m-**2b**, 13049-38-2; p-**2b**, 13049-40-6; p-**2c**, 14584-23-7; o-**2d**, 117712-96-6; p-**2d**, 117712-97-7; p-**2e**, 108292-13-3; o-**2f**, 57754-02-6; m-**2f**, 117712-98-8; p-**2f**, 61342-05-0; o-**2g**, 117712-99-9; p-**2g**, 117713-00-5; p-**2h**, 117713-01-6; o-**2i**, 117713-02-7; o-**3** (n=2), 776-35-2; o-**3** (n=3), 1015-80-1; o-**3** (n=4), 1082-12-8; o-**3** (n=5), 4444-45-5; o-**3** (n=6), 76692-01-8; o-**3** (n=7), 117713-05-0; m-**3** (n = 9), 117713-03-8; m-**3** (n = 10), 51739-47-0; p-**3** (n = 12), 2013-42-5; p-**3** (n=14), 2013-43-6; p-**3** (n=16), 117713-04-9; m-**4** (n=9), 117713-06-1; m-**4** (n=10), 117713-07-2; m-**4** (n=n'=2), 24656-54-0; p-**4** (n=2,n'=5), 117713-08-3; p-**4** (n=n'=5), 117713-09-4; p-**4** (n=n'=12), 117713-10-7; p-**4** (n=n'=14), 117713-11-8; p-**4** (n=n'=16), 117713-12-9; **5**, 90732-77-7; **6**, 117773-79-2; **7**, 61983-95-7; **8**, 117713-13-0; o-**9b**, 76708-83-3; m-**9b**, 7435-49-6; p-**9b**, 76708-90-2; p-**9c**, 117713-15-2; o-**9d**, 117713-20-9; p-**9d**, 117713-16-3; p-**9e**, 117713-17-4; m-**9f**, 117713-26-5; p-**9f**, 117713-18-5; p-**9g**, 117713-19-6; p-**9h**, 117713-14-1; o-**10**, 117713-21-0; p-**10**, 4040-29-3; p-**11a** (n=2), 43012-23-3; p-**11a** (n=3), 117713-24-3; p-**11e** (n=2), 117713-23-2; **12**, 113419-98-0; **13**, 2319-97-3; **14**, 117713-25-4; **15**, 4433-13-0; **16**, 31693-66-0; Me_2SO_4, 77-78-1; Et_2SO_4, 64-67-5; *i*-PrBr, 75-26-3; *t*-BuI, 558-17-8; Me_3SiCl, 75-77-4; Me_3GeBr, 1066-37-1; $H_2C{=}CHCH_2Cl$, 107-05-1; $C_5H_{11}Br$, 110-53-2; I_2, 7553-56-2; Cl_2CH_2, 75-09-2; $Cl(CH_2)_2Cl$, 107-06-2; $Br(CH_2)_2Br$, 106-93-4; $Br(CH_2)_3Br$, 109-64-8; $Br(CH_2)_4Br$, 110-52-1; $Br(CH_2)_5Br$, 111-24-0; $Br(CH_2)_7Br$, 4549-31-9; $Br(CH_2)_8Br$, 4549-32-0; $Br(CH_2)_{10}Br$, 4101-68-2; $Br(CH_2)_{12}Br$, 3344-70-5; $Br(CH_2)_{14}Br$, 37688-96-3; Me_2SiCl_2, 75-78-5; m-$C_6H_4(CH_2Br)_2$, 626-15-3; p-$C_6H_4(CH_2Cl)_2$, 623-25-6.

Supplementary Material Available: Calculated atomic coordinates of the low-energy conformations of o-**3** (n = 2–7) and o-**2i** depicted in Figure 1 (8 pages). Ordering information is given on any current masthead page.

Effect of Substituent on Reactions Remote from Silicon:[1] Regioselective α-Alkylation of α-Silylallyl Carbanions

Raymond F. Horvath and Tak Hang Chan*

Department of Chemistry, McGill University, Montreal, Quebec, Canada H3A 2K6

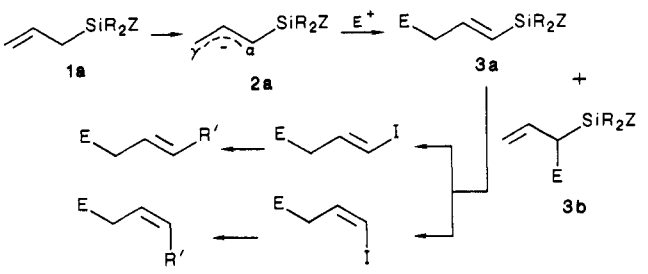
Received October 18, 1988

α-Silylallyl carbanions having metal-ion complexing substituents on silicon react with alkyl halides to give α-substituted allylsilanes regioselectively. The extent of α-selection depends significantly on the nature of the ligand and solvent. The synthetic utility of these systems is demonstrated by application in the synthesis of α-(*E*)-bisabolene.

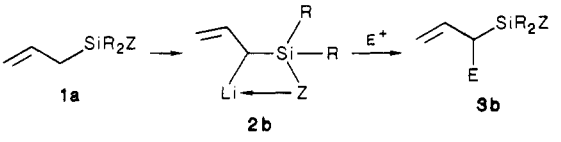
While organosilicon compounds have been used extensively in organic synthesis,[2] the substituents on silicon are typically alkyl or aryl groups. Substituent effects have been recognized and exploited to control reactions occurring at silicon. One good example is the use of a *tert*-butyl substituent to confer reasonable hydrolytic stability in *tert*-butyldimethylsilyl as a hydroxy protecting group.[3] On the other hand, the effect of silyl substituents on reactions occurring not at, or *remote* from, silicon is less known.[1]

An interesting area for the study of substituent effects is on the regiochemical control in substitution reactions of silylallyl anions.[4,5] Corriu has shown that the α-trimethylsilylallyl anion (**2a**, R, Z = CH_3) can be generated from allyltrimethylsilane (**1a**, R, Z = CH_3) and reacted with electrophiles.[6] The regioselectivity of the reaction depended on the nature of the electrophile. Carbonyl electrophiles gave regioselectively the γ-adducts[6] and, if complexed with a Lewis acid, the reaction gave the α-adducts.[7] More complicated were reactions with alkyl halides. Mixtures of α- and γ-alkylated products were obtained.[8] Our laboratory has demonstrated that by replacing the methyl groups on silicon by sterically larger groups (Et, Pr, or Ph), alkylation of the α-silylallyl anion gave higher γ-regioselection.[8] This observation has served as the basis of a useful method to prepare regio- and stereoselectively (*E*)-vinylsilanes and, after appropriate transformations, disubstituted alkenes (Scheme I).[9]

Scheme I



Scheme II



2b

Z = lithium chelating group

(1) For a preliminary report, see: Chan, T. H.; Koumaglo, K.; Horvath, R.; Wang, D.; Wei, Z. Y.; Yi, G. L.; Li, J. S. *Silicon Chemistry*; Corey, E. R., Corey, J. Y., Gaspar, P. P., Ed.; Ellis-Horwood: Chichester, 1988; Chapter 5; p 49.

(2) (a) Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981. (b) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983. (c) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(3) (a) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190. (b) Lalonde, M.; Chan, T. H. *Synthesis* **1985**, 817.

(4) For a general review on regiocontrol of allylic anions, see: (a) Biellmann, J.-F.; Ducep, J.-B. *Org. React. (N.Y.)* **1982**, *23*, 1. (b) Seebach, D.; Geiss, K.-H. *New Applications of Organometallic Reagents in Organic Synthesis*; Seyferth, D., Ed.; Elsevier: Amsterdam, 1976; p 1. (c) Gompper, R.; Wagner, H.-U. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 321.

(5) For recent examples of reactions of allylic anions, see: (a) Yamamoto, Y.; Yatagai, H.; Saito, Y.; Kazuhiro, M. *J. Org. Chem.* **1984**, *49*, 1096. (b) Horvath, R. F.; Chan, T. H. *J. Org. Chem.* **1987**, *52*, 4489.

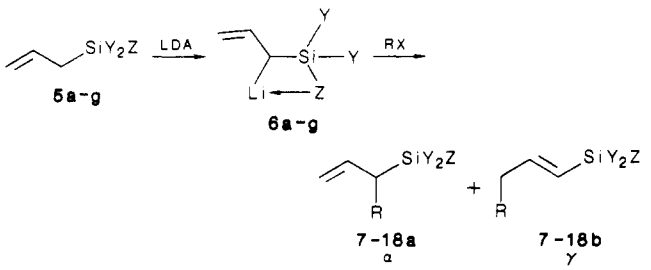
(6) (a) Corriu, R.; Masse, J. *J. Organomet. Chem.* **1973**, *57*, C5. (b) Corriu, R. J. P.; Maase, J.; Samate, D. *Ibid.* **1975**, *93*, 71.

(7) Lau, P. W. K.; Chan, T. H. *Tetrahedron Lett.* **1978**, 2383.

(8) Koumaglo, K.; Chan, T. H. *Tetrahedron Lett.* **1984**, *25*, 717.

0022-3263/89/1954-0317$01.50/0

Scheme III



5a, **6a**: Y = Z = OMe
5b, **6b**: Y = Z = OEt
5c, **6c**: Y = Z = OCH_2CH_2OMe
5d, **6d**: Y = Me; Z = $ONEt_2$
5e, **6e**: Y = Me; Z = OCH_2CH_2OMe
5f, **6f**: Y = Me; Z = $OCH_2CH_2NMe_2$
5g, **6g**: Y = Me; Z = $OCH_2CH_2OCH_2CH_2OEt$

Table I. Ratios and Yields of Products from Electrophilic Substitution of Lithiated Alkoxyallylsilanes with Various Electrophiles[a]

silane	electrophile	products[b]	α:γ_E[c]	% yield[d]
5a	CH_3I	**7a, 7b**	91:9	33
5b	CH_3OD	**8a, 8b**	81:19	26
5b	CH_3I	**9a, 9b**	82:18	71
5b	$CH_3(CH_2)_5I$	**10a, 10b**	34:66	84
5c	CH_3I	**11a, 11b**	74:26	[e]
5e	CH_3I	**12a, 12b**	86:14	[e]
5e	$CH_3(CH_2)_5I$	**13a, 13b**	65:35	[e]
5f	CH_3I	**14a, 14b**	86:14	[e]
5g	CH_3I	**15a, 15b**	87:13	78
5g	$CH_3(CH_2)_5I$	**16a, 16b**	61:39	76
5g	$CH_2{=}CHCH_2Br$	**17a, 17b**	41:59	63
5g	$(CH_3)_2C{=}CHCH_2Br$	**18a, 18b**	71:29	79

[a] Reactions were performed in THF with LDA as base. [b] Regioisomers were not separated. [c] Ratios were determined by capillary GC/MS and were confirmed by ^1H NMR data. [d] Yields are based on the weight of the mixture of regioisomers. Products, where yields are reported, are spectrally clean after workup. [e] Products were not isolated and were only detected by GC/MS.

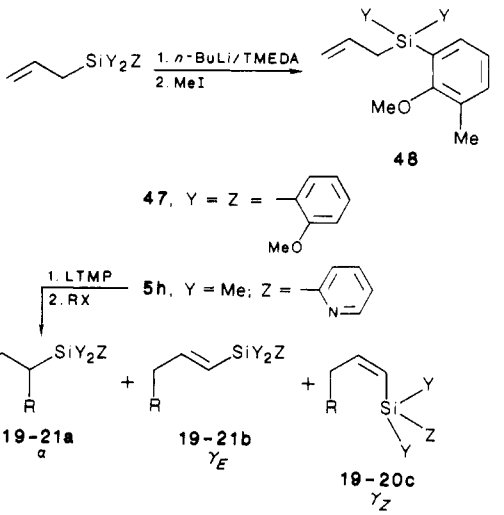
More demanding is the question of whether the alkylation of the α-silylallyl anion can be controlled to give regioselectively the α-isomer. Owing to the usefulness of allylsilanes in organic synthesis,[2] a convenient access to **3b** by regioselective alkylation of anion **2** would be considerably more interesting (Scheme II).

Complex induced proximity effects[10] in reactions of organometallic species having neighboring metal-ion binding groups have been proven to be useful for controlling regioselection in organic synthesis.[11,12] Given here is a study of the proximity effect of silyl functional groups (Z) on silylallyl anion **2b** in reactions with electrophiles (Scheme II).

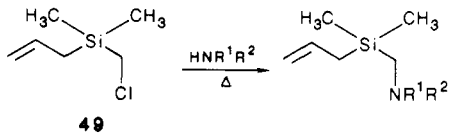
Results and Discussion

α-Alkylation of Alkoxy-Substituted Silylallyl Anions. Studies began by examining the effect of replacing alkyl groups on silicon with alkoxy groups. The results are summarized in Scheme III and Table I. Reaction of **5a** with lithium diisopropylamide (LDA) generated the anion **6a** at −78 °C (Scheme III).[13] The fact that LDA can deprotonate **5a** may be attributed to the enhanced acidity of **5a** over **1a** (R, Z = CH_3) by the inductive effect of the alkoxy groups and/or from the kinetic rate enhancement arising from complexation effects.[11,12] It is more interesting to note that quenching the anion with iodomethane gave regioselectively the α-isomer (**7a**:**7b** = 91:9, Table I). The yield was, however, not satisfactory, possibly due to the ease of polymerization of the trimethoxysilyl function. Compound **5d** also was not stable to the reaction conditions. The anions from compounds **5e** to **5g** with one multiheteroatom-containing alkoxy substituent on silicon have similar regiocontrol for methylation as do compounds with three alkoxy substituents. With iodomethane as the common electrophile, it appears that as the number of binding heteroatoms in the alkoxy substituent increases, the α-selectivity rises. These results suggest that the primary factor that controls α-regioselection is the ability of the chelating group to bind lithium in proximity to silicon. However, for larger electrophiles like iodohexane, even the most α-selective anion **6g** did not possess high enough selectivity to render the reaction synthetically useful. Finally, it is interesting to note that treatment of **6g** with 3,3-dimethylallyl bromide gave better α-selection than with the less bulky allyl bromide.

Scheme IV



Scheme V



Allylsilanes with Functionalized Aryl Groups. Allylsilanes in which silicon was substituted with a functionalized aromatic group were also examined. Treatment of compound **47** with *n*-butyllithium and TMEDA at 0 °C followed by iodomethane gave predominantly the ring-alkylated product **48** by orthometalation[11] (Scheme IV) and a small amount of dialkylated product. Compound **5h** could be deprotonated cleanly with lithium tetramethylpiperidide (LTMP) at −78 °C and less efficiently with LDA. Once again α-selectivity was observed when the anion was quenched with iodomethane (Table II).

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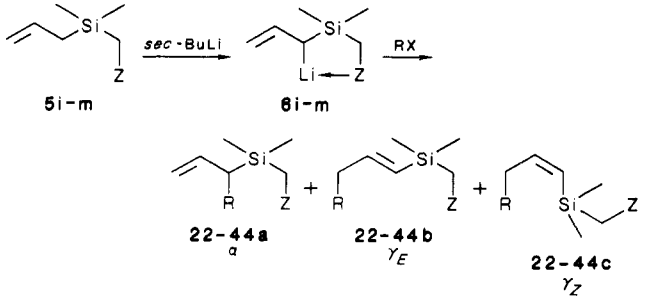
(10) Beak, P.; Meyers, A. I. *Acc. Chem. Res.* **1986**, *19*, 356.
(11) (a) Wakefield, B. J. *Chemistry of Organolithium Compounds*; Pergamon: Oxford, 1974; p 38. (b) Gschwend, H. W.; Rodriquez, H. R. *Org. React. (N.Y.)* **1979**, *26*, 1.
(12) For some examples of complex induced proximity effects, see: (a) Evans, D. A.; Andrews, G. C. *Acc. Chem. Res.* **1974**, *7*, 147. (b) Beak, P.; Hunter, J. E.; Young, M. J.; Wallin, A. P. *J. Am. Chem. Soc.* **1987**, *109*, 5403. (c) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306.
(13) The suggestion by Professor R. R. Fraser of using an alkoxy group on silicon to stabilize α-silylcarbanions is gratefully acknowledged. For a similar activating effect, see: Buell, G. R.; Corriu, R.; Guerin, C.; Spialter, L. *J. Am. Chem. Soc.* **1970**, *92*, 7424.

