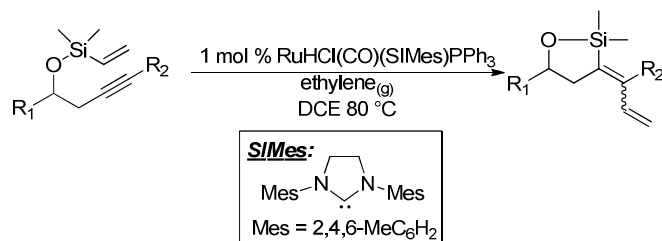# Ruthenium Hydride Catalyzed Silylvinylation of Internal Alkynes Using Ethylene as an Additive

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Abstract:

An efficient synthetic strategy for the regiospecific silylvinylation of internal alkynes is described. This transformation is catalyzed by RuHCl(CO)(SIMes)PPh$_3$ and provides a net 5-*exo-dig trans*-silylvinylation of internal alkynes. Ethylene was used to decrease reaction times and displayed altered selectivity at increased pressure. Furthermore, alkyl substituted alkynes were acceptable substrates at 80 psi of ethylene.

Introduction:

Alkenes are one of the most useful functional groups because they are incredibly versatile and known to undergo a variety of transformations.[1] Ethylene is the simplest alkene that is made in enormous quantities with nearly 150 million lbs produced daily.[2] It is an economical resource ideal for vinylation chemistry as only one hydrogen atom is lost during the process.[1] Ethylene has been utilized in numerous organic transformations including Mizoroki–Heck reactions,[3, 4] enyne metathesis[5] and hydrovinylation.[6-8] However, ethylene has not been thoroughly investigated for the silylvinylation of alkynes. A regio- and stereospecific silylvinylation of internal alkynes delivers a well-defined tetra-substituted olefin, a new vinyl group and vinylsilane of significantly increased complexity which functions as a useful

handle.[9] Vinyl silicon species are of particular interest due to their use in carbon-carbon bond forming reactions[10, 11] allowing for further elaboration.

Recently, we reported that ruthenium hydrides catalyze the silylvinylation of internal alkynes via intermolecular insertion of acrylates[12] and vinyl boronate esters.[13] These reactions both produce highly substituted dienes that possess unusual isomeric patterns formed through formal *trans-5-exo-dig* addition across the alkyne moiety. While screening catalysts for these transformations, we unearthed an intramolecular[14] vinylation of internal alkynes using RuHCl(CO)(SIMes)PPh$_3$ (complex **1),** which we refer to as "ethylene transposition". As observed previously, a formal *trans-5-exo-dig* cyclization occurred; however, the vinyl group (ethylene) was transferred across the alkyne instead of being released as in the intermolecular coupling (Figure 1). In addition, we observed cycloisomerization (isomer **B**) of the starting enyne as a minor byproduct of this process when aryl substituted alkynes were employed in these reactions.[15] Interestingly, when alkyl substituted alkynes were examined under analogous conditions, only cycloisomerization products **B** were obtained using this protocol. Mori and co-workers have observed similar reactivity of enynes in the presence of ruthenium hydrides.[16] An improved procedure for the formation of dienes **B** has recently been reported which relies on ruthenium complex Cp*RuCl(COD) and is compatible with both aryl- and alkyl-substituted alkynes.[15] Our main goal for this study was to improve the ethylene insertion process and to expand our repertoire of alkynes to include alkyl substituted substrates. Secondary goals included eradication of cycloisomerization byproducts **B**, reduction of catalyst loading and decreasing reaction times.
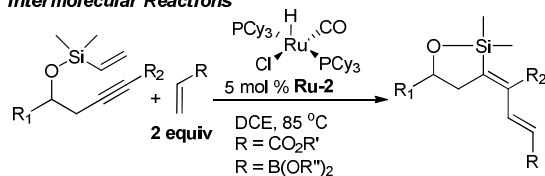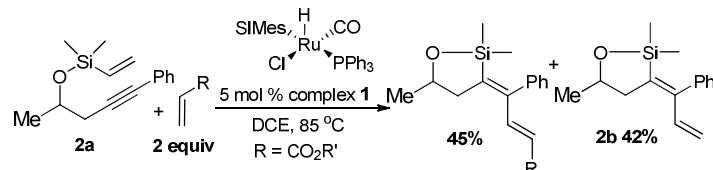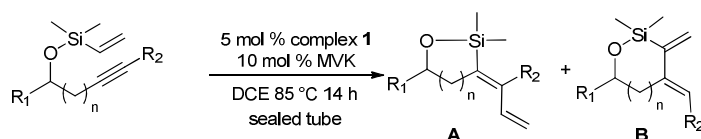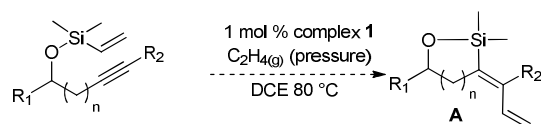
Figure 1. Silylvinylation of internal alkynes: discovery, previous work with methylvinylketone (MVK), and current work with ethylene.

Results and Discussion:

Based on the product formation observed previously, we suggest a mechanism which can illustrate the formation of diene **A** (Figure 2). Phosphine dissociation from complex **1** provides ruthenium complex **1a** which undergoes olefin insertion to provide alkyl-ruthenium **1b**. Silane **1b** extrudes ethylene and silicon is transferred to ruthenium to give silyl-ruthenium intermediate **1c**. Our mechanistic proposal suggests that *cis*-metallation (**1c** to **1d**) is followed by isomerization (**1d** to **1e**) and is supported by empirical data.[12, 14, 17] Although we do not favor a direct *trans*-addition across the alkyne pi-system, Trost,[18] Denmark,[19] and Chang[20] have observed anti-hydrosilylation products using various ruthenium catalysts. Direct *trans*-addition across alkynes has also been observed by Fu[21] and Mori[22] using rhodium, and Murakami[23] using gold. Subsequent insertion of ethylene into vinyl ruthenium **1e** and beta-hydride elimination of **1f** liberates the product and regenerates ruthenium hydride **1a** to complete the catalytic cycle. We anticipated that the addition of ethylene to the reaction would increase the production of diene **A** in preference to the undesired formation of diene **B**. Additionally, the use of

ethylene could provide some understanding of the mechanism of this reaction; our hypothesis being that increasing the amount of ethylene in the reaction would trap proposed "*cis*-siomer" **1d** prior to isomerization to "*trans*-isomer" **1e**; the stability of these proposed intermediates is currently not known. Using ethylene-d_4 we observed incorporation of exogenous ethylene into the product (Scheme 1). This outcome affirms that the ethylene being added to the system can be incorporated into the product. Another aspect of this study was to obtain silylvinylation of internal alkyl substituted alkynes. Previously, ethylene transposition of these alkynes provided solely cycloisomerization isomer **B** presumably through intermediates **1g** and **1h** (Figure 2).[14]
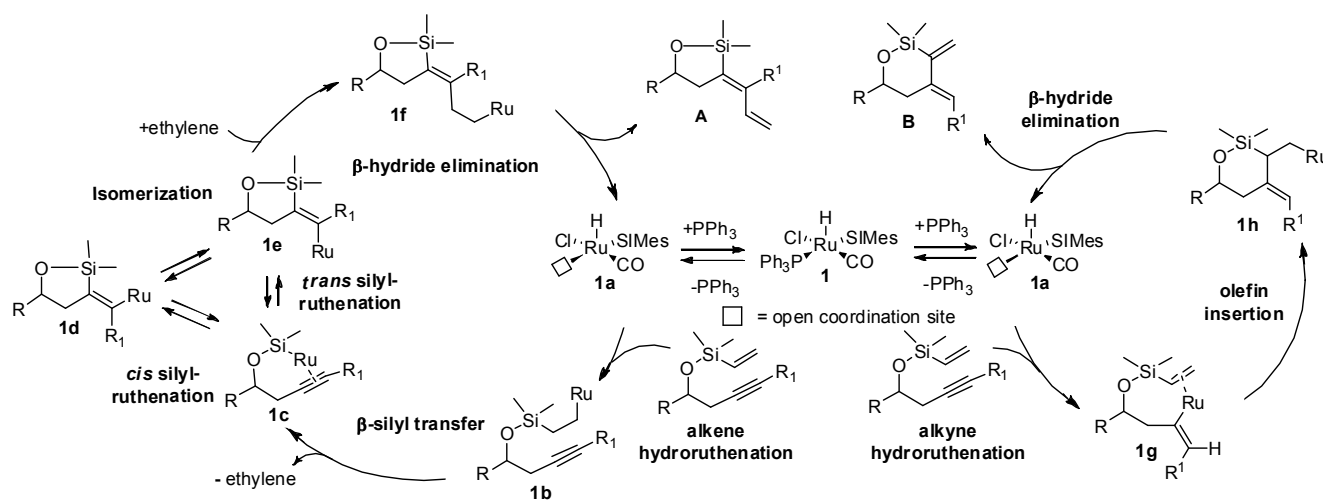

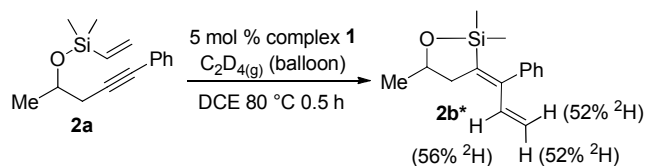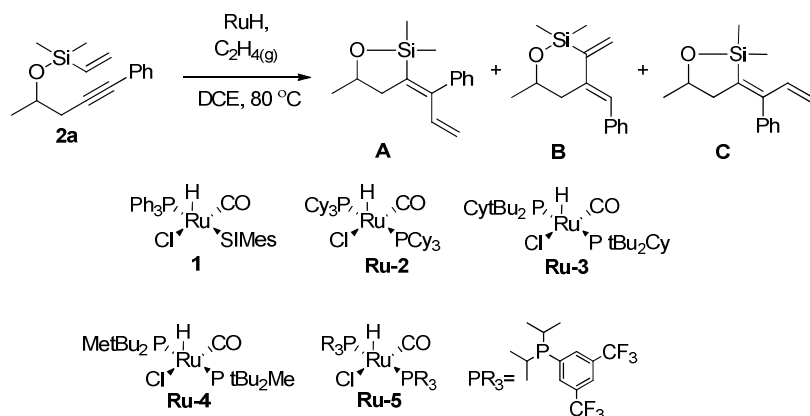**Figure 2.** Mechanistic hypothesis.

Scheme 1. Isotopic Labeling Experiment

Table 1. Catalyst Screen

RuH,
$C_2H_{4(g)}$

DCE, 80 °C

2a → A + B + C

Ph$_3$P, H, CO, Ru, Cl, SIMes — **1**

Cy$_3$P, H, CO, Ru, Cl, PCy$_3$ — **Ru-2**

CytBu$_2$ P, H, CO, Ru, Cl, P tBu$_2$Cy — **Ru-3**

MetBu$_2$ P, H, CO, Ru, Cl, P tBu$_2$Me — **Ru-4**

R$_3$P, H, CO, Ru, Cl, PR$_3$ — **Ru-5**

$PR_3 =$ (structure with CF$_3$ groups)

| entry	catalyst	time (h)	Conversion	A:B:C	yield A (%)[a]
1	**1**	1	100	18:1:2	91
2*	**Ru-2**	7	89	55:4:1	55
3*	**Ru-3**	7	43	1:0:0	23
4*	**Ru-4**	7	33	6:1:0	18
5*	**Ru-5**	7	29	1:0:0	11

[a]Yield determined by ^{1}H NMR vs mesitylene internal standard. *5 mol % catalyst was used.

