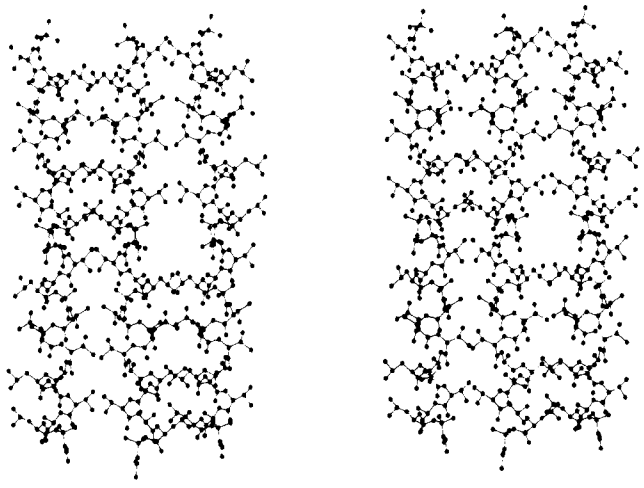

Figure 6. A sheet of parallel helices in crystal II with all N termini pointing upward (six molecules are drawn). Sheets of helices above and below the one shown are rotated by 180° to give an antiparallel arrangement. Water molecules in the head-to-tail region are omitted (see Figure 3). Axial directions of the cell are $a\rightarrow$, $b\uparrow$, and c up from the page.

had been rendered amphipathic by the insertion of water molecules into the helix.[19] In this case the leucyl side chains occur in every third position, therefore Leu[3] and Leu[6] are adjacent to each other on the helix. Since there is not sufficient space between adjacent leucyl side chains for others to penetrate in the same "plane", the interdigitating leucyl side chains from the neighboring molecule are offset, perpendicular to the view in Figure 3 of ref 19.

The loose, inefficient packing in the crystals of peptide II results in the occurrence of several water molecules in completely hydrophobic cavities, with at least some appearing to be uninvolved in hydrogen bonding. Presumably, the presence of water in hydrophobic holes does lead to some enthalpic stabilization by means of dipole–induced dipole (London) interactions with neighboring alkyl side chains.[20] These structures provide a high-resolution glimpse of water molecules in totally hydrophobic environments and may be of use in modeling trapped water in the apolar interior of globular proteins.[21,22] A recent analysis of protein crystal structures reveals that water molecules in the vicinity of apolar side chains lie predominantly at van der Waals contact distances, but most of these have a primary, shorter contact with a neighboring atom.[22] The unusual amount of water associated with the apolar peptide II is reminiscent of the antifreeze polypeptides (AFP) found in the blood of arctic fishes, which often are characterized by a very high alanine content and a high α-helical structure.[23] The first report on a crystal structure of an antifreeze polypeptide, at 2.5 Å, shows that the 36-residue peptide forms a single helix.[24] The water content and placement within the AFP crystal was not determined at this time.

The structures of I and II in crystals demonstrate that the incorporation of a few Aib residues permits the synthetic construction of largely α-helical structures. The length of the helices compares well with that found for helical segments in globular proteins.[25] Future studies will focus on the covalent linking of such helical modules and in the development of cylindrical peptide helices as a scaffold for the controlled orientation of functional residues and binding cavities.

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Supplementary Material Available: Tables of atomic coordinates, bond lengths, bond angles, anisotropic displacement coefficients, and H atom coordinates (23 pages); observed and calculated structure factors for peptides I and II (47 pages). Ordering information is given on any current masthead page.

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Unified Synthesis of Vinylsilanes and Silylated Butadienes. Nickel-Catalyzed Olefination and Silylolefination of Dithioacetals[1]

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Abstract: A simple unified reaction has been developed in the syntheses of various vinylsilanes and silylated butadienes by the nickel-catalyzed coupling of dithioacetals with appropriate Grignard reagents. Reactions of 2-aryl-2-(trimethylsilyl)dithianes with MeMgI or cyclopropyl Grignard reagent give in good yields 1-aryl-1-(trimethylsilyl)styrenes and 1-aryl-1-(trimethylsilyl)butadienes, respectively. Reactions of these substrates with Me_3SiCH_2MgCl afford 1,2-bis(silyl)styrenes. Allylic dithioacetals react with Me_3SiCH_2MgCl furnishing the synthesis of 1-(trimethylsilyl)butadienes. Reactions of 1-(trimethylsilyl)-substituted allylic dithioacetals with MeMgI or Me_3SiCH_2MgCl give internal (trimethylsilyl)butadienes or bis(trimethylsilyl)butadienes in satisfactory yields. Treatment of allylic orthothioester with Me_3SiCH_2MgCl under similar conditions provides a facile synthesis of compounds having both vinyl- and allylsilane functionalities in one step.

The synthetic utility of vinylsilanes is rich.[4] Various literature procedures are known for the preparation of this functionality,[4-7] but there seems to be no general method for the synthesis of different kinds of vinylsilanes and silylated butadienes. Occa-

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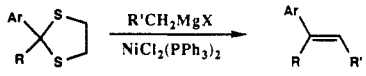
sionally, multistep synthesis are required and the starting materials or the reagents are not handily available.[4-7] It is noteworthy that the direct reactions of a carbonyl group with Me_3SiCH_2Li[8] or with $[(EtO)_2P(O)CHSiMe_3]^-$[9] give desilylated olefins. Several modified silyl-substituted reagents are known but are not readily accessible.[4-7] We are now pleased to report a unified procedure for the syntheses of vinylsilanes and silylated butadienes. Our approach is based on the nickel-catalyzed olefination reactions of dithioacetals with Grignard reagents recently developed in our laboratories (eq 1).[10,11] The reaction involves the nickel-catalyzed



(1)

displacement of one of the carbon–sulfur bonds in the dithioacetal with a carbon–carbon bond, the remaining carbon–sulfur bond being eliminated leading to the formation of the carbon–carbon double bond. Hence, by appropriate choice of the dithioacetal and/or the Grignard reagent, silylated styrenes and butadienes of different nature can be conveniently synthesized by this general procedure.[12]

Table I. Nickel-Catalyzed Synthesis of Silylstyrenes from Benzylic Dithioacetals

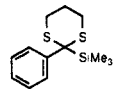
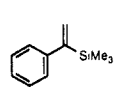
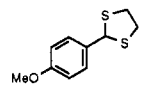
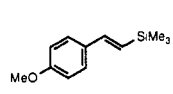
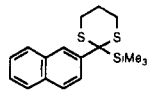
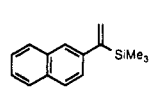
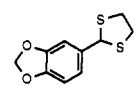
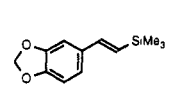
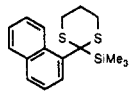
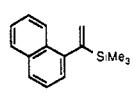
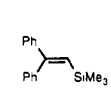
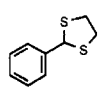
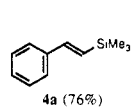
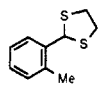
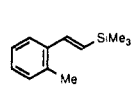
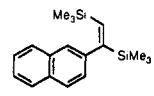
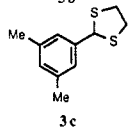
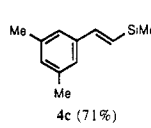
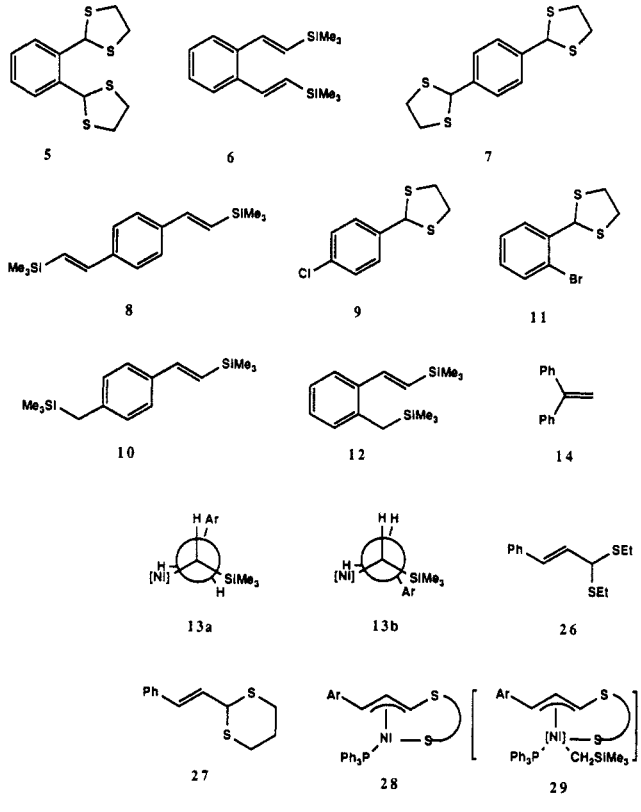
Dithioacetal	Product (%Yield)	Dithioacetal	Product (%Yield)
 1a	 2a (68%)	 3d	 4d (73%)
 1b	 2b (91%)	 3e	 4e (72%)
 1c	 2c (89%)	 3f	 4f (79%)
 3a	 4a (76%)	1a	 15a (56%)
 3b	 4b (71%)	1b	 15b (68%)
 3c	 4c (71%)		

Chart I



(1) Part 34 of the series Transition Metal Promoted Reactions.

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(3) Recipient of the Croucher Foundation Studentship, 1988–90.

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Results and Discussion

Silylstyrenes. The overnight reaction of 2-silyl-substituted dithiane **1** with MeMgI in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$ in refluxing toluene gave vinylsilanes **2** in good to excellent yields. The results are compiled in Table I. It is noted that an elevated temperature was necessary owing to the steric hindrance of the substrates and only starting materials were recovered, when benzene or THF was employed as the solvent.

The use of such olefination reaction in the synthesis of terminal vinylsilanes **4** from dithioacetals would require the presence of a silyl substituent at the α-position of the Grignard reagent. Thus, Me_3SiCH_2MgCl was chosen to react with various benzylic dithioacetals **3** in ether–benzene or ether–THF under refluxing conditions. The results are also outlined in Table I.

As can be seen from Table I, the silylolefination of dithioacetals is a facile process for the synthesis of vinylsilanes. The presence of alkoxy group or other electron-donating functionalities has no effect on the yields of the reactions. It is known that aryl methyl ethers are reactive under similar conditions;[13] however, such moieties apparently were less reactive than the dithioacetal group.

Substrates containing two dithioacetal functions behaved similarly. As a result, *o*-phthalaldehyde dithioacetal **5** afforded the bis-silylolefination product **6** in satisfactory yield. *p*-Bis(vinylsilane) **8** was isolated similarly from the reaction of **7**. These vinylsilanes could be useful building blocks in organic synthesis.

