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Palladium-catalyzed insertion reactions of trimethylsilyldiazomethane

Kevin L. Greenman, David S. Carter and David L. Van Vranken*

Department of Chemistry, University of California, Irvine, CA 92697-2025, USA

Dedicated to Professor Barry M. Trost on the occasion of his 60th birthday

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Abstract—Palladium(II) salts catalyze the Kirmse reaction of allylsulfides with trimethylsilyldiazomethane (TMSD) to give homoallylsulfides. Similarly, TMSD can intercept ArPdX intermediates generated during Stille couplings to give benzhydryl derivatives. The yields of this process are limited by overinsertion and β-elimination. Insertion and elimination can be harnessed to generate styrenes from benzylic halides in the presence of palladium (0) catalysts. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

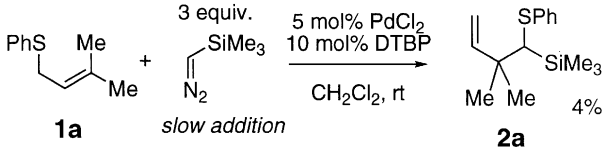
Many metals catalyze useful reactions of diazo compounds.[1,2] Cationic palladium can effect efficient cyclopropanation of olefins with low lying LUMOs (e.g. styrene,[3,4] acrylates,[5,6] and norbornenes[7–9]) or when the diazo compound has a high lying HOMO (e.g. diazomethane).[10,11] However, palladium is a poor catalyst for intermolecular cyclopropanation of simple alkenes with stabilized diazo compounds such as α-diazoesters.[12] Palladium-catalyzed cyclopropanation is less general than rhodium-catalyzed cyclopropanation, but the rich reactivity of palladium makes it an attractive catalyst for exploring new patterns of reactivity with diazo compounds.[13,14] In this manuscript, we describe three types of palladium catalyzed reactions with trimethylsilyldiazomethane: (1) insertion/rearrangement of allyl sulfides, (2) a low yielding Stille insertion reaction, and (3) a unique halide homologation.

2. Results and discussion

2.1. Pd(II)-Catalyzed Kirmse reaction

Many of the metals that efficiently catalyze cyclopropanation (e.g., rhodium, copper, cobalt) can also efficiently catalyze addition/rearrangement reactions of allyl sulfides with diazo compounds (the Kirmse reaction).[1,2,15] Even though thioethers bind to Pd(II) with high affinity McCrindle has shown that diazomethane inserts into the Pd–Cl and Pd–S bonds of R_2S–$PdCl_2$ complexes.[16] Recently, we reported stoichiometric addition/rearrangement of trimethylsilyldiazomethane (TMSD) to phenyl dimethallyl sulfide (**1a**) by slow addition of TMSD to a solution of sulfide **1a**, 10 mol% 2,6-di-*tert*-butyl-4-methylpyridine (DTBP), and 5 mol% $PdCl_2$ (Scheme 1).[17] The homoallylic sulfide product was formed in only 4% yield and most of the starting material (89%) was recovered.

Since the reaction remained homogeneous, it seemed likely that it might be possible to achieve turnover by increasing the reaction temperature. While benzene is known to undergo electrophilic substitution by palladium(II) in the presence of thioethers (in the absence of diazo compounds),[18] it is still a suitable solvent for the palladium chloride catalyzed process. When the same reaction was carried out in benzene at 80°C, the desired homoallylic sulfide was obtained in 67% yield with 12% recovered starting material. Not surprisingly, $Pd(Ph_3P)_4$ does not function as a catalyst under these conditions. Dichloroethane gave even better results with only 2% recovered starting material (Table 1). Other palladium salts were inferior to palladium



Scheme 1. Insertion/rearrangement without turnover.

Table 1. Palladium (II) salts in the Kirmse reaction at reflux

Catalyst	Solvent	[2,3] Yield (%)	Starting material (%)
$PdCl_2$	C_6H_6	67	12
$PdCl_2$	$ClCH_2CH_2Cl$	83	2
$Pd(O_2CCF_3)_2$	$ClCH_2CH_2Cl$	22	55
$Pd(O_2CCH_3)_2$	$ClCH_2CH_2Cl$	8	75

Keywords: insertion; carbenes; palladium.

