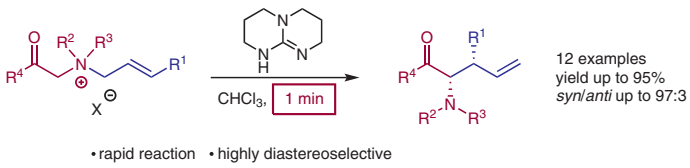
Synthesis A. Murre et al. Paper

Diastereoselective [2,3]-Sigmatropic Rearrangement of *N*-Allyl Ammonium Ylides

Aleksandra Murre
Kristin Erkman
Sandra Kaabel[1]
Ivar Järving
Tõnis Kanger*

Department of Chemistry and Biotechnology, Tallinn University of Technology, Akadeemia tee 15, 12618 Tallinn, Estonia
tonis.kanger@taltech.ee



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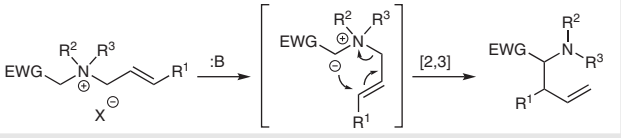
Abstract A rapid and diastereoselective method was developed for the [2,3]-sigmatropic rearrangement of *N*-allyl ammonium ylides, affording products in up to 95% isolated yields and up to 97:3 dr; most of the desired products were formed within 1 minute. For the asymmetric reaction, a chiral auxiliary was introduced to the starting compound, affording the rearrangement product with high diastereoselectivities.

Key words [2,3]-sigmatropic rearrangement, ammonium ylide, auxiliary, diastereoselectivity, oxazolidinyl group, α-amino ketones

Pericyclic reactions are considered to be one of the most useful organic reactions, as they give access to the formation of several new C–C or C–heteroatom bonds in a single step in 100% atom efficiency. The rearrangement of allylic or propargylic ethers (Wittig rearrangement) is one of the most studied of this type of reaction, as it can provide homoallyl alcohols in an enantioselective manner.[2] We have previously investigated the enantioselective [2,3]-Wittig rearrangement of oxindoles[3] and allyloxymalonates.[4] Contrary to a [2,3]-Wittig rearrangement reaction, its aza-analogue can only be performed under superbasic conditions,[5] with strained ring systems[6] or by inserting an alkylsilyl group on the allyl chain of the starting compound.[7] Unactivated acyclic amino compounds do not readily undergo [2,3]-rearrangement reactions. This problem can be bypassed by the quaternization of the tertiary amino group. Ammonium salts can be formed either by in situ quaternization or by alkylation. Alternatively, tertiary amine can be activated by Lewis acids, followed by the subsequent rearrangement reaction.[8–10]

The [1,2]-Stevens rearrangement and [2,3]-sigmatropic rearrangement of amines are transformations, in which, after quaternization, the ammonium ylide is generated either in situ or as an isolated intermediate (Scheme 1).[2b,11,12] Subsequently, the migration of the allyl group occurs, followed by the formation of a new C–C bond. In the case of substitution at the allylic position, the [2,3]-rearrangement leads to the formation of diastereomers. [1,2]- and [2,3]-Rearrangements are competitive with each other, but can be directed towards the desired reaction pathway by selecting suitable reaction conditions. In the rearrangement of *N*-benzylic ammonium ylides, a Sommelet–Hauser rearrangement can compete with [1,2]-Stevens reaction.[13]



Scheme 1 [2,3]-Rearrangement of *N*-allylic ammonium ylides

If the electron-withdrawing group is a carboxylic acid derivative, the [2,3]-rearrangement of *N*-allylic ammonium ylides affords homoallylic tertiary amines, which can also be considered to be α-amino acid derivatives. Often a rearrangement reaction occurs spontaneously after the ammonium ylides are formed. This makes performing Stevens rearrangement diastereoselectively challenging. The [2,3]-rearrangement of allylic ammonium ylides was initially studied by Ollis and Jemison.[14] Tambar and Soheili have shown that high diastereoselectivities were achieved through tandem Pd-catalytic amination, followed by [2,3]-sigmatropic rearrangement.[15] The stereoselectivity of the forming product can also be induced by chiral catalysts or auxiliaries, or through chirality transfer.[16–20] Somfai and co-workers have developed a stoichiometric asymmetric rearrangement reaction using Lewis acids to generate products with excellent enantioselectivities and diastereoselectivities.[10a,21] Sweeney and co-workers have utilized chiral

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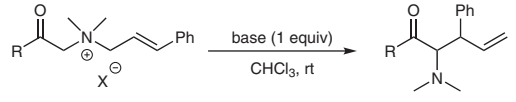
auxiliary control with camphorsultams, producing the rearranged products in excellent selectivities.[22] Up to now, only one catalytic asymmetric method has been developed by Smith and co-workers to achieve enantiomerically pure rearrangement products.[23]

To the best of our knowledge, systematic studies of diastereoselective base-catalyzed [2,3]-sigmatropic rearrangement reactions are mostly based on cyclic ammonium ylides[24] rather than acyclic ones.

Herein we present the results of the base-induced [2,3]-rearrangement of acyclic *N*-allylic ammonium ylides utilizing steric hindrance of the electron-withdrawing group to achieve a diastereoselective outcome (Scheme 2).

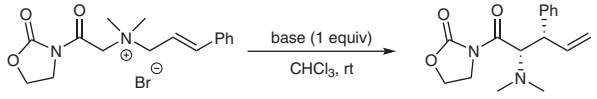


Scheme 2 [2,3]-Sigmatropic rearrangement of *N*-cinnamyl ammonium salts

Our preliminary experiments with cinnamyl-substituted methyl ester derivative **1a** showed that the use of methyl ester as an electron-withdrawing group (EWG) gave poor results. In 24 hours no reaction was observed in the presence of DIPEA, with DBU 84% conversion was reached within 2 hours, but the diastereoselectivity was only 40:60 (*syn*/*anti*). On that note, the ester moiety was replaced with a bulkier and stronger EWG group, oxazolidinyl, to influence both the reactivity of the substrate and the selectivity of the reaction. Subsequently, reaction conditions were screened with this more active starting compound (Table 1).

First, several organic bases were screened for the reaction. There was a clear correlation between the basicity of the used base and the reaction time. With weaker bases (imidazole, DABCO, and DMAP) only up to 46% conversion was obtained in 24 hours (Table 1, entries 1–3). In the case of imidazole, the diastereomeric ratio of the products was not determined, but for DABCO and DMAP, it was equally high. Tertiary amines Et_3N and DIPEA gave even higher diastereoselectivity in 24 hours (Table 1, entries 4 and 5). In terms of selectivity and reaction time, stronger bases, such as DBU and TBD, were equal, giving the rearranged product almost instantly. To determine the reaction time, a sample from the reaction mixture was quenched with acetic acid when the mixture turned from heterogeneous to homogeneous. ^{1}H NMR of the crude reaction mixture showed only the rearranged product after 1 minute (Table 1, entries 6 and 7). Since the reaction with the aforementioned bases was rapid, the reaction in the presence of TBD was also conducted at –45 °C (Table 1, entry 8). The diastereoselectivity rose from 93:7 to 97:3, but the reaction time increased to 2 hours. In the presence of *t*-BuOK the conversion remained

Table 1 Screening of the Reaction Conditions[a]



Entry	Base (1 equiv)	Time	Conversion (%)[b]	Ratio *syn*/*anti*[c]
1	imidazole	24 h	12	–[d]
2	DABCO	24 h	46	92:8
3	DMAP	24 h	28	92:8
4	Et_3N	24 h	100	93:7
5	DIPEA	24 h	100	93:7
6	DBU	1 min	100	92:8
7	TBD[e]	1 min	100	93:7
8[f]	TBD	2 h	100	97:3
9	*t*-BuOK	24 h	34	94:6
10	$NaHCO_3$	72 h	34	80:20
11	K_2CO_3	24 h	25	86:14
12	Cs_2CO_3	2 h	90	89:11
13	$K_3PO_4{\cdot}H_2O$	24 h	4	–[d]
14	K_2HPO_4	24 h	22	92:8

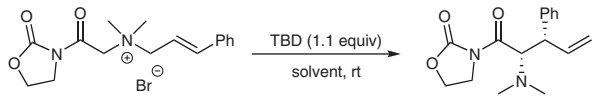
[a] Reaction conditions: **1b** (0.05 mmol), base (0.05 mmol), $CHCl_3$ (200 µL), rt, stirring.
[b] Conversion was determined by ^{1}H NMR of the crude product.
[c] Diastereomeric ratio was determined by ^{1}H NMR of the crude product; the major diastereomer is depicted in the scheme.
[d] Not determined.
[e] TBD = 1,5,7-triazabicyclo[4.4.0]dec-5-ene.
[f] Reaction was carried out at –45 °C.

low (34%) after 24 hours, due to the poor solubility of the base in $CHCl_3$ (Table 1, entry 9). The reaction with inorganic bases turned out to be less selective or slower (Table 1, entries 10–14) than with organic bases. More suitable solvents for inorganic bases (e.g. alcohols, water) could not be selected, as they would act as nucleophiles toward the oxazolidinone ring, resulting in its opening. No [1,2]-rearranged product was determined in the screening study. Based on the obtained results, TBD was chosen as the superior base as it gave the product in a high diastereomeric ratio in a very rapid reaction (reaction time only 1 minute). Next, a variety of solvents were screened.

In other chlorinated solvents, the rearrangement reaction was also complete within 1 minute (Table 2, entries 2 and 3), but the diastereoselectivity dropped compared to chloroform (Table 2, entry 1). The reaction was significantly slower in other organic solvents (Table 2, entries 4–6). As a result, the scope of the reaction was evaluated using TBD in chloroform (Scheme 3).

First we screened the influence of electron-withdrawing groups, starting from methyl ester **1a**. Under the optimal conditions, the reaction was completed in 1 minute, but the

Table 2 Screening of Different Solvents[a]

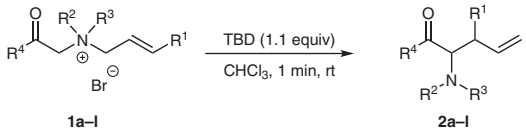


1b **2b**

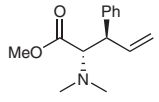
Entry	Solvent	Time	Conversion (%)[b]	Ratio *syn*/*anti*[c]
1	$CHCl_3$	1 min	100	93:7
2	CH_2Cl_2	1 min	100	87:13
3	DCE	1 min	100	86:14
4	DMSO	1 h	83	82:18
5	toluene	1 h	79	86:14
6	THF	1 h	82	82:18

[a] Reaction conditions: **1b** (0.05 mmol), TBD (0.05 mmol), solvent (200 μL), rt, stirring.
[b] Conversion was determined by ^{1}H NMR of the crude product.
[c] Diastereomeric ratio was determined by ^{1}H NMR of the crude product; the major diastereomer is depicted in the scheme.

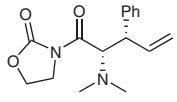
diastereoselectivity of product **2a** remained low (*syn*/*anti* 40:60). In the case of oxazolidinyl derivative **1b**, both geometric isomers *trans*-**1b** and *cis*-**1b** were equally reactive and afforded rearranged products in high yields and diastereoselectivities. In either case, the preferred diastereomer of **2b** was in *syn*-configuration, indicating that the product from *trans*-**1b** was formed through an *endo* transition state and the product from *cis*-**1b** through an *exo* transition state. When the EWG was changed to a Boc-protected amide (compound **1c**), two equivalents of base were required as the nitrogen atom in the amide moiety was also deprotonated by TBD. The yield of the product **2c** remained high (80%), but the diastereoselectivity was 50:50 as determined by ^{1}H and ^{13}C NMR. The 50:50 ratio of diastereomers was caused by enolization, which was additionally confirmed by IR analysis (see Supporting Information). Amide **1d** with the weakest electron-withdrawing group gave no reaction either at room temperature or at elevated temperature. The obtained results revealed that the diastereoselectivity of the rearrangement reaction could be easily directed towards the formation of the *syn*-product by using the oxazolidinyl group as the EWG. Next, we investigated the influence of the nitrogen atom substituents on the selectivity of the reaction. Pyrrolidinyl and benzyl(methyl)amino-substituted starting compounds afforded the products **2e** and **2f** in good yields and diastereoselectivities: 86% (dr 91:9) and 74% (dr 88:12), respectively. When the *N*-cinnamyl substituent was replaced with either *N*-crotyl or *N*-allyl group (**1g** and **1h**, respectively), the starting compounds were extremely moisture sensitive. While the reactions were conducted under typical reaction conditions, mainly the