Aryl halides are known to couple with Grignard reagents in the presence of the nickel catalyst.[14] Accordingly, an excess of Me_3SiCH_2MgCl underwent a double coupling reaction on dithioacetal **9** to give **10**. In a similar manner, the double coupling of dithioacetal **11** was executed to yield **12**. In these cases, both vinylsilane and benzylic silane functionalities were introduced in one step. Compound **12** could be useful in annulation reactions, related compounds having been employed as precursors of an *o*-quinodimethane intermediate used in polycyclic natural product syntheses.[15]

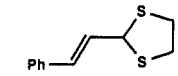
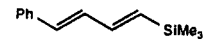
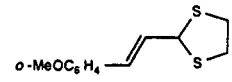
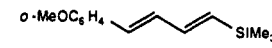
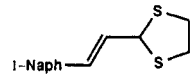
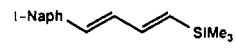
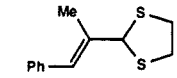
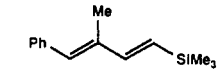
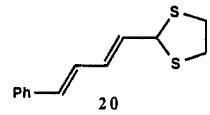
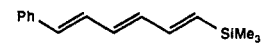
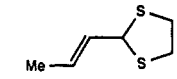
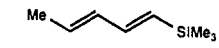
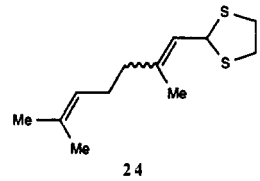
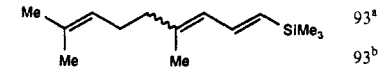
It is important to note that only (*E*)-vinylsilanes were isolated and no detectable quantity of *Z* isomers was observed in the reactions. The two olefinic protons showed a typical AB pattern with coupling constants in the range of 19–20 Hz. For most of the vinylsilanes, the chemical shifts of the olefinic proton α to the silyl group appeared at δ 6.26–6.54. The protons near the aryl group resonated at a lower field, at δ 6.81–7.20. The substituents in **4e** shifted the olefinic protons to higher fields at δ 5.90 and 6.22, respectively.

The formation of the vinylsilane may occur via a similar mechanism as that proposed for the olefination of dithioacetals.[10] Intermediate **13** may undergo the β-hydride elimination process to yield the corresponding vinylsilane. Since β-hydride elimination of transition-metal complexes generally needs the cis-coplanarity of the M–C–C–H unit[16] and conformer **13a** is more stable than **13b**, the stereochemical requirement determines the (*E*)-vinylsilanes would be formed.

It is noted that no trace of Peterson olefination products,[8] or desilylated products, was detected in the above reactions. The absence of the desilylated product indicated that β-hydride elimination is faster than β-silyl elimination under these conditions. In contrast, desilylated product has been occasionally the side product and sometimes even the major product in the palladium-catalyzed Heck reactions of vinylsilanes.[5d,e] The product distribution in the latter reactions depends on the nature of the catalyst ligands.[5d,e] Such desilylation can be avoided, when triphenylphosphine is the ligand.[5f] In our reaction, when $NiBr_2$·DME was employed as the catalyst, benzophenone dithioacetal (**3f**) gave 1,1-diphenylethene **14** in 3% yield in addition to the desired vinylsilane (**4f**) upon treatment with Me_3SiCH_2MgCl.

In similar manner, 1,2-bis-silylethenes **15** were prepared in good yields by means of the nickel-catalyzed olefination of appropriate dithioacetals **1**. The results are summarized in Table I. Elevated temperature (refluxing toluene), however, was essential in this transformation. It is noteworthy that the reaction is stereospecific and only *E* isomers were obtained. Presumably, the steric requirement determines the stereoselectivity.

Table II. Nickel-Catalyzed Silylolefination of Allylic Dithioacetals

Substrate	Product	%Yield
 **16a**	 **17a**	93
 **16b**	 **17b**	79
 **16c**	 **17c**	91
 **18**	 **19**	80
 **20**	 **21**	88
 **22**	 **23**	65
 **24**	 **25**	93[a] 93[b]

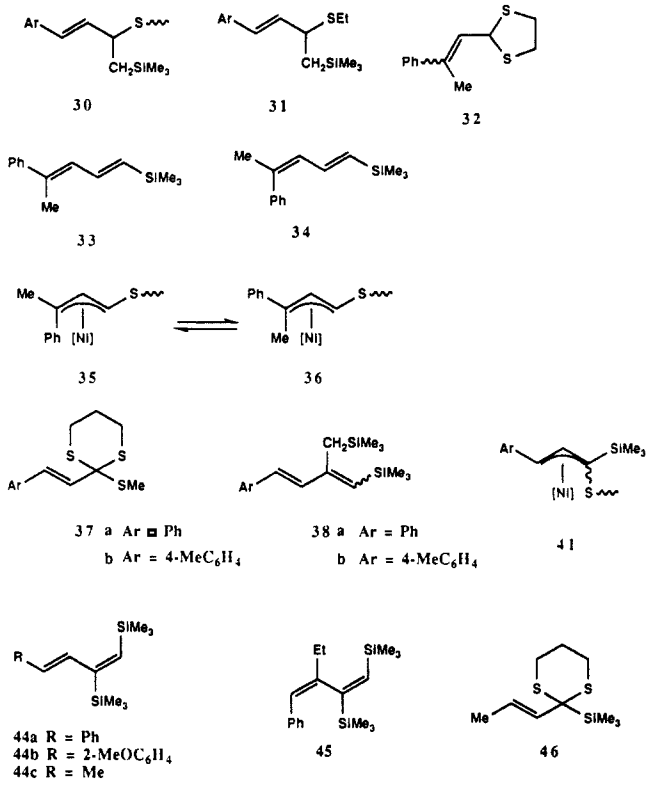
[a] **24**, E/Z = 21/79; **25**, E/Z = 21/79. [b] **24**, E/Z = 64/36; **25**, E/Z = 68/32.

Silylolefination of Allylic Dithioacetals. The extension of the silylolefination reaction to the synthesis of 1-(trimethylsilyl)butadienes has been carried out. Thus, treatment of allylic dithioacetals **16** with Me_3SiCH_2MgCl in the presence of 5 mol % of $NiCl_2(PPh_3)_2$ led directly to (1*E*,3*E*)-buta-1,3-dienes **17** in good to excellent yields. The results are summarized in Table II. In contrast to the Grignard reaction of allylic acetals,[17] the nickel catalyst was essential in the coupling reaction. The presence of C_2-substituted allylic dithioacetals did not affect the reaction. Thus, dithioacetal **18** was converted into **19** in good yield.

The reaction could be extended to dienyl dithioacetal derivatives. As illustration, **20** was converted into 1-silyl 1,3,5-triene **21** in 88% yield. It is known that vinylsilanes can be formylated to given enals,[18] which, in turn, may serve as precursors for higher homologues of vinylsilanes. A vinylsilane could also be transformed directly into the corresponding allylic dithioacetal by a similar

(13) Wenkert, E.; Michelotti, E. L.; Swindell, C. S. *J. Am. Chem. Soc.* **1979**, *101*, 2246.
(14) Kumada, M. *Pure Appl. Chem.* **1980**, *52*, 669.
(15) (a) Sano, H.; Ohtsuka, H.; Migita, T. *J. Am. Chem. Soc.* **1988**, *110*, 2014. (b) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863. (c) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 1043. (d) Djuric, S.; Sarkar, T.; Magnus, P. *J. Am. Chem. Soc.* **1980**, *102*, 6885.
(16) (a) Thorn, D. L.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 2079. (b) Koga, N.; Obara, S.; Morokuma, K. *J. Am. Chem. Soc.* **1984**, *106*, 4625.
(17) Wenkert, E.; Ferreira, T. W. *Organometallics* **1982**, *1*, 1670.
(18) (a) Chan, T. H.; Lau, P. W.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, *18*, 3317. (b) Pilot, J. P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143. (c) Yamamoto, K.; Nunokawa, O.; Tsuji, J. *Synthesis* **1977**, 721. (d) Yamamoto, K.; Yoshitake, J.; Qui, N. T.; Tsuji, J. *Chem. Lett.* **1978**, 859. (e) Yamamoto, K.; Ohta, M.; Tsuji, J. *Chem. Lett.* **1979**, 713.

Chart II



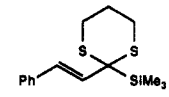
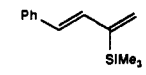
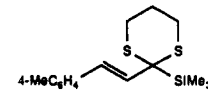
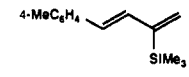
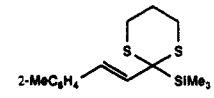
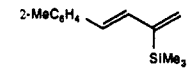
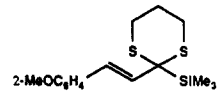
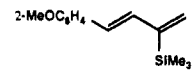
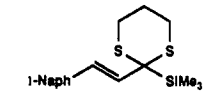
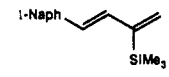
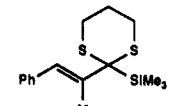
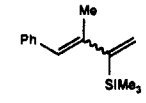
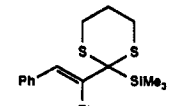
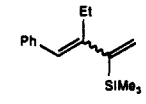
reaction.[19] Accordingly, by combining the silylolefination reaction with these procedures, homologation of an enal can be achieved.

As can be seen from Table II, the reaction furnishes a very efficient method for the synthesis of 1-silyl 1,3-dienes. More importantly, the reaction is regiospecific. The (trimethylsilyl)-methyl group attacked only at the C_1 position of the allylic system. It is noteworthy that the conjugative preference[19] is not essential in these reactions. For example, dithioacetal of crotonaldehyde **22** gave diene **23** in 65% yield. A similar regiospecificity was observed in the reaction of **24** to give **25**. The nature of the dithioacetal functionality has essentially no effect on the reaction. Either open-chain or six-membered-ring dithioacetals **26** and **27** afforded **17a** (in 82 and 76% yields, respectively).

The mechanism of the reaction may follow a pathway similar to that suggested for the benzylic case.[10] The first carbon–sulfur bond may undergo oxidative addition with a nickel(0) species to form an allylic intermediate **28**. The next step may involve the association of the Grignard reagent to give **29**, which undergoes reductive elimination to yield coupling product **30**. The nature of **29** is not clear. The remaining sulfur group in **29** may play a key role in the regioselective coupling at C_1. It is noted that the nickel- or palladium-catalyzed cross couplings of allylic acetals[19] or acetates[20] with nucleophiles are nonselective. It seems conceivalbe that the sulfur moiety in **29** may coordinate to the nickel. Related complexes are known.[21,22] Owing to such kind of coordination, the reductive elimination step may become regiospecific.

The evidence for the formation of allylic sulfide **30** during the course of the reaction was supported by an independent study of the reaction of an allylic thioether **31**. Treatment of **31** with Me_3SiCH_2MgCl under the usual conditions afforded **17a** in 76% yield. As discussed earlier,[10] benzylic thioethers were quite inert under similar conditions. Obviously, allylic substrates are more reactive than benzylic analogues.