* Corresponding author. Tel.: +949-824-5455; fax: +949-824-8571; e-mail: dlvanvra@uci.edu

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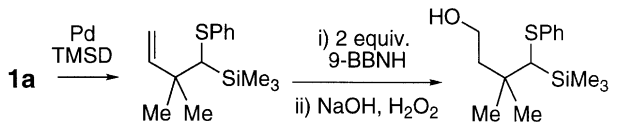
Table 2. Effect of ligands on conversion and ee



Catalyst	2a	ee[a]	1a
dppp+$PdCl_2$	64%	–	12%
(*R*)-BINAP+$PdCl_2$	40%	6%	41%
trans-$(Ph_3P)_2PdCl_2$	No *rxn.*	–	–
(*S,S*)-box+$PdCl_2$	70%	6%	6%

[a] $Eu(hfc)_3$ lanthanide shift study, **3a** *ortho* protons.

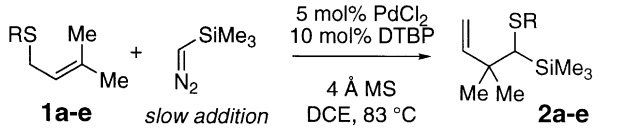
chloride. Unfortunately, with ethyl diazoacetate, the most common diazo compound, dimerization is the dominant reaction pathway, even when the diazo partner is added slowly to the reaction mixture using a syringe pump.

With a 20:1 excess of substrate to the initial catalyst complex it is reasonable to expect that the thioether might displace phosphine and nitrogen ligands in the course of the catalytic cycle. Addition of 1,3-bis(diphenylphosphino)propane gave a decreased yield of **2a** (Table 2). (*R*)-BINAP led to a more substantial reduction in yield with low levels of enantioselection. Although results with the (*S,S*)-box complex more closely paralleled those with the ligandless precursor, the enantiomeric excess of the product was still low. Interestingly, the *trans* bis(triphenylphosphine)–palladium chloride complex was not an effective catalyst precursor for this reaction. From these observations, it is unclear whether the ligands remain attached to the metal under the reaction conditions.

The conditions are fairly general for aryl and benzylic ethers of the type **1a**–**e** (Table 3). The products are thioethers, just like the starting material, so there is a tradeoff between consumption of starting material and the subsequent conversion of the product to a homoallyl ylide that cannot rearrange.

In support of this idea, the analogous Cu catalyzed reaction of allylic aryl sulfides with 3–4 equiv. of ethyl diazoacetate is known to proceed through the homoallylic sulfide which undergoes a second diazo insertion followed by elimination to generate the α,β,γ,δ-unsaturated ester.[19] With substrate

Table 3. Variation of sulfur substituents



	R	Equiv. TMSD	Yield (%)
1a	4-MeOPh		
1a	4-MeOPh	1.5	64
1a	4-MeOPh	2	62
1a	4-MeOPh	3	54
1b	Ph	2	84
1c	4-ClPh	2	75
1d	4-MeOBn	2	64
1e	Bn	2	80

1a the optimal balance was achieved using between 1.5 and 2 equiv. TMSD. The inclusion of molecular sieves generally leads to a slightly higher yield. For example, in the case of benzylic substrate **1e** the yield with 4 Å molecular sieves is 80%, versus 73% without molecular sieves.

A more pronounced effect arises on changing from the 3,3-dimethallyl substrates **1a**–**e** to other allylic groups (Table 4). The methallyl substrate **4a** and the geranyl substrate **5a** give yields around 60%. However, the hindered cyclohexenyl substrate **6a** leaves almost a third of the starting material un-reacted. In addition, only 24% of the starting material is successfully converted to product. Since the sulfur lone pairs of substrate **6a** are diastereotopic, it is possible that reaction of one lone pair leads to product **6b** while reaction of the other lone pair leads to other pathways or un-reactive ylide. The successful reaction of the cinnamyl substrate **7a** is compromised by the formation of a [1,2]-rearrangement product. [1,2]-Rearrangements of free ylides are common when the π component can form stable radicals. The results in Table 4 suggest that the palladium-catalyzed Kirmse reaction will work best with 3,3-dimethallyl and related substrates in which the sulfur lone pairs on the starting material are relatively accessible, but the lone pairs on the product are not.

