# RADICAL REACTION INITIATED AND STEREOCONTROLLED BY ZINC CHLORIDE†

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**Abstract** - The reaction of allyltributyltin with methyl 2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-2-bromoacetate (**5a**) was accelerated at -50℃ in the presence of AIBN and stopped in the presence of galvinoxyl, indicating that the reaction proceeds through a radical mechanism. The reaction was accelerated dramatically at -78℃ in the presence of $ZnCl_2$•$OEt_2$, and the $ZnCl_2$-mediated reaction was stopped in the presence of galvinoxyl. In the presence of 2 equiv $ZnCl_2$•$OEt_2$, the reaction afforded methyl (2*R*)-2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate {**6a**(*R*)} with high diastereoselectivity (93:7). Taken together, $ZnCl_2$•$OEt_2$ works as a radical initiator as well as chelating agent.

## INTRODUCTION

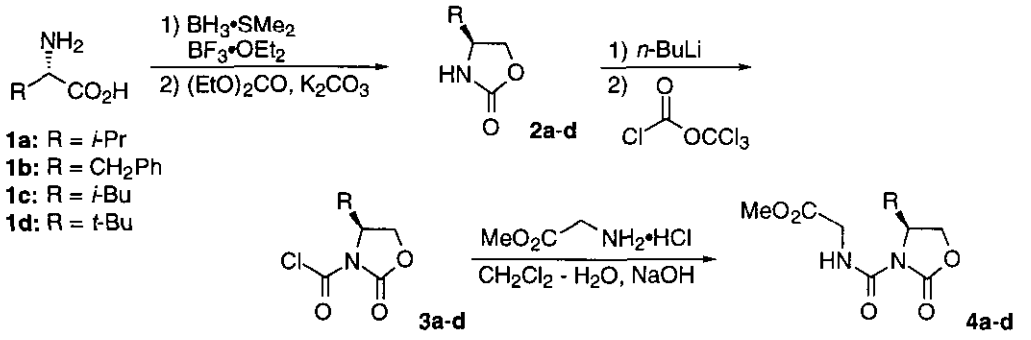
The control of stereochemistry in free radical reactions has been substantially advanced in recent years, and now there is an increase in interest in the problem of stereocontrol in reactions involving acyclic radicals.[1] It has been reported that chirality transfer is accomplished successfully using chiral auxiliaries[2] or stereogenic centers adjacent to the radical center.[3,4] Stereoselectivity enhancement has been observed in radical reactions based on complexation of the radical intermediate with Lewis acids.[5] More recently, enantioselective radical reactions have been achieved using chiral Lewis acids.[6] We previously reported that zinc chloride acts *as a radical initiator* as well as chelating agent in certain radical reactions of allylstannanes.[7] We now report on a detailed study of this work.[8]

## RESULTS AND DISCUSSIONS

### Reaction of Glycine Derivatives with Allyltributylstannane

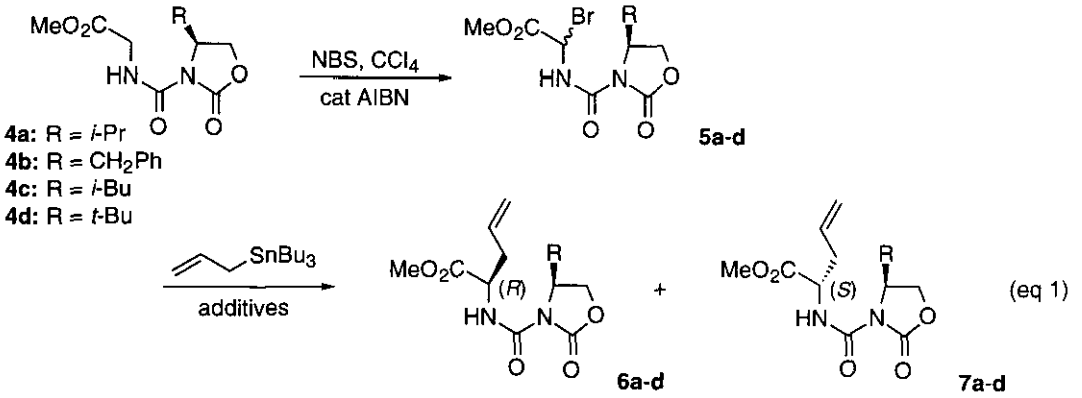
Hamon and coworkers reported that 8-phenylmenthyl *N*-Boc-2-bromoglycinate reacts with allylic stannanes to give the corresponding allylated products, without assistance of Lewis acids, with high diastereoselectivity.[2e] It occurred to us that the α-bromoglycine derivative having a chiral auxiliary on the nitrogen atom would also produce high diastereoselectivity in the free radical allylation with allylstannanes. The starting materials (**4a-d**) were prepared from the oxazolidinones (**2a-d**), which were synthesized from

the corresponding amino acids (**1a-d**) by the standard procedure.[9] Treatment of **2a-d** with *n*-BuLi followed by the reaction with trichloromethylchloroformate gave **3a-d** in good yields. The reaction of **3a-d** with glycine methyl ester hydrochloric acid salt afforded **4a-d** in high yields (Scheme 1).




Scheme 1

Treatment of **4a**, having the isopropyl group on oxazolidinone ring, with NBS in the presence of 10 mol % AIBN under reflux of $CCl_4$ afforded a 1 : 1 diastereoisomeric mixture of **5a** in essentially quantitative yield.[10] Without further purification, **5a** was treated with allyltributyltin under various conditions (eq 1, Table 1).




