A Platinum Open Access Journal for Organic Chemistry

Paper

Free to Authors and Readers | DOAJ Seal | *Arkivoc* **2025** (5) 202412349

The synthesis of α-vinyl-β-hydroxysilanes via chromium-catalyzed NHK reaction

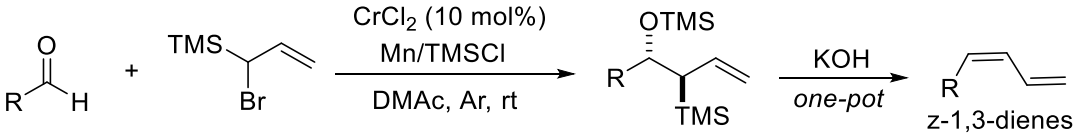
Jie Wang, Yang Luo, Xiaoqing Li,* and Xiangsheng Xu*

College of chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, P. R. China
Email: xqli@zjut.edu.cn future@zjut.edu.cn

Received 12-31-2024 **Accepted Manuscript** 03-15-2025 **Published on line** 03-22-2025

Abstract

α-Vinyl-β-hydroxysilanes are important organic compounds with broad applications in synthetic chemistry, especially in the construction of conjugated *Z*-diene-containing natural products and bioactive compounds. Conventional methods for their synthesis via Nozaki-Hiyama-Kishi Reaction (NHK reaction), often require a large excess of the toxic $CrCl_2$ reagent. Herein, we report the first chromium-catalyzed NHK reaction of 1-bromoallyltrimethylsilane with aldehydes for the synthesis of α-vinyl-β-hydroxysilanes. This reaction exhibits good substrate tolerance, enabling the use of various aldehydes, and thus provides a practical and relatively environmentally friendly method for the synthesis of α-vinyl-β-hydroxysilanes.

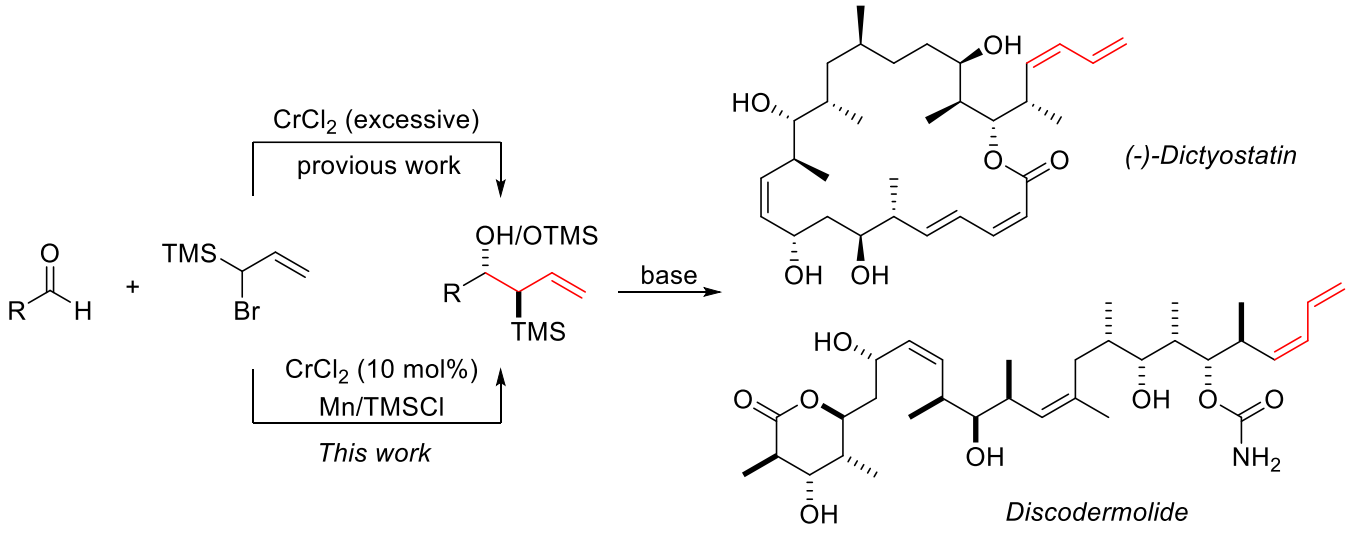


Keywords: Chromium catalysis; α-vinyl-β-hydroxysilanes; aldehyde; 1-bromoallyltrimethylsilan

Introduction

α-Vinyl-β-hydroxysilanes are a versatile class of organic compounds that have found broad applications in synthetic chemistry over time,[1-2] particularly for the construction of conjugated *Z*-diene containing natural products and bioactive compounds, such as (-)-dictyostatin and discodermolide via Peterson olefination.[3-8] Conventional methods to synthesize α-vinyl-β-hydroxysilanes are using a Nozaki-Hiyama-Kishi reaction (NHK reaction) of the *in situ* generated trimethylsilyl-substituted allyl-chromium reagents from 1-bromoallyltrimethylsilane to aldehydes.[3-9] However, a major drawback of this method lies in the utilization of a considerably excess of the toxic $CrCl_2$ reagent (generally 4-6 equivlents).

