, 26.2, 30.2, 32.1, 40.4, 66.8, 79.6, 125.9, 127.6, 127.7, 128.1, 128.2, 134.3, 134.5, 158.2; **36b**: δ = 10.9, 26.1, 26.4, 27.3, 30.5, 32.0, 32.4, 41.0, 66.6, 79.5, 126.0, 127.7, 127.8, 128.2, 128.4, 134.5, 134.8, 158.2 ppm. MS (EI): m/z (%) = 361 (3) [M$^+$], 278 (11), 234 (43), 180 (100), 165 (7), 132 (5), 104 (9), 77 (5) [Ph$^+$]. HMRS: [M]$^+$, found 361.20933, $C_{24}H_{27}NO_2$ calcd. 361.20417. $C_{24}H_{27}NO_2$ (361.48): calcd. C 79.74, H 7.53, N 3.87; found C 79.56, H 7.82, N 3.74.

(4*R*,5*S*)-4,5-Diphenyl-3-[(1*S*,2*R*)-2-phenylcyclopropyl]-2-oxazolidinone (37a), (4*R*,5*S*)-4,5-Diphenyl-3-[(1*R*,2*S*)-2-phenylcyclopropyl]-2-oxazolidinone (37b), (4*R*,5*S*)-4,5-Diphenyl-3-[(1*S*,2*S*)-2-phenylcyclopropyl]-2-oxazolidinone (37c) and (4*R*,5*S*)-4,5-Diphenyl-3-[(1*R*,2*R*)-2-phenylcyclopropyl]-2-oxazolidinone (37d): Fraction 1:

mixture of **37a**, **37b**, **37c** and **37d**, contaminated by traces of *N*-formyl-4,5-diphenyl-2-oxazolidinone, white solid; Fraction 2: **37a**, white solid; **37a**: m.p. 181–183 °C (EtOAc/hexane). $[\alpha]_D^{22}$ = +135.0 (c = 0.9, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3035 (w), 3000 (w), 2920 (w), 1738 (s), 1604 (w), 1499 (w), 1455 (m), 1403 (s), 1227 (m), 1194 (m), 1137 (w), 1134 (m) 1025 (s) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): **37a**: δ = 1.37 (dt, J = 7.4, 6.6 Hz, 1 H, C*H*HCHN), 1.37 (ddd, J = 10.0, 6.1, 4.2 Hz, 1 H, CH*H*CHN), 2.22 (ddd, J = 10.0, 6.6, 3.3 Hz, 1 H, C*H*CHN), 2.63 (dt, J = 7.4, 3.9 Hz, 1 H, CHN), 5.04 (d, J = 8.0 Hz, 1 H, CHNCO), 5.83 (d, J = 8.0 Hz, 1 H, CHOCO), 6.80–7.15 (m, 15 H, Ar-H); **37b**: δ = 1.05–1.29 (m, 2 H, C*H*$_2$CHN), 2.40–2.57 (m, 2 H, CHN and C*H*CHN), 4.94 (d, J = 7.9 Hz, 1 H, CHNCO), 5.81 (d, J = 7.9 Hz, 1 H, CHOCO), 6.72–7.44 (m, 15 H, Ar-H); **37c**: δ = 1.53 (dt, J = 9.0, 7.2 Hz, 1 H, C*H*HCHN), 1.96 (td, J = 7.2, 4.3 Hz, 1 H, CH*H*CHN), 2.15 (dt, J = 9.0, 7.2 Hz, 1 H, C*H*CHN), 2.60 (td, J = 7.2, 4.3 Hz, 1 H, CHN), 3.80 (d, J = 7.8 Hz, 1 H, CHNCO), 5.15 (d, J = 7.8 Hz, 1 H, CHOCO), 6.71–7.45 (m, 15 H, Ar-H); **37d**: δ = 1.05–1.15 (m, 2 H, C*H*$_2$CHN), 2.44 (dt, J = 8.8, 7.1 Hz, 1 H, C*H*CHN), 3.09 (ddd, J = 7.7, 7.1, 4.8 Hz, 1 H, CHN), 4.51 (d, J = 7.7 Hz, 1 H, CHNCO), 5.32 (d, J = 7.7 Hz, 1 H, CHOCO), 6.71–7.45 (m, 15 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): **37a**: δ = 15.9, 23.4, 33.9, 66.7, 79.7, 126.0, 126.3, 126.8, 127.6, 127.9, 128.1, 128.2, 128.4, 134.3, 134.4, 139.4, 157.9; **37b**: δ = 13.5, 24.9, 34.4, 66.4, 79.7, 126.3, 127.0, 127.4, 127.8, 127.9, 128.3, 129.0, 134.4, 134.6, 139.4, 158.6; **37c**: δ = 11.7, 22.5, 31.5, 65.4, 79.6, 125.8, 126.7, 127.6, 128.2, 128.3, 128.4, 133.8, 134.0, 136.5, 158.7; **37d**: δ = 9.9, 23.7, 31.7, 66.7, 79.7, 125.8, 126.0, 126.7, 127.0, 127.7, 128.2, 128.3, 128.4, 129.0, 134.0, 134.8, 136.5, 158.6 ppm. MS (EI): m/z (%) = 356 (2) [M + H], 240 (79), 220 (24), 180 (100), 117 (90), 91 (68), 77 (52). HMRS: [M + H], found 356.16306. $C_{24}H_{22}NO_2$ calcd. 356.16505. $C_{24}H_{21}NO_2$ (355.44): calcd. C 81.10, H 5.96, N 3.94; found C 80.91, H 5.92, N 3.95.

(±)-(4*S*,5*R*)-4,5-Diphenyl-3-[(1*S*,2*S*)-2-(trimethylsilyl)cyclopropyl]-oxazolidin-2-one (38): White solid; m.p. 145–146 °C. IR (film): $\tilde{\nu}_{max}$ = 3035 (w), 2955 (w), 1734 (s), 1499 (w), 1455 (w), 1409 (m), 1380 (m), 1247 (w), 1200 (m), 1135 (w), 1025 (w) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = –0.30 [s, 9 H, $Si(CH_3)_3$], –0.08 (ddd, J = 11.4, 8.2, 5.0 Hz, 1 H, C*H*CHN), 0.87 (ddd, J = 8.2, 6.2, 4.8 Hz, 1 H, C*H*HCHN), 1.23 (ddd, J = 11.4, 4.8, 3.2 Hz, 1 H, CH*H*CHN), 2.39 (ddd, J = 6.2, 5.0, 3.2 Hz, 1 H, CHN), 4.86 (d, J = 8.0 Hz, 1 H, CHNCO), 5.78 (d, J = 8.0 Hz, 1 H, CHNCO), 6.86–7.15 (m, 10 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 5.3, 11.5, 28.9, 66.9, 79.6, 125.9, 127.6, 127.8, 128.2, 128.3, 134.3, 134.4, 158.5 ppm. MS (CI^+): m/z (%) = 352 (100) [M + H], 308 (86), 292 (15), 230 (10), 180 (62), 130 (7), 100 (3), 73 (17). HMRS: [M + H], found 352.17348. $C_{21}H_{26}NO_2Si$ calcd. 352.17327. $C_{21}H_{25}NO_2Si$ (351.52): calcd. C 71.75, H 7.17, N 3.98; found C 71.92, H 7.18, N 3.98.

(±)-(4*S*,5*R*)-4,5-Diphenyl-3-[(1*S*,2*S*)-2-(tributylstannyl)cyclopropyl]-oxazolidin-2-one (39): White amorphous solid. IR (film): $\tilde{\nu}_{max}$ = 2959 (s), 2923 (s), 2872 (m), 2849 (m), 1748 (s), 1457 (m), 1374 (m), 1218 (m), 1025 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.02 (ddd, J = 11.5, 8.3, 5.1 Hz, 1 H, C*H*CHN), 0.48–0.64 (m, 6 H, 3 × CH_2), 0.82 (t, J = 7.2 Hz, 9 H, 3 × CH_3), 0.90 (ddd, J = 8.3, 5.9, 5.0 Hz, 1 H, C*H*HCHN), 1.10–1.33 (m, 13 H, 6 × CH_2 and CH*H*CHN), 2.44 (ddd, J = 5.9, 5.1, 3.0 Hz, 1 H, CHN), 4.80 (d, J = 7.9 Hz, 1 H, CHNCO), 5.73 (d, J = 7.9 Hz, 1 H, CHOCO), 6.86–6.90 (m, 2 H, Ar-H), 6.94–6.99 (m, 2 H, Ar-H), 7.01–7.11 (m, 6 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 0.8, 8.3, 11.9, 13.5, 27.1, 28.7, 29.1, 65.8, 79.7, 125.9, 127.5, 127.7, 127.8, 128.1, 128.2, 134.4, 134.5, 158.4 ppm. MS (EI): m/z (%) = 569 (2) [M^+], 512 (64), 398 (3), 332 (6), 288 (9), 234 (32), 180 (100), 143 (6), 91 (11). HMRS: [M + H], found 570.23942. $C_{30}H_{44}NO_2Sn$ calcd. 570.23885.

