

*Supporting Information I***Divergent Synthesis of Functionalized Carbocycles through Organosilane-Directed Asymmetric Alkyne-Alkene Reductive Coupling and Annulation Sequence***Jie Wu, Yi Pu and James S. Panek**

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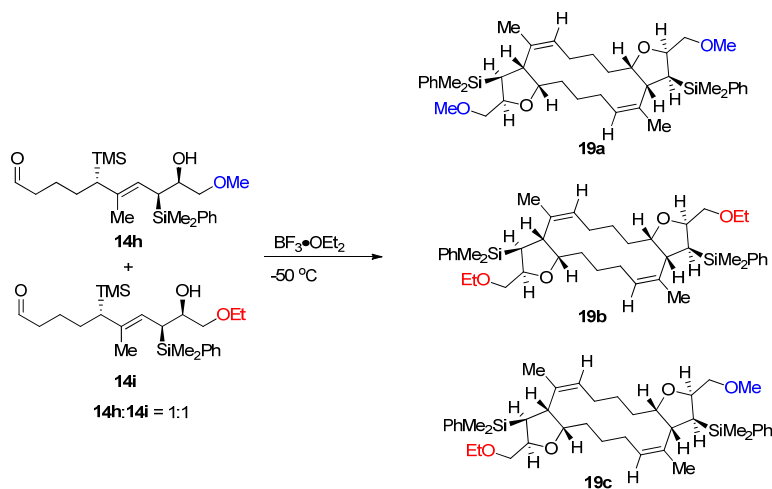
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Part I: General Information:

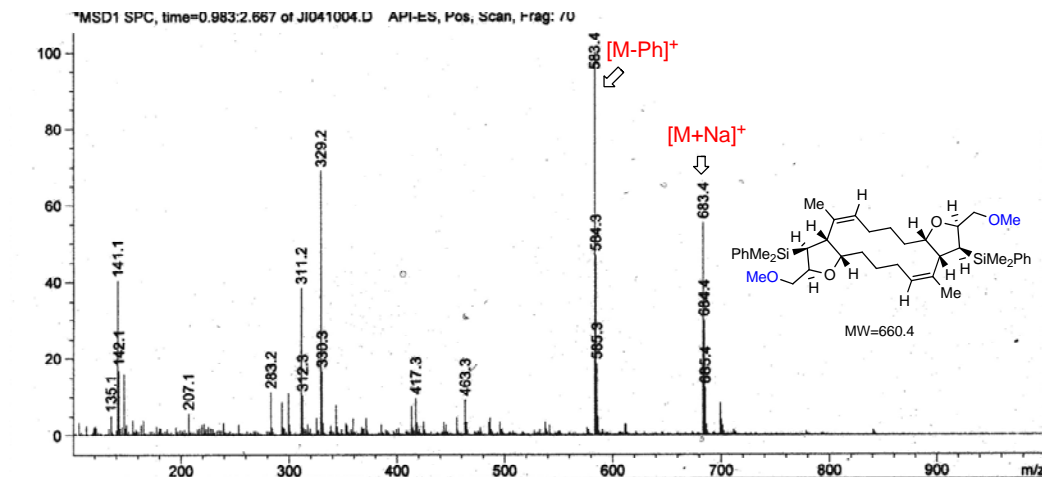
All reactions were carried out in oven or flame-dried glassware under argon atmosphere. *N,N*-dimethylformamide and dimethylsulfoxide were distilled over calcium hydride and stored over 4 Å molecular sieves. *n*-Butyllithium was purchased from Aldrich and was standardized by titration with menthol/2,2'-dipyridyl. All other reagents were used as supplied. Dichloromethane, toluene, diethyl ether, benzene, tetrahydrofuran, and acetonitrile were obtained from a dry solvent system (alumina) and used without further drying. Other ACS grade solvents were purchased from Clean Harbors. Unless otherwise noted, reactions were magnetically stirred and monitored by thin layer chromatography with Macherey Nagel Polygram 0.20 mm silica gel 60 Å plates. Analytical thin layer chromatography was performed using 0.25 mm silica gel 60-F plates. Flash chromatography was performed on Sorbent Technologies 32-63 µm 60 Å silica gel. Yields referred to chromatographically and spectroscopically pure compounds, unless otherwise noted. ¹H and ¹³C NMR spectra were taken in CDCl₃ at 400 or 500 MHz (as indicated) respectively, unless otherwise noted. Chemical shifts are reported in parts per million relative to CDCl₃ (¹H, δ 7.24; ¹³C, δ 77.0). Data are reported as follows: chemical shift, multiplicity (s = singlet, d= doublet, t= triplet, q = quartet, sept = septuplet, m = multiplet, br = broad), coupling constant, integration. Diastereomeric ratios were determined by ¹H NMR analysis of crude mixtures operating at a signal/noise ratio of 200:1. Infrared resonance spectra were recorded on a Nexus 670 FT-IR spectrometer. Optical rotations were recorded on an Autopol III digital polarimeter at 589 nm and reported as follows: [α]²⁰_D (concentration in g/100 mL solvent and solvent). High resolution mass-spectra were obtained on a Waters Q-TOF mass spectrometer at Boston University Chemical Instrumentation Center (CIC).

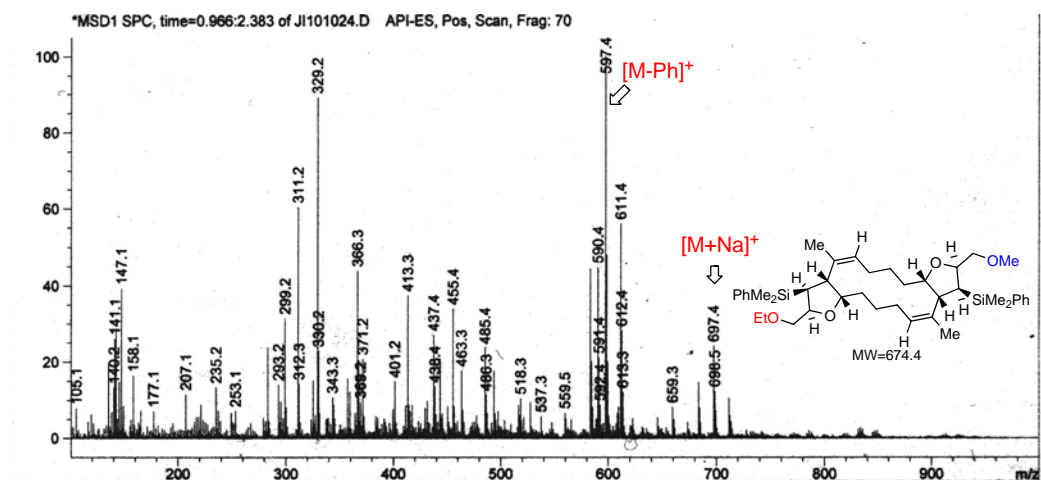
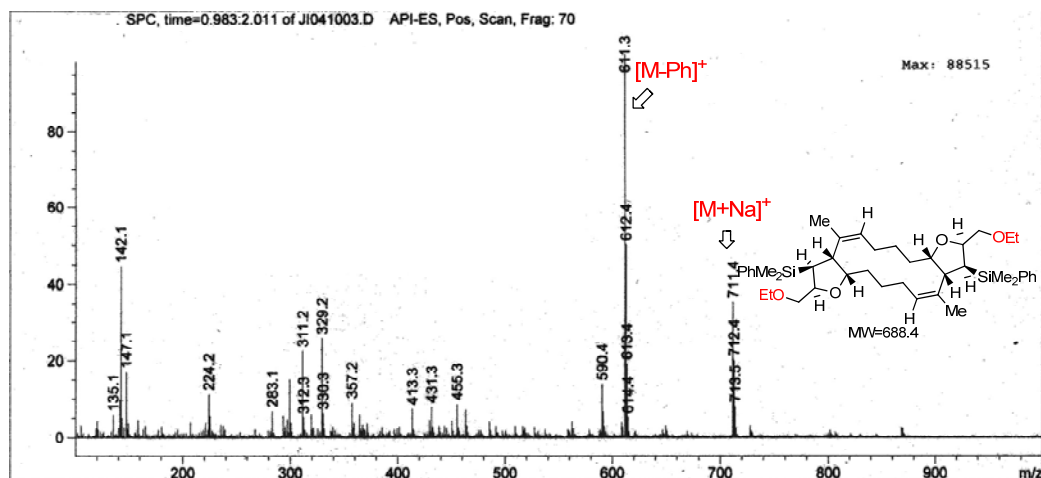
Part II : Control Experiments

Supplementary Scheme S1: Control Experiments to Support the Dimerization Process



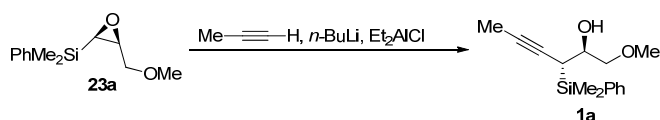
To support the production of dimer products, a control experiment was conducted using a mixture of silanes **14h** and **14i** (ratio 1:1). Under Lewis acid promotion, not only homo-dimers **19a** and **19b**, but also the hetero-dimer product **19c** should be generated in a dimerization process (Scheme S1). As anticipated, the reaction proceeded to deliver the dimerization products. Even though the dimers **19a-19c** could not be separated by column chromatography, we could detect the generation of heterodimer **19c** using mass spectral analysis (the other two dimers also showed mass hit in the third mass spectrum), thereby supporting the dimerization process.





Part III: Experimental Procedures:

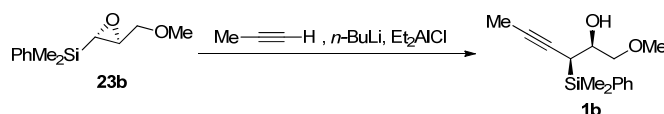
i. Preparation of Propargylic Silanes



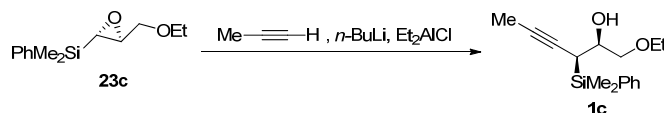
(2*S*,3*R*)-3-(Dimethyl(phenyl)silyl)-1-methoxyhex-4-yn-2-ol (1a): A solution of diethylpropynylaluminum in pentanes (0.4 M, 75 mL, 30 mmol, 3 equiv) was added into a round bottom flask under an argon atmosphere and cooled to 0 °C. A solution of epoxide **23a**¹

(1) For preparation of the silyl epoxide **23a** to **23c**, see: (a) Lowe, J. T.; Youngsaye, W.; Panek, J. S. *J. Org. Chem.* **2006**, *71*, 3639-3642. (b) Su, Q.; Panek, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 2425-2430.

(2.22 g, 10 mmol, 1 equiv) in pentanes (20 mL) was added over 5 minutes. The solution was stirred at room temperature for 12 hours after which time diethyl ether (50 mL) was added followed by the slow addition of an equal volume of a saturated solution of Rochelle's salt. The aqueous portion was then extracted with diethyl ether, combined and dried over MgSO_4 . The solution was then filtered and concentrated. Further purification over silica gel (hexanes/ethyl acetate: 90/10) afforded the desired propargyl silane **1a** (2.15 g, 82% yield) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.39 (s, 3H), 0.42 (s, 3H), 1.82 (d, $J = 2.8$ Hz, 3H), 2.20 (m, 1H), 3.23 (m, 1H), 3.28 (s, 3H), 3.29 (s, 3H), 3.52 (m, 2H), 7.34 (m, 3H), 7.56 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.2, -3.3, 3.8, 24.0, 58.0, 58.8, 74.0, 76.0, 78.3, 78.8, 127.5, 128.9, 133.7, 137.4 ppm; IR (neat) ν_{max} : 1113, 1246, 1428, 2918, 3069 cm^{-1} ; $[\alpha]_D^{20} = +0.60$ ($c = 2.3$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 299.1443, found 299.1436.

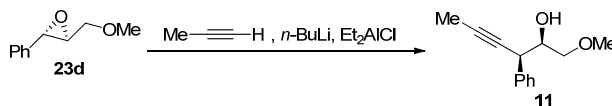


(2S,3S)-3-(Dimethyl(phenyl)silyl)-1-methoxyhex-4-yn-2-ol (1b): A solution of diethylpropynylaluminum in pentanes (0.4 M, 75 mL, 30 mmol, 3 equiv) was added into a round-bottom flask under an argon atmosphere and cooled to 0 °C. A solution of epoxide **23b** (2.22 g, 10 mmol, 1 equiv) in pentanes (20 mL) was added over 5 minutes. The solution was stirred at room temperature for 12 hours after which time diethyl ether (50 mL) was added followed by the slow addition of an equal volume of a saturated solution of Rochelle's salt. The aqueous portion was then extracted with diethyl ether, combined and dried over MgSO_4 . The solution was then filtered and concentrated. Further purification over silica gel (hexanes/ethyl acetate: 90/10) afforded the desired propargyl silane **1b** (2.23 g, 85% yield) as a slightly yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.42 (s, 6H), 1.77 (s, 3H), 2.11 (m, 1H), 2.28 (s, $J = 4.5$ Hz, 1H), 3.31 (s, 3H), 3.34 (m, 1H), 3.50 (m, 1H), 3.73 (m, 1H), 7.33 (m, 3H), 7.59 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.5, -3.4, 3.3, 24.3, 58.5, 70.6, 76.3, 76.7, 78.0, 127.2, 128.8, 133.9, 137.1 ppm; IR (neat) ν_{max} : 1114, 1247, 1428, 2856, 2917, 3070, 3453 cm^{-1} ; $[\alpha]_D^{20} = -18$ ($c = 4.0$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{15}\text{H}_{22}\text{O}_2\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 285.1287, found 285.1297.



(2S,3S)-3-(Dimethyl(phenyl)silyl)-1-ethoxyhex-4-yn-2-ol (1c): A solution of diethylpropynylaluminum in pentanes (0.4 M, 37.5 mL, 15 mmol, 3 equiv) was added into a round-bottom flask under an argon atmosphere and cooled to 0 °C. A solution of epoxide **23c** (1.18 g, 5 mmol, 1 equiv) in pentanes (10 mL) was added over 5 minutes. The solution was stirred at room temperature for 12 hours after which time diethyl ether (25 mL) was added followed by the slow addition of an equal volume of a saturated solution of Rochelle's salt. The aqueous portion was then extracted with diethyl ether, combined and dried over MgSO_4 . The solution was then filtered and concentrated. Further purification over silica gel (hexanes/ethyl acetate: 90/10) afforded the desired propargyl silane **1c** (1.10 g, 80% yield) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.45 (s, 6H), 1.17 (t, $J = 6.8$ Hz, 3H), 1.79 (d, $J = 2.8$ Hz, 3H), 2.13 (m, 1H), 2.55 (d, $J = 4.4$ Hz, 1H), 3.36 (m, 1H), 3.49 (m, 2H), 3.61 (m, 1H), 3.76 (m, 1H), 7.35 (m, 3H), 7.63 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.3, -3.2,

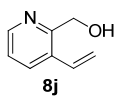
3.6, 15.0, 24.6, 66.5, 70.9, 74.2, 76.8, 78.4, 127.5, 129.0, 134.1, 137.3 ppm; IR (neat) ν_{max} : 1113, 1247, 1427, 2916, 2974, 3456 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -18$ ($c = 1.9$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 299.1443, found 299.1515.



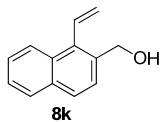
(2R,3S)-1-Methoxy-3-phenylhex-4-yn-2-ol (11): A solution of diethylpropynylaluminum in pentanes (0.4 M, 15 mL, 6 mmol, 3 equiv) was added into a round bottom flask under an argon atmosphere and cooled to 0 °C. A solution of phenyl epoxide **23d**² (328 mg, 2 mmol, 1 equiv) in pentanes (4 mL) was added over 5 minutes. The solution was stirred at room temperature for 12 hours after which time diethyl ether (10 mL) was added followed by the slow addition of an equal volume of a saturated solution of Rochelle's salt. The aqueous portion was then extracted with diethyl ether, combined and dried over MgSO_4 . The solution was then filtered and concentrated. Further purification over silica gel (hexanes/ethyl acetate: 90/10) afforded the desired product **11** (359 mg, 88% yield) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 1.87 (d, $J = 2.4$ Hz, 3H), 2.50 (m, 1H), 3.37 (s, 3H), 3.53 (m, 2H), 3.77 (m, 1H), 3.90 (m, 1H), 7.25 (m, 1H), 7.33 (m, 2H), 7.38 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 3.5, 41.6, 59.0, 73.8, 74.0, 77.4, 80.1, 127.1, 128.3, 128.3, 138.5 ppm; IR (neat) ν_{max} : 1123, 1453, 2918, 3439 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -3.7$ ($c = 0.9$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2$ $[\text{M} + \text{H}]^+$ 205.1229, found 205.1262.

ii. Preparation of Bis-Homoallylic Alcohols

Known olefins **8f**³ and **8g**⁴ were prepared according to literature procedures (see reference below). Olefins **8j** and **8k** were prepared using Stille coupling.⁵



(3-Vinylpyridin-2-yl)methanol (8j): ^1H NMR (400 MHz, CDCl_3) δ 4.76 (s, 2H), 5.43 (d, $J = 10.8$ Hz, 1H), 5.70 (d, $J = 17.6$ Hz, 1H), 6.68 (dd, $J = 17.6, 11.6$ Hz, 1H), 7.22 (m, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 8.44 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 561.4, 118.3, 122.3, 130.2, 130.3, 133.0, 146.7, 154.7 ppm; IR (neat) ν_{max} : 1057, 1398, 1442, 1628, 2955, 3385 cm^{-1} ; HRMS(CI/NH_3) m/z calcd for $\text{C}_8\text{H}_{10}\text{NO}$ $[\text{M} + \text{H}]^+$ 136.0762, found 136.0877.



