Supporting Information

Synthesis of Carbapenam Skeletons Using a Ruthenium-Catalyzed Cyclization

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General Information. ^{1}H NMR and ^{13}C NMR were recorded on a JEOL EX-270 (270 MHz (^{1}H), 67.5 MHz (^{13}C)), EX-270 (400 MHz (^{1}H), 100 MHz (^{13}C)), JEOL AL-400 (400 MHz (^{1}H), 100 MHz, ^{13}C), or Bruker ARX-500 (500 MHz (^{1}H), 125 MHz (^{13}C)) instrument in $CDCl_3$ with tetra-methylsilane as an internal standard otherwise mentioned. Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), coupling constant (Hz), integration. Infrared spectra (IR) were obtained on a Perkin Elmer 1605 FTIR spectrometer and absorptions are reported in reciprocal centimeters. Mass spectra were obtained on either a JEOL JMS-DX303 (EI) or a JEOL JMS-FABmate (EI and FAB). Elemental Analyses were performed at the Center for Instrumental Analysis of Hokkaido University. Melting points were recorded on a Yanagimoto Micro Melting Point Apparatus and those were uncorrected. Silica gel column chromatography was performed with Merck Silica Gel 60 (70-230 or 230-400 mesh ATM). For analytical or preparative TLC, Merck Silica Gel 60 PF_{254} was used.

Materials or Methods. All reactions were performed under an argon atmosphere using standard Schlenk techniques. Toluene was distilled under argon over sodium-benzophenone ketyl. $RuH_2(CO)(PPh_3)_3$ (**1**) was prepared according to the method described in the literature.[1]

- Spectral Data of Substrates for Ruthenium-catalyzed Cyclization-

Ethyl (2*E*)-8-(4-methoxyphenyl)-2-octen-7-ynoate (**2a**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.9 Hz, 2 H), 6.99 (dt, *J* = 8.9 Hz, 2 H), 6.82 (d, *J* = 8.9 Hz, 2 H), 5.88 (dt, *J* = 15.8, 1.7 Hz, 1 H), 4.20 (q, *J* = 7.3 Hz, 2 H), 3.80 (s, 3 H), 2.46-2.34 (m, 4 H), 1.76 (tt, *J* = 7.6, 6.9 Hz, 2 H), 1.29 (t, *J* = 7.3 Hz, 3 H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 166.36 (C), 158.99 (C), 147.96 (CH), 132.70 (CH), 121.85 (CH), 115.80 (C), 113.6 (CH), 87.31 (C), 80.99 (C), 60.00 (CH_2), 55.04 (CH_3), 31.03 (CH_2), 26.99 (CH_2), 18.73 (CH_2), 14.11 (CH_3). IR (film) 2936, 2836, 1718, 1654, 1606, 1510, 1290,

1246, 1172, 1036, 832 cm^{-1}. LR MS (EI, *m/z*) 272 (M^+), 243, 227, 215, 199, 158, 145, 135, 111, 77, 43. HR MS (EI) calcd for $C_{17}H_{20}O_3$ 272.1413, found 272.1413.

Ethyl (2*E*)-8-phenyl-5-(4-methylphenylsulfonyl)-5-aza-2-octen-7-ynoate (**2c**). ^1H NMR (270 MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.0 Hz, 3 H), 2.35 (s, 3 H), 4.04 (dd, *J* = 6.0, 1.5 Hz, 2 H), 4.19 (q, *J* = 7.0 Hz, 2 H), 4.31 (s, 2 H), 6.08 (dt, *J* = 15.5, 1.5, Hz, 1 H), 6.86 (dt, *J* = 15.5, 6.0 Hz, 1 H), 7.07 (br.d, *J* = 8.0 Hz, 2 H), 7.24 -7.29 (m, 5 H), 7.78 (br.d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 14.16, 21.40, 37.63, 47.42, 60.59, 81.22, 86.16, 121.92, 124.58, 127.78, 128.12, 128.53, 129.65, 131.50, 135.74, 141.46, 143.81, 165.59. IR (film) 2250, 1720, 1350, 1276, 1164 cm^{-1}. LR MS (EI, *m/z*) 397 (M^+), 368, 352, 324, 242. HR MS (EI) calcd for $C_{22}H_{23}NO_4S$ 397.1349, found 397.1357. Anal. Calcd for $C_{22}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52; S, 8.07. Found: C, 66.32; H, 5.88; N, 3.43; S, 8.11.

Ethyl (2*E*)-8-(4-methylphenyl)-5-(4-methylphenylsulfonyl)-5-aza-2-octen-7-ynoate (**2d**) ^1H NMR (270MHz, $CDCl_3$) δ 1.28 (t, *J* = 7.0 Hz, 3 H), 2.33 (s, 3 H), 2.36 (s, 3 H), 4.04 (dd, *J* = 6.0, 1.5 Hz, 2 H), 4.19 (q, *J* = 7.0 Hz, 2 H), 4.29 (s, 2 H), 6.07 (dt, *J* = 15.5, 1.5 Hz, 1 H), 6.86 (dt, *J* = 15.5, 6.0 Hz, 1 H), 6.97 (br.d, *J* = 8.0 Hz, 2 H), 7.05 (br.d, *J* = 8.0 Hz, 2 H), 7.27 (br.d, *J* = 8.0 Hz, 2 H) 7.77 (br.d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.16, 21.40, 37.67, 47.37, 60.58, 80.50, 86.31, 118.85, 124.55, 127.78, 128.88, 129.63, 131.41, 135.79, 138.72, 141.50, 143.74, 165.60. IR (film) 2243, 1720, 1350, 1276, 1162 cm^{-1}. LR MS: (EI, *m/z*) 411(M^+), 256. HR MS(EI) calcd for $C_{23}H_{25}NO_4S$ 411.1506, found 411.1513. Anal. Calcd for $C_{23}H_{25}NO_4S$: C, 67.13; H, 6.12; N, 3.40; S, 7.79. Found: C, 67.01; H, 6.17; N, 3.34; S, 7.66.

