Gold-Catalyzed Intramolecular Allylation of Silyl Alkynes Induced by Silane Alcoholysis

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Supporting Information

Materials and Methods

^1H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer. IR spectra were obtained on a Matteson Polaris FT-IR equipped with a DTGS detector. 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 and Strem. 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. Merck precoated silica gel 60 (particle size 0.040–0.063 mm).

General Procedure for the Preparation of Alkynyl Allyl Silanes

Synthesis of Allyl(methoxy)diphenylsilanes:

To a stirred Et₂O solution (100 mL) of dimethoxydiphenylsilane **S1** (2.44 g, 10.0 mmol) was added allylmagnesium bromide (3.5 mL, 3.0 M Et₂O solution, 10.5 mmol) at 0 °C. The reaction mixture was stirred for 30 min at 0 °C and for 2 h at room temperature. Then the salt was removed by filtration, the solvent was removed under reduced pressure and purification of the residue by column chromatography using silicagel afforded allyl(methoxy)diphenylsilane **S2** (colorless oil, 2.09 g, 8.2 mmol). Similarly, **S3** was prepared via allylation of **S1** with 2-methyl-1-propenylmagnesium chloride.

S2

Colorless Oil (82% yield); ¹H NMR (300 MHz, CDCl₃) δ 7.58–7.62 (m, 4H), 7.35–7.46 (m, 6H), 5.84 (ddt, *J* = 17.1, 10.2, 7.9 Hz, 1H), 4.88–5.00 (m, 2H), 3.57 (s, 3H), 2.19 (dt, *J* = 7.9, 1.3 Hz, 2H); ¹³C NMR (75 MHz, CDCl₃) δ 134.94, 134.35, 133.05, 128.07, 115.33, 51.80, 21.68; IR (neat, cm⁻¹) 3069, 2969, 2929, 2174, 1606, 1429, 1115, 1024; HRMS (ESI) calcd for C₁₆H₁₈OSiNa [M+Na]⁺ 277.1025, found 277.1014.

S3

Colorless Oil (71% yield); ¹H NMR (300 MHz, CDCl₃) δ 7.59–7.63 (m, 4H), 7.33–7.44 (m, 6H), 4.64 (s, 1H), 4.57 (s, 1H), 3.55 (s, 3H), 2.18 (s, 2H), 1.62 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 141.82, 134.96, 134.64, 130.12, 127.97, 110.81, 51.72, 25.49; IR (neat, cm⁻¹) 3074, 3052, 2940, 2840, 1645, 1431, 1124, 1091; HRMS (ESI) calcd for C₁₇H₂₀OSiNa [M+Na]⁺ 291.1181, found 291.1191.

Synthesis of But-2-enyl(methoxy)diphenylsilane:

Allyl(methoxy)diphenylsilane **S2** (1.27 g, 5.0 mmol) was dissolved in freshly distilled CH_2Cl_2 (0.02 M) and Grubbs 2nd generation catalyst, (H_2Imes) (PCy_3) $\text{Cl}_2\text{Ru}=\text{CHPh}$ (40 mg, 0.05 mmol, 1 mol %) was added. After refluxing under directly bubbled *cis*-2-butene for 2 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using mixture of hexanes and EtOAc (50:1 to 20:1 v/v) to yield the *cis/trans* (1:2) mixture of but-2-enyl(methoxy)diphenylsilane **S4** (colorless oil, 0.93 g) in 69% yield.

Colorless Oil ; ¹H NMR (300 MHz, CDCl_3) trans isomer δ 7.57–7.62 (m, 4H), 7.36–7.41 (m, 6H), 5.30–5.55 (m, 2H), 3.56 (s, 3H), 2.09 (d, $J = 7.2$ Hz, 2H), 1.60 (d, $J = 6.9$ Hz, 2H); ¹³C NMR (75 MHz, CDCl_3) *cis/trans* mixture δ 134.99, 134.97, 134.95, 134.70, 130.24, 130.17, 128.10, 128.07, 128.06, 125.91, 124.79, 124.79, 124.04, 123.78, 51.80, 19.67, 18.31, 15.28, 12.81; IR (neat, cm^{-1}) 3070, 3050, 2835, 1698, 1429, 1118, 1084; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{20}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 291.1181, found 291.1176.

Synthesis of Alkynyl Allyl Silanes:

(Alkyne addition was performed according to the literature procedure.¹)

Alkynyl allyl silanes **1a** was prepared via lithiated octyne addition to commercially available allyl(chloro)dimethylsilane. Colorless Oil; ¹H NMR (300 MHz, CDCl_3) δ 5.82 (ddt, $J = 17.0$, 10.4, 8.2 Hz, 1H), 4.84–4.92 (m, 2H), 2.21 (t, $J = 7.1$ Hz, 2H), 1.60 (d, $J = 8.0$ Hz, 2H), 1.25–1.56 (m, 8H), 0.89 (t, $J = 6.8$ Hz,

¹ Shibata, T.; Yamashita, K.; Takagi, K.; Ohta, T.; Soai, K. *Tetrahedron* **2000**, 56, 9259–9267.

3H), 0.13 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 134.57, 113.72, 108.96, 82.93, 31.50, 28.79, 28.66, 24.51, 22.74, 20.08, 14.23, -1.80; IR (neat, cm^{-1}) 2176, 1631, 1465, 1249, 1157.

