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Tandem dienyne ring-closing metathesis of alkynyl silaketals for the formation of bicyclic siloxanes

Jonathan B. Grimm, Ryan D. Otte, Daesung Lee *

Department of Chemistry, University of Wisconsin, 1101 University Avenue, Madison, WI 53706, USA

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Abstract

The tandem dienyne ring-closing metathesis of alkynyl silaketals containing two tethered olefins was achieved with second generation Grubbs NHC-ruthenium carbene complex to provide bicyclic siloxanes in good to excellent yield. Silaketals synthesized from homoallylic or bishomoallylic alcohols via base-catalyzed alcoholysis of trialkynylsilanes were well tolerated in the metathesis process and generated ring systems of various sizes. Removal of the silicon tether was achieved through protodesilylation with fluoride to afford stereochemically defined (1*E*,3*Z*)-dienes.

Keywords: Ruthenium carbene complexes; *N*-Heterocyclic carbenes; Enyne metathesis; Silicon tethering; 1,3-Dienes

1. Introduction

Olefin metathesis has emerged as one of the most powerful carbon–carbon bond-forming methods in the past decade, exerting a profound impact in synthetic chemistry [1]. The growing field of research in metathesis processes has been driven by the development of well-defined ruthenium [2], molybdenum [1d,3], and tungsten-based [1d,4] catalyst systems that show excellent reactivity and a wide range of functional group tolerance. Among these catalysts, ruthenium-based Grubbs and Hoveyda-type complexes **1**–**3** are most relevant for the metathesis between alkenes and alkynes (enyne metathesis) to generate 1,3-dienes [5] (see Fig. 1).

Recently, enyne metathesis has gained growing attention due to its inherently tandem bond-forming nature, allowing the synthesis of multiple conjugated bonds and rings per synthetic step. The limited substrate scope of enyne metathesis has been significantly broadened by the use of very reactive NHC-ruthenium carbene catalysts, subsequently becoming one of the most powerful and practical methods for the formation of 1,3-dienes from alkenes and alkynes [2,5]. Depending on the mode of bond formation between the reacting alkene and alkyne, either a 1,2- or 1,3-substituted 1,3-diene (**5** or **6**) can be formed (Scheme 1). There is, however, no mechanism within enyne metathesis for regio- and stereoselective generation of 1,4-substituted 1,3-dienes (**7**). Given that 1,4-substitution is more frequently found in many natural products and synthetic intermediates [6], this limitation of the scope of enyne ring-closing metathesis (RCM) is significant. Conceptually, this restriction can be eliminated if the temporary tether strategy is integrated into enyne metathesis, as demonstrated in Scheme 1. This process combines an enyne RCM and a diene RCM to generate a bicyclic structure (**8**) via *tandem dienyne metathesis* [5c,7]. Removal of the tethered X group would then provide a 1,4-substituted *E*,*Z*-diene **7**.

In choosing a tethering technology (“X”) for use in this application, the silyloxy functionality presents itself as an ideal choice. The silyl ether is one of the most

* Corresponding author. Tel.: +1 608 265 8431; fax: +1 608 265 4534.
E-mail address: dlee@chem.wisc.edu (D. Lee).

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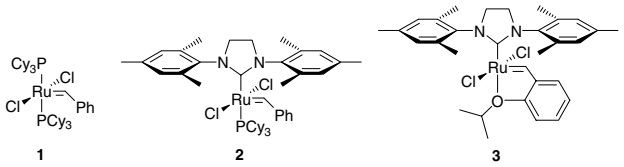
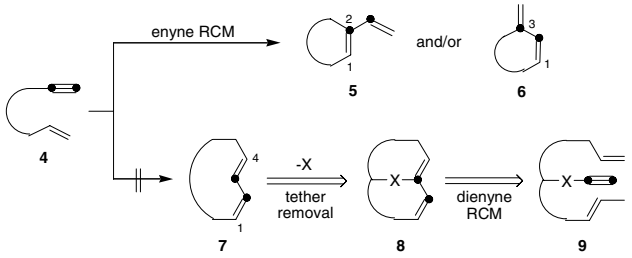


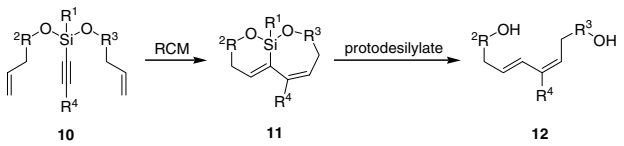
Fig. 1. Transition metal carbene catalysts for metathesis.



Scheme 1. Generation of disubstituted 1,3-dienes by ring-closing metathesis.

widely used protecting [8] and tethering [9] groups in modern synthetic chemistry due to the ease of its formation and removal; temporary silicon tethering (TST) with the silyl ether has become increasingly widespread in recent years. An extensive variety of transformations has been achieved with silyl ether and silaketal tethers, including Diels–Alder reactions [10], 1,3-dipolar cycloadditions of nitronates and nitrones [11], Heck couplings [12], silylformylation–allylsilylations [13], alkyne cyclocarbonylations [14], and metal-mediated cyclizations [15]. Various research groups have pursued the use of silicon tethering in diene ring-closing metathesis [16], but there are far fewer examples of silicon-tethered enyne RCM [17]. Previous work has also demonstrated the viability and utility of dienyne RCM in all-carbon systems [7,18], as well as those containing nitrogen [19] and phosphorus [20] "tethers." To broaden the scope of this strategy, we recently developed an efficient silicon tethering approach to form silaketal-based dienyne RCM substrates and briefly demonstrated the tandem metathesis of this new substrate class to form fused bicycles [21]. Herein we report the further exploration of the silicon-tethered dienyne RCM process and its application to the stereochemically controlled synthesis of 1,3-dienes.