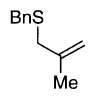
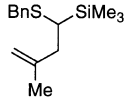
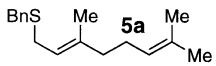
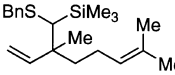
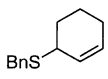
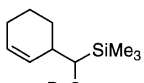
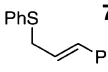
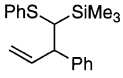
In the Kirmse reaction using rhodium dimer catalysts, the sulfide is required to react in a bimolecular fashion with the coordinatively saturated metal–carbene moiety. In contrast, copper, iron, and palladium catalysts with open coordination sites could potentially deliver a ligand internally (Scheme 2) as previously proposed by Hubert and Noels for cyclopropanation.[20]

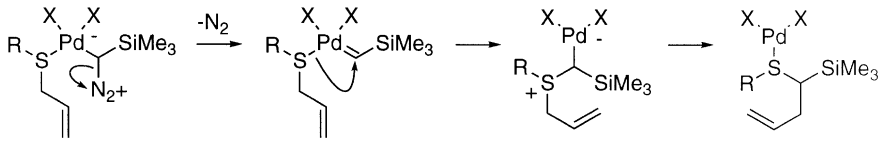
2.2. Participation of TMSD in Stille coupling reactions

If palladium can deliver sulfide ligands to carbene ligands, then ArPdX intermediates in the Stille coupling may be able to deliver aryl groups to carbene ligands as rationalized in Scheme 3.

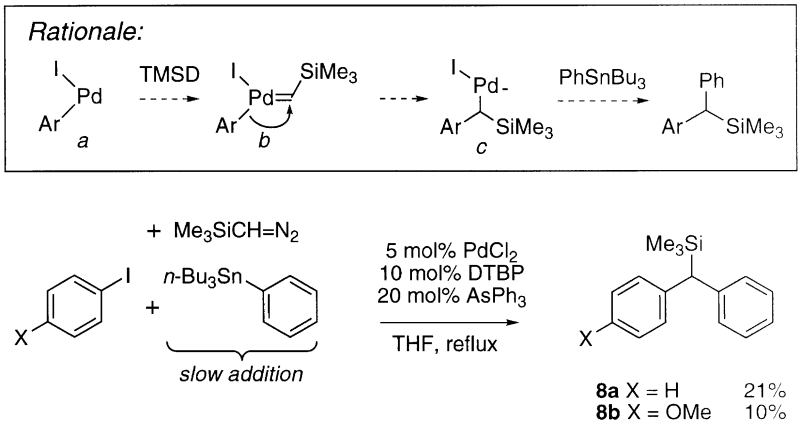
To explore the potential for trimethylsilyldiazomethane to participate in cross-coupling reactions 1 equiv. of TMSD

Table 4. Palladium catalyzed Kirmse reaction of various allyl sulfides

Starting material	Product	Yield	SM
 **4a**	 **4b**	60%	
 **5a**	 **5b** *ds* 5 : 1	65%	
 **6a**	 **6b** *ds* 1 : 1	24%	28%
 **7a**	 **7b** *ds* 3 : 1	54%	10%



Scheme 2. A plausible mechanistic pathway.



Scheme 3. Stille carbene insertion.

and 1 equiv. of tributylphenyltin were added by syringe pump to a refluxing solution of iodoanisole in THF. The desired insertion product **8a** was obtained in 21% yield along with the normal product, biphenyl, isolated in 10% yield. Under the same conditions, *p*-iodoanisole reacts to give 10% yield of the chiral benzhydryl derivative **8b**. The primary competing process in these reactions is the continued reaction of intermediate *c* with TMSD, followed by β-hydride or β-silyl elimination.

2.3. Participation of TMSD in a homologation reaction

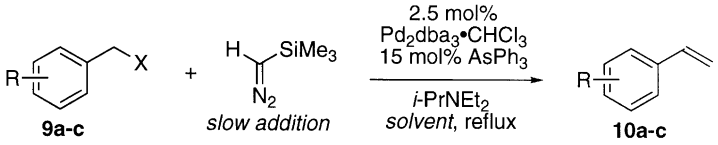
We decided to exploit this insertion/elimination process as a unique method for generating styrene derivatives. We envisioned that either an extra equivalent of TMSD or a hindered amine base could convert the H–Pd–X species back into Pd(0). Rather than adding 2 equiv. of TMSD to an aryl iodide, the reaction was simplified by starting with a benzyl bromide, requiring only one insertion for styrene formation. To our surprise, we found that when TMSD was slowly added to bromide **9a** in refluxing chloroform, the corresponding styrene **10a** was formed in 56% yield (Table 5), but none of the corresponding β-silylstyrene was detected by GCMS. No reaction occurred in the absence of palladium.