Based on our previous observations, we began our investigation with alkyne **2a** using ruthenium hydride **1** (1 mol %) under an atmosphere (balloon) of ethylene in 1,2-dichloroethane (DCE) at 80 °C.[14] We observed a rapid (1 h) reaction that produced silylvinylation product **2b** as a 9:1 mixture of E and Z isomers. This corroborates our assertion that syn-metallation (*i.e.* formation of **1d**) followed by isomerization occurs to give **1e** which proceeds to the silylvinylation products observed. Further examination of catalysts revealed that complex **1** was the optimum ruthenium hydride catalyst and in many cases 1 mol % was sufficient to provide the desired products (Table 1). However, the use of ruthenium complexes that bear two bulky phosphine moieties (**Ru-2** through **Ru-5**) do give some of the desired product. It was observed that the more electron rich complexes afforded higher conversion and larger quantities of **A-C** (Table 1). Presumably complex **1** is superior due to the greater donating ability of the NHC[24] and the enhanced lability of the less basic PPh$_3$ ligand.[25] Other solvents such as toluene and 1,4-dioxane were also found to be suitable for this reaction at 80 °C.

We examined the substrate scope using this protocol (Scheme 2) by keeping the aryl group constant and altering groups at the homo-propargyl and propargyl positions. The reaction tolerated methyl and cyclohexyl groups at the homo-propargyl position and gave **2b** and **3b** in 80% and 70% yield, respectively. Aryl groups were also well tolerated and **4b** was formed in 65% yield. Multiple

substitutions at the homopropargyl position afforded **5b** in 69% and **6b** in 76% yield. Previously only

partial conversion to diene **7b** was observed;[14] here **7b** was rapidly produced in 67% yield. Products **8b**

(78%) and **9b** (70%) demonstrate that the reaction works well with substitution in the *syn* or *anti*

relationship at the propargyl and homopropargyl locants. Next, variation of the aryl moiety at the alkyne

terminus was examined. As anticipated, *para*-substitution was well tolerated with the 4-fluorophenyl

providing **10b** in 69% yield as essentially a single isomer. Chlorines were also amenable to these

reaction conditions giving **11b** in 70% yield.

Scheme 2. Substrate Scope
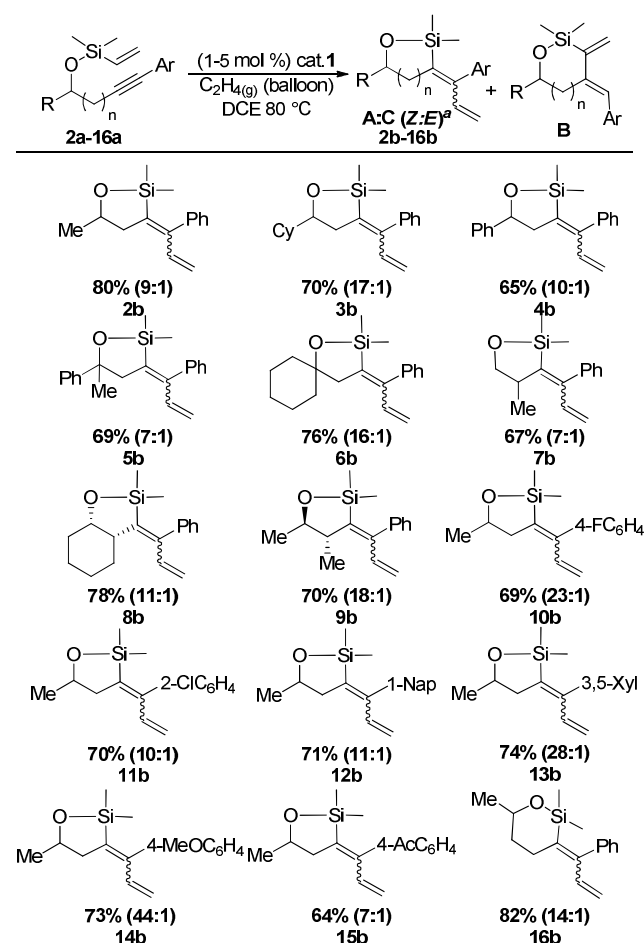
[a]Ratios determined by ^{1}H NMR using mesitylene as an internal standard. Products were isolated as a

mixture of *Z/E* isomers (A:C).

The bulk of the chlorine did not hamper the efficiency of the reaction, nor did other *ortho*-substituted

groups like 1-naphthyl which gave **12b** in 71% yield. The 3,5-xylyl moiety afforded **13b** in 74% yield

without difficulty. Electronics of the aryl group was also examined using 4-anisole and 4-acetophenone derivatives which provided **14b** in 73% yield and **15b** in 64% yield. Interestingly, although the yields are comparable, the ratio of isomers was substantially different in these cases. We posit that the electron donating methoxy-group in **14b** helps stabilize charge build-up in the isomerization pathway. Conversely, the electron withdrawing acetyl functionality destabilizes charge build-up in the same step. It has been reported previously that such isomerization events can occur through either zwitterionic or carbene type intermediates.[26] Finally, six membered oxasilacycle **16b** was formed in 82% yield under these conditions.

The aryl substrates provided excellent selectivity for silylvinylation versus cycloisomerization ($\geq$20:1) compared to previous results (5-8:1).[14] With these results we envisioned that higher concentration of ethylene (increased pressure) would further reduce or eliminate isomer **B**. Using alkyne **2a** the amount of ethylene was systematically increased by 20 psi; we observed increased amounts of isomer **C** as a function of pressure. Additionally, no undesired cycloisomerization product was observed over the pressure range studied (Table 2). To ascertain whether the pressure or concentration was influencing the outcome, a control experiment with increased argon pressure was conducted. At 80 psi of argon the reaction was retarded and approximately 23% conversion with only 11% of isomer **A** was observed by ^{1}H NMR. This supports the hypothesis that increased ethylene concentration increases the amount of syn-silylvinylation product. To the best of our knowledge increased ethylene pressure has not been shown to overcome inherent selectivity of a substrate for stereocontrol.

**Table 2. Sequential Increase of Ethylene Pressure**[a]
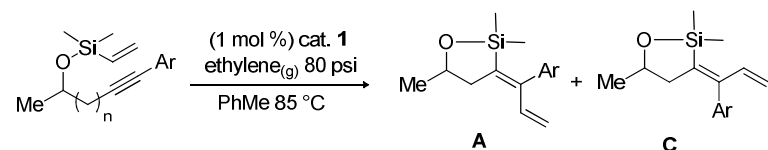
entry	pressure	ratio (A:C)[b]
1	balloon	9:1
2	20 psi	6:1

3	40 psi	2.5:1
4	60 psi	1:1.4
5	80 psi	1:1.7
6	80 psi (Ar$_{(g)}$)	1:0^c

^{a}Reactions were pressurized at room temperature prior to heating. ^{b}Determined by ^{1}H NMR. ^{c}23% conversion and 11% **A** observed.

The silylvinylation pressure study also unearthed an interesting electronic effect. The *E:Z* ratio of silylvinylation products was influenced by the electronics of the alkyne (Table 3). Alkynes substituted with electronically neutral and weakly withdrawing groups gave ~1:2 ratio of **A:C** (entry 1 and 2 respectively). Electron rich alkynes (entry 3) provide isomer **A** as the major product, while electron deficient alkynes provide major isomer **C** (entry 4). Increasing the ring size from five to six surprisingly yielded a 25:1 ratio of **A:C** (entry 5). These preliminary results warrant further examination i.e. higher pressures and increased reaction times, to determine the intrinsic electronic preference.

Table 3. Electronic Differentiation of Alkyne Terminus at 80 psi Ethylene
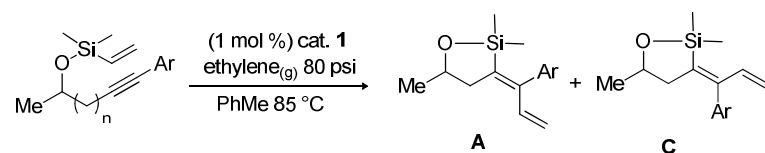
entry	substrate	time (h)	conv. (%)	ratio (A:C)	yield%^{a}
1	Ar = Ph	4	100	1:1.7	(99)
2	Ar = 4-F	4	100	1:1.3	85
3	Ar=4-OMe	6	100	3:1	91
4	Ar = 4-Ac	24	100	1:7	86
5	Ar = Ph, n= 2	24	100	25:1	72

^{a}Yield in parenthesis determined by ^{1}H NMR with mesitylene as an internal standard.

We continued by examining substrates that had previously formed isomer **B** preferentially (*i.e.* alkyl-substituted alkynes) or were aberrant at lower ethylene pressure.[14] To our delight, excellent results were obtained when alkyl-substituted alkynes were employed in this reaction (Figure 3). Methyl

substituted dienes **17b** and **18b** were formed in 84% yield, both favoring isomer **C** as the major product. Increasing the alkyl chain by one carbon to ethyl gave **19b** in 79% yield; adding three carbons gave *n*-butyl **20b** in 69% yield, and further extension to *n*-hexyl provided **21b** in 83% yield. In the later three cases, isomer **A** was the predominant product formed. Given the similar steric environment presented by these alkyl groups, we suggest that the observed product ratios are due to the subtle electronic changes in these substrates. We assume that the increased concentration of ethylene prevents unwanted hydroruthenation of the alkyne and thus inhibits the formation of isomer **B**.
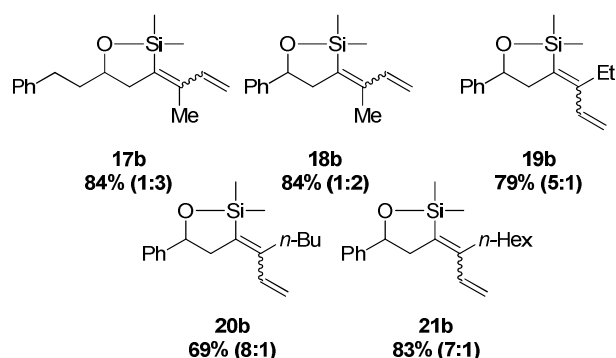

Figure 3. Reactions of internal alkyl alkynes at 80 psi. Ratio in parenthesis is isomers **A** to **C** determined by ^{1}H NMR and confirmed by nOe or NOESY experiments.

The synthetic utility of these systems was also explored. Fleming–Tamao oxidation[27, 28] under neutral conditions provided no oxidation products and slow decomposition of diene **4b** was observed. Utilizing basic conditions (Scheme 3, eq. 1) afforded α,β-epoxy ketone **22** in 70% yield. It was presumed that the excess basic peroxide facilitates a Michael-addition into the newly formed α,β-unsaturated ketone (i.e. **23**). To avoid this undesired Michael addition acidic conditions were used. These conditions utilized propionic anhydride and enone **23** was obtained in 85% isolated yield as a single isomer (eq. 2). These complementary methods provided access to β′-hydroxy-ketones in good yield. It was discovered that Heck product **24** was formed while attempting to utilize the silicon moiety of diene **4b** as a coupling partner in Hiyama–Denmark[29] chemistry. Using [(C$_3$H$_5$)PdCl]$_2$, CuI, KF·2H$_2$O, and 4-iodotoluene in DMF at room temperature gave Heck product **24** in low yield. After some experimentation the reaction of diene **4b** with Pd(OAc)$_2$, K$_2$CO$_3$, and 4-iodotoluene in DMF at 80 °C afforded **24** in 64% yield (eq.

3). We are currently exploring conditions that will selectively couple the silicon to directly access all carbon tetrasubstituted olefins. Additionally, Tamao oxidation was particularly useful with compound **17b** which was successfully converted into enone **25** (eq. 4). Apparently, introducing a mixture of isomers into the reaction was irrelevant as compound **25** was isolated in 73% yield as a single double bond isomer.