Table II. Ratios and Yields of Products from Electrophilic Substitution of Lithiated Aryl- and (Aminomethyl)allylsilanes with Various Electrophiles in THF[a]

silane	electrophile	products[b]	$\alpha:\gamma_E:\gamma_Z$[c]	% yield[d]
5h	CH_3OD	**19a, 19b, 19c**	31:57:12[e]	98[f]
5h	CH_3I	**20a, 20b, 20c**	69:28:3[e]	83[f]
5h	$CH_3(CH_2)_5I$	**21a, 21b**	40:60[e]	88[f]
5i	D_2O	**22a, 22b, 22c**	43:31:26	89
5i	CH_3OD	**22a, 22b, 22c**	39:45:16	93
5i	CH_3I	**23a, 23b, 23c**	68:26:6	94
5i	$CH_3(CH_2)_5Br$	**24a, 24b**	42:58	78
5j	CH_3OD	**25a, 25b, 25c**	23:64:13	86
5j	CH_3I	**26a, 26b, 26c**	58:38:4	88
5j	$CH_3(CH_2)_5Br$	**27a, 27b**	41:59	90
5k	CH_3I	**28a, 28b, 28c**	89:5:6	73
5k	$CH_3(CH_2)_5I$	**29a, 29b, 29c**	59:37:4	85
5k	$CH_2{=}CHCH_2Br$	**30a, 30b, 30c**	51:42:7	63
5k	$(CH_3)_2C{=}CHCH_2Br$	**31a, 31b, 31c**	79:15:6	50
5l	CH_3I	**32a, 32b, 32c**	87:3:10	86
5l	CH_3I	**32a, 32b, 32c**	78:8:14[e]	
5l	$(CH_3)_2C{=}CHCH_2Br$	**36a, 36b, 36c**	70:19:11	86
5m	CH_3OD	**37a, 37b, 37c**	54:17:29	90
5m	CH_3I	**38a, 38c**	90:0:10	89
5m	$CH_3(CH_2)_3I$	**39a, 39b**	70:30	85
5m	$CH_3(CH_2)_5Cl$	[g]		
5m	$CH_3(CH_2)_5Br$	**40a, 40b, 40c**	60:38:2	90
5m	$CH_3(CH_2)_5I$	**40a, 40b, 40c**	67:27:6	76
5m	$CH_3(CH_2)_9I$	**41a, 41b**	70:30	82
5m	$CH_2{=}CHCH_2Br$	**42a, 42b, 42c**	57:28:15	80
5m	$CH_2{=}CHCH_2I$	**42a, 42b, 42c**	59:14:27	87
5m	$(CH_3)_2C{=}CHCH_2Br$	**43a, 43b, 43c**	80:11:9	97
5m	$(CH_3)_2C{=}CHCH_2CH_2$-$C(CH_3){=}CHCH_2Br$	**44a, 44b, 44c**	80:13:7	94
5n	CH_3I	**45a, 45c**	85:0:15[h]	69
5n	$CH_3(CH_2)_5I$	**46a, 46b, 46c**	65:27:8[h]	83
56	CH_3I	**57a, 57b**	76:24	87
56	$(CH_3)_2C{=}CHCH_2Br$	**58a, 58b, 58c**	2:1[i]	90

[a] Reactions were done with *sec*-butyllithium as base, unless noted otherwise. [b] Regioisomers were not separated. [c] Ratios were determined by capillary GC/MS and were confirmed by ^1H NMR data. [d] Yields are based on the weight of the mixture of regioisomers. Products are spectrally clean after workup, except where indicated otherwise. [e] LTMP was the base used to generate anion **6**. [f] The yield was determined by GC analysis. [g] Products **40a, 40b,** and **40c** were not formed. Instead, starting material **5m** and the double bond isomers (*E* and *Z*) were obtained in the ratio 43:31:26, respectively. [h] Only one diastereomer of the α-isomer was detected by GC/MS, ^1H NMR, and ^{13}C NMR analyses. [i] The α/γ ratio was determined by ^1H NMR spectroscopy.

Scheme VI

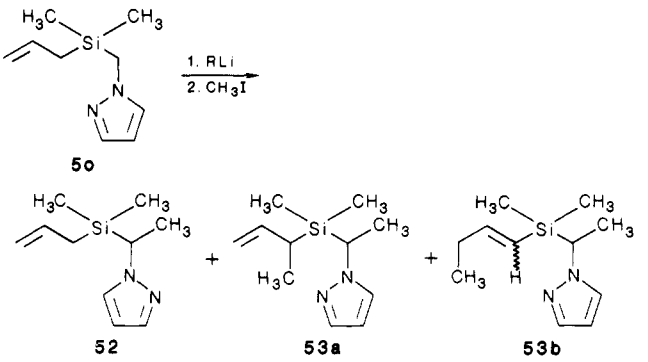


5i, 6i : Z = NEt_2
5j, 6j : Z = $N(CH_2)_4$
5k, 6k : Z = $N(Me)CH_2CH_2NMe_2$
5l, 6l : Z = $N(CH_2CH_2OMe)_2$
5m, 6m: Z = $N(CH_2CH_2OEt)_2$

With bromohexane as the electrophile, the α-selectivity decreased. Clearly, different substituents had to be sought for better α-selectivity.

α-Alkylation of Aminomethyl-Substituted Silylallyl Anions. A series of allyl(aminomethyl)dimethylsilanes (**5i–o**) were prepared from commercially available allyl(chloromethyl)dimethylsilane (**49**) according to Scheme V. Compound **5i** reacted cleanly after 3 h with *sec*-butyllithium[14] at −60 °C in THF to give the corresponding anion **6i** (Scheme VI). Treating **6i** with iodomethane at −78 °C gave three alkylation products **23a, 23b,** and **23c** in a ratio of 68:26:6, respectively (Table II). As with compound **5h** and others to follow, the γ-(*Z*)-isomer was formed in addition to the α- and the γ-(*E*)-isomers (vide infra). Electrophiles like bromohexane and D_2O gave poorer α-selection. In comparison, compound **5i** gave similar ratios to compound **5h**. Replacing the diethylamino group with the sterically less demanding pyrrolidino group (**5j**) gave poorer α-selection with the same electrophiles (Table II).

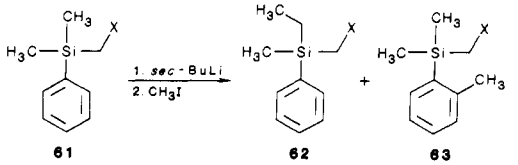
Scheme VII

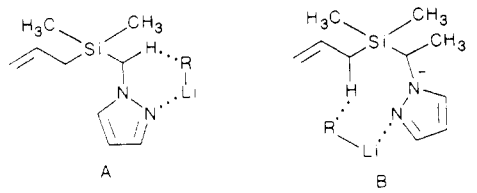


In an intramolecular complexation as in **6i–m**, a five-membered ring is involved. Designing a system that would complex lithium to form a six-membered intermediate may provide better α-selectivity. Moving the binding heteroatom away from silicon by one methylene unit would possibly give problems due to the propensity of β-elimination.[16] Compound **5o**, which has a pyrazole group, may offer a solution. The nitrogen in the 2-position of the pyrazole ring would compete for chelation. It was found that treatment of **5o** with LDA at −78 °C in THF and subsequent alkylation of the anion with iodomethane gave exclusively product **52**. When *sec*-butyllithium was used, the dialkylated products **53a** and **53b** were also obtained (Scheme VII). The pattern seemed to be similar to reactions involving compound **47** and other kinds of compounds.[17] It appears that the transition state A, the organolithium and silyl molecule six-membered complex, renders the anion leading to **52**. The alternative kinetically less-favored eight-membered cycle B results in the anion leading to **53**. The above situation is similar for compound **47**.

Indications from earlier work with alkoxyallylsilanes suggested that α-selection could be improved by having more binding heteroatoms in the ligand. It was pleasing

(14) *sec*-Butyllithium appears to give a cleaner product mixture than *n*-butyllithium.
(15) Hünig, S.; Klaunzer, N.; Schlund, R. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1281.
(16) Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1946**, *68*, 485.
(17) Metalation of compound **61** followed by reaction with iodomethane gave apparently did not take place to yield **63**. Linkletter, B.; Horvath, R. F.; Chan, T. H., unpublished results.





to find that compounds **5k**, **5l**, and **5m** gave enhanced α-selection with a variety of electrophiles. Metalation of these compounds could be carried out with *sec*-butyllithium in THF at −78 °C within 15 min. Furthermore, compound **5l** could also be metalated with LTMP in less than 1 h at −78 °C. Quenching anions **6k**, **6l**, and **6m** with iodomethane gave products **28a–c** in a ratio of 89:5:6, **32a–c** in a ratio of 87:3:10, and **38a,c** in a ratio of 90:10, respectively (Table II). Amide base conditions for **5l** gave slightly poorer α-selectivity (**32a:32b:32c** = 78:8:14).[18] As α-selectivity improves with better chelating groups, the proportion of the γ-(*Z*)-isomer also increases. Regioselectivity is also dependent on the nature of the electrophile.[19] As before, sterically larger electrophiles generally give poorer α-selectivity than smaller ones. Anion **6m** reacts with iodohexane to give products **40a–c** in the ratio 67:27:6, respectively. Electrophiles with good leaving groups like iodide give higher α-selectivity than those with poorer leaving groups such as chloride or bromide.

Solvent Effects. Effort was made to further improve α-regioselectivity by modifying the reaction conditions. Transmetalation of **6** with magnesium bromide or copper iodide followed by treatment with electrophile did not change selectivity by any significant amount. Neither did the use of potassium bis(trimethylsilyl)amide or *n*-butylpotassium[20] for metalation. However, upon changing the solvent from THF to diethyl ether, a significant improvement in α-selectivity was observed for compounds **5l** and **5m** (Table III). The use of dibutyl ether or diisopropyl ether gave ratios similar to diethyl ether; however, precipitation occurred during metalation. Diethyl ether appears to be superior to THF, probably because its larger steric size reduces solvation of the lithium cation. Hence, it competes less with the chelating ligand for coordination to the metal. Ether had little effect on regioselection in reactions with **5k**. This could be because the lithium ion in anion **6k** requires a solvent molecule to saturate the coordination, whereas in either anion **6l** or **6m**, the lithium ion can be tetracoordinated without the participation of solvent. The latter case is therefore sensitive to the solvent effect. Treatment of anion **6l** or **6m** with iodomethane both gave exclusively the corresponding α-product. They also reacted with iodohexane and 3,3-dimethylallyl bromide to give very high α-selection (Table III). Synthetically useful yields of α-substituted allylsilanes can thus be achieved with compounds **5l** and **5m**.

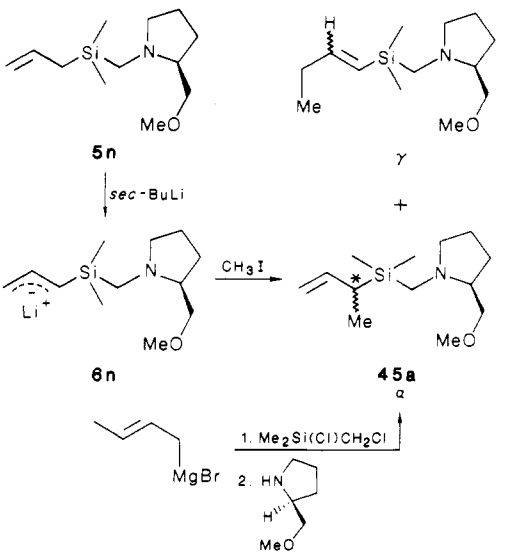
With use of **6k** as an example, it is possible that the (silylallyl)lithium exists as a mixture of complexes **50**, **51a**, and **51b** and possibly higher aggregates.[21] The relative

Table III. Ratios and Yields of Products from Electrophilic Substitution of Lithiated (Aminomethyl)allylsilanes with Various Electrophiles in Et_2O[a]

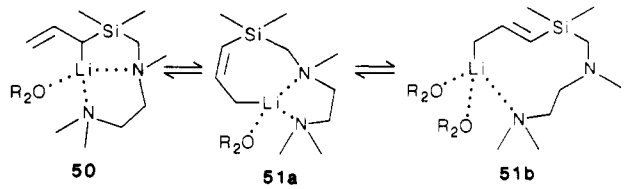
silane	electrophile	products[b]	α:γ_E:γ_Z[c]	% yield[d]
5k	CH_3I	**28a, 28b, 28c**	87:7:6	76
5k	$CH_3(CH_2)_5I$	**29a, 29b**	75:25	75
5k	$(CH_3)_2C{=}CHCH_2Br$	**31a, 31b, 31c**	74:18:8	91
5l	CH_3I	**32a**	100	78
5l	$CH_3(CH_2)_3I$	**33a, 33b, 33c**	91:6:3	83
5l	$CH_3(CH_2)_5I$	**34a, 34b, 35c**	95:3:2	81
5l	$CH_2{=}CHCH_2I$	**35a, 35b**	60:40	72
5l	$(CH_3)_2C{=}CHCH_2Br$	**36a, 36b, 36c**	87:11:2	68
5m	CH_3I	**38a**	100	98
5m	$CH_3(CH_2)_3I$	**39a, 39b**	90:10	96
5m	$CH_3(CH_2)_5I$	**40a, 40b**	90:10	96
5m	$CH_2{=}CHCH_2I$	**42a, 42b, 42c**	68:21:11	95
5m	$(CH_3)_2C{=}CHCH_2Br$	**43a, 43b**	91:9	94
5n	CH_3I	**45a, 45b, 45c**	87:6:7[e]	94
5n	$CH_3(CH_2)_5I$	**46a, 46b, 46c**	63:34:3[e]	66
56	CH_3I	**57a, 57b**	60:40	85

[a] Reactions were done with *sec*-butyllithium as base. [b] Regioisomers were not separated. [c] Ratios were determined by capillary GC/MS and were confirmed by ^1H NMR data. [d] Yields are based on the weight of the mixture of regioisomers. Products are spectrally clean after workup. [e] Only one diastereomer of the α-isomer was detected by GC/MS, ^1H NMR, and ^{13}C NMR analyses.

Scheme VIII



ratio of α-, γ-(*Z*)- and γ-(*E*)-isomers formed depends on the equilibrium of these species as well as the rate of reactions of these complexes with alkyl halides. If the reaction proceeds by an S_E2 mechanism, then it is possible that the cis product is formed from the seven-membered ring complex **51a** with the cis stereochemistry.[22] Geometrical restrictions of alkoxysilylallyl anions **6a–g** discussed earlier could prevent the cis complex from being



(18) Additives or amino compounds produced from metalation reactions with amide bases, can affect regioselectivity. See ref 12a and Atlani, P. M.; Biellmann, J. F.; Dube, S.; Vicens, J. J. *Tetrahedron Lett.* **1974**, 2665.

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(21) A recent X-ray structure of allyl(pentamethyldiethylenetriamine)lithium has revealed the first example of a monomeric allyllithium complex. This finding may indicate that anions **6l** and **6m** also exist as monomers in solution and can support the given explanation on the observed solvent effects. See: Schümann, U.; Weiss, E.; Dietrich, H.; Mahdi, W. *J. Organomet. Chem.* **1987**, *322*, 299.

