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Synthesis of *N*-Vinyloxazolidinones and Morpholines from Amino Alcohols and Vinylsulfonium Salts: Analysis of the Outcome's Dependence on the N-Protecting Group by Nanospray Mass Spectrometry

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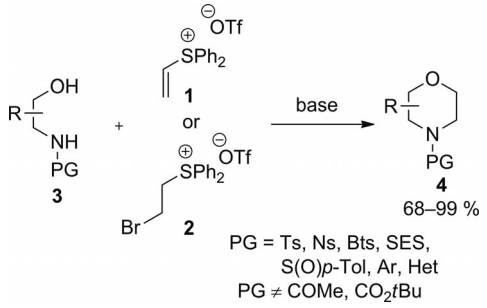
The effect of the nature of the N-protecting group on 1,2-amino alcohols in annulation reactions with diphenylvinylsulfonium triflate has been investigated. Although tosyl and sulfinamide groups give morpholines in high yields, the use of *N*-Cbz leads to a high-yielding synthesis of *N*-vinyloxazolidinones. The reactions were monitored by nanospray MS/MS, which revealed why reactions are successful and the fate of reactive intermediates in the unsuccessful reactions.

Introduction

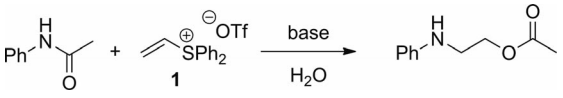
The direct conversion of 1,2-amino alcohols or 1,2-diamines into morpholines or piperazines are important transformations, particularly in the field of medicinal chemistry.[1,2] We recently reported a simple method for this transformation: the reaction of a 1,2-amino alcohol/1,2-diamine with diphenylvinylsulfonium triflate (**1**)[3–5] or bromoethyldiphenylsulfonium triflate (**2**) in the presence of base (Scheme 1).[6]



Scheme 1. Influence of the N-protecting group (N-PG) on the annulation reaction.

Although a range of amino substituents can be used in these transformations, including sulfonamides,[3a,6a] sulfinamides,[6b] aromatic and heteroaromatic groups,[6a] carbonyl-based protecting groups (e.g., amides and Boc-carbamates) cannot.[3a] We have therefore investigated these reactions in more detail and found that the use of *N*-Cbz-carbamates leads to a one-step high-yielding synthesis of *N*-vinyloxazolidinones, which are very useful intermediates in organic synthesis in their own right.[7] Furthermore, by monitoring the reaction by MS/MS analysis,[8] we were able to not only identify the events and therefore the mechanism of the successful reactions but also the competing reaction pathways that ultimately lead to undesired outcomes in the unsuccessful reactions.

The reactions reported herein are unique because related amides and carbamates give very different products. For example, it has been reported that the reactions of amides with diphenylvinylsulfonium triflate (**1**) lead to 1,2-amino esters[5k] [Equation (1)] and reactions of carbamates give oxazolidinones[5h] [Equation (2)].



(1)

(2)

Results and Discussion

We began our studies with a series of amide- and carbamate-derived amino alcohols **3a**–**f**[9] and tested them with sulfonium salt **1** in the presence of a range of bases (Et_3N, DBU, NaH, KO*t*Bu). Although the amino alcohol bearing an *N*-Ts group **3a** led to morpholine **4a** under a variety of

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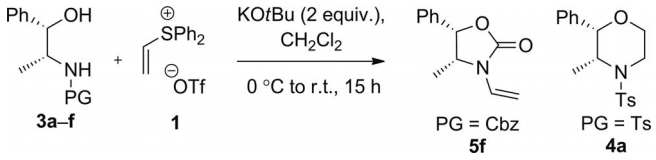
conditions (Table 1, Entry 1), the *N*-carbonyl compounds, except for the *N*-benzyloxy-carbamate, gave a mixture of highly polar compounds (Table 1, Entries 2–5). However, with KO*t*Bu as base the use of the benzyloxy-carbamate led to the formation of *N*-vinyloxazolidinone **5f** in high yield (Table 1, Entry 6). This reaction turned out to be general for a range of substituted *N*-benzyloxy-derived amino alcohols **3f**–**k**, which gave *N*-vinyloxazolidinones **5f**–**k** in good-to-high yields in all cases (Table 2, Entries 1–6).[10]

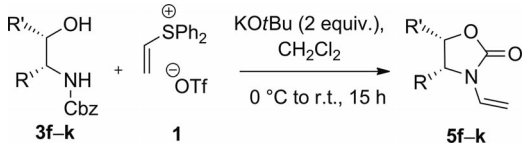
Table 1. Results of annulation reactions with vinylsulfonium triflate **1**.