Scheme 3. Synthetic Elaboration of Dienes
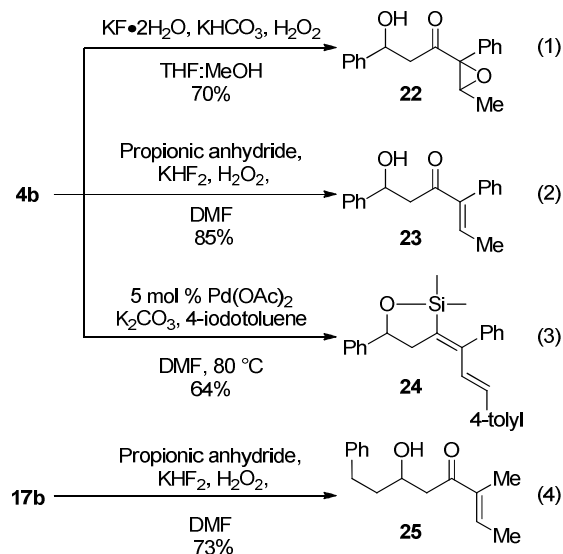
Conclusion:

In summary, we report that the use of ethylene gas can be successfully utilized in the ruthenium hydride catalyzed silylvinylation of internal alkynes. It was demonstrated that this protocol was useful for the synthesis of highly substituted conjugated dienes. When the reaction was conducted at increased pressure of ethylene (80 psi) competing cycloisomerization of the starting enyne was not observed. Additionally, it was demonstrated that alkyl substituted alkynes produced silylvinylation products in excellent yield. The resulting dienes were elaborated to epoxy-ketones and enones using complementary oxidation conditions. Finally, a regio- and stereoselective Heck coupling was reported which further enhances the scope of this chemistry beyond simple vinyl moieties. Future efforts in manipulating these dienes for complex molecule synthesis will be reported in due course.

Experimental Section:

General Procedures: Unless otherwise indicated, all reactions were conducted in oven (140 °C) or flame-dried glassware using distilled and degassed solvents under a positive pressure of dry argon with standard Schlenk techniques. All air-sensitive reagents were stored in a glovebox containing dry argon gas. Dry tetrahydrofuran (THF), toluene, acetonitrile (CH_3CN), and methylene chloride (DCM) were obtained by passing commercially available pre-dried, oxygen-free formulations through two activated alumina columns. Stainless steel syringes or cannulae that had been oven-dried (140 °C) and cooled under an argon atmosphere or in a desiccator were used to transfer air- and moisture-sensitive liquids. Yields refer to chromatographically and spectroscopically (^{1}H NMR) homogeneous materials, unless otherwise stated. Reactions were monitored by thin-layer chromatography (TLC) carried out on precoated glass plates of silica gel (0.25 mm) using the indicated solvent system. Visualization was accomplished with ultraviolet light (254 nm) or by treatment with one of the following solutions and carefully heating with a hot-air gun (450 °C): 10% phosphomolybdic acid in ethanol, 1% potassium permanganate/7% potassium carbonate/0.5% sodium hydroxide aqueous solution, or anisaldehyde in ethanol with 10% sulfuric acid. Flash column chromatography was performed using silica gel (40−63 μm). All workup and purification procedures were carried out with reagent grade solvents in air. Reagents were purchased and used without further purification, unless otherwise stated.

Silicon-Tethered Alkynes: Alkynes **2a, 3a, 4a, 5a, 6a, 8a, 10a, 11a, 14a, 16a, 17a** were prepared following the literature protocol.[12] Alkynes **9a, 12a, 13a, 15a, 18a** were prepared following the literature protocol.[14] Dienes **2b-6b** and **8b-16b** were previously prepared as the *Z* isomer by our group.[14] Ruthenium Hydride **Ru-3** was prepared according to literature procedure.[13]

Dimethyl((2-methyl-4-phenylbut-3-yn-1-yl)oxy)(vinyl)silane (7a): To a flame dried 50 mL round bottom flask with a magnetic stir bar was added alcohol **S5**[30] (1.08 g, 6.75 mmol), DCM (20 mL), DMAP (165 mg, 1.35 mmol) and imidazole (919 mg, 13.5 mmol). Vinyldimethylchlorosilane was added dropwise (1.39 mL, 10.13 mmol) to the resulting solution and the reaction stirred at RT for 2 h. The reaction mixture was poured into sat. $NH_4Cl_{(aq.)}$ (30 mL), extracted with DCM (2 x 20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo* to give a yellow residue. The yellow residue was

purified via flash column chromatography (1% diethyl ether/hexanes) to yield **7a** as a clear oil (1.37 g, 84%). R_f = 0.72 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.40-7.38 (m, 2H), 7.28-7.25 (m, 3H), 6.15 (dd, J = 20.0, 15.0 Hz, 1H), 6.03 (dd, J = 14.8, 4.0 Hz, 1H), 5.81 (dd, J =20.0, 4.2 Hz, 1H), 3.76 (dd, J = 9.8, 6.0 Hz, 1H), 3.53 (dd, J = 9.8, 7.6 Hz, 1H), 2.81 (sext., J = 6.8 Hz, 1H), 1.25 (d, J = 6.8 Hz, 3H), 0.22 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 137.4, 133.5, 131.7, 128.3, 127.7, 123.8, 92.1, 81.6, 67.1, 29.7, 17.5, -1.9; **IR** (film): v = 3053, 2967, 2909, 1596, 1490, 1253, 1086, 837 cm^{-1}; **Anal. calcd**. for C$_{15}$H$_{20}$OSi: C 73.71, H 8.25; found: C 73.83, H 8.19

Dimethyl((1-phenylhex-3-yn-1-yl)oxy)(vinyl)silane (19a): To a flame dried 250 mL 3-neck round bottom flask equipped with a pressure equalizing addition funnel, large magnetic stir bar and freshly prepared propargyl magnesium bromide (0.63M in Et$_2$O, 145 mmol) at -40 °C was added benzaldehyde (9.9 mL, 97 mmol) dropwise. The reaction stirred at RT for 4 h, then poured into 1M HCl (200 mL). The layers were separated and the organics were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a yellow oil (13.7 g). To a flame dried 500 mL round bottom flask with magnetic stir bar was added the resulting crude alcohol (13.7 g, 94 mmol), DCM (235 mL) and PPTS (2.36 g, 9.39 mmol). The yellow solution was cooled to 0 °C (ice/H$_2$O bath) and DHP (17.1 mL, 188 mmol) was added dropwise. The reaction mixture stirred at RT for 4 h and then was quenched by sat. NaHCO$_{3(aq)}$ (100 mL). The layers were separated and the organics were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a yellow oil (22.4 g). To a flame dried 500 mL 3-neck round bottom flask equipped with a pressure equalizing addition funnel and large magnetic stir bar was added the resulting crude alkyne (5.0 g, 21.7 mmol) and THF (130 mL). The yellow solution was cooled to -78 °C (dry ice/acetone bath) and *n*BuLi (10.4 mL, 2.5M, 26.0 mmol) was added dropwise. After stirring for 1 h, bromoethane (7.3 mL, 98 mmol) was added dropwise then the solution was warmed to RT and stirred overnight. The reaction mixture was quenched by the addition of sat. NH$_4$Cl$_{(aq)}$ (100 mL) at -78 °C (dry ice/acetone bath). The layers were separated and the aqueous was extracted with Et$_2$O (2 x 50 mL). The combined organics were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a orange oil (5.36 g). To an oven dried 100 mL round bottom flask with magnetic stir bar was added the resulting orange oil (5.36 g, 21

mmol), EtOH (50 mL) and PPTS (1.56 g, 6.2 mmol). The orange solution stirred at 50 $^\circ$C for 4 h, then was cooled to RT and concentrated *in vacuo*. The residue was dissolved in DCM and washed with brine (2 x 50 mL). The organics were dried over MgSO$_4$, filtered and concentrated *in vacuo* to give a brown oil. Purification via flash column chromatography (gradient elution with 5-10% EtOAc/hexanes) gave alcohol **S6** as a yellow oil (1.48 g, 41% over 3 steps). To an oven dried 100 mL round bottom flask with magnetic stir bar was added **S6** (1.48 g, 8.5 mmol), DCM (45 mL), imidazole (1.16 g, 17 mmol) and DMAP (208 mg, 1.7 mmol). The solution was cooled to 0 $^\circ$C (ice/H$_2$O bath) and vinyldimethylchlorosilane (1.8 mL, 12.7 mmol) was added dropwise. The resulting yellow suspension stirred at RT overnight. The reaction was quenched with sat. NH$_4$Cl$_{(aq)}$ (50 mL) and the organics were dried over Na$_2$SO$_4$, filtered and concentrated *in vacuo* to give a yellow residue. Purification via flash column chromatography (gradient elution with 1-3% diethyl ether/hexanes) gave alkyne **19a** as a pale yellow oil (1.39 g, 63%). **R$_f$** = 0.59 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.30 (m, 5H), 6.09 (dd, J = 20.0, 14.8 Hz, 1H), 5.97 (dd, J = 4.0, 14.8 Hz, 1H), 5.74 (dd, J = 4.0, 20.0 Hz, 1H), 4.78 (dd, J = 6.0, 7.6 Hz, 1H), 2.51 (m, 2H), 2.14 (qt, J = 10.0, 2.4 Hz, 2H), 1.09 (t, J = 7.6 Hz, 3H), 0.17 (s, 3H), 0.12 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 144.2, 137.9, 133.3, 128.2, 127.5, 126.2, 83.7, 76.8, 74.5, 31.2, 14.3, 12.7, -1.3, -1.4; **IR** (film): v = 3051, 2973, 2373, 1438, 1252, 1070 cm^{-1}; **Anal. calcd**. for C$_{16}$H$_{22}$OSi: C 74.36, H 8.58; found: C 74.31, H 8.58

Dimethyl((1-phenyloct-3-yn-1-yl)oxy)(vinyl)silane (20a): To a flame dried 250 mL 3-neck round bottom flask with a pressure equalizing addition funnel and magnetic stir bar was added 1-hexyne (4.1 g, 49.9 mmol) and THF (50 mL). The solution was cooled to -78 $^\circ$C (dry ice/acetone bath) and *n*BuLi (30 mL, 1.66M, 49.9 mmol) was added dropwise via addition funnel. After stirring at -78 $^\circ$C for 1 h, a solution of styrene oxide (5 g, 41.6 mmol) in HMPA (10.9 mL, 62.4 mmol) was added dropwise via addition funnel. After 10 min, the reaction mixture was allowed to warm to RT. The reaction was poured into 100 mL water and extracted with diethyl ether. The organic layer was washed with 1M HCl and brine, dried over MgSO$_4$, filtered and concentrated *in vacuo* to afford a yellow oil (1.57 g, 18%). To a flame-dried 250 mL round bottom flask with stir bar was added the crude alcohol (1.57 g, 7.76 mmol)

and DCM (50 mL). To the yellow solution was sequentially added imidazole (1.06 g, 15.52 mmol,) and DMAP (0.2 equiv). The resulting mixture was cooled to 0 °C (ice/H$_2$O bath) and vinyldimethylchlorosilane was added dropwise. After stirring at 0 °C for 10 min, the resulting suspension was allowed to warm to RT. After 4 h, the reaction was quenched with sat. NH$_4$Cl$_{(aq)}$ (30 mL) and extracted with DCM (3 x 30 mL). The combined organics were washed with brine (2 x 50 mL), dried with MgSO$_{4(s)}$, filtered and concentrated to yield a yellow oil. The oil was purified via flash column chromatography (2% diethyl ether/hexanes) to yield **20a** as a clear oil (1.73 g, 78%). **R$_f$** = 0.64 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.35-7.22 (m, 5H), 6.08 (dd, 1H, *J* = 20.0, 14.8 Hz), 5.96 (dd, 1H, *J* = 14.8, 4.2 Hz), 5.74 (dd, 1H, *J* = 20.0, 4.2 Hz), 4.77 (t, 1H, *J* = 6.3 Hz), 2.61-2.44 (m, 2H), 2.12 (tt, 2H, *J* = 9.2, 6.8, 2.4 Hz), 1.47-1.32 (m, 4H), 0.88 (t, 3H, *J* = 7.2 Hz), 0.16 (s, 3H), 0.11 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 144.1, 137.8, 133.2, 128.1, 127.4, 126.1, 82.2, 74.4, 31.1, 31.1, 22.0, 18.6, 13.8, -1.3, -1.5; **IR** (film): *v* = 3030, 2957, 2931, 2871 cm^{-1}; **Anal. calcd**. for C$_{18}$H$_{26}$OSi: C 75.46, H 9.15; found: C 75.29, H 9.05