We rationalize this result by the mechanism shown in Scheme 4. Following benzyl migration to the carbene ligand, β-hydride elimination could afford the β-silylstyrene as a complex with H–Pd–Br. The subsequent events follow from Karabelas and Hallberg's mechanistic study of the de-silylation of β-silylstyrenes[21] and are closely analogous to the mechanism proposed by Farina and Hossain for the abnormal cine substitution that is observed during Stille coupling of α-trimethylstannylstyrenes.[22]

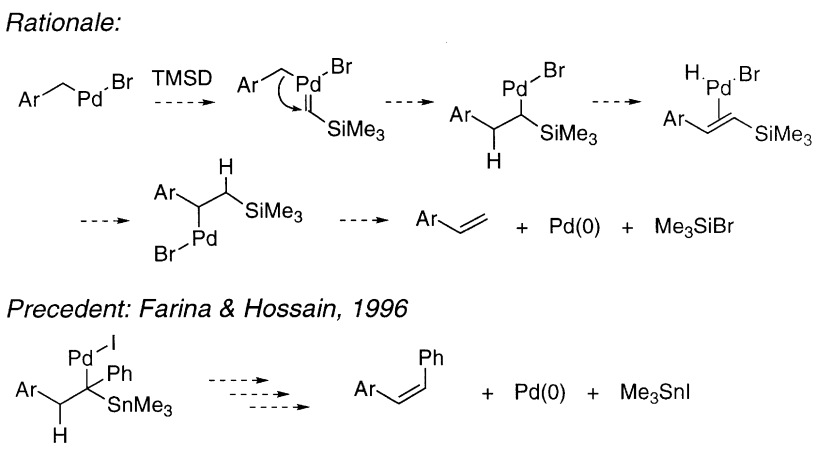
3. Conclusions

In conclusion, this work demonstrates for the first time that palladium can catalyze the addition and rearrangement of trimethylsilyldiazomethane to allylic sulfides. This reaction does not work with ethyl diazoacetate, a more common reagent. Yields are best with dimethallyl substrates that generate quaternary centers. Diastereoselection generally falls in the range of 3–5:1, but enantioselection was poor. The insertion concept can be extended to Stille reactions in

Table 5. Pd-catalyzed homologation of benzyl halides with TMSD



S.M.	X	R	Solvent	Time (h)	Yield (%)
9a	Br	4-MeO_2C	$CHCl_3$	12	56
9a	Br	4-MeO_2C	$ClCH_2CH_2Cl$	1	60
9b	Cl	4-O_2N	$ClCH_2CH_2Cl$	1	57
9c	Cl	3-MeO	$ClCH_2CH_2Cl$	1	54



Scheme 4. Palladium catalyzed benzyl homologation.

low yields. In contrast, the TMSD homologation of benzyl halides appears quite promising and may be of greater utility if applied to related aryl, vinyl and allyl halides.

4. Experimental

4.1. General

All reactions were run under an atmosphere of dry nitrogen unless otherwise noted. Trimethylsilyldiazomethane in hexanes and anhydrous 1,2-dichloroethane were purchased from Sigma–Aldrich. $PdCl_2$ and $(MeCN)_2PdCl_2$ were purchased from Strem Chemical. Deuterated NMR solvents with a 0.05% by volume tetramethylsilane standard were obtained from Cambridge Isotope Labs. All other reagents and solvents were purchased from Fisher Scientific. Dichloromethane was dried by passage over alumina as described by Grubbs.[23] Commercial reagents and solvents were used without further purification except as indicated. Chromatography solvents were prepared as volume to volume mixtures. Analtech 1.5 and 2.0 mm GF silica plates were used for preparative thin layer chromatography. Reverse phase HPLC was preformed on a C_{18} microsorb column with 1 mL/min (analytical) and 10 mL/min (preparative) flow rates. HPLC grade water and acetonitrile were filtered and degassed prior to use. All NMR spectra were taken with Bruker 500 or 400 MHz spectrometers. Mass spectra were obtained from a Micromass Analytica 7070E (LRMS/HRMS), Micromass Autospec (HRMS/LRMS), or a Perspective Biosystems Voyager DESTR (LCMS) using the indicated ionization method. Combustion analyses were performed by Atlantic Micro Labs, Atlanta, GA. Uncorrected melting points were determined in open capillary tubes.