(3*E*)-9-Phenyl-6-(4-methylphenylsulfonyl)-6-aza-2-oxo-3-nonen-8-yne (**2e**). ^1H NMR (270MHz, $CDCl_3$) δ 2.26 (s, 3 H), 2.36 (s, 3 H), 4.06 (dd, *J* = 5.7, 1.4 Hz, 2 H), 4.31 (s, 2 H), 6.27 (dt, *J* = 15.9, 1.4 Hz, 1 H), 6.71 (dt, *J* = 15.9, 5.7 Hz, 1 H), 7.06-7.10 (m, 2 H), 7.21-7.33 (m, 5 H), 7.78 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 21.51 (CH_3), 27.28 (CH_3), 37.86 (CH_2), 47.83 (CH_2), 81.13 (C), 86.22 (C), 121.75 (C), 127.71 (CH), 128.11 (CH), 128.55 (CH), 129.62 (CH), 131.42 (CH), 133.14 (CH), 135.53 (C), 140.46 (CH), 143.85 (C), 197.59 (C). IR (film) 3057, 2959, 2921, 2851, 2241, 1680, 1635, 1598 cm^{-1}. LRMS (EI, *m/z*) 367 $(M)^+$, 324 $(M\text{-}COMe)^+$, 298 $(M\text{-}CH{=}CHCOMe)^+$, 212 $(M\text{-}Ts)^+$. HRMS (EI) calcd for $C_{14}H_{14}NO$ 212.1075 $(M\text{-}Ts)^+$, found 212.1089.

***N,N*-Diethyl (2*E*)-8-phenyl-5-(4-methylphenylsulfonyl)-5-aza-2-octen-7-ynamide** (**2f**). ^1H

NMR (270MHz, $CDCl_3$) δ 1.14 (t, *J* = 7.0 Hz, 3 H), 1.15 (t, *J* = 7.0 Hz, 3 H), 2.35 (s, 3 H), 3.34 (q, *J* = 7.0 Hz, 2 H), 3.42 (q, *J* = 7.0 Hz, 2 H), 4.06 (dd, *J* = 5.7, 1.4 Hz, 2 H), 4.32 (s, 2 H), 6.50 (dt, *J* = 15.1, 1.4 Hz, 1 H), 6.78 (dt, *J* = 15.1, 5.7 Hz, 1 H), 7.05-7.10 (m, 2 H), 7.20-7.32 (m, 5 H), 7.78 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 13.12 (CH_3), 14.91 (CH_3), 21.46 (CH_3), 37.44 (CH_2), 40.83 (CH_2), 42.26 (CH_2), 47.63 (CH_2), 81.32 (C), 85.99 (C), 121.86 (C), 124.20 (CH), 127.68 (CH), 128.03 (CH), 128.39 (CH), 129.52 (CH), 131.33 (CH), 135.56 (C), 137.72 (CH), 143.63 (C), 164.60 (C). IR (film) 3061, 2974, 2931, 2873, 2240, 1664, 1618, 1598 cm^{-1}. LRMS (EI, *m*/*z*) 424 $(M)^+$, 352 $(M\text{-}NEt_2)^+$, 324 $(M\text{-}CONEt_2)^+$, 269 $(M\text{-}Ts)^+$. HRMS (EI) calcd for $C_{24}H_{28}N_2O_3S$ 424.1820 $(M)^+$, found 424.1829.

***N*-Ethyl (2*E*)-8-phenyl-5-(4-methylphenylsulfonyl)-5-aza-2-octen-7-ynamide** (**2g**) ^{1}H NMR (270MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.3 Hz, 3 H), 2.34 (s, 3 H), 3.35 (qd, *J* = 7.3, 5.9 Hz, 2 H), 4.03 (dd, *J* = 5.7, 1.4 Hz, 2 H), 4.31 (s, 2 H), 5.63 (bt, *J* = 5.9 Hz, 1 H), 6.07 (dt, *J* = 15.1, 1.4 Hz, 1 H), 6.73 (dt, *J* = 15.1, 5.7 Hz, 1 H), 7.05-7.10 (m, 2 H), 7.20-7.31 (m, 5 H), 7.77 (d, *J* = 8.4 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 14.81 (CH_3), 21.49 (CH_3), 34.53 (CH_2), 37.55 (CH_2), 47.24 (CH_2), 81.32 (C), 86.03 (C), 121.86 (C), 126.68 (CH), 127.67 (CH), 128.06 (CH), 128.44 (CH), 129.57 (CH), 131.41 (CH), 135.63 (C), 136.73 (CH), 143.71 (C), 164.56 (C). IR (film) 3288, 3064, 2974, 2936, 2875, 2240, 1677, 1632, 1599 cm^{-1}. LRMS (EI, *m*/*z*) 396 $(M)^+$, 352 $(M\text{-}NHEt)^+$, 241 $(M\text{-}Ts)^+$. HRMS (EI) calcd for $C_{22}H_{24}N_2O_3S$ 396.1507 $(M)^+$, found 396.1491.

