HETEROCYCLES, Vol. 59, No. 2, 2003, pp. 573 - 585, Received, 6th August, 2002

INVESTIGATION OF THE RING-OPENING CROSS-METATHESIS REACTION OF 2-AZABICYCLO[2.2.1]-HEPT-5-EN-3-ONE (ABH) WITH ALLYLSILANES

Minoru Ishikura,* Makoto Saijo, and Ayako Hino

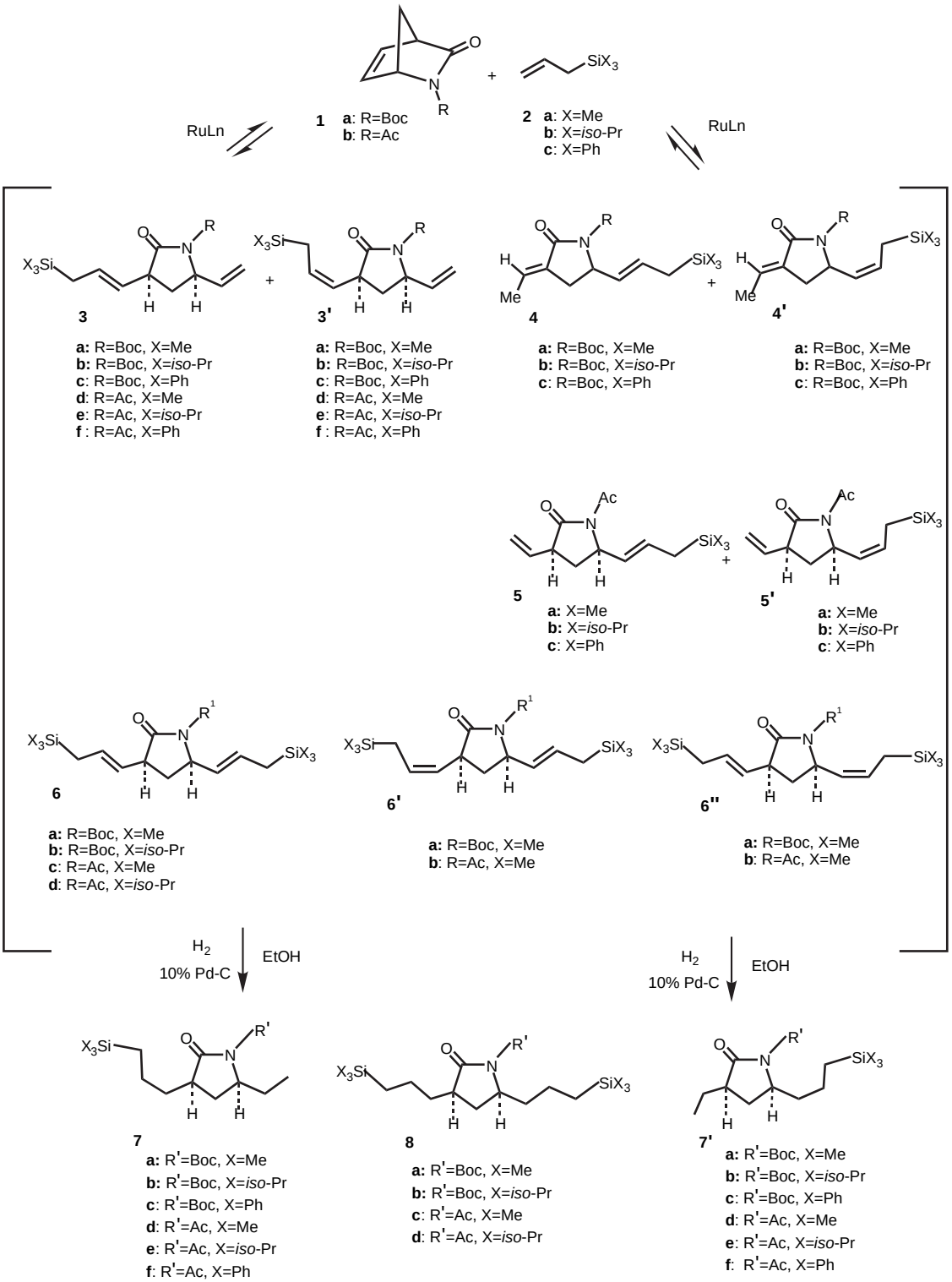
Faculty of Pharmaceutical Sciences, Health Sciences University of Hokkaido, Ishikari-Tobetsu, Hokkaido 061-0293, Japan

Abstract – An examination of the ring-opening cross-metathesis reaction of *N*-substituted 2-azabicyclo[2.2.1]hept-5-en-3-ones (ABH) (**1**) with allylsilanes (**2**) in the presence of ruthenium catalysts was undertaken.

Due to its lability across a range of chemical transformations, 2-azabicyclo[2.2.1]hept-5-en-3-ones (ABH) is not only a useful building block for the construction of various carbocyclic nuclesides, but also remains valuable for its synthetic potential.[1] During the recent remarkable progress in metathesis protocols in synthetic organic chemistry,[2] there has been a report by Blechert that the subjection of ABH (**1a**) to a ruthenium complex [$Cl_2(PCy_3)_2Ru$=CHPh]-catalyzed ring-opening cross-metathesis reaction with allyltrimethylsilane (**2a**) gave rise to regioselective formation of ring-opening products (**3a**,**3'a**).[3] In connection with our recent interest in extending the synthetic importance of ABH as a synthon,[1] Blechert's report prompted us to re-examine the ring-opening cross-metathesis process of **1a** with **2a** in the presence of Grubbs' catalyst, from which a pair of regioisomeric ring-opening products (**3a,3'a** and **4a,4'a**) were obtained instead of the known regioselective formation of **3a**,**3'a**.[4] Herein, further examination of the ring-opening cross-metathesis reaction of **1** with allylsilanes (**2**) using various ruthenium complexes was undertaken (Scheme 1), and the experimental results are described in this paper.

At first, the reaction of **1** with allylsilanes (**2**) catalyzed by Grubbs' catalyst in CH_2Cl_2 at room temperature under an argon atmosphere was examined. The reaction of **1a** with **2** allowed the isolation of **3a-c**, **3'a-c** and **4a-c**, **4'a-c**, and we assume that initial products from the reaction of **1a** with **2** isomerized to **4** and **4'** through double bond migration during silica gel column. Otherwise, a pair of regioisomeric ring-opening products (**3d-f**, **3'd-f** and **5a-c**, **5'a-c**) were the isolates from the reaction between **1b** and **2**. Because ring-opening products are intrinsically unstable due to the allylsilane functions, and are unable to be isolated without considerable decomposition during the separation by column chromatography, the ratios of regioisomeric ring-opening products were determined based on **7** and **7'** after catalytic hydrogenation of the reaction mixture as previously reported (Table 1).[4]

Treatment of **1a** with **2a**,**b** in the presence of 5 mol% of catalyst for 3.5 h provided a pair of regioisomers (**7a**,**b**) and (**7'a**,**b**) in ratios of approximately 2.2~2.5:1, respectively. Otherwise, a poor reaction rate was observed in the reaction of **1a** with **2c**, leading to **7c** and **7'c**, probably due to sterical encumbrance of


RuLn
1 a: R=Boc
b: R=Ac
2 a: X=Me
b: X=iso-Pr
c: X=Ph
RuLn
3
3'
4
4'
5
5'
6
6'
6''
H2
10% Pd-C
EtOH
H2
10% Pd-C
EtOH
7
8
7'

Scheme 1

triphenyl group in **2c**, unless increased amounts of catalyst (10 mol%) and a longer reaction time (10 h) were adopted. On the other hand, forcing the temperature to reflux complicated the reaction. Slightly increased propensity for **7c** resulted, in which a spatial interaction between *N*-Boc and Ph_3Si in complex (**A**) might exert an influence on the reaction outcome (Scheme 2).[5] Morever, **1b**, having less voluminous *N*-Ac, was treated with **2** similarly, leading to a pair of regioisomeric products (**7d-f**) and (**7'd-f**) in ratios of 1.3~2.0:1.

