An efficient access to functionally substituted 1,3-oxazolidin-2-ones via cyclization of 1-alkylamino- and 1-arylamino-3-[2-(vinyloxy)ethoxy)]propan-2-ols with dimethyl carbonate

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Abstract

One-step and solvent-free base-catalyzed cyclization of 1-alkylamino- and 1-arylamino-3-[2-(vinyloxy)ethoxy]propan-2-ols with dimethyl carbonate is reported to obtain N-substituted 5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-ones in 91-99% yield.

Keywords: Cyclization, 1,3-oxazolidin-2-one, vinyl ethers of amino alcohols, dimethyl carbonate, sodium methoxide

Introduction

Oxazolidin-2-ones are very interesting class of heterocyclic compounds that nuclei are generally used as pharmacophore units in drug discovery.[1-3] Among oxazolidin-2-ones derivatives there are new synthetic antibacterial agents active against gram-positive microorganisms, including multiple-antibiotic resistant strains (eg. linezolid which has been awarded the 2003 Prix Galien in Germany, as the prominent innovative drug),[4-6] as well as pharmaceuticals with different pharmacological activities e.g. drugs for prevention and treatment of heart disorders, anti-thrombotics[7,8] and anti-tumor remedies,[9,10] antidepressants.[11,12]

In addition, the oxazolidin-2-one heterocycles are also used as chiral auxiliaries in asymmetric synthesis.[2,3,13,14] Oxazolidin-2-one-containing polymers possess high heat resistance and thermal stability, high elasticity and improved physico-mechanical properties that allow them to be successfully applied as coatings, lacquers, electrically insulating materials, adhesives, foam plastics and so on.[1,15-18]

Therefore the development of new methods for the synthesis of oxazolidin-2-one derivatives have drawn much attention in recent years.

At the same time, it is well known that vinyl ethers belong to a valuable class of electron-rich alkenes possessing unique chemical reactivity that make them attractive not only as monomers for polymer chemistry, but also as reagents capable of executing a variety synthetic transformation (e.g. cycloadition,[19] hydroformylation,[20] metathesis,[21] Heck reaction[22]) for synthesis of complex organic molecules.[23,24]

Therefore, the introduction of the highly reactive vinyloxy fragment into the structure of oxazolidin-2-one allows to expand the scope of their applications as building blocks and monomers for organic chemistry.

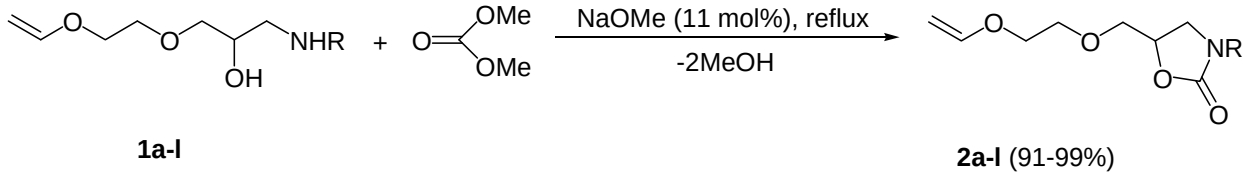
In spite of the occurrence of various methods to obtain oxazolidin-2-ones, the most widely used one is the heterocyclization of 1,2-amino alcohols.[2,25-29]

Recently the synthesis of 1,3-oxazolidin-2-one by the reaction of 1,2-amino alcohols with dimethyl carbonate in presence of phosphazene base was reported.[30]

Here we report a simple and efficient synthesis of the 3,5-substituted oxazolidin-2-ones containing vinyloxyalkyl moiety **2** from 1-alkylamino- and 1-arylamino-3-[2-(vinyloxy)ethoxy]-2-propanols (**1**) and dimethyl carbonate (DMC) in the presence of readily available inexpensive bases (sodium methoxide or metallic sodium). Starting vinyl ethers of amino alcohols **1** are also sufficient available**,** so they can be obtained from vinyloxyethyl glycidol ether (Vinylox),[31,32] the product of small-scale industry and from the large-scale produced primary amines.[33] Dimethyl carbonate is a well-known, inexpensive, nontoxic reagent that meets the requirements of green chemistry and it presents an eco-friendly alternative to carbonylating agents such as phosgene and its derivatives.[34,35]

Results and Discussion

The reaction of corresponding vinyl ethers **1a-j** and **1l** with DMC has been performed by the refluxing of the mixture of the reactants (1-7.5 h) in the presence of 11 mol% of sodium methoxide (Scheme 1). Target oxazolidin-2-ones of **2a-j, 2l** have been obtained with 93-99% yield.



1a-l **2a-l** (91-99%)

R = H, Me, CH_2CH_2OEt, $CH_2CH_2CH_2OH$, $CH_2CH=CH_2$, $CH_2CH_2OCH=CH_2$, $C(Me)_2CH_2OCH=CH_2$, $C(Et)CH_2OCH=CH_2$, $CH_2CH_2CH_2OCH=CH_2$, C_6H_{11}, Ph, CH_2Ph

Scheme 1. Synthesis of 5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one 2 by the reaction of vinyl ethers of amino alcohols 1 with dimethyl carbonate.

Difficulties have only arisen in the synthesis of 3-phenyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (**2k**) (Table 1, entries 11). The resinification of the reaction mass has been already observed in the first 10-15 min of the refluxing. This fact could be explained by low thermal stability of vinyl ether **1k** that completely decomposes at distillation with the removal of vinyl group.[33]

Table 1. List of 5-{[2-(Vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-ones **2**

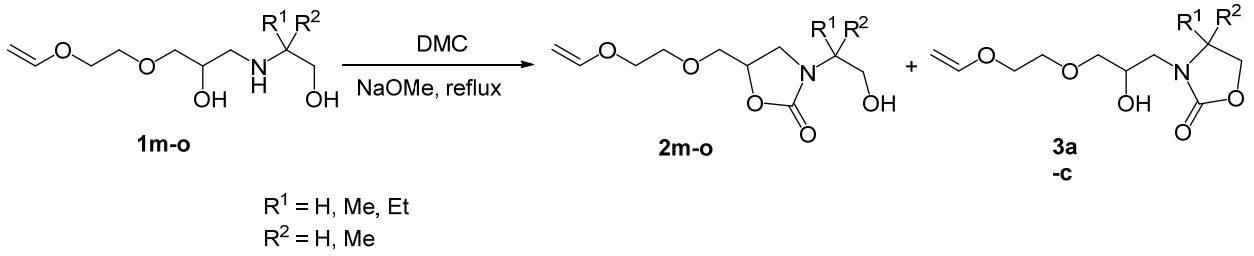
Entry [a]	Vinyl ether	R	Product	Time (h)	Yield [c] (%)
1	**1a**	H	**2a**	3	97
2	**1b**	Me	**2b**	2	95
3	**1c**	CH_2CH_2OEt	**2c**	4	98
4	**1d**	$CH_2CH_2CH_2OH$	**2d**	2	97
5	**1e**	$CH_2CH=CH_2$	**2e**	2	98
6	**1f**	$CH_2CH_2OCH=CH_2$	**2f**	2	94
7	**1g**	$C(Me)_2CH_2OCH=CH_2$	**2g**	2	99
8	**1h**	$C(Et)CH_2OCH=CH_2$	**2h**	7.5	93[d]
9	**1i**	$CH_2CH_2CH_2OCH=CH_2$	**2i**	1.5	98
10	**1j**	cyclohexyl	**2j**	2	98
11[b]	**1k**	Ph	**2k**	1.5	91
12	**1l**	CH_2Ph	**2l**	1	96

[a]Reaction conditions: **1** (0.01 mol), dimethyl carbonate (0.0125 mol), NaOMe (11 mol%), reflux.
[b]Reaction conditions: **1k** (0.01 mol), dimethyl carbonate (0.0125 mol), Na (11 mol%), benzene (20.0 mL), reflux.
[c]Yields of isolated products.
[d]Yields of mixture of diastereoisomers.

