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# New unsaturated amino acids containing an allylsilane moiety on the lateral chain

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**Abstract**—New enantiomerically enriched polyfunctionalized allylsilanes have been obtained from the synthetic elaboration of naturally occurring serine. In particular, an oxazolidine bearing an allylsilane framework on the lateral chain proved to be a suitable precursor for the corresponding silylated vinyl glycine derivatives.


## 1. Introduction

Amino acids have received great interest in the chiral pool of naturally occurring compounds.[1] For several reasons, silylated ones are particularly attractive. They can be highly valuable optically active starting materials as the synthetic usefulness of amino acids is enhanced by the rich reactivity known for organosilanes.[2] In addition, trialkylsilyl chains are known to have hydrophobic properties, which might be relevant for biological activity while some silylated amino acids have recently been developed in order to exploit new opportunities of silicon chemistry for drug design.[3] For instance, β-trimethylsilylalanine has been successfully employed as a *bio-isostere* for phenylalanine in the search for stable renin inhibitors.[4] More recently, silaproline has been found to lend unique properties to neurotensin analogues.[5]

Some examples of silylated amino acids have been reported in the literature so far, such as β-silylamino acids,[6–8] *p*-substituted phenylananine,[9] silaproline,[10,11] and *a*-silyl amino acids, which have been prepared both in racemic[12,13] and in the enantiomerically enriched forms.[14,15]

Recently we have been able to prepare some enantiomerically enriched new silicon-containing amino acids starting from enantiomerically pure oxazolidine **1**, a compound we synthesized for the first time some years ago,[16–18] which can be obtained on multigram scales from naturally occurring serine.[19] Oxazolidine **1** has been exploited as a helpful and versatile non-racemic building block to be used in the design and synthesis of non-natural α-amino acids.[20] In particular, silylcupration of compound **1** afforded intermediate vinyloxazolidine **2**, which, after reduction of the double bond, removal of the acetonide protecting group and oxidation, led to silylated amino acids **3**, bearing different trialkylsilyl substituents at the γ-position of the lateral chain[21] (Scheme 1).

Remarkably, the presence of a reactive double bond did not affect the yield of oxidation while unsaturated amino acid **4** could be recovered in satisfactory yield. This disclosed trialkylsilyl groups as suitable substituents for obtaining vinylglycine derivatives.

In view of these results we considered that the synthesis of novel silylated amino acids such as **5**, bearing an allylsilyl moiety on the backbone (Scheme 2), could be also possible and of valuable synthetic interest, as allylsilanes have proven to be very versatile silicon-containing carbon

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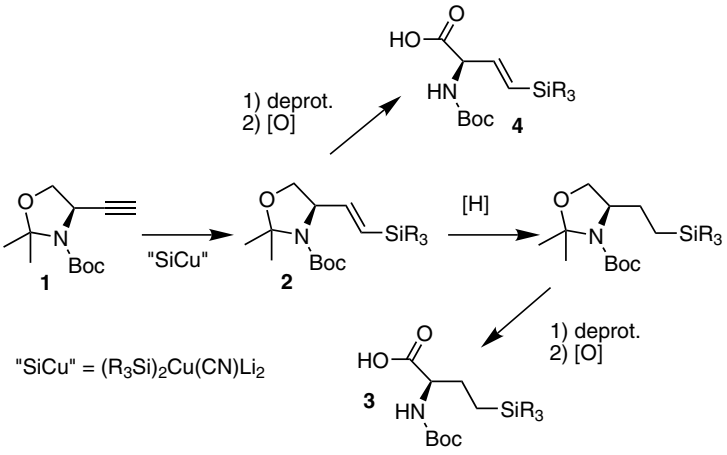
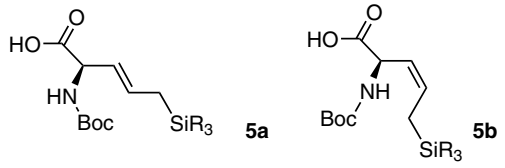