Table 1 Reaction of ABH (**1**) with allylsilanes (**2**) in the presence of Grubbs' catalyst[a]

1 + **2** $\xrightarrow[CH_2Cl_2,\ \text{at rt / 3.5 h}]{\text{Grubbs' catalyst}^b}$ [**3** + **3'** + **4** + **4'** + **5** + **5'**] $\xrightarrow[\text{EtOH}]{H_2\ /\ 10\%\ Pd\text{-}C}$ **7** + **7'**

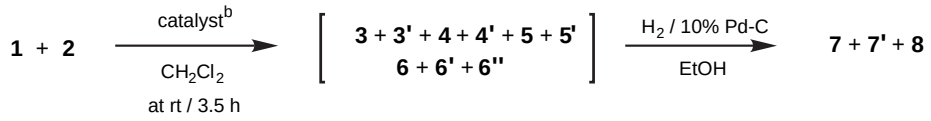
1	Catalyst (mol%)	**2** (eq.)	Yield (%)[c] **7**	**7'**
1a	5	**2a** (1)	52 (**7a**)	20 (**7'a**)
	5	**2a** (1.5)	54 (**7a**)	21 (**7'a**)
	1	**2a** (1)	52 (**7a**)	20 (**7'a**)
	1	**2a** (1.5)	50 (**7a**)	20 (**7'a**)
	5	**2a** (1.5)d	47 (**7b**)	23 (**7'b**)
	5	**2b** (1)	49 (**7b**)	21 (**7'b**)
	5	**2b** (1.5)	53 (**7b**)	27 (**7'b**)
	1	**2b** (1)	39 (**7b**)	18 (**7'b**)
	1	**2b** (1.5)	38 (**7b**)	19 (**7'b**)
	10	**2c** (1)	39 (**7c**)	14 (**7'c**)
	10	**2c** (1.5)	50 (**7c**)	13 (**7'c**)
	10	**2c** (1)e	57 (**7c**)	18 (**7'c**)
	10	**2c** (1.5)e	58 (**7c**)	17 (**7'c**)
1b	5	**2a** (1)	35 (**7e**)	23 (**7'e**)
	5	**2a** (1.5)	32 (**7e**)	19 (**7'e**)
	1	**2a** (1)	34 (**7e**)	22 (**7'e**)
	1	**2a** (1.5)	32 (**7e**)	19 (**7'e**)
	5	**2b** (1)	25 (**7f**)	22 (**7'f**)
	5	**2b** (1.5)	28 (**7f**)	27 (**7'f**)
	5	**2c** (1)	20 (**7g**)	10 (**7'g**)
	5	**2c** (1.5)[d]	28 (**7g**)	14 (**7'g**)

[a] reactions were carried out in CH_2Cl_2 at room temperature for 3.5 h under an argon atmosphere.
[b] $(PCy_3)_2Cl_2Ru{=}CHPh$ [c] isolated yields based on **1**. [d] in benzene [e] for 10 h

We next undertook the reaction of **1** with **2** in the presence of second generation ruthenium catalysts to clarify the effect of catalysts on the reaction outcome, still allowing for the isolation of bis-allylsilylane products (**6**, **6'**, **6''**) along with **3**,**3'**,**4**,**4'**,**5** and **5'**, which were in turn catalytically hydrogenated to **7**, **7'** and **8**, respectively, to determine the ratios of ring-opening products. The proportion of **8** increased under forcing reaction conditions (reflux in CH_2Cl_2 for 6 h). This might be ascribable to the known

thermal stability of second generation ruthenium catalyst,[6] enabling to force the cross-metathesis reaction of **3**, **3'**, **4**, **4'**, **5** and **5'** with **2** to lead to **6, 6', 6''**.

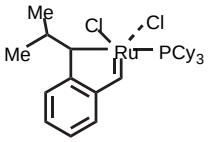
Table 2 Reaction of ABH (**1**) with allylsilanes (**2**) in the presence of the second generation ruthenium catalyst[a]

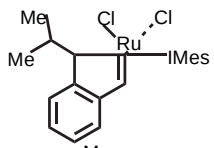


			Yield (%)[c]		
1	Catalyst	**2** (eq.)	**7**	**7'**	**8**
1a	A	**2a** (1.5)	38 (**7a**)	27 (**7'a**)	5 (**8a**)
	A	**2a** (2)	37 (**7a**)	24 (**7'a**)	10 (**8a**)
	A	**2a** (2)[d]	25 (**7a**)	10 (**7'a**)	15 (**8a**)
	A	**2a** (2)[e]	14 (**7a**)	5 (**7'a**)	50 (**8a**)
	A	**2a** (2)[f]	31 (**7a**)	22 (**7'a**)	14 (**8a**)
	A	**2a** (2)[g]	34 (**7a**)	30 (**7'a**)	3 (**8a**)
	A	**2a** (2)[h]	22 (**7a**)	15 (**7'a**)	15 (**8a**)
	B	**2a** (2)	40 (**7a**)	25 (**7'a**)	6 (**8a**)
	C	**2a** (2)	22 (**7a**)	9 (**7'a**)	6 (**8a**)
	D	**2a** (2)	18 (**7a**)	5 (**7'a**)	6 (**8a**)
	A	**2b** (1)	38 (**7b**)	15 (**7'b**)	17 (**8b**)
	A	**2b** (2)	30 (**7b**)	9 (**7'b**)	25 (**8b**)
	A	**2b** (2)[e]	25 (**7b**)	5 (**7'b**)	42 (**8b**)
1c	A	**2a** (1)	32 (**7e**)	13 (**7'e**)	5 (**8c**)
	A	**2a** (1.5)	34 (**7e**)	24 (**7'e**)	8 (**8c**)
	A	**2a** (2)	33 (**7e**)	25 (**7'e**)	10 (**8c**)
	A	**2a** (2)[e]	15 (**7e**)	3 (**7'e**)	50 (**8c**)
	A	**2a** (2)[g]	36 (**7e**)	23 (**7'e**)	7 (**8c**)
	A	**2a** (2)[l]	29 (**7e**)	6 (**7'e**)	12 (**8c**)
	A	**2b** (1)	14 (**7f**)	5 (**7'f**)	16 (**8d**)
	A	**2b** (2)[e]	21 (**7f**)	7 (**7'f**)	41 (**8d**)

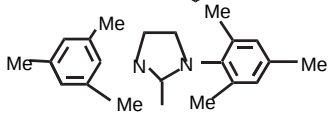
[a] reactions were carried out in CH_2Cl_2 in the presence of catalyst (5 mol%) at room temperature for 3.5 h under an argon atmosphere.

[b] Catalyst A: 

B: 

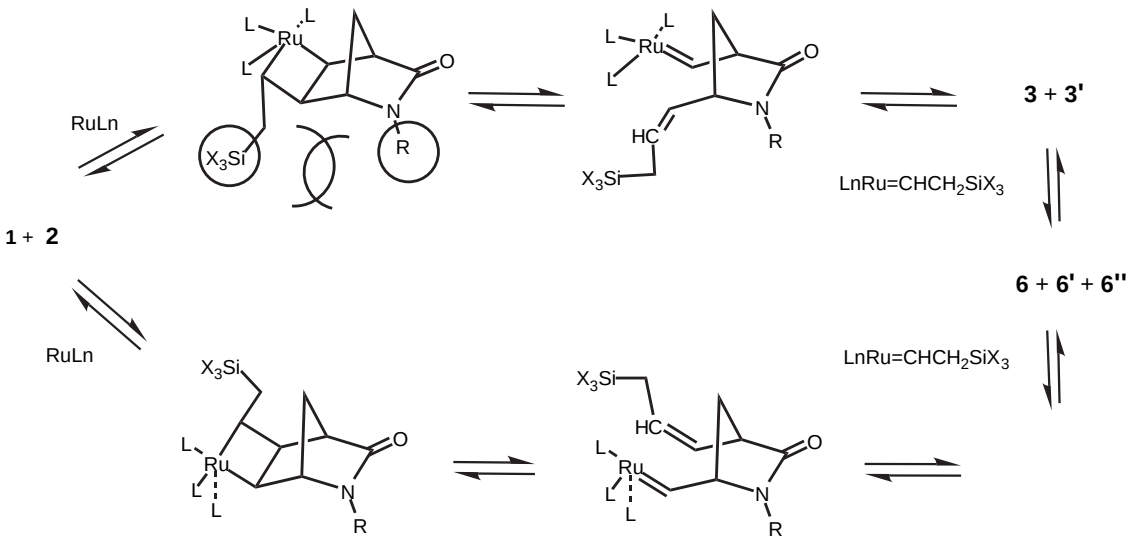
C: 

D: Grubbs' catalyst on polystyrene (1% DVB)

IMes = 

[c] yields based on ABH (**1**). [d] in benzene [e] reflux for 6 h [f] for 20 h [g] in $CHCl_3$ [h] in pentane

In summary, we undertook the metathesis reaction of **1a-c** with allylsilanes (**2**) in the presence of various ruthenium catalysts, still allowing for the isolation of a pair of regioisomeric ring-opening products. Further investigations on the regioselectivity of the reaction are in progress.



Scheme 2

ACKNOWLEDGEMENTS

This work was supported in part by a Grant-in Aid for Scientific Research (No. 13672226) from the Ministry of Education, Culture, Sports, Science and Technology of Japan. The authors thank Kuraray Co., Ltd. for providing the ABH.