The decrease of reaction temperature by refluxing in benzene has not led to the expected result, the yield of **2k** (according to the ^{1}H NMR spectrum of the reaction mixture) does not exceed 24% for 12.5 h. The lowered reactivity of the compound **1k** could be explained by the decrease of the nitrogen atom nucleophilicity through + M mesomeric effect of amino group. The catalyst replacement (metallic Na, 1 h, benzene, reflux) has allowed to obtain oxazolidin-2-one **2k** in 91% yield.

5-{[2-(Vinyloxy)ethoxy]methyl}-3-{1-[(vinyloxy)methyl]propyl}-1,3-oxazolidin-2-one **(2h**) is formed as the equimolar mixture of diastereomers (according to ^{1}H NMR spectrum). Thus, in the ^{1}H NMR spectrum of the product **2h** there are two triplets at 0.88 and 0.89 ppm, belonging to the protons of the methyl groups, the signals of the hydrogen atoms of other groups are overlapped forming the complex multiplets. In the ^{13}C NMR spectrum of the product **2h,** a doubling of all signals of carbon atoms is performed, except the signals of carbon atoms of vinyloxy-group containing in CH_2=$CHOCH_2CH_2O$ fragment.

In the reaction of the DMC with vinyl ethers of amino alcohols **1m-o**, containing two hydroxyl groups at β,β`-positions to the amino group, the formation of mixture of isomeric oxazolidin-2-ones **2m-o** and **3a-c** have occurred (Scheme 2).



Scheme 2. Reaction of 1-(alkylamino)-3-[2-(vinyloxy)ethoxy]propan-2-ol **1** with dimethyl carbonate.

Indeed, when vinyl ether of amino alcohol **1m** is used, the reaction occurs with the formation of mixture of two oxazolidin-2-ones with ratio **2m**/**3a** = 1 : 0.22 (Table 2, entry 1). The ratio has been determined by ^{1}H NMR from integrals of fully resolve signals of groups OCH (δ 4.57-4.64 m) at 5 position of oxazolidin-2-one ring in **2m** and CH_2 (δ 4.28 t) at 5 position of oxazolidin-2-one ring in **3a**. The mixture of **2m**/**3a** has been separated by column chromatography to afford pure **2m** and **3a**.

Table 2. Synthesized oxazolidin-2-ones **2** and **3**

Entry	Vinyl ether	R^1	R^2	Product **2**	Product **3**	Time (h)	Ratio **2**/**3**[a]	Yield (%)
1	**1m**	H	H	**2m**	**3a**	2	1 : 0.22	99[b]
2	**1n**	Me	Me	**2n**	**3b**	2	0 : 1	99
3	**1o**	Et	H	**2o**	**3c**	2	0.52 : 1	99[b]

[a]Determined by ^{1}H NMR.
[b]Mixture yield.

Vinyl ether of amino alcohol **1o** also gives a mixture of two oxazolidin-2-ones with ratio **2o**/**3c** = 0.52 : 1 (Table 2, entry 3). The ratio is determined by ^{1}H NMR as it has been previously described for mixture **2m**/**3a.**

Our attempts to separate mixture **2o/3c** are failed; the only fraction enriched with **3c** (**2o/3c =** 0.14 : 1) is obtained.

It is noteworthy that in the case of vinyl ether **1n,** containing in α-position of the amino group the carbon atom, having two methyl substituents (Table 2, entries 2), the cyclization reaction occurs selectively with the formation of the only oxazolidin-2-one **3b** as the result of gem-dialkyl effect.[36-38] The isomeric oxazolidin-2-one **2n** is not found, it results from NMR spectra data, e.g.

the absence of the distinctive proton signal of OCH-group of cycle **2n** at 4.47-4.73 ppm in ^{1}H NMR spectra and the absence of carbon atom signal of this group at 71.0-71.9 ppm in ^{13}C NMR spectra are the confirmations of that. At the same time, the proton signals of C*H*OH-group (**3b)** are presented at 3.91-4.03 ppm and the carbon atom signal of the same group is at 69.7 ppm.

Conclusions

It is shown that oxazolidin-2-ones **2a-m**, **2o**, **3a-c** containing the highly reactive vinyloxy-groups at 3- and 5-positions of oxazolidin-2-one ring have been synthesized in one-step with high yields from available vinyl ethers of amino alcohols **1a-o** and dimethyl carbonate. The compounds obtained are promising building blocks and monomers for the organic chemistry. Meanwhile, the protocols for their syntheses and the methods for the product isolations are common to be realized.

Experimental Section

General. The structures of the isolated products were unambiguously determined by NMR (^{1}H, ^{13}C) and IR spectroscopy. The elemental analyses for all the compounds confirmed their compositions. ^{1}H NMR (400.13 MHz) and ^{13}C NMR (100.62 MHz) spectra were recorded with Bruker DPX 400 spectrometer at ambient temperature for $CDCl_3$ solutions. Chemical shifts (δ) were presented in δ (ppm) relative to $CDCl_3$ (δ 7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). IR spectra were recorded with Bruker Vertex 70. Microanalyses were performed with Flash EA 1112 Series elemental analyzer. All starting materials were taken from commercial suppliers and used without further purification. Vinyl ethers of amino alcohols **1a-j**, **1l-o** were synthesized from vinyloxyethyl ether of glycidol and primary amines by the protocol.[33] 1-Anilino-3-[2-(vinyloxy)ethoxy]propan-2-ol **1k** was obtained for the first time.