(4*R*,5*S*)-3-[(1*S*,2*S*)-2-(Benzyldimethylsilanyl)cyclopropyl]-4,5-diphenyl-2-oxazolidinone (40): White solid; m.p. 149–151 °C (EtOAc). $[\alpha]_D^{18}$ = +84.5 (c = 1.06, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3025 (w), 2921 (w), 1735 (s), 1452 (m), 1405 (m), 1247 (w), 1247 (m), 1028 (w), 814 (m, Si–C) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = –0.46 (s, 3 H, CH_3), –0.37 (s, 3 H, CH_3), –0.11 (ddd, J = 11.4, 8.3, 5.0 Hz, 1 H, C*H*CHN), 0.83 (ddd, J = 8.3, 6.3, 5.0 Hz, 1 H, C*H*HCHN), 1.23 (ddd, J = 11.4, 5.0, 3.4 Hz, 1 H, CH*H*CHN), 1.81 (d, J = 13.6 Hz, 1 H, C*H*HPh), 1.85 (d, J = 13.6 Hz, 1 H, CH*H*Ph), 2.37 (ddd, J = 6.3, 5.0, 3.4 Hz, 1 H, CHN), 4.76 (d, J = 8.0 Hz, 1 H, CHNCO), 5.72 (d, J = 8.0 Hz, 1 H, CHOCO), 6.82–7.18 (m, 15 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = –5.3, –4.8, 4.1, 11.6, 24.8, 29.0, 66.9, 79.6, 124.0, 125.9, 127.6, 127.8, 128.0, 128.1, 128.2, 128.3, 134.3, 134.4, 139.4, 158.4 ppm. MS (CI): m/z (%) = 426 (29) [M – H], 382 (100), 308 (26), 238 (16), 195 (57). HMRS: M – H, found 426.18798. $C_{27}H_{28}NO_2Si$ calcd. 426.18892. $C_{27}H_{29}NO_2Si$: calcd. C 75.84, H 6.84, N 3.38; found C 76.09, H 6.93, N 3.30.

(4*R*,5*S*)-3-[(1*S*,2*S*)-2-(4-Methoxybenzyl)cyclopropyl]-4,5-diphenyl-oxazolidin-2-one (41): Mixture of **41**, (4*S*,5*R*)-3-methyl-4,5-diphenyloxazolidin-2-one and (4*S*,5*R*)-4,5-diphenyloxazolidin-2-one (63% yield based on ^1H NMR). A pure sample was obtained by recrystallisation from ethyl acetate/PE; white needles; m.p. 162–163 °C (EtOAc/PE). $[\alpha]_D^{18}$ = +57.6 (c = 0.55, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3267, 3035, 1746, 1512, 1455, 1410, 1351, 1293, 1217 cm^{-1}. cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (ddd, J = 7.2, 6.0, 5.7 Hz, 1 H, C*H*HCHN), 1.21 (ddddd, J = 9.2, 7.7, 6.0, 5.5, 3.3 Hz, 1 H, C*H*CH$_2$Ar), 1.29 (ddd, J = 9.2, 5.7, 3.6 Hz, 1 H, CH*H*CHN), 2.10 (dd, J = 14.5, 7.7 Hz, 1 H, C*H*HAr), 2.30 (ddd, J = 7.2, 3.6, 3.3 Hz, 1 H, C*H*NCH$_2$), 2.53 (dd, J = 14.5, 5.5 Hz, 1 H, CH*H*Ar), 3.75 (s, 3 H, OMe), 4.69 (d, J = 7.9 Hz, 1 H, NC*H*Ph), 5.69 (d, J = 7.9 Hz, 1 H, OC*H*Ph), 6.64 (br. d, J = 8.7 Hz, 2 H, Ar-H), 6.77 (t, J = 6.9 Hz, 2 H, Ph), 6.79 (d, J = 8.7 Hz, 2 H, Ar-H), 6.93–6.96 (m, 2 H, Ph), 7.03–7.12 (m, 6H×, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.1, 21.1, 31.0, 36.7, 55.1, 66.7, 79.6, 113.7, 125.9, 127.5, 127.5, 127.7, 128.0, 128.2, 129.1, 132.2, 134.1, 134.2, 157.8, 158.0 ppm. MS (CI): m/z (%) = 400 (22) [M + H], 240 (100), 196 (74), 107 (27). HMRS: [M + H], found 400.19183, $C_{26}H_{26}NO_3$ calcd. 400.19127.

(±)-(4*S*,5*R*)-3-[(1*S*,2*S*)-2-Benzylcyclopropyl]-4,5-diphenyloxazolidin-2-one (42a) and (±)-(4*S*,5*R*)-3-[(1*R*,2*R*)-2-Benzylcyclopropyl]-4,5-diphenyloxazolidin-2-one (42b): Mixture of **42a**, **42b** and (4*S*,5*R*)-3-formyl-4,5-diphenyl-2-oxazolidinone (83% yield by ^1H NMR). IR (film): $\tilde{\nu}_{max}$ = 3064 (w), 3031 (w), 2920 (w), 1756 (s), 1606 (w), 1497 (w), 1451 (w), 1405 (m), 1217 (w), 1194 (w), 1137 (w), 1079 (w), 1026 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): **42a**: δ = 0.93 (dt, J = 7.0, 5.9 Hz, 1 H, C*H*HCHN), 1.24 (m, 1 H, C*H*CH$_2$Ph), 1.31 (ddd, J = 9.4, 5.7, 3.7 Hz, 1 H, CH*H*CHN), 2.18 (dd, J = 14.5, 7.7 Hz, 1 H, C*H*HPh), 2.31 (dt, J = 7.0, 3.5 Hz, 1 H, CHN), 2.57 (dd, J = 14.5, 5.6 Hz, 1 H, CH*H*Ph), 4.68 (d, J = 7.9 Hz, 1 H, CHNCO), 5.69 (d, J = 7.9 Hz, 1 H, CHOCO), 6.72–6.78 (m, 2 H, Ar-H), 6.86–6.97 (m, 4 H, Ar-H), 7.03–7.14 (m, 9 H, Ar-H); **42b**: δ = 0.53 (dt, J = 7.1, 6.2 Hz, 1 H, C*H*HCHN), 0.85 (ddd, J = 9.4, 5.6, 3.7 Hz, 1 H, CH*H*CHN), 1.61 (ddddd, J = 9.4, 8.6, 6.2, 5.5, 3.1 Hz, 1 H, C*H*CH$_2$Ph), 2.29 (dd, J = 14.8, 8.6 Hz, 1 H, C*H*HPh), 2.35 (dt, J = 7.0, 3.4 Hz, 1 H, CHN), 3.05 (dd, J = 14.8, 5.5 Hz, 1 H, CH*H*Ph), 4.80 (d, J = 7.9 Hz, 1 H, CHNCO), 5.74 (d, J = 7.9 Hz, 1 H, CHOCO), 6.70–7.15 (m, 15 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): **42a**: δ = 14.2, 20.9, 31.2, 37.7, 66.8, 79.7, 126.0, 126.1, 127.6, 127.8, 128.1, 128.2, 128.3, 128.4,

134.3, 140.3, 158.0; **42b**: δ = 12.3, 21.5, 31.5, 37.9, 66.5, 79.7, 126.0, 127.6, 127.9, 128.3, 128.5, 134.7, 140.3, 158.3 ppm. MS (CI^+): *m*/*z* (%) = 370 (100) [M + H], 354 (8), 326 (52), 292 (13), 278 (17), 248 (12), 234 (19), 208 (7), 197 (12), 180 (37), 131 (17), 117 (11), 91 (19), 77 (4). HMRS: [M + H], found 370.18044. $C_{25}H_{24}NO_2$ calcd. 370.18069.

(4*R*,5*S*)-3-[(1*R*,2*S*)-1,1a,6,6a-Tetrahydrocyclopropainden-1-yl]-4,5-diphenyloxazolidin-2-one (43): White needles; m.p. 168–170 °C (Et_2O/PE). $[\alpha]_D^{22}$ = –27.4 (*c* = 0.19, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3066, 3031, 2907, 1749, 1497, 1478, 1455, 1436, 1386, 1352, 1312, 1213, 1193, 1141 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = –2.35 (dtd, *J* = 9.3, 6.7, 2.9 Hz, 1 H, C*H*CH_2Ar), 2.59 (t, *J* = 6.7 Hz, 1 H, CH_2CHC*H*N), 2.80 (t, *J* = 6.7 Hz, 1 H, C*H*Ar), 3.23–3.33 (m, 2 H, CH_2Ar), 3.82 (d, *J* = 7.7 Hz, NC*H*Ph), 4.91 (d, *J* = 7.7 Hz, OC*H*Ph), 6.75–6.80 (m, 2 H, Ar-H), 6.79–6.82 (m, 2 H, Ar-H), 6.98–7.00 (m, 3 H, Ar-H), 7.11–7.13 (m, 3 H, Ar-H), 7.24–7.29 (m, 3 H, Ar-H), 7.35–7.38 (m, 1 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 23.2, 29.0, 32.1, 33.6, 65.0, 79.9, 124.2, 124.7, 125.7, 126.1, 126.8, 127.6, 127.7, 127.7, 128.2, 128.3, 133.9, 134.3, 139.5, 144.4, 159.2 ppm. MS (EI): *m*/*z* (%) = 368 (60) [M + H], 324 (40), 180 (100). HMRS: [M + H], found 368.16426, $C_{25}H_{22}NO_2$ calcd. 368.16505.

