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Note

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Rhodium-Catalyzed Highly Regio- and Stereoselective Intermolecular Hydrosilylation of Internal Ynamides under Mild Conditions

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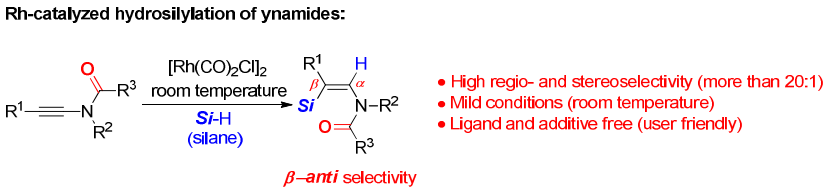
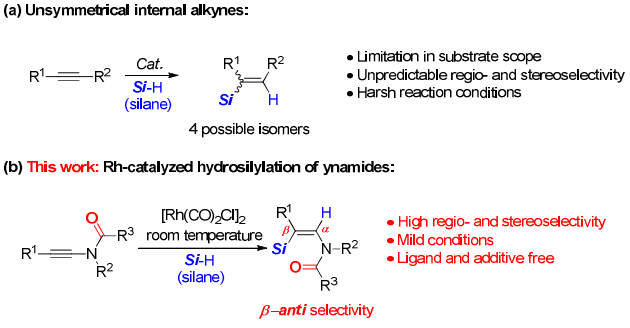
Supporting Information Placeholder



ABSTRACT: A rhodium-catalyzed highly regio- and stereoselective intermolecular hydrosilylation of internal ynamides has been developed. With the neutral rhodium complex $[Rh(CO)_2Cl]_2$ as catalyst and the bulky silanes as reactants, various ynamides underwent hydrosilylation smoothly at room temperature with excellent β regioselectivity and *anti* stereoselectivity. The synthetically versatile β-silyl (*Z*)-enamide products could be further transformed to diverse useful building blocks. Several possible mechanisms are proposed to rationalize this unique formal *trans*-addition-type selectivity.

Silyl-substituted organic molecules are widely applied in organic synthesis, materials and polymer science due to their non-toxicity, stability, easy accessibility and diverse transformations.[1] Therefore, various metal-catalyzed hydrosilylation of unsaturated functional groups, such as alkenes, alkynes, carbonyls, imines, epoxides and so on, have been developed in recent years.[2] Among these transformations, alkyne hydrosilylation could provide the vinylsilanes by the most straightforward and atom-economic strategy.[3] Vinylsilanes, as valuable synthetic precursors, are frequently used to participate in different cross-coupling reactions, Tamao-Fleming oxidations, electrophilic substitutions and group transfer polymerizations,[4] which furthermore highlight the notable significance of alkyne hydrosilylation. However, there still exist tremendous challenges for alkyne hydrosilylation. First, the substrate scopes are limited to the terminal alkynes and symmetrical alkynes.[2,5] If unsymmetrical internal alkynes are used as substrates, the regio- and stereoselectivity for alkyne hydrosilylation would drop dramatically. Second, most previous studies focused on the normal and electron-poor internal alkynes.[6] Only a few electron-rich internal alkyne hydrosilylations were reported under harsh conditions.[7] In addition, how to control the regio- and stereoselectivity for alkyne hydrosilylation is still the critical issue. Four possible isomers could be acquired from alkyne hydrosilylation (Scheme 1a). Limited protocols are used to obtain a single product with high regio- and stereoselectivity. Highly polarized or electron-deficient alkynes may give certain initial selectivities,[6] which could be further improved by internal directing group approach or intramolecular hydrosilylation.[8] But these substrates are complicated and usually hard to access. It is important to develop a general and novel control strategy to achieve high regio- and stereoselectivities. Third, recent examples on intermolecular hydrosilylation of internal alkynes mainly based on the catalysts like ruthenium,[5d,6d,7c,8a,8b] platinum,[5e,6c,8c,8e] iridium,[5c,7b] cobalt,[7d,7e,8d] manganese[5a] and other metals or metalloids,[7a] which generally require heating, ligands or additives. Consequently, it is quite urgent and meaningful to develop the new alkyne hydrosilylation which could occur smoothly under mild conditions without sophisticated promoting regents.