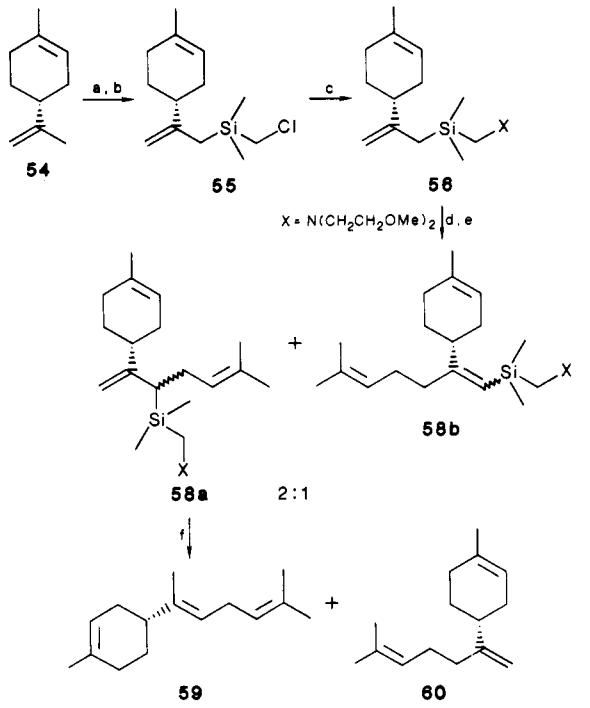
(22) Similar conclusions have been drawn by others. See: (a) Julia, M.; Schouteeten, A.; Baillarge, M. *Tetrahedron Lett.* **1974**, 3433. (b) Schouteeten, A.; Julia, M. *Ibid.* **1975**, 607. (c) Kloosterziel, H.; Van Drunen, J. A. A. *Recl. Trav. Chim. Pays-Bas* **1970**, *89*, 32.

formed and would explain why the corresponding cis products are not observed. The observed higher α-regioselection can be attributed to the predominance of the five-membered ring complex **50** in the equilibrium. Factors such as silatrane formation, which could affect regioselectivity, do not seem to be likely. Low-temperature ^{1}H NMR analysis of compound **5** does not suggest the formation of hypervalent silicon.[23] Only a slight change in the chemical shift of the olefinic protons can be observed.

Regio- and Stereoselective Alkylation of Chiral Silylallyl Anions. In a preliminary study to determine the effect of a chiral ligand on stereoselectivity, compound **5n** was prepared from compound **49** and (*S*)-(+)-2-(methoxymethyl)pyrrolidine. The metalation procedure was carried out as usual in THF (Scheme VIII). Subsequent quenching of anion **6n** with iodomethane not only gave good α-selectivity (**45a**:**45c** = 85:15) but gave only one stereoisomer of product **45a**. Neither the ^{1}H NMR spectrum nor the ^{13}C NMR spectrum showed doubling of any signal to indicate the presence of another diastereomer. In order to confirm that the other diastereomer of **45a** would show resonances at a different chemical shift, a mixture of diastereomers of **45a** was prepared by an alternative route. A racemic mixture of 3-[(chloromethyl)-dimethylsilyl]-1-butene was prepared[24] from crotylmagnesium bromide and chloro(chloromethyl)dimethylsilane and converted to **45a** by subsequent reaction with the chiral amine (Scheme VIII). Other crotylsilyl side products were formed in minor amounts and fortunately did not interfere in the spectral analysis. The ^{1}H NMR spectrum of this mixture clearly showed a doubling of the olefinic multiplet and the methyl doublet from the diastereomeric pair of **45a**. A similar doubling of lines was observed in the ^{13}C NMR spectrum. The absolute stereochemistry of **45a** has yet to be established in order to gain more information about the asymmetric reaction. With iodohexane as the electrophile α-selectivity dropped (**46a**:**46b**:**46c** = 65:27:8) while stereoselectivity appears to have remained good. As with compound **5k**, the use of ether solvent instead of THF did not improve α-selectivity. Again, these results can be explained in terms of incomplete internal solvation of the lithium cation by the ligand. The above reaction offers considerable potential as an approach to chiral allylsilanes.[25,26]

Stereoselective Synthesis of α-(*E*)-Bisabolene. In order to show the synthetic utility of this new methodology, the essential oil α-(*E*)-bisabolene was prepared in four simple steps (Schene IX). Treatment of (*R*)-(+)-limonene (**54**) with *n*-butyllithium and TMEDA,[27] followed by quenching the anion of **54** with chloro(chloromethyl)dimethylsilane gave compound **55**. Subsequent heating of **55** with an excess of bis(2-methoxyethyl)amine gave compound **56**. The silylallyl anion of **56** was then generated with *sec*-butyllithium. First, the alkylation reaction was probed with iodomethane as the electrophile to determine the effect of the cyclohexene substituent on regioselectivity. In THF, α-selectivity was good (**57a**:**57b** = 76:24), although

Scheme IX[a]



[a] (a) *n*-BuLi, TMEDA, 25 °C; (b) $Me_2Si(Cl)CH_2Cl$, Et_2O; (c) $HN(CH_2CH_2OMe)_2$, 120 °C; (d) *sec*-BuLi, THF, −78 °C; (e) $Me_2C{=}CHCH_2R$, THF, −78 °C; (f) HI, PhMe, −10 °C.

it was not as high as with compound **51** (Table II). Anomalously, lower α-selectivity was obtained in ether (**57a**:**57b** = 60:40, Table III). It appears that sterically large substituents on the allylic moiety affect the selectivity.[12a] With 3,3-dimethylallyl bromide as the electrophile, products **58a** and **58b** were obtained of the ratio 2:1 (by ^{1}H NMR) in THF (Table II). Desilylation of **58** with CsF in wet DMF at reflux gave a 50:50 mixture of **59** and **60** (β-bisabolene). The basic reaction conditions, which presumably generate the allyl anion, are likely to be the cause for the mixture obtained. Thus, selective protodesilylation could be achieved with hydroiodic acid[28] in toluene (**59**:**60** = 90:10) to give stereoselectively the sesquiterpene α-(*E*)-bisabolene (**59**).[29]

Summary and Conclusions

During the course of this work, several important conclusions have been reached. Allylsilanes having metal-ion complexing substituents on silicon can be readily prepared by rapid metalation with alkyllithium or lithium amide bases at low temperatures. If more than one acidic hydrogen exists in the molecule, the proton that will be removed is likely to be the one incorporated in the kinetically favored allylsilane–organolithium complex. The chelating ligands having two, or better, three appropriately positioned heteroatoms bind the lithium cation effectively enough to yield good α-selectivity in reactions with alkyl halides. Moreover, it appears that when the ligand is chiral, the reaction proceeds stereoselectively. Regioselectivity is also critically dependent upon the nature of solvent used. The utility of allylsilanes bearing metal-ion binding ligands on silicon has been demonstrated with the synthesis of α-(*E*)-bisabolene.

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Experimental Section

General Methods. Materials were obtained from commercial suppliers unless noted otherwise. Tetrahydrofuran was distilled from sodium benzophenone ketyl, and dimethylformamide was distilled from lithium aluminum hydride immediately prior to use. Tetramethylethylenediamine, triethylamine, and diisopropylamine were distilled from calcium hydride and stored over 3-Å molecular sieves. Other solvents were reagent grade or better. Organolithium reagents were ttitrated periodically according to literature procedure.[30] Melting points (mp), determined on a Gallenkamp block, and boiling points (bp) are uncorrected. Analytical thin-layer chromatography (TLC) was done with Merck silica gel 60 F_{254}. Iodine vapor or ceric acid mist was used for compound visualization. Flash chromatography[31] was done on Merck silica gel 60 (230–400 mesh ASTM). Capillary gas chromatography analysis was performed on a Hewlett-Packard 5890A instrument fitted with a 25 m × 0.2 mm high-performance column (cross-linked methylsilicon, film thickness of 0.33 μm). Optical rotations were determined on the JASCO DIP-140 digital polarimeter. Infrared (IR) spectra were recorded on an Analect FT, AQS-18 spectrophotometer with a MAP-67 data system and are reported in reciprocal centimeters (cm^{-1}). ^1H NMR, ^{13}C NMR, and ^{29}Si NMR spectra were recorded on Varian XL-200 or XL-300 instruments. All NMR spectra were done with $CDCl_3$ as the solvent and internal standard. Chemical shifts are expressed in parts per million (ppm). Significant ^1H NMR data are tabulated in the order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), a number of protons, and coupling constant in hertz. Decoupling experiments were performed to unambiguously assign selected spectra. Low- and high-resolution mass spectra (MS) were obtained with Du Pont 21-492B and ZAB 2F HS mass spectrometers (EI, 70 eV; CI, NH_3) and are reported as m/z (relative intensity in percent). Other mass spectra (GC/MS) were obtained on a Finnigan Mat 700 ion trap detector coupled to a Varian 3500 capillary (30 m × 0.25 mm, methylsilicon with 5% phenylsilicon, 0.25 μm) gas chromatograph or a Hewlett-Packard 5980A fitted with a packed column (6% OV-101, 2 m × 6 mm). Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario. All reactions were performed in oven-dried glassware. "Standard workup" will refer to treatment of the reaction mixture with brine, extraction of the aqueous phase with diethyl ether, drying the organic extract over magnesium sulfate, concentrating the extract with a rotary evaporator, and removal of volatile impurities with high vacuum.

Procedures for the preparation of compounds **5c–o** are general, and the reaction conditions have not been optimized for every case.

Allyltris(2-methoxyethoxy)silane (5c). Allyltrichlorosilane (5.0 mL, 34 mmol) was added to an ice-cooled solution of 2-methoxyethanol (80 mL) and triethylamine (15 mL, 104 mmol). A white precipitate was formed. The reaction mixture was allowed to stir and warm to room temperature overnight. The mixture was filtered, and the solvent was removed by evaporation under reduced pressure. Hexanes was added to the residue, and the solution was filtered again. After evaporation of the solvent, the crude product was purified by fractional distillation to yield 6.0 g (59%) of **5c**: bp 134–136 °C (15 mm); IR (film) 2882, 1635, 1458, 1099, 969, 845; ^1H NMR δ 5.82 (ddt, 1 H, J = 17.0, 10.2, 8.0), 4.97 (dm, 1 H, J = 17.0), 4.90 (dm, 1 H, J = 10.2), 3.90 (t, 6 H, J = 4.8), 3.47 (t, 6 H, J = 4.8), 3.35 (s, 9 H), 1.71 (dm, 2 H, J = 8.0); MS 253 (8 $M^+ - CH_2CH{=}CH_2$), 219 (3), 131 (8), 121 (18), 91 (3), 76 (12), 58 (14), 45 (100), 41 (9); exact mass for $C_9H_{21}O_6Si$ ($M^+ - CH_2CH{=}CH_2$) calcd 253.111, found 253.111. Anal. Calcd for $C_{12}H_{26}O_6Si$: C, 48.95; H, 8.90; Si, 9.54. Found: C, 48.64; H, 9.03; Si, 9.86.

Preparation of Alkoxyallylsilanes (5d–g). Allylchlorodimethylsilane (4.0 mL, 27 mml) was added dropwise to an ice-cooled solution of diethyl ether (70 mL), triethylamine (4.6 mL, 33 mmol), and the corresponding alcohol (33 mmol). A voluminous amount of white precipitate was formed as the reaction mixture was warmed to room temperature and allowed to stir overnight. The workup for **5c** was then followed, and the products were purified by fractional distillation.

Allyl[(*N*,*N*-diethylamino)oxy]dimethylsilane (5d): yield 67%; bp 58–60 °C (15 mm); ^1H NMR δ 5.79 (ddt, 1 H, J = 17.0, 10.0, 8.2), 4.87 (dm, 1 H, J =17.0), 4.85 (dm, 1 H, J = 10.0), 2.70 (br q, 4 H, J = 7.0), 1.66 (d, 2 H, J = 8.2), 1.14 (t, 3 H, J = 7.0), 1.02 (t, 3 H, J = 7.0), 0.13 (s, 6 H); MS 187 (14, M^+), 173 (69), 157 (6), 146 (78), 133 (50), 116 (9), 103 (24), 99 (35), 75 (93), 59 (64), 45 (57), 41 (40), 28 (100); exact mass for $C_9H_{21}NOSi$ calcd 187.139, found 187.139.

Allyldimethyl(2-methoxyethoxy)silane (5e): yield 43%; bp 170–174 °C; IR (film) 2923, 1629, 1457, 1252, 1105, 841; ^1H NMR δ 5.79 (ddt, 1 H, J = 17.3, 10.0, 8.0), 4.90 (dm, 1 H, J = 17.3), 4.86 (dm, 1 H, J = 10.0), 3.74 (t, 2 H, J = 5.0), 3.45 (t, 2 H, J = 5.0), 3.36 (s, 3 H), 1.63 (d, 2 H, J = 8.0), 0.12 (s, 6 H); MS 174 (1, M^+), 159 (6), 133 (31), 115 (26), (100), 75 (28), 45 (54), 41 (7); exact mass for $C_5H_{13}O_2Si$ ($M^+ - CH_2CH{=}CH_2$) calcd 133.068, found 133.070.

Allyldimethyl[2-(*N*,*N*-dimethylamino)ethoxy]silane (5f): yield 61%; bp 66–68 °C (15 mm); IR (film) 2955, 2769, 1629, 1458, 1255, 1104, 1058, 838; ^1H NMR δ 5.77 (ddt, 1 H, J = 17.2, 10.2, 8.0), 4.86 (dm, 1 H, J = 17.2), 4.84 (dm, 1 H, J = 10.2), 3.68 (t, 2 H, J = 6.4), 2.42 (t, 2 H, J = 6.4), 2.24 (s, 6 H), 1.61 (d, 2 H, J = 8.0), 0.10 (s, 6 H); MS 187 (10, M^+), 173 (6), 167 (2), 146 (13), 133 (2), 72 (15), 58 (100), 41 (11); exact mass for $C_9H_{21}NOSi$ calcd 187.139, found 187.136.

Allyldimethyl[2-(2-ethoxyethoxy)ethoxy]silane (5g): yield 27%; bp 112–114 °C (15 mm); IR (film) 2870, 1629, 1254, 1111, 838; ^1H NMR δ 5.78 (ddt, 1 H, J = 17.1, 10.2, 8.0), 4.87 (dm, 1 H, J = 17.1), 4.84 (dm, 1 H, J = 10.2), 3.76 (t, 2 H, J = 5.6), 3.59 (m, 6 H), 3.51 (q, 2 H, J = 7.0), 1.62 (d, 2 H, J = 8.0), 1.94 (t, 3 H, J = 7.0), 0.11 (s, 6 H); MS 191 (15, $M^+ - CH_2CH{=}CH_2$), 173 (4), 167 (4), 133 (3), 103 (20), 99 (16), 73 (60), 59 (36), 45 (100), 41 (19); exact mass for $C_8H_{19}O_3Si$ ($M^+ - CH_2CH{=}CH_2$) calcd 191.110, found 191.110.

Allyldimethyl(2-pyridyl)silane (5h). A solution of 2-bromopyridine (2.9 mL, 30 mmol) in THF (5 mL) was added dropwise to another solution of *tert*-butyllithium (67 mmol) in THF (190 mL) at −78 °C. The red-brown reaction mixture was stirred for 15 min. Afterwards, a solution of allylchlorodimethylsilane (7.1 mL, 49 mmol) in THF (5 mL) was added. The mixture slowly became yellow in color as the solution was allowed to warm to room temperature. After standard workup the crude product was purified by flash chromatography (10% ethyl acetate in hexanes) to yield 4.95 g (92%) of **5h**: bp 86–90 °C (15 mm); IR (film) 2931, 2867, 1682, 1629, 1248, 1115, 845; ^1H NMR δ 8.75 (dd, 1 H, J = 4.7, 1.8), 7.54 (m, 2 H), 7.19 (m, 1 H), 5.76 (ddt, 1 H, J = 16.8, 10.2, 8.0), 4.84 (dm, 1 H, J = 16.8), 4.82 (dm, 1 H, J = 10.2), 1.82 (dd, 2 H, J = 8.0, 1.0), 0.31 (s, 6 H); MS 177 (8, M^+), 162 (2 1), 149 (2), 136 (100), 122 (15), 117 (11), 106 (14), 80 (15), 59 (20); exact mass for $C_{10}H_{15}NSi$ calcd 177.097, found 177.101.