Table III. Synthesis of Trimethyl(1-aryl-1,3-butadien-3-yl)silanes

Substrate	Product	%Yield
 39a	 40a	61
 39b	 40b	74
 39c	 40c	86
 39d	 40d	78
 39e	 40e	87
 42a	 43a	97[a]
 42b	 43b	74[b]

[a] E/Z = 70/30. [b] E/Z = 57/43.

Oxidative addition of intermediate **30** and the nickel catalyst cleaves the second carbon–sulfur bond, followed by possible association of the Grignard reagent[10] and β-elimination to give the 1-silyl 1,3-diene.

The β-hydride elimination of the π-allylic metal system has been known for allylic substrates.[23] As shown in Table II, the silylolefination reaction was highly stereoselective. The configuration of the silyl-substituted double bond is always a trans configuration. These results are understandable within the framework of the steric requirement of the reaction and are compatible with the results of the silylolefination of the benzylic dithioacetal depicted earlier.

As can be seen from Table II, retention of the configuration at the olefinic carbon(s) has been found in most cases. It is interesting to note that a mixture of E/Z isomers of the dithioacetal **24** afforded a mixture of E/Z isomers **25**. The E/Z ratio of product **25** was found to be the same as the ratio of starting material **24**. However, exceptional cases have been found in the reactions of the geometrical isomers (*E*)-**32** and (*Z*)-**32**. Thus, the reaction of (*E*)-**32** led to in 88% yield (1*E*,3*E*)-1-silyl 1,3-diene **33** and 1*E*,3*Z* isomer **34** in a ratio of 92:8. In the reaction of (*Z*)-**32**, a similar product distribution was obtained (**33**:**34** = 94:6). Presumably, equilibration between intermediates **35** and **36** may occur to give the more stable *E* isomer as the major product.

The extension of this reaction to allylic orthothioesters has been executed. Thus, the reaction of **37** with an excess amount of Me_3SiCH_2MgCl under the usual conditions afforded **38**. The two carbon–sulfur bonds in **37** were replaced by two carbon–carbon bonds and the remaining carbon–sulfur bond underwent elimination to yield **38**. This reaction provides a facile synthesis of compounds having both vinylsilane and allylsilane functionalities

(19) Hirao, T.; Kohno, S.; Ohshiro, Y.; Agawa, T. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 1569.
(20) (a) Lu, X.; Huang, Y. *J. Organomet. Chem.* **1984**, *268*, 185. (b) Trost, B. M.; Vercauteran, J. *Tetrahedron Lett.* **1985**, *26*, 131.
(21) Alper, H.; Paik, H.-N. *J. Organomet. Chem.* **1976**, *122*, C31.
(22) (a) Huckett, S. C.; Saucer, N. N.; Angelici, R. J. *Organometallics* **1987**, *6*, 591. (b) Lesch, D. A.; Richardson, J. W., Jr.; Jacobson, R. A.; Angelici, R. J. *J. Am. Chem. Soc.* **1984**, *106*, 2901.
(23) Trost, B. M.; Schmuff, N. R.; Miller, M. J. *J. Am. Chem. Soc.* **1980**, *102*, 5979.

in one step. Unfortunately, the reaction gave a mixture of *E* and *Z* isomers. However, they were separated readily by preparative GC. The stereochemical assignments were based on NOE experiments.

2-(Trimethylsilyl)butadienes. The internal silylated dienes **40** were prepared from the reaction of the corresponding silylated dithioacetals **39** with MeMgI in the presence of a catalytic amount of $NiCl_2(PPh_3)_2$. The results are compiled in Table III. Again, the reaction is regiospecific. Although an allylic intermediate **41** may be involved in the reaction, the coupling reaction occurs at the more sterically crowded carbon where another sulfur atom is attached. These results adduce further evidence in support of assistance of the sulfur moiety in the cross-coupling process.

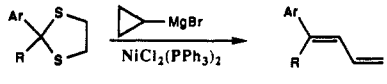
We have previously demonstrated that simple allylic dithioacetals undergo geminal dimethylation under similar conditions.[24] The more sterically hindered dithioacetals, however, gave a significant amount of butadienes as side products.[24] In this study, no geminal dimethylated products were detected. Presumably, an increase in crowding in intermediate **41** would be less favorable for the geminal coupling reaction. Hence, dienes were obtained exclusively.

The stereochemistry of the C_1–C_2 double bond in **40** from simple cinnamaldehyde derivatives was the same as that in the starting materials **39**. However, when the C_2 position was substituted with an alkyl group (e.g. **42**), a mixture of stereoisomers *E*-**43** and *Z*-**43** was obtained. Intermediate **41** becoming more sterically hindered causes the reaction to be less selective.

In a similar manner, the use of the above reaction in the synthesis of 1,2-bis(trimethylsilyl)butadienes has been carried out. Thus, the reactions of **39** with Me_3SiCH_2MgCl gave **44** stereospecifically in good yield. Similarly, **42b** gave **45** in 80% yield. The reaction with the crotonaldehyde derivative **46** is worth discussion. No desired coupling product **44c** was obtained. Instead, **47** was isolated exclusively. In order to avoid severe steric hindrance in the product, β-hydride elimination in the π-allyl intermediate **48** would arise at the methyl carbon to give the thermodynamically more stable **47**.

47 48

1-Aryl-1-(trimethylsilyl)butadienes. Our approach to the synthesis of 1-aryl-1-(trimethylsilyl)butadienes **49** relies on our recent discovery of the nickel-catalyzed reaction of cyclopropyl Grignard reagents with dithioacetals (eq 2).[25] Thus, dithianes



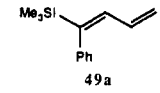
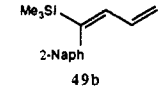
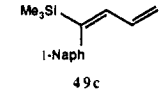
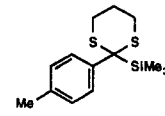
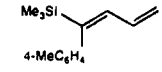
(2)

1a–d were allowed to react with 10 equiv of cyclopropylmagnesium bromide in the presence of 10 mol % of $NiCl_2(PPh_3)_2$ in refluxing benzene–toluene for 4 days. After the usual workup and chromatographic purification, **49a–d** were obtained in good yields. The results are given in Table IV. It is noted that the yields changed with the reaction conditions. If benzene was used as the solvent, the yields were about 30%, more than half of **1** being recovered. Apparently, the presence of the trimethylsilyl group generates a highly sterically hindered environment, such that a higher temperature and a longer reaction time were required. However, the conditions at refluxing toluene may be too vigorous and the cyclopropyl Grignard reagent may decompose to a certain extent leading to a lower yield of the reaction. The dilemma could be resolved by using benzene–toluene (1:1) mixed solvent.

It is noted that the reaction is again stereospecific. The assignments of *E* configuration of the C_1–C_2 double bond in **49** were based on a 2D-NOESY experiment. Taking **49c** as an example, the protons in the trimethylsilyl group correlate with the proton at C_2 (δ 6.78). The stereospecificity can be rationalized in the same manner as that in the related cases discerned earlier.[25]

(24) Yang, P.-F.; Ni, Z.-J.; Luh, T.-Y. *J. Org. Chem.* **1989**, *54*, 2261.

Table IV. Synthesis of (*E*)-Trimethyl(1-aryl-1,3-butadien-1-yl)silane (**49**)

Substrate	Product	%Yield
1a	 **49a**	70
1b	 **49b**	81
1c	 **49c**	79
 **1d**	 **49d**	74

Conclusion. We have demonstrated a unified synthesis of vinylsilanes, internal and terminal trimethylsilyl-substituted butadienes, and bis-silylated alkenes and dienes in good to excellent yields. The operations are simple and the starting materials are easily accessible.

Experimental Section

Melting and boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 283 spectrophotometer. ^1H NMR spectra were obtained on a JEOL PMX-60 (60 MHz) NMR spectrometer or a Bruker 250 WM (250 MHz) NMR spectrometer or a Bruker AC200 (200 MHz) NMR spectrometer. Chemical shifts are reported in δ scale with tetramethylsilane as the internal standard, and deuteriochloroform was used as the solvent. ^{13}C NMR spectra were recorded on a Bruker WM 250 spectrometer operating at 62.5 MHz or a Bruker AC200 spectrometer operating at 50 MHz with deuteriochloroform (δ 77.0) as the internal standard. Mass spectral data (MS) were obtained on a VG 7070F mass spectrometer or a Finigan TSQ-16C mass spectrometer or a JEOL JMS-HX110 mass spectrometer. Preparative GC was operated on a Hitachi G-3000 gas chromatograph with SE30 stationary phase (6 ft). All solvents were purified by standard methods.[26] Tetrahydrofuran was freshly distilled from sodium benzophenone ketyl. Benzene was distilled from sodium wire. Ether was treated with lithium aluminum hydride and distilled before use. $NiCl_2(PPh_3)_2$[27] was prepared according to literature methods. Grignard reagents were prepared and standardized according to previous procedures.[10,29]

Trimethyl(1-phenylethenyl)silane (2a). Methylmagnesium iodide in ether (3 mL, 1 M in ether, 3 mmol) was evaucated to remove ether. The residue was purged with nitrogen. A solution of **1a** (250 mg, 0.93 mmol) and $NiCl_2(PPh_3)_2$ (39 mg, 0.06 mmol) in toluene (5 mL) was then introduced. The mixture was refluxed for 16 h, quenched with saturated ammonium chloride, and diluted with ether (50 mL). The organic layer was washed twice with sodium hydroxide (10%) and water before drying over anhydrous sodium sulfate. After filtration and evaporation of the solvent, the residue was chromatographed on silica gel with hexane as eluent to give **2a** as a colorless oil (112 mg, 68%): IR (neat) ν 3062, 2954, 1602, 1492, 1254, 861, 837, 760, 700 cm^{-1}; ^1H NMR (60 MHz) δ 0.17 (s, 9 H), 5.57 (d, J = 3 Hz, 1 H), 5.78 (d, J = 3 Hz, 1 H), 7.17 (br s, 5 H); m/z 176 (31.0), 73 (base peak).[29]

Trimethyl[1-(2-naphthyl)ethenyl]silane (2b). According to the procedure for the preparation of **2a** described above, the reaction of **1b** (273 mg, 0.86 mmol) with MeMgI (3 mmol) in the presence of $NiCl_2(PPh_3)_2$ (30 mg, 0.05 mmol) in toluene (5 mL) afforded **2b** (177 mg, 91%): mp

