Synthesis of enantiomerically pure divinyl- and diallylcarbinols

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Acylated oxazolidinones and bornane sultams can be cleaved to divinyl- and diallylcarbinols by treatment with vinyl- or allylmetal compounds. For the preparation of divinylcarbinols, acylated bornane sultams are the starting materials of choice, while for the preparation of diallylcarbinols acylated oxazolidinones and bornane sultams work equally well.

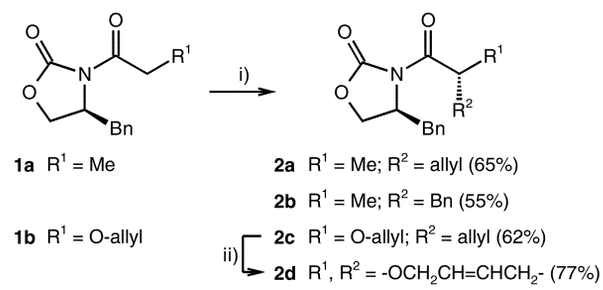
Introduction

Carbinols with unsaturated side chains are interesting starting materials for a variety of synthetic transformations. For example, divinylcarbinols have been employed in hydroacylation reactions,[1] formation of phosphorus heterocycles,[2] enantioselective epoxidation,[3–5] palladium-catalyzed malonate addition,[6] catalytic asymmetric intramolecular hydrosilation[7] and radical cyclizations.[8] Over the past few years several examples have been reported where divinylcarbinols played a key role in enantioselective[9,10] and diastereoselective ring closing metathesis reactions.[11–15] Diallylcarbinols have been used in silylformylation,[16,17] Pauson–Khand reactions,[18] Prins-cyclizations,[19] and various other reactions.[20–23] Applications in olefin metathesis have included the formation of cyclopentenols,[24] spirocyclic cyclopentenes[25] and oxacycles.[26,27] Carbinols are conveniently prepared from esters by treatment with excess organometallic reagent. Thus, enantiomerically pure carbinols with a stereogenic centre adjacent to the alcohol moiety become available from esters with a centre of chirality in the α-position, *e.g.* α-hydroxy carboxylic acid esters[13] or α-amino acid esters.[15,28] Well-established methods for the preparation of enantiomerically pure carboxylic acids and derivatives use chiral amine auxiliaries, such as oxazolidinones[29,30] or camphor sultams.[31] Standard methods for the cleavage of these auxiliaries are reduction to the primary alcohols, or hydrolysis to the free carboxylic acids. Surprisingly, the cleavage of oxazolidinones or camphor sultams using organometallic reagents has hardly been investigated. We are aware of only one example for each of these cases: Kashima *et al.* reported several years ago the formation of a diallylcarbinol by addition of an allylzinc reagent to achiral benzoylated oxazolidinone in excellent yield,[32] and the cleavage of an acylated sultam with methylmagnesium iodide to yield a dimethylcarbinol has been reported by Curran *et al.*[33] In this contribution we describe the scope and limitations of a novel synthesis of α-chiral divinyl- and diallylcarbinols.

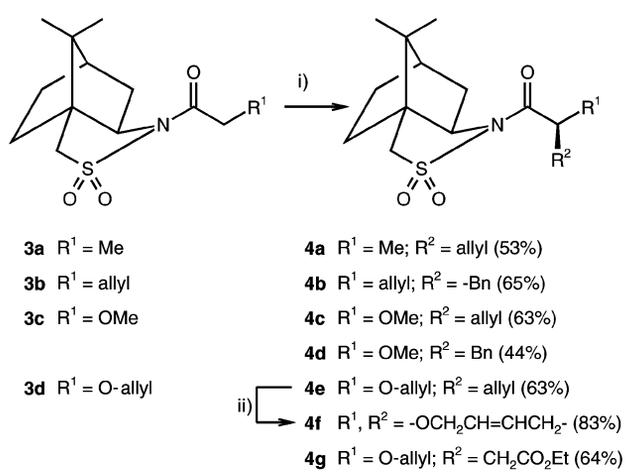
Results and discussion

Alkylation of acylated oxazolidinones and bornane sultams

Acylated oxazolidinones and sultams were obtained from the corresponding carboxylic acids *via* formation of the mixed anhydrides using pivaloyl chloride.[34] Alkylation of oxazolidinones **1a** and **1b** was achieved by treatment with NaHMDS, followed by allyl iodide or benzyl bromide, respectively, to give oxazolidinones **2a**–**c**. Dihydropyran **2d** was obtained from **2c** by ring closing metathesis using 3 mol% of Grubbs' catalyst (Scheme 1).[35] Alkylation of acylated bornane sultams **3a**–**d** was achieved under the same conditions. From sultams **3a**–**d** [derived from (*S*)-camphorsulfonic acid] alkylation products **4a**–**g** result, which have, compared to products **2a**–**d**, the opposite configuration of the α-position. **4f** was prepared by ring closing olefin metathesis of **4e** in the presence of Grubbs' catalyst (Scheme 2).



Scheme 1 *Reagents and conditions*: i, NaHMDS (1.5 equiv.), THF, −78 °C, then $ICH_2CH{=}CH_2$ or $BrCH_2Ph$; ii, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (3 mol%), DCM, 20 °C.



Scheme 2 *Reagents and conditions*: i, NaHMDS (1.5 equiv.), THF, −78 °C, then $ICH_2CH{=}CH_2$ or $BrCH_2Ph$ or $BrCH_2CO_2Et$; ii, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (3 mol%), DCM, 20 °C.

We also investigated the alkylation of oxazolidinones acylated with allylated lactic acid and mandelic acid. 2-Allyloxypropionic acid (**5a**) was converted into the acylated oxazolidinone **6a**. Allylation of **6a** to the metathesis precursor **7** was

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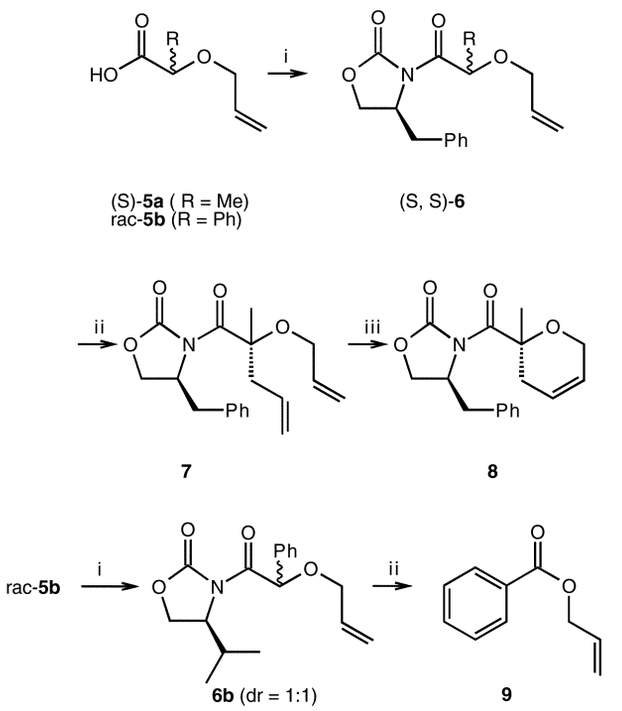
achieved in only moderate yield of 35% and a diastereomeric ratio of 10 : 1, using NaHMDS and allyl iodide. Ring closing metathesis of **7** gave the enantiomerically and diastereomerically pure dihydropyran **8**. 2-Allyloxymandelic acid (**5b**) was converted into the acylated valine-derived oxazolidinone analogously. However, the allylation reaction failed. Instead, allyl benzoate **9**, which was unambiguously identified by comparison of its spectroscopic data, was the only isolable product. The mechanism leading to the formation of allyl benzoate remains unclear (Scheme 3).



Scheme 3 *Reagents and conditions*: i, NEt_3, PivCl, then lithiated oxazolidinone [(*S*)-**6a**, 74%; **6b**, 57% (dr = 1 : 1)]; ii, NaHMDS (1.5 equiv.), THF, −78 °C, then $ICH_2CH{=}CH_2$ (**7a**, 35%; **9**, 47%); iii, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (3 mol%), DCM, 20 °C (80% of **8**).

Formation of diallylcarbinols

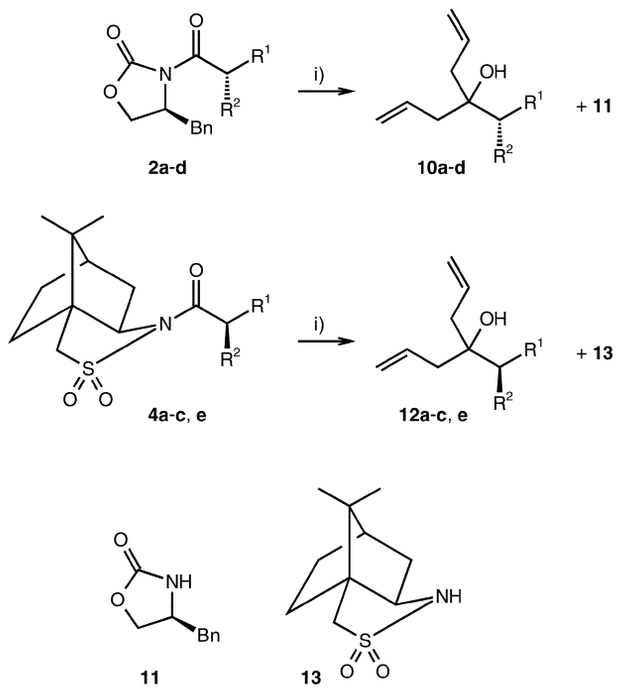
Upon treatment of an acylated oxazolidinone with excess organometallic reagent, cleavage of the heterocycle by nucleophilic attack at the carbonyl carbon may occur. The report by Kashima *et al.* demonstrates that this does not seem to be a problem if the allylzinc reagent is used, the corresponding magnesium compound, however, was not investigated previously. Treatment of acylated oxazolidinones **2a**–**d** with a fourfold excess of allylmagnesium bromide leads to a clean cleavage of the chiral auxiliary. Starting from (*S*)-phenylalanine-derived oxazolidinones, the *R*-configured products **10a**–**d** and the free oxazolidinone **11** are formed. The products are easily separated and no side products resulting from the cleavage of the heterocycle were detected. Cleavage of the acylated sultams **4a**–**c** and **4e** under the same conditions gives *S*-configured diallylcarbinols **12a**–**c** and **12e** and the free bornane sultams **13** in good yields. Examples **10a**/**12a** and **10c**/**12e** were obtained in both enantiomeric forms (Scheme 4 and Table 1). The values of the optical rotations are identical within the range of experimental error.

Formation of divinylcarbinols

After we had observed that cleavage of acylated oxazolidinones with allylmagnesium bromide is a very smooth process, we were very surprised to see that cleavage with the vinylmagnesium compound was not straightforward at all. The formation of butenones **15** was an expected side reaction, these products

Table 1 Formation of diallylcarbinols from oxazolidinones **2** or bornane sultams **4**

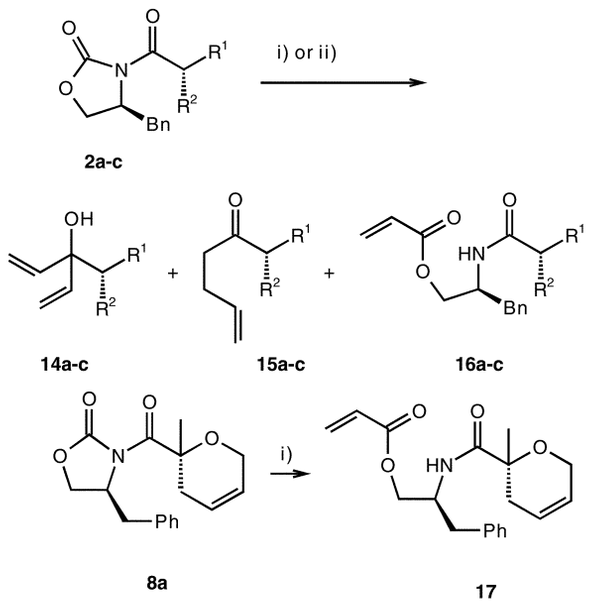
Starting material	Product	R^1	R^2	Yield (%)
2a	**10a**	Me	Allyl	70
2b	**10b**	Me	Bn	82
2c	**10c**	OAllyl	Allyl	76
2d	**10d**	$OCH_2CH{=}CHCH_2$		63
4a	**12a**	Me	Allyl	83
4b	**12b**	Allyl	Bn	64
4c	**12c**	OMe	Allyl	85
4e	**12e**	OAllyl	Allyl	96



Scheme 4 *Reagents and conditions*: i, AllylMgBr (1.0 M solution in ether, 4 equiv.), ether, −78 °C, then aq. NH_4Cl solution.

resulting from 1,4- rather than 1,2-addition of the second equivalent of vinylmagnesium chloride.[27] In the case of **2a**,**b**, however, neither the expected divinylcarbinol **14a**,**b** nor the expected side product, butenone **15a**,**b**, were observed. Instead, the oxazolidinone is cleaved to yield acrylates **16a**,**b**. The situation changes if an ether functionality is present in the α-position. **2c** is cleaved under the same conditions to yield all three products **14c**, **15c** and **16c** in a 1.5 : 1 : 1 ratio. It has been described in the literature that the formation of 1,4-addition products can be suppressed by transmetallation with ceric chloride.[36] When we repeated the cleavage of **2a**–**c** under these conditions, very similar results were obtained for **2a**,**b**. In the case of **2c** only the divinylcarbinol **14c** was isolated in moderate yield (40%). Formation of the corresponding 1,4-addition product **15c** and of acrylate **16c** was not observed under these conditions. In the case of sterically congested oxazolidinone **8a**, the acrylate **17** was formed exclusively, despite the chelating oxygen present in the molecule. It is interesting to note that similarly substituted esters react with vinylmagnesium chloride with exclusive formation of 1,4-addition products of type **15** (Scheme 5).