This study has been undertaken to investigate the dienyne ring-closing metathesis of alkynyl silaketals **10** with ruthenium carbene catalysts (**1**–**3**) to form bicyclic siloxanes represented by **11** (Scheme 2). Application of our previous work on the base-catalyzed alcoholysis of alkynylsilanes allows for efficient access to the unusual silaketal substrates [21]. The union of the silicon tether with the capacity of dienyne metathesis to form multiple carbon–carbon bonds in tandem fashion provides an



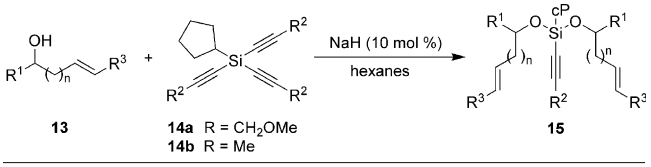
Scheme 2. Tandem dienyne RCM of alkynyl silaketals.

efficient tool to synthesize cyclic structures possessing a 1,4-disubstituted 1,3-diene. Protodesilylation would also provide straightforward access to dienes **12** free of the silicon tether. This process could be extremely useful to the synthetic organic chemist, as it meets many important goals simultaneously, including the synthesis of stereochemically defined alkenes, a rapid increase in molecular complexity, and annulation to form functionalized rings of various sizes.

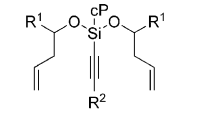
2. Results and discussion

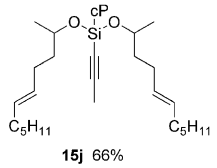
The silaketal substrates necessary for the exploration of this methodology (Table 1) were synthesized through the reaction of trialkynylsilanes with alcohols in the presence of a catalytic amount of base. The specific trialkynylsilanes – **14a** and **14b** – were chosen on the basis of their moderate reactivity and stability, as well as the high volatility of the alkyne byproduct of the alcoholysis reaction. A series of silylation reactions was performed with silanes **14a** and **14b** and a variety of secondary alcohols to generate silaketals **15a**–**15j** (Table 1). The

Table 1
Symmetrical alkynyl silaketals from trialkynylsilane

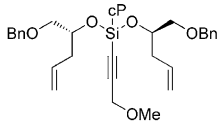


	R^1	R^2	
15a	Me	CH_2OMe	70%
15b	C_5H_{11}	CH_2OMe	71%
15c	CH_2CH_2Ph	CH_2OMe	74%
15d	C_5H_{11}	Me	79%
15e	CH_2CH_2Ph	Me	82%

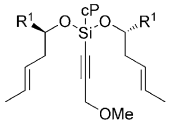




15j 66%



15f 67%

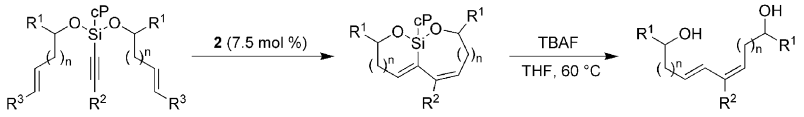


	R^1	
15g	C_5H_{11}	81%
15h	CH_2CH_2Ph	81%
15i	Ph	74%

optimal conditions involved the use of a catalytic amount of NaH (10 mol%) in hexanes. In nearly all cases, employment of two equivalents of alcohol cleanly afforded the desired alkynyl silaketal with only trace amounts of the trialkoxysilane, which was easily removed by chromatography. The transformation was generally complete in a few minutes at room temperature for **14a**; silane **14b** required an elevated reaction temperature (50 °C) for 1–2 h to achieve complete conversion. Because the secondary alcohols employed in the formation of silaketals **15a**–**15e** and **15j** were racemic, these alkynyl silaketals were obtained as diastereomeric mixtures (the two meso compounds *RS* and *SR* and the enantiomeric pair *RR*|*SS*). However, the ^{1}H and ^{13}C NMR spectra of these silaketals showed only small distinctions (if any) between the diastereomeric resonances. Only single sets of signals were seen in the NMR spectra of **15f**–**15i**, as they were derived from the corresponding enantiomerically pure secondary alcohols [22].

With the necessary silaketals in hand, we examined their reactivity in enyne ring-closing metathesis. When silaketals **15a**–**15j** were treated with a catalytic amount of second generation Grubbs catalyst (**2**), the bicyclic siloxanes **16a**–**16j** were universally provided in moderate to excellent yields in 3–4 h (Table 2). Small amounts of monocyclized material were isolated in most cases, and the desired product was purified by flash chromatography without difficulty. Cyclization of silaketals **15a**–**15f** proceeded easily at reflux (40 °C) in CH_2Cl_2 (2–3 mM), whereas reaction of those with disubstituted alkenes (**15g**–**15j**) required a higher reaction temperature (110 °C in toluene). These results indicated that the tandem enyne metathesis was amenable to terminal as well as internal double bonds. Although the majority of the siloxane products contain [5.4.0] ring systems,

Table 2
Tandem dienyne RCM of alkynyl silaketals and protodesilylation of siloxane products



15 **16** **17**

Alkynyl silaketal[a]	RCM conditions[b]	RCM product	Yield (%)	Protodesilylation diol	Yield (%)
15a R = Me	CH_2Cl_2, 40 °C	**16a**	75%	**17a**	68%
15b R = C_5H_{11}	CH_2Cl_2, 40 °C	**16b**	90%	**17b**	89%
15c R = CH_2CH_2Ph	CH_2Cl_2, 40 °C	**16c**	89%	**17c**	78%
15d R = C_5H_{11}	CH_2Cl_2, 40 °C	**16d**	73%	**17d**	70%
15e R = CH_2CH_2Ph	CH_2Cl_2, 40 °C	**16e**	88%	**17e**	65%
15f	CH_2Cl_2, 40 °C	**16f**	83%	**17f**	68%
15g R = C_5H_{11}	toluene, 110 °C	**16g**	96%	**17g**	87%
15h R = CH_2CH_2Ph	toluene, 110 °C	**16h**	88%	**17h**	83%
15i R = Ph	toluene, 110 °C	**16i**	75%	**17i**	88%
15j	toluene, 110 °C	**16j**	76%	**17j**	50%

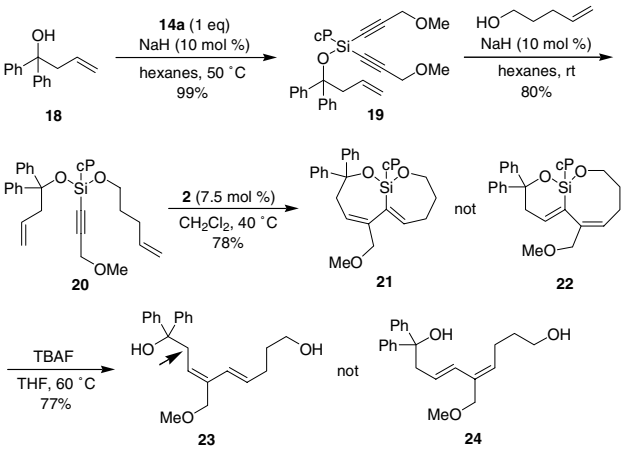
[a] cP, cyclopentyl.
[b] All reactions performed at 2–3 mM in the indicated solvent with 7.5 mol% of catalyst **2**.

silaketals with longer tethers were well tolerated (e.g., **16j**, a [6.5.0] bicycle).

