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A Tripartite Asymmetric Allylboration - Silicon Tethered Alkene Ring Closing Metathesis - *in situ* Ring Opening Protocol for the Regiospecific Generation of Functionalized (*E*)-Disubstituted Homoallylic Alcohols

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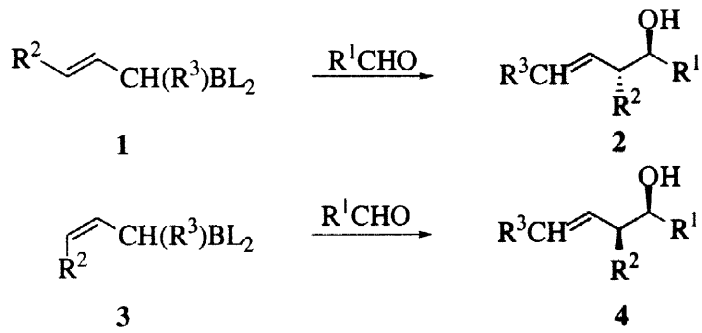
Abstract: Molybdenum carbene **6** catalyzed ring closing metathesis of (alkenyl)silyl ethers of homochiral allylic alcohols to afford 1,2-oxasilines which were elaborated *in situ* to give (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol and (*Z*)-4-alkyl-4-silyl-1,2-disubstituted 3-buten-1-ol derivatives as single geometric isomers.

Introduction

The reaction of chiral allylborane reagents, with aldehydes to give homochiral allylic alcohols is a powerful and versatile technique which has been widely applied in organic synthesis.[1] The relative stereochemistry of the product alcohol is determined by the geometry of the carbon-carbon double bond of the starting allylborane, with the (*E*)-isomer **1** providing the *anti*-product **2**, and the (*Z*)-isomer **3** providing *syn*-adduct **4**. Additionally, the absolute stereochemistry of the reaction may be controlled by the choice of chiral ligands attached to the boron (L) (Scheme 1). The process is tolerant of a range of substituents allowing the formation of a wide variety of polyfunctional allylic alcohols. However, the methodology suffers from a severe limitation in that, in order to form either **2** or **4** ($R^3 \neq H$) with control of the alkene geometry of the product, the absolute stereochemistry at the α-carbon of the starting allylborane must be fixed.[2] Whilst not impossible, preparation of chiral α-substituted allylboranes is non-trivial and the existing methodology for their synthesis is not general. Clearly, there is scope for the introduction of a general protocol for the preparation of **2** and **4** [$R^3 \neq H$] in homochiral form which removes the need for such reagents.



Scheme 1

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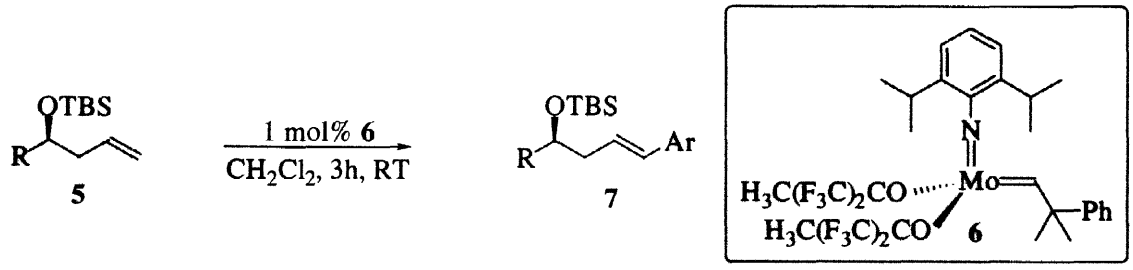
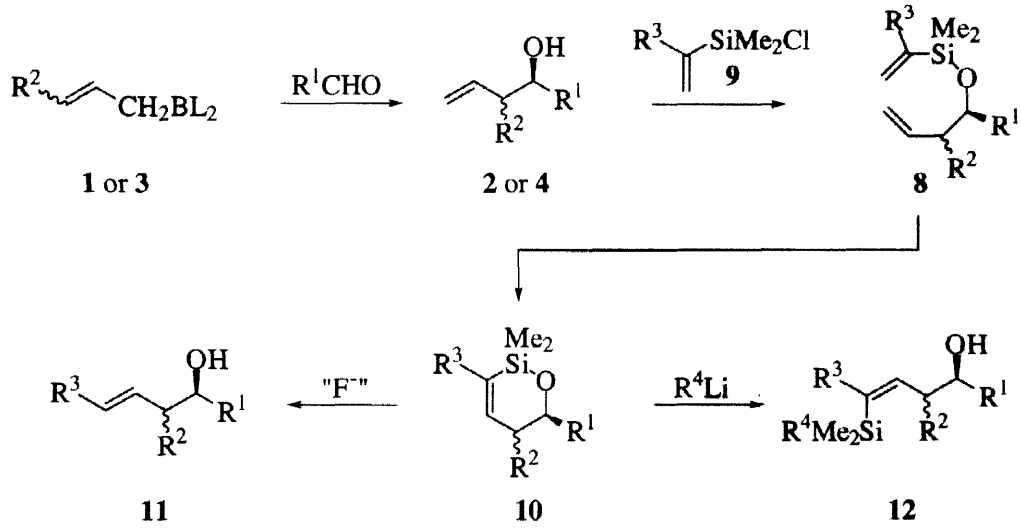


Scheme 2

We have previously reported[3] the cross-metathesis of chiral homoallylic silyl ethers **5** with *para*-substituted styrenes, employing Schrock's molybdenum carbene catalyst (**6**),[4] to give homochiral alkenes **7** with exclusive formation of the (*E*)-isomer (Scheme 2). Whilst this procedure represents an efficient route to such systems, it is reasonable to expect that the analogous reaction with the allylic alcohols **2** or **4** (R^3=H;R^2≠H) would not proceed with the same degree of efficiency, as the presence of a substituent in the allylic position is known to dramatically retard the rate of alkene cross-metathesis reactions.[5] In addition, Crowe and co-workers have shown[6] that although the cross-metatheses of both functionalized aryl/aryl- and aryl/alkyl-substituted alkenes proceeds with >95% *trans* selectivity, the cross-metathesis between two non-aryl substituted alkenes exhibits markedly poorer control of *E*/*Z* geometry of the product olefin.



Scheme 3

In order to obviate the difficulties associated with the control of the *E*/*Z* geometry of cross metathesis between two alkyl-substituted olefins it was reasoned that constraining the new carbon-carbon double bond to lie within a ring would ensure complete control of olefin geometry. Thus it was envisioned that the alkene cross coupling reaction would be carried out intramolecularly *via* ring-closing metathesis. The use of silicon tethers to facilitate intramolecular reactions is well established in organic synthesis[7] and such tethers have been employed in ring closing metathesis.[8] Whilst ring closing reactions of allyl silyl ethers of allylic alcohols have been extensively investigated, the analogous *vinyl* silyl ethers appear to have been much less well studied[8c] and we felt that these species should offer an attractive and efficient route to the desired 4-alkyl-1,2-disubstituted 3-buten-1-ol derivatives. Our general synthetic strategy is outlined above (Scheme 3). We envisaged that the key metathesis precursors **8** would be readily available from silylation (with the alkenylchlorosilane **9**) of homochiral

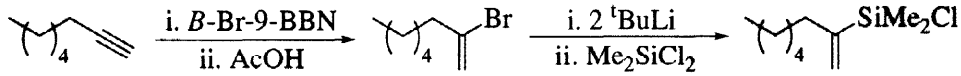
allylic alcohols **2** or **4**, themselves generated *via* a Brown condensation between the requisite homochiral allylborane **1** or **3** and an aldehyde.