(1-Vinylnaphthalen-2-yl)methanol (8k): ^1H NMR (400 MHz, CDCl_3) δ 2.51 (br, 1H), 4.81 (s, 2H), 5.44 (d, $J = 18.0$ Hz, 1H), 5.75 (d, $J = 11.6$ Hz, 1H), 7.07 (dd, $J = 17.6, 11.2$ Hz, 1H), 7.48 (m, 2H), 7.57 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.82 (m, 1H),

(2) For preparation of the phenyl epoxide **23d**, see: Balamurugan, R.; Kothapalli, R. B.; Thota, G. K. *Eur. J. Org. Chem.* **2011**, 1447-1569.

(3) Liu, G.; Stahl, S. S. *J. Am. Chem. Soc.* **2007**, 129, 6328-6335.

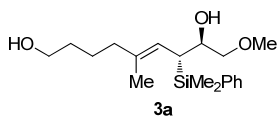
(4) Ma, S.; Liu, F.; Negishi, E. *Tetrahedron Lett.* **1997**, 38, 3829-3832.

(5) Molander, G. A.; Pack, S. K. *Tetrahedron* **2003**, 59, 10581-10591.

8.11 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 63.1, 121.9, 125.4, 125.6, 125.9, 126.0, 127.5, 128.0, 131.5, 132.8, 132.9, 134.6, 135.0 ppm; IR (neat) ν_{max} : 997, 1218, 1265, 1418, 1628, 2927, 3056, 3324 cm^{-1} ; HRMS(CI/ NH_3) m/z calcd for $\text{C}_{13}\text{H}_{11}$ $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ 167.0861, found 167.0860.

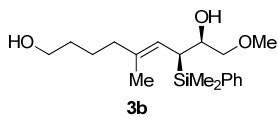
iii. Alkyne-Alkene Reductive Coupling with Mono-Substituted Olefins

The general procedure for alkyne-alkene reductive coupling between propargyl silanes and mono-substituted olefins: To a solution of propargyl silane **1** (262 mg, 1.0 mmol, 2 equiv) in Et_2O (10 mL) at -78°C was added sequentially $n\text{-BuLi}$ (2.5 M in hexanes, 400 μL , 1.0 mmol, 2 equiv), $\text{ClTi}(\text{OiPr})_3$ (1.0 M in hexanes, 2.0 mL, 2.0 mmol, 4 equiv) and $c\text{-C}_5\text{H}_9\text{MgCl}$ (2.0 M in Et_2O , 2.0 mL, 4.0 mmol, 8 equiv) dropwise. The resulting yellow solution turned brown while warming slowly to 0°C over 2 hours. The reaction mixture was stirred at 0°C for additional 2 hours producing a black solution. To a separate -78°C solution of the mono-substituted olefin (0.5 mmol, 1 equiv) in Et_2O (2 mL) was added $n\text{-BuLi}$ (2.5 M in hexanes, 200 μL , 0.5 mmol, 1 equiv) in a dropwise manner via gas-tight syringe. The resulting solution was warmed to 0°C , followed by slowly transfer via cannula into the original black solution at 0°C . The reaction mixture was further stirred at 0°C for another 2 hours. The reaction was quenched with saturated NH_4Cl solution (10 mL). The mixture was warmed to rt before extractive isolation with diethyl ether (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 30% or 50% EtOAc /hexanes as developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the coupled product.



(7R,8S,E)-7-(Dimethyl(phenyl)silyl)-9-methoxy-5-methylnon-5-

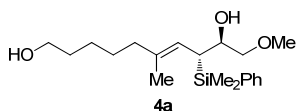
ene-1,8-diol (3a): Prepared by the *general procedure* using silane **1a**, silyl diol **3a** (123 mg, 73%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.28 (s, 3H), 0.35 (s, 3H), 1.38 (s, 3H), 1.46 (m, 4H), 1.98-2.05 (m, 4H), 3.17 (m, 2H), 3.24 (s, 3H), 3.61 (t, $J = 6.0$ Hz, 2H), 3.86 (m, 1H), 5.25 (d, $J = 11.2$ Hz, 1H), 7.31 (m, 3H), 7.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.0, -3.5, 16.1, 24.2, 32.1, 32.2, 39.7, 58.7, 62.6, 70.4, 76.9, 120.1, 127.5, 128.8, 133.9, 135.2, 138.4 ppm; IR (neat) ν_{max} : 1113, 1246, 1428, 2931, 3414 cm^{-1} ; $[\alpha]_D^{20} = -9.8$ ($c = 1.5$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{19}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 359.2018, found 359.2014.



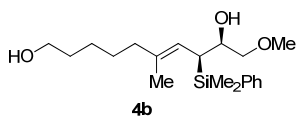
(7S,8S,E)-7-(Dimethyl(phenyl)silyl)-9-methoxy-5-methylnon-5-

ene-1,8-diol (3b): Prepared by the *general procedure* using silane **1b**, silyl diol **3b** (119 mg, 71%) was obtained as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.31 (s, 3H), 0.34 (s, 3H), 1.34 (m, 2H), 1.42 (s, 3H), 1.46 (m, 2H), 1.94 (t, $J = 7.5$ Hz, 2H), 2.17 (dd, $J = 11.5, 9.5$ Hz, 1H), 2.35 (br, 1H), 3.09 (m, 1H), 3.28 (s, 3H), 3.34 (m, 1H), 3.59 (t, $J = 6.5$ Hz, 2H), 3.71 (t, $J = 9.5$ Hz, 1H), 4.87 (d, $J = 11.5$ Hz, 1H), 7.30 (m, 3H), 7.51 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -3.0, 16.2, 24.2, 32.2, 33.2, 39.6, 58.7, 62.5, 72.1, 76.8, 121.5, 127.3, 128.6,

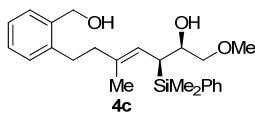
134.1, 134.7, 138.4 ppm; IR (neat) ν_{max} : 1112, 1246, 1427, 2933, 3426 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -5.9$ ($c = 1.0$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{19}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 359.2018, found 359.2018.



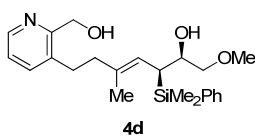
(8R,9S,E)-8-(Dimethyl(phenyl)silyl)-10-methoxy-6-methyldec-6-ene-1,9-diol (4a): Prepared by the *general procedure* using silane **1a**, silyl diol **4a** (119 mg, 68%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.28 (s, 3H), 0.35 (s, 3H), 1.28 (m, 4H), 1.37 (s, 3H), 1.53 (m, 2H), 1.98-2.16 (m, 4H), 3.15 (m, 2H), 3.23 (s, 3H), 3.61 (m, 2H), 3.85 (m, 1H), 5.25 (d, $J = 12.8$ Hz, 1H), 7.31 (m, 3H), 7.51 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ -4.1, -3.5, 16.4, 25.2, 27.8, 32.0, 32.5, 39.8, 58.6, 62.7, 70.4, 76.9, 119.8, 127.5, 128.8, 133.9, 135.3, 138.3 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 1450, 2930, 3404 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -14$ ($c = 2.0$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 373.2175, found 373.2172.



(8S,9S,E)-8-(Dimethyl(phenyl)silyl)-10-methoxy-6-methyldec-6-ene-1,9-diol (4b): Prepared by the *general procedure* using silane **1b**, silyl diol **4b** (113 mg, 65%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.30 (s, 3H), 0.34 (s, 3H), 1.27 (m, 4H), 1.41 (s, 3H), 1.53 (m, 2H), 1.92 (m, 2H), 2.16 (dd, $J = 11.6, 9.6$ Hz, 1H), 2.28 (d, $J = 4.4$ Hz, 1H), 3.09 (m, 1H), 3.28 (s, 3H), 3.34 (m, 1H), 3.60 (m, 2H), 3.71 (m, 1H), 4.87 (d, $J = 11.6$ Hz, 1H), 7.30 (m, 3H), 7.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.3, -2.9, 16.3, 25.4, 27.9, 32.6, 33.2, 39.8, 58.8, 62.8, 72.2, 76.8, 121.3, 127.4, 128.7, 134.1, 134.1, 135.0, 138.4 ppm; IR (neat) ν_{max} : 1113, 1246, 2930, 3422 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -7.5$ ($c = 2.6$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 373.2175, found 373.2180.

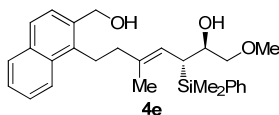


(2S,3S,E)-3-(Dimethyl(phenyl)silyl)-7-(2-(hydroxymethyl)phenyl)-1-methoxy-5-methylhept-4-en-2-ol (4c): Prepared by the *general procedure* using silane **1b**, silyl diol **4c** (135 mg, 68%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.33 (s, 3H), 0.37 (s, 3H), 1.52 (s, 3H), 2.23 (m, 3H), 2.68 (m, 2H), 3.03 (t, $J = 9.2$ Hz, 1H), 3.24 (m, 1H), 3.29 (s, 3H), 3.71 (t, $J = 9.2$ Hz, 1H), 4.70 (s, 2H), 4.89 (d, $J = 11.2$ Hz, 1H), 7.22 (m, 3H), 7.34 (m, 3H), 7.38 (m, 1H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -3.1, 16.4, 31.0, 33.4, 41.4, 58.8, 62.9, 72.0, 76.7, 122.1, 126.1, 127.4, 127.8, 128.0, 128.7, 129.2, 134.13, 134.2, 138.3, 140.2 ppm; IR (neat) ν_{max} : 1112, 1243, 1452, 2894, 3416 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +0.60$ ($c = 1.9$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{24}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 421.2175, found 421.2188.



(2S,3S,E)-3-(Dimethyl(phenyl)silyl)-7-(2-(hydroxymethyl)pyridin-3-yl)-1-methoxy-5-methylhept-4-en-2-ol (4d): Prepared by the *general procedure* using

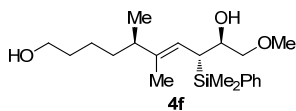
silane **1b** and olefin **8j**, silyl diol **4d** (58 mg, 29%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.28 (s, 3H), 0.33 (s, 3H), 1.45 (s, 3H), 2.15 (m, 3H), 2.30 (br, 1H), 2.42 (m, 2H), 3.01 (m, 1H), 3.21 (m, 1H), 2.61 (s, 3H), 3.67 (m, 1H), 3.76 (br, 1H), 4.66 (s, 2H), 4.85 (d, J = 11.6 Hz, 1H), 7.15 (m, 1H), 7.31 (m, 3H), 7.41 (m, 1H), 7.47 (m, 2H), 8.38 (d, J = 4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -3.0, 16.3, 28.8, 33.4, 39.7, 58.8, 61.1, 72.0, 76.8, 122.2, 123.1, 127.5, 128.8, 133.2, 133.6, 134.1, 136.4, 138.3, 145.2, 155.6 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2926, 3419 cm^{-1} ; $[\alpha]_{\text{D}}^{20}$ = +2.0 (c = 0.60, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{23}\text{H}_{33}\text{NO}_3\text{SiH}$ $[\text{M} + \text{H}]^+$ 400.2308, found 400.2311.



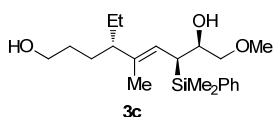
(2S,3R,E)-3-(Dimethyl(phenyl)silyl)-7-(2-(hydroxymethyl)naphthalen-1-yl)-1-methoxy-5-methylhept-4-en-2-ol (4e): Prepared by the *general procedure* using silane **1a** and olefin **8k**, silyl diol **4e** (157 mg, 70%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.36 (s, 3H), 0.40 (s, 3H), 1.55 (s, 3H), 2.11 (m, 1H), 2.32 (m, 2H), 3.16 (overlap, 4H), 3.26 (s, 3H), 3.91 (m, 1H), 4.86 (s, 2H), 5.37 (d, J = 10.08 Hz, 1H), 7.34 (m, 3H), 7.45-7.58 (m, 5H), 7.70 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.2 Hz, 1H), 8.03 (d, J = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.9, -3.5, 16.4, 27.5, 32.2, 41.5, 58.7, 63.1, 70.4, 76.8, 120.7, 123.9, 125.3, 126.0, 126.3, 126.5, 127.6, 128.6, 128.9, 131.9, 133.4, 134.0, 134.98, 135.19, 135.96, 138.21 ppm; IR (neat) ν_{max} : 1114, 1247, 1427, 2896, 3068, 3421 cm^{-1} ; $[\alpha]_{\text{D}}^{23}$ = -16 (c = 3.4, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{28}\text{H}_{36}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 471.2331, found 471.2351.

iv. Alkyne-Alkene Reductive Coupling with disubstituted Olefins

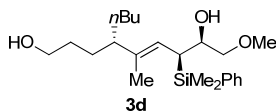
The general procedure for alkyne-alkene reductive coupling between propargyl silanes and disubstituted olefins: To a solution of propargyl silane **1** (262 mg, 1.0 mmol, 2 equiv) in Et_2O (10 mL) at -78°C was added sequentially $n\text{-BuLi}$ (2.5 M in hexanes, 400 μL , 1.0 mmol, 2 equiv), $\text{ClTi}(\text{O}i\text{Pr})_3$ (1.0 M in hexanes, 2.0 mL, 2.0 mmol, 4 equiv) and $c\text{-C}_5\text{H}_9\text{MgCl}$ (2.0 M in Et_2O , 2.0 mL, 4.0 mmol, 8 equiv) dropwise. The resulting yellow solution turned brown while warming slowly to 0°C over 2 hours. The reaction mixture was stirred at 0°C for additional 2 hours producing a black solution. To a separate -78°C solution of the disubstituted olefin (0.5 mmol, 1 equiv) in Et_2O (2 mL) was added $n\text{-BuLi}$ (2.5 M in hexanes, 200 μL , 0.5 mmol, 1 equiv) in a dropwise manner via gas-tight syringe. The resulting solution was warmed to 0°C , followed by slowly transfer via cannula into the original black solution at 0°C . The reaction mixture was further stirred at room temperature for another 1 to 3 hours. The reaction was quenched with saturated NH_4Cl solution (10 mL) at 0°C . The mixture was warmed to rt before extractive isolation with diethyl ether (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 40% EtOAc /hexanes as developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the coupled product.



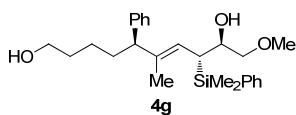
(5R,8R,9S,E)-8-(Dimethyl(phenyl)silyl)-10-methoxy-5,6-dimethyldec-6-ene-1,9-diol (4f): Prepared by the *general procedure* using silane **1a** and olefin **8a** or **8b**, silyl diol **4f** (86 mg, 47%) or (82 mg, 45%) respectively was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.29 (s, 3H), 0.34 (s, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 1.22 (m, 4H), 1.31 (s, 3H), 1.50 (m, 2H), 2.04 (dd, $J = 11.6, 3.6$ Hz, 1H), 2.11 (m, 1H), 3.18 (m, 2H), 3.24 (s, 3H), 3.59 (t, $J = 6.4$ Hz, 2H), 3.86 (m, 1H), 5.27 (d, $J = 11.2$ Hz, 1H), 7.31 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.9, -3.4, 12.8, 20.3, 23.8, 31.6, 32.8, 34.7, 43.1, 58.7, 62.8, 70.5, 76.8, 119.1, 127.6, 128.8, 134.0, 138.4, 139.6 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2929, 3425 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -13$ ($c = 2.3$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 387.2331, found 387.2335.