Entry	**3**	PG	Product	Yield [%]
1	**a**	Ts	**4a**	75
2	**b**	Boc	–	–[a]
3	**c**	CH_3CO	–	–[a]
4	**d**	PhCO	–	–[a]
5	**e**	CF_3CO	–	–[a]
6	**f**	$PhCH_2OCO$	**5f**	86[b]

[a] A mixture of highly polar compounds was obtained. Other bases (Et_3N, DBU, NaH) gave similar results. [b] Alternative bases were not effective in this reaction.

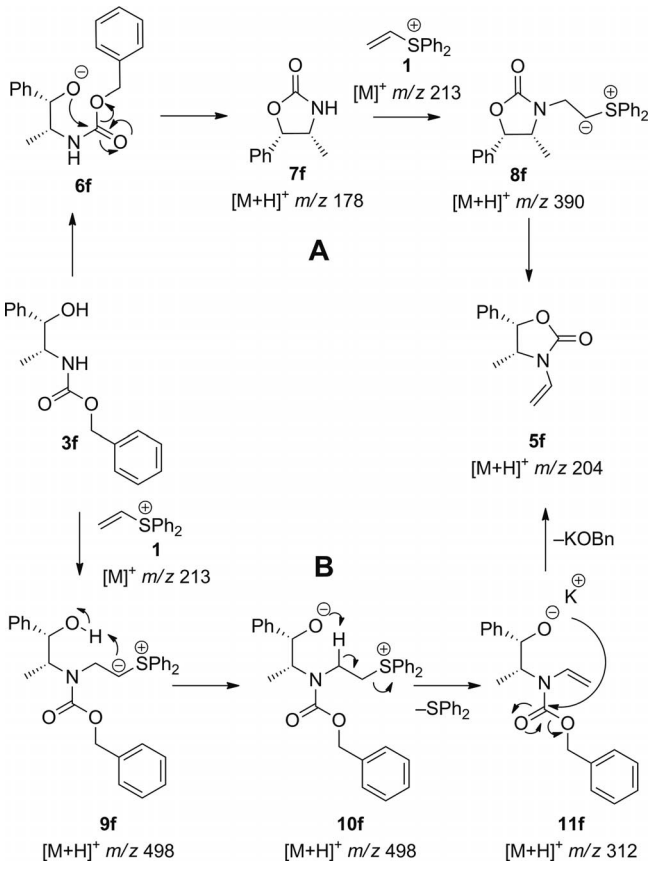
Table 2. Results of annulation reactions with vinylsulfonium triflate **1**.



Entry	R	R′	Product	Yield [%]
1	CH_3	Ph	**5f**	86
2	Ph	H	**5g**	89
3	Ph	Ph	**5h**	90
4	*i*Pr	H	**5i**	66
5	2,2-diMe	H	**5j**	70
6	H	H	**5k**	64

The simple and straightforward synthesis of *N*-vinyloxazolidinones is noteworthy as they have attracted significant attention in recent years. They have been used in [4+2] hetero-Diels–Alder reactions,[7a–7c] in palladium[7d,7e] and chromium[7f]-mediated transformations and in polymerisation reactions.[7g,7h] Although numerous methods have been reported for their synthesis,[11] our protocol is especially mild, practical and uses readily available starting materials.

Two possible pathways (A or B) can be advanced to account for the formation of *N*-vinyloxazolidinones **5f**–**k** (Scheme 2). Pathway A involves the initial formation of oxazolidinone **7f** followed by conjugate addition, proton transfer and subsequent elimination. However, treatment of preformed oxazolidinone **7f** with the vinylsulfonium salt **1** and KO*t*Bu did not furnish any *N*-vinyloxazolidinone **5f**, which suggests that this pathway is unlikely to be operative. Pathway B involves the initial conjugate addition of the *N*-carbamate **3f** to the vinylsulfonium salt **1** followed by ylide-alcohol proton transfer, alkoxide-promoted elimination and finally cyclisation. Indeed, by monitoring the reaction using nanospray MS/MS analysis[8] we were able to detect intermediates **10f** and **11f** along pathway B as well as the product **5f** (Figure 1). Taken together, these observations provide strong evidence that the reaction of the benzyloxy-carbamate **3f** with the vinylsulfonium salt **1** occurs along pathway B.



Scheme 2. Possible pathways for the formation of vinyloxazolidinone **5f**.

The nanospray MS/MS analysis allowed not only the identification of neutral species (e.g., [**5f** + H]$^+$), but also the easy identification of the cationic sulfonium salt intermediates (e.g., [**10f** + H]$^+$). We therefore sought to use this technique to try to discover the fate of unsuccessful reactions involving *N*-Boc-carbamate **3b** and amide **3d** and to identify the intermediates in the successful annulation reactions with sulfonamide **3a** groups (Scheme 3).

