JOC The Journal of Organic Chemistry

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

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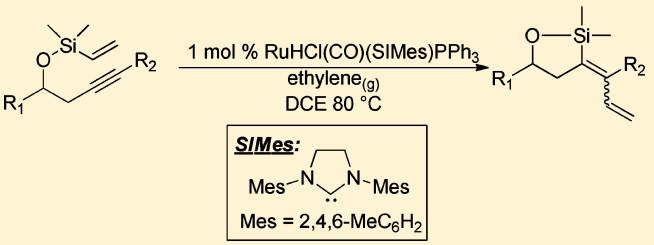
Supporting Information

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 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.

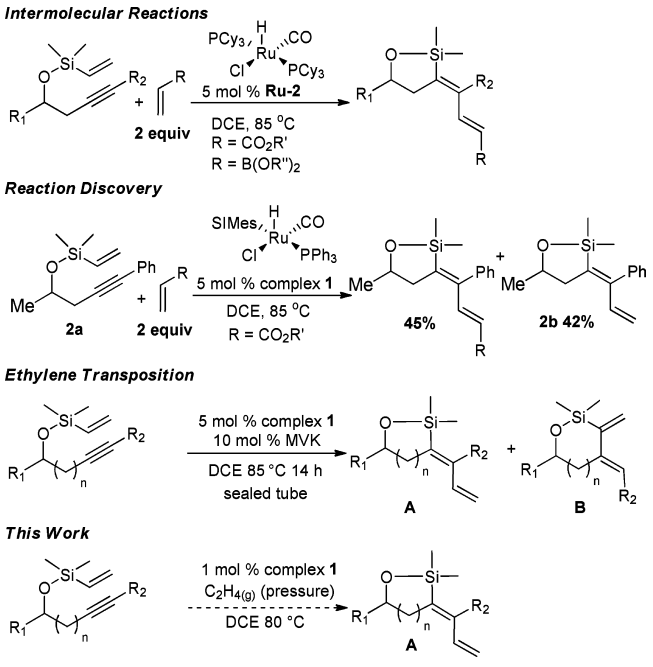


Figure 1. Silylvinylation of internal alkynes: discovery, previous work with methylvinylketone (MVK), and current work with ethylene.

Received: June 16, 2015
Published: August 4, 2015

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

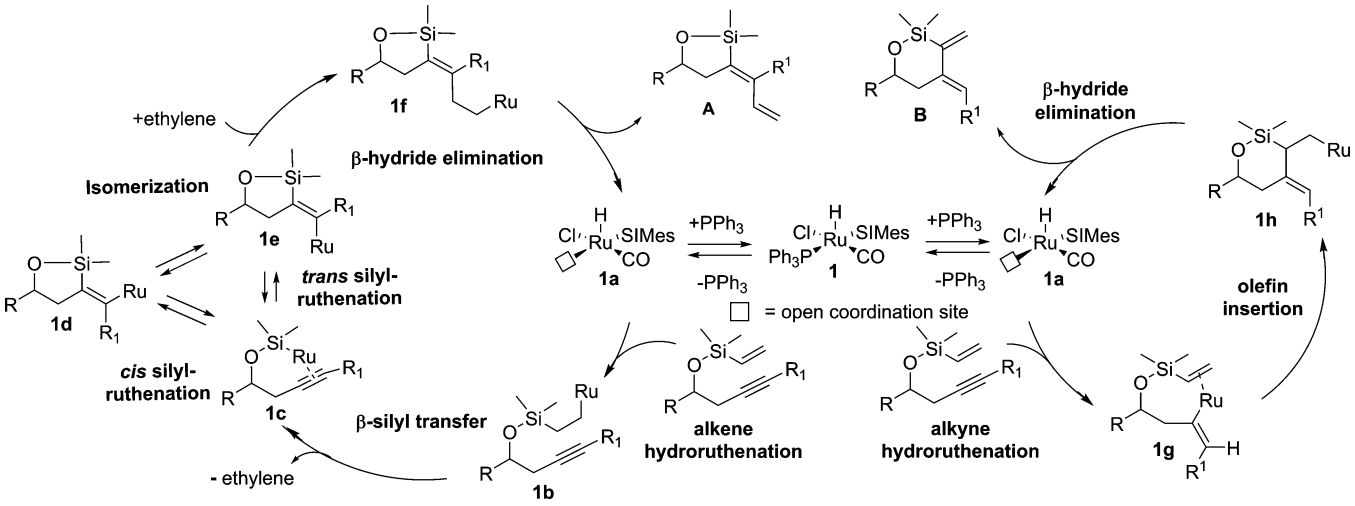
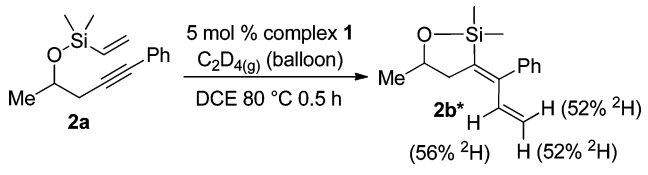