Synthesis of 1-anilino-3-[2-(vinyloxy)ethoxy]propan-2-ol (1k). Vinyloxyethyl ether of glycidol (4.33 g, 0.03 mol) was added to the aniline (8.38 g, 0.09 mol) and the mixture was stirred for 8 h at 30-40°C. The aniline excess was removed under reduce pressure (1 mm Hg, heating in water bath at 65-80°C). The residue was washed with hexane (3×5 mL) and dried under vacuum (1 mm Hg) to constant weight. The pure product was isolated as a pale yellow oil, yield 92%, 7.27 g, n_D^{20} 1.5502; IR (ν_{max}, cm^{-1}): 3380, 3115, 3086, 3052, 3026, 2920, 2875, 1636, 1620, 1604, 1507, 1501, 1467, 1455, 1435, 1358, 1322, 1279, 1260, 1201, 1182, 1133, 1086, 1040, 992, 974, 932, 875, 825, 752, 694, 507. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 2.91 (1H, br.s, OH), 3.16 (1H, dd, $^{2}J_{HH}$ 12.8 Hz, $^{3}J_{HH}$ 7.0 Hz, C*H*HN), 3.31 (1H, dd, $^{2}J_{HH}$ 12.8, $^{3}J_{HH}$ 4.3 Hz, CH*H*N), 3.54-3.66 (3H, m, OCH_2CH, NH), 3.74-3.77 (2H, m, =CHOCH_2CH_2), 3.87 (2H, m, =CHOCH_2), 4.02-4.07 (2H, m, cis-CH_2=, C*H*OH), 4.23 (1H, dd, $^{3}J_{trans}$ 14.3 Hz, $^{2}J_{gem}$ 1.9 Hz,

trans-CH_2=), 6.50 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C), 6.64-6.78 (3H, m, 2-H, 4-H, 6-H, Ph), 7.18 (2H, m, 3-H, 5-H, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 46.5 (CH_2N), 67.2 (=CHO*C*H_2), 68.8 (CHOH), 69.7 (=CHOCH$_2$*C*H_2), 73.6 (O*C*H_2CH), 86.9 (=CH_2), 113.0 (C-2, C-6, Ph), 117.5 (C-4, Ph), 129.1 (C-3, C-5, Ph), 148.2 (C-1, Ph), 151.5 (=CHO). Anal. Calcd for $C_{13}H_{19}NO_3$ (237.30): C, 65.80; H, 8.07; N, 5.90; O, 20.23%. Found: C, 65.85; H, 8.36; N, 5.56%.

General procedure for synthesis of 3-alkyl- and 3-arylamino-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2a-j, 2l). A mixture of the corresponding vinyl ether **1a-j**, **1l** (0.01 mol), DMC (1.13 g, 0.0125 mol) and MeONa (0.06 g, 0.0011 mol) was refluxed for 1-7.5 hours. Then MeONa was filtered and washed with methanol (2 mL). After removing methanol under reduced pressure, residue was washed with hexane (2×3 mL) and dried under vacuum to constant weight.

5-{[2-(Vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2a). Colourless oil, yield 97%, 1.82 g, n_D^{20} 1.4870; IR (ν_{max}, cm^{-1}): 3316, 3119, 2921, 2878, 1748, 1636, 1622, 1566, 1557, 1540, 1491, 1454, 1436, 1384, 1361, 1322, 1291, 1243, 1201, 1140, 1084, 1041, 1002, 967, 928, 892, 867, 829, 770, 705, 616, 524, 472. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 3.43 (1H, dd, $^2J_{HH}$ 8.6 Hz, $^3J_{HH}$ 6.9 Hz, C*H*HN), 3.61 (1H, t, $^2J_{HH}$ 8.6 Hz, CH*H*N), 3.67 (2H, d, $^3J_{HH}$ 4.8 Hz, OCH_2CH), 3.73-3.75 (2H, m, =CHOCH$_2$CH_2), 3.79-3.82 (2H, m, =CHOCH_2), 3.98 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.1 Hz, cis-CH_2=), 4.16 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-CH_2=), 4.73 (1H, m, OCH), 6.30 (1H, br.s, NH), 6.43 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 42.5 (CH_2N), 67.2 (=CHO*C*H_2), 70.1 (O*C*H_2CH), 71.5 (=CHOCH$_2$*C*H_2), 75.1 (OCH), 86.9 (=CH_2), 151.5 (=CHO), 159.9 (C=O). Anal. Calcd for $C_8H_{13}NO_4$ (187.19): C, 51.33; H, 7.00; N, 7.48; O, 34.19%. Found: C, 51.28; H, 7.27; N, 7.61%.

3-Methyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2b). Light yellow oil, yield 95%, 1.91 g, n_D^{20} 1.4740; IR (ν_{max}, cm^{-1}): 3117, 3041, 2928, 2879, 1749, 1635, 1621, 1524, 1498, 1452, 1437, 1409, 1379, 1358, 1322, 1290, 1267, 1202, 1137, 1087, 1068, 1028, 1003, 974, 900, 868, 826, 808, 763, 704, 669, 656, 522, 461. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 2.81 (3H, s, CH_3), 3.35 (1H, dd, $^2J_{HH}$ 8.7 Hz, $^3J_{HH}$ 6.5 Hz, C*H*HN), 3.53 (1H, t, $^2J_{HH}$ 8.7 Hz, CH*H*N), 3.62 (2H, d, $^3J_{HH}$ 4.8 Hz, OCH_2CH), 3.69-3.72 (2H, m, =CHOCH$_2$CH_2), 3.75-3.78 (2H, m, =CHOCH_2), 3.95 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.0 Hz, cis-CH_2=), 4.13 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-CH_2=), 4.56 (1H, m, OCH), 6.40 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 30.8 (CH_3), 48.5 (CH_2N), 67.2 (=CHO*C*H_2), 70.1 (O*C*H_2CH), 71.4 (=CHOCH$_2$*C*H_2), 71.5 (OCH), 86.8 (=CH_2), 151.5 (=CHO), 157.8 (C=O). Anal. Calcd for $C_9H_{15}NO_4$ (201.22): C, 53.72; H, 7.51; N, 6.96; O, 31.81%. Found: C, 53.64; H, 7.51; N, 6.99%.

3-(2-Ethoxyethyl)-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2c). Yellow oil, yield 98%, 2.54 g, n_D^{20} 1.4698; IR (ν_{max}, cm^{-1}): 3117, 3041, 2975, 2931, 2873, 1752, 1636, 1621, 1524, 1491, 1447, 1381, 1370, 1355, 1322, 1257, 1202, 1175, 1140, 1122, 1070, 1050, 1032, 1005, 973, 949, 923, 898, 843, 822, 797, 763, 703, 685, 668, 658, 497. ^{1}H NMR (400.13 MHz,

$CDCl_3$): δ_H 1.10 (3H, t, $^3J_{HH}$ 7.0 Hz, CH_3), 3.26-3.70 (12H, m, NCH_2CH_2OCH_2, CHCH_2N, =CHOCH$_2$CH_2OCH_2CH), 3.73-3.76 (2H, m, =CHOCH_2), 3.93 (1H, dd, $^3J_{cis}$ 6.7 Hz, $^2J_{gem}$ 2.1 Hz, cis-CH_2=), 4.11 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-CH_2=), 4.55 (1H, m, OCH), 6.38 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 15.0 (CH_3), 43.9 (NCH_2CH_2O), 47.7 (CH*C*H_2N), 66.2 (NCH$_2$*C*H_2O), 67.1 (=CHO*C*H_2), 68.5 (O*C*H_2CH$_3$), 70.1 (O*C*H_2CH), 71.5 (=CHOCH$_2$*C*H_2), 71.9 (OCH), 86.7 (=CH_2), 151.5 (=CHO), 157.6 (C=O). Anal. Calcd for $C_{12}H_{21}NO_5$ (259.30): C, 55.58; H, 8.16; N, 5.40; O, 30.86%. Found: C, 55.34; H, 8.15; N, 5.76%.

