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One-pot synthesis of heterocyclic compounds initiated by chemoselective addition to β-acyl substituted unsaturated aldehydes with nucleophilic tin complexes

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Abstract

β-Acyl substituted unsaturated aldehydes **1** were revealed to be good precursors for the synthesis of various heterocyclic compounds by the combination with tin nucleophiles. Various 2-monosubstituted pyrroles were prepared in an one-pot procedure via the reductive amination of formyl groups of **1** by using Bu_2SnIH–HMPA complex. One-pot synthesis of heterocycles was carried out initiated by chemoselective reduction of **1** with Bu_3SnH–HMPA complex and the subsequent reaction with heterocumulenes. Furthermore, the one-pot synthesis of nitrogen heterocyclic compounds accompanying chemo-, regio- and diastereoselective carbon–carbon bond formation in side chain moieties was effectively accomplished initiated by the regio- and diastereoselective allylation of the formyl group of **1** with allylic tin species.

Keywords: Heterocycle; Reductive amination; Reduction; Allylation; Tin hydride; Allylic tin

1. Introduction

Tin–heteroatom bonds can be easily generated by the addition of organotin nucleophiles to carbonyl compounds [1]. The reduction of carbonyl compounds by tributyltin hydride (Bu_3SnH) is a well-known method [2]. Although the reactions proceed under mild and neutral conditions, the resulting tin alkoxides have been scarcely used for further transformation in which most tin–oxygen bonds are hydrolyzed to alcohols. However, tin–oxygen and –nitrogen bonds bear high nucleophilicity. In some cases, their nucleophilicity is higher than that of the corresponding free alcohols and amines [3]. Herein we report the one-pot synthesis of heterocycles initiated by the chemoselective addition of bifunctional compounds **1**. The generated tin–heteroatom bonds worked as key intermediates (Scheme 1).

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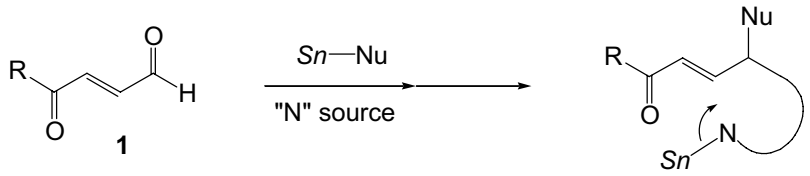
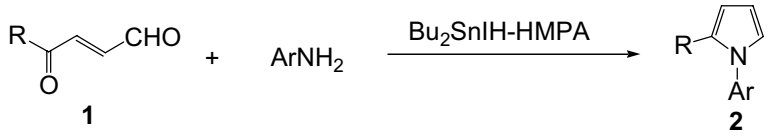
2. Results and discussion

2.1. One-pot synthesis of 2-monosubstituted pyrroles by reductive amination

We have been developing the unique reactivities of the halogen-substituted tin hydride systems such as Bu_2SnIH and Bu_2SnClH–HMPA which promote effective reduction of imines [4]. In particular, Bu_2SnClH–HMPA affords effective reductive amination to give a wide range of secondary and tertiary amines in one-pot procedures [5]. Pyrroles are important heterocycles broadly used in materials science [6] and found in naturally occurring and biologically important molecules [7]. Accordingly, substantial attention has been paid to develop efficient methods for the synthesis of pyrroles, most known methods are for forming 2,5-di- or polysubstituted pyrroles. Convenient methods have scarcely reported for the construction of 2-monosubstituted pyrrole ring [8]. Herein a novel, and



Scheme 1. Reaction concept for synthesis of heterocycles.



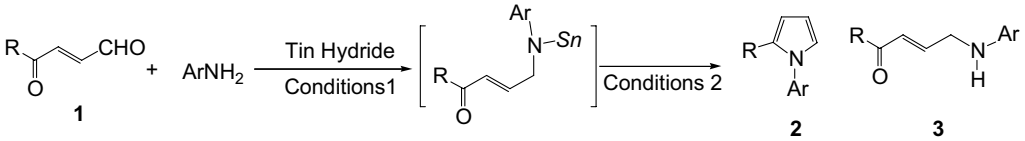
Scheme 2.

efficient method for construction of 2-monosubstituted pyrroles was developed via the reductive amination by dibutyliodotin hydride (Bu_2SnIH)–HMPA system (Scheme 2) [9].

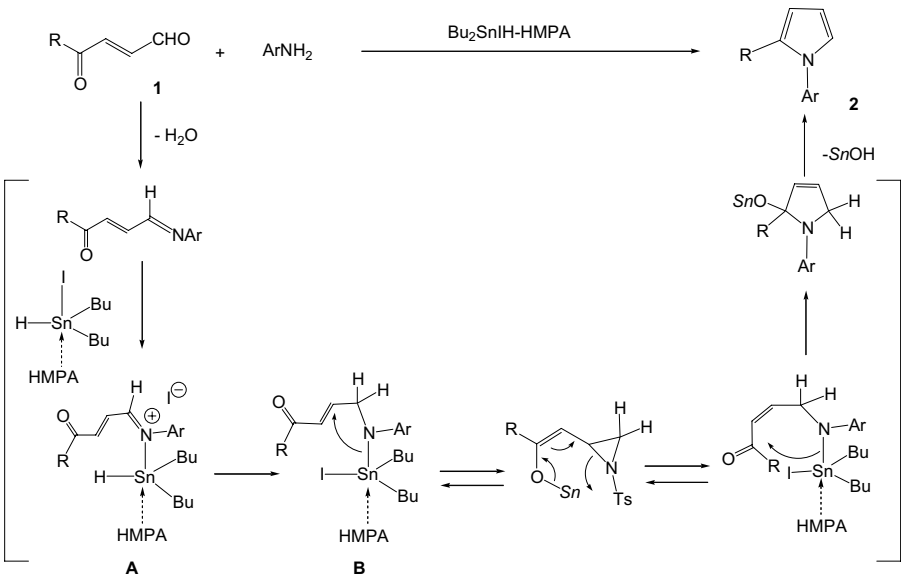
As shown in Table 1, first, it was found that enal **1a** in the presence of iodotin hydride in THF at 0 °C for 2 h underwent reductive amination with *p*-chloroaniline to give secondary amine **3a** in 74% yield (entry 1). Although no cyclization occurred, this result indicates that reductive amination was carried out effectively without affecting the remaining enone functionality in **1a**. Chloro-substituent on nitrogen aromatic ring was not reduced. After the reductive amination, heating the mixture at 80 °C for 2 h afforded pyrrole **2a** in 22% yield with 60% of **3a** (entry 2). In this case, 1,4-dioxane was used as a solvent to heat the reaction mixture at 80 °C. Noteworthy is that under the same conditions, pyrrole **2a** was obtained in 81% yield in the presence of an equimolar amount of HMPA (entry 3), in which non-cyclized product **3a** was not obtained at all. The iodo-substituent on the tin center was essential for the cyclization because chlorotin derivative, Bu_2SnClH–HMPA, gave no pyrrole **2a** at all where only **3a** was obtained under the same conditions (entry 4). Various aromatic amines were applicable to give pyrroles **2b–d** in one-pot procedures by the reductive amination of **1** using Bu_2SnIH–HMPA system followed by heating at 80 °C (entries 5–7). In the case of **1b**, pyrrole **2e** was also obtained (entry 8). Enal having aromatic ketone **1c** was also reactive to give the corresponding pyrroles **2f–h** where reductive amination was carried out at −40 °C (entries 9–11).

A plausible reaction course is indicated in Scheme 3. Initially, reductive amination occurs by mixing Bu_2SnIH–HMPA with starting substrate **1** and an aromatic amine. It is cleared that halogenotin hydride bears high imine-selectivity because formyl and enone groups of **1** were not reduced at all. In the next stage, the resulting tin–nitrogen bond adds to the remaining ketone moiety in **1** by heating. At the last stage, the elimination of tin hydroxide gives pyrroles **2**. The reaction was carried out in a one-pot procedure hence no intermediates were isolated. The substitu-

Table 1
One-pot synthesis of 2-monosubtituted pyrroles **2** (1 mmol of **1**, 1 mmol of $ArNH_2$, 1 mmol of tin hydride, 1 mmol of HMPA, 1 mL of solvent)



Entry	R	Ar	Tin hydride	Solvent	Conditions 1	Conditions 2	Product and yield (%)
1	n-C_8H_{17} (**1a**)	p-ClC_6H_4	Bu_2SnIH	THF	0 °C, 2 h	0 °C, 2 h	**3a** 74
2			Bu_2SnIH	Dioxane	0 °C, 2 h	80 °C, 2 h	**2a** 22, **3a** 60
3			Bu_2SnIH–HMPA	Dioxane	0 °C, 2 h	80 °C, 2 h	**2a** 81
4			Bu_2SnClH–HMPA	Dioxane	0 °C, 2 h	80 °C, 2 h	**3a** 98
5		Ph	Bu_2SnIH–HMPA	Dioxane	0 °C, 2 h	80 °C, 2 h	**2b** 54
6		p-Tol	Bu_2SnIH–HMPA	Dioxane	0 °C, 2 h	80 °C, 2 h	**2c** 60
7		p-$MeOC_6H_4$	Bu_2SnIH–HMPA	Dioxane	0 °C, 2 h	80 °C, 2 h	**2d** 66
8	$PhCH_2CH_2CH_2$ (**1b**)	p-ClC_6H_4	Bu_2SnIH–HMPA	THF	0 °C, 2 h	60 °C, 2 h	**2e** 60
9	Ph (**1c**)	p-ClC_6H_4	Bu_2SnIH–HMPA	THF	−40 °C, 2 h	60 °C, 2 h	**2f** 46
10		Ph	Bu_2SnIH–HMPA	THF	−40 °C, 2 h	60 °C, 2 h	**2g** 41
11		p-$MeOC_6H_4$	Bu_2SnIH–HMPA	THF	−40 °C, 2 h	60 °C, 2 h	**2h** 49



Scheme 3. A plausible reaction mechanism.

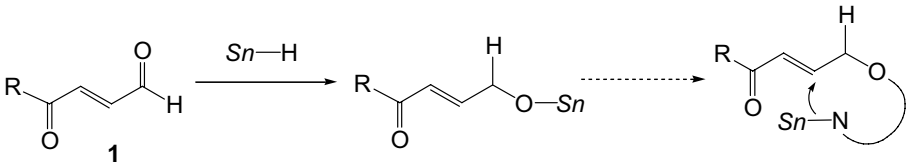
ent and ligand in the tin complex play important roles for the synthesis of pyrroles. Bu_2SnIH–HMPA is a trigonal bipyramidal structure in which iodine substituent occupy apical position [10]. The Sn–halogen bond is responsible for high imine-selectivity, which promotes the formation of an iminium ion **A**. As a result, electrophilicity of imine is increased [4,5]. The activated imine thus formed would be reduced more rapidly than any other functionalities such as starting formyl and enone moieties. After the imine-selective reduction, tin–nitrogen bond is formed. High coordination of tin is important for the intramolecular addition. Namely, in the pentavalent tin amide **B**, the tin–nitrogen bond occupying the apical position bears adequate nucleophilicity to the remaining carbonyl groups [11]. It seems that dibutylchlorotin amide moiety (Bu_2ClSnN–) does not have enough nucleophilicity to cause cyclization because of the electron-withdrawing character of Cl substituent (entry 4).

