PERKIN 1

Diazoketones as precursors in β-lactam synthesis. New insights into the mechanism of the photochemically induced Staudinger reaction

Michael R. Linder, Wolfgang U. Frey and Joachim Podlech *

Institut für Organische Chemie der Universität Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany. E-mail: joachim.podlech@po.uni-stuttgart.de; Fax: +711 685 4269; Tel: +711 685 4335

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Diazoketones **1**–**3**, derived from suitably protected amino acids (Ala, Val and Tle), have been photochemically rearranged in the presence of imines leading exclusively to *trans*-arranged 4-aryl- and cinnamoyl-substituted β-lactams **17**–**33** with up to 84% yield. Selectivities were dependent on the steric demand of the amino acid side-chain ranging from 65 : 35 to 90 : 10. The relative configurations were proved by several X-ray crystal structures and comparison of NMR spectra. Further reactions of the azetidinones at position C-4 have been performed: electron-rich aryl substituents (*e.g.*, 4-methoxyphenyl, furyl and thienyl) could be degraded to carboxylic acids **34** and **35** which were further transformed to acetoxy derivatives (compounds **36** and **37**) in a Kolbe reaction of type II. The cinnamoyl group could be oxidized to the formyl group by ozonolysis (⟶ **38**, **39**). The mechanism of the photochemically induced β-lactam formation is discussed in detail.

Introduction

β-Lactams (azetidin-2-ones) are one crucial structural element of natural products with antibiotic properties.[1] The resistance of bacteria to some β-lactam antibiotics can be overcome, *e.g.*, by using *trans*-configured β-lactam moieties in drugs which show much higher stability towards these resistant bacteria.[2] Thienamycin,[2] as well as the recently discovered trinems,[3] bear—contrary to the classical antibiotics like penicillin and cephalosporin—a *trans*-configured β-lactam moiety and contain a hydroxyalkyl substituent in position C-3 (Fig. 1).

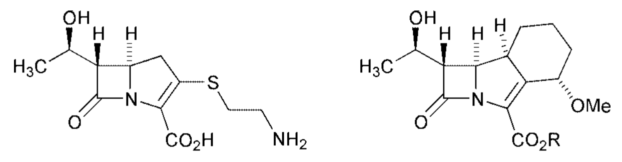

Fig. 1 Antibiotics bearing a *trans*-substituted β-lactam moiety.

The most frequently used method for the synthesis of β-lactams is the Staudinger reaction in which *in situ* generated ketenes—preferentially prepared from acid chlorides—are reacted with imines.[4] While several methods for the preparation of hydroxyalkyl-substituted β-lactams using the Staudinger reaction have been published,[5] direct methods for the stereoselective synthesis of aminoalkyl-substituted β-lactams using this transformation have, to the best of our knowledge, not been reported prior to our work. However, alternative routes to this class of compounds are known.[6] Recently, we presented a new method for the preparation of β-lactams using diazoketones prepared from amino acids as precursors for ketenes:[7] in a diastereoselective, photochemically induced reaction, exclusively *trans*-configured 3-aminoalkyl-substituted β-lactams were formed. This *trans*-substitution pattern is otherwise hard to achieve. In this paper we present a method for the preparation of 4-acetoxy- and 4-formyl-substituted β-lactams which should be possible precursors for the synthesis of bicyclic β-lactams.

Results and discussion

In our previous papers, we presented the synthesis of β-lactams bearing a phenyl substituent in position C-4.[7] Since this is not very advantageous for further reactions at this position, we looked for alternative substituents. Surprisingly, all attempts to use imines which are not derived from aromatic aldehydes failed. None of the aliphatic aldimines, imines or imidoesters prepared from crotonic aldehyde, glyoxalates or formates led to the formation of β-lactams. Consequently we made a virtue from necessity and used imines **4**–**16** prepared from substituted benzaldehydes in our reaction. Both electron-rich (*e.g.* 4-methoxy-substituted) and electron-deficient (*e.g.* 4-nitro-substituted) benzaldimines, as well as heteroaromatic (thienyl- or furyl-) carbaldimines could be successfully used (Table 1). Again, exclusively *trans*-configured β-lactams were obtained; the substitution pattern could be proved by the coupling constants between the hydrogen atoms attached at positions C-3 and C-4 of the β-lactam ring. The selectivities are obviously dependent on the steric demands of the side chain introduced with the amino acid derived diazoketones **1**–**3** (derived from alanine, valine and *tert*-leucine, respectively). The selectivities ranged from 65 : 35 (R = Me, derived from alanine) to 90 : 10 (R = *t*Bu, derived from *tert*-leucine). All isomers (except lactams **25**, **26** and **33**, entries 9, 10 and 17, respectively; see Experimental section) were separated by medium pressure liquid chromatography (MPLC) and were fully characterized. The configuration of the isomers could be proved by X-ray crystallographic analyses of **18b**, **19b**, **20b**, **21a** (Fig. 2), **22b**, **23a**, **26a** and **30b**[8] and by comparison of their NMR data.

We were especially interested in compounds with electron-rich aromatic substituents, since these can be easily degraded oxidatively to carboxylic acids with ruthenium tetraoxide (prepared *in situ* from $RuCl_3$–H_5IO_6 or $RuCl_3$–$NaIO_4$).[9] Under these conditions the electron-rich aromatic substituent is oxidized first, the product migrates into the aqueous phase and neither the benzyl group at the amide nitrogen, nor the Z group is attacked. Utilization of periodic acid instead of sodium periodate as the oxidizing agent seems to give slightly better

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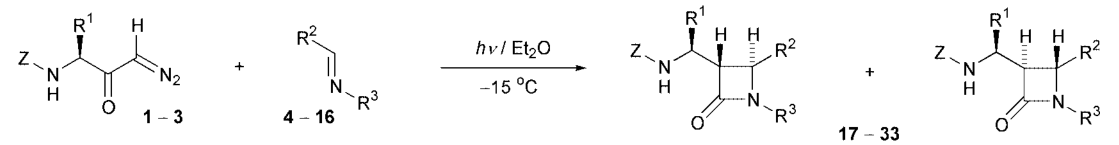
Table 1 Photochemically induced β-lactam synthesis starting with diazoketones



Entry	R^1	Diazoketone	R^2	R^3	Imine	Product	Yield (%)	dr[a]
1	Me	**1**	*p*-C_6H_4-NMe_2	Bn	**4**	**17**	72	70 : 30
2	Me	**1**	*p*-C_6H_4-OMe	Bn	**5**	**18**	50	70 : 30
3	Me	**1**	*p*-C_6H_4-Cl	Bn	**6**	**19**	55	70 : 30
4	Me	**1**	*p*-C_6H_4-NO_2	Bn	**7**	**20**	44	65 : 35
5	Me	**1**	2-Furyl	Bn	**9**	**21**	76	65 : 35
6	Me	**1**	2-Thienyl	Bn	**10**	**22**	54	65 : 35
7	Me	**1**	3-Thienyl	Bn	**11**	**23**	67	65 : 35
8	Me	**1**	(*E*)-Styryl	Bn	**12**	**24**	58	65 : 35
9	Me	**1**	Ph	*t*Bu	**13**	**25**	[b]	70 : 30
10	Me	**1**	Mesityl	*t*Bu	**14**	**26**	60	70 : 30
11	*i*Pr	**2**	2-Furyl	Bn	**9**	**27**	72	80 : 20
12	*i*Pr	**2**	2-Thienyl	Bn	**10**	**28**	72	75 : 25
13	*i*Pr	**2**	(*E*)-Styryl	Bn	**12**	**29**	70	80 : 20
14	*i*Pr	**2**	(*E*)-Styryl	Allyl	**15**	**30**	44	75 : 25
15	*t*Bu	**3**	2-Furyl	Bn	**9**	**31**	84	90 : 10
16	*t*Bu	**3**	2-Furyl	Allyl	**16**	**32**	84	90 : 10
17	*t*Bu	**3**	(*E*)-Styryl	Bn	**12**	**33**	60	87 : 13

[a] Determined from the crude product by HPLC and NMR analysis. [b] Crude product was not purified.

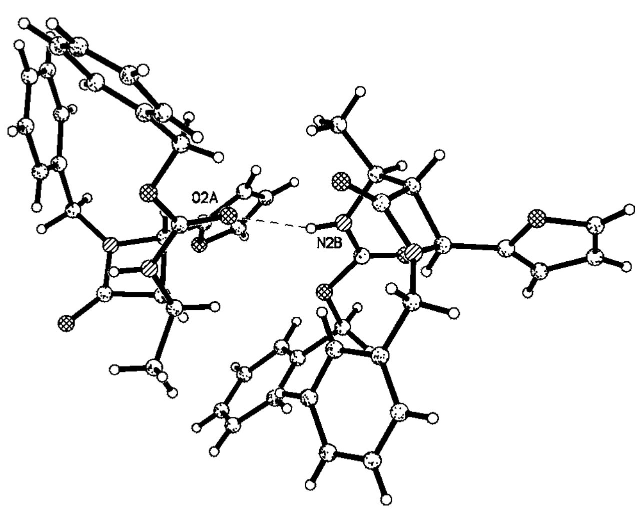
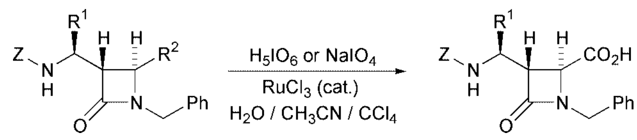


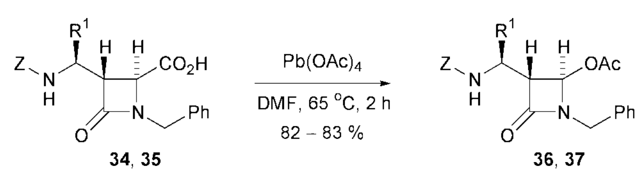
Fig. 2 Major isomer of the 2-furyl-substituted β-lactam **21a** (X-ray).[8]

Table 2 Oxidative degradation of aromatic and heteroaromatic substituents



Entry	R^1	R^2	Starting material	Reaction time/min	Product	Yield (%)
1	Me	*p*-C_6H_4-OMe	**18**	25[a]	**34**	70
2	Me	*p*-C_6H_4-OMe	**18**	60[b]	**34**	50
3	Me	2-Furyl	**21**	10[a]	**34**	Quant.
4	Me	2-Furyl	**21**	15[b]	**34**	90
5	Me	2-Thienyl	**22**	20[b]	**34**	80
6	*i*Pr	2-Furyl	**27**	10[a]	**35**	90
7	*i*Pr	2-Thienyl	**28**	10[a]	**35**	80
8	*i*Pr	2-Thienyl	**28**	15[b]	**35**	80

[a] Oxidant: H_5IO_6. [b] Oxidant: $NaIO_4$.



Scheme 1 Kolbe reaction of type II starting with azetidinecarboxylic acids.

results (Table 2, entries 1, 3 and 7). The best results were obtained, when furan or thiophene derivatives were used. The corresponding carboxylic acids **34** and **35** could be obtained in almost quantitative yield (*e.g.*, entries 3 and 6).

Azetidinecarboxylic acids are known to be suitable for a Kolbe reaction of type II,[10] leading to cyclic acyliminium compounds as intermediates which are usually trapped by acetate, yielding acetoxy-substituted β-lactams. This reaction can be performed electrochemically or with oxidizing agents such as lead tetraacetate[11] or peracids.[12] We oxidized the azetidinecarboxylic acids using lead tetraacetate and obtained *trans*-substituted 4-acetoxyazetidines **36** and **37** in 82 and 83% yield, respectively (Scheme 1, Fig. 3).[8] Obviously, the reaction proceeds stereoselectively with attack from the less hindered face of the iminium carbon (opposite to the substituent in position C-3). These acetoxy-substituted β-lactams are known to be well-suited for nucleophilic substitution with enolates[13] or organometallic compounds.[14] They have been used, *e.g.*, for the preparation of bicyclic β-lactams.[15]

Because the photochemical reaction of diazoketones with imines derived from crotonaldehyde did not lead to the formation of β-lactams, we used cinnamaldimines, which can be considered as vinylogous benzaldimines. Accordingly, β-lactam formation could be achieved under our reaction conditions. The resulting styryl-substituted β-lactams were formed in 55–70% yield. Selectivities were again ruled by the amino acid derivative employed in the reaction (Table 1). Cleavage of the double bond in styryl-substituted β-lactam **29a** by ozonolysis[16] led to the corresponding aldehyde **38** in 60% yield after reductive workup (dimethyl sulfide). *in situ* Formation of the corresponding dimethyl acetal **39** with trimethyl orthoformate facilitated purification by chromatography, leading to a slightly improved yield and analytically pure material (Scheme 2).

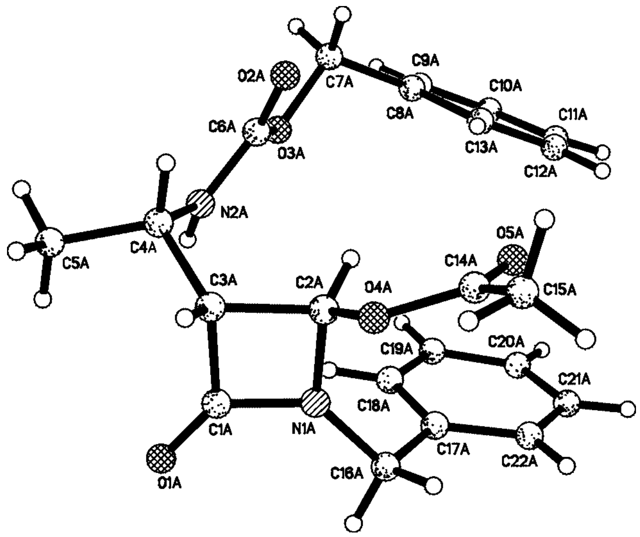
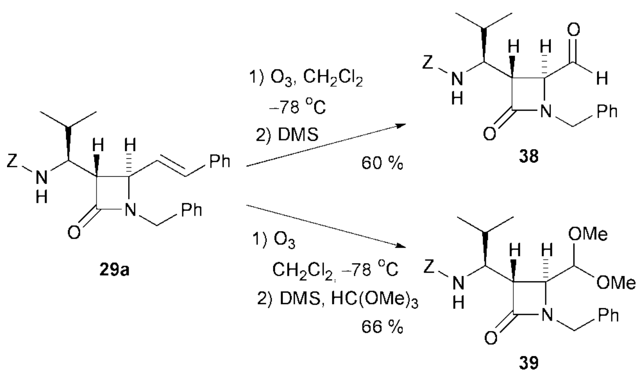


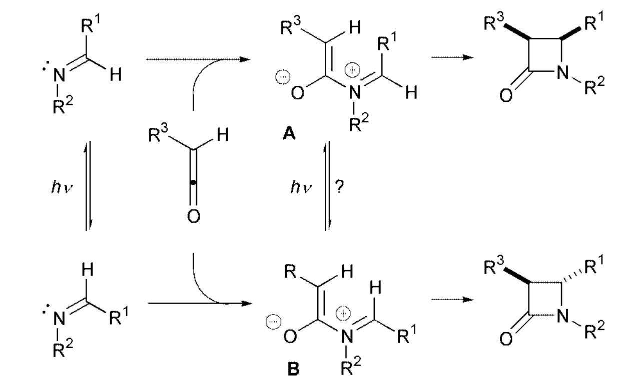
Fig. 3 The acetoxy-substituted β-lactam **36**.[8]



Scheme 2 Ozonolysis of styryl-substituted β-lactams.