EXPERIMENTAL

Melting points were recorded on a Yamato MP21 and are uncorrected. MS and high-resolution MS spectra were recorded on a Micromass AutoSpec 3100 mass spectrometer. IR spectra were measured on a Hitachi Model 270-30 spectrophotometer. The NMR experiments were performed with a JEOL JNM-LA300 or JNM-EX400 spectrometer, and chemical shifts are expressed in ppm (δ) with TMS as an internal reference. HPLC was performed on Mightysil Si-60 250-25 (7μm) (Kanto Chemical Co., Inc.) and a JASCO PU-1586 pump system equipped with a JASCO UV-1575 UV-VIS spectrometric and a JASCO RI-2031 differential refractive index detectors. Dehydrated solvents were purchased from Kanto Chemical Co. Inc.

Reaction of ABH (1) with allylsilanes (2) in the presence of ruthenium catalyst: General procedure:
To a mixture of **1** (1 mmol) and **2** (2 mmol) in CH_2Cl_2 (20 mL) at rt under an argon atmosphere, Grubbs' catalyst (0.05 mmol) was added, and the whole was stirred for 3.5 h. After passed through a short path silica gel column, the reaction mixture was immediately subjected to a catalytic hydrogenation on 10% Pd/C (20 mg) in EtOH (10 mL) under atmospheric pressure. The catalyst was removed by filtration, the solvent was removed, and the residue was separated by HPLC with AcOEt-hexane (1:10) as an eluent to give **7**, **7'** and/or **8**.

Soon after the elapse of the reaction time, the separation of the reaction mixture by HPLC with with AcOEt-hexane (1:10) as an eluent gave **3**, **3'**, **4**, **4'**, **5**, **5'**, and/or **6**, **6'**, **6''**.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*E*)-3-(trimethylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3a):** IR (neat): 1782, 1748, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.49 (s, 9H), 1.45-1.50 (m, 2H), 1.64 (ddd, 1H, *J*=6.8, 8.3, 13.3 Hz), 2.42 (ddd, 1H, *J*=7.8, 9.3, 13.3 Hz), 3.14 (q, 1H, *J*=8.3 Hz), 4.45 (q, 1H, *J*=7.3 Hz), 5.15 (d, 1H, *J*=10.2 Hz), 5.21 (d, 1H, *J*=17.5 Hz), 5.29 (dd, 1H, *J*=6.8, 15.3 Hz), 5.59 (tdt, 1H, *J*=1.5, 8.3, 15.3 Hz), 5.80 (ddd, 1H, *J*=7.3, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -1.9, 23.0, 27.9, 31.9, 46.2, 58.5, 82.9, 115.7, 124.1, 130.9, 138.8, 150.0, 174.7. HR-MS *m/z*: Calcd for $C_{17}H_{29}NO_3Si$: 323.1916. Found: 323.1923.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*E*)-3-(triisopropylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3b):** IR (neat): 1774, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (s, 21H), 1.49 (s, 9H), 1.58-1.68 (m, 3H), 2.41 (ddd, 1H, *J*=8.3, 9.3, 13.3 Hz), 3.08-3.18 (m, 1H), 4.40-4.47 (m, 1H), 5.15 (d, 1H, *J*=10.2 Hz), 5.20 (d, 1H, *J*=17.5 Hz), 5.34 (dd, 1H, *J*=7.3, 15.6 Hz), 5.66 (td, 1H, *J*=8.3, 15.6 Hz), 5.79 (ddd, 1H, *J*=7.3, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 10.8, 15.6, 18.5, 27.8, 31.7, 46.1, 58.7, 82.7, 115.5, 123.8, 131.8, 138.8, 150.0, 174.7. HR-MS *m/z*: Calcd for $C_{23}H_{41}NO_3Si$: 407.2855. Found: 407.2858 .

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*E*)-3-(triphenylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3c):** IR (neat): 1776, 1736 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.38-1.58 (m, 1H), 1.48 (s, 9H), 2.27 (ddd, 1H, *J*=7.8, 9.3, 13.3 Hz), 2.32-2.40 (m, 2H), 3.03-3.12 (m, 1H), 4.33-4.40 (m, 1H), 5.04 (d, 1H, *J*=10.2 Hz), 5.11 (d, 1H, *J*=17.5 Hz), 5.31 (dd, 1H, *J*=7.3, 15.3 Hz), 5.57-5.72 (m, 2H), 7.35-7.46 (m, 9H), 7.48-7.52 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 19.7, 28.1, 31.4, 46.2, 58.8, 82.9, 115.7, 126.4, 127.8, 129.4, 129.5, 134.3, 135.7, 138.7, 149.9, 174.5. HR-MS *m/z*: Calcd for $C_{32}H_{35}NO_3Si$: 509.2386. Found: 509.2375.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*E*)-3-(trimethylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3d):** IR (neat): 1732, 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.49 (d, 2H, *J*=8.3 Hz), 1.72 (ddd, 1H, *J*=5.4, 6.8, 13.3 Hz), 2.45 (ddd, 1H, *J*=8.3, 10.2, 13.3 Hz), 2.50 (s, 3H), 3.16-3.24 (m, 1H), 4.62-4.65 (m, 1H), 5.14 (d, 1H, *J*=10.2 Hz), 5.18 (d, 1H, *J*=17.5 Hz), 5.28 (dd, 1H, *J*=6.8, 15.3 Hz), 5.62 (ddd, 1H, *J*=1.5, 8.3, 15.3 Hz), 5.81 (ddd, 1H, *J*=6.8, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -1.9, 23.1, 25.6, 31.2, 46.7, 57.5, 115.5, 123.8, 131.3, 138.2, 171.3, 176.4. HR-MS *m/z*: Calcd for $C_{14}H_{23}NO_2Si$: 265.1498 Found: 265.1495.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*E*)-3-(triisopropylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3e):** IR (neat): 1738, 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.04 (s, 21H), 1.62 (d, 2H, *J*=8.3 Hz), 1.70 (ddd, 1H, *J*=6.4, 7.4, 13.3 Hz), 2.45 (td, 1H, *J*=8.3, 13.3 Hz), 2.50 (s, 3H), 3.21 (dt, 1H, *J*=7.4, 8.3 Hz), 4.65-4.72 (m, 1H), 5.16 (d, 1H, *J*=10.2 Hz), 5.18 (d, 1H, *J*=17.5 Hz), 5.34 (dd, 1H, *J*=7.4, 15.3 Hz), 5.71 (td, 1H, *J*=8.3, 15.3 Hz), 5.81 (ddd, 1H, *J*=6.5, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 10.9, 15.7, 18.6, 25.5, 31.1, 46.8, 57.5, 115.5, 123.7, 132.3, 138.1, 171.3, 176.3. HR-MS *m/z*: Calcd for $C_{20}H_{35}NO_2Si$: 349.2437. Found: 349.2457 .

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*E*)-3-(triphenylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3f):** IR (neat): 1734, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.53 (ddd, 1H, *J*=4.8, 5.8, 13.2 Hz), 2.28-2.40 (m, 3H), 2.47 (s, 3H), 3.13 (dt, 1H, *J*=6.4, 7.8 Hz), 4.57-4.62 (m, 1H), 5.03 (d, 1H, *J*=10.2 Hz), 5.06 (d, 1H, *J*=17.5 Hz), 5.31 (dd, 1H, *J*=7.4, 15.3 Hz), 5.62 (ddd, 1H, *J*=5.9, 10.2, 17.5 Hz), 5.69 (td, 1H, *J*=11.2, 15.3 Hz), 7.33-