At -78℃ the reaction did not occur (entry 1), whereas it started at -50℃ without additives (entry 2). The presence of AIBN (10 mol %) accelerated the allylation at -50℃ (entry 3), but the presence of galvinoxyl (5 mol %) halted the reaction completely (entry 4). Accordingly, it is clear that the allylation proceeds through a radical mechamism. The allylation at -78℃ was dramatically accelerated using 2 equiv $ZnCl_2$•$OEt_2$ (cf entry 5 vs 1). The use of 0.1 equiv $ZnCl_2$•$OEt_2$ also accelerated very much, but the diastereoselection was enhanced by using 2 equiv of the Lewis acid, as mentioned later. The allylation in the presence of $ZnCl_2$•$OEt_2$ was accelerated by AIBN (10 mol %), and stopped completely by galvinoxy (5 mol %) halted the reaction completely (entry 4). Accordingly, it is clear that the allylation proceeds through

Table 1. Zinc Chloride-Accelerated Radical Allylation of **5a**[a]

| entry | Lewis acid | Other additive (reactn, condn) | temp (°C) | yield (**6a**+**7a**)[b] |
|---|---|---|---|---|
| 1 | none | none | -78 | 0 |
| 2 | none | none | -50 | 11 |
| 3 | none | AIBN (*hν*) | -50 | 25 |
| 4 | none | galvinoxyl | -50 | 0 |
| 5 | $ZnCl_2$•$OEt_2$ | none | -78 | 40 |
| 6 | $ZnCl_2$•$OEt_2$ | AIBN (*hν*) | -78 | 60 |
| 7 | $ZnCl_2$•$OEt_2$ | galvinoxyl | -78 | 0 |

[a]To a $CH_2Cl_2$ solution of **5a** (0.5 mol) was added $ZnCl_2$•$OEt_2$ (2.2 M in $CH_2Cl_2$, 1 mmol) (in the case of entries 5-7) and allyltin (1 mmol) at -78°C. The reactions (entries 1, 5-7) were quenched with MeOH-$H_2O$ at -78°C after 10 min. AIBN (10 mol %) or galvinoxyl (5 mol %) was used. The reaction was conducted at -50°C and quenched at this temperature after 10 min (entries 2-4). [b]After quenching the reaction, the methoxy substituted glycine derivative of **5a** was afforded, *via* substitution of the carbon-bromine bond with methanol, along with **6a** and **7a**.

a radical mechamism. The allylation at -78℃ was dramatically accelerated using 2 equiv $ZnCl_2$•$OEt_2$ (cf entry 5 vs 1). The use of 0.1 equiv $ZnCl_2$•$OEt_2$ also accelerated very much, but the diastereoselection was enhanced by using 2 equiv of the Lewis acid, as mentioned later. The allylation in the presence of $ZnCl_2$•$OEt_2$ was accelerated by AIBN (10 mol %), and stopped completely by galvinoxy (5 mol %) (entries 6,7). Consequently, zinc chloride-diethyl ether complex acts as a radical initiator in the reaction of **5a** with allylstannanes. To the best of our knowledge, this is the first example of *the radical reaction of allylstannanes* in which the C-C bond formation is initiated by a Lewis acid, such as $ZnCl_2$•$OEt_2$.[11] The ether complex of $ZnBr_2$ and $ZnI_2$ also accelerated the reaction, whereas the acceleration was not observed in the case of $BF_3$•$OEt_2$ and $SnCl_4$.[12]

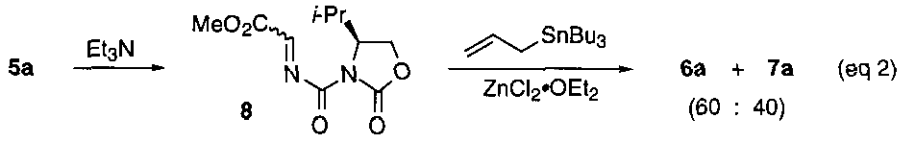
We next investigated the diastereoselectivities of the allylation of **5** in the presence of $ZnCl_2$•$OEt_2$ (eq 1, Table 2). When the reaction was stopped at the early stage (10 min) the highest selectivity was obtained (entry 3), whereas the diastereoselectivity was somewhat diminished at higher conversion (entry 1). We separated both stereoisomers (**6a** and **7a**) and then kept each of the diastereomers under the similar reaction conditions as the allylation. After several hours, we could recover each of the diastereomers quantitatively without isomerization. This clearly indicates that no isomerization of the diastereomers took place during the allylation process. Perhaps, the decrease of the diastereoselectivity at higher conversion is due to intervention of a non-radical by-pass to **6a**; the $ZnCl_2$ mediated allylation of imine (**8**), which may be formed in small amounts under the reaction conditions, may be involved. Actually, treatment of **5a** with triethylamine produced **8** quantitatively at -78℃, which reacted with allyltin in the presenceof 2 equiv of $ZnCl_2$•$OEt_2$ to give a 60 : 40 mixture of **6a** (*R*) and **7a** (*S*) (eq 2).[13] It is interesting that the Lewis acid mediated allylation of the imine (**8**) produces lower diastereoselectivity than the radical allylation of **5a**.

The reactions of **5a** with allyltin without any additives (entry 2), in the presence of 0.1 equiv $ZnCl_2$•$OEt_2$ (entry 4), or in the presence of AIBN (entry 5) afforded lower diastereoselectivities. The reactions of **5b-d** proceeded very smoothly, but the stereoselectivities were lower than those of **5a** (entries 6-8).

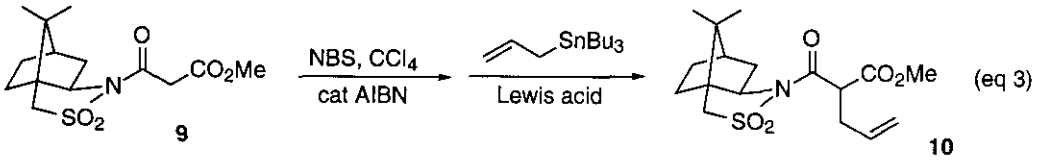
Table 2. Diastereoselective Allylation of **5** in the Presence of $ZnCl_2$•$OEt_2$

| entry | α-bromoglycine **5** | Lewis acid (equiv) | reactn conditions | yield (%) | isomer ratio **6** : **7** |
|---|---|---|---|---|---|
| 1 | **5a** | $ZnCl_2$•$OEt_2$ (2) | -78°C, 1 h | 85 | 87 : 13 |
| 2 | **5a** | none | -78°C → rt[a] | 56 | 52 : 48 |
| 3 | **5a** | $ZnCl_2$•$OEt_2$ (2) | -78°C, 10 min | 40 | 93 : 7 |
| 4 | **5a** | $ZnCl_2$•$OEt_2$ (0.1) | -78°C, 1 h | 65 | 67 : 33 |
| 5 | **5a** | none | AIBN (0.1 equiv) benzene 80°C, 1 h | 66 | 52 : 48 |
| 6 | **5b** | $ZnCl_2$•$OEt_2$ (2) | -78°C → rt | 92 | 74 : 26 |
| 7 | **5c** | $ZnCl_2$•$OEt_2$ (2) | -78°C → rt | 83 | 60 : 40 |
| 8 | **5d** | $ZnCl_2$•$OEt_2$ (2) | -78°C → rt | ~100 | 70 : 30 |

[a]rt, room temperature




Methallyltributyltin reacted similarly with **5a** in the presence of 2 equiv of $ZnCl_2$•$OEt_2$. Instead of the oxazolidinone auxiliary, we prepared the α-bromoglycine (**9**) having the Oppolzer's bornane-sultam,[14] but the allylation proceeded with lower diastereoselectivities (eq 3, Table 3).