Dimethyl((1-phenyldec-3-yn-1-yl)oxy)(vinyl)silane (21a): Prepared following the procedure for **20a**: 1-octyne (3.5 mL, 24 mmol), *n*BuLi (9.6 mL, 2.5M, 24 mmol), styrene oxide (2.28 mL, 20 mmol) in HMPA (5.2 mL, 30 mmol). The reaction was poured into 100 mL water and extracted with diethyl ether. The organic layer was washed with 1M HCl and brine, dried over MgSO$_4$, filtered and concentrated *in vacuo* to afford a yellow oil (2.74g, 59%). To a flame dried 100 mL round bottom flask was added the crude alcohol (1.39 g, 6.04 mmol), DCM (20 mL), DMAP (147 mg, 1.21 mmol) and imidazole (822 mg, 12.08 mmol). Vinyldimethylchlorosilane (1.25 mL, 9.06 mmol) was added dropwise to the yellow solution and the resulting suspension stirred overnight. The reaction mixture was poured into sat. NH$_4$Cl$_{(aq.)}$ (30 mL), extracted with DCM (2 x 20 mL), dried with MgSO$_4$, filtered and concentrated *in vacuo* to give a yellow residue. Purification via column chromatography (1% diethyl ether/hexanes) gave alkyne **20a** as a clear oil (1.21 g, 64%). **R$_f$** = 0.37 (2% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.35-7.28 (m, 3H), 7.25-7.22 (m, 2H), 6.08 (dd, *J* = 20.0, 15.2 Hz, 1H), 5.96 (dd, *J* = 14.8, 4.4 Hz, 1H), 5.81 (dd, *J* = 20.2, 4.2 Hz, 1H), 4.77 (t, *J* = 6.5 Hz, 1H), 2.60-2.44 (m,

2H), 2.13-2.08 (m, 2H), 1.47-1.23 (m, 8H), 0.89 (t, J = 6.6 Hz, 3H), 0.16 (s, 3H), 0.11 (s, 3H); [13]**C**

NMR (100 MHz, CDCl$_3$): δ = 144.1, 137.7, 133.2, 128.1, 127.4, 126.1, 82.2, 74.3, 31.5, 31.1, 29.0,

28.7, 22.7, 18.2, 14.2, -1.3, -1.5; **IR** (film): v = 2932, 2859, 1594, 1454, 1252, 1090, 836 cm^{-1};**Anal.**

calcd. for C$_{20}$H$_{30}$OSi: C 76.37, H 9.61; found: C 76.21, H 9.56

General procedure for Silylvinylation at 1 atmosphere ethylene (A): An oven dried 50 mL Schlenk

tube equipped with a magnetic stir bar was brought into an argon filled glove box. To the Schlenk tube

was added RuHCl(CO)(SIMes)(PPh$_3$) (**1**) (1-5 mol%) followed by the alkyne substrate (1.0 equivalent)

in 1,2-dichloroethane or toluene (0.25M). The Schlenk tube was sealed and removed from the glove

box. The solution was purged with ethylene gas for 1-5 minutes via balloon and steel needle. The needle

was removed from the solution and placed 3-4 cm above the solvent, then the apparatus was immersed

in an 80 °C oil bath. The reaction was stirred until complete consumption of the starting material was

visualized by thin layer chromatography. Upon completion, the reaction was filtered through a short

plug of silica gel (eluted with dichloromethane) and concentrated *in vacuo*. A crude yield was obtained

by ^{1}H NMR with mesitylene (0.33 equivalents) as an internal standard. The crude product was purified

via flash chromatography on silica gel.

2,2,5-trimethyl-3-(1-phenylallylidene)-1,2-oxasilolane (2b): Following the general procedure (**A**),

RuH **1** (35 mg, 0.046 mmol) and alkyne **2a** (1.12 g, 4.6 mmol) in toluene (4.6 mL) stirred under

ethylene (1 atm) at 80 °C for 1 h. Purification via flash column chromatography (2-3% diethyl

ether/hexanes) gave diene **2b** as a clear oil (896 mg, 80% as a *Z/E* mixture). **Crude ratio A:B:C =**

10:1:1; **R$_f$** = 0.40 (10% diethyl ether/hexanes); [1]**H NMR** (400 MHz, CDCl$_3$): δ = 7.34-7.28 (m, 3H),

7.13-7.10 (m, 2H), 6.86 (dd, J = 17.4, 10.8 Hz, 1H), 5.23 (dd, J = 10.8, 1.5 Hz, 1H), 4.87 (dd, J = 17.4,

1.5 Hz, 1H), 4.24-4.16 (m, 1H), 2.96 (dd, J = 15.9, 5.1 Hz, 1H), 2.32 (dd, J = 15.9, 8.4 Hz, 1H), 1.32 (d,

J = 6.0 Hz, 3H), -0.07 (s, 3H), -0.20 (s, 3H). **Minor isomer diagnostic peaks**: δ = 6.52 (dd, J = 16.8,

10.8 Hz, 1H), 5.08 (d, J = 10.5 Hz, 1H), 4.75 (d, J = 16.8 Hz, 1H), 1.20 (d, J = 6.0 Hz, 3H), 0.42 (s,

3H), 0.39 (s, 3H); [13]**C NMR** (100 MHz, CDCl$_3$): δ = 148.2, 147.2, 144.4, 143.5, 141.6, 139.8, 139.8,

135.9, 129.7, 128.9, 128.3, 127.9, 127.3, 126.9, 118.3, 116.4, 72.7, 72.5, 42.8, 40.7, 24.1, 23.8, 0.7, 0.6,

0.3, -0.3; **IR** (film): ν = 3056, 2964, 2873, 1581, 1249, 1035, 832 cm^{-1}; **Anal. calcd.** for $C_{15}H_{20}OSi$: C 73.71, H 8.25; found: C 73.71, H 8.34

Isotopic Labeled Diene (2b*): Following the general procedure **(A)**, RuH **1** (36 mg, 0.05 mmol) and alkyne **2a** (244 mg, 1.0 mmol) in DCE (4.0 mL) stirred under C_2D_4 (1 atm) at 80 °C for 30 min. Purification via flash column chromatography (1.5 x 15 cm, 2% diethyl ether/hexanes) gave diene **2b*** as a clear oil (155 mg, 63% as a *Z/E* mixture). % ^2H incorporation: 56%, 52% and 52%; **Crude ratio A:B:C =** 12:1:1; **R$_f$** = 0.40 (10% diethyl ether/hexanes); **^{1}H NMR** (600 MHz, CDCl$_3$): δ = 7.32-7.25 (m, 3H), 7.13-7.12 (m, 2H), 6.86 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.22 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.87 (dd, *J* = 17.4, 1.5 Hz, 1H), 4.23-4.17 (m, 1H), 2.93 (dd, *J* = 15.9, 5.1 Hz, 1H), 2.32 (dd, *J* = 15.9, 8.4 Hz, 1H), 1.32 (d, *J* = 6.0 Hz, 3H), -0.08 (s, 3H), -0.20 (s, 3H); **^{2}H NMR** (92 MHz, CHCl$_3$): δ = 6.87, 5.25, 4.87;

5-cyclohexyl-2,2-dimethyl-3-(1-phenylallylidene)-1,2-oxasilolane (3b): Following the general procedure (**A**), RuH **1** (4 mg, 0.006 mmol) and alkyne **3a** (78 mg, 0.25 mmol) in DCE (1.0 mL) stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via preparative TLC (1% diethyl ether/hexanes) gave diene **3b** as a clear oil (55 mg, 70% as a *Z/E* mixture). **Crude ratio A:B:C =** 16:2:1; **R$_f$** = 0.80 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.34-7.27 (m, 3H), 7.14-7.11 (m, 2H), 6.89 (dd, *J* = 17.4, 10.5 Hz, 1H), 5.23 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.87 (dd, *J* = 17.4, 1.5 Hz, 1H), 3.80-3.75 (m, 1H), 2.87 (dd, *J* = 16.2, 5.5 Hz, 1H), 2.45 (dd, *J* = 16.2, 8.7 Hz, 1H), 1.96-1.92 (m, 1H), 1.78-1.66 (m, 4H), 1.31-0.98 (m, 6H), -0.08 (s, 3H), -0.22 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.52 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.08 (d, *J* = 10.5 Hz, 1H), 4.75 (d, *J* = 16.8 Hz, 1H), 0.40 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 147.0, 143.7, 141.8, 135.9, 129.8, 127.9, 127.2, 118.2, 80.7, 44.8, 36.0, 29.3, 28.7, 26.3, 26.3, 0.4, -0.2; **IR** (film): ν = 2925, 2852, 1581, 1449, 1248, 1032 cm^{-1}; **Anal. calcd.** for $C_{20}H_{28}OSi$: C 76.86, H 9.03; found: C 76.52, H 8.82

2,2-dimethyl-5-phenyl-3-(1-phenylallylidene)-1,2-oxasilolane (4b): Following the general procedure (**A**), RuH **1** (2 mg, 0.0025 mmol) and alkyne **4a** (77 mg, 0.25 mmol) in DCE (1.0 mL) stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via preparative TLC (1:200 diethyl ether/hexanes) gave

diene **4b** as a clear oil (50 mg, 65% as a *Z/E* mixture). **Crude ratio A:B:C** = 10:1:1; **R$_f$** = 0.20 (5%

diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.44-7.28 (m, 8H), 7.19-7.16 (m, 2H), 6.87

(dd, *J* = 17.1, 10.5 Hz, 1H), 5.26 (d, *J* = 10.5 Hz, 1H), 5.08 (dd, *J* = 9.5, 5.5 Hz, 1H), 4.92 (d, *J* = 17.1

Hz, 1H), 3.29 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.61 (dd, *J* = 16.3, 9.5 Hz, 1H), -0.09 (s, 3H), -0.15 (s, 3H);

minor isomer diagnostic peaks: δ = 6.58 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.14 (d, *J* = 10.5 Hz, 1H), 4.81

(d, *J* = 17.1 Hz, 1H), 0.52 (s, 3H), 0.51 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 147.4, 144.4, 142.9,

141.6, 135.8, 129.8, 128.5, 128.0, 127.4, 127.4, 125.6, 118.8, 77.9, 42.0, 0.5, -0.4; **IR** (film): ν = 3060,

2961, 2880, 1582, 1420, 1250, 781 cm^{-1}; **Anal. calcd.** for C$_{20}$H$_{22}$OSi: C 78.38, H 7.24; found: C 78.43,

H 7.02

2,2,5-trimethyl-5-phenyl-3-(1-phenylallylidene)-1,2-oxasilolane   (5b):   Following   the   general

procedure (**A**), RuH **1** (2 mg, 0.0025 mmol) and alkyne **5a** (80 mg, 0.25 mmol) in DCE (1.0 mL) stirred

under ethylene (1 atm) at 80 °C for 1 h. Purification via preparative TLC (2% diethyl ether/hexanes)

gave diene **5b** as a clear oil (56 mg, 70% as a *Z/E* mixture). **Crude ratio A:B:C** = 16:2:1; **R$_f$** = 0.62

(10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.52-7.49 (m, 2H), 7.38-7.30 (m, 5H),

7.27-7.22 (m, 1H), 7.16-7.12 (m, 2H), 6.92 (dd, *J* = 17.4, 10.8 Hz, 1H), 5.27 (dd, *J* = 10.8, 1.2 Hz, 1H),

4.91 (dd, *J* = 17.4, 1.2 Hz, 1H), 3.14 (d, *J* = 16.2 Hz, 1H), 3.03 (d, *J* = 16.2 Hz, 1H), 1.58 (s, 3H), -0.07

(s, 3H), -0.10 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.55 (dd, *J* = 16.8, 10.8 Hz, 1H), 5.10 (dd, *J*

= 10.8, 0.9 Hz, 1H), 4.75 (d, *J* = 17.1 Hz, 1H), 2.72 (d, *J* = 16.5 Hz, 1H), 2.60 (d, *J* = 16.5 Hz, 1H),