2.2. One-pot synthesis of heterocycles initiated by chemoselective reduction

Next, the one-pot synthesis of heterocycles was carried out initiated by the chemoselective reduction of the formyl groups of bifunctional compounds **1** [12]. The generated tin–oxygen bonds worked as key intermediates. Heteroatom nucleophiles were generated by the combination of heterocumulenes (Scheme 4).

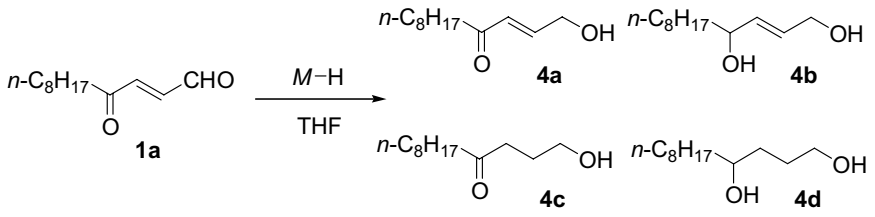
For the selective reduction of the formyl groups of **1**, the choice of reducing agents is important, because of coexistence reactive functionalities of enones. As shown in Table 2, use of conventional agents such as $LiAlH_4$ and $NaBH_4$ resulted in complex reactions (entries 1–3). Tributyltin hydride (Bu_3SnH) itself bears little reducing ability (entry 4). The Bu_3SnH reaction catalyzed by Lewis acid [13] gave only **4a**, though in moderate yields (entries 5 and 6). We had already developed Bu_3SnH–HMPA to effect chemoselective reduction of formyl groups under mild conditions [14], and here Bu_3SnH–HMPA was found to reduce the formyl group of **1a** in the highest yield (entry 7). Dibutylchlorotin hydride (Bu_2ClSnH) complex [15] also gave good yield of **4a** (entry 8). In these cases, other products than **4a**–**d** were not obtained and starting **1a** was recovered. This would be because of the decomposition of tin hydrides.

As shown in Scheme 5, we next tried to prepare heterocycles through initiation by tin hydride reduction in one-pot procedure. Thus, after the chemoselective reduction of the formyl group of **1**, the generated tin–oxygen bond of **C** was allowed to react with an isocyanate [16]. The resulting tin–nitrogen bond of **D** successively adds to the enone moiety in conjugate fashion to give 2-oxazolidinones

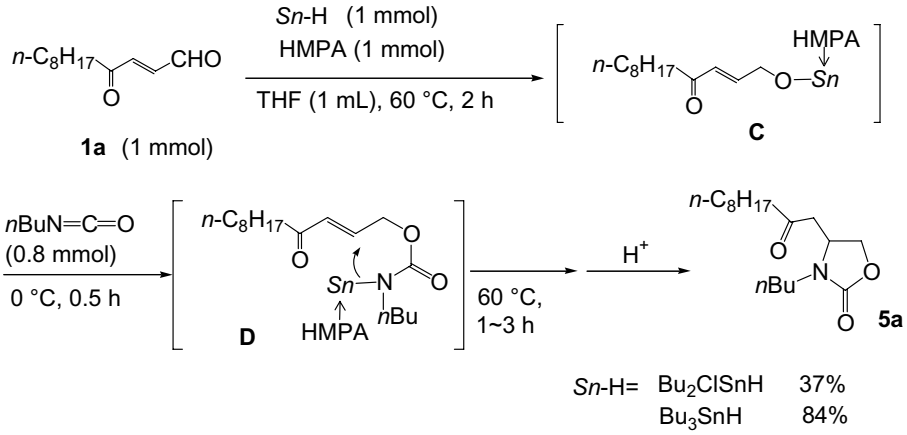


Scheme 4. Reaction concept for synthesis of heterocycles.

Table 2
Chemoselective reduction of formyl group of **1a**. (1 mmol of MH, 1 mmol of **1a**, 1 mL of THF)



Entry	Reducing agent (M–H)	Conditions	Product and yield (%)
1	DIBAL (1 mmol)	0 °C, 5 h	**4a** 25, **4b** 31
2	$NaBH_4$ (1 mmol)	rt, 1.5 h	**4d** 61
3	$LiAlH_4$ (1 mmol)	0 °C, 1 h	**4b** 33, **4c** 12
4	Bu_3SnH (1 mmol)	rt, 23 h	Trace
5	Bu_3SnH (1 mmol)–$ZnCl_2$ (0.1 mmol)	rt, 23 h	**4a** 40
6	Bu_3SnH (1 mmol)–$MgBr_2$ (0.1 mmol)	rt, 14 h	**4a** 35
7	Bu_3SnH–HMPA (1 mmol)	rt, 3 h	**4a** 56
8	Bu_2ClSnH–HMPA (1 mmol)	rt, 3 h	**4a** 51



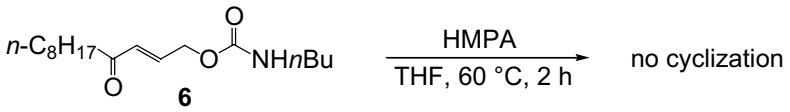
Scheme 5.

5. In the tin hydride initiated reductions presented here, use of dibutylchlorotin hydride system (Bu_2ClSnH–HMPA) and the subsequent treatment with BuN=C=O gave the desired 2-oxazolidone **5a** in only 37% yield, although the initial reduction of the formyl group proceeded effectively (see Table 2, entry 8). In contrast, the reduction of **1** with tributyltin nucleophile (Bu_3SnH–HMPA) and subsequent treatment with BuN=C=O afforded 2-oxazolidones **5a** in a good yield (84%). 2-Oxazolidones are important biologically active compounds and precursors of β-amino alcohols [17].

The role of the Sn–N bond of **D** is clearly important because linear compound **6** which bears no tin moiety did not afford intramolecular conjugate addition under the same conditions (Scheme 6).

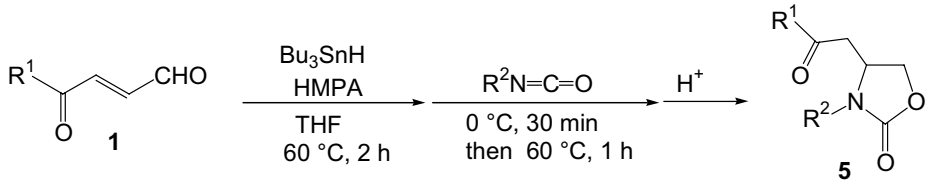
Bu_3SnN moieties have fundamentally higher nucleophilicity than $ClBu_2SnN$ moieties because of the presence of the electron-withdrawing Cl substituent in the latter case. Hence, Bu_3SnN moieties worked effectively in the presented conjugate addition. HMPA also plays an important role in the conjugate addition besides the chemoselective reduction of the formyl group in **1**, in the generation of nucleophilic pentacoordinate tin amides **D** [11]. It is clear that no intramolecular conjugate addition takes place in the absence of HMPA, because the $ZnCl_2$-catalyzed Bu_3SnH reduction (Table 2, entry 5) and the subsequent reaction with BuN=C=O at 60 °C for 2 h gave only the linear compound **6**. As shown in Table 3, various 2-oxazolidones **5** were prepared by Bu_3SnH–HMPA. Aliphatic, allylic, secondary alkyl and aromatic isocyanates were reactive towards **1a**, giving the corresponding 2-oxazolidones **5a**–**f** in good to excellent yields (entries 1–6). Use of substrates **1c**, **d** having aromatic ketone moieties also gave 2-oxazolidone **5h** and **5i** (entries 8 and 9).

The advantage of this method includes the potential to use other heterocumulenes instead of isocyanates, giving a variety of heterocycles. Use of phenyl isothiocyanate afforded oxazolidin-2-thione **7** (Scheme 7). In this case, it was known that tin–oxygen bond should add across the C=S bond of isothiocyanates to give **E** because strong affinity of tin to sulfur atom [16b]. The subsequent intramolecular conjugate addition occurs from the terminal imino-nitrogen



Scheme 6.

Table 3
Synthesis of 2-oxazolidones (1 mmol of **1**, 1 mmol of Bu_3SnH–HMPA, 0.8 mmol of isocyanate, 1 mL of THF)



Entry	R^1 (**1**)	R^2	Product and yield (%)	
1	*n*-C_8H_{17} (**1a**)	Bu	**5a**	84
2		$H_2C{=}CHCH_2$	**5b**	73
3		$ClCH_2CH_2$	**5c**	75
4		$PhCH_2$	**5d**	70
5		$(CH_3)_2CH$	**5e**	87
6		Ph	**5f**	85
7	$Ph(CH_2)_3$ (**1b**)	Bu	**5g**	56
8	Ph (**1c**)	Bu	**5h**	38
9	*p*-ClC_6H_4 (**1d**)	Bu	**5i**	42

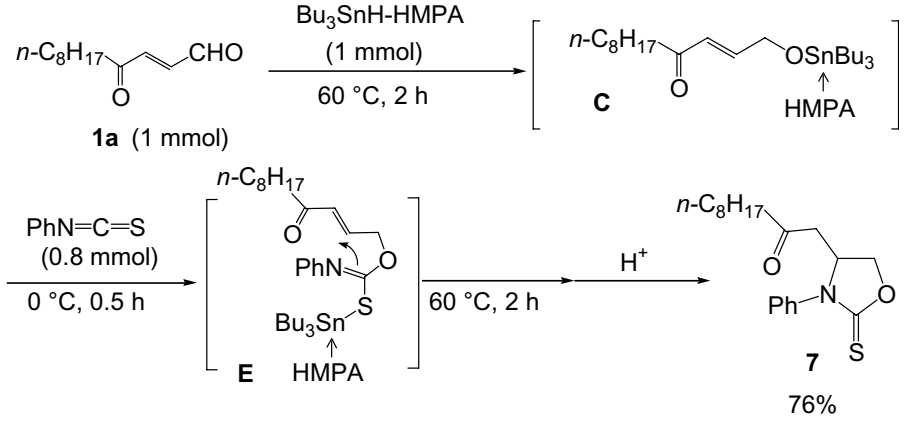
atom. The use of CO_2 as a heterocumulene did not afford cyclic products plausibly because of lower reactivity of tin–oxygen bond than Sn–N bonds in the conjugate addition.

As shown in Scheme 8, use of diphenylketene afforded the γ-lactone **8** through the intramolecular conjugate addition of tin enolate **F**. The conjugate addition occurred through *C*-alkylation of tin enolate. This result is in contrast to our previous intramolecular reaction with alkyl halides to cause *O*-alkylation [18].