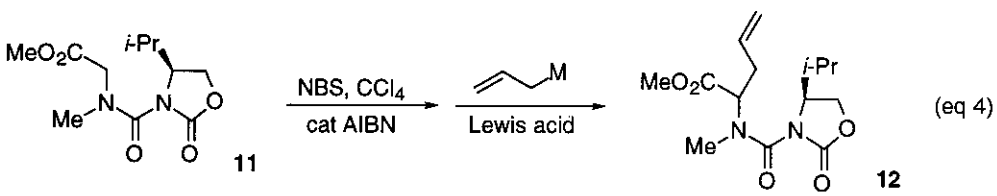

We examined the allylation reaction using **11**, which has a methyl group on nitrogen atom (eq 4). The results are summarized in Table 4. Although no reaction occurred without Lewis acid (entry 1), allylation product (**12**) was obtained as a mixture of stereoisomers (59:41) in the presence of $ZnCl_2$•$OEt_2$ (entry 2). However, no allylation reaction proceeded using allyltrimethylsilane instead of allyltributyltin even in the presence of $ZnCl_2$•$OEt_2$ (entry 3). If the reaction proceeds under ionic mechanism, acyliminium ion (**13**) would be formed as an intermediate. It is well known that allyltrimethylsilane reacts with acyliminium ion

Table 3. Diastereoselective Allylation of **9** Promoted by Lewis Acids

| entry | Lewis acid | condition | yield (%) | ratio of **10**[a] |
|---|---|---|---|---|
| 1 | none | rt | 85 | 56 : 44 |
| 2 | none | -78°C | 0 | — |
| 3 | $ZnCl_2$•$OEt_2$ | -78°C → rt | 70 | 52 : 48 |
| 4 | $EtAlCl_2$ | -78°C → rt | 54 | 26 : 74 |
| 5 | $Me_2AlCl$ | -78°C → rt | 74 | 44 : 56 |

[a]Stereochemistries were not determined.

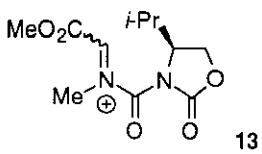
smoothly to give the allylation product.[15] The results strongly suggested that the reactions promoted by $ZnCl_2$•$OEt_2$ proceed *via* not ionic pathway but radical mechanism.



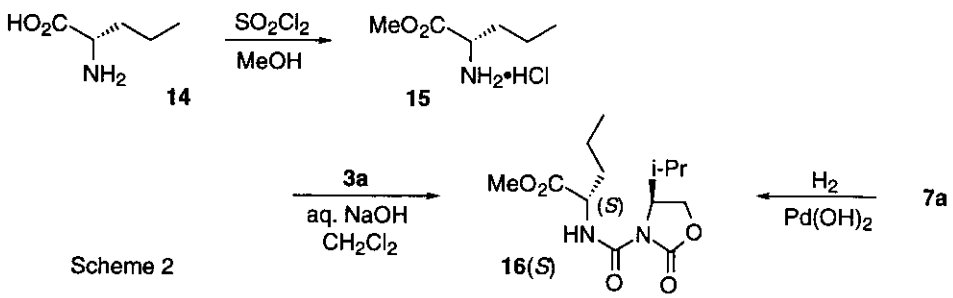

(eq 4)

Table 4. Zinc Chloride Promoted Allylation of **11**

| entry | allylmetal | Lewis acid | yield of **12** (%) |
|---|---|---|---|
| 1 | $SnBu_3$ | none | 0 |
| 2 | $SnBu_3$ | $ZnCl_2$•$OEt_2$ | 31 |
| 3 | $SiMe_3$ | $ZnCl_2$•$OEt_2$ | 0 |

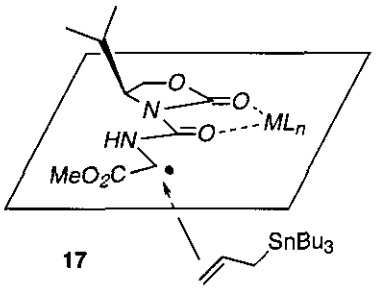



The stereochemistries of allylation products (**6**) and (**7**) were determined as shown in Scheme 2. The reaction of (*S*)-norvaline (**14**) with $SO_2Cl_2$ in MeOH gave the hydrogen chloride salt of (*S*)-norvaline methyl ester (**15**), which was converted to **16**(*S*) upon treatment with 4(*S*)-*N*-chloroformyl-4-isopropyl-2-




Scheme 2

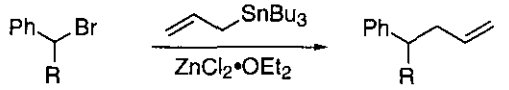
oxazolidinone (**3a**). Hydrogenation of **7a** (*S*) in methanol in the presence of $Pd(OH)_2$ catalyst gave **16**(*S*), and thus the absolute stereochemistries of **6** and **7** were determined unambiguously by comparing the hydrogenation product with the authentic sample. Since the major product of the allylation of **5a** is **6a**(*R*), the reaction presumably proceeds through the chelated transition state (**17**).




**17**

Reaction of Reactive Halides with Allyltributylstannane

It is now clear that $ZnX_2$ act as a radical initiator as well as a chelating agent in the reaction of **5** with allyltributyltin. The radical generated from **5** is stabilized by the capto-dative substituent.[16] To clarify whether $ZnCl_2$ works as a radical initiator even in the case of rather simple substrates, we investigated the allylation of reactive halides with allyltributyltin in the presence of $ZnCl_2$•$OEt_2$. The reaction of **18a-c** with allyltin in the presence of 0.1 (or 1.0) equiv of $ZnCl_2$•$OEt_2$ (at -78 ℃ to room temp) gave **19a-c** in 91%, 99%, and 30% yields respectively (eq 5). Without $ZnCl_2$•$OEt_2$, no reaction took place. Treatment of **18a** with 1.0 equiv $ZnCl_2$•$OEt_2$ afforded diphenylmethane (49%) along with benzhydryl chloride (9 %), whereas no reaction occurred by the use of $BF_3$•$OEt_2$ instead of $ZnCl_2$•$OEt_2$.

