Cross and Ring-Closing Metathesis of 1,3-Diynes: Metallotropic [1,3]-Shift of Ruthenium Carbenes

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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. Stable symmetrical/unsymmetrical diynes were synthesized according to the literature procedures unless otherwise indicated.¹ 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).

Representative Procedure for Cross Metathesis

Diyne **1c** (40 mg, 0.099 mmol) and 1-octene (28 mg, 0.322 mmol) were dissolved in freshly distilled CH_2Cl_2 (0.02 M). Grubbs 2nd generation catalyst **1**, (H_2Imes) (PCy_3) $\text{Cl}_2\text{Ru}=\text{CHPh}$, (4.2 mg, 0.005 mmol, 5 mol %) was added to the reaction mixture. After refluxing under nitrogen for 4 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 **2c** (oil, 45 mg, 88%).

^1H NMR (300 MHz, CDCl_3): (Z-isomer) δ 5.97 (t, $J = 7.4$ Hz, 1H), 5.46 (s, 1H), 4.95 (s, 1H), 2.45-2.12 (m, 6H), 1.63-1.21 (m, 16H), 0.96-0.82 (m, 9H) (E-isomer) δ 5.87 (t, $J = 7.6$ Hz, 1H), 5.01 (s, 1H), 4.80 (s, 1H), 2.45-2.12 (m, 6H), 1.63-1.21 (m, 16H), 0.96-0.82 (m, 9H); ^{13}C NMR (75 MHz, CDCl_3): (Z-isomer) δ 146.38, 136.56, 124.67, 113.16, 95.12, 77.40, 32.98, 31.95, 31.20, 31.11, 30.98, 29.28, 29.26, 22.86, 22.85, 22.24, 19.41, 14.30, 14.19, 13.83 (E-isomer) δ 146.30, 138.80, 125.33, 113.67, 88.09, 81.40, 35.62, 31.95, 31.20, 30.21, 29.98, 29.60, 29.30, 22.85, 22.65, 22.22, 19.28, 14.30, 14.16, 13.83
HRMS (EI) calcd for $\text{C}_{20}\text{H}_{34}$ $[\text{M}]^+$: 274.2661, found 274.2654.

¹ (a) Marino, J. P.; Nguyen, H. N. *J. Org. Chem.* **2002**, *67*, 6841. (b) Kim, S.; Kim, S.; Lee, T.; Ko, H.; Kim, D. *Org. Lett.* **2004**, *6*, 3601. (c) Rodríguez, D.; Castedo, L.; Saá, C. *Synlett.* **2004**, 377 and references cited therein.

¹H NMR (300 MHz, CDCl₃): (*Z*-isomer) δ 6.07 (t, J = 7.4 Hz, 1H), 5.66 (s, 1H), 5.32 (s, 1H), 4.90 (s, 2H), 4.78 (s, 2H), 2.45-2.35 (dt, J = 7.4, 7.3 Hz, 2H), 2.13 (s, 3H), 2.10 (s, 3H), 1.50-1.19 (m, 8H), 0.89 (t, J = 6.6 Hz, 3H) (*E*-isomer) δ 6.15 (t, J = 7.5 Hz, 1H), 5.37 (s, 1H), 5.11 (s, 1H), 4.80 (s, 2H), 4.70 (s, 2H), 2.11 (dt, J = 7.5, 7.4 Hz, 2H), 2.12 (s, 3H), 2.10 (s, 3H), 1.50-1.19 (m, 8H), 0.90 (t, J = 6.8 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** : (*Z*-isomer) δ 170.88, 170.42, 144.13, 140.40, 117.48, 117.40, 89.05, 82.57, 64.52, 53.00, 31.89, 31.27, 29.66, 29.15, 29.04, 22.83, 21.18, 21.00, 14.31 (*E*-isomer) δ 170.77, 170.35, 143.28, 139.63, 121.32, 121.68, 86.39, 81.63, 65.75, 53.06, 31.91, 31.27, 29.66, 29.20, 29.04, 22.83, 21.12, 21.01, 14.31 ; **HRMS (ESI)** calcd for C₁₈H₂₆O₄ [MNa]⁺: 329.1729, found 329.1733.

