Supporting Information

Regio- and Stereoselective Enyne Cross Metathesis of Silylated Internal Alkynes

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Materials and Methods

^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-250 or a Bruker AC-300 spectrometer. Tetramethylsilane (TMS) served as an internal standard ($\delta = 0$) for ^1H NMR and CDCl_3 was used as an internal standard ($\delta = 77.23$) for ^{13}C NMR. All reactions were run under an atmosphere of nitrogen, unless otherwise indicated. Flasks were oven-dried overnight and cooled under a stream of nitrogen. Compounds were purchased from Aldrich. Dichloromethane was distilled from CaH_2 . All other solvents were purified based on standard procedures. Flash chromatography was performed using silica gel 60 Å (32-63 mesh) from Sorbent Technologies. Reactions were monitored by thin layer chromatography (TLC) using 0.25 mm E. Merk precoated silica gel 60 (particle size 0.040-0.063 mm).

Representative Procedure for Cross Metathesis

Silylated alkyne **3a** (20 mg, 0.117 mmol) and 1-octene (92 mg, 0.819 mmol) were dissolved in freshly distilled CH_2Cl_2 (0.03 M). Grubbs 2nd generation catalyst, $(\text{H}_2\text{Imes})(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CHPh}$, (6.8 mg, 0.008 mmol, 7 mol %) was added to the reaction mixture. After stirring under reflux for 40 hours, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using pentane/ether (gradient elution) to yield the desired CM product **4a** (oil, 25 mg, 76%).

Note : Depending on the extent of dimerization of alkene, the initial amount of alkene was adjusted between 3 and 7 equivalents. For the reaction with slow conversion, an additional amount of alkene (up to 8 equiv) was added in order to get a satisfactory yield.

¹H NMR (300 MHz, CDCl₃): δ 6.00 (t, *J* = 7.6 Hz, 1H), 4.92 (s, 1H), 4.67(s, 1H), 4.49 (s, 2H), 2.13 (q, *J* = 7.6 Hz, 2H), 2.08 (s, 3H), 1.28 (m, 8H), 0.89 (t, *J* = 7 Hz, 3H), 0.15 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃) :** δ 170.80, 149.32, 146.73, 140.21, 110.06, 67.26, 32.37, 32.01, 30.00, 29.25, 22.84, 21.37, 14.30, 0.6 ; **HRMS (EI)** calcd for C₁₆H₃₀O₂Si [M-CH₃]^{•+}: 267.1780, found 267.1789.

¹H NMR (300 MHz, CDCl₃): δ 7.67 (d, *J* = 8.5 Hz, 2H), 7.31 (d, *J* = 8.5 Hz, 2H), 5.96 (t, *J* = 7.5 Hz, 1H), 4.86 (s, 1H), 4.71 (s, 1H), 3.54 (s, 2H), 4.54 (s, 2H), 2.63 (s, 3H), 2.43 (s, 3H), 1.28 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H), 0.17 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 149.17, 146.58, 143.36, 140.86, 135.04, 129.81, 127.69, 111.78, 55.72, 34.59, 32.42, 32.00, 30.00, 29.29, 22.84, 21.73, 14.31, 0.67 ; **HRMS (EI)** calcd for C₂₂H₃₇NO₂SSi [M-CH₃]^{•+}: 407.2314, found 407.2308.

¹H NMR (300 MHz, CDCl₃): δ 7.71-7.30 (m, 10H), 6.36 (t, *J* = 7.5 Hz, 1H), 4.94 (s, 1H), 4.91 (s, 1H), 3.82 (s, 2H), 3.66 (t, *J* = 6.5 Hz, 2H), 3.16 (s, 3H), 2.00 (q, *J* = 7.5 Hz, 2H), 1.51 (tt, *J* = 7.5 Hz, 2H), 1.35-0.98 (m, 14H), 0.85 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.5 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 151.20, 149.70, 136.30, 131.10, 134.98, 134.93, 134.55, 129.47, 127.90, 110.59, 75.54, 63.91, 57.95, 33.03, 32.64, 31.82, 31.81, 29.39, 25.71, 22.84, 22.72, 14.24 ; **HRMS (ESI)** calcd for C₃₀H₄₄O₂Si [M+Na]⁺: 487.3008, found 487.3006.