7.44 (m, 9H), 7.48-7.53 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 19.7, 25.5, 30.7, 46.8, 57.5, 115.6, 126.1, 127.8, 129.6, 129.7, 134.2, 135.7, 137.9, 171.2, 176.0. HR-MS *m/z*: Calcd for $C_{29}H_{29}NO_2Si$: 451.1967. Found: 451.1967.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(trimethylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'a):** IR (neat): 1786, 1750, 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: -0.01 (s, 9H), 1.46 (s, 9H), 1.40-1.60 (m, 3H), 2.38 (ddd, 1H, *J*=7.8, 9.2, 13.3 Hz), 3.33-3.42 (m, 1H), 4.40-4.48 (m, 1H), 5.13 (d, 1H, *J*=10.2 Hz), 5.19 (d, 1H, *J*=17.5 Hz), 5.22 (dd, 1H, *J*=8.8, 10.7 Hz), 5.63 (td, 1H, *J*=7.8, 10.7 Hz), 5.77 (ddd, 1H, *J*=7.3, 10.7, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -1.7, 18.9, 27.9, 32.5, 41.5, 58.8, 82.9, 115.7, 1232.2, 130.6, 138.8, 150.0, 174.8. HR-MS *m/z*: Calcd for $C_{17}H_{29}NO_3Si$: 323.1916. Found: 323.1914.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(triisopropylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'b):** IR (neat): 1782, 1724 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 21H), 1.50 (s, 9H), 1.46-1.63 (m, 2H), 1.68 (ddd, 1H, *J*=1.5, 10.2, 14.3 Hz), 2.45 (ddd, 1H, *J*=7.3, 8.8, 13.3 Hz), 3.48-3.57 (m, 1H), 4.44-4.52 (m, 1H), 5.15 (d, 1H, *J*=10.2 Hz), 5.21 (d, 1H, *J*=17.5 Hz), 5.15-5.25 (m, 1H), 5.70-5.85 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ: 11.3, 18.9, 28.2, 32.5, 41.8, 59.0, 83.2, 116.0, 123.7, 131.6, 139.0, 150.3, 174.9. HR-MS *m/z*: Calcd for $C_{23}H_{41}NO_3Si$ 407.2855. Found: 407.2856.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(triphenylsilanyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'c):** IR (neat): 1780, 1744, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.15 (ddd, 1H, *J*=7.3, 8.8, 13.3 Hz), 1.47 (s, 9H), 1.71 (ddd, 1H, *J*=7.3, 8.8, 13.3 Hz), 2.37 (ddd, 1H, *J*=1.3, 6.8, 14.5 Hz), 2.51 (ddd, 1H, *J*=1, 9.7, 14.5 Hz), 3.10-3.20 (m, 1H), 4.20-4.13 (m, 1H), 5.09 (d, 1H, *J*=10.2 Hz), 5.12 (d, 1H, *J*=17.5 Hz), 5.24 (dd, 1H, *J*=8.8, 11.2 Hz), 5.68 (ddd, 1H, *J*=7.3, 10.2, 17.5 Hz), 5.78-5.88 (m, 1H), 7.32-7.44 (m, 9H), 7.50-7.75 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 15.7, 27.9, 31.7, 41.8, 58.7, 82.9, 115.5, 125.2, 127.9, 128.0, 129.1, 129.6, 134.2, 135.7, 138.6, 150.0, 174.5. HR-MS *m/z*: Calcd for $C_{32}H_{35}NO_3Si$ 509.2386. Found: 509.2404.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(trimethylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3'd):** IR (neat): 1732, 1696 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.47-1.64 (m, 3H), 2.43 (ddd, 1H, *J*=8.3, 9.3, 13.3 Hz), 2.46 (s, 3H), 3.40-3.50 (m, 1H), 4.62-4.70 (m, 1H), 5.12 (d, 1H, *J*=10.2 Hz), 5.13 (d, 1H, *J*=17.5 Hz), 5.23 (dd, 1H, *J*=9.8, 10.2 Hz), 5.64 (q, 1H, *J*=10.2 Hz), 5.78 (ddd, 1H, *J*=6.5, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -1.8, 19.0, 25.5, 31.7, 42.0, 57.5, 115.5, 123.1, 130.8, 138.1, 171.3, 176.5. HR-MS *m/z*: Calcd for $C_{14}H_{23}NO_2Si$: 265.1498. Found: 265.1506.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(triisopropylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3'e):** IR (neat): 1738, 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.06 (s, 21H), 1.56-1.75 (m, 3H), 2.45-2.54 (m, 1H), 2.51 (s, 3H), 3.62 (ddt, 1H, *J*=1.5, 9.3, 10.2 Hz), 4.71 (dt, 1H, *J*=6.3, 7.3 Hz), 5.17 (d, 1H, *J*=10.2 Hz), 5.18 (d, 1H, *J*=17.5 Hz), 5.21 (dd, 1H, *J*=10.2, 11.2 Hz), 5.82 (ddd, 1H, *J*=6.3, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 11.1, 11.2, 18.7, 25.6, 31.5, 42.1, 57.6, 115.5, 123.3, 131.7, 138.1, 171.4, 176.5. HR-MS *m/z*: Calcd for $C_{20}H_{35}NO_2Si$: 349.2437. Found: 349.2437.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(triphenylsilanyl)propenyl]-5-vinylpyrrolidin-2-one (3'f):** IR (neat): 1734, 1698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.22 (ddd, 1H, *J*=6, 6.8, 13.3 Hz), 1.81 (td, 1H, *J*=8.5, 13.3 Hz), 2.40 (ddd, 1H, *J*=1.5, 6.8, 14.2 Hz), 2.54 (ddd, 1H, *J*=1.5, 10.2, 14.2 Hz), 2.46 (s, 3H), 3.20 (q, 1H, *J*=8.3 Hz), 4.48 (q, 1H, *J*=6.8 Hz), 5.08 (d, 1H, *J*=17.5 Hz), 5.09 (d, 1H, *J*=10.2 Hz), 5.26 (dd, 1H, *J*=10.2, 11.3 Hz), 5.70 (ddd, 1H, *J*=6.8, 10.2, 17.5 Hz), 5.84 (dt, 1H, *J*=6.5, 11.3 Hz), 7.34-7.45 (m, 9H), 7.51-7.57 (m,

6H). ^{13}C-NMR ($CDCl_3$) δ: 15.8, 25.5, 30.9, 42.3, 57.5, 115.3, 124.9, 127.9, 129.4, 129.7, 134.1, 135.7,m 138.0, 171.2, 176.2. HR-MS *m/z*: Calcd for $C_{29}H_{29}NO_2Si$: 451.1967. Found: 451.1979.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(trimethylsilanyl)propenyl]pyrrolidine-1-carboxylate (4a):** IR (neat):1776, 1742, 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.45 (d, 1H, *J*=7.5 Hz), 1.50-1.55(m, 1H), 1.53 (s, 9H), 1.81 (d, 3H, *J*=7.4 Hz), 2.39 (dd, 1H, *J*=1.5, 6.6 Hz), 2.78-2.88 (m, 1H), 4.60 (dt, 1H, *J*=2.1, 7.8 Hz), 5.18 (dd, 1H, *J*=7.8, 15.3 Hz), 5.63 (ddd, 1H, *J*=7.8, 8.3, 15.3 Hz), 6.72-6.80 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: -2.0, 14.8, 22.5, 28.1, 29.5, 56.6, 82.4, 127.8, 129.3, 131.4, 133.0, 150.5, 166.6. HR-MS *m/z*: Calcd for $C_{17}H_{29}NO_3Si$ 323.1916. Found: 323.1925.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(triisopropylsilanyl)propenyl]pyrrolidine-1-carboxylate (4b):** IR (neat):1768, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (s, 21H), 1.51 (s, 9H), 1.54-1.60 (m, 2H), 1.79 (d, 3H, *J*=7 .3 Hz), 2.37 (dd, 1H, *J*=1.5, 14.6 Hz), 2.74-2.84 (m, 1H), 4.58 (dt, 1H, *J*=1.9, 8.3 Hz), 5.25 (dd, 1H, *J*=7.3, 15.5 Hz), 5.68 (td, td, 1H, *J*=8.3, 15.5 Hz), 6.70-6.78 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 10.9, 15.2, 18.7, 28.0, 29.1, 56.5, 82.4, 127.9, 130.0, 133.0, 131.4, 150.5, 166.6. HR-MS *m/z*: Calcd for $C_{23}H_{41}NO_3Si$: 407.2856. Found: 407.2855.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(triphenylsilanyl)propenyl]pyrrolidine-1-carboxylate (4c):** IR (neat):1766, 1714 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.42 (s, 9H), 1.70 (d, 3H, *J*=6.8 Hz), 2.05 (dd, 1H, *J*=1.6, 16.2 Hz), 2.24-2.40 (m, 2H), 2.64 (tdd, 1H, *J*=2.9, 8.8, 16.2 Hz), 4.49 (dt, 1H, J=2.1, 9.3 Hz), 5.16 (dd, 1H, *J*=7.8, 15.3 Hz), 5.72 (td, 1H, *J*=7.3, 15.3 Hz), 6.62-6.72 (m, 1H), 7.32-7.44 (m, 9H), 7.46-7.51 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 14.8, 19.1, 27.9, 28.0, 56.4, 82.6, 127.3, 127.8, 129.6, 130.3, 131.2, 132.9, 134.2, 135.6, 138.2, 140.0, 150.4, 166.5. HR-MS *m/z*: Calcd for $C_{32}H_{35}NO_3Si$: 509.2386. Found: 509.2397.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(trimethylsilanyl)propenyl]pyrrolidine-1-carboxylate (4'a):** IR (neat): 1776, 1736, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.38 (ddd, 1H, *J*=2.1, 6.8, 13.5 Hz), 1.46 (s, 9H), 1.75 (d, 3H, *J*=7.3 Hz), 1.81 (d, 1H, *J*=13.5 Hz), 2.26(d, 1H, *J*=16.5 Hz), 2.75-2.82 (m, 1H), 4.83 (dt, 1H, *J*=2.1, 10.2 Hz), 5.15 (t, 1H, *J*=10.2 Hz), 5.47 (dt, 1H, *J*=7.8, 10.2 Hz), 6.66-6.74 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: -1.6, 14.9, 19.2, 28.1, 29.5, 51.6, 82.5, 127.9, 128.1, 131.3, 133.0, 150.8, 167.0. HR-MS *m/z*: Calcd for $C_{17}H_{29}NO_3Si$: 323.1916. Found: 323.1910.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(triisopropylsilanyl)propenyl]pyrrolidine-1-carboxylate (4'b):** IR (neat): 1766, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.05 (s, 21H), 1.49 (s, 9H), 1.50-1.60 (m, 1H), 1.73-1.80 (m, 3H), 1.83-1.93 (m, 1H), 2.25-2.35 (m, 1H), 2.78-2.90 (m, 1H), 4.90-5.00 (m, 1H), 5.30-5.40 (m, 1H), 5.50-5.62 (m, 1H), 6.67-6.78 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 11.0, 11.4, 14.9, 18.7, 28.1, 29.2, 30.9, 51.6, 82.5, 127.9, 128.6, 131.2, 133.0, 150.5, 166.8. HR-MS *m/z*: Calcd for $C_{23}H_{41}NO_3Si$: 4.702856. Found: 407.2853.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(triphenylsilanyl)propenyl]pyrrolidine-1-carboxylate (4'c):** IR (neat): 1768, 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.51 (s, 9H), 1.44-1.54 (m, 1H), 1.61 (d, 3H, *J*=6.8 Hz), 1.90-1.99 (m, 1H), 2.35 (ddd, 1H, *J*=2.1, 5.9, 14.5 Hz), 2.67 (dd, 1H, *J*=10.2, 14.5 Hz), 5.70 (td, 1H, *J*=5.9, 11.1 Hz), 6.57-6.65 (m, 1H), 7.34-7.46 (m, 9H), 7.53-7.58 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 14.8, 15.9, 28.1, 51.7, 852.5, 126.0, 127.9, 129.5, 129.7, 131.3, 132.6, 134.1, 135.8, 150.5, 166.8. HR-MS *m/z*: Calcd for $C_{32}H_{35}NO_3Si$: 509.2386. Found: 509.2394.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*E*)-3-(trimethylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5a):** IR (neat):