General Procedure for the Synthesis of Alkynyl Allyl Silanes 1b-j

To a stirred THF solution (10 mL) of alkyne (0.5 mmol) was added *n*-BuLi (0.2 mL, 2.5 M hexane solution, 0.5 mmol) at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was stirred for 30 min at $-78\text{ }^{\circ}\text{C}$ then a THF solution (5 mL) of allyl(methoxy)-, but-2-enyl(methoxy)-, methoxy(2-methylallyl)diphenylsilane **S2/S3/S4** (0.45 mmol) were added. The resulting solution was warmed slowly to $0\text{ }^{\circ}\text{C}$ and quenched with addition of 1 M HCl (10 mL). Organic materials were extracted with Et_2O (10 mL x 2) and the combined extracts were dried over anhydrous MgSO_4 . The solvent was removed under reduced pressure and purification of the residue by column chromatography using silica gel afforded alkynyl allyl silane.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.32–7.42 (m, 6H), 5.85 (ddt, J = 15.8, 10.2, 6.7 Hz, 1H), 4.87–4.97 (m, 2H), 2.35 (t, J = 7.0 Hz, 2H), 2.13 (d, J = 6.7 Hz, 2H), 1.60 (dt, J = 8.1, 7.0 Hz, 2H), 1.41–1.50 (m, 2H), 1.28–1.36 (m, 4H), 0.90 (t, J = 6.9 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.08, 134.58, 133.52, 129.83, 128.04, 115.08, 112.58, 79.30, 31.51, 28.73, 22.78, 22.55, 20.31, 14.25; IR (neat, cm^{-1}) 2931, 2360, 2174, 1632, 1429, 1113; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 355.1858, found 355.1869.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.34–7.44 (m, 6H), 5.85 (ddt, $J = 15.7, 10.1, 7.8$ Hz, 1H), 4.89–5.00 (m, 2H), 4.23 (s, 2H), 3.44 (s, 3H), 2.17 (d, $J = 7.6$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.09, 133.55, 133.02, 130.10, 128.15, 115.51, 105.88, 86.70, 60.69, 57.83, 22.15; IR (neat, cm^{-1}) 3070, 2174, 1631, 1429, 1107; HRMS (ESI) calcd for $\text{C}_{19}\text{H}_{20}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 315.1181, found 315.1168.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.64–7.68 (m, 4H), 7.34–7.44 (m, 6H), 5.85 (ddt, $J = 15.7, 10.2, 7.9$ Hz, 1H), 4.91–5.00 (m, 2H), 2.68 (s, 1H), 2.18 (d, $J = 7.8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.09, 133.15, 132.80, 130.22, 128.20, 115.68, 97.50, 85.28, 21.97; IR (neat, cm^{-1}) 3268, 2036, 1631, 1429, 1115; HRMS (ESI) calcd for $\text{C}_{17}\text{H}_{17}\text{Si}$ $[\text{M}+\text{H}]^+$ 249.1100, found 249.1107.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.66 (m, 4H), 7.33–7.42 (m, 6H), 5.85 (ddt, $J = 17.0, 10.1, 7.9$ Hz, 1H), 4.87–4.98 (m, 2H), 2.14 (dt, $J = 7.9, 1.2$ Hz, 2H), 2.01 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.09, 134.40, 133.47, 129.89, 128.06, 115.17, 107.70, 78.87, 22.44, 5.42; IR (neat, cm^{-1}) 3070, 2918, 2181, 1652, 1428, 1113; HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{18}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 285.1075, found 285.1063.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 7.89–7.92 (m, 4H), 7.71–7.74 (m, 2H), 7.52–7.58 (m, 6H), 7.45–7.48 (m, 3H), 6.11 (ddt, $J = 17.0, 10.1, 7.9$ Hz, 1H), 5.11–5.24 (m, 2H), 2.42 (dt, $J = 8.0, 1.3$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.20, 133.95, 133.25, 132.46, 130.07, 129.20, 128.51, 128.18, 123.00, 115.45, 109.46, 89.07, 22.37; IR (neat, cm^{-1}) 2923, 2155, 1652, 1115; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{20}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 347.1232, found 347.1234.

Colorless Oil; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.65–7.68 (m, 4H), 7.29–7.44 (m, 11H), 5.86 (ddt, $J = 16.8, 9.9, 7.7$ Hz, 1H), 4.90–5.01 (m, 2H), 4.66 (s, 2H), 4.29 (s, 2H), 2.19 (dt, $J = 7.9, 1.3$ Hz, 2H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 137.53, 135.11, 133.56, 133.04, 130.12, 128.65, 128.44, 128.31, 128.13, 115.54, 106.06, 86.92, 71.70, 58.11, 22.13; **IR** (neat, cm^{-1}) 3069, 2174, 1631, 1429, 1113; **HRMS** (ESI) calcd for $\text{C}_{25}\text{H}_{24}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 391.1494, found 391.1498.

Colorless Oil; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.31–7.40 (m, 6H), 5.84 (ddt, $J = 16.9, 9.9, 7.7$ Hz, 1H), 4.86–4.97 (m, 2H), 2.11 (dt, $J = 7.9, 1.3$ Hz, 2H), 1.31 (s, 9H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 135.06, 134.76, 133.56, 129.77, 128.02, 120.95, 114.95, 76.80, 31.13, 28.70, 22.69; **IR** (neat, cm^{-1}) 3070, 2155, 1631, 1429, 1253, 1115; **HRMS** (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 327.1545, found 327.1560.