¹H NMR (300 MHz, CDCl₃): δ 7.66-7.25 (m, 10H), 6.15 (d, *J* = 2.3 Hz, 1H), 5.68 (d, *J* = 2.3 Hz, 1H), 5.25 (s, 1H), 5.17 (s, 1H), 4.06 (s, 2H), 3.74 (t, *J* = 6.5 Hz, 2H), 3.26 (s, 3H), 1.57 (dt, *J* = 6.8, 6.5 Hz, 2H), 1.36-1.17 (m, 6H), 0.86 (t, *J* = 6.8 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 145.80, 144.87, 135.45, 134.73, 131.73, 130.03, 127.95, 116.77, 74.68, 64.28, 58.08, 32.67, 31.79, 25.68, 22.83, 14.23 ; **HRMS (ESI)** calcd for C₂₄H₃₂O₂Si [M+Na]⁺: 403.2069, found 403.2086.

4f

¹H NMR (300 MHz, CDCl₃): δ 5.97 (t, *J* = 7.5 Hz, 1H), 4.94 (s, 1H), 4.68 (s, 1H), 4.50 (s, 2H), 3.42 (t, *J* = 6.8 Hz, 2H), 2.31 (q, *J* = 7.5 Hz, 2H), 2.08 (s, 3H), 1.95 (tt, *J* = 6.8 Hz, 2H), 0.18 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 170.55, 149.04, 143.90, 142.52, 110.46, 67.13, 33.25, 32.96, 30.78, 21.15, 0.54 ; **HRMS (EI)** calcd for C₁₃H₂₃BrO₂Si [M-CH₃]^{•+}: 303.0416, found 303.0404.

4g

¹H NMR (300 MHz, CDCl₃): δ 5.98 (t, *J* = 7.4 Hz, 1H), 4.93 (s, 1H), 4.68 (s, 1H), 4.49 (s, 2H), 3.41 (t, *J* = 7.1 Hz, 2H), 2.17 (q, *J* = 7.4 Hz, 2H), 2.00 (s, 3H), 1.88 (tt, *J* = 7.1 Hz, 2H), 1.55 (tt, *J* = 7.1 Hz, 2H), 0.16 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 170.80, 149.08, 145.41, 141.49, 110.33, 67.18, 33.79, 32.57, 31.36, 28.49, 21.20, 0.58 ; **HRMS (EI)** calcd for C₁₄H₂₅BrO₂Si [M-CH₃]^{•+}: 317.0572, found 317.0586.

4h

¹H NMR (300 MHz, CDCl₃): δ 6.10 (t, *J* = 6.8 Hz, 1H), 5.00 (s, 1H), 4.77 (s, 1H), 4.67 (d, *J* = 6.8 Hz, 2H), 4.54 (s, 2H), 2.10 (s, 3H), 2.09 (s, 3H), 0.21 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 170.92, 170.67, 148.12, 146.44, 138.60, 111.13, 66.76, 63.45, 21.15, 21.09, 0.33 ; **HRMS (EI)** calcd for C₁₃H₂₂O₄Si [M-CH₃]^{•+}: 255.1053, found 255.1049.

4i

¹H NMR (300 MHz, CDCl₃): δ 5.99 (t, *J* = 7.5 Hz, 1H), 4.94 (s, 1H), 4.68 (s, 1H), 4.49 (s, 2H), 4.08 (t, *J* = 6.7 Hz, 2H), 2.23 (dt, *J* = 7.5, 6.4 Hz, 2H), 2.08 (s, 3H), 2.06 (s, 3H), 1.73 (tt, *J* = 6.7, 6.4 Hz, 2H), 0.17 (s, 9H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 171.81, 171.10, 149.00, 144.70, 141.77, 110.38, 67.14, 64.02, 28.93, 28.71, 21.19, 21.16, 0.48 ; **HRMS (EI)** calcd for C₁₅H₂₆O₄Si [M-CH₃]^{•+}: 283.1366, found 283.1369.

COC(=O)CC(C)=C(Si(C)(C)C)CCCCOC(=O)C

4k

41

4m

S-4

171.72, 149.18, 146.66, 143.37, 140.88, 135.14, 129.82, 127.69, 111.85, 64.87, 55.99, 53.64, 34.72, 32.41, 30.02, 29.71, 29.59, 29.48, 28.84, 26.14, 21.73, 21.26, 0.68 ; **HRMS (EI)** calcd for $C_{27}H_{45}NO_4SSi$ $[M]^{\bullet+}$: 507.2839, found 507.2848.