Scheme 1. Design of Intermolecular Hydrosilylation of Unsymmetrical Internal Alkyne

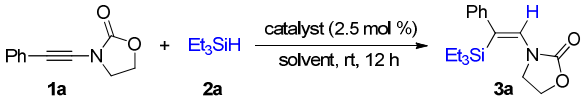


Despite the rhodium also a good catalyst in other silylation reaction,[9] the rhodium-catalyzed intermolecular regio- and stereoselective hydrosilylation of electron-rich internal alkynes

remains limitedly known today. Owing to our combined interest in the ynamides chemistry[10] and rhodium-catalyzed reactions,[11] we herein report the Rh(I)-catalyzed intermolecular hydrosilylation of internal ynamides (Scheme 1b). Remarkably, the hydrosilylation of internal ynamides could undergo efficiently in room temperature with high regio- and stereoselectivities to afford *β*-silyl (*Z*)-enamide products. Based on the mechanism studies, the chelation between carbonyl oxygen of ynamides and Rh catalyst may play the crucial control role. Several possible mechanisms are proposed to rationalize this unique formal *trans*-addition-type selectivity.

In order to achieve the hydrosilylation reaction for electron-rich internal alkynes, ynamide **1a** as the representative substrate and triethylsilane (**2a**) were chosen as model substrates to optimize the reaction parameters.[12] Rh(I) was first employed to catalyze this hydrosilylation (Table 1, entries 1-3). Only neutral catalyst $[Rh(CO)_2Cl]_2$ worked efficiently at room temperature to afford desired *β*-silyl (*Z*)-enamide **3a** with good regio- and stereoselectivity.[13] The cationic catalyst $[Rh(COD)_2]BF_4$ failed to mediate the reaction well. Another neutral catalyst $[Rh(COD)Cl]_2$ resulted in the decomposition of ynamide. Ir(I) as catalyst provided the hydrogenation product exclusively in good yield and stereoselectivity (Table 1, entry 4). Neutral [Cp*Ru(cod)Cl] could not give any desired hydrosilylation product, and the cationic $[Cp^*Ru(MeCN)_3]PF_6$ gave the lower regio- and stereoselectivity (Table 1, entries 5 and 6). Chloroplatinic acid or platinichloride were demonstrated to be ineffective for this transformation (Table 1, entries 7 and 8). It is noteworthy that previously well-defined Ir, Ru catalysts demonstrated to be either less selective or inactive at room temperature for ynamide hydrosilylation, which features this complementary approach for rhodium-catalyzed system. Other solvents could maintain the good regioselectivity but did not further improve the efficiency and stereoselectivity (Table 1, entries 9-12).

Table 1. Optimization of Reaction Conditions[a]



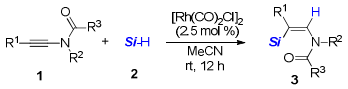
entry	catalyst	solvent	yield [%][b]	*β*/*α*[c]	*Z*/*E*[c]
1	$[Rh(CO)_2Cl]_2$	MeCN	80	> 20:1	15:1
2	$[Rh(COD)_2]BF_4$	MeCN	trace	-	-
3	$[Rh(COD)Cl]_2$	MeCN	0[d]	-	-
4	$[Ir(COD)Cl]_2$	MeCN	76[e]	-	11:1
5	[Cp*Ru(COD)Cl]	MeCN	trace	-	-
6	$[Cp^*Ru(MeCN)_3]PF_6$	MeCN	61	2.4:1	6.2:1
7	$H_2PtCl_6 \cdot 6H_2O$	MeCN	trace	-	-
8	$Na_2PtCl_6 \cdot 6H_2O$	MeCN	trace	-	-
9	$[Rh(CO)_2Cl]_2$	DCM	64	> 20:1	4.9:1
10	$[Rh(CO)_2Cl]_2$	$CHCl_3$	60	> 20:1	4.4:1
11	$[Rh(CO)_2Cl]_2$	THF	71	> 20:1	6.5:1
12	$[Rh(CO)_2Cl]_2$	Toluene	55	> 20:1	3.7:1

[a]Reaction conditions: **1a** (1.0 equiv), **2a** (2.0 equiv), solvent (0.1 M), catalyst (2.5 mol %), at rt under N_2 for 12 h. [b]Yields were determined by ^1H NMR of the crude mixture with an internal standard. [c]The ratio of *α*/*β* and *E*/*Z* were determined by ^1H NMR of the crude mixture. [d]The starting material decomposed. [e]Only the (*Z*)-hydrogenation product was detected in good NMR yield. Cp* = pentamethylcyclopentadiene, COD = 1,5-cyclooctadiene.

