# Direct synthesis of unprotected α-amino acids via allylation of hydroxyglycine[1]

**Masaharu Sugiura, Chieko Mori, Keiichi Hirano, and Shū Kobayashi**

**Abstract:** Hydroxyglycine, the ammonia adduct of glyoxylic acid, was found to react with various allylboronates in the presence of triethylamine in methanol to give unprotected α-amino acids directly with high stereoselectivity. For instance, the reactions with (*E*)- and (*Z*)-crotylboronates afforded the corresponding anti- and syn-crotylated products (isoleucine and alloisoleucine after hydrogenation) with high diastereoselectivity, respectively. Interestingly, it was found that isomerization of the products (γ-adducts to α-adducts) occurred under the reaction conditions in some cases. Control experiments have suggested that the isomerization took place via 2-aza (or azonia) Cope rearrangement of imines derived from γ-adducts and glyoxylic acid.

*Key words:* hydroxyglycine, glyoxylic acid, allylboronates, α-amino acids, allylglycines, isoleucine, alloisoleucine, stereoselective reactions, isomerization, 2-aza (azonia) Cope rearrangement.

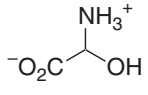
**Résumé :** On a trouvé que l'hydroxyglycine, le produit d'addition de l'ammoniac sur l'acide glyoxylique, réagit avec divers allylboronates, en présence de triéthylamine dans le méthanol, pour conduire directement à la formation d'acides α-aminés non protégés, avec une stéréosélectivité élevée. Par exemple, les réactions des (*E*)- et (*Z*)-crotylboronates conduisent respectivement aux produits anticrotylés et syncrotylés correspondants (isoleucine et alloisoleucine après hydrogénation) avec des diastéréosélectivités élevées. Fait intéressant, on a trouvé que, dans les conditions expérimentales et pour quelques cas, il se produit une isomérisation des produits (adduits γ en adduits α). Des expériences de contrôle ont suggéré que l'isomérisation se produit par un réarrangement 2-aza (ou azonia) de Cope des imines dérivées d'adduits γ et de l'acide glyoxylique.

*Mots clés :* hydroxyglycine, acide glyoxylique, allyboronates, acides α-aminés, allylglycines, isoleucine, alloisoleucine, réactions stéréosélectives, isomérisation, réarrangement 2-aza (ou azonia) de Cope.

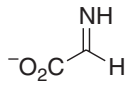
[Traduit par la Rédaction]

## Introduction

Hydroxyglycine (**1**), which is obtained as a zwitterionic solid under the isoelectronic conditions (pH ca. 6), is an equimolar adduct of glyoxylic acid and ammonia (1). It readily decomposes to glyoxylic acid in an aqueous media at pH < 6, while it oligomerizes via iminoacetate **2** (an assumed intermediate) at pH > 6. These compounds attracted us because we recently found that three-component reactions (α-aminoallylation) of glyoxylic acid (other aldehydes as well), ammonia, and allylboronates proceeded smoothly to afford allylglycines (homoallylic primary amines) in high yields (2). In these reactions, both **1** and **2** are supposed to serve as intermediates. However, despite their potential utility as intermediates for direct synthesis of *unprotected* α-amino acids, **1** and **2** have been barely utilized in organic synthesis (3). Herein, we report that nucleophilic addition of allylboronates to hydroxyglycine **1** provides an efficient, stereoselective route to unprotected allylglycines.




**1**




**2**

## Results and discussion

Initial attempts were made for allylation of hydroxyglycine **1** with allylboronate **3a** (4*a*). First, the effect of varying solvents was investigated by simply mixing **1** and **3a** (1.2 equiv.) in a solvent at 0 °C to room temperature (rt) for 15–18 h (Table 1, entries 1–6). Protic solvents (ethanol, methanol, and water) were found to be effective (Table 1, entries 1–3), whereas less polar solvents (toluene, THF, and acetonitrile) were much inferior (Table 1, entries 4–6). The reaction mixtures were suspensions in these solvents except for in water because of the low solubility of **1**. Among the solvents tested, methanol gave the highest yield and chemoselectivity (amine **4a** vs. alcohol **5a**) (Table 1, entry 2). To improve the yield, further optimization of the conditions were performed choosing methanol as a solvent. A longer reaction time (72 h) or a higher temperature (50 °C) dramatically improved the yield (Table 1, entries 7 and 8). It is also

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*This paper is dedicated to Professor Howard Alper for his great contributions to the fields of catalysis, organometallic, and organic chemistry.*

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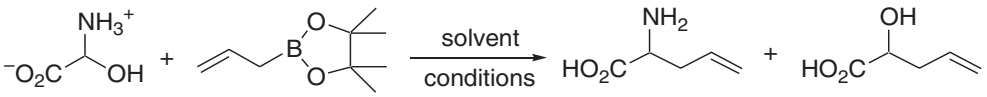
**Table 1.** Allylation of hydroxyglycine (**1**) with allylboronate **3a**.