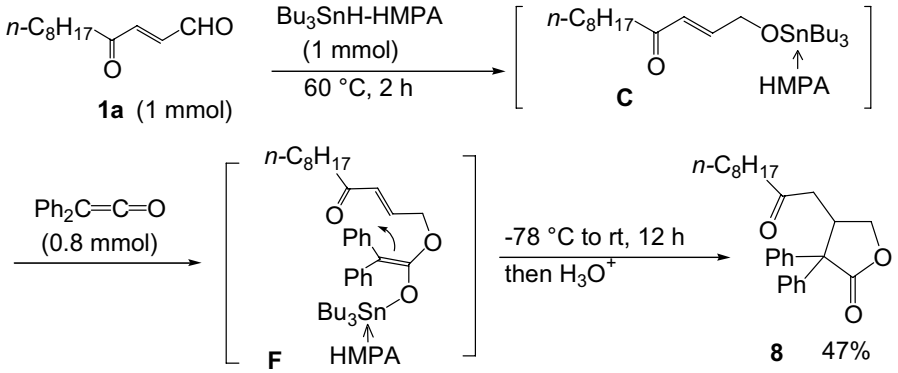
Electrophiles other than heterocumulenes were also applicable (Scheme 9). An electrophilic alkene reacted with the Sn–O bond of **C** to give intermediate **G**, and intramolecular addition proceeded to give cyclic ether **9** in a one-pot procedure. When **C** was treated with diketene, the α-acyl-γ-lactone **10** was obtained, so the ring cleavage of diketene occurred at the acyl carbon–oxygen bond [19]. After isomerization to the stable tin enolate **H**, the intramolecular conjugate addition took place.

2.3. One-pot synthesis of nitrogen heterocycles initiated by regio- and diastereoselective carbon–carbon bond formation

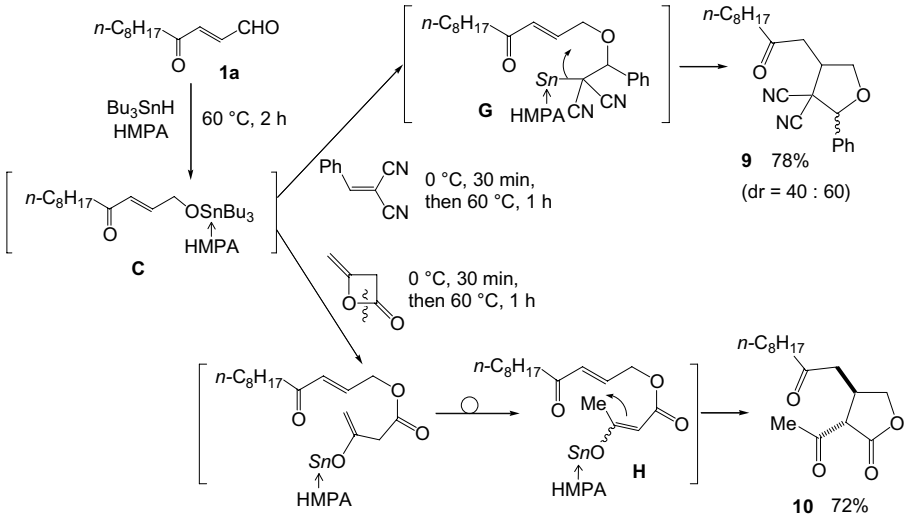
Next, a one-pot synthesis of nitrogen heterocyclic compounds was carried out initiated by the allylation of the formyl group of bifunctional carbonyl compounds **1** [20]. The generated tin–oxygen bonds worked as key intermediates to prepare various heterocyclic compounds accompanying chemo-, regio- and diastereoselective carbon–carbon bond formation in the side chain moieties. Allylic tributyltins bear low reactivities toward carbonyl groups. To achieve effective allylation, representative



Scheme 7.



Scheme 8.



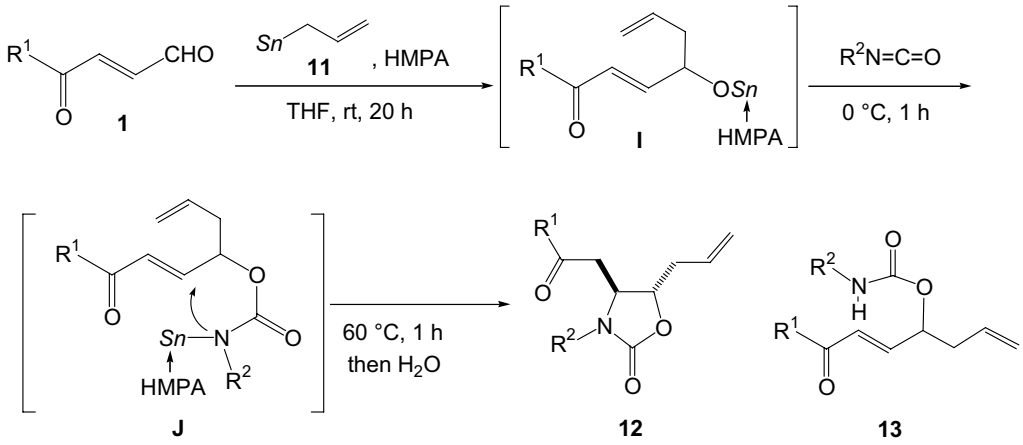
Scheme 9.

Lewis acids such as $TiCl_4$ and $BF_3 \cdot OEt_2$ have been used as activators of carbonyl substrates [21]. However, these conventional Lewis acids did not afford chemoselective allylation of the formyl groups of bifunctional substrates **1** because of their instability to acids. We fortunately found here that allylic chlorodibutyltin (**11**) system [22] effectively reacted with the formyl group of substrate **1** without any strong Lewis acids. The allylation was highly chemoselective to the formyl group where the enone moiety of **1a** did not react at all. As shown in Table 4, after the allylation, the successive reaction with an isocyanate followed by heating afforded 4,5-*trans*-disubstituted-2-oxazolidinones **12a** and **12b** selectively (entries 3 and 4). The chloro substituents on the tin center are essential because allyltributyltin (**11a**) was not reactive at all (entry 1). In addition, HMPA is essential to cause the cyclization to give **12** because only linear adduct **13** was obtained in the absence of HMPA (entry 2). The reaction course to **12** is explained as shown in the equation of Table 4. After the chemoselective allylation of the formyl group, the generated tin–oxygen bond of **I** reacts with an isocyanate spontaneously. As a result, an adduct **J** is formed. The resulting tin–nitrogen bond successively adds to the enone moieties of **1** in a fashion of conjugate addition to give 2-oxazolidinones **12** in a one-pot procedure. HMPA plays an important role for the conjugate addition of the stannylcarbamate **J** where HMPA coordinates to the tin center to form pentacoordinate tin amide species, increasing their nucleophilicity [11]. The intramolecular conjugate addition did not take place at all in the absence of HMPA. The activating effect of HMPA to silicon species was also discussed [23].

$[ClBu_2Sn]N-$ nucleophiles work well here in comparison with the reaction involving Bu_2SnClH-reduction (Scheme 5). The reason is not clear yet, however, allylic substituent would work well to orientate $ClBu_2SnN-$ group causing cyclization. In the 2-oxazolidinones **12**, 4,5-*trans*-disubstituted isomers predominated. The *trans* selectivity is explained in terms of 1, 3-allylic strain in the intramolecular addition (Scheme 10).

Next, we applied crotyltin reagents in the initial carbon–carbon bond formation. Crotylmetalation of the carbonyl functionality incurs problems of regio- and diastereoselectivities. A chloro substituent on the tin center is easily introduced by the redistribution of crotyltributyltin (**14**) with Bu_2SnCl_2 (Scheme 11) [24]. The redistribution pro-

Table 4
One-pot synthesis of 2-oxazolidinones (1 mmol of **1**, 1 mmol of **11**, 1 mmol of HMPA, 1 mmol of isocyanate, 1 mL of THF)



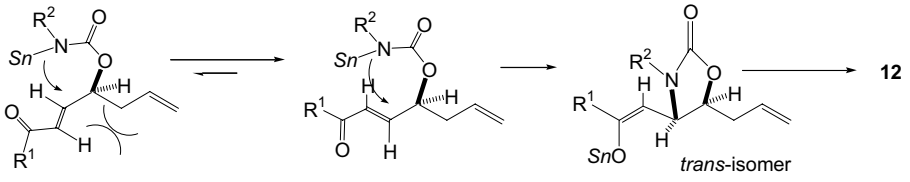
Entry	R^1	R^2	*Sn* (**11**)	Product and yield (%)
1	*n*-C_8H_{17} (**1a**)	Ph	Bu_3Sn (**11a**)	No reaction
2			Bu_2ClSn (**11b**)	**13a** 99 (without HMPA)
3			**11b**	**12a** 81 (*trans*:*cis* = 91:9)
4	*p*-ClC_6H_4 (**1d**)	Ts	**11b**	**12b** 54 (*trans*:*cis* = 100:0)

ceeds by the initial formation of chlorodibutyl (1-methylallyl)tin **K** through the reaction at the terminal γ-carbon of **14**, and the subsequent isomerization takes place to give (*Z*)-crotyldibutylchlorotin **L**. It has been reported that (*Z*)-isomers **L** are formed irrespective of the starting *E*/*Z*-crotyltin **14** [25]. Generated allylic tins **K** and **L** both work as nucleophiles to aldehydes, and here we controlled the reaction species by the order of the addition of Bu_2SnCl_2, determining α/γ regioselectivity of the products.

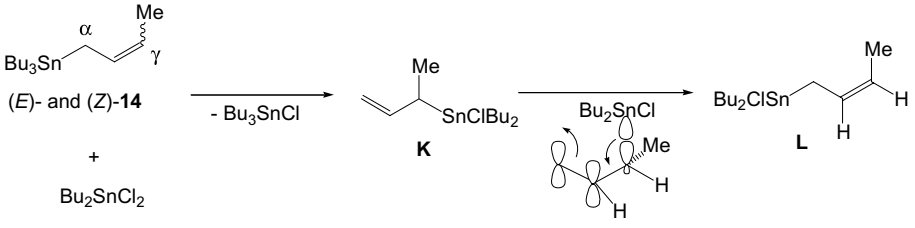
Initially, crotyltributyltin **14**, Bu_2SnCl_2, HMPA and the enone **1** were heated in one-portion at 60 °C for 3 h. The subsequent addition of RN=C=O at 0 °C followed by heating gave 4,5-*trans*-substituted 2-oxazolidones **15a**–**c** which include *Z*-crotyl and carbonylmethyl substituents on the rings (Scheme 12).

As shown in Scheme 13, it is considered that the *Z*-crotyl substituent in **15** is derived from the *in situ* generated chlorodibutyl(1-methylallyl)tin **K** which adds to the formyl group of **1** at the terminal γ-carbon. This regioselectivity is confirmed by quenching the mixture of the crotylation product of the carbonyl substrates, where *Z*-homocrotyl alcohols **16** were obtained. The stereoselectivity of the reactions between **K** and **1** is consistent with a six-membered, chair-like, cyclic transition state in which α-methyl substituent adopts a pseudo-axial position. The (*Z*)-preference is thought to be due to the steric congestion between the α-methyl group and the tin ligands in the transition state [26].