Formation of acrylates **16** is remarkable, because even in the presence of a fourfold excess of vinyl metal compound only one vinyl moiety is transferred to the oxazolidinone. A plausible explanation is the intermediate formation of stable tetrahedral intermediates **A**, which, analogously to the Weinreb-amides,[37] are stabilized by chelation and decompose upon hydrolysis to



Scheme 5 *Reagents and conditions*: i, H_2C=CHMgCl (2.1 equiv.), THF, −78 °C, then. aq. NH_4Cl solution: **2a** ⟶ **16a** (60%), **2b** ⟶ **16b** (70%), **2c** ⟶ **14c** (28%) + **15c** (19%) + **16c** (19%), **8a** ⟶ **17** (40%); ii, $CeCl_3$ (4.0 equiv.), H_2C=CHMgCl (3.6 equiv.), −78 °C, then aq. HCl (1 M): **2a** ⟶ **16a** (57%), **2b** ⟶ **16b** (67%), **2c** ⟶ **15c** (40%).

the acrylates **16**. In the case of **2c** an additional donor ligand (the ether moiety in the α-position) is able to coordinate to the metal and form a five-membered chelate complex (structure **B**). This might explain why acrylate **16c** is formed only in minor amounts or not at all in this case (Fig. 1).

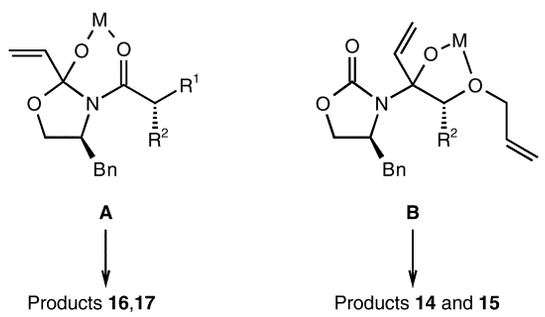


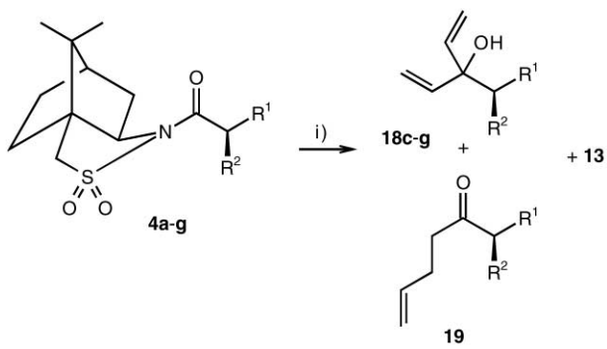
Fig. 1 Rationalization of different product distributions in the cleavage reactions of **2a**–**c**.

We saw a good chance to avoid this undesired acrylate formation by using the sultam- rather than the oxazolidinone-auxiliary. Surprisingly, the initially investigated acylated bornane sultams **4a**,**b** were recovered unchanged in nearly quantitative yield upon treatment with vinylmagnesium or vinylcerium reagent. In contrast, treatment of **4c**–**g** (which all have an oxygen atom in the α-position) with the vinyl metal compounds leads to a clean and rapid formation of the corresponding divinylcarbinols **18c**–**g** (when Grignard reagents are used, the butenone by-products **19** are observed) and the free camphor sultam **13**. The inertness of **4a**,**b** towards the vinyl metal compounds suggests that a chelation effect similar to the one described for the oxazolidinones is working here. Obviously, intramolecular coordination of the metal by an ether oxygen facilitates nucleophilic attack at the carbonyl carbon. The formation of **18g** is especially remarkable. This divinylcarbinol results from the chemoselective cleavage of the amide in **4g**. As long as stoichiometric amounts of vinyl metal compound are used, the ester group is not attacked. It might be speculated that this unusual chemoselectivity also originates from the intermediate formation of a chelate complex (Scheme 6 and Table 2).

Table 2 Formation of divinylcarbinols from bornane sultams **4**

Starting material	R^1	R^2	Conditions[a]	Yield (%) **18**	Yield (%) **19**
4a	Me	Allyl	i	[b]	
4a	Me	Allyl	ii	[b]	
4b	Allyl	Bn	i	[b]	
4b	Allyl	Bn	ii	[b]	
4c	OMe	Allyl	ii	70	—
4d	OMe	Bn	ii	73	—
4e	OAllyl	Allyl	i	59	20
4e	OAllyl	Allyl	ii	79	—
4f	–OCH_2CH=$CHCH_2$–		ii	62	—
4g	OAllyl	–CH_2CO_2Et	i	43	17

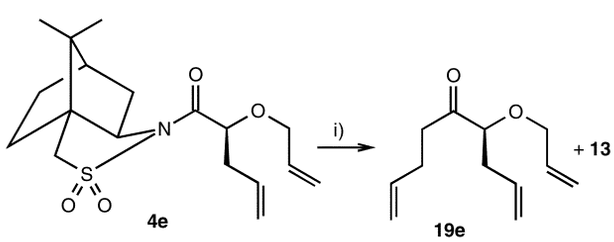
[a] Conditions i and ii as given in Scheme 6 [b] No conversion.



Scheme 6 *Reagents and conditions*: i, H_2C=CHMgCl (2.1 equiv.), THF, −78 °C, then. aq. NH_4Cl solution; ii, $CeCl_3$ (4.0 equiv.), H_2C=CHMgCl (3.6 equiv.), −78 °C, then aq. HCl (1 M).

Investigations directed towards the selective formation of butenones

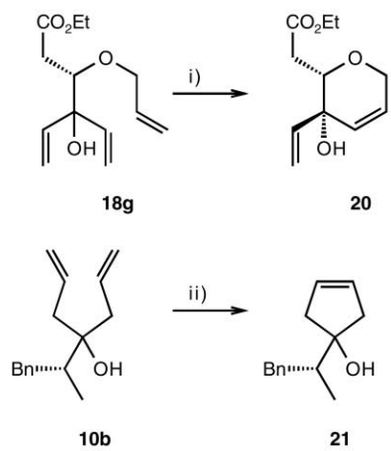
But-1-en-4-ones with a centre of chirality in the α-position are normally prepared in a two-step procedure by transamidation of acylated oxazolidinones or sultams with *N,O*-dimethylhydroxylamine to the corresponding Weinreb-amides, and subsequent addition of butenylmagnesium bromide.[38–40] Direct addition of butenylmagnesium bromide to the acylated oxazolidinones and sultams would result in the formation of the corresponding carbinols. A process leading directly from the acylated chiral auxiliaries to the butenones might be an attractive alternative. As outlined above, vinyl Grignard reagents normally give this transformation only as a side reaction.[41] A vinylcopper compound is the reagent of choice if selective 1,4-addition is the goal.[42] Thus, we investigated the cleavage of a bornane sultam auxiliary using a vinylcopper compound (obtained by transmetallation of vinylmagnesium chloride with copper iodide) for one example. Conversion of **4e** to butenone **19e** is highly regioselective, however, the reaction is rather slow. The butenone **19e** was isolated as the only product in 45% yield, along with 50% of the starting material **4e** (Scheme 7).



Scheme 7 *Reagents and conditions*: i, CuI (2.0 equiv.), H_2C=CHMgCl (5.0 equiv.), THF, −78 °C (45%).

Application of carbinols in ring closing metathesis reactions

Divinylcarbinols derived from α-hydroxy carboxylic acids are precursors for diastereoselective ring closing metathesis reactions, a field recently investigated by ourselves[14,43] and others.[12,26,44] The sequence outlined in this contribution makes starting materials conveniently accessible that are not directly prepared from commercially available or easily prepared enantiomerically pure α-hydroxy carboxylic acids. Ring closing metathesis of the divinylcarbinol **18g** in the presence of Grubbs' catalyst yields the dihydropyran **20** with an *exo*-vinyl side chain. Ring closing metathesis of the diallylcarbinol **10b** requires elevated temperatures: in the presence of Grubbs' catalyst, no conversion was observed at ambient temperature, while the reaction proceeded smoothly in refluxing toluene to give the enantiomerically pure cyclopentenol **21** (Scheme 8).



Scheme 8 *Reagents and conditions*: i, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (3 mol%), DCM, 20 °C (69%); ii, $[Cl_2(Cy_3P)_2Ru{=}CHPh]$ (5 mol%), toluene, 110 °C (79%).

In conclusion, we have developed a novel route to enantiomerically pure carbinols with unsaturated side chains. Synthetic concepts directed towards the differentiation of vinyl or allyl side chains using olefin metathesis and other transformations are currently under investigation in our laboratory.

Experimental

Instrumentation, product identification and general experimental methods have been described previously.[45] *J* values are given in Hz. The number of coupled protons was analyzed by APT experiments and is denoted by a number in parentheses following the δ_C value. Optical rotations are given in units of 10^{-1} deg cm^2 g^{-1}.

General procedure for the preparation of acylated oxazolidinones and sultams

To a solution of the corresponding acid (74 mmol) and triethylamine (12.2 ml, 87 mmol) in THF (100 ml) was slowly added pivaloyl chloride (9.20 ml, 74 mmol) at −78 °C under an atmosphere of dry argon. The mixture was stirred at this temperature for 5 min and then for 1 h at 0 °C. In a second flask, a solution of the corresponding (4*S*)-4-benzyloxazolidin-2-one or (2*S*)-bornane-10,2-sultam (62 mmol) in THF (100 ml) was cooled to −78 °C and *n*-BuLi (25.8 ml of a 2.4 M solution in hexanes, 62 mmol) was added *via* syringe. The solution was then stirred for 30 min at −78 °C. The first solution was re-cooled to −78 °C and then the cold solution of the lithium salt of the oxazolidinone or sultam was added rapidly. Stirring was continued at this temperature for 15 min and then at 0 °C until the starting material was fully consumed, as indicated by TLC (cyclohexane–methyl *tert*-butyl ether (MTBE) 2 : 1, approximately 30 min). The reaction was quenched by addition of water (100 ml). The aqueous layer was extracted with MTBE and the combined organic extracts were dried with $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography on silica using cyclohexane–MTBE mixtures as the eluent.

(4*S*)-4-Benzyl-3-propionyloxazolidin-2-one (1a)

From (4*S*)-4-benzyloxazolidin-2-one (5.00 g, 28.2 mmol) and propionic acid (2.10 ml, 28.2 mmol) **1a** (4.10 g, 62%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28–7.23 (2H, Ph), 7.19 (m, 1H, Ph), 7.15–7.11 (2H, Ph), 4.59 (dddd, 1H, *J* = 9.5, 9.0, 3.3, 3.0, *H*CN), 4.12 (dd, 1H, *J* = 9.0, 9.0, H_2COC=O), 4.08 (dd, 1H, *J* = 9.0, 3.3, H_2COC=O), 3.22 (dd, 1H, *J* = 13.3, 3.0, H_2CCHN), 2.91 (dm, 1H, *J* = 7.3, H_2CCH$_3$), 2.84 (dm, 1H, *J* = 7.3, H_2CCH$_3$), 2.69 (dd, 1H, *J* = 13.3, 9.5, H_2CCHN), 1.12 (t, 3H, *J* = 7.3, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$): δ 174.0 [(0), *C*CH$_2$], 153.4 [(0), *C*O], 135.2 [(0), Ph], 129.3, 128.8, 127.2 [(1), Ph], 66.1 [(2), *C*H$_2$O], 55.0 [(1), *C*HN], 37.8, 29.1 [(2), *C*H$_2$], 8.2 [(3), *C*H$_3$].

(4*S*)-3-(2-Allyloxyethanoyl)-4-benzyloxazolidin-2-one (1b)

From (4*S*)-4-benzyloxazolidin-2-one (4.50 g, 25.4 mmol) and 2-allyloxyacetic acid (2.95 g, 25.4 mmol), **1b** (5.45 g, 78%) was obtained. MS (EI) *m*/*z* (%) 275 (M$^+$, <5), 234 (100), 216 (60), 188 (40), 160 (80), 134 (99). IR (film): ν/cm^{-1} 1782s, 1662s, 1394m, 1263m, 1215m, 984m, 702m. Found: C, 65.8%; H, 6.6%; N, 4.9%. $C_{15}H_{17}O_4N$ requires C, 65.4%; H, 6.2%; N, 5.1%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.19 (3H, Ph), 7.17–7.10 (2H, Ph), 5.90 (dddd, 1H, *J* = 17.3, 10.5, 5.8, 5.8, *H*C=H$_2$), 5.28 (dddd, 1H, *J* = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.19 (dddd, 1H, *J* = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 4.61 (d, 2H, *J* = 3.0, H_2CC=O), 4.22 (dd, 1H, *J* = 9.0, 8.0, H_2COC=O), 4.16 (dd, 1H, *J* = 9.0, 3.0, H_2COC=O), 4.11 (m, 1H, H_2CO/*H*CN), 4.07 (m, 1H, H_2CO/*H*CN), 4.03 (m, 1H, H_2CO/*H*CN), 3.26 (dd, 1H, *J* = 13.3, 3.0, H_2CCHN), 2.75 (dd, 1H, *J* = 13.3, 8.8, H_2CCHN). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2 [(0), *C*CH$_2$], 153.4 [(0), *C*O], 134.9 [(0), Ph], 133.7 [(1), *C*H=CH$_2$], 129.4, 129.0, 127.4, [(1), Ph], 118.2 [(2), *C*H$_2$=CH], 72.5, 69.5, 67.2 [(2), *C*H$_2$O], 54.8 [(1), *C*HN], 37.7 [(2), *C*H$_2$CHN]. $[\alpha]_D^{20}$ + 66.2 (*c* 1.50 in CH_2Cl_2).