Additonally, it was proposed that ring closing metathesis of vinylsilyl ether **8** using either Grubbs' ruthenium carbene $[Cl_2(Cy_3P)_2Ru{=}CHPh]$[9] or Schrock's molybdenum catalyst **6**[4] would give the six-membered 2*H*-1,2-oxasiline intermediate **10**. Subsequent hydrolysis of **10** would lead to the regeneration of the alcohol with concomitant protodesilylation to provide the desired homochiral (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol derivative **11**. Alternatively, treatment of **10** with an alkyllithium reagent could be expected to lead to ring opening of the oxasiline with retention of the silyl moiety, to give the novel (*Z*)-4-alkyl-4-trialkylsilyl-1,2-disubstituted 3-buten-1-ol derivative **12**. In both cases, as a consequence of the intramolecular nature of the silicon-tethered metathesis reaction, it is clear that the olefin products **10** and **11** should be formed as single geometric isomers.

Results and Discussion

Synthesis of the ring closing metathesis precursors.

The construction of the desired dienes **8** necessitated the synthesis of the corresponding novel alkenylchloro(dimethyl)silane **9** ($R^3 \neq H$) (Scheme 4). Accordingly, as a representative example, 1-octyne was regioselectively bromoborated using *B*-bromo-9-borabicyclo[3.3.1]nonane[10] and subjected to *in situ* protodeboration to give 2-bromo-1-octene. This was transformed into the required chloro(dimethyl)-1-octen-2-ylsilane **9** by treatment with ^{t}BuLi followed by dichloro(dimethyl)silane.



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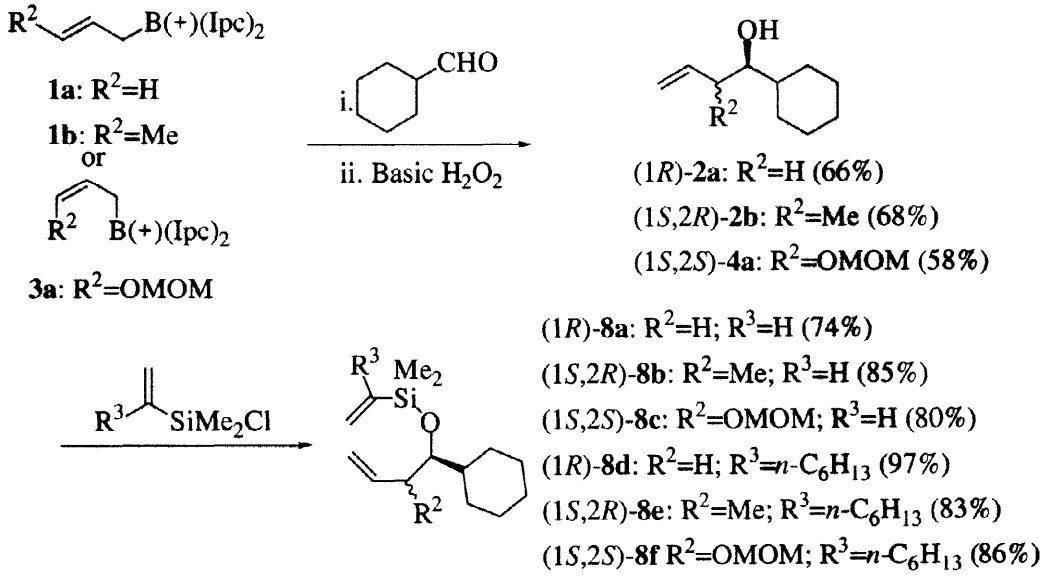
Scheme 4



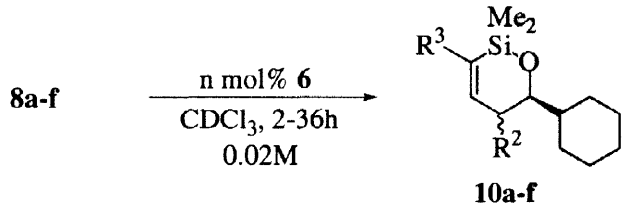
Scheme 5

Homochiral allylboranes **1a-b** and **3a** were synthesized from the appropriate olefin and (+)-*B*-methoxy(diisopinocamphenyl)borane based on existing literature procedures[11] and were allowed to react with cyclohexanecarboxaldehyde at between -85 and -78°C in the usual way to give homochiral alcohols **2a-b** and **4a** in good yield (Scheme 5). Each were treated with both commercially available chloro(dimethyl)vinylsilane and silyl chloride **9** to provide the metathesis precursors **8a-f** in good to excellent yield.

Ring closing metathesis reactions of dienes 8a-f.

With the silicon-tethered dienes **8a-f** in hand, attention turned to their reactivity towards ring closing metathesis. Grubbs' ruthenium benzylidene catalyst $(PCy_3)_2RuCl_2(=CHPh)$[9] has been shown to be singularly effective in the ring closing metathesis of allyl dimethylsilyl ethers of homoallylic alcohols.[8] Unfortunately, for the vinylsilanes **8a-f** all attempts to effect ring closure using this catalyst met with failure. However, on switching to Schrock's molybdenum catalyst (**6**),[4] we were delighted to find that the parent dienes **8a-c** cyclized smoothly to give the corresponding six-membered oxasilines **10a-c** in near quantitative conversions (> 99% conversion, no starting dienes were detectable by ^1H NMR) (Table 1, Entries 1-3). Similarly, dienes **8d-e**, having a hexyl side chain appended to the vinylsilane tether, also underwent efficient ring closing metathesis (Table 1, Entries 5-6). Whilst the cyclizations of dienes **8a-e** proceeded smoothly, diene **8f** bearing an α-OMOM functionality cyclized poorly giving the corresponding six-membered oxasiline **10f** in only 34% isolated yield (Table 1, Entry 6). Careful monitoring of the reaction by ^1H NMR revealed that the diene was undergoing a series of side reactions in the presence of catalyst **6**. It appeared that isomerisation of the allylic double bond of **8f** with concomitant loss of the MOM group was competing with the desired ring closing metathesis reaction. Furthermore, we speculate that this new diene also undergoes ring closure to the corresponding 5-membered siloxacycle under the influence of the catalyst as witnessed by the appearance of an increasingly intense ^1H NMR resonance located at δ_H 6.30 ppm (broad doublet), but we were unable to isolate this material to confirm our speculation. Such an isomerization event, followed by subsequent metathesis, has been previously noted.[12]

Table 1. Ring closing metathesis of dienes **8a-f**



10a-f

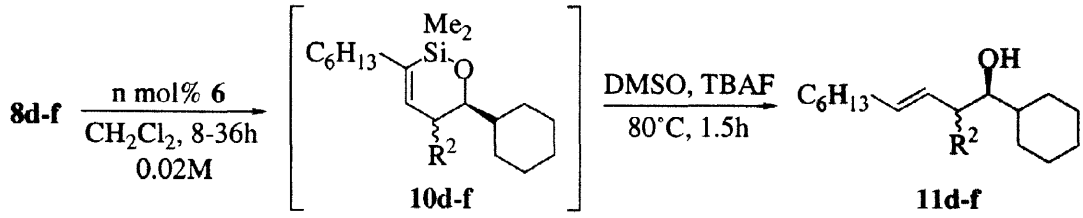
Entry	Diene	R^2	R^3	n	t/h	Oxasiline	% Conversion[a]
1	**8a**	H	H	2	10	**10a**	100
2	**8b**	*R*-Me	H	5	16	**10b**	100 (44)[b]
3	**8c**	*S*-OMOM	H	8	21	**10c**	>95
4	**8d**	H	C_6H_{13}	2	2	**10d**	>95
5	**8e**	*R*-Me	C_6H_{13}	5	24	**10e**	>95
6	**8f**	*S*-OMOM	C_6H_{13}	20	36	**10f**	55 (34)[b]

[a] Conversions observed by ^1H NMR; [b] Yield of isolated 1,2-oxasiline in parentheses.