1738, 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.46 (ddd, 2H, *J*=1, 3.4, 8.3 Hz), 1.76 (ddd, 1H, *J*=5.4, 6.3, 13.3 Hz), 2.45 (ddd, 1H, *J*=7.3, 10.2, 13.3 Hz), 2.49 (s, 3H), 3.21-3.29 (m, 1H), 4.66 (td, 1H, *J*=5.4, 7.8 Hz), 5.19 (dd, 1H, *J*=7.8, 15.5 Hz), 5.26 (d, 1H, *J*=17.5 Hz), 5.28 (d, 1H, *J*=10.2 Hz), 5.67 (td, 1H, *J*=8.3, 15.5 Hz), 5.94 (ddd, 1H, *J*=6.3, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: -2.0, 22.6, 25.7, 30.7, 47.2, 57.7, 117.9, 127.6, 130.2, 134.4, 171.1, 175.6. HR-MS *m/z*: Calcd for $C_{14}H_{23}NO_2Si$: 265.1498. Found: 265.1507.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*E*)-3-(triisopropylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5b):** IR (neat): 1736, 1706 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.03 (s, 21H), 1.58 (d, 2H, *J*=8.3 Hz), 1.74 (ddd, 1H, *J*=5.4, 7.8, 13.3 Hz), 2.41-2.48 (m, 1H), 2.47 (s, 3H), 3.22-3.28 (m, 1H), 4.66 (dt, 1H, *J*=5.4, 8.3 Hz), 5.25 (d, 1H, *J*=17.5 Hz), 5.26 (d, 1H, *J*=10.2 Hz), 5.20-5.30 (m, 1H), 5.75 (td, 1H, *J*=8.3, 15.5 Hz), 5.96 (ddd, 1H, *J*=6.4, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 10.9, 15.3, 18.6, 25.6, 30.5, 47.2, 57.7, 117.9, 127.7, 131.1, 134.4, 171.1, 175.5. HR-MS *m/z*: Calcd for $C_{20}H_{35}NO_2Si$: 349.2437. Found: 349.2424.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*E*)-3-(triphenylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5c):** IR (neat): 1730, 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.49 (ddd, 1H, *J*=4.9, 6.4, 13.2 Hz), 2.24-2.34 (m, 2H), 2.40 (s, 3H), 3.12-3.19 (m, 1H), 4.58 (dt, 1H, *J*=4.9, 7.8 Hz), 5.11 (d, 1H, *J*=17.5 Hz), 5.13 (d, 1H, *J*=10.2 Hz), 5.18 (dd, 1H, *J*=7.8, 15.3 Hz), 5.65-5.80 (m, 2H), 7.34-7.45 (m, 9H), 7.48-7.53 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 19.3, 25.6, 30.2, 47.0, 57.5, 117.8, 127.8, 128.1, 129.6, 130.1, 134.1, 135.7, 171.0, 175.4. HR-MS *m/z*: Calcd for $C_{29}H_{29}NO_2Si$: 451.1967. Found: 451.1956.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*Z*)-3-(trimethylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'a):** IR (neat): 1736, 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 0.00 (s, 9H), 1.47 (ddd, 1H, *J*=2.1, 7.8, 13.7 Hz), 1.65 (ddd, 1H, *J*=5.9, 7.8, 13.4 Hz), 1.75 (ddd, 1H, *J*=1.5, 10.2, 13.7 Hz), 2.42 (ddd, 1H, *J*=5.9, 9.5, 13.4 Hz), 2.43 (s, 3H), 3.18-3.26 (m, 1H), 4.80-4.89 (m, 1H), 5.09 (dd, 1H, *J*=9.5, 10.2 Hz), 5.20 (d, 1H, *J*=17.5 Hz), 5.22 (d, 1H, *J*=10.2 Hz), 5.49 (td, 1H, *J*=7.8, 10.2 Hz), 5.89 (ddd, 1H, *J*=6.3, 10.2, 17.5Hz). ^{13}C-NMR ($CDCl_3$) δ: -1.9, 18.8, 25.5, 30.4, 46.9, 52.7, 117.8, 127.5, 128.3, 133.9, 171.0, 175.2. HR-MS *m/z*: Calcd for $C_{14}H_{23}NO_2Si$: 265.1498. Found: 265.1500.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*Z*)-3-(triisopropylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'b):** IR (neat): 1736, 1710 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.07 (s, 21H), 1.58 (ddd, 1H, *J*=2.1, 6.8, 14.5 Hz), 1.72 (ddd, 1H, *J*=5.8, 7.8, 13.3 Hz), 1.88 (ddd, 1H, *J*=1.5, 8.8, 14.5 Hz), 2.49 (s, 3H), 2.48-2.56 (m, 1H), 3.25-3.34 (m, 1H), 4.98-5.15 (m, 2H), 5.26 (d, 1H, *J*=17.5 Hz), 5.28 (d, 1H, *J*=10.2 Hz), 5.64 (dd, 1H, *J*=6.8, 11.3 Hz), 5.94 (ddd, 1H, *J*=6.3, 10.2, 17.5 Hz). ^{13}C-NMR ($CDCl_3$) δ: 11.0, 11.1, 18.7, 25.7, 30.2, 47.1, 52.9, 118.0, 127.7, 129.5, 134.2, 171.2, 175.4. HR-MS *m/z*: Calcd for $C_{20}H_{35}NO_2Si$: 349.2437. Found: 349.2444.