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63–66 °C; IR (KBr) ν 3060, 2960, 2901, 1628, 1599, 1403, 1249, 932, 893, 855, 830, 750, 475 cm^{-1}; ^1H NMR (250 MHz) δ 0.21 (s, 9 H), 5.69 (d, J = 3.0 Hz, 1 H), 5.93 (d, J = 3.0 Hz, 1 H), 7.34 (dd, J = 1.7 and 8.4 Hz, 1 H), 7.40–7.57 (m, 2 H), 7.60 (br s, 1 H), 7.75–7.82 (m, 3 H); ^{13}C NMR (62.5 MHz) δ −0.8, 125.0, 125.3, 125.8, 126.0, 127.2, 127.4, 127.6, 127.9, 132.3, 133.7, 142.5, 153.8; m/z 227 (M + 1, 15.4), 226 (M, 71.8), 73 (base peak).[30]

Trimethyl[1-(1-naphthyl)ethenyl]silane (2c). Via the same procedure for the preparation of **2a**, a solution of **1c** (246 mg, 0.77 mmol) and $NiCl_2(PPh_3)_2$ (30 mg, 0.046 mmol) in toluene (5 mL) was allowed to react with MeMgI (3 mmol) under refluxing conditions for 16 h to give **2c** as a colorless oil (156 mg, 89%): IR (neat) ν 3062, 2962, 1600, 1560, 1410, 1389, 1251, 940, 871, 840, 778, 761 cm^{-1}; ^1H NMR (250 MHz) δ 0.09 (s, 9 H), 5.78 (d, J = 3.4 Hz, 1 H), 5.93 (d, J = 3.4 Hz, 1 H), 7.06 (dd, J = 1.1 and 6.4 Hz, 1 H), 7.36–7.90 (m, 3 H), 7.68 (d, J = 8.2 Hz, 1 H), 7.79–7.90 (m, 2 H); ^{13}C NMR (62.5 MHz) δ −1.2, 123.9, 125.1, 125.2, 125.5, 126.1, 126.5, 128.1, 129.1, 131.5, 133.9, 143.0, 153.4; accurate mass calcd for $C_{15}H_{18}Si$ 226.1178, found 226.1181. Anal. Calcd: C, 79.57; H, 8.02. Found: C, 79.76; H, 7.96.

General Procedure for the Preparation of Trimethyl(2-arylethenyl)silane. In a flask fitted with a reflux condenser, a rubber septum, and a magnet stirring bar were placed dithioacetal and a catalytic amount of $NiCl_2(PPh_3)_2$ (5 mol %). The flask was evacuated and filled with nitrogen three times. To the above mixture was added dry benzene, and the solution was then cooled in an ice bath. Freshly prepared Me_3SiCH_2MgCl in ether (3–4 equiv) was introduced via a syringe in one portion. The mixture was refluxed for 16 h and treated with saturated ammonium chloride. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic layers were washed with aqueous sodium hydroxide (10%), water, and brine and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to give the residue which was chromatographed on silica gel and eluted with hexane to give the desired product.

Trimethyl(2-phenylethenyl)silane (4a). According to the general procedure described above, a mixture of dithioacetal **3a** (189 mg, 1.04 mmol) and $NiCl_2(PPh_3)_2$ (26 mg, 0.043 mmol) in benzene (5 mL) was allowed to react with Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) for 16 h under refluxing to afford **4a** (140 mg, 76%): IR (neat) ν 3060, 3025, 2950, 1600, 1570, 1495, 1442, 1242, 1198, 983, 850, 750, 720, 682 cm^{-1}; ^1H NMR (60 MHz) δ 0.18 (s, 9 H), 6.38 (d, J = 20 Hz, 1 H), 6.92 (d, J = 20 Hz, 1 H), 7.12–7.51 (m, 5 H); m/z 176 (M, 45.3), 73 (100.0).[33]

Trimethyl[2-(2-methylphenyl)ethenyl]silane (4b). According to the general procedure described above, a solution of **3b** (246 mg, 1.25 mmol) and Me_3SiCH_2MgCl (4.5 mL, 1 M in ether, 4.5 mmol) in benzene (5 mL) in the presence of $NiCl_2(PPh_3)_2$ (31 mg, 0.05 mmol) was refluxed for 16 h to afford **4b** (170 mg, 71%): IR (neat) ν 3060, 2950, 1600, 1480, 1460, 1250, 1205, 985 cm^{-1}; ^1H NMR (60 MHz) δ 0.15 (s, 9 H), 2.35 (s, 3 H), 6.34 (d, J = 20 Hz, 1 H), 7.00–7.36 (m, 5 H, a doublet at δ 7.10, J = 20 Hz is apparently embodied in these multiplets); accurate mass calcd for $C_{12}H_{18}Si$ 190.1178, found 190.1178.

Trimethyl[2-(3,5-dimethylphenyl)ethenyl]silane (4c). According to the general procedure, the reaction of **3c** (221 mg, 1.05 mmol), $NiCl_2(PPh_3)_2$ (36 mg, 0.060 mmol), and Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) in THF (10 mL) afforded **4c** (154 mg, 71%) as an oil: IR (neat) ν 3035, 2945, 1585, 1485, 1435, 1240, 1200, 1035, 975 cm^{-1}; ^1H NMR (60 MHz) δ 0.15 (s, 9 H), 2.32 (s, 6 H), 6.45 (d, J = 20 Hz, 1 H), 6.82 (d, J = 20 Hz, 1 H), 6.88 (br s, 1 H), 7.05 (br s, 2 H); accurate mass calcd for $C_{13}H_{20}Si$ 204.1334, found 204.1332.

Trimethyl[2-(4-methoxyphenyl)ethenyl]silane (4d). According to the general procedure, a mixture of **3d** (211 mg, 1.00 mmol), $NiCl_2(PPh_3)_2$ (49 mg, 0.075 mmol), and Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) in THF (5 mL) was heated under reflux for 16 h to afford **4d** (150 mg, 73%);[32] IR (neat) ν 3040, 2955, 1605, 1574, 1508, 1441, 1308, 1250, 1175, 1030, 990, 827, 796, 722 cm^{-1}; ^1H NMR (60 MHz) δ 0.13 (s, 9 H), 3.78 (s, 3 H), 6.28 (d, J = 19 Hz, 1 H), 6.81 (d, J = 19 Hz, 1 H), 6.84 (d, J = 9 Hz, 2 H), 7.34 (d, J = 9 Hz, 2 H); accurate mass calcd for $C_{12}H_{18}OSi$ 206.1127, found 206.1129.

Trimethyl[2-(3,4-methylenedioxyphenyl)ethenyl]silane (4e). Via the general procedure described above, the reaction of **3e** (233 mg, 1.03 mmol) and $NiCl_2(PPh_3)_2$ (37.6 mg, 0.058 mmol) in benzene (5 mL) with Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) gave the crude **4e** which was purified by chromatography on silica gel and eluted with 10% ethyl acetate in hexane and then by molecule distillation to yield pure **4e** as a colorless oil (172 mg, 72%) which was unstable and rapidly became a brown oil: bp 80 °C (0.3 mm, Kugelrohr); IR (neat) ν 3035, 2945, 1585, 1485, 1435, 1240, 1200, 1035, 975 cm^{-1}; ^1H NMR (60 MHz) δ 0.15 (s, 9 H), 5.90 (s, 2 H), 6.22 (d, J = 19 Hz, 1 H), 6.73 (d, J = 19 Hz, 1 H), 6.70–7.23 (m, 3 H); accurate mass calcd for $C_{11}H_{13}O_2Si$ 205.0684, found 205.0685.

Trimethyl(2,2-diphenylethenyl)silane (4f). According to the general procedure described above, a solution of **3f** (259 mg, 1.0 mmol) and Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) in benzene (5 mL) in the presence of $NiCl_2(PPh_3)_2$ (32 mg, 0.05 mmol) was refluxed for 16 h to afford **4f** (199 mg, 79%): IR (neat) ν 3050, 2930, 1550, 1480, 1432, 1325, 1062, 1020, 830, 750, 680 cm^{-1}; ^1H NMR (60 MHz) δ −0.1 (s, 9 H), 6.28 (s, 1 H), 7.22 (s, 10 H); m/z 252 (M), 237 (M - CH_3), 135 (100.0).[31]

1,2-Bis[2-(trimethylsilyl)ethenyl]benzene (6). According to the general procedure, **5** (280 mg, 0.97 mmol) was allowed to react with Me_3SiCH_2MgCl (6.0 mL, 1 M in ether, 6.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (46 mg, 0.07 mmol) in THF (10 mL) to give **6** (212 mg, 80%) as an oil: IR (neat) ν 3040, 2950, 1580, 1240, 1205, 980 cm^{-1}; ^1H NMR (60 MHz) δ 0.16 (s, 18 H), 6.32 (d, J = 19 Hz, 2 H), 7.20 (d, J = 19 Hz, 2 H), 7.13–7.53 (m, 4 H); accurate mass calcd for $C_{16}H_{26}Si_2$ 274.1573, found 274.1575.

1,4-Bis[2-(trimethylsilyl)ethenyl]benzene (8). According to the general procedure, the reaction of dithiolane **7** (271 mg, 0.95 mmol), $NiCl_2(PPh_3)_2$ (65 mg, 0.10 mmol), and Me_3SiCH_2MgCl (6.0 mL, 1 M in ether, 6.0 mmol) in benzene (10 mL) gave **8** (180 mg, 69%) as a colorless oil: IR (neat) ν 3035, 2950, 1580, 1240, 1205, 980 cm^{-1}; ^1H NMR (60 MHz) δ 0.15 (s, 18 H), 6.54 (d, J = 19 Hz, 2 H), 6.93 (d, J = 19 Hz, 2 H), 7.47 (s, 4 H); accurate mass calcd for $C_{16}H_{26}Si_2$ 274.1573, found 274.1573.

Trimethyl[2-[4-((trimethylsilyl)methyl)phenyl]ethenyl]silane (10). Via the general procedure, a mixture of dithiolane **9** (245 mg, 1.13 mmol), $NiCl_2(PPh_3)_2$ (40 mg, 0.06 mmol), and Me_3SiCH_2MgCl (5.0 mL, 1 M in ether, 5.0 mmol) in THF (10 mL) was refluxed for 16 h to give **10** (146 mg, 50%) as an oil: IR (neat) ν 3040, 2945, 1600, 1245, 1200, 980 cm^{-1}; ^1H NMR (60 MHz) δ −0.02 (s, 9 H), 0.15 (s, 9 H), 2.05 (s, 2 H), 6.41 (d, J = 20 Hz, 1 H), 6.86 (d, J = 20 Hz, 1 H), 6.99 (d, J = 8 Hz, 2 H), 7.34 (d, J = 8 Hz, 2 H); accurate mass calcd for $C_{15}H_{26}Si_2$ 262.1573, found 262.1575.