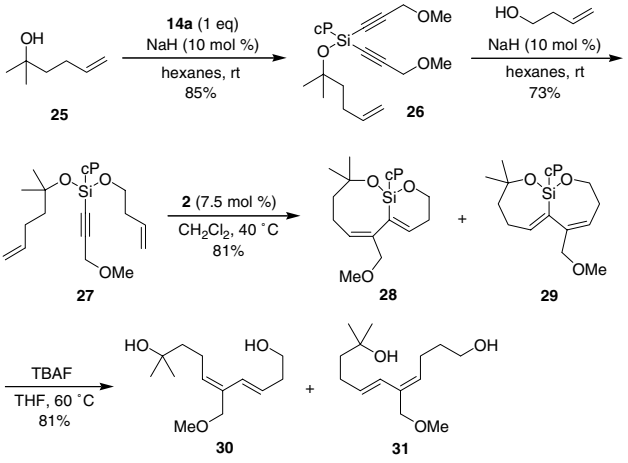
The siloxanes **16f–16i** derived from homochiral silaketals were formed as nearly 1:1 mixtures of diastereomers, where the two diastereomeric products were often separable on chromatography and allowed precise and unambiguous characterization of the bicycles. These results clearly indicated that the RCM reaction was not stereoselective for a particular configuration at silicon. Diastereomeric olefin resonances consistent with this lack of selectivity were also present in the spectra of **16a–16e** and **16j**, although the ^{1}H and ^{13}C NMR were more difficult to fully analyze due to the presence, in each case, of four nearly inseparable diastereomers.

Critical to the utility of a tethered RCM strategy is the removal of the temporary tether subsequent to the metathesis step. Excision of the silicon moiety from the bicyclic siloxanes was easily achieved through protodesilylation. Treatment of siloxanes **16a–16j** with an excess of TBAF in THF at reflux [13] yielded diols **17a–17j** in moderate to good yield after only 30–45 min (Table 2). Protodesilylation proceeded with retention of double bond configuration. This was evidenced by the coupling constants observed for the disubstituted alkene moieties, which were characteristic in magnitude of *trans* olefins (e.g., $J = 15.8$ Hz for **17f**). Notably, diols that existed as mixtures of two diastereomers (**17a–17f**, **17j**) behaved in the ^{1}H and ^{13}C NMR as essentially single compounds. This fortuity allowed for unequivocal characterization of the final products, particularly in those cases where it was not possible to fully characterize the siloxane intermediates (**16a–16f**, **16j**).

The tandem enyne RCM of *symmetrical* silaketals eschews a significant issue that becomes relevant when considering the same process in *unsymmetrical* silaketals: chemoselectivity (“group selectivity”). In order to begin to explore this matter, we synthesized two distinct, unsymmetrical silaketals (**20** and **27**), each containing two alkenes with tethers of different length and substitution (Schemes 3 and 4). Silane **14a** was first reacted with a single equivalent of tertiary alcohol **18** or **25** and catalytic NaH to give silyl ethers **19** and **26** in excellent yield (formation of the former required elevated temperature). The alcoholysis reaction was repeated a second time with either 3-buten-1-ol or 4-penten-1-ol (1 equivalent) to accrue the desired silaketals **20** and **27** in 73–80% yield. Exposure of **20** to ruthenium catalyst **2** in CH_2Cl_2 (3 mM) at 40 °C led to rapid formation of a single product **21** in 78% yield. This surprising result was further corroborated by protodesilylation with TBAF to afford only the diol **23** (77%). Unambiguous assignment of the product structures shown in Scheme 3 was achieved through a homonuclear decoupling experiment. When the vinyl proton of the trisubstituted double bond in **23** was radiated, loss of doublet splitting for the indicated methylene protons adjacent to the tertiary alkoxy



Scheme 3. Selective tandem dienyne RCM of an unsymmetrical silaketal.



Scheme 4. Nonselective tandem dienyne RCM of an unsymmetrical silaketal.

carbon was observed. This required that the siloxane RCM product was the [5.5.0] bicycle, which must result from initial enyne metathesis of the longer, less substituted tether of **20**. Unexpectedly, RCM of **27** (Scheme 4) did not possess the same selectivity, and a 1.5:1 mixture of the two possible siloxanes **28** and **29** was isolated (the identities of the major and minor products were not clear from the spectral data). Although protodesilylation of this mixture proceeded without incident to yield **30** and **31**, separation of the two diols was not possible. The reasons for the surprising selectivity seen in the RCM of **20** – and lack of such group selectivity in the case of **27** – are not yet clear, and work is ongoing to obtain more insight into the observed selectivity.

3. Conclusion

In summary, we have developed an efficient tandem dienyne ring-closing metathesis of alkynyl silaketals to

generate bicyclic siloxanes in the presence of Grubbs NHC-ruthenium catalyst. Removal of the silicon tether through protodesilylation allows for the generation of stereochemically defined 1,4-substituted 1,3-dienes. Further exploration of the derivatization and elaboration of these siloxanes – as well as the selectivity of the dienyne RCM of unsymmetrical alkynyl silaketals – is in progress.

4. Experimental

4.1. General information

Hexanes, dichloromethane (CaH_2), and THF (sodium/benzophenone) were freshly distilled prior to use. Reactions were monitored by thin layer chromatography (TLC) on precoated TLC glass plates (silica gel 60 F_{254}, 250 μm thickness). Silica gel (60 Å porosity, 32–63 μm particle size) was used for flash chromatography. ^1H and ^{13}C NMR were obtained on 250 and 300 MHz spectrometers; chemical shifts (δ) are reported relative to an internal standard of tetramethylsilane (TMS). High resolution mass spectra were obtained using Leu5-enkephalin or erythromycin as a lock mass on an ESI-TOF spectrometer equipped with Z-spray and a reflectron.