(4S,7S,8S,E)-7-(Dimethyl(phenyl)silyl)-4-ethyl-9-methoxy-5-methylnon-5-ene-1,8-diol (3c): Prepared by the *general procedure* using silane **1b** and olefin **8c** or **8d**, silyl diol **3c** (93 mg, 51%) or (100 mg, 55%) respectively was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.29 (s, 3H), 0.34 (s, 3H), 0.71 (t, $J = 7.6$ Hz, 3H), 1.26 (m, 6H), 1.34 (s, 3H), 1.74 (m, 1H), 2.25 (dd, $J = 12.0, 10.0$ Hz, 1H), 3.14 (m, 1H), 3.28 (s, 3H), 3.37 (m, 1H), 3.53 (t, $J = 2.0$ Hz, 2H), 3.71 (m, 1H), 4.87 (d, $J = 11.2$ Hz, 1H), 7.31 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.9, -2.6, 11.8, 12.5, 26.4, 29.6, 30.9, 32.9, 51.1, 58.8, 63.1, 72.3, 76.8, 123.4, 127.5, 128.7, 134.1, 136.8, 138.7 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2928, 3436 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -13$ ($c = 1.1$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 387.2331, found 387.2335.

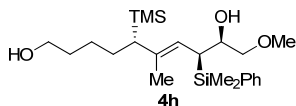


(4S,7S,8S,E)-4-Butyl-7-(dimethyl(phenyl)silyl)-9-methoxy-5-methylnon-5-ene-1,8-diol (3d): Prepared by the *general procedure* using silane **1b** and olefin **8e**, silyl diol **3d** (113 mg, 58%) was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.31 (s, 3H), 0.37 (s, 3H), 0.83 (t, $J = 7.6$ Hz, 3H), 1.08 (m, 2H), 1.26 (m, 8H), 1.34 (s, 3H), 1.83 (m, 1H), 2.24 (dd, $J = 11.6, 9.6$ Hz, 1H), 3.12 (m, 1H), 3.28 (s, 3H), 3.37 (m, 1H), 3.52 (t, $J = 6.4$ Hz, 2H), 3.71 (m, 1H), 4.86 (d, $J = 12.8$ Hz, 1H), 7.30 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.0, -2.6, 11.8, 14.1, 22.7, 29.8, 30.2, 30.9, 32.9, 33.3, 49.1, 58.8, 63.0, 72.3, 76.9, 123.1, 127.5, 128.7, 134.1, 137.0, 138.7 ppm; IR (neat) ν_{max} : 1113, 1457, 2921, 3396 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -10$ ($c = 3.3$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{23}\text{H}_{40}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 415.2644, found 415.2644.

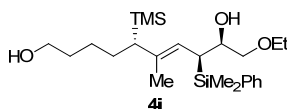


(5R,8R,9S,E)-8-(Dimethyl(phenyl)silyl)-10-methoxy-6-methyl-5-phenyldec-6-ene-1,9-diol (4g): Prepared by the *general procedure* using silane **1a** and olefin **8f**, silyl diol **4g** (78 mg, 37%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 3H), 0.17 (s, 3H), 1.37 (s, 3H), 1.44 (m, 4H), 2.01 (dd, $J = 11.2, 3.6$ Hz, 1H), 2.50 (m, 1H), 2.64 (m, 2H), 3.14 (m, 2H), 3.23 (s, 3H), 3.60 (m, 2H), 3.81 (m, 1H), 5.25 (d, J

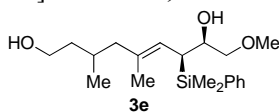
= 11.6 Hz, 1H), 7.16 (m, 4H), 7.27 (m, 2H), 7.31 (m, 2H), 7.43 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.3, -3.7, 12.1, 29.0, 30.9, 31.9, 40.7, 50.9, 58.7, 62.8, 70.3, 77.0, 122.7, 125.7, 127.6, 128.2, 128.8, 128.9, 134.0, 135.8, 138.3, 141.0 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 1496, 2930, 3418 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -16$ ($c = 1.5$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{26}\text{H}_{38}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 449.2488, found 449.2471.



(5S,8S,9S,E)-8-(Dimethyl(phenyl)silyl)-10-methoxy-6-methyl-5-(trimethylsilyl)dec-6-ene-1,9-diol (4h): Prepared by the *general procedure* using silane **1b** and olefin **8g**, silyl diol **4h** (65 mg, 31%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ -0.06 (s, 9H), 0.30 (s, 3H), 0.34 (s, 3H), 1.12 (m, 1H), 1.24 (m, 1H), 1.31 (m, 3H), 1.45 (s, 3H), 1.56 (m, 1H), 2.19 (m, 1H), 2.25 (m, 1H), 3.14 (m, 1H), 3.27 (s, 3H), 3.37 (m, 1H), 3.59 (t, $J = 6.0$ Hz, 2H), 3.70 (m, 1H), 4.77 (d, $J = 11.2$, 1H), 7.31 (m, 3H), 7.54 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.0, -2.3, -2.0, 16.4, 25.4, 27.7, 32.6, 33.7, 40.0, 58.8, 62.9, 72.5, 76.8, 120.5, 127.6, 128.8, 134.1, 136.3, 138.7 ppm; IR (neat) ν_{max} : 1113, 1247, 1457, 2931, 3433 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -5.6$ ($c = 0.8$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{23}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 445.2570, found 445.2578.

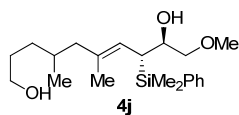


(5S,8S,9S,E)-8-(Dimethyl(phenyl)silyl)-10-ethoxy-6-methyl-5-(trimethylsilyl)dec-6-ene-1,9-diol (4i): Prepared by the *general procedure* using silane **1c** and olefin **8g**, silyl diol **4i** (87 mg, 40%) was obtained as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ -0.06 (s, 9H), 0.30 (s, 3H), 0.35 (s, 3H), 1.12 (t, $J = 7.0$ Hz, 3H), 1.40 (m, 5H), 1.43 (s, 3H), 1.55 (m, 1H), 1.71 (br, 1H), 2.23 (m, 1H), 2.33 (m, 1H), 3.13 (m, 2H), 3.42 (m, 2H), 3.59 (m, 2H), 3.69 (m, 1H), 4.77 (d, $J = 12.8$, 1H), 7.30 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.0, -2.3, -2.0, 15.1, 16.4, 25.4, 27.7, 32.6, 33.4, 40.0, 62.8, 66.4, 72.5, 74.8, 120.7, 127.5, 128.7, 134.1, 136.1, 138.7 ppm; IR (neat) ν_{max} : 1111, 1247, 1427, 2931, 3411 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -4.2$ ($c = 2.1$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{24}\text{H}_{44}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 459.2727, found 459.2745.

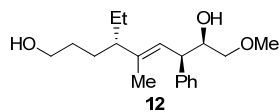


(7S,8S,E)-7-(Dimethyl(phenyl)silyl)-9-methoxy-3,5-dimethylnon-5-ene-1,8-diol (3e): Prepared by the *general procedure* using silane **1b** and olefin **8h**, silyl diol **3e** (94 mg, 54%) was obtained as a colorless oil. **Diastereomer 1:** ^1H NMR (400 MHz, CDCl_3) δ 0.31 (s, 3H), 0.35 (s, 3H), 0.77 (d, $J = 6.8$ Hz, 3H), 1.24 (m, 1H), 1.40 (s, 3H), 1.42 (m, 1H), 1.72 (m, 2H), 1.95 (m, 1H), 2.19 (t, $J = 10.8$ Hz, 1H), 2.37 (d, $J = 4.4$ Hz, 1H), 3.11 (m, 1H), 3.27 (s, 3H), 3.34 (m, 1H), 3.68 (overlap, 3H), 4.85 (d, $J = 11.6$ Hz, 1H), 7.30 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.0, -2.9, 16.3, 19.4, 27.5, 33.3, 39.7, 48.1, 58.8, 60.7, 72.3, 76.7, 123.1, 127.4, 128.7, 133.8, 134.2, 138.6 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2921, 3414 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -9.8$ ($c = 3.1$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 373.2175, found 373.2189. **Diastereomer 2:** ^1H NMR (400 MHz, CDCl_3) δ 0.31 (s, 3H), 0.35 (s, 3H), 0.78 (d, $J = 6.8$ Hz, 3H), 1.26 (m, 2H), 1.43 (s, 3H), 1.51 (m, 1H), 1.70 (m, 1H), 1.77 (m, 1H), 1.95 (m, 1H), 2.21 (m, 1H), 2.32 (d, $J = 4.4$ Hz, 1H), 3.11 (m, 1H), 3.27 (s, 3H), 3.34 (m, 1H), 3.65 (overlap, 3H), 4.87 (d, $J = 11.6$ Hz, 1H), 7.30 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -2.7, 16.3, 19.5, 27.6, 33.3, 39.67,

48.2, 58.8, 61.0, 72.2, 76.7, 123.0, 127.5, 128.8, 133.9, 134.1, 138.4 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2923, 3409 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -9.9$ ($c = 2.4$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 373.2175, found 373.2189.

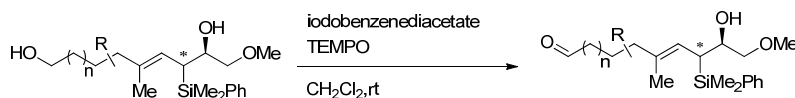


(8*R*,9*S*,*E*)-8-(Dimethyl(phenyl)silyl)-10-methoxy-4,6-dimethyldec-6-ene-1,9-diol (4j): Prepared by the *general procedure* using silane **1a** and olefin **8i**, silyl diol **4j** (80 mg, 44%) was obtained as a colorless oil. **Diastereomer 1**: ^1H NMR (500 MHz, CDCl_3) δ 0.30 (s, 3H), 0.37 (s, 3H), 0.82 (d, $J = 7.0$ Hz, 3H), 1.14 (m, 1H), 1.36 (m, 1H), 1.43 (s, 3H), 1.59 (m, 2H), 1.82 (m, 2H), 2.06 (m, 2H), 3.20 (m, 2H), 3.23 (s, 3H), 3.61 (t, $J = 6.5$ Hz, 2H), 3.87 (m, 1H), 5.26 (d, $J = 11.0$ Hz, 1H), 7.33 (m, 3H), 7.55 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.9, -3.3, 16.2, 19.5, 30.2, 30.7, 32.1, 32.7, 48.2, 58.8, 63.3, 70.6, 76.9, 121.5, 127.6, 128.9, 134.0, 134.4, 138.4 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2915, 3412 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -11$ ($c = 0.50$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 387.2331, found 387.2323. **Diastereomer 2**: ^1H NMR (500 MHz, CDCl_3) δ 0.28 (s, 3H), 0.35 (s, 3H), 0.81 (d, $J = 7.0$ Hz, 3H), 1.16 (m, 1H), 1.32 (m, 1H), 1.38 (s, 3H), 1.59 (m, 2H), 1.81 (m, 2H), 2.05 (m, 2H), 2.12 (br, 1H), 3.16 (m, 2H), 3.23 (s, 3H), 3.59 (t, $J = 6.5$ Hz, 2H), 3.85 (m, 1H), 5.24 (d, $J = 11.0$ Hz, 1H), 7.34 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.9, -3.3, 16.2, 19.5, 30.2, 30.7, 32.1, 32.7, 49.2, 59.8, 63.3, 70.6, 77.0, 121.5, 127.6, 128.9, 134.0, 134.4, 138.4 ppm; IR (neat) ν_{max} : 1113, 1246, 1427, 2917, 3402 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -11$ ($c = 0.60$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{36}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 387.2331, found 387.2323.



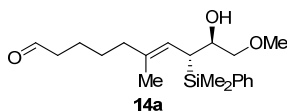
(4*S*,7*R*,8*R*,*E*)-4-Ethyl-9-methoxy-5-methyl-7-phenylnon-5-ene-1,8-diol (12): Prepared by the *general procedure* using alkyne **11** and olefin **8c** or **8d**, diol **12** (101 mg, 66%) or (89 mg, 58%) respectively was obtained as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.78 (t, $J = 7.2$ Hz, 3H), 1.14 (m, 1H), 1.30 (m, 5H), 1.47 (s, 3H), 1.67 (br, 1H), 1.84 (m, 1H), 2.08 (d, $J = 4.0$ Hz, 1H), 3.33 (m, 1H), 3.34 (s, 3H), 3.43 (m, 2H), 3.53 (m, 1H), 3.65 (t, $J = 9.2$ Hz, 1H), 3.96 (m, 1H), 5.38 (d, $J = 9.6$ Hz, 1H), 7.31 (m, 5H); ^{13}C NMR (100 MHz, CDCl_3) δ 11.8, 12.3, 26.1, 29.3, 30.7, 47.5, 50.8, 59.0, 62.8, 73.8, 74.7, 126.3, 126.4, 128.2, 128.5, 138.6, 142.1 ppm; IR (neat) ν_{max} : 1124, 1384, 1453, 2928, 3412 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -3.7$ ($c = 0.90$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 329.2093, found 329.2103.

v. The Experimental Procedure for Mono-Oxidation

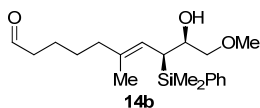


General procedure I for the selective mono-oxidation of allylsilane diols: To a stirred solution of the allylsilane diol (0.5 mmol, 1 equiv) in CH_2Cl_2 (10 mL) at room temperature was added iodobenzene diacetate (193 mg, 0.6 mmol, 1.2 equiv) followed by TEMPO (20 mg, 0.125 mmol, 0.25 equiv) and allowed the reaction mixture to stir further for another 7 hours. After

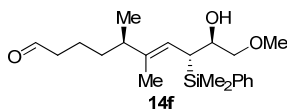
this reaction was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ solution and saturated NaHCO_3 solution, the mixture was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 20% EtOAc/hexane as developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the aldehyde product.



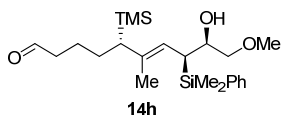
(8R,9S,E)-8-(Dimethyl(phenyl)silyl)-9-hydroxy-10-methoxy-6-methyldec-6-enal (14a): Prepared by the *general procedure I* using silyl diol **4a** to provide silyl aldehyde **14a** (139 mg, 80%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.28 (s, 3H), 0.35 (s, 3H), 1.35 (s, 3H), 1.40 (m, 2H), 1.54 (m, 2H), 2.04 (m, 3H), 2.11 (d, $J = 1.2$ Hz, 1H), 2.40 (m, 2H), 3.16 (m, 2H), 3.24 (s, 3H), 3.87 (m, 1H), 5.26 (d, $J = 11.2$ Hz, 1H), 7.31 (m, 3H), 7.51 (m, 2H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.0, -3.6, 15.9, 21.4, 27.4, 31.9, 39.5, 43.6, 58.7, 70.3, 76.9, 120.3, 127.4, 128.7, 133.9, 134.5, 138.2, 202.5 ppm; IR (neat) ν_{max} : 1116, 1244, 2930, 3447 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -4.7$ ($c = 0.90$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 371.2018, found 371.2008.



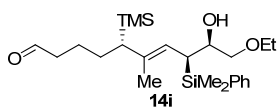
(8S,9S,E)-8-(Dimethyl(phenyl)silyl)-9-hydroxy-10-methoxy-6-methyldec-6-enal (14b): Prepared by the *general procedure I* using silyl diol **4b** to provide silyl aldehyde **14b** (130 mg, 75%) as a slightly yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.30 (s, 3H), 0.34 (s, 3H), 1.31 (m, 2H), 1.41 (s, 3H), 1.53 (m, 2H), 1.93 (t, $J = 7.0$ Hz, 2H), 2.16 (dd, $J = 11.5, 9.5$ Hz, 1H), 2.29 (br, 1H), 2.38 (t, $J = 7.5$ Hz, 2H), 3.09 (m, 1H), 3.28 (s, 3H), 3.36 (m, 1H), 3.71 (m, 1H), 4.87 (d, $J = 11.5$ Hz, 1H), 7.30 (m, 3H), 7.51 (m, 2H), 9.73 (t, $J = 1.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -3.0, 16.2, 21.6, 27.5, 33.3, 39.6, 43.7, 58.8, 72.2, 76.8, 121.8, 127.4, 128.7, 134.1, 134.4, 138.4, 202.6 ppm; IR (neat) ν_{max} : 1113, 1246, 1725, 2931, 3461 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -4.7$ ($c = 0.90$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 371.2018, found 371.2014.