**1** **3a** (1.2 equiv.) **4a** **5a**

| Entry | Solvent | Conditions | Yield (%) **4a**[a] | **5a**[b] |
|---|---|---|---|---|
| 1 | EtOH | rt, 18 h | 27 | 5 |
| 2 | MeOH | rt, 18 h | 42[c] | 3 |
| 3 | $H_2O$ | rt, 18 h | 39 | 67[d] |
| 4 | Toluene | rt, 18 h | 2 | Trace |
| 5 | THF | 0 °C, 15 h | 0 | 0 |
| 6 | $CH_3CN$ | rt, 18 h | 0 | 0 |
| 7 | MeOH | rt, 72 h | 73 | nd |
| 8 | MeOH | 50 °C, 18 h | 84 | nd |
| 9 | MeOH | $Et_3N$ (20 mol%), rt, 18 h | 90[c] | nd |

**Note:** nd = not detected.
[a]Isolated yield.
[b]Estimated by $^1$H NMR analysis of the crude product on the basis of the isolated yield of **4**.
[c]Average of two trials.
[d]Supposed to include an experimental error on integration of the $^1$H NMR spectrum.

noteworthy that only allylated amine **4a** was obtained exclusively in these entries. Furthermore, a catalytic amount of triethylamine (20 mol%) was found to accelerate the reaction showing the highest yield and selectivity of **4a** (Table 1, entry 9). It is presumable that the base promotes formation of an active intermediate, iminoacetate **2** from **1**.

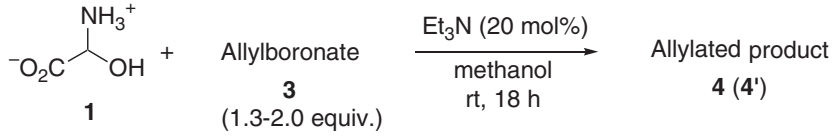
With the optimal conditions in hand, we then investigated reactions of **1** with various allylboronates **3** (4*b*–4*d*) (Table 2). Methallyboronate **3b** afforded the corresponding adduct **4b** in high yield (Table 2, entry 1). Triethylamine (1 equiv.) was used in this case to facilitate the desired reaction.[3] Significantly, (*Z*)-crotylboronate ((*Z*)-**3c**) provided syn-crotylated product (*syn*-**4c**) exclusively (>99% syn) along with a small amount of α-adduct (*Z*)-**4c′**, while anti-adduct (*anti*-**4c**) was obtained from (*E*)-crotylboronate ((*E*)-**3c**) in good yield with excellent selectivity (97% anti, Table 2, entries 2 and 3). In the later case, a very small amount of α-adduct **4c′** was yielded. Direct treatment of hydrogen (1 atm, 1 atm = 101.325 kPa) and Pd/C in the same pot successfully converted syn- and anti-adducts (*syn*- and *anti*-**4c**) to alloisoleucine (75%) and isoleucine (82%), respectively (Scheme 1). On the other hand, reactions of **1** with (*E*)-cinnamylboronate **3d** and cyclohexenylboronate **3e** provided **4d** and **4e**, respectively, in high yield with high diastereoselectivities (Table 2, entries 4 and 5). In the former case, 1 equiv. of triethylamine was effective to suppress formation of α-adduct **4d′**. Sterically more demanding prenylboronate **3f** also reacted with **1** in the presence of 2 equiv. of triethylamine to afford a mixture of the desired allylated product **4f** and α-adduct **4f′** (85:15) in high yield (Table 2, entry 6).