4.2. Synthesis of symmetrical silaketals *15a–15j*

The following procedure for **15a** is representative. Silane **14a** (200 mg, 0.66 mmol) and 4-penten-2-ol (114 mg, 1.32 mmol) were dissolved in hexanes (4 mL). Sodium hydride (60% dispersion in mineral oil, 5 mg, 0.13 mmol) was added, and the reaction was stirred at room temperature for 20 min. The solution was then filtered through a short plug of Celite, and evaporation of the solvent afforded a yellow residue. Flash chromatography of the crude product on silica gel with 99:1 to 97:3 hexanes:ether yielded 156 mg (70%) of **15a** as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.83 (2H, ddt, J = 17.2, 10.2, 7.1 Hz), 5.10–5.00 (4H, m), 4.23–4.10 (2H, m), 4.13 (2H, s), 3.39 (3H, s), 2.39–2.15 (4H, m), 1.85–1.70 (2H, m), 1.67–1.43 (6H, m), 1.21 (6H, d, J = 6.4 Hz) 1.11–0.97 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.3, 116.9, 101.4, 101.3, 101.2, 86.4, 86.3, 86.2, 69.5, 69.4, 60.4, 57.6, 43.9, 27.3, 27.2, 27.1, 24.7, 24.6, 23.0; HRMS (ESI) calc. for $C_{19}H_{32}O_3Si$ $[M + Na]^+$ 359.2024, found 359.2018.

15b *(71%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.85 (2H, ddt, J = 17.2, 10.4, 7.2 Hz), 5.10–4.98 (4H, m), 4.12 (2H, s), 4.01 (2H, pentet, J = 5.5 Hz), 3.39 (3H, s), 2.36–2.25 (4H, m), 1.84–1.69 (2H, m), 1.66–1.19 (22H, m), 1.10–0.97 (1H, m), 0.94–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.4, 116.81, 116.77, 101.3, 86.8, 73.1, 60.4, 57.6, 41.7, 41.6, 36.5, 36.4, 32.1, 27.4, 27.1, 25.13, 25.08, 24.9, 22.8, 14.2; HRMS (ESI) calc. for $C_{27}H_{48}O_3Si$ $[M + Na]^+$ 471.3270, found 471.3292.

15c *(74%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.30–7.12 (10H, m), 5.94–5.77 (2H, m), 5.13–4.99 (4H, m), 4.16–4.07 (4H, m), 3.363 (0.75H, s), 3.356 (1.50H, s), 3.351 (0.75H, s), 2.85–2.57 (4H, m), 2.48–2.30 (4H, m), 1.92–1.73 (6H, m), 1.69–1.46 (6H, m), 1.15–1.00 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.7, 134.9, 128.6, 128.5, 125.8, 117.3, 101.8, 86.62, 86.56, 86.49, 72.7, 60.3, 57.7, 41.7, 41.6, 38.3, 31.9, 27.4, 27.2, 24.9; HRMS (ESI) calc. for $C_{33}H_{44}O_3Si$ $[M + Na]^+$ 539.2957, found 539.2983.

15d *(79%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.95–5.76 (2 H, m), 5.09–4.97 (4H, m), 3.99 (2H, pentet, J = 5.6 Hz), 2.39–2.22 (4H, m), 1.89 (3H, s), 1.82–1.68 (2H, m), 1.63–1.19 (22H, m), 1.06–0.94 (1H, m), 0.93–0.84 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.6, 116.6, 103.0, 79.2, 72.9, 41.8, 41.7, 36.6, 36.4, 32.2, 27.5, 27.2, 25.1, 22.9, 14.3, 4.9; HRMS (ESI) calc. for $C_{26}H_{46}O_2Si$ $[M + Na]^+$ 441.3165, found 441.3157.

15e *(82%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.34–7.09 (10H, m), 5.96–5.76 (2H, m), 5.13–4.98 (4H, m), 4.17–4.02 (2H, m), 2.86–2.71 (2H, m), 2.70–2.56 (2H, m), 2.48–2.29 (4H, m), 1.88 (3H, s), 1.87–1.71 (6H, m), 1.68–1.45 (6H, m), 1.10–0.96 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.9, 135.2, 128.5, 125.8, 117.1, 103.5, 79.1, 72.5, 41.8, 38.4, 31.9, 27.5, 27.2, 25.1, 4.9; HRMS (ESI) calc. for $C_{32}H_{42}O_2Si$ $[M + Na]^+$ 509.2852, found 509.2856.

15f *(67%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37–7.22 (10H, m), 5.93–5.75 (2H, m), 5.13–4.98 (4H, m), 4.53–4.49 (4H, m), 4.22 (2H, sextet, J = 5.6 Hz), 4.07 (2H, s), 3.55–3.39 (4H, m), 3.35 (3H, s), 2.51–2.23 (4H, m), 1.82–1.67 (2H, m), 1.65–1.39 (6H, m), 1.14–0.99 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.7, 134.8, 128.4, 127.7, 127.6, 117.31, 117.26, 101.7, 86.0, 73.6, 73.5, 73.4, 72.0, 71.9, 60.3, 57.6, 38.9, 27.3, 27.2, 27.1, 24.6; HRMS (ESI) calc. for $C_{33}H_{44}O_5Si$ $[M + Na]^+$ 571.2856, found 571.2866.

15g *(81%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.53–5.35 (4H, m), 4.13 (2H, s), 4.00–3.89 (2H, m), 3.39 (3H, s), 2.30–2.14 (4H, m), 1.83–1.17 (30H, m), 1.10–0.96 (1H, m), 0.94–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 127.8, 127.22, 127.15, 101.1, 87.0, 73.55, 73.51, 60.4, 57.6, 40.5, 40.4, 36.6, 36.4, 32.21, 32.18, 27.4, 27.2, 25.2, 25.1, 25.0, 22.9, 18.2, 14.2; HRMS (ESI) calc. for $C_{29}H_{52}O_3Si$ $[M + Na]^+$ 499.3583, found 499.3562.