(2*R*)-*N*-Propionylbornane-10,2-sultam (3a)

From (2*S*)-Bornane-10,2-sultam (10.00 g, 46.4 mmol) and propionic acid (3.46 ml, 46.4 mmol) **3a** (10.37 g, 83%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.82 (dd, 1H, *J* = 7.8, 5.0, *H*CN), 3.46 (d, 1H, *J* = 14.0, H_2CS), 3.39 (d, 1H, *J* = 14.0, H_2CS), 2.76–2.64 (2H, H_2CC=O), 2.10 (dm, 1H, *J* = 14.0, H_2C), 2.03 (dd, 1H, *J* = 14.0, 7.8, H_2C), 1.91–1.81 (3H, H_2C, *H*C), 1.37 (dm, 1H, *J* = 9.8, H_2C), 1.31 (dm, 1H, *J* = 9.5, H_2C), 1.12 (t, 3H, *J* = 7.3, H_3CCH$_2$), 1.11 (s, 3H, H_3C), 0.97 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.6 [(0), *C*=O], 65.2 [(1), *C*HN], 52.8 [(2), *C*H$_2$S], 48.4, 47.7 [(0), *C*$_q$], 44.6 [(1), *C*H], 38.4, 32.8, 28.8, 26.4 [(2), *C*H$_2$], 20.5, 19.8, 8.3 [(3), *C*H$_3$].

(2*R*)-*N*-(Pent-4-enoyl)bornane-10,2-sultam (3b)

From (2*S*)-Bornane-10,2-sultam (12.00 g, 55.8 mmol) and pentenoic acid (5.70 ml, 55.8 mmol) **3b** (15.60 g, 94%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (dddd, 1H, *J* = 17.3, 10.3, 6.5, 6.5, *H*C=CH$_2$), 5.05 (dddd, 1H, *J* = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 4.97 (dddd, 1H, *J* = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.84 (dd, 1H, *J* = 7.3, 5.5, *H*CN), 3.48 (d, 1H, *J* = 13.8, H_2CS), 3.40 (d, 1H, *J* = 13.8, H_2CS), 2.84 (ddm, 1H, *J* = 16.8, 9.0, H_2C), 2.76 (ddm, 1H, *J* = 16.8, 9.3, H_2C), 2.44–2.36 (2H, H_2C), 2.09 (dm, 1H, *J* = 14.1, H_2C), 2.04 (ddm, 1H, *J* = 14.1, 7.8, H_2C), 1.92–1.81 (3H, H_2C, *H*C), 1.38 (dm, 1H, *J* = 8.5, H_2C), 1.35 (dm, 1H, *J* = 8.3, H_2C), 1.13 (s, 3H, H_3C), 0.94 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2 [(0), *C*=O], 136.4 [(1), *C*H=CH$_2$], 115.7 [(2), *C*H$_2$=CH], 65.2 [(1), *C*HN],

52.9 [(2), CH_2S], 48.4, 47.7 [(0), C_q], 44.6 [(1), CH], 38.5, 34.5, 32.8, 28.3, 26.4 [(2), CH_2], 20.8, 19.9 [(3), CH_3].

(2*R*)-*N*-(2-Methoxyethanoyl)bornane-10,2-sultam (3c)

From (2*S*)-Bornane-10,2-sultam (10.17 g, 47.2 mmol) and methoxyacetic acid (3.46 ml, 47.2 mmol) analytically pure **3c** (13.24 g, 98%) was obtained without further purification. Mp 118 °C. MS (EI) *m*/*z* (%) 288 (M^+ + 1, 100), 135 (90), 93 (40). IR (disk, KBr): ν/cm^{-1} 2956m, 1703s, 1330s, 1137s, 986m. Found: C, 54.3%; H, 7.5%; N, 5.0%. $C_{13}H_{21}O_4SN$ requires C, 54.3%; H, 7.4%; N, 4.9%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.41 (d, 1H, J = 16.5, H_2CO), 4.34 (d, 1H, J = 16.5, H_2CO), 3.87 (dd, 1H, J = 7.5, 5.0, HCN), 3.36 (d, 1H, J = 14.1, H_2CS), 3.42 (s, 3H, H_3CO), 3.40 (d, 1H, J = 14.1, H_2CS), 2.15 (dm, 1H, J = 14.1, H_2C), 2.07 (dd, 1H, J = 14.1, 7.5, H_2C), 1.90–1.80 (3H, H_2C, HC), 1.40 (ddm, 1H, J = 18.8, 9.5, H_2C), 1.30 (ddm, 1H, J = 18.8, 7.8, H_2C), 1.10 (s, 3H, H_3C), 0.93 (s, 3H, H_3C). ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.7 [(0), C=O], 70.9 [(2), CH_2O], 64.9 [(1), CHN], 59.5 [(3), CH_3O], 52.6 [(2), CH_2S], 49.2, 47.8 [(0), C_q], 44.5 [(1), CH], 38.1, 32.7, 26.3 [(2), CH_2], 20.7, 19.8 [(3), CH_3]. $[\alpha]_D^{23}$ −107.8 (*c* 1.28 in CH_2Cl_2).

(2*R*)-*N*-(2-Allyloxyethanoyl)bornane-10,2-sultam (3d)

From (2*S*)-Bornane-10,2-sultam (3.71 g, 17.2 mmol) and allyloxyacetic acid (2.00 g, 17.2 mmol) **3d** (4.32 g, 80%) was obtained. Mp 52 °C. MS (EI) *m*/*z* (%) 314 (M^+ + 1, 60), 135 (100), 93 (40), 79 (30). IR (disk, KBr): ν/cm^{-1} 2931s, 1719s, 1469s, 1332s, 1133s, 776m. Found: C, 57.5%, H, 7.3%; N, 4.5%. $C_{15}H_{23}O_4SN$ requires C, 57.5%; H, 7.4%; N, 4.5%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dddd, 1H, J = 17.1, 10.3, 5.8, 5.8, HC=CH_2), 5.27 (dddd, 1H, J = 17.1, 1.3, 1.3, 1.3, H_2C=CH), 5.18 (dddd, 1H, J = 10.3, 1.3, 1.3, 1.3, H_2C=CH), 4.46 (d, 1H, J = 16.5, H_2CC=O), 4.38 (d, 1H, J = 16.5, H_2CC=O), 4.09 (dddd, 1H, J = 12.5, 5.8, 1.3, 1.3, H_2CCH=CH_2), 4.03 (dddd, 1H, J = 12.5, 5.8, 1.3, 1.3, H_2CCH=CH_2), 3.85 (dd, 1H, J = 7.8, 5.0, HCN), 3.44 (d, 1H, J = 13.8, H_2CS), 3.38 (d, 1H, J = 13.8, H_2CS), 2.14 (ddm, 1H, J = 14.1, 5.0, H_2C), 2.05 (dd, 1H, J = 14.1, 8.0, H_2C), 1.92–1.80 (3H, H_2C, HC), 1.39 (dm, 1H, J = 10.0, H_2C), 1.31 (dm, 1H, J = 10.0, H_2C), 1.09 (s, 3H, H_3C), 0.93 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.9 [(0), C=O], 133.6 [(1), CH=CH_2], 118.2 [(2), CH_2=CH], 72.5, 68.3 [(2), CH_2O], 64.9 [(1), CHN], 52.6 [(2), CH_2S], 49.2, 47.4 [(0), C_q], 44.5 [(1), CH], 38.1, 32.7, 26.3 [(2), CH_2], 20.6, 19.8 [(3), CH_3]. $[\alpha]_D^{20}$ −115.0 (*c* 1.55 in CH_2Cl_2).

(4*S*)-3-[(2*S*)-2-Allyloxypropanoyl]-4-benzyloxazolidin-2-one (6a)

From (4*S*)-4-benzyloxazolidin-2-one (1.00 g, 5.6 mmol) and 2-allyloxypropionic acid (0.73 g, 5.6 mmol), **6a** (1.20 g, 74%) was obtained. MS (EI) *m*/*z* (%) 290 (M^+ + 1, <5), 248 (50), 178 (60), 117 (100), 91 (95). IR (film): ν/cm^{-1} 1781s, 1709s, 1393m, 1261m, 1220m, 1108m. Found: C, 65.7%, H, 6.7%; N, 4.6%. $C_{16}H_{19}O_4N$ requires C, 66.4%; H, 6.6%; N, 4.8%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.24 (2H, Ph), 7.22 (m, 1H, Ph), 7.17–7.14 (2H, Ph), 5.89 (dddd, 1H, J = 17.3, 10.5, 5.8, 5.8, HC=CH_2), 5.25 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.15 (dddd, 1H, J = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 5.08 (q, 1H, J = 6.5, $HCCH_3$), 4.62 (dddd, 1H, J = 9.5, 7.5, 3.3, 3.3, HCN), 4.18 (dd, 1H, J = 9.0, 7.5, H_2COC=O), 4.14 (dd, 1H, J = 9.0, 3.0, H_2COC=O), 4.04 (dddd, 1H, J = 12.3, 5.8, 1.5, 1.5, H_2COCH), 3.94 (dddd, 1H, J = 12.3, 5.8, 1.5, 1.5, H_2COCH), 3.28 (dd, 1H, J = 13.5, 3.3, H_2CCHN), 2.74 (dd, 1H, J = 13.5, 9.5, H_2CCHN), 1.37 (d, 3H, J = 6.5, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.5 [(0), CCH], 153.0 [(0), CO], 135.0 [(0), Ph], 134.3 [(1), CH=CH_2], 129.4, 129.0, 127.4 [(1), Ph], 117.9 [(2), CH_2=CH], 73.4 [(1), CHO], 71.2 [(2), CH_2OCH], 66.6 [(2), CH_2OC], 55.4 [(1), CHN], 37.7 [(2), CH_2Ph], 18.5 [(3), CH_3]. $[\alpha]_D^{20}$ +2.8 (*c* 1.20 in CH_2Cl_2).

(4*S*)-3-[(2*R*/*S*)-2-Allyloxy-2-phenylethanoyl]-4-isopropyloxazolidin-2-one (6b)

From (4*S*)-4-isopropyloxazolidin-2-one (5.20 g, 40.0 mmol) and 2-allyloxymandelic acid (7.69 g, 40.0 mmol), **6b** (6.92 g, 57%) was obtained as a 1 : 1 mixture of diastereoisomers. MS (EI) *m*/*z* (%) 304 (M^+ + 1, <5), 147 (25), 105 (100), 91 (50), 77 (20). IR (film): ν/cm^{-1} 1787s, 1709s, 1388s, 1205m, 1104m, 1025m, 723m. Found: C, 67.1%; H, 6.8%; N, 4.4%. $C_{17}H_{21}O_4N$ requires C, 67.3%; H, 7.0%; N, 4.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52–7.46 (4H, Ph), 7.31–7.28 (6H, Ph), 6.29 (s, 1H, HCO), 6.20 (s, 1H, HCO), 5.93 (ddm, 1H, J = 17.0, 10.5, HC=CH_2), 5.88 (ddm, 1H, J = 17.0, 10.5, HC=CH_2), 5.25 (dm, 2H, J = 17.0, H_2C=CH), 5.17 (dm, 2H, J = 10.5, H_2C=CH), 4.49 (ddd, 1H, J = 8.5, 4.0, 3.5, HCN), 4.30 (ddd, 1H, J = 8.5, 4.0, 3.5, HCN), 4.24 (dm, 1H, J = 8.5, H_2CO), 4.14 (dm, 1H, J = 8.5, H_2CO), 4.12 (dm, 1H, J = 9.0, H_2CO), 4.08 (dm, 1H, J = 9.0, H_2CO), 4.00 (br s, 4H, H_2CO), 2.48 [qqd, 1H, J = 7.0, 7.0, 3.5, $HC(CH_3)_2$], 2.08 [qqd, 1H, J = 7.0, 7.0, 3.5, $HC(CH_3)_2$], 0.89 (d, 6H, J = 7.0, H_3C), 0.73 (d, 3H, J = 7.0, H_3C), 0.36 (d, 3H, J = 7.0, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 170.7 [(0), CCH], 153.4, 153.4 [(0), CO], 135.8, 135.6 [(0), Ph], 134.0, 133.9 [(1), CH=CH_2], 128.8, 128.6, 128.5, 128.5, 128.4, 128.4 [(1), Ph], 118.1, 118.1 [(2), CH_2=CH], 78.0, 77.9 [(1), CHO], 70.5, 70.4 [(2), CH_2OCH], 63.6, 63.4 [(2), CH_2OC], 58.9, 57.8 [(1), CHN], 28.2, 28.0 [(1), $CH(CH_3)_2$], 17.9, 17.5, 14.5, 14.0 [(3), CH_3].

General procedure for the alkylation of acylated oxazolidinones or sultams

A solution of NaHMDS (2.72 ml of a 2.0 M solution in THF, 5.5 mmol) was diluted with THF (25 ml) and a solution of the corresponding *N*-acyl compound **1a**,**b** or **3a**–**d** (3.6 mmol) in THF (25 ml) was added dropwise at −78 °C. The mixture was stirred at this temperature for one hour. A solution of allyl iodide, benzyl bromide or ethyl 2-bromoacetate (18.2 mmol) in THF (5 ml) was added and the mixture was stirred until the reaction was complete as indicated by TLC. The reaction was quenched by addition of water and the aqueous layer was extracted with MTBE. The combined organic extracts were dried with $MgSO_4$, filtered and evaporated. The residue was purified by flash chromatography on silica.

General procedure for ring closing metathesis: preparation of 2d, 4f and 8a

To a solution of the corresponding metathesis precursor **2c**, **4e** or **7a** (12.7 mmol) in DCM (50 ml) was added Grubbs' catalyst (216 mg, 3 mol%). The mixture was stirred until the starting material was fully consumed, as indicated by TLC. The solvent was evaporated off and the residue purified by flash chromatography on silica.