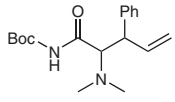
1a–l **2a–l**



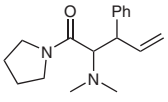
2a[a]
Yield 75%, *syn*/*anti* 40:60



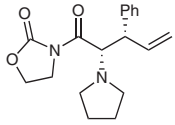
2b
From *trans*-**1b**:
Yield 95%, *syn*/*anti* 93:7
From *cis*-**1b**:
Yield 95%, *syn*/*anti* 94:6



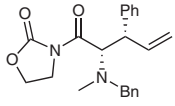
2c[b]
Yield 80%, *syn*/*anti* 50:50



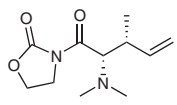
2d[c]
no reaction



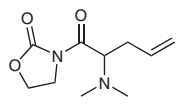
2e
Yield 86%, *syn*/*anti* 91:9



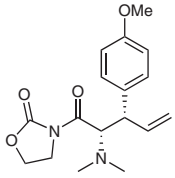
2f
Yield 74%, *syn*/*anti* 88:12



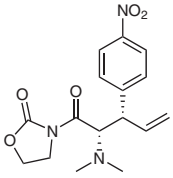
2g
From *trans*-**1g**:
Yield 61%, *syn*/*anti* 57:43[d]
From *cis*-**1g**:
Yield 52%, *syn*/*anti* 57:43[d]



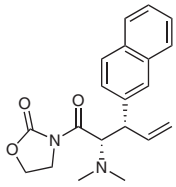
2h
Yield 80%[d,e]



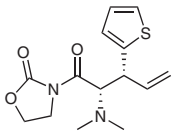
2i
Yield 68%, *syn*/*anti* 89:11



2j
Yield 90%, *syn*/*anti* 86:14



2k
Yield 87%, *syn*/*anti* 91:9



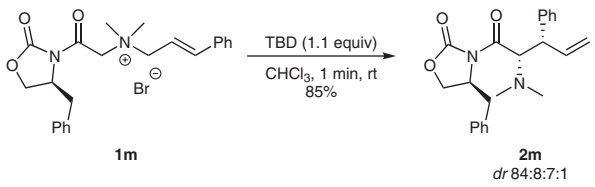
2l
Yield 83%, *syn*/*anti* 86:14

Scheme 3 Scope of the reaction. *Reagents and conditions*: **1a–l** (1 equiv), TBD (1.1 equiv), $CHCl_3$ (0.25 M solution), rt, stirring, 1 min; isolated yields are given. Diastereomeric ratio was determined by ^{1}H NMR of the crude product. Major diastereomers are depicted in the scheme. [a] Starting from the iodide salt of **1a**. [b] TBD (2 equiv), stirring, 30 min. [c] rt and 60 °C, 24 h. [d] Under Ar atmosphere with added molecular sieves (4 Å). [e] The purity of the product was 94%. The main impurity was oxazolidin-2-one, which has the same R_f value as compound **2h**.

formation of hydrolysis products of starting materials **1g** and **1h** (carboxylic acid and oxazolidin-2-one) was observed. It is assumed that in the case of *N*-cinnamyl-substituted starting compounds the phenyl ring shields the carbonyl group of the amide moiety and no nucleophilic side reaction is observed. Subsequently, the reactions were conducted under anhydrous conditions, resulting in product **2g** from *trans*-**1g** in 61% yield and 57:43 diastereoselectivity, and in product **2h** in 80% yield. When a crotyl derivative *cis*-**1g** was used as a starting compound, similar results to *trans*-**1g** were obtained, which showed that the presence of the phenyl ring in the starting compound was essential in order to favor one transition state and, consequently, high diastereoselectivity. Finally, the aromatic substitution effects were evaluated. The rearrangement reaction was not dependent on the electron density of the aromatic ring and both the electron-donating methoxy and the electron-withdrawing nitro group containing starting compounds **1i** and **1j** and naphthyl- and heteroaromatic thienyl-substituted ammonium salts **1k** and **1l** gave the desired products **2i–l** in high yields and dr values.

Since product **2c** was epimerized, causing a 50:50 ratio of diastereomers, additional epimerization studies were conducted with products **2a**, **2b**, **2i**, and **2k**. The experiments revealed that no epimerization occurred with any of the compounds under the reaction conditions.

In order to evaluate possible enantioselective outcome, a chiral auxiliary based approach utilizing (*S*)-4-benzyloxazolidin-2-one in the synthesis of the ammonium salt **1m** was studied (Scheme 4). Under the optimized conditions, the product **2m** was generated in 1 minute with a diastereomeric ratio of 84:8:7:1. The dr of the two *syn*-diastereomers is 84:8 or larger (84:7 or 84:1) which corresponds to at least 83% de. After removal of the auxiliary the *syn*-diastereomer should thus exhibit an enantiopurity of at least 83% ee.



Scheme 4 Auxiliary based [2,3]-sigmatropic rearrangement

The obtained results indicated that both oxazolidinyl and cinnamyl substituents in the starting compound are essential to achieve a high diastereoselectivity of the reaction. The relative *syn*-configuration of the product was determined by a single crystal X-ray structure analysis of compound **2i** (Figure 1a). According to these data, a possible transition state model (Figure 1b) can be proposed to explain the origin of high diastereoselectivity. The ratio of diastereomers was determined by the differences in energies between *endo*- and *exo*-transition states.[25] In the case of the *trans*-substituted double bond, the *endo* cyclic transition state led to the formation of the *syn*-product and the *exo* cyclic to the *anti*-product. The stacking between the phenyl ring and carbonyl group of the oxazolidinyl ring stabilized the *endo*-transition state, affording major diastereomer **2i** with *syn*-configuration. The substituents in the phenyl ring did not weaken the interaction between the phenyl ring and carbonyl group. The fact that starting compounds with an electron-rich and electron-poor phenyl ring (**1i** and **1j**, respectively) led to similar diastereoselectivities revealed that other factors should be also considered. The diastereoselectivity dropped drastically if the oxazolidinyl group was changed to the methoxy group (compound **2a**) or the vinylic aromatic ring was substituted for the methyl group

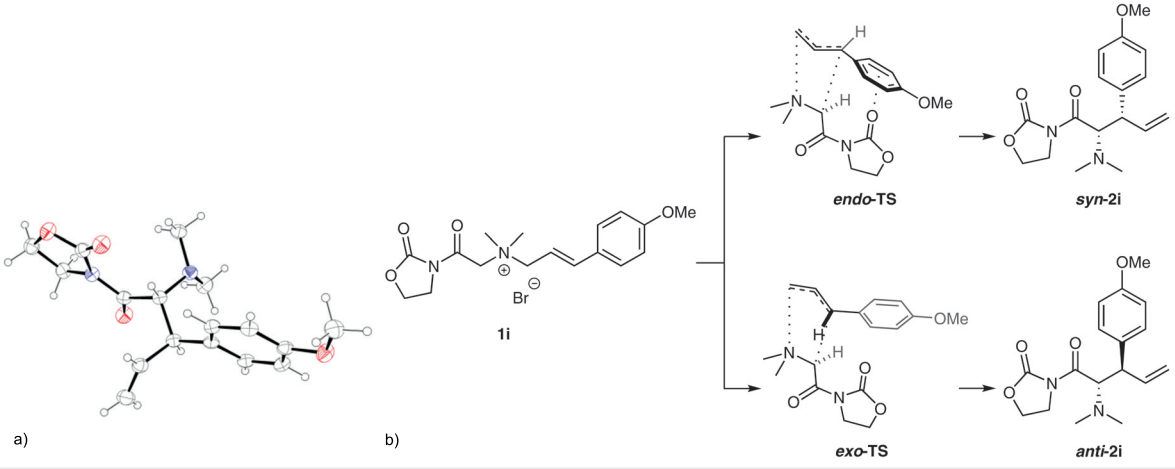


Figure 1 (a) Crystal structure of the major diastereomer of **2i**, showing only the (*R*,*R*)-enantiomer of the racemic *syn*-product. The anisotropic displacement ellipsoids are drawn at 50% probability level. (b) The proposed transition states for *N*-allylic ammonium ylide **1i**.

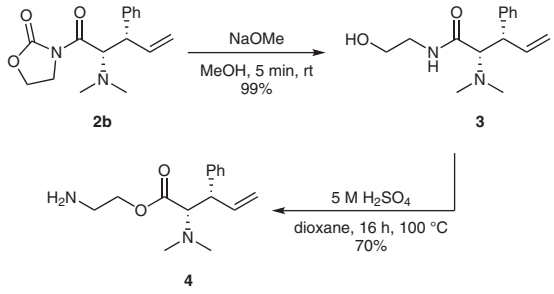
(compound **2g**). If either the oxazolidinyl or an aromatic moiety was absent from the structure, neither of the transition states was favored and diastereomers were formed in almost 1:1 ratio. It is assumed that in the case of *cis*-substituted double bond the reaction goes through an *exo*-transition state, leading to *syn*-products. In this case there are also possible interactions between the phenyl and oxazolidinyl rings.

The removal of the oxazolidinyl group from a bulky substrate in order to achieve carboxylic acid derivatives or alcohols has posed a problem[26] since the introduction of these types of auxiliaries. In general, there are two competitive reaction centers. In the case of the cleavage of the acyclic amide bond, an exocyclic cleavage product is formed. Alternatively, the reaction may occur via attack on the carbonyl group of the oxazolidinone ring, affording an endocyclic cleavage product.

Several attempts with numerous methods were made to cleave or reduce the oxazolidinyl group from compounds **2** (see Supporting Information). Firstly, the most commonly used method involving hydrolysis with $LiOH/H_2O_2$[27] afforded a mixture of different endocyclic cleavage products. Reduction with various hydrides[28] ($NaBH_4$, $LiBH_4$, $LiAlH_4$) at different temperatures (–40 °C to rt) in the presence or absence of various Lewis acids (I_2, $BF_3{\cdot}Et_2O$, BEt_3) gave a mixture of products. The reduction of **2b** with $NaBH_4$ in THF/H_2O provided the products in 66:34 ratio (respectively, *exo*- and *endo*-product). Although full conversion was achieved, the obtained products were inseparable by column chromatography. A recently published method utilizing $Yb(OTf)_3$[29,30] afforded mainly the endocyclic cleavage product. SmI_2 catalysis[31] led to the endocyclic cleavage product which reacted further giving a primary alcohol; additionally, the elimination of tertiary amine occurred. The removal of oxazolidin-2-one in the methoxide–dimethyl carbonate system affording methyl esters has been reported by Kanomata and co-workers.[32] In our case the method did not give the expected product, endocyclic cleavage product and its derivative were formed instead. It is assumed that substituents at the α-position of the carbonyl group shielded the exocyclic cleavage, providing preferably the endocyclic cleavage product.

In the presence of NaOMe in methanol, only the endocyclic cleavage product **3** was obtained in 99% yield (Scheme 5). When the obtained amide **3** was submitted to hydrolysis, a nucleophilic attack by the side chain hydroxyl group on the amide bond occurred, followed by an N–O acyl shift,[33] affording the desired amino ester **4** in 70% yield.

We have described a highly diastereoselective [2,3]-sigmatropic rearrangement of *N*-allyl ammonium ylides. The reaction is very fast, leading to full conversion of the starting material within 1 minute. The diastereoselectivity of the reaction was greatly influenced by the presence of an aromatic substituent on the allyl moiety and the oxazolidinyl group in the electron-withdrawing part of the starting compound. In the chiral auxiliary based approach obtained high dr value indicates at least 83% ee for the major diastereomer. Further insight into the enantioselective [2,3]-sigmatropic rearrangement reaction will be taken in the future. The removal of the oxazolidinyl group was achieved through endocyclic cleavage, followed by an N–O acyl shift, affording amino ester in 69% overall yield.



Scheme 5 The removal of oxazolidinyl group from compound **2b**

Full assignment of ^1H and ^{13}C chemical shifts is based on the 1D and 2D FT NMR spectra measured on a Bruker Avance III 400 MHz instrument. Residual solvent signals were used [$CDCl_3$ δ = 7.26 (^1H NMR), 77.16 (^{13}C NMR) and DMSO-d_6 δ = 2.50 (^1H NMR), 39.52 (^{13}C NMR)] as internal standards. All peak assignments are confirmed by 2D experiments (^1H-^1H COSY, ^1H-^{13}C HSQC, ^1H-^{13}C HMBC). In ^{13}C NMR, 2 C in brackets refers to either two chemically equivalent or two overlapping unique carbon signals. For the determination of diastereomeric ratio, CH integrals of the double bonds were used. If possible, the obtained ratio of diastereomers was also checked using the COCH or $N(CH_3)_2$ integrals. HRMS were recorded by using an Agilent Technologies 6540 UHD Accurate-Mass Q-TOF LC/MS spectrometer by using ESI ionization. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrophotometer. Optical rotations were obtained on an Anton Paar GWB Polarimeter MCP500 at 21 °C in $CHCl_3$ and calibrated with pure solvent as a blank. Precoated silica gel plates (Merck 60 F254) were used for TLC. Column chromatography was performed on a Biotage Isolera Prime preparative purification system with silica gel Kieselgel 63–200 µm. The measured melting points are uncorrected. Purchased chemicals and solvents were used as received. Petroleum ether has bp 40–60 °C. The reactions were performed under an air atmosphere without additional moisture elimination unless stated otherwise.