In 1996, Fürstner and co-workers[10-11] reported the first NHK reaction catalytic in chromium. The reaction is mediated by trimethylchlorosilane and, the active Cr^{2+} species is constantly recycled by means of the nontoxic, commercial manganese powder as the stoichiometric reductant.[12-14] Surprisingly, this chromium-catalyzed NHK reaction has not been applied to the synthesis of α-vinyl-β-hydroxysilanes. Herein, we present the first example of α-vinyl-β-hydroxysilanes synthesis using a chromium-catalzyed NHK reaction between 1-bromoallyltrimethylsilane and aldehydes.



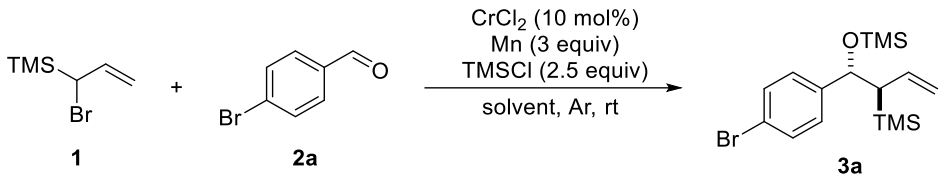
Scheme 1. The application and synthesis of α-vinyl-β-hydroxysilanes.

Results and Discussion

To assess the feasibility of the chromium-catalzyed NHK reaction of 1-bromoallyltrimethylsilane (3 equiv), 4-bromobenzaldehyde (**2a**) (1 equiv) was chosen as the model substrate using 10 mol % of $CrCl_2$ in the presence of 3 equiv. of Mn and 2.5 equiv. of TMSCl (Table 1). Firstly, it was observed that commonly utilized solvents like DME, DCE, and 1,4-dioxane exhibited minimal to no efficacy in facilitating the transformation. Intriguingly, the use of solvents such as DMAc, EtOAc, DMF, and MeCN led to relatively high yields. Notably, when DMAc was employed as the solvent, the yield 73% in **3a** was obtained . However, when the amount of the Cr-catalyst was reduced to 5.0 mol %, the yield dropped to 43%. Additionally, the quantity of (1-bromoallyl)trimethylsilane had a significant impact on the reaction outcome as the use of 1.5 equiv of **1a** instead of 3 equiv induced a decrease in the yield of **3a**. Different from the $CrCl_2$-mediated NHK reaction of 1-

bromoallyltrimethylsilane which led to α-vinyl-β-hydroxysilanes,[9] this $CrCl_2$-catalyzed reaction produced silyl ethers. But both the non-catalytic and catalytic reactions gave only the *anti*-products as they are coming from the same intermediate.

Table 1. Optimization of reaction conditions

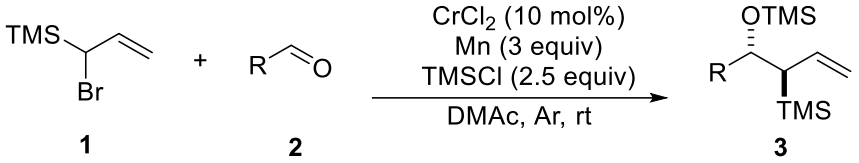


Entry	Variation from "standard conditions"	Yield (%)
1	None	73
2	EtOAc , instead of DMAc	61
3	DMF, instead of DMAc	59
4	MeCN, instead of DMAc	69
5	DME, instead of DMAc	0
6	DCE, instead of DMAc	0
7	1,4-dioxane, instead of DMAc	0
8	5.0 mol% $CrCl_2$	43
9	1.5 equiv., instead of 3.0 equiv. **1**	60

[a]Reaction conditions: **1** (0.60 mmol, 3 equiv), **2a** (0.20 mmol, 1 equiv), chromium catalyst (0.02 mmol, 10 mol%), Mn (0.60 mmol, 3 equiv) and TMSCl (0.48 mmol, 2.4 equiv) in DMAc (2.0 mL) at room temperature for 9 h, under argon. [b]Isolated yields.