4.1.1. General procedure for preparation of allylic sulfides 1a–e and 4a–7a. A flame dried flask with a magnetic stir bar was charged with methanol (50 mL) and cooled to 0°C. One equivalent of sodium metal was added to the flask. Upon complete reaction of the metal, 1.2 equiv. of the appropriate thiol was added and the solution maintained for 1 h. One equivalent of the corresponding allylic bromide was then added and the solution warmed to room temperature. After an additional 1 h, the solution was concentrated in vacuo, diluted with ether (100 mL) and washed with 2N sodium hydroxide (3×50 mL). The organic layer was dried ($MgSO_4$) and concentrated in vacuo. The resultant oils were purified by bulb to bulb distillation except for the solid **8a**, which was recrystallized from hexanes. Compounds **1a**,[24] **1b**,[25] **1c**,[26] **1e**,[27] **4a**,[28] **5a**,[29] **6a**[30] and **7a**[31] have been previously reported. Compound **1d** was obtained in 78% yield following bulb to bulb distillation: R_f=0.15 (hexanes); IR(neat) 3030, 2912, 2834, 1610, 1510 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, J=8.5 Hz, 2H), 6.83 (d, J=8.5 Hz, 2H), 5.23 (t, J=7.6 Hz, 1H), 3.78 (s, 3H), 3.63 (s, 2H), 3.03 (d, J=7.6 Hz, 2H), 1.73 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.5, 135.2, 130.5, 130.0, 129.9, 120.5, 113.8, 55.2, 35.0, 29.0, 25.7, 17.8; LRMS (EI) m/z 222 (50), 154 (50), 121 (100), 77 (80); HRMS(EI) calcd for $C_{13}H_{18}OS$ $[M]^+$ 222.1078, found: 222.1079; Anal. Calcd for $C_{13}H_{18}OS$: C, 70.23; H, 8.16; Found: C, 70.20, H, 8.20.

4.1.2. General procedure for [2,3]-sigmatropic rearrangement. A two-necked flask with 4 Å molecular sieve spheres and a magnetic stir bar was flame dried under vacuum. The vessel was then charged with 2,6-di-*tert*-butyl-4-methylpyridine (0.10 equiv.), $PdCl_2$ (0.05 equiv.) and purged with nitrogen. The corresponding allyl sulfide (1.0 equiv.) was added to the flask along with 1,2-dichloroethane (10 mL). The solution was then heated to reflux. Trimethylsilyldiazomethane in hexanes (2.0 equiv.) was added over 12 h by syringe pump. The resulting brown solution was cooled to room temperature, filtered through a pad of Celite, and concentrated in vacuo.

4.1.3. [1-(4-Methoxyphenylsulfanyl)-2,2-dimethylbut-3-enyl]trimethylsilane (2a). Following the above procedure, purification by preparative thin layer chromatography (98:2 hexanes/ether) afforded **2a** as a clear, colorless oil (169 mg, 64%): R_f=0.36 (98:2 hexanes/ether); IR (neat) 3082, 2960, 2835, 1634, 1593, 1284 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.34 (dt, J=8.8, 2.4 Hz, 2H), 6.81 (dt, J=8.8, 2.4 Hz, 2H), 5.89 (dd, J=17.5, 10.7 Hz, 1H), 4.97 (dd, J=17.5, 1.0 Hz, 1H), 4.91 (dd, J=10.7, 1.0 Hz, 1H), 3.79 (s, 3H), 2.27 (s, 1H), 1.13 (s, 3H), 1.10 (s, 3H), 0.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.3, 148.3, 132.1, 131.6, 114.5, 110.9, 55.4, 50.4, 42.7, 28.3, 26.3, 1.0; LRMS (EI) m/z 294 (16), 225 (56), 212 (86), 197 (64), 182 (68), 167 (30), 139 (24), 135 (22), 117 (14), 73 (100); HRMS (CI/NH_3)

calcd for $C_{16}H_{26}OSSi$ $[M]^+$ 294.1474, found 294.1472. Anal. Calcd for $C_{16}H_{26}OSSi$: C, 65.25; H, 8.90. Found: C, 65.25, H, 8.93.

4.1.4. (2,2-Dimethyl-1-phenylsulfanylbut-3-enyl)trimethylsilane (2b). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded the previously reported[17] **2b** as a clear, colorless oil (179 mg, 84%): R_f=0.57 (pentane); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38–7.36 (m, 2H), 7.26–7.23 (m, 2H), 7.14–7.13 (m, 1H), 5.94 (dd, J=17.4, 10.7 Hz, 1H), 5.00 (dd, J=17.4, 1.2 Hz, 1H), 4.93 (dd, J=10.7, 1.2 Hz, 1H), 2.46 (s, 1H), 1.15 (s, 3H), 1.12 (s, 3H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 140.6, 128.7, 128.6, 125.3, 111.0, 47.9, 42.7, 28.5, 26.5, 1.2.

