

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

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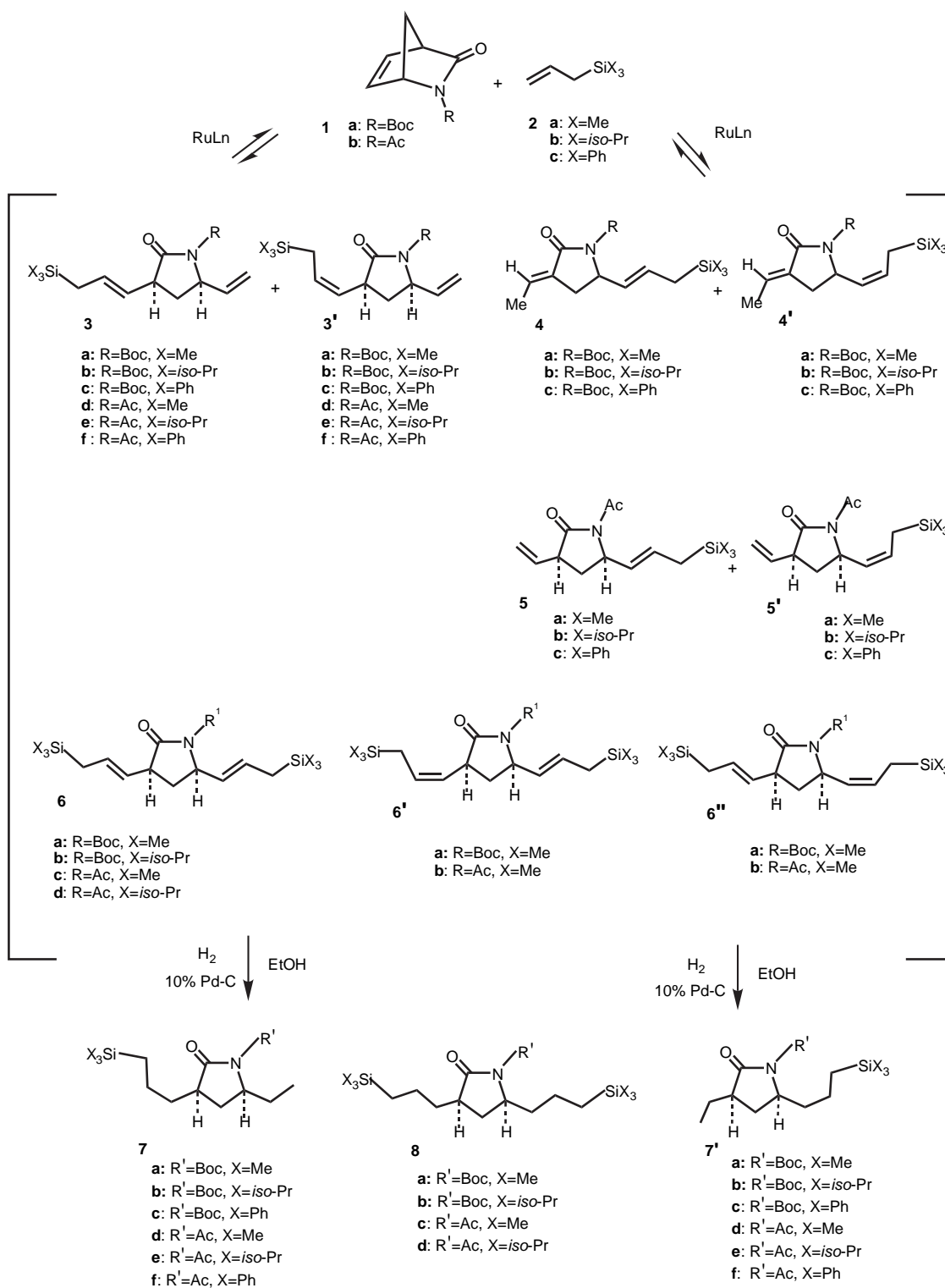
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Abstract – An examination of the ring-opening cross-metathesis reaction of *N*-substituted 2-azabicyclo[2.2.1]hept-5-en-3-ones (ABH) (**1**) with allylsilanes (**2**) in the presence of ruthenium catalysts was undertaken.