Colorless Oil; $^1\text{H NMR}$ (300 MHz, CDCl_3) trans isomer: δ 7.62–7.68 (m, 4H), 7.32–7.42 (m, 6H), 5.31–5.56 (overlapped m, 2H), 4.21 (s, 2H), 3.43 (s, 3H), 2.08 (d, $J = 6.6$ Hz, 2H), 1.60 (d, $J = 5.9$ Hz, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) – trans/cis mixture (2:1) 135.13, 135.06, 133.90, 133.86, 133.88, 130.05, 130.00, 128.10, 126.12, 124.82, 124.20, 124.09, 124.06, 105.60, 87.12, 60.73, 57.80, 20.22, 18.27, 15.77, 12.01; **IR** (neat, cm^{-1}) 3069, 3015, 2931, 2174, 1429, 1107; **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 329.1338, found 329.1347.

Colorless Oil; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.66–7.70 (m, 4H), 7.34–7.44 (m, 6H), 4.65 (s, 1H), 4.57 (s, 1H), 4.23 (s, 2H), 3.44 (s, 3H), 2.18 (s, 2H), 1.67 (m, 3H); $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 141.63, 135.08, 134.00, 130.05, 128.12, 111.02, 106.01, 87.18, 60.74, 57.87, 26.06, 25.42; **IR** (neat, cm^{-1}) 3070, 2174, 1639, 1429, 1108; **HRMS** (ESI) calcd for $\text{C}_{20}\text{H}_{22}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 329.1338, found 329.1348.

Representative Procedure for Gold-Catalyzed Intramolecular Allylation of Alkynyl Allyl Silanes:

To a mixture of silyl alkyne **1c** (147 mg, 0.5 mmol) and 4-penten-2-ol (43 mg, 0.5 mmol) under N_2 atmosphere, was added 5 mL of a pre-generated CH_2Cl_2 solution (1 mM) of $\text{Ph}_3\text{PAuSbF}_6$ (1 mol %), which is prepared by mixing stoichiometric amounts of Ph_3PAuCl and AgSbF_6 in CH_2Cl_2 followed by filtration through a plug of celite to remove precipitated AgCl . The resulting solution was stirred at room temperature for 10 min. The solvent was removed under reduced pressure, and the crude product was chromatographed with hexanes–EtOAc (50:1 v/v) to give alkoxy vinyl silane **4b** (colorless oil, 161 mg, 85%).

Colorless Oil (75% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.66 (m, 4H), 7.31–7.40 (m, 6H), 5.70 (br.s, 1H), 5.48 (ddt, $J = 17.1, 10.1, 6.9$ Hz, 1H), 4.85 (dq, $J = 10.1, 1.4$ Hz, 1H), 4.81 (dq, $J = 17.2, 1.5$ Hz, 1H), 4.12 (septet, $J = 6.1$ Hz, 1H), 2.87 (br.d, $J = 6.8$ Hz, 2H), 2.16 (t, $J = 6.6$ Hz, 2H), 1.41–1.54 (m, 2H), 1.26–1.36 (m, 6H), 1.15 (d, $J = 6.0$ Hz, 6H), 0.89 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 163.07, 137.19, 136.21, 135.11, 129.68, 127.90, 118.91, 116.37, 66.14, 41.46, 38.95, 32.00, 29.27, 28.13, 25.87, 22.79, 14.31; IR (neat, cm^{-1}) 3069, 2929, 2174, 1606, 1429, 1115, 1024; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{36}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 415.2433, found 415.2417.

Colorless Oil; ^1H NMR (300 MHz, CDCl_3) δ 5.82 (ddt, $J = 16.9, 10.1, 6.8$ Hz, 1H), 5.01–5.09 (m, 2H), 4.73–4.76 (m, 2H), 2.75 (d, $J = 7.1$ Hz, 2H), 2.01 (t, $J = 7.5$ Hz, 2H), 1.26–1.45 (m, 8H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.75, 136.85, 116.12, 109.91, 41.01, 36.24, 32.01, 29.28, 27.85, 22.87, 14.31.

Colorless Oil (81% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.63–7.66 (m, 4H), 7.32–7.41 (m, 6H), 6.00 (s, 1H), 5.80 (ddt, *J* = 17.0, 10.2, 6.8 Hz, 1H), 5.53 (ddt, *J* = 15.9, 11.0, 6.9 Hz, 1H), 5.03 (d, *J* = 17.1 Hz, 1H), 4.99 (d, *J* = 11.0 Hz, 1H), 4.89 (d, *J* = 10.6 Hz, 1H), 4.86 (d, *J* = 16.6 Hz, 1H), 3.93 (s, 2H), 3.75 (t, *J* = 6.8 Hz, 2H), 3.36 (s, 3H), 2.93 (d, *J* = 6.8 Hz, 2H), 2.31 (q, *J* = 6.8 Hz, 2H); **¹³C NMR (75 MHz, CDCl₃)** δ 157.81, 135.84, 135.61, 135.43, 135.12, 135.08, 129.98, 128.03, 118.68, 116.71, 76.35, 63.29, 58.43, 38.41, 37.26; **IR (neat, cm⁻¹)** 3070, 2928, 1617, 1429, 1266, 1115; **HRMS (ESI)** calcd for C₂₃H₂₈O₂SiNa [M+Na]⁺ 387.1756, found 387.1765.