The reactions of *N*-Boc **3b** and *N*-COPh **3d** amino alcohols with vinylsulfonium salt **1** followed the same pathway and initially mirrored the reaction of the *N*-benzyloxy-carbamate **3f** group (compare Figure 1 with Figures 2 and 3).

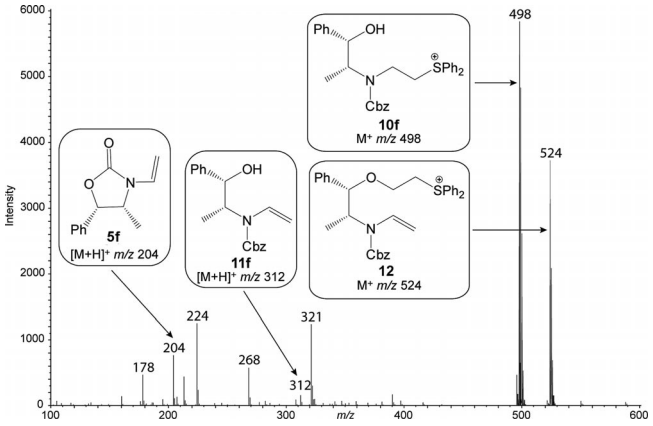


Figure 1. Nanospray MS spectrum of the reaction of hydroxycarbamate **3f** with vinylsulfonium salt **1**.

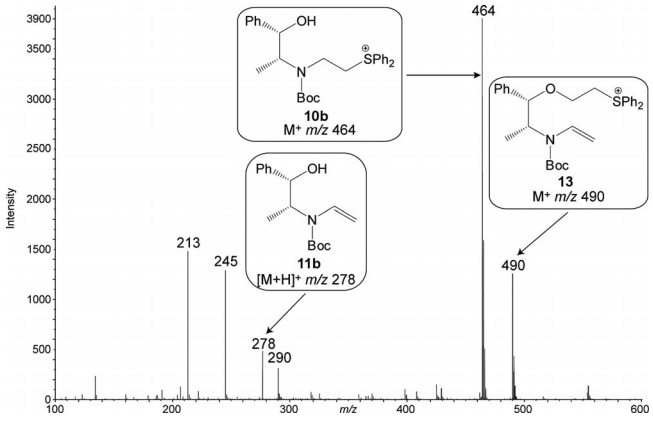
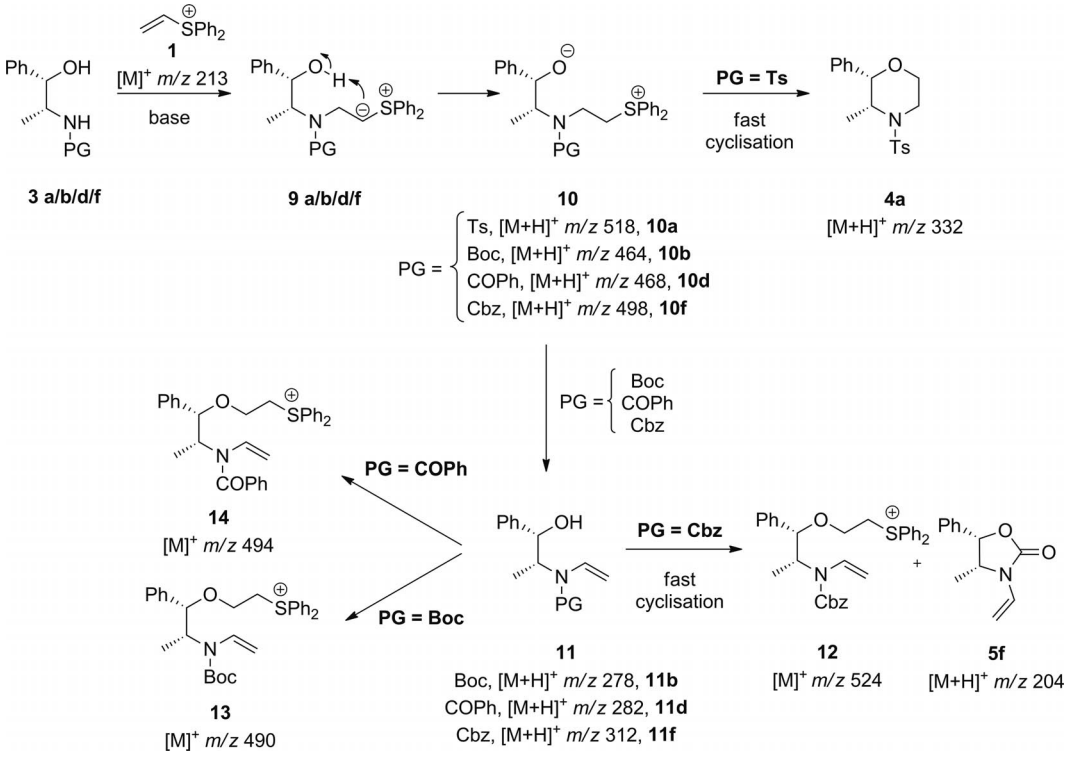


Figure 2. Nanospray MS spectrum of the reaction of *N*-Boc-carbamate **3b** with vinylsulfonium salt **1**.