Mechanistic considerations

The mechanism of the Staudinger reaction is well understood.[4] A ketene (usually generated by elimination of hydrogen chloride from an acid chloride) is attacked by the lone pair of an imine. The intermediate iminium enolate **A** is subsequently ring-closed to the corresponding β-lactam. The helical conformation of the iminium enolate (the double bonds are not co-planar, the dihedral angle is about 50°) allows—in accordance to the least-motion-principle—ring-closure to the *cis*-substituted β-lactams only (Scheme 3). The exclusive *trans*-substitution observed



Scheme 3 Proposed mechanism for the formation of *trans*-β-lactams.

with our reaction conditions might be explained by a *trans*⟶*cis*-isomerization of the imines, which is well known to occur during irradiation or heating.[17] The intermediacy of an isomeric iminium enolate **B** would consequently give rise to a *trans*-substituted β-lactam.[18]

To prove the proposed mechanism, we used cyclic imines

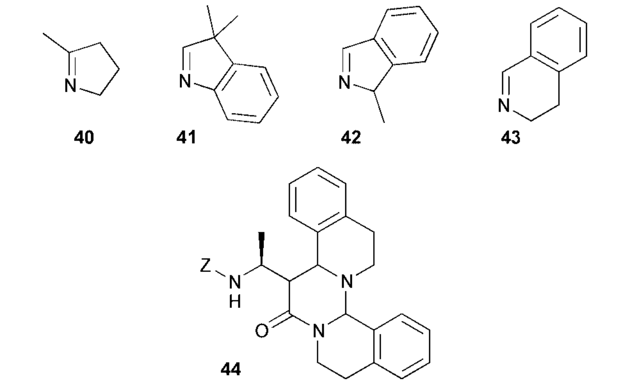
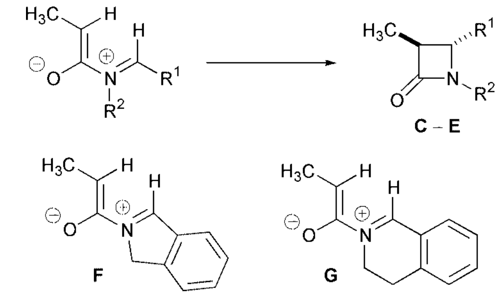


Fig. 4 Cyclic imines and a formal [2+2+2]-cycloadduct.

Table 3 Activation energy for the β-lactam formation



Entry	Substrate	R^1	R^2	Activation energy/ kJ mol^{-1} [a]
1	**C**	Ph	Me	61.6
2	**D**	Vinyl	Me	61.7
3	**E**	2,4,6-Trimethoxyphenyl	Me	67.4
4	**F**	—	—	75.3
5	**G**	—	—	73.3

[a] Calculated with AM1.[24] Force field calculations for the starting materials, transition states, and products, respectively, confirmed that these are extrema on the hypersurface.

(which are necessarily *cis*-substituted). Unfortunately, we could not achieve β-lactam formation with 5-methyl-3,4-dihydro-2*H*-pyrrole **40**,[19] 3,3-dimethyl-3*H*-indole **41**[20] or 1-methyl-1*H*-isoindole **42**[21] (Fig. 4). With 3,4-dihydroisoquinoline **43**[19] we observed the product of a [2+2+2]-cyclisation, pentacycle **44**,[22] with incorporation of two equivalents of imine (Fig. 4), a mode of reaction which has been observed previously by Padwa *et al.*[23]

We calculated the activation energies of the iminium enolate ring-closure (with a simplified substitution pattern) using semi-empirical methods (AM1,[24] Table 3). Interestingly, we found that the activation energies of acyclic iminium enolates **C** or **D** are about 12 kJ mol^{-1} lower than for the corresponding cyclic substrates **F** and **G**. Obviously these imines are too rigid to allow an unhindered ring-closure to β-lactams, which would explain why the cyclic imines did not yield any β-lactams. Consequently, we tested imines, that should be too sterically hindered for isomerization to *cis*-imines. However, with *N*-*tert*-butylmesitylenecarbaldimine, again exclusively *trans*-configured β-lactams were observed. It might be possible that the aromatic ring is not fully co-planar with the imine double bond, which would effectively reduce the steric hindrance. This seems to be rational, since even in *trans*-*N*-benzyl-2,4,6-trimethoxybenzaldimine **8**, an inclination of 27° of the aromatic ring is observed in the crystal (Fig. 5).[8] Nevertheless, β-lactam formation was not possible employing imine **8** (*cf.* entry 3 in Table 3).

Hegedus *et al.* performed photochemically induced Staudinger reactions starting with chromium carbene com-

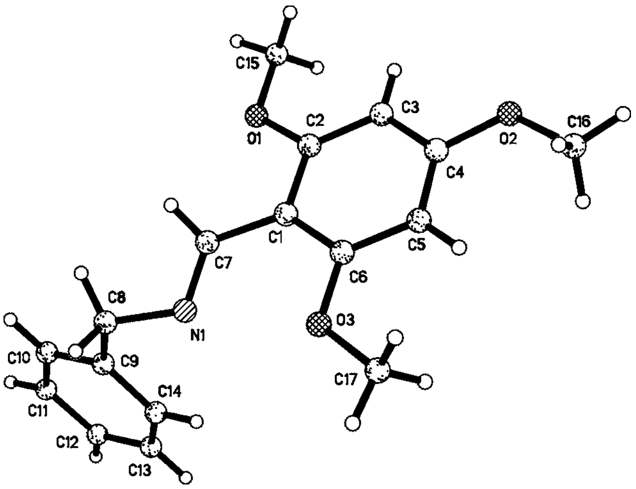
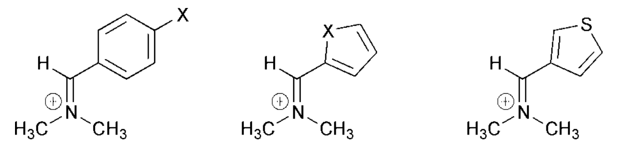


Fig. 5 Structure of imine **8** as determined by X-ray crystallographic analysis.[8]

Table 4 Bond order of C–N double bonds in iminium compounds



H **I** **J**

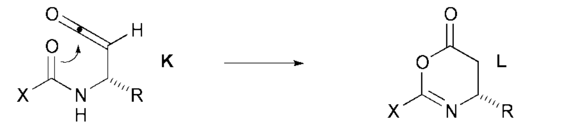
Entry	Substrate	X	Bond order[a] Ground state	Excited state[27]
1	**H**	H	1.70	1.18
2	**H**	NMe_2	1.54	1.63
3	**H**	NO_2	1.76	1.28
4	**I**	O	1.64/1.64[b]	1.24
5	**I**	S	1.65/1.66[b]	1.36
6	**J**	—	1.67/1.66[b]	1.23

[a] Calculated with PM3.[28] [b] Values for both planar conformations resulting from rotation around the C–C single bond are given.

plexes.[25] In their opinion, the phenyl substituent in the employed *N*-benzylbenzaldimine is responsible for the observed *trans*-substitution. The weakening of the double bond in the intermediate iminium enolate **A** (*cf.* Scheme 3) should allow rotation to the less hindered *trans*-intermediate **B**, which, after ring closure, should give rise to the *trans*-substituted β-lactam.[26] Other reactions employing *N*-benzylbenzaldimine, however, yielded *cis*-substituted β-lactams—obviously no isomerization **A**⟶**B** had occurred.[4,16]

In addition, if an isomerization of the iminium enolates occurred, we should observe a dependency of the *cis*/*trans*-selectivity on the substituents at the imine. These have an effect on the bond orders of the C–N double bond as has been shown by semi-empirical calculations (Table 4). In fact, although bond orders range from 1.54 to 1.76 for the ground state and from 1.18 to 1.63 for the excited state,[27] exclusively *trans*-substituted β-lactams were observed.[28]

It is quite astonishing that 3-aminoalkyl-substituted β-lactams have not been prepared *via* the Staudinger reaction before our work. A reason for this might be an intramolecular stabilization of the intermediate ketenes **K**. With acyl substituents at the nitrogen (*e.g.* protection as carbamates) attack of the acyl carbonyl on the electrophilic ketene centre leads to stable 4,5-dihydro-1,3-oxazin-6-ones **L** (Scheme 4).[29] With no nucleophile present, these are essentially stable; with protic nucleophiles they are ring-opened to the corresponding β-amino acid derivatives. Obviously, these heterocycles are not able to react with imines in a Staudinger reaction. It might be possible that



Scheme 4 Intramolecular stabilization of acyl-substituted aminoalkylketenes.

the proposed *cis*-substituted imines (which should be much more reactive than the *trans*-substituted imines, even if present only in a small fraction) react fast enough to avoid this oxazinone formation. Aliphatic aldimines are not isomerized by irradiation (in the solvents used in our reaction) and thus might be not reactive enough to compete with the intramolecular reaction (**K**⟶**L**).

In conclusion, we consider the isomerization of the respective imines most likely. This would further explain why the selectivities are somewhat lower than in other Staudinger reactions in which the ketenes had been generated from acid chlorides. Evans *et al.* and other groups reported that with glycine-derived acid chlorides attached to a chiral auxiliary, selectivities of up to 97 : 3 were observed.[16,30] Here a large substituent (R^1 in Scheme 3) approaches the stereogenic centre of the intermediate ketene. In the present case only a small hydrogen atom interacts with the ketene, consequently leading to reduced selectivities.

The presented Staudinger reaction in conjunction with the degradation of aromatic substituents supplies useful intermediates, *e.g.*, in the synthesis of bicyclic β-lactam antibiotics. Work in this direction is currently ongoing in our laboratories.

Experimental

General

Solvents for chromatography and for workup, *e.g.* ethyl acetate (EA) and light petroleum (PE) were distilled prior to use, diethyl ether (ether) was distilled over KOH–$FeSO_4$. Ether and THF used for reactions were distilled over Na–benzophenone. Amino acid derivatives were prepared by standard procedures.[31] Common amino acid abbreviations are used.[32] Diazoketones **1**–**3** were prepared in accordance with published procedures.[33] Moisture-sensitive reactions were performed in dried vessels (150 °C, 24 h) under a nitrogen atmosphere using syringe techniques. Flash column chromatography: Merck silica gel 60 (230–400 mesh). TLC: precoated sheets, Alugram SIL G/UV_{254} Macherey-Nagel; detection by UV extinction or by heating after dipping in a cerium molybdate solution [phosphomolybdic acid (25 g), $Ce(SO_4)_2 \cdot H_2O$ (10 g), conc. H_2SO_4 (60 ml), H_2O (940 ml)]. MPLC: detection with a UV detector. HPLC: analyses of diastereoisomer distribution were carried out with a Pharmacia LKB, RSD 2140 apparatus with a Pharmacia LKB, RSD 2249 mixer and diode-array detection (Pharmacia RSD 2140) on a LiChrosorb Si 60, Merck (hexane–EA, flow: 2.0 ml min^{-1}) chromatographic column. ^1H and ^{13}C NMR spectra were recorded at rt in $CDCl_3$ unless otherwise indicated; δ is given in ppm relative to internal TMS (0 ppm) or to resonances of the solvent (^1H: $CHCl_3$, 7.24 ppm; ^{13}C: $CDCl_3$, 77.0 ppm), *J* in Hz. Mass spectra were recorded using FAB or EI techniques. IR spectra were recorded with a FTIR instrument. Elemental analyses were performed by the service of the Institut für Organische Chemie, Stuttgart. Melting points are not corrected.

General procedure for the preparation of imines[34]

One equivalent of aldehyde was mixed with alumina (activity grade 1, 500 mg $mmol^{-1}$ aldehyde) and one equivalent of amine. The mixture was sealed with a stopper, shaken and kept for 12 h. Elution with CH_2Cl_2, filtration over Celite and evaporation yielded essentially pure imine (quantitative) which was used without further purification.

***N*-Benzyl-4-dimethylaminobenzaldehyde imine 4.**[35] δ_H (250 MHz; $CDCl_3$) 3.00 [6 H, s, $N(CH_3)_2$], 4.76 (2 H, d, CH_2), 6.69 (2 H, d, *J* 8.9, H-3, H-5), 7.19–7.33 (5 H, m, Ph), 7.66 (2 H, d, *J* 8.9, H-2, H-6) and 8.26 (1 H, s, N=CH); δ_C (63 MHz; $CDCl_3$) 40.2, 40.3 [2 q, $N(CH_3)_2$], 65.1 (t, CH_2), 111.1, 126.9, 128.0, 128.5, 129.8 (5 d, ar.), 124.5, 140.2, 152.2 (3 s, ar.) and 162.1 (d, N=C).

***N*-Benzylanisaldehyde imine 5.**[36] δ_H (250 MHz; $CDCl_3$) 3.83 (3 H, s, OCH_3), 4.79 (2 H, s, CH_2), 6.92 (2 H, d, *J* 4.8, H-3, H-5), 7.21–7.37 (5 H, m, Ph), 7.73 (2 H, d, *J* 4.8, H-2, H-6) and 8.32 (1 H, s, N=CH); δ_C (63 MHz; $CDCl_3$) 55.4 (q, OCH_3), 65.1 (t, CH_2), 114.1, 127.0, 128.1, 128.6, 129.3, 130.0 (5 d, 1 s, ar.), 139.7, 161.8 (2 s, ar.) and 161.4 (d, N=C).

***N*-Benzyl-4-chlorobenzaldehyde imine 6.**[35] δ_H (250 MHz; $CDCl_3$) 4.81 (2 H, s, CH_2), 7.26–7.35 (5 H, m, Ph), 7.38 (2 H, d, *J* 8.5, H-3, H-5), 7.71 (2 H, d, *J* 8.5, H-2, H-6) and 8.34 (1 H, s, N=CH); δ_C (63 MHz; $CDCl_3$) 65.1 (t, CH_2), 127.2, 128.1, 128.7, 129.0, 129.6 (5 d, ar.), 134.8, 136.8, 139.2 (3 s, ar.) and 160.6 (d, N=C).

***N*-Benzyl-4-nitrobenzaldehyde imine 7.**[34] δ_H (250 MHz; $CDCl_3$) 4.89 (2 H, s, CH_2), 7.30–7.41 (5 H, m, Ph), 7.94 (2 H, d, *J* 8.8, H-2, H-6), 8.27 (2 H, d, *J* 8.8, H-3, H-5) and 8.46 (1 H, s, N=CH); δ_C(63 MHz; $CDCl_3$) 65.2 (t, CH_2), 123.8, 127.3, 128.0, 128.6, 128.9 (5 d, ar.), 138.5, 141.6, 149.0 (3 s, ar.) and 159.5 (d, N=C).

***N*-Benzyl-2,4,6-trimethoxybenzaldehyde imine 8.**[37] Mp 83–85 °C (Found: C, 71.15; H, 6.7; N, 4.85; $C_{17}H_{19}NO_3$ requires C, 71.55; H, 6.7; N, 4.9%); ν_{max} (KBr)/cm^{-1} 2910 (CH), 2860 (CH), 2810 (CH), 1595 (C=N), 1215 (CO), 790 (aryl–CH); δ_H (500 MHz; $CDCl_3$) 3.83 (9 H, s, CH_3), 4.83 (2 H, s, CH_2), 6.13 (2 H, s, H-3, H-5), 7.31–7.37 (5 H, m, Ph) and 8.63 (1 H, s, N=CH); δ_C (126 MHz; $CDCl_3$) 55.5, 56.0 (3 q, CH_3), 66.7 (t, CH_2), 90.6 (d, C-3, C-5), 107.4 (s, C-1), 126.5, 127.9, 128.5 (3 d, Ph), 140.3 (s, *ipso*-Ph), 157.3 (d, N=C), 160.9 and 162.5 (2 s, C-2, C-4, C-6); *m*/*z* (FAB): 286 (100%, $[M + H]^+$) and 91 (18, $C_7H_7^+$).

***N*-Benzylfuran-2-carbaldehyde imine 9.**[38] δ_H (500 MHz; $CDCl_3$) 4.77 (2 H, s, CH_2), 6.45 (1 H, dd, *J* 3.5 and 1.3, H-4), 6.76 (1 H, d, *J* 3.5, H-3), 7.30–7.34 (5 H, m, Ph), 7.49 (1 H, d, *J* 1.3, H-5) and 8.15 (1 H, s, N=C-H); δ_C(63 MHz; $CDCl_3$) 64.4 (t, CH_2), 127.0, 127.3, 128.0, 128.5, 129.0, 130.6 (6 d, C-3–C-5, C-2′–C-6′), 139.0 (s, C-1′), 142.5 (s, C-2) and 155.2 (d, N=C).

***N*-Benzylthiophene-2-carbaldehyde imine 10.**[38] δ_H (250 MHz; $CDCl_3$) 4.79 (2 H, s, CH_2), 7.07 (1 H, dd, *J* 5.0 and 5.0, H-4), 7.22–7.41 (7 H, m, Ph, H-3, H-5) and 8.45 (1 H, d, *J* 1.0, N=C-H); δ_C (63 MHz; $CDCl_3$) 64.4 (t, CH_2), 127.0, 127.3, 128.0, 128.5, 129.0, 130.6 (6 d, C-3–C-5, C-2′–C-6′), 139.0 (s, C-1′), 142.5 (s, C-2) and 155.2 (d, N=C).