Synthesis of (E)-4-alkyl-1,2-disubstituted 3-buten-1-ol derivatives via protodesilylative ring opening of the intermediate oxasilines 10d-f.

Having demonstrated that dienes **8d-f** were viable substrates for ring closing metathesis, we now sought to elaborate the intermediate oxasilines so produced to give the desired (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol derivatives [Scheme 3; **10** ⇒ **11**]. Whilst the 2*H*-1,2-oxasiline intermediates could be isolated, it was found to be more convenient to proceed directly from the dienes **8d-f** to the desired homoallylic alcohols **11d-f** without purification of the intermediate heterocycles.

Table 2. One pot synthesis of (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol derivatives **11d-f**



Entry	Diene	R^2	n mol%	t/h	Product	% Yield[a]
1	**8d**	H	4	8	**11d**	87
2	**8e**	*R*-Me	5	24	**11e**	78
3	**8f**	*S*-OMOM	20[b]	36	**11f**	66[c] (34)[d]

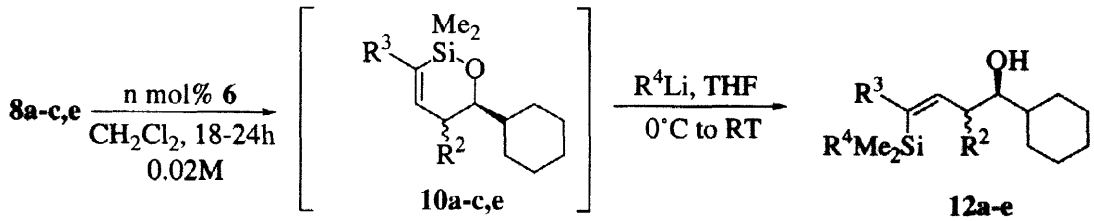
[a] Overall yield from **8d-f**; [b] 0.006 M; [c] From isolated siline **10f**; [d] Yield of isolated siline **10f**.

Thus, after ring closing metathesis had been deemed to have proceeded to completion (^{1}H NMR monitoring), the reaction mixture was evaporated to dryness, taken up in hexanes and filtered though a short silica column (failure to do so resulting in dramatically reduced efficiency of the subsequent step), and treated directly with tetrabutylammonium fluoride in DMSO[13] to furnish the desired (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol derivatives **11d-f** with complete control of the olefin geometry, in good to excellent overall yields (Table 2).

Synthesis of (Z)-4-alkyl-4-silyl-1,2-disubstituted 3-buten-1-ol derivatives 12a-e by in situ ring opening of the intermediate silines using organolithium reagents.

Attention now turned to the investigation of the reactivity of the six-membered siline systems towards organolithium reagents [Scheme 3; **10** ⇒ **12**]. Based on the observation that the Si-O bond of silyl ethers are cleaved by alkyllithium reagents,[14] we anticipated that treatment of the silines **10** with MeLi would afford (*Z*)-4-trimethylsilyl-1,2-disubstituted 3-buten-1-ol derivatives. Gratifyingly, it was found that addition of 1 equivalent of methyllithium to a THF solution of oxasiline **10b** maintained at 0 °C proceeded smoothly to give the corresponding ring-opened alkenylsilane **12b** in good yield. In practise, it was again found that the desired systems were more conveniently synthesized using the crude ring closing metathesis product without purification and direct reaction with the organolithium reagent. Accordingly, the crude mixture from the ring closing metathesis reaction was evaporated to dryness and treated with methyllithium to give the expected (*Z*)-4-trimethylsilyl-1,2-disubstituted 3-buten-1-ol derivative **12b** as a single geometric isomer (Table 3).

Table 3. One pot synthesis of (*Z*)-4-alkyl-4-silyl-1,2-disubstituted 3-buten-1-ol derivatives from dienes **8a-c,e**



Entry	Diene	R^2	R^3	n mol%	t/h	R^4Li	Product	%Yield[a]
1	**8a**	H	H	2	24	MeLi	**12a**	83
2	**8b**	*R*-Me	H	5	24	MeLi	**12b**	59
3	**8b**	*R*-Me	H	5	18	PhLi	**12c**	45
4	**8c**	*S*-OMOM	H	15[b]	24	MeLi	**12d**	51
5	**8e**	*R*-Me	C_6H_{13}	5	24	MeLi	**12e**	58

[a] Isolated yield from dienes **8a-c,e**; [b] Added batchwise (10 mol% + 5 mol%).

We were pleased to discover that not only was this protocol effective for the synthesis of the (*Z*)-alkenylsilanes **12a-b,d** (Entries 1,2 and 4), derived from dienes **8a-c** bearing an unsubstituted silicon tether, but that the same tandem reaction sequence also proceeded smoothly in the case of **8e** in which the vinylsilane moiety bears a *n*-hexyl-substituent, to provided exclusively the (*Z*)-trisubstituted olefin **12e** (Entry 5) in good overall yield. It was also found that the organolithium species used to effect ring opening of the intermediate oxasilines was not limited to MeLi. Ring closing metathesis of diene **8b** followed by treatment with phenyllithium afforded (*Z*)-alkenyl(phenyl)dimethylsilane **12c** (Entry 3) in good yield from the diene.

Conclusion

In summary, we have demonstrated novel and highly efficient tripartite routes to homochiral (*E*)-4-alkyl-1,2-disubstituted 3-buten-1-ol and (*Z*)-4-silyl-1,2-disubstituted 3-buten-1-ol derivatives. The starting dienes are readily available using well-established allylborane chemistry. Elaboration of these dienes *via* a one-pot ring closing metathesis/nucleophilic ring opening sequence may be carried out quickly and conveniently and allows rapid access to highly functionalized synthetic building blocks. Alkenylsilanes themselves are useful synthetic intermediates and have found increasing application in natural product synthesis *via* conversion to the corresponding vinyl halide[15] and as substrates in transition metal-catalyzed cross-coupling reactions.[16] This methodology further enhances the synthetic utility of the Brown allylboration reaction. Further studies on tethered alkene metathesis will be reported in due course.