Mixture of 4n and 5c' (2.2 :1)

1H NMR (300 MHz, $CDCl_3$): (4n, major compound) δ 7.67 (d, J = 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.95 (t, J = 7.4 Hz, 1H), 4.88 (s, 1H), 4.72 (s, 1H), 3.54 (s, 3H), 3.44 (t, J = 6.7 Hz, 2H), 2.63 (s, 3H), 2.44 (s, 3H), 2.20 (q, J = 7.4 Hz, 2H), 1.91 (tt, J = 7.4, 6.7 Hz, 2H), 1.57 (m, 2H), 0.19 (s, 9H) ; **^{13}C NMR (75 MHz, $CDCl_3$) : (Mixture)** δ 149.06, 148.98, 145.34, 143.41, 142.07, 141.73, 140.20, 134.92, 129.84, 127.65, 112.25, 111.90, 56.01, 55.72, 34.67, 34.05, 32.51, 31.38, 29.92, 28.43, 21.73, 18.14, 0.65, 0.443 ; **HRMS (EI)** calcd for $C_{20}H_{32}BrNO_2SSi(4n)$ $[M]^{\bullet+}$: 457.1106, found 457.1113.

1H NMR (300 MHz, $CDCl_3$): δ 7.68-7.26 (m, 10H), 6.30 (t, J = 7.7 Hz, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 3.81 (s, 2H), 3.65 (t, J = 6.5 Hz, 2H), 3.16 (s, 3H), 2.29 (q, J = 7.7 Hz, 2H), 2.14 (t, J = 7.7 Hz, 2H), 1.90 (s, 3H), 1.50 (tt, J = 6.5 Hz, 2H), 1.33-1.18 (m, 6H), 0.85 (t, J = 6.5 Hz, 3H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 151.09, 147.08, 138.69, 135.37, 135.06, 130.08, 128.06, 111.48, 75.47, 63.99, 57.97, 42.81, 32.61, 31.77, 29.93, 27.19, 25.68, 22.83, 14.24 ; **HRMS (EI)** calcd for $C_{28}H_{38}O_3Si$ $[M-CH_3]^{\bullet+}$: 435.2355, found 435.2372.

1H NMR (300 MHz, $CDCl_3$): δ 7.71-7.26 (m, 10H), 6.35 (t, J = 7.4 Hz, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 3.90 (t, J = 6.6 Hz, 2H), 3.77 (s, 2H), 3.65 (t, J = 6.6 Hz, 2H), 3.14 (s, 3H), 2.31 (dt, J = 7.4, 6.8 Hz, 2H), 1.98 (s, 3H), 1.50 (tt, J = 6.6 Hz, 2H), 1.33-1.16 (m, 6H), 0.85 (t, J = 6.5 Hz, 3H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 170.75, 150.60, 140.69, 139.78, 134.97, 134.38, 129.73, 127.65, 111.27, 74.98, 63.56, 63.33, 57.55, 32.17, 31.52, 31.35, 25.27, 22.41, 20.69, 18.82 ; **HRMS (EI)** calcd for $C_{28}H_{38}O_4Si$ $[M-CH_3]^{\bullet+}$: 451.2305, found 451.2322.

¹H NMR (300 MHz, CDCl₃): (**4q**, major compound) δ 7.70-7.35 (m, 10H), 6.38 (t, J = 7.2 Hz, 1H), 4.97 (s, 1H), 4.93 (s, 1H), 3.79 (s, 2H), 3.67 (t, J = 6.6 Hz, 2H), 3.16 (t, J = 7.2 Hz, 2H), 3.15 (s, 3H), 2.65 (q, J = 7.2 Hz, 2H), 1.52 (tt, J = 6.7 Hz, 2H), 1.34-1.19 (m, 6H), 0.86 (t, J = 6.7 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃) :** δ 150.71, 145.00, 140.60, 135.39, 134.59, 130.22, 128.11, 127.93, 111.91, 75.34, 64.02, 57.95, 35.41, 32.59, 31.96, 31.76, 25.69, 22.82, 14.24 ; **HRMS (EI)** calcd for C₂₆H₃₅BrO₂Si [M-Ph]^{•+}: 409.1198, found 409.1178.