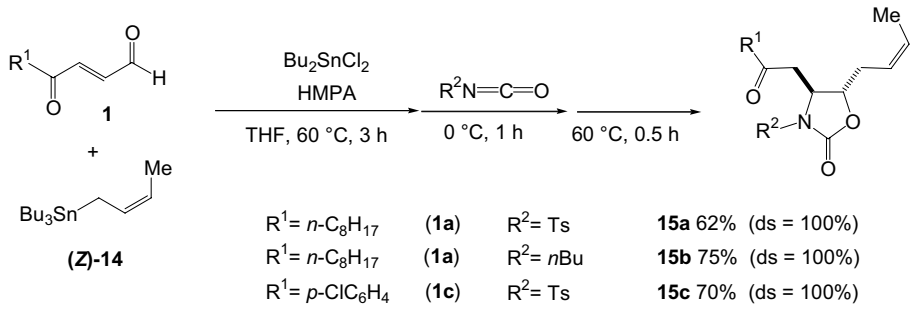
On the contrary, when crotyltributyltin **14** and *n*-Bu_2SnCl_2 were preheated at 60 °C for 2 h, the subsequent



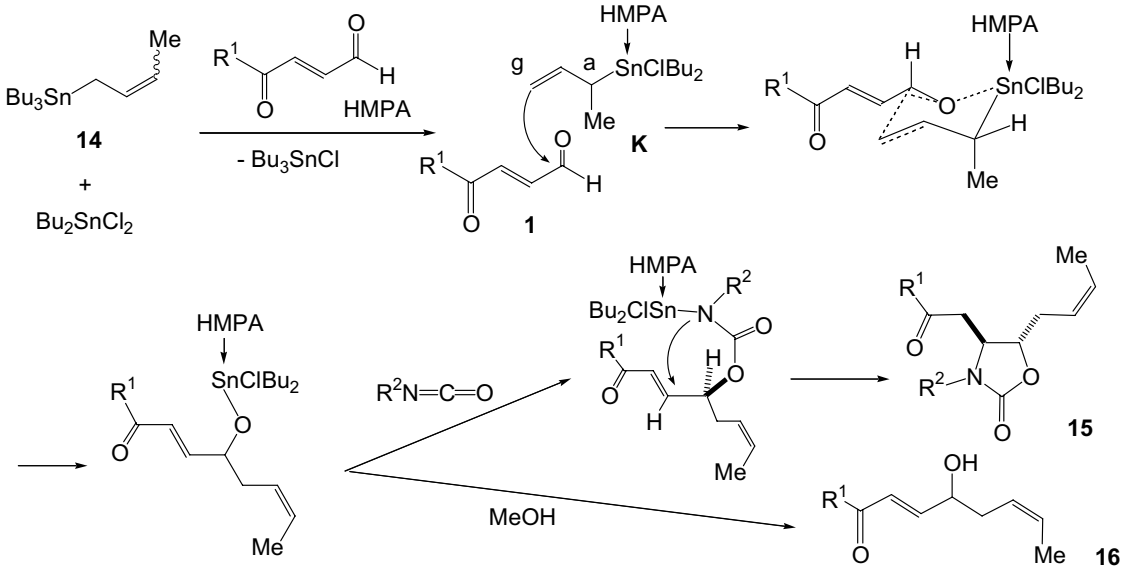
Scheme 10.



Scheme 11.



Scheme 12.

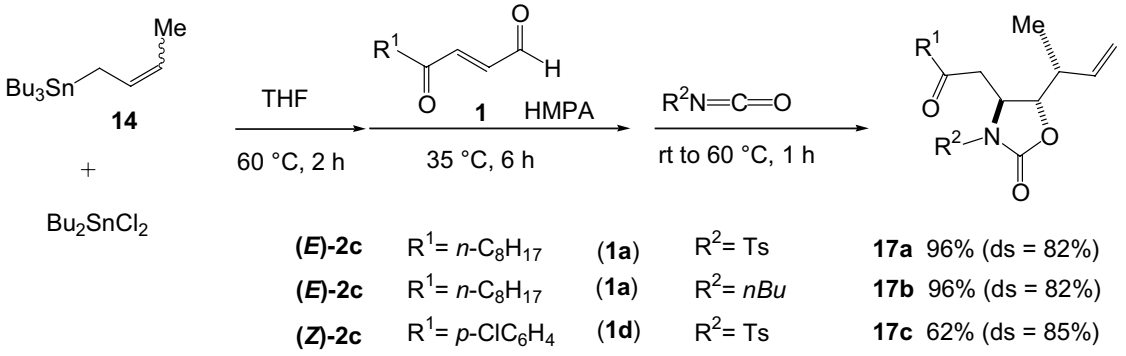


Scheme 13.

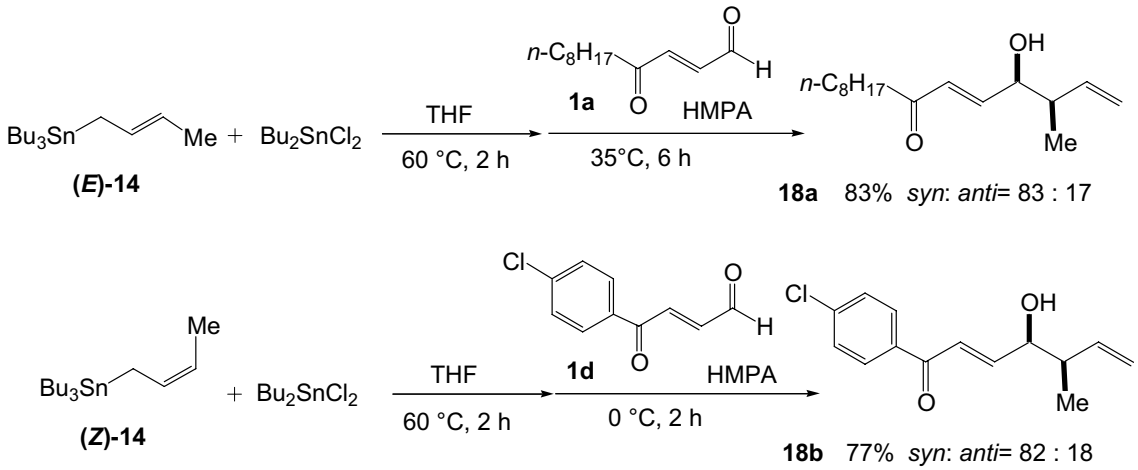
reaction with **1** followed by the addition to an isocyanate afforded 4,5-*trans*-disubstituted-2-oxazolidones **17a–c** which include carbonylmethyl- and 1-methylallyl groups on the ring (Scheme 14).

The regioselectivity to introduce a 1-methylallyl group on the ring of **17** is derived from the initial reaction of the *in situ* generated (*Z*)-crotyldibutylchlorotin **L** through preferential isomerization from **K** by preheating at 60 °C for 2 h. In addition, it is noted that high diastereoselectivity in the side chain, 1-methylallyl substituent, was obtained.

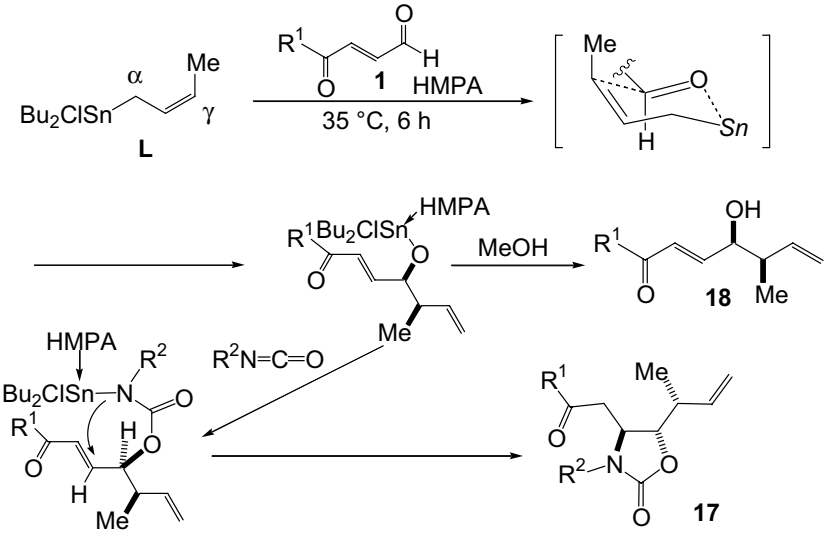
The same diastereoisomers of **17** predominated irrespective of the *E*/*Z*-stereochemistry of **14**. This diastereoselectivity is derived from the crotylation step. Thus, quenching the solution of crotylation of **1** gave the corresponding homoallylic alcohols **18** with high *syn* selectivities from both *E*- and *Z*-crotyltins **14** (Scheme 15). As



Scheme 14.



Scheme 15.



Scheme 16.

described in Scheme 11, (*Z*)-crotyltin **L** is formed by the redistribution of **14** with Bu_2SnCl_2 irrespective of the *E*/*Z*-stereochemistry of **14**, reacting with the formyl group of **1** at the terminal γ-carbon. As shown in Scheme 16, the crotylation of the (*Z*)-isomer **L** proceeds through a six-membered chair-like transition state, affording *syn* adducts predominantly [27].

3. Conclusion

In conclusion, various 2-monosubstituted pyrroles could be prepared in a one-pot procedure by the imine-selective reduction of *in situ* formed bifunctional substrates bearing imine and enone functionalities. One-pot synthesis of nitrogen heterocyclic compounds was initiated by chemoselective allylation of **1**. Regio- and diastereoselective carbon–carbon bond formation was established in the side chain of the rings. One-pot synthesis of a variety of heterocycles was established initiated by chemoselective reduction of enals **1**.

4. Experimental

4.1. Instrumentation

4.1.1. General procedures

IR spectra were recorded on a Horiba FT-720 spectrometer. All the ^1H and ^{13}C spectra of the products were recorded with a JEOL JNM-GSX-270 (270 and 67 MHz, respectively) in deuteriochloroform ($CDCl_3$) containing 0.03% (w/v) of tetramethylsilane. Mass spectra were recorded on a JEOL JMS-DS-303. Column chromatography was performed by using Fuji Davison gel FL-100DX. Preparative TLC was carried out on Wakogel B-5F silica gel. Yields were determined by ^1H NMR using internal standards.