Synthesis of Starting Materials 1a–l

The synthesis of ammonium salts **1a–l** was achieved as follows: amines were alkylated with unsaturated halides, which were then submitted to quaternization, affording the desired compounds **1**.

Tertiary Amines; General Procedure A (GPA)

Method A: To a solution of unsaturated chloride (1 equiv) in abs EtOH (1 M solution) was added NaI (0.2 equiv) and the mixture was stirred for 5 min at rt Then, secondary amine (5 equiv) was added and the mixture was stirred until the reaction was complete (TLC or ^1H NMR). The mixture was concentrated and the crude mixture was purified by column chromatography (silica gel).

Method B: To a solution of $Me_2NH{\cdot}HCl$ (2 equiv) in water (6 M solution) cooled to 0 °C was added NaOH (4 equiv) in portions. Then unsaturated halide (1 equiv) was added dropwise. The mixture was stirred at 0 °C until the reaction was complete (^1H NMR). The organic layer was separated, dried (NaOH), and filtered. The crude product was purified by distillation.

Method C: To a solution of unsaturated halide (1 equiv) in MeCN (0.5 M solution) was added secondary amine (2 equiv) and K_2CO_3 (1.5 equiv). The mixture was stirred at rt until the reaction was complete (TLC or ^1H NMR). The mixture was concentrated and the crude mixture was purified by column chromatography (silica gel) or by distillation.

(*E*)-*N*,*N*-Dimethyl-3-phenylprop-2-en-1-amine

Following GPA, method A, starting from (*E*)-(3-chloroprop-1-enyl)benzene (391 mg, 2.57 mmol) and Me_2NH (6.423 mL, 12.85 mmol, 2 M solution in THF), the mixture was stirred for 22 h. Purification by column chromatography (2% MeOH/NH_3 in CH_2Cl_2) gave the product (410 mg, 99%) as a yellow amorphous solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.34 (m, 2 H, Ar), 7.34–7.28 (m, 2 H, Ar), 7.26–719 (m, 1 H, Ar), 6.52 (d, *J* = 15.9 Hz, 1 H, ArC*H*), 6.27 (dt, *J* = 15.9, 6.7 Hz, 1 H, C*H*CH_2), 3.08 (dd, *J* = 6.7, 1.2 Hz, 2 H, CH_2), 2.28 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.1, 132.5, 128.6 (2 C), 127.48, 127.42, 126.3 (2 C), 62.1, 45.3 (2 C).

Analytical data are in agreement with the literature data.[23a]

***N*,*N*-Dimethyl-3-phenylprop-2-yn-1-amine**

Following GPA, method C, starting from (3-chloroprop-1-ynyl)benzene (690 mg, 4.58 mmol) and Me_2NH (4.582 mL, 9.16 mmol, 2 M solution in THF), the mixture was stirred for 2 h. Purification by column chromatography (1–2% MeOH/NH_3 in CH_2Cl_2) gave the product (467 mg, 59%) as a colorless oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.40 (m, 2 H, Ar), 7.33–7.27 (m, 3 H, Ar), 3.47 (s, 2 H, CH_2), 2.37 (s, 6 H, $N(CH_3)_2$).

Analytical data are in agreement with the literature data.[23a]

1-Cinnamylpyrrolidine

Following GPA, method A, starting from (*E*)-(3-chloroprop-1-enyl)benzene (100 mg, 0.66 mmol) and pyrrolidine (274 µL, 3.29 mmol), the mixture was stirred for 21 h. Purification by column chromatography (2–5% MeOH/NH_3 in CH_2Cl_2) gave the product (105 mg, 85%) as a pale yellow amorphous solid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.35 (m, 2 H, Ar), 7.35–7.26 (m, 2 H, Ar), 7.25–7.18 (m, 1 H, Ar), 6.54 (d, *J* = 15.8 Hz, 1 H, ArC*H*), 6.34 (dt, *J* = 15.8, 6.7 Hz, 1 H, C*H*CH_2), 3.27 (dd, *J* = 6.7, 1.3 Hz, 2 H, CHC*H*$_2$), 2.62–2.48 (m, 4 H, $N(CH_2)_2$), 1.89–1.73 (m, 4 H, $(CH_2)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 137.2, 131.8, 128.5 (2 C), 127.8, 127.3, 126.3 (2 C), 58.5, 54.1 (2 C), 23.5 (2 C).

Analytical data are in agreement with the literature data.[34]

(*E*)-*N*,*N*-Dimethylbut-2-en-1-amine

Following GPA, method B, starting from commercial (*E*)-1-chlorobut-2-ene (*cis*/*trans* (*Z*/*E*) mixture 15:85, 5 g, 55.22 mmol) and $Me_2NH{\cdot}HCl$ (9.005 g, 110.44 mmol), the mixture was stirred for 2 h. Distillation gave the product (1.538 g, 30%) as a colorless liquid; bp 90–93 °C; *cis*/*trans* (*Z*/*E*) mixture 15:85.

(*E*)-*N*,*N*-Dimethylbut-2-en-1-amine

^1H NMR (400 MHz, $CDCl_3$): δ = 5.64–5.52 (m, 1 H, CH), 5.52–5.41 (m, 1 H, CH), 2.81 (d, *J* = 6.5 Hz, 2 H, CH_2), 2.18 (s, 6 H, $N(CH_3)_2$), 1.68 (dd, *J* = 6.1, 1.1 Hz, 3 H, CH_3).

Analytical data are in agreement with the literature data.[35]

(*Z*)-*N*,*N*-Dimethylbut-2-en-1-amine

^1H NMR (400 MHz, $CDCl_3$): δ = 5.64–5.52 (m, 1 H, CH), 5.52–5.41 (m, 1 H, CH), 2.92 (d, *J* = 6.9 Hz, 2 H, CH_2), 2.21 (s, 6 H, $N(CH_3)_2$), 1.65–1.61 (m, 3 H, CH_3).

***N*,*N*-Dimethylbut-2-yn-1-amine**

Following GPA, method B, starting from 1-bromobut-2-yne (3.418 g, 25.70 mmol) and $Me_2NH{\cdot}HCl$ (4.191 g, 51.40 mmol), the mixture was stirred for 30 min. Distillation gave the product (1.937 g, 78%) as a colorless liquid; bp 90–92 °C.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.15 (q, *J* = 2.3 Hz, 2 H, CH_2), 2.27 (s, 6 H, $N(CH_3)_2$), 1.83 (t, *J* = 2.4 Hz, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 80.4, 74.1, 48.1, 44.1, 3.3.

Analytical data are in agreement with the literature data.[36]

(*E*)-3-(4-Methoxyphenyl)-*N*,*N*-dimethylprop-2-en-1-amine

Following GPA, method A, starting from (*E*)-1-(3-chloroprop-1-enyl)-4-methoxybenzene (263 mg, 1.44 mmol) and Me_2NH (3.560 mL, 7.20 mmol, 2 M solution in THF), the mixture was stirred for 2 h. Purification by column chromatography (1–4% MeOH/NH_3 in CH_2Cl_2) gave the product (131 mg, 48%) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 2 H, Ar), 6.89–6.81 (m, 2 H, Ar), 6.45 (d, *J* = 15.8 Hz, 1 H, ArC*H*), 6.12 (dt, *J* = 15.8, 6.8 Hz, 1 H, C*H*CH_2), 3.80 (s, 3 H, OCH_3), 3.05 (dd, *J* = 6.8, 1.2 Hz, 2 H, CH_2), 2.27 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 159.1, 132.0, 129.9, 127.5 (2 C), 125.2, 114.0 (2 C), 62.2, 55.3, 45.3 (2 C).

Analytical data are in agreement with the literature data.[23a]

(*E*)-*N*,*N*-Dimethyl-3-(4-nitrophenyl)prop-2-en-1-amine

Following GPA, method C, starting from (*E*)-1-(3-bromoprop-1-enyl)-4-nitrobenzene (146 mg, 0.60 mmol) and Me_2NH (603 µL, 1.21 mmol, 2 M solution in THF), the mixture was stirred for 30 min. Purification by column chromatography (2–5% MeOH in CH_2Cl_2) gave the product (74 mg, 60%) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 8.22–8.10 (m, 2 H, Ar), 7.50 (d, *J* = 8.8 Hz, 2 H, Ar), 6.60 (d, *J* = 16.1 Hz, 1 H, ArC*H*), 6.46 (dt, *J* = 15.9, 6.4 Hz, 1 H, C*H*CH_2), 3.14 (d, *J* = 5.3 Hz, 2 H, CH_2), 2.30 (s, 6 H, $N(CH_3)_2$).

Analytical data are in agreement with the literature data.[23a]

(*E*)-*N*,*N*-Dimethyl-3-(naphthalen-2-yl)prop-2-en-1-amine

Following GPA, method C, starting from (*E*)-2-(3-bromoprop-1-enyl)naphthalene (218 mg, 0.88 mmol) and Me_2NH (882 µL, 1.76 mmol, 2 M solution in THF), the mixture was stirred for 1 h. Purification by column chromatography (1–5% MeOH/NH_3 in CH_2Cl_2) gave the product (115 mg, 62%) as an off-white solid; mp 38–40 °C.

IR (KBr): 3055, 2971, 2940, 2853, 2813, 2769, 1455, 1366, 1019, 967, 854, 819, 795, 742 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.76 (m, 3 H, Ar), 7.72 (s, 1 H, Ar), 7.61 (dd, *J* = 8.6, 1.7 Hz, 1 H, Ar), 7.49–7.40 (m, 2 H, Ar), 6.68 (d, *J* = 15.9 Hz, 1 H, Ar*CH*), 6.39 (dt, *J* = 15.9, 6.8 Hz, 1 H, *CH*CH_2), 3.14 (dd, *J* = 6.7, 1.3 Hz, 2 H, CH_2), 2.31 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 134.6, 133.6, 132.9, 132.6, 128.2, 127.9 (2 C), 127.7, 126.2, 126.1, 125.8, 123.6, 62.2, 45.4 (2 C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{18}N$: 212.1434; found: 212.1437.

(*E*)-*N*,*N*-Dimethyl-3-(thiophen-2-yl)prop-2-en-1-amine

Following GPA, method A, starting from (*E*)-2-(3-chloroprop-1-enyl)thiophene (228 mg, 1.44 mmol) and Me_2NH (3.593 mL, 7.19 mmol, 2 M solution in THF), the mixture was stirred for 2 h. Purification by column chromatography (1–5% MeOH/NH_3 in CH_2Cl_2) gave the product (88 mg, 37%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.10–7.16 (m, 1 H, Ar), 6.98–6.89 (m, 2 H, Ar), 6.64 (d, *J* = 15.7 Hz, 1 H, Ar*CH*), 6.10 (dt, *J* = 15.7, 6.8 Hz, 1 H, *CH*CH_2), 3.04 (dd, *J* = 6.8, 1.3 Hz, 2 H, CH_2), 2.27 (s, 6 H, $N(CH_3)_2$).

Analytical data are in agreement with the literature data.[37]

Hydrogenation of Alkynamines

(*Z*)-*N*,*N*-Dimethyl-3-phenylprop-2-en-1-amine

H-cube system was charged with Lindlar CatCart column (5% Pd/$CaCO_3$/Pb) and the H_2 pressure was set to 1 bar with 75% of H_2 production. *N*,*N*-Dimethylbut-2-yn-1-amine (266 mg, 1.67 mmol) was dissolved in MeOH (53 mL) and the solution was pumped through the H-cube system twice with flow rate 1 mL/min. The collected solution was concentrated under reduced pressure and purified by column chromatography (2–5% MeOH in CH_2Cl_2) to give the product (233 mg, 87%) as a yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38–7.30 (m, 2 H, Ar), 7.28–7.20 (m, 3 H, Ar), 6.56 (d, *J* = 11.8 Hz, 1 H, Ar*CH*), 5.78 (dt, *J* = 11.9, 6.4 Hz, 1 H, *CH*CH_2), 3.21 (dd, *J* = 6.4, 2.0 Hz, 2 H, CH_2), 2.25 (s, 6 H, $N(CH_3)_2$).

Analytical data are in agreement with the literature data.[23a]

(*Z*)-*N*,*N*-Dimethylbut-2-en-1-amine

H-cube system was charged with Lindlar CatCart column (5% Pd/$CaCO_3$/Pb) and the H_2 pressure was set to 1 bar with 50% of H_2 production. *N*,*N*-Dimethylbut-2-yn-1-amine (1.275 g, 13.12 mmol) was dissolved in MeOH (255 mL) and the solution was pumped through the H-cube system twice with flow rate 1 mL/min. The collected solution was acidified with aq 1 M HCl and concentrated under reduced pressure. Aq 40% NaOH solution was added to the residue, the aqueous phase was additionally saturated with NaCl and the amine layer was separated. Distillation gave the product (530 mg, 41%) as a colorless liquid; bp 60–75 °C).