¹H NMR (300 MHz, CDCl₃): (*Z*-isomer) δ 7.75-7.35 (m, 10H), 6.34 (t, J = 7.7 Hz, 1H), 5.31 (s, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.34 (brs, 1H), 3.85 (t, J = 6.5 Hz, 2H), 3.81 (s, 2H), 3.15 (s, 3H), 2.05 (q, J = 7.7 Hz, 2H), 2.01 (s, 3H), 1.96-1.17 (m, 13H), 1.61 (s, 3H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 171.26, 151.69, 148.86, 138.05, 137.40, 135.86, 135.80, 129.87, 127.89, 125.04, 111.02, 75.50, 67.94, 64.55, 57.92, 32.56, 31.85, 30.16, 28.31, 25.76, 23.79, 21.15, 19.65 ; **HRMS (EI)** calcd for C₃₁H₄₀O₄Si [M]^{•+}: 504.2696, found 504.2717.

¹H NMR (300 MHz, CDCl₃): δ 7.73-7.26 (m, 15H), 6.38 (t, J = 7.8 Hz, 1H), 5.60 (d, J = 7.0 Hz, 1H), 5.31 (brs, 1H), 4.95 (s, 1H), 4.93 (s, 1H), 4.66 (tt, J = 7.0 Hz, 1H), 4.34 (brs, 1H), 3.79 (s, 2H), 3.14 (s, 3H), 2.75 (m, 2H), 2.43 (m, 2H), 2.02-1.39 (m, 8H), 1.61 (s, 3H), 0.93-0.76 (m, 4H), 0.82 (d, J = 7.0 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 172.11, 153.07, 151.25, 146.74, 139.43, 137.50, 135.60, 135.49, 133.56, 129.92, 128.95, 127.99, 125.84, 125.02, 111.25, 79.17, 75.43, 68.09, 58.01,

54.88, 34.94, 31.88, 30.22, 27.35, 23.82, 19.67, 14.73 ; **HRMS (ESI)** calcd for $C_{38}H_{43}NO_5Si$ $[M+Na]^+$: 644.2808, found 644.2793.

1H NMR (250 MHz, $CDCl_3$) : (Z-isomer) δ 7.70-7.30 (m, 10H), 6.37 (t, J = 7.5 Hz, 1H), 5.35 (brs, 1H), 4.93 (s, 1H), 4.88 (s, 1H), 4.23 (q, J = 6.4 Hz, 1H), 3.89 (t, J = 6.8 Hz, 2H), 3.77 (s, 1H), 3.13 (s, 3H), 2.40 (q, J = 6.8 Hz, 2H), 1.97 (s, 3H), 1.90-1.36 (m, 8H), 1.14(d, J = 6.4 Hz, 3H) ; **^{13}C NMR (62 MHz, $CDCl_3$):** δ 171.33, 151.30, 143.83, 140.78, 140.61, 135.58, 135.51, 130.00, 129.97, 129.93, 127.93, 127.81, 121.93, 111.48, 75.49, 74.50, 63.78, 57.97, 31.95, 25.03, 23.29, 23.00, 22.79, 22.70, 21.11 ; **HRMS (EI)** calcd for $C_{30}H_{38}O_4Si$ $[M]^+$: 490.2539, found 490.2515

1H NMR (300 MHz, $CDCl_3$) : (Z-isomer) δ 7.70-7.30 (m, 10H), 6.31 (t, J = 7.6 Hz, 1H), 5.37 (brs, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.24 (q, J = 6.4 Hz, 1H), 3.81 (s, 2H), 3.78 (t, J = 6.7 Hz, 2H), 3.16 (s, 3H), 2.08 (m, 3H), 1.84 (s, 3H), 1.87 (m, 3H), 1.85 (m, 3H), 1.16 (d, J = 6.4 Hz, 3H) ; **^{13}C NMR (75 MHz, $CDCl_3$):** δ 171.33, 151.58, 147.72, 140.71, 138.77, 135.51, 135.44, 129.91, 129.87, 127.89, 127.77, 121.78, 111.17, 64.20, 57.97, 29.43, 28.34, 25.03, 23.34, 23.05, 22.81, 22.72, 21.12; **HRMS (EI)** calcd for $C_{31}H_{40}O_4Si$ $[M]^+$: 504.2696, found 504.2710.