With the optimal condition in hand, we next evaluated the substrate scope of aldehydes (Table 2). Changing the 4-bromobenzaldehyde to other halogenated benzaldehyde (**2b** and **2c**), the yields were slightly decreased (**3b** and **3c**). It is noteworthy that benzaldehyde bearing an ester group (**2d**) was well tolerated and afforded product **3d** in 48% yield. 2-Naphthaldehyde (**2e**) was also a suitable substrate, affording product **3e** in 57% yield. Moreover, this transformation could also proceed efficiently with aliphatic aldehyde as **2f** was isolated in 56% yield. Importantly, aldehydes with Cbz protected amine (**2g**), especially aldehydes derived from amino acids (**2h** and **2i**) were also well tolerated, providing the desired α-vinyl-β-hydroxysilanes (**3g-i**) in moderate to good yields. Finally, this transformation can be applied to late-stage functionalization of drug molecules. For example, aldehyde **2j** derived from indobufen could be transformed to the corresponding α-vinyl-β-hydroxysilane **3j** in 86 yield.

Table 2. Substrate Scope of Aldehydes



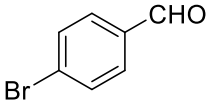
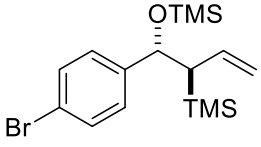
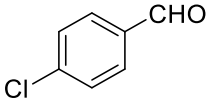
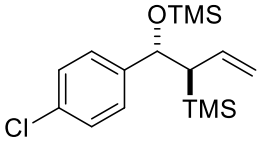
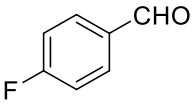
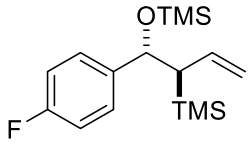
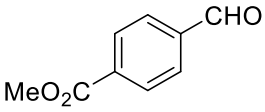
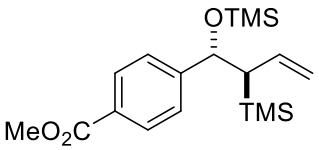
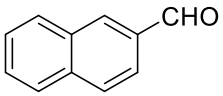
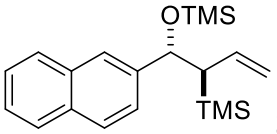
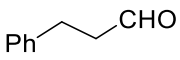
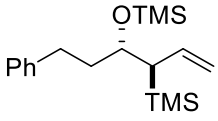
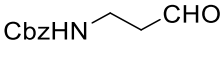
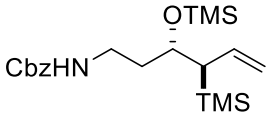
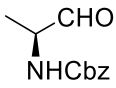
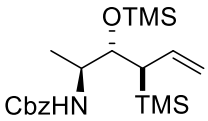
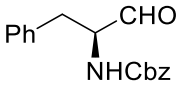
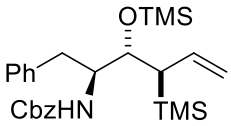
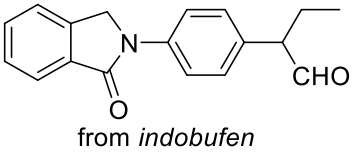
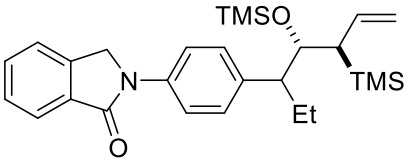
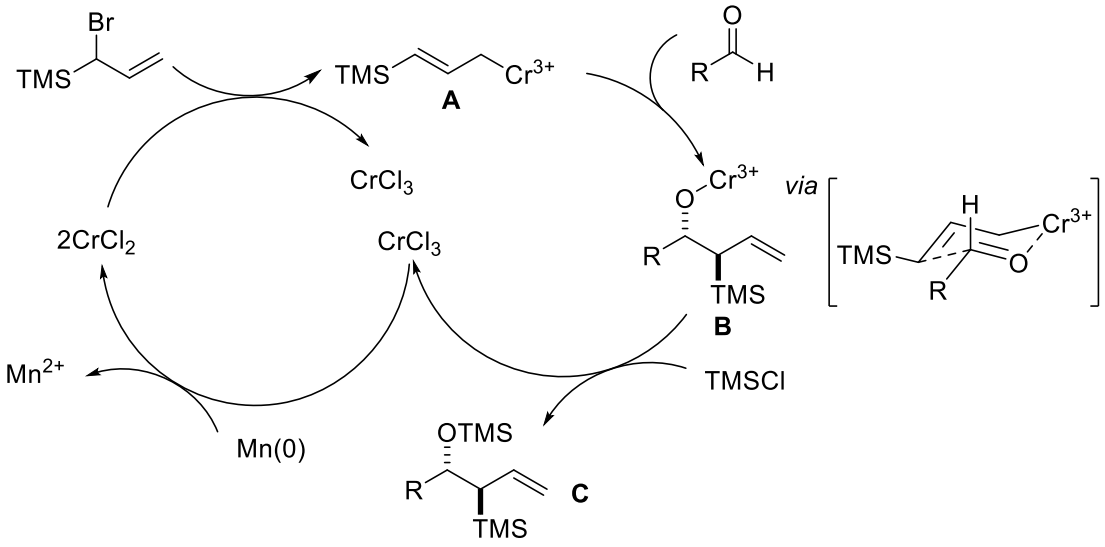
entry	Aldehyde	Product	Yield%; dr
1	 **2a**	 **3a**	**73**
2	 **2b**	 **3b**	**64**
3	 **2c**	 **3c**	**45**
4	 **2d**	 **3d**	**48**
5	 **2e**	 **3e**	**57**
6	 **2f**	 **3f**	**56**
7	 **2g**	 **3g**	**68**
8	 **2h**	 **3h**	**62** dr: 1:1
9	 **2i**	 **3i**	**80** dr: 3:2