(*Z*)-*N*,*N*-Dimethylbut-2-en-1-amine

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66–5.57 (m, 1 H, CH), 5.52–5.44 (m, 1 H, CH), 2.93 (d, *J* = 6.9 Hz, 2 H, CH_2), 2.22 (s, 6 H, $N(CH_3)_2$), 1.67–1.61 (m, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 127.4, 126.9, 55.7, 45.1 (2 C), 13.0.

(*E*)-*N*,*N*-Dimethylbut-2-en-1-amine

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66–5.57 (m, 1 H, CH), 5.52–5.44 (m, 1 H, CH), 2.93 (d, *J* = 6.9 Hz, 2 H, CH_2), 2.22 (s, 6 H, $N(CH_3)_2$), 1.67–1.61 (m, 3 H, CH_3).

Synthesis of Alkyl Halides

3-(2-Bromoacetyl)oxazolidin-2-one

To a suspension of NaH (293 mg, 7.32 mmol, 60% in mineral oil) in THF (5 mL) was added oxazolidin-2-one (490 mg, 5.63 mmol) under an argon atmosphere at 0 °C. The mixture was heated at reflux for 1 h, then cooled to 0 °C, followed by addition of 2-bromoacetyl bromide (515 μL, 5.91 mmol) solution in THF (600 μL). The mixture was stirred at 0 °C for 12 h, then it was diluted with EtOAc and sat. aq NH_4Cl solution was added. The aqueous phase was extracted with EtOAc (3 × 15 mL), the combined organic layers were washed with brine, dried (Na_2SO_4), filtered, and purified by column chromatography (silica gel, 30% EtOAc/petroleum ether) to give the product (764 mg, 65%) as a colorless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.50 (s, 2 H, CH_2Br), 4.52–4.44 (m, 2 H, CH_2O), 4.09–4.04 (m, 2 H, CH_2N).

Analytical data are in agreement with the literature data.[38]

***tert*-Butyl (2-Bromoacetyl)carbamate**

The solution of 2-bromoacetamide (1.000 g, 7.25 mmol) in DCE (7 mL) was cooled to 0 °C. Oxalyl chloride (736 μL, 8.70 mmol) was added dropwise under an argon atmosphere and the mixture was stirred at this temperature for 10 min, then the mixture was heated at 65 °C for 2.5 h. The mixture was cooled to 0 °C and *t*-BuOH (1.386 mL, 14.50 mmol) in DCE (1.5 mL) was added. The mixture was stirred at 0 °C for 25 min, then poured into ice-cold sat. aq $NaHCO_3$ solution. The organic layer was separated and washed with sat. aq $NaHCO_3$ and water, the organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The obtained solid was stirred overnight in hexanes (5 mL), then filtered and dried under reduced pressure to afford the product (1.131 g, 66%) as white crystals; mp 101–103 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.70 (br. s, 1 H, NH), 4.29 (s, 2 H, CH_2), 1.50 (s, 9 H, $C(CH_3)_3$).

Analytical data are in agreement with the literature data.[39]

(*S*)-4-Benzyl-3-(2-bromoacetyl)oxazolidin-2-one

The solution of (*S*)-4-benzyloxazolidin-2-one (300 mg, 1.69 mmol) in THF (8.5 mL) was cooled to –78 °C. BuLi (745 μL, 1.86 mmol, 2.5 M solution in hexane) was added dropwise under an argon atmosphere and the mixture was stirred at –78 °C for 1 h. Then, 2-bromoacetyl bromide (162 μL, 1.86 mmol) was added and the mixture was stirred at –78 °C for 30 min, the mixture was allowed to warm to rt and stirred for 16 h. Sat. aq NH_4Cl solution and water were added at 0 °C, and the aqueous phase was extracted with EtOAc (2 × 15 mL). The combined organic layers were dried ($MgSO_4$), filtered, and purified by column chromatography (silica gel, 5–25% EtOAc/petroleum ether) to give the product (467 mg, 92%) as a pale yellow oil.

$[\alpha]_D^{21}$ +47.1 (*c* 0.09, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37–7.26 (m, 3 H, Ar), 7.24–7.19 (m, 2 H, Ar), 4.74–4.66 (m, 1 H, NCH), 4.54 (d, *J* = 3.0 Hz, 2 H, CH_2Br), 4.31–4.20 (m, 2 H, OCH_2), 3.33 (dd, *J* = 13.4, 3.3 Hz, 1 H, $ArCH_2$), 2.81 (dd, *J* = 13.4, 9.5 Hz, 1 H, $ArCH_2$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{12}H_{13}NO_3$: 298.0073; found: 298.0078.

Analytical data are in agreement with the literature data.[40]

Ammonium Salts 1; General Procedure B (GPB)

To a solution of tertiary amine (1–1.5 equiv) in MeCN (1 M solution) was added a solution of alkyl halide (1 equiv) in MeCN (1 M solution). The mixture was stirred at rt until the reaction was complete by ^{1}H NMR. The solvent was removed under reduced pressure and the crude mixture was either used as received or purified by recrystallization or by stirring in a suitable solvent at rt or at reflux.

(*E*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]-3-phenylprop-2-en-1-aminium Bromide (*trans*-1b)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (469 mg, 2.91 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (605 mg, 2.91 mmol), the mixture was stirred for 2 h. Recrystallization (MeCN/EtOAc) gave the product (743 mg, 69%) as a white solid; mp 170–172 °C.

IR (KBr): 3007, 2972, 2942, 2868, 2789, 1781, 1679, 1638, 1475, 1453, 1390, 1367, 1269, 1215, 1204, 1112, 1041, 925, 704 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 7.62–7.56 (m, 2 H, Ar), 7.44–7.33 (m, 3 H, Ar), 6.89 (d, *J* = 15.7 Hz, 1 H, ArC*H*), 6.50 (dt, *J* = 15.4, 7.5 Hz, 1 H, C*H*CH$_2$), 4.81 (s, 2 H, COCH$_2$), 4.47 (t, *J* = 8.0 Hz, 2 H, CH$_2$O), 4.38 (d, *J* = 7.5 Hz, 2 H, CHC*H*$_2$), 3.95 (t, *J* = 8.0 Hz, 2 H, CH$_2$N), 3.33 (s, 6 H, N(CH$_3$)$_2$).

^{13}C NMR (101 MHz, DMSO): δ = 162.3, 151.2, 139.4, 133.1, 127.0, 126.6 (2 C), 125.2 (2 C), 114.1, 64.7, 61.5, 59.8, 48.7 (2 C), 40.1.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{16}H_{21}N_2O_3$: 289.1547; found: 289.1563.

(*Z*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]-3-phenylprop-2-en-1-aminium Bromide (*cis*-1b)

Following GPB, starting from (*Z*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (126 mg, 0.78 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (163 mg, 0.78 mmol), the mixture was stirred for 2 h. Recrystallization (MeCN/EtOAc) gave the product (236 mg, 82%) as a white solid; mp 157–159 °C.

IR (KBr): 3014, 2965, 2865, 2793, 1783, 1701, 1484, 1412, 1404, 1290, 1230, 1133, 1039, 895, 701 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 7.48–7.40 (m, 2 H, Ar), 7.40–7.33 (m, 1 H, Ar), 7.33–7.24 (m, 2 H, Ar), 7.00 (d, *J* = 11.8 Hz, 1 H, ArC*H*), 6.05 (dt, *J* = 12.3, 6.9 Hz, 1 H, C*H*CH$_2$), 4.80 (s, 2 H, COCH$_2$), 4.56 (d, *J* = 6.5 Hz, 2 H, CHC*H*$_2$), 4.46 (t, *J* = 8.0 Hz, 2 H, CH$_2$O), 3.80 (t, *J* = 8.0 Hz, 2 H, CH$_2$N), 3.27 (s, 6 H, N(CH$_3$)$_2$).

^{13}C NMR (101 MHz, DMSO): δ = 161.7, 150.8, 135.2, 132.4, 126.3 (2 C), 126.2 (2 C), 125.7, 115.7, 61.1, 59.4, 59.0, 48.7 (2 C), 39.7.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{16}H_{21}N_2O_3$: 289.1547; found: 289.1551.

(*E*)-*N*-{2-[(*tert*-Butoxycarbonyl)amino]-2-oxoethyl}-*N*,*N*-dimethyl-3-phenylprop-2-en-1-aminium Bromide (1c)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (140 mg, 0.87 mmol) and *tert*-butyl (2-bromoacetyl)carbamate (207 mg, 0.87 mmol), the mixture was stirred for 21 h. Refluxing in hexane gave the product (347 mg, 91%) as white crystals; mp 84–88 °C.

IR (KBr): 3122, 3061, 2978, 2937, 1777, 1751, 1726, 1705, 1516, 1482, 1455, 1370, 1255, 1232, 1145, 777, 757, 744 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 10.9 (s, 1 H, NH), 7.64–7.54 (m, 2 H, Ar), 7.45–7.32 (m, 3 H, Ar), 6.86 (d, *J* = 15.6 Hz, 1 H, ArC*H*), 6.50 (dt, *J* = 15.4, 7.4 Hz, 1 H, C*H*CH$_2$), 4.49 (s, 2 H, COCH$_2$), 4.33 (d, *J* = 7.3 Hz, 2 H, CHC*H*$_2$), 3.25 (s, 6 H, N(CH$_3$)$_2$), 1.43 (s, 9 H, C(CH$_3$)$_3$).

^{13}C NMR (101 MHz, DMSO): δ = 165.6, 150.1, 141.2, 135.2, 129.0, 128.7 (2 C), 127.2 (2 C), 116.2, 81.9, 66.7, 62.3, 50.7 (2 C), 27.6 (3 C).

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{27}N_2O_3$: 319.2016; found: 319.2030.

(*E*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(pyrrolidin-1-yl)ethyl]-3-phenylprop-2-en-1-aminium Bromide (1d)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (100 mg, 0.62 mmol) and 2-bromo-1-(pyrrolidin-1-yl)ethan-1-one (119 mg, 0.62 mmol). Recrystallization (Et$_2$O/EtOAc) gave the product (125 mg, 57%) as a white solid; mp 117–119 °C.

IR (KBr): 3055, 3010, 2934, 2886, 1651, 1480, 1451, 1370, 1232, 979, 749 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.50–7.41 (m, 2 H, Ar), 7.38–7.29 (m, 3 H, Ar), 7.03 (d, *J* = 15.2 Hz, 1 H, ArC*H*), 6.36–6.22 (m, 1 H, C*H*CH$_2$), 4.97 (s, 2 H, COCH$_2$), 4.88–4.74 (m, 2 H, CHC*H*$_2$), 3.68–3.60 (m, 2 H, CONCH$_2$), 3.57 (s, 6 H, N(CH$_3$)$_2$), 3.47–3.38 (m, 2 H, CONCH$_2$), 1.96–1.87 (m, 2 H, CH$_2$), 1.85–1.76 (m, 2 H, CH$_2$).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 161.7, 144.3, 134.5, 129.7, 128.9 (2 C), 127.3 (2 C), 114.0, 67.1, 61.6, 50.8 (2 C), 46.42, 46.36, 26.0, 23.8.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{17}H_{25}N_2O$: 273.1961; found: 273.1973.

1-Cinnamyl-1-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]pyrrolidin-1-ium Bromide (1e)

Following GPB, starting from 1-cinnamylpyrrolidine (99 mg, 0.53 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (110 mg, 0.53 mmol), the mixture was stirred overnight. Recrystallization (Et$_2$O/EtOAc) gave the product (169 mg, 81%) as a white solid; mp 154–155 °C.

IR (KBr): 3027, 2993, 2962, 2943, 1777, 1706, 1391, 1301, 1219, 1132, 1037, 984, 763 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.53–7.47 (m, 2 H, Ar), 7.39–7.31 (m, 3 H, Ar), 6.91 (d, *J* = 15.7 Hz, 1 H, ArC*H*), 6.41 (dt, *J* = 15.5, 7.6 Hz, 1 H, C*H*CH$_2$), 5.36 (s, 2 H, COCH$_2$), 4.55 (d, *J* = 7.7 Hz, 2 H, CHC*H*$_2$), 4.53–4.47 (m, 2 H, OCH$_2$), 4.29–4.19 (m, 2 H, NCH$_2$), 4.10–4.05 (m, 2 H, CONCH$_2$), 4.05–3.97 (m, 2 H, NCH$_2$), 2.43 (d, *J* = 6.9 Hz, 2 H, CH$_2$), 2.21–2.09 (m, 2 H, CH$_2$).