(*R*)-Ethyl 2-[(9*H*-Fluoren-9-yl)methoxycarbonyl]-3-{(1*R*,2*R*)-2-[(4*R*,5*S*)-2-oxo-4,5-diphenyloxazolidin-3-yl]cyclopropyl}propanoate (44): Colourless oil. $[\alpha]_D^9$ = +37.6 (*c* = 0.54, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3296, 2928, 1744, 1533, 1452, 1410 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.79–0.84 (m, 1 H, C*H*HCHNCH), 1.23–1.26 (m, 2 H, CH*H*CHNCH and C*H*CHN), 1.45 (t, *J* = 7.0 Hz, CH_3), 1.52–1.59 (m, 1 H, C*H*HCHCO$_2$Et), 2.00–2.06 (m, 1 H, CH*H*CHCO$_2$Et), 2.46–2.50 (m, 1 H, CHC*H*N), 4.25–4.36 (m, 3 H, CH_2CH$_3$ and CHC*H*HO), 4.41 = 4.47 (m, 2 H, C*H*CO$_2$Et and C*H*CHHO), 4.53 (dd, *J* = 10.1 and 6.7 Hz, 1 H, CHCH*H*O), 5.04 (br. d, *J* = 7.3 Hz, 1 H, NC*H*Ph), 5.80 (d, *J* = 7.6 Hz, 1 H, OC*H*Ph), 6.11 (br. d, *J* = 7.3 Hz, 1 H, NH), 6.91–6.93 (m, 2 H, Ar-H), 6.95–6.98 (m, 2 H, Ar-H), 7.05–7.08 (m, 6 H, Ar-H), 7.31–7.35 (m, 2 H, Ar-H), 7.41 (t, *J* = 7.3 Hz, 2 H, Ar-H), 7.63 (br. d, *J* = 6.7 Hz, 1 H, Ar-H), 7.65 (br. d, *J* = 6.7 Hz, 1 H, Ar-H), 7.76 (d, *J* = 7.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 12.2, 14.1, 31.8, 34.9, 47.1, 53.6, 61.5, 66.3, 66.9, 80.0, 120.0, 125.2, 125.4, 125.9, 127.0, 127.1, 127 ppm. 6, 127.7, 127.8, 128.3, 134.2, 134.7, 141.3, 143.7, 144.0, 156.1, 158.6, 171.7. MS (FAB): *m*/*z* (%) = 639 (100) [M + Na], 360 (15), 262 (17). HMRS: M + Na, found 639.24613, $C_{38}H_{36}N_2NaO_6$ calcd. 639.24709.

(*S*)-3-[(1*S*,2*S*)-2-Benzylcyclopropyl]-4-isopropyloxazolidin-2-one (45): Pale grey oil. $[\alpha]_D^{20}$ = –42.1 (*c* = 0.95, $CHCl_3$). IR (*trans*, film): $\tilde{\nu}_{max}$ = 2962, 1755 (s), 1420 (s), 1227, 1051 cm^{-1}. ^1H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.62 (d, *J* = 7.0 Hz, 3 H, CH_3CCH$_3$), 0.76 (d, *J* = 7.0 Hz, 3 H, CH$_3$CCH_3), 0.96–1.02 (m, 1 H, C*H*HCHN), 1.17–1.24 (m, 2 H, CH*H*CHN, C*H*CHN), 1.49–1.59 (m, 1 H, CHMe$_2$), 2.23 (dt, *J* = 7.0, 3.5 Hz, 1 H, CHN), 2.28–2.34 (m, 1 H, C*H*HPh), 2.86 (dd, *J* = 14.5, 5.4 Hz, 1 H, CH*H*Ph), 3.32 (dt, *J* = 8.9, 3.9 Hz, 1 H, C*H*CH$_2$O), 3.96 (dd, *J* = 8.9, 3.9 Hz, 1 H, C*H*HO), 4.03 (t, *J* = 8.9 Hz, 1 H, CH*H*O), 7.18–7.24 (m, 3 H, Ar-H), 7.27–7.32 (m, 2 H, Ar-H) ppm. ^{13}C NMR (*trans*, 125 HHz, $CDCl_3$): δ = 14.1, 15.6, 17.6, 20.5, 27.5, 29.6, 38.2, 60.9, 62.4, 126.3, 128.3, 128.5, 140.7, 158.0 ppm. MS (EI): *m*/*z* (%) = 260 (100) [M + H]. HRMS: [M + H], found 260.16466. $C_{16}H_{22}NO_2$ calcd. 260.16451.

(4S)-3-[(1*S*,2*R*)-1,1a,6,6a-Tetrahydro-cyclopropainden-1-yl]-4-isopropyloxazolidin-2-one (46): White solid; m.p. 87–89 °C diethyl ether). $[\alpha]_D^{20}$ = –13.5 (*c* = 1.02, $CHCl_3$). IR (*cis*, film): $\tilde{\nu}_{max}$ = 2964 (w), 1744 (s), 1412, 1227, 1047 cm^{-1}. ^1H NMR (*cis*, 500 MHz, $CDCl_3$): δ = 0.76 (d, *J* = 7.0 Hz, 3 H, CH_3CCH$_3$), 0.89 (d, *J* = 7.0 Hz, 3 H, CH$_3$CCH_3), 2.00–2.07 (m, 1 H, CHMe$_2$), 2.34 (qd, *J* = 6.8, 1.2 Hz, 1 H, C*H*CH$_2$Ar), 2.41 (dt, *J* = 8.6, 3.1 Hz, 1 H, C*H*CH$_2$O), 2.78 (td, *J* = 6.8, 1.4 Hz, 1 H, CHAr), 2.83 (t, *J* = 6.8 Hz, 1 H, CHN), 3.11 (br. d, *J* = 17.8 Hz, 1 H, C*H*HAr), 3.19 (dd, *J* = 17.8, 6.8 Hz, 1 H, CH*H*Ar) 3.48 (t, *J* = 8.8 Hz, 1 H, C*H*HO), 3.77 (dd, *J* = 8.8, 2.8 Hz, 1 H, CH*H*O), 7.10–7.20 (m, 3 H, Ar-H), 7.31 (d, *J* = 6.6 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (*cis*, 125 HHz, $CDCl_3$): δ = 15.3, 17.5, 23.3, 29.0, 29.2, 31.7, 32.9, 58.8, 63.4, 124.2, 124.5, 126.0, 126.7, 139.4, 144.2, 159.2 ppm. MS (CI^+): *m*/*z* (%) = 258 (100) [M + H], 142 (34), 129 (47), 85 (68). HRMS: [M + H], found 258.14954. $C_{16}H_{20}NO_2$ calcd. 258.14886.

(*S*)-3-[(1*S*,2*R*)-2-*tert*-Butylcyclopropyl]-4-isopropyloxazolidin-2-one (47): White solid; m.p. 53–55 °C (PE). $[\alpha]_D^{19}$ = –49.3 (*c* = 0.73, $CHCl_3$). IR (*trans*, film): $\tilde{\nu}_{max}$ = 2961, 1728 (s), 1423, 1236, 1055 (w) cm^{-1}. ^1H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.86 (br. s, 9 H, 3 × CCH$_3$), 0.87–0.92 (m, 9 H, 2 × CHCH_3, CH_2CHN, C*H*CHN), 2.20–2.25 (m, 1 H, CHMe$_2$), 2.27 (dt, *J* = 7.3, 3.6 Hz, 1 H, CHN), 3.51–3.56 (m, 1 H, C*H*CH$_2$O), 4.02–4.11 (m, 2 H, CH$_2$OCO) ppm. ^{13}C NMR (*trans*, 125 HHz, $CDCl_3$): δ = 10.9, 14.0, 17.7, 26.6, 27.9, 28.4, 29.0, 30.7, 61.2, 62.2, 158.0 ppm. MS (CI^+): *m*/*z* (%) = 226 (56) [M + H], 170 (100), 149 (46), 85 (81). HRMS: [M + H], found 226.17987. $C_{13}H_{24}NO_2$ calcd. 226.18070.

{(1*S*,2*S*)-2-[(*S*)-4-Isopropyl-2-oxooxazolidin-3-yl]cyclopropyl}methyl Benzoate (48): White solid; m.p. 58–59 °C diethyl ether). $[\alpha]_D^{20}$ = –9.6 (*c* = 0.8, $CHCl_3$). IR (*trans*, film): $\tilde{\nu}_{max}$ = 2885 (w), 1765 (s), 1726 (s), 1425, 1281, 1117 (w), 1049 (w) cm^{-1}. ^1H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.72 (d, *J* = 7.0 Hz, 3 H, CH_3CCH$_3$), 0.87 (d, *J* = 7.0 Hz, 3 H, CH$_3$CCH_3), 1.09–1.14 (m, 1 H, C*H*HCHN), 1.31–1.35 (m, 1 H, CH*H*CHN), 1.46–1.54 (m, 1 H, C*H*CHN), 2.18–2.25 (m, 1 H, CHMe$_2$), 2.47 (dt, *J* = 7.2, 3.6 Hz, 1 H, C*H*N), 3.56 (dt, *J* = 8.9, 3.9 Hz, 1 H, C*H*CH$_2$O), 3.88 (dd, *J* = 11.7, 9.2 Hz, 1 H, C*H*HOCOPh), 4.04 (dd, *J* = 8.9, 3.9 Hz, 1 H, C*H*HOCO), 4.12 (t, *J* = 8.9 Hz, 1 H, CH*H*OCO), 4.56 (dd, *J* = 11.7, 5.5 Hz, 1 H, CH*H*COOPh), 7.42–7.48 (m, 2 H, Ar-H), 7.55–7.60 (m, 1 H, Ar-H), 8.02–8.05 (m, 2 H, Ar-H) ppm. ^{13}C NMR (*trans*, 125 HHz, $CDCl_3$): δ = 13.2, 14.2, 17.6, 17.9, 27.8, 29.3, 61.1, 62.5, 66.5, 128.4, 129.5, 129.9, 133.2, 157.8, 166.4 ppm. MS (EI): *m*/*z* (%) = 326 (100) [M + Na], 301 (28), 247 (32), 212 (15), 182 (52), 166 (33). HRMS: M + Na, found 326.13712. $C_{17}H_{21}NNaO_4$ calcd. 326.13683.