Table 2. Continued

entry	Aldehyde	Product	Yield%; dr
10	 from *indobufen* **2j**	 **3j**	**86** dr: 3:1

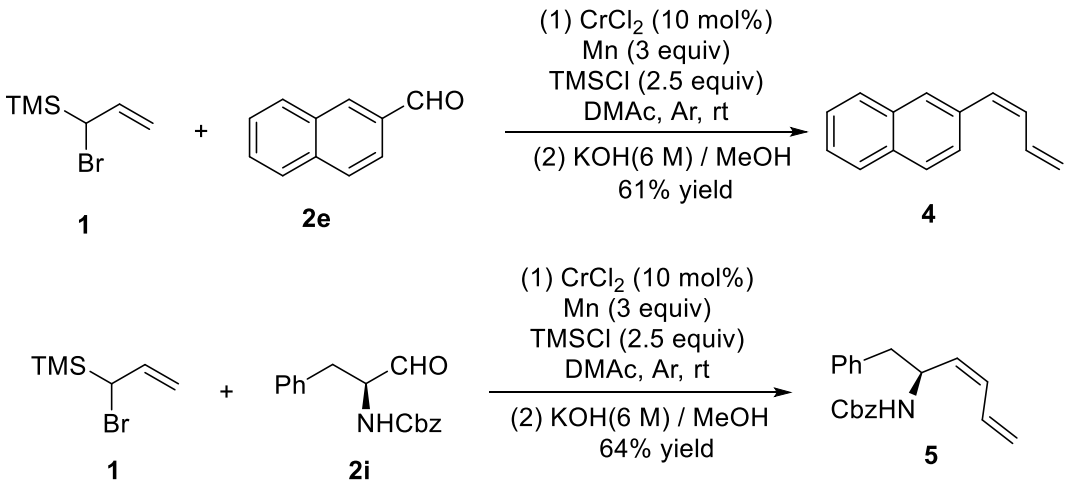
[a]Reaction conditions: **1** (0.60 mmol, 3 equiv), **2a** (0.20 mmol, 1 equiv), $CrCl_2$ (10 mol%), Mn (0.60 mmol, 3 equiv) and TMSCl (0.48 mmol, 2.4 equiv) in DMAc (2.0 mL) at room temperature for 9 h, under argon. [b]Isolated yields.

On the basis of previous related reports[10-11] and our experimental results presented above, a plausible reaction pathway is illustrated as shown in Scheme 2. The reaction of $CrCl_2$ with 1-bromoallyltrimethylsilane (**1**) giving rise to organochromium species A and CrX_3. Then, the intermediate **A** adds to the aldehydes (**2**) via Zimmerman-Traxler six-membered ring transition state[15] to form the chromium alkoxide **B**. Ligand exchanging between **B** and TMSCl releases the product and generates Cr^{3+}. Finally, reduction of Cr^{3+} by Mn(0) regenerated Cr^{2+}.



Scheme 2. Proposed mechanism.

In order to demonstrate the practicality of this simple protocol, the one-pot NHK reaction/basic elimination was conducted. The reaction of **2e** and **2i** with **1** under the standard conditions followed by treatment with KOH (6 M) in MeOH resulted in the conjugated *Z*-1,3-dienes **4** and **5** as single isomers in moderate yields.