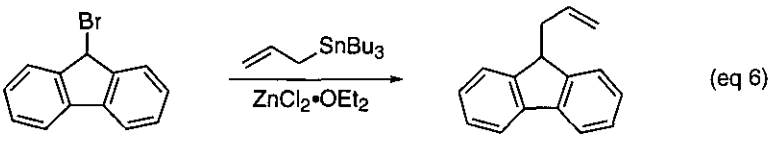



(eq 5)

**18a:** R = Ph
**18b:** R = Me
**18c:** R = *c*-$C_6H_{11}$

**19a:** R = Ph
**19b:** R = Me
**19c:** R = *c*-$C_6H_{11}$

Next, we examined the allylation of 9-bromofluorene (**20**) under various conditions and the results are summarized in Table 5. Without additives, the allylated product (**21**) was obtained at 80 °C in 28% yield (entry 1). Although the increase of chemical yield was observed by addition of catalytic amount of AIBN (entry 2), $ZnCl_2$•$OEt_2$ promoted reaction gave **21** in higher yield under even low temperature (at -78 ℃ to room temp) (entry 3). The best result was obtained using catalytic amount of $ZnCl_2$•$OEt_2$ (entry 4).

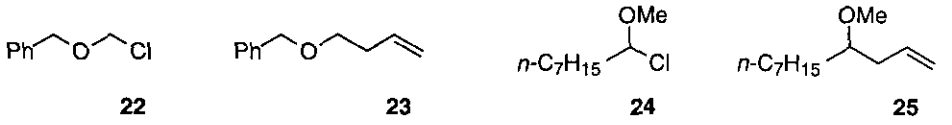



20 21 (eq 6)

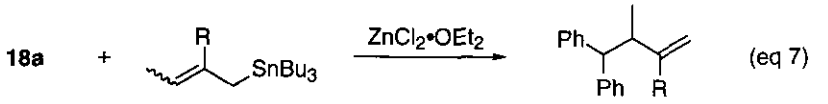
Table 5. Allylation Reaction of **20**

| entry | additive (equiv) | condition | yield (%) |
|---|---|---|---|
| 1 | none | benzene, 80°C | 28 |
| 2 | AIBN (0.1) | benzene, 80°C | 50 |
| 3 | $ZnCl_2$•$OEt_2$ (1.0) | -78°C → rt | 64 |
| 4 | $ZnCl_2$•$OEt_2$ (0.1) | -78°C → rt | 73 |

The reactions of α-alkoxy-alkyl halides (**22**) or (**24**) with allyltributyltin in the presence of 1.0 equiv. of $ZnCl_2$•$OEt_2$ also took place to give corresponding products (**23**) (83%) and (**25**) (60%). However, the $ZnCl_2$•$OEt_2$ catalyzed reaction of cyclohexyl bromide with allyltributyltin did not afford allylation product but cyclohexyl chloride. On the other hand, the reaction with 1-bromoadamantane gave 1-allyladamantane in 91% yield. Thus, the allylation proceeded in high yields in cases of sec-benzyl , α-alkoxy, and tertiary halides, whereas the reaction did not occur with primary and secondary halides. Interestingly, $ZnCl_2$•$OEt_2$ catalyzed reactions of crotyltin (**26a**) or (**26b**) with **18a** proceeded smoothly to give **27a** (88%) or **27b** (90%) respectively (eq 7). Is is well known that the crotyltin can not be used for radical reactions because the crotyltin is easy to decompose under normal radical conditions. This result indicates the advantage of $ZnCl_2$•$OEt_2$ catalyzed radical reactions for organic synthesis.




**22** **23** **24** **25**



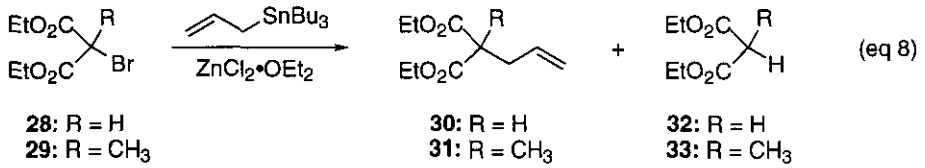

**26a:** R = H
**26b:** R = Me

**27a:** R = H
**27b:** R = Me

(eq 7)

The above results suggest that a radical process may be involved in the $ZnCl_2$ mediated allylation reaction of reactive halides. However, it is well known that $TiCl_4$ mediated reaction of reactive halides with allyltrimethylsilane proceeds through carbocation intermediates to give the corresponding allylated derivatives.[17] One can still be suspicious that similar cationic mechanism could be involved in the allyltin

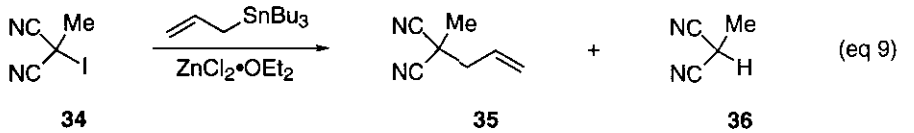
reactions.[18] The radicals, derived from bromomalonate and bromomalononitrile, are known to react well in radical processes, but a cationic pathway would be precluded. The reaction of **28** with allyltributyltin (1.5 equiv) in the presence of $ZnCl_2$•$OEt_2$ (1 equiv) in $CH_2Cl_2$ at room temperature gave **30** (30 %) and **32** (25 %) (eq 8). No reactions took place between allyltributyltin and **28** in the absence of $ZnCl_2$•$OEt_2$, and between allyltributyltin and $ZnCl_2$•$OEt_2$ without **28**. The zinc chloride mediated allylation of **29** under similar conditions afforded **31** in higher yield; **31** (59 %) and **33** (0 %). This is reasonable since the radical generated from **29** is stabilized, in comparison with the radical from **28**, by the capto-dative substituents. The reaction of **34** with allyltributyltin (1.5 equiv) in the presence of $ZnCl_2$•$OEt_2$ (1.0 equiv) in $CH_2Cl_2$ at -78 ℃ produced **35** (36 %) and **36** (44 %) (eq 9). Further, we examined the radical trap reaction using acrylonitrile and bromomalonate. The radical pathway should allow for the formation of **37**, while it should not be formed *via* sort of cationic pathway. The reaction of **28**, allyltin, and acrylonitrile (10 equiv) in the presence of $ZnCl_2$•$OEt_2$ at 0 ℃ afforded a mixture of **32** (13 %), **37** (16 %), and **28** (4 %) without forming **30** (eq 10). On the other hand, the reaction of **28** and acrylonitrile in the presence of $ZnCl_2$•$OEt_2$ under similar conditions resulted in recovery of **28**, indicating that the presence of allyltin is essential to formation of **37**.[19] Consequently, it is clear that the radical pathway is involved in the $ZnCl_2$ mediated reaction of allyltributyltin with reactive halides.