***N*-Benzylthiophene-3-carbaldehyde imine 11.** δ_H (500 MHz; $CDCl_3$) 4.75 (2 H, s, CH_2), 7.26–7.35 (6 H, m, Ph, H-2), 7.55–7.60 (2 H, m, H-4, H-5) and 8.35 (1 H, s, N=C-H); δ_C (126 MHz; $CDCl_3$) 64.9 (t, CH_2), 125.8, 126.4, 126.9, 127.9, 128.4, 128.6 (6 d, C-2, C-4, C-5, Ph), 139.2 (s, C-1′), 140.4 (s, C-3) and 156.2 (d, N=C).

***N*-Benzylcinnamaldehyde imine [(*E*,*E*)-4-aza-1,5-diphenylpenta-1,3-diene 12].**[34] δ_H (500 MHz; $CDCl_3$) 4.71 (2 H, s, H-5), 6.96 (1 H, d, *J* 4.9, H-2), 6.98 (1 H, s, H-1), 7.31–7.49 (10 H, m, 2 Ph) and 8.13 (dd, 1 H, *J* 5.0 and 1.4, H-3); δ_C (126 MHz; $CDCl_3$) 65.3 (t, C-5), 127.2, 127.8, 128.1, 128.5, 128.8, 129.1, 129.2 (7 d, C-2, Ph), 135.7 (s, *ipso*-Ph), 139.2 (s, *ipso*-Ph), 142.0 (d, C-1) and 163.4 (d, C-3).

***N*-*tert*-Butylbenzaldehyde imine 13.**[39] Deviating from the general procedure, benzaldehyde (531 mg, 5.00 mmol) and *tert*-butylamine (439 mg, 6.20 mmol) were heated for 10 h in benzene (8 mL) with a Dean–Stark trap filled with molecular sieve (4 Å). The solvent was removed *via* a rotary evaporator and subsequently *in vacuo* (with partial evaporation of the product) to yield the imine (484 mg, 60%) as a colourless oil: δ_H (500 MHz; $CDCl_3$) 1.30 [9 H, s, $C(CH_3)_3$], 7.38–7.40, 7.73–7.75 (5 H, 2 m, Ph) and 8.23 (1 H, s, N=CH); δ_C (126 MHz; $CDCl_3$) 30.1 [3 q, $C(CH_3)_3$], 57.6 [s, $C(CH_3)_3$], 128.3, 128.9, 130.1 (3 d, Ph), 137.6 (s, *ipso*-Ph) and 155.6 (s, N=C).

***N*-*tert*-Butylmesitylenecarbaldehyde imine 14.** Deviating from the general procedure, mesitylenecarbaldehyde (889 mg, 6.00 mmol) and *tert*-butylamine (527 mg, 7.20 mmol) were heated for 10 h in benzene (10 mL) with a Dean–Stark trap filled with molecular sieve (4 Å). The solvent was removed *via* a rotary evaporator and subsequently *in vacuo* to yield the imine (1.22 g, quant.) as a colourless oil: δ_H (500 MHz; $CDCl_3$) 1.31 [9 H, s, $C(CH_3)_3$], 2.26 (3 H, s, CH_3), 2.31 (6 H, s, 2 CH_3), 6.83 (2 H, s, H-3, H-5) and 8.50 (1 H, s, N=CH); δ_C (126 MHz; $CDCl_3$) 20.5 (2 q, 2 CH_3), 21.9 (q, CH_3), 30.1 [q, $C(CH_3)_3$], 58.3 [s, $C(CH_3)_3$], 129.4 (d, C-3, C-5), 133.0 (s, C-1), 136.9 (s, C-2, C-6), 138.3 (s, C-4) and 156.2 (N=C).

***N*-Allylcinnamaldehyde imine [(*E*,*E*)-4-aza-1-phenylhepta-1,3,6-triene 15].**[40] *N*-Allylcinnamaldehyde imine was prepared as described in the general procedure and purified by bulb-to-bulb distillation (60%): δ_H (500 MHz; $CDCl_3$) 4.14 (2 H, dd, *J* 5.8 and 1.3, H-5), 5.14 (1 H, dd, *J* 10.7 and 1.5 Hz, H_b-7), 5.20 (1 H, dd, *J* 17.2 and 1.5, H_a-7), 6.03 (1 H, ddt, *J* 17.1, 10.4 and 5.9, H-6), 6.93 (1 H, d, *J* 5.4, H-2), 6.94 (1 H, m, H-1), 7.30–7.47 (5 H, m, Ph) and 8.02 (1 H, dd, *J* 5.5 and 1.2, H-3); δ_C (126 MHz; $CDCl_3$) 65.5 (t, C-5), 116.1 (t, C-7), 127.2, 128.6, 129.1, 131.2 (4 d, C-2, Ph), 135.7, 135.8 (1 s, 1 d, *ipso*-Ph, C-6), 141.8 (d, C-1) and 163.5 (d, C-3).

***N*-Allylfuran-2-carbaldehyde imine 16.**[41] δ_H (500 MHz; $CDCl_3$) 4.21 (2 H, d, *J* 5.9, H-3), 5.15 (1 H, dd, *J* 10.2 and 1.6, H_b-5), 5.21 (1 H, dd, *J* 15.4 and 1.7, H_a-5), 6.04 (1 H, m, H-4), 6.46 (1 H, dd, *J* 3.3 and 1.7, H-4′), 6.75 (1 H, d, *J* 3.4, H-3′), 7.50 (1 H, d, *J* 1.6, H-5′) and 8.09 (1 H, s, H-1); δ_C (126 MHz; $CDCl_3$) 63.6 (t, C-3), 110.2, 114.0 (2 d, C-3′, C-4′), 116.5 (t, C-5), 135.6 (d, C-4), 144.7 (d, C-5′), 150.6 (d, C-1) and 151.6 (s, C-2′).

General procedure for the preparation of azetidinones

In a quartz photo-reactor diazoketone and imine were dissolved in Et_2O (300 mL), the mixture was cooled to −15 °C and irradiated for 90 min. The mixture was stirred for further 30 min at this temperature and then warmed to rt. The solvent was removed and the diastereomeric ratio was determined by HPLC and ^1H NMR spectroscopy. The diastereoisomers were separated by flash column chromatography or MPLC.