3-(3-Hydroxypropyl)-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2d). Yellow oil, yield 97%, 2.38 g, n_D^{20} 1.4865; IR (ν_{max}, cm^{-1}): 3432, 3117, 3041, 2931, 2876, 1749, 1636, 1621, 1524, 1492, 1454, 1356, 1322, 1266, 1201, 1141, 1059, 1004, 974, 950, 822, 763, 682, 653, 605, 561, 470. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 1.70 (2H, m, NCH$_2$C*H*$_2$), 3.00 (1H, br.s, OH), 3.24-3.68 (8H, m, NC*H*$_2$CH$_2$C*H*$_2$, CHC*H*$_2$N, OC*H*$_2$CH), 3.71-3.73 (2H, m, =CHOCH$_2$C*H*$_2$), 3.76-3.79 (2H, m, =CHOC*H*$_2$), 3.97 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.0 Hz, cis-CH_2=), 4.14 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-CH_2=), 4.61 (1H, m, OCH), 6.41 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 29.6 (NCH$_2$*C*H$_2$), 40.4 (N*C*H$_2$CH$_2$), 46.3 (CH*C*H$_2$N), 58.7 (CH$_2$OH), 67.2 (=CHO*C*H$_2$), 70.1 (O*C*H$_2$CH), 71.4 (=CHOCH$_2$*C*H$_2$), 71.9 (OCH), 86.8 (=CH_2), 151.4 (=CHO), 158.4 (C=O). Anal. Calcd for $C_{11}H_{19}NO_5$ (245.27): C, 53.87; H, 7.81; N, 5.71; O, 32.61%. Found: C, 53.55; H, 7.81; N, 5.99%.

3-Allyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2e). Light yellow oil, yield 98%, 2.22 g, n_D^{20} 1.4830; IR (ν_{max}, cm^{-1}): 3117, 3083, 3042, 3010, 2925, 2877, 1748, 1635, 1621, 1524, 1491, 1445, 1419, 1358, 1342, 1322, 1292, 1255, 1202, 1142, 1088, 1064, 997, 964, 929, 823, 763, 701, 605, 554, 499, 470. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 3.35 (1H, dd, $^2J_{HH}$ 8.6, $^3J_{HH}$ 6.9 Hz, CHC*H*HN), 3.50 (1H, t, $^2J_{HH}$ 8.6 Hz, CHCH*H*N), 3.63 (2H, d, $^3J_{HH}$ 4.6 Hz, OC*H*$_2$CH), 3.71-3.73 (2H, m, =CHOCH$_2$C*H*$_2$), 3.76-3.81 (4H, m, NC*H*$_2$CH=, =CHOC*H*$_2$), 3.96 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 1.4 Hz, cis-C*H*$_2$=CHO), 4.14 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 1.4 Hz, trans-C*H*$_2$=CHO), 4.59 (1H, m, OCH), 5.16-5.22 (2H, m, NCH$_2$CH=C*H*$_2$), 5.66-5.76 (1H, m, NCH$_2$C*H*=), 6.41 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 45.9 (N*C*H$_2$CH=), 46.6 (CH*C*H$_2$N), 67.2 (=CHO*C*H$_2$), 70.1 (O*C*H$_2$CH), 71.5 (=CHOCH$_2$*C*H$_2$), 71.7 (OCH), 86.7 (OCH=*C*H$_2$), 118.3 (NCH$_2$CH=*C*H$_2$), 131.7 (NCH$_2$*C*H=), 151.4 (=CHO), 157.3 (C=O). Anal. Calcd for $C_{11}H_{17}NO_4$ (227.26): C, 58.14; H, 7.54; N, 6.16; O, 28.16%. Found: C, 58.10; H, 7.54; N, 6.33%.

5-{[2-(Vinyloxy)ethoxy]methyl}-3-[2-(vinyloxy)ethyl]-1,3-oxazolidin-2-one (2f). Yellow oil, yield 94%, 2.43 g, n_D^{20} 1.4864; IR (ν_{max}, cm^{-1}): 3117, 3043, 3023, 2931, 2878, 1749, 1635, 1621, 1524, 1491, 1446, 1383, 1362, 1322, 1259, 1199, 1141, 1088, 1050, 1016, 958, 897, 882, 825, 763, 703, 685, 658, 608, 465. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 3.34-3.74 (12H, m, CHC*H*$_2$N, NCH$_2$CH$_2$O, OCH$_2$CH$_2$OCH$_2$), 3.89 (1H, dd, $^3J_{cis}$ 6.7, $^2J_{gem}$ 1.9 Hz, cis-C*H*$_2$=CHOCH$_2$CH$_2$N), 3.93 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.0 Hz, cis-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.07 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 1.9 Hz, trans-C*H*$_2$=CHOCH$_2$CH$_2$N), 4.09 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.52 (1H, m, OCH), 6.30-6.37 (2H, m, 2OCH=C). ^{13}C NMR (100.62

MHz, $CDCl_3$): δ_C 43.1 (N*C*H_2CH_2O), 47.3 (CH*C*H_2N), 65.9 (NCH$_2$C*H*$_2$O), 67.0 (=CHO*C*H_2CH_2O), 69.8 (O*C*H_2CH), 71.3 (=CHOCH$_2$*C*H_2O), 71.8 (OCH), 86.5 (OCH_2CH_2OCH=*C*H_2), 87.0 (NCH$_2$CH$_2$OCH=*C*H$_2$), 150.9 (OCH_2CH_2OCH=), 151.3 (NCH$_2$CH$_2$O*C*H=), 157.3 (C=O). Anal. Calcd for $C_{12}H_{19}NO_5$ (257.28): C, 56.02; H, 7.44; N, 5.44; O, 31.10%. Found: C, 56.50; H, 7.47; N, 5.58%.

3-[1,1-Dimethyl-2-(vinyloxy)ethyl]-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2g). Light yellow oil, yield 99%, 2.83 g, n_D^{20} 1.4796; IR (ν_{max}, cm^{-1}): 3117, 3043, 2978, 2932, 2878, 2822, 1745, 1636, 1620, 1530, 1476, 1461, 1415, 1368, 1322, 1295, 1271, 1238, 1202, 1144, 1083, 1044, 1013, 965, 949, 907, 880, 823, 766, 701, 660, 629, 534. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 1.35 (6H, s, 2CH$_3$), 3.48 (1H, dd, $^2J_{HH}$ 8.6 Hz, $^3J_{HH}$ 6.4 Hz, C*H*HN), 3.57-3.80 (9H, m, CH*H*N, NCCH$_2$O, OCH$_2$CH$_2$OCH$_2$), 3.93 (1H, dd, $^3J_{cis}$ 6.7 Hz, $^2J_{gem}$ 2.0 Hz, cis-C*H*$_2$=CHOCH$_2$CN), 3.95 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.1 Hz, cis-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.13 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.14 (1H, dd, $^3J_{trans}$ 14.2 Hz, $^2J_{gem}$ 2.0 Hz, trans-C*H*$_2$=CHOCH$_2$CN), 4.47 (1H, m, OCH), 6.38 (1H, dd, $^3J_{trans}$ 14.2 Hz, $^3J_{cis}$ 6.7 Hz, NCCH$_2$O*C*H=C), 6.41 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH$_2$CH$_2$O*C*H=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 23.0 (2CH$_3$), 46.1 (CH$_2$N), 55.3 (C), 67.1 (=CHO*C*H$_2$CH$_2$O), 70.0 (O*C*H$_2$CHO), 71.0 (OCH), 71.5(=CHOCH$_2$*C*H$_2$O), 72.7 (NC*C*H$_2$O), 86.7 (NCCH$_2$OCH=*C*H$_2$), 86.8 (OCH$_2$CH$_2$OCH=*C*H$_2$), 151.4 (OCH$_2$CH$_2$O*C*H=), 151.6 (NCCH$_2$O*C*H=), 156.2 (C=O). Anal. Calcd for $C_{14}H_{23}NO_5$ (285.34): C, 58.93; H, 8.12; N, 4.91; O, 28.04%. Found: C, 58.98; H, 8.20; N, 4.89%.