Methyl (2*E*)-4-{2-oxo-5-(4-methoxyphenyl)ethynylpyrrolidin-1-yl}-but-2-enoate (**7**). ^{1}H NMR (270MHz, $CDCl_3$) δ 2.16-2.28 (m, 1 H), 2.38-2.63 (m, 3 H), 3.73 (s, 3 H), 3.82 (s, 3 H), 3.93 (ddd, *J* = 16.5, 6.8, 1.9 Hz, 1 H), 4.45 (ddd, *J* = 16.5, 4.9, 1.9 Hz, 1 H), 4.53 (dd, *J* = 7.8, 4.9 Hz, 1 H), 5.96 (ddd, *J* = 15.7, 1.9, 1.9 Hz, 1 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 6.89 (ddd, *J* = 15.7, 6.8, 4.9 Hz, 1 H), 7.34 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 26.48 (CH_2), 29.67 (CH_2), 41.75 (CH_2), 49.80 (CH), 51.58 (CH_3), 55.24 (CH_3), 84.48 (C), 85.78 (C), 113.88 (CH), 121.02 (C), 122.79 (CH), 133.01 (CH), 142.15 (CH), 159.78 (C), 166.01 (C), 173.99 (C). IR (film) 2995, 2952, 2846, 2227, 1722, 1697, 1664, 1606 cm^{-1}. LRMS (EI, *m*/*z*) 313 $(M)^+$, 298 $(M\text{-}Me)^+$, 282 $(M\text{-}OMe)^+$. HRMS (EI) calcd for $C_{18}H_{19}NO_4$ 313.1314 $(M)^+$, found 313.1296.

Methyl
(2*E*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-phenylethynyl-azetidin-1-yl}-but-2-enoate** (**9a**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.27-7.46 (m, 5 H), 6.90 (dd, *J* = 15.4, 5.9, 5.9 Hz, 1 H), 6.08 (dd, *J* = 15.8, 1.6, 1.2 Hz, 1 H), 4.52 (d, *J* = 2.4 Hz, 1 H), 4.25-4.35 (m, 1 H),

4.16 (ddd, *J*= 16.9, 5.1, 1.6 Hz, 1 H), 3.93 (ddd, *J* = 16.9, 6.3, 1.2 Hz, 1 H), 3.71 (s, 3H), 3.35 (dd, *J* = 2.8, 2.8 Hz, 1 H), 1.28 (d, *J* = 6.3 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.93 (CH_3,), -4.49 (CH_3,), 17.91 (C), 22.33 (CH_3), 25.66 (CH_3), 41.30 (CH_2), 43.32 (CH), 51.47 (CH_3), 64.28 (CH), 66.66 (CH), 84.76 (C), 86.66 (C), 121.79 (C), 123.35 (C), 128.16 (CH), 128.58 (CH), 131.50 (CH), 141.13 (CH), 165.7 (C), 166.84 (C). IR (film) 2955, 2928, 2859, 2857, 2227, 1769, 1729, 1664, 1598 cm^{-1}. HR MS (EI) calcd for $C_{24}H_{33}NO_4Si$ 427.2179, found 427.2163. Anal. Calcd for $C_{24}H_{33}NO_4Si$: C, 67.41; H, 7.78; N, 3.28. Found: C, 67.56; H, 7.52; N, 3.37.

Methyl

(2*E*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-(4-methoxyphenyl)ethynylazetidin-1-yl}-but-2-enoate** (**9b**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.7 Hz, 2 H), 6.90 (ddd, *J* = 15.8, 6.7, 5.4 Hz, 1 H), 6.84(d, *J* = 8.7 Hz, 2 H), 4.51 (d, *J* = 2.4 Hz, 1 H), 4.25-4.34 (m, 1 H), 4.15 (ddd, *J* = 17.4, 5.5, 1.6 Hz, 1 H), 3.93 (ddd, *J* = 17.4, 6.7, 1.6 Hz, 1 H), 3.82 (s, 3 H), 3.72 (s, 3 H), 3.33 (dd, *J* = 2.4, 2.4 Hz, 1 H), 1.27 (d, *J* = 6.3 Hz, 3 H), 0.89 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H). ^{13}C NMR (100 MHz, $CDCL_3$) δ -4.95 (CH_3), -4.52 (CH_3), 17.88 (C), 22.29 (CH_3), 25.63 (CH_3), 41.19 (CH_2), 43.38 (CH), 51.44 (CH_3), 55.13 (CH_3), 64.25 (CH), 66.60 (CH), 83.30 (C), 86.61 (C), 113.77 (CH), 113.80 (C), 123.23 (CH), 132.99 (CH), 141.22 (CH), 159.69 (C), 165.78 (C), 166.91 (C). IR (film) 2955, 2932, 2898, 2857, 2227, 1765, 1726, 1608 cm^{-1}. HR MS (EI) calcd for $C_{25}H_{35}NO_5Si$ 457.2285, found 457.2267. Anal. Calcd for $C_{25}H_{35}NO_5Si$: C, 65.61; H, 7.71; N, 3.06. Found: C, 65.35; H, 7.63; N, 3.21.