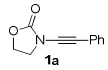
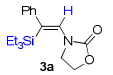
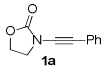
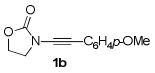
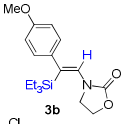
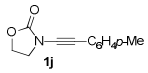
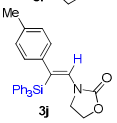
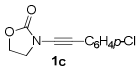
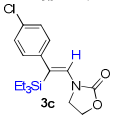
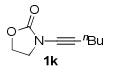
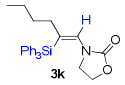
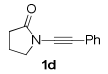
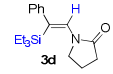
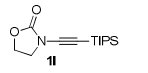
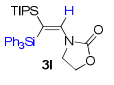
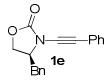
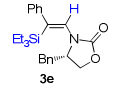
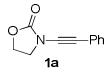
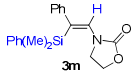
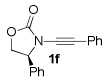
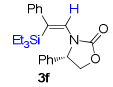
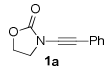
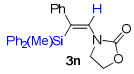
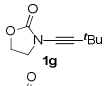
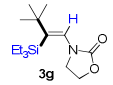
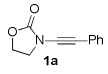
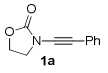
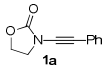
With the optimized condition in hand, we explored the substrate scope for Rh-catalyzed *β*-*anti* selective hydrosilylation of ynamides (Scheme 2). Aliphatic and aromatic tertiary silanes were successfully applied to this protocol. A variety of achiral and chiral ynamides with alkyl or aryl substituents could attend the reaction smoothly at room temperature to give (*Z*)-configured products with excellent *β*-regioselectivity (more than 20:1) and high *anti*-stereoselectivity (up to more than 20:1). Triethylsilane (**2a**) was firstly investigated as silicon source. The electronic effect was not obvious for aryl substituted ynamides (**3b** and **3c**). If pyrrolidinone was used instead of oxazolidinone, the yield and stereoselectivity of **3d** significantly dropped to 66% and 5:1 with extended reaction time. The bulky groups introduced to the adjacent position of ynamides could be well tolerated for this hydrosilylation (**3e** and **3f**). The structure of **3e** was unambiguously confirmed by X-ray crystallographic analysis.[14] However, the low yields and stereoselectivities for *t*-butyl substituted ynamides (**1g**) were observed, which may due to the combination of unfavorable steric and electronic factors. Besides *t*-butyl substituted ynamides, we also investigated *n*-butyl and cyclohexyl substituted ynamides. The inseparable mixture (*Z*/*E* = 1:1) were obtained for these alkyl-substituted ynamides. $(TMSO)_3SiH$ (**2h**), as the typical alkoxysilane, failed to attend this Rh-catalyzed hydrosilylation. Encouragingly, when triphenylsilane (**2i**) was used as silicon source, the stereoselectivities were as high as triethylsilane (**3i**, **3j**, **3k** and **3l**). The yield of *para*-methyl-phenyl substituted ynamide (**1j**) was similar with the phenyl one. Both yields and stereoselectivities could be increased for alkyl substituted ynamides (**1k** and **1l**). Noticeably, although *β*, *β*-disilylated enamide was unstable,[13] the reaction still occurred for triisopropylsilyl (TIPS) substituted ynamide at mild conditions. It provided a unique way to access *β*, *β*-disilylated enamide, which was usually hard to prepare under other harsh conditions. Other tertiary silanes, such as dimethylphenylsilane (**2m**) and methyldiphenylsilane (**2n**) were efficient for this hydrosilylation of ynamides. Secondary silane (diphenylsilane) and primary silane (phenylsilane) could not attend this transformation efficiently. The complex mixtures were acquired using **2o** or **2p** as hydrosilylating regents. In addition, we also explored the variation of acyclic ynamides, including *N*-sulfonyl or carboxyl ynamdies. Neither triethylsilane nor triphenylsilane could react with acyclic ynamides to afford desired hydrosilylation products. If an extra carbon was introduced between the alkyne and the nitrogen of amide, the reaction failed to occur. It discloses that the position of amide connected with alkyne is crucial for this hydrosilylation.