Scheme 3. Reaction pathways of various protected amino alcohols **3a**,**b**,**d**,**f** under annulation conditions.

Common intermediates **10b/d**, and **11b/d** were clearly identified. However, it seems that if cyclisation to the *N*-carbonyl substituent cannot occur (amide, **d** series) or is especially slow (*N*-Boc, **b** series), the alcohol preferentially reacts with another equivalent of the vinylsulfonium salt **1** leading to the polar sulfonium salts **13/14**, which were readily identified (Figure 2 and Figure 3).[12]

Monitoring the successful annulation reaction of the sulfonamide **3a** clearly revealed the sulfonium salt intermediate **10a** and the product **4a**. The MS/MS of the signal assigned to product **4a** gave the same fragmentation pattern as the isolated and fully characterised morpholine **4a** eliminating the possibility that it was the isomeric *N*-vinyltosylamide **11a** (Figure 4).

The final outcome of the reactions of protected amino alcohols with the vinylsulfonium salt **1** is thus dependent on the fate of the key alkoxide sulfonium salts **10a**,**b**,**d**,**f**. Up to that point, all of the protected amino groups behave in the same way, undergoing conjugate addition and subsequent alcohol-ylide proton transfer. In the case of sulfonamide groups, the key alkoxide **10a** acts as a nucleophile and leads to ring closure to give the morpholine. In the cases of the amide and carbamate groups, the alkoxide acts as a base, instead leading to *N*-vinyl amides/carbamates.

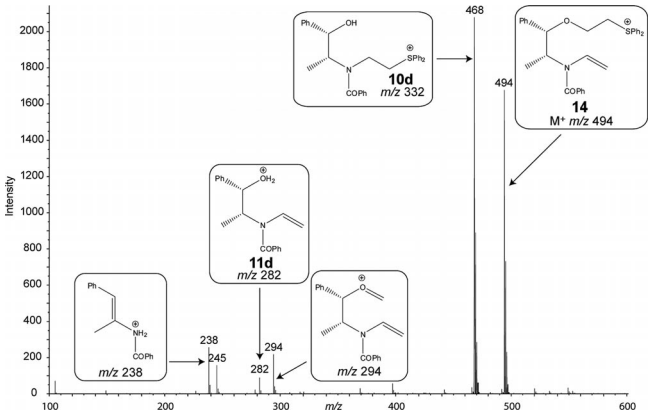


Figure 3. Nanospray MS spectrum of the reaction of *N*-COPh-carbamate **3d** with vinylsulfonium salt **1**.

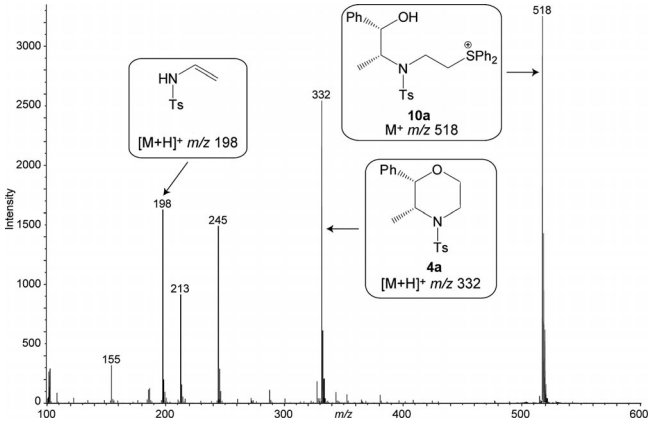


Figure 4. Nanospray MS spectrum of the reaction of sulfonamide **3a** with the vinylsulfonium salt **1**.

Unhindered carbamates can undergo ring closure to the oxazolidinones **5**, but with hindered carbamates and amides they undergo further addition to another vinylsulfonium salt to give the highly polar sulfonium salts **13** and **14** (Scheme 3).

Clearly the alkoxide **10** can act either as a nucleophile or base. We hypothesise that its behaviour is dependent on the nature of the N substituent. Amide/carbamate groups favour E2 elimination whereas sulfonamide and sulfinamide groups favour S_N2 displacement. The reasons for the differing behaviour of the different N substituents may be related to the conformation. In the case of amide or carbamate groups **15**, a hydrogen bond between the carbonyl and CH groups may favour a conformation in which S_N2 is not possible and E2 becomes the preferred pathway (Figure 5). Similar hydrogen bonds between sulfonium and phosphonium salts with carbonyl compounds and boranes have been found to be energetically favourable.[13] In the case of sulfonamides **16** the weaker hydrogen bond and the added steric hindrance arising from the bulkier sulfone may lead to a conformation in which E2 elimination is less favoured and so nucleophilic substitution occurs instead.