(*S*)-4-Isopropyl-3-[(1*R*,1a*R*,7b*R*)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-1-yl]oxazolidin-2-one (49a) and (*S*)-4-Isopropyl-3-[(1*S*,1a*R*,7b*R*)-1a,2,3,7b-tetrahydro-1*H*-cyclopropa[*a*]naphthalen-1-yl]oxazolidin-2-one (49b): Fraction 1: Mixture of **49a** and oxazolidinone **11**, white solid; Fraction 2: **49b**, yellow-orange oil; **49b**: $[\alpha]_D^{17}$ = –50.6 (*c* = 0.8, $CHCl_3$); **49b**: IR (film): $\tilde{\nu}_{max}$ = 2483 (w), 2928, 1747 (s), 1418 (s), 1229, 1107, 1051 cm^{-1}. **49a**: ^1H NMR (*endo*, 500 MHz, $CDCl_3$): δ = 0.67 (d, *J* = 7.0 Hz, 3 H, CH_3CCH$_3$), 0.87 (d, *J* = 7.0 Hz, 3 H, CH$_3$CCH_3), 1.87–2.00 (m, 1 H, C*H*CHN), 1.93–2.00 (m, 1 H, C*H*HCH$_2$Ar), 2.00–2.08 (m, 1 H, C*H*Me$_2$), 2.26 (br. t, *J* = 8.2 Hz, 1 H, CHN), 2.42–2.52 (m, 2 H, C*H*HAr, CH*H*CH$_2$Ar), 2.58 (dt, *J* = 8.7, 3.0 Hz, 1 H, C*H*CH$_2$O), 2.70–2.76 (m, 1 H, CH*H*Ar), 2.81 (t, *J* = 7.4 Hz, 1 H, CHAr), 3.75 (t, *J* = 8.8 Hz, 1 H, C*H*HO), 3.86 (dd, *J* = 9.0, 2.9 Hz, 1 H, CH*H*O); **49a**: ^{13}C NMR (125 HHz, $CDCl_3$): δ = 15.0, 17.3, 17.4, 19.0, 19.5, 27.4, 28.4, 35.4, 58.7, 63.7, 126.0, 126.4, 129.0, 130.0, 132.6, 135.6, 159.2 ppm. **49b**: ^1H NMR (500 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 7.0 Hz, 3 H, CH_3CCH$_3$), 0.90 (d, *J* = 7.0 Hz, 3 H, CH$_3$CCH_3), 1.77 (tdd, *J* = 13.4, 6.0, 3.0 Hz, 1 H, C*H*HCH$_2$Ar), 2.04–2.11 (m, 3 H, CHAr, C*H*CHN, C*H*Me$_2$), 2.42(ddt, *J* = 13.4, 6.6, 1.9 Hz, 1 H, CH*H*CH$_2$Ar), 2.46–2.57 (m, 1 H, C*H*HAr), 2.66 (t, *J* = 3.0 Hz, 1 H, CHN), 2.68–2.70 (m, 1 H, CH*H*Ar), 3.74 (dt, *J* = 8.8, 3.9 Hz,

1 H, C*H*CH_2O), 4.08 (dd, *J* = 9.0, 4.3 Hz, 1 H, C*H*HO), 4.21 (t, *J* = 8.9 Hz, 1 H, CH*H*O), 7.02 (d, *J* = 7.3 Hz, 1 H, Ar-H), 7.11–7.18 (m, 2 H, Ar-H), 7.25–7.28 (m, 1 H, Ar-H) ppm; **49b**: ^{13}C NMR (125 HHz, $CDCl_3$): δ = 15.0, 17.6, 18.1, 22.7, 24.3, 26.0, 28.4, 32.6, 60.8, 63.0, 125.9, 126.2, 128.5, 128.9, 134.2, 134.9, 157.8 ppm. MS (CI^+): *m*/*z* (%) = 272 (100) [M + H], 179 (37), 142 (40), 136 (24). HRMS: [M + H], found 272.16374. $C_{17}H_{22}NO_2$ calcd. 272.16505.

(4*S*,5*R*)-3-[(1*S*,2*R*)-2-*tert*-Butylcyclopropyl]-4-methyl-5-phenyloxazolidin-2-one (50): Obtained as a mixture with oxazoldinone **15**; Pale yellow semi-solid. IR (*trans*, film): $\tilde{\nu}_{max}$ = 2955, 1789, 1746, 1711, 1404, 1364, 1221, 1152, 1100 cm^{-1}. ^{1}H NMR (*trans*, 600 MHz, $CDCl_3$): δ = 0.86 (d, *J* = 6.7 Hz, 3 H, CHC*H*$_3$), 0.91 [s, 9 H, C(C*H*$_3$)$_3$], 0.95–1.00 (m, 3 H, C*H*$_2$CHN, C*H*CHN), 2.39 (dt, *J* = 6.8, 3.8 Hz, 1 H, CHN), 3.91–3.94 (m, 1 H, C*H*CH$_3$), 5.51 (d, *J* = 7.5 Hz, 1 H, CHO), 7.30–7.47 (m, 5 H, Ar-H) ppm. ^{13}C NMR (*trans*, 150 HHz, $CDCl_3$): δ = 11.2, 14.2, 26.7, 28.5, 30.5, 57.4, 78.3, 125.9, 128.6, 134.9, 157.7 ppm. MS (CI^+): *m*/*z* (%) = 274 (100) [M + H], 230 (30), 178 (57), 134 (70). HRMS: [M + H], found 274.17962, $C_{17}H_{24}NO_2$ calcd. 274.18070.

(*S*)-3-[(1*S*,2*S*)-2-Benzylcyclopropyl]-4-ethyloxazolidin-2-one (51): Pale yellow oil. $[\alpha]_D^{22}$ = –34.2 (*c* = 1.0, $CHCl_3$). IR (*trans*, film): $\tilde{\nu}_{max}$ = 2966 (w), 1755 (s), 1420, 1219 (w), 1061 cm^{-1}. ^{1}H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.71 (t, *J* = 7.5 Hz, 3 H, CH_3), 0.94–1.00 (m, 1 H, C*H*HCHN), 1.17–1.30 (m, 3 H, CH*H*CHN, C*H*CHN, C*H*HCH$_3$), 1.33–1.41 (m, 1 H, CH*H*CH$_3$), 2.25 (dt, *J* = 7.0, 3.5 Hz, 1 H, CHN), 2.38 (dd, *J* = 14.4, 7.8 Hz, 1 H, C*H*HPh), 2.83 (dd, *J* = 14.4, 6.0 Hz, 1 H, CH*H*Ph), 3.34–3.40 (m, 1 H, C*H*CH$_2$O), 3.88 (dd, *J* = 8.6, 4.6 Hz, 1 H, C*H*HO), 4.17 (t, *J* = 8.6 Hz, 1 H, CH*H*O), 7.19–7.25 (m, 3 H, Ar-H), 7.28–7.33 (m, 2 H, Ar-H) ppm. ^{13}C NMR (*trans*, 125 HHz, $CDCl_3$): δ = 8.0, 15.4, 20.4, 24.3, 29.6, 38.2, 57.6, 66.3, 126.3, 128.3, 128.5, 140.7, 157.8 ppm. MS (EI): *m*/*z* (%) = 268 (100) [M + Na], 246 (19). HRMS: M + Na, found 268.13074. $C_{15}H_{19}O_2Na$ calcd. 268.13080.

(*S*)-3-[(1*S*,2*R*)-2-Cyclohexylcyclopropyl]-4-isobutyloxazolidin-2-one (52): Pale yellow semi-solid. $[\alpha]_D^{20}$ = –74.0 (*c* = 1.71, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 2928, 1751, 1418, 1261, 1070, 1018 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.55–0.64 (m, 1 H, C*H*CHCHN), 0.70–0.77 (m, 2 H, C*H*CHN, C*H*HCHN), 0.90 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$CCH$_3$), 0.94 (d, *J* = 6.6 Hz, 3 H, CH$_3$CC*H*$_3$), 0.95–0.97 (m, 1 H, CH*H*CHN), 1.00–1.05 (m, 1 H, C*H*HCHCH$_2$), 1.08–1.20 (m, 4 H, C*H*HCH$_2$CH, C*H*HCH$_2$CH, C*H*HCH$_2$CH$_2$, C*H*HCHCH$_2$), 1.41 (ddd, *J* = 13.3, 11.0, 4.3 Hz, 1 H, C*H*HCHMe$_2$), 1.50–1.58 (m, 1 H, CHMe$_2$), 1.58–1.63 (m, 1 H, CH*H*CH$_2$CH$_2$), 1.65–1.72 (m, 3 H, CH*H*CH$_2$CH, CH*H*CH$_2$CH, CH*H*CHCH$_2$), 1.76 (ddd, *J* = 13.3, 9.8, 2.9 Hz, 1 H, CH*H*CHMe$_2$), 1.80–1.88 (m, 1 H, CH*H*CHCH$_2$), 2.15 (dt, *J* = 6.5, 3.6 Hz, 1 H, CHN), 3.56–3.66 (m, 1 H, C*H*CH$_2$O), 3.91 (dd, *J* = 8.6, 4.6 Hz, 1 H, CH*H*O), 4.19 (dd, *J* = 8.7, 8.3 Hz, 1 H, C*H*HO) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 21.7, 23.8, 24.6, 25.5, 25.9, 26.0, 26.3, 28.8, 32.2, 33.0, 40.7, 40.8, 55.5, 67.1, 157.7 ppm. MS (EI): *m*/*z* (%) = 266 (26) [M + H], 182 (100), 126 (31), 113 (23). HRMS: $[M]^+$, found 265.20434. $C_{16}H_{27}O_2N$ calcd. 265.20417.