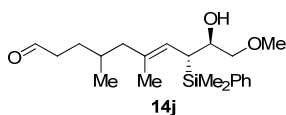
(5R,8R,9S,E)-8-(Dimethyl(phenyl)silyl)-9-hydroxy-10-methoxy-5,6-dimethyldec-6-enal (14f): Prepared by the *general procedure I* using silyl diol **4f** to provide silyl aldehyde **14f** (118 mg, 65%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.30 (s, 3H), 0.35 (s, 3H), 0.94 (d, $J = 6.8$ Hz, 3H), 1.25 (m, 2H), 1.30 (s, 3H), 1.61 (m, 2H), 2.11 (m, 3H), 3.36 (m, 1H), 3.18 (m, 2H), 3.26 (s, 3H), 3.88 (m, 1H), 5.29 (d, $J = 11.2$ Hz, 1H), 7.30 (m, 3H), 7.52 (m, 2H), 9.70 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.8, -3.5, 12.5, 20.2, 20.3, 31.5, 34.3, 43.0, 43.8, 58.8, 70.4, 76.8, 119.7, 127.6, 128.9, 134.0, 138.3, 139.0, 202.7 ppm; IR (neat) ν_{max} : 1113, 1246, 1724, 2864, 3467 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -20$ ($c = 1.3$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 385.2175, found 385.2183.



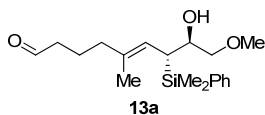
(5S,8S,9S,E)-8-(Dimethyl(phenyl)silyl)-9-hydroxy-10-methoxy-6-methyl-5-(trimethylsilyl)dec-6-enal (14h): Prepared by the *general procedure I* using silyl diol **4h** to provide bis-silyl aldehyde **14h** (121 mg, 58%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ -0.07 (s, 9H), 0.30 (s, 3H), 0.35 (s, 3H), 1.31 (m, 2H), 1.43 (s, 3H), 1.56 (m, 2H), 2.21-2.35 (m, 4H), 2.36 (3.14 (m, 1H), 3.28 (s, 3H), 3.38 (m, 1H), 3.71 (m, 1H), 4.78 (d, J = 11.6 Hz, 1H), 7.30 (m, 3H), 7.52 (m, 2H), 9.69 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.8, -2.8, -2.1, 15.9, 21.8, 27.3, 33.2, 39.9, 43.5, 58.7, 72.3, 76.7, 121.0, 127.4, 128.6, 134.0, 135.6, 138.6, 202.6 ppm; IR (neat) ν_{max} : 1114, 1247, 1725, 2951, 3455 cm^{-1} ; $[\alpha]_{\text{D}}^{23}$ = -6.8 (c = 1.5, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{23}\text{H}_{40}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 443.2414, found 443.2434.



(5S,8S,9S,E)-8-(Dimethyl(phenyl)silyl)-10-ethoxy-9-hydroxy-6-methyl-5-(trimethylsilyl)dec-6-enal (14i): Prepared by the *general procedure I* using silyl diol **4i** to provide bis-silyl aldehyde **14i** (130 mg, 60%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ -0.08 (s, 9H), 0.31 (s, 3H), 0.35 (s, 3H), 1.13 (t, J = 6.8 Hz, 4H), 1.34 (m, 4H), 1.43 (m, 3H), 2.2 (m, 4H), 3.14 (m, 1H), 3.42 (m, 3H), 3.70 (m, 1H), 4.77 (d, J = 11.6 Hz, 1H), 7.30 (m, 3H), 7.53 (m, 2H), 9.69 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.7, -2.6, -2.0, 15.1, 16.0, 21.9, 27.4, 33.4, 40.0, 43.6, 67.5, 72.8, 74.7, 121.2, 127.5, 128.7, 134.1, 135.5, 138.8, 202.6 ppm; IR (neat) ν_{max} : 1111, 1247, 1427, 2952 cm^{-1} ; $[\alpha]_{\text{D}}^{23}$ = -4.5 (c = 1.0, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{24}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$ $[\text{M} + \text{Na}]^+$ 457.2570, found 457.2578.

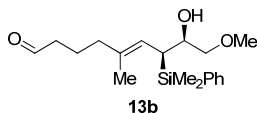


(8R,9S,E)-8-(Dimethyl(phenyl)silyl)-9-hydroxy-10-methoxy-4,6-dimethyldec-6-enal (14j): Prepared by the *general procedure I* using silyl diol **4j** to provide silyl aldehyde **14j** (116 mg, 64%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.29 (s, 3H), 0.35 (s, 3H), 0.80 (d, J = 6.0 Hz, 3H), 1.36 (s, 3H), 1.60 (m, 3H), 1.82 (m, 1H), 2.03 (m, 2H), 2.42 (m, 2H), 3.16 (m, 2H), 3.25 (s, 3H), 3.87 (m, 1H), 5.26 (d, J = 11.2 Hz, 1H), 7.31 (m, 3H), 7.53 (m, 2H), 9.74 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.9, -3.4, 16.1, 19.1, 28.7, 30.4, 32.1, 41.6, 48.0, 58.8, 70.5, 76.7, 121.9, 127.6, 128.9, 133.6, 134.0, 138.3, 202.8 ppm; IR (neat) ν_{max} : 1114, 1246, 1427, 2912, 3461 cm^{-1} ; $[\alpha]_{\text{D}}^{23}$ = -13 (c = 0.7, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 385.2175, found 385.2166

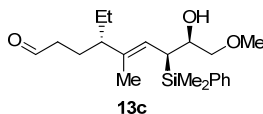


(7R,8S,E)-7-(Dimethyl(phenyl)silyl)-8-hydroxy-9-methoxy-5-methylnon-5-enal (13a): Prepared by the *general procedure I* using silyl diol **3a** to provide silyl aldehyde **13a** (117 mg, 70%) as a slightly yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.29 (s, 3H), 0.35 (s, 3H), 1.36 (s, 3H), 1.68 (m, 2H), 2.05 (m, 3H), 2.07 (br, 1H), 2.31 (m, 2H), 3.18 (m, 2H), 3.28 (s, 3H), 3.88 (m, 1H), 4.80 (d, J = 11.5 Hz, 1H), 7.31 (m, 3H), 7.52 (m, 2H), 9.73 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -4.0, -3.7, 15.8, 20.2, 31.9, 39.1, 43.0, 58.6, 70.1, 76.8, 121.0, 127.4, 127.5, 128.7, 133.8, 138.1, 202.2 ppm; IR (neat) ν_{max} : 1113, 1247,

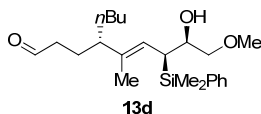
1427, 1722, 2896, 3470 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -13$ ($c = 1.8$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 357.1862, found 357.1859.



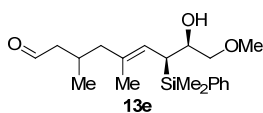
(7S,8S,E)-7-(Dimethyl(phenyl)silyl)-8-hydroxy-9-methoxy-5-methylnon-5-enal (13b): Prepared by the *general procedure I* using silyl diol **3b** to provide silyl aldehyde **13b** (128 mg, 77%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.31 (s, 3H), 0.35 (s, 3H), 1.42 (s, 3H), 1.62 (m, 2H), 1.94 (t, $J = 8.0$ Hz, 2H), 2.15-2.28 (m, 4H), 3.09 (m, 1H), 3.29 (s, 3H), 3.32 (m, 1H), 3.72 (m, 1H), 4.87 (d, $J = 11.6$ Hz, 1H), 7.30 (m, 3H), 7.50 (m, 2H), 9.70 (t, $J = 1.5$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -3.2, -2.9, 16.1, 20.3, 33.3, 39.1, 43.1, 58.8, 72.1, 76.8, 122.6, 127.4, 128.7, 133.8, 134.1, 138.4, 202.5 ppm; IR (neat) ν_{max} : 1111, 1255, 1727, 2913 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -4.6$ ($c = 1.7$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 357.1862, found 357.1855.



(4S,7S,8S,E)-7-(Dimethyl(phenyl)silyl)-4-ethyl-8-hydroxy-9-methoxy-5-methylnon-5-enal (13c): Prepared by the *general procedure I* using silyl diol **3c** to provide silyl aldehyde **13c** (121 mg, 67%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.42 (s, 3H), 0.47 (s, 3H), 0.80 (t, $J = 7.2$ Hz, 3H), 1.40 (s, 3H), 1.46 (m, 2H), 1.60 (m, 1H), 1.80 (m, 1H), 2.04 (m, 2H), 2.37 (t, $J = 10.0$ Hz, 2H), 2.48 (br, 1H), 3.23 (t, $J = 7.6$ Hz, 1H), 3.36 (s, 3H), 3.45 (d, $J = 9.2$ Hz, 1H), 4.97 (d, $J = 11.2$ Hz, 1H), 7.38 (m, 3H), 7.60 (m, 2H), 9.67 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -5.0, -3.3, 10.1, 11.0, 23.9, 24.9, 31.5, 40.5, 49.3, 57.5, 70.8, 75.4, 123.1, 126.2, 127.4, 132.6, 134.3, 137.4, 201.4 ppm; IR (neat) ν_{max} : 1115, 1240, 1727, 2929, 2957, 3460 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -10$ ($c = 2.5$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 385.2175, found 385.2187.

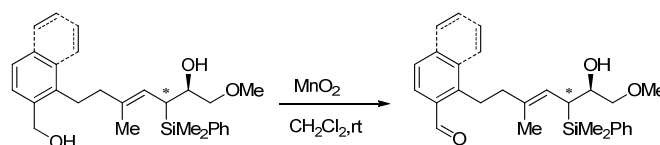


(4S,7S,8S,E)-4-Butyl-7-(dimethyl(phenyl)silyl)-8-hydroxy-9-methoxy-5-methylnon-5-enal (13d): Prepared by the *general procedure I* using silyl diol **3d** to provide silyl aldehyde **13d** (111 mg, 57%) as a slightly yellow oil. ^1H NMR (400 MHz, CDCl_3) δ 0.34 (s, 3H), 0.39 (s, 3H), 0.84 (t, $J = 7.2$ Hz, 3H), 1.08 (m, 2H), 1.26 (m, 4H), 1.32 (s, 3H), 1.38 (m, 1H), 1.50 (m, 1H), 1.83 (m, 1H), 1.91 (m, 1H), 1.99 (m, 1H), 2.27 (m, 1H), 2.32 (d, $J = 4.4$ Hz, 1H), 3.14 (m, 1H), 3.30 (s, 3H), 3.37 (m, 1H), 3.73 (m, 1H), 4.86 (d, $J = 11.6$ Hz, 1H), 7.30 (m, 3H), 7.52 (m, 2H), 9.59 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.7, -2.1, 11.5, 14.0, 22.5, 25.5, 30.0, 32.8, 33.1, 41.8, 48.7, 58.7, 72.2, 76.8, 124.2, 127.5, 128.7, 133.9, 135.9, 138.7, 202.6 ppm; IR (neat) ν_{max} : 1115, 1427, 1724, 2925 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -11$ ($c = 1.8$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{23}\text{H}_{38}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 413.2488, found 413.2488.

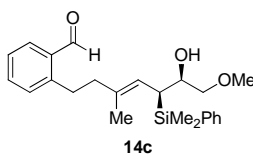


(7S,8S,E)-7-(Dimethyl(phenyl)silyl)-8-hydroxy-9-methoxy-3,5-dimethylnon-5-enal (13e): Prepared by the *general procedure I* using silyl diol **3e** to provide silyl aldehyde **13e** (108 mg, 62%) as a slightly yellow oil. **Diastereomer 1:** ^1H NMR (400

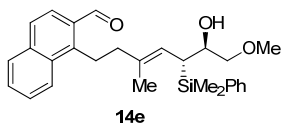
MHz, CDCl₃) δ 0.41 (s, 3H), 0.46 (s, 3H), 0.91 (d, J = 6.0 Hz, 3H), 1.51 (s, 3H), 1.95 (m, 2H), 2.08 (m, 1H), 2.17 (m, 2H), 2.31 (m, 1H), 3.21 (m, 1H), 3.37 (s, 3H), 3.44 (m, 1H), 3.82 (m, 1H), 4.97 (d, J = 11.2 Hz, 1H), 7.38 (m, 3H), 7.59 (m, 2H), 9.70 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ -6.2, -5.2, 13.4, 17.2, 23.3, 30.5, 44.9, 47.5, 56.2, 69.3, 74.1, 121.5, 124.7, 126.0, 130.0, 131.3, 135.8, 200.0 ppm; IR (neat) ν_{max} : 1115, 1246, 1427, 2953, 3448 cm⁻¹; [α]_D²³ = -8.2 (c = 3.1, CH₂Cl₂); HRMS(CI/NH₃) m/z calcd for C₂₀H₃₂O₃SiNa [M + Na]⁺ 371.2018, found 371.2040. **Diastereomer 2:** ¹H NMR (400 MHz, CDCl₃) δ 0.35 (s, 3H), 0.39 (s, 3H), 0.88 (d, J = 6.0 Hz, 3H), 1.46 (s, 3H), 1.92 (m, 2H), 2.26 (m, 4H), 3.13 (m, 1H), 3.30 (s, 3H), 3.34 (m, 1H), 3.75 (m, 1H), 4.93 (d, J = 11.2 Hz, 1H), 7.34 (m, 3H), 7.55 (m, 2H), 9.73 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ -4.0, -4.0, 15.2, 18.9, 25.2, 32.3, 46.6, 49.4, 57.7, 71.0, 75.7, 123.1, 126.4, 127.6, 131.7, 133.0, 137.2, 201.6 ppm; IR (neat) ν_{max} : 1115, 1246, 1427, 2894, 3448 cm⁻¹; [α]_D²³ = -4.5 (c = 2.2, CH₂Cl₂); HRMS(CI/NH₃) m/z calcd for C₂₀H₃₂O₃SiNa [M + Na]⁺ 371.2018, found 371.2040.



General procedure II for the selective mono-oxidation of allylsilane diols: To a stirred solution of the benzylic alcohol (0.5 mmol, 1 equiv) in CH₂Cl₂ (10 mL) at room temperature was added activated MnO₂ (645 mg, 7.5 mmol, 15 equiv) and allowed the reaction mixture to stir further for another 12 hours. After this reaction was filtered through celite, and washed with CH₂Cl₂ (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 20% EtOAc/hexane as developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the aldehyde product.

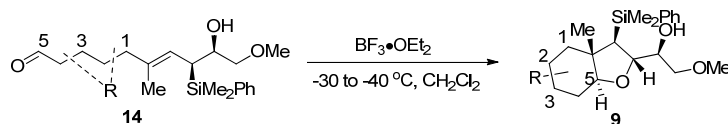


2-((5S,6S,E)-5-(Dimethyl(phenyl)silyl)-6-hydroxy-7-methoxy-3-methylhept-3-en-1-yl)benzaldehyde (14c): Prepared by the *general procedure II* using silyl diol **4c** to provide silyl aldehyde **14c** (168 mg, 85%) as a slightly yellow oil. ¹H NMR (500 MHz, CDCl₃) δ 0.30 (s, 3H), 0.34 (s, 3H), 1.50 (s, 3H), 2.15 (m, 2H), 2.23 (m, 2H), 3.02 (m, 3H), 3.21 (m, 1H), 3.26 (s, 3H), 3.68 (m, 1H), 4.88 (d, J = 12.5 Hz, 1H), 7.21 (d, J = 7.0 Hz, 1H), 7.31 (m, 3H), 7.35 (m, 1H), 7.50 (m, 3H), 7.80 (d, J = 7.5 Hz, 1H), 10.23 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ -3.2, -3.1, 16.4, 31.5, 33.5, 42.5, 58.8, 72.1, 76.7, 122.6, 126.5, 127.5, 128.8, 131.0, 131.9, 133.6, 133.8, 133.9, 134.2, 138.3, 145.1, 192.2 ppm; IR (neat) ν_{max} : 1115, 1245, 1600, 1696, 2894, 3462 cm⁻¹; [α]_D²⁰ = +3.5 (c = 1.1, CH₂Cl₂); HRMS(CI/NH₃) m/z calcd for C₂₄H₃₂O₃SiNa [M + Na]⁺ 419.2018, found 419.2008.