Scheme 3. The synthesis of Z-dienes via one-pot chromium-catalyzed NHK reaction/basic elimination.

Conclusions

In conclusion, the chromium-catalyzed reaction of 1-bromoallyltrimethylsilane with aldehydes was successfully achieved, leading to the efficient synthesis of α-vinyl-β-hydroxysilanes. The substrate scope of aldehydes was evaluated and it was found that various aldehydes, including halogenated benzaldehydes, methyl 4-formylbenzoate, 2-naphthaldehyde, aliphatic aldehyde, and aldehydes with protected amino groups, could be well tolerated, providing the desired products in moderate to good yields. Importantly, this transformation could be applied to the late-stage functionalization of drug molecules and to the one-pot synthesis of conjugated Z-dienes.

Experimental Section

General. Unless stated otherwise, all reactions were carried out under an argon atmosphere. All commercial reagents were used without additional purification. Flash chromatography was carried out with silica gel (300-400 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded with 400 MHz and 101 MHz spectrometers in $CDCl_3$ by using tetramethylsilane (TMS) as the internal standard, respectively.

Experimental procedures and characterization of products. To a dried reaction tube was added **2** (0.20 mmol, 1 equiv), $CrCl_2$ (10 mol %), Mn (0.60 mmol, 3 equiv). The tube was evacuated and backfilled with argon (three times). Then, anhydrous DMAc (2.0 mL), 1-trimethylsilylallyl bromide **1** (0.60 mmol, 3 equiv) and TMSCl (0.48 mmol, 2.4 equiv) was injected into the tube by syringe. The solution was kept at room temperature for 9 h. At the end of the reaction, water was added and the reaction mixure was extracted with ethyl acetate for three times, and the organic phase was combined. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by column chromatography on silica gel to give the products **3a-3j**.

((1*S*,2*R*)-1-(4-Bromophenyl)-1-((trimethylsilyl)oxy)but-3-en-2-yl)trimethylsilane (3a). Colorless liquid (73%), R_f=0.6 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.62 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 6.14 (dt, *J*

= 17.2, 10.4 Hz, 1H), 5.14 – 5.08 (m, 2H), 4.86 (dd, *J* = 17.2, 2.2 Hz, 1H), 1.96 (dd, *J* = 10.5, 4.0 Hz, 1H), 0.22 (s, 9H), 0.21 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 146.69, 137.78, 133.10, 130.55, 122.78, 116.70, 77.52, 48.66, 2.77, 0.00. HRMS (ESI) *m/z* calcd for $C_{16}H_{27}BrOSi_2Na^+$ $(M+Na)^+$ 393.0676; found 393.0676.

((1*S*,2*R*)-1-(4-Chlorophenyl)-1-((trimethylsilyl)oxy)but-3-en-2-yl)trimethylsilane (3b). Colorless liquid (64%), R_f= 0.6 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.28 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 5.97 (dt, *J* = 17.2, 10.4 Hz, 1H), 4.99 – 4.90 (m, 2H), 4.68 (dd, *J* = 17.2, 2.2 Hz, 1H), 1.79 (dd, *J* = 10.5, 4.0 Hz, 1H), 0.04 (s, 9H), 0.03 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 143.84, 135.52, 132.32, 127.84, 114.32, 75.15, 46.37, 0.42, -2.34. HRMS (ESI) *m/z* calcd for $C_{16}H_{27}ClOSi_2Na^+$ $(M+Na)^+$ 349.1181; found 349.1182.

((1*S*,2*R*)-1-(4-Fluorophenyl)-1-((trimethylsilyl)oxy)but-3-en-2-yl)trimethylsilane (3c). Colorless liquid (45%), R_f= 0.6 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.43 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.19 (t, *J* = 8.7 Hz, 2H), 6.17 (dt, *J* = 17.3, 10.4 Hz, 1H), 5.18 – 5.11 (m, 2H), 4.91 (dd, *J* = 17.2, 2.2 Hz, 1H), 2.02 (dd, *J* = 10.4, 4.4 Hz, 1H), 0.22 (s, 9H), 0.21 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 161.81(d, J_{C-F} = 245.4 Hz), 141.07(d, J_{C-F} = 3.03 Hz), 135.88, 128.05(d, J_{C-F} = 8.08 Hz), 114.51(d, J_{C-F} = 21.21 Hz), 114.21, 75.22, 46.52, 0.39, -2.32. HRMS (ESI) *m/z* calcd for $C_{16}H_{27}FOSi_2Na^+$ $(M+Na)^+$ 333.1477; found 333.1478.