Methyl

(2*E*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-(4-methylphenyl)ethynylazetidin-1-yl}-but-2-enoate** (**9c**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.89 (s, 9 H), 1.27 (d, *J* = 6.2 Hz, 3 H), 2.35 (s, 3 H), 3.34 (dd, *J* = 2.4 Hz, *J* = 2.4 Hz, 1H), 3.72 (s, 3 H), 3.92 (ddd, *J* = 17.0, 6.2, 1.6 Hz, 1H), 4.14 (ddd, *J* = 17.0Hz, 5.4, 1.6 Hz, 1 H), 4.26-4.34 (m, 1 H), 4.51 (d, *J* = 2.4 Hz, 1 H), 6.06 (ddd, *J* = 15.7 Hz, 1.6, 1.6 Hz, 1 H), 6.89 (ddd, *J* = 15.7, 6.2, 5.4 Hz, 1 H), 7.12 (d, *J* = 7.8 Hz, 2 H), 7.30 (d, *J* = 7.8 Hz, 2 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.8 (CH_3), -4.4 (CH_3), 18.0 (C), 21.5 (CH_3), 22.4 (CH_3), 25.7 (CH_3), 41.3 (CH_2), 43.5 (CH), 51.6 (CH_3), 64.4 (CH), 66.7 (CH), 84.1 (C), 86.9 (C), 118.8 (C), 123.4 (CH), 129.0 (CH), 131.5 (CH), 138.9 (C), 141.3 (CH), 165.9 (C), 167.0 (C). IR (film) 2953, 2928, 2889, 2855, 2225, 1765, 1726 , 1662 cm^{-1}. LR MS (FAB, *m/z*) 442 (M^++H), 426, 398, 384. HR MS (FAB) calcd for $C_{25}H_{36}NO_4Si$ (M^++H) 442.2414, found 442.2397.

Methyl (2*E*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-(3-triethylsilyloxypropyn-1-yl)azetidin-1-yl}-but-2-enoate** (**9d**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.07 (s, 3 H), 0.09 (s, 3 H), 0.64 (q, *J* = 8.1 Hz, 6 H), 0.87 (s, 9 H), 0.98 (t, *J* = 8.1 Hz, 9 H), 1.22 (d, *J* = 6.5 Hz, 3 H), 3.22-3.26 (m, 1 H), 3.74 (s, 3 H), 3.79 (ddd, *J* = 17.6, 6.5, 1.2 Hz, 1H), 4.16 (ddd, *J* = 17.6, 5.4, 1.4 Hz, 1 H), 4.22-4.29 (m, 1 H), 4.30-4.35 (m, 3 H), 6.01 (ddd, *J* = 15.9, 1.4, 1.2 Hz, 1 H), 6.83 (ddd, *J* = 15.9, 6.5, 5.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.8 (CH_3), -4.5 (CH_3), 4.5 (CH_3), 6.7 (CH_3), 18.0 (C), 22.3 (CH_3), 25.8 (CH_3), 41.2 (CH_2), 42.7 (CH), 51.2 (CH_2), 51.6 (CH_3), 64.2 (CH), 66.3 (CH), 80.4 (C), 85.5 (C), 123.4 (CH), 141.1 (CH), 165.9 (C), 166.9 (C). IR (film) 2954, 2932, 2878, 2856, 1768, 1729 , 1662 cm^{-1}. LR MS (FAB, *m/z*) 480 $(M\text{-}Me)^+$, 466 $(M\text{-}Et)^+$, 438 $(M\text{-}^tBu)^+$. HR MS (FAB) calcd for $C_{21}H_{36}NO_5Si_2$ $(M^+\text{-}^tBu)^+$ 438.2132, found 438.2144.

Methyl (2*E*)-(*3S*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-(4-methoxyphenyl)ethynylazetidin-1-yl}-pent-2-enoate** (**12a**). ^{1}H NMR (270MHz, $CDCl_3$) δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.89 (s, 9 H), 1.26 (d, *J* = 6.2 Hz, 3 H), 1.48 (d, *J* = 7.3 Hz, 3 H), 3.26 (dd, *J* = 2.7, 2.7 Hz, 1 H), 3.68 (s, 3 H), 3.81 (s, 3 H), 4.28 (qd, *J* =6.2, 2.7 Hz, 1 H), 4.47 (qd, *J* =7.3, 6.2 Hz, 1 H), 4.52 (d, *J* = 2.7 Hz, 1 H), 6.04 (d, *J* = 15.7 Hz, 1 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 7.02 (dd, *J* = 15.7, 6.2 Hz, 1 H), 7.35 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ -4.80 (CH_3), -4.44 (CH_3), 17.26 (CH_3), 17.99 (C), 22.42 (CH_3), 25.75 (CH_3), 41.52 (CH), 48.98 (CH), 51.54 (CH_3), 55.30 (CH_3), 64.37 (CH), 65.45 (CH), 84.63 (C), 86.39 (C), 113.85 (CH), 114.12 (C), 121.46 (CH), 133.02 (CH), 146.58 (CH), 159.73 (C), 166.34 (C), 166.54 (C). IR (film) 2953, 2930, 2893, 2856, 2225, 1761, 1728, 1662, 1607 cm^{-1}. LRMS (EI, *m*/*z*) 414 $(M\text{-}tBu)^+$. HRMS (EI) calcd for $C_{22}H_{28}NO_5Si$ 414.1737 $(M\text{-}tBu)^+$, found 414.1767.