Figure 2. Mechanistic hypothesis.

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*-metalation (**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 π-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 β-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]

Scheme 1. Isotopic Labeling Experiment



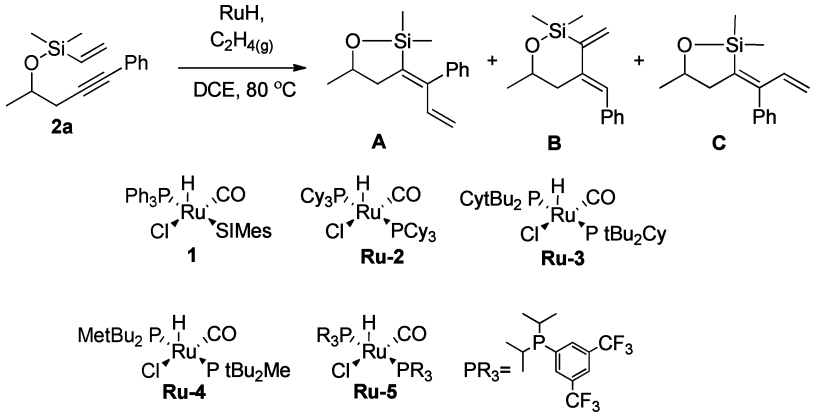
Based on our previous observations, we began our investigation with alkyne **2a** using ruthenium hydride **1** (1 mol %) under an atmosphere (balloon) of ethylene in 1,2-dichloroethane (DCE) at 80 °C.[14] We observed a rapid (1 h) reaction that produced silylvinylation product **2b** as a 9:1 mixture of *E* and *Z* isomers. This corroborates our assertion that *syn*-metalation (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 homopropargyl and propargyl positions. The reaction tolerated methyl and cyclohexyl groups at the homopropargyl 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.