5-{[2-(Vinyloxy)ethoxy]methyl}-3-{1-[(vinyloxy)methyl]propyl}-1,3-oxazolidin-2-one (2h). Light yellow oil, yield 93%, 2.66 g, n_D^{20} 1.4790; IR (ν_{max}, cm^{-1}): 3117, 3078, 3043, 2967, 2934, 2878, 2822, 1748, 1637, 1620, 1521, 1489, 1460, 1435, 1382, 1371, 1357, 1322, 1255, 1201, 1142, 1066, 1003, 964, 949, 897, 881, 823, 762, 703, 666, 616, 609, 528. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H (~ 1:1 mixture of diastereoisomers) 0.88 (1.5H, t, $^3J_{HH}$ 7.4 Hz, CH$_3$), 0.89 (1.5H, t, $^3J_{HH}$ 7.4 Hz, CH$_3$), 1.50-1.61 (2H, m, C*H*$_2$CH$_3$), 3.33-3.39 (1H, m, C*H*HN), 3.49-3.90 (10H, m, CH*H*N, OCH$_2$CH$_2$OCH$_2$, NCHCH$_2$O), 3.93-3.97 (2H, m, 2 trans-C*H*$_2$=CHO), 4.09-4.14 (2H, m, 2 trans-C*H*$_2$=CHO), 4.54-4.61 (1H, m, OC*H*CH$_2$), 6.35-6.42 (2H, m, 2OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C (~ 1:1 mixture of diastereoisomers) 10.3 and 10.4 (CH$_3$), 21.3 and 21.4 (*C*H$_2$CH$_3$), 42.9 and 43.4 (CH$_2$N), 53.9 and 54.0 (NCH), 67.1 (=CHO*C*H$_2$CH$_2$O), 67.8 and 68.0 (NCH*C*H$_2$O), 70.03 and 70.04 (O*C*H$_2$CHO), 71.5 and 71.6 (=CHOCH$_2$*C*H$_2$O), 71.9 and 72.0 (OCH), 86.7 (OCH$_2$CH$_2$OCH=*C*H$_2$), 86.85 and 86.90 (NCHCH$_2$OCH=*C*H$_2$), 151.2 (OCH$_2$CH$_2$O*C*H=), 151.40 and 151.43 (NCHCH$_2$O*C*H=), 157.5 and 157.6 (C=O). Anal. Calcd for $C_{14}H_{23}NO_5$ (285.34): C, 58.93; H, 8.12; N, 4.91; O, 28.04%. Found: C, 59.03; H, 8.17; N, 4.99%.

5-{[2-(Vinyloxy)ethoxy]methyl}-3-[3-(vinyloxy)propyl]-1,3-oxazolidin-2-one (2i). Light yellow oil, yield 98%, 2.66 g, n_D^{20} 1.4829; IR (ν_{max}, cm^{-1}): 3117, 3076, 3042, 2930, 2877, 1750, 1637, 1620, 1522, 1491, 1471, 1453, 1434, 1380, 1356, 1322, 1256, 1202, 1141, 1086, 1075, 1060, 1004, 976, 965, 884, 821, 762, 703, 683, 638, 608. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 1.88 (2H, m, NCH$_2$C*H*$_2$), 3.33 (2H, m, NC*H*$_2$CH$_2$), 3.41 (1H, dd, $^2J_{HH}$ 8.7 Hz, $^3J_{HH}$ 6.2 Hz,

CHC*H*HN), 3.57 (1H, t, $^2J_{HH}$ 8.7 Hz, CHCH*H*N), 3.64 (2H, d, $^3J_{HH}$ 4.5 Hz, OC*H*$_2$CH), 3.69 (2H, t, $^3J_{HH}$ 6.1 Hz, NCH$_2$CH$_2$C*H*$_2$O), 3.71-3.74 (2H, m, =CHOCH$_2$C*H*$_2$O), 3.77-3.80 (2H, m, =CHOC*H*$_2$CH$_2$O), 3.96 (1H, dd, $^3J_{cis}$ 6.7 Hz, $^2J_{gem}$ 2.0 Hz, cis-C*H*$_2$=CHOCH$_2$CH$_2$CH$_2$N), 3.98 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.1 Hz, cis-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.14 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-C*H*$_2$=CHOCH$_2$CH$_2$CH$_2$N), 4.15 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-C*H*$_2$=CHOCH$_2$CH$_2$O), 4.59 (1H, m, OCH), 6.37-6.45 (2H, m, 2OCH=C). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ_C 26.8 (NCH$_2$*C*H$_2$), 41.2 (N*C*H$_2$CH$_2$), 46.7 (CH*C*H$_2$N), 65.0 (NCH$_2$CH$_2$*C*H$_2$O), 67.2 (=CHO*C*H$_2$CH$_2$O), 70.1 (O*C*H$_2$CH), 71.5 (=CHOCH$_2$*C*H$_2$O), 71.7 (OCH), 86.7 (NCH$_2$CH$_2$CH$_2$OCH=*C*H$_2$), 86.8 (OCH$_2$CH$_2$OCH=*C*H$_2$), 151.4 (NCH$_2$CH$_2$CH$_2$O*C*H=), 151.5 (OCH$_2$CH$_2$O*C*H=), 157.6 (C=O). Anal. Calcd for $C_{13}H_{21}NO_5$ (271.31): C, 57.55; H, 7.80; N, 5.16; O, 29.49%. Found: C, 57.48; H, 7.32; N, 5.14%.