(4*S*)-4-Benzyl-3-[(2*R*)-2-methylpent-4-enoyl]oxazolidin-2-one (2a)

From **1a** (3.00 g, 12.9 mmol) and allyl iodide (4.70 ml, 51.4 mmol) **2a** (2.27 g, 65%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.07 (5H, Ph), 5.70 (dddd, 1H, J = 17.3, 10.3, 7.0, 7.0, CH=CH_2), 4.98 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, CH_2=CH), 4.94 (dm, 1H, J = 10.3, CH_2=CH), 4.56 (dddd, 1H, J = 9.5, 9.0, 3.3, 3.3, HCN), 4.06 (dd, 1H, J = 9.0, 9.0, H_2COC=O), 4.02 (dd, 1H, J = 9.0, 3.3, H_2COC=O), 3.74 (ddm, 1H, J = 7.0, 7.0, HCC=O), 3.16 (dd, 1H, J = 13.3, 3.3, H_2CCHN), 2.58 (dd, 1H, J = 13.3, 9.5, H_2CCHN), 2.40 (dddm, 1H, J = 14.0, 7.0, 7.0, H_2CCH=CH_2), 2.12 (dddm, 1H, J = 14.0, 7.0, 7.0, H_2CCH=CH_2), 1.06 (d, 3H, J = 7.0, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.4 [(0), CCH_2], 153.0 [(0), CO], 135.2 [(0), Ph], 135.2 [(1), CH=CH_2], 129.3, 128.8, 127.2 [(1), Ph], 117.1 [(2), CH_2=CH], 65.9 [(2), CH_2O], 55.3 [(1), CHN], 38.0, 37.9 [(2), CH_2], 37.0 [(1), $CHCH_3$], 16.3 [(3), CH_3].

(4*S*)-4-Benzyl-3-[(2*R*)-2-methyl-3-phenylpropanoyl]oxazolidin-2-one (2b)

From **1a** (0.50 g, 2.1 mmol) and benzyl bromide (1.30 ml, 10.7 mmol) **2b** (0.38 g, 55%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.11 (8H, Ph), 6.99–6.95 (2H, Ph), 4.58 (dddd, 1H, J = 9.5, 9.3, 3.3, 3.3, *H*CN), 4.11–4.04 (2H, *H*CCH$_3$, H_2COC=O), 4.02 (dd, 1H, J = 9.0, 3.0, H_2COC=O), 3.07 (dd, 1H, J = 13.3, 7.3, H_2CPh), 2.99 (dd, 1H, J = 13.5, 3.3, H_2CCHN), 2.60 (dd, 1H, J = 13.3, 7.8, H_2CPh), 2.48 (dd, 1H, J = 13.5, 9.3, H_2CCHN), 1.11 (d, 3H, J = 6.8, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5 [(0), *C*CH$_2$], 153.0 [(0), *C*O], 139.1, 135.1 [(0), Ph], 129.3, 129.3, 128.8, 128.3, 127.2, 126.4 [(1), Ph], 65.8 [(2), *C*H$_2$O], 55.0 [(1), *C*HN], 39.8 [(2), *C*H$_2$], 39.5 [(1), *C*HCH$_3$], 37.6 [(2), *C*H$_2$], 16.7 [(3), *C*H$_3$].

(4*S*)-3-[(2*R*)-2-Allyloxypent-4-enoyl)-4-benzyloxazolidin-2-one (2c)

From **1b** (1.00 g, 3.6 mmol) and allyl iodide (1.66 ml, 18.2 mmol) **2c** (0.71 g, 62%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (2H, Ph), 7.20 (m, 1H, Ph), 7.16–7.12 (2H, Ph), 5.91–5.80 (2H, *H*C=CH$_2$), 5.23 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.11 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.08 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.05 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.04 (dd, 1H, J = 7.0, 4.8, *H*CO), 4.66 (dddd, 1H, J = 10.0, 8.0, 3.5, 3.0, *H*CN), 4.19 (dd, 1H, J = 9.0, 8.0, H_2COC=O), 4.13 (dd, 1H, J = 9.0, 3.5, H_2COC=O), 4.04 (dddd, 1H, J = 12.3, 5.5, 1.5, 1.5, H_2COCH), 3.88 (dddd, 1H, J = 12.3, 5.8, 1.5, 1.5, H_2COCH), 3.22 (dd, 1H, J = 13.3, 3.0, H_2CCHN), 2.63 (dd, 1H, J = 13.3, 10.0, H_2CCHN), 2.55 (ddm, 1H, J = 14.3, 4.8, H_2CCHO), 2.46 (ddm, 1H, J = 14.3, 7.0, H_2CCHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 [(0), *C*CH], 153.0 [(0), *C*O], 134.9 [(0), Ph], 134.1, 132.9 [(1), *C*H=CH$_2$], 129.3, 128.9, 127.4 [(1), Ph], 118.1, 177.6 [(2), *C*H$_2$=CH], 76.7 [(1), *C*HO], 71.4, 66.8 [(2), *C*H$_2$O], 55.0 [(1), *C*HN], 38.0, 37.2 [(2), *C*H$_2$CHO, *C*H$_2$CHN].

(4*S*)-3-[(*R*)-(3,6-Dihydro-2*H*-pyran-2-ylmethanoyl]-4-benzyloxazolidin-2-one (2d)

From **2c** (0.30 g, 1.0 mmol) and Grubbs' catalyst (24 mg, 3 mol%) **2d** (0.21 g, 77%) was obtained. MS (EI) *m*/*z* (%) 288 (M$^+$ + 1, 40), 270 (30), 83 (70), 55 (100). IR (film): ν/cm^{-1} 3032w, 2929w, 2835w, 1790s, 1709s, 1398m, 1256m, 1103m, 705m. Found: C, 67.1%; H, 5.8%; N, 4.7%. $C_{16}H_{17}O_4N$ requires C, 66.9%; H, 6.0%; N, 4.9%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.23 (2H, Ph), 7.20 (m, 1H, Ph), 7.14–7.11 (2H, Ph); 5.79 (dm, 1H, J = 10.3, C*H*=CH), 5.70 (dm, 1H, J = 10.3, C*H*=CH), 5.06 (dd, 1H, J = 7.8, 5.5, C*H*O), 4.66 (dddd, 1H, J = 8.0, 8.0, 3.3, 3.3, *H*CN), 4.29 (dm, 1H, J = 16.5, H*H*CO), 4.22 (dm, 1H, J = 16.5, H*H*CO), 4.21 (dd, 1H, J = 9.0, 8.0, H_2COC=O), 4.14 (dd, 1H, J = 9.0, 3.3, H_2COC=O), 3.17 (dd, 1H, J = 13.3, 3.3, H_2CCHN), 2.76 (dd, 1H, J = 13.3, 8.0, H_2CCHN), 2.35–2.30 (2H, *HH*CCH=). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0 [(0), *C*CH], 152.7 [(0), *C*O], 134.8 [(0), Ph], 129.4, 128.8, 127.3 [(1), Ph], 126.0, 122.7 [(1), *C*H=*C*H], 71.6 [(1), *C*2], 66.6, 66.0 [(2), *C*H$_2$O], 54.9 [(1), *C*HN], 37.6 [(2), *C*H$_2$CHN], 26.9 [(2), HH*C*CH=]. $[\alpha]_D^{20}$ +132.4 (c 1.22 in CH_2Cl_2).

(2*R*)-*N*-[(2*S*)-2-Methylpent-4-enoyl]bornane-10,2-sultam (4a)

From **3a** (2.00 g, 7.4 mmol) and allyl iodide (2.71 ml, 29.6 mmol) **4a** (1.22 g, 53%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (dddd, 1H, J = 17.0, 10.0, 7.5, 6.3, *H*C=CH$_2$), 5.04 (dddd, 1H, J = 17.0, 1.5, 1.5, 1.5, H_2C=CH), 4.96 (dddd, 1H, J = 10.0, 1.5, 1.5, 1.5, H_2C=CH), 3.85 (dd, 1H, J = 7.3, 5.3, *H*CN), 3.47 (d, 1H, J = 13.8, H_2CS), 3.40 (d, 1H, J = 13.8, H_2CS), 3.19 (dqm, 1H, J = 7.5, 6.5, *H*CCH$_3$), 2.41 (dddm, 1H, J = 13.8, 7.5, 6.3, H_2CCHCH$_3$), 2.21 (dddm, 1H, J = 13.8, 7.5, 6.3, H_2CCHCH$_3$), 2.04–1.98 (2H, H_2C), 1.92–1.79 (3H, H_2C, *H*C), 1.38 (dm, 1H, J = 9.0, H_2C), 1.30 (dm, 1H, J = 9.0, H_2C), 1.14 (s, 3H, J = 6.5, H_3C), 1.13 (s, 3H, H_3C), 0.94 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.7 [(0), *C*=O], 135.0 [(1), *C*H=CH$_2$], 117.2 [(2), *C*H$_2$=CH], 65.3 [(1), *C*HN], 53.2 [(2), *C*H$_2$S], 48.2, 47.7 [(0), C_q], 44.6 [(1), *C*H], 39.4 [(2), *C*H$_2$], 39.3 [(1), *C*HCH$_3$], 38.5, 32.9, 26.4 [(2), *C*H$_2$], 20.8, 19.9, 16.1 [(3), *C*H$_3$].

(2*R*)-*N*-[(2*S*)-2-Benzylpent-4-enoyl]bornane-10,2-sultam (4b)

From **3b** (2.00 g, 6.7 mmol) and benzyl bromide (3.20 ml, 26.9 mmol) **4b** (1.70 g, 65%) was obtained. Mp 118 °C. MS (EI) *m*/*z* (%) 388 (M$^+$ + 1, 30), 135 (25), 105 (20), 91 (100), 67 (20). IR (disk, KBr): ν/cm^{-1} 1684s, 1331s, 1215s, 1135s, 1067m, 700m, 538s. Found: C, 67.9%; H, 7.5%; N, 3.5%. $C_{22}H_{29}O_3SN$ requires C, 68.2%; H, 7.5%; N, 3.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19–7.06 (5H, Ph), 5.74 (dddd, 1H, J = 17.1, 10.3, 7.0, 7.0, *C*H=CH$_2$), 5.03 (dddd, 1H, J = 17.1, 1.5, 1.5, 1.5, *C*H$_2$=CH), 4.98 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, *C*H$_2$=CH), 3.73 (m, 1H, *H*CN), 3.38 (m, 1H, *H*CC=O), 3.34 (d, 1H, J = 13.8, H_2CS), 3.30 (d, 1H, J = 13.8, H_2CS), 2.88 (dd, 1H, J = 13.8, 8.5, H_2CPh), 2.74 (dd, 1H, J = 13.8, 7.0, H_2CPh), 2.58 (dddm, 1H, J = 14.0, 7.0, 7.0, H_2CCH=CH$_2$), 2.14 (dddm, 1H, J = 14.0, 7.0, 7.0, H_2CCH=CH$_2$), 1.89 (dd, 1H, J = 13.3, 5.5, H_2C), 1.81–1.64 (4H, H_2C, *H*C), 1.26 (dm, 1H, J = 10.0, H_2C), 1.20 (dm, 1H, J = 7.8, H_2C), 0.80 (m, 3H, H_2C), 0.61 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.1 [(0), *C*=O], 138.3 [(0), Ph], 135.2 [(1), *C*H=CH$_2$], 129.4, 128.2, 126.4 [(1), Ph], 117.3 [(2), *C*H$_2$=CH], 65.0 [(1), *C*HN], 53.1 [(2), *C*H$_2$S], 48.0, 47.5 [(0), C_q], 46.7, 44.6 [(1), *C*H], 38.9, 38.3, 35.3, 32.8, 26.3 [(2), *C*H$_2$], 20.5, 19.8 [(3), *C*H$_3$]. $[\alpha]_D^{20}$ −27.9 (c 1.18 in CH_2Cl_2).

(2*R*)-*N*-[(2*S*)-2-Methoxypent-4-enoyl]bornane-10,2-sultam (4c)

From **3c** (1.50 g, 5.2 mmol) and allyl iodide (1.91 ml, 20.9 mmol) **4c** (1.07 g, 63%) was obtained. Mp 158 °C. MS (EI) *m*/*z* (%) 328 (M$^+$ + 1, 20), 296 (5), 222 (5), 85 (100), 55 (20). IR (disk, KBr): ν/cm^{-1} 3002s, 2973s, 1697s, 1393m, 1326s, 1222s, 1135s, 915s, 648m, 537s. Found: C, 58.8%; H, 7.6%; N, 4.2%. $C_{16}H_{25}O_4SN$ requires C, 58.7%; H, 7.7%; N, 4.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.83 (dddd, 1H, J = 17.0, 10.3, 7.5, 7.0, *H*C=CH$_2$), 5.09 (dm, 1H, J = 17.0, H_2C=CH), 5.06 (dm, 1H, J = 10.3, H_2C=CH), 4.49 (dd, 1H, J = 6.0, 5.5, *H*CO), 3.94 (dd, 1H, J = 7.5, 4.8, *H*CN), 3.48 (d, 1H, J = 13.8, H_2CS), 3.43 (d, 1H, J = 13.8, H_2CS), 3.35 (s, 3H, H_3CO), 2.56 (dm, 1H, J = 14.3, H_2CCHO), 2.48 (dd, 1H, J = 14.3, 7.0, H_2CCHO), 2.07 (dd, 1H, J = 14.0, 7.5, H_2C), 1.96 (dm, 1H, J = 14.0, H_2C), 1.92–1.83 (3H, H_2C, *H*C), 1.41 (dm, 1H, J = 9.0, H_2C), 1.34 (dm, 1H, J = 9.0, H_2C), 1.12 (s, 3H, H_3C), 0.95 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8 [(0), *C*=O], 132.7 [(1), *C*H=CH$_2$], 118.2 [(2), *C*H$_2$=CH], 79.7 [(1), *C*HO], 65.0 [(1), *C*HN], 58.0 [(3), *C*H$_3$O], 53.1 [(2), *C*H$_2$S], 47.8, 47.3 [(0), C_q], 44.5 [(1), *C*H], 38.2, 38.0, 32.8, 26.4 [(2), *C*H$_2$], 20.7, 19.9 [(3), *C*H$_3$]. $[\alpha]_D^{20}$ −10.2 (c 1.52 in CH_2Cl_2).