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(4-dimethylaminophenyl)azetidin-2-one 17a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **4** (953 mg, 4.00 mmol) were irradiated to give a mixture of **17a** and **17b** (720 mg, 79%, 70 : 30), which was separated by MPLC (PE–*i*-PrOH 9 : 1) yielding **17a** (456 mg, 50%) and **17b** (200 mg, 22%) as colourless solids. Compound **17a**: mp 148–149 °C; $[a]_D^{20}$ −31 (*c* 1, $CHCl_3$) (Found: C, 73.35; H, 6.95; N, 9.15; $C_{28}H_{31}N_3O_3$ requires C, 73.5; H, 6.85; N, 9.2%); ν_{max} (KBr)/cm^{-1} 3260 (NH), 1700 (CO), 1240 and 680; δ_H (500 MHz; $CDCl_3$) 1.31 (3 H, d, *J* 6.8, H-2′), 2.97 [6 H, s, $N(CH_3)_2$], 3.11 (1 H, dd, *J* 2.8 and 2.8, H-3), 3.66 (1 H, d, *J* 15.0, NCH_2Ph), 4.16 (2 H, m, H-4, H-1′), 4.81 (1 H, d, *J* 15.0, NCH_2Ph), 4.86 (1 H, d, *J* 8.8, NH), 4.92 (1 H, d, *J* 12.3, OCH_2Ph), 5.11 (1 H, d, *J* 12.3, OCH_2Ph), 6.70 [2 H, d, *J* 7.5, *p*-C_6H_4-N$(CH_3)_2$] and 7.12–7.37 [12 H, m, 2 Ph, *p*-C_6H_4-N$(CH_3)_2$]; δ_C (126 MHz; $CDCl_3$) 19.9 (q, C-2′), 40.5 [q, N$(CH_3)_2$], 44.0 (t, NCH_2Ph), 45.2 (d, C-1′), 56.7 (d, C-4), 64.9 (d, C-3), 66.7 (t, OCH_2Ph), 112.6 [d, C_6H_4-N$(CH_3)_2$], 123.9 [s, C_6H_4-N$(CH_3)_2$], 127.5, 127.7, 127.9, 128.1, 128.3, 128.5 [7 d, 2 Ph, C_6H_4-N$(CH_3)_2$, partly covered], 135.7, 136.5 (2 s, 2 Ph), 150.6 [s, C_6H_4-N$(CH_3)_2$], 155.5 (s, NH-C=O), 167.6 (s, C-2); *m*/*z* (FAB) 458 (100%, $[M + 1]^+$). Compound **17b**: mp 115–116 °C; $[\alpha]_D^{20}$ +27 (*c* 1, $CHCl_3$) (Found: C, 73.55; H, 6.95; N, 9.15; $C_{28}H_{31}N_3O_3$ requires C, 73.5; H, 6.85; N, 9.2%); ν_{max} (KBr)/cm^{-1} 3295 (NH), 1735 (CO), 1680 (CO), 1605, 1515, 1350, 1230 and 680; δ_H (500 MHz; $CDCl_3$) 1.27 (3 H, d, *J* 6.7, H-2′), 2.96 [6 H, s, N$(CH_3)_2$], 3.04 (1 H, dd, *J* 7.8 and 1.3, H-3), 3.70 (1 H, d, *J* 15.0, NCH_2Ph), 4.13 (1 H, m, H-1′), 4.23 (1 H, s, H-4), 4.78 (1 H, d, *J* 15.0, NCH_2Ph), 4.85 (1 H, d, *J* 8.9, NH), 5.04 (1 H, d, *J* 12.3, OCH_2Ph), 5.10 (1 H, d, *J* 12.3, OCH_2Ph), 6.67 [2 H, d, *J* 7.5, *p*-C_6H_4-N$(CH_3)_2$] and 7.14–7.36 [12 H, m, 2 Ph, *p*-C_6H_4-N$(CH_3)_2$]; δ_C (126 MHz; $CDCl_3$) 18.6 (q, C-2′), 40.5 [2 q, N$(CH_3)_2$], 44.1 (t, NCH_2Ph), 46.4 (d, C-1′), 57.9 (d, C-4), 65.2 (d, C-3), 66.6 (t, OCH_2Ph), 112.6 [d, *p*-C_6H_4-N$(CH_3)_2$], 124.1 [s, *p*-C_6H_4-N$(CH_3)_2$], 127.5, 127.6, 128.1, 128.4, 128.5, 128.7 [7 d, 2 Ph, *p*-C_6H_4-N$(CH_3)_2$, partly covered], 135.7, 136.5 (2 s, 2 Ph), 150.6 [s, *p*-C_6H_4-N$(CH_3)_2$], 155.5 (s, NH-C=O) and 167.6 (s, C-2); *m*/*z* (FAB) 458 (100%, $[M + 1]^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(4-methoxyphenyl)azetidin-2-one 18a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **5** (897 mg, 4.00 mmol) were irradiated to give a mixture of **18a** and **18b** (719 mg, 81%, 70 : 30), which was separated by MPLC (PE–*i*-PrOH 96 : 4) yielding **18a** (320 mg, 36%) and **18b** (128 mg, 14%) as colourless solids. Compound **18a**: mp 125–126 °C; $[\alpha]_D^{20}$ −5 (*c* 0.5 in $CHCl_3$) (Found: C, 72.95; H, 6.4; N, 6.25; $C_{27}H_{28}N_2O_4$ requires C, 72.95; H, 6.35; N, 6.3%); ν_{max} (KBr)/cm^{-1} 3270 (NH), 1720 (CO), 1700 (CO), 1535, 1505, 1240, 1045 and 682; δ_H (500 MHz; $CDCl_3$) 1.32 (3 H, d, *J* 6.8, H-2′), 3.11 (1 H, s, H-3), 3.68 (1 H, d, *J* 15.0, NCH_2Ph), 3.82 (3 H, s, OCH_3), 4.19 (2 H, m, H-4, H-1′), 4.81 (1 H, d, *J* 15.0, NCH_2Ph), 4.87 (1 H, d, *J* 8.5, NH), 4.92 (1 H, d, *J* 12.2, OCH_2Ph), 5.11 (1 H, d, *J* 12.2, OCH_2Ph), 6.88 (2 H, d, *J* 8.0, C_6H_4-OCH_3) and 7.10–7.38 (12 H, m, 2 Ph, C_6H_4-OCH_3); δ_C (126 MHz; $CDCl_3$) 19.9 (q, C-2′), 44.3 (t, NCH_2Ph), 45.1 (d, C-1′), 55.3 (q, OCH_3), 56.4 (d, C-4), 65.1 (d, C-3), 66.8 (t, OCH_2Ph), 114.3 (d, C_6H_4-OCH_3), 127.6, 127.8, 127.9, 128.1, 128.3, 128.5, 128.7, 128.9, 135.5, 136.3 (7 d, 3 s, 2 Ph, C_6H_4-OCH_3), 156.1 (s, NH-C=O), 159.8 (s, C_6H_4-OCH_3) and 167.7 (s, C-2); *m*/*z* (FAB) 445 (100%, $[M + 1]^+$), 353 (10, $[M - C_7H_7]^+$), 337 (5, $[M - C_7H_7O]^+$), 268 (100, $[M - C_{10}H_{12}NO_2]^+$), 226 (10, $[C_{10}H_{12}NO_2 - C_2H_4N]^+$), 161 (20, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$) and 91 (80, $C_7H_7^+$). Compound **18b**: mp 102–103 °C; $[\alpha]_D^{20}$ +4 (*c* 0.5, $CHCl_3$) (Found: C, 72.65; H, 6.35; N, 6.3; $C_{27}H_{28}N_2O_4$ requires C, 72.95; H, 6.35, N, 6.3%); ν_{max} (KBr)/cm^{-1} 3320 (NH), 1740 (CO), 1700 (CO), 1520, 1505, 1235, 1020 and 680; δ_H (500 MHz; $CDCl_3$) 1.28 (3 H, d, *J* 6.6, H-2′), 3.03 (1 H, dd, *J* 8.2 and 1.0, H-3), 3.73 (1 H, d, *J* 15.0, NCH_2Ph), 3.81 (3 H, s, OCH_3), 4.14 (1 H, m_c, H-1′), 4.27 (1 H, s, H-4), 4.77 (1 H, d, *J* 15.0, NCH_2Ph), 4.83 (1 H, d, *J* 8.8, NH), 5.03 (1 H, d, *J* 12.3, OCH_2Ph), 5.10 (1 H, d, *J* 12.3, OCH_2Ph), 6.83 (2 H, d, *J* 8.7, C_6H_4-OCH_3), 7.05 (2 H, d, *J* 8.2, C_6H_4-OCH_3), 7.11–7.13 and 7.25–7.36 (10 H, 2 m, 2 Ph); δ_C (126 MHz; $CDCl_3$) 18.6 (q, C-2′), 44.3 (t, NCH_2Ph), 46.3 (d, C-1′), 55.3 (q, OCH_3), 57.8 (d, C-4), 65.5 (d, C-3), 66.7 (t, OCH_2Ph), 114.4 (d, C_6H_4-OCH_3), 127.7, 128.1, 128.4, 128.5, 128.8, 129.0, 135.5, 136.4 (7 d, 3 s, 2 Ph, C_6H_4-OCH_3, partly covered), 155.5 (s, NH-C=O), 159.8 (s, C_6H_4-OCH_3) and 167.4 (s, C-2); *m*/*z* (FAB) 445 (67%, $[M + 1]^+$), 353 (13, $[M - C_7H_7]^+$), 268 (100, $[M - C_{10}H_{12}NO_2]^+$), 226 (11, $[C_{10}H_{12}NO_2 - C_2H_4N]^+$), 161 (25, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$) and 91 (92, $[C_7H_7]^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(4-chlorophenyl)azetidin-2-one 19a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **6** (915 mg, 4.00 mmol) were irradiated to give a mixture of **19a** and **19b** (707 mg, 79%, 70 : 30), which was separated by MPLC (PE–*i*-PrOH 97 : 3) yielding **19a** (304 mg, 34%) and **19b** (188 mg, 21%) as colourless solids. Compound **19a**: mp 134–135 °C; $[\alpha]_D^{20}$ −25 (*c* 1, $CHCl_3$) (Found: C, 69.65; H, 5.65; N, 6.2; $C_{26}H_{25}ClN_2O_3$ requires C, 69.55; H, 5.6; N, 6.25%); ν_{max} (KBr)/cm^{-1} 3270 (NH), 1725 (CO), 1700 (CO), 1535, 1240, 1045 and 680; δ_H (500 MHz; $CDCl_3$) 1.33 (3 H, d, *J* 6.9, H-2′), 3.10 (1 H, s, H-3), 3.71 (1 H, d, *J* 14.9, NCH_2Ph), 4.18 (1 H, m_c, H-1′), 4.22 (1 H, s, H-4), 4.82 (1 H, d, *J* 14.9, NCH_2Ph), 4.85 (1 H, d, *J* 9.4, NH), 4.91 (1 H, d, *J* 12.2, OCH_2Ph), 5.11 (1 H, d, *J* 12.2, OCH_2Ph) and 7.09–7.38 (14 H, m, 2 Ph, *p*-C_6H_4-Cl); δ_C (126 MHz; $CDCl_3$) 19.8 (q, C-2′), 44.5 (t, NCH_2Ph), 45.1 (d, C-1′), 56.1 (d, C-4), 65.4 (d, C-3), 66.9 (t, OCH_2Ph), 127.7, 127.9, 128.0, 128.2, 128.3, 128.6, 128.8, 129.2, 134.3, 135.1, 135.8, 136.2 (8 d, 4 s, 2 Ph, *p*-C_6H_4-Cl), 156.1 (s, NH-C=O) and 167.5 (s, C-2); *m*/*z* (EI, 70 eV) 448 (3%, M^+), 357 (23, $[M - C_7H_7]^+$), 270 (22, $[M - C_{10}H_{12}NO_2]^+$), 224 (9, $[C_{10}H_{12}NO_2 - C_2H_4N]^+$), 163 (12, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$) and 91 (100, $C_7H_7^+$). Compound **19b**: mp 125–126 °C; $[\alpha]_D^{20}$ +22 (*c* 1, $CHCl_3$) (Found: C, 69.55; H, 5.6; N, 6.15; $C_{26}H_{25}ClN_2O_3$ requires C, 69.55; H, 5.6; N, 6.25%); ν_{max} (KBr)/cm^{-1} 3320 (NH), 1740 (CO), 1680 (CO), 1515, 1230, 685 and 485; δ_H (500 MHz; $CDCl_3$) 1.29 (3 H, d, *J* 6.6, H-2′), 2.99 (1 H, dd, *J* 8.0 and 1.7, H-3), 3.78 (1 H, d, *J* 14.9, NCH_2Ph), 4.14 (1 H, m_c, H-1′), 4.37 (1 H, s, H-4), 4.76 (1 H, d, *J* 14.8, NCH_2Ph), 4.78 (1 H, d, *J* 6.3, NH), 5.02 (1 H, d, *J* 12.2, OCH_2Ph), 5.11 (1 H, d, *J* 12.2, OCH_2Ph), 7.03 (2 H, d, *J* 8.0, *p*-C_6H_4-Cl), 7.10 (2 H, m, *p*-C_6H_4-Cl) and 7.24–7.35 (10 H, m, 2 Ph); δ_C (126 MHz; $CDCl_3$) 18.6 (q, C-2′), 44.6 (t, NCH_2Ph), 46.4 (d, C-1′), 57.7 (d, C-4), 65.9 (d, C-3), 66.7 (t, OCH_2Ph), 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.8, 129.2, 134.2, 135.1, 135.9, 136.3 (8 d, 4 s, 2 Ph, *p*-C_6H_4-Cl), 155.1 (s, NH-C=O) and 167.1 (s, C-2); *m*/*z* (EI, 70 eV) 448 (1%, M^+), 420 (21, $[M - CO]^+$), 357 (12, $[M - C_7H_7]^+$), 270 (21, $[M - C_{10}H_{12}NO_2]^+$), 224 (6, $[C_{10}H_{12}NO_2 - C_2H_4N]^+$), 163 (9, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$) and 91 (100, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(4-nitrophenyl)azetidin-2-one 20a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **7** (957 mg, 4.00 mmol) were irradiated to give a mixture of **20a** and **20b** (620 mg, 67%, 65 : 35), which was separated by MPLC (PE–*i*-PrOH 97 : 3) yielding **20a** (255 mg, 28%) and **20b** (144 mg, 16%) as colourless solids. Compound **20a**: mp 163–164 °C; $[\alpha]_D^{20}$ −45 (*c* 1, $CHCl_3$) (Found: C, 67.7; H, 5.45; N, 9.1; $C_{26}H_{25}N_3O_5$ requires C, 67.95; H, 5.5; N, 9.15%); ν_{max} (KBr)/cm^{-1} 3360 (NH), 1730 (CO), 1710 (CO), 1505, 1340, 1235, 1045 and 680; δ_H (500 MHz; $CDCl_3$) 1.36 (3 H, d, *J* 7.0, H-2′), 3.14 (1 H, s, H-3), 3.80 (1 H, d, *J* 14.9, NCH_2Ph), 4.21 (1 H, m_c, H-1′), 4.37 (1 H, d, *J* 1.6, H-4), 4.83 (1 H, d, *J* 14.9, NCH_2Ph), 4.89 (1 H, d, *J* 8.3, NH), 4.91 (1 H, d, *J* 12.2, OCH_2Ph), 5.11 (1 H, d, *J* 12.2, OCH_2Ph), 7.09 (2 H, m_c, *p*-C_6H_4-NO_2), 7.20, 7.30–7.42 (10 H, 2 m, 2 Ph) and 8.19 (2 H, d, *J* 8.2, *p*-C_6H_4-NO_2); δ_C (126 MHz; $CDCl_3$) 19.6 (q, C-2′), 45.0 (t, NCH_2Ph), 45.0 (d, C-1′), 56.0 (d, C-4), 65.8 (d, C-3), 67.0 (t, OCH_2Ph), 124.2, 127.3, 127.9, 128.0, 128.3, 128.4, 128.6, 128.9, 134.7, 136.3 (8 d, 2 Ph, *p*-C_6H_4-NO_2), 145.1, 147.9 (2 s, *p*-C_6H_4-NO_2), 156.2 (s, NH-C=O) and 167.2 (s, C-2); *m*/*z* (EI, 70 eV) 459 (16%, M^+), 368 (9, $[M - C_7H_7]^+$), 281 (20, $[M - C_{10}H_{12}NO_2]^+$), 236 (3, $[C_{10}H_{12}NO_2 - NO_2]^+$), 174 (3, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$), 91 (100, $C_7H_7^+$) and 44 (3, NO_2^+). Compound **20b**: mp 160–161 °C; $[\alpha]_D^{20}$ +52 (*c* 1, $CHCl_3$) (Found: C, 67.9; H, 5.55; N, 9.05; $C_{26}H_{25}N_3O_5$ requires C, 67.95; H, 5.5; N, 9.15%); ν_{max} (KBr)/cm^{-1} 3305 (NH), 1740 (CO), 1680 (CO), 1505, 1340, 1235 and 680; δ_H (500 MHz; $CDCl_3$) 1.33 (3 H, d, *J* 6.8, H-2′), 2.98 (1 H, dd, *J* 8.9 and 2.2, H-3), 3.91 (1 H, d, *J* 14.9, NCH_2Ph), 4.16 (1 H, m_c, H-1′), 4.54 (1 H, d, *J* 1.5, H-4), 4.73 (1 H, d, J 14.9, NCH_2Ph), 4.78 (1 H, d, J 8.7, NH), 4.99 (1 H, d, J 12.2, OCH_2Ph), 5.15 (1 H, d, J 12.2, OCH_2Ph), 7.09 (2 H, m_c, p-C_6H_4-NO_2), 7.26–7.35 (10 H, 2 Ph) and 8.06 (2 H, d, J 8.5, p-C_6H_4-NO_2); δ_C (126 MHz; $CDCl_3$) 18.7 (q, C-2′), 45.1 (t, NCH$_2$Ph), 46.6 (d, C-1′), 58.0 (d, C-4), 66.5 (d, C-3), 66.8 (t, OCH$_2$Ph), 124.1, 127.2, 128.1, 128.3, 128.4, 128.5, 128.6, 128.9, 134.7, 136.3 (8 d, 2 s, Ph, p-C_6H_4-NO_2), 145.2, 147.8 (2 s, p-C_6H_4-NO_2), 155.6 (s, NH-C=O) and 166.8 (s, C-2); m/z (EI, 70 eV) 459 (14%, M^+), 368 (12, $[M - C_7H_7]^+$), 281 (19, $[M - C_{10}H_{12}NO_2]^+$), 236 (1, $[C_{10}H_{12}NO_2 - NO_2]^+$), 174 (3, $[C_{10}H_{12}NO_2 - C_7H_7O]^+$), 91 (100, $C_7H_7^+$) and 44 (3, NO_2^+).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[(1-benzyloxycarbonylamino)ethyl]-4-(2-furyl)azetidin-2-one 21a,b. Following the general procedure, diazoketone **1** (989 mg, 4.00 mmol) and imine **9** (1.48 g, 8.00 mmol) were irradiated to give a mixture of **21a** and **21b** (1.43 g, 88%, 65 : 35), which was separated by MPLC (PE–*i*-PrOH 97 : 3) yielding **21a** (803 mg, 50%) and **21b** (415 mg, 26%) as colourless solids. Compound **21a**: mp 109–110 °C; $[a]_D^{20}$ +25 (c 1, $CHCl_3$) (Found: C, 71.05; H, 6.0; N, 6.8; $C_{24}H_{24}N_2O_4$ requires C, 71.25; H, 6.0; N, 6.95%); ν_{max} (KBr)/cm^{-1} 3300 (NH), 1750 (CO), 1675 (CO), 1525, 1240, 1040, 990, 730 and 680; δ_H (500 MHz; $CDCl_3$) 1.35 (3 H, d, J 6.9, H-2′), 3.51 (1 H, s, H-3), 3.78 (1 H, d, J 15.1, NCH_2Ph), 4.18 (1 H, m_c, H-1′), 4.30 (1 H, s, H-4), 4.69 (1 H, d, J 15.1, NCH_2Ph), 4.89 (1 H, d, J 8.7, NH), 4.94 (1 H, d, J 12.3, OCH_2Ph), 5.11 (1 H, d, J 12.3, OCH_2Ph) and 7.12–7.38 (13 H, m, 2 Ph, furyl); δ_C (126 MHz; $CDCl_3$) 19.8 (q, C-2′), 44.7 (t, NCH$_2$Ph), 45.0 (d, C-1′), 50.2 (d, C-4), 61.3 (d, C-3), 66.9 (t, OCH$_2$Ph), 109.8, 110.5 (2 d, furyl), 127.6, 128.0, 128.2, 128.6, 128.7, 135.4, 136.3 (6 d, 2 s, 2 Ph, partly covered), 143.2 (s, furyl), 149.8 (d, furyl), 156.1 (s, NH-C=O) and 167.1 (s, C-2); m/z (FAB) 404 (100%, $[M + 1]^+$). Compound **21b**: mp 110–111 °C; $[a]_D^{20}$ −40 (c 1, $CHCl_3$) (Found: C, 71.15; H, 6.0; N, 6.85; $C_{24}H_{24}N_2O_4$ requires C, 71.25; H, 6.0; N, 6.95); ν_{max} (KBr)/cm^{-1} 3315 (NH), 1760 (CO), 1695 (CO), 1520, 1230, 1050, 700 and 680; δ_H (500 MHz; $CDCl_3$) 1.28 (3 H, d, J 6.7, H-2′), 3.42 (1 H, d, J 6.6, H-3), 3.85 (1 H, d, J 15.0, NCH_2Ph), 4.13 (1 H, m_c, H-1′), 4.38 (1 H, s, H-4), 4.65 (1 H, d, J 15.0, NCH_2Ph), 4.93 (1 H, d, J 8.5, NH), 5.06 (2 H, s, OCH_2Ph), 6.15 (1 H, s, furyl), 6.29 (1 H, m_c, furyl) and 7.25–7.36 (11 H, m, 2 Ph, furyl); δ_C (126 MHz; $CDCl_3$) 18.2 (q, C-2′), 44.8 (t, NCH$_2$Ph), 46.0 (d, C-1′), 51.3 (d, C-4), 61.7 (d, C-3), 66.7 (t, OCH$_2$Ph), 109.5, 110.5 (2 d, furyl), 127.7, 128.1, 128.2, 128.3, 128.5, 128.7, 135.4, 136.4 (6 d, 2 s, 2 Ph), 143.2 (s, furyl), 149.9 (d, furyl), 155.5 (s, NH-C=O) and 167.0 (s, C-2); m/z (FAB) 404 (100%, $[M + 1]^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(2-thienyl)azetidin-2-one 22a,b. Following the general procedure, diazoketone **1** (989 mg, 4.00 mmol) and imine **10** (1.61 g, 8.00 mmol) were irradiated to give a mixture of **22a** and **22b** (991 mg, 59%, 65 : 35), which was separated by MPLC (PE–*i*-PrOH 96 : 4) yielding **22a** (594 mg, 35%) and **22b** (320 mg, 19%) as colourless solids. Compound **22a**: mp 134–135 °C; $[a]_D^{20}$ +26 (c 1, $CHCl_3$) (Found: C, 68.4; H, 5.85; N, 6.7; $C_{24}H_{24}N_2O_3S$ requires C, 68.55; H, 5.75; N, 6.65%); ν_{max} (KBr)/cm^{-1} 3250 (NH), 1730 (CO), 1715 (CO), 1545, 1240, 1050, 725 and 680; δ_H (500 MHz; $CDCl_3$) 1.34 (3 H, d, J 6.8, H-2′), 3.30 (1 H, dd, J 2.9 and 2.9, H-3), 3.77 (1 H, d, J 15.1, NCH_2Ph), 4.21 (1 H, m_c, H-1′), 4.54 (1 H, d, J 1.1, H-4), 4.80 (1 H, d, J 15.1, NCH_2Ph), 4.87 (1 H, d, J 8.5, NH), 4.92 (1 H, d, J 12.3, OCH_2Ph), 5.11 (1 H, d, J 12.3, OCH_2Ph), 6.96 (2 H, s, thienyl) and 7.14–7.37 (m, 11 H, 2 Ph, thienyl); δ_C (126 MHz; $CDCl_3$) 19.8 (q, C-2′), 44.3 (t, NCH$_2$Ph), 45.1 (d, C-1′), 52.6 (d, C-4), 65.8 (d, C-3), 66.8 (t, OCH$_2$Ph), 125.8, 126.5, 127.3, 127.7, 128.0, 128.2, 128.3, 128.5, 128.7, 135.3, 136.2 (9 d, 2 s, 2 Ph, thienyl), 141.1 (s, thienyl), 156.1 (s, NH-C=O) and 167.1 (s, C-2); m/z (FAB) 420 (100%, $[M + 1]^+$). Compound **22b**: mp 105–106 °C; $[a]_D^{20}$ −35 (c 1, $CHCl_3$) (Found: C, 68.75; H, 5.85; N, 6.8; $C_{24}H_{24}N_2O_3S$ requires C, 68.55; H, 5.75; N, 6.65%); ν_{max} (KBr)/cm^{-1} 3320 (NH), 1760 (CO), 1690 (CO), 1525, 1240 and 680; δ_H (500 MHz; $CDCl_3$) 1.27 (3 H, d, J 6.7, H-2′), 3.19 (1 H, dd, J 8.1 and 1.5, H-3), 3.83 (1 H, d, J 15.1, NCH_2Ph), 4.14 (1 H, m_c, H-1′), 4.65 (1 H, s, H-4), 4.77 (1 H, d, J 15.1, NCH_2Ph), 4.93 (1 H, d, J 8.5, NH), 5.04 (1 H, d, J 12.3, OCH_2Ph), 5.08 (1 H, d, J 12.3, OCH_2Ph), 6.82 (1 H, s, thienyl), 6.92 (1 H, m_c, thienyl) and 7.15–7.33 (m, 11 H, 2 Ph, thienyl); δ_C (126 MHz; $CDCl_3$) 18.4 (q, C-2′), 44.4 (t, NCH$_2$Ph), 46.3 (d, C-1′), 53.9 (d, C-4), 66.2 (d, C-3), 66.7 (t, OCH$_2$Ph), 125.7, 126.1, 127.3, 127.8, 128.1, 128.2, 128.4, 128.5, 135.3, 136.3 (9 d, 2 s, 2 Ph, thienyl, partly covered), 141.2 (s, thienyl), 155.5 (s, NH-C=O) and 166.9 (s, C-2); m/z (FAB) (100%, $[M + 1]^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(3-thienyl)azetidin-2-one 23a,b. Following the general procedure, diazoketone **1** (989 mg, 4.00 mmol) and imine **11** (1.61 g, 8.00 mmol) were irradiated to give a mixture of **23a** and **23b** (1.41 g, 84%, 65 : 35), which was separated by MPLC (PE–*i*-PrOH 95 : 5) yielding **23a** (720 mg, 43%) and **23b** (398 mg, 24%) as colourless solids. Compound **23a**: mp 140–141 °C; $[a]_D^{20}$ +18 (c 1, $CHCl_3$) (Found: C, 68.45; H, 5.75; N, 6.6; $C_{24}H_{24}N_2O_3S$ requires C, 68.55; H, 5.75; N, 6.65%); ν_{max} (KBr)/cm^{-1} 3250 (NH), 1730 (CO), 1715 (CO), 1545, 1240, 1050, 725 and 680; δ_H (500 MHz; $CDCl_3$) 1.33 (3 H, d, J 6.9, H-2′), 3.21 (1 H, dd, J 2.6 and 2.6, H-3), 3.74 (1 H, d, J 15.0, NCH_2Ph), 4.19 (1 H, m_c, H-1′), 4.36 (1 H, s, H-4), 4.78 (1 H, d, J 15.0, NCH_2Ph), 4.93 (2 H, m, NH, OCH_2Ph), 5.11 (1 H, d, J 12.2, OCH_2Ph), 6.98 (1 H, d, J 3.8, thienyl) and 7.11–7.34 (12 H, m, 2 Ph, thienyl); δ_C (126 MHz; $CDCl_3$) 19.8 (q, C-2′), 44.4 (t, NCH$_2$Ph), 45.1 (d, C-1′), 52.7 (d, C-4), 64.3 (d, C-3), 66.8 (t, OCH$_2$Ph), 123.2, 125.3, 127.1, 127.6, 128.0, 128.2, 128.3, 128.5, 128.7, 135.4, 136.3 (9 d, 2 s, 2 Ph, thienyl), 138.8 (s, thienyl), 156.1 (s, NH-C=O) and 167.4 (s, C-2); m/z (FAB) 420 (100%, $[M + 1]^+$). Compound **23b**: mp 91–92 °C; $[a]_D^{20}$ −14 (c 1, $CHCl_3$) (Found: C, 68.45; H, 5.85; N, 6.55; $C_{24}H_{24}N_2O_3S$ requires C, 68.55; H, 5.75; N, 6.65%); ν_{max} (KBr)/cm^{-1} 3310 (NH), 1760 (CO), 1690 (CO), 1525, 1240, 725 and 680; δ_H (500 MHz; $CDCl_3$) 1.29 (3 H, d, J 6.8, H-2′), 3.09 (1 H, dd, J 8.2 and 2.0, H-3), 3.82 (1 H, d, J 15.0, NCH_2Ph), 4.14 (1 H, m_c, H-1′), 4.46 (1 H, d, J 2.0, H-4), 4.72 (1 H, d, J 15.0, NCH_2Ph), 4.87 (1 H, d, J 8.7, NH), 5.03 (2 H, m, NH, OCH_2Ph), 5.10 (1 H, d, J 12.3, OCH_2Ph), 6.87 (1 H, d, J 4.7, thienyl), 6.97 (1 H, s, thienyl), 7.12–7.14 and 7.25–7.35 (11 H, 2 m, 2 Ph, thienyl); δ_C (126 MHz; $CDCl_3$) 18.5 (q, C-2′), 44.5 (t, NCH$_2$Ph), 46.3 (d, C-1′), 54.1 (d, C-4), 64.8 (d, C-3), 66.7 (t, OCH$_2$Ph), 123.0, 125.1, 125.9, 127.2, 127.8, 128.2, 128.4, 128.5, 128.8, 135.4, 136.4 (9 d, 2 s, 2 Ph, thienyl), 138.9 (s, thienyl), 155.5 (s, NH-C=O), 167.2 (s, C-2); m/z (FAB) 421 (100%, $[M + 1]^+$).

