Cross-metathesis of unsaturated α-amino acid derivatives

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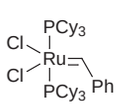
Cross-metathesis of homoallylglycine derivatives with aryl- and alkyl-substituted alkenes using the ruthenium catalyst $(Cy_3P)_2Cl_2Ru{=}CHPh$ 1 has been achieved in 43–55 and 55–66% yield respectively. Allylglycine, vinylglycine and dehydroalanine derivatives have also been examined. Whilst cross-metathesis of allylglycine derivatives with alkyl-substituted alkenes using catalyst 1 may be regarded as a synthetically useful procedure, cross-metathesis reactions of vinylglycine and dehydroalanine derivatives using catalyst 1 are non-viable. Attachment of FmocHagOH 13 to a capped Wang resin, cross-metathesis with dodec-1-ene, and product removal from the resin gives the cross-metathesis product in 74% yield based on FmocHagOH.

The ring-closing metathesis reaction has been rapidly accepted into mainstream organic synthesis[1] after pioneering studies indicated its potential earlier this decade.[2] In contrast, the entropically more challenging but equally promising cross-metathesis reaction has received much less attention from synthetic chemists and has been the subject of a relatively small number of investigations to date.[1b,3]

Cross-metathesis reactions using well-defined catalysts† began to receive more attention in 1993 when it was demonstrated that a tungsten carbene complex catalysed the cross-metathesis of allyl methyl sulfide with unfunctionalised alkenes.[4] Later that year the highly active but air-sensitive Schrock molybdenum carbene catalyst was used for cross-metathesis reactions between styrene and several functionalised terminal alkenes.[5] The Schrock catalyst has subsequently been shown to successfully cross-metathesise acrylonitrile,[6] allylsilane[7] and allylstannanes[8] with a variety of alkenes. Application of the styrene/molybdenum cross-metathesis system to the elaboration of homoallylic silyl ethers[9] and β-lactams[10] has also been reported.

The development of the benzylidene ruthenium catalyst, $(Cy_3P)_2Cl_2Ru{=}CHPh$ **1**[11] by Grubbs in 1995 resulted in the



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application of ruthenium catalysts in cross-metathesis reactions. This catalyst benefits from the same impressive tolerance of air and moisture, and the same stability towards functional groups as its predecessor $(Cy_3P)_2Cl_2Ru{=}CH\text{-}CH{=}CPh_2$, but in addition gives much improved initiation rates and is more easily prepared. The first report on the use of catalyst **1** in cross-metathesis reactions was towards the end of 1996.[12] This report was also noteworthy for its use of polymer-bound alkenes: tritylpolystyrene-bound *N*-Boc-*N*-allylglycinol was cross-metathesised with both unfunctionalised alkenes and unsaturated esters. The polymer-bound approach was later extended to an immobilised allylsilane.[13]

In view of the biological role of α-amino acids and their many uses in several branches of science, we recently initiated a programme designed to study the potential of the cross-metathesis reaction for the elaboration of α-amino acids. This paper describes the results of this study and compares them with results reported by other groups during the course of our study. Some of the results described herein have been the subject of a preliminary communication.[14]

Results and discussion

We decided to begin our investigation into the cross-metathesis reaction of unsaturated α-amino acids by exploring the reactivity of the amino acid homoallylglycine **5**. Homoallylglycine was chosen since its double bond is some distance from the amino acid moiety and it was anticipated that any reduction in metathesis reactivity that may arise due to the steric bulk, co-ordinating ability or electron withdrawing properties of the α-amino acid moiety would be reduced by separation of this group from the double bond.

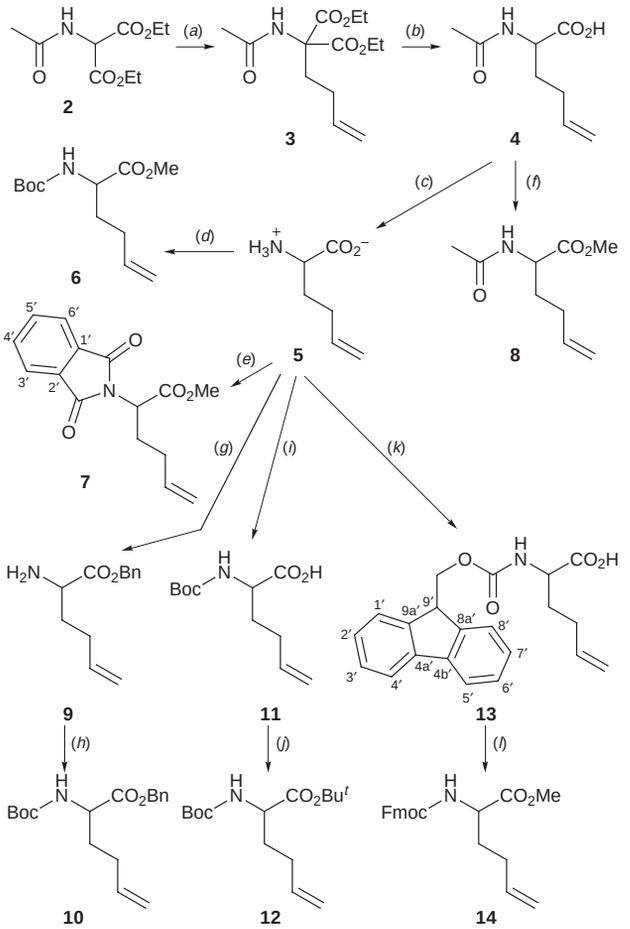
Homoallylglycine (2-aminohex-5-enoic acid) (Hag) **5** was readily prepared in multigram quantities from commercially available diethyl acetamidomalonate **2** (Scheme 1). Deprotonation of **2** and addition of 4-bromobut-1-ene to the anion generated to give **3**, and hydrolysis and decarboxylation of **3** to give AcHagOH **4** proceeded smoothly following a literature procedure.[15] Removal of the acetyl protecting group from **4** and neutralisation of the resulting hydrochloride salt with propene oxide gave unprotected homoallylglycine **5** in good yield.

We decided at the outset of this project that we would only use experimental conditions for cross-metathesis reactions that were relatively user-friendly. We thus confined ourselves to the ruthenium catalyst **1**, choosing not to investigate the chemistry of the more active but less stable molybdenum Schrock carbene which needs to be handled under glove-box conditions. Catalyst **1** was prepared according to a literature procedure[11] which we found readily gave gram quantities of the desired ruthenium benzylidene.

Initially, to ensure that the amino acid moiety of homoallylglycine **5** was tolerated by the ruthenium catalyst **1**, it was decided to Boc protect the amine group and protect the acid as its methyl ester. The compatibility of these protecting groups with the ruthenium vinylalkylidene predecessor to **1** had already been established for the ring-closing metathesis of α-amino acid substrates.[16] Thus homoallylglycine **5** was treated with potassium hydrogen carbonate and di-*tert*-butyl dicarbonate to yield BocHagOK, which was then methylated with iodomethane to give the required BocHagOMe **6**.

BocHagOMe **6** was reacted with 2 equiv. of styrene in the presence of the ruthenium catalyst **1** using a variety of solvents, temperatures, reaction times, catalyst loadings and BocHagOMe concentrations. The yields of the cross-metathesis product **15** were also measured from a reaction performed in a glove

† Strictly, this class of compounds should be referred to as 'initiators' or 'catalyst precursors'.



Scheme 1 *Reagents and conditions*: (*a*) i, NaH, DMF ii, CH_2=CH-CH_2CH_2Br (73%); (*b*) i, NaOH, H_2O–EtOH ii, 2 M HCl (82%); (*c*) i, aq. NaOH ii, 4 M HCl iii, propene oxide, EtOH (85%); (*d*) i, $KHCO_3$, $(Boc)_2O$, dioxane–H_2O ii, MeI, DMF (73%); (*e*) i, phthalic anhydride ii, $SOCl_2$, MeOH (88%); (*f*) $KHCO_3$, MeI, DMF (73%); (*g*) i, *p*-TsOH, TsCl, BnOH ii, aq. Na_2CO_3 (49%); (*h*) $(Boc)_2O$, dioxane–H_2O (95%); (*i*) 0.6 M NaOH, Bu′OH, $(Boc)_2O$ ii, $KHSO_4$ (72%); (*j*) $Cl_3CC(=NH)OBu'$, CH_2Cl_2–hexane, $F_3B{\cdot}OEt_2$ (81%); (*k*) i, Fmoc-ONSu, $NaHCO_3$, acetone–H_2O ii, conc. HCl (77%); (*l*) $KHCO_3$, MeI, DMF (77%)

box under nitrogen, and from reactions carried out using Schlenk line techniques under both a static pressure and a steady stream of both nitrogen and argon. Interestingly there was no advantage to working in the glove box or under argon and, more significantly, changing the nitrogen atmosphere from a static pressure (*ca.* 1 atm) to a steady stream across the reaction mixture led to a significant yield enhancement. The optimum conditions for the cross-metathesis reaction between BocHagOMe **6** and styrene were found to involve stirring a 0.25 M solution of **6** in dichloroethane with 2 equiv. of styrene and 5 mol% of catalyst **1** at room temperature with a steady stream of nitrogen blowing across the top of the reaction mixture for 30 h. These conditions gave a 52% isolated yield of the novel amino acid **15** (based on BocHagOMe **6**) and a 40% yield of the BocHagOMe self-metathesis product **16** (also based on **6**) (Table 1, entry 1). The cross-metathesis product **15** was found to be predominantly the *trans*-isomer (*trans* : *cis* = 19 : 1) whilst the self-metathesis product **16** was a complex mixture of isomers.

Once the optimum conditions for the cross-metathesis reaction of BocHagOMe with 2 equiv. of styrene had been determined, the effect of altering the amino acid protecting groups was explored.

To start with, *N*-(phthaloyl)homoallylglycine methyl ester **7** [methyl 2-(phthalimido)hex-5-enoate], which does not have an acidic carbamate or amide hydrogen, and *N*-(acetyl)homoallylglycine methyl ester **8**, containing the sterically smaller acetyl group, were prepared using standard protecting group procedures. The cross-metathesis reactions of PhthHagOMe **7** and AcHagOMe **8** with styrene were then performed using the optimised conditions outlined above. The reaction of **7** with styrene gave cross-metathesis product **17** and self-metathesis product **18** in very similar yields (Table 1, entry 2) to those recorded for the products from the BocHagOMe reaction, implying that the acidic carbamate hydrogen in BocHagOMe does not affect the cross-metathesis reaction. Compared with the other substrates, the reaction with AcHagOMe **8** afforded a slightly lower yield of the cross-metathesis product **19** and slightly more of the unwanted self-metathesis product **20** (Table 1, entry 3).

The protection of the acid moiety of homoallylglycine was investigated next. It was decided to determine whether protecting the acid group of Hag as benzyl and *tert*-butyl esters, which are widely used due to their ease of removal *via* hydrogenolysis and TFA cleavage respectively, was compatible with the cross-metathesis reaction. Thus BocHagOBn **10** and BocHagOBu′ **12** were synthesised *via* intermediates **9** and **11** respectively using standard protecting group chemistry and subjected to identical conditions to those used for previous cross-metathesis reactions. The cross-metathesis products **21** and **23** and the self-metathesis products **22** and **24** were obtained in almost identical yields to those recorded for the products obtained using BocHagOMe (Table 1, entries 4 and 5), and it was thus concluded that the cross-metathesis reactions of *N*-(Boc) homoallylglycines with styrene work equally well for the *tert*-butyl, benzyl and methyl ester.

Having established the cross-metathesis reaction of protected homoallylglycines with styrene, the focus of our investigations turned towards aliphatic alkenes. In order to determine whether the cross-metathesis reaction of homoallylglycine could also be used to introduce alkyl groups into the amino acid side-chain, BocHagOMe **6** was reacted with hex-1-ene using our standard conditions.

The yields of the cross-metathesis product **25** and the self-metathesis product **16** were almost identical to those observed in the analogous reaction of BocHagOMe **6** with styrene (Table 1, entry 6). When the aliphatic alkene was changed from hex-1-ene to oct-1-ene, however, there was a significant improvement in the yield of the cross-metathesis product. Thus the desired cross-metathesis product **26** was obtained in 66% yield whilst the undesired self-metathesis product **16** was isolated in 28% yield (Table 1, entry 7). As with the earlier reactions involving styrene, the yields of the cross-metathesis product **27** and the self-metathesis product **24** obtained using BocHagOBu′ **12** were very similar to those observed with the analogous methyl ester **6** (Table 1, entry 8). The lower yield observed for the reaction with hex-1-ene compared with those using oct-1-ene, was attributed to evaporation of the more volatile hex-1-ene from the reaction mixture. Cross-metathesis products **25**–**27** were predominantly *trans* (*trans* : *cis* = 4 : 1).

In order to confirm that the commonly used Fmoc (fluoren-9-ylmethoxycarbonyl) protecting group was also compatible with the cross-metathesis reaction, FmocHagOMe **14** was synthesised *via* acid **13**. Reaction of FmocHagOMe **14** with oct-1-ene yielded the cross-metathesis product **28** and the self-metathesis product **29** in comparable yields (Table 1, entry 9) to those obtained from the reaction of BocHagOMe **6** with oct-1-ene. The unprotected acid FmocHagOH **13** was also found to be a suitable substrate for the ruthenium-catalysed cross-metathesis reaction with oct-1-ene. In this case, however, the purification of the metathesis products proved a little more difficult, resulting in a cross-metathesis product **30** contaminated with 6% starting material and a relatively low isolated yield of the self-metathesis product **31** (Table 1, entry 10).

Having determined conditions for cross-metathesis of homoallylglycines, we turned our attention to more challenging unsaturated amino acids *i.e.* those with the double bond closer to the α-amino acid functionality. We thus synthesised the

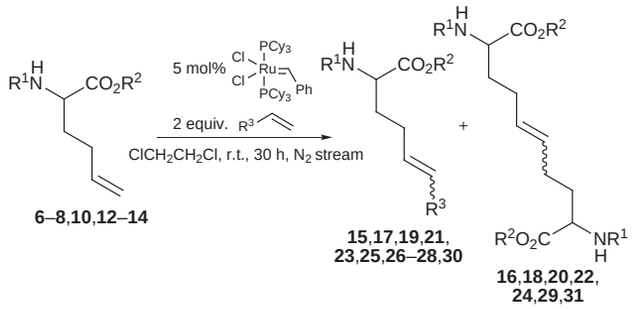


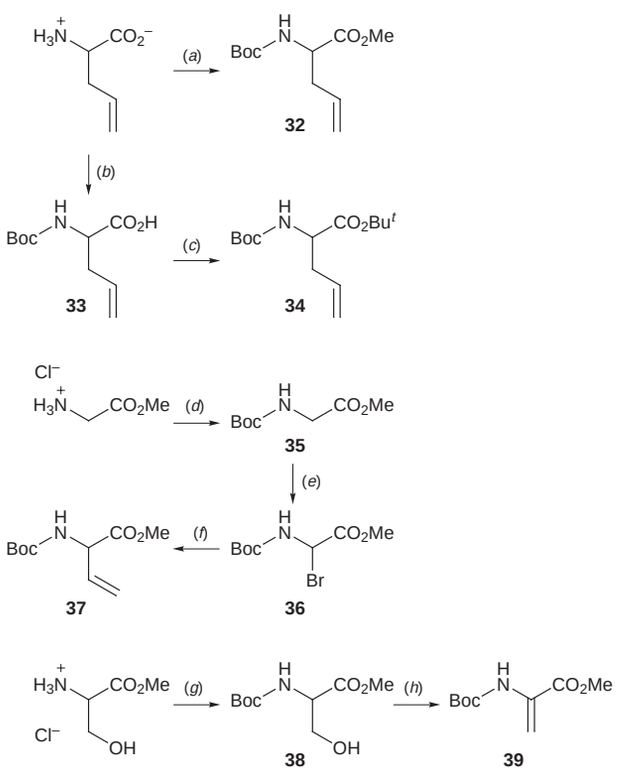
Table 1 Cross-metathesis of homoallylglycine derivatives with styrene, hex-1-ene and oct-1-ene

Entry	Substrate	R^1	R^2	Alkene R^3	Cross metathesis product	Isolated yield (%)[a]	Self metathesis product	Isolated yield (%)[a]
1	**6**	Boc	Me	Ph	**15**	52	**16**	40
2	**7**	Phth	Me	Ph	**17**	55	**18**	35
3	**8**	Ac	Me	Ph	**19**	43	**20**	48
4	**10**	Boc	$PhCH_2$	Ph	**21**	53	**22**	44
5	**12**	Boc	Bu^t	Ph	**23**	55	**24**	45
6	**6**	Boc	Me	Bu^n	**25**	55	**16**	43
7	**6**	Boc	Me	Hex	**26**	66	**16**	28
8	**12**	Boc	Bu^t	Hex	**27**	63	**24**	28
9	**14**	Fmoc	Me	Hex	**28**	58	**29**	25
10	**13**	Fmoc	H	Hex	**30**	58[b]	**31**	18

[a] Based on amino acid substrate. [b] Product contaminated with 6% starting material.

allylglycine derivative **32**, the vinylglycine derivative **37** and the dehydroalanine derivative **39**. These, together with the homoallylglycine derivative **6** form a series of identically protected unsaturated amino acids.

N-(Boc)allylglycine methyl ester **32** was prepared from commercially available allylglycine using the same procedure as for the synthesis of the analogous homoallylglycine **6** (Scheme 2). The vinylglycine derivative **37** was prepared in three steps



Scheme 2 *Reagents and conditions*: (*a*) i, $KHCO_3$, $(Boc)_2O$, 1,4-dioxane–H_2O ii, MeI, DMF (66%); (*b*) i, 0.6 M NaOH, Bu′OH, $(Boc)_2O$ ii, aq. NH_4Cl (94%); (*c*) $Cl_3CC(=NH)OBu^t$, CH_2Cl_2–hexane, $F_3B{\cdot}OEt_2$ (91%); (*d*) $NaHCO_3$, $(Boc)_2O$, NaCl, $CHCl_3$–H_2O (99%); (*e*) NBS, CCl_4, *hν* (99%); (*f*) i, 2.2 equiv. CH_2=CHMgBr, THF ii, 1 M citric acid (20%); (*g*) i, $(Boc)_2O$, py, CH_2Cl_2 ii, Et_3N (94%); (*h*) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide, $CHCl_3$, cat. CuCl (76%)

from glycine methyl ester hydrochloride, following a literature procedure for the synthesis of *N*-(Boc)vinylglycine *tert*-butyl ester.[17] Protection of the amine of the glycine methyl ester using sodium hydrogen carbonate and di-*tert*-butyl dicarbonate gave the fully protected glycine **35**. Bromination of **35** proceeded smoothly to provide **36** but, in our hands, subsequent addition of vinylmagnesium bromide to **36** proved to be a poor-yielding step. Nevertheless it proved possible to produce sufficient quantities of the desired vinylglycine derivative **37** for testing in the cross-metathesis reaction. The required dehydroalanine derivative **39** was prepared from serine methyl ester hydrochloride. Amine protection gave alcohol **38** which was subsequently dehydrated to give **39**.