¹H NMR (300 MHz, CDCl₃): δ 7.27-7.15 (m, 10H), 5.99 (t, J = 7.2 Hz, 1H), 5.58 (dd, J = 6.7, 6.5 Hz, 1H), 5.54 (t, J = 6.7 Hz, 1H), 5.52 (s, 1H), 5.22 (s, 1H), 2.80 (t, J = 8.0 Hz, 2H); 2.76-2.55 (m, 2H), 2.34 (dd, J = 7.2, 7.1 Hz, 2H), 2.19-2.09 (m, 2H), 2.08-1.96 (m, 2H), 2.07 (s, 3H), 2.06 (s, 3H), 1.41-1.26 (m, 8H), 0.87 (t, J = 6.8 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** : δ 170.23, 170.07, 144.72, 141.49, 141.00, 140.19, 128.71, 128.65, 128.63, 128.60, 126.35, 126.20, 121.44, 114.12, 92.27, 82.19, 72.66, 64.38, 36.65, 36.10, 32.09, 31.89, 31.65, 31.31, 29.29, 29.00, 22.81, 21.34, 21.17, 14.28 ; **HRMS (ESI)** calcd for C₃₄H₄₂O₄ [MNa]⁺: 537.2981, found 537.2970.

¹H NMR (300 MHz, CDCl₃): (*Z*-isomer) δ 6.09 (t, J = 7.7 Hz, 1H), 5.51 (s, 1H), 4.99 (s, 1H), 4.91 (s, 1H), 2.42 (dd, J = 7.7, 7.6 Hz, 2H), 2.26 (t, J = 7.1 Hz, 2H), 1.51-1.21 (m, 4H),

1.04 (t, $J = 8.2$ Hz, 9H), 0.96-0.86 (m, 6H), 0.65 (q, $J = 8.2$ Hz, 6H) (*E*-isomer) δ 6.04 (t, $J = 7.7$ Hz, 1H), 5.04 (s, 1H), 4.83 (s, 1H), 2.26 (t, $J = 7.1$ Hz, 2H), 2.20 (dd, $J = 7.7, 7.6$, 2H), 1.51-1.21 (m, 4H), 1.00 (t, $J = 8.2$ Hz, 9H), 0.96-0.86 (m, 6H), 0.61 (q, $J = 8.2$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3): (*Z*-isomer) δ 141.42, 138.84, 124.96, 113.61, 103.23, 97.42, 32.94, 31.93, 30.88, 29.80, 29.31, 22.85, 22.84, 14.27, 7.76, 4.80 (*E*-isomer) δ 145.54, 138.84, 125.28, 114.27, 107.89, 88.90, 35.69, 31.42, 30.26, 29.81, 29.30, 22.85, 22.66, 14.27, 7.76, 4.80; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{40}\text{Si}$ $[\text{M}]^{+}$: 332.2899, found 332.2911.

^1H NMR (300 MHz, CDCl_3): (*Z*-isomer) δ 6.04 (t, $J = 7.5$ Hz, 1H), 5.71 (s, 1H), 5.29 (s, 1H), 4.76 (s, 2H), 2.42 (dt, $J = 7.2$ Hz, 2H), 2.06 (s, 3H), 1.47-1.18 (m, 6H), 1.02 (t, $J = 7.9$ Hz, 9H), 0.87 (t, $J = 7.0$ Hz, 3H), 0.63 (q, $J = 7.6$ Hz, 8H) (*E*-isomer) δ 6.11 (t, $J = 7.7$ Hz, 1H), 5.33 (s, 1H), 5.08 (s, 1H), 4.69 (s, 2H), 2.18 (dt, $J = 7.2$ Hz, 2H), 2.06 (s, 3H), 1.47-1.18 (m, 6H), 0.98 (t, $J = 7.9$ Hz, 9H), 0.87 (t, $J = 7.0$ Hz, 3H), 0.58 (q, $J = 7.6$ Hz, 8H); ^{13}C NMR (75 MHz, CDCl_3): (*Z*-isomer) δ 170.89, 139.92, 139.72, 122.57, 117.40, 102.07, 98.06, 64.58, 31.92, 31.48, 29.72, 29.26, 22.85, 21.13, 14.28, 7.46, 4.76 (*E*-isomer) δ 170.66, 143.31, 139.78, 121.95, 116.98, 106.29, 90.17, 65.84, 31.92, 29.26, 22.85, 21.07, 14.28, 7.70, 4.70; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{36}\text{O}_2\text{Si}$ $[\text{M}]^{+}$: 348.2485, found 348.2490.