(*E*,3*R*,4*R*,1′*S*)- and (*E*,3*S*,4*S*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-4-(2-phenylethenyl)azetidin-2-one 24a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **12** (885 mg, 4.00 mmol) were irradiated to give a mixture of **24a** and **24b** (66 : 34), which was separated by MPLC (PE–*i*-PrOH 95 : 5) yielding **24a** (340 mg, 39%) and **24b** (171 mg, 19%) as colourless solids. Compound **24a**: mp 120–121 °C; $[a]_D^{20}$ −2 (c 0.6, $CHCl_3$) (Found: C, 76.2; H, 6.45; N, 6.3; $C_{28}H_{28}N_2O_3$ requires C, 76.35; H, 6.4; N, 6.35%); ν_{max} (KBr)/cm^{-1} 3260 (NH), 1725 (CO), 1702 (CO), 1545 and 1245; δ_H (500 MHz; $CDCl_3$) 1.34 (3 H, d, J 6.8, H-2′), 3.11 (1 H, dd, J 2.5 and 2.5, H-3), 3.91 (1 H, d, J 8.1, H-4), 3.96 (1 H, d, J 15.1, NCH_2Ph), 4.18 (1 H, m_c, H-1′), 4.67 (1 H, J 15.1, NCH_2Ph), 4.91 (1 H, d, J 8.6, NH), 4.95 (1 H, d, J 12.3, OCH_2Ph), 5.11 (1 H, d, J 12.2, OCH_2Ph), 6.04 (1 H, dd, J 15.5 and 8.7, CH=CHPh), 6.55 (1 H, d, J 15.8, CH=CHPh) and 7.21–7.36 (15 H, m, 3 Ph); δ_C (126 MHz; $CDCl_3$) 19.9 (q, C-2′), 44.6 (t, NCH$_2$Ph), 45.0 (d, C-1′), 56.3 (d, C-4), 62.5 (d, C-3), 66.8 (t, OCH$_2$Ph), 126.0 (d, CH=CHPh), 126.6, 127.6, 128.0, 128.2, 128.3, 128.4, 128.5, 128.7, 128.7, 135.7, 135.8, 136.3 (9 d, 3 s, 3 Ph), 134.8 (d, CH=CHPh), 156.1 (s, NH-C=O), 167.0 (s, C-2);

m/*z* (FAB) 882 (3%, $[2(M + 1)]^+$), 441 (68 $[M + 1]^+$), 264 (78) and 91 (100, $C_7H_7^+$). Compound **24b**: mp 109–110 °C; $[a]_D^{20}$ +10 (*c* 0.5, $CHCl_3$) (Found: C, 76.15; H, 6.45; N, 6.3; $C_{28}H_{28}N_2O_3$ requires C, 76.35; H, 6.4; N, 6.35%); ν_{max} (KBr)/cm^{-1} 3300 (NH), 1745 (CO), 1680 (CO), 1525 and 1233; δ_H (500 MHz; $CDCl_3$) 1.28 (3 H, d, *J* 6.7, H-2′), 3.05 (1 H, d, *J* 7.5, H-3), 4.00 (1 H, d, *J* 8.5, H-4), 4.03 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.13 (1 H, q, *J* 7.2, H-1′), 4.64 (1 H, d, *J* 15.0, NC*H*$_2$Ph), 4.94 (1 H, d, *J* 7.8, NH), 5.04–5.12 (2 H, m, OCH_2Ph), 5.99 (1 H, dd, *J* 15.7 and 8.7, C*H*=CHPh), 6.48 (1 H, d, *J* 15.8, CH=C*H*Ph), 7.22–7.33 (15 H, m, 3 Ph); δ_C (126 MHz; $CDCl_3$) 18.4 (q, C-2′), 44.7 (t, N*C*H$_2$Ph), 46.1 (d, C-1′), 57.5 (d, C-4), 62.7 (d, C-3), 66.7 (t, O*C*H$_2$Ph), 126.3 (d, *C*H=CHPh), 126.6, 127.8, 128.1, 128.1, 128.3, 128.5, 128.5, 128.7, 128.8, 135.7, 135.8, 136.3 (9 d, 3 s, 3 Ph), 134.6 (d, CH=*C*HPh), 155.5 (s, NH-C=O), 166.8 (s, C-2); *m*/*z* (FAB) 441 (100%, $[M + 1]^+$), 264 (43) and 91 (59, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-3-[1-(Benzyloxycarbonylamino)ethyl]-1-*tert*-butyl-4-phenylazetidin-2-one 25a,b. Following the general procedure, diazoketone **1** (268 mg, 1.08 mmol) and imine **13** (1.02 g, 4.32 mmol) were irradiated to give a mixture of **25a** and **25b**. The ratio of isomers was determined from the crude product (**25a** : **b** 74 : 26). Compound **25a**,**b**: δ_H (500 MHz; $CDCl_3$; index a: major isomer, index b: minor isomer) 1.17 [9 H, s, $C(CH_3)_3$], 1.31 (3 H, d, *J* 6.9, H-2′), 2.78 (1 H, dd, *J* 8.9 and 2.1, H_b-3), 2.87 (1 H, dd, *J* 3.2 and 2.2, H_a-3), 4.22 (1 H, m, H_b-1′), 4.23 (1 H, m, H_a-1′), 4.38 (1 H, d, *J* 2.2 Hz, H_a-4), 4.52 (1 H, d, *J* 2.3, H_b-4), 4.83 (1 H, d, *J* 9.0, NH_b), 4.88 (1 H, d, *J* 9.0, NH_a), 5.07–5.19 (2 H, m, CH_2) and 7.29–7.37 (10 H, m, Ph).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-3-[1-(Benzyloxycarbonylamino)ethyl]-1-*tert*-butyl-4-mesitylazetidin-2-one 26a,b. Following the general procedure, diazoketone **1** (495 mg, 2.00 mmol) and imine **14** (1.02 g, 5.00 mmol) were irradiated to give a mixture of **26a** and **26b** (550 mg, 65%, 66 : 34). Purification by MPLC (PE–*i*-PrOH 97 : 7) yielded **26a** (320 mg, 38%) as a colourless solid, whilst isomer **26b** could not be isolated diastereomerically pure. Compound **26a**: mp 122–124 °C; $[a]_D^{20}$ +34 (*c* 0.5, $CHCl_3$) (Found: C, 73.9; H, 8.15; N, 6.65; $C_{26}H_{34}N_2O_3$ requires C, 73.9; H, 8.1; N, 6.65%); ν_{max} (KBr)/cm^{-1} 3300 (NH), 2950 (CH), 1730 (C=O), 1705 (C=O, amide I), 1525 (NHCO, amide II), 1330 [$C(CH_3)_3$], 1230 (CO) and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 1.26 [9 H, s, $C(CH_3)_3$], 1.33 (3 H, d, *J* 7.0, H-2′), 2.25, 2.39, 2.45 [9 H, 3 s, $C_6H_2(CH_3)_3$], 3.17 (1 H, dd, *J* 2.6 and 2.6, H-3), 4.21 (1 H, ddq, *J* 9.4, 7.0 and 2.6, H-1′), 4.82 (1 H, d, *J* 2.5, H-4), 4.89 (1 H, d, *J* 9.6, NH), 5.04 (1 H, d, *J* 12.3, CH_AH_B), 5.21 (1 H, d, *J* 12.3, CH_AH_B), 6.81, 6.83 (2 H, 2 s, H-3″, H-5″) and 7.32–7.38 (5 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 20.5 [q, $C_6H_2(CH_3)_3$], 20.9 (q, C-2′), 21.1, 21.6 [2 q, $C_6H_2(CH_3)_3$], 27.8 [q, $C(CH_3)_3$], 45.7 (d, C-1′), 52.6 (d, C-4), 55.1 [s, *C*(CH$_3$)$_3$], 59.8 (d, C-3), 67.1 (t, O*C*H$_2$Ph), 128.5, 128.7, 128.9 (3 d, Ph), 130.2 (d, C-3″ or C-5″), 131.5 (s, *ipso*-Ph), 132.1 (d, C-3″ or C-5″), 136.9 (s, C-1″), 137.5, 137.6, 137.7 (3 s, C-2″, C-4″, C-6″), 156.6 (s, NHCO) and 168.9 (s, C-2); *m*/*z* (EI, 70 eV) 422 (30%, M^+) and 91 (95, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methylpropyl]-4-(2-furyl)azetidin-2-one 27a,b. Following the general procedure, diazoketone **2** (1.38 g, 5.00 mmol) and imine **9** (1.85 g, 10.0 mmol) were irradiated to give a mixture of **27a** and **27b** (8 : 20), which was separated by MPLC (PE–*i*-PrOH 97 : 3) yielding **27a** (1.17 g, 54%) as a slightly yellow oil and **27b** (380 mg, 18%) as a colourless solid. Compound **27a**: $[a]_D^{20}$ +44 (*c* 1, $CHCl_3$) (Found: C, 72.1; H, 6.6; N, 6.5; $C_{26}H_{28}N_2O_4$ requires C, 72.2; H, 6.5; N, 6.5%); ν_{max} (film)/cm^{-1} 3313 (NH), 3032 (CH), 2962 (CH), 1746 (C=O), 1713 (C=O, amide I), 1531 (NHCO, amide II), 1237 (CO), 739 and 698 (Ph); δ_H (500 MHz; $CDCl_3$) 0.96 [3 H, d, *J* 6.9, CH(C*H*$_3$)$_2$], 0.99 [3 H, d, *J* 6.7, CH(C*H*$_3$)$_2$], 1.97 (1 H, m, H-2′), 3.68 (1 H, dd, *J* 2.9 and 2.9, H-3), 3.76 (1 H, d, *J* 15.2, NC*H*$_2$Ph), 3.83 (1 H, ddd, *J* 10.4, 7.3 and 2.9, H-1′), 4.26 (1 H, d, *J* 2.4, H-4), 4.67 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.95 (1 H, d, *J* 10.1, NH), 4.96 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.14 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 6.25 (1 H, d, *J* 3.1, C_4H_3O), 6.32 (1 H, dd, *J* 2.9 and 1.9, C_4H_3O), 7.13 (2 H, m, C_4H_3O, Ph), 7.18 and 7.34–7.40 (9 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 18.9, 19.7 [2 q, CH(*C*H$_3$)$_2$], 32.0 (d, C-2′), 44.6 (t, N*C*H$_2$Ph), 50.8 (d, C-4), 54.9 (d, C-1′), 58.6 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 110.0 (d, C_4H_3O), 110.5 (d, C_4H_3O), 127.5, 127.8, 128.1, 128.2, 128.5, 128.6 (6 d, Ph), 135.4, 136.4 (2 s, *ipso*-Ph), 143.2 (d, C_4H_3O), 149.7 (s, *ipso*-C_4H_3O), 156.8 (s, NHCO) and 166.9 (s, C-2); *m*/*z* (FAB) 455 (9%, $[M + Na]^+$), 433 (75, $[M + H]^+$), 228 (98, $[M + H - C_{12}H_{15}NO_2]^+$), 91 (100, $C_7H_7^+$) and 77 (8, $C_6H_5^+$). Compound **27b**: mp 129–130 °C; $[a]_D^{20}$ −39 (*c* 1, $CHCl_3$) (Found: C, 72.45; H, 6.6; N, 6.35; $C_{26}H_{28}N_2O_4$ requires C, 72.2; H, 6.55; N, 6.5%); ν_{max} (KBr)/cm^{-1} 3358 (NH), 3130 (CH), 2940 (CH), 1742 (C=O), 1710 (C=O, amide I), 1520 (NHCO, amide II), 1230 (CO), 750 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.88 [3 H, d, *J* 6.9, CH(C*H*$_3$)$_2$], 0.93 [3 H, d, *J* 6.8, CH(C*H*$_3$)$_2$], 2.20 (1 H, m_c, *J* 6.7, H-2′), 3.46 (1 H, dd, *J* 9.3 and 2.2, H-3), 3.90 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.08 (1 H, ddd, *J* 9.7, 9.7 and 4.0, H-1′), 4.43 (1 H, d, *J* 2.3, H-4), 4.61 (1 H, d, *J* 14.9, NC*H*$_2$Ph), 4.63 (1 H, d, *J* 8.6, NH), 5.02 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.14 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 6.07 (1 H, d, *J* 3.1, C_4H_3O), 6.27 (1 H, dd, *J* 3.0 and 2.0, C_4H_3O), 7.12–7.14 (2 H, m, C_4H_3O, Ph) and 7.23–7.39 (9 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 19.3, 19.8 [2 q, CH(*C*H$_3$)$_2$], 30.1 (d, C-2′), 44.8 (t, N*C*H$_2$Ph), 51.7 (d, C-4), 55.3 (d, C-1′), 59.7 (d, C-3), 66.8 (t, O*C*H$_2$Ph), 109.4 (d, C_4H_3O), 110.5 (d, C_4H_3O), 127.6, 128.1, 128.2, 128.3, 128.5, 128.7 (6 d, Ph), 135.4, 136.4 (2 s, *ipso*-Ph), 143.1 (d, C_4H_3O), 150.0 (s, *ipso*-C_4H_3O), 156.3 (s, NHCO) and 166.9 (s, C-2); *m*/*z* (FAB) 455 (25%, $[M + Na]^+$), 433 (50, $[M + H]^+$), 228 (75, $[M + H - C_{12}H_{15}NO_2]^+$) and 91 (100, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)- and (3*S*,4*R*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methylpropyl]-4-(2-thienyl)azetidin-2-one 28a,b. Following the general procedure, diazoketone **2** (1.10 g, 4.00 mmol) and imine **10** (1.61 g, 8.00 mmol) were irradiated to give a mixture of **28a** and **28b** (82 : 18), which was separated by MPLC (PE–*i*PrOH 95 : 5) yielding **28a** (1.03 g, 57%) and **28b** (275 mg, 15%) as colourless solids. Compound **28a**: mp 119–121 °C; $[a]_D^{20}$ +53 (*c* 1, $CHCl_3$) (Found: C, 69.4; H, 6.2; N, 6.25; $C_{26}H_{28}N_2O_3S$ requires C, 69.6; H, 6.3; N, 6.25%); ν_{max} (KBr)/cm^{-1} 3250 (NH), 3025 (CH), 2940 (CH), 1725 (C=O), 1710 (C=O, amide I), 1590 (NHCO, amide II), 1240 (CO), 690 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.95 [3 H, d, *J* 6.8, CH(C*H*$_3$)$_2$], 0.97 [3 H, d, *J* 6.7, CH(C*H*$_3$)$_2$], 1.94 (1 H, q, *J* 6.8, H-2′), 3.44 (1 H, dd, *J* 2.7 and 2.7, H-3), 3.77 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 3.88 (1 H, ddd, *J* 10.3, 7.5 and 3.0, H-1′), 4.49 (1 H, d, *J* 2.3, H-4), 4.79 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.88 (1 H, d, *J* 10.2, NH), 4.93 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.15 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 6.97 (2 H, m, C_4H_3S), 7.12–7.41 (11 H, m, Ph, C_4H_3S); δ_C (126 MHz; $CDCl_3$) 18.9, 19.7 [2 q, CH(*C*H$_3$)$_2$], 32.0 (d, C-2′), 44.4 (t, N*C*H$_2$Ph), 53.2 (d, C-1′), 54.9 (d, C-4), 63.3 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 125.9, 126.7, 127.3, 127.6, 127.8, 128.1, 128.3, 128.6, 128.7 (9 d, Ph, C_4H_3S), 135.3, 136.3 (2 s, *ipso*-Ph), 141.1 (s, *ipso*-C_4H_3S), 156.7 (s, NHCO) and 166.9 (s, C-2); *m*/*z* (EI, 70 eV) 448 (1%, M^+), 377 (95, $[M - CO - C_3H_7]^+$), 91 (100, $C_7H_7^+$). Compound **28b**: mp 137–139 °C; $[a]_D^{20}$ −32 (*c* 1, $CHCl_3$) (Found: C, 69.5; H, 6.3; N, 6.2; $C_{26}H_{28}N_2O_3S$ requires C, 69.6; H, 6.3; N, 6.25%); ν_{max} (KBr)/cm^{-1} 3340 (NH), 2950 (CH), 1740 (C=O), 1710 (C=O, amide I), 1525 (NHCO, amide II), 1230 (CO), 730 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.86 [3 H, d, *J* 6.9, CH(C*H*$_3$)$_2$], 0.93 [3 H, d, *J* 6.9, CH(C*H*$_3$)$_2$], 2.20 (1 H, m, H-2′), 3.24 (1 H, dd, *J* 9.4 and 2.0, H-3), 3.87 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 3.88 (1 H, m, H-1′), 4.60 (1 H, d, *J* 10.0, NH), 4.67 (1 H, d, *J* 1.5, H-4), 4.75 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 5.04 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.16 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 6.74 (1 H, d, *J* 3.0, C_4H_3S), 6.91 (1 H, dd, *J* 5.0 and 3.6, C_4H_3S), 7.13–7.15 (2 H, m, Ph, C_4H_3S), 7.26 and 7.31–7.34 (9 H, m, Ph); δ_C (126