The cross-metathesis reactions of the series of unsaturated amino acids—homoallylglycine **6**, allylglycine **32**, vinylglycine **37** and dehydroalanine **39**—were examined under identical conditions. The reaction between homoallylglycine **6** and oct-1-ene is described above, but for ease of comparison, this experiment (which gave a 66% isolated yield of cross-metathesis product **26** and a 28% yield of self-metathesis product **16**) is also included in Table 2 (entry 1).

The first experiment conducted on allylglycine **32** was a cross-metathesis reaction with styrene. Disappointingly, this reaction gave a very low yield of the desired cross-metathesis product **40**, which was inseparable from unreacted starting material, although it did prove possible to isolate the self-metathesis product **41** (Table 2, entry 2). The reaction between allylglycine **32** and oct-1-ene proved to be more successful, however, and the cross-metathesis product **42** was isolated in 45% yield and the self-metathesis product **41** in 17% yield. It also proved possible to recover 31% of the starting material (Table 2, entry 3). Similarly a cross-metathesis reaction between oct-1-ene and the *tert*-butyl ester allylglycine **34** (prepared from allylglycine in two steps *via* the acid **33**), gave a 49% isolated yield of cross-metathesis product **43**, a 16% yield of self-metathesis product **44** and a recovered starting material yield of 33% (Table 2, entry 4). Thus, although allylglycines are clearly less reactive than homoallylglycines, the cross-metathesis reaction between allylglycine and alkyl-substituted alkenes under ruthenium catalysis should prove to be a synthetically viable reaction. In fact, two successful cross-reactions of an allylglycine derivative have recently been reported.[18]

Changing the amino acid substrate from allylglycine to

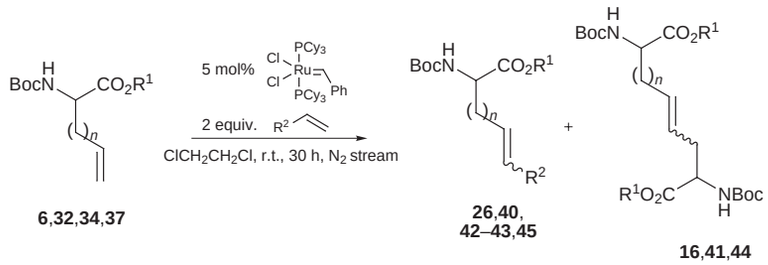


Table 2 Cross-metathesis of homoallylglycine, allylglycine and vinylglycine derivatives with oct-1-ene and styrene

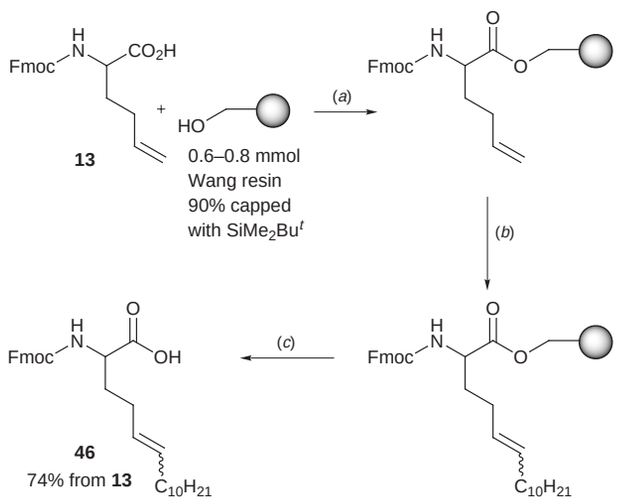
Entry	Substrate	R^1	*n*	Alkene R^2	Cross metathesis product	Isolated yield (%)[a]	Self metathesis product	Isolated yield (%)[a]	Substrate yield (%)
1	**6**	Me	2	Hex	**26**	66	**16**	28	0
2	**32**	Me	1	Ph	**40**	(15)[b]	**41**	21	(52)[b]
3	**32**	Me	1	Hex	**42**	45	**41**	17	31
4	**34**	Bu^t	1	Hex	**43**	49	**44**	16	33
5	**37**	Me	0	Hex	**45**	7	—	—	69

[a] Based on amino acid substrate. [b] Yields in parentheses were estimated from the ^{1}H NMR spectrum of a mixture of **40** and recovered substrate **32**.

vinylglycine resulted in a more serious decrease in metathesis reactivity. The reaction of vinylglycine **37** under the standard conditions gave only a 7% yield of the desired cross-metathesis product **45**. There was no observable formation of a vinylglycine self-metathesis product and the only other compound to be isolated from this reaction was recovered starting material (Table 2, entry 5). The most likely explanation for the low yield obtained for the cross-metathesis product **45** is that the sterically bulky amino acid moiety is hindering the approach of the catalytic ruthenium species to the double bond of the substrate. It is of note in this context that a previous attempt to form a five-membered ring *via* the ruthenium catalysed ring-closing metathesis reaction of a vinylglycine substrate proved unsuccessful.[19] A very high yield, however, has recently been reported for the cross-metathesis of a vinylglycine with allyltrimethylsilane using the less sterically sensitive and more active but less user-friendly molybdenum Schrock catalyst.[7b]

The reaction of the dehydroalanine derivative **39** with oct-1-ene, under identical conditions to those used for the analogous cross-metathesis reactions of vinylglycine **37**, allylglycines **32** and **34**, and homoallylglycine **6** resulted only in the isolation of unreacted starting material. A ^{1}H NMR spectrum recorded of the reaction mixture after 30 hours showed it to contain an approximately 1 : 1 mixture of dehydroalanine **39** and tetradec-7-ene, the self-metathesis product of oct-1-ene. This indicates that the absence of any amino acid metathesis products was simply due to the unreactivity of the dehydroalanine substrate rather than destruction of the catalyst.

Finally, in order to determine whether or not cross-metathesis of homoallylglycine can be performed attached to a readily-available solid support, we have conducted some preliminary experiments using Wang resins. Two initial experiments were performed using resins of 0.65 and 1.13 mmol g^{-1} loading but, disappointingly, analysis of the amino acid product after cross-metathesis with dodec-1-ene and release from the resin revealed that in each case a mixture of cross-metathesis and self-metathesis of the amino acid had been produced. As it appeared that site-isolation was not achieved on either of these resins, a sample of 0.6–0.8 mmol g^{-1} Wang resin was diluted *in extremis* by 90% capping using *tert*-butyldimethylsilyl chloride and triethylamine. Subsequent loading of FmocHagOH **13**, cross metathesis with dodec-1-ene using slightly modified conditions to those used for the solution-phase reactions described above (10% ruthenium catalyst **1**, 4 equiv. dodec-1-ene, CH_2Cl_2 at reflux, 16 h), and release of the amino acid using TFA gave a 74% yield of the cross-metathesis product **46** (Scheme 3). No amino acid self-metathesis product was observed. Thus the cross-metathesis of homoallylglycine



Scheme 3 *Reagents and conditions*: (*a*) 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide·HCl, DMAP, CH_2Cl_2; (*b*) 4 equiv. dodec-1-ene, cat. $(Cy_3P)_2Cl_2Ru{=}CHPh$, CH_2Cl_2, heat to reflux; (*c*) TFA, CH_2Cl_2

on a Wang resin is possible if site-isolation is achieved by capping of the commercially available resin. Optimisation, scope and limitation studies in this area are currently underway.

In conclusion, we have demonstrated that cross-metathesis of homoallylglycine derivatives in solution using the ruthenium catalyst **1** is a viable reaction for aryl- and alkyl-substituted alkenes. Although the efficiency of the reaction falls as the double bond is drawn closer to the amino acid head group, the cross-metathesis between allylglycines and alkyl-substituted alkenes with catalyst **1** is also a viable process. Preliminary results using Wang resins indicate that cross-metathesis of homoallylglycine on a solid support is a potentially attractive system if site-isolation can be achieved.

Experimental

Dichloromethane (DCM) and 1,4-dioxane were distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Diethyl ether, toluene and hexane were stored over sodium wire. 1,2-Dichloroethane was distilled from calcium hydride and stored over 4 Å molecular sieves. Styrene was washed sequentially with 1 M aqueous sodium hydroxide and water, dried ($MgSO_4$) and then distilled from calcium hydride. It was stored at 5 °C over molecular sieves. Triethylamine was distilled from and stored over potassium hydroxide pellets. Anhydrous methanol and *N*,*N*-dimethyl-

formamide (DMF) were purchased from Aldrich Chemical Company. Oxalyl chloride was freshly distilled at atmospheric pressure under an atmosphere of nitrogen. Sodium hydride was purchased as an oil dispersion (60% w/w), washed with hexane, decanted and filtered three times before use. Light petroleum, which refers to petroleum (bp 40–60 °C), was distilled before use. Deactivated alumina refers to Brockmann Grade IV alumina. Bis(tricyclohexylphosphine)benzylidene ruthenium dichloride **1** was prepared using a literature procedure.[11b]

Melting points, which are uncorrected, were measured using a Büchi 510 melting point apparatus. Elemental analyses were performed by the Imperial College Microanalytical Service. IR Spectra were recorded on a Mattson 5000 FTIR spectrometer. NMR Spectra were recorded in [^{2}H]chloroform (unless stated otherwise) at room temperature on JEOL GSX 270, Bruker DRX 300, Bruker DRX 400 and Bruker AM-500 spectrometers. Chemical shifts are given in ppm and coupling constants (J values) in Hz. Mass spectra were recorded on VG AutoSpec-Q and VG 70E instruments.

Diethyl 2-acetylamino-2-(but-3-enyl)malonate 3[15]

A stirred suspension of sodium hydride (2.76 g, 115 mmol) in anhydrous DMF (100 cm^3) was cooled to 0 °C, under an atmosphere of nitrogen, and a solution of diethyl acetamidomalonate (22.68 g, 105 mmol) in anhydrous DMF (100 cm^3) was then added over a period of 10 min *via* a cannula. The ice bath was removed and the reaction mixture stirred for 20 min before adding 4-bromobut-1-ene (11.8 cm^3, 116 mmol). The light brown solution was then stirred at 90 °C for 4 h before allowing to cool and concentrating *in vacuo*. The residual oil was partitioned between water (150 cm^3) and ethyl acetate (100 cm^3) and the two layers were separated. The aqueous layer was extracted with ethyl acetate (2 × 100 cm^3) and the combined organic extracts were washed with brine (150 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to yield a dark yellow oil. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 1:1) followed by recrystallisation from diethyl ether–pentane afforded the title compound **3** (20.81 g, 73%) as colourless crystals, mp 44–45 °C (lit.,[15] 39–41 °C); ν_{max}(Nujol mull)/cm^{-1} 3361vs (N–H), 1762s and 1739vs (2 × ester C=O) and 1661s (amide C=O and C=C); δ_H(270 MHz) 1.24 (6 H, t, J 7.2, 2 × OCH_2CH_3), 1.85–1.94 (2 H, m, CH_2CH_2CH=), 2.02 (3 H, s, CH_3C=O), 2.39–2.45 (2 H, m, CH_2CH_2CH=), 4.22 (4 H, q, J 7.2, 2 × OCH_2CH_3), 4.93 [1 H, ddt, J 10.2, 1.9 and 1, =C*H*H (*trans* to alkyl chain)], 5.00 [1 H, ddt, J 17.1, 1.9 and 1.6, =CH*H* (*cis* to alkyl chain)], 5.73 (1 H, ddt, J 17.1, 10.2 and 6.5, CH_2CH=) and 6.76 (1 H, s, NH); m/z (CI, NH_3) 289 (MNH_4^+, 4%), 272 (MH, 100), 156 (MH − H_2C=C=O − HCO_2Et, 36) and 82 [H_2C=CH$(CH_2)_2C\equiv$NH, 17].

2-(Acetylamino)hex-5-enoic acid 4[15]

Sodium hydroxide (2.54 g, 63.5 mmol) was added to a solution of diethyl 2-acetylamino-2-(but-3-enyl)malonate **3** (16.04 g, 59.2 mmol) in water–ethanol (1:1, 120 cm^3). After stirring the reaction mixture at reflux for 16 h it was allowed to cool and the ethanol was removed under reduced pressure. The remaining aqueous solution was washed with ethyl acetate (100 cm^3) and then acidified with 2 M hydrochloric acid (40 cm^3). The resulting cloudy aqueous mixture was extracted with ethyl acetate (3 × 100 cm^3) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to yield the title acid **4** (8.28 g, 82%) as a white solid, mp 113.5–115 °C (lit.,[15] 114–116 °C); ν_{max}(Nujol mull)/cm^{-1} 3346vs (N–H), 3100–2100br (O–H), 1716s (acid C=O), 1640w (C=C) and 1595vs (amide C=O); δ_H(270 MHz; [$^2H_6$]DMSO) 1.58–1.81 (2 H, m, CH_2CH_2CH=), 1.83 (3 H, s, CH_3CO), 1.94–2.08 (2 H, m, CH_2CH_2CH=), 4.14 (1 H, ddd, J 9, 7.6 and 5, $CHCO_2H$), 4.96 [1 H, ddt, J 10, 1.9 and 1, =C*H*H (*trans* to alkyl chain)], 5.02 [1 H, ddt, J 17.1, 1.9 and 1.6, =CH*H* (*cis* to alkyl chain)], 5.78 (1 H, ddt, J 17.1, 10 and 7, CH_2CH=), 8.11 (1 H, d, J 7.6, NH) and 12.0–12.9 (1 H, br s, CO_2H); m/z (CI, NH_3) 189 (MNH_4^+, 8%), 172 (MH, 100), 126 (MH − HCO_2H, 11) and 84 [H_2C=CH$(CH_2)_2CH$=NH_2, 30].

2-Aminohex-5-enoic acid 5

2-(Acetylamino)hex-5-enoic acid **4** (7.04 g, 41.2 mmol) was dissolved in aqueous sodium hydroxide (13.1 g, 330 mmol in 140 cm^3 of water) and the resulting solution was heated at reflux for 20 h. After allowing the mixture to cool, 4 M hydrochloric acid (100 cm^3) was added and the water was removed under reduced pressure. The residue was redissolved in water (*ca*. 200 cm^3) and concentrated *in vacuo* again to yield, after drying under vacuum overnight, a white solid. Ethanol (100 cm^3) was added to the solid and the resulting suspension was filtered, washing the insoluble sodium chloride with additional portions of ethanol (2 × 100 cm^3). The filtrates were combined, propene oxide (16.5 cm^3, 240 mmol) was added and the mixture was stirred for 20 h before concentrating *in vacuo*. Chloroform (100 cm^3) was added to the residual solid and the resulting suspension was stirred for 20 min. The solid was collected by filtration and then washed with chloroform a second time, using the same procedure. Upon filtration the title compound **5** (4.52 g, 85%) was isolated as a white powder, mp 275–276 °C (decomp.); ν_{max}(Nujol mull)/cm^{-1} 3200–2400br (N–H), 1646w (C=C) and 1584s (C=O); δ_H(270 MHz, D_2O) 1.68–1.94 (2 H, m, CH_2CH_2CH=), 2.03 (2 H, q, J 7, CH_2CH_2CH=), 3.60 (1 H, dd, J 6.7 and 5.6, $CHCO_2H$), 4.93 [1 H, dd, J 10.5 and 1, =C*H*H (*trans* to alkyl chain)], 5.00 [1 H, dd, J 17.1 and 1, =CH*H* (*cis* to alkyl chain)] and 5.74 (1 H, ddt, J 17.1, 10.5 and 7, CH_2CH=); m/z (CI, NH_3) 130 (MH^+, 100%) and 84 [H_2C=CH$(CH_2)_2CH$=NH_2, 33].

Methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 6

Potassium 2-(*tert*-butoxycarbonylamino)hex-5-enoate. 1,4-Dioxane (9 cm^3), potassium hydrogen carbonate (0.69 g, 6.9 mmol) and di-*tert*-butyl dicarbonate (1.95 g, 8.9 mmol) were added to a stirred solution of 2-aminohex-5-enoic acid **5** (0.79 g, 6.1 mmol) in water (20 cm^3). The resulting biphasic mixture was stirred for 16 h before concentrating *in vacuo*. Residual water and dioxane were removed by azeotroping with ethanol (2 × 50 cm^3) and the remaining solid was dried under vacuum (0.2 mmHg) overnight to give *potassium* 2-(tert-*butoxycarbonylamino)hex*-5-*enoate* as a white solid which was used, without further purification, in the following reaction; δ_H(270 MHz, D_2O) 1.26 (9 H, s, Bu^t), 1.44–1.59 (1 H, m, $CHHCH_2CH$=), 1.60–1.81 (1 H, m, $CHHCH_2CH$=), 1.88–2.03 (2 H, m, CH_2CH=), 3.66–3.75 (1 H, m, $CHCO_2K$), 4.86 [1 H, d, J 10.4, =C*H*H (*trans* to alkyl chain)], 4.92 [1 H, d, J 17.1, =CH*H* (*cis* to alkyl chain)] and 5.71 (1 H, ddt, J 17.1, 10.4, 6.7, CH_2CH=).

Methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 6. Iodomethane (5.5 cm^3, 88 mmol) and anhydrous DMF (30 cm^3) were added to the potassium 2-(*tert*-butoxycarbonylamino)hex-5-enoate prepared above, under an atmosphere of nitrogen. After stirring for 65 h the clear yellow solution was concentrated *in vacuo* and the residual oil was partitioned between water (15 cm^3) and DCM (15 cm^3). The two layers were separated and the aqueous phase was extracted with DCM (3 × 15 cm^3). The combined organic extracts were then washed with brine (15 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to yield a yellow oil. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 4:1) gave the title compound **6** (1.09 g, 73%) as a colourless oil [Found: m/z (MH^+) 244.1539; $C_{12}H_{22}NO_4$ requires 244.1549]; ν_{max}(neat)/cm^{-1} 3355s (N–H), 1739s (ester C=O), 1717vs (carbamate C=O) and 1642w (C=C); δ_H(270 MHz) 1.40 (9 H, s, Bu^t), 1.61–1.74 (1 H, m, $CHHCH_2CH$=), 1.80–1.93 (1 H, m, $CHHCH_2CH$=), 2.03–2.13 (2 H, m, CH_2CH_2CH=), 3.69 (3 H, s, OCH_3), 4.28 (1 H, br q, $CHCO_2Me$), 4.96 [1 H, ddt, J 10.4, 1.6 and 1, =C*H*H (*trans* to alkyl chain)], 5.01 [1 H, dq, J 17.1 and 1.6, =CH*H* (*cis* to alkyl chain)], 5.07 (1 H, br d, NH) and 5.75 (1 H, ddt, J 17.1, 10.4 and 6.7, CH_2CH=); m/z (CI, NH_3) 387 [$(2M + H)^+$ − Me_2C=CH_2 − CO_2, 30%], 327 [$(2M + H)^+$ − Me_2C=CH_2 − CO_2 −

HCO_2Me, 12], 261 (MNH_4, 43), 244 (MH, 53), 205 (MNH_4 − $Me_2C{=}CH_2$, 100), 188 (MH − $Me_2C{=}CH_2$, 35), 144 (MH − $Me_2C{=}CH_2$ − CO_2, 76) and 84 [$CH_2{=}CH(CH_2)_2CH{=}NH_2$, 24].

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 6 with styrene

A solution of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate **6** (122 mg, 0.50 mmol) and styrene (0.114 cm^3, 1.00 mmol) in 1,2-dichloroethane (2 cm^3) was degassed by three continuous freeze–pump–thaw cycles and then put under an atmosphere of nitrogen. The nitrogen-saturated solution was then added, *via* a cannula, to a nitrogen-filled Schlenk tube containing solid $Cl_2(PCy_3)_2Ru{=}CHPh$ **1** (21 mg, 0.026 mmol). After stirring under a steady stream of nitrogen for 30 h the resulting red solution was concentrated *in vacuo*. The residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight under air to effect decomposition of the catalyst. Removal of the diethyl ether *in vacuo* followed by column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–4 : 1–1 : 2 gradient elution) yielded *trans*-stilbene (10 mg, 11%) and *methyl* 2-tert-*butoxycarbonylamino*-6-*phenylhex*-5-*enoate* **15** (84 mg, 52%, *trans* : *cis* = 19 : 1) as white solids, and *dimethyl* 2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **16** (46 mg, 40%, mixture of *cis*- and *trans*-isomers) as a colourless gum. Crystallisation from pentane afforded an isolated sample of *dimethyl* trans-2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* as colourless needles.

Methyl 2-*tert*-butoxycarbonylamino-6-phenylhex-5-enoate 15. Mp 68–69 °C (from pentane) (Found: C, 67.55; H, 7.6; N, 4.3. $C_{18}H_{25}NO_4$ requires C, 67.69; H, 7.89; N, 4.39%); ν_{max}(Nujol mull)/cm^{-1} 3378s (N–H), 1741s (ester C=O) and 1693vs (carbamate C=O); δ_H(270 MHz, *trans*-isomer only) 1.43 (9 H, s, Bu^t), 1.75–1.91 (1 H, m, C*H*HCH_2CH=), 1.94–2.09 (1 H, m, CH*H*-CH_2CH=), 2.28 (2 H, q, *J* 7, CH_2CH=), 3.74 (3 H, s, OCH_3), 4.37 (1 H, br q, C*H*CO_2Me), 5.07 (1 H, br d, NH), 6.17 (1 H, dt, *J* 15.7 and 6.7, CH_2CH=), 6.41 (1 H, d, *J* 15.7, PhC*H*=) and 7.17–7.35 (5 H, m, Ph); $\delta_C\{^1H\}$ (67.9 MHz, *trans*-isomer only) 28.3 [C(CH_3)$_3$], 28.8 (C-4), 32.5 (C-3), 52.2 (OCH_3), 53.1 (C-2), 79.9 [$C(CH_3)_3$], 126.0 (C_{ortho}), 127.1 (C_{para}), 128.5 (C_{meta}), 128.7 (C-5), 131.0 (C-6), 137.4 (C_{ipso}), 155.3 (OCONH) and 173.2 (C-1); *m*/*z* (CI, NH_3) 337 (MNH_4^+, 16%), 320 (MH, 8), 281 (MNH_4 − $Me_2C{=}CH_2$, 65), 263 (MNH_4 − $Me_2C{=}CH_2$ − H_2O, 41), 220 (MH − $Me_2C{=}CH_2$ − CO_2, 63) and 128 (MH − CO_2 − $PhCH_3$ − $Me_2C{=}CH_2$, 100).

Dimethyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 16. (Found: C, 57.7; H, 8.1; N, 5.9. $C_{22}H_{38}N_2O_8$ requires C, 57.63; H, 8.35; N, 6.11%); ν_{max}(neat)/cm^{-1} 3364br (N–H), 1746s (ester C=O) and 1714vs (carbamate C=O); δ_H(270 MHz) 1.43 (18 H, s, 2 × Bu^t), 1.59–1.75 (2 H, m, 2 × C*H*HCH_2CH=), 1.75–1.91 (2 H, m, 2 × CH*H*CH_2CH=), 1.97–2.13 (4 H, m, 2 × CH_2CH=), 3.72 and 3.73 (6 H, 2 × s, 2 × OCH_3, *cis*- and *trans*-isomers), 4.26 (2 H, br s, 2 × C*H*CO_2Me), 5.00 (2 H, br d, 2 × NH) and 5.35–5.42 (2 H, m, 2 × CH=); $\delta_C\{^1H\}$ (67.9 MHz) 23.2 (C-4 and C-7, *cis*-isomer), 28.3 [C-4 and C-7, *trans*-isomer, and C(CH_3)$_3$], 32.4 (C-3 and C-8), 52.1 (OCH_3), 53.1 (C-2 and C-9), 79.8 [$C(CH_3)_3$], 129.3 (C-5 and C-6, *cis*-isomer), 129.8 (C-5 and C-6, *trans*-isomer), 155.3 (OCONH) and 173.2 (C-1 and C-10); *m*/*z* (CI, NH_3) 476 (MNH_4^+, 31%), 459 (MH, 100), 403 (MH − $Me_2C{=}CH_2$, 53), 359 (MH − $Me_2C{=}CH_2$ − CO_2, 68), 303 (MH − CO_2 − 2 × $Me_2C{=}CH_2$, 66), 243 (MH − CO_2 − 2 × $Me_2C{=}CH_2$ − HCO_2Me, 31) and 170 (MH − $Me_2C{=}CH_2$ − CO_2 − $BocNHCH_2CO_2Me$, 88).

Dimethyl *trans*-2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate. Mp 106–110 °C (Found: C, 57.8; H, 8.2; N, 6.0. $C_{22}H_{38}N_2O_8$ requires C, 57.63; H, 8.35; N, 6.11%); δ_H(270 MHz) 1.43 (18 H, s, 2 × Bu^t), 1.63–1.75 (2 H, m, 2 × C*H*HCH_2CH=), 1.78–1.94 (2 H, m, 2 × CH*H*CH_2CH=), 2.00–2.13 (4 H, m, 2 × CH_2CH=), 3.72 (6 H, s, 2 × OCH_3), 4.28 (2 H, br q, 2 × C*H*CO_2Me), 5.00 (2 H, d, *J* 8.1, 2 × NH) and 5.41 (2 H, t, *J* 3.7, 2 × CH=); $\delta_C\{^1H\}$ (75.4 MHz) 28.3 [C-4, C-7 and C(CH_3)$_3$], 32.4 (C-3 and C-8), 52.2 (OCH_3), 53.0 (C-2 and C-9), 79.8 [$C(CH_3)_3$], 129.8 (C-5 and C-6), 155.3 (OCONH) and 173.3 (C-1 and C-10). IR And mass spectral data matched that reported above for the *cis–trans* mixture **16**.

Methyl 2-(phthalimido)hex-5-enoate 7

A mixture of 2-aminohex-5-enoic acid **5** (709 mg, 5.50 mmol) and phthalic anhydride (815 mg, 5.51 mmol) was stirred at 140 °C for 40 min, under an atmosphere of nitrogen. After allowing the mixture to cool, the resulting gum was dissolved in anhydrous methanol (12.5 cm^3) and then added *via* a cannula to a stirred solution of thionyl chloride (0.55 cm^3, 7.5 mmol) in methanol (7.5 cm^3), keeping both solutions under an atmosphere of nitrogen. The reaction mixture was stirred for 17 h and the methanol was then removed under reduced pressure to yield a yellow oil. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 4 : 1) gave the *title compound* **7** (1.32 g, 88%) as a colourless oil (Found: C, 65.7; H, 5.5; N, 5.1. $C_{15}H_{15}NO_4$ requires C, 65.93; H, 5.53; N, 5.13%); ν_{max}(neat)/cm^{-1} 1777s (phthalimido C=O), 1747vs (ester C=O), 1717vs (phthalimido C=O), 1641w (C=C) and 1613w (aryl C–C); δ_H(270 MHz) 2.00–2.15 (2 H, m, CH_2CH_2CH=), 2.23–2.48 (2 H, m, CH_2CH_2CH=), 3.72 (3 H, s, OCH_3), 4.87 (1 H, dd, *J* 10 and 6, C*H*CO_2Me), 4.96 [1 H, ddt, *J* 10.2, 2 and 1, =C*H*H (*trans* to alkyl chain)], 5.00 [1 H, dq, *J* 17.1 and 2, =CH*H* (*cis* to alkyl chain)], 5.75 (1 H, ddt, *J* 17.1, 10.2 and 6.7, CH_2CH=), 7.74 (2 H, dd, *J* 5.3 and 3.2, aryl 4′-H and 5′-H) and 7.86 (2 H, dd, *J* 5.3 and 3.2, aryl 3′-H and 6′-H); $\delta_C\{^1H\}$ (67.9 MHz) 27.8 (C-3), 30.2 (C-4), 51.4 (C-2), 52.6 (OCH_3), 115.9 (C-6), 123.4 (aryl C-3′ and C-6′), 131.7 (aryl C-1′ and C-2′), 134.1 (aryl C-4′ and C-5′), 136.4 (C-5), 167.5 and 169.6 (NC=O and C-1); *m*/*z* (CI, NH_3) 291 (MNH_4^+, 100%) and 274 (MH, 60).

Methyl 2-(acetylamino)hex-5-enoate 8

Iodomethane (4.0 cm^3, 64 mmol) was added to a stirred suspension of potassium hydrogen carbonate (886 mg, 8.86 mmol) and 2-(acetylamino)hex-5-enoic acid **4** (720 mg, 4.21 mmol) in anhydrous DMF (20 cm^3), under an atmosphere of nitrogen. After stirring for 65 h the cloudy yellow solution was concentrated *in vacuo*. The residue was partitioned between water (15 cm^3) and DCM (15 cm^3) and the two layers were separated. The aqueous layer was then extracted with DCM (3 × 15 cm^3) and the combined organic extracts were washed with brine (15 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to yield a white solid. Recrystallisation from diethyl ether–pentane afforded the *title compound* **8** (570 mg, 73%) as fine colourless needles, mp 59.5–60.5 °C (Found: C, 58.65; H, 7.9; N, 7.5. $C_9H_{15}NO_3$ requires C, 58.36; H, 8.16; N, 7.56%); ν_{max}(Nujol mull)/cm^{-1} 3276s (N–H), 1753vs (ester C=O) and 1648vs (amide C=O and C=C); δ_H(270 MHz) 1.72–1.84 (1 H, m, C*H*HCH_2CH=), 1.88–2.00 (1 H, m, CH*H*CH_2CH=), 2.02 (3 H, s, CH_3C=O), 2.03–2.16 (2 H, m, CH_2CH=), 3.74 (3 H, s, OCH_3), 4.59–4.68 (1 H, m, C*H*CO_2Me), 5.00 [1 H, ddt, *J* 10.2, 1.9 and 1.2, =C*H*H (*trans* to alkyl chain)], 5.04 [1 H, ddt, *J* 17.1, 1.9 and 1.6, =CH*H* (*cis* to alkyl chain)], 5.77 (1 H, ddt, *J* 17.1, 10.2 and 7, CH_2CH=) and 6.02 (1 H, br s, NH); $\delta_C\{^1H\}$ (67.9 MHz) 23.0 (CH_3C=O), 29.4 (C-4), 31.4 (C-3), 51.7 (C-2), 52.2 (OCH_3), 115.6 (C-6), 136.8 (C-5), 169.8 (HNC=O) and 173.0 (C-1); *m*/*z* (CI, NH_3) 203 (MNH_4^+, 12%), 186 (MH, 100), 126 (MH − HCO_2Me, 17) and 84 {$H_2C{=}CH$-$[CH_2]_2CH{=}NH_2$, 53}.

Cross-metathesis of methyl 2-(phthalimido)hex-5-enoate 7 with styrene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(phthalimido)hex-5-enoate **7** (136 mg, 0.50 mmol), styrene (0.114 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2Ru{=}CHPh$ **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting purple solution was concentrated *in vacuo* and the

residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–4:1–1:2 gradient elution) yielded *trans*-stilbene (24 mg, 27%) as a white solid, *methyl* 6-*phenyl*-2-(*phthalimido*)*hex*-5-*enoate* **17** (95 mg, 55%, *trans*:*cis* = 21:1) as a colourless oil and *dimethyl* 2,9-*bis*(*phthalimido*)*dec*-5-*enedioate* **18** (45 mg, 35%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

Methyl 6-phenyl-2-(phthalimido)hex-5-enoate 17. (Found: C, 72.2; H, 5.2; N, 3.8. $C_{21}H_{19}NO_4$ requires C, 72.19; H, 5.48; N, 4.01%); ν_{max}(neat)/cm^{-1} 1758s (phthalimido C=O), 1741vs (ester C=O), 1719vs (phthalimido C=O) and 1617w (aryl C=C); δ_H(270 MHz, *trans*-isomer only) 2.26 (2 H, q, *J* 6.7, CH_2CH=), 2.37–2.52 (2 H, m, C$H_2$$CH_2$CH=), 3.74 (3 H, s, OCH_3), 4.93 (1 H, dd, *J* 10.4 and 5.1, C*H*CO_2Me), 6.12 (1 H, dt, *J* 15.7 and 6.7, CH_2C*H*=), 6.34 (1 H, d, *J* 15.7, PhC*H*=), 7.12–7.25 (5 H, m, *Ph*CH=), 7.68 (2 H, dd, *J* 5.3 and 3.2, aryl 4′-H and 5′-H) and 7.82 (2 H, dd, *J* 5.3 and 3.2, aryl 3′-H and 6′-H); $\delta_C\{^1H\}$ (67.9 MHz, *trans*-isomer only) 28.1 (C-3), 29.8 (C-4), 51.6 (C-2), 52.7 (OCH_3), 123.4 (aryl C-3′ and C-6′), 125.8 (styrene C_{ortho}), 126.9 (styrene C_{para}), 128.2 (C-5), 128.3 (styrene C_{meta}), 131.3 (C-6), 131.7 (aryl C-1′ and C-2′), 134.1 (aryl C-4′ and C-5′), 137.2 (styrene C_{ipso}), 167.6 and 169.7 (NC=O and C-1); *m*/*z* (CI, NH_3) 367 (MNH_4^+, 100%), 350 (MH, 56) and 219 (MH − PhCH=$CHCH_2CH_2$, 42).

Dimethyl 2,9-bis(phthalimido)dec-5-enedioate 18. [Found: *m*/*z* (MH^+) 519.1767; $C_{28}H_{27}N_2O_8$ requires 519.1767]; ν_{max}(neat)/cm^{-1} 1773s (phthalimido C=O), 1744vs (ester C=O), 1721vs (phthalimido C=O) and 1608w (aryl C=C); δ_H(270 MHz) 1.84–2.02 (4 H, m, 2 × CH_2CH=), 2.16–2.41 (4 H, m, 2 × CH_2-CH_2CH=), 3.70 and 3.71 (6 H, 2 × s, 2 × OCH_3, *cis*- and *trans*-isomers), 4.77–4.87 (2 H, m, 2 × C*H*CO_2Me), 5.25–5.34 (2 H, m, 2 × CH=), 7.69–7.76 [4 H, m, 2 × (aryl 4′-H and 5′-H)] and 7.82–7.88 [4 H, m, 2 × (aryl 3′-H and 6′-H)]; $\delta_C\{^1H\}$ (67.9 MHz) 24.0 (C-4 and C-7, *cis*-isomer), 28.1 (C-3 and C-8), 29.1 (C-4 and C-7, *trans*-isomer), 51.5 (C-2 and C-9), 52.7 (OCH_3), 123.5 (aryl C-3′ and C-6′), 129.2 (C-5 and C-6, *cis*-isomer), 129.8 (C-5 and C-6, *trans*-isomer), 131.8 (aryl C-1′ and C-2′), 134.1 (aryl C-4′ and C-5′), 167.6 and 169.8 (NC=O, C-1 and C-10); *m*/*z* (CI, NH_3) 536 (MNH_4^+, 100%), 519 (MH, 10) and 219 (PhthNC$H_2$$CO_2$Me, 68).