(*S*)-3-[(1*S*,2*S*)-2-(4-Methoxybenzyl)cyclopropyl]-4-isobutyloxazolidin-2-one (53): Obtained as a mixture with (*S*)-4-isobutyl-3-methyloxazolidin-2-one; pale orange oil. $[\alpha]_D^{10}$ = +10.68 (*c* = 1.46, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 2959, 1755 (s), 1512, 1417 (w), 1248, 1038. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.67 (d, *J* = 6.5 Hz, 3 H, CH$_3$CHC*H*$_3$), 0.82 (d, *J* = 6.5 Hz, 3 H, C*H*$_3$CHCH$_3$), 0.90–1.00 (m, 2 H, C*H*$_2$CHN), 1.1–1.35 (m, 4 H, CHMe$_2$, C*H*$_2$CHMe$_2$, C*H*CHN), 2.29 (dt, *J* = 6.9, 3.4 Hz, 1 H, CHN), 2.31 (dd, *J* = 14.4, 7.4 Hz, 1 H, CH*H*Ar), 2.77 (dd, *J* = 14.4, 5.8 Hz, 1 H, C*H*HAr), 3.42–3.51 (m, 1 H, C*H*CH$_2$O), 3.79 (s, 3 H, OCH$_3$), 3.89 (dd, *J* = 8.5, 5.2 Hz, 1 H, CH*H*O), 4.19 (t, *J* = 8.5 Hz, 1 H, C*H*HO), 6.85 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.13 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4, 21.0, 21.2, 23.6, 24.3, 29.2, 37.6, 40.5, 55.2, 67.8, 114.1, 129.4, 132.7, 157.7, 158.1 ppm. MS (CI^+): *m*/*z* (%) = 304 (75) [M + H], 182 (22), 134 (58), 121 (100). HRMS: [M + H], found 304.19154. $C_{18}H_{26}O_3N$ calcd. 304.19126.

(*R*)-3-[(1*R*,2*R*)-4-(Hydroxymethyl)-2-(4-methoxybenzyl)cyclopropyl]oxazolidin-2-one (54): Yellow oil. $[\alpha]_D^{20}$ = +13.0 (*c* = 0.55, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3408, 3057, 2924, 1736 (s), 1612 (w), 1512, 1427, 1267, 1244, 1092 (w), 1036 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.91–0.96 (m, 1 H, CH*H*CHN), 1.12–1.17 (m, 1 H, CH*H*CHN), 1.19–1.23 (m, 1 H, C*H*CHN), 2.25 (dt, *J* = 6.7, 3.5 Hz, 1 H, CHN), 2.38 (dd, *J* = 14.6, 7.6 Hz, 1 H, CH*H*Ph), 2.72 (dd, *J* = 14.6, 6.4 Hz, 1 H, C*H*HPh), 3.33 (dd, *J* = 10.7, 3.2 Hz, C*H*HOH) ppm. 3.36 (dd, *J* = 10.7, 5.0 Hz, CH*H*OH), 3.47–3.53 (m, 1 H, C*H*CH$_2$O), 3.79 (s, 3 H, OCH$_3$), 4.10 (dd, *J* = 8.6, 4.2 Hz, C*H*HOCO), 4.16 (t, *J* = 8.6, CH*H*OCO), 6.84 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.12 (d, *J* = 8.7 Hz, 2 H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.4, 20.4, 29.6, 37.3, 55.2, 57.5, 60.7, 64.6, 113.9, 129.3, 132.6, 158.1, 158.2 ppm. MS (CI^+): *m*/*z* (%) = 278 (33) [M + H], 161 (40), 134 (20), 121 (100). HRMS: M + H, found 278.13742. $C_{15}H_{20}O_4N$ calcd. 278.13868.

(*R*)-3-[(1*R*,2*R*)-2-Benzylcyclopropyl]-4-(4-methoxyphenyl)oxazolidin-2-one (55a) and (*R*)-3-[(1*S*,2*S*)-2-Benzylcyclopropyl]-4-(4-methoxyphenyl)oxazolidin-2-one (55b): Pale yellow oil. IR (mixture cyclopropanes, film): $\tilde{\nu}_{max}$ = 2917 (w), 1747 (s), 1612, 1513, 1407, 1245 (s), 1176, 1028 (s) cm^{-1}. **55a**: ^{1}H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.71–0.8 (m, 1 H, C*H*HCHN), 1.10–1.28 (m, 2 H, CH*H*CHN, C*H*CH$_2$Ph), 2.09 (dt, *J* = 7.1, 3.5 Hz, 1 H, C*H*N), 2.35 (dd, *J* = 14.5, 6.2 Hz, 1 H, C*H*HPh), 2.46 (dd, *J* = 14.5, 6.4 Hz, CH*H*Ph), 3.82 (s, 3 H, OCH$_3$), 4.02–4.08 (m, 1 H, C*H*HO), 4.42–4.48 (m, 2 H, CH*H*O, C*H*CH$_2$O), 6.81–6.92 (m, 2 H, Ar-H), 6.96–7.08 (m, 3 H, Ar-H), 7.09–7.30 (m, 4 H, Ar-H) ppm; **55a**: ^{13}C NMR (*trans*, 125 HHz, $CDCl_3$): δ = 13.7, 20.1, 30.6, 37.8, 55.4, 60.8, 69.7, 114.5, 126.1, 128.0, 128.4, 128.5, 130.6, 140.2, 157.9, 159.9 ppm; **55b**: ^{1}H NMR (*trans*, 500 MHz, $CDCl_3$): δ = 0.50–0.56 (m, 1 H, C*H*HCHN), 0.80–0.89 (m, 1 H, CH*H*CHN), 1.31–1.39 (m, 1 H, C*H*CH$_2$Ph), 2.14 (dt, *J* = 7.1, 3.5 Hz, 1 H, C*H*N), 2.23 (dd, *J* = 14.7, 8.0 Hz, 1 H, C*H*HPh), 2.78 (dd, *J* = 14.7, 5.6 Hz, CH*H*Ph), 3.81 (s, 3 H, OCH$_3$), 4.08–4.12 (m, 1 H, C*H*HO), 4.50–4.60 (m, 2 H, CH*H*O, C*H*CH$_2$O), 6.81–6.92 (m, 2 H, Ar-H), 6.96–7.08 (m, 3 H, Ar-H), 7.09–7.30 (m, 4 H, Ar-H) ppm; **55b**: ^{13}C NMR (*cis*, 125 HHz, $CDCl_3$): δ = 12.1, 20.6, 31.3, 38.0, 55.4, 61.0, 69.8, 114.5, 126.1, 128.1, 128.2, 128.3, 130.7, 140.3, 158.3, 160.0 ppm. MS (EI): *m*/*z* (%) = 323 (8) [M^+], 232 (55), 134 (100), 121 (50), 91 (25). HRMS: $[M]^+$, found 323.15083. $C_{20}H_{21}O_3N$ calcd. 323.15083.

(*R*)-3-[(1*R*,2*R*)-2-Benzylcyclopropyl]-4-(4-methoxyphenyl)-5,5-dimethyloxazolidin-2-one (56): Obtained as a mixture with 3-formyl-4-(4-methoxyphenyl)-5,5-dimethyloxazolidin-2-one (36% yield by ^{1}H NMR). Colourless oil. IR (film): $\tilde{\nu}_{max}$ = 2988, 2838, 1748, 1612, 1514, 1403, 1250, 1177 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.88 (s, 3 H, C*H*$_3$C), 1.06–1.15 (m, 1 H, C*H*CH$_2$Ph), 1.22–1.27 (m, 2 H, C*H*$_2$CHN), 1.41 (s, 3 H, C*H*$_3$C), 2.20 (dd, *J* = 14.6, 7.6 Hz, 1 H, C*H*HPh), 2.25 (dt, *J* = 7.1, 3.5 Hz, 1 H, CHN), 2.50 (dd, *J* = 14.6, 6.0 Hz, 1 H, CH*H*Ph), 3.83 (s, 3 H, CH$_3$O), 4.01 (s, 1 H, NC*H*Ar), 6.83–6.94 (m, 6 H, Ar), 7.14–7.17 (m, 3 H, Ar) ppm. ^{13}C NMR (100 HHz, $CDCl_3$): δ = 14.1, 20.7, 23.7, 28.4, 30.9, 37.8, 55.2, 70.4, 80.8, 114.1, 125.9, 127.7, 128.2, 128.3, 140.2, 157.3, 159.6 ppm. MS (EI): *m*/*z* (%) = 351 (5) [M^+], 249 (40), 216 (70), 191 (8), 162 (100). HRMS: M^+, found 351.18309, $C_{22}H_{25}NO_3$ calcd. 351.18343.