15h *(81%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.31–7.11 (10H, m), 5.56–5.38 (4H, m), 4.11 (2H, s), 4.10–4.01 (2H, m), 3.36 (3H, s), 2.85–2.71 (2H, ddd, J = 13.8, 10.2, 6.4 Hz), 2.69–2.56 (2H, m), 2.40–2.22 (4H, m), 1.91–1.47 (18H, m), 1.14–1.00 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.9, 128.6, 128.5, 127.7, 127.40, 127.38, 125.8, 101.6, 86.8, 73.2, 60.4, 57.6,

40.6, 40.4, 38.34, 38.27, 31.9, 27.4, 27.2, 25.0, 18.2; HRMS (ESI) calc. for $C_{35}H_{48}O_3Si$ $[M + Na]^+$ 567.3270, found 567.3276.

15i *(74%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.37–7.08 (10H, m), 5.50–5.12 (4H, m), 4.95 (1H, dd, $J = 6.8$, 6.0 Hz), 4.68 (1H, t, $J = 6.4$ Hz), 4.00 (2H, s), 3.25 (3H, s), 2.55–2.15 (4H, m), 1.71–1.33 (14H, m), 1.02–0.89 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 144.3, 144.2, 128.1, 127.9, 127.8, 127.6, 127.4, 127.2, 127.1, 127.0, 126.4, 126.3, 101.8, 86.1, 75.9, 75.6, 60.2, 57.5, 43.7, 43.5, 27.1, 24.5, 18.2, 18.1; HRMS (ESI) calc. for $C_{31}H_{40}O_3Si$ $[M + Na]^+$ 511.2644, found 511.2631.

15j *(66%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.49–5.32 (4H, m), 4.16–4.00 (2H, m), 2.12–1.92 (8H, m), 1.89 (3H, s), 1.82–1.69 (2H, m), 1.67–1.41 (10H, m), 1.40–1.23 (12H, m), 1.23–1.15 (6H, m), 1.05–0.93 (1H, m), 0.93–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 130.6, 130.2, 102.7, 79.0, 69.2, 39.5, 32.8, 31.6, 29.6, 29.0, 27.5, 27.2, 24.9, 23.5, 22.8, 14.3, 4.9; HRMS (EI) calc. for $C_{30}H_{54}O_2Si$ $[M]^+$ 474.3893, found 474.3879.

*4.3. Dienyne RCM of alkynyl silaketals to generate siloxanes **16a–16j, 21, 28, 29***

The following procedure for **16f** is representative. Silaketal **15f** (100 mg, 0.180 mmol) was dissolved in dry CH_2Cl_2 (90 mL) in a 200 mL round bottom flask equipped with a reflux condenser. Nitrogen was bubbled through the solution for 20 min before adding catalyst **2** (12 mg, 0.014 mmol) in CH_2Cl_2 (5 mL). The reaction was then stirred at reflux until complete by TLC (approximately 4 h). The solvent was removed to yield a brown residue that was flash chromatographed on silica with 95:5 to 85:15 hexanes:ether, affording 78 mg (83%) of **16f** as a colorless, viscous oil (diastereomers not separable). ^1H NMR ($CDCl_3$, 250 MHz) δ 7.37–7.22 (10H, m), 6.81–6.72 (1H, m), 5.68 (0.5H, t, $J = 7.0$ Hz), 5.59–5.52 (0.5H, m), 4.61–4.50 (4H, m), 4.37–4.25 (1H, m), 4.22–4.10 (1H, m), 4.08–3.90 (2H, m), 3.64–3.34 (4H, m), 3.320 (1.5H, s), 3.316 (1.5H, s), 2.67–2.15 (4H, m), 1.85–1.33 (8H, m), 1.14–0.96 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 143.0, 142.1, 140.8, 139.0, 138.62, 138.55, 136.9, 134.7, 134.4, 128.5, 127.9, 127.8, 127.7, 126.2, 124.7, 75.8, 74.6, 74.5, 74.3, 73.6, 73.5, 73.2, 72.8, 71.3, 70.7, 70.4, 58.0, 57.9, 37.0, 33.8, 33.6, 32.1, 27.5, 27.4, 27.2, 27.1, 27.0, 26.8, 24.6, 24.2; HRMS (ESI) calc. for $C_{31}H_{40}O_5Si$ $[M + Na]^+$ 543.2543, found 543.2558.

16g *(96%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) diastereomer 1: δ 6.77 (1H, dd, $J = 6.9$, 2.5 Hz), 5.64 (1H, t, $J = 6.7$ Hz), 4.11–3.88 (4H, m), 3.32 (3H, s), 2.50–2.31 (2H, m), 2.30–2.06 (2H, m), 1.81–1.19 (24H, m), 1.10–0.95 (1H, m), 0.94–0.82 (6H, m); diastereomer 2: δ 6.75 (1H, dd, $J = 5.5$, 3.5 Hz), 5.52 (1H, t, $J = 4.5$ Hz), 4.17–4.03 (2H, m), 4.03–3.91 (2H, AB of ABX, $\nu_A = 1198.8$, $J_{AX} = 1.1$, $\nu_B = 1183.5$, $J_{BX} = 0.9$, $J_{AB} = 11.8$ Hz), 3.33 (3H, s), 2.49 (1H, dt, $J = 17.7$, 4.1 Hz), 2.41–2.33 (2H, m), 2.24 (1H, ddd, $J = 17.7$, 5.5, 4.6 Hz), 1.82–1.20 (24H, m), 1.11–0.97 (1H, m), 0.93–0.84 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) diastereomer 1: δ 142.6, 138.1, 137.1, 125.3, 76.1, 73.9, 72.0, 57.8, 37.9, 36.8, 36.5, 32.1, 32.0, 27.4, 27.1, 27.0, 26.0, 25.8, 25.1, 24.4, 22.9, 22.8, 14.2; diastereomer 2: δ 141.8, 135.5, 134.4, 126.8, 77.4, 72.2, 71.4, 57.9, 40.1, 38.5, 37.1, 35.1, 32.1, 27.6, 27.3, 27.0, 26.8, 26.1, 25.7, 24.7, 22.9, 22.8, 14.3; HRMS (ESI) calc. for $C_{25}H_{44}O_3Si$ $[M + Na]^+$ 443.2957, found 443.2945.