**Scheme 1.**




**Scheme 2.**

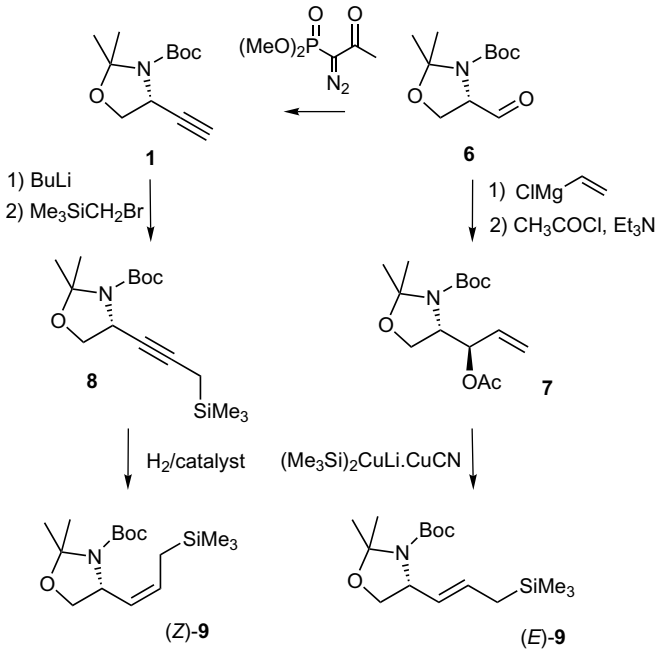
nucleophiles, often showing a high level of stereocontrol in reactions with electrophiles.[2,22]

The exploitation of these reagents in the synthesis of complex molecular structures is related to their availability as multifunctional enantiomerically enriched compounds. Although naturally occurring amino acids have been used, for instance, in the preparation of chiral amino silanes,[23] to the best of our knowledge, enantiomerically enriched allylsilanes bearing an amino acid moiety have not been reported so far. Herein we report a convenient and stereoselective synthesis of *Z*- and *E*-unsaturated silicon-containing amino acids **5a** and **5b** using commercially available L-serine as the starting material.

## 2. Results and discussion

Two different pathways have been considered for the synthesis of *E*-**5a** and *Z*-**5b** diastereoisomers. In both cases Garner's aldehyde **6**, prepared from naturally occurring L-serine via standard methods,[24] provided an attractive starting point.

Our approaches are described in Scheme 3. Vinyloxazolidines **9a** and **b** were focused as key intermediate. Silylcuprates displacement of an allylic acetate is a well-established procedure for allylsilane synthesis.[25] The reaction is *anti*-stereospecific and can be performed on acetate **7** to provide oxazolidine **9a** as a direct precursor of the desired *E*-amino acid **5a**. On the other hand *syn*-hydrogenation of alkyne **8**, which can in turn be obtained from compound **1** through metalation and reaction with a suitable electrophile, was envisaged as a simple way to obtain oxazolidine **9b** and thus the opposite *Z*-isomer **5b**.