General Procedure for Hydrogenolysis of the Diphenyloxazolidinone Auxiliary: A mixture of cyclopropane (0.3 mmol, 1 equiv.), di-*tert*-

butyl dicarbonate (131 mg, 0.6 mmol, 2 equiv.), $Pd(OH)_2$/C (20%, 52 wt.-% water, 86 mg, 0.06 mmol, 0.2 equiv.) and THF (10 mL) was hydrogenated at 5.5 bar/35 °C for 8 h. The reaction mixture was filtered, concentrated in vacuo and purified by flash column chromatography to give the carbamate.

***exo-tert*-Butyl *N*-(Bicyclo[4.1.0]hept-7-yl)carbamate (60):** White solid; m.p. 103–104 °C (hexane); R_f (PE 30–40 °C/diethyl ether, 85:15) = 0.38. IR (film): $\tilde{\nu}_{max}$ = 3340 (br., NH), 2925 (m), 2852 (w), 1682 (s), 1518 (m), 1366 (m), 1251 (m), 1170 (m), 1143 (m) 1058 (w) cm^{-1}. ^1H NMR (500 MHz, 330 K, $CDCl_3$): δ = 0.93–0.96 (m, 2 × CH), 1.04–1.13 (m, 2 H), 1.17–1.25 (m, 2 H), 1.42 (s, 9 H, 3 × CH_3), 1.64–1.71 (m, 2 H), 1.80–1.88 (m, 2 H), 2.16–2.19 (m, 1 H, C*H*NH), 4.53 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, 330 K, $CDCl_3$): δ = 19.4, 21.5, 22.5, 28.5, 34.8, 79.1, 156.6 ppm. MS (CI^+): *m*/*z* (%) = 212 (92) [M + H], 184 (18), 156 (94), 138 (15), 112 (92), 110 (90), 74 (47), 57 (100). HMRS: [M + H], found 212.16589. $C_{12}H_{22}NO_2$ calcd. 212.16505. $C_{12}H_{21}NO_2$: calcd. C 68.21, H 10.02, N 6.63.; found C 68.28, H 10.21, N 6.66.

***tert*-Butyl *N*-[(1*S*,2*R*)-2-Cyclohexylcyclopropyl]carbamate (61):** (±)-**61**: Yellow oil; (+)-**61** and (–)-**61**, white solid; m.p. (+)-**61**: 64–67 °C, (–)-**61**: 65–67 °C; (+)-**61**: $[\alpha]_D^{20}$ = +47.0 (*c* = 1.32, $CHCl_3$), (–)-**61**: $[\alpha]_D^{20}$ = –47.7 (*c* = 1.32, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3335 (br., NH), 2978 (m), 2924 (s), 2851 (w), 1705 (s), 1514 (m), 1365 (m), 1171 (m) cm^{-1}. ^1H NMR (500 MHz, 330 K, $CDCl_3$): δ = 0.47–0.53 (m, 2 H, CH_2CHN), 0.59–0.68 (m, 2 H, C*H*CHN and C*H*CHCHN), 0.95–1.19 (m, 5 H), 1.40 (s, 9 H, 3 × CH_3), 1.54–1.71 (m, 4 H), 1.84–1.89 (m, 1 H), 2.23–2.28 (m, 1 H, CHN), 4.54 (br. s, 1 H, NH) ppm. ^{13}C NMR (125 MHz, 330 K, $CDCl_3$): δ = 12.3, 26.1, 26.2, 26.5, 27.2, 28.4, 32.1, 32.7, 40.7, 79.1, 156.4 ppm. MS (CI^+): *m*/*z* (%) = 240 (36) [M + H], 184 (100), 140 (41), 57 (36). HMRS: [M + H], found 240.19634. $C_{14}H_{26}NO_2$ calcd. 240.19634. $C_{14}H_{25}NO_2$ (239.36): calcd. C 70.25, H 10.53, N 5.83; found C 70.08, H 10.61, N 5.82.

(±)-*tert*-Butyl *N*-[(1*S*,2*R*)-2-(Trimethylsilyl)cyclopropyl]carbamate (62): Amorphous solid. IR (film): $\tilde{\nu}_{max}$ = 3348 (br.), 2956 (m), 1701 (s), 1406 (w), 1366 (m), 1249 (s), 1172 (s), 1096 (m), 1077 (m), 836 (s, Si–C) cm^{-1}. ^1H NMR (400 MHz, 328 K, $CDCl_3$): δ = –0.27 (ddd, *J* = 11.2, 8.0, 5.0 Hz, 1 H, C*H*CHN), –0.05 [s, 9 H, Si(CH_3)$_3$], 0.56 (ddd, *J* = 8.0, 6.5, 4.6 Hz, 1 H, C*H*HCHN), 0.67 (ddd, *J* = 11.2, 4.6, 3.4 Hz, 1 H,CH*H*CHN), 1.42 [s, 9 H, C(CH_3)$_3$], 2.42–2.48 (m, 1 H, CHN), 4.62 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, 328 K, $CDCl_3$): δ = –2.4, 7.0, 10.6, 27.3, 28.5, 79.2, 156.5 ppm. MS (EI): *m*/*z* (%) = 252 (100) [M + Na], 217 (6). HMRS: [M + Na], found 252.13933. $C_{11}H_{23}NNaO_2Si$ calcd. 252.13903.

***tert*-Butyl *N*-[(1*S*,2*S*)-2-(Benzyldimethylsilanyl)cyclopropyl]carbamate (63):** Colourless oil. $[\alpha]_D^{18}$ = +16.3 (*c* = 1.0, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3327 (br., NH), 2976 (m), 2895 (w), 1705 (s), 1493 (s), 1452 (m), 1365 (s), 1247 (s), 1171 (s), 1078 (m), 833 (s, Si–C) cm^{-1}. ^1H NMR (400 MHz, 328 K, $CDCl_3$): δ = –0.28 (ddd, *J* = 11.2, 8.1, 4.9 Hz, 1 H, C*H*CHN), –0.09 (s, 3 H, CH_3), –0.06 (s, 3 H, CH_3), 0.57 (ddd, *J* = 8.1, 6.3, 4.7 Hz, 1 H,C*H*HCHN), 0.69 (ddd, *J* = 11.2, 4.7, 3.3 Hz, 1 H, CH*H*CHN), 1.44 [s, 9 H, C(CH_3)$_3$], 2.11 (d, *J* = 13.6 Hz, 1 H, C*H*HPh), 2.15 (d, *J* = 13.6 Hz, 1 H, CH*H*Ph), 2.46 (ddd, *J* = 6.3, 4.9, 3.3 Hz, 1 H, CHN), 4.53 (br. s, 1 H, NH), 7.00–7.07 (m, 3 H, Ar-H), 7.15–7.21 (m, 2 H, Ar-H) ppm. ^{13}C NMR (100 MHz, 328 K, $CDCl_3$): δ = –4.5, 5.8, 10.6, 25.5, 27.2, 28.5, 79.3, 124.1, 128.1, 128.2, 140.0, 156.4 ppm. MS (EI): *m*/*z* (%) = 305 (5) [M^+], 249 (22), 204 (43), 149 (100), 114 (100), 98 (42), 75 (22). HMRS: $[M]^+$, found 305.18162. $C_{17}H_{27}NO_2Si$ calcd. 305.18110.

***exo*-Bicyclo[4.1.0]hept-7-ylamine Hydrochloride (64):**[32] Protected amine **60** (38 mg, 0.18 mol) in a solution of hydrochloric acid (5–6 M solution in 2-propanol, 2 mL) was heated with a heat gun for a few seconds in order to dissolve all organic material and then stirred for 10 min. The solvent was removed in vacuo and the residue triturated in dry diethyl ether (2 mL). The resulting precipitate was filtered, washed with dry diethyl ether (2 × 4 mL) and dried in vacuo to give **64** (19.5 mg, 0.13 mmol, 74%) as a colourless solid; m.p. (dec.) 225–227 °C [ref.[32] 224–225 °C (dec.)]. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 3430 (br.), 2922 (w), 2855 (w), 1590 (w), 1496 (w), 1160 (w), 1124 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO): δ = 1.03–1.20 (m, 4 H), 1.21–1.28 (m, 2 H), 1.52–1.60 (m, 2 H), 1.75–1.84 (m, 2 H), 2.23 (m, 1 H, C*H*NH_3^+), 8.23 (br. s, 3 H, NH_3^+) ppm. ^{13}C NMR (75 MHz, DMSO): δ = 15.7, 21.4, 22.0, 32.9 ppm. MS (EI): *m*/*z* (%) = 111 (28) [M – HCl]$^+$, 94 (17), 82 (16) (100) 69. HMRS: [M – HCl]$^+$, found 111.10458. $C_7H_{13}N$ calcd. 111.104795.