^1H NMR (300 MHz, CDCl_3): (*Z*-isomer) δ 7.67 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 8.3$ Hz, 2H), 6.46 (t, $J = 7.5$ Hz, 1H), 5.70 (s, 1H), 5.10 (s, 1H), 3.77 (s, 2H), 2.57 (s, 3H), 2.15 (dt, $J = 7.5, 7.4$ Hz, 2H), 1.55-1.15 (m, 8H), 1.02 (t, $J = 7.5$ Hz, 9H), 0.91-0.86 (m, 3H), 0.64 (q, $J = 7.5$ Hz, 6H) (*E*-isomer) δ 7.68 (d, $J = 8.3$ Hz, 2H), 7.31 (d, $J = 8.3$ Hz, 2H), 6.07 (t, $J = 7.7$ Hz, 1H), 5.37 (s, 1H), 5.10 (s, 1H), 3.76 (s, 2H), 2.70 (s, 3H), 2.43 (dt, $J = 7.7, 7.6$ Hz, 2H), 1.55-1.15 (m, 8H), 0.95 (t, $J = 7.5$ Hz, 9H), 0.91-0.86 (m, 3H), 0.57 (q,

$J = 7.5$ Hz, 6H) ; ^{13}C NMR (75 MHz, CDCl_3) : (Z-isomer) δ 143.62, 141.78, 138.94, 133.94, 129.88, 127.83, 121.91, 118.58, 102.52, 97.58, 53.03, 34.26, 31.87, 29.71, 29.26, 22.80, 21.70, 14.26, 7.74, 4.72 (E-isomer) δ 143.43, 143.05, 138.34, 134.88, 129.71, 127.71, 122.67, 117.04, 106.31, 90.13, 53.79, 35.22, 31.66, 29.67, 28.92, 22.78, 21.70, 14.26, 7.67, 4.60 ; HRMS (EI) calcd for $\text{C}_{27}\text{H}_{43}\text{NO}_2\text{SSi}$ $[\text{M}]^{+}$: 473.2784, found 473.2791.

^1H NMR (300 MHz, CDCl_3): δ 6.10 (t, $J = 7.5$ Hz, 1H), 5.69 (q, $J = 7.4$ Hz, 1H), 5.59 (s, 1H), 5.27 (s, 1H), 2.42 (dd, $J = 7.5, 7.4$ Hz, 2H), 2.06 (s, 3H), 2.03-1.90 (m, 2H), 1.39 (d, $J = 7.4$ Hz, 3H), 1.49-1.24 (m, 8H), 1.03 (t, $J = 7.9$ Hz, 9H), 0.88 (t, $J = 6.7$ Hz, 3H), 0.64 (q, $J = 7.9$ Hz, 6H) ; ^{13}C NMR (75 MHz, CDCl_3) : 170.28, 145.78, 139.84, 122.54, 113.71, 102.49, 97.86, 69.35, 31.86, 31.40, 29.11, 29.00, 22.79, 21.45, 20.35, 14.23, 7.71, 4.70 ; MS (EI) calcd for $\text{C}_{22}\text{H}_{38}\text{O}_3\text{Si}$ $[\text{M} - \text{COCH}_3]^+$: 319.2, found 319.2.

Chemical derivation to confirm the structural assignment

nOe data of **3h'** to confirm the stereochemistry of **3h**:

Downfield shifts upon MnO_2 oxidation

- H_a : 0.22 ppm

- $\text{H}_b/\text{H}_{b'}$: 0.49/0.55 ppm

¹H NMR (300 MHz, CDCl₃): δ 6.32 (t, *J* = 7.3 Hz, 1H), 5.97 (s, 1H), 5.86 (s, 1H), 3.24 (s, 1H), 2.42 (dd, *J* = 7.5, 7.4 Hz, 2H), 2.39 (s, 3H), 1.50-1.23 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H) ; **¹³C NMR (75 MHz, CDCl₃) :** 200.2, 147.2, 141.5, 123.5, 119.18, 83.1, 80.1, 31.9, 31.4, 29.2, 28.8, 28.7, 22.8, 14.3 ; **HRMS (EI)** calcd for C₁₄H₂₀O [*M*⁺]: 204.1514, found 204.1511