Preparation of (Aminomethyl)allyldimethylsilanes (5i–o). A neat mixture of allyl(chloromethyl)dimethylsilane (**49**) in an excess amount of the corresponding secondary amine was heated between 80 and 120 °C with magnetic stirring for about 24 h. Variation in reaction temperature and reaction time is noted in parentheses following the reported yield for the individual products. After standard workup, the crude products were further purified by fractional distillation.

Allyl[(*N*,*N*-diethylamino)methyl]dimethylsilane (5i): yield 71% (120 °C); bp 68 °C (15 mm); IR (film) 2970, 2793, 1629, 1380, 1247, 1152, 893, 844; ^1H NMR δ 5.78 (ddt, 1 H, J = 16.5, 10.0, 8.4), 4.83 (dm, 1 H, J = 16.5), 4.82 (dm, 1 H, J = 10.0), 2.43 (q, 4 H, J = 7.2), 1.93 (s, 2 H), 1.55 (d, 2 H, J = 8.4), 0.97 (t, 6 H, J = 7.2), 0.04 (s, 6 H); MS 185 (4, M^+), (9), 144 (12), 86 (100), 58 (16), 45 (11); exact mass for $C_{10}H_{23}NSi$ calcd 185.160, found 185.160.

2,2-Dimethyl-1-(1-pyrrolidinyl)-2-sila-4-pentene (5j): yield 63% (120 °C); bp 76 °C (15 mm); IR (film) 2959, 2776, 1629, 1249, 844; ^1H NMR δ 5.78 (ddt, 1 H, J = 16.7, 10.8, 7.6), 4.83 (dm, 1 H, J = 16.7), 4.82 (dm, 1 H, J = 10.8), 2.44 (m, 4 H), 2.01 (s, 2 H), 1.74 (m, 4 H), 1.56 (d, 2 H, J = 7.6), 0.06 (s, 6 H); MS 183 (8, M^+), 168 (8), 142 (23), 138 (12), 128 (6), 99 (12), 84 (100), 73 (20), 59 (22), 42 (14); exact mass for $C_{10}H_{22}NSi$ (M^+ + H) calcd 184.152, found 184.152.

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(31) Clark, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Allyldimethyl[[*N'*-[2-(*N*,*N*-dimethylamino)ethyl]-*N'*-methylamino]methyl]silane (5k): yield 44% (80 °C); bp 94 °C (15 mm); IR (film) 2970, 2766, 1629, 1458, 1249, 1154, 1030, 893, 844; ^{1}H NMR δ 5.76 (ddt, 1 H, *J* = 16.4, 10.6, 8.0), 4.82 (dm, 1 H, *J* = 16.4), 4.81 (dm, 1 H, *J* = 10.6), 2.38 (m, 4 H), 2.21 (s, 6 H), 2.20 (s, 3 H), 1.91 (s, 2 H), 1.54 (d, 2 H, *J* = 8.0), 0.04 (s, 6 H); MS 214 (2, M$^+$), 199 (3), 173 (5), 156 (88), 140 (4), 128 (20), 114 (6), 98 (35), 85 (30), 72 (36), 58 (100), 42 (61); exact mass for $C_{11}H_{26}N_2Si$ calcd 214.186, found 214.188.

Allyl[[bis(2-methoxyethyl)amino]methyl]dimethylsilane (5l): yield 89% (120 °C); bp 73–74 °C (0.08 mm); IR (film) 2875, 1629 1458, 1249, 1195, 1121, 893, 844; ^{1}H NMR δ 5.77 (ddt, 1 H, *J* = 16.6, 10.4, 8.0), 4.83 (dm, 1 H, *J* = 16.6), 4.81 (dm, 1 H, *J* = 10.4), 3.43 (t, 4 H, *J* = 6.4), 3.32 (s, 6 H), 2.62 (t, 4 H, *J* = 6.4), 2.07 (s, 2 H), 1.54 (dm, 2 H, *J* = 8.0), 0.04 (s, 6 H); MS 245 (2, M$^+$), 200 (62), 188 (3), 146 (42), 133 (3), 125 (7), 114 (7), 100 (43), 88 (90), 75 (39), 59 (82), 43 (50), 28 (100); exact mass for $C_{12}H_{27}NO_2Si$ calcd 245.181, found 245.181.

Allyl[[bis(2-ethoxyethyl)amino]methyl]dimethylsilane (5m): yield 73% (120 °C); bp 150 °C (20 mm); IR (film) 2975, 2867, 1682, 1629, 1248, 1115, 845; ^{1}H NMR δ 5.78 (ddt, 1 H, *J* = 16.6, 10.8, 8.4), 4.84 (dm, 1 H, *J* = 16.6), 4.82 (dm, 1 H, *J* = 10.8), 3.47 (m, 8 H), 2.64 (t, 4 H, *J* = 6.5), 2.09 (s, 2 H), 1.56 (dm, 2 H, *J* = 8.2), 1.18 (t, 6 H, *J* = 7.0), 0.04 (s, 6 H); MS 274 (4, M$^+$ + H), 273 (1, M$^+$), 232 (8), 214 (100), 202 (10), 174 (58), 140 (39), 130 (13), 114 (10), 102 (57), 86 (13), 72 (50), 59 (66), 45 (91), 29 (59); exact mass for $C_{14}H_{32}NO_2Si$ (M$^+$ + H) calcd 274.220, found 274.220.

2,2Dimethyl-1-[1-[(*S*)-2-(methoxymethyl)pyrrolidinyl]]-2-sila-4-pentene (5n): yield 74% (80 °C); bp 128–130 °C (20 mm); $[\alpha]^{20}_D$ −72.2° (ethanol, 130 mg/10 mL); IR (film) 2959, 2875, 1629, 1458, 1249, 1113, 893, 841; ^{1}H NMR δ 5.79 (ddt, 1 H, *J* = 16.7, 10.2, 8.2), 4.84 (dm, 1 H, *J* = 16.7), 4.82 (dm, 1 H, *J* = 10.2), 3.40 (dd, 1 H, *J* = 9.2, 4.4), 3.34 (s, 3 H), 3.21 (dd, 1 H, *J* = 9.2, 6.6), 3.05 (m, 1 H), 2.46 (d, 1 H, *J* = 14.2), 2.33 (m, 1 H), 2.13 (dt, 1 H, *J* = 8.4, 8.4), 1.95–1.50 (m, 4 H), 1.70 (d, 1 H, *J* = 14.2), 1.56 (dm, 2 H, *J* = 8.2), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR δ 135.02, 112.86, 76.31, 67.63, 59.09, 57.54, 44.81, 28.35, 23.18, 23.08; MS 227 (1, M$^+$), 191 (22), 182 (96), 163 (34), 148 (12), 128 (67), 111 (14), 99 (13), 83 (18), 70 (50), 59 (85), 43 (88), 28 (100); exact mass for $C_{12}H_{25}NOSi$ calcd 227.170, found 227.170.

2,2-Dimethyl-1-(1-pyrazolyl)-2-sila-4-pentene (5o): yield after flash chromatography (10% ethyl acetate in hexanes) 33% (80 °C); bp 178–184 °C (15 mm); IR (film) 2958, 1629, 1510, 1410, 1250, 1157, 1044, 847, 745; ^{1}H NMR δ 7.44 (d, 1 H, *J* = 1.0), 7.26 (d, 1 H, *J* = 1.0), 6.21 (t, 1 H, *J* = 1.0), 5.75 (ddt, 1 H, *J* = 11.7, 6.2, 5.4), 4.88 (dm, 1 H, *J* = 11.7), 4.87 (dm, 1 H, *J* = 6.2), 3.78 (s, 2 H), 1.63 (dd, 2 H, *J* = 5.4, 1.0), 0.10 (s, 6 H); MS 180 (2, M$^+$), 165 (17), 139 (100), 120 (10), 112 (11), 105 (18), 99 (13), 84 (25), 71 (17), 59 (40), 43 (40); exact mass for $C_9H_{16}N_2Si$ calcd 180.108, found 180.106.

Procedures for Metalation Reactions. Typical metalation reactions were performed under argon with 100 mg of allylsilane and 2 molar equiv[32] of organolithium reagent, by using standard syringe–septum techniques.[33]

Procedure A. In one flask, allylsilane was dissolved in THF (1 mL). In another flask, LDA was prepared from a solution of diisopropylamine (2 molar equiv) in THF (1 mL), cooled to −78 °C and then treated with *n*-butyllithium (2 molar equiv, 1.4 M). After 5 min, the solution of allylsilane was added to the LDA. The yellow reaction mixture was stirred for 15 min. Treatment with electrophile (2 molar equiv) as a neat liquid gave a cloudy-white solution, which was then subjected to standard workup.[34]

Procedure B. Similar to procedure A except LTMP generated from 2,2,6,6-tetramethylpiperidine was used. Metalation time was 1 h.

Procedure C. To allylsilane in THF (2 mL) was added *sec*-butyllithium (2 molar equiv, 1.4 M) at −60 °C. The yellow solution was stirred for 3 h and subsequently cooled to −78 °C. Then procedure A was followed.

Procedure D. To allylsilane in diethyl ether or THF (2 mL) was added *sec*-butyllithium (2 molar equiv, 1.4 M) at −78 °C. The yellow solution was stirred for 15 min, and then procedure A was followed.

3-(Trimethoxysilyl)-1-butene (7a) and (*E*)-1-(Trimethoxysilyl)-1-butene (7b). Procedure A: ^{1}H NMR δ 6.50 (dt, 1 H, *J* = 18.0, 6.0, **7b**), 5.95 (ddd, 1 H, *J* = 16.0, 11.0, 8.0, **7a**), 5.39 (dm, 1 H, *J* = 18.0, **7b**), 4.97 (dm, 1 H, *J* = 16.0, 11.0, **7a**), 3.57 (s, 9 H, **7a**), 3.56 (s, 9 H, **7b**), 1.86 (m, 1 H, **7a**), 1.16 (d, 1 H, *J* = 7.0, **7a**); GC/MS (**7a**) 176 (2, M$^+$), 145 (26), 121 (100), 107 (3), 91 (16), 61 (44).

3-Deuterio-3-(triethoxysilyl)-1-propene (8a) and (*E*)-3-Deuterio-1-(triethoxysilyl)-1-propene (8b). Procedure A: ^{1}H NMR δ 6.46 (m, 1 H, **8b**), 5.83 (m, 1 H, **8a**), 5.45 (dm, 1 H, *J* = 18.0, **8b**), 4.97 (dm, 1 H, *J* = 18.0, **8a**), 4.92 (dm, 1 H, *J* = 10.0, **8a**), 3.84 (q, 6 H, *J* = 7.0, **8a**), 3.83 (q, 6 H, *J* = 7.0, **8b**), 1.75 (m, 2 H, **8b**), 1.67 (m, 1 H, **8a**), 1.23 (t, 9 H, *J* = 7.0); GC/MS (**8a**) 205 (5, M$^+$), 190 (5), 163 (57), 135 (10), 119 (100), 107 (55), 91 (11), 79 (58), 63 (87); GC/MS (**8b**) 205 (2, M$^+$), 163 (30), 147 (36), 135 (30), 119 (67), 103 (53), 91 (19), 79 (31), 63 (100).

3-(Triethoxysilyl)-1-butene (9a) and (*E*)-1-(Triethoxysilyl)-1-butene (9b). Procedure A: ^{1}H NMR δ 6.48 (dt, 1 H, *J* = 18.8, 5.6, **9b**), 5.98 (ddd, 1 H, *J* = 16.8, 10.6, 7.0, **9a**), 5.40 (dt, 1 H, *J* = 18.8, 1.7, **9b**), 4.93 (dm, 1 H, *J* = 16.8, **9a**), 4.91 (dm, 1 H, *J* = 10.6, **9a**), 3.82 (q, 6 H, *J* = 7.0, **9a**), 3.81 (q, 6 H, *J* = 7.0, **9b**), 2.15 (m, 2 H, **9b**), 1.81 (m, 1 H, **9a**), 1.21 (t, 9 H, *J* = 6.8, **9b**), 1.20 (t, 9 H, *J* = 6.8, **9a**), 1.14 (d, 3 H, *J* = 7.4, **9a**), 1.00 (t, 3 H, *J* = 7.4, **9b**); GC/MS (**9a**) 218 (9, M$^+$), 163 (90), 119 (100), 107 (66), 79 (57), 63 (95); GC/MS (**9b**) 218 (5, M$^+$), 173 (20), 163 (45), 147 (14), 135 (14), 119 (49), 103 (44), 79 (32), 63 (100).

3-(Triethoxysilyl)-1-nonene (10a) and (*E*)-1-(Triethoxysilyl)-1-nonene (10b). Procedure A: ^{1}H NMR δ 6.39 (dt, 1 H, *J* = 18.8, 6.4, **10b**), 5.69 (ddd, 1 H, *J* = 17.8, 9.2, 8.9, **10a**), 5.37 (dt, 1 H, *J* = 18.8, 1.4, **10b**), 4.91 (dm, 1 H, *J* = 17.8, **10a**), 4.90 (dm, 1 H, *J* = 9.2, **10a**), 3.79 (q, 6 H, *J* = 7.0, **10b**), 3.78 (q, 6 H, *J* = 7.0, **10a**), 2.11 (dt, 2 H, *J* = 6.4, 6.4, **10b**), 1.19–0.84 (m, 13 H); GC/MS (**10a**) 288 (8, M$^+$), 253 (38), 163 (60), 119 (100), 107 (34), 79 (21), 63 (54); GC/MS (**10b**) 288 (8, M$^+$), 273 (9), 253 (20), 190 (10), 163 (78), 135 (19), 119 (100), 107 (34), 79 (31), 63 (79).

3-[Dimethyl(2-methoxyethoxy)silyl]-1-butene (12a) and (*E*)-1-[Dimethyl(2-methoxyethoxy)silyl]-1-butene (12b). Procedure A: ^{1}H NMR δ 6.12 (m, 1 H, **12b**), 5.88 (ddd, 1 H, *J* = 16.0, 10.0, 8.0, **12a**), 5.40 (dm, 1 H, *J* = 18.0, **12b**), 4.86 (dm, 1 H, *J* = 10.0, **12a**), 4.84 (dm, 1 H, *J* = 16.0, **12a**), 3.74 (t, 2 H, *J* = 5.0), 3.44 (t, 2 H, *J* = 5.0), 3.34 (s, 3 H), 1.06 (d, 3 H, *J* = 8.0, **12a**), 0.12 (s, 6 H, **12b**), 0.07 (s, 6 H, **12a**); GC/MS (**12a**) 133 (16, M$^+$ − $CH_3CHCH{=}CH_2$), 127 (3), 89 (100), 75 (15), 59 (48); GC/MS (**12b**) 188 (7, M$^+$), 173 (34), 153 (11), 133 (59), 129 (77), 113 (41), 101 (26), 89 (89), 75 (94), 59 (100).

3-[Dimethyl(2-methoxyethoxy)silyl]-1-nonene (13a) and (*E*)-1-[Dimethyl(2-methoxyethoxy)silyl]-1-nonene (13b). Procedure A: ^{1}H NMR δ 6.18 (dt, 1 H, *J* = 18.0, 6.0, **13b**), 5.67 (m, 1 H), 4.90 (dm, 1 H, *J* = 17.0, **13a**), 4.86 (dm, 1 H, *J* = 17.0, **13a**), 3.75 (t, 2 H, *J* = 5.0), 3.46 (t, 2 H, *J* = 5.0), 3.38 (s, 3 H), 2.12 (m, 2 H, **13b**), 1.25–0.89 (m, 13 H), 0.18 (s, 6 H, **12b**), 0.09 (s, 6 H, **12a**); GC/MS (**13a**) 243 (3, M$^+$ − CH_3), 133 (57), 103 (4), 89 (100), 75 (14), 59 (39); GC/MS (**13b**) 243 (29, M$^+$ − CH_3), 199 (28), 183 (7), 133 (100), 117 (8), 103 (10), 89 (69), 75 (73), 59 (63).