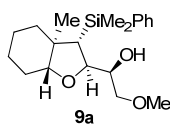


2-((5R,6S,E)-5-(Dimethyl(phenyl)silyl)-6-hydroxy-7-methoxy-3-methylhept-3-en-1-yl)benzaldehyde (14e): Prepared by the *general procedure II* using silyl diol **4e** to provide silyl aldehyde **14e** (183 mg, 82%) as a slightly yellow oil. ^1H NMR (500 MHz, CDCl_3) δ 0.37 (s, 3H), 0.40 (s, 3H), 1.55 (s, 3H), 2.09 (m, 1H), 2.21 (br, 1H), 2.41 (m, 2H), 3.18 (m, 2H), 3.29 (s, 3H), 3.50 (m, 1H), 3.59 (m, 1H), 3.93 (m, 1H), 5.42 (d, $J = 11.5$ Hz, 1H), 7.34 (m, 3H), 7.58 (m, 4H), 7.77 (m, 1H), 7.86 (m, 1H), 7.91 (m, 1H), 8.18 (m, 1H), 10.57 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ -3.8, -3.6, 16.4, 26.1, 32.3, 42.7, 58.8, 70.4, 76.9, 122.5, 124.3, 124.9, 126.9, 127.1, 127.6, 128.5, 129.0, 130.5, 131.8, 134.0, 136.3, 138.2, 144.6, 191.7 ppm; IR (neat) ν_{max} : 1116, 1428, 1683, 2896, 3446 cm^{-1} ; $[\alpha]_{\text{D}}^{20} = -15$ ($c = 1.9$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 469.2175, found 469.2172.

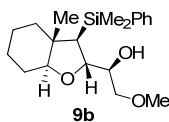
vi. [3 + 2] Annulation of Complex Silyl Aldehydes



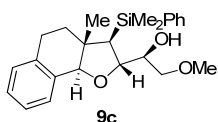
General procedure for the [3 + 2] annulation: Aldehyde **14** (0.2 mmol, 1 equiv) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to -30 °C under an argon atmosphere. $\text{BF}_3 \cdot \text{OEt}_2$ (50 μL , 0.4 mmol, 2 equiv) was added to the mixture at -30 or -40 °C, and the solution was stirred at that temperature for 1 to 1.5 hours. The reaction was diluted with a solution of saturated NaHCO_3 (10 mL) and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 30% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the bicyclic product **9**.



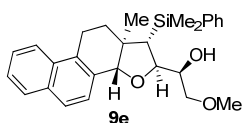
(S)-1-((2R,3S,3aR,7aR)-3-(Dimethyl(phenyl)silyl)-3a-methyloctahydrobenzofuran-2-yl)-2-methoxyethanol (9a): Prepared by the *general procedure* using silyl aldehyde **14a** to provide bicyclic product **9a** (57 mg, 82%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.37 (s, 3H), 0.39 (s, 3H), 0.85 (s, 3H), 1.18 (m, 2H), 1.35 (m, 3H), 1.51 (m, 1H), 1.68 (m, 2H), 1.78 (m, 1H), 2.05 (br, 1H), 3.19 (dd, $J = 12.0$, 3.6 Hz, 1H), 3.29 (s, 3H), 3.35 (m, 2H), 3.46 (m, 1H), 4.03 (d, $J = 10.8$ Hz, 1H), 7.33 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (100 MHz, C_6D_6) δ -1.8, -1.6, 15.7, 21.0, 24.5, 25.6, 36.30, 40.5, 45.2, 58.6, 71.6, 75.7, 79.0, 87.5, 128.1, 129.3, 134.3, 139.0 ppm; IR (neat) ν_{max} : 1110, 1250, 1427, 1733, 2932, 3445 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +8.0$ ($c = 1.2$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 371.2018, found 371.2019.



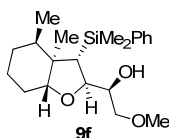
(S)-1-((2S,3R,3aS,7aS)-3-(Dimethyl(phenyl)silyl)-3a-methyloctahydrobenzofuran-2-yl)-2-methoxyethanol (9b): Prepared by the *general procedure* using silyl aldehyde **14b** to provide bicyclic product **9b** (47 mg, 68%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.38 (s, 3H), 0.42 (s, 3H), 0.86 (s, 3H), 1.09-1.23 (m, 3H), 1.30-1.41 (m, 3H), 1.54 (m, 1H), 1.74 (m, 2H), 2.17 (d, $J = 4.4$ Hz, 1H), 2.97 (dd, $J = 11.6, 3.6$ Hz, 1H), 3.24 (s, 3H), 3.38 (m, 1H), 3.50 (m, 2H), 4.13 (dd, $J = 10, 5.2$ Hz, 1H), 7.33 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.0, -1.4, 15.1, 20.7, 24.1, 24.9, 36.1, 42.9, 45.3, 58.8, 72.9, 73.3, 80.6, 86.5, 127.8, 129.0, 133.0, 139.1 ppm; IR (neat) ν_{max} : 1109, 1249, 1456, 1734, 2930, 3447 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -19$ ($c = 0.50$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{20}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 371.2018, found 371.2003.



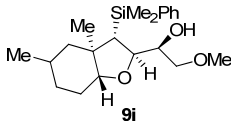
(S)-1-((2S,3R,3aS,9bS)-3-(Dimethyl(phenyl)silyl)-3a-methyl-2,3,3a,4,5,9b-hexahydronaphtho[1,2-b]furan-2-yl)-2-methoxyethanol (9c): Prepared by the *general procedure* using silyl aldehyde **14c** to provide bicyclic product **9c** (47 mg, 59%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.43 (s, 3H), 0.45 (s, 3H), 0.64 (s, 3H), 1.45 (d, $J = 10.0$ Hz, 1H), 1.66 (m, 2H), 2.28 (br, 1H), 2.77 (m, 2H), 3.28 (s, 3H), 3.48 (m, 1H), 3.63 (m, 2H), 4.31 (s, 1H), 4.39 (dd, $J = 10.0, 5.5$ Hz, 1H), 7.04 (m, 1H), 7.12 (m, 2H), 7.29 (m, 1H), 7.35 (m, 3H), 7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ -1.9, -1.6, 16.2, 26.2, 32.2, 42.5, 45.8, 58.9, 73.1, 73.5, 82.8, 85.5, 123.7, 125.6, 126.3, 127.7, 127.9, 129.1, 134.0, 135.07, 136.9, 138.8 ppm; IR (neat) ν_{max} : 1114, 1249, 1456, 1733, 2924, 3447 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +5.6$ ($c = 0.60$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{24}\text{H}_{32}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 419.2018, found 419.2036.



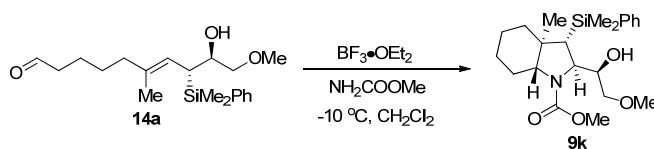
(S)-1-((2R,3S,3aR,11bR)-3-(Dimethyl(phenyl)silyl)-3a-methyl-2,3,3a,4,5,11b-hexahydrophenanthro[1,2-b]furan-2-yl)-2-methoxyethanol (9e): Prepared by the *general procedure* using silyl aldehyde **14e** to provide bicyclic product **9e** (49 mg, 55%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.47 (s, 6H), 0.74 (s, 3H), 1.88 (m, 2H), 2.01 (d, $J = 10.8$ Hz), 3.16 (m, 2H), 3.40 (s, 3H), 3.54 (m, 2H), 3.68 (m, 1H), 4.39 (d, $J = 10.4$ Hz, 1H), 4.72 (s, 1H), 7.38-7.54 (m, 6H), 7.59 (m, 2H), 7.71 (d, $J = 8.4$ Hz, 1H), 7.81 (d, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ -2.2, -1.9, 15.8, 24.0, 32.1, 39.9, 45.0, 59.0, 71.6, 75.5, 81.3, 87.1, 122.5, 123.2, 124.8, 125.8, 126.2, 127.9, 128.8, 129.3, 129.4, 131.6, 132.4, 133.9, 134.2, 138.2 ppm; IR (neat) ν_{max} : 1114, 1250, 1427, 1641, 2926, 3443 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -14$ ($c = 0.60$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{28}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 469.2175, found 469.2189.



(S)-1-((2R,3S,3aR,4R,7aR)-3-(Dimethyl(phenyl)silyl)-3a,4-dimethyloctahydrobenzofuran-2-yl)-2-methoxyethanol (9f): Prepared by the *general procedure* using silyl aldehyde **14f** to provide bicyclic product **9f** (46 mg, 63%) as a white solid. Melting Point: 47 °C to 49 °C; ^1H NMR (400 MHz, CDCl_3) δ 0.37 (s, 3H), 0.41 (s, 3H), 0.97 (s, 3H), 0.99 (d, $J = 7.2$ Hz, 3H), 1.16(m, 1H), 1.41 (m, 2H), 1.57 (m, 2H), 1.72 (m, 1H), 1.78 (m, 1H), 2.02 (m, 2H), 3.28 (s, 3H), 3.34 (m, 2H), 3.43 (m, 1H), 3.53 (m, 1H), 3.98 (d, $J = 10.8$ Hz, 1H), 7.33 (m, 3H), 7.52 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 14.5, 15.3, 18.4, 19.9, 25.7, 27.6, 34.7, 36.2, 47.3, 58.9, 65.9, 71.3, 75.6, 78.9, 81.1, 127.9, 129.1, 133.8, 138.7 ppm; IR (neat) ν_{max} : 1124, 1456, 1734, 2926, 3481, 3853 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +6.0$ ($c = 0.30$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 385.2175, found 385.2187.

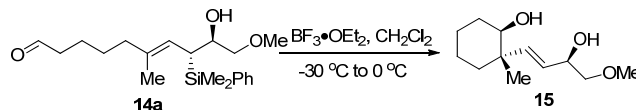


(1S)-1-((2R,3S,3aR,7aR)-3-(Dimethyl(phenyl)silyl)-3a,5-dimethyloctahydrobenzofuran-2-yl)-2-methoxyethanol (9j): Prepared by the *general procedure* using silyl aldehyde **14j** to provide bicyclic product **9j** (54 mg, 75%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.37 (s, 3H), 0.39 (s, 3H), 0.79 (d, $J = 6.4$ Hz, 3H), 0.87 (s, 3H), 0.91 (m, 2H), 1.40 (m, 1H), 1.53 (m, 1H), 1.67 (m, 2H), 1.76 (m, 1H), 2.08 (d, $J = 6.4$ Hz, 1H), 3.21 (dd, $J = 12, 3.6$ Hz, 1H), 3.28 (s, 3H), 3.35 (m, 2H), 3.44 (m, 1H), 4.04 (d, $J = 10.4$ Hz, 1H), 7.32 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ -2.4, -1.5, 16.3, 22.2, 24.5, 27.1, 33.1, 40.5, 44.8, 45.4, 58.9, 71.3, 75.6, 79.7, 87.6, 127.8, 129.1, 133.8, 138.5 ppm; IR (neat) ν_{max} : 1113, 1249, 1457, 1734, 2949, 3441, 3853 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +10$ ($c = 0.50$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{21}\text{H}_{34}\text{O}_3\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 385.2175, found 385.2187.



Procedure of the [3+2] annulation to achieve perhydroindol: (2R,3S,3aR,7aR)-Methyl 3-(dimethyl(phenyl)silyl)-2-((R)-1-hydroxy-2-methoxyethyl)-3a-methyloctahydro-1H-indole-1-carboxylate (9k): Aldehyde **14a** (70 mg, 0.2 mmol, 1 equiv) and NH_2COOMe (60 mg, 0.8 mmol, 4 equiv) was dissolved in CH_2Cl_2 (10 mL). The solution was cooled to -30 °C under an argon atmosphere. $\text{BF}_3 \cdot \text{OEt}_2$ (50 μL , 0.4 mmol, 2 equiv) was added to the mixture at -30 °C, and the solution was stirred at -10 °C for 2 hours. A solution of saturated NaHCO_3 (10 mL) was added and the mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 30% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated under reduced pressure to obtain the perhydroindol product **9k** (49 mg, 61%) as a single diastereomer. ^1H NMR (400 MHz, CD_3CN) δ 0.41 (s, 3H), 0.44 (s, 3H), 0.90 (s, 3H), 1.15 (m, 2H), 1.39 (m, 2H), 1.55 (m, 1H), 1.65 (m, 2H), 1.88 (m, 1H), 2.22 (d, $J = 10.4$ Hz, 1H), 2.80 (d, $J = 4.8$ Hz, 1H), 3.15 (t, $J = 9.6$ Hz, 1H), 3.22 (s, 3H), 3.42 (m, 3H), 3.60 (s, 3H), 3.98 (d, $J = 10.4$ Hz, 1H), 7.40 (m, 3H),

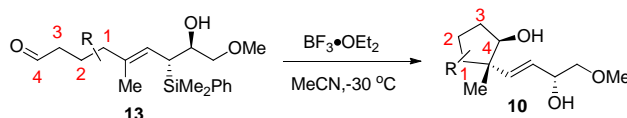
7.60 (m, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ -2.3, -1.5, 21.1, 24.2, 27.1, 28.1, 29.7, 34.1, 43.6, 51.7, 57.8, 61.6, 67.0, 70.8, 76.4, 127.8, 129.0, 133.9, 139.3 ppm; IR (neat) ν_{max} : 1112, 1254, 1448, 1698, 2924, 3447 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -4.6$ ($c = 0.50$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{22}\text{H}_{35}\text{NO}_4\text{SiNa}$ $[\text{M} + \text{Na}]^+$ 428.2233, found 428.2231.



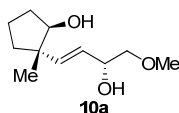
(1R,2S)-2-((R,E)-3-Hydroxy-4-methoxybut-1-en-1-yl)-2-methylcyclohexanol (15):

Aldehyde **14a** (0.2 mmol, 1 equiv) was dissolved in CH_2Cl_2 (20 mL). The solution was cooled to $-30\text{ }^\circ\text{C}$ under an argon atmosphere. $\text{BF}_3 \cdot \text{OEt}_2$ (50 μL , 0.4 mmol, 2 equiv) was added to the mixture at $-30\text{ }^\circ\text{C}$, and the solution was stirred at that temperature for 1 hour, at which time, another portion of $\text{BF}_3 \cdot \text{OEt}_2$ (25 μL , 0.2 mmol, 1 equiv) was added into the mixture. The reaction was warmed to $0\text{ }^\circ\text{C}$ and further stirred for 30 min. A solution of saturated NaHCO_3 (10 mL) was added and the mixture was extracted with CH_2Cl_2 (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 80% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the product **15** (20 mg, 46%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.99 (s, 3H), 1.30 (m, 2H), 1.41 (m, 4H), 1.73 (m, 2H), 3.28 (t, $J = 8.0$ Hz, 1H), 3.38 (s, 3H), 3.39 (m, 2H), 4.29 (m, 1H), 5.50 (dd, $J = 15.6, 6.0$ Hz, 1H), 5.72 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 15.4, 20.9, 24.4, 29.1, 36.6, 41.4, 59.0, 71.3, 74.9, 77.0, 126.8, 142.3 ppm; IR (neat) ν_{max} : 1124, 1197, 1450, 2920, 3444 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -3.7$ ($c = 0.20$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{12}\text{H}_{22}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 237.1467, found 237.1555.

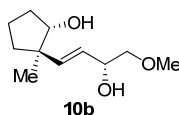
vii. Intramolecular Allylation



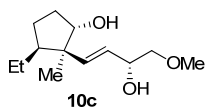
General procedure of the intramolecular allylation to achieve cyclopentyl alcohols: Aldehyde **13** (0.2 mmol, 1 equiv) was dissolved in MeCN (20 mL). The solution was cooled to $-30\text{ }^\circ\text{C}$ under an argon atmosphere. $\text{BF}_3 \cdot \text{OEt}_2$ (50 μL , 0.4 mmol, 2 equiv) was added to the mixture at $-30\text{ }^\circ\text{C}$, and the solution was stirred at that temperature for 1 to 1.5 hours. A solution of saturated NaHCO_3 (20 mL) was added and the mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 70% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the cyclopentanol product **10**.



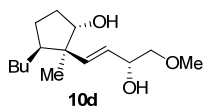
(1R,2S)-2-((R,E)-3-Hydroxy-4-methoxybut-1-en-1-yl)-2-methylcyclopentanol (10a): Prepared by the *general procedure* using silyl aldehyde **13a** to provide cyclopentanol **10a** (25 mg, 61%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 1.01 (s, 3H), 1.58 (m, 4H), 1.71 (m, 1H), 2.01 (m, 1H), 3.26 (t, $J = 8.4$ Hz, 1H), 3.38 (s, 3H), 3.83 (t, $J = 6.8$ Hz, 1H), 4.28 (m, 1H), 5.43 (dd, $J = 15.6, 6.4$ Hz, 1H), 5.74 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.4, 19.3, 31.2, 36.0, 47.3, 59.0, 71.4, 76.7, 79.6, 125.8, 141.5 ppm; IR (neat) ν_{max} : 1124, 1457, 1668, 2929, 3402 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -13$ ($c = 0.30$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{11}\text{H}_{20}\text{O}_3\text{Na}$ $[\text{M} + \text{Na}]^+$ 223.1310, found 223.1484.