Cross-metathesis of methyl 2-(acetylamino)hex-5-enoate 8 with styrene

A solution of styrene (0.114 cm^3, 1.00 mmol) in 1,2-dichloroethane (2 cm^3) was degassed by three continuous freeze–pump–thaw cycles and then put under an atmosphere of nitrogen. The nitrogen-saturated solution was then added, *via* a cannula, to a nitrogen-filled Schlenk tube containing solid methyl 2-(acetylamino)hex-5-enoate **8** (93 mg, 0.50 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol). After stirring under a steady stream of nitrogen for 30 h the resulting purple solution was concentrated *in vacuo*. The residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight under air to effect decomposition of the catalyst. Removal of the diethyl ether *in vacuo* followed by column chromatography (SiO_2; light petroleum–diethyl ether–ethyl acetate, 1:1:0–0:1:0–0:1:1–0:0:1 gradient elution) yielded *trans*-stilbene (17 mg, 19%) and *methyl* 2-*acetylamino*-6-*phenylhex*-5-*enoate* **19** (57 mg, 43%, *trans*:*cis* = 16:1) as white solids, and *dimethyl* 2,9-*bis*(*acetylamino*)*dec*-5-*enedioate* **20** (41 mg, 48%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

Methyl 2-acetylamino-6-phenylhex-5-enoate 19. Mp 46–47.5 °C (from diethyl ether) (Found: C, 68.9; H, 7.1; N, 5.3. $C_{15}H_{19}NO_3$ requires C, 68.94; H, 7.33; N, 5.36%); ν_{max}(neat)/cm^{-1} 3285s (N–H), 1746vs (ester C=O) and 1652vs (amide C=O); δ_H(270 MHz, *trans*-isomer only) 1.77–1.95 (1 H, m, C*H*HCH_2CH=), 1.97–2.13 (1 H, m, CH*H*CH_2CH=), 2.03 (3 H, s, CH_3C=O), 2.17–2.38 (2 H, m, CH_2CH=), 3.74 (3 H, s, OCH_3), 4.69 (1 H, td, *J* 7.5 and 5, C*H*CO_2Me), 6.12 (1 H, br s, NH), 6.16 (1 H, dt, *J* 15.9 and 6.7, CH_2C*H*=), 6.40 (1 H, d, *J* 15.9, PhC*H*=) and 7.17–7.35 (5 H, m, Ph); $\delta_C\{^1H\}$ (67.9 MHz, *trans*-isomer only) 23.2 (*C*H_3C=O), 28.7 (C-4), 32.1 (C-3), 51.8 (C-2), 52.4 (OCH_3), 126.0 (C_{ortho}), 127.1 (C_{para}), 128.5 (C_{meta}), 128.6 (C-5), 131.0 (C-6), 137.3 (C_{ipso}), 169.7 (HNC=O) and 172.9 (C-1); *m*/*z* (CI, NH_3) 279 (MNH_4^+, 25%), 262 (MH, 100) and 131 (MH − PhCH=$CHCH_2CH_2$, 34).

Dimethyl 2,9-bis(acetylamino)dec-5-enedioate 20. (Found: C, 56.1; H, 7.4; N, 7.9. $C_{16}H_{26}N_2O_6$ requires C, 56.13; H, 7.65; N, 8.18%); ν_{max}(neat)/cm^{-1} 3284br (N–H), 1746vs (ester C=O) and 1656vs (amide C=O); δ_H(300 MHz, [$^2H_6$]DMSO) 1.52–1.73 (4 H, m, 2 × C$H_2$$CH_2$CH=), 1.83 (6 H, s, 2 × CH_3C=O), 1.93–2.05 (4 H, m, 2 × CH_2CH=), 3.60 (6 H, s, 2 × OCH_3), 4.10–4.23 (2 H, m, 2 × C*H*CO_2Me), 5.30–5.40 (2 H, m, 2 × CH=) and 8.24 (2 H, d, *J* 7.2, 2 × NH); $\delta_C\{^1H\}$ (75.4 MHz) 23.1 (*C*H_3C=O), 23.3 (C-4 and C-7, *cis*-isomer), 28.2 (C-4 and C-7, *trans*-isomer), 32.1 (C-3 and C-8), 51.6 (C-2 and C-9, *trans*-isomer), 51.8 (C-2 and C-9, *cis*-isomer), 52.3 (OCH_3), 129.3 (C-5 and C-6, *cis*-isomer), 129.8 (C-5 and C-6, *trans*-isomer), 169.8 (HNC=O) and 173.0 (C-1 and C-10); *m*/*z* (CI, NH_3) 343 (MH^+, 100%), 212 (MH − AcNHC$H_2$$CO_2$Me, 23) and 170 (MH − H_2C=CO − AcNHC$H_2$$CO_2$Me, 9).

Benzyl 2-aminohex-5-enoate 9

A solution of *p*-toluenesulfonic acid (0.86 g, 5.0 mmol), 2-aminohex-5-enoic acid **5** (0.64 g, 5.0 mmol) and *p*-toluenesulfonyl chloride (1.15 g, 6.0 mmol) in benzyl alcohol (18 cm^3) was stirred at 80 °C for 1.5 h, under an atmosphere of nitrogen. After allowing to cool, the reaction mixture was diluted with diethyl ether (300 cm^3) and left to stand at −25 °C overnight. The white precipitate that formed was collected by filtration and then suspended in water (50 cm^3). The stirred suspension was basified to pH 9 by addition of 10% w/v aqueous sodium carbonate and the resulting cloudy solution was extracted with DCM (3 × 30 cm^3). The combined organic extracts were dried ($MgSO_4$) and concentrated *in vacuo* to yield the title compound **9** (0.535 g, 49%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3483w and 3317w (2 × N–H), 1736vs (C=O), 1639w (C=C) and 1608w (aryl C=C); δ_H(270 MHz) 1.58 (2 H, s, NH_2), 1.59–1.72 (1 H, m, C*H*HCH_2CH=), 1.78–1.92 (1 H, m, CH*H*CH_2CH=), 2.14 (2 H, q, *J* 7, CH_2CH_2CH=), 3.49 (1 H, dd, *J* 8 and 5, C*H*CO_2Bn), 4.97 [1 H, ddt, *J* 10.2, 1.9 and 1.2, =C*H*H (*trans* to alkyl chain)], 5.02 [1 H, ddt, *J* 17.1, 1.9 and 1.6, =CH*H* (*cis* to alkyl chain)], 5.15 (2 H, s, OCH_2Ph), 5.78 (1 H, ddt, *J* 17.1, 10.2 and 6.7, CH_2C*H*=) and 7.35 (5 H, m, Ph); *m*/*z* (CI, NH_3) 220 (MH^+, 100%), 91 ($PhCH_2$, 16) and 84 {CH_2=CH[CH_2]$_2$CH=NH_2, 54}.

Benzyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 10

Di-*tert*-butyl dicarbonate (389 mg, 1.78 mmol) was added to a stirred solution of benzyl 2-aminohex-5-enoate **9** (260 mg, 1.19 mmol) in water (3 cm^3) and 1,4-dioxane (6 cm^3). After stirring for 3 h the reaction mixture was concentrated *in vacuo*. The residual oil was partitioned between water (10 cm^3) and ethyl acetate (5 cm^3) and the two layers were separated. The aqueous phase was then extracted with ethyl acetate (2 × 5 cm^3) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to yield a pale yellow oil. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 4:1) gave the title compound **10** (361 mg, 95%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3364br (N–H), 1741s (ester C=O), 1716vs (carbamate C=O) and 1641w (C=C); δ_H(270 MHz) 1.44 (9 H, s, Bu^t), 1.66–1.80 (1 H, m, C*H*HCH_2CH=), 1.84–2.03 (1 H, m, CH*H*-CH_2CH=), 2.03–2.15 (2 H, m, CH_2CH_2CH=), 4.37 (1 H, br q, C*H*CO_2Bn), 4.90–5.09 (3 H, m, =CH_2 and NH), 5.13 (1 H, d, *J* 12.5, OC*H*HPh), 5.21 (1 H, d, *J* 12.5, OCH*H*Ph), 5.76 (1 H, ddt, *J* 17, 10 and 7, CH_2C*H*=) and 7.35 (5 H, m, Ph); *m*/*z* (CI, NH_3) 337 (MNH_4^+, 12%), 320 (MH, 12), 281 (MNH_4 − Me_2C=CH_2, 27), 264 (MH − Me_2C=CH_2, 16), 220 (MH − Me_2C=CH_2 − CO_2, 18), 91 ($PhCH_2$, 50) and 84 {CH_2=CH-[CH_2]$_2$CH=NH_2, 100}.

2-(*tert*-Butoxycarbonylamino)hex-5-enoic acid 11

2-Aminohex-5-enoic acid **5** (0.354 g, 2.74 mmol) was dissolved in 0.6 M aqueous sodium hydroxide (5 cm^3) and the resulting solution was diluted with 2-methylpropan-2-ol (2 cm^3). Di-*tert*-butyl dicarbonate (0.801 g, 3.67 mmol) was added and the reaction mixture was stirred for 18 h. The resulting mixture was then concentrated *in vacuo* and the residue remaining was dissolved in water (20 cm^3) and washed with diethyl ether (10 cm^3). Solid potassium hydrogen sulfate was added to acidify the aqueous solution to pH 3 and the resulting cloudy mixture was then extracted with ethyl acetate (3 × 10 cm^3). The combined organic extracts were washed with water (10 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to yield the *title acid* **11** (0.45 g, 72%) as a white solid, mp 59–62 °C (from pentane) (Found: C, 57.9; H, 8.2; N, 6.2. $C_{11}H_{19}NO_4$ requires C, 57.63; H, 8.35; N, 6.11%); ν_{max}(Nujol mull)/cm^{-1} 3365s (N–H), 3400–2400br (O–H), 1730s (acid C=O), 1678vs (carbamate C=O) and 1640w (C=C); δ_H(300 MHz, [$^2H_6$]DMSO) 1.37 (9 H, s, Bu^t), 1.56–1.77 (2 H, m, C$H_2$$CH_2$CH=), 1.99–2.12 (2 H, m, CH_2-CH_2CH=), 3.80–3.89 (1 H, m, C*H*CO_2H), 4.96 [1 H, d, *J* 10, =C*H*H (*trans* to alkyl chain)], 4.99 [1 H, d, *J* 17, =CH*H* (*cis* to alkyl chain)], 5.77 (1 H, ddt, *J* 17, 10 and 7, CH_2C*H*=), 7.11 (1 H, d, *J* 8.1, NH) and 12.47 (1 H, br s, CO_2H); δ_C\{^{1}H\} (75.4 MHz) 28.3 [C(*C*H_3)$_3$], 29.4 (C-4), 31.6 (C-3), 52.9 (C-2), 80.2 [*C*(CH_3)$_3$], 115.8 (C-6), 136.8 (C-5), 155.5 (OCONH) and 177.6 (C-1); *m*/*z* (CI, NH_3) 247 (MNH_4^+, 19%), 230 (MH, 13), 191 (MNH_4 − Me_2C=CH_2, 100), 174 (MH − Me_2C=CH_2, 12), 130 (MH − Me_2C=CH_2 − CO_2, 22) and 84 {H_2C=CH[CH_2]$_2$CH=NH_2, 18}.

***tert*-Butyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 12**

A solution of *tert*-butyl 2,2,2-trichloroacetimidate (0.79 g, 3.6 mmol) in hexane (8 cm^3) was added *via* a cannula to a stirred solution of 2-(*tert*-butoxycarbonylamino)hex-5-enoic acid **11** (0.412 g, 1.80 mmol) in DCM (4 cm^3), under an atmosphere of nitrogen. Boron trifluoride–diethyl ether (0.033 cm^3, 0.27 mmol) was added and the resulting suspension was stirred for 19 h. The reaction was quenched by addition of sodium hydrogen carbonate (0.5 g) and the mixture was then filtered through a short pad of silica (light petroleum–diethyl ether, 4:1). After concentrating the filtrate *in vacuo* the residual oil was purified by column chromatography (SiO_2; light petroleum–diethyl ether, 6:1) to give the *title compound* **12** (0.413 g, 81%) as a colourless oil (Found: C, 62.9; H, 9.45; N, 4.9. $C_{15}H_{27}NO_4$ requires C, 63.13; H, 9.54; N, 4.91%); ν_{max}(neat)/cm^{-1} 3367br (N–H), 1716vs (carbamate and ester C=O) and 1645w (C=C); δ_H(270 MHz) 1.44 (9 H, s, carbamate Bu^t), 1.46 (9 H, s, ester Bu^t), 1.61–1.74 (1 H, m, C*H*HCH_2CH=), 1.77–1.94 (1 H, m, CH*H*CH_2CH=), 2.00–2.22 (2 H, m, CH_2CH_2CH=), 4.19 (1 H, br q, C*H*CO_2Bu^t), 4.94–5.04 [2 H, br d, =C*H*H (*trans* to alkyl chain) and NH], 5.05 [1 H, dq, *J* 17 and 1, =CH*H* (*cis* to alkyl chain)] and 5.80 (1 H, ddt, *J* 17, 10 and 7, CH_2C*H*=); δ_C\{^{1}H\} (75.4 MHz) 28.0 and 28.3 [2 × C(*C*H_3)$_3$], 29.4 (C-4), 32.2 (C-3), 53.5 (C-2), 79.5 [carbamate *C*(CH_3)$_3$], 81.6 [ester *C*(CH_3)$_3$], 115.3 (C-6), 137.2 (C-5), 155.2 (OCONH) and 171.8 (C-1); *m*/*z* (CI, NH_3) 303 (MNH_4^+, 6%), 286 (MH, 33), 230 (MH − Me_2C=CH_2, 19), 191 (MNH_4 − 2 × Me_2C=CH_2, 24), 186 (MH − Me_2C=CH_2 − CO_2, 21) and 84 {CH_2=CH[CH_2]$_2$CH=NH_2, 100}.

Cross-metathesis of benzyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 10 with styrene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of benzyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate **10** (160 mg, 0.50 mmol), styrene (0.114 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting purple solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–4:1–1:2 gradient elution) yielded *trans*-stilbene (14 mg, 16%) and *benzyl* 2-tert-*butoxycarbonylamino*-6-*phenylhex*-5-*enoate* **21** (105 mg, 53%, *trans*:*cis* = 19:1) as white solids, and *dibenzyl* 2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **22** (67 mg, 44%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

Benzyl 2-*tert*-butoxycarbonylamino-6-phenylhex-5-enoate 21. Mp 60–62 °C (Found: C, 72.6; H, 7.6; N, 3.6. $C_{24}H_{29}NO_4$ requires C, 72.89; H, 7.39; N, 3.54%); ν_{max}(Nujol mull)/cm^{-1} 3373s (N–H), 1725s (ester C=O) and 1685vs (carbamate C=O); δ_H(270 MHz, *trans*-isomer only) 1.45 (9 H, s, Bu^t), 1.74–1.92 (1 H, m, C*H*HCH_2CH=), 1.92–2.12 (1 H, m, CH*H*CH_2CH=), 2.15–2.32 (2 H, m, CH_2CH=), 4.42 (1 H, br q, C*H*CO_2Bn), 5.10 (1 H, br d, NH), 5.13 (1 H, d, *J* 12.2, OC*H*HPh), 5.21 (1 H, d, *J* 12.2, OCH*H*Ph), 6.14 (1 H, dt, *J* 15.7 and 6.7, CH_2C*H*=), 6.36 (1 H, d, *J* 15.7, PhC*H*=) and 7.18–7.42 (5 H, m, Ph); δ_C\{^{1}H\} (67.9 MHz, *trans*-isomer only) 28.3 [C(*C*H_3)$_3$], 28.7 (C-4), 32.4 (C-3), 53.2 (C-2), 67.0 (O*C*H_2Ph), 79.9 [*C*(CH_3)$_3$], 126.0 (styrene C_{ortho}), 127.1 (styrene C_{para}), 128.3, 128.5 and 128.6 (styrene C_{meta} and benzyl C_{ortho}, C_{meta} and C_{para}), 128.7 (C-5), 131.0 (C-6), 135.4 (benzyl C_{ipso}), 137.4 (styrene C_{ipso}), 155.3 (OCONH) and 172.5 (C-1); *m*/*z* (CI, NH_3) 413 (MNH_4^+, 22%), 396 (MH, 18), 357 (MNH_4 − Me_2C=CH_2, 61), 340 (MH − Me_2C=CH_2, 13), 296 (MH − Me_2C=CH_2 − CO_2, 42), 204 (MH − CO_2 − $PhCH_3$ − Me_2C=CH_2, 100) and 91 (Ph*C*H_2, 34).

Dibenzyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 22. (Found: C, 66.9; H, 7.5; N, 4.3. $C_{34}H_{46}N_2O_8$ requires C, 66.86; H, 7.59; N, 4.59%); ν_{max}(neat)/cm^{-1} 3372s (N–H), 1747s (ester C=O) and 1704vs (carbamate C=O); δ_H(300 MHz) 1.43 (18 H, s, 2 × Bu^t), 1.59–1.72 (2 H, m, 2 × C*H*HCH_2CH=), 1.77–1.91 (2 H, m, 2 × CH*H*CH_2CH=), 1.93–2.06 (4 H, m, 2 × CH_2CH=), 4.24–4.38 (2 H, m, 2 × C*H*CO_2Bn), 5.00 (2 H, d, *J* 8.5, 2 × NH), 5.12 (2 H, d, *J* 12.3, 2 × OC*H*HPh), 5.19 (2 H, d, *J* 12.3, 2 × OCH*H*Ph), 5.32 (2 H, t, *J* 3.6, 2 × CH=) and 7.35 (10 H, s, 2 × Ph); δ_C\{^{1}H\} (75.4 MHz) 23.1 (C-4 and C-7, *cis*-isomer), 28.3 [C-4 and C-7, *trans*-isomer, and C(*C*H_3)$_3$], 32.4 (C-3 and C-8), 53.1 (C-2 and C-9), 79.8 [*C*(CH_3)$_3$], 128.2, 128.4 and 128.5 (C_{ortho}, C_{meta} and C_{para}), 129.2 (C-5 and C-6, *cis*-isomer), 129.7 (C-5 and C-6, *trans*-isomer), 135.4 (C_{ipso}), 155.3 (OCONH) and 172.6 (C-1 and C-10); *m*/*z* (CI, NH_3) 611 (MH^+, 3%), 511 (MH − Me_2C=CH_2 − CO_2, 21), 319 (MH − CO_2 − 2 × Me_2C=CH_2 − HCO_2Bn, 12), 246 (MH − Me_2C=CH_2 − CO_2 − BocNHCH_2CO_2Bn, 20) and 91 ($PhCH_2$, 100).