4.1.5. [1-(4-Chlorophenylsulfanyl)-2,2-dimethylbut-3-enyl]trimethylsilane (2c). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded **2c** as a clear, colorless oil (222 mg, 75%): R_f=0.56 (hexanes); IR(neat) 3082, 2965, 2897, 1636, 1475, 1250 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 (d, J=8.6 Hz, 2H), 7.21 (d, J=8.6 Hz, 2H), 5.89 (dd, J=17.4, 10.7 Hz, 1H), 4.98 (d, J=17.4 Hz, 1H), 4.92 (d, J=10.7 Hz, 1H), 2.37 (s, 1H), 1.13 (s, 3H), 1.10 (s, 3H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 139.5, 131.3, 130.3, 128.9, 111.3, 48.5, 42.5, 28.2, 26.3, 0.9; LRMS (EI) m/z 298 (16), 229 (40), 216 (60), 201 (86), 165 (60), 73 (100); HRMS (EI) calcd for $C_{15}H_{23}ClSSi$ $[M]^+$ 298.0978, found 298.0974. Anal. Calcd for $C_{15}H_{23}ClSSi$: C, 60.27; H, 7.75. Found: C, 60.37, H, 7.73.

4.1.6. [1-(4-Methoxybenzylsulfanyl)-2,2-dimethylbut-3-enyl]trimethylsilane (2d). Following the above procedure, purification by preparative thin layer chromatography (99:1 hexanes/ether) afforded **2d** as a clear, colorless oil (162 mg, 64%): R_f=0.21 (99:1 hexanes/ether); IR(neat) 3080, 2957, 2835, 1634, 1610, 1301 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.19 (d, J=8.6 Hz, 2H), 6.83 (d, J=8.6 Hz, 2H), 5.94 (dd, J=17.5, 10.7 Hz, 1H), 4.97 (d, J=17.5 Hz), 4.93 (d, J=10.7 Hz, 1H), 3.79 (s, 3H), 3.75 (d, J=12.4 Hz, 1H), 3.62 (d, J=12.4 Hz, 1H), 1.65 (s, 1H), 1.15 (s, 3H), 1.13 (s, 3H), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 148.6, 130.6, 130.5, 113.9, 110.7, 55.4, 44.0, 42.2, 40.9, 27.8, 26.4, 0.7; LRMS (EI) m/z 308 (2), 239 (46), 187 (64), 121 (100), 113 (66), 73 (88); HRMS (EI) calcd for $C_{17}H_{28}OSSi$ $[M]^+$ 308.1630, found 308.1636. Anal. Calcd for $C_{17}H_{28}OSSi$: C, 66.18; H, 9.15. Found: C, 66.14, H, 9.17.

4.1.7. (1-Benzylsulfanyl-2,2-dimethylbut-3-enyl)trimethylsilane (2e). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded **2e** as a clear, colorless oil (244 mg, 80%): R_f=0.43 (hexanes); IR(neat) 3083, 3028, 2962, 1635, 1602, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.25 (m, 5H), 5.94 (dd, J=17.5, 10.7 Hz, 1H), 5.00 (dd, J=17.6, 1.2 Hz, 1H), 4.96 (dd, J=10.7, 1.2 Hz, 1H), 3.78 (d, J=12.0 Hz, 1H), 3.65 (d, J=12.0 Hz, 1H), 1.66 (s, 1H), 1.15 (s, 3H), 1.13 (s, 3H), 0.00 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 138.5, 129.5, 128.5, 127.0, 110.8, 44.0, 42.2, 41.5, 27.8, 26.4, 0.7; LRMS (CI/NH_3) m/z 296 (2), 279 (100), 226 (37), 209 (90), 90 (32); HRMS (CI/NH_3) calcd for $C_{16}H_{26}SSi$ $[M+H]^+$ 279.1603, found 279.1599. Anal. Calcd for $C_{16}H_{26}SSi$: C, 69.00; H, 9.41. Found: C, 68.88, H, 9.41.