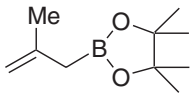
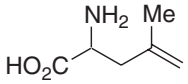
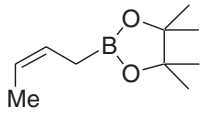
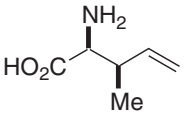
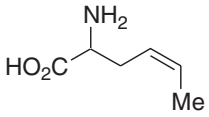
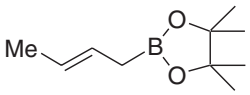
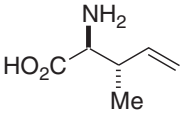
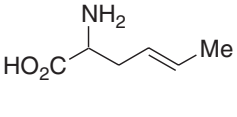
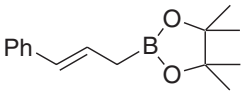
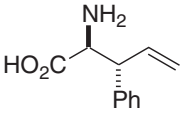
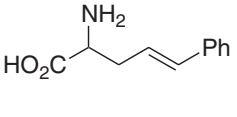
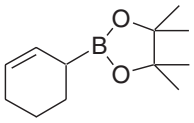
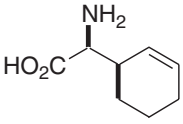
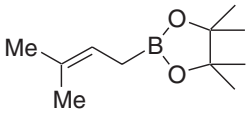
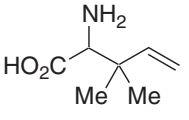
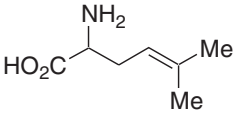
We were then interested in the mechanism of the formation of α-adduct **4′**. It was found that the formation of α-adduct **4′** became prominent when the reaction mixtures were concentrated with heating before purification. In the reaction of **1** with **3f**, for example, this manipulation led to only formation of **4f′**. In contrast, the formation of **4′** was suppressed to a large extent when the reaction mixture was directly purified by ion exchange resin (Dowex 50W-X2). Addition of a stoichiometric amount of triethylamine in allylations was also effective to suppress the formation of **4′** (vide supra). These observations indicated that some impurity involved in the reaction mixture promoted the isomerization on heating. We speculated that glyoxylic acid (or hydroxyglycine) formed an imine with allylated product **4**, which could undergo 2-aza (or azonia) Cope rearrangement leading to the isomerization (Scheme 2) (5, 6). To prove this hypothesis, purified *syn*- and *anti*-**4c** were treated with glyoxylic acid (0.1 equiv.) in $D_2O$ at 50 °C (Fig. 1). Monitoring by $^1$H NMR spectroscopy clearly showed gradual isomerization of *syn*- and *anti*-**4c** to α-adduct **4c′** (first order in [**4c**]; $t_{1/2}$ = 78 min for *syn*-**4c**, 34 min for *anti*-**4c**), whereas no isomerization was observed in the absence of glyoxylic acid.

It should also be noted that (*Z*)-**4c′** was predominantly obtained from *syn*-**4c**, whereas *anti*-**4c** gave (*E*)-**4c′** with high selectivity (also see the Experimental section). Chair-like transition states **TS-*syn*** with the pseudo-axial methyl group[4] and **TS-*anti*** with the pseudo-equatorial methyl group could account for the observed stereochemical outcomes (Scheme 3). We also found that the rate of the isomerization of *anti*-**4c** to (*E*)-**4c′** was faster than that of *syn*-**4c** to (*Z*)-

[3] When a catalytic amount of triethylamine was used, an unidentified product was obtained along with **4b**. The $^1$H and $^{13}$C NMR spectra of this by-product suggested a Prins-type cyclization product. Further structural elucidation is now in progress.
[4] The preference of the equatorial $CO_2H$ group might be ascribed to the acid–base interaction of the $CO_2H$ group with the imino nitrogen.