^{13}C NMR (101 MHz, CDCl$_3$): δ = 164.9, 153.6, 143.1, 134.6, 129.6, 128.9 (2 C), 127.4 (2 C), 115.1, 63.63 (2 C), 63.57, 63.3, 61.9, 42.6, 22.5 (2 C).

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{18}H_{23}N_2O_3$: 315.1703; found: 315.1708.

(*E*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]but-2-en-1-aminium Bromide (*trans*-1g)

Following GPB, starting from (*E*)-*N*,*N*-dimethylbut-2-en-1-amine (105 mg, 1.06 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (200 mg, 0.96 mmol), the mixture was stirred for 2 h. The crude product was dried under reduced pressure (295 mg, quantitative) as a yellow amorphous solid.

IR (KBr): 3015, 2970, 2948, 2916, 1778, 1704, 1476, 1417, 1390, 1300, 1226, 1122, 1038, 880, 755 cm^{-1}.

***trans*-1g**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.38–6.16 (m, 1 H, CH_3CH), 5.71–5.53 (m, 1 H, $CHCH_2$), 5.31 (s, 2 H, $COCH_2$), 4.61–4.55 (m, 2 H, CH_2O), 4.52 (d, *J* = 7.6 Hz, 2 H, $CHCH_2$), 4.17–3.97 (m, 2 H, CH_2N), 3.49 (s, 6 H, $N(CH_3)_2$), 1.82 (dd, *J* = 6.8, 1.4 Hz, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.5, 153.5, 143.0, 117.1, 66.9, 63.6, 63.4, 50.7 (2 C), 42.5, 18.5.

***cis*-1g**

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.38–6.16 (m, 1 H, CH_3CH), 5.71–5.53 (m, 1 H, $CHCH_2$), 5.42 (s, 2 H, $COCH_2$), 4.62–4.53 (m, 4 H, $CHCH_2$, CH_2O), 4.17–3.97 (m, 2 H, CH_2N), 3.52 (s, 6 H, $N(CH_3)_2$), 1.92–1.87 (m, 3 H, CH_3).

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{19}N_2O_3$: 227.1390; found: 227.1395.

(*Z*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]but-2-en-1-aminium Bromide (*cis*-1g)

Following GPB, starting from (*Z*)-*N*,*N*-dimethylbut-2-en-1-amine (59 mg, 0.60 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (83 mg, 0.40 mmol), the mixture was stirred for 2 h. Drying under reduced pressure gave the crude product (123 mg, quantitative) as a white amorphous solid.

IR (KBr): 3015, 2970, 2922, 1779, 1704, 1477, 1417, 1390, 1298, 1227, 1122, 1038, 882, 755 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.25 (dq, *J* = 11.1, 7.1 Hz, 1 H, CH_3CH), 5.67–5.58 (m, 1 H, $CHCH_2$), 5.43 (s, 2 H, $COCH_2$), 4.64–4.54 (m, 4 H, $CHCH_2$, CH_2O), 4.10 (t, *J* = 8.0 Hz, 2 H, CH_2N), 3.53 (s, 6 H, $N(CH_3)_2$), 1.90 (dd, *J* = 7.1, 1.6 Hz, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 162.6, 151.5, 138.1, 114.1, 61.7, 61.4, 59.1, 48.8 (2 C), 40.5, 12.3.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{11}H_{19}N_2O_3$: 227.1390; found: 227.1392.

***N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]prop-2-en-1-aminium Bromide (1h)**

Following GPB, starting from *N*,*N*-dimethylprop-2-en-1-amine (90 mg, 1.06 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (200 mg, 0.96 mmol), the mixture was stirred for 2 h. Drying under reduced pressure gave the crude product (282 mg, quantitative) as a yellow amorphous solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.17–5.93 (m, 1 H, NCH_2CH), 5.84–5.73 (m, 1 H, $CHCH_2$), 5.78–5.71 (m, 1 H, $CHCH_2$), 5.34 (s, 2 H, $COCH_2$), 4.68–4.49 (m, 4 H, $CHCH_2$, CH_2O), 4.19–4.00 (m, 2 H, CH_2N), 3.54 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (400 MHz, $CDCl_3$): δ = 162.5, 151.5, 128.4, 122.5, 65.02, 61.8, 61.7, 49.2 (2 C), 40.6.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{10}H_{17}N_2O_3$: 213.1234; found: 213.1237.

(*E*)-3-(4-Methoxyphenyl)-*N*,*N*-dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]prop-2-en-1-aminium Bromide (1i)

Following GPB, starting from (*E*)-3-(4-methoxyphenyl)-*N*,*N*-dimethylprop-2-en-1-amine (127 mg, 0.66 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (138 mg, 0.66 mmol). The mixture was stirred for 2 h, then dried under reduced pressure. The obtained solid was stirred in EtOAc, filtered under argon, and dried under reduced pressure, to afford the product (213 mg, 80%) as an off-white amorphous solid.

IR (KBr): 3010, 2963, 2934, 2838, 1778, 1704, 1605, 1513, 1391, 1296, 1250, 1123, 1035, 883, 755 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 7.53 (d, *J* = 8.7 Hz, 2 H, Ar), 6.96 (d, *J* = 8.7 Hz, 2 H, Ar), 6.82 (d, *J* = 15.6 Hz, 1 H, ArC*H*), 6.33 (dt, *J* = 15.4, 7.6 Hz, 1 H, $CHCH_2$), 4.79 (s, 2 H, $COCH_2$), 4.46 (t, *J* = 8.0 Hz, 2 H, CH_2O), 4.34 (d, *J* = 7.5 Hz, 2 H, $CHCH_2$), 3.95 (t, *J* = 8.0 Hz, 2 H, CH_2N), 3.78 (s, 3 H, OCH_3), 3.27 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, DMSO): δ = 164.4, 160.0, 153.3, 141.3, 128.8 (2 C), 127.8, 114.1 (2 C), 113.3, 67.1, 63.5, 61.8, 55.3, 50.7 (2 C), 42.2.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{17}H_{23}N_2O_4$: 319.1652; found: 319.1657.

(*E*)-*N*,*N*-Dimethyl-3-(4-nitrophenyl)-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]prop-2-en-1-aminium Bromide (1j)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-(4-nitrophenyl)prop-2-en-1-amine (71 mg, 0.34 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (72 mg, 0.34 mmol). The mixture was stirred for 2 h, then dried under reduced pressure. The obtained solid was stirred in EtOAc, filtered, and dried under reduced pressure, to afford the product (100 mg, 70%) as an off-white solid; mp 151–152 °C.

IR (KBr): 3061, 3032, 3008, 2923, 1792, 1714, 1599, 1516, 1474, 1343, 1289, 1186, 1107, 1023, 936, 873, 739 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 8.27 (d, *J* = 8.8 Hz, 2 H, Ar), 7.88 (d, *J* = 8.8 Hz, 2 H, Ar), 7.02 (d, *J* = 15.7 Hz, 1 H, ArC*H*), 6.78 (dt, *J* = 15.5, 7.4 Hz, 1 H, $CHCH_2$), 4.85 (s, 2 H, $COCH_2$), 4.55–4.46 (m, 2 H, CH_2O), 4.46–4.41 (m, 2 H, $CHCH_2$), 3.96 (t, *J* = 8.0 Hz, 2 H, CH_2N), 3.31 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, DMSO): δ = 164.3, 153.2, 147.3, 141.7, 138.8, 128.4 (2 C), 123.9 (2 C), 121.4, 66.1, 63.6, 62.1, 51.1 (2 C), 42.2.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{16}H_{20}N_3O_5$: 334.1397; found: 334.1405.

(*E*)-*N*,*N*-Dimethyl-3-(naphthalen-2-yl)-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]prop-2-en-1-aminium Bromide (1k)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-(naphthalen-2-yl)prop-2-en-1-amine (114 mg, 0.54 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (112 mg, 0.54 mmol), the mixture was stirred for 1.5 h. Recrystallization (MeCN/EtOAc) gave the product (176 mg, 78%) as a white solid; mp 165–166 °C.

IR (KBr): 3050, 3010, 2954, 2920, 1780, 1704, 1386, 1300, 1219, 1127, 1036, 861, 816, 759, 702 cm^{-1}.

^{1}H NMR (400 MHz, DMSO): δ = 8.02 (s, 1 H, Ar), 7.97–7.90 (m, 3 H, Ar), 7.89–7.83 (m, 1 H, Ar), 7.58–7.50 (m, 2 H, Ar), 7.05 (d, *J* = 15.6 Hz, 1 H, ArC*H*), 6.65 (dt, *J* = 15.3, 7.5 Hz, 1 H, $CHCH_2$), 4.85 (s, 2 H, $COCH_2$), 4.52–4.46 (m, 2 H, CH_2O), 4.46–4.41 (m, 2 H, $CHCH_2$), 3.96 (t, *J* = 8.0 Hz, 2 H, CH_2N), 3.32 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, DMSO): δ = 164.4, 153.3, 141.4, 133.1, 132.9, 132.7, 128.2, 128.1, 127.8, 127.6, 126.7, 126.7, 123.8, 116.7, 66.8, 63.6, 61.9, 50.8 (2 C), 42.2.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{20}H_{23}N_2O_3$: 339.1703; found: 339.1714.

(*E*)-*N*,*N*-Dimethyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]-3-(thiophen-2-yl)prop-2-en-1-aminium Bromide (1l)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-(thiophen-2-yl)prop-2-en-1-amine (80 mg, 0.48 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (100 mg, 0.48 mmol). The mixture was stirred for 2 h,

EtOAc was added and the solid was filtered. Drying under reduced pressure gave the product (115 mg, 64%) as a fine white solid; mp 163–164 °C.

IR (KBr): 3088, 3010, 2959, 2914, 1779, 1761, 1709, 1638, 1390, 1302, 1226, 1133, 1037, 865, 728, 704 cm^{-1}.

^1H NMR (400 MHz, DMSO): δ = 7.60 (d, *J* = 4.9 Hz, 1 H, Ar), 7.31 (d, *J* = 3.2 Hz, 1 H, Ar), 7.14–7.09 (m, 1 H, Ar), 7.09–7.04 (m, 1 H, ArC*H*), 6.18 (dt, *J* = 15.4, 7.6 Hz, 1 H, C*H*CH_2), 4.79 (s, 2 H, $COCH_2$), 4.47 (t, *J* = 8.0 Hz, 2 H, CH_2O), 4.35 (d, *J* = 7.6 Hz, 2 H, CHCH_2), 3.95 (t, *J* = 8.0 Hz, 2 H, CH_2N), 3.26 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, DMSO): δ = 164.4, 153.3, 139.6, 134.7, 128.8, 128.0, 127.5, 114.7, 66.8, 63.6, 61.9, 50.7 (2 C), 42.2.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{19}N_2O_3S$: 295.1111; found: 295.1118.

(*S*,*E*)-*N*-[2-(4-Benzyl-2-oxooxazolidin-3-yl)-2-oxoethyl]-*N*,*N*-dimethyl-3-phenylprop-2-en-1-aminium Bromide (1m)

Following GPB, starting from (*E*)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-amine (54 mg, 0.34 mmol) and (*S*)-4-benzyl-3-(2-bromoacetyl)oxazolidin-2-one (100 mg, 0.34 mmol). The mixture was stirred for 15 min, then dried under reduced pressure. The obtained solid was refluxed in EtOAc, filtered, and dried under reduced pressure to afford the product (113 mg, 73%) as an off-white solid; mp 151–153 °C.

$[\alpha]_D^{21}$ +15.2 (*c* 0.06, $CHCl_3$).

IR (KBr): 3061, 3030, 2985, 2799, 1773, 1693, 1384, 1361, 1213, 1202, 1103, 1040, 795, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.51–7.43 (m, 2 H, Ar), 7.39–7.27 (m, 5 H, Ar), 7.26–7.21 (m, 1 H, Ar), 7.21–7.14 (m, 2 H, Ar), 7.06 (d, *J* = 15.7 Hz, 1 H, ArC*H*), 6.34 (dt, *J* = 15.6, 7.7 Hz, 1 H, C*H*CH_2), 5.48 (d, *J* = 17.7 Hz, 1 H, $COCH_2$), 5.37 (d, *J* = 17.8 Hz, 1 H, $COCH_2$), 4.88–4.78 (m, 2 H, CHCH_2), 4.78–4.70 (m, 1 H, NCH), 4.51 (t, *J* = 8.3 Hz, 1 H, CH_2O), 4.12 (dd, *J* = 8.8, 2.5 Hz, 1 H, CH_2O), 3.61 (s, 3 H, NCH_3), 3.59 (s, 3 H, NCH_3), 3.30 (dd, *J* = 13.6, 3.4 Hz, 1 H, ArCH_2), 2.82 (dd, *J* = 13.4, 9.8 Hz, 1 H, ArCH_2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.6, 153.5, 144.2, 135.1, 134.8, 129.6, 129.5 (2 C), 129.0 (2 C), 128.9 (2 C), 127.38 (2 C), 127.36, 114.2, 67.8, 67.2, 63.9, 55.5, 51.2, 50.8, 38.0.