Colorless Oil (85% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.63–7.68 (m, 4H), 7.32–7.42 (m, 6H), 6.04 (br.s, 1H), 5.69–5.82 (m, 1H), 5.46 (ddt, *J* = 17.0, 10.2, 6.9 Hz, 1H), 4.94–5.02 (m, 2H), 4.79–4.89 (m, 2H), 4.01 (sextet, *J* = 6.1 Hz, 1H), 3.93 (d, *J* = 1.2 Hz, 2H), 3.37 (s, 3H), 2.88 (d, *J* = 6.9 Hz, 2H), 2.14–2.31 (m, 2H), 1.12 (d, *J* = 6.3 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 157.46, 136.50, 135.32, 135.19, 135.08, 129.89, 127.95, 119.49, 117.02, 116.71, 76.40, 69.49, 58.40, 44.13, 38.54, 23.15; **IR (neat, cm⁻¹)** 3070, 2936, 2174, 1430, 1122; **HRMS (ESI)** calcd for C₂₄H₃₁O₂Si [M+H]⁺ 379.2093, found 379.2106.

Colorless Oil (75% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.63–7.67 (m, 4H), 7.32–7.42 (m, 6H), 6.05 (t, *J* = 1.4 Hz, 1H), 5.71 (ddt, *J* = 16.8, 10.1, 6.6 Hz, 1H), 5.45 (ddt, *J* = 17.0, 10.3, 7.0 Hz, 1H), 4.78–4.96 (m, 4H), 3.96 (sextet, *J* = 6.1 Hz, 1H), 3.93 (d, *J* = 1.5 Hz, 2H), 3.37 (s, 3H), 2.88 (d, *J* = 6.9 Hz, 2H), 1.95–2.14 (m, 2H), 1.43–1.67 (m, 2H), 1.13 (d, *J* = 6.3 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 157.34, 138.90, 136.53, 135.41, 135.18, 129.87, 127.94, 119.55, 116.76, 114.45, 76.35, 69.36, 58.41, 38.73, 38.55, 29.94, 23.54; **IR (neat, cm⁻¹)** 3070, 2977, 2928, 1617, 1429, 1116; **HRMS (ESI)** calcd for C₂₅H₃₂O₂SiNa [M+Na]⁺ 415.2069, found 415.2071.

Colorless Oil (87% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.64–7.67 (m, 4H), 7.32–7.42 (m, 6H), 6.06 (br.s, 1H), 5.75 (ddt, J = 16.3, 10.7, 7.2 Hz, 2H), 5.43 (ddt, J = 17.0, 10.1, 6.9 Hz, 1H), 4.98 (d, J = 10.7 Hz, 2H), 4.96 (d, J = 16.4 Hz, 2H), 4.84 (br.d, J = 10.1 Hz, 1H), 4.80 (dq, J = 17.0, 1.5 Hz, 1H), 3.92 (overlapped pentet, J = 5.9 Hz, 1H), 3.92 (d, J = 1.4 Hz, 2H), 3.36 (s, 3H), 2.86 (d, J = 7.0 Hz, 2H), 2.34 (m, 4H); **¹³C NMR (75 MHz, CDCl₃)** 157.52, 136.30, 135.36, 135.25, 135.00, 129.94, 127.89, 119.39, 117.28, 116.74, 72.74, 58.38, 41.03, 38.62; **IR (neat, cm⁻¹)** 3071, 2978, 2930, 1617, 1429, 1114; **HRMS (ESI)** calcd for C₂₆H₃₂O₂SiNa [M+Na]⁺ 427.2069, found 427.2062.

Colorless Oil (86% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.64–7.68 (m, 4H), 7.33–7.43 (m, 6H), 6.04 (s, 1H), 5.47 (ddt, J = 17.1, 10.0, 6.9 Hz, 1H), 4.87 (br.d, J = 10.2 Hz, 1H), 4.83 (br.d, J = 17.0 Hz, 1H), 4.11 (sextet, J = 6.1 Hz, 1H), 3.93 (d, J = 1.5 Hz, 2H), 3.37 (s, 3H), 2.88 (d, J = 6.7 Hz, 2H), 2.41 (ddd, J = 16.5, 5.0, 2.7 Hz, 1H), 2.29 (ddd, J = 16.5, 7.4, 2.6 Hz, 1H), 1.94 (t, J = 2.7 Hz, 1H), 1.25 (d, J = 6.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 157.89, 136.02, 135.38, 135.14, 130.03, 128.06, 118.84, 116.81, 81.61, 76.27, 70.26, 68.31, 58.45, 38.57, 29.23, 23.01 **IR (neat, cm⁻¹)** 3069, 1618, 1429, 1116; **HRMS (ESI)** calcd for C₂₄H₂₈O₂SiNa [M+Na]⁺ 399.1756, found 399.1761.

Colorless Oil (70% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.67–7.70 (m, 4H), 7.33–7.42 (m, 6H), 6.05 (br.s, 1H), 5.52 (ddt, J = 17.1, 10.6, 7.0 Hz, 1H), 4.87 (br.d, J = 10.7 Hz, 1H), 4.85 (br.d, J = 16.9 Hz, 1H), 4.57 (qq, J = 6.4, 2.0 Hz, 1H), 3.94 (d, J = 1.4 Hz, 2H), 3.38 (s, 3H), 2.91 (d, J = 6.9 Hz, 2H), 1.70 (d, J = 2.0 Hz, 3H), 1.39 (d, J = 6.4 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 157.60, 135.98, 135.63, 135.26, 130.06, 127.90, 119.17, 116.66, 81.73, 80.44, 76.34, 60.19, 58.38, 38.53, 25.67, 3.65; **IR (neat, cm⁻¹)** 3070, 2925, 1617, 1428, 1116; **HRMS (ESI)** calcd for C₂₃H₂₅O₂Si [M-CH₃]⁺ 361.1624, found 361.1619.