Subsequently, the applicability of this reaction was examined. It was very easy to remove the silyl groups from the obtained vinylsilane products under mild conditions.[7a] Treating **3f** with 1.5 equiv silver fluoride in room temperature, corresponding (*E*)-enamides **4f** were acquired and the olefin configurations were perfectly maintained. The (*E*)-enamides **4f** could be further transformed to chiral *α*-fluorinated imides in one step according to the known literature.[15] The Hiyama cross-coupling reaction is the typical organosilicon-based cross-coupling. We screened different conditions and found triethylsilane derivate **3f** could not achieve this cross-coupling with 4-iodoanisole efficiently, because the transmetalation was reluctant to occur without the activating agent (such as fluoride or hydroxide) in organosilicons (Scheme 3).[16]

Scheme 2. Substrate Scope of the Hydrosilylation of Ynamides with Silane[a]



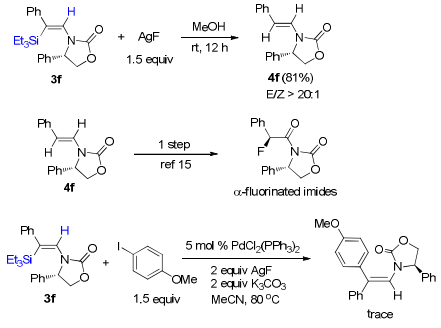
1 2 3

entry	substrate 1	substrate 2	product	yield and *Z*/*E*	entry	substrate 1	substrate 2	product	yield and *Z*/*E*
1	 1a	Et_3SiH 2a	 3a	76% *Z*/*E* = 15:1	9	 1a	Ph_3SiH 2i	 3i	78% *Z*/*E* = 16:1
2	 1b	Et_3SiH 2a	 3b	70% *Z*/*E* > 20:1	10	 1j	Ph_3SiH 2i	 3j	72% *Z*/*E* = 17:1
3	 1c	Et_3SiH 2a	 3c	69% *Z*/*E* = 18:1	11	 1k	Ph_3SiH 2i	 3k	70% *Z*/*E* > 20:1
4	 1d	Et_3SiH 2a	 3d	66%[b] *Z*/*E* = 5:1	12	 1l	Ph_3SiH 2i	 3l	74%[c] *Z*/*E* > 20:1
5	 1e	Et_3SiH 2a	 3e	74% *Z*/*E* > 20:1	13	 1a	$Ph(Me)_2SiH$ 2m	 3m	70% *Z*/*E* = 15:1
6	 1f	Et_3SiH 2a	 3f	81% *Z*/*E* > 20:1	14	 1a	$Ph_2(Me)SiH$ 2n	 3n	72% *Z*/*E* = 17:1
7	 1g	Et_3SiH 2a	 3g	65%[d] *Z*/*E* = 1:1	15	 1a	Ph_2SiH_2 2o	a complex mixture	-
8	 1a	$(TMSO)_3SiH$ 2h	no reaction	-	16	 1a	$PhSiH_3$ 2p	a complex mixture	-

[a]Standard conditions unless otherwise noted: **1** (0.2 mmol), **2** (0.4 mmol), MeCN (2 mL), $[Rh(CO)_2Cl]_2$ (2.5 mol %), at rt under N_2 for 12 h. Combined isolated yields were shown. The ratio of α/β and *E*/*Z* were determined by ^{1}H NMR of the crude mixture. The ratio of β/α > 20:1 unless otherwise noted. [b]For 24 h. [c]For 18 h, TIPS = triisopropylsilyl. [d]Inseparable mixture.

The Rh-catalyzed hydrosilylation of internal ynamides could result in excellent regio- and stereoselectivities under mild conditions. To further understand this Rh-catalyzed process, we investigated the mechanism. We firstly concluded one possible isomerization process may be involved to afford the β-silyl (*Z*)-enamide products **3**.[6b, 9b] The initial hydrosilylation provides β-silyl (*E*)-enamides **3'**. Then the second hydrosilylation followed by β-hydride elimination gives β-silyl (*Z*)-enamides. β-Silyl (*E*)-enamide **3a'** was treated under the standard condition in order to demonstrate this mechanism. Unfortunately, no reaction occurred under the standard condition. Hence the isomerization mechanism may be excluded (for details, see the SI).