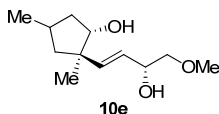
((1S,2R)-2-((R,E)-3-Hydroxy-4-methoxybut-1-en-1-yl)-2-methylcyclopentanol (10b): Prepared by the *general procedure* using silyl aldehyde **13b** to provide cyclopentanol **10b** (23 mg, 58%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.98 (s, 3H), 1.56 (m, 4H), 1.70 (m, 1H), 1.97 (m, 2H), 2.67 (br, 1H), 3.25 (t, $J = 9.0$ Hz, 1H), 3.36 (s, 3H), 3.38 (m, 1H), 3.80 (t, $J = 7.5$ Hz, 1H), 4.25 (m, 1H), 5.41 (dd, $J = 16.0, 6.5$ Hz, 1H), 5.72 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 19.3, 31.3, 35.9, 47.3, 59.0, 71.1, 76.8, 79.5, 125.7, 141.0 ppm; IR (neat) ν_{max} : 1123, 1457, 1663, 2930, 3403 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +2.5$ ($c = 0.20$, CH_2Cl_2).



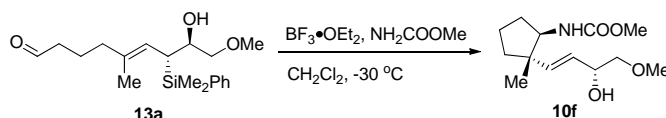
(1S,2R,3S)-3-Ethyl-2-((R,E)-3-hydroxy-4-methoxybut-1-en-1-yl)-2-methylcyclopentanol (10c): Prepared by the *general procedure* using silyl aldehyde **13c** to provide cyclopentanol **10c** (23 mg, 51%) as a colorless oil. ^1H NMR (400 MHz, CDCl_3) δ 0.85 (t, $J = 8.0$ Hz, 3H), 1.00 (m, 1H), 1.08 (s, 3H), 1.24 (m, 1H), 1.36 (m, 1H), 1.56 (m, 2H), 1.70 (m, 1H), 2.00 (m, 1H), 2.09 (m, 1H), 2.33 (br, 1H), 3.23 (t, $J = 9.2$ Hz, 1H), 3.37 (m, 1H), 3.38 (s, 3H), 3.82 (m, 1H), 4.26 (m, 1H), 5.39 (dd, $J = 16.0, 6.4$ Hz, 1H), 5.65 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 13.3, 18.2, 23.6, 27.7, 31.7, 48.7, 50.7, 59.0, 71.5, 76.9, 80.8, 126.9, 136.8 ppm; IR (neat) ν_{max} : 1118, 1655, 2872, 2954, 3413 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +2.0$ ($c = 0.30$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{13}\text{H}_{25}\text{O}_3$ $[\text{M} + \text{H}]^+$ 229.1804, found 229.1806.



(1S,2R,3S)-3-Butyl-2-((R,E)-3-hydroxy-4-methoxybut-1-en-1-yl)-2-methylcyclopentanol (10d): Prepared by the *general procedure* using silyl aldehyde **13d** to provide cyclopentanol **10d** (24 mg, 47%) as a colorless oil. ^1H NMR (500 MHz, CDCl_3) δ 0.85 (t, $J = 7.0$ Hz, 3H), 1.00 (m, 1H), 1.08 (s, 3H), 1.29 (m, 6H), 1.51 (br, 1H), 1.58 (m, 1H), 1.74 (m, 1H), 1.98 (m, 1H), 2.08 (m, 1H), 2.50 (br, 1H), 3.25 (t, $J = 9.0$ Hz, 1H), 3.37 (m, 1H), 3.39 (s, 3H), 3.83 (m, 1H), 4.28 (m, 1H), 5.39 (dd, $J = 16.0, 6.5$ Hz, 1H), 5.66 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 14.1, 18.3, 22.9, 28.1, 30.4, 31.1, 31.7, 46.7, 50.7, 59.0, 71.6, 76.8, 80.8, 126.8, 136.8 ppm; IR (neat) ν_{max} : 1124, 1452, 1737, 2925, 3402 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +8.2$ ($c = 0.40$, CH_2Cl_2).

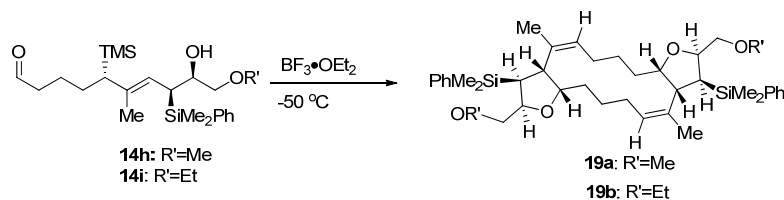


(1S,2R)-2-((R,E)-3-Hydroxy-4-methoxybut-1-en-1-yl)-2,4-dimethylcyclopentanol (10e): Prepared by the *general procedure* using silyl aldehyde **13e** to provide cyclopentanol **10e** (30 mg, 70%) as a colorless oil. **Diastereomer a:** ^1H NMR (500 MHz, CDCl_3) δ 1.00 (overlap, 6H), 1.23 (m, 2H), 1.82 (m, 1H), 1.97 (m, 1H), 2.14 (m, 1H), 2.64 (br, 1H), 3.23 (m, 1H), 3.35 (s, 3H), 3.36 (m, 1H), 3.80 (t, $J = 7.0$ Hz, 1H), 4.23 (m, 1H), 5.37 (dd, $J = 16.0, 6.5$ Hz, 1H), 5.72 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 20.3, 22.3, 28.4, 41.4, 45.1, 47.6, 60.0, 71.1, 76.8, 79.7, 125.0, 141.5 ppm; IR (neat) ν_{max} : 1124, 1456, 1653, 2951, 3398 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +2.5$ ($c = 1.9$, CH_2Cl_2). **Diastereomer b:** ^1H NMR (500 MHz, CDCl_3) δ 0.98 (overlap, 6H), 1.17 (m, 1H), 1.60 (m, 1H), 1.69 (m, 1H), 1.80 (m, 2H), 2.19 (m, 1H), 2.60 (br, 1H), 3.25 (m, 1H), 3.37 (s, 3H), 3.38 (m, 1H), 3.89 (t, $J = 7.0$ Hz, 1H), 4.26 (m, 1H), 5.40 (dd, $J = 16.0, 6.5$ Hz, 1H), 5.76 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 17.4, 22.5, 27.9, 39.8, 45.9, 48.2, 60.0, 71.1, 76.8, 78.8, 126.6, 141.5 ppm; IR (neat) ν_{max} : 1194, 1456, 1655, 2949, 3389 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +9.0$ ($c = 1.3$, CH_2Cl_2).

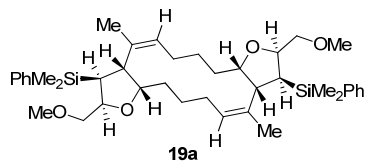


Procedure of the intramolecular allylation to achieve cyclopentyl carbamate: **Methyl (1R,2S)-2-((R,E)-3-hydroxy-4-methoxybut-1-enyl)-2-methylcyclopentylcarbamate (10f):** Aldehyde **13a** (67 mg, 0.2 mmol, 1 equiv) and NH_2COOMe (30 mg, 0.4 mmol, 2 equiv) was dissolved in CH_2Cl_2 (10 mL). The solution was cooled to -30 °C under an argon atmosphere. $\text{BF}_3 \cdot \text{OEt}_2$ (50 μL , 0.4 mmol, 2 equiv) was added to the mixture at -30 °C, and the solution was stirred at that temperature for 1 hour. The reaction was diluted with a solution of saturated NaHCO_3 (10 mL) and the mixture was extracted with diethyl ether (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 70% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the carbamate product **10f** (35 mg, 68%) as a single diastereomer. ^1H NMR (500 MHz, CDCl_3) δ 0.99 (s, 3H), 1.42 (m, 1H), 1.49 (m, 1H), 1.66 (m, 3H), 2.08 (m, 1H), 3.30 (m, 1H), 3.36 (s, 3H), 3.37 (m, 1H), 3.59 (s, 3H), 3.78 (m, 1H), 4.25 (m, 1H), 4.54 (d, $J = 9.0$ Hz, 1H), 5.38 (dd, $J = 16.0, 6.5$ Hz, 1H), 5.77 (d, $J = 16.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 17.6, 19.4, 29.2, 29.8, 37.2, 46.2, 52.1, 53.8, 59.0, 59.3, 71.2, 125.9, 141.3, 156.9 ppm; IR (neat) ν_{max} : 1055, 1125, 1260, 1541, 1702, 2960, 3320 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = +6.3$ ($c = 1.1$, CH_2Cl_2); HRMS(CI/NH_3) m/z calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_4\text{Na}$ $[\text{M} + \text{Na}]^+$ 280.1525, found 280.1514.

viii. Sakurai-Like Dimerization



Aldehyde **14h** or **14i** (0.1 mmol, 1 equiv) was dissolved in CH₂Cl₂ (1 mL). The solution was cooled to -50 °C under an argon atmosphere. BF₃·OEt₂ (25 μL, 0.2 mmol, 2 equiv) was added to the mixture at -50 °C, and the solution was stirred at that temperature for 2 hours. A solution of saturated NaHCO₃ (2 mL) was added and the mixture was extracted with CH₂Cl₂ (3 x 5 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 20% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated under reduced pressure to obtain the dimerization product **19**.

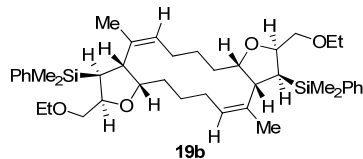


((2*S*,3*S*,3*aR*,4*Z*,8*aS*,10*S*,11*S*,11*aR*,12*Z*,16*aS*)-2,10-

Bis(methoxymethyl)-4,12-dimethyl-2,3,3*a*,6,7,8,8*a*,10,11,11*a*,14,15,16,16*a*-

tetradecahydrocyclooctadeca[1,2-*b*:8,9-*b'*]difuran-3,11-diyl)bis(dimethyl(phenyl)silane)

(19a): ¹H NMR (400 MHz, CDCl₃) δ 0.26 (s, 6H), 0.32 (s, 6H), 1.23 (m, 2H), 1.39 (m, 4H), 1.50 (s, 6H), 1.72 (m, 2H), 1.84 (m, 2H), 1.92 (dd, *J* = 10.8, 8.4 Hz, 2H), 2.35 (q, *J* = 11.2 Hz, 2H), 3.18 (s, 6H), 3.22 (m, 4H), 3.47 (m, 2H), 4.01 (t, *J* = 8.4 Hz, 2H), 4.34 (m, 2H), 5.03 (d, *J* = 9.6 Hz, 2H), 7.31 (m, 6H), 7.47 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ -2.9, -1.9, 21.9, 24.5, 24.6, 28.4, 30.8, 44.5, 58.8, 74.4, 78.2, 80.0, 127.7, 129.0, 130.3, 133.7, 134.1, 138.7 ppm; IR (neat) ν_{max}: 1112, 1248, 1428, 2928 cm⁻¹; [α]_D²³ = -5.0 (c = 0.20, CH₂Cl₂); HRMS(CI/NH₃) *m/z* calcd for C₄₀H₆₀O₄Si₂Na [M + Na]⁺ 683.3928, found 683.3943.



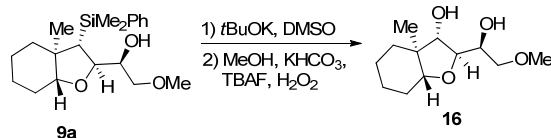
((2*S*,3*S*,3*aR*,4*Z*,8*aS*,10*S*,11*S*,11*aR*,12*Z*,16*aS*)-2,10-

Bis(ethoxymethyl)-4,12-dimethyl-2,3,3*a*,6,7,8,8*a*,10,11,11*a*,14,15,16,16*a*-

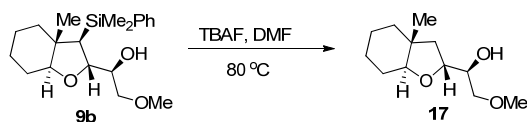
tetradecahydrocyclooctadeca[1,2-*b*:8,9-*b'*]difuran-3,11-diyl)bis(dimethyl(phenyl)silane)

(19b): ¹H NMR (500 MHz, CDCl₃) δ 0.27 (s, 6H), 0.32 (s, 6H), 1.08 (t, *J* = 7.0 Hz, 6H), 1.19 (m, 2H), 1.40 (m, 4H), 1.49 (s, 6H), 1.69 (m, 2H), 1.83 (m, 2H), 1.91 (dd, *J* = 11.0, 8.0 Hz, 2H), 2.34 (q, *J* = 11.5 Hz, 2H), 3.24 (m, 4H), 3.32 (m, 4H), 3.52 (m, 2H), 4.01 (t, *J* = 8.0 Hz, 2H), 4.32 (m, 2H), 5.02 (d, *J* = 9.5 Hz, 2H), 7.30 (m, 6H), 7.47 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ -2.8, -2.1, 15.1, 21.8, 24.7, 28.5, 30.3, 31.3, 44.4, 66.3, 72.4, 78.3, 80.3, 127.7, 128.9, 130.2, 133.7, 134.4, 138.8 ppm; IR (neat) ν_{max}: 1113, 1247, 1384, 2920 cm⁻¹; [α]_D²³ = -5.7 (c = 0.40, CH₂Cl₂); HRMS(CI/NH₃) *m/z* calcd for C₄₂H₆₄O₄Si₂Na [M + Na]⁺ 711.4241, found 711.4242.

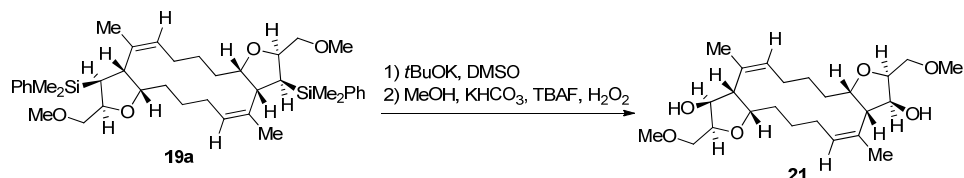
ix. Tamao Oxidation and Protodesilylation



(2*S*,3*S*,3*aS*,7*aR*)-2-((*S*)-1-Hydroxy-2-methoxyethyl)-3*a*-methyloctahydrobenzofuran-3-ol (16): To a solution of dimethylphenylsilyl-substituted tetrahydrofuran **9a** (35 mg, 0.1 mmol, 1 equiv) in DMSO (2 mL) was added potassium *t*-butoxide (25 mg, 0.22 mmol, 2.2 equiv). The mixture was stirred for 7 hours at room temperature, and then diluted with diethyl ether (10 mL) and phosphate buffer solution (pH 7, 10 mL). After the aqueous layer was extracted with diethyl ether (2 x 10 mL), the combined organic layer was evaporated. MeOH (2 mL), KHCO₃ (30 mg, 0.3 mmol, 3 equiv), TBAF (1.0 M in THF, 450 μ L, 0.45 mmol, 4.5 equiv) and H₂O₂ (30% in water, 170 μ L, 1.5 mmol, 15 equiv) were added to the residue. The mixture was stirred for 24 hours at 40 °C, then poured into saturated Na₂S₂O₃ solution and extracted with diethyl ether. The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 70% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the oxidation product **16** (14 mg, 60%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 0.94 (s, 3H), 1.14 (m, 2H), 1.46 (m, 2H), 1.55 (m, 2H), 1.77 (m, 2H), 2.52 (br, 1H), 2.57 (br, 1H), 3.33 (m, 1H), 3.40 (s, 3H), 3.49 (m, 1H), 3.59 (m, 2H), 3.81 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 10.9, 20.4, 24.1, 25.1, 34.0, 43.9, 59.4, 71.1, 74.2, 80.7, 83.1, 83.4 ppm; IR (neat) ν_{max} : 1046, 1456, 1559, 1653, 2926, 3407 cm⁻¹; [α]_D²³ = +8.4 (c = 0.40, CH₂Cl₂); HRMS(CI/NH₃) *m/z* calcd for C₁₂H₂₂O₄Na [M + Na]⁺ 253.1416, found 253.1421.