16h *(88%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) diastereomer 1: δ 7.31–7.10 (10H, m), 6.73 (1H, t, $J = 5.1$ Hz), 5.63 (1H, t, $J = 6.9$ Hz), 4.08–3.91 (4H, m), 3.31 (3H, s), 2.88–2.62 (4H, m), 2.52–2.28 (2H, m), 2.25–2.17 (2H, m), 2.04–1.32 (12H, m), 1.13–0.99 (1H, m); diastereomer 2: δ 7.31–7.11 (10H, m), 6.70 (1H, t, $J = 4.5$ Hz), 5.49 (1H, t, $J = 4.5$ Hz), 4.24–4.06 (2H, m), 4.01–3.88 (2H, AB of ABX, $\nu_A = 1190.2$, $J_{AX} = 1.1$, $\nu_B = 1176.1$, $J_{BX} = 1.0$, $J_{AB} = 12.0$ Hz), 3.32 (3H, s), 2.94–2.58 (4H, m), 2.49–2.19 (4H, m), 2.12–1.97 (1H, m), 1.93–1.38 (11H, m), 1.14–1.00 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) diastereomer 1: δ 142.7, 142.6, 142.5, 138.6, 137.1, 128.8, 128.7, 128.4, 125.8, 124.8, 75.9, 73.2, 70.9, 57.9, 39.7, 39.5, 36.8, 36.7, 32.3, 31.5, 27.5, 27.1, 27.03, 26.99, 24.4; diastereomer 2: δ 142.6, 142.2, 135.2, 134.6, 128.9, 128.6, 128.5, 128.3, 126.1, 125.9, 125.8, 77.3, 71.3, 70.5, 57.9, 40.14, 40.08, 38.8, 35.6, 32.3, 32.1, 27.7, 27.4, 27.0, 26.8, 24.9; HRMS (ESI) calc. for $C_{31}H_{40}O_3Si$ $[M + Na]^+$ 511.2644, found 511.2654.

16i *(75%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) diastereomer 1: δ 7.46–7.17 (10H, m), 6.81 (1H, dd, $J = 6.6$, 2.8 Hz), 5.81 (1H, t, $J = 7.3$ Hz), 5.17 (1H, d, $J = 8.1$ Hz), 5.06 (1H, dd, $J = 10.2$, 3.0 Hz), 4.05 (2H, s), 3.37 (3H, s), 2.88–2.75 (1H, m), 2.53–2.32 (3H, m), 1.91–1.75 (2H, m), 1.71–1.46 (6H, m), 1.31–1.16 (1H, m); diastereomer 2: δ 7.41–7.11 (10H, m), 6.90 (1H, t, $J = 4.4$ Hz), 5.51 (1H, t, $J = 4.3$ Hz), 5.27 (1H, t, $J = 5.1$ Hz), 4.87 (1H, dd, $J = 9.8$, 2.0 Hz), 4.09–3.94 (2H, AB of ABX, $\nu_A = 1213.4$, $J_{AX} = 1.0$, $\nu_B = 1191.6$, $J_{BX} = 1.0$, $J_{AB} = 11.7$ Hz), 3.36 (3H, s), 2.78 (2H, t, $J = 4.9$ Hz), 2.63–2.39 (2H, m), 1.95–1.78 (2H, m), 1.70–1.45 (6H, m), 1.28–1.14 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) diastereomer 1: δ 145.0, 144.4, 143.5, 140.0, 137.7, 128.4, 128.3, 127.4, 127.1, 125.7, 125.6, 124.1, 76.3, 75.7, 74.2, 58.2, 39.8, 39.5, 27.5, 27.3, 27.1, 24.2; diastereomer 2: δ 144.8, 143.4, 142.7, 135.5, 134.3, 128.3, 128.1, 127.0, 126.3, 126.1, 125.7, 77.4, 73.1, 72.0, 58.1, 43.4, 35.9, 27.7, 27.4, 27.1, 26.9, 24.7; HRMS (ESI) calc. for $C_{27}H_{32}O_3Si$ $[M + Na]^+$ 455.2018, found 455.2032.

21 *(78%, colorless oil)*. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.55–7.42 (4H, m), 7.32–7.11 (6H, m), 6.52 (1H, t, $J = 7.1$ Hz), 5.44 (1H, t, $J = 7.7$ Hz), 3.97 (1H, td,

J = 11.4, 4.5 Hz), 3.91 (2H, s), 3.75 (1H, ddd, J = 11.6, 6.2, 2.2 Hz), 3.25–3.14 (5H, m), 2.55–2.40 (1H, m), 2.33–2.20 (1H, m), 1.99–1.42 (10H, m), 1.28–1.10 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 148.8, 146.7, 143.8, 141.7, 140.8, 128.1, 127.9, 126.6, 126.5, 126.1, 125.6, 120.9, 80.5, 76.0, 61.3, 57.8, 40.9, 28.4, 27.73, 27.66, 27.2, 27.1, 26.5, 25.5; HRMS (ESI) calc. for $C_{28}H_{34}O_3Si$ $[M + Na]^+$ 469.2175, found 469.2154.

4.4. Protodesilylation to form diols *17a–17j, 23, 30, 31*

The following procedure for **17a** is representative. Siloxane **16a** (104 mg, 0.34 mmol) was taken up in dry THF (3 mL), and TBAF (1.0 M in THF, 1.35 mL, 1.35 mmol) was added. The solution was stirred at reflux for 45 min. It was then diluted with EtOAc and saturated NH_4Cl. The organic layer was removed, and the aqueous layer was extracted twice more with EtOAc. The combined organic layers were dried over $MgSO_4$ and evaporated to give a yellow oil. Flash chromatography of the crude product on silica with 1:1 to 1:0 EtOAc:hexanes yielded diene **17a** (49 mg, 68%) as a thick, colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.38 (1H, dd, J = 15.8, 1.0 Hz), 5.85 (1H, dt, J = 15.8, 7.4 Hz), 5.60 (1H, t, J = 7.7 Hz), 4.06 (2H, s), 3.93–3.80 (2H, m), 3.32 (3H, s), 2.46–2.18 (6H, m), 1.22 (3H, d, J = 5.9 Hz), 1.20 (3H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.1, 128.0, 127.8, 127.7, 75.2, 67.8, 67.4, 57.8, 43.5, 37.3, 23.2, 23.0; HRMS (ESI) calc. for $C_{12}H_{22}O_3$ $[M + Na]^+$ 237.1467, found 237.1479.