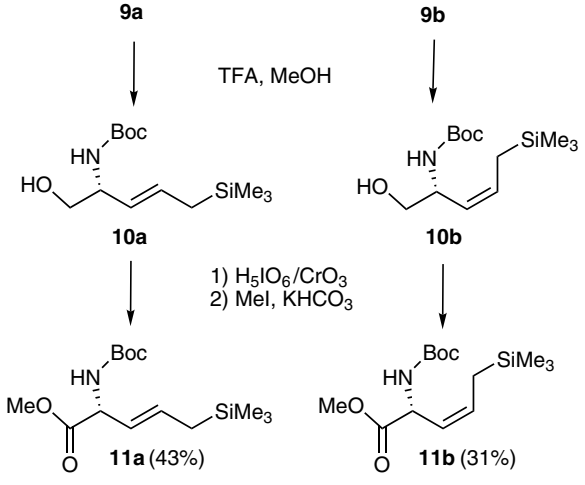

**Scheme 3.**

In agreement with what has already been reported,[26,27] the addition of vinyl magnesium chloride onto Garner aldehyde **6** and esterification with acetylchloride gave *anti*-**7** with a moderate selectivity (*syn*/*anti* = 1/2.5) and no racemization. As expected, trimethylsilylcyanocuprate reacted at low temperature with acetate **7** to afford, after hydrolytic work-up, allylsilanes **9** in a 95/5 mixture of *E*- and *Z*-isomers, as determined by $^1$H NMR analysis of the crude mixture. The desired isomer, **9a** was finally obtained in 84% yield after chromatography. The double bond *trans* geometry was easily confirmed from the 15.2 Hz coupling constant we observed for the vinyl protons, which could be clearly measured by performing the $^1$H NMR experiment

at 50 °C in order to obtain the averaged spectrum of the slowly interconverting rotamers.

Alkylation of lithiated ethynyloxazolidine **1** with (bromomethyl)trimethylsilane gave the corresponding propargylsilane **8** in 57% yield, after purification. Lower yield were obtained when (chloromethyl)- or (iodomethyl)-trimethylsilanes were used. Catalytic hydrogenation of the corresponding alkynylsilanes is a widely used procedure for the preparation of *Z*-substituted allylsilanes. Hydrogenation is normally run in the presence of a palladium catalyst such as the Lindlar catalyst,[28] or P-2 nickel (nickel boride).[29] Reduction of our substrate **8** needed harsh conditions, but we were finally able to quantitatively obtain the desired **9b** by performing the hydrogenation at 50 °C in the presence of Lindlar catalyst and quinoline and under 50 bar of $H_2$ pressure. Also in this case the double bond *cis* geometry was confirmed from the 10.8 Hz coupling constant we observed for the vinyl protons, in the $^1$H NMR experiment, at 50 °C.

Finally opening of the oxazolidine ring and oxidation were performed using standard conditions.[21] Treatment of each starting material with an excess of $CF_3COOH$ in MeOH at 0 °C gave essentially pure amino alcohols **10a** and **b**, which were used without further purification in the subsequent oxidative step. This was performed using periodic acid ($H_5IO_6$) as the stoichiometric oxidant together with a catalytic amount of $CrO_3$. Clean and high yielding oxidation occurred as shown in Scheme 4. For characterization purposes, crude protected amino acids were treated with excess MeI in the presence of $KHCO_3$ and the corresponding methyl esters **11a** and **b** were isolated in pure form after chromatography. Again we found that the presence of a reactive double bond in **10a** and **b** did not affect the yield of oxidation while the corresponding amino esters, bearing an allylsilyl moiety on the lateral chain were recovered in satisfactory overall yield.




**Scheme 4.**

Crude amino acids **11a** and **b** showed, however, sufficient purity for further uses. To confirm this, compound **11a** was coupled with L-leucine methyl ester using EDC/HOBT coupling conditions to produce dipeptide **12**, in 23% overall yield after purification (Scheme 5).

$^1$H and $^{13}$C NMR analysis of **12** indicated the absence (within limits of detection, i.e., 5%) of peaks due to epimerization at the α carbon of the silylated amino acid. This confirmed that during our synthetic sequence no racemization of the starting material occurred and showed that our silylated amino acid was not affected by coupling conditions usually associated with peptides synthesis.