***rel*-(3*S*,5*R*)-1-Acetyl-5-[(1*Z*)-3-(triphenylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'c):** IR (neat): 1732, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ: 1.11 (ddd, 1H, *J*=5.9, 7.8, 13.7 Hz), 1.55 (ddd, 1H, *J*=7.8, 9.3, 13.7 Hz), 2.45 (s, 3H), 2.41 (ddd, 1H, *J*=1.5, 6.4, 14.2 Hz), 2.72 (ddd, 1H, *J*=1.5, 11.2, 14.2 Hz), 2.98-3.06 (m, 1H), 4.65-4.73 (m, 1H), 5.09 (d, 1H *J*=17.5 Hz), 5.19 (d, 1H, *J*=10.2 Hz), 5.05-5.15 (m, 1H), 5.71 (ddt, 1H, *J*=1.5, 6.3, 10.2 Hz), 5.83 (ddd, 1H, *J*=6.3, 10.2, 17.5 Hz), 7.34-7.44 (m, 9H), 7.52-7.58 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ: 15.7, 25.5, 29.3, 30.9, 46.8, 52.9, 117.7, 127.3, 127.9, 128.9, 129.7, 134.1, 134.2, 135.8, 171.3, 175.5. HR-MS *m/z*: Calcd for $C_{29}H_{29}NO_2Si$: 451.1967. Found: 451.1979.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3,5-bis[(1*E*)-3-(trimethylsilanyl)propenyl]pyrrolidine-1-carboxylate**

(6a): IR (neat): 1784, 1748, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : -0.02 (s, 18H), 1.42-1.50 (m, 3H), 1.47 (s, 9H), 1.51-1.63 (m, 2H), 2.36 (ddd, 1H, *J*=7.3, 8.8, 12.7 Hz), 3.04-3.13 (m, 1H), 4.33-4.42 (m, 1H), 5.18 (dd, 1H, *J*=7.8, 15.3 Hz), 5.28 (dd, 1H, *J*=6.8, 15.3 Hz), 5.50-5.64 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : -1.9, 22.6, 23.0, 28.0, 32.6, 46.3, 58.6, 82.5, 124.4, 128.6, 129.9, 130.6, 150.2, 174.8. HR-MS *m/z*: Calcd for $C_{21}H_{39}NO_3Si_2$: 409.2468. Found: 409.2473.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3,5-bis[(1*E*)-3-(triisopropylsilanyl)propenyl]pyrrolidine-1-carboxylate (6b):** IR (neat): 1776, 1726 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 1.04 and 1.05 (two s, 42H), 1.49 (s, 9H), 1.48-1.66 (m, 5H), 2.35 (ddd, 1H, *J*=7.8, 9.3, 13.2 Hz), 3.05-3.13 (m, 1H), 4.33-4.40 (m, 1H), 5.25 (dd, 1H, *J*=7.8, 15.1 Hz), 5.36 (dd, 1H, *J*=7.3, 15.6 Hz), 5.60-5.78 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : 10.9, 15.2, 15.6, 18.6, 27.9, 32.2, 46.1, 58.6, 82.4, 124.2, 128.5, 130.5, 131.6, 150.1, 174.6. HR-MS *m/z*: Calcd for $C_{33}H_{63}NO_3Si_2$: 577.4346. Found: 577.4351.

***rel*-(3*S*,5*R*)-1-Acetyl-3,5-bis[(1*E*)-3-(trimethylsilanyl)propenyl]pyrrolidin-2-one (6c):** IR (neat): 1734, 1704 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : -0.02 (s, 18H), 1.44 (ddd, 2H, *J*=1.5, 3.4, 7.3 Hz), 1.49 (d, 2H, *J*=7.9 Hz), 1.65 (ddd, 1H, *J*=5.3, 6.3, 13.2 Hz), 2.41 (ddd, 1H, *J*=8.3, 10.2, 13.2 Hz), 2.46 (s, 3H), 3.16 (td, 1H, *J*=7.3, 8.8 Hz), 5.31 (dd, 1H, *J*=7.8, 15.1 Hz), 5.56-5.68 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : -1.8, 19.0, 22.7, 25.7, 32.5, 42.0, 57.5, 123.4, 127.9, 129.7, 130.6, 171.2, 176.7. HR-MS *m/z*: Calcd for $C_{18}H_{33}NO_2Si_2$: 351.2049. Found: 351.2039.

***rel*-(3*S*,5*R*)-1-Acetyl-3,5-bis[(1*E*)-3-(triisopropylsilanyl)propenyl]pyrrolidin-2-one (6d):** IR (neat): 11734, 1708 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.95-1.16 (m, 42H), 1.56-1.68 (m, 1H), 1.61 (dd, 4H, *J*=7.8, 19.1 Hz), 2.35-2.50 (m, 1H), 2.46 (s, 3H), 3.10-3.20 (m, 1H), 4.62 (dt, 1H, *J*=5.8, 7.8 Hz), 5.26 (dd, 1H, *J*=7.8, 14.7 Hz), 5.38 (dd, 1H, *J*=6.8, 15.3 Hz), 5.66-5.78 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : 10.9, 15.4, 15.8, 18.6, 25.7, 31.5, 46.6, 57.6, 124.1, 128.0, 130.7, 132.0, 171.3, 176.4. HR-MS *m/z*: Calcd for $C_{30}H_{57}NO_2Si_2$: 519.3927. Found: 519.3947.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(trimethylsilanyl)propenyl]-5-[(1*E*)-3-(trimethylsilanyl)propenyl]pyrrolidine-1-carboxylate (6'a):** IR (neat): 1774, 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : -0.02 and -0.00 (two s, 18H), 1.49 (s, 9H), 1.43-1.50 (m, 5H), 2.36 (ddd, 1H, *J*=7.8, 9.3, 13.2 Hz), 3.25-3.40 (m, 1H), 4.35-4.45 (m, 1H), 5.17 (dd, 1H, *J*=7.8, 15.5 Hz), 5.26 (dd, 1H, *J*=8.8, 10.3 Hz), 5.57-5.69 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : -1.6, -1.9, 19.0, 22.6, 28.0, 33.3, 41.7, 58.6, 82.6, 123.6, 128.5, 129.9, 130.4, 150.2, 174.9. HR-MS *m/z*: Calcd for $C_{21}H_{39}NO_3Si_2$: 409.2468. Found: 409.2457.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(trimethylsilanyl)propenyl]-5-[(1*E*)-3-(trimethylsilanyl)propenyl]-pyrrolidin-2-one (6'b):** IR (neat): 1728, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : - 0.04 (s, 18H), 1.40-1.75 (m, 5H), 2.48 (s, 3H), 2.40-2.55 (n, 1H), 3.42-3.50 (m, 1H), 4.61-4.69 (m, 1H), 5.21 (dd, 1H, *J*=7.3, 15.1 Hz), 5.31 (dd, 1H, *J*=9.3, 10.7 Hz), 5.58-5.75 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : -1.8, 19.0, 22.7, 25.7, 32.5, 42.0, 57.5, 123.4, 127.9, 129.7, 130.6, 171.2, 176.7. HR-MS *m/z*: Calcd for $C_{18}H_{33}NO_2Si_2$: 351.2049. Found: 351.2041.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*E*)-3-(trimethylsilanyl)propenyl]-5-[(1*Z*)-3-(trimethylsilanyl)propenyl]pyrrolidine-1-carboxylate (6''a):** IR (neat): 1784, 1746, 1722cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : -0.02 and –0.04 (two s, 18H), 1.19-1.58 (m, 4H), 1.46 (s, 9H), 1.69-1.80 (m, 1H), 2.38 (ddd, 1H, *J*=7.3, 8.8, 12.7 Hz), 3.05-3.15 (m, 1H), 4.63-4.72 (m, 1H), 5.21 (dd, 1H, *J*=8.3, 10.2 Hz), 5.28 (td, 1H, *J*=6.8, 15.5 Hz), 5.44-5.62 (m, 2H). ^{13}C-NMR ($CDCl_3$) δ : -1.9, -1.6, 19.1, 23.1, 28.1, 32.4, 46.2, 53.4, 82.7, 124.2,

127.7, 128.6, 130.7, 150.1, 174.9. HR-MS *m/z*: Calcd for $C_{21}H_{39}NO_3Si_2$: 409.2468. Found: 409.2454.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*E*)-3-(trimethylsilanyl)propenyl]-5-[(1*Z*)-3-(trimethylsilanyl)propenyl]-pyrrolidin-2-one (6''b):** IR (neat): 1730, 1698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.00 (s, 18H), 1.44-1.55 (m, 3H), 1.58-1.65 (m, 1H), 1.78 (dd, 1H, *J*=11.2, 13.7 Hz), 2.38-2.50 (m, 1H), 2.47 (s, 3H), 3.14-3.23 (m, 1H), 4.80-4.88 (m, 1H), 5.14 (dd, 1H, *J*=9.3, 10.7 Hz), 5.30 (dd, 1H, *J*=6.8, 15.6 Hz), 5.46-5.55 (m, 1H), 5.62 (dt, 1H, *J*=15.6, 8.3 Hz). ^{13}C-NMR ($CDCl_3$) δ : -1.9, -1.7, 19.0, 23.1, 25.7, 31.8, 46.7, 52.9, 124.0, 128.1, 128.2, 131.1, 171.4, 176.4. HR-MS *m/z*: Calcd for $C_{18}H_{37}NO_2Si_2$: 355.2362. Found: 355.2373.