Methyl 4-((1*S*,2*R*)-2-(trimethylsilyl)-1-((trimethylsilyl)oxy)but-3-en-1-yl)benzoate (3d). Colorless liquid (48%), R_f= 0.6 (petroleum ether/ethyl acetate 20:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 5.97 (dt, *J* = 17.2, 10.4 Hz, 1H), 5.04 (d, *J* = 3.8 Hz, 1H), 4.90 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.65 (dd, *J* = 17.2, 2.2 Hz, 1H), 3.94 (s, 3H), 1.81 (dd, *J* = 10.5, 3.9 Hz, 1H), 0.04 (s, 9H), 0.03 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.11, 150.61, 135.28, 129.15, 128.67, 126.44, 114.43, 75.44, 51.97, 46.26, 0.43, -2.32. HRMS (ESI) *m/z* calcd for $C_{18}H_{30}O_3Si_2Na^+$ $(M+Na)^+$ 373.1626; found 373.1629.

Trimethyl((1*S*,2*R*)-1-(naphthalen-2-yl)-1-((trimethylsilyl)oxy)but-3-en-2-yl)silane (3e). Colorless liquid (57%), R_f= 0.5 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.94 (dd, *J* = 16.9, 8.1 Hz, 3H), 7.80 (s, 1H), 7.63 – 7.54 (m, 3H), 6.18 (dt, *J* = 17.1, 10.3 Hz, 1H), 5.27 (d, *J* = 4.3 Hz, 1H), 5.02 (dd, *J* = 10.3, 2.1 Hz, 1H), 4.80 (dd, *J* = 17.2, 2.1 Hz, 1H), 2.08 (dd, *J* = 10.4, 4.3 Hz, 1H), 0.15 (s, 9H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.95, 135.99, 133.11, 132.81, 127.90, 127.73, 127.36, 125.80, 125.42, 125.40, 124.81, 114.07, 76.02, 46.43, 0.54, -2.22. HRMS (ESI) *m/z* calcd for $C_{20}H_{30}OSi_2Na^+$ $(M+Na)^+$ 365.1727; found 365.1728.

Trimethyl((3R**,4**S**)-6-phenyl-4-((trimethylsilyl)oxy)hex-1-en-3-yl)silane (3f).** Colorless liquid (56%),R_f= 0.6 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 (t, *J* = 7.6 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 3H), 5.98 (dt, *J* = 17.2, 10.4 Hz, 1H), 5.10 (dd, *J* = 10.3, 2.3 Hz, 1H), 4.99 (dd, *J* = 17.2, 2.3 Hz, 1H), 4.04 – 3.97 (m, 1H), 2.72 – 2.50 (m, 2H), 2.04 – 1.94 (m, 1H), 1.92 – 1.80 (m, 2H), 0.19 (s, 9H), 0.11 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.33, 136.26, 128.39, 128.35, 125.78, 113.92, 72.91, 41.26, 38.64, 32.09, 1.00, -2.00. HRMS (ESI) *m/z* calcd for $C_{18}H_{32}OSi_2Na^+$ $(M+Na)^+$ 343.1884; found 343.1884.

Benzyl ((3*S*,4*R*)-4-(trimethylsilyl)-3-((trimethylsilyl)oxy)hex-5-en-1-yl)carbamate (3g). Colorless liquid (68%), R_f=0.5 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.51 – 7.41 (m, 5H), 5.95 (dt, *J* = 17.3, 10.4 Hz, 1H), 5.23 (s, 2H), 5.15 – 4.90 (m, 3H), 4.09 (s, 1H), 3.30 (q, *J* = 6.8 Hz, 2H), 2.03 – 1.74 (m, 3H), 0.25 (s, 9H), 0.15 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ 156.32, 136.72, 136.21, 128.51, 128.07, 114.27, 71.72, 66.55, 41.83, 38.10, 36.56, 0.83, -1.93. HRMS (ESI) *m/z* calcd for $C_{20}H_{35}NO_3Si_2Na^+$ $(M+Na)^+$ 416.2048; found 416.2044.