Experimental

General. Molybdenum carbene **6** was prepared by the method of Schrock.[4] (1*R*)-1-Cyclohexyl-3-buten-1-ol[17] (**2a**) and (1*S*,2*R*)-1-cyclohexyl-2-methyl-3-buten-1-ol[18] (**2b**) were prepared using Brown asymmetric allylboration methodology.[11] (1*S**,2*R**)-1-cyclohexyl-2-methyl-3-buten-1-ol[19] and allyl methoxymethyl ether[20]

were prepared according to the literature procedures. All chemicals were purchased from the Aldrich Chemical Co. and used as received unless otherwise stated. Dichlorodimethylsilane was distilled immediately before use. Organolithium reagents were titrated against 2-pentanol employing 1,10-phenanthroline as the indicator immediately before use.

*(1S,2S)-1-Cyclohexyl-2-[(methoxymethyl)oxy]-but-3-en-1-ol (**4a**).* Following a modified procedure of Brown,[11] *sec*-BuLi (7.7 mL, 1.3 M, 10.1 mmol) was added slowly with stirring to a solution of allyl methoxymethyl ether (1.1 g, 11.0 mmol) in THF (4 mL) at -85 °C under N_2. After 3.5 h (+)-*B*-methoxydiisopinocampheylborane (3.32 g, 10.5 mmol) in THF (8 mL) was added to the yellow solution at -85 °C over 1 h ensuring that the internal temperature of the solution did not exceed -78 °C. The resulting white suspension in a colorless solution was stirred for a further 3 h at -85 °C, and treated with $BF_3{\cdot}OEt_2$ (1.39 mL, 11.0 mmol). After 0.25 h, cyclohexanecarboxaldehyde (1.21 mL, 10.0 mmol) in THF (10 mL), was added over a period of 1 h and the mixture was stirred for 18 h at -85 °C, quenched with aqueous NaOH (3.0M, 10 mL) followed by aqueous H_2O_2 (27.5% wt., 8 mL), allowed to warm to room temperature and stirred for a further 24 h. The mixture was diluted with Et_2O (50 mL) and the separated aqueous phase extracted with Et_2O (2 × 50 mL). The combined ethereal extracts were washed with water (50 mL) and brine (50 mL), dried ($MgSO_4$) and evaporated. Chromatography gave **4a** (1.34 g, 63%) as a colorless oil: R_f (1:4 EtOAc:hexane) 0.33; $[\alpha]_D^{25}$ +81.5° ($CHCl_3$, *c* 1.00); IR (film) 3600-3200, 3078, 2927, 2853, 1742, 1644 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.80-5.66 (m, 1H), 5.33-5.26 (m, 2H), 4.73 (d, *J* = 6.7 Hz, 1H), 4.56 (d, *J* = 6.7 Hz, 1H), 4.08 (m, 1H), 3.39 (s, 3H), 3.29 (m, 1H), 2.33 (d, *J* = 4.6, 1H), 1.74-1.11 (m, 11H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 135.1, 119.4, 93.9, 78.5, 55.8, 39.4, 30.0, 26.8, 26.4, 26.1; *m/z* (CI^+, NH_3) 232 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{12}H_{26}NO$ ($M+NH_4^+$): 232.1912. Found: 232.1921 ($M+NH_4^+$). Mosher's ester analysis[21] revealed that **4a** had been produced in >95% ee.

*General Procedure for the Preparation of Siladienes **8a-c**.* To a solution of homoallylic alcohol **2a-b, 4a** (0.75 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added sequentially Et_3N (131 μL, 0.94 mmol) and chloro(dimethyl)vinylsilane (130 μL, 0.94 mmol) and stirred for 18 h. The mixture was diluted with Et_2O (5 mL), filtered, evaporated and chromatographed.

*[(1R)-Cyclohexyl-3-buten-1-yloxy](dimethyl)ethenylsilane (**8a**).* 74%: R_f (1:99 CH_2Cl_2:hexane) 0.28; $[\alpha]_D^{25}$ -9.0° ($CHCl_3$, *c* 1.00); IR (film) 3077, 3050, 2928, 2854 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.16 (dd, *J* = 19.8, 14.9 Hz, 1H), 5.98 (dd, *J* = 14.9, 4.5 Hz, 1H), 5.90-5.73 (m, 1H), 5.75 (dd, *J* =19.8, 4.5 Hz, 1H) 5.08-5.00 (m, 2H), 3.46 (q, *J* = 5.7 Hz, 1H), 2.21 (m, 2H), 1.80-1.59 (m, 5H), 1.36-0.85 (m, 6H), 0.17 (s, 6H) ; ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 138.5, 135.7, 132.5, 116.5, 77.5, 42.8, 38.9, 29.3, 28.3, 26.6, 26.4, 26.3, -1.2; *m/z* (CI^+, NH_3) 256 ($M+NH_4^+$), 239 ($M+H^+$), 137, 102.

*[(1S,2R)-1-Cyclohexyl-2-methyl-3-buten-1-yloxy](dimethyl)ethenylsilane (**8b**).* 85%: R_f (1:199 Et_2O:hexane) 0.55; $[\alpha]_D^{25}$ -7.4° ($CHCl_3$, *c* 1.00); IR (film) 3073, 3050, 2926, 2853, 1593 cm^{-1}; ^1H NMR (270 MHz, $CDCl_3$) δ 6.17 (dd, *J* = 20.0, 14.8 Hz, 1H), 5.96 (dd, *J* = 14.7, 4.2 Hz, 1H), 5.78 (m, 1H), 5.73 (dd, *J* = 20.0, 4.2 Hz, 1H), 4.94 (m, 2H), 3.22 (dd, *J* = 6.7, 4.3 Hz, 1H), 2.39 (m, 1H), 1.85-0.85 (m, 11H), 0.98 (d, *J* = 6.9Hz, 3H), 0.18 (s, 6H); ^{13}C NMR (67.5 MHz, $CDCl_3$) δ 141.2, 138.8, 132.3, 114.2, 81.7, 41.3,

40.9, 30.0, 28.8, 26.6, 26.4, 26.2, 18.3, -0.8; *m/z* (CI^+, NH_3) 270 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{15}H_{29}OSi$ ($M+H^+$): 253.1987. Found: 253.1991 ($M+NH_4^+$).

[(1S,2S)-1-Cyclohexyl-2-(methoxymethyl)oxy-3-buten-1-yloxy](dimethyl)ethenylsilane (8c). 80%: R_f (1:4 EtOAc:hexane) 0.57; $[\alpha]_D^{25}$ +25.2° ($CHCl_3$, *c* 1.00); IR (film) 3079, 3050, 2927, 2854, 2823, 1595 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.18 (dd, *J* = 20.1, 14.9 Hz, 1H), 6.00 (dd, *J* = 14.9, 4.3 Hz, 1H), 5.82-5.67 (m, 2H), 5.29-5.21 (m, 2H), 4.68 (d, *J* = 6.8 Hz, 1H), 4.56 (d, *J* = 6.8 Hz, 1H), 4.07 (dd, *J* = 7.6, 4.5 Hz, 1H), 3.38 (dd, *J* = 6.2, 4.5 Hz, 1H), 3.36 (s, 3H), 1.84-1.52 (m, 6H), 1.29-0.94 (m, 5H), 0.20 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 136.4, 132.4, 118.3, 94.1, 80.0, 78.5, 55.8, 39.8, 30.0, 28.2, 26.5, 26.3, 26.1, -1.0, -1.0; *m/z* (CI^+, NH_3) 316 ($M+NH_4^+$), 299 ($M+H^+$); HRMS (CI^+, NH_3) Calcd for $C_{16}H_{34}NO_3Si$ ($M+NH_4^+$): 316.2308. Found: 316.2307 ($M+NH_4^+$).