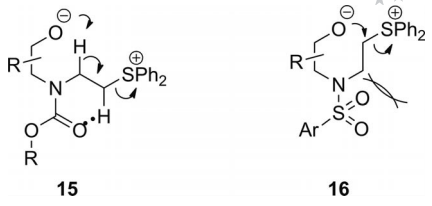


Figure 5. Proposed major conformation of alkoxide intermediates derived from carbamate- (**15**) and sulfonamide-protected (**16**) amino alcohols.

Conclusions

We have discovered a new, facile, one-step synthesis of *N*-vinyloxazolidinones **5f**–**k** from simple *N*-Cbz-amino alcohols **3f**–**k** and vinylsulfonium salt **1**. The pathway for their formation has been mapped out by monitoring the reactions by nanospray MS/MS analysis. More importantly, this technique has enabled us to identify the products and therefore understand why reactions with sulfonamide or *N*-Cbz groups succeed (although give different products) and why others with *N*-Boc and amide groups do not.

Experimental Section

General Procedure A

Cbz Protection of β-Amino Alcohols: β-Amino alcohol (6.6 mmol, 1 equiv.) was dissolved in a 1 M aqueous NaOH solution (7.3 mmol, 1.1 equiv.), stirred for 5 min at 0 °C and then benzyl chloroformate (7.3 mmol, 1.1 equiv.) was added dropwise. A solid material appeared immediately. The reaction mixture was stirred for 2 h at room temperature. The product was separated by filtration, washed with water, dried under high vacuum and recrystallised from ethanol or purified by flash chromatography to afford the target compound.

Benzyl [(1*S*,2*R*)-2-Hydroxy-1-methylphenylethyl]carbamate (3f):[14] Following general procedure A. Yield 93%; white solid. R_f = 0.20 (EtOAc/PE, 3:7). M.p. 114–116 °C (ethanol) (ref.[14] 111–113 °C). $[\alpha]_D^{22}$ = +41 (*c* = 1.5, $CHCl_3$) {ref.[14] $[\alpha]_D^{25}$ = –38.7 (*c* = 1.5, $CHCl_3$) for the enantiomer}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 10 H, ArH), 5.13 (s, 2 H, PhC*H*$_2$), 5.06 (br. d, *J* = 7.5 Hz, 1 H, NH), 4.92–4.85 (m, 1 H, PhC*H*OH), 4.11–4.05 (m, 1 H, NCH), 2.72 (br. s, 1 H, OH), 1.01 (d, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.6 (C=O), 140.7 (C), 136.4 (C), 128.6 (CH), 128.3 (CH), 128.3 (CH), 128.2 (CH), 127.7 (CH), 126.3 (CH), 76.7 (*C*HOH), 66.9 (*C*H$_2$Ph), 52.4 (N*C*H), 14.5 (CH_3) ppm. The spectroscopic data are consistent with those reported.[14]

Benzyl (*R*)-2-Hydroxy-1-phenylethylcarbamate (3g):[15] Following general procedure A. Yield 87%; white solid. R_f = 0.26 (EtOAc/PE, 3:7). M.p. 98–100 °C (ethanol) [ref.[15] 111–113 °C (EtOAc/hexane)]. $[\alpha]_D^{22}$ = –36 (*c* = 1.0, CH_3OH) {ref.[15] $[\alpha]_D^{20}$ = –35.1 (*c* = 1, CH_3OH)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.24 (m, 10 H, ArH), 5.59 (br. s, 1 H, NH), 5.11 (d, *J* = 12.0 Hz, 1 H, PhCH*H*O), 5.06 (d, *J* = 12.0 Hz, 1 H, PhC*H*HO), 4.87–4.80 (m, 1 H, NCH), 3.90–3.75 (m, 2 H, C*H*$_2$OH), 2.30 (br. t, *J* = 6.0 Hz, 1 H, OH) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5 (C=O), 139.2 (C), 136.2 (C), 128.9 (CH), 128.6 (CH), 128.3 (CH), 128.0 (CH), 126.72 (CH), 126.68 (CH), 67.1 (Ph*C*H$_2$), 66.5 (*C*H$_2$OH), 57.2 (N*C*H) ppm. The spectroscopic data are consistent with those reported.[15]