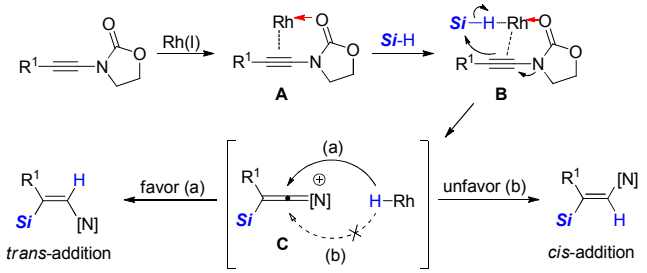
Scheme 3. Application of Rh-catalyzed Hydrosilylation of Internal Ynamides



The Crabtree-Ojima mechanism is the most classic and ubiquitous mechanism suitable for the hydrosilylation of alkynes and alkenes.[17] But it fails to explain the results why triphenylsilane **2i** works better than triethylsilane **2a** for some substrates in this Rh-catalyzed hydrosilylation of ynamides (for details, see the SI).

We rationalize that a ketene iminium intermediate forming *in situ* may be an alternative explanation for affording β-silyl (*Z*)-enamide products.[7a,12,18] From the ^{1}H-NMR study (for details, see the SI), the Rh carbonyl complex **A** is generated firstly. It could activate the ynamide to attack silane in intermediate **B**, generating the ketene iminium species **C** *in situ*.[19] Then the hydride selectively attacks the ketene iminium **C** by pathway (a) due to the combination of steric and β-silicon effect, which determines the (*Z*)-enamides geometry.[7a] For the TIPS-substituted ynamide **1l**, β, β-silyl-disubstituted ketene iminium intermediate would be formed. Triphenyl group is more bulky than the triisopropyl one, which control the hydride attacking by pathway (a) efficiently. Although the alkyl group is less steric hindrance than aryl group, the poor selectivity was acquired for treating *t*-butyl-substituted ynamide **1g** with triethylsilane **2a**. It may be due to the unfavorable electronic factors. Although the reason for these interesting phenomena is not clear at this stage, we also consider the critical factor may change depending on the substrate (Scheme 4).

Scheme 4. Plausible Ketene Iminium Mechanism



In summary, we have developed a rhodium-catalyzed highly regio- and stereoselective intermolecular hydrosilylation of internal ynamides under mild conditions. This reaction is unique to provide a straightforward and efficient entry to access the related *β*-silyl (*Z*)-enamides. With the neutral rhodium complex $[Rh(CO)_2Cl]_2$ as catalyst and the bulky silanes as reactants, various ynamides underwent hydrosilylation smoothly at room temperature with excellent *β* regioselectivities and *anti* stereoselectivities. The synthetically versatile *β*-silyl (Z)-enamide products could be further transformed to the useful building blocks. Based on the detailed mechanism study, several possible mechanisms are proposed. The high regio- and stereoselectivities may be derived from the strong coordination between the ynamides and rhodium, followed by the hydride selectively attacking the ketene iminium intermediate. The comprehensive mechanistic studies and advanced theoretical calculations for the catalysts and intermediates are underway in our laboratory.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all reactions in non-aqueous media were conducted under a positive pressure of dry nitrogen in glassware that had been oven dried prior to use. Anhydrous solutions were transferred via an oven dried syringe or cannula. All solvents were dried prior to use unless noted otherwise. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm). ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Bruker Avance II 400 MHz or Bruker Avance III 500 MHz recorded in ppm (δ) downfield of TMS (δ=0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), multiplet (m), and broad (br) with coupling constants (*J*) in hertz (Hz). High resolution mass spectra (HRMS) were performed by Micromass apparatus (TOF mass analyzer type) on an Electron Impact (EI) mass spectrometer or Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer. Melting points were determined by XP-4 melting point apparatus. Optical rotations were measured on a Rudolph Autopol IV automatic polarimeter.

General Procedure of Rhodium-catalyzed Hydrosilylation. Standard conditions: To a vial containing $[Rh(CO)_2Cl]_2$ (2.0 mg, 0.025 eq, 0.005 mmol) in MeCN (2 mL) under N_2 was added 3-(phenylethynyl)oxazolidin-2-one (37.4 mg, 1 eq, 0.2 mmol) and triethylsilane (46.5 mg, 2 eq, 0.4 mmol). The mixture was stirred at room temperature for 12 h. Then the mixture was concentrated in vacuo and purified with flash column chromatography (10% EtOAc in PE) to give the pure product (46.1 mg, 76%) as yellow oil.