**Table 2.** Allylation of hydroxyglycine (**1**) with various allylboronates **3**.



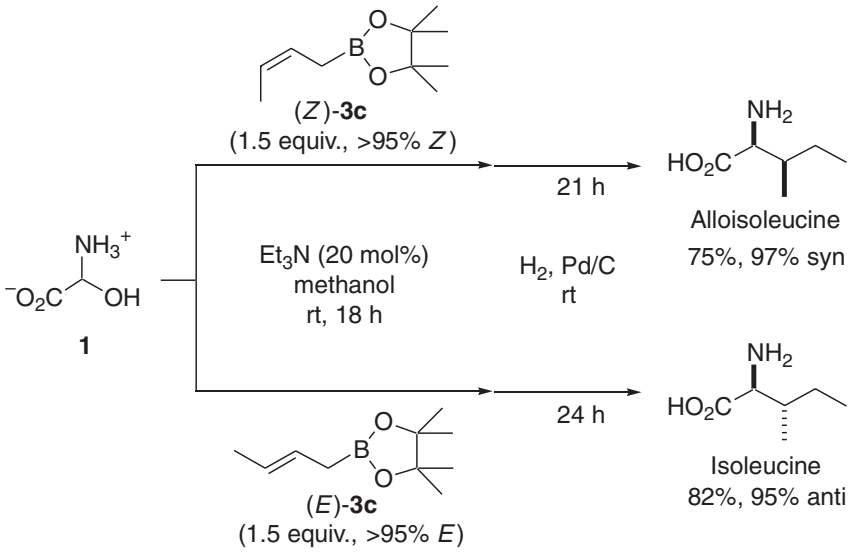

| Entry | Allylboronate | Yield (%)[a] | Allylated products | 4/4'[b] |
|---|---|---|---|---|
| 1[c] |  **3b** | 81 |  **4b** 2-Amino-4-methyl-pent-4-enoic acid | — |
| 2 |  (*Z*)-**3c** (>95% *Z*) | 73 |  *syn*-**4c** (>99% syn) +  **4c'** (77% *Z*) | 95/5 |
| 3 |  (*E*)-**3c** (>95% *E*) | 66 |  *anti*-**4c** (97% anti) +  **4c'** (>97% *E*) | 98/2 |
| 4[c] |  **3d** (>99% *E*) | 93 |  **4d** (>99% anti) +  **4d'** (>99% *E*) | 93/7 |
| 5 |  **3e** | 88 |  **4e** (>99% syn) | — |
| 6[d,e] |  **3f** | 92 |  **4f** +  **4f'** | 85/15 |

[a]Combined yields of **4** and **4′**.
[b]Determined by $^1$H NMR analyses.
[c]Triethylamine (1 equiv.) was used.
[d]Triethylamine (2 equiv.) was used.
[e]The reaction was conducted for 6 h.

**4c′**. This rate difference would be ascribed to the fact that **TS-*anti*** is more stable than **TS-*syn*** because of the number of pseudo-equatorial substituents. In addition, the higher isomerization tendency of **4f** could be explained by the mechanism via 2-aza (or azonia) Cope rearrangement in which the equilibrium favors release of the steric hindrance to the more stable trisubstituted alkene **4f′**.

In summary, we have demonstrated that hydroxyglycine (**1**), the ammonia adduct of glyoxylic acid, reacts with various allylboronates in the presence of a tertiary amine to give

**Scheme 1.** Stereoselective synthesis of alloisoleucine and isoleucine.




**Scheme 2.** Assumed mechanism for isomerization via 2-aza Cope rearrangement.

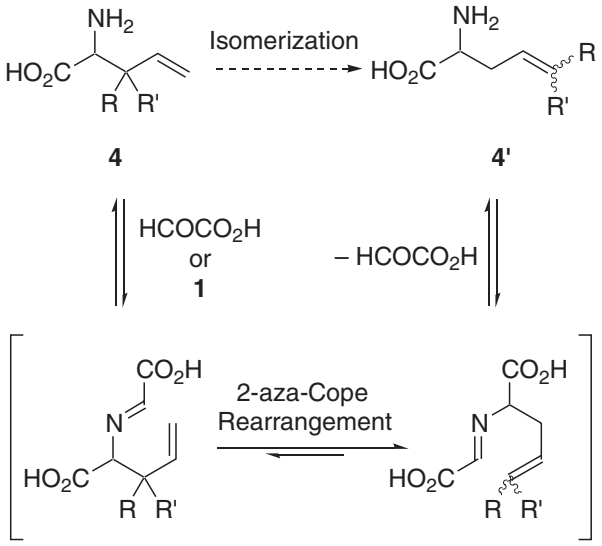
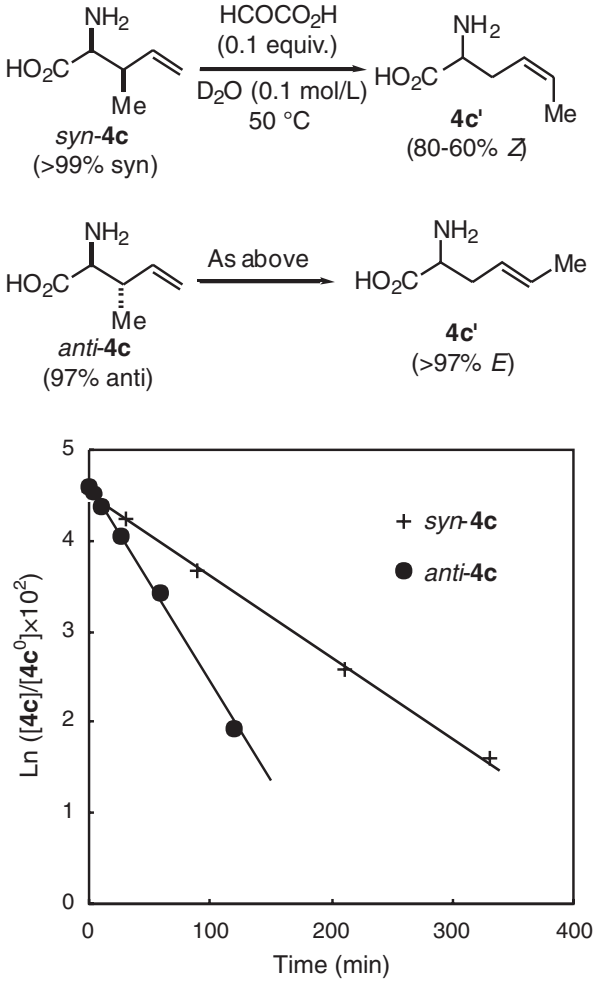