Methyl (2*E*)-(*3R*)-4-{(3*S,4*R**)-3-[(*1R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-oxo-4-(4-methoxyphenyl)ethynylazetidin-1-yl}-pent-2-enoate** (**12b**). ^{1}H NMR (270MHz, $CDCl_3$) δ 0.08 (s, 3 H), 0.09 (s, 3 H), 0.88 (s, 9 H), 1.25 (d, *J* = 6.5 Hz, 3 H), 1.51 (d, *J* = 6.8 Hz, 3 H), 3.25 (dd, *J* = 2.7, 2.7 Hz, 1 H), 3.73 (s, 3 H), 3.81 (s, 3 H), 4.23-4.32 (m, 1 H), 4.46-4.52 (m, 2 H), 5.99 (d, *J* = 15.9 Hz, 1 H), 6.84 (d, *J* = 8.9 Hz, 2 H), 7.00 (dd, *J* = 15.9, 6.8 Hz, 1 H), 7.33 (d, *J* = 8.9 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ -4.76 (CH_3), -4.48 (CH_3), 18.00 (C), 18.22 (CH_3), 22.44 (CH_3), 25.76 (CH_3), 42.00 (CH), 49.46 (CH), 51.63 (CH_3), 55.29 (CH_3), 64.44 (CH), 65.90 (CH), 85.02 (C), 85.93 (C), 113.89 (CH), 114.19 (C), 122.14 (CH), 132.96 (CH), 145.73 (CH), 159.75 (C), 166.20 (C), 166.48 (C). IR (film)

2953, 2930, 2895, 2855, 2224, 1760, 1729, 1662, 1606 cm^{-1}. LRMS (EI, *m*/*z*) 414 $(M\text{-}tBu)^+$. HRMS (EI) calcd for $C_{22}H_{28}NO_5Si$ 414.1737 $(M\text{-}tBu)^+$, found 414.1760.

- Procedures for Cyclization -

Typical Procedure for the Cyclization of 2c. To a solution of **2c** (127 mg, 0.32 mmol) in toluene (2 mL) was added RuH_2 (CO) $(PPh_3)_3$ **1** (15 mg, 0.016 mmol) under a flow of argon. The mixture was heated under vigorous reflux (135 °C, oil bath temperature) with stirring. After heating for 18 hr, the mixture was allowed to cool to room temperature, and solvent was removed in vacuo. A concentrated residue was purified by silica gel column chromatography (eluent, hexane/ethyl acetate = 5/1) to afford cylized product **3c** (105 mg, 83 %) as a colorless oil.

Typical Procedure for the Cyclization of 9a. To a suspension of catalyst **1** (10.7 mg, 0.012 mmol) in toluene (1 mL) was added a solution of **9a (**50.0 mg, 0.12 mmol) in toluene (1 mL). The mixture was heated under vigorous reflux (135 °C, oil bath temperature) with stirring. After heating for 12 hr, the mixture was allowed to cool to room temperature , and solvent was removed in vacuo. A concentrated residue was purified by silica gel column chromatography eluent, hexane/ethyl acetate = 6/1) to afford cylized product **10a** (22.1 mg, 44 %) as a slightly yellow oil along with **11a**.

- Spectral Data of Cyclized Products-

Ethyl (*E*)-2-[(*E*)-4-methoxybenzylidene]cyclopentylideneethanoate (**3a**). mp 57.0-59.0 °C (recryst. from $MeOH/H_2O$ = 4/1). ^1H NMR (400 MHz, $CDCl_3$) δ 7.36 (br.d, *J* = 9.0 Hz, 2 H), 7.04 (t, *J* = 2.5 Hz, 1 H), 6.90 (br.d, *J* = 9.0 Hz, 1 H), 6.23 (t, *J* = 2.5 Hz, 1 H), 4.20 (q, *J* = 7.0 Hz, 2H), 3.82 (s, 3 H), 3.00 (td, *J* = 7.5, 2.5 Hz, 2H), 2.70 (td, *J* = 7.5, 2.5 Hz, 2H), 1.83 (tt, *J* = 7.5, 7.5 Hz, 2 H), 1.31 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.39 (C), 163.06 (C), 159.22 (C), 140.27 (C), 130.85 (C), 129.97 (CH), 123.72 (CH), 113.97 (CH), 106.99 (CH), 59.58 (CH_2), 55.29 (CH_3), 32.54 (CH_2), 31.88 (CH_2), 24.45 (CH_2), 14.43 (CH_3). IR (nujor) 2956, 1704, 1640, 1510, 1252, 1150, 872, 850, 826 cm^{-1}. LR MS (EI, *m/z*) 242 (M^+ -30), 197, 169. HR MS calcd for $C_{17}H_{22}O_3$ 272.1413, found 272.1397. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.94; H, 7.40. Found: C, 74.77; H, 7.49.

3-Phenylpropyl (*E*)-2-[(*E*)-ethylidene]cyclopentylideneethanoate (**3b**). ^1H NMR (500 MHz, $CDCl_3$) δ 7.30-7.24 (m, 2 H), 7.22-7.15 (m, 3 H), 6.22 (qt, *J* = 7.0, 2.5 Hz, 1 H), 6.05 (br.s, 1 H) 4.13 (t, *J* = 7.0 Hz, 2 H), 2.95 (td, *J* = 7.5, 2.5 Hz, 2 H), 2.71 (t, *J* = 7.5 Hz, 2 H), 2.37 (br.t, *J* = 7.0

Hz, 2 H), 1.99 (tt, *J* = 7.5, 7.5 Hz, 2 H), 1.80 (tt, *J* = 7.5, 7.0 Hz, 2H), 1.70 (t, *J* = 7.0 Hz, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.53 (C), 161.77 (C), 142.09 (C), 141.45 (C), 128.45 (CH), 128.43 (CH), 125.95 (CH), 120.39 (CH), 106.44 (CH), 63.03 (CH_2), 33.50 (CH_2), 32.34 (CH_2), 30.52 (CH_2), 29.11 (CH_2), 23.67 (CH_2), 14.43 (Me). IR (film) 2954, 1706, 1654, 1618, 1496, 1454, 1358, 1240, 1186, 1158, 1108, 1030, 912, 866, 850, 816, 734, 700 cm^{-1}. LR MS (EI, *m/z*) 270 (M^+), 176, 152, 118, 107, 91, 79, 67, 53, 41. HR MS calcd for $C_{18}H_{20}O_2$ 270.1621, found 270.1622.