3-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1-butene (15a) and (*E*)-1-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1-butene (15b). Procedure A: ^{1}H NMR δ 5.88 (ddd, 1 H, *J* = 16.6, 10.9, 7.4, **15a**), 4.82 (dm, 1 H, *J* = 16.6, **15a**), 4.80 (dm, 1 H, *J* = 10.9, **15a**), 3.74 (t, 2 H, *J* = 5.6), 3.56 (m, 6 H), 3.49 (q, 2 H, *J* = 7.0), 2.12 (m, 2 H, **15b**), 1.76 (m, 1 H, **15a**), 1.17 (t, 3 H, *J* = 7.0), 1.05 (d, 3 H, *J* = 7.2, **15a**), 0.94 (t, 3 H, *J* = 7.0, **15b**), 0.11 (s, 6 H, **15b**), 0.06 (s, 6 H, **15a**); GC/MS (**15a**) 217 (10, M$^+$ − CH_2CH_3), 191 (14), 129 (7), 103 (20), 99 (24), 73 (100), 59 (40); GC/MS (**15b**) 246 (7, M$^+$), 231 (6), 191 (7), 133 (19), 115 (6), 103 (13), 99 (18), 73 (100), 59 (26).

3-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1-nonene (16a) and (*E*)-1-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1-nonene (16b). Procedure A: ^{1}H NMR δ 6.14 (dt, 1 H, *J* = 18.8, 6.5, **10b**), 5.63 (m, 1 H, **11a**), 4.87 (dm, 1 H, *J* = 8.4, **16a**), 4.84 (dm, 1 H, *J* = 18.0, **16a**), 3.74 (t, 2 H, *J* = 5.6), 3.57 (m, 6

(32) One equivalent of organolithium base is sufficient for reactions which are done on a scale larger than 100 mg; no changes in regioselection occur by varying the amount of base used.

(33) Aldrich Technical Information Bulletin Number AL-134, Handling Air-Sensitive Reagents.

(34) The workup should be done immediately after completing the reaction while the mixture is still cold.

H), 3.50 (q, 2 H, J = 7.0), 2.10 (dt, 2 H, J = 6.5, 6.5, **16b**), 1.24–0.85 (m, 13 H), 1.82 (t, 3 H, J = 7.0), 0.14 (s, 6 H, **16b**), 0.07 (s, 3 H, **16a**), 0.06 (s, 3 H, **16a**); GC/MS (**16a**) 191 (30, $M^+ - (C_6H_{13})$-$CHCH{=}CH_2$), 147 (4), 117 (6), 103 (14), 73 (100), 59 (17); GC/MS (**16b**) 301 (3, $M^+ - CH_3$), 217 (2), 191 (29), 131 (4), 117 (10), 103 (17), 73 (100), 59 (34).

3-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1,5-hexadiene (17a) and (*E*)-1-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-1,5-hexadiene (17b). Procedure A: ^{1}H NMR δ 6.15 (dt, 1 H, J = 18.8, 6.5, **17b**), 5.75–4.94 (m, 10 H, **17a,b**), 3.75 (t, 2 H, J = 5.6), 3.58 (m, 6 H), 3.51 (q, 2 H, J = 7.0), 2.18 (m, 6 H, **17a,b**), 1.70 (m, 1 H, **17a**), 1.19 (t, 3 H, J = 7.0), 0.14 (s, 6 H, **17b**), 0.09 (s, 3 H, **17a**), 0.08 (s, 3 H, **17a**); GC/MS (**17a**) 191 (13, $M^+ - (CH_2{=}CHCH_2)CHCH{=}CH_2$), 168 (2), 147 (4), 117 (6), 103 (17), 73 (100), 59 (27); GC/MS (**17b**) 257 (12, $M^+ - CH_3$), 227 (4), 191 (34), 147 (4), 117 (14), 103 (14), 89 (5), 73 (100), 59 (21).

3-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-6-methyl-1,5-heptadiene (18a) and (*E*)-1-[Dimethyl[2-(2-ethoxyethoxy)ethoxy]silyl]-6-methyl-1,5-heptadiene (18b). Procedure A: ^{1}H NMR δ 6.13 (m, 11 H, **18a**), 5.09 (t, 1 H, J = 7.4), 4.85 (m, 2 H, **18a**), 3.73 (t, 2 H, J = 5.6), 3.57 (m, 6 H), 3.50 (q, 2 H, J = 7.0), 1.65 (s, 3 H), 1.58 (s, 3 H), 1.17 (t, 3 H, J = 7.0), 0.12 (s, 6 H, **18b**), 0.07 (s, 6 H, **18a**); GC/MS (**18a**) 241 (7, $M^+ - CH_2OCH_2CH_3$), 225 (7), 187 (5), 171 (3), 157 (15), 149 (8), 133 (100), 107 (11), 73 (16), 69 (22), 59 (7); GC/MS (**18b**) 241 (4, $M^+ - CH_2OCH_2CH_3$), 199 (4), 171 (5), 157 (19), 149 (9), 133 (100), 119 (28), 107 (12), 73 (20), 69 (77), 59 (10).

3-Deuterio-3-[dimethyl(2-pyridyl)silyl]-1-propene (19a) and (*E*)- and (*Z*)-3-Deuterio-1-[dimethyl(2-pyridyl)silyl]-1-propene (19b and 19c). Procedure B: ^{1}H NMR δ 8.69 (d, 1 H, J = 4.7), 8.51 (d, 1 H, J = 4.7, **19c**), 7.45 (m, 2 H), 7.18 (m, 1 H, **19c**), 7.09 (m, 1 H), 6.48 (m, 1 H, **19c**), 6.12 (m, 1 H, **19b**), 5.75 (d, 1 H, J = 10.0, **19b**), 5.66 (m, 1 H, **19a**), 4.76 (m, 2 H, **19a**), 1.75 (m, 2 H, **19b**), 1.57 (m, 1 H, **19a**), 0.35 (s, 6 H, **19c**), 0.28 (s, 6 H, **19b**), 0.24 (s, 6 H, **19a**); GC/MS (**19a**) 178 (3, M^+), 163 (10), 136 (100), 120 (3), 106 (7), 59 (9); GC/MS (**19b**) 178 (39, M^+), 163 (100), 147 (4), 136 (70), 122 (43), 106 (11), 80 (13), 74 (3), 59 (28); GC/MS (**19c**) 178 (10, M^+), 162 (100), 147 (5), 136 (41), 122 (26), 106 (9), 80 (11), 74 (3), 59 (18).

3-[Dimethyl(2-pyridyl)silyl]-1-butene (20a) and (*E*)- and (*Z*)-1-[Dimethyl(2-pyridyl)silyl]-1-butene (20b and 20c). Procedure B: ^{1}H NMR δ 8.73 (d, 1 H, J = 4.7), 7.47 (m, 2 H), 7.12 (m, 1 H), 6.41 (dt, 1 H, J = 7.0, 14.0, **20c**), 6.20 (dt, 1 H, J = 5.0, 19.0, **20b**), 5.82 (ddd, 1 H, J = 7.4, 10.0, 17.4, **20a**), 5.78 (d, 1 H, J = 19.0, **20b**), 4.78 (m, 2 H, **20a**), 1.99 (m, 1 H, **20a**), 1.03 (d, 3 H, J = 6.8, **20a**), 0.38 (s, 6 H, **20c**), 0.33 (s, 6 H, **20b**), 0.25 (s, 6 H, **20a**); GC/MS (**20a**) 191 (1, M^+), 176 (5), 160 (2), 136 (100), 122 (3), 109 (14), 80 (4), 59 (39); GC/MS (**20b**) 191 (2, M^+), 176 (18), 162 (95), 147 (4), 136 (75), 122 (47), 106 (36), 80 (31), 59 (100); GC/MS (**20c**) 176 (100, $M^+ - CH_2CH_3$), 136 (60), 120 (45), 109 (12), 94 (22), 59 (79).

3-[Dimethyl(2-pyridyl)silyl]-1-nonene (21a) and (*E*)-1-[Dimethyl(2-pyridyl)silyl]-1-nonene (21b). Procedure B: ^{1}H NMR δ 8.68 (d, 1 H, J = 5.0), 7.44 (m, 2 H), 7.08 (m, 1 H), 6.11 (dt, 1 H, J = 5.0, 12.5, **21b**), 5.73 (d, 1 H, J = 12.5, **21b**), 5.52 (ddd, 1 H, J = 7.0, 9.0, 10.5, **21a**), 4.78 (dm, 1 H, J = 9.0, **21a**), 4.72 (dm, 1 H, J = 10.5, **21a**), 2.08 (dt, 2 H, J = 5.0, 5.0, **21b**), 1.2–0.8 (m, 13 H), 0.30 (s, 6 H, **21b**), 0.23 (s, 3 H, **21a**), 0.22 (s, 3 H, **21a**); GC/MS (**21a**) 261 (4, M^+), 202 (1), 190 (4), 176 (10), 162 (5), 136 (100), 122 (1), 106 (3), 80 (1), 59 (7); GC/MS (**21b**) 261 (20, M^+), 246 (2), 218 (5), 204 (5), 190 (3), 176 (49), 162 (75), 136 (100), 122 (10), 108 (5), 80 (9), 59 (16); exact mass for $C_{16}H_{28}NSi$ (M^+ + H) calcd 262.199, found 262.199.

3-Deuterio-3-[[(*N*,*N*-diethylamino)methyl]dimethylsilyl]-1-propene (22a) and (*E*)- and (*Z*)-3-Deuterio-1-[[(*N*,*N*-diethylamino)methyl]dimethylsilyl]-1-propene (22b and 22c). Procedure C: ^{1}H NMR δ 6.39 (dtm, 1 H, J = 14.0, 6.6, **22c**), 6.07 (dtm, 1 H, J = 18.4, 4.8, **22b**), 5.64 (m, 1 H, **22a**), 5.64 (dm, 1 H, J = 18.4, **22b**), 5.51 (dm, 1 H, J = 14.0, **22c**), 4.82 (dm, 1 H, J = 16.8, **22a**), 4.80 (dm, 1 H, J = 10.0, **22a**), 2.43 (q, 4 H, J = 7.0, **22a**), 2.41 (q, 4 H, J = 7.0, **22b,c**), 1.99 (s, 2 H, **22c**), 1.94 (s, 2 H, **22b**), 1.92 (s, 2 H, **22a**), 1.77 (m, 2 H, **22b,c**), 1.53 (m, 1 H, **22a**), 0.95 (t, 6 H, J = 7.0), 0.15 (s, 6 H, **22c**), 0.07 (s, 6 H, **22b**), 0.02 (s, 6 H, **22a**); GC/MS (**22a**) 187 (28, M^+ + H), 186 (16, M^+), 171 (52), 144 (100), 86 (96), 58 (32); GC/MS (**22b**) 187 (33, M^+ + H), 186 (22, M^+), 171 (46), 144 (59), 130 (18), 86 (100), 58 (35); GC/MS (**22c**) 187 (29, M^+ + H), 186 (21, M^+), 171 (41), 144 (67), 130 (13), 86 (100), 58 (36).

3-[[(*N*,*N*-Diethylamino)methyl]dimethylsilyl]-1-butene (23a) and (*E*)- and (*Z*)-1-[[(*N*,*N*-Diethylamino)methyl]dimethylsilyl]-1-butene (23b and 23c). Procedure C: ^{1}H NMR δ 6.10 (dt, 1 H, J = 19.0, 5.0, **23b**), 5.87 (ddd, 1 H, J = 17.4, 9.9, 7.0, **23a**), 5.61 (dm, 1 H, J = 19.0, **23b**), 5.44 (dm, 1 H, J = 14.0, **23c**), 4.80 (m, 2 H, **23a**), 2.41 (q, 4 H, J = 7.0), 2.09 (m, 2 H, **23b**), 1.96 (s, 2 H, **23b**), 1.93 (s, 2 H, **23a**), 1.67 (m, 1 H, **23a**), 1.05 (d, 3 H, J = 6.6, **23a**), 0.95 (t, 6 H, J = 7.0), 0.14 (s, 6 H, **23c**), 0.07 (s, 6 H, **23b**), 0.00 (s, 6 H, **23a**); GC/MS (**23a**) 200 (13, M^+ + H), 199 (3, M^+), 184 (12), 144 (14), 130 (10), 86 (100), 58 (33), 42 (18); GC/MS (**23b**) 200 (29, $M^+ + {}^H$) (6, M^+), 185 (18), 144 (100), 130 (3), 86 (65), 58 (12), 42 (11); GC/MS (**23c**) 200 (3, M^+ + H), 144 (16), 86 (100), 58 (41), 42 (21); exact mass for $C_{11}H_{26}NSi$ (M^+ + H) calcd 200.183, found 200.183.

3-[[(*N*,*N*-Diethylamino)methyl]dimethylsilyl]-1-nonene (24a) and (*E*)-1-[[(*N*,*N*-Diethylamino)methyl]dimethylsilyl]-1-nonene (24b). Procedure C: ^{1}H NMR δ 6.06 (dt, 1 H, J = 18.4, 6.4, **24b**), 5.62 (dm, 1 H, J = 18.4, **24b**), 5.60 (m, 1 H, **24a**), 4.82 (m, 2 H, **24a**), 2.41 (q, 4 H, J = 7.0), 2.08 (dt, 2 H, J = 6.8, 6.4, **24b**), 1.25–0.86 (m, 13 H), 0.96 (t, 6 H, J = 7.0), 0.08 (s, 6 H, **24b**), 0.01 (s, 6 H, **24a**); GC/MS (**24a**) 269 (2, M^+), 144 (37), 100 (4), 86 (100), 73 (7), 58 (22); GC/MS (**24b**) 269 (2, M^+), 254 (7), 130 (6), 86 (100), 73 (2), 58 (22); exact mass for $C_{16}H_{36}NSi$ (M^+ + H) calcd 270.262, found 270.262.

3-Deuterio-2,2-dimethyl-1-(1-pyrrolidinyl)-2-sila-4-pentene (25a) and (*E*)- and (*Z*)-5-Deuterio-2,2-dimethyl-1-(1-pyrrolidinyl)-2-sila-3-pentene (25b and 25c). Procedure C: ^{1}H NMR δ 6.39 (dtm, 1 H, J = 14.0, 6.0, **25c**), 6.07 (dtm, 1 H, J = 18.2, 6.6, **25b**), 5.74 (m, 1 H, **25a**), 5.65 (dm, 1 H, J = 18.2, **25b**), 5.50 (dm, 1 H, J = 14.0, **25c**), 4.82 (dm, 1 H, J = 16.6, **25a**), 4.80 (dm, 1 H, J = 9.6, **25a**), 2.42 (m, 4 H), 2.06 (s, 2 H, **25c**), 2.01 (s, 2 H, **25b**), 2.00 (s, 2 H, **25a**), 1.71 (m, 4 H), 0.17 (s, 6 H, **25c**), 0.08 (s, 6 H, **25b**), 0.04 (s, 6 H, **25a**); GC/MS (isomers **25a** and **25b** were not resolved) 185 (4, M^+ + H), 184 (1, M^+), 169 (4), 142 (4), 128 (12), 113 (2), 100 (5), 84 (100), 74 (3), 59 (14), 55 (16); GC/MS (**25c**) 185 (3, M^+ + H), 184 (1, M^+), 169 (2), 142 (4), 128 (9), 113 (2), 84 (100), 74 (2), 59 (13), 55 (15).