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{23}H_{27}N_2O_3$: 379.2016; found: 379.2029.

(*E*)-*N*-(2-Methoxy-2-oxoethyl)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-aminium Iodide (1a)

Methyl Cinnamylglycinate

To a solution of methyl glycinate hydrochloride (1.435 g, 11.43 mmol) in MeCN (29 mL) was added (*E*)-(3-chloroprop-1-enyl)benzene (435 mg, 2.86 mmol) and Et_3N (1.912 mL, 13.72 mmol). The mixture was stirred at reflux for 2 h. Then, the solvent was removed under reduced pressure, H_2O was added and the aqueous layer was extracted with CH_2Cl_2 (7 × 30 mL). The combined organic phases were washed with sat. aq $NaHCO_3$ solution and brine, dried ($MgSO_4$), filtered, and purified by column chromatography (silica gel, 3–10% MeOH/CH_2Cl_2) to give the product (586 mg, 47%) as a yellow oil.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.39–7.35 (m, 2 H, Ar), 7.33–7.28 (m, 2 H, Ar), 7.25–7.19 (m, 1 H, Ar), 6.54 (d, *J* = 15.9 Hz, 1 H, ArC*H*), 6.25 (dt, *J* = 15.9, 6.4 Hz, 1 H, C*H*CH_2), 3.73 (s, 3 H, OCH_3), 3.46 (s, 2 H, $COCH_2$), 3.44 (dd, *J* = 6.4, 1.3 Hz, 2 H, CHCH_2).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 173.0, 136.9, 131.9, 128.5 (2 C), 127.6, 127.5, 126.3 (2 C), 51.8, 51.3, 49.8.

Analytical data are in agreement with the literature data.[41]

(*E*)-*N*-(2-Methoxy-2-oxoethyl)-*N*,*N*-dimethyl-3-phenylprop-2-en-1-aminium Iodide (1a)

To a solution of methyl cinnamylglycinate (1.024 g, 4.99 mmol) in MeCN (100 mL) was added K_2CO_3 (655 mg, 4.74 mmol) and MeI (2.485 mL, 39.91 mmol) under an argon atmosphere. The mixture was stirred at reflux for 2 h. After cooling to rt, K_2CO_3 was removed by filtration, the solvent was removed under reduced pressure, and the crude was purified by recrystallization (MeCN/Et_2O) to give the product (1.044 g, 90%) as fine yellow crystals; mp 162–165 °C.

^1H NMR (400 MHz, DMSO): δ = 7.60 (d, *J* = 7.1 Hz, 2 H, Ar), 7.46–7.31 (m, 3 H, Ar), 6.89 (d, *J* = 15.7 Hz, 1 H, ArC*H*), 6.50 (dt, *J* = 15.4, 7.5 Hz, 1 H, C*H*CH_2), 4.44 (s, 2 H, $COCH_2$), 4.32 (d, *J* = 7.5 Hz, 2 H, CHCH_2), 3.77 (s, 3 H, OCH_3), 3.24 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, DMSO): δ = 165.3, 141.4, 135.1, 129.1, 128.7 (2 C), 127.3 (2 C), 116.1, 66.5, 60.3, 52.9, 50.7 (2 C).

HRMS (ESI): *m*/*z* $[M]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1489; found: 234.1499.

(*E*)-*N*-Benzyl-*N*-methyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]-3-phenylprop-2-en-1-aminium Bromide (1f)

(*E*)-*N*-Methyl-3-phenylprop-2-en-1-amine

To a solution of (*E*)-(3-chloroprop-1-enyl)benzene (468 mg, 3.08 mmol) in abs EtOH (3 mL) was added NaI (92 mg, 0.62 mmol) and the mixture was stirred 15 min at rt. The mixture was then cooled to 0 °C and $MeNH_2$ (2.636 mL, 30.75 mmol, 40 wt% in H_2O) was added dropwise. When the addition was complete, the mixture was allowed to warm to rt and it was stirred for 20 h. The mixture was concentrated, and the residue was taken up in CH_2Cl_2. The organic layer was washed with aq 1 M HCl , then the aqueous layer was washed with CH_2Cl_2 and the combined organic layers were washed with aq 1 M HCl. The pH of the combined aqueous layers was adjusted to 12 with aq NH_4OH solution and the aqueous phase was extracted with CH_2Cl_2 (3 × 15 mL), dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the product (231 mg, 51%) as a pale yellow liquid.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.36 (m, 2 H, Ar), 7.33–7.28 (m, 2 H, Ar), 7.25–7.19 (m, 1 H, Ar), 6.53 (d, *J* = 15.9 Hz, 1 H, ArC*H*), 6.29 (dt, *J* = 15.9, 6.3 Hz, 1 H, C*H*CH_2), 3.38 (dd, *J* = 6.3, 1.4 Hz, 2 H, CHCH_2), 2.48 (s, 3 H, CH_3).

Analytical data are in agreement with the literature data.[42]

3-(*N*-Cinnamyl-*N*-methylglycyl)oxazolidin-2-one

To a solution of (*E*)-*N*-methyl-3-phenylprop-2-en-1-amine (231 mg, 1.57 mmol) in MeCN (5.2 mL) was added DIPEA (410 µL, 2.35 mmol) and 3-(2-bromoacetyl)oxazolidin-2-one (326 mg, 1.57 mmol). The mixture was stirred at rt for 2 h, then the solvent was removed under reduced pressure, the residue was taken up in CH_2Cl_2 and sat. aq NH_4Cl was added. The aqueous phase was extracted with CH_2Cl_2 (10 × 10 mL), the combined organic layers were dried (Na_2SO_4), filtered, and purified by column chromatography (silica gel, 5–15% EtOAc/$CHCl_3$) to give the product (319 mg, 74%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.36 (m, 2 H, Ar), 7.34–7.28 (m, 2 H, Ar), 7.26–7.20 (m, 1 H, Ar), 6.55 (d, *J* = 15.9 Hz, 1 H, ArC*H*), 6.31 (dt, *J* = 15.9, 6.8 Hz, 1 H, C*H*CH_2), 4.40 (t, *J* = 8.1 Hz, 2 H, CH_2O), 4.00 (t, *J* = 8.1 Hz, 2 H, CH_2N), 3.91 (s, 2 H, $COCH_2$), 3.38 (d, *J* = 6.5 Hz, 2 H, CHCH_2), 2.48 (s, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 153.5, 136.7, 133.6, 128.6 (2 C), 127.7, 126.4 (2 C), 126.3, 62.6, 60.0, 58.8, 42.9, 42.3.

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{15}H_{18}NaN_2O_3$: 297.1210; found: 297.1214.

(*E*)-*N*-Benzyl-*N*-methyl-*N*-[2-oxo-2-(2-oxooxazolidin-3-yl)ethyl]-3-phenylprop-2-en-1-aminium Bromide (1f)

To a solution of 3-(*N*-cinnamyl-*N*-methylglycyl)oxazolidin-2-one (119 mg, 0.43 mmol) in MeCN (870 μL) was added BnBr (52 μL, 0.43 mmol). The mixture was stirred at rt for 24 h, then dried under reduced pressure and the residue was refluxed in EtOAc to give the product (150 mg, 78%) as fine white crystals; mp 91–94 °C.

IR (KBr): 3061, 3027, 3007, 2962, 2920, 1778, 1702, 1453, 1391, 1298, 1224, 1127, 1038, 803, 736, 703 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68–7.28 (m, 10 H, Ar), 6.96 (d, *J* = 15.6 Hz, 1 H, ArC*H*), 6.41 (dt, *J* = 15.4, 7.5 Hz, 1 H, C*H*CH_2), 5.35–5.19 (m, 2 H, $ArCH_2$), 5.19–5.02 (m, 2 H, $COCH_2$), 4.93–4.80 (m, 1 H, CHC*H*$_2$), 4.63–4.55 (m, 1 H, CHC*H*$_2$), 4.55–4.44 (m, 2 H, CH_2O), 4.13–4.03 (m, 2 H, CH_2N), 3.43 (s, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 164.5, 153.3, 144.0, 134.7, 133.3 (2 C), 131.0, 129.6, 129.5 (2 C), 128.9 (2 C), 127.5 (2 C), 127.1, 114.2, 66.2, 64.5, 63.5, 59.9, 48.0, 42.6.

HRMS (ESI): *m*/*z* [M]$^+$ calcd for $C_{22}H_{25}N_2O_3$: 365.1860; found: 365.1873.

Diastereomeric [2,3]-Sigmatropic Rearrangement Reaction of Ammonium Salts 1a–l; General Procedure

The solution or suspension of ammonium salt **1** (1 equiv) and TBD (1.1 equiv) was stirred in $CHCl_3$ (0.25 M solution) at rt for 1 min. The mixture was concentrated and the crude was purified by column chromatography (silica gel). Diastereomers were not separable by column chromatography. A diastereomeric ratio after the purification is shown.

Methyl 2-(Dimethylamino)-3-phenylpent-4-enoate (2a)

Following the general procedure, starting from **1a** (36 mg, 0.10 mmol). Purification by column chromatography (1–5% EtOAc/CH_2Cl_2) gave the product (15 mg, 75%) as a white solid; dr *syn*/*anti* 42:58 (^{1}H NMR).

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.07 (m, 5 H, Ar), 6.18 (ddd, *J* = 17.0, 10.1, 8.4 Hz, 1 H, CH_2CH), 5.23–5.13 (m, 2 H, CH_2CH), 3.87–3.77 (m, 1 H, COCH), 3.71–3.59 (m, 1 H, ArCH), 3.47 (s, 3 H, OCH_3), 2.45 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.1, 140.8, 138.9, 128.55 (2 C), 128.2 (2 C), 126.9, 116.1, 71.8, 50.6, 49.8, 41.3 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.07 (m, 5 H, Ar), 5.97–5.86 (m, 1 H, CH_2CH), 5.14–5.02 (m, 2 H, CH_2CH), 3.87–3.77 (m, 1 H, COCH), 3.75 (s, 3 H, OCH_3), 3.71–3.59 (m, 1 H, ArCH), 2.30 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.2, 140.8, 138.6, 128.54 (2 C), 127.9 (2 C), 126.7, 116.6, 70.9, 50.7, 50.1, 41.4 (2 C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{20}NO_2$: 234.1489; found: 234.1478.

3-[2-(Dimethylamino)-3-phenylpent-4-enoyl]oxazolidin-2-one (2b)

Following the general procedure, starting from *trans*-**1b** (74 mg, 0.20 mmol) or *cis*-**1b** (74 mg, 0.20 mmol). Purification by column chromatography (5–15% EtOAc/CH_2Cl_2) gave the product (55 mg, 95% from *trans*-**1b**; 55 mg, 95% from *cis*-**1b**) as a white solid; dr *syn*/*anti* 92:8 (from *trans*-**1b**), 95:5 (from *cis*-**1b**) (^{1}H NMR).

IR (KBr): 2980, 2937, 2867, 2831, 2789, 1769, 1689, 1484, 1387, 1365, 1218, 1205, 1108, 1041, 932, 758, 703, 668 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.23 (m, 4 H, Ar), 7.21–7.15 (m, 1 H, Ar), 5.84 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1 H, CH_2CH), 5.36 (d, *J* = 11.3 Hz, 1 H, COCH), 5.02 (dt, *J* = 17.0, 1.0 Hz, 1 H, C*H*$_2$CH), 4.92 (dd, *J* = 10.1, 1.4 Hz, 1 H, C*H*$_2$CH), 4.38–4.29 (m, 2 H, CH_2O), 4.06–3.88 (m, 2 H, CH_2N), 3.79 (dd, *J* = 11.2, 8.9 Hz, 1 H, ArCH), 2.22 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 153.6, 140.9, 138.7, 128.6 (2 C), 128.1 (2 C), 126.7, 116.8, 65.2, 61.9, 50.4, 42.1, 41.2 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31–7.23 (m, 4 H), 7.21–7.15 (m, 1 H), 6.12 (ddd, *J* = 16.5, 10.7, 8.6 Hz, 1 H), 5.29 (d, *J* = 11.5 Hz, 1 H), 5.12–5.09 (m, 1 H), 5.09–5.05 (m, 1 H), 4.20–4.09 (m, 1 H), 3.95–3.87 (m, 1 H), 3.77–3.71 (m, 2 H), 3.52–3.35 (m, 1 H), 2.41 (s, 6 H).