¹H NMR (300 MHz, CDCl₃): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.3 Hz, 2H), 6.41 (t, *J* = 7.7 Hz, 1H), 5.70 (s, 1H), 5.14 (s, 1H), 5.13 (q, *J* = 6.9 Hz, 1H), 2.53 (s, 3H), 2.42 (s, 3H), 2.38 (dt, *J* = 7.7, 7.6 Hz, 2H), 1.48-1.24 (m, 8H), 1.15 (d, *J* = 6.9 Hz, 3H), 1.03 (t, *J* = 7.9 Hz, 9H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.65 (q, *J* = 7.9 Hz, 2H) ; **¹³C NMR (75 MHz, CDCl₃) :** δ 144.75, 143.11, 141.36, 137.35, 129.67, 127.70, 122.97, 116.54, 103.10, 97.56, 52.36, 31.89, 31.61, 29.31, 28.94, 28.41, 22.81, 21.68, 15.36, 14.28, 7.75, 4.72 ; **HRMS (EI)** calcd for C₂₈H₄₅NO₂SSi [*M*⁺]: 487.2940, found 487.2934.

Representative Procedures for Ring-Closing Metathesis

(A) For stable compounds:

Enediyne **18g** (90 mg, 0.437 mmol) were dissolved in freshly distilled CH₂Cl₂ (0.02 M). Grubbs 2nd generation catalyst **1**, (H₂Imes) (PCy₃)Cl₂Ru=CHPh, (18 mg, 0.022 mmol, 5 mol %) was added to the reaction mixture. After stirring under reflux for 3.5 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 RCM-[1,3]-shift product **19g** (oil, 80 mg, 89%).

(B) For unstable compounds (**19a**, **19b**, **19c**, **19d**, **19e**, **19i**)²

Alcohol and silane were mixed together with 1 mol % of [Cl₂Ru(*p*-cymene)]₂ catalyst and left to react 3-4 hours. The reddish oil was then filtered through a short pad of silica gel with a 1: 1 mixture of hexane and diethyl ether. After concentrating the silyl ether, freshly distilled CH₂Cl₂ was added to make a solution of 0.003M concentration and 7.5

² Miller, R. L.; Maifeld, S. V.; Lee, D. *Org. Lett.* **2004**, *6*, 2773.

mol % of Grubbs 2nd generation catalyst **1**, (H₂Imes) (PCy₃)Cl₂Ru=CHPh, was added. The reaction was refluxed for 4-6 hours or until the starting material was consumed. Solvent was removed, and characterization was done with the crude material because of the sensitivity of the products. Yields were determined by ¹H NMR based on internal standard added to the reaction.

12a

¹H NMR (300 MHz, CDCl₃) : δ 5.80 (ddt, *J* = 16.8, 10.1, 8.2 Hz, 1H), 4.92 (m, 2H), 4.38 (t, *J* = 0.8 Hz, 2H), 4.17 (s, 2H), 3.39 (s, 3H), 1.68 (b d, *J* = 8.2 Hz, 2H), 0.18 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) : δ 133.2, 114.0, 77.1, 75.1, 70.4, 69.1, 60.0, 57.6, 51.5, 24.1, -2.6; HRMS (ESI) calcd for C₁₂H₁₈O₂Si [MNa⁺] 245.0974, found 245.0971.

15

¹H NMR (300 MHz, CDCl₃) : δ 6.35 (tt, *J* = 5.61, 1.8 Hz, 1H), 5.49 (m, 2H), 4.41 (m, 2H), 3.94 (t, *J* = 1.3 Hz, 2H), 3.38 (s, 3H), 1.40 (dt, *J* = 5.4, 2.6 Hz, 2H), 0.07 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) : δ 134.3, 129.3, 123.6, 122.5, 89.7, 87.6, 75.6, 66.0, 59.2, 14.2, 2.0, -0.01; HRMS (ESI) calcd for C₁₂H₁₈O₂Si [MeOH+NaM⁺] 277.1236, found 277.1249.