4.2. Materials

Dibutyltin dihydride was prepared by dibutyltin dichloride (Bu_2SnCl_2) with $LiAlH_4$ [28]. Dibutyltin diiodide (Bu_2SnI_2) was prepared according to described method [29]. Dibutyltin halide hydrides (Bu_2SnXH) were synthesized *in situ* by the redistribution reaction between Bu_2SnH_2 and Bu_2SnX_2 (X=Cl, I) [30]. Allyltributyltin (**11a**) was prepared by the reaction of tributyltin chloride (Bu_3SnCl) with the corresponding allylic Grignard reagents [31]. Allyldibutylchlorotin was synthesized by the redistribution reaction between Bu_2SnCl_2 and diallyldibutyltin (**11b**). THF was freshly distilled from sodium benzophenone ketyl. Crotyltributyltin (*E*)-**14** [32] and (*Z*)-**14** [33] were prepared by known methods. For the preparation of (*E*)-**14**, starting substrate, crotyl chloride, was used as sterically (*E*)-pure form which was provided by the reduction of commercially available (*E*)-crotylaldehyde with $LiAlH_4$ and subsequent chlorination of the (*E*)-crotyl alcohol with PCl_3. Substrates **1a** and **1b** were prepared according to reported methods starting from the alkylation of furan [34]. Substrates **1c**, **1d** were prepared by our original method via Wittig reaction as follows.

4.2.1. Synthesis of (*E*)-4-oxo-4-phenyl-but-2-enal (*1c*)

To a dry nitrogen-filled 300-mL round-bottomed flask containing Ph_3P (33.11 g, 126.23 mmol) in $CHCl_3$ (150 mL) was added 2-bromo-propiophenone (25.1 g, 126 mmol) at rt. After stirring at rt for 4 h, 500 mL of ether was added to form white precipitates. After separation, the resulting white precipitate was added to 1 L water containing Na_2CO_3 (101 g), which was stirred at rt for 15 h. Ylide was obtained as a white solid which was filtered and dried. To a dry nitrogen-filled 300-mL round-bottomed flask containing 40 wt% glyoxal (145 g, 1 mol) in dichloromethane (100 mL) was added a CH_2Cl_2 solution of the ylide (38.0 g, 100 mmol) dropwise at rt for 1 h. The solution was stirred overnight at rt and poured into a mixture of ether and water with vigorous stirring. The resulting white solid (Ph_3PO) was filtered off. Ether layer was separated, and the aqueous layer was extracted with ether. The combined ether solution was dried over $MgSO_4$ and concentrated to give an oil. Purification was performed by column chromatography on silica-gel column (FL100-DX (Fuji silysia)). Elution with hexane removed other unknown by-products and elution hexane/EtOAc = 7/3 gave **1c** as a pure form (see Scheme 17).

4.2.1.1. (E)-4-Oxo-4-phenyl-but-2-enal (1c). Colorless wax; IR 1697, 1670 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.99 (dd, $J = 7.32$ and 15.62 Hz, 1H), 7.53–8.00 (m, 5H), 7.72 (d, $J = 15.62$ Hz, 1H), 9.99 (d, $J = 7.32$ Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 128.86, 129.01, 134.14, 136.24, 139.14, 142.04, 189.75, 192.74; HRMS calcd for $C_{10}H_8O_2$ 160.054; found 160.0528.

4.3. Typical experimental procedure to prepare pyrrole (*2*)

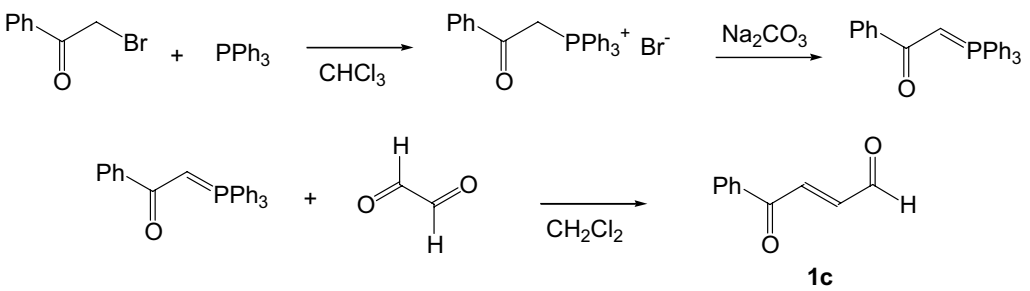
To a dry nitrogen-filled 10-mL round-bottomed flask containing dibutyltin dihydride (Bu_2SnH_2, 0.166 g, 0.5 mmol) in 1,4-dioxane (1 mL) was added dibutyltin diiodide (Bu_2SnI_2, 0.243 g, 0.5 mmol) and HMPA (0.180 g, 1 mmol) at rt. After stirring at rt for 10 min, the resulting solution of dibutyliodotin hydride (Bu_2SnIH, 1 mmol) was cooled to 0 °C. Carbonyl substrate **1a** (0.196 g, 1 mmol), and *p*-chloroaniline (0.128 g) were added successively, and stirring was continued at 0 °C for 2 h. The IR absorption band of Sn–H (1850 cm^{-1}) disappeared, which indicated the formation of stannylamide(II). The mixture was heated to 80 °C and stirred for 2 h. The reaction was quenched by MeOH (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). Elution with hexane gave pyrrole **2a** (0.234 g, 81%).

4.3.1. 1-(4-Chlorophenyl)-2-octyl-1H-pyrrole (*2a*)

Colorless wax; IR 1596, 1496 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, $J = 6.83$ Hz, 3H), 1.21–1.30 (m, 10H), 1.44–1.55 (m, 2H), 2.49 (t, $J = 7.81$ Hz, 2H), 6.04–6.06 (m, 1H), 6.21 (t, $J = 2.93$ Hz, 1H), 6.67–6.69 (m, 1H), 7.22 (d, $J = 8.79$ Hz, 2H), 7.39 (d, $J = 8.79$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 14.08, 22.63, 26.65, 29.13, 29.27, 29.30, 31.57, 31.80, 107.10, 108.26, 121.30, 127.30, 129.18, 132.77, 134.21, 139.06; HRMS calcd for $C_{18}H_{24}NCl$ 289.1597; found 289.1597.

4.3.2. 2-Octyl-1-phenyl-1H-pyrrole (*2b*)

Colorless wax; IR 1516 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.86 (t, $J = 6.83$ Hz, 3H), 1.21–1.30 (m, 10H), 1.45–1.56 (m,



Scheme 17.

2H), 2.52 (t, $J = 7.81$ Hz, 2H), 6.05–6.07 (m, 1H), 6.21 (t, $J = 2.93$ Hz, 1H), 6.72–6.73 (m, 1H), 7.27–7.45 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 14.03, 22.60, 26.67, 29.11 (d), 29.25, 29.30, 31.79, 106.69, 107.84, 121.34, 126.09, 126.89, 128.93, 134.16, 140.50; HRMS calcd for $C_{18}H_{25}N$ 255.1987; found 255.1993.

*4.3.3. 2-Octyl-1-p-tolyl-1H-pyrrole (**2c**)*

Colorless wax; IR 1520 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, $J = 6.83$ Hz, 3H), 1.21–1.30 (m, 10H), 1.45–1.55 (m, 2H), 2.40 (s, 3H), 2.50 (t, $J = 7.81$ Hz, 2H), 6.03–6.05 (m, 1H), 6.19 (t, $J = 2.93$ Hz, 1H), 6.69–6.71 (m, 1H), 7.15–7.24 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.05, 20.98, 22.62, 26.65, 29.11, 29.14, 29.28, 29.31, 31.81, 106.38, 107.59, 121.40, 125.97, 129.53, 134.28, 136.71, 137.97; HRMS calcd for $C_{19}H_{27}N$ 269.2144; found 269.2148.

*4.3.4. 1-(4-Methoxy-phenyl)-2-octyl-1H-pyrrole (**2d**)*

Colorless wax; IR 1500 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.86 (t, $J = 6.83$ Hz, 3H), 1.21–1.30 (m, 10H), 1.44–1.54 (m, 2H), 2.46 (t, $J = 7.81$ Hz, 2H), 3.85 (s, 3H), 6.01–6.03 (m, 1H), 6.18 (t, $J = 2.93$ Hz, 1H), 6.67–6.69 (m, 1H), 6.92–7.22 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.06, 22.63, 26.59, 29.14, 29.30, 29.34, 29.68, 31.82, 55.45, 106.11, 107.42, 114.07, 121.57, 127.42, 133.51, 134.54, 158.53; HRMS calcd for $C_{19}H_{27}NO$ 285.2093; found 285.2086.

*4.3.5. 1-(4-Chloro-phenyl)-2-(3-phenyl-propyl)-1H-pyrrole (**2e**)*

Colorless wax; IR 1496 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.75–1.87 (m, 2H), 2.51–2.59 (m, 4H), 6.06–6.09 (m, 1H), 6.18–6.21 (m, 1H), 6.66–6.68 (m, 1H), 7.050–7.352 (m, 9H); ^{13}C NMR ($CDCl_3$) δ 26.09, 30.67, 35.29, 107.39, 108.32, 121.46, 125.71, 127.19, 128.25, 128.31, 129.20, 132.76, 133.49, 138.87, 141.86; HRMS calcd for $C_{19}H_{18}NCl$ 295.1128; found 295.1125.

*4.3.6. 1-(4-Chloro-phenyl)-2-phenyl-1H-pyrrole (**2f**)*

Colorless wax; IR 1600, 1492 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.35–6.38 (m, 1H), 6.42–6.44 (m, 1H), 6.90–6.91 (m, 1H), 7.09 (d, $J = 8.40$ Hz, 2H), 7.13–7.24 (m, 5H), 7.28 (d, $J = 8.40$ Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 109.60, 110.99, 124.16, 126.49, 126.76, 128.18, 128.32, 129.13, 132.19, 132.59, 133.79, 139.01; HRMS calcd for $C_{16}H_{12}NCl$ 253.0658; found 253.0653.

4.4. Representative procedure for the preparation of 2-oxazolidinone initiated by chemoselective reduction

To a dry nitrogen-filled 10-mL round-bottomed flask containing triibutyltin hydride (0.291 g, 1 mmol) in THF (1 mL) was added and HMPA (0.180 g, 1 mmol) at rt. To the resulting solution was added carbonyl substrate (**1a**) (0.196 g, 1 mmol), and stirred at 60 °C for 2 h. The reaction mixture was cooled to 0 °C. To this mixture was added butyl isocyanate (0.0975 g, 0.8 mmol) and stirred for 0.5 h. The IR absorption band of NCO (2200 cm^{-1}) disappeared, which indicated the formation of stannylcarbamate adduct (II). The mixture was heated to 60 °C and stirred for 1 h. The reaction was quenched by MeOH (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elution with EtOAc gave 2-oxazolidonone **5a** (0.199 g, 84% based on BuN=C=O).