4.1.8. (1-Benzylsulfanyl-3-methylbut-3-enyl)trimethylsilane (4b). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded **4b** as a clear, colorless oil (155 mg, 60%): R_f=0.25 (hexanes); IR(neat) 3072, 3028, 2955, 1648, 1248 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.28 (m, 4H), 7.24–7.21 (m, 1H), 4.86 (d, J=1.0 Hz, 1H), 4.83 (d, J=1.0 Hz, 1H), 3.77 (d, J=13.0 Hz, 1H), 3.75 (d, J=13.0 Hz, 1H), 2.41 (dd, J=14.3, 5.8 Hz, 1H), 2.32 (dd, J=14.3, 9.0 Hz, 1H), 1.93 (dd, J=9.0, 5.8 Hz, 1H), 1.70 (s, 3H), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 138.7, 129.3, 128.4, 126.9, 112.6, 41.1, 37.48, 28.1, 22.3, −2.3; LRMS (EI) m/z 264 (4), 209 (8), 181 (14), 173 (66), 99 (40), 91 (74) 73 (100); HRMS (EI) calcd for $C_{15}H_{24}SSi$ $[M]^+$ 264.1368, found 264.1363. Anal. Calcd for $C_{15}H_{24}SSi$: C, 68.12; H, 9.15. Found: C, 67.72, H, 9.05.

4.1.9. (1-Benzylsulfanyl-2,6-dimethyl-2-vinylhept-5-enyl)trimethylsilane (5b). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded the clear, colorless oil **5b** as an inseparable mixture of diastereomers (112 mg, 65%): R_f=0.25 (hexanes); IR(neat) 3082, 3062, 3028, 2967, 1634, 1494, 1248 cm^{-1}; ^{1}H NMR indicated a 5:1 mixture of diastereomers; ^{1}H NMR, major diastereomer (500 MHz, $CDCl_3$) δ 7.31–7.20 (m, 5H), 5.85 (dd, J=17.5, 11.0 Hz, 1H), 5.08–5.04 (m, 2H), 4.97 (d, J=17.5 Hz, 1H), 3.77 (d, J=12.3 Hz, 1H), 3.66 (d, J=12.3 Hz, 1H), 1.88–1.85 (m, 2H), 1.74 (s, 1H), 1.71 (s, 3H), 1.60 (s, 3H), 1.50 (m, 2H), 1.30 (s, 3H), 0.03 (s, 9H); ^{13}C NMR, major diastereomer (125 MHz, $CDCl_3$) δ 146.0, 138.2, 131.0, 129.3, 128.3, 126.8, 124.8, 112.5, 45.6, 44.2, 41.6, 40.5, 26.1, 23.4, 21.3, 18.1, 1.1; LRMS (EI) m/z 346 (5), 255 (45), 209 (38), 181 (55), 149 (36), 107 (40), 91 (100), 73 (80); HRMS (EI) calcd for $C_{21}H_{34}SSi$ $[M]^+$ 346.2151, found 346.2148. Anal. Calcd for $C_{21}H_{34}SSi$: C, 72.76; H, 9.89. Found: C, 73.04, H, 9.97.

4.1.10. (Benzylsulfanylcyclohex-2-enylmethyl)trimethylsilane (6b). Following the above procedure, purification by preparative thin layer chromatography (hexanes) afforded the clear colorless oil **6b** as an inseparable mixture of diastereomers (67.7 mg, 24%): R_f=0.33 (hexanes); IR(neat) 3061, 3025, 2931, 1602, 1248 cm^{-1}; ^{1}H NMR indicated a 1:1 mixture of diastereomers; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.23 (m, 10H), 5.80–5.76 (m, 1H), 5.72–5.68 (m, 1H), 5.57 (dd, J=10.4, 2.0 Hz, 1H), 5.46 (dt, J=10.4, 2.0 Hz, 1H), 3.76–3.66 (m, 4H), 2.78–2.50 (m, 2H), 2.03–2.00 (m, 4H), 1.86–1.79 (m, ^{1}H and d, J=2.8 Hz, 2H), 1.74 (d, J=3.2 Hz, 2H), 1.62–1.51 (m, 5H), 0.01 (s, 18H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.8, 138.6, 132.4, 131.6, 129.5, 128.4, 128.2, 126.9, 39.2, 39.1, 38.7, 38.6, 29.1, 27.8, 25.4, 25.0, 22.9, 22.7; LRMS (EI) m/z 209 (60), 199 (65), 181 (60), 91 (100), 73 (90); HRMS (EI) calcd for $C_{17}H_{26}SSi$ $[M+H]^+$ 291.1603, found 291.1610. Anal. Calcd for $C_{17}H_{26}SSi$: C, 70.28; H, 9.02. Found: C, 70.51, H, 9.04.