**Fig. 1.** Isomerization of *syn*- and *anti*-**4c**.



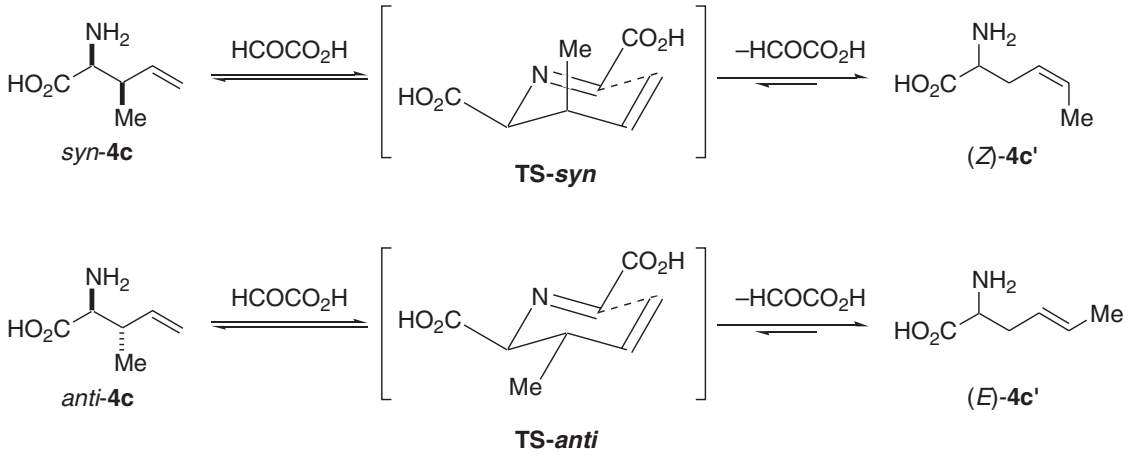

the corresponding unprotected α-amino acids directly. Reactions with γ-substituted allylboronates showed high diastereoselectivity, while isomerization of γ-adducts to α-adducts was accompanied to some extent. Further studies regarding its application to asymmetric synthesis are now in progress.

## Experimental section

### General methods

Melting points (mp) are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on JEOL ECX-400 or ECX-600 spectrometers in $D_2O$. 1,4-Dioxane served as the internal standard (δ 3.75 ppm for $^1$H NMR and δ 67.19 ppm for $^{13}$C NMR). High-resolution electrospray ionization mass spectra (HR-ESI-MS) were measured with a Bruker Daltonics BioTOF II mass spectrometer. Methanol was distilled from magnesium–iodine and stored over 3 Å MS. Purified water was employed for work-up and purification. All other solvents were purified based on standard procedures. Hydroxyglycine (**1**) (1) and allylboronates **3a**–**3f** (4) were prepared according to literature procedures.