(±)-*trans*-Cyclohexylcyclopropylamine Hydrochloride (65): Protected amine (±)-**61** (38 mg, 0.18 mol) in a solution of hydrochloric acid (5–6 M solution in 2-propanol, 2 mL) was stirred for 10 min. The solvent was removed in vacuo and the residue triturated in dry diethyl ether (5 mL). The resulting precipitate was filtered, washed with dry diethyl ether (2 × 4 mL) and dried in vacuo to give (±)-**65** (19.5 mg, 0.13 mmol, 74%) as a white solid; m.p. 182–184 °C. IR (CH_2Cl_2): $\tilde{\nu}_{max}$ = 2922 (s), 1620 (w), 1520 (w), 1446 (w), 1020 (w) cm^{-1}. ^1H NMR (500 MHz, DMSO): δ = 0.53 (dt, *J* = 7.6, 5.9 Hz,C*H*HCHN), 0.58–0.68 (m, 1 H, C*H*CHCHN), 0.81 (ddd, *J* = 9.4, 5.7, 3.8 Hz, 1 H,CH*H*CHN), 0.95 (dddd, *J* = 12.8, 9.4, 6.1, 3.4 Hz, 1 H, C*H*CHN), 0.95–1.20 (m, 5 H, cy-H), 1.50–1.72 (m, 4 H, cy-H), 1.75–1.79 (m, 1 H, cy-H), 2.27 (dt, *J* = 7.6, 3.7 Hz, 1 H, CHN), 8.37 (br. s, 3 H, NH_3^+) ppm. ^{13}C NMR (125 MHz, DMSO): δ = 8.7, 23.0, 25.5, 25.8, 26.6, 31.5, 32.1, 39.4 ppm. MS (EI): *m*/*z* (%) = 139 (2) [[M + H – HCl]$^+$], 110 (4), 96 (5), 82 (7), 67 (5), 56 (100). HMRS: [M + H – HCl]$^+$, found 140.14343. $C_9H_{18}N$ calcd. 140.14338.

(±)-(1*R*,2*S*)-2-{(1*S*,6*R*,7*R*)-Bicyclo[4.1.0]heptan-7-ylamino}-1,2-diphenylethanol (66): Lithium hydroxide monohydrate (0.566 g, 13.5 mmol) was added in one portion to a suspension of cyclopropane **35a** (0.15 g, 0.45 mmol) in a mixture of absolute ethanol (7 mL) and water (3 mL). The reaction mixture was heated at reflux for 24 h and then cooled to room temperature. Most of the ethanol was removed in vacuo and saturated aqueous NH_4Cl solution (5 mL) was added to the residue. The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (DCM/MeOH, 96:4) to give the amino alcohol **66** (0.116 g, 0.38 mmol, 84%) as a white solid; m.p. 154–156 °C. IR (film): $\tilde{\nu}_{max}$ = 3427 (br.), 2987 (m), 2926 (w), 1660 (m), 1541 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.81–0.87 (m, 2 H, 2 × C*H*CHN), 0.88–0.99 (m, 2 H, cy-H), 1.03–1.07 (m, 2 H, cy-H), 1.36–1.49 (m, 2 H, cy-H), 1.64–1.72 (m, 1 H, cy-H), 1.67 (t, *J* = 3.4 Hz, 1 H, CHN), 1.76–1.83 (m, 1 H, cy-H), 3.97 (d, *J* = 5.4 Hz, 1 H, NHC*H*Ph), 4.89 (d, *J* = 5.4 Hz, 1 H, C*H*OH), 6.99–7.02 (m, 2 H, Ar-H), 7.03–7.06 (m, 2 H, Ar-H), 7.16–7.23 (m, 6 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 18.9, 19.0, 21.5, 21.6, 22.6, 22.8, 41.1, 69.1, 75.3, 125.9, 126.6, 127.3, 127.4, 127.8, 128.0, 128.2, 139.4, 140.4 ppm. MS (EI): *m*/*z* (%) = 307 (3) [M^+], 200 (100), 149 (15), 117 (12), 106 (52), 91 (100), 77 (37), 67 (21), 55 (16). HMRS: $[M]^+$, found 307.19268. $C_{21}H_{25}NO$ calcd. 307.19307.

(±)-(1*R*,2*S*)-2-[(1*S*,2*S*)-2-Cyclohexylcyclopropylamino]-1,2-diphenylethanol (67): Lithium hydroxide monohydrate (0.745 g, 17.7 mmol) was added in one portion to a suspension of cyclopropane (±)-**36**

(0.214 g, 0.59 mmol) in a mixture of absolute ethanol (8 mL) and water (3.5 mL). The reaction mixture was heated at reflux for 48 h and then cooled to room temperature. Most of the ethanol was removed in vacuo and saturated aqueous NH_4Cl solution (5 mL) was added to the residue. The aqueous layer was extracted with dichloromethane (3 × 10 mL) and the combined organic extracts were then dried (Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (PE 30–40 °C/EtOAc, 4:1 to 7:3) to give the amino alcohol (±)-**67** (0.155 g, 0.44 mmol, 74%) as a white solid; m.p. 90–92 °C. IR (film): $\tilde{\nu}_{max}$ = 3380 (br.), 3028 (w), 2922 (s), 2850 (m), 1495 (m), 1450 (m), 1100 (w), 1053 (w), 1028 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.23–0.30 (m, 1 H, C*H*HCHN), 0.34–0.42 (m, 1 H, C*H*CHCHN), 0.50–0.58 (m, 2 H, CH*H*CHN and C*H*CHN), 0.96–1.18 (m, 5 H, cy-H), 1.57–1.72 (m, 5 H, cy-H), 1.79 (dt, *J* = 6.9, 3.2 Hz, 1 H, CHN), 2.07 (br. s, 1 H), 3.62 (br. s, 1 H), 4.04 (d, *J* = 4.7 Hz, 1 H, NHC*H*Ph), 4.91 (d, *J* = 4.7 Hz, 1 H, C*H*OH), 6.91–6.95 (m, 2 H, Ar-H), 6.98–7.01 (m, 2 H, Ar-H), 7.14–7.24 (m, 6 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 12.5, 26.1, 26.4, 27.7, 32.4, 32.8, 34.3, 40.8, 68.6, 75.2, 126.5, 127.0, 127.1, 127.5, 127.8, 127.9, 139.3, 140.3 ppm. MS (EI): *m*/*z* = 336 (100) [M + H]. HMRS: [M + H], found 336.23246. $C_{23}H_{30}NO$ calcd. 336.23219.

(1*S*,2*R*)-1,2-Diphenyl-2-[(1*S*,2*R*)-2-phenylcyclopropylamino]ethanol (68): Potassium trimethylsilanolate (90% purity, 323 mg, 2.52 mmol) was added to a solution of cyclopropane (+)-**37** (112 mg, 0.315 mmol) in dry THF (1.6 mL) under nitrogen. The reaction mixture was heated at 60 °C for 3.5 h and, as the reaction was not complete (as determined by TLC), additional potassium trimethylsilanolate (90% pure, 81 mg, 0.63 mmol, 2 equiv.) was added. The mixture was heated for a further 30 min and then cooled to room temperature. EtOAc (10 mL) and water (5 mL) were added and the mixture was transferred into a separating funnel. The organic layer was separated and the aqueous layer was extracted with EtOAc (5 mL). The combined organic extracts were washed with brine (5 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude product was purified by flash column chromatography (PE 40–60 °C/EtOAc, 4:1 to 7:3) to give the amino alcohol (+)-**68** (73 mg, 0.22 mmol, 70%) as a white solid; m.p. 138–141 °C. $[\alpha]_D^{32}$ = +22.0 (*c* = 1.0, $CHCl_3$). IR ($CHCl_3$): $\tilde{\nu}_{max}$ = 3405 (br.), 3066 (w), 3018 (m), 1558 (m), 1499 (m), 1051 (w), 1028 (w) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.92 (ddd, *J* = 7.2, 5.8, 5.3 Hz, 1 H,C*H*HCHN), 1.05 (ddd, *J* = 9.3, 5.3, 4.2 Hz, 1 H,CH*H*CHN), 1.90 (ddd, *J* = 9.3, 5.8, 3.1 Hz, 1 H, C*H*CHN), 2.24 (ddd, *J* = 7.2, 4.2, 3.1 Hz, 1 H, CHN), 3.00 (br. s, 2 H, OH and NH), 4.08 (d, *J* = 5.3 Hz, 1 H, NHC*H*Ph), 4.93 (d, *J* = 5.3 Hz, 1 H, CHOH), 6.83–7.31 (m, 15 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.8, 25.4, 39.3, 69.1, 75.6, 125.5, 125.9, 126.6, 127.5, 127.8, 128.0, 128.1, 128.2, 139.1, 140.2, 141.7 ppm. MS (EI): *m*/*z* (%) = 329 (6) [M^+] 222 (100), 132 (52), 117 (98), 91 (86), 77 (32). HMRS: [M + H], found 329.17795. $C_{23}H_{23}NO$ calcd. 329.17742.