17b *(89%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.38 (1H, d, J = 15.9 Hz), 5.86 (1H, dt, J = 15.9, 7.4 Hz), 5.61 (1H, t, J = 7.7 Hz), 4.07 (2H, s), 3.73–3.60 (2H, m), 3.32 (3H, s), 2.42–2.31 (3H, m), 2.27–2.14 (1H, m), 1.96 (2H, bs), 1.54–1.21 (16H, m), 0.96–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.1, 128.1, 127.85, 127.79, 75.2, 71.8, 71.2, 57.8, 41.8, 37.2, 37.1, 35.6, 32.0, 25.5, 22.8, 14.1; HRMS (ESI) calc. for $C_{20}H_{38}O_3$ $[M + Na]^+$ 349.2719, found 349.2714.

17c *(78%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.14 (10H, m), 6.38 (1H, d, J = 15.8 Hz), 5.84 (1H, dt, J = 15.8, 7.1 Hz), 5.59 (1H, t, J = 7.6 Hz), 4.04 (2H, s), 3.74–3.62 (2H, m), 3.30 (3H, s), 2.87–2.74 (2H, m), 2.74–2.61 (2H, m), 2.44–2.32 (3H, m), 2.31–2.18 (1H, m), 2.06 (1H, bs), 1.98 (1H, bs), 1.86–1.72 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.3, 142.1, 135.3, 128.6, 127.9, 127.6, 126.01, 125.97, 75.1, 71.0, 70.5, 57.9, 41.9, 38.7, 35.7, 32.2; HRMS (ESI) calc. for $C_{26}H_{34}O_3$ $[M + Na]^+$ 417.2406, found 417.2422.

17d *(70%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.52 (1H, d, J = 15.4 Hz), 5.72 (1H, dt, J = 15.4, 7.5 Hz), 5.35 (1H, t, J = 7.7 Hz), 3.72–3.56 (2H, m), 2.43–2.15 (4H, m), 1.86 (3H, s), 1.80 (2H, bs), 1.54–1.22 (16H, m), 0.95–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 134.8, 130.4, 127.1, 125.3, 72.0, 71.4, 41.5, 37.1, 35.6, 32.1, 25.6, 22.8, 21.0, 14.2; HRMS (ESI) calc. for $C_{19}H_{36}O_2Si$ $[M + Na]^+$ 319.2613, found 319.2617.

17e *(65%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.34–7.12 (10H, m), 6.52 (1H, d, J = 15.8 Hz), 5.70 (1H, dt, J = 15.8, 7.5 Hz), 5.33 (1H, t, J = 7.7 Hz), 3.74–3.58 (2H, m), 2.88–2.74 (2H, m), 2.74–2.60 (2H, m), 2.45–2.19 (4H, m), 2.03 (2H, bs), 1.89–1.70 (7H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.2, 135.0, 130.5, 128.6, 126.9, 126.0, 125.0, 71.1, 70.6, 41.6, 38.7, 38.6, 35.7, 32.3, 21.0; HRMS (ESI) calc. for $C_{25}H_{32}O_2Si$ $[M + Na]^+$ 387.2300, found 387.2299.

17f *(68%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.40–7.27 (10H, m), 6.36 (1H, d, J = 15.8 Hz), 5.85 (1H, dt, J = 15.8, 7.6 Hz), 5.58 (1H, t, J = 7.5 Hz), 4.56 (2H, s), 4.55 (2H, s), 4.03 (2H, s), 3.95–3.84 (2H, m), 3.54–3.47 (2H, m), 3.38 (2H, dd, J = 9.5, 7.3 Hz), 3.28 (3H, s), 2.46 (2H, bs), 2.40 (2H, t, J = 7.1 Hz), 2.33 (2H, t, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 138.14, 138.07, 134.9, 128.6, 127.9, 127.4, 126.8, 75.0, 74.1, 74.0, 73.5, 70.4, 70.2, 57.8, 37.8, 31.6; HRMS (ESI) calc. for $C_{26}H_{34}O_5$ $[M + Na]^+$ 449.2304, found 449.2315.

17g *(87%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.38 (1H, d, J = 15.8 Hz), 5.86 (1H, dt, J = 15.8, 7.3 Hz), 5.61 (1H, t, J = 7.6 Hz), 4.07 (2H, s), 3.73–3.60 (2H, m), 3.32 (3H, s), 2.42–2.31 (3H, m), 2.27–2.14 (1H, m), 1.86 (1H, bs), 1.77 (1H, bs), 1.54–1.21 (16H, m), 0.96–0.83 (6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 135.2, 128.1, 127.8, 75.2, 71.8, 71.3, 57.8, 41.8, 37.2, 37.1, 35.6, 32.0, 25.6, 22.8, 14.2; HRMS (ESI) calc. for $C_{20}H_{38}O_3$ $[M + Na]^+$ 349.2719, found 349.2709.

17h *(83%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.32–7.14 (10H, m), 6.38 (1H, d, J = 15.8 Hz), 5.84 (1H, dt, J = 15.8, 7.4 Hz), 5.59 (1H, t, J = 7.6 Hz), 4.04 (2H, s), 3.74–3.62 (2H, m), 3.30 (3H, s), 2.87–2.74 (2H, m), 2.74–2.61 (2H, m), 2.44–2.32 (3H, m), 2.31–2.11 (3H, m), 1.86–1.72 (4H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 142.2, 142.1, 135.3, 128.6, 127.9, 127.6, 125.99, 125.97, 75.1, 70.9, 70.5, 57.9, 41.9, 38.7, 35.7, 32.2; HRMS (ESI) calc. for $C_{26}H_{34}O_3$ $[M + Na]^+$ 417.2406, found 417.2415.