**Scheme 3.** Chair-like transition state models for 2-aza Cope rearrangement.




## General procedure for allylation of hydroxyglycine

Under an argon atmosphere, to a suspension of hydroxyglycine (**1**) (45.5 mg, 0.5 mmol) in dry methanol (2 mL), were added allylboronate **3** (1.2–2.0 equiv.) and triethylamine (0.1–2.0 equiv.) successively at ambient temperature. The mixture was stirred at that temperature for the indicated time, diluted with water, and charged on a cationic ion exchange resin column (Dowex 50W-X2, 50–100 mesh, $H^+$ form; ca. 5 g/wet) with water. After washing with a sufficient amount of water, α-amino acid **4** was eluted with 1.0 mol/L aqueous ammonia (fractions were checked by 0.1 wt% ninhydrine in acetone–water (4:1)), and concentrated to dryness.

## Physical data of allylglycines

### *2-Aminopent-4-enoic acid (4a)*

See ref. 2.

### *2-Amino-4-methylpent-4-enoic acid (4b)*

mp 228–231 °C. $^1$H NMR (400 MHz) δ: 5.00 (s, 1H), 4.90 (s, 1H), 3.85 (dd, *J* = 9.6, 4.6 Hz, 1H), 2.68 (dd, *J* = 14.7, 4.6 Hz, 1H), 2.50 (dd, *J* = 14.7, 9.6 Hz, 1H), 1.77 (s, 3H). $^{13}$C NMR (100 MHz) δ: 175.2, 140.7, 116.0, 53.2, 39.7, 21.3. HR-ESI-MS calcd. for $C_6H_{12}NO_2$: 130.0863 (M + $H^+$); found: 130.0867.

### syn-*2-Amino-3-methylpent-4-enoic acid (*syn-*4c)*

mp 224–227 °C. $^1$H NMR (400 MHz) δ: 5.84 (ddd, *J* = 17.9, 10.1, 6.4 Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H), 5.25 (d, *J* = 17.9 Hz, 1H), 3.76 (d, *J* = 4.1 Hz, 1H), 2.94–2.82 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz) δ: 174.0, 138.2, 118.2, 59.0, 38.4, 13.6. HR-ESI-MS calcd. for $C_6H_{12}NO_2$: 130.0863 (M + $H^+$); found: 130.0866.

### anti-*2-Amino-3-methylpent-4-enoic acid (*anti-*4c)*

mp 220–223 °C. $^1$H NMR (400 MHz) δ: 5.75 (ddd, *J* = 17.4, 10.1, 7.3 Hz, 1H), 5.25 (d, *J* = 17.4 Hz, 1H), 5.24 (d, *J* = 10.1 Hz, 1H), 3.61 (d, *J* = 5.5 Hz, 1H), 2.87–2.74 (m, 1H), 1.16 (d, *J* = 7.3 Hz, 3H). $^{13}$C NMR (100 MHz) δ: 174.4, 137.3, 118.8, 59.8, 39.1, 16.0. HR-ESI-MS calcd. for $C_6H_{12}NO_2$: 130.0863 (M + $H^+$); found: 130.0862.

### *2-Aminohex-4-enoic acid (4c′)*

$^1$H NMR (400 MHz) (*E*-isomer) δ: 5.74 (dqt, *J* = 15.1, 6.4, 1.4 Hz, 1H), 5.38 (dtq, *J* = 15.1, 7.3, 1.8 Hz, 1H), 3.83 (dd, *J* = 6.7, 5.3 Hz, 1H), 2.67–2.49 (m, 2H), 1.67 (d, *J* = 6.4 Hz, 3H); (*Z*-isomer, a representative signal) δ: 1.63 (d, *J* = 6.9 Hz, 3H).

### anti-*2-Amino-3-phenylpent-4-enoic acid (4d) and (*E*)-2-amino-5-phenylpent-4-enoic acid (4d′) (4d:4d′ = 93:7)*

mp 172–176 °C. $^1$H NMR (400 MHz) δ: 7.52–7.28 (m, 5.00H), 6.65 (d, *J* = 15.6 Hz, 0.07H), 6.29–6.14 (m, 1.00H), 5.36 (d, *J* = 17.4 Hz, 0.93H), 5.34 (d, *J* = 10.1 Hz, 0.93H), 3.98 (d, *J* = 7.8 Hz, 0.93H), 3.91–3.83 (m, 1.00H), 2.89–2.71 (m, 0.14H). For **4d**: $^{13}$C NMR (150 MHz) δ: 173.6, 139.2, 135.3, 129.8, 128.54, 128.47, 120.6, 60.0, 51.8; for **4d′**: (distinguishable signals) δ: 174.7, 137.2, 129.5, 127.0, 123.6, 54.9, 34.7. HR-ESI-MS calcd. for $C_{11}H_{14}NO_2$: 192.1019 (M + $H^+$); found: 192.1021.