1.48 (s, 3H), 0.54 (s, 3H), 0.38 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 149.5, 147.6, 143.1, 141.7,

135.8, 129.8, 128.2, 128.0, 127.4, 126.5, 124.8, 118.6, 81.5, 46.5, 32.2, 1.0, 0.8; **IR** (film): ν = 3057,

2965, 2887, 1599, 1582, 1492, 1250, 962 cm^{-1}; **Anal. calcd.** for C$_{21}$H$_{24}$OSi: C 78.70, H 7.55; found: C

79.07, H 7.75

2,2-dimethyl-3-(1-phenylallylidene)-1-oxa-2-silaspiro[4.5]decane   (6b):   Following   the   general

procedure (**A**), RuH **1** (2 mg, 0.0025 mmol) and alkyne **6a** (74 mg, 0.25 mmol) in DCE (1.0 mL) stirred

under ethylene (1 atm) at 80 °C for 3 h. Purification via flash column chromatography (1% diethyl

ether/hexanes) gave diene **6b** as a clear oil (56 mg, 76% as a *Z/E* mixture). **Crude ratio A:B:C =** 16:2:1; **R$_f$** = 0.42 (5% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.34-7.25 (m, 3H), 7.15-7.12 (m, 2H), 6.89 (dd, *J* = 17.1, 10.8 Hz, 1H), 5.24 (dd, *J* = 10.8, 1.5 Hz, 1H), 4.87 (dd, *J* = 17.1, 1.5 Hz, 1H), 2.65 (s, 2H), 1.70-1.41 (m, 10H), -0.16 (s, 6H); **minor isomer diagnostic peaks:** δ = 6.54 (dd, *J* = 16.8, 10.2 Hz, 1H), 5.06 (d, *J* = 10.8 Hz, 1H), 4.71 (d, *J* = 16.8 Hz, 1H), 2.22 (s, 3H), 0.40 (s, 6H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 146.5, 143.0, 140.8, 134.9, 128.8, 126.9, 126.2, 117.0, 78.8, 42.7, 38.7, 24.7, 22.2, 0.1; **IR** (film): ν = 3055, 2931, 2857, 1582, 1443, 1249, 891 cm^{-1}; **Anal. calcd.** for C$_{19}$H$_{26}$OSi: C 76.45, H 8.78; found: C 76.29, H 8.47

2,2,4-trimethyl-3-(1-phenylallylidene)-1,2-oxasilolane (7b): Following the general procedure (**A**), RuH **1** (9.0 mg, 0.0125 mmol) and alkyne **7a** (75 mg, 0.25 mmol) in DCE (1.0 mL) stirred under ethylene (1 atm) at 80 °C for 1.5 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave diene **7b** as a clear oil (50 mg, 67% as a *Z/E* mixture). **Crude ratio A:B:C =** 13:1:2; **R$_f$** = 0.36 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.33-7.25 (m, 3H), 7.14-7.10 (m, 2H), 6.90 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.25 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.87 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.00 (dd, *J* = 9.3, 5.1 Hz, 1H), 3.85 (d, *J* = 9.6 Hz, 1H), 3.18-3.09 (m, 1H), 1.21 (d, *J* = 7.2 Hz, 3H), 0.14 (s, 3H), -0.41 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.49 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.09 (dd, *J* = 10.5, 0.9 Hz, 1H), 4.69 (dd, *J* = 17.1, 1.2 Hz, 1H), 2.60-2.52 (m, 1H), 0.85 (d, *J* = 7.2 Hz, 3H), 0.46 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 148.3, 147.0, 141.5, 135.3, 129.7, 127.9, 127.3, 118.7, 72.5, 38.2, 21.1, 1.6, -1.2; **IR** (film): ν = 3025, 2960, 2867, 1581, 1490, 1250, 842 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{20}$OSi: C 73.71, H 8.25; found: C 73.97, H 8.35

2,2-dimethyl-3-(1-phenylallylidene)octahydrobenzo[d][1,2]oxasilole (8b): Following the general procedure, RuH **1** (9.0 mg, 0.0125 mmol) and alkyne **8a** (71 mg, 0.25 mmol) in DCE (1.0 mL) stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via flash column chromatography (2% diethyl ether/hexanes) gave diene **8b** as a clear oil (55 mg, 78% as a *Z/E* mixture). **Crude ratio A:B:C =** 34:1:3; **R$_f$** = 0.34 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.34-7.26 (m, 3H),

7.14-7.10 (m, 2H), 6.89 (dd, J = 17.1, 10.5 Hz, H), 5.20 (dd, J = 10.5, 1.5 Hz, 1H), 4.85 (dd, J = 17.1,

1.5 Hz, 1H), 4.07-4.06 (m, 1H), 2.89-2.82 (m, 1H), 2.08-2.03 (m, 1H), 1.74-1.72 (m, 1H), 1.65-1.50 (m,

4H), 1.40-1.26 (m, 2H), 0.17 (s, H), -0.39 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.47 (dd, J =

16.8, 10.5 Hz, 1H), 5.07 (dd, J = 10.8, 1.2 Hz, 1H), 4.65 (dd, J = 16.8, 1.5 Hz, 1H), 0.48 (s, 3H), 0.39

(s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 150.0, 146.3, 141.6, 135.5, 129.9, 128.0, 127.3, 118.3, 74.1,

44.3, 31.3, 28.4, 25.6, 19.7, 1.7, -1.1; **IR** (film): ν = 3054, 2931, 2851, 1582, 1491, 1441, 1249 cm^{-1};

Anal. calcd. for C$_{18}$H$_{24}$OSi: C 76.00, H 8.56; found: C 75.94, H 8.79

2,2,4,5-tetramethyl-3-(1-phenylallylidene)-1,2-oxasilolane (9b): Following the general procedure (**A**),

RuH **1** (2 mg, 0.005 mmol) and alkyne **9a** (65 mg, 0.25 mmol) in DCE (1.0 mL) stirred under ethylene

(1 atm) at 80 °C for 1 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave

diene **9b** as a clear oil (45 mg, 70% as a *Z/E* mixture). **Crude ratio A:B:C = 18:2:1; R$_f$** = 0.38 (10%

diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.33-7.27 (m, 3H), 7.15-7.12 (m, 2H), 6.88

(dd, J = 17.1, 10.5 Hz, 1H), 5.24 (dd, J = 10.5, 1.5 Hz, 1H), 4.88 (dd, J = 17.4, 1.8 Hz, 1H), 4.11-4.06

(m, 1H), 2.86-2.83 (m, 1H), 1.21 (d, J = 7.2 Hz, 3H), 1.17 (d, J = 6.6 Hz, 3H), 0.15 (s, 3H), -0.43 (s,

3H); **minor isomer diagnostic peaks:** δ = 6.52 (dd, J = 17.1, 10.5 Hz, 1H), 5.08 (dd, J = 10.2, 1.2 Hz,

1H), 4.67 (dd, J = 17.1, 1.2 Hz, 1H), 0.44 (s, 3H), 0.42 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 148.1,

148.1, 141.8, 135.4, 129.8, 127.9, 127.3, 118.7, 80.0, 44.3, 24.6, 21.3, 2.3, 0.7; **IR** (film): ν = 3025,

2960, 2867, 1581, 1490, 1250, 842 cm^{-1}; **Anal. calcd.** for C$_{16}$H$_{22}$OSi: C 74.36, H 8.58; found: C 74.34,

H 8.89

3-(1-(4-fluorophenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (10b): Following the general

procedure (**A**), RuH **1** (4 mg, 0.006 mmol) and alkyne **10a** (79 mg, 0.3 mmol) in toluene (1.2 mL)

stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via preparative TLC (1% diethyl

ether/hexanes) gave diene **10b** as a clear oil (55 mg, 69% as a *Z/E* mixture). **Crude ratio A:B:C =**

23:3:1; **R$_f$** = 0.27 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.11-7.07 (m, 2H),

7.04-6.99 (m, 2H), 6.84 (dd, J = 17.1, 10.5 Hz, 1H), 5.23 (d, J = 10.5 Hz, 1H), 4.82 (dd, J = 17.4, 1.8

Hz, 1H), 4.24-4.16 (m, 1H), 2.94 (dd, J = 16.1, 5.0 Hz, 1H), 2.31 (dd, J = 16.1, 8.2 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H), -0.06 (s, 3H), -0.18 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.50 (dd, J = 16.8, 10.5 Hz, 1H), 5.08 (d, J = 10.8 Hz, 1H), 4.73 (d, J = 17.1 Hz, 1H), 0.41 (s, 3H), 0.38 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 162.0 (d, J_{C-F} = 249.7 Hz), 146.2, 144.3, 137.7 (d, J_{C-F} = 3.4 Hz), 136.0, 131.5 (d, J_{C-F} = 8.5 Hz), 118.4, 115.1 (d, J_{C-F} = 22.1 Hz), 72.6, 40.8, 24.2, 0.7, -0.1; **^{19}F NMR** (376.4 MHz, CDCl$_3$): δ = (-115.2)-(-115.2)(m); (-115.6)-(-115.7)(m); **IR** (film): ν = 3044, 2928, 1507, 1452, 1256, 910 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{19}$FOSi: C 68.66, H 7.30; found: C 68.82, H 7.26

3-(1-(2-chlorophenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (11b): Following the general procedure (**A**), RuH **1** (11.0 mg, 0.015 mmol) and alkyne **11a** (84 mg, 0.30 mmol) in 1,4-dioxane (1.2 mL) stirred under ethylene (1 atm) at 100 °C for 30 min. Purification via preparative TLC (1% diethyl ether/hexanes) gave diene **11b** as a clear oil (59 mg, 70% as a *Z/E* mixture). **Crude ratio A:B:C =** 12:1:3; **R$_f$** = 0.46 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$, mixture of rotamers): δ = 7.40-7.37 (m, 1H), 7.28-7.23 (m, 2H), 7.13-7.11 (m, 1H), 6.81 (ddd, J = 17.2, 10.5, 2.7 Hz, 1H), 5.20 (d, J = 7.9 Hz, 1H), 4.69 (d, J = 12.9 Hz, 1H) 4.33-4.25 (m, 0.5H), 4.25-4.17 (m, 0.5H), 3.05 (dd, J = 16.2, 5.2 Hz, 0.5H), 2.94 (dd, J = 16.2, 5.7 Hz, 0.5H), 2.47 (dd, J = 16.2, 7.1 Hz, 0.5H), 2.30 (dd, J = 16.1, 8.9 Hz, 0.5H), 1.35 (d, J = 6.1 Hz, 1.5H), 1.32 (d, J = 6.1 Hz, 1.5H), 0.00 (s, 1.5H), -0.08 (s, 1.5H), -0.16 (s, 1.5H), -0.25 (s, 1.5H); **minor isomer diagnostic peaks:** δ = 6.49 (dd, J = 16.8, 10.4 Hz, 1H), 5.07 (d, J = 10.5 Hz, 1H), 4.60 (d, J = 17.0 Hz, 1H), 4.15-4.12 (m, 1H), 0.44 (s, 3H), 0.41 (s, 3H); **^{13}C NMR** (75 MHz, CDCl3): δ = 144.8, 144.6, 144.2, 140.0, 140.0, 134.7, 134.6, 134.2, 134.1, 132.2, 129.8, 129.6, 129.5, 129.0, 128.6, 126.6, 126.5, 117.6, 117.6, 116.0, 72.8, 72.7, 40.8, 40.3, 24.2, 24.1, 23.9, 1.1, 0.4, -1.1, -1.9; **IR** (film): ν = 2966, 2926, 2876, 1584, 1471, 1436, 1250, 835 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{19}$ClOSi: C 64.61, H 6.87; found: C 64.56, H 6.76