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,

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290–8299

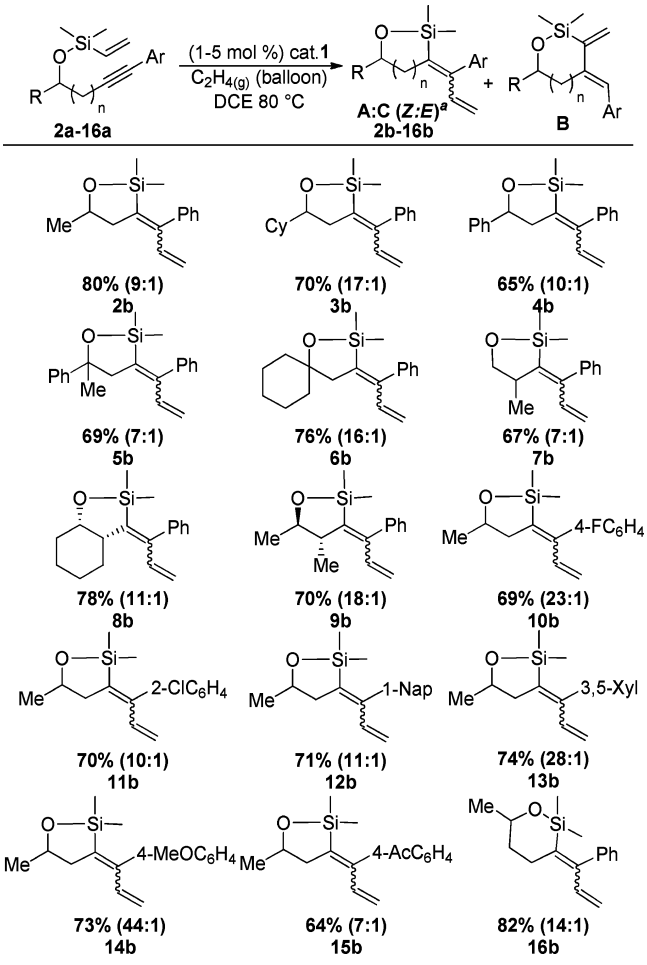
Table 1. Catalyst Screen



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

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

Scheme 2. Substrate Scope

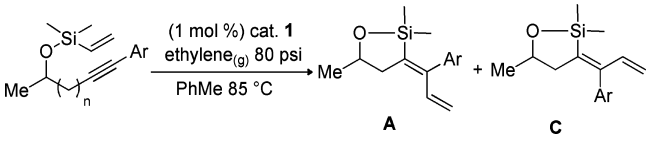


[a]Ratios determined by ^{1}H NMR using mesitylene as an internal standard. Products were isolated as a mixture of *Z*/*E* isomers (**A**/**C**).

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 buildup in the isomerization pathway. Conversely, the electron-withdrawing acetyl functionality destabilizes charge buildup 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 (≥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

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]

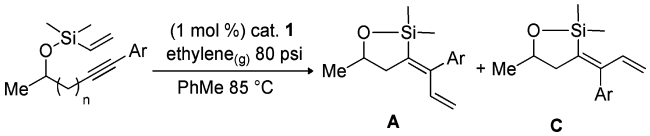
[a]Reactions were pressurized at room temperature prior to heating. [b]Determined by ^{1}H NMR. [c]23% conversion and 11% of **A** observed.

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

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.

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

Table 3. Electronic Differentiation of Alkyne Terminus at 80 psi Ethylene



entry	substrate	time (h)	conversion (%)	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 parentheses determined by ^{1}H NMR with mesitylene as an internal standard.

withdrawing groups gave ∼1:2 ratio of **A**/**C** (entries 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, that is, higher pressures and increased reaction times, to determine the intrinsic electronic preference.

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

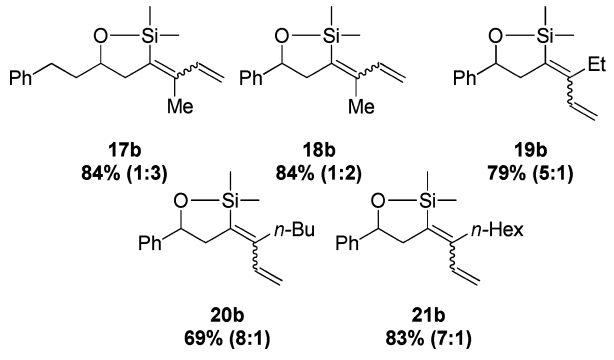
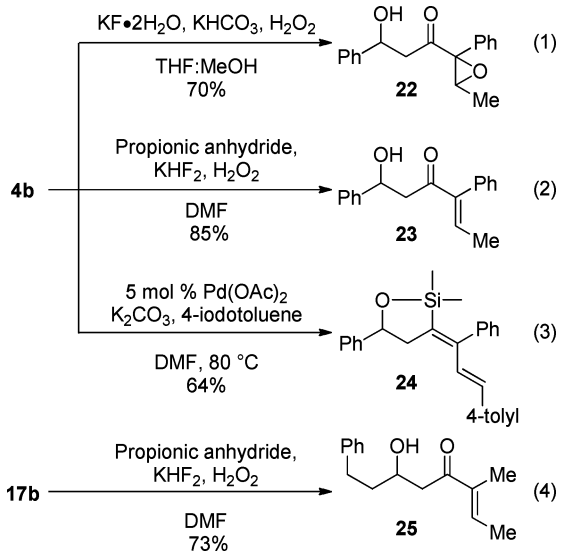