## 3. Experimental

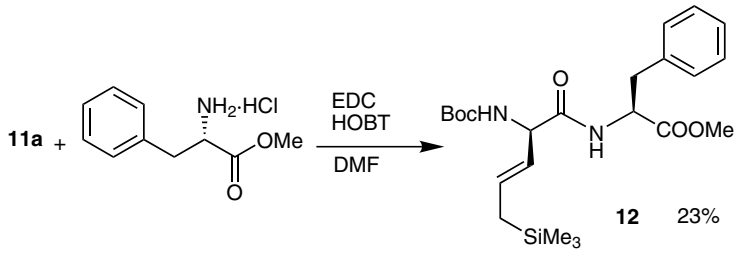
### 3.1. General methods and materials

All reactions were carried out under a positive pressure of dry nitrogen. Ether extracts were dried over $Na_2SO_4$. Reactions were monitored by TLC on $SiO_2$; detection was made using a $KMnO_4$ basic solution. Flash column chromatography[30] was performed using glass columns (10–50 mm wide) and $SiO_2$ 230–400 mesh. $^1$H NMR spectra were recorded at 200 or 400 MHz. $^{13}$C NMR spectra were recorded at 50.3 MHz. Chemical shifts were determined relative to the residual solvent peak ($CHCl_3$ $\delta$ 7.26 for $^1$H NMR; $CHCl_3$ $\delta$ 77.0 for $^{13}$C NMR). For those compounds, which are present as slowly interconverting rotamers, $^1$H NMR experiments were performed at 50 °C ($CDCl_3$) and the signals of the averaged spectrum reported when possible. Coupling constants (*J*) are reported in Hertz. When necessary, *J* values were obtained through selective decoupling. Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br s (broad singlet). Mass spectra were obtained at a 70 eV ionization potential and are reported in the form *m*/*z* (intensity relative to base = 100). Polarimetric measurements were performed in $CHCl_3$ solution at $\lambda = 589$ nm, while the temperature is specified case by case.

Starting materials **1** and **7** were prepared according to the literature.[18,26] THF was dried by distillation over sodium benzophenone ketyl. Petroleum ether, unless specified, is the 40–70 °C boiling fraction.

### 3.2. (4*R*)-2,2-Dimethyl-4-(*E*-3-trimethylsilanyl-propenyl)-oxazolidine-3-carboxylic acid *tert*-butyl ester 9a

Trimethylsilylcyanocuprate was prepared according to the general route,[21] using hexamethyldisilane (0.307 mL, 1.5 mmol), MeLi (1.6 M solution in THF, 0.46 mL, 0.74 mmol), and CuCN (33 mg, 0.37 mmol). Oxazolidine **7** (*syn*/*anti* = 1/2.5, 100 mg, 0.33 mmol) was dissolved in THF (0.6 mL) added at −23 °C and left at this temperature for 30 min. The reaction mixture was hydrolyzed with $NH_4Cl/NH_4OH$ buffer solution, extracted with $Et_2O$, then washed with brine, and dried over $Na_2SO_4$. After solvent evaporation and purification (petroleum ether/ethyl acetate = 10/1) 88 mg of **9a** were recovered as a colorless oil (yield: 84%). $^1$H NMR (400 MHz, 50 °C) $\delta$: 5.65–5.56 [m, 1H]; 5.32–5.26 [dd, $J_{trans} = 15.2$ Hz, $J = 7.6$ Hz, 1H]; 4.33–4.22 [m, 1H]; 4.01–3.97 [m, $J_{AB} = 8.8$ Hz, $J_{BX} = 6.0$ Hz, 1H]; 3.70–3.67 [m, $J_{AB} = 8.8$ Hz, $J_{AX} = 2.2$ Hz,




**Scheme 5.**

1H]; 1.58 [s, 3H]; 1.50 [s, 3H]; 1.49–1.45 [br m, 2H + 9H]; 0.01 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 152.0; 128.6; 126.1; 93.8; 79.9; 68.7; 59.3; 28.5; 27.7; 24.0; 22.6; −1.9. MS *m*/*e*: 257 (4); 57 (100); 73 (54). $[\alpha]_D^{26} = -22.0$ (*c* 1.31, $CHCl_3$). Anal. Calcd for $C_{16}H_{31}NO_3Si$: C, 61.30; H, 9.97; N, 4.47. Found: C, 61.42; H, 9.93; N, 4.51.