2-Bromo-1-octene. Following the procedure of Hara,[10] a solution of 1-octyne (1.5 g, 13.6 mmol) in CH_2Cl_2 (10 mL) was added dropwise with stirring and *via* cannula to *B*-bromo-9-borobicyclo[3.3.1]nonane in CH_2Cl_2 (1.0 M, 16.3 mL, 16.3 mmol), pre-diluted with CH_2Cl_2 (60 mL), at 0 °C. After 3.5 h at 0 °C, AcOH (9 mL) was added, the mixture stirred for 1 h at 0 °C, followed by the addition of aq. NaOH (3M, 110 mL) and H_2O_2 (27% wt, 20 mL), and stirred for 0.5 h at room temperature. The mixture was extracted with hexanes (3 × 75 mL), and the combined organics washed successively with water (75 mL), aq. $NaHCO_3$ (75 mL) and water (75 mL), dried ($MgSO_4$), evaporated and chromatographed (hexane) to provide **13** (1.96 g, 75%) as a colorless oil: R_f (hexanes) 0.62; IR (film) 2930, 2859, 1629 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.55 (br s, 1H) 5.38 (br s, 1H), 2.41 (br t, *J* = 7.5 Hz, 2H), 1.54 (m, 2H), 1.29 (m, 6H), 0.88 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 134.9, 116.2, 41.4, 31.5, 28.1, 27.8, 22.5, 14.0; *m/z* (CI^+, NH_3) 192, 190, 122, 120; HRMS (CI^+, NH_3) Calcd for $C_8H_{15}{}^{81}Br$ ($M+H^+$): 192.0337. Found: 192.0344 ($M+H^+$), Calcd for $C_8H_{15}{}^{79}Br$ ($M+H^+$): 190.0357. Found: 190.0372 ($M+H^+$);

Chloro(dimethyl)(1-octen-2-yl)silane (9). *tert*-Butyllithium (24.6 mL, 1.7M solution in pentanes, 42 mmol) was added dropwise to a stirred solution of 2-bromo-1-octene (4.0 g, 21 mmol) in Et_2O (20 mL) at -78 °C. After 0.5 h, the resulting yellow solution was transferred *via* cannula to dichloro(dimethyl)silane (5.68 g, 52 mmol) in Et_2O (30 mL) at -78 °C and the mixture was allowed to warm to room temperature. The mixture was concentrated to approximately quarter volume, followed by the addition of pentane (150 mL). Cannula filtration under N_2, evaporation of the filtrate and vacuum distillation provided **9** (2.65 g, 62%) as a colorless oil: B.P. 55-58°C (5 mmHg); IR (film) 3053, 2975, 2928, 2857 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.70 (br s, 1H), 5.52 (br s, 1H), 2.21 (br t, *J* = 7.3 Hz, 2H), 1.48-1.29 (m, 8H), 0.91 (m, 3H), 0.49 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 148.9, 126.8, 34.9, 31.7, 29.1, 28.8, 22.6, 14.1, 1.7. The silyl chloride **9** was used directly without further purification.

General Procedure for the Preparation of Siladienes 8d-f. To homoallylic alcohol **2a-b, 4a** (1.9 mmol) and (dimethylamino)pyridine (0.3 mmol) in CH_2Cl_2 (2 mL) at 0 °C was added sequentially Et_3N (400 μL, 2.9 mmol) and **9** (600 mg, 2.9 mmol) and stirred for 18 h. The solvent was evaporated, the residue taken up in pentanes (10 mL), filtered, evaporated and chromatographed.

[(1R)-1-Cyclohexyl-3-buten-1-yloxy](dimethyl)(1-octen-2-yl)silane (8d). 97%: R_f (1:99 CH_2Cl_2:hexane) 0.28; $[\alpha]_D^{25}$ -7.2° ($CHCl_3$, *c* 1.00); IR (film) 3077, 3051, 2926, 2854, 1640 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.89-5.75 (m, 1H), 5.60 (m, 1H), 5.41 (m, 1H), 5.07-4.99 (m, 2H), 3.46 (q, *J* = 5.5 Hz, 1H), 2.24-2.11 (m, 4H), 1.76-1.55 (m, 5H), 1.45-0.86 (m, 17H), 0.17 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.3, 135.8, 125.0, 116.4, 76.6, 42.6, 38.6, 31.8, 29.3, 29.1, 28.9, 28.1, 26.6, 26.4, 26.3, 22.7, 14.1, -1.0, -1.2; *m/z* (CI^+, NH_3) 340 ($M+NH_4^+$), 323 ($M+H^+$), 186, 137; HRMS (CI^+, NH_3) Calcd for $C_{20}H_{39}OSi$ ($M+H^+$): 323.2770. Found: 323.2770 ($M+H^+$).

[(1S,2R)-1-Cyclohexyl-2-methyl-3-buten-1-yloxy](dimethyl)(1-octen-2-yl)silane (8e). 83%: R_f (1:99 CH_2Cl_2:hexane) 0.50; $[\alpha]_D^{25}$ -3.5° ($CHCl_3$, *c* 1.00); IR (film) 3072, 3049, 2927, 2853, 1639 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.93-5.78 (m, 1H), 5.57 (m, 1H), 5.39 (m, 1H), 5.00-4.92 (m, 2H), 3.23 (dd, *J* = 6.5, 4.0 Hz, 1H), 2.41-2.33 (m, 1H), 2.18-2.12 (m, 2H), 1.83-0.85 (m, 25H), 0.18 (s, 6H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.6, 141.4, 124.6, 113.9, 81.6, 41.6, 41.1, 35.6, 31.8, 30.1, 29.3, 28.9, 26.6, 26.5, 26.3, 22.7, 18.1, 14.1, -0.71; *m/z* (CI^+, NH_3) 337 ($M+H^+$), 186, 151; HRMS (CI^+, NH_3) Calcd for $C_{21}H_{41}OSi$ ($M+H^+$): 337.2927. Found: 337.2923 ($M+H^+$).

[(1S,2S)-1-Cyclohexyl-2-(methoxymethyl)oxy-3-buten-1-yloxy](dimethyl)(1-octen-2-yl)silane (8f). 86%: $[\alpha]_D^{25}$ +14.2° ($CHCl_3$, *c* 1.00); IR (film) 2927, 2854 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.83-5.68 (m, 1H), 5.60 (m, 1H), 5.42 (m, 1H), 5.29-5.21 (m, 2H), 4.67 (d, *J* = 6.7 Hz, 1H), 4.56 (d, *J* = 6.7 Hz, 1H), 4.02 (dd, *J* = 7.7, 5.4 Hz), 3.42 (t, *J* = 5.3 Hz, 1H), 3.35 (s, 3H), 2.15 (m, 2H), 1.72-0.85 (m, 22H), 0.21 (s, 3H), 0.19 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 151.3, 136.1, 125.0, 118.1, 94.4, 79.5, 55.7, 40.0, 35.5, 31.8, 30.4, 29.3, 28.9, 27.7, 26.5, 26.2, 22.7, 14.1, -0.8, -0.9; *m/z* (CI^+, NH_3) 400 ($M+NH_4^+$), 383 ($M+H^+$), 186; HRMS (CI^+, NH_3) Calcd for $C_{22}H_{43}O_3Si$ ($M+H^+$): 383.2982. Found: 383.2984 ($M+H^+$).