Colorless Oil (73% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.67–7.70 (m, 4H), 7.32–7.41 (m, 6H), 6.04 (t, *J* = 1.8 Hz, 1H), 5.52 (ddt, *J* = 16.6, 10.8, 7.0 Hz, 1H), 4.87 (br.d, *J* = 10.6 Hz, 1H), 4.85 (dq, *J* = 16.9, 1.6 Hz, 1H), 4.60 (qt, *J* = 6.4, 1.8 Hz, 1H), 3.93 (d, *J* = 1.3 Hz, 2H), 3.36 (s, 3H), 2.91 (br.d, *J* = 6.9 Hz, 2H), 2.07 (td, *J* = 6.8, 2.0 Hz, 2H), 1.29–1.42 (overlapped m, 4H), 1.41 (d, *J* = 6.4 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 157.50, 135.97, 135.64, 135.26, 129.92, 127.92, 119.31, 116.63, 84.89, 82.51, 76.44, 60.23, 58.37, 38.81, 30.81, 25.79, 22.12, 18.56, 13.83; **IR (neat, cm⁻¹)** 3069, 1617, 1429, 1115; **HRMS (ESI)** calcd for C₂₇H₃₄O₂Si Na [M+Na]⁺ 441.2226, found 441.2223.

Colorless Oil (75% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.63–7.68 (m, 4H), 7.30–7.39 (m, 6H), 6.16 (s, 1H), 5.91 (ddt, *J* = 17.4, 10.2, 7.1 Hz, 1H), 5.39 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.04 (br.d, *J* = 10.2 Hz, 1H), 4.99 (br.d, *J* = 17.4 Hz, 1H), 4.83 (br.d, *J* = 10.1 Hz, 1H), 4.79 (br.d, *J* = 16.9 Hz, 1H), 3.91 (s, 2H), 3.36 (s, 3H), 2.87 (d, *J* = 6.7 Hz, 2H), 2.25 (d, *J* = 7.1 Hz, 2H), 1.19 (s, 6H); **¹³C NMR (75 MHz, CDCl₃)** 156.45, 138.22, 135.43, 135.13, 135.09, 129.59, 127.82, 121.34, 117.39, 116.63, 76.51, 75.61, 58.36, 49.69, 38.36, 29.90; **IR (neat, cm⁻¹)** 3070, 2976, 2927, 1617, 1429, 1113, 1040; **HRMS (ESI)** calcd for C₂₅H₃₂O₂SiNa [M+Na]⁺ 415.2069, found 415.2084.

Colorless Oil (79% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.63–7.69 (m, 4H), 7.30–7.41 (m, 6H), 6.13 (br.s, 1H), 5.42 (ddt, *J* = 17.2, 10.3, 7.1 Hz, 1H), 4.77–4.86 (m, 2H), 3.92 (d, *J* = 1.5 Hz, 2H), 3.36 (s, 3H), 2.89 (d, *J* = 7.1 Hz, 2H), 1.25 (s, 9H); **¹³C NMR (75 MHz, CDCl₃)** 156.31, 138.33, 135.16, 129.53, 128.16, 127.81, 121.49, 116.56, 76.57, 73.96, 58.37, 38.29, 32.29; **IR (neat, cm⁻¹)** 3070, 2976, 1429, 1189, 1115; **HRMS (ESI)** calcd for C₂₃H₃₀O₂SiNa [M+Na]⁺ 389.1913, found 389.1924.

Colorless Oil (71% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.32–7.41 (m, 6H), 5.69–5.90 (m, 1H), 5.71 (br.s, 1H), 5.46 (ddt, $J = 16.8, 10.1, 6.8$ Hz, 1H), 4.95–5.02 (m, 2H), 4.75–4.88 (m, 2H), 3.99 (sextet, $J = 6.1$ Hz, 1H), 2.86 (br.d, $J = 7.1$ Hz, 2H), 2.11–2.32 (m, 2H), 2.16 (t, $J = 6.8$ Hz, 2H), 1.48 (m, 2H), 1.26–1.35 (m, 6H), 1.12 (d, $J = 5.9$ Hz, 3H), 0.89 (t, $J = 6.9$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 163.19, 137.08, 136.13, 135.47, 135.08, 129.83, 127.90, 118.83, 116.93, 116.41, 69.38, 44.18, 41.52, 38.93, 32.00, 29.26, 28.14, 23.17, 22.89, 14.31; IR (neat, cm^{-1}) 3070, 2929, 2174, 1607, 1429, 1115; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{38}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 441.2590, found 441.2576.