Cross-metathesis of *tert*-butyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 12 with styrene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of *tert*-butyl 2-(*tert*-butoxycarbonylamino)-hex-5-enoate **12** (143 mg, 0.50 mmol), styrene (0.114 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting purple solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–6:1–1:2 gradient elution) yielded *trans*-stilbene (14 mg, 16%) as a white solid, tert-*butyl* 2-tert-*butoxycarbonylamino*-6-*phenylhex*-5-*enoate* **23** (100 mg, 55%, *trans*:*cis* = 19:1) as a colourless oil and *di*-tert-*butyl* 2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **24** (61 mg, 45%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

***tert*-Butyl 2-*tert*-butoxycarbonylamino-6-phenylhex-5-enoate 23.** (Found: C, 69.7; H, 8.4; N, 3.9. $C_{21}H_{31}NO_4$ requires C, 69.78; H, 8.64; N, 3.87%); ν_{max}(neat)/cm^{-1} 3358br (N–H) and 1715vs (carbamate and ester C=O); δ_H(270 MHz, *trans*-isomer only) 1.45 (9 H, s, carbamate Bu^t), 1.48 (9 H, s, ester Bu^t), 1.71–1.86 (1 H, m, C*H*HCH_2CH=), 1.86–2.06 (1 H, m, CH*H*-

CH_2CH=), 2.15–2.40 (2 H, m, CH_2CH=), 4.24 (1 H, br q, CHCO$_2$Bu^t), 5.08 (1 H, br d, NH), 6.19 (1 H, dt, *J* 15.7 and 6.7, CH_2CH=), 6.41 (1 H, d, *J* 15.7, PhCH=) and 7.19–7.36 (5 H, m, Ph); $\delta_C\{^1H\}$ (75.4 MHz, *trans*-isomer only) 28.0 and 28.3 [2 × C(CH_3)$_3$], 28.8 (C-4), 32.7 (C-3), 53.7 (C-2), 79.6 [carbamate $C(CH_3)_3$], 81.8 [ester $C(CH_3)_3$], 126.0 (C_{ortho}), 127.0 (C_{para}), 128.4 (C_{meta}), 129.1 (C-5), 130.7 (C-6), 137.5 (C_{ipso}), 155.3 (OCONH) and 171.8 (C-1); *m*/*z* (CI, NH_3) 379 (MNH_4^+, 18%), 362 (MH, 30), 323 (MNH_4 − Me_2C=CH_2, 10), 306 (MH − Me_2C=CH_2, 11), 267 (MNH_4 − 2 × Me_2C=CH_2, 29), 262 (MH − Me_2C=CH_2 − CO_2, 13) 206 (MH − CO_2 − 2 × Me_2C=CH_2, 31), 160 {PhCH=CH[CH_2]$_2$CH=NH_2, 18} and 114 (MH − CO_2 − $PhCH_3$ − 2 × Me_2C=CH_2, 100).

Di-*tert*-butyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 24. [Found: *m*/*z* (MH^+) 543.3642. $C_{28}H_{51}N_2O_8$ requires 543.3645]; ν_{max}(neat)/cm^{-1} 3363br (N–H) and 1711vs (carbamate and ester C=O); δ_H(270 MHz) 1.43 (18 H, s, 2 × carbamate Bu^t), 1.45 (18 H, s, 2 × ester Bu^t), 1.55–1.89 (4 H, m, 2 × CH_2CH$_2$CH=), 1.97–2.16 (4 H, m, 2 × CH_2CH=), 4.15 (2 H, br q, 2 × CHCO$_2$Bu^t), 5.01 (2 H, d, *J* 8.3, 2 × NH) and 5.41 (2 H, t, *J* 3.7, 2 × CH=); $\delta_C\{^1H\}$ (75.4 MHz) 23.1 (C-4 and C-7, *cis*-isomer), 28.0 and 28.3 [C-4 and C-7, *trans*-isomer, and carbamate and ester C(CH_3)$_3$], 32.8 (C-3 and C-8), 53.6 (C-2 and C-9), 79.5 [carbamate $C(CH_3)_3$], 81.7 [ester $C(CH_3)_3$], 129.3 (C-5 and C-6, *cis*-isomer), 129.8 (C-5 and C-6, *trans*-isomer), 155.3 (OCONH) and 171.9 (C-1 and C-10); *m*/*z* (CI, NH_3) 560 (MNH_4^+, 16%), 543 (MH, 88), 443 (MH − Me_2-C=CH_2 − CO_2, 64), 387 (MH − CO_2 − 2 × Me_2C=CH_2, 26), 341 (MH − CO_2 − 2 × Me_2C=CH_2 − HCO_2H, 45), 285 (MH − CO_2 − 3 × Me_2C=CH_2 − HCO_2H, 58), 229 (MH − CO_2 − 4 × Me_2C=CH_2 − HCO_2H, 90), 212 (MH − Me_2C=CH_2 − CO_2 − BocNHCH$_2$CO$_2$Bu^t, 28), 185 (MH − 2 × CO_2 − 4 × Me_2C=CH_2 − HCO_2H, 46) and 156 (MH − 2 × Me_2C=CH_2 − CO_2 − BocNHCH$_2$CO$_2$Bu^t, 100).

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 6 with hex-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate **6** (121 mg, 0.50 mmol), hex-1-ene (0.125 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–4 : 1–1 : 2 gradient elution) yielded *methyl* 2-(tert-*butoxycarbonylamino*)-*dec*-5-*enoate* **25** (82 mg, 55%, mixture of *cis*- and *trans*-isomers) as a colourless oil and *dimethyl* 2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **16** (49 mg, 43%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

Methyl 2-(tert-butoxycarbonylamino)dec-5-enoate 25. (Found: C, 64.0; H, 9.6; N, 4.8. $C_{16}H_{29}NO_4$ requires C, 64.19; H, 9.76; N, 4.68%); ν_{max}(neat)/cm^{-1} 3370br (N–H), 1746s (ester C=O) and 1718vs (carbamate C=O); δ_H(270 MHz) 0.84–0.94 {3 H, m, [CH_2]$_2$CH_3}, 1.25–1.38 {4 H, m, [CH_2]$_2$CH$_3$}, 1.44 (9 H, s, Bu^t), 1.59–1.75 (1 H, m, CHHCHCO$_2$), 1.78–1.91 (1 H, m, CHHCHCO$_2$), 1.91–2.13 (4 H, m, CH_2CH=CHCH_2), 3.72 (3 H, 2 × s, OCH_3, *cis*- and *trans*-isomers), 4.29 (1 H, br q, CHCO$_2$Me), 4.99 (1 H, br d, NH) and 5.24–5.49 (2 H, m, HC=CH); $\delta_C\{^1H\}$ (67.9 MHz, [$^2H_6$]benzene) 14.1 (C-10), 22.4 (C-9, *trans*-isomer), 22.6 (C-9, *cis*-isomer), 23.5 (C-4, *cis*-isomer), 27.1 (C-7, *cis*-isomer), 28.3 [C(CH_3)$_3$], 28.7 (C-4, *trans*-isomer), 31.9 (C-8, *trans*-isomer), 32.0 (C-8, *cis*-isomer), 32.5 and 32.8 (C-7, *trans*-isomer, and C-3), 51.5 (OCH_3), 53.3 (C-2), 79.2 [$C(CH_3)_3$], 128.1 (HC=, *cis*-isomer), 128.7 (HC=, *trans*-isomer), 131.4 (=CH, *cis*-isomer), 132.0 (=CH, *trans*-isomer), 155.5 (OCONH) and 173.2 (C-1); *m*/*z* (CI, NH_3) 317 (MNH_4^+, 18%), 300 (MH, 69), 261 (MNH_4 − Me_2C=CH_2, 70), 244 (MH − Me_2C=CH_2, 91), 200 (MH − Me_2C=CH_2 − CO_2, 86) and 140 {CH_3[CH_2]$_3$$CH_2$CH=CH[$CH_2$]$_2$CH=$NH_2$, 100}.

Dimethyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 16. The ^1H NMR spectrum was identical to that of the sample isolated from the cross-metathesis reaction of amino acid **6** with styrene.

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 6 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate **6** (121 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–red solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–5 : 1–1 : 2 gradient elution) yielded *methyl* 2-(tert-*butoxycarbonylamino*)*dodec*-5-*enoate* **26** (108 mg, 66%, mixture of *cis*- and *trans*-isomers) as a colourless oil and *dimethyl* 2,9-*bis*(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **16** (32 mg, 28%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

Methyl 2-(*tert*-butoxycarbonylamino)dodec-5-enoate 26. (Found: C, 66.0; H, 10.2; N, 4.3. $C_{18}H_{33}NO_4$ requires C, 66.02; H, 10.16; N, 4.28%); ν_{max}(neat)/cm^{-1} 3365br (N–H), 1746s (ester C=O) and 1722vs (carbamate C=O); δ_H(270 MHz) 0.87 {3 H, t, *J* 7, [CH_2]$_4$CH_3}, 1.26 {8 H, br s, [CH_2]$_4$CH$_3$}, 1.43 (9 H, s, Bu^t), 1.55–1.74 (1 H, m, CHHCHCO$_2$), 1.74–1.91 (1 H, m, CHHCHCO$_2$), 1.91–2.12 (4 H, m, CH_2CH=CHCH_2), 3.72 and 3.73 (3 H, 2 × s, OCH_3, *cis*- and *trans*-isomers), 4.29 (1 H, br q, CHCO$_2$Me), 5.00 (1 H, br d, NH) and 5.24–5.50 (2 H, m, HC=CH); $\delta_C\{^1H\}$ (67.9 MHz) 14.0 (C-12), 22.6 (C-11), 23.1 (C-4, *cis*-isomer), 27.2 (C-7, *cis*-isomer), 28.2 [C(CH_3)$_3$], 28.3 (C-4, *trans*-isomer), 28.8, 28.9, 29.4 and 29.5 (C-8 and C-9, *cis*- and *trans*-isomers), 31.7 (C-10), 32.5 and 32.6 (C-7, *trans*-isomer, and C-3), 52.1 (OCH_3), 53.1 (C-2), 79.7 [$C(CH_3)_3$], 127.5 (HC=, *cis*-isomer), 128.1 (HC=, *trans*-isomer), 131.5 (=CH, *cis*-isomer), 132.0 (=CH, *trans*-isomer), 155.2 (OCONH) and 173.3 (C-1); *m*/*z* (CI, NH_3) 345 (MNH_4^+, 3%), 328 (MH, 17), 289 (MNH_4 − Me_2C=CH_2, 100), 272 (MH − Me_2C=CH_2, 19), 228 (MH − Me_2C=CH_2 − CO_2, 84) and 168 {CH_3[CH_2]$_5$-CH_2CH=CH[CH_2]$_2$CH=NH_2, 14}.

Dimethyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 16. The ^1H NMR spectrum was identical to that of the sample isolated from the cross-metathesis reaction of amino acid **6** with styrene.

Cross-metathesis of *tert*-butyl 2-(*tert*-butoxycarbonylamino)hex-5-enoate 12 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of *tert*-butyl 2-(*tert*-butoxycarbonylamino)-hex-5-enoate **12** (143 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–red solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–9 : 1–1 : 2 gradient elution) yielded tert-*butyl* 2-(tert-*butoxycarbonylamino*)*dodec*-5-*enoate* **27** (116 mg, 63%, mixture of *cis*- and *trans*-isomers) as a colourless oil and *di*-tert-*butyl* 2,9-*bis*-(tert-*butoxycarbonylamino*)*dec*-5-*enedioate* **24** (38 mg, 28%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

***tert*-Butyl 2-(*tert*-butoxycarbonylamino)dodec-5-enoate 27.** [Found: *m*/*z* (MH^+) 370.2957. $C_{21}H_{41}NO_4$ requires 370.2957]; ν_{max}(neat)/cm^{-1} 3362br (N–H) and 1718vs (carbamate and ester C=O); δ_H(300 MHz) 0.88 {3 H, t, *J* 7, [CH_2]$_4$CH_3}, 1.26 {8 H, br

s, [CH_2]$_4$CH_3}, 1.44 (9 H, s, carbamate Bu^t), 1.46 (9 H, s, ester Bu^t), 1.55–1.70 (1 H, m, CHHCHCO$_2$), 1.74–1.87 (1 H, m, CHHCHCO$_2$), 1.91–2.10 (4 H, m, CH_2CH=CHCH_2), 4.17 (1 H, br q, CHCO$_2$Bu^t), 5.00 (1 H, br d, NH) and 5.29–5.50 (2 H, m, HC=CH); δ_C\{^{1}H\} (67.9 MHz) 14.0 (C-12), 22.6 (C-11), 23.0 (C-4, *cis*-isomer), 27.2 (C-7, *cis*-isomer), 28.0 and 28.3 [C-4, *trans*-isomer, and 2 × C(*C*H$_3$)$_3$], 28.8, 28.9, 29.4 and 29.6 (C-8 and C-9, *cis*- and *trans*-isomers), 31.7 (C-10), 32.5 (C-7, *trans*-isomer), 32.9 (C-3), 53.7 (C-2), 79.4 [carbamate *C*(CH$_3$)$_3$], 81.5 [ester *C*(CH$_3$)$_3$], 127.9 (HC=, *cis*-isomer), 128.5 (HC=, *trans*-isomer), 131.2 (=CH, *cis*-isomer), 131.7 (=CH, *trans*-isomer), 155.3 (OCONH) and 172.0 (C-1); *m*/*z* (CI, NH$_3$) 387 (MNH$_4^+$, 9%), 370 (MH, 71), 331 (MNH$_4$ − Me$_2$C=CH$_2$, 11), 314 (MH − Me$_2$C=CH$_2$, 29), 275 (MNH$_4$ − 2 × Me$_2$C=CH$_2$, 40), 270 (MH − Me$_2$C=CH$_2$ − CO$_2$, 25), 258 (MH − 2 × Me$_2$C=CH$_2$, 18) and 168 {CH$_3$[CH$_2$]$_5$CH$_2$CH=CH[CH$_2$]$_2$CH=NH$_2$, 100}.

Di-*tert*-butyl 2,9-bis(*tert*-butoxycarbonylamino)dec-5-enedioate 24. The ^{1}H NMR spectrum was identical to that of the sample isolated from the cross-metathesis reaction of amino acid **12** with styrene.

2-(Fluoren-9-ylmethoxycarbonylamino)hex-5-enoic acid 13

N-(Fluoren-9-ylmethoxycarbonyloxy)succinimide (Fmoc-ONSu) (818 mg, 2.43 mmol) was added to a stirred suspension of 2-aminohex-5-enoic acid **5** (313 mg, 2.43 mmol) and sodium hydrogen carbonate (207 mg, 2.46 mmol) in water–acetone (1:1, 8 cm^3). After stirring for 20 h the reaction mixture was acidified to pH 2 by careful addition of concentrated hydrochloric acid and the acetone was removed *in vacuo*. Chloroform (30 cm^3) was added to the resulting aqueous suspension and the biphasic mixture was washed with 0.1 M hydrochloric acid (10 cm^3). The organic layer was then washed with water (10 cm^3), dried (MgSO$_4$) and concentrated *in vacuo* to yield a white foam. Recrystallisation from DCM–pentane afforded the *title acid* **13** (658 mg, 77%) as colourless crystals, mp 128–129.5 °C (Found: C, 71.6; H, 5.8; N, 3.9. C$_{21}$H$_{21}$NO$_4$ requires C, 71.78; H, 6.02; N, 3.99%); ν_{max}(Nujol mull)/cm^{-1} 3300–2400br (O–H), 3326s (N–H), 1692vs (acid and carbamate C=O) and 1642w (C=C); δ_H(270 MHz, [^{2}H$_6$]DMSO) 1.66–1.82 (2 H, m, CH_2CH$_2$CH=), 2.00–2.16 (2 H, m, CH$_2$CH_2CH=), 3.93 (1 H, ddd, *J* 9, 8 and 5, CHCO$_2$H), 4.18–4.30 (3 H, m, CHCH$_2$O), 4.98 [1 H, ddt, *J* 10, 2 and 1, =CHH (*trans* to alkyl chain)], 5.00 [1 H, ddt, *J* 17, 2 and 1, =CHH (*cis* to alkyl chain)], 5.78 (1 H, ddt, *J* 17, 10 and 7, CH$_2$CH=), 7.32 (2 H, t, *J* 7.4, fluorenyl 2′-H and 7′-H), 7.41 (2 H, t, *J* 7.4, fluorenyl 3′-H and 6′-H), 7.67 (1 H, d, *J* 8, NH), 7.72 (2 H, d, *J* 7.4, fluorenyl 1′-H and 8′-H), 7.89 (2 H, d, *J* 7.4, fluorenyl 4′-H and 5′-H) and 12.2–12.8 (1 H, br s, CO$_2$H); δ_C\{^{1}H\} (67.9 MHz, [^{2}H$_6$]DMSO) 29.8 and 30.1 (C-3 and C-4), 46.9 (C-9′), 53.3 (C-2), 65.7 (CH$_2$O), 115.7 (C-6), 120.3, 125.5, 127.2 and 127.8 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 137.7 (C-5), 140.9 and 144.0 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 156.3 (OCONH) and 174.1 (C-1); *m*/*z* (FAB positive) 703 [(2 M + H)$^+$, 6%], 352 (MH, 29) and 179 [(fluoren-9-ylmethyl) + H, 100].