HRMS (ESI): *m*/*z* [M + Na]$^+$ calcd for $C_{16}H_{20}NaN_2O_3$: 311.1366; found: 311.1371.

tert-Butyl [2-(Dimethylamino)-3-phenylpent-4-enoyl]carbamate (2c)

Following a modification of the general procedure, starting from **1c** (80 mg, 0.20 mmol), the mixture was stirred in the presence of TBD (56 mg, 0.40 mmol) for 30 min. Purification by column chromatography (10–15% EtOAc/CH_2Cl_2) gave the product (51 mg, 80%) as a white solid; dr 50:50 (^{1}H NMR).

IR (KBr): 3106, 3076, 2996, 2936, 2882, 2838, 2785, 1742, 1691, 1502, 1455, 1370, 1236, 1152, 1073, 987, 914, 856, 752, 697 cm^{-1}.

IR (film): 3272, 2980, 2935, 2834, 2791, 1755, 1694, 1514, 1455, 1393, 1231, 1147, 989, 917, 857, 756, 700 cm^{-1}.

Diastereomer 1 (I1)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (br s, 1 H, NH), 7.37–7.13 (m, 5 H, Ar), 6.23–6.12 (m, 1 H, CH_2CH), 5.17–5.09 (m, 2 H, C*H*$_2$CH), 3.89–3.83 (m, 1 H, ArCH), 2.44 (s, 6 H, $N(CH_3)_2$), 1.41 (s, 9 H, $C(CH_3)_3$).

Diastereomer 2 (I2)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.88 (br s, 1 H, NH), 7.37–7.13 (m, 5 H, Ar), 6.08–5.95 (m, 1 H, CH_2CH), 5.13–5.00 (m, 2 H, C*H*$_2$CH), 3.85–3.78 (m, 1 H, ArCH), 2.28 (s, 6 H, $N(CH_3)_2$), 1.51 (s, 9 H, $C(CH_3)_3$).

Both Isomers

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.9 (2 C) (CHCO), 150.0 (OCO), 149.8 (OCO), 141.5 (I2, *i*-Ar), 140.7 (I1, *i*-Ar), 138.9 (I2, CH_2CH), 138.5 (I1, CH_2CH), 128.5 (4 C) (*m*-Ar), 128.4 (2 C) (*o*-Ar), 128.2 (2 C) (*o*-Ar),

126.8 (*p*-Ar), 126.6 (*p*-Ar), 116.8 (I1, *C*H_2CH), 116.2 (I2, *C*H_2CH), 82.5 (I2, *C*$(CH_3)_3$), 82.3 (I1, *C*$(CH_3)_3$), 69.9 (*C*HCO), 68.8 (*C*HCO), 49.9 (I2, Ar*C*H), 49.8 (I1, Ar*C*H), 41.9 (2 C) (I1, N$(CH_3)_2$), 41.4 (2 C) (I2, N$(CH_3)_2$), 28.0 (3 C) (I2, C$(CH_3)_3$), 27.9 (3 C) (I1, C$(CH_3)_3$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{27}N_2O_3$: 319.2016; found: 319.2024.

3-[3-Phenyl-2-(pyrrolidin-1-yl)pent-4-enoyl]oxazolidin-2-one (2e)

Following the general procedure, starting from **1e** (37 mg, 0.09 mmol). Purification by column chromatography (20–25% EtOAc/CH_2Cl_2) gave the product (25 mg, 86%) as a white solid; dr *syn*/*anti* 90:10 (^{1}H NMR).

IR (KBr): 3027, 2966, 2831, 2801, 1774, 1693, 1385, 1360, 1216, 1201, 1105, 1040, 759, 702 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.12 (m, 5 H, Ar), 6.01–5.91 (m, 1 H, CH_2CH), 5.46 (d, *J* = 10.5 Hz, 1 H, COCH), 5.08–5.01 (m, 1 H, *CH*$_2$CH), 4.96 (dd, *J* = 10.2, 1.3 Hz, 1 H, *CH*$_2$CH), 4.35–4.27 (m, 1 H, CH_2O), 4.28–4.22 (m, 1 H, CH_2O), 4.01–3.94 (m, 1 H, CH_2N), 3.90–3.81 (m, 2 H, ArCH, CH_2N), 2.72–2.63 (m, 2 H, NCH_2), 2.58–2.49 (m, 2 H, NCH_2), 1.53–1.44 (m, 4 H, $(CH_2)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 153.5, 141.2, 138.5, 128.4 (2 C), 128.1 (2 C), 126.5, 116.7, 63.2, 61.9, 51.5, 48.9 (2 C), 42.2, 23.5 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.11 (m, 5 H), 6.17 (ddd, *J* = 16.9, 10.4, 8.2 Hz, 1 H), 5.51 (d, *J* = 11.4 Hz, 1 H), 5.06–4.99 (m, 2 H), 4.19–4.09 (m, 1 H), 4.01–3.92 (m, 1 H), 3.90–3.81 (m, 1 H), 3.79–3.71 (m, 1 H), 3.46–3.36 (m, 1 H), 2.97–2.84 (m, 2 H), 2.75–2.63 (m, 2 H), 1.74–1.62 (m, 4 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{18}H_{23}N_2O_3$: 315.1703; found: 315.1713.

3-{2-[Benzyl(methyl)amino]-3-phenylpent-4-enoyl}oxazolidin-2-one (2f)

Following the general procedure, starting from **1f** (42 mg, 0.09 mmol). Purification by column chromatography (1–2% EtOAc/CH_2Cl_2) gave the product (25 mg, 74%) as a colorless oil; dr (*syn*/*anti*) 85:15 (^{1}H NMR).

IR (KBr): 3062, 3027, 2982, 2924, 2799, 1775, 1693, 1453, 1385, 1217, 1104, 1041, 759, 701 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36–7.15 (m, 5 H, Ar), 7.07–6.98 (m, 3 H, Ar), 6.71–6.61 (m, 2 H, Ar), 5.87 (ddd, *J* = 17.1, 9.9, 8.9 Hz, 1 H, CH_2CH), 5.50 (d, *J* = 11.4 Hz, 1 H, COCH), 5.07–5.00 (m, 1 H, *CH*$_2$CH), 4.95–4.89 (dd, *J* = 10.3, 1.1 Hz, 1 H, *CH*$_2$CH), 4.40–4.28 (m, 2 H, CH_2O), 4.04–3.91 (m, 2 H, CH_2N), 3.91–3.82 (m, 1 H, ArCH), 3.75 (d, *J* = 13.8 Hz, 1 H, $ArCH_2$), 3.36 (d, *J* = 13.8 Hz, 1 H, $ArCH_2$), 2.08 (s, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.3, 153.6, 140.7, 139.5, 138.6, 128.6 (2 C), 128.4 (2 C), 128.2 (2 C), 127.9 (2 C), 126.6 (2 C), 116.8, 65.3, 61.9, 57.4, 50.9, 42.1, 37.8.

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.08 (m, 10 H), 6.23 (ddd, *J* = 18.1, 10.1, 8.3 Hz, 1 H), 5.44 (d, *J* = 11.5 Hz, 1 H), 5.16–5.06 (m, 2 H), 4.17–4.08 (m, 1 H), 4.05–3.92 (m, 1 H), 3.97–3.90 (m, 1 H), 3.93–3.85 (m, 1 H), 3.80–3.69 (m, 1 H), 3.60 (d, *J* = 13.6 Hz, 1 H), 3.50–3.40 (m, 1 H), 2.25 (s, 3 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{25}N_2O_3$: 365.1860; found: 365.1867.

3-[2-(Dimethylamino)-3-methylpent-4-enoyl]oxazolidin-2-one (2g)

Following a modification of the general procedure, starting from *trans*-**1g** (127 mg, 0.41 mmol) or *cis*-**1g** (118 mg, 0.38 mmol), the reaction was stirred in freshly distilled $CHCl_3$ (1.6 mL and 1.5 mL, respectively) under an argon atmosphere in the presence of powdered 4 Å molecular sieves (300 mg and 220 mg, respectively). Purification by column chromatography (5–15% EtOAc/CH_2Cl_2) gave the product (57 mg, 61% from *trans*-**1g**; 45 mg, 52% from *cis*-**1g**) as a pale yellow amorphous solid; dr *syn*/*anti* 60:40 (*trans*-**1g**), 58:42 (*cis*-**1g**) (^{1}H NMR).

IR (KBr): 2979, 2934, 2871, 2831, 2791, 1776, 1692, 1454, 1385, 1361, 1218, 1204, 1104, 1040, 920, 761 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.66 (ddd, *J* = 17.2, 10.1, 8.7 Hz, 1 H, CH_2CH), 5.01 (dd, *J* = 17.1, 2.7 Hz, 1 H, *CH*$_2$CH), 4.93 (dd, *J* = 10.2, 1.8 Hz, 1 H, *CH*$_2$CH), 4.66 (d, *J* = 10.8 Hz, 1 H, COCH), 4.37 (dd, *J* = 8.8, 7.3 Hz, 2 H, CH_2O), 4.12–3.98 (m, 2 H, CH_2N), 2.71–2.57 (m, 1 H, CH_3CH), 2.36 (s, 6 H, N$(CH_3)_2$), 1.10 (d, *J* = 6.7 Hz, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.2, 153.5, 140.4, 116.0, 66.3, 61.8, 42.0, 41.1 (2 C), 38.6, 17.2.

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.85 (ddd, *J* = 17.3, 10.2, 8.5 Hz, 1 H, CH_2CH), 5.15–5.09 (m, 1 H, *CH*$_2$CH), 5.07 (dd, *J* = 10.2, 1.8 Hz, 1 H, *CH*$_2$CH), 4.72 (d, *J* = 10.7 Hz, 1 H, COCH), 4.46–4.38 (m, 2 H, CH_2O), 4.01–3.87 (m, 2 H, CH_2N), 2.85–2.70 (m, 1 H, CH_3CH), 2.35 (s, 6 H, N$(CH_3)_2$), 0.94 (d, *J* = 6.7 Hz, 3 H, CH_3).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 153.4, 141.1, 114.7, 66.6, 61.84, 42.2, 41.1 (2 C), 37.6, 17.6.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{11}H_{19}N_2O_3$: 227.1390; found: 227.1393.

3-[2-(Dimethylamino)pent-4-enoyl]oxazolidin-2-one (2h)

Following a modification of the general procedure, starting from **1h** (118 mg, 0.40 mmol), the mixture was stirred in freshly distilled $CHCl_3$ (1.6 mL) under an argon atmosphere in the presence of powdered 4 Å molecular sieves (300 mg). Purification by column chromatography (50–55% EtOAc/CH_2Cl_2) gave the product (68 mg, 80%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.83–5.68 (m, 1 H, CH_2CH), 5.09 (dd, *J* = 17.0, 1.5 Hz, 1 H, *CH*$_2$CH), 5.02 (dd, *J* = 10.2, 1.4 Hz, 1 H, *CH*$_2$CH), 4.72 (dd, *J* = 8.9, 5.7 Hz, 1 H, COCH), 4.42–4.34 (m, 2 H, CH_2O), 4.05–3.95 (m, 2 H, CH_2N), 2.59–2.48 (m, 1 H, COCH*CH*$_2$), 2.42–2.32 (m, 1 H, COCH*CH*$_2$), 2.36 (s, 6 H, N$(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 172.1, 153.2, 134.4, 117.6, 62.7, 61.9, 42.4, 41.4 (2 C), 30.8.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{10}H_{17}N_2O_3$: 213.1234; found: 213.1236.

3-[2-(Dimethylamino)-3-(4-methoxyphenyl)pent-4-enoyl]oxazolidin-2-one (2i)

Following the general procedure, starting from **1i** (80 mg, 0.20 mmol), Purification by column chromatography (10% EtOAc/CH_2Cl_2) gave the product (43 mg, 68%) as a white solid; dr (*syn*/*anti*) 86:14 (^{1}H NMR).

IR (KBr): 3079, 2982, 2937, 2833, 2786, 1770, 1691, 1514, 1478, 1395, 1370, 1243, 1224, 1205, 1105, 1044, 1029, 917, 812, 656 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.26–7.20 (m, 2 H, Ar), 6.92–6.83 (m, 2 H, Ar), 5.87 (ddd, *J* = 17.1, 10.1, 8.8 Hz, 1 H, CH_2CH), 5.36 (d, *J* = 11.3 Hz, 1 H, COCH), 5.07–5.01 (m, 1 H, CH_2CH), 4.95 (dd, *J* = 10.1, 1.5 Hz, 1 H, CH_2CH), 4.45–4.35 (m, 2 H, CH_2O), 4.11–3.94 (m, 2 H, CH_2N), 3.79 (s, 3 H, OCH_3), 3.83–3.77 (m, 1 H, ArCH), 2.28 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.9, 158.3, 153.7, 139.0, 132.9, 129.0 (2 C), 116.4, 114.1 (2 C), 65.3, 61.9, 55.2, 49.5, 42.1, 41.2 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.18–7.11 (m, 2 H), 6.83–6.76 (m, 2 H), 6.21–6.09 (m, 1 H), 5.30 (d, *J* = 11.5 Hz, 1 H), 5.14–5.07 (m, 2 H), 4.26–4.17 (m, 1 H), 4.11–3.94 (m, 1 H), 3.93–3.85 (m, 1 H), 3.83–3.76 (m, 1 H), 3.76 (s, 3 H), 3.59–3.50 (m, 1 H), 2.45 (s, 6 H, $N(CH_3)_2$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{17}H_{23}N_2O_4$: 319.1652; found: 319.1656.