¹H NMR (250 MHz, CDCl₃) : (Z-isomer) δ 7.71-7.32 (m, 10H), 6.31 (t, *J* = 7.6 Hz, 1H), 5.37 (brs, 1H), 4.95 (s, 1H), 4.91 (s, 1H), 4.24 (q, *J* = 6.4 Hz, 1H), 3.83 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 2H), 3.17 (s, 3H), 2.07- 1.14 (m, 18H), 2.00 (s, 3H), 1.16 (d, *J* = 6.4 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃) :** δ 170.87, 151.33, 148.24, 140.34, 137.81, 135.12, 129.45, 127.44, 127.32, 121.34, 110.62, 75.22, 73.96, 64.18, 57.58, 32.16, 27.94, 25.38, 24.63, 22.95, 22.66, 22.42, 22.33, 20.78; **HRMS (EI)** calcd for C₃₂H₄₂O₄Si [M]⁺: 518.2852, found 518.2858.

¹H NMR (300 MHz, CDCl₃) : (Z-isomer) δ 7.74-7.32 (m, 10H), 6.35 (t, *J* = 7.6 Hz, 1H), 5.42 (brs, 1H), 4.96 (s, 1H), 4.94 (s, 1H), 4.04 (s, 2H), 3.84 (t, *J* = 6.3 Hz, 2H), 3.83 (s, 2H), 2.33 (dt, *J* = 8.3, 5.4 Hz, 1H), 2.27-2.19 (m, 2H), 2.12-1.93 (m, 7H), 2.00 (s, 3H), 1.39-1.16 (m, 7H), 1.24 (s, 3H), 1.11 (d, *J* = 8.4 Hz, 1H), 0.77 (s, 3H) ; **¹³C NMR (62 MHz, CDCl₃):** δ 151.32, 149.04, 147.11, 137.51, 135.33, 130.02, 127.95, 116.74, 111.40, 75.54, 66.30, 64.55, 57.95, 43.15, 41.24, 38.25, 32.48, 31.64, 31.28, 28.30, 26.39, 25.79, 21.16; **HRMS (EI)** calcd for C₃₄H₄₄O₄Si [M]⁺: 544.3009, found 544.2984.

¹H NMR (300 MHz, CDCl₃) : δ 7.72-7.28 (m, 10H), 6.50 (t, *J* = 7.8 Hz, 1H), 5.74 (brs, 1H), 4.76 (brq, *J* = 6.8 Hz, 1H), 4.21 (s, 2H), 3.75 (t, *J* = 6.4, 2H), 3.37 (s, 3H), 1.99 (q, *J* = 7.8 Hz, 2H), 1.98 (s, 3H), 1.34 (d, *J* = 6.8 Hz, 3H), 1.25-1.02 (m, 4H), **¹³C NMR (62 MHz, CDCl₃):** δ 171.26, 142.20, 135.44, 135.40, 134.72, 134.64, 133.10, 130.40, 130.37, 128.18, 128.09, 127.40, 75.05, 69.08, 64.43, 57.92, 33.72, 28.20, 25.82, 24.92, 21.18.

Desilylation of compound **4i**

To a solution of compound **4i** (30 mg, 0.101 mmol) in THF was added n-BuN₄F (1.0 M in THF, 0.12 mL) at room temperature. After stirring for 4 hours, the reaction mixture was concentrated under reduced pressure. The residue was directly purified by flash column chromatography using pentane/ether (10:1) to afford the desilylated product **4i'** (oil, 22 mg, 97%).

4i'

¹H NMR (300 MHz, CDCl₃): δ 6.11 (d, *J* = 15.8 Hz, 1H), 5.70 (dt, *J* = 15.8, 6.6 Hz, 1H), 5.16 (s, 1H), 5.13 (s, 1H), 4.74 (s, 2H), 4.08 (t, *J* = 6.6 Hz, 2H), 2.10 (q, *J* = 6.6 Hz, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 1.75 (tt, *J* = 6.6 Hz, 2H) ; **¹³C NMR (75 MHz, CDCl₃):** δ 171.34, 170.97, 140.31, 130.25, 130.18, 116.28, 64.25, 64.04, 29.54, 28.29, 21.18 ; **(EI)** calcd for C₁₂H₁₈O₄ [M]^{•+}: 226.1205, found 226.1206.