Methyl 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoate 14

Iodomethane (0.50 cm^3, 8.0 mmol) was added to a stirred suspension of potassium hydrogen carbonate (68 mg, 0.68 mmol) and 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoic acid **13** (200 mg, 0.57 mmol) in anhydrous DMF (5 cm^3), under an atmosphere of nitrogen. After stirring for 23 h the cloudy yellow solution was concentrated *in vacuo*. The residue was partitioned between water (5 cm^3) and DCM (5 cm^3) and the two layers were separated. The aqueous layer was then extracted with DCM (3 × 5 cm^3) and the combined organic extracts were washed with brine (5 cm^3), dried (MgSO$_4$) and concentrated *in vacuo* to yield a yellow oil. Purification by column chromatography (SiO$_2$; light petroleum–diethyl ether, 3:2) gave the *title compound* **14** (160 mg, 77%) as a white solid, mp 98–100 °C (Found: C, 72.1; H, 6.4; N, 4.1. C$_{22}$H$_{23}$NO$_4$ requires C, 72.31; H, 6.34; N, 3.83%); ν_{max}(Nujol mull)/cm^{-1} 3311s (N–H), 1737s (ester C=O), 1688vs (carbamate C=O) and 1639w (C=C); δ_H(270 MHz) 1.69–1.84 (1 H, m, CHHCH$_2$CH=), 1.88–2.06 (1 H, m, CHHCH$_2$CH=), 2.06–2.19 (2 H, m, CH$_2$CH_2CH=), 3.76 (3 H, s, OCH$_3$), 4.23 (1 H, t, *J* 6.9, CHCH$_2$O), 4.41 (3 H, d, *J* 6.9, CHCH_2O and CHCO$_2$Me), 5.02 [1 H, d, *J* 10, =CHH (*trans* to alkyl chain)], 5.06 [1 H, d, *J* 17, =CHH (*cis* to alkyl chain)], 5.32 (1 H, d, *J* 8.3, NH), 5.79 (1 H, ddt, *J* 17, 10 and 7, CH$_2$CH=), 7.32 (2 H, t, *J* 7.4, fluorenyl 2′-H and 7′-H), 7.41 (2 H, t, *J* 7.4, fluorenyl 3′-H and 6′-H), 7.60 (2 H, d, *J* 7.4, fluorenyl 1′-H and 8′-H) and 7.77 (2 H, d, *J* 7.4, fluorenyl 4′-H and 5′-H); δ_C\{^{1}H\} (67.9 MHz) 29.3 (C-4), 31.8 (C-3), 47.1 (C-9′), 52.4 (OCH$_3$), 53.4 (C-2), 67.0 (CH$_2$O), 115.8 (C-6), 119.9, 125.0, 127.0 and 127.7 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 136.8 (C-5), 141.3 and 143.7 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 155.8 (OCONH) and 172.9 (C-1); *m*/*z* (CI, NH$_3$) 383 (MNH$_4^+$, 14%), 366 (MH, 16), 179 [(fluoren-9-ylmethyl) + H, 74], 144 [MH − (fluoren-9-ylmethyl) − CO$_2$, 100] and 84 {CH$_2$=CH[CH$_2$]$_2$CH=NH$_2$, 12}.

Cross-metathesis of methyl 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoate 14 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoate **14** (182 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and Cl$_2$(PCy$_3$)$_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–red solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca.* 50 cm^3) and stirred overnight, under air. Column chromatography (SiO$_2$; light petroleum–diethyl ether, 1:0–5:2–1:3 gradient elution) yielded *methyl* 2-(*fluoren*-9-*ylmethoxycarbonylamino*)*dodec*-5-*enoate* **28** (130 mg, 58%, *trans*:*cis* = 9:2) as a gummy white solid and *dimethyl* 2,9-*bis*-(*fluoren*-9-*ylmethoxycarbonylamino*)*dec*-5-*enedioate* **29** (43 mg, 25%, mixture of *cis*- and *trans*-isomers) as a white foam.

Methyl 2-(fluoren-9-ylmethoxycarbonylamino)dodec-5-enoate 28. (Found: C, 74.6; H, 7.6; N, 3.1. C$_{28}$H$_{35}$NO$_4$ requires C, 74.80; H, 7.85; N, 3.12%); ν_{max}(Nujol mull)/cm^{-1} 3320s (N–H), 1737s (ester C=O) and 1692vs (carbamate C=O); δ_H(270 MHz) 0.88 {3 H, t, *J* 7, [CH$_2$]$_4$CH_3}, 1.26 {8 H, br s, [CH_2]$_4$CH$_3$}, 1.65–1.83 (1 H, m, CHHCHCO$_2$), 1.83–2.15 (5 H, m, CHH-CHCO$_2$ and CH_2CH=CHCH_2), 3.75 (3 H, s, OCH$_3$), 4.23 (1 H, t, *J* 7.2, CHCH$_2$O), 4.41 (3 H, d, *J* 7.2, CHCH_2O and CHCO$_2$Me), 5.29 (1 H, d, *J* 8.2, NH), 5.31–5.53 (2 H, m, HC=CH), 7.32 (2 H, t, *J* 7.4, fluorenyl 2′-H and 7′-H), 7.41 (2 H, t, *J* 7.4, fluorenyl 3′-H and 6′-H), 7.61 (2 H, d, *J* 7.4, fluorenyl 1′-H and 8′-H) and 7.77 (2 H, d, *J* 7.4, fluorenyl 4′-H and 5′-H); δ_C\{^{1}H\} (67.9 MHz) 14.0 (C-12), 22.6 (C-11), 23.0 (C-4, *cis*-isomer), 27.2 (C-7, *cis*-isomer), 28.2 (C-4, *trans*-isomer), 28.8, 28.9, 29.4 and 29.5 (C-8 and C-9, *cis*- and *trans*-isomers), 31.7 (C-10), 32.4 and 32.5 (C-7, *trans*-isomer, and C-3), 47.1 (C-9′), 52.3 (OCH$_3$), 53.4 (C-2, *trans*-isomer), 53.6 (C-2, *cis*-isomer), 66.9 (CH$_2$O), 119.9, 125.0, 127.0 and 127.6 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 127.4 (CH$_2$*C*H=, *cis*-isomer), 127.9 (CH$_2$*C*H=, *trans*-isomer), 131.6 (=*C*HCH$_2$, *cis*-isomer), 132.2 (=*C*HCH$_2$, *trans*-isomer), 141.3 and 143.7 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 155.8 (OCONH) and 173.0 (C-1); *m*/*z* (CI, NH$_3$) 467 (MNH$_4^+$, 2%), 450 (MH, 2), 228 [MH − (fluoren-9-ylmethyl) − CO$_2$, 100], 179 [(fluoren-9-ylmethyl) + H, 71] and 168 {CH$_2$=CH-[CH$_2$]$_2$CH=NH$_2$, 11}.

Dimethyl 2,9-bis(fluoren-9-ylmethoxycarbonylamino)dec-5-enedioate 29. (Found: C, 71.5; H, 5.75; N, 3.7. C$_{42}$H$_{42}$N$_2$O$_8$ requires C, 71.78; H, 6.02; N, 3.99%); ν_{max}(neat)/cm^{-1} 3338br (N–H) and 1723vs (carbamate and ester C=O); δ_H(270 MHz) 1.67–1.82 (2 H, m, 2 × CHHCH$_2$CH=), 1.85–2.01 (2 H, m, 2 × CHHCH$_2$CH=), 2.01–2.17 (4 H, m, 2 × CH_2CH=), 3.74

(6 H, s, 2 × OCH_3), 4.23 (2 H, t, *J* 7, 2 × C*H*CH_2O), 4.32–4.51 [6 H, m, 2 × (C*H*CO_2Me and CHC*H*$_2$O)], 5.31 (2 H, br d, 2 × NH), 5.39–5.49 (2 H, m, 2 × CH=), 7.32 [4 H, t, *J* 7.4, 2 × (fluorenyl 2′-H and 7′-H)], 7.41 [4 H, t, *J* 7, 2 × (fluorenyl 3′-H and 6′-H)], 7.61 [4 H, d, *J* 7.4, 2 × (fluorenyl 1′-H and 8′-H)] and 7.77 [4 H, d, *J* 7.2, 2 × (fluorenyl 4′-H and 5′-H)]; $\delta_C\{^1H\}$ (67.9 MHz) 23.1 (C-4 and C-7, *cis*-isomer), 28.2 (C-4 and C-7, *trans*-isomer), 32.3 (C-3 and C-8), 47.2 (C-9′), 52.3 (OCH_3), 53.3 (C-2 and C-9, *trans*-isomer), 53.6 (C-2 and C-9, *cis*-isomer), 67.0 (CH_2O), 120.0, 125.0, 127.0 and 127.7 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 129.4 (C-5 and C-6, *cis*-isomer), 129.8 (C-5 and C-6, *trans*-isomer), 141.3 and 143.7 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 155.8 (OCONH) and 172.9 (C-1); *m*/*z* (FAB positive) 703 (MH^+, 39%), 481 [MH − (fluoren-9-ylmethyl) − CO_2, 15] and 178 (fluoren-9-ylmethyl, 100).

Cross-metathesis of 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoic acid 13 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of 2-(fluoren-9-ylmethoxycarbonylamino)-hex-5-enoic acid **13** (176 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting yellow suspension was concentrated *in vacuo* and the residue was purified by column chromatography (SiO_2; 0.5% v/v acetic acid in DCM–methanol, 1:0–39:1–9:1 gradient elution) to yield 2-(*fluoren-9-ylmethoxycarbonylamino*)*dodec-5-enoic acid* **30** (133 mg, contaminated with a small amount of starting material **13**, **30**:**13** = 12:1, which implies a 58% yield of **30**) as a colourless gum and 2,9-*bis*(*fluoren-9-ylmethoxycarbonylamino*)*dec-5-enedioic acid* **31** (30 mg, 18%, mixture of *cis*- and *trans*-isomers) as a beige solid.

2-(Fluoren-9-ylmethoxycarbonylamino)dodec-5-enoic acid 30. ν_{max}(neat)/cm^{-1} 3500–2700br (O–H), 3319br (N–H) and 1718vs (carbamate and acid C=O); δ_H(270 MHz) 0.83–0.92 {3 H, m, $[CH_2]_4CH_3$}, 1.26 {8 H, br s, $[CH_2]_4CH_3$}, 1.69–2.19 (6 H, m, CH_2CHCO_2 and CH_2CH=CHCH_2), 4.23 (1 H, t, *J* 7, C*H*CH_2O), 4.38–4.50 (3 H, m, CHCH_2O and C*H*CO_2H), 5.31–5.53 (3 H, m, NH and HC=CH), 7.31 (2 H, t, *J* 7, fluorenyl 2′-H and 7′-H), 7.40 (2 H, t, *J* 7, fluorenyl 3′-H and 6′-H), 7.60 (2 H, d, *J* 7, fluorenyl 1′-H and 8′-H), 7.76 (2 H, d, *J* 7, fluorenyl 4′-H and 5′-H) and 8.6–9.4 (1 H, br s, CO_2H); $\delta_C\{^1H\}$ (75.4 MHz) 14.1 (C-12), 22.6 (C-11), 23.1 (C-4, *cis*-isomer), 27.2 (C-7, *cis*-isomer), 28.3 (C-4, *trans*-isomer), 28.8, 28.9, 29.4 and 29.5 (C-8 and C-9, *cis*- and *trans*-isomers), 31.7 (C-10), 32.1 and 32.5 (C-7, *trans*-isomer, and C-3), 47.1 (C-9′), 53.4 (C-2), 67.1 (CH_2O), 120.0, 125.0, 127.0 and 127.7 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 127.3 (CH_2CH=, *cis*-isomer), 127.9 (CH_2CH=, *trans*-isomer), 131.6 (=*C*HCH_2, *cis*-isomer), 132.4 (=*C*HCH_2, *trans*-isomer), 141.3 and 143.6 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 156.0 (OCONH) and 177.2 (C-1); *m*/*z* (CI, NH_3) 453 (MNH_4^+, 8%), 436 (MH, 3), 257 [MNH_4 − (fluoren-9-ylmethyl) − H_2O, 49], 214 [MH − (fluoren-9-ylmethyl) − CO_2, 99] and 179 [(fluoren-9-ylmethyl) + H, 100].

2,9-Bis(fluoren-9-ylmethoxycarbonylamino)dec-5-enedioic acid 31. ν_{max}(neat)/cm^{-1} 3500–2700br (O–H), 3321br (N–H) and 1699vs (carbamate and acid C=O); δ_H(270 MHz, [$^2H_6$]-DMSO) 1.58–1.79 (4 H, m, 2 × CH_2CH_2CH=), 1.95–2.14 (4 H, m, 2 × CH_2CH=), 3.87–3.99 (2 H, m, 2 × C*H*CO_2H), 4.15–4.31 (6 H, m, 2 × $CHCH_2O$), 5.33–5.43 (2 H, m, 2 × CH=), 7.31 [4 H, t, *J* 7, 2 × (fluorenyl 2′-H and 7′-H)], 7.36–7.43 [4 H, m, 2 × (fluorenyl 3′-H and 6′-H)], 7.56–7.75 [6 H, m, 2 × (NH, fluorenyl 1′-H and 8′-H)], 7.89 [4 H, dd, *J* 7 and 3, 2 × (fluorenyl 4′-H and 5′-H)] and 12.2–12.7 (2 H, br s, 2 × CO_2H); $\delta_C\{^1H\}$ (75.4 MHz, [$^2H_6$]acetone) 24.3 (C-4 and C-7, *cis*-isomer), 29.3 (C-4 and C-7, *trans*-isomer), 32.4 (C-3 and C-8), 47.9 (C-9′), 54.1 (C-2 and C-9), 67.1 (CH_2O), 120.7, 126.1, 127.9 and 128.4 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 130.3 (C-5 and C-6, *cis*-isomer), 130.8 (C-5 and C-6, *trans*-isomer), 142.0 and 144.9 (fluorenyl C-4a′, C-4b′, C-8a′ and C-9a′), 157.1 (OCONH) and 174.0 (C-1); *m*/*z* (FAB positive) 675 (MH^+, 4%) and 179 [(fluoren-9-ylmethyl) + H, 25].

Methyl 2-(*tert*-butoxycarbonylamino)pent-4-enoate 32

Potassium 2-(*tert*-butoxycarbonylamino)pent-4-enoate.[20] 1,4-Dioxane (24 cm^3), potassium hydrogen carbonate (1.90 g, 19.0 mmol) and di-*tert*-butyl dicarbonate (5.26 g, 24.1 mmol) were added to a stirred solution of 2-aminopent-4-enoic acid (1.93 g, 16.8 mmol) in water (50 cm^3). The resulting biphasic mixture was stirred for 15 h before concentrating *in vacuo*. Residual water and dioxane were removed by azeotroping with ethanol (2 × 100 cm^3) and the remaining solid was dried under vacuum (0.2 mmHg) overnight to give potassium 2-(*tert*-butoxycarbonylamino)pent-4-enoate (3.96 g) as a white solid which was used, without further purification, in the subsequent reaction; δ_H(270 MHz) 1.27 (9 H, s, Bu′), 2.13–2.41 (2 H, m, CH_2CH=), 3.79 (1 H, dd, *J* 7.4 and 5.1, C*H*CO_2K), 4.98 [1 H, d, *J* 10, =C*H*H (*trans* to alkyl chain)], 5.01 [1 H, d, *J* 17, =CH*H* (*cis* to alkyl chain)] and 5.62 (1 H, ddt, *J* 17, 10 and 7, CH_2CH=).

Methyl 2-(*tert*-butoxycarbonylamino)pent-4-enoate 32. Iodomethane (8.0 cm^3, 129 mmol) was added to a stirred solution of potassium 2-(*tert*-butoxycarbonylamino)pent-4-enoate (3.96 g) in anhydrous DMF (30 cm^3), under an atmosphere of nitrogen. After stirring for 66 h the clear yellow solution was diluted with water (50 cm^3) and extracted with diethyl ether (3 × 50 cm^3). The combined organic extracts were washed sequentially with saturated aqueous sodium hydrogen carbonate (50 cm^3), water (30 cm^3) and brine (50 cm^3). Drying ($MgSO_4$) and concentrating *in vacuo* yielded a pale yellow oil, which slowly solidified upon standing at −25 °C. Recrystallisation from pentane afforded the *title compound* **32** (2.54 g, 66%) as colourless crystals, mp 30–32 °C (Found: C, 57.9; H, 8.1; N, 6.15. $C_{11}H_{19}NO_4$ requires C, 57.63; H, 8.35; N, 6.11%); ν_{max}(Nujol mull)/cm^{-1} 3357s (N–H), 1741s (ester C=O), 1708vs (carbamate C=O) and 1643w (C=C); δ_H(270 MHz) 1.44 (9 H, s, Bu′), 2.40–2.61 (2 H, m, CH_2CH=), 3.74 (3 H, s, OCH_3), 4.38 (1 H, q, *J* 6.7, C*H*CO_2Me), 5.02 (1 H, br d, *J* 6.7, NH), 5.13 [1 H, d, *J* 17, =CH*H* (*cis* to alkyl chain)], 5.14 [1 H, d, *J* 10, =C*H*H (*trans* to alkyl chain)] and 5.69 (1 H, ddt, *J* 17, 10 and 7, CH_2CH=); $\delta_C\{^1H\}$ (67.9 MHz) 28.2 [C(*C*H_3)$_3$], 36.7 (C-3), 52.1 (OCH_3), 52.9 (C-2), 79.8 [*C*(CH_3)$_3$], 119.0 (C-5), 132.3 (C-4), 155.1 (OCONH) and 172.5 (C-1); *m*/*z* (CI, NH_3) 359 [(2 M + H)$^+$ − Me_2C=CH_2 − CO_2, 13%], 247 (MNH_4, 72), 230 (MH, 85), 191 (MNH_4 − Me_2C=CH_2, 100), 174 (MH − Me_2C=CH_2, 39), 130 (MH − Me_2C=CH_2 − CO_2, 29), 88 (H_2N=$CHCO_2$Me, 14) and 70 (CH_2=$CHCH_2CH$=NH_2, 25).

N-(*tert*-Butoxycarbonyl)glycine methyl ester 35

A solution of sodium hydrogen carbonate (5.88 g, 70.0 mmol) in water (100 cm^3), a solution of di-*tert*-butyl dicarbonate (15.25 g, 70.0 mmol) in chloroform (10 cm^3) and sodium chloride (14.0 g) were added to a stirred suspension of glycine methyl ester hydrochloride (8.79 g, 70.0 mmol) in chloroform (70 cm^3). The resulting biphasic mixture was stirred vigorously at reflux for 1.5 h, allowed to cool and the two layers were separated. The aqueous phase was extracted with chloroform (2 × 50 cm^3) and the combined organic layers were dried ($MgSO_4$) and concentrated *in vacuo* to yield the title compound **35** (13.10 g, 99%) as a viscous colourless oil; ν_{max}(neat)/cm^{-1} 3500–3100br (N–H), 1759vs (ester C=O) and 1718 (carbamate C=O); δ_H(270 MHz) 1.43 (9 H, s, Bu′), 3.73 (3 H, s, OCH_3), 3.89 (2 H, d, *J* 5.8, CH_2) and 5.06 (1 H, br s, NH); *m*/*z* (CI, NH_3) 279 [(2 M + H)$^+$ − Me_2C=CH_2 − CO_2, 11%], 207 (MNH_4, 100), 190 (MH, 73), 151 (MNH_4 − Me_2C=CH_2, 59), 134 (MH − Me_2C=CH_2, 71) and 90 (MH − Me_2C=CH_2 − CO_2, 74).