2,2,5-trimethyl-3-(1-(naphthalen-1-yl)allylidene)-1,2-oxasilolane (12b): Following the general procedure (**A**), RuH **1** (11.0 mg, 0.015 mmol) and alkyne **12a** (88 mg, 0.30 mmol) in 1,4-dioxane (1.2 mL) stirred under ethylene (1 atm) at 100 °C for 1 h. Purification via flash column chromatography (2%

diethyl ether/hexanes) gave diene **12b** as a clear oil (62 mg, 71% as a *Z/E* mixture). **Crude ratio A:B:C** = 23:1:5; **R$_f$** = 0.44 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$) (mixture of rotamers): δ = 7.85-7.76 (m, 3H), 7.51-7.38 (m, 3H), 7.25 (d, *J* = 6.7 Hz, 1H), 7.01 (ddd, *J* = 17.2, 10.4, 2.4 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.67 (d, *J* = 17.2 Hz, 1H), 4.39-4.30 (m, 0.5H), 4.28-4.19 (m, 0.5H), 3.16 (dd, *J* = 16.1, 5.1 Hz, 0.5H), 2.42 (dd, *J* = 16.5, 5.7 Hz, 0.5H), 1.39 (d, *J* = 6.1 Hz, 1.5H), 1.36 (d, *J* = 6.1 Hz, 0.5H), 0.00 (s, 1.5H), -0.1 (s, 1.5H), -0.7 (s, 1.5H), -0.8 (1.5H); **minor isomer diagnostic peaks:** δ = 6.70 (ddd, *J* = 16.6, 10.4, 2.4 Hz, 1H), 5.28 (d, *J* = 10.2 Hz, 1H), 4.90 (d, *J* = 17.2 Hz, 1H), 1.16 (d, *J* = 6.1 Hz, 3H), 1.13 (d, *J* = 6.1 Hz, 3H), -0.1 (s, 3H), -0.2 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 145.8, 145.6, 145.1, 144.7, 139.2, 139.0, 135.9, 135.8, 133.6, 133.5, 132.7, 132.7, 128.2, 127.9, 127.9, 127.8, 126.8, 126.7, 125.9, 125.9, 125.3, 125.2, 118.6, 118.6, 72.8, 72.6, 40.9, 40.5, 24.3, 24.2, 1.1, 0.4, -1.1, -1.8; **IR** (film): *v* = 3046, 2966, 2927, 1585, 1507, 1395, 1376, 1249, 1104, 1037, 944, 781 cm^{-1}; **Anal. calcd.** for C$_{19}$H$_{22}$OSi: C 77.50, H 7.53; found: C 77.48, H 7.48

3-(1-(3,5-dimethylphenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (13b): Following the general procedure (**A**), RuH **1** (2 mg, 0.0025 mmol) and alkyne **13a** (68 mg, 0.25 mmol) in toluene (1.0 mL) stirred under ethylene (1 atm) at 85 °C for 1 h. Purification via flash column chromatography (2% diethyl ether/hexanes) gave diene **13b** as a clear oil (50 mg, 74% as a *Z/E* mixture). **Crude ratio A:B:C** = 28:3:1; **R$_f$** = 0.29 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 6.92 (s, 1H), 6.84 (dd, *J* = 10.5, 17.2 Hz, 1H), 6.74 (s, 2H), 5.23 (dd, *J* = 1.4, 10.6 Hz, 1H), 4.95 (dd, *J* = 1.5, 17.2 Hz, 1H), 4.23-4.15 (m, 1H), 2.93 (dd, *J* = 5.4, 16.1 Hz, 1H), 2.33-2.30 (m, 1H), 2.30 (s, 3H), 2.30 (s, 3H), 1.32 (d, *J* = 6.08 Hz, 3H), -0.07 (s, 3H), -0.21 (s, 3H); **minor isomer diagnostic peaks:** δ = 6.50 (dd, *J* = 10.4, 17.0 Hz, 1H), 5.07 (d, *J* = 10.1 Hz, 1H), 4.78 (d, *J* = 17.0 Hz, 1H), 0.41 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ =147.6, 143.1, 141.6, 137.3, 135.8, 128.7, 127.5, 118.2, 72.6, 40.7, 24.1, 21.4, 0.7, -0.3; **IR** (film): *v* = 3012, 2925, 1601, 1248, 823 cm^{-1}; **Anal. calcd.** for C$_{17}$H$_{24}$OSi: C 74.94, H 8.88; found: C 74.85, H 8.64

3-(1-(4-methoxyphenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (14b): Following the general procedure (**A**), RuH **1** (4 mg, 0.005 mmol) and alkyne **14a** (82 mg, 0.3 mmol) in DCE (1.2 mL) stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via preparative TLC (3% diethyl ether/hexanes) gave diene **14b** as a clear oil (60 mg, 73%). **Crude ratio A:B:C** = 44:3:1; R_f = 0.26 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.05-7.01 (m, 2H), 6.89-6.80 (m, 3H), 5.22 (dd, J = 10.5, 1.5 Hz, 1H), 4.88 (dd, J = 17.1, 1.5 Hz, 1H), 4.25-4.14 (m, 1H), 3.82 (s, 3H), 2.93 (dd, J = 16.5, 5.4 Hz, 1H), 2.30 (dd, J = 16.5, 8.4 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H), -0.05 (s, 3H), -0.18 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 158.9, 146.8, 143.4, 136.1, 134.1, 130.8, 118.1, 113.2, 72.5, 55.3, 40.7, 24.1, 0.7, -0.1; **IR** (film): ν = 3087, 2968, 2835, 1608, 1508, 1458, 1246, 1036 cm^{-1}; **Anal. calcd.** for C$_{16}$H$_{22}$O$_2$Si: C 70.03, H 8.08; found: C 70.03, H 7.81

1-(4-(1-(2,2,5-trimethyl-1,2-oxasilolan-3-ylidene) allyl) phenyl) ethanone (15b): Following the general procedure (**A**), RuH **1** (2 mg, 0.0025 mmol) and alkyne **15a** (72 mg, 0.25 mmol) in DCE (1.0 mL) was stirred under ethylene (1 atm) at 80 °C for 3 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave diene **15b** as a clear oil (46 mg, 64% as a *Z/E* mixture). **Crude ratio A:B:C** = 7:1:1; R_f = 0.20 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.92 (d, J = 8.4 Hz, 2H), 7.24 (d, J = 8.4 Hz, 2H), 6.85 (dd, J = 17.1, 10.5 Hz, 1H), 5.24 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 18.0 Hz, 1H), 4.24-4.17 (m, 1H), 2.96 (dd, J = 16.2, 5.4 Hz, 1H), 2.62 (s, 3H), 2.34 (dd, J = 16.2, 8.2 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H), -0.07 (s, 3H), -0.19 (s, 3H); **minor isomer diagnostic peaks:** δ = 7.97 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.51 (dd, J = 16.8, 10.5 Hz, 1H), 5.11 (d, J = 10.5 Hz, 1H), 4.70 (d, J = 17.4 Hz, 1H), 4.11-4.04 (m, 1H), 1.20 (d, J = 6.0 Hz, 3H), 0.42 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 198.0, 198.0, 146.9, 146.9, 146.2, 145.5, 145.2, 144.5, 139.2, 136.2, 135.9, 135.6, 130.1, 129.3, 128.6, 128.2, 118.6, 116.8, 72.8, 72.5, 42.8, 41.0, 26.8, 26.8, 24.1, 23.8, 0.7, 0.3, -0.0; **IR** (film): ν = 3087, 2964, 2871, 1684, 1601, 1264, 944 cm^{-1}; **Anal. calcd.** for C$_{17}$H$_{22}$O$_2$Si: C 71.28, H 7.74; found: C 70.99, H 7.75

2,2,6-trimethyl-3-(1-phenylallylidene)-1,2-oxasilinane (16b): Following the general procedure (**A**), RuH **1** (4 mg, 0.006 mmol) and alkyne **16a** (77 mg, 0.3 mmol) in DCE (1.2 mL) stirred under ethylene (1 atm) at 80 °C for 1 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave diene **16b** as a clear oil (63 mg, 82%). **Crude ratio A:B:C** = 14:1:1; R_f = 0.74 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.30-7.26 (m, 3H), 7.09-7.02 (m, 3H), 5.21 (dd, J = 10.8, 1.8 Hz, 1H), 4.73 (dd, J = 17.1, 1.8 Hz, 1 H), 4.10-4.03 (m, 1H), 3.08 (ddd, J = 15.9, 5.4, 3.3 Hz, 1H), 2.47 (ddd, J = 15.9, 12.6, 3.3 Hz, 1H), 1.90-1.83 (m, 1H), 1.61-1.51 (m, 1H), 1.21 (d, J = 6.3 Hz, 3H), -0.14 (s, 3H), -0.37 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 147.2, 141.6, 140.3, 134.3, 130.6, 127.9, 127.3, 118.7, 70.5, 36.1, 29.1, 24.7, 1.6, 0.2; **IR** (film): ν = 3080, 2965, 2846, 1558, 1490, 1248, 829 cm^{-1}; **Anal. calcd.** for C$_{16}$H$_{22}$OSi: C 74.36, H 8.58; found: C 74.39, H 8.69

General Procedure for high pressure reactions (B): An oven dried Fischer Porter bottle equipped with a magnetic stir bar was brought into an argon filled glove box. To the Fischer Porter bottle was added RuHCl(CO)(SIMes)PPh$_3$ (**1**) and the alkyne in toluene. The bottle was plugged with a septum and removed from the glove box. The septum was replaced with a Swagelok regulator and the system was purged with ethylene (80 psi) and vented three times, then refilled to 80 psi and heated to 80 °C for the allotted time. Upon completion by TLC, the reaction was filtered through a short plug of silica gel (eluted with dichloromethane), concentrated *in vacuo* and a crude yield was obtained by ^{1}H NMR with mesitylene (0.33 equivalents) as an internal standard. The crude product was purified by flash chromatography on silica gel.

3-(1-(4-fluorophenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (Diene Mixture 10b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **10a** (66 mg, 0.25 mmol) in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 4 h. Purification via flash column chromatography (10% diethyl ether/hexanes) gave the diene mixture **10b** as a clear oil (56 mg, 85% as a *Z/E* mixture). **Crude ratio A:C** = 1:1.3; R_f = 0.27 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): **isomer A:** δ = 7.12-6.99 (m, 4H), 6.85 (dd, J = 17.4, 10.8 Hz, 1H), 5.24 (dd, J = 10.8, 1.5 Hz, 1H), 4.82 (dd, J = 17.4,

1.2 Hz, 1H), 4.24-4.17 (m, 1H), 2.95 (dd, J = 16.2, 5.4 Hz, 1H), 2.31 (dd, J = 16.2, 8.4 Hz, 1H), 1.32 (d, J = 6.0 Hz, 3H), -0.05 (s, 3H), -0.17 (s, 3H); **isomer C:** δ = 7.12-6.99 (m, 4H), 6.51 (dd, J = 17.1, 10.5 Hz, 1H), 5.09 (dd, J = 10.8, 0.6 Hz, 1H), 4.74 (dd, J = 17.1, 0.6 Hz, 1H), 4.11-4.02 (m, 1H), 2.38 (dd, J = 17.4, 5.1 Hz, 1H), 2.02 (dd, J = 16.8, 8.4 Hz, 1H), 1.21 (d, J = 6.0 Hz, 3H), 0.42 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 163.7, 163.4, 160.1, 146.9, 146.1, 145.0, 144.1, 139.7, 137.5, 137.5, 135.9, 135.6, 135.5, 131.3, 131.2, 130.5, 130.4, 118.3, 116.4, 115.4, 115.1, 115.0, 114.7, 72.7, 72.5, 42.8, 40.7, 24.0, 23.7, 0.7, 0.6, 0.3, -0.2; **^{19}F NMR** (282.3 MHz, CDCl$_3$): δ = (-115.6)-(-115.7)(m); δ = (-116.1)-(-116.2)(m); **IR** (film): ν = 2966, 2927, 1601, 1506, 1252 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{19}$FOSi: C 68.66, H 7.30; found: C 68.52, H 7.12