Colorless Oil (85% yield); ^1H NMR (300 MHz, CDCl_3) trans isomer: δ 7.59–7.63 (m, 4H), 7.30–7.43 (m, 6H), 6.27 (dt, $J = 18.6, 5.8$ Hz, 1H), 6.05 (ddd, $J = 18.6, 1.5, 1.3$ Hz, 1H), 5.72–5.91 (overlapped m, 2H), 4.95–5.09 (overlapped m, 4H), 4.02 (sextet, $J = 6.0$ Hz, 1H), 2.92–2.98 (m, 2H), 2.26 (overlapped m, 2H), 1.66 (d, $J = 6.3$ Hz, 3H); cis isomer : δ 7.63–7.67 (m, 4H), 7.30–7.43 (m, 6H), 6.61 (dt, $J = 14.1, 7.1$ Hz, 1H), 5.98 (ddd, $J = 14.1, 1.6, 1.2$ Hz, 1H), 5.72–5.91 (overlapped m, 1H), 5.63 (ddt, $J = 16.7, 10.2, 6.4$ Hz, 1H), 4.95–5.09 (overlapped m, 2H), 4.89 (ddt, $J = 10.2, 3.1, 1.5$ Hz, 1H), 4.83 (ddt, $J = 17.1, 3.2, 1.7$ Hz, 1H), 4.02 (sextet, $J = 6.0$ Hz, 1H), 2.79–2.85 (m, 2H), 2.21–2.35 (overlapped m, 2H), 1.66 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) – cis/trans mixture (1:1.7) 151.07, 150.69, 136.40, 135.99, 135.82, 135.70, 135.65, 135.41, 135.33, 135.29, 135.07, 129.92, 127.94, 125.69, 124.68, 117.02, 116.31, 115.66, 69.52, 69.48, 44.21, 44.14, 40.90, 38.59, 23.36, 23.18; IR (neat, cm^{-1}) 3069, 1614, 1428, 1116; HRMS (ESI) calcd for $\text{C}_{22}\text{H}_{27}\text{O}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 335.1831, found 335.1823.

Colorless Oil (80% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.32–7.41 (m, 6H), 5.76 (overlap m, 1H), 5.71 (s, 1H), 5.49 (ddt, $J = 17.2, 10.2, 6.9$ Hz, 1H), 4.98 (overlapped m, 2H), 4.87 (ddt, $J = 10.1, 2.1, 1.0$ Hz, 1H), 4.81 (ddt, $J = 17.0, 3.3, 1.6$ Hz, 1H), 4.00 (sextet, $J = 6.0$ Hz, 1H), 2.84 (br.d, $J = 7.1$ Hz, 2H), 2.23 (m, 2H), 1.91

(d, $J = 1.3$ Hz, 3H), 1.12 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 159.02, 136.92, 135.89, 135.43, 135.17, 129.77, 127.91, 120.51, 116.94, 116.54, 69.37, 44.17, 42.90, 26.68, 23.14; IR (neat, cm^{-1}) 3069, 1612, 1429, 1116, 1085; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{29}\text{OSi}$ $[\text{M}+\text{H}]^+$ 349.1987, found 349.2003.

Colorless Oil (55% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.30–7.80 (m, 15H), 6.29 (s, 1H), 5.71–5.74 (m, 1H), 5.47 (ddt, $J = 16.7$, 10.2, 6.4 Hz, 1H), 4.95–5.10 (m, 2H), 4.75 (dq, $J = 10.3$, 1.6 Hz, 1H), 4.69 (dq, $J = 16.9$, 1.6 Hz, 1H), 4.05 (sextet, $J = 6.0$ Hz, 1H), 3.39 (br.d, $J = 6.4$ Hz, 2H), 2.27 (m, 2H), 1.15 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 159.42, 143.27, 136.42, 135.72, 135.21, 134.98, 130.46, 129.97, 128.40, 128.05, 126.77, 123.56, 117.09, 116.53, 70.32, 44.17, 39.71, 23.22; IR (neat, cm^{-1}) 3070, 2973, 1429, 1117, 1083; HRMS (ESI) calcd for $\text{C}_{28}\text{H}_{30}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 433.1964, found 433.1976.

Colorless Oil (68% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.65–7.72 (m, 4H), 7.48–7.51 (m, 2H), 7.22–7.43 (m, 9H), 6.28 (s, 1H), 5.49 (ddt, $J = 16.8$, 10.4, 6.5 Hz, 1H), 4.77 (ddt, $J = 10.6$, 1.8, 1.4 Hz, 1H), 4.71 (ddt, $J = 17.0$, 1.8, 1.6 Hz, 1H), 4.19 (m, 1H), 3.41 (dt, $J = 6.6$, 1.6 Hz, 2H), 1.18 (d, $J = 5.0$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 159.31, 143.24, 136.54, 135.82, 135.20, 134.52, 130.11, 128.38, 127.84, 126.76, 123.66, 116.48, 66.64, 39.64, 25.89; IR (neat, cm^{-1}) 3070, 2836, 1591, 1429, 1117, 1080; HRMS (ESI) calcd for $\text{C}_{26}\text{H}_{28}\text{OSiNa}$ $[\text{M}+\text{Na}]^+$ 407.1807, found 407.1797.

Colorless Oil (73% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.64–7.68 (m, 4H), 7.25–7.42 (m, 11H), 6.13 (t, $J = 1.4$ Hz, 1H), 5.46 (ddt, $J = 17.1$, 10.2, 6.9 Hz, 1H), 4.95–5.02 (triplet of septet, $J = 7.1$, 1.4 Hz, 1H), 4.77–4.86 (m, 2H), 4.53 (s, 2H), 4.04 (d, $J = 1.3$ Hz, 2H), 3.95 (sextet, $J = 6.1$ Hz, 1H), 2.91 (d, $J = 6.9$ Hz, 2H), 1.96 (m, 2H), 1.63 (d, $J = 1.2$ Hz, 3H), 1.38–1.64 (m, 2H), 1.52 (s, 3H), 1.14 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 157.37, 138.57, 136.63,

135.45, 135.21, 131.53, 129.85, 128.65, 128.58, 128.01, 127.93, 127.89, 120.24, 116.74, 74.17, 72.44, 69.66, 39.75, 38.55, 25.86, 24.39, 23.57, 17.81; **IR (neat, cm⁻¹)** 3068, 2968, 2926, 1617, 1429, 1266, 1114; **HRMS (ESI)** calcd for C₃₃H₄₀O₂SiNa [M+Na]⁺ 519.2695, found 519.2675.