2-Bromo-*N*-(*tert*-butoxycarbonyl)glycine methyl ester 36

N-Bromosuccinimide (12.46 g, 70.0 mmol) was added to a stirred solution of *N*-(*tert*-butoxycarbonyl)glycine methyl ester **35** (13.07 g, 69.2 mmol) in carbon tetrachloride (120 cm^3), under an atmosphere of nitrogen. The resulting stirred pale yellow solution was illuminated with a 500 W lamp for 1 h, keeping the reaction mixture between 10–30 °C (water bath). The orange reaction mixture was then filtered and the filtrate concentrated *in vacuo* to yield a pale yellow oil, which solidified, upon storing at −25 °C, to give the title compound **36** (18.3 g, 99%) as a hygroscopic beige solid, which was used without purification in the next step; ν_{max}(Nujol mull)/cm^{-1} 3365w (N−H), 1749vs (ester C=O) and 1687s (carbamate C=O); δ_H(270 MHz) 1.47 (9 H, s, Bu^t), 3.85 (3 H, s, OCH_3), 5.98 and 6.35 (2 H, 2 × br d, C*H*CO_2Me and NH); $\delta_C\{^1H\}$ (67.9 MHz) 27.9 [C(CH_3)$_3$], 53.3 and 53.8 (OCH_3 and CHBr), 82.1 [*C*(CH_3)$_3$], 152.1 (OCONH) and 166.5 (*C*O_2Me).

Methyl 2-(*tert*-butoxycarbonylamino)but-3-enoate 37

Vinylmagnesium bromide (25.0 cm^3 of a 1.0 M solution in THF, 25 mmol) was added dropwise to a stirred solution of 2-bromo-*N*-(*tert*-butoxycarbonyl)glycine methyl ester **36** (3.07 g, 11.5 mmol) in THF (60 cm^3), cooled to −78 °C under an atmosphere of nitrogen. The resulting solution was stirred at −78 °C for 2 h before quenching with 1 M aqueous citric acid (50 cm^3) and then extracting with diethyl ether (100 cm^3). The organic extract was washed with water (2 × 20 cm^3) and brine (20 cm^3), dried ($MgSO_4$) and then concentrated *in vacuo* to yield an orange gum. Purification by column chromatography (SiO_2; light petroleum–diethyl ether, 3:1) gave the title compound **37** (503 mg, 20%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3364s (N−H), 1752vs (ester C=O), 1719vs (carbamate C=O) and 1644w (C=C); δ_H(270 MHz) 1.45 (9 H, s, Bu^t), 3.76 (3 H, s, OCH_3), 4.87 (1 H, br t, C*H*CO_2Me), 5.18 (1 H, br s, NH), 5.26 [1 H, ddd, *J* 10.4, 1.6 and 0.7, CH=C*H*H (*trans* to alkyl chain)], 5.35 [1 H, ddd, *J* 17.1, 1.6 and 0.7, CH=CH*H* (*cis* to alkyl chain)] and 5.89 (1 H, ddd, *J* 17.1, 10.4 and 5.5, C*H*=CH_2); *m*/*z* (CI, NH_3) 431 [(2 M + H)$^+$, 14%], 271 [(2 M + H) − Me_2C=CH_2 − CO_2 − HCO_2Me, 34], 233 (MNH_4, 44), 216 (MH, 70), 177 (MNH_4 − Me_2C=CH_2, 35), 160 (MH − Me_2C=CH_2, 43), 156 (MH − HCO_2Me, 38), 116 (MH − Me_2C=CH_2 − CO_2, 41) and 56 (H_2C=CHCH=NH_2, 100).

***N*-(*tert*-Butoxycarbonyl)serine methyl ester 38**

A suspension of serine methyl ester hydrochloride (2.02 g, 13.0 mmol) and di-*tert*-butyl dicarbonate (3.24 g, 14.9 mmol) in DCM (40 cm^3) was cooled to 0 °C, under an atmosphere of nitrogen. Pyridine (1.15 cm^3, 14.3 mmol) was added and the mixture stirred for 10 min before adding triethylamine (1.85 cm^3, 13.3 mmol). The ice bath was removed and the reaction mixture was stirred for 2.5 h before partitioning between DCM (80 cm^3) and water (80 cm^3). The two layers were separated and the aqueous phase was extracted with DCM (40 cm^3). The combined organic extracts were dried (Na_2SO_4) and concentrated *in vacuo* to yield a yellow oil. Purification by column chromatography (SiO_2; light petroleum–ethyl acetate, 1:2) gave the title compound **38** (2.67 g, 94%) as a viscous colourless oil; ν_{max}(neat)/cm^{-1} 3600–3100br (N−H and O−H), 1747s (ester C=O) and 1712vs (carbamate C=O); δ_H(270 MHz) 1.45 (9 H, s, Bu^t), 2.47 (1 H, t, *J* 6, CH_2O*H*), 3.78 (3 H, s, CO_2CH_3), 3.85–3.98 (2 H, m, C*H*$_2$OH), 4.38 (1 H, br s, C*H*CO_2Me) and 5.45 (1 H, br s, NH); *m*/*z* (CI, NH_3) 339 [(2 M + H)$^+$ − Me_2-C=CH_2 − CO_2, 25%], 237 (MNH_4, 40), 220 (MH, 91), 181 (MNH_4 − Me_2C=CH_2, 100), 164 (MH − Me_2C=CH_2, 82), 160 (MH − HCO_2Me, 19), 120 (MH − Me_2C=CH_2 − CO_2, 94) and 60 ($HOCH_2CH$=NH_2, 51).

Methyl 2-(*tert*-butoxycarbonylamino)prop-2-enoate 39

Copper(I) chloride (32 mg, 0.32 mmol) and EDCI (690 mg, 3.59 mmol) were added to a stirred solution of *N*-(*tert*-butoxycarbonyl)serine methyl ester **38** (643 g, 2.94 mmol) in chloroform (30 cm^3), under an atmosphere of nitrogen. The resulting solution was stirred for 5 h and then concentrated *in vacuo*. The residue remaining was partitioned between ethyl acetate (50 cm^3) and 1 M hydrochloric acid (25 cm^3). The two layers were separated and the organic phase was washed with 1 M hydrochloric acid (25 cm^3) and water (25 cm^3) before drying ($MgSO_4$) and concentrating *in vacuo*. The resulting pale yellow oil was purified by column chromatography (SiO_2; light petroleum–diethyl ether, 9:1) to give the title compound **39** (449 mg, 76%) as a colourless oil; ν_{max}(neat)/cm^{-1} 3424s (N−H), 1735s (ester C=O), 1716vs (carbamate C=O) and 1633s (C=C); δ_H(270 MHz) 1.48 (9 H, s, Bu^t), 3.83 (3 H, s, OCH_3), 5.72 (1 H, d, *J* 1.6, C=C*H*H), 6.16 (1 H, s, C=CH*H*) and 7.01 (1 H, br s, NH); *m*/*z* (CI, NH_3) 202 (MH$^+$, 33%), 163 (MNH_4 − Me_2C=CH_2, 100), 146 (MH − Me_2C=CH_2, 32) and 102 (MH − Me_2C=CH_2 − CO_2, 63).

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)pent-4-enoate 32 with styrene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)-pent-4-enoate **32** (113 mg, 0.49 mmol), styrene (0.114 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting purple solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–4:1–1:2 gradient elution) yielded *trans*-stilbene (7 mg, 8%) as a white solid, an inseparable mixture of methyl *trans*-2-*tert*-butoxycarbonylamino-5-phenylpent-4-enoate **40** and starting material **32** (81 mg, **40**:**32** = 2:7) as a colourless oil, and *dimethyl* 2,7-*bis*(tert-*butoxycarbonylamino*)*oct*-4-*enedioate* **41** (22 mg, 21%, mixture of *cis*- and *trans*-isomers) as a gummy white solid.

Methyl *trans*-2-*tert*-butoxycarbonylamino-5-phenylpent-4-enoate 40. δ_H(270 MHz) 1.42 (9 H, s, Bu^t), 2.59–2.78 (2 H, m, C*H*$_2$CH=), 3.75 (3 H, s, OCH_3), 4.46 (1 H, br q, C*H*CO_2Me), 5.05 (1 H, br d, NH), 6.06 (1 H, dt, *J* 15.7 and 7.4, CH_2C*H*=), 6.46 (1 H, d, *J* 15.7, PhC*H*=) and 7.19–7.36 (5 H, m, Ph); $\delta_C\{^1H\}$ (75.4 MHz) 28.3 [C(*C*H_3)$_3$], 36.2 (C-3), 52.3 (OCH_3), 53.2 (C-2), 79.9 [*C*(CH_3)$_3$], 123.7 (C-4), 126.2 (C_{ortho}), 127.5 (C_{para}), 128.5 (C_{meta}), 134.0 (C-5), 136.9 (C_{ipso}), 155.1 (OCONH) and 172.5 (C-1).

Dimethyl 2,7-bis(*tert*-butoxycarbonylamino)oct-4-enedioate 41. [Found: *m*/*z* (MH$^+$) 431.2398. $C_{20}H_{35}N_2O_8$ requires 431.2393]; ν_{max}(neat)/cm^{-1} 3363br (N−H), 1747s (ester C=O) and 1716vs (carbamate C=O); δ_H(300 MHz) 1.45 (18 H, 2 × s, 2 × Bu^t, *cis*- and *trans*-isomers), 2.39–2.64 (4 H, m, 2 × C*H*$_2$CH=), 3.74 and 3.75 (6 H, 2 × s, 2 × OCH_3, *cis*- and *trans*-isomers), 4.30–4.46 (2 H, m, 2 × C*H*CO_2Me), 5.08–5.21 (2 H, m, 2 × NH) and 5.36–5.52 (2 H, m, 2 × CH=); $\delta_C\{^1H\}$ (75.4 MHz) 28.3 [C(*C*H_3)$_3$], 30.3 (C-3 and C-6, *cis*-isomer), 35.5 (C-3 and C-6, *trans*-isomer), 52.3 (OCH_3), 53.0 (C-2 and C-7), 79.9 [*C*(CH_3)$_3$], 127.3 (C-4 and C-5, *cis*-isomer), 128.5 (C-4 and C-5, *trans*-isomer), 155.1 (OCONH) and 172.4 (C-1 and C-8); *m*/*z* (CI, NH_3) 431 (MH$^+$, 1%), 275 (MH − CO_2 − 2 × Me_2C=CH_2, 9), 88 (H_2N=$CHCO_2$Me, 74) and 57 (Me_2C=CH_2 + H, 100).

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)pent-4-enoate 32 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)-pent-4-enoate **32** (114 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2$Ru=CHPh **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–red solution was con-

centrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–5:1–1:2 gradient elution) yielded *methyl* 2-(tert-*butoxycarbonylamino*)*undec*-4-*enoate* **42** (70 mg, 45%, mixture of *cis*- and *trans*-isomers) as a colourless oil, recovered starting material **32** (35 mg, 31%) as a white solid and *dimethyl* 2,7-*bis*(tert-*butoxycarbonylamino*)*oct*-4-*enedioate* **41** (17 mg, 16%, mixture of *cis*- and *trans*-isomers) as a gummy beige solid.

Methyl 2-(*tert*-butoxycarbonylamino)undec-4-enoate 42. (Found: C, 65.15; H, 9.7; N, 4.4. $C_{17}H_{31}NO_4$ requires C, 65.14; H, 9.97; N, 4.47%); ν_{max}(neat)/cm^{-1} 3373br (N–H), 1747s (ester C=O) and 1720 (carbamate C=O); δ_H(270 MHz) 0.87 {3 H, t, *J* 7, $[CH_2]_4CH_3$}, 1.19–1.38 {8 H, m, $[CH_2]_4CH_3$}, 1.43 (9 H, s, Bu′), 1.98 {2 H, q, *J* 6.5, $=CHCH_2[CH_2]_4$}, 2.34–2.66 (2 H, m, $=CHCH_2CHCO_2$), 3.72 and 3.73 (3 H, 2 × s, OCH_3, *cis*- and *trans*-isomers), 4.23–4.43 (1 H, m, $CHCO_2Me$), 5.00 (1 H, br d, NH), 5.18–5.32 (1 H, m, $=CHCH_2CHCO_2$) and 5.45–5.61 {1 H, m, $=CH[CH_2]_5$}; δ_C\{^{1}H\} (67.9 MHz) 14.0 (C-11), 22.6 (C-10), 27.3 (C-6, *cis*-isomer), 28.3 [$C(CH_3)_3$], 28.7, 28.9, 29.2 and 29.5 (C-7 and C-8, *cis*- and *trans*-isomers), 30.1 (C-3, *cis*-isomer), 31.6 (C-9), 32.5 (C-6, *trans*-isomer), 35.6 (C-3, *trans*-isomer), 52.1 (OCH_3, *trans*-isomer), 52.2 (OCH_3, *cis*-isomer), 53.2 (C-2), 79.8 [$C(CH_3)_3$], 122.5 (C-4, *cis*-isomer), 123.3 (C-4, *trans*-isomer), 134.5 (C-5, *cis*-isomer), 135.6 (C-5, *trans*-isomer), 155.2 (OCONH) and 172.7 (C-1); *m*/*z* (CI, NH_3) 331 (MNH_4^+, 13%), 314 (MH, 46), 275 ($MNH_4 - Me_2C{=}CH_2$, 100), 258 ($MH - Me_2C{=}CH_2$, 52), 214 ($MH - Me_2C{=}CH_2 - CO_2$, 83), 154 {$CH_3[CH_2]_5CH{=}CHCH_2CH{=}NH_2$, 22} and 88 ($H_2N{=}CHCO_2Me$, 22).

Dimethyl 2,7-bis(*tert*-butoxycarbonylamino)oct-4-enedioate 41. The ^{1}H NMR spectrum was identical to that of the sample isolated from the above cross-metathesis reaction of amino acid **33** with styrene.

2-(*tert*-Butoxycarbonylamino)pent-4-enoic acid 33

2-Aminopent-4-enoic acid (1.88 g, 16.4 mmol) was dissolved in 0.6 M aqueous sodium hydroxide (30 cm^3) and the resulting solution was diluted with 2-methylpropan-2-ol (13 cm^3). Di-*tert*-butyl dicarbonate (4.78 g, 21.9 mmol) was added and the reaction mixture was stirred for 16 h. The resulting aqueous mixture was washed with diethyl ether (10 cm^3) and then concentrated *in vacuo*. The residue remaining was treated with saturated aqueous ammonium chloride (30 cm^3) and then extracted with ethyl acetate (3 × 20 cm^3). The combined organic layers were washed with water (20 cm^3), dried ($MgSO_4$) and concentrated *in vacuo* to yield the title compound **33** (3.31 g, 94%) as a white solid, mp 106–107.5 °C (lit.,[21] 109–111 °C) (Found: C, 55.8; H, 7.7; N, 6.4. $C_{10}H_{17}NO_4$ requires C, 55.80; H, 7.96; N, 6.51%); ν_{max}(Nujol mull)/cm^{-1} 3367s (N–H), 3250–2400br (O–H), 1726vs (acid C=O), 1691vs (carbamate C=O) and 1640w (C=C); δ_H(300 MHz, [$^2H_6$]DMSO) 1.36 (9 H, s, Bu′), 2.23–2.45 (2 H, m, $CH_2CH{=}$), 3.90 (1 H, td, *J* 8 and 5, $CHCO_2H$), 5.02 [1 H, d, *J* 10, $=CHH$ (*trans* to alkyl chain)], 5.07 [1 H, d, *J* 17, $=CHH$ (*cis* to alkyl chain)], 5.75 (1 H, ddt, *J* 17, 10 and 7, $CH_2CH{=}$), 7.07 (1 H, d, *J* 8, NH) and 12.54 (1 H, br s, CO_2H); *m*/*z* (CI, NH_3) 233 (MNH_4^+, 36%), 216 (MH, 16), 177 ($MNH_4 - Me_2C{=}CH_2$, 100), 160 ($MH - Me_2C{=}CH_2$, 13), 133 ($MNH_4 - Me_2C{=}CH_2 - CO_2$, 12), 116 ($MH - Me_2C{=}CH_2 - CO_2$, 52) and 70 ($H_2C{=}CHCH_2CH{=}NH_2$, 27).

tert-Butyl 2-(*tert*-butoxycarbonylamino)pent-4-enoate 34

A solution of *tert*-butyl 2,2,2-trichloroacetimidate (2.80 cm^3, 15.6 mmol) in hexane (32 cm^3) was added *via* a cannula to a stirred solution of 2-(*tert*-butoxycarbonylamino)pent-4-enoic acid **33** (1.67 g, 7.8 mmol) in DCM (16 cm^3), under an atmosphere of nitrogen. Boron trifluoride–diethyl ether (0.155 cm^3, 1.26 mmol) was added and the resulting suspension was stirred for 18 h. The reaction was quenched by addition of sodium hydrogen carbonate (2 g) and the mixture was then filtered through a short pad of silica (light petroleum–diethyl ether, 4:1). After evaporation of the solvents under reduced pressure, the crude product was taken up in pentane (50 cm^3) and filtered (washing the insoluble 2,2,2-trichloroacetamide at the pump with a further 50 cm^3 of pentane). Concentrating the filtrate *in vacuo* yielded the *title compound* **34** (1.92 g, 91%) as a colourless oil (Found: C, 61.8; H, 9.1; N, 5.3. $C_{14}H_{25}NO_4$ requires C, 61.97; H, 9.29; N, 5.16%); ν_{max}(neat)/cm^{-1} 3365br (N–H), 1717vs (carbamate and ester C=O) and 1647w (C=C); δ_H(270 MHz) 1.43 (9 H, s, carbamate Bu′), 1.45 (9 H, s, ester Bu′), 2.22–2.62 (2 H, m, $CH_2CH{=}$), 4.24 (1 H, br q, $CHCO_2Bu'$), 5.04 (1 H, br d, NH), 5.07 [1 H, d, *J* 17, $=CHH$ (*cis* to alkyl chain)], 5.10 [1 H, d, *J* 10, $=CHH$ (*trans* to alkyl chain)] and 5.70 (1 H, ddt, *J* 17, 10 and 7, $CH_2CH{=}$); δ_C\{^{1}H\} (75.4 MHz) 28.0 and 28.3 [2 × $C(CH_3)_3$], 37.0 (C-3), 53.3 (C-2), 79.5 [carbamate $C(CH_3)_3$], 81.8 [ester $C(CH_3)_3$], 118.7 (C-5), 132.5 (C-4), 155.1 (OCONH) and 171.1 (C-1); *m*/*z* (CI, NH_3) 289 (MNH_4^+, 6%), 272 (MH, 76), 216 ($MH - Me_2C{=}CH_2$, 26), 160 ($MH - 2 \times Me_2C{=}CH_2$, 25), 70 ($CH_2{=}CHCH_2CH{=}NH_2$, 81) and 57 ($Me_2C{=}CH_2$ + H, 100).