*4.4.1. 3-Butyl-4-(2-oxo-decyl)-oxazolidin-2-one (**5a**)*

Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.85–0.96 (m, 6H, $2CH_3$), 1.21–1.60 (m, 16H, CH_2), 2.45 (t, 2H, $J = 7.3$ Hz, C=OCH_2), 2.61 (dd, 1H, $J = 9.3$ and 18.1 Hz, one of C=OCH_2), 2.88–2.96 (m, 1H, one of NCH_2), 3.01 (dd, 1H, $J = 3.9$ and 18.1 Hz, one of C=OCH_2), 3.37–3.50 (m, 1H, one of NCH_2), 3.84 (dd, 1H, $J = 5.9$ and 8.8 Hz, one of OCH_2), 4.12–4.22 (m, 1H, CHN), 4.52 (dd, 1H, $J = 8.3$ and 8.8 Hz, one of CH_2O); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.45, 13.83, 19.66, 22.38, 22.39, 28.85, 28.90, 29.08, 29.19, 31.56, 41.61, 43.02, 45.22, 50.64, 67.89, 157.73, 207.93; HRMS calcd for $C_{17}H_{31}NO_3$ 297.2304, found 297.2298.

*4.4.2. 3-Allyl-4-(2-oxo-decyl)-oxazolidin-2-one (**5b**)*

Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.11–1.56 (m, 12H, CH_2), 2.42 (t, 2H, $J = 7.3$ Hz, C=OCH_2), 2.58 (dd, 1H, $J = 9.8$ and 18.1 Hz, one of C=OCH_2), 3.01 (dd, 1H, $J = 3.9$ and 18.1 Hz, one of C=OCH_2), 3.63 (dd, 1H, $J = 6.8$ and 15.6 Hz, one of C=CCH_2), 3.87 (dd, 1H, $J = 6.3$ and 8.8 Hz, one of CH_2O), 4.06 (dd, 1H, $J = 5.4$ and 15.6 Hz, one of C=CCH_2), 4.12–4.33 (m, 1H, one of CH_2N), 4.57 (t, 1H, $J = 8.8$ Hz, one of CH_2O), 5.08–5.29 (m, 2H, C=CH_2), 5.68–5.85 (m, 1H, C*H*=CH_2); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.78, 22.30, 23.25, 28.77, 28.78, 28.99, 31.47, 42.79, 44.82, 45.10, 50.78, 67.96, 118.12, 132.04, 157.58, 207.79; HRMS calcd for $C_{16}H_{27}NO_3$ 281.1991, found 281.1988.

*4.4.3. 3-(2-Chloro-ethyl)-4-(2-oxo-decyl)-oxazolidin-2-one (**5c**)*

Colorless wax; IR (neat) 2931, 1754, 1712 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.88 (t, 3H, $J = 6.4$ Hz, CH_3), 1.22–1.58 (m, 12H, CH_2), 2.47 (t, 2H, $J = 7.3$ Hz, C=OCH_2), 2.69 (dd, 1H, $J = 8.8$ and 18.1 Hz, one of C=OCH_2), 3.13 (dd, 1H, $J = 4.4$ and 18.1 Hz, one of C=OCH_2), 3.30–3.44 (m, 1H, one of CH_2N), 3.64–3.76 (m, 3H, CH_2Cl and one of CH_2N), 3.91 (dd, 1H, $J = 6.3$ and 8.8 Hz, one of CH_2O), 4.26–4.39 (m, 1H, CHN), 4.58 (t, 1H, $J = 8.8$ Hz, one of CH_2O); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.91, 22.45, 23.46, 28.92, 28.96, 29.13, 31.62, 41.31, 43.05, 44.15, 45.59, 51.64, 68.31, 157.47, 207.91; HRMS calcd for $C_{15}H_{26}ClNO_3$ 303.1601, found 303.1609.

*4.4.4. 3-Benzyl-4-(2-oxo-decyl)-oxazolidin-2-one (**5d**)*

Colorless wax; IR (neat) 2927, 1758, 1712 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.08–1.48 (m, 12H, CH_2), 2.24 (t, 2H, $J = 8.3$ Hz, C═OCH_2), 2.50 (dd, 1H, $J = 9.3$ and 18.1 Hz, one of C═OCH_2), 2.87 (dd, 1H, $J = 3.9$ and 18.1 Hz, one of C═OCH_2), 3.87 (dd, 1H, $J = 6.6$ and 8.6 Hz, one of CH_2O), 3.97–4.11 (m, 1H, CHN), 4.21 (d, 1H, $J = 15.7$ Hz, one of CH_2Ph), 4.54 (t, 1H, $J = 8.6$ Hz, one of CH_2O), 4.21 (d, 1H, $J = 15.7$ Hz, one of CH_2Ph), 7.20–7.83 (m, 5H, Ph); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.99, 22.53, 23.41, 28.94, 29.18, 29.29, 31.67, 42.97, 45.33, 46.49, 50.82, 68.16, 127.77, 127.92, 127.77, 128.78, 158.31, 207.84; HRMS calcd for $C_{20}H_{29}NO_3$ 331.2147, found 331.2136.

*4.4.5. 3-Isopropyl-4-(2-oxo-decyl)-oxazolidin-2-one (**5e**)*

Colorless wax; IR (neat) 2927, 1751, 1712 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.81 (t, 3H, $J = 6.8$ Hz, CH_3), 1.03–1.29 (m, 18H, CH_2 and CH(CH_3)$_2$), 2.37 (t, 2H, $J = 7.3$ Hz, C═OCH_2), 2.65 (dd, 1H, $J = 10.3$ and 18.6 Hz, one of C═OCH_2), 2.92 (dd, 1H, $J = 3.4$ and 18.6 Hz, one of C═OCH_2), 3.71–3.85 (m, 2H, one of CH_2O and $CHMe_2$), 4.10–4.19 (m, 1H, CHN), 4.41 (t, 1H, $J = 8.8$ Hz, one of CH_2O); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.99, 19.19, 21.32, 22.52, 23.51, 28.98, 29.01, 29.19, 31.67, 43.21, 45.85, 47.31, 50.32, 68.35, 157.29, 208.33; HRMS calcd for $C_{16}H_{29}NO_3$ 283.2147, found 283.2136.

*4.4.6. 3-(4-Phenyl)-4-(2-oxo-decyl)-oxazolidin-2-one (**5f**)*

Colorless wax; IR (neat) 2927, 1758, 1709, 755 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.87 (t, 3H, $J = 6.8$ Hz, CH_3), 1.17–1.55 (m, 12H, CH_2), 2.32 (t, 2H, $J = 7.3$ Hz, C═OCH_2), 2.65 (dd, 1H, $J = 9.8$ and 18.1 Hz, one of C═OCH_2), 2.97 (dd, 1H, $J = 2.9$ and 18.1 Hz, one of C═OCH_2), 4.01 (dd, 1H, $J = 5.4$ and 8.8 Hz, one of CH_2O), 4.67 (dd, 1H, $J = 8.3$ and 8.8 Hz, one of CH_2O), 4.75–4.85 (m, 1H, CHN), 7.14–7.41 (m, 5H, arom); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.81, 22.34, 23.26, 28.80(d), 28.99, 31.50, 42.87, 44.68, 52.16, 67.67, 121.68, 125.22, 129.06, 136.05, 155.29, 208.13; HRMS calcd for $C_{21}H_{27}NO_3$ 317.1991, found 317.1991.

*4.4.7. 3-Butyl-4-(2-oxo-5-phenylpentyl)-oxazolidin-2-one (**5g**)*

Colorless wax; IR (neat) 2931, 1751, 1712 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.92 (t, 3H, $J = 7.2$ Hz, CH_3), 1.24–1.38 (m, 2H, CH_2), 1.41–1.54 (m, 2H, CH_2), 1.91 (tt, 2H, $J = 7.3$ and 7.4 Hz, CH_2CH_2Ph), 2.43 (t, 2H, $J = 7.3$ Hz, C═OCH_2CH_2), 2.53 (dd, 1H, $J = 9.4$ and 18.8 Hz, one of C═OCH_2), 2.61 (t, 2H, $J = 7.4$ Hz, $PhCH_2$), 2.88 (m, 1H, one of NCH_2), 2.90 (dd, 1H, $J = 3.9$ and 18.8 Hz, one of C═OCH_2), 3.37–3.45 (m, 1H, one of NCH_2), 3.78 (dd, 1H, $J = 6.0$ and 8.9 Hz, one of OCH_2), 4.06–4.16 (m, 1H, CHN), 4.48 (t, 1H, $J = 8.9$ and 8.9 Hz, one of CH_2O); 7.12–7.31 (m, 5H, Ph); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.50, 19.62, 24.60, 29.14, 34.70, 41.56, 42.02, 45.21, 50.52, 67.87, 125.76, 128.45, 128.58, 140.90, 157.75, 207.48; HRMS calcd for $C_{18}H_{25}NO_3$ 303.1834, found 303.1834.

*4.4.8. 3-Butyl-4-(2-oxo-2-phenyl-ethyl)-oxazolidin-2-one (**5h**)*

Colorless wax; IR (neat) 2958, 1747, 1678 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.93 (t, 3H, $J = 7.3$ Hz, CH_3), 1.26–1.61 (m, 4H, CH_2), 2.96–3.06 (m, 1H, one of NCH_2), 3.14 (dd, 1H, $J = 9.3$ and 17.6 Hz, one of C═OCH_2), 3.45–3.55 (m, 1H, one of NCH_2), 3.55 (dd, 1H, $J = 3.9$ and 17.6 Hz, one of C═OCH_2), 3.95 (dd, 1H, $J = 5.9$ and 8.8 Hz, one of OCH_2), 4.32–4.43 (m, 1H, CHN), 4.63 (t, 1H, $J = 8.8$ Hz, one of OCH_2), 7.49–7.94 (m, 5H, Ph); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.64, 19.80, 29.34, 41.51, 41.81, 51.22, 68.23, 127.91, 128.81, 133.93, 137.22, 157.95, 196.93; HRMS calcd for $C_{15}H_{19}NO_3$ 261.1365, found 261.1368.

*4.4.9. 3-Butyl-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-oxazolidin-2-one (**5i**)*

Colorless wax; IR (neat) 2958, 1747, 1681 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.94 (t, 3H, $J = 7.3$ Hz, CH_3), 1.22–1.61 (m, 4H, $2CH_2$), 2.94–3.05 (m, 1H, one of NCH_2), 3.13 (dd, 1H, $J = 9.3$ and 18.1 Hz, one of C═OCH_2), 3.46–3.57 (m, 1H, one of NCH_2), 3.52 (dd, 1H, $J = 3.4$ and 18.1 Hz, one of C═OCH_2), 3.95 (dd, 1H, $J = 5.4$ and 8.8 Hz, one of OCH_2), 4.33–4.42 (m, 1H, CHN), 4.63 (t, 1H, $J = 8.8$ Hz, one of OCH_2), 7.47 (d, 2H, $J = 8.3$ Hz, arom), 7.90 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.63, 19.81, 29.34, 41.47, 41.81, 51.13, 68.14, 129.17, 129.33, 134.21, 140.47, 157.89, 195.74; HRMS calcd for $C_{15}H_{18}ClNO_3$ 295.0975, found 295.0976.