### 3.3. Synthesis of (4*R*)-2,2-dimethyl-4-(3-trimethylsilanyl-prop-1-ynyl)-oxazolidine-3-carboxylic acid *tert*-butyl ester 8

Oxazolidine **1** (175 mg, 1.0 mmol) was dissolved in THF (4 mL) and after cooling at −78 °C reacted with BuLi (1.6 M, 0.48 mL, 1 mmol). The mixture was stirred at −78 °C for 60 min, then after the temperature had risen to −23 °C, left to react for further 30 min. $Me_3SiCH_2Br$ (158 mg, 1.2 mmol) was then added, and after rising to room temperature, left to react for 18 h. The reaction mixture was hydrolized with water, extracted with $Et_2O$, then washed with brine, and dried over $Na_2SO_4$. After solvent evaporation and purification (petroleum ether/ethyl acetate = 7/1), 178 mg of **8** were recovered as a colorless oil (yield: 57%). $^1$H NMR (400 MHz, 50 °C) $\delta$: 4.58–4.42 [m, 1H]; 3.96–3.92 [m, $J_{AB} = 8.4$ Hz, $J_{AX} = 6.2$ Hz, 1H]; 3.87–3.84 [m, $J_{AB} = 8.4$ Hz, $J_{BX} = 1.2$ Hz, 1H]; 1.57 [br s, 6H]; 1.44–1.40 [br m, 9H + 2H]; 0.05 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 151.4; 93.9; 93.4; 79.8; 77.9; 69.5; 48.8; 28.3; 25.2; 24.2; 6.8; −2.2. MS *m*/*e*: 255 (3); 57 (100); 73 (34). $[\alpha]_D^{24} = -108.5$ (*c* 1.38, $CHCl_3$). Anal. Calcd for $C_{16}H_{29}NO_3Si$: C, 61.69; H, 9.38; N, 4.50. Found: C, 61.65; H, 9.59; N, 4.47.

### 3.4. (4*R*)-2,2-Dimethyl-4-[(*Z*)-3-trimethylsilanyl-prop-1-enyl]-oxazolidine-3-carboxylic acid *tert*-butyl ester 9b

Alkyne **8** (121 mg, 0.39 mmol) was dissolved in ethyl acetate (4 mL) together with the catalyst ($Pd/BaSO_4$, 4 mg, 10%) and 2–3 drops of quinoline. The solution was reacted under $H_2$ (50 atm) at 50 °C for 20 h then filtered over Celite and evaporated. Purification (petroleum ether/ethyl acetate = 20/1) afforded 109 mg **9b** as a colorless oil (yield: 90%). $^1$H NMR (400 MHz, 50 °C) $\delta$: 5.54–5.47 [m, 1H]; 5.36–5.30 [dd, $J_{cis} = 10.8$ Hz, $J = 9.9$ Hz, 1H]; 4.64–4.56 [m, 1H]; 4.07–4.02 [m, $J_{AB} = 8.4$ Hz, $J_{BX} = 6.4$ Hz, 1H]; 3.66–3.62 [m, $J_{AB} = 8.4$ Hz, $J_{AX} = 3.0$ Hz, 1H]; 1.59 [s, 3H]; 1.52 [s, 3H]; 1.49–1.45 [br m, 9H + 2H]; 0.01 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 151.9; 126.9 (2C), 97.4; 79.6; 68.9; 54.1; 28.5; 26.7; 24.5; 18.9; −1.7. MS *m*/*e*: 257 (6); 57 (100); 73 (53). $[\alpha]_D^{25} = -152.3$ (*c* 0.7, $CHCl_3$). Anal. Calcd for $C_{16}H_{31}NO_3Si$: C, 61.30; H, 9.97; N, 4.47. Found: C, 61.46; H, 10.01; N, 4.45.