Chemical derivation to confirm the structural assignment of compound 15

nOe data of compound **17** :

12b

16

CC(C)(C)SiC#CC1=CC=C(C=C1)O[C@H]1C=CC(C1)Si(C)C

18a

Chemical structure of 18a: A silicon atom is bonded to a methyl group, a tert-butyl group, and an allyloxy group (-OCH₂CH=CH₂). It is also bonded to a propargyl group (-CH₂C≡CH) via a single bond, and to a 4-tert-butylphenylethynyl group (-C≡C-CH₂-C₆H₄-tBu) via a triple bond.

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19a

¹H NMR (300 MHz, CDCl₃) : δ 7.00 (t, *J* = 2.0 Hz, 1H), 5.54 (m, 1H), 5.48 (m, 1H), 4.72 (t, *J* = 3.4 Hz, 1H), 4.68 (d, *J* = 2.0 Hz, 2H), 4.25 (dt, *J* = 13.2, 1.6 Hz, 1H), 4.05 (dt, *J* = 13.2, 1.3 Hz, 1H), 3.82 (m, 1H), 3.54 (m, 1H), 1.62-1.94 (m, 6H), 0.33 (s, 6H); **¹³C NMR (CDCl₃, 75 MHz)** : δ 151.8, 128.4, 121.9, 120.3, 96.5, 91.7, 86.0, 71.9, 68.2, 61.5, 29.7, 24.8, 18.4, -0.6.

18b

¹H NMR (300 MHz, CDCl₃) : δ 5.80 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.06 (m, 2H), 4.80 (t, *J* = 3.0 Hz, 1H), 4.33 (s, 2H), 3.81 (ddd, *J* = 11.8, 9.1, 3.4 Hz, 1H), 3.74 (t, *J* = 6.8 Hz, 2H), 3.54 (m, 1H), 2.32 (m, 2H), 1.71-1.87 (m, 2H), 1.55-1.65 (m, 4H), 0.27 (s, 6H); **¹³C NMR (75 MHz, CDCl₃)** : δ 135.1, 116.8, 97.1, 87.6, 84.3, 75.2, 70.6, 63.3, 62.2, 54.5, 37.0, 30.3, 25.4, 19.1, -0.01; **HRMS (ESI)** calcd for C₁₆H₂₄O₃Si [MNa⁺] 315.1392, found 315.1404.

19b

¹H NMR (300 MHz, CDCl₃) : δ 6.97 (t, *J* = 4.6 Hz, 1H), 5.49 (dd, *J* = 3.4, 1.7 Hz, 1H), 5.42 (s, 1H), 4.69 (t, *J* = 3.4 Hz, 1H), 4.21 (dt, *J* = 13.3, 1.5 Hz, 1H), 4.00 (dt, *J* = 13.3, 1.3 Hz, 1H), 3.93 (t, *J* = 5.3 Hz, 2H), 3.88 (m, 1H), 3.52 (m, 2H), 2.35 (ABq, *J* = 5.1 Hz, 2H), 1.76-1.93 (m, 2H), 1.49-1.74 (m, 4H), 0.27 (s, 6H); **¹³C NMR (75 MHz, CDCl₃)** δ 153.5, 131.1, 124.7, 122.5, 99.7, 92.5, 91.9, 70.9, 64.0, 63.3, 32.9, 32.6, 27.5, 21.3, -0.02 ; **HRMS (ESI)** calcd for C₁₆H₂₄O₃Si [MNa⁺] 315.1392, found 315.1407.

¹H NMR (300 MHz, CDCl₃) : δ 5.82 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.00 (m, 2H), 4.81 (t, *J* = 3.0 Hz, 1H), 4.33 (s, 2H), 3.82 (ddd, *J* = 11.8, 9.1, 3.4 Hz, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 3.55 (m, 1H), 2.11 (m, 2H), 1.71-1.87 (m, 2H), 1.52-1.69 (m, 6H), 0.27 (s, 6H); **¹³C NMR (75 MHz, CDCl₃)** : δ 138.4, 115.9, 97.2, 87.6, 84.4, 75.2, 70.7, 63.2, 62.2, 54.5, 31.6, 30.4, 30.1, 25.5, 19.1, -0.01; **HRMS (ESI)** calcd for C₁₇H₂₆O₃Si [MNa⁺] 329.1549, found 329.1538.