*4.4.10. 1-(3-Phenyl-2-thioxo-oxazolidin-4-yl)-decan-2-one (**7**)*

Mp 80 °C; IR (neat) 2927, 1743, 1700 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.87 (t, 3H, $J = 7.3$ Hz, CH_3), 1.16–1.53 (m, 12H, CH_2), 2.20–2.40 (m, 2H, C═OCH_2), 2.71 (dd, 1H, $J = 9.8$ and 18.1 Hz, one of C═OCH_2), 2.85 (dd, 1H, $J = 3.4$ and 18.1 Hz, one of C═OCH_2), 4.24 (dd, 1H, $J = 6.8$ and 9.3 Hz, one of CH_2O), 4.73–4.85 (m, 1H, CHN), 5.01 (t, 1H, $J = 9.3$ Hz, one of CH_2O), 7.14–7.55 (m, 5H, arom); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 14.05, 22.56, 23.41, 28.99(d), 29.19, 31.71, 43.00, 45.51, 58.56, 72.91, 121.91, 128.54, 129.62, 136.85, 187.70, 207.51; HRMS calcd for $C_{19}H_{27}NO_sS$ 333.1762, found 333.1755. Anal. Calc. for $C_{19}H_{27}NO_sS$: C, 68.43; H, 8.16; N, 4.20. Found: C, 68.20; H, 7.96; N, 4.14.

*4.4.11. 4-(2-Oxo-decyl)-3,3-diphenyl-dihydro-furan-2-one (**8**)*

Bp 190 °C/0.1 mmHg; IR (neat) 2923, 1778, 1712 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.87 (t, 3H,

$J = 6.9$ Hz, CH_3), 1.16–1.52 (m, 12H, CH_2), 2.04 (dd, 1H, $J = 10.4$ and 18.3 Hz, one of C=OCH_2), 2.24 (t, 2H, $J = 7.4$ Hz, C=OCH_2), 2.48 (dd, 1H, $J = 3.5$ and 18.3 Hz, one of C=OCH_2), 3.84–3.92 (m, 2H, one of CH_2O and CHN), 4.66 (dd, 1H, $J = 5.9$ and 8.4 Hz, one of CH_2O), 7.05–7.50 (m, 10H, Ph); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 14.07, 22.60, 23.53, 29.03, 29.11, 29.24, 31.78, 38.44, 42.58, 43.14, 58.59, 69.83, 127.42, 127.90, 128.10, 128.45, 128.56, 128.62, 138.72, 139.18, 177.11, 208.63; HRMS calcd for $C_{26}H_{32}O_3$ 392.2351, found 392.2356.

4.4.12. 4-(2-Oxo-decyl)-2-phenyl-dihydrofuran-3,3-dicarbonitrile (*9*)

(Major isomer) colorless wax; IR (neat) 2923, 1708 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.18–1.62 (m, 12H, CH_2), 2.45–2.53 (m, 2H, C=OCH_2), 2.87 (dd, 1H, $J = 9.3$ and 18.1 Hz, one of C=OCH_2), 3.15 (dd, 1H, $J = 3.5$ and 18.1 Hz, one of C=OCH_2), 3.39–3.48 (m, 1H, CCH), 3.85 (dd, 1H, $J = 8.3$ and 9.3 Hz, one of CH_2O), 4.54 (t, 1H, $J = 9.3$ Hz, one of CH_2O), 5.18 (s, 1H, CH), 7.38–7.54 (m, 5H, Ph); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 14.00, 22.53, 23.57, 29.01 (d), 29.19, 31.68, 42.67, 43.13, 45.29, 46.91, 71.68, 86.55, 113.21, 126.06, 128.72, 129.98, 132.79, 206.95; HRMS calcd for $C_{22}H_{28}N_2O_2$ 352.2151, found 352.2145.

4.4.13. 3-Acetyl-4-(2-oxo-decyl)-dihydro-furan-2-one (*10*)

Colorless wax; IR (neat) 1774, 1716, 1643 cm^{-1}; ^{1}H NMR (270 MHz, $CDCl_3$, 25 °C) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.18–1.60 (m, 12H, CH_2), 2.28 (s, 3H, C=OCH_3), 2.34–2.79 (m, 4H, C=OCH_2), 3.26–3.40 (m, 1H, ring CH), 3.48 (d, 1H, $J = 7.8$ Hz, CHAc), 3.91 (t, 1H, $J = 8.5$ Hz, one of CH_2O), 4.61 (t, 1H, $J = 8.5$ Hz, one of CH_2O); ^{13}C NMR (67.9 MHz, $CDCl_3$, 25 °C) δ 13.91, 22.47, 23.51, 28.93, 28.98, 29.14, 29.48, 31.62, 32.77, 42.73, 44.32, 58.08. 71.59, 171.89, 200.05, 208.51; HRMS calcd for $C_{16}H_{26}O_4$ 282.1831, found 282.1823.

4.5. Representative procedure for the preparation of 2-oxazolidinone initiated by allylation

To a dry nitrogen-filled 10-mL round-bottomed flask containing diallyldibutyltin (0.166 g, 0.5 mmol) in THF (1 mL) was added dibutyltin dichloride (0.151 g, 0.5 mmol) and HMPA (0.180 g, 1 mmol) at rt. After stirring at rt for 10 min, to the resulting solution of allyldibutylchlorotin (**11b**) (1 mmol) was added carbonyl substrate (**1a**) (0.196 g, 1 mmol), and stirred at rt for 20 h. The reaction mixture was cooled to 0 °C. To this mixture was added phenyl isocyanate (0.119 g, 1 mmol) and stirred for 1 h. The IR absorption band of NCO (2200 cm^{-1}) disappeared, which indicated the formation of stannylcarbamate adduct **J**. The mixture was heated to 60 °C and stirred for 1 h. The reaction was quenched by MeOH (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elution with EtOAc gave 2-oxazolidonone (**12a**) (0.273 g, 81%). The stereochemistry of the major diastereoisomer of **12a** was determined by NOE. As for product **12b**, the structure was indicated by X-ray analysis.

4.5.1. 5-Allyl-4-(2-oxo-decyl)-3-phenyl-oxazolidin-2-one (*12a*)

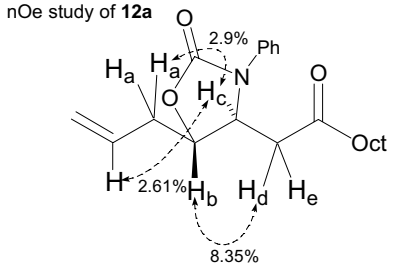
Bp 135 °C/0.1 mmHg; IR (neat) 2927, 1758, 1712, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, $J = 6.4$ Hz, CH_3), 1.28–1.57 (m, 12H, CH_2), 2.34 (t, 2H, $J = 7.3$ Hz, C=OCH_2), 2.55–2.70 (m, 2H, CH_2C=C), 2.73 (dd, 1H, $J = 9.8$ and 18.1 Hz, one of C=OCH_2), 2.92 (dd, 1H, $J = 3.0$ and 18.1 Hz, one of C=OCH_2), 4.30 (ddd, $J = 3.0$, 3.2 and 9.0 Hz, 1H, CHO), 4.55 (ddd, 1H, $J = 3.0$, 3.2 and 9.8 Hz, CHN), 5.20–5.33 (m, 2H, allyl C=CH_2), 5.81–5.96 (m, 1H, allyl CH=C), 7.15–7.46 (m, 5H, arom); ^{13}C NMR ($CDCl_3$) δ 14.07, 22.61, 23.48, 29.04(d), 29.25, 31.74, 38.77, 43.39, 44.70, 56.16, 78.51, 119.87, 121.40, 125.28, 129.36, 131.09, 136.22, 154.62, 208.57; HRMS calcd for $C_{22}H_{31}NO_3$ 357.2304, found 357.2309 (see Scheme 18).

4.5.2. 5-Allyl-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-3-(toluene-4-sulfonyl)-oxazolidin-2-one (*12b*)

Mp 183 °C; IR (neat) 3070, 1778, 1677, 1168, 663 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.47 (s, 3H, CH_3), 2.44–2.51 (m, 2H, C=CCH_2), 3.47 (dd, 1H, $J = 10.3$ and 18.1 Hz, one of C=OCH_2), 3.96 (dd, 1H, $J = 2.4$ and 18.1 Hz, one of C=OCH_2), 4.34 (td, 1H, $J = 2.4$ and 4.9 Hz, 1H, CHO), 4.57 (td, 1H, $J = 2.4$ and 10.3 Hz, 1H, CHN), 4.92–5.16 (m, 2H, allyl C=CH_2), 5.45–5.60 (m, 1H, allyl CH=C), 7.38 (d, 2H, $J = 8.3$ Hz, arom), 7.49 (d, 2H, $J = 8.3$ Hz, arom), 7.89 (d, 2H, $J = 8.3$ Hz, arom), 7.94 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR ($CDCl_3$) δ 21.74, 38.25, 43.72, 57.09, 79.72, 120.76, 123.37, 129.26, 129.44, 129.65, 129.81, 134.01, 134.57, 140.67, 145.86, 151.36, 195.77; HRMS calcd for $C_{21}H_{20}ClNO_5S$ 433.0751, found (CI) 434.0834. Anal. Calc. for $C_{21}H_{20}ClNO_5S$: C, 58.13; H, 4.65; N, 3.23. Found: C, 58.16; H, 4.68; N, 3.22.

4.6. Representative procedure for the preparation of 2-oxazolidinone (*15c*) initiated by crotylation

To a dry nitrogen-filled 10 mL round-bottomed flask containing crotyltributyltin (*Z*)-**14** (0.345 g, 1 mmol), car-



Scheme 18.

bonyl substrate (**1b**) (0.195 g, 1 mmol) in THF (1 mL) were added dibutyltin dichloride (Bu_2SnCl_2) (0.303 g, 1 mmol) and HMPA (0.180 g, 1 mmol) at rt. After stirring at 60 °C for 3 h, the reaction mixture was cooled to 0 °C. To this mixture was added tosyl isocyanate (0.197 g, 1 mmol) and stirred for 1 h. IR absorption band of NCO (2200 cm^{-1}) had disappeared, which indicated the formation of stannylcarbamate adduct. The mixture was warmed to 60 °C and stirred for 0.5 h. The reaction was quenched by MeOH (0.5 mL), and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). By-products such as organotin compounds were removed by eluting with hexane. Subsequent elusion with EtOAc gave 5-(*Z*)-crotyl substituted 2-oxazolidonone **15c** (0.312 g, 70%). Further purification of **15c** was performed by recrystallization. The structure of crystalline product **15c** was indicated by X-ray analysis. Conjugate addition using other substrates were performed in a similar manner. Spectral data of products obtained are listed from the following pages.