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 nucleosides, 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 $[\text{Cl}_2(\text{PCy}_3)_2\text{Ru}=\text{CHPh}]$ -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

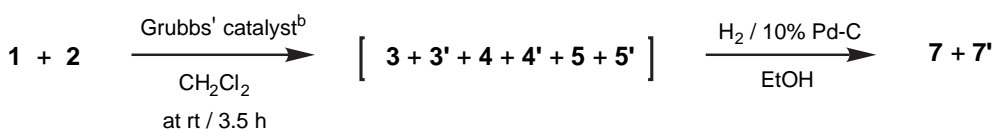
Treatment of **1a** with **2a,b** in the presence of 5 mol% of catalyst for 3.5 h provided a pair of regioisomers (**7a,b**) and (**7'a,b**) in ratios of approximately 2.2~2.5:1, respectively. Otherwise, a poor reaction rate was observed in the reaction of **1a** with **2c**, leading to **7c** and **7'c**,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



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 Ph₃Si in complex (**A**) might exert an influence on the reaction outcome (Scheme 2).⁵ Moreover, **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	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)
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 CH₂Cl₂ at room temperature for 3.5 h under an argon atmosphere.

^b (PCy₃)₂Cl₂Ru=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-allylsilylamine 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 CH₂Cl₂ for 6 h). This might be ascribable to the known

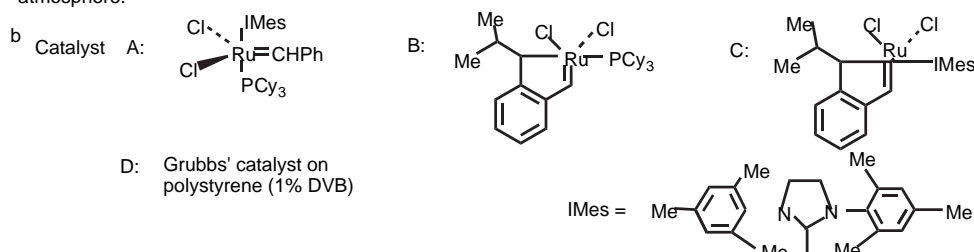
thermal stability of second generation ruthenium catalyst,⁶ enabling to force the cross-metathesis reaction of **3**, **3'**, **4**, **4'**, **5** and **5'** with **2** to lead to **6**, **6'**, **6''**.

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

$$\begin{array}{c}
 \mathbf{1} + \mathbf{2} \xrightarrow[\text{at rt / 3.5 h}]{\text{catalyst}^b, \text{CH}_2\text{Cl}_2} \left[\begin{array}{c} \mathbf{3} + \mathbf{3}' + \mathbf{4} + \mathbf{4}' + \mathbf{5} + \mathbf{5}' \\ \mathbf{6} + \mathbf{6}' + \mathbf{6}'' \end{array} \right] \xrightarrow[\text{EtOH}]{\text{H}_2 / 10\% \text{ Pd-C}} \mathbf{7} + \mathbf{7}' + \mathbf{8}
 \end{array}$$