Benzyl (1*R*,2*S*)-2-Hydroxy-1,2-diphenylethylcarbamate (3h):[16] Following general procedure A, except in this case the β-amino alcohol was dissolved in THF/H_2O (5 mL, 3:1) and then 1 M aqueous NaOH was added. Yield 85%; white solid. R_f = 0.71 (EtOAc/PE, 3:7). M.p. 173–174 °C (ethanol) [ref.[16] 172–173 °C (ethanol)]. $[\alpha]_D^{22}$ = –61 (*c* = 1.0, $CHCl_3$) {ref.[16] $[\alpha]_D^{22}$ = –67.4 (*c* = 1, $CHCl_3$)}. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.30–7.20 (m, 5 H, ArH), 7.16–7.13 (m, 6 H, ArH), 6.96–6.93 (m, 4 H, ArH), 5.55 (br. d, *J* = 7.5 Hz, 1 H), 5.20–5.02 (m, 4 H, PhCH_2, 2 PhC*H*), 2.50 (br. s, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.1 (C=O), 139.8 (C), 137.4 (C), 136.4 (C), 128.6 (CH), 128.2 (CH), 128.0 (CH), 127.9 (CH), 126.6 (CH), 76.9 (O*C*H), 67.1 (Ph*C*H_2), 60.9 (N*C*H) ppm. The spectroscopic data are consistent with those reported.[17]

Benzyl (±)-1-Hydroxy-3-methylbutan-2-ylcarbamate (3i):[17] Following general procedure A. Yield 74%; white solid. R_f = 0.25 (EtOAc/PE, 3:7). M.p. 48–50 °C (CH_2Cl_2) [ref.[17] 57–59 °C (benzene/hexane)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.37 (m, 5 H, ArH), 5.46 (d, *J* = 9.2 Hz, 1 H, NH), 4.96–5.19 (m, 2 H, CH_2), 3.34–3.73 (m, 4 H, NCH, PhCH_2, OH), 1.80 (sept., *J* = 7.0 Hz, 1 H, Me_2CH), 0.91 (d, *J* = 11.5 Hz, 3 H, CH_3), 0.88 (d, *J* = 11.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2 (CO), 136.3 (C), 128.2 (CH), 127.8 (CH), 127.7 (CH), 66.4 (CH_2), 62.9 (CH_2), 58.2 (CH), 28.9 (CH), 19.2 (CH_3), 18.3 (CH_3) ppm. The spectroscopic data are consistent with those reported.[17]

Benzyl 1-Hydroxy-2-methylpropan-2-ylcarbamate (3j):[18] Following general procedure A. Yield 81%; clear oil. R_f = 0.31 (EtOAc/PE, 3:7). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22–7.41 (m, 5 H, ArH), 5.27 (s, 1 H, NH), 5.05 (s, 2 H, CH_2), 4.09 (br. s, 1 H, OH), 3.56 (d, *J* = 4.2 Hz, 2 H, PhCH_2), 1.27 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.9 (CO), 136.2 (C), 128.3 (CH), 127.9 (CH), 127.8 (CH), 69.8 (CH_2), 66.3 (CH_2), 54.1 (C), 24.0 (CH_3) ppm. The spectroscopic data are consistent with those reported.[18]

Benzyl 2-Hydroxyethylcarbamate (3k):[19] Following general procedure A. Yield 68%; white solid. R_f = 0.12 (EtOAc/PE, 3:7). M.p. 52–54 °C (CH_2Cl_2) [ref.[19] 62–63 °C (benzene/hexane)]. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.19–7.41 (m, 5 H, ArH), 5.75 (t, *J* = 5.1 Hz, 1 H, NH), 5.06 (s, 2 H, PhCH_2), 3.69 (br. s, 1 H, OH), 3.61 (t, *J* = 5.1 Hz, 2 H, CH_2), 3.27 (q, *J* = 5.3 Hz, 2 H, CH_2) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.9 (CO), 136.2 (C), 128.2 (CH), 127.81 (CH), 127.76 (CH), 66.5 (CH_2), 61.4 (CH_2), 43.2 (CH_2) ppm. The spectroscopic data are consistent with those reported.[19]

General Procedure B

Synthesis of *N*-Vinyloxazolidinones: A stirred solution of *N*-protected β-amino alcohol (1.0 equiv.) in CH_2Cl_2 (0.06 M) was treated with base (2.0 equiv.) at 0 °C under nitrogen. After 10 min a solution of diphenylvinylsulfonium salt **1** (1.2 equiv.) in CH_2Cl_2 (0.1 M) was added dropwise over 2 min and the reaction was stirred for 3 h at 0 °C and then for 12 h at room temp. The reaction was then quenched with saturated ammonium chloride solution (5 mL), extracted with CH_2Cl_2 (3 × 30 mL), washed with brine (10 mL), dried with $MgSO_4$, filtered and concentrated under vacuum. The product was then purified by using flash column chromatography on silica.