3-Cyclohexyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2j). Light yellow oil, yield 98%, 2.63 g, n_D^{20} 1.4908; IR (ν_{max}, cm^{-1}): 3117, 3075, 3042, 2932, 2857, 1740, 1637, 1620, 1524, 1488, 1465, 1452, 1430, 1377, 1355, 1321, 1271, 1248, 1202, 1142, 1088, 1063, 1061, 998, 975, 964, 948, 894, 873, 826, 792, 763, 692, 601, 577, 507, 445. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ_H 0.98-1.74 (10H, m, 2-H$_2$, 3-H$_2$, 4-H$_2$, 5-H$_2$, 6-H$_2$, cyclohexyl), 3.34 (1H, m, C*H*HN), 3.50 (1H, t, $^2J_{HH}$ 8.7 Hz, CH*H*N), 3.58-3.62 (3H, m, OC*H*$_2$CH, 1-H, cyclohexyl), 3.71-3.73 (2H, m, =CHOCH$_2$C*H*$_2$), 3.76-3.78 (2H, m, =CHOC*H*$_2$), 3.97 (1H, dd, $^3J_{cis}$ 6.8 Hz, $^2J_{gem}$ 2.0 Hz, cis-CH$_2$=), 4.14 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-CH$_2$=), 4.53-4.60 (1H, m, OCH), 6.42 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ_C 25.14 (C-3, cyclohexyl), 25.15 (C-5, cyclohexyl), 25.2 (C-4, cyclohexyl), 29.9 (C-2, cyclohexyl), 30.2 (C-6, cyclohexyl), 42.4 (CH$_2$N), 52.3 (C-1, cyclohexyl), 67.1 (=CHO*C*H$_2$), 70.1 (O*C*H$_2$CH), 71.6 (=CHOCH$_2$*C*H$_2$), 71.8 (OCH), 86.7 (=CH$_2$), 151.4 (=CHO), 156.9 (C=O). Anal. Calcd for $C_{14}H_{23}NO_4$ (269.34): C, 62.43; H, 8.61; N, 5.20; O, 23.76%. Found: C, 62.55; H, 8.69; N, 5.48%.

Synthesis of 3-phenyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2k). Na metal (0.026 g, 0.0011 mol) was added to the solution of 1-anilino-3-[2-(vinyloxy)ethoxy]propan-2-ol (**1k**) (2.37 g, 0.01 mol) in anhydrous benzene (20.0 mL), the mixture was stirred at room temperature for 30 min. DMC was then added (1.13 g, 0.0125 mol) and the mixture was refluxed for 1 h. The precipitate was filtered. After the benzene was removed under reduce pressure, residue was washed with hexane (2×3 mL) and dried in vacuum to constant weight to afford pure product **2k** as yellow oil, yield 91%, 2.40 g, n_D^{20} 1.5420; IR (ν_{max}, cm^{-1}): 3116, 3066, 3047, 2922, 2876, 1752, 1636, 1620, 1600, 1504, 1490, 1460, 1413, 1376, 1358, 1320, 1286, 1227, 1202, 1139, 1085, 1045, 1002, 979, 899, 827, 758, 693, 671, 617, 586, 509. ^{1}H NMR (400.13 MHz, CDCl$_3$): δ_H 3.67 (2H, d, $^3J_{HH}$ 4.3 Hz, OC*H*$_2$CH), 3.69-3.71 (2H, m, =CHOCH$_2$C*H*$_2$), 3.74-3.77 (2H, m, =CHOC*H*$_2$), 3.81 (1H, dd, $^2J_{HH}$ 8.8 Hz, $^3J_{HH}$ 6.7 Hz, C*H*HN), 3.91-3.96 (2H, m, CH*H*N, cis-CH$_2$=), 4.13 (1H, dd, $^3J_{trans}$ 14.4 Hz, $^2J_{gem}$ 2.0 Hz, trans-CH$_2$=), 4.66 (1H, m, OCH), 6.38 (1H, dd, $^3J_{trans}$ 14.4 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C), 7.06 (1H, m, 4-H, Ph), 7.30 (2H, m, 2-H, 6-H, Ph), 7.47-7.49 (2H, m, 3-H, 5-H, Ph). ^{13}C NMR (100.62 MHz, CDCl$_3$): δ_C 46.6 (CH$_2$N), 67.0 (=CHO*C*H$_2$), 69.9 (O*C*H$_2$CH), 71.0 (=CHOCH$_2$*C*H$_2$), 71.1 (OCH), 86.6 (=CH$_2$), 117.8 (C-2, C-

6, Ph), 123.5 (C-4, Ph), 128.6 (C-3, C-5, Ph), 137.9 (C-1, Ph), 151.3 (=CHO), 154.2 (C=O). Anal. Calcd for $C_{14}H_{17}NO_4$ (263.29): C, 63.87; H, 6.51; N, 5.32; O, 24.30%. Found: C, 63.81; H, 6.70; N, 5.29%.

3-Benzyl-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2l). Yellow oil, yield 96%, 2.65 g, n_D^{20} 1.5260; IR (ν_{max}, cm^{-1}): 3115, 3087, 3064, 3031, 2926, 2876, 1749, 1636, 1620, 1521, 1496, 1444, 1359, 1322, 1256, 1202, 1141, 1088, 1063, 1004, 966, 894, 868, 841, 820, 761, 741, 702, 673, 619, 605, 534, 459. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 3.27 (1H, dd, $^2J_{HH}$ 8.6 Hz, $^3J_{HH}$ 6.7 Hz, CHC*H*HN), 3.41 (1H, t, $^2J_{HH}$ 8.6 Hz, CHCH*H*N), 3.60 (2H, d, $^3J_{HH}$ 4.0 Hz, OC*H*$_2$CH), 3.68-3.71 (2H, m, =CHOCH$_2$C*H*$_2$), 3.74-3.77 (2H, m, =CHOC*H*$_2$), 3.97 (1H, dd, $^3J_{cis}$ 6.7 Hz, $^2J_{gem}$ 2.0 Hz, cis-CH$_2$=), 4.14 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-CH$_2$=), 4.38 (2H, m, NC*H*$_2$Ph), 4.53-4.61 (1H, m, OCH), 6.40 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C), 7.23-7.33 (5H, m, Ph). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 45.6 (N*C*H$_2$Ph), 48.0 (CH*C*H$_2$N), 67.1 (=CHO*C*H$_2$), 70.0 (O*C*H$_2$CH), 71.4 (=CHOCH$_2$*C*H$_2$), 71.7 (OCH), 86.7 (=CH$_2$), 127.7 (C-4, Ph), 127.8 (C-2, C-6, Ph), 128.6 (C-3, C-5, Ph), 135.5 (C-1, Ph), 151.4 (=CHO), 157.6 (C=O). Anal. Calcd for $C_{15}H_{19}NO_4$ (277.32): C, 64.97; H, 6.91; N, 5.05; O, 23.07%. Found: C, 64.87; H, 7.07; N, 5.03%.

General procedure for Reaction of Vinyl Ethers 1m-o with Dimethyl Carbonate. A mixture of the corresponding vinyl ether **1m-o** (0.01 mol), DMC (0.90 g, 0.01 mol) and MeONa (0.06 g, 0.0011 mol) was refluxed for 2 h. MeONa was filtered and washed with methanol (2 mL). MeOH was removed under reduce pressure. The residue was washed with hexane (2×3 mL) and dried under vacuum to constant weight.