Trimethyl[2-[2-((trimethylsilyl)methyl)phenyl]ethenyl]silane (12). By using the same procedure as described above, the reaction of **11** (266 mg, 0.98 mmol) and Me_3SiCH_2MgCl (5.0 mL, 1 M in ether, 5.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (62 mg, 0.094 mmol) in THF (10 mL) afforded **12** (208 mg, 82%) as an oil: IR (neat) ν 3040, 2940, 1590, 1240, 1200, 980 cm^{-1}; ^1H NMR (250 MHz) δ −0.03 (s, 9 H), 0.15 (s, 9 H), 2.18 (s, 2 H), 6.30 (d, J = 19 Hz, 1 H), 6.91–7.58 (m, 5 H, a doublet at 7.08, J = 19 Hz, is apparently embodied in these multiplets); accurate mass calcd for $C_{15}H_{26}Si_2$ 262.1573, found 262.1578.

1-Phenyl-1,2-bis(trimethylsilyl)ethene (15a). By using the general procedure a mixing of **1a** (250 mg, 0.9 mmol) and $NiCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) was allowed to react under reflux with Me_3SiCH_2MgCl (2.0 mL, 2 M in ether, 4.0 mmol) to give **15a** (130 mg, 56%): ^1H NMR (250 MHz) δ −0.19 (s, 9 H), 0.06 (s, 9 H), 6.33 (s, 1 H), 6.92–7.31 (m, 5 H); ^{13}C NMR (62.5 MHz) δ −1.6, 0.03, 127.4, 127.5, 127.6, 144.0; IR (neat) 3079, 3027, 2961, 2903, 1600, 1488, 1260, 1249, 933, 835 cm^{-1}; accurate mass calcd for $C_{14}H_{24}Si_2$ 248.1416, found 248.1410.

1-(2-Naphthyl)-1,2-bis(trimethylsilyl)ethene (15b). By using the general procedure, **1b** (300 mg, 0.9 mmol) and $NiCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) in toluene (5 mL) were treated under reflux for 16 h with Me_3SiCH_2MgCl (2.0 mL, 2 M in ether, 4.0 mmol) to yield **15b** (190 mg, 68%) and **2b** (28 mg, 13%). **15b**: IR (KBr) ν 3056, 2956, 2900, 1630, 1599, 1499, 1247, 927, 834 cm^{-1}; ^1H NMR (250 MHz) δ −0.21 (s, 9 H), 0.10 (s, 9 H), 6.42 (s, 1 H), 7.06–8.00 (m, 7 H); ^{13}C NMR (62.5 MHz) δ −1.5, 0.1, 125.1, 125.2, 125.9, 126.7, 127.0, 127.7, 132.0, 133.4, 143.2, 144.5, 166.7; accurate mass calcd for $C_{18}H_{26}Si_2$ 298.1573, found 298.1581.

(*E*,*E*)-Trimethyl(4-phenyl-1,3-butadien-1-yl)silane (17a). In a 1-L, two-necked, round-bottomed flask fitted with a reflux condenser, a rubber septum, and a magnet stirring bar were placed **16a** (14.6 g, 0.070 mmol) and $NiCl_2(PPh_3)_2$ (2.3 g, 0.0035 mmol). The flask was evacuated and flushed with nitrogen three times. To the above mixture was added anhydrous THF (200 mL), and the solution was then cooled in an ice bath. The ether solution of Me_3SiCH_2MgCl, freshly prepared from magnesium turning (5.2 g, 0.22 g-atom) and Me_3SiCH_2Cl (25.8 g, 0.21 mol), was introduced with a double-ended needle in one portion. The mixture was refluxed for 10 h, cooled to room temperature, and then treated with saturated ammonium chloride solution (200 mL). The organic layer was separated and the aqueous layer was extracted with

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ether (3 × 200 mL). The combined organic layers were washed with aqueous sodium hydroxide solution (10%, 2 × 100 mL) and brine (2 × 100 mL). The organic solution was dried over anhydrous magnesium sulfate. The solvent is removed in vacuo, and the residue is filtered through a short silica gel column (30 g) and flushed under positive nitrogen pressure with hexane (300 mL). After evaporation of the solvent in vacuo, the yellowish residue was distilled to give **17a** as a colorless liquid which solidified on standing (12.9 g, 91%): bp 99–101 °C (0.6 mmHg); mp <37 °C [lit.[18b] bp 70 °C (0.1 mmHg)]; IR (neat) ν 3030, 2855, 1628, 1605, 1450, 1249, 1002, 872, 843, 728, 690 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.13 (s, $-Si(CH_3)_3$, 9 H), 6.01 (d, J = 17.8 Hz, $=CHSiMe_3$, 1 H), 6.58 (d, J = 15.1 Hz, PhCH=, 1 H), 6.69 (dd, J = 9.8 and 17.8 Hz, $-CH$=CHSiMe$_3$, 1 H), 6.80 (dd, J = 9.8 and 15.1 Hz, PhCH=CH–, 1 H), 7.23–7.45 (m, aromatic, 5 H); ^{13}C NMR (62.5 MHz) δ 1.3, 126.6, 127.6, 128.6, 131.8, 132.9, 134.9, 137.4, 144.2; accurate mass calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1185. Anal. Calcd: C, 77.18; H, 8.97. Found: C, 76.83; H, 9.10.

General Procedure for the Reaction of Allylic Dithioacetal with Me_3SiCH_2MgCl. In a flask fitted with a reflux condenser, a rubber septum, and a magnet stirring bar were placed allylic dithioacetal and a catalytic amount of $NiCl_2(PPh_3)_2$ (5 mol %). The flask was evacuated and filled with nitrogen three times. To the above mixture was added dry benzene, and the solution was then cooled with an ice bath. Freshly prepared Me_3SiCH_2MgCl (3–4 equiv) was introduced via a syringe in one portion. The mixture was refluxed for 16 h and then treated with saturated ammonium chloride (60 mL). The organic layer was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with aqueous sodium hydroxide (10%), water, and brine and then dried over anhydrous magnesium sulfate. The solvent was removed in vacuo to leave the residue which was chromatographed on silica gel (eluted with hexane unless otherwise stated) to give the product.

(*E*,*E*)-Trimethyl[4-(2-methylphenyl)-1,3-butadien-1-yl]silane (19). According to the general procedure, a mixture of **18** (331 mg, 1.49 mmol) and $NiCl_2(PPh_3)_2$ (32 mg, 0.05 mmol) in benzene (6 mL) was allowed to react with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) under refluxing conditions for 16 h to give **19** (258 mg, 80%): IR (neat) ν 3033, 2961, 1605, 1440, 1245, 980, 865, 835, 720, 690 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.13 (s, 9 H, $-Si(CH_3)_3$), 2.00 (br s, 3 H, PhCH=CCH_3–), 5.97 (d, J = 18.8 Hz, 1 H, $=CHSiMe_3$), 6.57 (br s, 1 H, PhCH=), 6.73 (dd, J = 18.8 and 0.4 Hz, 1 H, $-CH$=CHSiMe$_3$), 7.19–7.37 (m, 5 H, aromatic); ^{13}C NMR (62.5 MHz) δ −1.2, 13.3, 126.6, 128.1, 128.4, 129.2, 132.3, 137.2, 138.0, 148.9; accurate mass calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1355.

(*E*,*E*)-Trimethyl[4-(2-methoxyphenyl)-1,3-butadien-1-yl]silane (17b). By using the general procedure described above, a mixture of **16b** (271 mg, 1.13 mmol) and Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (23 mg, 0.04 mmol) in benzene (5 mL) was refluxed for 16 h. After the usual workup, the crude product was chromatographed on silica gel and eluted with 10% ethyl acetate in hexane to yield **17b** (211 mg, 79%): IR (neat) ν 3041, 3007, 2945, 1621, 1602, 1573, 1486, 1439, 1251, 1190, 1098, 1001, 887, 749, 720, 690 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.11 (s, 9 H, $-Si(CH_3)_3$), 3.71 ($-OCH_3$), 5.86 (d, J = 16.5 Hz, 1 H, $=CHSiMe_3$), 6.56–6.85 (m, 5 H, olefinic and aromatic), 7.08 (t, J = 7.4 Hz, 1 H), 7.35 (d, J = 7.6 Hz, 1 H); ^{13}C NMR (62.5 MHz) δ −1.2, 55.5, 111.1, 121.0, 126.5, 126.6, 127.9, 128.6, 132.4, 133.9, 145.1, 157.1; accurate mass calcd for $C_{14}H_{29}OSi$ 232.1283, found 232.1281.

(*E*,*E*)-Trimethyl[4-(1-naphthyl)-1,3-butadien-1-yl]silane (17c). Via the general procedure described above, the reaction of **16c** (342 mg, 1.28 mmol) and $NiCl_2(PPh_3)_2$ (66 mg, 0.1 mmol) with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) in refluxing benzene (7 mL) for 16 h gave **17c** (303 mg, 91%): IR (neat) ν 3065, 2969, 2902, 1616, 1577, 1510, 1395, 1242, 1006, 887, 751, 720, 690 cm^{-1}; ^{1}H NMR (250 MHz) δ[33] 0.15 (s, $-Si(CH_3)_3$, 9 H), 5.96 (dd, J = 17.8 and 1.2 Hz, $=CHSiMe_3$, 1 H), 6.74 (m, $=CHCH=$, 2 H), 7.31–7.37 (m, 8 H, an olefinic proton at δ 7.34, dd, J = 15.0 and 1.2 Hz was embodied in these multiplets); ^{13}C NMR (62.5 MHz) δ 1.5, 123.4, 123.6, 125.6, 125.8, 126.0, 128.0, 128.6, 129.7, 131.3, 133.8, 134.5, 135.3, 144.4; accurate mass calcd for $C_{17}H_{20}Si$ 252.1334, found 252.1342.

(*E*,*E*,*E*)-Trimethyl(6-phenyl-1,3,5-hexatrien-1-yl)silane (21). By employing the general procedure described above, the reaction of dithiolane **20** (230 mg, 0.98 mmol) and $NiCl_2(PPh_3)_2$ (35 mg, 0.055 mmol) in benzene (5 mL) with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) afforded **21** (198 mg, 88%): mp 84–87 °C; IR (KBr) ν 3018, 2961, 1613, 1449, 1247, 1011, 976, 833, 748, 689 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.10 (s, $Si(CH_3)_3$, 9 H), 5.94 (d, J = 18.1 Hz, $=CHSiMe_3$, 1 H), 6.35 (dd, J = 9.5 and 15.8 Hz, Me_3SiCH=CHCH, 1 H), 6.41 (dd, J = 9.6 and 15.8 Hz, PhCH=CHCH, 1 H), 6.58 (d, J = 15.5 Hz, PhCH=, 1 H), 6.61 (dd, J = 18.1 and 9.5 Hz, $-CH$=CHSiMe$_3$, 1 H), 6.80 (dd, J = 15.5 and 9.6 Hz, PhCH=CH–, 1 H), 7.22–7.43 (m, 5 H, aromatic); ^{13}C NMR (62.5 MHz) δ −1.4, 126.5, 127.6, 128.7, 129.1, 133.3, 133.5, 135.0, 135.2, 137.6, 144.1; accurate mass calcd for $C_{15}H_{20}Si$ 228.1334, found 228.1338.