¹H NMR (300 MHz, CDCl₃) : δ 5.82 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 5.00 (m, 2H), 4.81 (t, *J* = 3.0 Hz, 1H), 4.33 (s, 2H), 3.82 (ddd, *J* = 11.8, 9.1, 3.4 Hz, 1H), 3.70 (t, *J* = 6.6 Hz, 2H), 3.55 (m, 1H), 2.11 (m, 2H), 1.71-1.87 (m, 2H), 1.52-1.69 (m, 6H), 0.27 (s, 6H); **¹³C NMR (75 MHz, CDCl₃)** : δ 154.9, 130.4, 126.7, 121.3, 98.9, 92.9, 91.0, 70.1, 65.4, 63.2, 31.7, 31.6, 30.6, 26.7, 20.5, -0.01 ; **HRMS (ESI)** calcd for C₁₇H₂₆O₃Si [MNa⁺] 329.1549, found 329.1544.

¹H NMR (300 MHz, CDCl₃) : δ 5.81 (ddt, *J* = 17.1, 10.3, 6.8 Hz, 1H), 4.98 (m, 2H), 4.80 (t, *J* = 3.0 Hz, 1H), 4.33 (s, 2H), 3.82 (ddd, *J* = 11.8, 9.1, 3.1 Hz, 1H), 3.69 (t, *J* = 6.5 Hz, 2H), 3.54 (m, 1H), 2.07 (m, 2H), 1.70-1.83 (m, 2H), 1.52-1.69 (m, 6H), 1.45 (m, 2H), 0.27 (s, 6H) ; **¹³C NMR (75 MHz, CDCl₃)** : δ 139.0, 114.7, 97.2, 87.5, 84.5, 75.2, 70.7, 63.7, 62.2, 54.5, 33.6, 31.9, 30.3, 25.3, 25.2, 19.1, -0.01; **HRMS (ESI)** calcd for C₁₈H₂₈O₃Si [MNa⁺] 343.1705, found 343.1706.

19d

^1H NMR (300 MHz, CDCl_3) : δ 6.74 (t, J = 8.5 Hz, 1H), 5.49 (m, 1H), 5.41 (m, 1H), 4.70 (t, J = 3.2 Hz, 1H), 4.42 (d, J = 13.1 Hz, 1H), 4.15 (d, J = 13.1 Hz, 1H), 3.96 (t, J = 5.3 Hz, 2H), 8.86 (m, 1H), 3.54 (m, 1H), 2.40 (m, 2H), 1.53-1.94 (m, 10H), 0.30 (s, 6H); **^{13}C NMR (75 MHz, CDCl_3)** : δ 151.8, 129.9, 128.9, 119.8, 98.6, 84.8, 84.3, 68.4, 65.8, 61.7, 30.4, 30.3, 27.1, 25.2, 21.9, 19.2, -0.77 ; **HRMS (ESI)** calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$ [MNa^+] 343.1705, found 343.1706.

19d'

^1H NMR (300 MHz, CDCl_3) : δ 6.52 (t, J = 7.5 Hz, 1H), 5.61 (s, 1H), 5.31 (s, 1H), 4.65 (t, J = 3.5 Hz, 1H), 4.42 (d, J = 13.1 Hz, 1H), 4.15 (d, J = 13.1 Hz, 1H), 3.96 (t, J = 5.3 Hz, 2H), 8.86 (m, 1H), 3.54 (m, 1H), 2.40 (m, 2H), 1.53-1.94 (m, 10H), 0.31 (s, 6H); **^{13}C NMR (75 MHz, CDCl_3)** : δ 140.0, 139.7, 125.1, 115.6, 104.6, 102.8, 97.5, 66.5, 62.0, 59.9, 30.4, 30.3, 27.1, 25.2, 21.9, 19.2, -0.77 ; **HRMS (ESI)** calcd for $\text{C}_{18}\text{H}_{28}\text{O}_3\text{Si}$ [MNa^+] 343.1705, found 343.1706.

18e

^1H NMR (300 MHz, CDCl_3) : δ 5.83 (ddt, J = 17.0, 10.0, 8.0 Hz, 1H), 4.93 (m, 2H), 4.37 (d, J = 1.0 Hz, 2H), 2.18 (t, J = 1.0 Hz, 1H), 1.69 (b d, J = 7.9 Hz, 2H), 0.20 (s, 6H); **^{13}C NMR (75 MHz, CDCl_3)** : δ 135.8, 116.6, 77.0, 71.7, 70.4, 69.9, 54.0, 26.7, -0.17.