1-(1-Pyrrolidinyl)-2-sila-2,2,3-trimethyl-4-pentene (26a) and (*E*)- and (*Z*)-2,2-Dimethyl-1-(1-pyrrolidinyl)-2-sila-3-hexene (26b and 26c). Procedure C: ^{1}H NMR δ 6.10 (dt, 1 H, J = 19.0, 5.8, **26b**), 5.86 (ddd, 1 H, J = 16.8, 9.8, 7.2, **26a**), 5.60 (dm, 1 H, J = 19.0, **26b**), 5.4 (dm, 1 H, J = 14.0, **26c**), 4.78 (m, 2 H, **26a**), 2.41 (m, 4 H), 2.08 (m, 2 H, **26b**), 1.71 (m, 4 H), 1.04 (d, 3 H, J = 7.2, **26a**), 0.95 (t, 3 H, J = 7.0, **26b**), 0.15 (s, 6 H, **26c**), 0.08 (s, 6 H, **26b**), 0.01 (s, 6 H, **26a**); GC/MS (**26a**) 198 (2, M^+ + H), 197 (1, M^+), 182 (2), 142 (40), 128 (3), 114 (2), 100 (1), 84 (100), 73 (15), 59 (17), 55 (11); GC/MS (**26b**) 198 (2, M^+ + H), 197 (1, M^+), 182 (3), 168 (1), 142 (3), 128 (13), 113 (3), 100 (1), 84 (100), 73 (2), 59 (13), 55 (10); GC/MS (**26c**) 198 (1, M^+ + H), 182 (1), 142 (9), 128 (8), 113 (3), 100 (1), 84 (100), 73 (3), 59 (12), 55 (11); exact mass for $C_{11}H_{24}NSi$ (M^+ + H) calcd 198.168, found 198.168.

2,2-Dimethyl-1-(1-pyrrolidinyl)-2-sila-3-vinylnonane (27a) and (*E*)-2,2-Dimethyl-1-(1-pyrrolidinyl)-2-sila-3-undecene (27b). Procedure C: ^{1}H NMR δ 6.05 (dt, 1 H, J = 19.2, 5.6, **27b**), 5.61 (dm, 1 H, J = 19.2, **27b**), 5.60 (m, 1 H, **27a**), 4.82 (m, 2 H, **27a**), 2.42 (m, 4 H), 2.08 (dt, 2 H, J = 6.0, 6.0, **27b**), 2.02 (s, 2 H, **27b**), 1.99 (s, 2 H, **27a**), 1.71 (m, 4 H), 1.24–0.85 (m, 13 H), 0.08 (s, 6 H, **27b**), 0.03 ns, 3 H, **27a**), 0.02 (s, 3 H, **27a**); GC/MS (**27a**) 268 (3, M^+ + H), 267 (1, M^+), 142 (76), 128 (3), 113 (3), 102 (3), 84 (100), 73 (12), 59 (14), 55 (7); GC/MS (**27b**) 268 (2, M^+ + H), 267 (1, M^+), 252 (3), 142 (4), 128 (13), 113 (2), 100 (2), 84 (100), 73 (2), 59 (10), 55 (6); exact mass for $C_{16}H_{34}NSI$ (M^+ + H) calcd 268.246, found 268.246.

3-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1-butene (28a) and (*E*)- and (*Z*)-1-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1-butene (28b and 28c). Procedure C: NMR δ 5.84 (ddd, 1 H, J = 17.0, 10.1, 7.3, **28a**), 5.59 (dm, 1 H, J = 18.6, **28b**), 5.43 (dm, 1 H, J = 12.8, **28c**), 4.80 (m, 2 H, **28a**), 2.35 (m, 4 H), 2.19 (s, 6 H), 2.18 (s, 3 H), 1.90 (s, 2 H), 1.68 (m, 1 H, **28a**), 1.03 (d, 3 H, J = 7.2, **28a**), 0.14 (s, 6 H, **28c**), 0.07 (s, 6 H, **28b**), 0.01 (s, 6 H, **28a**); GC/MS (**28a**) 229 (10, M^+ + H), 228 (4, M^+), 184 (4), 170 (67), 142 (5), 128 (8), 102 (21), 85 (11),

72 (27), 58 (100); GC/MS (**28b**) 229 (4, $M^+ + H$), 170 (66), 142 (5), 127 (8), 112 (10), 102 (45), 85 (13), 72 (30), 58 (100); GC/MS (**28c**) 228 (10, M^+), 170 (95), 142 (18), 127 (20), 99 (53), 72 (40), 58 (100); exact mass for $C_{11}H_{25}N_2Si$ ($M^+ - CH_3$) calcd 213.178, found 213.178.

3-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1-nonene (29a) and (*E*)- and (*Z*)-1-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1-nonene (29b and 29c). Procedure C: ^1H NMR δ 6.25 (dt, 1 H, *J* = 12.6, 7.8, **29c**), 6.00 (dt, 1 H, *J* = 18.6, 6.4, **29b**), 5.55 (dm, 1 H, *J* = 18.6, **29b**), 5.53 (m, 1 H, **29a**), 4.76 (m, 2 H, **29a**), 2.31 (m, 4 H), 2.16 (s, 6 H), 2.14 (s, 3 H), 1.88 (s, 2 H, **29b**), 1.85 (s, 2 H, **29a**), 1.82–0.80 (m, 13 H), 0.11 (s, 6 H, **29c**), 0.02 (s, 6 H, **29b**), –0.03 (s, 3 H, **29a**), –0.04 (s, 3 H, **29a**); GC/MS (**29a**) 283 (3, $M^+ - CH_3$), 240 (83), 173 (7), 140 (9), 116 (13), 102 (18), 85 (7), 72 (32), 58 (100); GC/MS (isomers **29b** and **29c** were not resolved) 240 (100, $M^+ - CH_2N(CH_3)_2$), 212 (4), 140 (5), 127 (5), 116 (8), 102 (22), 85 (10), 72 (29), 58 (87).

3-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1,5-hexadiene (30a) and (*E*)- and (*Z*)-1-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-1,5-hexadiene (30b and 30c). Procedure C or D: ^1H NMR δ 6.26 (dt, 1 H, *J* = 14.0, 7.6, **30c**), 6.01 (dt, 1 H, *J* = 18.6, 5.8, **30b**), 5.65 (m, 6 H, **30a–c**), 4.87 (m, 8 H, **30a–c**), 2.32 (m, 4 H), 2.16 (s, 6 H), 2.15 (s, 3 H), 1.88 (s, 2 H), 0.11 (s, 6 H, **30c**), 0.04 (s, 6 H, **30b**), 0.00 (s, 3 H, **30a**), –0.01 (s, 3 H, **30a**); GC/MS (**30a**) 254 (3, M^+), 237 (2), 210 (2), 196 (53), 173 (10), 154 (7), 140 (7), 125 (4), 116 (11), 102 (16), 85 (5), 72 (28), 58 (100); GC/MS (**30b**) 255 (7, $M^+ + H$), 239 (7), 210 (9), 196 (77), 154 (11), 140 (10), 125 (8), 116 (15), 100 (34), 88 (9), 72 (46), 58 (100); GC/MS (**30c**) 196 (53, $M^+ - CH_2N(CH_3)_2$), 154 (10), 140 (10), 127 (11), 102 (48), 95 (11), 72 (33), 67 (10), 58 (100); exact mass for $C_{14}H_{31}N_2Si$ ($M^+ + H$) calcd 255.226, found 255.226.

3-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-6-methyl-1,5-heptadiene (31a) and (*E*)- and (*Z*)-1-[Dimethyl[[*N*′-[2-(*N*,*N*-dimethylamino)ethyl]-*N*′-methylamino]methyl]silyl]-6-methyl-1,5-heptadiene (31b and 31c). Procedure C or D: ^1H NMR δ 6.28 (dt, 1 H, *J* = 13.8, 6.4, **31c**), 6.03 (dt, 1 H, *J* = 18.2, 6.0, **31b**), 5.62 (ddd, 1 H, *J* = 17.0, 9.2, 10.4, **31a**), 5.06 (tm, 1 H, *J* = 7.0, **31a**), 4.83 (dm, 1 H, *J* = 9.2, **31a**), 4.76 (dm, 1 H, *J* = 17.0, **31a**), 2.36 (m, 4 H), 2.19 (s, 6 H), 2.17 (s, 3 H), 1.90 (s, 2 H), 1.61 (s, 3 H, **31a**), 1.54 (s, 3 H, **31a**), 0.12 (s, 6 H, **31c**), 0.06 (s, 6 H, **31b**), 0.01 (s, 3 H, **31a**), 0.00 (s, 3 H, **31a**); GC/MS (**31a**) 224 (59, $M^+ - CH_2N(CH_3)_2$), 173 (6), 154 (4), 140 (9), 116 (26), 102 (24), 95 (7), 73 (31), 58 (100); GC/MS (isomers **31b** and **31c** were not resolved), 283 (4, $M^+ + H$), 224 (57), 154 (7), 140 (10), 127 (5), 116 (24), 102 (33), 86 (10), 73 (33), 58 (100); exact mass for $C_{16}H_{35}N_2Si$ ($M^+ + H$) calcd 283.257, found 258.257.

3-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-butene (32a) and (*E*)- and (*Z*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-butene (32b and 32c). Procedure B, C or D: ^1H NMR δ 6.28 (dt, 1 H, *J* = 14.0, **32c**), 6.30 (m, 1 H, **32b**), 5.86 (ddd, 1 H, *J* = 17.0, 10.4, 7.3, **32a**), 5.60 (dm, 1 H, *J* = 18.6, **32b**), 5.42 (dm, 1 H, *J* = 14.0, **32c**), 4.79 (m, 2 H, **32a**), 3.41 (t, 4 H, *J* = 6.2), 3.29 (s, 6 H), 2.60 (t, 4 H, *J* = 6.2), 2.06 (s, 2 H), 1.69 (m, 1 H, **32a**), 1.04 (d, 3 H, *J* = 7.3, **32a**), 0.95 (t, 3 H, *J* = 7.4, **32b,c**), 0.13 (s, 6 H, **32c**), 0.06 (s, 6 H, **32b**), 0.00 (s, 6 H, **32a**); GC/MS (**32a**) 2.60 (16, $M^+ + H$), 259 (7, M^+), 228 (7), 214 (100), 204 (57), 172 (8), 146 (76), 130 (5), 114 (37), 100 (17), 69 (12), 59 (56); GC/MS (**32b**) 214 (64, $M^+ - CH_2OCH_3$), 182 (7), 146 (70), 130 (6), 114 (65), 100 (6), 589 (13), 59 (100); GC/MS (**32c**) 260 (5, $M^+ + H$), 228 (10), 214 (56), 182 (13), 146 (68), 130 (10), 114 (79), 73 (20), 59 (100); exact mass for $C_{11}H_{24}NO_2Si$ ($M^+ - CH_2OCH_3$) calcd 214.162, found 214.162.

3-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-heptene (33a) and (*E*)- and (*Z*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-heptene (33b and 33c). Procedure C or D: ^1H NMR δ 5.57 (ddd, 1 H, *J* = 16.5, 10.4, 9.4, **33a**), 5.21 (dm, 1 H, *J* = 17.4, **33b**), 5.06 (dm, 1 H, *J* = 10.6, **33c**), 4.80 (m, 2 H), 3.40 (t, 4 H, *J* = 6.4), 3.29 (s, 6 H), 2.59 (t, 4 H, *J* = 6.4), 2.05 (s, 2 H), 1.40–0.80 (m, 9 H), 0.00 (s, 3 H, **33a**), –0.01 (s, 3 H, **33a**); GC/MS (**33a**) 256 (56, $M^+ - CH_2OCH_3$), 204 (47), 146 (100), 114 (36), 100 (15), 89 (23), 69 (65), 59 (91); GC/MS (**33b**) 256 (50, $M^+ - CH_2OCH_3$), 204 (23), 160 (7), 146 (83), 128 (13), 114 (30), 100 (15), 89 (33), 69 (54), 59 (100); exact mass for $C_{16}H_{36}NO_2Si$ ($M^+ + H$) calcd 302.251, found 302.251.

3-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-nonene (34a) and (*E*)- and (*Z*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-nonene (34b and 34c). Procedure C or D: ^1H NMR δ 5.59 (ddd, 1 H, *J* = 16.9, 10.2, 9.3, **34a**), 5.22 (dm, 1 H, *J* = 17.0, **34b**), 5.08 (dm, 1 H, *J* = 10.6, **34c**), 4.81 (m, 2 H, **34a**), 3.42 (t, 4 H, *J* = 6.2), 3.31 (s, 6 H), 2.61 (t, 4 H, *J* = 6.2), 2.07 (s, 2 H), 1.23–0.85 (m, 13 H), 0.02 (s, 3 H, **34a**), –0.01 (s, 3 H, **34a**); GC/MS (**34a**) 284 (100, $M^+ - CH_2OCH_3$), 252 (8), 204 (25), 172 (7), 146 (89), 114 (26), 100 (14), 89 (26), 69 (25), 59 (80); exact mass for $C_{18}H_{40}NO_2Si$ ($M^+ + H$) calcd 330.283, found 330.283.

3-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1,5-hexadiene (35a) and (*E*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1,5-hexadiene (35b). Procedure C or D: ^1H NMR δ 6.07 (dt, 1 H, *J* = 18.6, 5.6, **35b**), 5.70 (m, 4 H, **35a,b**), 4.92 (m, 6 H, **35a,b**), 3.42 (t, 4 H, *J* = 6.2), 3.31 (s, 6 H), 2.64 (t, 4 H, *J* = 6.2, **35b**), 2.61 (t, 4 H, *J* = 6.2, **35a**), 2.09 (s, 2 H), 1.68 (m, 1 H, **35a**), 0.08 (s, 6 H, **35b**), 0.04 (s, 3 H, **35a**), 0.03 (s, 3 H, **35a**); GC/MS (**35a**) 240 (56, $M^+ - CH_2OCH_3$), 204 (19), 146 (81), 114 (30), 100 (19), 89 (26), 67 (62), 59 (100); GC/MS (**35b**) 240 (71, $M^+ - CH_2OCH_3$), 208 (6), 146 (81), 114 (61), 89 (21), 75 (15), 67 (42), 59 (100).

3-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-6-methyl-1,5-heptadiene (36a) and (*E*)- and (*Z*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-6-methyl-1,5-heptadiene (36b and 36c). Procedure C or D: ^1H NMR δ 6.28 (dt, 1 H, *J* = 14.0, 7.0, **36c**), 6.04 (dt, 1 H, *J* = 18.6, 5.8, **36b**), 5.64 (ddd, 1 H, *J* = 16.9, 10.6, 9.1, **36a**), 5.07 (t, 1 H, *J* = 7.0), 4.84 (dm, 1 H, *J* = 9.1, **36a**), 4.78 (dm, 1 H, *J* = 10.6, **36a**), 3.40 (t, 4 H, *J* = 6.2), 3.28 (s, 6 H), 2.59 (t, 4 H, *J* = 6.2), 2.06 (s, 2 H), 1.63 (s, 3 H), 1.56 (s, 3 H), 0.13 (s, 6 H, **36c**), 0.07 (s, 6 H, **36b**), 0.02 (s, 3 H, **36a**), 0.01 (s, 3 H, **36a**); GC/MS (**36a**) 314 (44, $M^+ + H$), 313 (7, M^+), 282 (30), 268 (71), 254 (9), 204 (88), 172 (12), 160 (21), 146 (100), 100 (19), 59 (60); GC/MS (**36b**) 314 (9, $M^+ + H$), 268 (86), 146 (100), 130 (7), 114 (57), 100 (23), 69 (70), 59 (77); GC/MS (**36c**) 268 (68, $M^+ - CH_2OCH_3$), 146 (100), 114 (52), 100 (14), 69 (49), 59 (78); exact mass for $C_{17}H_{35}NO_2Si$ ($M^+ - CH_2OCH_3$) calcd 268.208, found 268.209.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-3-deuterio-1-propene (37a) and (*E*)- and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-3-deuterio-1-propene (37b and 37c). Procedure C or D: ^1H NMR δ (dtm, 1 H, *J* = 14.6, 8.8, **37c**), 6.05 (dtm, 1 H, *J* = 16.2, 8.8, **37b**), 5.70 (m, 1 H, **37a**), 5.61 (dm, 1 H, *J* = 16.2, **37b**), 5.47 (dm, 1 H, *J* = 14.6, **37c**), 4.80 (dm, 1 H, *J* = 17.0, **37a**), 4.78 (dm, 1 H, *J* = 9.8, **37a**), 3.43 (m, 8 H), 2.60 (m, 4 H), 2.12 (s, 2 H, **37b,c**), 2.05 (s, 2 H, **37a**), 1.72 (m, 2 H, **37b,c**), 1.50 (H, **37a**), 1.34 (t, 6 H, *J* = 7.0), 0.12 (s, 6 H, **37c**), 0.04 (s, 6 H, **37b**), 0.00 (s, 6 H, **37a**); GC/MS (**37a**) 275 (11, $M^+ + H$), 274 (2, M^+), 229 (17), 215 (27), 186 (2), 174 (10), 144 (7), 130 (28), 114 (20), 100 (100), 86 (11), 73 (34), 59 (58); GC/MS (**37b**) 275 (7, $M^+ + H$), 274 (2, M^+), 229 (16), 215 (23), 169 (15), 114 (5), 130 (35), 114 (92), 103 (30), 86 (15), 73 (37), 56 (100); GC/MS (**37c**) 275 (17, $M^+ + H$), 274 (3, M^+), 229 (28), 215 (24), 186 (3), 174 (16), 144 (3), 130 (39), 114 (89), 103 (28), 86 (19), 76 (46), 56 (100).