***tert*-Butyl *rel*-(3*R*,5*S*)-5-Ethyl-2-oxo-3-[3-(trimethylsilanyl)propyl]pyrrolidine-1-carboxylate (7a):** IR (neat): 1784, 1744, 1722 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.00 (s, 9H), 0.45-0.59 (m, 2H), 0.91 (t, 3H, *J*=7.8 Hz), 1.30-1.60 (m, 5H), 1.55 (s, 9H), 1.90-2.30 (m, 2H), 2.31 (ddd, 1H, *J*=7.8, 9.8, 13.5 Hz), 2.43 -2.53 (m, 1H), 3.85-3.95 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : -1.9, 8.7, 16.4, 21.8, 27.2, 27.9, 28.0, 28.9, 35.3, 42.3, 57.2, 82.5, 150.4, 176.6. HR-MS *m/z*: Calcd for $C_{17}H_{33}NO_3Si$: 327.2229. Found: 327.2220.

***tert*-Butyl *rel*-(3*R*,5*S*)-5-Ethyl-2-oxo-3-[3-(triisopropylsilanyl)propyl]pyrrolidine-1-carboxylate (7b):** IR (neat): 1784, 1745, 1720 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.50-0.68 (m, 2H), 0.89 (t, 3H, *J*=7.8 Hz), 1.03 (s, 21H), 1.28-1.60 (m, 5H), 1.53 (s, 9H), 1.90-2.80 (m, 2H), 2.30 (ddd, 1H, *J*=7.8, 10.2, 14.3 Hz), 2.42-2.52 (m, 1H), 3.85-3.93 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : 8.7, 9.1, 10.9, 18.8, 22.2, 27.7, 28.0, 28.9, 36.3, 42.2, 57.2, 82.6, 150.5, 176.8. HR-MS *m/z*: Calcd for $C_{23}H_{45}NO_3Si$: 411.3169. Found: 411.3170.

***tert*-Butyl *rel*-(3*R*,5*S*)-5-Ethyl-2-oxo-3-[3-(triphenylsilanyl)propyl]pyrrolidine-1-carboxylate (7c):** IR (neat): 1772, 1714 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.82 (t, 3H, *J*=7.8 Hz), 1.14-1.28 (m, 1H), 1.32-1.60 (m, 5H), 1.51 (s, 9H), 1.90-2.06 (m, 2H), 2.16 (ddd, 1H, *J*=7.8, 10.2, 12.7 Hz), 2.41 (ddd, 1H, *J*=4.4, 9.8, 19.1 Hz), 3.76-3.86 (m, 1H), 7.32-7.40 (m, 9H), 7.48-7.54 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ : 8.7, 13.0, 21.9, 28.0, 28.8, 35.5, 42.2, 57.2, 82.6, 127.9, 129.4, 135.0, 135.5, 150.4, 176.5. HR-MS *m/z*: Calcd for $C_{26}H_{34}NO_3Si$ (M^+-C_6H_5): 436.2307. Found: 436.2311.

***rel*-(3*R*,5*S*)-1-Acetyl-5-ethyl-3-[3-(trimethylsilanyl)propyl]pyrrolidin-2-one (7d):** IR (neat): 1732, 1698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.00 (s, 9H), 0.45-0.60 (m, 2H), 0.88 (t, 3H, *J*=7.8 Hz), 1.35-1.50 (m, 5H), 1.88-1.96 (m, 1H), 2.02-2.12 (m, 1H), 2.14-2.20 (m, 1H), 2.33 (ddd, 1H, *J*=8.3, 9.7, 13.3 Hz), 2.49 (s, 3H), 2.44-2.58 (m, 1H), 4.04-4.12 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : -1.6, 8.8, 16.5, 21.9, 25.8, 27.1, 28.2, 35.6, 42.6, 56.7, 169.9, 178.5. HR-MS *m/z*: Calcd for $C_{14}H_{27}NO_2Si$: 269.1811. Found: 269.1805.

***rel*-(3*R*,5*S*)-1-Acetyl-5-ethyl-3-[3-(tritriisopropylsilanyl)propyl]pyrrolidin-2-one (7e):** IR (neat): 1736, 1698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.52-0.70 (m, 2H), 0.87 (t, 3H, *J*=7.8 Hz), 1.04 (s, 21H), 1.37-1.55 (m, 5H), 1.88-1.99 (m, 1H), 2.06 (ddd, 1H, *J*=3.8, 7.8, 13.5 Hz), 2.32 (ddd, 1H, *J*=8.3, 9.7, 13.5 Hz), 2.49 (s, 3H), 2.50-2.59 (m, 1H), 4.03-4.11 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : 8.8, 9.1, 10.9, 18.8, 27.2, 25.8, 27.0, 28.1, 30.9, 36.4, 42.4, 56.7, 171.8, 178.5. HR-MS *m/z*: Calcd for $C_{17}H_{32}NO_2Si$: 310.2202. Found: 310.2192.

***rel*-(3*R*,5*S*)-1-Acetyl-5-ethyl-3-[3-(triphenylsilanyl)propyl]pyrrolidin-2-one (7f):** IR (neat): 1728, 1692 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.80 (t, 3H, *J*=7.4 Hz), 1.26 (ddd, 1H, *J*=6.3, 8.3, 14.3 Hz), 1.34-1.70 (m, 6H), 1.94-2.06 (m, 2H), 2.19 (ddd, 1H, *J*=7.3, 11.5, 14.3 Hz), 2.46 (s, 3H), 2.42-2.52 (m, 1H), 3.96-4.04 (m, 1H), 7.33-7.44 (m, 9H), 7.49-7.54 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ : 8.7, 13.0, 21.9, 25.8, 26.9, 28.0, 35.6, 42.4, 56.6, 127.9, 129.5, 134.9, 135.5, 171.8, 178.3. HR-MS *m/z*: Calcd for $C_{23}H_{28}NO_2Si$ (M^+-C_6H_5): 378.1889. Found: 378.1873.

***tert*-Butyl *rel*-(3*R*,5*S*)-3-Ethyl-2-oxo-5-[3-(trimethylsilanyl)propyl]pyrrolidine-1-carboxylate (7'a):** IR (neat): 1784, 1746, 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.00 (s, 9H), 0.46-0.62 (m, 2H), 1.00 (t, 3H, *J*=7.8 Hz), 1.25-1.41 (m, 3H), 1.41-1.60 (m, 2H), 1.54 (s, 9H), 1.90-2.10 (m, 2H), 2.28-2.42 (m, 2H), 3.91-3.99 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : -1.7, 11.7, 16.6, 19.2, 24.5, 28.0, 29.0, 39.0, 44.2, 56.0, 82.6, 150.5, 176.5. HR-MS *m/z*: Calcd for $C_{17}H_{33}NO_3Si$: 327.2229. Found: 327.2219.

***tert*-Butyl *rel*-(3*R*,5*S*)-3-Ethyl-2-oxo-5-[3-(triisopropylsilanyl)propyl]pyrrolidine-1-carboxylate (7'b):** IR (neat): 1784, 1750, 1724 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.52-0.70 (m, 2H), 0.99 (t, 3H, *J*=7.9 Hz), 1.03 (s, 21H), 1.26-1.60 (m, 5H), 1.53 (s, 9H), 1.86-1.98 (m, 1H), 1.98-2.09 (m, 1H), 2.25-2.44 (m, 2H), 3.92-4.00 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : 9.4, 10.9, 11.7, 19.1, 19.6, 24.6, 28.0, 28.9, 39.8, 44.2, 55.8, 82.7, 150.4, 176.5. HR-MS *m/z*: Calcd for $C_{23}H_{45}NO_3Si$: 411.3169. Found: 411.3169.