(2*R*)-*N*-[(2*S*)-2-Methoxy-3-phenylpropanoyl]bornane-10,2-sultam (4d)

From **3c** (4.00 g, 13.9 mmol) and benzyl bromide (8.30 ml, 69.6 mmol) **4d** (2.33 g, 44%) was obtained. Mp 160 °C. MS (EI) *m*/*z* (%) 378 (M$^+$ + 1, 40), 346 (20), 216 (40), 135 (100), 91 (30). IR (disk, KBr): ν/cm^{-1} 3002m, 2966m, 1694s, 1330s, 1284s, 1218s, 1137s, 700m, 534s. Found: C, 63.6%; H, 7.1%; N, 3.7%. $C_{20}H_{27}O_4SN$ requires C, 63.6%; H, 7.2%; N, 3.7%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (4H, Ph), 7.18 (m, 1H, Ph), 4.61 (dd, 1H, J = 9.5, 3.5, *H*CO), 3.94 (dd, 1H, J = 7.5, 4.8, *H*CN), 3.49 (d, 1H, J = 13.8, H_2CS), 3.44 (d, 1H, J = 13.8, H_2CS), 3.27 (s, 3H, H_3CO), 3.06 (dd, 1H, J = 13.8, 3.5, H_2CPh), 2.87 (dd, 1H, J = 13.8, 9.5, H_2CPh), 2.08 (dd, 1H, J = 13.8, 7.5, H_2C), 1.95 (dm, 1H, J = 13.8, H_2C), 1.91–1.83 (3H, H_2C, *H*C), 1.41 (dm, 1H, J = 9.5, H_2C), 1.33 (dm, 1H, J = 9.5, H_2C), 1.01 (s, 3H, H_3C), 0.94 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2

[(0), *C*=O], 136.9 [(0), Ph], 129.6, 128.2, 126.7 [(1), Ph], 81.4 [(1), *C*HO], 65.0 [(1), *C*HN], 58.2 [(3), CH_3O], 53.1 [(2), CH_2S], 48.7, 47.6 [(0), C_q], 44.5 [(1), *C*H], 39.8, 38.1, 32.8, 26.4 [(2), CH_2], 20.7, 19.8 [(3), CH_3]. $[\alpha]_D^{25}$ −76.4 (*c* 1.00 in CH_2Cl_2).

(2*R*)-*N*-[(2*S*)-2-Allyloxypent-4-enoyl]bornane-10,2-sultam (4e)

From **3d** (6.00 g, 19.1 mmol) and allyl iodide (8.75 ml, 95.7 mmol) **4e** (4.25 g, 63%) was obtained. Mp 93 °C. MS (EI) *m*/*z* (%) 354 (M^+ + 1, 35), 135 (30), 111 (100), 93 (40), 67 (50), 55 (55). IR (disk, KBr): ν/cm^{-1} 2941m, 1695s, 1330s, 1273m, 1138s, 1062m, 914m, 545s. Found: C, 61.1%; H, 7.7%; N, 3.9%. $C_{18}H_{27}O_4SN$ requires C, 61.2%; H, 7.7%; N, 4.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91–5.79 (2H, *H*C=CH_2), 5.27 (dddd, 1H, *J* = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.15 (dm, 1H, *J* = 10.3, H_2C=CH), 5.08 (dm, 1H, *J* = 17.3, H_2C=CH), 5.04 (dm, 1H, *J* = 10.1, H_2C=CH), 4.61 (dd, 1H, *J* = 7.0, 5.0, *H*CO), 4.07 (dddd, 1H, *J* = 12.8, 5.5, 1.5, 1.5, H_2CO), 3.91 (dd, 1H, *J* = 7.8, 5.0, *H*CN), 3.87 (dddd, 1H, *J* = 12.8, 6.0, 1.5, 1.5, H_2CO), 3.47 (d, 1H, *J* = 13.8, H_2CS), 3.41 (d, 1H, *J* = 13.8, H_2CS), 2.57 (ddm, 1H, *J* = 13.8, 5.0, H_2C), 2.50 (ddm, 1H, *J* = 13.8, 7.0, H_2C), 2.05 (dd, 1H, *J* = 14.1, 7.8, H_2C), 1.95 (dm, 1H, *J* = 14.1, H_2C), 1.90–1.81 (3H, H_2C, *H*C), 1.40 (m, 1H, H_2C), 1.33 (m, 1H, H_2C), 1.11 (s, 3H, H_3C), 0.94 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.1 [(0), *C*=O], 133.9, 132.9 [(1), *C*H=CH_2], 118.0, 117.7 [(2), CH_2=CH], 77.6 [(1), *C*HO], 71.1 [(2), CH_2O], 65.0 [(1), *C*HN], 53.1 [(2), CH_2S], 48.6, 47.8 [(0), C_q], 44.5 [(1), *C*H], 38.2, 38.1, 32.8, 26.4 [(2), CH_2], 20.7, 19.8 [(3), CH_3]. $[\alpha]_D^{20}$ −96.6 (*c* 1.55 in CH_2Cl_2).

(2*R*)-*N*-[(1*S*)-3,6-Dihydro-2*H*-pyran-2-ylmethanoyl]bornane-10,2-sultam (4f)

From **4e** (4.48 g, 12.7 mmol) and Grubbs' catalyst (216 mg, 3 mol%) **4f** (3.44 g, 83%) was obtained. Mp 168 °C. MS (EI) *m*/*z* (%) 326 (M^+ + 1, 80), 216 (15), 135 (10), 83 (85), 55 (100). Found: C, 59.2%; H, 7.1%; N, 4.2%. $C_{16}H_{23}O_4SN$ requires C, 59.1%; H, 7.1%; N, 4.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 (ddm, 1H, *J* = 10.3, 2.0, C*H*=C*H*), 5.72 (dm, 1H, *J* = 10.3, C*H*=C*H*), 4.68 (dd, 1H, *J* = 10.3, 3.8, *H*CO), 4.33 (dm, 1H, *J* = 16.5, H*H*CO), 4.25 (dm, 1H, *J* = 16.5, H*H*CO), 3.92 (dd, 1H, *J* = 7.8, 4.8, *H*CN), 3.47 (d, 1H, *J* = 13.8, H_2CS), 3.42 (d, 1H, *J* = 13.8, H_2CS), 2.41 (dm, 1H, *J* = 16.8, H*H*CCH=), 2.28 (dm, 1H, *J* = 16.8, H*H*CCH=), 2.09 (dd, 1H, *J* = 14.0, 7.8, H_2C), 1.97 (dm, 1H, *J* = 14.0, H_2C), 1.91–1.83 (3H, H_2C, *H*C), 1.45–1.30 (2H, H_2C), 1.09 (s, 3H, H_3C), 0.94 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.6 [(0), *C*=O], 126.0, 122.7 [(1), *C*H=*C*H], 72.8 [(1), H*C*O], 65.7 [(2), HH*C*O], 64.9 [(1), *C*HN], 53.0 [(2), CH_2S], 48.7, 47.8 [(0), C_q], 44.4 [(1), *C*H], 38.0, 32.6, 28.6, 26.4 [(2), CH_2, *C*3], 20.7, 19.8 [(3), CH_3]. $[\alpha]_D^{20}$ −179.0 (*c* 1.75 in CH_2Cl_2).

(2*R*)-*N*-[(2*S*)-2-Allyloxy-3-ethoxycarbonylpropanoyl]bornane-10,2-sultam (4g)

From **3d** (3.00 g, 9.6 mmol) and ethyl 2-bromoacetate (5.31 ml, 47.9 mmol) **4g** (2.45 g, 64%) was obtained. MS (EI) *m*/*z* (%) 401 (M^+ + 1, 80), 399 (100), 390 (100), 354 (85), 296 (100). IR (disk, KBr): ν/cm^{-1} 2961m, 1744s, 1708s, 1337m, 1135m, 538m. Found: C, 57.2%; H, 7.4%; N, 3.7%. $C_{19}H_{29}NO_6S$ requires C, 57.1%; H, 7.3%; N, 3.5%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86 (dddd, 1H, *J* = 17.1, 10.7, 6.0, 6.0, C*H*=CH_2), 5.25 (dd, 1H, *J* = 17.1, 1.5, CH_2=CH), 5.15 (dd, 1H, *J* = 10.6, 1.5, CH_2=CH), 4.88 (1H, dd, *J* = 8.2, 4.0, C*H*C=O), 4.07–4.17 (4H, OCH_2), 3.92 (1H, dd, *J* = 6.2, 6.0, C*H*N), 3.47 (d, 1H, *J* = 14.0, CH_2SO_2), 3.42 (d, 1H, *J* = 13.7, CH_2SO_2), 2.79 (1H, dd, *J* = 15.7, 4.0, CH_2CHO), 2.72 (1H, dd, *J* = 15.7, 8.1, CH_2CHO), 2.00–2.11 (2H, CH_2CHN), 1.80–1.93 (3H, Sul), 1.20–1.27 (2H, Sul & 3H, CH_3CH$_2$), 1.09 (s, 3H, Sul), 0.93 (s, 3H, Sul); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.8 [(0), *C*=O], 169.3 [(0), *C*=O], 133.6 [(1), *C*H=CH_2], 118.1 [(2), CH_2=CH], 74.9 [(1), *C*HO], 71.7 [(2), CH_2O], 65.0 [(1), *C*HN], 60.8 [(2), CH_2O], 53.0 [(2), CH_2SO_2], 48.9 [(0), Sul], 47.8 [(0), Sul], 44.4 [(1), Sul], 38.4 [(2), Sul], 34.1 [(2), CH_2C=O], 32.7 [(2), Sul], 26.4 [(2), Sul], 20.5 [(3), Sul], 19.8 [(3), Sul], 14.1 [(3), CH_3CH_2]. $[\alpha]_D^{20}$ −62.6 (*c* 1.40 in CH_2Cl_2).

(4*S*)-3-[(2*R*)-2-Allyloxy-2-methylpent-4-enoyl]-4-benzyloxazolidin-2-one (7)

From **6a** (1.18 g, 4.1 mmol) and allyl iodide (1.87 ml, 20.5 mmol), **7** (0.45 g, 35%) was obtained. MS (EI) *m*/*z* (%) 329 (M^+, <5), 270 (100), 218 (90), 157 (50), 129 (30), 91 (50). IR (film) ν/cm^{-1} 3079w, 2964w, 2914w, 1790s, 1692s, 1348m, 1256m, 1182m, 1105m, 1004m, 917m, 734m. Found: C, 69.0%; H, 7.3%; N, 4.1%. $C_{19}H_{23}O_4N$ requires C, 69.3%; H, 7.0%; N, 4.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.15 (5H, Ph), 5.85 (dddd, 1H, *J* = 17.3, 10.3, 5.5, 5.5, *H*C=CH_2), 5.72 (dddd, 1H, *J* = 17.3, 10.0, 7.5, 7.5, *H*C=CH_2), 5.22 (dddd, 1H, *J* = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.09 (dddd, 1H, *J* = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.08 (dddd, 1H, *J* = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 5.04 (dddd, 1H, *J* = 10.0, 1.5, 1.5, 1.5, H_2C=CH), 4.57 (dddd, 1H, *J* = 10.0, 7.0, 3.5, 3.5, *H*CN), 4.07 (dd, 1H, *J* = 9.0, 7.0, H_2COC=O), 4.03 (dd, 1H, *J* = 9.0, 3.3, H_2COC=O), 3.98 (dddd, 1H, *J* = 12.3, 5.5, 1.5, 1.5, H_2COC), 3.84 (dddd, 1H, *J* = 12.3, 5.5, 1.5, 1.5, H_2COC), 3.23 (dd, 1H, *J* = 13.0, 3.5, H_2CCHN), 3.03 (dd, 1H, *J* = 14.0, 7.5, H_2CCO), 2.71 (dd, 1H, *J* = 14.0, 7.0, H_2CCO), 2.66 (dd, 1H, *J* = 13.0, 10.0, H_2CCHN), 1.52 (s, 3H, H_3CC). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5 [(0), *C*CCH$_3$], 151.4 [(0), *C*O], 135.4 [(0), Ph], 134.6, 132.7 [(1), *C*H=CH_2], 129.3, 128.8, 127.2 [(1), Ph], 118.7, 116.5 [(2), CH_2=CH], 82.7 [(0), *C*CH$_3$], 66.1, 65.4 [(2), CH_2O], 57.5 [(1), *C*HN], 40.5, 37.8 [(2), CH_2C], 20.8 [(3), CH_3]. $[\alpha]_D^{20}$ +38.4 (*c* 1.13 in CH_2Cl_2).

(4*S*)-3-[(2*R*)-2-Methyl-3,6-diyhdro-2*H*-pyran-2-ylmethanoyl]-4-benzyloxazolidin-2-one (8)

From **7** (0.94 g, 2.8 mmol) and Grubbs' catalyst (70 mg, 3 mol%) **8** (0.68 g, 80%) was obtained. MS (EI) *m*/*z* (%) 302 (M^+ + 1, 60), 97 (100). IR (film) ν/cm^{-1} 2926m, 1789s, 1349m, 1190s, 1093s, 703m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.24 (2H, Ph), 7.21 (m, 1H, Ph), 7.17–7.13 (2H, Ph); 5.79 (dm, 1H, *J* = 10.5, HC=C*H*), 5.66 (dm, 1H, *J* = 10.5, HC=C*H*), 4.60 (dddd, 1H, *J* = 10.0, 9.0, 3.0, 3.0, *H*CN), 4.39 (dm, 1H, *J* = 17.0, H*H*CO), 4.22 (dm, 1H, *J* = 17.0, H*H*CO), 4.13 (dd, 1H, *J* = 9.0, 9.0, H_2COC=O), 4.08 (dd, 1H, *J* = 9.0, 3.0, H_2COC=O), 3.26 (dd, 1H, *J* = 13.3, 3.0, H_2CCHN), 2.88 (dm, 1H, *J* = 17.5, *H*HCCH=), 2.68 (dd, 1H, *J* = 13.3, 10.0, H_2CCHN), 2.19 (dm, 1H, *J* = 17.5, *H*HCCH=), 1.61 (3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.5 [(0), *C*CCH$_3$], 151.8 [(0), *C*O], 135.3 [(0), Ph], 129.3, 128.9, 127.3 [(1), Ph], 125.0, 122.0 [(1), H*C*=*C*H], 76.8 [(0), C(CH$_3$)O], 66.4, 62.4 [(2), CH_2O], 57.4 [(1), *C*HN], 37.8 [(2), CH_2CHN)], 31.9 [(2), HH*C*CH=], 22.2 [(3), CH_3]. $[\alpha]_D^{20}$ +42.7 (*c* 1.45 in CH_2Cl_2).