General Procedure of Protodesilylation. To a solution of **3f** (37.9 mg, 0.1 mmol) in MeOH (1 mL) under N_2 was added AgF (19 mg, 1.5 eq, 0.15 mmol). The mixture was stirred at room temperature for 12 h. Then the mixture was concentrated *in vacuo* and purified with flash column chromatography (5% EtOAc in PE) to give the pure product **4f** (21.5 mg, 81%) as white solid.

General Procedure of the Stoichiometric Reactions for Mechanism Investigation. To a solution of **1a** (7.48 mg, 0.04 mmol) in CD_3CN (0.4 mL) under N_2 was added $[Rh(CO)_2Cl]_2$ (15.5 mg, 1 eq, 0.04 mmol). The mixture was tested by ^{1}H-NMR at 0, 3, 6, 12 h.

(Z)-3-(2-phenyl-2-(triethylsilyl)vinyl)oxazolidin-2-one ***(3a)***. 46.1 mg, *Z*/*E* = 15:1. 76% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.29-7.25 (m, 2H), 7.22-7.20 (m, 1H), 7.11-7.08 (m, 2H), 6.65 (s, 1H), 4.42 (t, *J* = 8.0 Hz, 2H), 3.85 (t, *J* = 8.0 Hz, 2H), 0.92 (t, *J* = 8.0 Hz, 9H), 0.65 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 143.7, 136.7, 136.0, 128.0, 128.0, 126.0, 62.1, 47.4, 7.6, 4.4. IR (KBr) ν 2955, 2359, 1761, 1598, 1398, 1265, 1080, 741, 703 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{25}NO_2Si$ 303.1655; Found 303.1664.

(Z)-3-(2-(4-methoxyphenyl)-2-(triethylsilyl)vinyl)oxazolidin-2-one ***(3b)***. 46.6 mg, *Z*/*E* > 20:1. 70% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.02 (d, *J* = 10.0 Hz, 2H), 6.81 (d, *J* = 10.0 Hz, 2H), 6.60 (s, 1H), 4.41 (t, *J* = 10.0 Hz, 2H), 3.82 (t, *J* = 10.0 Hz, 2H), 3.80 (s, 3H), 0.92 (t, *J* = 10.0 Hz, 9H), 0.65 (q, *J* = 10.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.0, 157.5, 136.6, 135.9, 129.8, 129.0, 113.4, 62.1, 56.2, 47.5, 7.6, 4.3. IR (KBr) ν 2956, 2359, 1762, 1590, 1265, 1110, 742, 701 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{27}NO_3Si$ 333.1760; Found 333.1764.

(Z)-3-(2-(4-chlorophenyl)-2-(triethylsilyl)vinyl)oxazolidin-2-one ***(3c)***. 46.5 mg, *Z*/*E* = 18:1. 69% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.24 (d, *J* = 10.0 Hz, 2H), 7.02 (d, *J* = 10.0 Hz, 2H), 6.65 (s, 1H), 4.42 (t, *J* = 10.0 Hz, 2H), 3.85 (t, *J* = 10.0 Hz, 2H), 0.92 (t, *J* = 10.0 Hz, 9H), 0.64 (q, *J* = 10.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.3, 142.3, 137.1, 134.2, 132.0, 129.4, 128.1, 62.1, 47.2, 7.6, 4.4. IR (KBr) ν 2957, 2305, 1762, 1481, 1264, 749, 705 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{17}H_{24}ClNO_2Si$ 337.1265; Found 337.1257.

(Z)-1-(2-phenyl-2-(triethylsilyl)vinyl)pyrrolidin-2-one ***(3d)***. 39.7 mg, *Z*/*E* = 5:1. 66% yield. Yellow oil. Major isomer: ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.50-7.33 (m, 5H), 7.28 (s, 1H), 3.86 (t, *J* = 10.0 Hz, 2H), 2.60 (t, *J* = 10.0 Hz, 2H), 2.24 (t, *J* = 10.0 Hz, 2H), 0.98 (t, *J* = 10.0 Hz, 9H), 0.81 (q, *J* = 10.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 175.1, 146.4, 130.3, 128.2, 127.1, 126.5, 126.1, 49.4, 31.3, 18.5, 6.8, 5.3. IR (KBr) ν 2876, 1710, 1461, 1384, 1265, 737, 703 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{18}H_{27}NOSi$ 301.1862; Found 301.1870.