MHz; $CDCl_3$) 16.3, 19.8 [2 q, CH(C*H*$_3$)$_2$], 30.0 (d, C-2′), 44.4 (d, C-1′), 54.2 (t, N*C*H$_2$Ph), 55.5 (d, C-4), 64.2 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 125.7, 126.0, 127.3, 127.7, 128.2, 128.3, 128.5, 128.8 (9 d, Ph, C_4H_3S, partly covered), 135.3, 136.4 (2 s, *ipso*-Ph), 141.4 (s, *ipso*-C_4H_3S), 156.2 (s, NHCO) and 166.8 (s, C-2); *m*/*z* (FAB) 471 (45%, $[M + Na]^+$), 449 (95, $[M + H]^+$), 244 (84, $[M + 2 H - C_{12}H_{16}NO_2]^+$) and 91 (100, $C_7H_7^+$).

(*E*,3*R*,4*R*,1′*S*)- and (*E*,3*S*,4*S*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methylpropyl]-4-(2-phenylethenyl)azetidin-2-one 29a,b. Following the general procedure, diazoketone **2** (551 mg, 2.00 mmol) and imine **12** (885 mg, 4.00 mmol) were irradiated to give a mixture of **29a** and **29b** (80 : 20), which was separated by MPLC (PE–*i*-PrOH 95 : 5 and PE–EA 4 : 1) yielding **29a** (530 mg, 57%) as a colourless oil and **29b** (126 mg, 13%) as a colourless solid. Compound **29a**: $[\alpha]_D^{20}$ +29 (*c* 1, $CHCl_3$) (Found: C, 76.15; H, 6.95; N, 5.8; $C_{30}H_{32}N_2O_3$ requires C, 76.9; H, 6.9; N, 6.0%); ν_{max} (film)/cm^{-1} 3313 (NH), 3062 (CH), 3030 (CH), 2962 (CH), 2930 (CH), 1746 (C=O), 1650 (C=O, amide I), 1531 (NHCO, amide II), 1236 (CO) and 969 (C=C); δ_H (500 MHz; $CDCl_3$) 0.96 [3 H, d, *J* 6.7, CH(C*H*$_3$)$_2$], 0.99 [3 H, d, *J* 6.8, CH(C*H*$_3$)$_2$], 1.95 (1 H, m, H-2′), 3.25 (1 H, dd, *J* 2.2 and 2.2, H-3), 3.83 (1 H, ddd, *J* 10.4, 7.5 and 2.9, H-1′), 3.87 (1 H, dd, *J* 8.8 and 1.8, H-4), 3.97 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.66 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.89 (1 H, d, *J* 10.2, NH), 4.97 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.15 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 6.05 (1 H, dd, *J* 15.8 and 8.8, H-1″), 6.56 (1 H, d, *J* 15.8, H-2″) and 7.20–7.41 (15 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 19.0, 19.6 [2 q, CH(*C*H$_3$)$_2$], 32.0 (d, C-2′), 44.6 (t, N*C*H$_2$Ph), 54.9 (d, C-1′), 57.0 (d, C-4), 59.8 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 126.0 (d, C-1″), 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7 (9 d, Ph), 134.9 (d, C-2″), 135.7, 135.8, 136.4 (3 s, *ipso*-Ph), 156.7 (s, NHCO) and 166.8 (s, C-2); *m*/*z* (FAB) 469.2490; $^{12}C_{30}{}^{1}H_{33}{}^{14}N_2{}^{16}O_3$ requires 469.2491; *m*/*z* (FAB) 491 (4%, $[M + Na]^+$), 469 (38, $[M + H]^+$), 264 (60, $[M + H - C_{12}H_{15}NO_2]^+$) and 91 (100, $C_7H_7^+$). Compound **29b**: mp 64–66 °C; $[\alpha]_D^{20}$ +26 (*c* 0.5, $CHCl_3$) (Found: C, 76.5; H, 6.9; N, 6.0; $C_{30}H_{32}N_2O_3$ requires C, 76.9; H, 6.9; N, 6.0%); ν_{max} (KBr)/cm^{-1} 3322 (NH), 3062 (CH), 3030 (CH), 2961 (CH), 2930 (CH), 1717 (C=O), 1637 (C=O, amide I), 1496 (NHCO, amide II), 1237 (CO), 750 and 696 (Ph); δ_H (500 MHz; $CDCl_3$) 0.88 [3 H, d, *J* 6.9, CH(C*H*$_3$)$_2$], 0.95 [3 H, d, *J* 6.8, CH(C*H*$_3$)$_2$], 2.18 (1 H, dsept, *J* 6.8 and 4.3, H-2′), 3.08 (1 H, dd, *J* 9.4 and 1.5, H-3), 4.04 (1 H, ddd, *J* 10.4, 9.3 and 4.4, H-1′), 4.05 (1 H, dd, *J* 8.9 and 1.5, H-4), 4.10 (1 H, d, *J* 15.0, NC*H*$_2$Ph), 4.59 (1 H, d, *J* 15.3, NC*H*$_2$Ph), 4.61 (1 H, d, *J* 10.6, NH), 5.03 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.17 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.96 (1 H, dd, *J* 15.8 and 8.9, H-1″), 6.42 (1 H, d, *J* 15.8, H-2″) and 7.19–7.43 (15 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 16.3, 19.8 [2 q, CH(*C*H$_3$)$_2$], 30.1 (d, C-2′), 44.7 (t, N*C*H$_2$Ph), 55.3 (d, C-1′), 57.9 (d, C-4), 60.6 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 126.5 (d, C-1″), 127.7, 128.2, 128.4, 128.5, 128.8 (9 d, Ph, partly covered), 134.9 (d, C-2″), 135.9, 136.4 (3 s, *ipso*-Ph, partly covered), 156.3 (s, NHCO) and 166.7 (s, C-2); *m*/*z* (FAB) 491 (2%, $[M + Na]^+$), 469 (12, $[M + H]^+$), 264 (36, $[M + H - C_{12}H_{15}NO_2]^+$) and 91 (100, $C_7H_7^+$).

(*E*,3*R*,4*R*,1′*S*)- and (*E*,3*S*,4*S*,1′*S*)-1-Allyl-3-[1-(benzyloxycarbonylamino)-2-methylpropyl]-4-(2-phenylethenyl)azetidin-2-one 30a,b. Following the general procedure, diazoketone **2** (851 mg, 3.09 mmol) and imine **15** (793 mg, 4.63 mmol) were irradiated to give a mixture of **30a** and **30b** (720 mg, 56%, 75 : 25), which was separated by MPLC (PE–*i*-PrOH 98 : 2) yielding **30a** (460 mg, 36%) as a colourless oil and **30b** (109 mg, 8%) as a colourless solid. Compound **30a**: $[\alpha]_D^{20}$ +125 (*c* 1.02, $CHCl_3$) (Found: C, 74.6; H, 7.35; N, 6.7; $C_{26}H_{30}N_2O_3$ requires C, 74.6; H, 7.2; N, 6.7%); ν_{max} (film)/cm^{-1} 3306 (NH), 3031 (CH), 2961 (CH), 1732 (C=O), 1644 (C=O, amide I), 1538 (NHCO, amide II), 1237 (C-O), 749 and 695 (Ph); δ_H (500 MHz; $CDCl_3$) 0.97, 1.00 [6 H, 2 d, *J* 6.7, CH(C*H*$_3$)$_2$], 1.95 (1 H, sept, *J* 6.8, H-2′), 3.22 (1 H, dd, *J* 2.7 and 2.7, H-3), 3.46 (1 H, dd, *J* 15.8 and 6.8, H-1′), 3.88 (1 H, ddd, *J* 10.4, 7.5, and 2.8, H-1′), 3.99 (1 H, dd, *J* 8.8 and 2.4, H-4), 4.03 (1 H, dd, *J* 15.8 and 5.1, H-1″), 4.92 (1 H, d, *J* 10.2, NH), 5.13 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.07 (1 H, d, *J* 10.2, H-3″), 5.14 (1 H, dd, *J* 17.2 and 1.0, H-3″), 5.18 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.65 (1 H, dddd, *J* 17.2, 10.3, 6.6 and 5.2, H-2″), 6.10 (1 H, dd, *J* 15.8 and 8.8, H-1‴), 6.66 (1 H, d, *J* 15.8, H-2‴) and 7.25–7.42 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 19.0, 19.8 [2 q, CH(*C*H$_3$)$_2$], 32.0 (d, C-2′), 42.9 (t, C-1″), 54.9 (d, C-1′), 57.2 (d, C-4), 59.8 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 118.2 (t, C-3″), 126.1 (d, C-1‴), 126.6, 128.0, 128.1, 128.3, 128.5, 128.7 (6 d, Ph), 131.7 (d, C-2″), 134.8, 135.8 (2 s, *ipso*-Ph), 136.5 (d, C-2‴), 156.8 (s, NHCO) and 166.8 (s, C-2); *m*/*z* (FAB) 441 (6%, $[M + Na]^+$), 419 (58, $[M + H]^+$), 214 (100, $[M + H - C_{12}H_{15}NO_2]^+$), 91 (100, $C_7H_7^+$). Compound **30b**: mp 100–101 °C; $[\alpha]_D^{20}$ −94 (*c* 1, $CHCl_3$) (Found: C, 74.55; H, 7.3; N, 6.65; $C_{26}H_{30}N_2O_3$ requires C, 74.6; H, 7.2; N, 6.7%); ν_{max} (film)/cm^{-1} 3320 (NH), 3031 (CH), 2950 (CH), 1745 (C=O), 1680 (C=O, amide I), 1525 (NHCO, amide II), 1237 (CO), 732 and 675 (Ph); δ_H (500 MHz; $CDCl_3$) 0.89, 0.96 [6 H, 2 d, *J* 6.8, CH(C*H*$_3$)$_2$], 2.24 (1 H, dsept, *J* 6.9 and 3.6, H-2′), 3.02 (1 H, dd, *J* 10.1 and 2.1, H-3), 3.55 (1 H, dd, *J* 15.8 and 6.7, H-1″), 4.00 (1 H, dd, *J* 15.8 and 5.4, H-1″), 4.09 (1 H, ddd, *J* 10.1, 10.1, 3.7, H-1′), 4.19 (1 H, dd, *J* 8.8 and 2.0, H-4), 4.78 (1 H, d, *J* 10.1, NH), 5.03 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.18 (1 H, d, *J* 10.2, H-3″), 5.19 (1 H, d, *J* 17.1, H-3″), 5.20 (1 H, d, *J* 12.2, OC*H*$_2$Ph), 5.74 (1 H, dddd, *J* 17.1, 10.2, 6.9 and 5.5, H-2″), 6.06 (1 H, dd, *J* 15.7 and 8.8, H-1‴), 6.52 (1 H, d, *J* 15.8, H-2‴) and 7.23–7.41 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 16.0, 19.9 [2 q, CH(*C*H$_3$)$_2$], 29.9 (d, C-2′), 43.3 (t, C-1″), 55.7 (d, C-1′), 58.4 (d, C-4), 60.6 (d, C-3), 66.9 (t, O*C*H$_2$Ph), 118.5 (t, C-3″), 126.6 (d, C-1‴), 126.8, 128.1, 128.2, 128.3, 128.6, 128.7 (6 d, Ph), 131.8 (d, C-2″), 134.2, 135.8 (2 s, *ipso*-Ph), 136.4 (d, C-2‴), 156.4 (s, NHCO) and 166.7 (s, C-2); *m*/*z* (FAB) 441 (13%, $[M + Na]^+$), 419 (38, $[M + H]^+$), 214 (90, $[M + H - C_{12}H_{15}NO_2]^+$), 91 (100, $C_7H_7^+$).