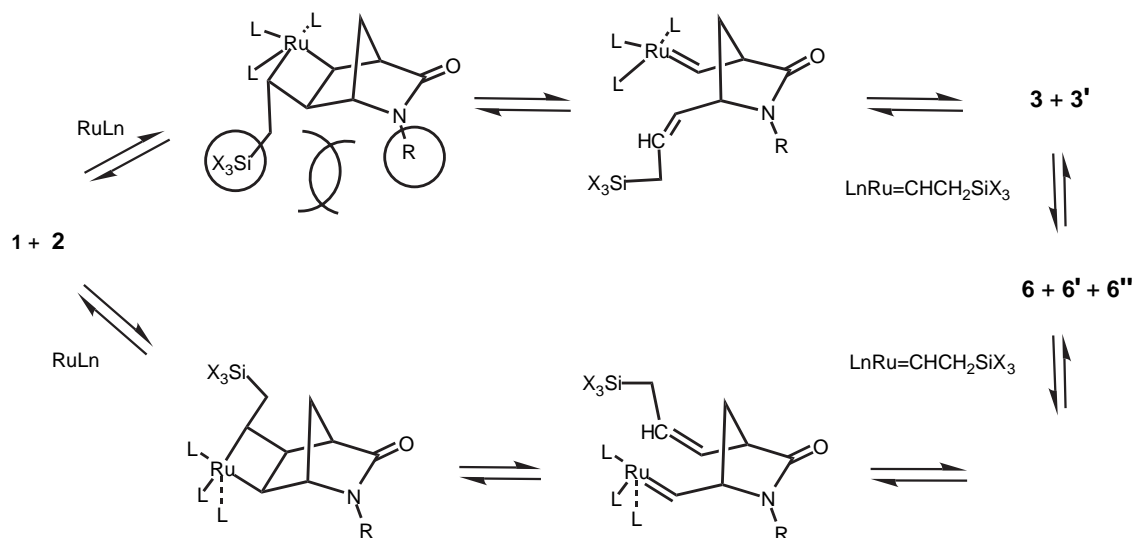
1	Catalyst	2 (eq.)	Yield (%) ^c		
			7	7'	8
1a	A	2a (1.5)	38 (7a)	27 (7'a)	5 (8a)
	A	2a (2)	37 (7a)	24 (7'a)	10 (8a)
	A	2a (2) ^d	25 (7a)	10 (7'a)	15 (8a)
	A	2a (2) ^e	14 (7a)	5 (7'a)	50 (8a)
	A	2a (2) ^f	31 (7a)	22 (7'a)	14 (8a)
	A	2a (2) ^g	34 (7a)	30 (7'a)	3 (8a)
	A	2a (2) ^h	22 (7a)	15 (7'a)	15 (8a)
	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 CH₂Cl₂ in the presence of catalyst (5 mol%) at room temperature for 3.5 h under an argon atmosphere.



^c yields based on ABH (**1**). ^d in benzene ^e reflux for 6 h ^f for 20 h ^g in CHCl₃ ^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

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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 (7 μ m) (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 CH₂Cl₂ (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-(3S,5R)-2-Oxo-3-[(1E)-3-(trimethylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3a): IR (neat): 1782, 1748, 1720 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{Si}$: 323.1916. Found: 323.1923.

tert-Butyl rel-(3S,5R)-2-Oxo-3-[(1E)-3-(triisopropylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3b): IR (neat): 1774, 1720 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{23}\text{H}_{41}\text{NO}_3\text{Si}$: 407.2855. Found: 407.2858.

tert-Butyl rel-(3S,5R)-2-Oxo-3-[(1E)-3-(triphenylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3c): IR (neat): 1776, 1736 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{32}\text{H}_{35}\text{NO}_3\text{Si}$: 509.2386. Found: 509.2375.

rel-(3S,5R)-1-Acetyl-3-[(1E)-3-(trimethylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3d): IR (neat): 1732, 1704 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{Si}$: 265.1498 Found: 265.1495.

rel-(3S,5R)-1-Acetyl-3-[(1E)-3-(triisopropylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3e): IR (neat): 1738, 1704 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{35}\text{NO}_2\text{Si}$: 349.2437. Found: 349.2457.

rel-(3S,5R)-1-Acetyl-3-[(1E)-3-(triphenylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3f): IR (neat): 1734, 1700 cm^{-1} . $^1\text{H-NMR}$ (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). ¹³C-NMR (CDCl₃) 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 C₂₉H₂₉NO₂Si: 451.1967. Found: 451.1967.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(trimethylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'a)**: IR (neat): 1786, 1750, 1722 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₁₇H₂₉NO₃Si: 323.1916. Found: 323.1914.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(triisopropylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'b)**: IR (neat): 1782, 1724 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₃H₄₁NO₃Si: 407.2855. Found: 407.2856.