17i *(88%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.22 (10H, m), 6.34 (1H, d, J = 15.7 Hz), 5.81 (1H, dt, J = 15.7, 7.4 Hz), 5.57 (1H, d, J = 7.6 Hz), 4.72 (2H, dd, J = 7.6, 5.4 Hz), 3.99 (2H, s), 3.22 (3H, s), 2.75–2.46 (4H, m), 2.28 (2H, bs); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 144.1, 135.3, 128.6, 128.5, 128.0, 127.8, 127.6, 127.5, 126.0, 75.0, 74.1, 73.7, 57.8, 43.7, 37.5; HRMS (ESI) calc. for $C_{22}H_{26}O_3$ $[M + Na]^+$ 361.1780, found 361.1782.

17j *(50%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 6.54–6.45 (1H, m), 5.76–5.62 (1H, m), 5.27 (1H, t, J = 7.5 Hz), 3.90–3.74 (2H, m), 2.35–2.14 (4H, m), 1.80 (3H, s), 1.66 (2H, bs), 1.62–1.44 (4H, m), 1.24–1.15

(6H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 132.5, 130.3, 128.5, 127.7, 67.9, 67.7, 39.1, 29.8, 23.7, 20.8; HRMS (ESI) calc. for $C_{13}H_{24}O_2Si$ $[M + Na]^+$ 235.1674, found 235.1682.

23 *(77%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.49–7.39 (4H, m), 7.36–7.17 (6H, m), 6.36 (1H, d, J = 15.7), 5.89 (1H, dt, J = 15.7, 7), 5.42 (1H, t, J = 7.4), 3.96 (2H, s), 3.62 (2H, t, J = 6.4), 3.20 (2H, d, J = 7.4), 3.15 (3H, s), 2.68 (1H, s), 2.21 (2H, q, J = 7), 1.75 (1H, bs), 1.66 (2H, pentet, J = 7.0); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ HRMS (ESI) calc. for $C_{23}H_{28}O_3$ $[M + Na]^+$ 375.1953, found 375.1936. 146.8, 136.7, 132.5, 128.4, 127.1, 126.2, 125.7, 125.1, 78.1, 75.2, 62.5, 57.6, 40.1, 32.3, 30.1.

4.5. Synthesis of silyl ethers *19* and *26*

The following procedure for **19** is representative. Silane **14a** (500 mg, 1.64 mmol) and alcohol **18** (368 mg, 1.64 mmol) were combined in hexanes (10 mL), and sodium hydride (60% dispersion in mineral oil, 6 mg, 0.16 mmol) was added. The reaction was stirred at 50 °C until complete by TLC (approximately 2.5 h). The solution was then filtered through Celite. Evaporation of the solvent gave a yellow oil that was chromatographed on silica gel with 95:5 to 90:10 hexanes:ether to obtain 750 mg (99%) of a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.39–7.15 (10 H, m), 5.72 (1H, ddt, J = 17.1, 10.3, 6.8 Hz), 5.03–4.89 (2H, m), 3.99 (4H, s), 3.35 (2H, d, J = 6.8 Hz), 3.31 (6H, s), 1.85–1.70 (2H, m), 1.67–1.45 (6H, m), 1.12–0.98 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.3, 134.0, 127.8, 127.4, 127.0, 118.0, 102.0, 87.3, 82.4, 60.3, 57.7, 45.2, 27.25, 27.22, 26.5; HRMS (ESI) calc. for $C_{29}H_{34}O_3Si$ $[M + Na]^+$ 481.2175, found 481.2186.

26 *(85%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.84 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.03 (1H, ddt, J = 16.9, 2.0, 1.7 Hz), 4.94 (1H, ddt, J = 10.2, 2.0, 1.1 Hz), 4.13 (4H, s), 3.39 (6H, s), 2.20–2.09 (2H, m), 1.87–1.72 (2H, m), 1.70–1.45 (8H, m), 1.38 (6H, s), 1.19–1.04 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.5, 114.1, 101.6, 88.6, 76.3, 60.5, 57.7, 43.4, 29.4, 28.8, 27.2, 26.5; HRMS (ESI) calc. for $C_{20}H_{32}O_3Si$ $[M + Na]^+$ 371.2018, found 371.2022.

4.6. Synthesis of unsymmetrical silaketals *20* and *27*

The following procedure for **20** is representative. Silyl ether **19** (750 mg, 1.64 mmol) and 4-penten-1-ol (141 mg, 1.64 mmol) were combined in hexanes (10 mL). Sodium hydride (60% dispersion in mineral oil, 6 mg, 0.16 mmol) was added. After stirring for 45 min at room temperature, the solution was filtered through Celite. Removal of the solvent gave a yellow residue. Chromatography on silica with 98:2 hexanes:ether afforded **20** (622 mg, 80%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 7.39–7.14 (10H, m), 5.86–5.60 (2H, m), 5.03–4.88 (4H, m), 4.01 (2H, s), 3.52–3.19 (4H, m), 3.33 (3H, s), 2.06–1.94 (2H, m), 1.80–1.40 (10H, m), 1.00–0.81 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 146.9, 146.7, 138.6, 134.2, 127.8, 127.3, 127.2, 126.93, 126.89, 117.8, 114.6, 101.1, 86.7, 81.7, 63.1, 60.3, 57.6, 45.6, 31.6, 30.1, 27.5, 27.20, 27.15, 25.4; HRMS (ESI) calc. for $C_{30}H_{38}O_3Si$ $[M + Na]^+$ 497.2488, found 497.2469.

27 *(73%, colorless oil)*. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.842 (1H, ddt, J = 16.9, 10.2, 6.6 Hz), 5.838 (1H, ddt, J = 17.2, 10.2, 6.9 Hz), 5.14–4.89 (4H, m), 4.13 (2H, m), 4.13 (2H, s), 3.89–3.75 (2H, m), 3.39 (3H, s), 2.39–2.30 (2H, m), 2.20–2.09 (2H, m), 1.83–1.68 (2H, m), 1.67–1.42 (6H, m), 1.34 (3H, s), 1.33 (3H, s), 1.08–0.94 (1H, m); ^{13}C NMR ($CDCl_3$, 75.4 MHz) δ 139.5, 135.4, 116.6, 114.0, 100.8, 87.6, 75.4, 63.0, 60.4, 57.6, 43.7, 37.2, 29.7, 29.6, 28.9, 27.4, 27.3, 27.1, 25.3; HRMS (ESI) calc. for $C_{20}H_{34}O_3Si$ $[M + Na]^+$ 373.2159, found 373.2175.

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