(*S*)-2-[(1*S*,2*S*)-2-(4-Methoxybenzyl)cyclopropylamino]-4-methylpentan-1-ol (69): Lithium hydroxide monohydrate (789 mg, 18.79 mmol) was added in one portion to a suspension of the amidocyclopropane **53** (190 mg, 0.57 mmol) in a mixture of ethanol (8.55 mL) and water (3.8 mL). The reaction was heated at 84 °C for 36 h and then cooled to room temperature. The volume of the solution was concentrated to *ca.* one third of its volume and an aqueous saturated solution of ammonium chloride (6 mL) was added. The aqueous layer was extracted with dichloromethane (3 × 5 mL) and the combined organic extracts dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (2% triethylamine in ethyl acetate) to give the aminocyclopropane as a yellow solid (106 mg, 67%); m.p. 56–59 °C. $[\alpha]_D^{20}$ = +31.3 (*c* = 1.01, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3364 (w), 2959, 1612 (w), 1512, 1468 (w), 1265, 1246, 1177 (w), 1036 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.41–0.48 (m, 1 H, C*H*HCHN), 0.62 (ddd, *J* = 8.8, 4.9, 3.8 Hz, 1 H, CH*H*CHN), 0.85 (d, *J* = 6.6 Hz, 3 H, CH_3CHCH$_3$), 0.87 (d, *J* = 6.6 Hz, 3 H, CH$_3$CHC*H*$_3$), 0.92–1.00 (m, 1 H, C*H*CHN), 1.16 (dt, *J* = 13.9, 7.0 Hz, 1 H, CH*H*CHMe$_2$), 1.36 (ddd, *J* = 13.9, 7.6, 6.6 Hz, 1 H, C*H*HCHMe$_2$), 153–1.63 (m, 1 H, CHMe$_2$), 2.04 (dt, *J* = 6.7, 3.3 Hz, 1 H, CHN), 2.10 (br. s, 2 H, NH, OH), 2.41–2.53 (m, 2 H, C*H*$_2$Ar), 2.62–2.70 (m, 1 H, C*H*CH$_2$OH), 3.11 (dd, *J* = 10.5, 6.7 Hz, 1 H, CH*H*OH), 3.50 (dd, *J* = 10.5, 4.2 Hz, 1 H, C*H*HOH), 3.79 (s, 3 H, OCH_3), 6.82 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.12 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7, 22.6, 23.0, 22.4, 24.9, 35.2, 37.5, 41.5, 55.3, 57.4, 63.2, 113.8, 129.3, 133.5, 157.9 ppm. MS (CI^+): *m*/*z* (%) = 278 (100) [M + H], 260 (18), 220 (12), 170 (14), 156 (90). HRMS: [M + H], found 278.21125. $C_{17}H_{28}NO_2$ calcd. 278.21199.

***N*-*tert*-Butoxycarbonyl-(*S*)-2-[(1*S*,2*S*)-2-(4-methoxybenzyl)cyclopropylamino]-4-methylpentan-1-ol (70):** A solution of di-*tert*-butyl dicarbonate (96 mg, 0.44 mmol) in dichloromethane (2.5 mL) was added to a solution of the aminocyclopropane **69** (104 mg, 0.37 mmol) in dichloromethane (2.5 mL). The resulting mixture was left at reflux for 24 h. The reaction was treated with a saturated aqueous solution of sodium hydrogen carbonate (3 mL). The resulting aqueous phase was extracted with dichloromethane (2 × 4 mL) and the combined organic layers washed with water and brine, dried with $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography using PE/ethyl acetate (3:1) to give the boc-protected aminocyclopropane as a pale yellow oil (111 mg, 80%). $[\alpha]_D^{27}$ = –48.11 (*c* = 0.85, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3019, 1685 (w), 1653 (w), 1513, 1216 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.68–0.74 (m, 1 H, C*H*HCHN), 0.85 (d, *J* = 6.6 Hz, 3 H, CH$_3$CC*H*$_3$), 0.87 (d, *J* = 6.6 Hz, 3 H, C*H*$_3$CCH$_3$), 0.86–0.89 (m, 1 H, CH*H*CHN), 1.19–1.28 (m, 1 H, C*H*CHN), 1.47 (s, 9 H, 3 × CCH$_3$), 1.48–1.55 (m, 2 H, CHMe$_2$, C*H*HCHMe$_2$), 1.61 (ddd, *J* = 13.8, 8.7, 5.8 Hz, 1 H, CH*H*CHMe$_2$), 2.30 (dt, *J* = 6.9, 3.4 Hz, 1 H, CHN), 2.35 (dd, *J* = 14.5, 8.2 Hz, 1 H, CH*H*Ar), 2.81 (dd, *J* = 14.5, 5.6 Hz, 1 H, C*H*HAr), 3.45–3.58 (m, 2 H, C*H*CH$_2$OH, C*H*HOH), 3.59–3.67 (m, 1 H, CH*H*OH), 3.78 (s, 3 H, OCH_3), 6.83 (d, *J* = 8.7 Hz, 2 H, Ar-H), 7.11 (d, *J* = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 16.2, 22.6, 22.9, 25.0, 28.3, 28.5, 36.4, 37.0, 37.1, 55.2, 60.1, 65.6, 80.0, 113.8, 129.7, 132.6, 157.9, 158 ppm. MS (CI^+): *m*/*z* (%) = 378 (97) [M + H], 322 (99), 306 (65), 278 (100), 156 (54), 121 (27). HRMS: [M + H], found 378.26454. $C_{22}H_{36}NO_4$ calcd. 378.26442.

***N*-*tert*-Butoxycarbonyl-(*S*)-2-[(1*R*,2*S*)-2-(4-methoxybenzyl)cyclopropylamino]-4-methylpentanoic Acid (71):** Sodium (meta)periodate (250 mg, 1.17 mmol) was added portionwise to a mixture of the aminocyclopropane **70** (110 mg, 0.29 mmol), ruthenium(IV) oxide hydrate (2.2 mol-%) in carbon tetrachloride (0.58 mL), acetonitrile (0.58 mL) and water (0.87 mL). The resulting mixture was left to stir vigorously for 45 min at room temperature. Then dichloromethane (3 mL) was added, and the phases separated. The upper aqueous phase was extracted with dichloromethane (3 × 3 mL). The combined organic extracts were dried ($MgSO_4$) and concentrated. The resulting residue was diluted with diethyl ether (6 mL), filtered through a Celite pad and concentrated. The residue was purified by column chromatography (0.25:4.75:95 acetic acid/ethanol/dichloromethane) to give the cyclopropyl amino acid as a pale brown oil (74 mg, 65%). $[\alpha]_D^{27}$ = –38.1 (*c* = 0.73, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3018, 1691 (w), 1512 (w), 1215 (s) cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ = 0.69–0.75 (m, 1 H, C*H*HCHN), 0.85 (d, *J*

= 6.6 Hz, 3 H, CH_3CHCH_3), 0.89 (d, J = 6.6 Hz, 3 H, CH_3CHCH_3), 0.93–1.00 (m, 1 H, CHCHN), 1.33–1.41 (m, 1 H, CHCHN), 1.47 (s, 9 H, $3 \times CH_3$), 1.51–1.59 (m, 2 H, $CHMe_2$, $CHCHMe_2$), 1.71–1.81 (m, 1 H, $CHCHMe_2$), 2.33 (dd, J = 14.6, 8.5 Hz, 1 H, CHHAr), 2.36–2.41 (m, 1 H, CHN), 2.86 (dd, J = 14.6, 5.3 Hz, 1 H, CHHAr), 3.79 (s, 3 H, OCH_3), 3.92–4.09 (m, 1 H, $CHCO_2H$) 6.83 (d, J = 8.5 Hz, 2 H, Ar-H), 7.12 (d, J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 15.6, 21.8, 22.9, 25.1, 27.6, 28.4, 29.3, 29.7, 36.9, 38.0, 55.2, 61.2, 81.1, 113.8, 129.4, 132.9, 158.0, 179.6 ppm. MS (CI^+): *m/z* (%) = 392 (5) [M + H], 336 (32), 292 (72), 170 (52), 121 (37). HRMS: [M + H], found 392.24436. $C_{22}H_{34}NO_5$ calcd. 392.24369.

***tert*-Butyl *N*-[(1*S*,2*S*)-2-(Hydroxycyclopropyl)]carbamate (72):** Tetrabutylammonium fluoride (1 M *solution* in THF, 0.33 mL, 0.33 mmol) was added to a solution of cyclopropane (+)-**63** (50 mg, 0.164 mmol) in THF (0.08 mL) under nitrogen. After 30 min of stirring, methanol (0.41 mL), potassium hydrogencarbonate (32.8 mg, 0.33 mmol) and hydrogen peroxide (30% solution in water, 0.34 mL, 3.28 mmol) were added to the solution. The reaction mixture was stirred for 16 h and then sodium thiosulfate pentahydrate (0.9 g, 3.62 mmol) was added. After stirring for 30 min the mixture was filtered and concentrated in vacuo. The crude product was purified by flash column chromatography (PE 40–60 °C/EtOAc, 4:1 to 1:1) to give **72** (25 mg, 0.144 mmol, 88%) as a colourless oil. $[\alpha]_D^{25}$ = –14.6 (c = 0.99, $CHCl_3$). IR (film): $\tilde{\nu}_{max}$ = 3327 (br., NH), 2978 (m), 2931 (w), 1690 (s), 1522 (m), 1367 (m), 1278 (m), 1256 (m), 1171 (s), 1020 (w) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 0.71 (td, J = 7.0, 4.6 Hz, 1 H, CHHCHN), 0.99 (ddd, J = 8.5, 6.8, 3.9 Hz, 1 H,CHHCHN), 1.40 [s, 9 H, $C(CH_3)_3$], 2.48–2.54 (m, 1 H, CHN), 3.36 (ddd, J = 7.2, 3.9, 1.4 Hz, 1 H, CHOH), 4.09 (br. s, 1 H, OH), 4.68 (br. s, 1 H, NH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.7, 28.3, 30.5, 52.6, 79.9, 156.7 ppm. MS (EI): *m/z* (%) = 173 (100) [M^+]; HMRS: [M]$^+$. found 173.10521. $C_8H_{15}NO_3$ calcd. 173.10519.

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