***tert*-Butyl *rel*-(3*S*,5*R*)-2-Oxo-3-[(1*Z*)-3-(triphenylsilyl)propenyl]-5-vinylpyrrolidine-1-carboxylate (3'c)**: IR (neat): 1780, 1744, 1720 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₃₂H₃₅NO₃Si: 509.2386. Found: 509.2404.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(trimethylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3'd)**: IR (neat): 1732, 1696 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₁₄H₂₃NO₂Si: 265.1498. Found: 265.1506.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(triisopropylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3'e)**: IR (neat): 1738, 1704 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₀H₃₅NO₂Si: 349.2437. Found: 349.2437.

***rel*-(3*S*,5*R*)-1-Acetyl-3-[(1*Z*)-3-(triphenylsilyl)propenyl]-5-vinylpyrrolidin-2-one (3'f)**: IR (neat): 1734, 1698 cm⁻¹. ¹H-NMR (CDCl₃) 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{Si}$: 451.1967. Found: 451.1979.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(trimethylsilyl)propenyl]pyrrolidine-1-carboxylate (4a)**: IR (neat): 1776, 1742, 1718 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{Si}$: 323.1916. Found: 323.1925.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(triisopropylsilyl)propenyl]pyrrolidine-1-carboxylate (4b)**: IR (neat): 1768, 1710 cm^{-1} . $^1\text{H-NMR}$ (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, 1H, $J=8.3, 15.5$ Hz), 6.70-6.78 (m, 1H). $^{13}\text{C-NMR}$ (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 $\text{C}_{23}\text{H}_{41}\text{NO}_3\text{Si}$: 407.2856. Found: 407.2855.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*E*)-3-(triphenylsilyl)propenyl]pyrrolidine-1-carboxylate (4c)**: IR (neat): 1766, 1714 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{32}\text{H}_{35}\text{NO}_3\text{Si}$: 509.2386. Found: 509.2397.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(trimethylsilyl)propenyl]pyrrolidine-1-carboxylate (4'a)**: IR (neat): 1776, 1736, 1720 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{17}\text{H}_{29}\text{NO}_3\text{Si}$: 323.1916. Found: 323.1910.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(triisopropylsilyl)propenyl]pyrrolidine-1-carboxylate (4'b)**: IR (neat): 1766, 1720 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{23}\text{H}_{41}\text{NO}_3\text{Si}$: 407.2856. Found: 407.2853.

***tert*-Butyl *rel*-(5*R*)-(3*E*)-3-Ethylidene-2-oxo-5-[(1*Z*)-3-(triphenylsilyl)propenyl]pyrrolidine-1-carboxylate (4'c)**: IR (neat): 1768, 1718 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (CDCl_3) δ : 14.8, 15.9, 28.1, 51.7, 82.5, 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 $\text{C}_{32}\text{H}_{35}\text{NO}_3\text{Si}$: 509.2386. Found: 509.2394.

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

1738, 1702 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{Si}$: 265.1498. Found: 265.1507.

rel-(3S,5R)-1-Acetyl-5-[(1E)-3-(triisopropylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5b): IR (neat): 1736, 1706 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{35}\text{NO}_2\text{Si}$: 349.2437. Found: 349.2424.

rel-(3S,5R)-1-Acetyl-5-[(1E)-3-(triphenylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5c): IR (neat): 1730, 1702 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{Si}$: 451.1967. Found: 451.1956.

rel-(3S,5R)-1-Acetyl-5-[(1Z)-3-(trimethylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'a): IR (neat): 1736, 1702 cm^{-1} . $^1\text{H-NMR}$ (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, $J=6.3, 10.2, 17.5$ Hz). $^{13}\text{C-NMR}$ (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 $\text{C}_{14}\text{H}_{23}\text{NO}_2\text{Si}$: 265.1498. Found: 265.1500.