### 3.5. Deprotection to amino alcohols

A solution of oxazolidine **9** in MeOH was cooled to 32 °C and then treated with an excess of $CF_3COOH$. After completion, volatile components were evaporated under reduced pressure and the residue was redissolved in ethyl acetate. The organic layer was washed with saturated $NaHCO_3$ aqueous solution and brine, then dried over $Na_2SO_4$ and evaporated to afford pure amino alcohols **10a**,**b**, which were oxidized without further purification.

**3.5.1. ((*E*)-(*R*)-1-Hydroxymethyl-4-trimethylsilanyl-but-2-enyl)-carbamic acid *tert*-butyl ester 10a.** Oxazolidine **9a** (168 mg, 0.54 mmol) was deprotected to afford crude **10a** (146 mg, quantitative). $^1$H NMR (200 MHz) $\delta$: 5.72–5.54 [m, 1H]; 5.21–5.10 [dd, $J_{trans} = 15.4$ Hz, $J = 6.6$ Hz, 1H]; 4.18–4.02 [m, 1H]; 3.70–3.45 [m, 2H]; 1.50–1.41 [br m, 9H + 2H]; −0.03 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 156.0; 129.9; 124.8; 79.6; 65.8; 54.9; 28.4; 22.9; −1.9.

**3.5.2. ((*Z*)-(*R*)-1-Hydroxymethyl-4-trimethylsilanyl-but-2-enyl)-carbamic acid *tert*-butyl ester 10b.** Oxazolidine **9b** (47 mg, 0.15 mmol) was deprotected to afford crude **10b** (40 mg, quantitative). $^1$H NMR (200 MHz) $\delta$: 5.71–5.55 [m, 1H]; 5.19–5.09 [dd, $J_{cis} = 10.6$ Hz, $J = 8.8$ Hz, 1H]; 4.60–4.48 [m, 1H]; 3.75–3.55 [m, 2H]; 1.57 [d, 2H, $J = 8.8$ Hz]; 1.45 [s, 9H]; −0.02 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 156.3; 132.6; 121.0; 79.9; 64.5; 50.7; 28.4; 19.6; −1.8.

### 3.6. Oxidation of amino alcohols

To a solution of amino alcohol in wet acetonitrile, cooled to 0 °C, were added $H_5IO_6$ (2.6 equiv) and $CrO_3$ (2%). After 30 min, the mixture was diluted with ethyl acetate and the organic layer washed with water, brine and dried over $Na_2SO_4$. After evaporation of the solvent, crude amino acid was redissolved in dry DMF, then $NaHCO_3$ (2 equiv) and MeI (2 equiv) were added at room temperature. The mixture was left to react for 18 h, then ethyl acetate was added and the organic layer washed with saturated $NH_4Cl$ aqueous solution, brine and dried over $Na_2SO_4$. Evaporation afforded crude amino ester, which was purified by flash chromatography.

**3.6.1. (2*R*)-2-*tert*-Butoxycarbonylamino-5-trimethylsilanyl-*E*-pent-3-enoic acid methyl ester 11a.** Amino alcohol **10a** (73 mg, 0.26 mmol) was oxidized to the corresponding amino acid (68 mg, 88% yield) and converted to amino ester.

Purification (*n*-pentane/ethyl acetate = 15/1) afforded **11a** (34 mg, 43% overall yield) as a colorless oil. : $^1$H NMR (400 MHz) $\delta$: 5.82–5.72 [m, 1H, $J_{trans} = 15.2$ Hz]; 5.27–5.21 [dd, 1H, $J_{trans} = 15.2$ Hz, $J = 7.2$ Hz]; 5.14–5.10 [m, 1H]; 3.73 [s, 3H]; 1.49 [d, 2H, $J = 9.6$ Hz]; 1.43 [s, 9H]; −0.01 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 172.1; 154.7; 132.3; 122.2; 79.8; 55.7; 52.3; 28.3; 23.0; −1.9. MS *m*/*e*: 245 (7); 213 (5); 186 (17); 142 (28); 112 (43); 73 (100); 57 (83). $[\alpha]_D^{24} = -125.4$ (*c* 0.69, $CHCl_3$). Anal. Calcd for $C_{14}H_{27}NO_4Si$: C, 55.78; H, 9.03; N, 4.65. Found: C, 55.87; H, 10.04, N, 4.63.