Benzyl ((2*S*,3*S*,4*R*)-4-(trimethylsilyl)-3-((trimethylsilyl)oxy)hex-5-en-2-yl)carbamate (3h). Colorless liquid (62%),R_f= 0.6 (heptane). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.53 – 7.40 (m, 5H), 5.86 (dt, *J* = 17.1, 10.5 Hz, 1H), 5.29 – 5.16 (m, 2H), 5.10 (dd, *J* = 10.2, 2.1 Hz, 1H), 5.06 – 4.82 (m, 2H), 4.05 – 3.94 (m, 1H), 3.90 (ddd, *J* = 8.9, 6.6, 2.3 Hz, 1H), 2.05 – 1.87 (m, 1H), 1.25 (dd, *J* = 28.7, 6.7 Hz, 3H), 0.27 (s, 4H), 0.23 (s, 5H), 0.20 (s, 4H), 0.15 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.88, 155.68, 137.81, 137.32, 136.81, 136.71, 128.52, 128.47, 128.21, 128.10, 128.06, 128.00, 114.12, 113.53, 75.67, 74.77, 66.57, 66.39, 52.38, 51.16, 40.79, 39.77, 19.13, 15.62, 0.97, 0.79, -1.96, -2.09. HRMS (ESI) *m/z* calcd for $C_{20}H_{35}NO_3Si_2Na^+$ $(M+Na)^+$ 416.2048; found 416.2044.

Benzyl ((2*S*,3S,4R)-1-phenyl-4-(trimethylsilyl)-3-((trimethylsilyl)oxy)hex-5-en-2-yl)carbamate (3i). Colorless liquid (80%), R_f= 0.5 (petroleum ether/ethyl acetate 20:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.79 – 7.50 (m, 10H), 6.08 (dt, *J* = 17.0, 10.5 Hz, 1H), 5.62 (d, *J* = 8.9 Hz, 1H), 5.47 (s, 2H), 5.44 – 5.13 (m, 2H), 4.43 – 4.26 (m, 2H), 3.35 – 3.24 (m, 1H), 3.18 (dt, *J* = 14.5, 7.5 Hz, 1H), 2.31 (dd, *J* = 10.9, 7.1 Hz, 1H), 0.61 (s, 5H), 0.48 (s, 4H), 0.43 (s, 4H), 0.34 (s, 5H). ^{13}C NMR (101 MHz, Chloroform-d) δ 155.98, 138.50, 137.27, 129.36, 128.99, 128.55, 128.47, 128.45, 128.20, 128.12, 127.92, 126.46, 126.44, 114.06, 72.94, 72.56, 66.57, 66.34, 58.63, 57.19, 41.00, 38.98, 38.93, 37.15, 1.33, 0.74, -1.96, -2.25. HRMS (ESI) *m/z* calcd for $C_{26}H_{39}NO_3Si_2Na^+$ $(M+Na)^+$ 492.2361; found 492.2365.

2-(4-((4*S*,5*R*)-5-(Trimethylsilyl)-4-((trimethylsilyl)oxy)hept-6-en-3-yl)phenyl)isoindolin-1-one (3j). Colorless liquid (86%) , R_f= 0.3 (petroleum ether/ethyl acetate 20:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.94 (d, *J* = 8.5 Hz, 2H), 7.73 – 7.66 (m, 1H), 7.65 – 7.56 (m, 2H), 7.40 (d, *J* = 8.6 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 2H), 5.93 (dt, *J* = 17.2, 10.4 Hz, 1H), 5.05 (ddd, *J* = 16.3, 10.2, 2.3 Hz, 1H), 4.96 (s, 2H), 4.87 (ddd, *J* = 28.6, 17.3, 2.3 Hz, 1H), 4.26 – 4.14 (m, 1H), 2.92 – 2.70 (m, 1H), 1.86 (ddd, *J* = 25.2, 10.5, 3.4 Hz, 1H), 1.04 – 0.97 (m, 2H), 0.84 (q, *J* = 7.3, 6.4 Hz, 3H), 0.26 (s, 2H), 0.23 (s, 7H), 0.13 (s, 7H), 0.07 (s, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 167.31, 139.98, 139.33, 137.56, 136.77, 133.27, 131.85, 129.79, 129.30, 128.22, 123.91, 122.46, 119.02, 118.89, 113.97, 77.78, 53.13, 50.62, 40.96, 23.60, 12.06, 1.51, 0.84, -1.98, -2.42. HRMS (ESI) *m/z* calcd for $C_{27}H_{39}NO_2Si_2Na^+$ $(M+Na)^+$ 488.2412; found 488.2413.

(*Z*)-2-(Buta-1,3-dien-1-yl)naphthalene (4).[16] Colorless liquid(61%), R_f= 0.6 (petroleum ether/ethyl acetate 50:1). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.86 – 7.71 (m, 4H), 7.52 – 7.36 (m, 3H), 7.05 – 6.90 (m, 1H), 6.59 (d, *J* = 11.5 Hz, 1H), 6.34 (t, *J* = 11.4 Hz, 1H), 5.42 (dd, *J* = 16.9, 1.9 Hz, 1H), 5.26 (d, *J* = 10.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 134.96, 133.34, 132.47, 131.18, 130.47, 128.03, 127.95, 127.78, 127.66, 127.21, 126.24, 125.99, 123.51, 119.96.