rel-(3S,5R)-1-Acetyl-5-[(1Z)-3-(triisopropylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'b): IR (neat): 1736, 1710 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{20}\text{H}_{35}\text{NO}_2\text{Si}$: 349.2437. Found: 349.2444.

rel-(3S,5R)-1-Acetyl-5-[(1Z)-3-(triphenylsilanyl)propenyl]-3-vinylpyrrolidin-2-one (5'c): IR (neat): 1732, 1700 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{29}\text{H}_{29}\text{NO}_2\text{Si}$: 451.1967. Found: 451.1979.

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

(6a): IR (neat): 1784, 1748, 1720 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{21}\text{H}_{39}\text{NO}_3\text{Si}_2$: 409.2468. Found: 409.2473.

tert-Butyl rel-(3S,5R)-2-Oxo-3,5-bis[(1E)-3-(triisopropylsilyl)propenyl]pyrrolidine-1-carboxylate (6b): IR (neat): 1776, 1726 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{33}\text{H}_{63}\text{NO}_3\text{Si}_2$: 577.4346. Found: 577.4351.

rel-(3S,5R)-1-Acetyl-3,5-bis[(1E)-3-(trimethylsilyl)propenyl]pyrrolidin-2-one (6c): IR (neat): 1734, 1704 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{18}\text{H}_{33}\text{NO}_2\text{Si}_2$: 351.2049. Found: 351.2039.

rel-(3S,5R)-1-Acetyl-3,5-bis[(1E)-3-(triisopropylsilyl)propenyl]pyrrolidin-2-one (6d): IR (neat): 11734, 1708 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{30}\text{H}_{57}\text{NO}_2\text{Si}_2$: 519.3927. Found: 519.3947.

tert-Butyl rel-(3S,5R)-2-Oxo-3-[(1Z)-3-(trimethylsilyl)propenyl]-5-[(1E)-3-(trimethylsilyl)propenyl]pyrrolidine-1-carboxylate (6'a): IR (neat): 1774, 1722 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{21}\text{H}_{39}\text{NO}_3\text{Si}_2$: 409.2468. Found: 409.2457.

rel-(3S,5R)-1-Acetyl-3-[(1Z)-3-(trimethylsilyl)propenyl]-5-[(1E)-3-(trimethylsilyl)propenyl]pyrrolidin-2-one (6'b): IR (neat): 1728, 1700 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{18}\text{H}_{33}\text{NO}_2\text{Si}_2$: 351.2049. Found: 351.2041.

tert-Butyl rel-(3S,5R)-2-Oxo-3-[(1E)-3-(trimethylsilyl)propenyl]-5-[(1Z)-3-(trimethylsilyl)propenyl]pyrrolidine-1-carboxylate (6''a): IR (neat): 1784, 1746, 1722 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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-(3S,5R)-1-Acetyl-3-[(1E)-3-(trimethylsilyl)propenyl]-5-[(1Z)-3-(trimethylsilyl)propenyl]-pyrrolidin-2-one (6''b): IR (neat): 1730, 1698 cm^{-1} . 1H -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-(3R,5S)-5-Ethyl-2-oxo-3-[3-(trimethylsilyl)propyl]pyrrolidine-1-carboxylate (7a): IR (neat): 1784, 1744, 1722 cm^{-1} . 1H -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-(3R,5S)-5-Ethyl-2-oxo-3-[3-(triisopropylsilyl)propyl]pyrrolidine-1-carboxylate (7b): IR (neat): 1784, 1745, 1720 cm^{-1} . 1H -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-(3R,5S)-5-Ethyl-2-oxo-3-[3-(triphenylsilyl)propyl]pyrrolidine-1-carboxylate (7c): IR (neat): 1772, 1714 cm^{-1} . 1H -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-(3R,5S)-1-Acetyl-5-ethyl-3-[3-(trimethylsilyl)propyl]pyrrolidin-2-one (7d): IR (neat): 1732, 1698 cm^{-1} . 1H -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-(3R,5S)-1-Acetyl-5-ethyl-3-[3-(triisopropylsilyl)propyl]pyrrolidin-2-one (7e): IR (neat): 1736, 1698 cm^{-1} . 1H -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-(3R,5S)-1-Acetyl-5-ethyl-3-[3-(triphenylsilyl)propyl]pyrrolidin-2-one (7f): IR (neat): 1728, 1692 cm^{-1} . 1H -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-(trimethylsilyl)propyl]pyrrolidine-1-carboxylate (7'a):**