Figure 3. Reactions of internal alkyl alkynes at 80 psi. Ratio in parentheses is isomers **A** to **C** determined by ^{1}H NMR and confirmed by NOE or NOESY experiments.

carbons gave *n*-butyl **20b** in 69% yield, and further extension to *n*-hexyl provided **21b** in 83% yield. In the latter 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**.

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,

Scheme 3. Synthetic Elaboration of Dienes



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*′-hydroxyketones 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 $[(C_3H_5)PdCl]_2$, CuI, $KF{\cdot}2H_2O$, 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_2CO_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.

■ 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

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

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 epoxyketones 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 predried, 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**, and **17a** were prepared following the literature protocol.[12] Alkynes **9a**, **12a**, **13a**, **15a**, and **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 the 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 were 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 was stirred at rt for 2 h. The reaction mixture was poured into saturated $NH_4Cl_{(aq)}$ (30 mL), extracted with DCM (2 × 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) ν = 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 three-neck round-bottom flask equipped with a pressure equalizing addition funnel, large magnetic stir bar, and freshly prepared propargyl magnesium bromide (0.63 M in Et_2O, 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 1 M 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 were 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_2O 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 saturated $NaHCO_{3(aq)}$ (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 three-neck round-bottom flask equipped with a pressure equalizing addition funnel and large magnetic stir bar were 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, 2.5 M, 26.0 mmol) was added dropwise. After being stirred for 1 h, bromoethane (7.3 mL, 98 mmol) was added dropwise, and then the solution was warmed to rt and stirred overnight. The reaction mixture was quenched by the addition of saturated $NH_4Cl_{(aq)}$ (100 mL) at −78 °C (dry ice/acetone bath). The layers were separated, and the aqueous phase was extracted with Et_2O (2 × 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 were added the resulting orange oil (5.36 g, 21 mmol), EtOH (50 mL), and PPTS (1.56 g, 6.2 mmol). The orange solution was stirred at 50 °C for 4 h and then was cooled to rt and concentrated in vacuo. The residue was dissolved in DCM and washed with brine (2 × 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 were 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 °C (ice/H_2O bath), and vinyldimethylchlorosilane (1.8 mL, 12.7 mmol) was added dropwise. The resulting yellow suspension was stirred at rt overnight. The reaction was quenched with saturated $NH_4Cl_{(aq)}$ (50 mL), and the organics were dried over Na_2SO_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) ν = 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 three-neck round-bottom flask with a pressure equalizing addition funnel and magnetic stir bar were added 1-hexyne (4.1 g, 49.9 mmol) and THF (50 mL). The solution was cooled to −78 °C (dry ice/acetone bath), and *n*BuLi (30 mL, 1.66 M, 49.9 mmol) was added dropwise via addition funnel. After being stirred at −78 °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 of water and extracted with diethyl ether. The organic layer was washed with 1 M 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 were added the crude alcohol (1.57 g, 7.76 mmol) and DCM (50 mL). To the yellow solution were sequentially added imidazole (1.06 g, 15.52 mmol) and DMAP (0.2 equiv). The resulting mixture was cooled to 0 °C (ice/H_2O bath), and vinyldimethylchlorosilane was added dropwise. After being stirred at 0 °C for 10 min, the resulting suspension was allowed to warm to rt. After 4 h, the reaction was