Ethyl (*Z*)-[(*Z*)-4-benzylidene-1-(4-methylphenylsulfonyl)pyrrolidin-3-ylidene]ethanoate (**3c**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.0 Hz, 3 H), 2.42 (s, 3 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 4.34 (d, *J* = 2.5 Hz, 2 H), 4.50 (d, *J* = 2.5 Hz, 2 H), 6.18 (t, *J* = 2.5 Hz, 1 H), 7.04 (t, *J* = 2.5 Hz, 1 H), 7.24 - 7.34 (m, 5 H), 7.39 (br.d, *J* = 8.0 Hz, 2 H), 7.74 (br.d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.28, 21.50, 51.26, 52.33, 60.36, 108.60, 126.00, 126.09, 126.47, 127.79, 128.89, 129.33, 129.81, 133.66, 135.16, 143.86, 153.47, 166.04. IR (film): 1700, 1606, 1348, 1164 cm^{-1}. LR MS (EI, *m/z*) 397 (M^+), 352, 306, 242. H RMS (EI) calcd for $C_{23}H_{23}NO_4S$ 397.1349, found 397.1366 . Anal. Calcd for $C_{23}H_{23}NO_4S$: C, 66.48; H, 5.83; N, 3.52; S, 8.07. Found: C, 66.34; H, 5.75; N, 3.48; S, 8.08.

Ethyl

(2*Z*)-[(*Z*)-4-(4-methylbenzylidene)-1-(4-methylphenylsulfonyl)pyrrolidin-3-ylidene]ethanoate (**3d**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.30 (t, *J* = 7.0 Hz, 3 H), 2.39 (s, 3 H), 2.42 (s, 3 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 4.33 (d, *J* = 2.5 Hz, 2 H), 4.50 (d, *J* = 2.5 Hz, 2 H), 6.16 (t, *J* = 2.5 Hz, 1 H), 7.01 (br., 1 H), 7.15 (br.d, *J* = 8.0 Hz, 2 H), 7.22 (br.d, *J* = 8.0 Hz, 2 H), 7.31 (br.d, *J* = 8.0 Hz, 2 H), 7.75 (br.d, *J* = 8.0 Hz, 2 H). ^{13}C NMR (125MHz, $CDCl_3$) δ 14.30, 21.37, 21.51, 51.35, 52.37, 60.31, 108.09, 126,04, 126.50, 127.80, 129.39, 129.66, 129.81, 132.44, 132.58, 139.34, 143.82, 153.71, 166.13. IR (film): 1700, 1596, 1348, 1162 cm^{-1}. LR MS (EI, *m/z*) 411 (M^+), 366, 338, 256, 155, 91. HR MS (EI) calcd for $C_{23}H_{25}NO_4S$ 411.1506, found 411.1521.

***N,N*-Diethyl**

(2*Z*)-[(*Z*)-4-(4-methylbenzylidene)-1-(4-methylphenylsulfonyl)pyrrolidin-3-ylidene]ethanamid

e (**3f**). ^{1}H NMR (270MHz, $CDCl_3$) δ 1.16 (t, *J* = 7.3 Hz, 3 H), 1.23 (t, *J* = 7.3 Hz, 3 H), 2.40 (s, 3 H), 3.41 (q, *J* = 7.3 Hz, 2 H), 3.43 (q, *J* = 7.3 Hz, 2 H), 4.30 (d, *J* = 2.4 Hz, 2 H), 4.48 (d, *J* = 2.4 Hz, 2 H), 6.48 (t, *J* = 2.4 Hz, 1 H), 6.95 (t, *J* = 2.4 Hz, 1 H), 7.24-7.44 (m, 7 H), 7.76 (d, *J* = 8.1 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 13.32 (CH_3), 15.02 (CH_3), 21.60 (CH_3), 40.69 (CH_2), 42.57 (CH_2), 51.27 (CH_2), 52.40 (CH_2), 108.34 (CH), 123.91 (CH), 127.88 (CH), 128.42 (CH), 128.75 (CH),

129.05 (CH), 129.70 (CH), 132.55 (C), 134.55 (C), 135.37 (C), 143.61 (C), 149.57 (C), 165.11 (C). IR (film) 3058, 3026, 2974, 2929, 2873, 2238, 1649, 1621, 1597 cm^{-1}. LRMS (EI, *m*/*z*) 424 $(M)^+$, 269 $(M\text{-}Ts)^+$. HRMS (EI) calcd for $C_{24}H_{28}N_2O_3S$ 424.1820 $(M)^+$, found 424.1813.

***N*-Ethyl**

(2*Z*)-[(*Z*)-4-(4-methylbenzylidene)-1-(4-methylphenylsulfonyl)pyrrolidin-3-ylidene]ethanamide (**3g**). ^1H NMR (270MHz, $CDCl_3$) δ 0.94 (t, *J* = 7.3 Hz, 3 H), 2.42 (s, 3 H), 3.08 (qd, *J* = 7.3, 5.7 Hz, 2 H), 3.19 (s, 2 H), 3.66 (s, 2 H), 5.12 (bd, *J* = 5.7 Hz, 1 H), 6.91 (s, 1 H), 7.08 (s, 1 H), 7.20-7.45 (m, 7 H), 7.73 (d, *J* = 8.4 Hz, 2 H). IR (film) 3400-3100, 3062, 2969, 2924, 2873, 2852, 1648, 1595 cm^{-1}. LRMS (EI, *m*/*z*) 396 $(M)^+$, 324 $(M\text{-}CONHEt)^+$, 241 $(M\text{-}Ts)^+$. HRMS (EI) calcd for $C_{22}H_{24}N_2O_3S$ 396.1507 $(M)^+$, found 396.1532.