(4*R*,5*S*)-4-Methyl-5-phenyl-3-vinyloxazolidin-2-one (5f):[20] Following general procedure B using benzyl (1*S*,2*R*)-1-hydroxy-1-phenylpropan-2-ylcarbamate (**3f**; 20 mg, 0.07 mmol), KO*t*Bu (16 mg, 0.14 mmol) and diphenylvinylsulfonium salt **1** (26 mg, 0.073 mmol). After column chromatography (EtOAc/PE, 3:7) the title compound (12 mg, 86%) was isolated as a colourless gummy solid. R_f = 0.4 (EtOAc/PE, 3:7). $[\alpha]_D^{24}$ = +25 (*c* = 1.0, CH_2Cl_2) {ref.[20] $[\alpha]_D^{25}$ = –26 (*c* = 1.1, CH_2Cl_2) for the enantiomer}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45–7.31 (m, 5 H, ArH), 6.83 (dd, *J* = 16.5, 9.5 Hz, 1 H, C*H*=CH_2), 5.71 (d, *J* = 7.5 Hz, 1 H, PhC*H*), 4.50 (dd, *J* = 9.5, 1.5 Hz, 1 H, CH=CH*H*), 4.41 (dd, *J* = 16.5, 1.5 Hz, 1 H, CH=CH*H*), 4.35–4.41 (m, 1 H, NCH), 0.86 (d, *J* = 6.5 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 134.1 (C), 128.78 (CH), 128.73 (CH), 128.70 (CH), 125.9 (CH), 94.1 (CH_2), 79.2 (CH), 53.9 (CH), 12.9 (CH_3) ppm. The spectroscopic data are consistent with those reported.[20]

(*S*)-4-Phenyl-3-vinyloxazolidin-2-one (5g):[21] Following general procedure B using benzyl (*R*)-2-hydroxy-1-phenylethylcarbamate (**3g**; 40 mg, 0.15 mmol), KO*t*Bu (36 mg, 0.32 mmol) and diphenylvinylsulfonium salt **1** (79 mg, 0.22 mmol). After column chromatography (EtOAc/PE, 3:7) the title compound (25 mg, 89%) was isolated as a white solid. R_f = 0.07 (EtOAc/PE, 3:7). $[\alpha]_D^{22}$ = +112 (*c* = 1.25, CH_2Cl_2) {ref.[21] [α] = +113 (*c* = 1.25, CH_2Cl_2)}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.32 (m, 5 H, ArH), 6.83 (dd, *J* = 16.0, 9.5 Hz, 1 H, *H*C=CH_2), 5.02 (dd, *J* = 9.0, 5.5 Hz, 1 H, PhCH), 4.72 (dd, *J* = 9.0, 9.0 Hz, 1 H, CH*H*O), 4.31 (dd, *J* = 9.5, 1.5 Hz, 1 H, HC=CH*H*), 4.13 (dd, *J* = 9.0, 5.5 Hz, 1 H, C*H*HO), 4.08 (dd, *J* = 16.0, 1.5, Hz, 1 H, HC=CH*H*) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 155.9 (C=O), 138.1 (C), 129.5 (CH), 128.9 (CH), 128.8 (CH), 125.9 (CH), 96.0 (CH_2), 70.7 (CH_2), 58.3 (CH) ppm. The spectroscopic data are consistent with those reported.[21]

(4*R*,5*S*)-4,5-Diphenyl-3-vinyloxazolidin-2-one (5h):[22] Following general procedure B using benzyl (1*R*,2*S*)-2-hydroxy-1,2-diphenylethylcarbamate (**3h**; 60 mg, 0.18 mmol), KO*t*Bu (40 mg, 0.36 mmol) and diphenylvinylsulfonium salt **1** (77 mg, 0.21 mmol). After column chromatography (EtOAc/PE, 3:7) the title compound (43 mg, 90%) was isolated as a white solid. R_f = 0.85 (EtOAc/PE, 3:7). M.p. 169–171 °C (EtOAc) (ref.[21] m.p. 170–171 °C). $[\alpha]_D^{22}$ = +22 (*c* = 1, $CHCl_3$) {ref.[22] $[\alpha]_D$ = +21.7 (*c* = 0.775, $CHCl_3$)}. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.12–6.83 (m, 11 H, ArH, C*H*=CH_2), 5.91 (d, *J* = 8.5 Hz, 1 H, CH), 5.24 (d, *J* = 8.5 Hz, 1 H, CH), 4.36 (dd, *J* = 9.5, 1.0 Hz, 1 H, CH=CH*H*), 4.08 (dd, *J* = 16.0, 1.0 Hz, 1 H, CH=CH*H*) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 155.5 (CO), 133.8 (C), 133.4 (C), 128.7 (CH), 128.5 (CH), 128.4 (CH), 128.3 (CH), 128.0 (CH), 127.1 (CH), 126.4 (CH), 96.3 (CH_2), 80.6 (CH), 63.3 (CH) ppm. The spectroscopic data are consistent with those reported.[22]