Attempted allylation of acylated oxazolidinone 6b

From **6b** (1.80 g, 5.9 mmol) and allyl iodide (2.71 ml, 29.7 mmol) only allyl benzoate **9** (0.50 g, 47%) was obtained. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–8.03 (2H, Ph), 7.55 (m, 1H, Ph), 7.45–7.40 (2H, Ph), 6.03 (dddd, 1H, *J* = 17.1, 10.5, 5.8, 5.5, *H*C=CH_2), 5.40 (dddd, 1H, *J* = 17.1, 1.5, 1.5, 1.5, H_2C=CH), 5.27 (dddd, 1H, *J* = 10.5, 1.5, 1.5, 1.5, H_2C=CH), 4.84 (dddd, 1H, *J* = 19.8, 5.8, 1.5, 1.5, H_2CO), 4.79 (dddd, 1H, *J* = 19.8, 5.5, 1.5, 1.5, H_2CO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2 [(0), *C*=O], 133.0, 132.2 [(1), Ph/*C*H=CH_2], 130.1 [(0), Ph], 129.6, 128.3 [(1), Ph/*C*H=CH_2], 118.2 [(2), CH_2=CH], 65.2 [(2), CH_2O].

General procedure for the preparation of diallylcarbinols

A solution of allylmagnesium bromide (1.0 M solution in ether, 7.6 ml, 7.6 mmol) was added to a solution of the corresponding oxazolidinone **2** or bornane sultam **4** (1.90 mmol) in ether

(5 ml) at −78 °C. When the reaction was complete as indicated by TLC, the mixture was poured into aqueous NH_4Cl solution and extracted. After evaporation, the residue was purified by flash chromatography on silica to give the corresponding *S*- or *R*-configured diallylcarbinols, along with the free oxazolidinone or bornane sultam, respectively.

(*R*)-4-Allyl-5-methylocta-1,7-dien-4-ol (10a)

From **2a** (4.21 g, 15.4 mmol) **10a** (1.94 g, 70%) was obtained. MS (EI) *m*/*z* (%) 179 ($M^+ - 1$, <5), 139 (100), 69 (40). IR (film): ν/cm^{-1} 3485br m, 3076s, 2977s, 2937s, 1640s, 1383m, 996s, 911s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92–5.81 (2H, *H*C=CH_2), 5.70 (ddm, 1H, *J* = 17.3, 10.3, *H*C=CH_2), 5.13 (dm, 1H, *J* = 10.3, H_2C=CH), 5.13 (dm, 1H, *J* = 10.3, H_2C=CH), 5.09 (dm, 1H, *J* = 17.8, H_2C=CH), 5.09 (dm, 1H, *J* = 17.8, H_2C=CH), 5.00 (dm, 1H, *J* = 17.3, H_2C=CH), 4.97 (dm, 1H, *J* = 10.8, H_2C=CH), 2.43 (m, 1H, H_2C), 2.32–2.25 (2H, H_2C), 2.23–2.17 (2H, H_2C), 1.76 (dm, 1H, *J* = 13.3, H_2C), 1.64 (dqm, 1H, *J* = 7.0, 2.8, *H*CCH_3), 1.57 (br s, 1H, *H*O), 0.89 (d, 3H, *J* = 7.0, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 133.9, 133.8 [(1), *C*H=CH_2], 118.6, 118.6, 115.7 [(2), *C*H_2=CH], 75.4 [(0), *C*OH], 41.4, 40.6 [(2), *C*H_2], 40.1 [(1), *C*HCH_3], 35.5 [(2), *C*H_2], 13.6 [(3), *C*H_3]. +4.3 (*c* 1.20 in CH_2Cl_2).

(*R*)-4-Allyl-2-benzylhex-5-en-3-ol (10b)

From **2b** (0.53 g, 1.6 mmol) **10b** (0.31 g, 82%) was obtained. MS (EI) *m*/*z* (%) 231 ($M^+ + 1$, <5), 189 (100), 171 (70), 119 (80), 91 (25). IR (film): ν/cm^{-1} 3476br m, 2976s, 2937s, 1639m, 999s, 914s, 711s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.26 (2H, Ph), 7.21–7.16 (3H, Ph), 6.02–5.89 (2H, *H*C=CH_2), 5.22 (dm, 1H, *J* = 10.0, H_2C=CH), 5.20 (dm, 1H, *J* = 17.1, H_2C=CH), 5.18 (dm, 1H, *J* = 10.0, H_2C=CH), 5.17 (dm, 1H, *J* = 17.0, H_2C=CH), 3.12 (dd, 1H, *J* = 13.0, 2.5, H_2CPh), 2.41 (dm, 2H, *J* = 14.0, H_2C), 2.33 (dd, 2H, *J* = 14.0, 7.5, H_2C), 2.19 (dd, 1H, *J* = 13.0, 11.3, H_2CPh), 1.89 (dqd, 1H, *J* = 11.3, 7.0, 2.5, *H*CCH_3), 1.67 (br s, 1H, *H*O), 0.84 (d, 1H, *J* = 7.0, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.8 [(0), Ph], 133.9, 133.7 [(1), *C*H=CH_2], 129.1, 128.2, 125.7 [(1), Ph], 118.8, 118.7 [(2), *C*H_2=CH], 75.3 [(0), *C*OH], 42.8 [(1), *C*HCH_3], 41.3, 40.8, 37.2 [(2), *C*H_2], 13.2 [(3), *C*H_3]. $[\alpha]_D^{22}$ −2.5 (*c* 1.70 in CH_2Cl_2).

(*R*)-4-Allyl-5-allyloxyocta-1,7-dien-4-ol (10c)

From **2c** (0.60 g, 1.9 mmol) **10c** (0.32 g, 76%) was obtained. MS (EI) *m*/*z* (%) 221 ($M^+ - 1$, <5), 205 (100), 177 (40), 149 (20), 91 (20). IR (film) ν/cm^{-1} 3483br w, 3078m, 2926m, 1640m, 1261m, 1087m, 998m, 925s, 804m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95–5.81 (4H, *H*C=CH_2), 5.23 (dddd, 1H, *J* = 17.3, 1.8, 1.8, 1.8, H_2C=CH), 5.14–5.03 (6H, H_2C=CH), 5.02 (dm, 1H, *J* = 10.3, H_2C=CH), 4.18 (dddd, 1H, *J* = 12.5, 5.3, 1.5, 1.5, H_2CO), 3.97 (dddd, 1H, *J* = 12.5, 5.8, 1.5, 1.5, H_2CO), 3.29 (dd, 1H, *J* = 8.0, 3.5, *H*CO), 2.43–2.29 (3H, H_2C), 2.31 (ddm, 1H, *J* = 13.5, 7.0, H_2C), 2.27 (br s, 1H, *H*O), 2.24 (ddm, 1H, *J* = 14.3, 7.5, H_2C), 2.12 (dd, 1H, *J* = 14.3, 8.0, H_2C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 134.8, 133.9, 133.7 [(1), *C*H=CH_2], 118.3, 118.0, 116.7, 116.4 [(2), *C*H_2=CH], 83.4 [(1), *C*HO], 75.7 [(0), *C*OH], 73.0 [(2), *C*H_2O], 40.8, 40.0, 34.9 [(2), *C*H_2]. $[\alpha]_D^{22}$ −28.3 (*c* 1.25 in CH_2Cl_2).

(*R*)-4-(3,6-Dihydro-2*H*-pyran-2-yl)hepta-1,6-dien-4-ol (10d)

From **2d** (0.96 g, 3.3 mmol) **10d** (0.38 g, 63%) was obtained. MS (EI) *m*/*z* (%) 195 ($M^+ + 1$, <5), 177 (90), 55 (100). IR (film): ν/cm^{-1} 3440s, 2937s, 1648m, 915m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92–5.78 (3H, *H*C=CH_2), 5.68 (dm, 1H, *J* = 10.0, *H*C=), 5.15–5.03 (4H, H_2C=CH), 4.22 (d, 1H, *J* = 16.2, OC*H*H), 4.15 (d, 1H, *J* = 16.2, OCH*H*), 3.40 (dd, 1H, *J* = 10.7, 3.0, *H*CO), 2.40–2.18 (5H, CH_2, O*H*), 2.09 (dd, 1H, *J* = 14.2, 8.2, CH_2), 1.91 (dm, 1H, *J* = 17.0, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.6, 133.5, 125.9, 124.4 [(1), *C*H=CH_2], 118.3, 118.0 [(2), *C*H_2=CH], 76.8 [(1), *C*HO], 74.6 [(0), *C*OH], 66.4 [(2), *C*H_2O], 40.4, 39.0, 24.5 [(2), *C*H_2]. $[\alpha]_D^{22}$ +14.5 (*c* 1.00 in CH_2Cl_2).

(*S*)-4-Allyl-5-methylocta-1,7-dien-4-ol (12a)

From **4a** (1.50 g, 4.8 mmol) **12a** (0.73 g, 83%) was obtained. Spectroscopic data are identical to those observed for the enantiomer (**10a**). $[\alpha]_D^{22}$ −3.2 (*c* 1.00 in CH_2Cl_2).

(*S*)-4-Allyl-5-benzylocta-1,7-dien-4-ol (12b)

From **4b** (0.50 g, 1.3 mmol) **12b** (0.22 g, 64%) was obtained. MS (EI) *m*/*z* (%) 256 (M^+, 40), 244 (90), 216 (90), 135 (100), 93 (50), 57 (50). IR (film): ν/cm^{-1} 3480br m, 3079m, 2934s, 1643s, 925s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (2H, Ph), 7.19–7.14 (3H, Ph), 5.96–5.84 (2H, *H*C=CH_2), 5.71 (dddd, 1H, *J* = 17.1, 10.0, 7.0, 7.0, *H*C=CH_2), 5.17 (dm, 1H, *J* = 17.1, H_2C=CH), 5.12 (dm, 1H, *J* = 10.0, H_2C=CH), 5.12 (dm, 1H, *J* = 17.1, H_2C=CH), 5.10 (dm, 1H, *J* = 10.0, H_2C=CH), 4.94 (ddm, 1H, *J* = 17.1, 1.5, H_2C=CH), 4.90 (dm, 1H, *J* = 10.0, H_2C=CH), 2.98 (dd, 1H, *J* = 13.8, 3.8, H_2CPh), 2.44 (dd, 1H, *J* = 14.1, 9.8, H_2C), 2.39 (dd, 2H, *J* = 14.1, 7.3, H_2C), 2.34–2.23 (3H, *H*CCOH, H_2C), 2.08 (dm, 1H, *J* = 14.3, H_2C), 1.98 (dm, 1H, *J* = 14.3, H_2C), 1.73 (br s, 1H, *H*O). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.6 [(0), Ph], 138.4, 133.9, 133.8 [(1), *C*H=CH_2], 129.2, 128.3, 125.8 [(1), Ph], 118.7, 118.6, 115.8 [(2), *C*H_2=CH], 76.2 [(0), *C*OH], 47.3 [(1), *C*HCOH], 41.8, 41.5, 35.4, 33.7 [(2), *C*H_2]. $[\alpha]_D^{21}$ −7.1 (*c* 1.30 in CH_2Cl_2).

(*S*)-4-Allyl-5-methoxyocta-1,7-dien-4-ol (12c)

From **4c** (0.59 g, 1.8 mmol) **12c** (0.30 g, 85%) was obtained. MS (EI) *m*/*z* (%) 195 ($M^+ - 1$, <5), 179 (20), 147 (40), 137 (50), 85 (100). IR (film) ν/cm^{-1} 3480br m, 2978m, 2935m, 1639m, 1437m, 1098s, 914s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95–5.80 (3H, *H*C=CH_2), 5.13–5.07 (4H, H_2C=CH), 5.06 (dm, 1H, *J* = 17.8, H_2C=CH), 5.03 (dm, 1H, *J* = 17.0, H_2C=CH), 3.42 (s, 3H, H_3C), 3.12 (dd, 1H, *J* = 8.3, 3.5, *H*CO), 2.41–2.32 (3H, H_2C), 2.27 (dm, 1H, *J* = 9.0, H_2C), 2.23 (br s, 1H, *H*O), 2.21 (dm, 1H, *J* = 8.3, H_2C), 2.10 (dd, 1H, *J* = 14.1, 8.3, H_2C). ^{13}C NMR (100 MHz, $CDCl_3$) 136.1, 133.9, 133.6 [(1), *C*H=CH_2], 118.3, 118.0, 116.6 [(2), *C*H_2=CH], 85.1 [(1), *C*HO], 75.8 [(0), *C*OH], 60.0 [(2), *C*H_3O], 40.7, 39.9, 34.6 [(2), *C*H_2]. $[\alpha]_D^{22}$ +23.3 (*c* 1.25 in CH_2Cl_2).

(*S*)-4-Allyl-5-allyloxyocta-1,7-dien-4-ol (12e)

From **4e** (0.50 g, 1.3 mmol) **12e** (0.29 g, 96%) was obtained. Spectroscopic data are identical to those observed for the enantiomer (**10c**). $[\alpha]_D^{20}$ +30.3 (*c* 1.45 in CH_2Cl_2).

Preparation of divinylcarbinols

Procedure A. A solution of vinylmagnesium chloride (1.7 M solution in THF, 1.85 ml, 3.2 mmol) was added to a solution of the corresponding oxazolidinone **2** or bornane sultam **4** (1.50 mmol) in ether (15 ml) at −78 °C. When the reaction was complete as indicated by TLC, the mixture was poured into aqueous NH_4Cl solution and extracted. After evaporation, the residue was purified by flash chromatography on silica to give the corresponding *S*- or *R*-configured divinylcarbinols, along with a butenone by-product. When oxazolidinones **2a**,**b** and **8a** were used, acrylates **16a**,**b** and **17** were formed exclusively.