3-(2-Hydroxyethyl)-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2m) and 3-{2-hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-1,3-oxazolidin-2-one (3a). Mixture of **2m**/**3a** (1:0.22), light yellow oil, yield of mixture 99%, 2.31 g; IR (ν_{max}, cm^{-1}): 3418, 3117, 3042, 2927, 2879, 1741, 1731, 1635, 1621, 1490, 1452, 1361, 1322, 1269, 1201, 1137, 1067, 1045, 1004, 974, 952, 863, 827, 797, 763, 699, 640, 615, 536, 472. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H (0.82:0.18 mixture of products **2m***/**3a**) 3.23-3.73 [10.64H, m, NCH$_2$CH$_2$OH*, OC*H*$_2$CH(O*H*)C*H*$_2$N, OC*H*$_2$CHO*, OCHC*H*$_2$N*, NC*H*$_2$CH$_2$O, =CHOCH$_2$C*H*$_2$*, =CHOCH$_2$C*H*$_2$], 3.77-3.80 (2H, m, =CHOC*H*$_2$CH$_2$*, =CHOC*H*$_2$CH$_2$), 3.92-3.98 (1.18H, m, C*H*OH, cis-CH$_2$*=, cis-CH$_2$=), 4.12-4.16 (1H, m, trans-CH$_2$*=, trans-CH$_2$=), 4.28 (0.36H, t, $^3J_{HH}$ 8.0 Hz, NCH$_2$C*H*$_2$O), 4.61 (0.82H, m, OCH*), 6.41 (0.82H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C*), 6.42 (0.18H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C (0.82:0.18 mixture of products **2m***/**3a**) 46.2 (N*C*H$_2$CH$_2$O), 46.4 (N*C*H$_2$CH$_2$OH*), 47.2 [CH(OH)*C*H$_2$N], 47.3 (OCH*C*H$_2$N*), 60.0 (CH$_2$OH*), 62.1 (NCH$_2$*C*H$_2$O), 67.2 (br.s, =CHO*C*H$_2$*, =CHO*C*H$_2$), 69.0 (CHOH), 69.7 (=CHOCH$_2$*C*H$_2$), 70.1 (O*C*H$_2$CHO*), 71.7 (=CHOCH$_2$*C*H$_2$*), 72.1 (OCH*), 72.9 [O*C*H$_2$CH(OH)], 86.9 (br.s, =CH$_2$*, =CH$_2$), 151.4 (=CHO*), 151.5 (=CHO), 158.2 (C=O*), 159.2 (C=O). Anal. Calcd for $C_{10}H_{17}NO_5$ (231.25): C, 51.94; H, 7.41; N, 6.06; O, 34.59%. Found: C, 51.27; H, 7.43; N, 6.11%.

The mixture of **2m**/**3a** was separated by column chromatography (silica gel, chloroform-methanol 95:5) to afford pure **2m** and **3a**.

3-(2-Hydroxyethyl)-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2m). Colourless oil, yield 11%, 0.20 g; IR (ν_{max}, cm^{-1}): 3426, 3117, 3041, 2930, 2879, 1731, 1636, 1622, 1524, 1491, 1453, 1379, 1360, 1322, 1258, 1201, 1140, 1068, 1043, 1003, 973, 952, 898, 864, 828, 796, 763, 735, 690, 649, 607, 579, 473. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 2.68 (1H, br.s, OH), 3.28-3.35 (1H, m, NC*H*HCH$_2$), 3.40-3.47 (1H, m, NCH*H*CH$_2$), 3.60 (1H, dd, $^2J_{HH}$ 8.6 Hz, $^3J_{HH}$ 5.8 Hz, CHC*H*HN), 3.65-3.83 (9H, m, CHCH*H*N, NCH$_2$C*H*$_2$, =CHOC*H*$_2$C*H*$_2$OC*H*$_2$), 4.02 (1H, dd, $^3J_{cis}$ 6.7 Hz, $^2J_{gem}$ 1.9 Hz, cis-CH$_2$=), 4.18 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 1.9 Hz, trans-CH$_2$=), 4.61-4.67 (1H, m, OCH), 6.46 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 46.5 (N*C*H$_2$CH$_2$OH), 47.4 (OCH*C*H$_2$N), 60.2 (CH$_2$OH), 67.2 (=CHO*C*H$_2$), 70.1 (O*C*H$_2$CHO), 71.8 (=CHOCH$_2$*C*H$_2$), 72.1 (OCH), 87.0 (=CH$_2$), 151.4 (=CHO), 158.3 (C=O). Anal. Calcd for $C_{10}H_{17}NO_5$ (231.25): C, 51.94; H, 7.41; N, 6.06; O, 34.59%. Found: C, 51.74; H, 7.40; N, 6.19%.

3-{2-Hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-1,3-oxazolidin-2-one (3a). Colourless oil, yield 16%, 0.29 g; IR (ν_{max}, cm^{-1}): 3416, 3117, 3040, 2921, 2879, 1740, 1636, 1621, 1526, 1487, 1444, 1425, 1377, 1364, 1323, 1270, 1200, 1133, 1101, 1052, 974, 918, 888, 841, 825, 764, 732, 701, 619, 535, 486. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 3.02 (1H, d, $^3J_{HH}$ 3.6 Hz, OH), 3.30 (1H, dd, $^2J_{HH}$ 14.5 Hz, $^3J_{HH}$ 6.9 Hz, CHC*H*HN), 3.39 (1H, dd, $^2J_{HH}$ 14.5 Hz, $^3J_{HH}$ 3.6 Hz, CHCH*H*N), 3.46 (1H, dd, $^2J_{HH}$ 9.8 Hz, $^3J_{HH}$ 6.8 Hz, NC*H*HCH$_2$O), 3.57 (1H, dd, $^2J_{HH}$ 9.8 Hz, $^3J_{HH}$ 4.2 Hz, NCH*H*CH$_2$O), 3.69-3.77 (4H, m, =CHOCH$_2$C*H*$_2$OC*H*$_2$), 3.81-3.84 (2H, m, =CHOC*H*$_2$), 3.98-4.03 (2H, m, C*H*OH, cis-CH$_2$=), 4.19 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 1.9 Hz, trans-CH$_2$=), 4.32 (2H, t, $^3J_{HH}$ 8.1 Hz, NCH$_2$C*H*$_2$O), 6.46 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.8 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 46.4 (N*C*H$_2$CH$_2$O), 47.2 (CH*C*H$_2$N), 62.1 (NCH$_2$*C*H$_2$O), 67.2 (=CHO*C*H$_2$), 69.4 (CHOH), 69.9 (=CHOCH$_2$*C*H$_2$), 72.9 (O*C*H$_2$CH), 87.0 (=CH$_2$), 151.6 (=CHO), 159.2 (C=O). Anal. Calcd for $C_{10}H_{17}NO_5$ (231.25): C, 51.94; H, 7.41; N, 6.06; O, 34.59%. Found: C, 51.58; H, 7.61; N, 6.24%.