(±)-4-Isopropyl-3-vinyloxazolidin-2-one (5i):[23] Following general procedure B using benzyl (±)-1-hydroxy-3-methylbutan-2-ylcarbamate (**3i**; 100 mg, 0.42 mmol), KO*t*Bu (95 mg, 0.85 mmol) and diphenylvinylsulfonium salt **1** (185 mg, 0.51 mmol). After column chromatography (Et_2O/hexanes, 75:25) the title compound (43 mg, 66%) was isolated as a clear oil. R_f = 0.70 (Et_2O/hexanes, 75:25). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.69 (dd, *J* = 16.0, 9.5 Hz, 1 H, C*H*=CH_2), 4.30–4.44 (m, 2 H, CH=CH*H*, CH*H*), 4.08–4.24 (m, 2 H, CH=CH*H*, CH*H*), 3.97 (dt, *J* = 8.5, 3.5 Hz, 1 H, NCH), 2.36 (sept.d, *J* = 7.0, 3.5 Hz, 1 H, Me_2CH), 0.85 (d, *J* = 7.0 Hz, 3 H, CH_3), 0.77 (d, *J* = 7.0 Hz, 3 H, CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 155.6 (CO), 128.8 (CH), 94.0 (CH_2), 62.9 (CH_2), 57.9 (CH), 25.9 (CH), 17.8 (CH_3), 13.8 (CH_3) ppm. The spectroscopic data are consistent with those reported.[23]

4,4-Dimethyl-3-vinyloxazolidin-2-one (5j):[24] Following general procedure B using benzyl 1-hydroxy-2-methylpropan-2-ylcarbamate (**3j**; 100 mg, 0.44 mmol), KO*t*Bu (99 mg, 0.88 mmol) and diphenylvinylsulfonium salt **1** (195 mg, 0.54 mmol). After column chromatography (Et_2O/hexanes, 75:25) the title compound (44 mg, 70%) was isolated as a clear oil. R_f = 0.52 (Et_2O/hexanes, 75:25).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.46 (dd, J = 16.5, 10.0 Hz, 1 H, C*H*=CH_2), 4.94 (dd, J = 16.5, 1.0 Hz, 1 H, CH=CH*H*), 4.54 (dd, J = 10.0, 1.0 Hz, 1 H, CH=CH*H*), 4.03 (s, 2 H, CH_2), 1.49 (s, 6 H, 2 CH_3) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 155.1 (CO), 127.6 (CH), 96.5 (CH_2), 75.2 (CH_2), 58.5 (C), 24.7 (CH_3) ppm. The spectroscopic data are consistent with those reported.[24]

3-Vinyloxazolidin-2-one (5k):[25] Following general procedure B using benzyl 2-hydroxyethylcarbamate (**3k**; 700 mg, 3.57 mmol), KO*t*Bu (801 mg, 7.14 mmol) and diphenylvinylsulfonium salt **1** (1546 mg, 4.27 mmol). After column chromatography (Et_2O/hexanes, 75:25) the title compound (258 mg, 64%) was isolated as a yellow oil. R_f = 0.45 (Et_2O/hexanes, 1:1). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.73 (dd, J = 15.8, 8.9 Hz, 1 H, C*H*=CH_2), 4.28–4.40 (m, 3 H, CH=CH*H*, CH_2), 4.21 (dd, J = 15.8, 1.2 Hz, 1 H, CH=CH*H*), 3.58–3.66 (m, 2 H, CH_2) ppm. ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 155.1 (CO), 129.3 (N*C*H), 93.2 (CH=*C*H_2), 62.0 (CH_2), 41.6 (CH_2) ppm. The spectroscopic data are consistent with those reported.[25]

General Procedure C

Preparation of Sample Reactions for the Tandem MS Investigation: A stirred solution of the *N*-protected β-amino alcohol (1.0 equiv.) in CH_2Cl_2 (0.07 M) was treated with base (2.0 equiv.) at 0 °C under nitrogen. After 10 min a solution of diphenylvinylsulfonium salt **1** (1.2 equiv.) in CH_2Cl_2 (0.1 M) was added dropwise over 2 min, the reaction was stirred at 0 °C for 3 h and then warmed to room temperature. Aliquots of the reaction solution were diluted with CH_2Cl_2 (HPLC grade) and subjected to tandem MS analysis.

Major peaks in the mass spectra were assigned to the proposed structures based on fragmentation in the MS/MS experiments.

Supporting Information (see footnote on the first page of this article): General methods, experimental procedures, and spectroscopic and analytical data for all compounds.

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