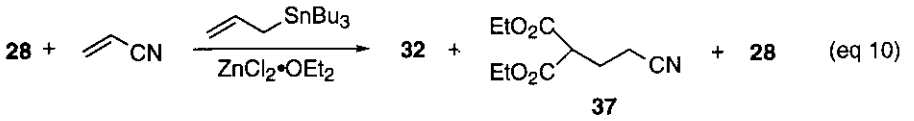

**28:** R = H
**29:** R = $CH_3$

**30:** R = H
**31:** R = $CH_3$

**32:** R = H
**33:** R = $CH_3$




**34** **35** **36**




**37**

## EXPERIMENTAL

$^1$H-NMR spectra were recorded with a JEOL GSX-270 and JEOL GX-400 spectrometer with tetramethylsilane as an internal standard. Chemical shifts are given on the δ scale (ppm). IR spectra were measured with Hitachi model 260-10 spectrophotometer. MS spectra were taken with Hitachi M-52 and JEOL JMS-HX110 spectrometer.

**Synthesis of the glycine derivatives (4) having oxazolidinone auxiliaries**

The oxazolidinones (**2a-d**) were prepared by the reported procedure.[8] The conversion of **2a** to **4a** is representative.

To a THF (20 mL) solution of **2a** (1.3g, 10 mmol), coold at 0℃, was added slowly *n*-BuLi (1.64 M in hexane, 6.1 mL, 10 mmol) under Ar. The mixture was stirred for 20 min and then coold to -78℃. TCF (trichloromethyl chloroformate, 1.2 mL, 10 mmol) was added rapidly, and the mixture was stirred for 30 min at -78℃ and then allowed to warm to rt. THF solvent and phosgene generated were removed using a water-aspirator. **3a** was obtained as a white solid including LiCl, which was used for further transformation without purification.

Glycine methyl ester hydrochloride (3.1 g, 25 mmol) and sodium hydroxide (1.0 g, 25 mmol) were dissolved in 10 mL of water. To this solution was added at 0℃ a $CH_2Cl_2$ (20 mL) solution of **3a** (25 mmol) all at once. The mixture was stirred for 30 min at 0℃, and 1 h at rt. The organic layer was separated, washed with brine, dried with $MgSO_4$, and the solvent was removed under reduced pressure. Purification of the crude product by silica gel column chromatography (hexane / ethyl acetate 2:1) afforded **4a** (3.9 g, 78 %).

**Methyl 2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)]aminoacetate (4a)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.31 (br s, 1 H), 4.42 (ddd, 1 H, $J$ = 8.5, 4.0, and 3.5 Hz), 4.33 (dd, 1 H, $J$ = 8.5 and 8.5 Hz), 4.24 (dd, 1 H, $J$ = 8.5 and 3.5 Hz), 4.08 (dd, 2 H, $J$ = 5.5 and 5.5 Hz), 3.78 (s, 3 H), 2.45 (m, 1 H), 0.90 (d, 3 H, $J$ = 7.0 Hz), 0.92 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3350, 2590, 1750, 1690, and 1530 cm$^{-1}$. HRMS calcd for $C_{10}H_{16}N_2O_5$: 244.1059. Found: 244.1059.

**Methyl 2-[*N*-((4*S*)-4-phenylmethyl-2-oxazolidinone-3-carbamoyl)]aminoacetate (4b)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.26 (m, 1 H), 7.40-7.20 (m, 5 H), 4.68 (dddd, 1 H, $J$ = 9.0, 9.0, 3.5, and 3.5 Hz), 4.27 (dd, 1 H, $J$ = 9.5 and 9.0 Hz), 4.20 (dd, 1 H, $J$ = 9.5 and 3.5 Hz), 4.12 (d, 2 H, $J$ = 5.5 Hz), 3.79 (s, 3 H), 3.33 (dd, 1 H, $J$ = 13.5 and 3.5 Hz), 2.89 (dd, 1 H, $J$ = 13.5 and 9.0 Hz); IR (neat) 3350, 2960, 1745, 1700, and 1525 cm$^{-1}$.

**Methyl 2-[*N*-((4*S*)-4-(2-methylpropyl)-2-oxazolidinone-3-carbamoyl)]aminoacetate (4c)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.25 (br s, 1 H), 4.46 (m, 2 H), 4.14 (m, 1 H), 4.06 (d, 2 H, $J$ = 5.5 Hz), 3.77 (s, 3 H), 1.90 (m, 1 H), 1.70-1.47 (m, 2 H), 0.96 (d, 6 H, $J$ = 7.0 Hz); IR (neat) 3370, 2980, 2900, 1775, 1710, 1540, and 1410 cm$^{-1}$. HRMS calcd for $C_{11}H_{18}N_2O_5$: 258.1216. Found: 258.1237.

**Methyl 2-[*N*-((4*S*)-4-(1,1-dimethylethyl)-2-oxazolidinone-3-carbamoyl)]aminoacetate**

**(4d)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.20 (br s, 1 H), 4.39-4.31 (m, 3 H), 4.07 (d, 2 H, $J$ = 6.0 Hz), 3.77 (s, 3 H), 0.96 (s, 9 H); IR (neat) 3450, 2960, 1750, 1700, and 1525 cm$^{-1}$. HRMS calcd for $C_{11}H_{18}N_2O_5$: 258.1216. Found: 258.1216.