Methyl (3*Z*,4*Z*)-{4-(4-methoxybenzylidene)-8-oxo-1-azabicyclo[3.3.0]oct-3-ylidene}ethanoate (**8**). ^1H NMR (270MHz, $CDCl_3$) δ 1.50-1.64 (m, 1 H), 2.17-2.31 (m, 1 H), 2.48-2.75 (m, 2 H), 3.77 (s, 3 H), 3.85 (s, 3 H), 4.07 (dd, *J* = 18.9, 2.4 Hz, 1 H), 5.04-5.16 (m, 2 H), 6.22 (dd, *J* = 2.4, 2.4 Hz, 1 H), 6.92 (d, *J* = 9.2 Hz, 2 H), 7.13 (d, *J* = 2.4 Hz, 1 H), 7.28 (d, *J* = 9.2 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ 27.57 (CH_2), 33.19 (CH_2), 47.58 (CH_2), 51.57 (CH_3), 55.38 (CH_3), 63.03 (CH), 108.13 (CH), 114.02 (CH), 125.95 (CH), 127.45 (C), 131.03 (CH), 137.63 (C), 156.31 (C), 159.90 (C), 166.46 (C), 175.23 (C). IR (film) 2950, 2840, 1702, 1594 cm^{-1}. LRMS (EI, *m*/*z*) 313 $(M)^+$, 298 $(M\text{-}Me)^+$. HRMS (EI) calcd for $C_{18}H_{19}NO_4$ 313.1314 $(M)^+$, found 313.1306.

Methyl

(3*Z*,4*Z*,5*R,6*S**)-{4-benzylidene-6-[(1*R**)-1-*tert*-butyldimethylsilyloxyethyl]-7-oxo-1-azabicyclo[3.2.0]hept-3-ylidene}ethanoate** (**10a**). ^1H NMR (270 MHz, $CDCl_3$) δ 7.29-7.47 (m, 5 H), 7.24 (d, *J* = 2.4 Hz, 1 H), 6.25 (dd, *J* = 2.4, 2.4 Hz, 1 H), 4.95 (dd, *J* = 18.6, 2.4 Hz, 1 H), 4.62 (dd, *J* = 2.9, 1.4 Hz, 1 H), 4.23 (td, *J* = 6.4, 4.4 Hz, 1 H), 3.97 (dd, *J* = 18.6, 2.4 Hz, 1 H), 3.76 (s, 3 H), 2.86 (dd, *J* = 4.4, 1.9 Hz, 1 H), 1.09 (d, *J* = 6.4 Hz, 3 H), 0.90 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H). ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 177.3 (C), 177.5 (C), 160.1 (C), 137.9 (C), 134.6 (C), 129.7 (CH), 128.9 (CH), 128.8 (CH), 128.5 (CH), 109.2 (CH), 65.9 (CH), 65.5 (CH), 56.1 (CH), 51.5 (CH_3), 50.0 (CH_2), 35.8 (CH_3), 22.9 (CH_3), 18.1 (C), -4.6 (CH_3), -4.9 (CH_3). IR (film) 3060, 3024 2952, 2928, 2989, 1770, 1709, 1669, 1644, 1602 cm-1. HR MS (EI) calcd for $C_{24}H_{33}O_4NSi$ 427.2179, found 427.2162. Anal. Calcd for $C_{24}H_{33}O_4NSi$: C, 67.41; H, 7.78; N, 3.28. Found: C, 67.22; H, 7.97; N, 3.31.

Methyl

(3*Z*,4*Z*,5*R,6*S**)-{4-(4-methoxybenzylidene)-6-[(1*R**)-1-*tert*-butyldimethylsilyloxyethyl]-7-oxo-1-azabicyclo[3.2.0]hept-3-ylidene}ethanoate** (**10b**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 7.38 (d, *J* = 9.1 Hz, 2 H), 7.17 (br.s, 1 H), 6.92 (d, *J* = 9.1 Hz, 2 H), 6.20 (t, *J* = 2.3 Hz, 1 H), 4.93 (dd, *J* = 18.6, 2.3 Hz, 1 H), 4.57 (br.s, 1 H), 4.27 (dq, *J* = 6.3, 5.1 Hz, 1H), 3.95 (dd, *J* = 18.6, 2.3 Hz, 1 H), 3.83 (s, 3 H), 3.74 (s, 3 H), 2.89 (dd, *J* = 5.1, 2.0 Hz, 1 H), 1.21 (d, *J* = 6.2 Hz, 3 H), 0.92 (s, 9 H), 0.09 (s, 3 H), 0.07 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3 (C), 166.4 (C), 160.4 (C), 160.1 (C), 134.9, (C), 131.5 (CH), 128.2, (CH), 127.1 (C), 114.2 (CH), 104.6 (CH), 66.6 (CH), 65.0 (CH), 56.5 (CH), 55.3 (CH_3), 51.4 (CH_3), 50.1 (CH_2), 25.9 (CH_3), 25.2 (CH_3), 18.2 (C), -4.5 (CH_3), -4.7 (CH_3). IR (film) 2959, 2934, 2901, 1768, 1705, 1643, 1590. HR MS (EI) calcd for $C_{25}H_{35}NO_5Si$ 457.2285, found 457.2292. Anal. Calcd for $C_{25}H_{35}NO_5Si$: C, 65.61; H, 7.71; N, 3.06. Found: C, 65.83; H, 7.59; N, 2.96.