### 3.6.2. (2*R*)-2-*tert*-Butoxycarbonylamino-5-trimethylsilanyl-*Z*-pent-3-enoic acid methyl ester 11b.

Amino alcohol **10b** (47 mg, 0.15 mmol) was oxidized to the corresponding amino acid (41 mg, 95% yield) and converted to amino ester. Purification (*n*-pentane/ethyl acetate = 15/1) afforded **11b** (16 mg, 31% overall yield) as a colorless oil. $^1$H NMR (400 MHz) $\delta$: 5.76–5.69 [m, 1H, $J_{cis} = 10.4$ Hz]; 5.19–5.14 [dd, 1H, $J_{cis} = 10.4$ Hz, $J = 9.2$ Hz]; 5.02–4.91 [m, 1H]; 3.72 [s, 3H]; 1.51–1.43 [br m, 2H + 9H]; 0.03 [s, 9H]. $^{13}$C NMR (50.3 MHz) $\delta$: 172.6; 154.9; 133.4; 120.7; 79.2; 52.3; 51.1; 28.3; 19.5; −1.8. MS *m*/*e*: 245 (8); 242 (4); 228 (2); 186 (21); 142 (27); 112 (49); 73 (100); 57 (94). $[\alpha]_D^{24} = -81.2$ (*c* 0.52, $CHCl_3$). Anal. Calcd for $C_{14}H_{27}NO_4Si$: C, 55.78; H, 9.03; N, 4.65. Found: C, 55.90; H, 9.09; N, 4.72.

### 3.7. (2*S*,2′*R*)-2-(2′-*tert*-Butoxycarbonylamino-5-trimethylsilanyl-*E*-pent-3-enoylamino)-3-phenyl-propionic acid methyl ester 12

To a solution of crude amino acid derivative **11a** (81 mg, 0.28 mmol) in dry DMF (0.7 mL), L-phenylalanine methyl ester hydrochloride (61 mg, 0.28 mmol), and DIPEA (40 mg, 0.31 mmol) were added and then cooled to 0 °C. EDC (60 mg, 0.31 mmol) and HOBt (11 mg, 0.08 mmol) were added and the mixture was allowed to react at room temperature for 3 days, then the solvent was evaporated and the residue redissolved in ethyl acetate. The organic layer was washed with water, HCl 0.1 M, NaOH 0.1 M, brine and dried over $Na_2SO_4$. Purification (petroleum ether/ethyl acetate = 5/1) afforded 29 mg of **12** as a colorless oil (yield: 23%). $^1$H NMR (400 MHz) $\delta$: 7.31–7.06 [m, 5H]; 6.38–6.27 [m, 1H]; 5.81–5.70 [m, 1H]; 5.19–5.14 [dd, $J_{trans} = 15.0$ Hz, $J = 7.8$ Hz, 1H]; 4.88–4.81 [m, 1H]; 4.58–4.45 [m, 1H]; 3.70 [s, 3H]; 3.18–3.02 [m, 2H]; 1.51–1.39 [br m, 2H + 9H]; −0.01 [s, 9H]; $^{13}$C NMR (50.3 MHz) $\delta$: 171.5; 170.1; 154.8; 135.5; 133.1; 129.2; 128.4; 127.1; 123.6; 79.7; 57.0; 53.2; 52.3; 37.9; 28.3; 23.1; −1.9. MS *m*/*e*: 200 (3); 156 (2); 144 (3); 114 (3); 100 (11); 83 (4); 57 (100). $[\alpha]_D^{25} = -11.2$ (*c* 0.69, $CHCl_3$). Anal. Calcd for $C_{23}H_{36}N_2O_5Si$: C, 61.58; H, 8.09; N, 6.24. Found: C, 61.66; H, 8.12; N, 6.18.

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