Benzyl (*S,Z*)-(1-phenylhexa-3,5-dien-2-yl)carbamate (5). White solid(64%), mp: 85-87 °C, R_f= 0.3 (petroleum ether/ethyl acetate 20:1) ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.38 – 7.13 (m, 10H), 6.55 (dt, *J* = 16.9, 10.5 Hz, 1H), 5.97 (d, *J* = 11.0 Hz, 1H), 5.37 (t, *J* = 10.1 Hz, 1H), 5.23 – 5.03 (m, 2H), 5.02 – 4.90 (m, 2H), 4.62 (p, *J* = 8.1 Hz, 1H), 2.84 (dd, *J* = 13.4, 7.8 Hz, 1H), 2.66 (dd, *J* = 13.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.71, 138.51, 137.67, 132.87, 132.45, 130.01, 129.76, 128.77, 128.55, 128.16, 128.03, 126.58, 119.36, 65.53, 50.26, 41.43. HRMS (ESI) *m/z* calcd for $C_{20}H_{21}NO_2Na^+$ $(M+Na)^+$ 330.1465; found 330.1467.

Acknowledgements

X. L. Thanks the Hangzhou Zhongmeihuadong Pharmaceutical Co., (KYY-HX-20220125) for financial support.

Supplementary Material

Supplemental material for this article is available online.

References

1. Pursera, S.; Wilsona C.; Mooreb P. R.; Gouverneur, V. *Synlett*. **2007**, 1166-1168.

https://doi.org/10.1055/s-2007-977428.
2. Han, S. B.; Gao, X.; Krische, M. J. *J. Am. Chem. Soc.* **2010**, 132, 26, 9153-9156. https://doi.org/10.1021/ja103299f
3. Smith, A.; Xian, M.; Liu F. H. *Org. Lett.* **2005**, 7, 4613-4616. https://doi.org/10.1021/ol051691c
4. Paterson, I.; Delgado, O.; Florence, G.; Lyothier, I.; O'Brien, M.; Scott, J.; Sereinig, N. *J. Org. Chem.* **2005**, 70, 150-160. https://doi.org/10.1021/jo048534w
5. Ramachandran P.; Srivastava, A.; Hazra D. *Org. Lett.* **2007**, 9, 157-160. https://doi.org/10.1021/ol062737k
6. Zanato, C.; Pignataro, L.; Ambrosi, A.; Hao, Z.; Trigili, C.; Díaz, J.; Barasoain, I.; Gennari, C. *Eur. J. Org. Chem.* **2011**, 2643-2661. https://doi.org/10.1002/ejoc.201100244
7. Shin, Y.; Fournier, J.-H.; Fukui, Y.; Brückner, A.M.; Curran, D.P. *Angew. Chem. Int. Ed.* **2004**, 43, 4634-4637. https://doi.org/10.1002/anie.200460593.
8. Prantz, K.; Mulzer, J. *Chem. Eur. J.* **2010**, 16, 485-506. https://doi.org/10.1002/chem.200901567
9. Hodgson, D. M.; Wells C. *Tetrahedron Lett.* **1992**, 33, 4761-4762. https://doi.org/10.1016/S0040-4039(00)61279-0
10. Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, 118, 2533-2534. https://doi.org/10.1021/ja9537538
11. Fürstner, A.; Shi, N. *J. Am. Chem. Soc.* **1996**, 118, 12349-12357. https://doi.org/10.1021/ja9625236
12. Inoue, M.; Suzuki, T.; Nakada, M. *J. Am. Chem. Soc*. **2003**, 125, 1140-1141. https://doi.org/10.1021/ja021243p
13. Berkessel, A.; Menche, D.; Sklorz, C. A.; Schröder, M.; Paterson, I. *Angew. Chem. Int. Ed.* **2003**, 42, 1032-1035. https://doi.org/10.1002/anie.200390265
14. Miller, J. J.; Sigman, M. S. *J. Am. Chem. Soc.* **2007**, 129, 2752-2753. https://doi.org/10.1021/ja068915m
15. Takai, K. *Org. React.* **2004**, 253-612. https://doi.org/10.1002/0471264180.or064.03
16. Wang, J. S.; Na, Y.; Ying, J.; Wu, X. F. *Org. Chem. Front.* **2021**, 8, 2429-2433. https://doi.org/10.1039/D1QO00290B