General Procedure for the monitoring of ring closing metatheses by ^1H NMR. In a glove box, molybdenum catalyst **6** (0.7 mg, 2 mol%) was added to siladienes **8a-f** (0.04 mmol) in degassed $CDCl_3$. The solution was transferred to a 5 mm NMR tube fitted with a Youngs' tap and sealed under N_2. The extent of ring closing metathesis was monitored by ^1H NMR. Additional portions of catalyst **6** were added, where necessary, incrementally as 2-3 mol% loadings (see Table 1), as dictated by the NMR experiments.

(6R)-6-Cyclohexyl-2,2-dimethyl-5,6-dihydro-2H-1,2-oxasiline (10a). IR (film) 2988, 2926, 2853, 1587 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.77 (dt, *J* = 14.1, 4.4 Hz, 1H), 5.75 (dt, *J* = 14.1, 1.9 Hz, 1H), 3.60 (q, *J* = 6.5 Hz, 1H), 2.16-2.11 (m, 2H), 1.96-1.91 (m, 1H), 1.96-1.64 (m, 4H), 1.40-0.91 (m, 6H), 0.16 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 147.5, 127.1, 15.6, 44.0, 33.2, 28.9, 28.7, 26.6, 26.2, 26.1, -0.57; *m/z* (CI^+, NH_3) 228 ($M+NH_4^+$), 211 ($M+H^+$), 178; HRMS (CI^+, NH_3) Calcd for $C_{12}H_{23}OSi$ ($M+H^+$): 211.1518. Found: 211.1515 ($M+H^+$).

(5R,6S)-6-Cyclohexyl-2,2,5-trimethyl-5,6-dihydro-2H-1,2-oxasiline (10b). $[\alpha]_D^{25}$ -62.5° ($CHCl_3$, *c* 1.00); IR (film) 2958, 2928, 2854, 1585 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.60 (dd, *J* = 14.2, 3.4 Hz, 1H), 5.69 (dd, *J* = 14.2, 2.0 Hz, 1H), 3.33 (dd, *J* = 6.9, 4.3 Hz, 1H), 2.41-2.33 (m, 1H), 1.75-1.13 (m, 11H), 1.00 (d, *J* = 7.3 Hz, 3H), 0.14 (s, 3H), 0.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 126.4, 81.6,

40.3, 35.2, 30.2, 26.6, 26.5, 26.3, 26.2, 18.5, -0.3, -1.2; *m/z* (CI^+, NH_3) 242 ($M+NH_4^+$), 225 ($M+H^+$); HRMS (CI^+, NH_3) Calcd for $C_{13}H_{25}OSi$ ($M+H^+$): 225.1675. Found: 225.1670 ($M+H^+$).

*(5S,6S)-6-Cyclohexyl-2,2-dimethyl-5-[(methoxymethyl)oxy]-5,6-dihydro-2H-1,2-oxasiline (**10c**).* ^1H NMR (250 MHz, $CDCl_3$) δ 6.94 (dd, *J* = 14.1, 5.6 Hz, 1H), 6.02 (d, *J* = 14.1 Hz, 1H), 4.82 (d, *J* = 6.9 Hz, 1H), 4.64 (d, *J* = 6.9 Hz, 1H), 4.03 (dd, *J* = 5.6, 1.5 Hz, 1H), 3.48 (dd, *J* = 9.4, 1.4 Hz, 1H), 3.37 (s, 3H), 2.18 (br d, *J* = 13.0 Hz, 1H), 1.80-1.64 (m, 4H), 1.28-1.11 (m, 4H), 0.90-0.82 (m, 2H), 0.24 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 146.6, 132.3, 95.3, 78.3, 70.0, 55.6, 39.4, 29.6, 28.9, 26.6, 25.9, 25.8, 22.4, -0.8, -0.18; *m/z* (CI^+, NH_3) 288 ($M+NH_4^+$), 271 ($M+H^+$); HRMS (CI^+, NH_3) Calcd for $C_{14}H_{27}O_3Si$ ($M+H^+$): 271.1729 Found: 271.1737 ($M+NH_4^+$).

*(6R)-6-Cyclohexyl-2,2-dimethyl-3-hexyl-5,6-dihydro-2H-1,2-oxasiline (**10d**).* IR (film) 2926, 2854, 1606 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.32 (m, 1H), 3.52 (q, *J* = 6.5 Hz, 1H), 2.14-1.91 (m, 5H), 1.76-1.59 (m, 4H), 1.42-0.85 (m, 17H), 0.17 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 139.7, 139.3, 75.8, 43.9, 35.4, 32.7, 31.7, 29.5, 29.2, 29.0, 28.7, 26.6, 26.2, 26.1, 22.6, 14.1, -0.76, -0.91; *m/z* (CI^+, NH_3) 312 ($M+NH_4^+$), 295 ($M+H^+$), 211; HRMS (CI^+, NH_3) Calcd for $C_{28}H_{35}OSi$ ($M+H^+$): 295.2457. Found: 295.2453 ($M+H^+$).

*(5R,6S)-6-Cyclohexyl-3-hexyl-2,2,5-trimethyl-5,6-dihydro-2H-1,2-oxasiline (**10e**).* IR (film) 2957, 2926, 2854, 1602 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.14 (m, 1H), 3.27 (dd, *J* = 6.7, 4.4 Hz, 1H), 2.36 (m, 1H), 2.00 (m, 2H), 1.75-1.64 (m, 4H) 1.47-1.14 (m, 18H), 0.98 (d, *J* = 7.2 Hz, 3H), 0.88 (m, 3H), 0.15 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 146.3, 140.0, 81.8, 40.4, 35.5, 34.8, 31.7, 30.2, 29.6, 29.1, 25.6, 26.5, 26.3, 22.7, 19.1, 14.1, -0.36; *m/z* (CI^+, NH_3) 326 ($M+NH_4^+$), 309 ($M+H^+$), 186; HRMS (CI^+, NH_3) Calcd for $C_{19}H_{37}OSi$ ($M+H^+$): 309.2614. Found: 309.2617 ($M+H^+$).

*(5S,6S)-6-Cyclohexyl-2,2-dimethyl-3-hexyl-5-[(methoxymethyl)oxy]-5,6-dihydro-2H-1,2-oxasiline (**10f**).* IR (film) 2924, 2852, 1450 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.53 (dt, *J* = 5.9, 1.3 Hz, 1H), 4.82 (d, *J* = 6.9 Hz, 1H), 4.60 (d, *J* = 6.9 Hz, 1H), 4.04 (dd, *J* = 5.9, 1.2 Hz, 1H), 3.42-3.35 (m, 1H), 3.36 (s, 3H), 2.21-2.03 (m, 3H), 1.78-1.57 (m, 4H), 1.40-1.11 (m, 13H), 0.93-0.74 (m, 6H), 0.24 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 145.8, 138.9, 95.0, 78.4, 70.1, 55.5, 39.4, 35.2, 31.7, 29.7, 29.2, 29.0, 28.9, 26.6, 26.0, 25.8, 22.6, 14.0, -1.0, -2.0; *m/z* (CI^+, NH_3) 372 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{20}H_{42}NO_3Si$ ($M+NH_4^+$): 372.2934. Found: 372.2937 ($M+NH_4^+$).