***tert*-Butyl *rel*-(3*R*,5*S*)-3-Ethyl-2-oxo-5-[3-(triphenylsilanyl)propyl]pyrrolidine-1-carboxylate (7'c):** IR (neat):1780, 1742, 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.91 (t, 3H, *J*=7.3 Hz), 1.14-1.28 (m, 1H), 1.30-1.60 (m 6H), 1.49 (s, 9H), 1.80-1.90 (m, 1H), 2.06-2.15 (m, 1H), 2.17 (ddd, 1H, *J*=7.8, 10.2, 13.8 Hz), 2.31 (ddd, 1H, *J*=4.9, 9.3, 12.7 Hz), 3.84-3.93 (m, 1H), 7.32-7.44 (m, 9H), 7.47-7.54 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ : 11.7, 13.2, 19.3, 24.5, 28.0, 28.9, 39.1, 44.1, 55.8, 82.7, 127.9, 129.5, 134.8, 135.5, 150.4, 176.4. HR-MS *m/z*: Calcd for $C_{28}H_{30}NO_3Si$ (M^+-C_4H_9): 456.1994. Found: 456.1994.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(trimethylsilanyl)propyl]pyrrolidin-2-one (7'd):** IR (neat): 1736, 1694 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.00 (s, 9H), 0.47-0.62 (m, 2H), 0.99 (t, 3H, *J*=7.8 Hz), 1.30-1.50 (m, 4H), 1.75-1.83 (m, 1H), 1.85-2.00 (m, 1H), 2.04 (dd, 1H, *J*=8.6, 13 Hz), 2.50 (s, 3H), 2.57-2.63 (m, 1H), 4.23 (dt, 1H, *J*=3.5, 8.6 Hz). ^{13}C-NMR ($CDCl_3$) δ : -1.8, 11.3, 16.4, 20.6, 23.5, 25.4, 28.6, 36.4, 43.5, 54.6, 170.9, 177.4. HR-MS *m/z*: Calcd for $C_{14}H_{27}NO_2Si$: 269.1811. Found: 269.1821.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(triisopropylsilanyl)propyl]pyrrolidin-2-one (7'e):** IR (neat): 1736, 1702 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.50-0.70 (m, 2H), 1.01 (t, 3H, *J*=7.8 Hz), 1.03 (s, 21H), 1.30-1.55 (m, 5H), 1.93 (ddd, 1H, *J*=5.4, 7.8, 13.3 Hz), 2.08-2.17 (m, 1H), 2.33 (ddd, 1H, *J*=8.3, 10.2, 13.3 Hz), 2.40-2.50 (m, 1H), 2.48 (s, 3H), 4.07-4.16 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : 9.3, 10.9, 11.7, 18.8, 19.7, 24.7, 25.8, 28.2, 39.1, 44.4, 55.3, 171.8, 178.1. HR-MS *m/z*: Calcd for $C_{17}H_{32}NO_2Si$: 310.2202. Found: 310.2199.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(triphenylsilanyl)propyl]pyrrolidin-2-one (7'f):** IR (neat): 1728, 1697 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.93 (t, 3H, *J*=7.3 Hz), 1.25 (ddd, 1H, *J*=6.3, 8.2, 14.6 Hz), 1.30-1.50 (m, 6H), 1.85 (ddd, 1H, *J*=4.8, 7.3, 14.6 Hz), 2.12-2.24 (m, 2H), 2.36 (ddt, 1H, *J*=4.8, 8.2, 9.3 Hz), 2.44 (s, 3H), 4.02-4.11 (m, 1H), 7.33-7.44 (m, 9H), 7.48-7.53 (m, 6H). ^{13}C-NMR ($CDCl_3$) δ : 11.7, 12.9, 19.2, 24.6, 25.8, 28.1, 38.3, 44.3, 55.2, 127.9, 129.4, 134.9, 135.5, 171.8, 178.1. HR-MS *m/z*: Calcd for $C_{29}H_{33}NO_2Si$ (M^+-C_6H_5): 378.1889. Found: 378.1888.

***tert*-Butyl *rel*-(3*R*,5*S*)-2-Oxo-3,5-bis[3-(trimethylsilanyl)propyl]pyrrolidine-1-carboxylate (8a):** IR (neat): 1786, 1744, 1716 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : -0.04 (s, 18H), 0.39-0.56 (m, 4H), 1.16-1.50 (m, 7H), 1.50 (s, 9H), 1.83-2.02 (m, 2H), 2.27-2.37 (m, 1H), 2.36-2.46 (m, 1H), 3.90-3.98 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ : 0.04, 18.1, 18.3, 20.8, 23.6, 29.7, 31.2, 37.1, 40.7, 44.23, 57.7, 84.3, 152.1, 178.4. HR-MS *m/z*: Calcd for $C_{21}H_{43}NO_3Si_2$: 413.2781. Found: 413.2779.

***tert*-Butyl *rel*-(3*R*,5*S*)-2-Oxo-3,5-bis[3-(triisopropylsilanyl)propyl]pyrrolidine-1-carboxylate (8b):** IR (neat): 1786, 1746, 1718 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ : 0.45-0.65 (m, 4H), 1.02 and 1.03 (two s, 42H),

1.22-1.47 (m, 5H), 1.54 (s, 9H), 1.88-2.08 (m, 2H), 2.30 (ddd, 1H, *J*=7.8, 9.3, 12.7 Hz), 2.42-2.54 (m, 1H), 3.92-3.98 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 9.1, 9.3, 10.8, 18.8, 19.6, 22.2, 28.0, 29.3, 36.3, 39.8, 42.2,55.9, 82.6, 150.4, 176.8. HR-MS *m/z*: Calcd for $C_{33}H_{67}NO_3Si_2$: 581.4659. Found: 581.4676.

***rel*-(3*R*,5*S*)-1-Acetyl-3,5-bis[3-(trimethylsilanyl)propyl]pyrrolidin-2-one (8c):** IR (neat): 1736, 1698 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ:0.00 (s, 18H), 0.39-0.59 (m, 4H), 1.17-1.50 (m, 5H), 1.80-1.95 (m, 1H), 2.00-2.12 (m, 1H), 2.31 (ddd, 1H, *J*=8.3, 10.3, 13.3 Hz), 2.46 (s, 3H), 2.41-2.55 (m, 1H), 4.06-4.14 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ:-1.7, 16.4, 19.3, 21.9, 25.7, 28.8, 35.6, 38.3, 42.7, 55.5, 171.7, 178.4. HR-MS *m/z*: Calcd for $C_{18}H_{37}NO_2Si_2$: 355.2362. Found: 355.2373.

***rel*-(3*R*,5*S*)-1-Acetyl-3,5-bis[3-(triisopropylsilanyl)propyl]pyrrolidin-2-one (8d):** IR (neat): 1734, 1700 cm^{-1}. ^{1}H-NMR ($CDCl_3$) δ:0.48-0.72 (m, 4H), 0.95-1.10 (m, 42H), 1.27-1.57 (m, 4H), 1.86-1.99 (m, 1H), 2.03-2.18 (m, 1H), 2.32 (ddd, 1H, *J*=8.8, 10.3, 13.3 Hz), 2.49 (s, 3H), 2.50-2.60 (m, 1H), 4.09-4.18 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ:9.1, 9.2, 10.9, 18.8, 19.7, 22.2, 25.8, 28.5, 36.4, 39.1, 42.5, 55.4, 171.7, 178.5. HR-MS *m/z*: Calcd for $C_{30}H_{61}NO_2Si_2$: 523.4240. Found: 523.4227.

REFERENCES AND NOTES

1. B. M. Domingueg and P. M. Cullis, *Tetrahedron Lett*., 1999, **40**, 5783; N., Katagiri, Y. Yamatoya, and M. Ishikura, *Tetrahedron Lett*., 1999, **40**, 9069; S. M. Daluge, M. T. Martin, B. R. Sickles, and D. A. Livingston, *Nucleosides, Nucleotides & Nucleic Acids*, 2000, **19**, 297; J. Qiu and R. B. Silverman, *J. Med. Chem.*, 2000, **43**, 706; M. E.B. Smith, M. C. Lloyd, N. Derrien, R. C. Llyoid, S. J. C. Taylor, D. A. Chaplin, G. Casy, and R. McCague, *Tetrahedron, Asymmetry*, 2001, **12**, 703; J. Shi and R. F. Schinazi, *Nucleotides & Nucleic Acids*, 2001, **20**, 1367; M. Ishikura, S. Kudo, N. Ohnuki, and N. Katagiri, *Heterocycles*, 2002, **57**, 241.
2. R. H. Grubbs, S. J. Miller, and G. C. Fu, *Acc. Chem. Res.*, 1995, **28**, 446; S. K. Armstrong, *J. Chem. Soc., Perkin Trans. 1*, 1998, 371; S. Blechert, *Pure Appl. Chem*., 1999, **71**, 1393; A. Fürstner, Eds., *Alkene Metathesis in Organic Synthesis*, Springer-Verlag, Berlin, 1998; A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, **39**, 3013; T. M. Trnka and R. H. Gribbs, *Acc. Chem. Res*., 2001, **34**, 18.
3. M. F. Schneider, N. Lucas, J. Velder, and S. Blechert, *Angew. Chem., Int. Ed*., 1997, **36**, 257.
4. M. Ishikura, M. Saijo, and A. Hino, *Heterocycles*, 2002, **57**, 241.
5. E. L. Dias, S. T. Nguyen, and R. H. Grubbs, *J. Am. Chem. Soc*., 1997, **119**, 3887; O. M. Aagaard, R. J. Meier, and F. Buda, *J. Am. Chem. Soc*., 1998, **120**, 7174; M. S. Sanford, J. A. Love, and R. H. Grubbs, *J. Am. Chem. Soc*., 2001, **123**, 6543.
6. M. Ulman and R. H. Grubbs, *J. Org. Chem*., 1999, **64**, 7202; Q. Yao, *Angew. Chem., Int. Ed*., 2000, **39**, 3896; L. Jafarpour and S. P. Nolan, *Org. Lett*., 2000, **2**, 4075; S. B. Garber, J. S. Kingsbury, B. L. Gray, and A. H. Hoveyda, *J. Am. Chem. Soc*., 2000, **122**, 8186; L. Jafarpour and S. P. Nolan, *J. Organomet. Chem*., 2001, **717-718**, 17.