(*E*,*E*)-Trimethyl(1,3-pentadien-1-yl)]silane (23). According to the general procedure, the reaction of dithioacetal **22** (1.51 g, 10.3 mmol) with Me_3SiCH_2MgCl (30 mL, 1 M in ether, 30 mmol) in the presence of $NiCl_2(PPh_3)_2$ (252 mg, 0.40 mmol) in ether (20 mL) afforded **23** (0.69 g, 48%; GC yield 65%): bp 43 °C (20 mmHg) (lit.[6c] bp 50 °C (23 mmHg); IR (neat) ν 3020, 2958, 1648, 1582, 1249, 999, 869, 768, 724, 689 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.10 (s, 1 H, $-Si(CH_3)_3$), 1.79 (d, J = 6.8 Hz, CH_3CH=, 3 H), 5.73 (d, J = 18.3 Hz, 1 H, $=CHSiMe_3$), 5.77 (qd, 6.8 and 15.2 Hz, 1 H, CH_3CH=CH–), 6.11 (dd, J = 9.9 and 15.2 Hz, 1 H, CH_3CH=CH–), 6.51 (dd, J = 9.9 and 18.3 Hz, 1 H, $-CH$=CHSiMe$_3$); ^{13}C NMR (62.5 MHz) δ −1.9, 18.0, 130.2, 130.8, 134.8, 144.3; m/z 140 (M), 125 (M - CH_3), 73 (base peak).

Trimethyl(4,8-dimethyl-1(*E*),3(*Z*),7-nonatrien-1-yl)silane and Trimethyl(4,8-dimethyl-1(*E*),3(*E*),7-nonatrien-1-yl)silane (25). According to the general procedure the reaction of citral dithioacetal **24** (Z/E = 79/21, 225 mg, 0.98 mmol) and $NiCl_2(PPh_3)_2$ (31 mg, 0.049 mmol) with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) in benzene (5 mL) yielded a mixture of (1*E*,3*Z*,7)-**25** and (1*E*,3*E*,7)-**25** (206 mg, 93%) in a ratio of 79/21 as determined by the ^{1}H NMR spectral data: IR (neat) ν 3005, 2960, 1642, 1575, 1350, 1380, 1249, 979, 872, 835, 737, 722, 689 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.01 (s, $-Si(CH_3)_3$, 9 H), 1.53 (s, CH_3C=, 3 H), 1.61 (s, CH_3C=, 3 H); 1.70 (3*E*) and 1.73 (3*Z*) (s, $-CH_2C(CH_3)$=, 3 H), 1.96–2.15 (m, $=CHCH_2CH_2C(CH_3)$=, 4 H), 5.00–5.06 (m, Me_2C=CH–, 1 H), 5.62 (3*Z*) and 5.66 (3*E*) (d, J = 18.2, $=CHSiMe_3$, 1 H), 5.81 (br d, J = 9.6 Hz, $=CHCH=CHSiMe_3$, 1 H), 6.68 (3*Z*) and 6.70 (3*E*) (dd, J = 9.6 and 18.2 Hz, $-CH$=CHSiMe$_3$, 1 H); ^{13}C NMR (62.5 MHz) δ −1.1, 16.8, 17.7, 23.8, 25.7, 26.6, 26.9, 32.6, 40.0, 124.0, 127.9, 128.9, 130.7, 131.1, 131.7, 131.9, 139.9, 140.0, 140.2, 140.4; accurate mass calcd for $C_{14}H_{26}Si$ 222.1804, found 222.1809.

By employing the same procedure described above, a solution of neral dithioacetal **24** (Z/E = 36/64, 252 mg, 1.10 mmol) and $NiCl_2(PPh_3)_2$ (35 mg, 0.055 mmol) with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) in benzene (5 mL) under refluxing conditions for 16 h gave rise to a mixture of (1*E*,3*Z*,7)-**25** and (1*E*,3*E*,7)-**25** (206 mg, 93%) in a ratio of 32/68 as determined by the ^{1}H NMR spectra.

Reaction of 26 with Me_3SiCH_2MgCl. According to the general procedure described above, the reaction of **26** (248 mg, 1.04 mmol) with Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (31 mg, 0.05 mmol) in benzene (5 mL) gave **17a** (172 mg, 82%), which showed identical spectroscopic data with those of the authentic sample.

Reaction of 27 with Me_3SiCH_2MgCl. By employing the general procedure described above, the reaction of **27** (241 mg, 1.02 mmol) with Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (32 mg, 0.05 mmol) in benzene (5 mL) gave **17a** (157 mg, 76%), which exhibited the same spectroscopic data as those of the authentic sample.

Reaction of Ethyl 1-Phenyl-4-(trimethylsilyl)-1-buten-3-yl Sulfide (31) with Me_3SiCH_2MgCl. A mixture of **31** (286 mg, 1.08 mmol), $NiCl_2(PPh_3)_2$ (33 mg, 0.05 mmol), and Me_3SiCH_2MgCl (2.0 mL, 1 M in ether, 2.0 mmol) in benzene (5 mL) was refluxed for 16 h to give **17a** (192 mg, 88%) which showed identical spectroscopic data with those of the authentic sample.

Reaction of (*E*)-2-(2-Phenyl-1-propen-1-yl)-1,3-dithiolane (*E*-32) with Me_3SiCH_2MgCl. According to the general procedure the reaction of *E*-**32** (230 mg, 1.04 mmol) and $NiCl_2(PPh_3)_2$ (32 mg, 0.05 mmol) in benzene (4 mL) with Me_3SiCH_2MgCl (4.0 mL, 1 M in ether, 4.0 mmol) gave a mixture of (1*E*,3*E*)-4-phenyl-1-(trimethylsilyl)-1,3-pentadiene (**33**) and (1*E*,3*Z*)-4-phenyl-1-(trimethylsilyl)-1,3-pentadiene (**34**) (197 mg, 88%, **33**/**34** = 92/8). **33**: IR (neat) ν 3066, 3033, 2961, 160, 1495, 1448, 1265, 1124, 1028, 842, 764, 701 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.12 (s, $-Si(CH_3)_3$, 9 H), 2.21 (d, J = 1.0 Hz, PhC(CH_3)=, 3 H), 6.00 (br d, J = 18.1 Hz, $=CHSiMe_3$, 1 H), 6.46 (br d, J = 10.5 Hz, PhMeC=CH–, 1 H), 6.95 (dd, J = 18.1, 10.5 Hz, $-CH$=CHSiMe$_3$, 1 H), 7.20–7.46 (m, aromatic, 5 H); ^{13}C NMR (62.5 MHz) δ −1.0, 16.3, 125.9, 127.4, 128.5, 130.2, 135.2, 136.9, 140.5, 143.3; accurate mass calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1326. The presence of *Z* isomer **34** was determined by the ^{1}H NMR spectrum of the mixture. It showed characteristic absorptions at δ 2.11 (s, PhC(CH_3)=, 3 H), 5.83 (d, J = 18.3, $=CHSiMe_3$, 1 H), 6.16 (br d, J = 10.5 Hz, PMeC=CH–, 1 H), 6.61 (dd, J = 10.5, 18.3 Hz, $-CH$=CHSiMe$_3$).

Reaction of (*Z*)-2-(2-Phenyl-1-propen-1-yl)-1,3-dithiolane (*Z*-32) with Me_3SiCH_2MgCl. The reaction of dithioacetal *Z*-**32** (153 mg, 0.69 mmol) and $NiCl_2(PPh_3)_2$ (25 mg, 0.039 mmol) in benzene (3 mL) with Me_3SiCH_2MgCl (3.0 mL, 1 M in ether, 3.0 mmol) was carried out by employing the general procedure, giving a mixture of **33** and **34** (130 mg

87%, **33**:**34** = 94/6). The ratio of *E*/*Z* isomers was determined by the ^{1}H NMR spectrum as described above.

(*E*)- and (*Z*)-Trimethyl[4-phenyl-2-(trimethylsilyl)methyl-1,3-butadien-1-yl]silane (38a). According to a similar procedure described above, a mixture of orthothioester **37a** (423 mg, 1.58 mmol), $NiCl_2(PPh_3)_2$ (110 mg, 0.17 mmol), and Me_3SiCH_2MgCl (4.0 mL, 2 M in ether, 8.0 mmol) in toluene (25 mL) was refluxed for 16 h to give a mixture of *E*- and *Z*-**38a** (*E*/*Z* = 39/61) (168 mg, 37%). The two isomers were separated by preparative GC (oven temperature 180 °C). *E*-**38a**: IR (neat) ν 2953, 1548, 1421, 1248, 1156, 961, 838, 753, 692 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.02 (s, 9 H), 0.20 (s, 9 H), 1.94 (s, 2 H), 5.38 (s, 1 H), 6.50 (d, J = 16 Hz, 1 H), 7.06 (d, J = 16 Hz, 1 H), 7.26–7.42 (m, 5 H); *m*/*z* 288 (89), 215 (19), 201 (34), 185 (26), 73 (100); accurate mass calcd for $C_{17}H_{28}Si_2$ 288.1730, found 288.1714. *Z*-**38a**: IR (neat) ν 2953, 1548, 1421, 1248, 961, 838, 753, 692 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.08 (s, 9 H), 0.16 (s, 9 H), 2.03 (s, 2 H, 4.2% NOE enhancement upon irradiation at δ 0.16), 5.48, (s, 1 H, 4.6% NOE enhancement upon irradiation at δ 0.16), 6.46 (d, J = 16 Hz, 1 H, 18.6% NOE enhancement upon irradiation at δ 2.03), 6.76 (d, J = 16 Hz, 1 H, 16% NOE enhancement upon irradiation at δ 5.48), 7.21–7.43 (m, 5 H); ^{13}C NMR (50 MHz) δ −0.3, 0.4, 22.5, 126.4, 127.3, 128.4, 128.6, 129.5, 134.6, 135.5, 137.4; *m*/*z* 288 (39), 287 (46), 214 (23), 201 (36), 200 (33), 185 (34), 168 (15), 73 (100); accurate mass calcd for $C_{17}H_{28}Si_2$ 288.1730, found 288.1734.