General procedure for tandem ring closing metathesis - fluoride mediated protodesilylation. To a stirred solution of siladiene **8d-f** (0.31 mmol) in CH_2Cl_2 (1 mL) was added molybdenum carbene **6** (n mol%, Table 2). Once the reaction was deemed complete by ^1H NMR analysis of an aliquot, the solvent was evaporated under reduced pressure and the residue passed through a short pad of silica (eluant: 1:4 EtOAc:hexane) to remove catalyst residues and re-evaporated. The resultant oil was taken up in DMSO (3 mL), treated with TBAF (1.5 mL, 1.0 M solution in THF, *ca.* 5% water content) and heated to 80 °C for 1.5 h. The mixture was cooled, partitioned between H_2O (15 mL) and Et_2O (15 mL), separated, and the aqueous phase extracted with Et_2O (2 ×

15 mL). The combined organics were washed with water (2 × 15 mL), dried ($MgSO_4$), evaporated and chromatographed.

*(1R)-(E)-1-Cyclohexyl-3-decen-1-ol (**11d**).* 87%: R_f (1:4 EtOAc:hexane) 0.45; $[\alpha]_D^{25}$ +6.7° ($CHCl_3$, *c* 1.00); IR (film) 3600-3100, 2924, 2853, 1450 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.61-5.33 (m, 2H), 3.36-3.27 (m, 1H), 2.29-2.21 (m, 1H), 2.10-1.98 (m, 3H), 1.88-1.56 (m, 6H), 1.41-1.02 (m, 14H), 0.88 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 134.6, 126.2, 74.8, 42.9, 37.5, 32.6, 31.7, 29.4, 29.0, 28.8, 28.1, 26.5, 26.3, 26.1, 22.6, 14.0; *m/z* (CI^+, NH_3) 256 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{16}H_{34}NO$ ($M+NH_4^+$): 256.2640. Found: 256.2643 ($M+NH_4^+$).

*(1S,2R)-(E)-1-Cyclohexyl-2-methyl-3-decen-1-ol (**11e**).* 78%: R_f (1:4 EtOAc:hexane) 0.57; $[\alpha]_D^{25}$ +18.4° ($CHCl_3$, *c* 1.00); IR (film) 3600-3100, 2925, 2853, 1450 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.57-5.45 (m, 1H), 5.35-5.26 (m, 1H), 3.06 (m, 1H), 2.36-2.22 (m, 1H), 2.05-1.97 (m, 2H), 1.79-1.63 (m, 5H), 1.49 (d, *J* = 4.2 Hz, 1H), 1.42-1.04 (m, 14H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 132.8, 131.7, 78.9, 40.2, 29.7, 32.7, 31.7, 30.1, 29.5, 28.8, 26.8, 26.5, 26.2, 22.6, 22.6, 17.5, 14.1; *m/z* (CI^+, NH_3) 270 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{17}H_{36}NO$ ($M+NH_4^+$): 270.2797. Found: 270.2797 ($M+NH_4^+$).

*(1S,2S)-(E)-1-Cyclohexyl-2-[(methoxymethyl)oxy]-3-decen-1-ol (**11f**).* 66% from isolated siline **10f**: R_f (1:4 EtOAc:hexane) 0.33; $[\alpha]_D^{25}$ +76.4° ($CHCl_3$, *c* 1.00); IR (film) 2925, 2853, 1608 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 5.77-5.65 (m, 1H), 5.34-5.24 (m, 1H), 4.75 (d, *J* = 6.6 Hz, 1H), 4.52 (d, *J* = 6.6 Hz, 1H), 4.02 (dd, *J* = 8.5, 6.6 Hz, 1H), 3.37 (s, 3H), 3.31-3.25 (m, 1H), 2.38 (d, *J* = 6.9 Hz, 1H), 2.11-2.03 (m, 2H), 1.74-1.56 (m, 5H), 1.40-1.15 (m, 14H), 0.85 (m, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 137.1, 126.4, 93.3, 78.2, 77.8, 55.7, 39.4, 32.4, 31.6, 30.1, 29.0, 28.8, 26.5, 26.2, 22.6, 14.1.

General procedure for tandem ring-closing metathesis - in situ organolithium ring opening. To siladiene **8a-c,e** (0.4 mmol) in CH_2Cl_2 (1 mL) with stirring was added molybdenum carbene **6** (n mol%, Table 3). After 18-24 h, the solvent was removed under reduced pressure, the residue taken up in THF (2.5 mL) and cooled to 0 °C. Organolithium (1.1 equiv.) was added, the solution allowed to warm to room temperature and stirred for 18 h. Solid ammonium chloride was added (50 mg), the mixture diluted with Et_2O, filtered, evaporated and chromatographed.

*(1R)-(Z)-1-Cyclohexyl-4-(trimethylsilyl)-3-buten-1-ol (**12a**).* 83%: R_f (1:9 EtOAc:hexane) 0.46; $[\alpha]_D^{25}$ -2.6° ($CHCl_3$, *c* 1.00); IR (film) 3600-3100, 2927, 2853 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.35 (ddd, *J* = 14.5, 8.3, 6.6 Hz, 1H), 5.70 (br d, *J* = 14.1 Hz, 1H), 3.42 (m, 1H), 2.39-2.17 (m, 2H), 1.87-1.61 (m, 5H), 1.49 (d, *J* = 3.9 Hz, 1H), 1.45-1.01 (m, 6H), 0.13 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 145.1, 132.9, 75.243, 43.3, 37.9, 29.1, 28.1, 26.5, 26.3, 26.2, 0.3.

*(1S,2R)-(Z)-1-Cyclohexyl-2-methyl-4-(trimethylsilyl)-3-buten-1-ol (**12b**).* 59%: R_f (1:9 EtOAc:hexane) 0.39; $[\alpha]_D^{25}$ +1.9° ($CHCl_3$, *c* 1.00); IR (film) 3450-3200, 2955, 2927, 2853, 1607 cm^{-1}; ^1H NMR (250 MHz, $CDCl_3$) δ 6.14 (dd, *J* = 14.0, 10.3 Hz, 1H), 5.64 (d, *J* = 14.0 Hz, 1H), 3.11 (dt, *J* = 8.2, 2.7 Hz, 1H), 2.57-

2.41 (m, 1H), 1.78-1.16 (m, 12H), 0.93 (d, J = 6.7 Hz, 3H), 0.13 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 131.9, 78.3, 41.0, 39.3, 30.7, 26.7, 26.5, 26.2, 25.1, 17.1, 0.4; *m/z* (CI^+, NH_3) 258 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{14}H_{32}NOSi$ ($M+NH_4^+$): 258.2253. Found: 258.2264 ($M+NH_4^+$).