19e

^1H NMR (300 MHz, CDCl_3) : δ 6.34 (b t, J = 5.6 Hz, 1H), 5.89 (dd, J = 17.5, 11.1 Hz, 1H), 5.61 (dd, J = 17.5, 2.0 Hz, 1H), 5.45 (dd, J = 11.0, 2.0 Hz, 1H), 4.41 (m, 2H), 1.89 (m, 2H), 0.20 (s, 6H); **^{13}C NMR (75 MHz, CDCl_3)** : δ 134.0, 129.4, 127.6, 123.8, 118.1,

89.7, 88.2, 65.9, 14.0, -0.16 ; **HRMS (ESI)** calcd for C₁₀H₁₄OSi [M]⁺, 178.0814 found 178.0821.

¹H NMR (300 MHz, CDCl₃) : δ 6.19 (t, *J* = 4.0 Hz, 1H), 5.26 (m, 1H), 5.18 (m, 1H), 4.19 (m, 1H), 2.16 (m, 3H), 2.07 (m, 1H), 1.73-1.81 (m, 3H), 1.51 (m, 3H), 1.34 (m, 2H), 0.92 (s, 9H), 0.90 (m, 3H), 0.15 (s, 3H), 0.12 (s, 3H); **¹³C NMR (75 MHz, CDCl₃)** : δ 142.0, 136.7, 129.3, 124.6, 94.7, 93.2, 72.2, 41.8, 36.9, 35.1, 34.4, 30.6, 26.7, 22.9, 22.2, 18.6, 0.3, -0.01 ; **HRMS (ESI)** calcd for C₂₀H₃₄OSi [MNa⁺] 341.2277, found 341.2293.

¹H NMR (300 MHz, CDCl₃) : δ 6.15 (tt, *J* = 2.2 Hz, 1H), 5.53 (s, 1H), 5.50 (s, 1H), 5.35 (q, *J* = 6.4 Hz, 1H), 4.76 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.74 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.63 (dd, *J* = 5.0, 2.1 Hz, 1H), 4.61 (dd, *J* = 5.0, 2.1 Hz, 1H), 2.07 (s, 3H), 1.39 (d, *J* = 6.4 Hz, 3H); **¹³C NMR (75 MHz, CDCl₃)** : δ 170.2, 132.3, 131.6, 122.6, 121.3, 90.7, 83.4, 76.9, 76.5, 71.7, 21.4, 19.8. **MS (ESI)** calcd for C₁₂H₁₄O₃ [MMeOH+2Na⁺] 293.2, [MMeOHNa⁺] 261.1, [MK⁺] 245.1, found 293.2, 261.1, 245.1, respectively.

¹H NMR (300 MHz, CDCl₃) : δ 5.80 (ddt, *J* = 16.9, 10.2, 8.1 Hz, 1H), 5.34 (m, 1H), 4.92 (m, 2H), 4.38 (d, *J* = 0.5 Hz, 2H), 4.21 (m, 2H), 3.96 (dd, *J* = 11.2, 7.5 Hz, 1H), 1.75 (s, 3H), 1.70 (s, 3H), 1.68 (m, 2H), 1.44 (d, *J* = 6.6 Hz, 3H), 0.19 (s, 6H); **¹³C NMR (CDCl₃, 75 MHz)** : δ 138.4, 133.7, 120.6, 114.4, 79.9, 77.3, 69.5, 69.1, 65.6, 64.7, 52.0, 26.1, 24.5, 22.1, 18.3, -2.2; **HRMS (ESI)** calcd for C₁₇H₂₆O₂Si [MNa⁺] 313.1600, found 313.1586.

19i

¹H NMR (300 MHz, CDCl₃) : δ 6.36 (tt, *J* = 5.6, 1.7 Hz, 1H), 6.06 (m, 1H), 4.70 (m, 1H), 4.41 (m, 2H), 4.20 (m, 1H), 3.96 (dd, *J* = 11.4, 7.9 Hz, 1H), 1.76 (m, 2H), 1.33 (d, *J* = 6.3 Hz, 3H), 0.20 (s, 6H); **¹³C NMR (CDCl₃, 75 MHz)** : δ 136.0, 133.0, 130.5, 127.7, 94.6, 85.6, 83.6, 77.1, 67.3, 23.0, 15.6, 1.4.