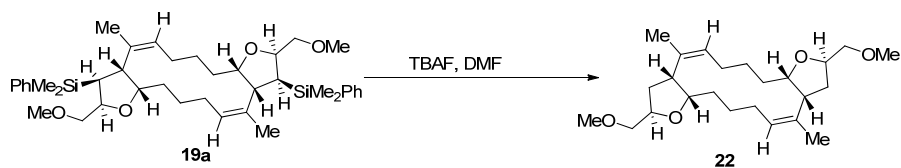


(*S*)-2-Methoxy-1-((2*R*,3*aR*,7*aS*)-3*a*-methyloctahydrobenzofuran-2-yl)ethanol (17): To a solution of dimethylphenylsilyl-substituted tetrahydrofuran **9b** (35 mg, 0.1 mmol, 1 equiv) in DMF (2 mL) was added TBAF as a 1.0 M solution in THF (0.5 mL, 0.5 mmol, 5 equiv). The resulting dark brown solution was stirred at 80 °C for 12 hours, cooled to room temperature, diluted with EtOAc, and washed successively with saturated NH₄Cl solution, saturated NaHCO₃ solution. The resulting organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 40% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the protidesilylation product **17** (15 mg, 71%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 0.88 (s, 3H), 1.23 (m, 2H), 1.43 (m, 3H), 1.60 (m, 1H), 1.76 (m, 3H), 2.33 (br, 1H), 3.19 (dd, *J* = 12.0, 3.5 Hz, 1H), 3.37 (s, 3H), 3.37 (m, 1H), 3.52 (dd, *J* = 9.5, 3.0 Hz, 1H), 3.82 (m, 1H), 4.00 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 17.1, 20.8, 24.4, 25.3, 35.6, 41.3, 42.4, 59.1, 72.8, 74.1, 76.7, 84.7 ppm; IR (neat) ν_{max} : 1066, 1124, 1457, 2929, 3430 cm⁻¹; [α]_D²³ = -9.5 (c = 0.30, CH₂Cl₂); HRMS(CI/NH₃) *m/z* calcd for C₁₂H₂₂O₃Na [M + Na]⁺ 237.1467, found 237.1475.



(2*S*,3*S*,3*aS*,4*Z*,8*aS*,10*S*,11*S*,11*aS*,12*Z*,16*aS*)-2,10-Bis(methoxymethyl)-4,12-dimethyl-2,3,3*a*,6,7,8*a*,10,11,11*a*,14,15,16,16*a*-tetradecahydrocycloclotetradeca[1,2-*b*:8,9-*b'*]difuran-3,11-diol (21**):**

To a solution of dimethylphenylsilyl-substituted dimer **19a** (33 mg, 0.05 mmol, 1 equiv) in DMSO (2 mL) was added potassium *t*-butoxide (25 mg, 0.22 mmol, 4.4 equiv). The mixture was stirred for 7 hours at room temperature, and then diluted with diethyl ether (10 mL) and phosphate buffer solution (pH 7, 10 mL). After the aqueous layer was extracted with diethyl ether (2 x 10 mL), the combined organic layer was evaporated. MeOH (2 mL), KHCO₃ (30 mg, 0.3 mmol, 6 equiv), TBAF (1.0 M in THF, 450 μ L, 0.45 mmol, 9 equiv) and H₂O₂ (30% in water, 170 μ L, 1.5 mmol, 30 equiv) were added to the residue. The mixture was stirred for 24 hours at 40 °C, then poured into a saturated solution of Na₂S₂O₃ and extracted with diethyl ether. The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 80% EtOAc/hexane as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the oxidation product **21** (10 mg, 48%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.32 (m, 4H), 1.42 (m, 2H), 1.62 (m, 2H), 1.73 (s, 6H), 1.93 (m, 2H), 2.25 (q, *J* = 12.0 Hz, 2H), 2.91 (d, *J* = 6.0 Hz, 2H), 3.17 (t, *J* = 7.0 Hz, 2H), 3.40 (s, 6H), 3.65 (m, 4H), 4.16 (m, 4H), 4.55 (m, 2H), 5.17 (d, *J* = 10.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 22.7, 24.5, 25.0, 27.5, 52.2, 59.5, 72.7, 76.0, 77.6, 77.8, 130.5, 131.5 ppm; IR (neat) ν_{max} : 1095, 1384, 2921, 3412 cm⁻¹; [α]_D²³ = -18 (*c* = 0.30, CH₂Cl₂); HRMS(CI/NH₃) *m/z* calcd for C₂₄H₄₀O₆Na [M + Na]⁺ 447.2723, found 447.2739.

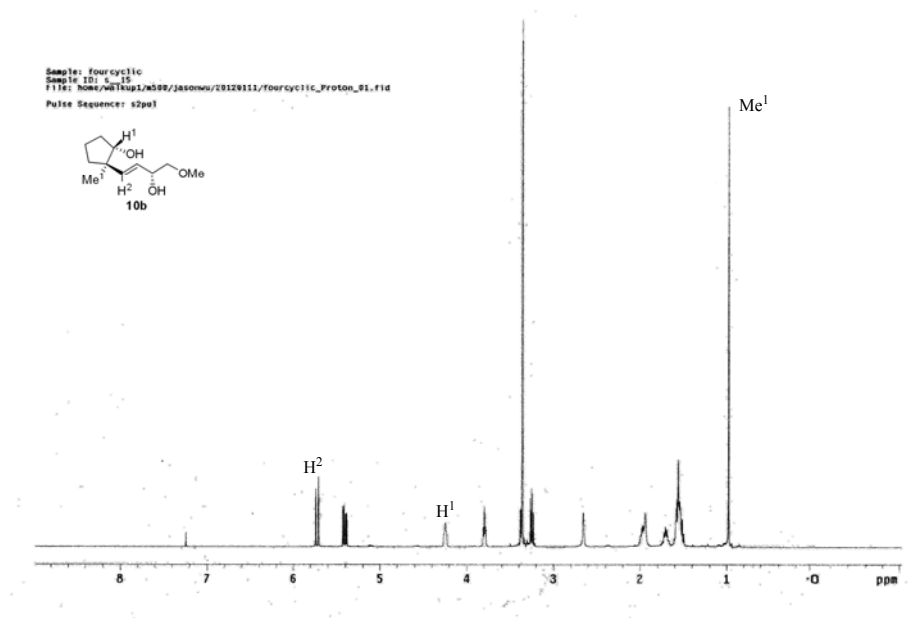


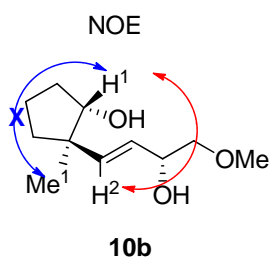
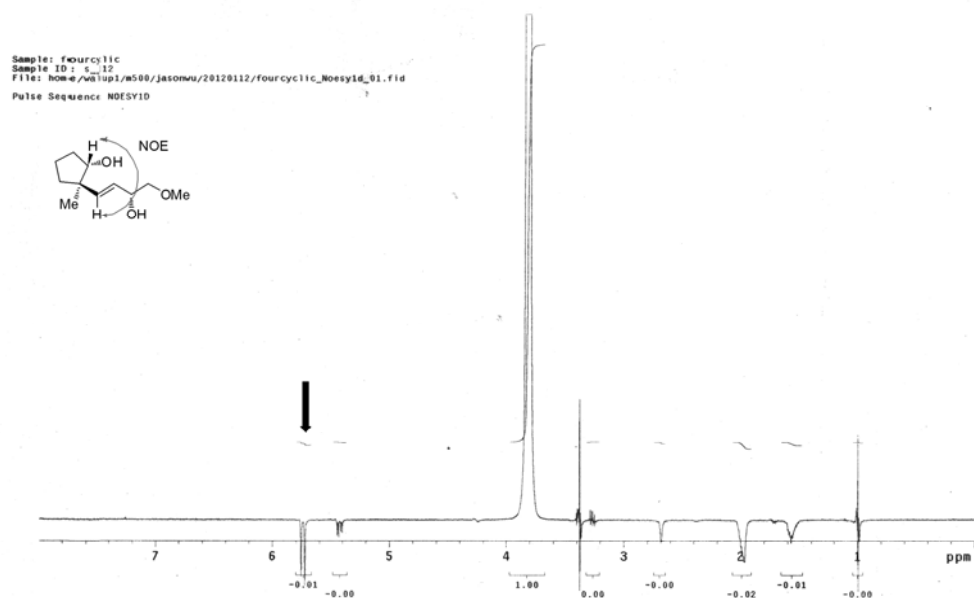
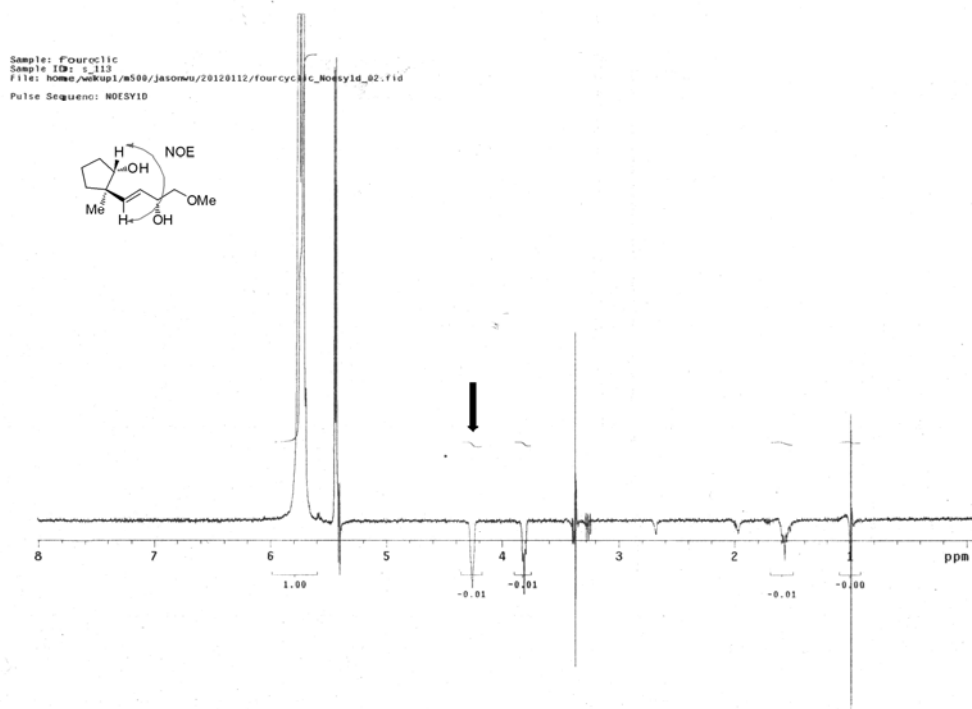
(2*R*,3*aR*,4*Z*,8*aS*,10*R*,11*aR*,12*Z*,16*aS*)-2,10-Bis(methoxymethyl)-4,12-dimethyl-2,3,3*a*,6,7,8*a*,10,11,11*a*,14,15,16,16*a*-tetradecahydrocycloclotetradeca[1,2-*b*:8,9-*b'*]difuran (22**):**

To a solution of dimethylphenylsilyl-substituted tetrahydrofuran **19a** (33 mg, 0.05 mmol, 1 equiv) in DMF (2 mL) was added TBAF as a 1.0 M solution in THF (0.5 mL, 0.5 mmol, 10 equiv). The resulting dark brown solution was stirred at 80 °C for 12 hours, cooled to room temperature, diluted with EtOAc, and washed successively with saturated NH₄Cl, saturated NaHCO₃ solution. The resulting organic layer was dried over MgSO₄, filtered and concentrated under reduced pressure. The residue was purified by preparative thin layer chromatography in the dark, using 40% EtOAc/hexanes as the developing solvent system. The product band was eluted with EtOAc (5 x 2 mL), and the EtOAc was evaporated to obtain the protidesilylation product **22** (13 mg, 68%) as a colorless oil. ¹H NMR (500 MHz, CDCl₃) δ 1.23 (m, 2H), 1.41 (m, 4H), 1.63 (m, 2H), 1.67 (s, 6H), 1.73 (m, 2H), 1.86 (m, 2H), 2.07 (m, 2H), 2.26 (m, 2H), 3.24 (q, *J* = 7.5 Hz, 2H), 3.31 (m, 2H), 3.37 (m, 2H), 3.38 (s, 6H), 4.05 (m, 2H), 4.26 (m, 2H), 5.10 (d, *J* = 9.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 22.8, 24.9, 25.2, 27.3, 31.1, 41.9, 59.3, 76.0, 76.1, 80.1, 129.0, 134.3 ppm; IR (neat) ν_{max} : 1093,

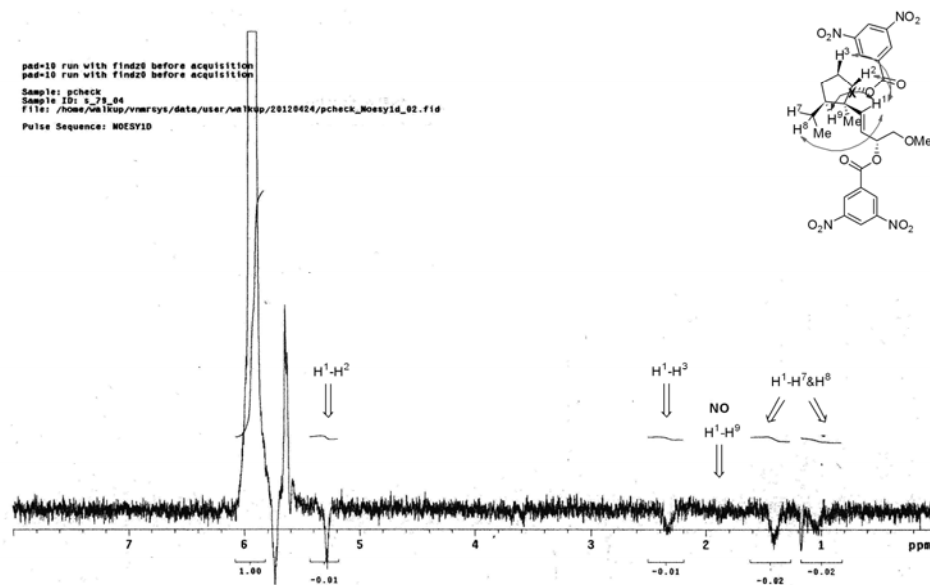
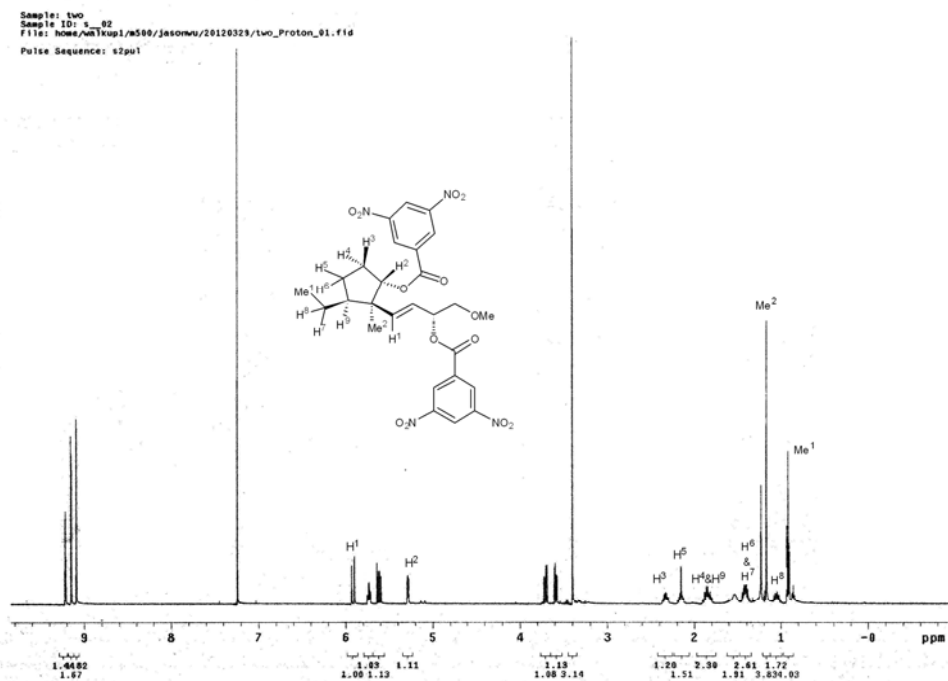
1456, 1734, 2923 cm^{-1} ; $[\alpha]_{\text{D}}^{23} = -16$ ($c = 0.20$, CH_2Cl_2); HRMS(CI/ NH_3) m/z calcd for $\text{C}_{24}\text{H}_{41}\text{O}_4$ $[\text{M} + \text{H}]^+$ 393.3005, found 393.3020.