**Methyl 2-[*N*-(bornane-10,2-sultam)-12-carbamoyl]aminoacetate (9)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 6.40 (br s, 1 H), 4.15 (dd, 1 H, $J$ = 18.0 and 6.0 Hz), 3.93 (dd, 1 H, $J$ = 18.0 and 5.5 Hz), 3.82 (dd, 1 H, $J$ = 7.5 and 4.5 Hz), 3.76 (s, 3 H), 3.39 (s, 2 H), 2.20-1.80 (m, 5 H), 1.50 (m, 1 H), 1.36 (m, 1 H), 1.14 (s, 3 H), 0.95 (s, 3 H); IR (neat) 3400, 2970, 1760, 1700, 1530, 1330, and 1140 cm$^{-1}$. HRMS calcd for $C_{14}H_{22}N_2O_5S$: 330.1250. Found: 330.1250.

**Methyl 2-[*N*-methyl-*N*-((4*S*)-4-isopropyl-2-oxazolidinone-3-carbamoyl)]aminoacetate (11)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 4.50 (m, 1 H), 4.41 (m, 2 H), 4.12 (m, 2 H), 3.76 (s, 3 H), 3.15 (s, 3 H), 0.94 (br d, 6 H, $J$ = 7.0 Hz); IR (neat) 2960, 1755, 1680, 1480 and 1200 cm$^{-1}$. HRMS calcd for $C_{11}H_{18}N_2O_5$: 258.1216. Found: 258.1213.

**The reaction of 5 with allyltributyltin**

A mixture of **4** (0.5 mmol), AIBN (23 mg, 0.05 mmol), and NBS (89 mg, 0.5 mmol) in $CCl_4$ (5 mL) was irradiated with a 250 W sun lamp for 30 min under reflux. The mixture was cooled to rt, and the solvent was removed *in vacuo*. The NMR spectrum of pale yellow solid, which was decomposed by column chromatography (silica, alumina, on florisil), indicated formation of a 1 : 1 diastereomeric mixture of **5**. To a $CH_2Cl_2$ (5 mL) solution of **5** (0.5 mmol) under Ar, cooled at -78℃, were added $ZnCl_2$•$OEt_2$ (1 mmol, 0.45 mL of 2.2 M $CH_2Cl_2$ solution) and then allyltributyltin (0.3 mL, 1 mmol). The mixture was stirred at -78℃ for 1 h and then the reaction was quenched by adding MeOH-$H_2O$. The usual work-up gave a mixture of **6** and **7**; the diastereomer ratio was determined by capillary GLPC (Shimazu GC-12A, column CBPI-M25-025).

**Methyl (2*R*)-2-[*N*-((4*S*)-4-isopropyl-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (6a)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.35 (d, 1 H, $J$ = 7.0 Hz), 5.74 (dddd, 1 H, $J$ = 17.0, 10.5, 7.0, and 7.0 Hz), 5.19 (br d, 1 H, $J$ = 17.0 Hz), 5.17 (br d, 1 H, $J$ = 10.5 Hz), 4.55 (ddd, 1 H, $J$ = 7.0, 7.0, and 5.5 Hz), 4.39 (ddd, 1 H, $J$ = 8.5, 4.0, and 3.5 Hz), 4.31 (dd, 1 H, $J$ = 8.5 and 8.5 Hz), 4.22 (dd, 1 H, $J$ = 8.5 and 3.5 Hz), 3.76 (s, 3 H), 2.60 (m, 2 H), 2.44 (m, 1 H), 0.91 (d, 3 H, $J$ = 7.0 Hz), 0.88 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3335, 2970, 1760, 1710, 1645, 1530, 1440, 1410, 1370, and 1220 cm$^{-1}$. HRMS

calcd for $C_{13}H_{20}N_2O_5$: 284.1372. Found: 284.1379.

**Methyl (2*S*)-2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (7a)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.32 (d, 1 H, $J$ = 7.0 Hz), 5.73 (dddd, 1 H, $J$ = 17.0, 10.5, 7.0 and 7.0 Hz), 5.18 (dm, 1 H, $J$ = 17.0 Hz), 5.17 (dm, 1 H, $J$ = 10.5 Hz), 4.56 (ddd, 1 H, $J$ = 7.0, 7.0, and 5.5 Hz), 4.40 (ddd, 1 H, $J$ = 8.5, 4.0, and 3.5 Hz), 4.31 (dd, 1 H, $J$ = 8.5 and 8.5 Hz), 4.22 (dd, 1 H, $J$ = 8.5 and 3.5 Hz), 3.76 (s, 3 H), 2.59 (m, 2 H), 2.43 (m, 1 H), 0.91 (d, 3 H, $J$ = 7.0 Hz), 0.90 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3330, 2960, 1750, 1700, 1640, 1525, 1435, 1400, 1370, and 1210 cm$^{-1}$. HRMS calcd for $C_{13}H_{20}N_2O_5$: 284.1372. Found: 284.1378.

**Methyl 2-[*N*-((4*S*)-4-phenylmethyl-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (6b and 7b)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.3 (d, 1 H, $J$ = 6.0 Hz), 7.40-7.20 (m, 5 H), 5.77 (m, 1 H), 5.23 and 5.20 (d, totally 2 H, $J$ = 13.5 Hz), 4.62 (m, 1 H), 4.25 (dd, 1 H, $J$ = 9.0 and 8.0 Hz), 4.18 (dd, 1 H, $J$ = 9.0 and 3.5 Hz), 3.80 and 3.78 (s, totally 3 H), 3.32 (dd, 1 H, $J$ = 13.5 and 3.5 Hz), 2.86 (dd, 1 H, $J$ = 13.5 and 9.0 Hz); IR (neat) 3330, 2950, 1748, 1690, and 1520 cm$^{-1}$.

**Methyl 2-[*N*-((4*S*)-4-(2-methylpropyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (6c and 7c)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.27 (d, 1 H, $J$ = 7.0 Hz), 5.80-5.65 (m, 1 H), 5.25-5.15 (m, 2 H), 4.56 (m, 1 H), 4.44 (m, 2 H), 4.13 (m, 1 H), 3.76 and 3.75 (s, totally 3 H), 2.60 (m, 2 H), 1.90 (m, 1 H), 1.68-1.47 (m, 2 H), 0.96 (d, 6 H, $J$ = 7.0 Hz); IR (neat) 3400, 2980, 1770, 1645, and 1540 cm$^{-1}$. HRMS calcd for $C_{14}H_{22}N_2O_5$: 298.1529. Found: 298.1532.