*4.6.1. 5-But-2-enyl-4-(2-oxo-decyl)-3-(toluene-4-sulfonyl)-oxazolidin-2-one (**15a**)*

Bp 150 °C/0.1 mmHg; IR (neat) 2927, 1785, 1712, 1173, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 1.23–2.53 (m, 12H, CH_2), 1.56 (d, 1H, $J = 6.9$ Hz, CH_3), 2.46 (s, 3H, arom-CH_3), 2.35–2.52 (m, 4H, C=CCH_2 and C=OCH_2C_7), 2.93 (dd, 1H, $J = 10.4$ and 18.3 Hz, one of C=OCH_2), 3.41 (dd, 1H, $J = 3.0$ and 18.3 Hz, one of C=OCH_2), 4.22 (td, 1H, $J = 4.9$ and 3.0 Hz, CHO), 4.34 (td, 1H, $J = 3.0$ and 10.4 Hz, CHN), 5.06–5.16 (m, 1H, C=CH), 5.34–5.46 (m, 1H, CH=C), 7.36 (d, 2H, $J = 8.3$ Hz, arom), 7.91 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR ($CDCl_3$) δ 12.99, 14.07, 21.67, 22.60, 23.48, 29.05, 29.05, 29.27, 31.16, 31.75, 43.04, 47.35, 56.76, 80.32, 120.89, 128.30, 129.72, 129.79, 134.65, 145.69, 151.41, 208.32; HRMS calcd for $C_{24}H_{35}NO_5S$ 449.2236, found 449.2240. Anal. Calc. for $C_{24}H_{35}NO_5S$: C, 64.11; H, 7.85; N, 3.12. Found: C, 64.31; H, 7.7, N, 3.02.

*4.6.2. 5-But-2-enyl-3-butyl-4-(2-oxo-decyl)-oxazolidin-2-one (**15b**)*

Colorless wax; IR (neat) 2958, 1751, 1712, 1427 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 0.93 (t, 3H, $J = 6.8$ Hz, CH_3), 1.23–1.58 (m, 16H, CH_2), 1.67 (d, 3H, $J = 6.8$ Hz, CH_3), 2.43 (t, 2H, $J = 7.3$ Hz, C_7CH_2C=O), 2.49–2.54 (m, 2H, C=CCH_2), 2.60 (dd, 1H, $J = 8.8$ and 18.1 Hz, one of C=OCH_2), 2.79–2.87 (m, 1H, one of NCH_2), 2.87 (dd, 1H, $J = 5.0$ and 18.1 Hz, one of C=OCH_2), 3.40–3.55 (m, 1H, one of NCH_2), 3.86 (ddd, 1H, $J = 5.0$, 5.6 and 8.8 Hz, CHN), 4.10 (td, $J = 3.4$ and 5.6 Hz 1H, CHO), 5.38–5.50 (m, 1H, C=CH), 5.62–5.75 (m, 1H, CH=C); ^{13}C NMR ($CDCl_3$) δ 13.11, 13.70, 14.08, 19.88, 22.62, 23.58, 29.08, 29.11, 29.30, 29.39, 31.71, 31.77, 41.60, 43.55, 45.36, 54.58, 79.17, 122.80, 128.49, 157.18, 208.32; HRMS calcd for $C_{21}H_{37}NO_3$ 351.2773, found 351.2764.

*4.6.3. 5-But-2-enyl-4-[2-(4-chloro-phenyl)-2-oxo-ethyl]-3-(toluene-4-sulfonyl)-oxazolidin-2-one (**15c**)*

Mp 160 °C; IR (neat) 3023, 1774, 1673, 1168, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.57 (d, 3H, $J = 6.8$ Hz, C=CCH_3), 2.47 (s, 3H, CH_3), 2.47–2.52 (m, 2H, CH_2), 3.47 (dd, 1H, $J = 10.7$ and 18.1 Hz, one of C=OCH_2), 3.97 (dd, 1H, $J = 3.0$ and 18.1 Hz, one of C=OCH_2), 4.34 (td, 1H, $J = 3.0$ and 7.8 Hz, CHO), 4.53 (td, 1H, $J = 3.0$ and 10.7 Hz, CHN), 5.07–5.17 (m, 1H, C=CH), 5.32–5.44 (m, 1H, CH=C), 7.37 (d, 2H, $J = 8.3$ Hz, arom), 7.48 (d, 2H, $J = 8.3$ Hz, arom), 7.90 (d, 2H, $J = 8.3$ Hz, arom), 7.93 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR ($CDCl_3$) δ 13.01, 21.72, 31.24, 43.87, 57.21, 80.30, 120.82, 128.33, 129.21, 129.44, 129.75, 129.91, 134.04, 134.62, 140.60, 145.79, 151.38, 195.82; HRMS calcd for $C_{22}H_{22}ClNO_5S$ 447.0907, found (CI) 448.0985; Anal. Calc. for $C_{22}H_{22}ClNO_5S$: C, 58.99; H, 4.95; N, 3.13. Found: C, 58.79; H, 4.92; N, 3.19.

*4.7. Representative procedure for the preparation of 2-oxazolidinone (**17c**) initiated by 1-methylallylation*

To a dry nitrogen-filled 10-mL round-bottomed flask containing crotylbutyltin (*Z*)-**12c** (0.345 g, 1 mmol) in THF (1 mL) was added dibutyltin dichloride (Bu_2SnCl_2) (0.303 g, 1 mmol) at rt. After stirring at 60 °C for 2 h, the reaction mixture was cooled to rt (35 °C) and carbonyl substrate (**1b**) (0.195 g, 1 mmol) and HMPA (0.180 g, 1 mmol) were added. To this mixture was added tosyl isocyanate (0.197 g, 1 mmol). The IR absorption band of NCO (2200 cm^{-1}) disappeared, which indicated the formation of stannylcarbamate adduct. The mixture was warmed to 60 °C and stirring was continued for 1 h. The reaction was quenched by MeOH, and the residue was chromatographed on silica-gel column (FL100-DX (Fuji silysia)). Removal of by-products such as organotin compounds was performed by eluting with hexane. Subsequent elution with EtOAc gave 2-oxazolidonone **17c** (0.277 g, 62%). Diastereomer ratio was determined by ^1H NMR. Further purification of the main diastereo isomer of **17 c** was performed by recrystallization. The structure of the crystalline product was indicated by X-ray analysis. Conjugate 1-methylallylation using other substrates was performed in a similar manner. Spectral data of products obtained are listed in the following pages.

*4.7.1. 5-(1-Methyl-allyl)-4-(2-oxo-decyl)-3-(toluene-4-sulfonyl)-oxazolidin-2-one (**17a**)*

Mp 160 °C; IR (neat) 2927, 1786, 1712, 1172, 667 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 0.88 (t, 3H, $J = 6.9$ Hz, CH_3), 0.94 (d, 3H, $J = 6.9$ Hz, CH_3), 1.24–1.61 (m, 12H, CH_2), 2.46 (s, 3H, CH_3), 2.33–2.51 (m, 3H, CHMe and C_7CH_2C=O), 2.95 (dd, 1H, $J = 8.9$ and 17.8 Hz, one of C=OCH_2), 3.28 (dd, 1H, $J = 3.0$ and 17.8 Hz, one of C=OCH_2), 4.07 (dd, 1H, $J = 3.0$ and 5.5 Hz, CHO), 4.45 (td, 1H, $J = 3.0$ and 8.9 Hz, CHN), 4.92–5.06 (m, 2H, allyl C=CH_2), 5.54 (ddd, 1H, $J = 7.8$, 10.4, and 16.8 Hz, allyl C=CH), 7.37 (d, 2H, $J = 8.3$ Hz, arom), 7.90 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR ($CDCl_3$) δ 14.02, 14.05,

21.68, 22.60, 23.40, 29.03, 29.04, 29.27, 31.75, 41.91, 43.17, 46.89, 55.24, 83.05, 117.71, 128.27, 129.62, 134.69, 136.67, 145.72, 151.39, 207.70; HRMS calcd for $C_{24}H_{35}NO_5S$ 449.2236, found 449.0985.

*4.7.2. 3-Butyl-5-(1-methyl-allyl)-4-(2-oxo-decyl)-oxazolidin-2-one (**17b**)*

Colorless wax; IR (neat) 2927, 1780, 1712, 1172, 732 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 0.88 (t, 3H, $J = 6.8$ Hz, CH_3), 0.93 (t, 3H, $J = 7.3$ Hz, CH_3), 1.10 (d, 3H, $J = 6.8$ Hz, CH_3), 1.24–1.65 (m, 16H, CH_2), 2.43 (t, 2H, $J = 7.3$ Hz, C═OCH_2C_7), 2.41–2.53 (m, 1H, CHMe), 2.59 (dd, 1H, $J = 7.3$ and 18.1 Hz, one of C═OCH_2), 2.76–2.83 (m, 1H, one of NCH_2), 2.81 (dd, 1H, $J = 4.9$ and 18.1 Hz, one of C═OCH_2), 3.41–3.51 (m, 1H, one of NCH_2), 3.90–3.94 (m, 1H), 3.96–4.02 (m, 1H), 5.07–5.23 (m, 2H, allyl C═CH_2), 5.67–5.80 (m, 1H, allyl CH═C); ^{13}C NMR ($CDCl_3$) δ 13.68, 14.06, 14.60, 19.90, 22.60, 23.61, 29.07(d), 29.28, 29.37, 31.76, 41.73, 42.15, 43.61, 45.75, 53.04, 82.10, 116.96, 137.91, 157.21, 207.95; HRMS calcd for $C_{21}H_{37}NO_3$ 351.2773, found 351.2772.

*4.7.3. 4-[2-(4-Chloro-phenyl)-2-oxo-ethyl]-5-(1-methyl-allyl)-3-(toluene-4-sulfonyl)-oxazolidin-2-one (**17c**)*

Mp 139 °C; IR (neat) 2977, 1774, 1681, 1365, 667 cm^{-1}; ^1H NMR ($CDCl_3$) major isomer δ 0.96 (d, 3H, $J = 6.8$ Hz, CH_3), 2.35–2.42 (m, 1H, CHMe), 2.46 (s, 3H, CH_3), 3.48 (dd, 1H, $J = 9.8$ and 17.6 Hz, one of C═OCH_2), 3.83 (dd, 1H, $J = 3.0$ and 17.6 Hz, one of C═OCH_2), 4.18 (dd, 1H, $J = 2.4$ and 5.9 Hz, CHO), 4.61 (td, 1H, $J = 3.0$ and 9.8 Hz, CHN), 4.90–5.06 (m, 2H, arom C═CH_2), 5.51–5.64 (m, 1H, arom CH═C), 7.35 (d, 2H, $J = 8.3$ Hz, arom), 7.48 (d, 2H, $J = 8.3$ Hz, arom), 7.89 (d, 2H, $J = 8.3$ Hz, arom), 7.93 (d, 2H, $J = 8.3$ Hz, arom); ^{13}C NMR ($CDCl_3$) δ 13.85, 21.54, 41.80, 42.99, 55.52, 82.70, 117.63, 128.05, 128.95, 129.35, 129.65, 134.04, 134.54, 136.50, 140.18, 145.64, 151.29, 195.17; HRMS calcd for $C_{22}H_{22}ClNO_5S$ 447.0907, found (CI) 448.0988; Anal. Calc. for $C_{22}H_{22}ClNO_5S$: C, 58.99; H, 4.95; N, 3.13. Found: C, 58.78; H, 4.89; N, 3.11.

Acknowledgments

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