3-{2-Hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-4,4-dimethyl-1,3-oxazolidin-2-one (3b). Colourless oil, yield 99%, 2.31 g, n_D^{20} 1.4762; IR (ν_{max}, cm^{-1}): 3427, 3117, 3042, 2971, 2931, 2877, 1748, 1728, 1636, 1621, 1542, 1479, 1464, 1452, 1441, 1408, 1387, 1372, 1322, 1297, 1258, 1227, 1200, 1129, 1094, 1042, 1014, 974, 949, 914, 883, 827, 773, 749, 701, 596, 581, 559, 482. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 1.27 (3H, s, CH$_3$), 1.28 (3H, s, CH$_3$), 3.15 (1H, dd, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 7.1 Hz, C*H*HN), 3.26 (1H, dd, $^2J_{HH}$ 14.7 Hz, $^3J_{HH}$ 3.8 Hz, CH*H*N), 3.45-3.52 (2H, m, OC*H*$_2$CH), 3.68-3.71 (3H, m, =CHOCH$_2$C*H*$_2$, OH), 3.79-3.81 (2H, m, =CHOC*H*$_2$), 3.91-4.03 (4H, m, C*H*OH, cis-CH$_2$=, NCC*H*$_2$O), 4.16 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-CH$_2$=), 6.43 (1H, dd, $^3J_{trans}$ 14.3 Hz, $^3J_{cis}$ 6.7 Hz, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 24.77 (CH$_3$), 24.79 (CH$_3$), 43.8 (CH$_2$N), 58.9 (C), 67.2 (=CHO*C*H$_2$), 69.7 (CHOH), 69.9 (=CHOCH$_2$*C*H$_2$), 72.7 (O*C*H$_2$CH), 75.3 (NC*C*H$_2$O), 86.8 (=CH$_2$), 151.6 (=CHO), 159.4 (C=O). Anal. Calcd for $C_{12}H_{21}NO_5$ (259.30): C, 55.58; H, 8.16; N, 5.40; O, 30.86%. Found: C, 55.55; H, 8.11; N, 5.84%.

3-[1-(Hydroxymethyl)propyl]-5-{[2-(vinyloxy)ethoxy]methyl}-1,3-oxazolidin-2-one (2o) and 4-Ethyl-3-{2-hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-1,3-oxazolidin-2-one (3c). Mixture of **2o**/**3c** (0.52:1), light yellow oil, yield of mixture 99%, 2.58 g; IR (ν_{max}, cm^{-1}): 3417, 3118, 3075, 3041, 2965, 2933, 2879, 1746, 1731, 1635, 1621, 1527, 1485, 1442, 1373, 1359, 1322, 1267, 1201, 1136, 1076, 1055, 1040, 976, 915, 883, 846, 831, 793, 764, 705, 616, 593, 581, 544. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H (0.34:0.66 mixture of products **2o***/**3c**) 0.76-0.86 (3H, m, CH_3, CH_3^*), 1.30-1.74 (2H, m, C*H*$_2$CH$_3$, C*H*$_2$CH$_3^*$), 2.97-3.75 [10.02H, m, CH(OH)C*H*$_2$N, NC*H*(CH$_2$CH$_3$)CH$_2$OH*, OCHC*H*$_2$N*, OC*H*$_2$C*H*$_2$OC*H*$_2$CHO*H*, OCH$_2$CH$_2$OCH$_2^*$, CH$_2$OH*], 2.97-3.93 [2.98H, m, NC*H*C*H*HO, C*H*OH, cis-C*H*$_2$=CHO*, cis-C*H*$_2$=CHO], 4.08 (0.34H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.1 Hz, trans-C*H*$_2$=CHO*), 4.10 (0.66H, dd, $^3J_{trans}$ 14.3 Hz, $^2J_{gem}$ 2.0 Hz, trans-C*H*$_2$=CHO), 4.29 (0.66H, t, $^3J_{HH}$ 8.4 Hz, NCHCH*H*O), 4.57 (0.34H, m, OC*H*CH$_2$N*), 6.32-6.39 (1H, m, =CHO*, =CHO). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C (0.34:0.66 mixture of products **2o***/**3c**) 7.4 and 7.5 (CH_3), 10.2 and 10.4 (CH_3^*), 20.9 and 21.0 (*C*H$_2$CH$_3^*$), 24.0 (*C*H$_2$CH$_3$), 42.3 and 42.5 (OCH*C*H$_2$N*), 44.4 and 44.7 (CH$_2$N), 56.3, 56.8, 56.9 and 57.1 (m, N*C*HCH$_2$O, N*C*HCH$_2$OH*), 62.1 and 62.3 (CH$_2$OH*), 66.8 and 66.9 (=CHO*C*H$_2^*$), 67.0 (br.s, =CHO*C*H$_2$), 68.2 (CHOH), 69.4 (O*C*H$_2$CHO*), 69.5 and 69.6 (NCH*C*H$_2$O), 69.9 (=CHOCH$_2$*C*H$_2$), 71.5 (=CHOCH$_2$*C*H$_2^*$), 71.9 and 72.0 (O*C*HCH$_2$N*), 72.8 and 72.9 [O*C*H$_2$CH(OH)], 86.6, 86.7 and 86.8 (m, =CH$_2^*$, =CH$_2$), 151.2, 151.3 and 151.4 (m, =CHO*, =CHO), 158.2 and 158.3 (C=O*), 158.9 and 159.1 (C=O). Anal. Calcd for $C_{12}H_{21}NO_5$ (259.30): C, 55.58; H, 8.16; N, 5.40; O, 30.86%. Found: C, 55.90; H, 8.05; N, 5.49%.

The separation of mixture **2o**/**3c** by column chromatography (silica gel, chloroform-methanol 95:5) afforded fraction enriched with **3c**.

4-Ethyl-3-{2-hydroxy-3-[2-(vinyloxy)ethoxy]propyl}-1,3-oxazolidin-2-one (3c). Light yellow oil, yield 20%, 0.52 g; IR (ν_{max}, cm^{-1}): 3419, 3118, 2966, 2931, 2880, 1746, 1636, 1621, 1531, 1483, 1440, 1384, 1360, 1322, 1269, 1201, 1181, 1137, 1046, 974, 825, 792, 765, 705, 668, 606, 540, 534. ^{1}H NMR (400.13 MHz, $CDCl_3$): δ_H 0.89 (3H, t, $^3J_{HH}$ 7.5 Hz, CH_3), 1.51-1.60 (2H, m, C*H*HCH$_3$, OH), 1.76-1.83 (1H, m, CH*H*CH$_3$), 3.10-3.62 (5H, m, OC*H*$_2$CHC*H*$_2$N, NC*H*CH$_2$O), 3.72-3.85 (4H, m, OCH$_2$CH$_2$O), 3.96-4.04 (3H, m, cis-C*H*$_2$=CHO, C*H*OH, NCHC*H*HO), 4.18-4.23 (1H, m, trans-C*H*$_2$=CHO), 4.39 (1H, t, $^3J_{HH}$ 8.4 Hz, NCHCH*H*O), 6.44-6.50 (1H, m, OCH=C). ^{13}C NMR (100.62 MHz, $CDCl_3$): δ_C 7.8 and 7.9 (CH_3), 24.4 (*C*H$_2$CH$_3$), 44.7 and 45.1 (CH$_2$N), 57.1 and 57.5 (N*C*HCH$_2$O), 67.2 and 67.3 (=CHO*C*H$_2$), 69.2 (CHOH), 69.9 and 70.0 (NCH*C*H$_2$O), 70.1 (=CHOCH$_2$*C*H$_2$), 72.9 [O*C*H$_2$CH(OH)], 87.0 (br.s, =CH$_2$), 151.7 (=CHO), 159.3 (C=O).

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