Colorless Oil (56% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.69–7.74 (m, 4H), 7.32–7.43 (m, 6H), 5.83 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1H), 5.04 (ddt, *J* = 17.3, 2.2, 1.5 Hz, 1H), 5.01 (ddt, *J* = 10.4, 2.2, 1.5 Hz, 1H), 4.12 (sextet, *J* = 6.1 Hz, 1H), 2.20–2.43 (m, 2H), 1.32 (s, 9H), 1.21 (d, *J* = 6.1 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 135.58, 135.41, 134.94, 130.17, 127.77, 119.83, 116.88, 77.94, 69.99, 43.94, 30.98, 28.63, 22.95; **IR (neat, cm⁻¹)** 2970, 2916, 2154, 1541, 1429, 1253, 1121; **HRMS (ESI)** calcd for C₂₃H₂₈OSiNa [M+Na]⁺ 371.1807, found 371.1815.

Colorless Oil (86% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.77–7.80 (m, 4H), 7.45–7.51 (m, 6H), 6.17 (t, *J* = 1.5 Hz, 1H), 5.79 (ddd, *J* = 17.2, 10.5, 5.8 Hz, 1H), 4.99 (dt, *J* = 10.4, 1.6 Hz, 1H), 4.89 (dt, *J* = 17.3, 1.6 Hz, 1H), 4.25 (septet, *J* = 6.1 Hz, 1H), 4.07 (dd, *J* = 14.8, 1.6 Hz, 1H), 4.00 (dd, *J* = 14.7, 1.6 Hz, 1H), 3.58 (qd, *J* = 6.1, 5.7 Hz, 1H), 3.48 (s, 3H), 1.26 (dd, *J* = 6.1, 1.5 Hz, 6H), 1.04 (d, *J* = 7.0 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** 161.66, 140.74, 136.82, 135.22, 129.78, 127.95, 117.88, 114.10, 72.79, 66.21, 58.46, 42.48, 25.93, 17.29; **IR (neat, cm⁻¹)** 3070, 2970, 1616, 1429, 1116; **HRMS (ESI)** calcd for C₂₃H₃₀O₂SiNa [M+Na]⁺ 389.1913, found 389.1925.

Colorless Oil (85% yield); **¹H NMR (300 MHz, CDCl₃)** δ 7.65–7.68 (m, 4H), 7.32–7.42 (m, 6H), 6.07 (t, *J* = 1.5 Hz, 1H), 5.67–5.82 (m, 2H), 5.64 (ddd, *J* = 17.4, 10.5, 5.9 Hz, 1H), 4.98 (d, *J* = 10.3 Hz, 2H), 4.97 (d, *J* = 17.3 Hz, 2H), 4.87 (dt, *J* = 10.3, 1.6 Hz, 1H), 4.75 (dt, *J* = 17.4, 1.6 Hz, 1H), 3.85–3.97

(overlapped m, 3H), 3.36–3.46 (overlapped m, 1H), 3.36 (s, 3H), 2.16–2.33 (m, 4H), 0.89 (d, $J = 7.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 161.73, 140.60, 136.41, 135.35, 135.02, 129.89, 127.90, 117.72, 117.26, 114.14, 72.69, 58.45, 42.54, 41.03, 17.24; IR (neat, cm^{-1}) 3070, 2929, 1615, 1429, 1115; HRMS (ESI) calcd for $\text{C}_{27}\text{H}_{34}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 441.2226, found 441.2221.

Colorless Oil (62% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.76–7.68 (m, 4H), 7.46–7.32 (m, 6H), 5.82 (ddt, $J = 17.1, 9.9, 7.3$ Hz, 1H), 5.08–4.98 (m, 2H), 4.22 (s, 2H), 4.17 (sextet, $J = 6.1$ Hz, 1H), 3.43 (s, 3H), 2.43–2.20 (m, 2H), 1.22 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 135.20, 134.89, 134.84, 134.33, 134.20, 130.47, 128.09, 117.09, 105.01, 87.25, 70.28, 60.58, 57.85, 43.85, 22.97; IR (neat, cm^{-1}) 3070, 2975, 1617, 1429, 1115; HRMS (ESI) calcd for $\text{C}_{21}\text{H}_{24}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 359.1443, found 359.1429.

Representative Procedure for Ring-Closing Metathesis of Alkoxy Vinyl Silane:

Alkoxy vinyl silane **4c** (98 mg, 0.25 mmol) was dissolved in freshly distilled CH_2Cl_2 (0.002 M) and Grubbs 2nd generation catalyst **22**, (H_2Imes) $(\text{PCy}_3)\text{Cl}_2\text{Ru}=\text{CHPh}$ (10 mg, 0.012 mmol, 5 mol %) was added. After stirred at room temperature under nitrogen for 4 h, the reaction mixture was concentrated under reduced pressure. The residue was purified by flash column chromatography using mixture of hexane and EtOAc (50:1 to 10:1 vol/vol) yield the cyclic siloxane **23** (colorless oil, 67 mg, 74%).