Part VI: 1D and 2D NMR Spectroscopic Analysis; Assignment of Stereochemistry

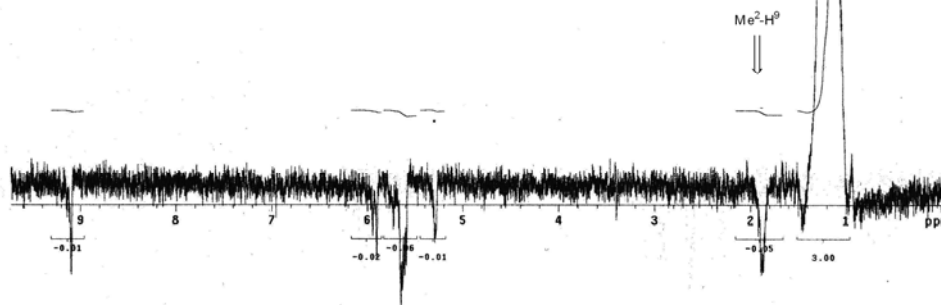
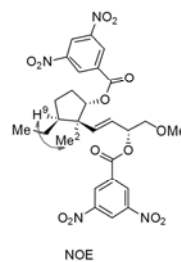




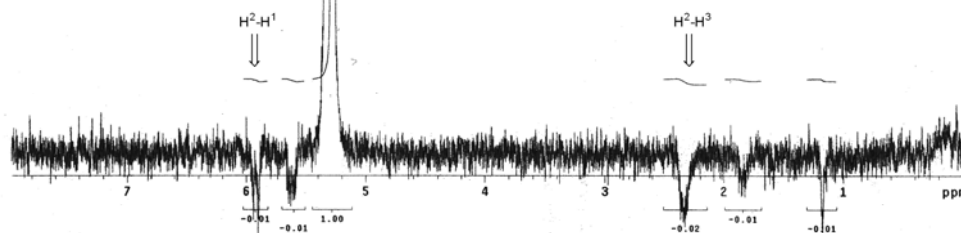
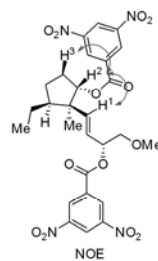
The proton assignment on ¹H NMR of **10b** was confirmed by GCOSY NMR analysis. As shown above, the NOE measurement indicated that H¹ and H² has NOE with each other, but no NOE was observed between H¹ and Me¹ group, thus indicated the *cis* configuration of Me¹ and OH groups on cyclopentane **10b**.

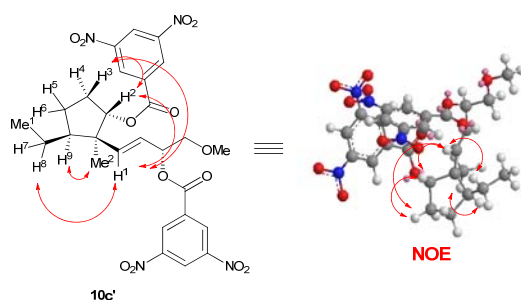


pad-10 run with find20 before acquisition
 pad-10 run with find20 before acquisition
 Sample: pcheck
 Sample ID: s_78_66
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 Pulse Sequence: NOESY1D

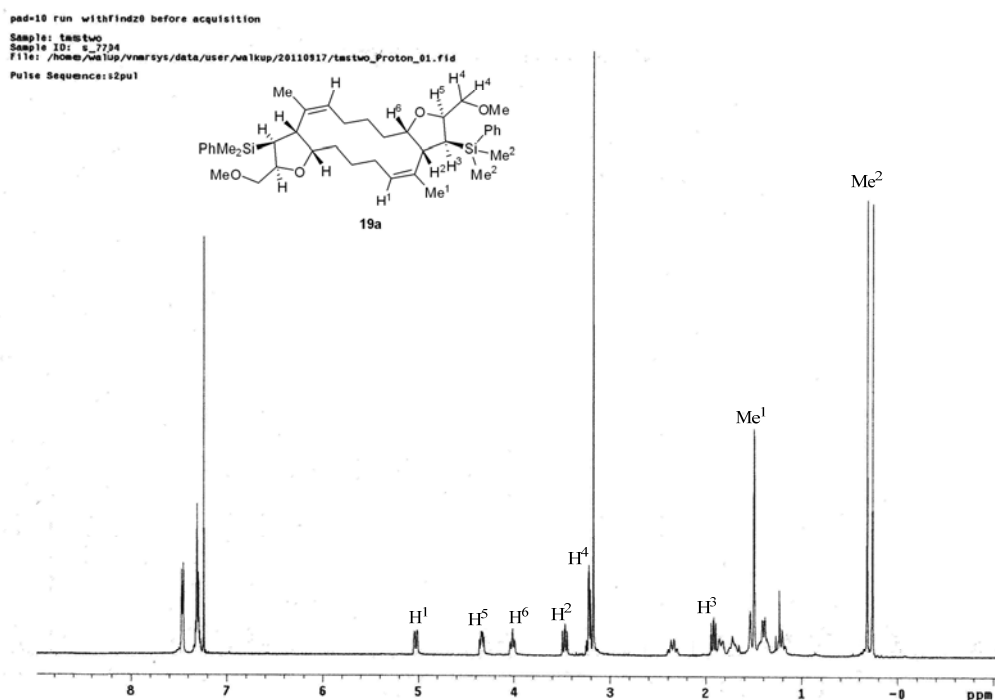


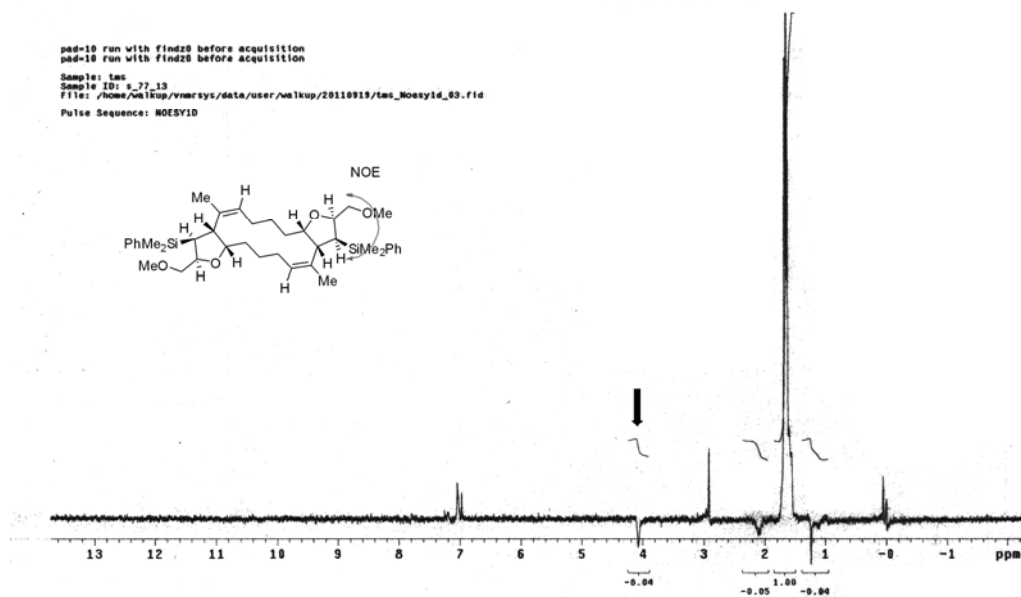
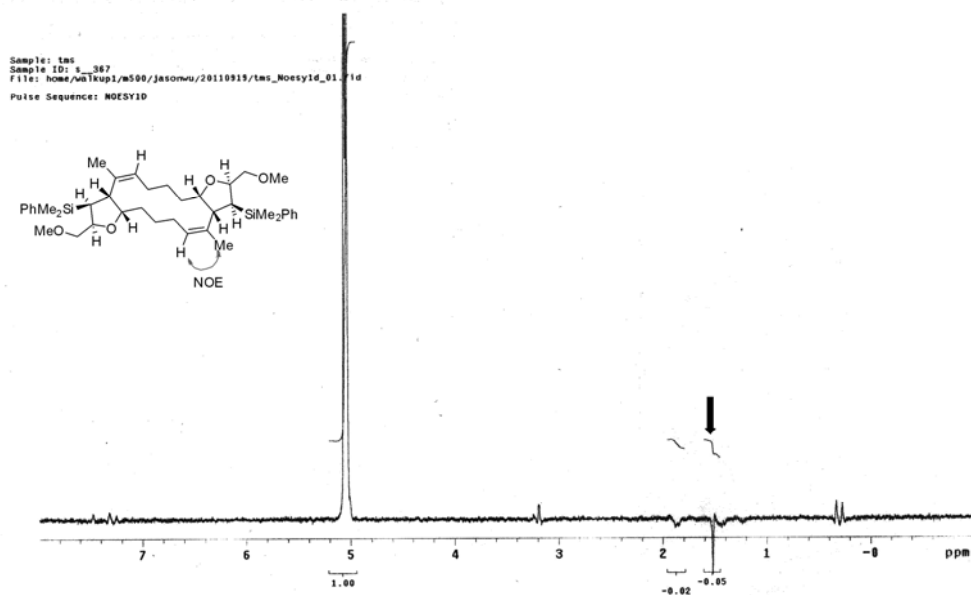
pad-10 run with find20 before acquisition
 pad-10 run with find20 before acquisition
 Sample: pcheck
 Sample ID: s_78_63
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 Pulse Sequence: NOESY1D

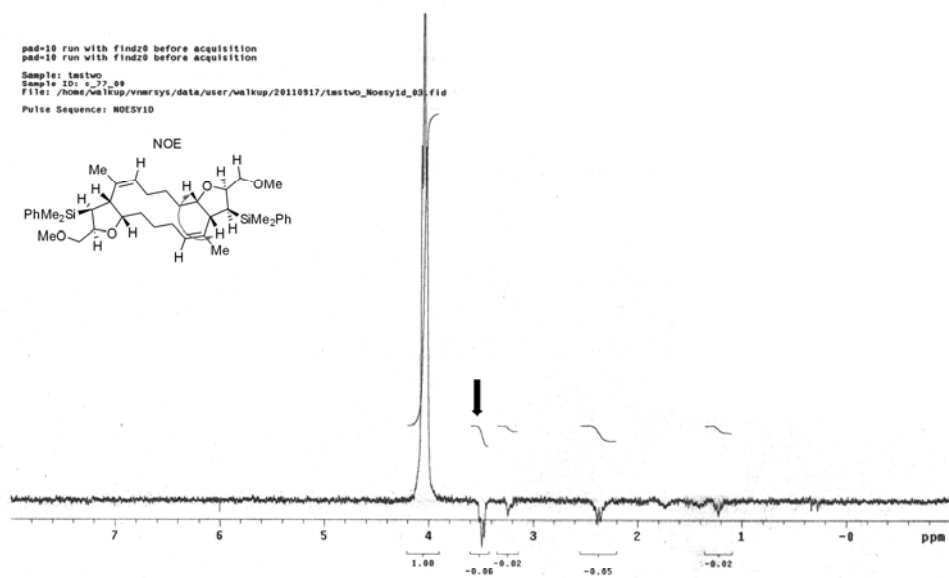
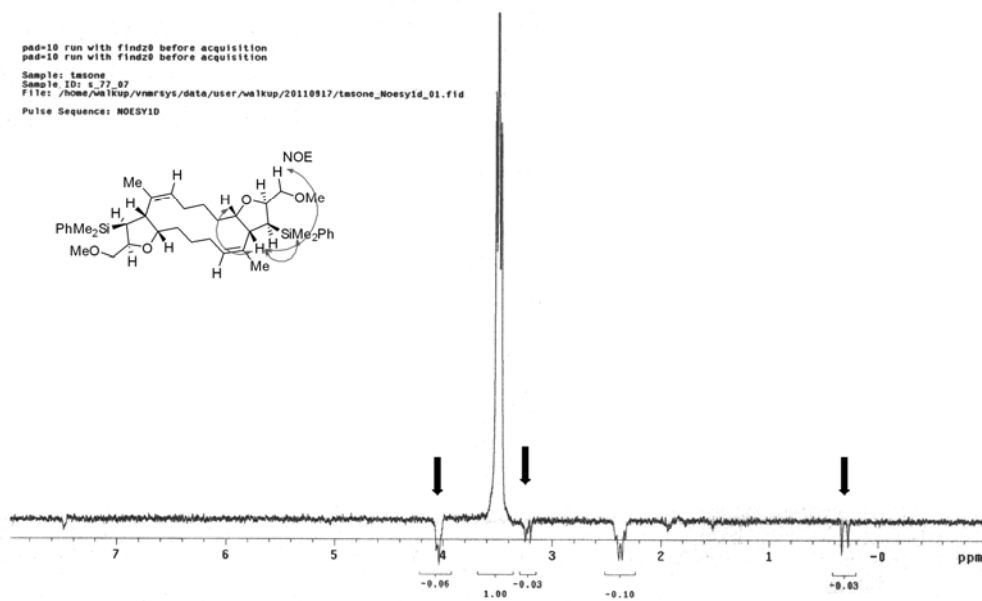


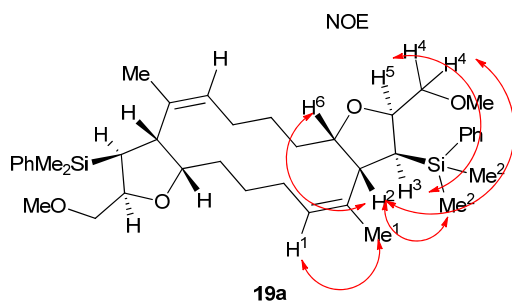


The proton assignment on ¹H NMR of **10c'** was confirmed by GCOSY NMR analysis. As shown above, the NOE measurement indicated that H¹-H², H¹-H³, H¹-H⁷ or H⁸, H²-H³, H⁹-Me² have NOE with each other, but no NOE was observed between H¹ and H⁹, thus indicated the relative *cis* stereochemistry of the ethyl and vinyl groups on **10c'**.





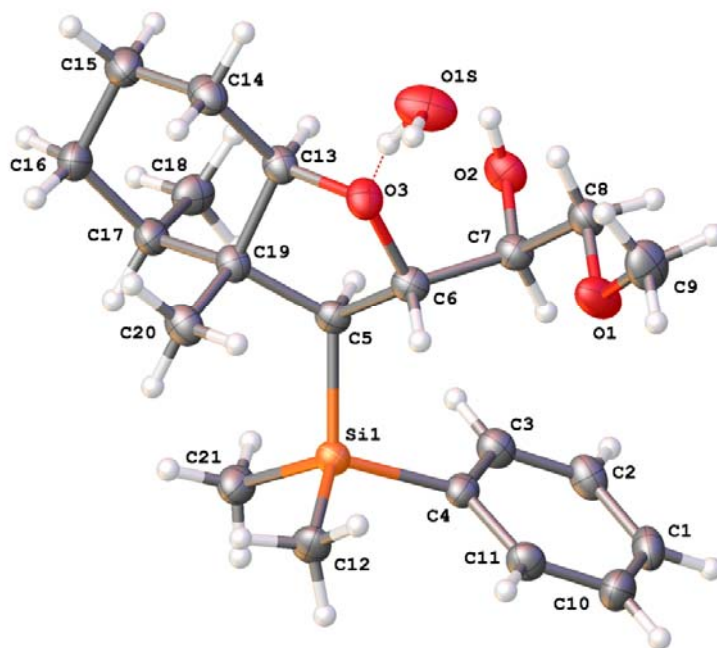




The proton assignment on ^1H NMR of **19a** was confirmed by GCOSY NMR analysis. As shown above, the NOE measurement indicated that H^1 -Me¹, H^2 -Me², H^2 -H⁴, H^2 -H⁶, and H^3 -H⁵ have NOE with each other, thus indicated the relative stereochemistry of **19a**.

Part V: X-ray Crystal Structure

X-ray crystal structure for **9f**



Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC 869781). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.) or via www.ccdc.cam.ac.uk/data_request/cif.

Crystal data for 9f

$C_{21}H_{34}O_3Si \cdot H_2O$	$V = 2146.84 (15) \text{ \AA}^3$
$M_r = 380.59$	$Z = 4$
Orthorhombic, $P2_12_12_1$	Cu $K\alpha$ radiation, $\lambda = 1.54184 \text{ \AA}$
$a = 7.2946 (3) \text{ \AA}$	$\mu = 1.14 \text{ mm}^{-1}$
$b = 13.3574 (5) \text{ \AA}$	$T = 100 \text{ K}$
$c = 22.0331 (9) \text{ \AA}$	$\times \times \text{ mm}$

Data collection

Bruker APEX-II CCD diffractometer	3286 reflections with $I > 2\sigma(I)$
17867 measured reflections	$R_{\text{int}} = 0.058$
3702 independent reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.100$	$\Delta\rho_{\text{max}} = 0.29 \text{ e \AA}^{-3}$
$S = 1.02$	$\Delta\rho_{\text{min}} = -0.19 \text{ e \AA}^{-3}$
3702 reflections	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
247 parameters	Flack parameter: 0.03 (3)
3 restraints	

Data reduction: *SAINT* v7.68A (Bruker, 2009); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.; software used to prepare material for publication: O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. J. Appl. Cryst. (2009). 42, 339-341.