3-(1-(4-methoxyphenyl)allylidene)-2,2,5-trimethyl-1,2-oxasilolane (Diene Mixture 14b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **14a** (72 mg, 0.25 mmol) in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 4 h. Purification via flash column chromatography (10% diethyl ether/hexanes) gave the diene mixture **14b** as a clear oil (66 mg, 91% as a *Z/E* mixture). **Crude ratio A:C** = 3:1; **R$_f$** = 0.26 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): **isomer A:** δ = 7.06-7.03 (m, 2H), 6.92-6.80 (m, 3H), 5.21 (d, J = 10.5 Hz, 1H), 4.87 (dd, J = 17.1, 1.5 Hz, 1H), 4.24-4.14 (m, 1H), 3.81 (s, 3H), 2.93 (dd, J = 16.2, 5.4 Hz, 1H), 2.29 (dd, J = 16.2, 8.4 Hz, 1H), 1.31 (d, J = 6.0 Hz, 3H), -0.05 (s, 3H), -0.17 (s, 3H); **isomer C:** δ = 7.06-7.03 (m, 2H), 6.92- 6.80 (m, 2H), 6.51 (dd, J = 16.8, 10.5 Hz, 1H), 5.07 (d, J = 10.5 Hz, 1H), 4.79 (d, J = 17.1 Hz, 1H), 4.10-4.03 (m, 1H), 3.82 (s, 3H) 2.43 (dd, J = 16.8, 5.1 Hz, 1H), 2.06 (dd, J = 16.5, 8.4 Hz, 1H), 1.20 (d, J = 6.0 Hz, 3H), 0.41 (s, 3H), 0.38 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 158.7, 158.3, 147.4, 146.7, 143.3, 139.9, 136.0, 133.9, 130.7, 129.9, 118.0, 116.1, 113.5, 113.1, 72.6, 72.4, 55.2, 55.2, 42.8, 40.6, 24.0, 23.7, 0.7, 0.6, 0.2, -0.3; **IR** (film): ν = 2963, 2929, 1608, 1509, 1248 cm^{-1}; **Anal. calcd.** for C$_{16}$H$_{22}$O$_2$Si: C 70.03, H 8.08; found: C 70.41, H 7.80

1-(4-(1-(2,2,5-trimethyl-1,2-oxasilolan-3-ylidene)allyl)phenyl)ethanone (Diene Mixture 15b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **15a** (72 mg, 0.25 mmol)

in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 24 h. Purification via flash column chromatography (10% diethyl ether/hexanes) gave the diene mixture **15b** as a clear oil (62 mg, 86% as a *Z/E* mixture). **Crude ratio A:C** = 1:7; **R$_f$** = 0.20 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): **isomer A:** δ = 7.92 (d, *J* = 8.4 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 6.85 (dd, *J* = 17.1, 10.5 Hz, 1H), 5.24 (d, *J* = 10.5 Hz, 1H), 4.79 (d, *J* = 18.0 Hz, 1H), 4.24-4.17 (m, 1H), 2.96 (dd, *J* = 16.2, 5.4 Hz, 1H), 2.62 (s, 3H), 1.32 (d, *J* = 6.0 Hz, 3H), -0.07 (s, 3H), -0.19 (s, 3H); **isomer C:** δ = 7.97 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 6.51 (dd, *J* = 16.8, 10.5 Hz, 1H), 5.11 (d, *J* = 10.5 Hz, 1H), 4.70 (d, *J* = 17.4 Hz, 1H), 4.12-4.02 (m, 1H), 2.62 (s, 3H), 2.34 (dd, *J* = 16.8, 5.1 Hz, 1H), 2.00 (dd, *J* = 16.8, 5.4 Hz, 1H), 1.19 (d, *J* = 6.0 Hz, 3H), 0.42 (s, 3H), 0.39 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 197.8, 145.8, 145.0, 139.0, 135.7, 129.1, 128.4, 116.6, 72.6, 42.7, 26.6, 23.6, 0.6, 0.1; **IR** (film): ν = 2964, 2925, 1684, 1264 cm^{-1}; **Anal. calcd.** for C$_{17}$H$_{22}$O$_2$Si: C 71.28, H 7.74; found: C 71.03, H 7.40

2,2,6-trimethyl-3-(1-phenylallylidene)-1,2-oxasilinane (Diene Mixture 16b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **16a** (57 mg, 0.22 mmol) in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 24 h. (25:1). Purification via flash column chromatography (10% diethyl ether/hexanes) gave the diene mixture **16b** as a clear oil (41 mg, 72%). **Crude ratio A:C** = 25:1; **^{1}H NMR** (300 MHz, CDCl$_3$): δ = 7.28-7.27 (m, 3H), 7.09-7.00 (m, 3H), 5.20 (dd, *J* = 10.5, 1.5 Hz, 1H), 4.72 (dd, *J* = 17.1, 1.5 Hz, 1H), 4.11-4.00 (m, 1H), 3.06 (ddd, *J* = 16.2, 5.1, 3.3 Hz, 1H), 2.45 (ddd, *J* = 15.9, 12.6, 3.3 Hz, 1H), 1.90-1.81 (m, 1H), 1.62-1.48 (m, 1H), 1.20 (d, *J* = 6.0 Hz, 3H), -0.15 (s, 3H), -0.38 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ = 147.1, 141.5, 140.2, 134.1, 130.4, 127.8, 127.2, 118.7, 70.4, 36.0, 29.0, 24.6, 1.5, 0.1;

3-(but-3-en-2-ylidene)-2,2-dimethyl-5-phenethyl-1,2-oxasilolane (Diene Mixture 17b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **17a** (68 mg, 0.25 mmol) in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 24 h. Purification via flash column chromatography (2% diethyl ether/hexanes) gave the diene mixture **17b** as a clear oil (57 mg, 84% as a *Z/E* mixture). **Crude ratio A:C** = 1:3; **R$_f$** = 0.64 (10% diethyl ether/hexanes); **^{1}H NMR** (300 MHz, CDCl$_3$): **major**

isomer C: δ = 7.32-7.16 (m, 5H), 6.35 (dd, J = 16.8, 10.2 Hz, 1H), 5.23 (d, J = 17.3 Hz, 1H), 5.06 (d, J = 10.7 Hz, 1H), 4.12-4.02 (m, 1H), 2.88-2.67 (m, 4H), 2.27 (dd, J = 16.2, 7.6 Hz, 1H), 1.86 (s, 3H), 0.37 (s, 3H), 0.32 (s, 3H); **minor isomer A:** δ = 6.70 (dd, J = 17.3, 10.7 Hz, 1H), 5.28 (d, J = 16.8 Hz, 1H), 5.17 (d, J = 10.8 Hz, 1H), 1.91 (s, 3H), 0.36 (s, 3H), 0.32 (s, 3H); **^{13}C NMR** (75 MHz, CDCl$_3$): δ= 142.8, 142.4, 141.7, 140.4, 140.1, 139.4, 136.1, 128.6, 128.4, 125.8, 114.4, 112.5, 76.0, 75.7, 40.2, 40.1, 39.9, 38.4, 32.3, 20.0, 15.3, 0.9, 0.5, 0.4, 0.0; **IR** (film): ν = 2957, 2931, 1585, 1453, 1250, 866 cm^{-1}; **Anal. calcd.** for C$_{17}$H$_{24}$OSi: C 74.94, H 8.88; found C 74.88, H 8.99

3-(but-3-en-2-ylidene)-2,2-dimethyl-5-phenyl-1,2-oxasilolane (Diene Mixture 18b): Following the general procedure (B), RuH **1** (4 mg, 0.005 mmol) and alkyne **18a** (80 mg, 0.32 mmol) in toluene (1.3 mL) stirred under ethylene (80 psi) at 80 °C for 24 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave the diene mixture **18b** as a clear oil (67 mg, 84% as a *Z/E* mixture). **Crude ratio A:C** = 1:2; **R$_f$** = 0.52 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): **major isomer C:** δ = 7.39-7.32 (m, 4H), 7.27-7.23 (m, 1H), 6.36 (dd, J = 17.1, 10.8 Hz, 1H), 5.23 (d, J = 16.9 Hz, 1H), 5.06 (d, J = 11.0 Hz, 1H), 5.05-5.00 (m, 1H), 3.02 (dd, J = 16.8, 5.7 Hz, 1H), 2.50-2.44 (m, 1H), 1.86 (dd, J = 1.6, 0.7 Hz, 3H), 0.41 (s, 3H), 0.39 (s, 3H); **minor isomer A:** δ = 6.68 (dd, J = 17.3, 10.6 Hz, 1H), 5.28 (d, J = 17.3 Hz, 1H), 5.15 (d, J = 10.6 Hz, 1H) 3.13 (ddd, J = 16.2, 5.5, 1.0 Hz, 1H), 1.92 (dd, J = 2.2, 1.0 Hz, 3H), 0.40 (s, 3H), 0.38 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 144.3, 144.2, 142.2, 141.3, 139.8, 139.6, 139.1, 135.5, 128.0, 126.9, 125.1, 114.3, 112.5, 77.7, 77.3, 42.5, 41.1, 19.6, 14.9, 0.0, 0.0, -0.3, -0.4; **IR** (film): ν = 3088, 3029, 2956, 2877, 1588, 1251, 1036, 868 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{20}$OSi: C 73.71, H 8.21; found C 73.43, H 8.20

2,2-dimethyl-3-(pent-1-en-3-ylidene)-5-phenyl-1,2-oxasilolane (Diene Mixture 19b): Following the general procedure (B), RuH **1** (4 mg, 0.005 mmol) and alkyne **19a** (77 mg, 0.3 mmol) in toluene (1.2 mL) stirred under ethylene (80 psi) at 80 °C for 1 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave the diene mixture **19b** as a clear oil (61 mg, 79% as a *Z/E* mixture). **Crude ratio A:C** = 5:1; **R$_f$** = 0.63 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): **isomer A:** δ =

7.38-7.31 (m, 4H), 7.25-7.23 (m, 1H), 6.52 (dd, J = 17.7, 11.0 Hz, 1H), 5.29 (d, J = 17.7 Hz, 1H), 5.17 (d, J = 11.0 Hz, 1H), 5.00 (dd, J = 9.0, 5.5 Hz, 1H), 3.10 (dd, J = 16.1, 5.5 Hz, 1H), 2.49-2.41 (m, 1H), 2.38-2.24 (m, 2H), 1.10 (t, J = 7.8 Hz, 3H), 0.39 (s, 3H), 0.37 (s, 3H); **isomer C:** δ = 6.25 (dd, J = 17.3, 10.6 Hz, 1H), 5.25 (d, J = 17.3 Hz, 1H), 5.06 (d, J = 11.0 Hz, 1H), 3.01 (dd, J = 16.5, 5.5 Hz, 1H), 1.01 (t, J = 7.8 Hz, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 148.2, 146.2, 144.7, 144.7, 141.4, 139.2, 138.8, 134.2, 128.4, 127.3, 125.5, 125.4, 114.9, 112.6, 78.0, 77.8, 42.2, 41.7, 28.2, 22.7, 14.9, 13.0, 0.4, 0.1; **IR** (film): ν = 3088, 2966, 2876, 1586, 1251, 1061, 907 cm^{-1}; **Anal. calcd.** for C$_{16}$H$_{22}$OSi: C 74.36, H 8.58; found: C 74.55, H 8.74