(Z)-(S)-4-benzyl-3-(2-phenyl-2-(triethylsilyl)vinyl)oxazolidin-2-one ***(3e)***. 58.2 mg, *Z*/*E* > 20:1. 74% yield. White solid, mp = 115-116 °C. $[\alpha]_D^{23}$= +30.8 (*c* = 0.52, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.37-7.12 (m, 10H), 6.44 (s, 1H), 4.30-4.14 (m, 3H), 3.23 (t, *J* = 8.0 Hz, 1H), 2.83-2.77 (m, 1H), 0.97 (t, *J* = 8.0 Hz, 9H), 0.74 (q, *J* = 8.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.8, 143.2, 143.1, 135.6, 135.1, 129.1, 129.1, 128.0, 127.8, 127.3, 126.3, 66.5, 60.4, 38.3, 7.6, 3.6. IR (KBr) ν 2961, 2359, 1759, 1420, 1265, 1110, 748, 704 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{24}H_{31}NO_2Si$ 393.2124; Found 393.2133.

(Z)-(S)-4-phenyl-3-(2-phenyl-2-(triethylsilyl)vinyl)oxazolidin-2-one ***(3f)***. 61.4 mg, *Z*/*E* > 20:1. 81% yield. White solid, mp = 48-49 °C. $[\alpha]_D^{23}$= +94.3 (*c* = 0.32, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.40-7.36 (m, 3H), 7.35-7.29 (m, 2H), 7.22-7.14 (m, 3H), 6.99 (d, *J* = 5.0 Hz, 2H), 6.09 (s, 1H), 4.89-4.86 (m, 1H), 4.67 (t, *J* = 10.0 Hz, 1H), 4.29-4.26 (m, 1H), 0.92 (t, *J* = 10.0 Hz, 9H), 0.71 (q, *J* = 10.0 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 143.6, 143.2, 137.5, 134.6, 129.3, 129.1, 127.9, 127.8, 126.8, 126.2, 69.5, 63.1, 7.6, 3.5. IR (KBr) ν 2955, 2359, 1762, 1539, 1441, 1263, 1102, 876, 749 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{23}H_{29}NO_2Si$ 379.1968; Found 379.1967.

(Z)-3-(2-phenyl-2-(triphenylsilyl)vinyl)oxazolidin-2-one ***(3i)***. 69.7 mg, *Z*/*E* = 16:1. 78% yield. Yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.57-7.55 (m, 6H), 7.40-7.35 (m, 5H), 7.35-7.29 (m, 6H), 7.00-6.98 (m, 4H), 3.61 (t, *J* = 10.0 Hz, 2H), 3.34 (t, *J* = 10.0 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 143.2, 139.4, 136.1, 134.3, 129.7, 129.2, 127.9, 127.6, 125.8, 122.9, 62.2, 46.9. IR (KBr) ν 2920, 2851, 1765, 1590, 1390, 1102, 700 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{29}H_{25}NO_2Si$ 447.1655; Found 447.1650.

(Z)-3-(2-(p-tolyl)-2-(triphenylsilyl)vinyl)oxazolidin-2-one ***(3j)***. 66.4 mg, *Z*/*E* = 17:1. 72% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.57-7.55 (m, 6H), 7.38-7.26 (m, 9H), 6.88-6.76 (m, 4H), 3.59 (t, *J* = 8.0 Hz, 2H), 3.34 (t, *J* = 8.0 Hz, 2H), 2.19 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 139.2, 136.5, 136.1, 134.4, 129.7, 129.0, 128.3, 127.9, 127.7, 123.7, 62.1, 47.1, 20.9. IR (KBr) ν 2986, 1760, 1595, 1428, 1399, 1107, 1039, 744 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{30}H_{27}NO_2SiNa$ 484.1703; Found 484.1703.

(Z)-3-(2-(triphenylsilyl)hex-1-en-1-yl)oxazolidin-2-one ***(3k)***. 59.8 mg, *Z*/*E* > 20:1. 70% yield. White solid, mp = 106-107 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.63-7.61 (m, 6H), 7.42-7.36 (m, 9H), 7.20 (s, 1H), 3.49 (t, *J* = 10.0 Hz, 2H), 3.22 (t, *J* = 10.0 Hz, 2H), 2.07 (t, *J* = 5.0 Hz, 2H), 1.24-1.22 (m, 2H), 1.07-1.04 (m, 2H), 0.65 (t, *J* = 5.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.0, 136.8, 136.1, 134.4, 129.8, 128.0, 121.4, 62.0, 47.2, 36.8, 33.4, 22.3, 13.6. IR (KBr) ν 2956, 2359, 1761, 1476, 1399, 1107, 761, 639 cm^{-1}. HRMS (EI-TOF) m/z: $[M]^+$ Calcd for $C_{27}H_{29}NO_2Si$ 427.1968; Found 427.1965.