3-[2-(Dimethylamino)-3-(4-nitrophenyl)pent-4-enoyl]oxazolidin-2-one (2j)

Following the general procedure, starting from **1j** (83 mg, 0.20 mmol). Purification by column chromatography (2–5% EtOAc/CH_2Cl_2) gave the product (60 mg, 90%) as a yellow amorphous solid; dr (*syn*/*anti*) 83:17 (^{1}H NMR).

IR (KBr): 3080, 2984, 2933, 2838, 2794, 1783, 1769, 1690, 1523, 1387, 1344, 1197, 1105, 1038, 920, 802, 729 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.23–8.15 (m, 2 H, Ar), 7.49–7.43 (m, 2 H, Ar), 5.82 (ddd, *J* = 17.0, 10.1, 8.8 Hz, 1 H, CH_2CH), 5.46 (d, *J* = 11.5 Hz, 1 H, COCH), 5.16–5.09 (m, 1 H, CH_2CH), 5.04 (dd, *J* = 10.1, 1.6 Hz, 1 H, CH_2CH), 4.49–4.39 (m, 2 H, CH_2O), 4.13–3.93 (m, 3 H, CH_2N, ArCH), 2.25 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.7, 153.7, 148.8, 146.8, 137.0, 129.0 (2 C), 123.9 (2 C), 118.4, 64.9, 62.0, 50.3, 42.1, 41.0 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14–8.10 (m, 2 H), 7.43–7.40 (m, 2 H), 6.19–6.08 (m, 1 H), 5.40 (d, *J* = 11.5 Hz, 1 H), 5.21–5.16 (m, 1 H), 5.13–5.07 (m, 1 H), 4.33–4.24 (m, 1 H), 4.24–4.17 (m, 1 H), 4.13–3.93 (m, 1 H), 3.92–3.86 (m, 1 H), 3.70–3.59 (m, 1 H), 2.44 (s, 6 H).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{16}H_{20}N_3O_5$: 334.1397; found: 334.1411.

3-[2-(Dimethylamino)-3-(naphthalen-2-yl)pent-4-enoyl]oxazolidin-2-one (2k)

Following the general procedure, starting from **1k** (84 mg, 0.20 mmol). Purification by column chromatography (10% EtOAc/CH_2Cl_2) gave the product (59 mg, 87%) as a white solid; dr (*syn*/*anti*) 87:13 (^{1}H NMR).

IR (KBr): 3004, 2972, 2931, 2832, 2785, 1778, 1684, 1388, 1358, 1202, 1120, 1043, 918, 823, 749 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.64 (m, 4 H, Ar), 7.51–7.34 (m, 3 H, Ar), 5.98 (ddd, *J* = 17.1, 10.1, 8.8 Hz, 1 H, CH_2CH), 5.55 (d, *J* = 11.3 Hz, 1 H, COCH), 5.15–5.09 (m, 1 H, CH_2CH), 5.00 (dd, *J* = 10.2, 1.4 Hz, 1 H, CH_2CH), 4.47–4.35 (m, 2 H, CH_2O), 4.14–3.97 (m, 2 H, CH_2N), 4.08–3.97 (m, 1 H, ArCH), 2.29 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 169.6, 151.6, 136.4, 136.3, 131.6, 130.5, 126.2, 125.6 (2 C), 124.8, 124.0, 123.8, 123.4, 114.9, 63.0, 59.8, 48.5, 40.0, 39.1 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.64 (m, 4 H), 7.51–7.34 (m, 3 H), 6.31–6.21 (m, 1 H), 5.48 (d, *J* = 11.5 Hz, 1 H), 5.19–5.15 (m, 2 H), 4.14–4.07 (m, 1 H), 3.76–3.70 (m, 2 H), 3.43–3.36 (m, 2 H), 2.50 (s, 6 H, $N(CH_3)_2$).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{20}H_{23}N_2O_3$: 339.1703; found: 339.1708.

3-[2-(Dimethylamino)-3-(thiophen-2-yl)pent-4-enoyl]oxazolidin-2-one (2l)

Following the general procedure, starting from **1l** (75 mg, 0.20 mmol). Purification by column chromatography (5–7% EtOAc/CH_2Cl_2) gave the product (49 mg, 83%) as a white solid; dr (*syn*/*anti*) 85:15 (^{1}H NMR).

IR (KBr): 2977, 2937, 2876, 2803, 1770, 1682, 1454, 1394, 1369, 1223, 1110, 1045, 922, 712 cm^{-1}.

Major Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.23–7.18 (m, 1 H, Ar), 6.98–6.93 (m, 2 H, Ar), 5.90 (ddd, *J* = 17.1, 10.1, 8.9 Hz, 1 H, CH_2CH), 5.22 (d, *J* = 11.2 Hz, 1 H, COCH), 5.19–5.12 (m, 1 H, CH_2CH), 5.09 (dd, *J* = 10.1, 1.3 Hz, 1 H, CH_2CH), 4.45–4.35 (m, 2 H, CH_2O), 4.12 (dd, *J* = 11.1, 8.9 Hz, 1 H, ArCH), 4.09–3.94 (m, 2 H, CH_2N), 2.35 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 153.5, 143.8, 137.7, 126.3, 125.0, 124.6, 118.0, 66.0, 61.9, 44.8, 42.1, 41.1 (2 C).

Minor Diastereomer

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.15–7.11 (m, 1 H), 6.91–6.87 (m, 2 H), 6.10 (ddd, *J* = 16.9, 10.2, 8.5 Hz, 1 H), 5.30 (d, *J* = 11.4 Hz, 1 H), 5.20–5.14 (m, 2 H), 4.33–4.25 (m, 1 H), 4.23–4.15 (m, 2 H), 3.96–3.88 (m, 1 H), 3.77–3.69 (m, 1 H), 2.44 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.3, 153.2, 143.5, 138.7, 126.9, 124.7, 124.1, 116.0, 66.2, 61.8, 44.6, 42.2, 41.0 (2 C).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{14}H_{19}N_2O_3S$: 295.1111; found: 295.1115.

(4*S*)-4-Benzyl-3-[2-(dimethylamino)-3-phenylpent-4-enoyl]-oxazolidin-2-one (2m)

Following the general procedure, starting from **1m** (200 mg, 0.44 mmol). Purification by column chromatography (5–10% EtOAc/CH_2Cl_2) gave the product (140 mg, 85%) as a white solid; dr (*syn*/*anti*) 84:8:7:1.

IR (KBr): 3027, 2978, 2937, 2867, 2834, 2793, 1769, 1688, 1390, 1365, 1197, 1106, 922, 758, 703 cm^{-1}.

Major Diastereomer

^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.14 (m, 10 H, Ar), 5.85 (ddd, *J* = 17.1, 10.0, 8.9 Hz, 1 H, CH_2CH), 5.37 (d, *J* = 11.3 Hz, 1 H, COCH), 5.07–5.01 (m, 1 H, CH_2CH), 4.93 (dd, *J* = 10.2, 1.4 Hz, 1 H, CH_2CH), 4.66 (ddt, *J* = 10.7, 7.4, 3.8 Hz, 1 H, NCH), 4.12–4.02 (m, 2 H, OCH_2), 3.82 (dd, *J* = 11.2, 8.8 Hz, 1 H, ArCH), 3.36 (dd, *J* = 13.3, 3.5 Hz, 1 H, $ArCH_2$), 2.64 (dd, *J* = 13.3, 10.2 Hz, 1 H, $ArCH_2$), 2.29 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.5, 153.7, 140.9, 138.7, 135.4, 129.4 (2 C), 129.0 (2 C), 128.6 (2 C), 128.1 (2 C), 127.4, 126.7, 116.9, 66.1, 65.4, 55.3, 50.4, 41.2 (2 C), 39.0.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{27}N_2O_3$: 379.2016; found: 379.2024.

3-[2-(Dimethylamino)-3-phenylpent-4-enoyl]oxazolidin-2-one (2b); 1-mmol Scale Reaction

Following the general procedure, starting from *trans*-**1b** (369 mg, 1.00 mmol). Purification by column chromatography (10% EtOAc/CH_2Cl_2) gave the product (270 mg, 94%) as a white solid; dr (*syn*/*anti*) 93:7 (^1H NMR).

Epimerization Assay

To a solution of compound **2a**, **2b**, **2i**, or **2k** (the dr of the isolated compounds) (1 equiv) in $CDCl_3$ (0.25 M solution) was added TBD (1 equiv). The mixture was stirred at rt for 24 h. The dr of **2a**, **2b**, **2i** or **2k** was determined by ^1H NMR and it did not change during the reaction.

2-(Dimethylamino)-*N*-(2-hydroxyethyl)-3-phenylpent-4-enamide (3) from 2b

To a solution of **2b** (190 mg, 0.66 mmol) in MeOH (1.3 mL) was added NaOMe (43 mg, 0.79 mmol). The mixture was stirred at rt for 5 min, after this time TLC showed full consumption of the starting compound. The mixture was dried under reduced pressure and the obtained residue was purified by column chromatography (7–10% MeOH/CH_2Cl_2) to give the product (172 mg, 99%) as a white solid; dr (*syn*/*anti*) 90:10 (^1H NMR).

IR (KBr): 3300, 3033, 2935, 2875, 2830, 2785, 1645, 1544, 1452, 1267, 1216, 1063, 915, 757, 700 cm^{-1}.

Major Diastereomer

^1H NMR (400 MHz, $CDCl_3$): δ = 7.35–7.28 (m, 2 H, Ar), 7.28–7.19 (m, 3 H, Ar), 6.41 (br s, 1 H, NH), 6.17–6.07 (m, 1 H, CH_2CH), 5.11–5.07 (m, 1 H, CH_2CH), 5.08–5.02 (m, 1 H, CH_2CH), 3.82 (t, *J* = 8.4 Hz, 1 H, ArCH), 3.71–3.61 (m, 2 H, CH_2OH), 3.44–3.35 (m, 2 H, $NHCH_2$), 3.18 (d, *J* = 8.2 Hz, 1 H, COCH), 2.29 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 171.7, 141.7, 138.4, 128.5 (2 C), 128.2 (2 C), 126.6, 116.7, 73.8, 62.5, 50.1, 42.6 (2 C), 42.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{23}N_2O_2$: 263.1754; found: 263.1746.

2-Aminoethyl 2-(Dimethylamino)-3-phenylpent-4-enoate (4) from 3

To a solution of **3** (400 mg, 1.52 mmol) in dioxane (9 mL) was added aq 5 M H_2SO_4 (9.148 mL, 45.74 mmol). The mixture was stirred at 100 °C for 16 h. The mixture was cooled and the pH of the solution was regulated to 7 with sat. aq $NaHCO_3$ solution. The organic phase was extracted promptly with CH_2Cl_2 (7 ×) and dried (Na_2SO_4). After filtration, the residue was purified by column chromatography (silica gel, 1–3% MeOH/NH_3 in CH_2Cl_2) to give the product (281 mg, 70%) as an orange oil; dr (*syn*/*anti*) 89:11 (^1H NMR).

IR (KBr): 3293, 3028, 2935, 2869, 2838, 2788, 1730, 1649, 1557, 1453, 1257, 1213, 1162, 921, 757, 700 cm^{-1}.

Major Diastereomer

^1H NMR (400 MHz, $CDCl_3$): δ = 7.34–7.28 (m, 2 H, Ar), 7.23–7.19 (m, 3 H, Ar), 5.89 (ddd, *J* = 17.1, 10.2, 8.4 Hz, 1 H, CH_2CH), 5.08 (dt, *J* = 17.0, 1.3 Hz, 1 H, CH_2CH), 5.02 (dd, *J* = 10.2, 2.0 Hz, 1 H, CH_2CH), 4.21–4.07 (m, 2 H, NH_2CH_2), 3.76 (dd, *J* = 11.2, 8.5 Hz, 1 H, ArCH), 3.61 (d, *J* = 11.2 Hz, 1 H, COCH), 2.92 (t, *J* = 5.5 Hz, 2 H, OCH_2), 2.26 (s, 6 H, $N(CH_3)_2$).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 170.6, 140.7, 138.6, 128.6, 127.9, 126.7, 116.7, 71.0, 66.4, 50.1, 41.4, 41.1.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{23}N_2O_2$: 263.1754; found: 263.1758.

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