Cross-metathesis of *tert*-butyl 2-(*tert*-butoxycarbonylamino)-pent-4-enoate 34 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of *tert*-butyl 2-(*tert*-butoxycarbonylamino)-pent-4-enoate **35** (136 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2Ru{=}CHPh$ **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–red solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1:0–9:1–1:2 gradient elution) yielded tert-*butyl* 2-(tert-*butoxycarbonylamino*)*undec*-4-*enoate* **43** (88 mg, 49%, mixture of *cis*- and *trans*-isomers) and recovered starting material **34** (45 mg, 33%) as colourless oils, and *di*-tert-*butyl* 2,7-*bis*(tert-*butoxycarbonylamino*)*oct*-4-*enedioate* **44** (20 mg, 16%, mixture of *cis*- and *trans*-isomers) as a colourless gum.

***tert*-Butyl 2-(*tert*-butoxycarbonylamino)undec-4-enoate 43.** (Found: C, 67.7; H, 10.6; N, 3.8. $C_{20}H_{37}NO_4$ requires C, 67.57; H, 10.49; N, 3.94%); ν_{max}(neat)/cm^{-1} 3365br (N–H) and 1716vs (carbamate and ester C=O); δ_H(270 MHz) 0.87 {3 H, t, *J* 7, $[CH_2]_4CH_3$}, 1.22–1.38 {8 H, m, $[CH_2]_4CH_3$}, 1.43 (9 H, s, carbamate Bu′), 1.45 (9 H, s, ester Bu′), 1.98 {2 H, q, *J* 7, $=CHCH_2[CH_2]_4$}, 2.34–2.66 (2 H, m, $=CHCH_2CHCO_2$), 4.11–4.29 (1 H, m, $CHCO_2Me$), 5.01 (1 H, br d, NH), 5.30 (1 H, dt, *J* 15.3 and 7.2, $=CHCH_2CHCO_2$) and 5.45–5.61 {1 H, m, $=CH[CH_2]_5$}; δ_C\{^{1}H\} (75.4 MHz) 14.0 (C-11), 22.6 (C-10), 27.3 (C-6, *cis*-isomer), 28.0 and 28.3 [2 × $C(CH_3)_3$], 28.8, 28.9, 29.2 and 29.5 (C-7 and C-8, *cis*- and *trans*-isomers), 30.3 (C-3, *cis*-isomer), 31.7 (C-9), 32.5 (C-6, *trans*-isomer), 35.8 (C-3, *trans*-isomer), 53.6 (C-2), 79.4 [carbamate $C(CH_3)_3$], 81.6 [ester $C(CH_3)_3$, *trans*-isomer], 81.7 [ester $C(CH_3)_3$, *cis*-isomer], 122.8 (C-4, *cis*-isomer), 123.5 (C-4, *trans*-isomer), 134.0 (C-5, *cis*-isomer), 135.1 (C-5, *trans*-isomer), 155.1 (OCONH) and 171.3 (C-1); *m*/*z* (CI, NH_3) 611 [$(2\ M + H)^+ - Me_2C{=}CH_2 - CO_2$, 16%], 373 ($MNH_4$, 14), 356 (MH, 100), 317 ($MNH_4 - Me_2C{=}CH_2$, 36), 300 ($MH - Me_2C{=}CH_2$, 40), 261 ($MNH_4 - 2 \times Me_2C{=}CH_2$, 87), 256 ($MH - Me_2C{=}CH_2 - CO_2$, 62), 244 ($MH - 2 \times Me_2C{=}CH_2$, 17), 200 ($MH - CO_2 - 2 \times Me_2C{=}CH_2$, 38), 182 ($MH - CO_2 - H_2O - 2 \times Me_2C{=}CH_2$, 19), 154 {$CH_3[CH_2]_5CH{=}CHCH_2CH{=}NH_2$, 70} and 130 ($H_2N{=}CHCO_2Bu'$, 30).

Di-*tert*-butyl 2,7-bis(*tert*-butoxycarbonylamino)oct-4-enedioate 44. (Found: C, 60.5; H, 9.3; N, 5.3. $C_{26}H_{46}N_2O_8$ requires C, 60.68; H, 9.01; N, 5.44%); ν_{max}(neat)/cm^{-1} 3384br (N–H) and 1716vs (carbamate and ester C=O); δ_H(270 MHz) 1.44 (2 × s) and 1.45 (2 × s) [36 H, 4 × s, 2 × (carbamate and ester Bu′), *trans*- and *cis*-isomers], 2.30–2.66 (4 H, m, 2 × $CH_2CH{=}$), 4.12–

4.32 (2 H, m, 2 × C*H*CO_2Bu^t), 5.00–5.21 (2 H, m, 2 × NH) and 5.37–5.51 (2 H, m, 2 × CH=); $\delta_C\{^1H\}$ (67.9 MHz) 28.0 and 28.3 [carbamate and ester C(CH_3)$_3$], 30.6 (C-3 and C-6, *cis*-isomer), 35.7 (C-3 and C-6, *trans*-isomer), 53.5 (C-2 and C-7), 79.6 [carbamate $C(CH_3)_3$], 81.8 [ester $C(CH_3)_3$, *trans*-isomer], 82.0 [ester $C(CH_3)_3$, *cis*-isomer], 127.2 (C-4 and C-5, *cis*-isomer), 128.4 (C-4 and C-5, *trans*-isomer), 155.2 (OCONH) and 171.1 (C-1 and C-8); *m*/*z* (CI, NH_3) 515 (MH^+, 60%), 459 (MH − $Me_2C{=}CH_2$, 47), 415 (MH − $Me_2C{=}CH_2$ − CO_2, 100), 403 (MH − 2 × $Me_2C{=}CH_2$, 30), 359 (MH − CO_2 − 2 × $Me_2C{=}CH_2$, 93), 315 (MH − 2 × CO_2 − 2 × $Me_2C{=}CH_2$, 48), 303 (MH − CO_2 − 3 × $Me_2C{=}CH_2$, 29), 257 (MH − CO_2 − 3 × $Me_2C{=}CH_2$ − HCO_2H, 27), 201 (MH − CO_2 − 4 × $Me_2C{=}CH_2$ − HCO_2H, 29), 157 (MH − 2 × CO_2 − 4 × $Me_2C{=}CH_2$ − HCO_2H, 22) and 130 ($H_2N{=}CHCO_2Bu^t$, 33).

Cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)but-3-enoate 37 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)but-3-enoate **37** (108 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2Ru{=}CHPh$ **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–brown solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–5 : 1–1 : 2 gradient elution) gave two separate compounds as green oils. Both of these were decolourised by treating separately with activated charcoal (stirring for 30 min in 5 cm^3 of DCM) to yield *methyl* trans-2-(tert-*butoxycarbonylamino*)*dec*-3-*enoate* **45** (11 mg, 7%) and recovered starting material **37** (75 mg, 69%) as colourless oils.

Methyl *trans*-2-(*tert*-butoxycarbonylamino)dec-3-enoate 45. [Found: *m*/*z* (MH^+) 300.2164. $C_{16}H_{30}NO_4$ requires 300.2175]; ν_{max}(neat)/cm^{-1} 3365br (N–H), 1747s (ester C=O) and 1720vs (carbamate C=O); δ_H(270 MHz) 0.87 {3 H, t, *J* 7, $[CH_2]_4CH_3$}, 1.19–1.41 {8 H, m, $[CH_2]_4CH_3$}, 1.44 (9 H, s, Bu^t), 2.03 {2 H, q, *J* 7, $=CHCH_2[CH_2]_4$}, 3.75 (3 H, s, OCH_3), 4.77 (1 H, br t, C*H*CO_2Me), 5.10 (1 H, br s, NH), 5.44 (1 H, dd, *J* 15.5 and 6.0, =C*H*CHCO_2Me) and 5.76 (1 H, dtd, *J* 15.5, 7 and 1, $=CHCH_2$); $\delta_C\{^1H\}$ (67.9 MHz) 14.0 (C-10), 22.6 (C-9), 28.3 [C(CH_3)$_3$], 28.7 (2 × s, C-6 and C-7), 31.6 (C-8), 32.1 (C-5), 52.4 (OCH_3), 55.4 (C-2), 80.0 [$C(CH_3)_3$], 124.1 (C-3), 135.0 (C-4), 154.9 (OCONH) and 172.0 (C-1); *m*/*z* (CI, NH_3) 317 (MNH_4^+, 29%), 300 (MH, 74), 261 (MNH_4 − $Me_2C{=}CH_2$, 100), 244 (MH − $Me_2C{=}CH_2$, 43), 200 (MH − $Me_2C{=}CH_2$ − CO_2, 27) and 140 $\{CH_3[CH_2]_5CH{=}CHCH{=}NH_2$, 79$\}$.

Attempted cross-metathesis of methyl 2-(*tert*-butoxycarbonylamino)prop-2-enoate 39 with oct-1-ene

The general procedure was the same as that described for the cross-metathesis of amino acid **6** with styrene. A nitrogen-saturated solution of methyl 2-(*tert*-butoxycarbonylamino)-prop-2-enoate **39** (101 mg, 0.50 mmol), oct-1-ene (0.156 cm^3, 1.00 mmol) and $Cl_2(PCy_3)_2Ru{=}CHPh$ **1** (21 mg, 0.026 mmol) in 1,2-dichloroethane (2 cm^3) was stirred under a steady stream of nitrogen for 30 h. The resulting orange–brown solution was concentrated *in vacuo* and the residual oil was taken up in diethyl ether (*ca*. 50 cm^3) and stirred overnight, under air. Column chromatography (SiO_2; light petroleum–diethyl ether, 1 : 0–9 : 1 gradient elution) yielded recovered starting material **39** (92 mg, 91%) as a colourless oil.

Cross-metathesis using Wang ester 0.65 mmol g^{-1}

***N*-Fmoc-homoallylglycine, Wang ester 0.65 mmol g^{-1}.** Wang resin (100–200 mesh 1% DVB 0.65 mmol g^{-1}) (2.16 g, 1.4 mmol) was swelled in dichloromethane (25 cm^3) for 5 min at room temperature, then treated sequentially with 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoic acid **13** (0.60 g, 1.68 mmol), 1-(3′-dimethylaminopropyl)-3-ethylcarbodiimide·HCl (0.35 g, 1.8 mmol) and 4-dimethylaminopyridine (85 mg, 0.7 mmol). The reaction mixture was shaken at room temperature for 24 h, filtered through a sinter, and the resin washed sequentially with three cycles of dichloromethane (2 × 15 cm^3) and diethyl ether (2 × 15 cm^3), followed by a final wash with dichloromethane (2 × 15 cm^3). The title resin was then dried for 1 h at room temperature *in vacuo*.

Cross-metathesis reaction. Dodec-1-ene (178 ml, 0.8 mmol) was dissolved in anhydrous dichloromethane (8.5 cm^3) and degassed using the freeze–thaw (3 cycles) method. The solution was added *via* cannula to a mixture of *N*-Fmoc-homoallylglycine, Wang ester (736 mg, 0.4 mmol) and $(Cy_3P)_2Cl_2Ru{=}CHPh$ **1** (16 mg, 0.02 mmol) under nitrogen. The reaction mixture was stirred and heated to reflux for 13 h. The reaction mixture was cooled, filtered through a sinter and washed sequentially with three cycles of dichloromethane (2 × 15 cm^3) and diethyl ether (2 × 15 cm^3), followed by a final wash with dichloromethane (2 × 15 cm^3).

Hydrolysis of the resin product. The resin was swelled in dichloromethane (5 cm^3) for 5 min, then treated with trifluoroacetic acid (5 cm^3). After a few minutes the reaction mixture turned a deep purple colour. The mixture was stirred for 4 h in ambient conditions, then filtered through a sinter and washed sequentially with three cycles of dichloromethane (2 × 15 cm^3) and diethyl ether (2 × 15 cm^3), followed by a final wash with dichloromethane (2 × 15 cm^3). The purple colour was lost during the washing process. The filtrate was concentrated and dried *in vacuo*. This yielded the product (131 mg) as an oil. The ^{1}H NMR spectrum showed the presence of a mixture of a self-metathesis product **31** and the cross-metathesis product **46** in a 3 : 2 ratio respectively.

Cross-metathesis using Wang ester 1.13 mmol g^{-1}

The above procedure was essentially repeated using Wang resin (100–200 mesh 1% DVB 1.13 mmol g^{-1}). This lead to a mixture of self-metathesis product **31** and the cross-metathesis product **46** in a 1 : 3 ratio respectively.

Cross-metathesis using capped Wang ester

Capping of active sites on Wang resin. Wang resin (200–400 mesh 1% DVB 0.6–0.8 mmol g^{-1}) (2.4 g, 1.44 mmol) was swelled in dichloromethane (23 cm^3) and treated at room temperature with *tert*-butyldimethylsilyl chloride (195 mg, 1.3 mmol) and triethylamine (81 ml, 1.3 mmol). The reaction mixture was shaken for 18 h, then filtered through a sinter and washed sequentially with three cycles of dichloromethane (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3), followed by a final wash with dichloromethane (2 × 20 cm^3).

***N*-Fmoc-homoallylglycine, capped Wang ester.** The above Wang resin was swelled in dichloromethane (25 cm^3) for five minutes at room temperature, then treated sequentially with 2-(fluoren-9-ylmethoxycarbonylamino)hex-5-enoic acid **13** (70 mg,0.2mmol),1-(3′-dimethylaminopropyl)-3-ethylcarbodiimde·HCl (50 mg, 0.26 mmol) and 4-dimethylaminopyridine (12 mg, 0.1 mmol). The reaction mixture was shaken at room temperature for 24 h, filtered through a sinter, and the resin washed sequentially with three cycles of dichloromethane (2 × 20 cm^3) and diethyl ether (2 × 20 cm^3), followed by a final wash with dichloromethane (2 × 20 cm^3). The title resin was then dried for an hour at room temperature *in vacuo*.

Cross-metathesis reaction. Dodec-1-ene (178 ml, 0.8 mmol) was dissolved in anhydrous dichloromethane (10 cm^3) and degassed using the freeze–thaw (3 cycles) method. The solution was added *via* cannula to a mixture of *N*-Fmoc-homoallylglycine, capped Wang ester (0.2 mmol) and $(Cy_3P)_2Cl_2Ru{=}CHPh$ **1** (16 mg, 0.02 mmol) under nitrogen. The reaction mixture was stirred and heated to reflux for 16 h. The reaction mixture was cooled, filtered through a sinter and

washed sequentially with three cycles of dichloromethane (2×20 cm^3) and diethyl ether (2×20 cm^3), followed by a final wash with dichloromethane (2×20 cm^3).

Hydrolysis of the resin product. The resin was swelled in dichloromethane (10 cm^3) for 5 min, then treated with trifluoroacetic acid (10 cm^3). After a few minutes the reaction mixture turned a deep purple colour. The mixture was stirred for 4 h in ambient conditions, then filtered through a sinter and washed sequentially with three cycles of dichloromethane (2×15 cm^3) and diethyl ether (2×15 cm^3), followed by a final wash with dichloromethane (2×15 cm^3). The purple colour was lost during the washing process. The filtrate was concentrated and dried *in vacuo*. This yielded 2-(*fluoren*-9-*ylmethoxycarbonylamino*)-*hexadec*-5-*enoic acid* **46** (73 mg, 0.15 mmol, 74 %) as a waxy oil {Found: *m*/*z* [MNH_4^+ − (fluoren-9-ylmethyl) − H_2O] 313.2491. $C_{17}H_{29}NO_3{\cdot}NH_4$ requires 313.2491}; $\nu_{max}(CHCl_3)$/cm^{-1} 3700–3200br (O-H), 1717s (carbamate and acid C=O); δ_H(300 MHz) 0.89 [3H, t, *J* 7, $(CH_2)_9CH_3$], 1.20–2.21 [20 H, m, $(CH_2)_8CH_3$, $CHCH_2CH_2$), 4.24 (1 H, br t, $CHCH_2O$), 4.39–4.53 (3 H, m, $CHCO_2H$ and $CHCH_2O$), 5.13–5.27 (3 H, m, NH and HC=CH), 7.33 (2 H, t *J* 7, fluorenyl 2′-H and 7′H), 7.42 (3 H, t, *J* 7, fluorenyl 3′-H and 6′-H), 7.60 (2 H, br d, fluorenyl 1′-H and 8′-H), 7.78 (2H, d, *J* 7, fluorenyl 4′-H and 5′H) and 8.3–9.4 (1 H, br s, CO_2H); $\delta_C\{^1H\}$ (75.4 MHz) 14.1 (C-16), 22.7 (C-15), 29.3, 29.4, 29.6, 29.7 (m, C-8 to C-14 including *cis*- and *trans*-isomers), 32.0 (C-3), 32.2 and 32.6 (C-4, *cis*- and *trans*-isomer), 47.2 (C-9′), 53.5 (C-2), 67.2 (CH_2O), 120.0, 127.1, 127.8 (fluorenyl C-1′, C-2′, C-3′, C-4′, C-5′, C-6′, C-7′ and C-8′), 125.1 (=$CHCH_2$), 132.5 (=$CHCH_2$), 141.3 and 143.7 (C-4′ and C-8′), 156.1 (OCONH) and 177 (C-1); *m*/*z* (CI, NH_3) 313 {[MNH_4 − (fluoren-9-ylmethyl) − H_2O]$^+$, 45%}, 297 [M − (fluoren-9-ylmethyl), 85], 281 [MH − (fluoren-9-ylmethyl) − OH, 65], 179 [(fluoren-9-ylmethyl) + H, 100].

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