**Methyl 2-[*N*-((4*S*)-4-(1,1-dimethylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (6d and 7d)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 8.29 and 8.14 (d, totally, 1 H, $J$ = 7.0 Hz), 5.74 (m, 1 H), 5.19 (br d, 1 H, $J$ = 17.0 Hz), 5.18 (br d, 1 H, $J$ = 10.5 Hz), 4.54 (m, 1 H), 4.37-4.29 (m, 3 H), 3.75 (s, 3 H), 2.60 (m, 2 H), 0.94 (s, 9 H); IR (neat) 3350, 2990, 1775, 1715, 1530, 1395, and 1210 cm$^{-1}$. HRMS calcd for $C_{14}H_{22}N_2O_5$: 298.1529. Found: 298.1528.

**Methyl 2-[*N*-((bornane-10,2-sultam)-12-carbamoyl)amino]-4-pentenoate (10)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 6.48 and 6.44 (d, totally 1 H, $J$ = 7.5 Hz), 5.71 (m, 1 H), 5.20 and 5.14 (m, totally 2 H), 4.55 (m, 1 H), 3.90 and 3.80 (dd, totally 1 H, $J$ = 7.5 and 4.5 Hz), 3.75 (s, 3 H), 3.38 (s,

2 H), 2.60 (m, 1 H), 2.30-1.80 (m, 5 H), 1.49 (m, 1 H), 1.35 (m, 1 H), 1.14 and 1.11 (s, totally 3 H), 0.95 (s, 3 H); IR ($CCl_4$) 3400, 3040, 2970, 1755, 1710, 1520, 1335, 1220, and 1140 $cm^{-1}$. HRMS calcd for $C_{17}H_{26}N_2O_5S$: 370.1563. Found: 370.1549.

**Methyl 2-[*N*-methyl-*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentenoate (12)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 5.85 (m, 1 H), 5.15 (m, 2 H), 3.74 (s, 3 H), 3.73 (s, 3 H), 3.08 (br s, 3 H), 2.76 (m, 2 H), 2.06 (m, 1 H), 0.95-0.88 (m, 6 H); IR (neat) 2960, 1740, 1680, 1540, and 1210 $cm^{-1}$.

**Structural Determination, 16(*S*) and 16(*R*)**

To a methyl alcohol (10mL) was added slowly sulfuryl chloride (2.6 mL, 35 mmol) at -10°C. After stirring for 10 min at this temperature, L-norvaline (500 mg, 4.27 mmol) was added to the mixture. The reaction mixture was stirred for overnight at rt. Then the solvent was removed under reduced pressure and the remaining residue was purified by recrystallization from chloroform to give **15** as a white crystal (593 mg, 83% yield). The obtained **15** was treated with **3a** under same condition with the reaction for preparation of **4** from **3** to give crude material. Purification of the crude product by silica gel column chromatography (hexane / ethyl acetate 2:1) afforded **16** (*S*) (183 mg, 71%).

A mixture of **7a** (60 mg) and $Pd(OH)_2$ on charcol (20%, 20 mg) in methyl alcohol (5 mL) was stirred for 3 h under $H_2$ atmosphere. After filtration, the solvent was evaporated to give **16** (*S*) quantitatively. Same reaction using **6a** was carried out to give **16** (*R*) quantitatively.

**Methyl (2*S*)-2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentanoate (16 (*S*))**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 8.28 (d, 1 H, $J$ = 7.0 Hz), 4.49 (td, 1 H, $J$ = 8.0 and 5.5 Hz), 4.40 (ddd, 1 H, $J$ = 8.5, 4.0, and 3.5 Hz), 4.32 (dd, 1 H, $J$ = 8.5 and 8.5 Hz), 4.23 (dd, 1 H, $J$ = 8.5 and 3.5 Hz), 3.75 (s, 3 H), 2.44 (m, 1 H), 1.79 (tq, 2 H, $J$ = 8.0 and 7.8 Hz), 1.40 (td, 2 H, $J$ = 8.0 and 8.0 Hz), 0.94 (t, 3 H, $J$ = 7.8 Hz), 0.91 (d, 3 H, $J$ = 7.0 Hz), 0.90 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3340, 2960, 2880, 1740, 1700, and 1530 $cm^{-1}$.

**Methyl (2*R*)-2-[*N*-((4*S*)-4-(1-methylethyl)-2-oxazolidinone-3-carbamoyl)amino]-4-pentanoate (16 (*R*))**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 8.28 (d, 1 H, $J$ = 7.0 Hz), 4.46 (td, 1 H, $J$ = 8.0 and 5.5 Hz), 4.40 (ddd, 1 H, $J$ = 8.5, 4.0, and 3.5 Hz), 4.31 (dd, 1 H, $J$ =8.5 and 8.5 Hz), 4.22 (dd, 1 H, $J$ = 8.5 and 3.5 Hz), 3.75 (s, 3 H), 2.44 (m, 1 H), 1.80 (tq, 2 H, $J$ = 8.0 and 7.8 Hz), 1.41 (td, 2 H, $J$ = 8.0 and 8.0 Hz), 0.96

(t, 3 H, $J$ = 7.8 Hz), 0.91 (d, 3 H, $J$ = 7.0 Hz), 0.89 (d, 3 H, $J$ = 7.0 Hz); IR ($CCl_4$) 3310, 2940, 1770, 1700, and 1390 $cm^{-1}$.

**The reaction of reactive alkyl halides with allyltributylstannane**

The preparation of **19a** is representative. To a $CH_2Cl_2$ (3 mL) solution of **18a** (82 mg, 0.33 mmol) under Ar, cooled at -78℃, were added $ZnCl_2$•$OEt_2$ (0.33 mmol, 0.14 mL of 2.2 M $CH_2Cl_2$ solution) and then allyltributyltin (0.1 mL, 0.33 mmol). The mixture was stirred at -78℃ for 10 min and then the reaction was quenched by adding MeOH-$H_2O$. After the usual work-up, purification of the crude product by column chromatography on silica gel (hexane / ethyl acetate = 6/1) afforded **19a** (63 mg, 91%).

**4,4-Diphenyl-1-butene (19a)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.30-7.15 (m, 10 H), 5.72 (ddd, 1 H, $J$ = 17.0, 10.5, and 7.0 Hz), 5.03 (dddd, 1 H, $J$ = 17.0, 1.5, 1.5, and 1.5 Hz), 4.95 (dddd, 1 H, $J$ = 10.5, 1.5, 1.0, and 1.0 Hz), 4.00 (t, 1 H, $J$ = 7.5 Hz), 2.81 (dddd, 2 H, $J$ = 7.5, 7.0, 1.5, and 1.5 Hz); IR (neat) 3070, 2940, 1642, 1600, 1495, 1455, and 742 $cm^{-1}$; HRMS calcd for $C_{16}H_{16}$: 208.1252. Found: 208.1251.