IR (neat): 1784, 1746, 1718 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₁₇H₃₃NO₃Si: 327.2229. Found: 327.2219.

***tert*-Butyl *rel*-(3*R*,5*S*)-3-Ethyl-2-oxo-5-[3-(triisopropylsilyl)propyl]pyrrolidine-1-carboxylate (7'b):**

IR (neat): 1784, 1750, 1724 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₃H₄₅NO₃Si: 411.3169. Found: 411.3169.

***tert*-Butyl *rel*-(3*R*,5*S*)-3-Ethyl-2-oxo-5-[3-(triphenylsilyl)propyl]pyrrolidine-1-carboxylate (7'c):**

IR (neat): 1780, 1742, 1716 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₈H₃₀NO₃Si (M⁺-C₄H₉): 456.1994. Found: 456.1994.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(trimethylsilyl)propyl]pyrrolidin-2-one (7'd):**

IR (neat): 1736, 1694 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₁₄H₂₇NO₂Si: 269.1811. Found: 269.1821.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(triisopropylsilyl)propyl]pyrrolidin-2-one (7'e):**

IR (neat): 1736, 1702 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₁₇H₃₂NO₂Si: 310.2202. Found: 310.2199.

***rel*-(3*R*,5*S*)-1-Acetyl-3-ethyl-5-[3-(triphenylsilyl)propyl]pyrrolidin-2-one (7'f):**

IR (neat): 1728, 1697 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₉H₃₃NO₂Si (M⁺-C₆H₅): 378.1889. Found: 378.1888.

***tert*-Butyl *rel*-(3*R*,5*S*)-2-Oxo-3,5-bis[3-(trimethylsilyl)propyl]pyrrolidine-1-carboxylate (8a):**

IR (neat): 1786, 1744, 1716 cm⁻¹. ¹H-NMR (CDCl₃) 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). ¹³C-NMR (CDCl₃) 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 C₂₁H₄₃NO₃Si₂: 413.2781. Found: 413.2779.

***tert*-Butyl *rel*-(3*R*,5*S*)-2-Oxo-3,5-bis[3-(triisopropylsilyl)propyl]pyrrolidine-1-carboxylate (8b):**

IR (neat): 1786, 1746, 1718 cm⁻¹. ¹H-NMR (CDCl₃) 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). $^{13}\text{C-NMR}$ (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 $\text{C}_{33}\text{H}_{67}\text{NO}_3\text{Si}_2$: 581.4659. Found: 581.4676.

rel-(3R,5S)-1-Acetyl-3,5-bis[3-(trimethylsilyl)propyl]pyrrolidin-2-one (8c): IR (neat): 1736, 1698 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{18}\text{H}_{37}\text{NO}_2\text{Si}_2$: 355.2362. Found: 355.2373.

rel-(3R,5S)-1-Acetyl-3,5-bis[3-(triisopropylsilyl)propyl]pyrrolidin-2-one (8d): IR (neat): 1734, 1700 cm^{-1} . $^1\text{H-NMR}$ (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). $^{13}\text{C-NMR}$ (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 $\text{C}_{30}\text{H}_{61}\text{NO}_2\text{Si}_2$: 523.4240. Found: 523.4227.

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