Procedure B. The vinylcerium reagent was prepared from $CeCl_3 \cdot 7H_2O$ (2.73 g, 7.3 mmol) and vinylmagnesium chloride (1.7 M solution in THF, 3.77 ml, 6.4 mmol) as described by Lautens *et al.*[36] Acylated oxazolidinones **2** or bornane sultams **4** (1.8 mmol) were added in dry, degassed THF (22 ml) at −78 °C. The reaction mixture was stirred until the starting material was fully consumed, as indicated by TLC. Water (30 ml) was added dropwise and the minimum amount of hydrochloric acid (1M)

was added to ensure solution of inorganic precipitates. The aqueous layer was extracted and the combined organic extracts were dried with $MgSO_4$, filtered and evaporated. The resulting divinylcarbinols were easily separated from the oxazolidinone **11** or bornane sultam **13**, respectively, by flash chromatography on silica. When oxazolidinones **2a**,**b** were used, acrylates **16a**,**b** were formed exclusively.

(*S*)-2-[(*R*)-2-Methylpent-4-enamido]-3-phenylpropyl acrylate (16a)

Following procedure A, from **2a** (0.80 g, 2.9 mmol) **16a** (0.53 g, 60%) was obtained. Following procedure B, from **2a** (0.80 g, 2.9 mmol) **16a** (0.50 g, 57%) was obtained. Mp 107 °C. MS (EI, 70 eV): *m*/*z* (%) = 302 (M^+ + 1, 100), 230 (20), 138 (40), 114 (30), 91 (30), 69 (65), 55 (70). IR (disk, KBr): ν/cm^{-1} 3287s, 2965w, 1725s, 1648s, 1552m, 1299m, 1211m, 700m. Found: C, 71.7%; H, 7.6%; N, 4.6%. $C_{18}H_{23}O_3N$ requires C, 71.7%; H, 7.7%; N, 4.7%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25–7.12 (5H, Ph), 6.37 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 6.08 (dd, 1H, J = 17.3, 10.3, *H*C=CH_2), 5.82 (dd, 1H, J = 10.3, 1.5, H_2C=CH), 5.60–5.52 (m, 2H, *H*N, *H*C=CH_2), 4.94 (dddd, 1H, J = 17.3, 1.8, 1.8, 1.8, H_2C=CH), 4.90 (dddd, 1H, J = 10.3, 1.8, 1.8, 1.8, H_2C=CH), 4.42 (m, 1H, *H*CN), 4.13 (dd, 1H, J = 11.5, 5.8, H_2CO), 4.05 (dd, 1H, J = 11.5, 4.5, H_2CO), 2.83 (dd, 1H, J = 13.8, 6.5, H_2CPh), 2.75 (dd, 1H, J = 13.8, 7.8, H_2CPh), 2.23 (ddm, 1H, J = 13.8, 7.3, H_2CCHCH_3), 2.12 (dm, 1H, J = 6.8, *H*CCH_3), 2.00 (ddm, 1H, J = 13.8, 6.3, H_2CCHCH_3), 1.02 (d, 3H, J = 6.8, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 166.2 [(0), *C*=O], 136.9 [(0), Ph], 135.7 [(1), *C*H=CH_2], 131.6 [(2), *C*H_2=CH], 129.2, 128.6, 127.9, 126.8, [(1), Ph, *C*H=CH_2], 116.8 [(2), *C*H_2=CH], 64.9 [(2), *C*H_2O], 49.4 [(1), *C*HN], 41.3 [(1), *C*HCH_3], 38.2, 37.6 [(2), *C*H_2], 17.3 [(3), *C*H_3]. $[\alpha]_D^{22}$ −28.9 (*c* 1.40 in CH_2Cl_2).

(*S*)-2-[(*R*)-2-Methyl-3-phenylpropanamido]-3-phenylpropyl acrylate (16b)

Following procedure A, from **2b** (0.56 g, 1.5 mmol) **16b** (0.43 g, 70%) was obtained. Following procedure B, from **2b** (0.56 g, 1.5 mmol) **16b** (0.41 g, 67%) was obtained. Mp 89 °C. MS (EI) *m*/*z* (%) 352 (M^+ + 1, 40), 280 (30), 188 (60), 119 (30), 91 (100), 55 (50). IR (disk, KBr) ν/cm^{-1} 3298s, 2964w, 1726s, 1648s, 1545m, 1409m, 1300m, 1216m, 703s. Found: C, 74.5%; H, 7.2%; N, 3.9%. $C_{22}H_{25}O_3N$ requires C, 75.1 %; H, 7.2%; N, 4.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.08 (8H, Ph), 6.94–6.90 (2H, Ph), 6.31 (dd, 1H, J = 17.3, 1.3, H_2C=CH), 6.02 (dd, 1H, J = 17.3, 10.3, *H*C=CH_2), 5.79 (dd, 1H, J = 10.3, 1.3, H_2C=CH), 5.34 (d, 1H, J = 8.3, *H*N), 4.33 (m, 1H, *H*CN), 3.99 (dd, 1H, J = 11.5, 6.0, H_2CO), 4.96 (dd, 1H, J = 11.5, 4.3, H_2CO), 2.83 (dd, 1H, J = 13.8, 8.8, H_2CPh), 2.68 (dd, 1H, J = 13.8, 5.3, H_2CPh), 2.57 (dd, 1H, J = 13.8, 6.3, H_2CPh), 2.45 (dd, 1H, J = 13.8, 8.0, H_2CPh), 2.31 (dm, 1H, J = 7.0, *H*CCH_3), 1.07 (d, 3H, J = 7.0, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.1, 166.1 [(0), *C*=O], 139.8, 136.7 [(0), Ph], 131.5 [(2), *C*H_2=CH], 129.2, 129.0, 128.6, 128.4, 127.8, 126.7, 126.3, [(1), Ph, *C*H=CH_2], 64.4 [(2), *C*H_2O], 49.6 [(1), *C*HN], 44.0 [(1), *C*HCH_3], 40.4, 37.2 [(2), *C*H_2], 17.7 [(3), *C*H_3]. $[\alpha]_D^{22}$ −39.5 (*c* 1.06 in CH_2Cl_2).

Attempted cleavage of oxazolidinone 2c

Following procedure A, from **2c** (0.47 g, 1.5 mmol) an inseparable 1.5 : 1 : 1 mixture of **14c**, **15c** and **16c** was obtained, along with the oxazolidinone **11**. Following procedure B, from **2c** (0.80 g, 2.5 mmol) only the *R*-configured divinylcarbinol **14c** (0.19 g, 40%) was obtained. Spectroscopic data were identical to those observed for **12e**. $[\alpha]_D^{22}$ +13.3 (*c* 1.10 in CH_2Cl_2).

(*S*)-2-{1-[(*S*)-2-Methyl-3,6-dihydro-2*H*-pyran-2-yl]methanoylamino}-3-phenylpropyl acrylate (17)

Following procedure A, from **8a** (0.39 g, 1.3 mmol) **17** (0.17 g, 40%) was obtained. Mp 79 °C. MS (EI) *m*/*z* (%) 329 (M^+, <5), 301 (20), 238 (40), 166 (70), 97 (100). IR (disk, KBr): ν/cm^{-1} 3353m, 2844w, 1720s, 1648s, 1408m, 1300m, 1079s, 811m, 703m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (2H, Ph), 7.23–7.18 (3H, Ph), 6.78 (d, 1H, J = 8.8, *H*N), 6.43 (dd, 1H, J = 17.5, 1.5, H_2C=CH), 6.16 (dd, 1H, J = 17.5, 10.5, *H*C=CH_2), 5.87 (dd, 1H, J = 10.5, 1.5, H_2C=CH), 5.76 (dm, 1H, J = 10.5, C*H*=CH), 5.63 (dm, 1H, J = 10.5, C*H*=CH), 4.58 (m, 1H, *H*CN), 4.20–4.13 (3H, H_2CO, H*H*CO), 4.09 (dm, 1H, J = 16.5, *H*6), 2.88 (d, 2H, J = 7.3, H_2CPh), 2.32 (dm, 1H, J = 17.5, H*H*CCH=), 2.08 (dm, 1H, J = 17.5, H*H*CCH=), 1.36 (s, 3H, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 165.9 [(0), *C*=O], 137.0 [(0), Ph], 131.4 [(2), *C*H_2=CH], 129.2, 128.6, 128.0, 126.7, 124.3, 122,7 [(1), Ph, *C*H=CH, *C*H=CH_2], 74.6 [(0), *C*(CH_3)O], 64.9, 61.7 [(2), *C*H_2O], 48.8 [(1), *C*HN], 37.6, 31.8 [(2), *C*H_2Ph, HH*C*CH=], 21.7 [(3), *C*H_3]. $[\alpha]_D^{22}$ −51.2 (*c* 0.86 in CH_2Cl_2).

(4*S*)-4-Methoxy-3-vinylhepta-1,6-dien-3-ol (18c)

Following procedure B, from **4c** (0.66 g, 2.0 mmol) 0.24 g (70%) of **18c** were obtained. MS (EI) *m*/*z* (%) 167 (M^+ − 1, <5), 151 (40), 119 (95), 85 (100), 55 (45). IR (film) ν/cm^{-1} 3479br m, 2933m, 1413w, 1102s, 922s, 799w. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.95 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.86 (dddd, 1H, J = 17.3, 10.3, 7.0, 7.0, *H*C=CH_2), 5.34 (dm, 1H, J = 17.3, H_2C=CH), 5.34 (dm, 1H, J = 17.3, H_2C=CH), 5.17 (dm, 1H, J = 17.3, H_2C=CH), 5.17 (dm, 1H, J = 10.8, H_2C=CH), 5.07 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.01 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 3.41 (s, 3H, H_3CO), 3.14 (dd, 1H, J = 7.5, 3.8, *H*CO), 2.40–2.32 (2H, *H*O, H_2CCH=CH_2), 2.21 (dm, 1H, J = 14.8, H_2CCH=CH_2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.0, 139.0, 135.9 [(1), *C*H=CH_2], 116.7, 114.5, 114.5 [(2), *C*H_2=CH], 86.7 [(1), *C*HO], 78.1 [(0), *C*OH], 60.3 [(3), *C*H_3O], 35.0 [(2), *C*H_2CH=CH_2]. $[\alpha]_D^{23}$ −10.7 (*c* 1.52 in CH_2Cl_2).

(4*S*)-4-Methoxy-5-phenyl-3-vinylpent-1-en-3-ol (18d)

Following procedure B, from **4d** (0.67 g, 2.0 mmol) **18d** (0.28 g, 73%) was obtained. MS (EI) *m*/*z* (%) 217 (M^+ − 1, <5), 169 (100). IR (film): ν/cm^{-1} 3470br m, 2931s, 1496m, 1454m, 1105s, 924m, 700s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.19 (5H, Ph), 6.08 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 6.05 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.43 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.42 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.26 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 5.24 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 3.32 (dd, 1H, J = 9.8, 2.8, *H*CO), 3.10 (s, 3H, H_3CO), 2.94 (dd, 1H, J = 14.3, 2.8, H_2CPh), 2.67 (dd, 1H, J = 14.3, 9.8, H_2CPh), 2.46 (br s, 1H, *H*O). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1 [(1), *C*H=CH_2], 139.7 [(0), Ph], 139.1 [(1), *C*H=CH_2], 129.4, 128.3, 126.0 [(1), Ph], 114.6, 114.6 [(2), *C*H_2=CH], 88.8 [(1), *C*HO], 78.2 [(0), *C*OH], 61.1 [(3), *C*H_3O], 37.1 [(2), *C*H_2Ph].

(4*S*)-4-Allyloxy-3-vinylhepta-1,6-dien-3-ol (18e) and (*S*)-4-Allyloxynona-1,8-dien-5-one (19e)

Following procedure A, from **4e** (0.72 g, 2.0 mmol) a mixture of **18e** (59%) and **19e** (20%) was obtained. The compounds were separated by column chromatography on silica. Following procedure B, from **4e** (0.72 g, 2.0 mmol) **18e** (0.31 g, 79%) was obtained as a single isomer. Spectroscopic data for **18e**: MS (EI) *m*/*z* (%) 195 (M^+ + 1, <5), 137 (60), 93 (40), 81 (50), 67 (50), 55 (100). IR (film) ν/cm^{-1} 3465br w, 3079w, 2923m, 1088m, 995m, 921s, 805w. Found: C, 73.6%; H, 9.2%. $C_{12}H_{18}O_2$ requires C, 74.2%; H, 9.3%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.00 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.96 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.90–5.80 (2H, *H*C=CH_2), 5.34 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.33 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.21 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.17 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 5.17 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 5.12 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 5.06 (dddd, 1H, J = 17.3,

1.5, 1.5, 1.5, H_2C=CH), 5.00 (dddd, 1H, J = 10.0, 1.5, 1.5, 1.5, H_2C=CH), 4.11 (dddd, 1H, J = 12.5, 5.5, 1.5, 1.5, H_2CO), 4.02 (dddd, 1H, J = 12.5, 5.5, 1.5, 1.5, H_2CO), 3.30 (dd, 1H, J = 8.5, 3.5, *H*CO), 2.45 (br s, 1H, *H*O), 2.36 (dm, 1H, J = 14.5, H_2CCHO), 2.24 (dm, 1H, J = 14.5, H_2CCHO). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.1, 139.1, 135.9, 134.7 [(1), *C*H=CH_2], 116.8, 116.7, 114.4, 114.4 [(2), *C*H_2=CH], 84.6 [(1), *C*HO], 78.1 [(0), *C*OH], 73.3 [(2), *C*H_2O], 35.3 [(2), *C*H_2CHO]. $[\alpha]_D^{22}$ −12.8 (*c* 1.90 in CH_2Cl_2). Spectroscopic data for **19e** are reported below.