Methyl
(3*Z*,4*Z*,5*R,6*S**)-{4-(4-methylbenzylidene)-6-[(1*R**)-1-*tert*-butyldimethylsilyloxyethyl]-7-oxo-1-azabicyclo[3.2.0]hept-3-ylidene}ethanoate** (**10c**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.04 (s, 3 H), 0.07 (s, 3 H), 0.91 (s, 9 H), 1.16 (d, *J* = 6.5 Hz, 3 H), 2.17 (s, 3 H), 2.87 (dd, *J* = 4.9, 2.2 Hz, 1 H), 3.76 (s, 3 H), 3.96 (dd, *J* = 18.6, 2.4 Hz, 1 H), 4.24 (qd, *J* = 6.2, 4.9 Hz, 1 H), 4.60 (m, 1 H), 4.94 (dd, *J* = 18.6, 2.4 Hz, 1 H), 6.23 (dd, *J* = 2.2, 2.2 Hz, 1 H), 7.18-7.33 (m, 5 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ -4.8 (CH_3), -4.5 (CH_3), 18.2 (C), 21.5 (CH_3), 23.0 (CH_3), 25.9 (CH_3), 50.1 (CH_2), 51.5 (CH_3), 56.4 (CH), 65.3 (CH), 66.2 (CH), 108.6 (CH), 128.5 (CH), 129.5 (CH), 129.7 (CH), 131.6 (C), 136.6 (C), 139.3 (C), 160.3 (C), 166.4 (C), 177.3 (C) IR (film) 2952, 2928, 2893, 2856, 1769, 1711, 1642, 1593 cm^{-1}. LR MS (EI, *m/z*) 441 (M^+), 426, 410, 398, 384. HR MS (EI) calcd for $C_{25}H_{35}NO_4Si$ 441.2335, found 442.2361.

Methyl
(3*Z*,4*Z*,5*R,6*S**)-{4-(2-triethylsilyloxyethylidene)-6-[(1*R**)-1-*tert*-butyldimethylsilyloxyethyl]-7-oxo-1-azabicyclo[3.2.0]hept-3-ylidene}ethanoate** (**10d**). ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.10 (s, 3 H), 0.11 (s, 3 H), 0.62 (q, *J* = 8.1 Hz, 6 H), 0.91 (s, 9 H), 0.97 (t, *J* = 8.1 Hz, 9 H), 1.32 (d, *J* = 6.2 Hz, 3 H), 3.02 (dd, *J* = 5.9, 2.4 Hz, 1 H), 3.74 (s, 3 H), 3.87 (dd, *J* = 18.6, 2.4 Hz, 1 H), 4.23-4.47 (m, 4 H), 4.94 (dd, *J* = 18.6, 2.4 Hz, 1 H), 6.13 (dd, *J* = 2.4, 2.4 Hz, 1 H), 6.37 (td, *J* = 6.5, 1.9 Hz, 1 H). IR (film) 2951, 2930, 2877, 2856, 1773, 1714, 1622 cm^{-1}. LR MS (EI, *m/z*) 480 $(M\text{-}Me)^+$, 466 $(M\text{-}Et)^+$, 438 $(M\text{-}^tBu)^+$. HR MS (EI) calcd for $C_{21}H_{36}NO_5Si_2$ 438.2132 $(M\text{-}^tBu)^+$, found 438.2134.

Methyl

(2*S,3*Z*,4*Z*,5*R**,6*S**)-{4-(4-methoxybenzylidene)-6-[(1*R**)-1-*tert*-butyldimethylsilyloxyethyl]-2-methyl-7-oxo-1-azabicyclo[3.2.0]hept-3-ylidene}ethanoate (13a).** ^{1}H NMR (270MHz, $CDCl_3$) δ 0.09 (s, 3 H), 0.10 (s, 3 H), 0.93 (s, 9 H), 1.22 (d, *J* = 6.2 Hz, 3 H), 1.28 (d, *J* = 6.8 Hz, 3 H), 2.89 (dd, *J* = 4.1, 2.2 Hz, 1 H), 3.75 (s, 3 H), 3.84 (s, 3 H), 4.31 (qd, *J* =6.2, 4.1 Hz, 1 H), 4.63-4.68 (m, 1 H), 5.39 (qd, *J* =6.8, 1.6 Hz, 1 H), 6.13 (d, *J* = 1.6 Hz, 1 H), 6.93 (d, *J* = 8.6 Hz, 2 H), 7.18 (d, *J* = 1.6 Hz, 1 H), 7.41 (d, *J* = 8.6 Hz, 2 H). ^{13}C NMR (100MHz, $CDCl_3$) δ -4.73 (CH_3), -4.43 (CH_3), 18.26 (C), 18.83 (CH_3), 23.46 (CH_3), 25.94 (CH_3), 51.46 (CH_3), 53.94 (CH), 55.40 (CH_3), 56.00 (CH), 65.61 (CH), 65.96 (CH), 107.12 (CH), 114.28 (CH), 127.59 (C), 128.51 (CH), 131.34 (CH), 135.01 (C), 160.13 (C), 164.16 (C), 165.93 (C), 176.83 (C). IR (film) 2953, 2930, 2895, 2856, 1766, 1709, 1642, 1590 cm^{-1}. LRMS (EI, *m*/*z*) 471 $(M)^+$, 456 $(M\text{-}Me)^+$, 440 $(M\text{-}OMe)^+$, 428, 414 $(M\text{-}tBu)^+$. HRMS (EI) calcd for $C_{26}H_{37}NO_5Si$ 471.2441 $(M)^+$, found 471.2429.

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