### syn-*Aminocyclohex-2-enyl-acetic acid (4e)*

mp 233–236 °C. $^1$H NMR (400 MHz) δ: 6.07–5.96 (m, 1H), 5.54 (d, *J* = 10.1 Hz, 1H), 3.78 (d, *J* = 4.1 Hz, 1H), 2.94–2.80 (m, 1H), 2.08–1.90 (m, 2H), 1.85–1.74 (m, 1H), 1.72–1.61 (m, 1H), 1.60–1.46 (m, 1H), 1.40–1.25 (m, 1H). $^{13}$C NMR (100 MHz) δ: 174.4, 133.7, 126.1, 58.9, 37.1, 24.8, 23.2, 21.6. HR-ESI-MS calcd. for $C_8H_{14}NO_2$: 156.1019 (M + $H^+$); found: 156.1015.

### *2-Amino-3,3-dimethylpent-4-enoic acid (4f)*

mp 212–216 °C. $^1$H NMR (400 MHz) δ: 5.86 (dd, *J* = 17.4, 11.0 Hz, 1H), 5.24 (d, *J* = 11.0 Hz, 1H), 5.21 (d, *J* = 17.4 Hz, 1H), 3.52 (s, 1H), 1.21 (s, 3H), 1.14 (s, 3H). $^{13}$C NMR (100 MHz) δ: 173.4, 143.0, 116.0, 62.9, 38.8, 25.0, 22.0. HR-ESI-MS calcd. for $C_7H_{14}NO_2$: 144.1019 (M + $H^+$); found: 144.1020 (checked as an 85:15 mixture of **4f** and **4f′**).

### *2-Amino-5-methylhex-4-enoic acid (4f′)*

mp 198–202 °C. $^1$H NMR (400 MHz) δ: 5.10 (t, *J* = 7.8 Hz, 1H), 3.74 (t, *J* = 6.0 Hz, 1H), 2.68–2.50 (m, 2H), 1.74 (s, 3H), 1.65 (s, 3H). $^{13}$C NMR (100 MHz) δ: 175.1, 139.6, 116.7, 55.3, 29.7, 25.7, 17.7. HR-ESI-MS calcd. for $C_7H_{14}NO_2$: 144.1019 (M + $H^+$); found: 144.1021.

**Table 3.** Isomerization of *syn*-**4c**.

| Time (min) | *syn*-**4c**:**4c′** | *E*:*Z* ratio of **4c′** |
|---|---|---|
| 0 | 94:6 | 20:80 |
| 30 | 70:30 | 33:67 |
| 90 | 39:61 | 37:63 |
| 210 | 13:87 | 40:60 |
| 330 | 5:95 | 38:62 |

**Table 4.** Isomerization of *anti*-**4c**.

| Time (min) | *anti*-**4c**:**4c′** | *E*:*Z* ratio of **4c′** |
|---|---|---|
| 0 | 98:2 | >97:<3 |
| 4 | 93:7 | >97:<3 |
| 10 | 81:19 | >97:<3 |
| 28 | 57:43 | >97:<3 |
| 59 | 31:69 | >97:<3 |
| 120 | 7:93 | >97:<3 |
| 180 | 3:97 | >97:<3 |

### *(±)-Alloisoleucine and (±)-isoleucine*

Prepared according to the reported method (2).

### Monitoring isomerization of 4c to 4c′ by $^1$H NMR spectroscopy

A solution of *syn*- or *anti*-**4c** (7.7 mg, 0.06 mmol including a small amount of **4c′**) in deuterium oxide (0.6 mL) in a NMR sample tube was heated at 50 °C for 1 h and checked by $^1$H NMR spectroscopy. No isomerization between **4c** and **4c′** was observed. Then, glyoxylic acid (0.1 equiv., 60 µL of a 0.1 mol/L solution in deuterated oxide) was added to the solution. The mixture was heated at 50 °C and monitored by $^1$H NMR spectroscopy intermittently. Gradual changes of the **4c**:**4c′** ratio was observed as shown in Tables 3 and 4 (see also Fig. 1). Epimerization between *syn*- and *anti*-**4c** was not observed during the reaction.

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