(3*R*,4*S*,1′*R*)- and (3*S*,4*R*,1′*R*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2,2-dimethylpropyl]-4-(2-furyl)azetidin-2-one 31a,b. Following the general procedure, diazoketone **3** (2.03 g, 7.00 mmol) and imine **9** (2.59 g, 14.0 mmol) were irradiated to give a mixture of **31a** and **31b** (90 : 10), which was separated by MPLC (PE–*i*-PrOH 98 : 2) yielding **31a** (2.35 g, 75%) as a colourless oil and **31b** (270 mg, 9%) as a colourless solid. Compound **31a**: $[\alpha]_D^{20}$ +61 (*c* 1, $CHCl_3$) (Found: C, 72.5; H, 6.85; N, 6.2; $C_{27}H_{30}N_2O_4$ requires C, 72.6; H, 6.75; N, 6.25%); ν_{max} (film)/cm^{-1} 3317 (NH), 3031 (CH), 2962 (CH), 1750 (C=O), 1713 (C=O, amide I), 1504 (NHCO, amide II), 1234 (CO), 736 and 698 (Ph); δ_H (500 MHz; $CDCl_3$) 0.97 [9 H, s, C(CH_3)$_3$], 3.74 (1 H, dd, *J* 2.5 and 2.5 Hz, H-3), 3.76 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 3.87 (1 H, dd, *J* 10.7 and 2.4, H-1′), 4.25 (1 H, d, *J* 2.5, H-4), 4.66 (1 H, d, *J* 15.1, NC*H*$_2$Ph), 4.96 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 5.04 (1 H, d, *J* 10.7, NH), 5.17 (1 H, d, *J* 12.3, OC*H*$_2$Ph), 6.26 (1 H, d, *J* 3.3, C_4H_3O), 6.33 (1 H, dd, *J* 3.3 and 1.8, C_4H_3O), 7.12 (2 H, m, C_4H_3O, Ph), 7.18, 7.20–7.41 (9 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 26.8 [q, C(*C*H$_3$)$_3$], 34.8 (s, C-2′), 44.7 (t, N*C*H$_2$Ph), 51.6 (d, C-4), 57.4 (d, C-3), 58.0 (d, C-1′), 66.9 (t, O*C*H$_2$Ph), 110.2 (d, C_4H_3O), 110.5 (d, C_4H_3O), 127.5, 127.8, 128.1, 128.2, 128.5, 128.8 (6 d, Ph), 135.4, 136.4, 143.3, 149.6 (1 d, 3 s, C_4H_3O, *ipso*-C_4H_3O, *ipso*-Ph), 156.8 (s, NHCO) and 166.6 (s, C-2); *m*/*z* (FAB) 469 (8%, $[M + Na]^+$), 447 (50, $[M + H]^+$), 228 (100, $[M + 2 H - C_{13}H_{18}NO_2]^+$), 91 (100, $C_7H_7^+$). Compound **31b**: mp 160–161 °C; $[\alpha]_D^{20}$ −103 (*c* 1, $CHCl_3$) (Found: C, 72.55; H, 6.8; N, 6.25; $C_{27}H_{30}N_2O_4$ requires C, 72.6; H, 6.75; N, 6.25%); ν_{max} (KBr)/cm^{-1} 3315 (NH), 2940 (CH), 1735 (C=O), 1705 (C=O, amide I), 1523 (NHCO, amide II), 1235 (CO), 750 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.88 [9 H, s, C(C*H*$_3$)$_3$], 3.70 (1 H, dd, *J* 4.7 and 2.6, H-3), 3.72 (1 H, d, *J* 15.2, NC*H*$_2$Ph), 4.15 (1 H, dd, *J* 10.6 and 4.7 Hz, H-1′), 4.17 (1 H, d, *J* 2.4, H-4), 4.65 (1 H, d, *J* 10.6, NH), 4.72 (1 H, d, *J* 15.2, NC*H*$_2$Ph), 5.11 (1 H, d, *J* 12.1, OC*H*$_2$Ph), 5.19 (1 H, d, *J* 12.1, OC*H*$_2$Ph), 6.13 (1 H, d, *J* 3.0, C_4H_3O), 6.31 (1 H, dd, *J* 3.0 and

1.8, C_4H_3O), 7.10 (2 H, m, C_4H_3O, Ph), 7.16 (3 H, m, Ph) and 7.33–7.38 (6 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 26.7 [q, C(CH$_3$)$_3$], 34.7 (s, C-2′), 44.6 (t, NCH$_2$Ph), 50.0 (d, C-4), 57.1 (d, C-3), 58.0 (d, C-1′), 67.1 (t, OCH$_2$Ph), 109.6 (d, C_4H_3O), 110.5 (d, C_4H_3O), 127.6, 128.2, 128.3, 128.4, 128.6, 128.7 (6 d, Ph), 135.5, 136.4, 143.3, 149.8 (1 d, 3 s, C_4H_3O, *ipso*-C_4H_3O, *ipso*-Ph), 156.0 (s, NHCO) and 167.4 (s, C-2); *m/z* (EI, 70 eV) 446 (1%, M^+), 91 (100, $C_7H_7^+$).

(3*R*,4*S*,1′*R*)- and (3*S*,4*R*,1′*R*)-1-Allyl-3-[1-(benzyloxycarbonylamino)-2,2-dimethylpropyl]-4-(2-furyl)azetidin-2-one 32a,b. Following the general procedure, diazoketone **3** (700 mg, 2.42 mmol) and imine **16** (426 mg, 3.15 mmol) were irradiated to give a mixture of **32a** and **32b** (90 : 10), which was separated by MPLC (PE–*i*-PrOH 98 : 2) yielding **32a** (730 mg, 76%) as a colourless solid and **32b** (80 mg, 8%) as a colourless oil. Compound **32a**: mp 138–141 °C; $[\alpha]_D^{20}$ +105 (*c* 1, $CHCl_3$) (Found: C, 69.65; H, 7.1; N, 6.9; $C_{23}H_{28}N_2O_4$ requires C, 69.65; H, 7.1; N, 7.05%); ν_{max} (KBr)/cm^{-1} 3250 (NH), 2915 (CH), 1750 (C=O), 1705 (C=O, amide I), 1540 (NHCO, amide II), 1235 (CO), 725 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.98 [9 H, s, C(CH$_3$)$_3$], 3.30 (1 H, dd, *J* 15.9 and 6.8, H-1″), 3.69 (1 H, dd, *J* 2.5 and 2.5, H-3), 3.91 (1 H, dd, *J* 10.7 and 2.5, H-1′), 3.99 (1 H, dd, *J* 15.9 and 5.0, H-1″), 4.37 (1 H, d, *J* 2.5, H-4), 5.01 (1 H, d, *J* 10.7, NH), 5.01 (1 H, dd, *J* 10.2 and 1.5, H-3″), 5.06 (1 H, dd, *J* 17.1 and 1.5, H-3″), 5.12 (1 H, d, *J* 12.2, OCH_2Ph), 5.17 (1 H, d, *J* 12.2, OCH_2Ph), 5.54 (1 H, dddd, *J* 17.1, 10.2, 6.8 and 5.0, H-2″), 6.35 (2 H, m, C_4H_3O) and 7.33–7.41 (6 H, m, C_4H_3O, Ph); δ_C (126 MHz; $CDCl_3$) 26.8 [q, C(CH$_3$)$_3$], 34.7 (s, C-2′), 43.1 (t, C-1″), 51.9 (d, C-4), 57.5 (d, C-3), 58.1 (d, C-1′), 66.9 (t, OCH$_2$Ph), 110.0 (d, C_4H_3O), 110.5 (d, C_4H_3O), 118.1 (t, C-3″), 128.0, 128.2, 128.5 (3 d, Ph), 131.3 (s, *ipso*-Ph), 136.4 (d, C-2″), 143.2, 149.8 (d, s, C_4H_3O, *ipso*-C_4H_3O), 157.0 (s, NHCO) and 166.6 (s, C-2); *m/z* (FAB) 419 (33%, [M + Na]$^+$), 397 (36, [M + H]$^+$), 220 (50, $C_{13}H_{18}NO_2^+$), 178 (50, [M + 2 H − $C_{13}H_{18}NO_2$]$^+$), 91 (100, $C_7H_7^+$). Compound **32b**: $[\alpha]_D^{20}$ −80 (*c* 0.35, $CHCl_3$) (Found: C, 69.75; H, 7.2; N, 6.7; $C_{23}H_{28}N_2O_4$ requires C, 69.65; H, 7.1; N, 7.0%); ν_{max} (film)/cm^{-1} 3250 (NH), 2940 (CH), 1745 (C=O), 1735 (C=O, amide I), 725 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.92 [9 H, s, C(CH$_3$)$_3$], 3.35 (1 H, dd, *J* 15.6 and 6.9, H-1″), 3.69 (1 H, dd, *J* 5.6 and 2.4, H-3), 4.01 (1 H, dd, *J* 15.8 and 5.5 Hz, H-1″), 4.10 (1 H, dd, *J* 10.6 and 5.7, H-1′), 4.36 (1 H, d, *J* 2.5, H-4), 4.76 (1 H, d, *J* 10.6, NH), 5.01 (1 H, dd, *J* 10.2 and 1.5, H-3″), 5.08 (1 H, dd, *J* 17.1 and 1.4, H-3″), 5.08 (1 H, d, *J* 12.2, OCH_2Ph), 5.18 (1 H, d, *J* 12.2, OCH_2Ph), 5.54 (1 H, dddd, *J* 17.1, 10.2, 7.0 and 5.1, H-2″), 6.20 (1 H, d, *J* 3.2, C_4H_3O), 6.33 (1 H, dd, *J* 3.3 and 1.9, C_4H_3O) and 7.33–7.40 (6 H, m, C_4H_3O, Ph); δ_C (126 MHz; $CDCl_3$) 26.7 [q, C(CH$_3$)$_3$], 34.6 (s, C-2′), 43.2 (t, C-1″), 50.6 (d, C-4), 57.4 (d, C-3), 58.2 (d, C-1′), 67.0 (t, OCH$_2$Ph), 109.6 (d, C_4H_3O), 110.6 (d, C_4H_3O), 118.3 (t, C-3″), 128.3, 128.6 (3 d, Ph, partly covered), 131.3 (s, *ipso*-Ph), 136.4 (d, C-2″), 143.2, 150.1 (d, s, C_4H_3O, *ipso*-C_4H_3O), 156.1 (s, NHCO) and 167.2 (s, C-2); *m/z* (FAB) 397 (17%, [M + H]$^+$) and 91 (100, $C_7H_7^+$).

(*E*,3*R*,4*R*,1′*R*)- and (*E*,3*S*,4*S*,1′*R*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2,2-dimethylpropyl]-4-(2-phenylethenyl)azetidin-2-one 33a,b. Following the general procedure, diazoketone **3** (579 mg, 2.00 mmol) and imine **12** (885 mg, 4.00 mmol) were irradiated to give a mixture of **33a** and **33b** (87 : 13), which was purified by MPLC (PE–*i*-PrOH 99 : 1). Separation of the isomers could not be achieved (579 mg, 60%). Compound **33a/b** (87 : 13): $[\alpha]_D^{20}$ +54 [(**33a** : **b**, 87 : 13), *c* 0.5, $CHCl_3$] (Found: C, 77.0; H, 7.15; N, 5.75; $C_{31}H_{34}N_2O_3$ requires C, 77.15; H, 7.1; N, 5.8%); ν_{max} [film, (**33a** : **b**, 87 : 13)]/cm^{-1} 3300 (NH), 3020 (CH), 3000 (CH), 2970 (CH), 1745 (C=O), 1625 (C=O, amide I), 1500 (NHCO, amide II), 1220 (CO), 730 and 680 (Ph); δ_H (major isomer, 500 MHz; $CDCl_3$) 0.98 [9 H, s, C(CH$_3$)$_3$], 3.30 (1 H, dd, *J* 2.4 and 2.4, H-3), 3.85 (1 H, dd, *J* 9.2 and 2.5, H-4), 3.86 (1 H, dd, *J* 10.7 and 2.5, H-1′), 3.99 (1 H, d, *J* 15.1, NCH_2Ph), 4.64 (1 H, d, *J* 15.1, NCH_2Ph), 4.96 (1 H, d, *J* 12.3, OCH_2Ph), 5.02 (1 H, d, *J* 10.7, NH), 5.18 (1 H, d, *J* 12.4, OCH_2Ph), 6.04 (1 H, dd, *J* 15.8 and 8.9, H-1″), 6.58 (1 H, d, *J* 15.8, H-2″) and 7.19–7.40 (15 H, m, Ph); δ_C (major isomer, 126 MHz; $CDCl_3$) 27.1 [q, C(CH$_3$)$_3$], 35.2 (s, C-2′), 45.0 (t, NCH$_2$Ph), 58.1, 58.3 (2 d, C-4, C-1′), 59.1 (d, C-3), 67.2 (t, OCH$_2$Ph), 125.9 (d, C-1″), 127.6, 127.8, 128.1, 128.3, 128.4, 128.5, 128.6, 128.7, 128.8 (9 d, Ph), 135.5 (d, C-2″), 136.2, 136.2, 136.8 (3 s, *ipso*-Ph), 157.2 (s, NHCO) and 166.9 (s, C-2); *m/z* [(**33a** : **b**, 87 : 13), FAB] 483 (48%, [M + H]$^+$), 264 (70, [M + H − $C_{13}H_{17}NO_2$]$^+$) and 91 (100, $C_7H_7^+$).

(3′*R*,4′*S*,1″*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)ethyl]-2-oxoazetidine-4-carboxylic acid 34

(a) β-Lactam **21a** (402 mg, 1.00 mmol) and periodic acid (3.42 g, 15.0 mmol) were dissolved in a mixture of acetonitrile, CCl_4 and H_2O (2 : 2 : 3, 14 mL) and stirred, until a clear solution had formed (5 min). $RuCl_3 \cdot H_2O$ (4.5 mg, 20 μmol) was added and the mixture was stirred at room temperature. After the evolution of gas stopped (10 min), the black mixture was cooled (0 °C) and Et_2O (5 mL) was added. The organic phase was separated and the aqueous phase was extracted with Et_2O (2 × 5 mL). The combined organic layers were washed with brine (2 × 5 mL), dried ($MgSO_4$) and concentrated. The residue was triturated with saturated $NaHCO_3$ solution (10 mL) and extracted with Et_2O (3 × 10 mL). The aqueous phase was acidified to pH 2 with 6 M HCl and extracted with Et_2O (3 × 10 mL). The combined organic layers were dried ($MgSO_4$) and concentrated to yield the carboxylic acid **34** (383 mg, quant.) as a colourless foam.

(b) Utilization of sodium periodate as oxidation agent (further experimental details as described above) led within 15 min to the carboxylic acid **34** (344 mg, 90%).

(c) Further starting materials for the preparation of carboxylic acid **34** are summarized in Table 2. Compound **34**: softening range 40–50 °C; ν_{max} (KBr)/cm^{-1} 3400 (NH), 3020 (CH), 2920 (CH), 1740 (C=O), 1715 (C=O), 1515 (NHCO, amide II), 1230 (CO) and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 1.22 (1 H, d, *J* 6.7, H-2″), 3.34 (1 H, dd, *J* 2.8 and 2.8, H-3′), 3.77 (1 H, d, *J* 2.6, H-4′), 3.99 (1 H, d, *J* 15.0, NCH_2Ph), 4.14 (1 H, m, H-1″), 4.77 (1 H, d, *J* 15.0, NCH_2Ph), 4.83 (1 H, d, *J* 12.3, OCH_2Ph), 5.01 (1 H, d, *J* 12.3, OCH_2Ph), 5.18 (1 H, d, *J* 8.9, NH), 7.13–7.28 (10 H, m, Ph) and 8.86 (1 H, br s, COOH); δ_C (126 MHz; $CDCl_3$) 19.0 (q, C-2″), 45.2 (d, C-1″), 45.3 (t, NCH$_2$Ph), 52.6 (d, C-4′), 60.1 (d, C-3′), 67.2 (t, OCH$_2$Ph), 128.0, 128.3, 128.4, 128.6, 128.9, 130.0 (6 d, 2 Ph), 134.5, 136.0 (2 s, *ipso*-Ph), 156.4 (s, NHCO), 166.6 (s, C-2′) and 173.4 (s, C-1); *m/z* (EI, 70 eV) 382 (1%, M^+) and 91 (42, $C_7H_7^+$).