(*E*)- and (*Z*)-Trimethyl[4-(4-methylphenyl)-2-((trimethylsilyl)-methyl)-1,3-butadien-1-yl]silane (38b). By employing the general procedure described above, the reaction of **37b** (141 mg, 0.51 mmol) with Me_3SiCH_2MgCl (1.5 mL, 2 M in ether, 3 mmol) in the presence of $NiCl_2(PPh_3)_2$ (33 mg, 0.05 mmol) in refluxing toluene (10 mL) for 16 h gave a mixture of *E*- and *Z*-**38b** (*E*/*Z* = 32/68) (44 mg, 29%). The two isomers were separated by preparative GC (oven temperature 200 °C). *E*-**38b**: IR (neat) ν 2952, 1551, 1511, 1414, 1248, 1156, 961, 839, 767, 690, 621 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.02 (s, 9 H), 0.19 (s, 9 H), 1.93 (s, 2 H), 2.35 (s, 3 H), 5.35 (s, 1 H, 20% NOE enhancement upon irradiation at δ 1.93), 6.48 (d, J = 16 Hz, 1 H, 25% NOE enhancement upon irradiation at δ 1.93), 7.01 (d, J = 16 Hz, 1 H, 2% NOE enhancement upon irradiation at δ 0.19), 7.14 (d, J = 8 Hz, 2 H), 7.28 (d, J = 8 Hz, 2 H); ^{13}C NMR (50 MHz) δ −1.1, 0.9, 21.2, 126.4, 129.4, 129.7, 129.8, 134.9, 137.4; *m*/*z* 302 (51), 215 (30), 73 (100); accurate mass calcd for $C_{18}H_{30}Si_2$ 302.1886, found 302.1889. *Z*-**38b**: IR (neat) ν 2951, 1551, 1492, 1412, 1247, 1226, 1157, 1111, 961, 840, 766, 721, 621 cm^{-1}; ^{1}H NMR (200 MHz) δ 0.07 (s, 9 H), 0.15 (s, 9 H), 2.02 (s, 2 H), 2.33 (s, 3 H), 5.47 (s, 1 H), 6.43 (d, J = 16.1 Hz, 1 H), 6.72 (d, J = 16.1 Hz, 1 H), 7.12 (d, J = 8.1 Hz, 2 H), 7.30 (d, J = 8.1 Hz, 2 H); *m*/*z* 302 (56), 215 (29), 73 (100); accurate mass calcd for $C_{18}H_{30}Si_2$ 302.1886, found 302.1885.

Trimethyl(1-phenyl-1,3-butadien-3-yl)silane (40a). According to the general procedure, **39a** (250 mg, 0.85 mmol) was treated with MeMgI (2.0 mL, 2 M in ether, 4.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) in benzene (8 mL) for 20 h to give **40a** (105 mg, 61%): IR (neat) ν 3065, 3031, 2962, 1600, 1578, 1449, 1263, 1251, 980, 963, 841 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.50 (s, 9 H), 5.86 (d, J = 3.1 Hz, 1 H), 6.21 (d, J = 3.1 Hz, 1 H), 6.96 (d, J = 16.4 Hz, 1 H), 7.27 (d, J = 16.4 Hz, 1 H), 7.53–7.78 (m, 5 H); ^{13}C NMR (62.5 MHz) δ −0.80, 126.0, 126.3, 127.3, 128.1, 128.6, 130.5, 134.0; accurate mass calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1177.

Trimethyl[1-(4-methylphenyl)-1,3-butadien-3-yl]silane (40b). Via the general procedure, **39b** (250 mg, 0.81 mmol) was allowed to react with MeMgI (2.0 mL, 2 M in ether, 4.0 mmol) in the presence of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) in benzene (8 mL) for 48 h to give **40b** (130 mg, 74%): ^{1}H NMR (250 MHz) δ 0.26 (s, 9 H), 2.35 (s, 3 H), 5.51 (d, J = 3.1 Hz, 1 H), 5.85 (d, J = 3.1 Hz, 1 H), 6.80 (d, J = 16.0 Hz, 1 H), 6.87 (d, J = 16.0 Hz, 1 H), 7.06 (d, J = 8 Hz, 2 H), 7.33 (d, J = 8 Hz, 2 H); *m*/*z* 216 (12), 201 (8), 142 (59), 128 (8), 73 (100); accurate mass calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1330.

Trimethyl[1-(2-methylphenyl)-1,3-butadien-3-yl]silane (40c). In the presence of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), **39c** (250 mg, 0.81 mmol) was treated, according to the general procedure, with MeMgI (2.0 mL, 2 M in ether, 4.0 mmol) in benzene (8 mL) for 48 h to give **40c** (154 mg, 86): ^{1}H NMR (250 MHz) δ 0.26 (s, 9 H), 2.36 (s, 3 H), 5.51 (d, J = 3.1 Hz, 1 H), 5.85 (d, J = 3.1 Hz, 1 H), 6.79 (d, J = 16.4 Hz, 1 H), 6.86 (d, J = 16.4 Hz, 1 H), 7.11–7.52 (m, 4 H); *m*/*z* 216 (12), 201 (8), 142 (59), 73 (100); accurate mass calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1336.

Trimethyl[1-(2-methoxyphenyl)-1,3-butadien-3-yl]silane (40d). Under the same conditions as described in the general procedure, a mixture of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), **39d** (250 mg, 0.77 mmol), and MeMgI (2.0 mL, 2 M in ether, 4.0 mmol) in benzene (8 mL) was refluxed for 48 h to give **40d** (140 mg, 78%): ^{1}H NMR (250 MHz) δ 0.26 (s, 9 H), 3.86 (s, 3 H), 5.40 (d, J = 3.1 Hz, 1 H), 5.85 (d, J = 3.1 Hz, 1 H), 6.82 (d, J = 16.4 Hz, 1 H), 6.90–7.53 (m, 5 H); *m*/*z* 232 (7), 217 (19), 202 (6), 159 (18), 73 (100); accurate mass calcd for $C_{14}H_{20}OSi$ 232.1283, found 232.1270.

Trimethyl[1-(1-naphthyl)-1,3-butadien-3-yl]silane (40e). Under the same conditions as described in the general procedure, a mixture of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), **39e** (250 mg, 0.73 mmol), and MeMgI (2.0 mL, 2 M in ether, 4.0 mmol) in benzene (8 mL) was heated under reflux for 48 h and the usual workup to afford **40e** (160 mg, 87%): ^{1}H NMR (250 MHz) δ 0.74 (s, 9 H), 5.98 (d, J = 3.1 Hz, 1 H), 6.34 (d, J = 3.1 Hz, 1 H), 7.36 (d, J = 16.1 Hz, 1 H), 7.80 (d, J = 16.1 Hz, 1 H), 7.83–8.50 (m, 7 H); *m*/*z* 252 (10), 178 (52), 152 (5), 73 (100); accurate mass calcd for $C_{17}H_{20}Si$ 252.1334, found 252.1326.

Trimethyl[2-methyl-1-phenyl-1,3-butadien-3-yl]silanes (*E*- and *Z*-43a). To a mixture of **42a** (250 mg, 0.8 mmol) and $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) in a 25-mL round-bottomed flask was syringed MeMgI (2.0 mL, 2 M in ether, 4.0 mmol). The system was evacuated and ether was removed. Toluene (8 mL) was then introduced and the mixture was heated under reflux for 16 h. Workup as usual afforded a mixture of *E*- and *Z*-**43a** (*E*/*Z* = 70/30) (170 mg, 97%). *E*-**43a**: ^{1}H NMR (250 MHz) δ 0.24 (s, 9 H), 2.01 (s, 3 H), 5.49 (d, J = 2.70 Hz, 1 H), 5.83 (d, J = 2.70 Hz, 1 H), 6.54 (s, 1 H), 7.11–7.63 (m, 5 H). *Z*-**43a**: ^{1}H NMR (250 MHz) δ 0.00 (s, 9 H), 1.96 (s, 3 H), 5.59 (d, J = 3.3 Hz, 1 H), 5.74 (d, J = 3.3 Hz, 1 H), 6.19 (s, 1 H), 7.11–7.63 (m, 5 H); *m*/*z* 216 (7), 142 (70), 73 (100).

Trimethyl[2-ethyl-1-phenyl-1,3-butadien-3-yl]silanes (*E*- and *Z*-43b). Via similar conditions as described above, a mixture of $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol) and **42b** (250 mg, 0.8 mmol) was allowed to react with MeMgI (4.0 mmol) in toluene (8 mL) to give a mixture of *E*- and *Z*-**43b** (*E*/*Z* = 57/43) (130 mg, 73%). *E*-**43b**: ^{1}H NMR (250 MHz) δ 0.20 (s, 9 H), 1.09 (t, J = 7.5 Hz, 3 H), 2.38 (q, J = 7.5 Hz, 2 H), 5.58 (d, J = 3 Hz, 1 H), 5.78 (d, J = 3 Hz, 1 H), 6.28 (s, 1 H), 7.19–7.40 (m, 5 H). *Z*-**43b**: ^{1}H NMR (250 MHz) δ 0.00 (s, 9 H), 1.04 (t, J = 6.3 Hz, 3 H), 2.21 (q, J = 6.3 Hz, 2 H), 5.62 (d, J = 3.3 Hz, 1 H), 5.70 (d, J = 3.3 Hz, 1 H), 6.15 (s, 1 H), 7.19–7.40 (m, 5 H).

4-Phenyl-1,2-bis(trimethylsilyl)-1,3-butadiene (44a). With use of the general procedure, a mixture of **39a** (250 mg 0.85 mmol), $NiCl_2(PPh_3)_2$ (60 mg, 0.09 mmol), and Me_3SiCH_2MgCl (2.0 mL, 2 M in ether, 4.0 mmol) in benzene (8 mL) was allowed to reflux for 48 h to yield **44a** (205 mg, 88%): IR (neat) ν 3032, 2961, 2903, 1600, 1514, 1251, 960, 831 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.23 (s, 9 H), 0.25 (s, 9 H), 6.30 (s, 1 H), 6.59 (d, J = 16.4 Hz, 1 H), 7.24–7.44 (m, 6 H); ^{13}C NMR (62.5 MHz) δ −1.6, 0.1, 125.7, 126.4, 127.4, 127.6, 128.2, 144.0, 145.5, 166.7; *m*/*z* 274 (12), 200 (45), 186 (67), 171 (43), 145 (12), 128 (6), 73 (100); accurate mass calcd for $C_{16}H_{26}Si_2$ 274.1573, found 274.1566.

4-(2-Methoxyphenyl)-1,2-bis(trimethylsilyl)-1,3-butadiene (44b). A mixture of **39d** (125 mg, 0.40 mmol), $NiCl_2(PPh_3)_2$ (35 mg, 0.05 mmol), and Me_3SiCH_2MgCl (2 mL 2 M in ether, 4.0 mmol) in benzene (8 mL) was allowed to reflux for 48 h, according to the procedure described above, to give **44b** (75 mg, 64%): IR (KBr) ν 2953, 2900, 2840, 1598, 1485, 1465, 1246, 966, 831 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.21 (s, 9 H), 0.24 (s, 9 H), 3.85 (s, 3 H), 6.23 (s, 1 H), 6.89–7.53 (m, 6 H); accurate mass calcd for $C_{17}H_{28}OSi_2$ 304.1679, found 304.1677.