*(1S,2R)-(Z)-1-Cyclohexyl-4-[dimethyl(phenyl)silyl]-2-methyl-3-buten-1-ol (**12c**).* **45%**: R_f (1:9 EtOAc:hexane) 0.39; $[\alpha]_D^{25}$ -12.9° ($CHCl_3$, *c* 1.00); IR (film) 3600-3300, 3068, 2925, 2851, 1605 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.34 (m, 3H), 6.24 (dd, J = 13.9, 10.3 Hz, 1H), 5.78 (d, J = 13.9 Hz, 1H), 3.05 (m, 1H), 2.47-2.32 (m, 1H), 1.70-1.00 (m, 12H), 0.84 (d, J = 6.7 Hz, 3H), 0.41 (s, 3H), 0.40 (s, 3H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 152.8, 139.5, 133.7, 129.0, 128.9, 127.9, 78.6, 40.9, 39.5, 30.5, 26.7, 26.5, 26.2, 25.2, 17.0, -0.8, -0.9; *m/z* (CI^+, NH_3) 320 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{19}H_{34}NOSi$ ($M+NH_4^+$): 320.2410. Found: 320.2408 ($M+NH_4^+$).

*(1S,2S)-(Z)-1-Cyclohexyl-2-[(methoxymethyl)oxy]-4-(trimethylsilyl)-3-buten-1-ol (**12d**).* **51%**: R_f (1:9 EtOAc:hexane) 0.20; $[\alpha]_D^{25}$ +64.6° ($CHCl_3$, *c* 1.00); IR (film) 3600-3100, 2924, 2852, 1650 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 6.24 (dd, J = 14.5, 9.6 Hz, 1H), 5.84 (d, J = 14.5 Hz, 1H), 4.71 (d, J = 6.8 Hz, 1H), 4.52 (d, J = 6.8 Hz, 1H), 4.26 (dd, J = 9.6, 4.2 Hz, 1H), 3.36 (s, 3H), 3.22 (m, 1H), 2.17 (d, J =6.5 Hz, 1H), 1.74-1.09 (m, 11H), 0.14 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 144.6, 135.2, 93.2, 78.9, 75.4, 55.5, 40.0, 29.9, 28.1, 26.4, 26.1, 0.1;*m/z* (CI^+, NH_3) 304 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{15}H_{34}NO_3Si$ ($M+NH_4^+$): 304.2308 Found: 304.2312 ($M+NH_4^+$).

*(1S,2R)-(Z)-1-Cyclohexyl-2-methyl-4-(trimethylsilyl)-3-decen-1-ol (**12e**).* **58%**: R_f (1:19 EtOAc:hexane) 0.28; $[\alpha]_D^{25}$ +29.4° ($CHCl_3$, *c* 1.00); IR (film) 3600-3400 cm^{-1}; ^{1}H NMR (250 MHz, $CDCl_3$) δ 5.75 (d, J = 10.5 Hz, 1H), 3.09 (d, J = 8.8 Hz, 1H), 2.58-2.47 (m, 1H), 2.05 (m, 2H), 1.77 (m, 2H),1.66-1.38 (m, 6H), 1.26-1.07 (m, 12H), 0.88 (m, 6H), 0.15 (s, 9H); ^{13}C NMR (62.9 MHz, $CDCl_3$) δ 145.1, 143.2, 78.7, 39.4, 39.1, 38.6, 31.7, 31.0, 30.9, 29.1, 26.9, 26.5, 26.4, 24.9, 22.6, 17.1, 14.1, 0.7; *m/z* (CI^+, NH_3) 342 ($M+NH_4^+$); HRMS (CI^+, NH_3) Calcd for $C_{20}H_{44}NOSi$ ($M+NH_4^+$): 342.3192 Found: 342.3190 ($M+NH_4^+$).

*General procedure for the determination of enantiomeric excess of homoallylic alcohols **2a-b**, **4a** via formation of α-methoxy-α-(trifluoromethyl)phenylacetic (MTPA) ester derivatives (Mosher esters).*[21] To homoallylic alcohol (1*R*)-**2a**, (1*S*,2*R*)-**2b**, (1*S**,2*R**)-**2b** or (1*S*,2*S*)-**4a** (0.036 mmol), (dimethylamino)pyridine (3 mg) and pyridine (32 μL, 0.04 mmol) in CH_2Cl_2 (0.5 mL) was added either (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride or (*R*)-(-)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (10 μL, 1.5 equiv.). After the esterification had proceeded to completion (tlc analysis) the mixture was diluted with Et_2O (10 mL) and washed with saturated aqueous $NaHCO_3$ (2 × 2 mL) followed by saturated aqueous $CuSO_4$ solution (2 × 2 mL), water (2 × 2 mL) and brine (2 mL). The separated organic phase was dried, evaporated and the residue taken up in Et_2O (5 mL), filtered through a short pad of silica, re-evaporated and directly analyzed by ^{1}H NMR without any purification.

(S)-[(1R)-1-Cyclohexyl-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenylacetate. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58-7.55 (m, 2H), 7.44-7.39 (m, 3H), 5.72-5.58 (m, 1H), 5.04-4.98 (m, 3H), 3.55 (s, 3H), 2.39-2.29 (m, 2H), 1.77-1.58 (m, 5H), 1.27-1.02 (m, 6H).

(R)-[(1R)-1-Cyclohexyl-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenylacetate. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.56 (m, 2H), 7.43-7.38 (m, 3H), 5.84-5.70 (m, 1H), 5.15-5.01 (m, 3H), 3.58 (s, 3H), 2.46-2.40 (m, 2H), 1.71-1.55 (m, 5H), 1.28-0.88 (m, 6H).

(S)-[(1S,2R)-1-Cyclohexyl-2-methyl-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenylacetate. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61-7.59 (m, 2H), 7.44-7.40 (m, 3H), 5.74-5.62 (m, 1H), 5.03-4.90 (m, 3H), 3.54 (s, 3H), 2.59-2.52 (m, 1H), 1.69-1.56 (m, 5H), 1.37-0.75 (m, 9H).

(S)-[(1S,2R*)-1-Cyclohexyl-2-methyl-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenylacetate.* 1:1 Mixture of diastereoisomers ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.60 (m, 4H), 7.44-7.39 (m, 6H), 5.80-5.62 (m, 6H), 3.56 (s, 3H), 3.54 (s, 3H), 2.62-2.29 (m, 2H), 1.69-1.59 (m, 10H), 1.27-0.88 (m, 18H).

(S)-[(1S,2S)-1-Cyclohexyl-2-(methoxymethyl)oxy-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenyl acetate. Major diastereoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62-7.59 (m, 2H), 7.44-7.40 (m, 3H), 5.62-5.44 (m, 1H), 5.33-5.28 (m, 1H), 5.11-5.07 (m, 1H), 4.53 (d, J = 6.8 Hz, 1H), 4.39 (d, J = 6.8 Hz, 1H), 4.20 (t, J = 7.5 Hz, 1H), 3.59 (s, 3H), 3.17 (s, 3H), 1.77-1.65 (m, 5H), 1.27-1.08 (m, 6H).

(R)-[(1S,2S)-1-Cyclohexyl-2-(methoxymethyl)oxy-3-buten-1-yl] α-methoxy-α-(trifluoromethyl)phenyl acetate. Major diasteoreoisomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2H), 7.44-7.39 (m, 3H), 5.67-5.61 (m, 1H), 5.39-5.33 (m, 2H), 5.13-5.09 (m, 1H), 4.69 (d, J = 6.7 Hz, 1H), 4.53 (d, J = 6.7 Hz, 1H), 4.66 (t, J = 7.5 Hz, 1H), 3.69 (s, 3H), 3.29 (s, 3H), 1.73-1.59 (m, 5H), 1.27-1.03 (m, 6H).

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