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

quenched with saturated $NH_4Cl_{(aq)}$ (30 mL) and extracted with DCM (3 × 30 mL). The combined organics were washed with brine (2 × 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) ν = 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**, with 1-octyne (3.5 mL, 24 mmol), *n*BuLi (9.6 mL, 2.5 M, 24 mmol), styrene oxide (2.28 mL, 20 mmol) in HMPA (5.2 mL, 30 mmol). The reaction was poured into 100 mL of water and extracted with diethyl ether. The organic layer was washed with 1 M 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 were 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 was stirred overnight. The reaction mixture was poured into saturated $NH_4Cl_{(aq)}$ (30 mL), extracted with DCM (2 × 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) ν = 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 atm Ethylene (A). An oven-dried 50 mL Schlenk tube equipped with a magnetic stir bar was brought into an argon-filled glovebox. To the Schlenk tube was added RuHCl(CO)(SIMes)(PPh_3) (**1**) (1−5 mol %) followed by the alkyne substrate (1.0 equiv) in 1,2-dichloroethane or toluene (0.25M). The Schlenk tube was sealed and removed from the glovebox. The solution was purged with ethylene gas for 1−5 min 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 equiv) 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) were 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) were stirred under C_2D_4 (1 atm) at 80 °C for 30 min. Purification via flash column chromatography (1.5 × 15 cm, 2% diethyl ether/hexanes) gave diene **2b*** as a clear oil (155 mg, 63% as a *Z*/*E* mixture): % ^{2}H 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) were 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) were 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) were 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.

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

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) were 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) were 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) were 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) were 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) were 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) were 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, $CDCl_3$) 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) were 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) ν = 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) were stirred under ethylene (1 atm) at 85 °C for 1 h. Purification via flash column chromatography (2% diethyl ether/hexanes) gave

DOI: 10.1021/acs.joc.5b01374
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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) ν = 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) werestirred 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 $C_{16}H_{22}O_2Si$: 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) were 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 $C_{17}H_{22}O_2Si$: 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) were 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 glovebox. To the Fischer−Porter bottle were added RuHCl(CO)(SIMes)PPh_3 (**1**) and the alkyne in toluene. The bottle was plugged with a septum and removed from the glovebox. 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) and concentrated in vacuo, and a crude yield was obtained by ^{1}H NMR with mesitylene (0.33 equiv) 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) were 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) were 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 $C_{16}H_{22}O_2Si$: 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) were 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 $C_{17}H_{22}O_2Si$: C, 71.28; H, 7.74. Found: C, 71.03; H, 7.40.

DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299

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) were 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) were 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) were 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) were 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) were 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) were 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 were added sequentially MeOH (2.7 mL), KF·H_2O (282 mg, 3.0 mmol), $KHCO_3$ (300 mg, 3.0 mmol), and H_2O_2 (2.5 mL, ∼23 mmol) dropwise with vigorous stirring. After being stirred, the cloudy white suspension for 4 h TLC indicated consumption of the starting diene. $Na_2S_2O_{3(s)}$ (∼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 × 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 were 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 × 15 mL), washed with saturated $NaHCO_{3(aq)}$ (20 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude oil was purified

DOI: 10.1021/acs.joc.5b01374
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via flash column chromatography (silica gel 1.5 × 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); ^{1}H 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); ^{13}C 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 were 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 × 30 mL), dried over $MgSO_4$, filtered, and concentrated in vacuo. The crude oil was purified via flash column chromatography (silica gel 2.5 × 12 cm; 3% EtOAc/hexanes) to afford diene **24** as a yellow oil (126 mg, 64%): R_f = 0.51 (10% EtOAc/hexanes); ^{1}H NMR (400 MHz, C_6D_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); ^{13}C NMR (100 MHz, C_6D_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 were 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_2O_2 (1.1 mL, 9.75 mmol) sequentially. The reaction was stirred at rt overnight then poured into water (25 mL), extracted with Et_2O (3 × 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 × 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.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01374.

^{1}H and ^{13}C NMR spectra for all new compounds (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to the donors of the ACS PRF (DNI 50787), the NSF (CAREER CHE-1352432), and Syracuse University for generous financial support. We thank Alexandre D.C. Dixon for the synthesis of compounds **18a** and **20a**, and Daniel D. Nguyen for the synthesis of **19a**. We thank Prof. John Chisholm for critical reading of this manuscript.

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DOI: 10.1021/acs.joc.5b01374
J. Org. Chem. 2015, 80, 8290−8299