3-[(2*S*)-3,6-Dihydro-2*H*-pyran-2-yl)penta-1,4-dien-3-ol (18f) and 1-[(2*S*)-3,6-Dihydro-2*H*-pyran-2-yl)pent-4-en-1-one (19f)

Following procedure A, from **4f** (0.55 g, 1.7 mmol) a mixture of **18f** (0.12 g, 43%) and **19f** (0.05 g, 19%) was obtained. The compounds were separated by column chromatography on silica. Following procedure B, from **4f** (0.60 g, 1.8 mmol) **18f** (0.19 g, 62%) was obtained as a single isomer. Spectroscopic data for **18f**: MS (EI) *m*/*z* (%) 167 (M^+ + 1, <5), 83 (70), 55 (100). IR (film) ν/cm^{-1} 3477br m, 2938m, 1727m, 1092s, 924m, 800w, 656m. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.97 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.92 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.78 (dm, 1H, J = 10.0, HC=C*H*), 5.65 (dm, 1H, J = 10.0, HC=C*H*), 5.36 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.35 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.19 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 5.18 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 4.21 (dm, 1H, J = 16.3, H*H*CO), 4.16 (dm, 1H, J = 16.3, H*H*CO), 3.48 (dd, 1H, J = 10.8, 3.3, *H*CO), 2.61 (br s, 1H, *H*O), 2.22 (m, 1H, HCOC*H*H), 1.91 (dm, 1H, J = 17.5, HCOC*H*H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.8, 138.2 [(1), *C*H=CH_2], 125.6, 124.2 [(1), H*C*=*C*H], 115.0, 114.6 [(2), *C*H_2=CH], 78.2 [(1), H*C*O], 76.8 [(0), *C*OH], 66.5 [(2), HH*C*O], 25.0 [(2), HH*C*CH=]. $[\alpha]_D^{24}$ −103.6 (*c* 1.12 in CH_2Cl_2).

Spectroscopic data for **19f**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (dm, 1H, J = 10.0, C*H*=C*H*), 5.78 (dddd, 1H, J = 17.0, 10.5, 6.5, 6.5, *H*C=CH_2), 5.71 (dm, 1H, J = 10.0, C*H*=C*H*), 5.00 (dm, 1H, J = 17.3, H_2C=CH), 4.94 (dm, 1H, J = 10.5, H_2C=CH), 4.30 – 4.17 (2H, H*H*CO), 3.97 (dd, 1H, J = 10.3, 4.5, *H*CO), 2.68 (dd, 1H, J = 7.3, 7.3, H_2CC=O), 2.32 (dm, 1H, J = 7.3, H_2C), 2.29 (dm, 1H, J = 7.3, H_2C), 2.22–2.12 (3H, 3 × CH*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7 [(0), *C*=O], 137.1 [(1), *C*H=CH_2], 126.1, 123.3 [(1), *C*H=*C*H], 115.1 [(2), *C*H_2=CH], 78.4 [(1), *H*CO], 65.9 [(2), HH*C*O], 37.1, 27.0, 26.9 [(2), *C*H_2].

(3*S*)-3-Allyloxy-4-hydroxy-4-vinylhex-5-enoic acid ethyl ester (18g) and (3*S*)-3-Allyloxy-4-oxooct-7-enoic acid ethyl ester (19g)

Following procedure A, from **4g** (1.51 g, 3.8 mmol) a mixture of **18g** (0.39 g, 43%) and **19g** (0.15 g, 17%) was obtained. The compounds were separated by column chromatography on silica. Spectroscopic data for **18g**: MS (EI) *m*/*z* (%) 241 (M^+ + 1, <5), 115 (80), 83 (40), 55 (100). IR (film): ν/cm^{-1} 3503br w, 2983w, 1732s, 1307m, 1182m, 926m. Found: C, 64.4%; H, 8.1%. $C_{13}H_{20}O_4$ requires C, 64.5%; H, 8.4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.89 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.79 (dddd, 1H, J = 17.3, 10.3, 5.8, 5.8, *H*C=CH_2), 5.33 (dd, 1H, J = 17.3, 1.3, H_2C=CH), 5.32 (dd, 1H, J = 17.3, 1.3, H_2C=CH), 5.18 (dddd, 1H, J = 17.3, 1.5, 1.5, 1.5, H_2C=CH), 5.16 (dd, 1H, J = 10.8, 1.3, H_2C=CH), 5.13 (dd, 1H, J = 10.8, 1.3, H_2C=CH), 5.08 (dddd, 1H, J = 10.3, 1.5, 1.5, 1.5, H_2C=CH), 4.14–4.02 (4H, H_2CO), 3.81 (dd, 1H, J = 8.0, 4.0, *H*CO), 2.62 (dd, 1H, J = 16.1, 4.0, H_2CC=O), 2.46 (br s, 1H, *H*O), 2.42 (dd, 1H, J = 16.1, 8.0, H_2CC=O), 1.20 (t, 3H, J = 7.3, H_3CCH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.3 [(0), C=O], 139.8, 138.8, 134.5 [(1), *C*H=CH_2], 116.9, 114.7, 114.6 [(2), *C*H_2=CH], 81.1 [(1), *C*HO], 77.7 [(0), *C*OH], 73.2, 60.6 [(2), *C*H_2O], 36.1 [(2), *C*H_2C=O], 14.1 [(3), *C*H_3]. $[\alpha]_D^{25}$ −22.1 (*c* 1.10 in CH_2Cl_2).

Spectroscopic data for **19g**: MS (EI) *m*/*z* (%) 241 (M^+ + 1, <5), 157 (20), 138 (40), 115 (100), 71 (30), 55 (80). IR (film) ν/cm^{-1} 2981m, 2931m, 1729s, 1373m, 1184m, 995m, 921m. Found: C, 64.4%; H, 8.4%. $C_{13}H_{20}O_4$ requires C, 64.5%; H, 8.4%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.84 (dddd, 1H, J = 17.1, 10.5, 5.8, 5.8, *H*C=CH_2), 5.76 (dddd, 1H, J = 17.1, 10.3, 6.5, 6.5, *H*C=CH_2), 5.24 (dm, 1H, J = 17.1, H_2C=CH), 5.16 (dm, 1H, J = 10.5, H_2C=CH), 4.99 (dm, 1H, J = 17.1, H_2C=CH), 4.92 (dm, 1H, J = 10.3, H_2C=CH), 4.11 (dd, 1H, J = 6.5, 5.3, *H*CO), 4.10 (q, 2H, J = 7.0, H_2CCH$_3$), 4.03 (dm, 2H, J = 6.5, H_2CCHO), 2.80–2.55 (4H, H_2C), 2.28 (ddm, 2H, J = 14.8, 7.0, H_2C), 1.20 (t, 3H, J = 7.0, H_3CCH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 170.3 [(0), C=O], 137.0, 133.7 [(1), *C*H=CH_2], 117.9, 115.2 [(2), *C*H_2=CH], 80.5 [(1), *C*HO], 71.8, 60.8 [(2), *C*H_2O], 37.6, 36.8, 27.0 [(2), *C*H_2], 14.0 [(3), *C*H_3]. $[\alpha]_D^{25}$ −19.4 (*c* 1.10 in CH_2Cl_2).

Procedure for the selective preparation of 19e by vinylcuprate addition to 4e

To a suspension of CuI (0.53 g, 2.8 mmol) in THF (40 ml) was added a solution of vinylmagnesium chloride (4.1 ml of a 1.7 M solution in THF, 6.9 mmol) at −78 °C. After 30 min at this temperature, **4e** (0.49 g, 1.4 mmol) in THF (5 ml) was added. After 24 h at −10 °C the reaction was quenched at 50% conversion by addition of water. After usual aqueous work-up the product **19e** (0.12 g, 45%) was isolated by column chromatography on silica, along with recovered starting material **4e** (0.22 g, 45%) and bornane sultam **13** (0.12 g, 40%). MS (EI) *m*/*z* (%) 195 (M^+ + 1, 5%), 137 (55), 55 (100). IR (film) ν/cm^{-1} 2962s, 1719s, 1261s, 803s. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (dddd, 1H, J = 17.5, 10.5, 5.7, 5.3, =C*H*CH_2O), 5.81–5.70 (2H, *H*C=CH_2), 5.26 (dm, 1H, J = 17.2, =CH_2), 5.17 (dm, 1H, J = 10.5, =CH_2), 5.08 (dm, 1H, J = 17.0, =CH_2), 5.04 (dm, 1H, J = 10.2, =CH_2), 5.01 (dm, 1H, J = 17.2, =CH_2), 4.94 (dm, 1H, J = 10.2, =CH_2), 4.01 (ddm, 1H, J = 12.7, 5.5, OCH_2), 3.93 (ddm, 1H, J = 12.7, 5.7, OCH_2), 3.79 (dd, 1H, J = 6.2, 6.2, CHO), 2.62–2.25 (6H, H_2C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4 [(0), *C*=O], 137.1, 133.9, 133.0 [(1), *C*H=CH_2], 117.9, 117.6, 115.2 [(2), *C*H_2=CH], 84.2 [(1), *C*HO], 71.3 [(2), *C*H_2O], 37.3, 36.4, 27.0 [(2), *C*H_2]. $[\alpha]_D^{22}$ −27.4 (c 1.35 in CH_2Cl_2).

[(2*S*,3*S*)-3-Hydroxy-3-vinyl-3,6-dihydro-2*H*-pyran-2-yl)acetic acid ethyl ester (20)

Following the general procedure for ring closing metathesis reactions, from **18g** (0.13 g, 0.54 mmol) and Grubbs' catalyst (13 mg, 3 mol%) a mixture of diastereoisomers of **20** [(2*S*,3*S*):(2*S*,3*R*) = 3 : 1) (77 mg, 67%) was isolated. MS (EI) *m*/*z* (%) 211 (M^+ − 1, <5), 107 (20), 95 (100), 77 (50), 67 (70). IR (film) ν/cm^{-1} 3469br m, 2983w, 1744s, 1300m, 1182m, 929m. Found: C, 61.8%; H, 7.2%. $C_{11}H_{16}O_4$ requires C, 62.2%; H, 7.6%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dm, 1H, J = 10.0, CHC*H*), 5.71 (ddd, 1H, J = 10.0, 2.0, 2.0, CHC*H*), 5.71 (dd, 1H, J = 17.3, 10.8, *H*C=CH_2), 5.37 (dd, 1H, J = 17.3, 1.5, H_2C=CH), 5.18 (dd, 1H, J = 10.8, 1.5, H_2C=CH), 4.16–4.08 (4H, H_2CO, H*H*CO), 3.85 (dd, 1H, J = 7.3, 5.0, *H*CO), 2.53 (dm, 1H, J = 7.3, H_2CC=O), 2.52 (dm, 1H, J = 5.0, H_2CC=O), 2.30 (br s, 1H, *H*O), 1.20 (t, 3H, J = 7.3, H_3CCH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.9 [(0), C=O], 138.4 [(1), *C*H=CH_2], 130.1, 128.6 [(1), H*C*=*C*H], 116.0 [(2), *C*H_2=CH], 78.2 [(1), H*C*O], 69.7 [(0), –*C*HHCH=], 66.0, 60.5 [(2), *C*H_2O], 34.6 [(2), *C*H_2C=O], 14.1 [(3), *C*H_3].

NMR spectroscopic data for the minor diastereomer (obtained from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.89 (dd, 1H, J = 17.5, 10.5, *H*C=CH_2), 5.76 (dm, 1H, J = 10.0, *C*H=*C*H), 5.56 (ddd, 1H, J = 10.0, 2.3, 2.3, *C*H=*C*H), 5.28 (dd, 1H, J = 17.5, 1.5, H_2C=CH), 5.17 (dd, 1H, J = 10.5, 1.5, H_2C=CH), 4.14–4.04 (4H, H_2CO), 3.84 (dd, 1H, J = 7.0, 4.3, H*C*O), 2.69 (br s, 1H, *H*O), 2.61 (dd, 1H, J = 16.1, 4.3, H_2CC=O), 2.35 (dm, 1H, J = 16.1, H_2CC=O), 1.20 (t, 3H, J = 7.3, H_3CCH$_2$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.2 [(0), C=O],

137.8 [(1), *C*H=CH$_2$], 130.9, 126.1 [(1), *C*4, *C*5], 114.9 [(2), *C*H$_2$=CH], 77.6 [(1), *C*2], 71.2 [(0), *C*3], 65.8, 60.7 [(2), *C*H$_2$O, *C*6], 35.634.6 [(2), *C*H$_2$C=O], 14.0 [(3), *C*H$_3$].

1-[(*R*)-1-Methyl-2-phenylethyl]cyclopent-3-enol (21)

No conversion of diallylcarbinol **10b** to cyclopentenol **21** was observed at ambient temperature. In refluxing toluene (20 ml) in the presence of Grubbs' catalyst (253 mg, 5 mol%) **10b** (1.42 g, 6.2 mmol) reacted smoothly to give **21** (0.99 g, 79%). MS (EI) *m*/*z* (%) 202 (M$^+$, <5), 186 (100), 91 (20). IR (film) ν/cm^{-1} 3454 bm, 3060m, 3026m, 2967m, 2933m, 1464m, 885m, 702s. Found: C, 82.4%; H, 8.4%. $C_{14}H_{18}O$ requires C, 83.1%; H, 9.0%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.25 (2H, Ph), 7.21–7.15 (3H, Ph), 5.74 (s, 2H, *H*C=CH), 2.99 (dd, 1H, J = 13.3, 3.0, H_2CPh), 2.61 (d, 1H, J = 16.5, H_2C), 2.56 (d, 2H, J = 16.5, H_2C), 2.43 (d, 1H, J = 16.8, H_2C), 2.36 (dd, 1H, J = 13.3, 10.8, H_2CPh), 2.33 (d, 1H, J = 16.8, H_2C), 1.89 (dqd, 1H, J = 10.8, 6.5, 3.0, *H*CCH$_3$), 1.75 (br s, 1H, *H*O), 0.86 (d, 1H, J = 6.5, H_3C). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.5 [(0), Ph], 129.6, 128.7, 128.6, 128.1, 125.6 [(1), Ph, *C*H=CH$_2$], 84.0 [(0), *C*OH], 46.3, 46.0 [(2), *C*H$_2$], 44.4 [(1), *C*HCH$_3$], 38.3 [(2), *C*H$_2$], 14.1 [(3), *C*H$_3$]. $[\alpha]_D^{24}$ +4.5 (c 1.55 in CH_2Cl_2).

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