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-butene (38a) and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-butene (38c). Procedure C or D: ^1H NMR δ 6.27 (dt, 1 H, *J* = 13.4, 7.6, **38c**), 5.86 (ddd, 1 H, *J* = 17.1, 10.6, 7.4, **38a**), 5.42 (dm, 1 H, *J* = 13.4, **38c**), 4.78 (m, 2 H, **38a**), 3.44 (m, 8 H), 2.60 (t, 4 H, *J* = 7.0), 2.08 (s, 2 H), 1.67 (m, 1 H, **38a**), 1.14 (t, 6 H, *J* = 6.8), 1.04 (d, 3 H, *J* = 7.4, **38a**), 0.12 (s, 6 H, **38c**), 0.01 (s, 6 H, **38a**); GC/MS (**38a**) 288 (20, $M^+ + H$), 287 (4, M^+), 242 (27), 232 (20), 205 (2), 174 (11), 144 (5), 130 (22), 114 (51), 103 (36), 86 (9), 69 (100), 5.5 (72); GC/MS (**38c**) 288 (5, $M^+ + H$), 287 (3, M^+), 269 (2), 242 (4), 228 (14), 174 (11), 160 (7), 144 (6), 130 (43), 114 (100), 100 (35), 86 (11), 69 (64), 55 (46); exact mass for $C_{15}H_{33}NO_2Si$ calcd 287.228, found 287.224; exact mass for $C_{11}H_{26}NO_2Si$ ($M^+ - CH_3CHCH{=}CH_2$) calcd 232.174, found 232.174; exact mass for $C_{12}H_{26}NOSi$ ($M^+ - CH_2OCH_2CH_3$) calcd 228.182, found 228.180.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-heptene (39a) and (*E*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-heptene (39b). Procedure C or D: ^1H NMR δ 6.04 (dt, 1 H, *J* = 18.4, 6.2, **39b**), 5.59 (m, 2 H, **39a,b**),

4.80 (m, 2 H, **39a**), 3.44 (m, 8 H), 2.60 (t, 4 H, J = 6.4), 2.07 (s, 2 H), 1.50–0.80 (m, 9 H), 1.15 (t, 6 H, J = 7.0), 0.06 (s, 6 H, **39b**), 0.01 (s, 3 H, **39a**), 0.00 (s, 3 H, **39a**); GC/MS (**39a**) 330 (6, M^+ + H), 284 (9), 270 (100), 232 (26), 224 (11), 174 (25), 160 (12), 144 (15), 130 (37), 114 (26), 100 (18), 86 (20), 69 (62), 59 (62); GC/MS (**39b**) 284 (5, $M^+ - OCH_2CH_3$), 270 (100), 224 (9), 174 (29), 160 (15), 144 (9), 130 (35), 114 (54), 100 (16), 86 (14), 69 (33), 59 (53); exact mass for $C_{18}H_{40}NO_2Si$ (M^+ + H) calcd 330.283, found 330.283.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-nonene (40a) and (*E*)- and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-nonene (40b and 40c). Procedure C or D: ^{1}H NMR δ 6.29 (dt, 1 H, J = 13.6, 7.6, **40c**), 6.04 (dt, 1 H, J = 18.2, 6.4, **40b**), 5.60 (m, 2 H, **40a,b**), 4.80 (m, 2 H, **40a**), 3.44 (m, 8 H), 2.60 (t, 4 H, J = 6.4), 2.07 (s, 2 H), 1.50–0.80 (m, 13 H), 1.15 (t, 6 H, J = 7.0), 0.14 (s, 6 H, **40c**), 0.06 (s, 6 H, **40b**), 0.00 (s, 6 H, **40a**); GC/MS (**40a**) 358 (9, M^+ + H), 357 (1, M^+), 312 (5), 298 (100), 254 (4), 232 (17), 202 (2), 174 (22), 130 (25), 114 (24), 102 (14), 83 (15), 69 (21), 55 (71); GC/MS (**40b**) 258 (18, M^+ + H), 257 (3, M^+), 312 (11), 298 (100), 270 (4), 252 (14), 232 (7), 174 (32), 160 (12), 130 (34), 114 (83), 100 (18), 73 (17), 55 (73); GC/MS (**40c**) 358 (3, M^+ + H), 357 (1, M^+), 298 (100), 270 (3), 252 (10), 232 (3), 174 (22), 160 (8), 130 (22), 114 (55), 100 (11), 69 (12), 55 (37); exact mass for $C_{17}H_{36}NOSi$ ($M^+ - CH_2OCH_2CH_3$) calcd 298.255, found 298.256.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-tridecene (41a) and (*E*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1-tridecene (41b). Procedure C or D: ^{1}H NMR δ 6.04 (dt, 1 H, J = 18.4, 6.4, **41b**), 5.58 (m, 2 H, **41a,b**), 4.82 (m, 2 H, **41a**), 3.45 (m, 8 H), 2.60 (t, 4 H, J = 6.4), 2.07 (s, 2 H), 1.50–0.80 (m, 21 H), 1.16 (t, 6 H, J = 7.0), 0.06 (s, 6 H, **41b**), 0.00 (s, 6 H, **41a**); GC/MS (**41a**) 414 (4, M^+ + H), 354 (100), 308 (6), 232 (17), 207 (4), 174 (25), 130 (24), 102 (11), 73 (19), 59 (39); GC/MS (**41b**) 354 (100, $M^+ - CH_2OCH_2CH_3$), 281 (10), 232 (6), 207 (14), 174 (21), 160 (8), 130 (20), 114 (28), 100 (15), 73 (35), 59 (40); exact mass for $C_{24}H_{52}NO_2Si$ (M^+ + H) calcd 414.377, found 414.377.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1,5-hexadiene (42a) and (*E*)- and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-1,5-hexadiene (42b and 42c). Procedure C or D: ^{1}H NMR δ 6.28 (dt, 1 H, J = 14.0, 6.8, **42c**), 6.04 (dt, 1 H, J = 18.4, 6.0, **42b**), 5.68 (m, 6 H, **42a–c**), 4.90 (m, 8 H, **42a–c**), 3.44 (m, 8 H), 2.60 (t, 4 H, J = 6.4), 2.09 (s, 2 H), 1.67 (m, 1 H, **42a**), 1.15 (t, 6 H, J = 7.0), 0.13 (s, 6 H, **42c**), 0.06 (s, 6 H, **42b**), 0.02 (s, 3 H, **42a**), 0.01 (s, 3 H, **42a**); GC/MS (**42a**) 314 (13, M^+ + H), 268 (17), 254 (100), 232 (31), 208 (13), 186 (9), 174 (38), 144 (14), 130 (40), 114 (34), 100 (28), 86 (17), 73 (29), 59 (60); GC/MS (**42b**) 314 (9, M^+ + H), 268 (9), 254 (100), 208 (9), 174 (33), 160 (11), 144 (7), 130 (46), 114 (64), 100 (26), 86 (24), 73 (35), 59 (74); GC/MS (**42c**) 314 (8, M^+ + H), 268 (8), 254 (100), 208 (11), 174 (32), 160 (11), 144 (9), 130 (53), 114 (7), 100 (24), 86 (28), 67 (45), 59 (73); exact mass for $C_{14}H_{28}NOSi$ ($M^+ - CH_2OCH_2CH_3$) calcd 254.200, found 254.197.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-6-methyl-1,5-heptadiene (43a) and (*E*)- and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-6-methyl-1,5-heptadiene (43b and 43c). Procedure C or D: ^{1}H NMR δ (dt, 1 H, J = 13.8, 7.8, **43c**), 6.01 (dt, 1 H, J = 18.6, 6.0, **43b**), 5.59 (ddd, 1 H, J = 16.9, 9.2, 10.4, **43a**), 5.02 (tm, 1 H, J = 7.0, **43a**), 4.79 (dm, 1 H, J = 9.2, **43a**), 4.73 (dm, 1 H, J = 16.9, **43a**), 3.41 (t, 4 H, J = 6.2), 3.38 (q, 4 H, J = 7.0), 2.60 (t, 4 H, J = 6.2), 2.06 (s, 2 H), 1.58 (s, 3 H), 1.50 (s, 3 H), 1.09 (t, 6 H, J = 7.0), 0.09 (s, 6 H, **43c**), 0.03 (s, 6 H, **43b**), 0.02 (s, 3 H, **43a**), –0.03 (s, 3 H, **43a**); GC/MS (**43a**) 242 (17, M^+ + H), 296 (11), 282 (100), 232 (40), 174 (43), 154 (9), 130 (49), 100 (33), 81 (34), 59 (51); GC/MS (**43b**) 296 (8, $M^+ - OCH_2CH_3$), 282 (100), 254 (8), 232 (12), 174 (39), 160 (21), 130 (51), 114 (47), 100 (30), 59 (82), 59 (60); GC/MS (**43c**) 282 (100, $M^+ - CH_2OCH_2CH_3$), 254 (8), 174 (50), 160 (24), 144 (11), 130 (57), 114 (76), 100 (29), 69 (92), 59 (68); exact mass for $C_{19}H_{40}NO_2Si$ (M^+ + H) calcd 342.283, found 342.283.

3-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-6,10-dimethyl-1,5,9-undecatriene (44a) and (*E*)- and (*Z*)-1-[[[Bis(2-ethoxyethyl)amino]methyl]dimethylsilyl]-6,10-dimethyl-1,5,9-undecatriene (44b and 44c). Procedure C or D: ^{1}H NMR δ 6.33 (dt, 1 H, J = 12.8, 6.6, **44c**), 6.11 (dt, 1 H, J = 18.8, 6.2, **44b**), 5.49 (ddd, 1 H, J = 17.0, 9.4, 9.4, **44a**), 4.94 (m, 2 H), 4.83 (dm, 1 H, J = 9.4, **44a**), 4.77 (dm, 1 H, J = 17.0, **44a**), 3.78 (t, 4 H, J = 5.0), 3.39 (q, 4 H, J = 7.0), 3.25 (t, 4 H, J = 5.0), 2.76 (s, 2 H), 1.86 (m, 4 H), 1.53 (s, 3 H), 1.45 (s, 6 H), 1.06 (t, 6 H, J = 7.0), 0.24 (s, 3 H, **44a**), 0.19 (s, 3 H, **44a**); GC/MS (isomer **44a–c** were not resolved) 410 (7, M^+ + H), 350 (100), 340 (9), 232 (34), 174 (50), 160 (13), 130 (44), 100 (28), 69 (97); exact mass for $C_{21}H_{40}NOSi$ ($M^+ - CH_2OCH_2CH_3$) calcd 350.296, found 350.292.

1-[1-[2(*S*)-(Methoxymethyl)pyrrolidinyl]]-2,2,3-trimethyl-2-sila-4-pentene (45a) and (*E*)- and (*Z*)-2,2-Dimethyl-1-[1-[2(*S*)-(methoxymethyl)pyrrolidinyl]]-2-sila-3-hexene (45b and 45c). Procedure C or D: ^{1}H NMR δ 6.31 (dt, 1 H, J = 14.0, 7.2, **45c**), 6.12 (dt, 1 H, J = 18.4, 5.8, **45b**), 5.90 (ddd, 1 H, J = 16.9, 10.7, 7.4, **45a**), 5.62 (dm, 1 H, J = 18.4, **45b**), 5.46 dm, 1 H, J = 14.0, **45c**), 3.41 (dd, 1 H, J = 9.2, 4.8), 3.34 (s, 3 H), 3.22 (dd, 1 H, J = 9.3, 6.6), 3.05 (m, 1 H), 3.51 (d, 1 H, J = 14.4), 2.35 (m, 1 H), 2.10 (dt, 1 H, J = 8.4, 8.4), 1.72 (d, 1 H, J = 14.4), 1.07 (d, 3 H, J = 7.2, **45a**), 0.98 (t, 3 H, J = 7.4, **45b,c**), 0.16 (s, 6 H, **45c**), 0.10 (s, 3 H, **45b**), 0.08 (s, 3 H, **45b**), 0.04 (s, 3 H, **45a**), –0.02 (s, 3 H, **45a**); ^{13}C NMR (**45a**) δ 141.57, 110.03, 76.43, 67.63, 59.06, 57.52, 43.69, 28.39, 26.40, 23.23, 12.84; GC/MS (**45a**) 242 (11, M^+ + H), 226 (4), 210 (12), 196 (100), 186 (25), 154 (7), 140 (5), 128 (33), 96 (6), 73 (12), 59 (26); GC/MS (**45b**) 196 (100, $M^+ - CH_2OCH_3$), 153 (4), 128 (24), 113 (4), 99 (31), 85 (13), 75 (10), 59 (49), 55 (15); GC/MS (**45c**) 196 (100, $M^+ - CH_2OCH_3$), 128 (32), 99 (20), 85 (13), 73 (12), 59 (40); exact mass for $C_{11}H_{22}NSi$ ($M^+ - CH_2OCH_3$) calcd 196.152, found 196.152.

Diastereoisomeric Mixture of 1-[1-[2(*S*)-(Methoxymethyl)pyrrolidinyl]]-2,2,3-trimethyl-2-sila-4-pentene (45a). The procedure was similar to that for compound **5n**. Treatment of **64** (see below) with (*S*)-2-(methoxymethyl)pyrrolidine at 80 °C overnight gave **45a** in 51% yield after distillation: bp 56–58 °C (0.02 mm); ^{1}H NMR spectrum was similar to that of **45a** above, except for the additional signals from the diastereomer **45a′** at δ 5.89 (ddd, 1 H, J = 16.9, 10.7, 7.4, **45a′**) and 1.08 (d, 3 H, J = 7.2, **45a′**); ^{13}C NMR spectrum was similar to that of **45a** above except for the additional signals from the diastereomer **45a′** at δ 141.48, 110.14, 76.33, and 12.95.