**4-Phenyl-1-pentene (19b)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.30-7.15 (m, 5 H), 5.71 (dddd, 1 H, $J$ = 17.0, 10.0, 7.5, and 7.5 Hz), 4.99 (dddd, 1 H, $J$ = 17.0, 1.5, 1.5, and 1.5 Hz), 4.95 (dddd, 1 H, $J$ = 10.0, 1.5, 1.5, and 1.0 Hz), 2.79 (ddq, 1 H, $J$ = 7.5, 7.5, and 7.0 Hz), 2.33 (dddd, 2 H, $J$ = 7.5, 7.5, 1.5, and 1.5 Hz); IR (neat) 3040, 2980, 1730, 1610, 1495, and 1455 $cm^{-1}$.

**4-Cyclohexyl-4-phenyl-1-butene (19c)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.50-7.05 (m, 5 H), 5.58 (dddd, 1 H, $J$ = 17.0, 10.0, 6.5, and 6.5 Hz), 4.91 (dddd, 1 H, $J$ = 17.0, 2.0, 2.0, and 1.5 Hz), 4.84 (dddd, 1 H, $J$ = 10.0, 2.0, 2.0, and 1.0 Hz), 2.54 (m, 1 H), 2.39 (m, 2 H), 1.90-0.85 (m, 10 H).

**9-(1-Propenyl)fluorene (21)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.76-7.30 (m, 8 H), 5.74 (ddt, 1 H, $J$ = 17.5, 10.0, and 7.0 Hz), 5.02 (br d, 1 H, $J$ = 17.5 Hz), 4.97 (br d, 1 H, $J$ = 10.0 Hz), 4.00 (t, 1 H, $J$ = 6.2 Hz), 2.73 (dddd, 2 H, $J$ = 7.0, 6.2, 1.0, and 1.0 Hz); IR (neat) 3080, 2945, 1645, 1615, 1485, 1455, and 750 $cm^{-1}$; HRMS calcd for $C_{16}H_{14}$: 206.1096. Found: 206.1093.

**4,4-Diphenyl-3-methyl-1-butene (27a)**

$^1$H NMR (270 MHz, $CDCl_3$) $\delta$ 7.30-7.10 (m, 10 H), 5.68 (ddd, 1 H, $J$ = 17.0, 10.5, and 7.5 Hz), 4.96 (ddd, 1 H, $J$ = 17.0, 1.5, and 1.5 Hz), 4.86 (ddd, 1 H, $J$ = 10.5, 1.5, and 1.0 Hz), 3.63 (d, 1 H, $J$ = 10.5

Hz), 3.07 (m, 1 H), 0.97 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3050, 1650, 1610, 1500, 1455, and 750 $cm^{-1}$; HRMS calcd for $C_{17}H_{18}$: 222.1409. Found: 222.1404.

**4,4-Diphenyl-2,3-dimethyl-1-butene (27b)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 7.35-7.10 (m, 10 H), 4.74 (m, 1 H), 4.62 (br d, 1 H, $J$ = 1.5 Hz), 3.77 (d, 1 H, $J$ = 10.5 Hz), 3.13 (dq, 1 H, $J$ = 10.5 and 7.0 Hz), 1.59 (s, 3 H), 0.96 (d, 3 H, $J$ = 7.0 Hz); IR (neat) 3080, 3050, 2990, 1650, 1610, 1495, 1458, and 750 $cm^{-1}$; HRMS calcd for $C_{16}H_{20}$: 236.1565. Found: 236.1561.

**Diethyl 2-allylpropanedionate (30)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 5.79 (ddt, 1 H, $J$ = 17.1, 10.2, and 6.9 Hz), 5.13 (ddt, 1 H, $J$ = 17.1, 1.8, and 1.5 Hz), 5.06 (ddt, 1 H, $J$ = 10.2, 1.8, and 1.2 Hz), 4.21 (dq, 2 H, $J$ = 11.1 and 7.2 Hz), 4.19 (dq, 2 H, $J$ = 11.1 and 7.2 Hz), 3.42 (t, 1 H, $J$ = 7.5 Hz), 2.65 (dddd, 2 H, $J$ = 7.5, 6.9, 1.5, and 1.2 Hz), 1.27 (t, 6 H, $J$ = 7.2 Hz); IR (neat) 2984, 1736, 1034, 922, and 858 $cm^{-1}$.

**Diethyl 2-allyl-2-methylpropanedionate (31)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 5.70 (ddt, 1 H, $J$ = 16.5, 10.5, and 7.5 Hz), 5.12 (ddt, 1 H, $J$ = 7.5, 2.1, and 0.9 Hz), 5.08 (m, 1 H), 4.19 (q, 4 H, $J$ = 6.9 Hz), 2.61 (dt, 2 H, $J$ = 7.5 and 1.2 Hz), 1.39 (s, 3 H), 1.25 (t, 6 H, $J$ = 6.9 Hz); IR (neat) 2984, 1732, 1069, 922, and 860 $cm^{-1}$.

**Pent-4-ene-2,2-dicarbonytrile (35)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 5.89 (ddt, 1 H, $J$ = 16.8, 10.0, and 7.3 Hz), 5.43 (m, 1 H), 2.69 (d, 1 H, $J$ = 7.3 Hz), 1.80 (s, 3 H).

**Diethyl 2-cyanoethylmalonate (37)**

$^1H$ NMR (270 MHz, $CDCl_3$) $\delta$ 4.23 (dq, 2 H, $J$ = 10.8, and 7.2 Hz), 4.22 (dq, 2 H, $J$ = 10.8, and 7.2 Hz), 3.50 (t, 1 H, $J$ = 7.2 Hz), 2.50 (t, 2 H, $J$ = 6.6 Hz), 2.25 (dt, 2 H, $J$ = 6.6 and 7.2 Hz), 1.28 (t, 6 H, $J$ = 7.2 Hz); IR (neat) 2986, 2249, 1732, 1049, 1024, and 862 $cm^{-1}$.

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†Dedicated to Prof. Koji Nakanishi on the occasion of his 75th birthday.

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