Colorless Oil (74% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.71–7.74 (m, 2H), 7.61–7.64 (m, 2H), 7.30–7.41 (m, 6H), 6.01 (s, 1H), 5.63 (dt, $J = 11.3, 4.6$ Hz, 1H), 5.38 (tdd, $J = 11.0, 5.7, 1.6$ Hz, 1H), 4.11 (dd, $J = 14.0, 1.3$ Hz, 1H), 4.02 (dd, $J = 14.0, 1.2$ Hz, 1H), 4.00–4.10 (overlapped m, 1H), 3.37–3.47 (overlapped m, 1H), 3.39 (s, 3H), 2.76 (qd, $J = 13.4, 2.5$ Hz, 1H), 2.36 (dd, $J = 13.3, 3.3$ Hz, 1H), 1.82–1.91 (m, 1H), 1.67–1.78 (m, 1H), 1.28–1.39 (m, 1H), 1.01 (d, $J = 4.3, 3\text{H}$); ^{13}C NMR (75 MHz, CDCl_3) 160.32, 138.64, 137.47, 134.67, 129.66, 127.94, 126.96, 116.84, 76.45, 67.23, 58.48, 38.35, 32.93, 24.41, 23.14; IR (neat, cm^{-1}) 2933, 2360, 1616, 1429, 1113; HRMS (ESI) calcd for $\text{C}_{23}\text{H}_{28}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 387.1756, found 387.1746.

Colorless Oil (85% yield); ^1H NMR (300 MHz, CDCl_3) δ 7.65–7.69 (m, 2H), 7.44–7.47 (m, 2H), 7.24–7.41 (m, 6H), 5.95 (br.s, 1H), 5.76 (dd, $J = 11.0, 7.4$ Hz, 1H), 4.70 (q, $J = 6.5$ Hz, 1H), 4.52 (s, 1H), 4.39 (s, 1H), 4.16 (t, $J = 11.9$ Hz, 1H), 4.04 (dd, $J = 14.0, 1.5$ Hz, 1H), 3.97 (dd, $J = 14.0, 1.4$ Hz, 1H), 3.41 (s, 3H), 2.43 (dd, $J = 12.6, 7.4$ Hz, 1H), 1.54 (s, 3H), 1.47 (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) 158.80, 145.92, 143.18, 136.69, 135.56, 134.57, 129.69, 128.06, 120.82, 111.25, 78.83, 70.50, 58.42, 30.73, 24.38, 21.94; IR (neat, cm^{-1}) 2924, 2155, 1541, 1114; HRMS (ESI) calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2\text{SiNa}$ $[\text{M}+\text{Na}]^+$ 399.1756, found 399.1742.

(Cyclic siloxane **25** was characterized as its ring-opened form **25'** after treatment with $\text{HF}\cdot\text{Pyridine}$.)
Colorless Oil, ^1H NMR (300 MHz, CDCl_3) δ 7.63–7.67 (m, 4H), 7.38–7.50 (m, 6H), 5.92 (d, $J = 6.6$ Hz, 1H), 5.12 (dd, $J = 8.4, 6.8$ Hz, 1H), 4.78–4.82 (m, 2H), 4.67 (q, $J = 6.6$ Hz, 1H), 4.12 (d, $J = 13.5$ Hz, 1H), 3.93 (d, $J = 13.7$ Hz, 1H), 3.36 (s, 3H), 3.16 (dd, $J = 14.4, 8.5$ Hz, 1H), 3.08 (dd, $J = 14.8, 6.6$ Hz, 1H), 2.57 (br.s, 1H), 2.06–2.20 (m, 2H), 1.23–1.36 (m, 4H), 1.19 (d, $J = 6.7$ Hz, 3H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (75

MHz, CDCl₃) 160.58, 150.06, 146.60, 134.63, 130.96, 128.37, 125.38, 119.8, 118.34, 112.72, 65.56, 58.14, 42.71, 36.37, 32.56, 30.58, 22.55, 21.64, 14.23 **IR (neat, cm⁻¹)** 3416, 2931, 1541, 1429, 1118; **LRMS (ESI)** calcd for C₂₈H₃₈O₃SiNa [M-F+MeO]⁺ 473.7, found 473.7 (Fluoride was displaced by methanol solvent during sampling).

(Compound **26** was characterized as its acetate **26'**.)
 Colorless Oil, **¹H NMR (300 MHz, CDCl₃)** δ 7.64–7.68 (m, 4H), 7.29–7.39 (m, 6H), 6.11 (br.s, 1H), 4.96–5.16 (m, 2H), 3.97 (t, *J* = 6.7 Hz, 2H), 3.87–3.94 (m, 2H), 3.36 (s, 3H), 2.82 (d, *J* = 6.4 Hz, 2H), 2.00–2.06 (m, 2H), 2.04 (s, 3H), 1.55 (m, 2H), 1.25 (s, 9H); **¹³C NMR (75 MHz, CDCl₃)** 171.30, 157.44, 138.44, 135.14, 131.02, 129.54, 127.80, 127.36, 121.30, 76.65, 73.93, 64.16, 58.37, 36.97, 32.30, 28.90, 28.36, 21.20; **IR (neat, cm⁻¹)** 2933, 2360, 1738, 1617, 1429, 1242, 1116; **HRMS (ESI)** calcd for C₂₈H₃₈O₄SiNa [M+Na]⁺ 489.2437, found 489.2433.

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