2,2-Dimethyl-1-[1-[2(*S*)-(methoxymethyl)pyrrolidinyl]]-3-vinyl-2-silanone (46a) and (*E*)- and (*Z*)-2,2-Dimethyl-1-[1-[2(*S*)-(methoxymethyl)pyrrolidinyl]]-2-sila-3-undecene (46b and 46c). Procedure C or D: ^{1}H NMR δ 6.29 (dt, 1 H, J = 14.2, 7.2, **46c**), 6.04 (dt, 1 H, J = 18.4, 6.2, **46b**), 5.60 (m, 3 H, **46a–c**), 4.82 (m, 2 H, **46a**), 3.38 (dd, 1 H, J = 9.2, 4.2), 3.32 (s, 3 H), 3.19 (m, 1 H), 3.01 (m, 1 H), 2.47 (d, 1 H, J = 14.4, **46a**), 2.44 (d, 1 H, J = 14.4, **46b**), 2.33 (m, 1 H), 2.08 (m, 1 H), 1.67 (d, 1 H, J = 14.4, **46a**), 1.23–0.85 (m, 1o H), 0.13 (s, 6 H, **46c**), 0.07 (s, 3 H, **46b**), 0.05 (s, 3 H, **46b**), 0.01 (s, 3 H, **46a**), –0.04 (s, 3 H, **46a**); GC/MS (**46a**) 266 (100, $M^+ - CH_2OCH_3$), 186 (6), 154 (5), 140 (6), 128 (26), 113 (4), 99 (6), 89 (7), 73 (17), 59 (26); GC/MS (**46b**) 266 (100, $M^+ - CH_2OCH_3$), 128 (21), 96 (8), 85 (9), 73 (14), 59 (32); GC/MS (**46c**) 266 (100, $M^+ - CH_2OCH_3$), 207 (5), 128 (28), 111 (5), 96 (7), 83 (7), 70 (20), 59 (31).

Allyltris(2-methoxyphenyl)silane (47). A solution of *o*-anisyllithium in diethyl ether (350 mmol, 1 M), prepared according to literature procedure,[35] was added to allyltrichlorosilane (10 mL, 69 mmol) in diethyl ether (50 mL) at room temperature. The mixture was then refluxed overnight and carefully hydrolyzed with a minimum amount of ammonium chloride solution. The solution was filtered, and solvent was removed. Hexanes was added to the residue, and the mixture was filtered and stripped of solvent again. The crude material was washed with ammonium chloride solution and extracted with methylene chloride. The combined extract was dried over magnesium sulfate and concentrated by evaporation of the solvent under reduced pressure. The product was purified by flash chromatography (10% ethyl acetate in hexanes) and then by recrystallization from absolute ethanol and diethyl ether to yield 18.5 g (69%) of product: mp 101–102 °C; IR (KBr) 3068, 2833, 1587, 1569, 1473, 1426, 1240, 1023, 758; ^{1}H NMR δ 7.35 (m, 3 H), 7.10 (m, 3 H), 6.86 (m, 6 H), 5.88 (ddt, 1 H, J = 16.9, 10.4, 7.4), 4.87 (dm, 1 H, J = 16.9), 4.70 (dm, 1 H, J = 10.4), 3.61 (s, 9 H), 2.45 (dm, 2 H, J = 7.4); MS 349 (100, $M^+ - CH_2CH{=}CH_2$), 287 (49), 257 (44), 227 (44), 211 (36), 197 (32), 181 (23), 152 (23), 91 (41), 59 (25), 45 (40), 41 (35), 31 (36); exact

(35) Gilman, H.; Zoellner, E. A.; Selby, W. M. *J. Am. Chem. Soc.* **1933**, *55*, 1252.

mass for $C_{21}H_{21}O_3Si$ ($M^+ - CH_2CH{=}CH_2$) calcd 349.126, found 349.126.

Allylbis(2-methoxyphenyl)(2-methoxy-3-methylphenyl)-silane (48). To a solution of allyltris(2-methoxyphenyl)silane (**47**) (101 mg, 0.26 mmol) and TMEDA (0.65 mL, 1.29 mmol) in THF (1.5 mL) was added *n*-butyllithium (0.65 mL, 1.29 mmol) at 0 °C. The yellow solution was stirred for 4 h and then quenched at −78 °C with an excess of iodomethane (0.5 mL) to give a cloudy white mixture. After standard workup the crude product was purified by flash chromatography (10% ethyl acetate in hexanes) to yield 484 mg of **48** and a dialkylated product **48b**: ^{1}H NMR δ 7.40–6.80 (m, 11 H), 5.84 (m, 1 H), 4.84 (m, 2 H), 3.61 (s, 9 H), 3.19 (d, 2 H, J = 9.6), 2.28 (s, 3 H); GC/MS (**48**) 363 (100, $M^+ - CH_2CH{=}CH_2$), 333 (6), 301 (15), 271 (17), 142 (5), 91 (9), 59 (12); GC/MS (**48b**) 377 (100, $M^+ - CH_2CH{=}CH_2$), 362 (4), 347 (7), 315 (22), 285 (24), 269 (4), 165 (3), 105 (16), 91 (7), 59 (7).

3,3-Dimethyl-2-(1-pyrazolyl)-3-sila-5-hexene (52), 2-(1-Pyrazolyl)-3,3,4-trimethyl-3-sila-5-hexene (53a) and 3,3-Dimethyl-2-(1-pyrazolyl)-3-sila-4-heptene (53b). Procedure B (with LDA) or C (1 h metalation): ^{1}H NMR δ 7.44 (d, 1 H, J = 1.8, **52**), 7.34 (d, 1 H, J = 1.8, **53**), 7.29 (d, 1 H, J = 1.8, **52**), 6.19 (t, 1 H, J = 1.8, **52**), 5.70 (ddt, 1 H, J = 17.5, 9.6, 8.0, **52**), 4.86 (m, 1 H, **52**), 4.79 (m, 1 H, **52**), 3.91 (q, 1 H, J = 7.6, **52**), 3.69 (q, 1 H, J = 7.2, **53**), 1.54 (br d, 2 H, J = 8.0, **52**), 1.53 (d, 3 H, J = 7.6, **52**), 1.44 (d, 3 H, J = 7.4, **53a**), 0.10 (s, 3 H, **53**), 0.07 (s, 3 H, **52**), 0.05 (s, 3 H, **53**), 0.02 (s, 3 H, **52**); GC/MS (**52**) 195 (4, M^+ + H), 194 (2, M^+), 179 (17), 153 (100), 125 (17), 111 (4), 100 (28), 86 (4), 71 (4), 59 (45); GC/MS (**53a**) 209 (4, M^+ + H), 208 (1, M^+), 193 (15), 181 (1), 167 (93), 152 (2), 139 (28), 125 (4), 100 (55), 85 (11), 71 (8), 59 (100); GC/MS (**53b**) 209 (7, M^+ + H), 193 (14), 181 (1), 167 (84), 151 (8), 140 (11), 125 (44), 114 (36), 100 (33), 83 (5), 73 (74), 59 (100).

1-[(Chloromethyl)dimethylsilyl]-2-(4-methyl-3-cyclohexenyl)-2-propene (55). Literature procedure for the preparation of metalated limonene was followed.[27] To a solution of *n*-butyllithium in hexanes (55 mL, 110 mmol) was added TMEDA (17 mL, 110 mmol) in a dropwise fashion. To this yellow solution was added (*R*)-(+)-limonene (**54**) (36 mL, 220 mmol). After stirring at room temperature overnight, the dark red mixture was transferred to a solution of chloro(chloromethyl)dimethylsilane (17 mL, 132 mmol) in diethyl ether (100 mL) at −78 °C with a cannula. A cloudy solution developed as the reaction mixture warmed to room temperature overnight. The mixture was filtered and subjected to standard workup. The product was purified by fractional distillation to yield 10.0 g (37%) of material: bp 90–94 °C (0.10 mm); IR (film) 2923, 1629, 1436, 1250, 877, 845, 797; ^{1}H NMR δ 5.39 (m, 1 H), 4.66 (s, 1 H), 4.59 (s, 1 H), 2.79 (s, 2 H), 2.2–1.2 (m, 7 H), 1.69 (s, 2 H), 1.64 (s, 3 H), 0.13 (s, 6 H); MS 244 (1, M^+ + 2), 242 (4, M^+), 201 (2), 187 (4), 174 (3), 163 (3), 149 (7), 135 (6), 121 (18), 107 (80), 93 (100), 81 (36), 67 (27), 55 (39), 41 (37); exact mass for $C_{13}H_{23}{}^{35}ClSi$ calcd 242.126, found 242.122.

1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-2-(4-methyl-3-cyclohexenyl)-2-propene (56). The procedure was similar to that for compound **51**. Treatment of **55** with bis(2-methoxyethyl)amine at 120 °C overnight gave **56** in 69% yield after distillation: bp 130–134 °C (0.05 mm); IR (film) 2920, 1629, 1452, 1247, 1121, 845; ^{1}H NMR δ 5.38 (m, 1 H), 4.60 (s, 1 H), 4.55 (s, 1 H), 3.42 (t, 4 H, J = 6.2), 3.31 (s, 6 H), 2.62 (t, 4 H, J = 6.2), 2.2–1.2 (m, 7 H), 2.07 (s, 2 H), 1.63 (s, 3 H), 1.60 (s, 2 H), 0.06 (s, 6 H); MS 339 (2, M^+), 294 (100), 279 (3), 219 (4), 204 (13), 188 (36), 146 (97), 114 (12), 100 (32), 93 (56), 75 (32), 59 (97), 41 (35); exact mass for $C_{19}H_{38}NO_2Si$ (M^+ + H) calcd 340.267, found 340.267.

1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-1-methyl-2-(4-methyl-3-cyclohexenyl)-2-propene (57a) and (*E*)-1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-2-(4-methyl-3-cyclohexenyl)-1-butene (57b). Procedure D: ^{1}H NMR δ 5.36 (br, 1 H), 5.14 (s, 1 H, **57b**), 4.69 (s, 1 H, **57a**), 4.55 (s, 1 H, **57a**), 3.40 (t, 4 H, J = 6.2), 3.29 (s, 6 H), 2.60 (t, 4 H, J = 6.2), 2.15 (q, 2 H, J = 7.5, **57b**), 2.09 (s, 2 H, **57b**), 2.06 (s, 2 H, **57a**), 1.70 (s, 3 H, **57b**), 1.61 (s, 3 H, **57a**), 1.11 (d, 3 H, J = 7.4, **57a**), 0.98 (t, 3 H, J = 7.5, **57b**), 0.12 (s, 6 H, **57b**), 0.02 (s, 3 H, **57a**), 0.00 (s, 3 H, **57a**); another diastereomer **57a′** was detected by ^{1}H NMR δ 4.68 (s, 1 H, **57a′**), 4.52 (s, 1 H, **57a′**), 2.05 (s, 2 H, **57a′**), 1.10 (d, 3 H, J = 7.4, **57a′**); GC/MS (diastereomers **57a** and **57a′** were not resolved) 354 (8 M^+ + H), 308 (58), 204 (40), 172 (11), 146 (100), 114 (30), 89 (17), 59 (76); GC/MS (**57b**) 308 (58, $M^+ - OCH_2CH_3$), 204 (5), 146 (100), 114 (33), 107 (9), 93 (16), 67 (25), 59 (75).

1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-4-methyl-1-[1-(4-methyl-3-cyclohexenyl)ethenyl]-3-pentene (58a) and 1-[[[Bis(2-methoxyethyl)amino]methyl]dimethylsilyl]-6-methyl-2-(4-methyl-3-cyclohexenyl)-1,5-heptadiene (58b). Procedure D: ^{1}H NMR δ 5.36 (br, 1 H), 5.19 (s, 1 H, **58b**), 5.06 (t, 1 H, J = 6.8), 4.73 (s, 1 H, **58a**), 4.57 (s, 1 H, **58a**), 3.40 (t, 4 H, J = 6.2), 3.28 (s, 6 H), 2.62 (t, 4 H, J = 6.2, **58b**), 2.59 (t, 4 H, J = 6.2, **58a**), 2.08 (s, 2 H, **58b**), 2.07 (s, 2 H, **58a**), 1.65 (s, 3 H), 1.61 (s, 3 H), 1.56 (s, 3 H), 0.11 (s, 6 H, **58b**), 0.02 (s, 6 H, **58a**); another diastereomer **58a′** was detected by ^{1}H NMR δ 4.66 (s, 1 H, **58a′**), 4.53 (s, 1 H, **58a′**); ^{29}Si NMR 0.79 and 0.75 (for diastereomers of **58a**), −12.28 (for **58b**); GC/MS (diastereomers **58a** and **58a′** were not resolved) 362 (42, $M^+ - CH_2OCH_3$), 281 (12), 204 (88), 172 (18), 160 (28), 146 (100), 114 (21), 89 (23), 69 (48), 59 (100); GC/MS (**58b**) 363 (32, $M^+ - CH_2OCH_3$), 264 (4), 204 (16), 146 (100), 69 (22), 59 (46).

α-(*E*)-Bisabolene (59).[29] A solution of **58** (579 mg, 1.42 mmol) in toluene (20 mL), cooled to −10 °C, was treated with hydroiodic acid (0.34 mL, 57%). More HI was added dropwise as needed while the reaction was followed by GC (3 h), until all of **58a** was selectively protodesilylated to give **59**. The mixture was quenched with buffer solution (pH 7), followed by treatment with sodium thiosulfate solution, and then subjected to standard workup. The product was purified by flash chromatography (hexanes) to yield 106 mg (55% after correcting for unreacted **58b**) of **59**: ^{1}H NMR δ 5.39 (br s, 1 H), 5.13 (t, 1 H, J = 7.0), 5.10 (t, 1 H, J = 7.0), 2.69 (t, 2 H, J = 7.0), 2.1–1.8 (m, 5 H), 1.69 (s, 3 H), 1.63 (s, 3 H), 1.62 (s, 3 H), 1.60 (s, 3 H), 1.5 (m, 2 H); ^{13}C NMR δ 139.26, 133.65, 131.23, 123.50, 121.74, 120.90, 42.80, 30.78, 27.96, 26.94, 25.69, 23.48, 17.71, 14.14; MS 204 (10, M^+), 189 (9), 133 (8), 121 (16), 119 (38), 109 (18), 93 (100), 80 (24), 69 (12), 55 (22); exact mass for $C_{15}H_{24}$ calcd 204.188, found 204.186.

3-[(Chloromethyl)dimethylsilyl]-1-butene (67) and (*E*)- and (*Z*)-1-[(Chloromethyl)dimethylsilyl]-2-butene (68 and 69).[24] To a solution of magnesium powder (13.7 g, 564 mmol) in diethyl ether (40 mL) was added a solution of *trans*-crotyl bromide (29 mL, 282 mmol) in diethyl ether (250 mL) in a dropwise fashion. After the addition was completed, the Grignard reaction heated to reflux for another 0.5 h. The crotylmagnesium bromide solution was then transferred dropwise with a cannula to another solution of chloro(chloromethyl)dimethylsilane (45 mL, 338 mmol) in diethyl ether (110 mL). The mixture was stirred at room temperature overnight and then filtered. Solvent was removed, hexanes was added, and the mixture was filtered again. After hexanes was removed, the crude residue was subjected to standard workup. The product was purified by distillation to give 17.0 g (37%) of a mixture of **67** to **69** in the ratio 62:17:21, respectively, in close agreement with literature values:[24] bp 64–70 °C (20 mm); ^{1}H NMR δ 5.84 (ddd, 1 H, J = 16.9, 10.7, 7.6, **67**), 5.37 (m, 4 H, **68**, **69**), 4.89 (dm, 1 H, J = 10.7, **67**), 4.87 (dm, 1 H, J = 16.9, **67**), 2.80 (s, 2 H, **67**), 2.77 (s, 2 H, **69**), 2.73 (s, 2 H, **68**), 1.84 (m, 1 H, **67**), 1.58 (m, 4 H, **68**, **69**), 1.58 (m, 6 H, **68**, **69**), 1.10 (d, 3 H, J = 7.2, **67**), 0.21 (s, 6 H, **68**), 0.11 (s, 6 H, **69**), 0.09 (s, 3 H, **67**), 0.08 (s, 3 H, **67**); GC/MS (**67**) 127 (3, M^+ − Cl), 119 (2), 111 (4), 107 (15), 99 (100), 93 (4), 85 (14), 79 (9), 59 (8); GC/MS (**68**) 127 (7, M^+ − Cl), 119 (1), 113 (8), 107 (15), 99 (100), 93 (7), 85 (16), 79 (10), 59 (9); GC/MS (**69**) 127 (3, M^+ − Cl), 119 (2), 111 (7), 107 (22), 99 (100), 93 (9), 85 (23), 79 (23), 59 (15).

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