(Z)-3-(2-(triisopropylsilyl)-2-(triphenylsilyl)vinyl)oxazolidin-2-one ***(3l)***. 78.0 mg, *Z*/*E* > 20:1. 74% yield. White solid, mp = 119-120 °C. ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.68 (d, *J* = 5.0 Hz, 6H), 7.43-7.37 (m, 9H), 6.40 (s, 1H), 3.88 (t, *J* = 10.0 Hz, 2H), 3.36 (t, *J* = 10.0 Hz, 2H), 1.20-1.15 (m, 3H), 1.06 (d, *J* = 10.0 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.7, 151.7, 149.2, 135.1, 132.4, 128.9, 126.9, 60.7, 46.5, 17.9, 10.9. IR (KBr) ν 2943, 2341, 1749, 1428, 1108, 882, 740 cm^{-1}. HRMS (EI-TOF) m/z: $[M-i\text{Pr}]^+$ Calcd for $C_{29}H_{34}NO_2Si_2$ 484.2128; Found 484.2133.

(Z)-3-(2-(dimethyl(phenyl)silyl)-2-phenylvinyl)oxazolidin-2-one ***(3m)***. 45.2 mg, *Z*/*E* = 15:1. 70% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.63-7.62 (m, 2H), 7.39-7.18 (m, 8H), 6.77 (s, 1H), 3.84 (t, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 2H), 0.34 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.6, 144.2, 139.5, 137.2, 134.4, 130.1, 129.0, 128.8, 127.0, 125.0, 113.6, 62.6, 47.3, 0.0. IR (KBr) ν 2986, 2359, 1758, 1417, 1265, 1111, 814, 747 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{19}H_{21}NO_2SiNa$ 346.1234, found 346.1239.

(Z)-3-(2-(methyldiphenylsilyl)-2-phenylvinyl)oxazolidin-2-one ***(3n)***.55.4 mg, *Z*/*E* = 17:1. 70% yield. Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.66-7.64 (m, 4H), 7.40-7.38 (m, 6H), 7.22-7.16 (m, 6H), 3.66 (t, *J* = 8.0 Hz, 2H), 3.33 (t, *J* = 8.0 Hz, 2H), 0.39 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 156.9, 143.3, 138.4, 136.2, 134.9, 129.6, 128.4, 128.1, 127.1, 126.3, 112.8, 62.0, 46.9, -0.5. IR (KBr) ν 2985, 1759, 1398, 1109, 1039, 747, 703 cm^{-1}. HRMS (ESI-TOF) m/z: $[M+Na]^+$ Calcd for $C_{24}H_{23}NO_2Si$ 408.1390; Found 408.1392.

(E)-(S)-4-phenyl-3-styryloxazolidin-2-one ***(4f)***. 21.5 mg, *E*/*Z* > 20:1. 81% yield. White solid, mp = 122-123 °C. $[\alpha]_D^{23}$= +91.3 (*c* = 1.45, MeOH). ^{1}H NMR (500 MHz, $CDCl_3$, TMS): δ 7.44-7.40 (m, 2H), 7.39-7.31 (m, 4H), 7.22 (t, *J* = 10.0 Hz, 2H), 7.17-7.13 (m, 3H), 5.58 (d, *J* = 15.0 Hz, 1H), 5.16 (dd, *J* = 5.0, 10.0 Hz, 1H), 4.78 (t, *J* = 10.0 Hz, 1H), 4.20 (dd, *J* = 5.0, 10.0 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.8, 138.0, 135.8, 129.5, 129.0, 128.6, 126.7, 125.9, 125.6, 123.0, 113.0, 70.8, 58.6. IR (KBr) ν 2986, 2359, 1760, 1403, 1265, 747 cm^{-1}. Compound **4f** is known compound, and the proton and carbon spectrum is fully consistent with literature reported.[15]

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Other plausible mechanism, ^{1}H NMR, ^{13}C NMR spectra of new compounds and X-ray crystallographic data for **3e**.

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Notes

The authors declare no competing financial interests.

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