(3′*R*,4′*S*,1″*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methylpropyl]-2-oxoazetidine-4-carboxylic acid 35

Carboxylic acid **35** was obtained as described for compound **34**. Starting azetidinones, reaction conditions and yields for these syntheses are summarized in Table 2. Compound **35**: softening range 65–67 °C; $[\alpha]_D^{20}$ −28 (*c* 1, $CHCl_3$) (Found: C, 66.3; H, 6.4; N, 6.55; $C_{23}H_{26}N_2O_5$ requires C, 67.3; H, 6.4; N, 6.8%); ν_{max} (KBr)/cm^{-1} 3300 (NH), 2950 (CH), 1740 (C=O), 1720 (C=O), 1525 (NHCO, amide II), 1225 (CO), 720 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.95 [3 H, d, *J* 6.8, CH(CH_3)$_2$], 0.98 [3 H, d, *J* 6.7, CH(CH_3)$_2$], 1.94 (1 H, dsept, *J* 7.7 and 6.8, H-2″), 3.57 (1 H, dd, *J* 3.0 and 3.0, H-3′), 3.81 (1 H, d, *J* 2.5, H-4′), 3.88 (1 H, ddd, *J* 10.6, 7.8 and 3.2, H-1″), 4.07 (1 H, d, *J* 14.9, NCH_2Ph), 4.84 (1 H, d, *J* 15.1, NCH_2Ph), 4.92 (1 H, d, *J* 12.4, OCH_2Ph), 5.13 (1 H, d, *J* 12.4, OCH_2Ph), 5.21 (1 H, d, *J* 10.1, NH), 7.20–7.36 (10 H, m, Ph) and 8.84 (1 H, br s, COOH); δ_C (126 MHz; $CDCl_3$) 19.4, 20.2 [2 q, CH(CH$_3$)$_2$], 32.1 (d, C-2″), 45.7 (t, NCH$_2$Ph), 53.8 (d, C-4′), 55.7 (d, C-1″), 57.8 (d, C-3′), 67.6

(t, OCH$_2$Ph), 128.2, 128.3, 128.5, 128.6, 128.7, 129.0 (6 d, Ph), 134.5, 136.1 (2 s, *ipso*-Ph), 156.9 (s, NHCO), 166.0 (s, C-2′) and 173.5 (s, C-1); *m*/*z* (FAB) 433 (12%, $[M + Na]^+$), 411 (83, $[M + H]^+$) and 91 (100, $C_7H_7^+$).

Methyl (3′*R*,4′*S*,1″*S*)-1-benzyl-3-[1-(benzyloxycarbonylamino)-ethyl]-2-oxoazetidine-4-carboxylate 45

To enable purification a solution of carboxylic acid **34** (80 mg, 209 μmol) in THF (5 mL) was treated with a 0.4 M solution of CH_2N_2 in Et_2O until the yellow colour persisted. The solution was stirred for a further 5 min, concentrated and purified by MPLC (PE–EA 80 : 20) to yield the methyl ester **45** (82 mg, 99%) as a colourless solid. Compound **45**: mp 134–135 °C; $[a]_D^{20}$ +18 (*c* 1, $CHCl_3$) (Found: C, 66.7; H, 6.2; N, 7.0; $C_{22}H_{24}N_2O_5$ requires C, 66.65; H, 6.1; N, 7.05%); ν_{max} (KBr)/cm^{-1} 3280 (NH), 3021 (CH), 3004 (CH), 2980 (CH), 1740 (C=O), 1729 (C=O), 1695 (C=O, amide I), 1535 (NHCO, amide II), 1240 (CO), 720 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 1.34 (3 H, d, *J* 6.7, H-2″), 3.38 (1 H, s, H-3′), 3.70 (3 H, s, OCH_3), 3.85 (1 H, s, H-4′), 4.09 (1 H, d, *J* 14.9, NCH_2Ph), 4.22 (1 H, br s, H-1″), 4.82 (1 H, d, *J* 15.0, NCH_2Ph), 4.86 (1 H, d, *J* 8.7, NH), 4.91 (1 H, d, *J* 12.3, OCH_2Ph), 5.09 (1 H, d, *J* 12.3, OCH_2Ph) and 7.19–7.37 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 19.8 (q, C-2″), 45.5 (d, C-1″), 45.7 (t, NCH$_2$Ph), 52.8 (q, OCH_3), 53.2 (d, C-4′), 60.6 (d, C-3′), 67.3 (t, OCH$_2$Ph), 128.3, 128.4, 128.6, 128.8, 129.0, 129.2 (6 d, Ph), 135.2, 136.6 (2 s, *ipso*-Ph), 156.4 (s, NHCO), 166.5 (s, C-2′) and 171.0 (s, C-1); *m*/*z* (EI, 70 eV) 396 (14%, M^+) and 91 (100, $C_7H_7^+$).

(3*R*,4*R*,1′*S*)-4-Acetoxy-1-benzyl-3-[1-(benzyloxycarbonyl-amino)ethyl]azetidin-2-one 36

To a solution of carboxylic acid **34** (1.30 g, 3.40 mmol) in DMF (70 mL) were added at 70 °C in 10 portions within 1 h $Pb(OAc)_4$ (10.2 g, 23.0 mmol) and HOAc (27 mL). The reaction was terminated by addition of H_2O (140 mL). The mixture was extracted with Et_2O (3 × 50 mL) and the organic layers were washed with saturated $NaHCO_3$ solution (3 × 30 mL) and brine (30 mL), dried ($MgSO_4$), concentrated and filtrated through a short SiO_2 pad. Purification by MPLC (PE–EA 90 : 10) yielded the acetoxy-substituted β-lactam **36** (1.12 g, 83%) as a colourless oil: mp 89–91 °C; $[a]_D^{20}$ +15 (*c* 1, $CHCl_3$) (Found: C, 66.55; H, 6.1; N, 7.05; $C_{22}H_{24}N_2O_5$ requires C, 66.65; H, 6.1; N, 7.05%); ν_{max} (KBr)/cm^{-1} 3280 (NH), 3000 (CH), 2960 (CH), 1760 (C=O), 1680 (C=O, amide I), 1535 (NHCO, amide II), 740 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 1.27 (3 H, d, *J* 6.9, H-2′), 1.97 (3 H, s, $COCH_3$), 3.28 (1 H, d, *J* 3.3, H-3), 4.20 (1 H, d, *J* 15.1, NCH_2Ph), 4.26 (1 H, m, H-1′), 4.52 (1 H, d, *J* 15.1, NCH_2Ph), 4.96 (1 H, d, *J* 12.2, OCH_2Ph), 5.08 (1 H, d, *J* 11.8, OCH_2Ph), 5.71 (1 H, s, H-4) and 7.23–7.38 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 19.0 (q, C-2′), 20.6 (q, COCH$_3$), 44.0 (d, C-1′), 44.9 (t, NCH$_2$Ph), 62.8 (d, C-3), 66.8 (t, OCH$_2$Ph), 79.1 (d, C-4), 127.8, 128.1, 128.1, 128.3, 128.5, 128.7 (6 d, Ph), 135.6, 136.3 (2 s, *ipso*-Ph), 155.8 (s, NHCO), 165.5 (s, C-2) and 170.7 (s, COCH$_3$); *m*/*z* (FAB) 419 (4%, $[M + Na]^+$), 397 (7, $[M + H]^+$), 337 (100, $[M - C_2H_3O_2]^+$) and 91 (58, $C_7H_7^+$).

(3*R*,4*R*,1′*S*)-4-Acetoxy-1-benzyl-3-[1-(benzyloxycarbonyl-amino)-2-methylpropyl]azetidine-2-one 37

Carboxylic acid **35** (410 mg, 1.00 mmol) was dissolved in DMF (20 mL) and reacted with $Pb(OAc)_4$ (3.13 g, 7.07 mmol) and HOAc (8 mL) as described for compound **36**, yielding the acetoxy-substituted β-lactam **37** (348 mg, 82%) as a colourless oil: $[a]_D^{20}$ +35 (*c* 1, $CHCl_3$) (Found: C, 67.75; H, 6.7; N, 6.6; $C_{24}H_{28}N_2O_5$ requires C, 67.9; H, 6.65; N, 6.6%); ν_{max} (film)/cm^{-1} 3334 (NH), 3065 (CH), 3034 (CH), 2966 (CH), 1768 (C=O), 1729 (C=O), 1712 (C=O, amide I), 1538 (NHCO, amide II), 1236 (CO), 736 and 698 (Ph); δ_H (500 MHz; $CDCl_3$) 0.95, 0.99 [6 H, 2 d, *J* 6.7, CH(CH_3)$_2$], 1.93 (1 H, dsept, *J* 7.3 and 6.7, H-2′), 1.94 (3 H, s, $COCH_3$), 3.41 (1 H, d, *J* 3.3, H-3), 3.97 (1 H, ddd, *J* 10.4, 7.6 and 3.3, H-1′), 4.25 (1 H, d, *J* 15.2, NCH_2Ph), 4.43 (1 H, d, *J* 15.2, NCH_2Ph), 4.75 (1 H, d, *J* 10.2, NH), 4.96 (1 H, d, *J* 12.3, OCH_2Ph), 5.10 (1 H, d, *J* 12.3, OCH_2Ph), 5.72 (1 H, d, *J* 1.3, H-4) and 7.20–7.38 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 18.6, 19.6 [2 q, CH(CH$_3$)$_2$], 20.0 (q, COCH$_3$), 31.7 (d, C-2′), 45.0 (t, NCH$_2$Ph), 54.0 (d, C-1′), 60.3 (d, C-3), 66.9 (t, OCH$_2$Ph), 79.3 (d, C-4), 127.6, 127.9, 128.1, 128.2, 128.5, 128.7 (6 d, Ph), 135.8, 136.4 (2 s, *ipso*-Ph), 156.5 (s, NHCO), 165.7 (s, C-2) and 170.5 (s, COCH$_3$); *m*/*z* (FAB) 447 (100%, $[M + Na]^+$), 387 (100, $[M + Na - C_2H_3O_2]^+$) and 91 (32, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methyl-propyl]-2-oxoazetidine-4-carbaldehyde 38

Ozone was passed for 2 min through a cooled (−78 °C) solution of β-lactam **29a** (797 mg, 1.70 mmol) in CH_2Cl_2 (40 mL). Me_2S (311 mg, 5.00 mmol) was added to the deep-blue solution and stirring was continued for 30 min at −78 °C and 1 h at room temperature. The solvents were removed on a rotary evaporator and the crude product was purified by chromatography (PE–EA 3 : 1) to yield carbaldehyde **38** (402 mg, 60%) as a colourless oil: ν_{max} (film)/cm^{-1} 3321 (NH), 3064 (CH), 3032 (CH), 2962 (CH), 1731 (C=O), 1538 (NHCO, amide II), 1239 (CO), 736 and 697 (Ph); δ_H (500 MHz; $CDCl_3$) 0.98, 1.01 [6 H, 2 d, *J* 6.8, CH(CH_3)$_2$], 1.97 (1 H, m, H-2′), 3.19 (1 H, dd, *J* 7.0, 2.2, H-3), 3.74 (1 H, m, H-1′), 3.85 (1 H, d, *J* 1.9, H-4), 4.22 (1 H, d, *J* 14.8, NCH_2Ph), 4.69 (1 H, d, *J* 14.8, NCH_2Ph), 4.88 (1 H, d, *J* 10.2, NH), 4.96 (1 H, d, *J* 12.1, OCH_2Ph), 5.13 (1 H, d, *J* 12.4, OCH_2Ph), 7.13–7.40 (10 H, m, Ph) and 9.57 (1 H, d, *J* 1.7, CHO); δ_C (126 MHz; $CDCl_3$) 19.1, 19.8 [2 q, CH(CH$_3$)$_2$], 31.8 (d, C-2′), 45.9 (t, NCH$_2$Ph), 55.3 (d, C-1′), 55.4 (d, C-3), 59.8 (d, C-4), 67.1 (t, OCH$_2$Ph), 128.2, 128.3, 128.4, 128.6, 128.7, 128.9 (6 d, Ph), 134.6, 136.1 (2 s, *ipso*-Ph), 156.7 (s, NHCO), 165.3 (s, C-2) and 197.8 (d, CHO); *m*/*z* (EI, 70 eV) 394.1892; $^{12}C_{23}{}^{1}H_{26}{}^{14}N_2{}^{16}O_4$ requires 394.1893; *m*/*z* (EI, 70 eV) 394 (5%, M^+) and 91 (100, $C_7H_7^+$).

(3*R*,4*S*,1′*S*)-1-Benzyl-3-[1-(benzyloxycarbonylamino)-2-methyl-propyl]-4-dimethoxymethylazetidin-2-one 39

Ozone was passed for 2 min through a cooled (−78 °C) solution of β-lactam **29a** (220 mg, 470 μmol) in MeOH (8 mL). Me_2S (51 mg, 0.82 mmol), trimethyl orthoformate (578 mg, 5.45 mmol) and 1 M HCl in MeOH (0.8 mL) were added to the deep-blue solution and stirring was continued for 12 min with warming to room temperature. The solvents were removed on a rotary evaporator and the crude product was triturated in saturated $NaHCO_3$ solution (50 mL). The mixture was extracted with Et_2O (3 × 50 mL) and the organic layers were dried ($MgSO_4$), concentrated and purified by chromatography (PE–EA 3 : 1) to yield acetal **39** (137 mg, 66%) as a colourless oil: $[a]_D^{20}$ +35 (*c* 1, $CHCl_3$) (Found: C, 68.15; H, 7.25; N, 6.35; $C_{25}H_{32}N_2O_5$ requires C, 68.15; H, 7.3; N, 6.35%); ν_{max} (film)/cm^{-1} 3315 (NH), 3054 (CH), 2962 (CH), 2834 (OCH_3), 1745 (C=O), 1719 (C=O, amide I), 1509 (NHCO, amide II), 1265 (CO), 736 and 680 (Ph); δ_H (500 MHz; $CDCl_3$) 0.96 [3 H, d, *J* 6.8, CH(CH_3)$_2$], 1.01 [3 H, d, *J* 6.7, CH(CH_3)$_2$], 1.96 (1 H, sept, *J* 6.9, H-2′), 3.24 (3 H, s, OCH_3), 3.30 (1 H, dd, *J* 2.5 and 2.5, H-3), 3.31 (3 H, s, OCH_3), 3.47 (1 H, dd, *J* 6.1 and 2.3, H-4), 3.77 (1 H, ddq, *J* 10.3, 7.6 and 2.8, H-1′), 4.12 (1 H, d, *J* 15.0, NCH_2Ph), 4.30 (1 H, d, *J* 6.1, H-1″), 4.57 (1 H, d, *J* 15.0, NCH_2Ph), 4.77 (1 H, d, *J* 10.2, NH), 4.91 (1 H, d, *J* 12.3, OCH_2-Ph), 5.11 (1 H, d, *J* 12.3, OCH_2Ph) and 7.16–7.39 (10 H, m, Ph); δ_C (126 MHz; $CDCl_3$) 18.9, 19.8 [2 q, CH(CH$_3$)$_2$], 31.7 (d, C-2′), 45.2 (t, NCH$_2$Ph), 53.6 (d, C-3), 54.1 (2 q, OCH_3), 54.3 (d, C-4), 55.0 (d, C-1′), 66.7 (t, OCH$_2$Ph), 104.4 (d, C-1″), 127.8, 128.1, 128.2, 128.5, 128.6, 128.9 (6 d, Ph), 136.2, 136.4 (2 s, *ipso*-Ph), 156.6 (s, NHCO) and 167.2 (s, C-2); *m*/*z* (EI, 70 eV) 440 (1%, M^+), 91 (100, $C_7H_7^+$) and 75 (65, $C_3H_7O_2^+$).

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