4.1.11. (2-Phenyl-1-phenylsulfanylbut-3-enyl)trimethylsilane (7b). Following the above procedure, purification

by preparative thin layer chromatography (hexanes) afforded previously reported[17] clear, colorless oil **7b** as an inseparable mixture of diastereomers (371 mg, 54%): R_f=0.24 (hexanes); ^{1}H NMR indicated a 3:1 mixture of diastereomers; ^{1}H NMR, major diastereomer (500 MHz, $CDCl_3$) δ 7.27–7.24 (m, 2H), 7.21–7.17 (m, 2H), 7.14–7.09 (m, 1H), 7.09–7.05 (m, 2H), 7.04–7.00 (m, 1H), 6.98–6.96 (m, 2H), 6.31 (ddd, J=17.0, 10.2, 9.1 Hz, 1H), 5.15–5.09 (m, 2H), 3.79 (dd, J=9.1, 5.1 Hz, 1H), 2.74 (d, J=5.1 Hz, 1H), 0.07 (s, 9H); ^{13}C NMR, major diastereomer (125 MHz, $CDCl_3$) δ 144.0, 139.8, 138.8, 129.4, 128.3, 128.2, 128.1, 126.5, 125.4, 116.3, 51.6, 43.2, −1.6.

4.1.12. Benzhydryltrimethylsilane (8a). A two-necked flask with 4 Å molecular sieve spheres and a magnetic stir bar was flame dried under vacuum. $PdCl_2$ (9 mg, 0.06 mmol), triphenylarsine (62 mg, 0.20 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (21 mg, 0.10 mmol) were sequentially added. The flask was purged with nitrogen, charged with iodobenzene (203 mg, 1.0 mmol), tetrahydrofuran (10 mL), and heated to reflux. Phenyl-tri-*n*-butyltin (393 mg, 1.1 mmol), and trimethylsilyldiazomethane in hexanes (0.5 mL, 1.0 mmol) were each diluted to 1 mL with tetrahydrofuran and added through separate syringes over 15 h. The black solution was cooled to room temperature, filtered through a pad of Celite and concentrated in vacuo to give a yellow oil, which was subsequently purified by preparative thin layer chromatography (hexanes) to give the previously reported[32] **8a** as a white solid (50 mg, 21%): mp (methanol) 72–74°C; lit.[33] mp 73–75°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28–7.24 (m, 8H), 7.16–7.10 (m, 2H), 3.53 (s, 1H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9, 128.7, 128.3, 125.0, 46.1, −1.7.

4.1.13. [(4-Methoxyphenyl)phenylmethyl]trimethylsilane (8b). A two-necked flask with 4 Å molecular sieve spheres and a magnetic stir bar was flame dried under vacuum. 4-Iodoanisole (231 mg, 1.0 mmol), $PdCl_2$ (10 mg, 0.06 mmol), triphenylarsine (59 mg, 0.20 mmol), and 2,6-di-*tert*-butyl-4-methylpyridine (19 mg, 0.10 mmol) were sequentially added. The flask was purged with nitrogen, charged with tetrahydrofuran (10 mL), and heated to reflux. Phenyl-tri-*n*-butyltin (410 mg, 1.1 mmol), and trimethylsilyldiazomethane in hexanes (0.5 mL, 1.0 mmol) were each diluted to 1 mL with tetrahydrofuran and added through separate syringes over 15 h. The black solution was cooled to room temperature, filtered through a pad of Celite and concentrated in vacuo to give a yellow oil, which was subsequently purified by preparative thin layer chromatography (99:1 hexanes/ether) to give a white solid. Further purification by reverse phase HPLC (90:10 MeCN/H_2O) afforded (4-phenyl)-anisole (19 mg, 10%) and **8b** as a white solid (26 mg, 10%): mp (pentane) 57–58°C; lit.[34] mp 57–58°C; R_f=0.30 (99:1 hexane/ether); IR(KBr) 3027, 2957, 1656, 1604, 1509, 1457, 1253, 839; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.19–7.18 (m, 2H), 7.15 (d, J=8.5 Hz, 2H), 6.81 (d, J=8.5 Hz, 2H), 3.76 (s, 3H), 3.44 (s, 1H), 0.02 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.1, 143.3, 135.0, 129.7, 128.4, 128.2, 124.9, 113.7, 55.4, 45.2, −1.2; LRMS (EI) m/z 270 (10), 255 (100), 197 (10), 73 (20);); HRMS (EI) calcd for $C_{17}H_{22}OSi$ $[M]^+$ 270.1440, found 270.1445.

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