3-(hept-1-en-3-ylidene)-2,2-dimethyl-5-phenyl-1,2-oxasilolane (Diene Mixture 20b): Following the general procedure (B), RuH **1** (4 mg, 0.005 mmol) and alkyne **20a** (86 mg, 0.3 mmol) in toluene (1.2 mL) stirred under ethylene (80 psi) at 80 °C for 1 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave the diene mixture **20b** as a clear oil (59 mg, 69% as a *Z/E* mixture). **Crude ratio A:C = 8:1**; **R$_f$** = 0.36 (10% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): **isomer A:** δ = 7.31-7.24 (m, 4H), 7.19-7.15 (m, 1H), 6.46 (dd, J = 17.6, 10.8 Hz, 1H), 5.21 (d, J = 17.6 Hz, 1H), 5.09 (d, J = 10.8 Hz, 1H), 4.93 (dd, J = 9.5, 5.4 Hz, 1H), 3.02 (dd, J = 16.2, 5.4 Hz, 1H), 2.37 (dd, J = 16.2, 5.4 Hz, 1H), 2.25-2.13 (m, 2H), 1.43-1.35 (m, 2H), 1.33-1.24 (m, 2H), 0.86 (t, J = 7.5 Hz, 3H), 0.32 (s, 3H), 0.30 (s, 3H); **isomer C:** δ = 6.19 (dd, J = 17.2, 10.4 Hz, 1H), 4.99 (d, J = 10.8 Hz, 1H), 2.93 (dd, J = 16.7, 5.4 Hz, 1H), 0.82 (t, J = 7.1 Hz, 3H), 0.33 (s, 3H), 0.31 (s, 3H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 146.8, 145.1, 144.7, 142.0, 139.4, 139.2, 134.7, 128.4, 127.3, 127.3, 125.5, 114.8, 112.7, 78.0, 77.8, 42.5, 41.8, 35.3, 32.6, 30.8, 29.5, 23.3, 23.2, 14.1, 14.1, 0.4, 0.3; **IR** (film): ν = 3087, 2957, 2873, 1585, 1250, 1036, 867 cm^{-1}; **Anal. calcd.** for C$_{18}$H$_{26}$OSi: C 75.46, H 9.15; found: C 75.65, H 9.26

2,2-dimethyl-3-(non-1-en-3-ylidene)-5-phenyl-1,2-oxasilolane (Diene Mixture 21b): Following the general procedure (B), RuH **1** (2 mg, 0.0025 mmol) and alkyne **21a** (78 mg, 0.25 mmol) in toluene (1.0 mL) stirred under ethylene (80 psi) at 80 °C for 24 h. Purification via flash column chromatography (1% diethyl ether/hexanes) gave the diene mixture **21b** as a clear oil (65 mg, 83% as a *Z/E* mixture). **Crude**

ratio A:C = 7:1; R_f = 0.78 (10% diethyl ether/hexanes); ^{1}H NMR (300 MHz, CDCl$_3$): **isomer A:** δ =

7.40-7.31 (m, 5H), 6.54 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.30 (d, *J* = 17.4 Hz, 1H), 5.17 (d, *J* = 10.9 Hz,

1H), 5.01 (dd, *J* = 9.6, 5.6 Hz, 1H), 3.11 (dd, *J* = 16.2, 5.3 Hz, 1H), 2.46 (dd, *J* = 16.2, 9.6 Hz, 1H),

2.32-2.23 (m, 2H), 1.53-1.43 (m, 2H), 1.40-1.26 (m, 7H), 0.93-0.87 (m, 3H), 0.40 (s, 3H), 0.38 (s, 3H);

isomer C: δ = 6.27 (dd, *J* = 17.4, 10.9 Hz, 1H), 5.07 (d, *J* = 10.9 Hz, 1H), 3.00 (dd, *J* = 16.8, 5.6 Hz,

1H), 0.41 (s, 3H), 0.39 (s, 3H); ^{13}C NMR (75 MHz, CDCl$_3$): δ = 145.2, 144.7, 139.4, 134.8, 128.5,

127.3, 125.5, 114.9, 78.0, 41.8, 35.7, 31.9, 30.5, 30.0, 22.8, 14.2, 0.3, 0.3; **IR** (film) ν = 2957, 2931,

1585, 1453, 1250, 866 cm^{-1}; **Anal. calcd.** for C$_{20}$H$_{30}$OSi: C 76.37, H 9.61; found C 76.24, H 9.79

3-hydroxy-1-(3-methyl-2-phenyloxiran-2-yl)-3-phenylpropan-1-one (22): To an oven dried 25 mL

round bottom flask equipped with a magnetic stir bar was added diene **4b** (92 mg, 0.3 mmol) in THF

(1.3 mL). To the stirred solution was added sequentially MeOH (2.7 mL), KF·H$_2$O (282 mg, 3.0 mmol),

KHCO$_3$ (300 mg, 3.0 mmol), and H$_2$O$_2$ (2.5 mL, ~23 mmol) dropwise with vigorous stirring. After

stirring the cloudy white suspension for 4 h TLC indicated consumption of the starting diene. Na$_2$S$_2$O$_{3(s)}$

(~1.0 g) was carefully added in small portions to consume remaining peroxides. The reaction was

diluted with EtOAc (20 mL) and washed with brine. The organics were dried over MgSO$_4$, filtered and

concentrated *in vacuo*. The crude oil was purified via flash column chromatography (silica gel 2.5 x 15

cm, eluted with 10% EtOAc/hexanes) to give ketone **22** as a clear oil (59 mg, 70% as a mixture of

diastereoisomers). R_f = 0.25 (20% EtOAc/hexanes); ^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.45-7.32 (m,

10H), 5.15 (t, *J* = 3.7 Hz, 0.5H), 5.12 (t, *J* = 3.7 Hz, 1H), 3.50 (q, *J* = 5.2 Hz, 0.5H), 3.43 (q, *J* = 5.2 Hz,

0.5H), 3.08-2.82 (m, 3H), 1.06 (d, *J* = 5.3 Hz, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ = 207.8, 207.8,

142.7, 142.6, 131.8, 128.6, 128.6, 128.5, 128.3, 128.1, 128.1, 127.8, 127.8, 125.8, 125.7, 69.9, 69.7,

68.1, 59.1, 58.8, 46.3, 45.9, 14.5, 14.4; **IR** (film): ν = 3511, 3060, 2967, 2926, 1708, 1494, 1022 cm^{-1};

Anal. calcd. for C$_{18}$H$_{18}$O$_3$: C 76.57, H 6.43; found: C 76.44, H 6.41

(E)-1-hydroxy-1,4-diphenylhex-4-en-3-one (23): To a flame dried 50 mL round bottom flask equipped

with a magnetic stir bar was added diene **4b** (92 mg, 0.3 mmol, 10:1, *Z:E*), DMF (15 mL), KHF$_2$ (71

mg, 0.9 mmol), propionic anhydride (0.96 mL, 7.5 mmol) and H_2O_2 (0.85 mL, 7.5 mmol) sequentially. The reaction was stirred at rt for 14 h then poured into water (15 mL), extracted with Et_2O (3 x 15 mL) washed with saturated $NaHCO_{3(aq)}$ (20 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified via flash column chromatography (silica gel 1.5 x 12 cm, gradient elution with 10-20% EtOAc/hexanes) to afford ketone **23** as a clear oil (68 mg, 85%, 13:1 mixture of double bond isomers). R_f = 0.22 (20% EtOAc/hexanes); **¹H NMR** (400 MHz, CDCl$_3$): δ = 7.41-7.28 (m, 8H), 7.09-7.07 (m, 2H), 7.04 (q, *J* = 7.2 Hz, 1H), 5.18 (dd, *J* = 7.4, 4.8 Hz, 1H) 3.65 (s, 1H), 2.98 (s, 1H), 2.96 (d, *J* = 3.3 Hz, 1H), 1.73 (d, *J* = 7.0 Hz, 3H); **minor isomer diagnostic peaks** δ = 5.53 (q, *J* = 7.4 Hz, 1H), 1.82 (d, *J* = 7.2 Hz, 3H); **¹³C NMR** (100 MHz, CDCl$_3$): δ = 200.7, 143.7, 142.9, 140.2, 135.1, 129.6, 128.4, 128.4, 127.7, 127.5, 125.7, 70.2, 47.8, 15.7; **IR** (film): ν = 3412, 3058, 2912, 1773, 1670, 1597, 1137, 700 cm^{-1}; **Anal. calcd.** for $C_{18}H_{18}O_2$: C 81.17, H 6.81; found: C 81.34, H 6.83

2,2-dimethyl-5-phenyl-3-((E)-1-phenyl-3-(p-tolyl)allylidene)-1,2-oxasilolane (24): To an oven dried 50 mL Schlenk tube equipped with magnetic stir bar was added 4-iodotoluene (164 mg, 0.75 mmol), K_2CO_3 (138 mg, 1.0 mmol), Pd(OAc)$_2$ (6.0 mg, 0.025 mmol) and diene **4b** (180 mg, 0.58 mmol) in DMF (5.0 mL). The reaction mixture was evacuated and purged with argon$_{(g)}$ three times, then stirred at 80 °C for 8 h. Once cooled to rt, the solution was diluted with EtOAc (20 mL), washed with water (2 x 30 mL), dried over $MgSO_4$, filtered and concentrated *in vacuo*. The crude oil was purified via flash column chromatography (silica gel 2.5 x 12 cm; 3% EtOAc/hexanes) to afford diene **24** as a yellow oil (126 mg, 64%). R_f = 0.51 (10% EtOAc/hexanes); **¹H NMR** (400 MHz, C$_6$D$_6$): δ = 7.44 (d, *J* = 8.2 Hz, 2H), 7.40-7.35 (m, 5H), 7.30-7.28 (m, 1H),7.25-7.21 (m, 5H), 7.08 (d, *J* = 7.8 Hz, 2H), 6.19 (d, *J* = 16.0 Hz, 1H), 5.11 (dd, *J* = 9.3, 5.3 Hz, 1H), 3.38 (dd, *J* = 16.3, 5.5 Hz, 1H), 2.69 (dd, *J* = 16.3, 9.5 Hz, 1H), 2.31 (s, 3H), 0.08 (s, 3H), -0.13 (s, 3H); **¹³C NMR** (100 MHz, C$_6$D$_6$): δ = 147.3, 144.8, 142.8, 142.0, 137.9, 134.6, 133.4, 129.8, 129.4, 128.5, 128.1, 127.4, 127.4, 127.0, 126.7, 125.5, 77.9, 42.3, 21.3, 0.5, 0.3; **IR** (film): ν = 3027, 2958, 1583, 1249, 1031, 862 cm^{-1}; **Anal. calcd.** for $C_{27}H_{28}OSi$: C 81.77, H 7.12; found: C 81.52, H 7.18

(E)-6-hydroxy-3-methyl-8-phenyloct-2-en-4-one (25): To a flame dried 50 mL round bottom flask equipped with a magnetic stir bar was added diene **17b** (105 mg, 0.39 mmol), DMF (15 mL), KHF$_2$ (91.3 mg, 1.17 mmol), propionic anhydride (1.6 mL, 9.75 mmol) and H$_2$O$_2$ (1.1 mL, 9.75 mmol) sequentially. The reaction was stirred at rt overnight then poured into water (25 mL), extracted with Et$_2$O (3 x 25 mL) washed with brine (25 mL), dried over MgSO$_4$, filtered and concentrated *in vacuo*. The crude oil was purified via flash column chromatography (silica gel 2.5 x 15 cm, gradient elution with 15-30% diethyl ether/hexanes) to afford ketone **25** as a clear oil (66 mg, 73%). **R$_f$** = 0.12 (20% diethyl ether/hexanes); **^{1}H NMR** (400 MHz, CDCl$_3$): δ = 7.30-7.16 (m, 5H), 6.75 (dq, *J* = 6.8, 1.6 Hz, 1H), 4.11-4.05 (m, 1H), 3.47 (br s, 1H), 2.88-2.81 (m, 2H), 2.75-2.67 (m, 2H), 1.91-1.82 (m, 4H), 1.77 (t, *J* = 1.2 Hz, 3H), 1.75-1.71 (m, 1H); **^{13}C NMR** (100 MHz, CDCl$_3$): δ = 202.5, 142.3, 139.0, 138.7, 128.7, 128.6, 126.0, 67.5, 43.6, 38.4, 32.1, 15.1, 11.0; **IR** (film): ν = 3496, 3061, 3026, 2927, 2860, 1655, 1496, 1451, 1073, 700 cm^{-1}; **Anal. calcd.** for C$_{15}$H$_{20}$O$_2$: C 77.55, H 8.68; found: C 77.71, H 8.54

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Supporting Information Available

^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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