3-Ethyl-4-phenyl-1,2-bis(trimethylsilyl)-1,3-butadiene (45). Via the procedure described above, a mixture of **42b** (200 Mg, 0.6 mmol), $NiCl_2(PPh_3)_2$ (42 mg, 0.06 mmol), and Me_3SiCH_2MgCl (4.0 mmol) in toluene (8 mL) was allowed to reflux for 16 h to give **45** (150 mg, 80%): IR (neat) ν 3062, 3028, 1601, 1494, 1249, 928, 836 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.05 (s, 9 H), 0.08 (s, 9 H), .0.97 (t, J = 7.5 Hz, 3 H), 2.35 (q, J = 7.5 Hz, 2 H), 6.03 (s, 1 H), 7.12–7.31 (m, 6 H); ^{13}C NMR (62.5 MMz) δ −0.5, 0.8, 12.7, 24.7, 124.1, 126.0, 128.8, 142.7, 148.8, 168.0, 171.8; accurate mass calcd for $C_{18}H_{30}Si_2$ 302.1886, found 302.1880.

4,5-Bis(trimethylsilyl)-1,3-pentadiene (47). According to the procedure described above, a mixture of **46** (250 mg, 1.1 mmol), $NiCl_2(PPh_3)_2$, and Me_3SiCH_2MgCl (4.0 mmol) in toluene was allowed to react for 48 h to yield **47** (110 mg, 48%): IR (neat) ν 2960, 1411, 1249, 991, 926, 834 cm^{-1}; ^{1}H NMR (250 MHz) δ 0.03 (s, 9 H), 0.09 (s, 9 H), 1.84 (s, 2 H), 5.11 (dd, J = 10.6, 2.0 Hz, 1 H), 5.16 (dd, J = 16.7, 2.0 Hz, 1 H), 6.24 (d, J = 10.6 Hz, 1 H), 6.51–6.62 (dt, J = 16.7, 10.6 Hz, 1 H); ^{13}C NMR (62.5 MHz) δ −1.1, −0.2, 21.3, 115.8, 133.8, 135.5, 143.2; accurate mass calcd for $C_{11}H_{24}Si_2$ 212.1416, found 212.1407.

General Procedure for the Coupling Reaction of Dithiane 1 with Cyclopropyl Magnesium Bromide. To a 50-mL two-necked flask equipped with a stirrer and a condenser was placed magnesium turning (0.24 g, 10 g-atom). The setup was flame-dried and flushed with dry nitrogen. Cyclopropyl bromide (0.8 mL, 10 mmol) in THF (6 mL) was then added under nitrogen and the mixture was stirred for 0.5 h until all the magnesium turning was dissolved. The solvent was removed in vacuo. Dithiane **1** (1.0 mmol) and $NiCl_2(PPh_3)_2$ (0.067 g, 0.1 mmol) in benzene (4 mL) and toluene (4 mL) were added and the mixture was heated under reflux for 4 days. The mixture was quenched with saturated NH_4Cl (10 mL) and diluted with ether (60 mL). The organic portion

was washed with aqueous NaOH (3 × 30 mL) and water (2 × 30 mL), dried over anhydrous $MgSO_4$, and filtered, and the filtrate was evaporated in vacuo. The residue was purified by chromatographic separation with hexane as eluent to give **49**.

(*E*)-Trimethyl(1-phenyl-1,3-butadien-1-yl)silane (49a). According to the general procedure, **1a** (0.269 g, 1.0 mmol) was converted to **49a** (0.142 g, 70%): IR (neat) ν 3065, 2956, 1600, 1565, 1494, 1248, 941, 898, 836, 701 cm^{-1}; ^1H NMR (250 MHz) δ[34] 0.10 (s, 9 H), 5.08 (dd, J = 1.9, 9.9 Hz, 1 H), 5.30 (dd, J = 1.9, 16.9 Hz, 1 H), 6.25 (quasi dt, J = 16.9, 10.3 Hz, 1 H), 6.53 (d, J = 10.7 Hz, 1 H), 6.96-6.99 (m, 2 H), 7.20-7.35 (m, 3 H); ^{13}C NMR (62.5 MHz) δ -1.6, 118.5, 125.6, 127.9 (two overlapping signals), 134.5, 138.9, 142.3, 147.8; accurate mass calcd for $C_{13}H_{18}Si$ 202.1178, found 202.1178.

(*E*)-Trimethyl[1-(2-naphthyl)-1,3-butadien-1-yl]silane (49b). Following the general procedure, **1b** (0.319 g, 1 mmol) was transformed to **49b** (0.204 g, 81%): mp 52-54 °C; IR (KBr) ν 3054, 2956, 1728, 1628, 1597, 1562, 1502, 1247, 931, 864, 853, 838, 807, 742 cm^{-1}; ^1H NMR δ 0.13 (s, 9 H), 5.07 (dd, J = 1.9, 10.0 Hz, 1 H), 5.33 (dd, J = 1.9, 16.9 Hz, 1 H), 6.26 (quasi dt, J = 16.9, 10.3 Hz, 1 H), 6.60 (d, J = 10.6 Hz, 1 H), 7.13 (dd, J = 1.6, 8.4 Hz, 1 H), 7.41-7.48 (m, 3 H), 7.78-7.85 (m, 3 H); ^{13}C NMR δ -1.15, 118.8, 125.2, 125.9, 127.1, 127.6, 127.7, 131.9, 133.5, 134.6, 139.3, 140.0, 147.8; accurate mass calcd for $C_{17}H_{20}Si$ 252.1334, found 252.1331. Anal. Calcd: C, 80.89; H, 7.99. Found: C, 80.29; H, 8.10.

(*E*)-Trimethyl[1-(1-naphthyl)-1,3-butadien-1-yl]silane (49c). Via the general procedure, **1c** (0.319 g, 1 mmol) was converted to **49c** (0.199 g, 70%): IR (neat) ν 3057, 2955, 1589, 1577, 1561, 1504, 1403, 1390, 1248, 928, 898, 839, 791, 774, 755 cm^{-1}; ^1H NMR (250 MHz) δ 0.07 (s, 9 H), 4.98 (dd, J = 1.8, 9.9 Hz, 1 H), 5.30 (dd, J = 1.8, 17.0 Hz, 1 H), 5.91 (quasi dt, J = 17.0, 10.3 Hz, 1 H), 6.78 (d, J = 10.6 Hz, 1 H), 7.04 (dd, J = 1.1, 7.0 Hz, 1 H), 7.40-7.48 (m, 3 H), 7.71-7.86 (m, 3 H); ^{13}C NMR (62.5 MHz) δ -1.5, 118.8, 124.6, 125.3, 125.4, 125.6, 126.0, 126.5, 128.2, 131.4, 133.7, 134.8, 139.8, 140.5, 145.9; accurate mass calcd for $C_{17}H_{20}Si$ 252.1334, found 252.1338. Anal. Calcd: C, 80.89; H, 7.99. Found: C, 80.28; H, 8.11.

(*E*)-Trimethyl[1-(4-methylphenyl)-1,3-butadien-1-yl]silane (49d). Via the general procedure, **1d** (0.283 g, 1 mmol) was transformed to **49d** (0.160 g, 74%): IR (neat) ν 2957, 2925, 1728, 1566, 1508, 1457, 1248, 912, 840 cm^{-1}; ^1H NMR (250 MHz) δ 0.09 (s, 9 H), 2.33 (s, 3 H), 5.07 (dd, J = 2.0, 10.1 Hz, 1 H), 5.29 (dd, J = 2.0, 16.8 Hz, 1 H), 6.26 (quasi dt, J = 16.8, 10.3 Hz, 1 H), 6.52 (d, J = 10.7 Hz, 1 H), 6.87 (d, J = 8.0 Hz, 2 H), 7.12 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (62.5 MHz) δ -1.6, 21.1, 118.3, 127.8, 128.7, 134.6, 135.1, 138.8, 139.1, 147.8; accurate mass calcd for $C_{14}H_{20}Si$ 216.1334, found 216.1328.

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5-(Aminomethyl)-3-aryl-2-oxazolidinones. A Novel Class of Mechanism-Based Inactivators of Monoamine Oxidase B

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Abstract: The mechanism of inactivation of monoamine oxidase (MAO) by 5-(aminomethyl)-3-aryl-2-oxazolidinones has been investigated. (*R*)- and (*S*)-3-[4-[(3-chlorophenyl)methoxy]phenyl]-5-[(methylamino)methyl]-2-oxazolidinone (**1**) exhibit all of the properties of a mechanism-based inactivator. Several other analogues of **1** also inactivate MAO. Inactivation of MAO by (*R*)- and (*S*)-[*methoxy*-^3H]-**1** and by [*methoxy*-^3H]-3-(4-methoxyphenyl)-5-[(methylamino)methyl]-2-oxazolidinone (**15**, R = ^3H) led to incorporation of 1.0, 1.2, and 2.1 equiv of tritium per enzyme molecule after denaturation, indicating that a covalent bond between the oxazolidinones and MAO is formed. The partition ratios, determined from the amount of radioactive non-amines generated per tritium incorporated into the enzyme, were 17.6 and 10.9 for the *R* and *S* isomers, respectively. Inactivation of MAO by (*R*)- and (*S*)-[*carboxy*-^{14}C]-**1** resulted in release of 4.5 and 3.0 equiv of $^{14}CO_2$, respectively. However, in addition to the loss of $^{14}CO_2$ there also was incorporation of 1.5 and 1.0 equiv of ^{14}C, respectively, into the enzyme after denaturation. The flavin spectrum indicated that the flavin was reduced after inactivation, but upon denaturation the spectrum returned to that of the oxidized form, suggesting that attachment is to an amino acid residue, not to the flavin. 5-(Aminomethyl)-3-(4-cyanophenyl)-2-oxazolidinone inactivates MAO at a rate comparable to or faster than does the corresponding 4-methoxyphenyl analogue, suggesting that there is little or no electronic effect of ring substitution on the rate of inactivation. All of these results support an inactivation mechanism that involves one-electron oxidation of the amine to the amine radical cation, followed by proton removal to give the α radical, which can partition among three pathways (Scheme V): radical combination with an active-site amino acid residue radical to give inactive enzyme, decomposition of the oxazolidinone ring with loss of CO_2, and second electron transfer to give the corresponding aldehyde product.

Monoamine oxidase (MAO; EC 1.4.3.4) is responsible for the deactivation of amine neurotransmitters as well as the metabolism of certain exogenous amines.[1] The enzyme exists in two different isoenzymic forms, designated MAO A and MAO B, which differ in substrate specificity, distribution among tissues, and structure.[2] Nonspecific or MAO A specific inhibitors have been shown to be clinically useful as antidepressants; the clinical usefulness of MAO B specific inhibitors in the treatment of depression remains to be demonstrated.[3] Recently, however, it has become clear that there are other important uses for MAO B specific inhibitors in medicine, namely, as adjuncts to L-dopa treatment of Parkinson's disease.[4,5] Furthermore, it was shown that administration of

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